

SUPPORTING INFORMATION

Base-Catalyzed Thio-Lactamization of 2-(1-Arylvinyl)anilines with CS₂ for the Synthesis of Quinoline-2-thiones

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Experimental

1.1. General information

¹H NMR and ¹³C NMR data analyses were performed with a Varian Mercury plus-400 and Agilent 600 MHz DD2 instruments unless otherwise specified. CDCl₃ and DMSO-*d*₆ as solvent and tetramethylsilane (TMS) as the internal standard were employed. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ¹H NMR spectrum as 0.00 ppm. The data of ¹H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant (*J* values) in Hz and integration. Chemical shift for ¹³C NMR spectra were recorded in ppm from TMS using the central peak of CDCl₃ (77.0 ppm) as the internal standard. ¹⁹F NMR spectra were recorded on a Varian Mercury 400 plus instrument. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Melting points were measured with an XT-4 apparatus. High-resolution mass spectra (HRMS) (ESI) were obtained with a Bruker Daltonics APEX II 47e and Orbitrap Elite mass spectrometer. Column chromatography was generally performed on silica gel (200-300 mesh) and TLC analyses were conducted on silica gel GF254 plates. All reagents were directly used from purchased without any further purification unless otherwise specified.

1.2 General procedure for the synthesis of 2-(1-aryvinyl)aniline 1. Starting materials **1** was prepared according to the reported procedures.¹ 1.0 g of montmorillonites K10 was added to a solution of phenylacetylene (1.0 g, 10.0 mmol) and *para*-tolftidine (1.1 g, 10.0 mmol) in the xylene (10.0 mL). The mixture was heated at the 140 °C under stirring for 5 hours. After cooling to room temperature, filtration, washing with diethyl ether and distillation of the solvents. The volatiles were removed in vacuum. The residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether 1:5) to give the corresponding products.

1.3 General procedure for the synthesis of 4-phenylquinoline-2(1H)-thione 2a. Under an atmosphere of air, 2-(1-phenylvinyl) aniline **1a** (0.5 mmol, 0.0095 g), CS₂ (2.4 eq. 0.6 mmol, 0.0046 g), DBU (5 mol%, 0.00018 g) were added to a tube. DMF (3.0 mL) was added by dropper and the mixture was stirred for 8 h at 140 °C and the reaction was monitored by TLC analysis. Then, 2.0 mL ammonium chloride were added to the mixture to quench the reaction and extracted with ethyl acetate (3×25 mL). The combined organic layers were washed with aqueous NaHCO₃ and brine, dried over MgSO₄, filtered, and the volatiles were removed in vacuum. The residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether 1:5) to give the corresponding products. All of the products **2b-v** were synthesized according to above described procedure.

1.4 General procedure for the synthesis of 6-methyl-2-(methylthio)-4-phenylquinoline 3

6-Methyl-4-phenylquinoline-2(1H)-thione **2b** (1.0 mmol, 0.0251 g), MeI (1.2 mmol, 0.01692 g), K₂CO₃ (1.5 equiv, 1.5 mmol, 0.0207 g), EtOH (3.0 mL) was added by dropper and the mixture was

stirred at 80 °C for 5 h. And the progress of the reaction was monitored by TLC (silica gel). After completion of the reaction, mixture was cooled to ambient temperature, quenched by addition of saturated NH₄Cl (2.0 mL), and extracted with ethyl acetate (3×10 ml). The organic layers were combined and dried with anhydrous MgSO₄ and concentrated in vacuo, the resulting residue was purified by silica gel column chromatography using ethyl acetate/petroleum ether (1:5) as eluent to afford the products.

1.5 Procedure for the synthesis of 6-methyl-2,4-diphenylquinoline 4

6-Methyl-4-phenylquinoline-2(1H)-thione **2b** (1.0 mmol, 0.0251 g), phenylboronic acid (1.2 mmol, 0.0167 g), Pd(OAc)₂ (5 mol%, 0.025 mmol, 0.0175 g), CuTC (2.5 equiv, 2.5 mmol, 0.0475 g) was added to the sealed tube, PPh₃ (10 mol%, 0.1 mmol, 0.0262 g), The mixture was stirred at 120 °C for 16 h. And the progress of the reaction was monitored by TLC (silica gel). After completion of the reaction, mixture was cooled to ambient temperature, quenched by addition of saturated NH₄Cl (2.0 ml), and extracted with ethyl acetate (3×10 mL). The organic layers were combined and dried with anhydrous MgSO₄ and concentrated in vacuo, the resulting residue was purified by silica gel column chromatography using ethyl acetate/petroleum ether(1:20) as eluent to afford the products.

1.6 Procedure for the synthesis of 6-methyl-4-phenyl-2-(phenylthio)quinoline 5

6-Methyl-4-phenylquinoline-2(1H)-thione **2b** (1.0 mmol, 0.0251 g), phenylboronic acid (1.2 mmol, 0.0167 g), Cu(OAc)₂ (1.0 equiv, 1.0 mmol, 0.0123 g), 1,10-phenanthroline monohydrate (5 mol%, 0.05 mmol, 0.0099 g) was added to the sealed tube, DCE (3.0 ml) was added by dropper and the mixture was stirred at 110 °C for 30 h. And the progress of the reaction was monitored by TLC (silica gel). After completion of the reaction, mixture was cooled to ambient temperature, quenched by addition of saturated NH₄Cl (2.0 mL), and extracted with ethyl acetate (3×10 mL). The organic layers were combined and dried with anhydrous MgSO₄ and concentrated in vacuo, the resulting residue was purified by silica gel column chromatography using ethyl acetate/petroleum ether (1:20) as eluent to afford the products.

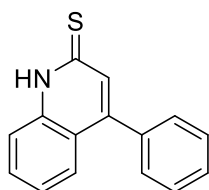
1.7 Procedure for the synthesis of methyl 3-(6-methyl-4-phenyl-2-thioxoquinolin-1(2H)-yl) propanoate 6

6-Methyl-4-phenylquinoline-2(1H)-thione **2b** (1.0 mmol, 0.0251 g), methyl acrylate (1.2 mmol, 0.01032 g), K₂CO₃ (30 mol%, 0.3 mmol, 0.00414 g), PEG-400 (3.0 mL) was added by dropper and the mixture was stirred at rt for 18 h. And the progress of the reaction was monitored by TLC (silica gel). After completion of the reaction, mixture was cooled to ambient temperature, quenched by addition of saturated NH₄Cl (2.0 mL), and extracted with ethyl acetate (3×10 mL). The organic layers were combined and dried with anhydrous MgSO₄ and concentrated in vacuo, the resulting residue was purified by silica gel column chromatography using ethyl acetate/petroleum ether (1:5) as eluent to afford the products.

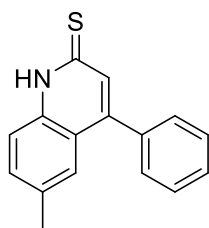
1.8 Procedure for the synthesis of

6-methyl-2-((6-methyl-4-phenyl-4a,8a-dihydroquinolin-2-yl)disulfanyl)-4-phenylquinoline 7

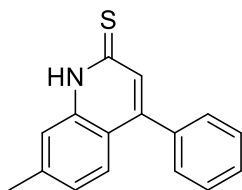
6-Methyl-4-phenylquinoline-2(1H)-thione **2b** (1.0 mmol, 0.0251 g), DDQ (0.5 mmol, 0.0113 g), NaH (0.5 mmol, 0.0012 g), diaoxane (5 mL) was added by dropper and the mixture was stirred at room temperature for 8 h. And the progress of the reaction was monitored by TLC (silica gel). After completion of the reaction, mixture was cooled to ambient temperature, quenched by addition of saturated NH₄Cl (2.0 mL), and extracted with ethyl acetate (3×10 mL). The organic layers were combined and dried with anhydrous MgSO₄ and concentrated in vacuo, the resulting residue was purified by silica gel column chromatography using ethyl acetate/petroleum ether (1:5) as eluent to afford the products.



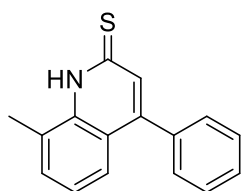
4-Phenylquinoline-2(1H)-thione (2a). Yellow solid (94%, 111.4 mg): mp 187-188 °C. ¹H NMR (600 MHz, CDCl₃) δ: 7.97 (d, *J* = 9.0 Hz, 1H), 7.79 (d, *J* = 2.4 Hz, 1H), 7.75 (s, 1H), 7.63 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.49 (dd, *J* = 4.8, 1.8 Hz, 3H), 7.40 – 7.38 (m, 2H). ¹³C NMR (150 MHz, CDCl₃) δ: 158.93, 149.16, 146.84, 136.76, 132.34, 131.04, 130.32, 129.33, 128.96, 128.80, 125.98, 124.82, 118.21. HRMS (ESI⁺) *m/z*: Calcd for C₁₅H₁₂NS 238.0685 [M+H]⁺, Found 238.0683.



6-Methyl-4-phenylquinoline-2(1H)-thione (2b). Yellow solid (93%, 116.7 mg): mp 215-217 °C. ¹H NMR (600 MHz, DMSO-*d*₆) δ: 13.68 (s, 1H), 7.60 (d, *J* = 2.4 Hz, 1H), 7.54 – 7.51 (m, 3H), 7.48-7.46 (m, 3H), 7.25 (s, 1H), 7.08 (s, 1H), 2.27 (s, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ: 184.48, 150.91, 143.17, 141.21, 138.83, 137.89, 136.13, 134.21, 134.00, 130.40, 130.38, 126.40, 121.82, 26.01. HRMS (ESI⁺) *m/z*: Calcd for C₁₆H₁₄NS 252.0841 [M+H]⁺, Found 252.0845.

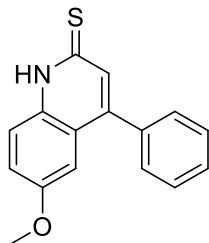


7-Methyl-4-phenylquinoline-2(1H)-thione (2c). Yellow solid (85%, 106.7 mg): mp 252-254 °C. ¹H NMR (600 MHz, DMSO-*d*₆) δ: 13.52 (s, 1H), 7.52 (d, *J* = 7.2 Hz, 3H), 7.46 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.39 (d, *J* = 9.0 Hz, 1H), 7.21 (d, *J* = 2.4 Hz, 1H), 6.97 (s, 1H), 6.93 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.82 (s, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ: 180.55, 161.93, 146.59, 141.96, 136.58, 129.48, 129.23, 129.19, 128.72, 127.98, 116.05, 114.28, 99.23, 56.05. HRMS (ESI⁺) *m/z*: Calcd for C₁₆H₁₄NS 252.0841 [M+H]⁺, Found 252.0843.



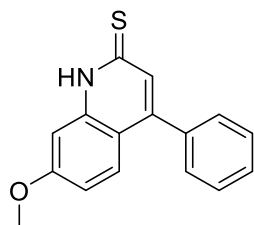
8-Methyl-4-phenylquinoline-2(1H)-thione (2d). Yellow solid (88%, 110.4 mg): mp

185-187 °C. ¹H NMR (600 MHz, CDCl₃) δ: 13.01 (s, 1H), 7.67 (d, *J* = 9.0 Hz, 1H), 7.53-7.47 (m, 6H), 7.27 – 7.23 (m, 1H), 7.03 (d, *J* = 3.0 Hz, 1H), 3.73 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ: 177.34, 156.63, 147.48, 136.37, 131.39, 129.25, 129.16, 128.81, 128.80, 128.64, 121.15, 117.94, 107.50, 55.59. HRMS (ESI⁺) *m/z*: Calcd for C₁₆H₁₄NS 252.0841 [M+H]⁺, Found 252.0845.



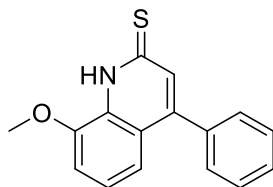
6-Methoxy-4-phenylquinoline-2(1H)-thione (2e). Yellow solid (90%, 120.2 mg): mp

181-182 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ: 13.75 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 4.0 Hz, 5H), 7.36 (dd, *J* = 12, 4.0 Hz, 1H), 7.15 (s, 1H), 6.92 (d, *J* = 2.8 Hz, 1H), 3.70 (s, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ: 178.38, 156.09, 145.83, 136.42, 135.23, 131.70, 129.57, 129.32, 129.18, 122.54, 121.16, 118.72, 107.34, 55.76. HRMS (ESI⁺) *m/z*: Calcd for C₁₆H₁₄NOS 268.0791 [M+H]⁺, Found 268.0794.



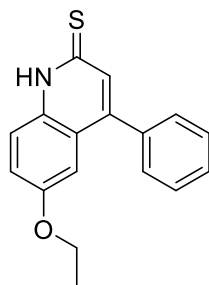
7-Methoxy-4-phenylquinoline-2(1H)-thione (2f). Yellow solid (85%, 113.5 mg): mp

256-258 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ: 12.10 (s, 1H), 7.57 – 7.50 (m, 5H), 7.30 – 7.28 (m, 2H), 7.19 (s, 1H), 7.08 (dd, *J* = 7.2, 2.4 Hz, 1H), 4.00 (s, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ: 180.20, 146.42, 146.32, 136.37, 132.00, 130.39, 129.57, 129.25, 129.21, 124.84, 122.30, 118.00, 112.00, 56.89. HRMS (ESI⁺) *m/z*: Calcd for C₁₆H₁₄NOS 268.0791 [M+H]⁺, Found 268.0793.



8-Methoxy-4-phenylquinoline-2(1H)-thione (2g). Yellow solid (82%, 109.5 mg): mp

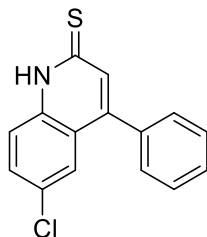
216-218 °C. ¹H NMR (400 MHz, CDCl₃) δ: 10.96 (s, 1H), 7.51 – 7.44 (m, 6H), 7.20 (d, *J* = 6.8 Hz, 2H), 7.04 (dd, *J* = 6.8, 2.4 Hz, 1H), 4.04 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ: 180.04, 147.14, 136.29, 131.97, 130.00, 129.10, 128.90, 128.65, 123.99, 118.45, 110.17, 56.21. HRMS (ESI⁺) *m/z*: Calcd for C₁₆H₁₄NOS 268.0791 [M+H]⁺, Found 268.0792.



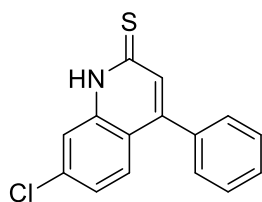
6-Ethoxy-4-phenylquinoline-2(1H)-thione (2h). Yellow solid (79%, 110.9 mg): mp

159-162 °C. ¹H NMR (600 MHz, DMSO-*d*₆) δ: 13.68 (s, 1H), 7.65 (d, *J* = 6.0 Hz, 1H), 7.54-7.49 (m, 5H), 7.31 (dd, *J* = 6.0, 6.0 Hz, 1H), 7.10 (s, 1H), 6.85 (d, *J* = 3.0 Hz, 1H), 3.89 (q, *J* = 6.6 Hz, 2H), 1.25 (t, *J* = 6.6 Hz, 3H).

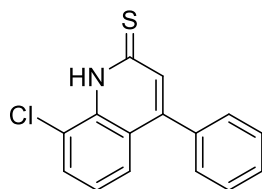
^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ : 178.35, 155.37, 145.84, 136.43, 135.13, 131.63, 129.56, 129.32, 129.16, 122.58, 121.41, 118.69, 108.03, 63.87, 14.87. HRMS (ESI⁺) m/z : Calcd for $\text{C}_{17}\text{H}_{16}\text{NOS}$ 282.0947 $[\text{M}+\text{H}]^+$, Found 282.0949.



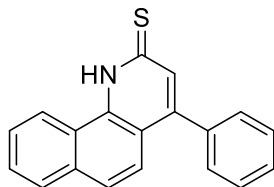
6-Chloro-4-phenylquinoline-2(1H)-thione (2i). Yellow solid (60%, 81.3 mg): mp 213-215 °C. ^1H NMR (400 MHz, CDCl_3) δ : 7.97 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 4.0 Hz, 1H), 7.76 (s, 1H), 7.63 (dd, J = 8.0, 4.0 Hz, 1H), 7.50-7.48 (m, 3H), 7.39 (dd, J = 8.0, 4.0 Hz, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ : 158.94, 149.14, 146.86, 136.77, 132.33, 131.03, 130.33, 129.33, 128.96, 128.80, 125.98, 124.81, 118.21. HRMS (ESI⁺) m/z : Calcd for $\text{C}_{15}\text{H}_{11}\text{ClNS}$ 272.0295 $[\text{M}+\text{H}]^+$, Found 272.0297.



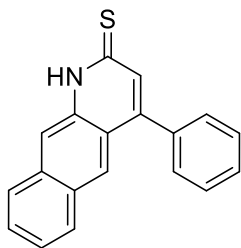
7-Chloro-4-phenylquinoline-2(1H)-thione (2j). Yellow solid (67%, 90.8 mg): mp 243-245 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 13.96 (s, 1H), 7.73 (dd, J = 8.4, 1.2 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.45-7.43 (m, 3H), 7.35-7.32 (m, 3H), 7.05 (s, 1H). ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ : 180.19, 144.95, 142.11, 139.35, 135.18, 131.92, 131.44, 128.57, 128.54, 128.33, 127.49, 119.10, 116.76. HRMS (ESI⁺) m/z : Calcd for $\text{C}_{15}\text{H}_{11}\text{ClNS}$ 272.0295 $[\text{M}+\text{H}]^+$, Found 272.0297.



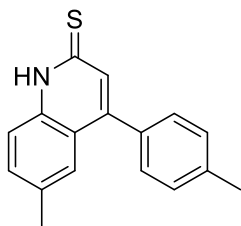
8-Chloro-4-phenylquinoline-2(1H)-thione (2k). Yellow solid (41%, 55.6 mg): mp 187-188 °C. ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ : 13.73 (s, 1H), 7.68 (d, J = 2.4 Hz, 1H), 7.54 – 7.51 (m, 3H), 7.48 – 7.45 (m, 3H), 7.30 (dd, J = 1.8, J = 8.4 Hz, 1H), 7.10 (d, J = 1.2 Hz, 1H). ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ : 186.36, 150.52, 145.49, 140.98, 140.64, 136.39, 134.43, 134.03 (d, J = 8.6 Hz), 133.16, 129.56, 125.25, 120.93. HRMS (ESI⁺) m/z : Calcd for $\text{C}_{15}\text{H}_{11}\text{ClNS}$ 272.0295 $[\text{M}+\text{H}]^+$, Found 272.0297.



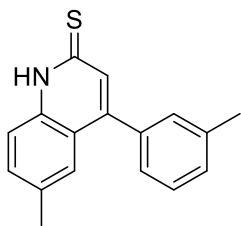
4-Phenylbenzo[h]quinoline-2(1H)-thione (2l). Yellow solid (80%, 114.8 mg): mp 180-184 °C. ^1H NMR (400 MHz, CDCl_3) δ : 9.24 (d, J = 12.0 Hz, 1H), 7.90 (s, 1H), 7.84 (d, J = 11.6 Hz, 1H), 7.17 – 7.56 (m, 5H), 7.44 (s, 5H). ^{13}C NMR (150 MHz, CDCl_3) δ : 157.37, 149.56, 146.89, 137.96, 133.59, 130.90, 129.58, 128.53, 128.48, 128.42, 127.40, 127.16, 127.02, 125.21, 122.73 (d, J = 30.0 Hz), 118.73. HRMS (ESI⁺) m/z : Calcd for $\text{C}_{19}\text{H}_{14}\text{NS}$ 288.0841 $[\text{M}+\text{H}]^+$, Found 288.0844.



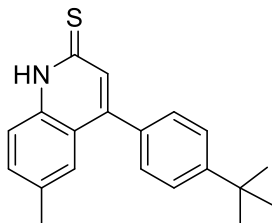
4-Phenylbenzo[g]quinoline-2(1H)-thione (2m). Yellow solid (92%, 132.0 mg): mp 244-246 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ: 14.07 (s, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 9.2 Hz, 1H), 7.58 – 7.57 (m, 3H), 7.47-7.40 (m, 3H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 2H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ: 178.13, 147.36, 141.06 (d, *J* = 1.5 Hz), 134.19, 134.00, 131.23, 129.70 (d, *J* = 3.0 Hz), 129.11 (d, *J* = 11.0 Hz), 127.99, 127.07, 126.11, 125.85, 117.32, 116.64. HRMS (ESI⁺) *m/z*: Calcd for C₁₉H₁₄NS 288.0841 [M+H]⁺, Found 288.0843.



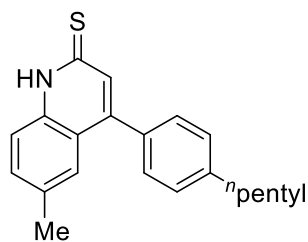
6-Methyl-4-(p-tolyl)quinoline-2(1H)-thione (2n). Yellow solid (89%, 129.9 mg): mp 194-196 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.93 (d, *J* = 8.4 Hz, 1H), 7.72 (s, 1H), 7.60 (d, *J* = 1.6 Hz, 1H), 7.51 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.31-7.27 (m, 4H), 2.42 (d, *J* = 1.6 Hz, 6H). ¹³C NMR (150 MHz, CDCl₃) δ: 157.74, 149.39, 147.03, 138.47, 136.21, 134.74, 132.22, 129.39, 129.25, 128.42, 125.23, 124.80, 117.36, 21.74, 21.28. HRMS (ESI⁺) *m/z*: Calcd for C₁₇H₁₆NS 266.0998 [M+H]⁺, Found 266.1002.



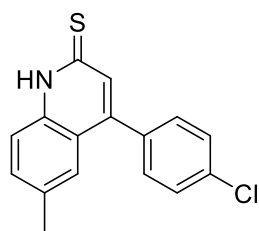
6-Methyl-4-(m-tolyl)quinoline-2(1H)-thione (2o). Yellow solid (84%, 111.3 mg): mp 242-244 °C. ¹H NMR (600 MHz, CDCl₃) δ: 12.99 (s, 1H), 7.62 (d, *J* = 9.0 Hz, 1H), 7.41 (dd, *J* = 18.0, 10.8 Hz, 4H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 2H), 2.45 (s, 3H), 2.36 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ: 178.62, 148.02, 138.54, 137.77, 136.36, 134.67, 132.83, 131.00, 129.78, 129.56, 128.49, 126.10 (d, *J* = 2.7 Hz), 122.49, 116.41, 21.40. HRMS (ESI⁺) *m/z*: Calcd for C₁₇H₁₆NS 266.0998 [M+H]⁺, Found 266.1000.



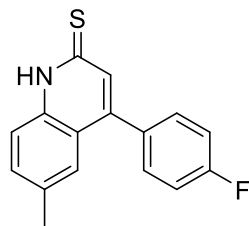
4-(4-(*Tert*-butyl)phenyl)-6-methylquinoline-2(1H)-thione (2p). Yellow solid (88%, 135.1 mg): mp 253-255 °C. ¹H NMR (600 MHz, CDCl₃) δ: 13.34 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.48 (s, 1H), 7.46 (s, 1H), 7.11 (t, *J* = 8.4 Hz, 3H), 2.37 (s, 3H), 1.40 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ: 178.34, 152.30, 147.91, 137.91, 134.62, 133.43, 132.78, 130.97, 128.80, 126.11, 125.66, 122.47, 116.54, 34.81, 31.31, 21.35. HRMS (ESI⁺) *m/z*: Calcd for C₂₀H₂₂NS 322.1624 [M+H]⁺, Found 322.1621.



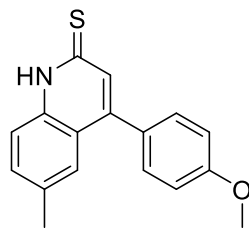
6-Methyl-4-(4-pentylphenyl)quinoline-2(1H)-thione (2q). Yellow solid (88%, 141.2 mg): mp 215-217 °C. ¹H NMR (600 MHz, CDCl₃) δ: 13.0 (s, 1H), 7.64–7.61 (m, 1H), 7.45 (d, *J* = 10.2 Hz, 2H), 7.40 (m, 3H), 7.32 (d, *J* = 7.8 Hz, 2H), 2.78–2.61 (m, 1H), 2.36 (s, 2H), 1.79–1.65 (m, 1H), 1.38 (dd, *J* = 7.4, 3.6 Hz, 2H), 0.97–0.86 (m, 2H). ¹³C NMR (150 MHz, CDCl₃) δ: 178.55, 147.97, 144.19, 137.80, 134.62, 133.63, 132.78, 130.97, 128.93, 128.72, 126.15, 122.48, 116.42, 35.77, 31.58, 31.01, 22.54, 21.33, 14.03. HRMS (ESI⁺) *m/z*: Calcd for C₂₁H₂₄NS 322.1624 [M+H]⁺, Found 322.1626.



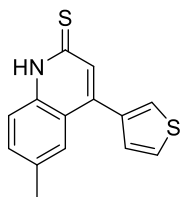
4-(4-Chlorophenyl)-6-methylquinoline-2(1H)-thione (2r). Yellow solid (87%, 123.9 mg): mp 240-243 °C. ¹H NMR (600 MHz, CDCl₃) δ: 13.16 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.46–7.32 (m, 4H), 7.35 (s, 1H), 7.22 (t, *J* = 8.4 Hz, 2H), 2.36 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ: 178.55, 164.03, 162.37, 146.76, 137.81, 134.90, 133.00, 132.33 (d, *J* = 3.4 Hz), 131.18, 130.79 (d, *J* = 8.4 Hz), 125.78, 122.37, 116.52, 115.97, 115.82, 21.35. HRMS (ESI⁺) *m/z*: Calcd for C₁₆H₁₃ClNS 286.0452 [M+H]⁺, Found 286.0454.



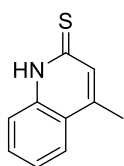
4-(2-Fluorophenyl)-6-methylquinoline-2(1H)-thione (2s). Yellow solid (78%, 104.9 mg): mp 230-233 °C. ¹H NMR (600 MHz, CDCl₃) δ: 11.86 (s, 1H), 7.51-7.34 (m, 8H), 2.38 (s, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ: 179.73, 144.93, 135.27, 134.28 (d, *J* = 66.0 Hz), 133.23, 131.46, 131.17, 129.30, 125.49, 121.48, 117.08, 21.23. ¹⁹F NMR (CDCl₃, 376.5 MHz) δ: -112.22 – (-)112.27 (m). HRMS (ESI⁺) *m/z*: Calcd for C₁₆H₁₃FNS 270.0747 [M+H]⁺, Found 270.0743.



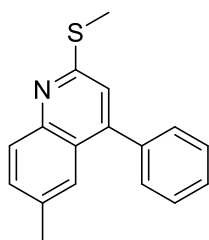
4-(4-Methoxyphenyl)-6-methylquinoline-2(1H)-thione (2t). Yellow solid (95%, 133.5 mg): mp 192-194 °C. ¹H NMR (600 MHz, CDCl₃) δ: 7.91 (d, *J* = 9.0 Hz, 1H), 7.52–7.46 (m, 8H), 7.14 (s, 1H), 2.72 (s, 3H), 2.42 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ: 179.69, 146.16, 143.90, 138.44, 134.00, 133.76, 133.07, 131.27, 129.17 (d, *J* = 10.1 Hz), 125.69, 121.66, 117.07, 35.34, 21.27. HRMS (ESI⁺) *m/z*: Calcd for C₁₇H₁₆NOS 282.0947 [M+H]⁺, Found 282.0951.



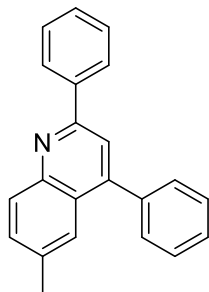
6-methyl-4-(thiophen-3-yl)quinoline-2(1H)-thione (2u). Yellow solid (75%, 96.4 mg): mp 333-335 °C. ¹H NMR (600 MHz, CDCl₃) δ = 10.91 (s, 1H), 7.93 (d, *J* = 6.0 Hz, 1H), 7.79 (s, 1H), 7.73 (s, 1H), 7.54 (d, *J* = 6.0 Hz, 1H), 7.52 (d, *J* = 0.6 Hz, 1H), 7.45 – 7.42 (m, 2H), 7.23 (dd, *J* = 1.2, 1.2 Hz, 1H), 2.46 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ = 157.81, 147.11, 144.00, 138.10, 136.44, 132.33, 128.78, 128.53, 126.21, 125.21, 125.16, 124.57, 117.19, 21.78. HRMS (ESI⁺) *m/z*: Calcd for C₁₄H₁₂NS₂ 258.0406 [M+H]⁺, Found 258.0409.



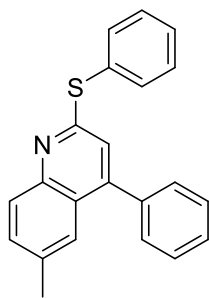
4-methylquinoline-2(1H)-thione (2v). Yellow solid (85%, 74.4 mg): mp 265-267 °C. ¹H NMR (600 MHz, DMSO-*d*₆) δ = 13.44 (s, 1H), 7.76 (d, *J* = 6.0 Hz, 1H), 7.60 – 7.56 (m, 2H), 7.31 (m, 1H), 7.17 (s, 1H), 2.41 (s, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ = 180.75, 143.68, 139.26, 131.38, 131.37, 125.09, 124.41, 122.91, 116.81, 18.38. HRMS (ESI⁺) *m/z*: Calcd for C₁₉H₁₃NS 176.0528 [M+H]⁺, Found 176.0530.



6-Methyl-2-(methylthio)-4-phenylquinoline (3). White solid (79%, 209.4 mg): mp 158-160 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.91 (d, *J* = 8.4 Hz, 1H), 7.55 – 7.45 (m, 7H), 7.13 (s, 1H), 2.72 (s, 3H), 2.41 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ: 158.28, 147.40, 147.10, 137.96, 134.94, 131.53, 129.40, 128.49, 128.28, 128.11, 124.77, 124.58, 120.56, 21.63, 12.93. HRMS (ESI⁺) *m/z*: Calcd for C₁₇H₁₆NS 266.0998 [M+H]⁺, Found 266.0995.

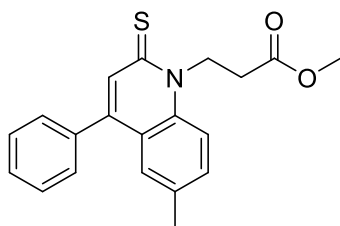


6-Methyl-2,4-diphenylquinoline (4). White solid (69%, 283.6 mg): mp 126-128 °C. ¹H NMR (600 MHz, CDCl₃) δ: 8.22 – 8.18 (m, 2H), 8.16 (d, *J* = 8.64 Hz, 1H), 7.79 (s, 1H), 7.67 (s, 1H), 7.59 – 7.51 (m, 8H), 7.46 (t, *J* = 7.2 Hz, 1H), 2.48 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ: 156.00, 148.43, 147.40, 139.76, 138.65, 136.26, 131.75, 129.87, 129.55, 129.14, 128.79, 128.57, 128.28, 127.48, 125.71, 124.38, 119.40, 21.83. HRMS (ESI⁺) *m/z*: Calcd for C₂₂H₁₈N 296.1434 [M+H]⁺, Found 296.1435.



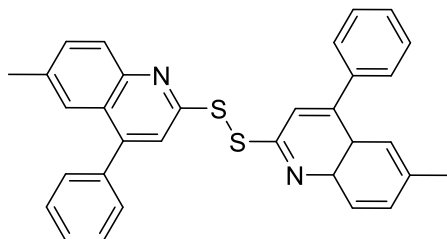
6-Methyl-4-phenyl-2-(phenylthio)quinoline (5). White solid (74%, 242.0 mg): mp

180-184 °C. ¹H NMR (600 MHz, CDCl₃) δ: 7.91 (d, *J* = 8.4 Hz, 1H), 7.68 – 7.64 (m, 2H), 7.53 – 7.44 (m, 5H), 7.40 (m, 5H), 6.94 (s, 1H), 2.42 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ: 159.60, 148.33, 147.16, 137.86, 135.74, 134.69, 131.98, 131.24, 129.50, 129.36, 128.93, 128.52 (d, *J* = 11.5 Hz), 128.32, 124.63 (d, *J* = 10.4 Hz), 119.83, 21.70. HRMS (ESI⁺) *m/z*: Calcd for C₂₂H₁₈NS 328.1154 [M+H]⁺, Found 328.1156



Methyl 3-(6-methyl-4-phenyl-2-thioxoquinolin-1(2H)-yl)propanoate (6).

Oil (67%, 225.8 mg): ¹H NMR (400 MHz, CDCl₃) δ: 7.92–7.88 (d, *J* = 7.6 Hz, 1H), 7.52 – 7.45 (m, 7H), 7.25 (s, 1H), 7.10 (d, *J* = 2.4 Hz, 1H), 3.73 (d, *J* = 2.4 Hz, 3H), 3.61 (td, *J* = 7.0, 2.2 Hz, 2H), 2.93 (td, *J* = 7.0, 2.2 Hz, 2H), 2.42 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ: 172.75, 156.68, 137.84, 135.11, 131.54, 130.87, 129.36, 128.81, 128.49, 128.26 (d, *J* = 14.0 Hz), 124.72, 120.90, 65.54, 51.73, 34.48, 21.63. HRMS (ESI⁺) *m/z*: Calcd for C₂₀H₂₀NO₂S 338.1209 [M+H]⁺, Found 338.1211.

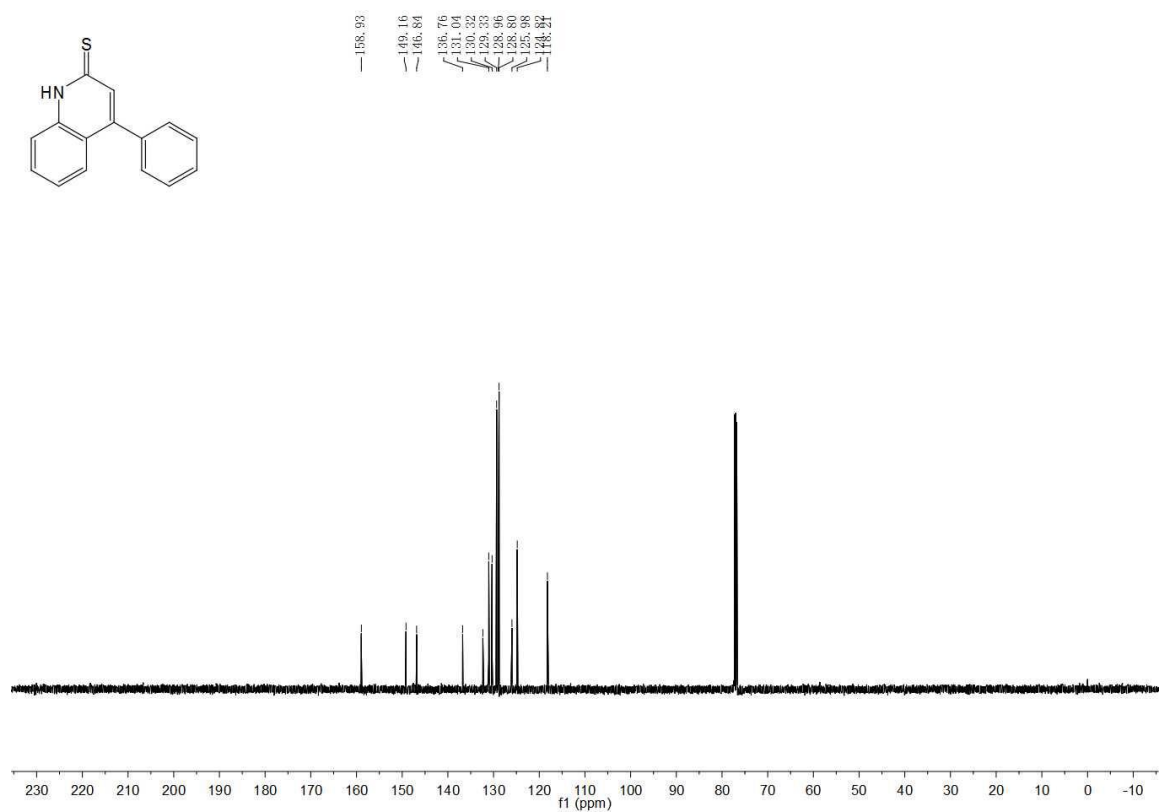
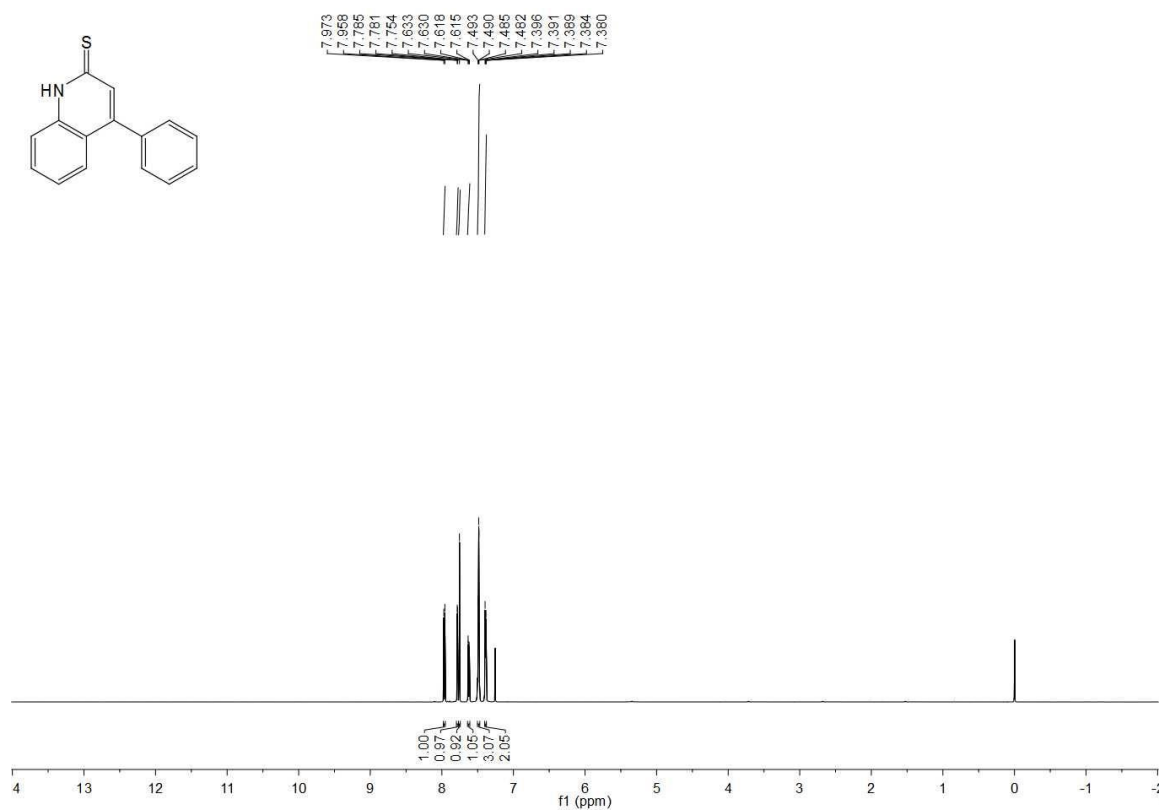


6-Methyl-2-((6-methyl-4-phenyl-4a,8a-dihydroquinolin-2-yl)disulfanyl)-4-phenylquinoline (7). White solid (92%, 460.0 mg) : mp 199-201 °C. ¹H NMR (600 MHz, CDCl₃) δ: 7.94 (d, *J* = 8.8 Hz, 1H), 7.75 (s, 1H), 7.57 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.46 (m, 3H), 7.42 – 7.38 (m, 2H), 2.42 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ: 157.75, 149.28, 147.07, 137.68, 136.33, 132.28, 129.46, 128.51 (d, *J* = 6.5 Hz), 125.13, 124.72, 117.43, 21.74. HRMS (ESI⁺) *m/z*: Calcd for C₃₂H₂₇N₂S₂ 503.1610 [M+H]⁺, Found 503.1613.

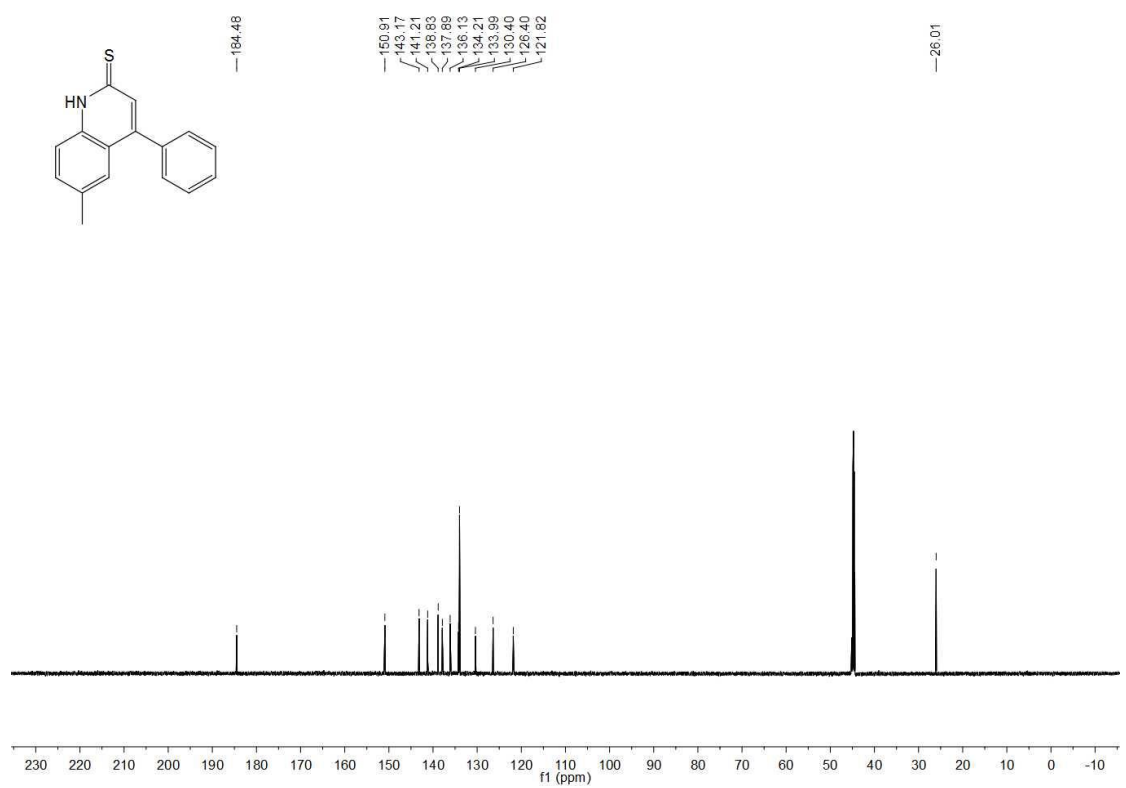
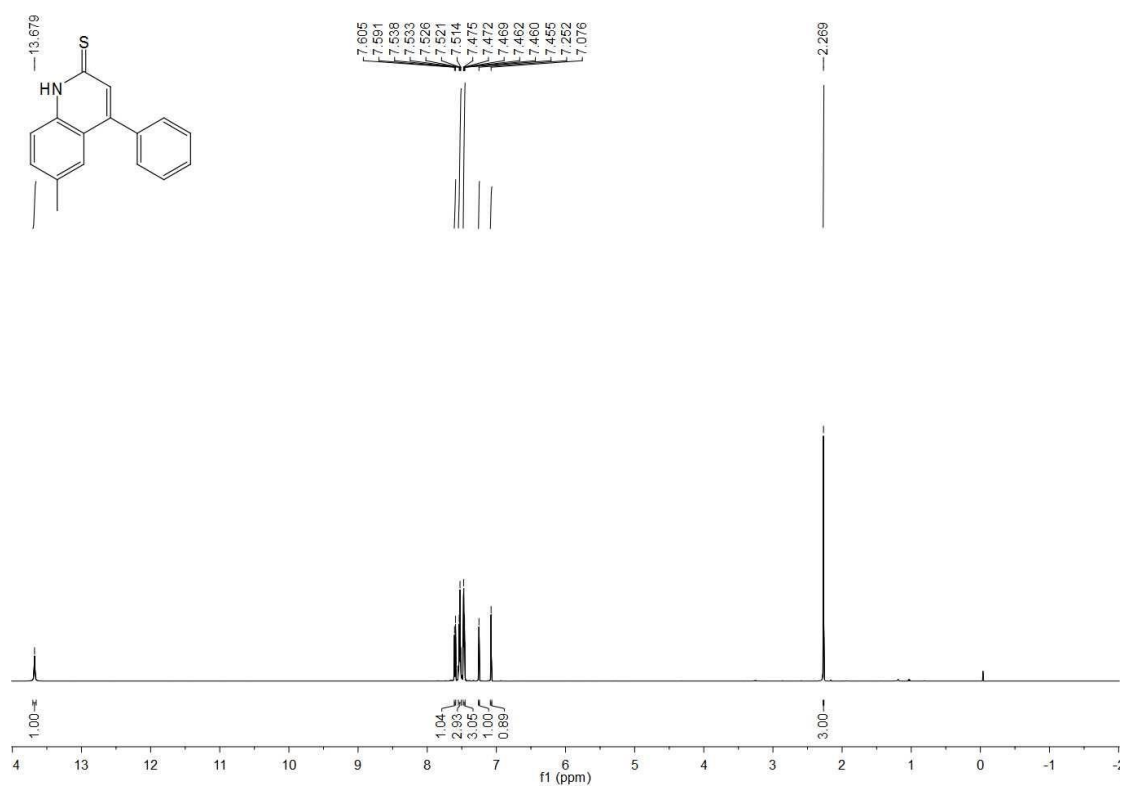
References

- (a) Mameda, N.; Peraka, S.; Kodumuri, S.; Chevella, D.; Marri, M. R.; Nama, N. *RSC Adv.* **2015**, *5*, 78374. (b) Arienti, A. Bigi, F.; Maggi, R.; Marzi, E.; Moggi, P.; Rastelli, M.; Sartori, G.; Tarantola, F. *Tetrahedron* **1997**, *53*, 3795.

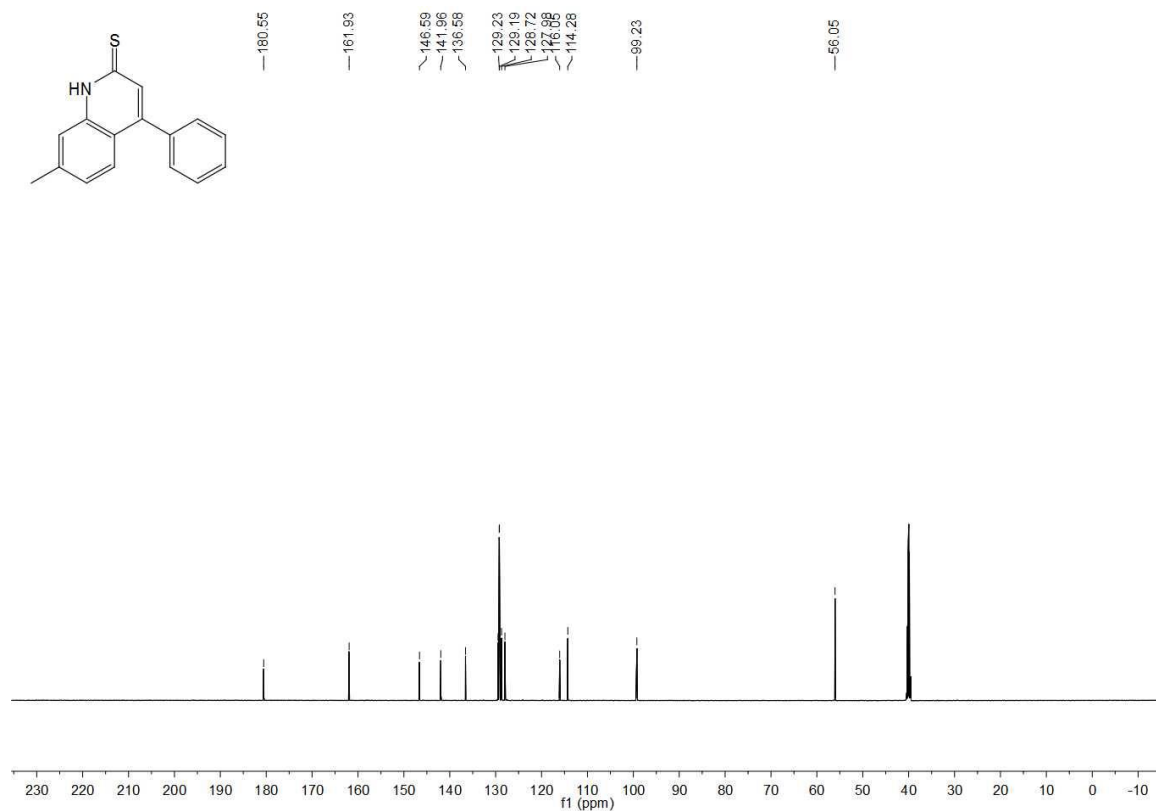
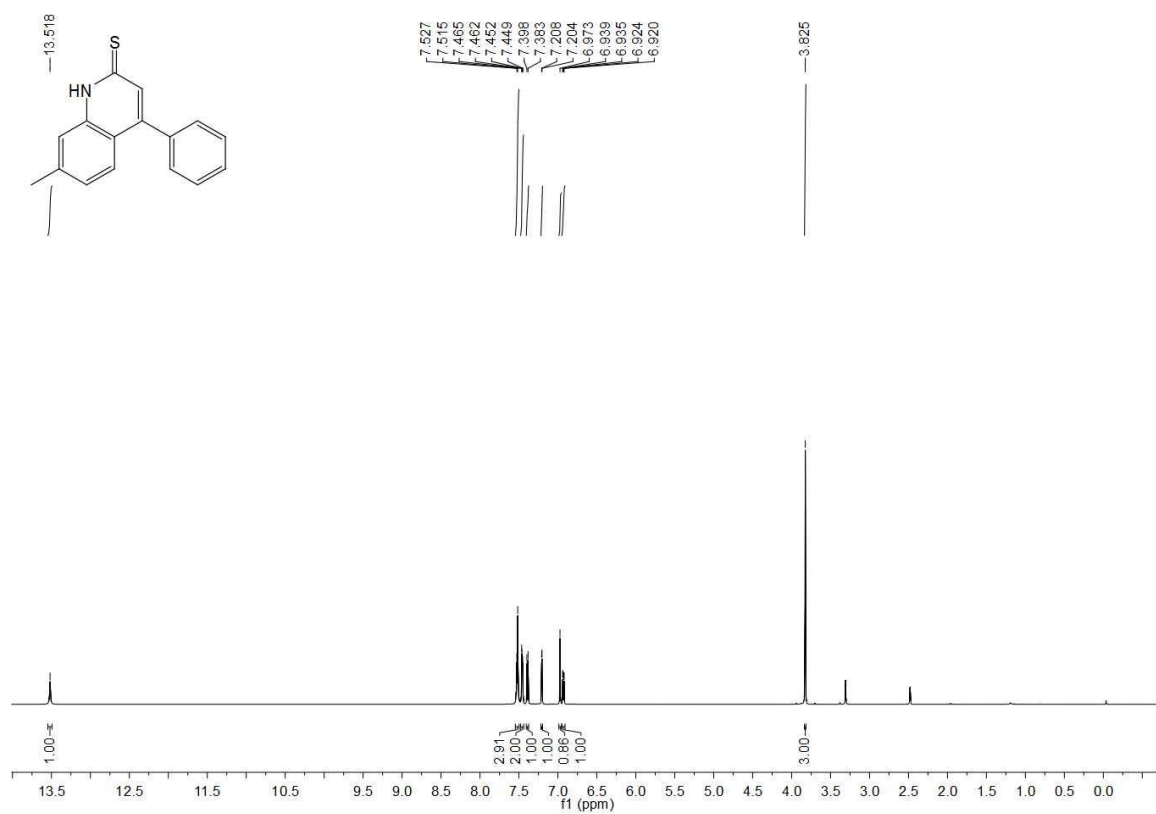
Copies of NMR of compound **2a**.



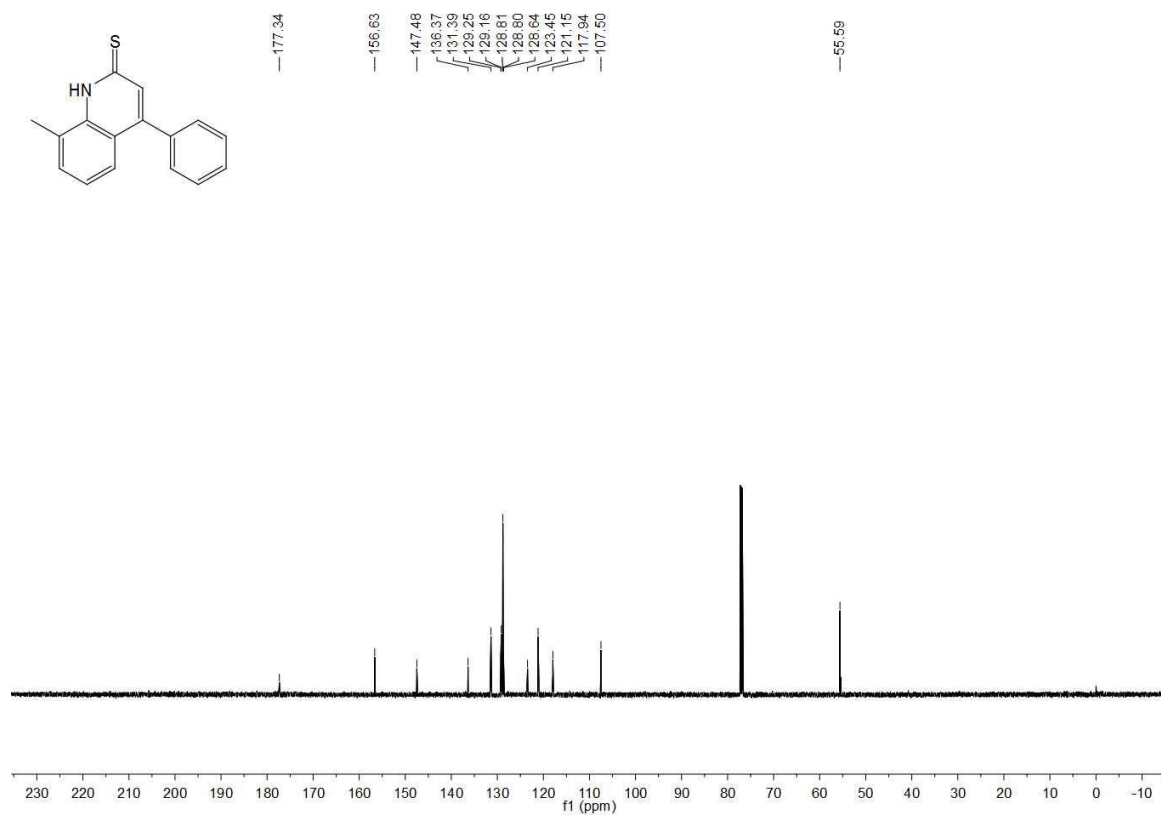
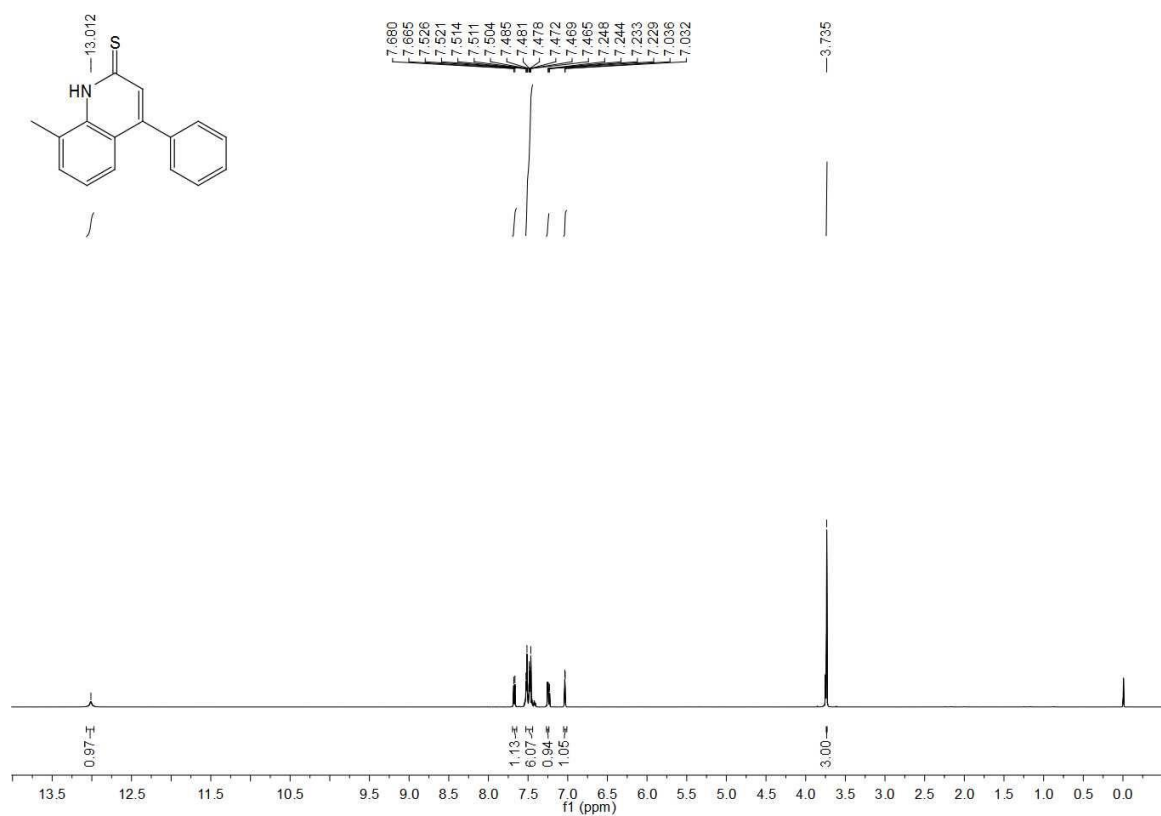
Copies of NMR of compound **2b**.



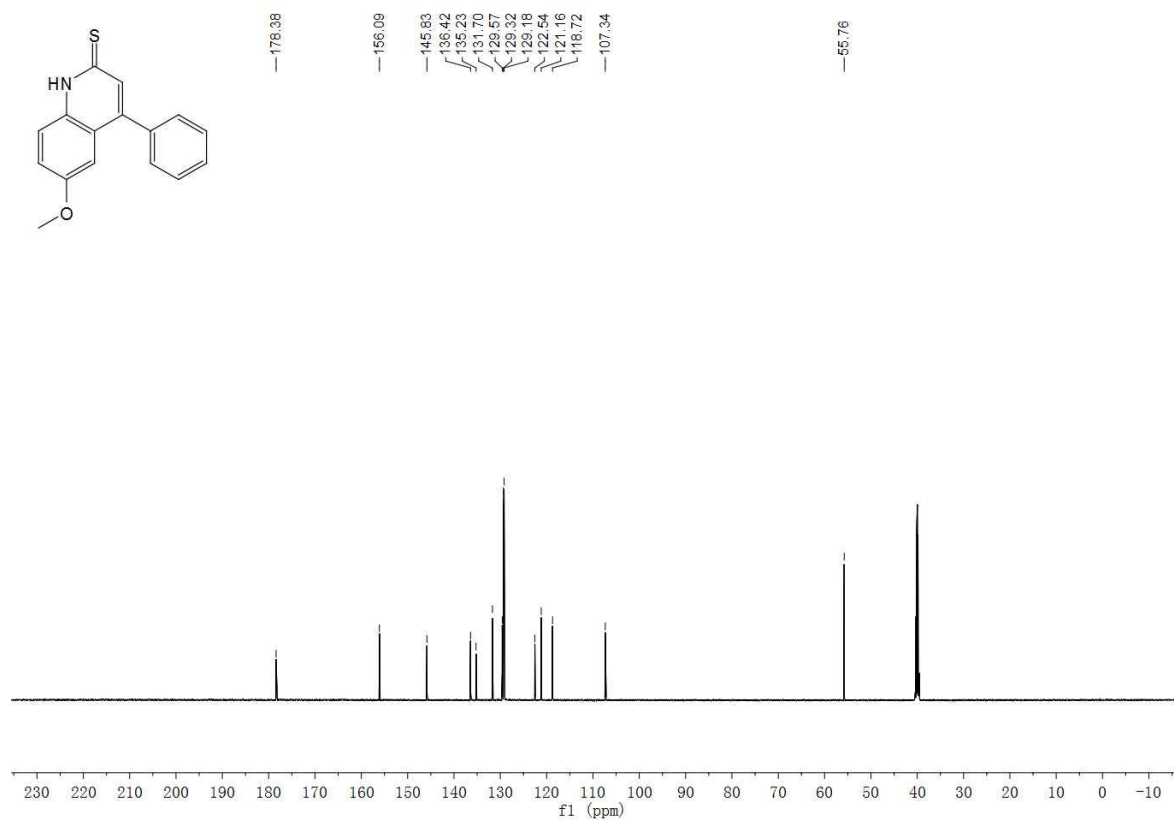
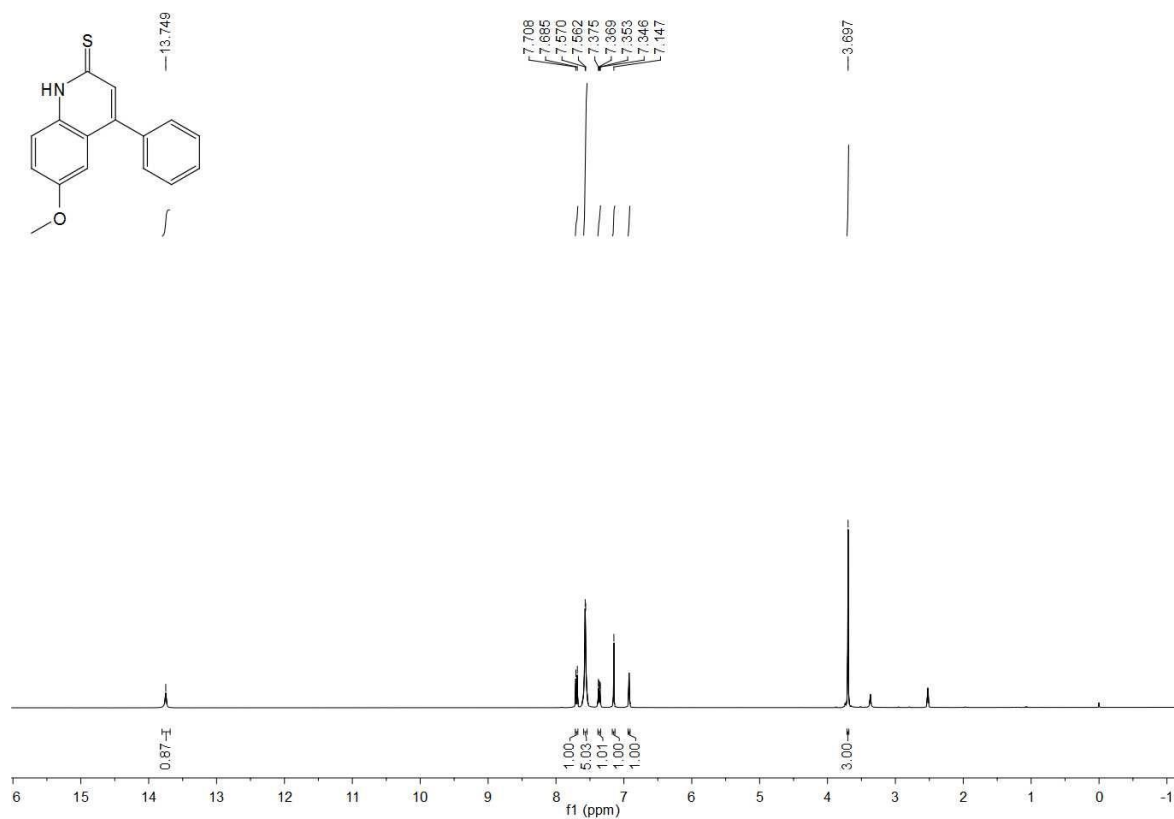
Copies of NMR of compound **2c**.



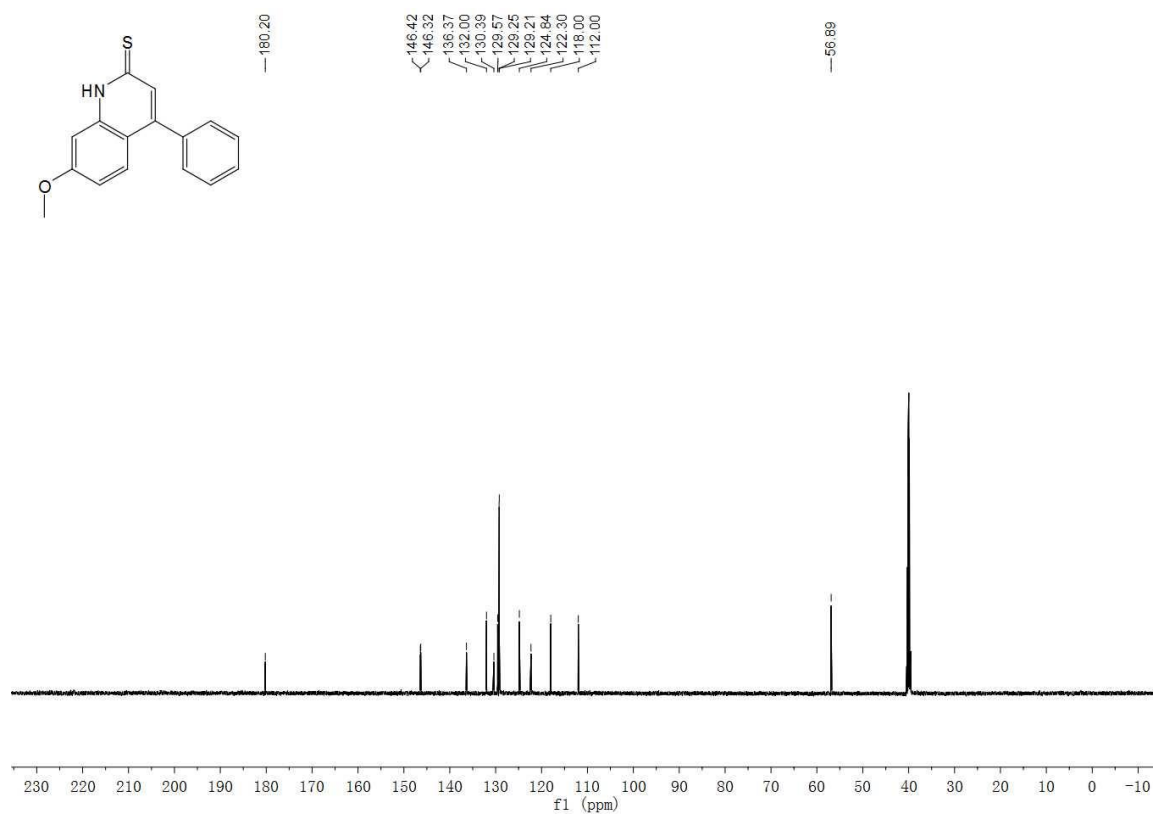
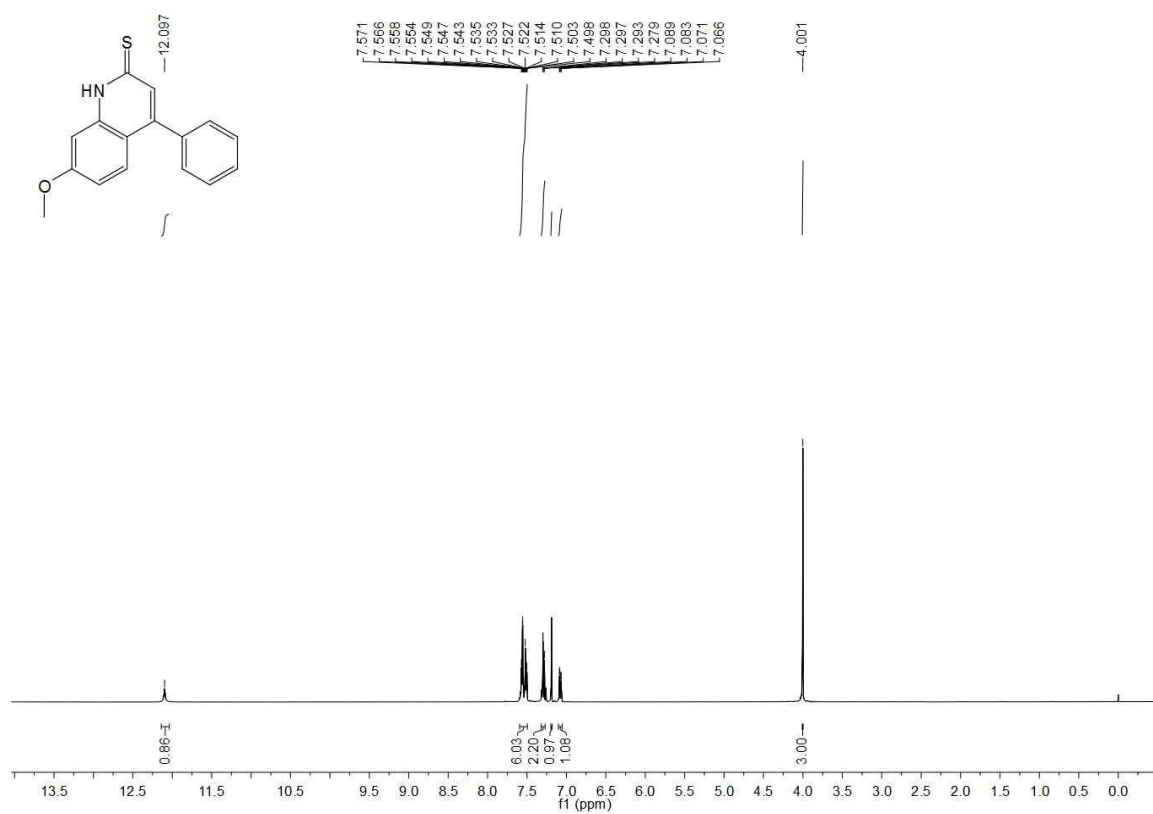
Copies of NMR of compound **2d**.



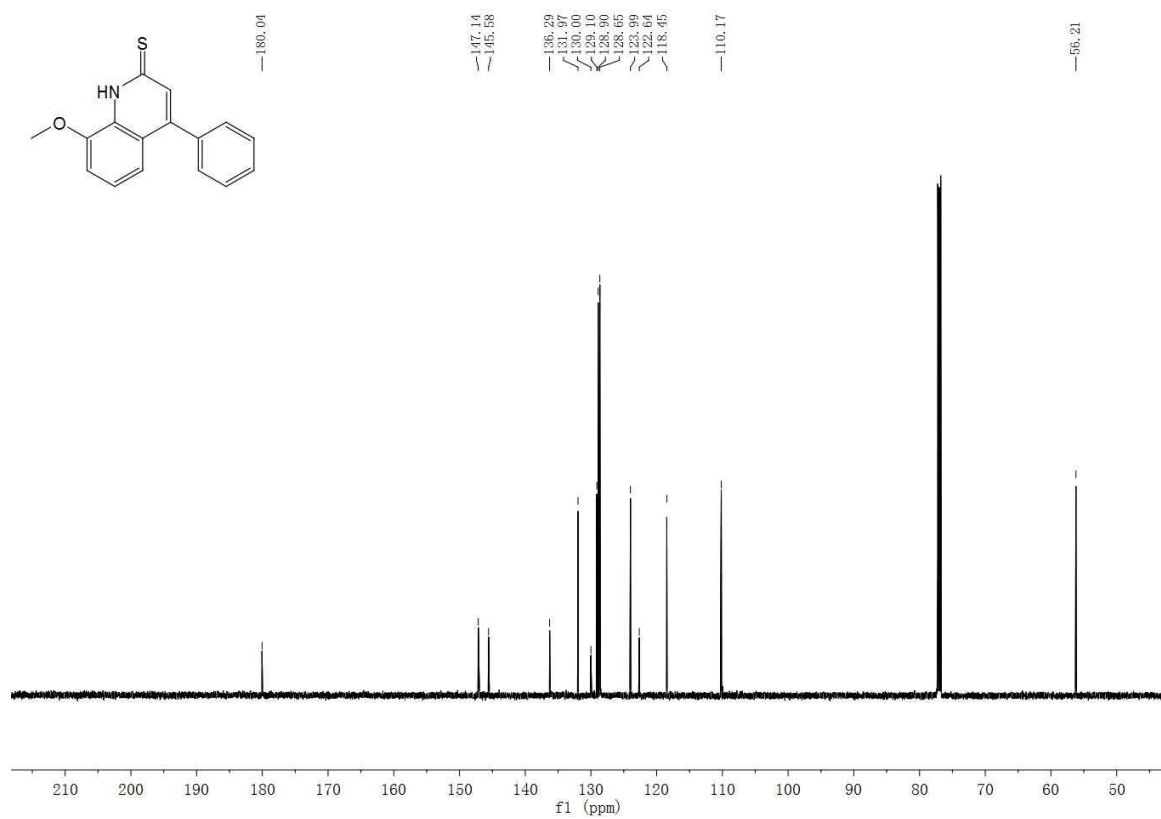
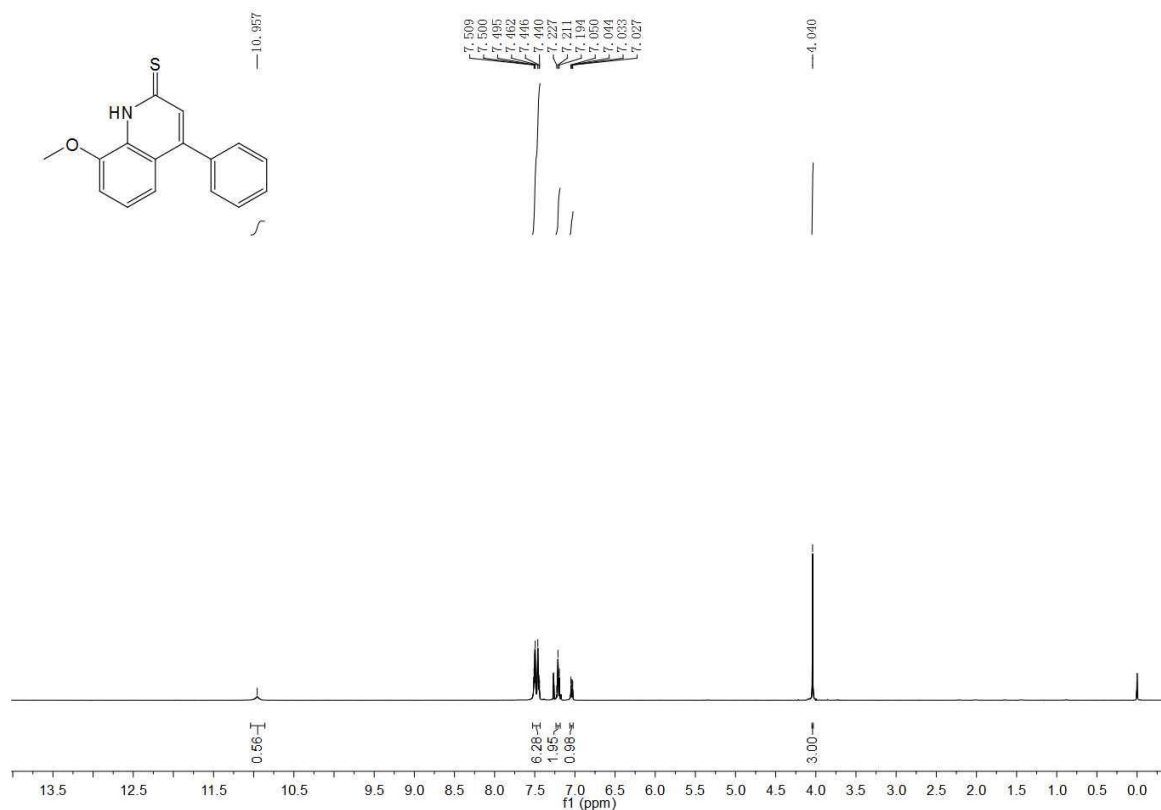
Copies of NMR of compound **2e**.



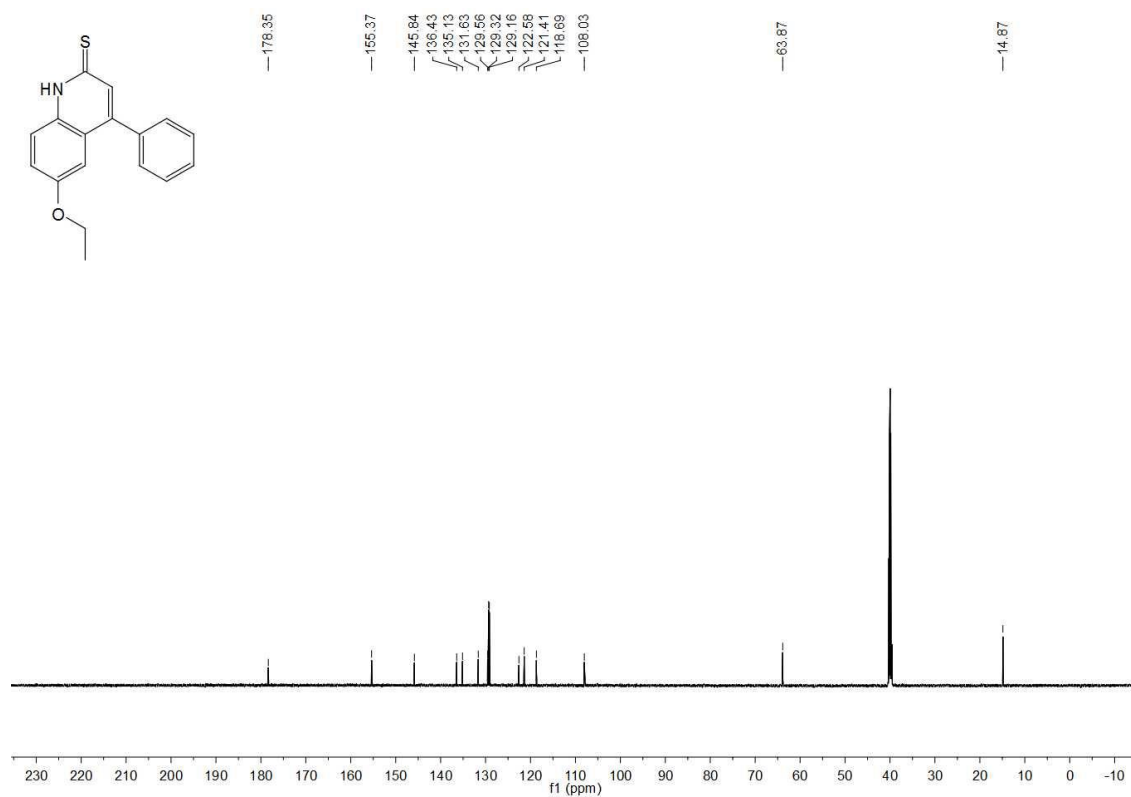
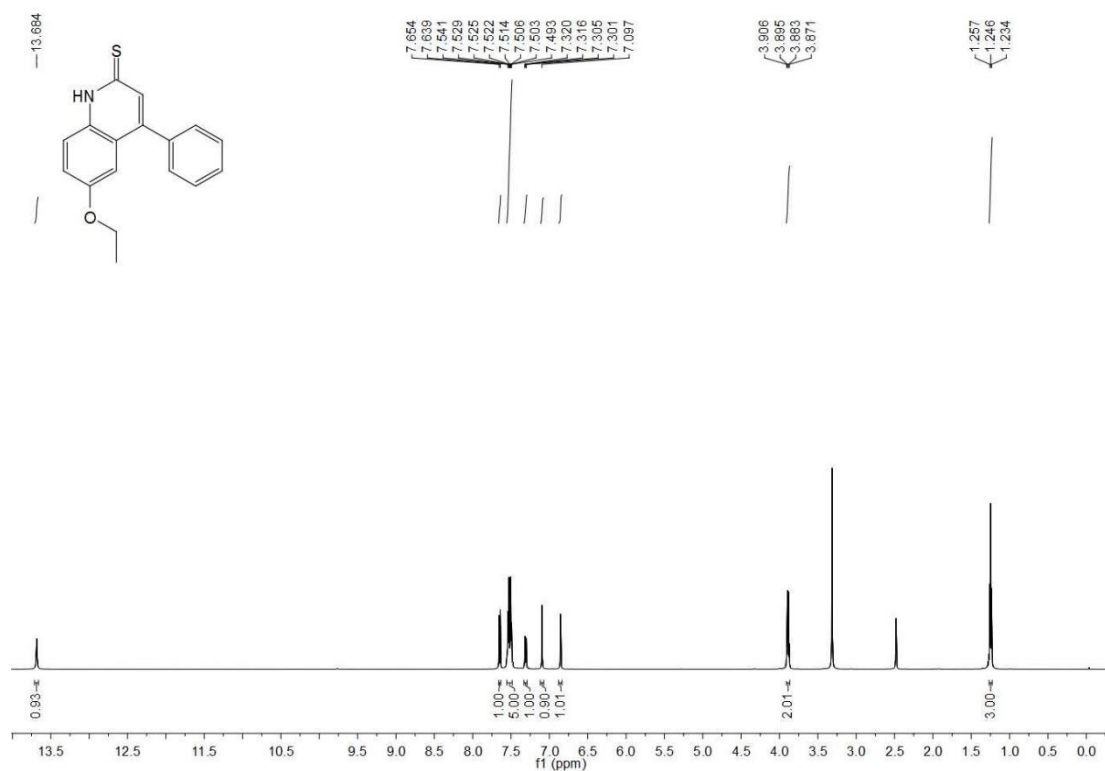
Copies of NMR of compound **2f**.



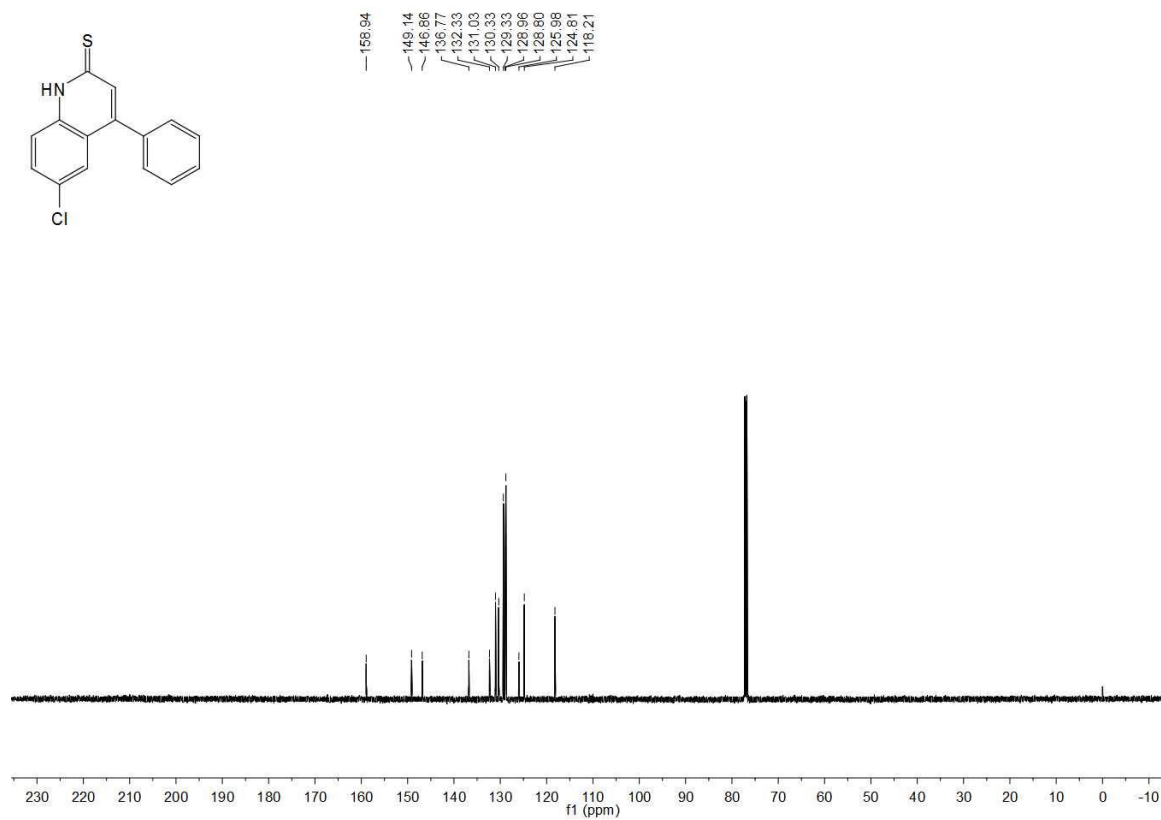
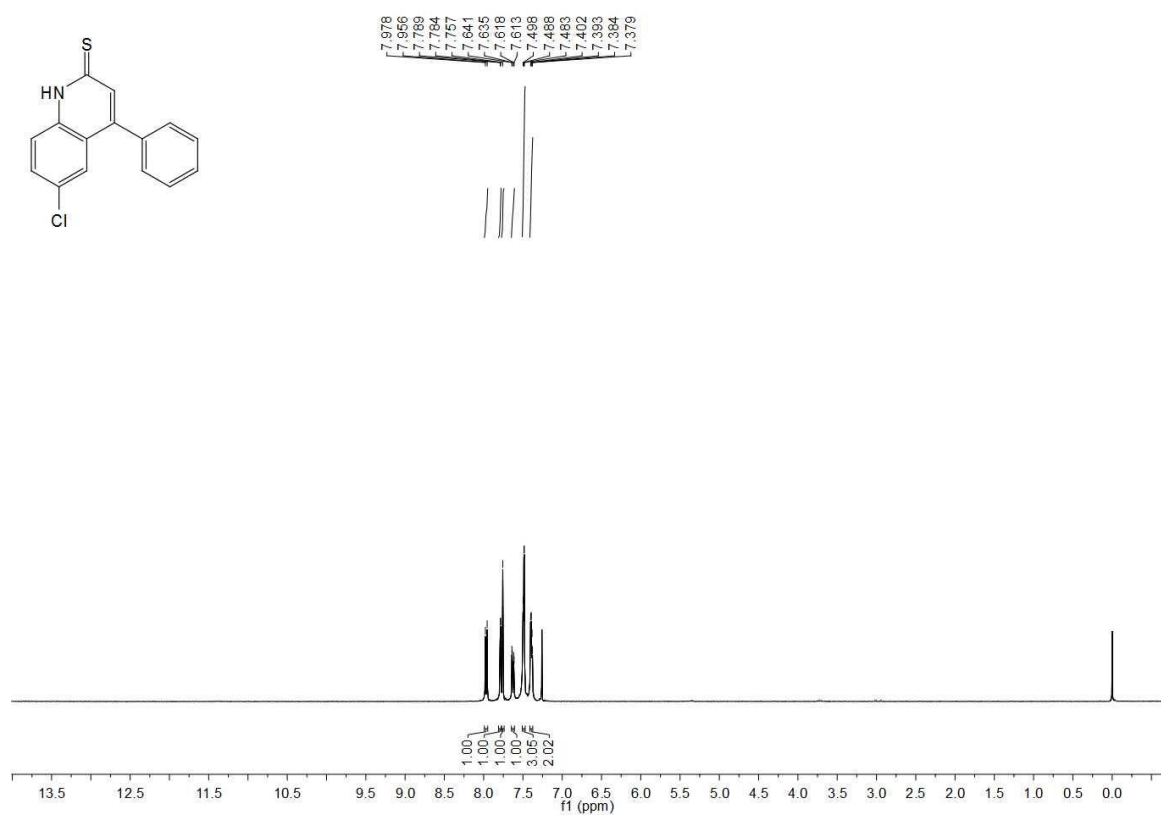
Copies of NMR of compound **2g**.



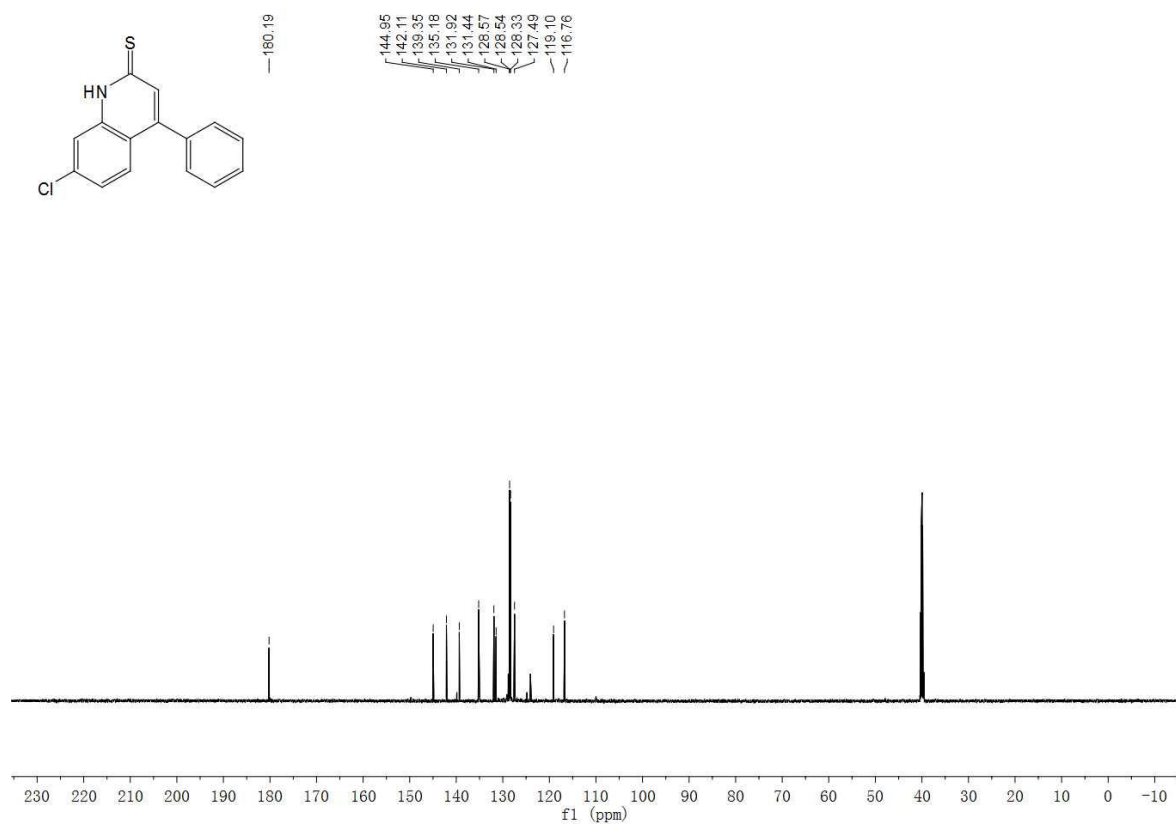
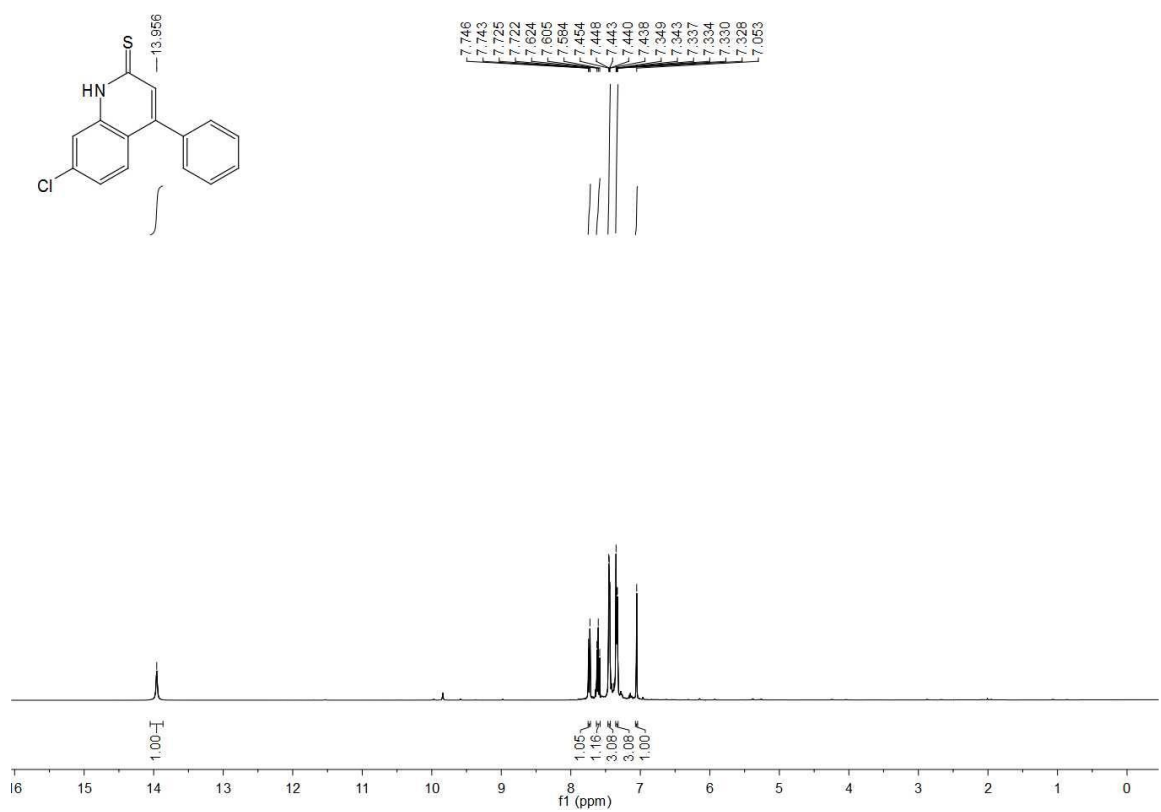
Copies of NMR of compound **2h**.



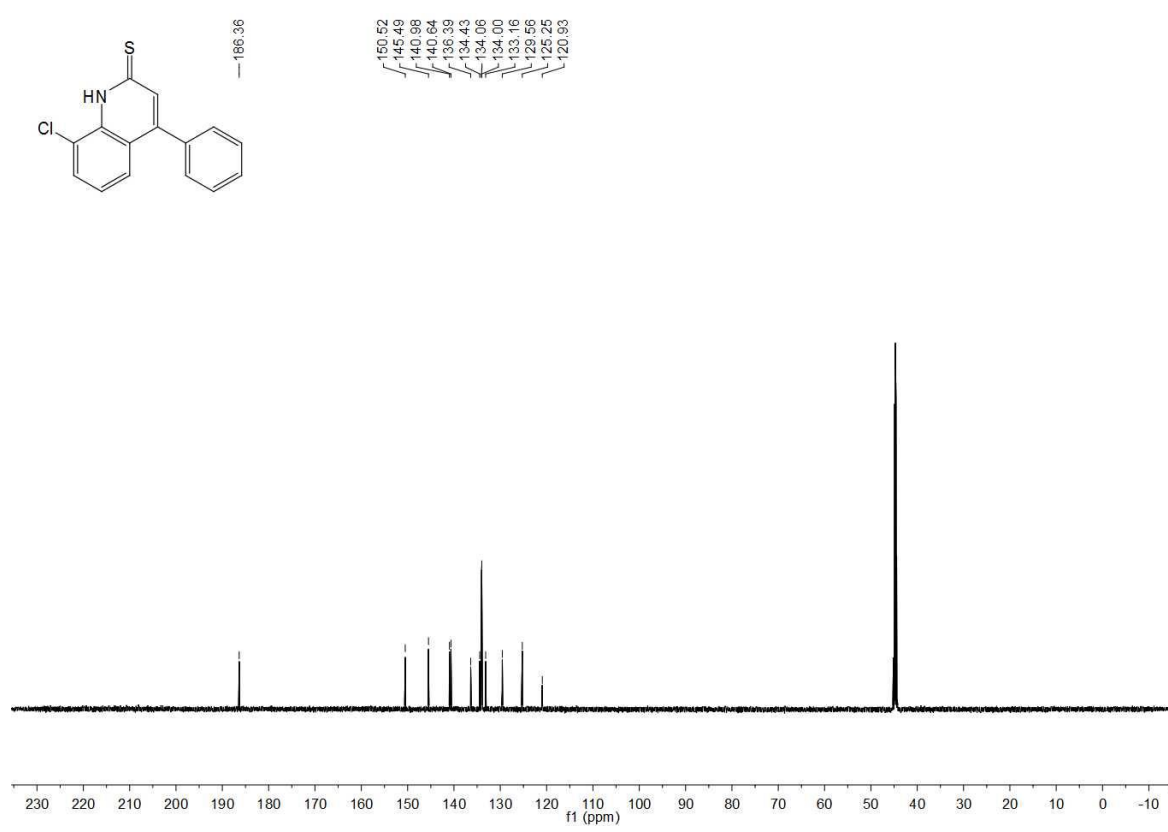
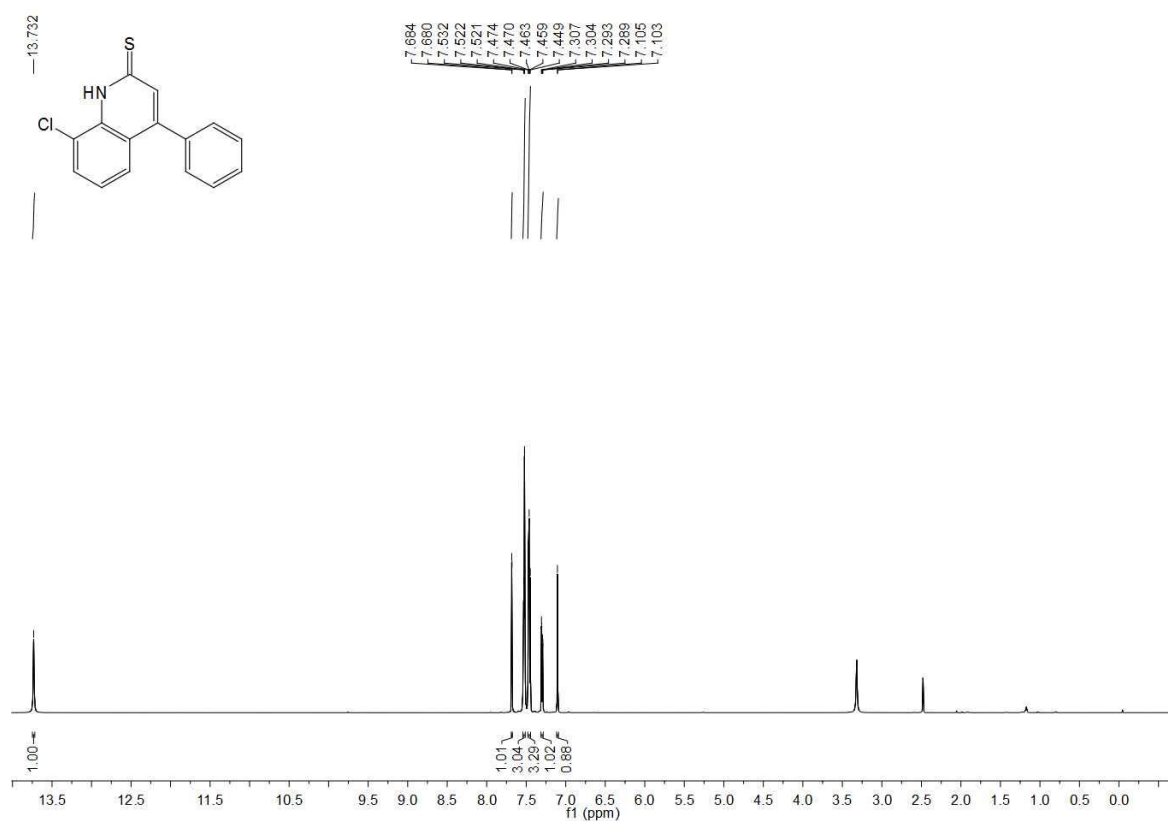
Copies of NMR of compound **2i**.



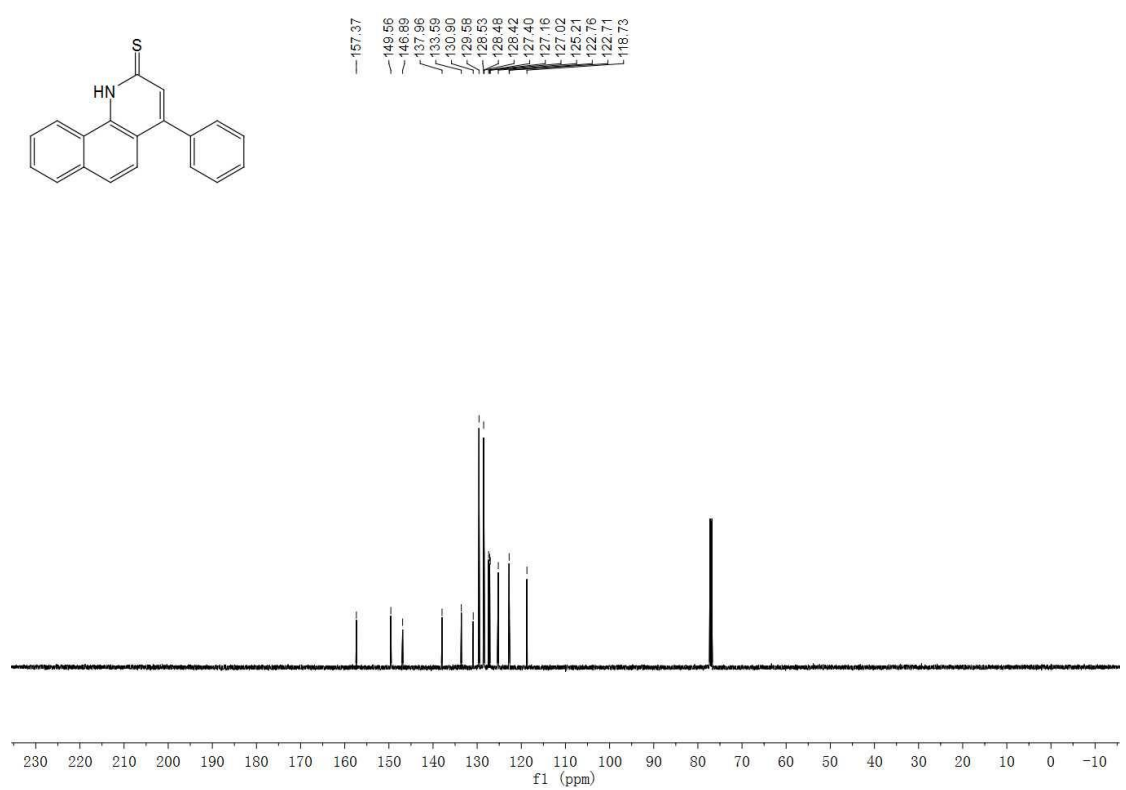
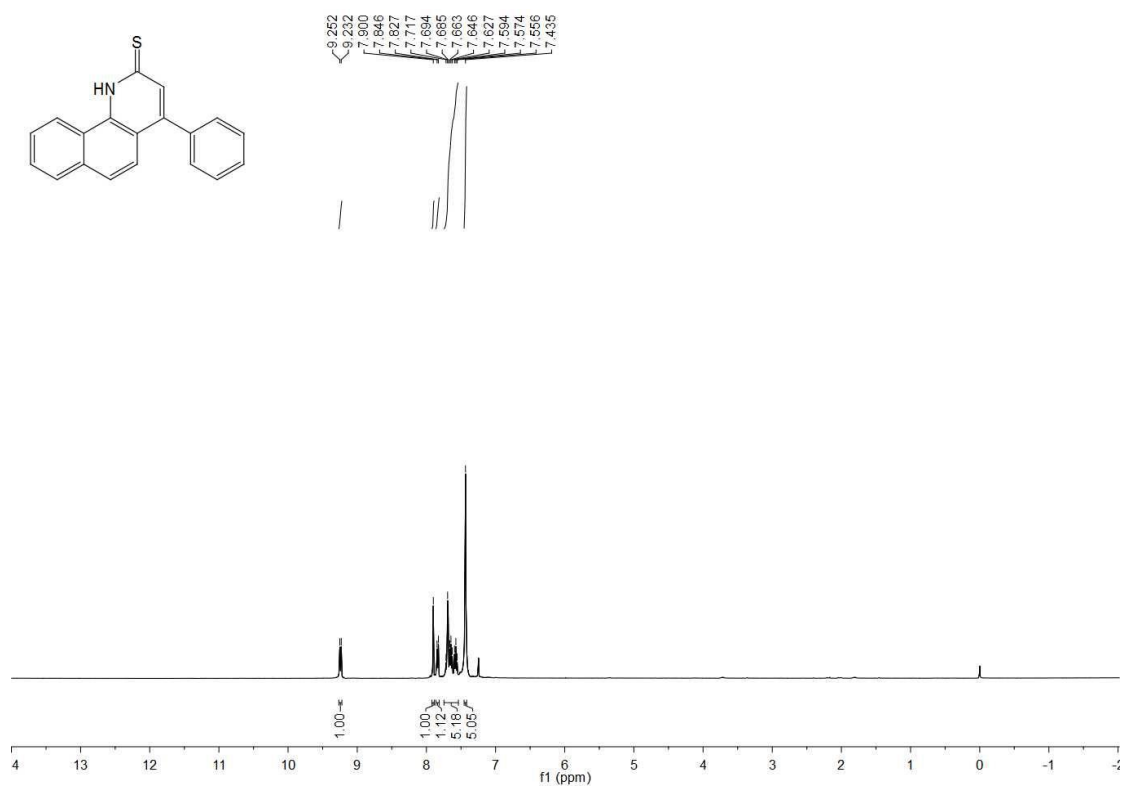
Copies of NMR of compound **2j**.



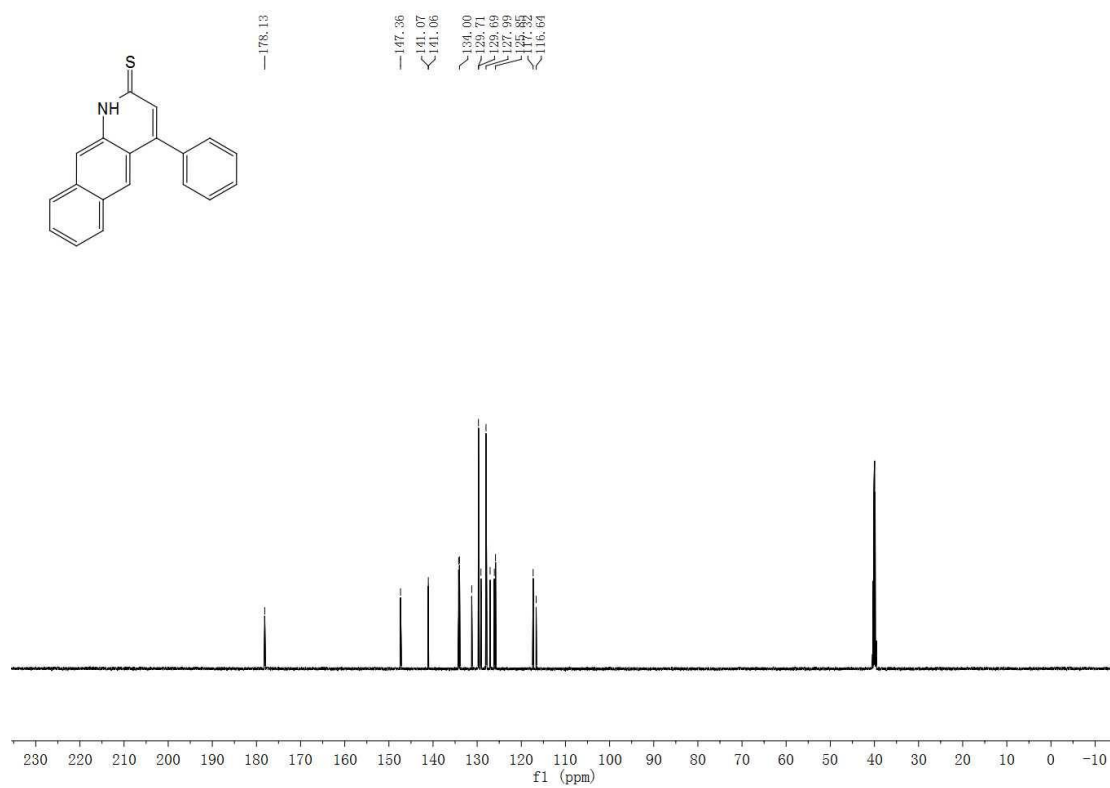
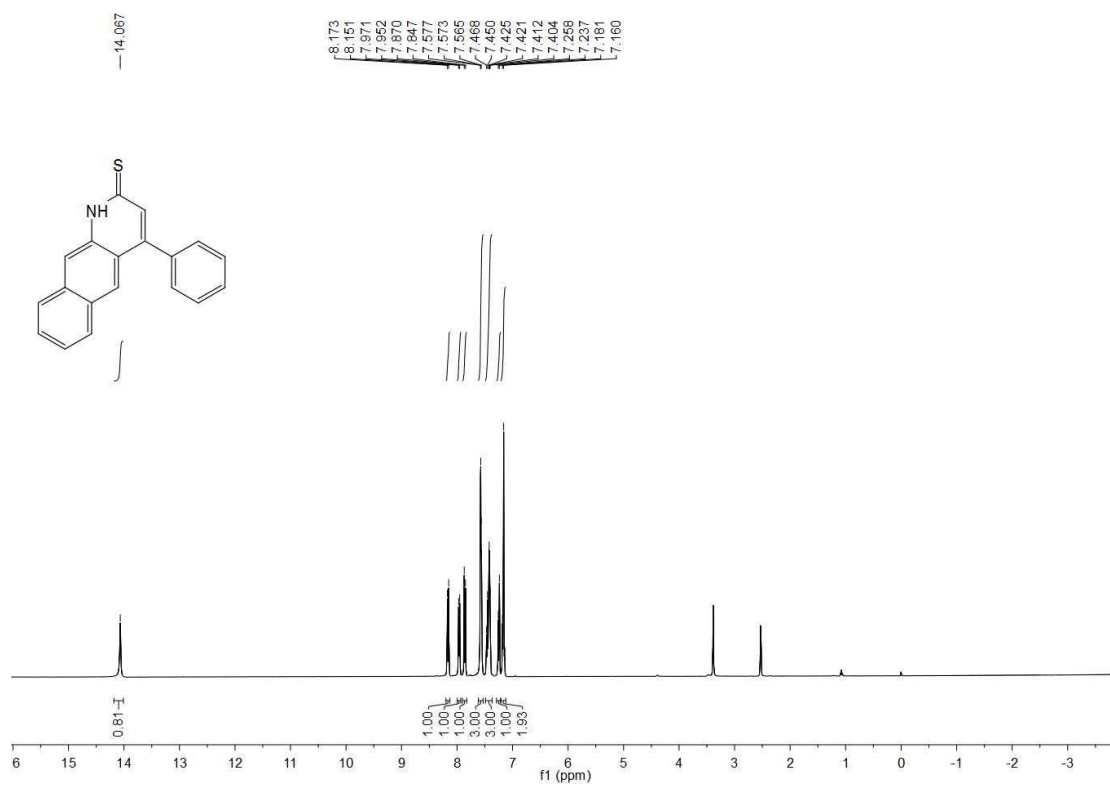
Copies of NMR of compound **2k**.



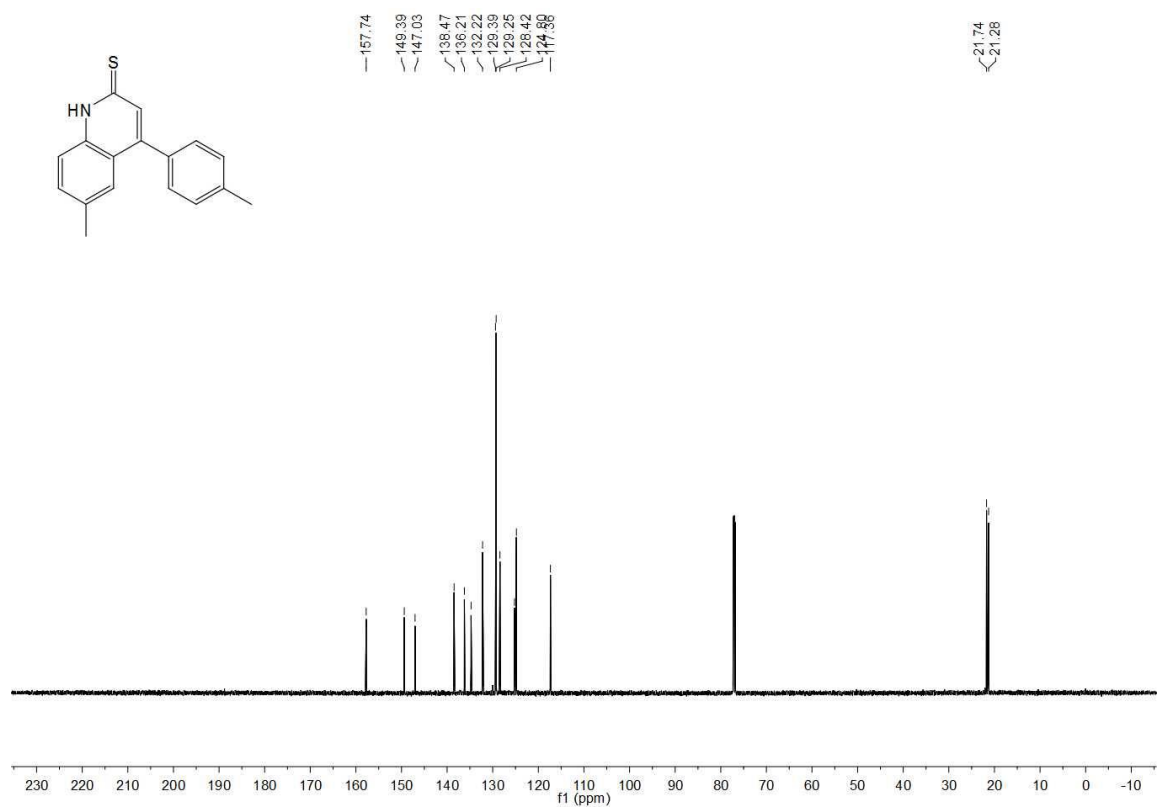
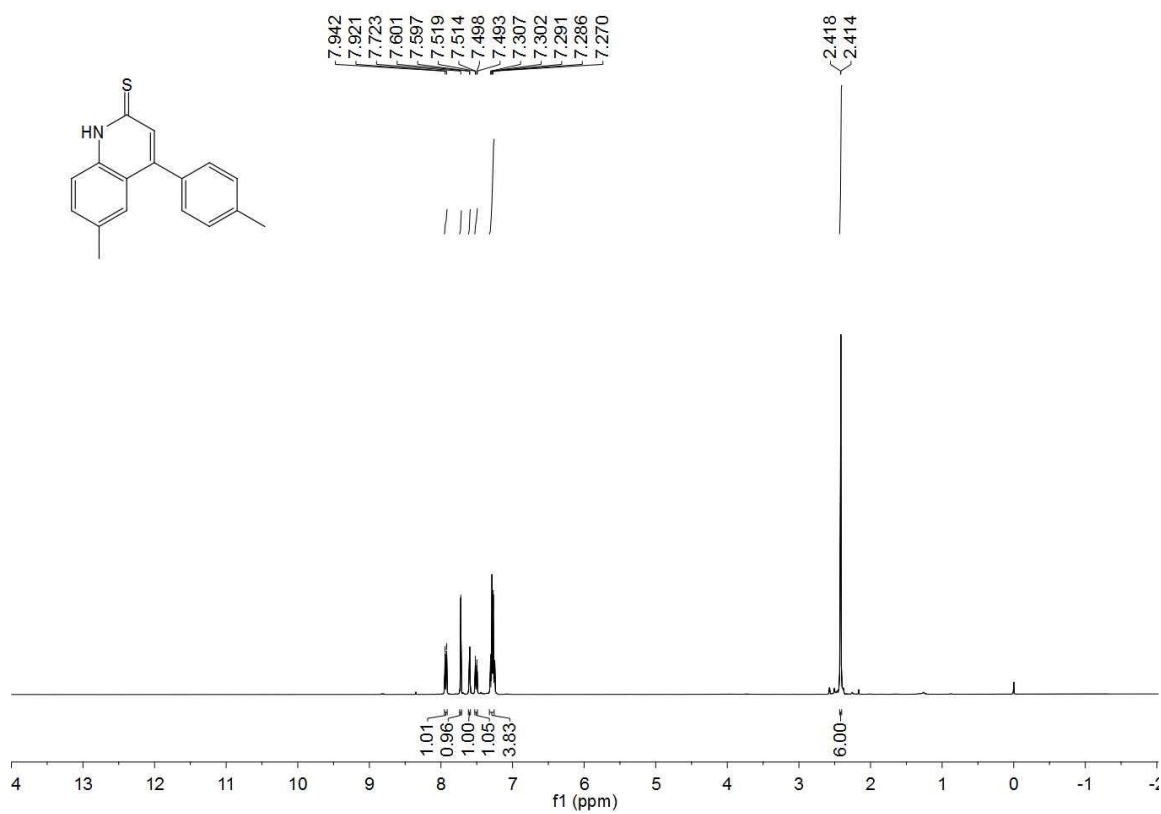
Copies of NMR of compound **2l**.



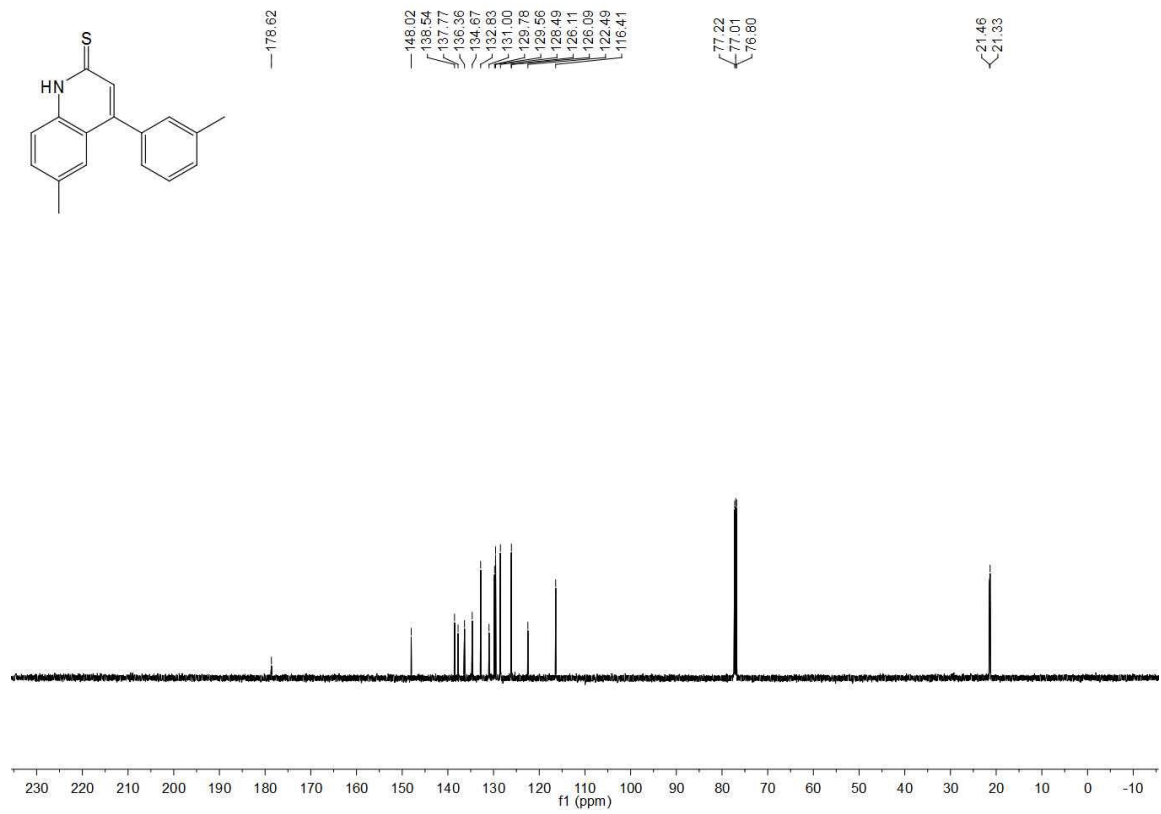
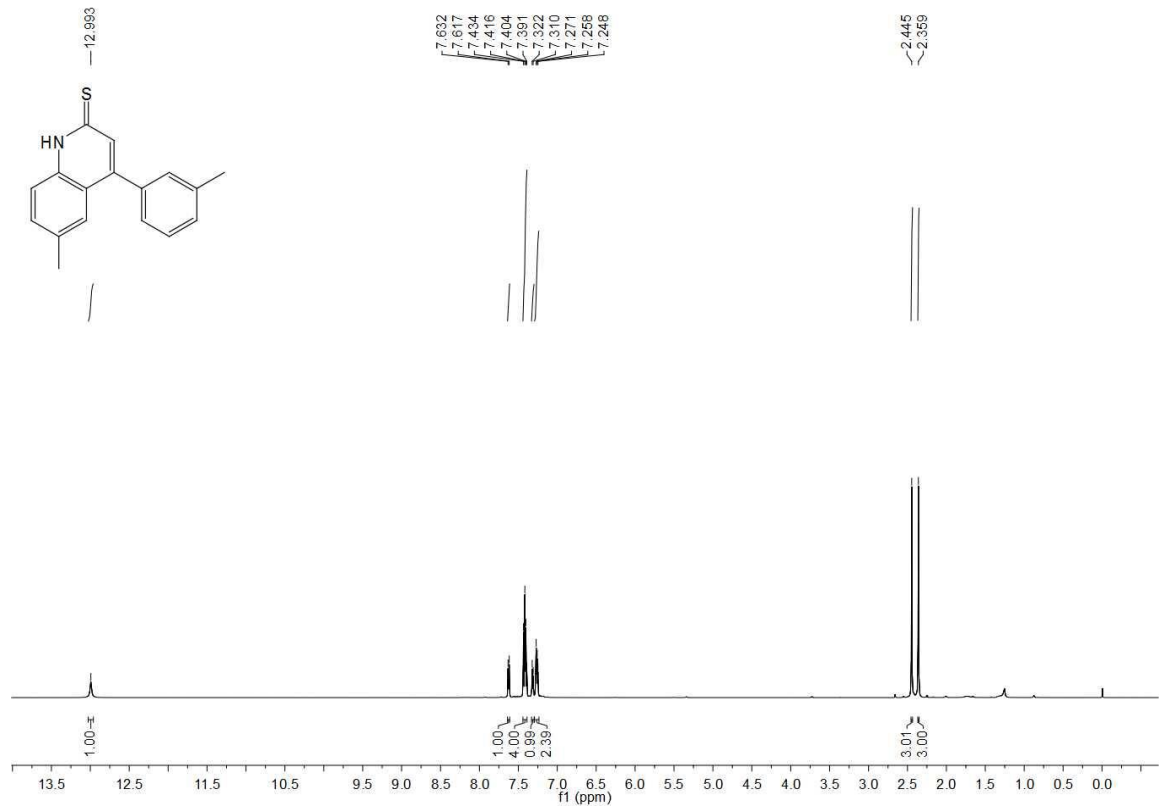
Copies of NMR of compound **2m**.



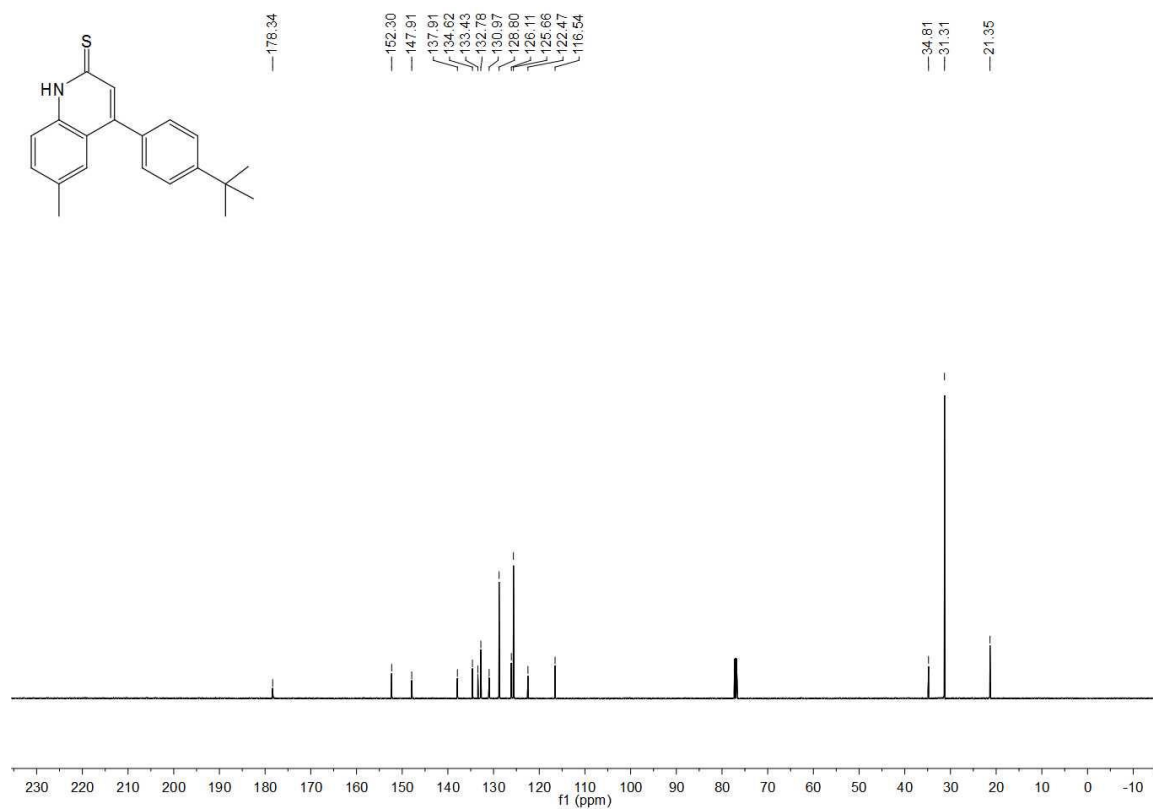
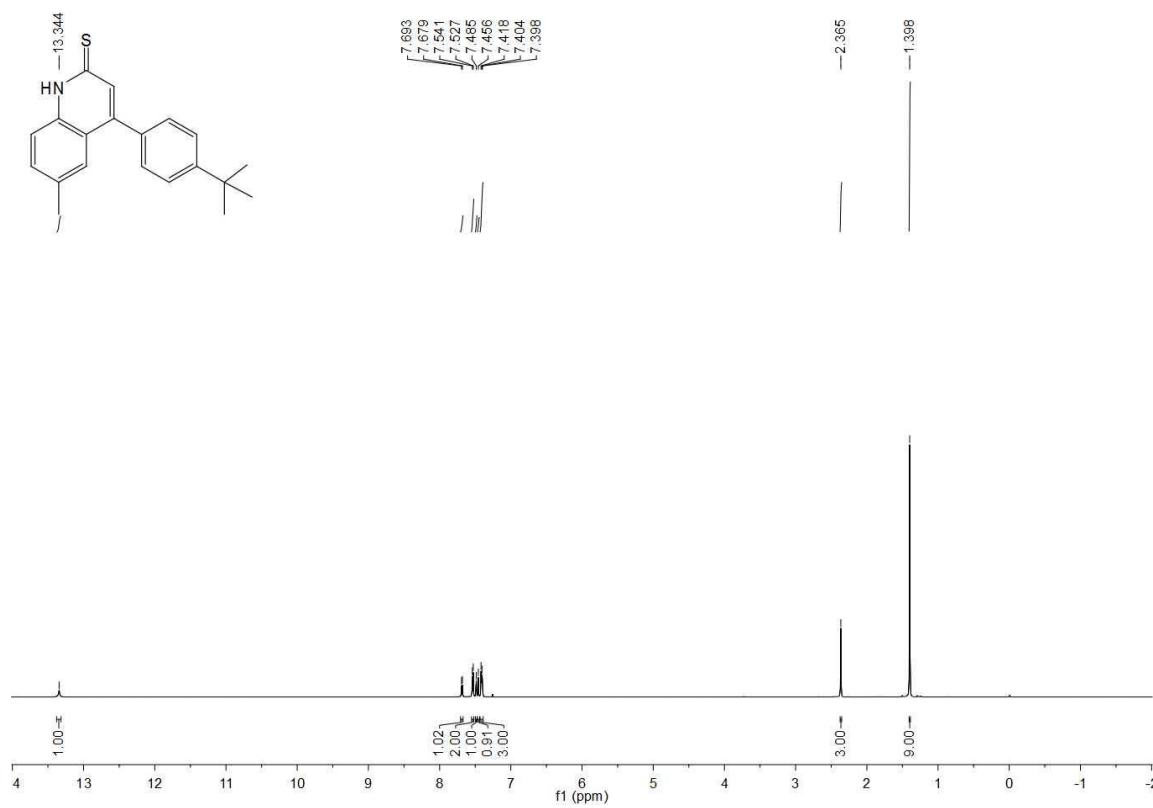
Copies of NMR of compound **2n**.



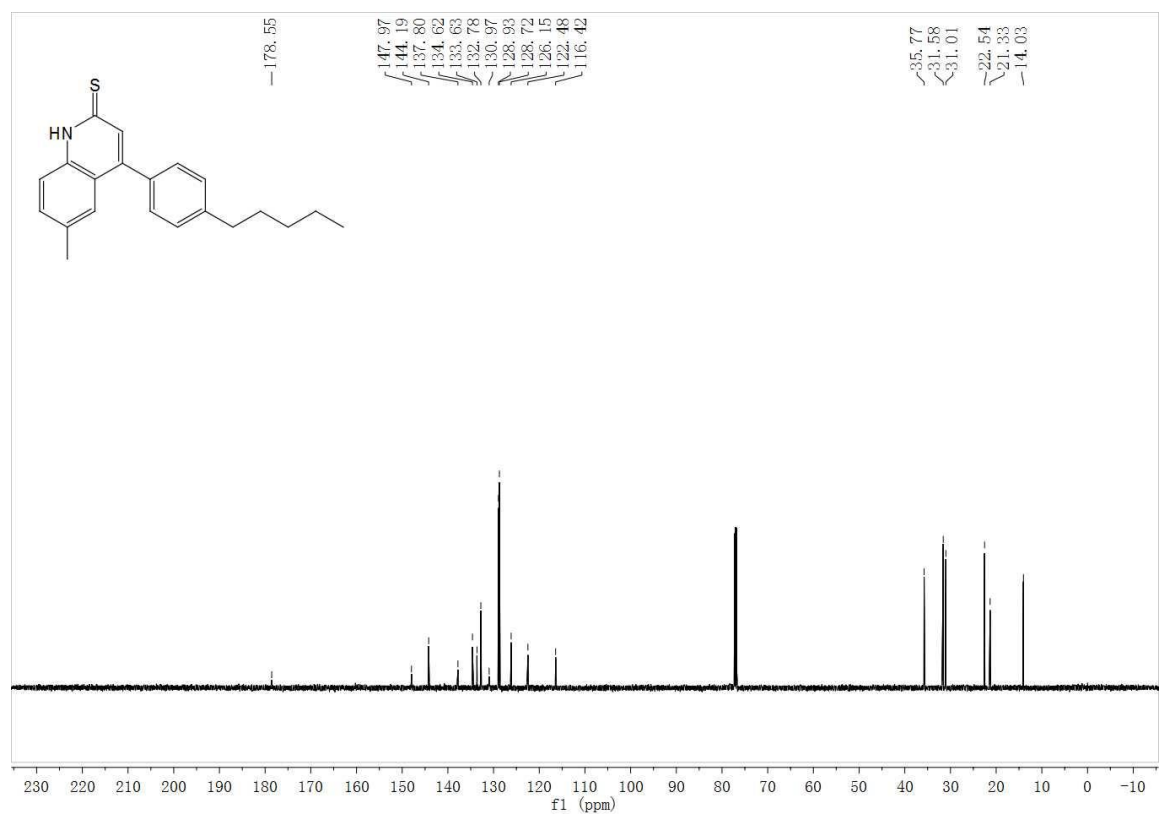
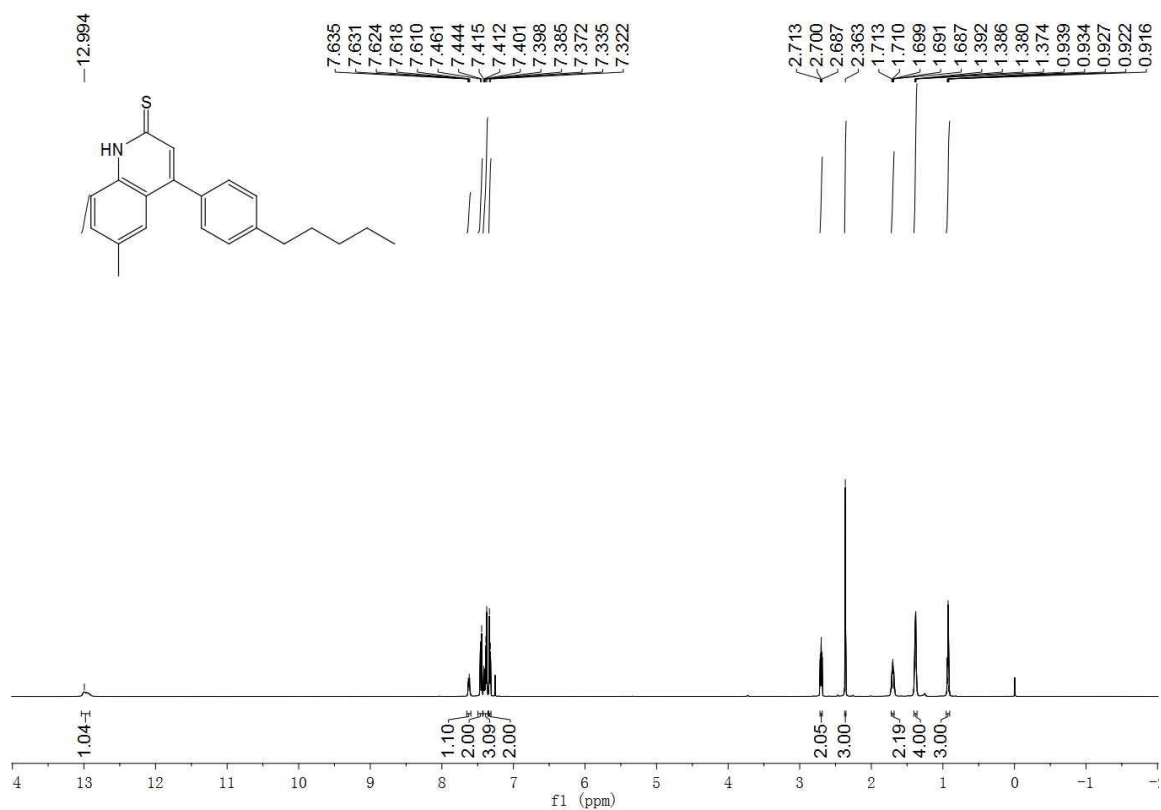
Copies of NMR of compound **20**.



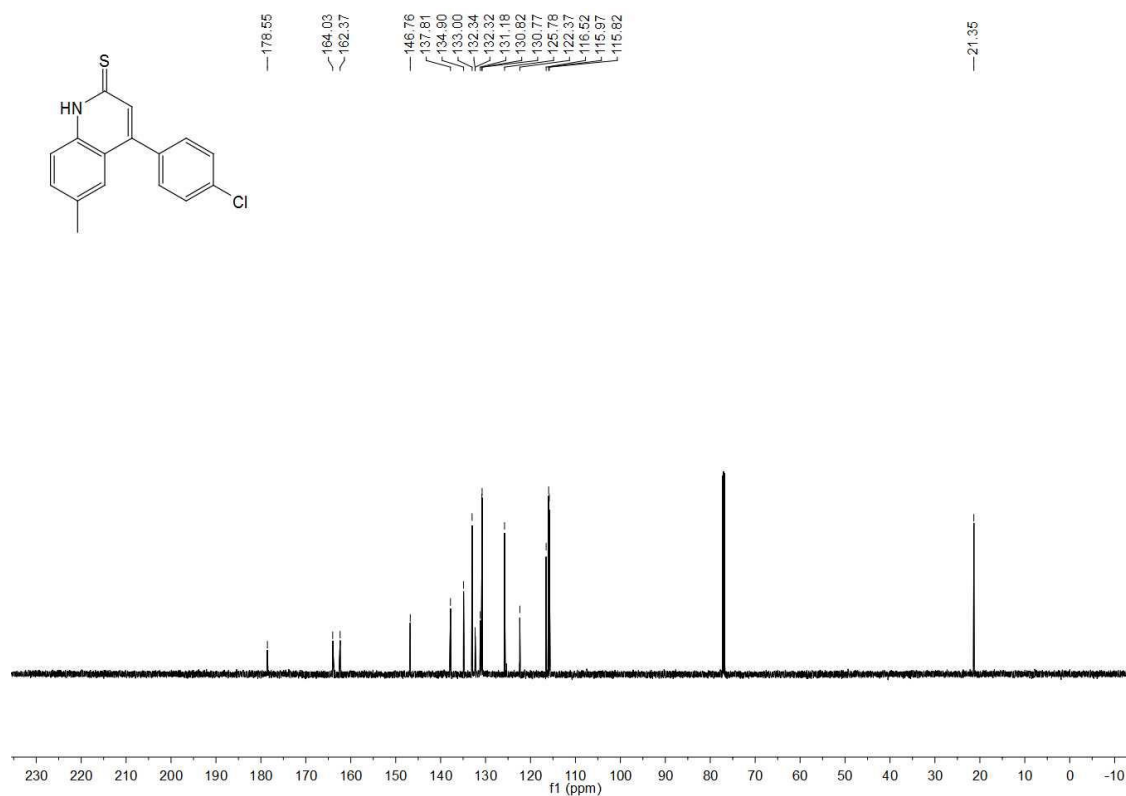
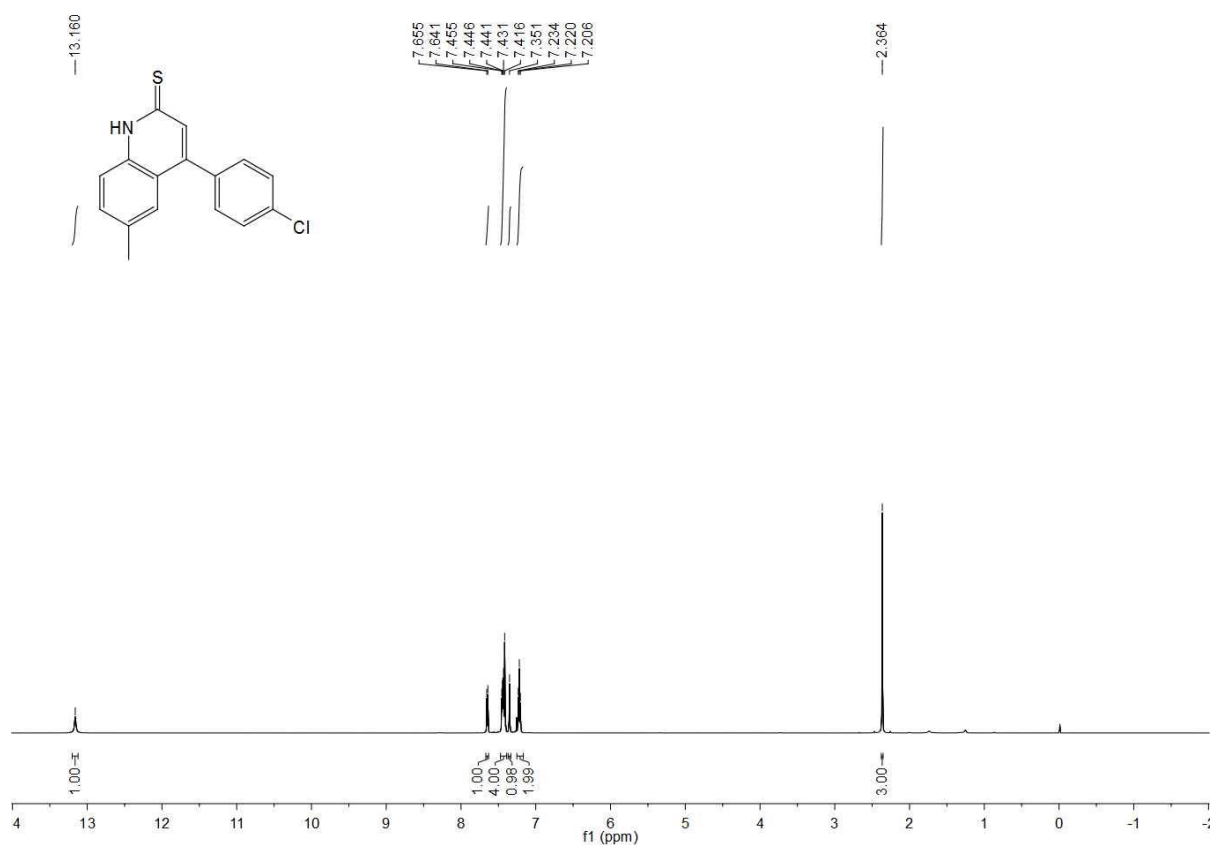
Copies of NMR of compound **2p**.



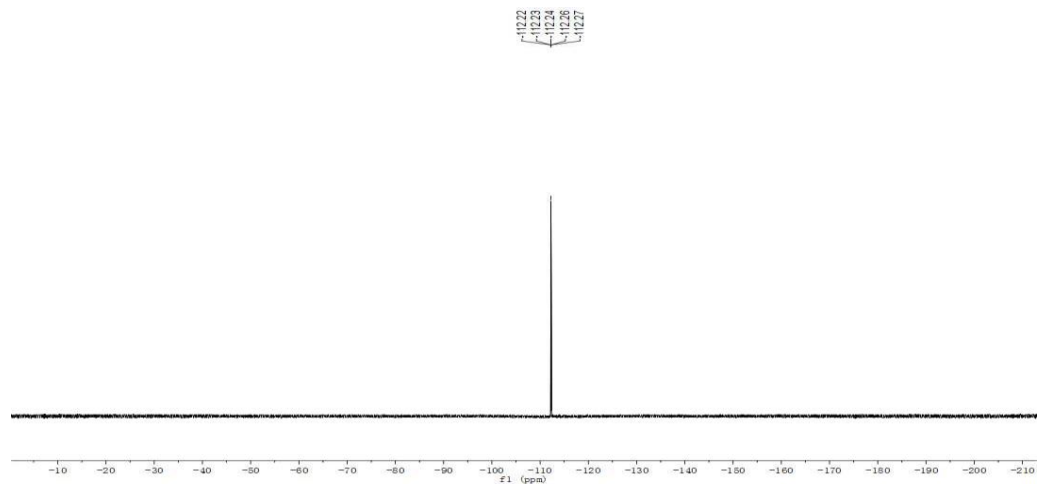
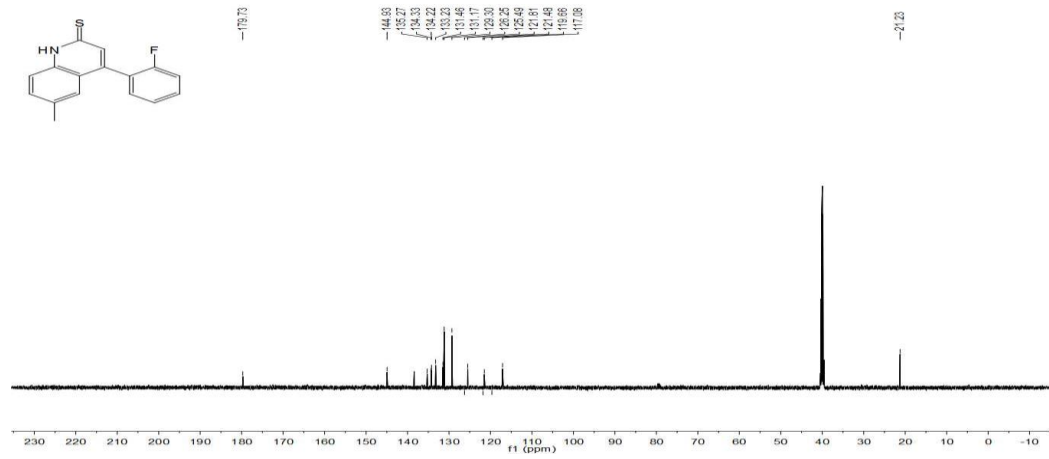
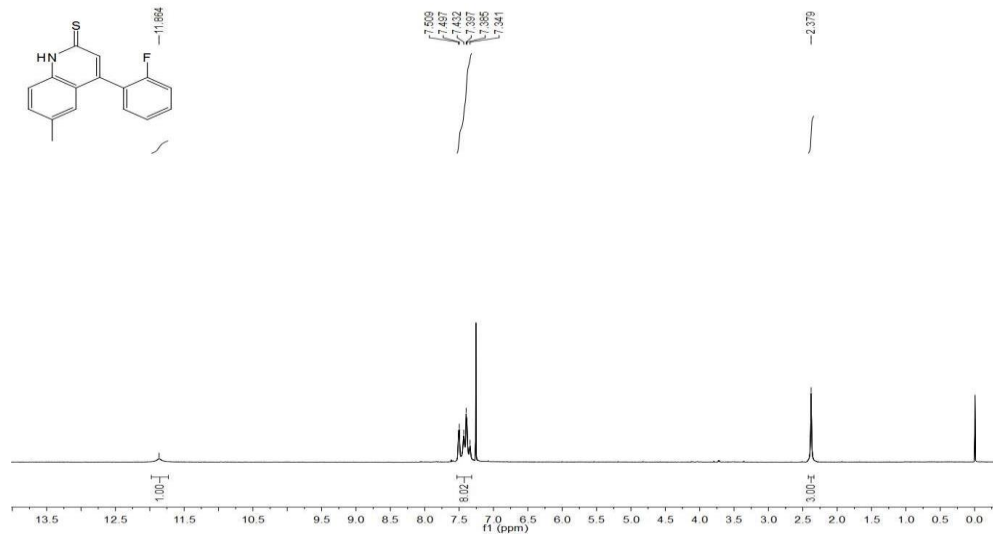
Copies of NMR of compound **2q**.



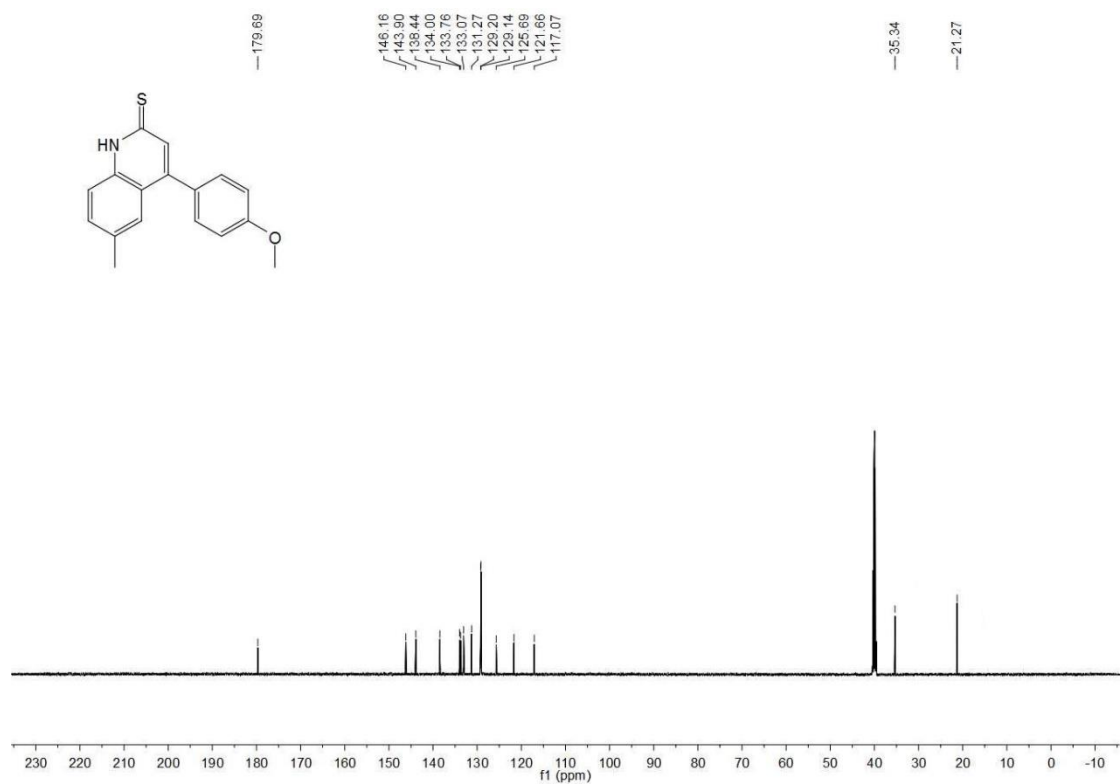
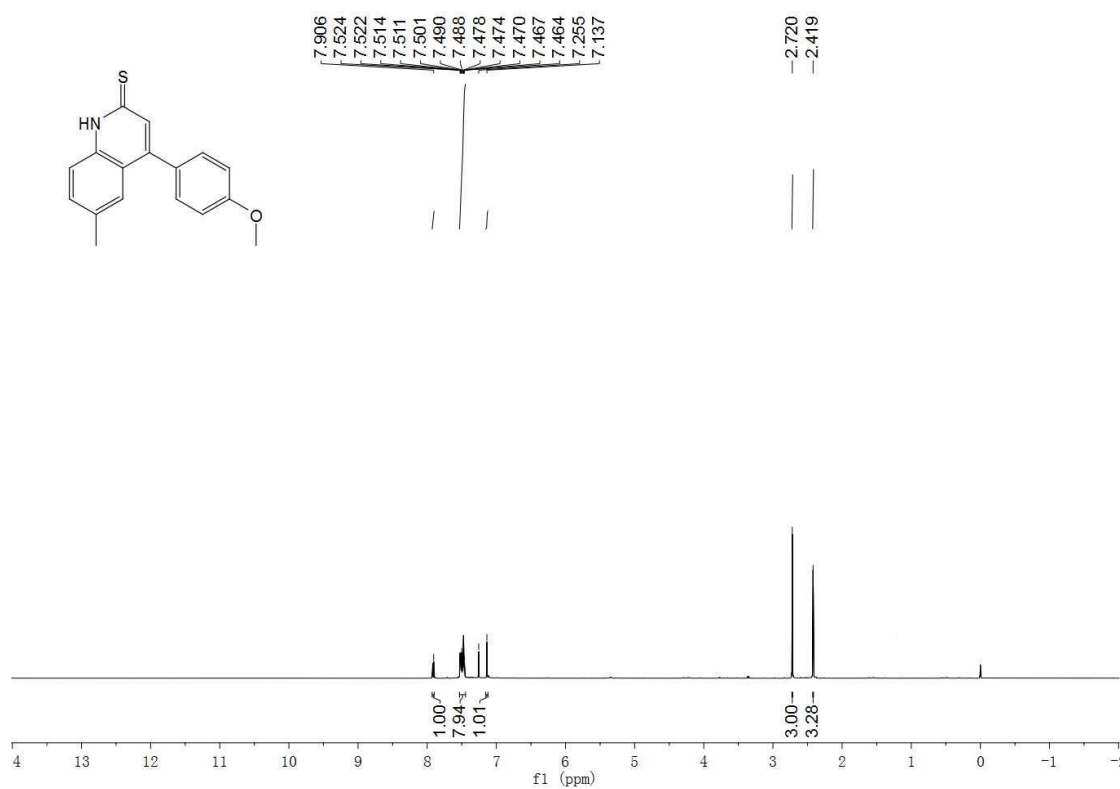
Copies of NMR of compound **2r**.



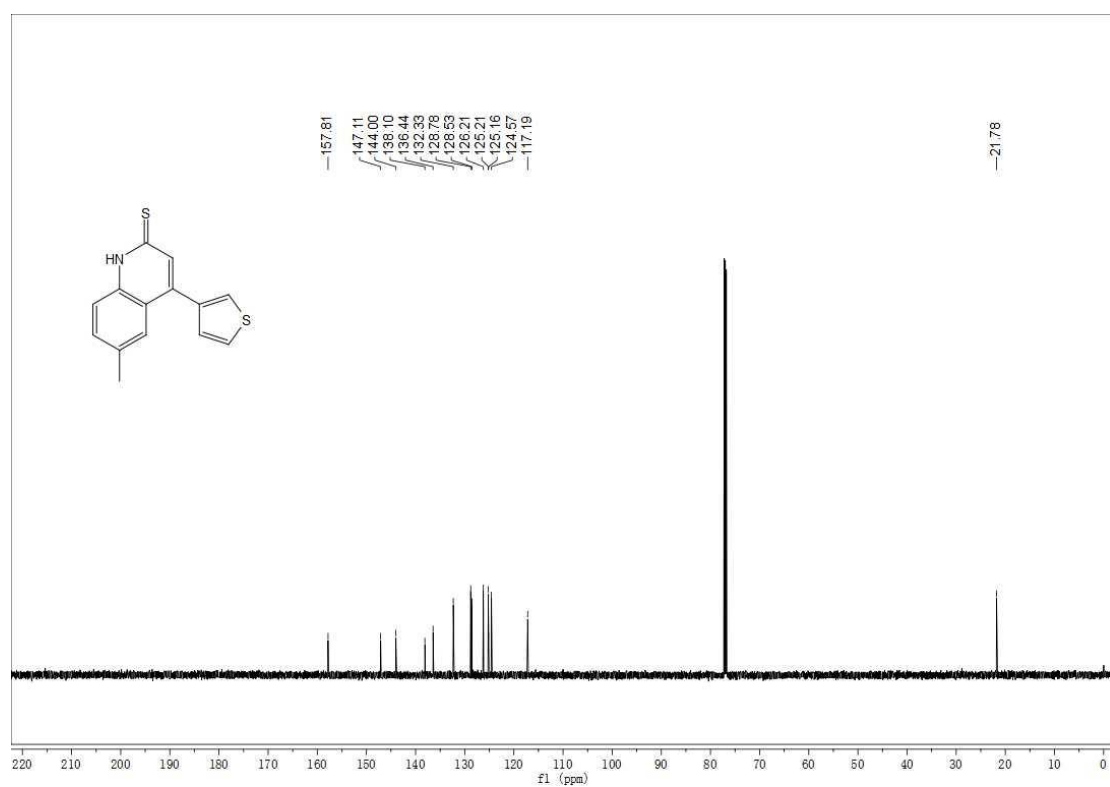
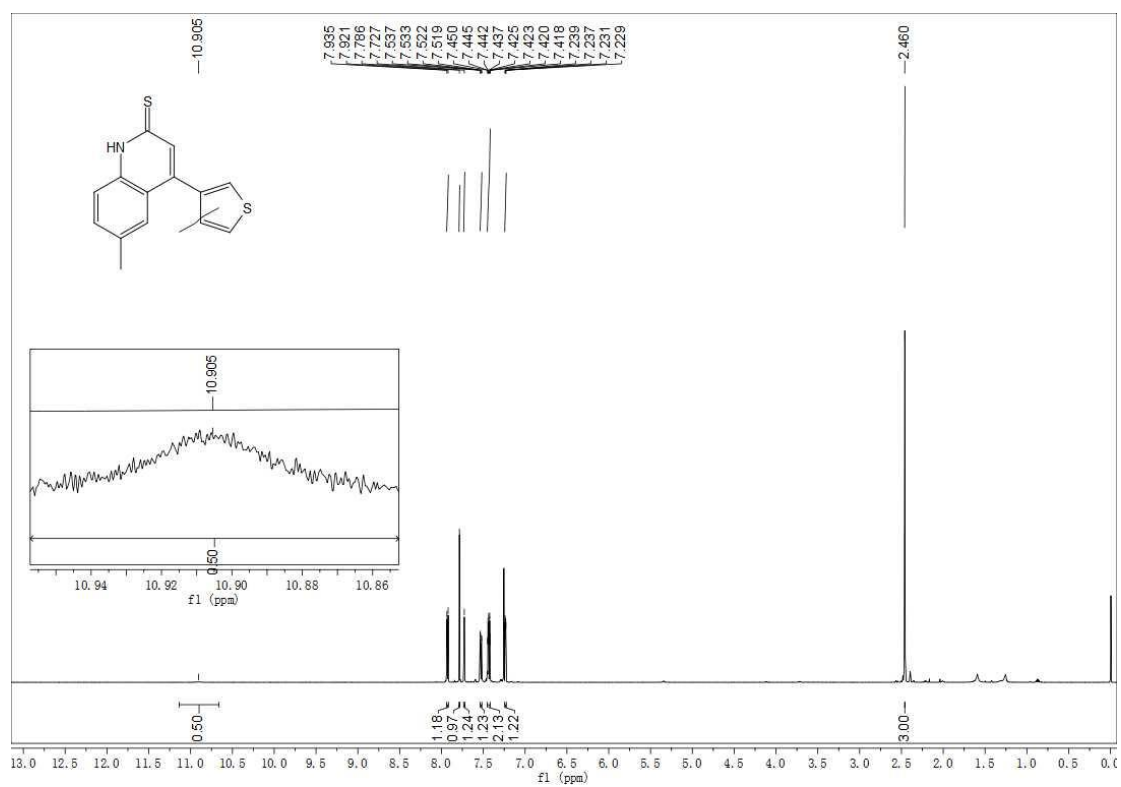
Copies of NMR of compound **2s**.



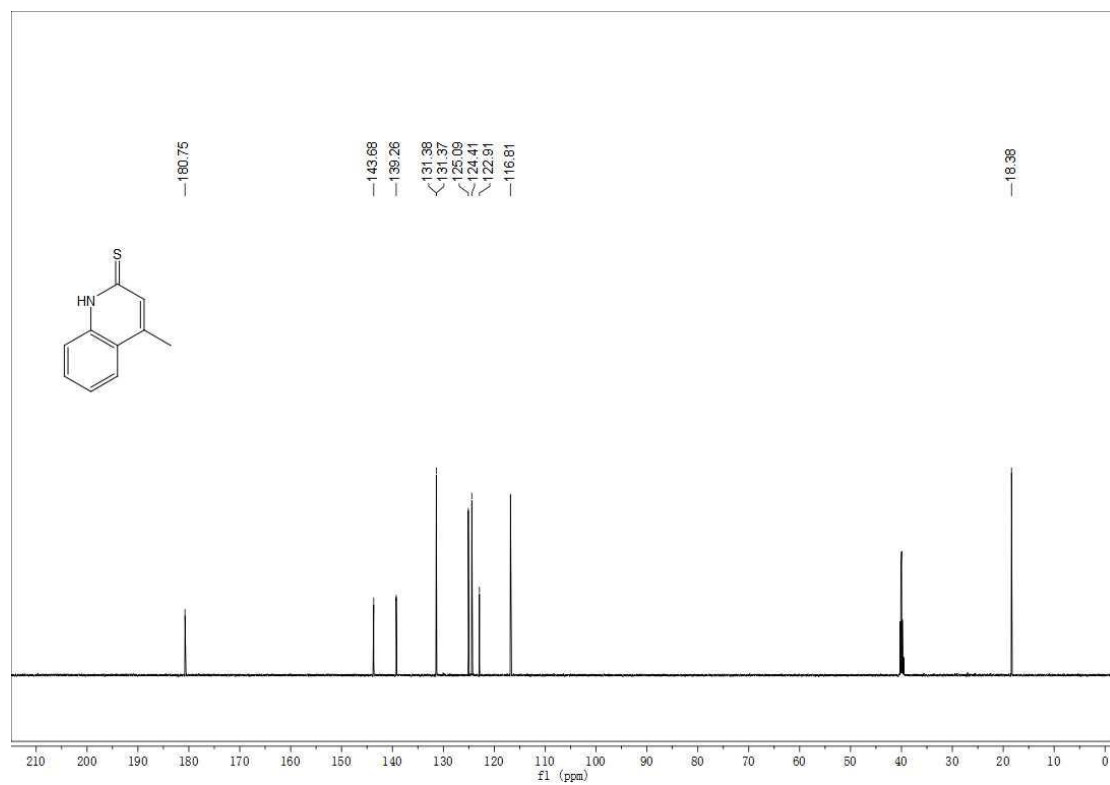
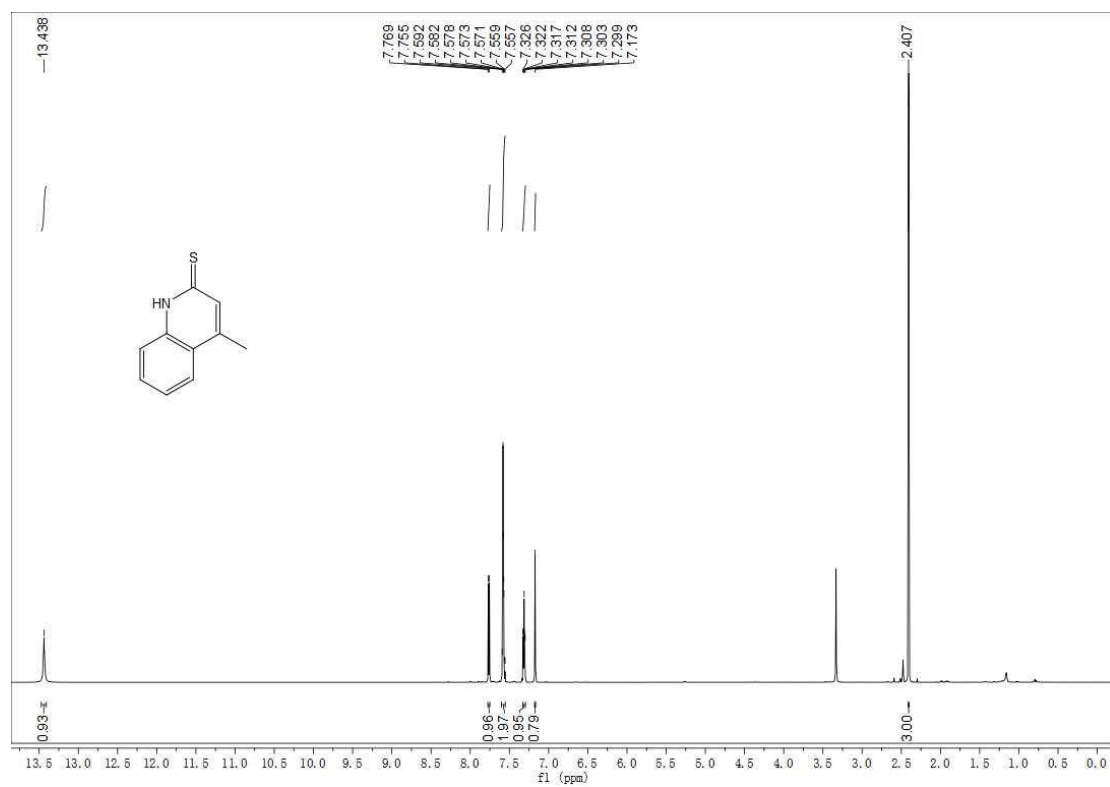
Copies of NMR of compound **2t**.



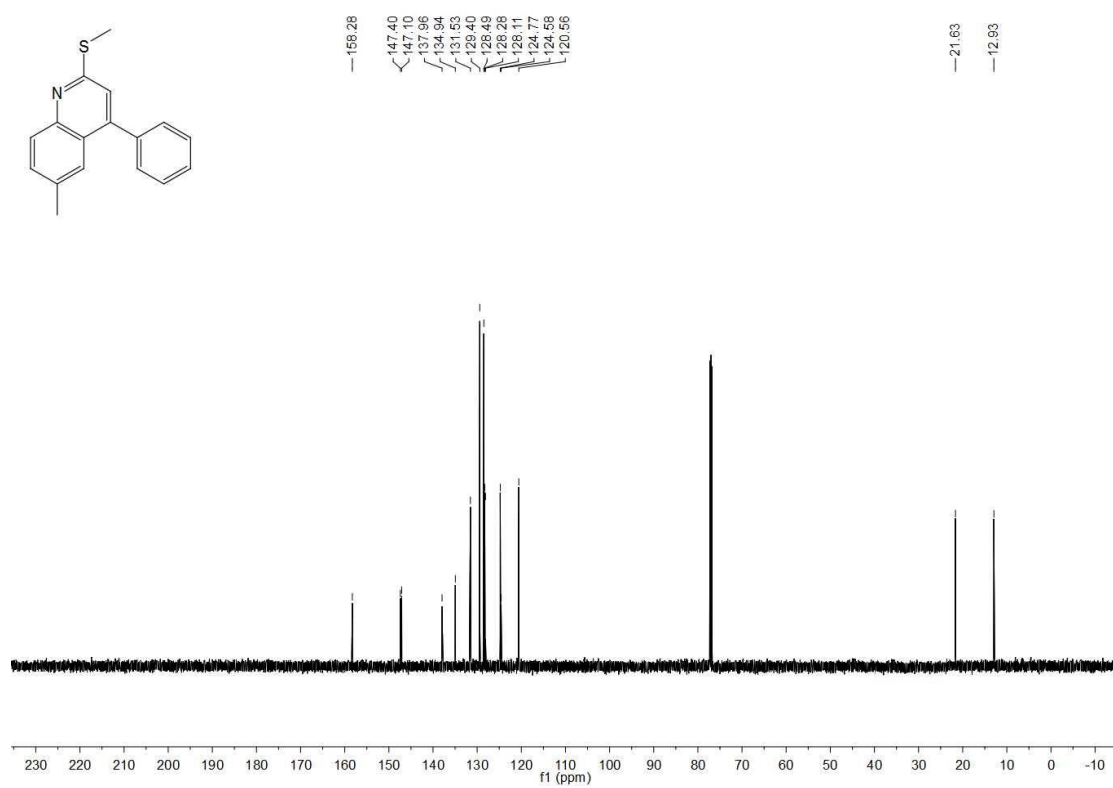
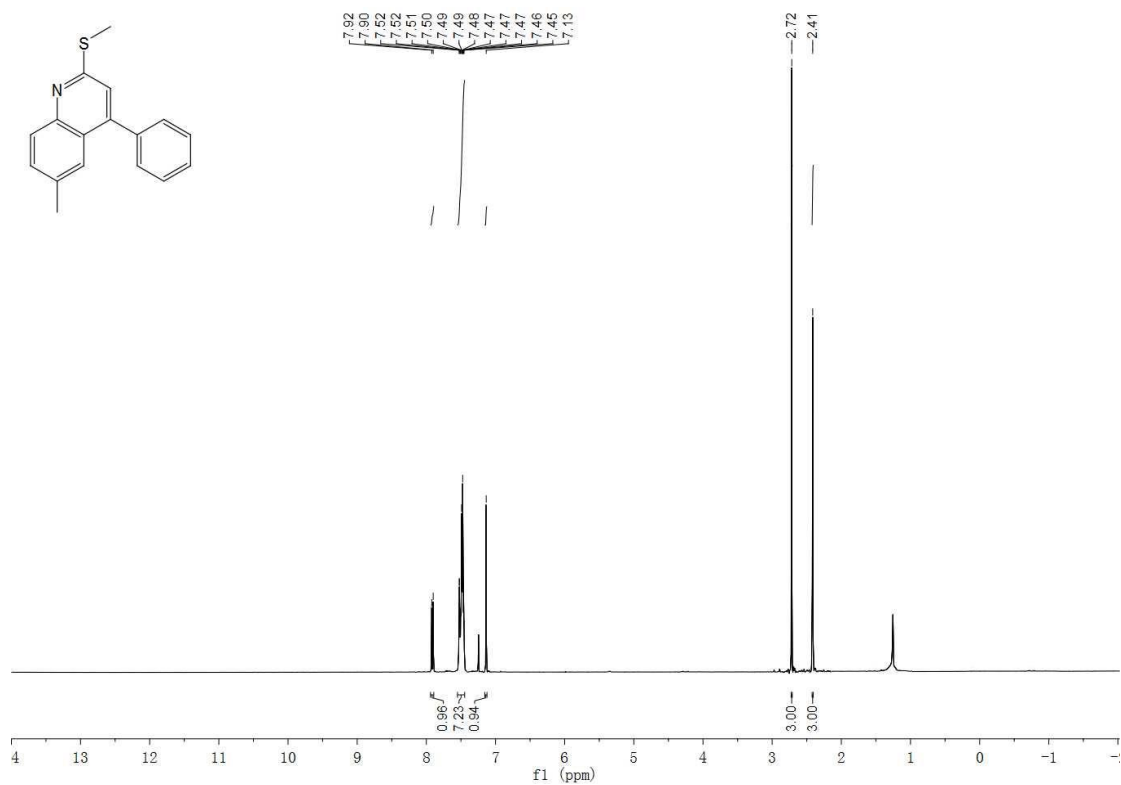
Copies of NMR of compound **2u**.



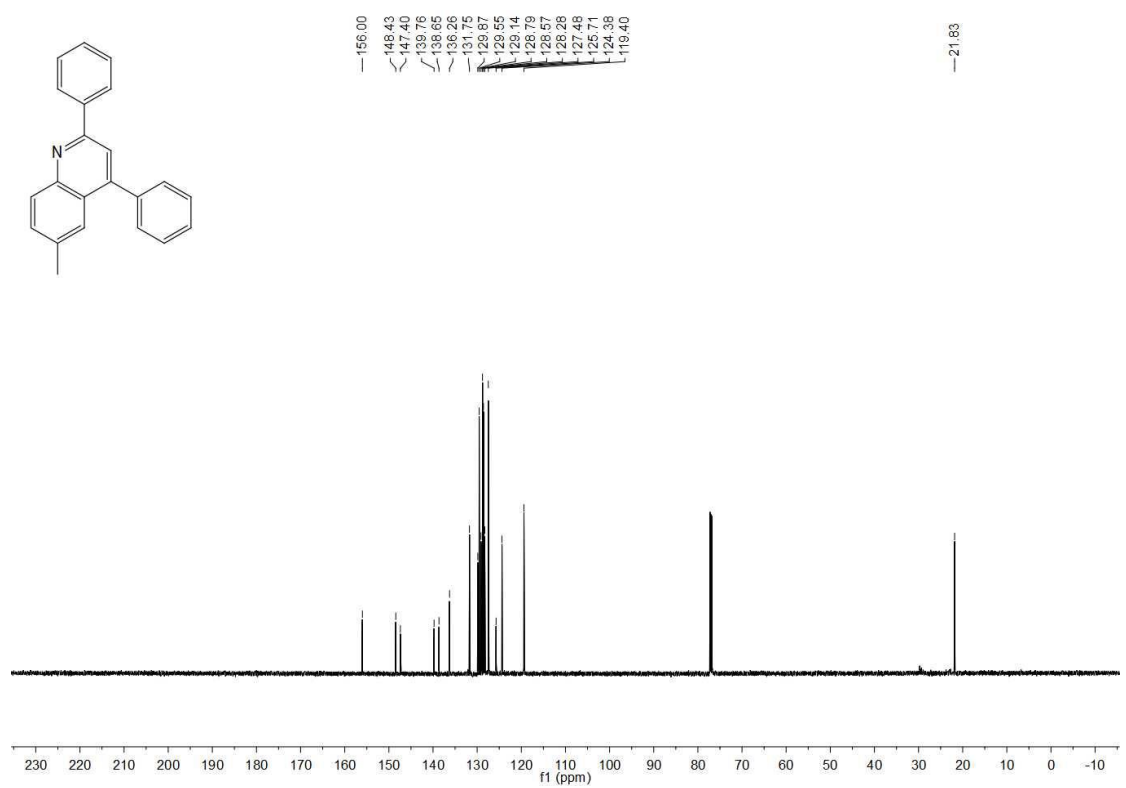
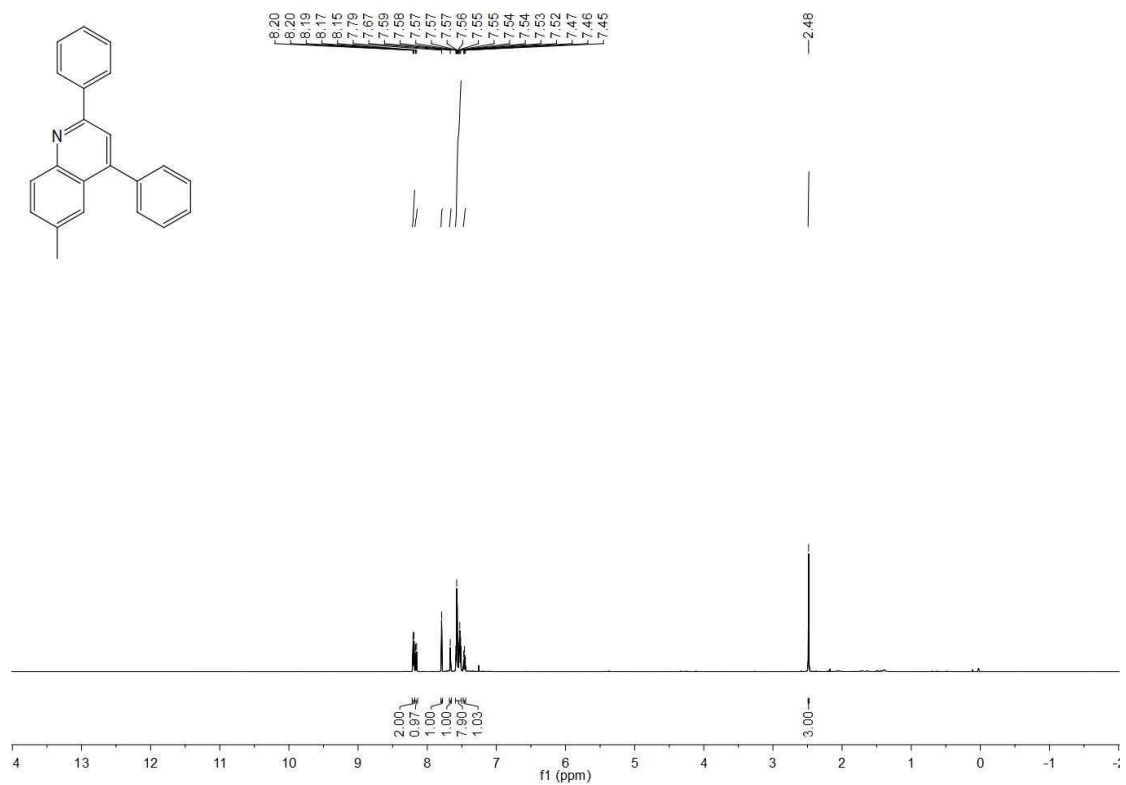
Copies of NMR of compound **2v**.



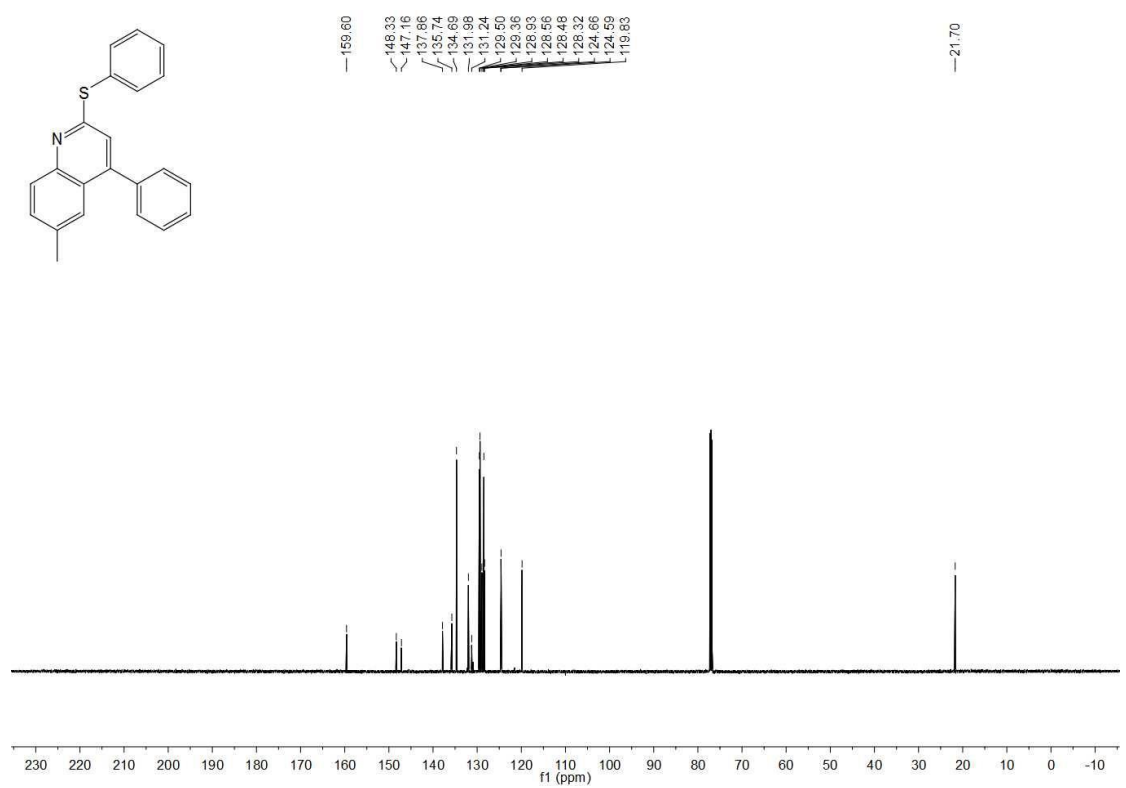
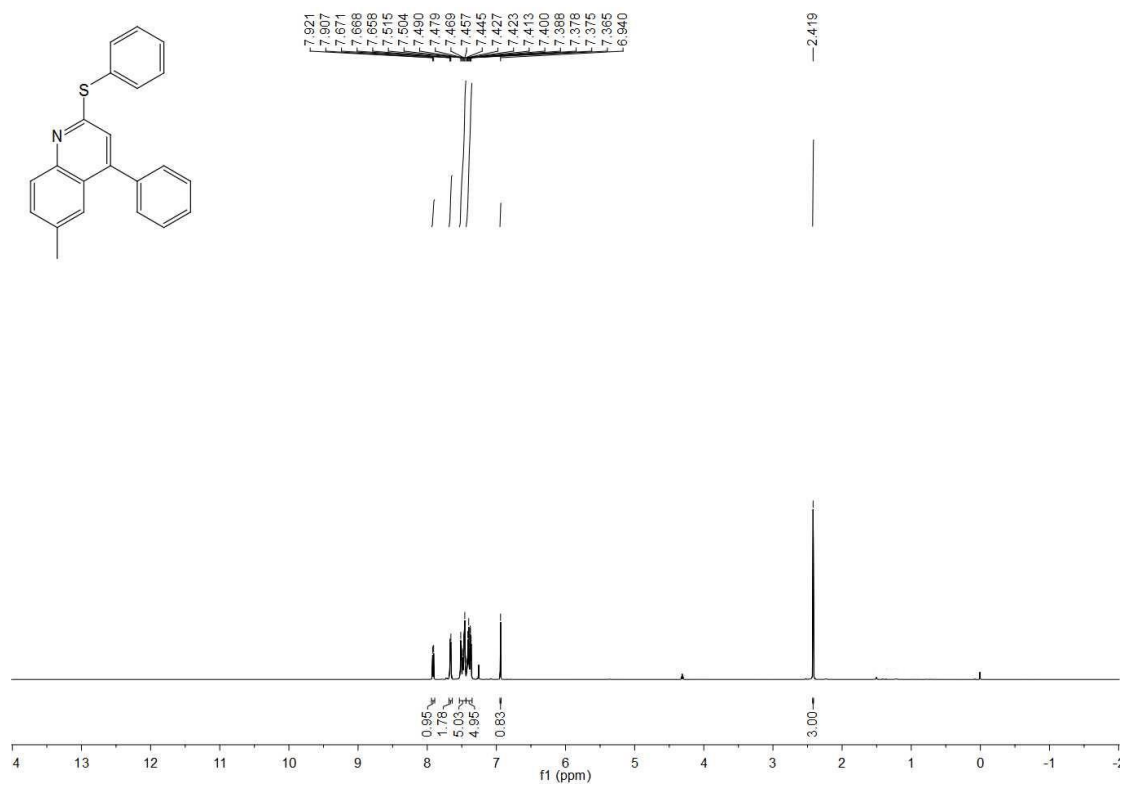
Copies of NMR of compound **3**.



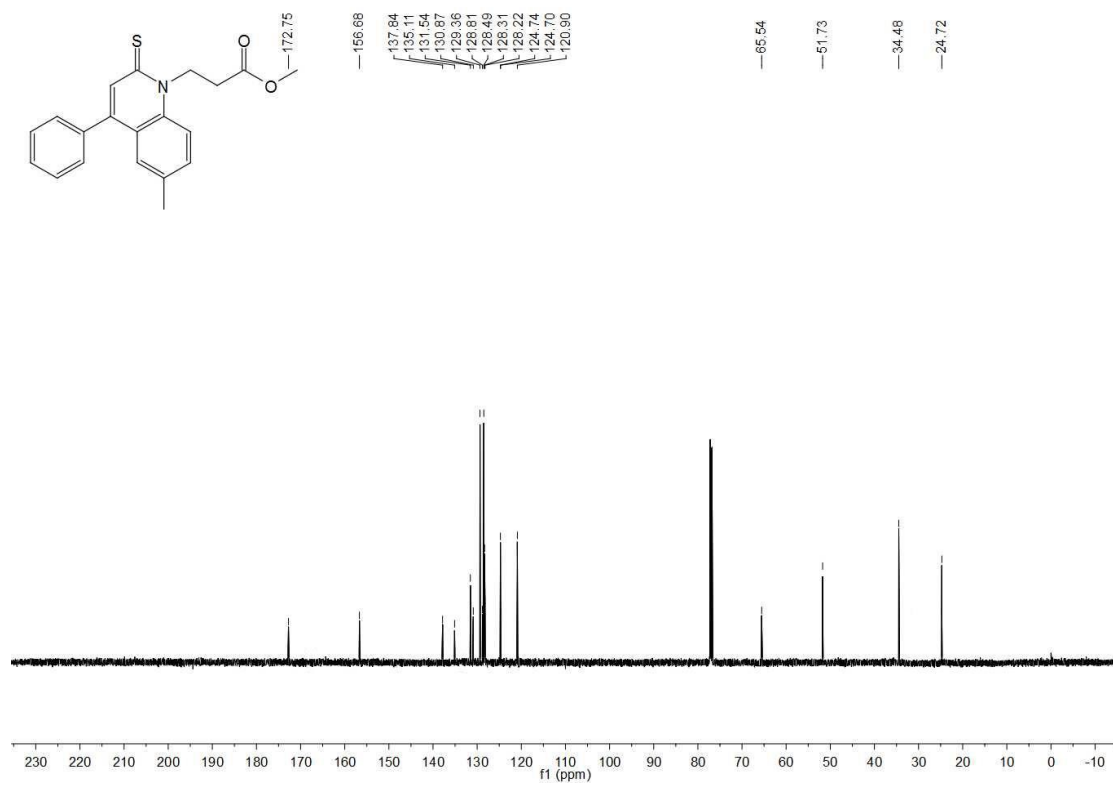
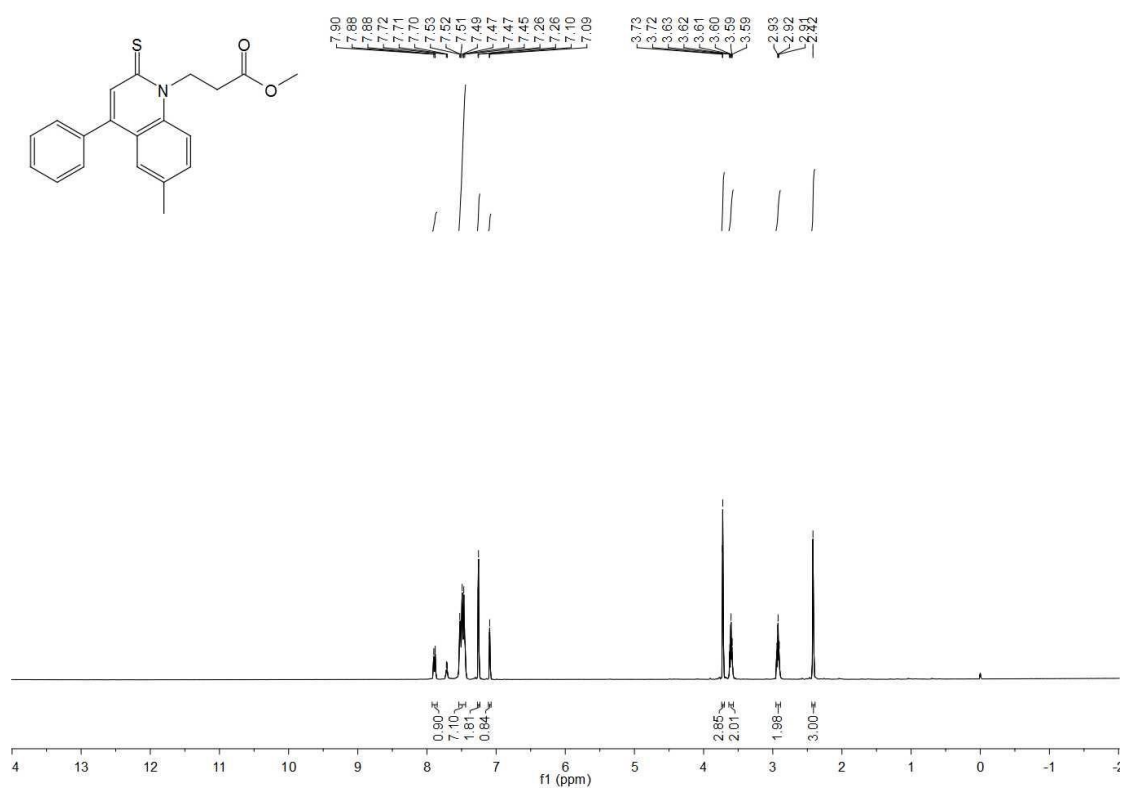
Copies of NMR of compound **4**.



Copies of NMR of compound **5**.



Copies of NMR of compound **6**.



Copies of NMR of compound 7.

