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SUPPORTING INFORMATION

Metal-free Hypervalent Iodine-promoted Tandem Carbonyl Migration and Unactivated C(Ph)-C(Alkyl) Bond Cleavage for Quinolone Scaffold Synthesis

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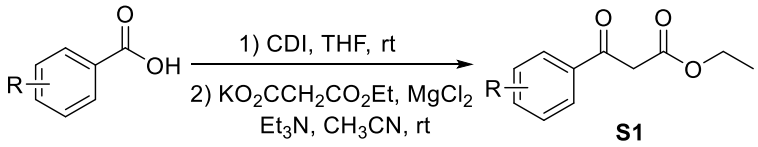
1. General Methods, Materials, and Instrumentations

Unless otherwise specified, all reactions were carried out in oven-dried glassware with magnetic stirring. All reagents were weighed and handled in air at room temperature. Unless otherwise stated, commercially obtained materials were used without further purification. Column chromatography was performed on silica gel (200-300 mesh). The column output was monitored by TLC on silica gel (100-200 mesh) precoated on glass plates (15 x 50 mm), and spots were visualized by UV light at 254 nm. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, 1D NOE, NOESY and low/high resolution mass spectroscopy. NMR spectra were recorded on Brucker AVANCE 300 NMR spectrometer or Brucker AVANCE III 400 NMR spectrometer. Chemical shifts for proton magnetic resonance spectra (^{1}H NMR) were quoted in parts per million (ppm) referenced to the signals of residual chloroform (7.26 ppm), dimethyl sulfoxide (2.50 ppm) or methanol (3.30 ppm). ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm), dimethyl sulfoxide (39.52 ppm) or methanol (49.00 ppm). The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multriplet, dd = doublet of doublet. Coupling constants, *J*, were reported in hertz unit (Hz). Mass spectra were recorded using an ESI ion source unless stated otherwise. Some products were isolated by semi-preparative HPLC on a EasySepTM-1010 with XBridge^{TM} Prep C18 reversed-phase column (19 × 150 mm) in the solvent systems of solvent A, water; solvent B, acetonitrile; flow rate, 8 mL/min; UV decetor 254 nm. All melting points were measured using a BÜCHI 510 melting point apparatus. The yields in this paper refer to isolated yields of compounds estimated to be ≥95% pure as determined by ^{1}H NMR.

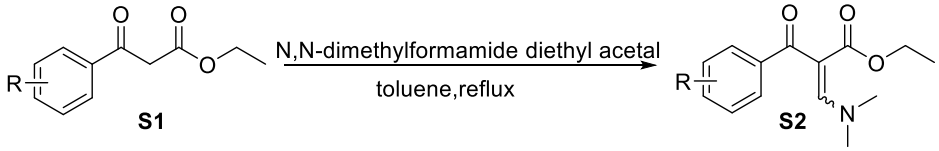
2. General Procedures for Synthesis of Substrates and Products

2.1 General procedure A for preparation of the substituted ethyl 3-oxo-3-phenylpropanoates S1



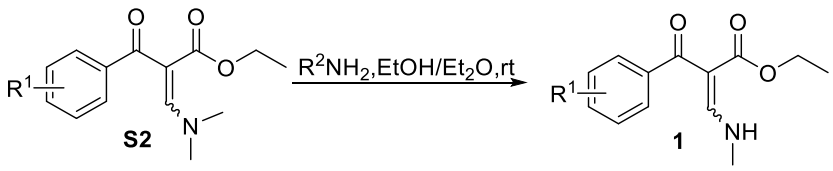
Carbonyldiimidazole (6 mmol) was added to a solution of the corresponding benzoic acid (1 equiv) in THF (6 mL) and stirred at room temperature for 12 h. A mixture of magnesium chloride (2.5 equiv), triethylamine (3 equiv) and potassium monoethyl malonate (2 equiv) in CH_3CN (0.1 M) was stirred for 4 h. Then the suspension was cooled in ice bath, and the solution of the active ester was added dropwise. The mixture was stirred for additional 12 h at room temperature and then quenched by diluted hydrochloric acid at 0 ℃. The resulting mixture was extracted with EA. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. Filtrated and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the corresponding product **S1**.

2.2 General procedure B for the preparation of the substituted ethyl 2-benzoyl-3-(dimethylamino)acrylates S2



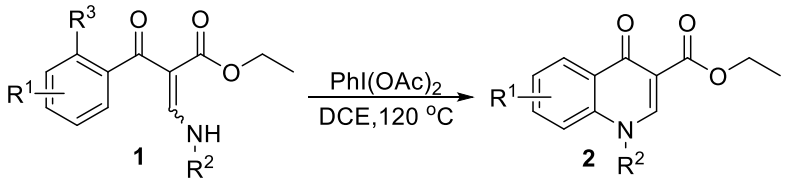
To a solution of the corresponding ethyl 3-oxo-3-phenylpropanoate (2 mmol) in toluene (0.2 M) was added *N*,*N*-dimethylformamide diethyl acetal (1.3 equiv). The reaction mixture was heated at 110 ℃ for 2 h and subsequently cooled to room temperature, then diluted with ethyl acetate. The resulting mixture was washed with brine and the organic layer was dried over anhydrous Na_2SO_4. After removal of the drying agent, the filtrate was concentrated under reduced pressure leaving the yellow oil **S2**, which could be used for next step without further purification.

2.3 General procedure C for the preparation of the substrates 1



The corresponding ethyl 2-benzoyl-3-(dimethylamino)acrylate **S2** was dissolved in EtOH/Et_2O=3:1 (0.2 M), then 2 equiv of the amine was added. The mixture was stirred at room temperature for 15 min and then evaporated to remove the solvent. The residue was purified by silica gel chromatography to afford the product. The product **1** was obtained as the mixture of the (E/Z) isomers.

2.4 General procedure D for the synthesis of the products 2

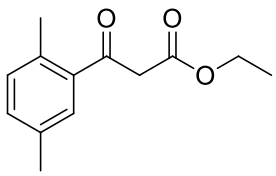


A mixture of the corresponding substrate **1** (0.3 mmol, 1 equiv) and $PhI(OAc)_2$ (0.9 mmol, 3 equiv) in DCE (15 mL) was stirred at 120 ℃ for the corresponding reaction time listed in the tables in a sealed tube. After cooling to room temperature, the reaction mixture was diluted with DCM and quenched by saturated $Na_2S_2O_3$ (aq.). Extracted with DCM and the combined organic layer was dried over anhydrous Na_2SO_4. Filtrated and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give the product **2**.

2.5 General procedure E for the synthesis of the products 2

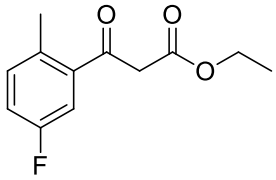
Procedure D was used with following modifications: $PhI(OCO^tBu)_2$ (0.9 mmol, 3 equiv) was used instead of $PhI(OAc)_2$ (0.9 mmol, 3 equiv) and the temperature was decreased to 100℃ .

3. Characterization Data for All of the Substrates and Products

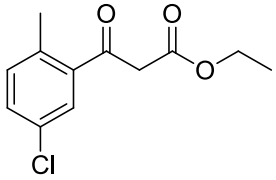


Ethyl 3-(2,5-dimethylphenyl)-3-oxopropanoate (S1e): Yellow oil, yield: 86% (ketone:enol=15:4). ^{1}H NMR (300 MHz, $CDCl_3$): ketone δ 7.43 (s, 1H), 7.20 (d, *J* = 8.5 Hz, 1H), 7.14 (d, *J* = 8.5 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 2H), 2.47 (s, 3H), 2.34 (s, 3H), 1.23 (t, *J*

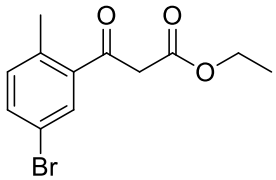
= 7.1 Hz, 3H). Enol δ 12.45 (s, 1H), 7.24 (s, 1H), 7.11 (d, *J* = 8.5 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 1H), 5.25 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.45 (s, 3H), 2.39 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H).



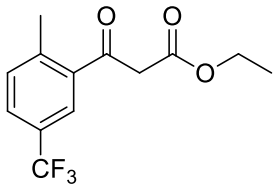
Ethyl 3-(5-fluoro-2-methylphenyl)-3-oxopropanoate (S1f): Yellow oil, yield: 90% (ketone:enol=3:1). ^{1}H NMR (400 MHz, $CDCl_3$): ketone δ 7.35 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.17 – 7.13 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 2H), 2.50 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). Enol δ 12.49 (s, 1H), 7.27 (d, *J* = 6.9 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.03 (td, *J* = 8.0, 4.0 Hz, 1H), 5.29 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).



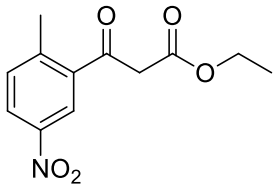
Ethyl 3-(5-chloro-2-methylphenyl)-3-oxopropanoate (S1g): Yellow oil, yield: 78% (ketone:enol=3:1). ^{1}H NMR (400 MHz, $CDCl_3$): ketone δ 7.61 (s, 1H), 7.43 – 7.35 (m, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 2H), 2.50 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). Enol δ 12.47 (s, 1H), 7.41 (s, 1H), 7.31 – 7.26 (m, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 5.29 (s, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).



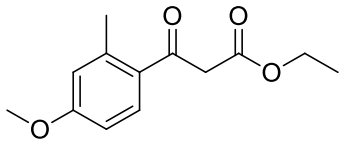
Ethyl 3-(5-bromo-2-methylphenyl)-3-oxopropanoate (S1h): Yellow oil, yield: 85% (ketone:enol=2:1). ^{1}H NMR (400 MHz, $CDCl_3$): ketone δ 7.03 (d, *J* = 8.0 Hz, 2H), 6.64 (d, *J* = 8.2 Hz, 1H), 3.71 (q, *J* = 7.1 Hz, 2H), 3.43 (s, 2H), 1.97 (s, 3H), 0.76 (t, *J* = 7.1 Hz, 3H). Enol δ 11.99 (s, 1H), 7.05 (s, 1H), 6.91 (d, *J* = 9.8 Hz, 1H), 6.59 (d, *J* = 8.2 Hz, 1H), 4.78 (s, 1H), 3.78 (q, *J* = 7.1 Hz, 2H), 1.90 (s, 3H), 0.84 (t, *J* = 7.1 Hz, 3H).



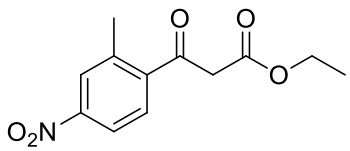
Ethyl 3-(2-methyl-5-(trifluoromethyl)phenyl)-3-oxopropanoate (S1i): Yellow oil, yield: 73% (ketone:enol=2:1). ^{1}H NMR (300 MHz, $CDCl_3$): ketone δ 7.87 (s, 1H), 7.66 – 7.63 (m, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 2H), 2.59 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). Enol δ 12.49 (s, 1H), 7.66 – 7.63 (m, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 5.31 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.51 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).



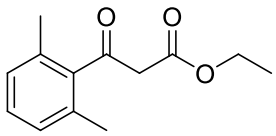
Ethyl 3-(2-methyl-5-nitrophenyl)-3-oxopropanoate (S1j): Yellow oil, yield: 79% (ketone:enol=1.5:1). ^{1}H NMR (300 MHz, $CDCl_3$): ketone δ 8.50 (d, *J* = 2.1 Hz, 1H), 8.26 (d, *J* = 8.7 Hz 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 2H), 2.63 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). Enol δ 12.51 (s, 1H), 8.23 (s, 1H), 8.15 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 5.35 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.63 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).



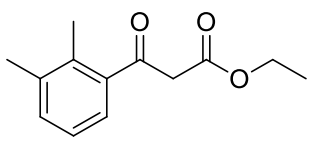
Ethyl 3-(4-methoxy-2-methylphenyl)-3-oxopropanoate (S1k): Yellow oil, yield: 54% (ketone:enol=10:1). ^{1}H NMR (300 MHz, $CDCl_3$): ketone δ 7.70 (d, *J* = 9.4 Hz, 1H), 6.81 – 6.72 (m, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 2H), 3.85 (s, 3H), 2.58 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). Enol δ 12.52 (s, 1H), 7.70 (s, 1H), 7.39 (d, *J* = 9.5 Hz, 1H), 7.17 (d, *J* = 7.0 Hz, 1H), 5.25 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 2.46 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H).



Ethyl 3-(2-methyl-4-nitrophenyl)-3-oxopropanoate (S1m): Yellow oil, yield: 81% (ketone:enol=1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.48 (s, 0.5H), 8.11 – 8.03 (m, 2H), 7.74 (d, *J* = 8.6 Hz, 0.5H), 7.54 (d, *J* = 8.5 Hz, 0.5H), 5.31 (s, 0.5H), 4.28 (q, *J* = 7.2 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 1H), 3.95 (s, 1H), 2.59 (s, 1.5H), 2.55 (s, 1.5H), 1.33 (t, *J* = 7.1 Hz, 1.5H), 1.22 (t, *J* = 7.1 Hz, 1.5H).

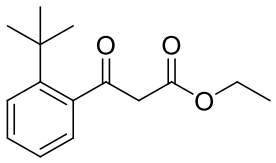


Ethyl 3-(2,6-dimethylphenyl)-3-oxopropanoate (S1n): To a suspension of NaH (55% dispersion in mineral oil, 462 mg, 10.6 mmol) in 12 mL toluene was added carbonic acid diethyl ester (652 μL, 5.3 mmol) and 2,6-dimethylacetophenone (392 mg, 2.6 mmol), and then the resulting mixture was heated at 100℃ for 30 min. After cooling to room temperature, the reaction mixture was quenched by saturated NH_4Cl (aq). Extracted with EA and the organic layer was washed with saturated NH_4Cl (aq) and brine for 3 times respectively, then dried over anhydrous Na_2SO_4. After removal of the drying agent, the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography, yield: 79% (ketone:enol=1:1), yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.35 (s, 0.5H), 7.21 – 7.14 (m, 1H), 7.07 – 6.99 (m, 2H), 5.12 (s, 0.5H), 4.27 (q, *J* = 7.1 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 1H), 3.74 (s, 1H), 2.33 (s, 3H), 2.29 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 1.5H), 1.24 (t, *J* = 7.1 Hz, 1.5H).

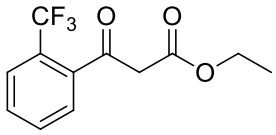


Ethyl 3-(2,3-dimethylphenyl)-3-oxopropanoate (S1o): Yellow oil, yield: 86% (ketone:enol=3:1). ^{1}H NMR (300 MHz, $CDCl_3$): ketone δ 7.37 (d, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.20 – 7.06 (m, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 2H), 2.35 (s, 3H), 2.29 (s, 3H), 1.21 (t, *J* = 7.4 Hz, 3H). Enol δ 12.45 (s, 1H), 7.20 – 7.06 (m, 3H), 5.22 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H),

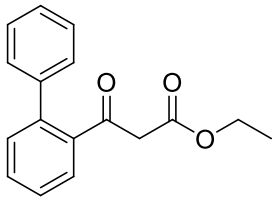
2.31 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H).



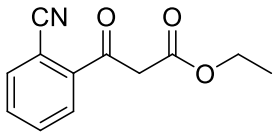
Ethyl 3-(2-tert-butylphenyl)-3-oxopropanoate (S1p): Yellow oil , yield: 26% (ketone:enol=10:3). ^{1}H NMR (300 MHz, $CDCl_3$): ketone δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.31 (m, 1H), 7.25 – 7.17 (m, 2H), 4.24 (q, *J* = 7.2 Hz, 3H), 3.90 (s, 2H), 1.39 (s, 9H), 1.28 (t, *J* = 7.1 Hz, 3H). Enol δ 12.57 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.31 (m, 1H), 7.25 – 7.17 (m, 3H), 5.23 (s, 1H), 4.24 (q, *J* = 7.2 Hz, 3H) , 1.43 (s, 9H), 1.28 (t, *J* = 7.1 Hz, 3H).



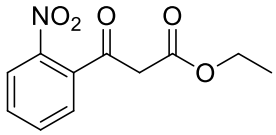
Ethyl 3-oxo-3-(2-(trifluoromethyl)phenyl)propanoate (S1r): Yellow oil, yield: 90% (ketone:enol=1.5:1). ^{1}H NMR (300 MHz, $CDCl_3$): ketone δ 7.73 – 7.72 (m, 1H), 7.62-7.61 (m, 1H), 7.58 – 7.52 (m, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.90 (s, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). Enol δ 12.41 (s, 1H), 7.71 – 7.52 (m, 4H), 5.30 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H).



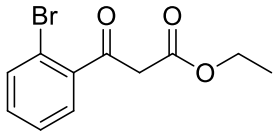
Ethyl 3-(biphenyl-2-yl)-3-oxopropanoate (S1s): Yellow oil, yield: 74% (ketone:enol=11:2). ^{1}H NMR (400 MHz, $CDCl_3$): ketone δ 7.61 (ddd, *J* = 7.6, 1.4, 0.4 Hz, 1H), 7.55 (td, *J* = 7.5, 1.4 Hz, 1H), 7.46 – 7.34 (m, 7H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.27 (s, 2H), 1.16 (t, *J* = 7.1 Hz, 3H). Enol δ 12.25 (s, 1H), 7.59 (ddd, *J* = 7.6, 1.4, 0.4 Hz, 1H), 7.50 – 7.33 (m, 8H), 5.07 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).



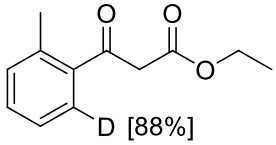
Ethyl 3-(2-cyanophenyl)-3-oxopropanoate (S1t): Yellow oil, yield: 57% (ketone:enol=1.6:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.62 (s, 0.38H), 7.95 – 7.93 (m, 0.62H), 7.86 – 7.84 (m, 0.62H), 7.80 – 7.64 (m, 2.38H), 7.57– 7.53 (m, 0.62H), 5.76 (s, 0.38H), 4.28 – 4.18 (m, 2H), 3.43 (s, 1.24H), 1.36 – 1.29 (m, 3H).



Ethyl 3-(2-nitrophenyl)-3-oxopropanoate (S1u): Yellow oil, yield: 74% (ketone:enol=5:1). ^{1}H NMR (300 MHz, $CDCl_3$): ketone δ 8.16 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.77 – 7.71 (m, 1H), 7.68 – 7.61 (m, 1H), 7.52 (dd, *J* = 7.4, 1.3 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). Enol δ 12.32 (s, 1H), 7.88 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.77 – 7.71 (m, 1H), 7.67 – 7.66 (m, 1H), 7.58 – 7.55 (m, 1H), 5.41 (s, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

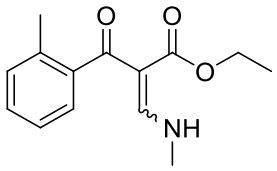


Ethyl 3-(2-bromophenyl)-3-oxopropanoate (S1w): Yellow oil, yield: 80% (ketone:enol=2:1). ^{1}H NMR (300 MHz, $CDCl_3$): ketone δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.50 (td, *J* = 6.0, 3.0 Hz, 1H), 7.43 – 7.31 (m, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.01 (s, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). Enol δ 12.42 (s, 1H), 7.53 – 7.48 (m, 2H), 7.43 – 7.31 (m, 2H), 5.45 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 6.9 Hz, 3H).

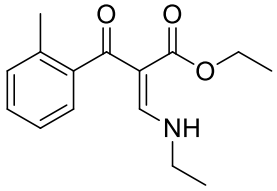


Deutero ethyl 3-oxo-3-(o-tolyl)propanoate (S1a-[D]): Yellow oil (2-deutero-6-methylbenzoic acid was 88% deuterium incorporation), yield: 90% (ketone:enol=4:1). ^{1}H NMR (300 MHz,

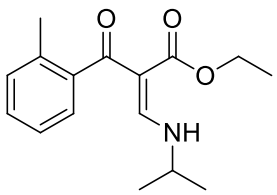
$CDCl_3$): δ 7.41 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 2H), 2.55 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). Enol δ 12.48 (s, 1H), 7.33 (d, *J* = 7.3 Hz, 1H), 7.23-7.19(m, 2H), 5.28 (s, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.46 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H).



Ethyl 3-(methylamino)-2-(2-methylbenzoyl)acrylate (1a): White solid, yield: 74% (major: minor=5:1). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 10.99 (br, 1H), 8.04 (d, *J* = 13.8 Hz, 1H), 7.23 – 7.12 (m, 4H), 3.89 (t, *J* = 7.1 Hz, 2H), 3.23 (d, *J* = 5.1 Hz, 3H), 2.26 (s, 3H), 0.84 (t, *J* = 7.1 Hz, 3H). Minor isomer δ 9.25 (br, 1H), 8.09 (d, *J* = 13.8 Hz, 1H), 7.23 – 7.12 (m, 3H), 7.05 (d, *J* = 7.5 Hz, 1H), 3.91 (t, *J* = 7.1 Hz, 2H), 3.18 (d, *J* = 5.1 Hz, 3H), 2.29 (s, 3H), 0.80 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 248.1 ($[M+H]^+$), 270.1 ($[M+Na]^+$).

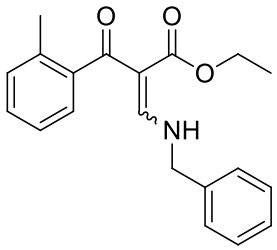


Ehyl 3-(ethylamino)-2-(2-methylbenzoyl)acrylate (1b): White solid, yield: 93% (major: minor=3.5:1). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 11.10 (br, 1H), 8.15 (d, *J* = 13.9 Hz, 1H), 7.26 – 7.20 (m, 1H), 7.19 – 7.12 (m, 2H), 7.10 – 7.05 (m, 1H), 3.90 (q, *J* = 7.2 Hz, 2H), 3.52 (q, *J* = 7.2 Hz, 2H), 2.29 (s, 3H), 1.38 (t, *J* = 7.3 Hz, 3H), 0.86 (t, *J* = 7.1 Hz, 3H). Minor isomer δ 9.40 (br, 1H), 8.13 (d, *J* = 13.9 Hz, 1H), 7.26 – 7.20 (m, 1H), 7.19 – 7.12 (m, 3H), 3.90 (q, *J* = 7.2 Hz, 2H), 3.52 (q, *J* = 7.2 Hz, 2H), 2.32 (s, 3H), 1.33 (t, *J* = 7.3 Hz, 3H), 0.81 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 262.0 ($[M+H]^+$), 284.0 ($[M+Na]^+$).

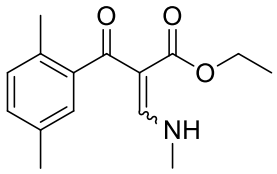


Ehyl 3-(isopropylamino)-2-(2-methylbenzoyl)acrylate (1c): White solid, yield: 90% (major:

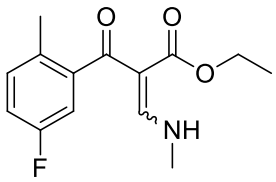
minor=3.8:1). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 11.03 (br, 1H), 8.13 (d, *J* = 14.0 Hz, 1H), 7.22 – 7.15 (m, 1H), 7.15 – 7.07 (m, 2H), 7.06 – 7.01 (m, 1H), 3.89 – 3.84 (m, 3H), 2.25 (s, 3H), 1.35 (d, *J* = 6.6 Hz, 6H), 0.81 (t, *J* = 7.1 Hz, 3H). Minor isomer δ 9.31 (br, 1H), 8.13 (d, *J* = 14.0 Hz, 1H), 7.22 – 7.15 (m, 1H), 7.15 – 7.07 (m, 3H), 3.71 – 3.61 (m, 3H), 2.28 (s, 3H), 1.31 (d, *J* = 6.6 Hz, 6H), 0.76 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 276.0 ($[M+H]^+$), 298.2 ($[M+Na]^+$).



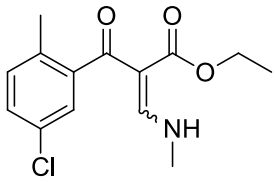
Ehyl 3-(benzylamino)-2-(2-methylbenzoyl)acrylate (1d): White solid, yield: 94% (major: minor=5.5:1). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 11.28 (br, 1H), 8.19 (d, *J* = 13.7 Hz, 1H), 7.43 – 7.27 (m, 5H), 7.25 – 7.19 (m, 1H), 7.17 – 7.11 (m, 2H), 7.10 – 7.05 (m, 1H), 4.60 (d, *J* = 6.1 Hz, 2H), 3.90 (q, *J* = 7.2 Hz, 2H), 2.28 (s, 3H), 0.84 (t, *J* = 7.1 Hz, 3H). Minor isomer δ 9.58 (br, 1H), 8.14 (d, *J* = 13.7 Hz, 1H), 7.43 – 7.27 (m, 5H), 7.25 – 7.19 (m, 1H), 7.17 – 7.11 (m, 3H), 4.56 (d, *J* = 6.1 Hz, 2H), 3.90 (q, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 0.80 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 324.1 ($[M+H]^+$).



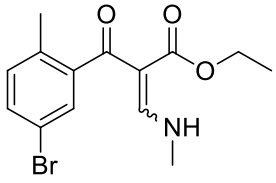
Ethyl 2-(2,5-dimethylbenzoyl)-3-(methylamino)acrylate (1e): White solid, yield: 93% (major: minor=15:4). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 10.97 (br, 1H), 8.08 (d, *J* = 13.8 Hz, 1H), 7.01 (s, 2H), 6.87 (s, 1H), 3.90 (q, *J* = 7.1 Hz, 2H), 3.22 (d, *J* = 5.1 Hz, 3H), 2.28 (s, 3H), 2.20 (s, 3H), 0.86 (t, *J* = 7.1 Hz, 3H). Minor isomer δ 9.21 (br, 1H), 8.00 (d, *J* = 14.4 Hz, 1H), 7.01 (s, 2H), 6.94 (s, 1H), 3.95 (q, *J* = 7.1 Hz, 2H), 3.17 (d, *J* = 5.0 Hz, 3H), 2.27 (s, 3H), 2.24 (s, 3H), 0.82 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 262.1 ($[M+H]^+$), 284.0 ($[M+Na]^+$), 260.1 ($[M-H]^-$).



Ethyl 2-(5-fluoro-2-methylbenzoyl)-3-(methylamino)acrylate (1f): White solid, yield: 93% (major: minor=4:1). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 10.99 (br, 1H), 8.12 (d, *J* = 13.9 Hz, 1H), 7.08 (dd, *J* = 8.4, 5.5 Hz, 1H), 6.90 (td, *J* = 8.5, 2.6 Hz, 1H), 6.77 (dd, *J* = 8.9, 2.7 Hz, 1H), 3.92 (q, *J* = 7.1 Hz,2H), 3.25 (d, *J* = 5.1 Hz, 3H), 2.20 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H). Minor isomer δ 9.32 (br, 1H), 8.07 (d, *J* = 13.9 Hz, 1H), 7.08 (dd, *J* = 8.4, 5.5 Hz, 1H), 6.90 (td, *J* = 8.5, 2.6 Hz, 1H), 6.83 (dd, *J* = 8.9, 2.7 Hz, 1H), 3.90 (q, *J* = 7.1 Hz, 2H), 3.21 (d, *J* = 5.0 Hz, 3H), 2.23 (s, 3H), 0.81 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 266.2($[M+H]^+$), 288.1($[M+Na]^+$), 264.1 ($[M-H]^-$).

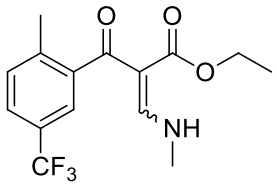


Ethyl 2-(5-chloro-2-methylbenzoyl)-3-(methylamino)acrylate (1g): White solid, yield: 82% (major: minor=15:4). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 10.99 (br, 1H), 8.12 (d, *J* = 13.9 Hz, 1H), 7.17 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.10 – 7.03 (m, 2H), 3.92 (q, *J* = 7.1 Hz, 2H), 3.24 (d, *J* = 5.1 Hz, 3H), 2.21 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H). Minor isomer δ 9.34 (br, 1H), 8.12 (d, *J* = 13.9 Hz, 1H), 7.18 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.10 – 7.03 (m, 2H), 3.89 (q, J = 7.2 Hz, 2H), 3.21 (d, J = 5.1 Hz, 3H), 2.24 (s, 3H), 0.81 (t, J = 7.1 Hz, 3H). ESI-MS *m/z*: 280.2 ($[M-H]^-$), 282.1 ($[M+2-H]^-$).

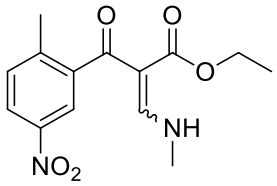


Ethyl 2-(5-bromo-2-methylbenzoyl)-3-(methylamino)acrylate (1h): White solid, yield: 76% (major: minor=15:4). ^{1}H NMR (400 MHz, $CDCl_3$)**:** major isomer δ 10.98 (br, 1H), 8.11 (d, *J* = 13.9 Hz, 1H), 7.33 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.18 (d, *J* = 2.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 3.92 (q, *J* = 7.1 Hz, 2H), 3.24 (d, *J* = 5.1 Hz, 3H), 2.19 (s, 3H), 0.88 (t, *J* = 7.1 Hz, 3H). Minor

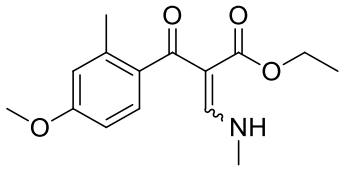
isomer δ 9.34 (br, 1H), 8.11 (d, *J* = 13.9 Hz, 1H), 7.33 (dd, *J* = 8.0, 2.0 Hz,1H), 7.24 (d, *J* = 2.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 3.89 (q, *J* = 7.1 Hz, 2H), 3.21 (d, *J* = 5.1 Hz, 3H), 2.22 (s, 3H), 0.81 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 326.0($[M+H]^+$), 328.0($[M+2+H]^+$), 347.9($[M+Na]^+$), 349.9($[M+2+Na]^+$), 324.0 ($[M-H]^-$), 326.0 ($[M+2-H]^-$).



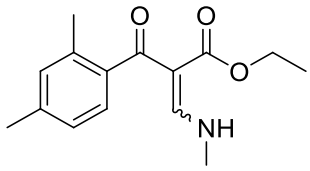
Ethyl 2-(2-methyl-5-(trifluoromethyl)benzoyl)-3-(methylamino) acrylate (1i): White solid, yield: 86% (major: minor=15:4). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 11.01 (br, 1H), 8.15 (d, *J* = 13.8 Hz, 1H), 7.46 (dd, *J* = 8.0, 2.0 Hz,1H), 7.31 (s, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 3.89 (q, *J* = 7.0 Hz, 2H), 3.26 (d, *J* = 5.1 Hz, 3H), 2.31 (s, 3H), 0.81 (t, *J* = 7.1 Hz, 3H). Minor isomer δ 9.41 (br, 1H), 8.20 (d, *J* = 13.8 Hz, 1H), 7.47 (dd, *J* = 8.0, 2.0 Hz,1H), 7.37 (d, *J* = 2.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 3.24 (d, *J* = 5.1 Hz, 3H), 2.34 (s, 3H), 0.70 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 314.2 ($[M-H]^-$).



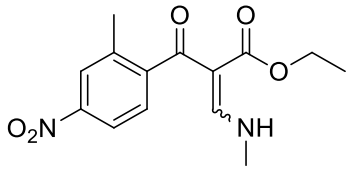
Ethyl 2-(2-methyl-5-nitrobenzoyl)-3-(methylamino)acrylate (1j): White solid, yield: 84% (major: minor=5:1). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 11.06 (br, 1H), 8.17 (d, *J* = 14.2 Hz, 1H), 8.07 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.93 (d, *J* = 2.3 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 3.92 (q, *J* = 7.1 Hz, 2H), 3.28 (d, *J* = 5.1 Hz, 3H), 2.34 (s, 3H), 0.91 (t, *J* = 7.1 Hz, 3H). Minor isomer δ 9.47 (br, 1H), 8.23 (d, *J* = 14.2 Hz, 1H), 8.09 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.98 (d, *J* = 2.2 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 3.85 (q, *J* = 7.1 Hz, 2H), 3.25 (d, *J* = 5.1 Hz, 3H), 2.38 (s, 3H), 0.70 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 293.0 ($[M+H]^+$), 315.0 ($[M+Na]^+$), 291.0 ($[M-H]^-$).



Ethyl 2-(4-methoxy-2-methylbenzoyl)-3-(methylamino)acrylate (1k): White solid, yield: 80% (major: minor=10:3). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 10.86 (br, 1H), 8.05 (d, *J* = 13.8 Hz, 1H), 7.02 (d, *J* = 8.8 Hz, 1H), 6.68 – 6.63 (m, 2H), 3.92 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 3.19 (d, *J* = 5.1 Hz, 3H), 2.26 (s, 3H), 0.92 (t, *J* = 7.2 Hz, 3H). Minor isomer δ 9.10 (br, 1H), 7.89 (d, *J* = 14.4 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 1H), 6.68 – 6.63 (m, 2H), 3.96 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.14 (d, *J* = 5.1 Hz, 3H), 2.31 (s, 3H), 0.87 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 278.0 ($[M+H]^+$), 300.0 ($[M+Na]^+$), 276.1 ($[M-H]^-$).

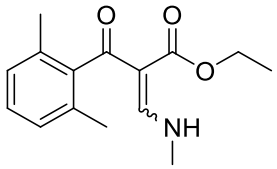


Ethyl 2-(2,4-dimethylbenzoyl)-3-(methylamino)acrylate (1l): White solid, yield: 58% (major: minor=4:1). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 10.95 (br, 1H), 8.07 (d, *J* = 13.8 Hz, 1H), 6.97 – 6.91 (m, 3H), 3.92 (q, *J* = 7.1 Hz, 3H), 3.20 (d, *J* = 5.1 Hz, 3H), 2.30 (s, 3H), 2.23 (s, 3H), 0.90 (t, *J* = 7.1 Hz, 3H). Minor isomer δ 10.95 (br, 1H), 7.94 (d, *J* = 13.8 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.97 – 6.91 (m, 2H), 3.93 (q, *J* = 7.1 Hz, 3H), 3.20 (d, *J* = 5.1 Hz, 3H), 2.30 (s, 3H), 2.27 (s, 3H), 0.85 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 262.2 ($[M+H]^+$), 284.1 ($[M+Na]^+$).

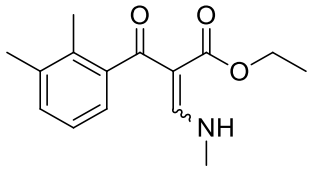


Ethyl 2-(2-methyl-4-nitrobenzoyl)-3-(methylamino)acrylate (1m): White solid, yield: 57% (major: minor=5:1). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 11.08 (br, 1H), 8.16 (d, *J* = 14.0 Hz, 1H), 8.04 – 7.93 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 3.93 (q, *J* = 7.1 Hz, 2H), 3.28 (d, *J* = 5.1 Hz, 3H), 2.33 (s, 3H), 0.92 (t, *J* = 7.1 Hz, 3H). Minor isomer δ 9.47 (br, 1H), 8.22 (d, *J* = 14.7 Hz, 1H), 8.04 – 7.93 (m, 2H), 7.22 (d, *J* = 8.1 Hz, 1H), 3.85 (q, *J* = 7.1 Hz, 2H), 3.25 (d, *J* = 5.1 Hz,

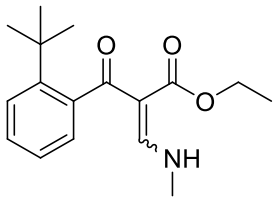
3H), 2.35 (s, 3H), 0.71 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 291.1 ([M-H]$^-$).



Ethyl 2-(2,6-dimethylbenzoyl)-3-(methylamino)acrylate (1n): White solid, yield: 63% (major: minor=5.2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.26 (br, 0.84H), 9.41 (br, 0.16H), 8.13 (d, *J* = 13.8 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 2H), 3.88 (q, *J* = 7.1 Hz, 2H), 3.24 (d, *J* = 5.1 Hz, 3H), 2.16 (s, 6H), 0.83 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 262.0 ([M+H]$^+$), 284.0 ([M+Na]$^+$), 260.2 ([M-H]$^-$).

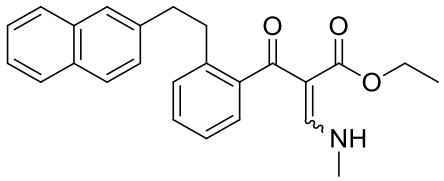


Ethyl 2-(2,3-dimethylbenzoyl)-3-(methylamino)acrylate (1o): White solid, yield: 93% (major: minor=4:1). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 11.02 (br, 1H), 8.09 (d, *J* = 13.8 Hz, 1H), 7.11 – 7.03 (m, 2H), 6.89 (d, *J* = 7.3 Hz, 1H), 3.88(q, *J* = 7.1 Hz, 2H), 3.23 (d, *J* = 5.1 Hz, 3H), 2.26 (s, 3H), 2.15 (s, 3H), 0.84 (t, *J* = 7.1 Hz, 3H). Minor isomer δ 9.27 (br, 1H), 8.04 (d, *J* = 14.4 Hz, 1H), 7.11 – 7.03 (m, 2H), 6.94 (d, *J* = 7.5 Hz, 1H), 3.92 (q, *J* = 7.1 Hz, 2H), 3.17 (d, *J* = 5.1 Hz, 3H), 2.27 (s, 3H), 2.17 (s, 3H), 0.80 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 262.2 ([M+H]$^+$), 284.1 ([M+Na]$^+$).

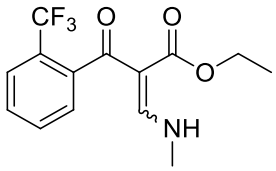


Ethyl 2-(2-tert-butylbenzoyl)-3-(methylamino)acrylate (1p): White solid, yield: 66% (major: minor=5:1). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 10.92 (br, 1H), 8.11 (d, *J* = 13.8 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 3.91 – 3.77 (m, 2H), 3.22 (d, *J* = 5.0 Hz, 3H), 1.36 (s, 9H), 0.78 (t, *J* = 7.1 Hz, 3H). Minor

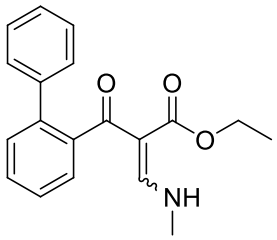
isomer δ 9.34 (br, 1H), 8.20 (d, *J* = 13.8 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 3.91 – 3.77 (m, 2H), 3.20 (d, *J* = 5.0 Hz, 4H), 1.37 (s, 11H), 0.70 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 288.2 ($[M-H]^-$).



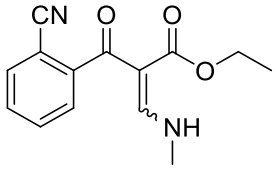
Ethyl 3-(methylamino)-2-(2-(2-(naphthalen-2-yl)ethyl)benzoyl) acrylate (1q): Colorless oil, yield: 77% (major: minor=3.5:1). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 11.02 (br, 1H), 8.12 (d, *J* = 13.9 Hz, 1H), 7.82 – 7.71 (m, 3H), 7.61 (s, 1H), 7.47 – 7.16 (m, 6H), 7.10 (d, *J* = 7.4 Hz, 1H), 3.89 (q, *J* = 7.1 Hz, 2H), 3.24 (d, *J* = 5.1 Hz, 3H), 3.09 – 2.96 (m, 4H), 0.84 (t, *J* = 7.1 Hz, 3H). Minor isomer δ 9.23 (br, 1H), 8.01 (d, *J* = 13.9 Hz, 1H), 7.82 – 7.71 (m, 3H), 7.61 (s, 1H), 7.47 – 7.16 (m, 7H), 3.90 (q, *J* = 7.1 Hz, 2H), 3.14 (d, *J* = 5.1 Hz, 3H), 3.09 – 2.96 (m, 4H), 0.80 (t, *J* = 7.1 Hz, 3H). HRMS (ESI) Calcd for $C_{25}H_{26}NO_3$ $[M+H]^+$: 388.1913, found 388.1902.



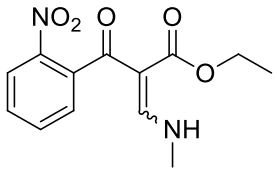
Ethyl 3-(methylamino)-2-(2-(trifluoromethyl)benzoyl)acrylate (1r): White solid, yield: 88% (major: minor=5:1). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 10.92 (br, 1H), 8.14 (d, *J* = 14.0 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.42 (m, 2H), 7.21 (d, *J* = 4.0 Hz, 1H),, 3.87 (q, *J* = 7.1 Hz, 2H), 3.25 (d, *J* = 5.1 Hz, 3H), 0.81 (t, *J* = 7.1 Hz, 3H). Minor isomer δ 9.47 (br, 1H), 8.26 (d, *J* = 14.5 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.42 (m, 2H), 7.22 (d, *J* = 4.0 Hz, 1H), 3.81 (q, *J* = 7.1 Hz, 2H), 3.23 (d, *J* = 5.1 Hz, 3H), 0.64 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 302.1 ($[M+H]^+$), 324.1 ($[M+Na]^+$).



Ethyl 2-(biphenylcarbonyl)-3-(methylamino)acrylate (1s): White solid, yield: 59% (major: minor=4.5:1). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 10.67 (br, 1H), 7.86 (d, *J* = 13.9 Hz, 1H), 7.42 – 7.23 (m, 9H), 3.87 (q, *J* = 7.1 Hz, 2H), 3.10 (d, *J* = 5.1 Hz, 3H), 0.86 (t, *J* = 7.1 Hz, 3H). Minor isomer δ 9.00 (br, 1H), 7.88 (d, *J* = 13.9 Hz, 1H), 7.42 – 7.23 (m, 9H), 3.87 (q, *J* = 7.1 Hz, 2H), 3.06 (d, *J* = 5.1 Hz, 3H), 0.79 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 310.2 ($[M+H]^+$), 332.1 ($[M+Na]^+$).

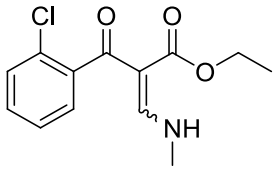


Ethyl 2-(2-cyanobenzoyl)-3-(methylamino)acrylate (1t): Yellow solid, yield: 18% (major: minor=4.2:1). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 10.97 (s, 1H), 8.18 (d, *J* = 14.1 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 3.98 (q, *J* = 7.0 Hz, 2H), 3.26 (d, *J* = 5.0 Hz, 3H), 0.97 (t, *J* = 7.1 Hz, 3H). Minor isomer 9.48 (br, 1H), 8.18 (d, *J* = 14.1 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.47 – 7.42 (m, 2H), 3.91 (q, *J* = 7.0 Hz, 2H), 3.25 (d, *J* = 5.0 Hz, 3H), 0.75 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 259.1 ($[M+H]^+$), 281.2 ($[M+Na]^+$).

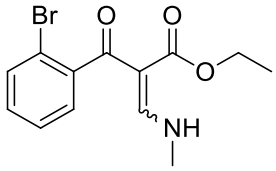


Ethyl 3-(methylamino)-2-(2-nitrobenzoyl)acrylate (1u): Yellow solid, yield: 87% (major: minor=5:1). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 10.86 (br, 1H), 8.13 (d, *J* = 16.0 Hz, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 3.87 (q, *J* = 7.1 Hz, 2H), 3.22 (d, *J* = 5.1 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H). Minor isomer δ

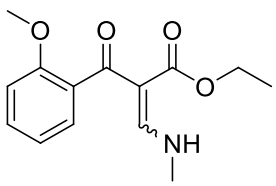
9.44 (br, 1H), 8.34 (d, *J* = 12.0 Hz, 1H), 8.09 (d, *J* = 6.4 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 7.4 Hz, 1H), 3.78 (q, *J* = 7.1 Hz, 2H), 3.20 (d, *J* = 5.1 Hz, 3H), 0.65 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 279.1 ($[M+H]^+$), 301.1 ($[M+Na]^+$).



Ethyl 2-(2-chlorobenzoyl)-3-(methylamino)acrylate (1v): White solid, yield: 79% (major: minor=5.8:1). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 10.98 (br, 1H), 8.13 (dd, *J* = 14.0, 0.7 Hz, 1H), 7.35 – 7.23 (m, 3H), 7.20 – 7.16 (m, 1H), 3.94 (q, *J* = 7.1 Hz, 2H), 3.25 (dd, *J* = 5.1, 0.6 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H). Minor isomer δ 9.40 (br, 1H), 8.19 (dd, *J* = 14.0, 0.7 Hz, 1H), 7.35 – 7.23 (m, 4H), 3.90 (q, *J* = 7.1 Hz, 2H), 3.22 (dd, *J* = 5.1, 0.6 Hz, 3H), 0.77 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 268.2 ($[M+H]^+$), 270.1 ($[M+2+H]^+$), 290.1 ($[M+Na]^+$), 292.1 ($[M+2+Na]^+$).

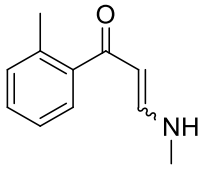


Ethyl 2-(2-bromobenzoyl)-3-(methylamino)acrylate (1w): White solid, yield: 94% (major: minor=5:1). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 10.98 (br, 1H), 8.13 (d, *J* = 14.0 Hz, 1H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.20 – 7.14 (m, 2H), 3.92 (q, *J* = 7.3 Hz, 2H), 3.22 (d, *J* = 5.1 Hz, 3H), 0.87 (t, *J* = 6.9 Hz, 3H). Minor isomer δ 9.43 (br 1H), 8.20 (d, *J* = 14.6 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.20 – 7.14 (m, 2H), 3.87 (q, *J* = 7.3 Hz, 2H), 3.20 (d, *J* = 5.2 Hz, 3H), 0.75 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 312.1 ($[M+H]^+$), 334.0 ($[M+Na]^+$), 336.0 ($[M+2+Na]^+$).

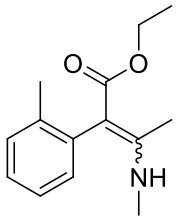


Ethyl 2-(2-methoxybenzoyl)-3-(methylamino)acrylate (1x): White solid yield: 45% (major:

minor=5.6:1). ^{1}H NMR (300 MHz, $CDCl_3$): major isomer δ 10.84 (br, 1H), 8.00 (d, *J* = 13.8 Hz, 1H), 7.31 (ddd, *J* = 8.3, 7.5, 1.7 Hz, 1H), 7.21 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.95 (td, *J* = 7.4, 0.8 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 3.93 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 3.20 (d, *J* = 5.1 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H). Minor isomer δ 9.08 (br, 1H), 8.05 (d, *J* = 13.8 Hz, 1H), 7.34 – 7.26 (m, *2*H), 6.94 (td, *J* = 7.4, 0.8 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 3.93 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 3.18 (d, *J* = 5.1 Hz, 3H), 0.81 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 264.0 ($[M+H]^+$), 286.0 ($[M+Na]^+$).

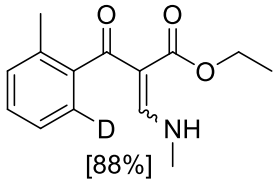


3-(methylamino)-1-o-tolylprop-2-en-1-one (1y): preparation according to the corresponding reference[1], white solid (Z/E=2.6:1). ^{1}H NMR (400 MHz, $CDCl_3$): Z isomer δ 10.09 (br, 1H), 7.39 (d, *J* = 7.1 Hz, 1H), 7.31 – 7.13 (m, 3H), 6.86 (dd, *J* = 12.9, 7.3 Hz, 1H), 5.31 (d, *J* = 7.3 Hz, 1H), 3.07 (d, *J* = 5.1 Hz, 3H), 2.46 (s, 3H). E isomer δ 7.31 – 7.13 (m, 5H), 5.48 (d, *J* = 13.2 Hz, 1H), 5.14 (br, 1H), 2.79 (d, *J* = 4.2 Hz, 3H), 2.37 (s, 3H). HRMS (ESI) Calcd for $C_{11}H_{14}NO$ $[M+H]^+$: 176.1075, found 176.1072.

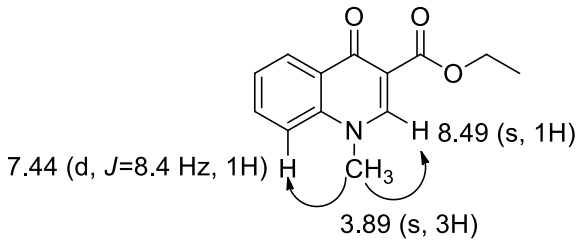


Ethyl 3-(methylamino)-2-phenylbut-2-enoate (1z): A mixture of ethyl 3-oxo-2-phenylbutanoate [2](105 mg, 0.48 mmol), methylamine (about 30% in EtOH(w/w), 94 μL, 0.72 mmol) and acetic acid (41 μL, 0.72 mmol) in 2.5 mL EtOH was stirred at 60℃ for 5 h. After cooling to room temperature, the mixture was poured into saturated $NaHCO_3$ (aq). EA was used to extract the mixture for 3 times and the combined organic layer was dried with Na_2SO_4. After removal of the drying agent, the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography, white solid, yield: 40%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.39 (br, 1H), 7.22 – 7.09 (m, 3H), 7.02 (d, *J* = 7.0 Hz, 1H), 4.11 (dq, *J* = 10.8, 7.0 Hz, 1H), 3.97 (dq, *J*

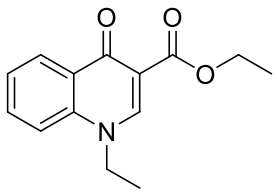
= 10.8, 7.0 Hz, 1H), 2.96 (d, *J* = 5.1 Hz, 3H), 2.14 (s, 3H), 1.65 (s, 3H), 1.10 (t, *J* = 7.0 Hz, 3H). HRMS (ESI) Calcd for $C_{14}H_{19}NO_2$ $[M+H]^+$: 234.1494, found 234.1491.



Deturo ethyl 3-(methylamino)-2-(2-methylbenzoyl)acrylate (1a-[D]): White solid, yield: 78% (major: minor=3.3:1). ^{1}H NMR (400 MHz, $CDCl_3$): major isomer δ 10.99 (br, 1H), 8.10 (d, *J* = 13.7 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.16-7.12 (m, 2H), 3.89 (q, *J* = 7.1 Hz, 2H), 3.24 (d, *J* = 5.2 Hz, 3H), 2.26 (s, 3H), 0.85 (t, *J* = 7.2 Hz, 3H). Minor isomer δ 10.99 (br, 1H), 8.03 (d, *J* = 13.7 Hz, 1H), 7.16-7.12 (m, 2H), 3.89 (q, *J* = 7.1 Hz, 2H), 3.19 (d, *J* = 5.2 Hz, 3H), 2.26 (s, 3H), 0.80 (t, *J* = 7.2 Hz, 3H). ESI-MS *m/z*: 278.0($[M+H]^+$), 300.0($[M+Na]^+$), 276.1 ($[M-H]^-$).

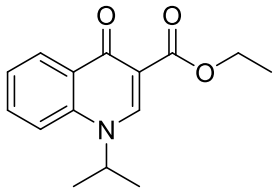


Ethyl 1-methyl-4-oxo-1,4-dihydroquinoline-3-carboxylate (2a): White solid, m.p. 124-127 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 7.6 Hz, 1H), 8.48 (s, 1H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.49 – 7.42 (m, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.5, 166.0, 149.9, 139.9, 132.8, 129.1, 128.1, 125.4, 115.7, 111.1, 61.1, 41.5, 14.6. Selective irradiation of the N-CH_3 resonance at δ 3.89 resulted in NOE enhancement for Ph-H at δ 7.44 and C=C-H at δ 8.49.HRMS (ESI) Calcd for $C_{13}H_{14}NO_3$ $[M+H]^+$: 232.0497, found 232.0968.

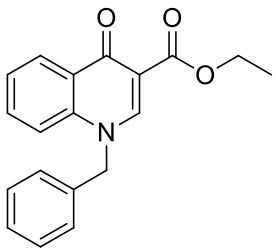


Ehyl 1-ethyl-4-oxo-1,4-dihydroquinoline-3-carboxylate (2b): Colorless oil. ^{1}H NMR (400 MHz,

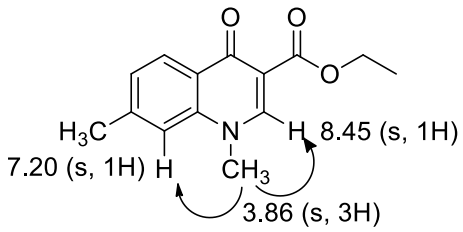
$CDCl_3$): δ 8.51 (d, *J* = 7.9 Hz, 1H), 8.47 (s, 1H), 7.71 – 7.61 (m, 1H), 7.49 – 7.35 (m, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.52 (t, *J* = 7.2 Hz, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 174.3, 166.0, 148.6 138.6, 132.6 129.4 128.2 125.0, 115.5, 111.1, 60.9, 48.9, 14.5, 14.4. HRMS (ESI) Calcd for $C_{14}H_{16}NO_3$ $[M+H]^+$: 246.1125, found 246.1132.



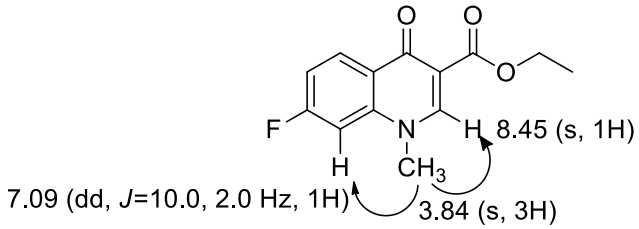
Ethyl 1-isopropyl-4-oxo-1,4-dihydroquinoline-3-carboxylate (2c): White solid, m.p. 83-85 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (s, 1H), 8.58 (d, *J* = 7.8 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 8.6 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 4.91 (hept, *J* = 6.7 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.61 (d, *J* = 6.6 Hz, 6H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.1, 166.5, 144.1, 139.3, 132.6, 129.6, 128.5, 125.0, 115.0, 111.2, 61.1, 51.2, 22.2, 14.6. HRMS (ESI) Calcd for $C_{15}H_{18}NO_3$ $[M+H]^+$: 260.1287, found 260.1280.



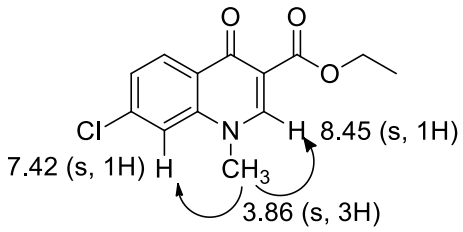
Ethyl 1-benzyl-4-oxo-1,4-dihydroquinoline-3-carboxylate (2d): White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 1H), 8.52 (d, *J* = 8.1 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.42 – 7.27 (m, 5H), 7.16 (d, *J* = 7.2 Hz, 2H), 5.40 (s, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ESI-MS *m/z*: 308.1($[M+H]^+$), 330.1 ($[M+Na]^+$). The spectra were in agreement with those described in the literature. [3]



Ethyl 1,7-dimethyl-4-oxo-1,4-dihydroquinoline-3-carboxylate (2e): White solid, m.p. 160-162 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 8.32 (d, *J* = 9.1 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 7.13 (s, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.46 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.4, 165.8, 149.6, 143.7, 139.8, 127.6, 126.8, 115.7, 110.6, 60.8, 41.4, 22.1, 14.5. Selective irradiation of the N-CH_3 resonance at δ 3.86 resulted in NOE enhancement for Ph-H at δ 7.20 and C=C-H at δ 8.45.HRMS (ESI) Calcd for $C_{14}H_{16}NO_3$ $[M+H]^+$: 246.1130, found 246.1122.

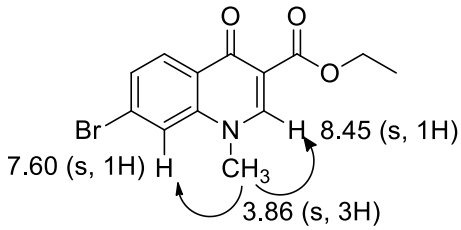


Ethyl 7-fluoro-1-methyl-4-oxo-1,4-dihydroquinoline-3-carboxylate (2f): White solid, m.p. 163-164 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (dd, *J* = 8.9, 6.5 Hz, 1H), 8.46 (s, 1H), 7.17 (td, *J* = 8.0, 4.0 Hz, 1H), 7.08 (dd, *J* = 10.0, 1.6 Hz, 1H), 4.39 (q, *J* = 7.0 Hz, 2H), 3.84 (s, 3H), 1.41 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 165.5, 165.3 (d, *J*=252.0 Hz), 150.1, 141.3 (d, *J*=11.3 Hz), 130.9 (d, *J*=10.4 Hz), 125.6, 113.6 (d, *J*=23.0 Hz), 111.6, 102.1 (d, *J*=26.5 Hz), 61.0, 41.4, 14.4. Selective irradiation of the N-CH_3 resonance at δ 3.84 resulted in NOE enhancement for Ph-H at δ 7.09 and C=C-H at δ 8.45. HRMS (ESI) Calcd for $C_{13}H_{13}FNO_3$ $[M+H]^+$: 250.0879, found 250.0879.

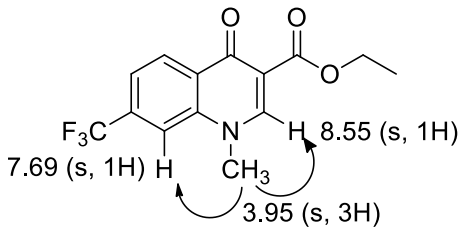


Ethyl 7-chloro-1-methyl-4-oxo-1,4-dihydroquinoline-3-carboxylate (2g): White solid, m.p.

176-180 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, 1H), 8.36(d, *J* = 8.0 Hz, 1H), 7.37 (s, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 165.1, 150.0, 140.3, 139.0, 129.2, 127.0, 125.7, 115.6, 111.2, 60.9, 41.4, 14.3. The NOESY spectrum revealed the following pairs of cross peaks: between N-CH_3 at δ 3.86 and Ph-H at δ 7.42 and N-CH_3 at δ 3.86 between C=C-H at δ 8.45. HRMS (ESI) Calcd for $C_{13}H_{13}ClNO_3$ $[M+H]^+$: 266.0584, found 266.0583.

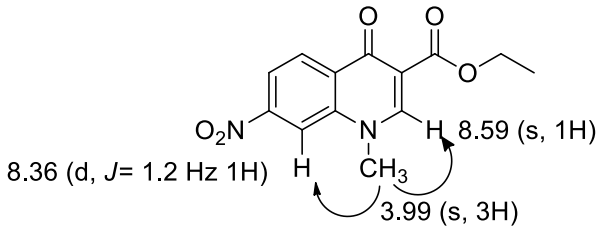


Ethyl 7-bromo-1-methyl-4-oxo-1,4-dihydroquinoline-3-carboxylate (2h): Light yellow solid, m.p. 202-204 °C ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 8.32 (d, *J* = 8.6 Hz, 1H), 7.56 (s, 1H), 7.52 (d, *J* = 8.6 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 165.2, 149.9, 140.5, 129.3, 128.5, 127.5, 118.6, 111.4, 60.9, 41.3, 14.3. Selective irradiation of the N-CH_3 resonance at δ 3.86 resulted in NOE enhancement for Ph-H at δ 7.60 and C=C-H at δ 8.45. HRMS (ESI) Calcd for $C_{13}H_{13}BrNO_3$ $[M+H]^+$: 310.0079, found 310.0076.

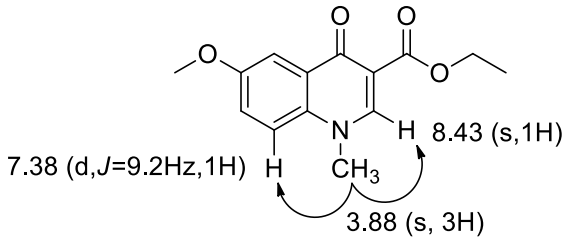


Ethyl 1-methyl-4-oxo-7-(trifluoromethyl)-1,4-dihydroquinoline-3- carboxylate (2i): White solid, m.p. 234-236 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, *J* = 8.5 Hz, 1H), 8.55 (s, 1H), 7.69 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 4.41 (q, *J* = 6.8 Hz, 2H), 3.95 (s, 3H), 1.42 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.4, 165.3, 150.5, 139.6, 134.4 (q, *J*= 33.0 Hz), 131.0, 129.3, 123.4 (q, *J*= 271.0 Hz), 121.4 (q, *J*= 3.3 Hz), 113.2 (q, *J*= 4.0 Hz), 112.1, 61.2, 41.5, 14.4. Selective irradiation of the N-CH_3 resonance at δ 3.95 resulted in NOE enhancement for Ph-H at δ 7.69 and C=C-H at δ 8.55. HRMS (ESI) Calcd for $C_{14}H_{13}F_3NO_3$ $[M+H]^+$: 300.0848, found

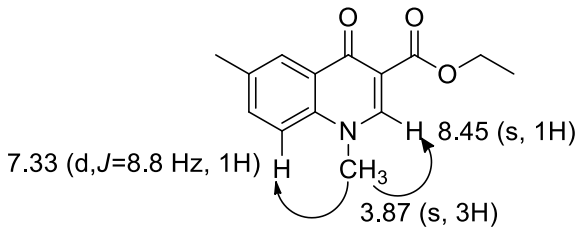
300.0843.



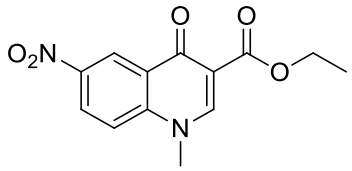
Ethyl 1-methyl-7-nitro-4-oxo-1,4-dihydroquinoline-3-carboxylate (2j): Light yellow solid, m.p. 259-261 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 8.8 Hz, 1H), 8.57 (s, 1H), 8.35 (d, *J* = 1.4 Hz, 1H), 8.23 (dd, *J* = 9.1, 1.4 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.99 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.9, 164.8, 150.9, 150.0, 139.8, 132.3, 130.0, 119.0, 112.6, 111.8, 61.2, 41.6, 14.3. Selective irradiation of the N-CH_3 resonance at δ 3.99 resulted in NOE enhancement for Ph-H at δ 8.36 and C=C-H at δ 8.59. HRMS (ESI) Calcd for $C_{13}H_{13}N_2O_5$ $[M+H]^+$: 277.0824, found 277.0820.



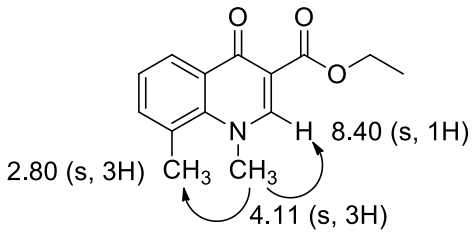
Ethyl 6-methoxy-1-methyl-4-oxo-1,4-dihydroquinoline-3-carboxylate (2k): White solid, m.p. 169-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 7.96 (d, *J* = 2.9 Hz, 1H), 7.38 (d, *J* = 9.1 Hz, 1H), 7.30 (dd, *J* = 9.1, 3.0 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 3.88 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.1, 166.3, 157.6, 148.6, 134.3, 130.5, 122.9, 117.3, 110.0, 107.6, 60.9, 55.9, 41.6, 14.6. The NOESY spectrum revealed the following pairs of cross peaks: between N-CH_3 at δ 3.88 and Ph-H at δ 7.38 and N-CH_3 at δ 3.88 between C=C-H at δ 8.43. HRMS (ESI) Calcd for $C_{14}H_{16}NO_4$ $[M+H]^+$: 262.1079, found 262.1072.



Ethyl 1,6-dimethyl-4-oxo-1,4-dihydroquinoline-3-carboxylate (2l): White solid, m.p. 171-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 8.26 (s, 1H), 7.47 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 2.45 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.5, 165.9, 149.3, 137.8, 135.4, 133.9, 128.8, 127.4, 115.7, 110.7, 60.8, 41.4, 21.1, 14.6. Selective irradiation of the N-CH_3 resonance at δ 3.87 resulted in NOE enhancement for Ph-H at δ 7.33 and C=C-H at δ 8.45. HRMS (ESI) Calcd for $C_{14}H_{16}NO_3$ $[M+H]^+$: 246.1130, found 246.1124.

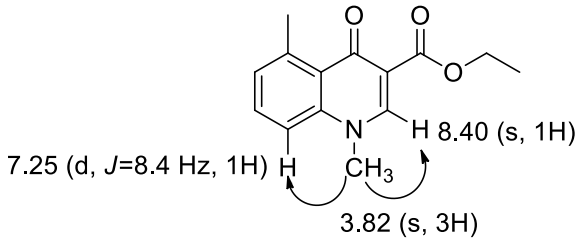


Ethyl 1-methyl-6-nitro-4-oxo-1,4-dihydroquinoline-3-carboxylate (2m): White solid, m.p. 268-271 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.93 (d, *J* = 2.8 Hz, 1H), 8.79 (s, 1H), 8.55 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.97 (d, *J* = 9.3 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 172.2, 163.9, 151.5, 143.8, 143.7, 127.6, 126.6, 121.9, 119.6, 111.2, 60.1, 41.3, 14.3. HRMS (ESI) Calcd for $C_{13}H_{13}N_2O_5$ $[M+H]^+$: 277.0284, found 277.0816.

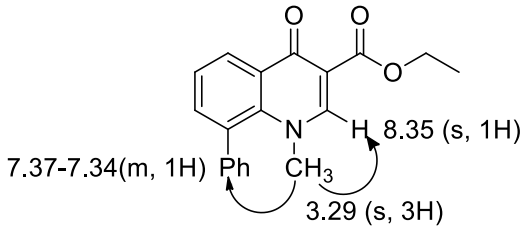


Ethyl 1,8-dimethyl-4-oxo-1,4-dihydroquinoline-3-carboxylate (2n): White solid, m.p. 135-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, *J* = 7.8 Hz, 1H), 8.39 (s, 1H), 7.45 (d, *J* = 7.1 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 4.10 (s, 3H), 2.80 (s, 3H), 1.41 (t, *J* =

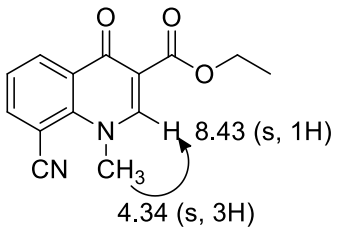
7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 174.4, 165.9, 152.5, 140.5, 137.5, 130.9, 126.6, 126.41, 125.4, 110.5, 61.0, 47.0, 24.2, 14.5. Selective irradiation of the N-CH_3 resonance at δ 4.11 resulted in NOE enhancement for Ph-CH_3 at δ 2.80 and C=C-H at δ 8.40. HRMS (ESI) Calcd for $C_{14}H_{16}NO_3$ $[M+H]^+$: 246.1130, found 246.1123.



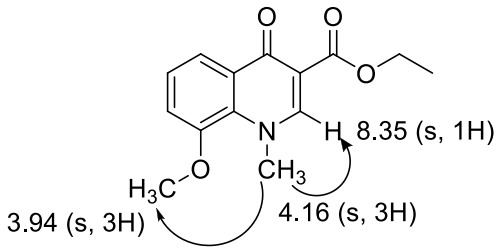
Ethyl 1,5-dimethyl-4-oxo-1,4-dihydroquinoline-3-carboxylate (2o): White solid, m.p. 129-131 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38 (s, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.5 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 2.97 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 177.2, 166.1, 149.0, 143.3, 141.5, 131.7, 128.7, 127.4, 113.7, 112.2, 60.9, 42.2, 24.6, 14.7. Selective irradiation of the N-CH_3 resonance at δ 3.82 resulted in NOE enhancement for Ph-H at δ 7.25 and C=C-H at δ 8.40. HRMS (ESI) Calcd for $C_{14}H_{16}NO_3$ $[M+H]^+$: 246.1130, found 246.1123.



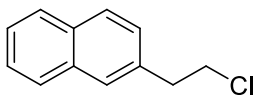
Ethyl 1-methyl-4-oxo-8-phenyl-1,4-dihydroquinoline-3-carboxylate (3s): White solid, m.p. 143-144 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (dd, *J* = 7.9, 1.8 Hz, 1H), 8.32 (s, 1H), 7.50 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.47 – 7.38 (m, 4H), 7.36 – 7.30 (m, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.27 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.2, 165.8, 152.4, 141.2, 138.7, 136.8, 132.4, 130.6, 129.5, 128.6, 128.1, 127.4, 124.6, 110.9, 60.9, 47.2, 14.5. HRMS (ESI) Calcd for $C_{19}H_{18}NO_3$ $[M+H]^+$: 308.1287, found 308.1279.



Ethyl 8-cyano-1-methyl-4-oxo-1,4-dihydroquinoline-3-carboxylate (3t): White solid, m.p. 235-237 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, *J* = 8.0 Hz, 1H), 8.42 (s, 1H), 8.06 (d, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.33 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.9, 164.8, 152.1, 141.1, 140.4, 133.9, 130.5, 124.9, 118.5, 112.7, 100.9, 61.5, 45.2, 14.5. Selective irradiation of the N-CH_3 resonance at δ 4.34 resulted in NOE enhancement for C=C-H at δ 8.43. HRMS (ESI) Calcd for $C_{14}H_{13}N_2O_3$ $[M+H]^+$: 257.0926, found 257.0919.



Ethyl 8-methoxy-1-methyl-4-oxo-1,4-dihydroquinoline-3-carboxylate (3x): White solid，m.p. 126-129℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 4.15 (s, 3H), 3.93 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.8, 166.1, 152.1, 150.6, 131.7, 130.9, 125.7, 119.9, 114.6, 110.3, 60.9, 56.5, 47.9, 14.6. Selective irradiation of the N-CH_3 resonance at δ 4.16 resulted in NOE enhancement for O-CH_3 at δ 3.94 and C=C-H at δ 8.35. HRMS (ESI) Calcd for $C_{14}H_{16}NO_4$ $[M+H]^+$: 262.1079, found 262.1073.



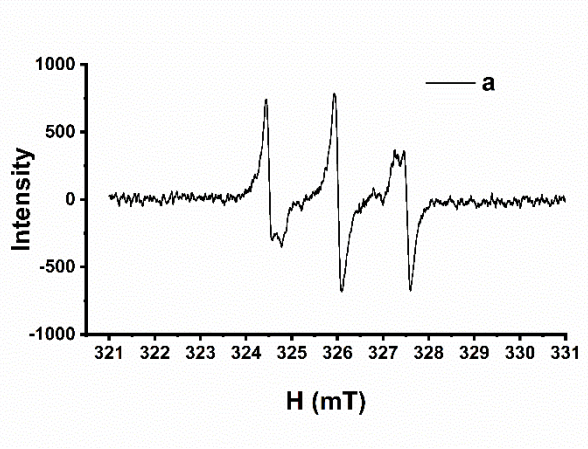
2-(2-chloroethyl)naphthalene (4): White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 – 7.81 (m, 3H), 7.69 (s, 1H), 7.51 – 7.45 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 3.83 (t, *J* = 7.4 Hz, 2H), 3.25 (t, *J* = 7.4 Hz, 2H). EI-MS *m/z*: 190 ($[M]^+$), 192 ($[M+2]^+$). The spectra were in agreement with those described in the literature.[4]

4. EPR experiment

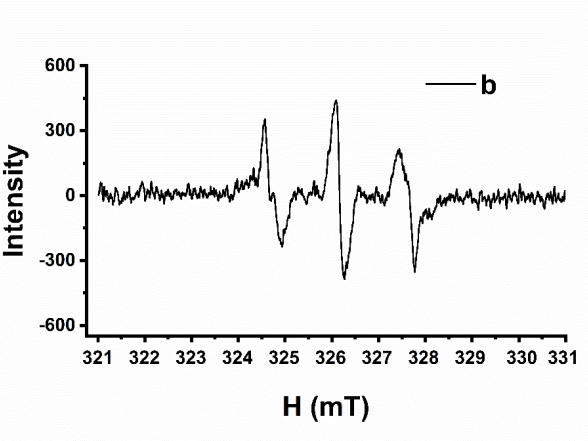
General procedure for EPR experiments

Sample A: The mixture of ethyl 3-(methylamino)-2-(2-methylbenzoyl)acrylate (**1a**) (0.3 mmol, 1.0 equiv.), diacetoxyiodobenzene (PIDA) (0.9 mmol, 3.0 equiv.), 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) (0.6 mmol, 2.0 equiv.), and DCE(10.0 mL) were loaded in a sealed tube. Then the tube was placed in the thermostatic oil bath and stirred at 120 °C for 15 minutes. After reaction completion, the mixture was packed in the capillary and detected by EPR.

Sample B: A mixture of ethyl 3-(methylamino)-2-(2-methylbenzoyl)acrylate (**1a**) (0.3 mmol, 1.0 equiv.), diacetoxyiodobenzene (PIDA) (0.9 mmol, 3.0 equiv.), and DCE (10.0 mL) were loaded in another sealed tube. The tube was placed in the thermostatic oil bath and stirred at 120 °C for 10 minutes. Then 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) (0.6 mmol, 2.0 equiv.) was added and the mixture was allowed to stirred at 120 °C for another 10 minutes. After reaction completion, the mixture was packed in the capillary and detected by EPR.



A. **1a** + PIDA + DMPO under standard conditions for 15 min



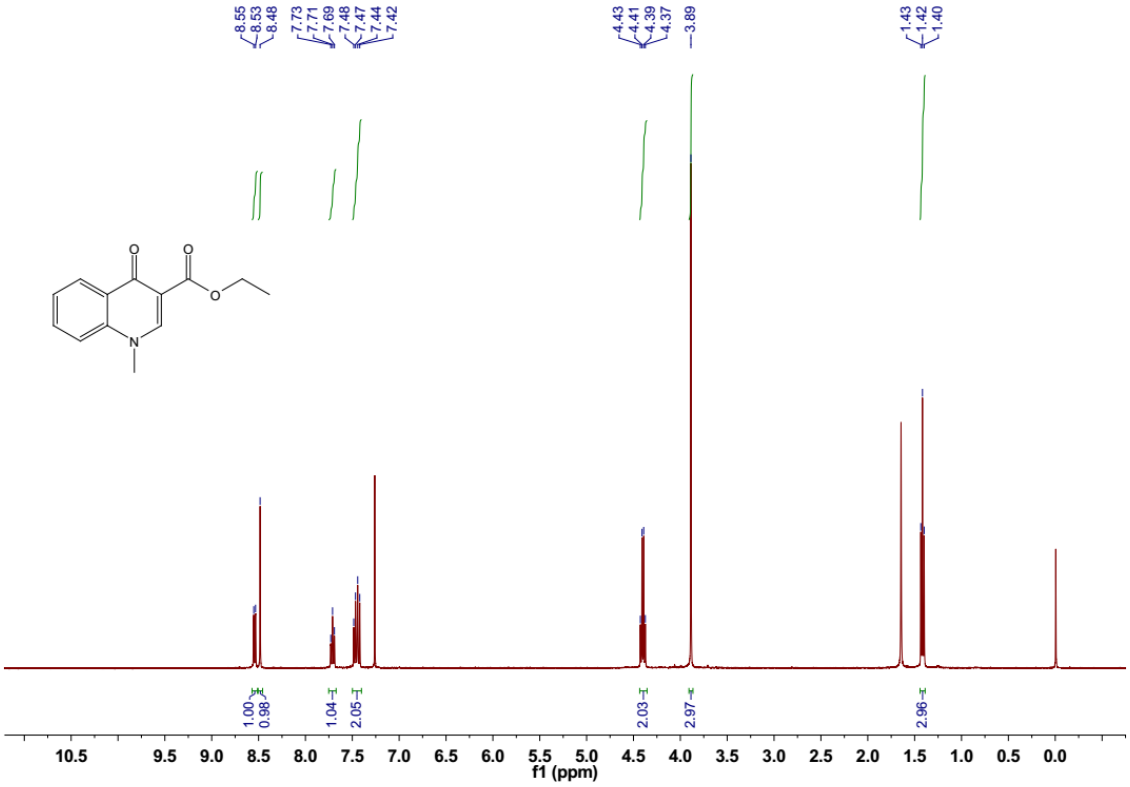
B. **1a** + PIDA under standard conditions for 10 min then DMPO was added, the mixture under standard conditions for another 10 min

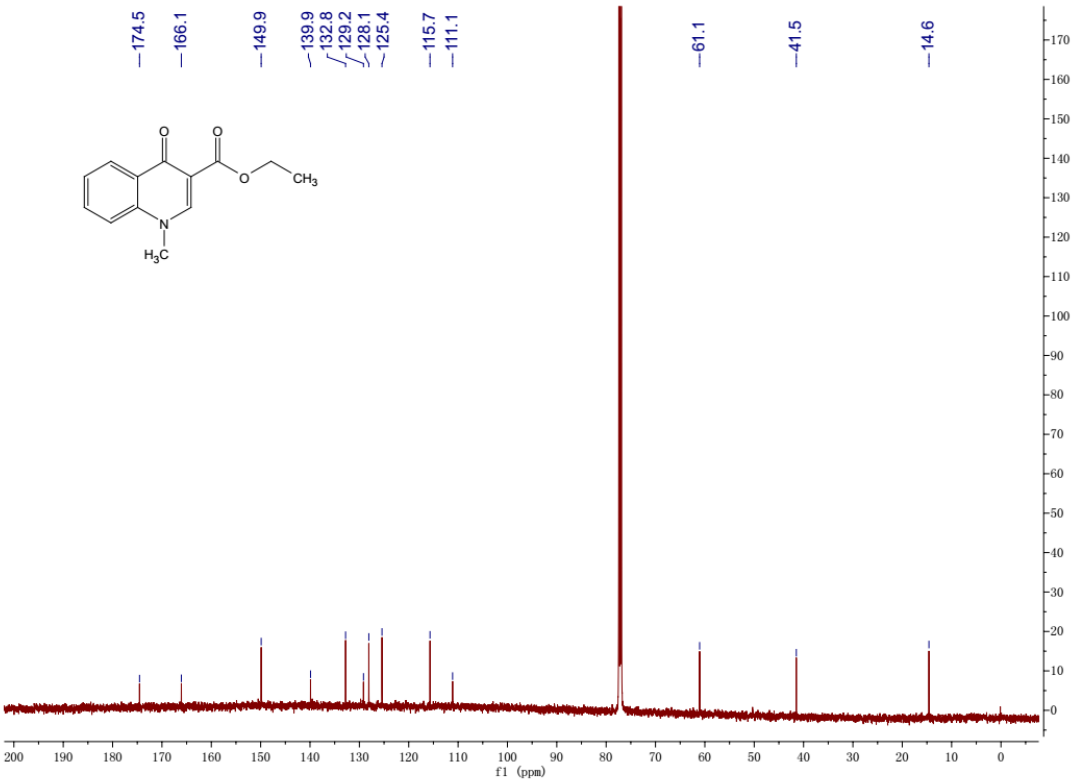
5. References

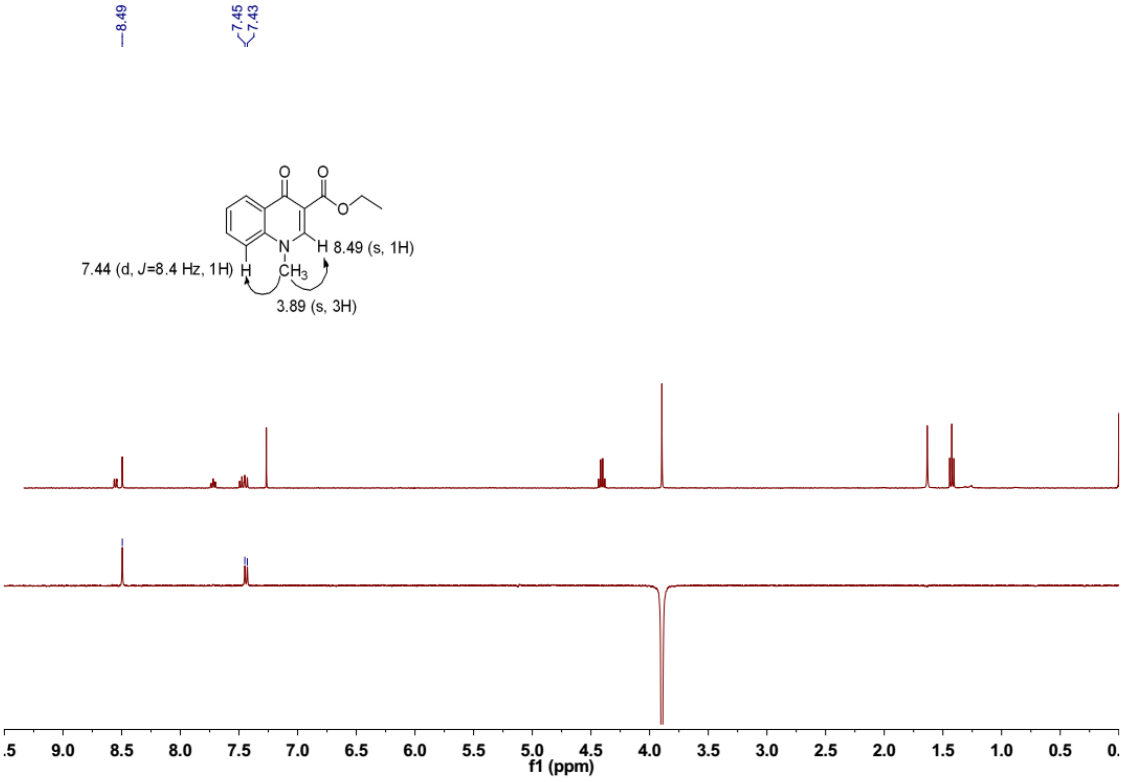
[1] H. Geng, X. Zhang, M. Chang, L. Zhou, W. Wu, X. Zhang, *Adv. Synth. Catal.* **2011**, *353*, 3039.
[2] J. G. Zeevaart, C. J. Parkinson, C. B. de Koning, *Tetrahedron Lett.* **2007**, *48*, 3289.
[3] R. A. Bunce, E. J. Lee, M. T. Grant, *J. Heterocyclic Chem.* **2011**, *48*, 620.
[4] M. Murakami, S. Kadowaki, A. Fujimoto, M. Ishibashi, T. Matsuda, *Org. Lett.* **2005**, *7*, 2059.

6. Copies of NMR Spectra Data

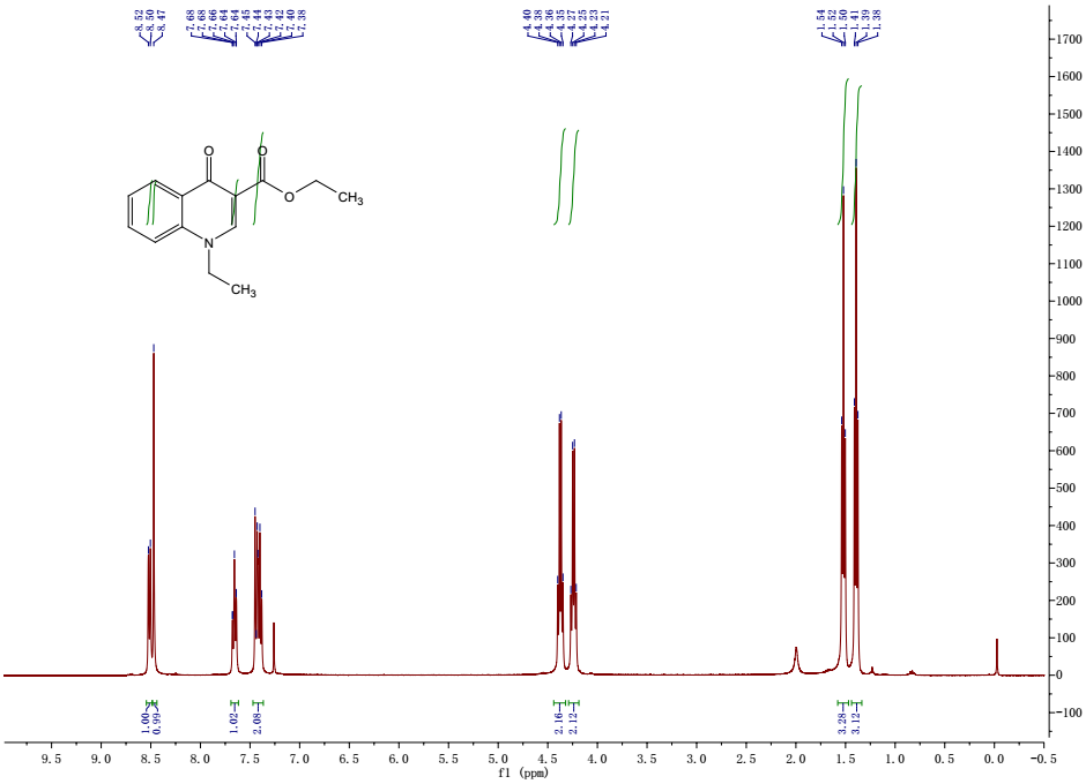
^{1}H and ^{13}C NMR spectra of compound 2a

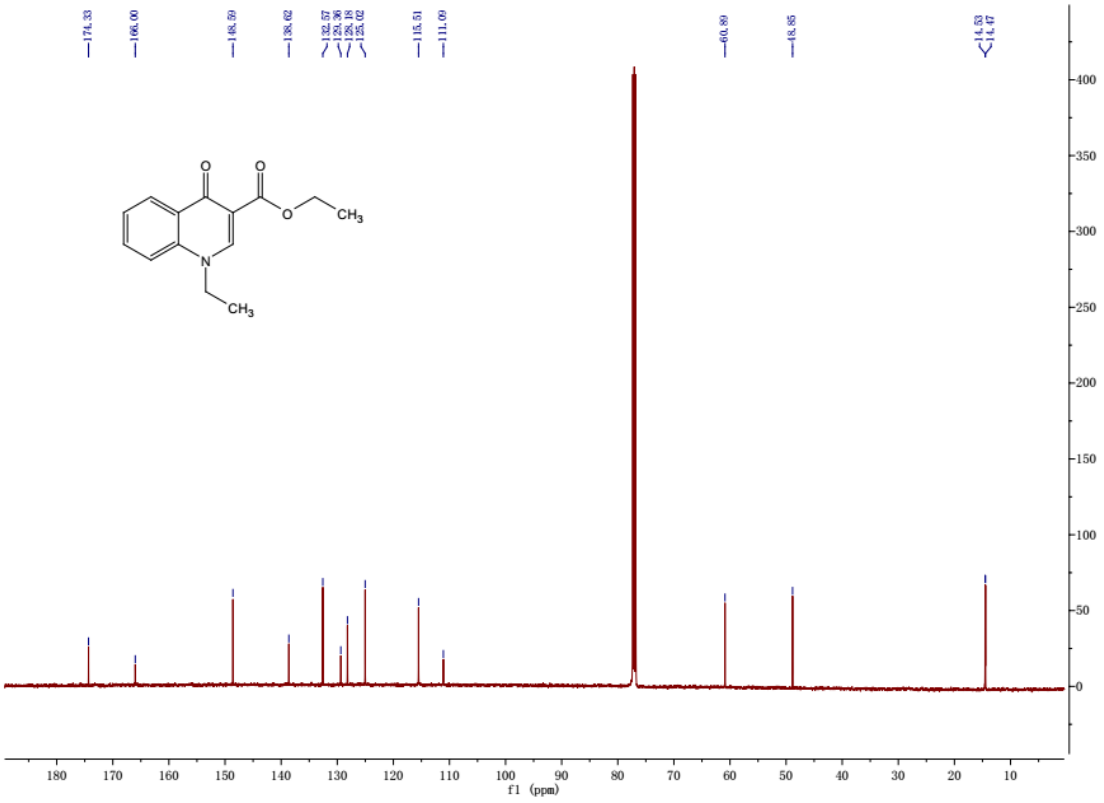




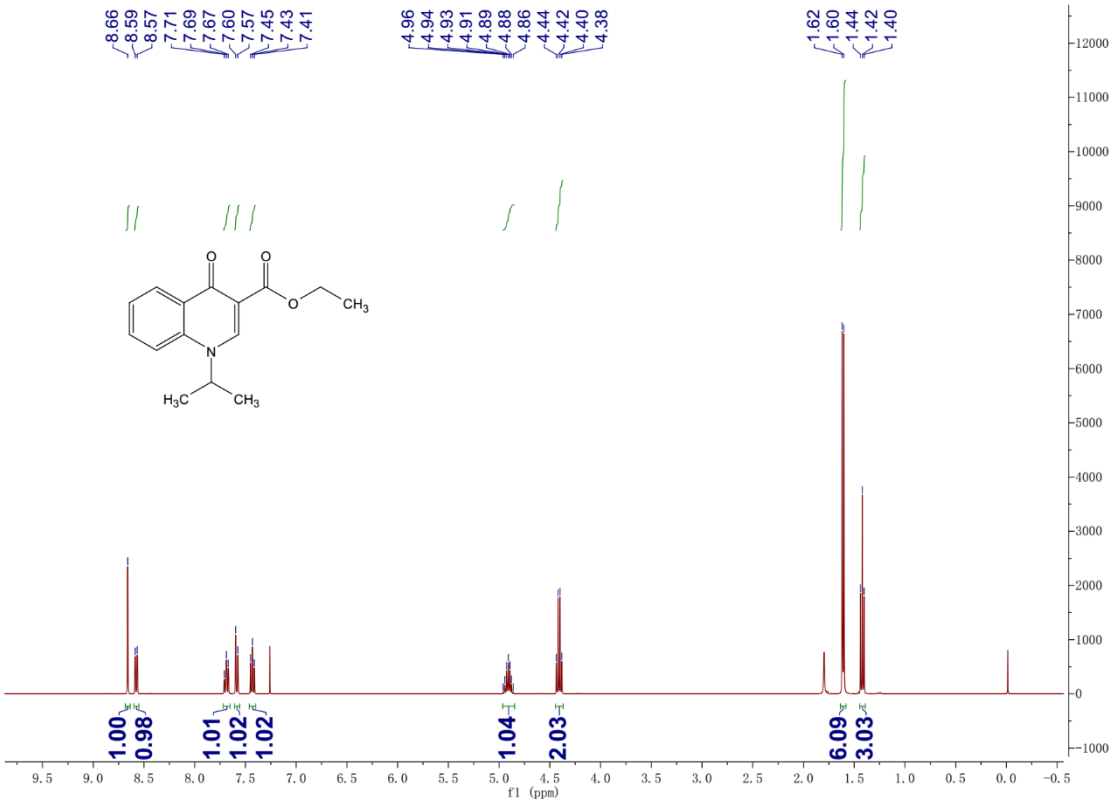

8.49
7.45
7.43
O
O
O
N
H 8.49 (s, 1H)
7.44 (d, J=8.4 Hz, 1H) H
CH3
3.89 (s, 3H)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

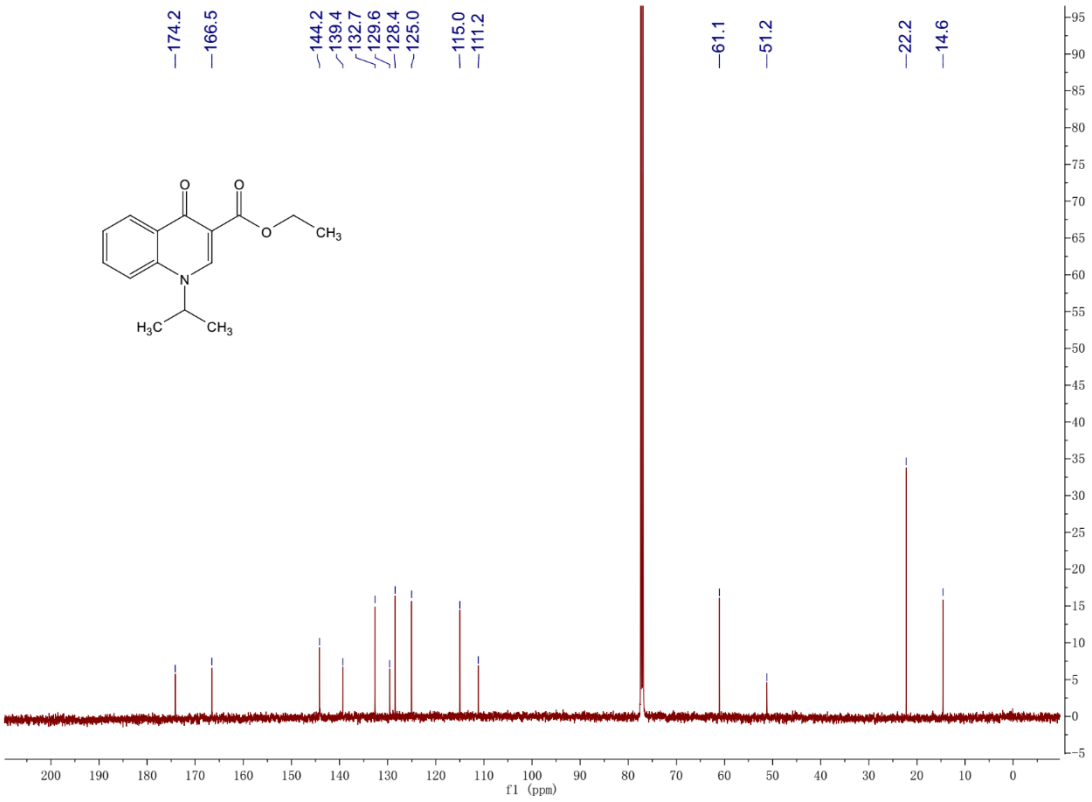
^{1}H and ^{13}C NMR spectra of compound 2b



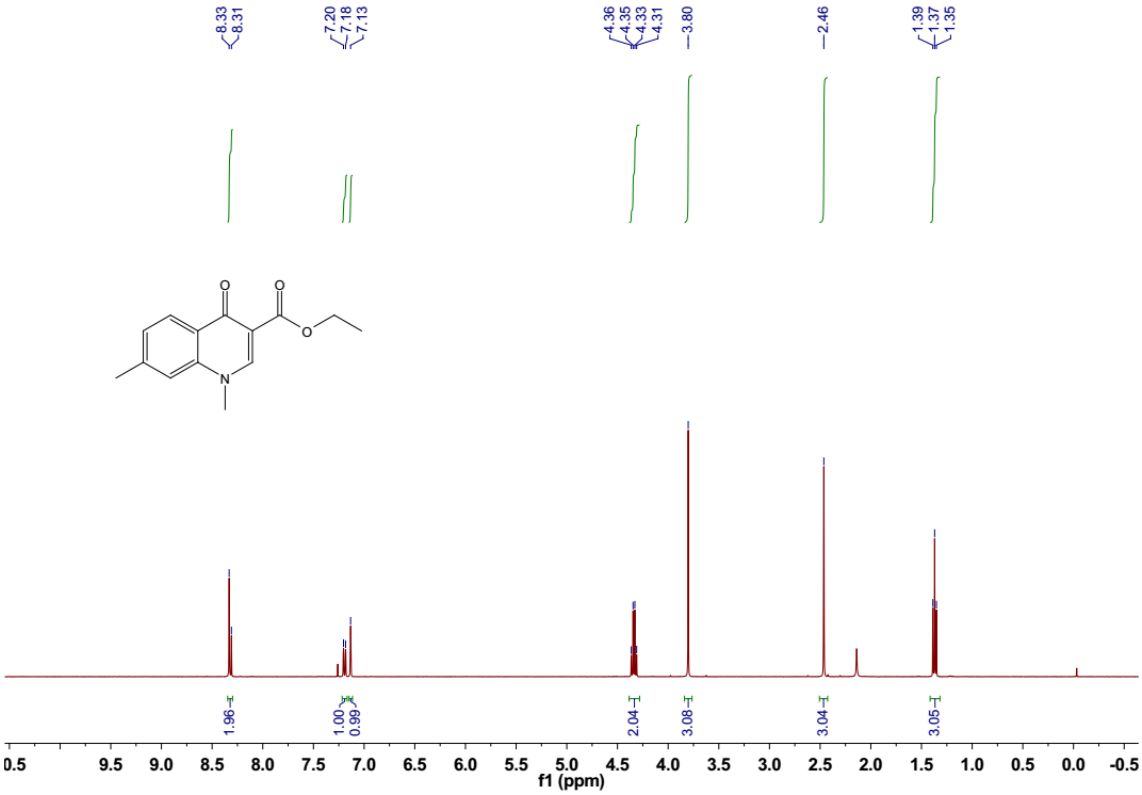


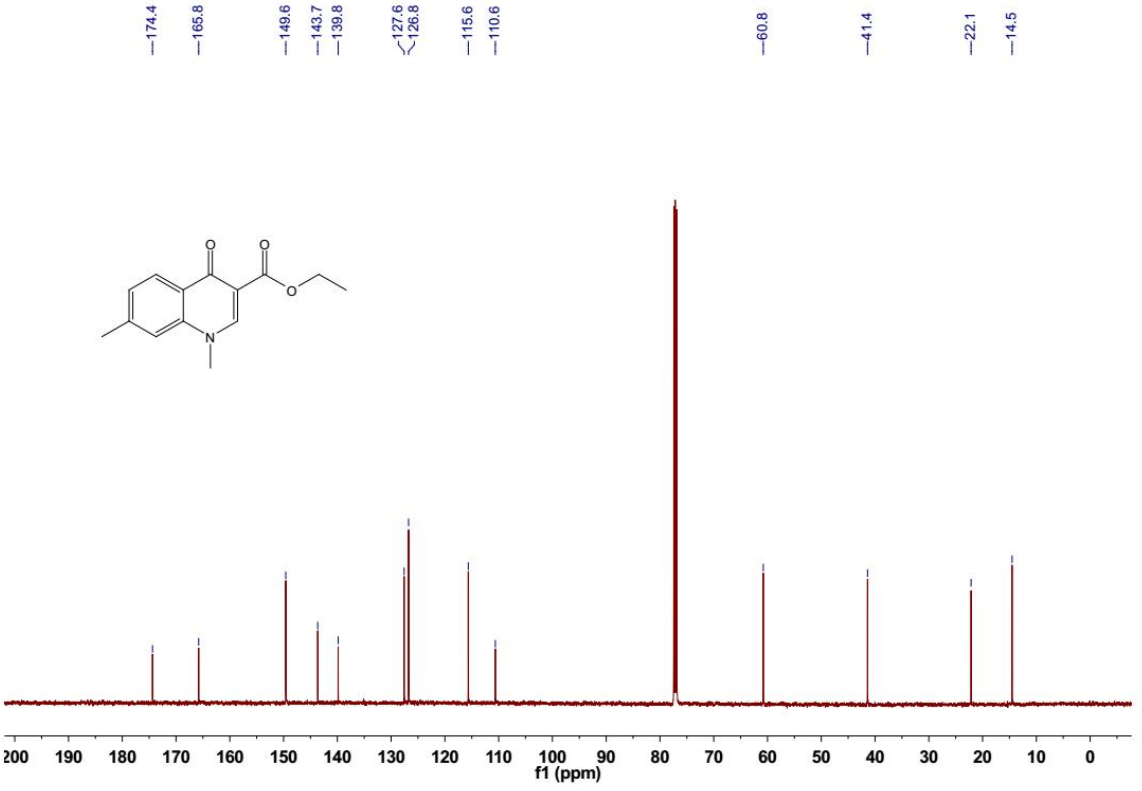
^{1}H and ^{13}C NMR spectra of compound 2c

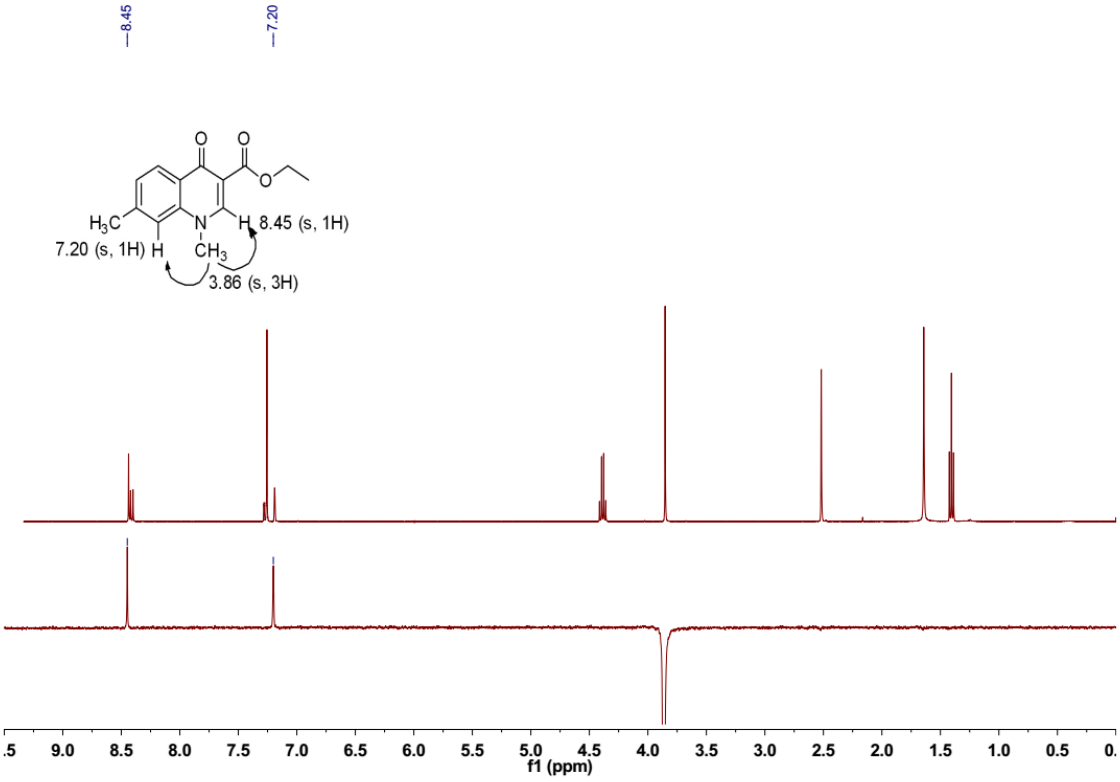




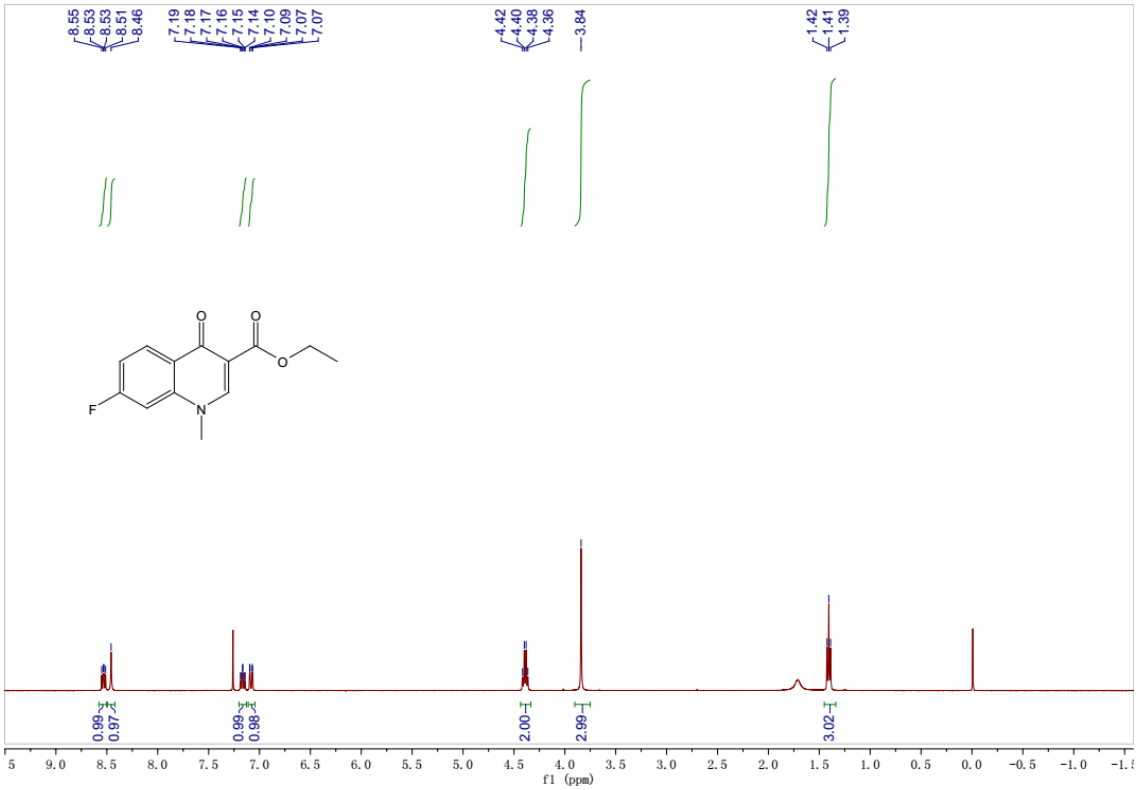
^{1}H and ^{13}C NMR spectra of compound 2e

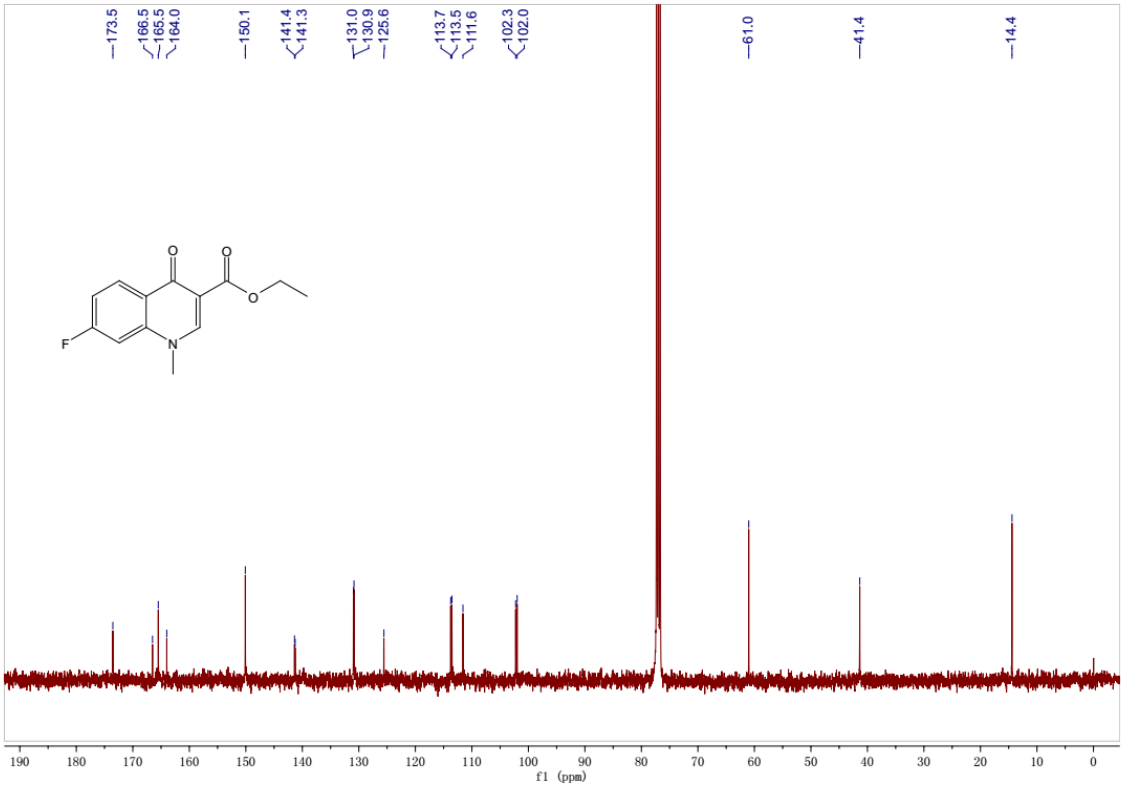


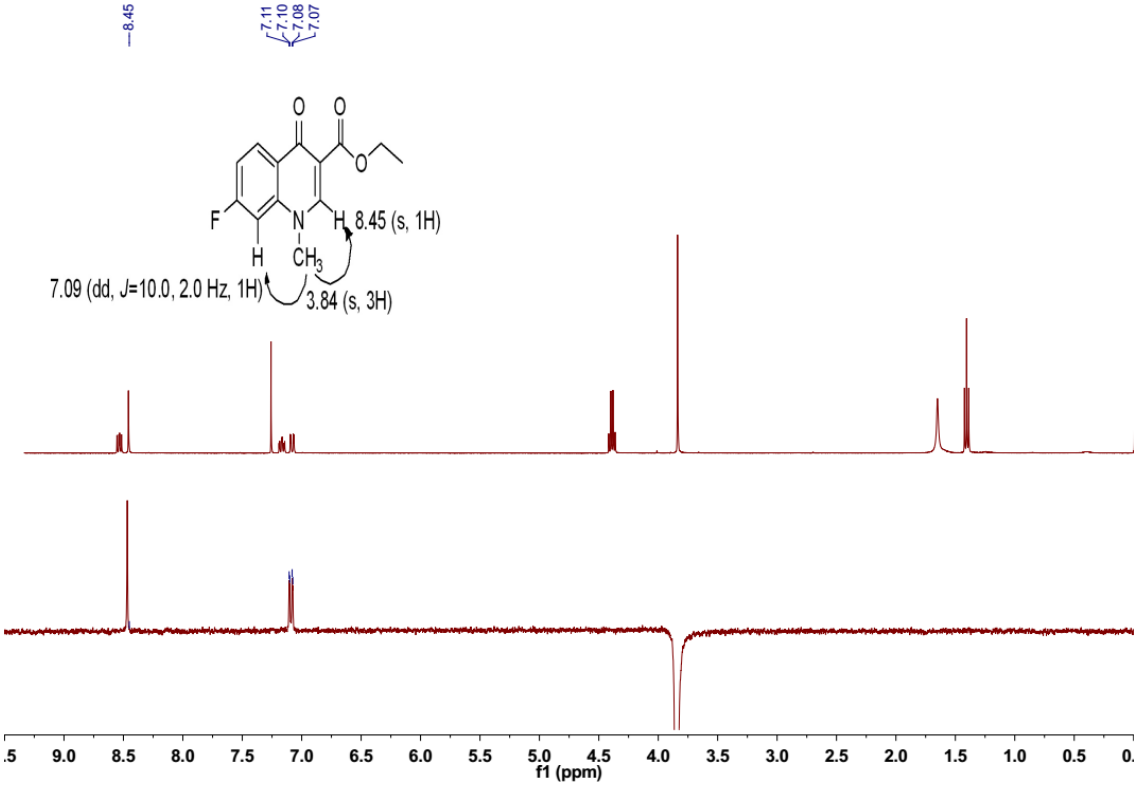



8.45
7.20
O
O
O
H3C
N
H
8.45 (s, 1H)
7.20 (s, 1H)
H
CH3
3.86 (s, 3H)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

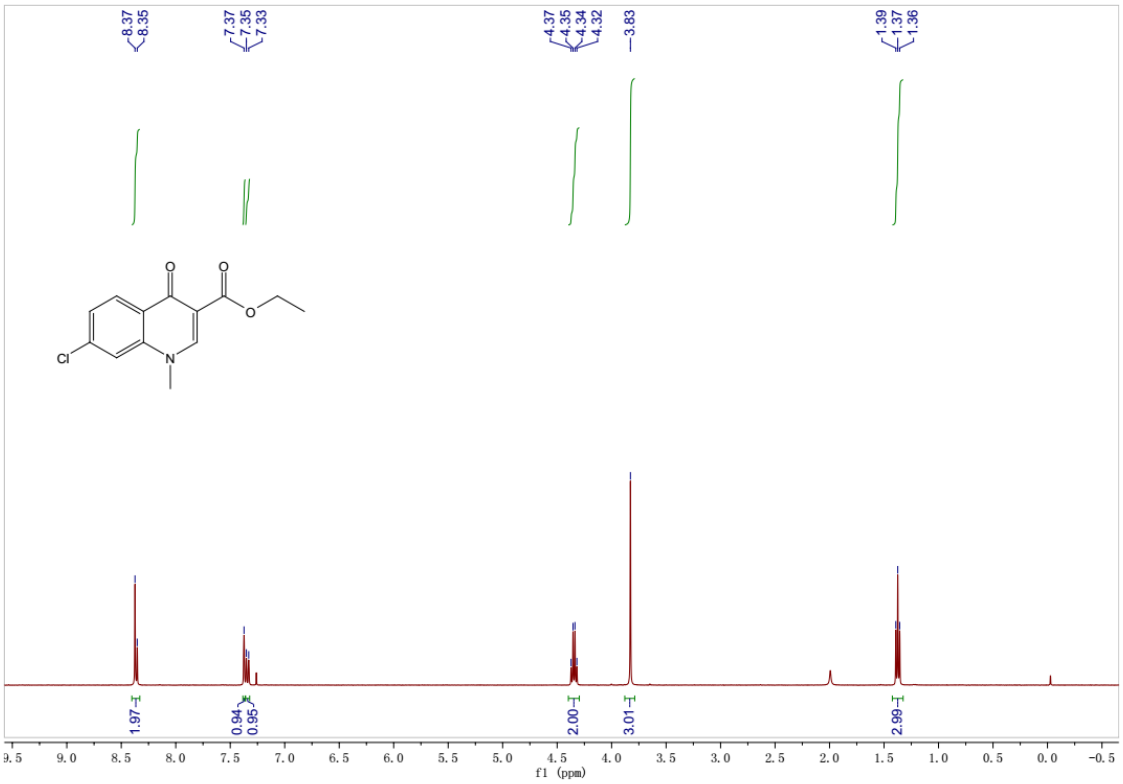
^{1}H and ^{13}C NMR spectra of compound 2f

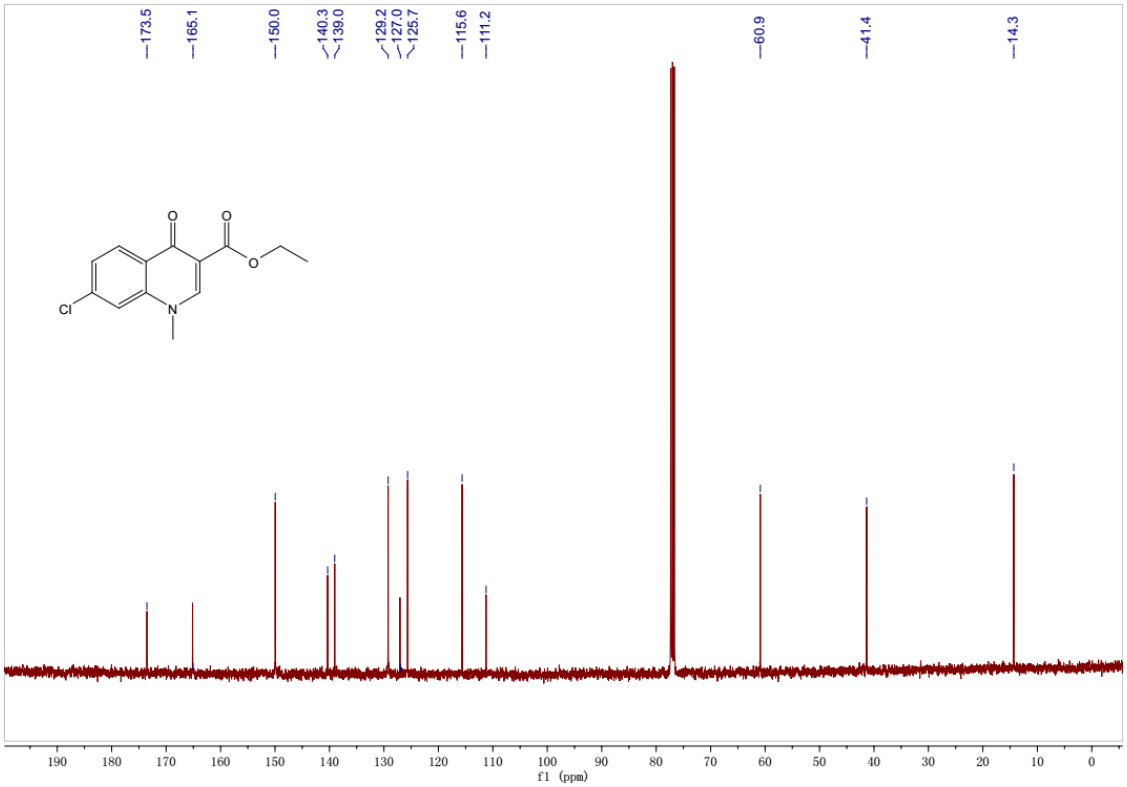


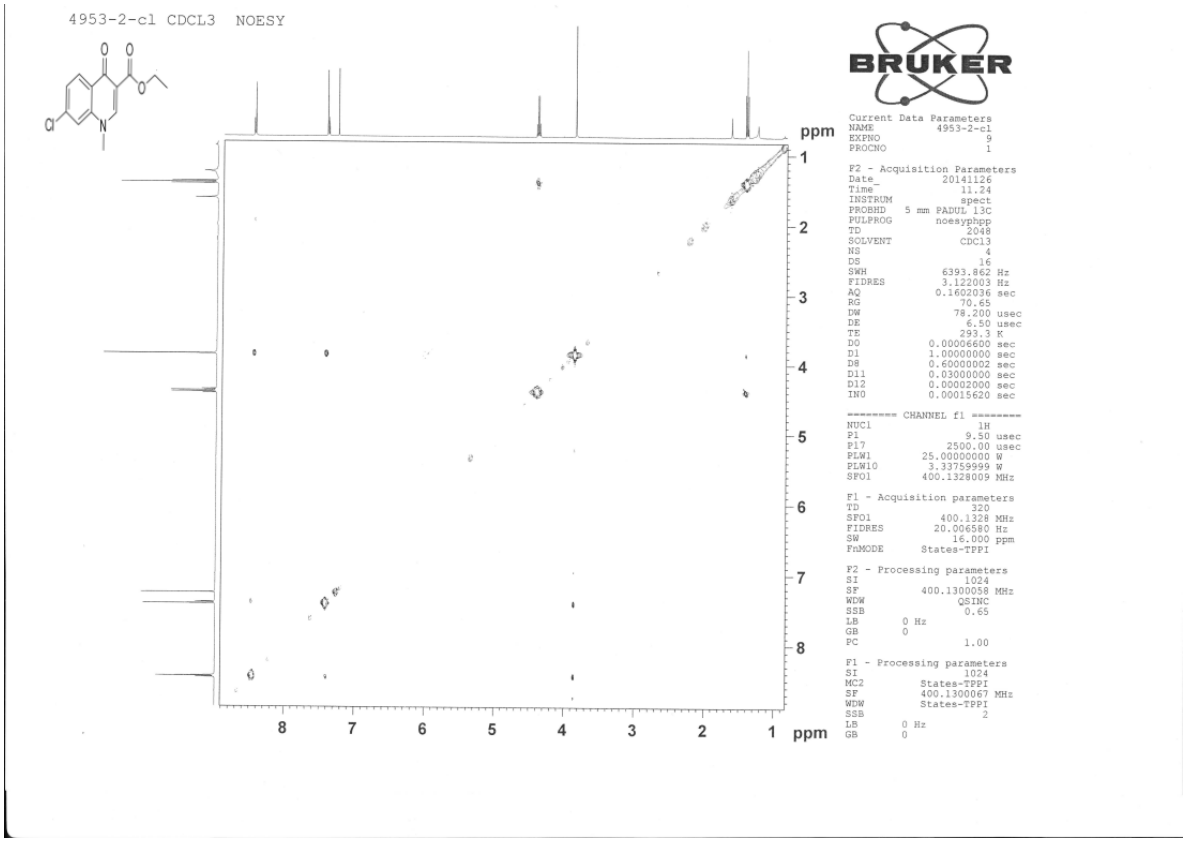



8.45
7.11
7.10
7.08
7.07
O
O
O
F
N
H
8.45 (s, 1H)
H
CH3
7.09 (dd, J=10.0, 2.0 Hz, 1H)
3.84 (s, 3H)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

^{1}H and ^{13}C NMR spectra of compound 2g







BRUKER

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SOLVENT                   CDCl3
NS                            4
DS                           16
SWH                   6393.862 Hz
FIDRES                3.122003 Hz
AQ                    0.1602036 sec
RG                        70.65
DW                       78.200 usec
DE                        6.50 usec
TE                       293.3 K
D0                    0.00006600 sec
D1                    1.00000000 sec
D8                    0.60000002 sec
D11                   0.03000000 sec
D12                   0.00002000 sec
IN0                   0.00015620 sec

======== CHANNEL f1 ========
NUC1                         1H
P1                         9.50 usec
P17                     2500.00 usec
PLW1                25.00000000 W
PLW10                3.33759999 W
SFO1                400.1328009 MHz

F1 - Acquisition parameters
TD                          320
SFO1                  400.1328 MHz
FIDRES               20.006580 Hz
SW                       16.000 ppm
FnMODE             States-TPPI

F2 - Processing parameters
SI                         1024
SF                  400.1300058 MHz
WDW                      QSINC
SSB                       0.65
LB            0 Hz
GB            0
PC                         1.00

F1 - Processing parameters
SI                         1024
MC2                States-TPPI
SF                  400.1300067 MHz
WDW                States-TPPI
SSB                           2
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GB            0
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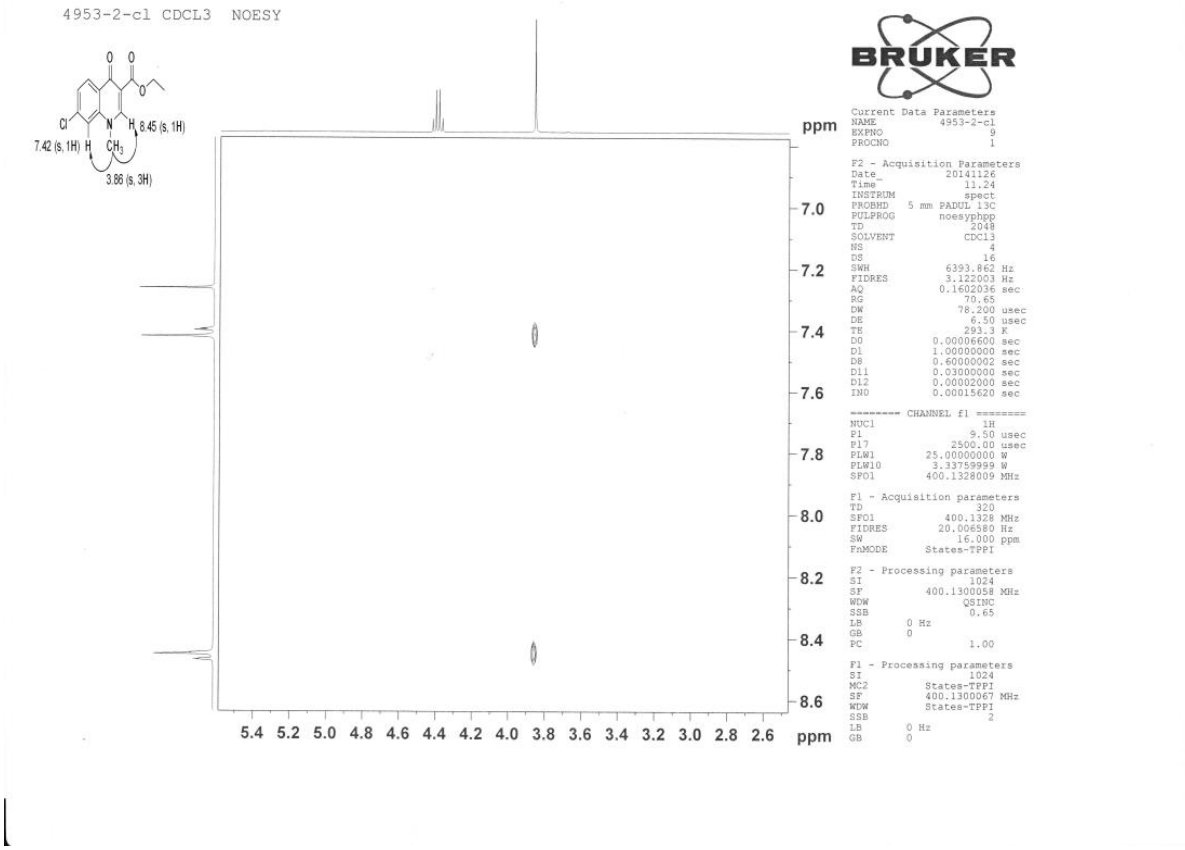

BRUKER

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Current Data Parameters
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EXPNO                         9
PROCNO                        1

F2 - Acquisition Parameters
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Time                      11.24
INSTRUM                   spect
PROBHD    5 mm PADUL 13C
PULPROG              noesyphpp
TD                         2048
SOLVENT                   CDCl3
NS                            4
DS                           16
SWH                   6393.862 Hz
FIDRES                3.122003 Hz
AQ                    0.1602036 sec
RG                        70.65
DW                       78.200 usec
DE                        6.50 usec
TE                       293.3 K
D0                    0.00006600 sec
D1                    1.00000000 sec
D8                    0.60000002 sec
D11                   0.03000000 sec
D12                   0.00002000 sec
IN0                   0.00015620 sec

======== CHANNEL f1 ========
NUC1                         1H
P1                         9.50 usec
P17                     2500.00 usec
PLW1                25.00000000 W
PLW10                3.33759999 W
SFO1                400.1328009 MHz

F1 - Acquisition parameters
TD                          320
SFO1                  400.1328 MHz
FIDRES               20.006580 Hz
SW                       16.000 ppm
FnMODE             States-TPPI

F2 - Processing parameters
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SF                  400.1300058 MHz
WDW                      QSINC
SSB                       0.65
LB            0 Hz
GB            0
PC                         1.00

F1 - Processing parameters
SI                         1024
MC2                States-TPPI
SF                  400.1300067 MHz
WDW                States-TPPI
SSB                           2
LB            0 Hz
GB            0
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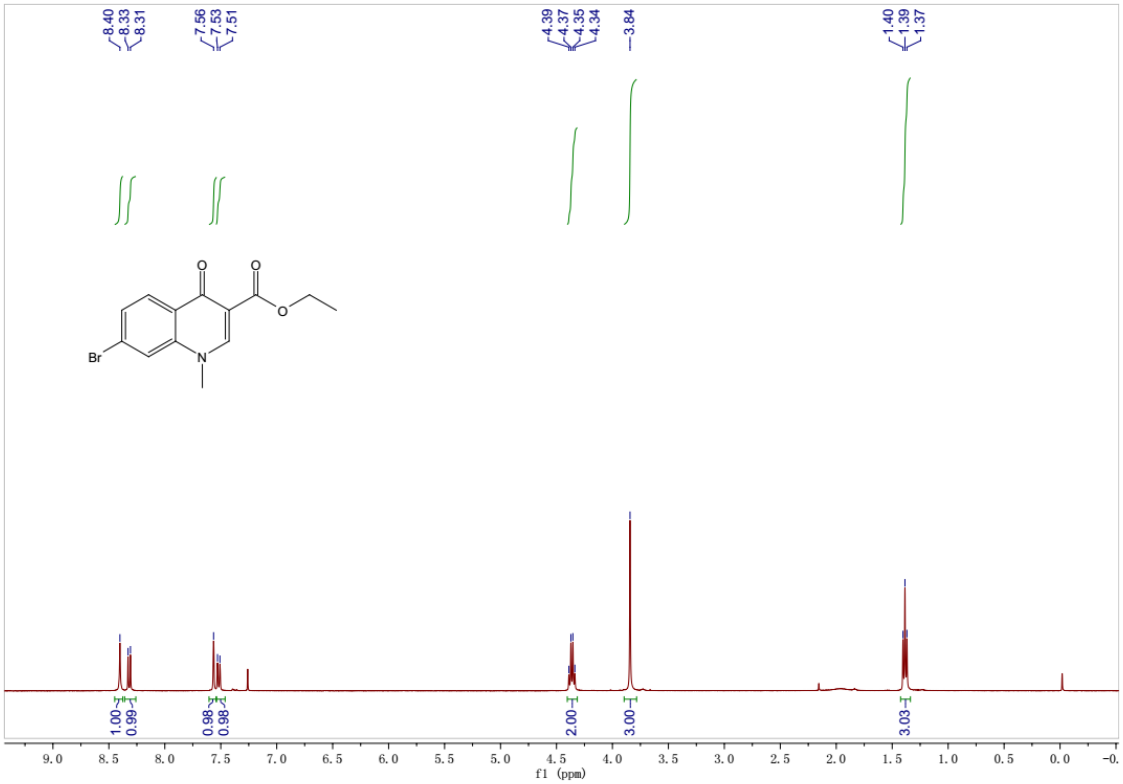
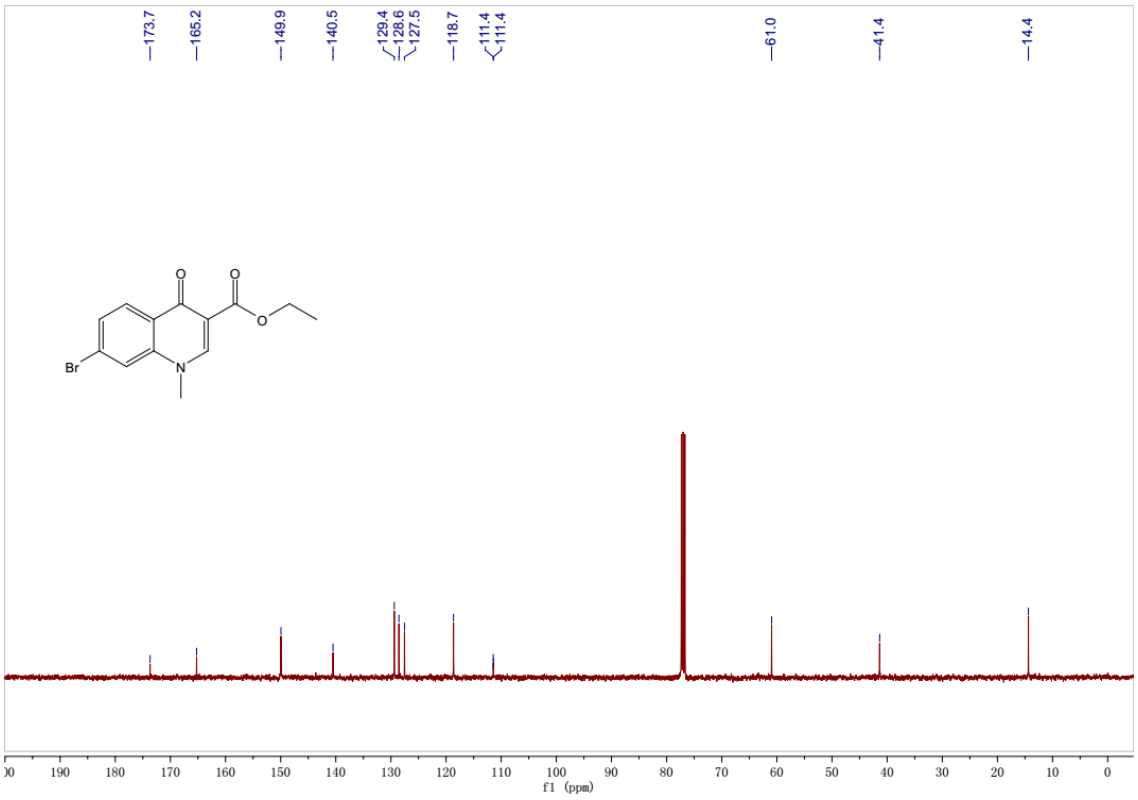
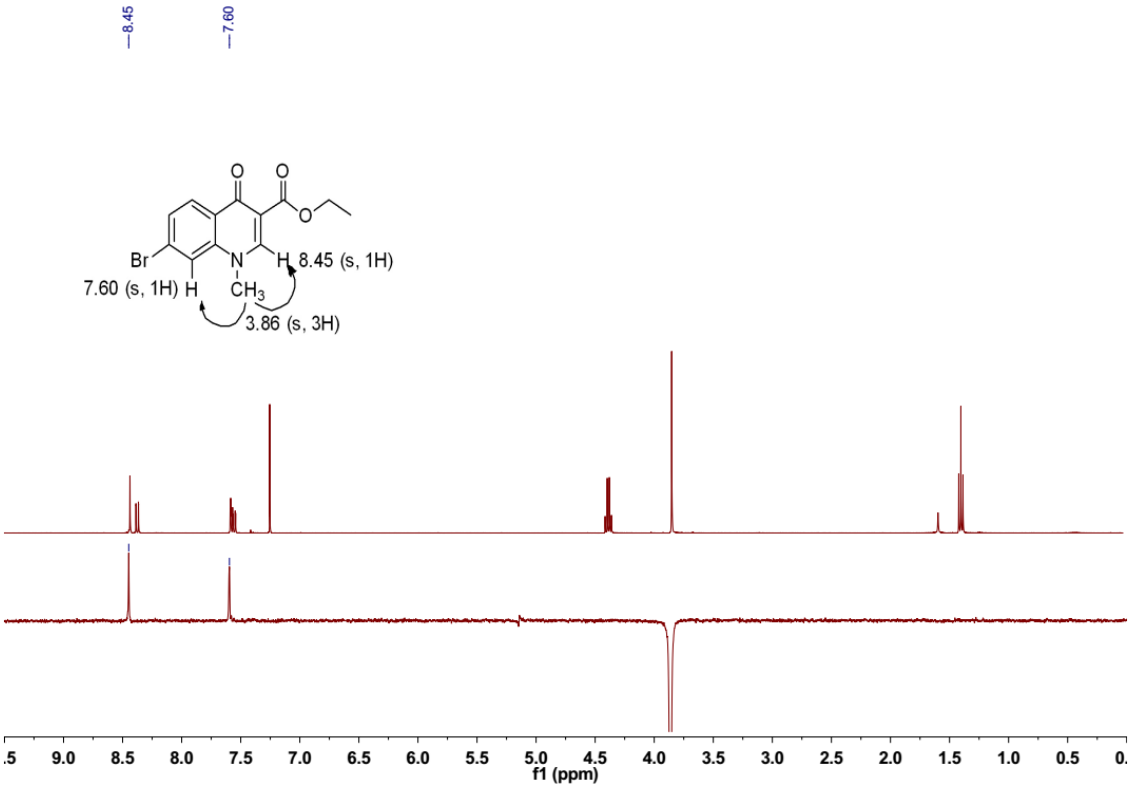
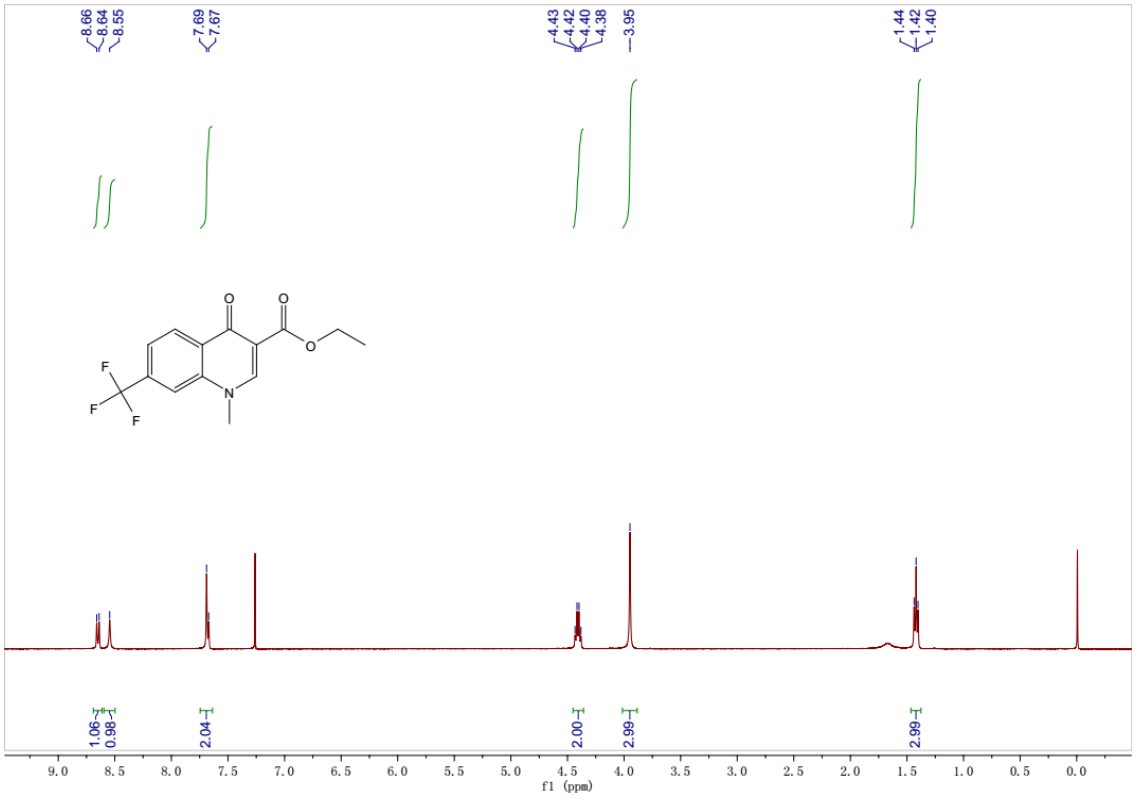
^{1}H and ^{13}C NMR spectra of compound 2h

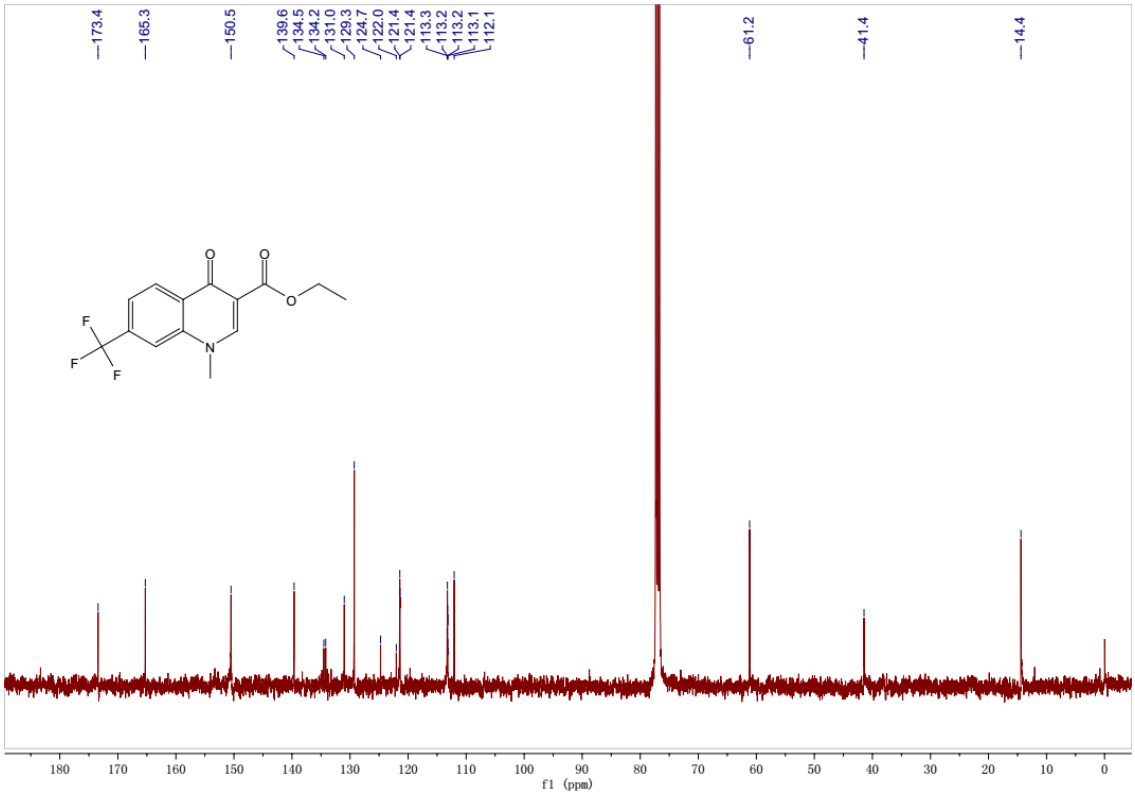


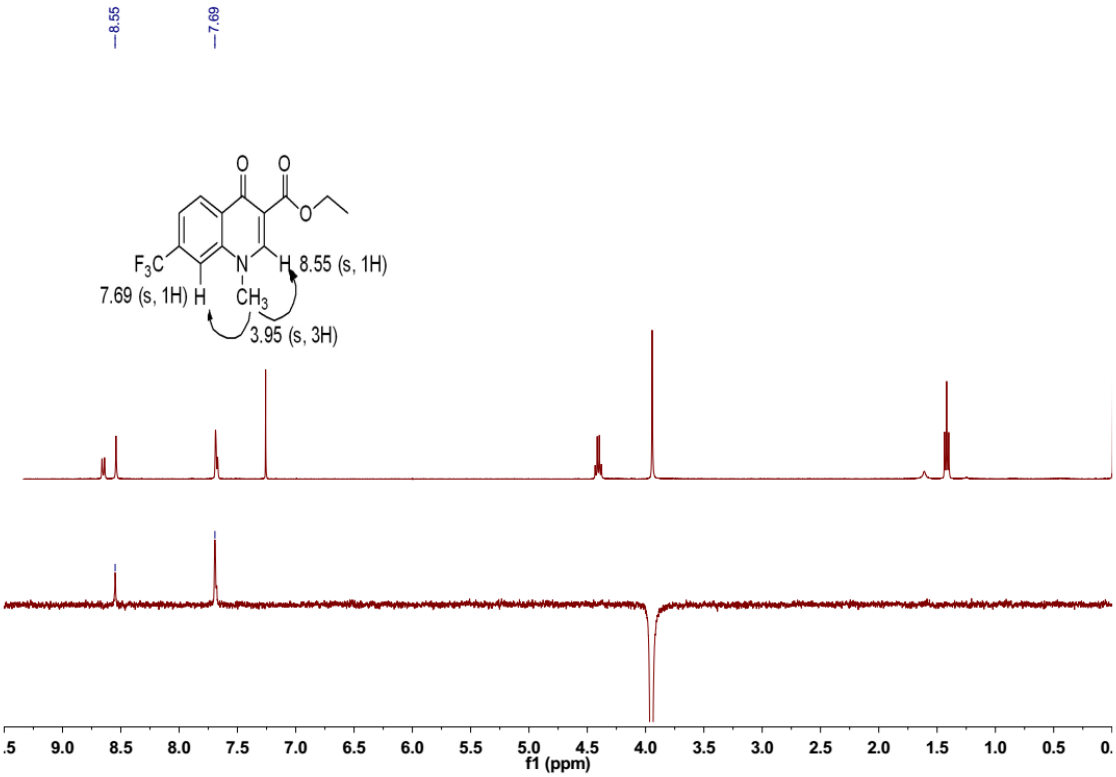



8.45
7.60
O
O
O
Br
N
H
8.45 (s, 1H)
7.60 (s, 1H) H
CH3
3.86 (s, 3H)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

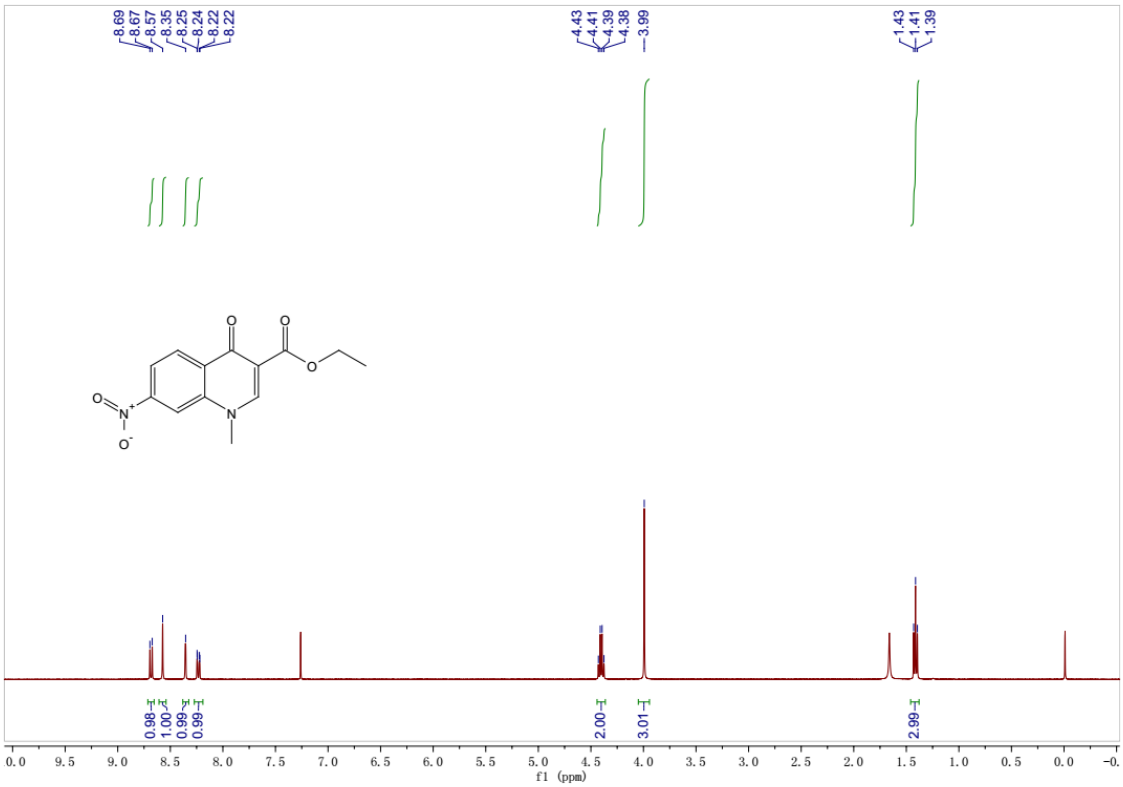
^{1}H and ^{13}C NMR spectra of compound 2i

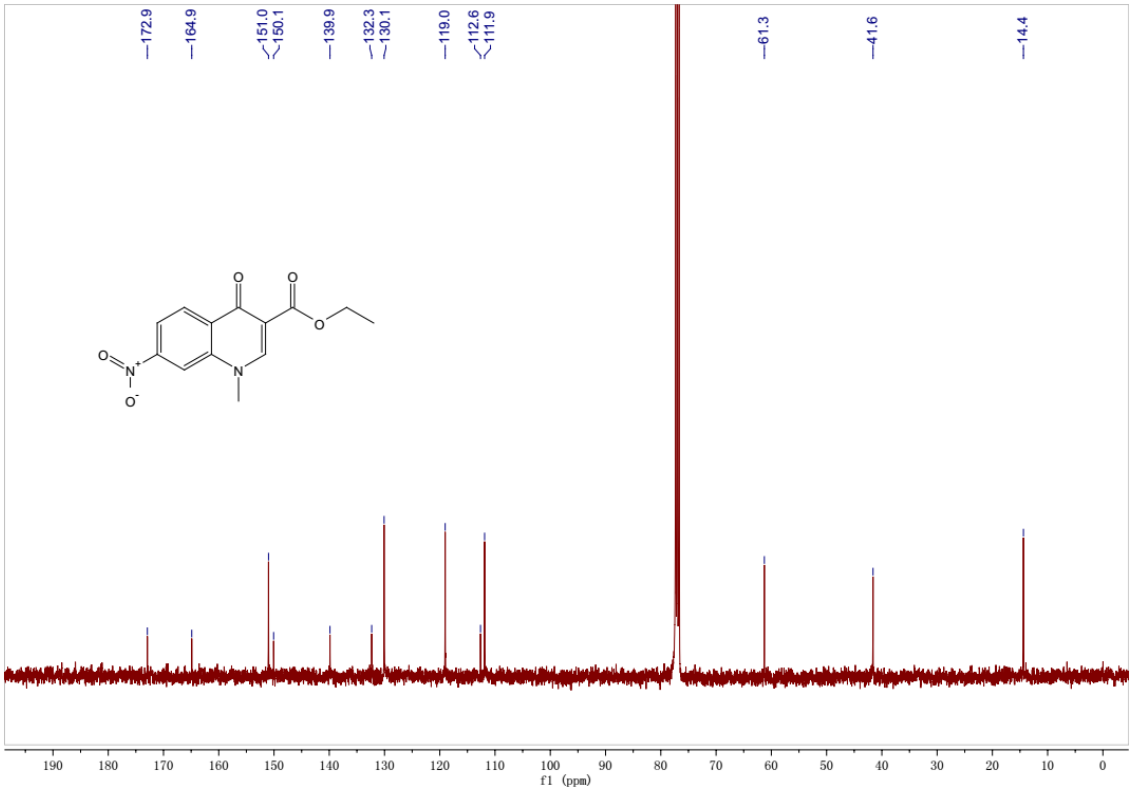


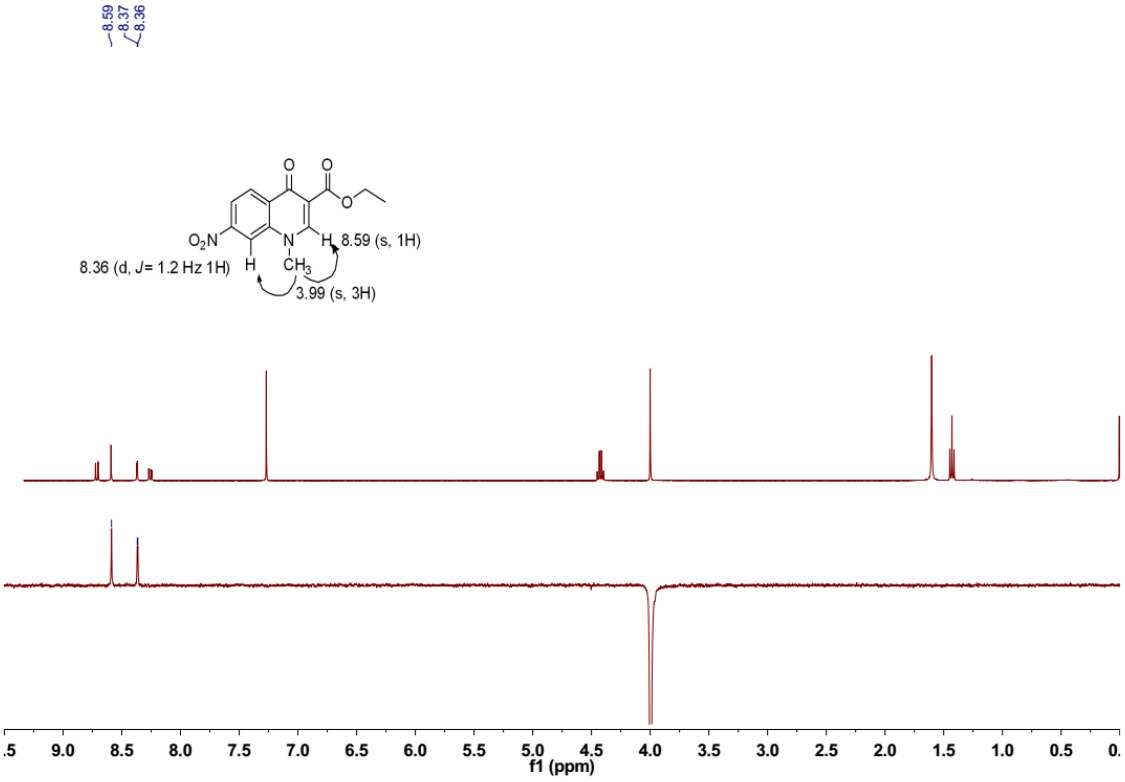



8.55
7.69
O
O
O
F3C
N
H 8.55 (s, 1H)
7.69 (s, 1H) H
CH3
3.95 (s, 3H)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

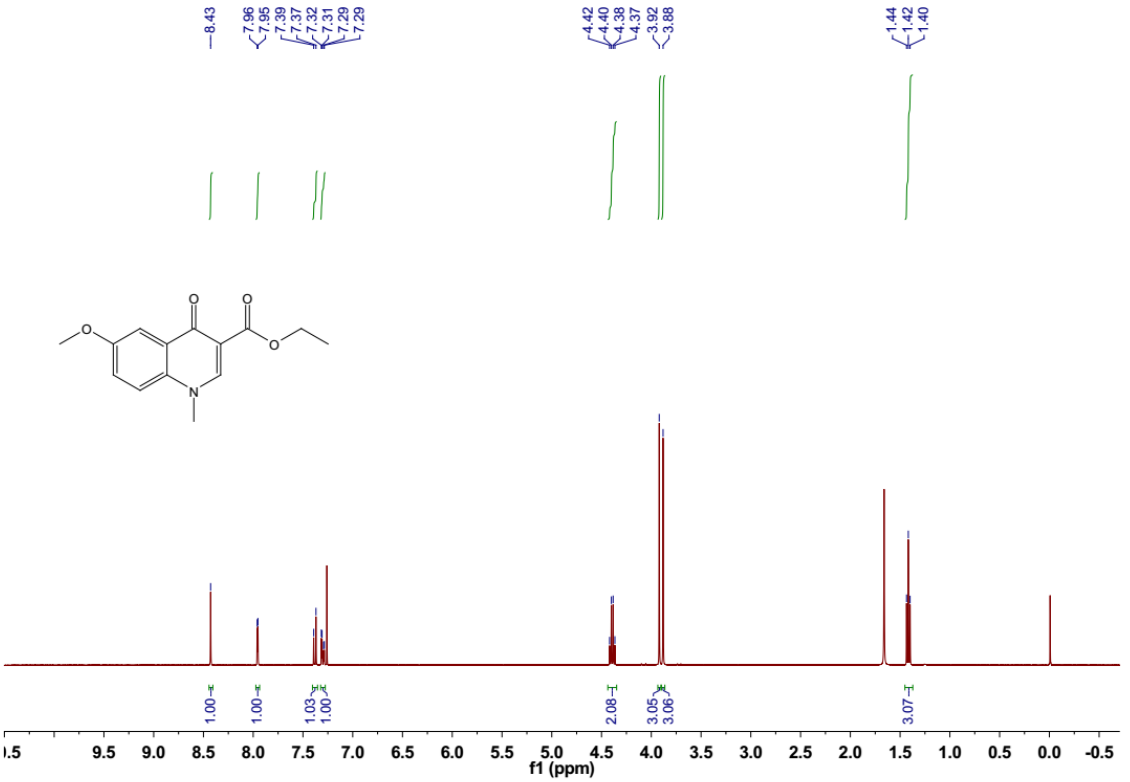
^{1}H and ^{13}C NMR spectra of compound 2j

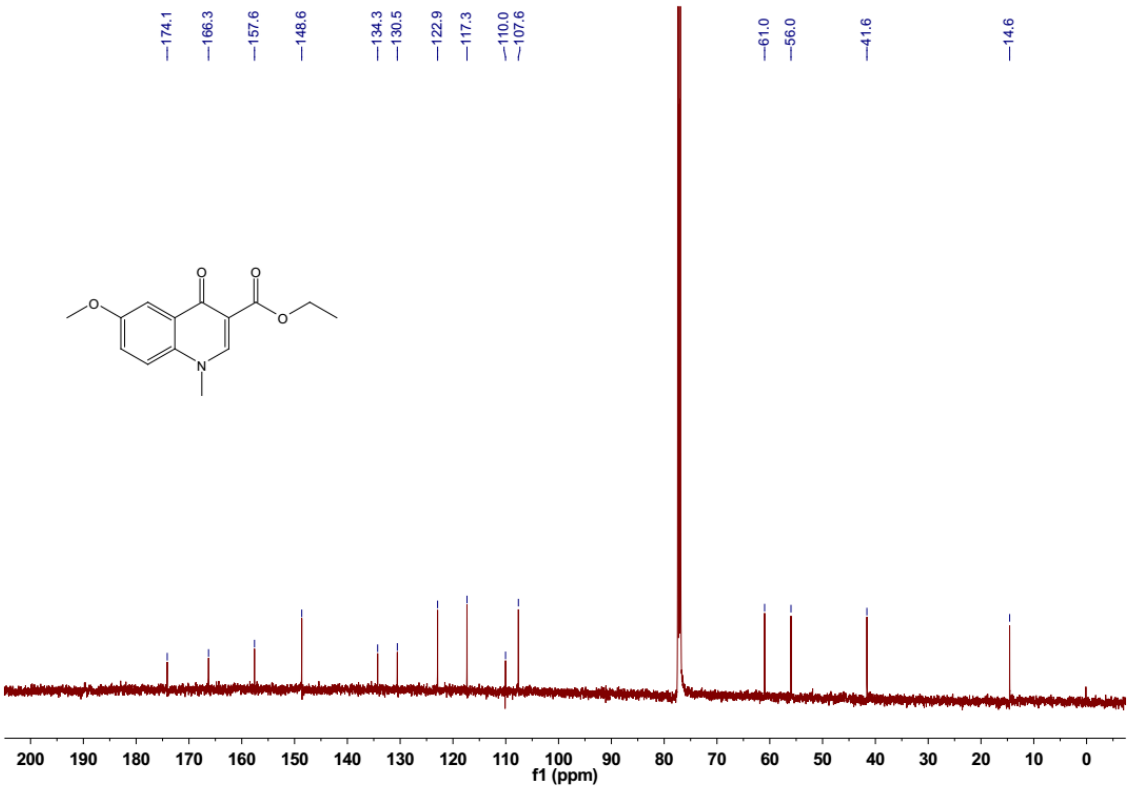


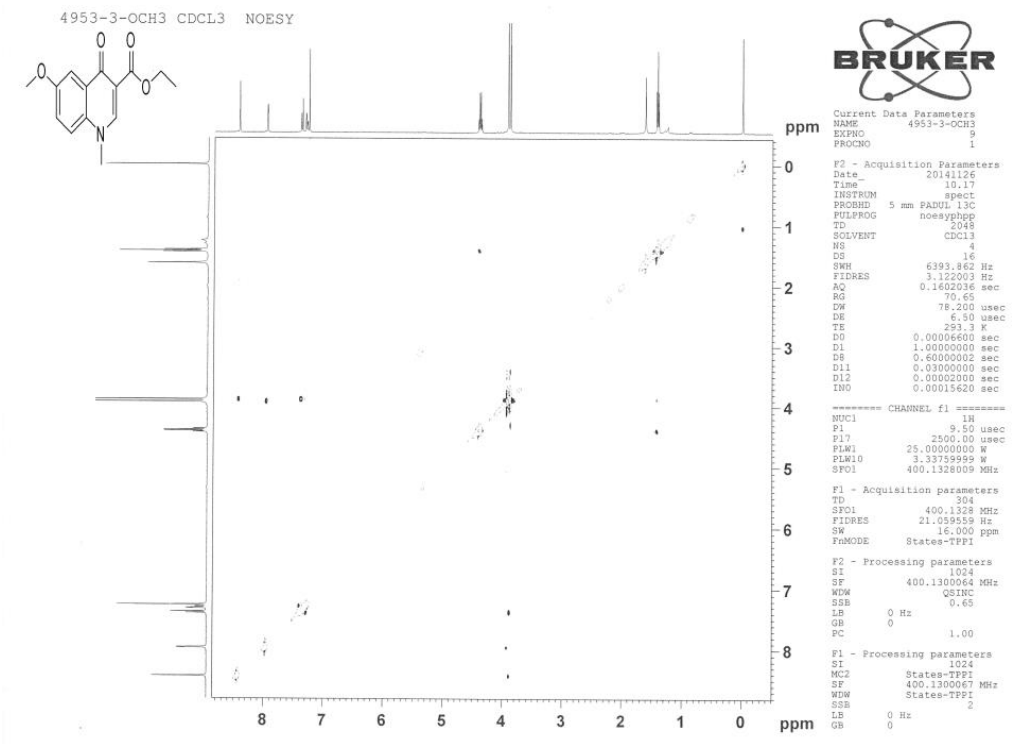



8.59
8.37
8.36
O
O
O
O2N
N
H
8.59 (s, 1H)
8.36 (d, J= 1.2 Hz 1H)
H
CH3
3.99 (s, 3H)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

^{1}H and ^{13}C NMR spectra of compound 2k





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TD                      2048
SOLVENT                 CDCl3
NS                         4
DS                        16
SWH                6393.862 Hz
FIDRES             3.122003 Hz
AQ                 0.1602036 sec
RG                     70.65
DW                    78.200 usec
DE                     6.50 usec
TE                    293.3 K
D0                 0.00006600 sec
D1                 1.00000000 sec
D8                 0.60000002 sec
D11                0.03000000 sec
D12                0.00002000 sec
IN0                0.00015620 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                       9.50 usec
P17                   2500.00 usec
PLW1              25.00000000 W
PLW10              3.33759999 W
SFO1             400.1328009 MHz

F1 - Acquisition parameters
TD                        304
SFO1             400.1328 MHz
FIDRES           21.059559 Hz
SW                   16.000 ppm
FnMODE           States-TPPI

F2 - Processing parameters
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SF               400.1300064 MHz
WDW                     QSINC
SSB                      0.65
LB          0 Hz
GB          0
PC                       1.00

F1 - Processing parameters
SI                       1024
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WDW              States-TPPI
SSB                         2
LB          0 Hz
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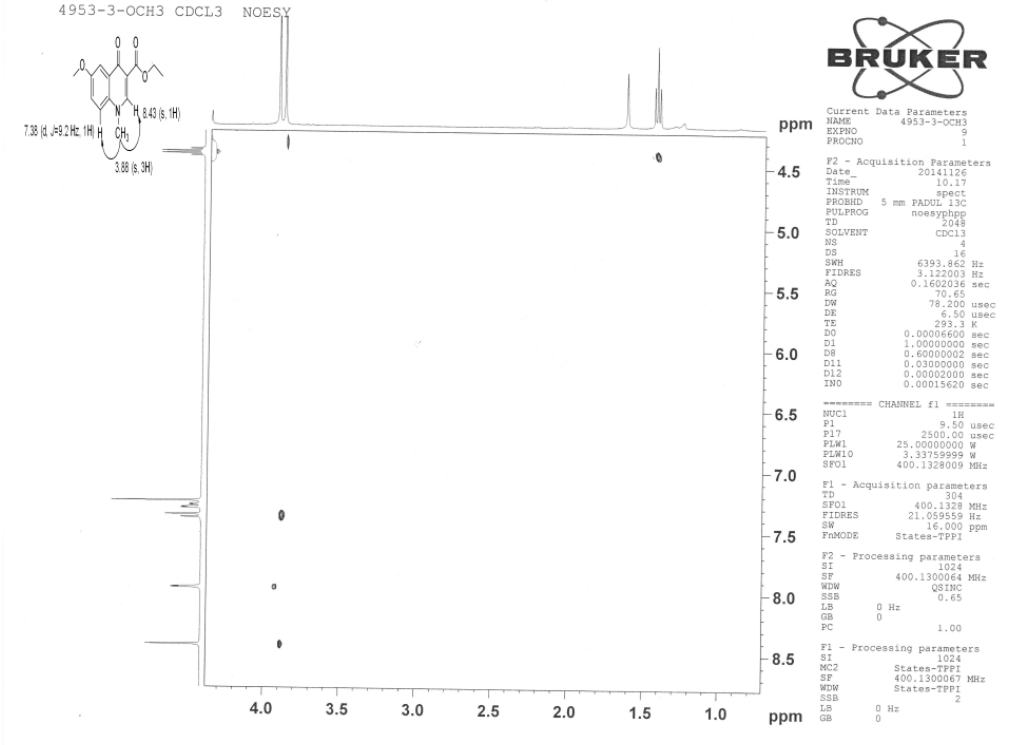


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PROCNO                          1

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TD                      2048
SOLVENT                 CDCl3
NS                         4
DS                        16
SWH                6393.862 Hz
FIDRES             3.122003 Hz
AQ                 0.1602036 sec
RG                     70.65
DW                    78.200 usec
DE                     6.50 usec
TE                    293.3 K
D0                 0.00006600 sec
D1                 1.00000000 sec
D8                 0.60000002 sec
D11                0.03000000 sec
D12                0.00002000 sec
IN0                0.00015620 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                       9.50 usec
P17                   2500.00 usec
PLW1              25.00000000 W
PLW10              3.33759999 W
SFO1             400.1328009 MHz

F1 - Acquisition parameters
TD                        304
SFO1             400.1328 MHz
FIDRES           21.059559 Hz
SW                   16.000 ppm
FnMODE           States-TPPI

F2 - Processing parameters
SI                       1024
SF               400.1300064 MHz
WDW                     QSINC
SSB                      0.65
LB          0 Hz
GB          0
PC                       1.00

F1 - Processing parameters
SI                       1024
MC2              States-TPPI
SF               400.1300067 MHz
WDW              States-TPPI
SSB                         2
LB          0 Hz
GB          0
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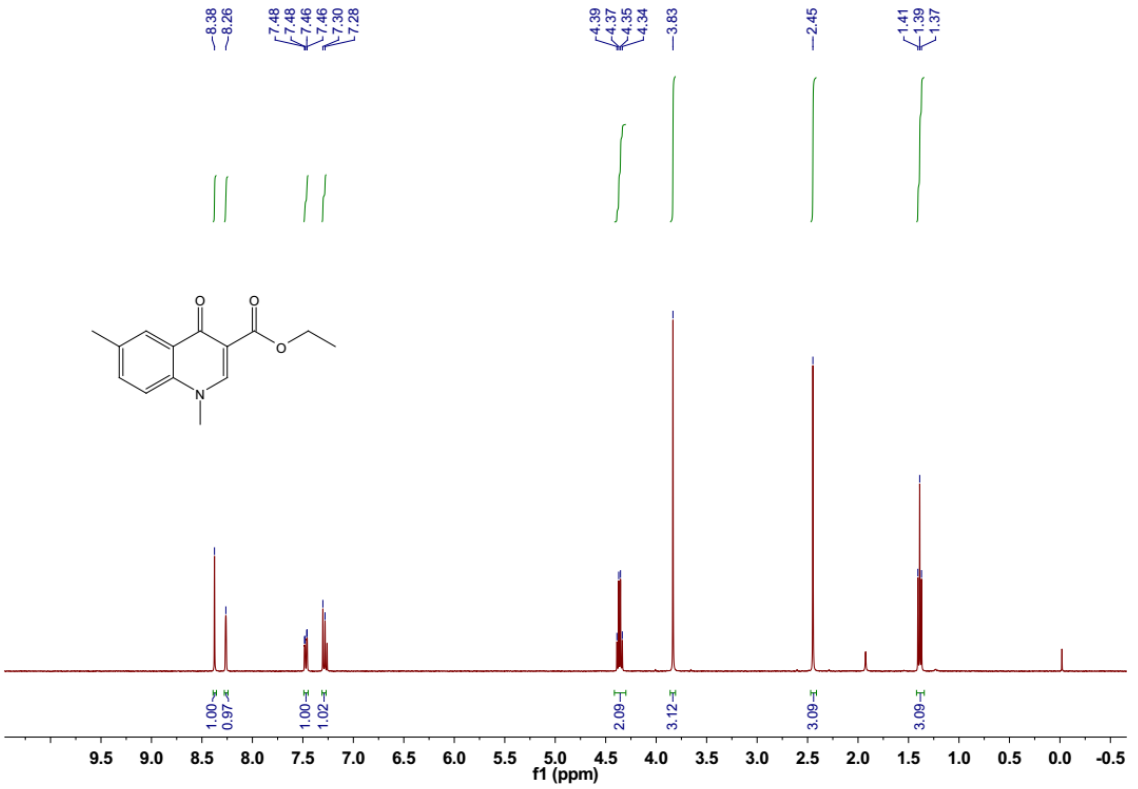
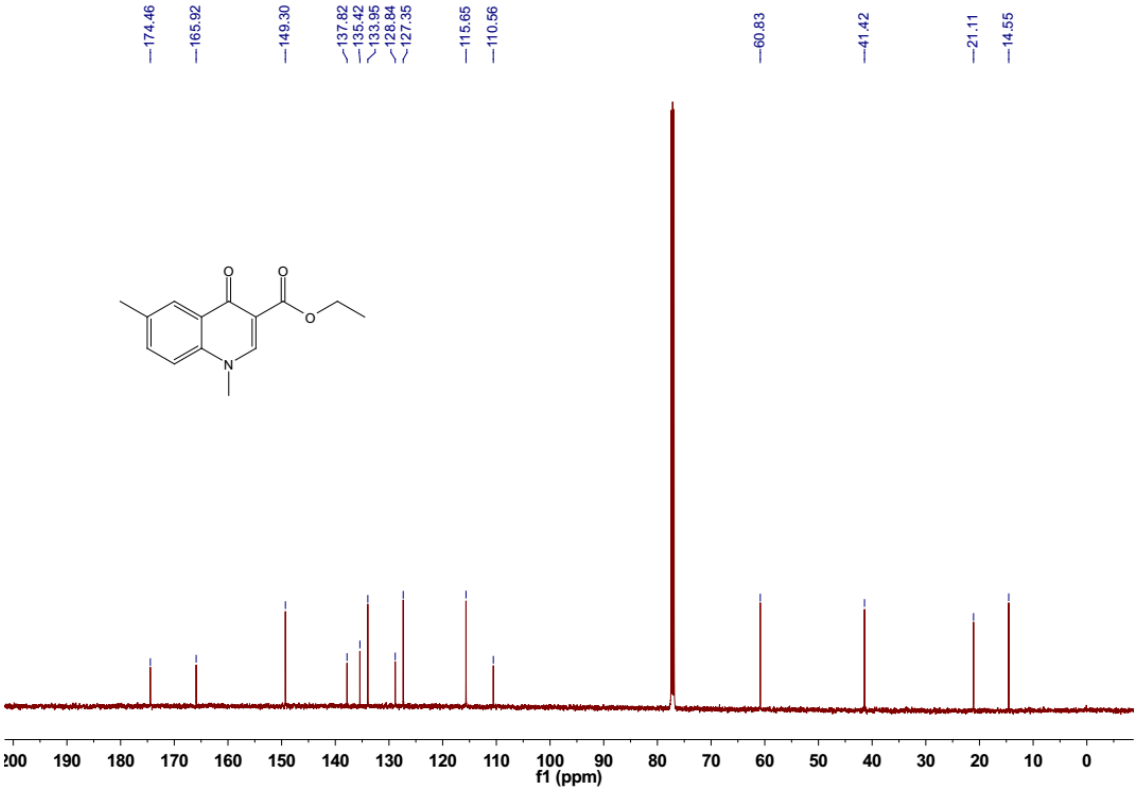
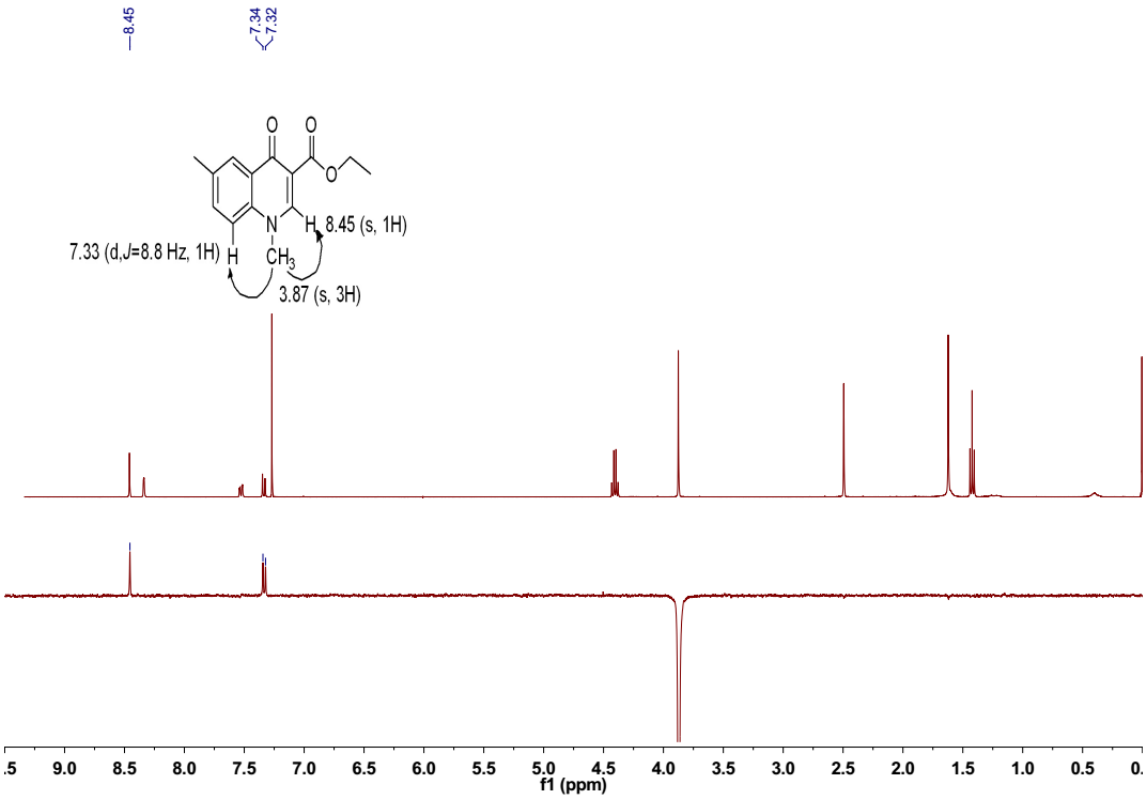
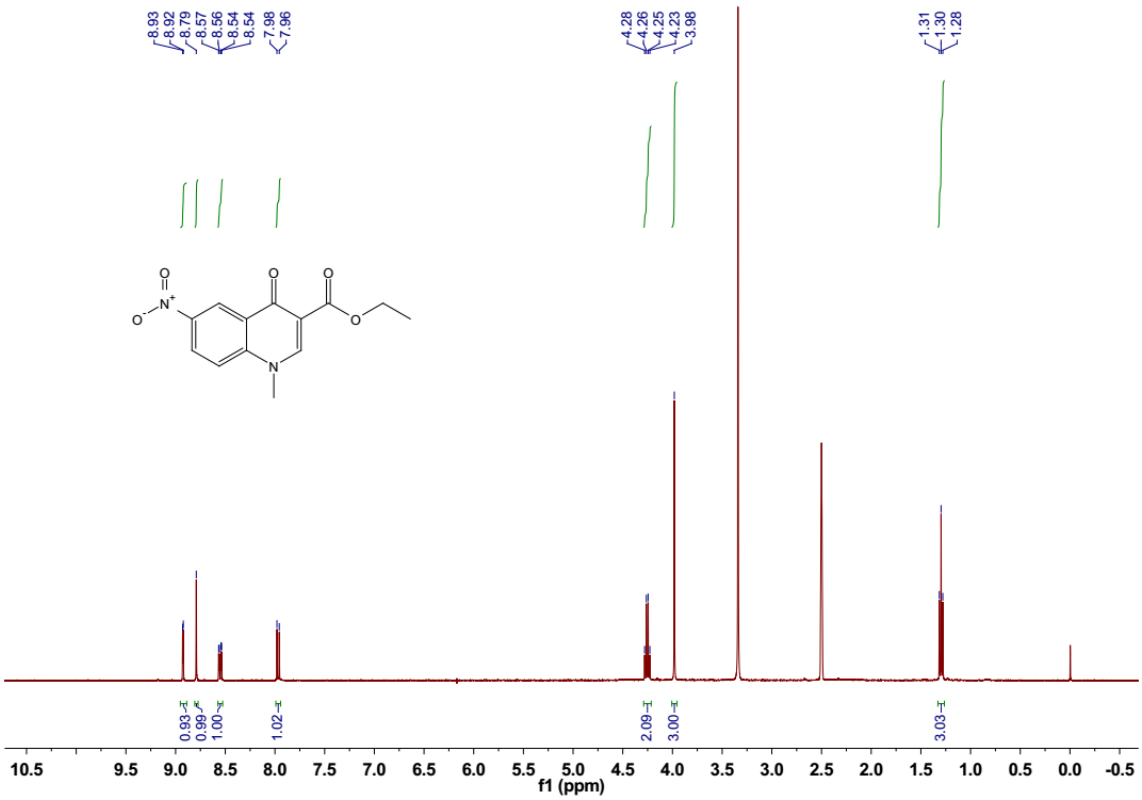
^{1}H and ^{13}C NMR spectra of compound 2l

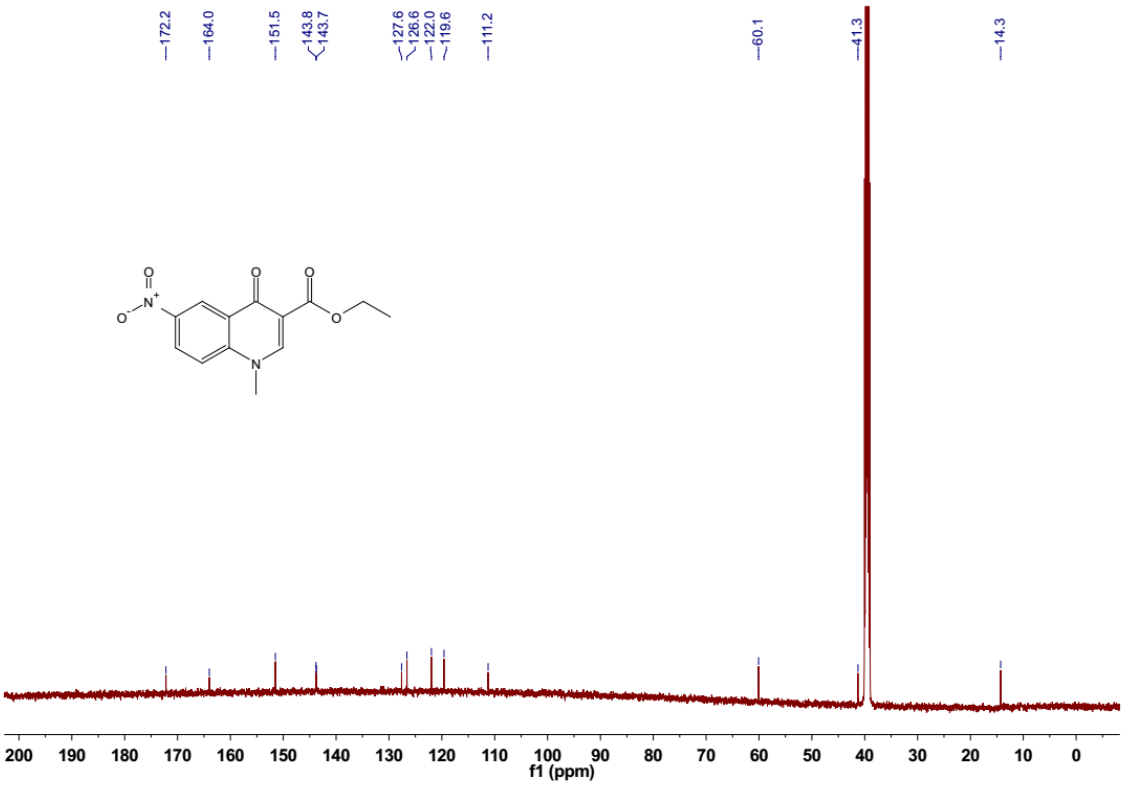




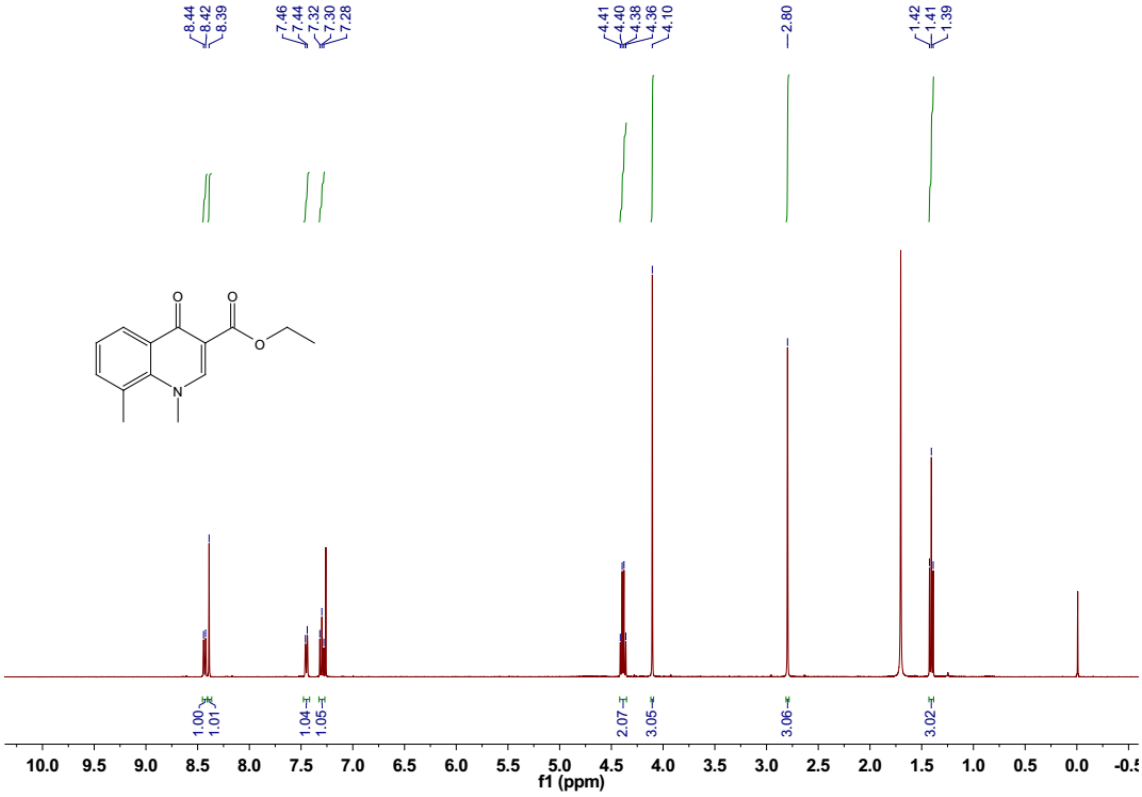

8.45
7.34
7.32
O
O
O
N
H
8.45 (s, 1H)
7.33 (d,J=8.8 Hz, 1H)
H
CH3
3.87 (s, 3H)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

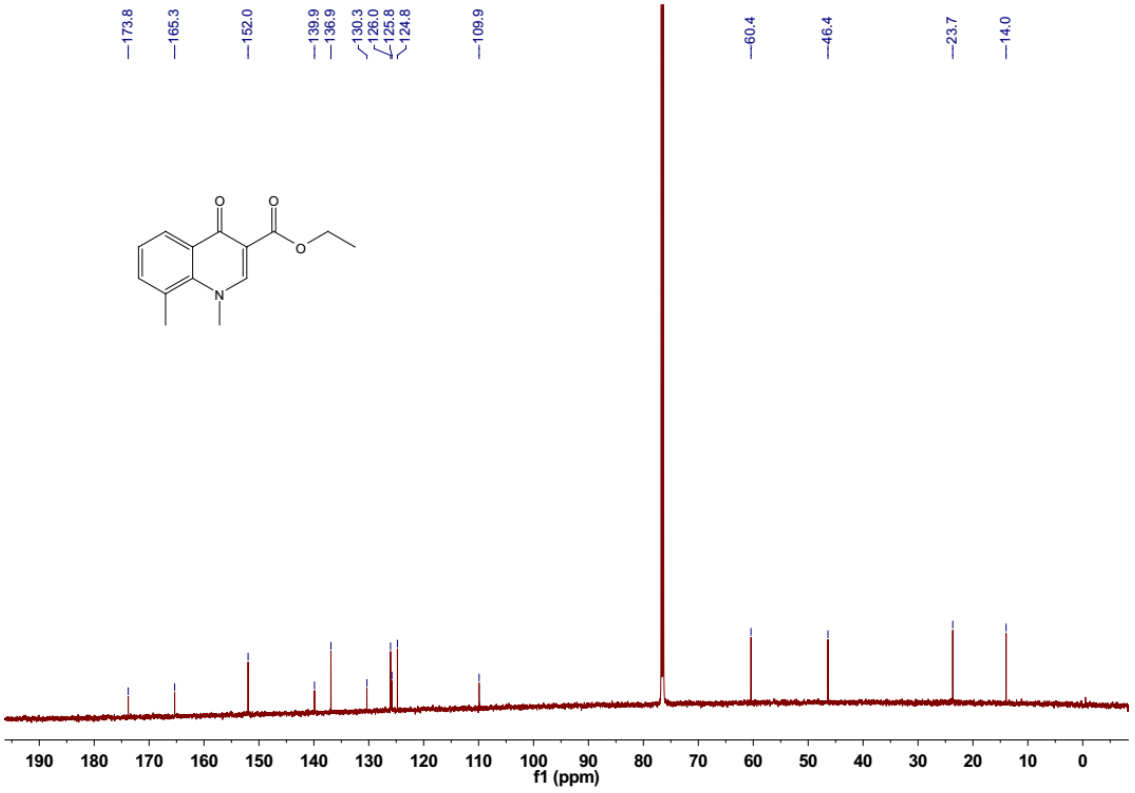
^{1}H and ^{13}C NMR spectra of compound 2m

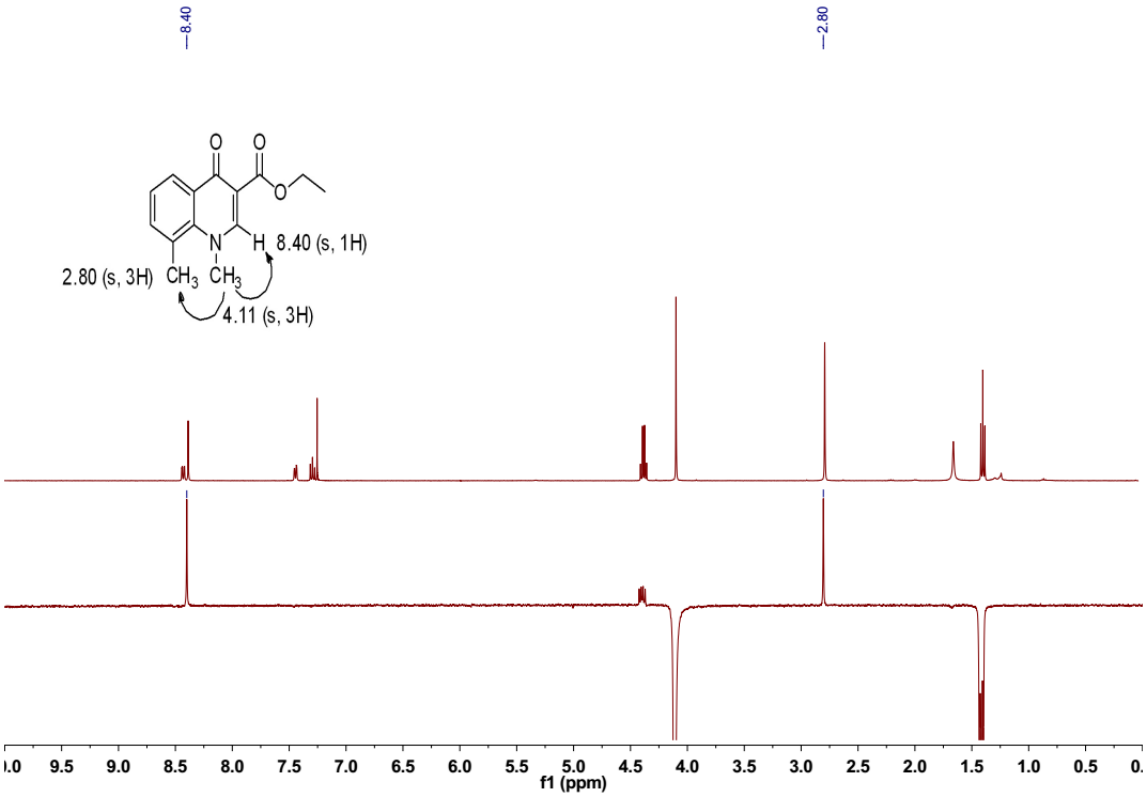




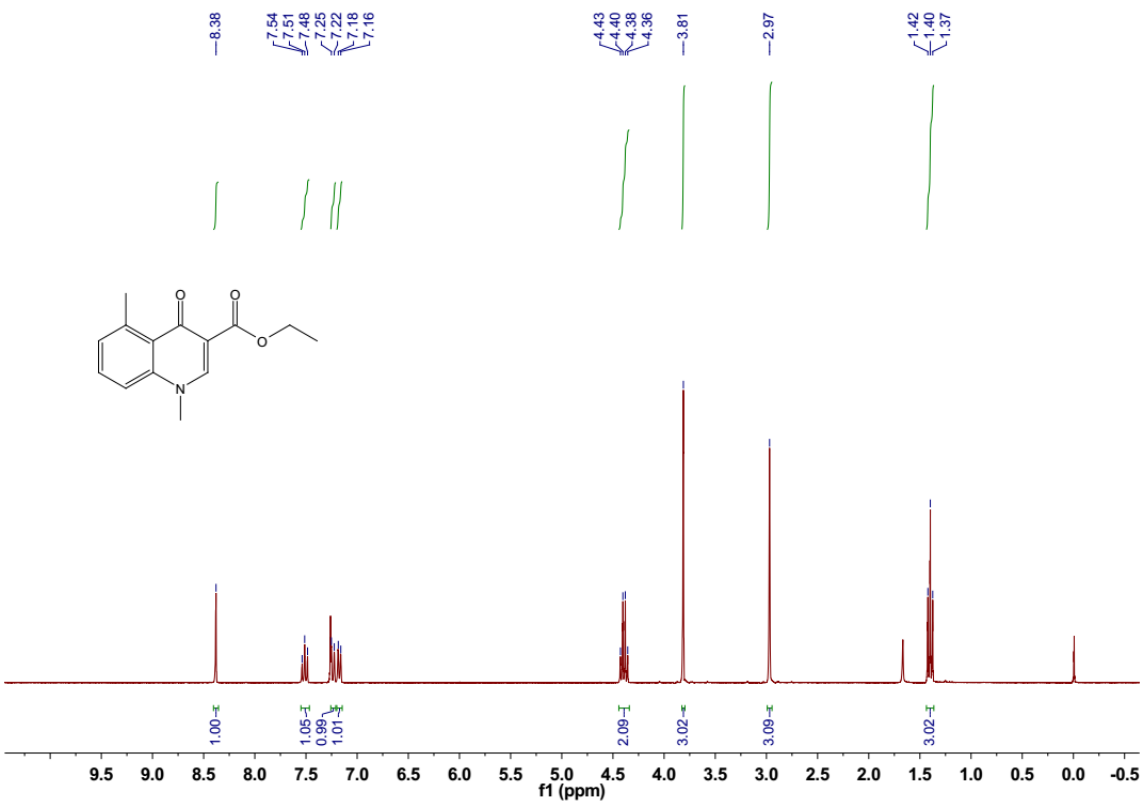
^{1}H and ^{13}C NMR spectra of compound 2n

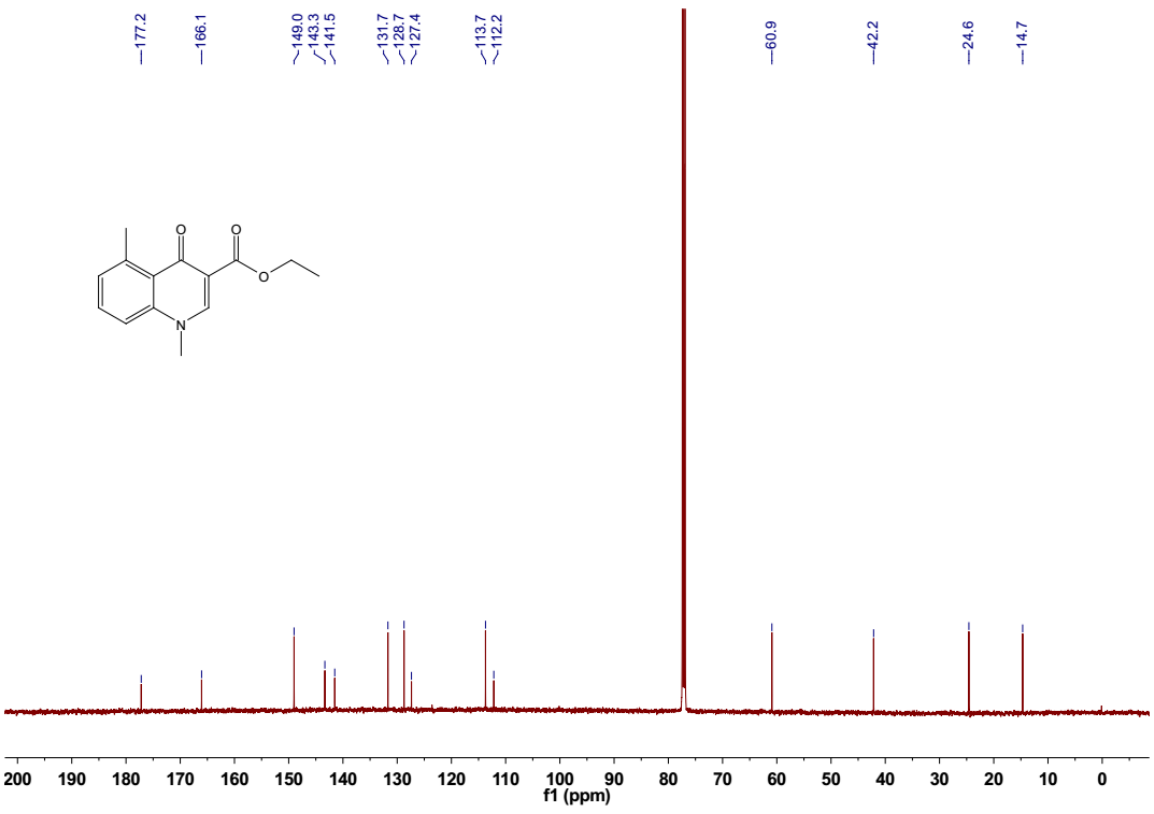


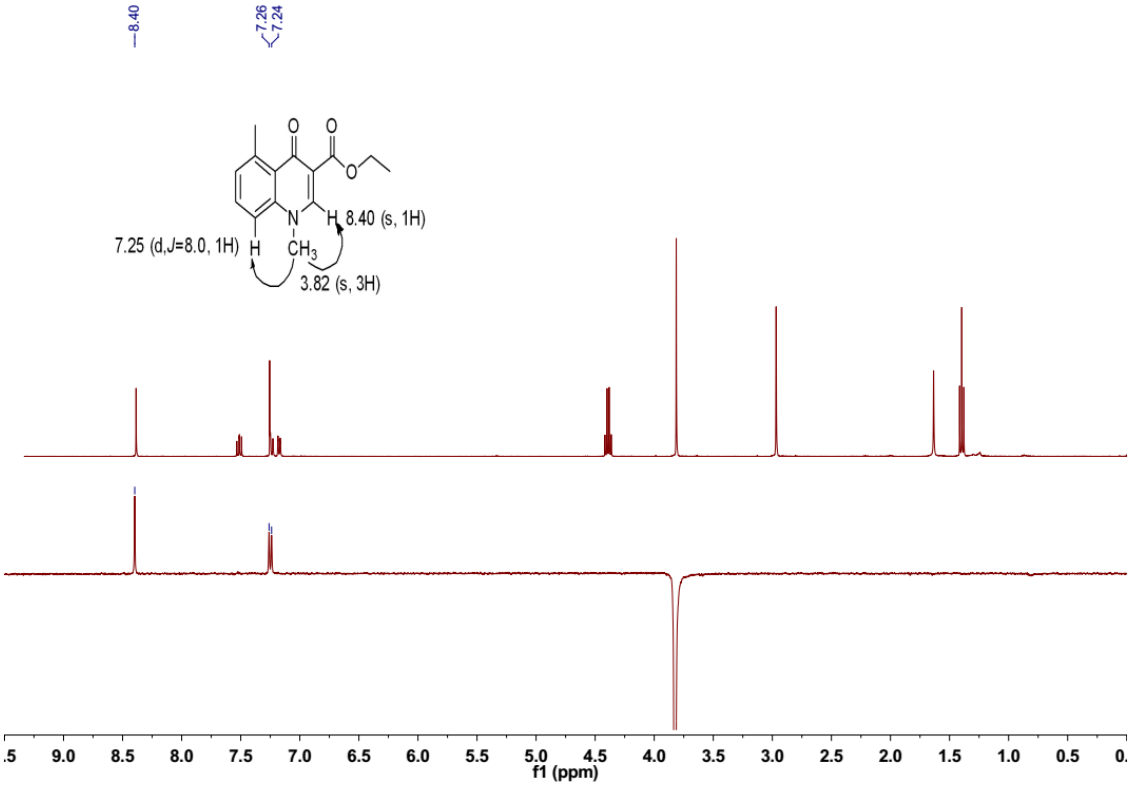



8.40
2.80
O
O
O
N
H
8.40 (s, 1H)
2.80 (s, 3H)
CH3
CH3
4.11 (s, 3H)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

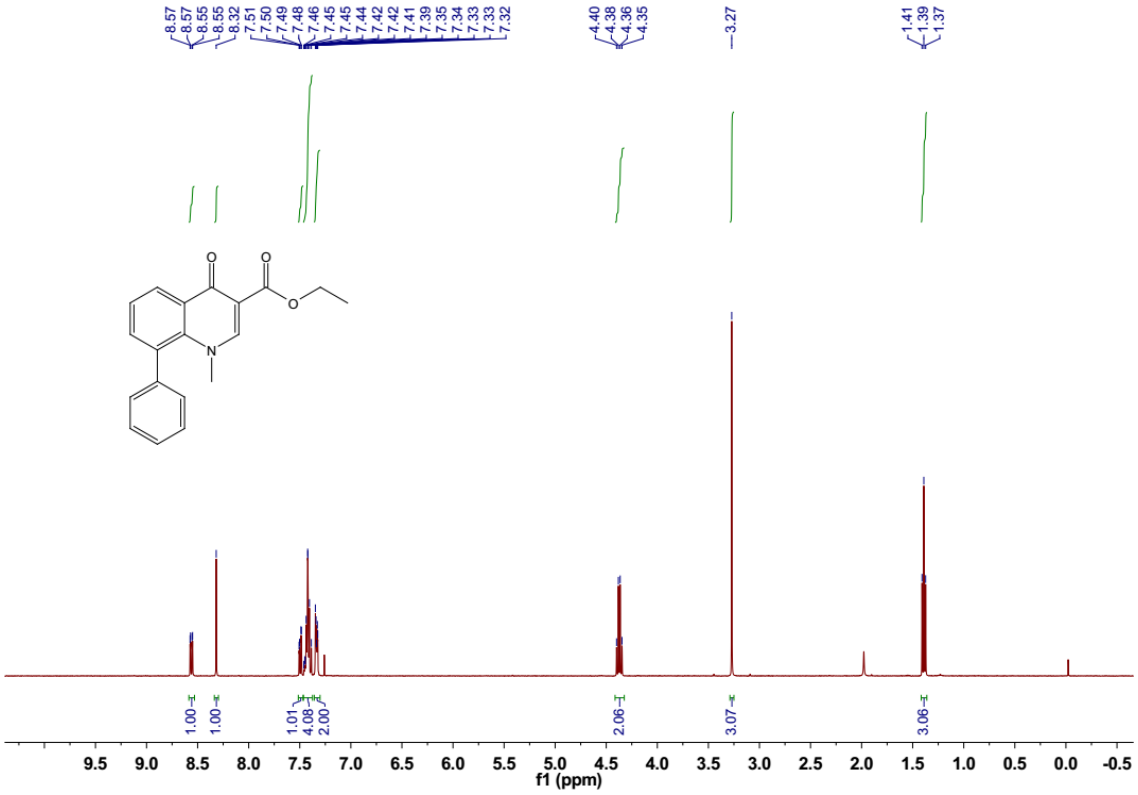
^{1}H and ^{13}C NMR spectra of compound 2o

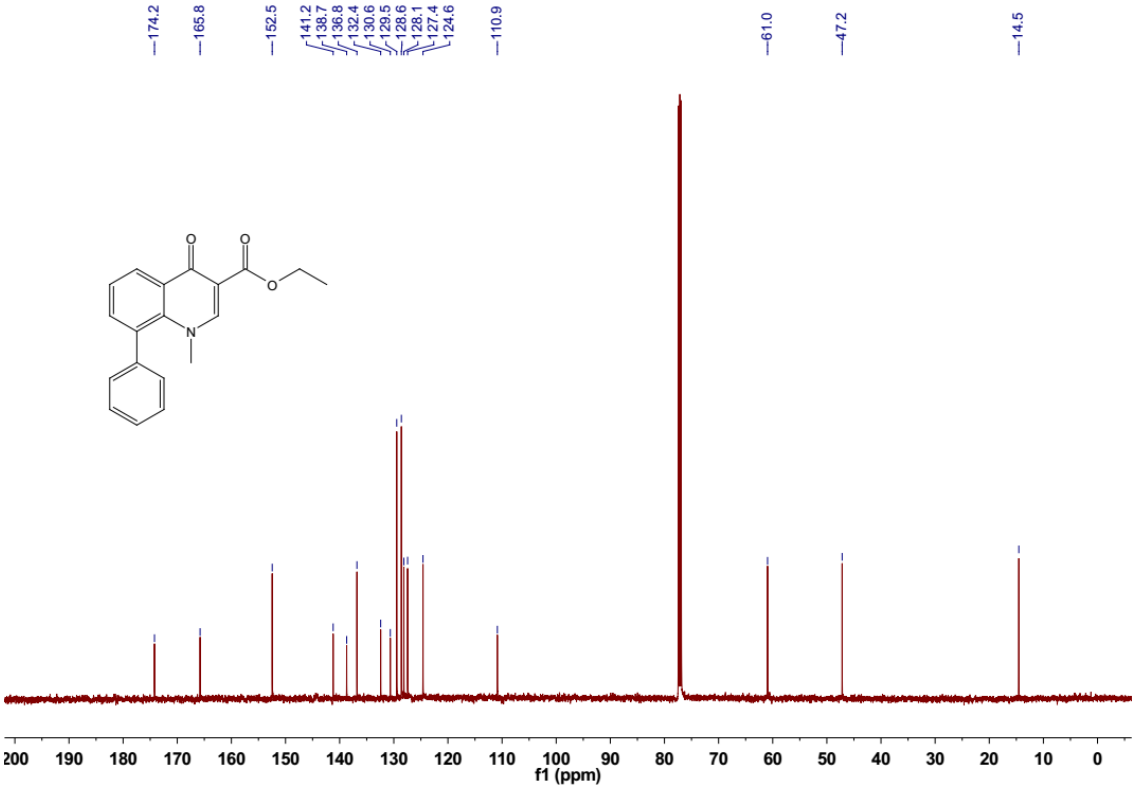


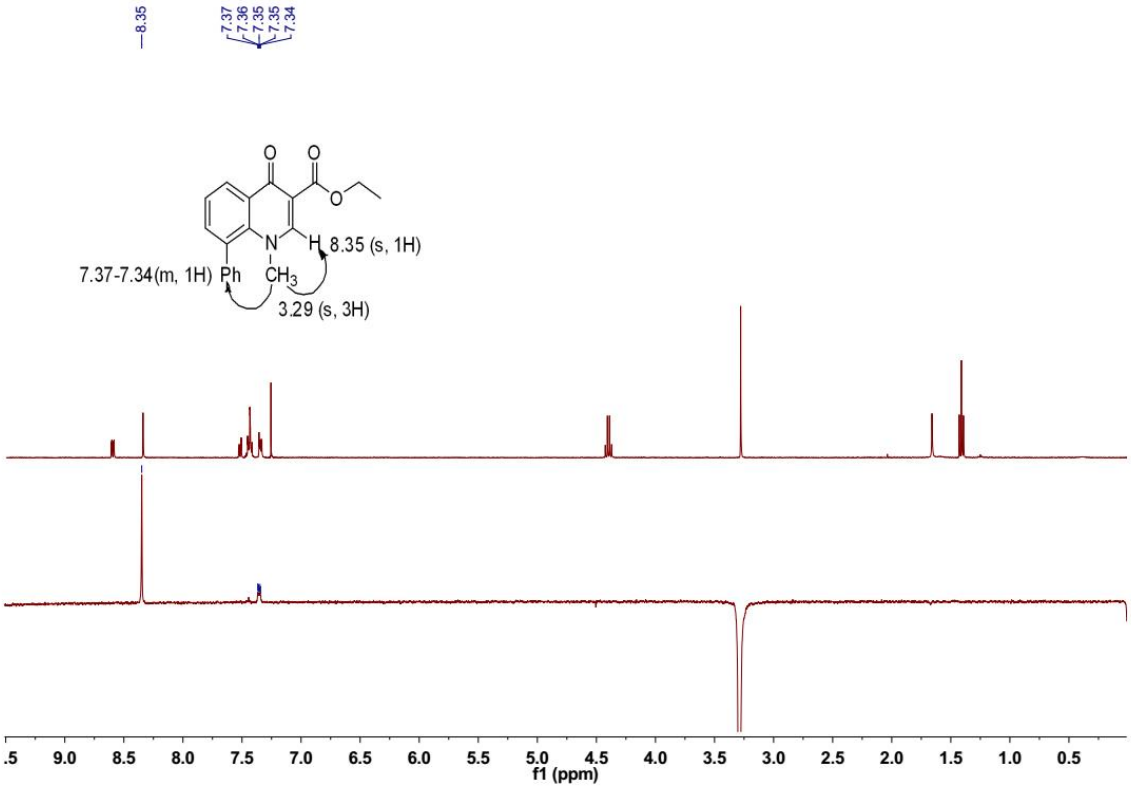



8.40
7.26
7.24
O
O
O
N
H
8.40 (s, 1H)
7.25 (d,J=8.0, 1H)
H
CH3
3.82 (s, 3H)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

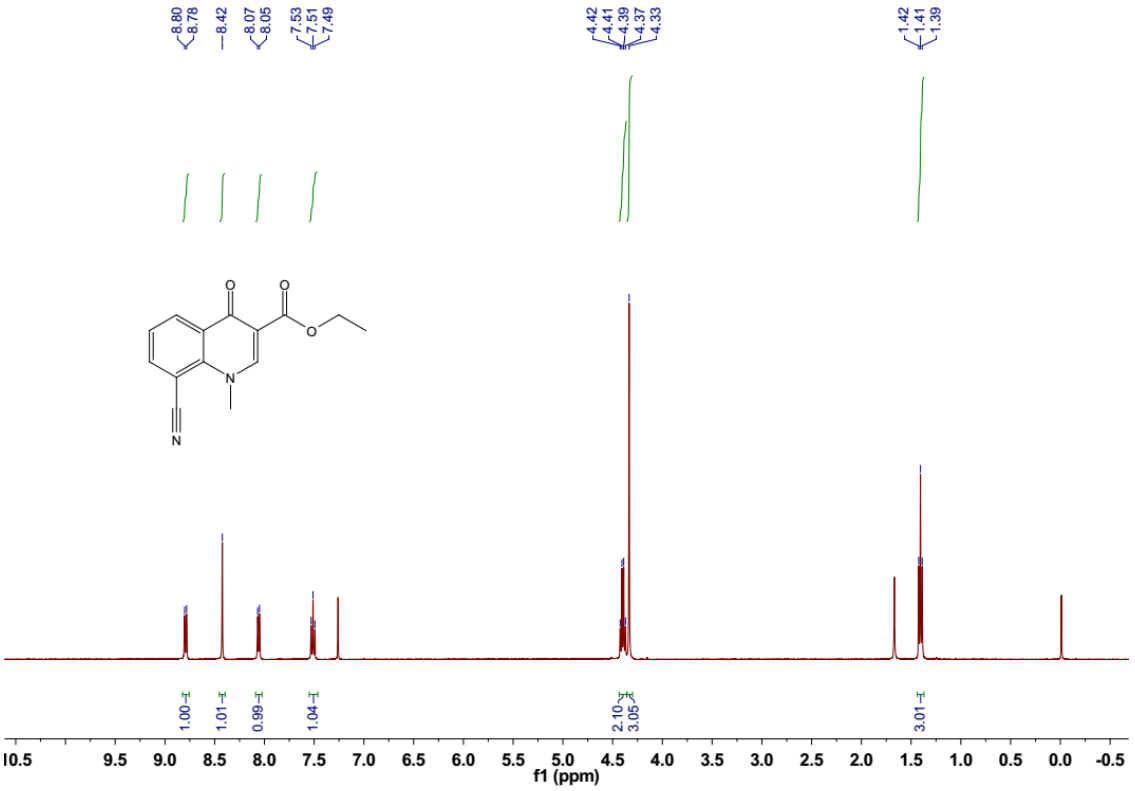
^{1}H and ^{13}C NMR spectra of compound 3s

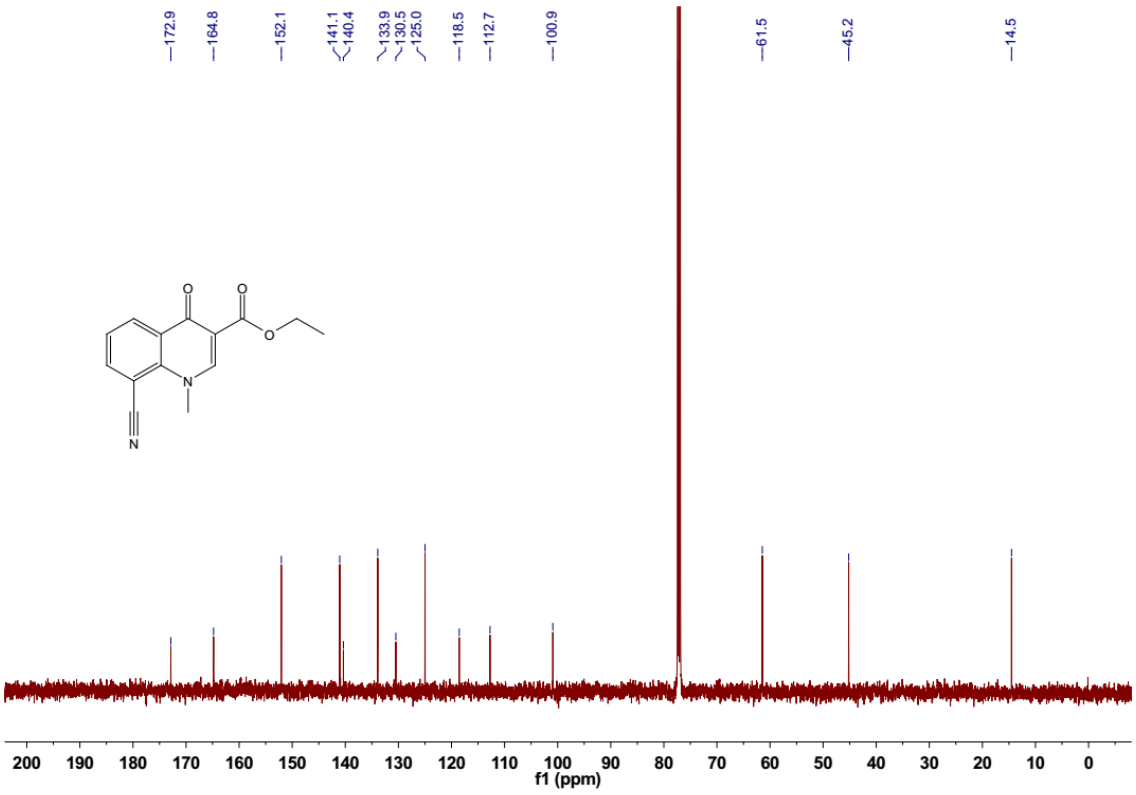


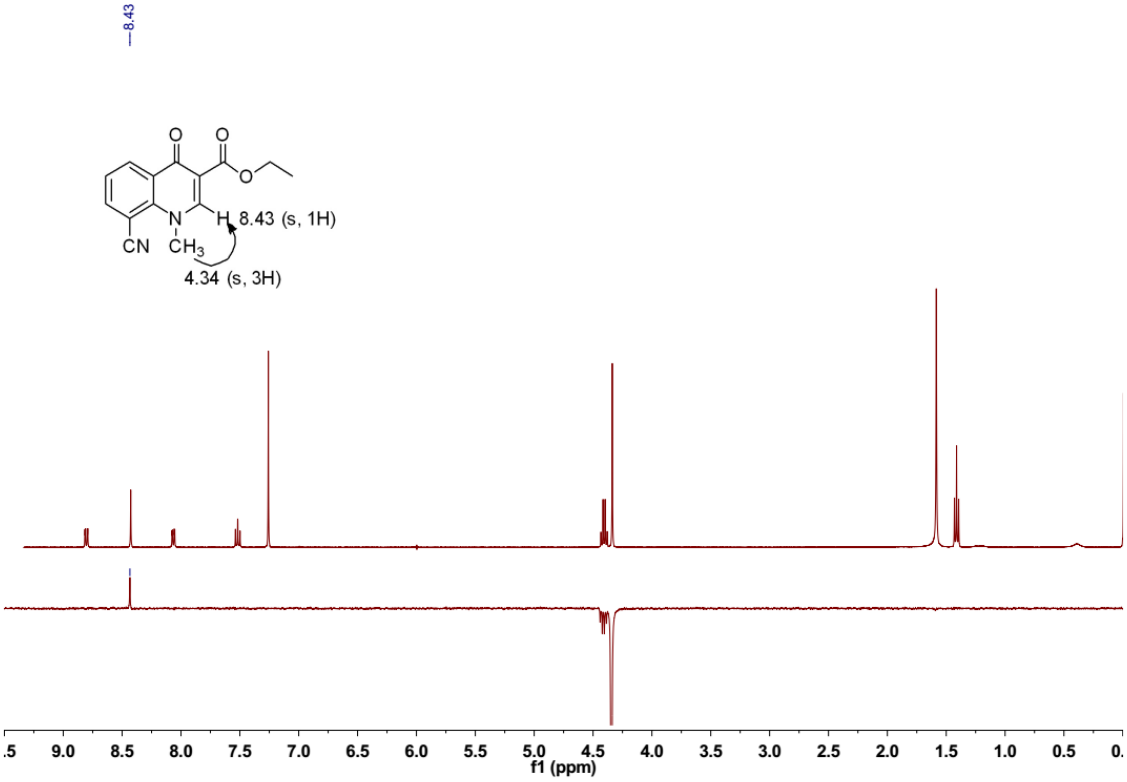



8.35
7.37
7.36
7.35
7.35
7.34
O
O
O
N
H
8.35 (s, 1H)
7.37-7.34(m, 1H)
Ph
CH3
3.29 (s, 3H)
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

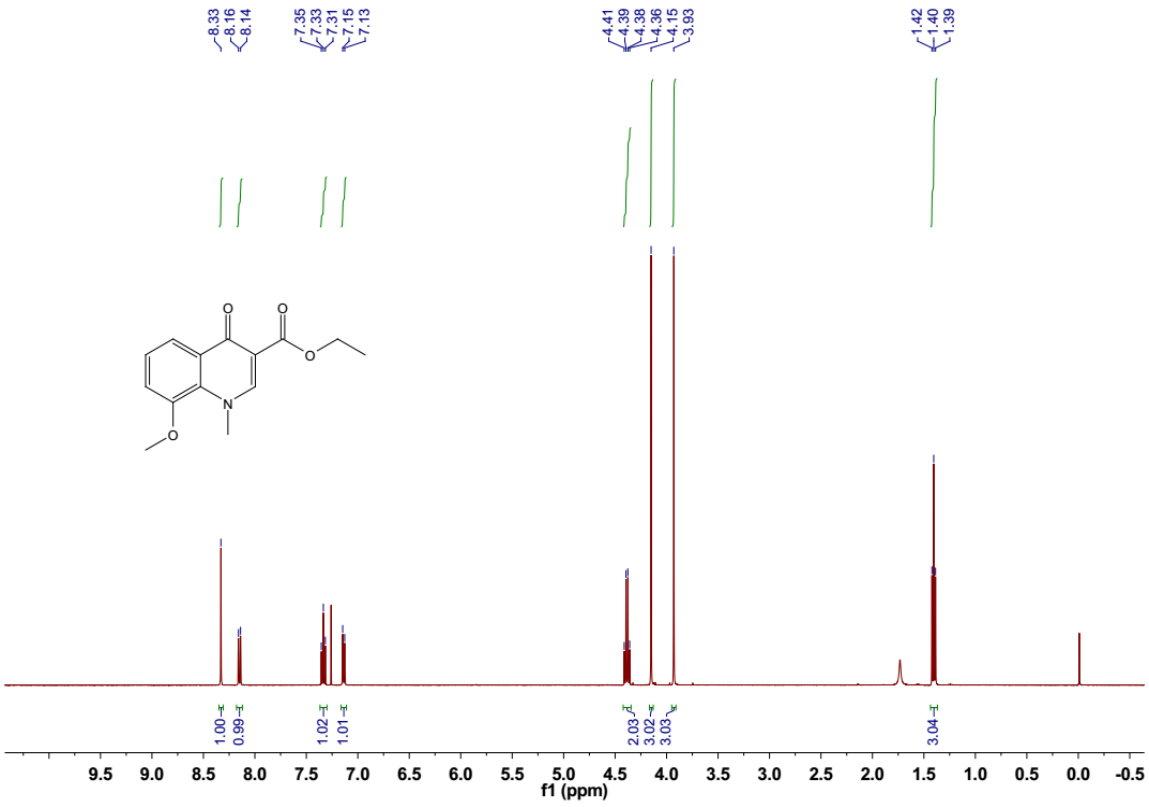
^{1}H and ^{13}C NMR spectra of compound 3t

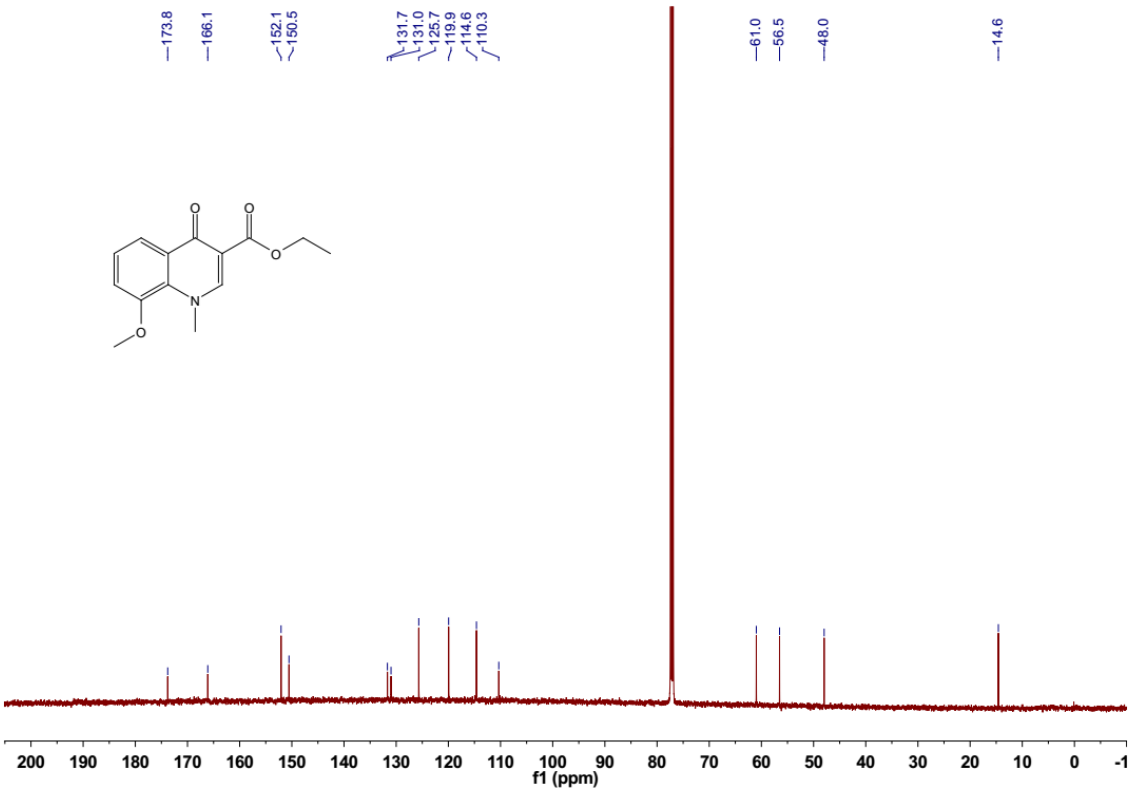


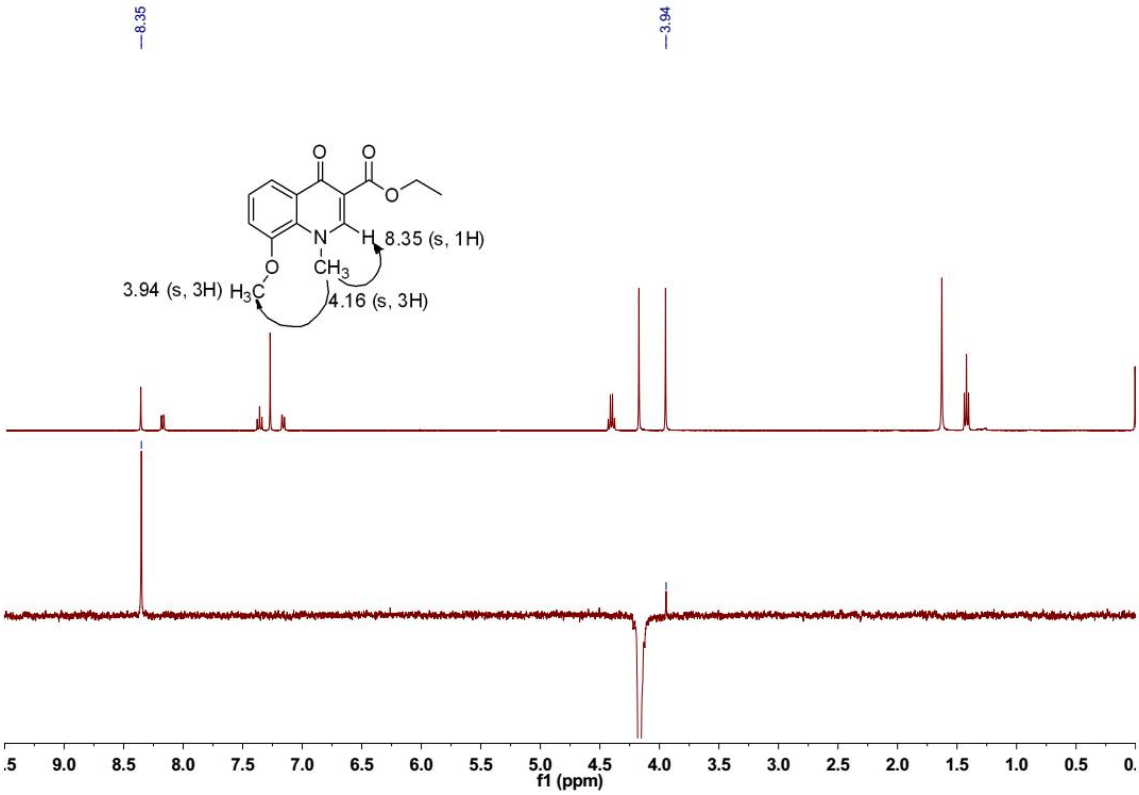



8.43
O
O
O
N
H
8.43 (s, 1H)
CN
CH3
4.34 (s, 3H)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

^{1}H and ^{13}C NMR spectra of compound 3x






8.35
3.94
8.35 (s, 1H)
3.94 (s, 3H)
4.16 (s, 3H)
f1 (ppm)

7. Crystal Structure Report for 2a

A specimen of $C_{13}H_{13}NO_4$, approximate dimensions 0.020 mm x 0.050 mm x 0.350 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 7.14 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 9968 reflections to a maximum θ angle of 27.56 ° (0.77 Å resolution), of which 2782 were independent (average redundancy 3.583, completeness = 98.0%, R_{int} = 5.31%, R_{sig} = 7.30%) and 1251 (44.97%) were greater than $2\sigma(F^2)$. The final cell constants of a = 7.0946(6) Å, b = 9.7401(7) Å, c = 10.3943(8) Å, α = 62.776(5)°, β = 77.724(5)°, γ = 74.122(6)°, volume = 611.11(8) $Å^3$, are based upon the refinement of the XYZ-centroids of 1287 reflections above 20 σ(I) with 4.430° < 2θ < 43.67°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.870.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, $C_{13}H_{13}NO_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 173 variables converged at R1 = 5.49%, for the observed data and wR2 = 17.15% for all data. The goodness-of-fit was 0.942. The largest peak in the final difference electron density synthesis was 0.228 $e^-/Å^3$ and the largest hole was -0.180 $e^-/Å^3$ with an RMS deviation of 0.041 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.344 g/cm^3 and F(000), 260 e^-.

Table 1. Sample and crystal data for 2a.

Identification code	**2a**	
Chemical formula	$C_{13}H_{13}NO_4$	
Formula weight	247.24	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.020 x 0.050 x 0.350 mm	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.0946(6) Å	α = 62.776(5)°
	b = 9.7401(7) Å	β = 77.724(5)°
	c = 10.3943(8) Å	γ = 74.122(6)°
Volume	611.11(8) $Å^3$	
Z	2	
Density (calculated)	1.344 Mg/cm^3	
Absorption coefficient	0.101 mm^{-1}	
F(000)	260	

Table 2. Data collection and structure refinement for 2a.

Theta range for data collection	2.22 to 27.56 °
Index ranges	-8<=h<=9, -12<=k<=12, -13<=l<=13
Reflections collected	9968
Independent reflections	2782 [R(int) = 0.0531]
Coverage of independent reflections	98.0%
Absorption correction	multi-scan
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-97 (Sheldrick, 2008)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	2782 / 2 / 173
Goodness-of-fit on F^2	0.942
Δ/σ_{max}	0.005

Final R indices	1251 data; I>2σ(I)	R1 = 0.0549, wR2 = 0.1321
	all data	R1 = 0.1456, wR2 = 0.1715
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0828P)^2+0.0000P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.228 and -0.180 eÅ^{-3}	
R.M.S. deviation from mean	0.041 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 2a.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
O1S	0.9449(6)	0.0968(3)	0.2785(3)	0.0975(9)
O1	0.5788(3)	0.30963(19)	0.85991(17)	0.0512(5)
O2	0.6947(3)	0.1204(2)	0.7829(2)	0.0724(7)
O3	0.8585(3)	0.2270(2)	0.49183(19)	0.0675(6)
N1	0.6897(3)	0.6656(2)	0.4850(2)	0.0434(6)
C4	0.9296(4)	0.7629(3)	0.1138(3)	0.0559(8)
C5	0.8345(4)	0.7816(3)	0.2352(3)	0.0515(7)
C6	0.7891(4)	0.6503(3)	0.3602(2)	0.0410(6)
C1	0.8478(3)	0.4999(3)	0.3620(2)	0.0396(6)
C9	0.8072(4)	0.3590(3)	0.4927(3)	0.0434(6)
C8	0.7084(3)	0.3867(3)	0.6167(2)	0.0394(6)
C11	0.6617(4)	0.2574(3)	0.7582(3)	0.0450(7)
C12	0.5358(5)	0.1913(3)	0.0051(3)	0.0604(8)
C13	0.4578(6)	0.2703(4)	0.1026(3)	0.0871(12)
C10	0.6152(5)	0.8237(3)	0.4841(3)	0.0633(9)
C7	0.6541(4)	0.5379(3)	0.6046(2)	0.0417(6)
C3	0.9861(4)	0.6165(3)	0.1131(3)	0.0563(8)
C2	0.9471(4)	0.4863(3)	0.2353(3)	0.0499(7)

Table 4. Bond lengths (Å) for 2a.

O1S-H1S	0.856(19)	O1S-H2S	0.87(2)
O1-C11	1.337(3)	O1-C12	1.450(3)
O2-C11	1.201(3)	O3-C9	1.240(3)
N1-C7	1.334(3)	N1-C6	1.391(3)
N1-C10	1.481(3)	C4-C5	1.364(3)
C4-C3	1.375(3)	C4-H3	0.93
C5-C6	1.398(3)	C5-H4	0.93
C6-C1	1.401(3)	C1-C2	1.401(3)
C1-C9	1.469(3)	C9-C8	1.434(3)
C8-C7	1.368(3)	C8-C11	1.479(3)
C12-C13	1.473(4)	C12-H9	0.97
C12-H10	0.97	C13-H12	0.96
C13-H11	0.96	C13-H13	0.96
C10-H7	0.96	C10-H6	0.96
C10-H5	0.96	C7-H8	0.93
C3-C2	1.367(3)	C3-H2	0.93
C2-H1	0.93		

Table 5. Bond angles (°) for 2a.

H1S-O1S-H2S	98.(6)	C11-O1-C12	116.57(19)
C7-N1-C6	119.88(19)	C7-N1-C10	119.7(2)
C6-N1-C10	120.35(19)	C5-C4-C3	121.2(2)
C5-C4-H3	119.4	C3-C4-H3	119.4
C4-C5-C6	119.6(2)	C4-C5-H4	120.2
C6-C5-H4	120.2	N1-C6-C5	121.0(2)
N1-C6-C1	119.0(2)	C5-C6-C1	120.0(2)
C2-C1-C6	118.4(2)	C2-C1-C9	120.2(2)
C6-C1-C9	121.4(2)	O3-C9-C8	124.2(2)
O3-C9-C1	120.5(2)	C8-C9-C1	115.3(2)
C7-C8-C9	119.3(2)	C7-C8-C11	118.4(2)
C9-C8-C11	122.3(2)	O2-C11-O1	122.6(2)
O2-C11-C8	125.5(2)	O1-C11-C8	112.0(2)
O1-C12-C13	108.4(2)	O1-C12-H9	110.0
C13-C12-H9	110.0	O1-C12-H10	110.0
C13-C12-H10	110.0	H9-C12-H10	108.4

C12-C13-H12	109.5	C12-C13-H11	109.5
H12-C13-H11	109.5	C12-C13-H13	109.5
H12-C13-H13	109.5	H11-C13-H13	109.5
N1-C10-H7	109.5	N1-C10-H6	109.5
H7-C10-H6	109.5	N1-C10-H5	109.5
H7-C10-H5	109.5	H6-C10-H5	109.5
N1-C7-C8	125.1(2)	N1-C7-H8	117.5
C8-C7-H8	117.5	C2-C3-C4	120.1(2)
C2-C3-H2	120.0	C4-C3-H2	120.0
C3-C2-C1	120.8(2)	C3-C2-H1	119.6
C1-C2-H1	119.6		

Table 6. Torsion angles ( ) for 2a.

C3-C4-C5-C6	-1.6(4)	C7-N1-C6-C5	-177.7(2)
C10-N1-C6-C5	5.1(4)	C7-N1-C6-C1	0.9(4)
C10-N1-C6-C1	-176.3(2)	C4-C5-C6-N1	-179.1(2)
C4-C5-C6-C1	2.4(4)	N1-C6-C1-C2	179.8(2)
C5-C6-C1-C2	-1.7(4)	N1-C6-C1-C9	-0.2(4)
C5-C6-C1-C9	178.3(2)	C2-C1-C9-O3	-0.8(4)
C6-C1-C9-O3	179.2(3)	C2-C1-C9-C8	178.8(2)
C6-C1-C9-C8	-1.2(3)	O3-C9-C8-C7	-178.4(3)
C1-C9-C8-C7	2.1(3)	O3-C9-C8-C11	1.3(4)
C1-C9-C8-C11	-178.2(2)	C12-O1-C11-O2	2.1(4)
C12-O1-C11-C8	-177.0(2)	C7-C8-C11-O2	177.4(3)
C9-C8-C11-O2	-2.3(4)	C7-C8-C11-O1	-3.5(3)
C9-C8-C11-O1	176.8(2)	C11-O1-C12-C13	176.4(2)
C6-N1-C7-C8	0.1(4)	C10-N1-C7-C8	177.3(2)
C9-C8-C7-N1	-1.7(4)	C11-C8-C7-N1	178.6(2)
C5-C4-C3-C2	0.1(4)	C4-C3-C2-C1	0.6(4)
C6-C1-C2-C3	0.2(4)	C9-C1-C2-C3	-179.9(2)

Table 7. Anisotropic atomic displacement parameters (Å^2) for 2a.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1S	0.138(3)	0.0747(16)	0.0799(18)	-0.0408(14)	-0.0118(17)	-0.0063(16)
O1	0.0672(13)	0.0430(10)	0.0370(9)	-0.0148(8)	0.0051(9)	-0.0131(9)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	0.1083(18)	0.0371(11)	0.0598(12)	-0.0197(9)	0.0192(11)	-0.0196(11)
O3	0.0986(17)	0.0410(11)	0.0563(12)	-0.0251(9)	0.0136(11)	-0.0125(10)
N1	0.0550(15)	0.0328(11)	0.0399(12)	-0.0160(10)	-0.0036(10)	-0.0051(10)
C4	0.065(2)	0.0503(17)	0.0431(15)	-0.0117(13)	0.0021(14)	-0.0184(15)
C5	0.064(2)	0.0398(15)	0.0458(16)	-0.0131(13)	-0.0046(14)	-0.0138(14)
C6	0.0458(17)	0.0387(14)	0.0370(13)	-0.0144(11)	-0.0056(12)	-0.0080(12)
C1	0.0419(16)	0.0390(14)	0.0376(14)	-0.0160(12)	-0.0066(11)	-0.0061(12)
C9	0.0503(17)	0.0381(14)	0.0412(14)	-0.0188(12)	0.0011(12)	-0.0088(12)
C8	0.0439(16)	0.0349(13)	0.0371(13)	-0.0139(11)	-0.0039(11)	-0.0074(11)
C11	0.0486(17)	0.0426(16)	0.0394(14)	-0.0156(12)	-0.0010(12)	-0.0085(12)
C12	0.078(2)	0.0502(17)	0.0348(15)	-0.0070(13)	0.0049(14)	-0.0133(15)
C13	0.127(3)	0.082(2)	0.0444(17)	-0.0268(17)	0.0136(18)	-0.026(2)
C10	0.095(2)	0.0355(15)	0.0571(17)	-0.0246(13)	0.0028(16)	-0.0098(15)
C7	0.0487(17)	0.0403(14)	0.0337(13)	-0.0157(11)	-0.0023(11)	-0.0070(12)
C3	0.067(2)	0.0621(18)	0.0378(15)	-0.0211(14)	0.0081(13)	-0.0198(15)
C2	0.0543(18)	0.0518(16)	0.0460(15)	-0.0257(13)	0.0034(13)	-0.0119(13)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for 2a.

	x/a	y/b	z/c	U(eq)
H1S	0.898(7)	0.115(6)	0.354(4)	0.16(2)
H3	0.9566	0.8508	0.0300	0.067
H4	0.8000	0.8810	0.2348	0.062
H9	0.6548	0.1136	1.0388	0.072
H10	0.4396	0.1377	1.0042	0.072
H12	0.5597	0.3111	1.1130	0.131
H11	0.4130	0.1959	1.1962	0.131
H13	0.3497	0.3554	1.0623	0.131
H7	0.5508	0.8129	0.5784	0.095
H6	0.5231	0.8853	0.4127	0.095
H5	0.7234	0.8754	0.4605	0.095
H8	0.5872	0.5527	0.6859	0.05
H2	1.0510	0.6061	0.0293	0.068
H1	0.9869	0.3875	0.2344	0.06
H2S	1.069(4)	0.089(11)	0.283(10)	0.35(5)