Supporting information

Solvent-Controlled Chemoselectively Constructing C-S/S-S Bonds via Michael Reaction/Thiol Coupling of Quinoline-2-thiones

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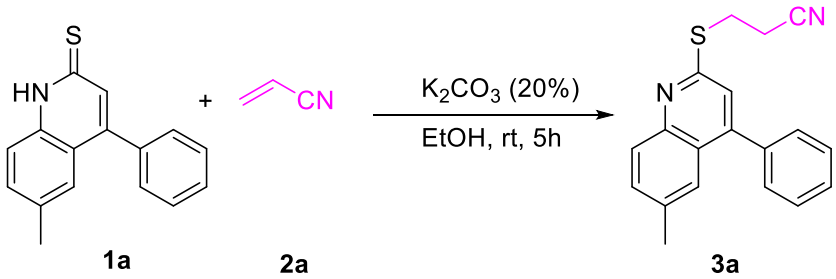
1. General Information

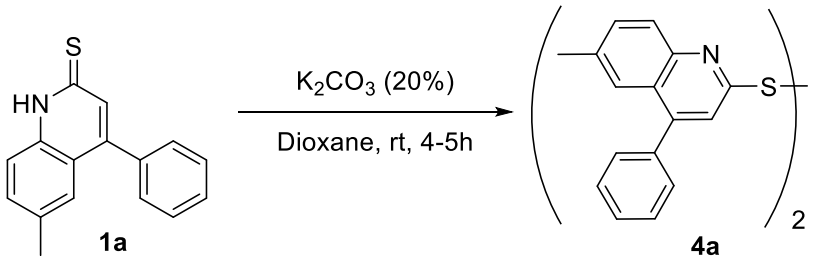
Unless otherwise noted, all commercially available compounds were used as provided without further purification. ^{1}H NMR and ^{13}C NMR data analyses were performed with a Varian Mercury plus-400 and Agilent 600 MHz DD2 instruments $CDCl_3$ and DMSO-*d*6 as solvent and tetramethylsilane (TMS) as the internal standard were employed. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H 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 ^{13}C NMR spectra were recorded in ppm from TMS using the central peak of $CDCl_3$ (77.0 ppm) as the internal standard. ^{19}F 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.

2. Typical Procedure for the Synthesis of 3



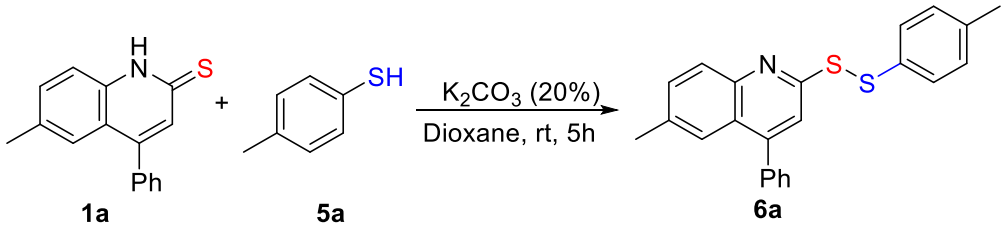
The mixture of quinoline-2-thione **1a** (0.2 mmol, 50 mg), acrylonitrile **2a** (0.24 mmol, 13 mg) and K_2CO_3 (20%, 6 mg) in EtOH (2 mL) was stirred at room temperature for 5 hours under air atmosphere. After the reaction completed (monitored by TLC analysis), saturated aq. NH_4Cl was added to the mixture to quench the reaction and extracted with ethyl acetate (3×25 mL). The combined organic layers were washed with aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, and the volatiles were removed in vacuum. The mixture was purified by using silica gel column chromatography (ethyl acetate: petroleum ether = 1:30). The corresponding product **3a** was obtained as a white solid (55 mg, 90% yield).

3. Typical Procedure for the Synthesis of 4



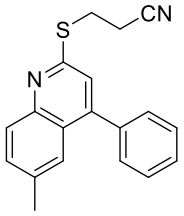
The mixture of Quinoline-2-thione **1a** (0.2 mmol, 50 mg), and K_2CO_3 (20%, 6 mg) was dissolved in 1,4-dioxane (2 mL) and stirred at room temperature for 5 hours under air atmosphere. After the reaction completed (monitored by TLC analysis), saturated aq. NH_4Cl was added to the mixture to quench the reaction and extracted with ethyl acetate (3×25 mL). The combined organic layers were washed with aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, and the volatiles were removed in vacuum. The mixture was purified using silica gel column chromatography (ethyl acetate: petroleum ether = 1:30). The corresponding product **4a** was obtained as a white solid (80 mg, 80% yield)

4. Typical Procedure for the Synthesis of 6

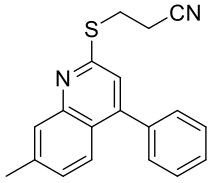


The mixture of quinoline-2-thione **1a** (0.2 mmol, 50 mg), thiophenol **5a** (0.3 mmol, 13 mg) and K_2CO_3 (20%, 6 mg) in 1,4-dioxane (2 mL) was stirred at room temperature for 5 hours under air. After the completion of the reaction was monitored by TLC analysis, 2.0 mL saturated aq. NH_4Cl was added to the mixture to quench the reaction and extracted with ethyl acetate (3×25 mL). The combined organic layers were washed with aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, and the volatiles were removed in vacuum. The mixture was purified by using silica gel column chromatography (ethyl acetate: petroleum ether = 1:30). The corresponding product **6a** was obtained as a colourless oil (40 mg, 55% yield).

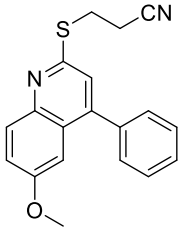
5. Spectroscopic Data of Compounds



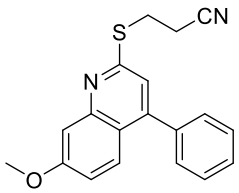
3-((6-methyl-4-phenylquinolin-2-yl)thio)propanenitrile (3a). White solid. mp: 114-116℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (d, *J* = 8.4 Hz, 1H), 7.57–7.44 (m, 7H), 7.11 (s, 1H), 3.58 (t, *J* = 7.2 Hz, 2H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ = 155.47, 148.13, 147.48, 137.83, 135.82, 132.09, 129.58, 128.81, 128.72, 128.40, 125.11, 121.03, 119.02, 25.71, 21.92, 18.78. HRMS (ESI) m/z: Calcd for $C_{19}H_{16}N_2S$: 305.1107 $[M+H]^+$, Found 305.1110.



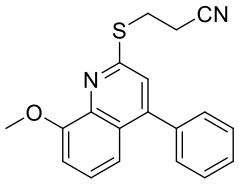
3-((7-methyl-4-phenylquinolin-2-yl)thio)propanenitrile (3a). White solid. mp: 136-137℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.79 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.53 – 7.42 (m, 5H), 7.24 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.09 (s, 1H), 3.58 (t, *J* = 7.2 Hz, 2H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.55 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 156.25, 148.86, 148.25, 140.15, 137.54, 129.32, 128.54, 128.50, 127.78, 127.65, 125.67, 122.87, 119.91, 118.73, 25.48, 21.62, 18.51. HRMS (ESI) m/z: Calcd for $C_{19}H_{16}N_2S$: 305.1107 $[M+H]^+$, Found 305.11101.



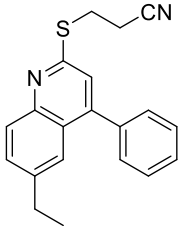
3-((6-methoxy-4-phenylquinolin-2-yl)thio)propanenitrile (3c). White solid. mp: 104-106℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 (d, *J* = 9.2 Hz, 1H), 7.55–7.45 (m, 5H), 7.33 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.12 (s, 1H), 7.11 (s, 1H), 3.76 (s, 3H), 3.56 (t, *J* = 7.2 Hz, 2H), 2.99 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (150MHz, $CDCl_3$) δ =157.25, 153.50, 147.41, 144.74, 137.67, 129.85, 129.14, 128.67, 128.54, 125.74, 121.45, 121.09, 118.73, 104.60, 55.45, 25.51, 18.58. HRMS (ESI) m/z: Calcd for $C_{19}H_{16}N_2OS$: 321.1056 $[M+H]^+$, Found 321.1058.



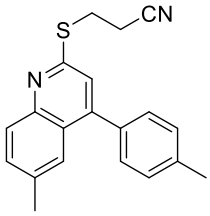
3-((7-methoxy-4-phenylquinolin-2-yl)thio)propanenitrile (3d). White solid. mp: 138-140℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (d, *J* = 9.2 Hz, 1H), 7.53–7.41 (m, 5H), 7.33 (d, *J* = 2.8 Hz, 1H), 7.05 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.03 (s, 1H), 3.98 (s, 3H), 3.59 (t, *J* = 7.2 Hz, 2H), 3.01 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 160.96, 156.65, 150.50, 148.33, 137.58, 129.28, 128.55, 128.52, 127.11, 119.77, 118.75, 118.60, 118.14, 107.08, 55.58, 25.42, 18.60. HRMS (ESI) m/z: Calcd for $C_{19}H_{16}N_2OS$: 321.1056 $[M+H]^+$, Found 321.1060.



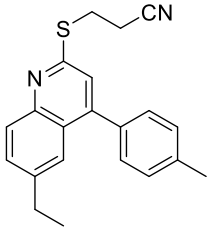
3-((8-methoxy-4-phenylquinolin-2-yl)thio)propanenitrile (3e). White solid. mp: 106-108℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53–7.42 (m, 5H), 7.38–7.29 (m, 2H), 7.18 (s, 1H), 7.06 (dd, *J* = 7.6, 1.4 Hz, 1H), 4.06 (s, 3H), 3.60 (t, *J* = 6.8 Hz, 2H), 3.14 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 155.47, 154.80, 148.47, 140.46, 137.73, 129.34, 128.49, 125.97, 125.56, 121.18, 118.86, 117.81, 108.83, 56.26, 26.12, 18.10. HRMS (ESI) m/z: Calcd for $C_{19}H_{16}N_2OS$: 321.1056 $[M+H]^+$, Found 321.1059.



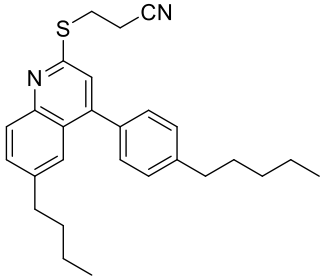
3-((6-ethyl-4-phenylquinolin-2-yl)thio)propanenitrile (3f). White solid. mp: 108-110℃. IR (KBr) 2972, 2900, 2162, 1581, 1543, 1047, 702 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.45 (m, 7H), 7.12 (s, 1H), 3.58 (t, *J* = 7.2 Hz, 2H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 155.28, 148.03, 147.45, 141.89, 137.61, 130.68, 129.34, 128.56, 128.47, 128.32, 124.87, 123.70, 120.77, 118.73, 28.98, 25.48, 18.53, 15.61. HRMS (ESI) m/z: Calcd for $C_{20}H_{18}N_2S$: 319.1263 $[M+H]^+$, Found 319.1266.



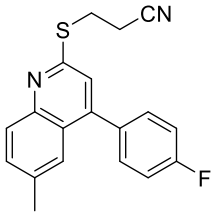
3-((6-methyl-4-(p-tolyl)quinolin-2-yl)thio)propanenitrile (3g). White solid. mp: 109-110℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.88 (d, *J* = 8.4 Hz, 1H), 7.58 (s, 1H), 7.50 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.38–7.30 (m, 4H), 7.09 (s, 1H), 3.57 (t, *J* = 7.2 Hz, 2H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.46 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ =155.21, 147.95, 147.26, 138.40, 135.45, 134.65, 131.75, 129.26, 129.25, 128.15, 124.97, 124.93, 120.71, 118.74, 25.48, 21.64, 21.29, 18.54. HRMS (ESI) m/z: Calcd for $C_{20}H_{18}N_2S$: 319.1263 $[M+H]^+$, Found 319.1267.



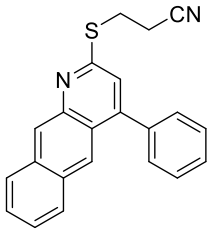
3-((6-ethyl-4-(p-tolyl)quinolin-2-yl)thio)propanenitrile (3h). White solid. mp: 89-91℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.91 (d, *J* = 8.4 Hz, 1H), 7.61 (s, 1H), 7.57–7.52 (m, 1H), 7.39–7.30 (m, 4H), 7.10 (s, 1H), 3.58 (t, *J* = 6.8 Hz, 2H), 3.00 (t, *J* = 6.8 Hz, 2H), 2.73 (q, *J* = 7.6 Hz, 2H), 2.46 (s, 3H), 1.24 (t, *J* = 8.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ =155.25, 148.09, 147.47, 141.78, 138.41, 134.67, 130.60, 129.28, 129.26, 128.31, 124.98, 123.78, 120.71, 118.75, 28.99, 25.48, 21.30, 18.53, 15.65. HRMS (ESI) m/z: Calcd for $C_{21}H_{20}N_2S$: 333.1420 $[M+H]^+$, Found 333.1424.



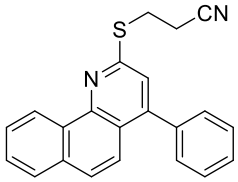
3-((6-butyl-4-(4-pentylphenyl)quinolin-2-yl)thio)propanenitrile (3i). Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.90 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.52 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.41–7.30 (m, 4H), 7.11 (s, 1H), 3.57 (t, *J* = 6.8 Hz, 2H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.69 (q, *J* = 7.6 Hz, 4H), 1.75–1.66 (m, 2H), 1.64–1.56 (m, 2H), 1.41–1.30 (m, 6H), 0.96–0.88 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ =155.24, 148.08, 147.48, 143.46, 140.42, 134.86, 131.00, 129.27, 128.61, 128.21, 124.90, 124.46, 120.74, 118.75, 35.74, 35.72, 33.58, 31.59, 31.07, 25.49, 22.56, 22.33, 18.54, 14.04, 13.90. HRMS (ESI) m/z: Calcd for $C_{27}H_{32}N_2S$: 417.2359 $[M+H]^+$, Found 417.2362.



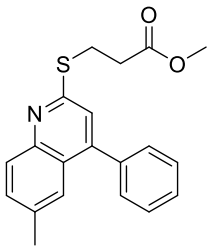
3-((4-(4-fluorophenyl)-6-methylquinolin-2-yl)thio)propanenitrile (3j). White solid. mp: 110-112℃**.** IR (KBr) 3047, 2248, 1602, 1544, 1510, 839 cm^{-1} .^{1}H NMR (400 MHz, $CDCl_3$) δ =7.89 (d, *J* = 8.4 Hz, 1H), 7.53–7.48 (m, 2H), 7.45–7.41 (m, 2H), 7.21 (t, *J* = 8.4 Hz, 2H), 7.08 (s, 1H), 3.57 (t, *J* = 7.2 Hz, 2H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ =163.72, 162.08, 155.29, 147.02 (d, *J* = 64.5 Hz), 135.73, 133.52 (d, *J* = 3.3 Hz), 131.93, 131.05 (d, *J* = 8.1 Hz), 128.25, 124.82, 124.59, 120.82, 118.69, 115.66 (d, *J* = 21.3 Hz), 25.48, 21.67, 18.52. HRMS (ESI) m/z: Calcd for $C_{19}H_{15}FN_2S$: 322.0940 $[M+H]^+$, Found 322.0944.



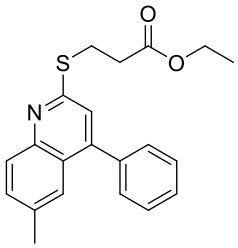
3-((4-phenylbenzo[g]quinolin-2-yl)thio)propanenitrile(3k). White solid. mp: 139-141℃**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.98–7.87 (m, 2H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.50–7.42 (m, 3H), 7.38–7.34 (m, 2H), 7.18 (s, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 3.60 (t, *J* = 7.2 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 155.09, 149.71, 148.70, 142.03, 132.48, 131.82, 129.79, 129.20, 128.65, 128.30, 128.19, 127.82, 127.68, 126.20, 125.68, 123.31, 121.39, 118.68, 25.53, 18.66. HRMS (ESI) m/z: Calcd for $C_{22}H_{16}N_2S$: 341.1107 $[M+H]^+$, Found 341.1111.



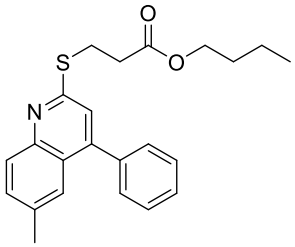
3-((4-phenylbenzo[h]quinolin-2-yl)thio)propanenitrile(3l). White solid. mp: 94-97℃**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ =9.21 (d, *J* = 8.0 Hz, 1H), 7.89 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.77–7.68 (m, 4H), 7.57–7.45 (m, 5H), 7.32 (s, 1H), 3.76 (t, *J* = 7.1 Hz, 2H), 3.13 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ =154.92, 148.84, 146.64, 137.72, 133.69, 130.81, 129.46, 128.60, 128.53, 128.39, 127.75, 127.08, 126.48, 124.29, 122.97, 122.18, 121.30, 118.63, 25.82, 18.39. HRMS (ESI) m/z: Calcd for $C_{22}H_{16}N_2S$: 341.1107 $[M+H]^+$, Found 341.1110.



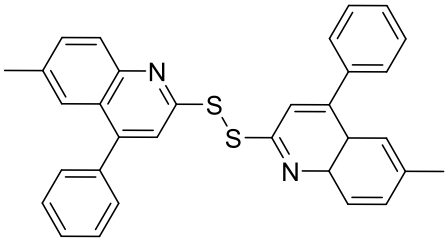
methyl 3-((6-methyl-4-phenylquinolin-2-yl)thio)propanoate(3m). White solid mp: 58-60℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (d, *J* = 8.0 Hz, 1H), 7.54–7.42 (m, 7H), 7.09 (s, 1H), 3.72 (s, 3H), 3.61 (t, *J* = 7.2 Hz, 2H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.03, 156.91, 147.57, 138.07, 135.36, 131.79, 129.61, 128.75, 128.56, 128.47, 124.99, 124.93, 121.15, 52.01, 34.72, 24.95, 21.89. HRMS (ESI) m/z: Calcd for $C_{20}H_{19}NO_2S$: 338.1209 $[M+H]^+$, Found 338.1211.



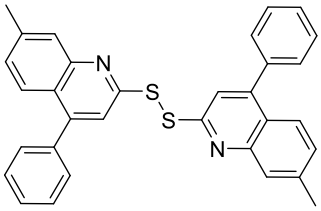
ethyl 3-((6-methyl-4-phenylnaphthalen-2-yl)thio)propanoate(3n). White solid. mp: 80-82℃. ^{1}H NMR (400 MHz,$CDCl_3$) δ =7.89 (d, *J* = 8.4 Hz, 1H), 7.55–7.44 (m, 7H), 7.10 (s, 1H), 4.19 (q, *J* = 6.8 Hz, 2H), 3.60 (t, *J* = 6.8 Hz, 2H), 2.90 (t, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ =172.29, 156.77, 147.33, 137.86, 135.08, 131.52, 129.36, 128.48, 128.30, 128.23, 124.73, 124.69, 120.91, 60.58, 34.71, 24.74, 21.62, 14.22. HRMS (ESI) m/z: Calcd for $C_{21}H_{21}O_2S$: 352.1366 $[M+H]^+$, Found 352.1368.



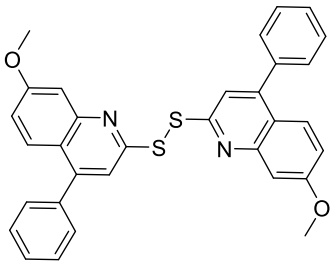
butyl 3-((6-methyl-4-phenylnaphthalen-2-yl)thio)propanoate(3o). Colourless Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.89 (d, *J* = 8.4 Hz, 1H), 7.55–7.44 (m, 7H), 7.10 (s, 1H), 4.13 (t, *J* = 6.4 Hz, 2H), 3.61 (t, *J* = 6.8 Hz, 2H), 2.90 (t, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.63–1.58 (m, 2H), 1.44–1.33 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ =172.37, 156.76, 147.32, 147.31, 137.86, 135.08, 131.51, 129.36, 128.48, 128.29, 128.22, 124.73, 124.69, 120.92, 64.51, 34.73, 30.64, 24.77, 21.62, 19.13, 13.68. HRMS (ESI) m/z: Calcd for $C_{23}H_{25}NO_2S$: 380.1679 $[M+H]^+$, Found 380.1680.



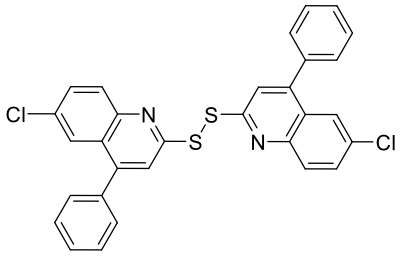
1,2-bis(6-methyl-4-phenylquinolin-2-yl)disulfane (4a). White solid. mp: 199-201°C. IR (KBr) 2924, 2850, 1577, 1546, 1323, 819 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 8.8Hz, 1H), 7.75 (s, 1H), 7.57 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.46 (m, 3H), 7.42 – 7.38 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) 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 $C_{32}H_{24}N_2S_2$ 501.1454 $[M+H]^+$, Found 501.1458.



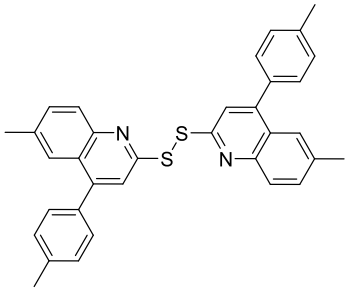
1,2-bis(7-methyl-4-phenylquinolin-2-yl)disulfane(4b). White solid. mp : 144-146℃**.** ^1H NMR (400 MHz, $CDCl_3$) δ = 7.85–7.80 (m, 1H), 7.74–7.69 (m, 2H), 7.47–7.38 (m, 5H), 7.27–7.24 (m, 1H), 2.53 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 158.73, 149.66, 148.71, 140.54, 137.63, 129.45, 128.52, 128.50, 127.87, 125.60, 123.16, 116.48, 21.68. HRMS (ESI^+) m/z: Calcd for $C_{32}H_{24}N_2S_2$ 501.1454 $[M+H]^+$, Found 501.1456



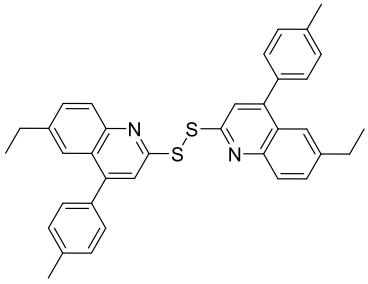
1,2-bis(6-methoxy-4-phenylquinolin-2-yl)disulfane(4c). White solid. mp: 148-150℃**.** ^1H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 9.2 Hz, 1H), 7.65 (s, 1H), 7.46–7.36 (m, 6H), 7.07 (dd, *J* = 9.2, 2.4 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 161.18, 159.16, 150.33, 149.77, 137.65, 129.41, 128.51, 127.04, 120.16, 119.23, 115.09, 106.91, 55.58. HRMS (ESI^+) m/z: Calcd for $C_{32}H_{24}N_2O_2S_2$ 533.1352 $[M+H]^+$, Found 533.1355.



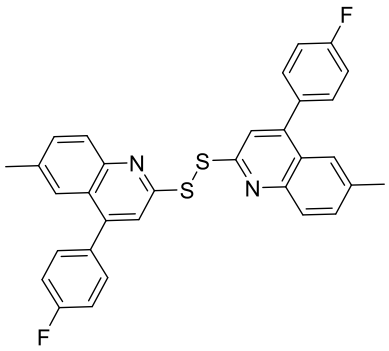
1,2-bis(6-chloro-4-phenylquinolin-2-yl)disulfane (4d). White solid. mp: 200-203℃**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 2.4 Hz, 1H), 7.76 (s, 1H), 7.62 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.52–7.45 (m, 3H), 7.41–7.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.18, 149.38, 147.10 , 137.00, 132.56, 131.29, 130.57, 129.59, 129.21, 129.05, 126.21, 125.06, 118.41. HRMS (ESI) m/z: Calcd for $C_{30}H_{18}Cl_2N_2S_2$: 541.0361 $[M+H]^+$, Found 541.0365.



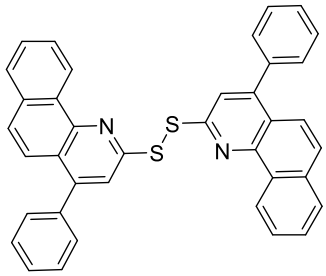
1,2-bis(6-methyl-4-(p-tolyl)quinolin-2-yl)disulfane (4e). White solid. mp: 178-180℃**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93 (d, *J* = 8.4 Hz, 1H), 7.72 (s, 1H), 7.60 (s, 1H), 7.51 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.31–7.24 (m, 4H), 2.42 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 157.76, 149.33, 147.08, 138.44, 136.17, 134.76, 132.18, 129.38, 129.23, 128.46, 125.22, 124.79, 117.32, 21.73, 21.27. HRMS (ESI) m/z: Calcd for $C_{34}H_{28}N_2S_2$: 529.1767 $[M+H]^+$, Found 529.1770.



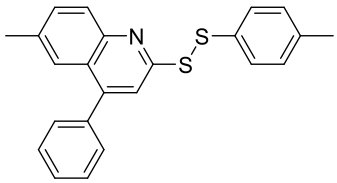
1,2-bis(6-ethyl-4-(p-tolyl)quinolin-2-yl)disulfane (4f). White solid. mp: 150-152℃**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 0.8 Hz, 1H), 7.62 (s, 1H), 7.56 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.33–7.26 (m, 4H), 2.72 (q, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 157.82, 149.48, 147.27, 142.44, 138.43, 134.77, 131.04, 129.39, 129.23, 128.60, 125.23, 123.63, 117.27, 29.04, 21.26, 15.54. HRMS (ESI) m/z: Calcd for $C_{36}H_{32}N_2S_2$: 557.2080 $[M+H]^+$, Found 557.2084.



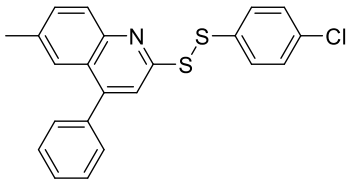
1,2-bis(4-(4-fluorophenyl)-6-methylquinolin-2-yl)disulfane (4g). White solid. mp: 197-200℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93 (d, *J* = 8.0 Hz, 1H), 7.72 (s, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 7.52 (s, 1H), 7.40–7.35 (m, 2H), 7.16 (t, *J* = 8.8 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 163.74, 162.09, 157.71, 148.21, 147.0, 136.56, 133.56(d, *J* = 13.8 Hz), 132.40, 131.16(d, *J* = 34.2 Hz), 128.54, 125.10, 124.46, 117.50, 115.65(d, *J* = 85.2 Hz), 21.75. HRMS (ESI) m/z: Calcd for $C_{32}H_{22}F_2N_2S_2$: 537.1265 $[M+H]^+$, Found 537.1269.



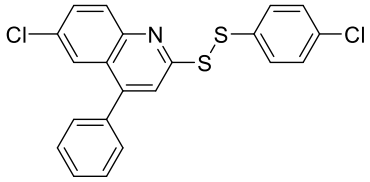
1,2-bis(4-phenylbenzo[h]quinolin-2-yl)disulfane (4h). White solid. mp: 190-192℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.24 (d, *J* = 6.8 Hz, 1H), 7.90 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 2.8 Hz, 2H), 7.68–7.63 (m, 1H), 7.60–7.55 (m, 1H), 7.44 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 157.36, 149.56, 146.88, 137.95, 133.59, 130.89, 129.57, 128.52, 128.47, 128.41, 127.39, 127.15, 127.02, 125.20, 122.75, 122.70, 118.71. HRMS (ESI) m/z: Calcd for $C_{38}H_{24}N_2S_2$: 573.1454 $[M+H]^+$, Found 573.1458.



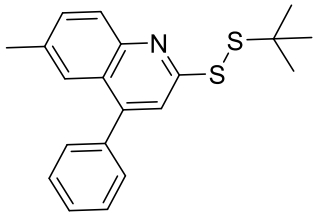
6-methyl-4-phenyl-2-(p-tolyldisulfanyl)quinoline. (6a). Colourless Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 8.8 Hz, 1H), 7.73 (s, 1H), 7.58 (s, 1H), 7.56–7.43 (m, 8H), 7.09 (d, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 158.50, 148.95, 147.15, 137.87, 137.76, 136.13, 133.12, 132.18, 130.85, 129.85, 129.46, 128.72, 128.56, 128.48, 124.70, 117.32, 21.73, 21.03. HRMS (ESI) m/z: Calcd for $C_{23}H_{19}NS_2$: 374.1032 $[M+H]^+$, Found 374.1035.



2-((4-chlorophenyl)disulfanyl)-6-methyl-4-phenylquinoline (6b). White solid. mp: 173-175℃**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 8.4 Hz, 1H), 7.62 (s, 1H), 7.58 (s, 1H), 7.56–7.49 (m, 6H), 7.46–7.43 (m, 2H), 7.26 (s, 1H), 7.24–7.23 (m, 1H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 157.48, 149.19, 147.19, 137.73, 136.38, 135.17, 133.50, 132.34, 129.42, 129.38, 129.20, 128.61, 128.57, 128.49, 125.14, 124.74, 117.26, 21.74. HRMS (ESI) m/z: Calcd for $C_{22}H_{16}ClNS_2$: 394.0485 $[M+H]^+$, Found 394.0489.



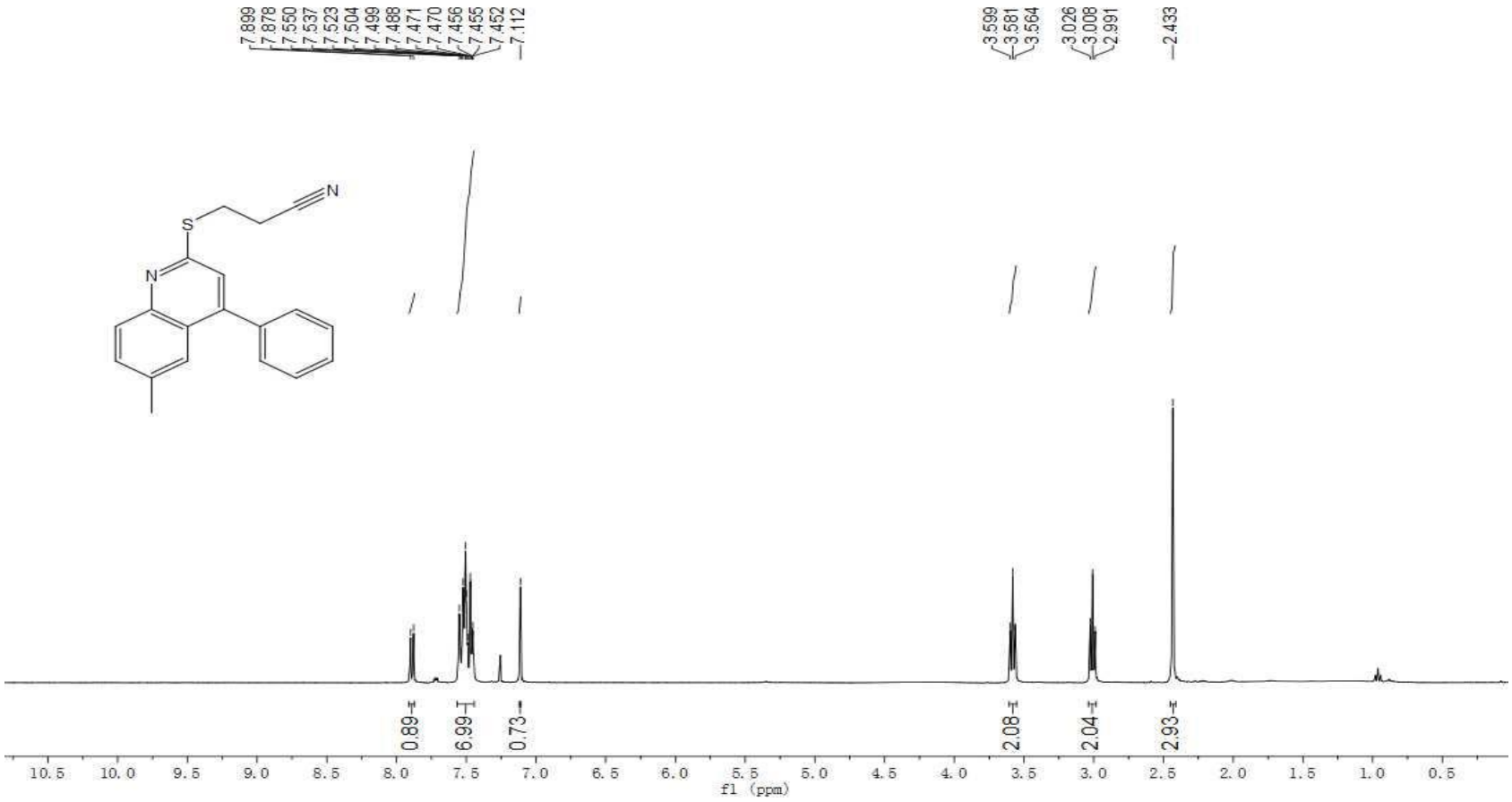
6-chloro-2-((4-chlorophenyl)disulfanyl)-4-phenylquinoline (6c) Colourless Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 2.4 Hz, 1H), 7.68 (s, 1H), 7.64 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.57 – 7.49 (m, 6H), 7.45 – 7.41 (m, 2H), 7.28 (s, 1H), 7.26 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 159.16, 149.01, 146.98, 136.85, 134.82, 133.75, 132.26, 131.03, 130.33, 129.55, 129.31, 129.28, 128.99, 128.85, 125.94, 124.82, 117.98. HRMS (ESI) m/z: Calcd for $C_{21}H_{13}Cl_2NS_2$: 413.9939 $[M+H]^+$, Found 413.9942.

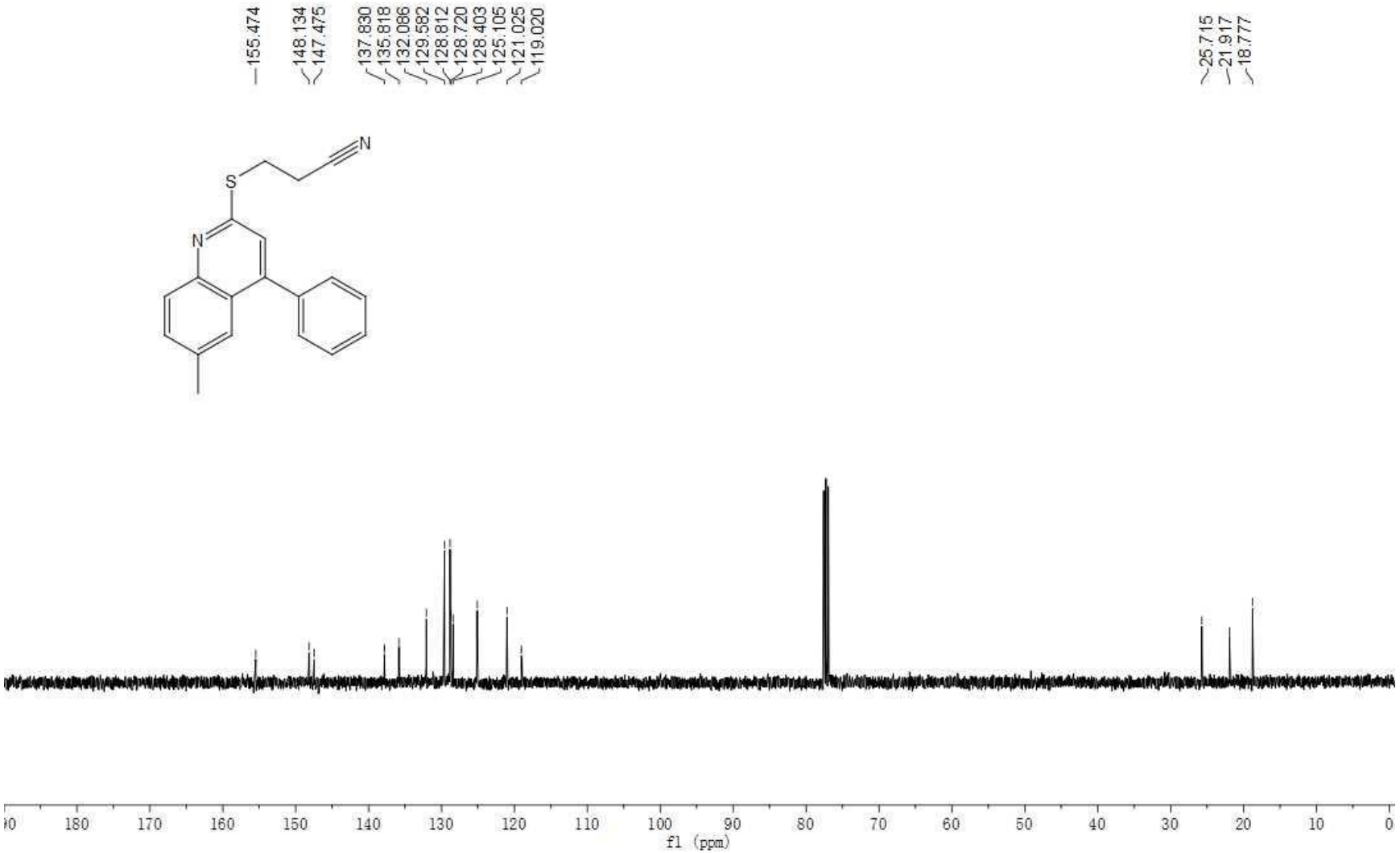


2-(tert-butyldisulfanyl)-6-methyl-4-phenylquinoline (6d) White solid. mp: 83-85℃**.** ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.95 (d, *J* = 9.0 Hz, 1H), 7.84 (s, 1H), 7.58 – 7.50 (m, 5H), 7.50 – 7.47 (m, 2H), 2.44 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 160.31, 148.47, 146.91, 138.07, 135.91, 132.07, 129.42, 128.58, 128.42, 128.37, 124.86, 124.70, 117.34, 49.25, 29.80, 21.70. HRMS (ESI) m/z: Calcd for $C_{20}H_{21}NS_2$: 340.1188 $[M+H]^+$, Found 340.1193.

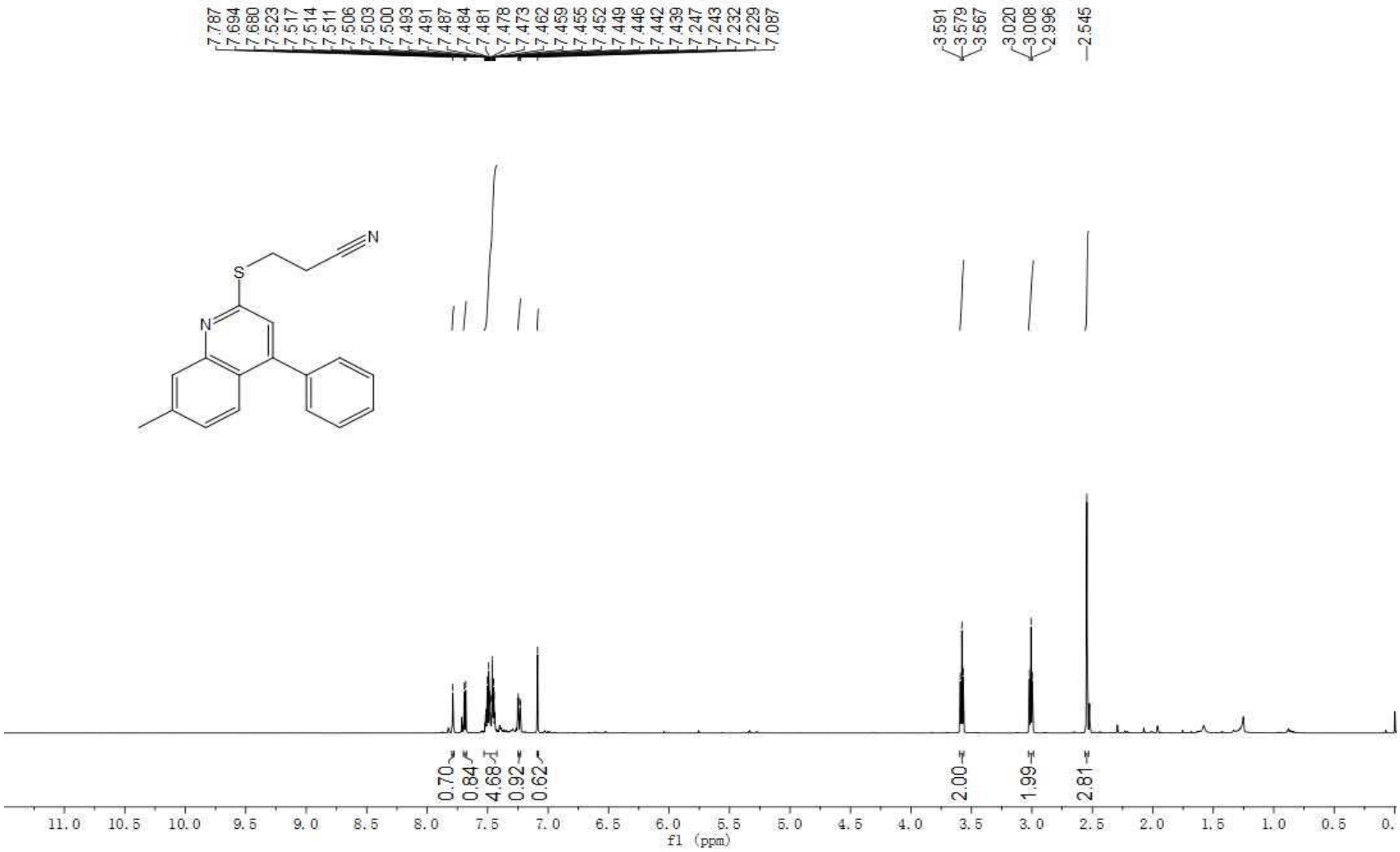
6. Copies of ^{1}H NMR and ^{13}C NMR Spectra for Compounds

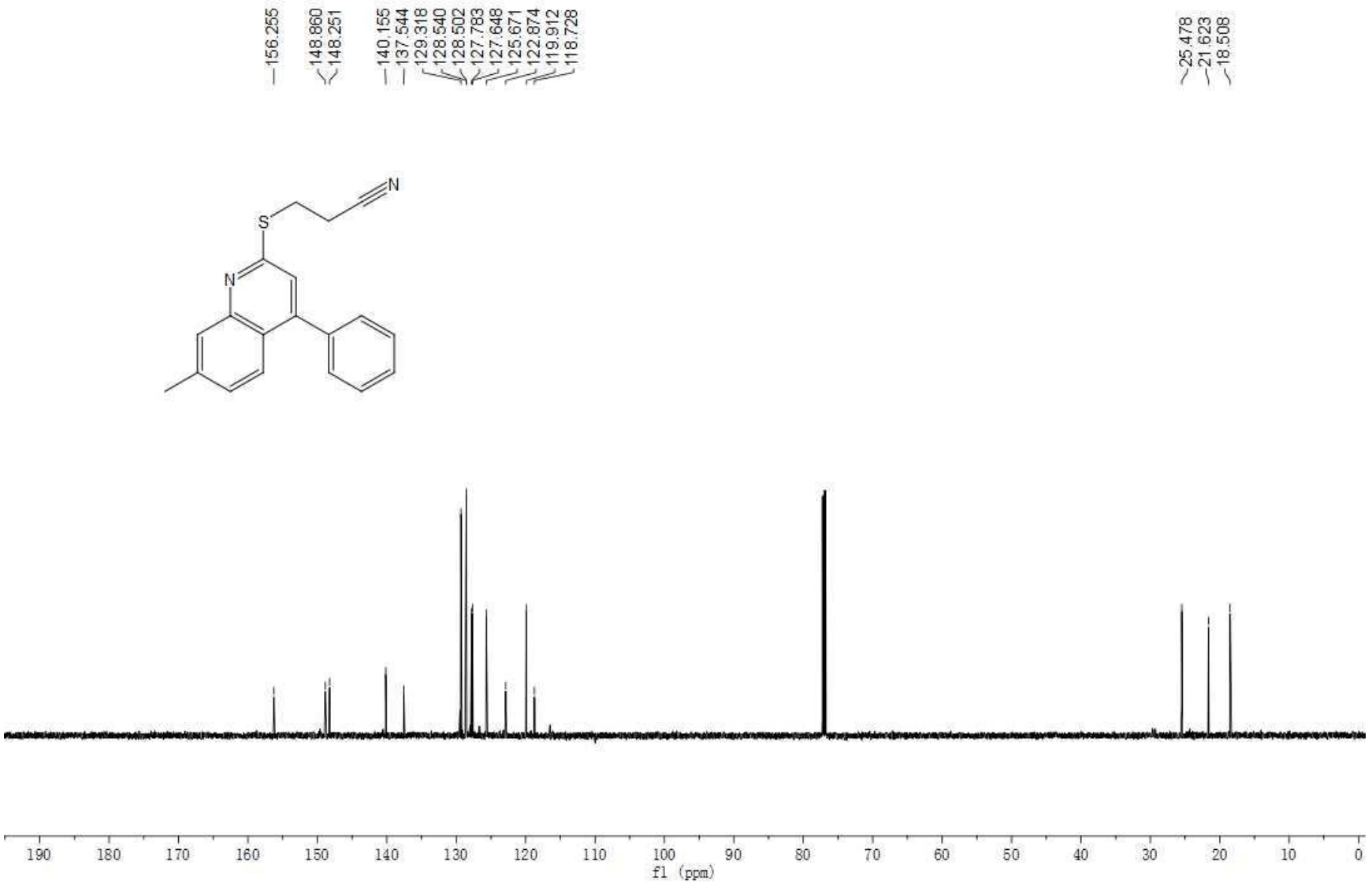
^{1}H and ^{13}C Spectra of compound 3a ($CDCl_3$)



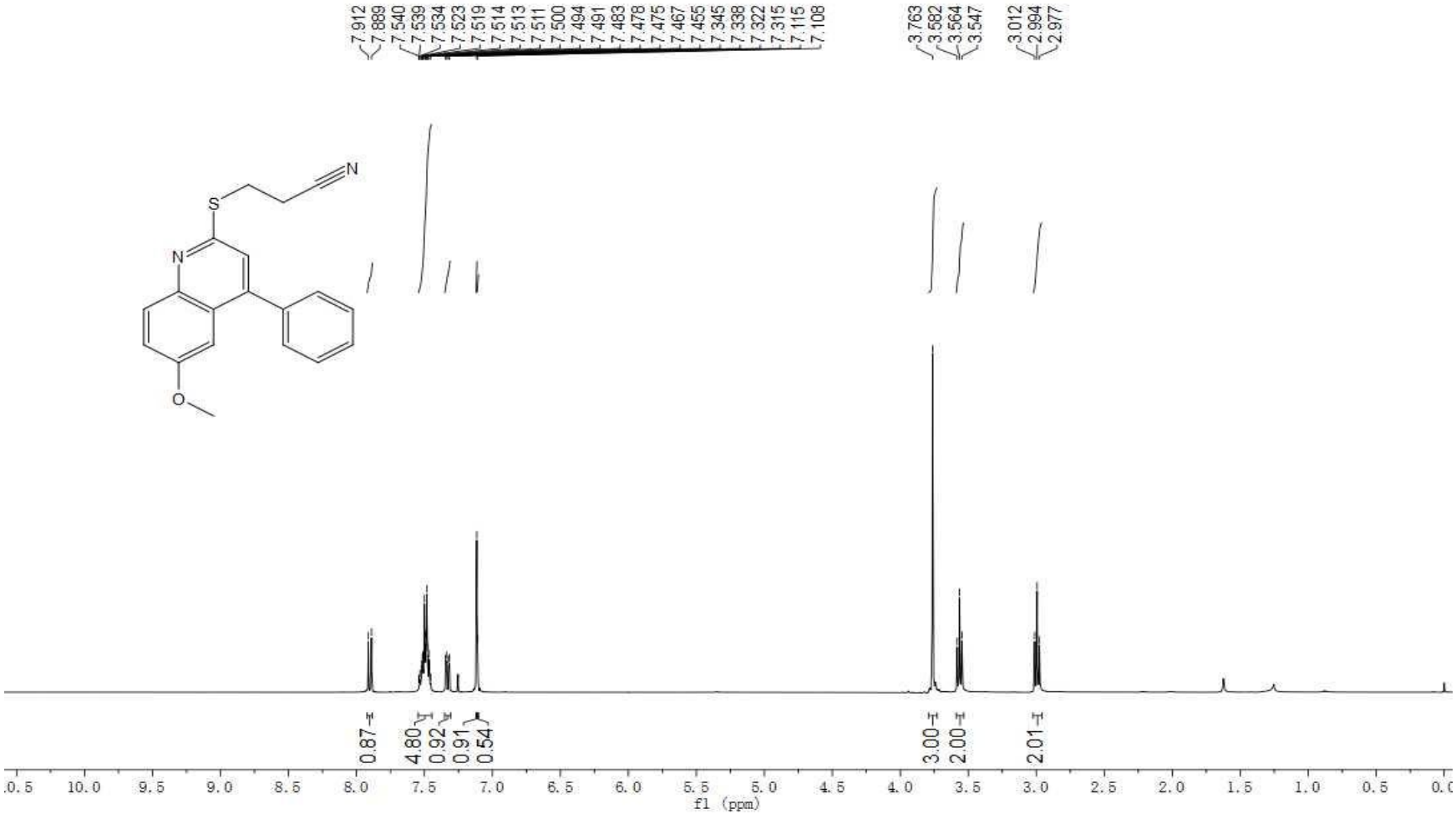

155.474
148.134
147.475
137.830
135.818
132.086
129.582
128.812
128.720
128.403
125.105
121.025
119.020
25.715
21.917
18.777
N
S
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

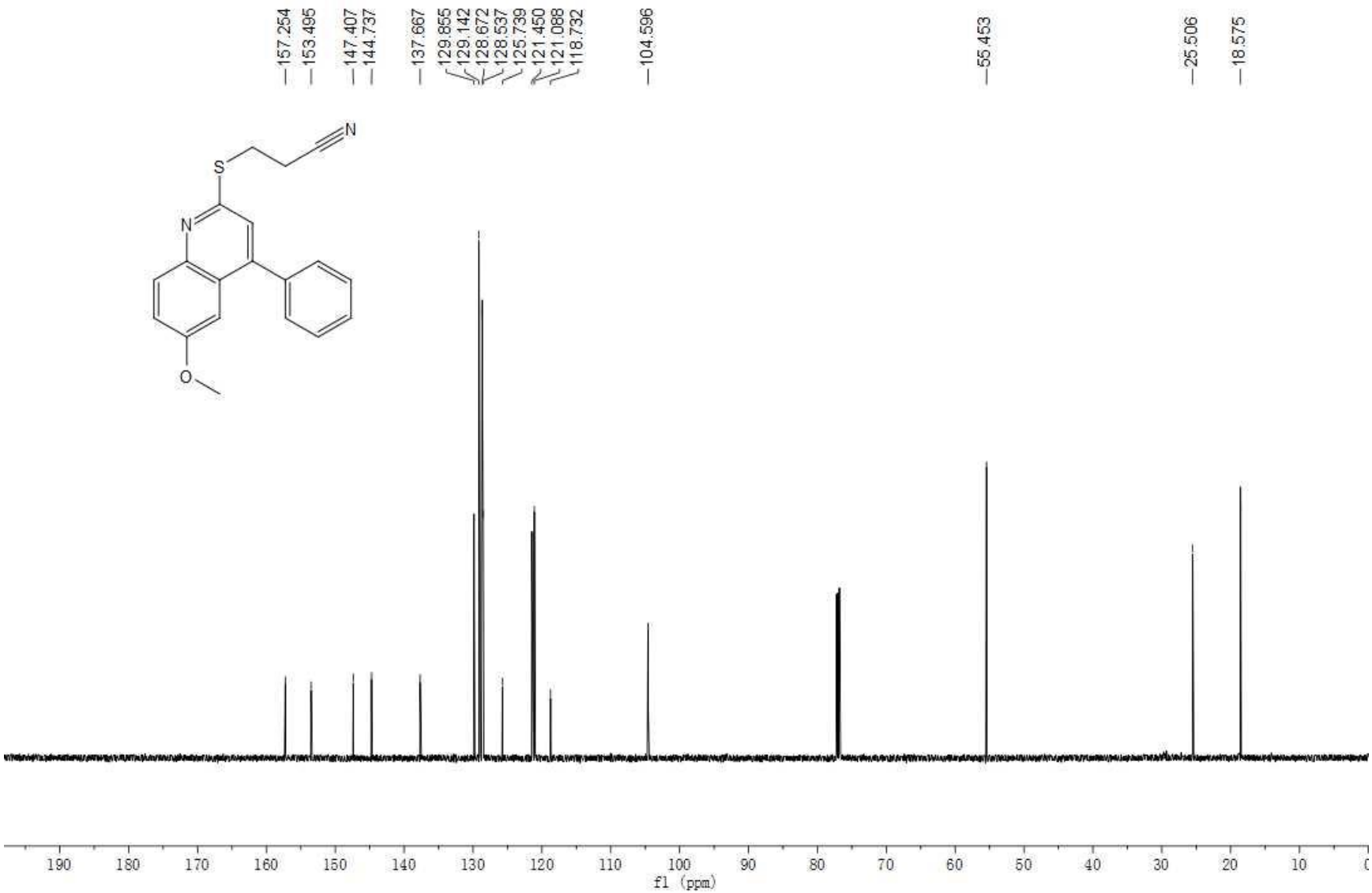
^{1}H and ^{13}C Spectra of compound 3b ($CDCl_3$)



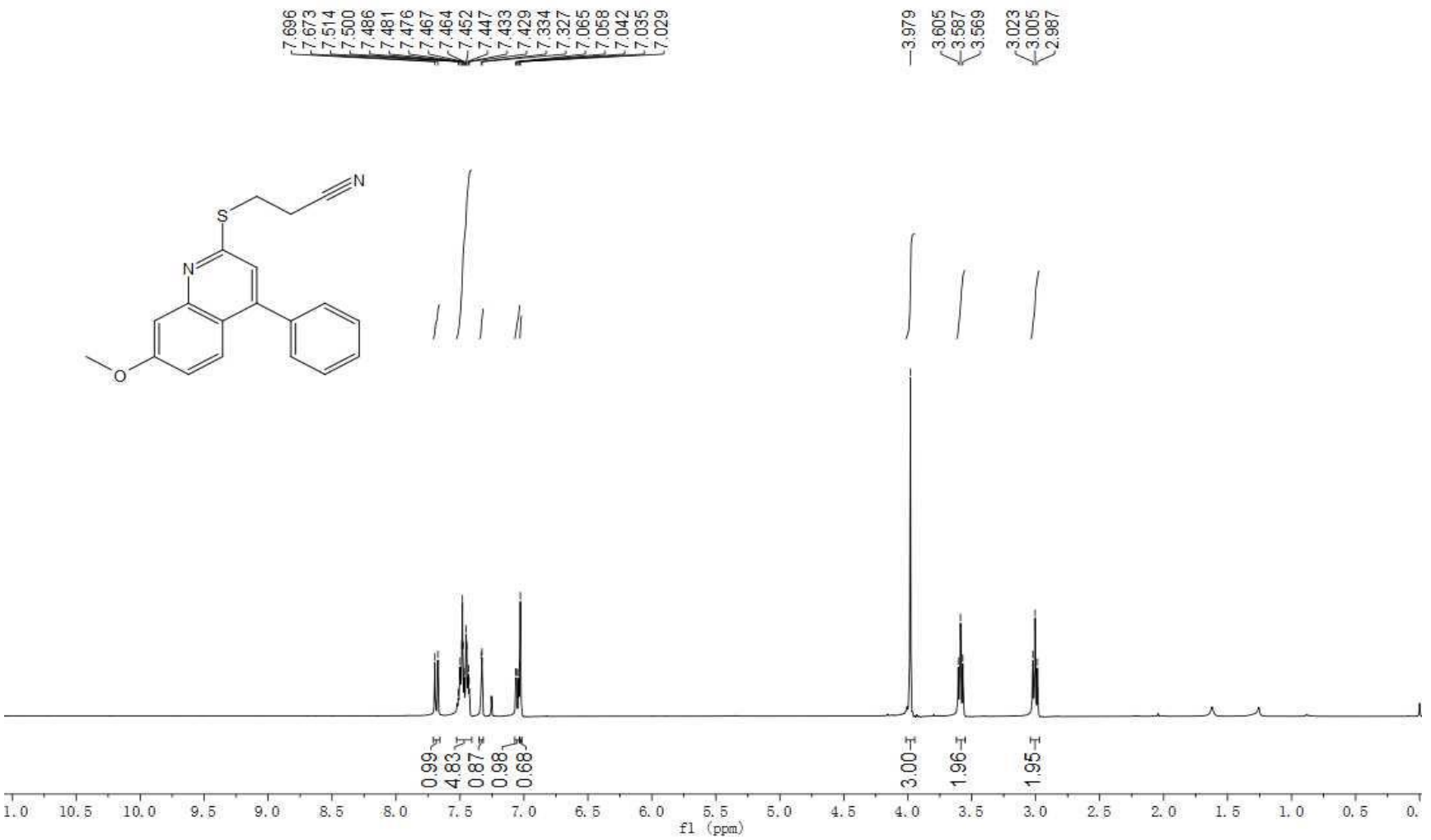

156.255
148.860
148.251
140.155
137.544
129.318
128.540
128.502
127.783
127.648
125.671
122.874
119.912
118.728
25.478
21.623
18.508
N
S
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

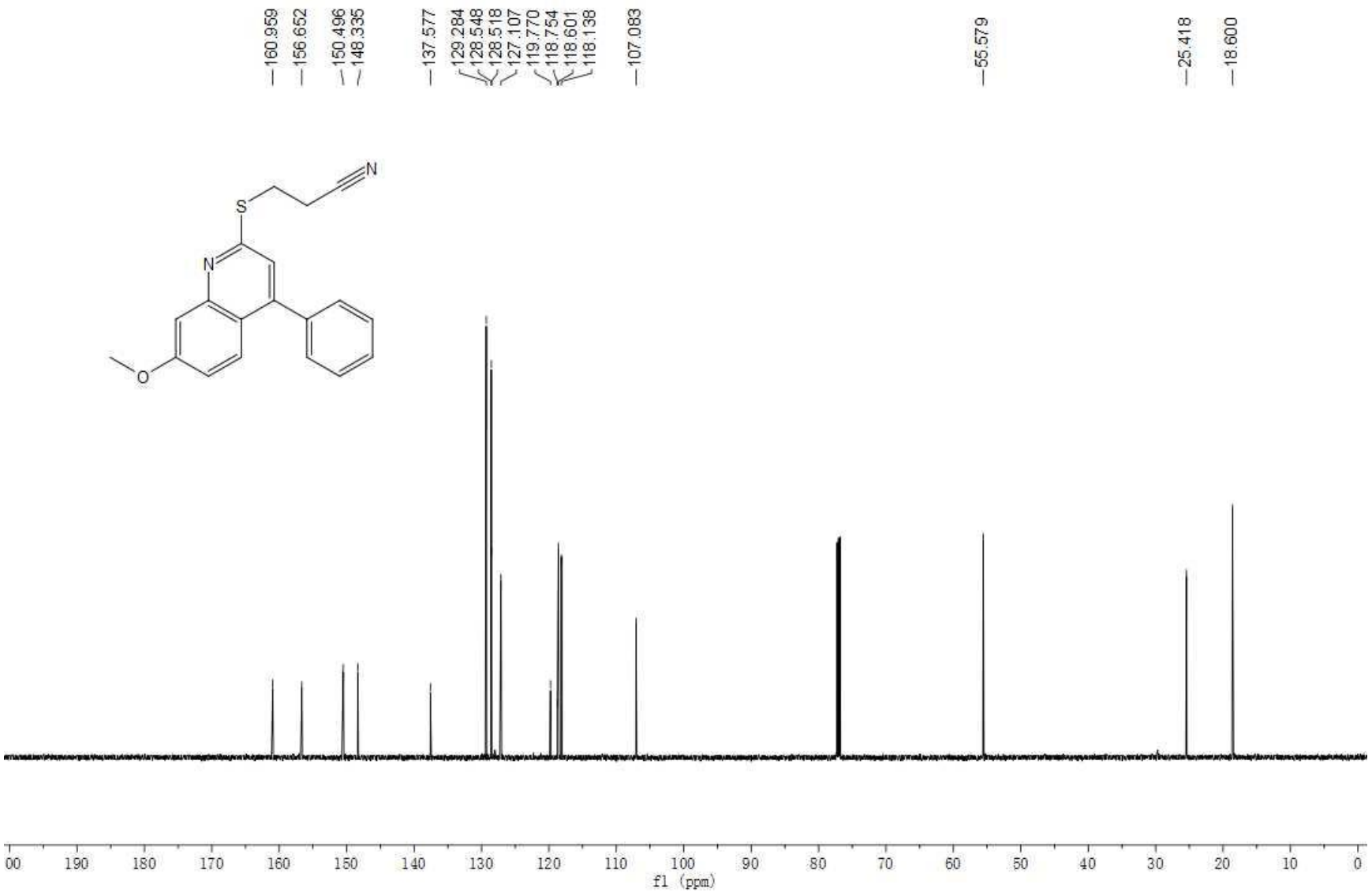
^{1}H and ^{13}C Spectra of compound 3c ($CDCl_3$)



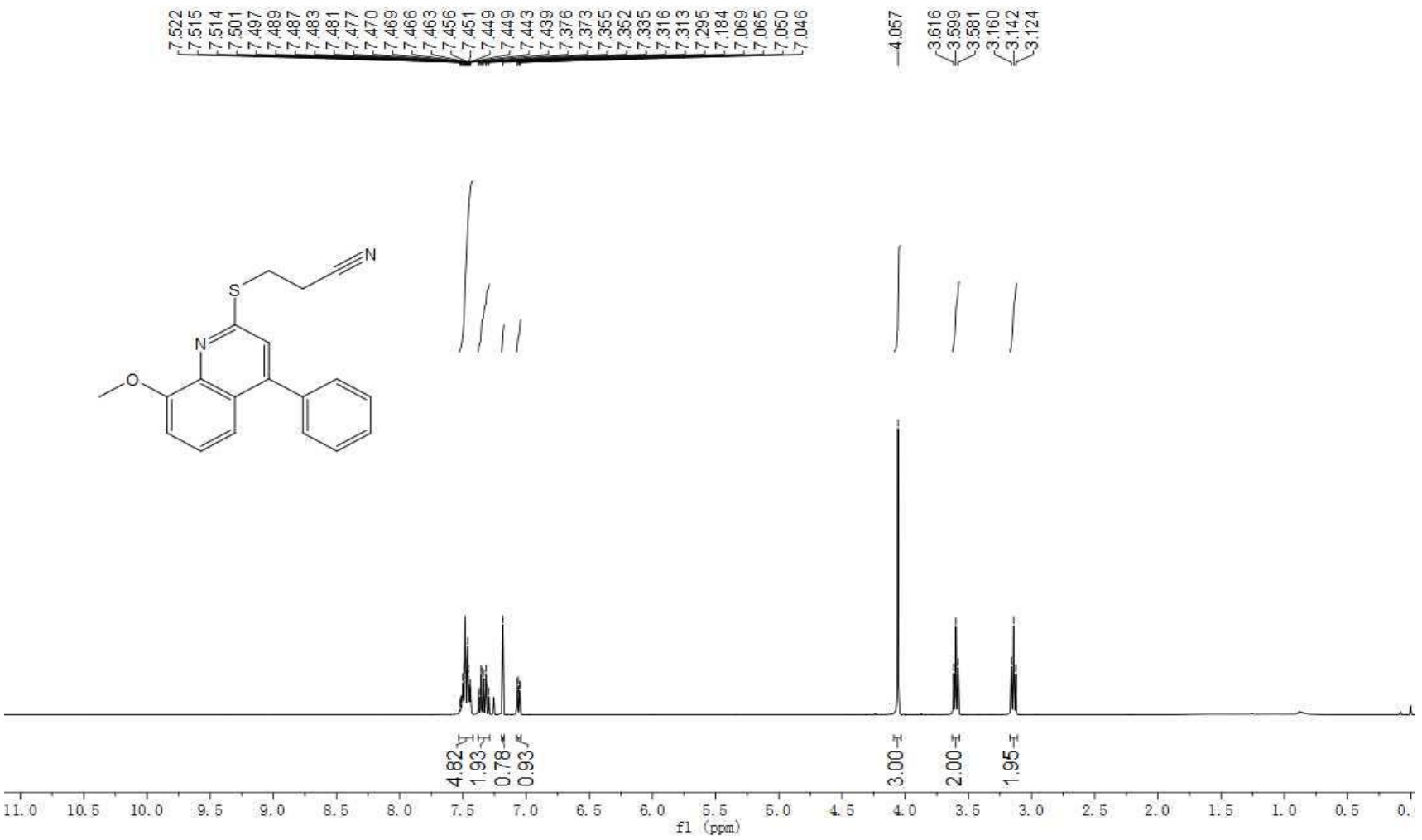

157.254
153.495
147.407
144.737
137.667
129.855
129.142
128.672
128.537
125.739
121.450
121.088
118.732
104.596
55.453
25.506
18.575
N
S
N
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

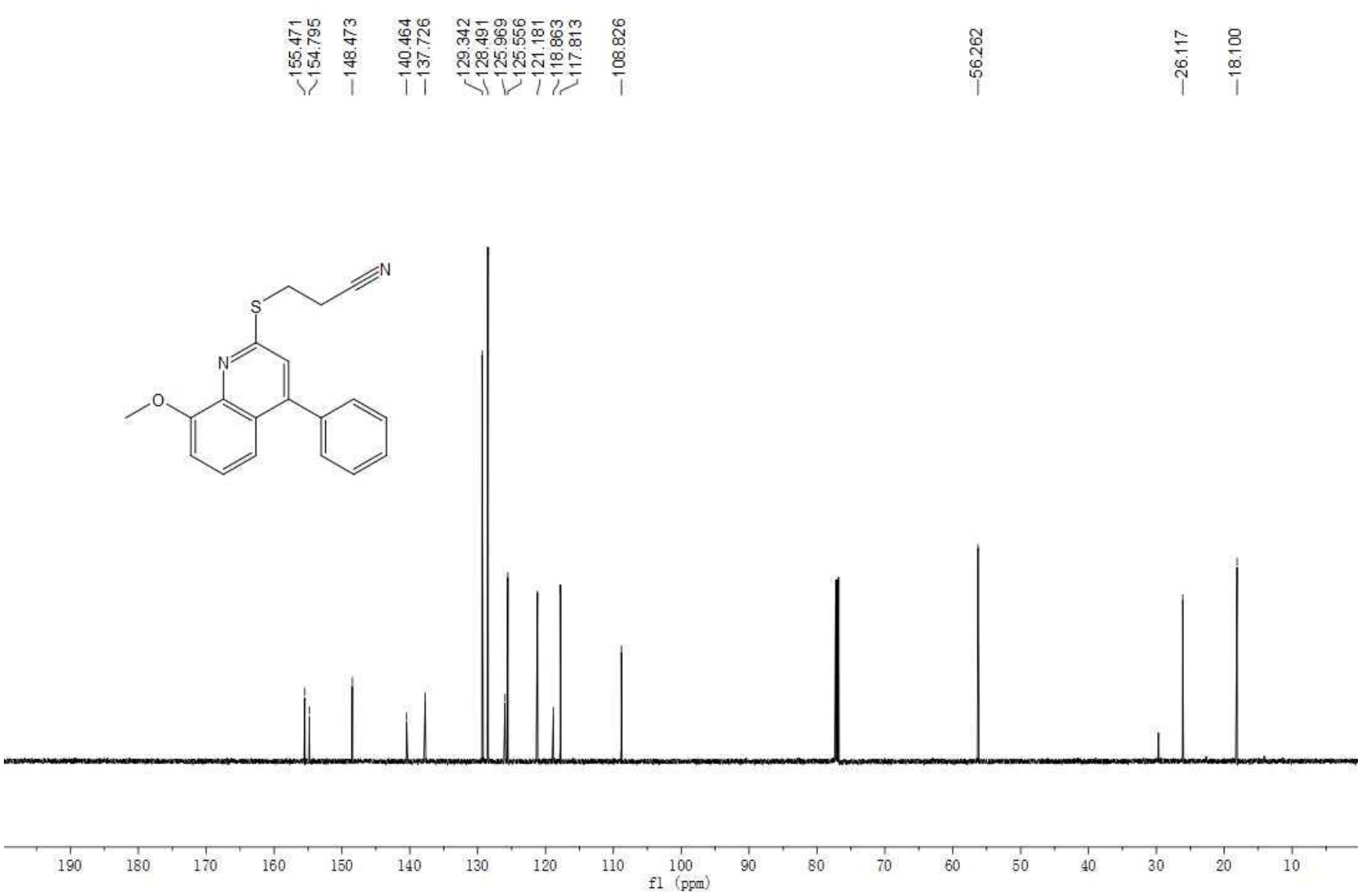
^{1}H and ^{13}C Spectra of compound 3d ($CDCl_3$)



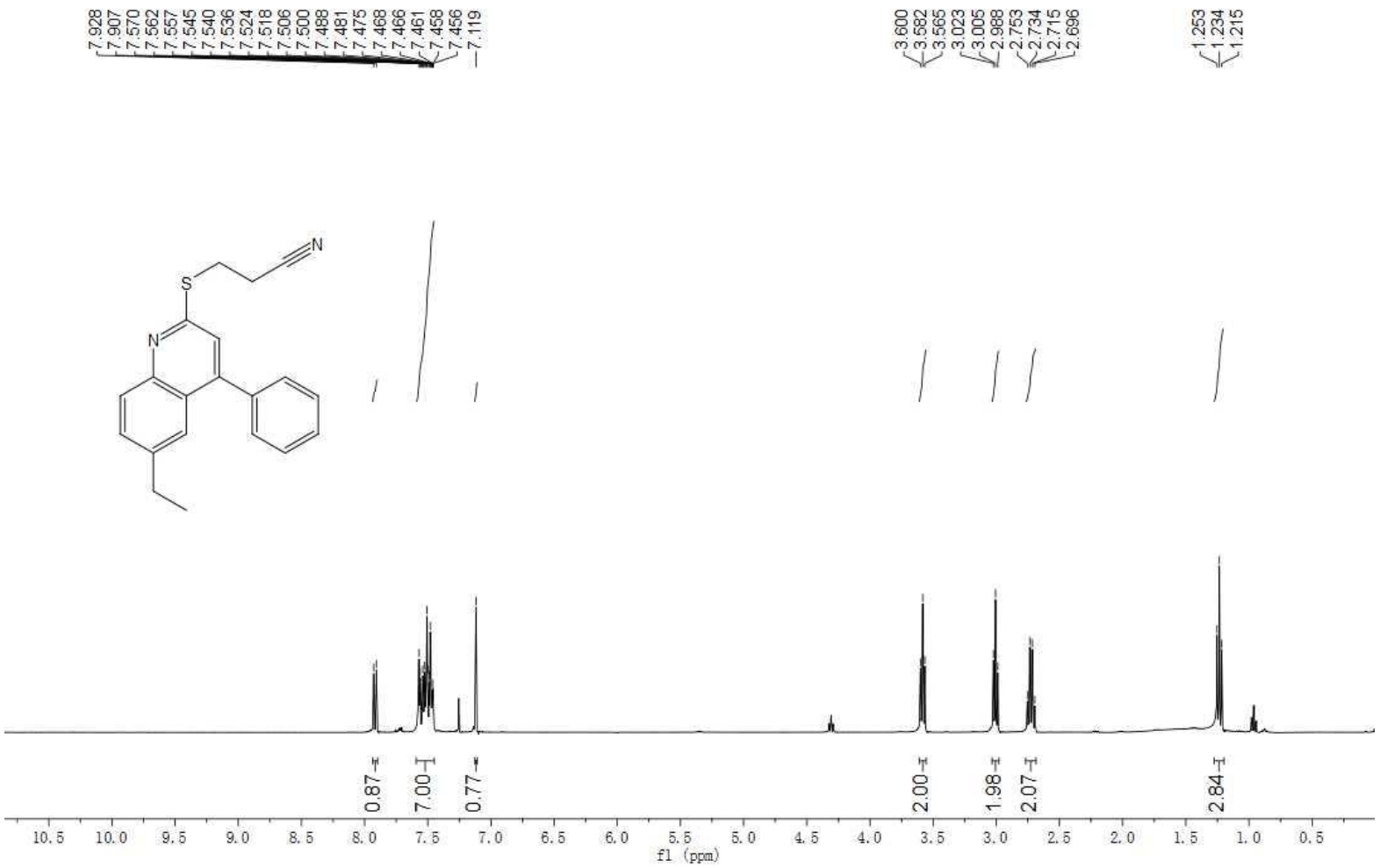

160.959
156.652
150.496
148.335
137.577
129.284
128.548
128.518
127.107
119.770
118.754
118.601
118.138
107.083
55.579
25.418
18.600
N
S
N
O
f1 (ppm)

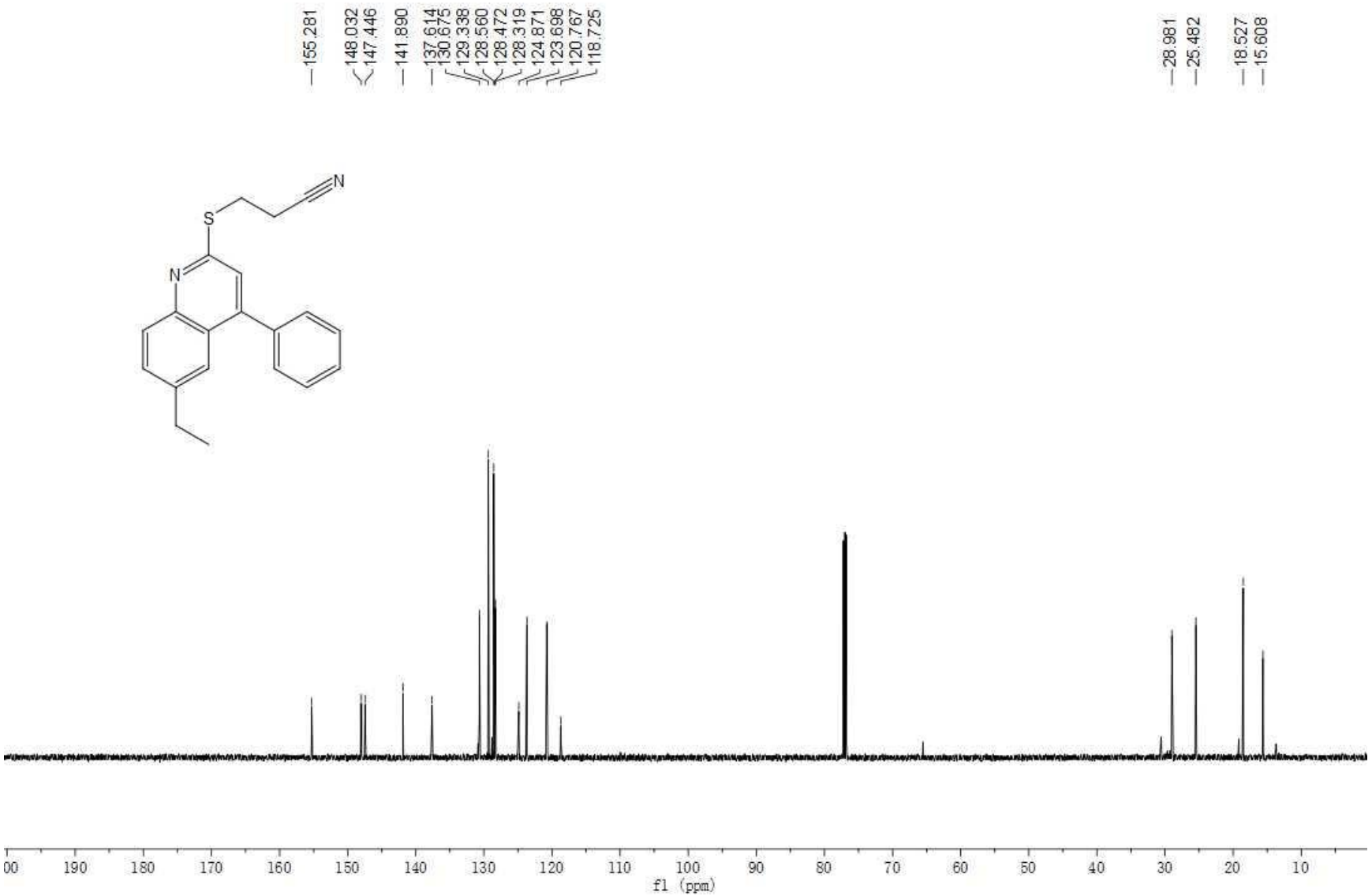
^{1}H and ^{13}C Spectra of compound 3e ($CDCl_3$)

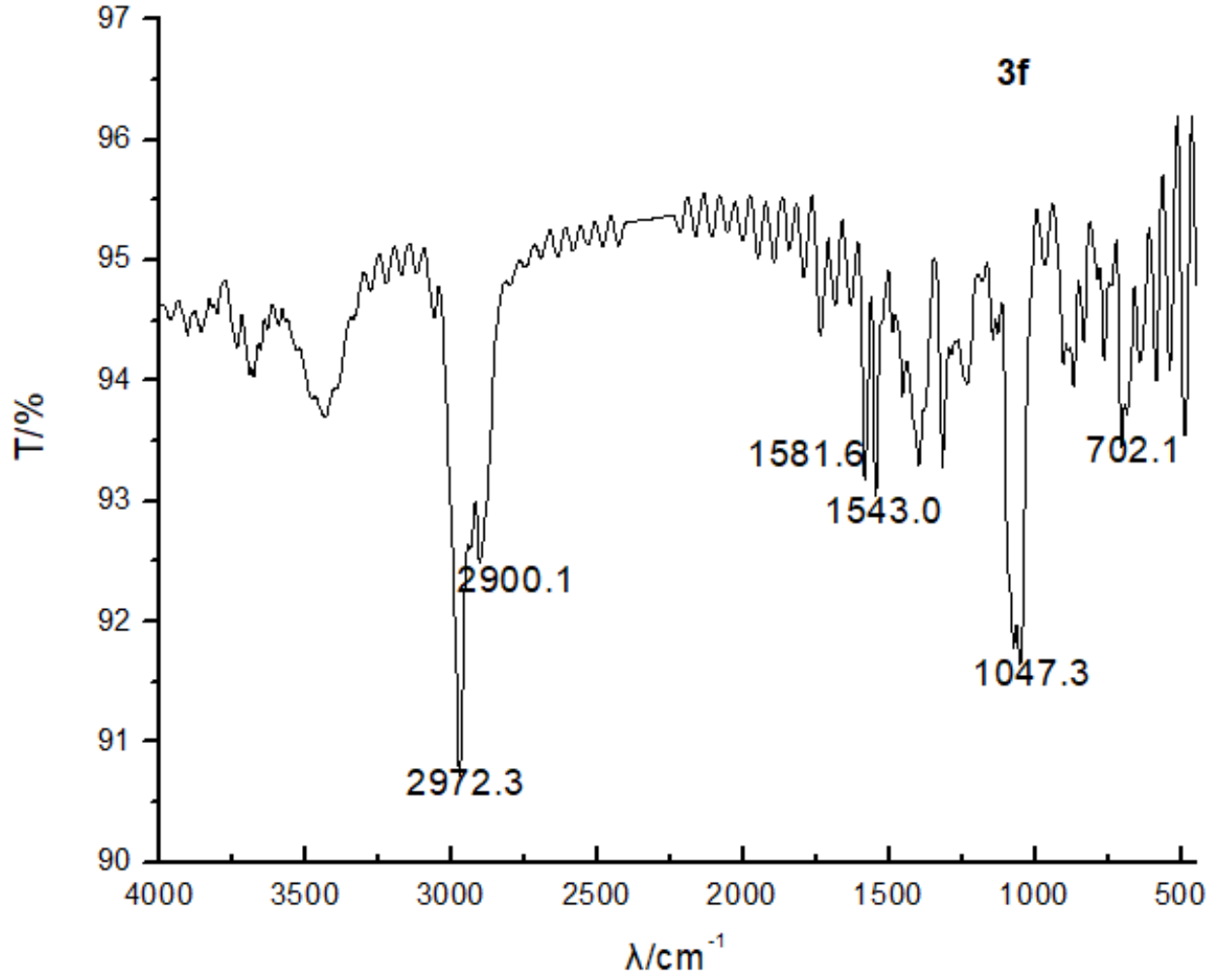



155.471
154.795
148.473
140.464
137.726
129.342
128.491
125.969
125.556
121.181
118.863
117.813
108.826
56.262
26.117
18.100
N
S
N
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

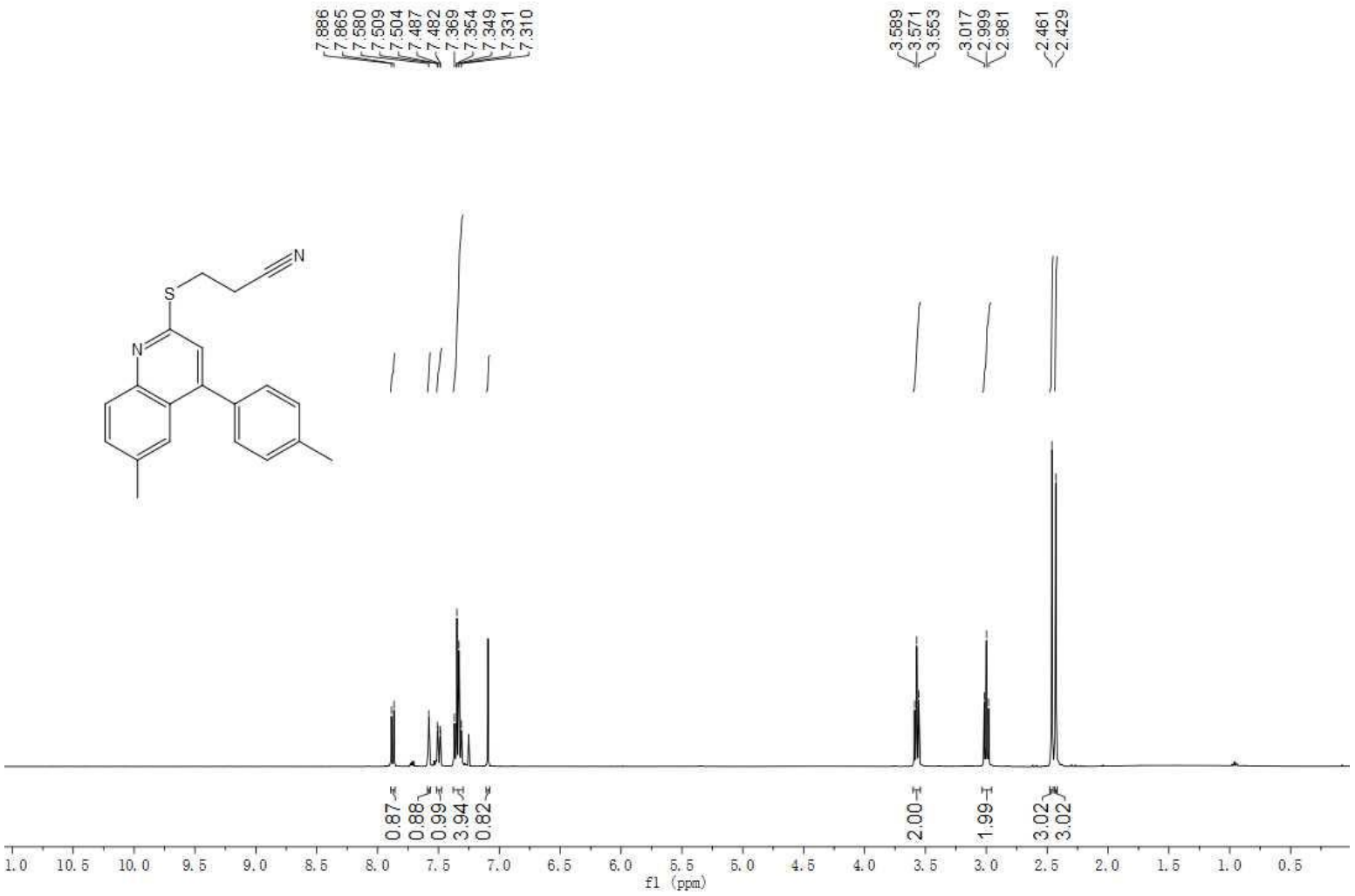
^{1}H and ^{13}C Spectra of compound 3f ($CDCl_3$)

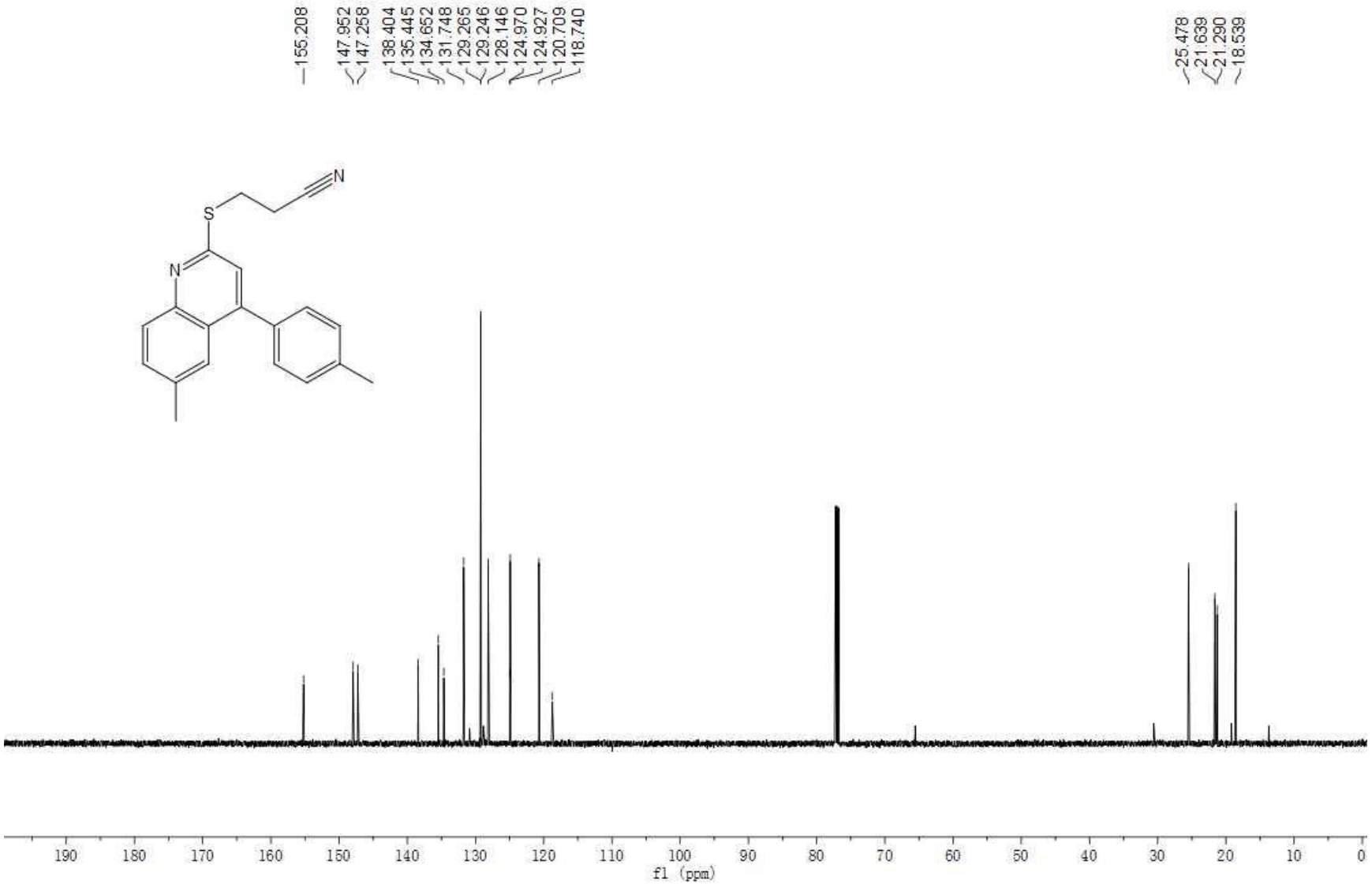



155.281
148.032
147.446
141.890
137.614
130.675
129.338
128.560
128.472
128.319
124.871
123.698
120.767
118.725
28.981
25.482
18.527
15.608
N
S
N
f1 (ppm)

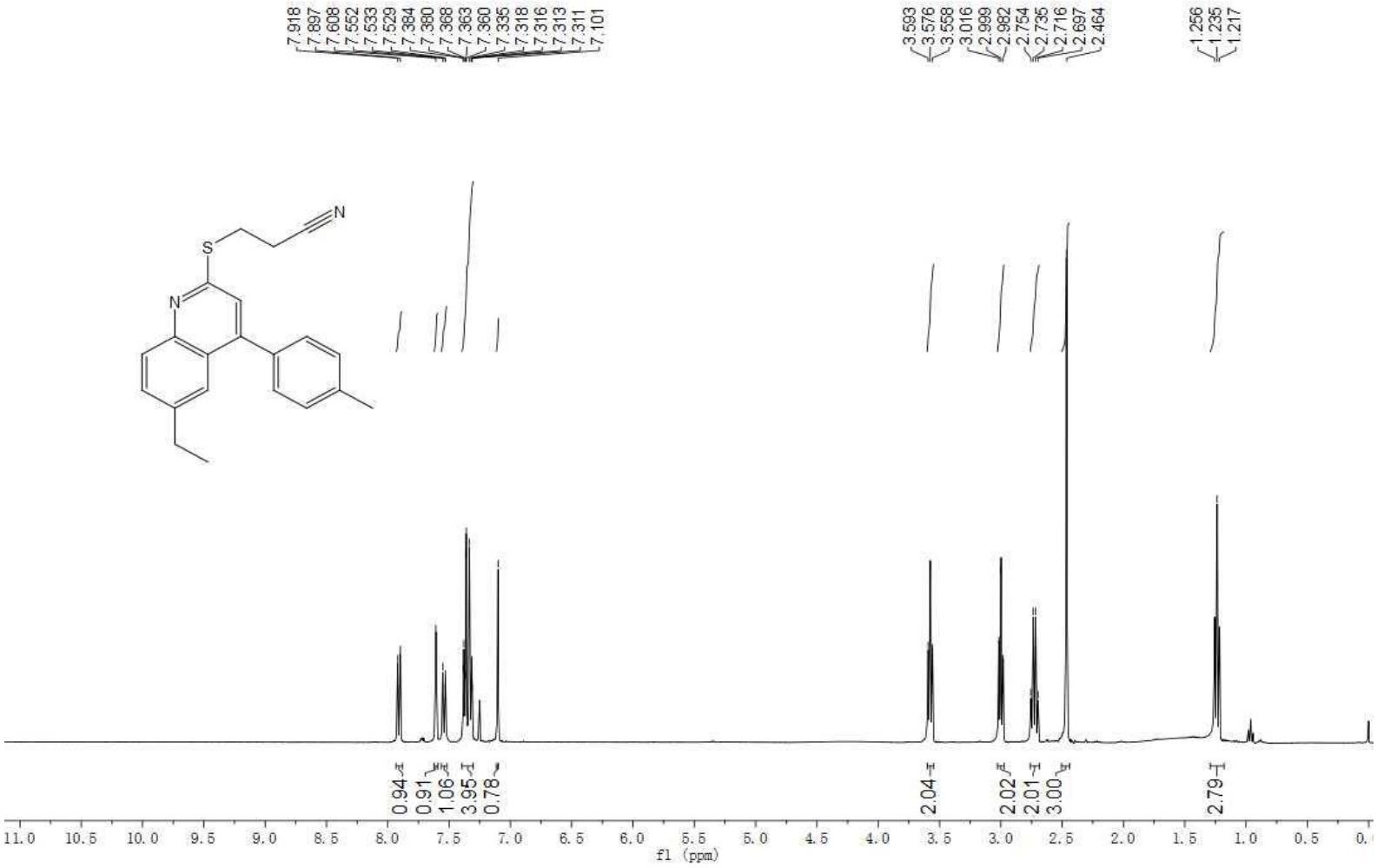

3f
T/%
λ/cm-1
97
96
95
94
93
92
91
90
4000
3500
3000
2500
2000
1500
1000
500
2972.3
2900.1
1581.6
1543.0
1047.3
702.1

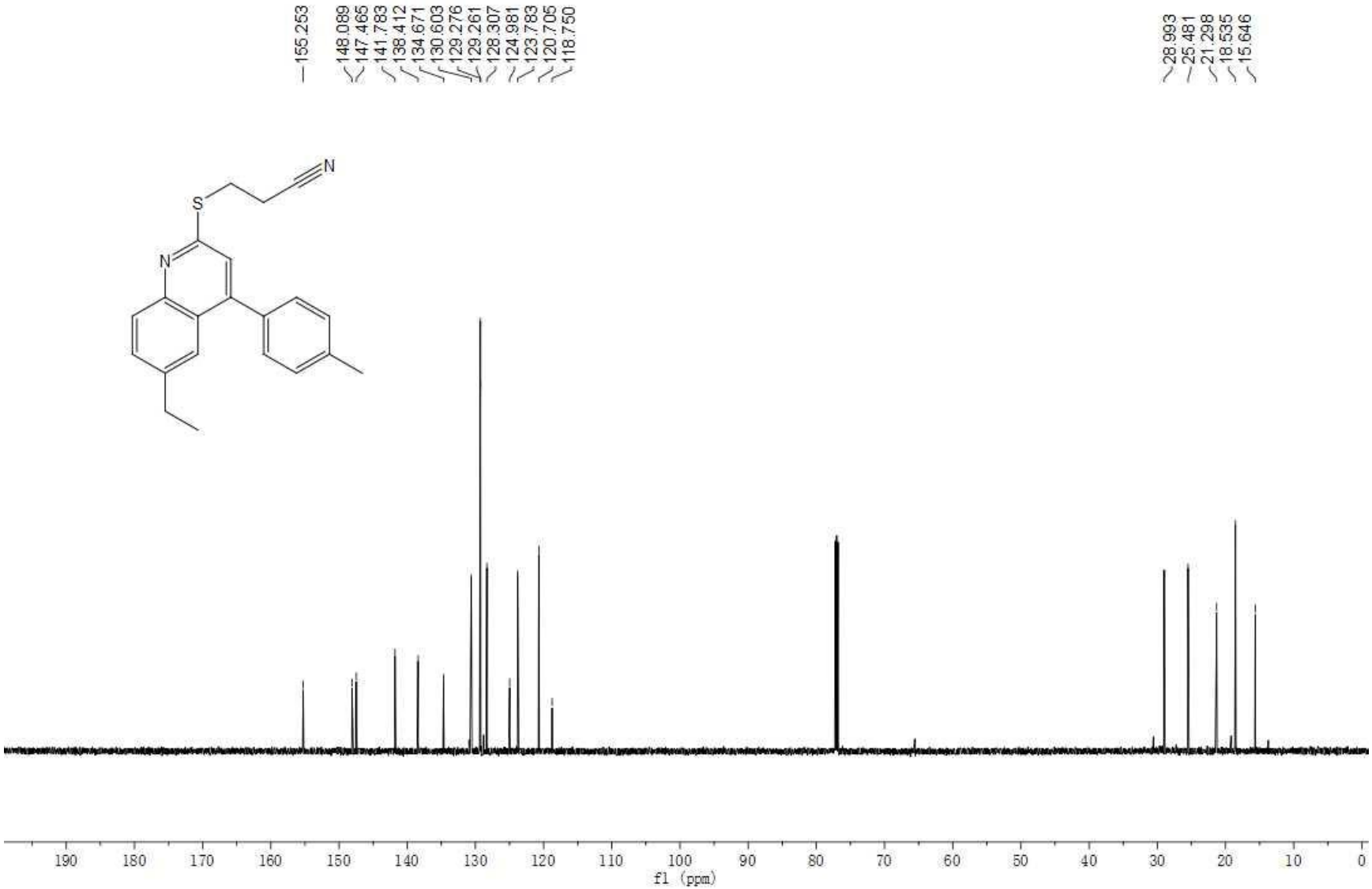
^{1}H and ^{13}C Spectra of compound 3g ($CDCl_3$)



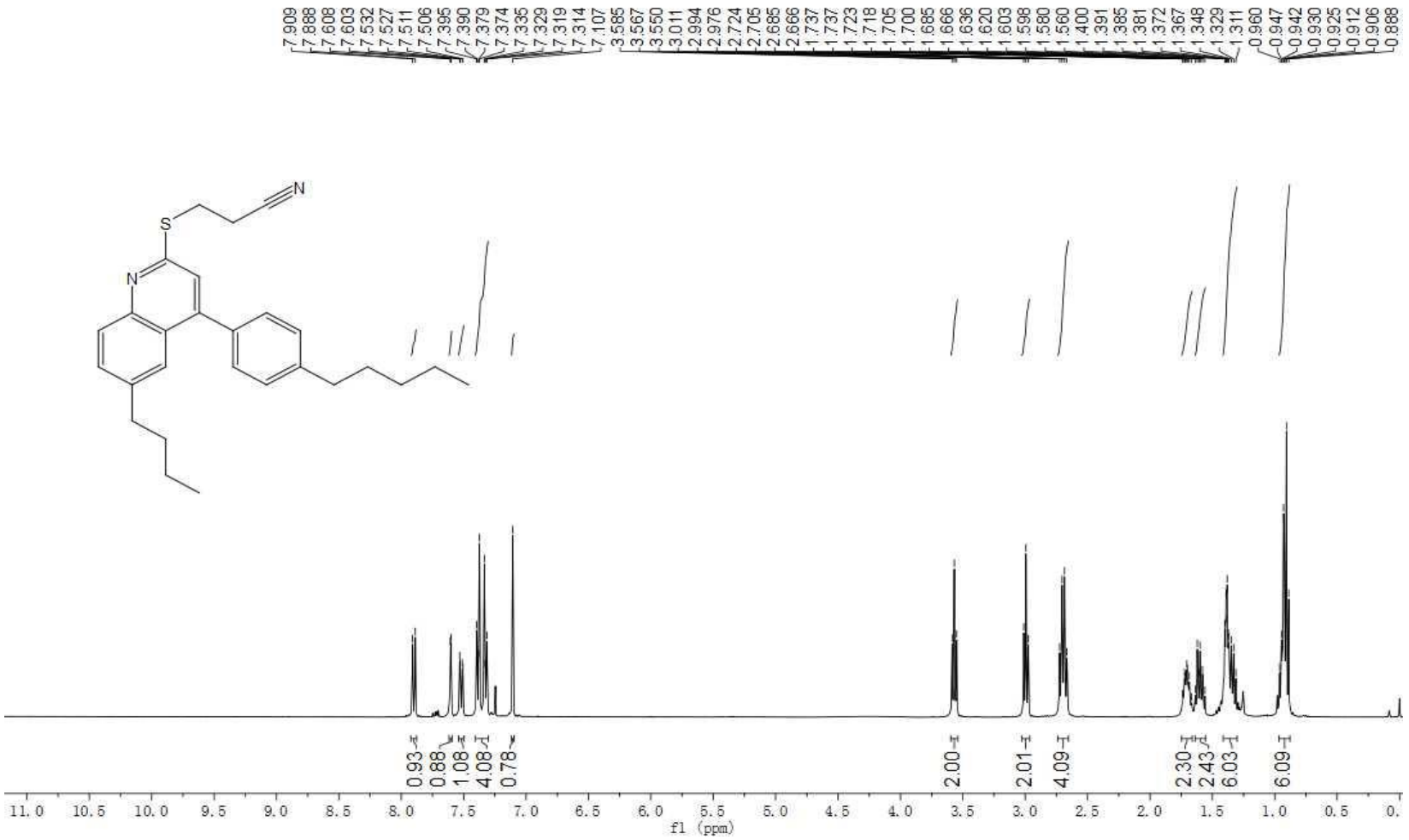

155.208
147.952
147.258
138.404
135.445
134.652
131.748
129.265
129.246
128.146
124.970
124.927
120.709
118.740
25.478
21.639
21.290
18.539
N
S
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

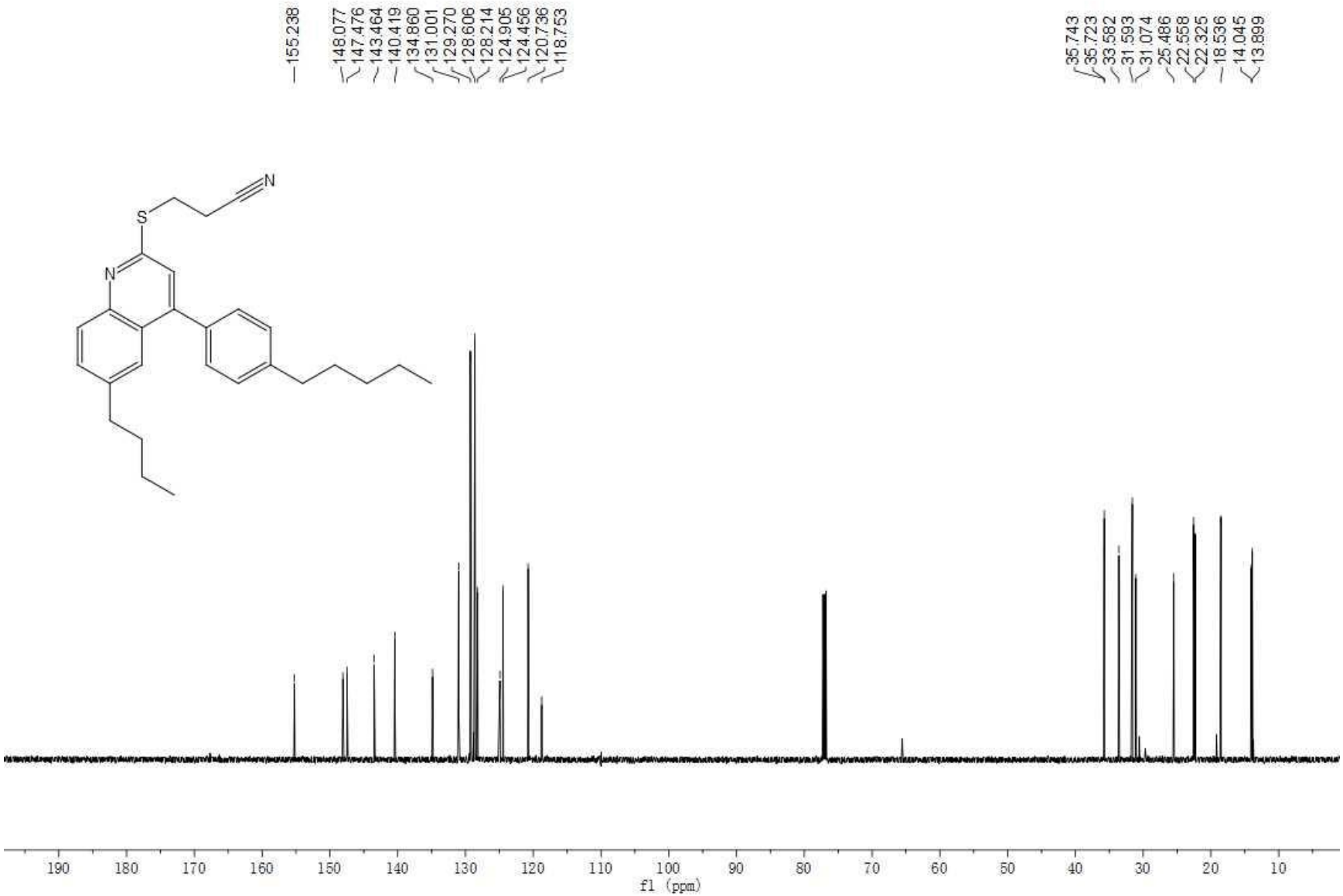
^{1}H and ^{13}C Spectra of compound 3h ($CDCl_3$)



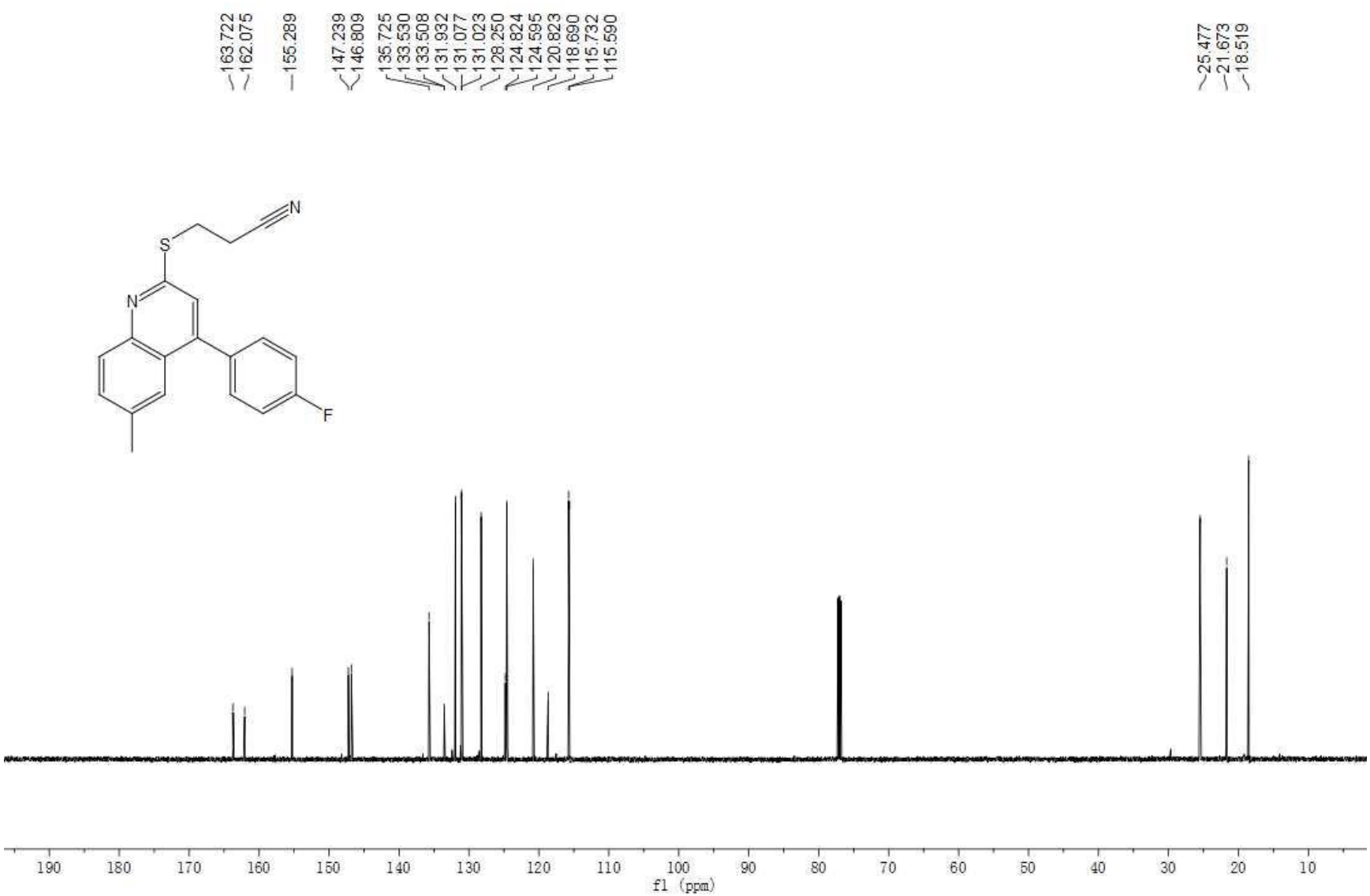

155.253
148.089
147.465
141.783
138.412
134.671
130.603
129.276
129.261
128.307
124.981
123.783
120.705
118.750
28.993
25.481
21.298
18.535
15.646
N
S
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

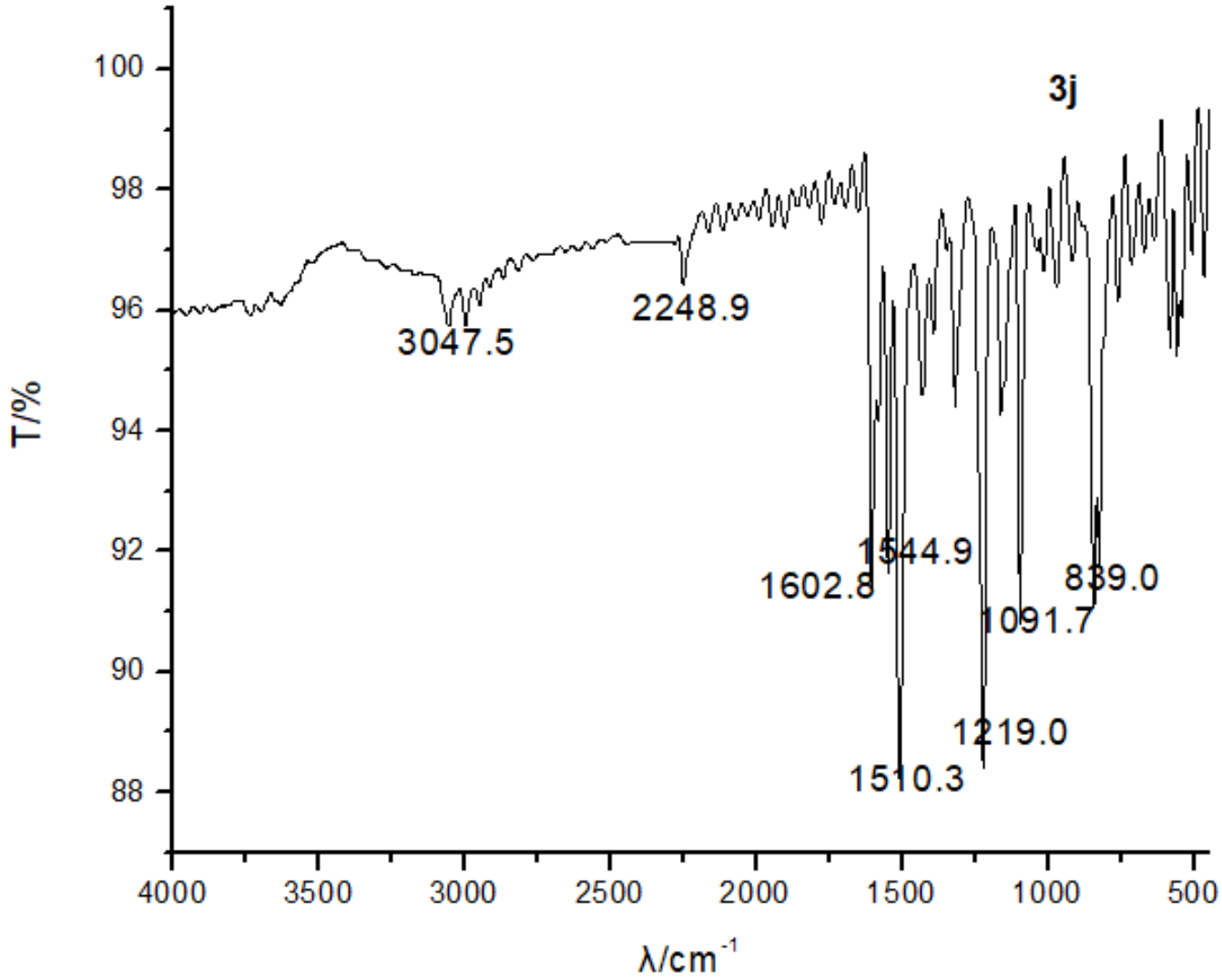
^{1}H and ^{13}C Spectra of compound 3i ($CDCl_3$)



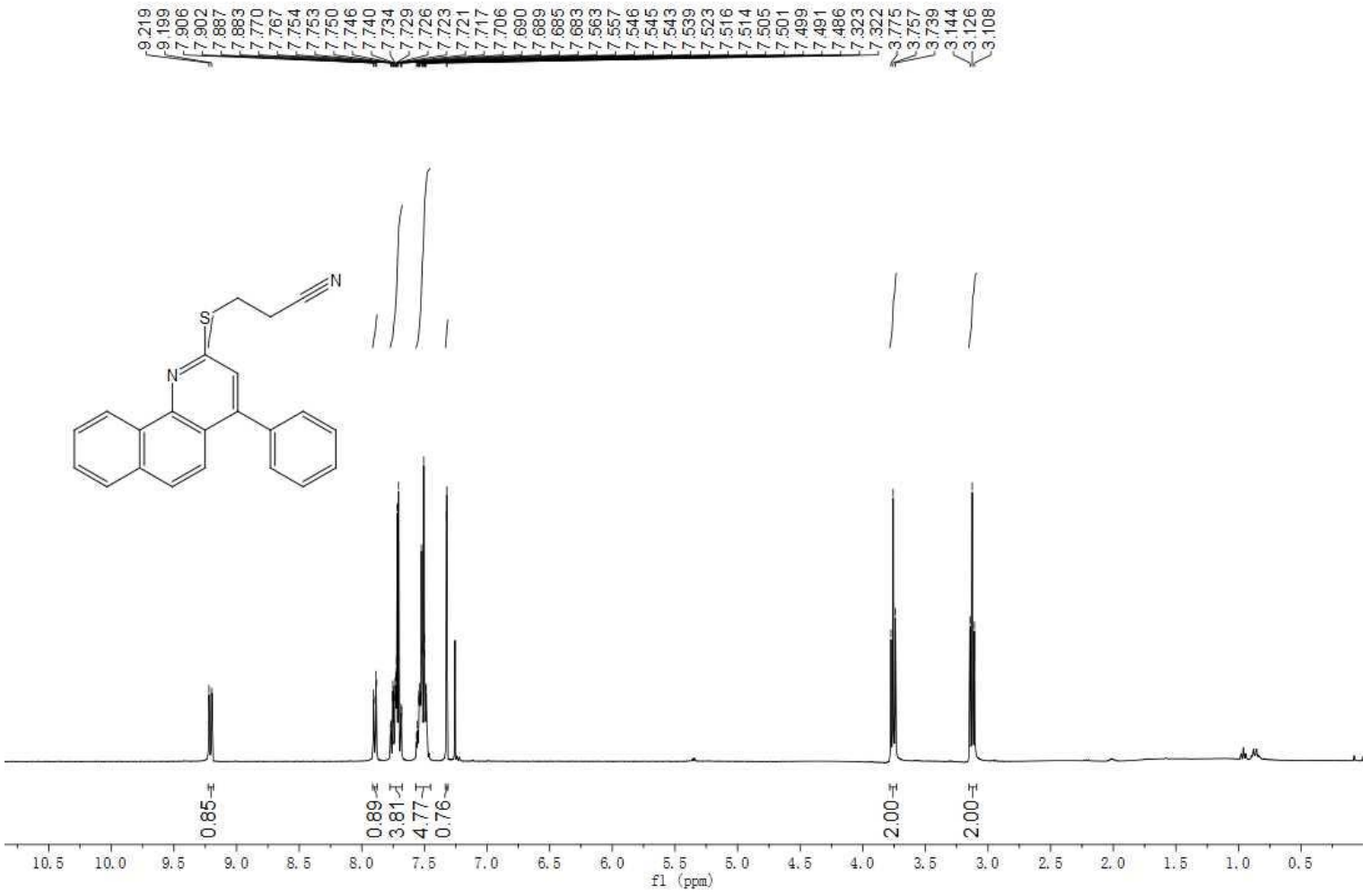

155.238
148.077
147.476
143.464
140.419
134.860
131.001
129.270
128.606
128.214
124.905
124.456
120.736
118.753
35.743
35.723
33.582
31.593
31.074
25.486
22.558
22.325
18.536
14.045
13.899
S
N
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

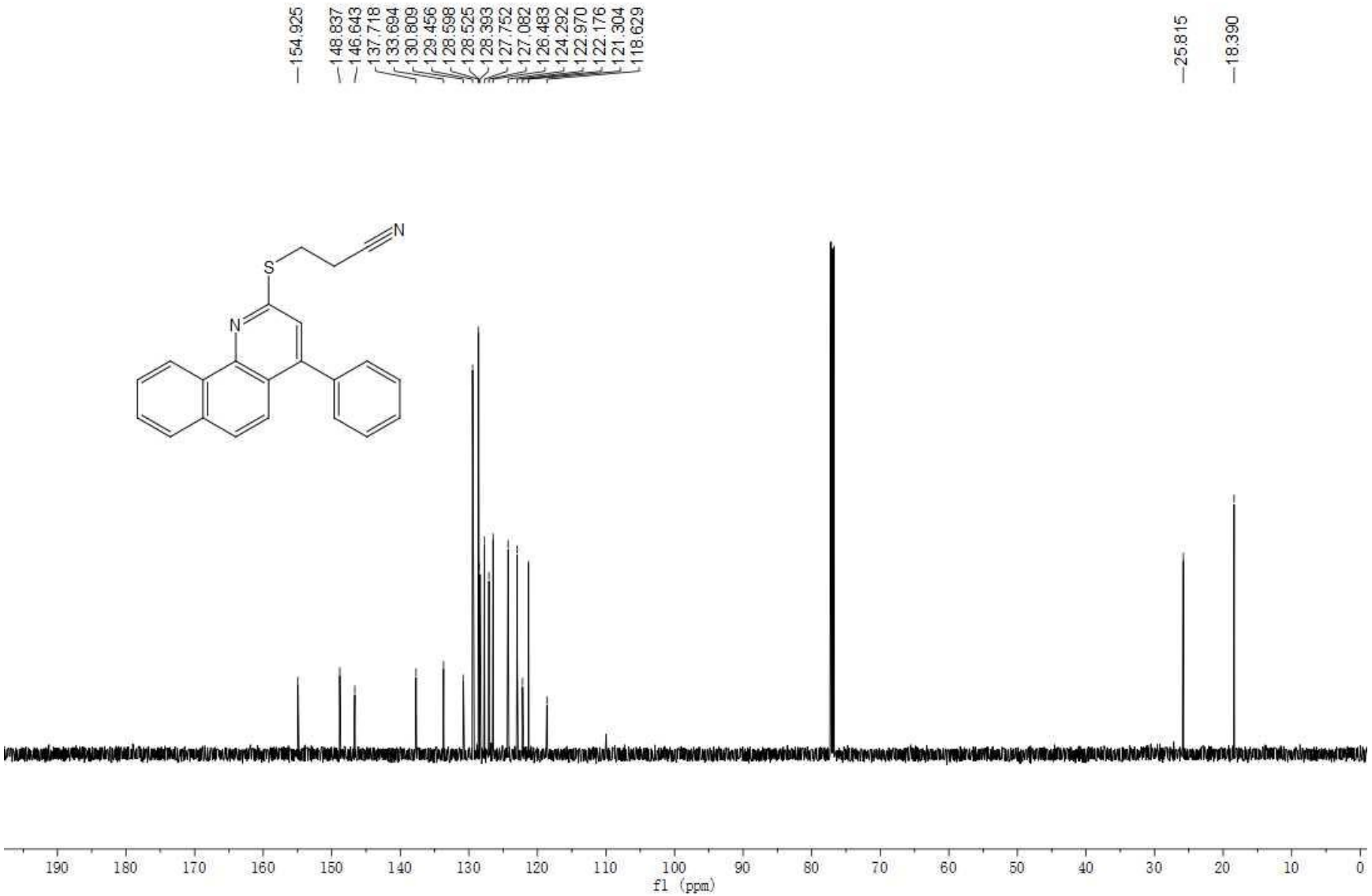
^{1}H and ^{13}C Spectra of compound 3j ($CDCl_3$)


163.722
162.075
155.289
147.239
146.809
135.725
133.530
133.508
131.932
131.077
131.023
128.250
124.824
124.595
120.823
118.690
115.732
115.590
25.477
21.673
18.519
N
S
N
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

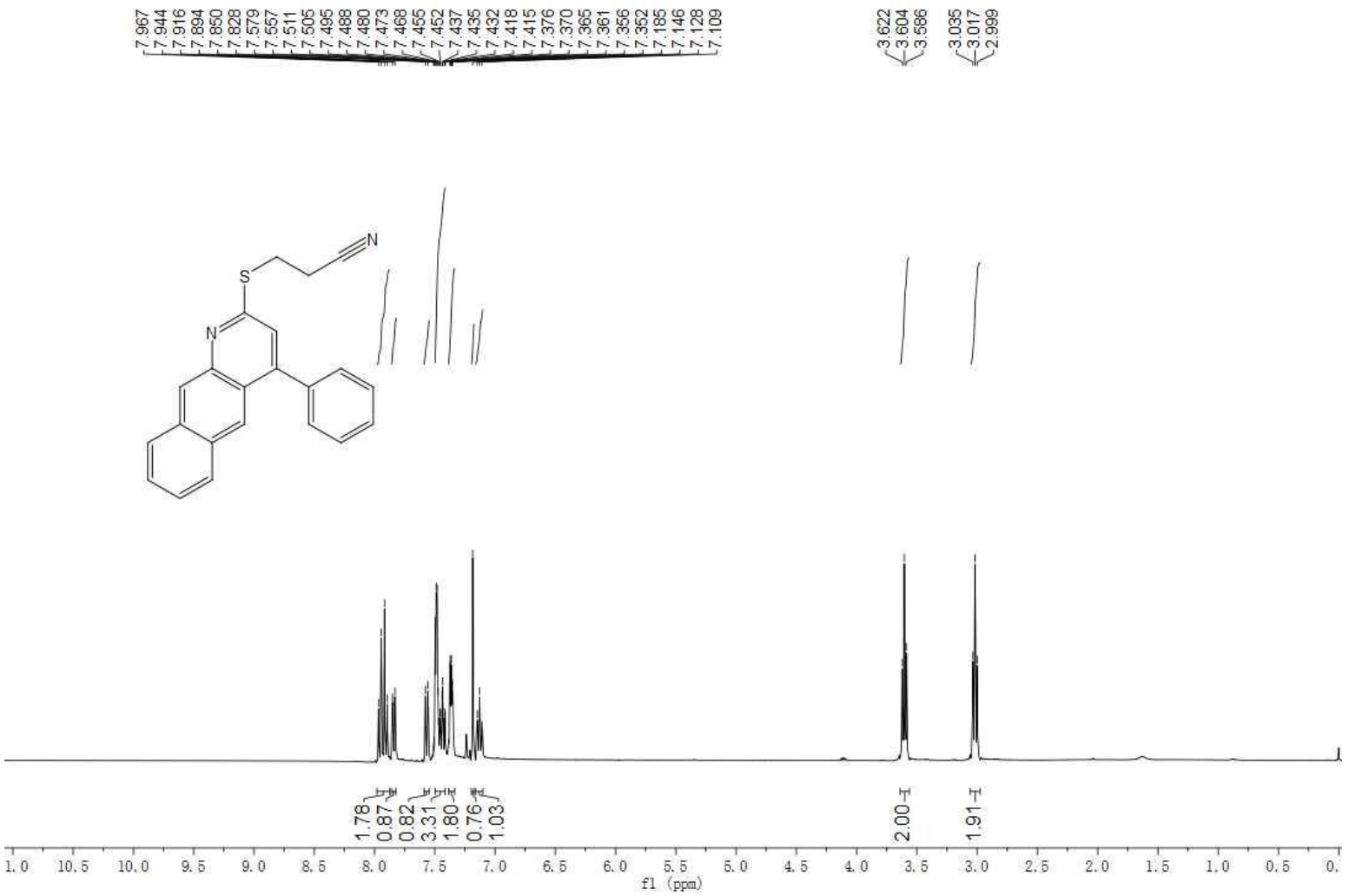

3j
100
98
96
94
92
90
88
T/%
3047.5
2248.9
1602.8
1544.9
1510.3
1219.0
1091.7
839.0
4000
3500
3000
2500
2000
1500
1000
500
λ/cm-1

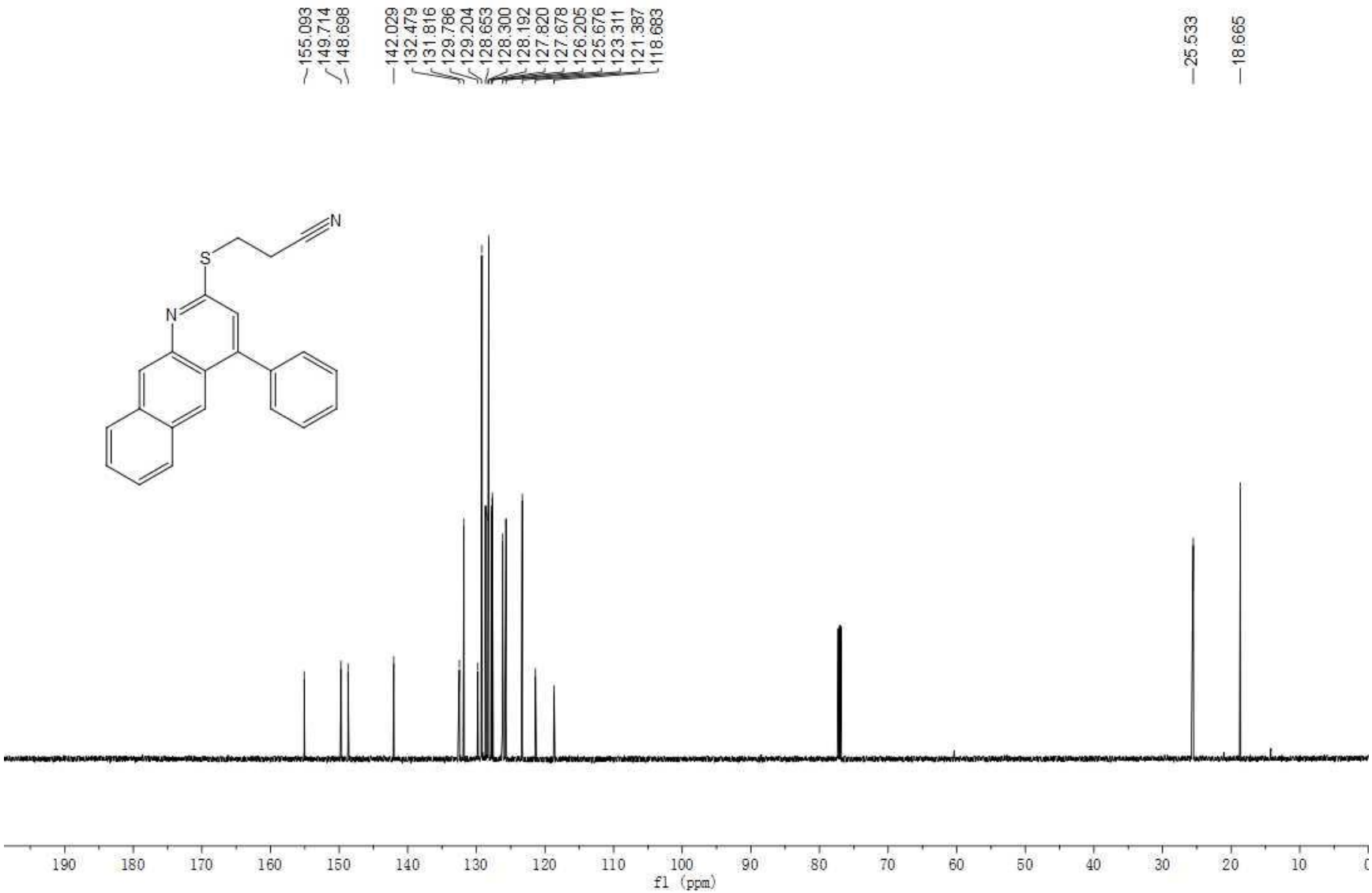
^{1}H and ^{13}C Spectra of compound 3k ($CDCl_3$)



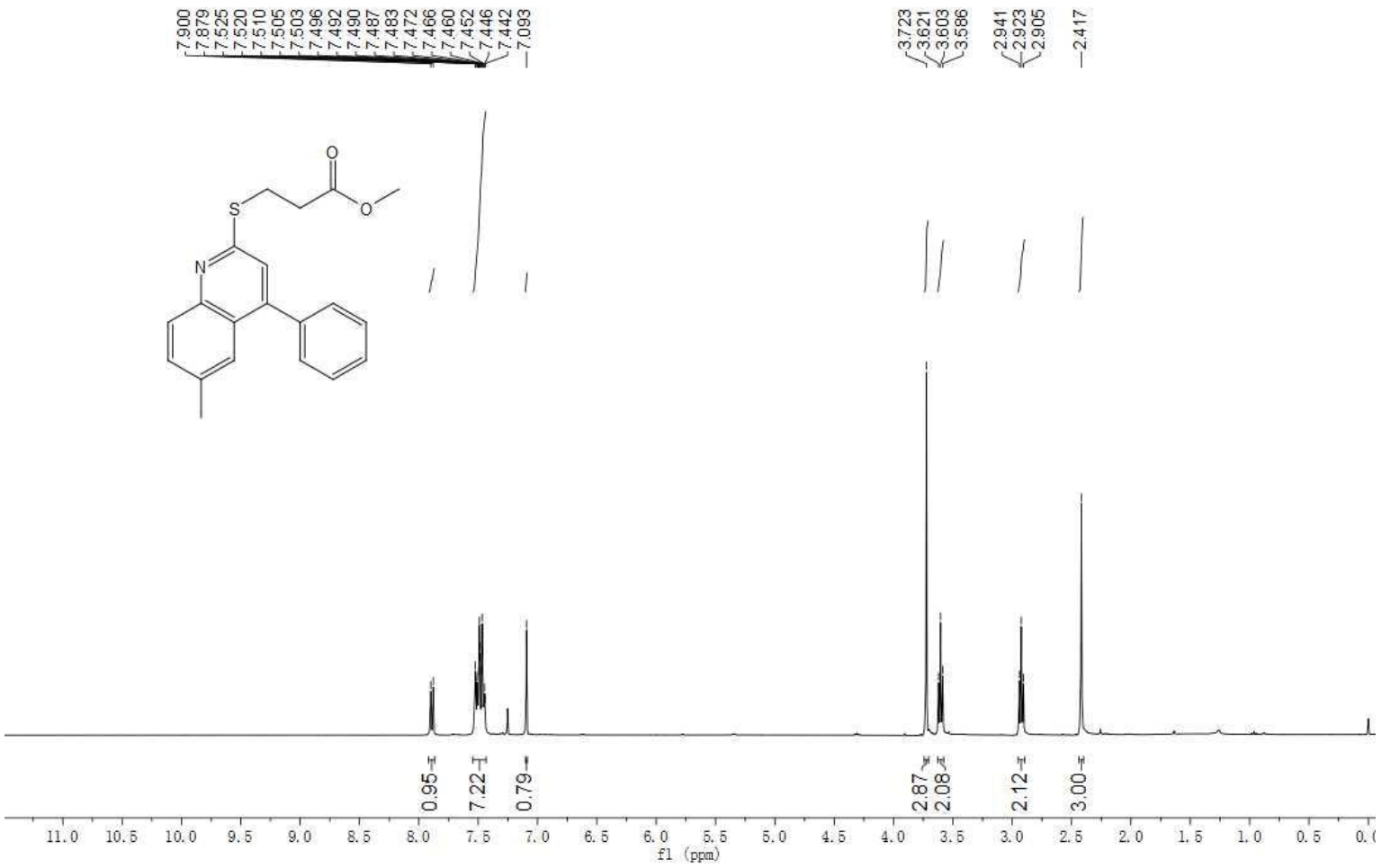

154.925
148.837
146.643
137.718
133.694
130.809
129.456
128.598
128.525
128.393
127.752
127.082
126.483
124.292
122.970
122.176
121.304
118.629
25.815
18.390
N
S
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

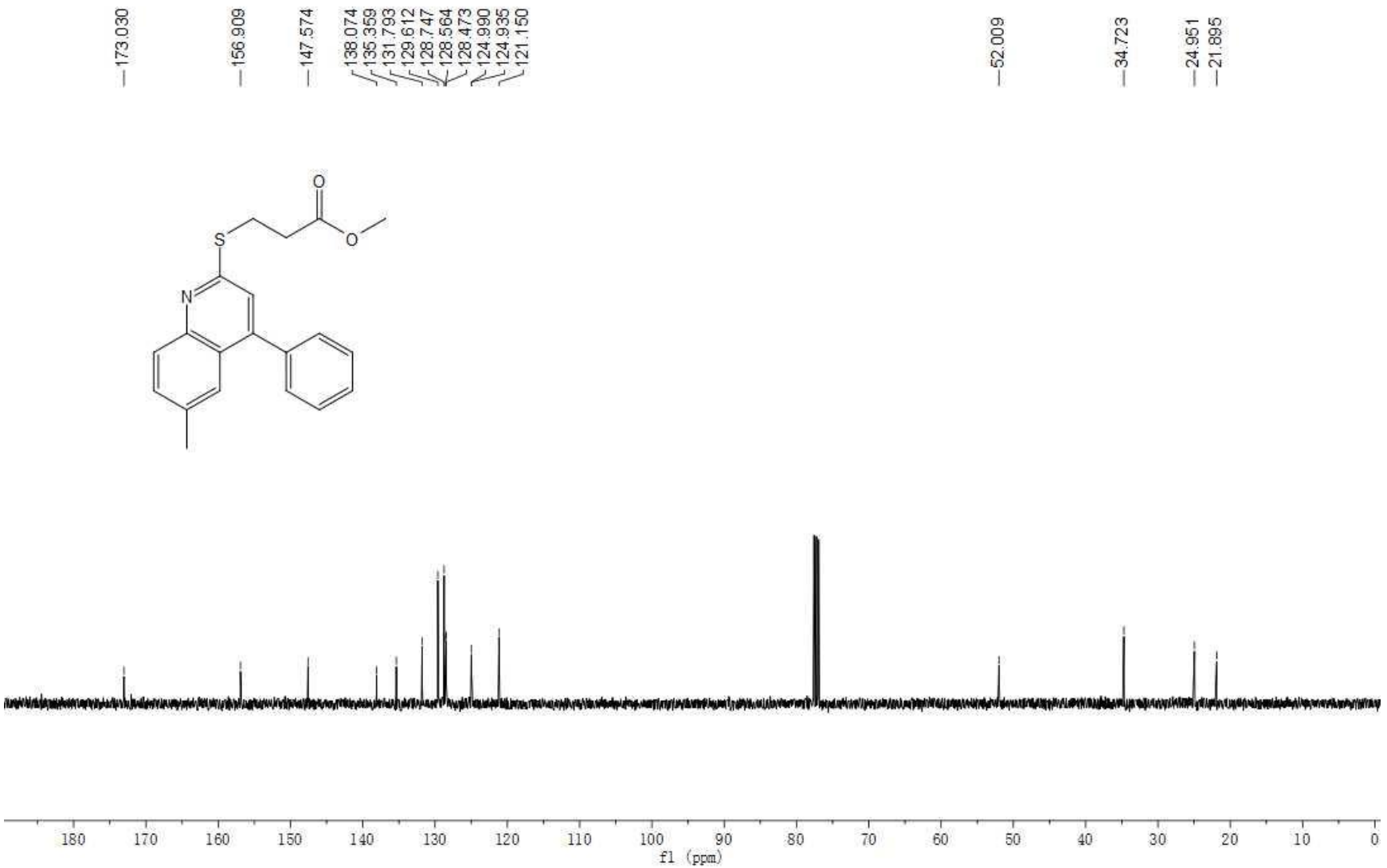
^{1}H and ^{13}C Spectra of compound 3l ($CDCl_3$)



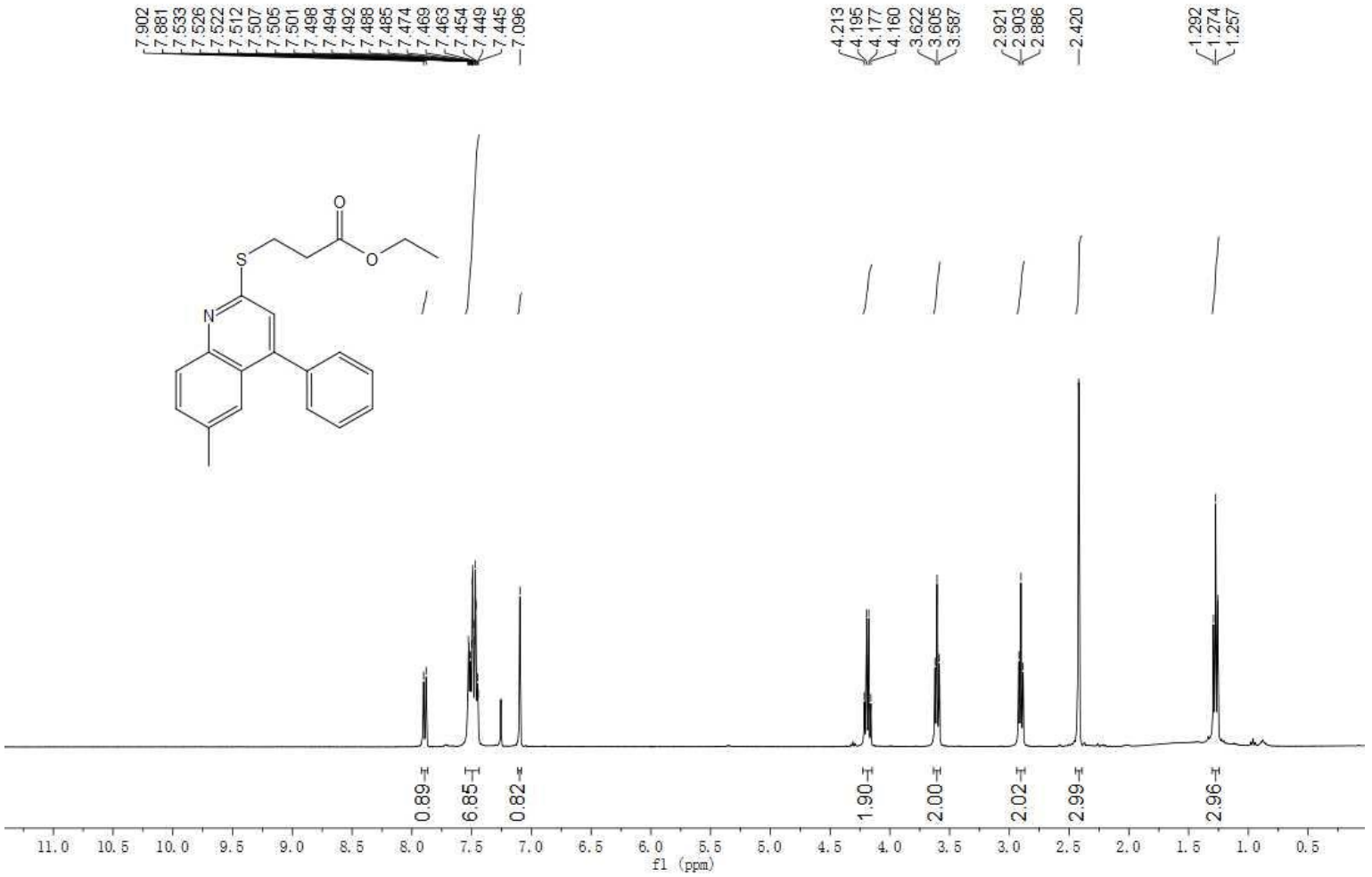

155.093
149.714
148.698
142.029
132.479
131.816
129.786
129.204
128.653
128.300
128.192
127.820
127.678
126.205
125.676
123.311
121.387
118.683
25.533
18.665
N
S
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

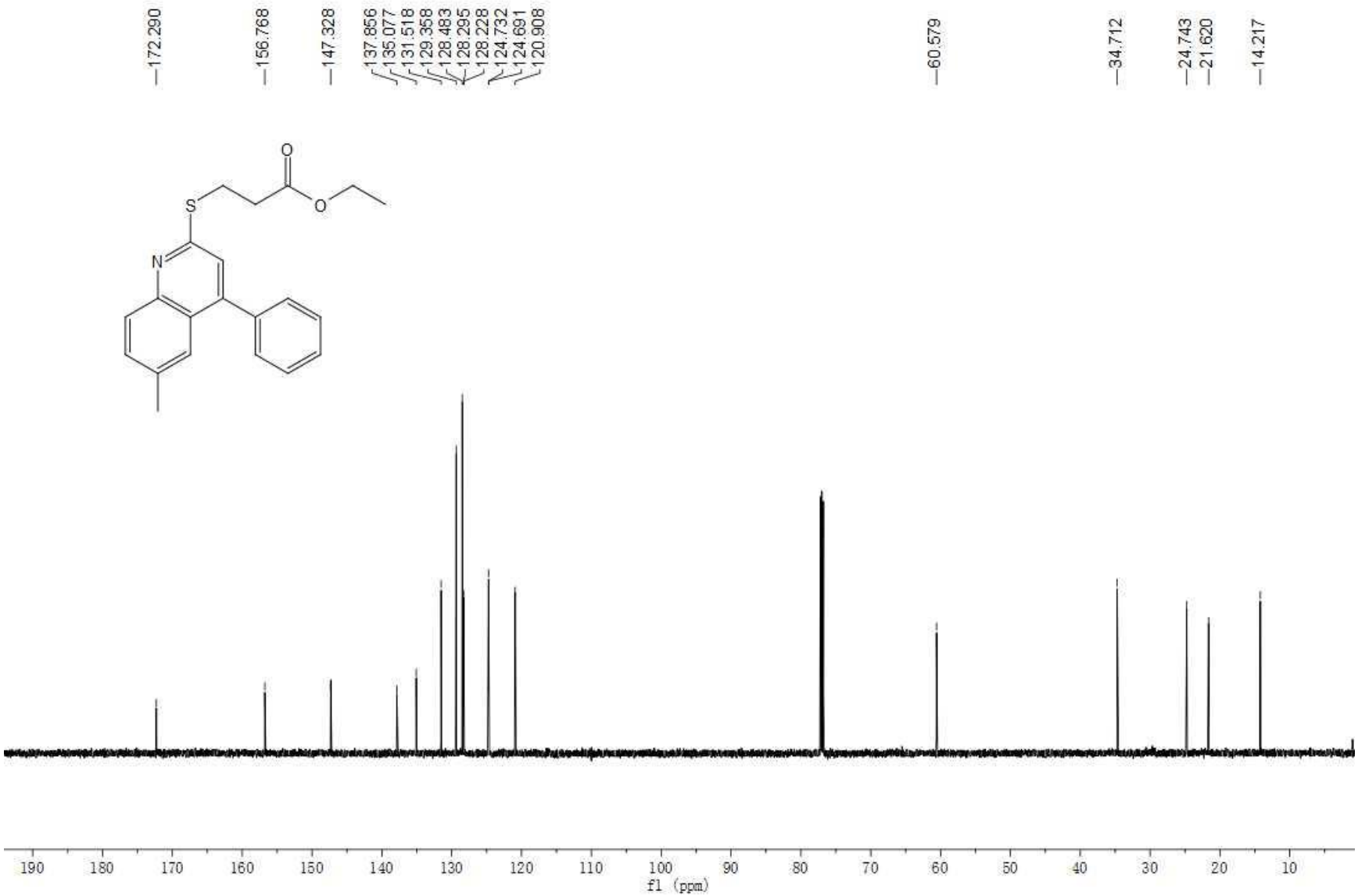
^{1}H and ^{13}C Spectra of compound 3m ($CDCl_3$)



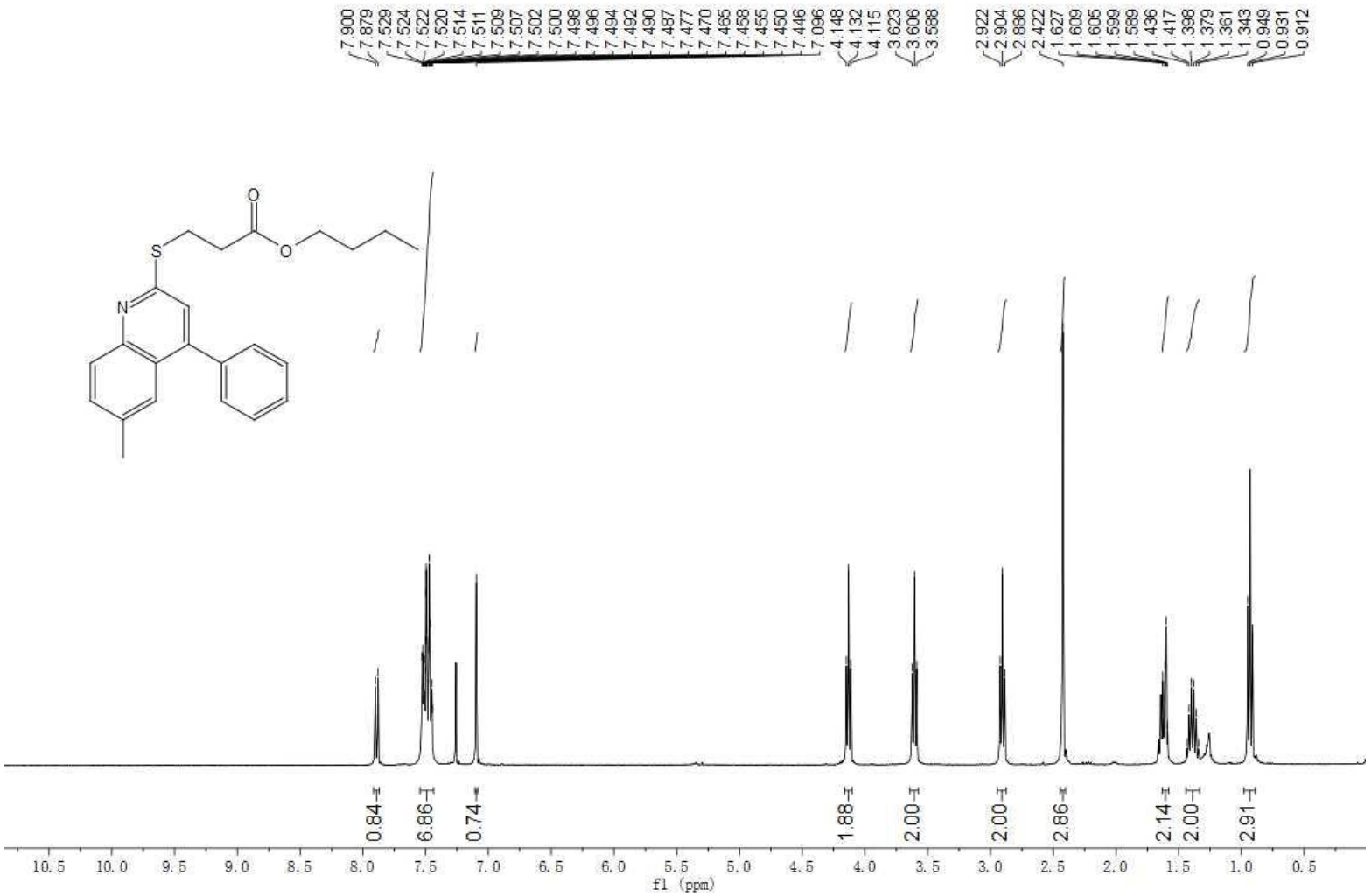

173.030
156.909
147.574
138.074
135.359
131.793
129.612
128.747
128.564
128.473
124.990
124.935
121.150
52.009
34.723
24.951
21.895
O
S
O
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

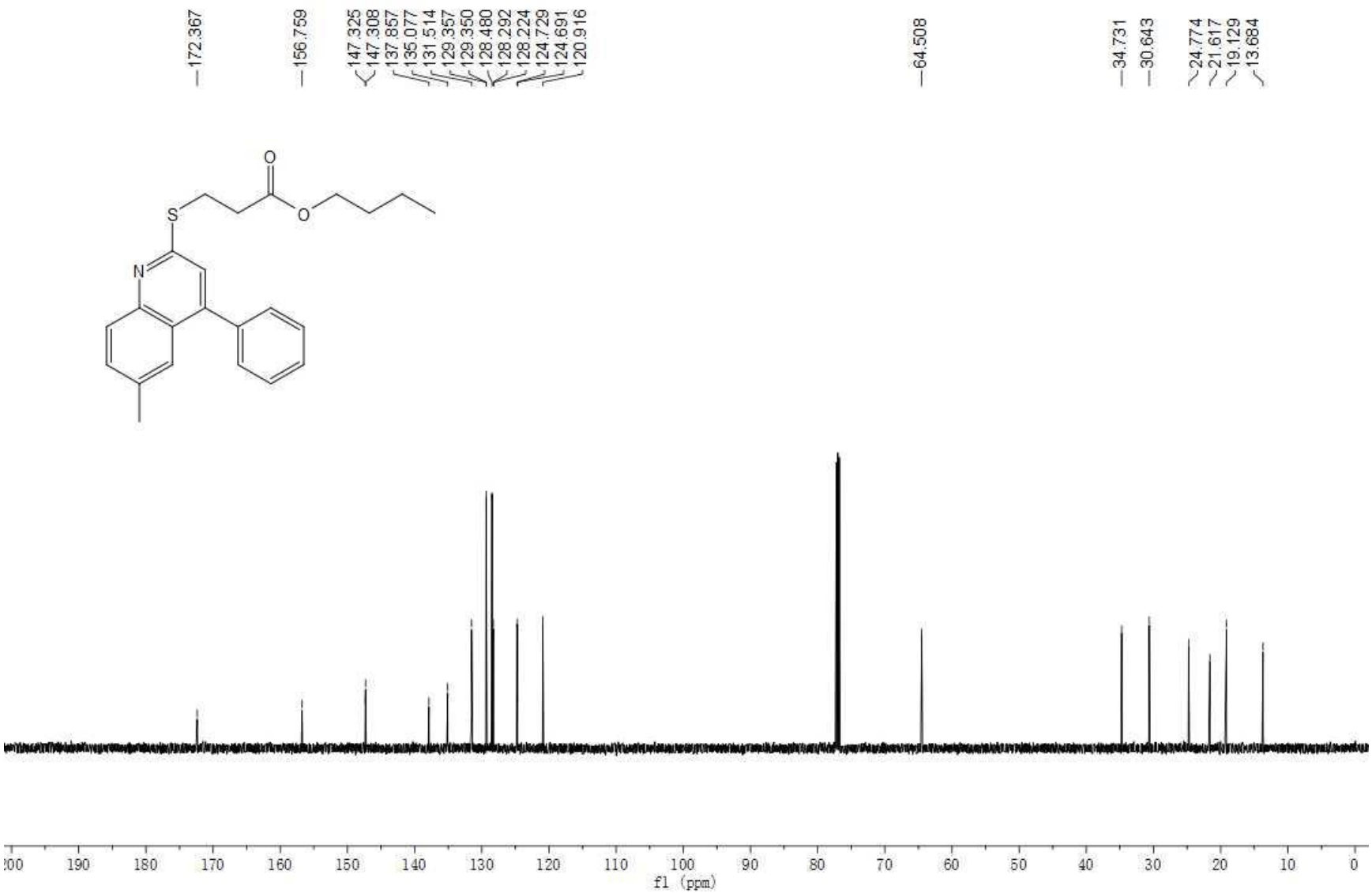
^{1}H and ^{13}C Spectra of compound 3n ($CDCl_3$)



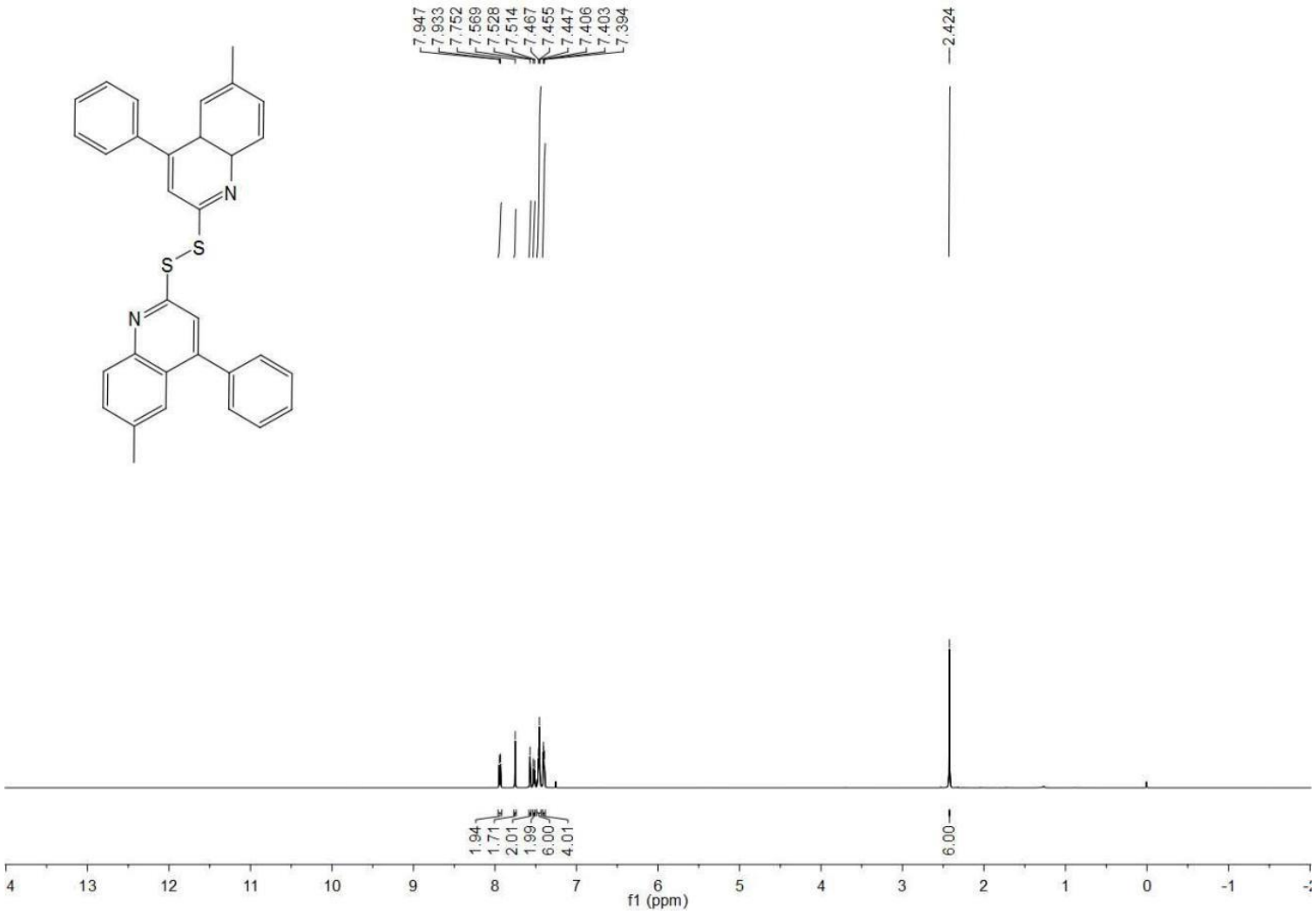

172.290
156.768
147.328
137.856
135.077
131.518
129.358
128.483
128.295
128.228
124.732
124.691
120.908
60.579
34.712
24.743
21.620
14.217
O
S
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

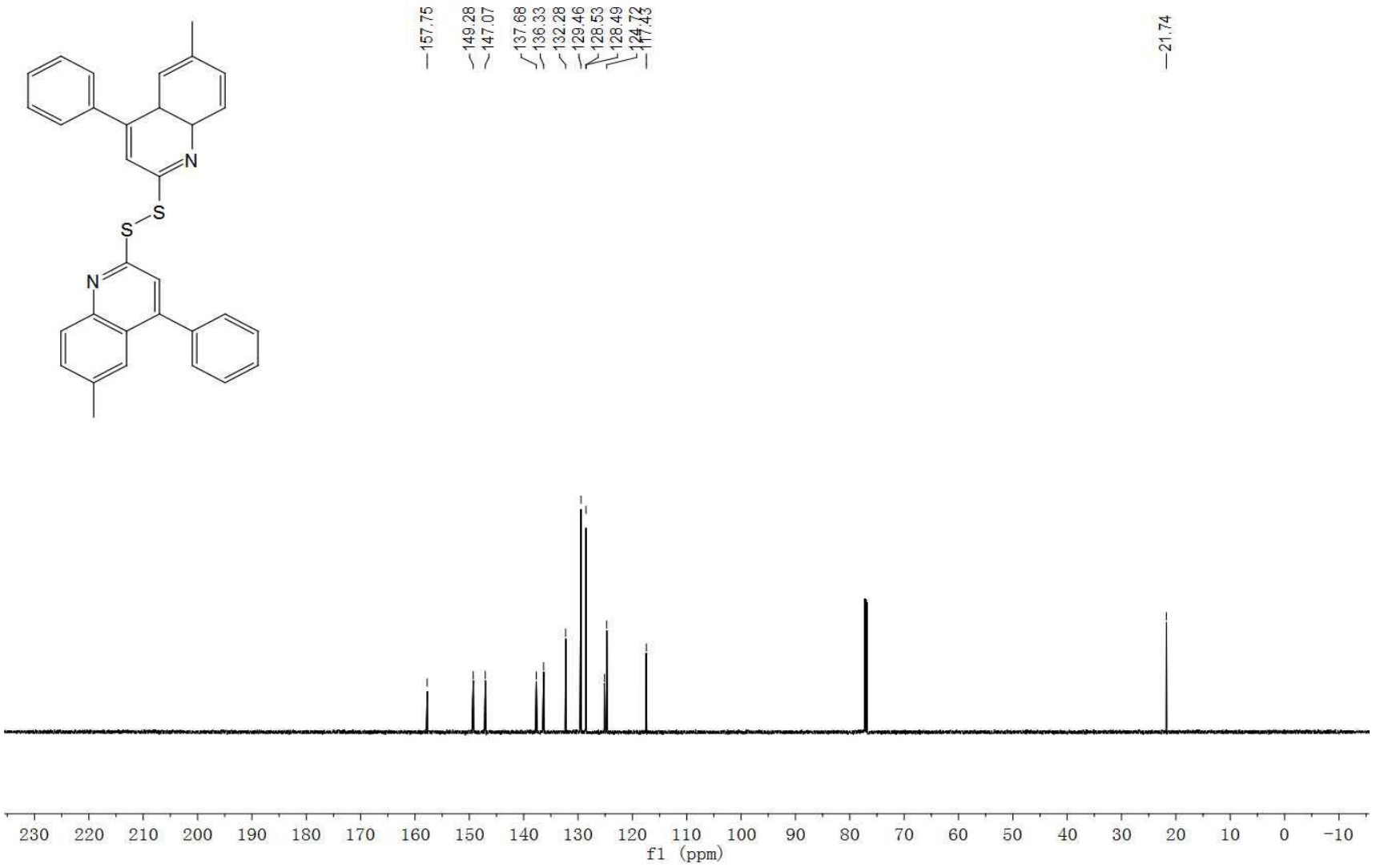
^{1}H and ^{13}C Spectra of compound 3o ($CDCl_3$)

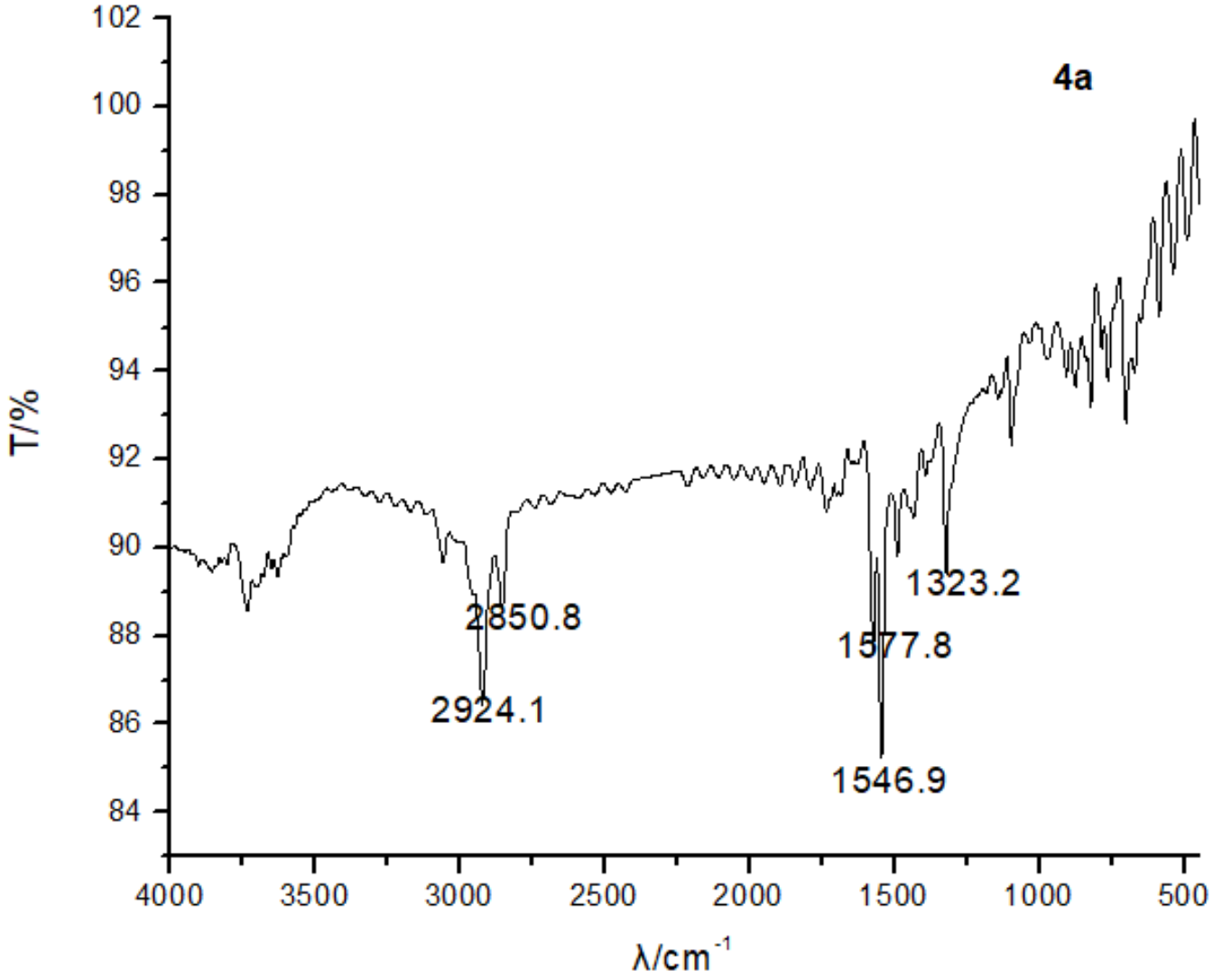



172.367
156.759
147.325
147.308
137.857
135.077
131.514
129.357
129.350
128.480
128.292
128.224
124.729
124.691
120.916
64.508
34.731
30.643
24.774
21.617
19.129
13.684
O
O
S
N
f1 (ppm)

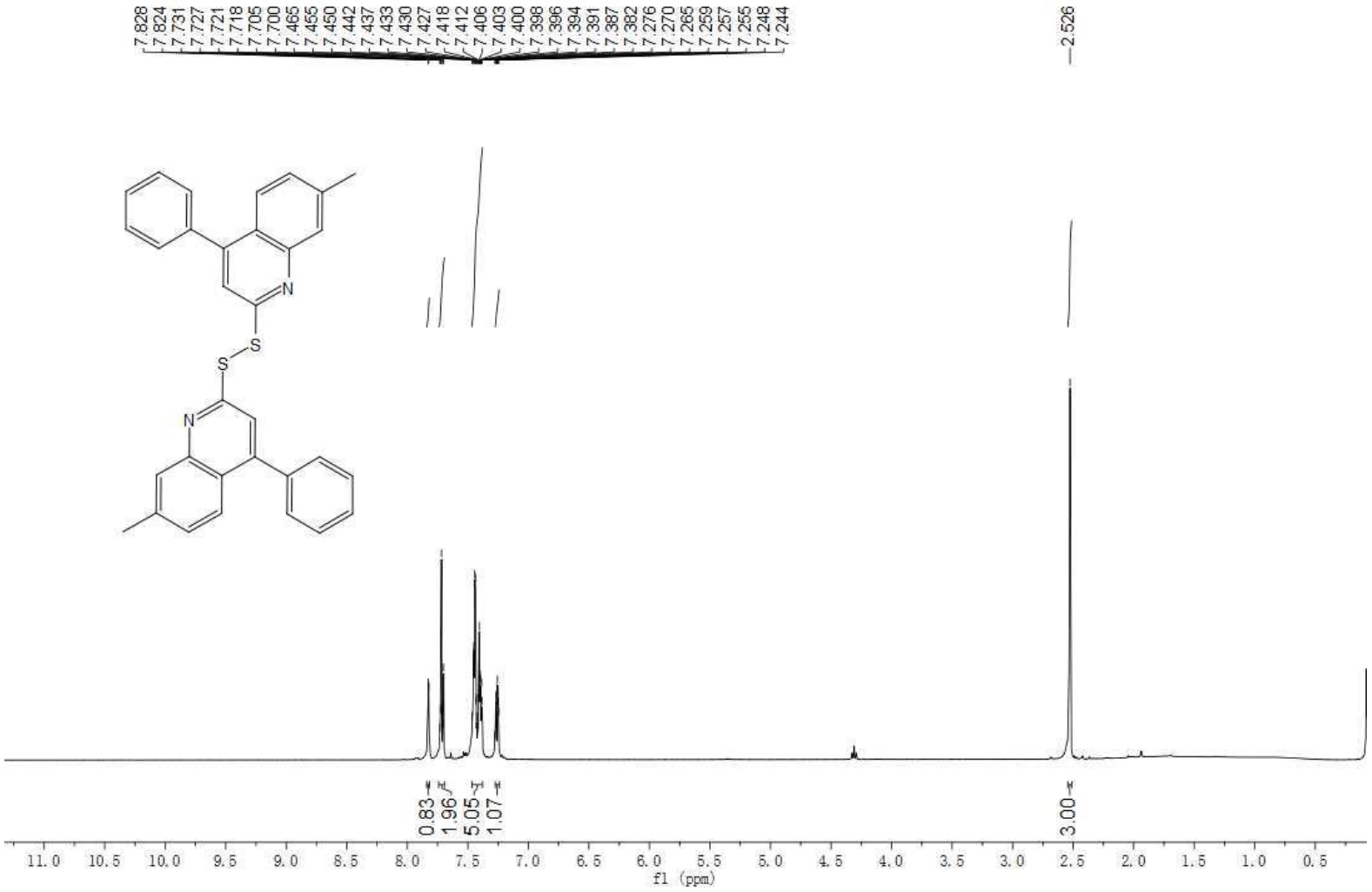
^{1}H and ^{13}C Spectra of compound 4a ($CDCl_3$)

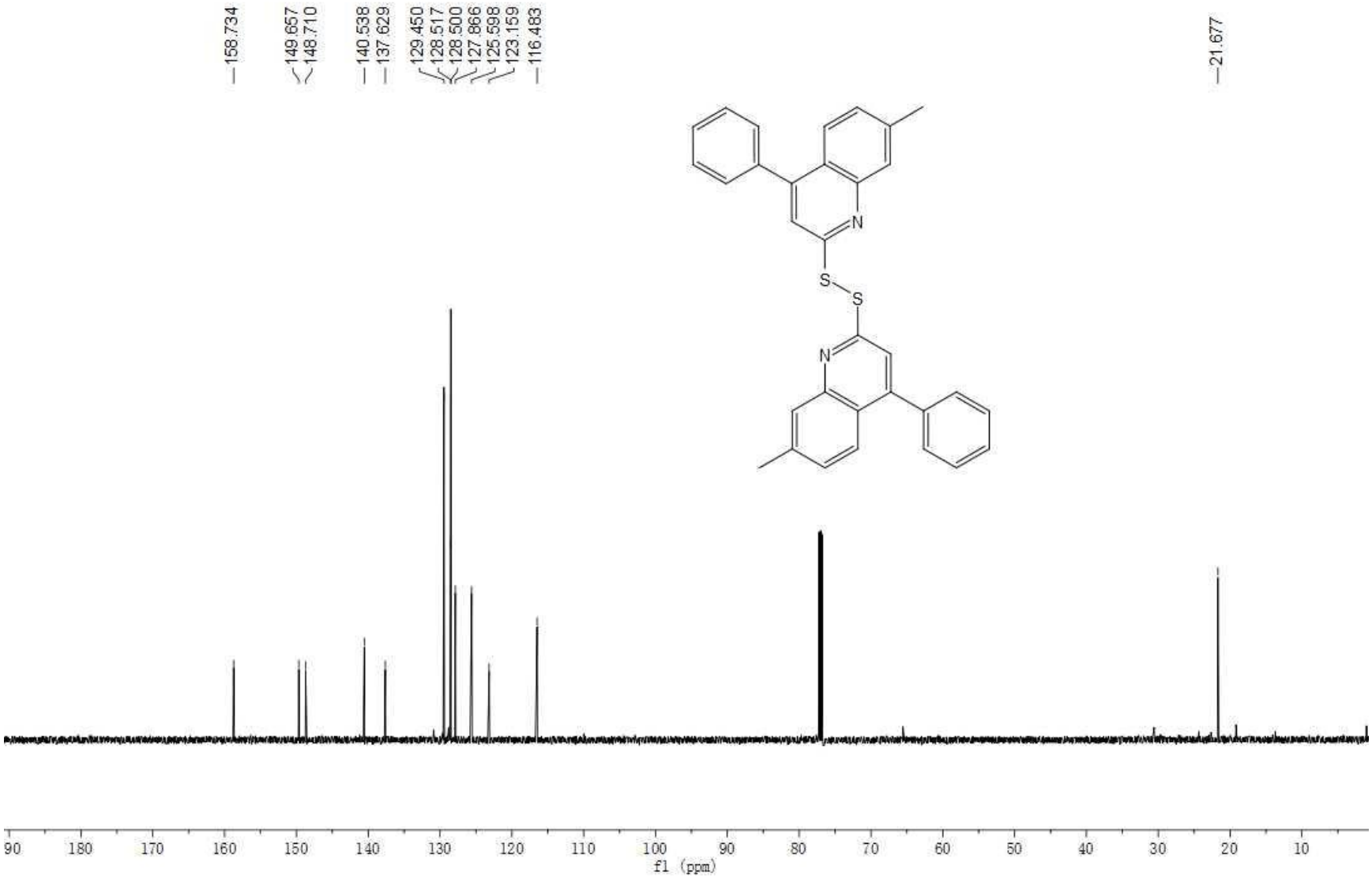



157.75
149.28
147.07
137.68
136.33
132.28
129.46
128.53
128.49
124.72
117.43
21.74
N
S
S
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

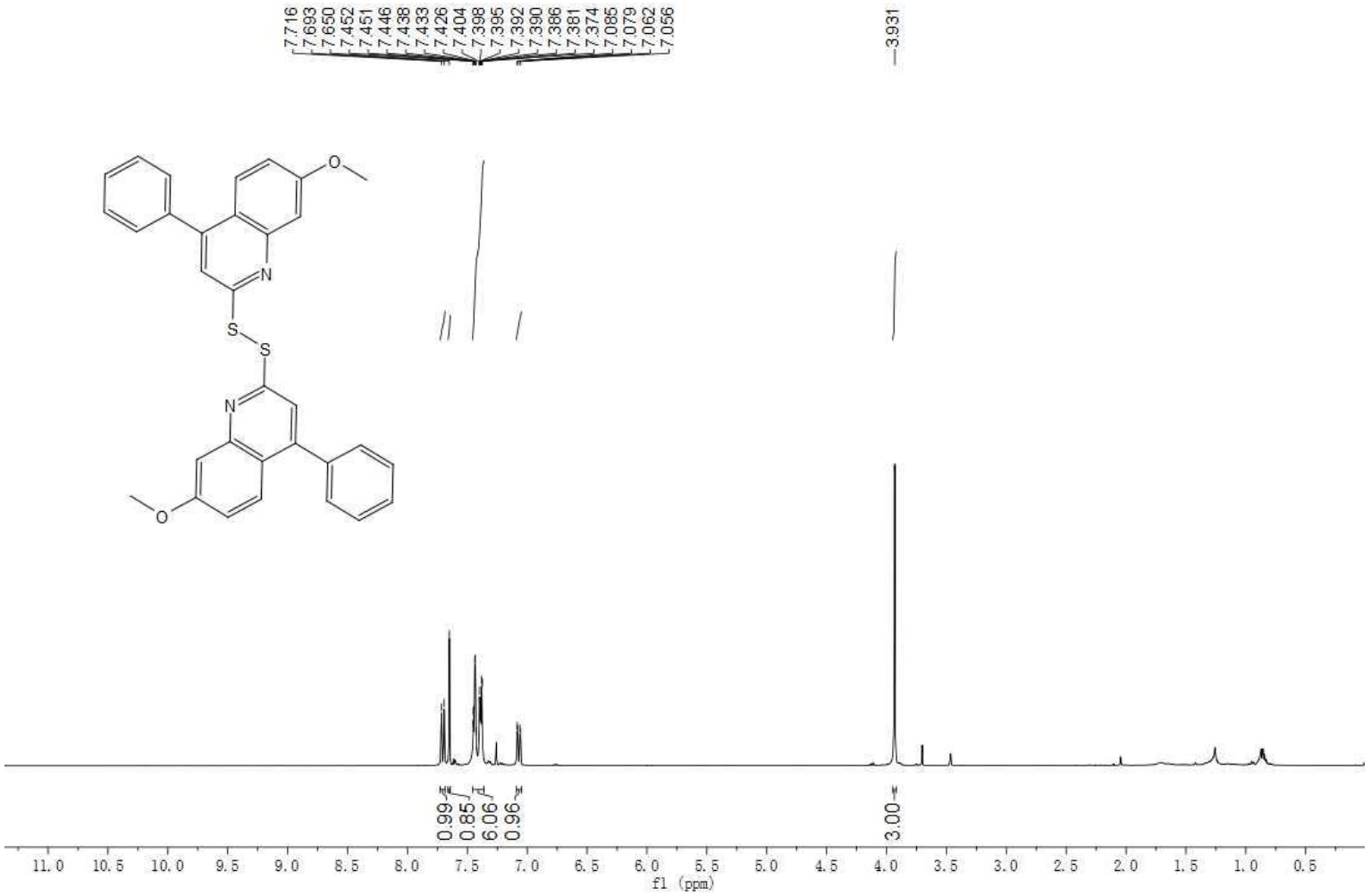

4a
T/%
102
100
98
96
94
92
90
88
86
84
2850.8
2924.1
1577.8
1323.2
1546.9
4000
3500
3000
2500
2000
1500
1000
500
λ/cm-1

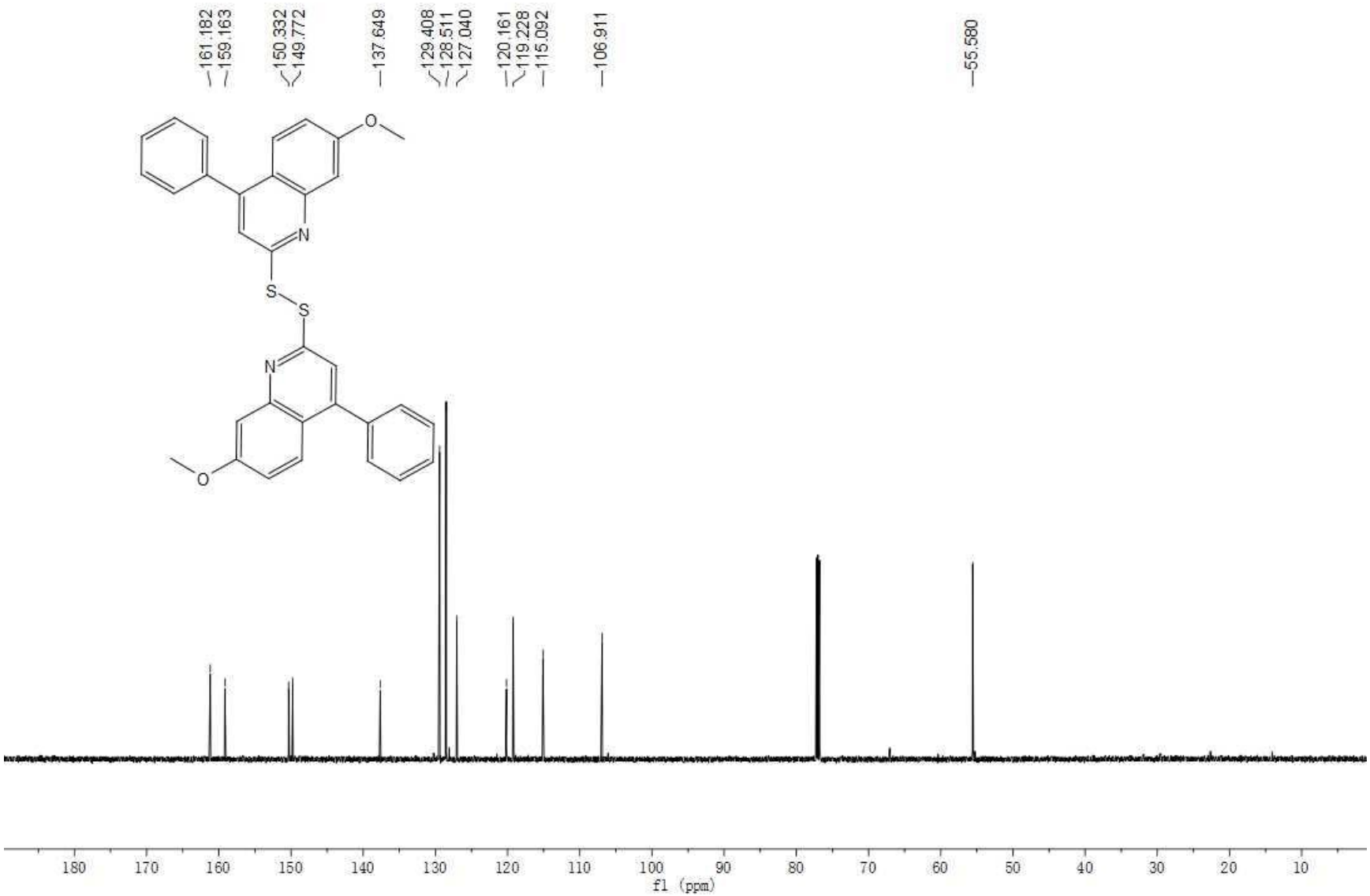
^{1}H and ^{13}C Spectra of compound 4b ($CDCl_3$)



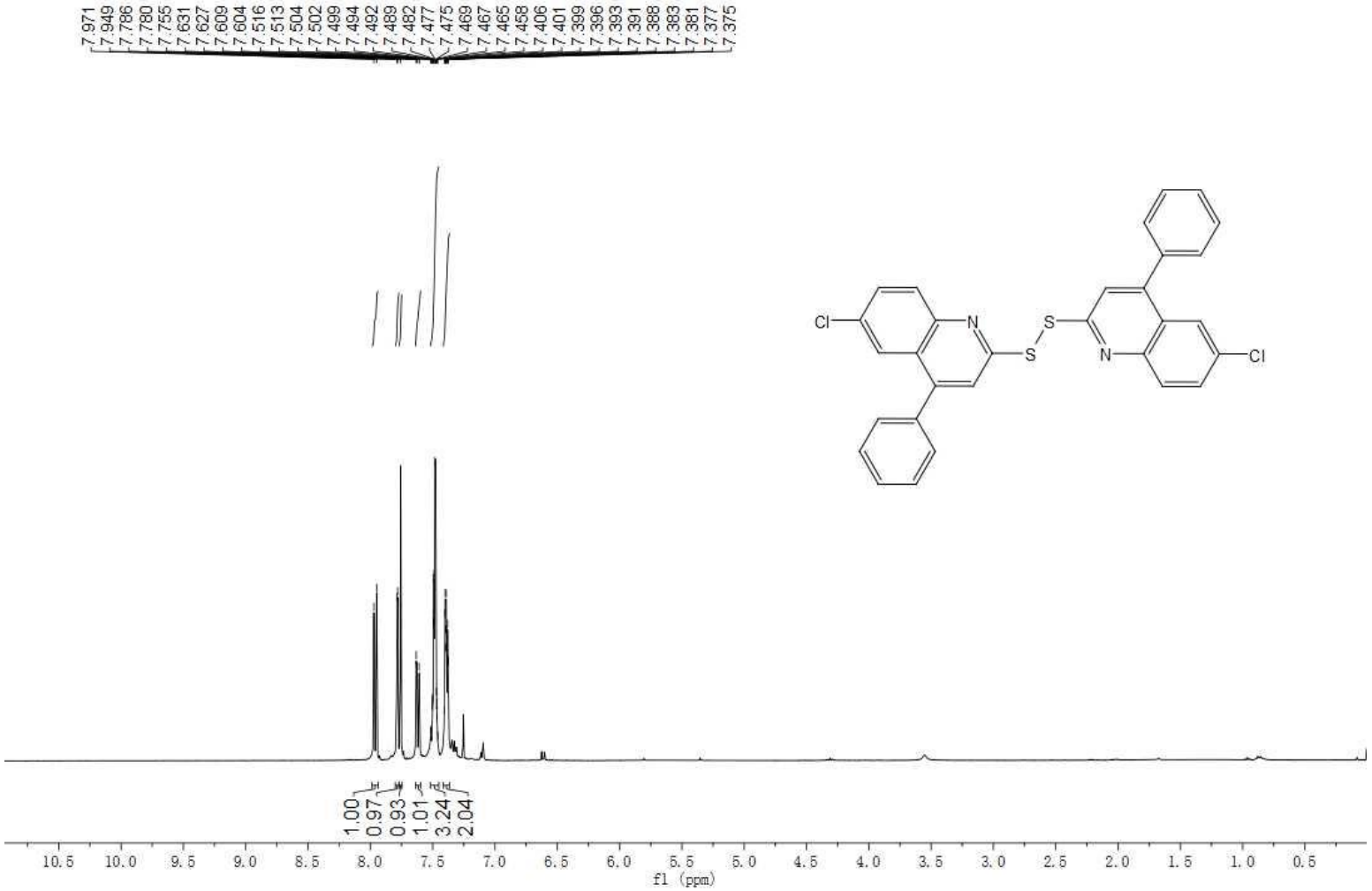

158.734
149.657
148.710
140.538
137.629
129.450
128.517
128.500
127.866
125.598
123.159
116.483
21.677
N
S
S
N
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

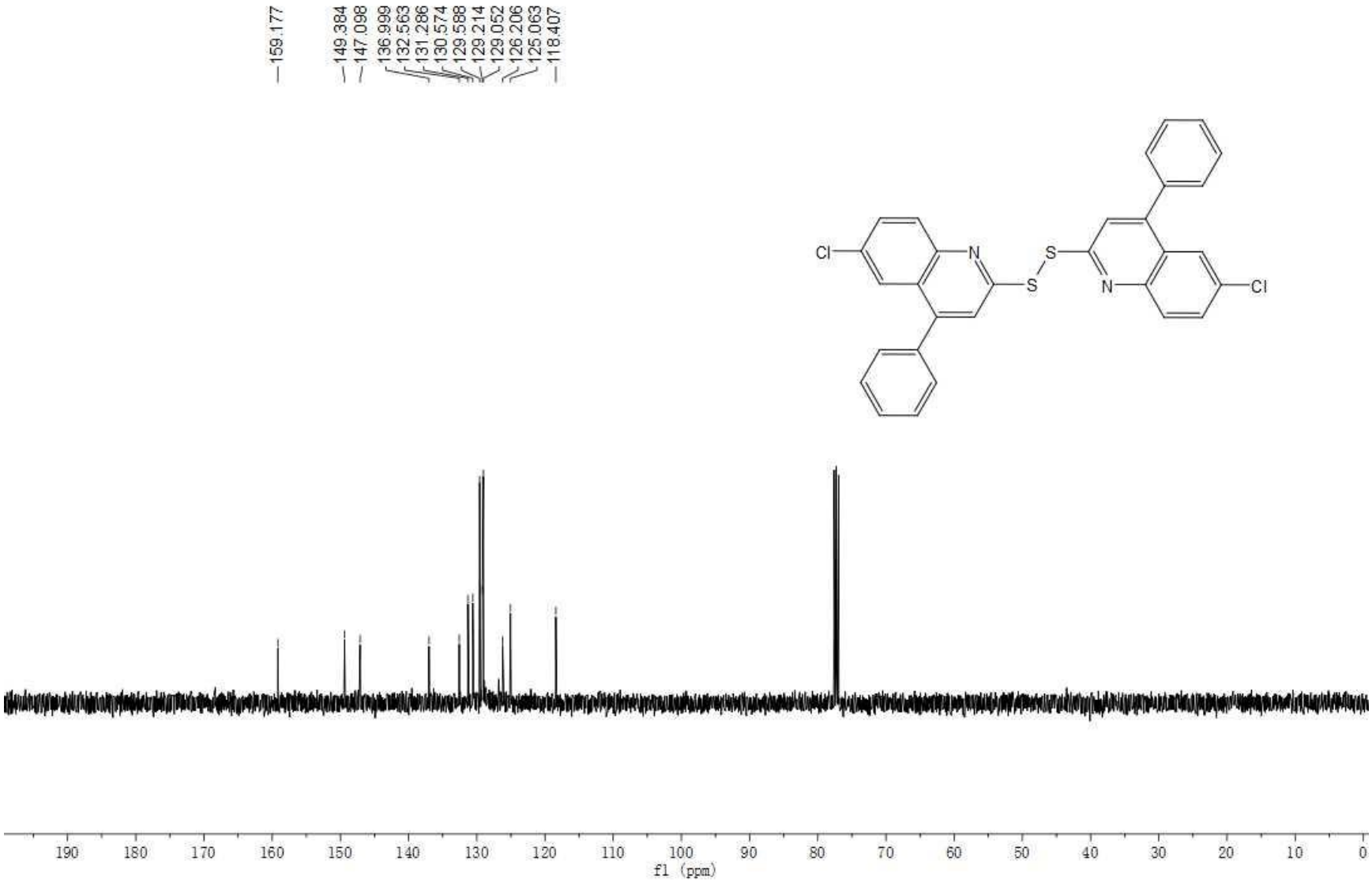
^{1}H and ^{13}C Spectra of compound 4c ($CDCl_3$)



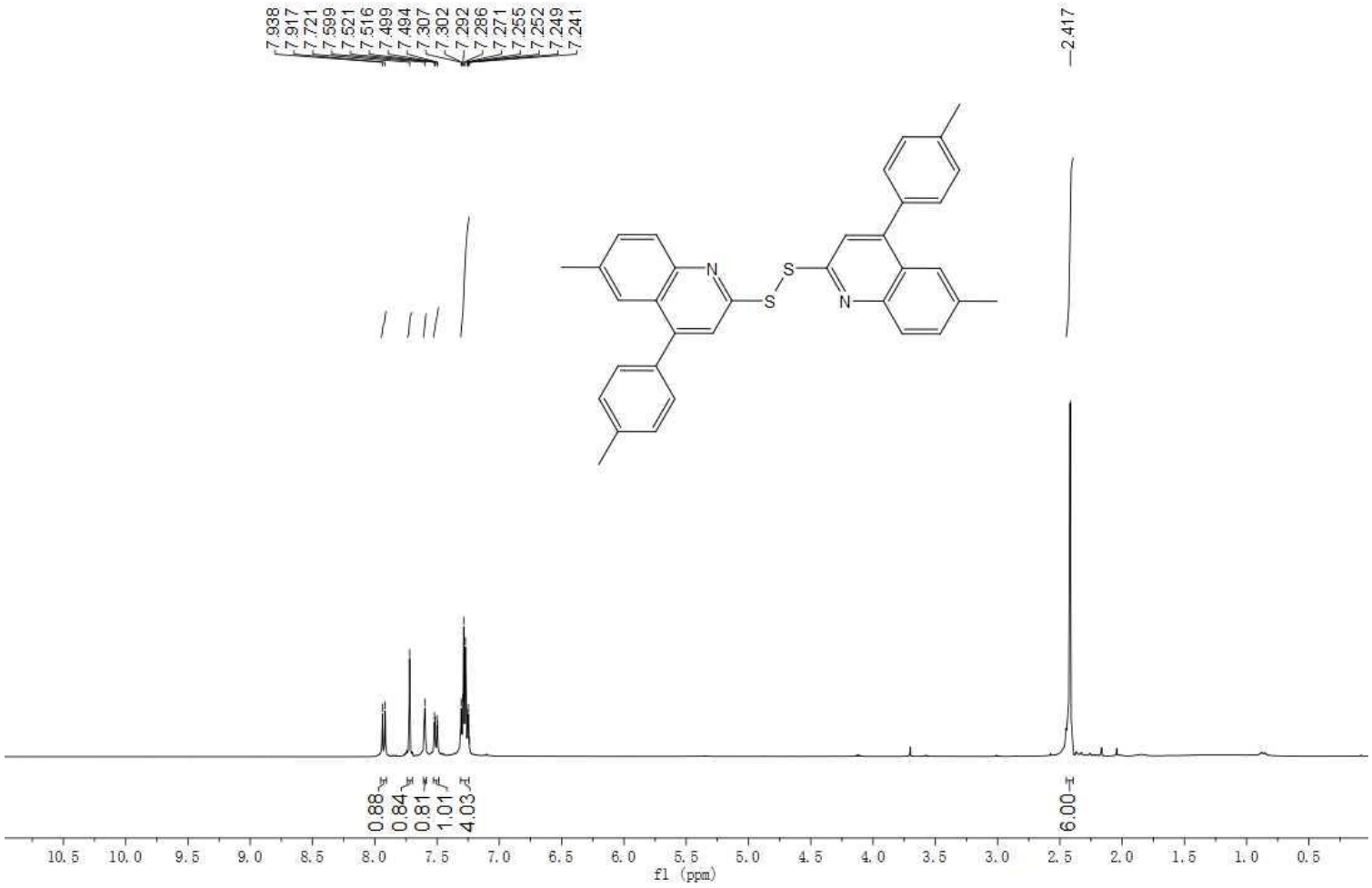

161.182
159.163
150.332
149.772
137.649
129.408
128.511
127.040
120.161
119.228
115.092
106.911
55.580
O
N
S
S
N
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

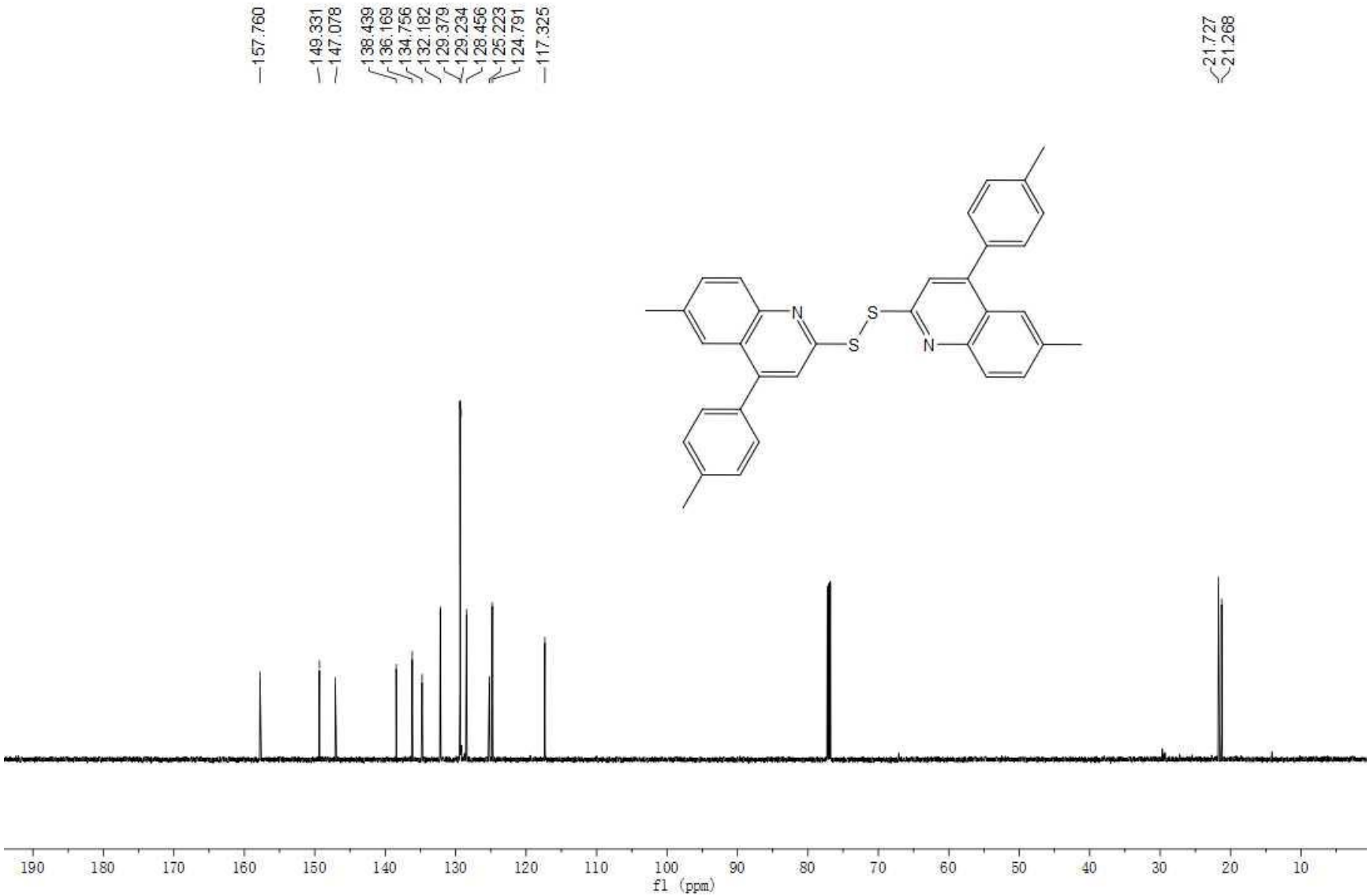
^{1}H and ^{13}C Spectra of compound 4d ($CDCl_3$)



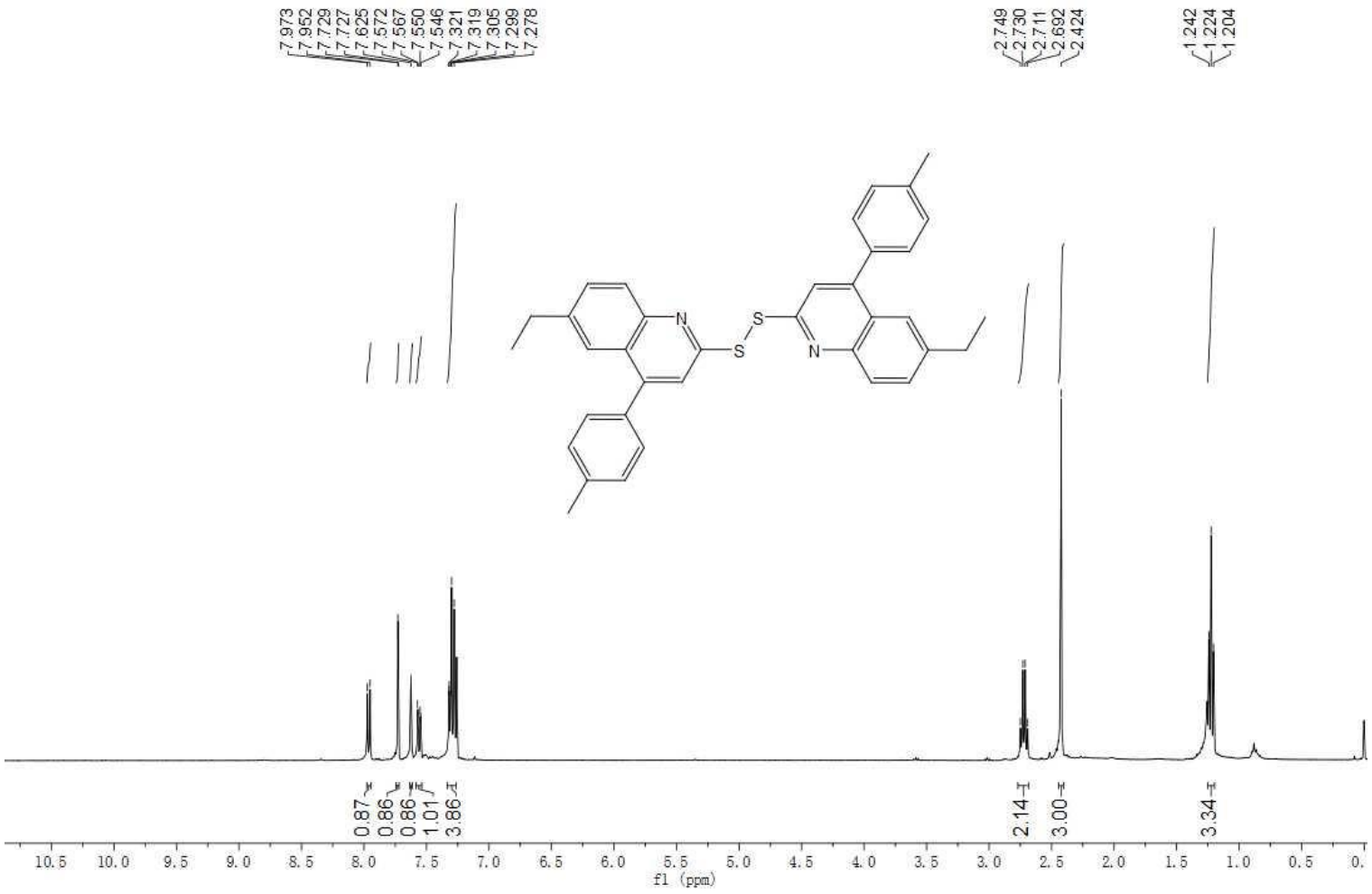

159.177
149.384
147.098
136.999
132.563
131.286
130.574
129.588
129.214
129.052
126.206
125.063
118.407
Cl
N
S
S
N
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

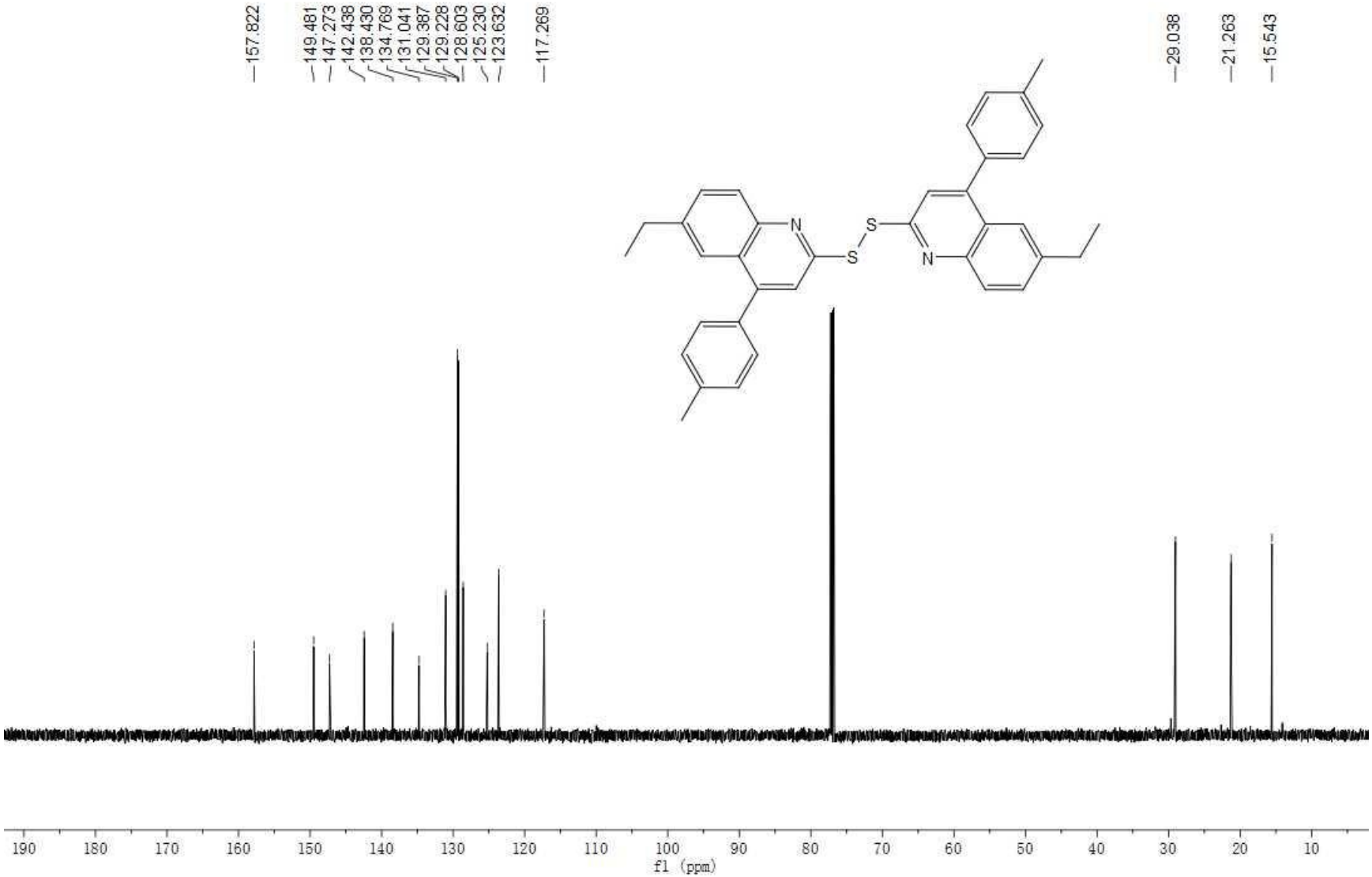
^{1}H and ^{13}C Spectra of compound 4e ($CDCl_3$)



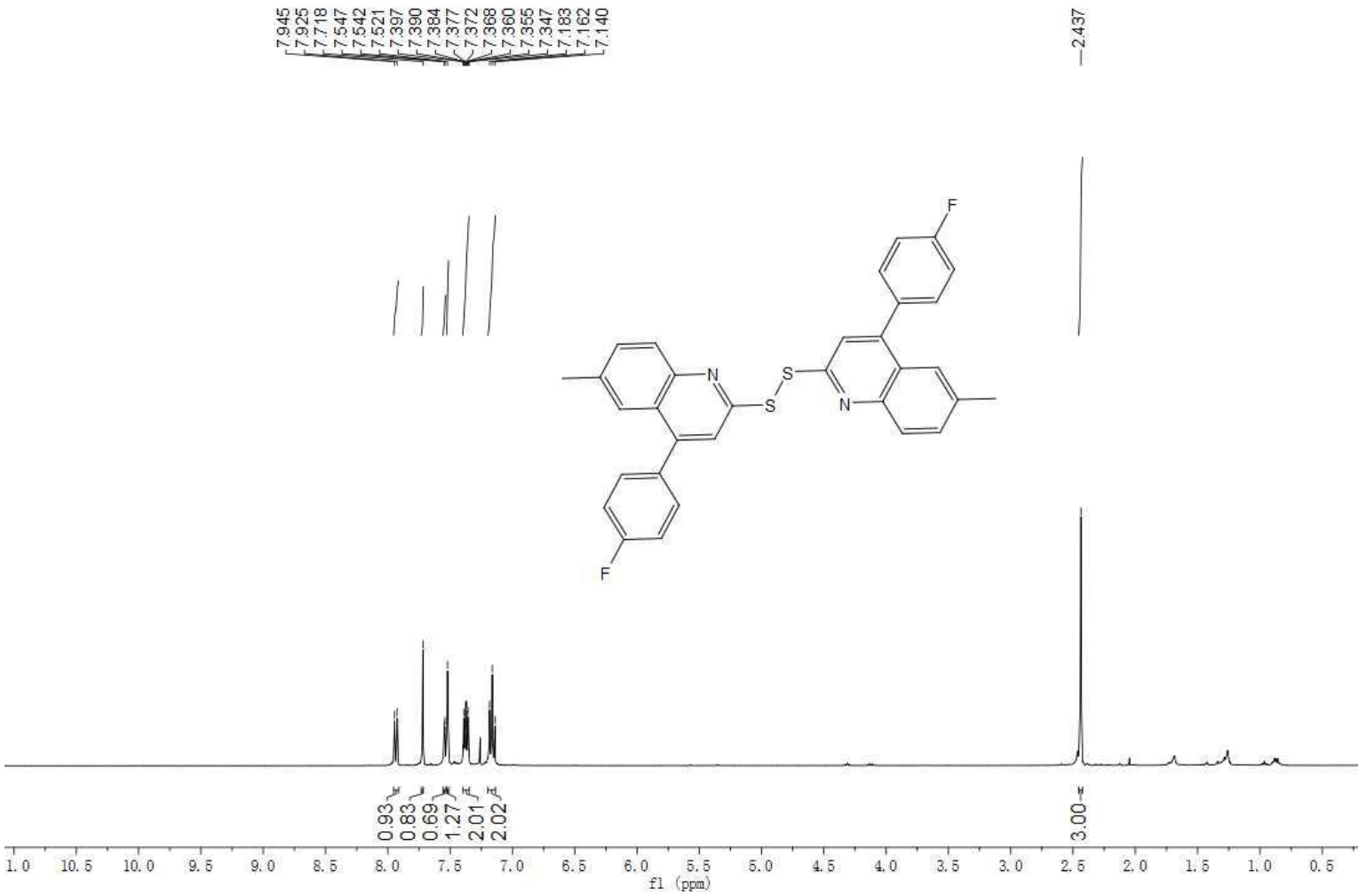

157.760
149.331
147.078
138.439
136.169
134.756
132.182
129.379
129.234
128.456
125.223
124.791
117.325
21.727
21.268
N
S
S
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

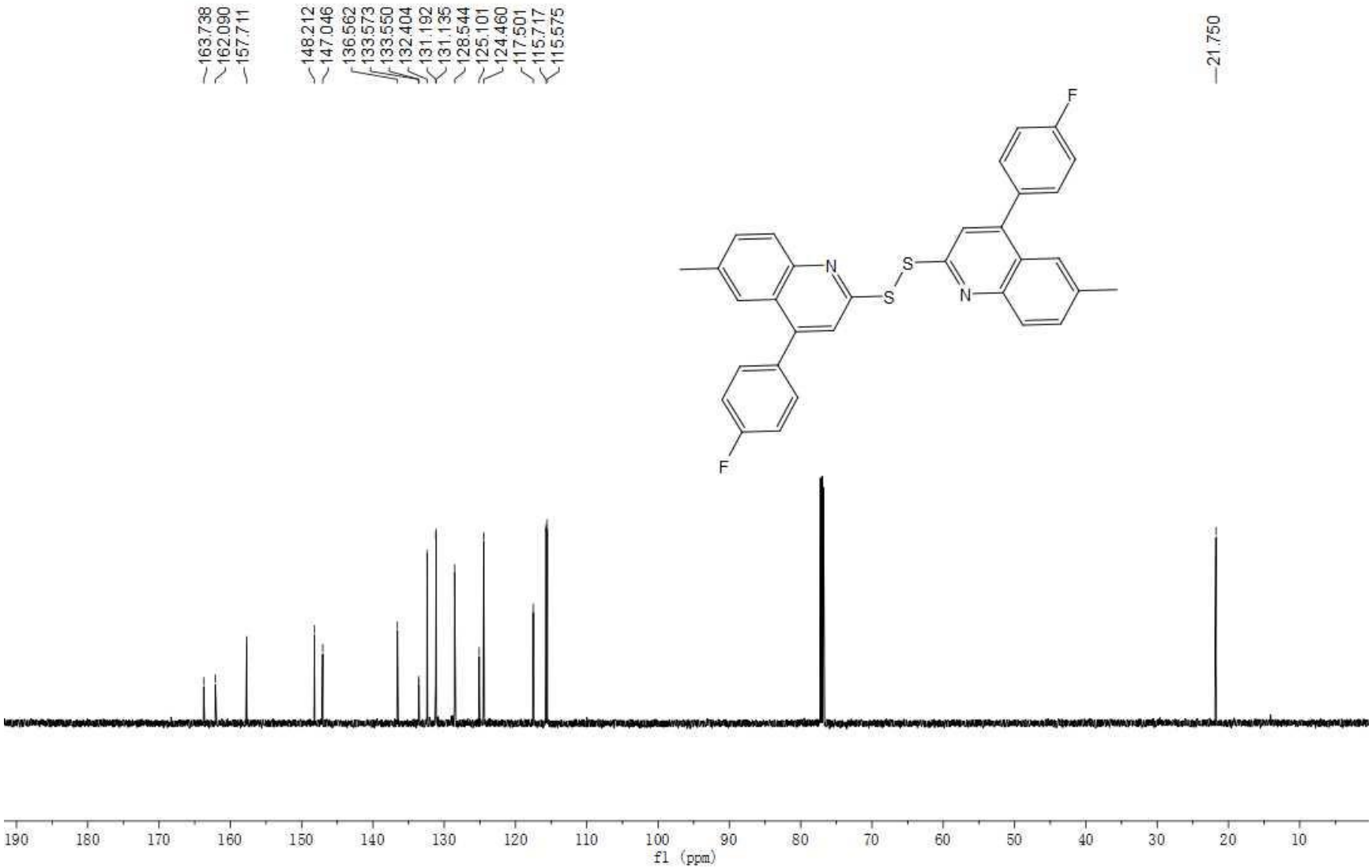
^{1}H and ^{13}C Spectra of compound 4f ($CDCl_3$)



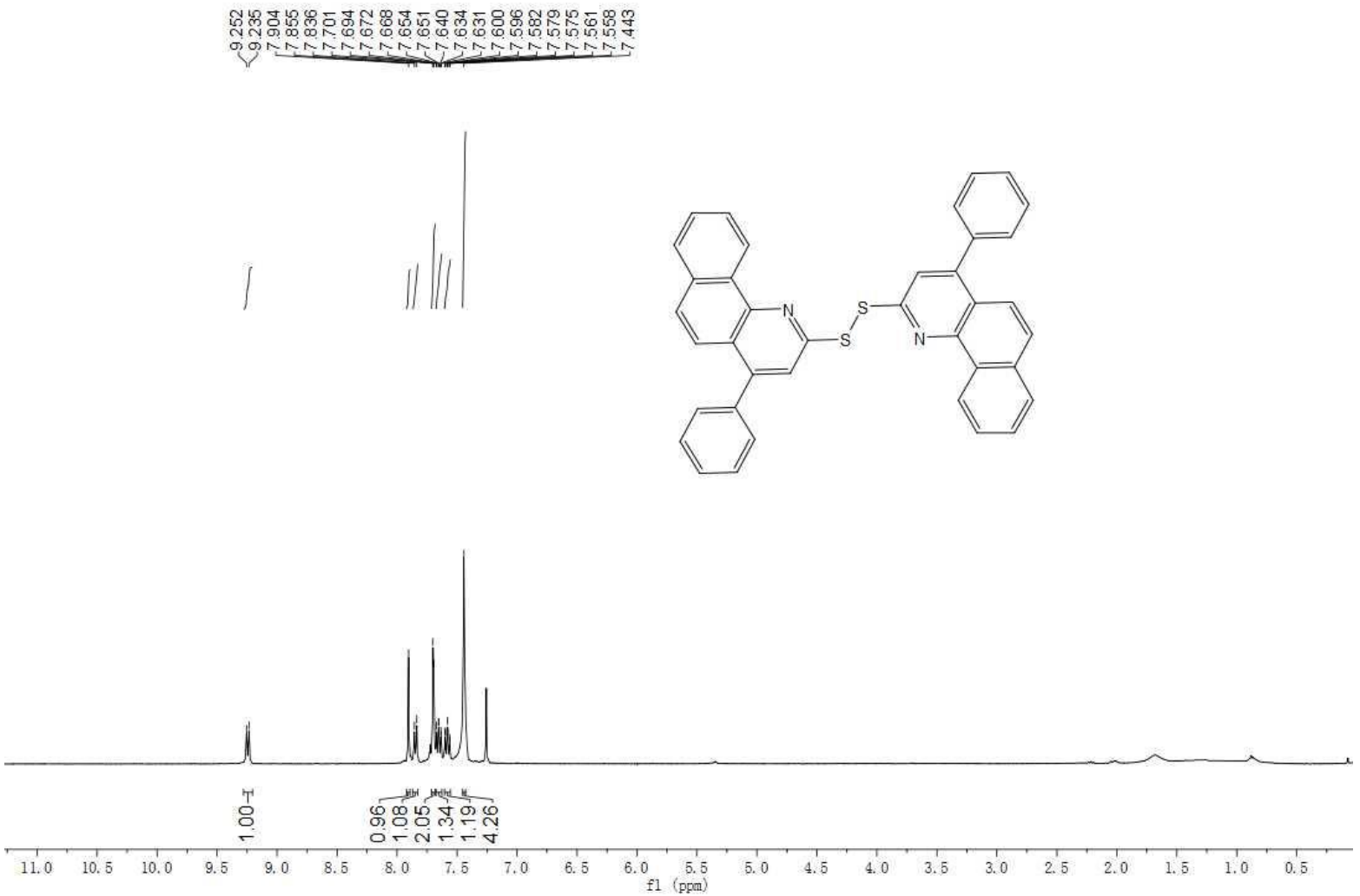

157.822
149.481
147.273
142.438
138.430
134.769
131.041
129.387
129.228
128.603
125.230
123.632
117.269
29.038
21.263
15.543
N
S
S
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

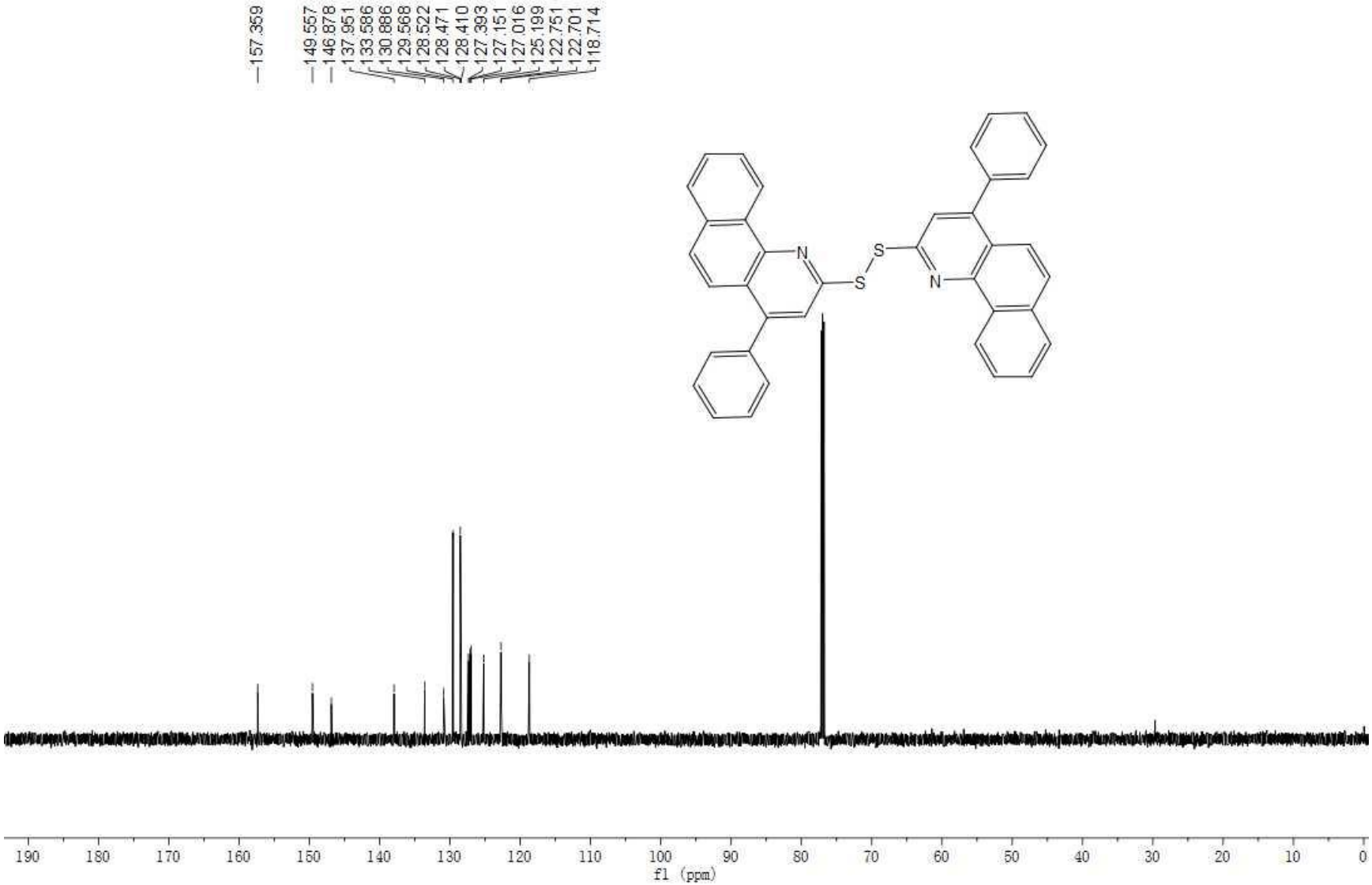
^{1}H and ^{13}C Spectra of compound 4g ($CDCl_3$)



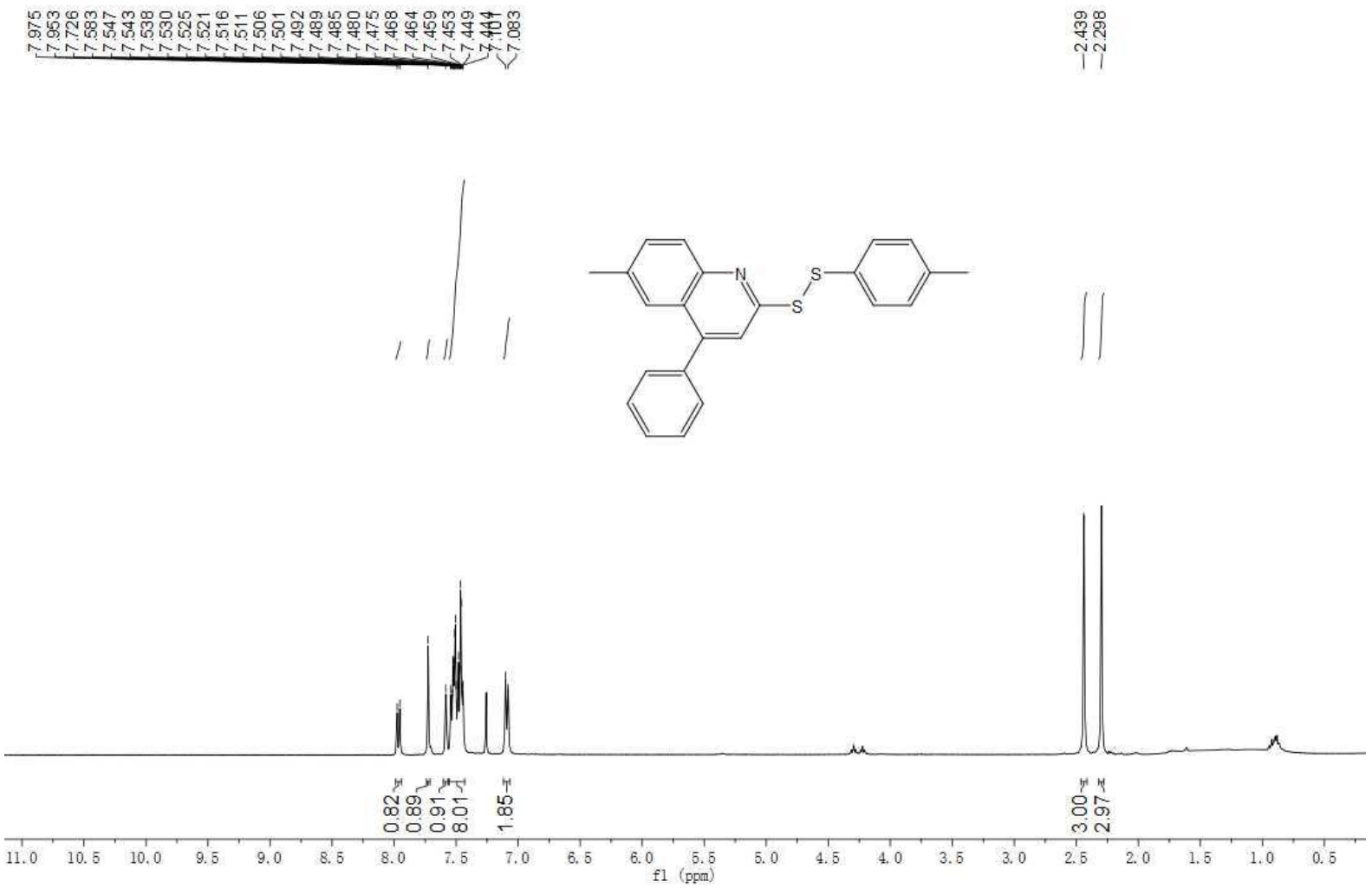

163.738
162.090
157.711
148.212
147.046
136.562
133.573
133.550
132.404
131.192
131.135
128.544
125.101
124.460
117.501
115.717
115.575
21.750
F
N
S
S
N
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

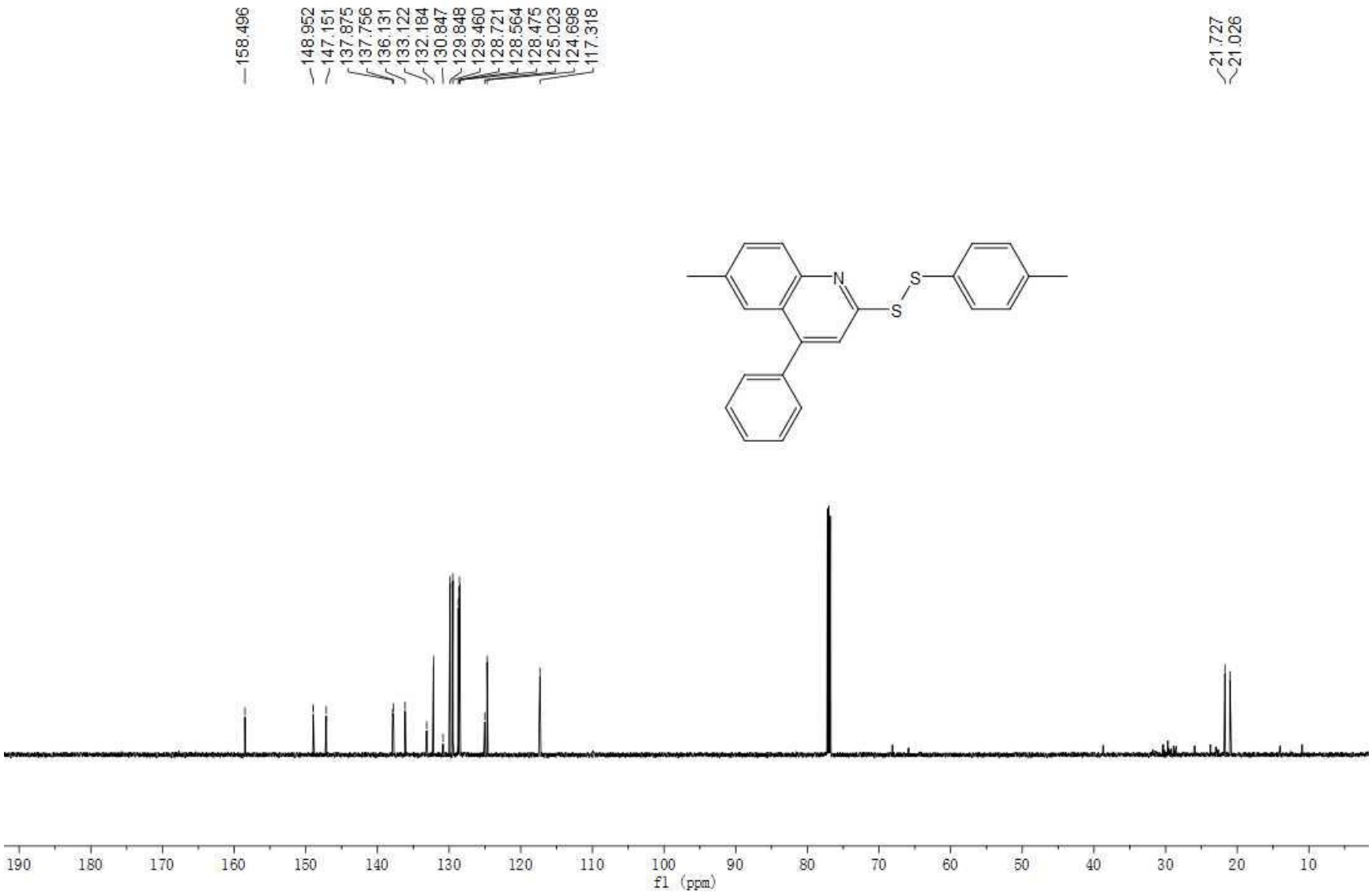
^{1}H and ^{13}C Spectra of compound 4h ($CDCl_3$)



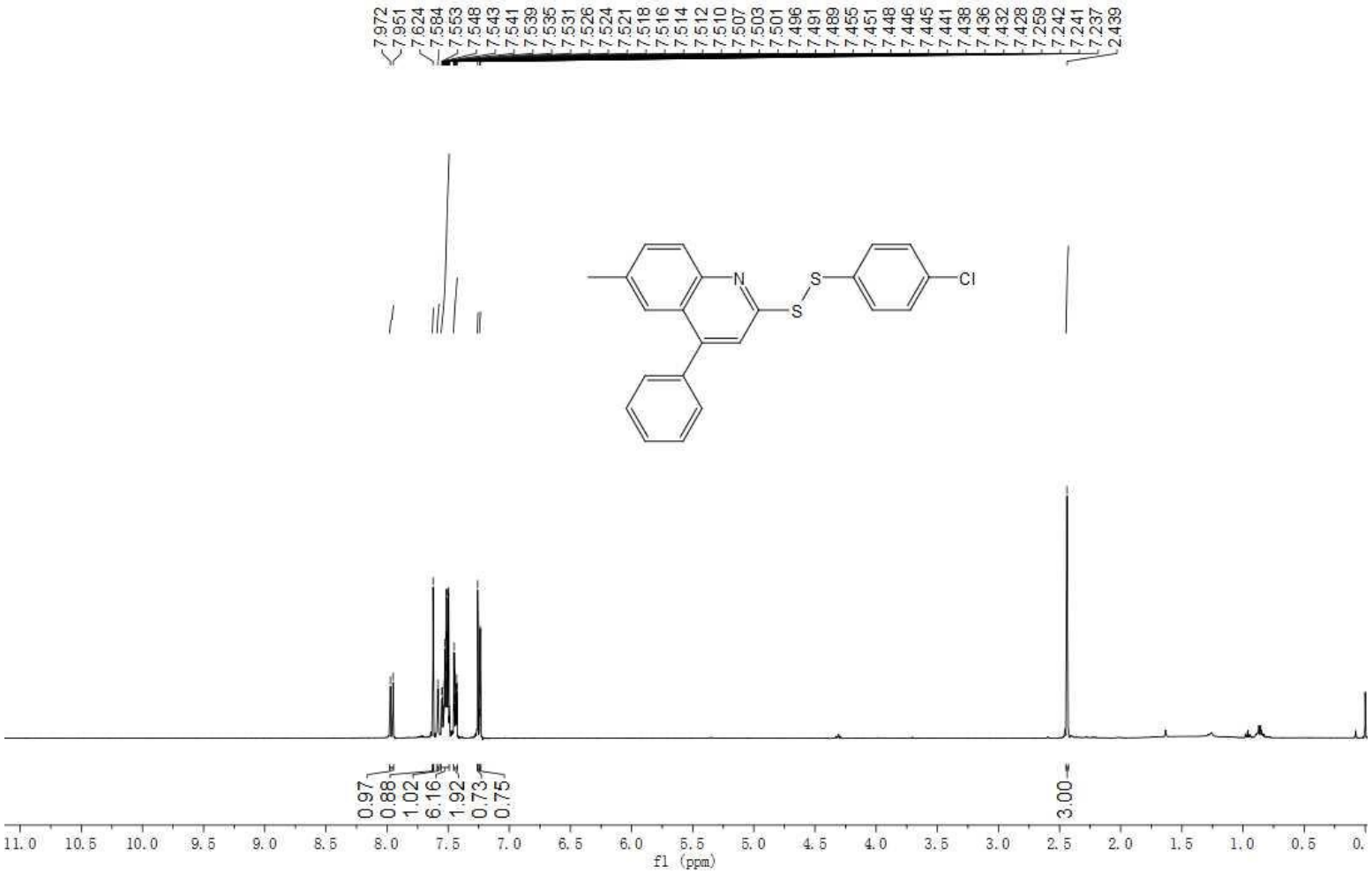

157.359
149.557
146.878
137.951
133.586
130.886
129.568
128.522
128.471
128.410
127.393
127.151
127.016
125.199
122.751
122.701
118.714
N
S
S
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

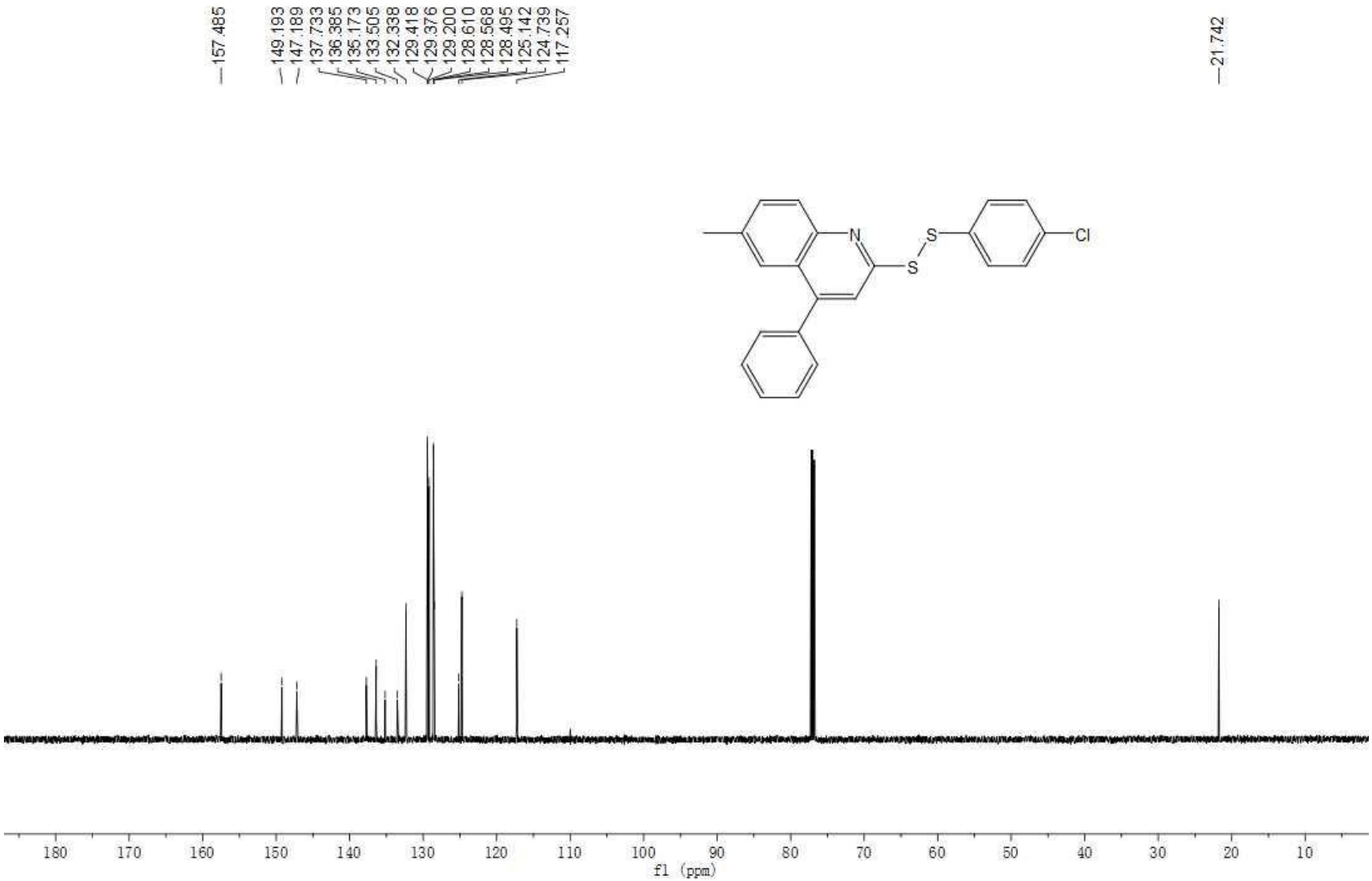
^{1}H and ^{13}C Spectra of compound 6a ($CDCl_3$)



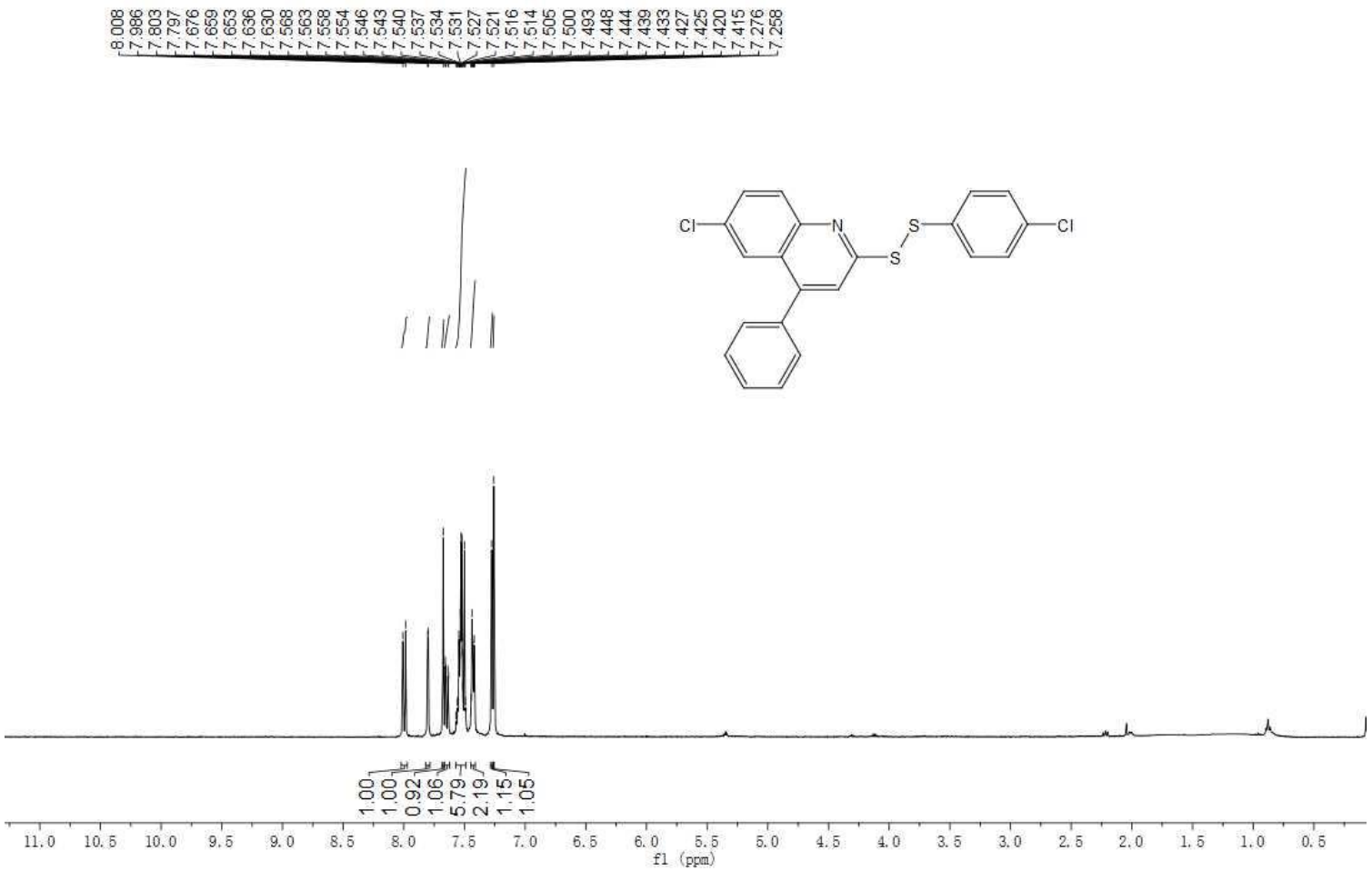

158.496
148.952
147.151
137.875
137.756
136.131
133.122
132.184
130.847
129.848
129.460
128.721
128.564
128.475
125.023
124.698
117.318
21.727
21.026
N
S
S
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

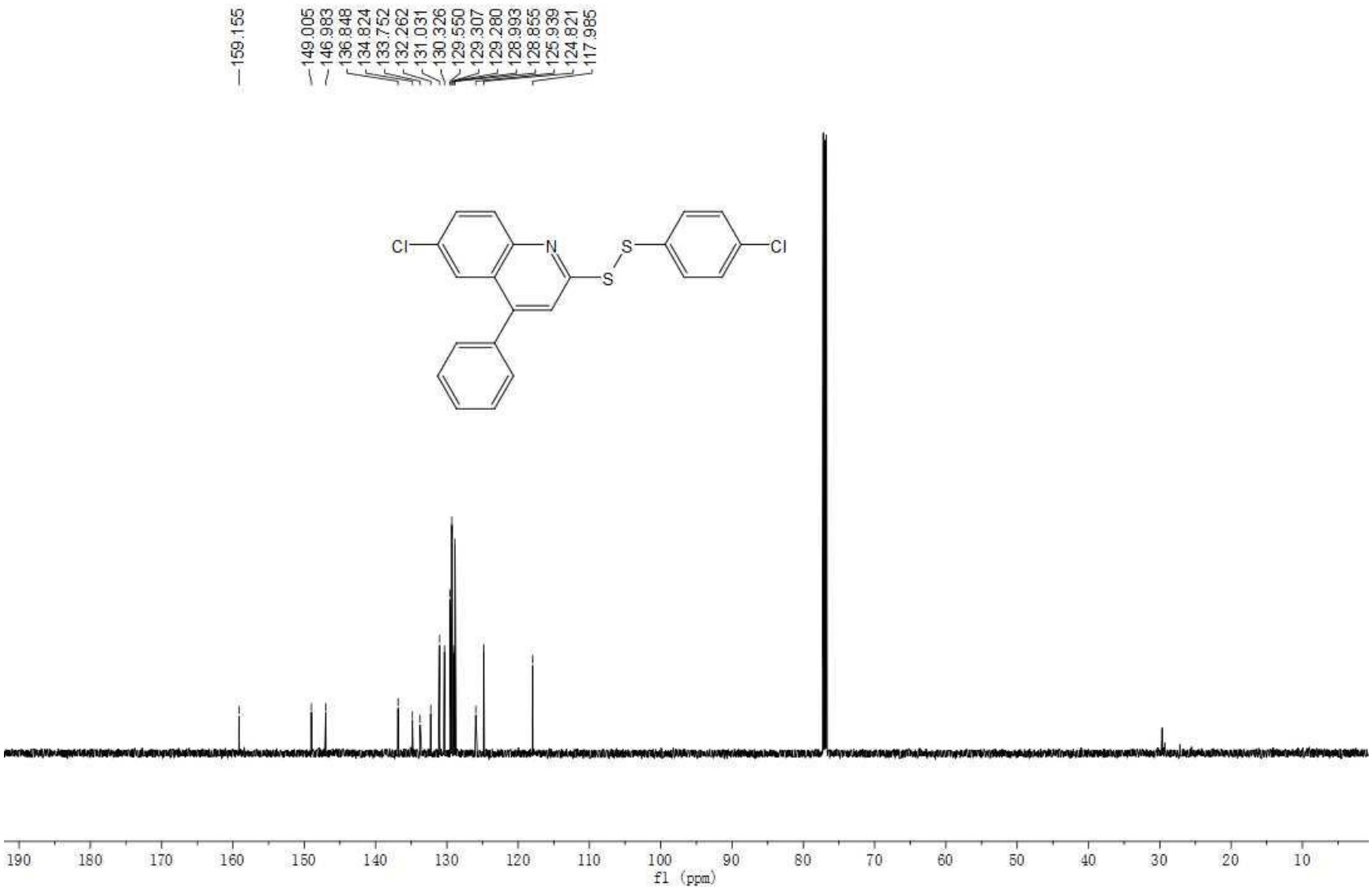
^{1}H and ^{13}C Spectra of compound 6b ($CDCl_3$)



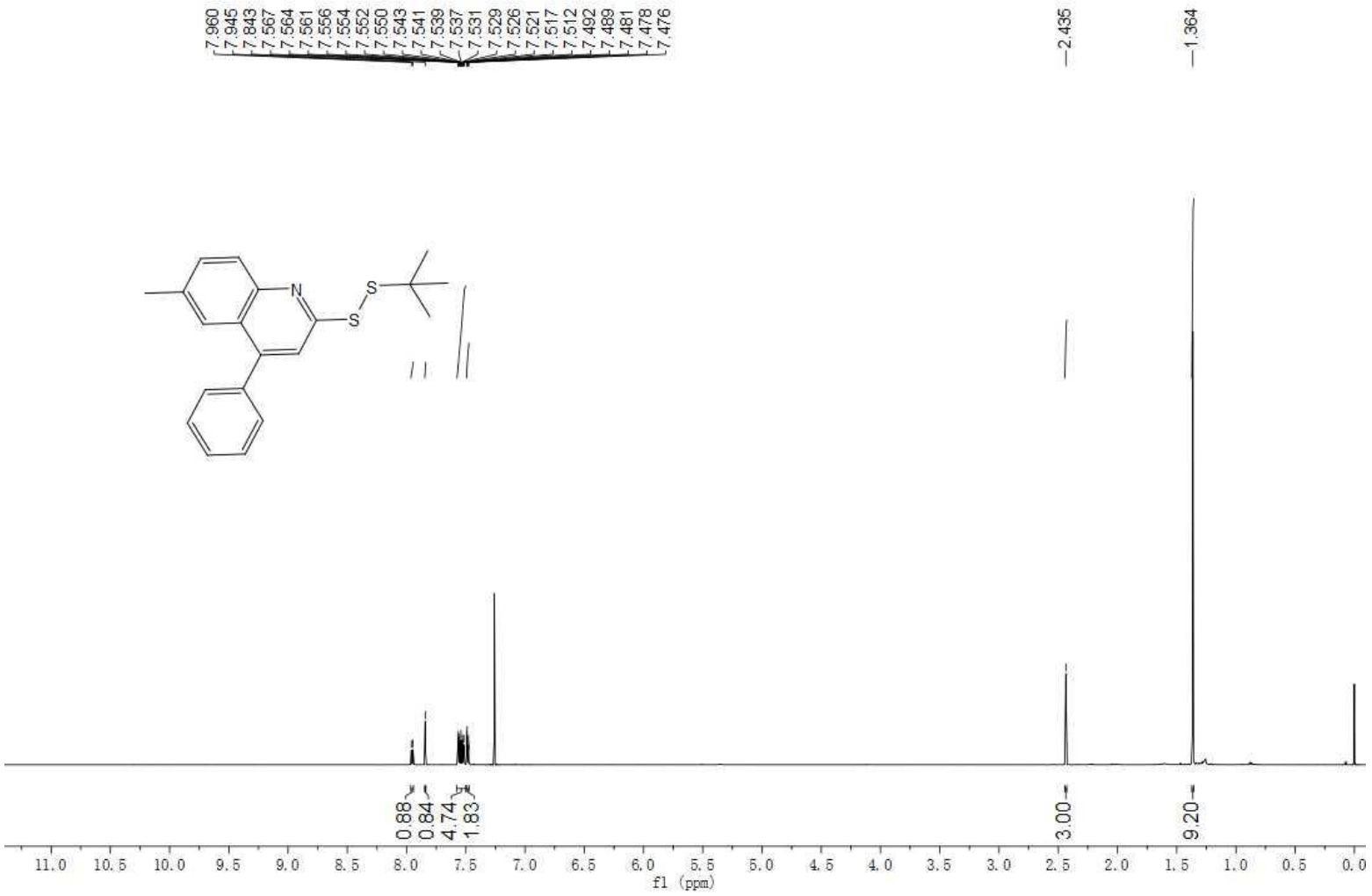

157.485
149.193
147.189
137.733
136.385
135.173
133.505
132.338
129.418
129.376
129.200
128.610
128.568
128.495
125.142
124.739
117.257
21.742
N
S
S
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

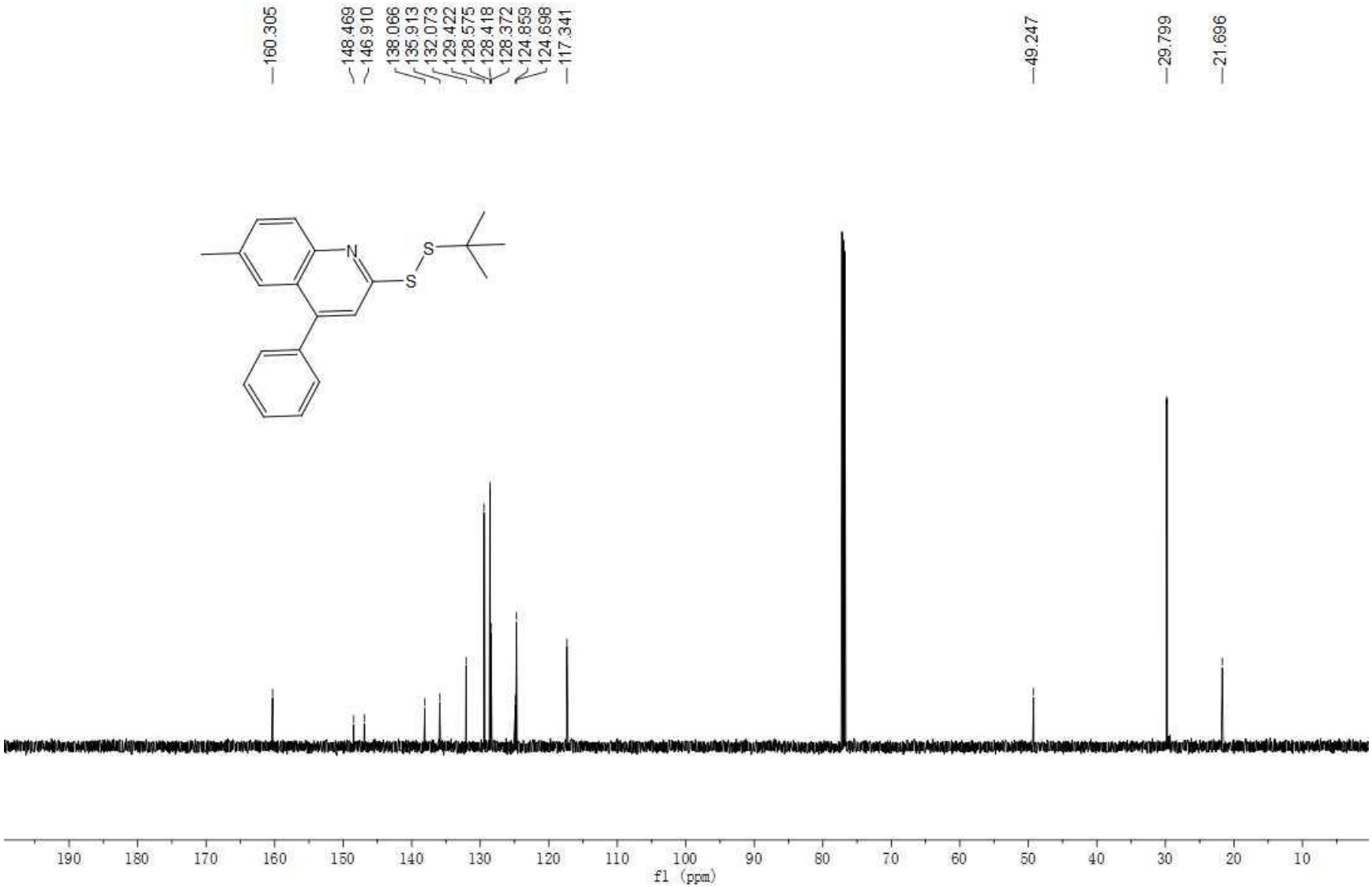
^{1}H and ^{13}C Spectra of compound 6c ($CDCl_3$)




159.155
149.005
146.983
136.848
134.824
133.752
132.262
131.031
130.326
129.550
129.307
129.280
128.993
128.855
125.939
124.821
117.985
Cl
N
S
S
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{1}H and ^{13}C Spectra of compound 6d ($CDCl_3$)




160.305
148.469
146.910
138.066
135.913
132.073
129.422
128.575
128.418
128.372
124.859
124.698
117.341
49.247
29.799
21.696
N
S
S
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)