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Supporting Information

Highly Selective Fluorescent Probes for Visualizing Intracellular Mg^{2+} Dynamics without Interference from Ca^{2+} Fluctuation

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1. Supplemental Figures

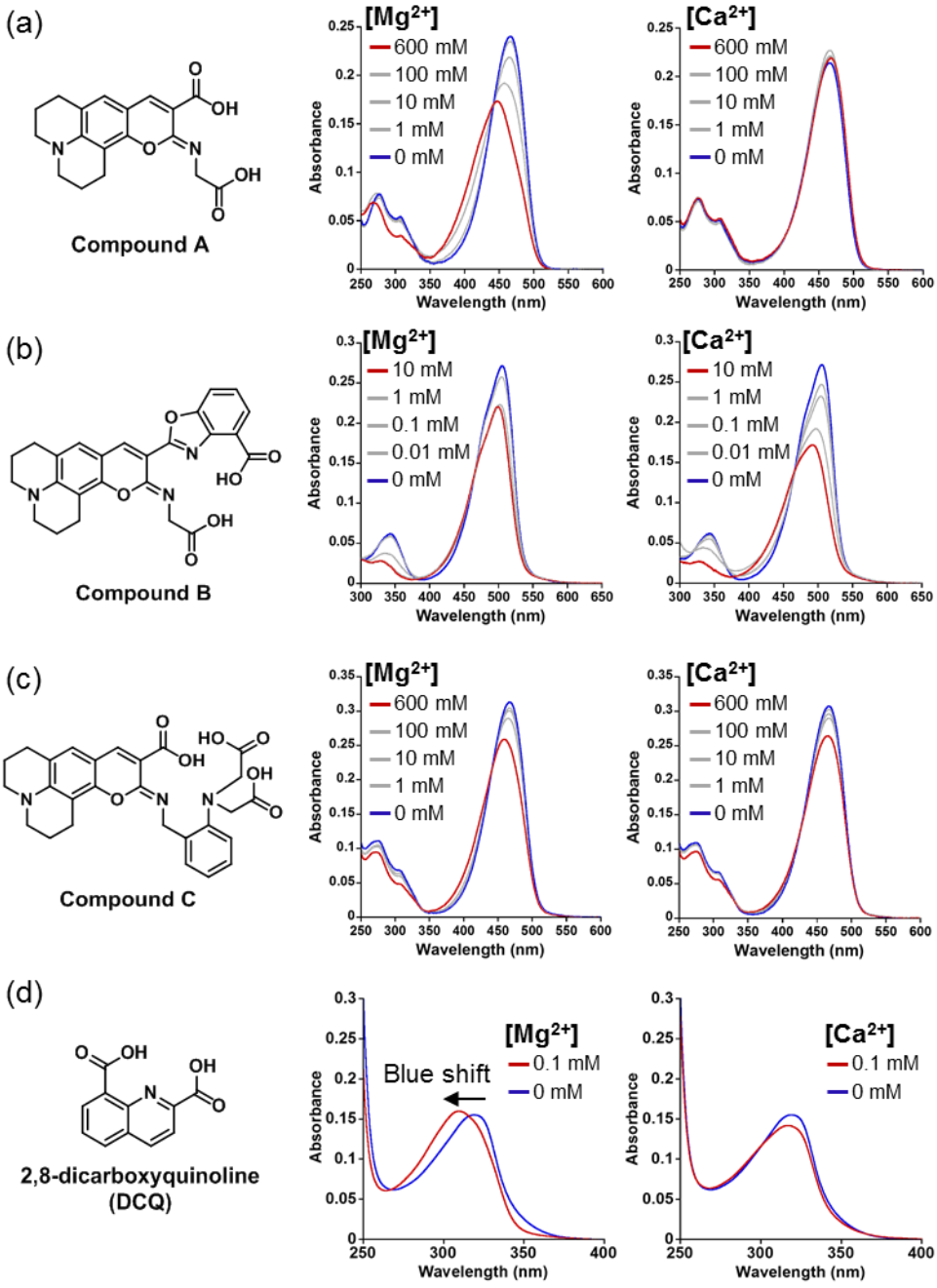


Fig. S1 UV-vis absorption spectra of (a) 10 μM compound A, (b) 5 μM compound B, (c) 10 μM compound C and (d) 10 μM 2,8-dicarboxyquinoline in the presence and absence of Mg^{2+} or Ca^{2+} in 100 mM HEPES buffer (pH 7.4) at 37 °C.

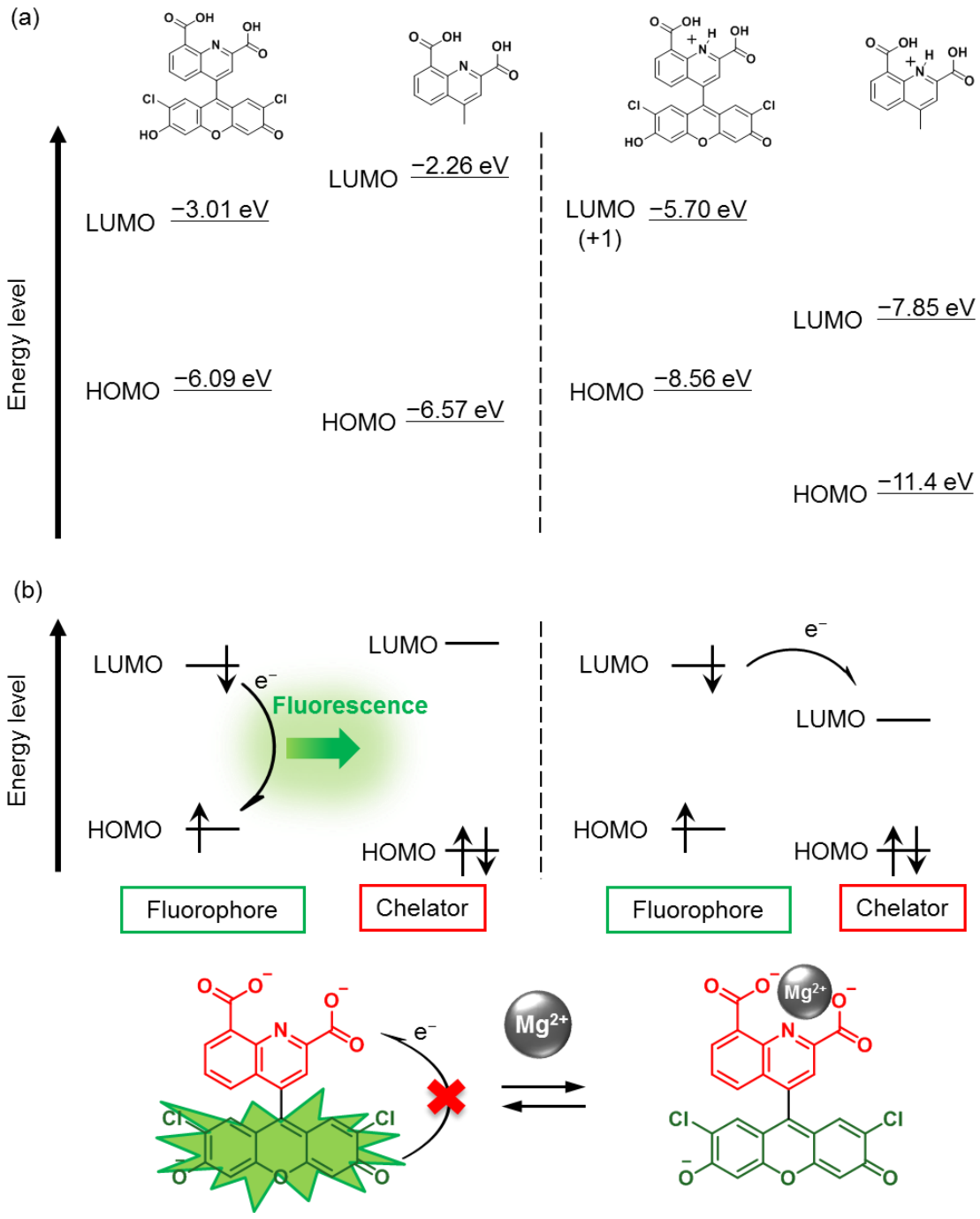


Fig. S2 (a) Quantum chemical calculation of HOMO and LUMO energy levels of MGQ-1 and protonated MGQ-1 in water (B3LYP/6-31G(d)). (b) Turn-off mechanism of MGQ-1 caused by d-PeT.

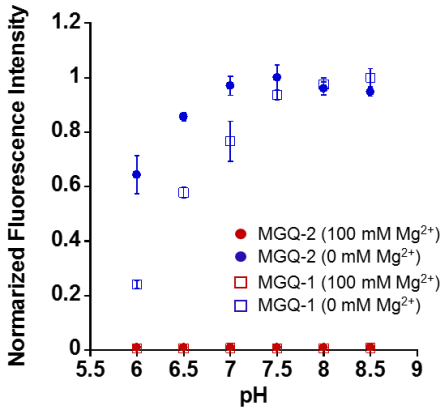


Fig. S3 Effect of the pH on the fluorescence intensity of MGQ-1 and MGQ-2 between pH 6.0–6.5 (in 100 mM MES buffer, 115 mM KCl, 20 mM NaCl) and pH 7.0–8.5 (in 100 mM HEPES buffer, 115 mM KCl, 20 mM NaCl), with or without 100 mM of Mg^{2+}. The error bars denote SD (n = 3).

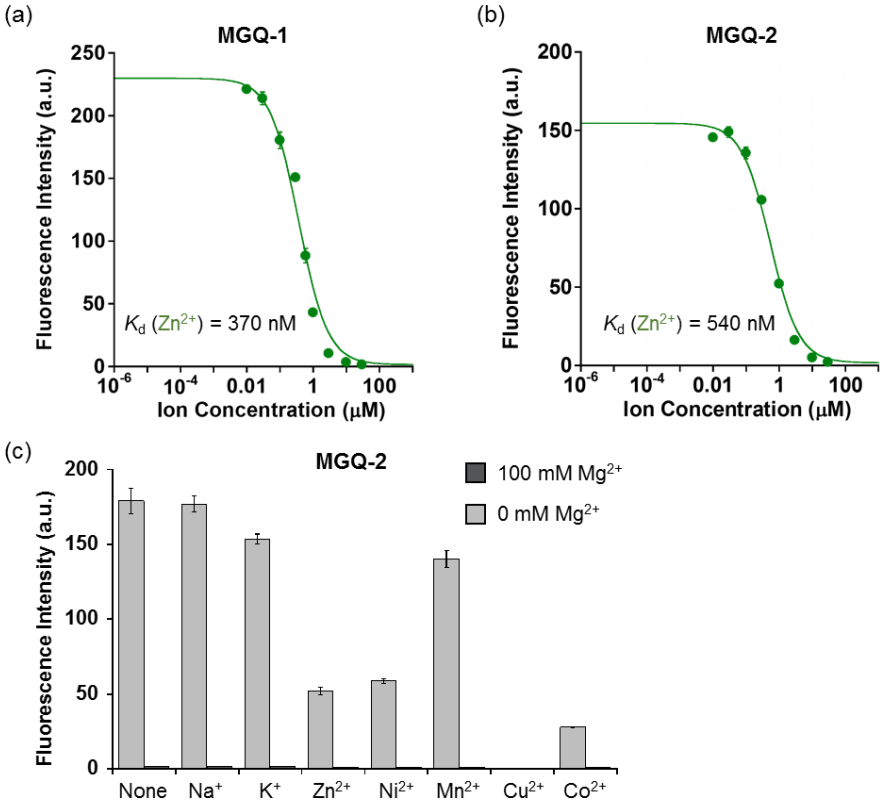


Fig. S4 Zn^{2+}-titration curves of (a) MGQ-1 and (b) MGQ-2 measured from their emissions at 536 nm (100 mM HEPES buffer, 115 mM KCl, 20 mM NaCl, pH7.4, 37 °C). [Zn^{2+}] = 0, 0.01, 0.03, 0.1, 0.3, 0.6, 1, 3, 10, 30 μM. λ_{ex} = 515 nm. (c) Metal ion selectivity of 1 μM MGQ-2 in the presence and absence of 100 mM Mg^{2+}. Na^{+} was added at 20 mM, and K^{+} was added at 115 mM (100 mM HEPES buffer, pH 7.4, 37 °C). Zn^{2+}, Ni^{2+}, Mn^{2+}, Cu^{2+} or Co^{2+} were added to a final concentration of 1 μM (100 mM HEPES buffer, 115 mM KCl, 20 mM NaCl, pH7.4, 37 °C). The error bars denote SD (n = 3).

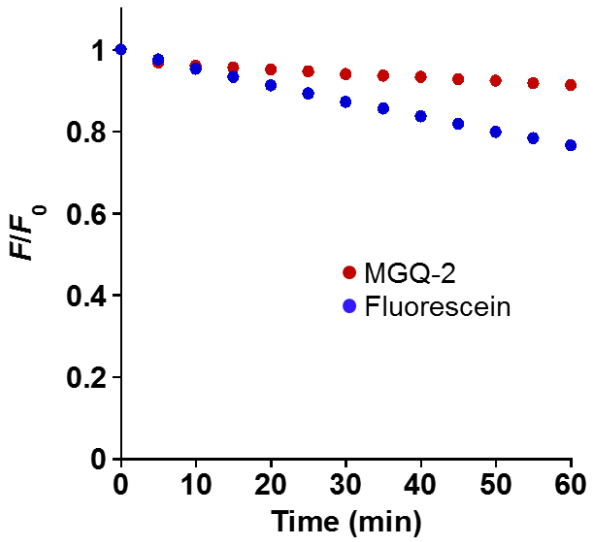


Fig. S5 Photostability of MGQ-2 during continuous irradiation (4.0 mW/cm^2). Changes in the fluorescence intensity (F) were normalized by the initial fluorescence intensity (F_0). The error bars denote SD (n = 3).

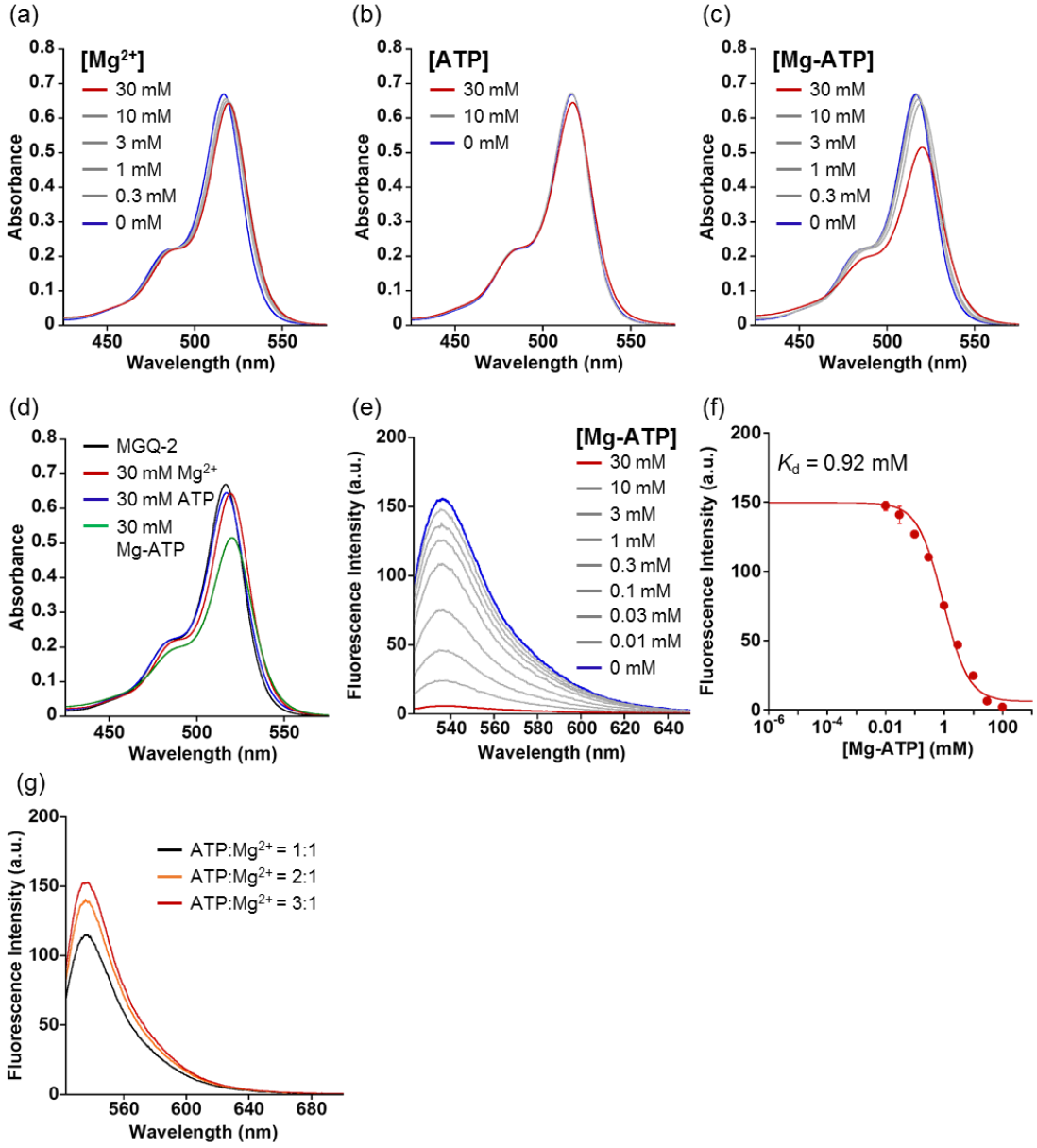


Fig. S6 UV-vis absorption spectra of 10 μM MGQ-2 in the presence of (a) Mg^{2+}, (b) ATP, (c) Mg-ATP (100 mM HEPES, 115 mM KCl, 20 mM NaCl, pH 7.4, 37 °C). [Mg^{2+}] or [Mg-ATP] = 0, 0.3, 1, 3, 10, 30 mM. [ATP] = 0, 10, 30 mM. (d) UV-vis absorption spectra of 10 μM MGQ-2 in the presence of 30 mM Mg^{2+}, ATP or Mg-ATP. (e) Emission spectra of 1 μM MGQ-2 in the presence of Mg-ATP (100 mM HEPES, 115 mM KCl, 20 mM NaCl, pH 7.4, 37 °C). [Mg-ATP] = 0, 0.01, 0.03, 0.1, 0.3, 1, 3, 10, 30 mM. λ_{ex} = 515 nm. (f) Mg-ATP-titration curve of MGQ-2 measured from its emission at 536 nm. The error bars denote SD (n = 3). (g) Emission spectra of 1 μM MGQ-2 in the presence of different ratios of ATP to Mg^{2+}. Black line; 0.3 mM ATP and 0.3 mM Mg^{2+} (1:1). Orange line; 0.6 mM ATP and 0.3 mM Mg^{2+} (2:1). Red line; 0.9 mM ATP and 0.3 mM Mg^{2+} (3:1).

2. Supporting Methods

Materials and instruments

General chemicals for organic synthesis were of the best grade available, supplied by Tokyo Chemical Industries, Wako Pure Chemical, or Sigma-Aldrich Chemical Co, and were used without further purification. Analytical thin-layer chromatography was performed on 60F254 silica plates (Merck & Co., Inc.). Silica gel column chromatography was performed using BW-300 (Fuji Silysia Chemical Ltd.). MGQ-1, MGQ-2 and MGQ-2(AM) were dissolved in DMSO (biochemical grade, Wako) before fluorescence measurements to facilitate solubilization in aqueous solution. Magnesium Green(AM) was purchased from Thermo Fisher Scientific. Ionomycin was purchased from Wako. CMV-R-GECO1.0 was purchased from Addgene. ATP was obtained from Wako Pure Chemical as its disodium salt.

GPC purifications were performed with a JAIGEL 1H-2H column (Japan Analytical Industry Co., Ltd.) using a GPC system that was comprised of a pump (LC-6AD, Shimadzu) and a detector (SPD-20A, Shimadzu). HPLC analyses were performed with an Inertsil ODS-3 (4.6 mm×250 mm) column (GL Sciences Inc.) using an HPLC system that was comprised of a pump (PU-2080, Jasco) and a detector (MD-2010, Jasco). Preparative HPLC was performed with an Inertsil ODS-3 (10.0 mm × 250 mm) column (GL Sciences Inc.) using an HPLC system that comprised a pump (PU-2087, JASCO) and a detector (UV-2075, JASCO). Buffer A was 0.1% HCOOH in H_2O (for MGQ-2(AM)) or 50 mM triethylammonium acetate in H_2O (for MGQ-1 and MGQ-2); Buffer B was 0.1% HCOOH in acetonitrile (for MGQ-2(AM)) or pure acetonitrile (for MGQ-1 and MGQ-2). NMR spectra were recorded on a Bruker Avance 500 instrument at 500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR, using tetramethylsilane as an internal standard. Mass spectra were measured on a Waters LCT-Premier XE mass spectrometer or on a JMS-700 (JEOL).

Fluorescence spectra were measured using a Hitachi F7000 spectrometer. The slit widths were 2.5 nm for both excitation and emission, and the photomultiplier voltage was 700 V. UV-visible absorbance spectra were measured using a Jasco aV-650 spectrophotometer. For photostability analysis of MGQ-2, the light irradiation was performed by using a xenon light source (MAX-303, Asahi Spectra) equipped with a band pass filter (490/5 nm for MGQ-2 and fluorescein).

Fluorescence microscopic images were recorded using a confocal fluorescence microscopic imaging system including a fluorescence microscope (IX71, Olympus), an EMCCD (iXon3, Andor Technology), a confocal scanner unit (CSU-X1, Yokogawa Electric Corporation), and a multispectral LED light source (Spectra X light engine, Lumencor). The filter sets were BP488 ± 3/DM488/BA520 ± 17.5 (for MGQ-2 and Magnesium Green) and BP560 ± 13/DM561/BA624 ± 20 (for R-GECO1.0). The whole system was controlled using MetaMorph 7.6 software (Molecular Devices).

Fluorometric analysis

The relative fluorescence quantum yields of the compounds were obtained by comparing the area under the emission spectrum. The following equation was used to calculate quantum yield:

$$\Phi_x = \Phi_{st} (I_x/I_{st})(A_{st}/A_x)(n_x^2/n_{st}^2)$$

where Φ_{st} is the reported quantum yield of the standard, I is the integrated emission spectrum, A is the absorbance at the excitation wavelength, and n is the refractive index of the solvent used. The subscripts x and st denote sample and standard, respectively. Fluorescein (Φ = 0.85 when excited at 492 nm in 100 mM NaOH aq.) was used as the standard.

Photostability of MGQ-2 (1 μM, 2 mL) was examined with a 100 mM HEPES buffer (pH 7.4) with 115 mM KCl and 20 mM NaCl at 25 °C under continuous light irradiation through a band pass filter (490 ± 2.5 nm, 4.0 mW/cm^2) using a xenon light source. The fluorescence intensity (λ_{ex} = 515 nm, λ_{em} = 536 nm) was measured every 5 min for 1 h.

Determination of dissociation constants

The apparent dissociation constants (K_d) of MGQ-1 and MGQ-2 for metal ions in 100 mM HEPES buffer (pH 7.4) containing 115 mM KCl and 20 mM NaCl were calculated using the following equation,

$$[M^{n+}] = K_d (F - F_{min})/(F_{max} - F)$$

,where F is the fluorescence intensity at each metal ion concentration, F_{min} is the fluorescence intensity before addition of the metal ions, and F_{max} is the fluorescence intensity at the saturation point.

Metal ion selectivity study

Metal ion selectivity was measured by adding either $MgCl_2$, NaCl, KCl, $ZnCl_2$, $CoCl_2$, $MnCl_2$, $NiCl_2$ or $CuCl_2$ to 1 μM MGQ-2 solution. The fluorescence intensity of MGQ-2 with 20 mM Na^+ or 115 mM K^+ was measured in 100 mM HEPES buffer (pH 7.4). The fluorescence intensity with 1 μM Zn^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, or Cu^{2+} was measured in 100 mM HEPES buffer (pH 7.4) with 115 mM KCl and 20 mM NaCl.

Quantum chemical calculation

All calculations of HOMO and LUMO energy levels were performed using the Gaussian 09 program. The geometries of the ground state structures were optimized using Density Functional Theory (DFT) at the B3LYP level. The 6-31G(d) basis set was used for all atoms.

Cell culture

HEK293 cells were cultured in high-glucose Dulbecco's modified Eagle medium (DMEM) plus Gluta Max-I supplemented with 10% fetal bovine serum (FBS), 100 U/mL penicillin, and 100 μg/mL

streptomycin. Cells were incubated at 37 °C in a humidified atmosphere with 5% CO_2. A subculture was performed every 2–3 days from subconfluent (<80%) cultures using a trypsin-ethylenediamine tetraacetic acid solution. Transfection of plasmids was carried out in a glass-bottomed dish using Lipofectamine 3000 according to the standard protocol.

Live-cell fluorescence imaging of MGQ-2(AM)

HEK293 cells maintained in 10% FBS in DMEM at 37 °C in 5% CO_2 were washed three times with HBSS and incubated in FBS-free DMEM containing 2 μM MGQ-2(AM) for 45 min in a CO_2 incubator. After washing with HBSS, the medium was replaced with DMEM and the fluorescence images were captured using a confocal fluorescence microscope.

Mg^{2+} export experiment

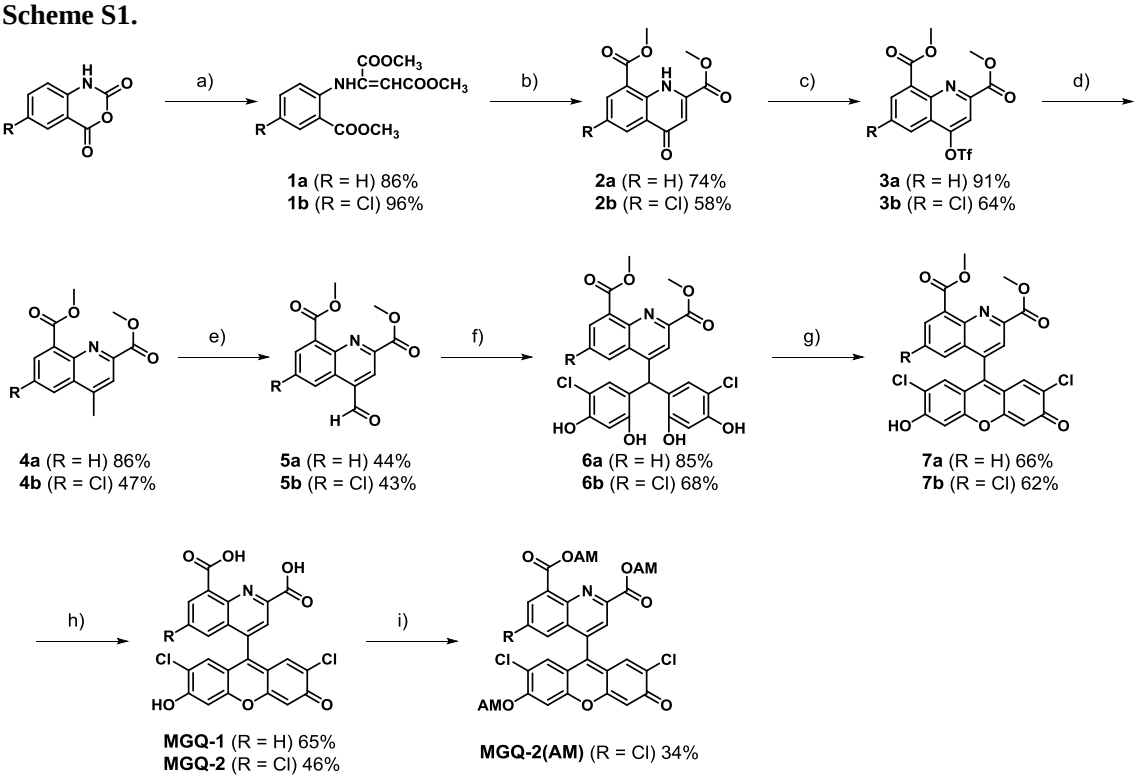
HEK293 cells were transfected with pCMV-CNNM4-FLAG using Lipofectamine 3000, and the cells were incubated at 37 °C for 24 h. Then, the cells were incubated with Mg^{2+}-loading buffer (78.1 mM NaCl, 5.4 mM KCl, 1.8 mM $CaCl_2$, 40 mM $MgCl_2$, 5.5 mM glucose, 5.5 mM HEPES-KOH, pH 7.4), including 2 μM MGQ-2(AM) or 2 μM Magnesium Green(AM), for 45 min at 37 °C. The cells were rinsed once with loading buffer and the fluorescence images were captured every 20 s using a confocal fluorescence microscope. Then, the buffer was changed to a Mg^{2+}-free buffer ($MgCl_2$ in the loading buffer was replaced with 60 mM NaCl).

Responsivity of MGQ-2 for $[Ca^{2+}]_i$ change

HEK293 cells were transfected with pCMV-R-GECO1.0 using Lipofectamine 3000, and the cells were incubated at 37 °C for 24 h. Then, the cells were incubated FBS-free DMEM containing 2 μM MGQ-2(AM) or 2 μM Magnesium Green(AM) for 45 min at 37 °C. The cells were rinsed twice with Mg^{2+}- and Ca^{2+}-free HEPES-buffered Hanks balanced salt solution (HHBSS), then 10 mM Ca^{2+} in Mg^{2+}-free HHBSS was added to the cells. Then, time lapse images were taken with 5 μM ionomycin added after 1 min. The fluorescence images were captured every 10 s using a confocal fluorescence microscope.

Chemical synthesis

Scheme S1.



a) dimethyl acetylenedicarboxylate, sodium methoxide, MeOH, reflux; b) diphenyl ether, reflux; c) trifluoromethanesulfonic anhydride, 2,6-lutidine, DMAP, DCM, 0 °C→r.t.; d) methylboronic acid, K_2CO_3, Pd(dppf)Cl_2·CH_2Cl_2, dioxane, 100 °C; e) SeO_2, dioxane, 80 °C; f) 4-chlororesorcinol, 8% (v/v) $MeSO_3H$, DCM/Et_2O (1:1), r.t.; g) *p*-TsOH·H_2O, AcOH, 60 °C; h) 2 M NaOH aq., MeOH/H_2O (3:1), r.t.; i) bromomethyl acetate, DIEA, DMF, r.t.

Synthesis of compound 1a

Isatic anhydride (4.08 g, 25.0 mmol), dimethyl acetylenedicarboxylate (4.60 mL, 37.5 mmol) and sodium methoxide (54.0 mg, 1.00 mmol) were stirred in MeOH (40 mL) at reflux temperature for 3 h. After cooling, the solvent was evaporated. The residue was then purified by flash column chromatography on silica gel (ethyl acetate/hexane) and subsequently by GPC. Compound **1a** (6.45 g, 86% yield) was obtained as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.4 (s, 1H), 7.98 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.36 (m, 1H), 7.00 (m, 1H), 6.66 (m, 1H), 5.60 (s, 1H), 3.96 (s, 1H), 3.79 (s, 1H), 3.73 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 167.4, 165.4, 144.7, 142.5, 133.1, 131.5, 121.6, 118.5, 117.2, 99.2, 52.9, 52.4, 51.6; MS(FAB+): Calcd for $[M+H]^+$ 294.0899, found 294.0981.

Synthesis of compound 1b

5-chloroisatic anhydride (2.51 g, 12.7 mmol), dimethyl acetylenedicarboxylate (1.87 mL, 15.3 mmol) and sodium methoxide (27.4 mg, 0.508 mmol) were stirred in MeOH (30 mL) at reflux temperature for 2 h. After cooling, the solvent was evaporated. The residue was then purified by flash column chromatography on silica gel (ethyl acetate/hexane). Compound **1b** (4.01 g, 96%) was obtained as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.4 (s, 1H), 7.95 (dd, *J* = 2.0 Hz, 1H), 7.31 (dd, *J* = 6.5, 2.0 Hz 1H), 7.58 (d, *J* = 6.5 Hz, 1H), 5.66 (s, 1H), 3.96 (s, 1H), 3.79 (s, 1H), 3.75 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 166.4, 165.0, 144.1, 141.2, 133.0, 131.1, 126.7, 119.7, 118.1, 100.3, 53.01, 52.64, 51.68; MS(FAB+): Calcd for $[M+H]^+$ 328.0510, found 328.0592.

Synthesis of compound 2a

Compound **1a** (5.67 g, 21.7 mmol) was stirred in diphenyl ether (18.1 g) at reflux temperature for 3 h. After cooling, the reaction mixture was purified by flash column chromatography on silica gel (ethyl acetate/hexane). Compound **2a** (4.19 g, 74%) was obtained as a colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 12.4 (s, 1H), 8.61 (m, 1H), 8.45 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.41 (dd, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 2.0 Hz, 1H), 4.06 (s, 3H), 4.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.0, 167.7, 162.8, 140.1, 137.2, 136.1, 132.8, 127.2, 123.0, 115.9, 112.5, 53.8, 52.8; MS(FAB+): Calcd for $[M+H]^+$ 262.0637, found 262.0720.

Synthesis of compound 2b

Compound **1b** (3.98 g, 12.1 mmol) was stirred in diphenyl ether (15.0 g) at reflux temperature for 3 h. After cooling, the reaction mixture was purified by flash column chromatography on silica gel (ethyl acetate/hexane). Compound **2b** (2.08 g, 58%) was obtained as a colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 12.3 (s, 1H), 8.61 (m, 1H), 8.38 (d, *J* = 2.5 Hz, 1H), 7.01 (d, *J* = 2.0 Hz, 1H), 4.06 (s, 3H), 4.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.8, 166.6, 162.5, 138.4, 137.3, 136.1, 131.9, 129.3, 128.2, 117.5, 112.5, 53.9, 55.1; MS(FAB+): Calcd for $[M+H]^+$ 296.0248, found 296.0327.

Synthesis of compound 3a

Compound **2a** (3.24 g, 12.4 mmol), 2,6-lutidine (2.16 mL, 18.6 mmol) and 4-(dimethylamino)pyridine (303 mg, 2.48 mmol) were dissolved in DCM (33 mL), and the solution was cooled to 0 °C. Trifluoromethanesulfonic anhydride (3.05 mL, 18.6 mmol) was added dropwise, and the reaction mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (ethyl acetate/hexane). Compound **3a** (4.43 g, 91%) was obtained as a brown solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.0 Hz, 2H), 8.23 (s, 1H), 7.86 (dd, *J* = 8.0 Hz, 1H), 4.09 (s, 3H), 4.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 164.4, 153.6, 149.7, 146.7, 133.0, 132.9, 129.6, 124.0, 122.5, 112.7, 53.6, 53.0; MS(FAB+): Calcd for $[M+H]^+$ 393.0130, found 393.0217.

Synthesis of compound 3b

Compound **2b** (1.98 g, 6.68 mmol), 2,6-lutidine (1.17 mL, 10.0 mmol) and 4-(dimethylamino)pyridine (163 mg, 1.34 mmol) were dissolved in DCM (22 mL), and the solution was cooled to 0 °C. Trifluoromethanesulfonic anhydride (1.64 mL, 10.0 mmol) was added dropwise, and the reaction mixture was stirred at room temperature for 3 h. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (ethyl acetate/hexane). Compound **3a** (1.82 g, 64%) was obtained as a brown solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.20 (s, 2H), 4.09 (s, 3H), 4.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.4, 164.1, 152.5, 149.7, 145.1, 136.3, 134.4, 134.0, 123.3, 122.7, 113.3, 53.7, 53.2; MS(FAB+): Calcd for $[M+H]^+$ 427.9740, found 427.9825.

Synthesis of compound 4a

Compound **3a** (2.21 g, 5.62 mmol) was dissolved in dioxane (40 mL), and methylboronic acid (1.01 g, 16.9 mmol), K_2CO_3 (3.11 g, 22.5 mmol), and [1,1'-bis(diphenylphosphino)ferrocene] dichloropalladium(II) complex with dichloromethane (459 mg, 0.562 mmol) were added to the solution. The solution was heated to reflux for 2 h. After cooling, the organic layer was washed with water, dried with Na_2SO_4 and evaporated. The residue was then purified by flash column chromatography on silica gel (ethyl acetate/hexane). Compound **4a** (1.25 g, 86%) was obtained as a brown solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.15 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.10 (s, 1H), 7.69 (dd, *J* = 8.5 Hz, 1H), 4.09 (s, 3H), 4.05 (s, 3H), 2.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 166.1, 148.3, 146.1, 144.8, 132.8, 131.3, 129.4, 127.3, 127.2, 122.2, 53.1, 52.7, 19.2; MS(FAB+): Calcd for $[M+H]^+$ 260.0845, found 260.0927.

Synthesis of compound 4b

Compound **3b** (1.61 g, 3.75 mmol) was dissolved in dioxane (20 mL), and methylboronic acid (449 mg, 7.5 mmol), K_2CO_3 (2.07 g, 15.0 mmol), and [1,1'-bis(diphenylphosphino)ferrocene] dichloropalladium(II) complex with dichloromethane (306 mg, 0.375 mmol) were added to the solution. The solution was heated to reflux for 7 h. After cooling, the organic layer was washed with water, dried with Na_2SO_4 and evaporated. The residue was then purified by flash column chromatography on silica gel (ethyl acetate/hexane). Compound **4b** (705 mg, 64%) was obtained as a brown solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 2.5 Hz, 1H), 8.11 (s, 1H), 8.08 (d, *J* = 2.5 Hz, 1H), 4.08 (s, 3H), 4.04 (s, 3H), 2.77 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 165.7, 148.5, 145.4, 143.3, 134.4, 133.6, 132.1, 130.3, 126.1, 122.9, 53.18, 52.93, 19.15; MS(FAB+): Calcd for $[M+H]^+$ 294.0455, found 294.0535.

Synthesis of compound 5a

Compound **4a** (500 mg, 1.93 mmol) and selenium dioxide (429 mg, 3.86 mmol) were stirred in dioxane (8 mL) at 80 ºC for 3 h. After cooling, the solution was filtered and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (ethyl acetate/hexane). Compound **5a** (232 mg, 44%) was obtained as a colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.5 (s, 1H), 9.27 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.64 (s, 1H), 8.22 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.88 (dd, *J* = 8.5 Hz, 1H), 4.11 (s, 3H), 4.09 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.4, 167.3, 165.0, 149.2, 154.9, 137.9, 132.9, 131.8, 130.6, 128.0, 126.7, 124.7, 53.5, 52.9; MS(FAB+): Calcd for $[M+H]^+$ 274.0637, found 274.0718.

Synthesis of compound 5b

Compound **4b** (251 mg, 0.856 mmol) and selenium dioxide (104 mg, 0.942 mmol) were stirred in dioxane (8 mL) at 80 ºC for 3 h. After cooling, the solution was filtered and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (ethyl acetate/hexane). Compound **5b** (113 mg, 43%) was obtained as a colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.5 (s, 1H), 9.32 (d, *J* = 2.5 Hz, 1H), 8.64 (s, 1H), 8.16 (d, *J* = 2.5 Hz, 1H), 4.10 (s, 3H), 4.09 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.0, 164.9, 164.7, 149.2, 144.4, 137.6, 136.9, 134.2, 132.8, 127.8, 127.1, 125.3, 53.54, 53.10; MS(FAB+): Calcd for $[M+H]^+$ 308.0248, found 308.0326.

Synthesis of compound 6a

Compound **5a** (97.8 mg, 0.358 mmol) and 4-chlororesorcinol (114 mg, 0.788 mmol) were added to a flame-dried three-necked flask under N_2. A DCM/Et_2O (1:1) (10 mL) mixture was added to the flask, and then $MeSO_3H$ (800 μL) was added dropwise at room temperature. The solution was stirred for 17 h. After confirming the completion of the reaction, the solution was diluted with Et_2O, poured into saturated aqueous $NaHCO_3$ and acidified with 2 M HCl aq. to pH 5~6. The solution was extracted with ethyl acetate, and the combined organic extracts were dried with Na_2SO_4 and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (DCM/MeOH). Compound **6a** (166 mg, 85%) was obtained as a pink solid.

^{1}H NMR (500 MHz, Acetone-d_6) δ 8.24 (dd, *J* = 9.0, 1.5 Hz, 1H), 7.92 (dd, *J* = 7.0, 1.5 Hz, 1H), 7.77 (s, 1H), 7.70 (dd, *J* = 9.0, 7.0 Hz, 1H), 6.76 (s, 1H), 6.71 (s, 2H), 6.70 (s, 2H), 3.96 (s, 3H), 3.91 (s,

3H); ^{13}C NMR (125 MHz, Acetone-d_6) δ 170.0, 167.4, 156.0, 154.5, 154.1, 150.3, 146.5, 137.1, 132.1, 130.5, 129.9, 129.5, 128.1, 122.6, 122.0, 112.4, 106.0, 53.87, 53.47, 40.46; MS(FAB+): Calcd for $[M+H]^+$ 544.0488, found 544.0575.

Synthesis of compound 6b

Compound **5b** (101 mg, 0.330 mmol) and 4-chlororesorcinol (105 mg, 0.725 mmol) were added to a flame-dried three-necked flask under N_2. A DCM/Et_2O (1:1) (10 mL) mixture was added to the flask, and then $MeSO_3H$ (800 μL) was added dropwise at room temperature. The solution was stirred for 20 h. After confirming the completion of the reaction, the solution was diluted with Et_2O, poured into saturated aqueous $NaHCO_3$ and acidified with 2 M HCl aq. to pH 5~6. The solution was extracted with ethyl acetate, and the combined organic extracts were dried with Na_2SO_4 and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (DCM/MeOH). Compound **6b** (130 mg, 68%) was obtained as a pink solid.

^{1}H NMR (500 MHz, Acetone-d_6) δ 8.24 (d, J = 2.5 Hz, 1H), 7.93 (d, J = 2.5 Hz, 1H), 7.81 (s, 1H), 6.76 (s, 2H), 6.71 (s, 2H), 6.68 (s, 1H), 3.98 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (125 MHz, Acetone-d_6) δ 168.5, 167.1, 155.9, 154.6, 153.6, 150.7, 145.0, 138.9, 134.9, 132.2, 131.0, 130.9, 126.9, 122.8, 122.0, 112.6, 106.0, 53.99, 53.82, 40.31; MS(FAB+): Calcd for $[M+H]^+$ 578.0098, found 578.0182.

Synthesis of compound 7a

Compound **6a** (122 mg, 0.223 mmol) and *p*-TsOH·H_2O (4.25 mg, 22.3 μmol) were dissolved in CH_3COOH (6 mL) and stirred at 60 °C under N_2 for 19 h. After cooling, the solution was evaporated under reduced pressure and purified by flash column chromatography on silica gel (DCM/MeOH). Compound **7a** (77.0 mg, 66%) was obtained as an orange solid.

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.25 (s, 1H), 8.01 (dd, J = 7.0, 1.5 Hz, 1H), 7.83 (dd, J = 8.5, 1.5 Hz, 1H), 7.71 (dd, J = 7.0, 8.5 Hz, 1H), 7.06 (s, 2H), 6.83 (s, 2H), 4.00 (s, 3H), 3.97 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 167.1, 164.0, 147.6, 143.7, 143.3, 139.4, 133.3, 129.7, 128.5, 127.5, 127.4, 126.4, 122.1, 103.4, 52.27, 51.88; MS(FAB+): Calcd for $[M+H]^+$ 524.0226, found 524.0314.

Synthesis of compound 7b

Compound **6b** (120 mg, 0.207 mmol) and *p*-TsOH·H_2O (3.94 mg, 20.7 μmol) were dissolved in CH_3COOH (8 mL) and stirred at 60 °C under N_2 for 19 h. After cooling, the solution was evaporated under reduced pressure and purified by flash column chromatography on silica gel (DCM/MeOH). Compound **7b** (71.7 mg, 62%) was obtained as an orange solid.

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.25 (s, 1H), 8.17 (d, J = 2.5 Hz, 1H), 8.01 (d, J = 2.5 Hz, 1H), 7.08 (s, 2H), 6.78 (s, 2H), 4.01 (s, 3H), 3.97 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.8, 164.9, 148.9, 144.1, 143.2, 140.2, 136.3, 134.2, 131.1, 128.8, 128.5, 126.9, 124.1, 104.4, 53.41, 53.22; MS(FAB+):

Calcd for $[M+H]^+$ 557.9836, found 557.9905.

Synthesis of MGQ-1

Compound **7a** (20.0 mg, 38.1 μmol) was dissolved in 4 mL of MeOH/H_2O (3:1). A 2 M NaOH solution (300 μL) was added dropwise at 0 °C. The reaction mixture was then warmed to room temperature. After stirring for 3 h, the solution was acidified with 2 M HCl aq. and then extracted with ethyl acetate. The combined organic extracts were dried with Na_2SO_4 and evaporated under reduced pressure. The residue was purified by reversed-phase HPLC under the following conditions: A/B = 10/90 (0 min), 30/70 (30 min) (solvent A: MeCN; solvent B: 50 mM trimethylamine acetate (TEAA)). After lyophilization, MGQ-1·2.5Et_3N (18.6 mg, 65%) was obtained as a purple powder.

^1H NMR (500 MHz, CD_3CN) δ 8.71 (dd, *J* = 7.0, 1.5 Hz, 1H), 8.26 (s, 1H), 7.88 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.86 (dd, *J* = 7.0, 8.0 Hz, 1H), 6.79 (s, 2H), 6.39 (s, 2H); ^{13}C NMR (125 MHz, CD_3CN) δ 174.7, 167.7, 167.2, 157.5, 154.3, 145.6, 145.2, 144.3, 135.4, 130.9, 129.1, 128.8, 127.7, 127.6, 126.1, 123.4, 110.4, 104.5; MS(FAB+): Calcd for $[M+H]^+$ 495.9913, found 495.9998.

Synthesis of MGQ-2

Compound **7b** (13.9 mg, 24.9 μmol) was dissolved in 4 mL of MeOH/H_2O (3:1). A 2 M NaOH solution (300 μL) was added dropwise at 0 °C. The reaction mixture was then warmed to room temperature. After stirring for 3 h, the solution was acidified with 2 M HCl aq. and then extracted with ethyl acetate. The combined organic extracts were dried with Na_2SO_4 and evaporated under reduced pressure. The residue was purified by reversed-phase HPLC under the following conditions: A/B = 15/85 (0 min), 45/55 (30 min) (solvent A: MeCN; solvent B: 50 mM TEAA). After lyophilization, MGQ-2·2.5Et_3N (8.98 mg, 46%) was obtained as a purple powder.

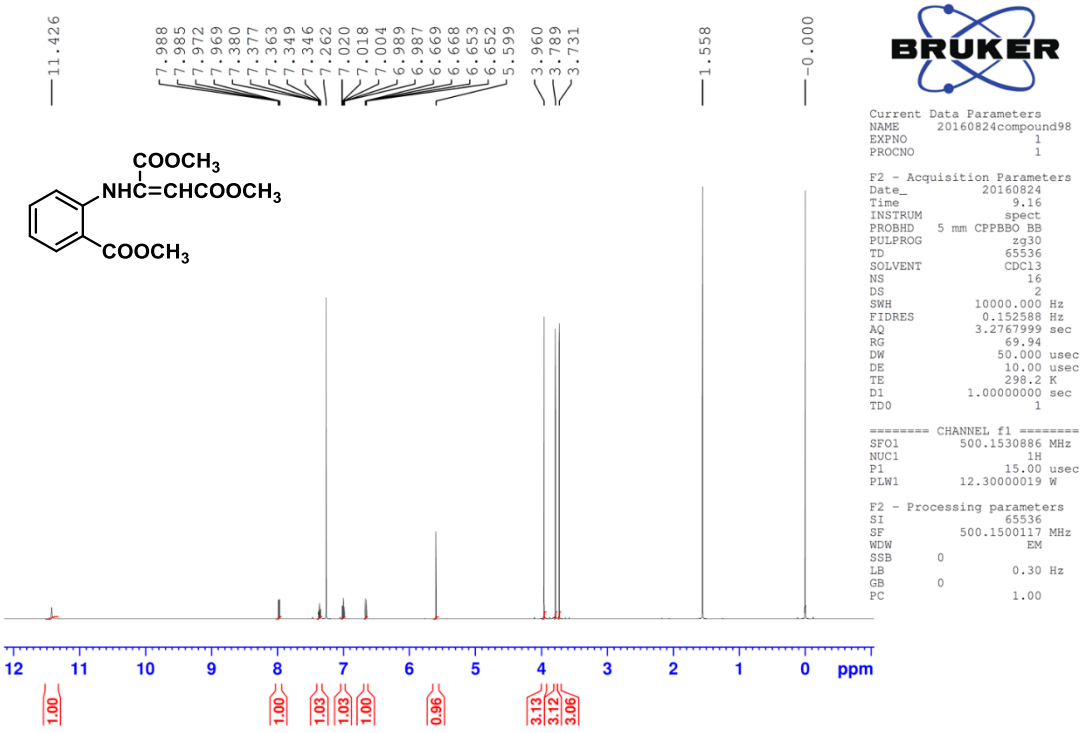
^1H NMR (500 MHz, CD_3CN) δ 8.55 (d, *J* = 2.5 Hz, 1H), 8.27 (s, 1H), 7.88 (d, *J* = 2.5 Hz, 1H), 6.78 (s, 2H), 6.39 (s, 2H); ^{13}C NMR (125 MHz, CD_3CN) δ 174.7, 167.1, 166.8, 157.6, 154.6, 144.9, 143.9, 143.5, 135.2, 134.6, 129.2, 129.0, 128.9, 127.5, 124.4, 110.5, 104.5; MS(FAB+): Calcd for $[M+H]^+$ 529.9523, found 529.9593.

Synthesis of MGQ-2(AM)

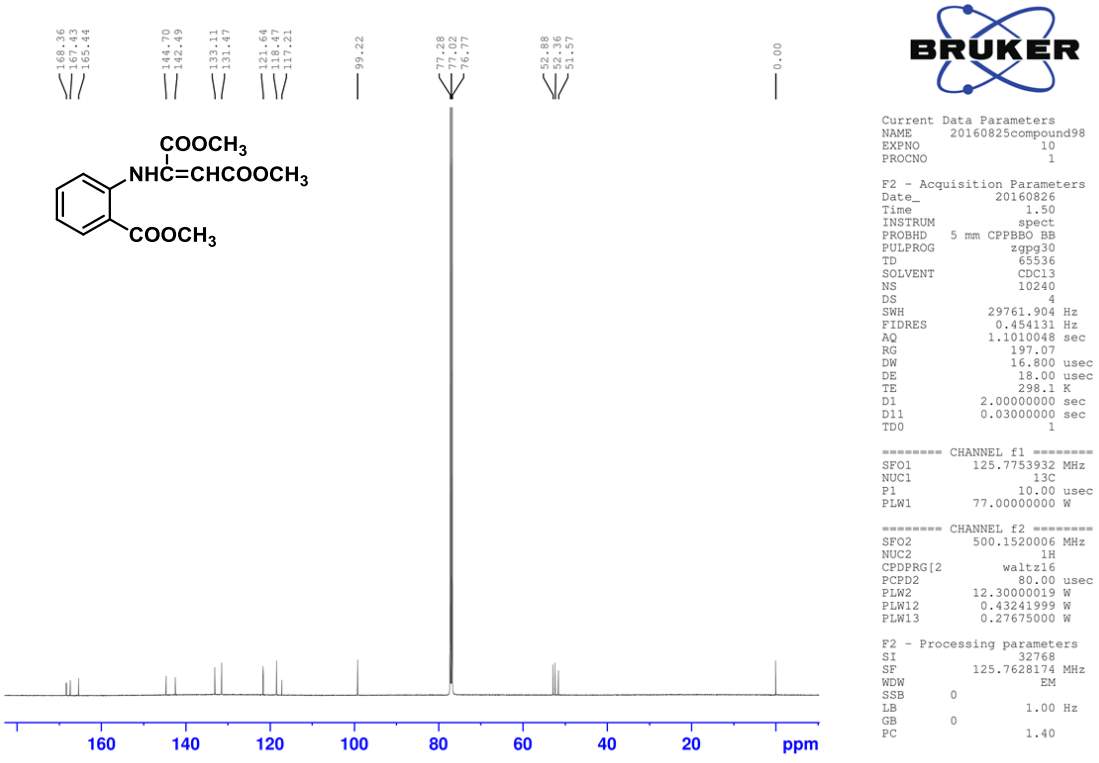
MGQ-2 (8.50 mg, 16.0 μmol) and DMF (1.5 mL) was added to a flame-dried three-necked flask under N_2. DIEA (13.8 μL, 80.0 μmol) and bromomethyl acetate (7.84 μL, 80.0 μmol) were added at room temperature. After stirring for 18 h, the solvent was removed under reduced pressure, and ethyl acetate was added to the residue and then it was washed with water. The organic layer was washed with brine, dried with Na_2SO_4 and evaporated. The residue was purified by HPLC under the following conditions: A/B = 55/45 (0 min), 65/35 (30 min) (solvent A: 0.1% HCOOH in MeCN; solvent B: 0.1% HCOOH in H_2O). After lyophilization, MGQ-2(AM) (4.06 mg, 34%) was obtained as an orange solid.

^{1}H NMR (500 MHz, CD_3CN) δ 8.12 (s, 1H), 8.03 (d, *J* = 2.0 Hz, 1H), 7.45 (d, *J* = 2.0 Hz, 1H), 7.35 (s, 1H), 7.03 (s, 1H), 6.92 (s, 1H), 6.46 (s, 1H), 5.97 (s, 2H), 5.94 (s, 2H), 5.84 (s, 2H), 2.10 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (125 MHz, CD_3CN) δ 177.8, 170.3, 170.2, 170.1, 165.2, 163.5, 158.6, 157.4, 153.0, 148.6, 144.2, 142.6, 140.6, 136.4, 135.7, 135.1, 132.7, 129.3, 129.2, 128.2, 127.7, 124.4, 121.2, 121.0, 116.4, 105.9, 104.0, 85.69, 81.12, 80.57, 20.59, 20.50; MS(FAB+): Calcd for $[M+H]^+$ 746.0157, found 746.0234.

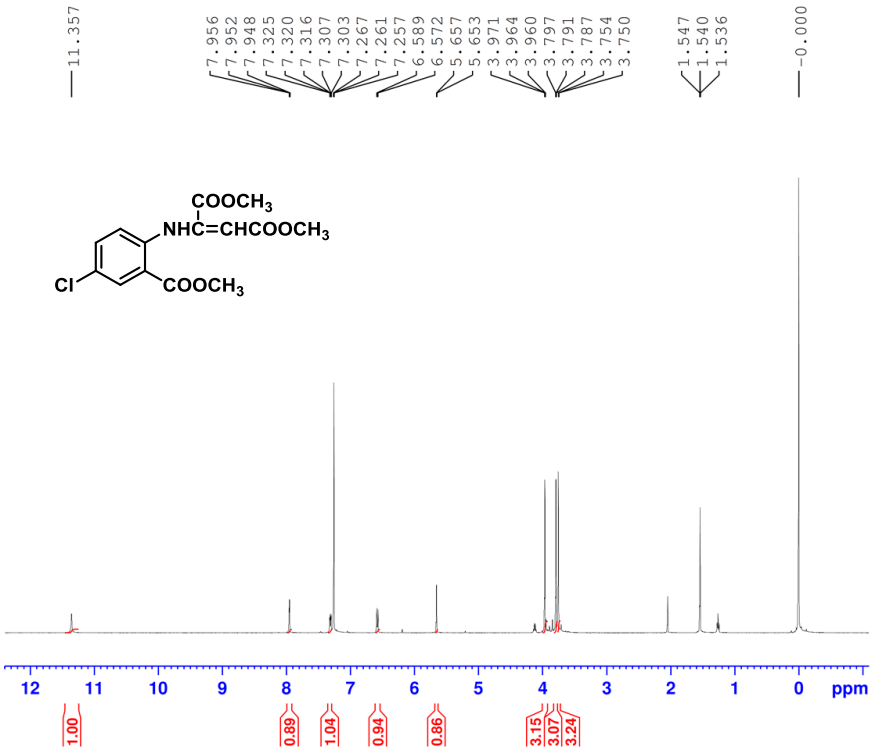
3. NMR Spectra of Compounds

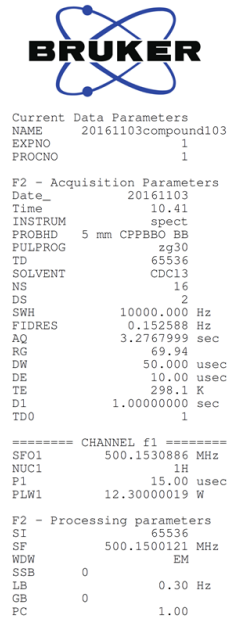


^{1}H NMR spectrum of compound **1a**

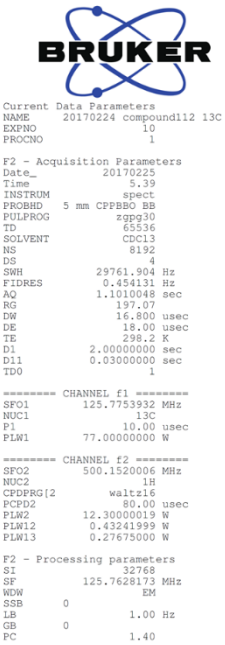


^{13}C NMR spectrum of compound **1a**





^{1}H NMR spectrum of compound **1b**



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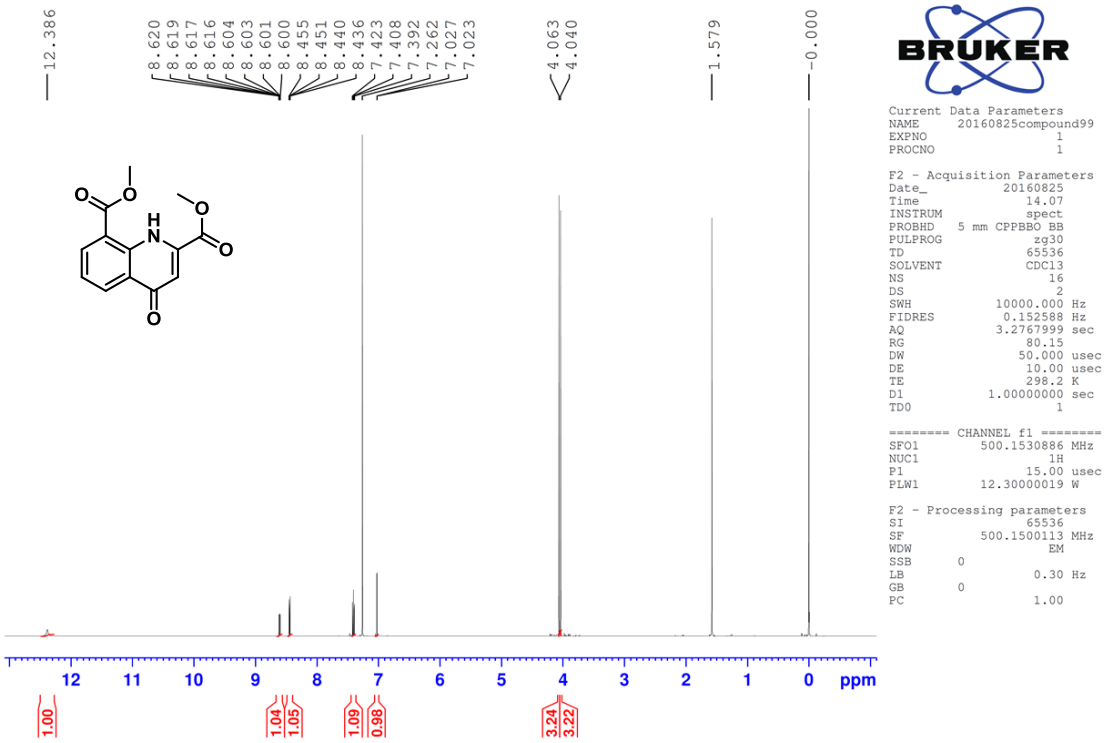
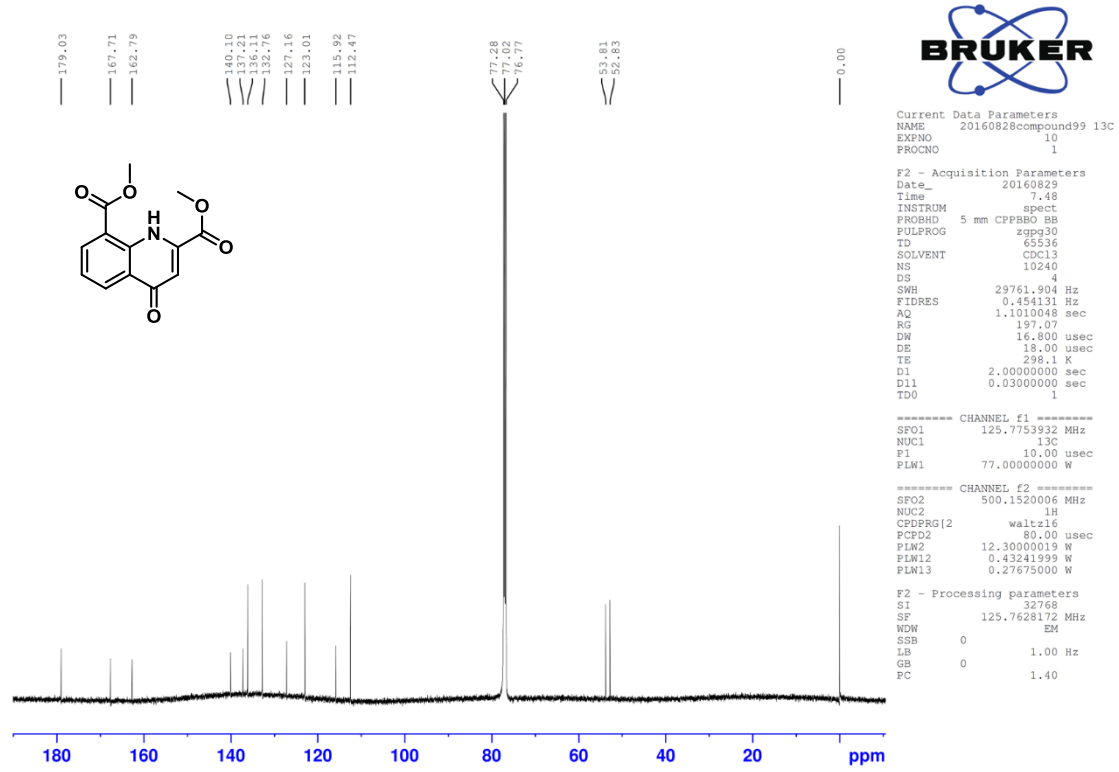
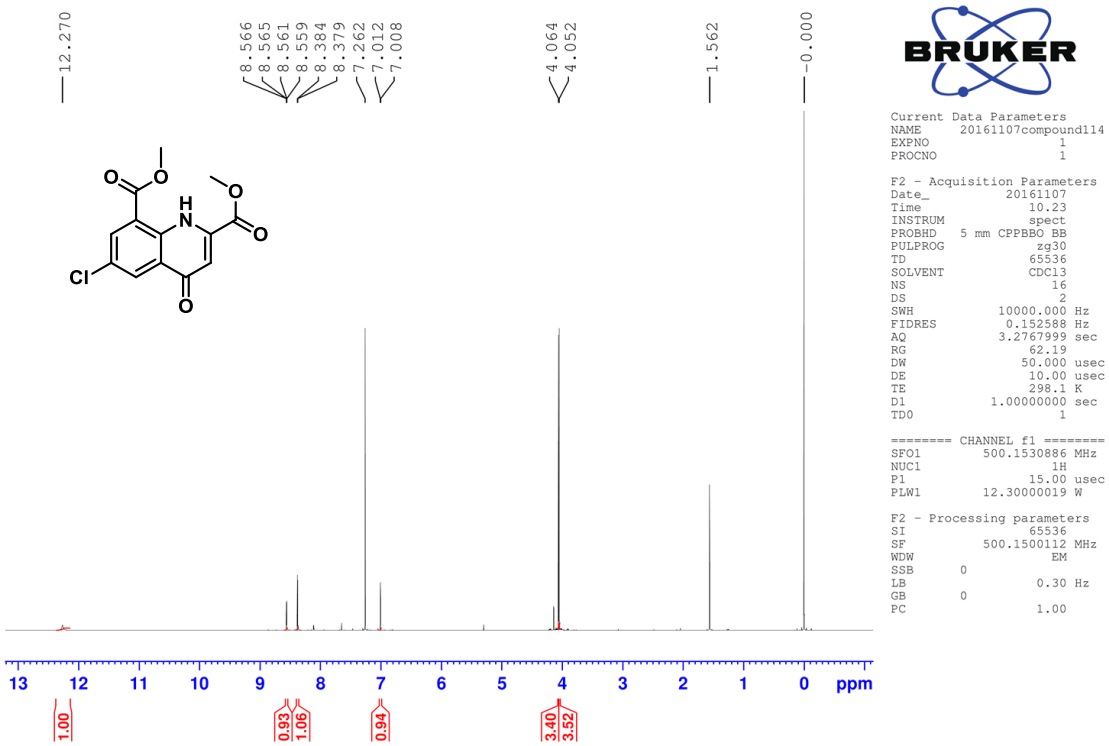


^{1}H NMR spectrum of compound **2a**



^{13}C NMR spectrum of compound **2a**



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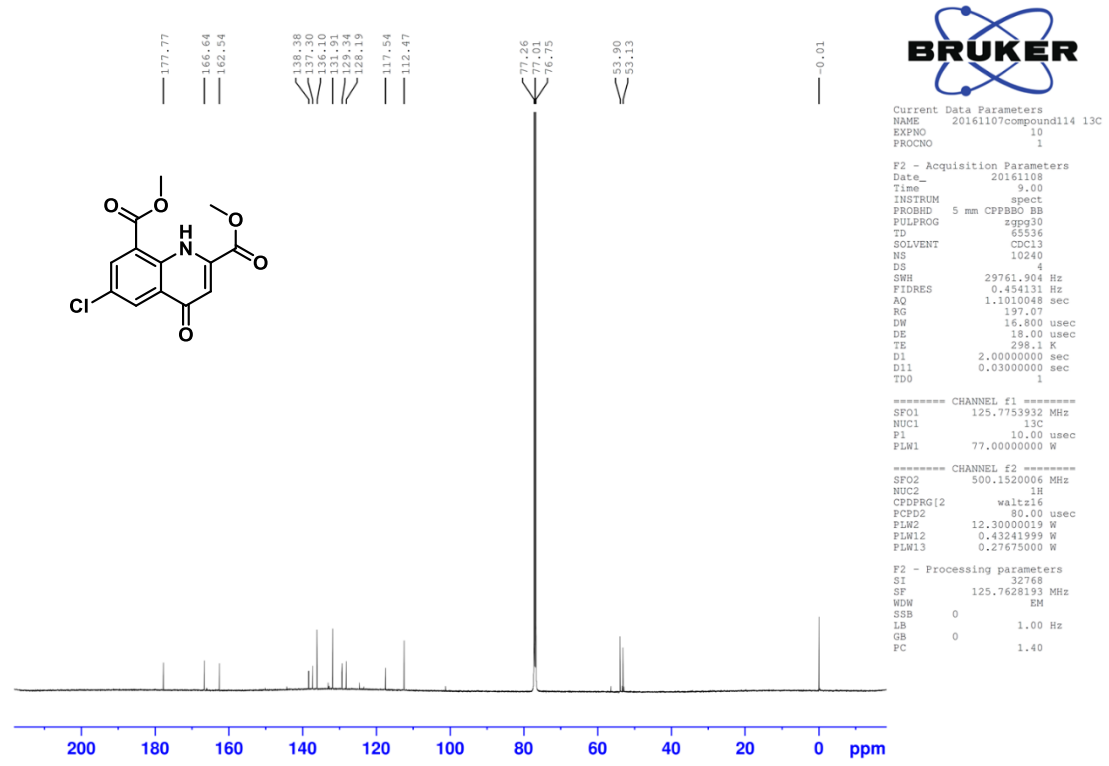
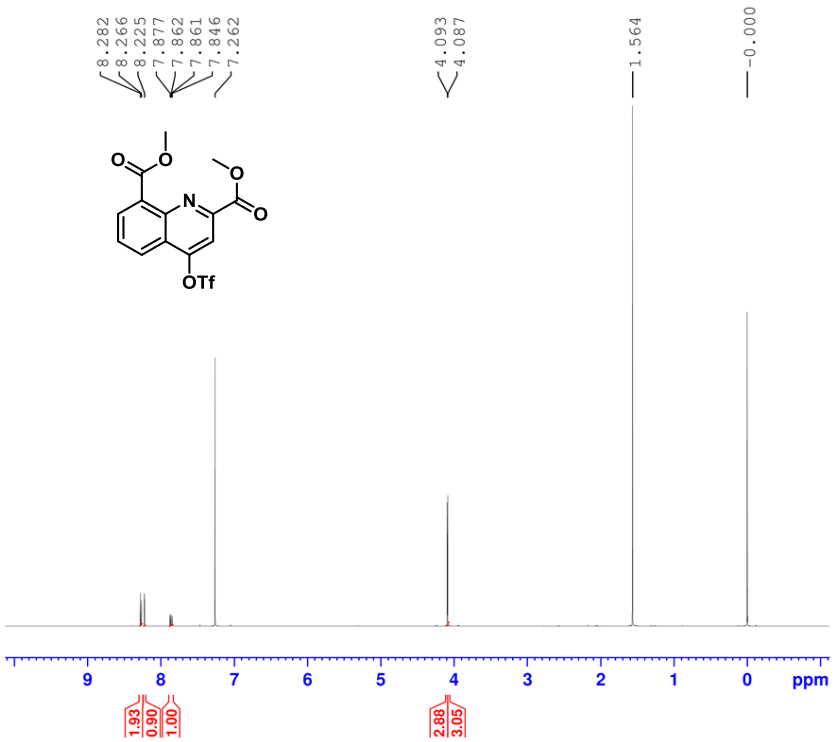


^{13}C NMR spectrum of compound **2b**



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PROCNO 1

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F2 - Processing parameters
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LB 0.30 Hz
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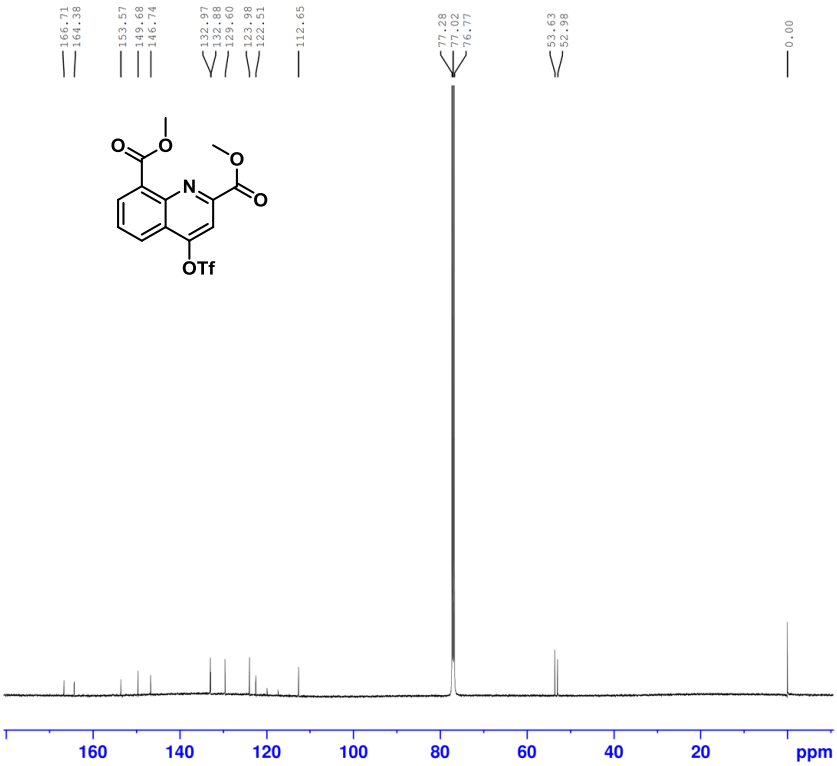

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EXPNO 10
PROCNO 1

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FIDRES 0.454131 Hz
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TE 298.1 K
D1 2.00000000 sec
D11 0.03000000 sec
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NUC1 13C
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======== CHANNEL f2 ========
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NUC2 1H
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PCPD2 80.00 usec
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PLW12 0.43241999 W
PLW13 0.27675000 W

F2 - Processing parameters
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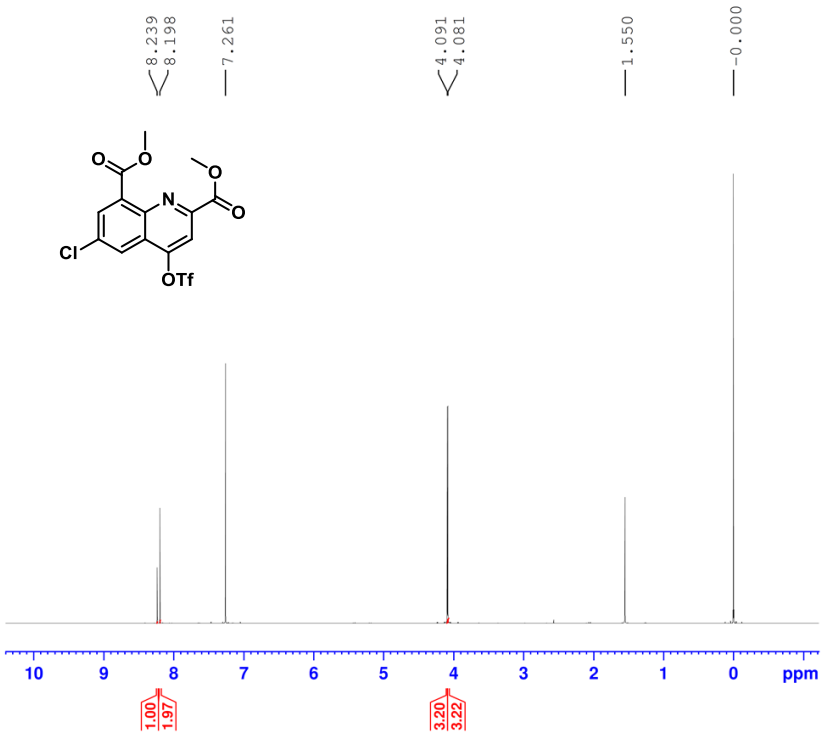
^{13}C NMR spectrum of compound **3a**



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PROCNO 1

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SOLVENT CDCl3
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DS 2
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FIDRES 0.152588 Hz
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RG 69.94
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D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
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NUC1 1H
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PLW1 12.30000019 W

F2 - Processing parameters
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LB 0.30 Hz
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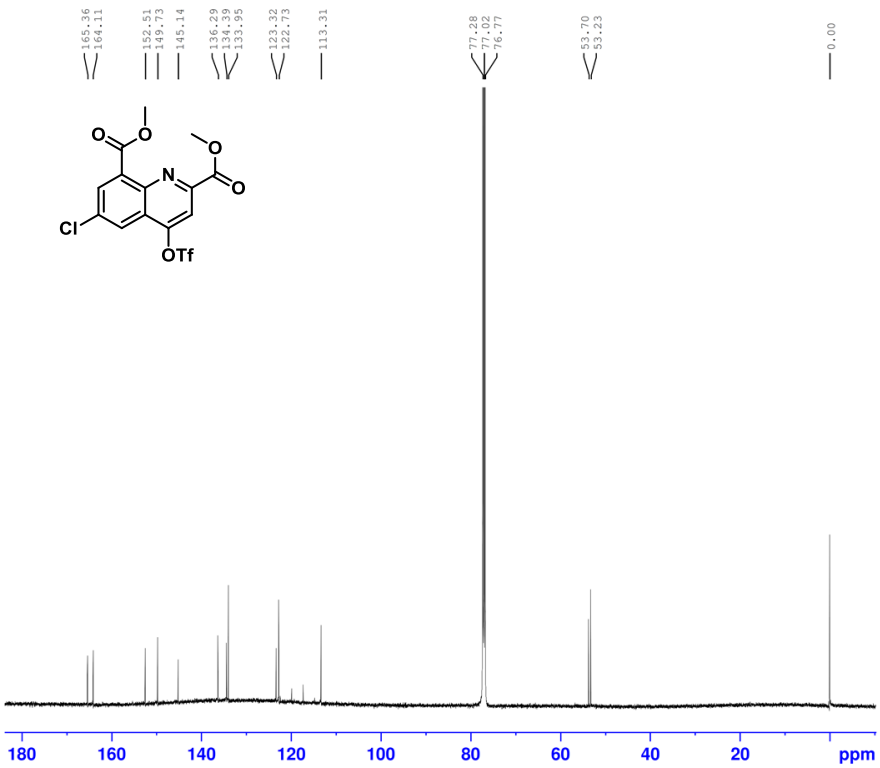
^{1}H NMR spectrum of compound **3b**



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PROCNO 1

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SOLVENT CDCl3
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RG 197.07
DW 16.800 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

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NUC1 13C
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PLW1 77.00000000 W

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NUC2 1H
CPDPRG[2 waltz16
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PLW12 0.43241999 W
PLW13 0.27675000 W

F2 - Processing parameters
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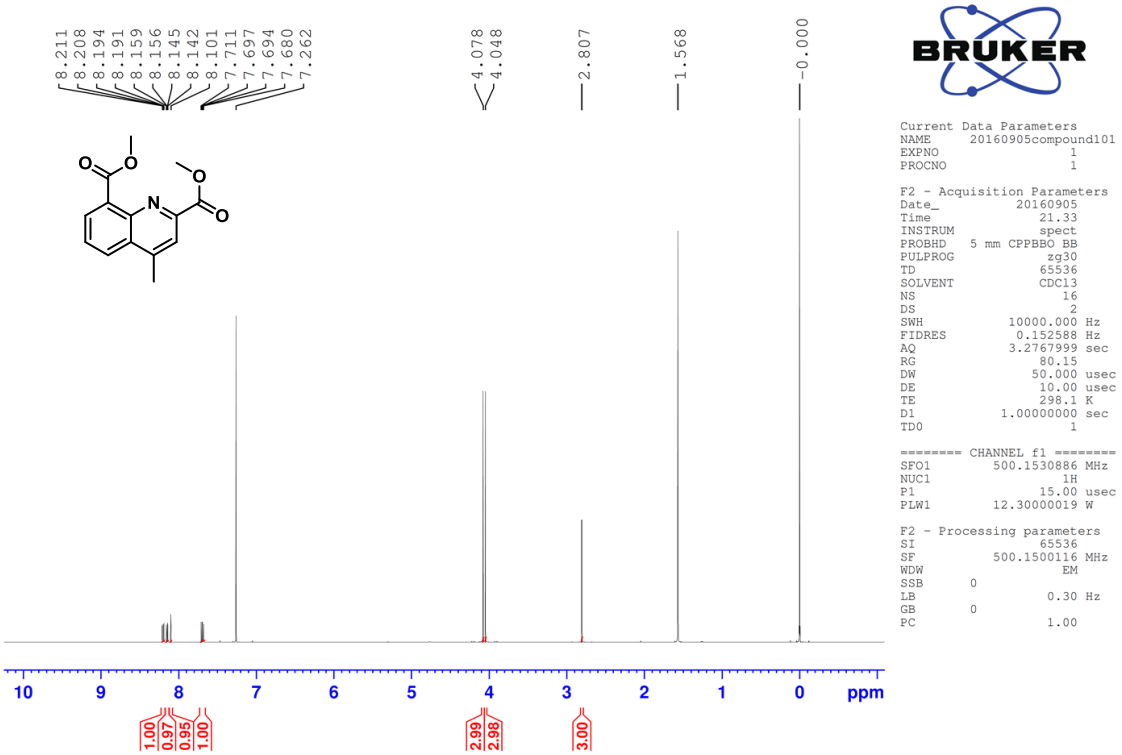
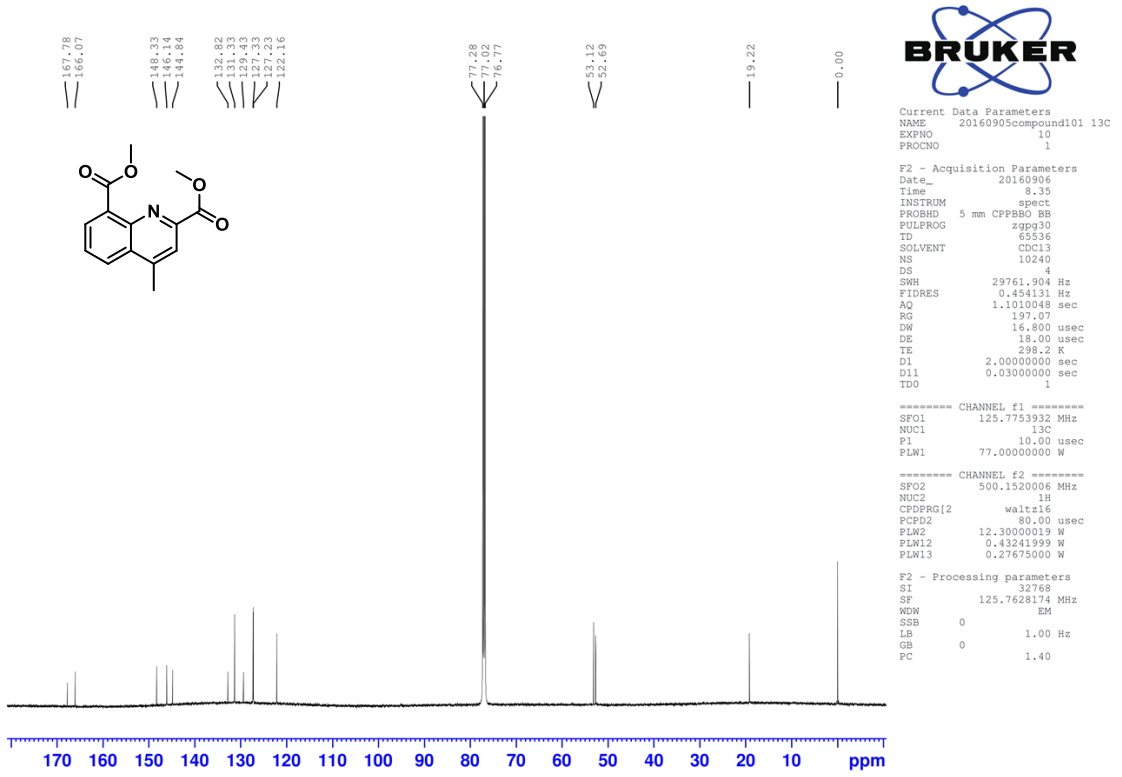
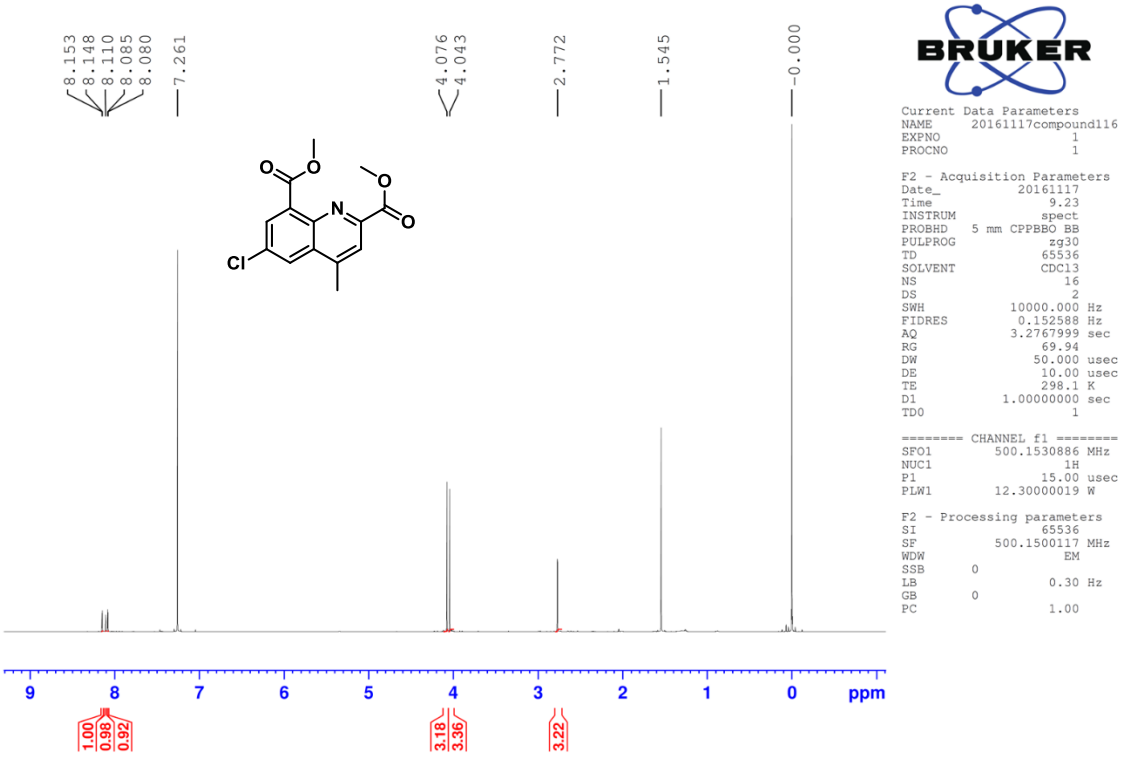
^{13}C NMR spectrum of compound **3b**



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



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



BRUKER

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PROCNO                      1

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TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
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FIDRES            0.152588 Hz
AQ                3.2767999 sec
RG                     69.94
DW                  50.000 usec
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TE                  298.1 K
D1                1.00000000 sec
TD0                       1

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NUC1                      1H
P1                   15.00 usec
PLW1           12.30000019 W

F2 - Processing parameters
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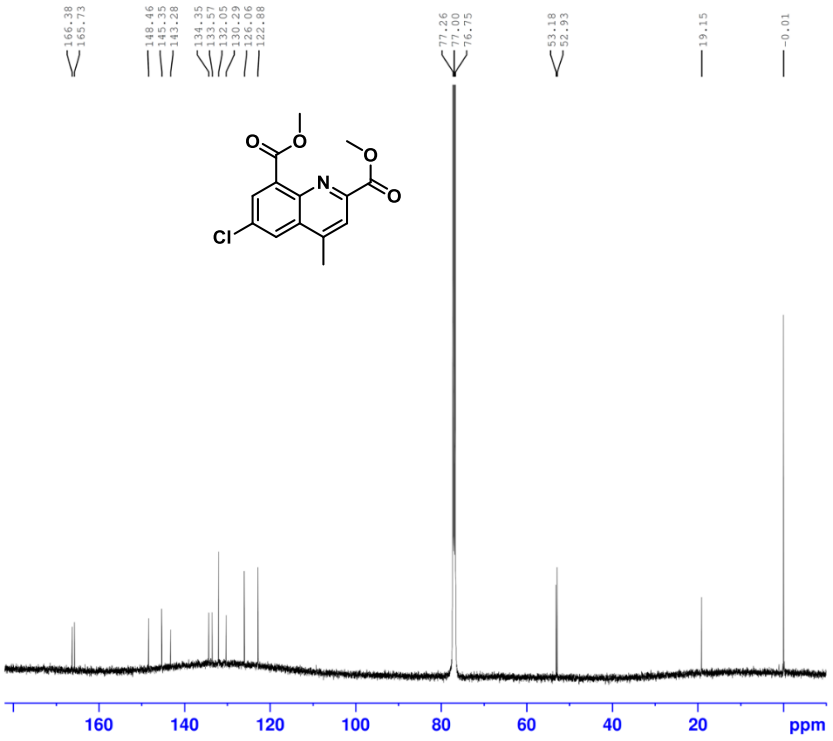
^{1}H NMR spectrum of compound **4b**



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PROCNO                      1

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INSTRUM               spect
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PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     8192
DS                        4
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FIDRES            0.454131 Hz
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RG                    197.07
DW                  16.800 usec
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TD0                       1

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F2 - Processing parameters
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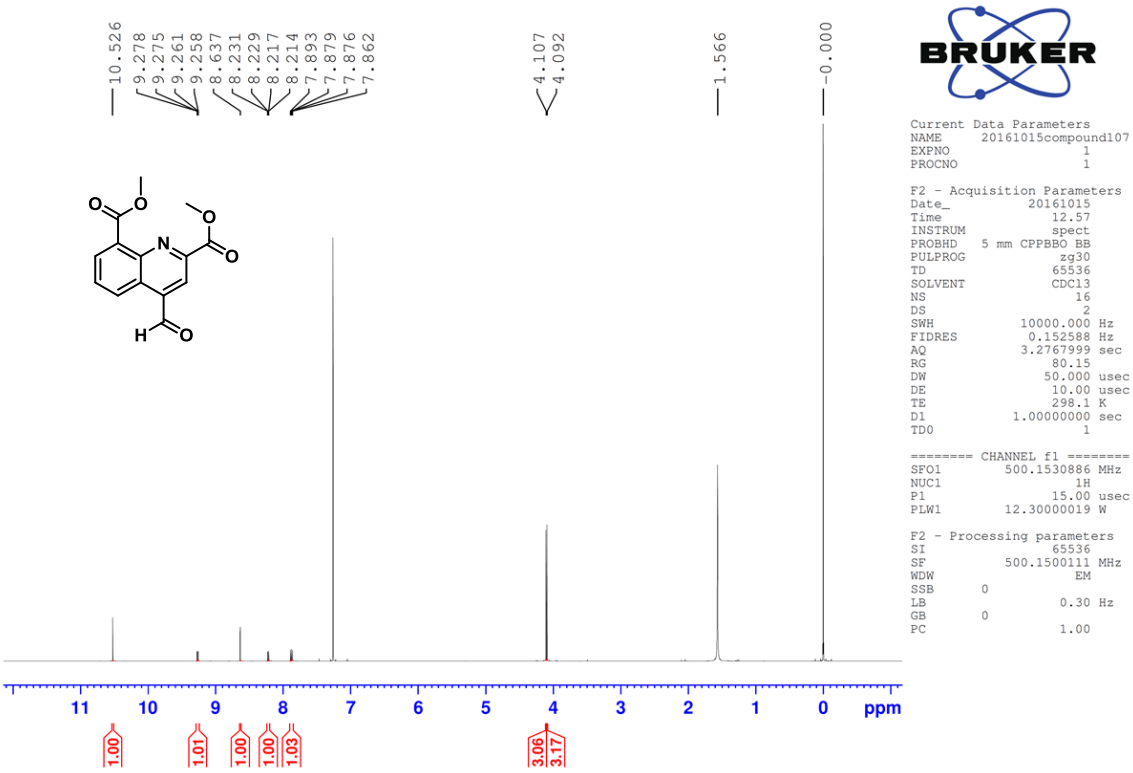
^{13}C NMR spectrum of compound **4b**



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EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
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FIDRES 0.152588 Hz
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RG 80.15
DW 50.000 usec
DE 10.00 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1

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NUC1 1H
P1 15.00 usec
PLW1 12.30000019 W

F2 - Processing parameters
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LB 0.30 Hz
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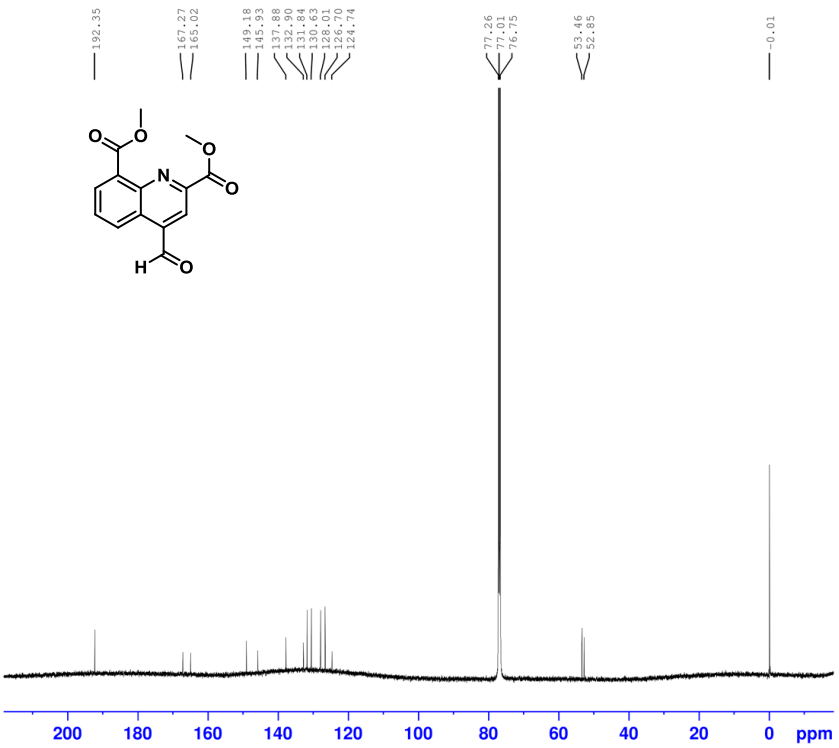
^{1}H NMR spectrum of compound **5a**



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PROCNO 1

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FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 197.07
DW 16.800 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
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======== CHANNEL f1 ========
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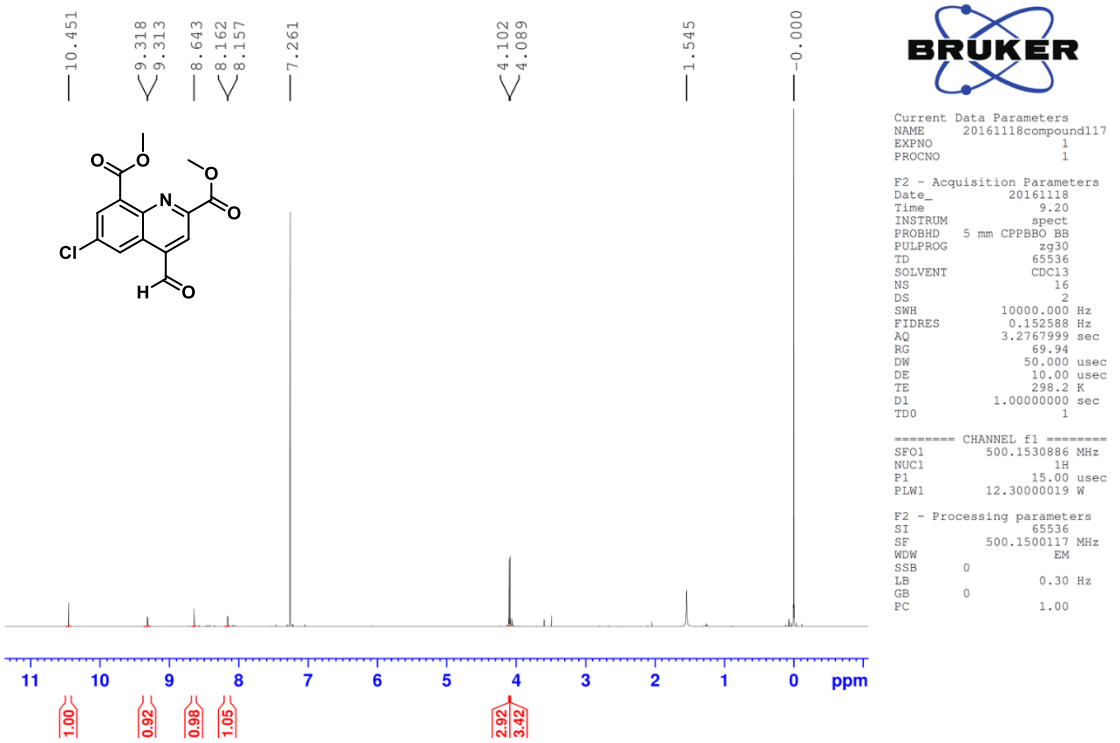
^{13}C NMR spectrum of compound **5a**



BRUKER

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PROCNO                      1

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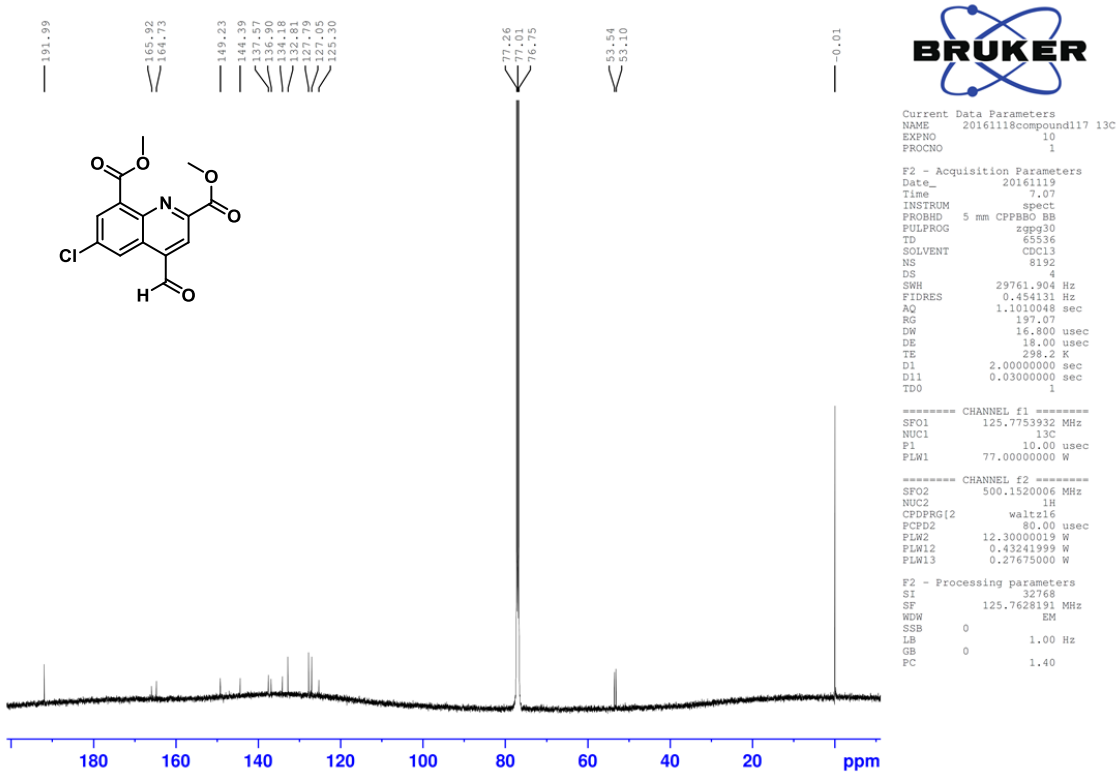
RG                 69.94
DW                 50.000 usec
DE                 10.00 usec
TE                 298.2 K
D1              1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          500.1530886 MHz
NUC1                   1H
P1                  15.00 usec
PLW1          12.30000019 W

F2 - Processing parameters
SI                 65536
SF            500.1500117 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

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



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```
Current Data Parameters
NAME      20161118compound117 13C
EXPNO                      10
PROCNO                      1

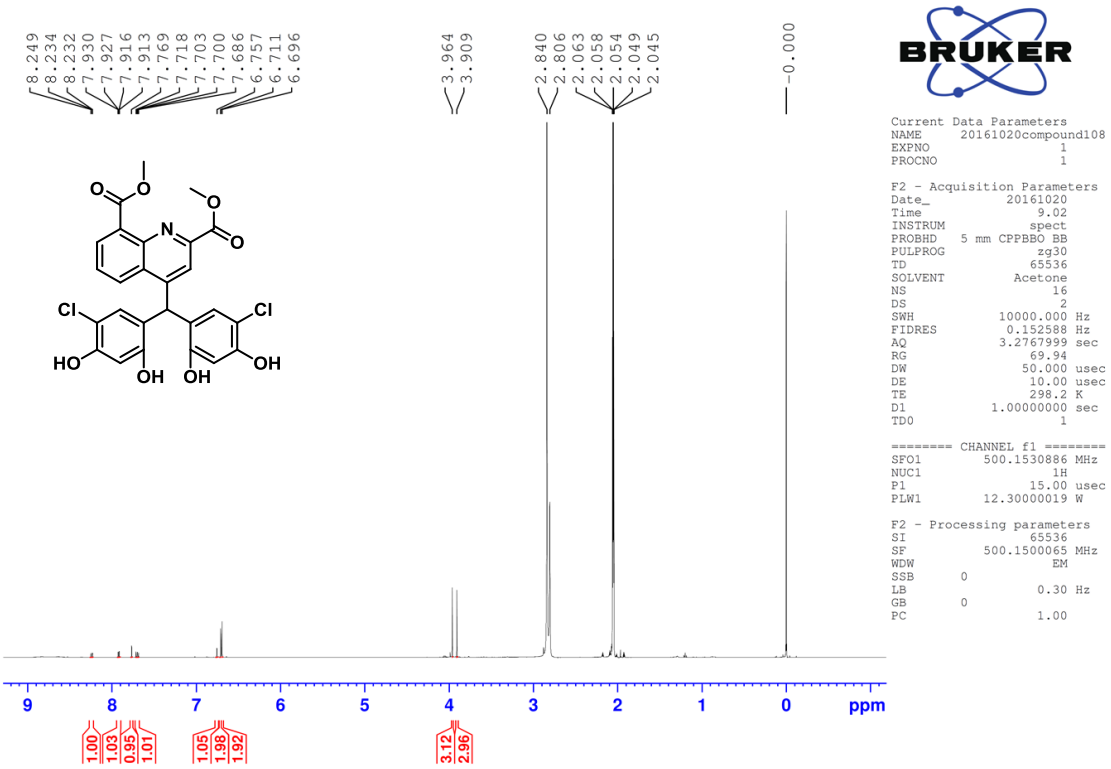
F2 - Acquisition Parameters
Date_           20161119
Time                7.07
INSTRUM            spect
PROBHD   5 mm CPPBBO BB
PULPROG           zgpg30
TD                 65536
SOLVENT            CDC13
NS                  8192
DS                     4
SWH            29761.904 Hz
FIDRES             0.454131 Hz
AQ              1.1010048 sec
RG                197.07
DW                 16.800 usec
DE                 18.00 usec
TE                 298.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          125.7753932 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          77.00000000 W

======== CHANNEL f2 ========
SFO2          500.1520006 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          12.30000019 W
PLW12          0.43241999 W
PLW13          0.27675000 W

F2 - Processing parameters
SI                 32768
SF            125.7628191 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

^{13}C NMR spectrum of compound **5b**



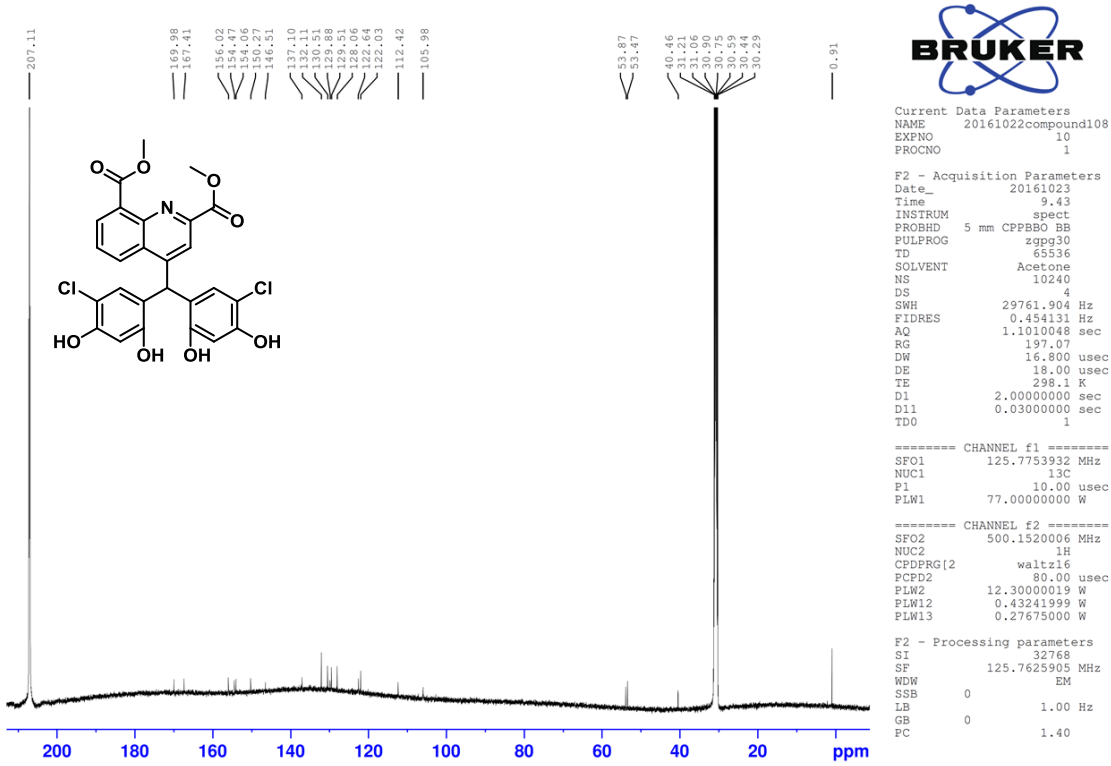
Current Data Parameters
NAME 20161020compound108
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20161020
Time 9.02
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 69.94
DW 50.000 usec
DE 10.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 500.1530886 MHz
NUC1 1H
P1 15.00 usec
PLW1 12.30000019 W

F2 - Processing parameters
SI 65536
SF 500.1500065 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

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



Current Data Parameters
NAME 20161022compound108
EXPNO 10
PROCNO 1

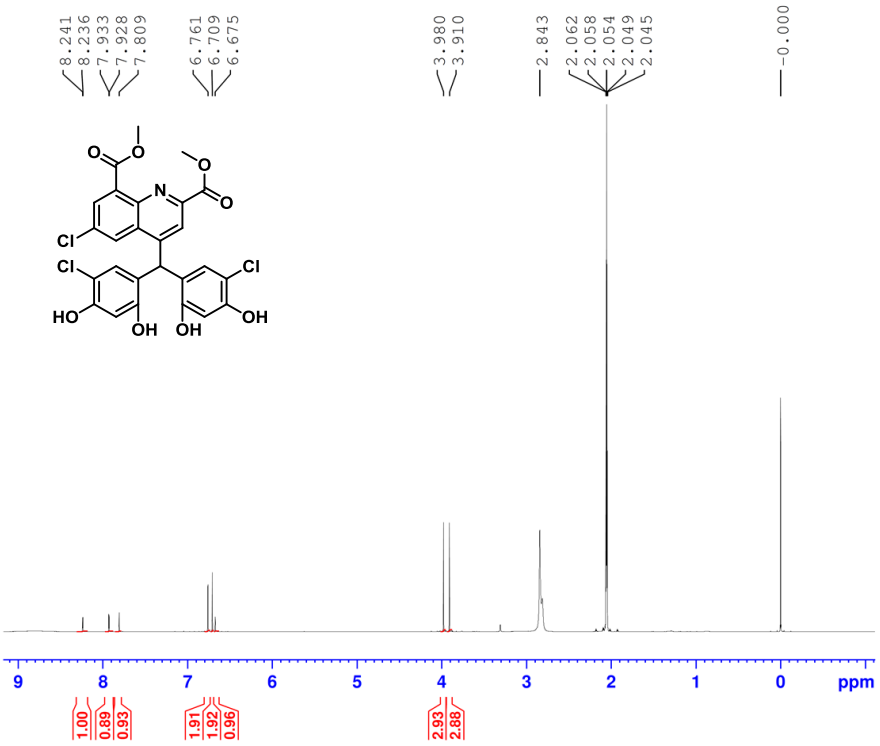
F2 - Acquisition Parameters
Date_ 20161023
Time 9.43
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 10240
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 197.07
DW 16.800 usec
DE 18.00 usec
TE 298.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 125.7753932 MHz
NUC1 13C
P1 10.00 usec
PLW1 77.00000000 W

======== CHANNEL f2 ========
SFO2 500.1520006 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 12.30000019 W
PLW12 0.43241999 W
PLW13 0.27675000 W

F2 - Processing parameters
SI 32768
SF 125.7625905 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{13}C NMR spectrum of compound **6a**



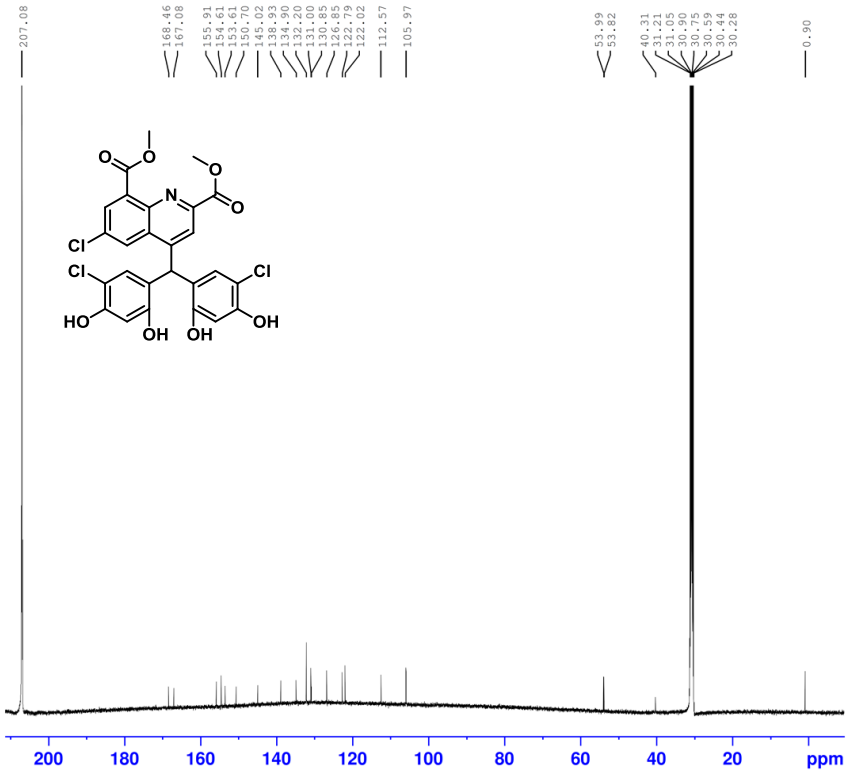
```
Current Data Parameters
NAME      20161120compound118
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20161120
Time                 21.13
INSTRUM              spect
PROBHD    5 mm CPPBBO BB
PULPROG              zg30
TD                  65536
SOLVENT           Acetone
NS                     16
DS                      2
SWH             10000.000 Hz
FIDRES              0.152588 Hz
AQ                  3.2767999 sec
RG                     69.94
DW                  50.000 usec
DE                  10.00 usec
TE                  298.2 K
D1                1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1           500.1530886 MHz
NUC1                     1H
P1                   15.00 usec
PLW1           12.30000019 W

F2 - Processing parameters
SI                      65536
SF             500.1500066 MHz
WDW                     EM
SSB          0
LB                   0.30 Hz
GB           0
PC                   1.00
```

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



```
Current Data Parameters
NAME      20161120compound118
EXPNO                      10
PROCNO                      1

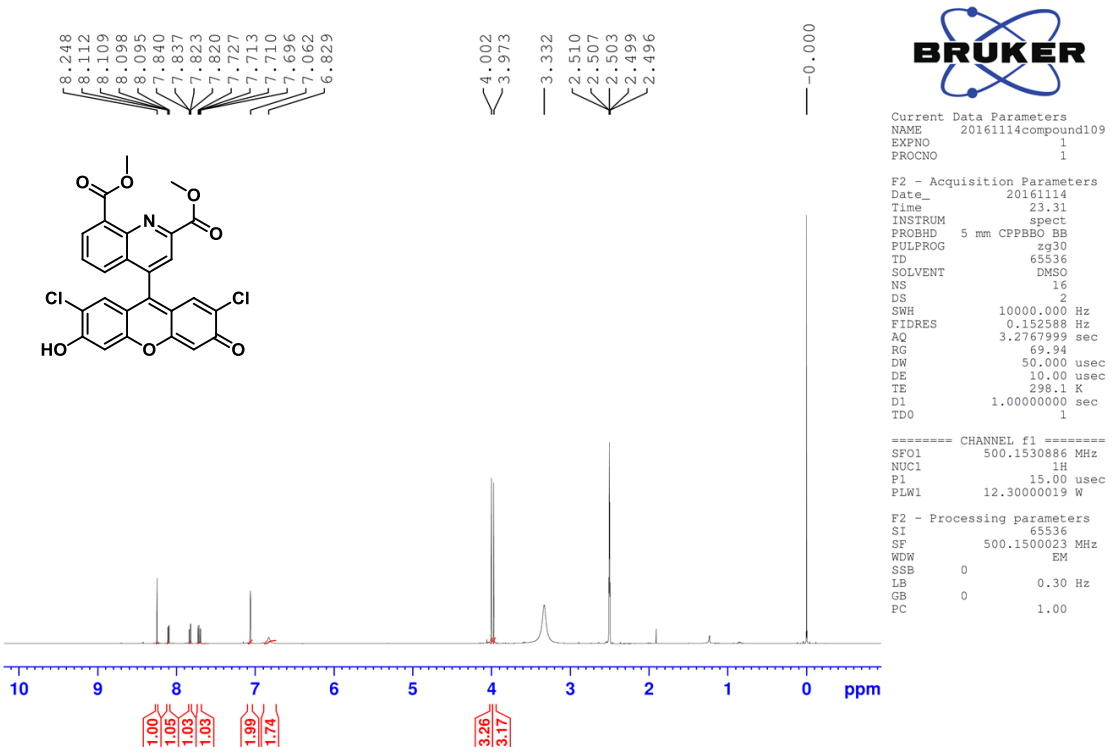
F2 - Acquisition Parameters
Date_              20161121
Time                  8.53
INSTRUM              spect
PROBHD    5 mm CPPBBO BB
PULPROG            zgpg30
TD                  65536
SOLVENT           Acetone
NS                   4096
DS                      4
SWH             29761.904 Hz
FIDRES              0.454131 Hz
AQ                  1.1010048 sec
RG                    197.07
DW                  16.800 usec
DE                  18.00 usec
TE                  298.2 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1           125.7753932 MHz
NUC1                     13C
P1                   10.00 usec
PLW1           77.00000000 W

======== CHANNEL f2 ========
SFO2           500.1520006 MHz
NUC2                     1H
CPDPRG[2          waltz16
PCPD2                80.00 usec
PLW2           12.30000019 W
PLW12           0.43241999 W
PLW13           0.27675000 W

F2 - Processing parameters
SI                      32768
SF             125.7625906 MHz
WDW                     EM
SSB          0
LB                   1.00 Hz
GB           0
PC                   1.40
```

^{13}C NMR spectrum of compound **6b**



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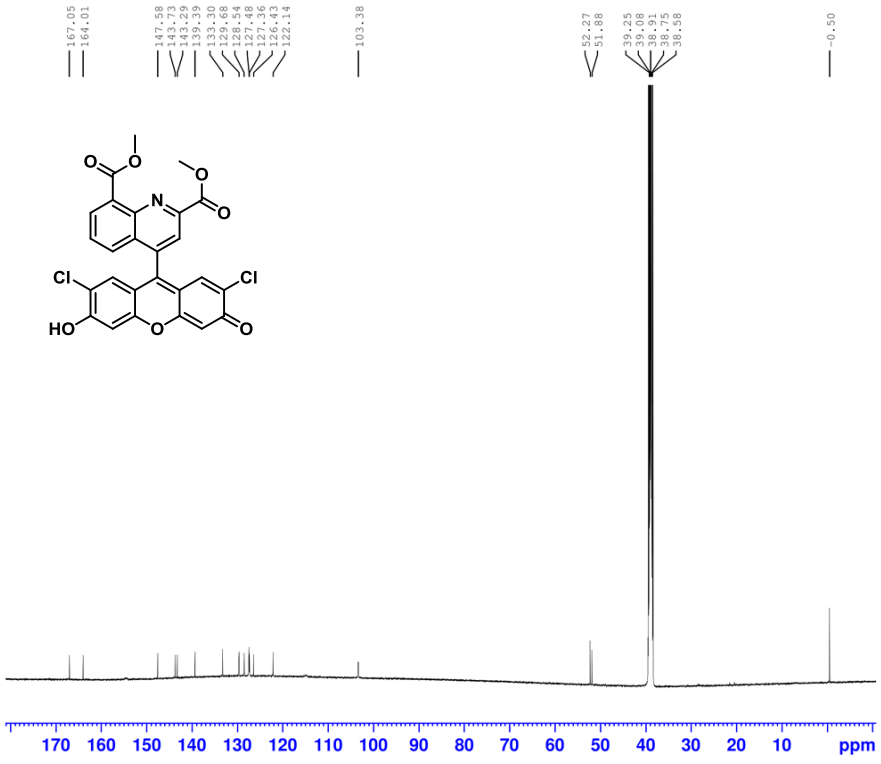
```
Current Data Parameters
NAME      20161114compound109
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_            20161114
Time                23.31
INSTRUM             spect
PROBHD    5 mm CPPBBO BB
PULPROG             zg30
TD                 65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH            10000.000 Hz
FIDRES             0.152588 Hz
AQ              3.2767999 sec
RG                  69.94
DW                 50.000 usec
DE                 10.00 usec
TE                298.1 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          500.1530886 MHz
NUC1                    1H
P1                  15.00 usec
PLW1          12.30000019 W

F2 - Processing parameters
SI                 65536
SF            500.1500023 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

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



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```
Current Data Parameters
NAME      20161114compound109 13C
EXPNO                        10
PROCNO                        1

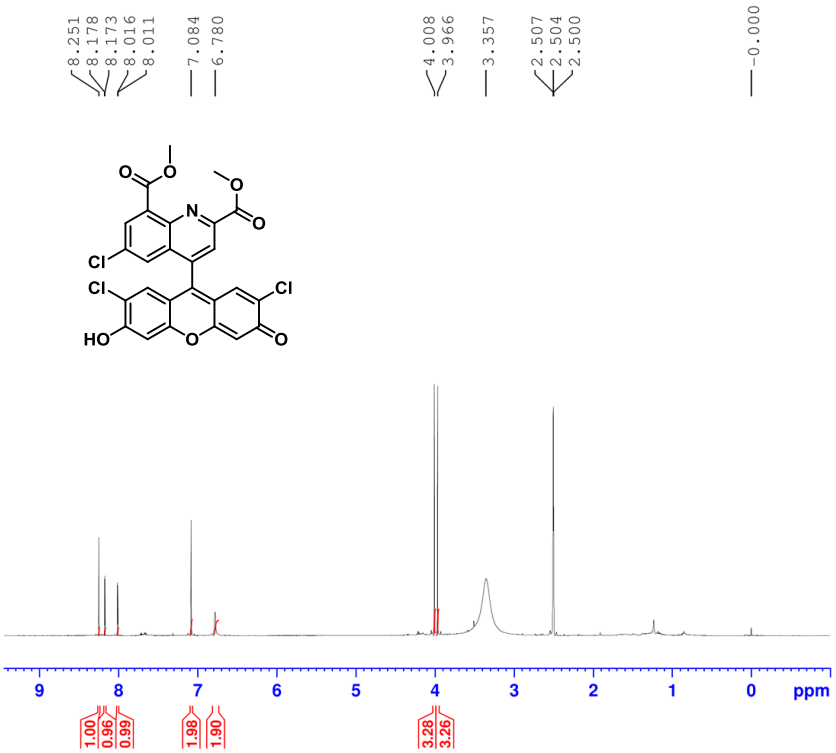
F2 - Acquisition Parameters
Date_            20161115
Time                 8.37
INSTRUM             spect
PROBHD    5 mm CPPBBO BB
PULPROG          zgpg30
TD                 65536
SOLVENT             DMSO
NS                 10240
DS                     4
SWH            29761.904 Hz
FIDRES             0.454131 Hz
AQ              1.1010048 sec
RG                 197.07
DW                 16.800 usec
DE                 18.00 usec
TE                298.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          125.7753932 MHz
NUC1                   13C
P1                  10.00 usec
PLW1          77.00000000 W

======== CHANNEL f2 ========
SFO2          500.1520006 MHz
NUC2                    1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          12.30000019 W
PLW12          0.43241999 W
PLW13          0.27675000 W

F2 - Processing parameters
SI                 32768
SF            125.7629527 MHz
WDW                    EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

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



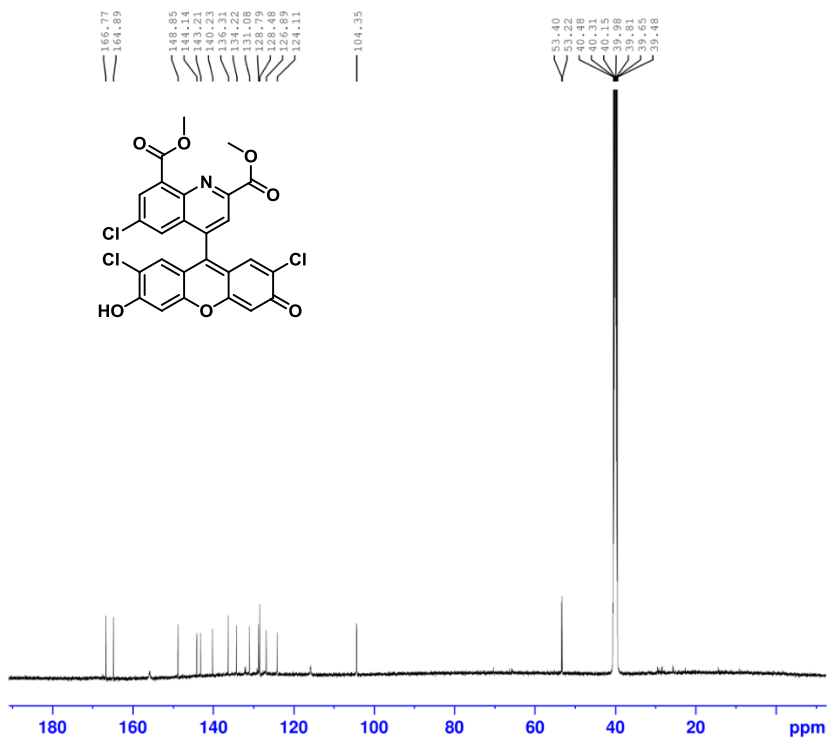

```
Current Data Parameters
NAME      20170627compound119
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20170627
Time                   9.20
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH               10000.000 Hz
FIDRES            0.152588 Hz
AQ                3.2767999 sec
RG                     69.94
DW                  50.000 usec
DE                  10.00 usec
TE                   298.1 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1          500.1530886 MHz
NUC1                     1H
P1                    15.00 usec
PLW1          12.30000019 W

F2 - Processing parameters
SI                    65536
SF            500.1500022 MHz
WDW                      EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

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




```
Current Data Parameters
NAME      20170627compound119
EXPNO                      20
PROCNO                      1

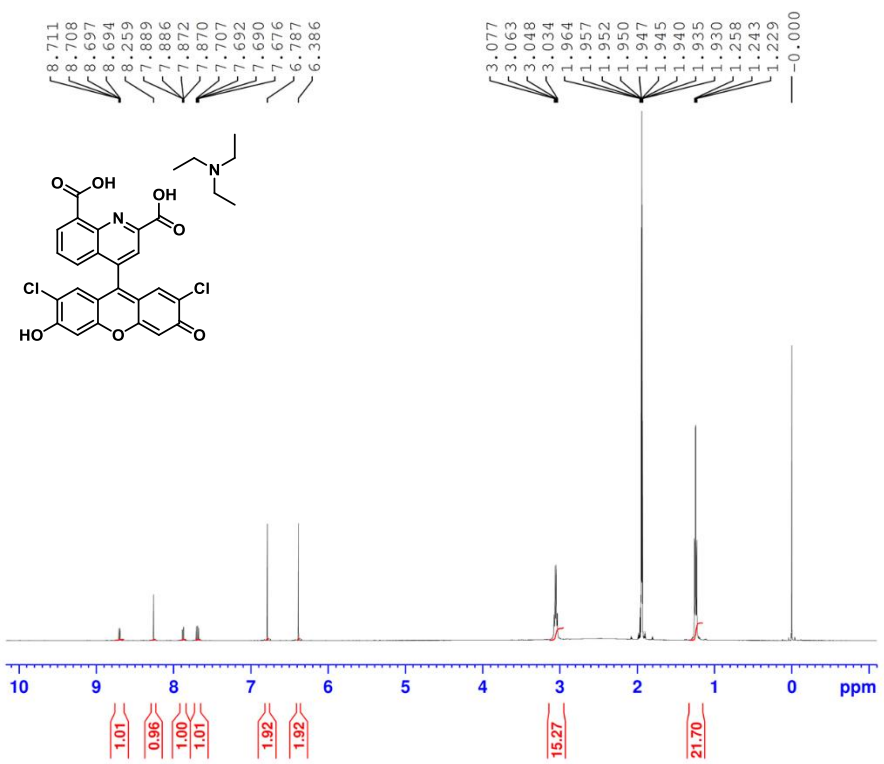
F2 - Acquisition Parameters
Date_              20170628
Time                   5.39
INSTRUM               spect
PROBHD    5 mm CPPBBO BB
PULPROG            zgpg30
TD                    65536
SOLVENT                DMSO
NS                     8192
DS                        4
SWH               29761.904 Hz
FIDRES            0.454131 Hz
AQ                1.1010048 sec
RG                    197.07
DW                  16.800 usec
DE                  18.00 usec
TE                   298.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

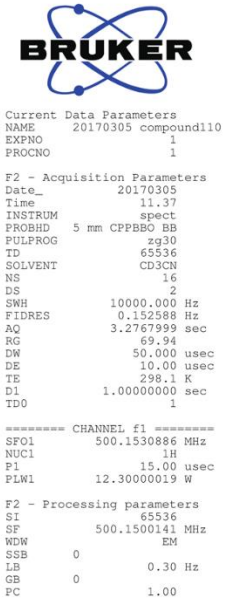
======== CHANNEL f1 ========
SFO1          125.7753932 MHz
NUC1                     13C
P1                    10.00 usec
PLW1          77.00000000 W

======== CHANNEL f2 ========
SFO2          500.1520006 MHz
NUC2                     1H
CPDPRG[2          waltz16
PCPD2                 80.00 usec
PLW2          12.30000019 W
PLW12          0.43241999 W
PLW13          0.27675000 W

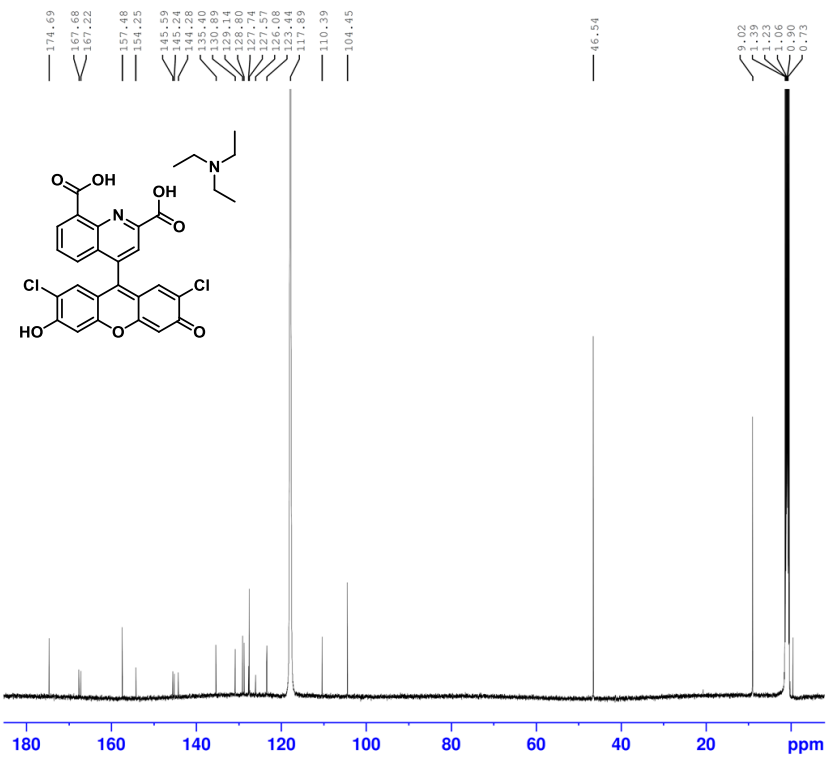
F2 - Processing parameters
SI                    32768
SF            125.7628175 MHz
WDW                      EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

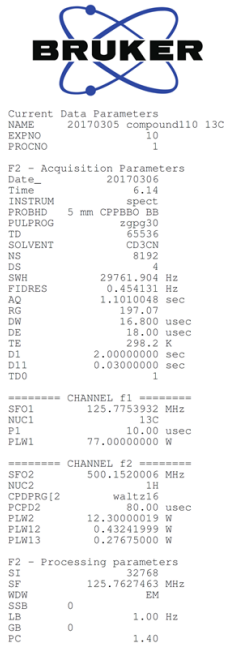
^{13}C NMR spectrum of compound **7b**



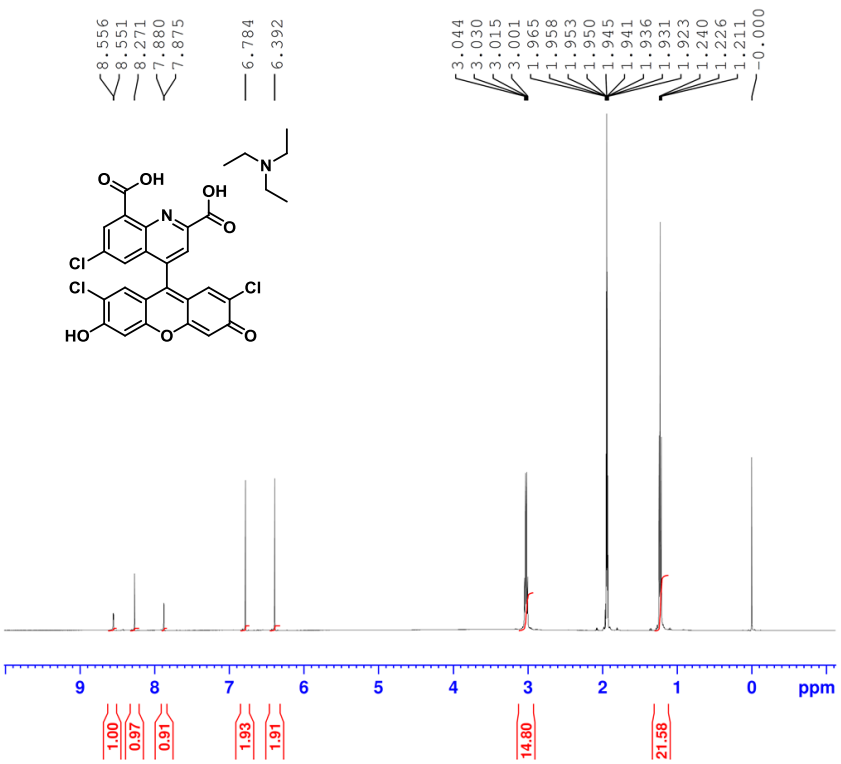


^{1}H NMR spectrum of MGQ-1





^{13}C NMR spectrum of MGQ-1



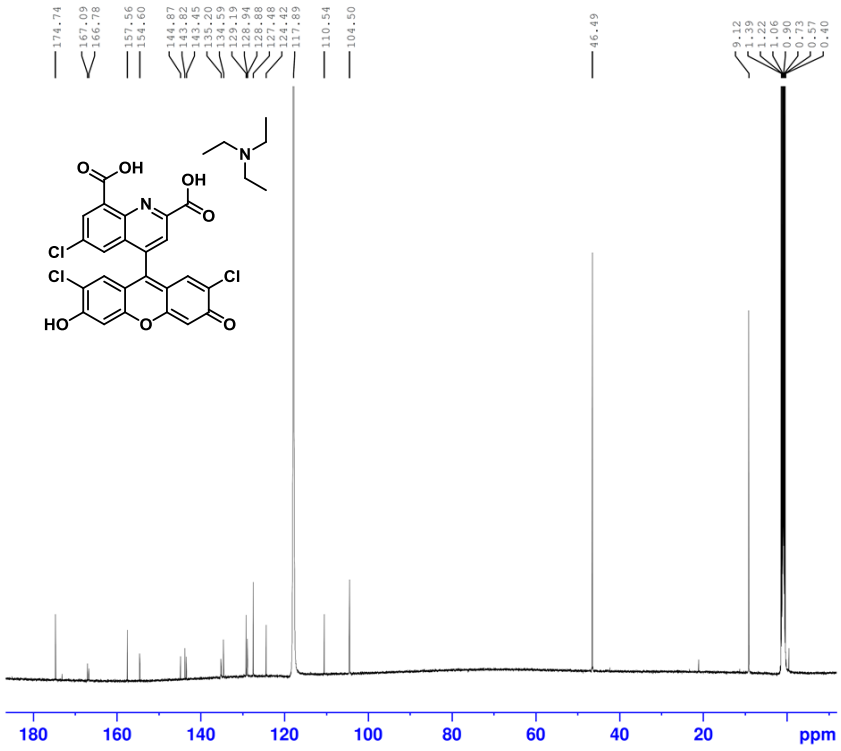
Current Data Parameters
NAME 20170312 compound120
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170312
Time 12.39
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zg30
TD 65536
SOLVENT CD3CN
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 62.19
DW 50.000 usec
DE 10.00 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 500.1530886 MHz
NUC1 1H
P1 15.00 usec
PLW1 12.30000019 W

F2 - Processing parameters
SI 65536
SF 500.1500139 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H NMR spectrum of MGQ-2



Current Data Parameters
NAME 20170312 compound120 13C
EXPNO 10
PROCNO 1

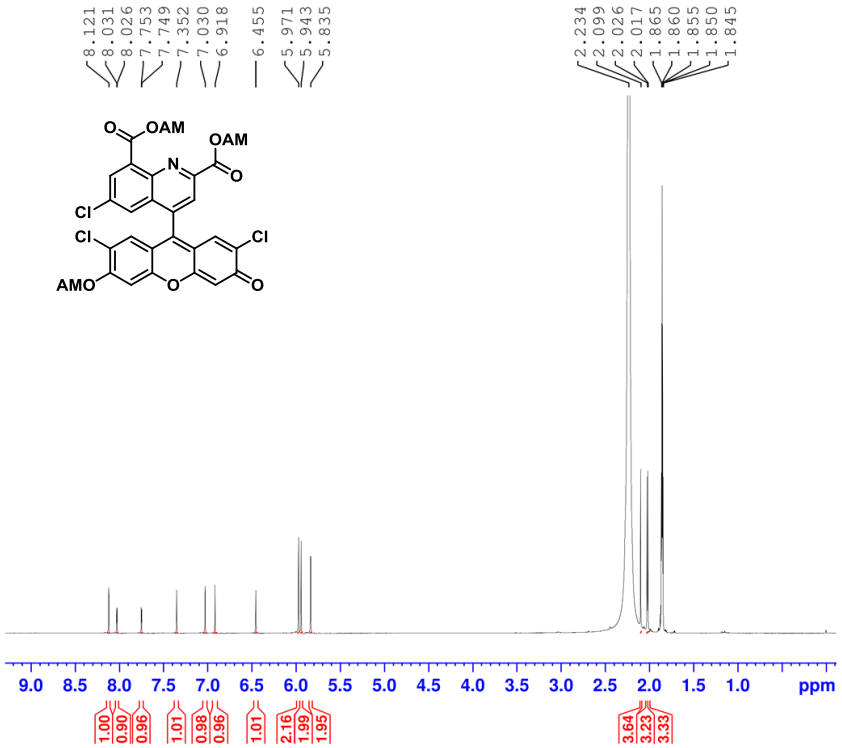
F2 - Acquisition Parameters
Date_ 20170313
Time 6.14
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPROG zgpg30
TD 65536
SOLVENT CD3CN
NS 8192
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 197.07
DW 16.800 usec
DE 18.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

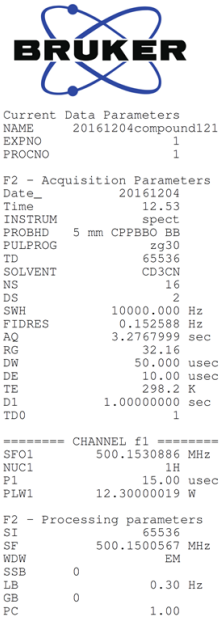
======== CHANNEL f1 ========
SFO1 125.7753932 MHz
NUC1 13C
P1 10.00 usec
PLW1 77.00000000 W

======== CHANNEL f2 ========
SFO2 500.1520006 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 12.30000019 W
PLW12 0.43241999 W
PLW13 0.27675000 W

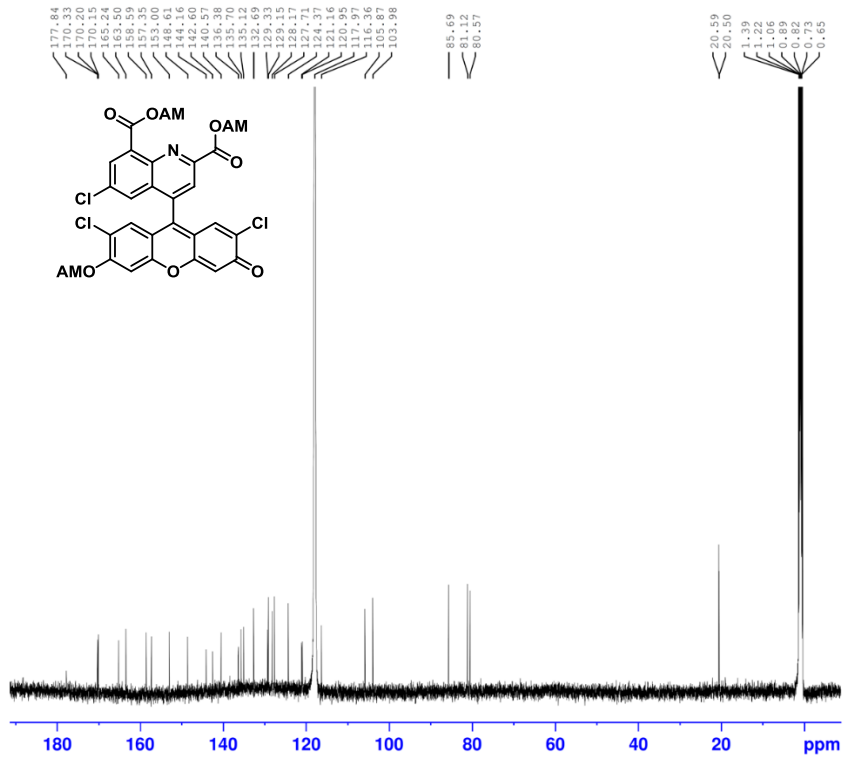
F2 - Processing parameters
SI 32768
SF 125.7627466 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

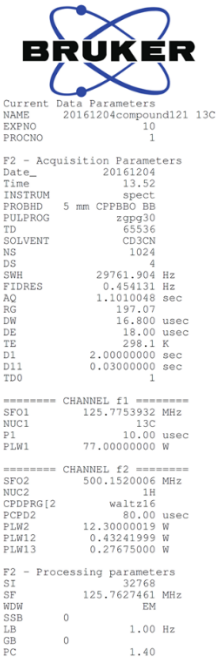
^{13}C NMR spectrum of MGQ-2





^{1}H NMR spectrum of MGQ-2(AM)





^{13}C NMR spectrum of MGQ-2(AM)