Supporting Information

Facile synthesis of tetrahydroquinoline containing dithiocarbamate derivatives *via* one-pot sequential multicomponent reaction

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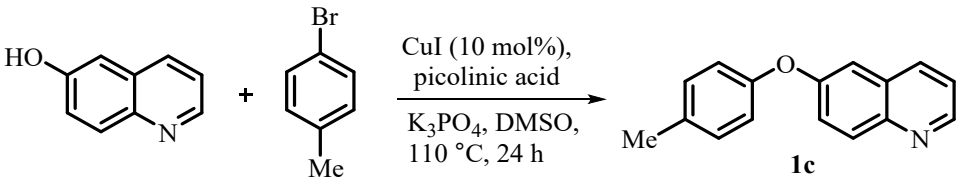
1. General Information

All the reagents and chemicals were purchased from common commercial suppliers like Sigma-Aldrich, Alfa Aesar, Merck, Spectrochem, Avra Synthesis Pvt. Ltd., Finar Chemicals, and BLD Pharma directly used as received without any further purification unless otherwise mentioned. ^{1}H, ^{13}C, and ^{19}F NMR spectra of the compounds were measured in $CDCl_3$, D_2O, as a solvent by using TMS as an internal standard. Chemical shifts, δ (in ppm), are reported relative to TMS δ (^{1}H) 0.0 ppm, δ (^{13}C) 0.0 ppm, which was used as the internal reference. Otherwise the solvents residual proton resonance and carbon resonance ($CHCl_3$, δ (^{1}H) 7.26 ppm, δ (^{13}C) 77.16 ppm; D_2O, (^{1}H) 4.790 ppm, were also used for calibration. Bruker Avance III 600, 500 and 400 spectrometers were used to record the NMR spectra. Chemical shifts (δ) values were reported in ppm and spin-spin coupling constant (J) were expressed in Hz, and other data were reported as follows: s = singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, t = triplet, m = multiplet, q = quartet, pent = pentate, sext = sextet, br = broad, and brs = broad singlet. IR spectra were recorded on Perkin Elmer Instrument at normal temperature making KBr pellet grinding the sample with KBr (IR Grade). MS (ESI-HRMS): Mass spectra were recorded on an Agilent Accurate-Mass (UHPLC - Q-TOF - HRMS). Merck silica gel 60 - 120 was used for column chromatography. otherwise stated. All the final reactions were carried out under air and in preheated oil baths unless otherwise mentioned. Completion of reactions was examined by thin layer chromatography carried out on pre-coated Merck silica gel-60 F_{254} aluminium plates with ultraviolet light (UV) or iodine as visualizing agents.

2. Synthesis of starting material

Synthesis of 6-(*p*-tolyloxy) quinoline [1]

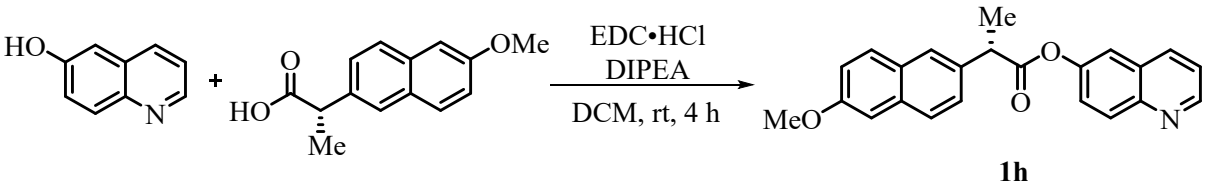


Scheme S1. Synthesis of 6-(*p*-tolyloxy) quinoline

Experimental procedure: 6-hydroxyquinoline (0.400 g, 2.75 mmol, 1.0 equiv.), picolinic acid (0.068 g, 0.55 mmol, 20 mol%), copper(I) iodide (0.052 g, 0.275 mmol, 10 mol%), potassium phosphate (1.172 g, 5.51 mmol, 2.0 equiv.), and 1-bromo-4- methylbenzene (0.471 g, 2.75 mmol,1.0 equiv.) in dimethyl sulfoxide (5.0 mL) was taken in a 15 ml reaction tube, Solution was stirred at 110 °C with reflux condenser. After 24 h, the reaction mixture was cooled to room temperature and quenched with water (1 mL). The aqueous layer was extracted with ethyl acetate, and the combined organic layer was washed with saturated ammonium chloride solution (20 mL × 2). The resulting mixture was dried over anhydrous Na_2SO_4, and then filtered. The resulting filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel to afford the product as brownish oil. Isolated yield: (0.543 g, 84%)

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.79 (dd, J = 4.1, 1.4 Hz, 1H), 8.07 (d, J = 9.1 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.47 (dd, J = 9.1, 2.7 Hz, 1H), 7.30 (dd, J = 8.3, 4.2 Hz, 1H), 7.17 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 2.6 Hz, 1H), 6.99 (d, J = 8.4 Hz, 2H), 2.35 (s, 3H).

Preparation of quinolin-6-yl 2-(6-methoxynaphthalen-2-yl) propanoate (1h)



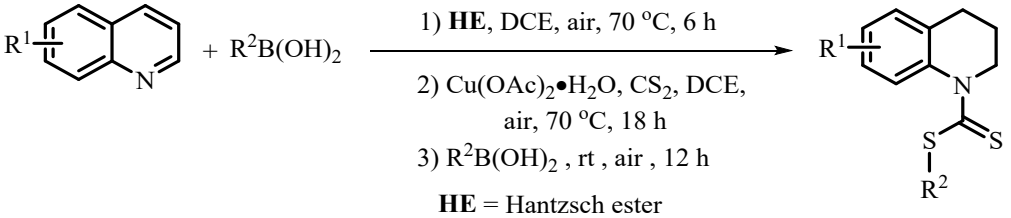
1h

Scheme S2. Preparation of quinolin-6-yl 2-(6-methoxynaphthalen-2-yl) propanoate

Experimental procedure: A mixture of 6-hydroxy quinoline (0.189 g, 1.0 mmol, 1.0 equiv.), (S)-6-methoxy-α-methyl-2-naphthaleneacetic acid (0.253 g, 1.1 mmol, 1.1 equiv.), EDC·HCl (0.230 g, 1.2 mmol, 1.2 equiv.) were combined in a round bottom flask and DCM (25 mL) and DIPEA (0.53 mL, 3.0 mmol, 3.0 equiv.) were added. The reaction mixture was stirred at room temperature for 4 h. 1N HCl (50 mL) and DCM (50 mL) were added to the reaction mixture. The organic layer is washed with saturated $NaHCO_3$ (25 mL) and brine (25 mL) then dried and concentrated under reduced pressure. The crude compound was purified through silica gel column chromatography as brownish solid (0.321 g, 90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 – 8.87 (m, 1H), 8.08 – 8.05 (m, 2H), 7.81 – 7.75 (m, 3H), 7.54 (dd, J = 8.5, 1.7 Hz, 1H), 7.47 (d, J = 2.5 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.20 – 7.16 (m, 2H), 4.17 (q, J = 7.1 Hz, 1H), 3.93 (s, 3H), 1.74 (d, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 173.3, 158.0, 150.3, 148.8, 146.4, 135.9, 135.0, 134.0, 131.1, 129.5, 129.2, 128.6, 127.6, 126.3, 126.2, 124.7, 121.7, 119.3, 118.4, 105.8, 55.5, 45.8, 18.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{23}H_{20}NO_3$: 358.1438; found: 358.1439.

3. General procedure for synthesis of tetrahydroquinoline containing dithiocarbamate derivatives (GP)

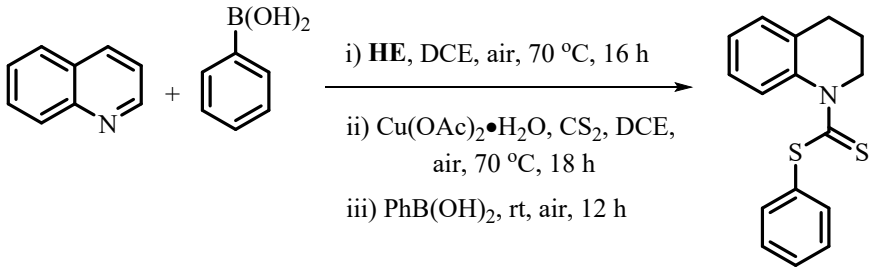


Scheme S3. Synthesis of *S*-aryl/alkyl dithiocarbamate THQ derivatives

Reaction condition: A mixture of substituted quinoline (1.0 mmol, 1.0 equiv.), **HE** (2.2 mmol, 2.2 equiv.), boronic acid (0.30 mmol, 30 mol%) and DCE (2 mL) were added into a reaction tube (15 mL) equipped with stirring bar. The reaction tube was properly closed and placed in a preheated oil bath at 70 °C with continuous stirring for 6 h. To the reaction mixture, copper

(II) acetate monohydrate (1.0 mmol) and carbon disulphide (2.2 mmol) was added and stirred at 70 °C for 18 h. To the resulting mixture, remaining boronic acid (0.70 mmol, 70 mol%) was added and stirred at room temperature for 12 h. The reaction was monitored by thin layered chromatography (TLC) in petroleum ether and ethyl acetate solvent system. After completion of the reaction, all the solvent and volatiles were removed under reduced pressure. The crude compound was purified through silica gel column chromatography.

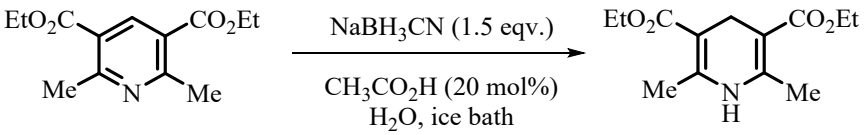
4. Gram-scale reaction



Scheme S4. Gram-scale reaction

Experimental procedure: A mixture of quinoline (1.000 gm, 7.742 mmol, 1.0 equiv.), **HE** (4.324 gm, 17.03 mmol, 2.2 equiv.), phenyl boronic acid (0.283 gm, 2.323 mmol, 30 mol%) and DCE (10 mL) were added into a reaction tube (15 mL) equipped with stirring bar. The reaction tube was properly closed and placed in a preheated oil bath at 70 ºC with continuous stirring for 16 hours. To the reaction mixture, copper (II) acetate monohydrate (1.545 gm, 7.742 mmol, 1.0 equiv.) and carbon disulphide (1.296 gm, 17.03 mmol, 2.2 equiv.) was added and stirred at 70 ºC for 18 hours. To the resulting mixture, phenyl boronic acid (0.661 gm, 5.42 mmol, 70 mol%) was added and stirred at room temperature for 12 hours. The reaction was monitored by thin layered chromatography (TLC) in petroleum ether and ethyl acetate solvent system. After completion of the reaction, all the solvent and volatiles were removed under reduced pressure. The crude compound was purified through silica gel column chromatography to get pure compound as yellow oil of (1.834 g, 82%).

5. Procedure for oxidised Hantzsch ester (OHE) to Hantzsch-1,4-dihydropyridine (H.E) recovery [2]



OHE **HE**, 91%

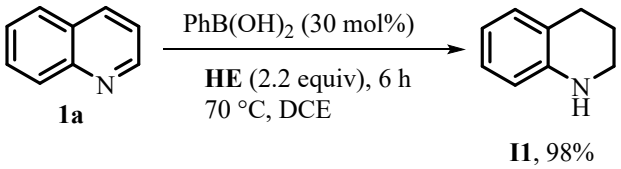
Scheme S5. Reduction of oxidised Hantzsch ester (**OHE**) to Hantzsch ester (**HE**)

Experimental procedure: In a 50 mL round bottom flask, **OHE** (1 gm, 3.9 mmol), water (10 mL) and acetic acid (45 µL, 20 mol%) were charged and placed in an ice bath. In the reaction mixture $NaBH_3CN$ (0.294 gm, 1.2 equiv.) was slowly added and stirred for overnight. The reaction was monitored by thin layered chromatography (TLC) in hexane and ethyl acetate solvent system. Once the reaction was completed, solid precipitate was filtered, washed

thoroughly by water and ice-cold acetone and dried on vacuum desiccator. Isolated yield: (0.899 g, 91%).

6. Reaction mechanistic studies

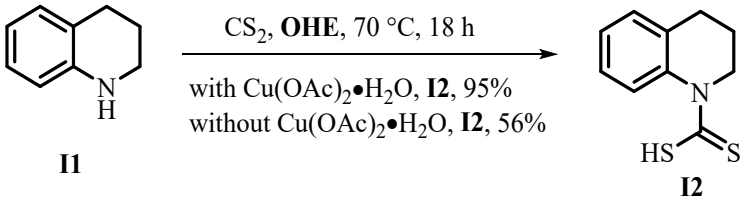
6.1. Proof of 1,2,3,4 THQ as the reaction intermediate



Scheme S6. The proof of 1,2,3,4 THQ as the reaction intermediate

In a reaction tube (15 mL), quinoline (0.065 g, 0.5 mmol, 1.0 equiv.), **HE** (0.280 g, 1.1 mmol, 2.2 equiv.), phenylboronic acid (0.018 g, 0.15 mmol, 30 mol%) and DCE (2 mL) were charged. The reaction tube was properly closed and placed in a preheated oil bath (70 °C) with continuous stirring. After completion of the reaction, the crude compound was purified by column chromatography on silica gel for pure compound as yellow oil of **I1** (0.065 g, 98%).

6.2. Proof of 3,4-dihydroquinoline-1(2H)-carbodithioic acid I2 as the reaction intermediate

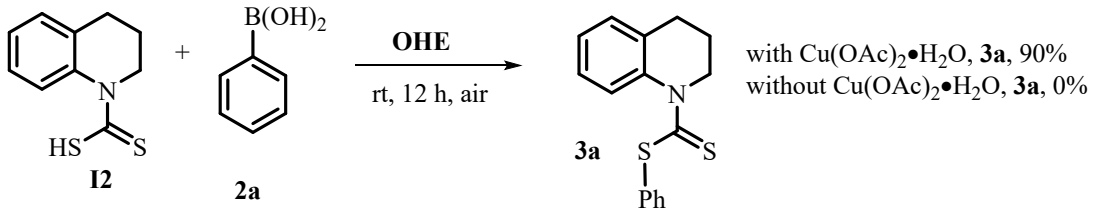


Scheme S7. The proof of dithiocarbamic acid as the reaction intermediate

In a reaction tube (15 mL), 1,2,3,4 tetrahydroquinoline (0.066 g, 0.5 mmol, 1.0 equiv.), Carbon disulphide (0.084 g, 1.1 mmol, 2.2 equiv.), copper (II) acetate monohydrate (0.099 g, 0.5 mmol, 1.0 equiv.), **OHE** (0.188 g, 0.75 mmol, 1.5 equiv.) and DCE (2 mL) were added. The reaction tube was properly closed and placed in a preheated oil bath at 70 °C with continuous stirring for 18 hours. The reaction was monitored by thin layered chromatography (TLC) in petroleum ether and ethyl acetate solvent system. After completion of the reaction, all the volatiles were removed under reduced pressure. The crude compound was purified through silica gel to get pure compound as yellow powder of **I2** (0.099 g, 95%). Under the identical reaction condition in the absence of copper salt, the intermediate **I2** was obtained in 56% yield (0.058 g).

^{1}H NMR (400 MHz, D_2O): δ 7.67 – 7.65 (m, 1H), 7.29 – 7.26 (m, 1H), 7.22 – 7.19 (m, 2H), 4.40 (t, J = 6.7 Hz, 2H), 2.71 (t, J = 7.0 Hz, 2H), 2.05 (pent, J = 6.8 Hz, 2H). ^{13}C NMR (151 MHz, D_2O): δ 212.6, 143.3, 134.4, 128.2, 127.4, 126.4, 125.1, 52.6, 25.4, 23.6. Characteristic IR band: $\nu_{(C=S)}$: 973 cm^{-1}. Spectral data is in accordance with the lietrature.[3]

6.3. Role of copper salt in the *S*-arylation step

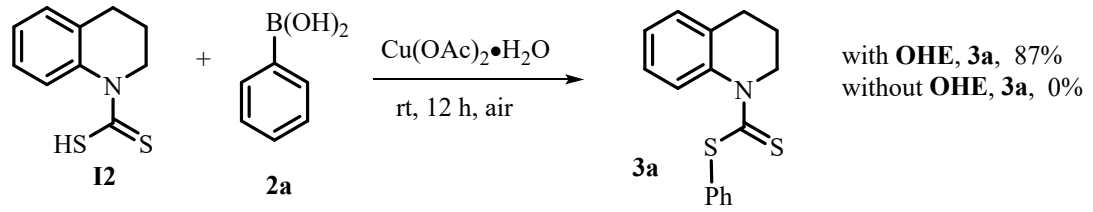


Scheme S8. The role of copper salt in the *S*-arylation step

In a reaction tube (15 mL), **I2** (0.104 g, 0.5 mmol, 1.0 equiv.), **2a** (0.061 g, 0.5 mmol, 1.0 equiv.), copper (II) acetate monohydrate (0.099 g, 0.5 mmol, 1.0 equiv.), **OHE** (0.277 g, 0.75 mmol, 1.5 equiv.) and DCE (2 mL) were added. The reaction tube was properly closed and placed in a preheated oil bath at rt with continuous stirring for 12 hours. After completion of the reaction, the crude compound was purified through silica gel to get pure compound as yellow oil of (0.128 g, 90%).

Under the same reaction condition in the absence of copper salt, there is no conversion of desired product **3a**. Both the study suggests that role of copper (II) acetate monohydrate is significant in nucleophic addition reaction as well as C-S coupling reaction.

6.4. Role of oxidised Hantzsch ester in the *S*-arylation step

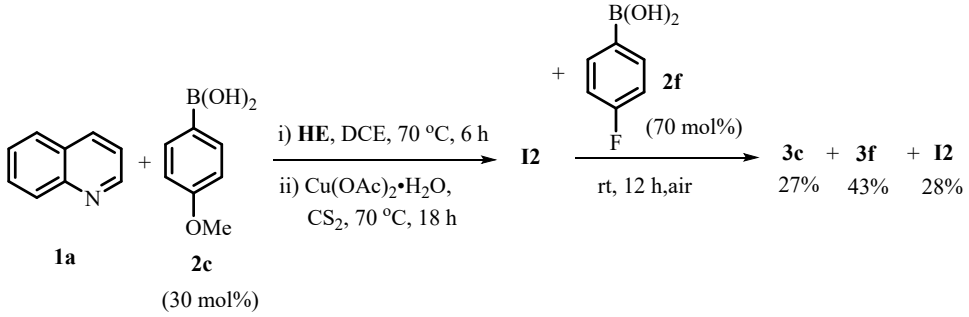


Scheme S9. The role of oxidised Hantzsch ester (**OHE**) in the *S*-arylation step

In a reaction tube (15 mL), **I2** (0.104 g, 0.5 mmol, 1.0 equiv.), **2a** (0.061 g, 0.5 mmol, 1.0 equiv.), copper (II) acetate monohydrate (0.100 g, 0.5 mmol, 1.0 equiv.), **OHE** (0.188 g, 0.75 mmol, 1.5 equiv.) and DCE (2 mL) were added. The reaction tube was properly closed and placed in a preheated oil bath at room temperature with continuous stirring for 12 hours. The reaction was monitored by thin layered chromatography (TLC) in petroleum ether and ethyl acetate solvent system. After completion of the reaction, the crude compound was purified through silica gel column chromatography to get the pure compound **3a** as yellow oil (0.124 g, 87%).

Under the same reaction condition in the absence of **OHE**, there is no formation of desired product **3a**. Study suggests that role of in-stu generated **OHE** in the *S*-arylation step is critical.

6.5. Reactivity studies with two different arylboronic acid



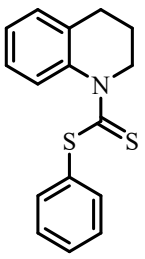
Scheme S10. The reactivity studies with two different arylboronic acids

1a (0.065 g, 0.5 mmol, 1.0 equiv.), **HE** (0.280 g, 1.1 mmol, 2.2 equiv.), **2c** (0.023 g, 0.15 mmol, 30 mol%) and DCE (2 mL) were added into a reaction tube (15 mL) equipped with stirring bar. The reaction tube was properly closed and placed in a preheated oil bath at 70 °C with continuous stirring for 6 hours. To the resulting mixture, copper (II) acetate monohydrate (0.099 g, 0.5 mmol, 1.0 equiv.) and carbon disulphide (0.084 g, 1.1 mmol, 2.2 equiv.) was added and stirred at 70 °C for 18 hours. To the resulting mixture, **2f** (0.049 g, 0.35 mmol, 70 mol%) was added and stirred at room temperature for 12 hours. After completion of the reaction, the crude compound was purified through silica gel column chromatography.

Gratifyingly, analytically pure *S*-aryl dithiocarbamate **3c** and **3f** were isolated in 27% (0.042 g) and 43% (0.067 g) yields, respectfully along with 28% (0.030 g) of **I2** intermediate. The result suggests that the reactivity of the boronic acid containing an electron-donating group is likely to be higher than that with an electron-withdrawing substituent in the *S*-arylation segment.

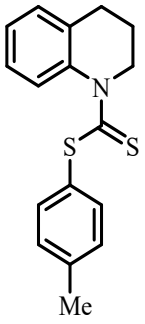
7. Analytical data of the products

Phenyl 3,4-dihydroquinoline-1(2H)-carbodithioate (3a)



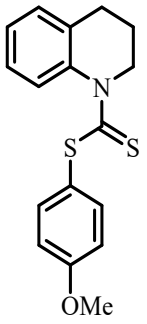
By following the **GP**, the title compound **3a** was isolated as light-yellow oil (0.259 g, 91%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.75 – 7.73 (m, 1H), 7.45 – 7.39 (m, 5H), 7.29 – 7.24 (m, 3H), 4.43 – 4.41 (m, 2H), 2.76 (t, J = 6.8 Hz, 2H), 2.09 (pent, J = 6.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 199.3, 140.4, 136.8, 134.9, 132.5, 130.0, 129.1, 128.7, 127.7, 126.5, 126.1, 52.8, 26.5, 23.8. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{16}NS_2$: 286.0719; found: 286.0742. Significant IR band: $\nu_{(C=S)}$: 974 cm^{-1}.

***p*-tolyl 3, 4-dihydroquinoline-1(2H)-carbodithioate (3b)**



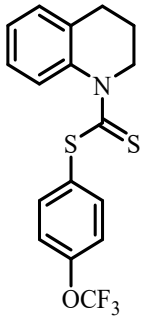
By following the **GP**, the title compound **3b** was isolated as light-yellow oil (0.260 g, 87%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 – 7.73 (m, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.27 – 7.21 (m, 5H), 4.42 (t, J = 6.5 Hz, 2H), 2.76 (t, J = 6.8 Hz, 2H), 2.39 (s, 3H), 2.09 (pent, J = 6.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 199.9, 140.4, 140.3, 136.7, 135.0, 130.1, 129.1, 128.7, 127.7, 126.6, 126.0, 52.8, 26.5, 23.8, 21.7. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{17}H_{18}NS_2$: 300.0876; found: 300.0875. Significant IR band: $\nu_{(C=S)}$: 974 cm^{-1}.

Phenyl 4-methoxy-3, 4-dihydroquinoline-1(2H)-carbodithioate (3c)



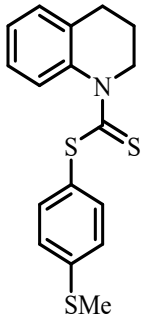
By following the **GP**, the title compound **3c** was isolated as light-yellow oil (0.300 g, 95%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.66). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 – 7.73 (m, 1H), 7.34 (d, 8.7 Hz, 2H), 7.28 – 7.24 (m, 3H), 6.95 (d, J = 8.8 Hz, 2H), 4.43 (m, 2H), 3.84 (s, 3H), 2.76 (t, J = 6.8 Hz, 2H), 2.09 (pent, J = 6.8 Hz, 2H).^{13}C NMR (151 MHz, $CDCl_3$): δ 200.4, 161.1, 140.5, 138.4, 134.9, 128.7, 127.7, 126.6, 126.0, 123.4, 114.8, 55.4, 52.9, 26.6, 23.8. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{17}H_{18}NOS_2$: 316.0825; found: 316.0823. Significant IR band: $\nu_{(C=S)}$: 974 cm^{-1}.

4-(trifluoromethoxy) phenyl 3, 4-dihydroquinoline-1(2H)-carbodithioate (3d)



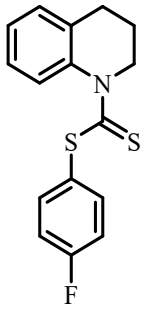
By following the **GP**, the title compound **3d** was isolated as light-yellow oil (0.277 g, 75%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.71 – 7.69 (m, 1H), 7.44 (d, J = 8.5 Hz, 2H), 7.28 – 7.25 (m, 3H), 7.22 (d, J = 8.1 Hz, 2H), 4.42 – 4.40 (m, 2H), 2.75 (t, J = 6.8 Hz, 2H), 2.09 (pent, J = 6.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 198.2, 150.5, 140.3, 138.4, 135.0, 130.9, 128.8, 127.9, 126.4, 126.2, 121.2, 52.9, 26.5, 23.8. ^{19}F NMR (377 MHz, $CDCl_3$): δ -57.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{17}H_{15}F_3NOS_2$: 370.0542; found: 370.0545. Significant IR band: $\nu_{(C=S)}$: 975 cm^{-1}.

4-(methylthio) phenyl 3,4-dihydroquinoline-1(2H)-carbodithioate (3e)



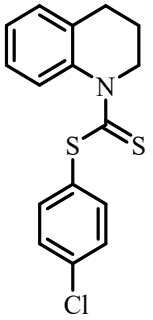
By following the **GP**, the title compound **3e** was isolated as light-yellow oil (0.292 g, 88%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.70). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 – 7.71 (m, 1H), 7.33 – 7.31 (m, 2H), 7.28 – 7.23 (m, 5H), 4.42 (t, J = 6.6 Hz, 2H), 2.76 (t, J = 6.8 Hz, 2H), 2.50 (s, 3H), 2.09 (pent, J = 6.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 199.5, 141.7, 140.4, 137.0, 135.0, 128.7, 128.2, 127.7, 126.5, 126.2, 126.1, 52.9, 26.5, 23.8, 15.2. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{17}H_{18}NS_3$: 332.0596; found 332.0595. Significant IR band: $\nu_{(C=S)}$: 975 cm^{-1}.

4-fluorophenyl 3, 4-dihydroquinoline-1(2H)-carbodithioate (3f)



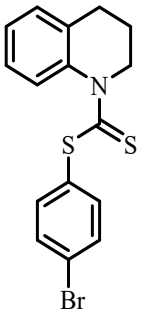
By following the **GP**, the title compound **3f** was isolated as light-yellow oil (0.188 g, 62%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72 – 7.71 (m, 1H), 7.41 – 7.39 (m, 2H), 7.28 – 7.25 (m 3H), 7.09 (t, 8.6 Hz, 2H), 4.43 – 4.40 (m, 2H), 2.76 (t, J =6.8 Hz, 2H), 2.09 (pent, J = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.1, 165.2 – 162.7 (C-F, $^1J_{C\text{-}F}$ = 251.7 Hz), 140.3, 139.0 – 138.9 (C-F, $^2J_{C\text{-}F}$ = 8.8 Hz), 135.0, 128.7, 128.0 – 127.9 (C-F, $^3J_{C\text{-}F}$ = 3.5 Hz), 127.8, 126.4, 126.1, 116.5, 116.3, 52.9, 26.5, 23.8.^{19}F NMR (377 MHz, $CDCl_3$): δ -110.3. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{16}H_{15}FNS_2$: 304.0625; found: 304.0624. Significant IR band: $\nu_{(C=S)}$: 973 cm^{-1}.

4-chlorophenyl 3, 4-dihydroquinoline-1(2H)-carbodithioate (3g)



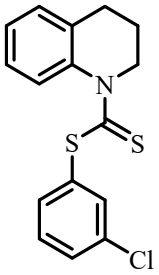
By following the **GP**, the title compound **3g** was isolated as light-yellow oil (0.243 g, 76%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 – 7.69 (m, 1H), 7.38 – 7.34 (m, 4H), 7.27 – 7.25 (m, 3H), 4.43 – 4.40 (m, 2H), 2.77 – 2.75 (m, 2H), 2.12 – 2.07 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 198.4, 140.2, 138.1, 136.5, 135.0, 130.9, 129.4, 128.7, 127.9, 126.4, 126.1, 52.9, 26.5, 23.8. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{16}H_{15}ClNS_2$: 320.0329; found: 320.0328. Significant IR band: $\nu_{(C=S)}$: 974 cm^{-1}.

4-bromophenyl 3, 4-dihydroquinoline-1(2H)-carbodithioate (3h)



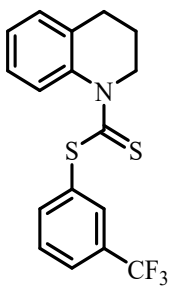
By following the **GP**, the title compound **3h** was isolated as light-yellow oil (0.306 g, 84%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.71 – 7.69 (m, 1H), 7.53 (d, 8.4 Hz, 2H), 7.29 – 7.26 (m, 5H), 4.42 – 4.40 (m, 2H), 2.76 (t, J = 6.8 Hz, 2H), 2.09 (pent, J = 6.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 198.2, 140.2, 138.3, 135.0, 132.4, 131.5, 128.8, 127.9, 126.4, 126.1, 124.9, 52.9, 26.5, 23.8. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{16}H_{15}BrNS_2$: 363.9824; found: 363.9825. Significant IR band: $\nu_{(C=S)}$: 975 cm^{-1}.

3-chlorophenyl 3, 4-dihydroquinoline-1(2H)-carbodithioate (3i)



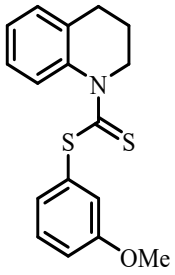
By following the **GP**, the title compound **3i** was isolated as light-yellow oil (0.265 g, 83%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75).^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (s, 1H), 7.42 – 7.24 (m, 7H), 4.42 – 4.39 (m, 2H), 2.75 (t, J = 6.9 Hz, 2H), 2.12 – 2.06 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.9, 140.4, 136.4, 135.0, 134.8, 134.5, 134.2, 130.1, 130.0, 128.7, 127.8, 126.4, 126.2, 52.9, 26.5, 23.8. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{16}H_{15}ClNS_2$: 320.0329; found: 320.0328. Significant IR band: $\nu_{(C=S)}$: 978 cm^{-1}.

3-(trifluoromethyl) phenyl 3, 4-dihydroquinoline-1(2H)-carbodithioate (3j)



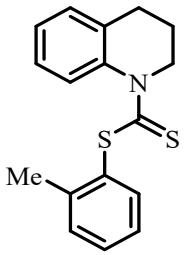
By following the **GP**, the title compound **3j** was isolated as light-yellow oil (0.300 g, 85%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 – 7.70 (m, 1H), 7.67 (d, 9.0 Hz, 2H), 7.61 (d, J = 7.7 Hz, 1H), 7.51 (t, J = 7.7 Hz, 1H), 7.29 – 7.25 (m, 3H), 4.41 (t, J = 6.8 Hz, 2H), 2.76 (t, J = 6.8 Hz, 2H), 2.10 (pent, J = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.4, 140.2, 140.1, 135.0, 133.8, 133.5 (C-F, q, $^1J_{C\text{-}F}$ = 3.8 Hz), 131.6, 131.3, 129.4, 128.7, 127.9, 126.7 (C-F, q, $^2J_{C\text{-}F}$ = 3.7 Hz), 126.3, 126.2, 52.9, 26.5, 23.8. ^{19}F NMR (565 MHz, $CDCl_3$): δ -62.6. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{17}H_{15}F_3NS_2$: 354.0593; found: 354.0594. Significant IR band: $\nu_{(C=S)}$: 974 cm^{-1}.

Phenyl 3-methoxy-3, 4-dihydroquinoline-1(2H)-carbodithioate (3k)



By following the **GP**, the title compound **3k** was isolated as light-yellow oil (0.271 g, 86%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:1, R_f = 0.66).^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 – 7.71 (m, 1H), 7.31 – 7.23 (m, 4H), 7.03 (d, J = 7.5 Hz, 1H), 6.98 – 6.95 (m, 2H), 4.41 (t, J = 6.9 Hz, 2H), 3.80 (s, 3H), 2.74 (t, J = 6.9 Hz, 2H), 2.11 – 2.06 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.0, 159.9, 140.5, 134.9, 133.4, 129.8, 128.9, 128.6, 127.6, 126.5, 126.1, 121.7, 116.2, 55.5, 52.7, 26.5, 23.9. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{17}H_{18}NOS_2$: 316.0825; found: 316.0830. Significant IR band: $\nu_{(C=S)}$: 974 cm^{-1}.

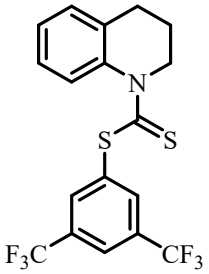
***O*-tolyl 3,4-dihydroquinoline-1(2H)-carbodithioate (3l)**



By following the **GP**, the title compound **3l** was isolated as light-yellow oil (0.240 g, 80%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 – 7.73 (m, 1H), 7.40 – 7.35 (m, 2H), 7.32 – 7.30 (m, 1H), 7.29 – 7.21 (m, 4H), 4.43 (t, J = 6.6 Hz, 2H), 2.77 (t, J = 6.8 Hz, 2H), 2.41 (s, 3H), 2.09 (pent, J = 6.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 198.3, 143.7, 140.6, 137.6, 134.9, 131.9, 130.8, 130.7, 128.7, 127.7, 126.8, 126.4, 126.1, 52.7, 26.6, 23.9, 21.0. HRMS (ESI) *m/z*:

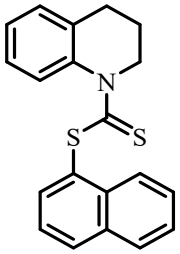
$[M+H]^+$ calculated for: $C_{17}H_{18}NS_2$: 300.0876; found: 300.0873. Significant IR band: $\nu_{(C=S)}$: 974 cm^{-1}.

3,5-bis(trifluoromethyl)phenyl 3,4-dihydroquinoline-1(2H)-carbodithioate (3m)



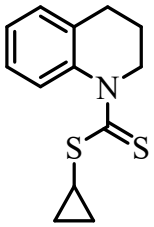
By following the **GP**, the title compound **3m** was isolated as light-yellow oil (0.346 g, 82%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 25:1, R_f = 0.66). ^1H NMR (600 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.86 (s, 2H), 7.69 – 7.67 (m, 1H), 7.30 – 7.25 (m, 3H), 4.42 – 4.39 (m, 2H), 2.76 (t, J = 6.7 Hz, 2H), 2.10 (pent, J = 6.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 195.5, 139.9, 136.78, 136.76, 135.5, 135.1, 132.07 (C-F, q, $^1J_{C\text{-}F}$ = 33.6 Hz), 128.8, 128.2, 126.3, 126.2, 124.0, 123.6 (C-F, q, $^2J_{C\text{-}F}$ = 3.4 Hz), 122.2, 53.1, 26.5, 23.8. ^{19}F NMR (565 MHz, $CDCl_3$): δ -62.8. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{18}H_{14}F_6NS_2$: 422.0467; found: 422.0466. Significant IR band: $\nu_{(C=S)}$: 974 cm^{-1}.

Naphthalen-1-yl 3, 4-dihydroquinoline-1(2H)-carbodithioate (3n)



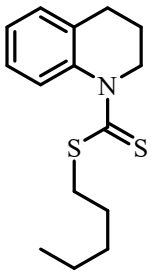
By following the **GP**, the title compound **3n** was isolated as light-yellow oil (0.292 g, 87%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^1H NMR (500 MHz, $CDCl_3$): δ 8.22 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 8.3 Hz, 1H), 7.86 (d , J =7.8 Hz, 2H), 7.65 (d, J =7.1Hz, 1H), 7.56 – 7.54 (m, 1H), 7.50 (s, 1H), 7.45 – 7.44 (m, 1H), 7.30 – 7.27 (m, 3H), 7.23 – 7.21 (m, 1H), 4.40 (t, J = 6.6 Hz, 2H), 2.69 (t, J = 6.7 Hz, 2H), 2.07 (pent, J = 6.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 198.2, 140.5, 136.5, 135.0, 134.9, 134.2, 131.3, 129.9, 128.8, 128.6, 127.6, 127.3, 126.4, 126.3, 126.2, 125.9, 125.8, 52.7, 26.5, 24.0. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{20}H_{18}NS_2$: 336.0876; found: 336.0877. Significant IR band: $\nu_{(C=S)}$: 971 cm^{-1}.

Cyclopropyl 3,4-dihydroquinoline-1(2H)-carbodithioate (3o)



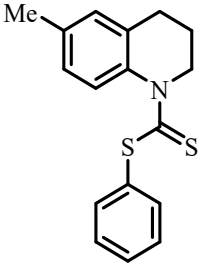
By following the **GP**, the title compound **3o** was isolated as light-yellow oil (0.167 g, 67%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.80). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (d, J = 6.9 Hz, 1H), 7.21 – 7.17 (m, 3H), 4.41 (t, J = 6.6 Hz, 2H), 2.71 (t, J = 6.8 Hz, 2H), 2.44 – 2.39 (m, 1H), 2.06 (pent, J = 6.7 Hz, 2H), 1.12 – 1.08 (m, 2H), 0.69 – 0.66 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 200.9, 140.4, 134.7, 128.7, 127.5, 126.3, 125.9, 51.8, 26.5, 23.8, 17.5, 8.3. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for: $C_{13}H_{16}NS_2$: 250.0719; found: 250. 0721. Significant IR band: $\nu_{(C=S)}$: 977 cm^{-1}.

Pentyl 3,4-dihydroquinoline-1(2H)-carbodithioate (3p)



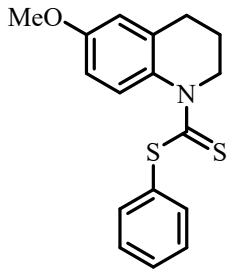
By following the **GP**, the title compound **3p** was isolated as light-yellow oil (0.217 g, 78%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.80). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.60 (m, 1H), 7.22 – 7.20 (m, 3H), 4.43 (t, J = 6.7 Hz, 2H), 3.28 – 3.20 (m, 2H), 2.72 (t, J = 6.8 Hz, 2H), 2.07 (pent, J = 6.8 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.39 – 1.30 (m, 4H), 0.90 – 0.87 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 199.8, 140.5, 134.8, 128.7, 127.4, 126.6, 125.8, 52.0, 37.9, 31.4, 28.2, 26.4, 23.7, 22.4, 14.1. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{15}H_{22}NS_2$: 280.1189; found: 280. 1191.Significant IR band: $\nu_{(C=S)}$: 978 cm^{-1}.

Phenyl 6-methyl-3, 4-dihydroquinoline-1(2H)-carbodithioate (4a)



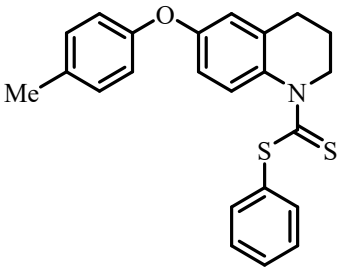
By following the **GP**, the title compound **4a** was isolated as light-yellow oil (0.266 g, 89%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, J = 8.0 Hz, 1H), 7.45 – 7.38 (m, 5H), 7.11 – 7.06 (m, 2H), 4.41 (t, J = 6.8 Hz, 2H), 2.72 (t, J = 6.6 Hz, 2H), 2.37 (s, 3H), 2.10 – 2.05 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 199.0, 137.9, 137.7, 136.9, 134.7, 132.6, 129.9, 129.4, 129.3, 129.1, 126.7, 126.2, 122.7, 52.9, 26.5, 23.8, 21.3. HRMS (ESI) *m/z*: $[M+H]^+$calculated for $C_{17}H_{18}NS_2$: 300.0876; found: 300.0848. Significant IR band: $\nu_{(C=S)}$: 973 cm^{-1}.

Phenyl 6-methoxy-3, 4-dihydroquinoline-1(2H)-carbodithioate(4b)



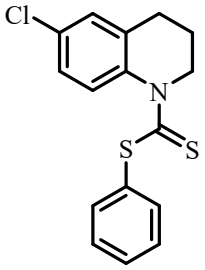
By following the **GP**, the title compound **4b** was isolated as light-yellow oil (0.284 g, 90%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.66). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 8.8 Hz, 1H), 7.45 – 7.38 (m, 5H), 6.82 – 6.77 (m, 2H), 4.41 (t, J = 6.8 Hz, 2H), 3.84 (s, 3H), 2.73 (t, J = 6.8 Hz, 2H), 2.07 (pent, J = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.9, 158.9, 136.9, 136.5, 133.5, 132.7, 129.9, 129.1, 127.6, 113.6, 111.4, 55.6, 52.8, 26.9, 23.7. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{17}H_{18}NOS_2$: 316.0825; found: 316.0828. Significant IR band: $\nu_{(C=S)}$: 974 cm^{-1}.

phenyl 6-(*p*-tolyloxy)-3,4-dihydroquinoline-1(2H)-carbodithioate (4c)



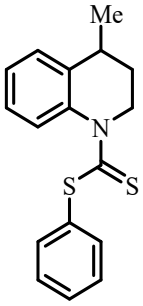
By following the **GP**, the title compound **4c** was isolated as light-yellow oil (0.337 g, 86%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.66). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.7 Hz, 1H), 7.46 – 7.38 (m, 5H), 7.18 (d, J = 8.1 Hz, 2H), 6.97 (d, J = 8.5 Hz, 2H), 6.86 – 6.81 (m, 2H), 4.41 (t, J = 6.6 Hz, 2H), 2.69 (t, J = 6.8 Hz, 2H), 2.36 (s, 3H), 2.07 (pent, J = 6.7 Hz, 2H).^{13}C NMR (151 MHz, $CDCl_3$): δ 199.0, 157.3, 154.0, 136.8, 136.6, 134.9, 133.8, 132.5, 130.6, 130.0, 129.2, 127.7, 119.9, 117.3, 115.2, 52.8, 26.8, 23.7, 20.9. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{23}H_{22}NOS_2$: 392.1138; found: 392.1139. Significant IR band: $\nu_{(C=S)}$: 977 cm^{-1}.

Phenyl 6-chloro-3,4-dihydroquinoline-1(2H)-carbodithioate (4d)



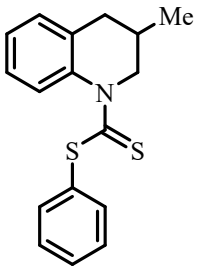
By following the **GP**, the title compound **4d** was isolated as light-yellow oil (0.243 g, 76%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.42 – 7.40 (m, 2H), 7.28 (d, J = 7.4 Hz, 1H), 7.20 – 7.19 (m, 1H), 7.15 (dd, J = 8.8, 2.4 Hz, 1H), 7.09 (d, J = 8.5 Hz, 2H), 4.29 (t, J = 6.3 Hz, 2H), 2.83 (t, J = 6.7 Hz, 2H), 2.13 – 2.09 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 187.6, 154.0, 136.8, 134.1, 131.4, 129.5, 129.2, 128.6, 127.1, 126.3, 126.2, 122.6, 52.6, 27.0, 23.5. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{16}H_{15}ClNS_2$: 320.0329; found: 320.0325. Significant IR band: $\nu_{(C=S)}$: 963 cm^{-1}.

Phenyl 4-methyl-3, 4-dihydroquinoline-1(2H)-carbodithioate (4e)



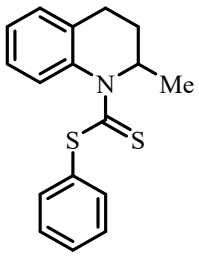
By following the **GP**, the title compound **4e** was isolated as light-yellow oil (0.264 g, 88%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75).^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 7.4 Hz, 1H), 7.44 – 7.38 (m, 5H), 7.31 – 7.29 (m, 3H), 4.63 – 4.58 (m, 1H), 4.33 – 4.26 (m, 1H), 2.90 – 2.83 (m, 1H), 2.29 – 2.22 (m, 1H), 1.70 – 1.63 (m, 1H), 1.37 (d, J = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 199.3, 139.7, 139.6, 136.9, 132.5, 129.9, 129.4, 129.1, 127.9, 126.5, 126.2, 126.1, 122.7, 52.3, 32.4, 31.0, 19.3. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{17}H_{18}NS_2$: 300.0876; found: 300.0900. Significant IR band: $\nu_{(C=S)}$: 970 cm^{-1}

Phenyl 3-methyl-3, 4-dihydroquinoline-1(2H)-carbodithioate (4f)



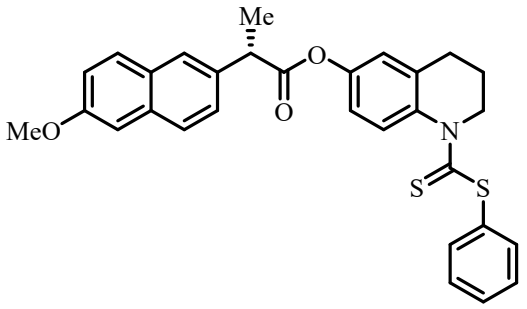
By following the **GP**, the title compound **4f** was isolated as light-yellow oil (0.246 g, 82%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 – 7.75 (m, 1H), 7.44 – 7.39 (m, 4H), 7.26 – 7.23 (m, 4H), 4.74 – 4.71(m, 1H), 3.82 – 3.78 (m, 1H), 2.89 (dd, J = 15.5, 5.8 Hz, 1H), 2.44 – 2.40 (m, 1H), 2.31 – 2.25 (m, 1H), 1.11 (d, J = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 199.4, 140.0, 136.8, 134.2, 132.6, 130.0, 129.4, 129.2, 128.9, 127.5, 126.4, 126.0, 122.7, 59.7, 35.4, 31.1, 20.0. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{17}H_{18}NS_2$: 300.0876; found: 300.0885. Significant IR band: $\nu_{(C=S)}$: 960 cm^{-1}.

Phenyl 2-methyl-3,4-dihydroquinoline-1(2H)-carbodithioate (4g)



By following the **GP**, the title compound **4g** was isolated as light-yellow oil (0.243 g, 81%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 50:1, R_f = 0.75). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 – 7.62 (m, 1H), 7.45 – 7.37 (m, 4H), 7.31 – 7.26 (m, 3H), 7.22 – 7.17 (m, 1H), 5.76 – 5.71 (m, 1H), 2.73 – 2.57 (m, 2H), 2.54 – 2.47 (m, 1H), 1.43 – 1.33 (m, 1H), 1.21 (d, J = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 198.9, 138.2, 137.2, 137.0, 132.5, 129.9, 129.4, 129.1, 128.1, 128.0, 127.6, 126.3, 122.7, 58.3, 33.1, 26.5, 20.0. HRMS (ESI) *m/z*: $[M+H]^+$ calculated for $C_{17}H_{18}NS_2$: 300.0876; found: 300.0875. Significant IR band: $\nu_{(C=S)}$: 957 cm^{-1}.

1-((phenylthio)carbonothioyl)-1, 2, 3,4-tetrahydroquinolin-6-yl 2-(6-methoxynaphthalen-2-yl) propanoate (4h)



By following the **GP**, the title compound **4h** was isolated as light-yellow oil (0.267 g, 52%) using silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 10:1, R_f = 0.48). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 – 7.72 (m, 4H), 7.50 – 7.48 (m, 2H), 7.40 – 7.38 (m, 1H), 7.26 (s, 4H), 7.17 – 7.14 (m, 2H), 6.81 – 6.77 (m, 1H), 4.09 – 4.05 (m, 1H), 3.92 (s, 3H), 3.84 – 3.81 (m, 2H), 2.76 – 2.73 (m, 2H), 2.03 – 1.97 (m, 2H), 1.68 (d, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 204.3, 173.4, 157.1, 144.7, 143.7, 136.7, 134.00, 133.98, 131.4, 134.0, 129.5, 129.21, 129.16, 129.1, 127.5, 126.3, 125.9, 121.9, 121.4, 119.3, 119.1, 116.0, 110.5, 105.8, 55.5, 45.7, 29.8, 27.1, 23.5, 18.7. HRMS (ESI) *m/z*: $[M+H]^+$calculated for $C_{30}H_{28}NO_3S_2$: 514.1506; found: 514.1505. Significant IR band: $\nu_{(C=S)}$: 963 cm^{-1}.

8. ^{1}H, ^{13}C and ^{19}F NMR spectra of the products

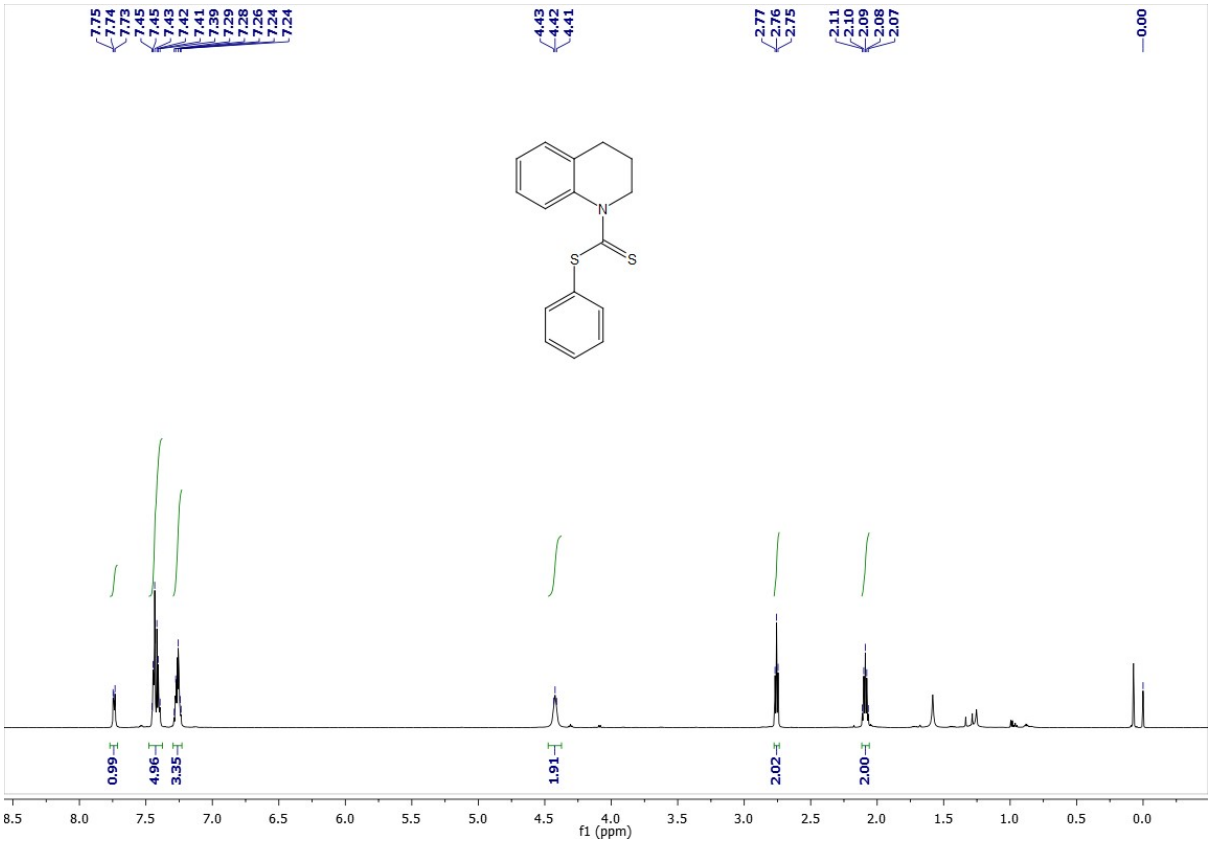


Figure S1: ^{1}H NMR Spectrum of **3a** ($CDCl_3$, 600 MHz, 298 K)

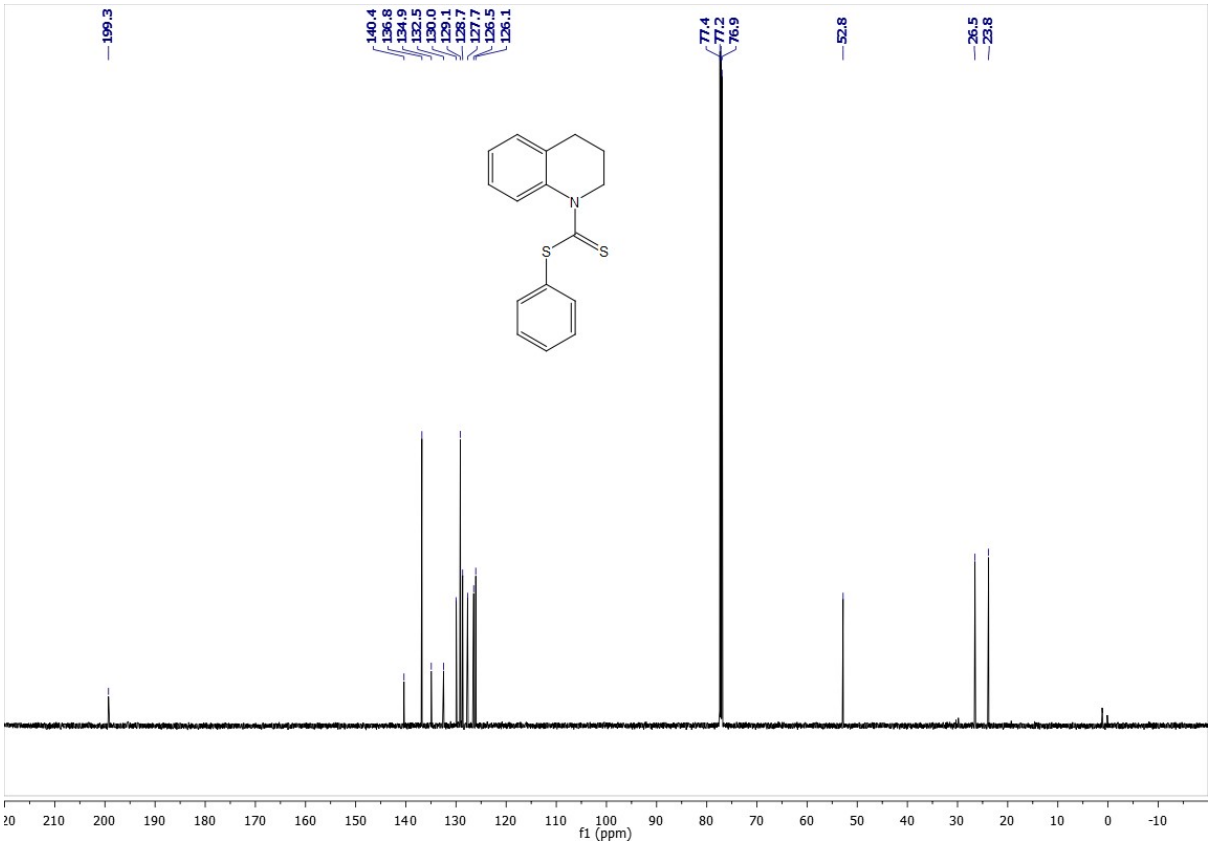


Figure S2: ^{13}C {^{1}H} NMR Spectrum of **3a** ($CDCl_3$, 151 MHz, 298 K)

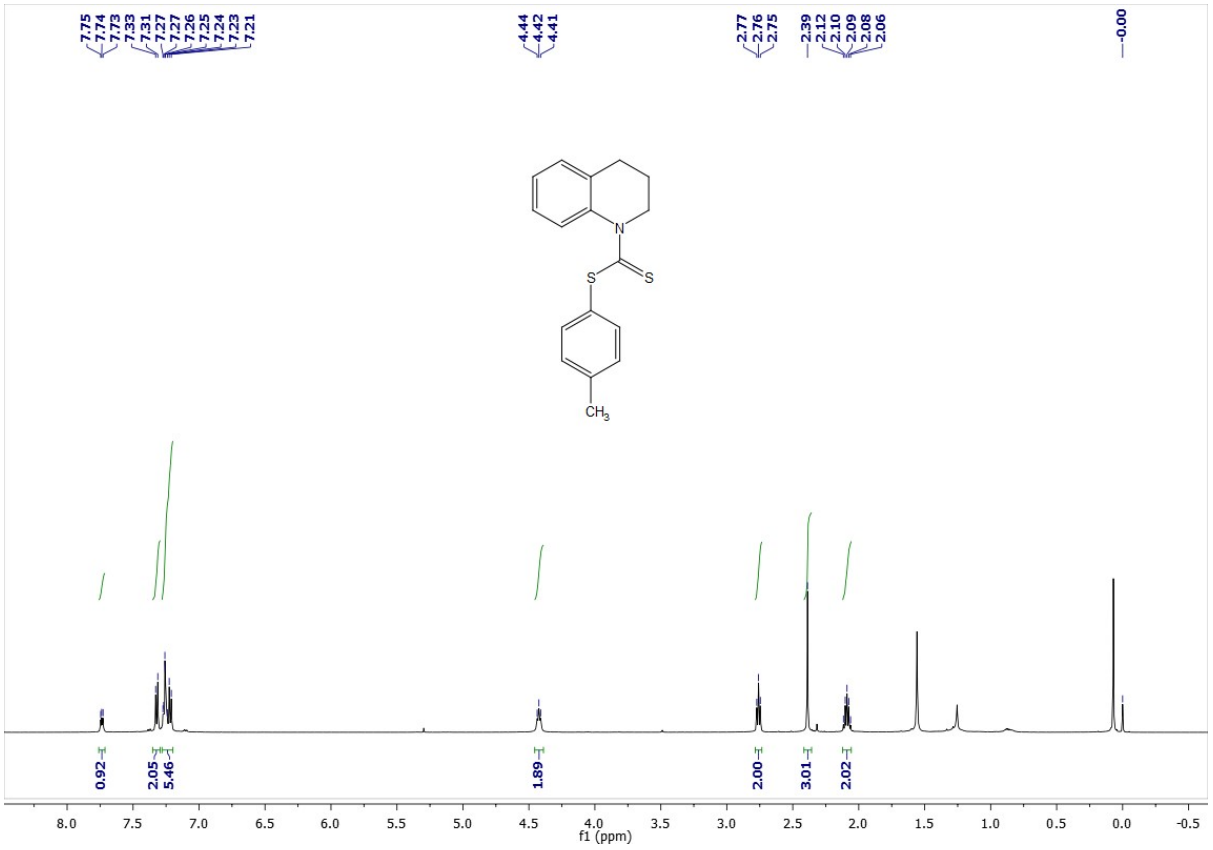


Figure S3: ^{1}H NMR Spectrum of **3b** ($CDCl_3$, 500 MHz, 298 K)

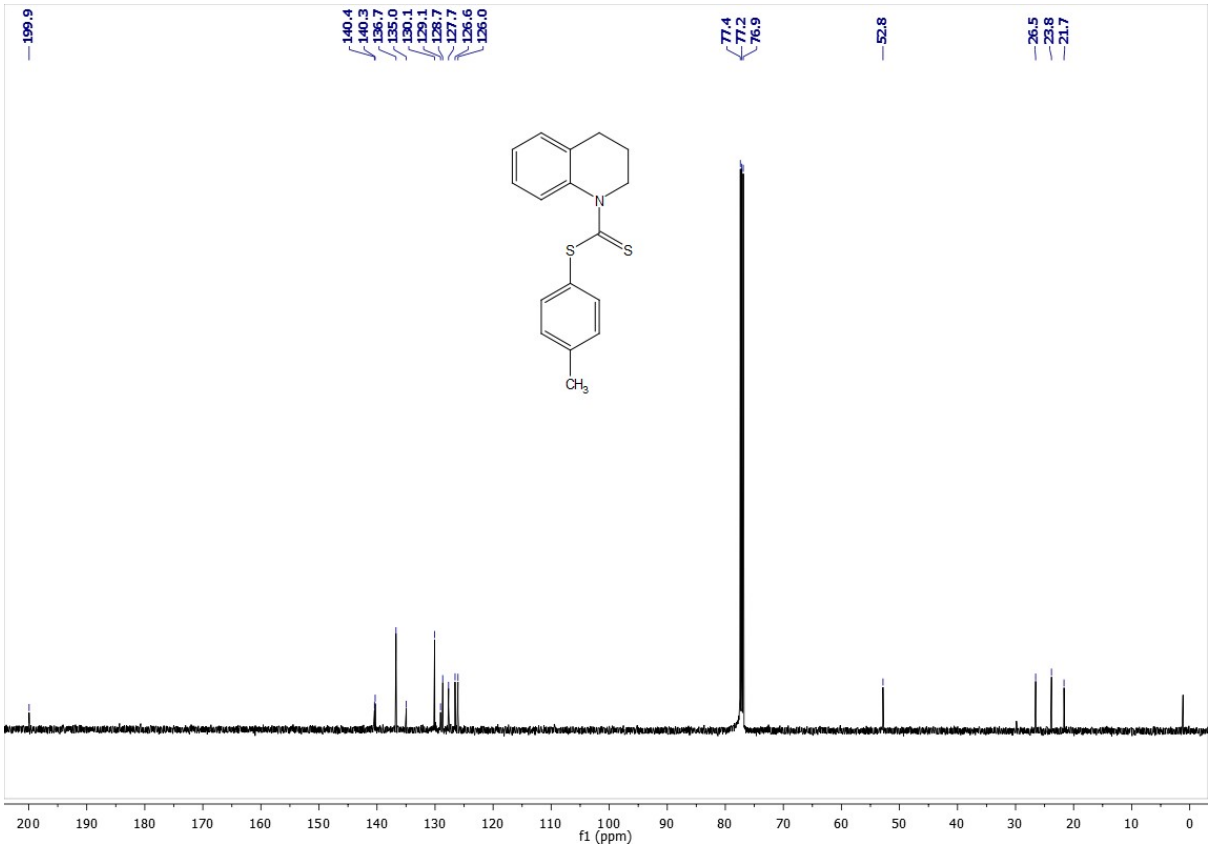


Figure S4: ^{13}C {^{1}H} NMR Spectrum of **3b** ($CDCl_3$, 126 MHz, 298 K)

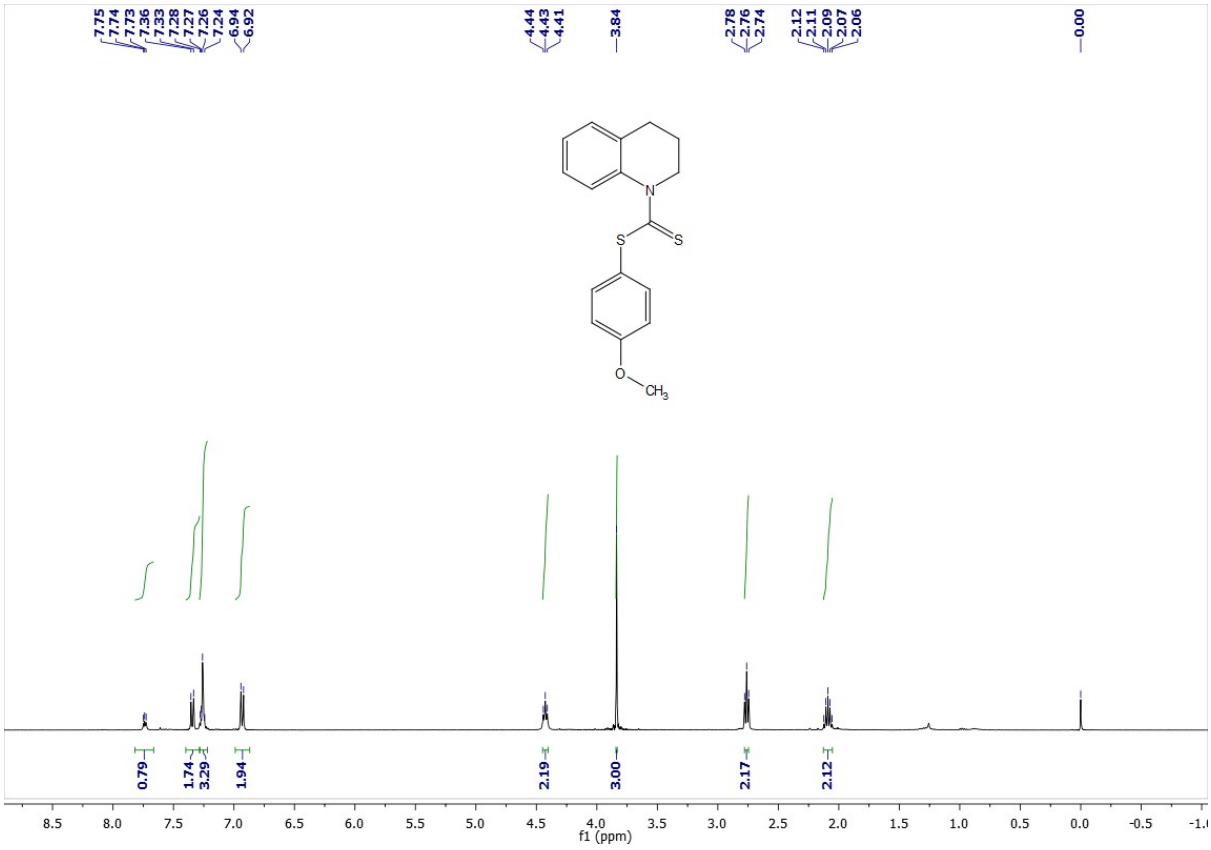


Figure S5: ^{1}H NMR Spectrum of **3c** ($CDCl_3$, 400 MHz, 298 K)

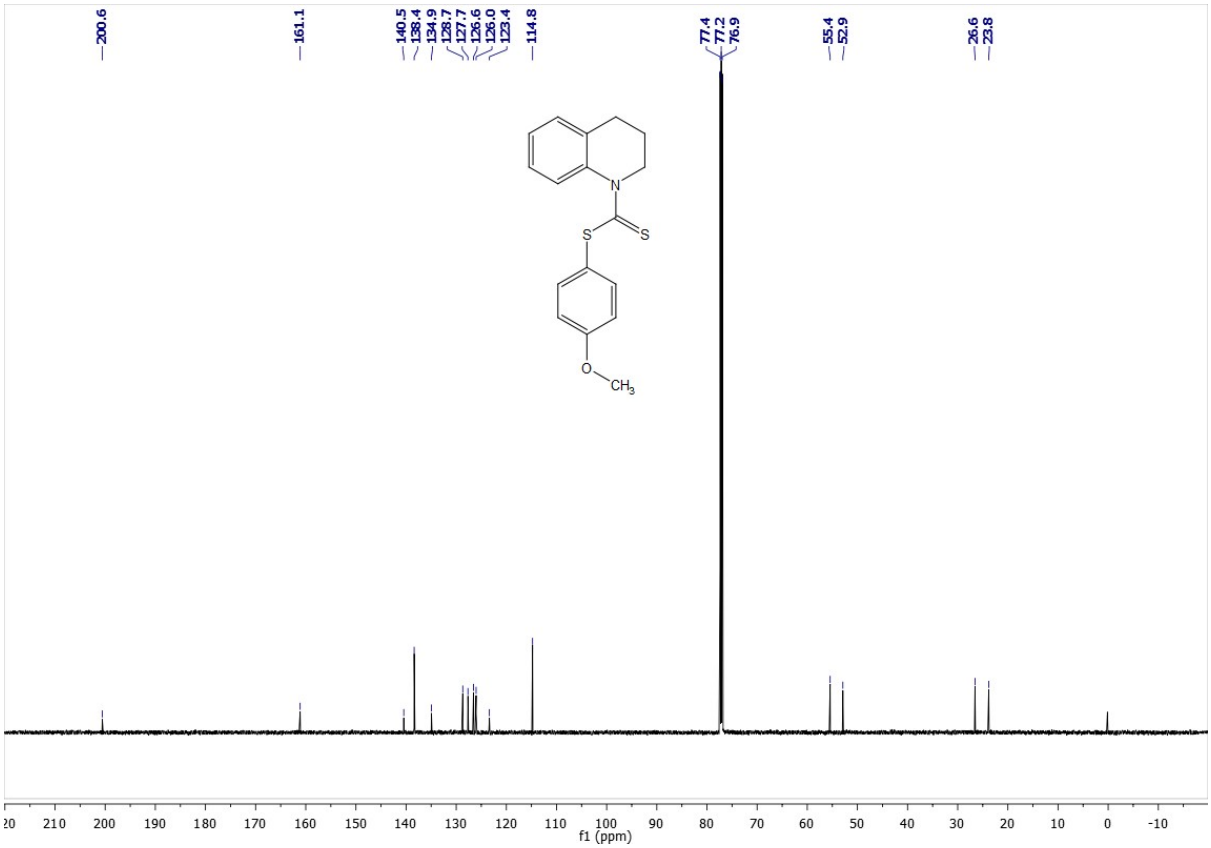


Figure S6: ^{13}C $\{^{1}H\}$ NMR Spectrum of **3c** ($CDCl_3$, 151 MHz, 298 K)

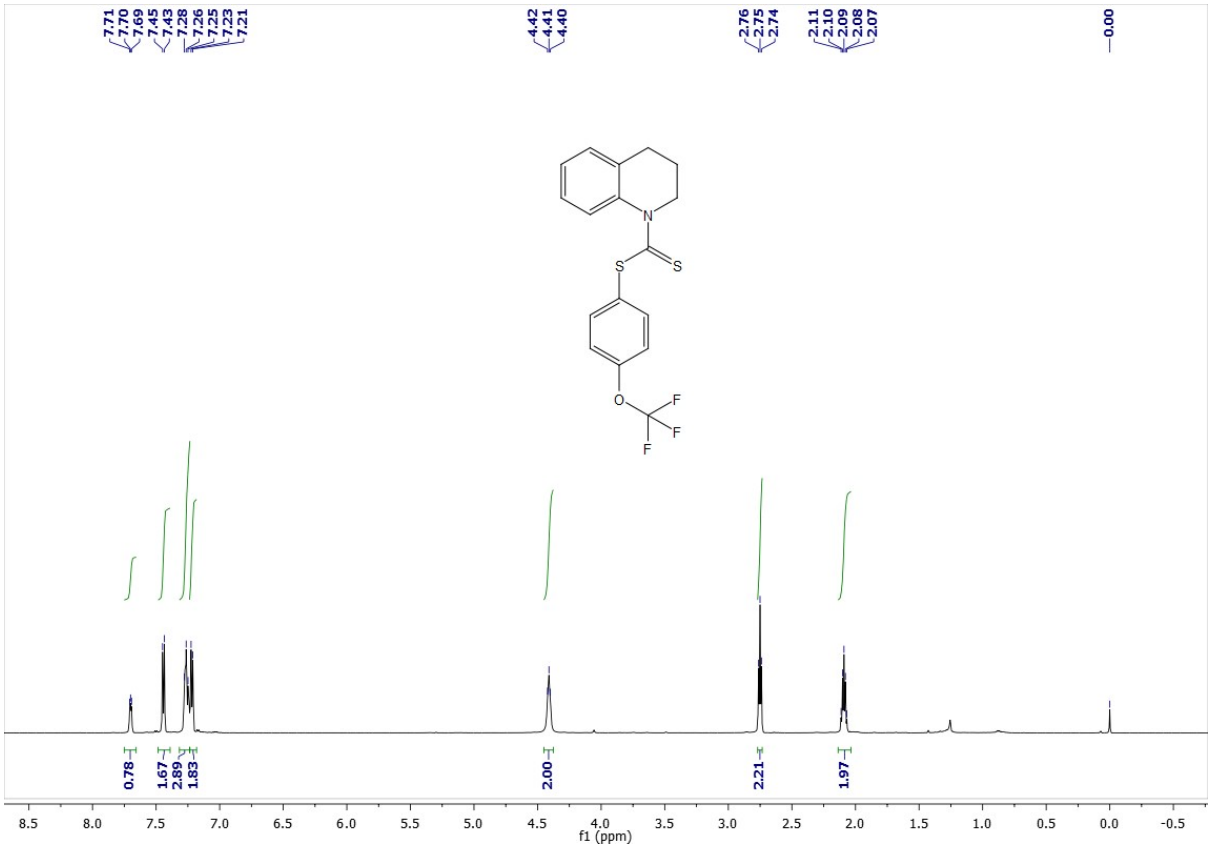


Figure S7: ^{1}H NMR Spectrum of **3d** ($CDCl_3$, 600 MHz, 298 K)

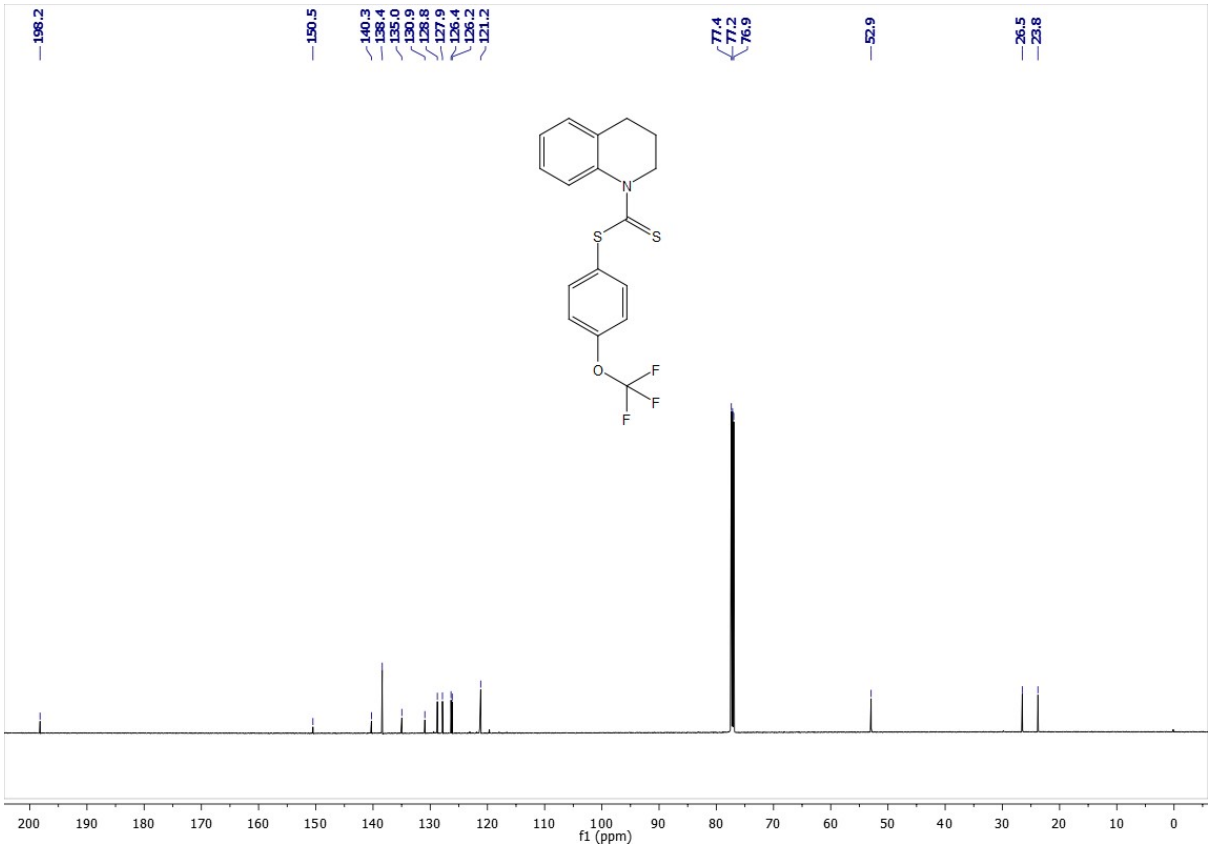


Figure S8: ^{13}C {^{1}H} NMR Spectrum of **3d** ($CDCl_3$, 151 MHz, 298 K)

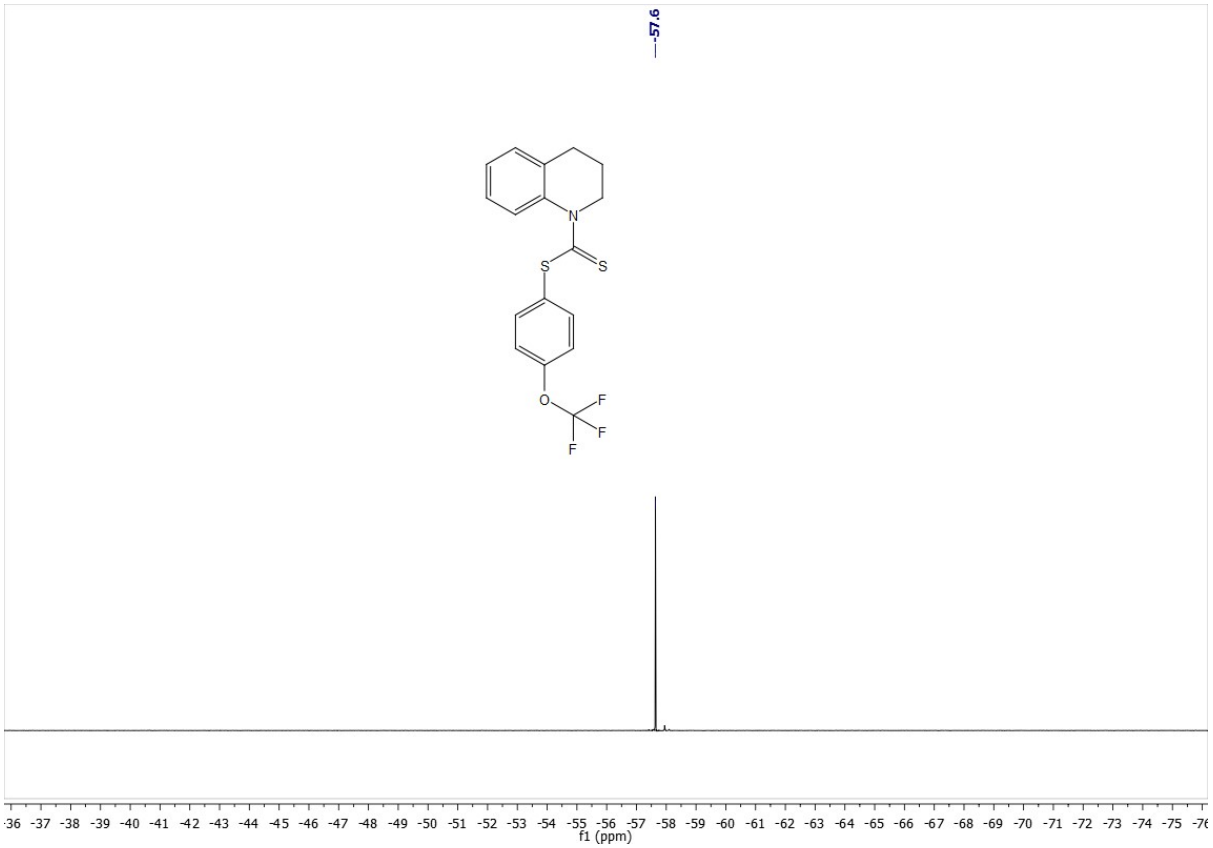


Figure S9: ^{19}F $\{^{1}H\}$ NMR Spectrum of **3d** ($CDCl_3$, 377 MHz, 298 K)

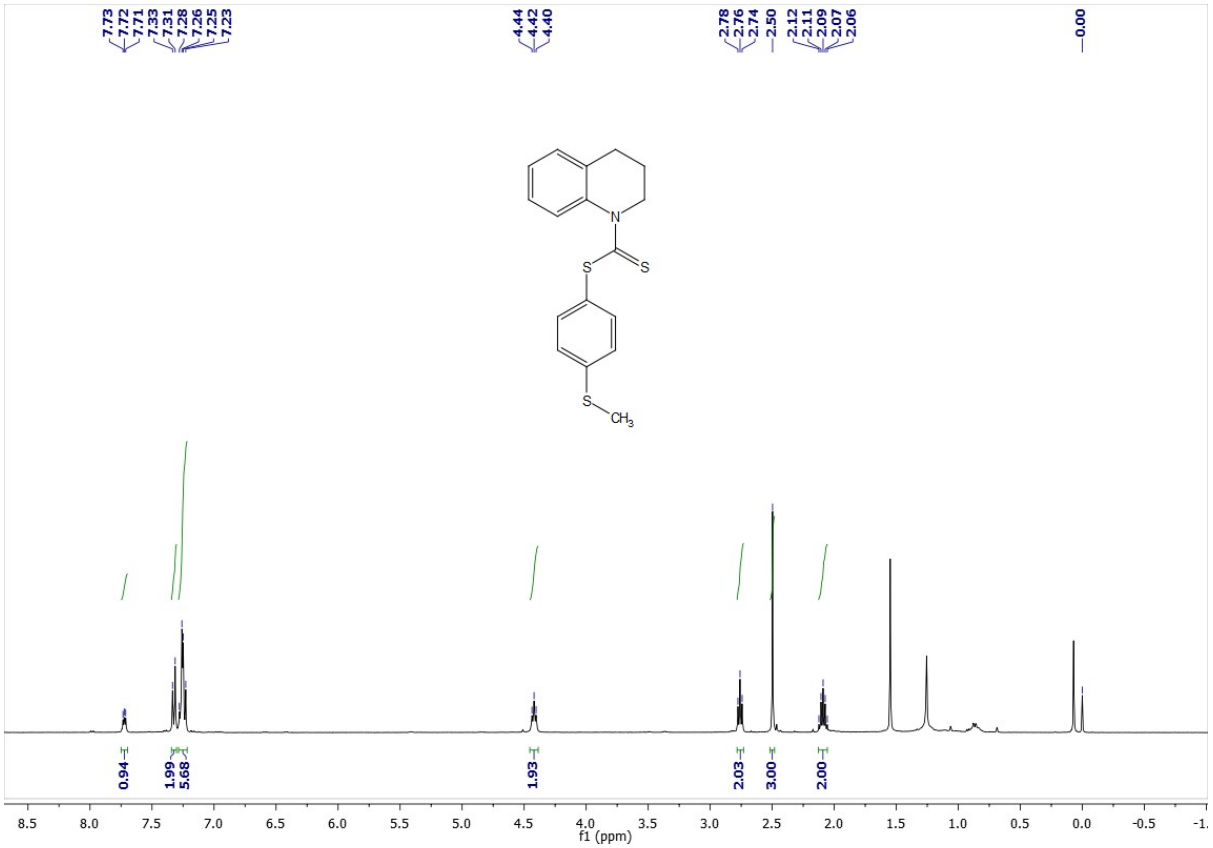


Figure S10: ^{1}H NMR Spectrum of **3e** ($CDCl_3$, 400 MHz, 298 K)

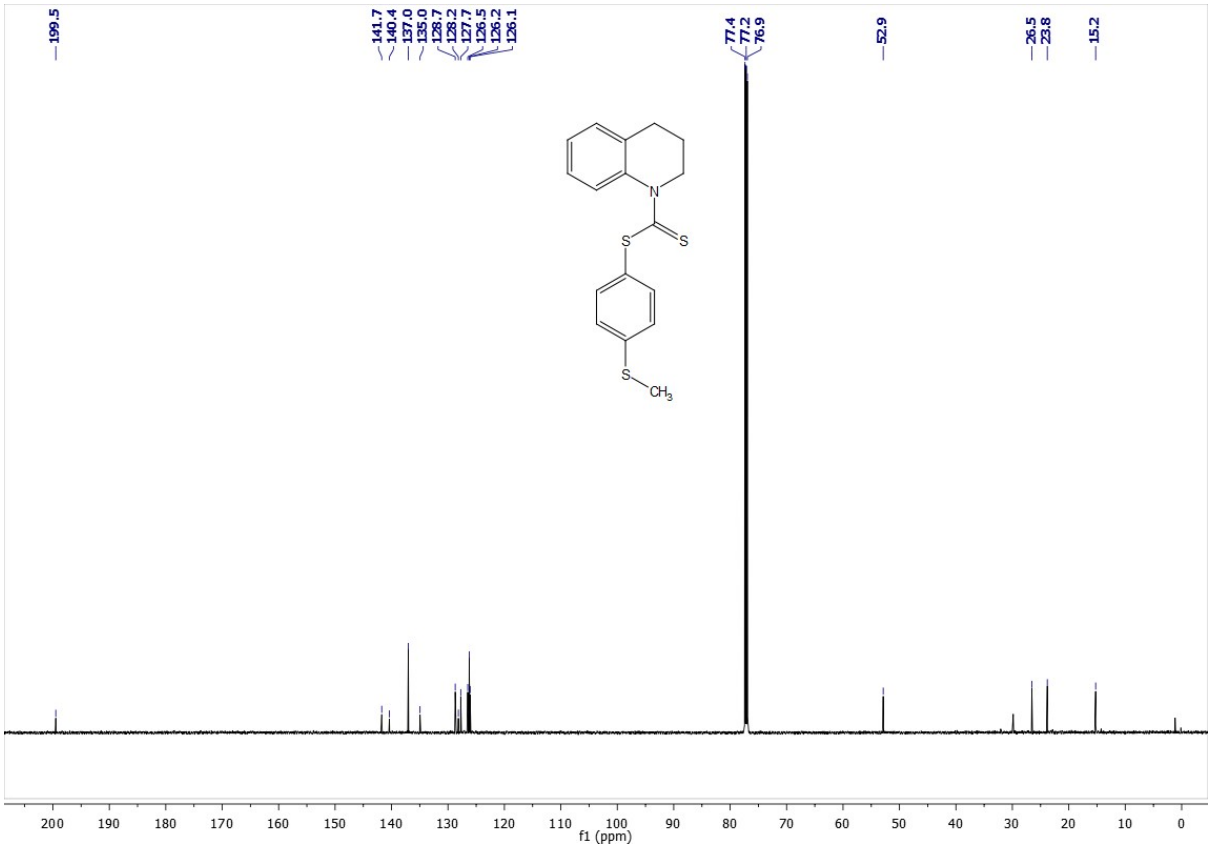


Figure S11: ^{13}C {^{1}H} NMR Spectrum of **3e** ($CDCl_3$, 151 MHz, 298 K)

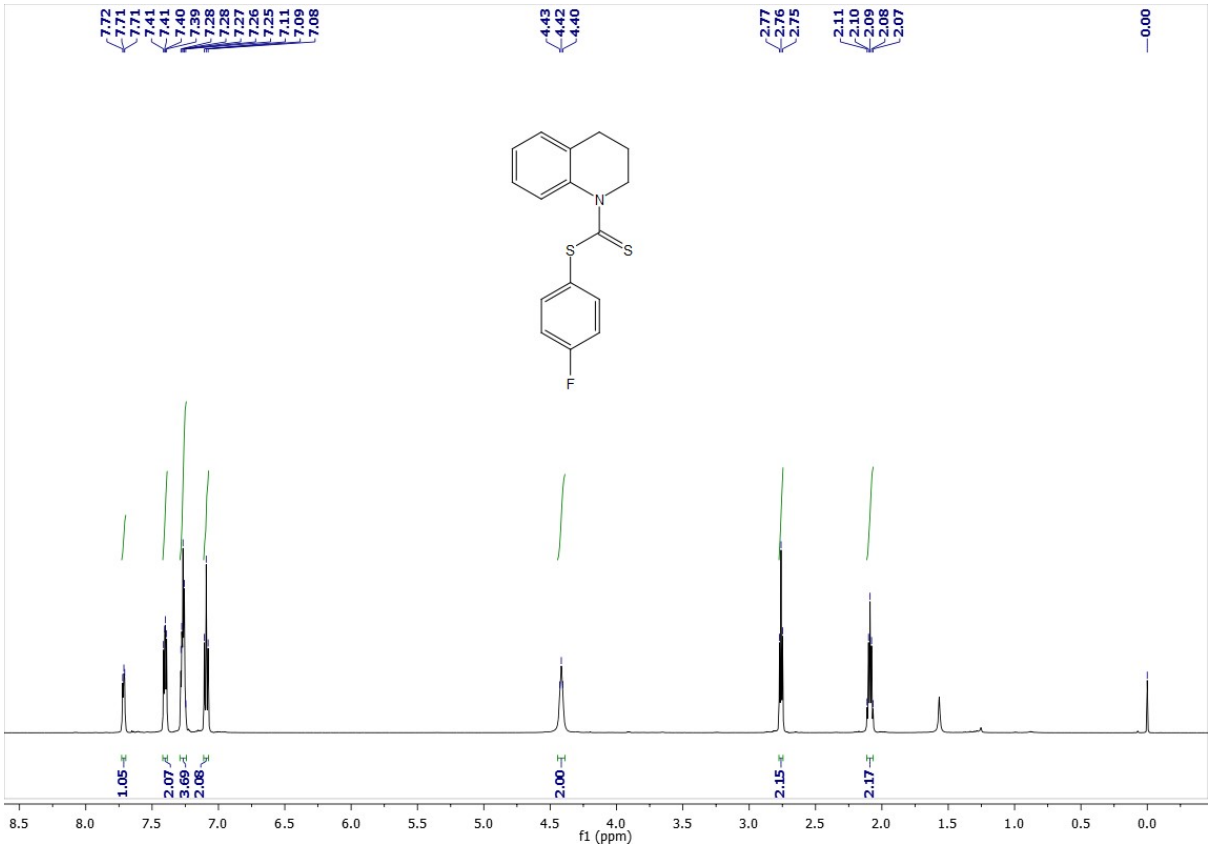


Figure S12: ^{1}H NMR Spectrum of **3f** ($CDCl_3$, 600 MHz, 298 K)

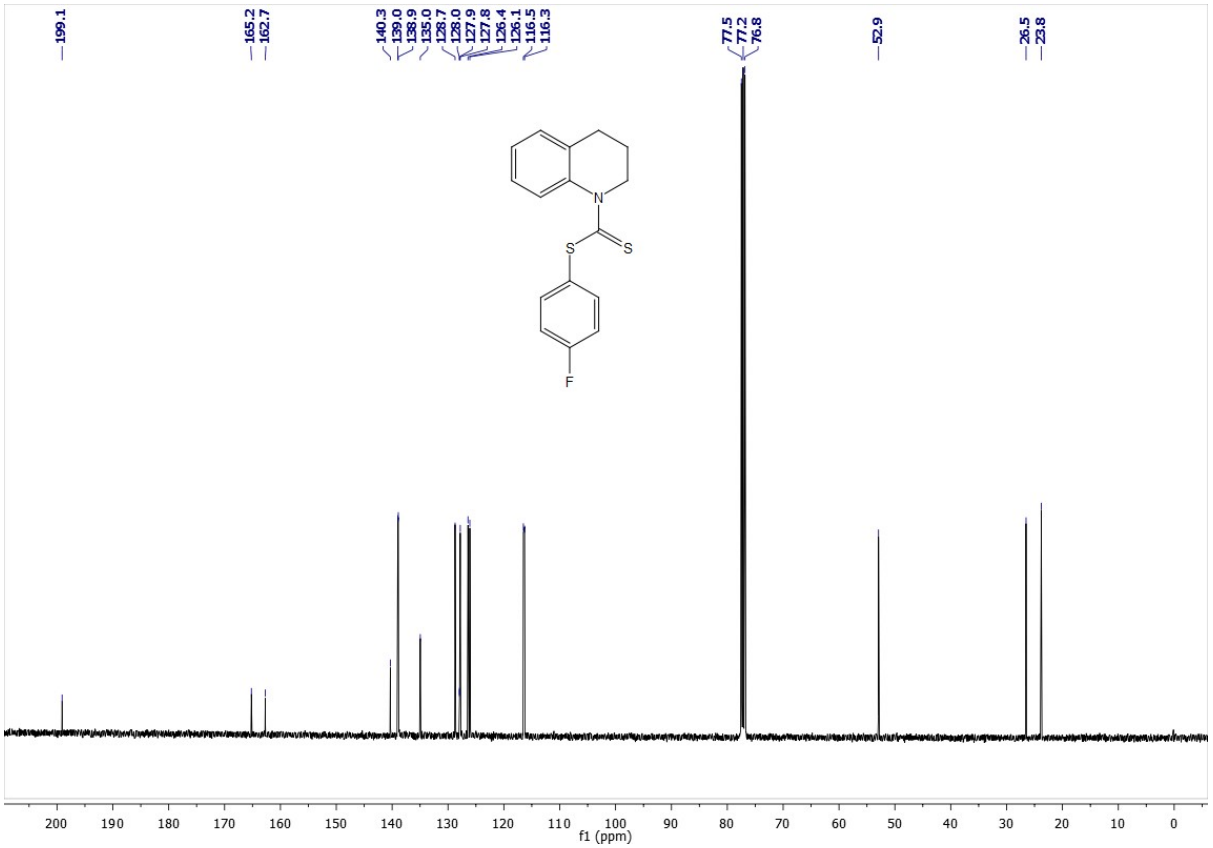


Figure S13: ^{13}C $\{^{1}H\}$ NMR Spectrum of **3f** ($CDCl_3$, 101 MHz, 298 K)

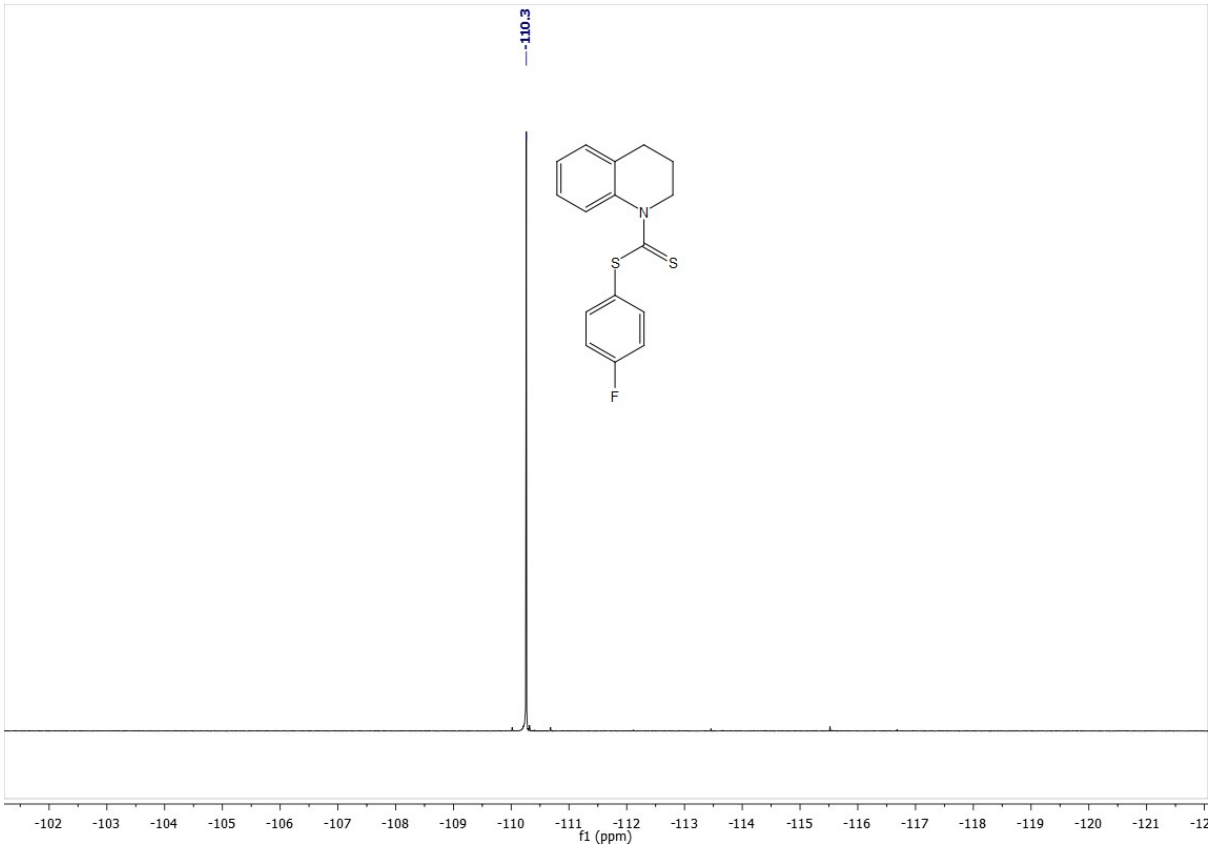


Figure S14: ^{19}F $\{^{1}H\}$ NMR Spectrum of **3f** ($CDCl_3$, 377 MHz, 298 K)

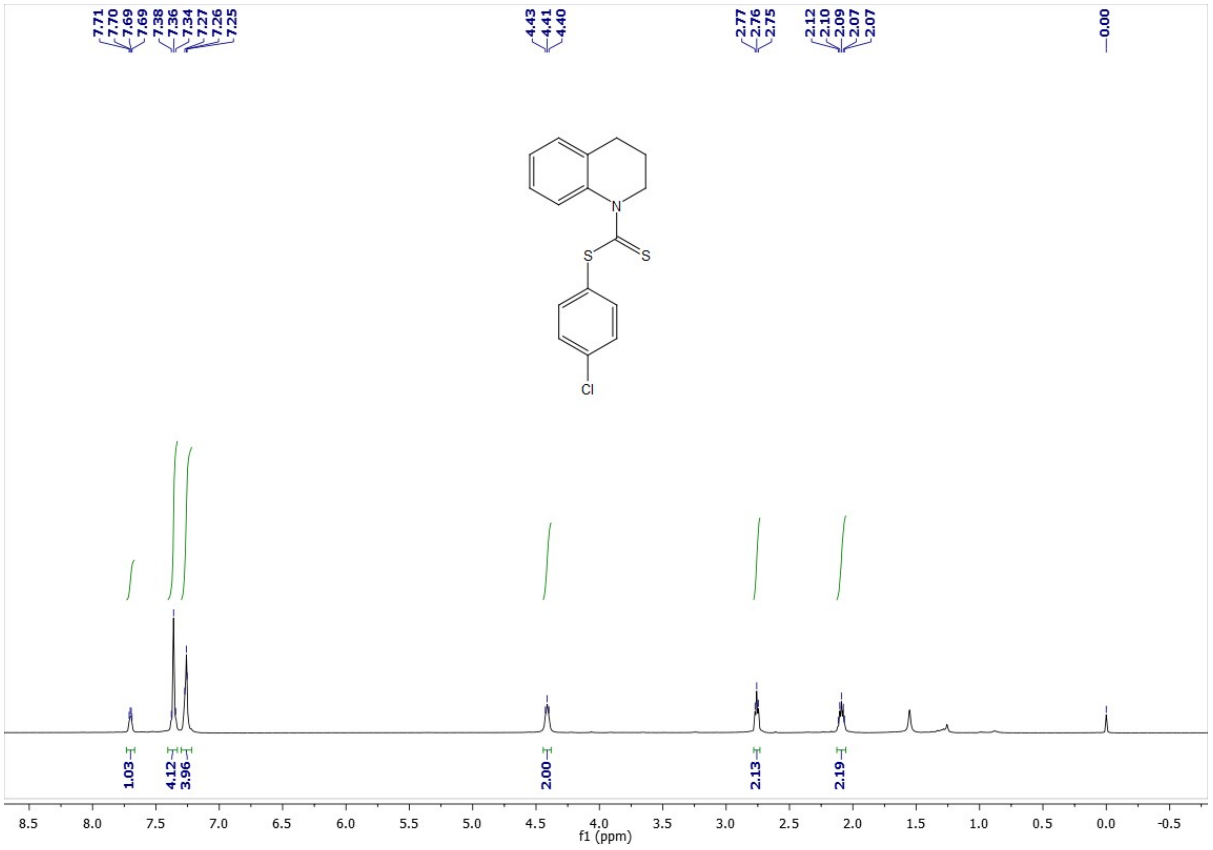


Figure S15: ^{1}H NMR Spectrum of **3g** ($CDCl_3$, 500 MHz, 298 K)

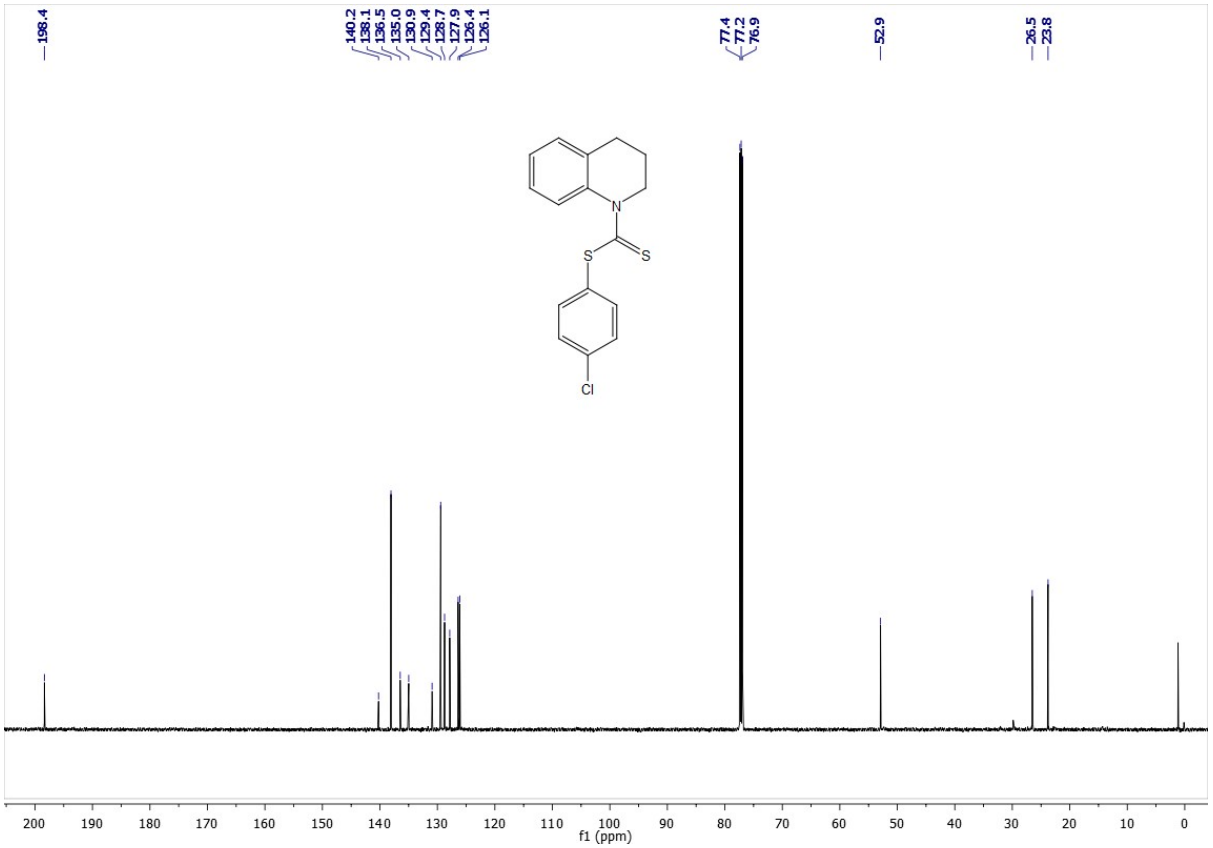


Figure S16: ^{13}C $\{^{1}H\}$ NMR Spectrum of **3g** ($CDCl_3$, 151 MHz, 298 K)

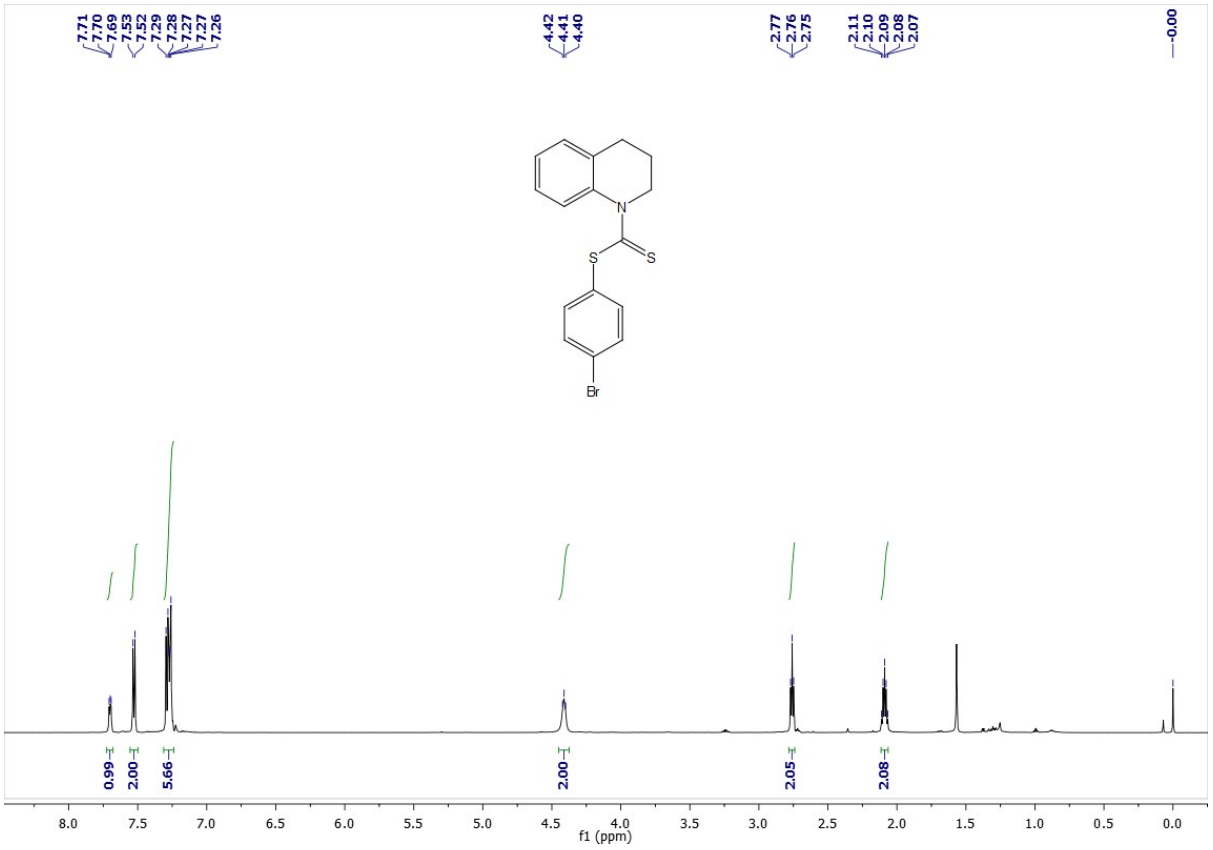


Figure S17: ^{1}H NMR Spectrum of **3h** ($CDCl_3$, 600 MHz, 298 K)

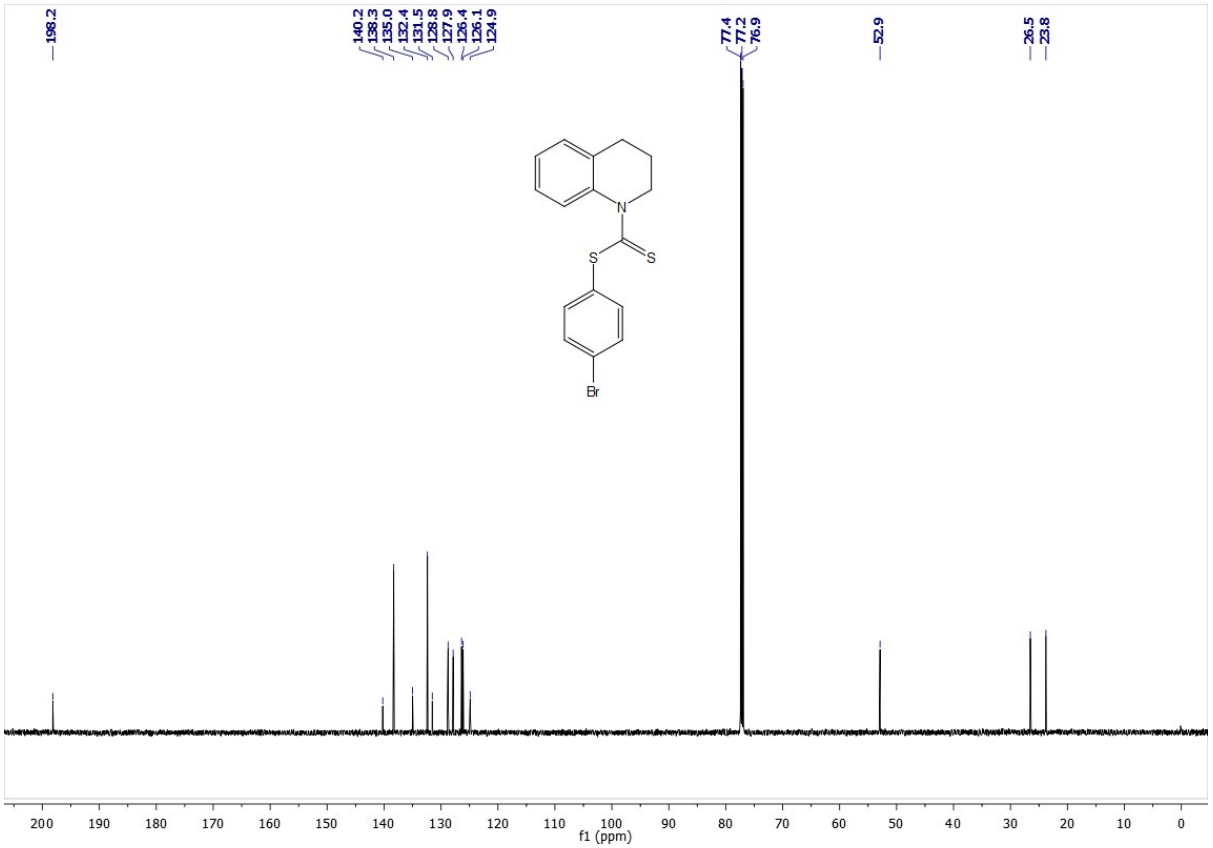


Figure S18: ^{13}C {^{1}H} NMR Spectrum of **3h** ($CDCl_3$, 151 MHz, 298 K)

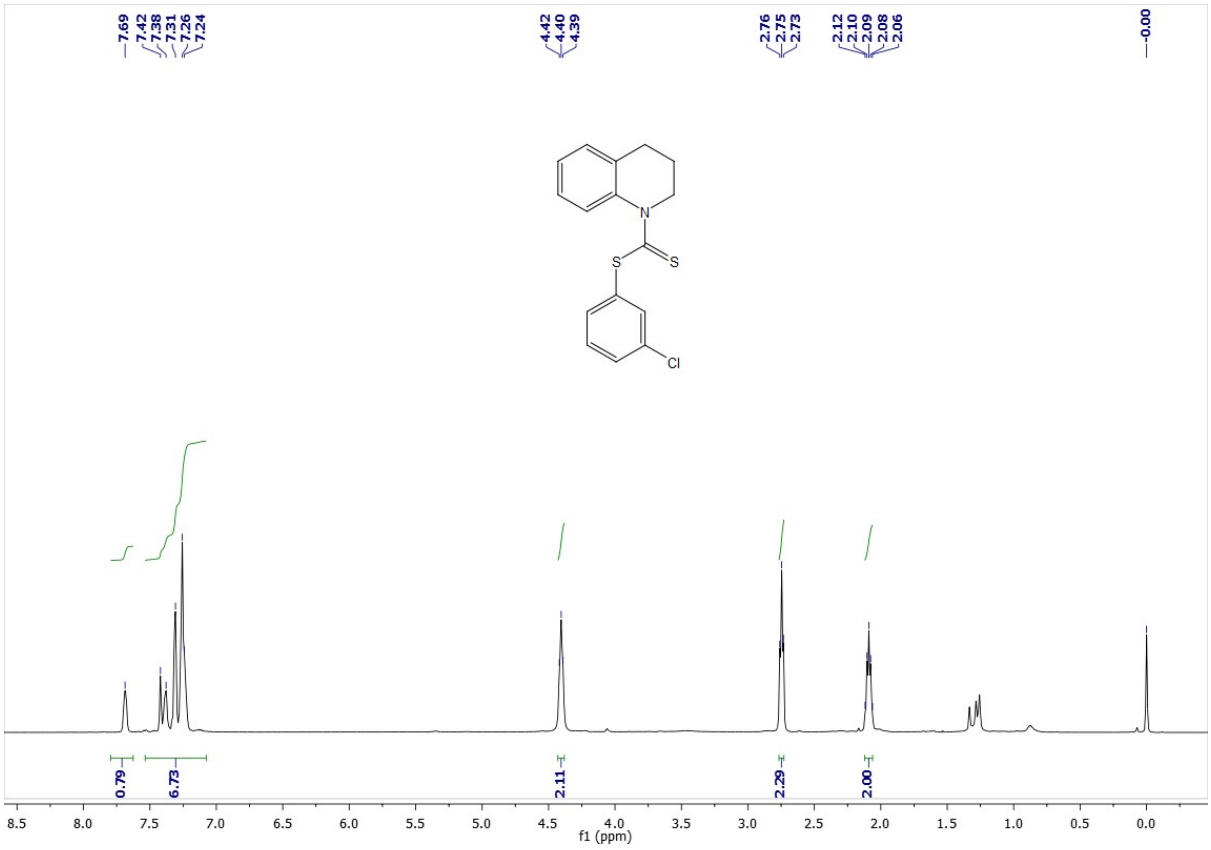


Figure S19: ^{1}H NMR Spectrum of **3i** ($CDCl_3$, 500 MHz, 298 K)

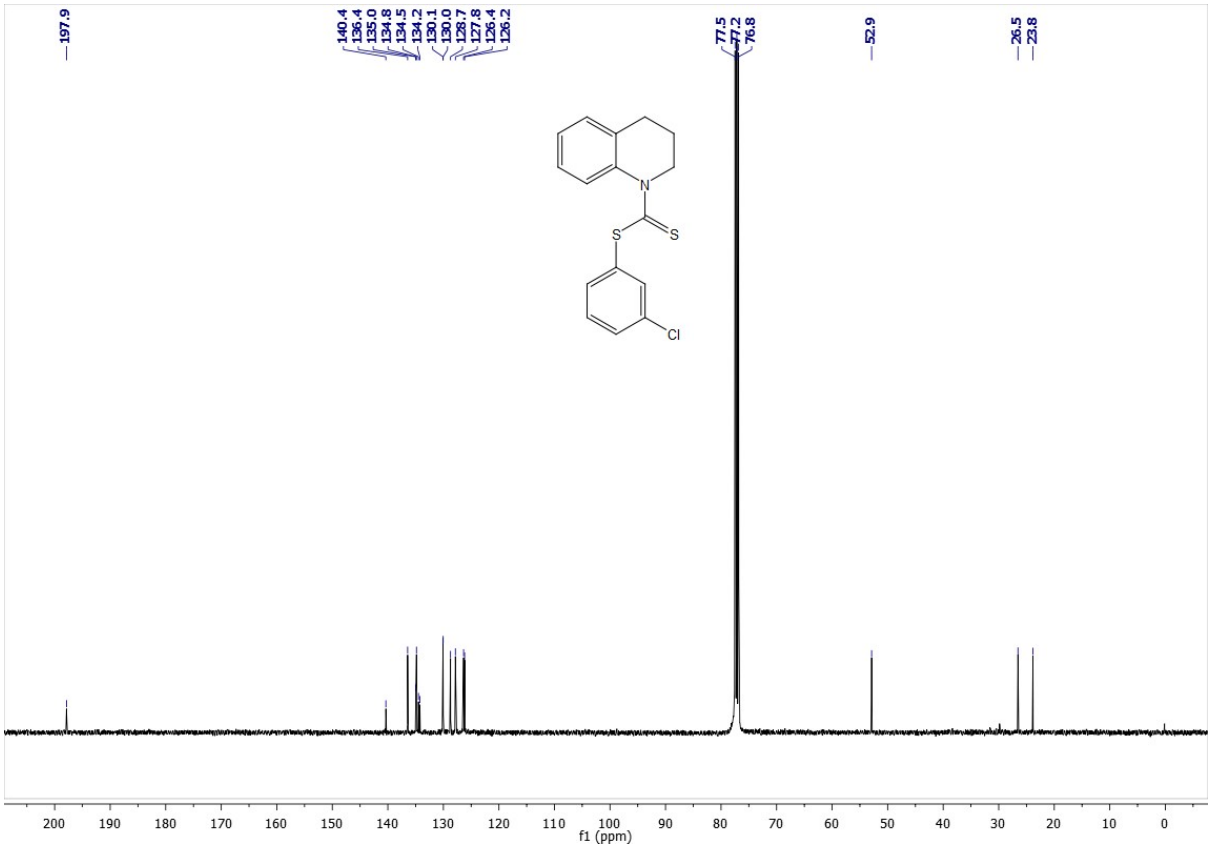


Figure S20: ^{13}C $\{^{1}H\}$ NMR Spectrum of **3i** ($CDCl_3$, 101 MHz, 298 K)

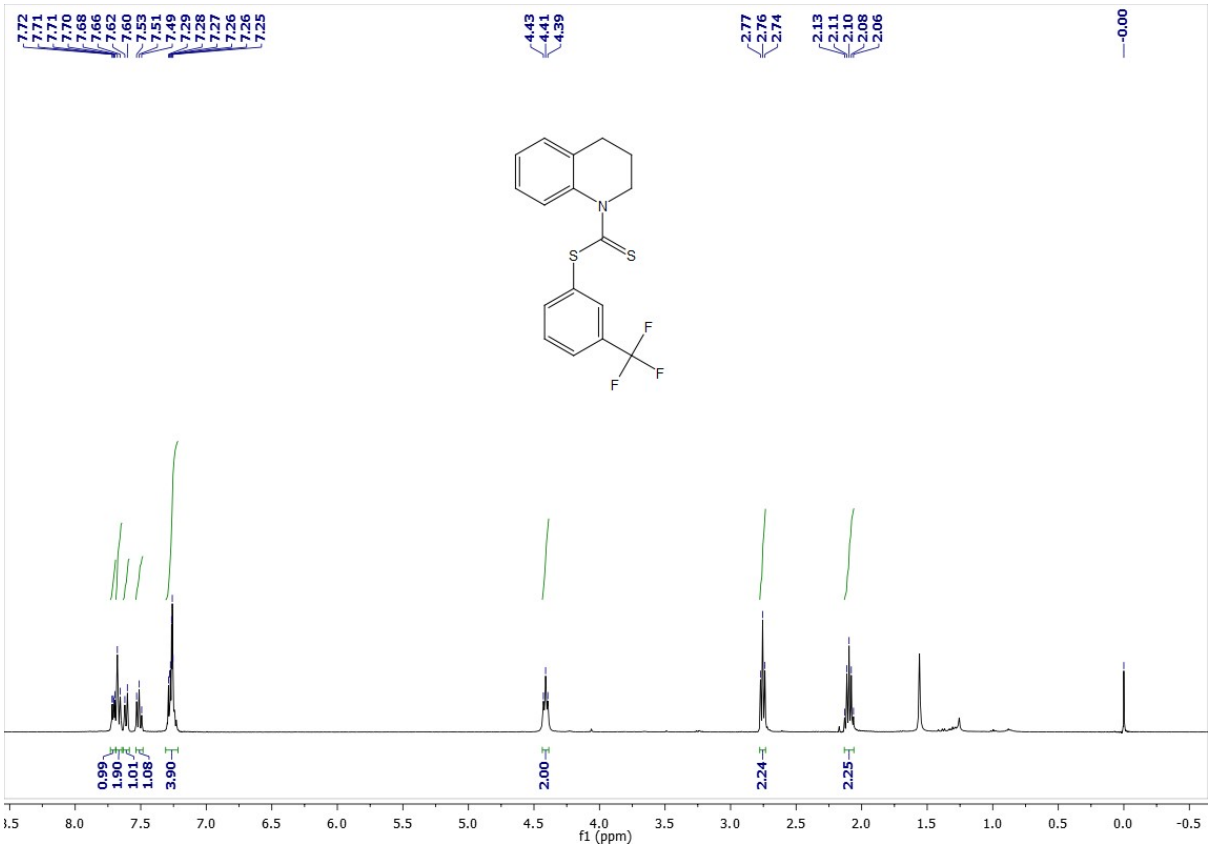


Figure S21: ^{1}H NMR Spectrum of **3j** ($CDCl_3$, 400 MHz, 298 K)

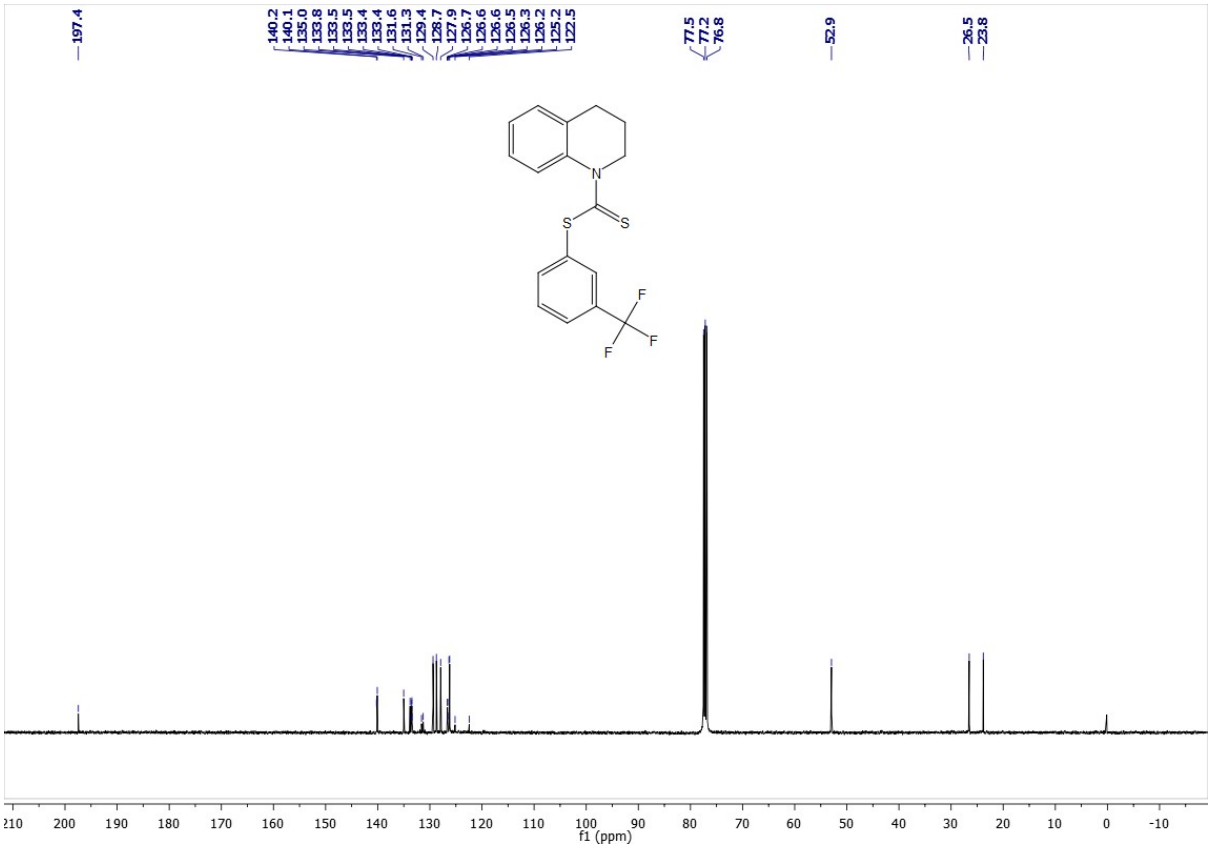


Figure S22: ^{13}C {^{1}H} NMR Spectrum of **3j** ($CDCl_3$, 101 MHz, 298 K)

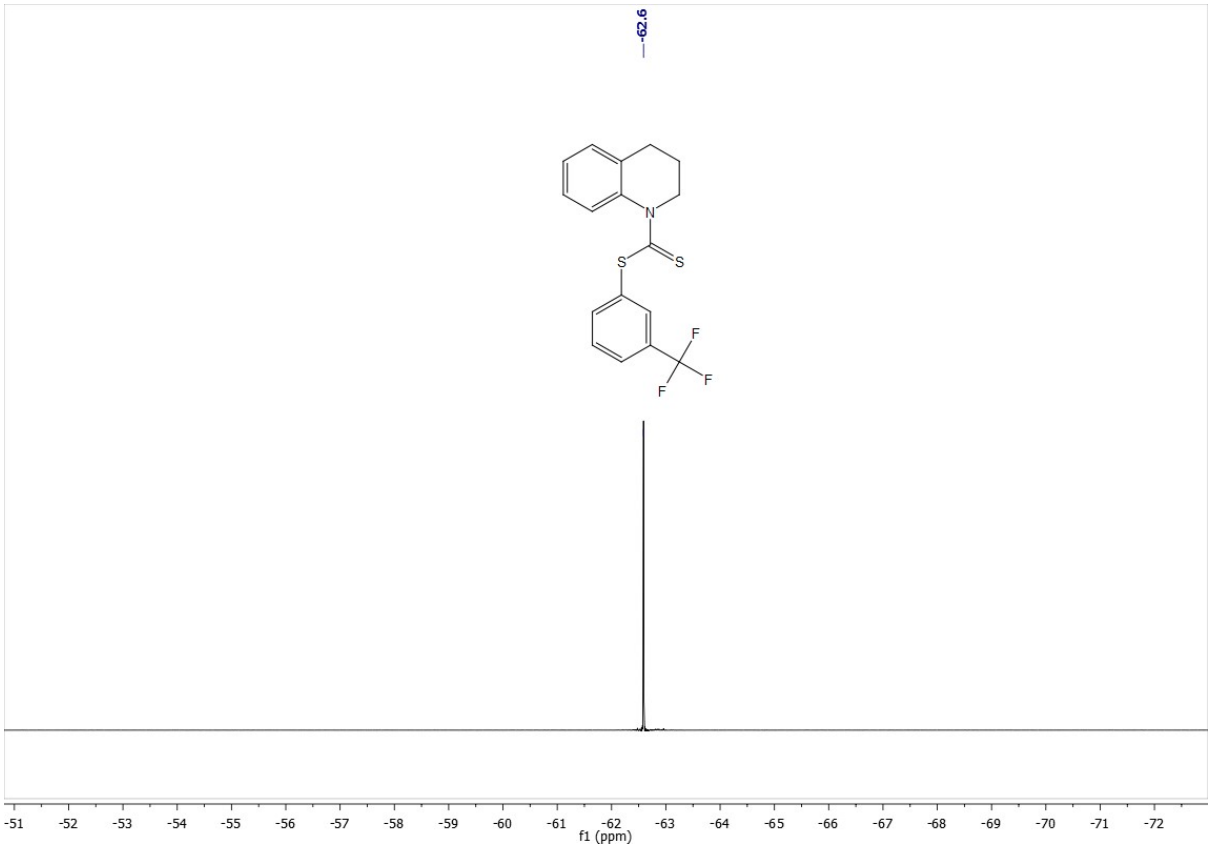


Figure S23: ^{19}F {^{1}H} NMR Spectrum of **3j** ($CDCl_3$, 565 MHz, 298 K)

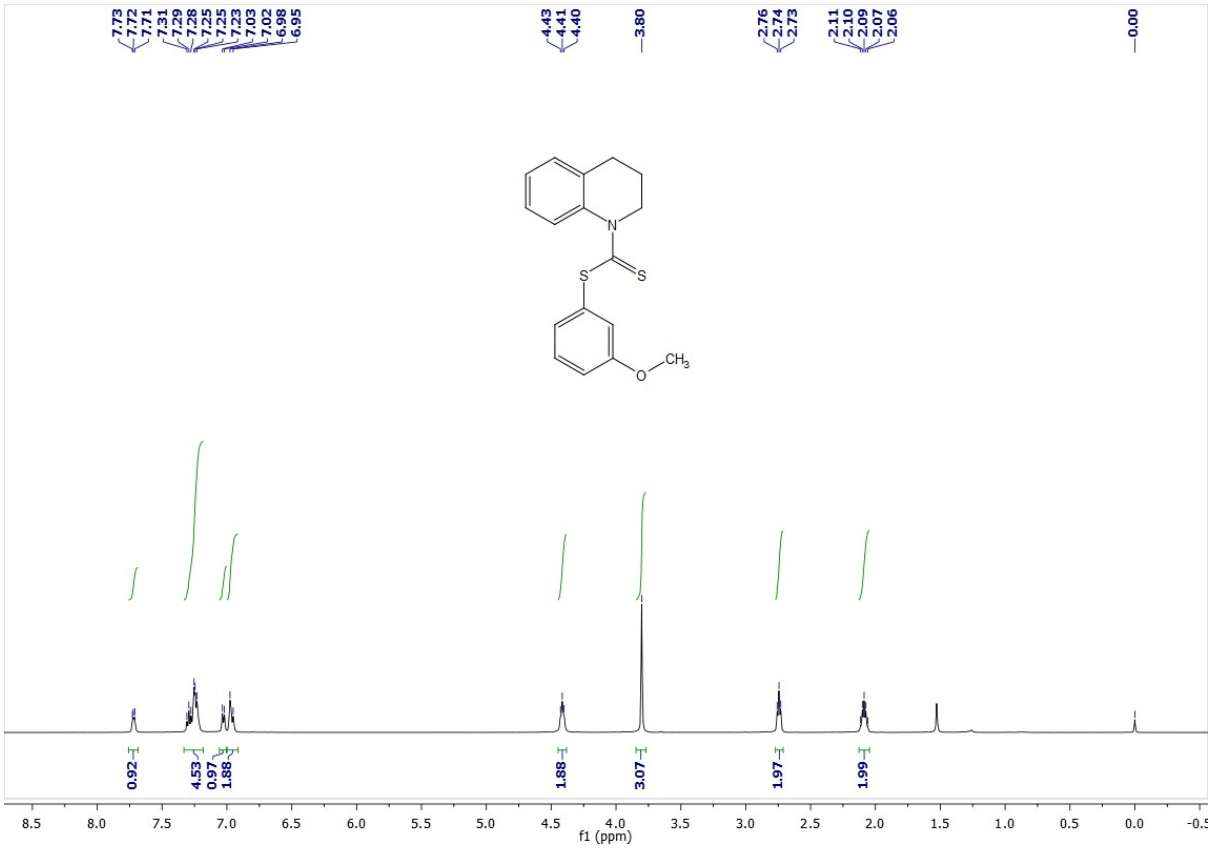


Figure S24: ^{1}H NMR Spectrum of **3k** ($CDCl_3$, 500 MHz, 298 K)

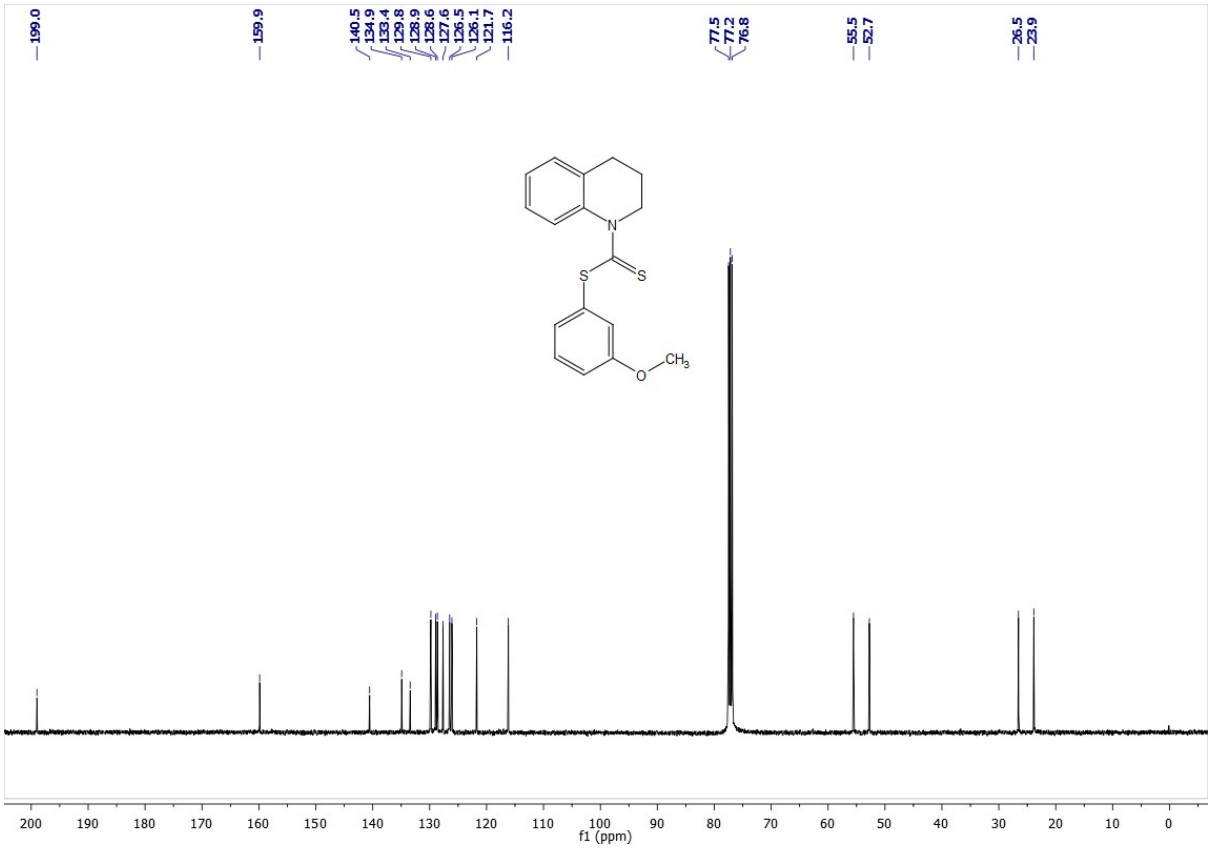


Figure S25: ^{13}C {^{1}H} NMR Spectrum of **3k** ($CDCl_3$, 101 MHz, 298 K)

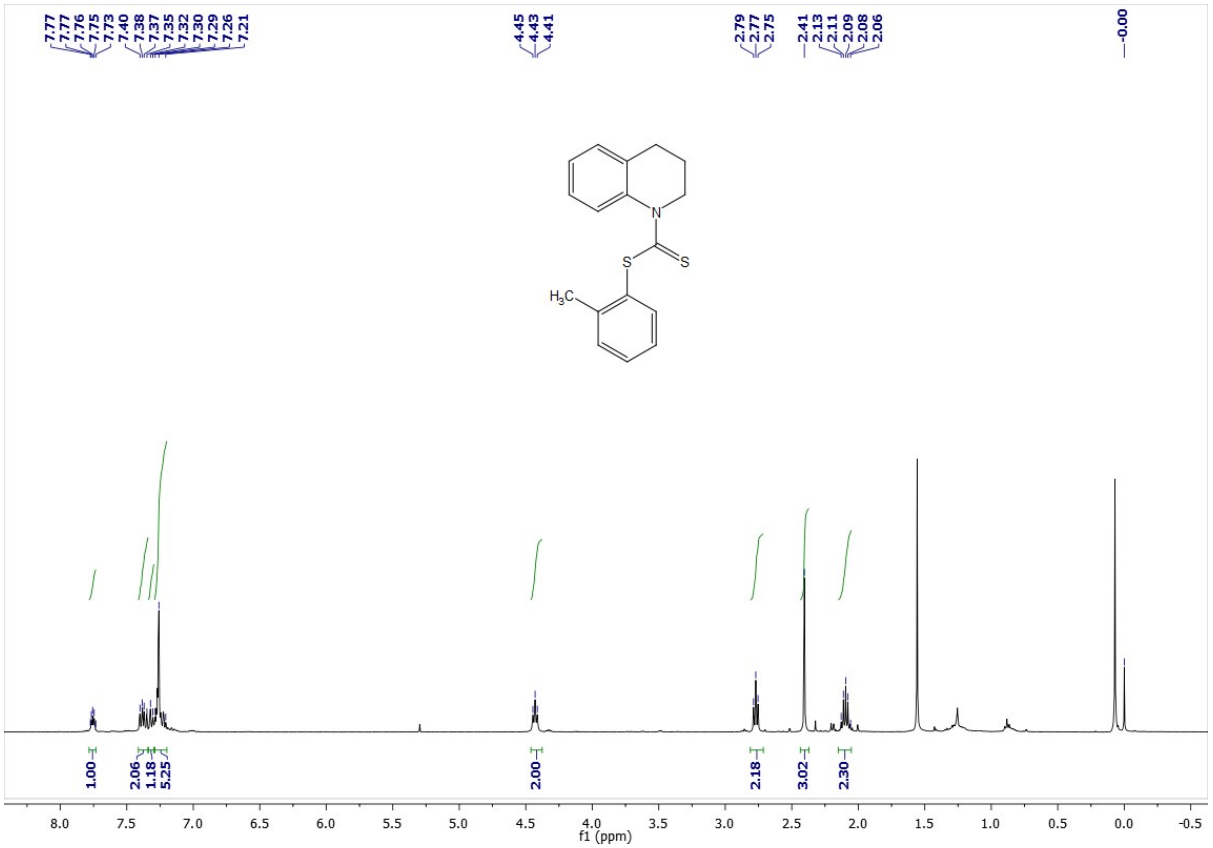


Figure S26: ^{1}H NMR Spectrum of **3l** ($CDCl_3$, 400 MHz, 298 K)

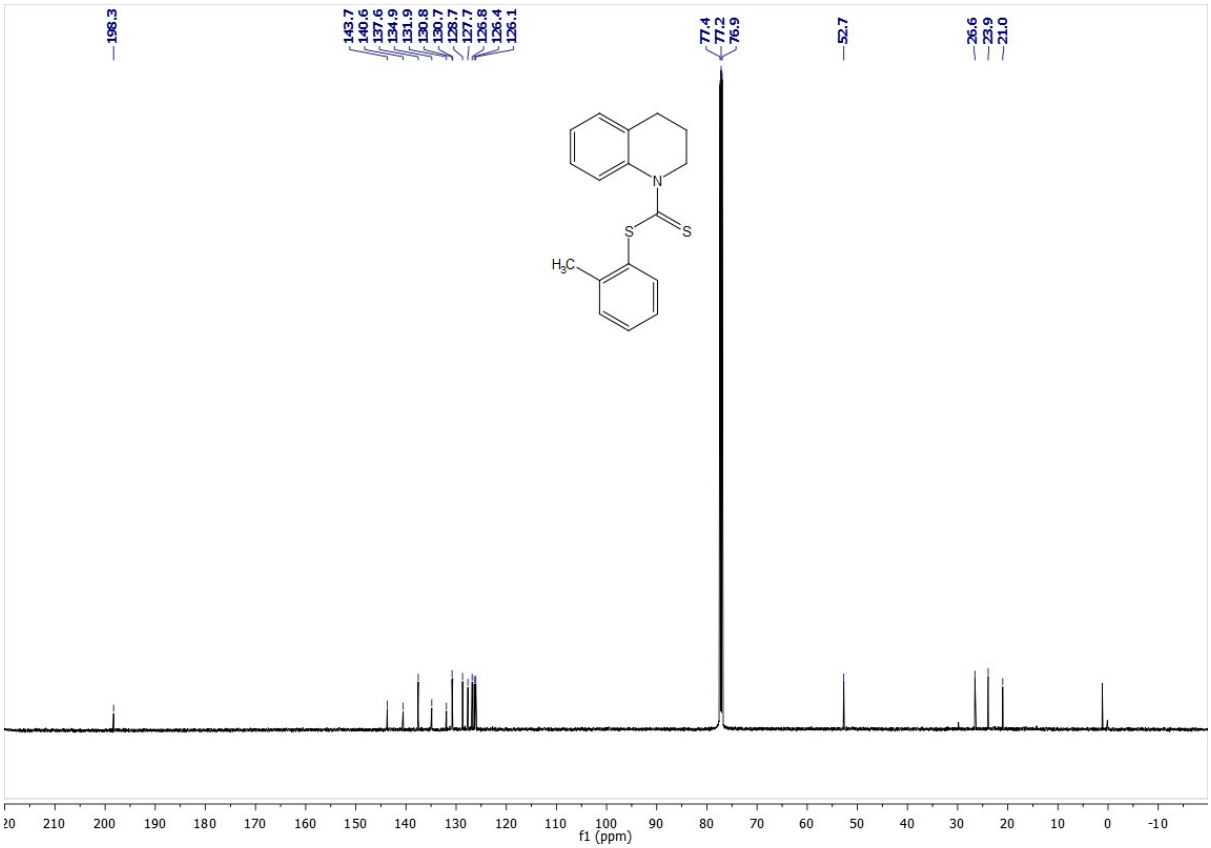


Figure S27: ^{13}C {^{1}H} NMR Spectrum of **3l** ($CDCl_3$, 151 MHz, 298 K)

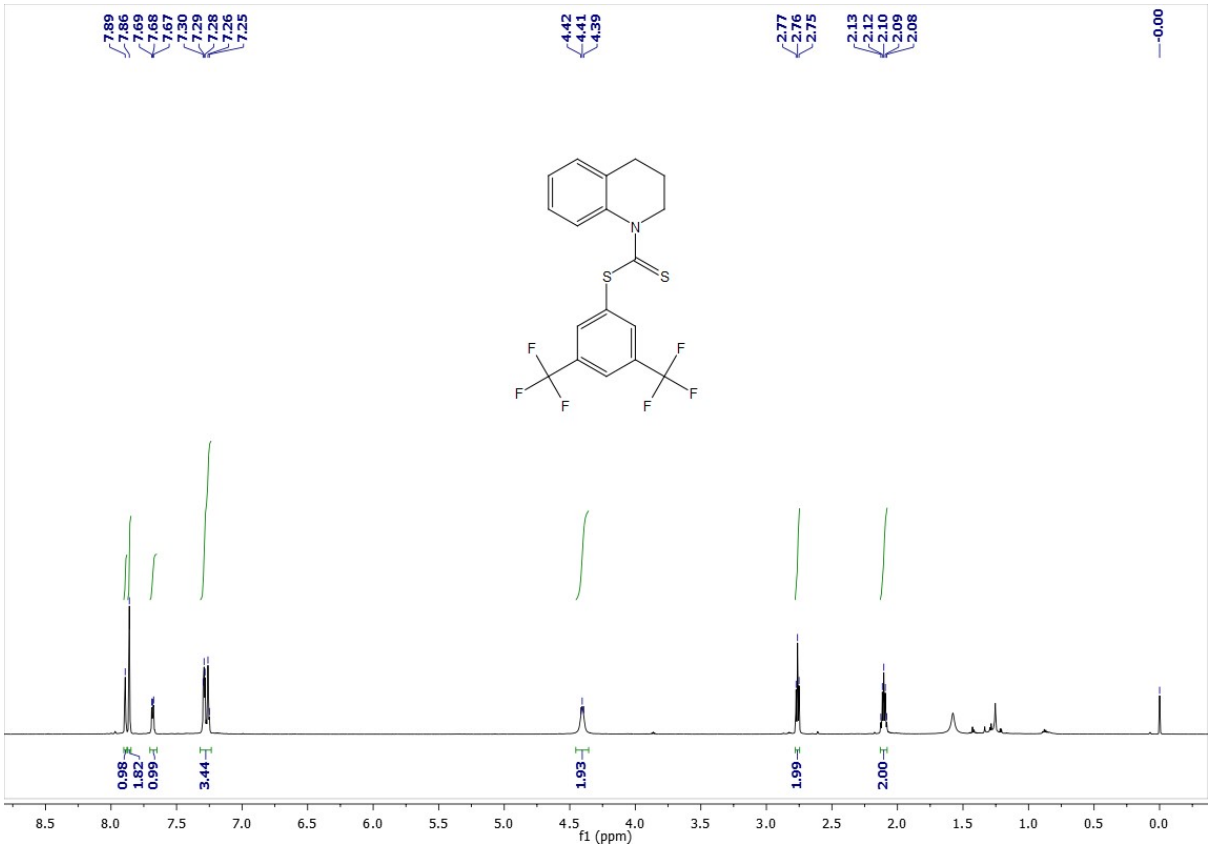


Figure S28: ^{1}H NMR Spectrum of **3m** ($CDCl_3$, 600 MHz, 298 K)

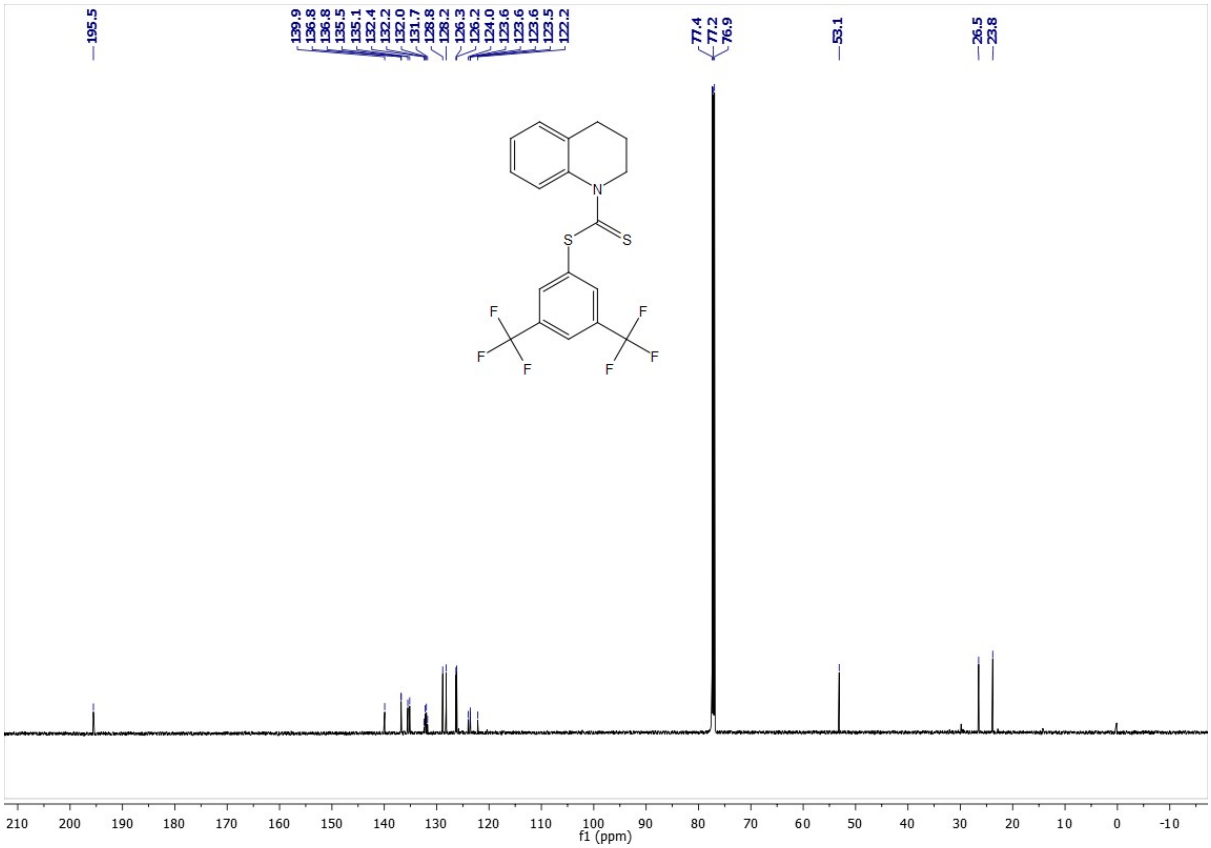


Figure S29: ^{13}C {^{1}H} NMR Spectrum of **3m** ($CDCl_3$, 151 MHz, 298 K)

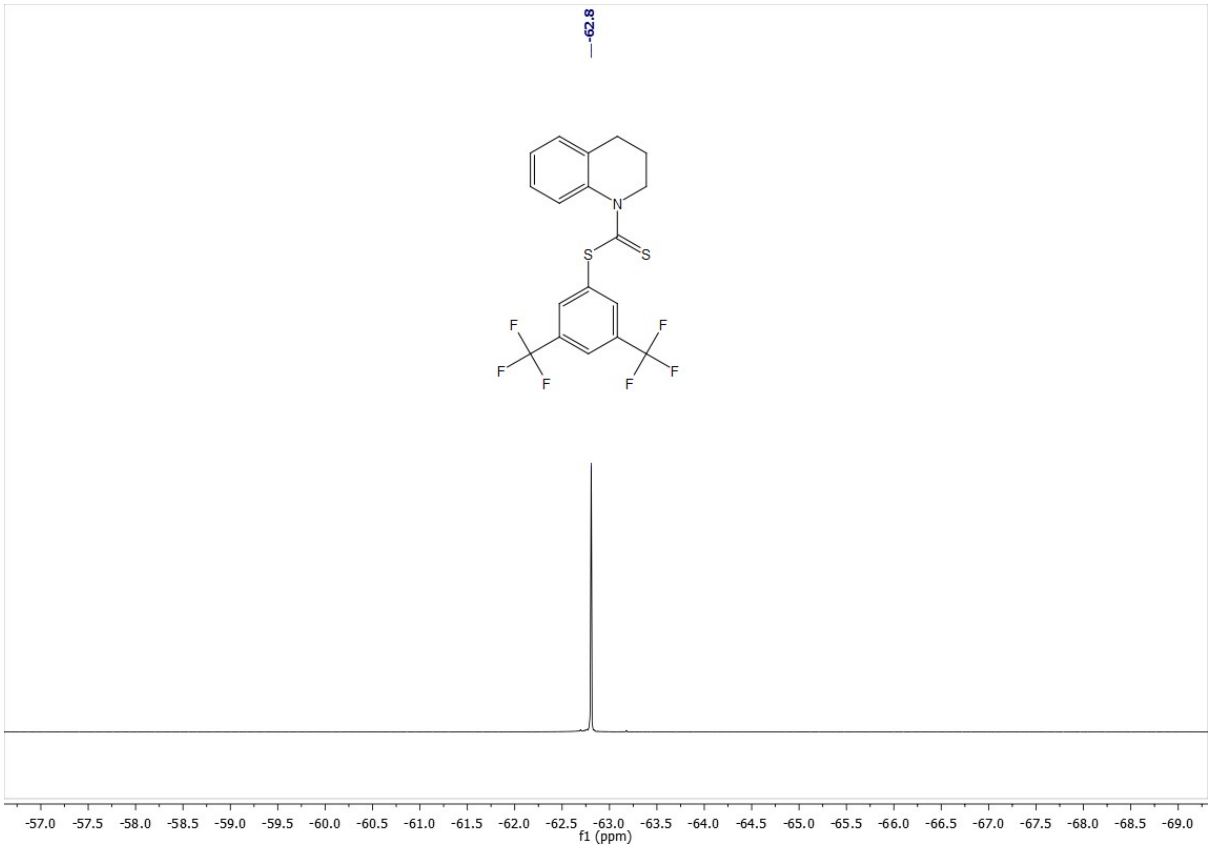


Figure S30: ^{19}F {^{1}H} NMR Spectrum of **3m** ($CDCl_3$, 565 MHz, 298 K)

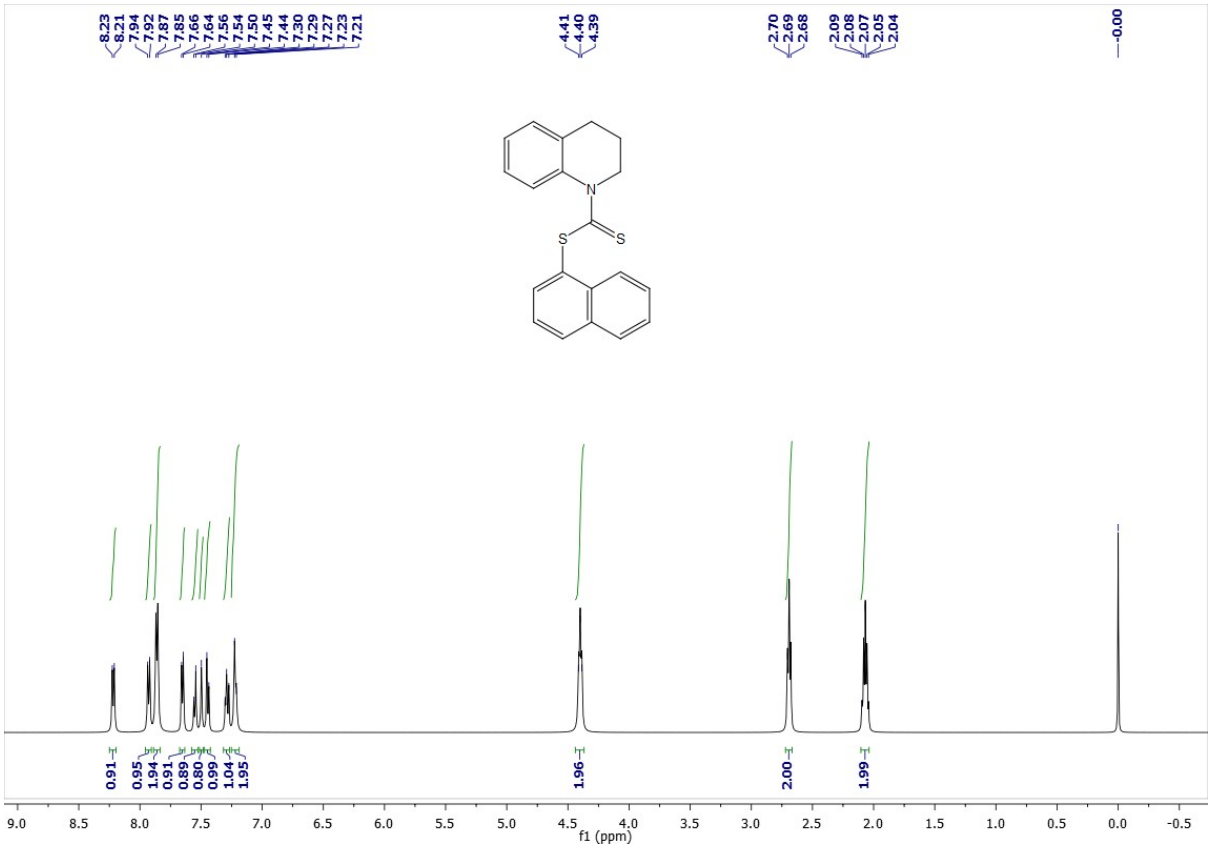


Figure S31: ^{1}H NMR Spectrum of **3n** ($CDCl_3$, 500 MHz, 298 K)

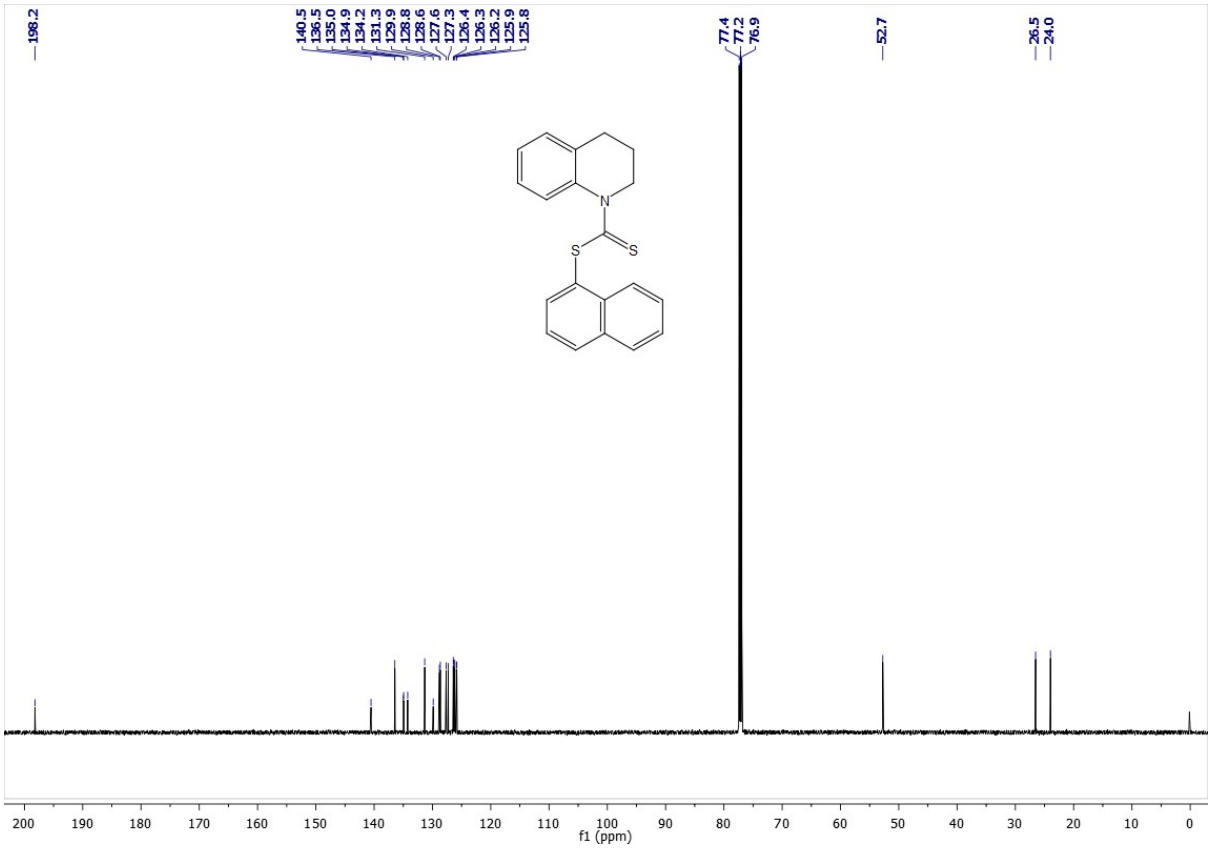


Figure S32: ^{13}C $\{^{1}H\}$ NMR Spectrum of **3n** ($CDCl_3$, 151 MHz, 298 K)

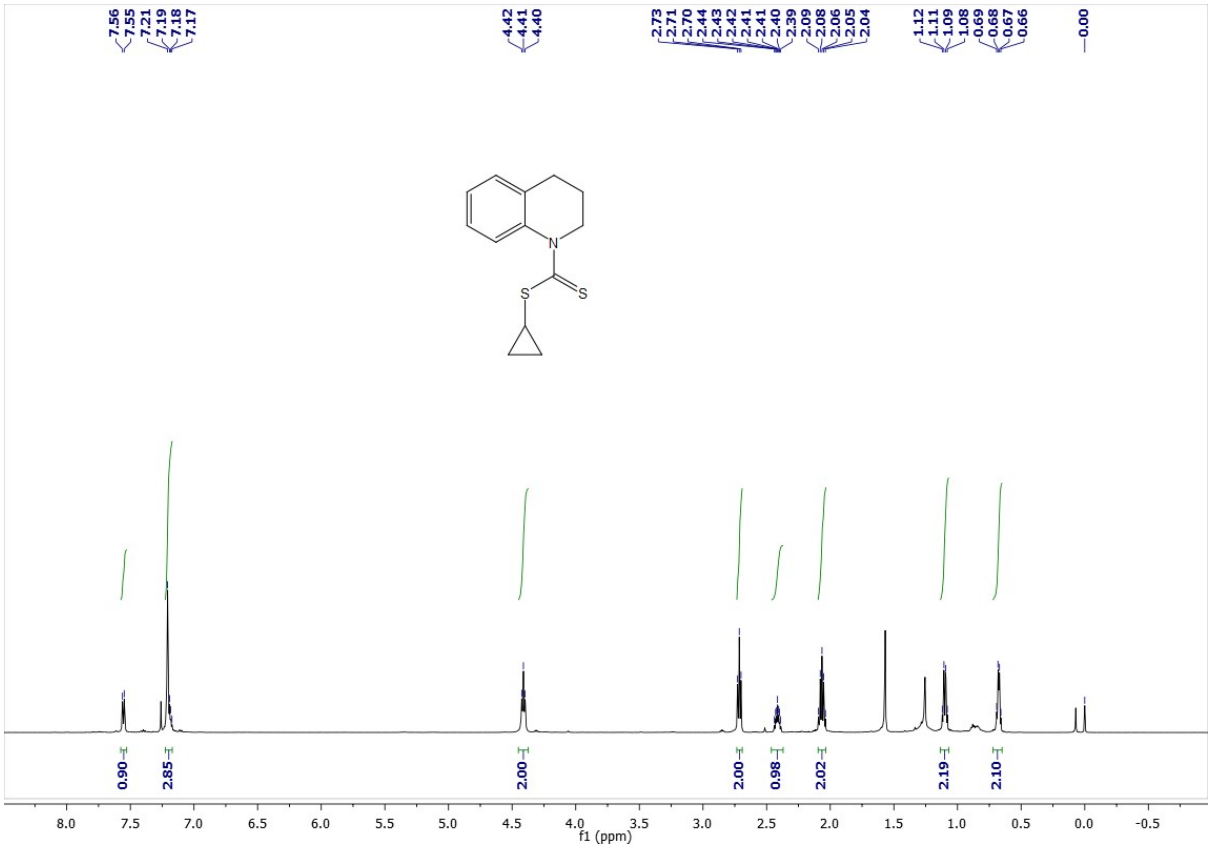


Figure S33: ^{1}H NMR Spectrum of **3o** ($CDCl_3$, 500 MHz, 298 K)

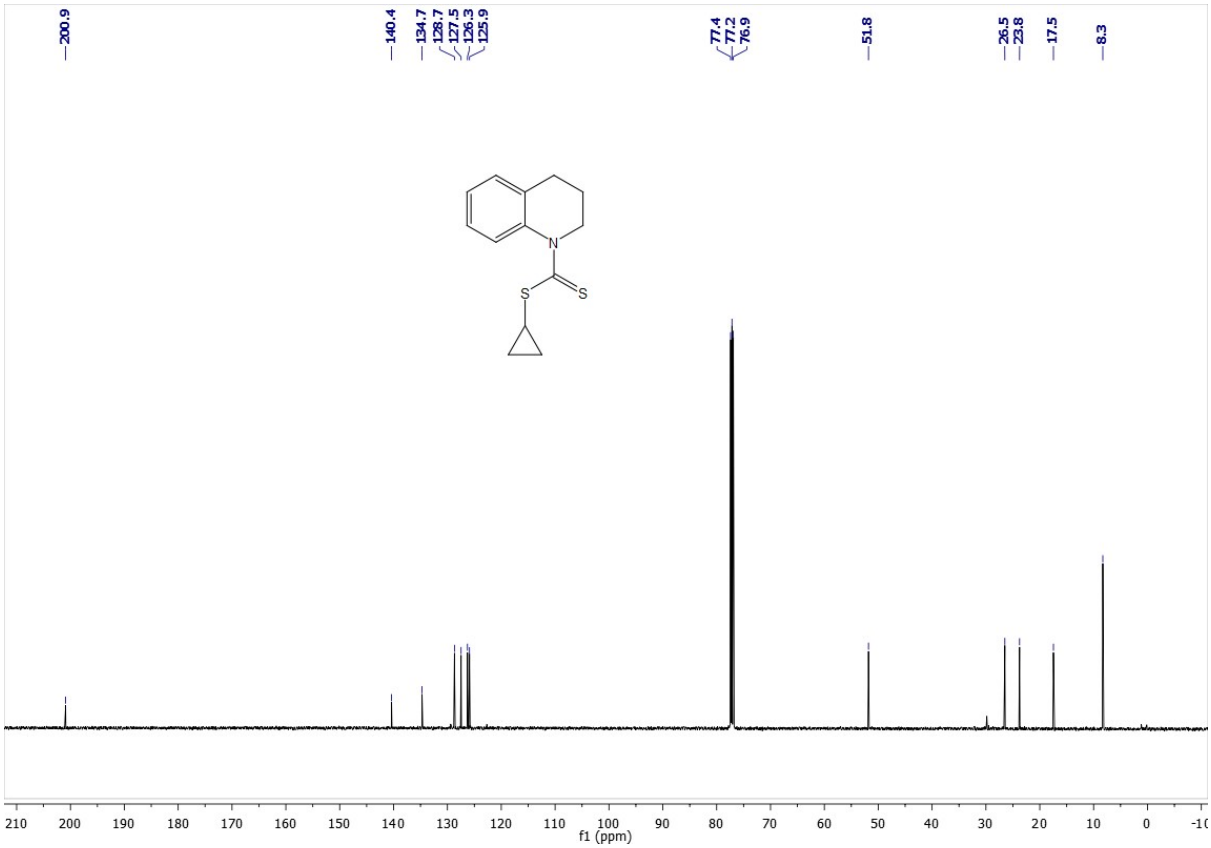


Figure S34: ^{13}C $\{^{1}H\}$ NMR Spectrum of **3o** ($CDCl_3$, 126 MHz, 298 K)

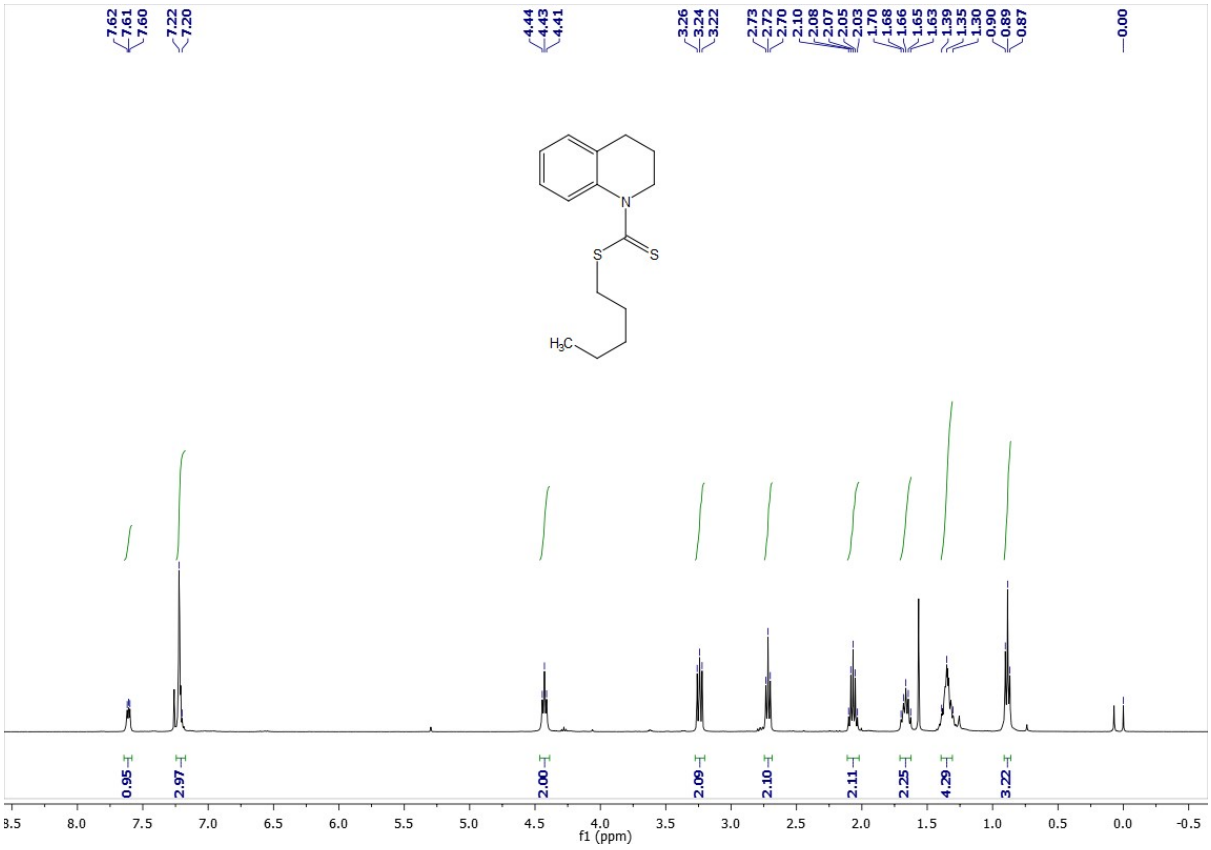


Figure S35: ^{1}H NMR Spectrum of **3p** ($CDCl_3$, 400 MHz, 298 K)

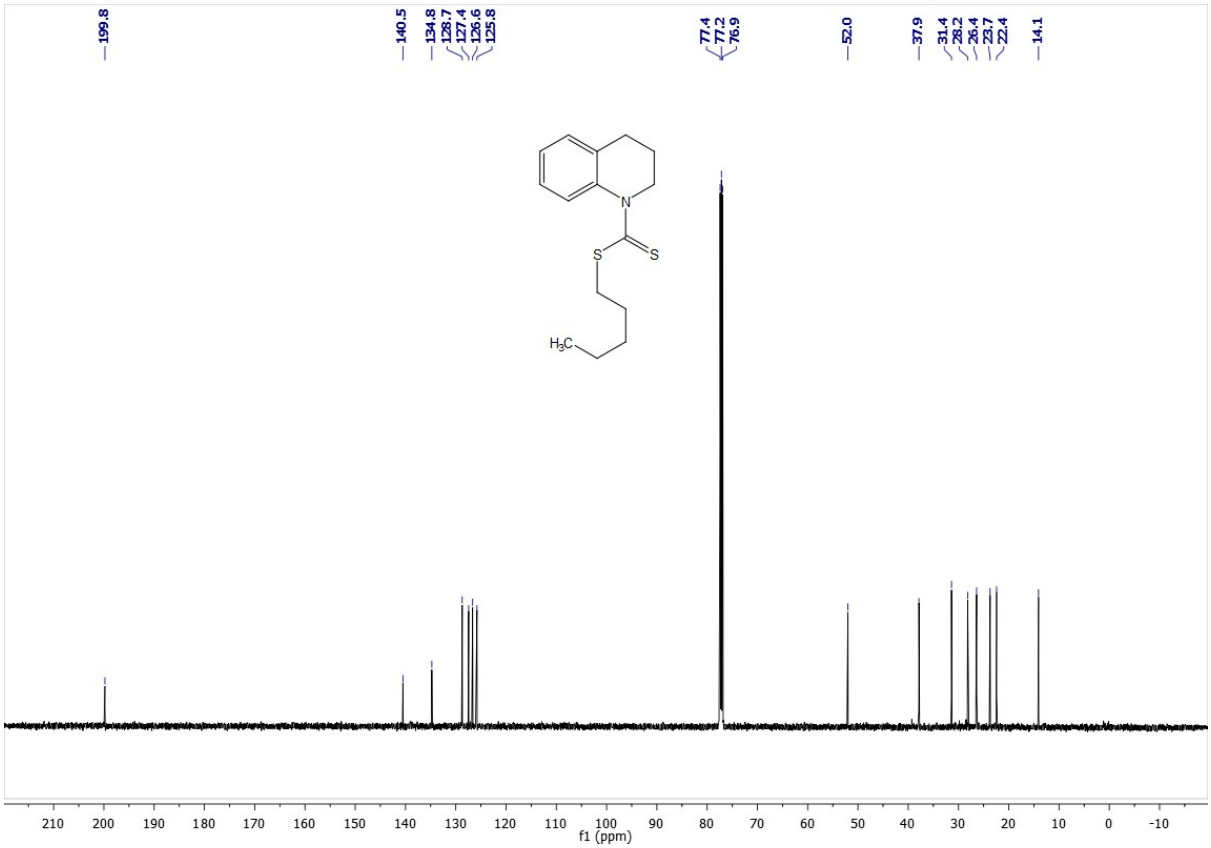


Figure S36: ^{13}C $\{^{1}H\}$ NMR Spectrum of **3p** ($CDCl_3$, 126 MHz, 298 K)

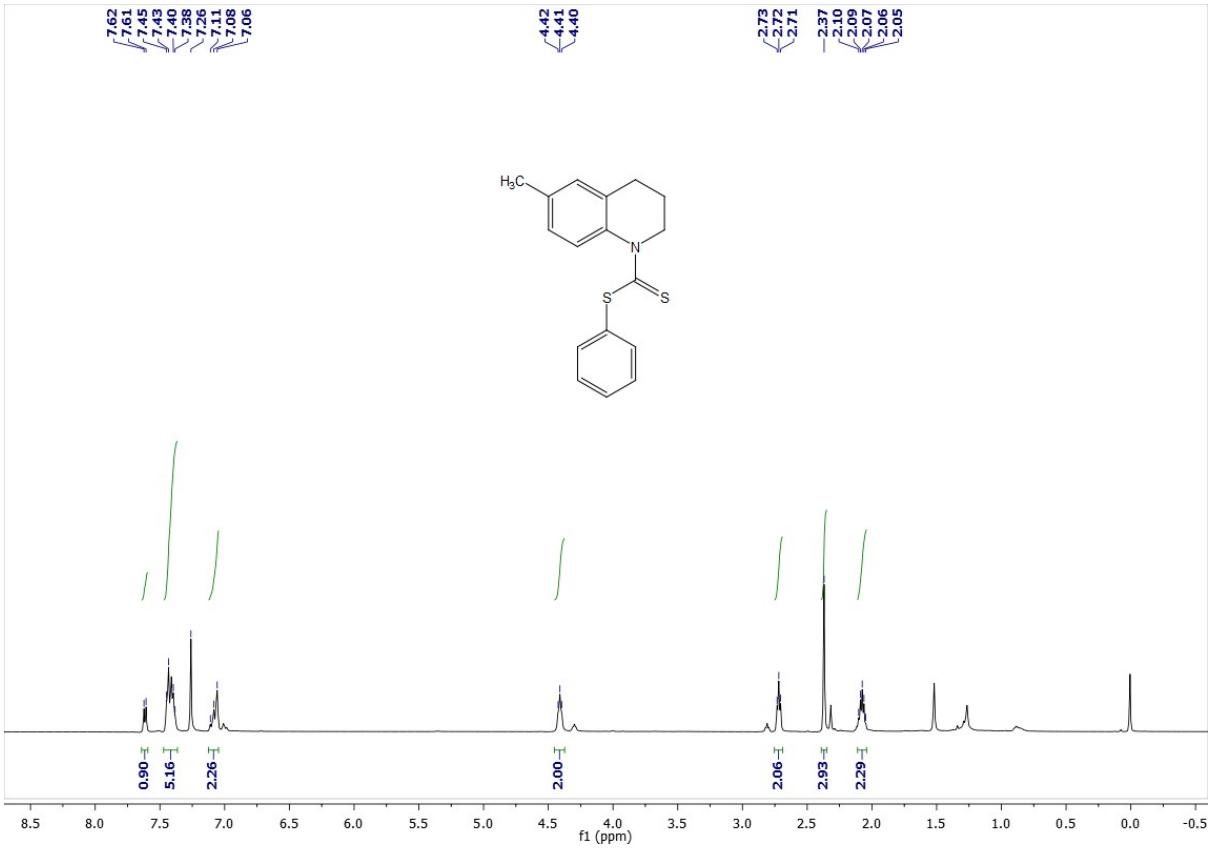


Figure S37: ^{1}H NMR Spectrum of **4a** ($CDCl_3$, 500 MHz, 298 K)

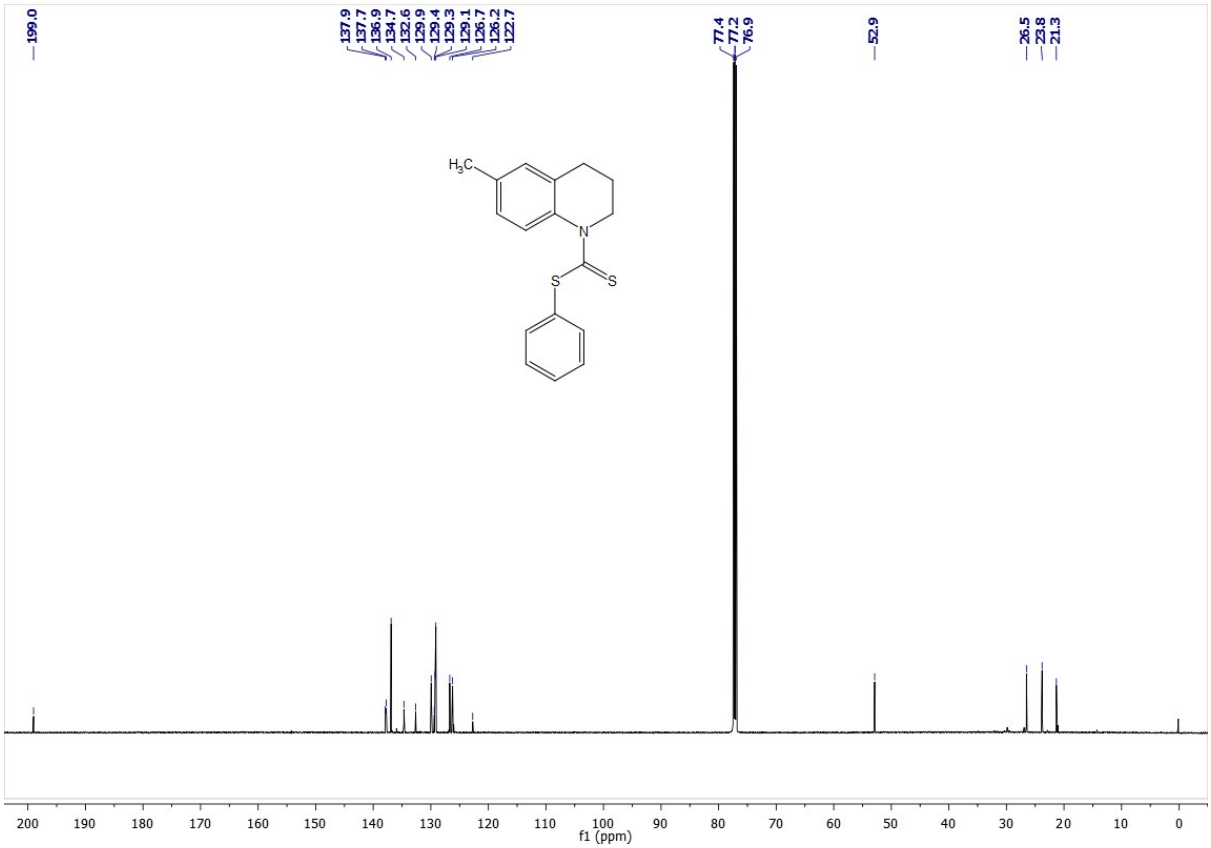


Figure S38: ^{13}C {^{1}H} NMR Spectrum of **4a** ($CDCl_3$, 151 MHz, 298 K)

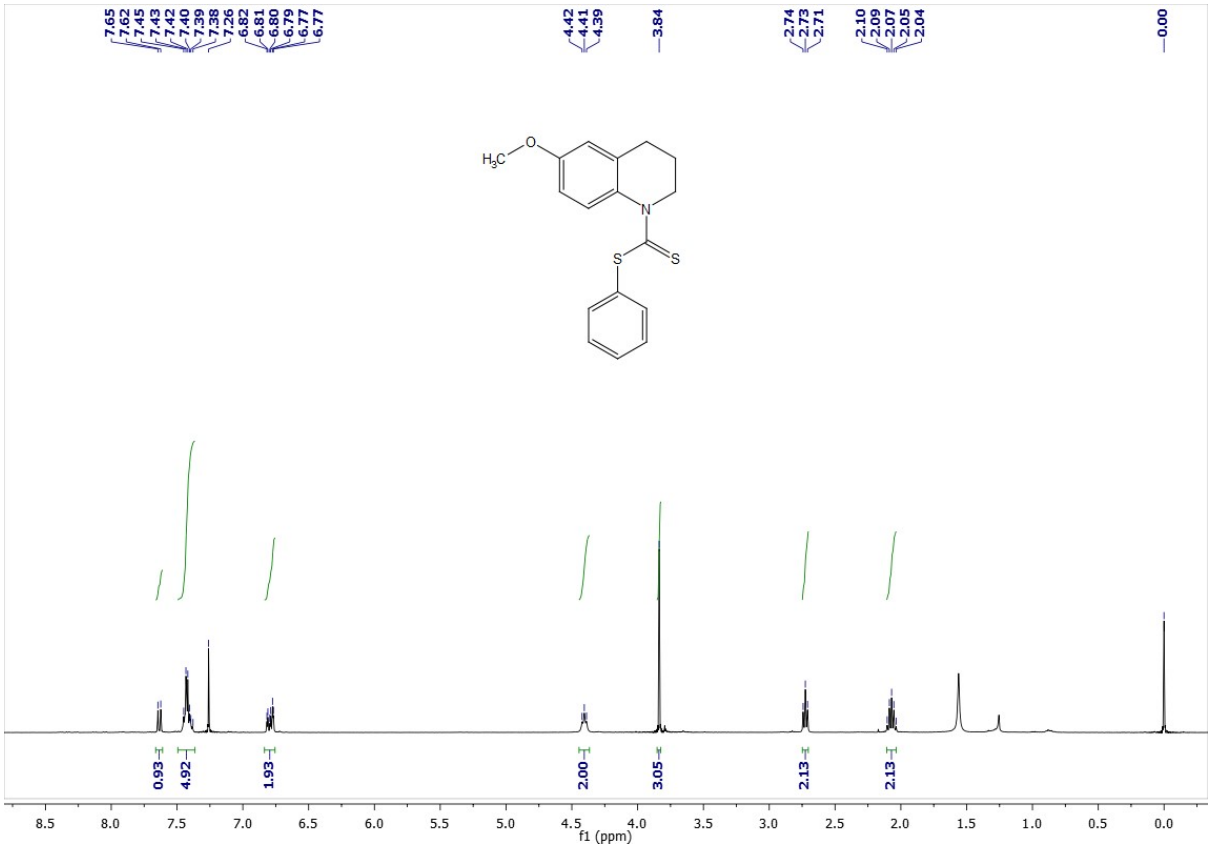


Figure S39: ^{1}H NMR Spectrum of **4b** ($CDCl_3$, 400 MHz, 298 K)

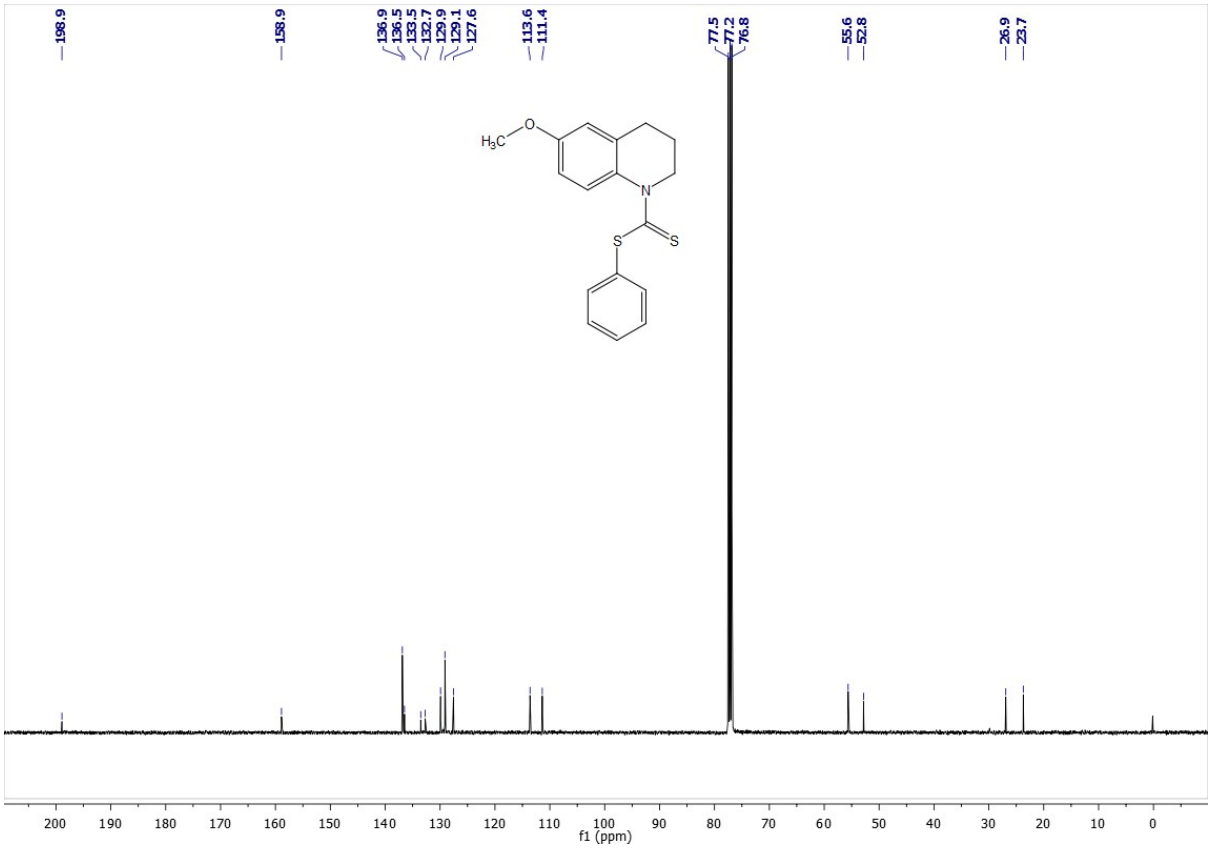


Figure S40: ^{13}C $\{^{1}H\}$ NMR Spectrum of **4b** ($CDCl_3$, 101 MHz, 298 K)

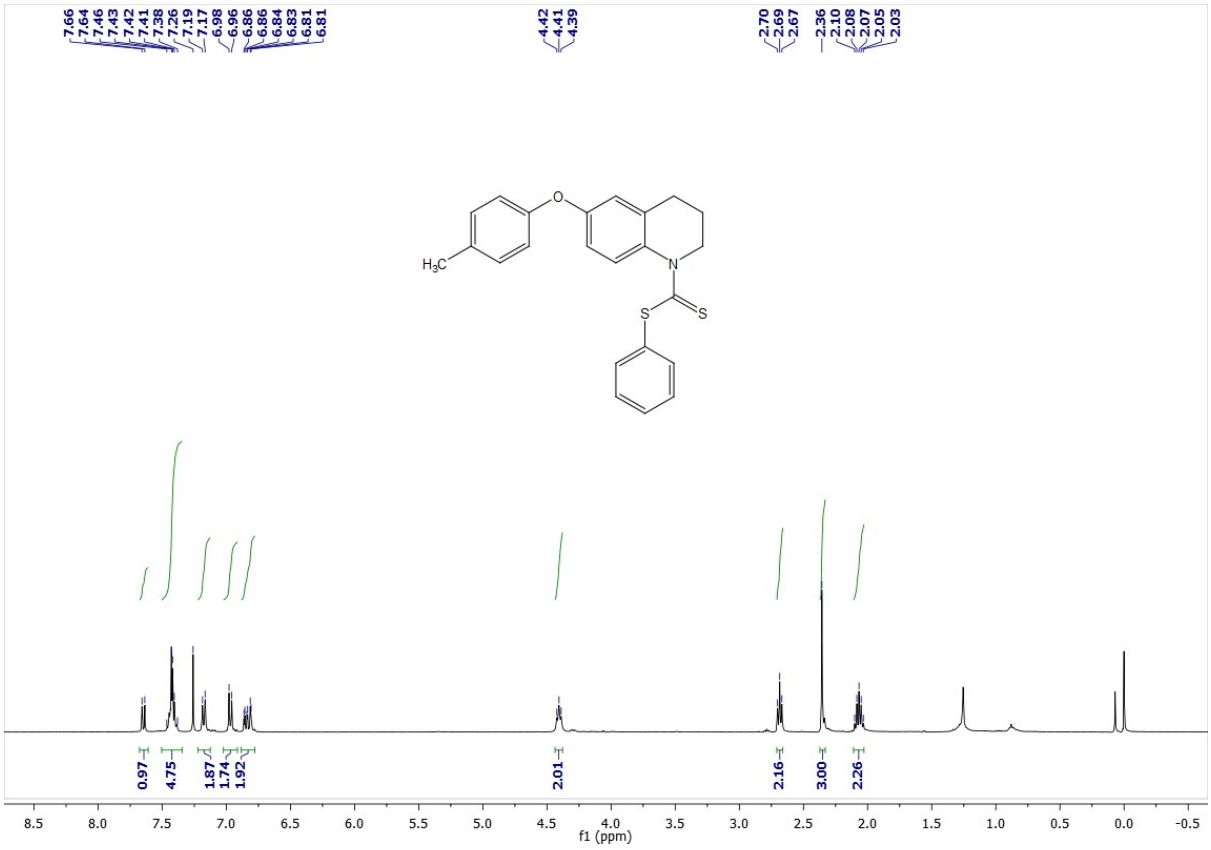


Figure S41: ^{1}H NMR Spectrum of **4c** ($CDCl_3$, 400 MHz, 298 K)

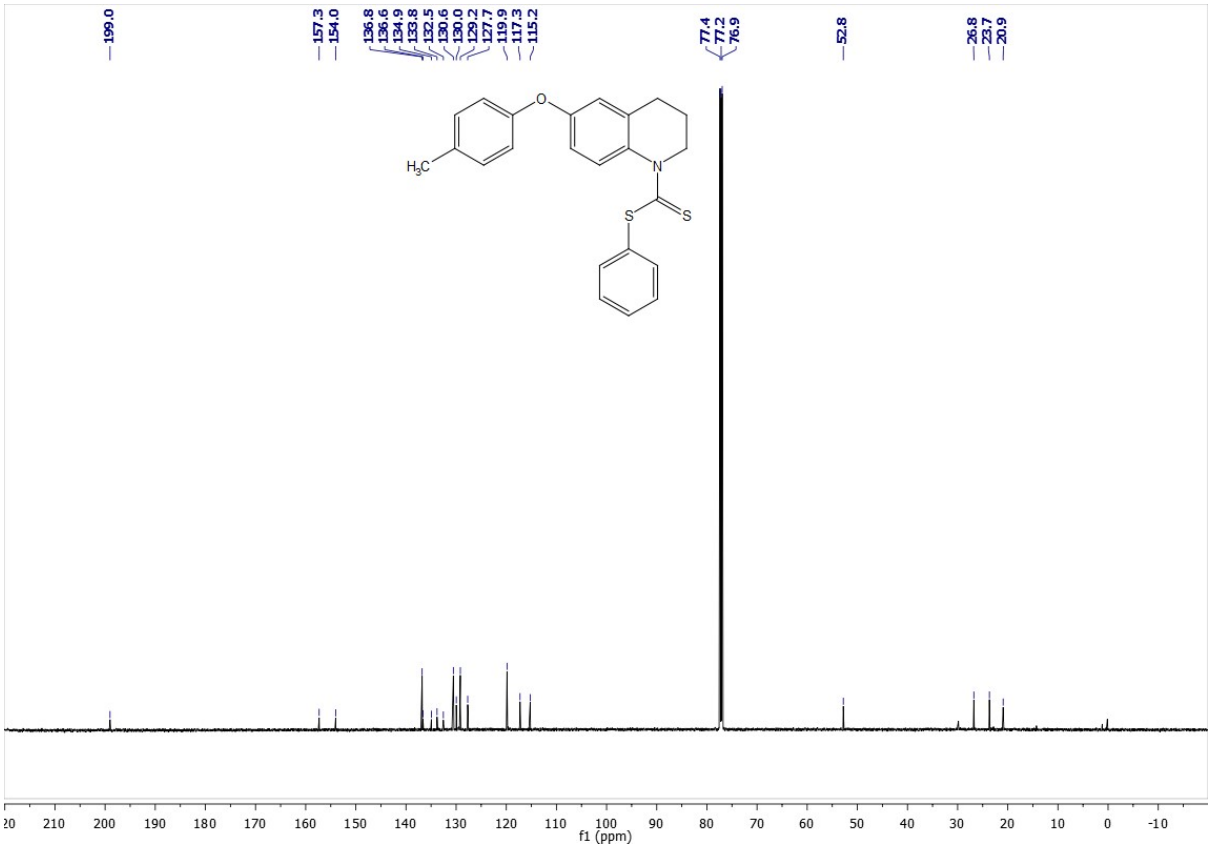


Figure S42: ^{13}C $\{^{1}H\}$ NMR Spectrum of **4c** ($CDCl_3$, 151 MHz, 298 K)

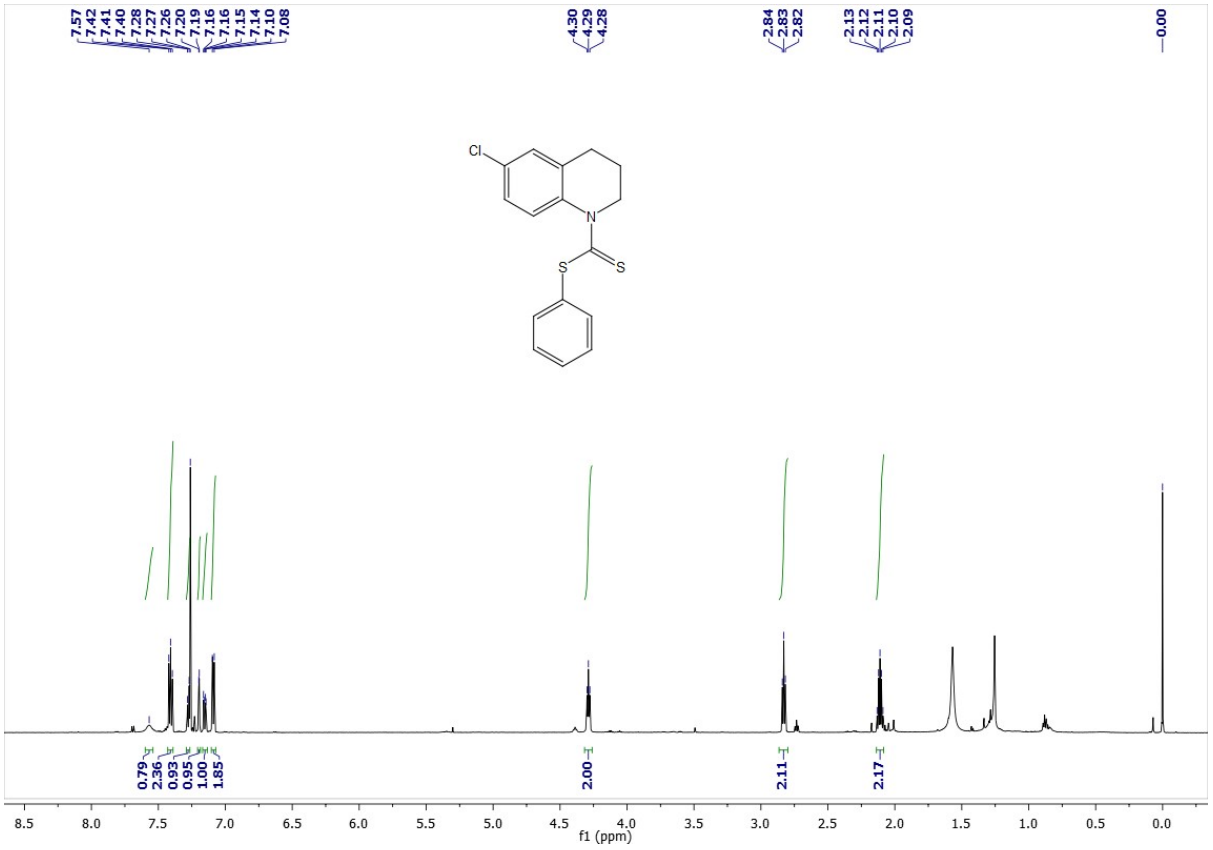


Figure S43: ^{1}H NMR Spectrum of **4d** ($CDCl_3$, 600 MHz, 298 K)

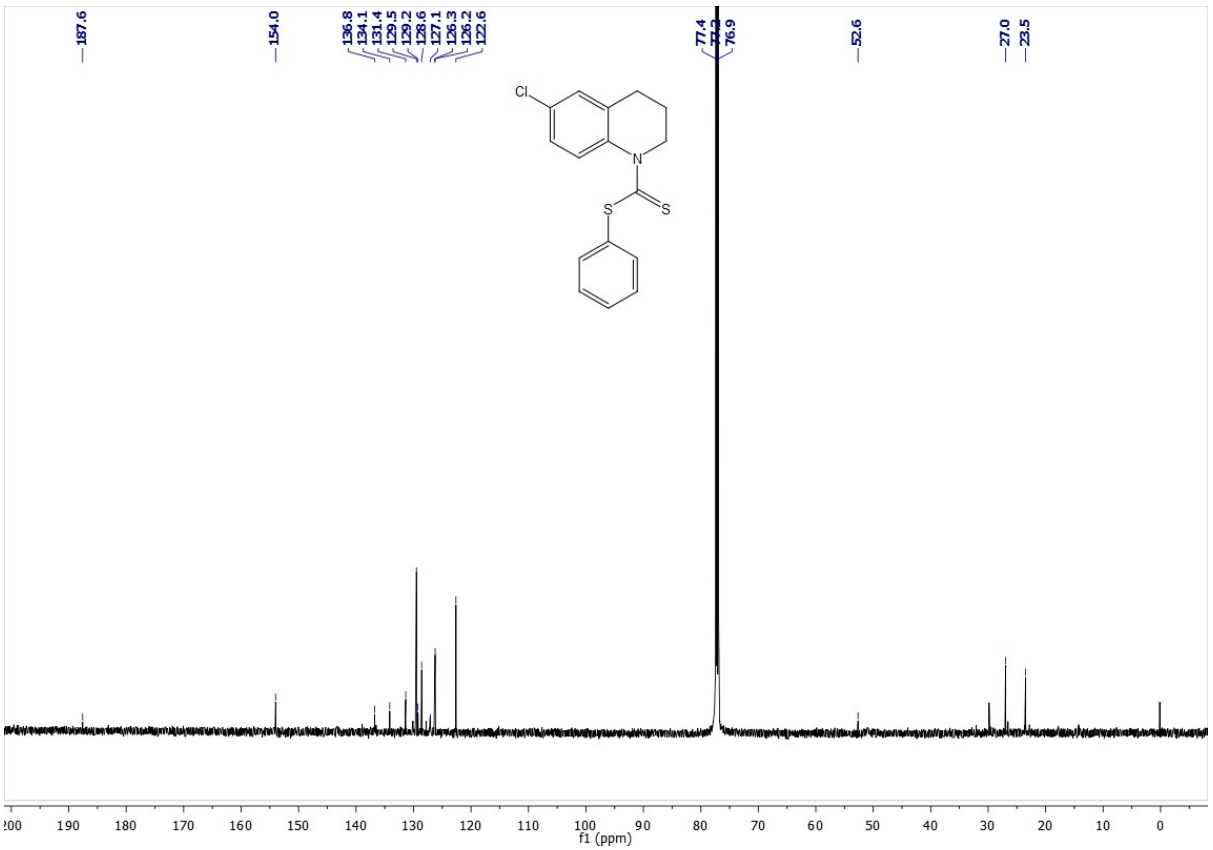


Figure S44: ^{13}C $\{^{1}H\}$ NMR Spectrum of **4d** ($CDCl_3$, 151 MHz, 298 K)

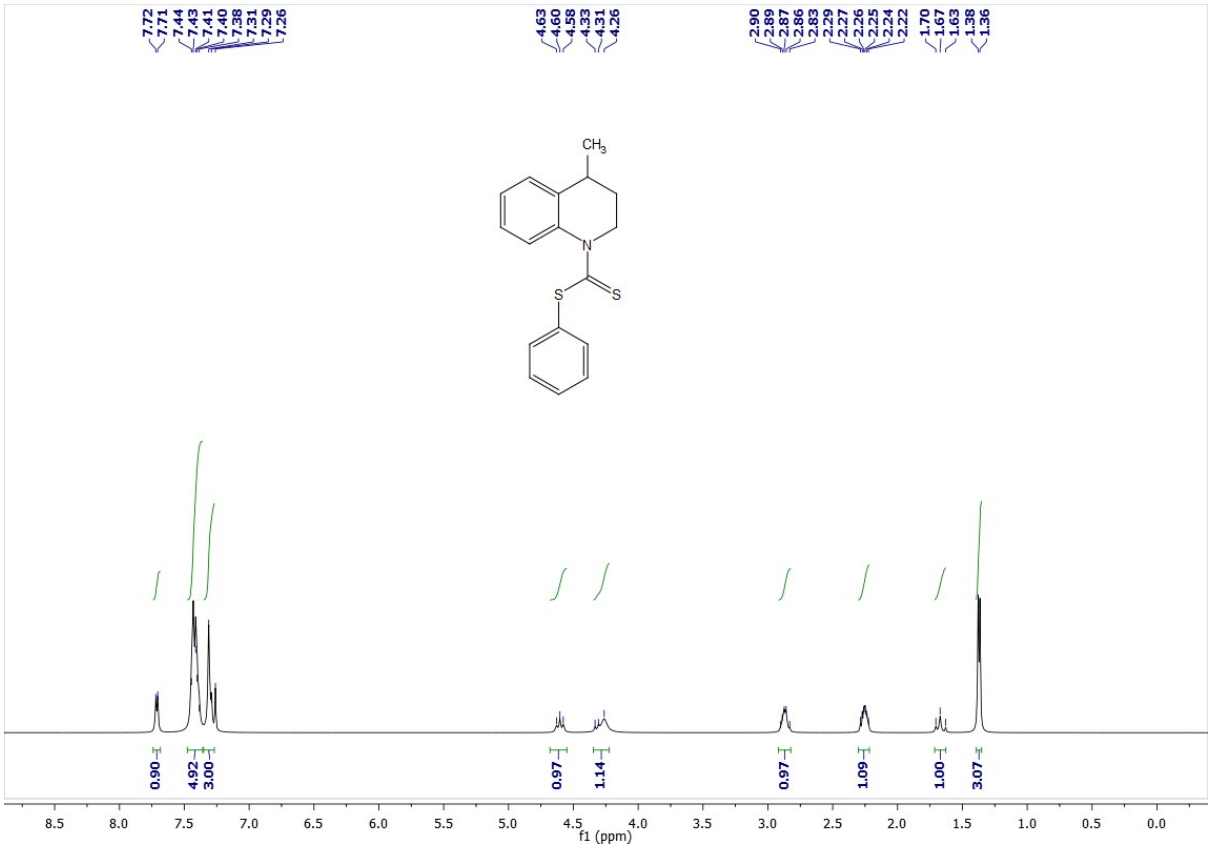


Figure S45: ^{1}H NMR Spectrum of **4e** ($CDCl_3$, 500 MHz, 298 K)

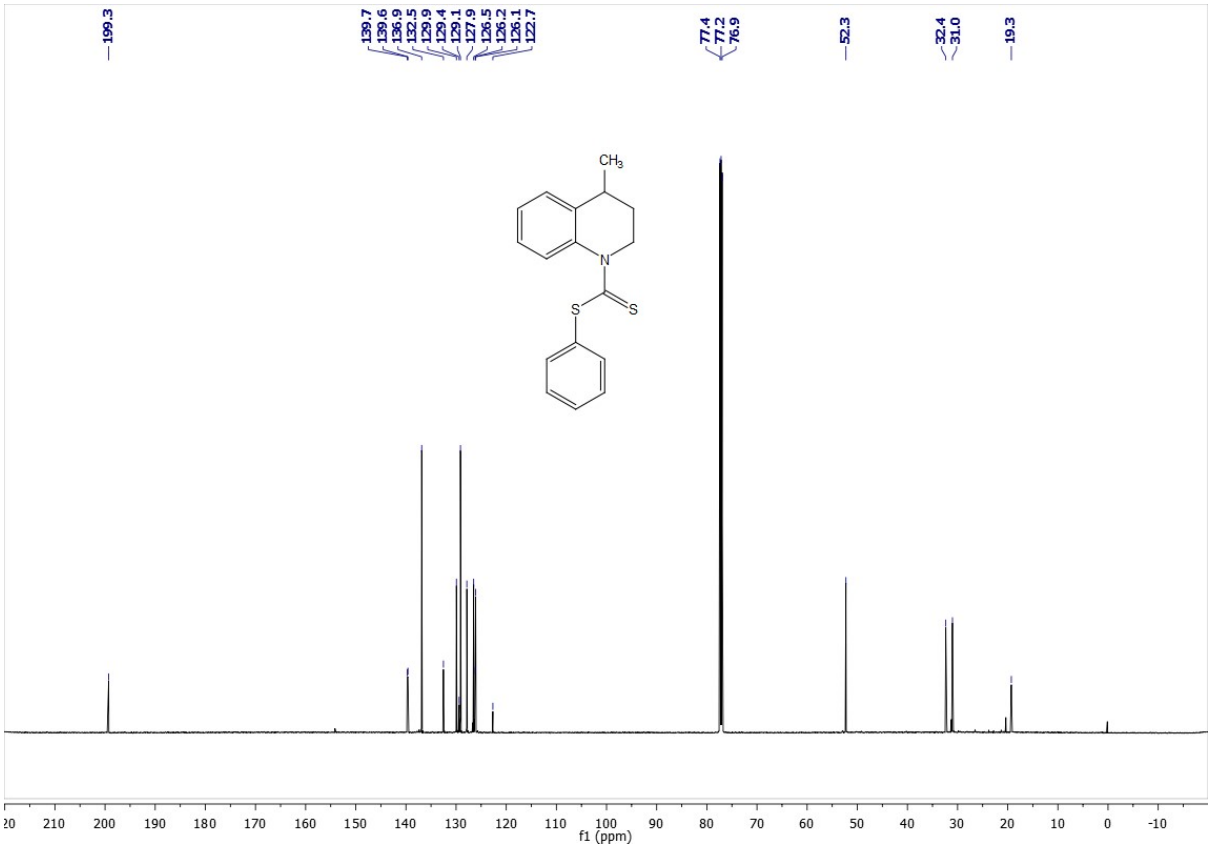


Figure S46: ^{13}C {^{1}H} NMR Spectrum of **4e** ($CDCl_3$, 151 MHz, 298 K)

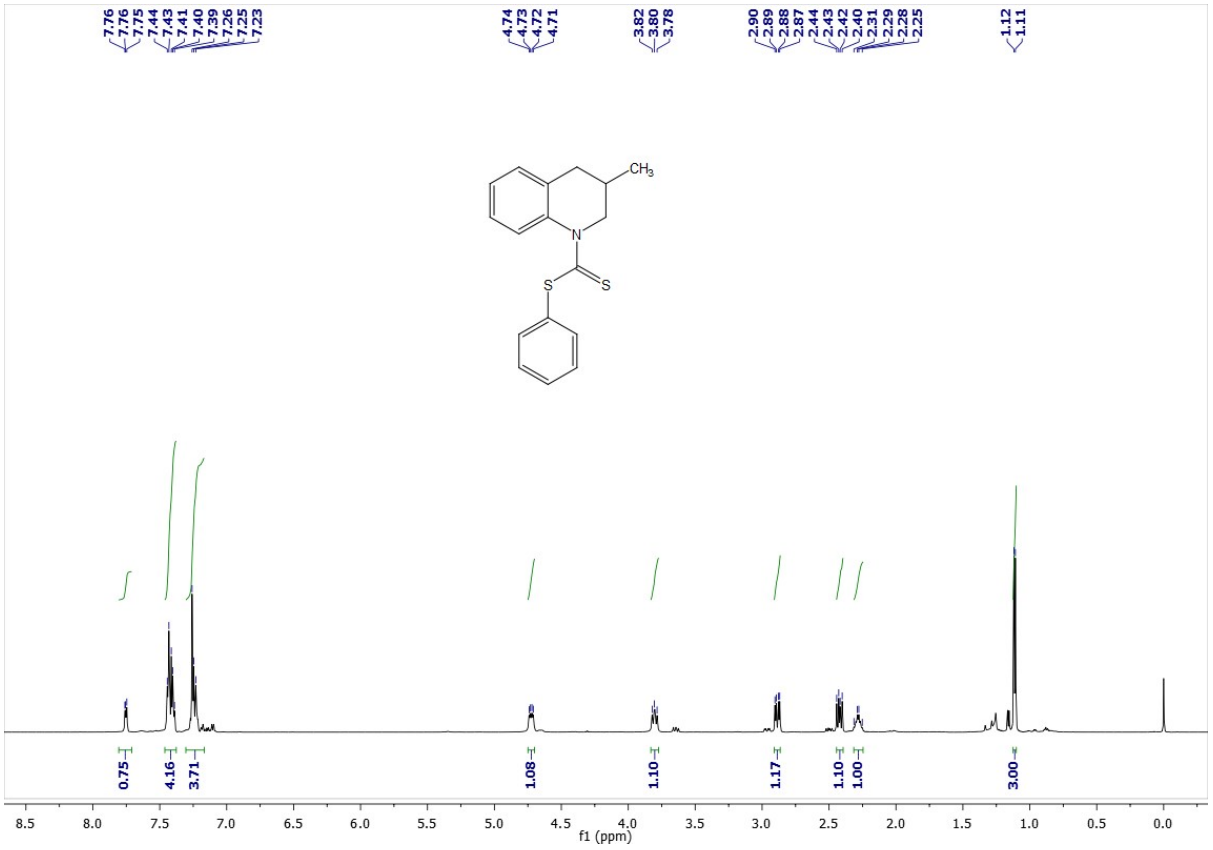


Figure S47: ^{1}H NMR Spectrum of **4f** ($CDCl_3$, 600 MHz, 298 K)

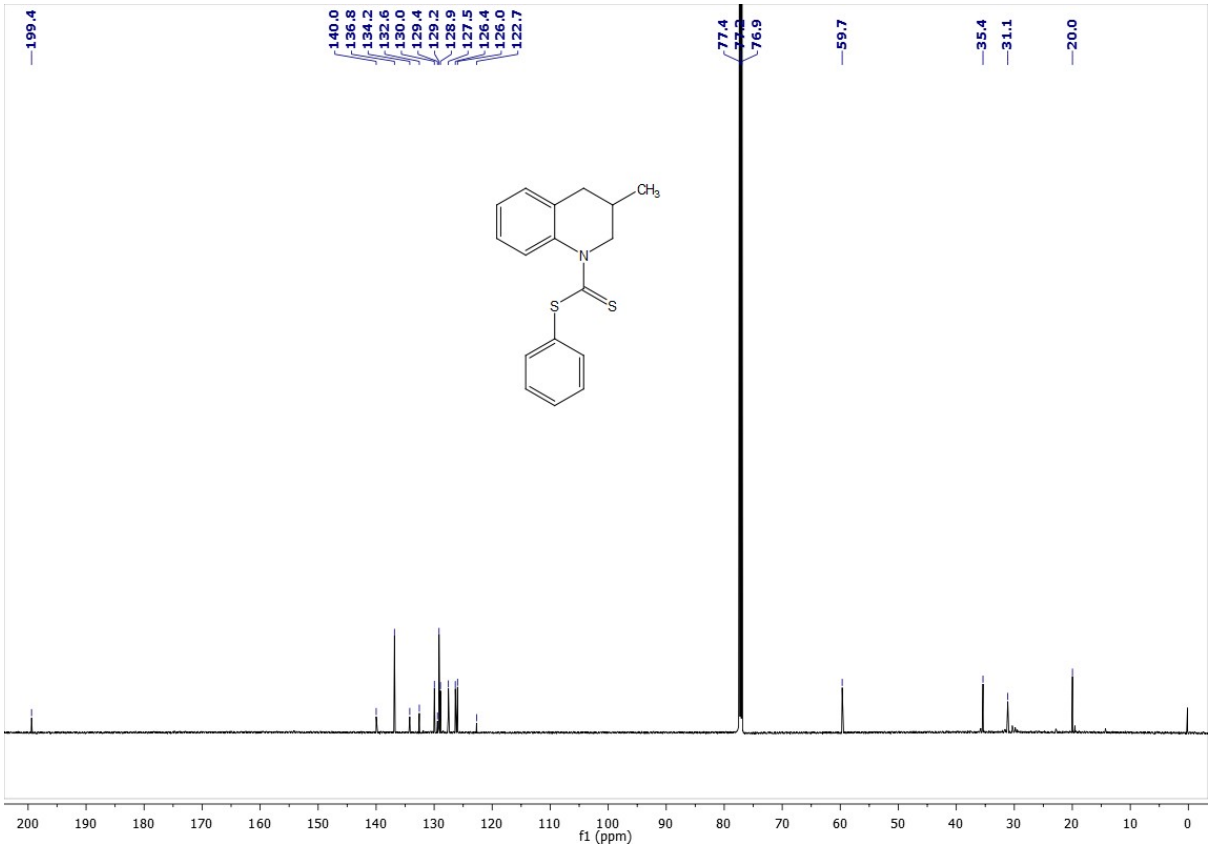


Figure S48: ^{13}C {^{1}H} NMR Spectrum of **4f** ($CDCl_3$, 151 MHz, 298 K)

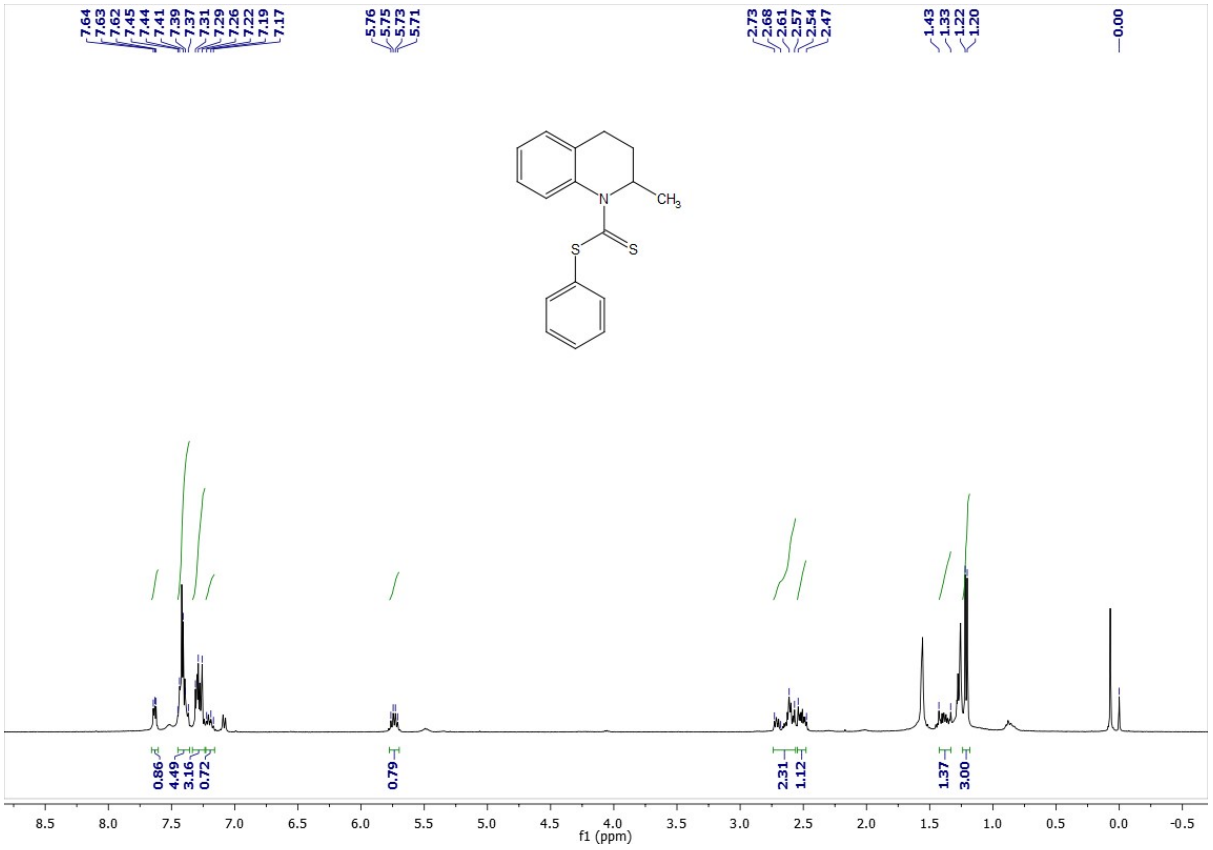


Figure S49: ^{1}H NMR Spectrum of **4g** ($CDCl_3$, 400 MHz, 298 K)

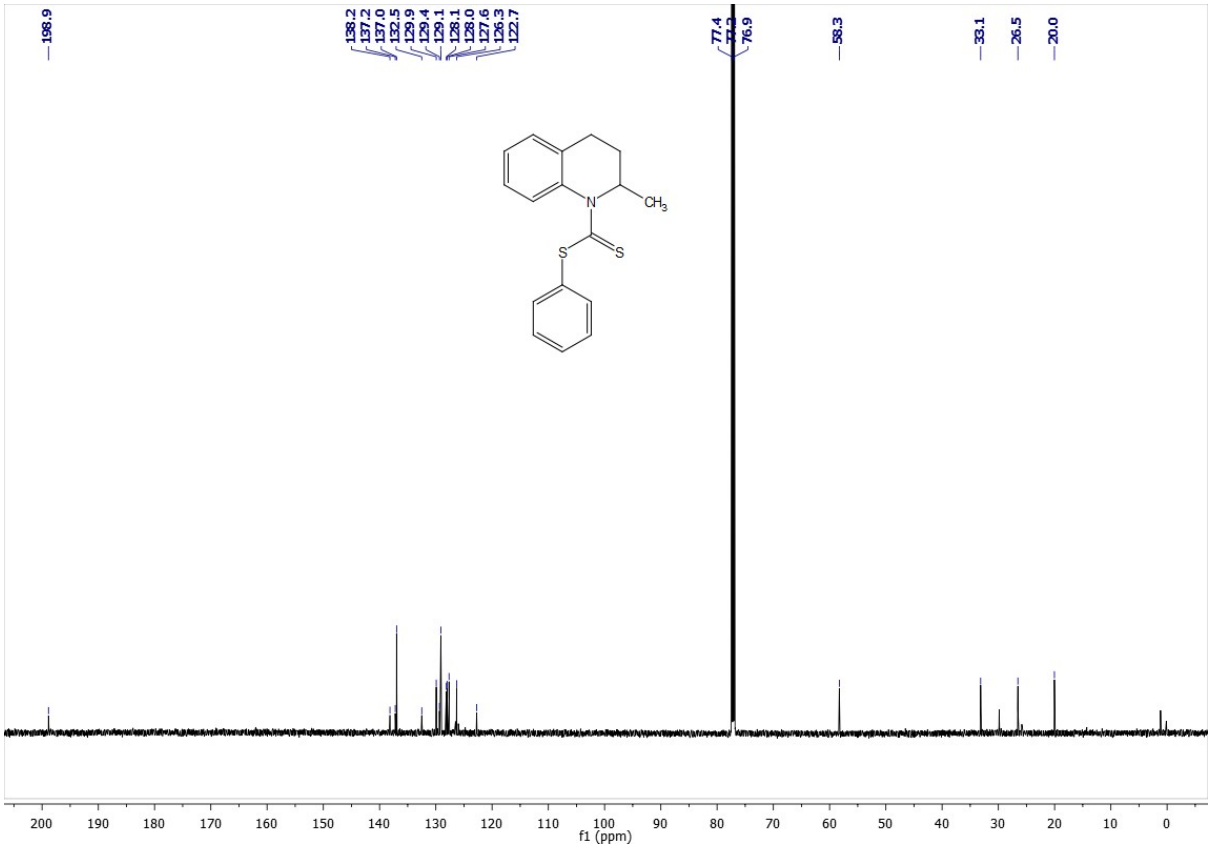


Figure S50: ^{13}C {^{1}H} NMR Spectrum of **4g** ($CDCl_3$, 151 MHz, 298 K)

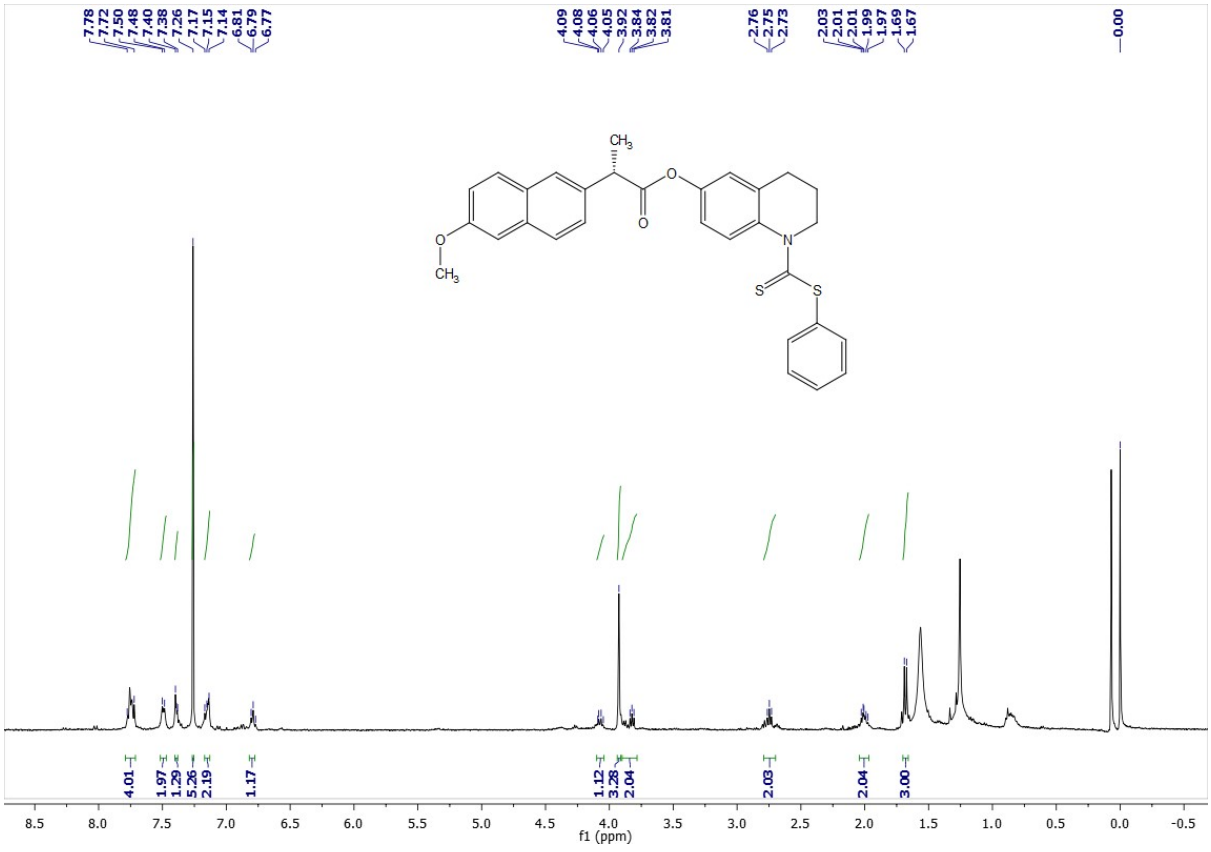


Figure S51: ^{1}H NMR Spectrum of **4h** ($CDCl_3$, 400 MHz, 298 K)

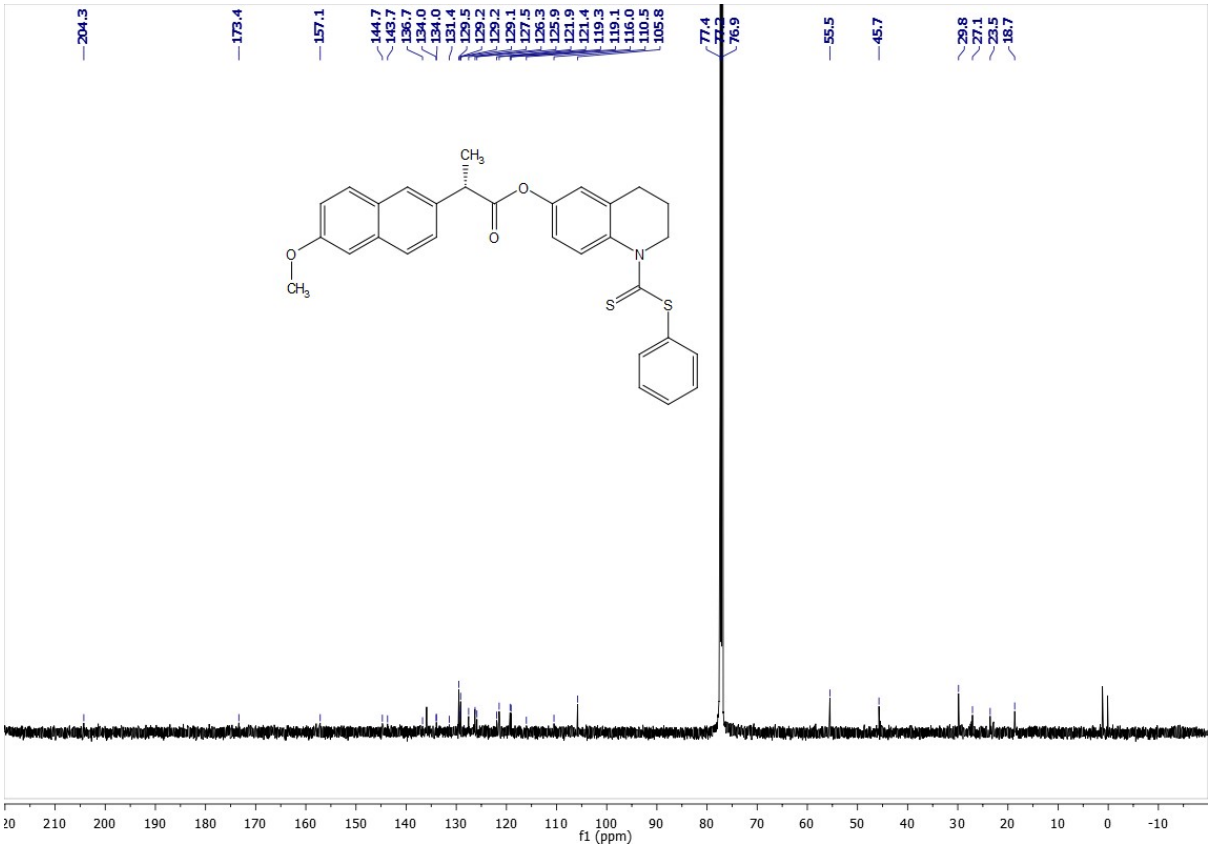


Figure S52: ^{13}C $\{^{1}H\}$ NMR Spectrum of **4h** ($CDCl_3$, 151 MHz, 298 K)

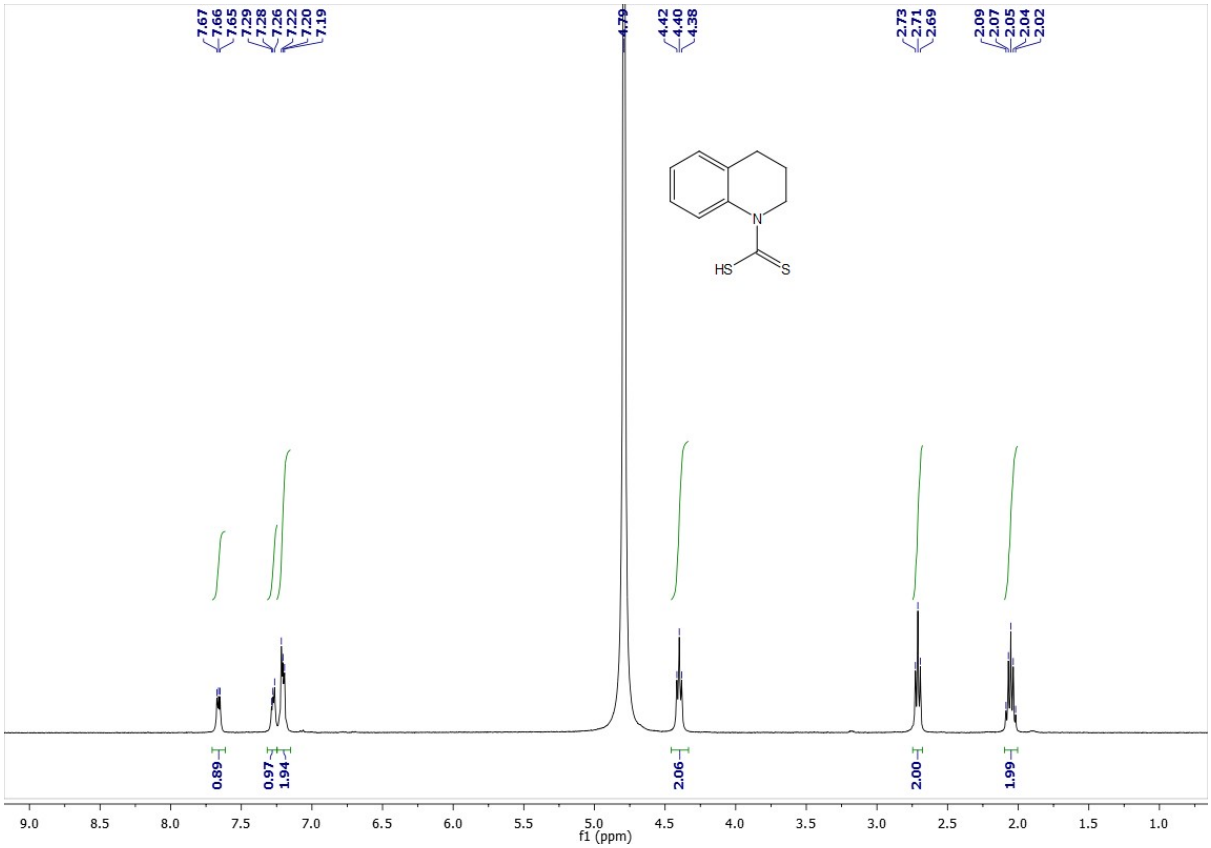


Figure S53: ^{1}H NMR Spectrum of **I2** (D_2O, 400 MHz, 298 K)

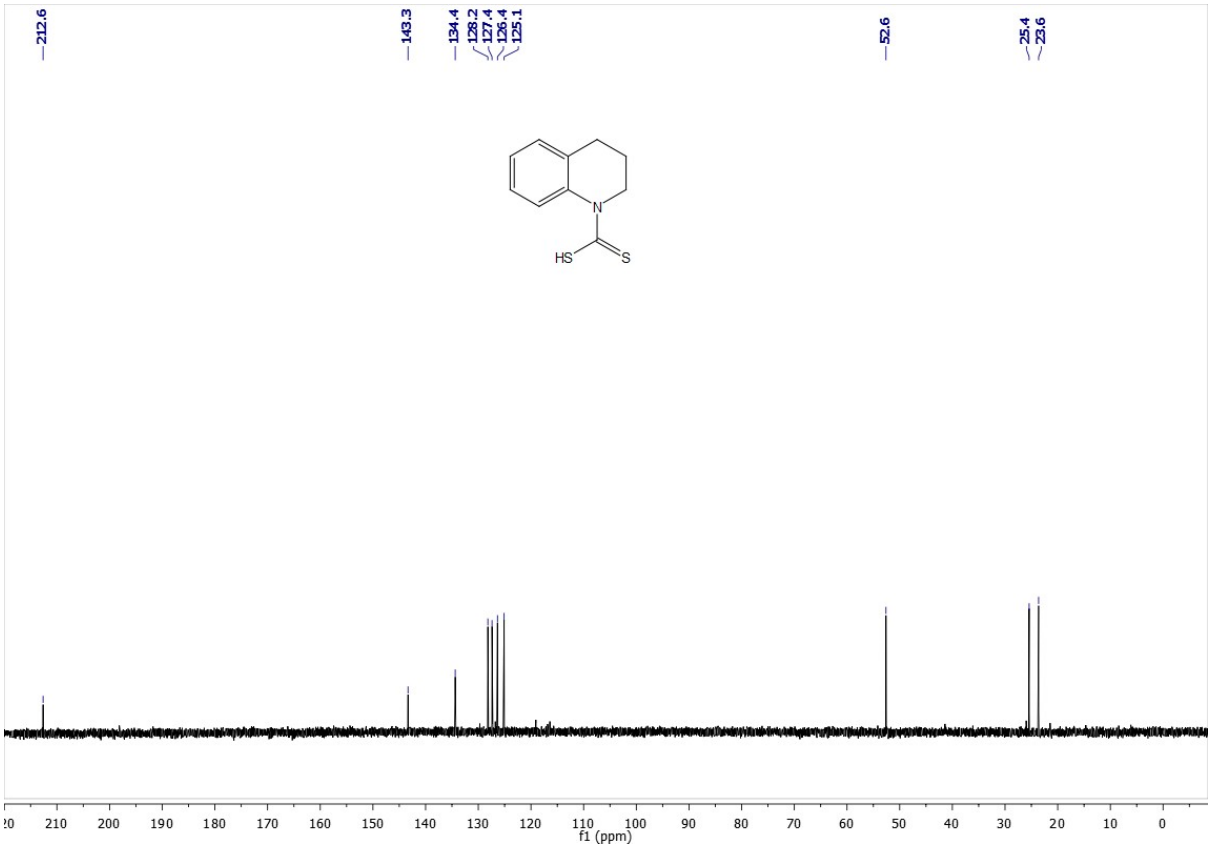


Figure S54: ^{13}C {^{1}H} NMR Spectrum of **I2** (D_2O, 151 MHz, 298 K)

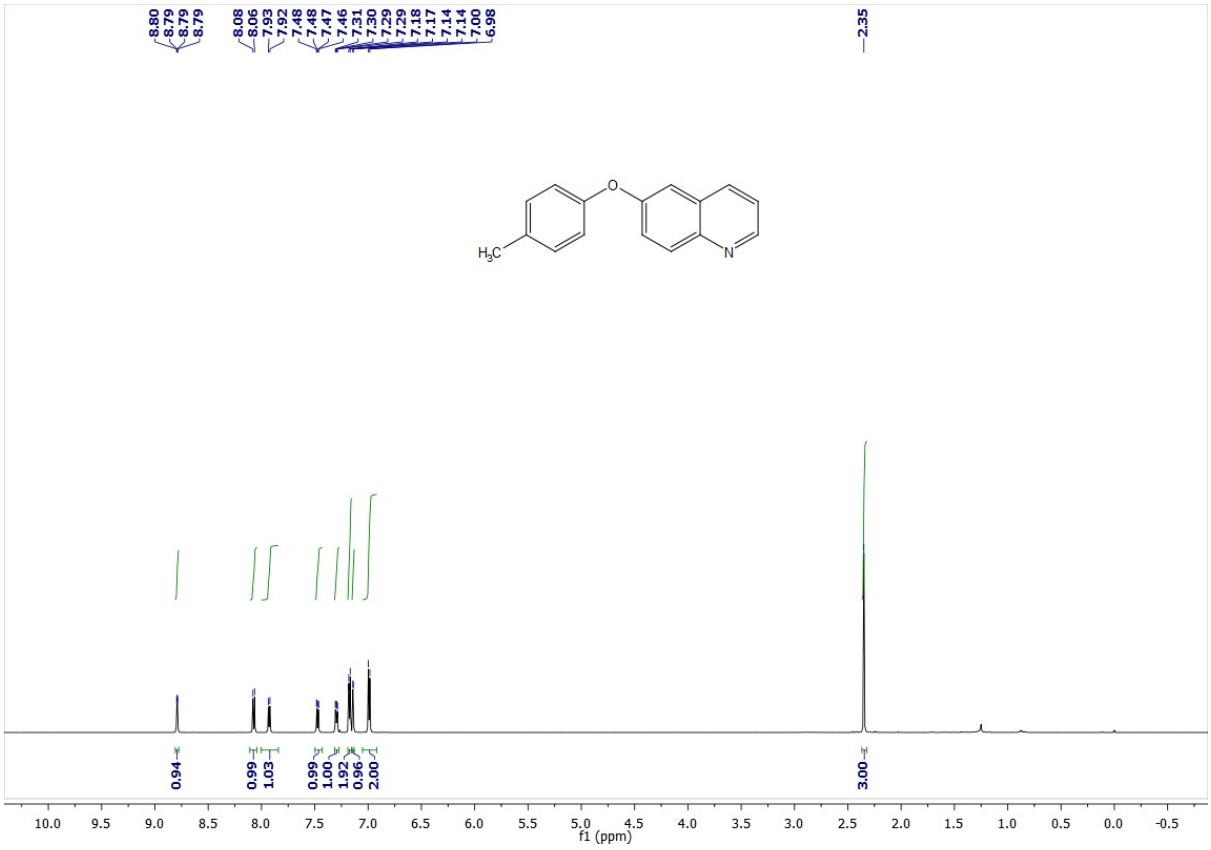


Figure S55: ^{1}H NMR Spectrum of **1c** ($CDCl_3$, 600 MHz, 298 K)

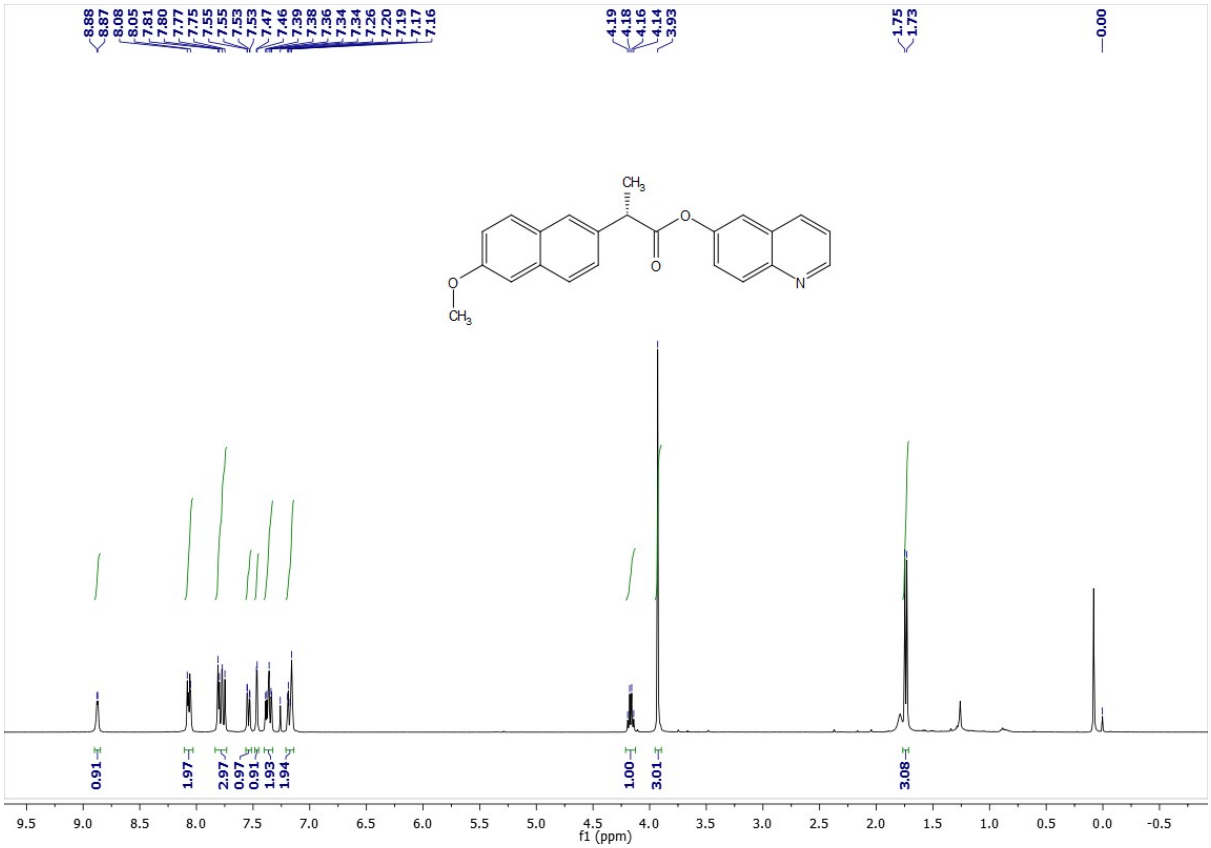


Figure S56: ^{1}H NMR Spectrum of **1h** ($CDCl_3$, 400 MHz, 298 K)

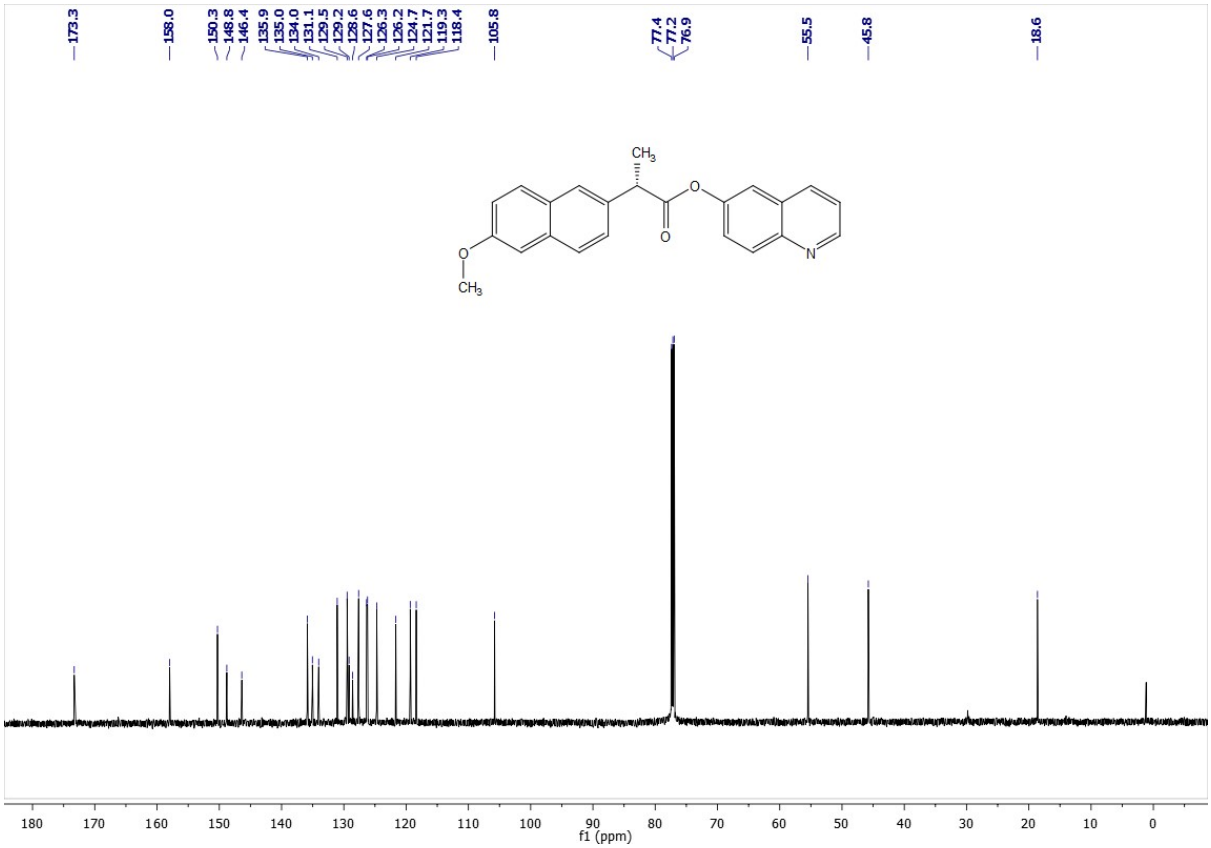


Figure S57: ^{13}C {^{1}H} NMR Spectrum of **1h** ($CDCl_3$, 151 MHz, 298 K)

9. References

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