Supporting Information

Visible Light-Induced Radical Cyclization of *o*-Alkenyl Aromatic Isocyanides with Thioethers: Direct Synthesis of 2-Thioquinolines

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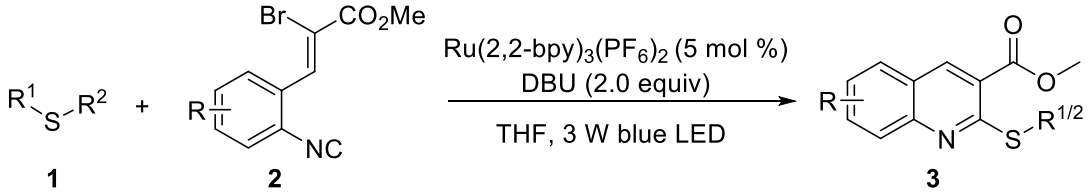
Table of contents

I. General Information:

All reagents were commercial and were used without further purification. Isocyanides **1** were synthesized according to known literature procedure.[1] Thioethers **2a-p**, **2s-v**, **2x-z** were commercial reagents and were used as such without further purification. Thioethers **2q**, **2r** and **2w** were prepared according to the previous method reported.[2] Chromatography was carried on flash silica gel (300-400 mesh). All reactions were monitored by TLC, which was performed on percolated aluminum sheets of silica gel 60 (F254). Unless noted, the ^{1}H NMR spectra were recorded at 500 MHz，600 MHz in $CDCl_3$, the ^{13}C NMR spectra were recorded at 151 MHz in $CDCl_3$ with TMS as internal standard, and the ^{19}F NMR spectra were recorded at 565 MHz in $CDCl_3$. All coupling constants (*J* values) were reported in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI). The compound **3ab** were glued on a glass fiber. Data were collected at 293 K using graphite-monochromated Mo Kradiation (λ = 0.71073Å) and IP technique in the range $2.19° < \theta < 27.48°$. Empirical absorption correction was applied. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXS 97 crystallographic software package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps.

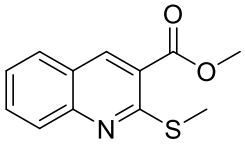
II. Synthetic Procedures and Analytical Data of Compounds 3 (3aa as example):



1 2 3

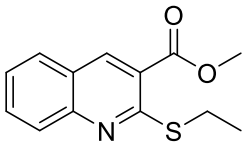
A flame-dried, Schlenk tube equipped with a magnetic stir bar was charged with **1a** (12.4 mg, 0.2 mmol), $Ru(2,2\text{-bpy})_3(PF_6)_2$ (8.6 mg, 0.01mmol) and **2a** (159.7 mg, 0.6 mmol) under nitrogen atmosphere. Solutions of the DBU (60.9 mg, 0.4 mmol) in 2 mL anhydrous THF were added via syringe in rapid succession. The reaction was stirred at room temperature and irradiated with 3 W blue LEDs for 16 h. After the reaction was completed, the reaction mixture was poured into saturated aqueous NaCl (5.0 mL), extracted with CH_2Cl_2 (5.0 mL × 3). The combined organic extracts were dried over anhydrous $NaSO_4$, filtered and concentrated under reduced pressure to yield the corresponding crude product, which was purified by silica gel chromatography (EtOAc/petroleum ether = 1/10, V/V) to give **3aa** (38.2 mg, 82%) as a white solid.

Methyl 2-(methylthio)quinoline-3-carboxylate (3aa):



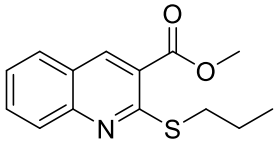
Following the general procedure, **3aa** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (38.2 mg, 82%); mp 107-109 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.62 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.65 (m, 1H), 7.40 – 7.37 (m, 1H), 3.91 (s, 3H), 2.59 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.74, 160.18, 149.03, 140.02, 132.11, 128.73, 127.96, 125.80, 124.07, 121.67, 52.41, 14.08; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{11}NNaO_2S^+$ 256.0403; Found 256.0408.

Methyl 2-(ethylthio)quinoline-3-carboxylate (3ba):



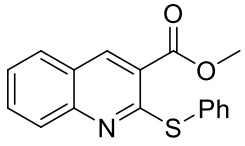
Following the general procedure, **3ba** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow liquid (31.2 mg, 63% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.62 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 3.91 (s, 3H), 3.26 (q, *J* = 7.3 Hz, 2H), 1.36 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.76, 159.75, 149.03, 140.04, 132.04, 128.72, 128.69, 127.97, 125.76, 124.12, 121.84, 52.38, 24.63, 13.91; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{14}NO_2S^+$ 248.0740; Found 248.0748.

Methyl 2-(propylthio)quinoline-3-carboxylate (3ca):



Following the general procedure, **3ca** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow liquid (23.5 mg, 45% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.61 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 8.3 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 3.91 (s, 3H), 3.26 – 3.22 (m, 2H), 1.74 (h, *J* = 7.4 Hz, 2H), 1.03 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.77, 159.87, 148.97, 140.01, 132.02, 128.68, 127.96, 125.73, 124.10, 121.90, 52.37, 32.26, 22.27, 13.87; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{15}NNaO_2S^+$ 284.0716; Found 284.0723.

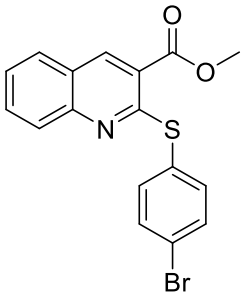
Methyl 2-(phenylthio)quinoline-3-carboxylate (3da):



Following the general procedure, **3da** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (41.3 mg, 70% yield); mp >240 °C; ^{1}H NMR (600

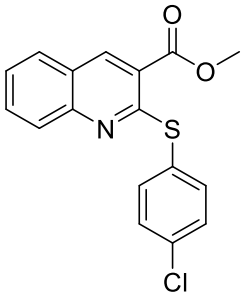
MHz, $CDCl_3$) δ = 8.74 (s, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.61 (m, 3H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.45 – 7.43 (m, 4H), 4.03 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.79, 159.57, 148.88, 140.34, 135.89, 132.00, 130.97, 128.73, 128.68, 128.50, 128.46, 126.14, 124.61, 121.34, 52.58; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{13}NNaO_2S^+$ 318.0559; Found 318.0556.

Methyl 2-((4-bromophenyl)thio)quinoline-3-carboxylate (3ea):



Following the general procedure, **3ea** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (53.9 mg, 72% yield); mp 157-158 °C; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.76 (s, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.61 (m, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.47 – 7.44 (m, 1H), 4.03 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.69, 158.87, 148.83, 140.50, 137.46, 132.21, 131.89, 130.15, 128.55, 128.42, 126.34, 124.65, 123.22, 121.12, 52.63; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{12}BrNNaO_2S^+$ 395.9664; Found 395.9655.

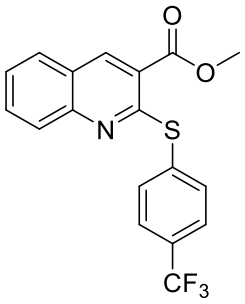
Methyl 2-((4-chlorophenyl)thio)quinoline-3-carboxylate (3fa):



Following the general procedure, **3fa** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (40.2 mg, 61% yield); mp 116-118 °C; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.75 (s, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.61 (m, 2H),

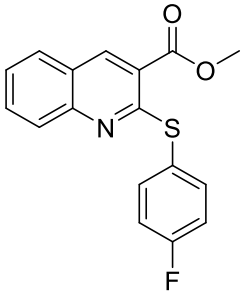
7.55 (d, J = 8.4 Hz, 2H), 7.45 (t, J = 7.3 Hz, 1H), 7.41 (d, J = 8.5 Hz, 2H), 4.03 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.69, 159.02, 148.84, 140.47, 137.20, 134.95, 132.17, 129.52, 128.93, 128.53, 128.41, 126.31, 124.66, 121.16, 52.60; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}ClNO_2S^+$ 330.0350; Found 330.0358.

Methyl 2-((4-(trifluoromethyl)phenyl)thio)quinoline-3-carboxylate (3ga):



Following the general procedure, **3ga** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (37.8 mg, 52% yield); mp 111-113 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.72 (s, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.64 – 7.59 (m, 3H), 7.55 (d, J = 8.4 Hz, 1H), 7.43 – 7.37 (m, 1H), 3.97 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.63, 158.32, 148.78, 140.58, 135.85, 132.30, 130.55 (d, J = 32.5 Hz), 128.47 (d, J = 28.3 Hz), 126.49, 125.46, 125.42 (q, J = 3.8 Hz), 124.15 (q, J = 272.1 Hz), 121.21, 52.65; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -62.62; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{13}F_3NO_2S^+$ 364.0614; Found 364.0625.

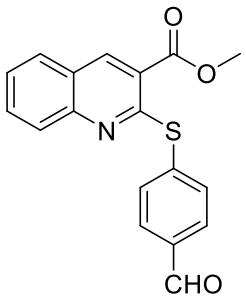
Methyl 2-((4-fluorophenyl)thio)quinoline-3-carboxylate (3ha):



Following the general procedure, **3ha** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (31.3 mg, 50% yield); mp 103-105 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.68 (s, 1H), 7.75 – 7.70 (m, 1H), 7.61 – 7.56 (m, 1H), 7.54 –

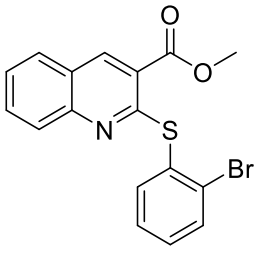
7.49 (m, 3H), 7.38 (t, J = 7.4 Hz, 1H), 7.07 (t, J = 8.6 Hz, 2H), 3.97 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.73, 163.29 (d, J = 248.5 Hz), 159.49, 148.85, 140.43, 138.02 (d, J = 8.15 Hz), 132.13, 128.46 (d, J = 20.3 Hz), 126.23, 126.18 (d, J = 3.5 Hz), 124.61, 121.12, 115.88 (d, J = 21.9 Hz), 52.59; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -112.58 – 112.63 (m, 1F); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}FNO_2S^+$ 314.0646; Found 314.0661.

Methyl 2-((4-formylphenyl)thio)quinoline-3-carboxylate (3ia):



Following the general procedure, **3ia** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (27.2 mg, 42% yield); mp 186-188 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 10.02 (s, 1H), 8.73 (s, 1H), 7.86 (d, J = 8.3 Hz, 2H), 7.76 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.2 Hz, 2H), 7.63 – 7.60 (m, 1H), 7.55 (d, J = 8.1 Hz, 1H), 7.43 – 7.40 (m, 1H), 3.98 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 190.81, 164.58, 157.08, 147.75, 139.58, 138.46, 134.97, 134.67, 131.32, 128.61, 127.57, 127.33, 125.56, 123.78, 120.34, 51.66; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{14}NO_3S^+$ 324.0689; Found 324.0687.

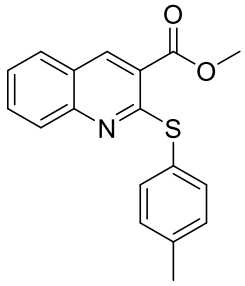
Methyl 2-((2-bromophenyl)thio)quinoline-3-carboxylate (3ja):



Following the general procedure, **3ja** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white soild (38.2 mg, 51% yield); mp 105-107 °C; ^{1}H NMR

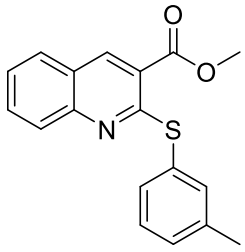
(600 MHz, $CDCl_3$) δ = 8.71 (s, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.58 – 7.56 (m, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.33 – 7.30 (m, 1H), 7.25 – 7.23 (m, 1H), 3.98 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.72, 158.29, 148.94, 140.49, 138.03, 133.24, 132.78, 132.06, 131.64, 130.42, 128.54, 127.71, 126.21, 124.61, 121.11, 52.61; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}BrNO_2S^+$ 373.9845; Found 373.9843

Methyl 2-(*p*-tolylthio)quinoline-3-carboxylate (3ka):



Following the general procedure, **3ka** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a pale yellow soild (44.6 mg, 72% yield); mp 120-122 °C; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.65 (s, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 3.3 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.33 (m, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 3.95 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.82, 159.88, 148.91, 140.29, 138.73, 135.79, 131.93, 129.57, 128.48, 128.47, 127.36, 126.06, 124.58, 121.38, 52.55, 21.42; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{16}NO_2S^+$ 310.0896; Found 310.0904.

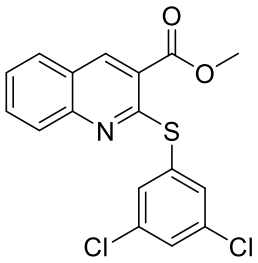
Methyl 2-(*m*-tolylthio)quinoline-3-carboxylate (3la):



Following the general procedure, **3la** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white soild (43.3 mg, 70% yield); mp 97-99 °C; ^1H NMR

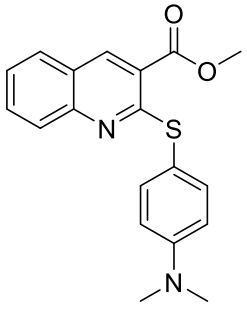
(500 MHz, $CDCl_3$) δ = 8.66 (s, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.39 – 7.34 (m, 3H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 3.95 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.80, 159.68, 148.90, 140.29, 138.44, 136.21, 132.88, 131.95, 130.62, 129.48, 128.52, 128.49, 126.11, 124.61, 121.46, 52.55, 21.37; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{16}NO_2S^+$ 310.0896; Found 310.0905.

Methyl 2-((3,5-dichlorophenyl)thio)quinoline-3-carboxylate (3ma):



Following the general procedure, **3ma** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white soild (43.7 mg, 60% yield); mp 158-160 °C; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.75 – 8.70 (m, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.47 (d, *J* = 1.8 Hz, 2H), 7.44 – 7.41 (m, 1H), 7.36 (t, *J* = 1.7 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.56, 157.98, 148.77, 140.66, 134.60, 134.34, 133.81, 132.41, 128.84, 128.58, 128.49, 126.60, 124.78, 120.98, 52.68; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{12}Cl_2NO_2S^+$ 363.9960; Found 363.9956.

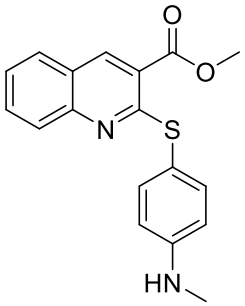
Methyl 2-((4-(dimethylamino)phenyl)thio)quinoline-3-carboxylate (3na):



Following the general procedure, **3na** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow soild (46.0 mg, 68% yield); mp 164-166°C; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.11 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.63 – 7.56 (m, 2H),

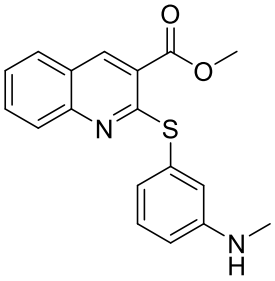
7.26 (t, J = 7.2 Hz, 1H), 7.12 (d, J = 8.6 Hz, 2H), 6.95 (d, J = 8.6 Hz, 2H), 3.56 (s, 3H), 3.28 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.57, 154.20, 148.35, 146.31, 140.18, 133.61, 131.32, 128.26, 128.07, 127.07, 124.15, 123.88, 123.26, 119.57, 51.88, 40.53, 16.65; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{19}N_2O_2S^+$ 339.1162; Found 339.1166.

Methyl 2-((4-(methylamino)phenyl)thio)quinoline-3-carboxylate (3oa):



Following the general procedure, **3oa** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow soild (41.5 mg, 64% yield); mp 153-155 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 10.18 (s, 1H), 8.70 (s, 1H), 7.86 (s, 2H), 7.71 (d, J = 8.3 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.26 (d, J = 8.7 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 3.93 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.64, 152.40, 149.74, 142.64, 138.18, 132.65, 130.84, 128.90, 128.77, 126.87, 123.44, 122.33, 120.72, 110.33, 52.59, 17.49; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}N_2O_2S^+$ 325.1005; Found 325.1016.

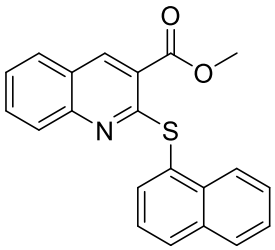
Methyl 2-((3-(methylamino)phenyl)thio)quinoline-3-carboxylate (3pa):



Following the general procedure, **3pa** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow soild (40.2 mg, 62% yield); mp 125-127 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 10.21 (s, 1H), 8.70 (s, 1H), 8.08 (s, 1H), 7.69 (d, J = 8.3 Hz,

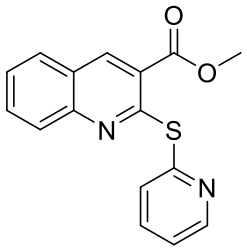
1H), 7.62 – 7.57 (m, 2H), 7.54 – 7.52 (m, 1H), 7.24 – 7.21 (m, 1H), 7.21 – 7.17 (m, 1H), 6.89 (d, J = 8.6 Hz, 1H), 3.92 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.61, 152.39, 149.60, 142.64, 140.71, 138.90, 132.68, 128.97, 128.91, 126.89, 123.55, 122.35, 120.66, 117.70, 116.78, 110.37, 52.62, 15.88; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}N_2O_2S^+$ 325.1005; Found 325.1016.

Methyl 2-(naphthalen-1-ylthio)quinoline-3-carboxylate (3qa):



Following the general procedure, **3qa** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white soild (38.0 mg, 55% yield); mp 149-151 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.70 (s, 1H), 8.09 (s, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.79 (t, J = 7.9 Hz, 2H), 7.72 (d, J = 7.9 Hz, 1H), 7.58 – 7.56 (m, 1H), 7.54 – 7.51 (m, 1H), 7.49 – 7.42 (m, 3H), 7.37 – 7.34 (m, 1H), 3.98 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.80, 159.62, 148.91, 140.39, 134.63, 133.78, 133.23, 133.01, 132.02, 128.75, 128.50, 128.45, 128.01, 127.84, 127.71, 126.68, 126.18, 126.09, 124.67, 121.36, 52.60; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{16}NO_2S^+$ 346.0896; Found 346.0888.

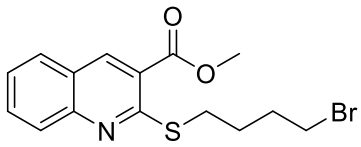
Methyl 2-(pyridin-2-ylthio)quinoline-3-carboxylate (3ra):



Following the general procedure, **3ra** was isolated by flash chromatography on silica (EtOAc/PE = 2/10) as a white soild (31.4 mg, 53% yield); mp >240 °C; ^{1}H NMR (500

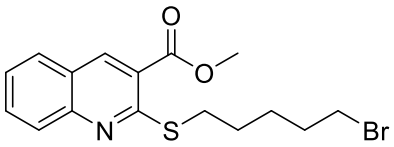
MHz, $CDCl_3$) δ = 8.69 (s, 1H), 8.59 (d, *J* = 4.8 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.65 (m, 2H), 7.61 – 7.57 (m, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.24 – 7.22 (m, 1H), 3.93 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.66, 158.41, 154.99, 150.20, 148.84, 140.34, 136.60, 132.01, 130.75, 128.52, 128.48, 126.49, 124.88, 122.74, 122.26, 52.58; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{13}N_2O_2S^+$ 297.0692; Found 297.0703.

Methyl 2-((4-bromobutyl)thio)quinoline-3-carboxylate (3sa):



Following the general procedure, **3sa** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow oil (48.2 mg, 68% yield); ^1H NMR (500 MHz, $CDCl_3$) δ = 8.61 (s, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.67 – 7.64 (m, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 3.89 (s, 3H), 3.39 (t, *J* = 6.7 Hz, 2H), 3.26 (t, *J* = 7.2 Hz, 2H), 2.00 (p, *J* = 6.8 Hz, 2H), 1.86 (p, *J* = 7.2, 6.8 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.69, 159.32, 148.93, 140.20, 132.19, 128.73, 127.96, 125.91, 124.18, 121.78, 52.44, 33.37, 32.12, 29.13, 27.60; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{17}BrNO_2S^+$ 354.0158; Found 354.0164.

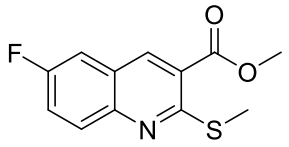
Methyl 2-((5-bromopentyl)thio)quinoline-3-carboxylate (3ta):



Following the general procedure, **3ta** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a yellow oil (47.9 mg, 65% yield); ^1H NMR (500 MHz, $CDCl_3$) δ = 8.64 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.70 – 7.65 (m, 1H), 7.42 – 7.39 (m, 1H), 3.91 (s, 3H), 3.37 (t, *J* = 6.9 Hz, 2H), 3.29 – 3.23 (m, 2H), 1.92 – 1.86 (m, 2H), 1.75 (q, *J* = 7.5 Hz, 2H), 1.60 (q, *J* = 8.0 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.72, 159.56, 148.96, 140.14, 132.15, 128.73, 127.94, 125.84,

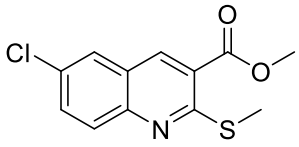
124.15, 121.83, 58.47, 52.42, 33.67, 32.46, 29.83, 28.14, 27.75; HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{16}H_{18}BrNNaO_2S^+$ 390.0134; Found 390.0134.

Methyl 6-fluoro-2-(methylthio)quinoline-3-carboxylate (3ab):



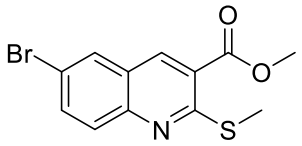
Following the general procedure, **3ab** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (46.2 mg, 92% yield); mp 139-141 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.59 (s, 1H), 7.73 – 7.70 (m, 1H), 7.51 – 7.49 (m, 1H), 7.18 – 7.14 (m, 1H), 3.90 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.54, 164.96 (d, *J* = 253.5 Hz), 161.80, 150.14 (d, *J* = 13.4 Hz), 139.69, 130.90 (d, *J* = 10.4 Hz), 121.03, 121.00 (d, *J* = 2.7 Hz), 116.22 (d, *J*= 25.5 Hz), 112.01 (d, *J*= 20.6 Hz), 52.46, 14.15; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -105.37 – 105.41 (m, 1F); HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{12}H_{10}FNNaO_2S^+$ 274.0308; Found 274.0308.

Methyl 6-chloro-2-(methylthio)quinoline-3-carboxylate (3ac):



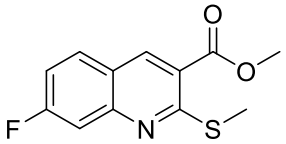
Following the general procedure, **3ac** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (44.4 mg, 83% yield); mp 164-167 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.60 (s, 1H), 7.91 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.36 – 7.34 (m, 1H), 3.92 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.45, 161.80, 149.22, 139.60, 138.21, 129.85, 127.14, 126.85, 122.41, 121.79, 52.52, 14.17; HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{12}H_{10}ClNNaO_2S^+$ 290.0013; Found 290.0011.

Methyl 6-bromo-2-(methylthio)quinoline-3-carboxylate (3ad):



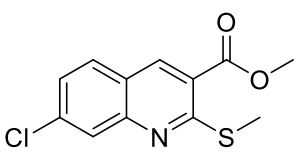
Following the general procedure, **3ad** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (45.0 mg, 72% yield); mp 172-175 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.53 (s, 1H), 8.03 (d, *J* = 1.8 Hz, 1H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.45 – 7.43 (m, 1H), 3.90 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.39, 161.71, 149.25, 139.64, 130.39, 129.80, 129.31, 126.65, 122.59, 121.82, 52.52, 14.17; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{10}BrNNaO_2S^+$ 333.9508; Found 333.9499.

Methyl 7-fluoro-2-(methylthio)quinoline-3-carboxylate (3ae):



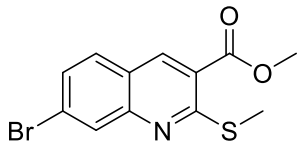
Following the general procedure, **3ae** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (47.7 mg, 95% yield); mp 138-140 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.45 (s, 1H), 7.80 – 7.77 (m, 1H), 7.39 – 7.35 (m, 1H), 7.26 – 7.24 (m, 1H), 3.88 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.35, 159.72 (d, *J* = 247.8Hz), 159.43 (d, *J* = 2.6 Hz), 146.04, 139.07 (d, *J* = 5.3 Hz), 130.24 (d, *J* = 8.9 Hz), 124.36 (d, *J* = 10.1 Hz), 122.27, 121.91 (d, *J* = 25.7 Hz), 111.53 (d, *J* = 21.9 Hz), 52.46, 13.99; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -114.31 – 114.35 (m, 1F); HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{10}FNNaO_2S^+$ 274.0308; Found 274.0308.

Methyl 7-chloro-2-(methylthio)quinoline-3-carboxylate (3af):



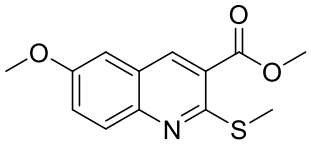
Following the general procedure, **3af** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (51.9 mg, 97% yield); mp 167-169 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.42 (s, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.60 (d, *J* = 2.3 Hz, 1H), 7.54 – 7.52 (m, 1H), 3.89 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.28, 160.66, 147.23, 138.76, 132.71, 131.21, 129.45, 127.12, 124.54, 122.36, 52.52, 14.09; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{10}ClNNaO_2S^+$ 290.0013; Found 290.0019.

Methyl 7-bromo-2-(methylthio)quinoline-3-carboxylate (3ag):



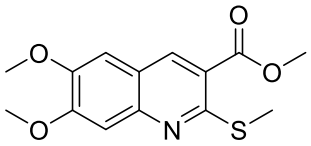
Following the general procedure, **3ag** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (57.4 mg, 92% yield); mp 171-174 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.51 (s, 1H), 7.86 (s, 1H), 7.77 – 7.68 (m, 2H), 3.92 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.38, 160.91, 147.55, 138.79, 135.35, 130.54, 129.66, 125.20, 122.43, 119.22, 52.59, 14.15; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{10}BrNNaO_2S^+$ 333.9508; Found 333.9505.

Methyl 6-methoxy-2-(methylthio)quinoline-3-carboxylate (3ah):



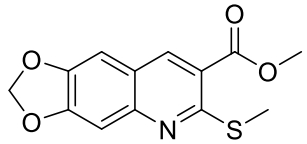
Following the general procedure, **3ah** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (48.4 mg, 92% yield); mp 178-180 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.51 (s, 1H), 7.77 (d, *J* = 9.2 Hz, 1H), 7.32 – 7.29 (m, 1H), 6.96 (d, *J* = 2.8 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.86, 157.27, 157.17, 145.37, 138.88, 129.38, 124.86, 124.65, 121.74, 105.92, 55.59, 52.37, 14.00; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{13}NNaO_3S^+$ 286.0508; Found 286.0515.

Methyl 6,7-dimethoxy-2-(methylthio)quinoline-3-carboxylate (3ai):



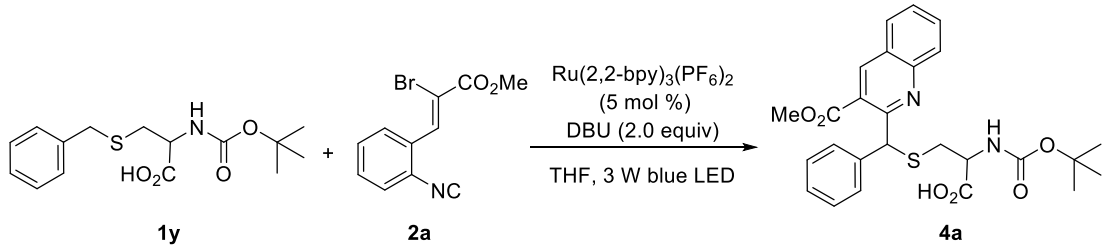
Following the general procedure, **3ai** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (29.3 mg, 50% yield); mp >240 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.52 (s, 1H), 7.24 (s, 1H), 6.98 (s, 1H), 4.00 (s, 3H), 3.93 (s, 3H), 3.90 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.03, 158.19, 154.62, 149.23, 146.76, 138.25, 119.60, 119.23, 107.03, 105.88, 56.32, 56.11, 52.24, 14.04; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{15}NNaO_4S^+$ 316.0614; Found 316.0618.

Methyl 6-(methylthio)-[1,3]dioxolo[4,5-g]quinoline-7-carboxylate (3aj):



Following the general procedure, **3aj** was isolated by flash chromatography on silica (EtOAc/PE = 1/10) as a white solid (52.7 mg, 95% yield); mp 233-235 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.44 (s, 1H), 7.19 (s, 1H), 6.96 (s, 1H), 6.04 (s, 2H), 3.89 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.93, 158.24, 152.88, 148.03, 147.29, 138.57, 120.58, 119.64, 105.02, 103.43, 101.98, 52.25, 13.98; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{11}NNaO_4S^+$ 300.0301; Found 300.0301.

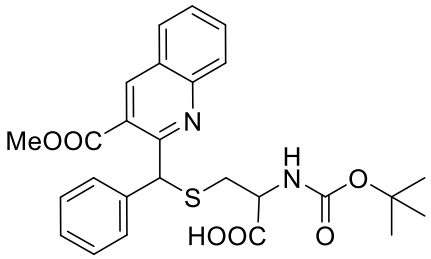
III. Synthetic Procedures and Analytical Data of Compounds 4a:



1y **2a** **4a**

A flame-dried, Schlenk tube equipped with a magnetic stir bar was charged with **1y** (62.3 mg, 0.2 mmol), $Ru(2,2\text{-}bpy)_3(PF_6)_2$ (8.6 mg, 0.01 mmol) and **2a** (159.7 mg, 0.6 mmol) under nitrogen atmosphere. Solutions of the DBU (60.9 mg, 0.4 mmol) in 2 mL anhydrous THF were added via syringe in rapid succession. The reaction was stirred at room temperature and irradiated with 3 W blue LEDs for 16 h. After the reaction was completed, the reaction mixture was poured into saturated aqueous NaCl (5 mL), extracted with CH_2Cl_2 (5 mL × 3). The combined organic extracts were dried over anhydrous $NaSO_4$, filtered and concentrated under reduced pressure to yield the corresponding crude product, which was purified by silica gel chromatography (EtOAc/petroleum ether = 3/10, V/V) to give **4a** (40.7 mg, 41%) as a white solid.

N-(*tert*-butoxycarbonyl)-S-((3-(methoxycarbonyl)quinolin-2-yl)(phenyl)methyl)cysteine (4a):



Following the general procedure, **4a** was isolated by flash chromatography on silica (EtOAc/PE = 3/10) as a white solid (40.7 mg, 41% yield); mp 136-138 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.66 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.77 – 7.72 (m, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.25 (s, 5H), 6.34 (s, 1H), 5.09 (d, *J* = 14.2 Hz, 2H), 4.70 (s, 1H), 3.91 (s, 3H), 3.82 – 3.78 (m, 1H), 3.62 – 3.58 (m, 1H), 1.32 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 171.17, 165.40, 158.65, 155.45, 148.54,

140.61, 135.47, 132.41, 128.66, 128.47, 128.20, 128.15, 127.87, 126.36, 124.48, 121.77, 79.65, 67.11, 54.28, 52.52, 32.41, 28.30; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{28}N_2NaO_6S^+$ 519.1560; Found 519.1557.

IV. The X-ray Analytical data of Compound 3ab:

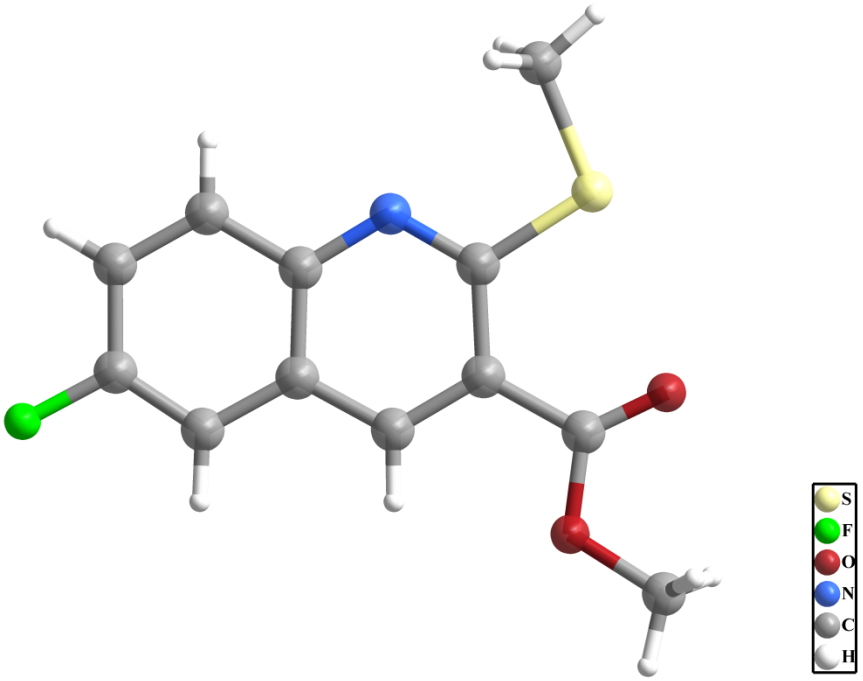


Figure 1. The ORTEP drawing of crystal (The ellipsoid contour percent probability level is 50%).

Method of Crystallization: The **3ab** was recrystallized from mixed solvents of acetate and petroleum ether at 25 ˚C.

V. Mechanism Studies:

1. BHT Trapping Experiments:

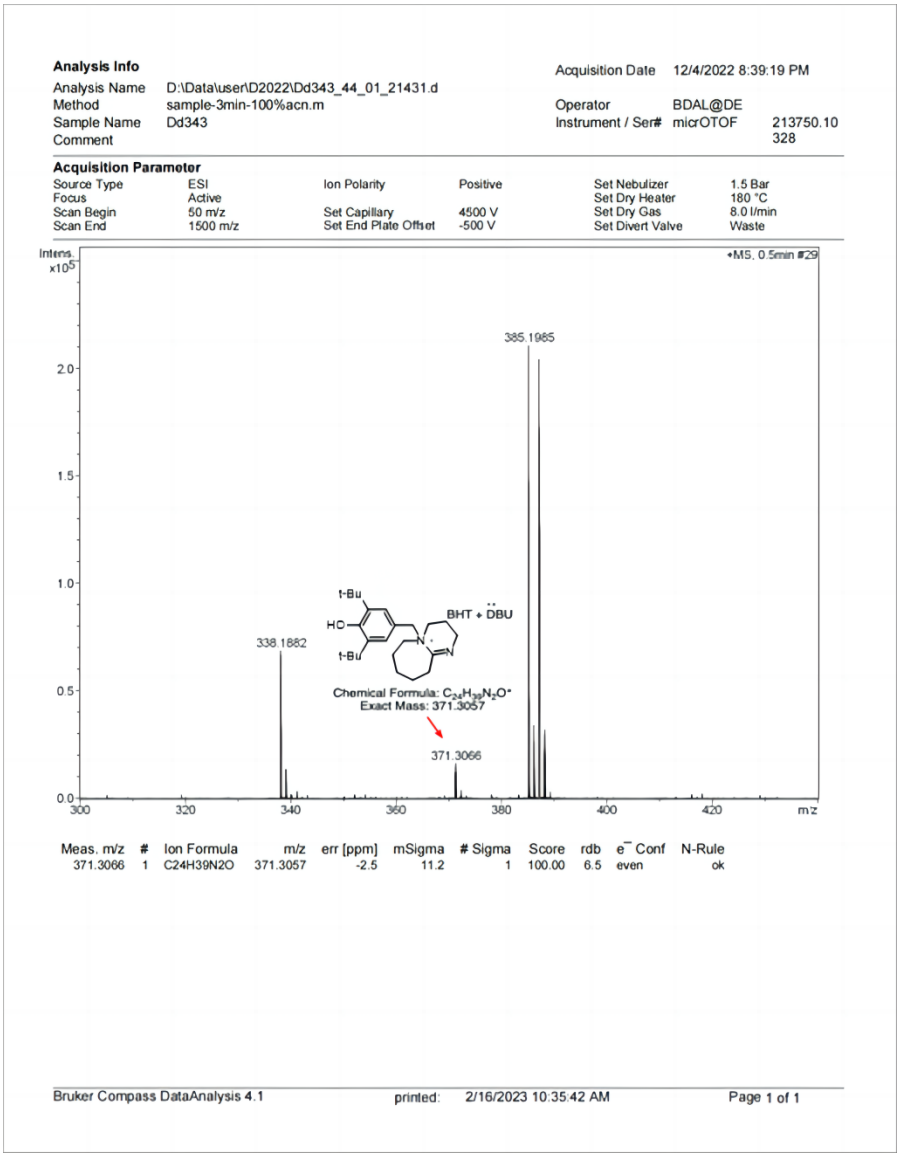


Figure 2. Mass spectrometry of the coupling product of the DBU cation radical and BHT.

2. Stern-Volmer Quenching Experiments:

Emission intensities were recorded using a spectrofluorimeter. All $Ru(2,2\text{-bpy})_3(PF_6)_2$ solutions were excited at 480 nm and the emission intensity at 561 nm was observed. First the emission spectrum of a 5×10^{-5} M solution of $Ru(2,2\text{-bpy})_3(PF_6)_2$ in THF was collected. Then appropriate amount of quencher was added to the measured solution and the emission spectrum of the sample was collected.

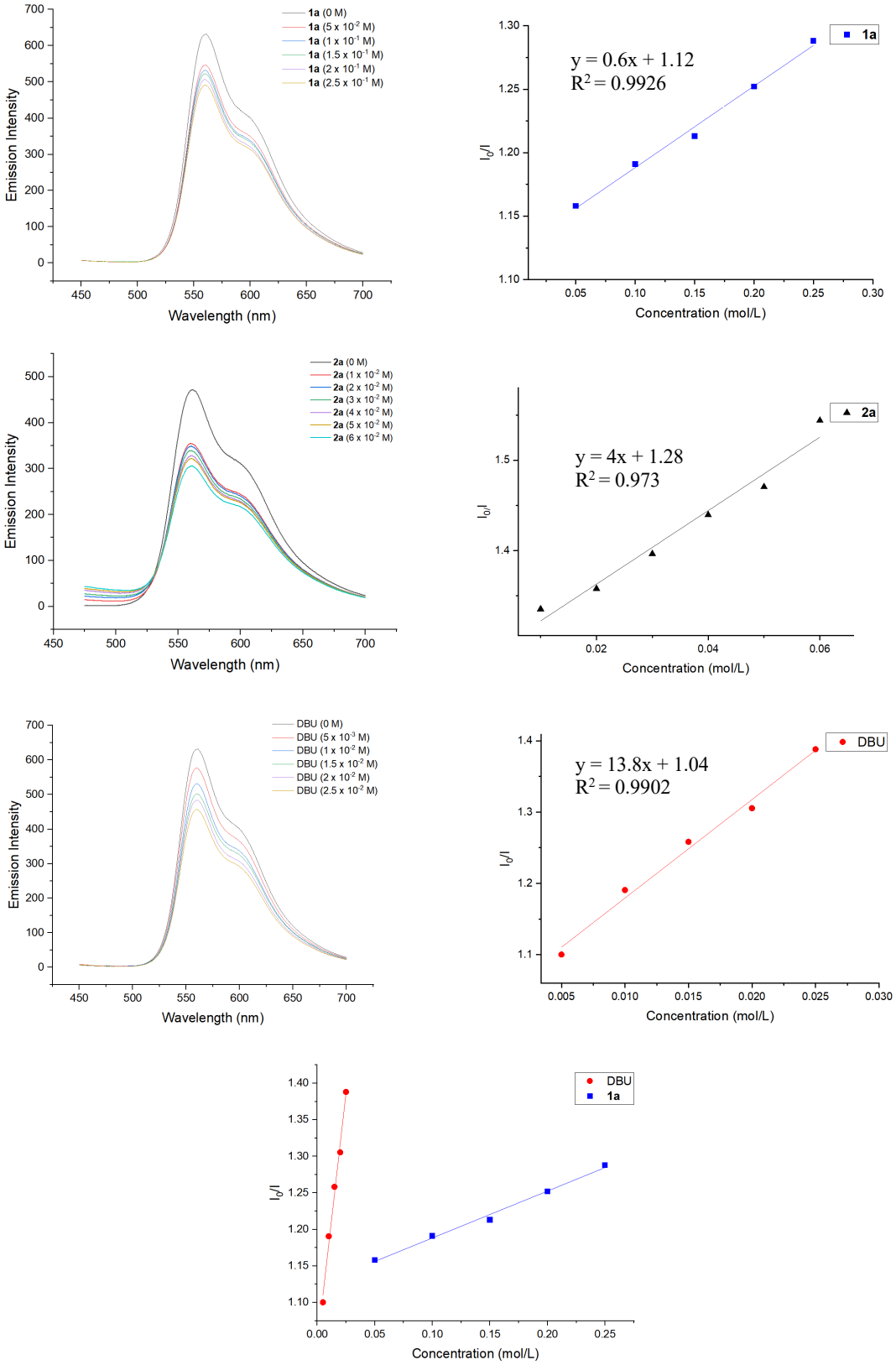


Figure 3. $Ru(2,2\text{-}bpy)_3(PF_6)_2$ Emission Quenching by 1a, 2a and DBU

VI. References:

1. Vidyasagar, A.; Shi, J.; Kreitmeier, P.; Reiser, O. Bromo- or Methoxy-Group-Promoted Umpolung Electron Transfer Enabled, Visible-Light-Mediated Synthesis of 2-Substituted Indole-3-glyoxylates. *Org. Lett.* **2018**, *20*, 6984-6989.

2. (a) Barbero, N.; Martin. R. Ligand-Free Ni-Catalyzed Reductive Cleavage of Inert Carbon−Sulfur Bonds. *Org. Lett.* **2012,** *14*, 796-799. (b) Morgan, K. F.; Hollingsworth, I. A.; Bull, J. A. Studies on the Synthesis, Stability and Conformation of 2-Sulfonyl-Oxetane Fragments. *Org. Biomol. Chem.* **2015**, *13*, 5265-5272.

VII. Copies of ^{1}H NMR and ^{13}C NMR Spectra of 3 and 4:

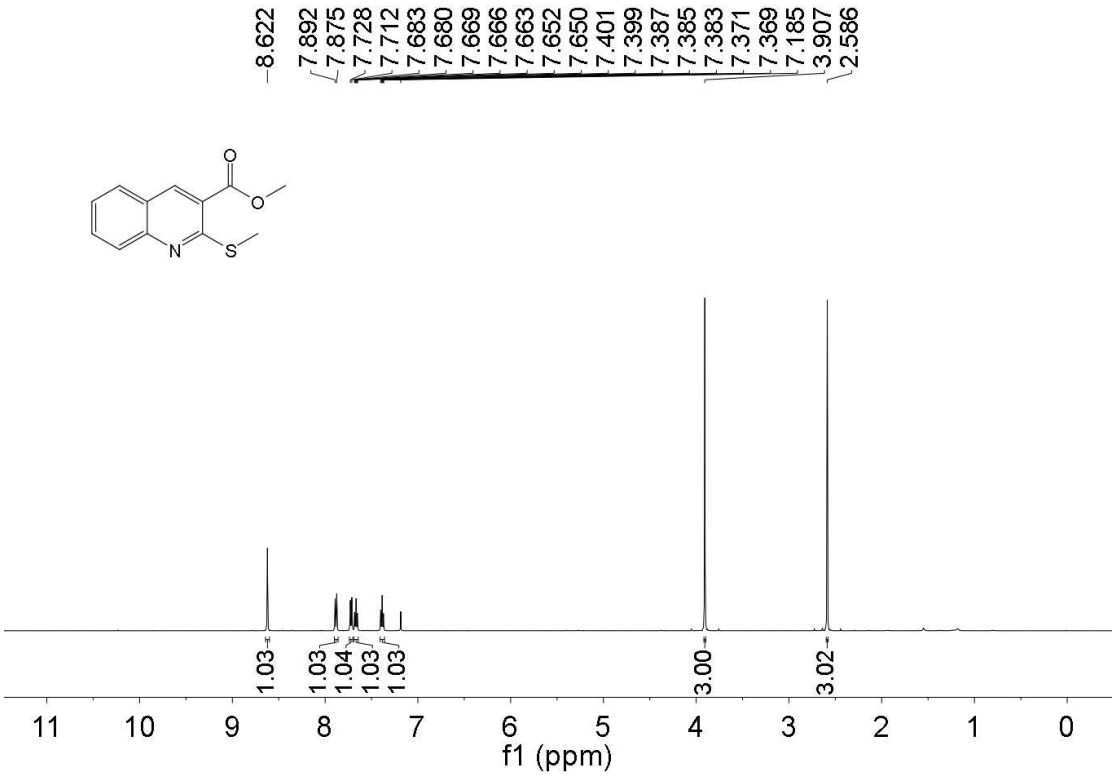


Figure 5. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3aa**

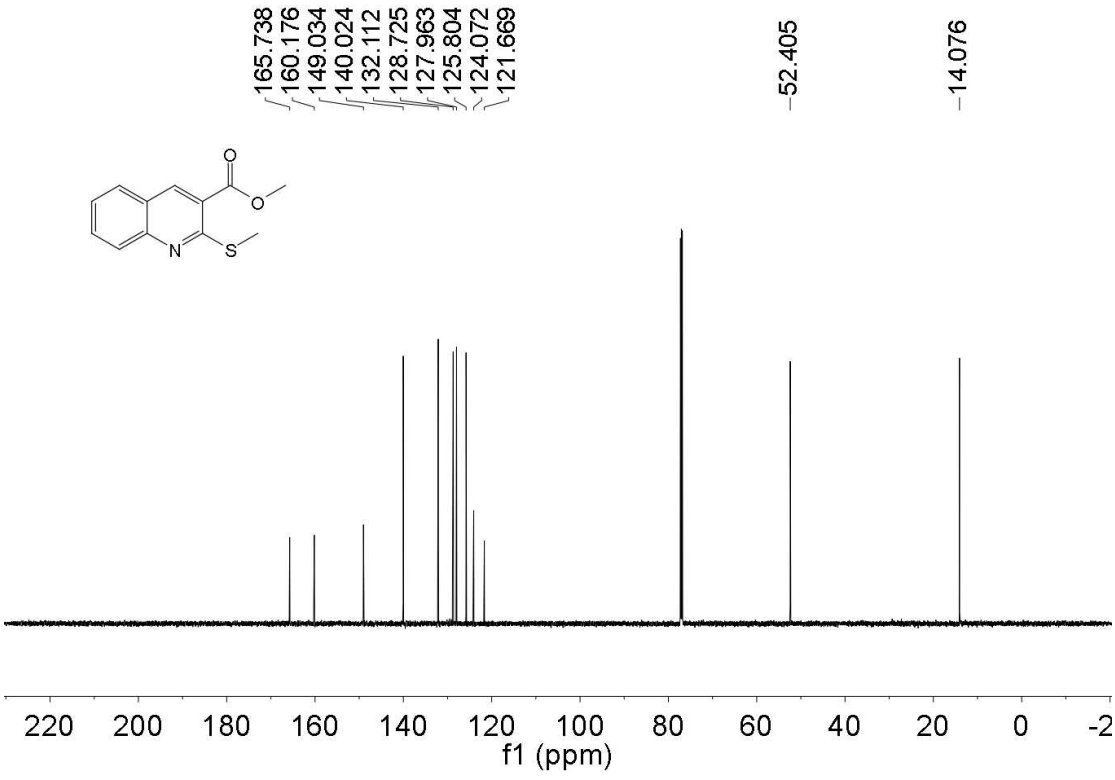


Figure 6. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3aa**

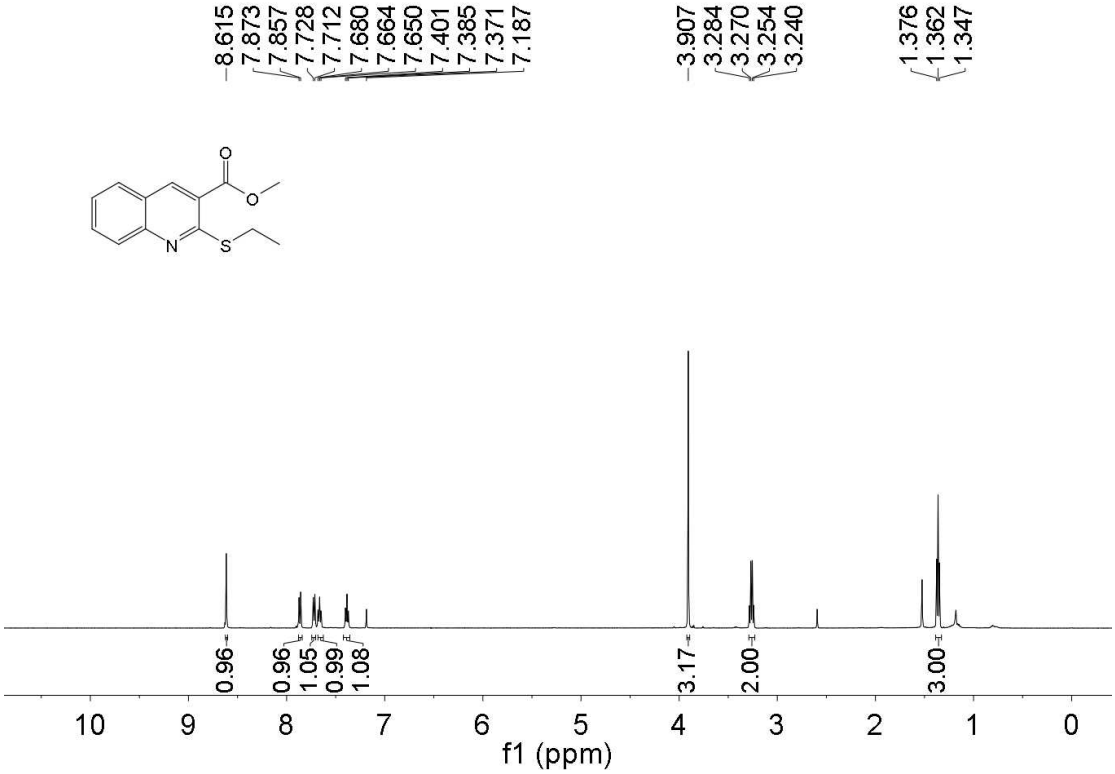


Figure 7. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ba**

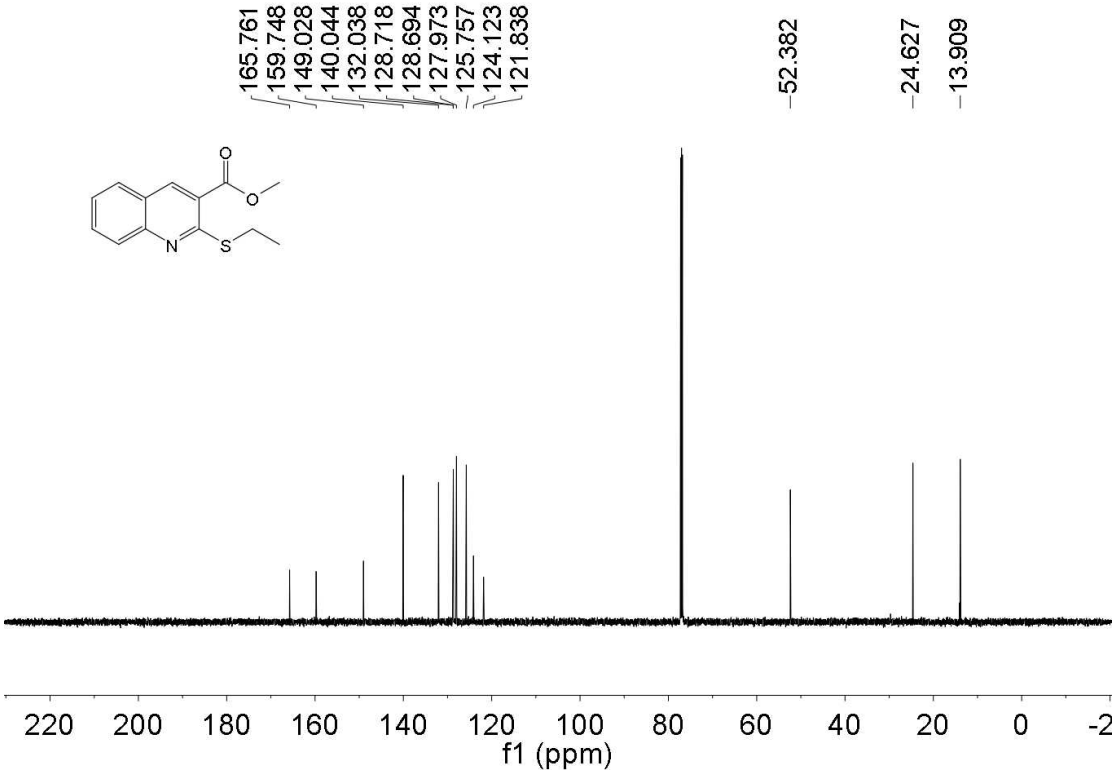


Figure 8. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ba**

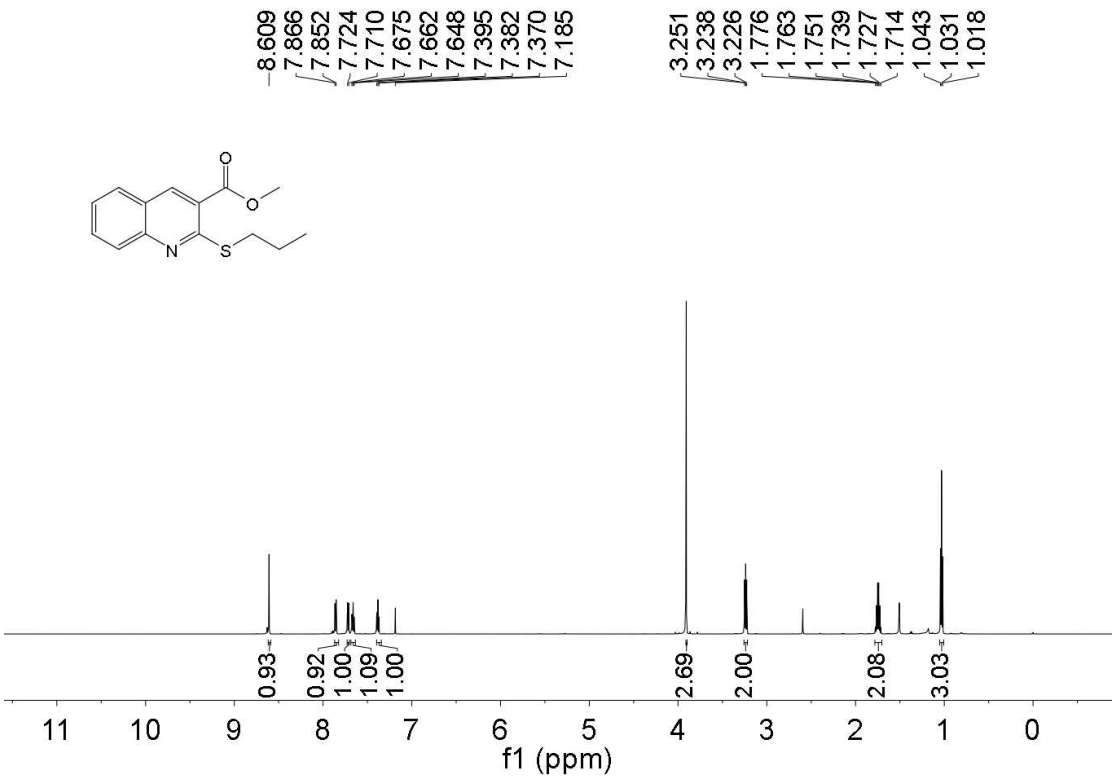


Figure 9. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ca**

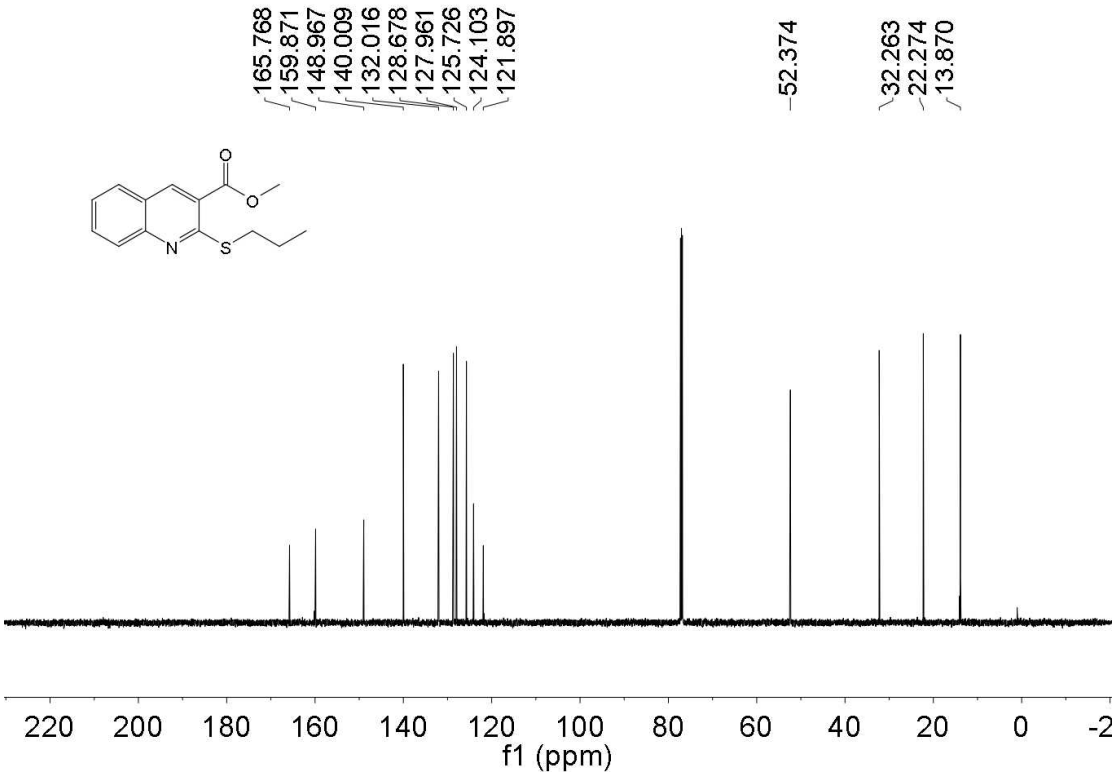


Figure 10. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ca**

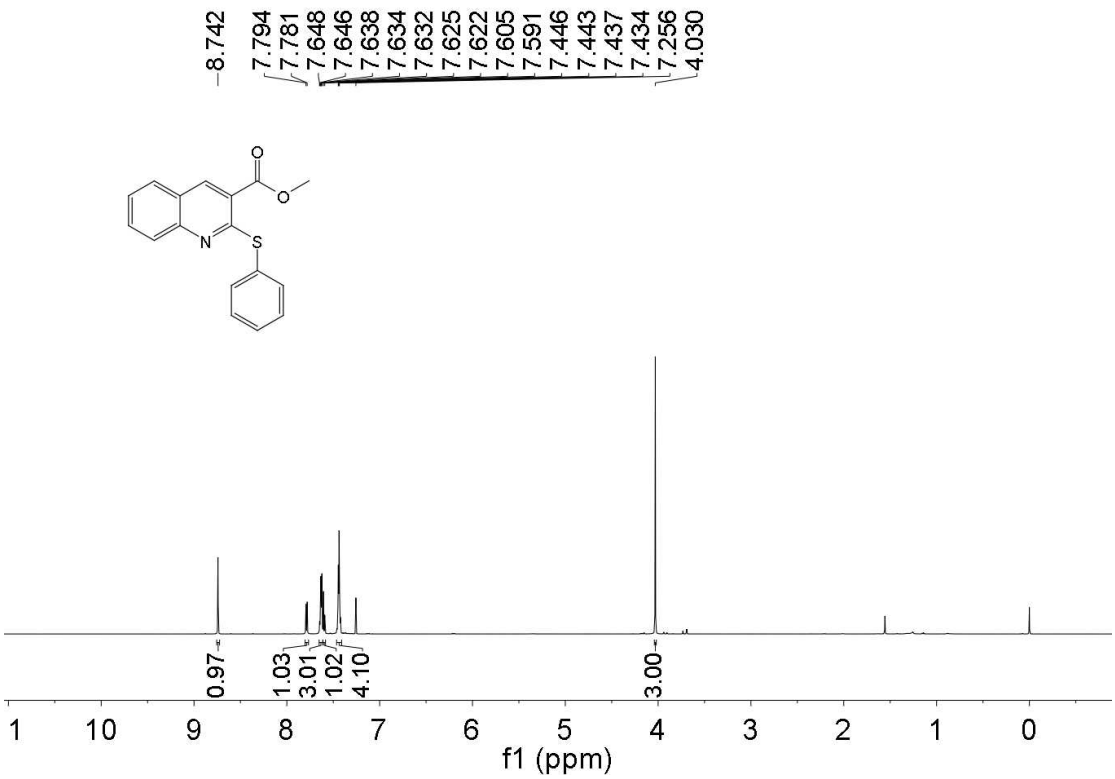


Figure 11. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3da**

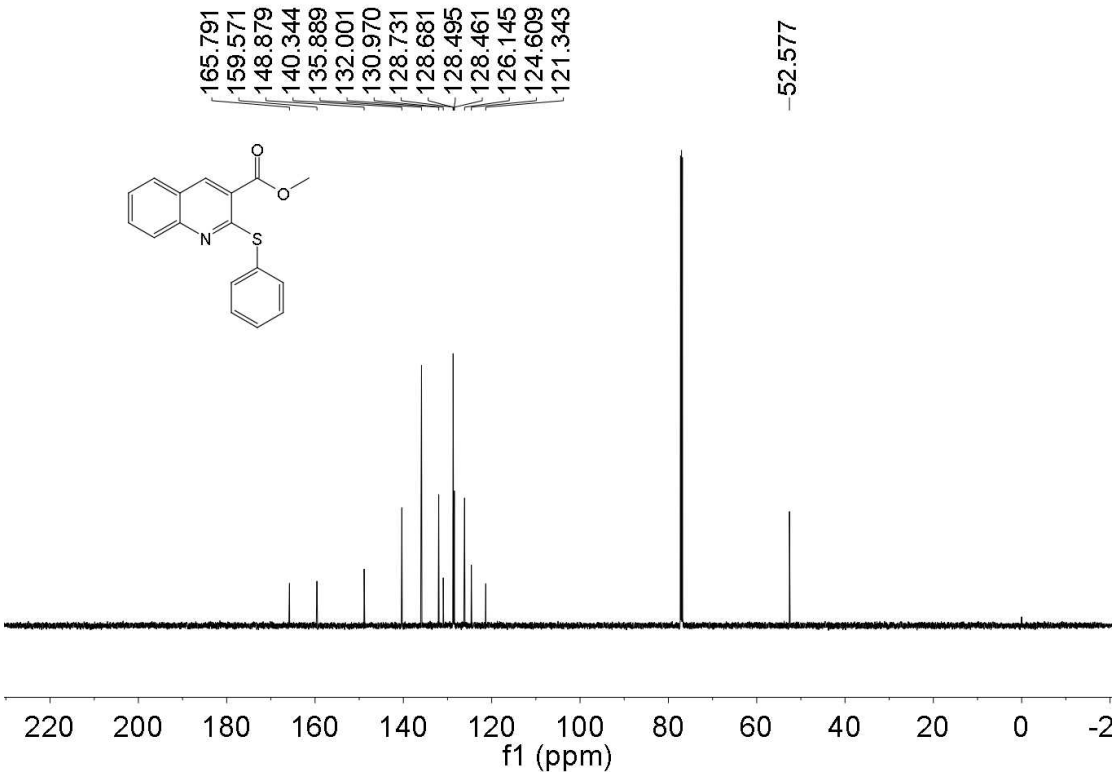


Figure 12. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3da**

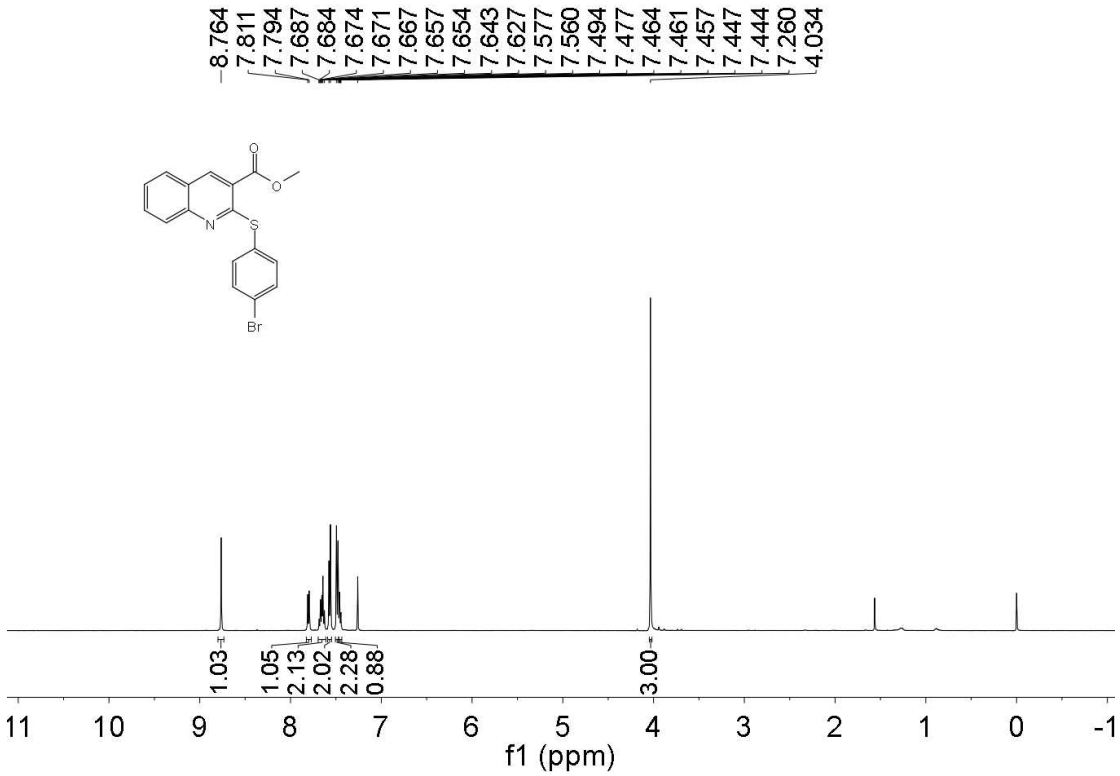


Figure 13. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ea**

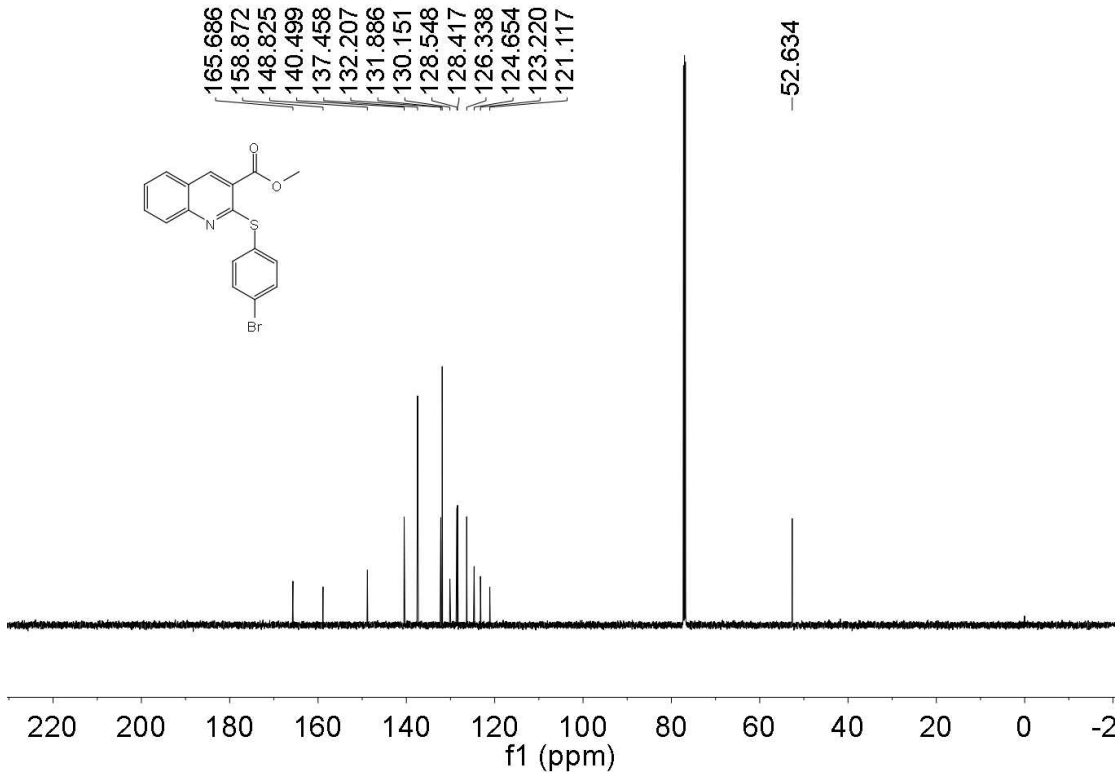


Figure 14. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ea**

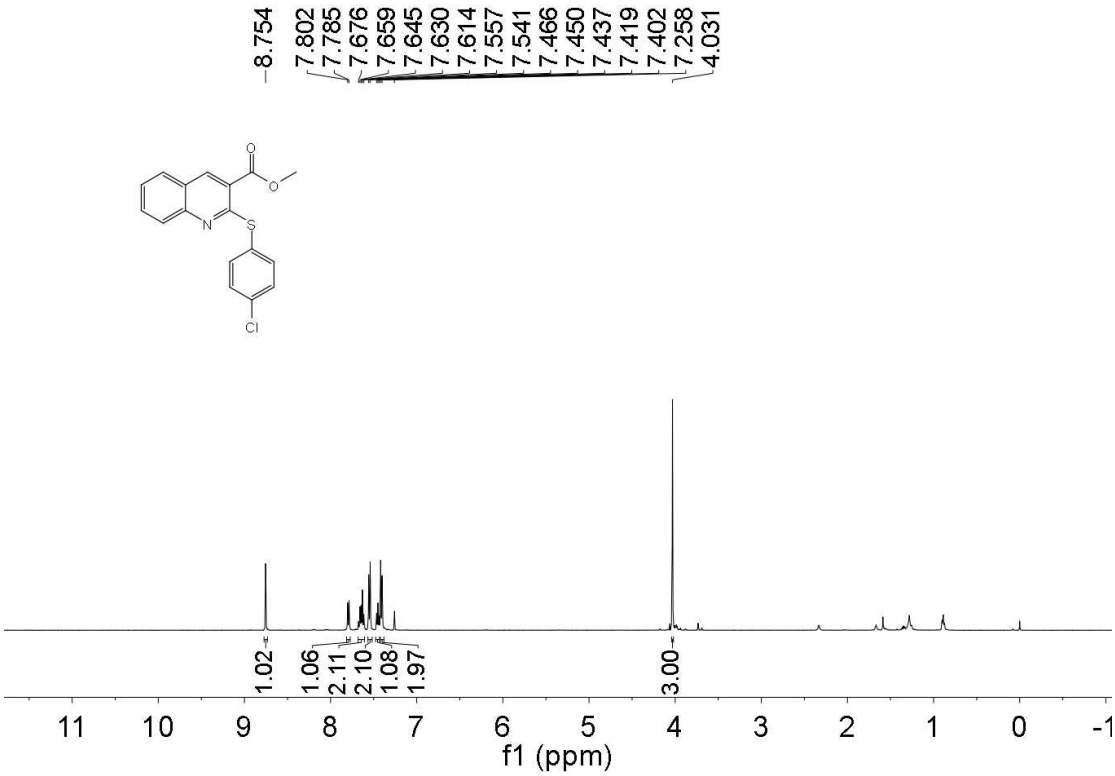


Figure 15. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3fa**

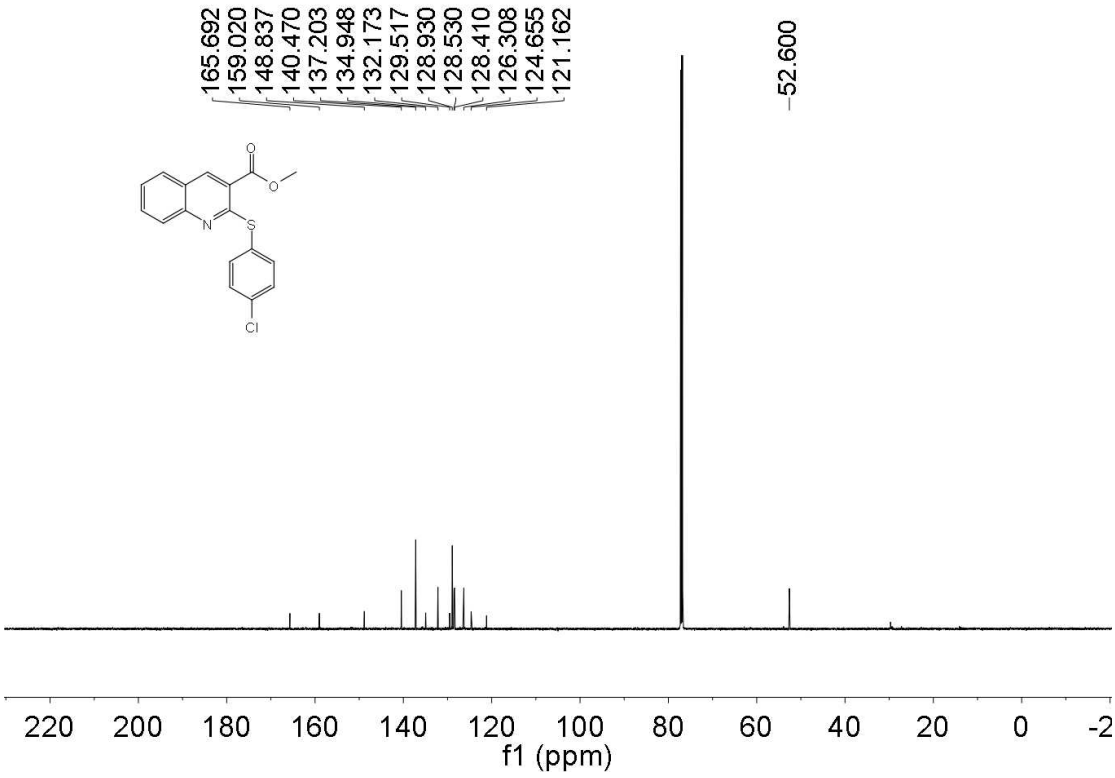


Figure 16. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3fa**

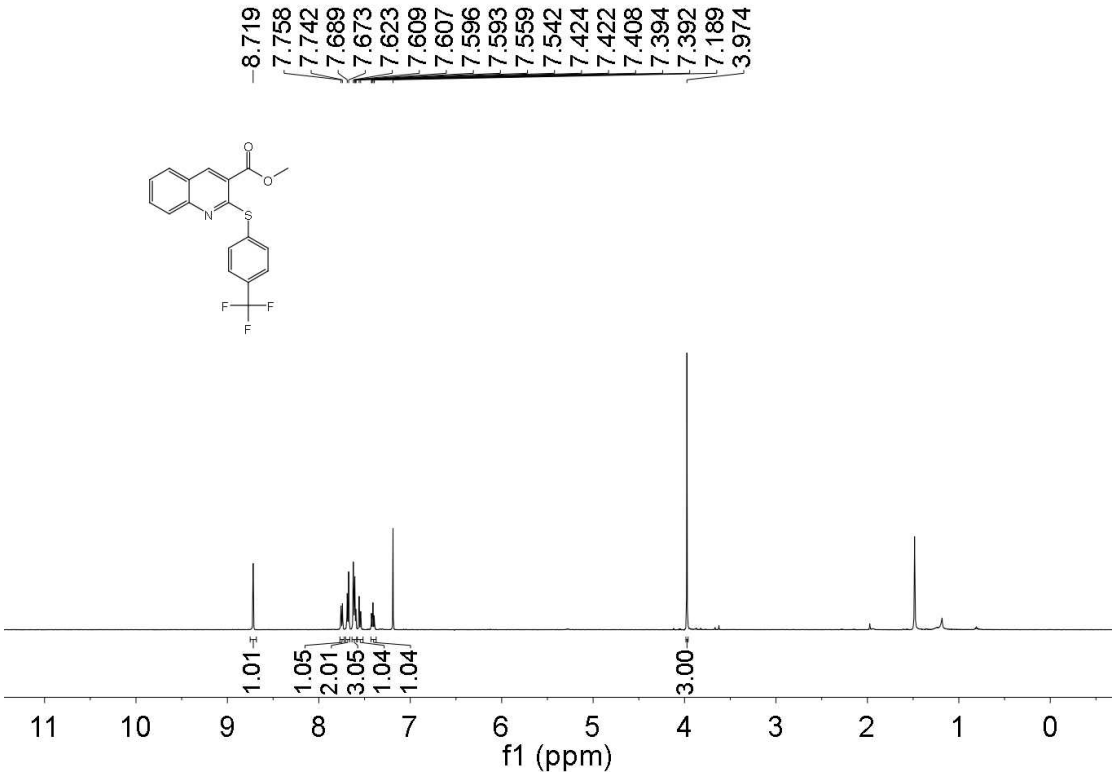


Figure 17. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ga**

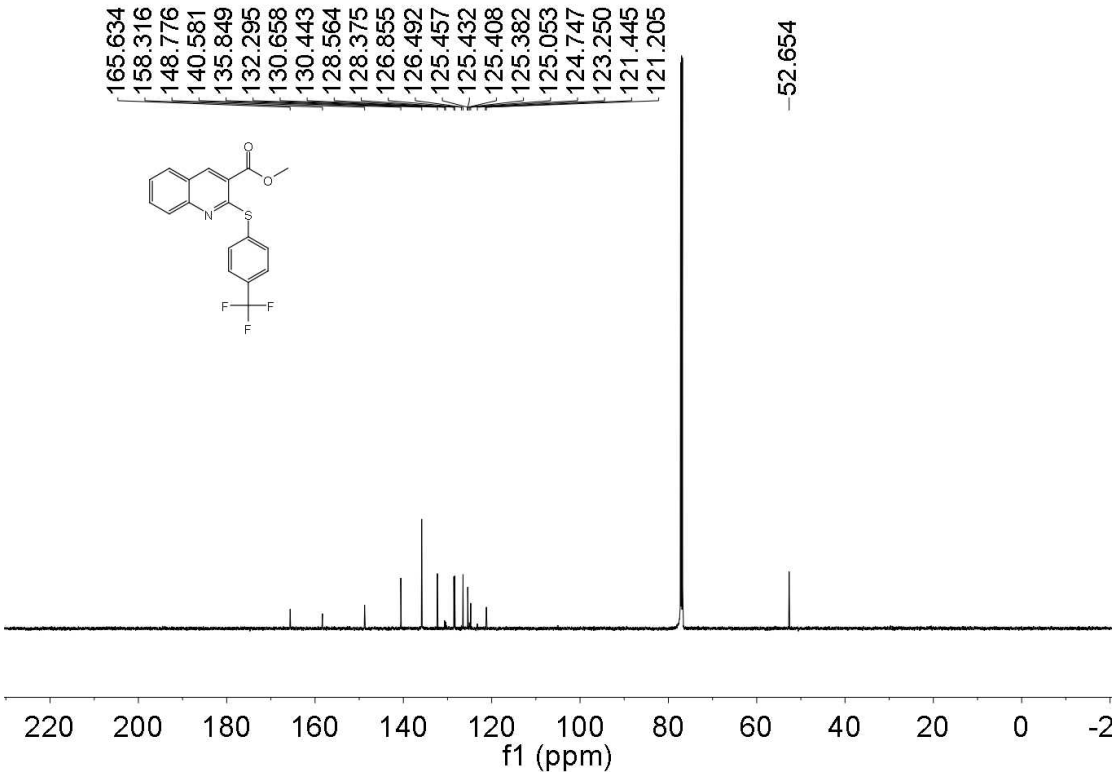


Figure 18. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ga**

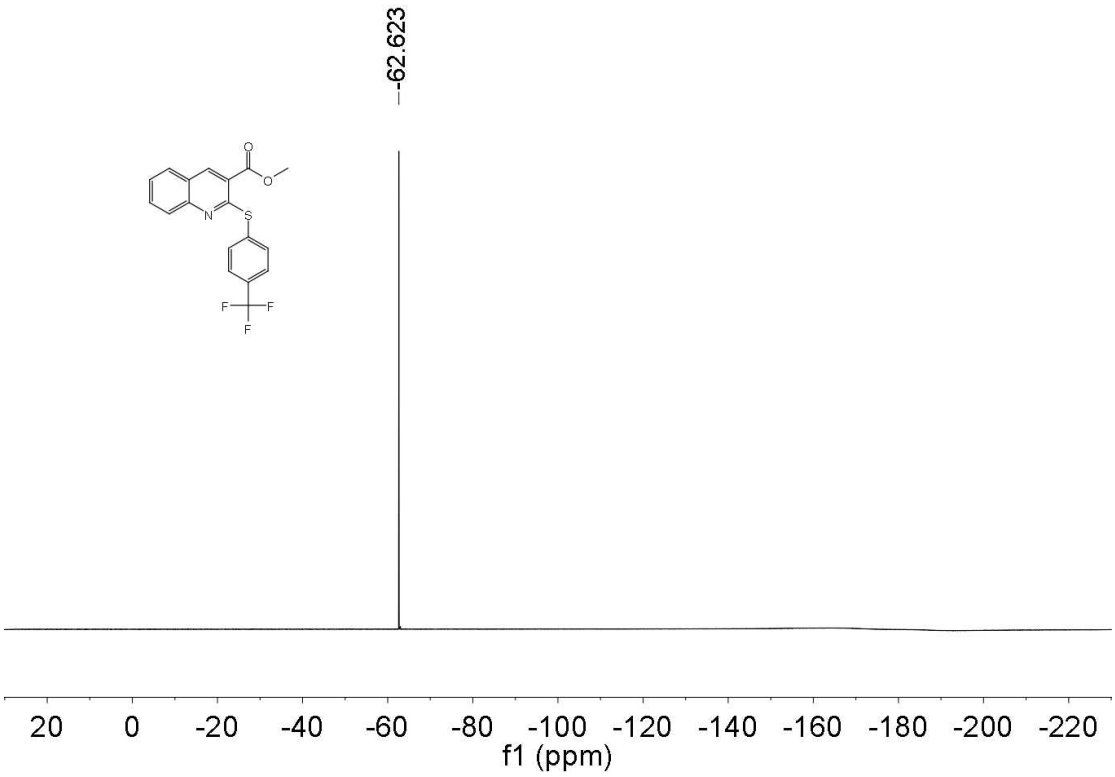


Figure 19. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ma**

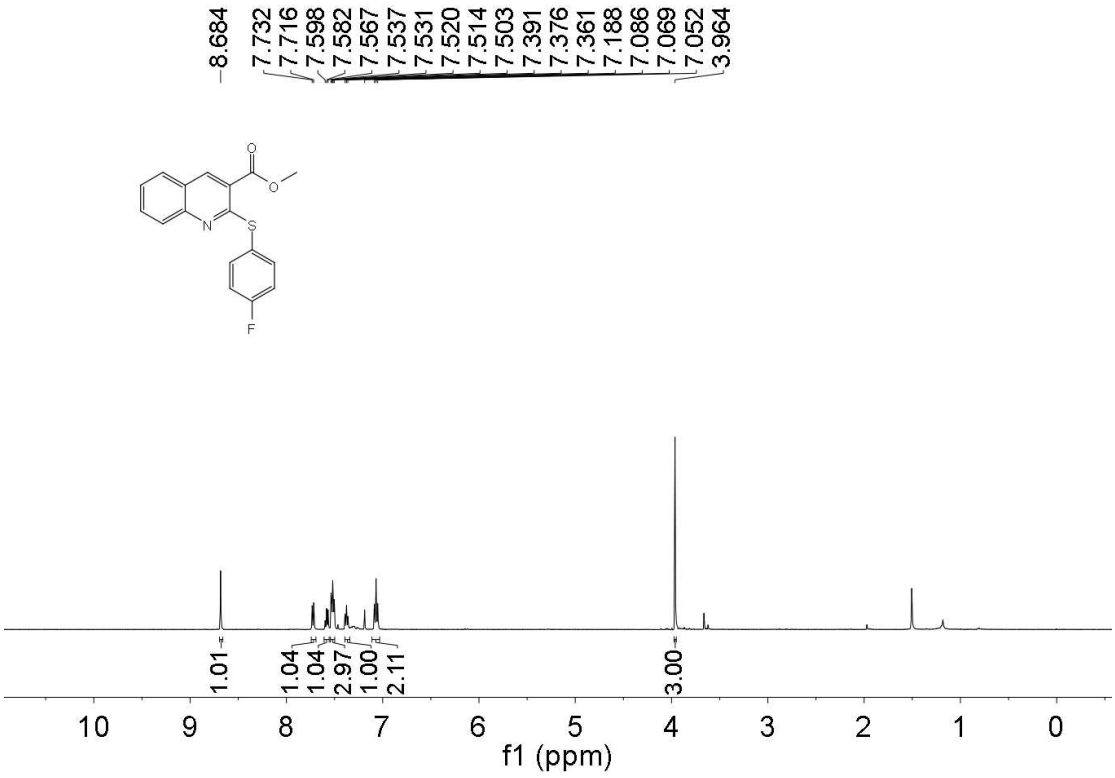


Figure 20. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ha**

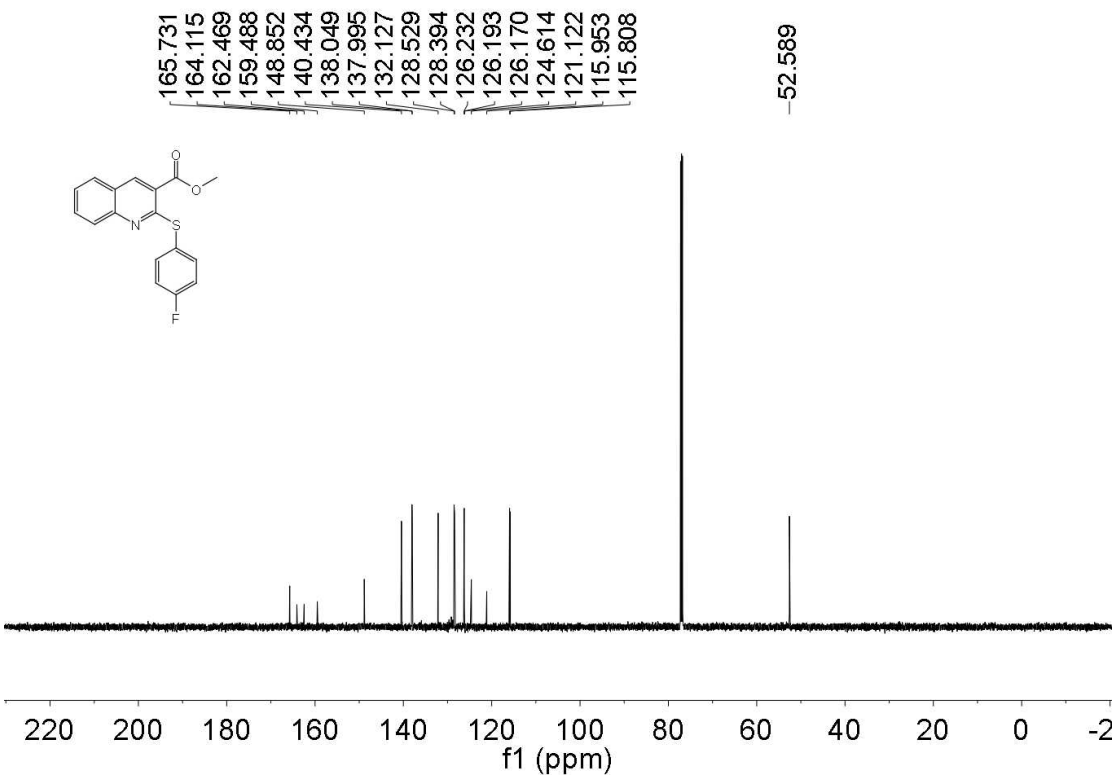


Figure 21. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ha**

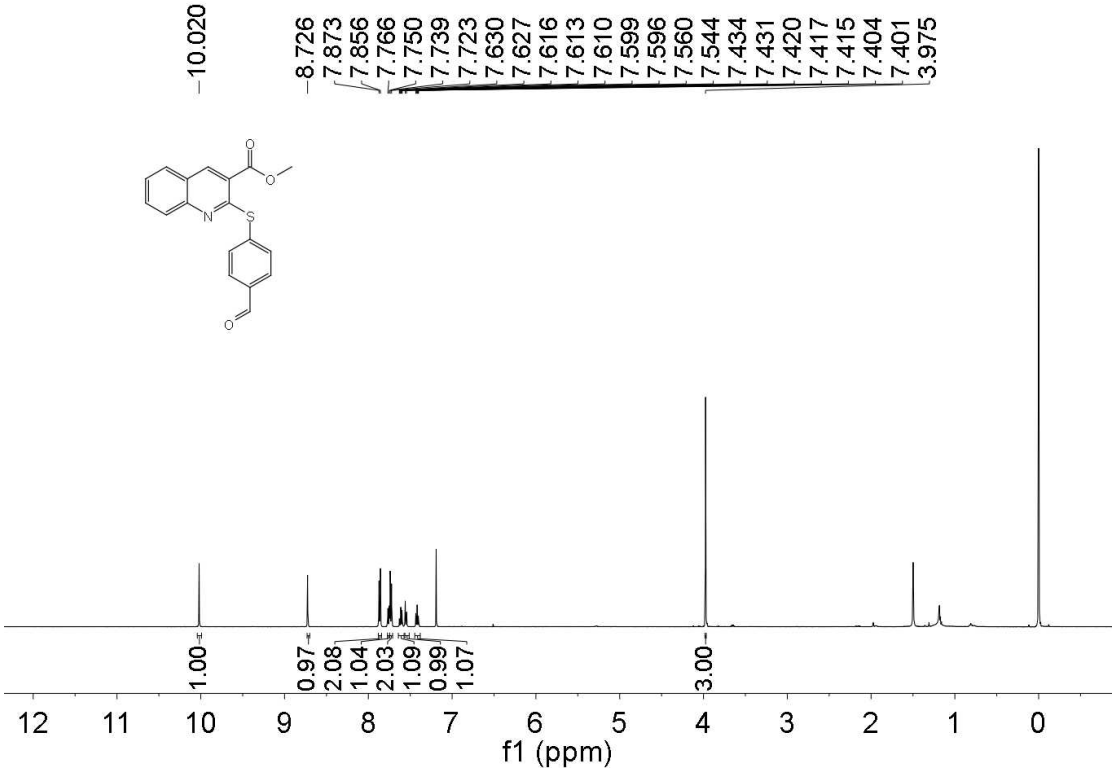


Figure 22. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ia**

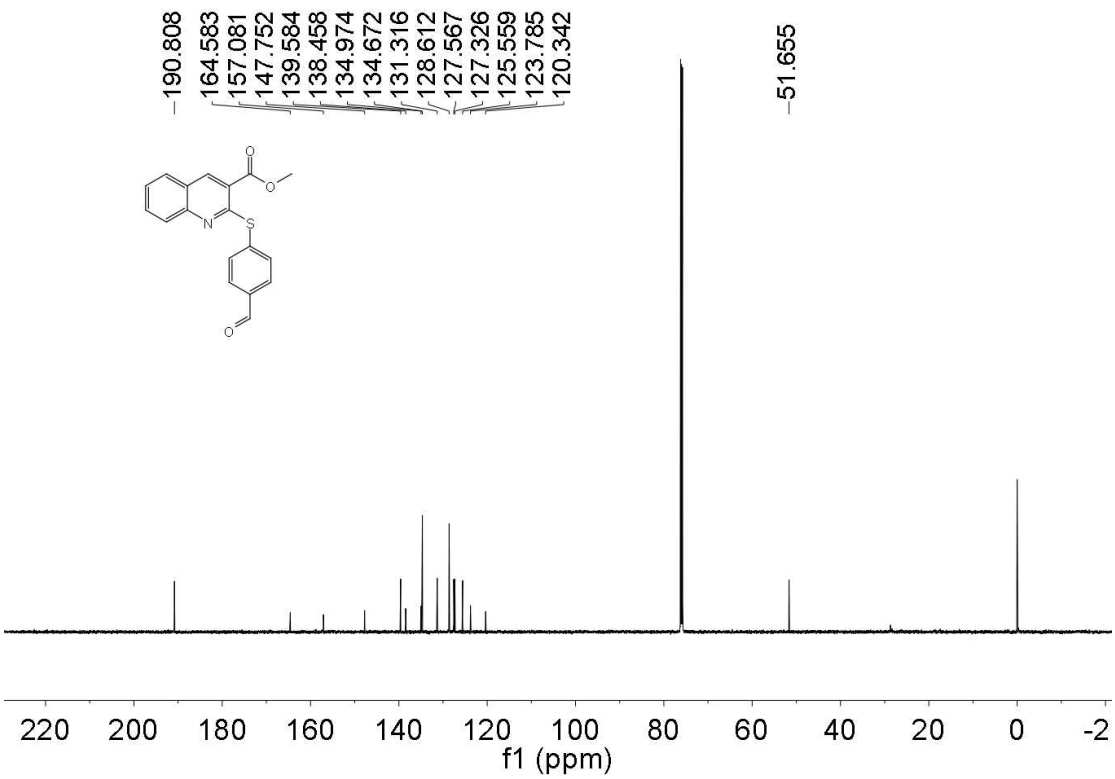


Figure 23. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ia**

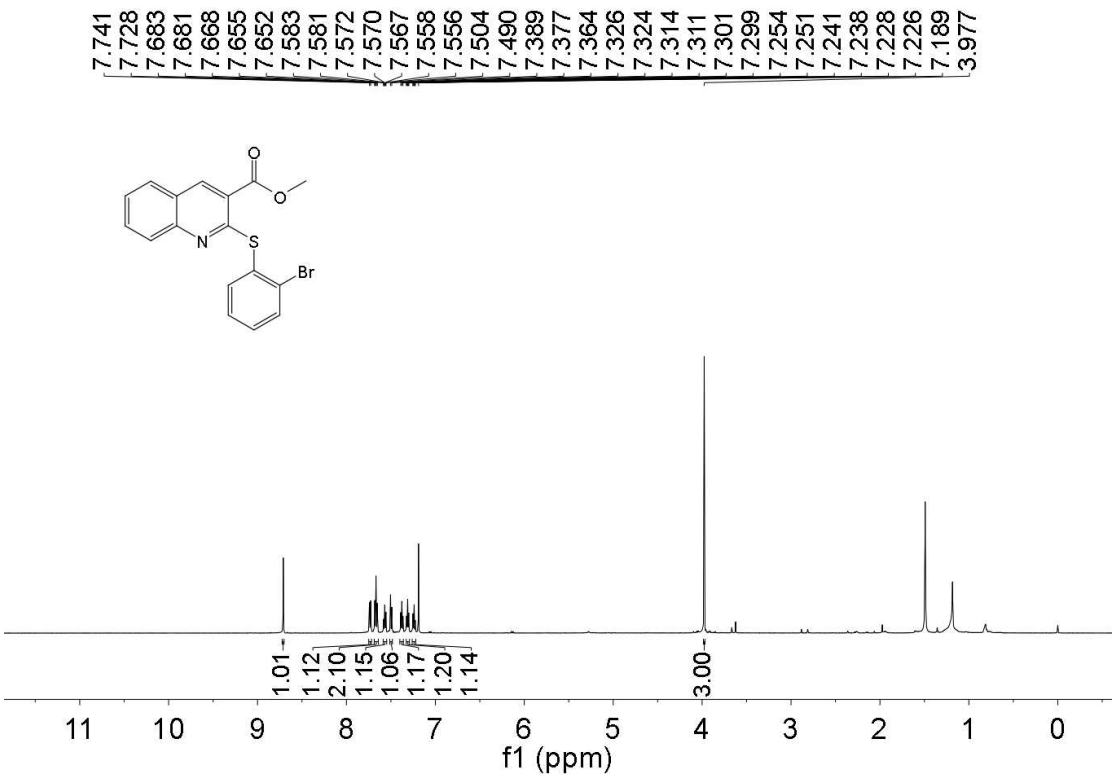


Figure 24. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ja**

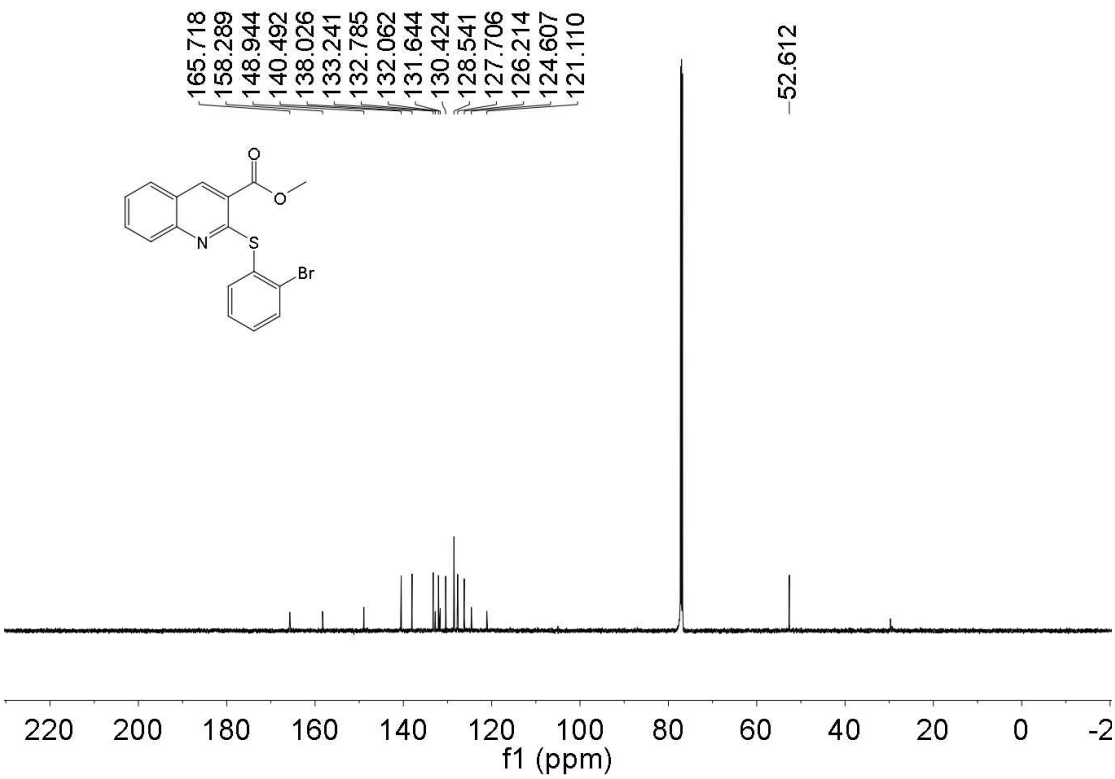


Figure 25. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ja**

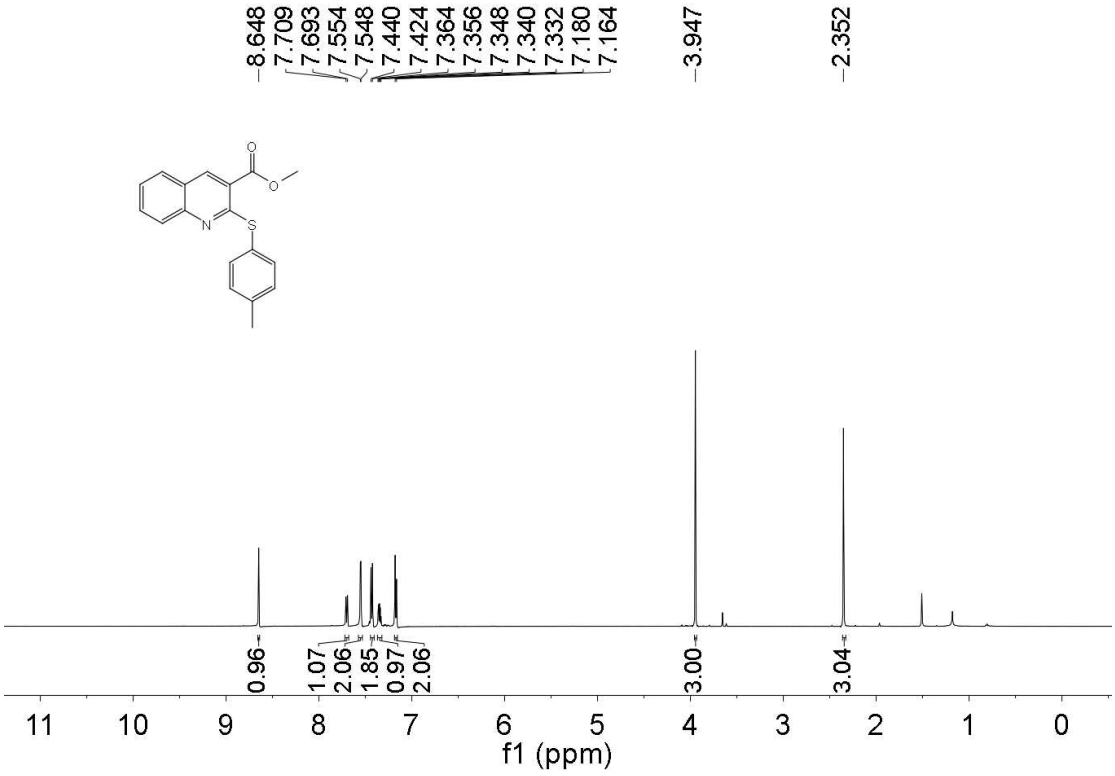


Figure 26. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ka**

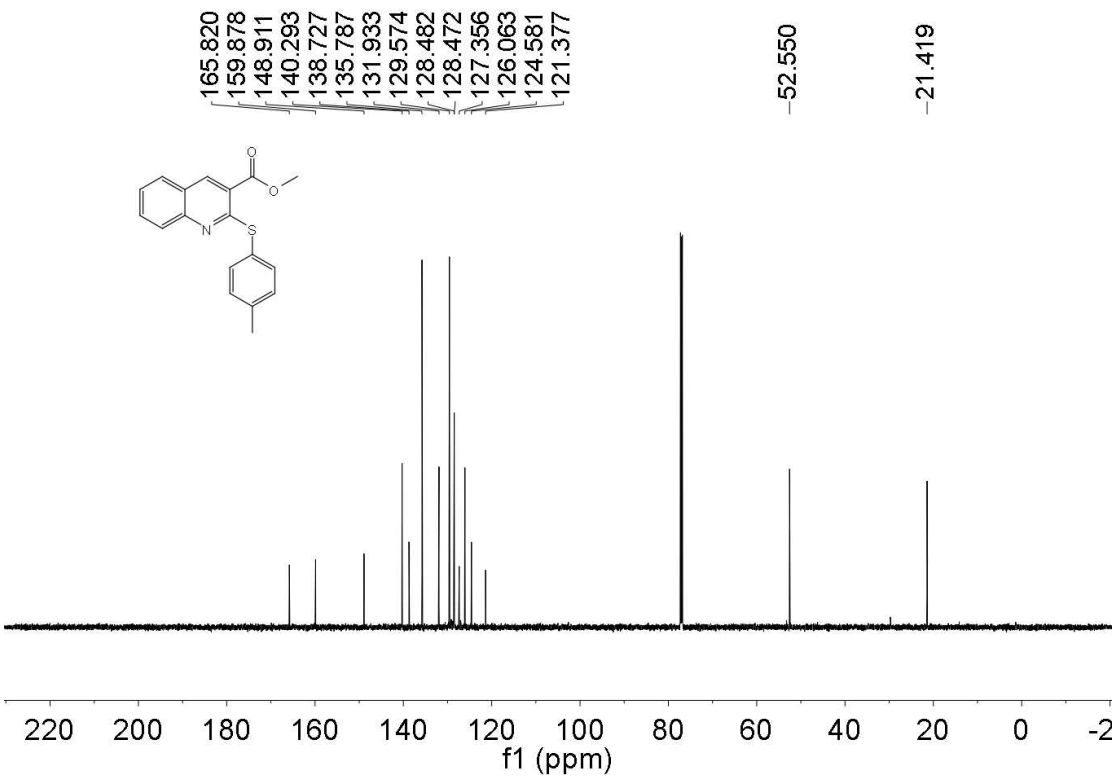


Figure 27. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ka**

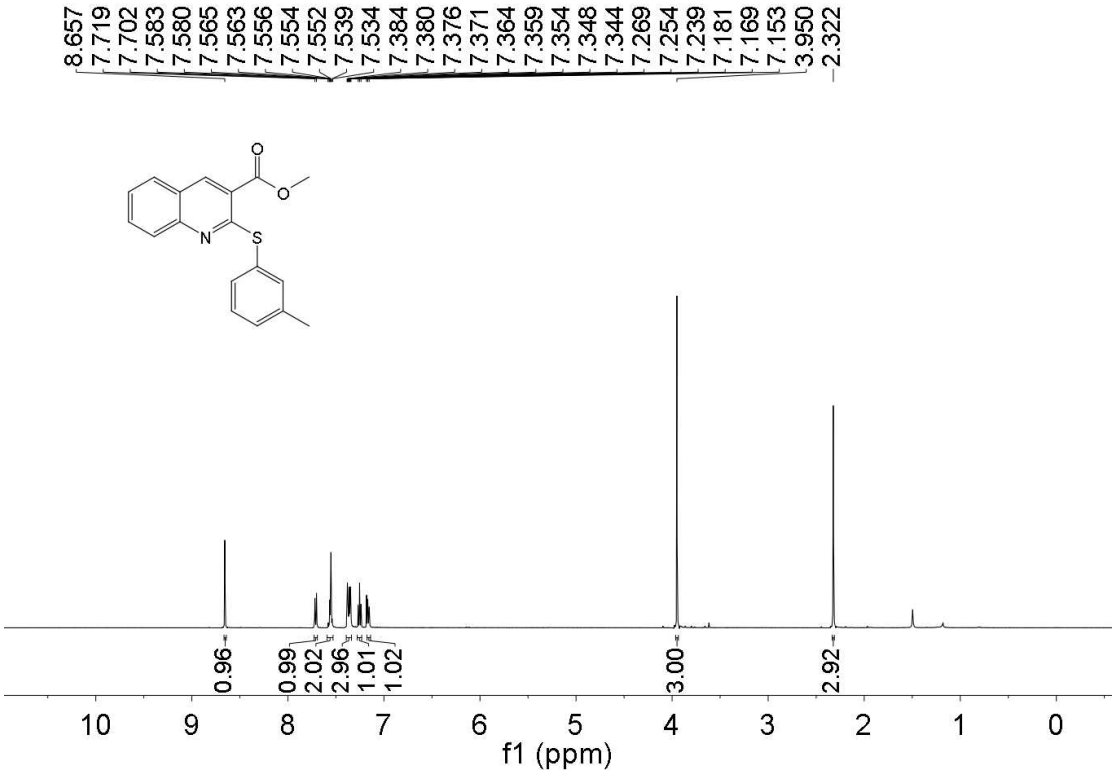


Figure 28. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3la**

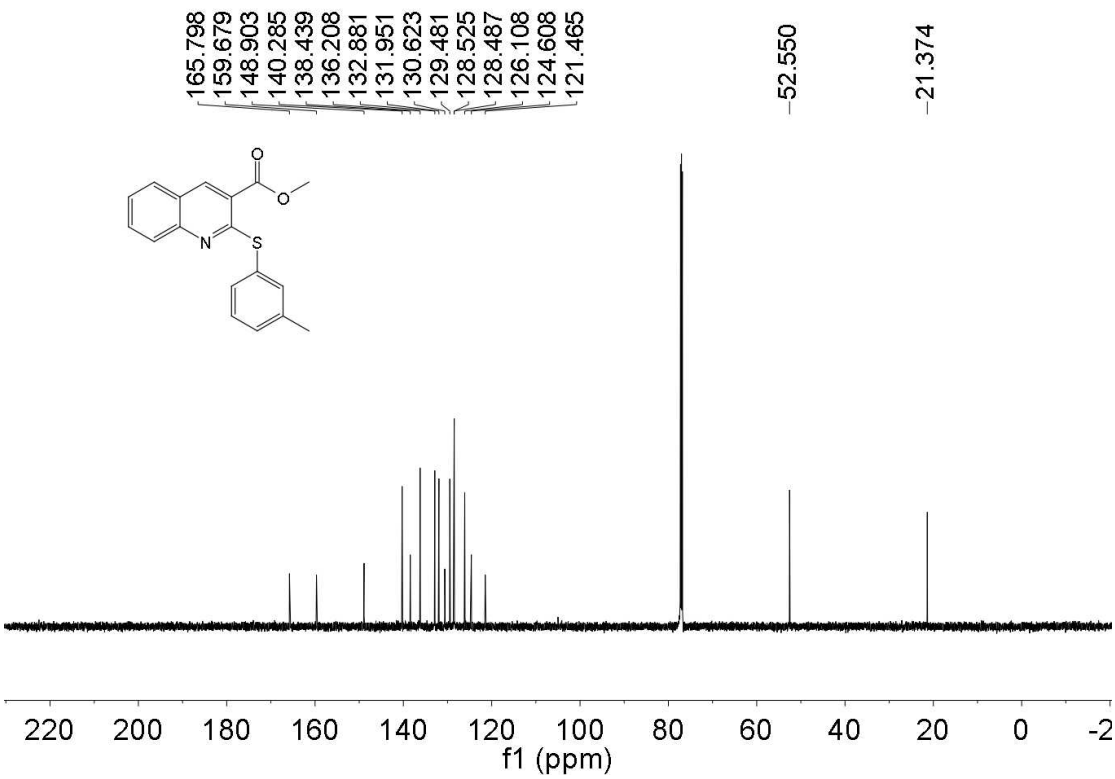


Figure 29. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3la**

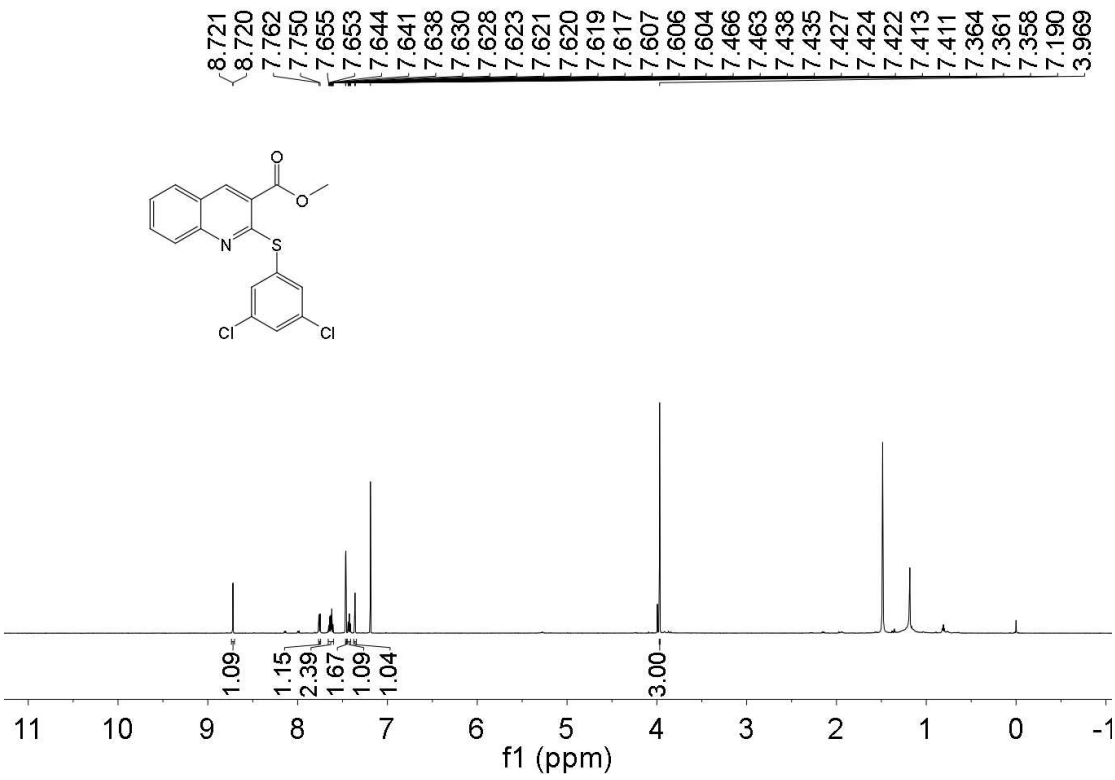


Figure 30. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ma**

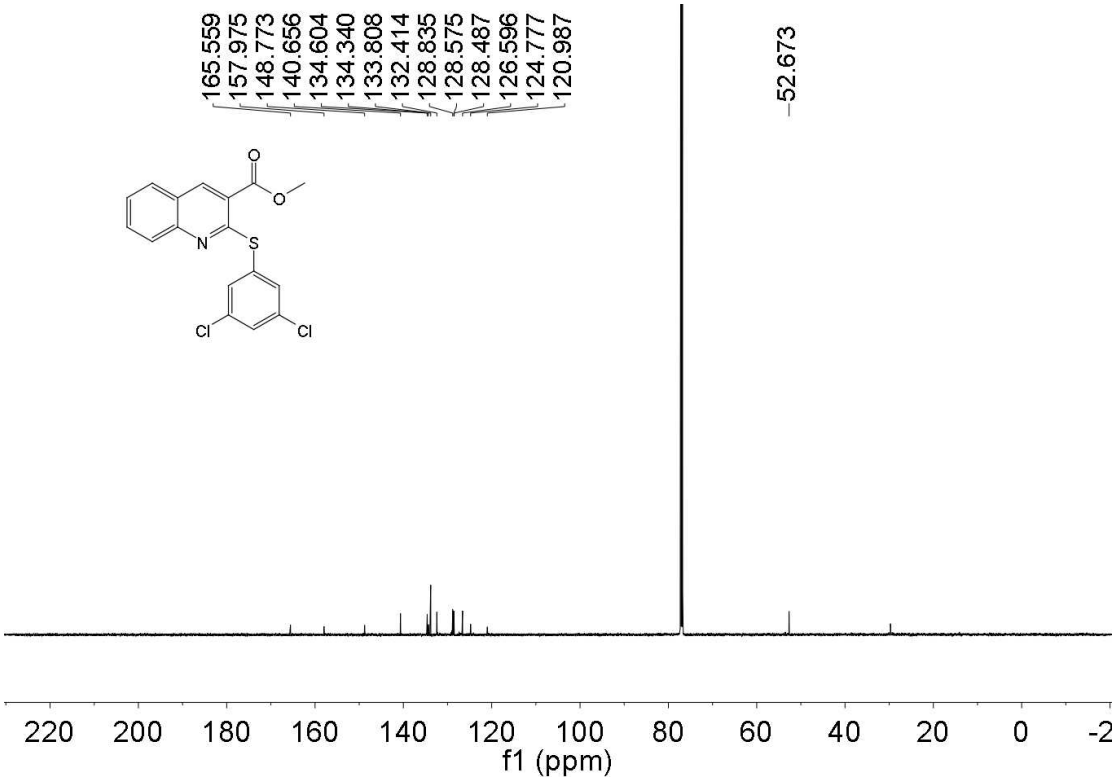


Figure 31. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ma**

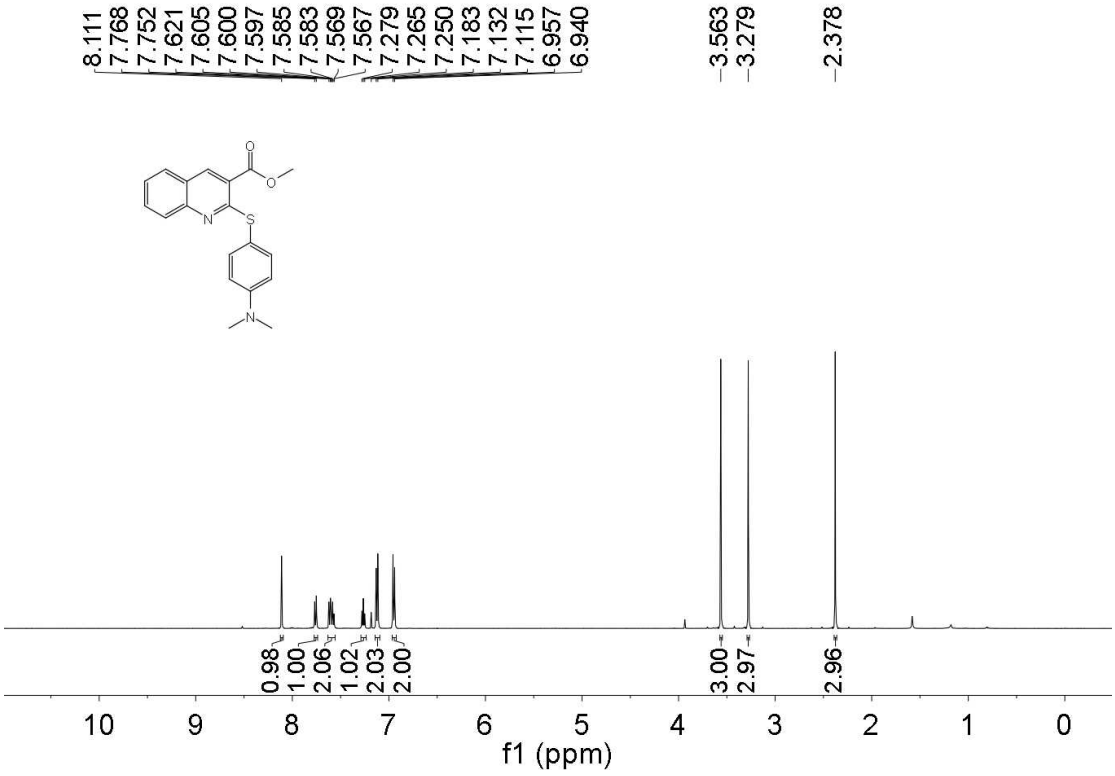


Figure 32. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3na**

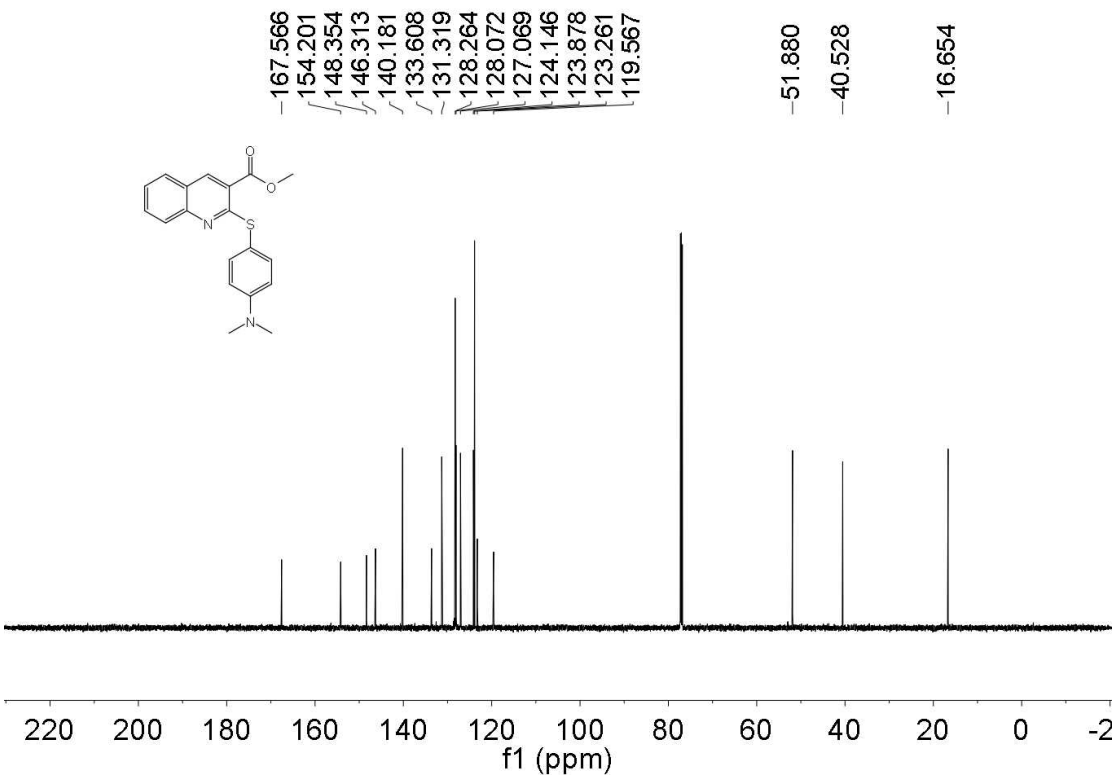


Figure 33. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3na**

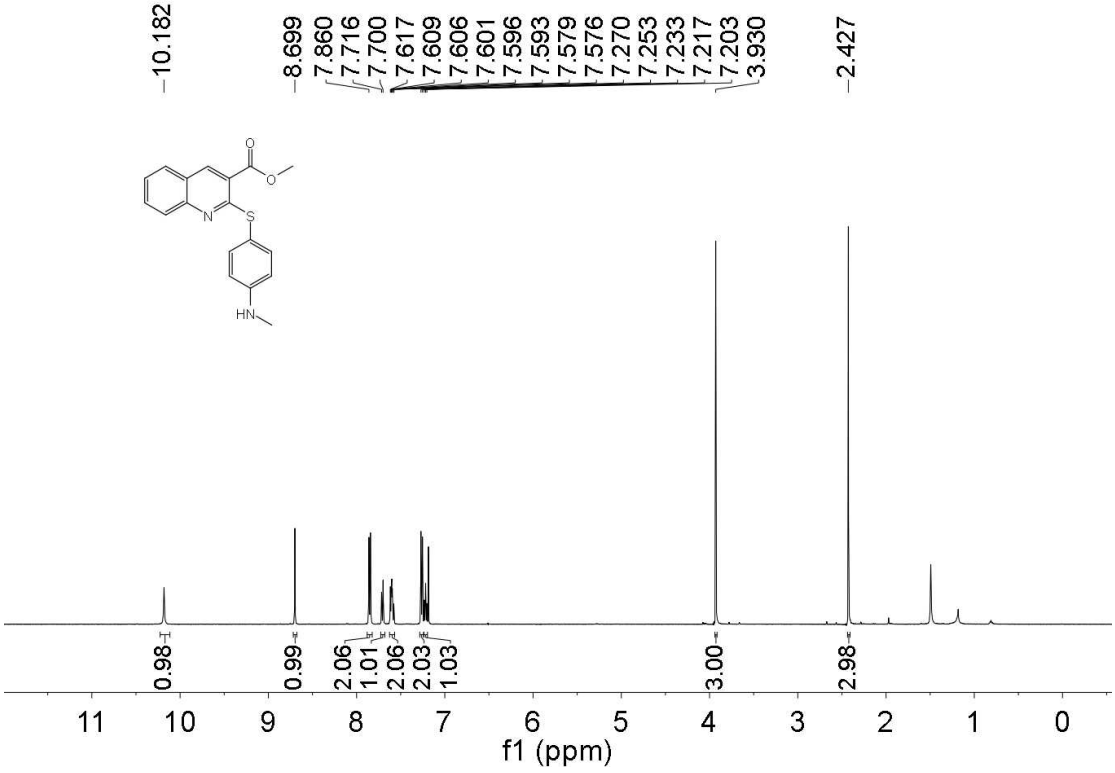


Figure 34. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3oa**

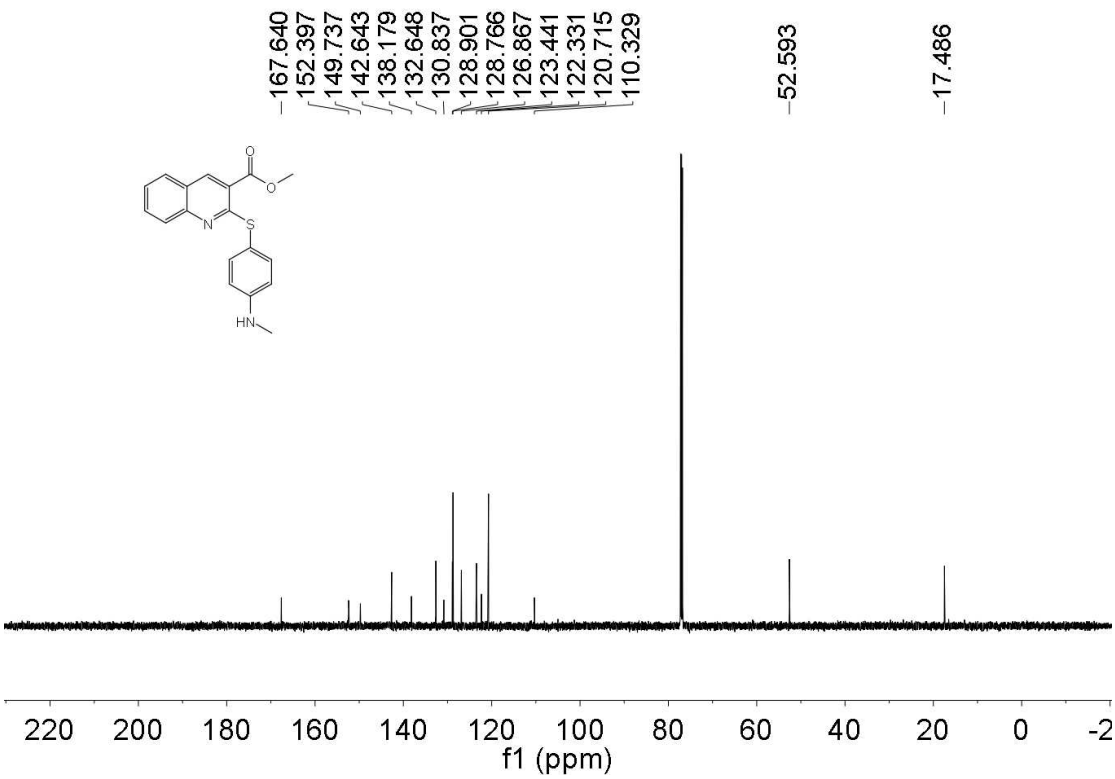


Figure 35. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3oa**

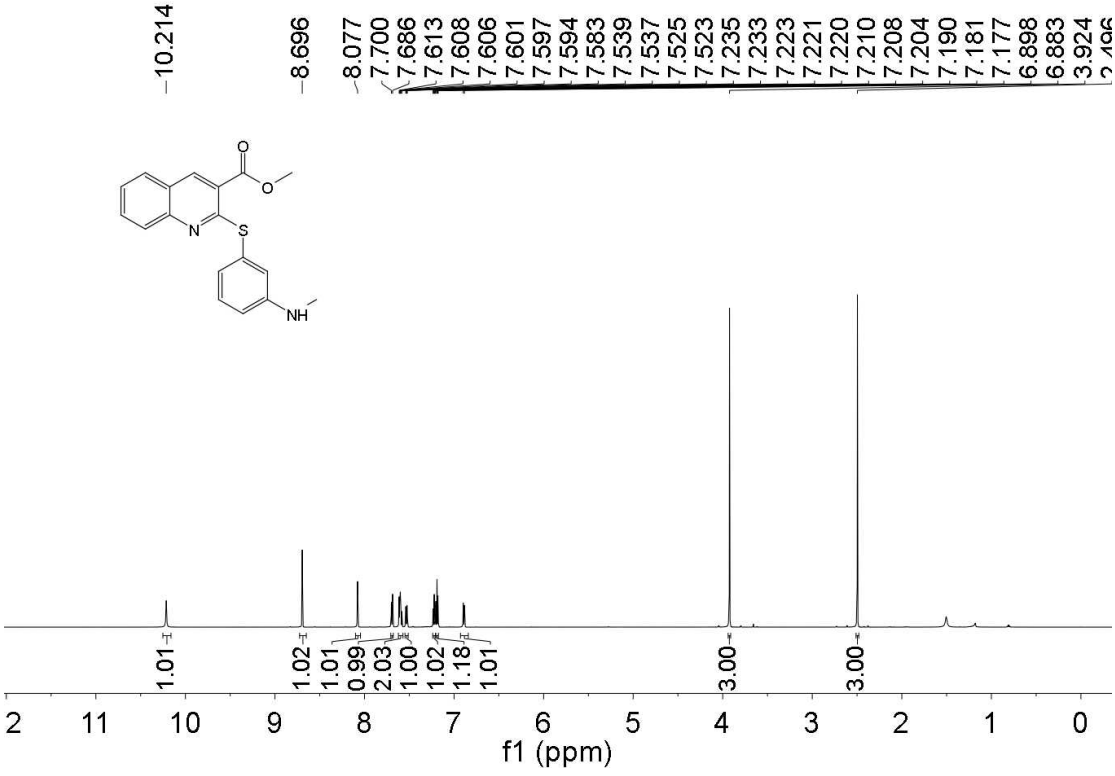


Figure 36. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3pa**

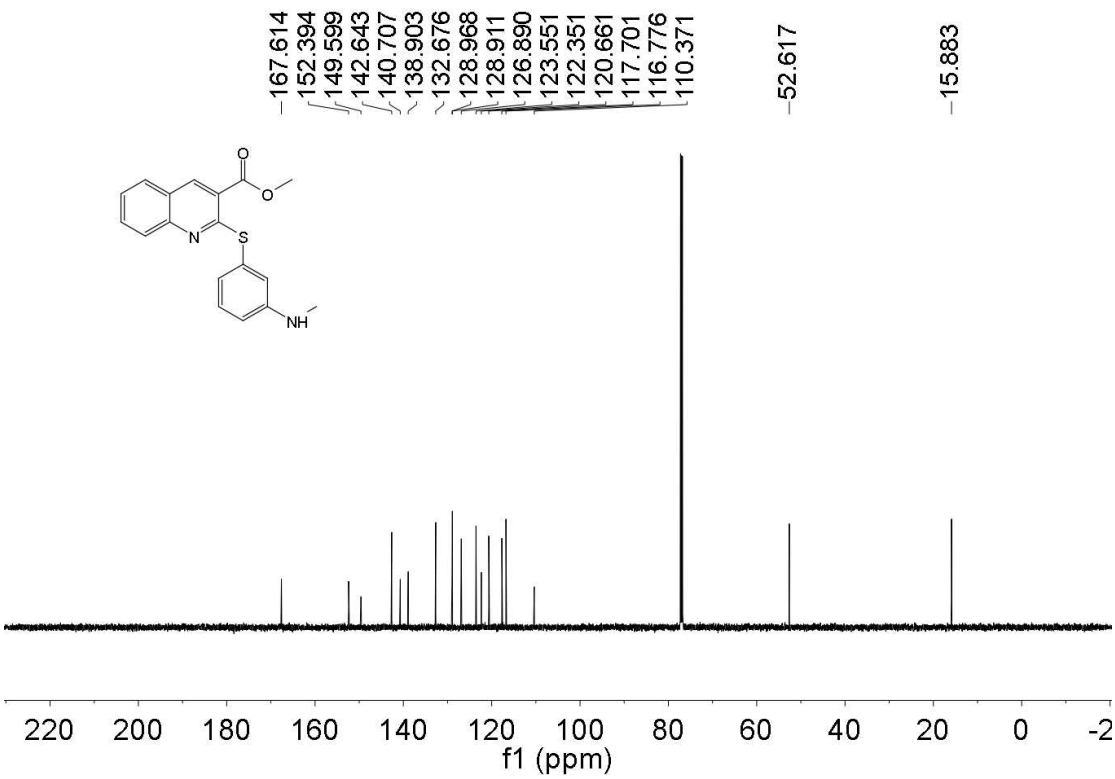


Figure 37. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3pa**

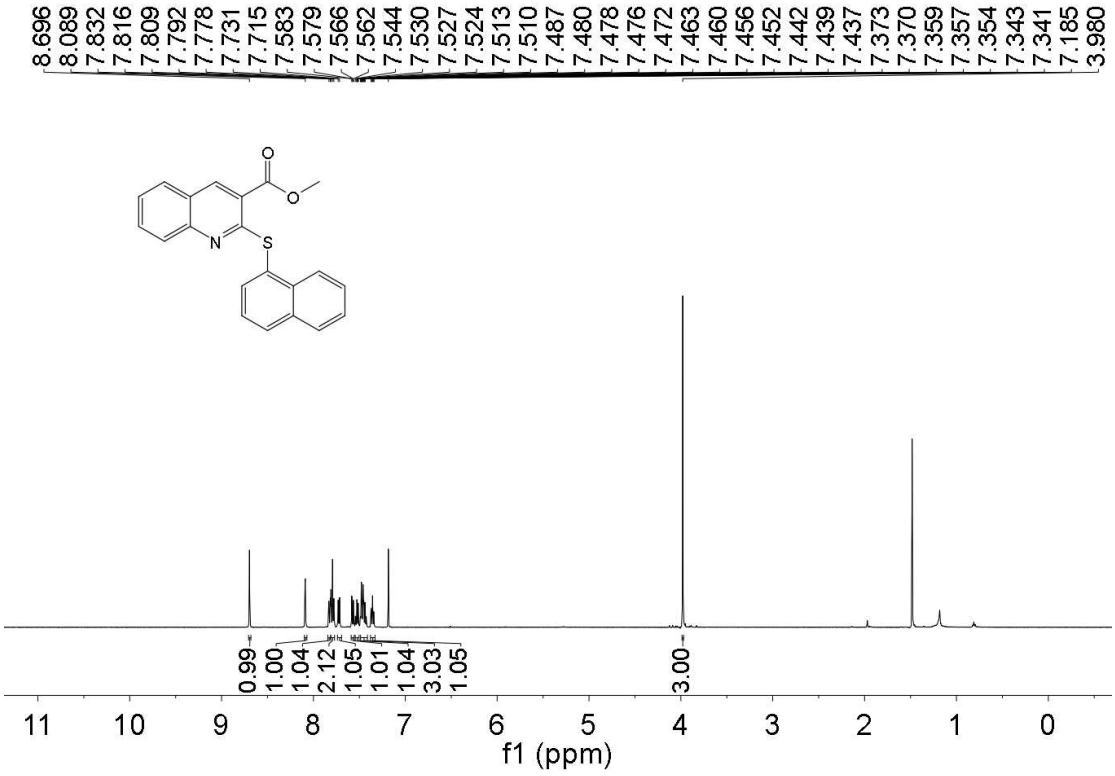


Figure 38. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3qa**

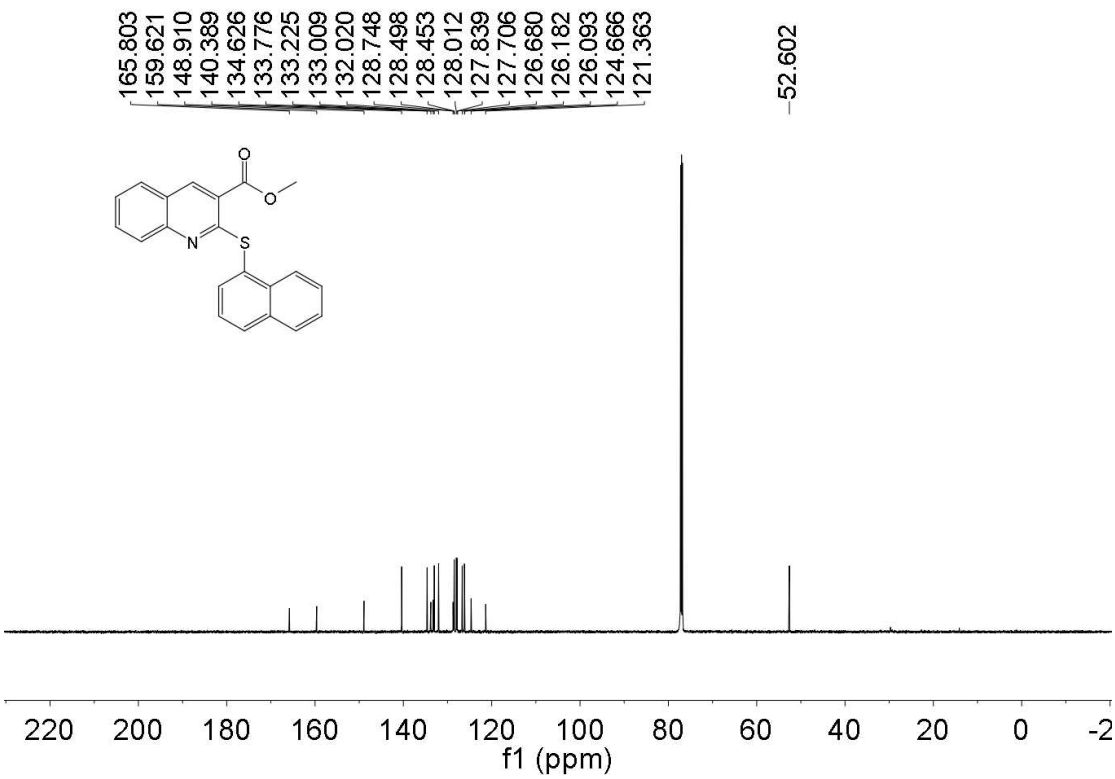


Figure 39. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3qa**

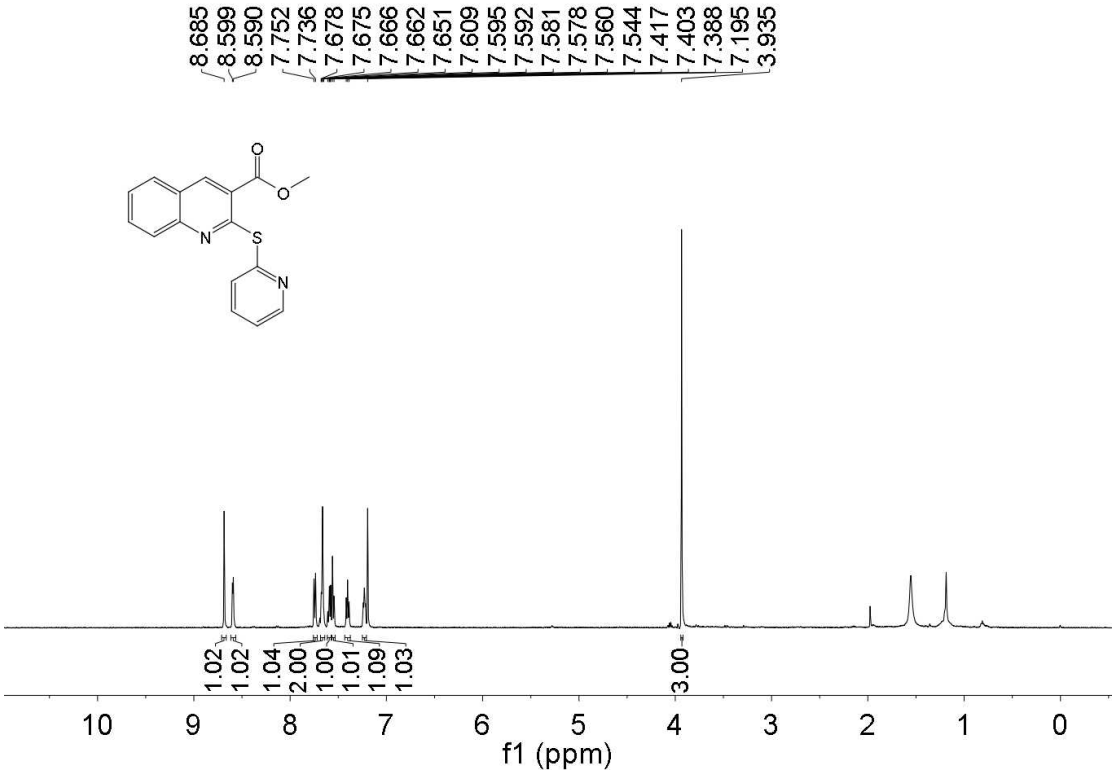


Figure 40. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ra**

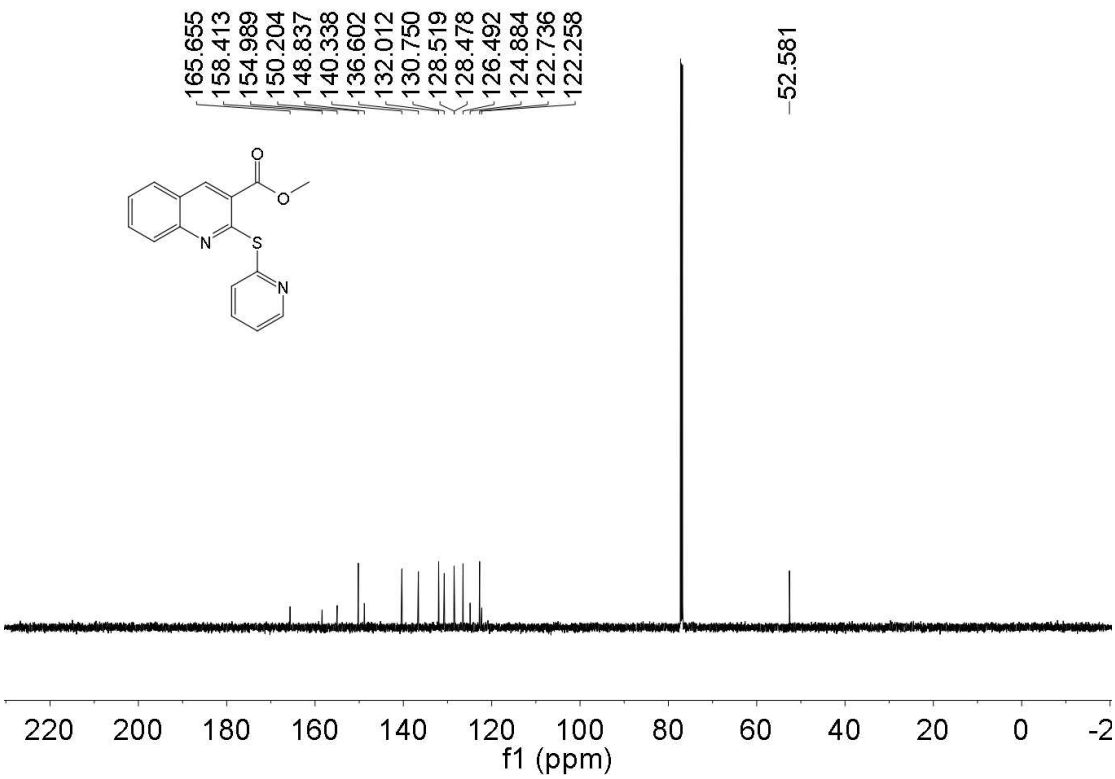


Figure 41. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ra**

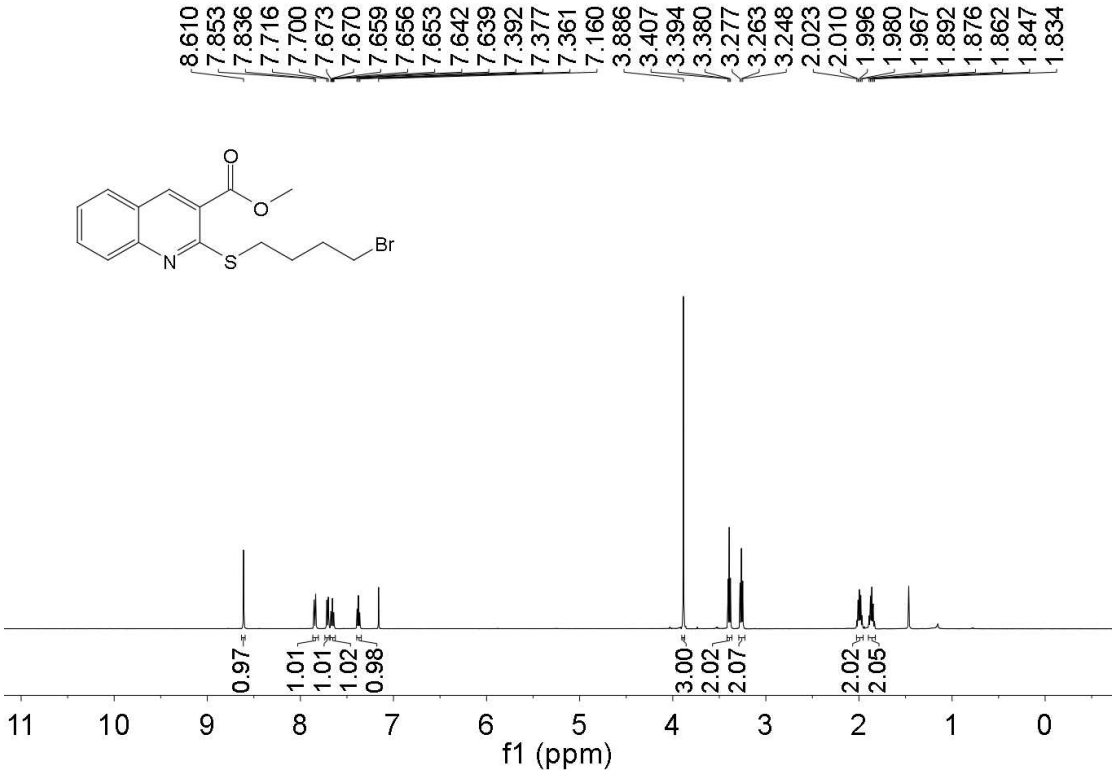


Figure 42. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3sa**

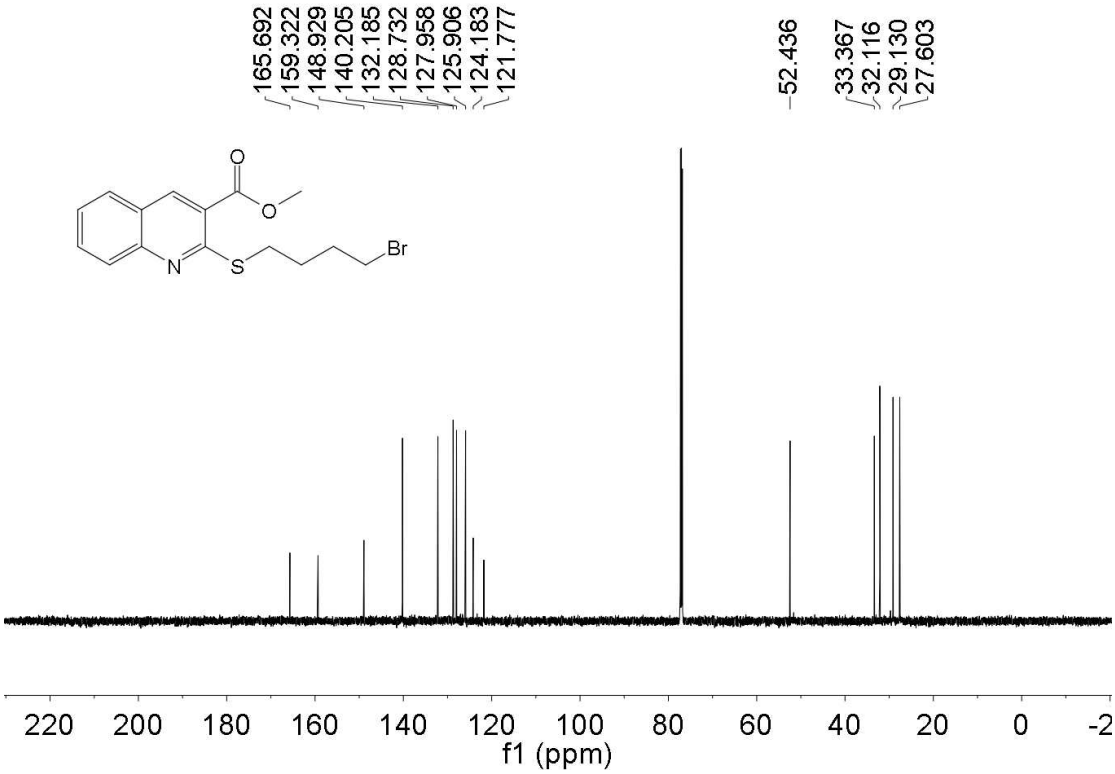


Figure 43. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3sa**

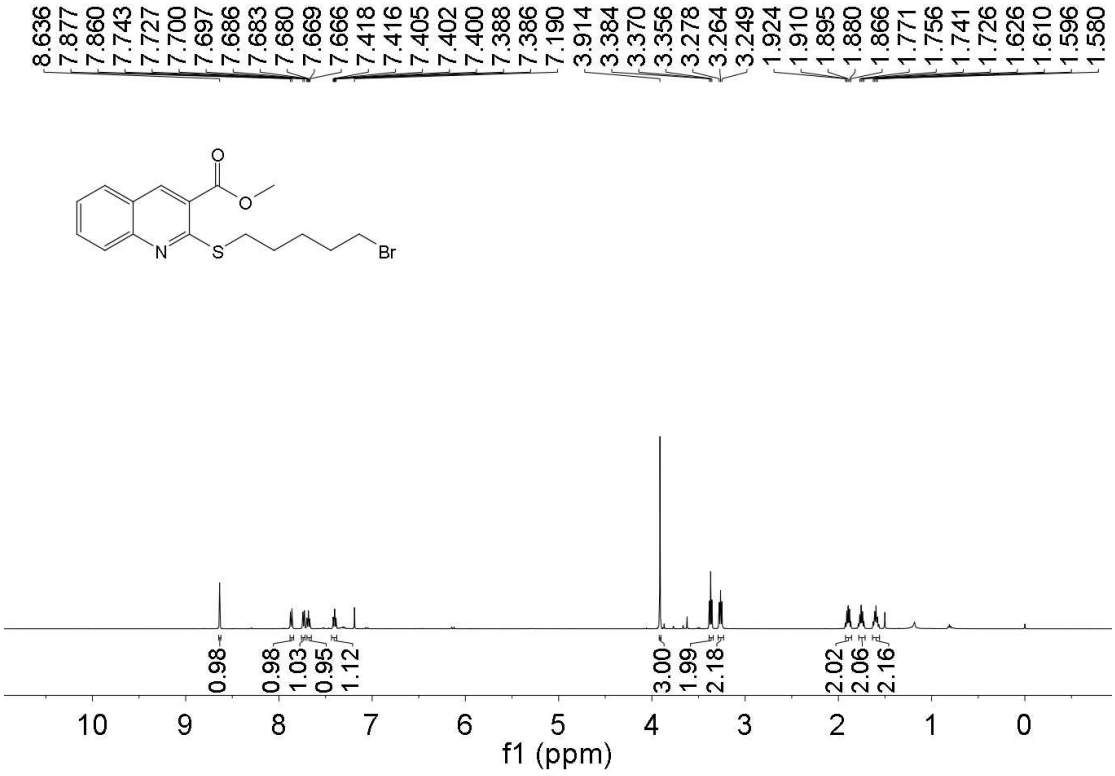


Figure 44. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ta**

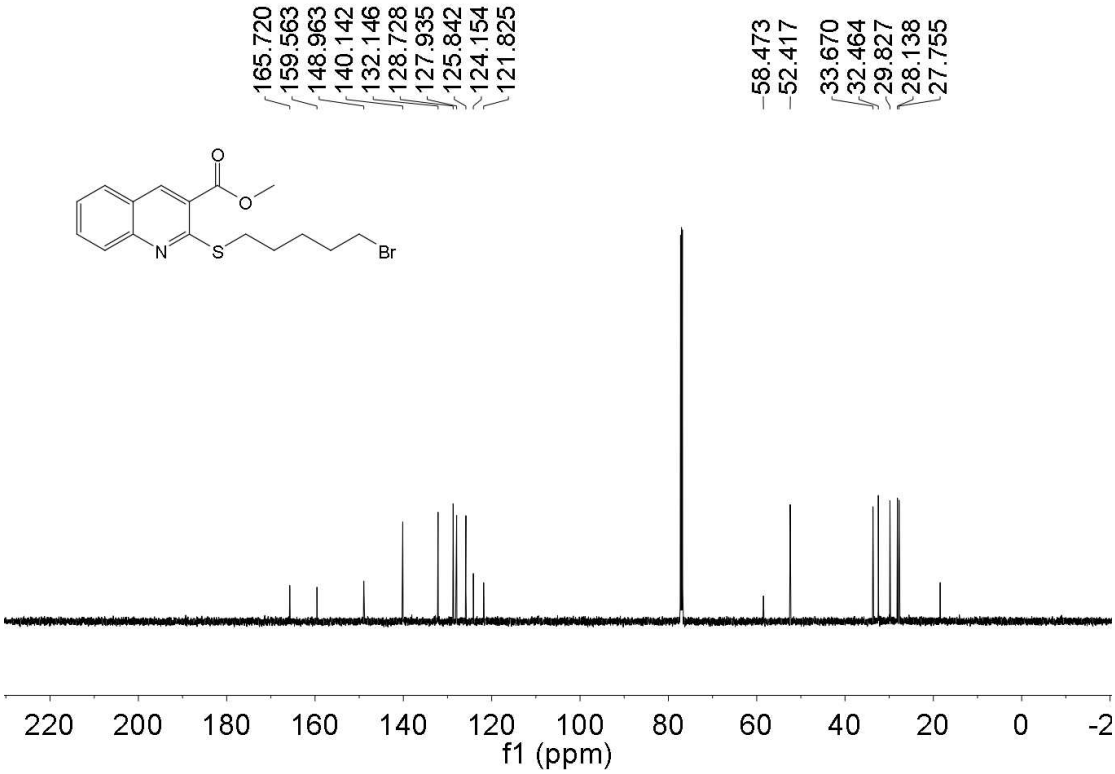


Figure 45. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ta**

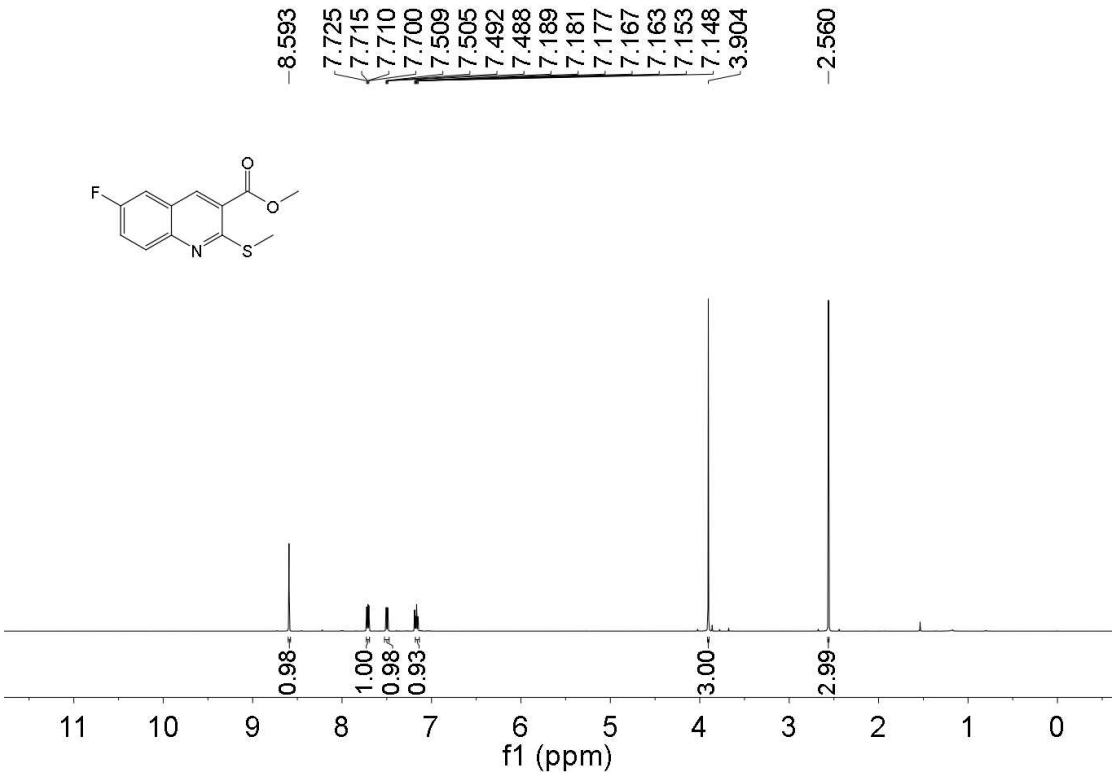


Figure 46. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ab**

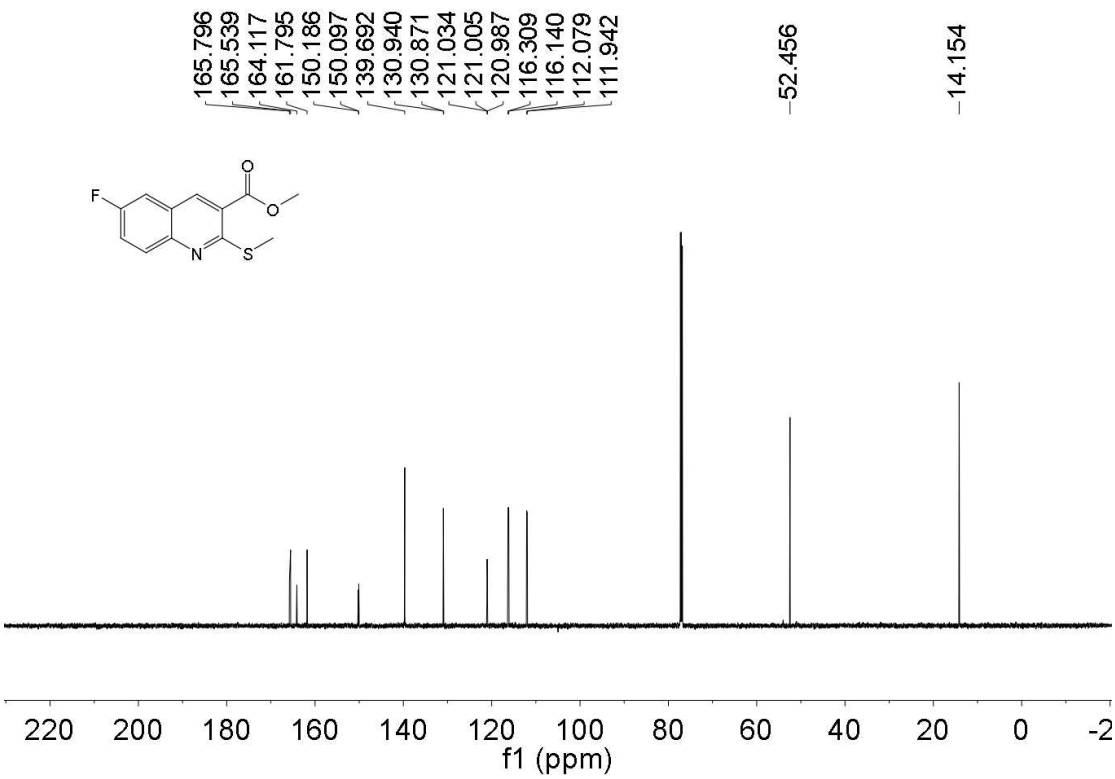


Figure 47. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ab**

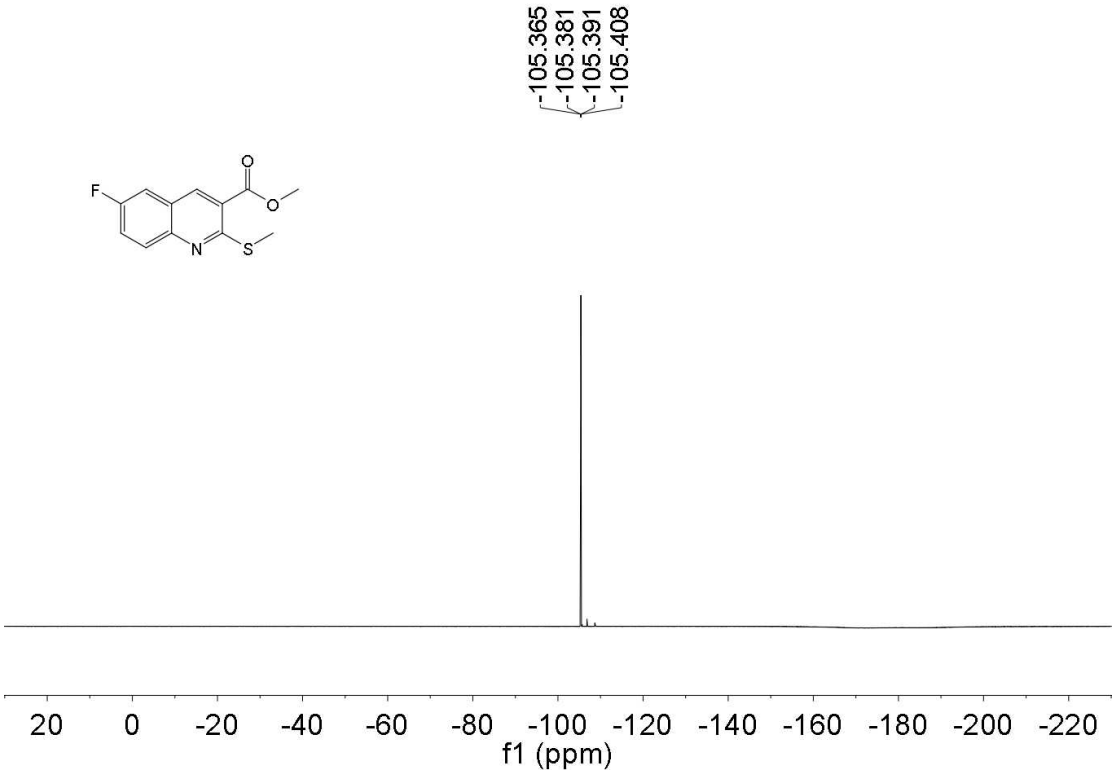


Figure 48. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ab**

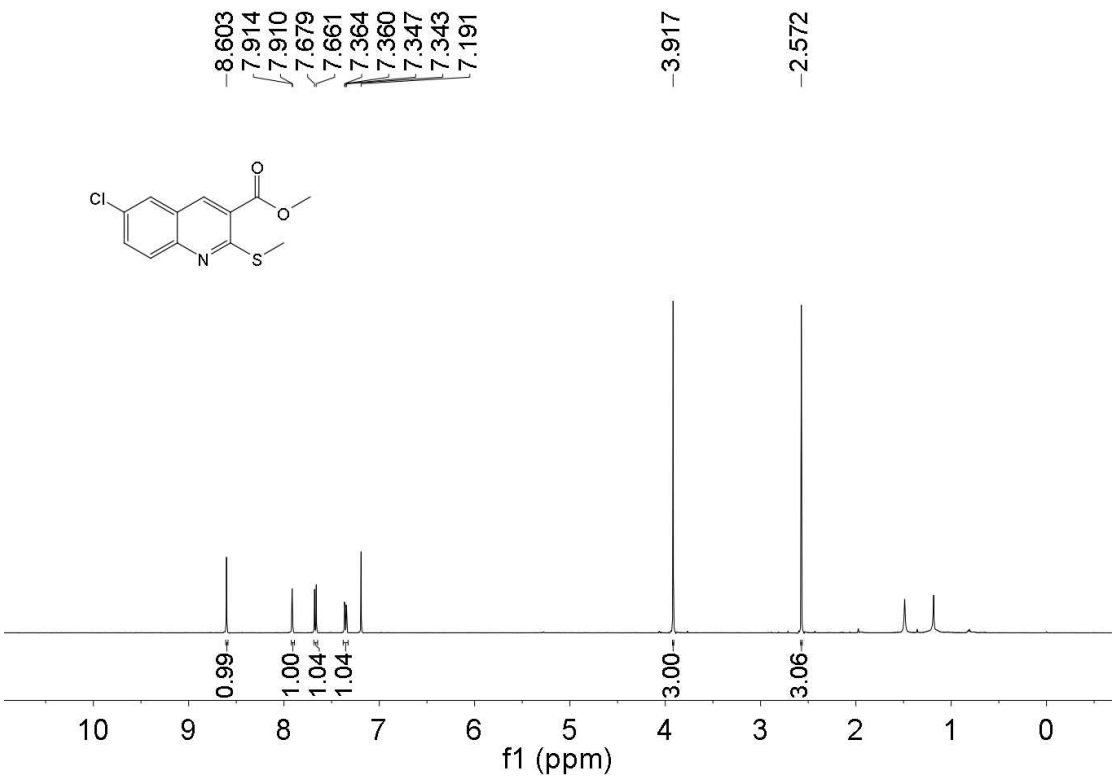


Figure 49. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ac**

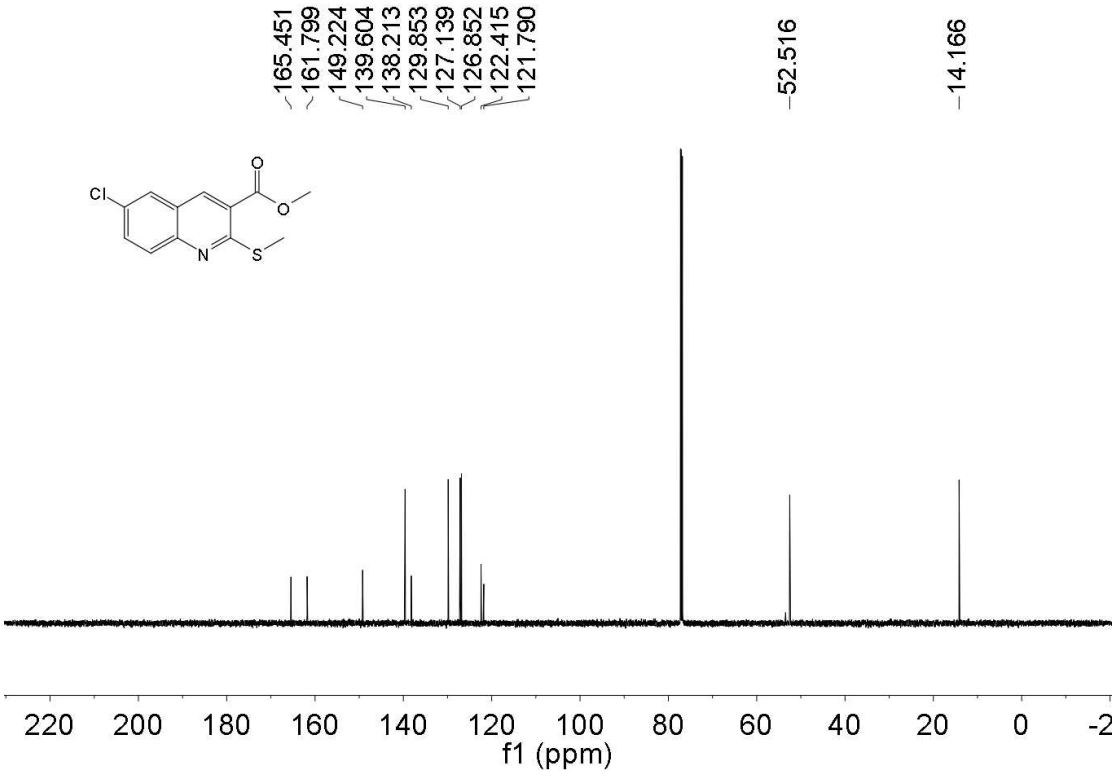


Figure 50. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ac**

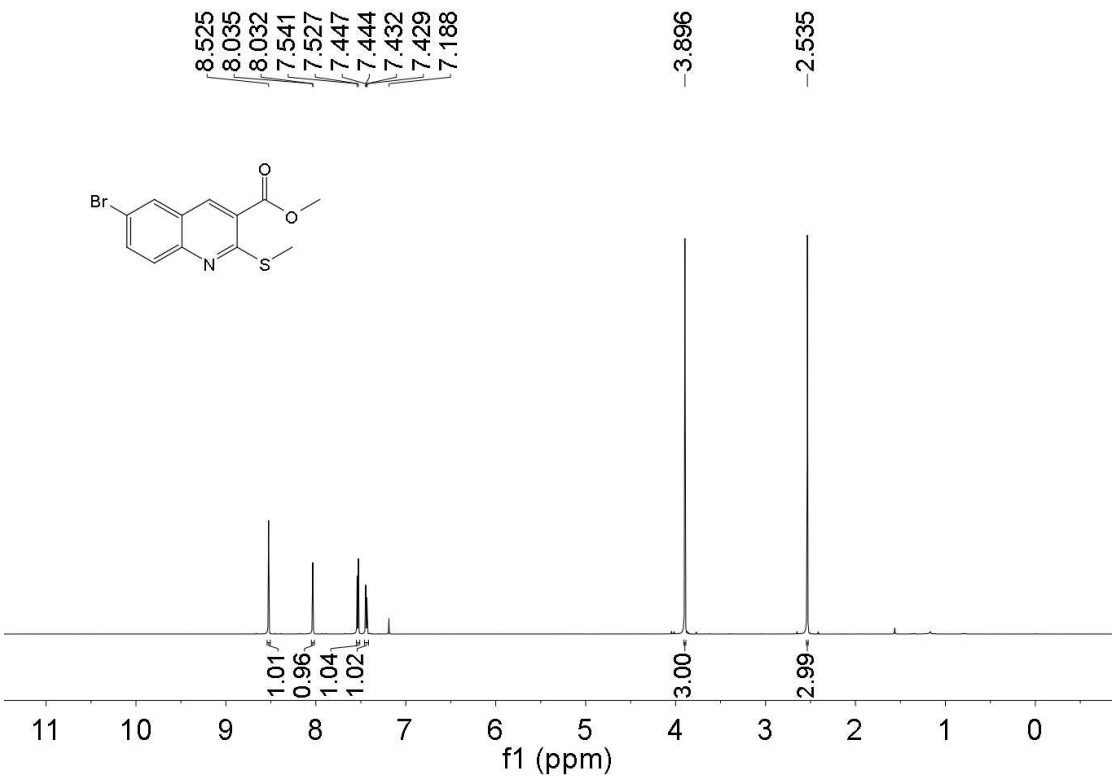


Figure 51. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3ad**

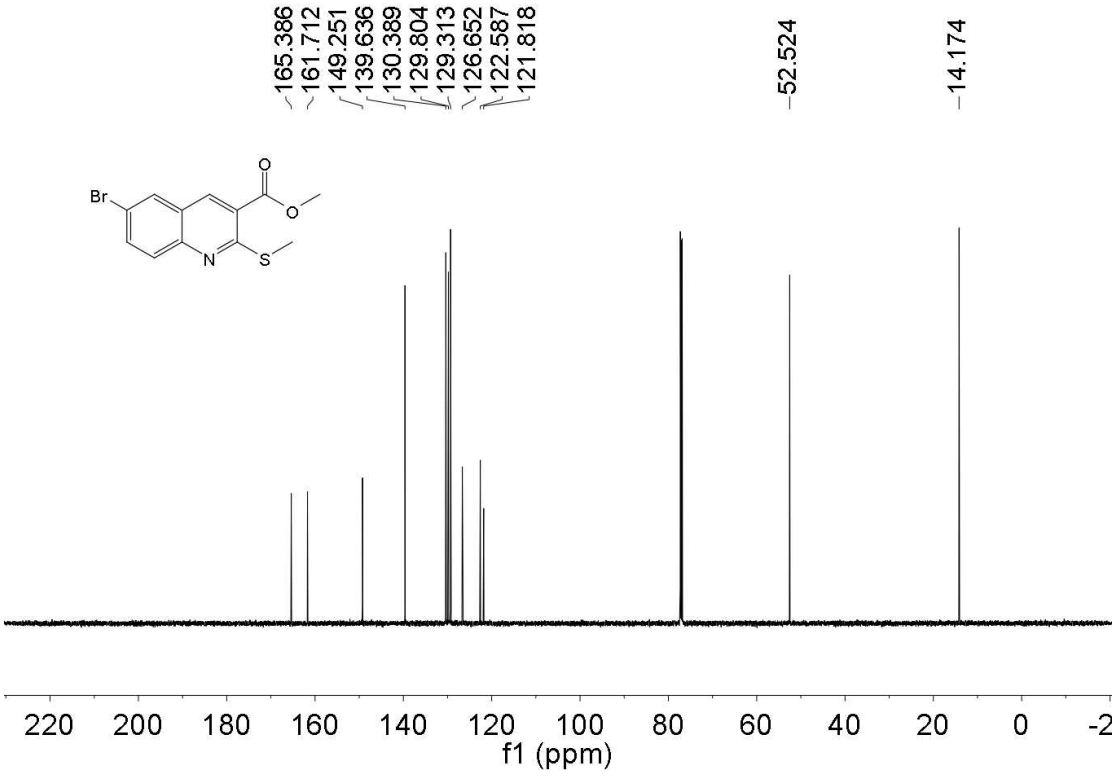


Figure 52. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ad**

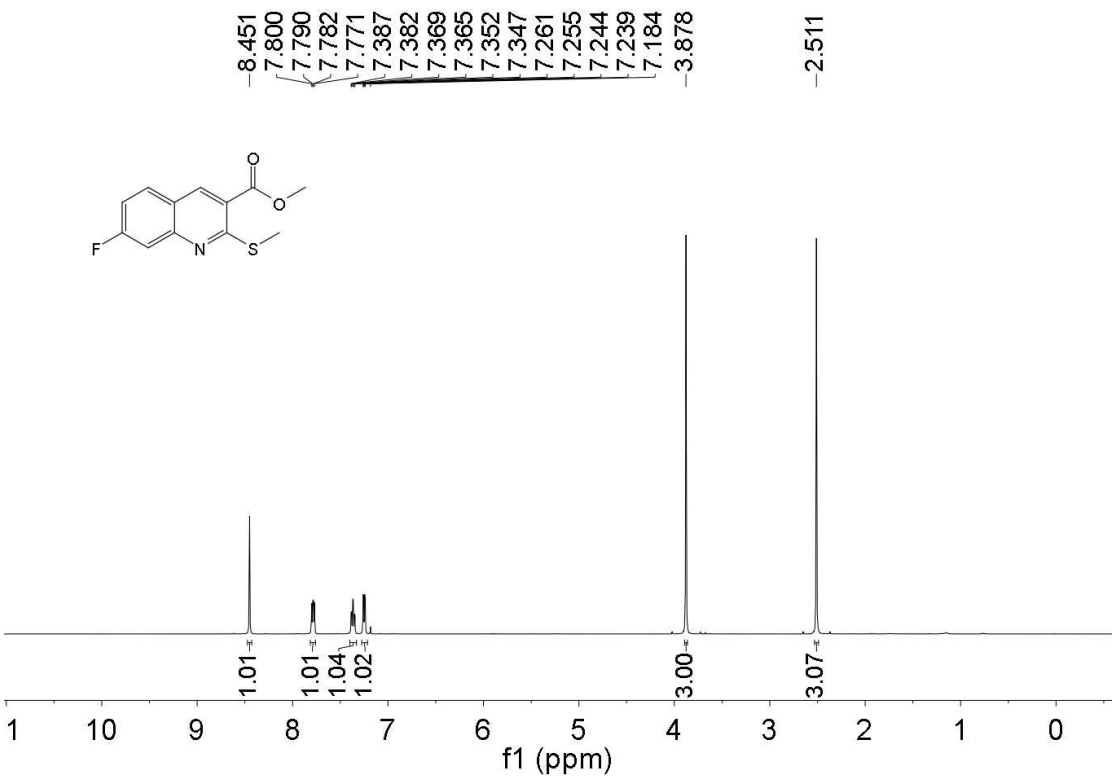


Figure 53. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ae**

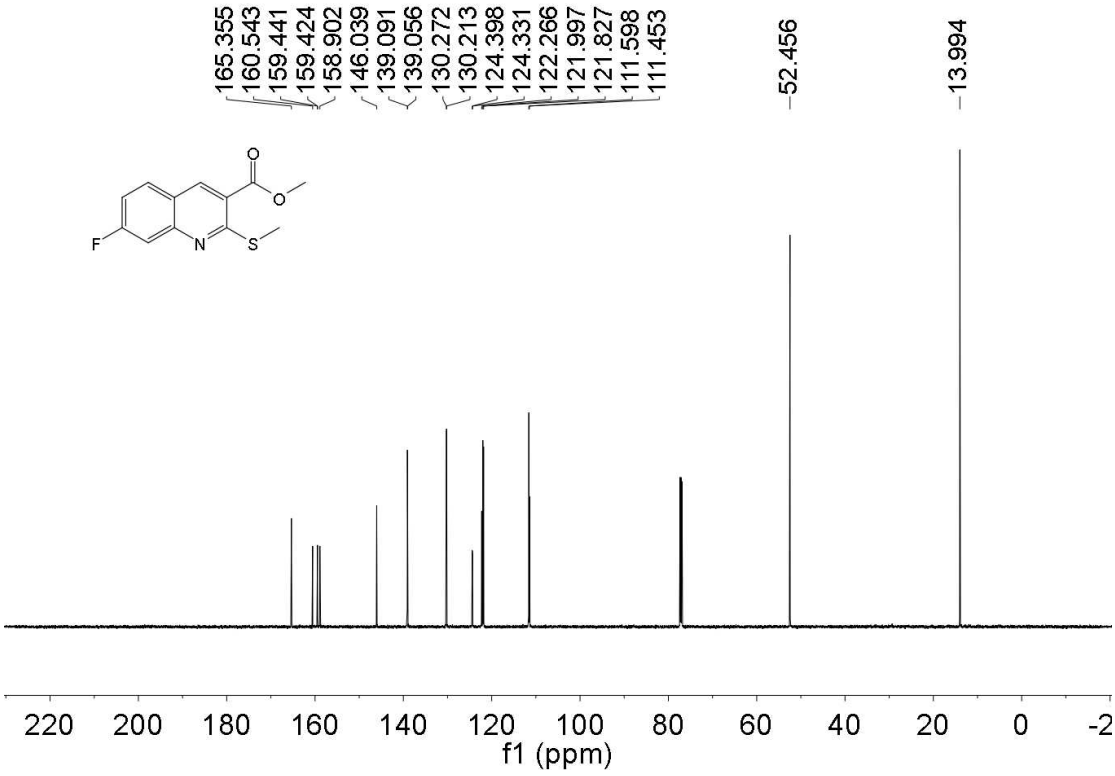


Figure 54. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ae**

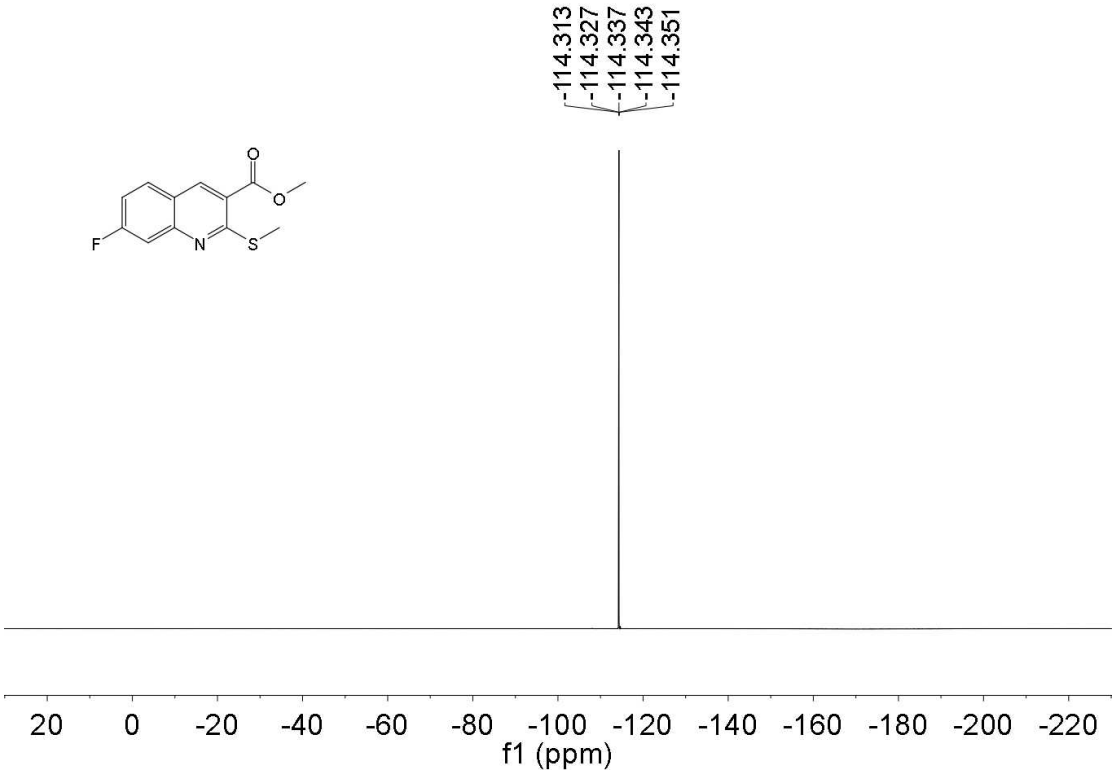


Figure 55. ^{19}F NMR spectrum (565 MHz, $CDCl_3$) of **3ae**

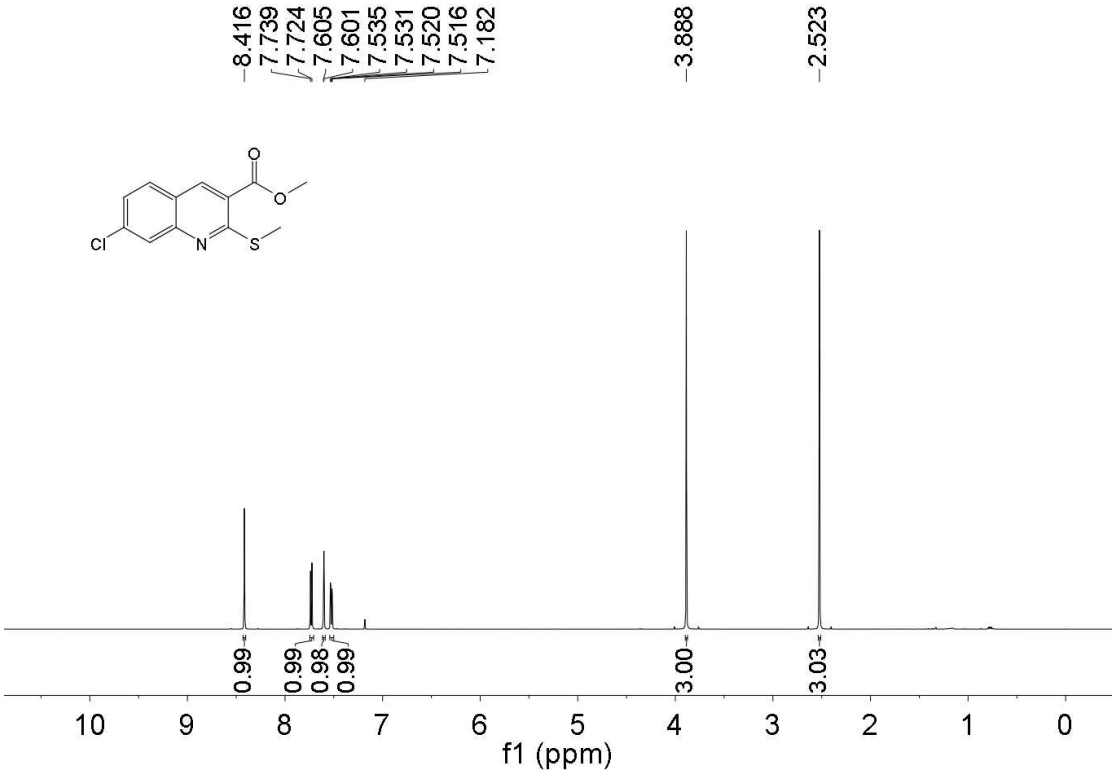


Figure 56. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3af**

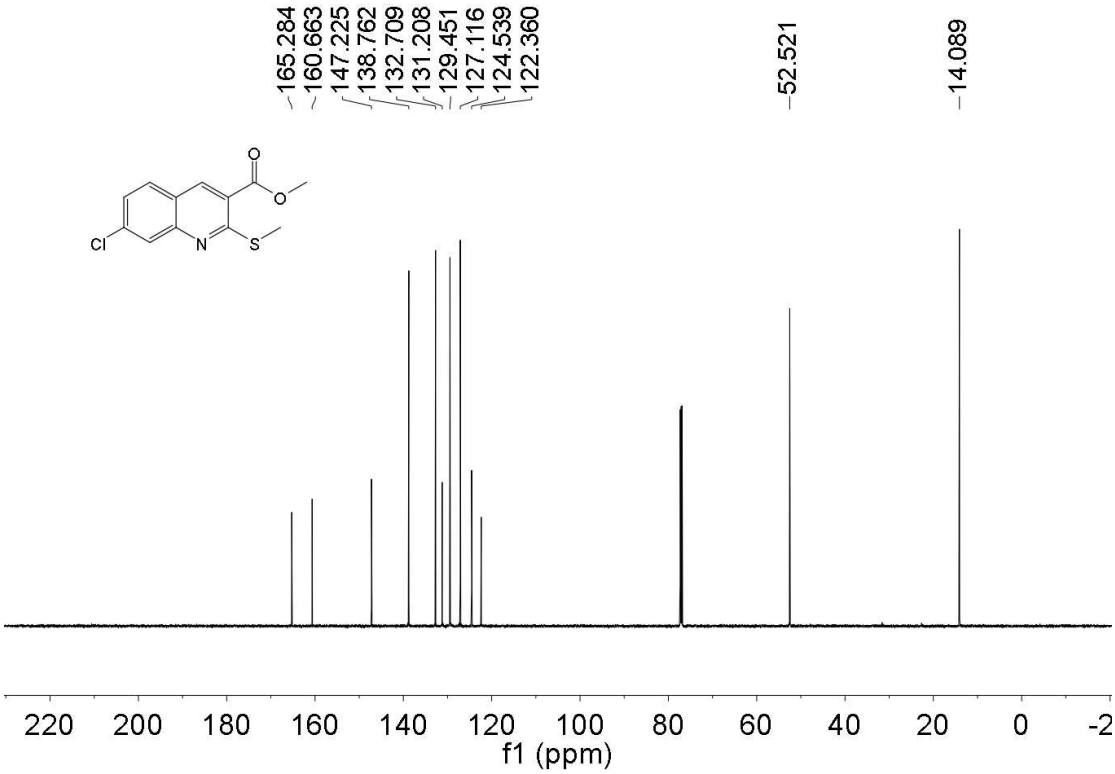


Figure 57. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3af**

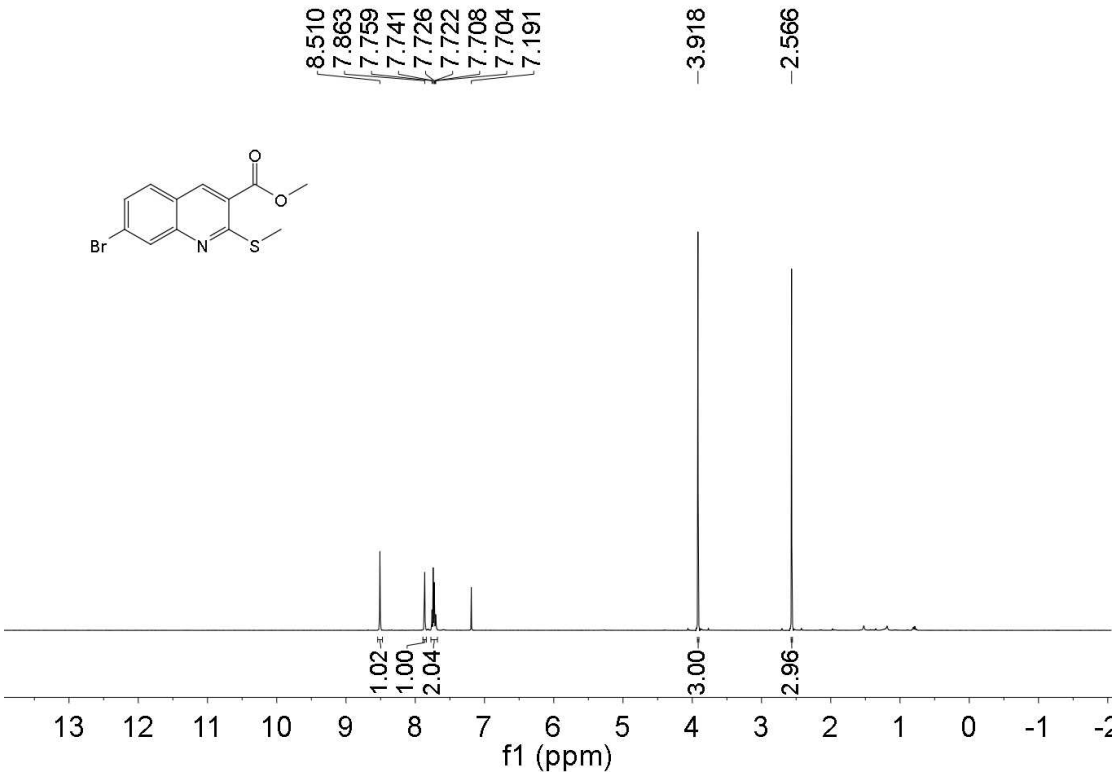


Figure 58. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ag**

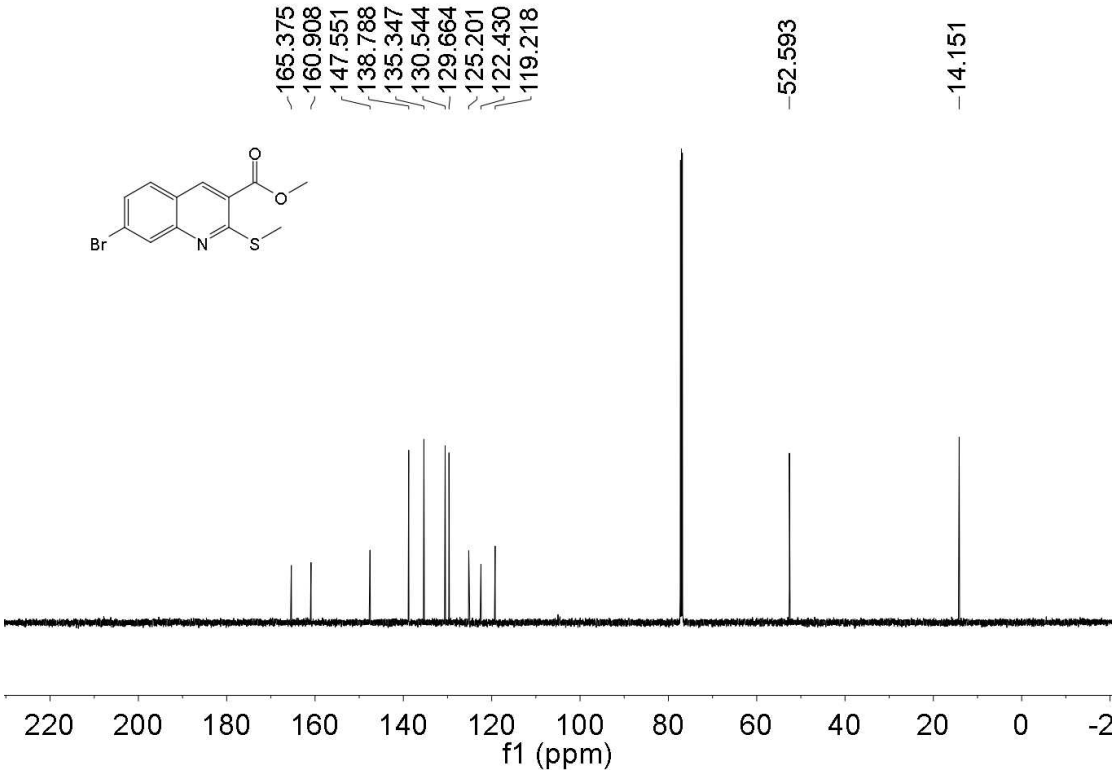


Figure 59. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ag**

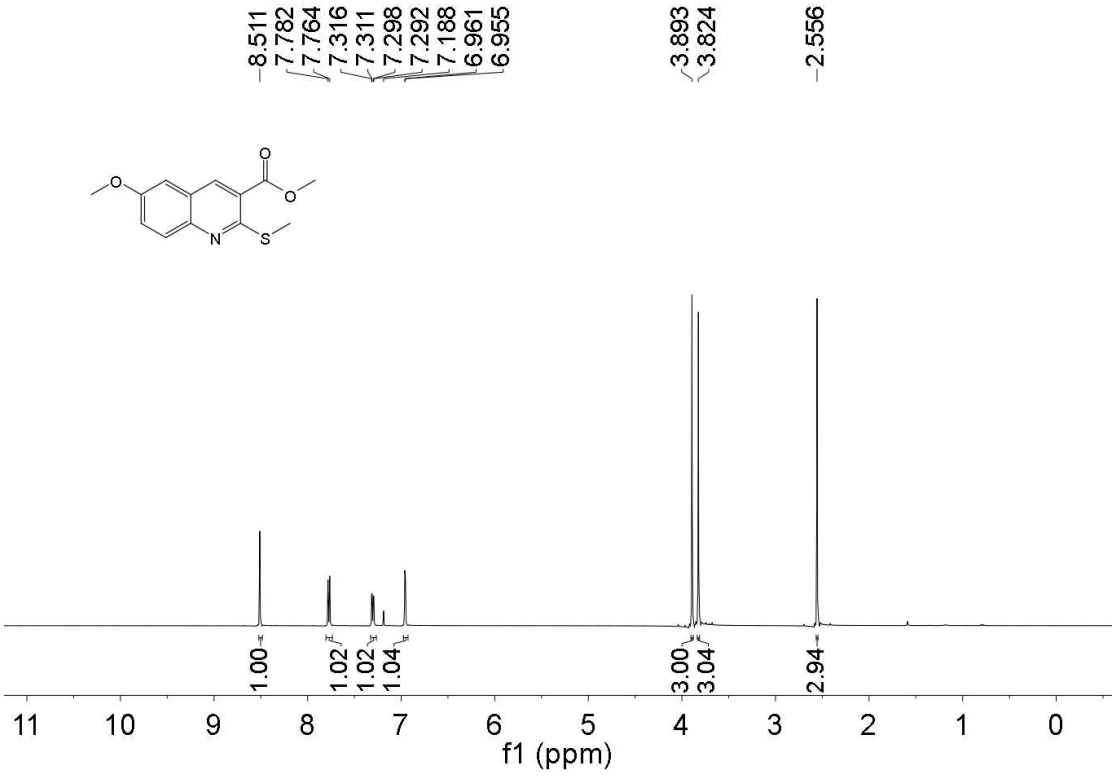


Figure 60. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ah**

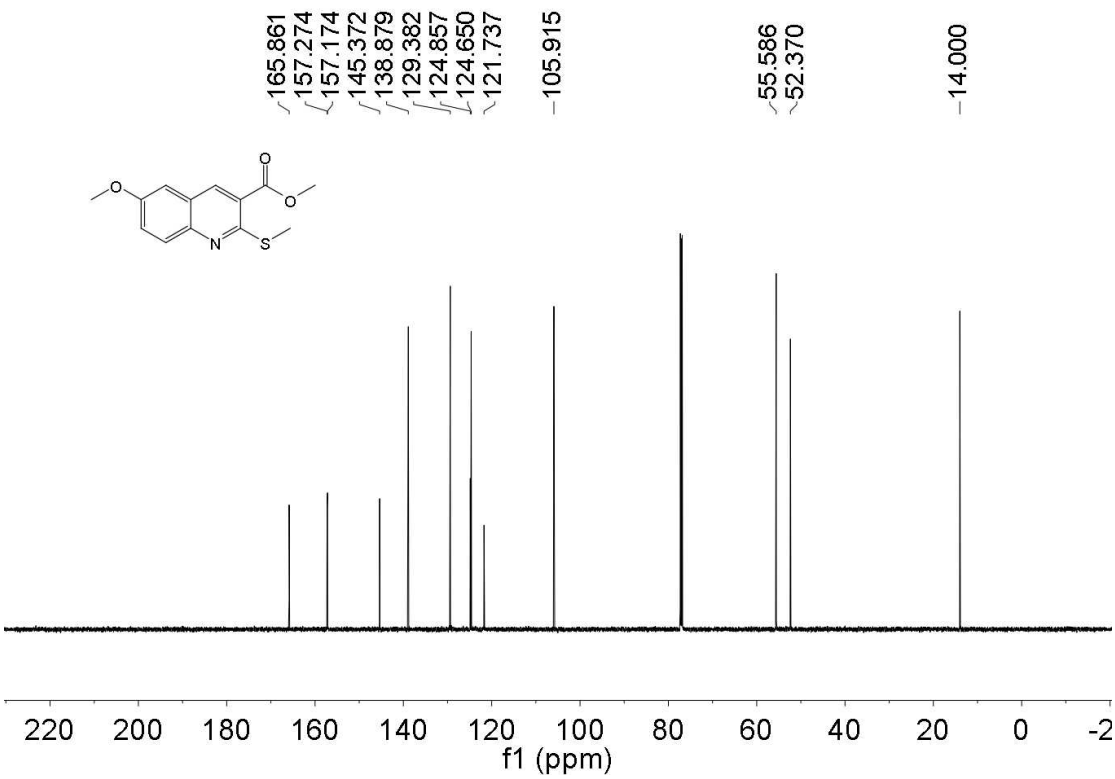


Figure 61. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ah**

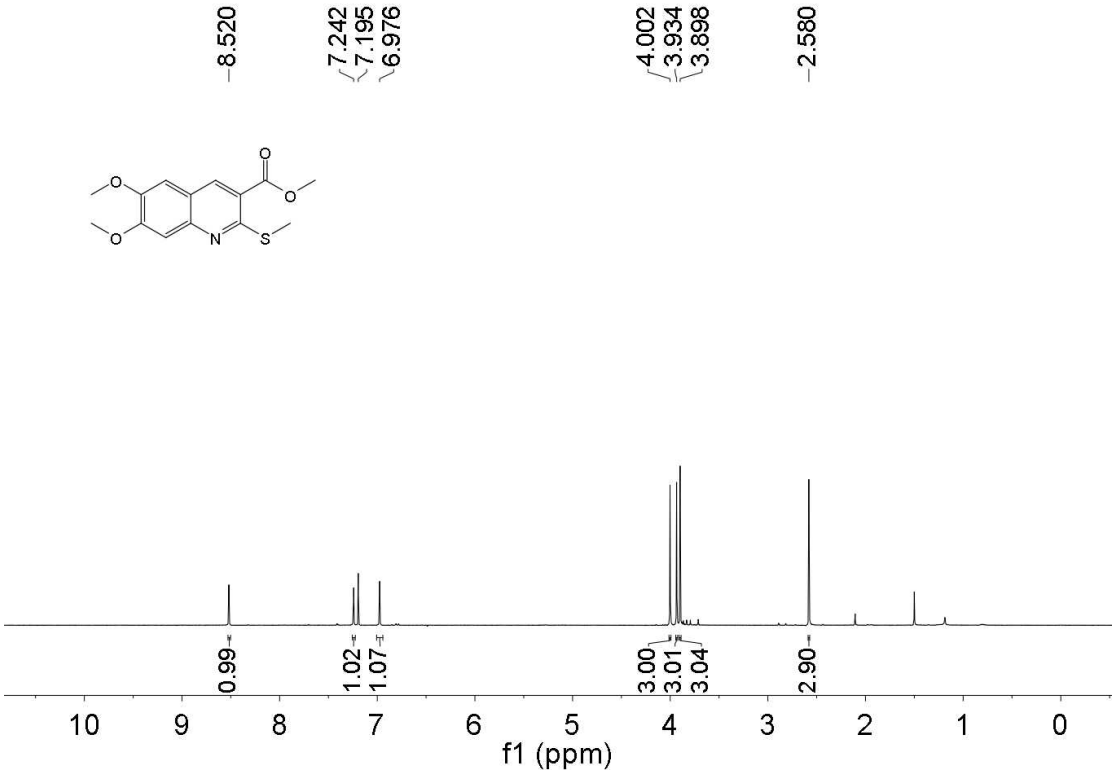


Figure 62. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3ai**

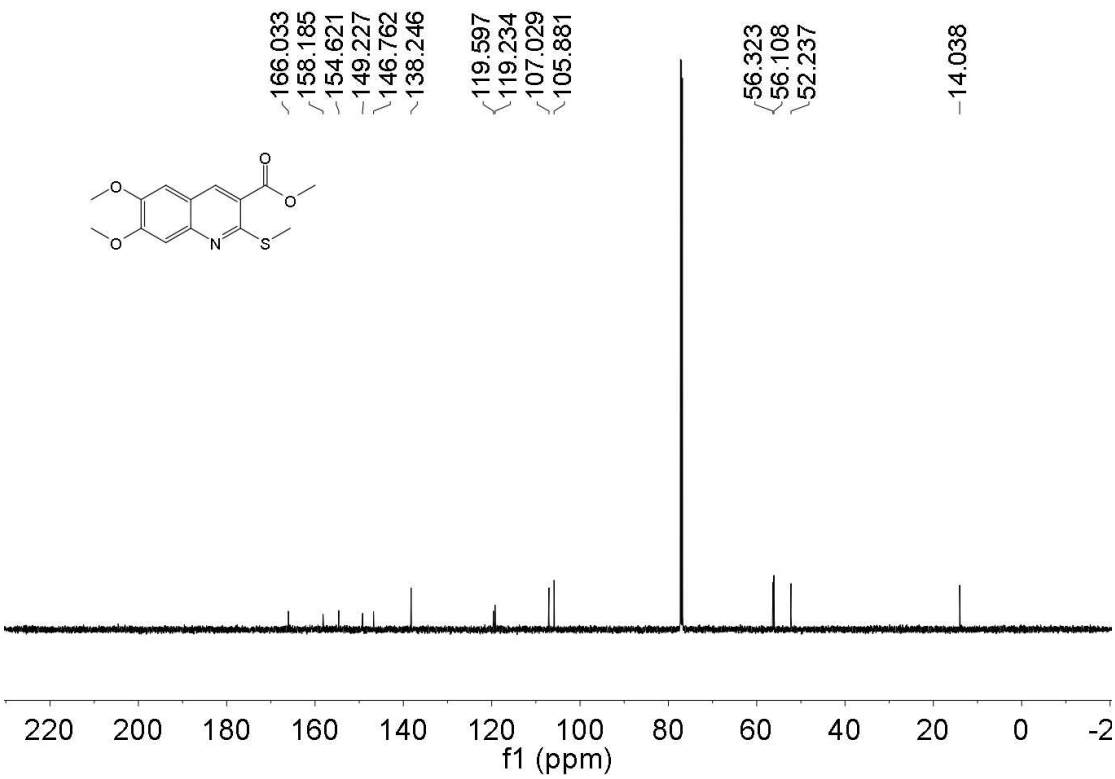


Figure 63. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3ai**

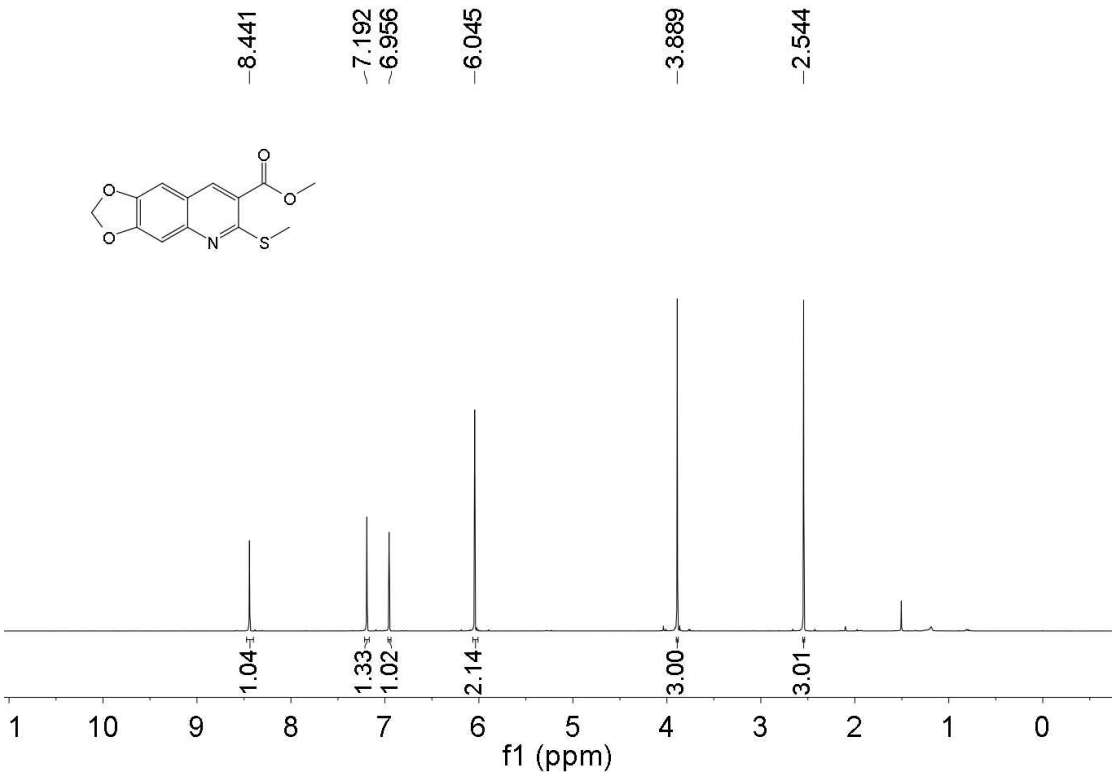


Figure 64. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **3aj**

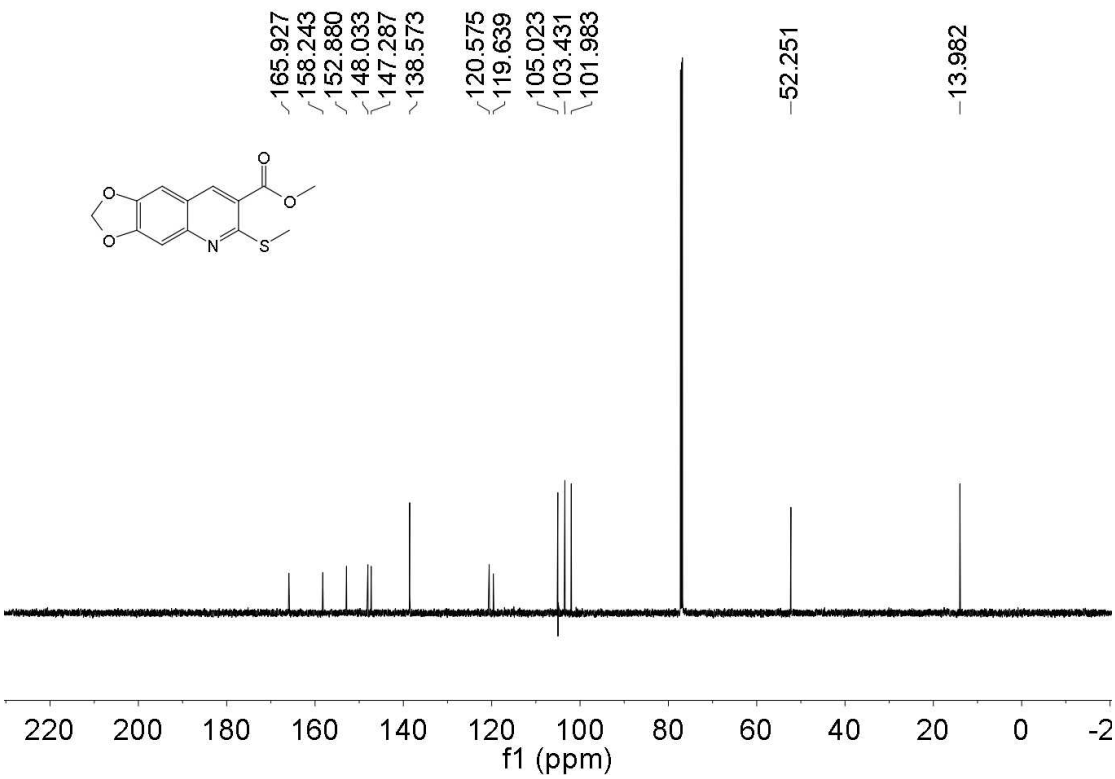


Figure 65. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **3aj**

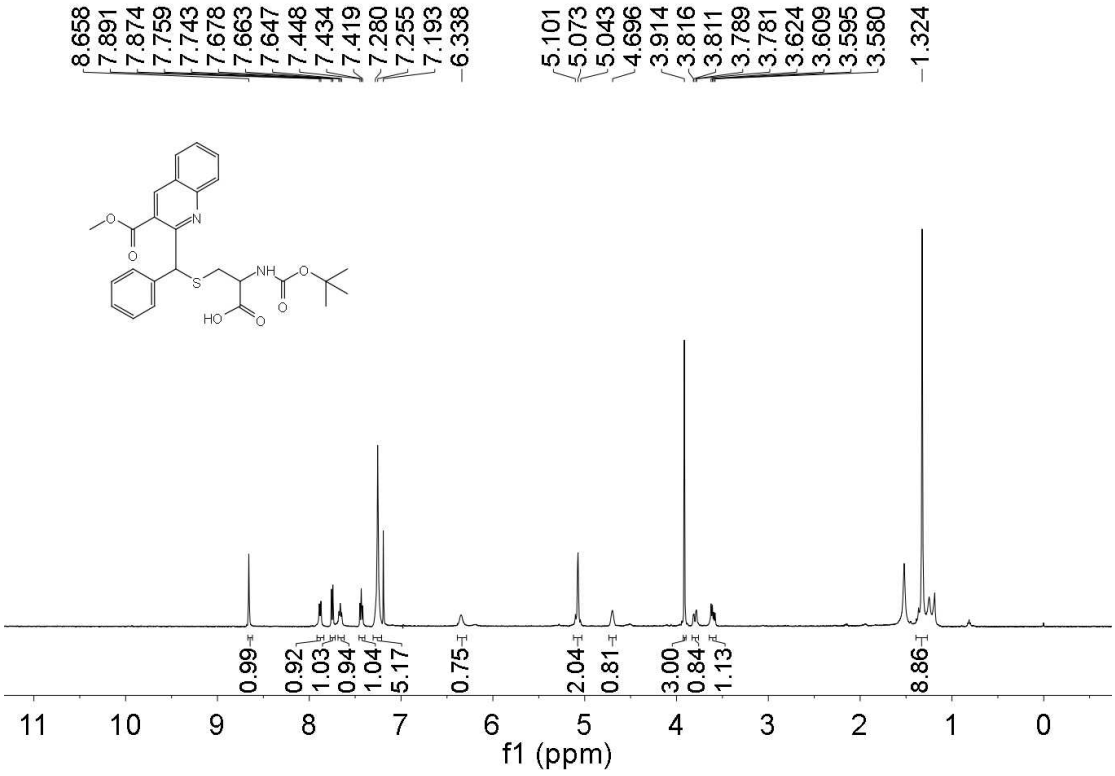


Figure 66. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4a**

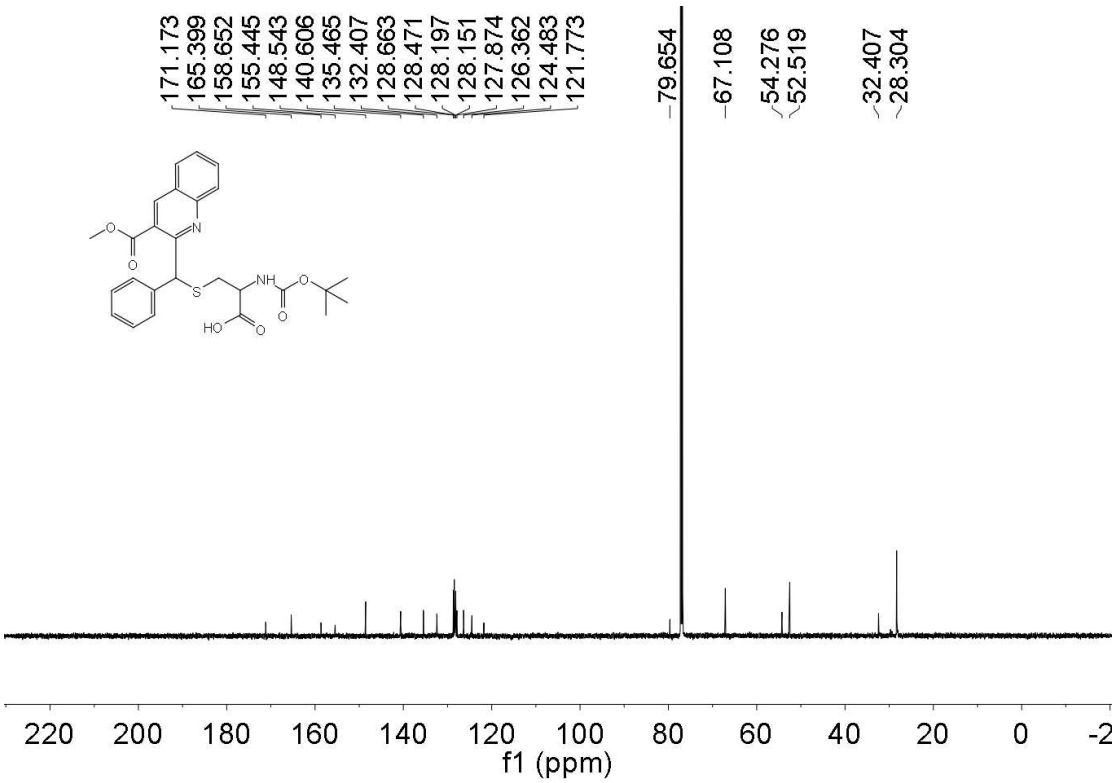


Figure 67. ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of **4a**