

A Visible-light-induced photosensitizer-free decarbonylative Minisci-type reaction

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Content

1. General information.....	2
2. General procedure for synthesis of the products	3
3. Radical trapping experiment.....	3
4. Determination of electron spin resonance (ESR)	4
4.1 Determination of superoxide radicals and alkyl radicals	4
4.2 Determination of singlet oxygen pieces	5
5 Light/dark experiments.....	5
6 UV-Vis	6
7. Characterization of products.....	7

1. General information

Unless otherwise noted, all reagents were obtained from commercial suppliers (Macklin) and used without further purification. The photocatalytic reaction were performed on WATTCAS Parallel Photocatalytic Reactor (WP-TEC-HSL) with 20W COB LED. The distance from light source to the irradiation vessel is 5 mm. The reaction product was isolated by column chromatography on a silica gel (236–400 mesh) column using petroleum ether (PE) with a boiling range from 60 to 90 °C and EtOAc. ^1H NMR and ^{13}C NMR were recorded on a Bruker-400MHz Spectrometer (^1H NMR: 400MHz, ^{13}C NMR: 100MHz) using TMS as internal reference. The Electron Spin Resonance (ESR) Spectra were recorded on JEOL JES-FA200 ESR. In addition, ^1H , and ^{13}C NMR spectra used tetramethylsilane as the internal standard. HRMS (ESI) were recorded on a WatersTM Q-TOF Premier.

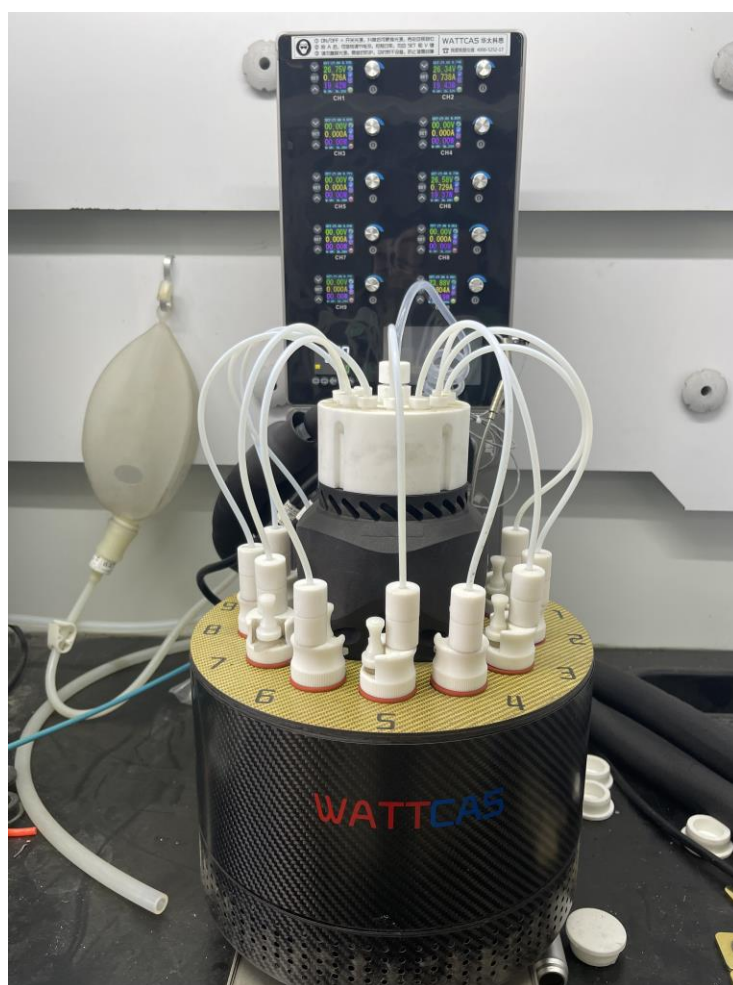


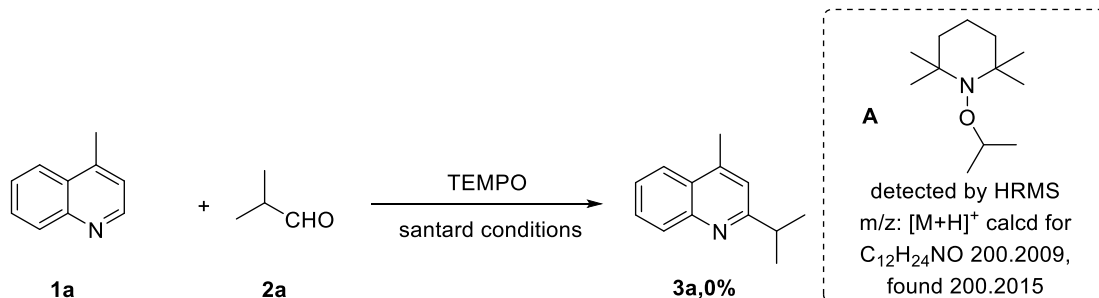
Figure S1 The reaction apparatus

2. General procedure for synthesis of the products

A Schlenk-tube was equipped with a magnetic stir bar and charged with N-heteroarene (0.1 mmol, 1.0 equiv.), DCE (1mL), TFA (2.0 equiv.) and aldehyde (5.0 equiv.). The resulting mixture was stirred under ambient air for 18 h under irradiation with a 20 W blue lamp (450 nm). After the reaction ended, the reaction solution was quenched with saturated sodium carbonate and extracted with DCE for three times. The extracts were combined, dried over sodium sulfate, filtered and the volatiles were removed under reduced pressure. The mixture was purified by silica gel column chromatography to give the desired product.

3. Radical trapping experiment

A Schlenk-tube was equipped with a magnetic stir bar and charged with N-heteroarene (0.1 mmol, 1.0 equiv.), DCE (1mL), TFA (2.0 equiv.), aldehyde (5.0 equiv.) and TEMPO (2.0 equiv.). The resulting mixture was stirred under ambient air for 18 h under irradiation with a 20 W blue lamp (450 nm). The solvent was removed, which residue was used directly for HRMS analysis. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{24}NO$: 200.2009 Found: 200.2015.



Scheme S1 The radical trapping experiment

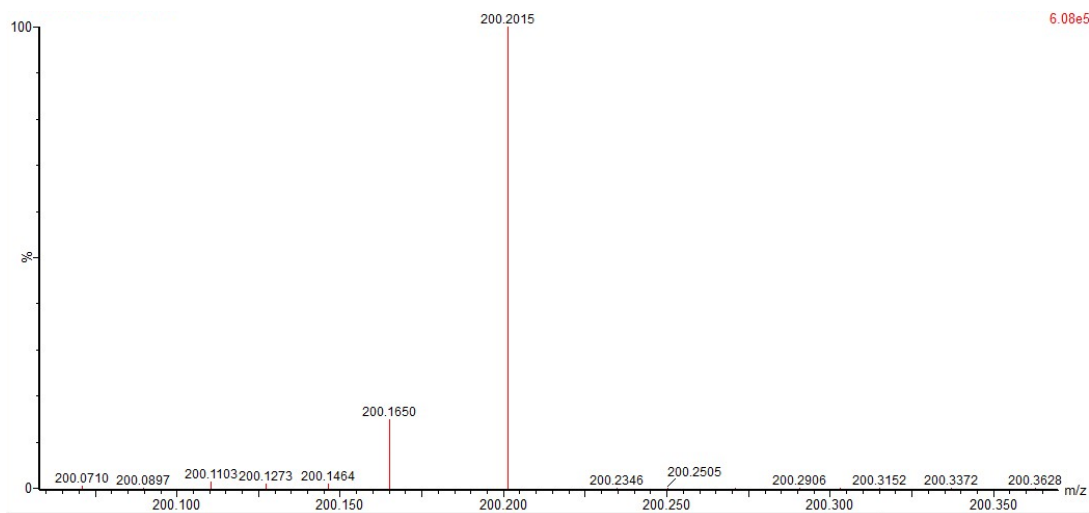


Figure S2 HRMS spectrum analysis of reaction in the presence of TEMPO.

4. Determination of electron spin resonance (ESR)

4.1 Determination of superoxide radicals and alkyl radicals

In order to determine the active species of oxygen involved in the present reaction, 5,5-dimethyl-pyrroline-N-oxide (DMPO) were employed to capture $O_2^{\cdot-}$ and alkyl radicals. There was a small signal when DMPO was added into a solution of isobutyraldehyde (**2a**) and TFA in DCE without light irradiation. Irradiation of the above solution in air with Xe lamp resulted in the formation of a strong characteristic signal of alkyl radical adduct with DMPO (Figure S3). And there is no $O_2^{\cdot-}$ generated.

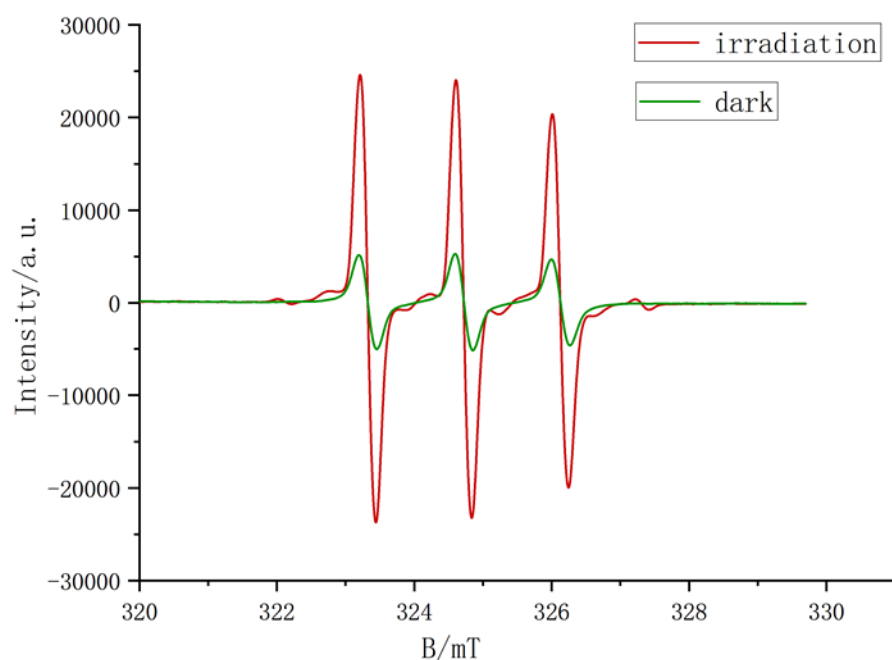


Figure S3. Electron spin resonance (ESR) spectra of DMPO with $O_2^{\cdot-}$

- (A) Green line - A solution of DMPO (0.10 mol/L) with isobutyraldehyde (**2a**) and TFA in DCE without light irradiation.
- (B) Red line - A solution of DMPO (0.10 mol/L) with isobutyraldehyde (**2a**) and TFA in DCE under Xe lamp irradiation.

4.2 Determination of singlet oxygen pieces

For further explore the active species of singlet oxygen involved in the reaction, 2,2,6,6-tetramethylpiperidine (TEMP) were used to trap $^1\text{O}_2$. Irradiation of reaction solution of TEMP, isobutyraldehyde (**2a**) and TFA in DCE under air with Xe lamp could not result in the formation of a strong characteristic signal $^1\text{O}_2$ adduct with TEMP (Figure S4), implying that $^1\text{O}_2$ is not present during the reaction.

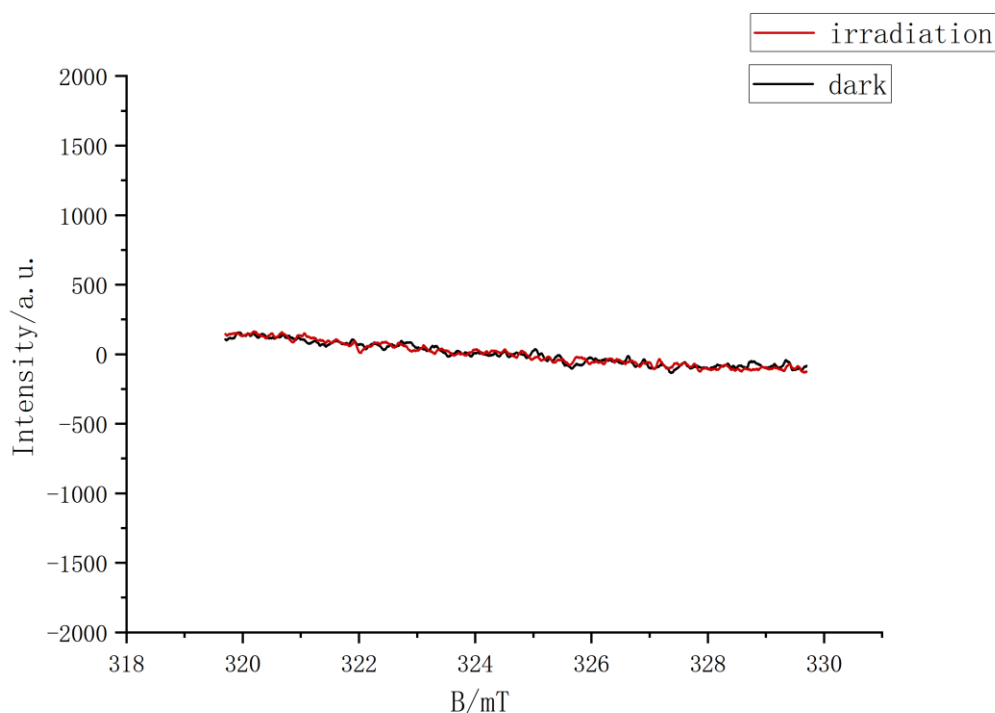


Figure S4. Electron spin resonance (ESR) spectra of DMPO with $^1\text{O}_2$
(A) Black line - A solution of TEMP (0.20 mol/L) with isobutyraldehyde (**2a**) and TFA in DCE without light irradiation.
(B) Red line - A solution of TEMP (0.20 mol/L) with isobutyraldehyde (**2a**) and TFA in DCE under Xe lamp irradiation.

5 Light/dark experiments



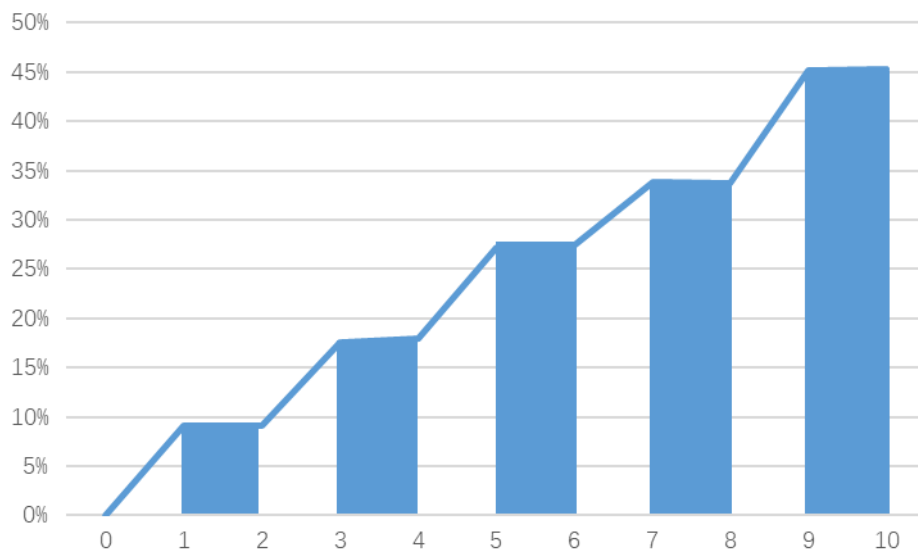


Figure S5 Light/dark experiments

6 UV-Vis

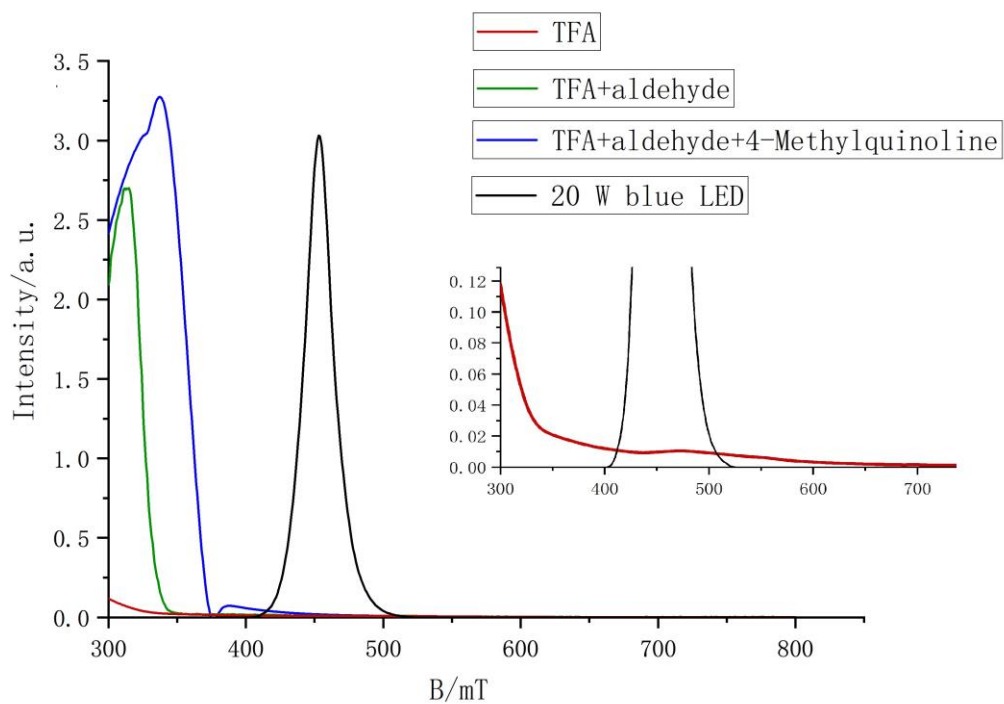
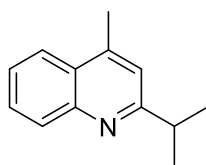
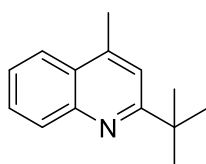


Figure S6 UV-Vis experiments.

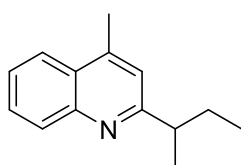
7. Characterization of products



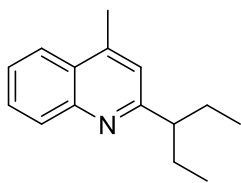
3a: 16.7 mg, 91%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 8.4$ Hz, 1H), 7.95 (dd, $J = 8.3, 0.9$ Hz, 1H), 7.67 (ddd, $J = 8.4, 6.9, 1.4$ Hz, 1H), 7.50 (ddd, $J = 8.2, 6.9, 1.2$ Hz, 1H), 7.18 (s, 1H), 3.21 (dq, $J = 13.9, 7.0$ Hz, 1H), 2.69 (d, $J = 0.8$ Hz, 3H), 1.39 (d, $J = 7.0$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.35, 147.44, 144.45, 129.41, 128.99, 127.00, 125.43, 123.56, 119.72, 37.22, 22.55, 18.88. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{15}\text{N}$, 186.1277; found, 186.1279.



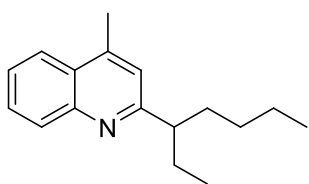
3b: 17.1 mg, 86%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 8.2$ Hz, 1H), 7.86 (dd, $J = 8.3, 0.7$ Hz, 1H), 7.66 – 7.44 (m, 1H), 7.48 – 7.35 (m, 1H), 7.27 (s, 1H), 2.61 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.88, 146.22, 142.59, 128.87, 127.67, 125.50, 124.36, 122.35, 117.87, 36.87, 29.08, 17.95. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{17}\text{N}$, 200.1434; found, 200.1437.



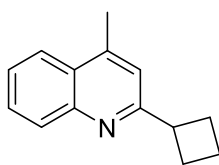
3c: 14.3 mg, 72%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 8.4$ Hz, 1H), 7.95 (d, $J = 8.3$ Hz, 1H), 7.74 – 7.59 (m, 1H), 7.53 – 7.38 (m, 1H), 7.14 (s, 1H), 3.06 – 2.85 (m, 1H), 2.69 (s, 3H), 1.78 (ddt, $J = 28.0, 13.7, 7.3$ Hz, 2H), 1.35 (d, $J = 7.0$ Hz, 3H), 0.89 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.75, 147.53, 144.34, 129.48, 128.97, 127.06, 125.43, 123.61, 120.17, 44.57, 29.97, 20.45, 18.92, 12.31. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{17}\text{N}$, 200.1434; found, 200.1433.



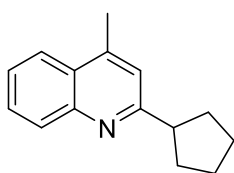
3d: 18.3 mg, 86%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 8.4$ Hz, 1H), 7.88 (dd, $J = 8.3, 0.9$ Hz, 1H), 7.59 (ddd, $J = 8.3, 6.9, 1.4$ Hz, 1H), 7.42 (ddd, $J = 8.2, 6.9, 1.2$ Hz, 1H), 7.02 (s, 1H), 2.66 (td, $J = 8.3, 4.1$ Hz, 1H), 2.61 (d, $J = 0.7$ Hz, 3H), 1.80 – 1.57 (m, 5H), 0.75 (t, $J = 7.4$ Hz, 7H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.60, 146.60, 142.93, 128.53, 127.80, 126.02, 124.30, 122.55, 119.67, 51.18, 27.22, 17.85, 11.22. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{19}\text{N}$, 214.1590; found, 214.1591.



3e: 19.8 mg, 82%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, $J = 8.4$ Hz, 1H), 7.88 (d, $J = 8.3$ Hz, 1H), 7.59 (dd, $J = 11.2, 4.0$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 1H), 7.03 (s, 1H), 2.73 (dd, $J = 14.5, 7.2$ Hz, 1H), 2.62 (s, 3H), 1.69 (dd, $J = 15.8, 7.8$ Hz, 5H), 1.24 – 1.11 (m, 5H), 0.75 (t, $J = 7.3$ Hz, 7H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.89, 147.54, 144.10, 129.51, 128.89, 127.07, 125.38, 123.61, 120.68, 50.49, 35.19, 29.94, 28.63, 22.90, 18.94, 14.03, 12.28. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{23}\text{N}$, 242.1903; found, 242.1902.

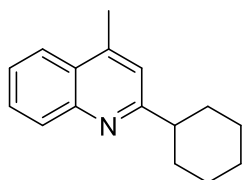


3f: 10.6 mg, 54%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, $J = 8.4$ Hz, 1H), 7.87 (dd, $J = 8.3, 0.9$ Hz, 1H), 7.60 (ddd, $J = 8.3, 6.9, 1.4$ Hz, 1H), 7.43 (ddd, $J = 8.2, 6.9, 1.2$ Hz, 1H), 7.14 (s, 1H), 3.77 (p, $J = 8.9$ Hz, 1H), 2.62 (d, $J = 0.8$ Hz, 3H), 2.41 – 2.33 (m, 4H), 2.05 (tt, $J = 20.1, 9.2$ Hz, 1H), 1.88 (tdd, $J = 11.9, 8.5, 3.2$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.68, 147.38, 144.41, 129.39, 129.09, 126.88, 125.50, 123.59, 120.24, 42.57, 28.26, 18.85, 18.38. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{15}\text{N}$, 198.1277; found, 198.1278.

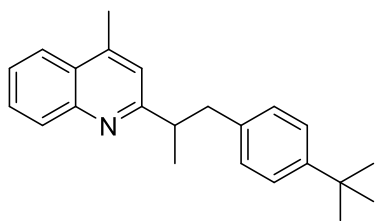


3g: 13.1 mg, 62%, colorless oil liquid. Purification by flash column

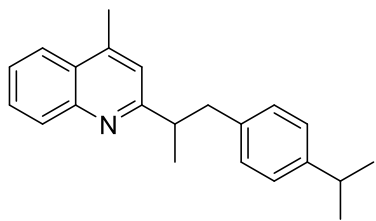
chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 8.4$ Hz, 1H), 7.93 (d, $J = 8.3$ Hz, 1H), 7.70 – 7.62 (m, 1H), 7.53 – 7.45 (m, 1H), 7.18 (s, 1H), 3.43 – 3.23 (m, 1H), 2.68 (s, 3H), 2.25 – 2.07 (m, 3H), 1.93 – 1.80 (m, 5H), 1.79 – 1.67 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.95, 147.44, 144.23, 129.42, 128.99, 126.98, 125.40, 123.57, 120.64, 48.81, 33.63, 26.07, 18.88. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{17}\text{N}$, 212.1434; found, 212.1435.



3h: 15.1 mg, 67%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 7.7$ Hz, 1H), 7.70 – 7.60 (m, 1H), 7.53 – 7.43 (m, 1H), 7.17 (s, 1H), 2.88 (tt, $J = 12.2, 3.4$ Hz, 1H), 2.69 (s, 3H), 2.01 (d, $J = 11.4$ Hz, 2H), 1.89 (dd, $J = 9.9, 3.0$ Hz, 2H), 1.62 (ddd, $J = 24.7, 12.4, 2.7$ Hz, 2H), 1.54 – 1.41 (m, 2H), 1.34 (ddd, $J = 10.8, 8.0, 3.4$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.48, 146.48, 143.34, 128.37, 127.96, 126.01, 124.37, 122.54, 119.20, 46.54, 31.80, 25.52, 25.09, 17.85. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{19}\text{N}$, 226.1590; found, 226.1592.

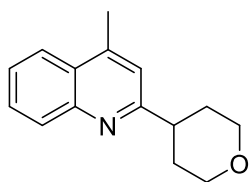


3i: 20.0 mg, 62%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 8.4$ Hz, 1H), 7.95 (d, $J = 8.2$ Hz, 1H), 7.73 – 7.60 (m, 1H), 7.51 (t, $J = 7.2$ Hz, 1H), 7.26 (t, $J = 5.5$ Hz, 2H), 7.13 (d, $J = 8.7$ Hz, 3H), 3.35 (dd, $J = 14.9, 6.8$ Hz, 1H), 3.21 (dd, $J = 13.5, 6.0$ Hz, 1H), 2.86 (dd, $J = 13.5, 8.9$ Hz, 1H), 2.66 (s, 3H), 1.33 (d, $J = 6.9$ Hz, 3H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, CH_3CN) δ 166.07, 148.66, 147.59, 144.36, 137.52, 129.52, 129.04, 128.90, 127.09, 125.74, 125.54, 125.10, 123.65, 120.85, 44.37, 42.39, 34.38, 31.44, 31.38, 20.00, 18.86. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{27}\text{N}$, 318.2216; found, 318.2215.

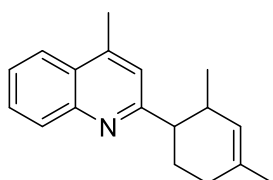


3j: 21.5 mg, 71%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 8.3$ Hz, 1H), 7.68 (t, $J = 7.6$ Hz, 1H), 7.50 (t, $J = 7.5$ Hz, 1H), 7.11 (s, 5H), 3.34 (dq, $J = 13.7, 6.7$ Hz, 1H), 3.20 (dd, $J = 13.5, 6.0$ Hz, 1H), 2.85 (ddd, $J = 13.5, 7.9, 5.2$ Hz, 2H), 2.66 (s, 3H), 1.33

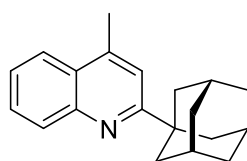
(d, $J = 6.9$ Hz, 3H), 1.22 (d, $J = 7.0$ Hz, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.06, 147.62, 146.39, 144.32, 137.92, 129.54, 129.34, 129.17, 129.02, 127.09, 126.87, 126.24, 125.52, 123.64, 120.85, 50.68, 44.44, 42.52, 33.71, 24.10, 24.09, 19.99, 18.85. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{25}\text{N}$, 304.2060; found, 304.2058.



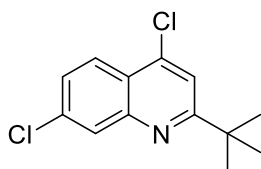
3k: 11.4 mg, 50%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 8.4$ Hz, 1H), 7.92 – 7.85 (m, 1H), 7.66 – 7.57 (m, 1H), 7.48 – 7.40 (m, 1H), 7.12 (s, 1H), 4.06 (dd, $J = 11.0, 3.8$ Hz, 2H), 3.53 (td, $J = 11.7, 2.2$ Hz, 2H), 3.08 (tt, $J = 11.8, 4.0$ Hz, 1H), 2.63 (s, 3H), 1.91 (dtd, $J = 14.8, 13.1, 3.1$ Hz, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.23, 147.42, 144.99, 129.37, 129.30, 127.14, 125.79, 123.67, 119.91, 68.16, 44.34, 32.32, 18.98. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{17}\text{NO}$, 228.1383; found, 228.1384.



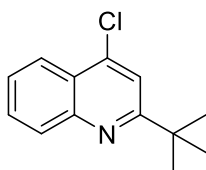
3l: 13.8 mg, 55%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 8.12 (d, $J = 8.3$ Hz, 1H), 8.01 (d, $J = 8.4$ Hz, 1H), 7.73 – 7.61 (m, 1H), 7.51 (t, $J = 7.6$ Hz, 1H), 7.33 (s, 1H), 5.26 (s, 1H), 2.64 – 2.49 (m, 1H), 2.15 – 2.02 (m, 1H), 1.98 – 1.82 (m, 4H), 1.66 (s, 3H), 0.80 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.17, 148.70, 142.68, 133.20, 130.24, 129.37, 127.17, 126.71, 125.21, 123.95, 120.32, 51.37, 35.58, 30.37, 30.00, 23.56, 20.34. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{21}\text{N}$, 252.1747; found, 252.1749.



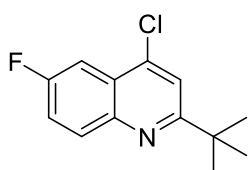
3m: 16.2 mg, 58%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 8.07 – 7.92 (m, 1H), 7.87 (d, $J = 8.1$ Hz, 1H), 7.58 (t, $J = 7.2$ Hz, 1H), 7.42 (t, $J = 7.3$ Hz, 1H), 7.26 (s, 1H), 2.62 (s, 3H), 2.08 (s, 3H), 2.04 (s, 6H), 1.75 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.71, 160.46, 147.51, 143.62, 129.93, 128.66, 126.72, 125.36, 123.46, 118.58, 41.80, 39.56, 36.90, 28.85. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{23}\text{N}$, 278.1903; found, 278.1906.



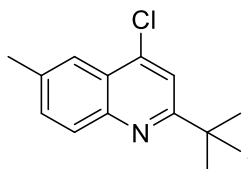
3p: 21.2 mg, 86%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.11 – 7.83 (m, 1H), 7.50 (s, 1H), 7.43 (dd, $J = 9.0, 2.0$ Hz, 1H), 1.36 (s, 5H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.71, 147.63, 141.25, 134.94, 127.64, 126.53, 124.10, 122.13, 117.61, 37.35, 28.86. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{13}\text{Cl}_2\text{N}$, 254.0498; found, 254.0499.



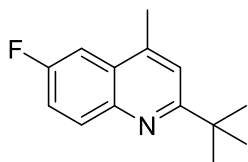
3q: 18.6 mg, 85%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.09 (d, $J = 8.3$ Hz, 1H), 8.00 (d, $J = 8.4$ Hz, 1H), 7.65 (dd, $J = 11.2, 4.1$ Hz, 1H), 7.57 – 7.44 (m, 2H), 1.38 (s, 10H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.33, 147.25, 141.26, 128.91, 128.66, 125.59, 123.62, 122.68, 117.45, 37.22, 28.96. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{14}\text{ClN}$, 220.0888; found, 220.0889.



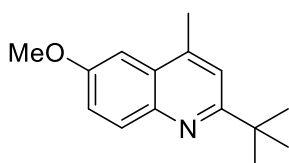
3r: 20.0 mg, 83%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.99 (dd, $J = 9.1, 5.4$ Hz, 1H), 7.71 (dd, $J = 9.4, 2.7$ Hz, 1H), 7.55 (s, 1H), 7.41 (td, $J = 8.8, 2.8$ Hz, 1H), 1.37 (s, 10H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 167.70, 159.7 ($^1J_{\text{CF}} = 248.5$ Hz), 144.30, 131.28 ($^3J_{\text{CF}} = 9.1$ Hz), 124.49, 124.39, 119.04 ($^2J_{\text{CF}} = 26.3$ Hz), 118.07, 106.46 ($^2J_{\text{CF}} = 24.2$ Hz), 37.18, 28.93. $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -112.66. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{13}\text{ClFN}$, 238.0793; found, 238.0796.



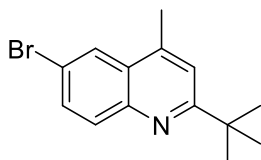
3s: 20.1 mg, 86%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.98 – 7.76 (m, 1H), 7.59 – 7.38 (m, 1H), 2.49 (s, 2H), 1.37 (s, 5H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 167.32, 145.85, 140.53, 135.60, 131.12, 128.39, 123.49, 121.52, 117.38, 37.07, 28.99. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{16}\text{ClN}$, 234.1044; found, 234.1046.



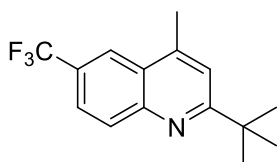
3t: 15.6 mg, 72%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 7.97 (dd, $J = 8.5, 5.7$ Hz, 1H), 7.45 (dd, $J = 9.9, 2.8$ Hz, 1H), 7.34 (td, $J = 8.8, 2.8$ Hz, 1H), 7.29 (s, 1H), 2.56 (s, 3H), 1.37 (s, 11H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.19, 158.99 ($^1J_{\text{CF}} = 247.5$ Hz), 143.29, 131.19 ($^3J_{\text{CF}} = 9.1$ Hz), 126.13 ($^3J_{\text{CF}} = 9.1$ Hz), 118.45, 117.52 ($^2J_{\text{CF}} = 25.3$ Hz), 105.93 ($^2J_{\text{CF}} = 22.2$ Hz), 36.82, 29.04, 17.97. ^{19}F NMR (377 MHz, CDCl_3) δ -114.75. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{16}\text{FN}$, 218.1340; found, 218.1343.



3u: 18.5 mg, 81%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, $J = 8.9$ Hz, 1H), 7.28 – 7.21 (m, 2H), 7.08 (d, $J = 2.8$ Hz, 1H), 3.86 (s, 4H), 2.56 (s, 4H), 1.37 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.48, 157.08, 143.16, 142.30, 131.36, 127.23, 120.65, 119.14, 101.84, 55.51, 37.65, 30.21, 19.21. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{19}\text{NO}$, 230.1539; found, 230.1538.

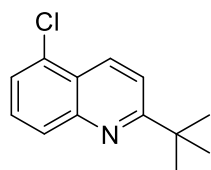


3v: 17.5 mg, 63%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 8.18 (s, 1H), 7.71 (d, $J = 8.8$ Hz, 1H), 7.48 (dd, $J = 8.8, 2.0$ Hz, 1H), 7.27 (s, 1H), 2.59 (s, 4H), 1.36 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.14, 147.04, 142.77, 131.12, 127.72, 124.19, 123.83, 121.72, 118.22, 36.99, 28.98, 17.87. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{16}\text{BrN}$, 278.0539; found, 278.0541.

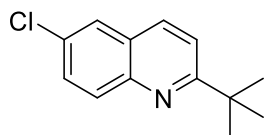


3w: 19.5 mg, 73%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 8.15 (s, 1H), 8.08 (d, $J = 8.6$ Hz, 1H), 7.75 (dd, $J = 8.8, 1.6$ Hz, 1H), 7.36 (s, 1H), 2.65 (s, 4H), 1.38 (s, 10H). ^{19}F NMR (377 MHz, CDCl_3) δ -61.88. ^{13}C NMR (101 MHz, CDCl_3) δ 170.31, 145.50, 129.98, 126.10 ($^2J_{\text{CF}} = 32.3$ Hz), 124.66

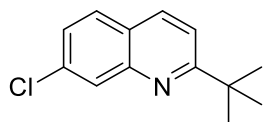
($^3J_{\text{CF}} = 8.0$ Hz), 123.35, 120.51 ($^1J_{\text{CF}} = 299$ Hz), 120.43 ($4J_{\text{CF}} = 8.1$ Hz), 120.21 ($4J_{\text{CF}} = 9.0$ Hz), 37.16, 28.95, 17.87. ^{19}F NMR (377 MHz, CDCl_3) δ -61.88. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{16}\text{F}_3\text{N}$, 268.1308; found, 268.1340.



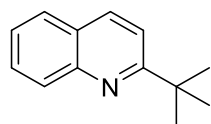
3x: 17.7 mg, 81%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 8.39 (d, $J = 8.9$ Hz, 1H), 7.91 (d, $J = 7.9$ Hz, 1H), 7.56 – 7.43 (m, 3H), 1.39 (s, 10H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.03, 147.08, 131.66, 129.94, 127.65, 127.57, 124.62, 123.54, 118.09, 37.11, 29.00. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{14}\text{ClN}$, 220.0888; found, 220.0889.



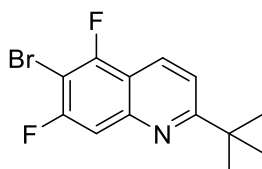
3y: 13.6 mg, 62%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 7.90 (dd, $J = 8.7, 5.0$ Hz, 1H), 7.66 (d, $J = 2.3$ Hz, 1H), 7.51 (dd, $J = 9.0, 2.3$ Hz, 1H), 7.46 (d, $J = 8.7$ Hz, 1H), 1.38 (s, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.58, 144.73, 133.93, 130.14, 129.98, 128.78, 125.97, 124.85, 118.09, 37.15, 29.01. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{14}\text{ClN}$, 220.0888; found, 220.0890.



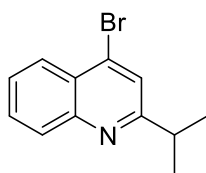
3z: 17.1 mg, 78%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 8.08 – 7.90 (m, 1H), 7.62 (d, $J = 8.6$ Hz, 1H), 7.44 (d, $J = 8.7$ Hz, 1H), 7.35 (dd, $J = 8.6, 1.7$ Hz, 1H), 1.38 (s, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.40, 146.75, 134.62, 133.72, 127.42, 127.38, 126.35, 125.59, 123.74, 117.40, 37.20, 29.01. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{14}\text{ClN}$, 220.0888; found, 220.0891.



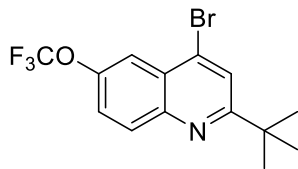
3aa: 11.8 mg, 64%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 8.6$ Hz, 1H), 7.67 (d, $J = 8.1$ Hz, 1H), 7.61 – 7.56 (m, 1H), 7.44 (d, $J = 8.7$ Hz, 1H), 7.39 (t, $J = 7.5$ Hz, 1H), 1.39 (s, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.20, 146.34, 134.84, 128.33, 127.96, 126.18, 125.39, 124.59, 117.19, 37.08, 29.10. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{15}\text{N}$, 186.1277; found, 186.1278.



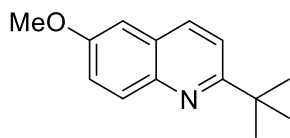
3ab: 23.6 mg, 79%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.19 (d, $J = 8.9$ Hz, 1H), 7.54 (dd, $J = 9.6, 1.2$ Hz, 1H), 7.49 (d, $J = 8.9$ Hz, 1H), 1.37 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 171.99, 158.58 ($^1J_{\text{CF}} = 247.5$ Hz), 156.70 ($^1J_{\text{CF}} = 256.5$ Hz), 154.16, 146.59 ($^3J_{\text{CF}} = 13.1$ Hz), 128.76 ($^4J_{\text{CF}} = 3.0$ Hz), 118.46 ($^4J_{\text{CF}} = 3.0$ Hz), 114.44 ($^2J_{\text{CF}} = 18.2$ Hz), 110.10 ($^4J_{\text{CF}} = 4.0$ Hz), 109.88 ($^4J_{\text{CF}} = 4.0$ Hz), 95.35 ($^4J_{\text{CF}} = 25.8$ Hz), 38.48, 29.91. $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -105.85, -113.67. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{12}\text{BrF}_2\text{N}$, 300.0194; found, 300.0193.



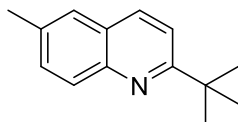
3ac: 12.5 mg, 50%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.14 (d, $J = 8.3$ Hz, 1H), 8.04 (d, $J = 8.5$ Hz, 1H), 7.75 – 7.68 (m, 1H), 7.64 (s, 1H), 7.58 (t, $J = 7.6$ Hz, 1H), 3.23 (dt, $J = 13.9, 6.9$ Hz, 1H), 1.39 (d, $J = 6.9$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.57, 147.32, 133.29, 129.20, 128.32, 125.90, 125.52, 125.43, 122.24, 36.03, 21.37. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{12}\text{BrN}$, 250.0226; found, 250.0229.



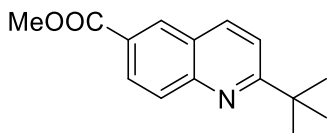
3ad: 20.5 mg, 59%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.07 (dd, $J = 17.9, 5.2$ Hz, 2H), 7.50 – 7.38 (m, 2H), 1.38 (s, 9H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -57.87. $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 167.70, 159.7 ($^1J_{\text{CF}} = 248.4$ Hz), 144.30, 140.47, 131.28 ($^3J_{\text{CF}} = 9.0$ Hz), 124.44 ($^3J_{\text{CF}} = 10.0$ Hz), 119.04 ($^2J_{\text{CF}} = 26.3$ Hz), 118.07, 106.46 ($^2J_{\text{CF}} = 24.4$ Hz), 37.18, 28.93. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{13}\text{BrF}_3\text{NO}$, 348.0205; found, 348.0206.



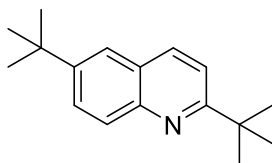
3ae: 19.4 mg, 90%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.6$ Hz, 1H), 7.48 (d, $J = 8.7$ Hz, 1H), 7.34 – 7.25 (m, 1H), 7.04 (d, $J = 2.7$ Hz, 1H), 3.92 (s, 2H), 1.46 (s, 5H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.76, 156.12, 142.34, 133.77, 129.71, 126.17, 120.44, 117.41, 103.86, 54.44, 36.79, 29.17. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{17}\text{NO}$, 216.1383; found, 216.1382.



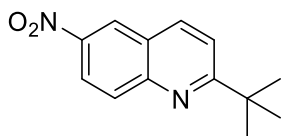
3af: 18.1 mg, 91%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 7.88 (t, $J = 7.7$ Hz, 1H), 7.41 (dd, $J = 13.5, 5.6$ Hz, 1H), 2.43 (s, 2H), 1.38 (s, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.34, 145.98, 135.31, 135.27, 131.24, 129.08, 126.45, 126.15, 118.21, 38.02, 30.21, 21.53. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{17}\text{N}$, 200.1434; found, 200.1433.



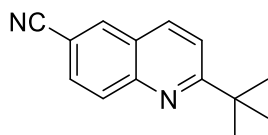
3ag: 23.1 mg, 95%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 8.53 (d, $J = 1.5$ Hz, 1H), 8.25 (dd, $J = 8.8, 1.8$ Hz, 1H), 8.16 (d, $J = 8.7$ Hz, 1H), 8.09 (d, $J = 8.8$ Hz, 1H), 7.58 (d, $J = 8.7$ Hz, 1H), 3.98 (s, 3H), 1.47 (s, 10H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.83, 166.94, 149.38, 137.09, 130.51, 129.67, 128.58, 127.15, 125.56, 119.11, 52.34, 38.46, 30.04. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_2$, 244.1332; found, 244.1333.



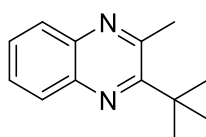
3ah: 20.0 mg, 83%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 7.95 (t, $J = 10.2$ Hz, 1H), 7.68 (dd, $J = 8.9, 2.1$ Hz, 1H), 7.60 (d, $J = 2.1$ Hz, 1H), 7.41 (d, $J = 8.6$ Hz, 1H), 1.38 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.64, 148.43, 135.97, 128.84, 127.97, 126.76, 126.09, 122.24, 118.11, 38.02, 34.83, 31.29, 30.23. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{23}\text{N}$, 242.1903; found, 242.1906.



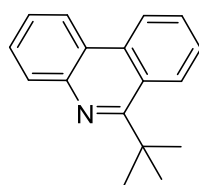
3ai: 7.0 mg, 30%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 8.67 (s, 1H), 8.36 (d, $J = 9.1$ Hz, 1H), 8.18 (d, $J = 8.7$ Hz, 1H), 8.09 (d, $J = 9.2$ Hz, 1H), 7.61 (d, $J = 8.7$ Hz, 1H), 1.41 (s, 11H). ^{13}C NMR (101 MHz, CDCl_3) δ 173.52, 149.64, 137.54, 131.13, 125.15, 124.15, 122.52, 120.26, 38.74, 29.94. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_2$, 231.1128; found, 231.1130.



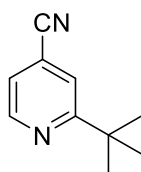
3aj: 5.9 mg, 28%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 8.08 (dd, $J = 19.7, 5.0$ Hz, 1H), 7.74 (dd, $J = 8.7, 1.7$ Hz, 1H), 7.58 (d, $J = 8.8$ Hz, 1H), 1.40 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.72, 135.11, 132.51, 128.80, 124.75, 118.99, 117.90, 108.20, 37.58, 28.91. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{14}\text{N}_2$, 211.1230; found, 211.1231.



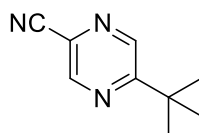
3ak: 12.2 mg, 61%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 8.03 – 7.79 (m, 1H), 7.66 – 7.43 (m, 1H), 2.87 (s, 3H), 1.48 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 160.90, 151.60, 139.04, 138.91, 127.97, 127.92, 127.58, 126.69, 37.75, 28.38, 25.20. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{16}\text{N}_2$, 201.1386; found, 201.1387.



3al: 10.6 mg, 45%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 8.76 – 8.47 (m, 3H), 8.12 (d, $J = 7.9$ Hz, 1H), 7.78 (t, $J = 7.3$ Hz, 1H), 7.73 – 7.56 (m, 3H), 1.73 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.60, 132.95, 129.21, 128.22, 127.33, 127.21, 127.11, 126.99, 125.41, 125.15, 124.90, 123.26, 122.69, 122.36, 121.93, 120.56, 120.45, 117.45, 39.15, 39.06, 34.26, 30.20, 30.15. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{17}\text{N}$, 236.1434; found, 236.1433.

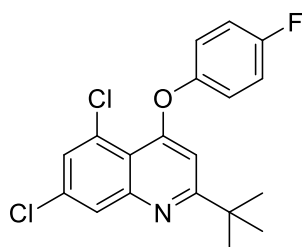


3am: 3.9 mg, 24%, colorless oil liquid. Purification by flash column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 8.73 (d, $J = 4.9$ Hz, 1H), 7.56 (s, 1H), 7.33 (d, $J = 4.6$ Hz, 1H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.03, 148.56, 121.06, 120.05, 119.51, 116.06, 36.88, 28.83. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{12}\text{N}_2$, 161.1073; found, 161.1076.



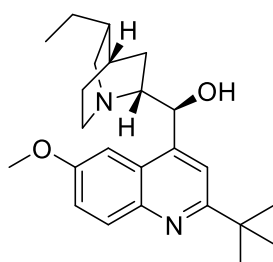
3an: 5.6 mg, 35%, colorless oil liquid. Purification by flash column

chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^{13}C NMR (101 MHz, CDCl_3) δ 166.17, 148.38, 145.22, 129.28, 116.24, 37.64, 29.51. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_9\text{H}_{11}\text{N}_3$, 162.1026; found, 162.1029.



5a: 25.4 mg, 70%, colorless oil liquid. Purification by flash

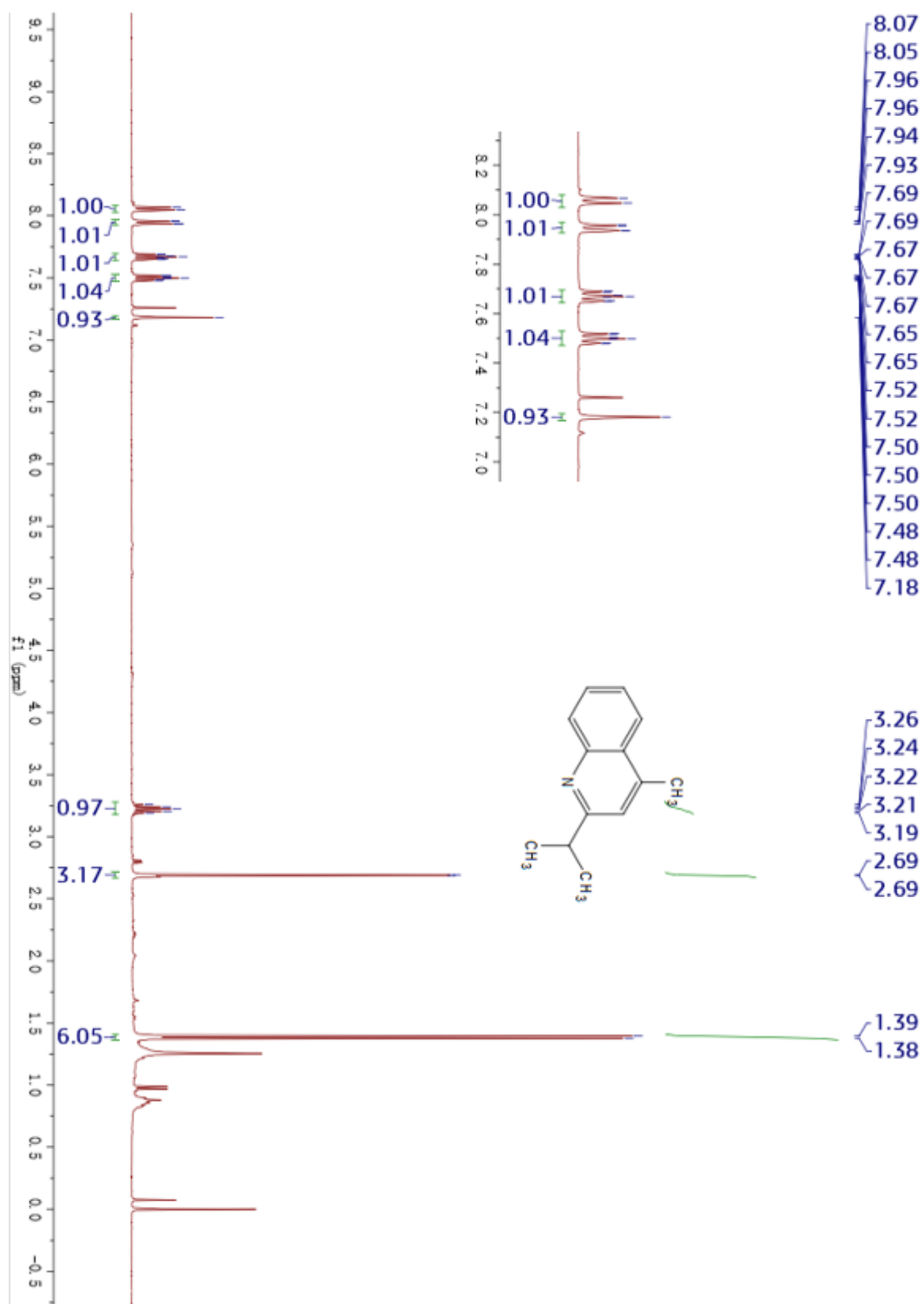
column chromatography on silica gel (eluent: Petroleum ether/ EtOAc = 60/1). ^1H NMR (400 MHz, CDCl_3) δ 7.91 (s, 1H), 7.43 (d, $J = 2.0$ Hz, 1H), 7.14 – 6.95 (m, 4H), 6.68 (s, 1H), 1.23 (s, 10H). ^{19}F NMR (377 MHz, $\text{CH}_3\text{CN} + \text{D}_2\text{O}$) δ -120.24. ^{13}C NMR (101 MHz, $\text{CH}_3\text{CN} + \text{D}_2\text{O}$) δ 169.65, 159.47, 157.18 ($^1J_{\text{CF}} = 246.44$ Hz), 148.49, 148.08, 132.06, 127.14, 126.14, 125.36, 119.10 ($^3J_{\text{CF}} = 8.0$ Hz), 114.43 ($^2J_{\text{CF}} = 23.2$ Hz), 102.14, 35.76, 27.19. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{16}\text{Cl}_2\text{FNO}$, 364.0666; found, 364.0665.

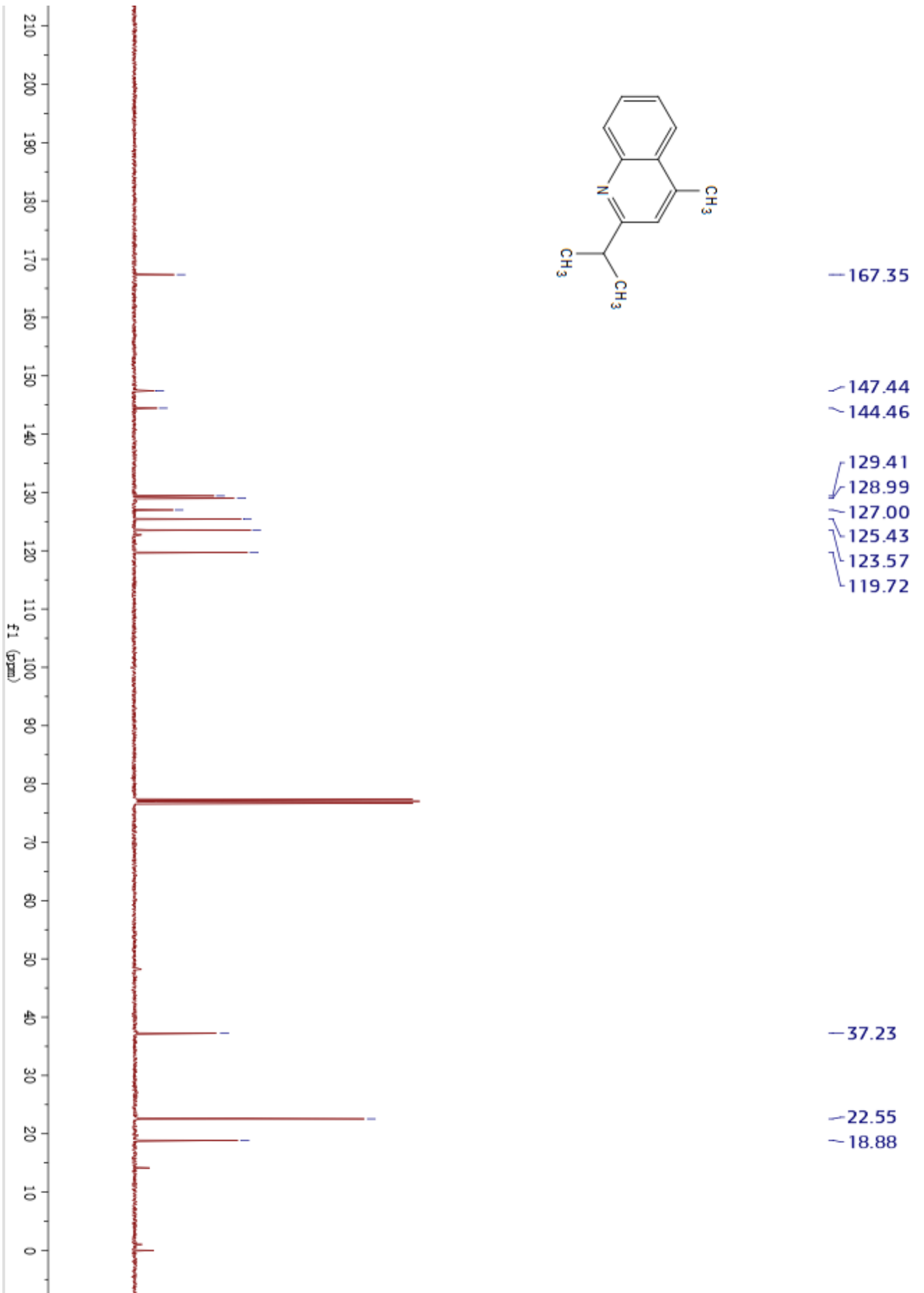
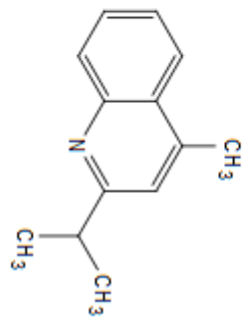


5b: 30. mg, 79%, yellow oil liquid. Purification by flash column

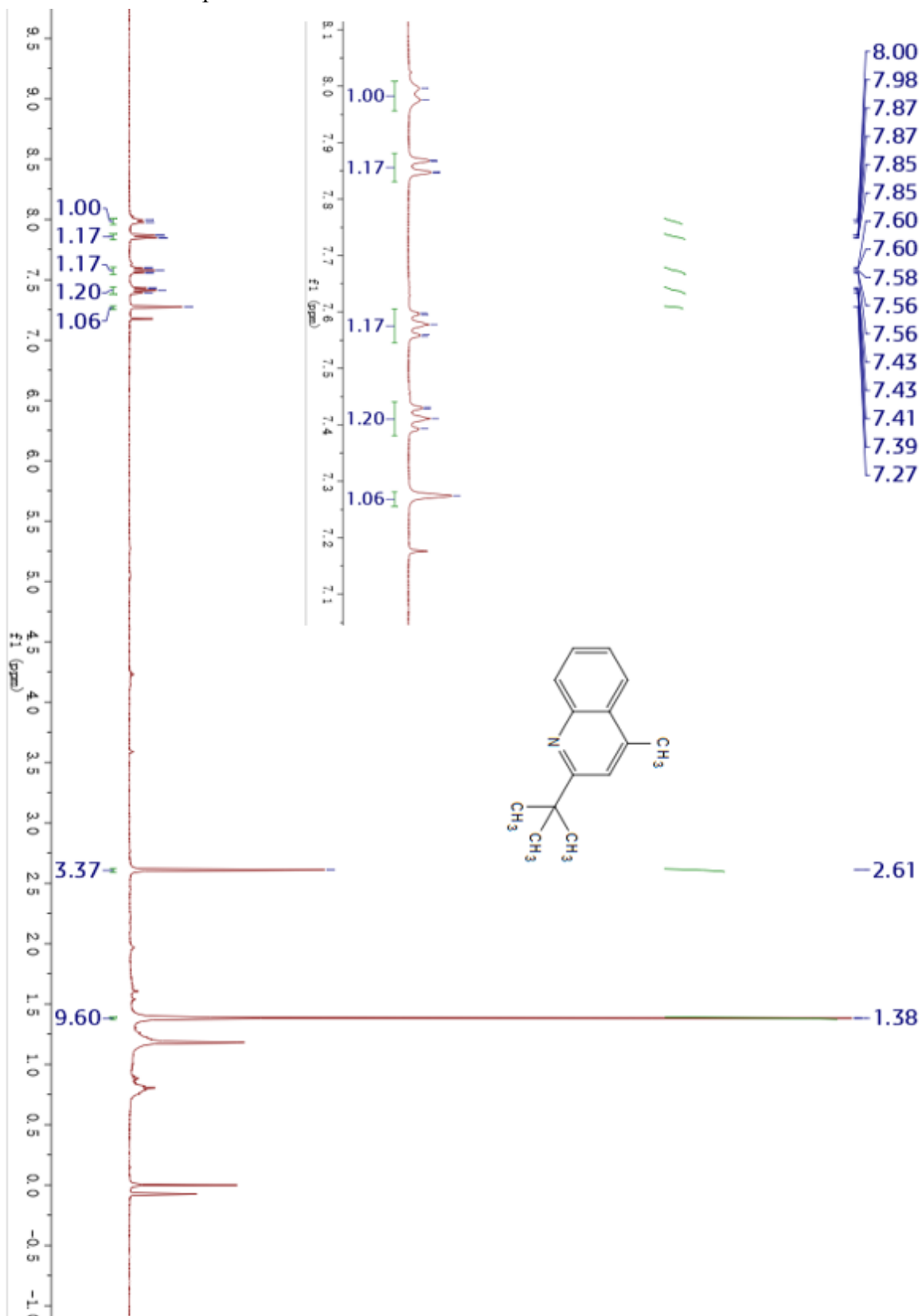
chromatography on silica gel (eluent: DCM/ MeOH = 30/1). ^1H NMR (400 MHz, CDCl_3) δ 7.82 – 7.49 (m, 1H), 6.93 (d, $J = 9.2$ Hz, 1H), 6.79 (s, 1H), 6.34 (s, 1H), 6.01 (s, 1H), 4.09 (dt, $J = 21.4, 10.6$ Hz, 1H), 3.60 (s, 1H), 3.45 – 2.93 (m, 2H), 2.44 – 2.20 (m, 1H), 1.91 (s, 1H), 1.83 – 1.51 (m, 3H), 1.46 (s, 4H), 1.24 (t, $J = 7.1$ Hz, 1H), 0.93 (t, $J = 6.9$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.84, 157.46, 131.15, 128.87, 123.17, 121.50, 115.31, 98.95, 66.52, 60.42, 60.35, 55.96, 49.93, 49.32, 37.85, 35.30, 30.18, 25.31, 24.32, 23.94, 17.39, 11.55. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{34}\text{N}_2\text{O}_2$, 383.2693; found, 383.2694.

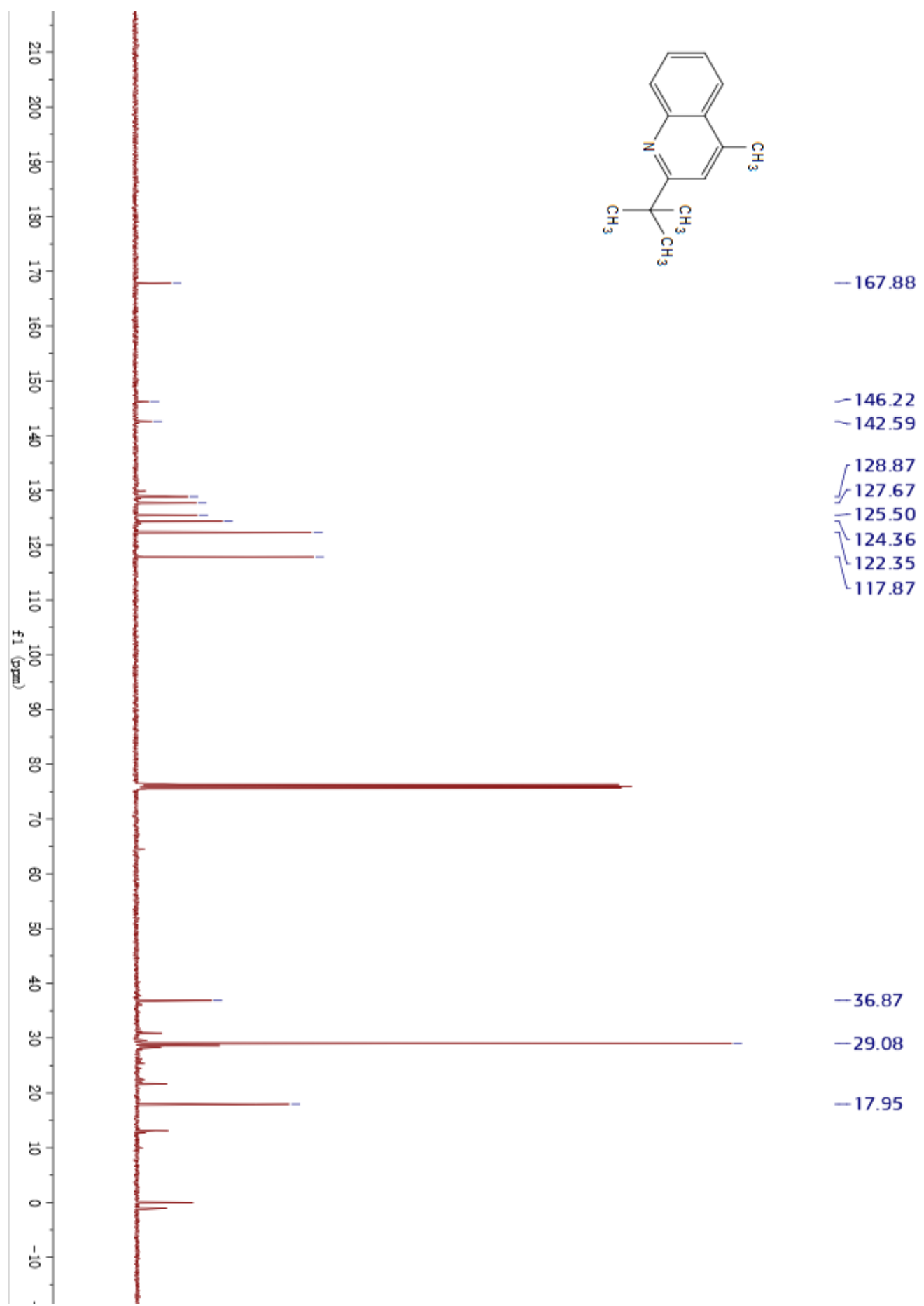
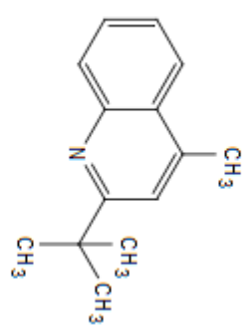
^1H and ^{13}C NMR spectra of **3a**



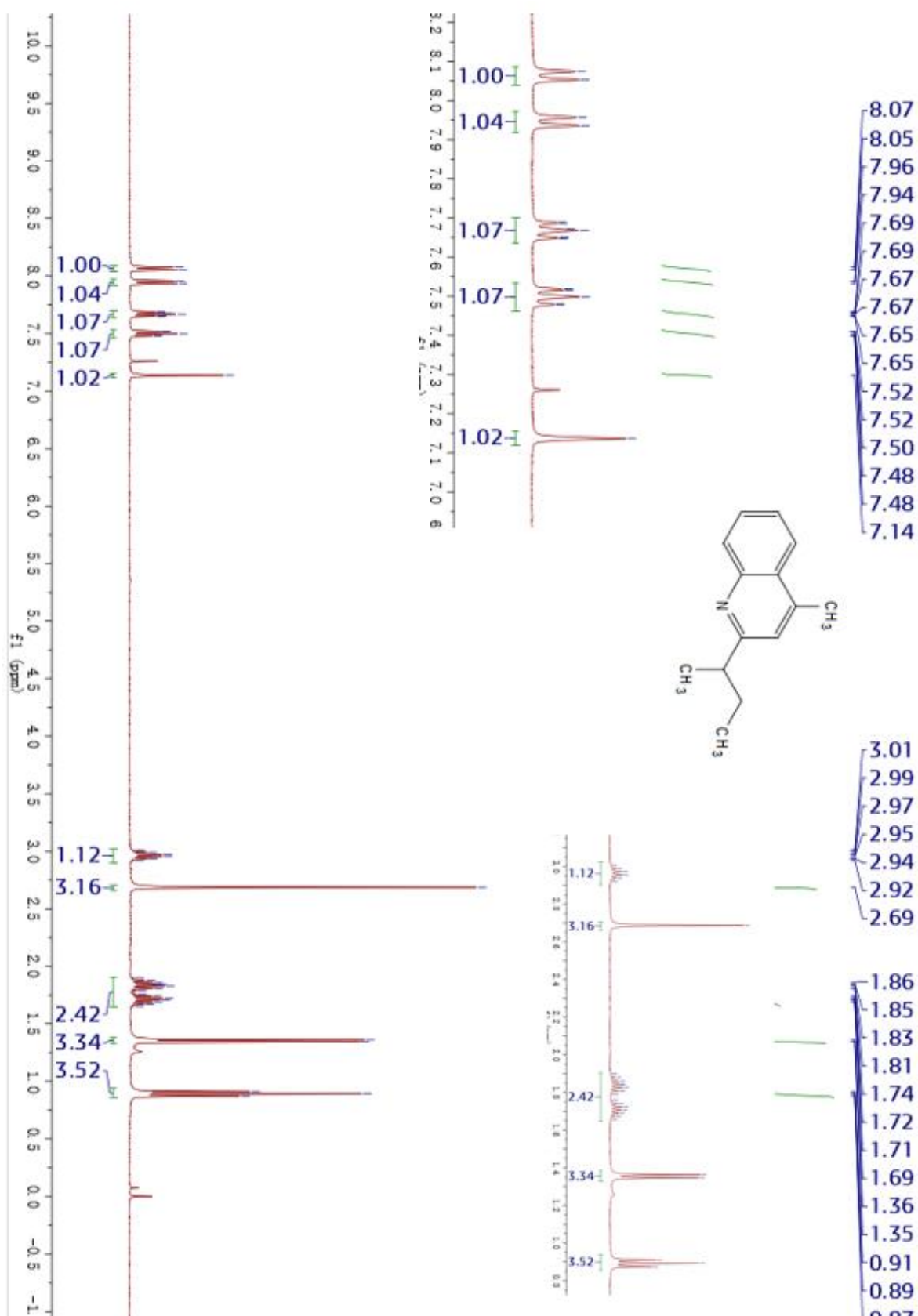


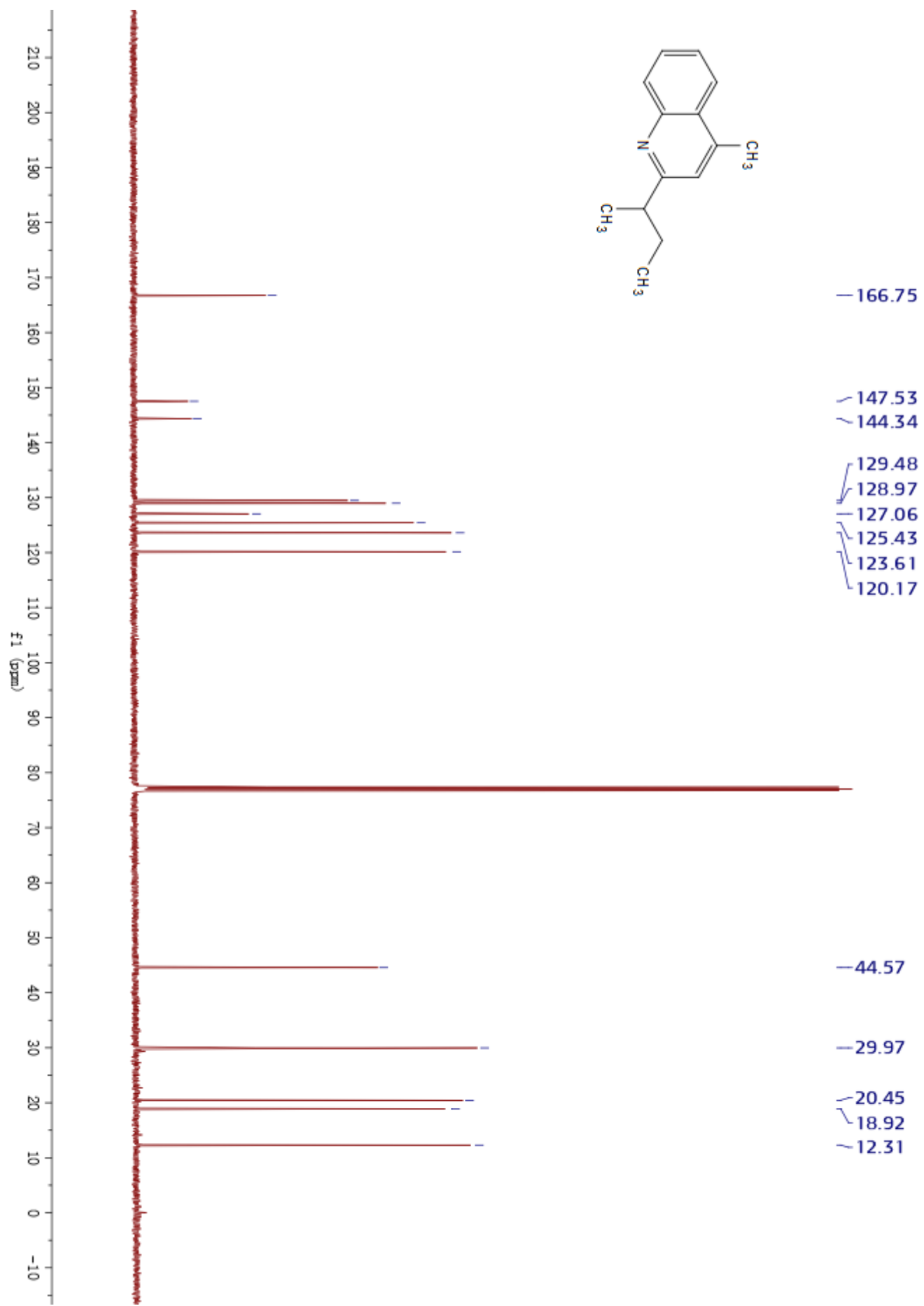
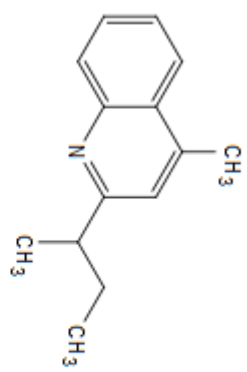
^1H and ^{13}C NMR spectra of **3b**



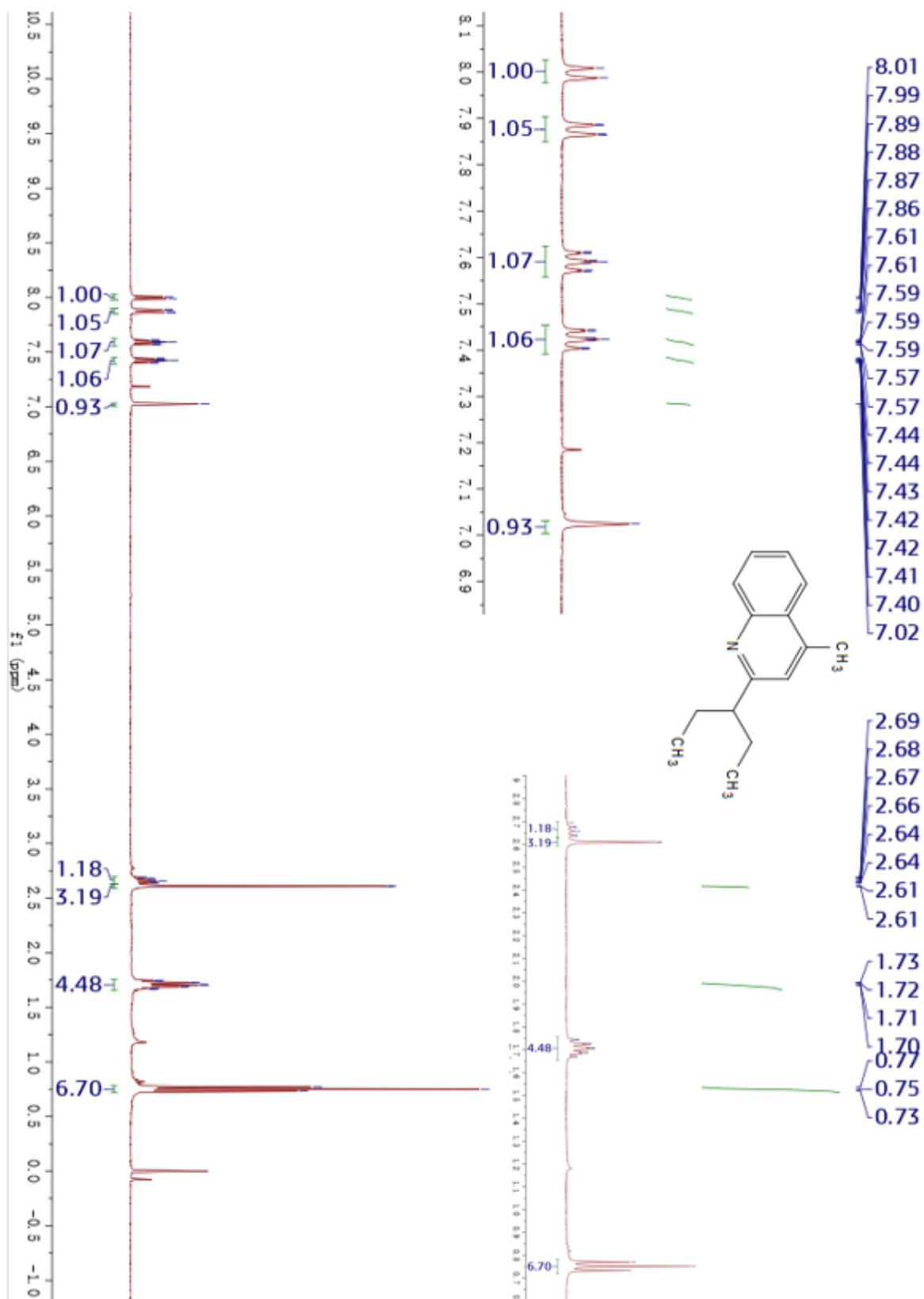


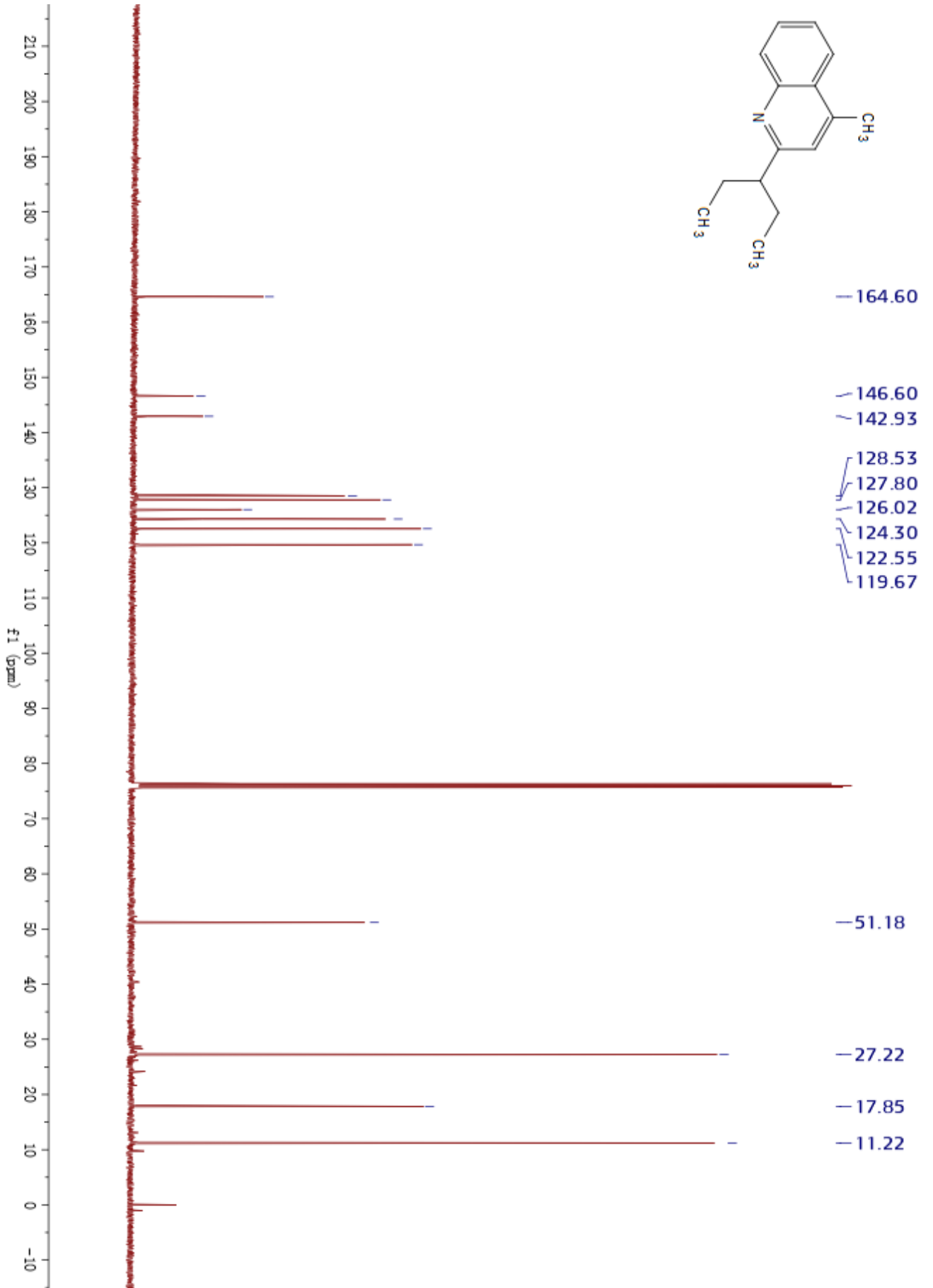
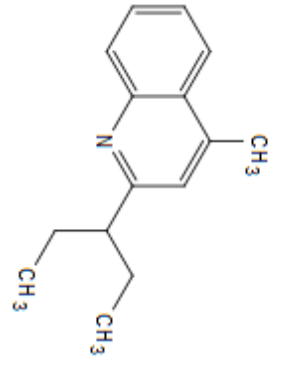
^1H and ^{13}C NMR spectra of **3c**



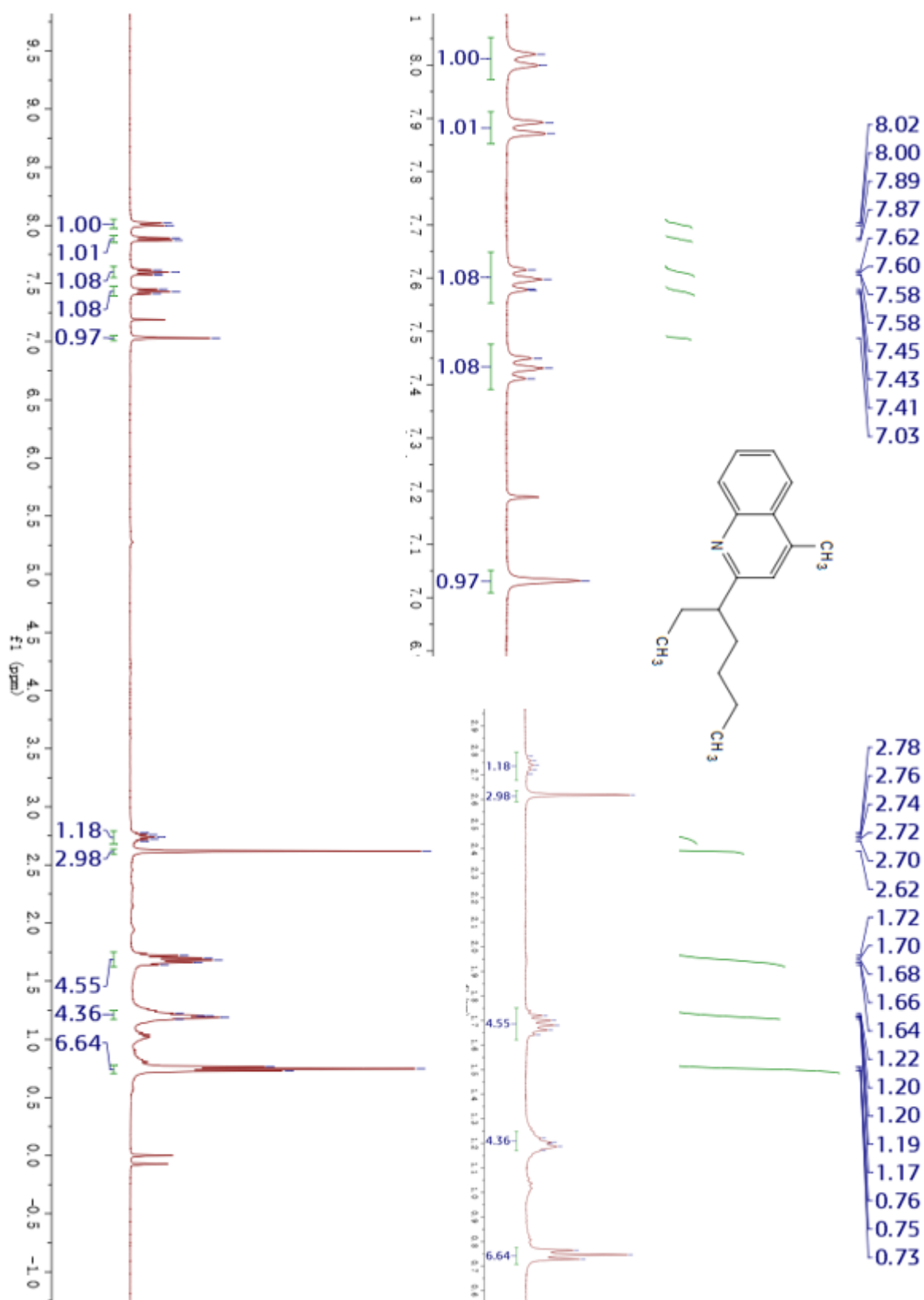


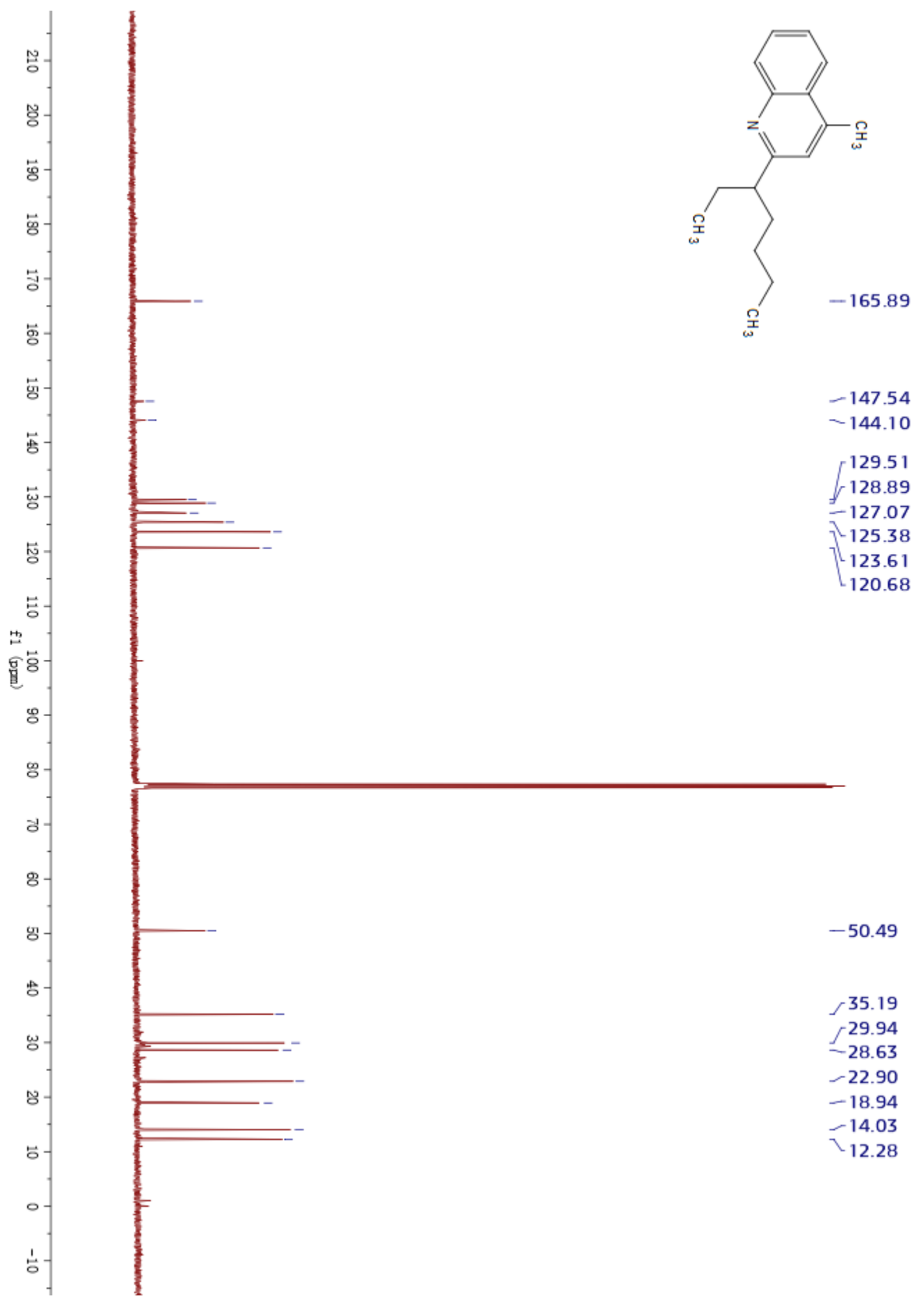
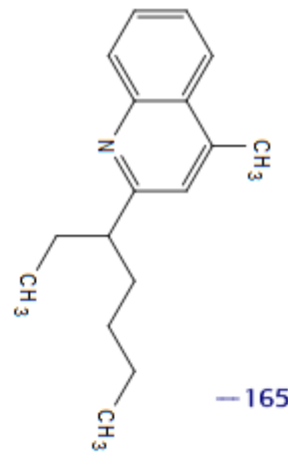
^1H and ^{13}C NMR spectra of **3d**



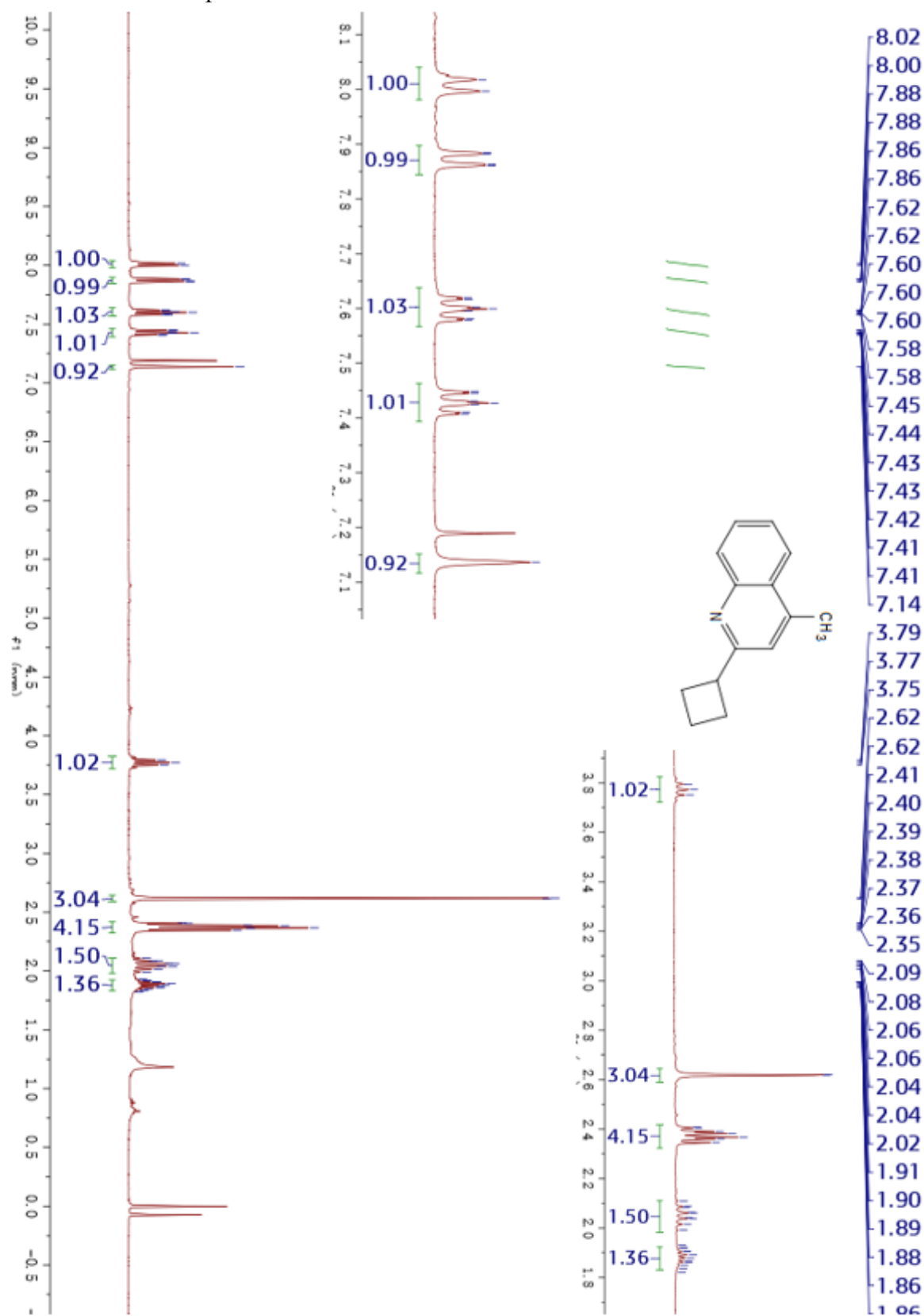


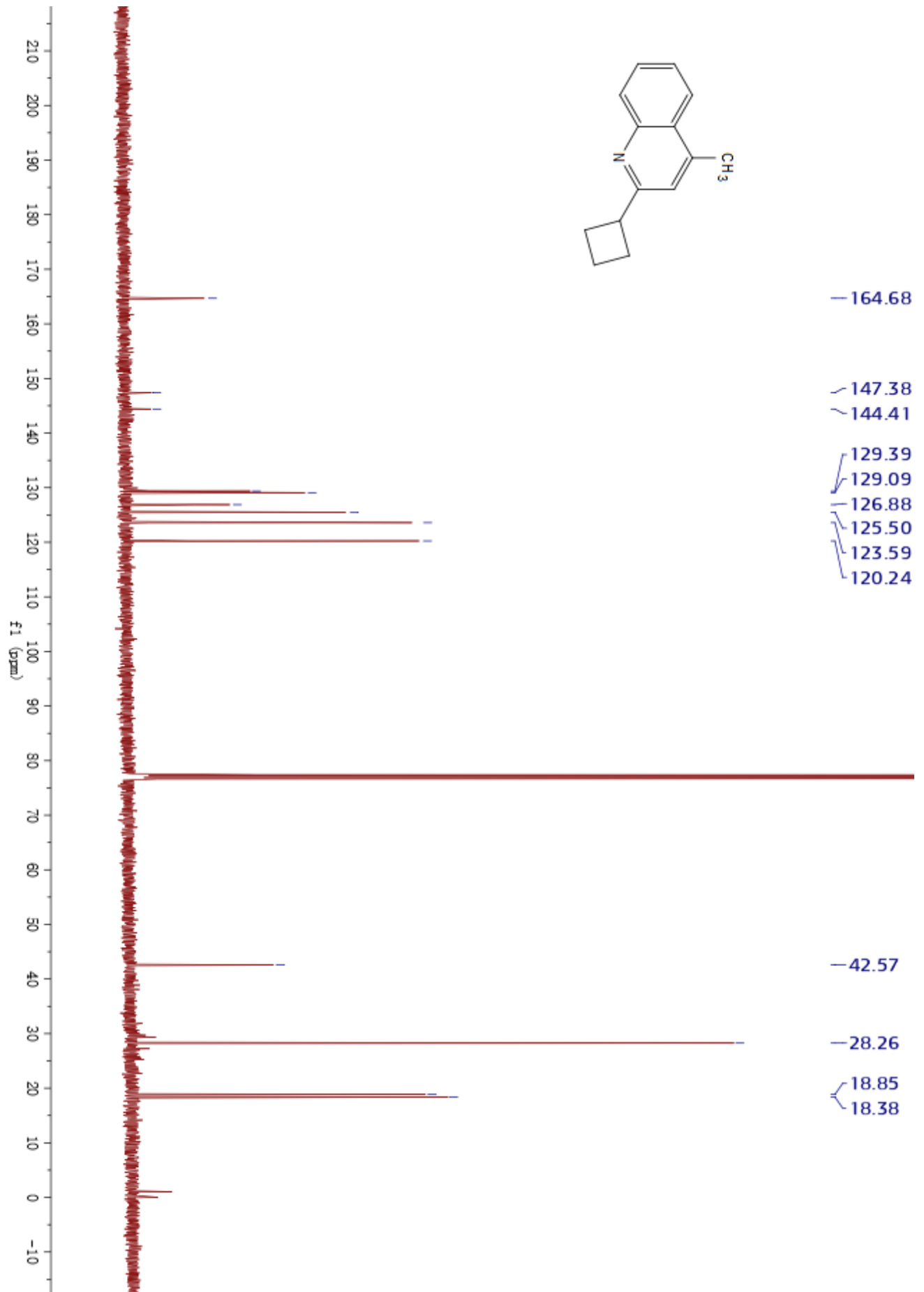
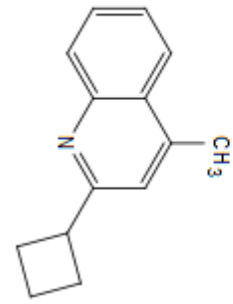
^1H and ^{13}C NMR spectra of **3e**



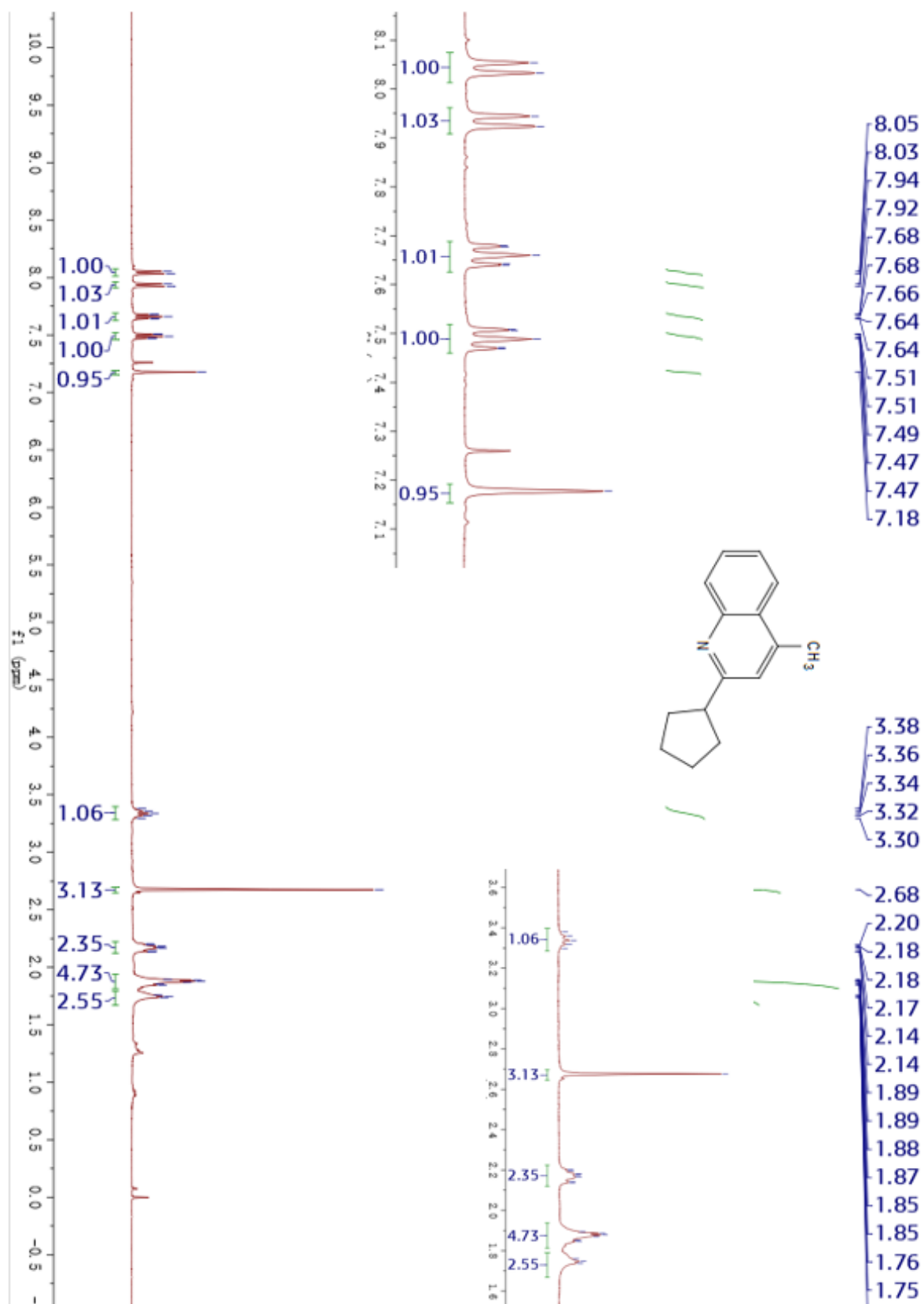


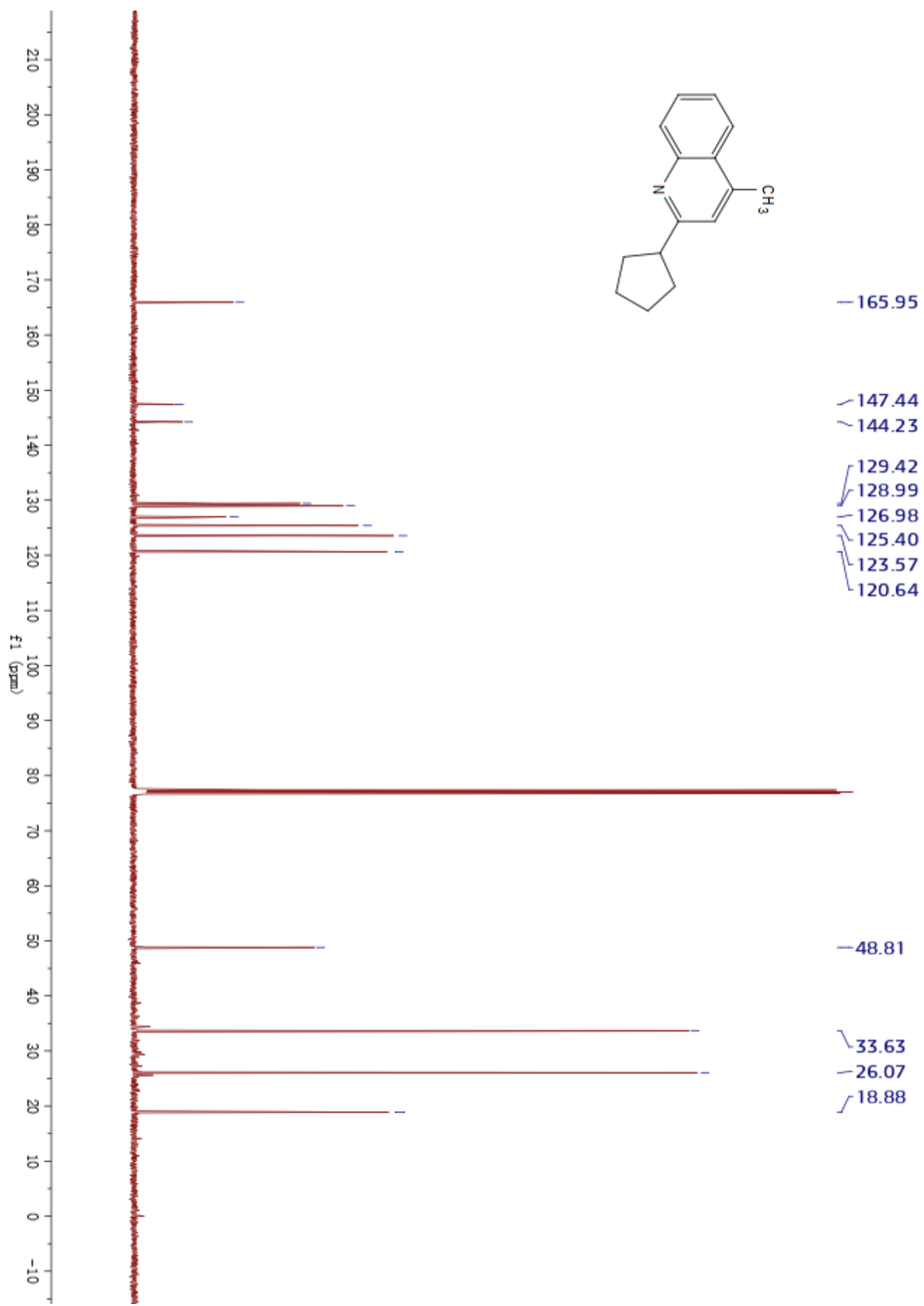
^1H and ^{13}C NMR spectra of **3f**



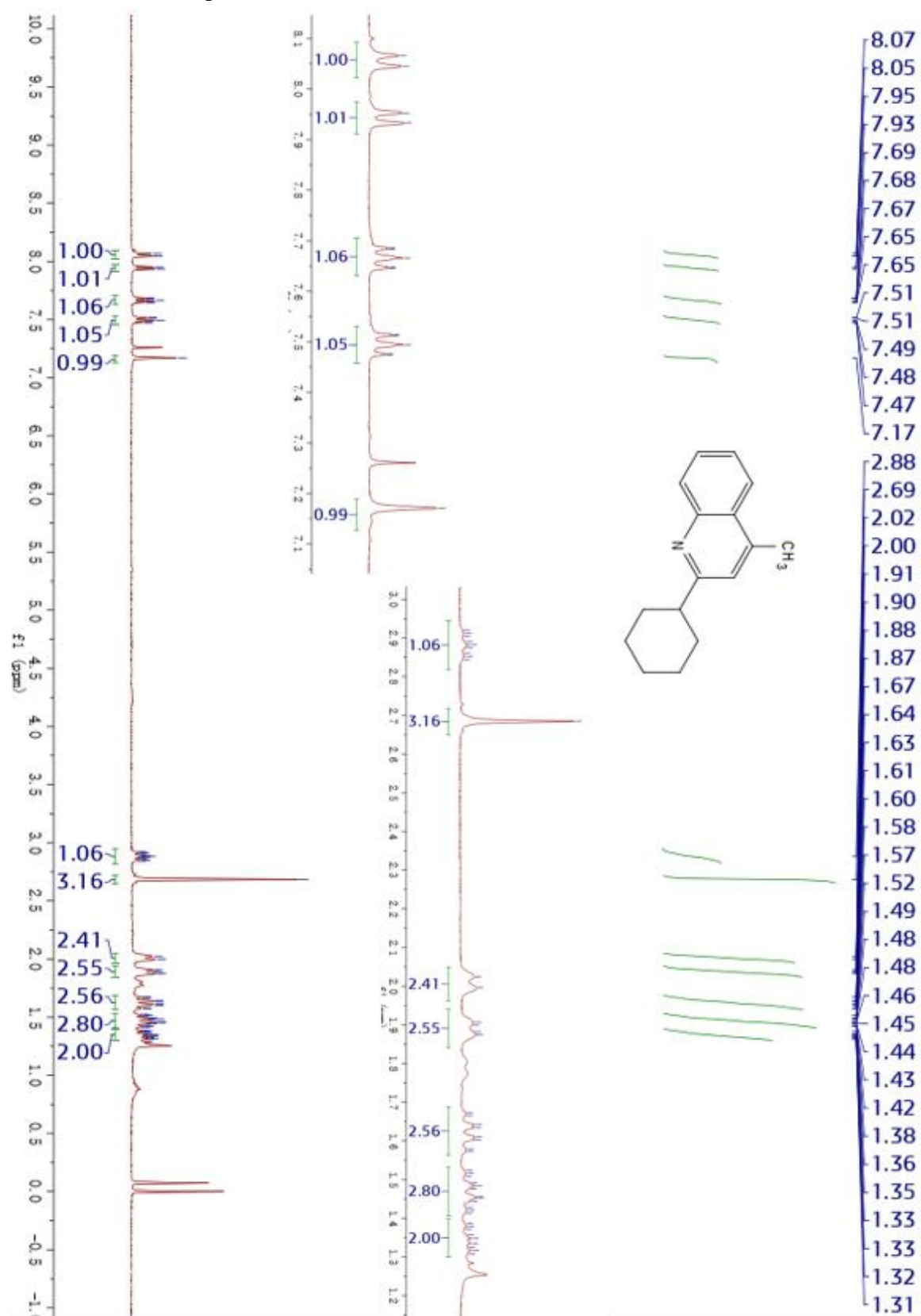


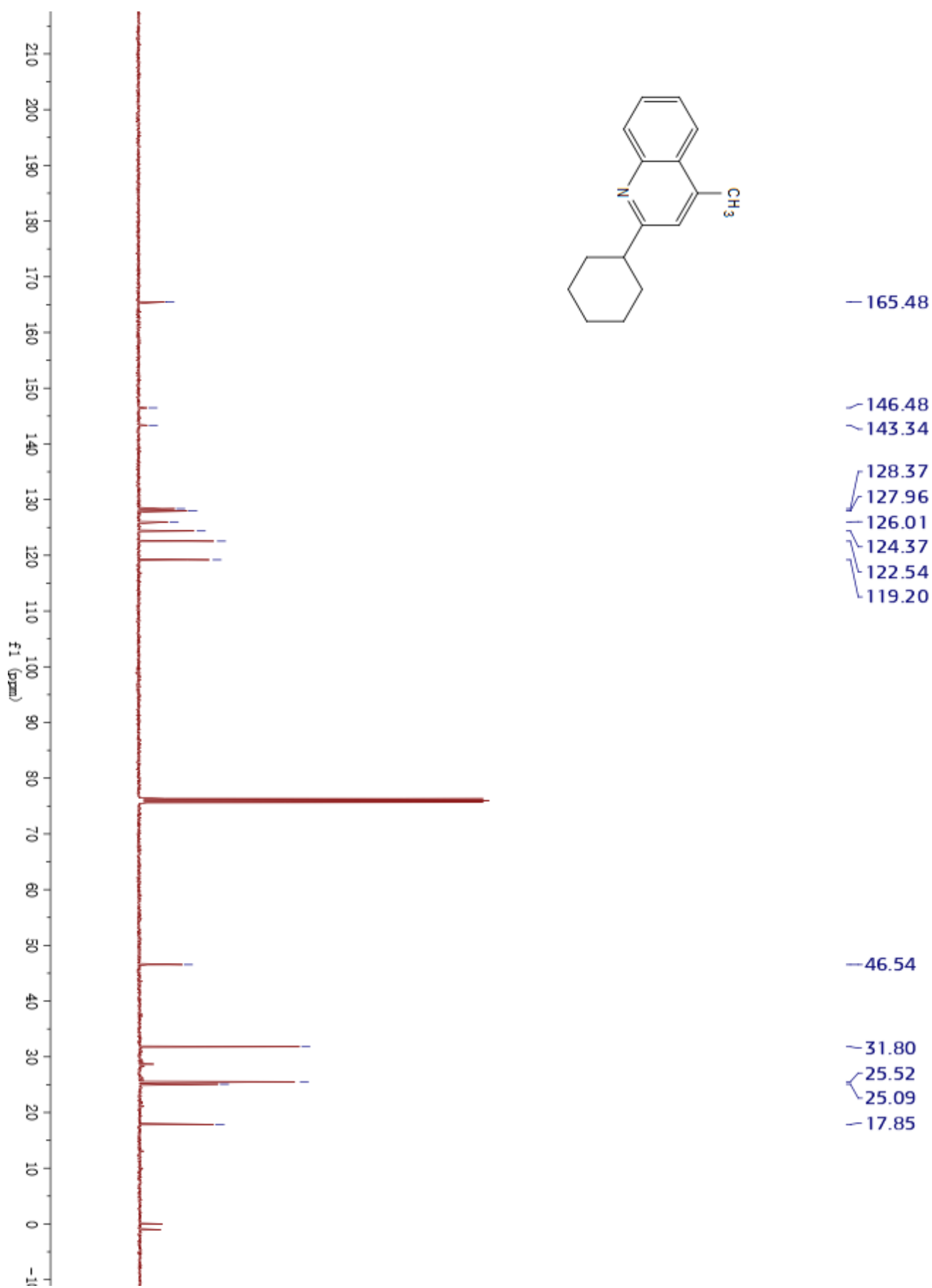
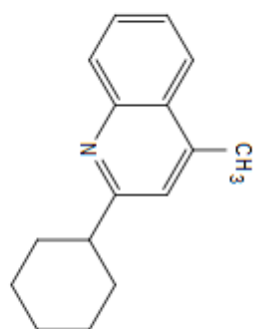
^1H and ^{13}C NMR spectra of **3g**



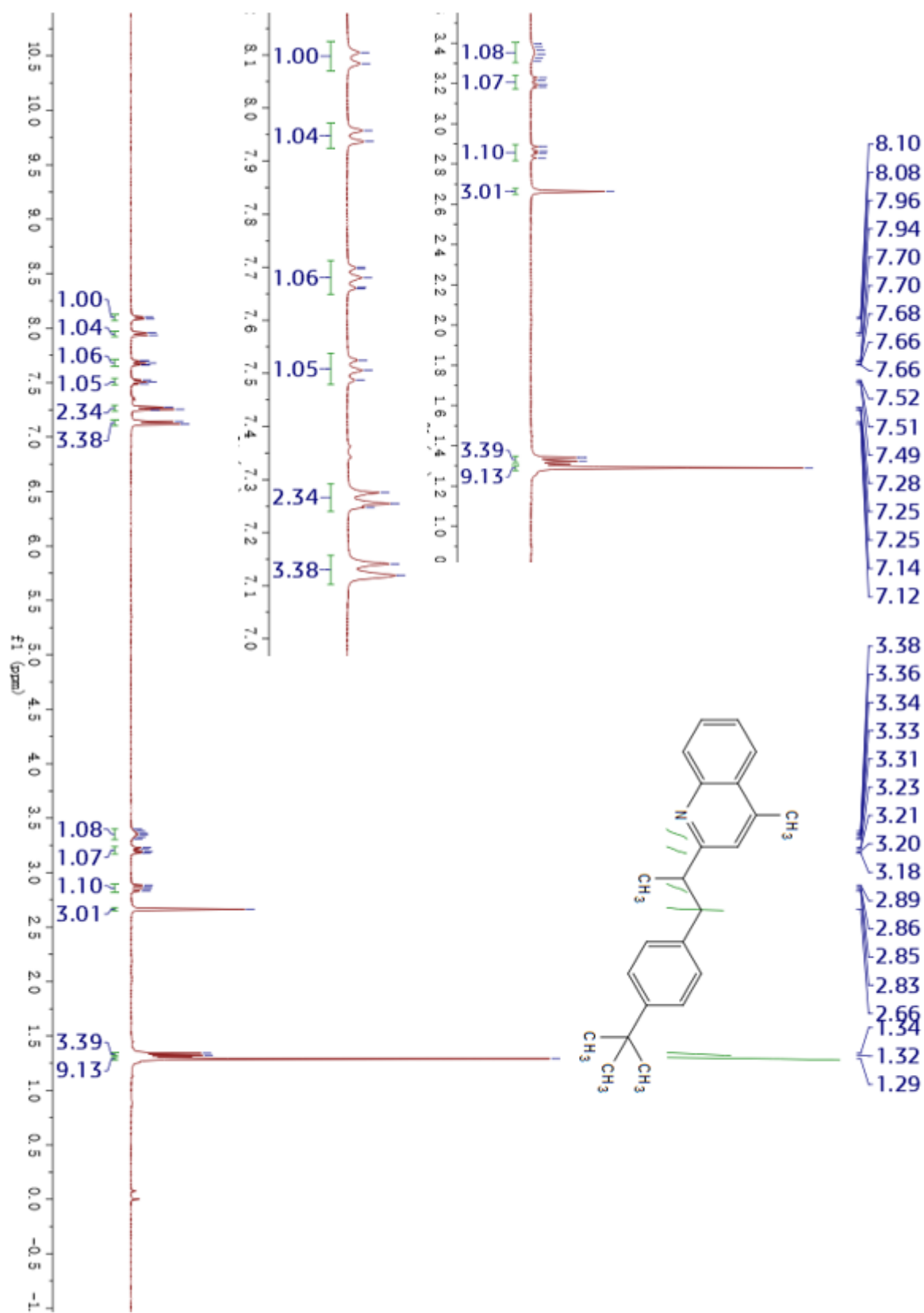


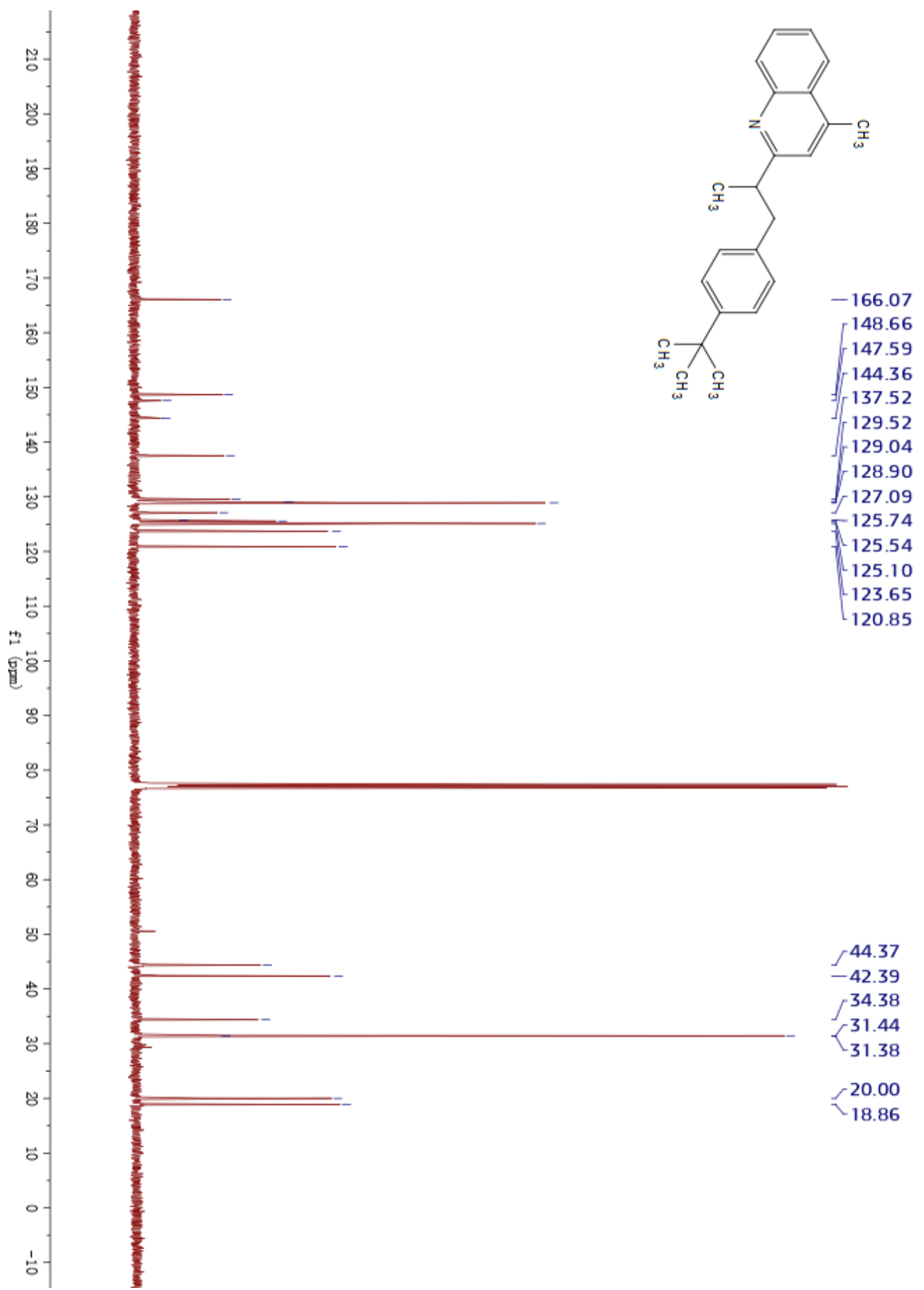
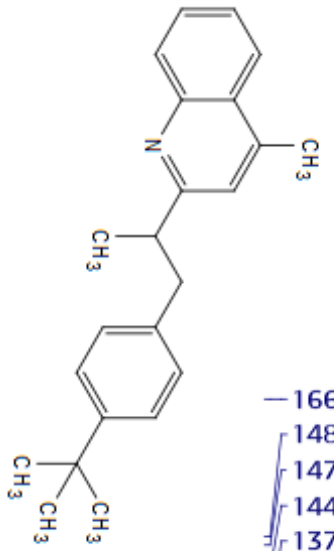
^1H and ^{13}C NMR spectra of **3h**



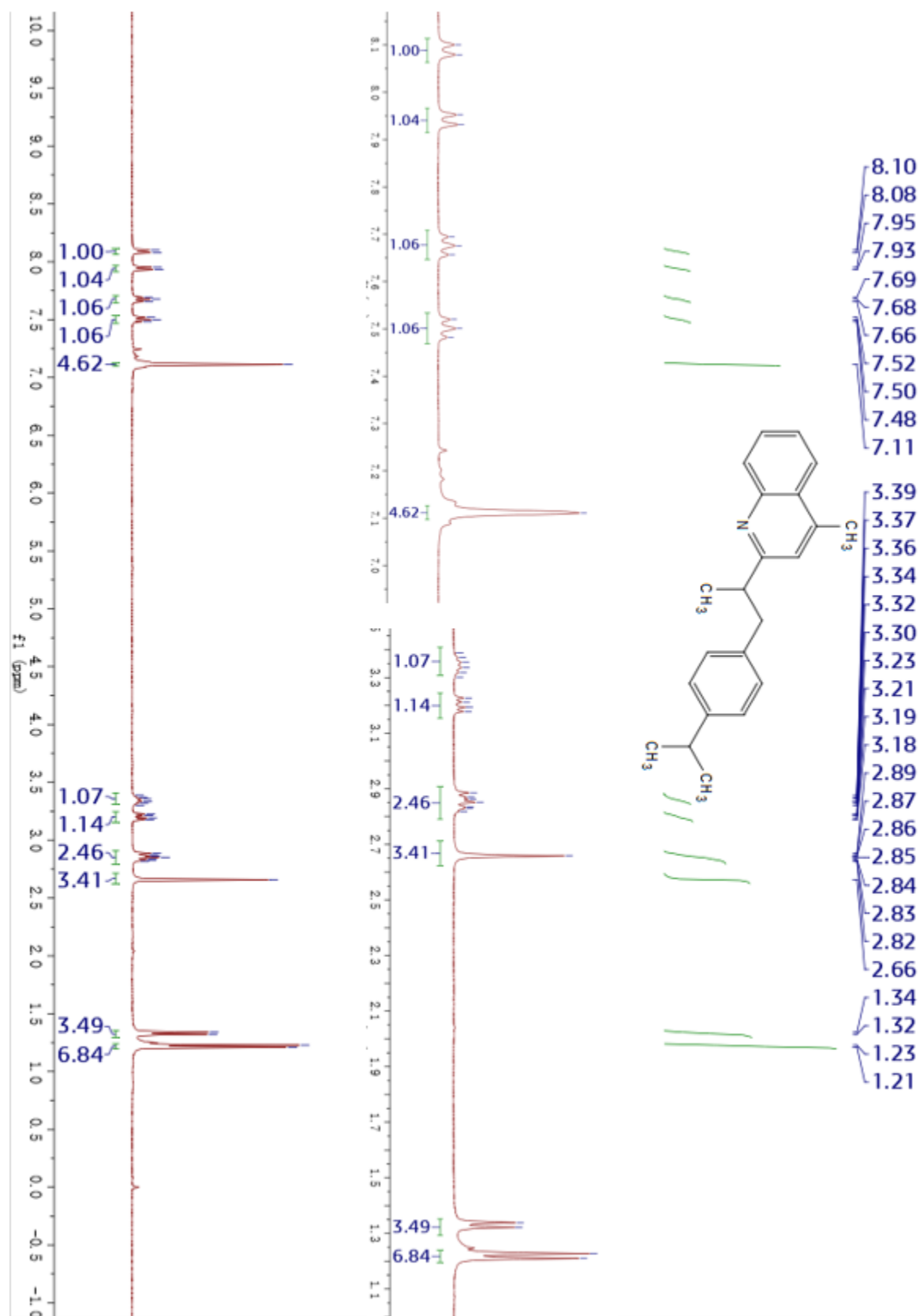


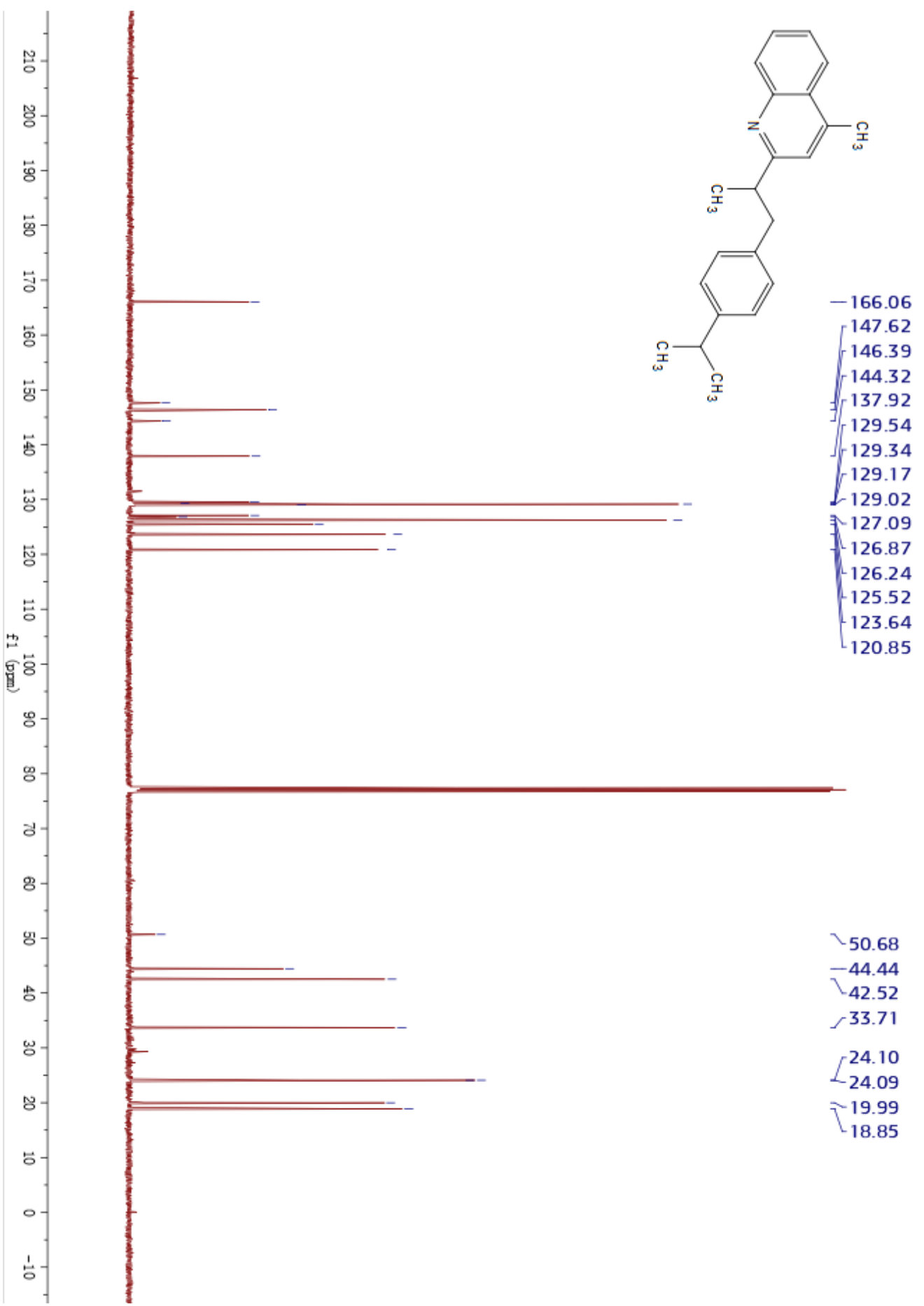
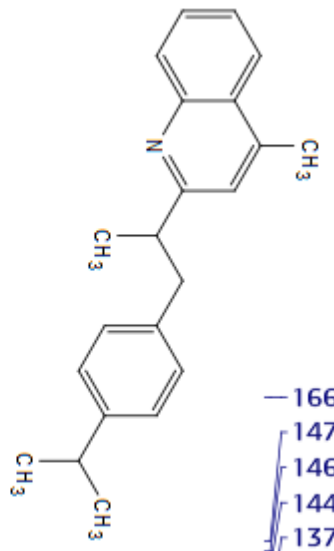
^1H and ^{13}C NMR spectra of **3i**



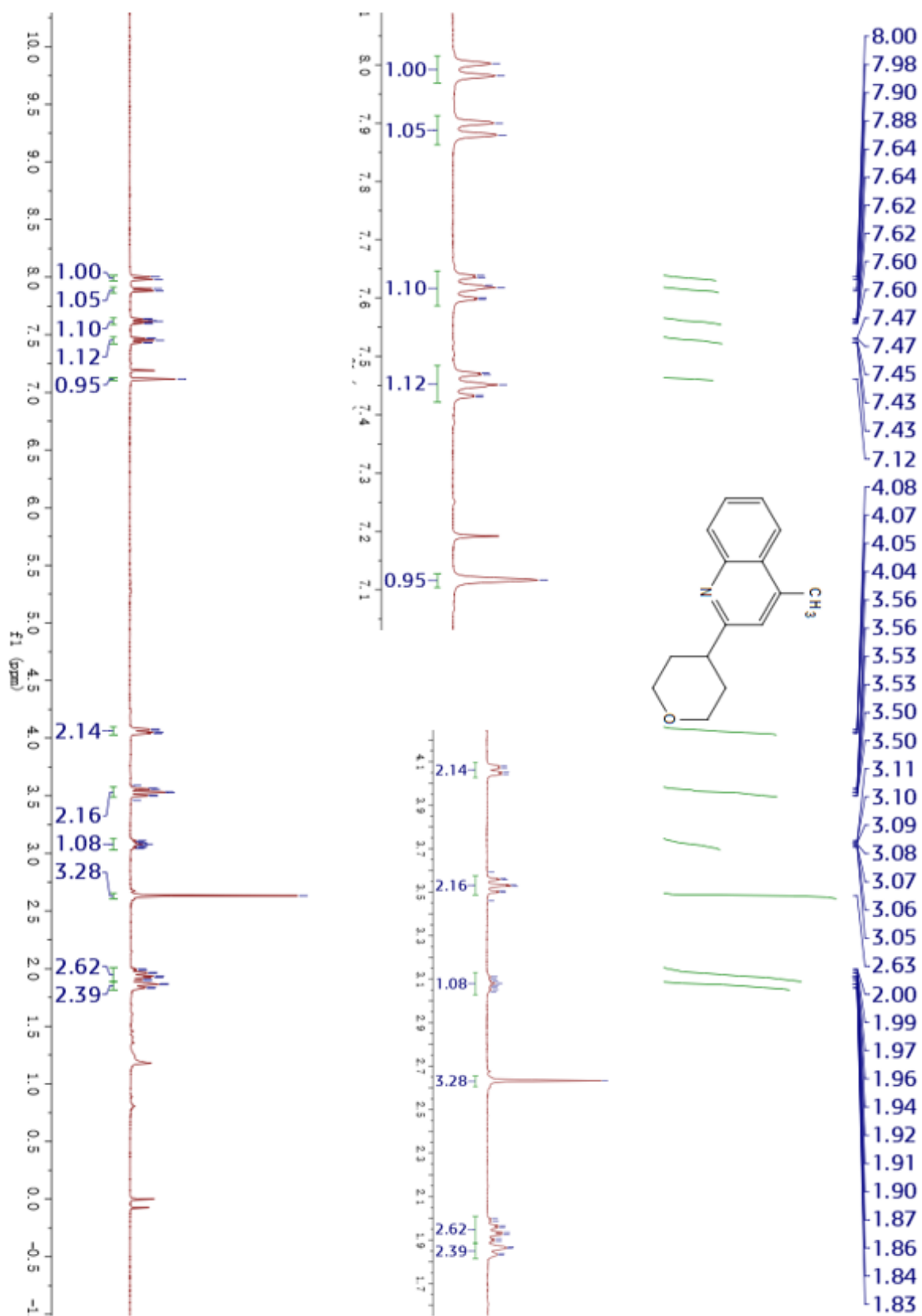


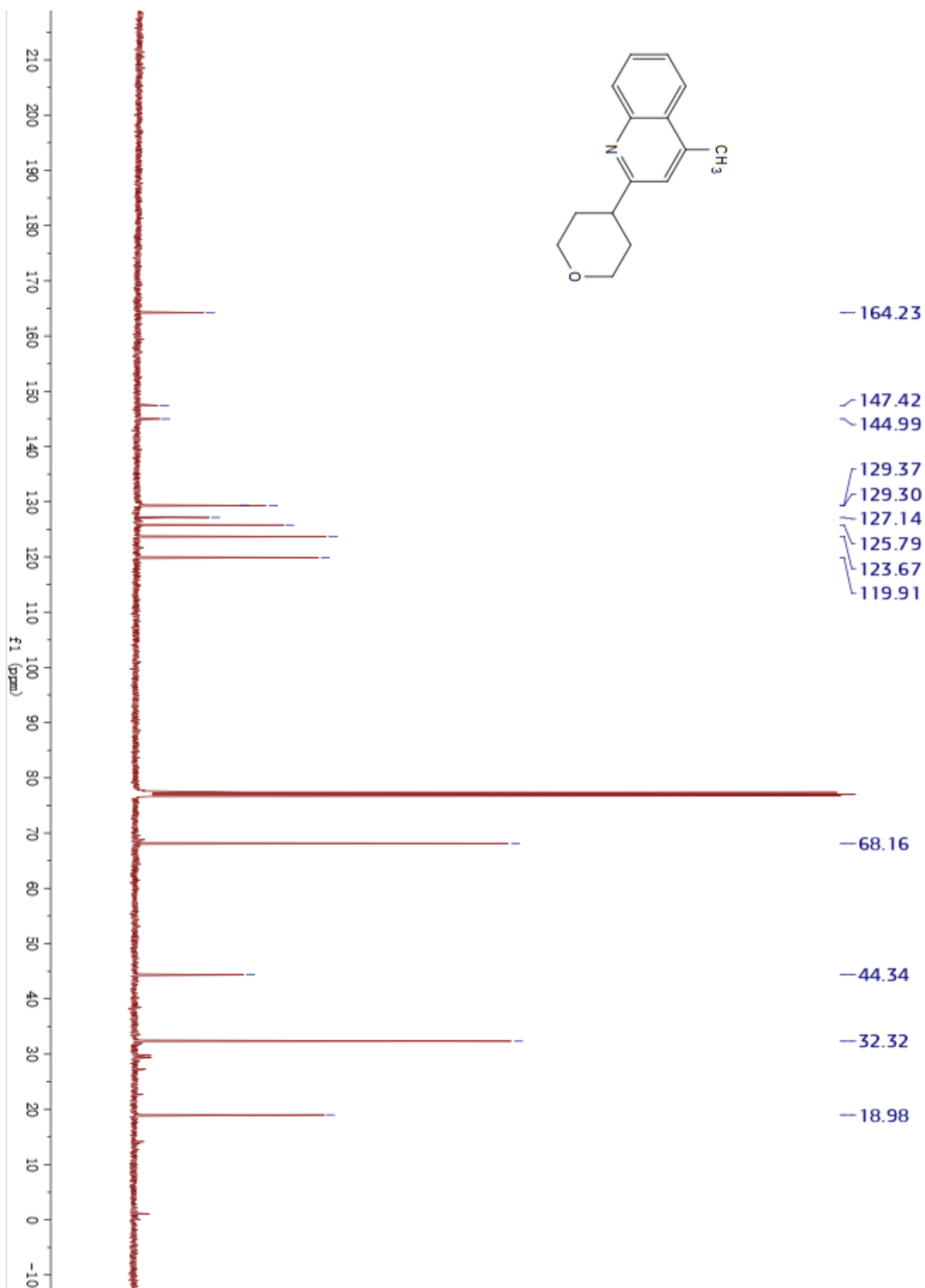
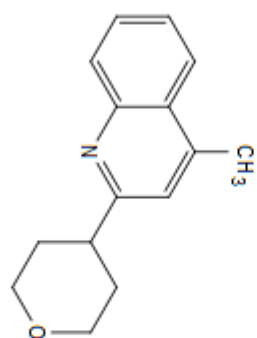
^1H and ^{13}C NMR spectra of **3j**



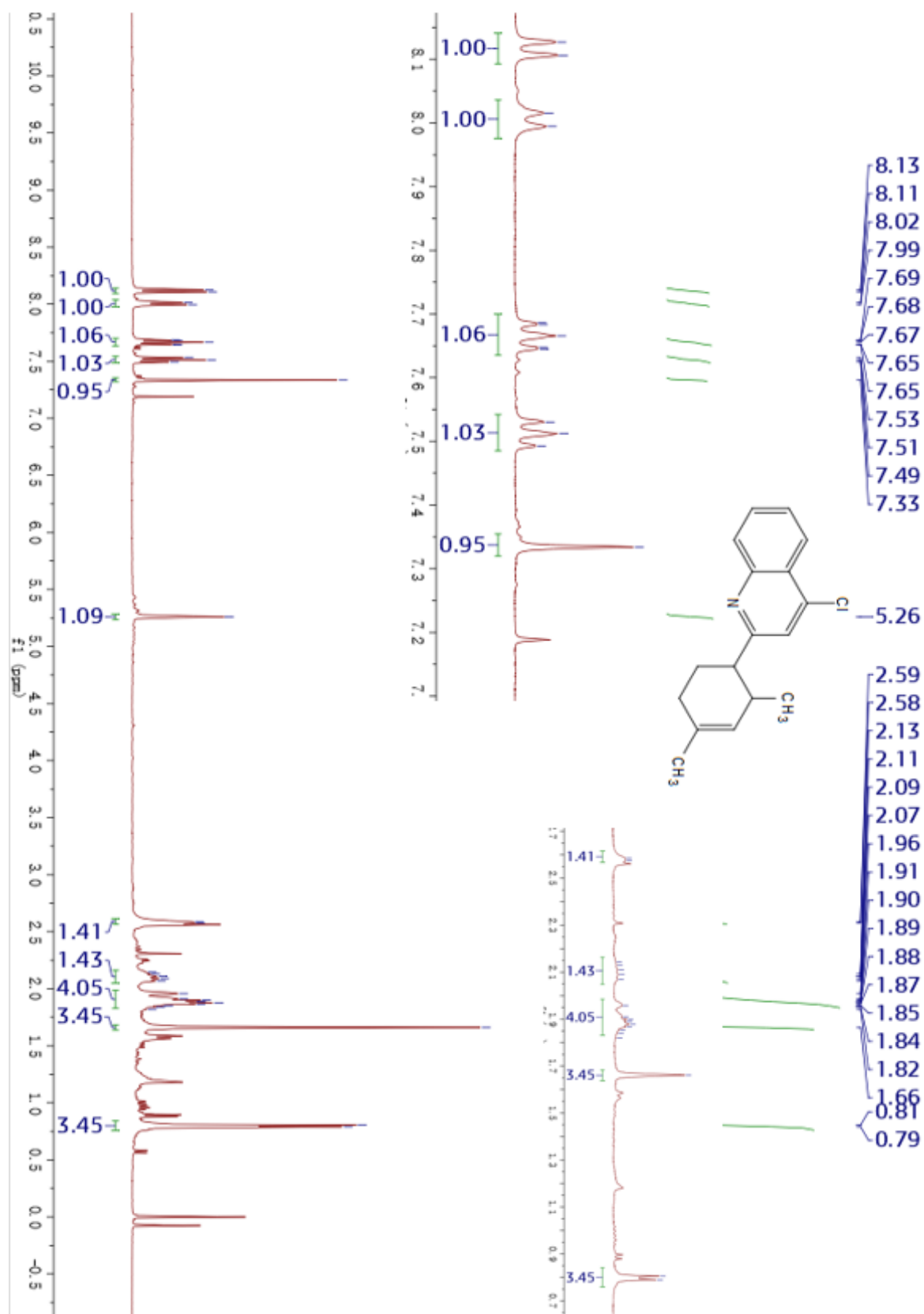


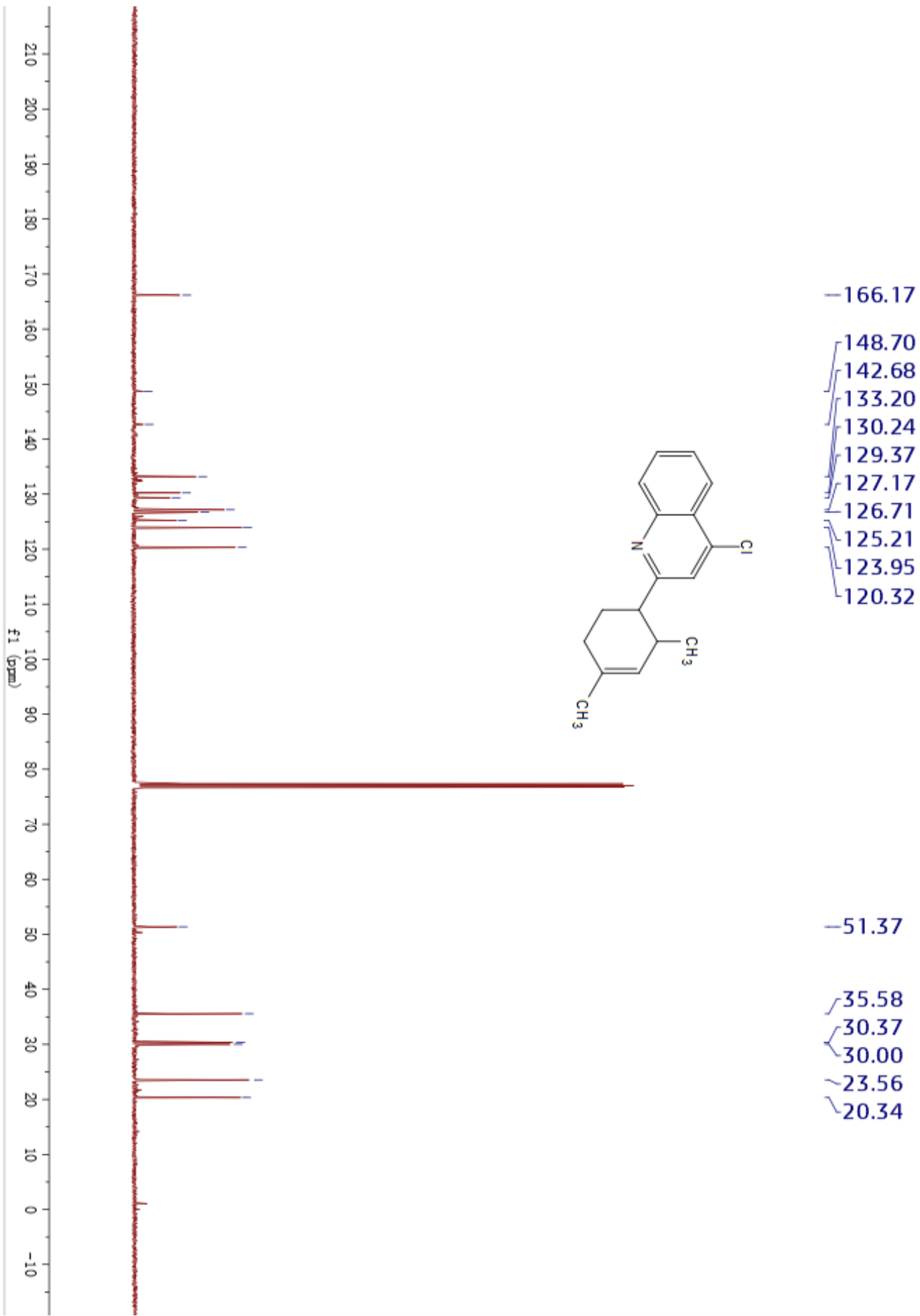
^1H and ^{13}C NMR spectra of **3k**



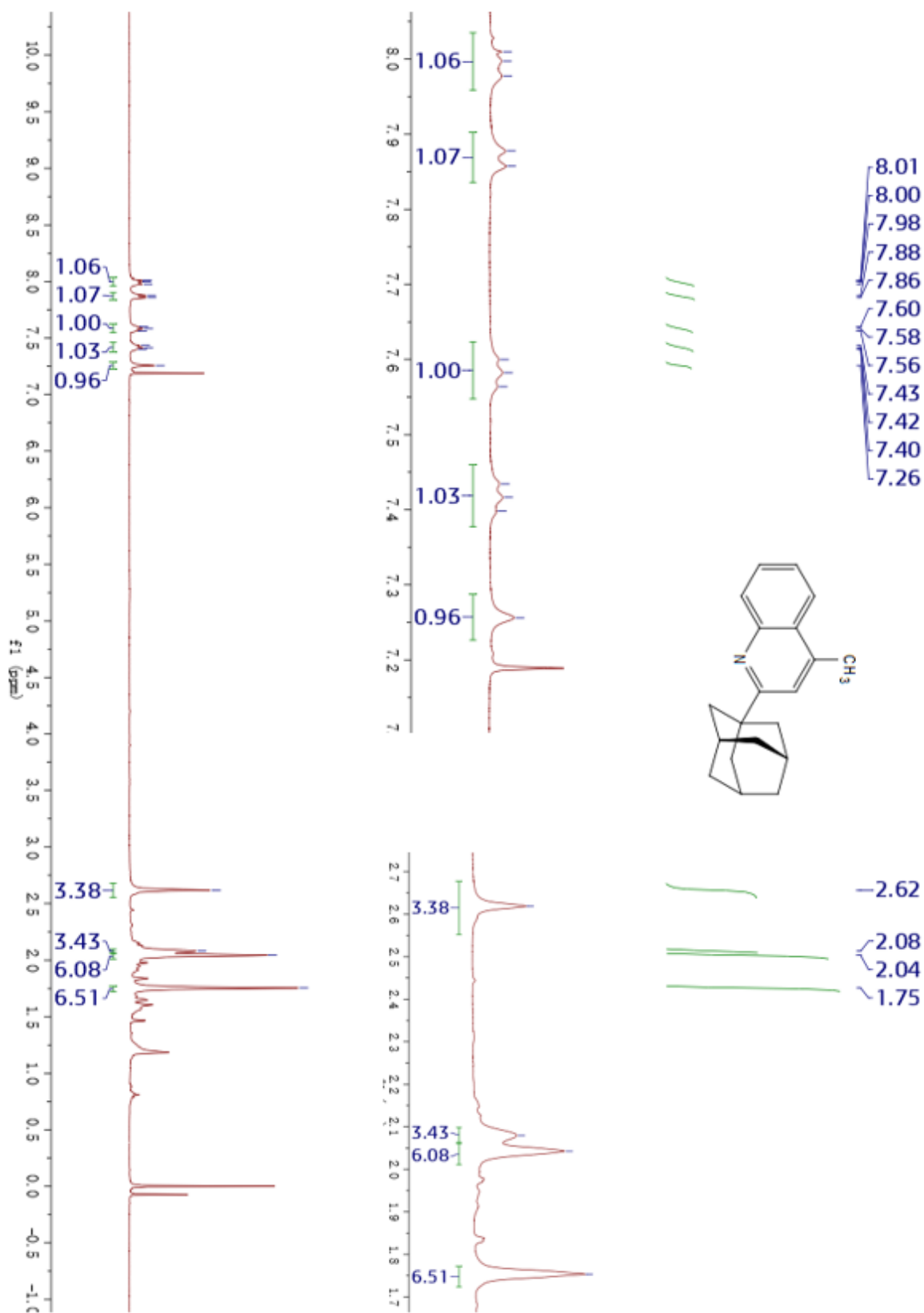


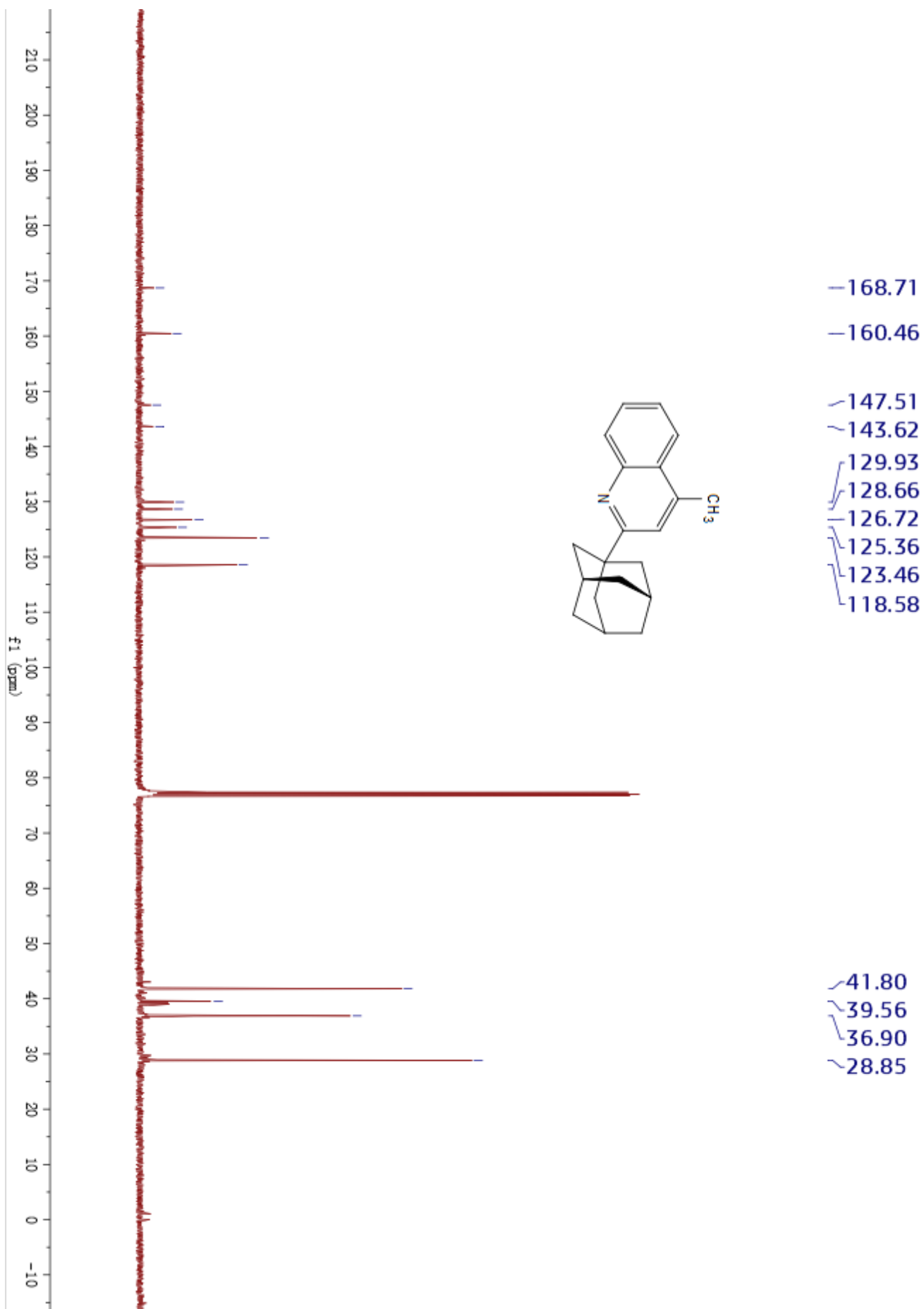
^1H and ^{13}C NMR spectra of **3I**



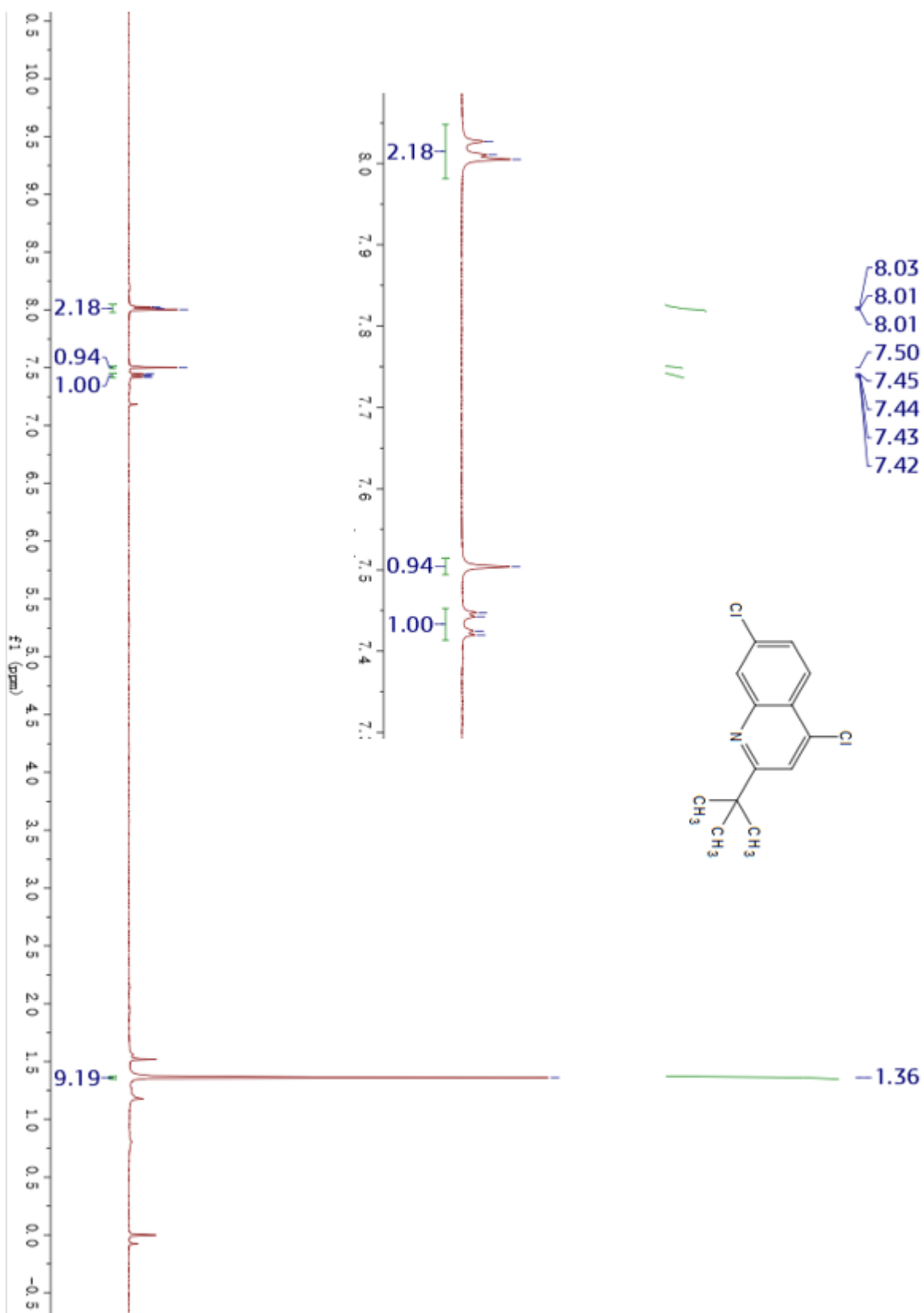


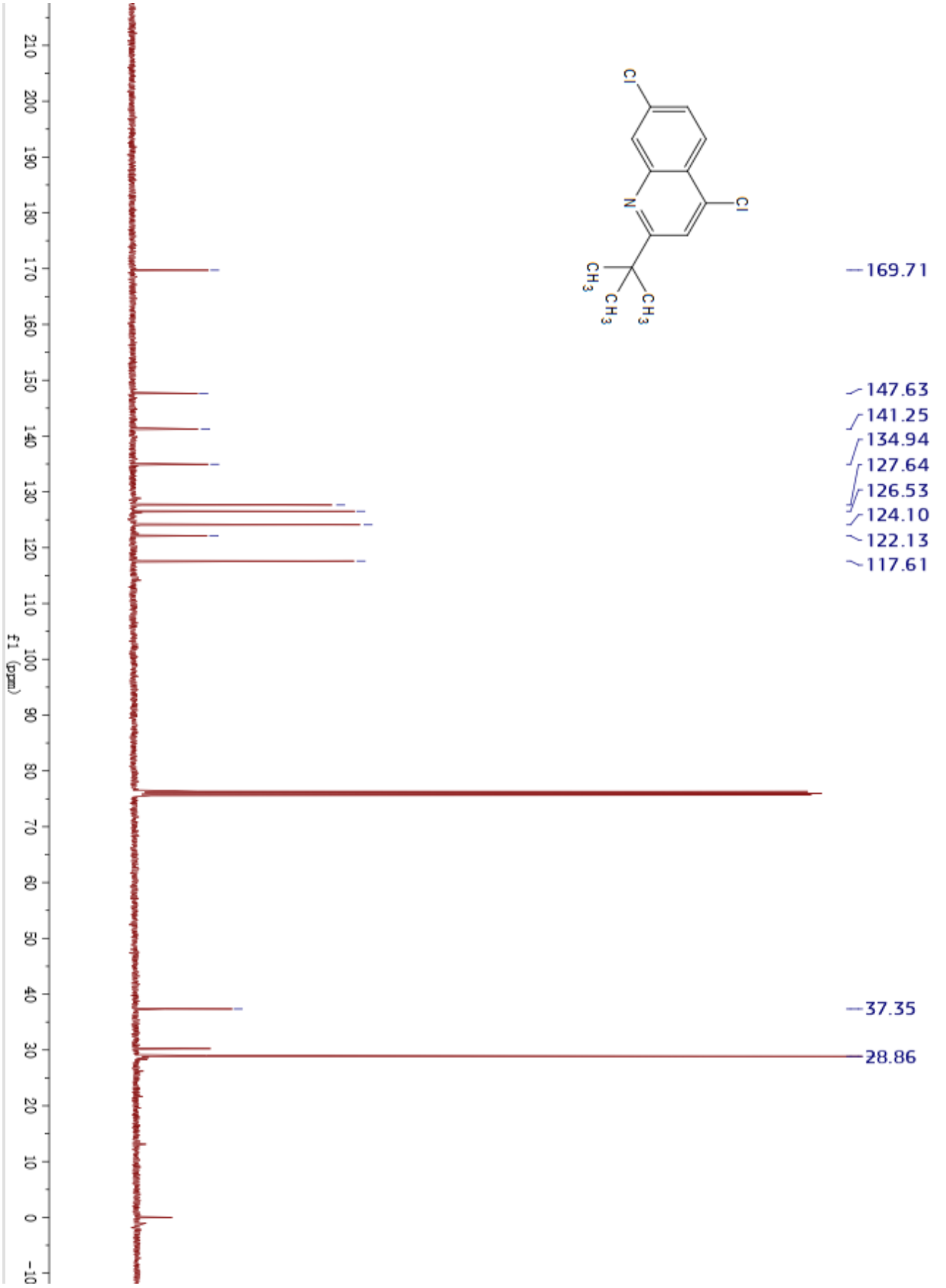
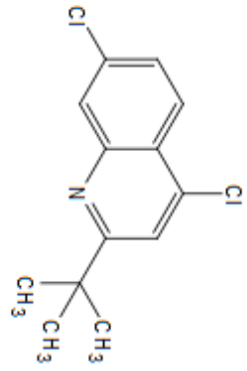
^1H and ^{13}C NMR spectra of **3m**



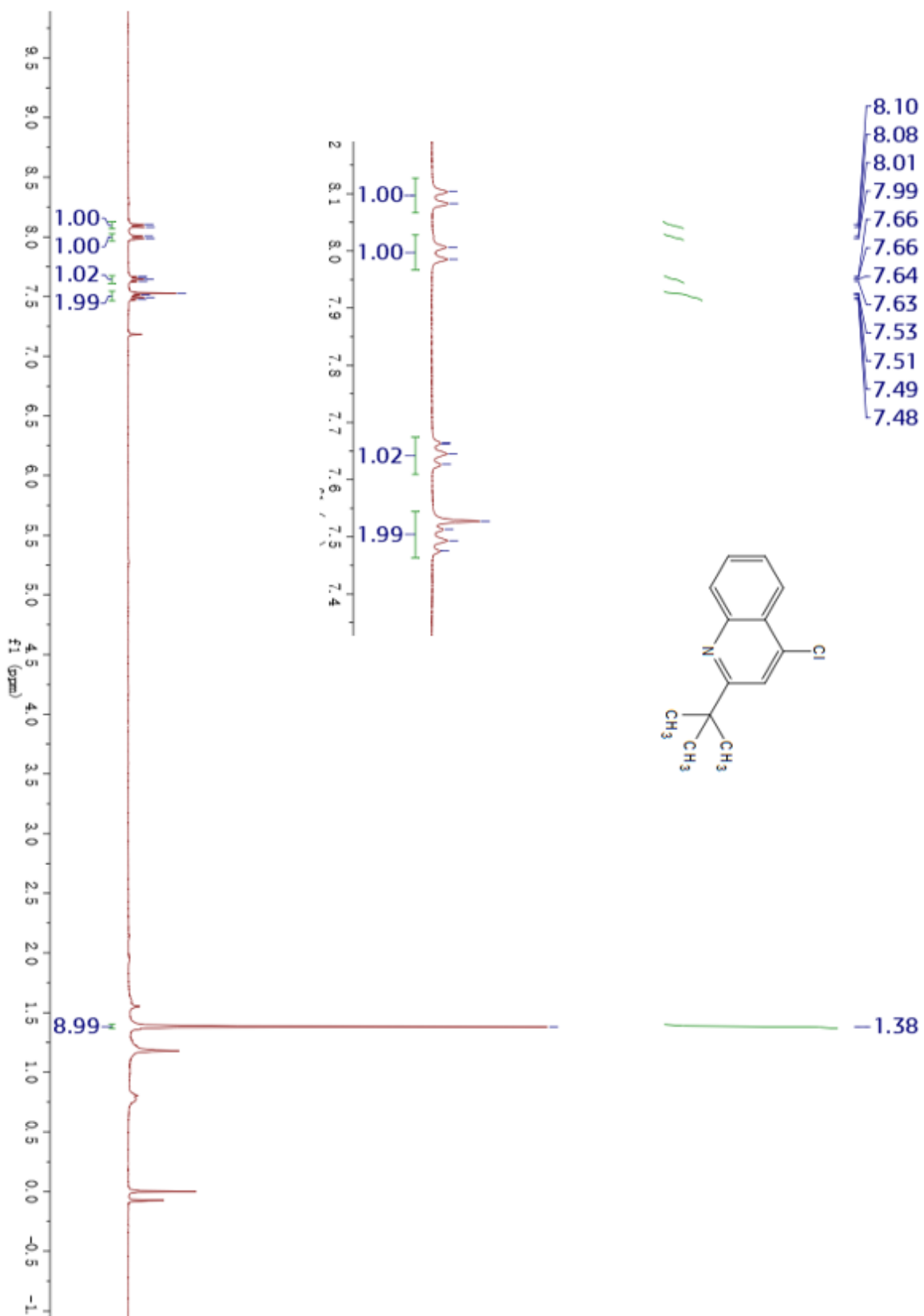


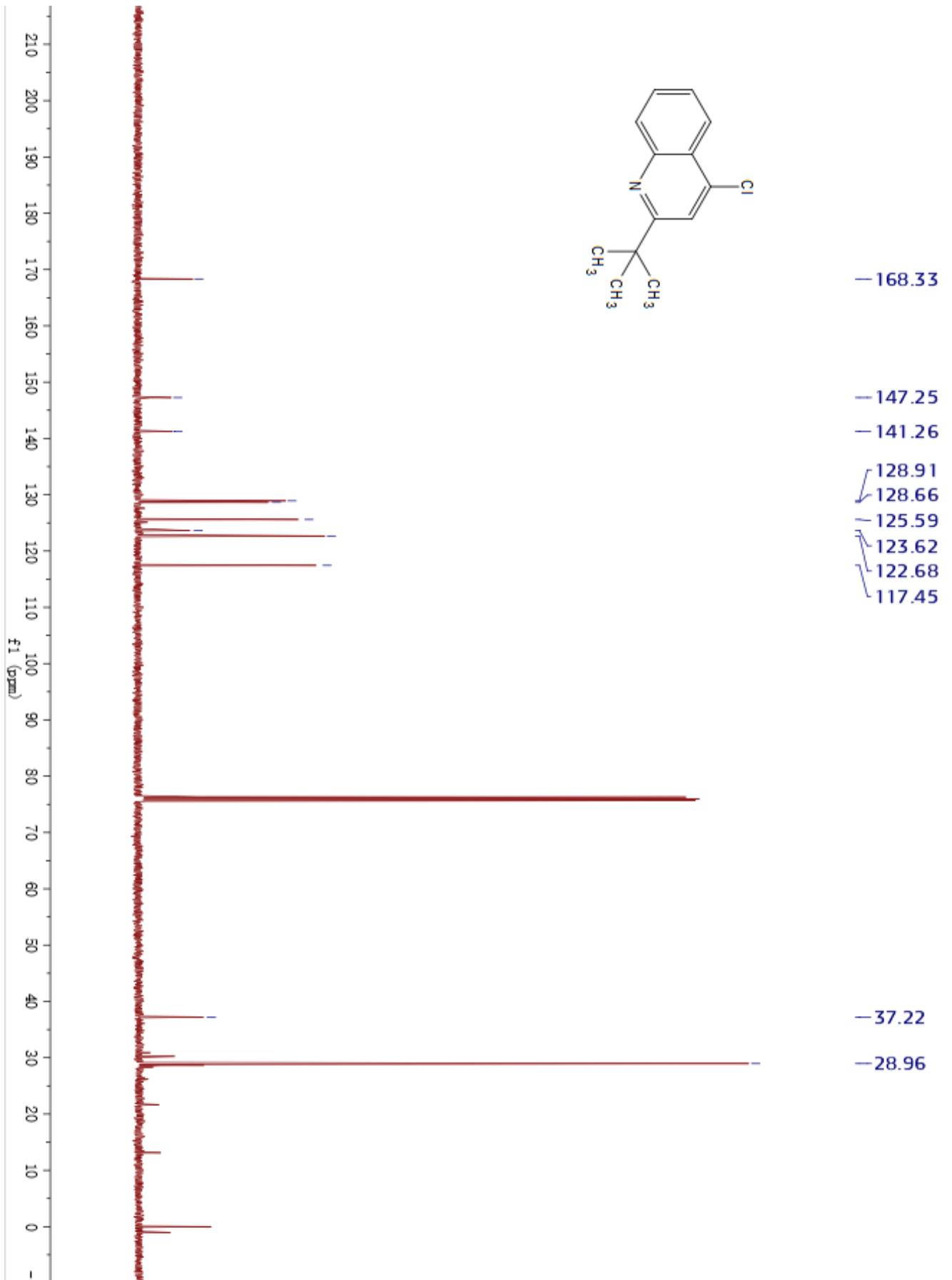
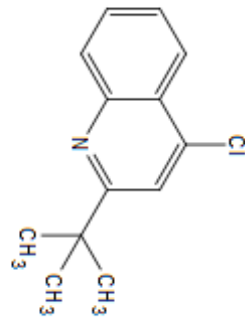
^1H and ^{13}C NMR spectra of **3p**



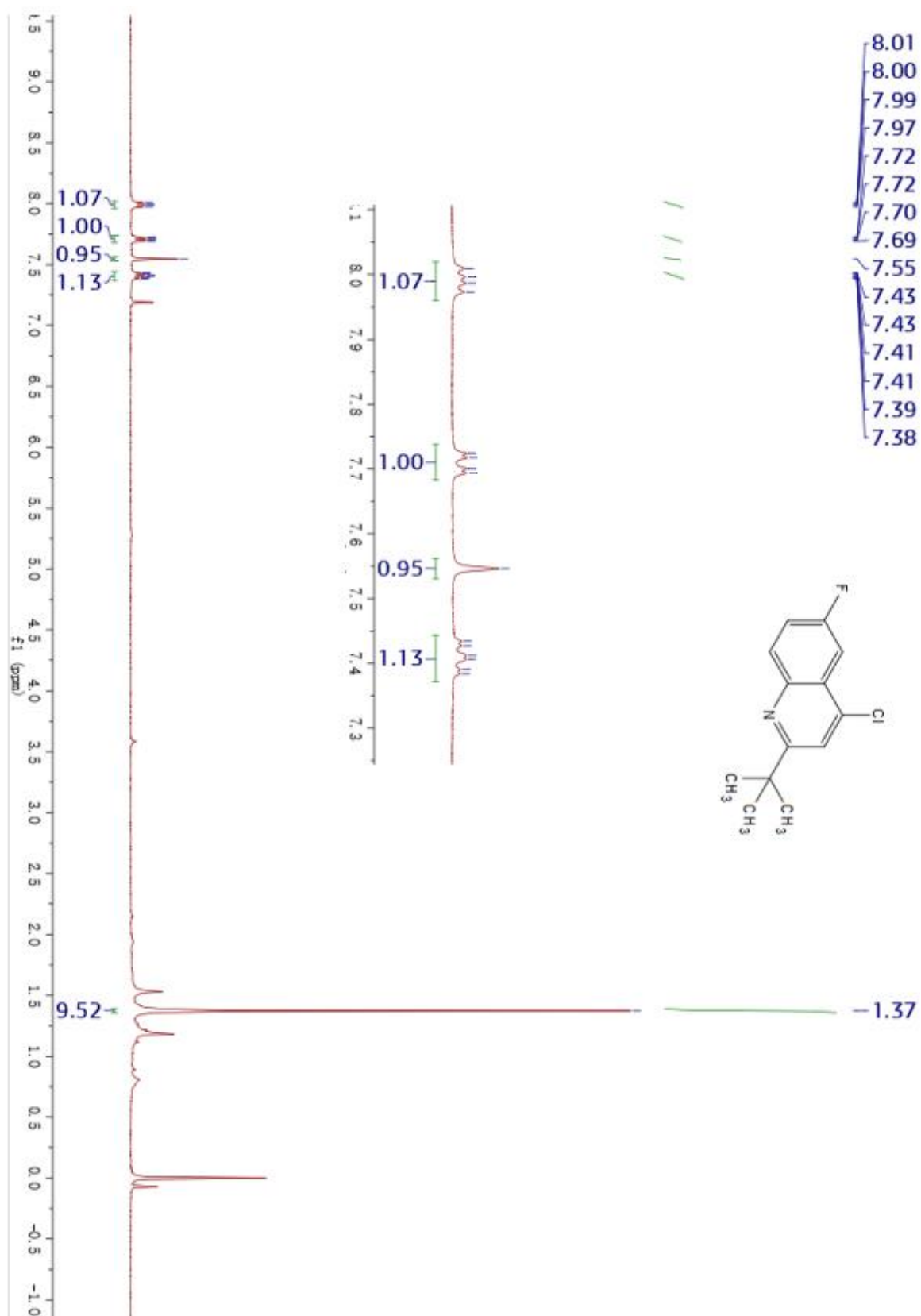


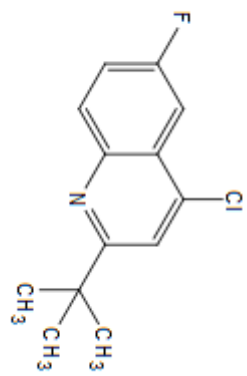
^1H and ^{13}C NMR spectra of **3q**





^1H , ^{13}C and ^{19}F NMR spectra of **3r**





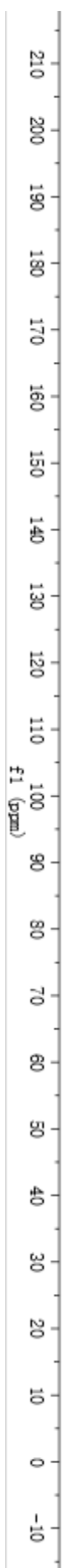
— 167.70
— 160.93
— 158.47

— 144.30

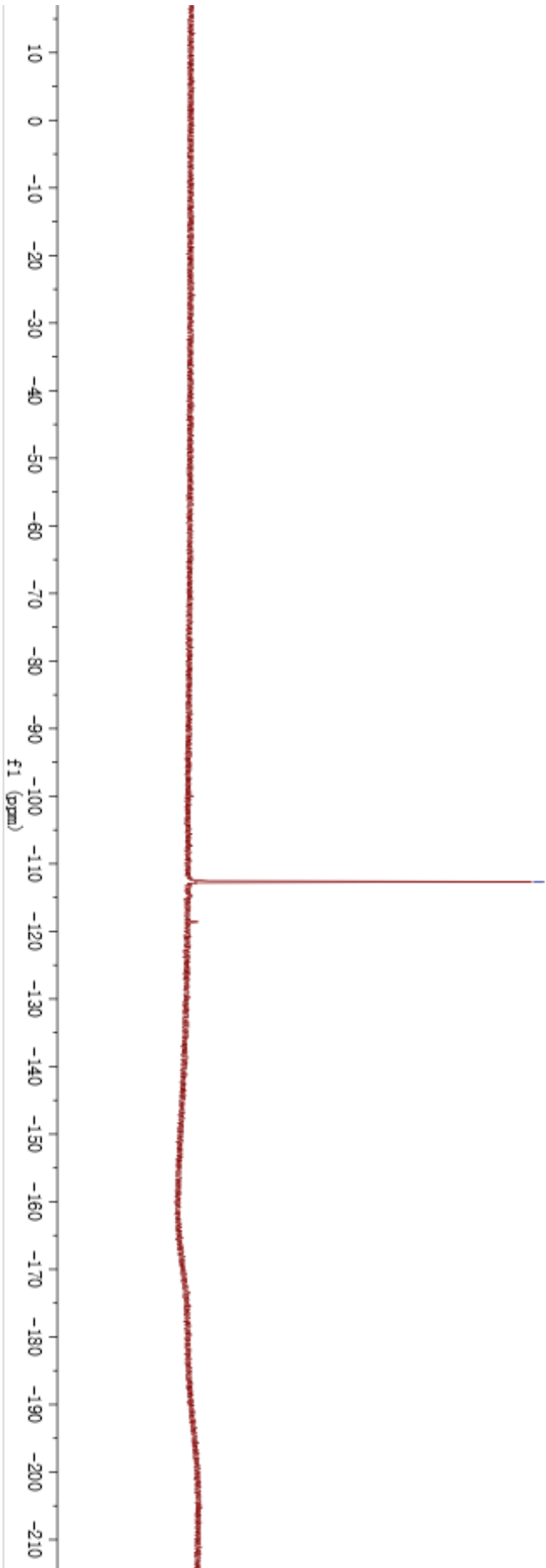
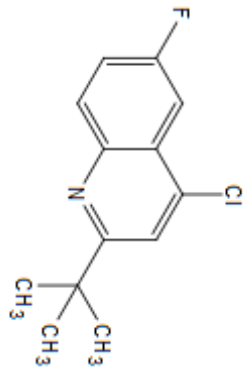
— 131.32
— 131.23
— 124.49
— 119.17
— 118.91
— 118.07
— 106.58
— 106.34

— 37.18

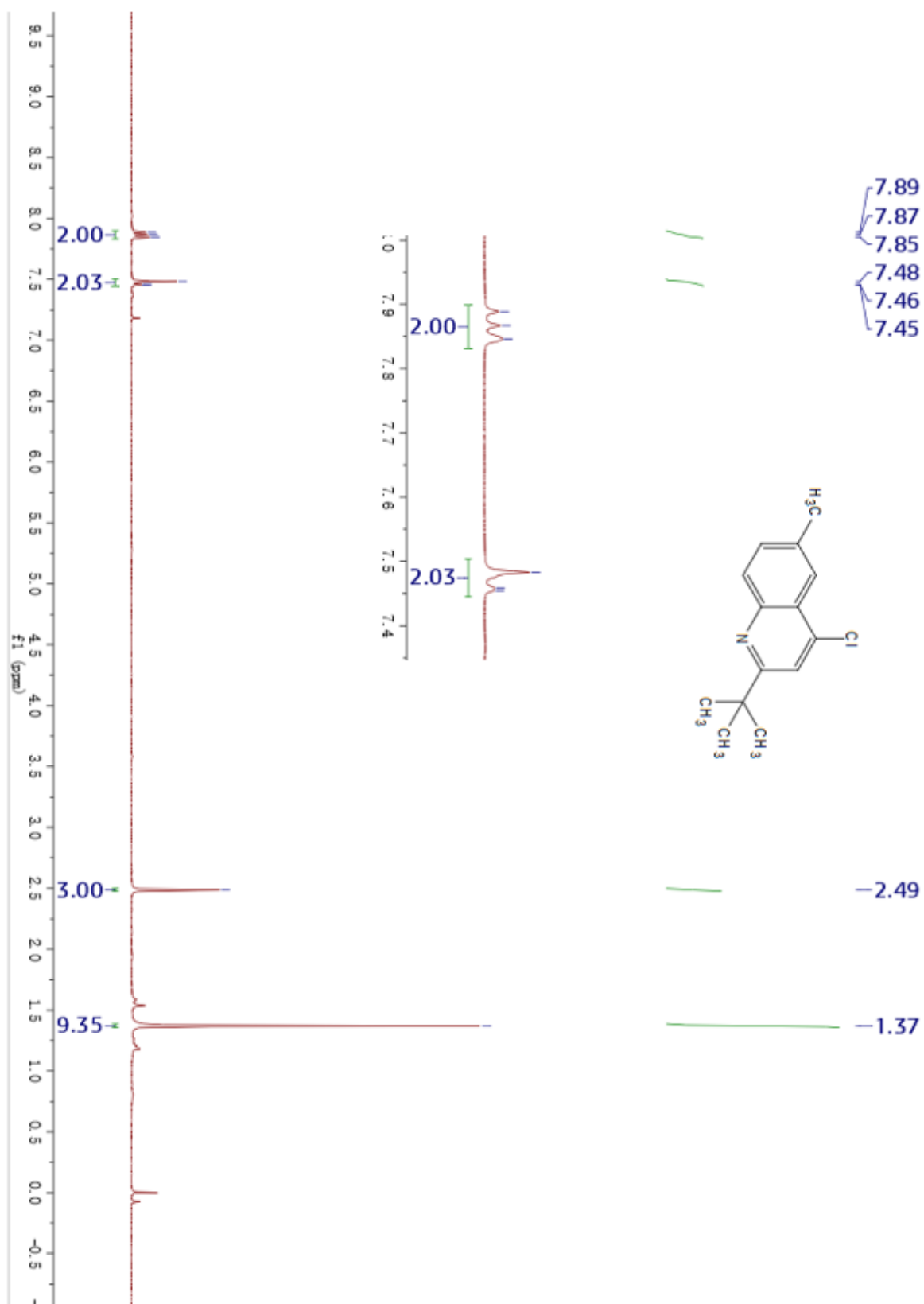
— 28.93

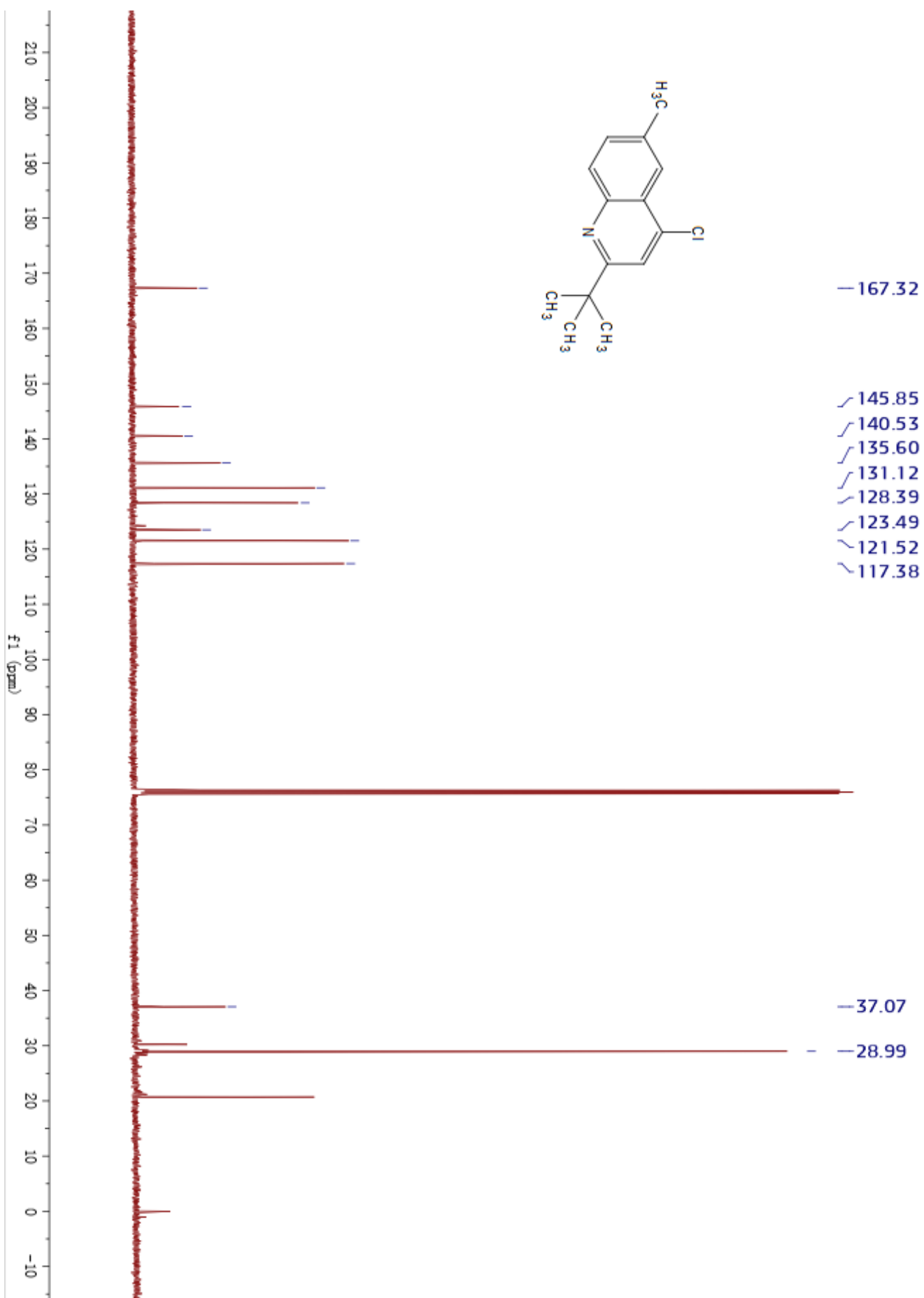
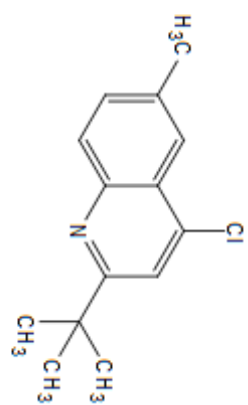


-112.66

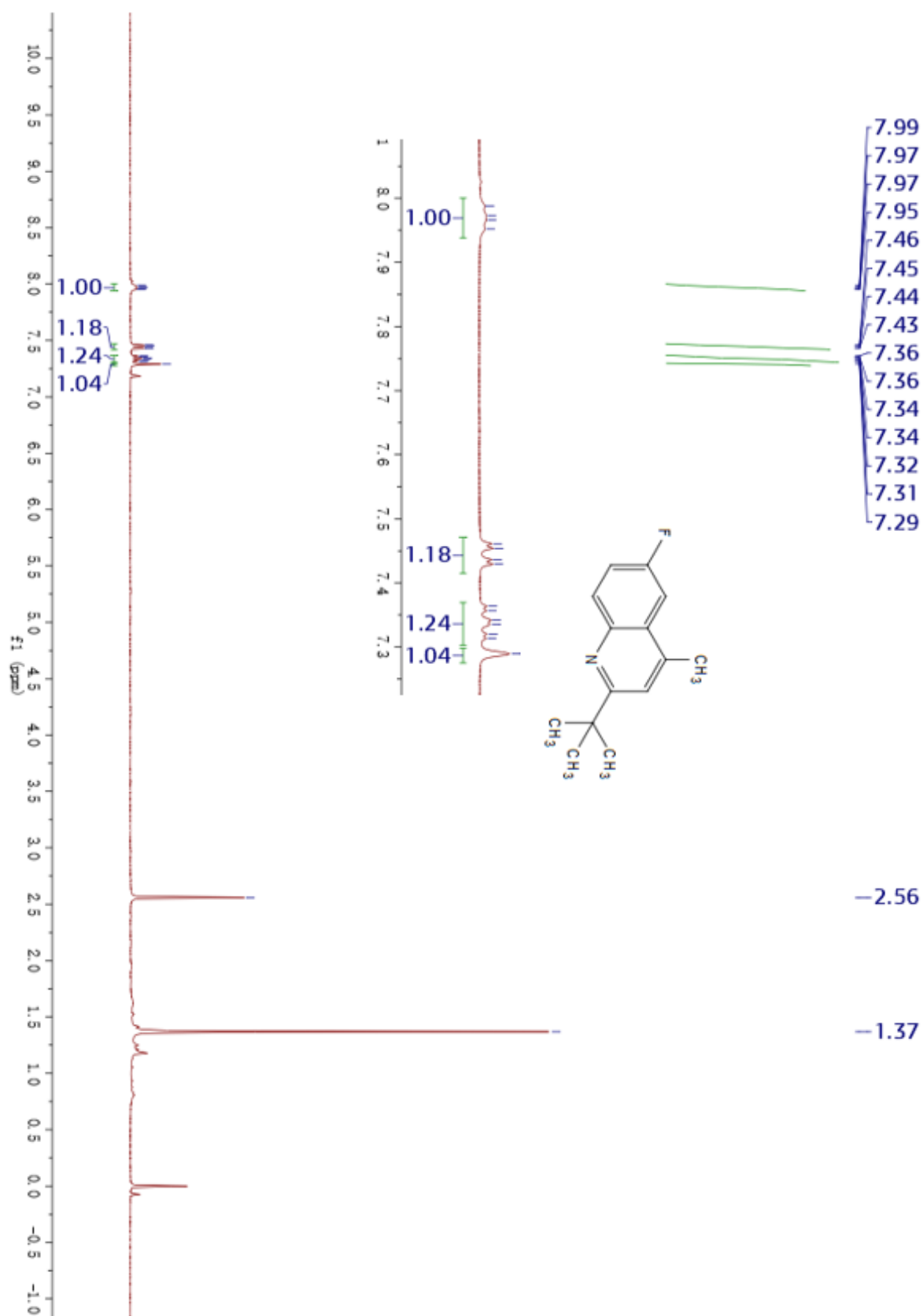


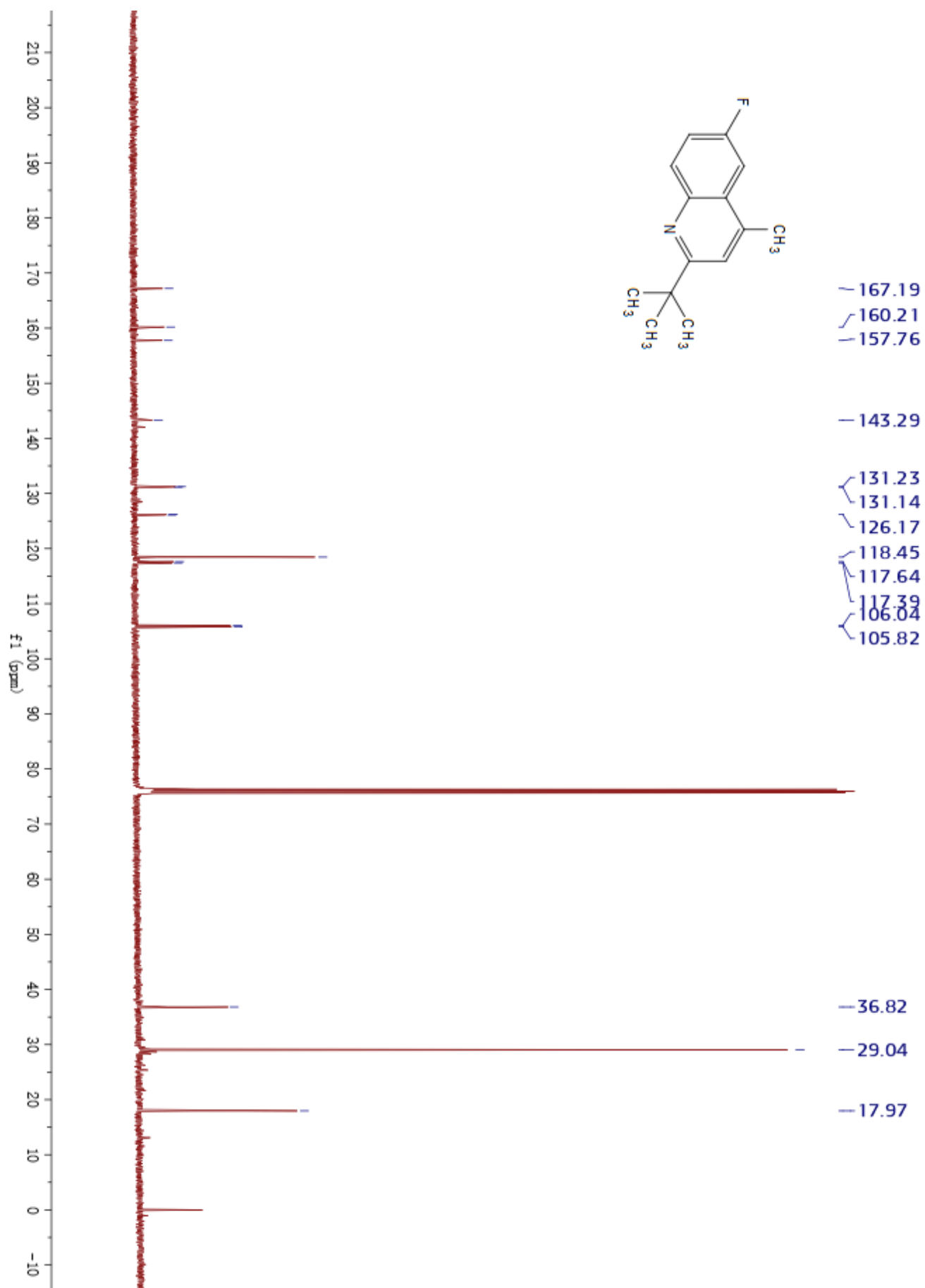
^1H and ^{13}C NMR spectra of **3s**

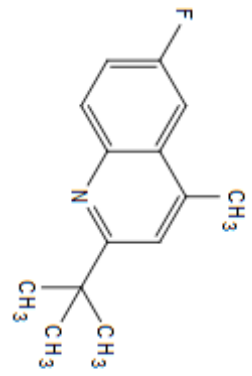




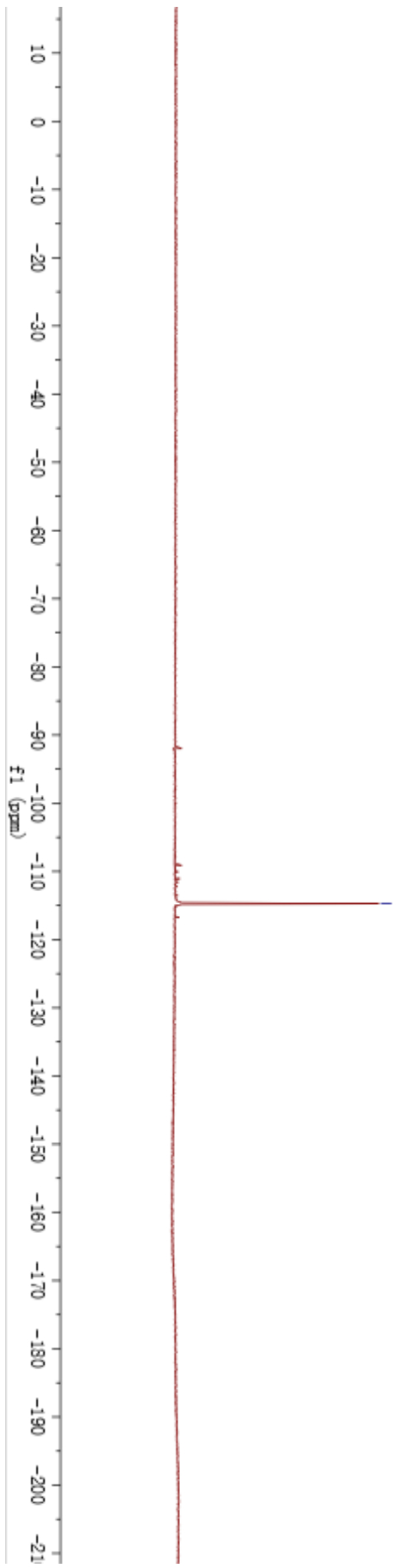
^1H , ^{13}C and ^{19}F NMR spectra of **3t**



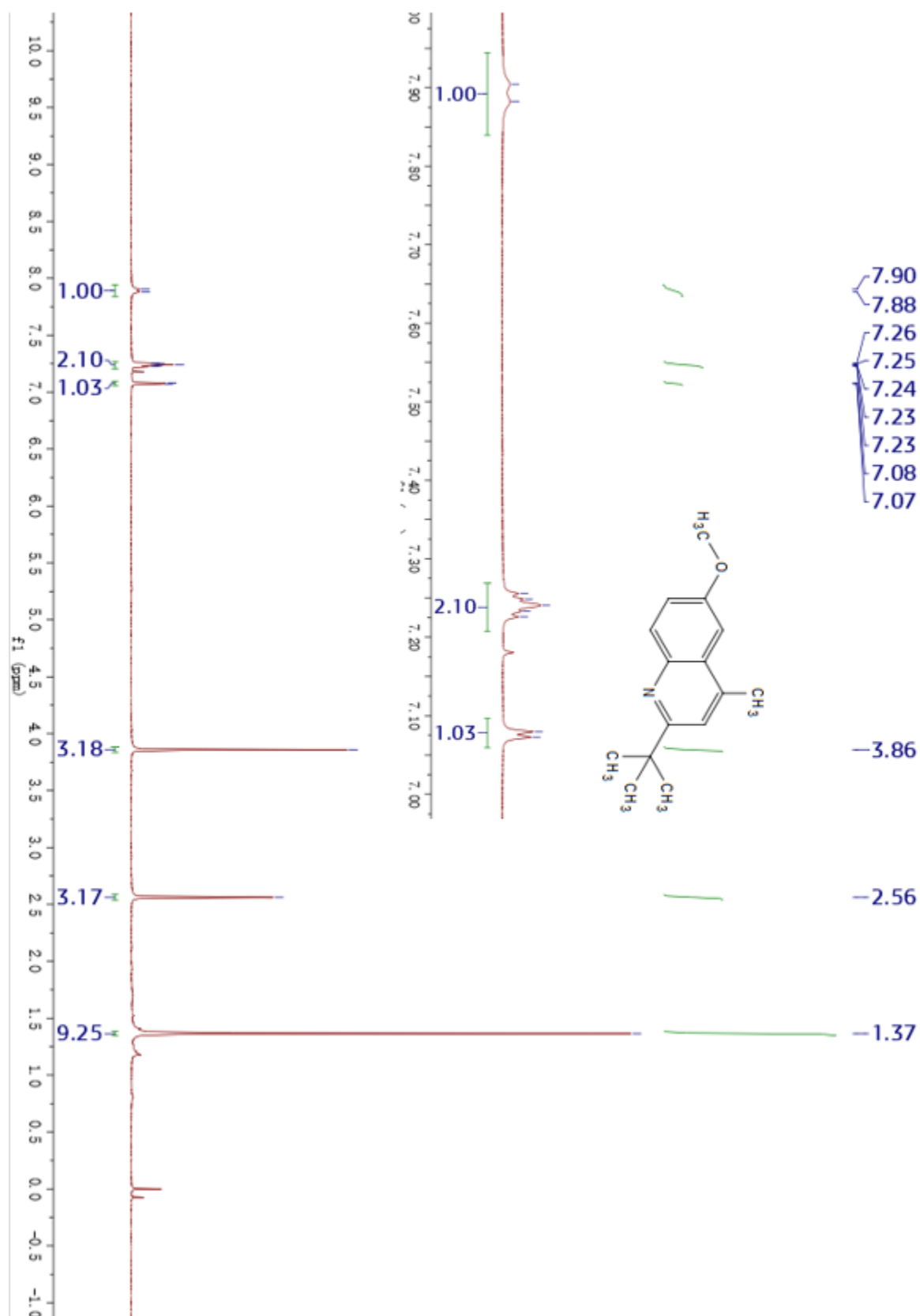


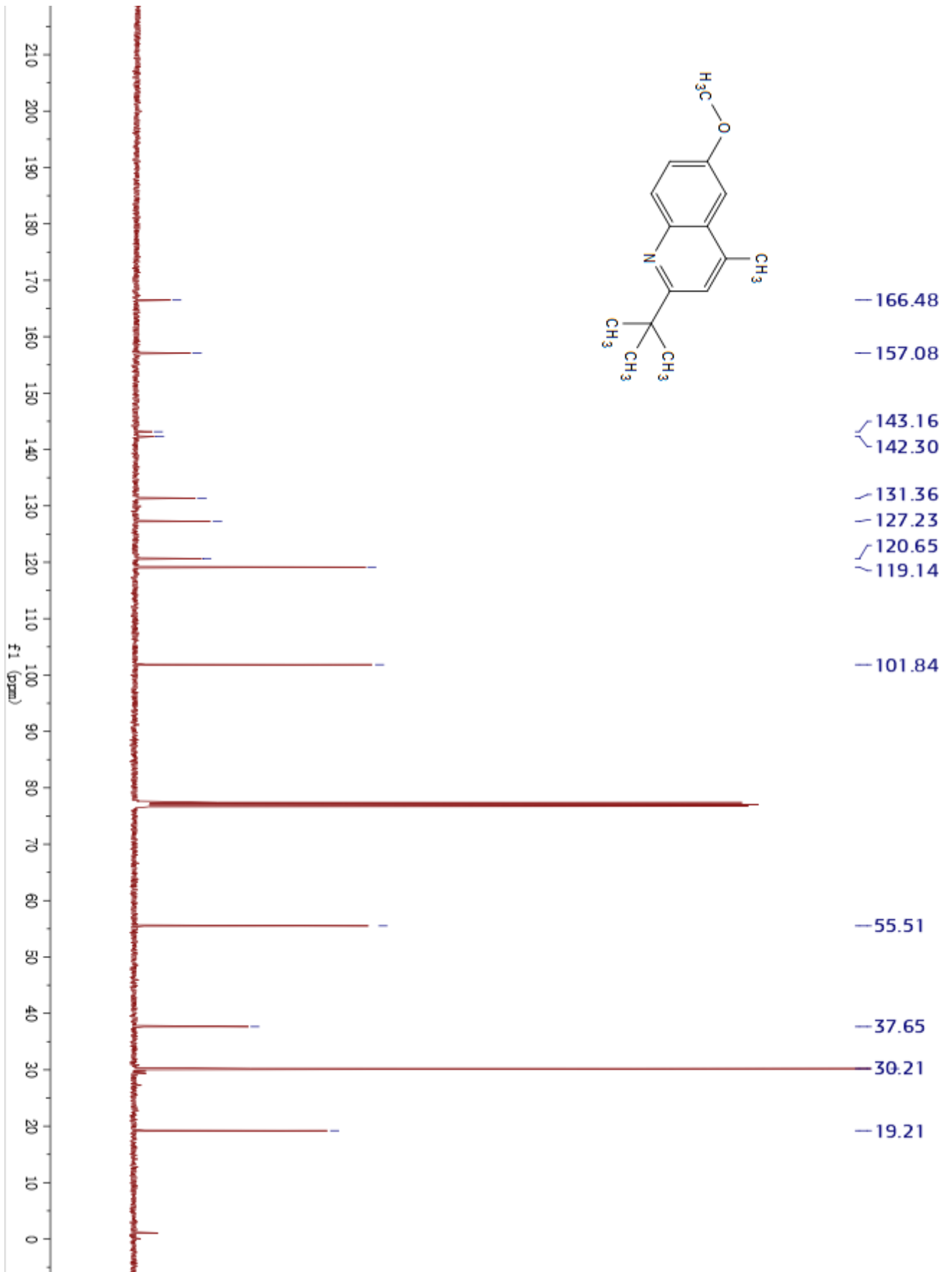
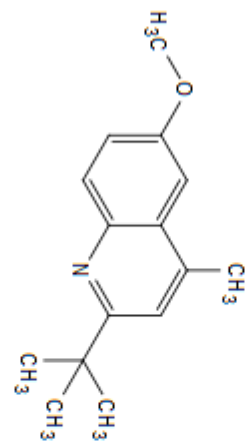


--114.75

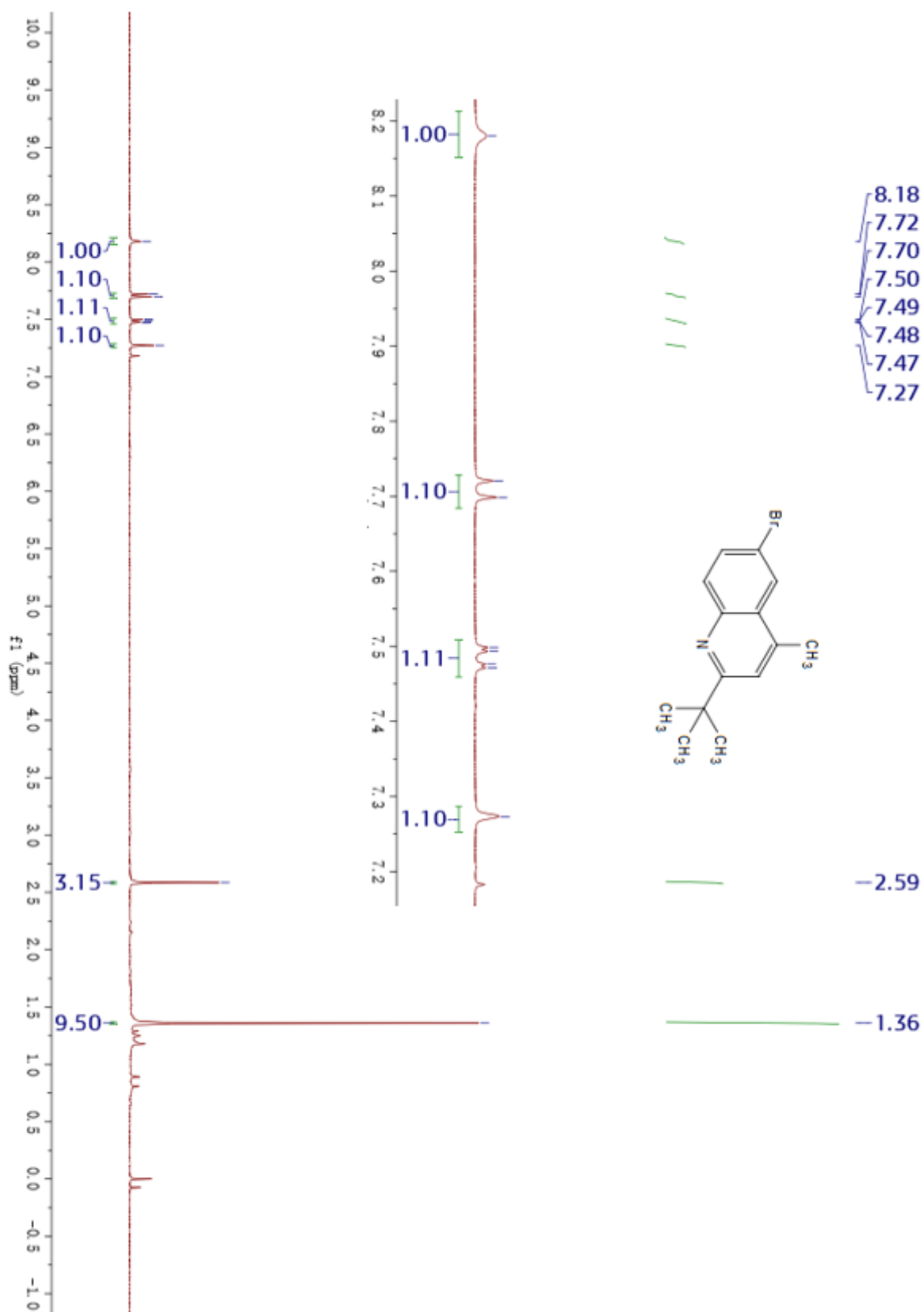


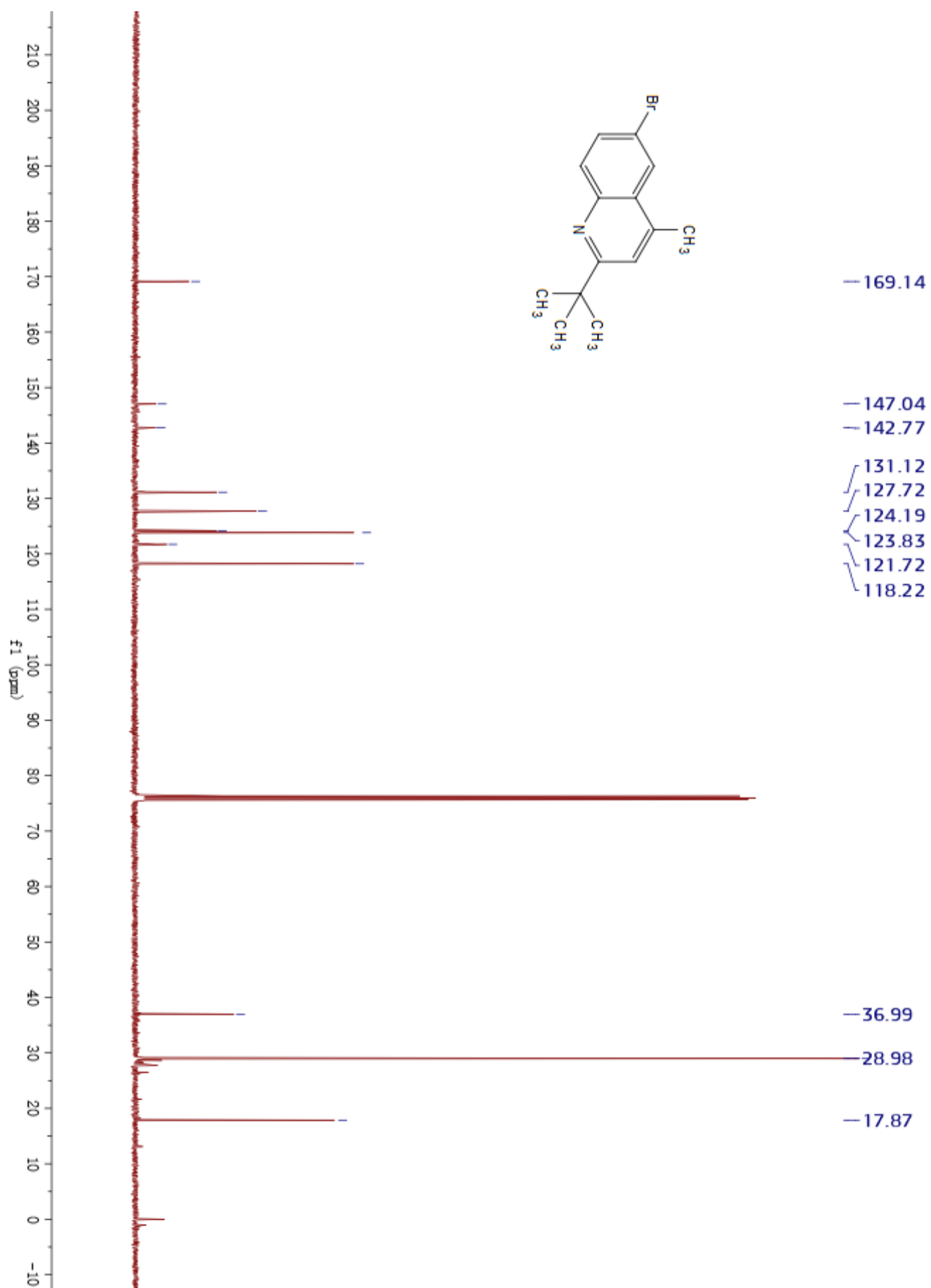
^1H and ^{13}C NMR spectra of **3u**



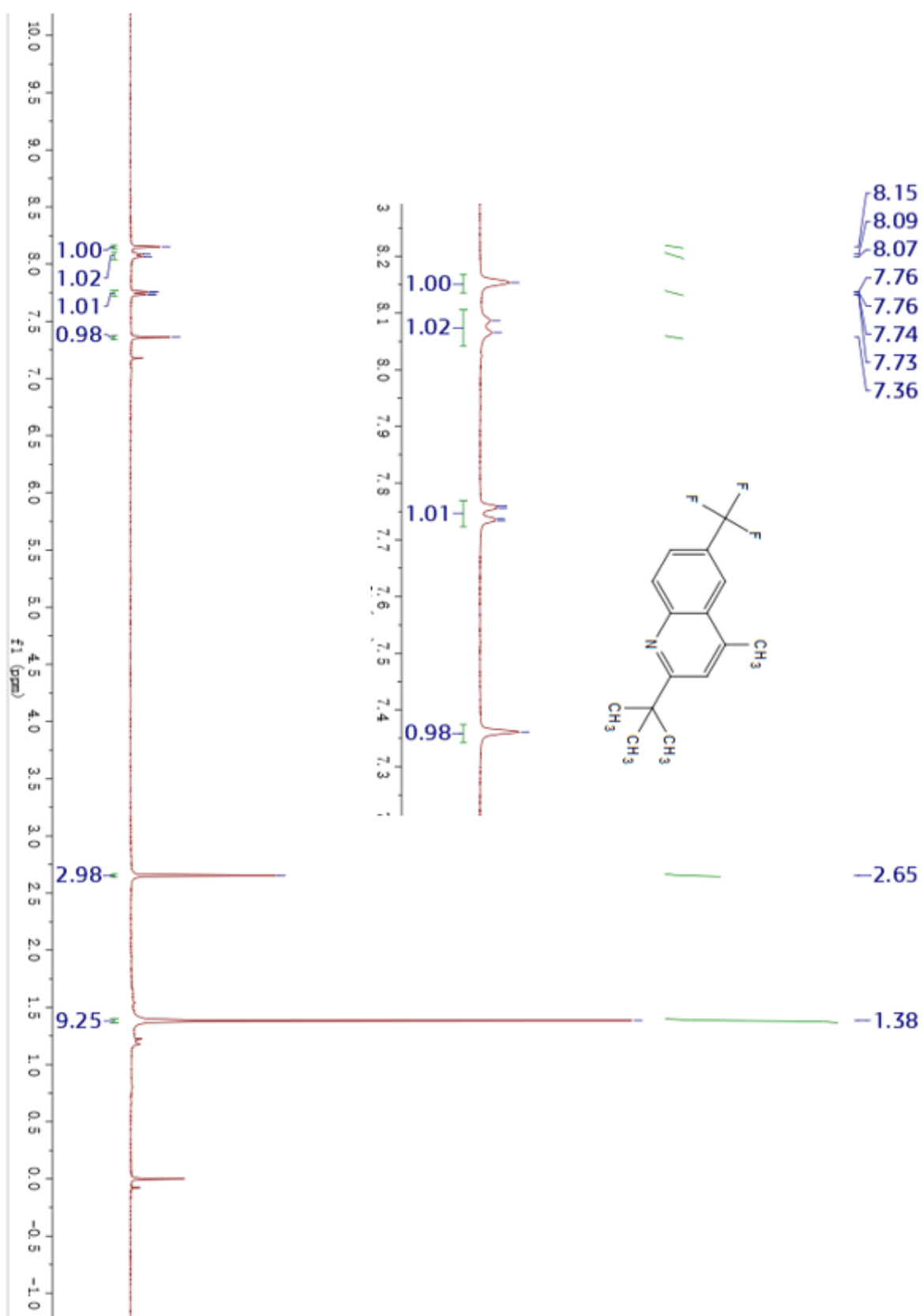


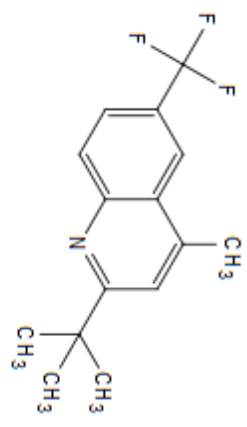
^1H and ^{13}C NMR spectra of **3v**



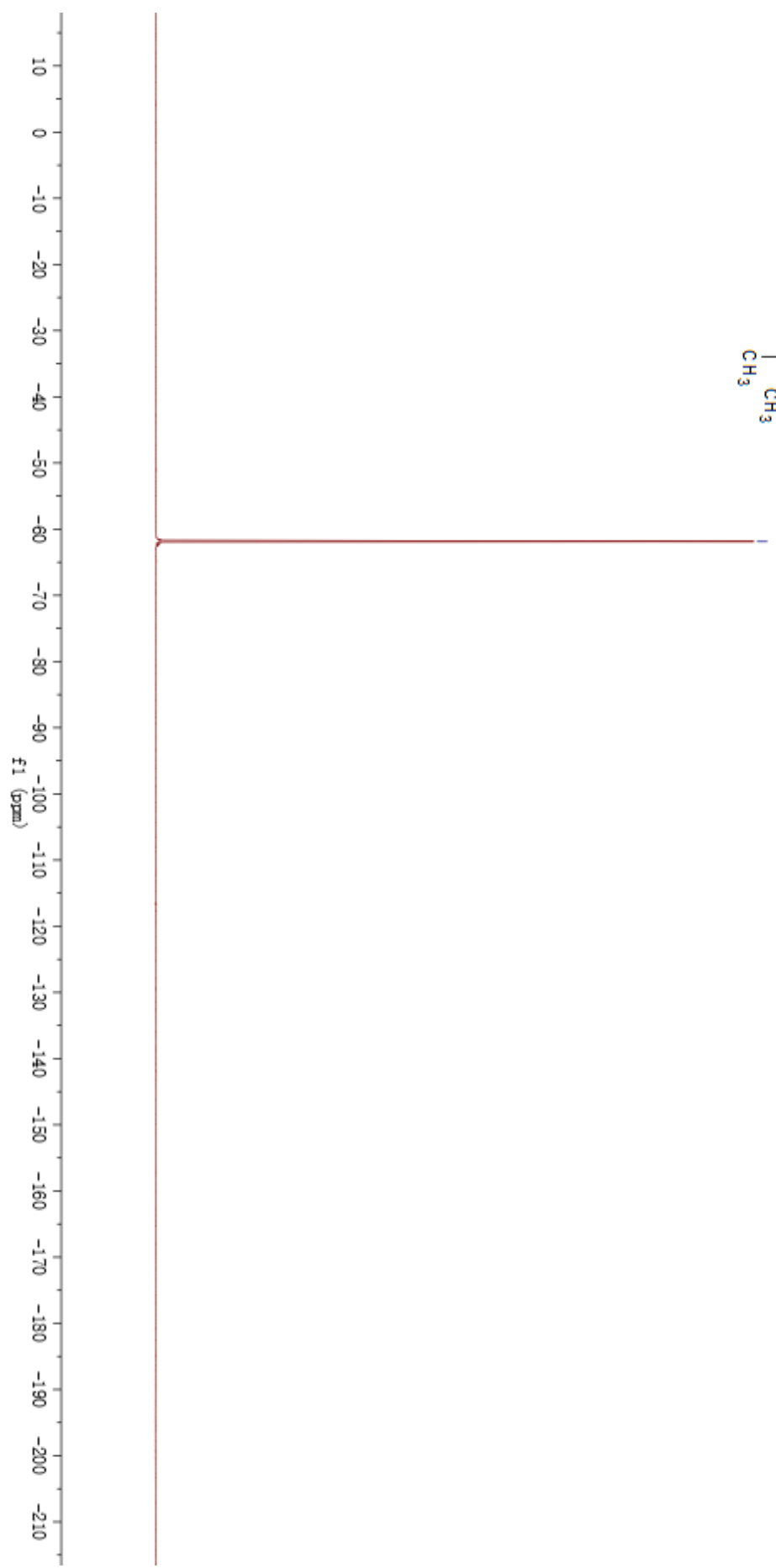


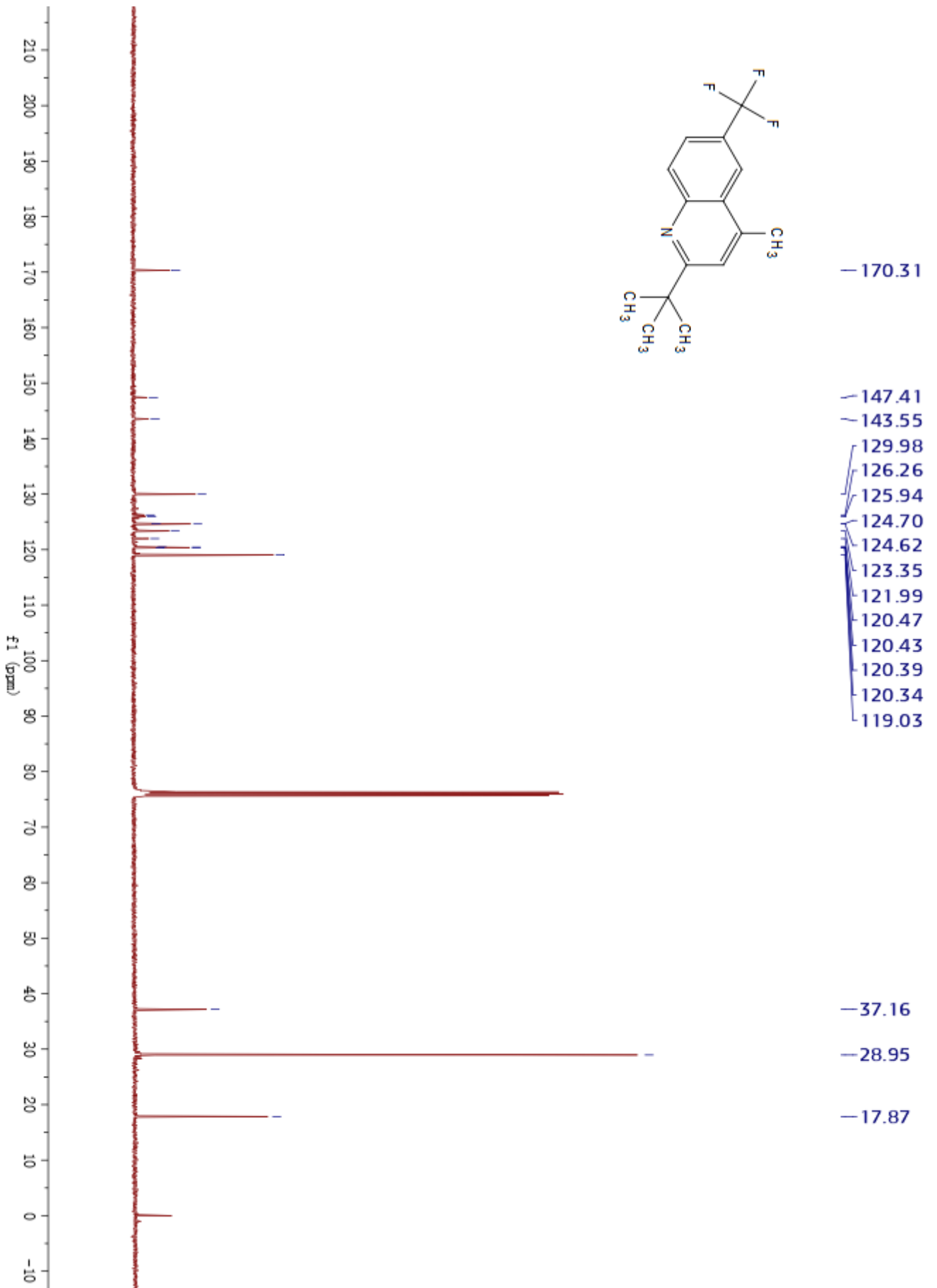
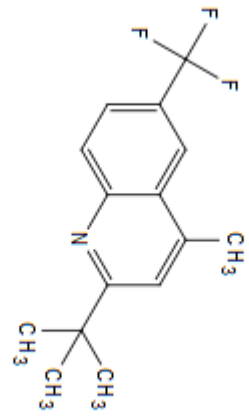
^1H , ^{19}F and ^{13}C NMR spectra of **3w**



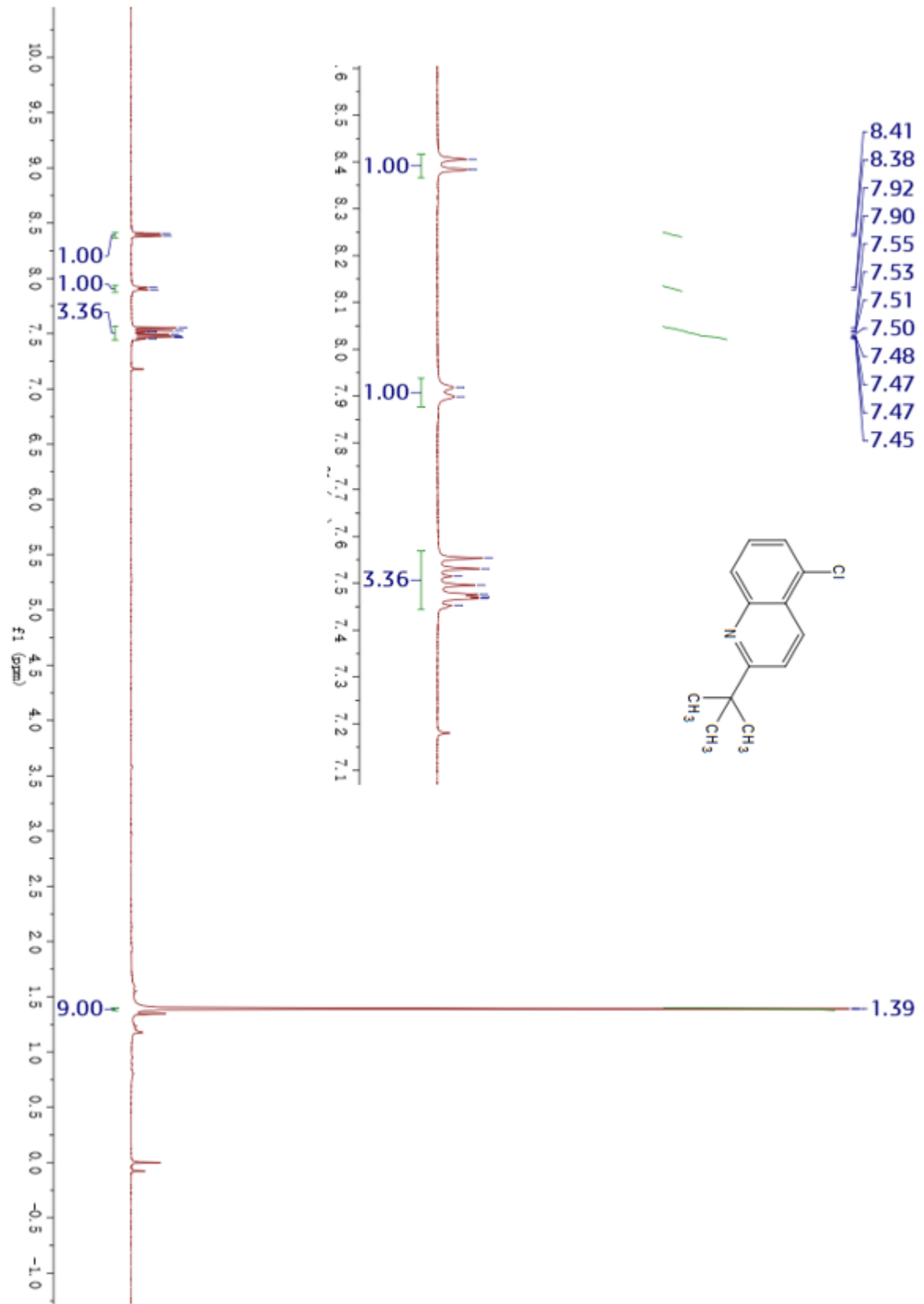


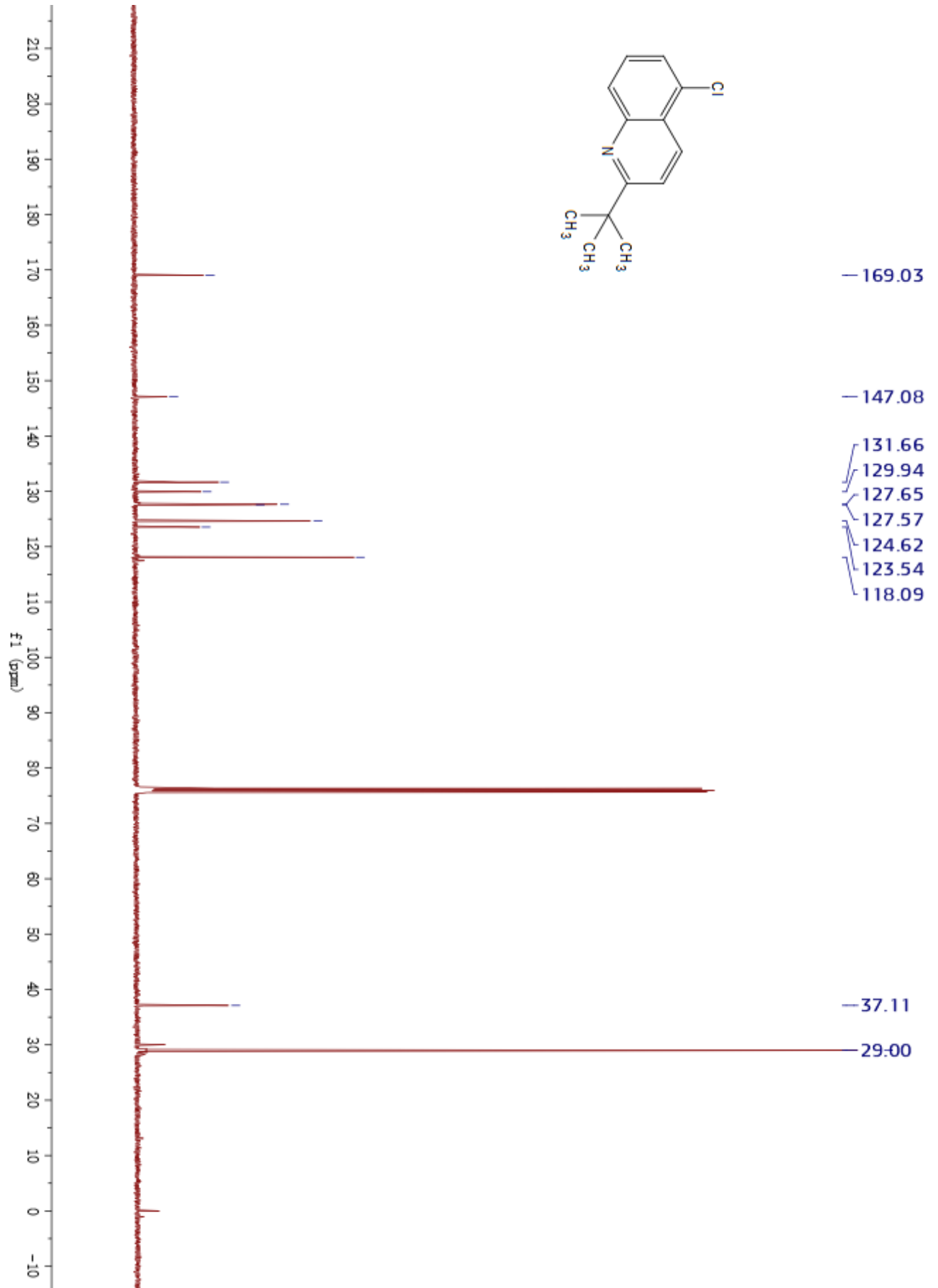
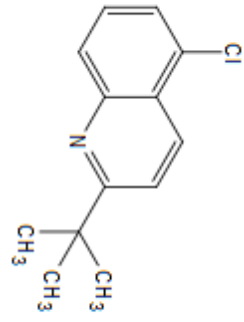
—61.88



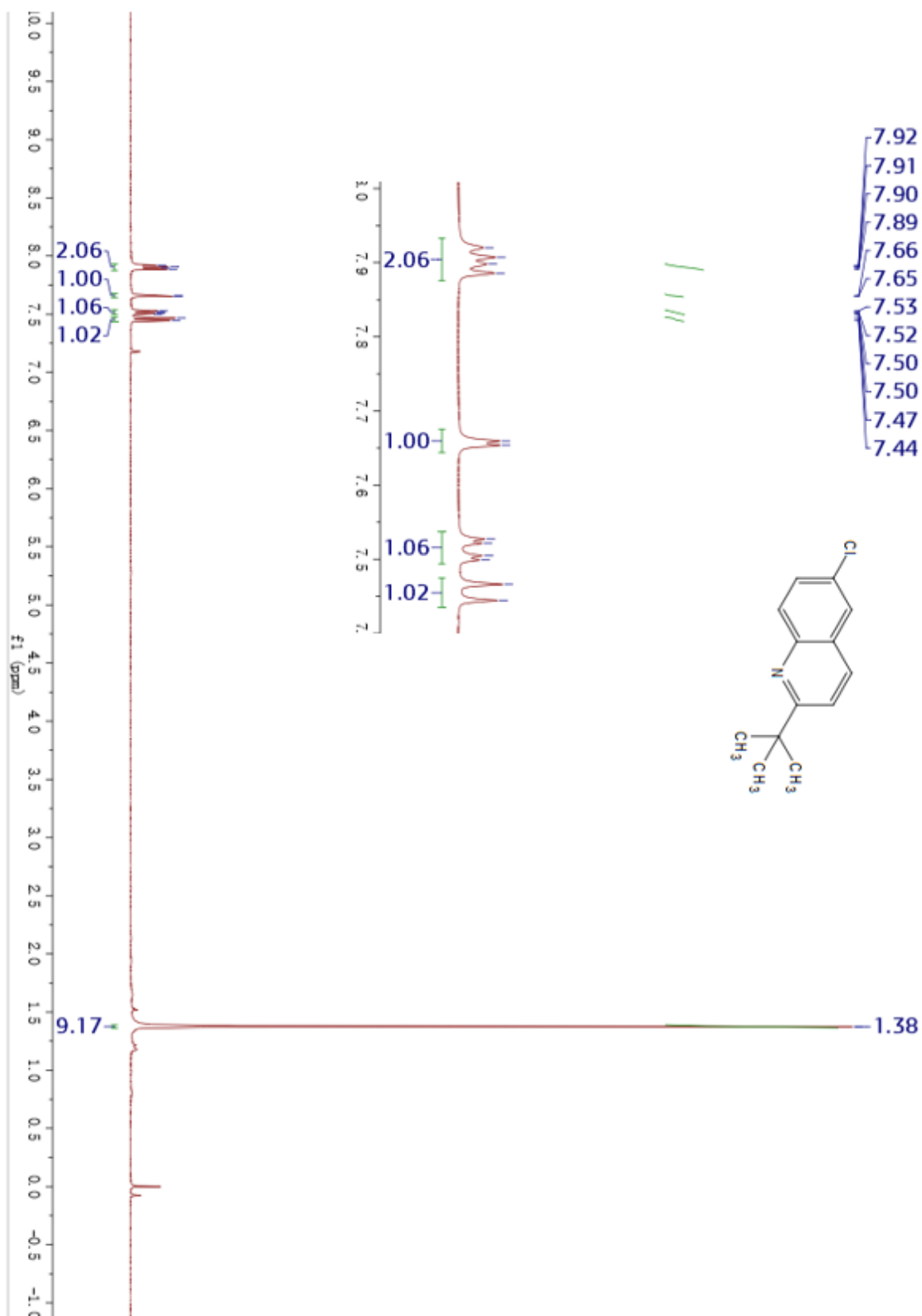


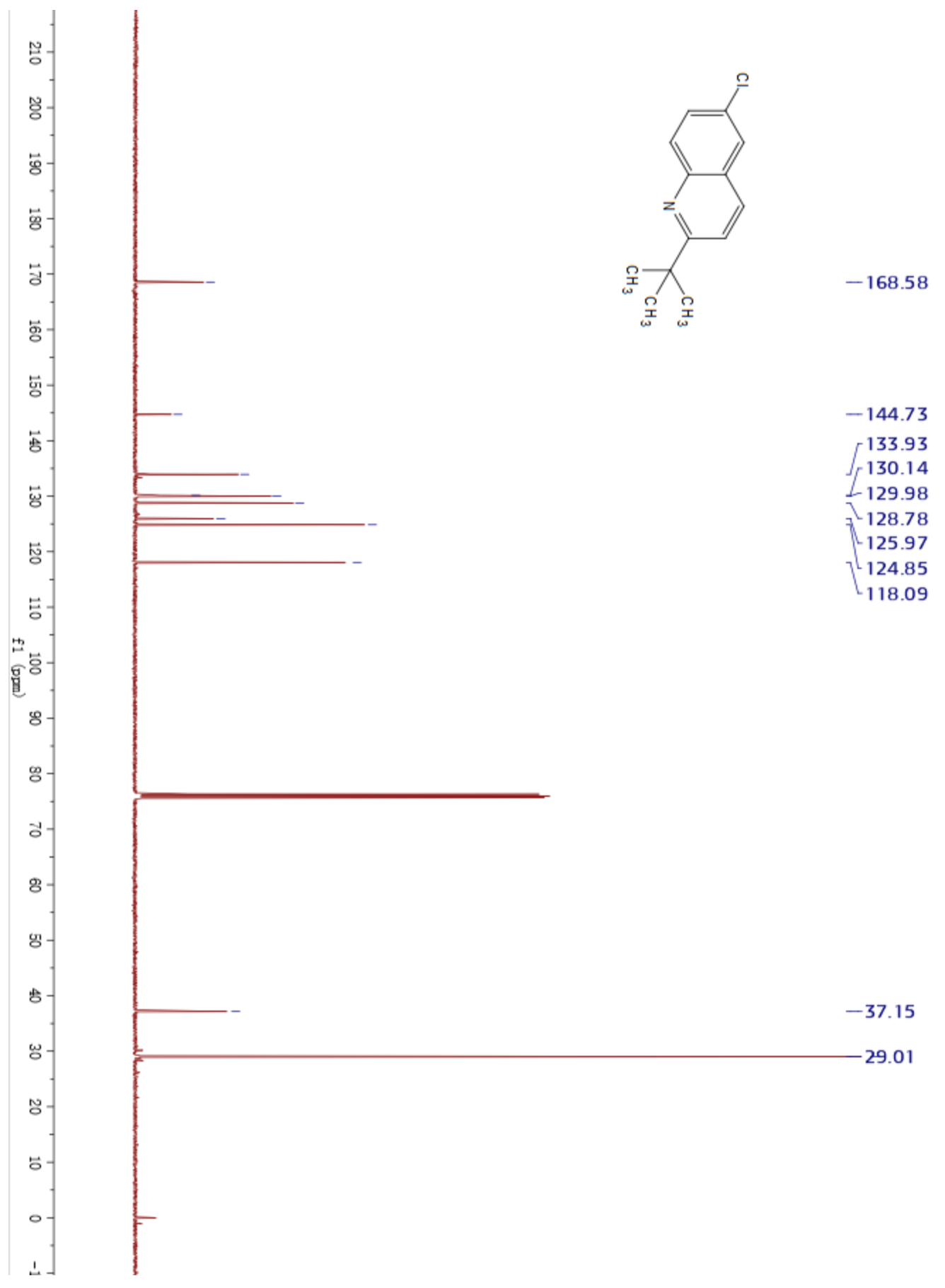
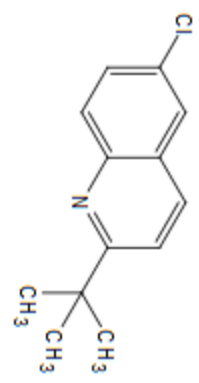
^1H and ^{13}C NMR spectra of **3x**



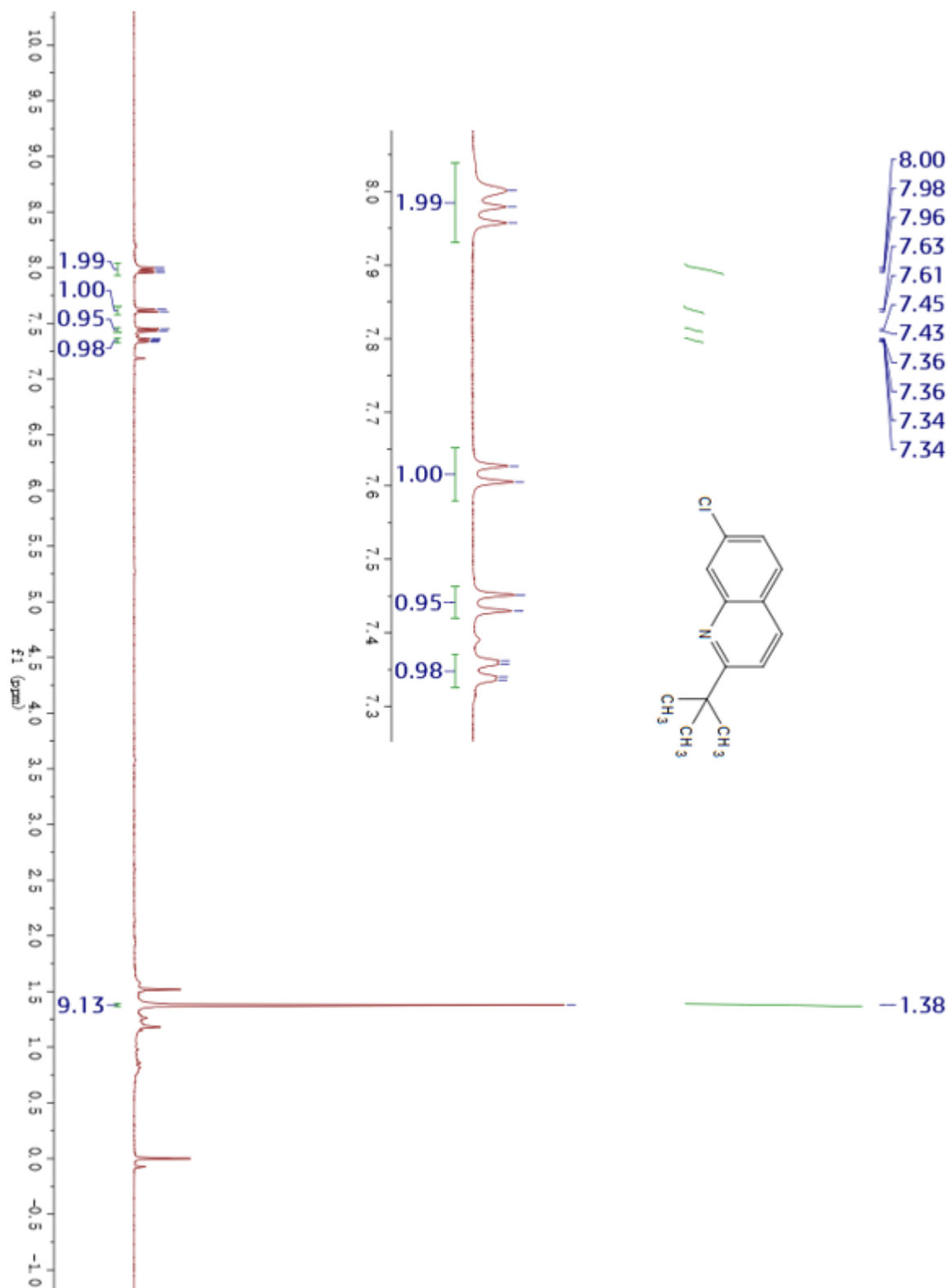


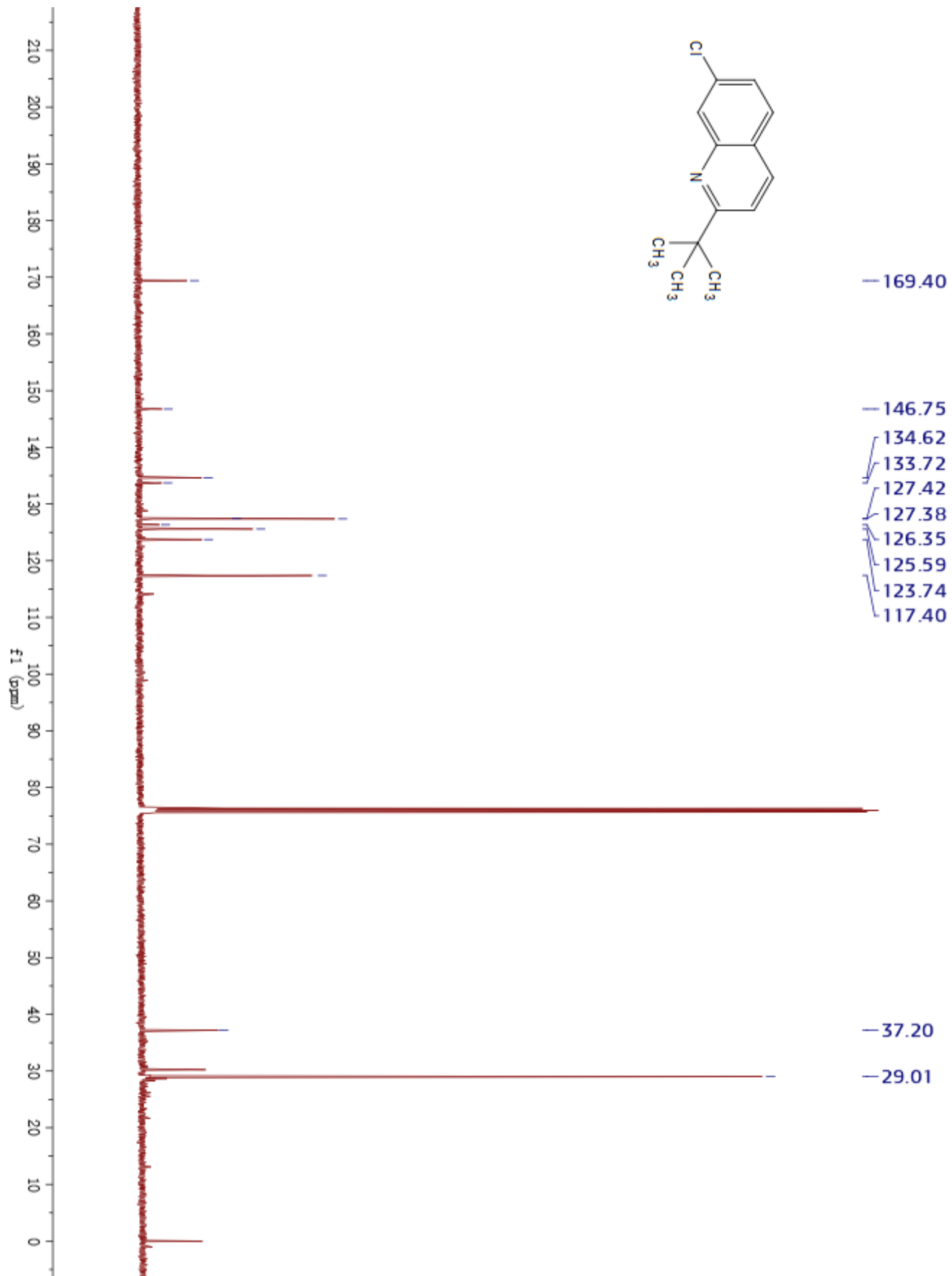
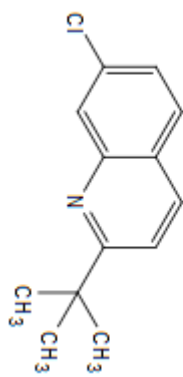
^1H and ^{13}C NMR spectra of **3y**



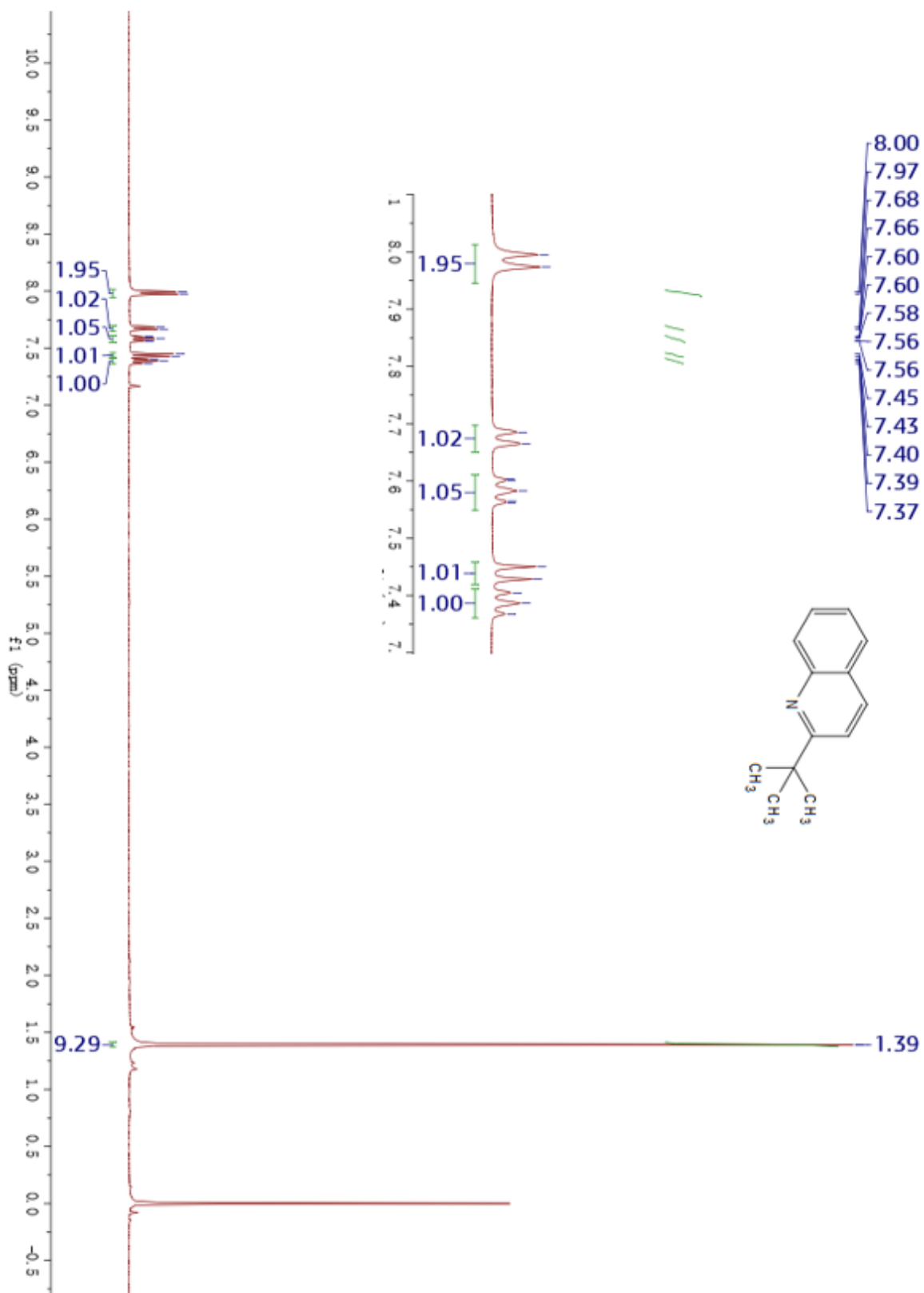


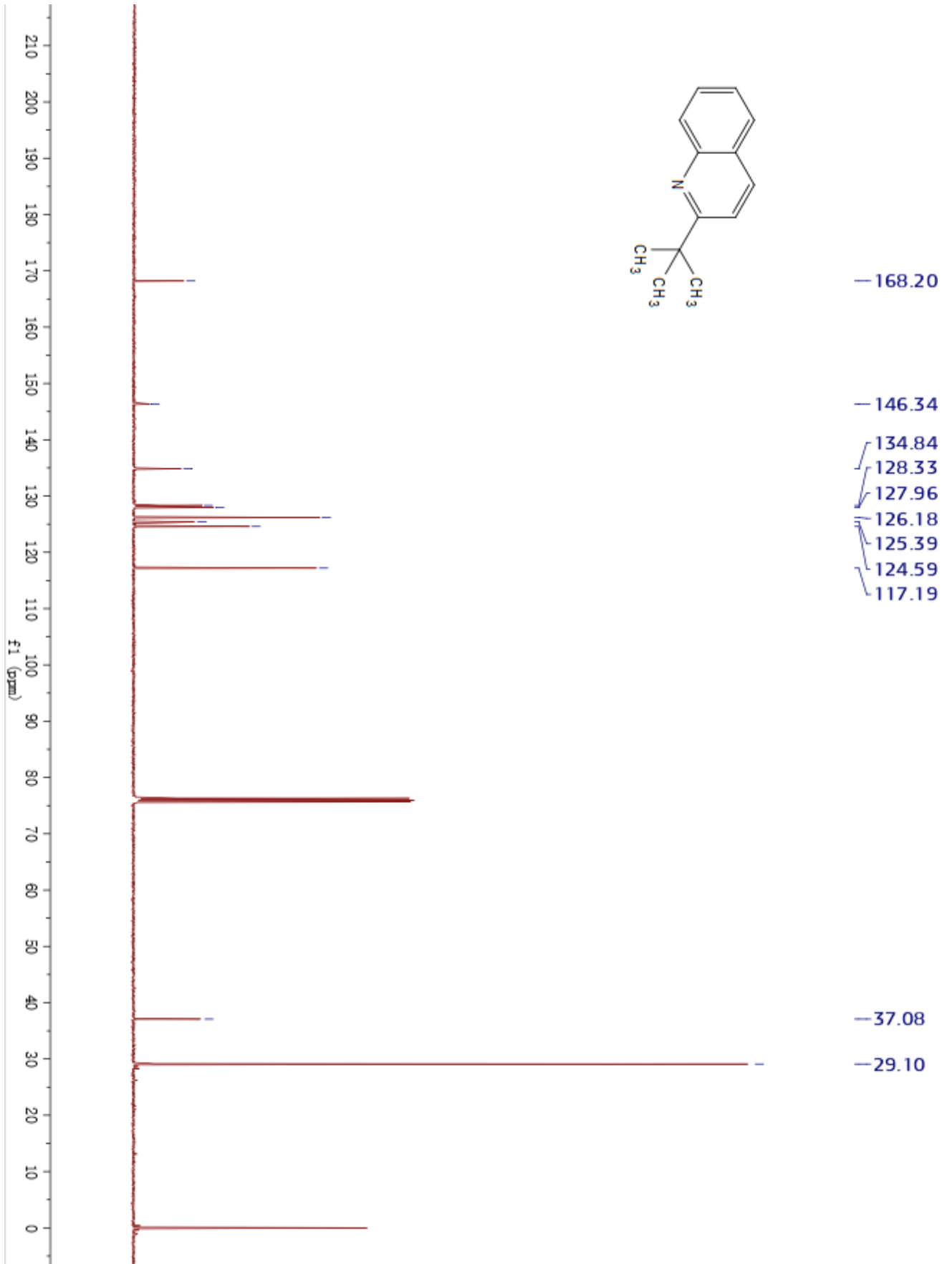
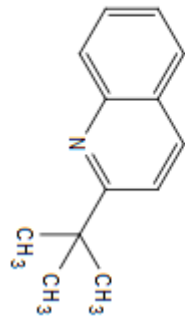
^1H and ^{13}C NMR spectra of **3z**



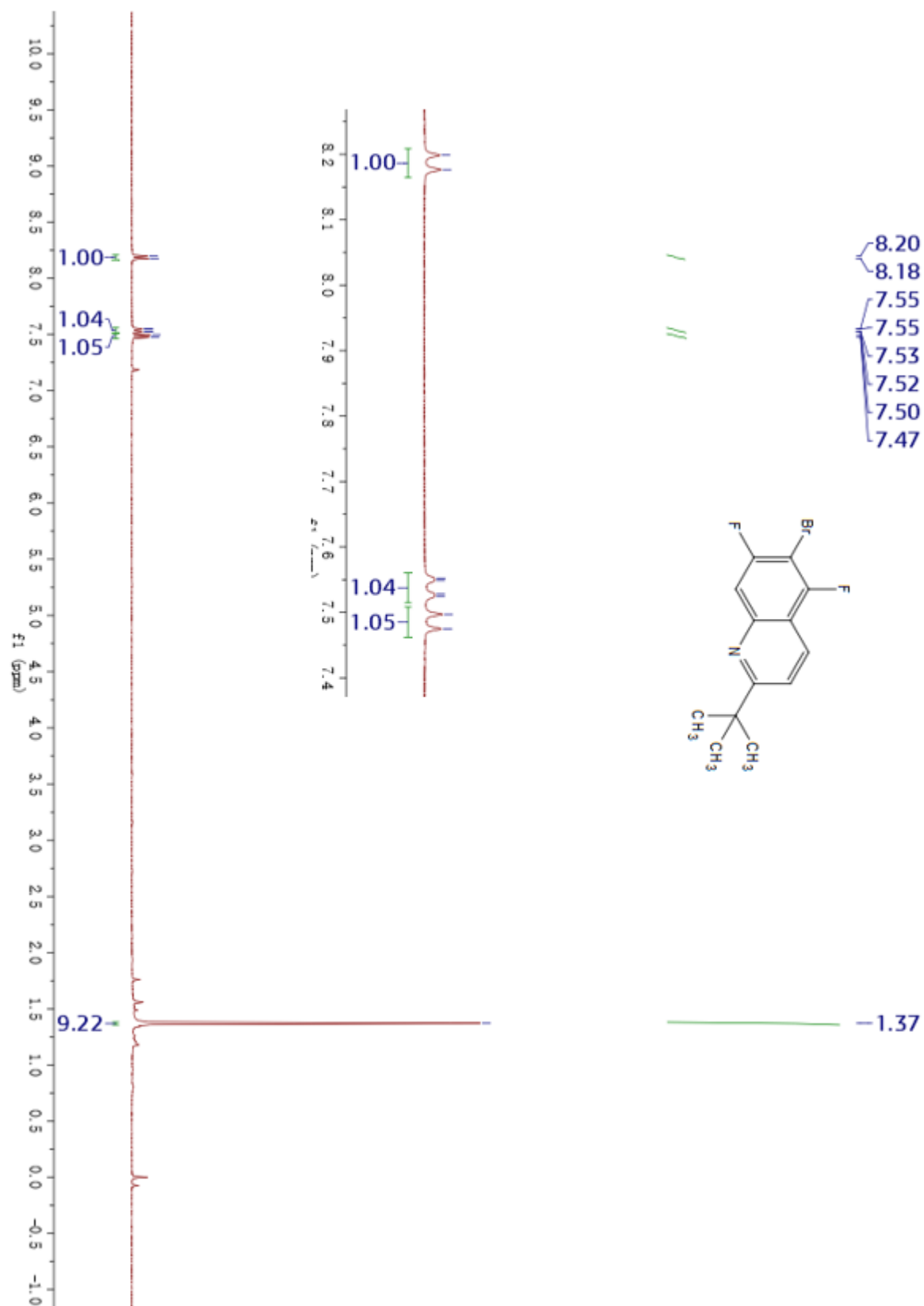


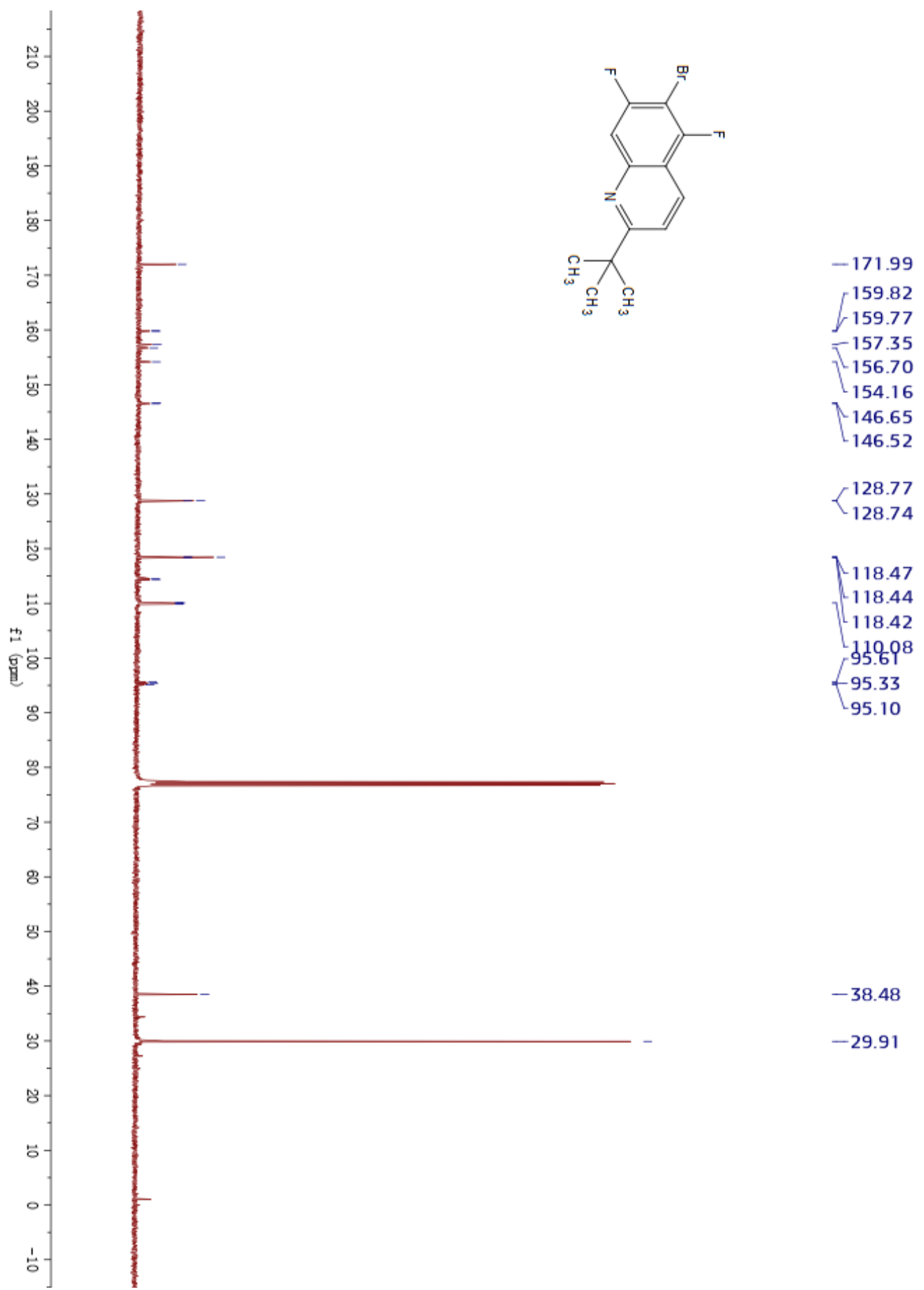
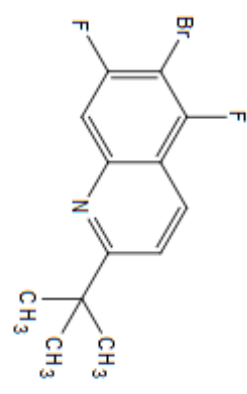
^1H and ^{13}C NMR spectra of **3aa**

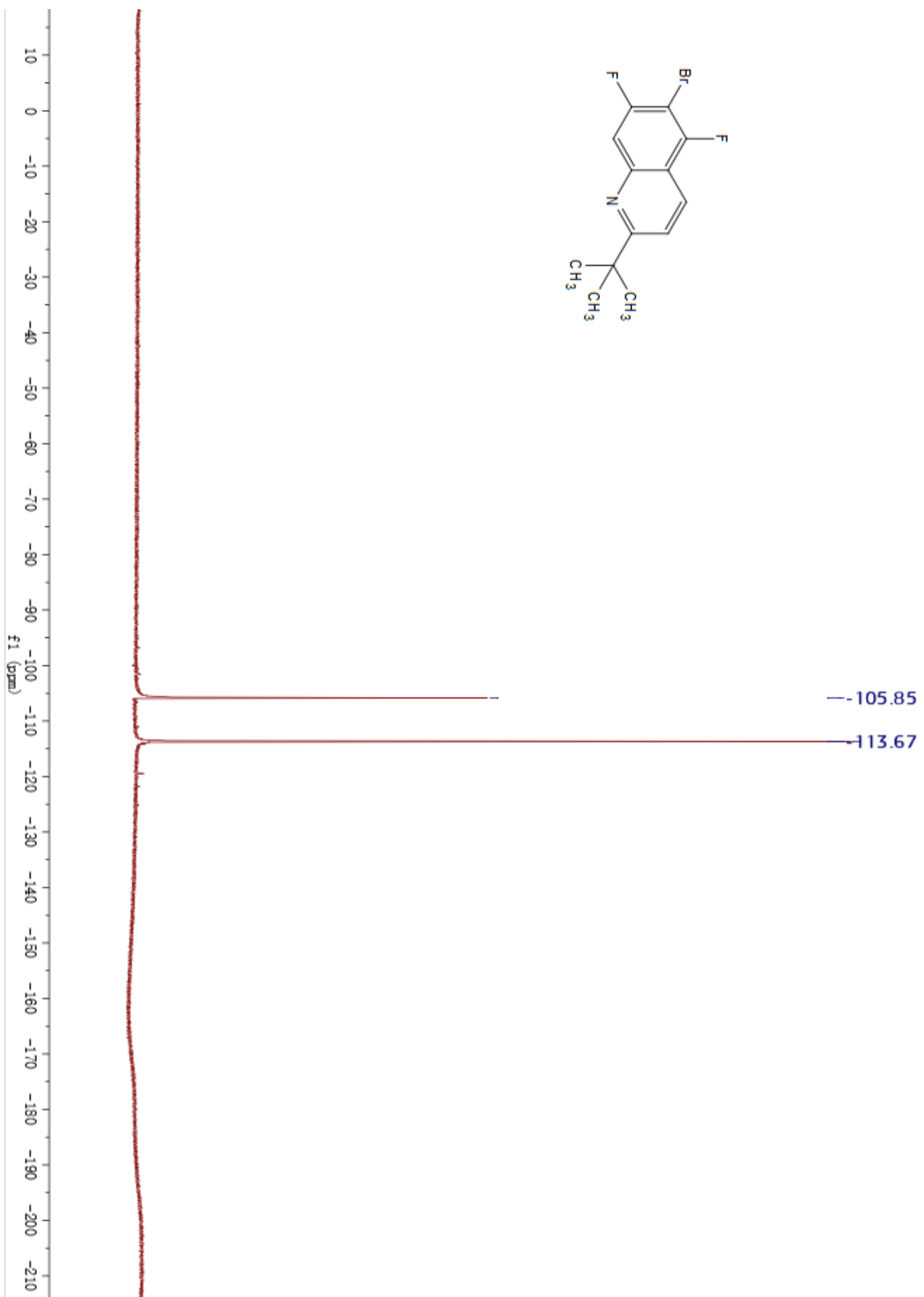
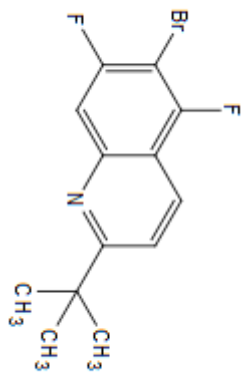




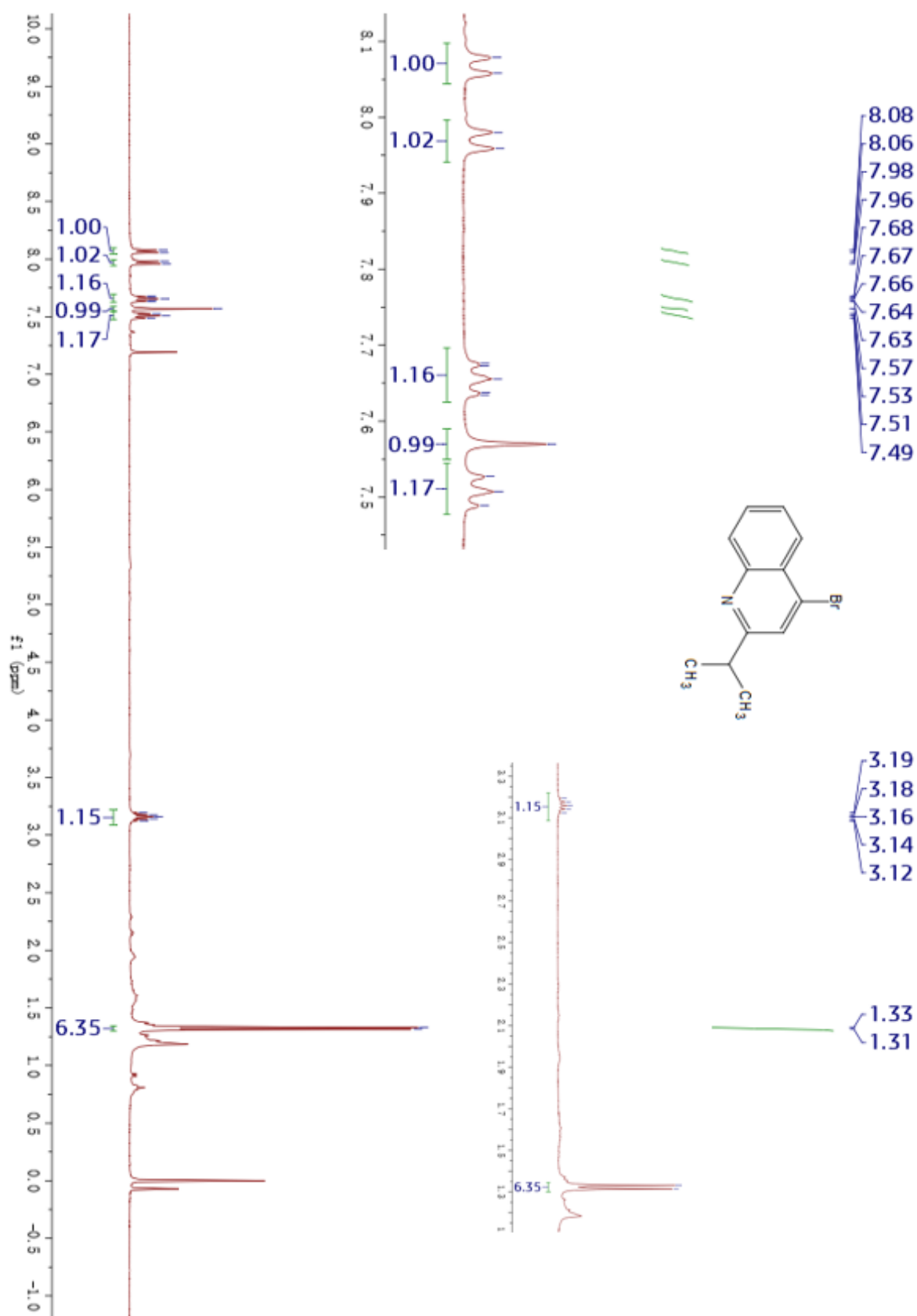
^1H , ^{19}F and ^{13}C NMR spectra of **3ab**

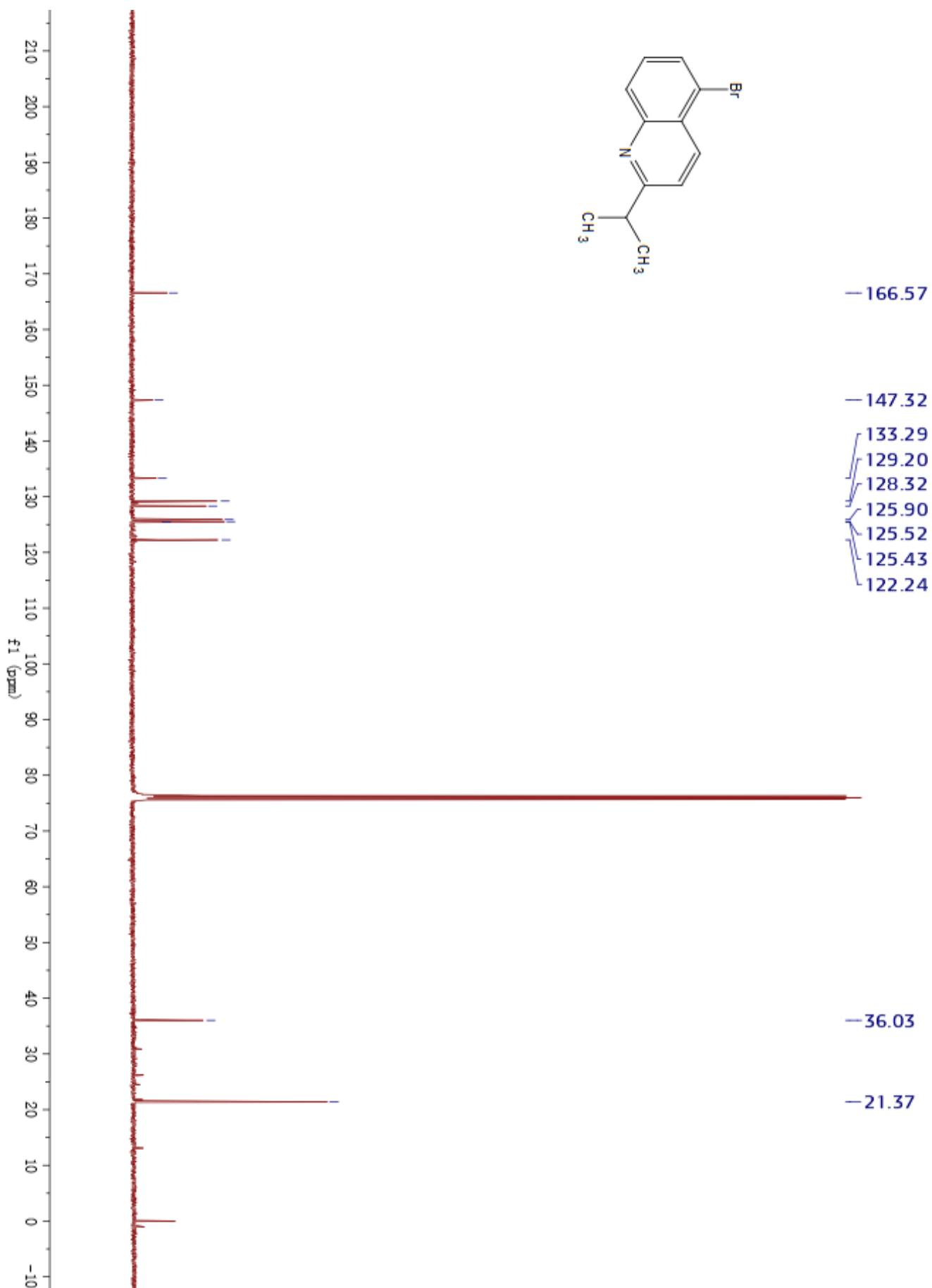
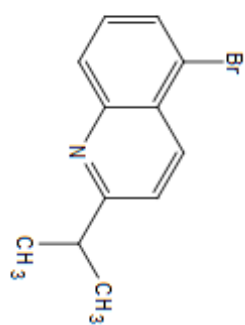




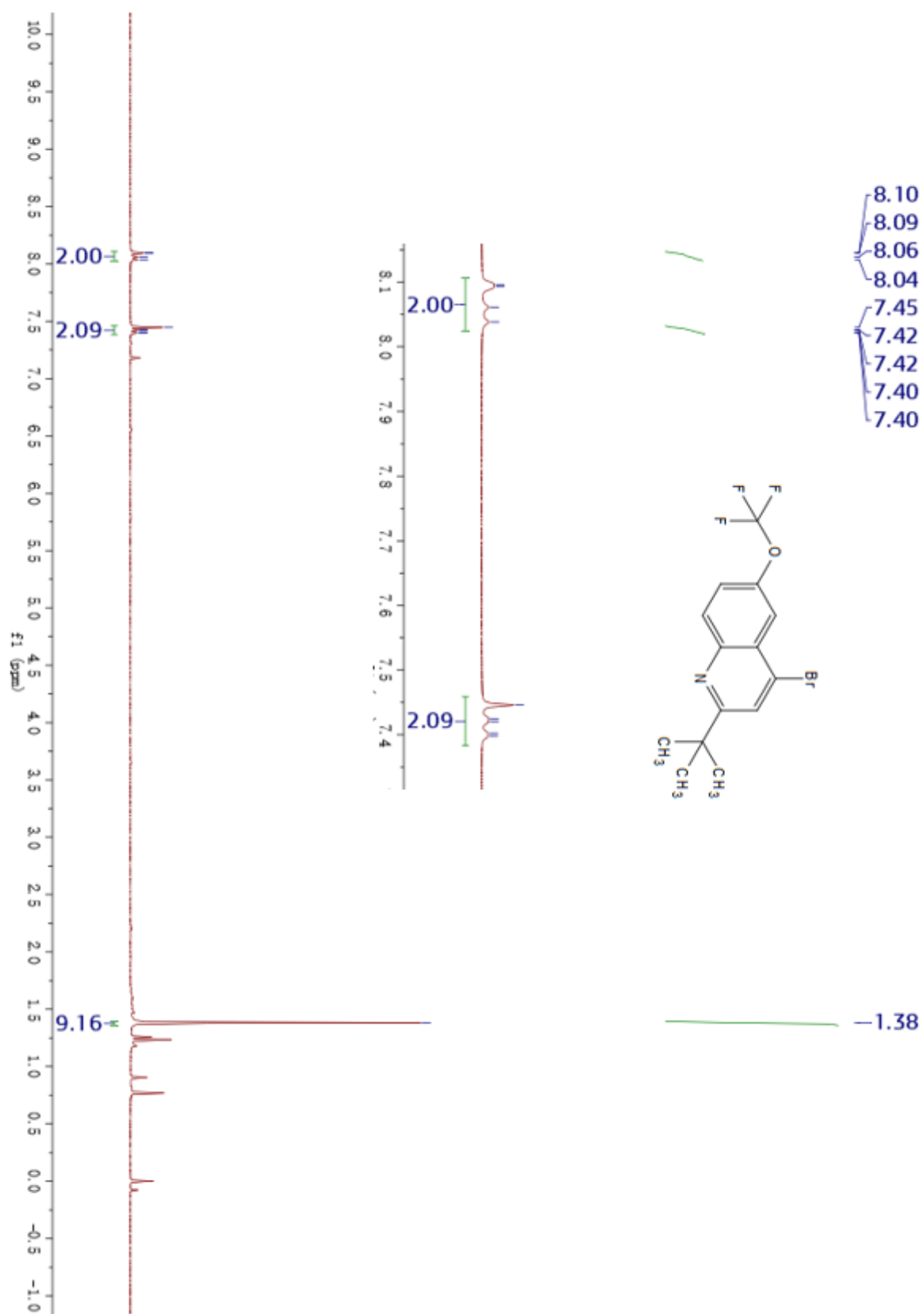


^1H and ^{13}C NMR spectra of **3ac**

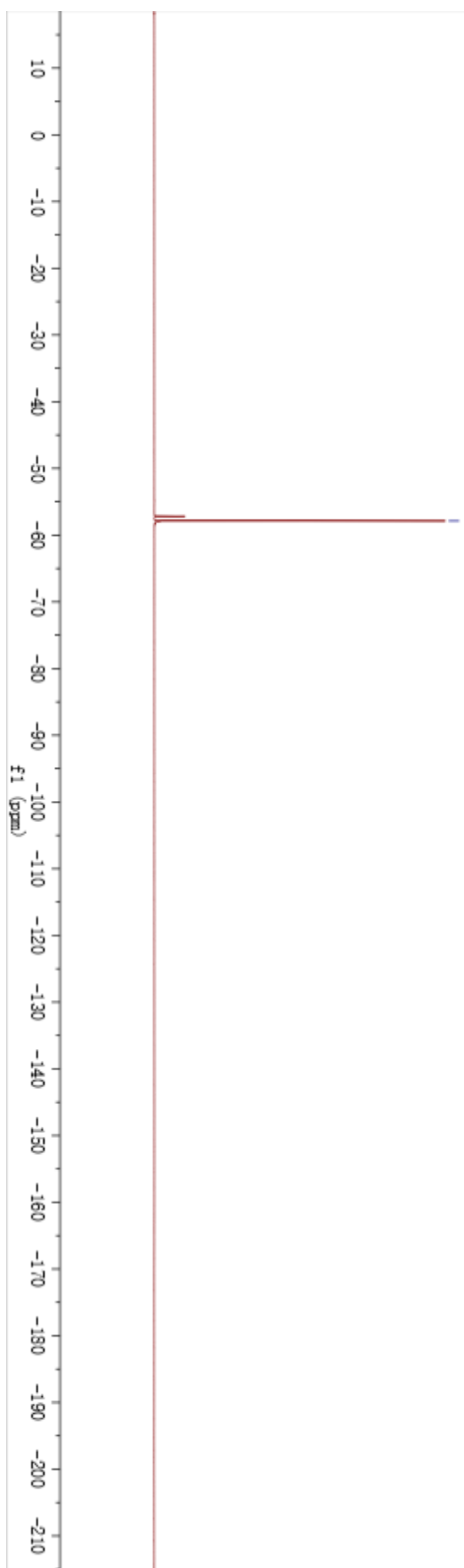
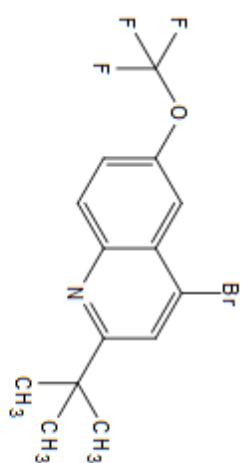


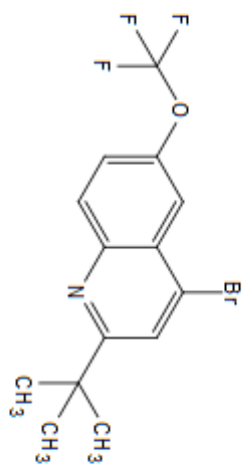


^1H , ^{19}F and ^{13}C NMR spectra of **3ad**

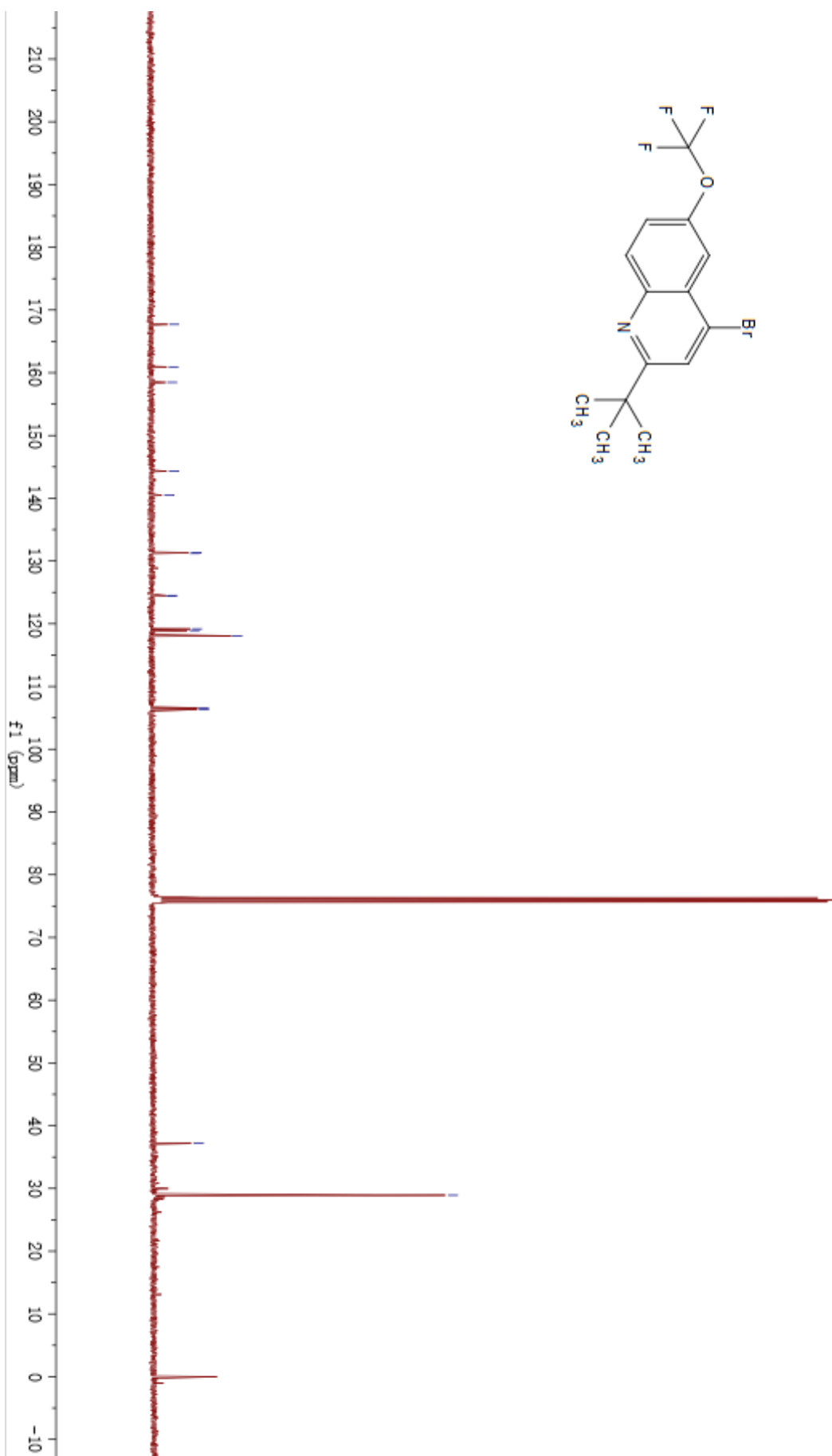


-57.87



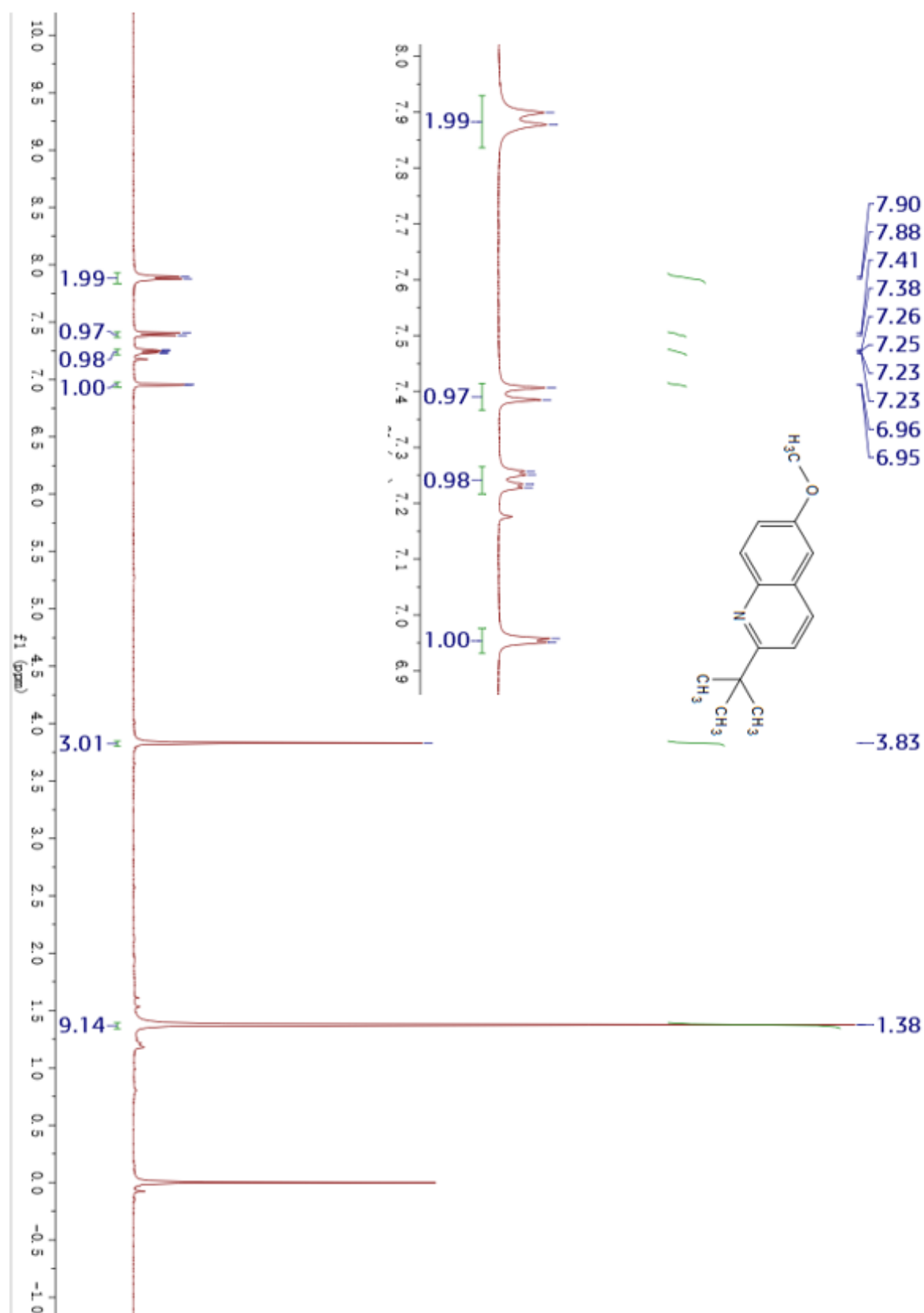


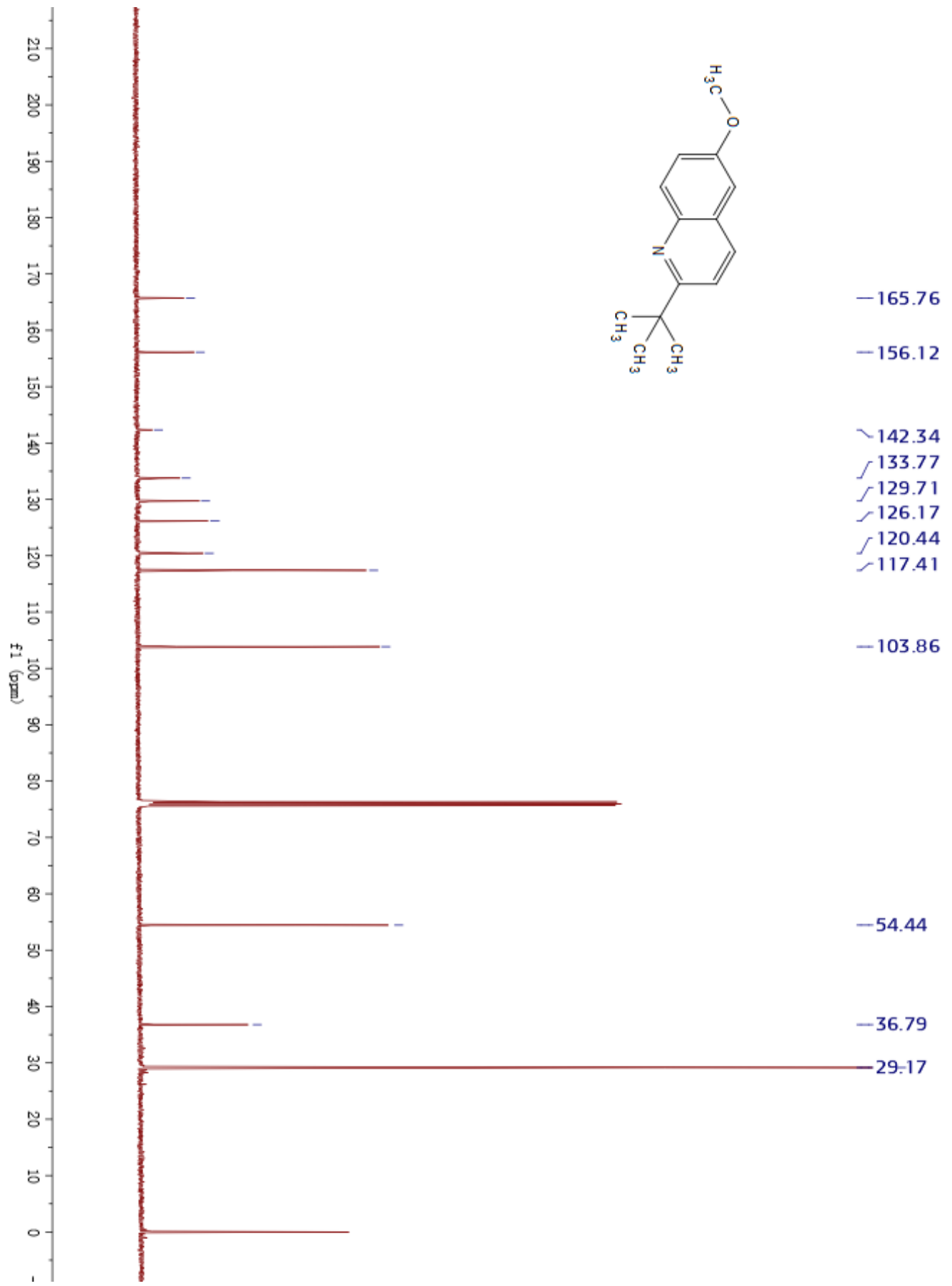
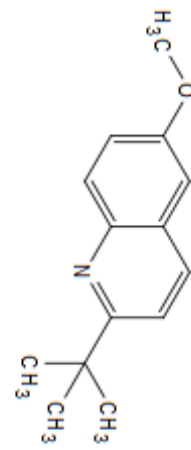
- 167.70
- 160.93
- 158.47
- 144.30
- 140.47
- 131.32
- 131.23
- 119.17
- 118.91
- 118.07
- 106.58
- 106.34



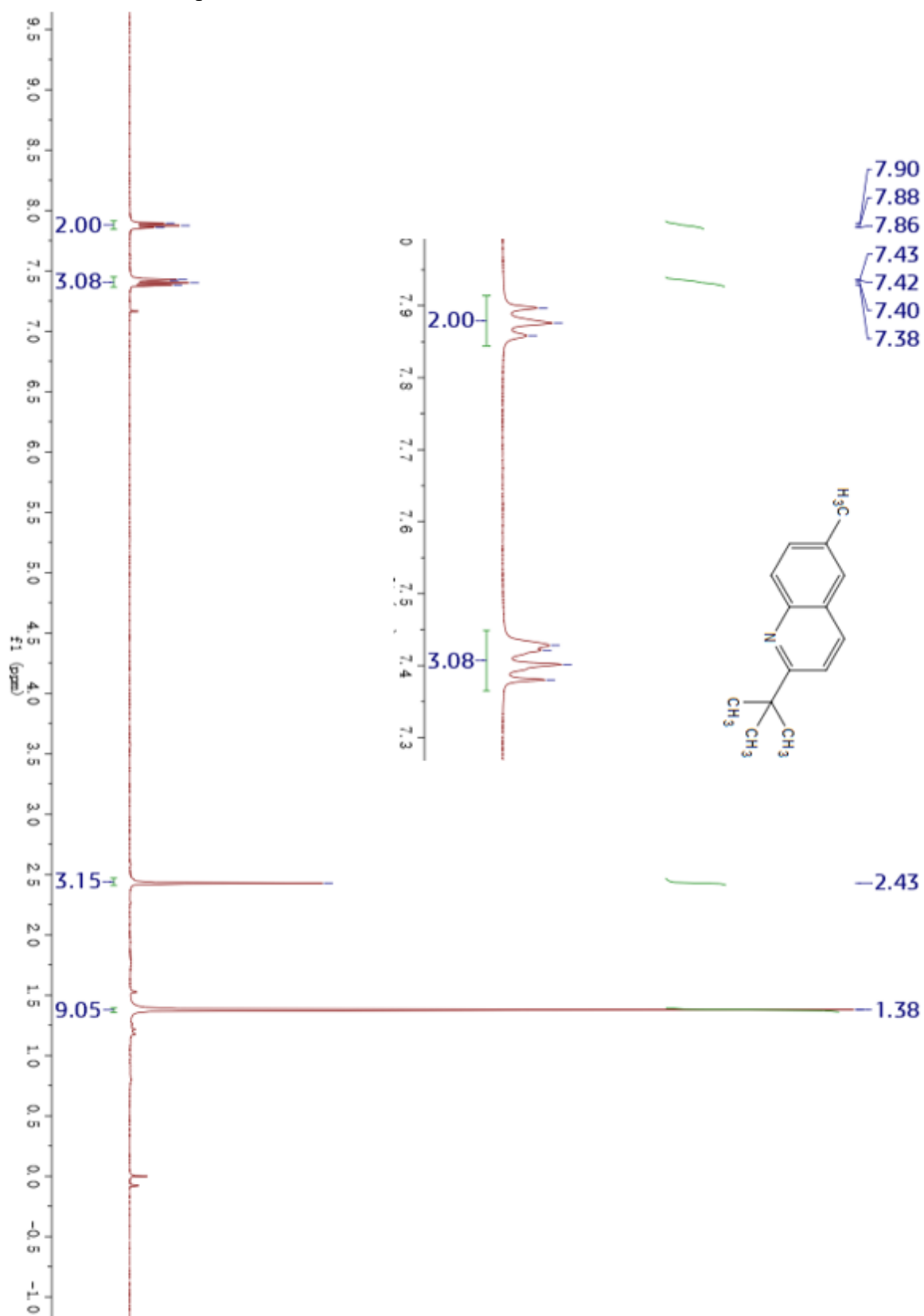
- 37.18
- 28.93

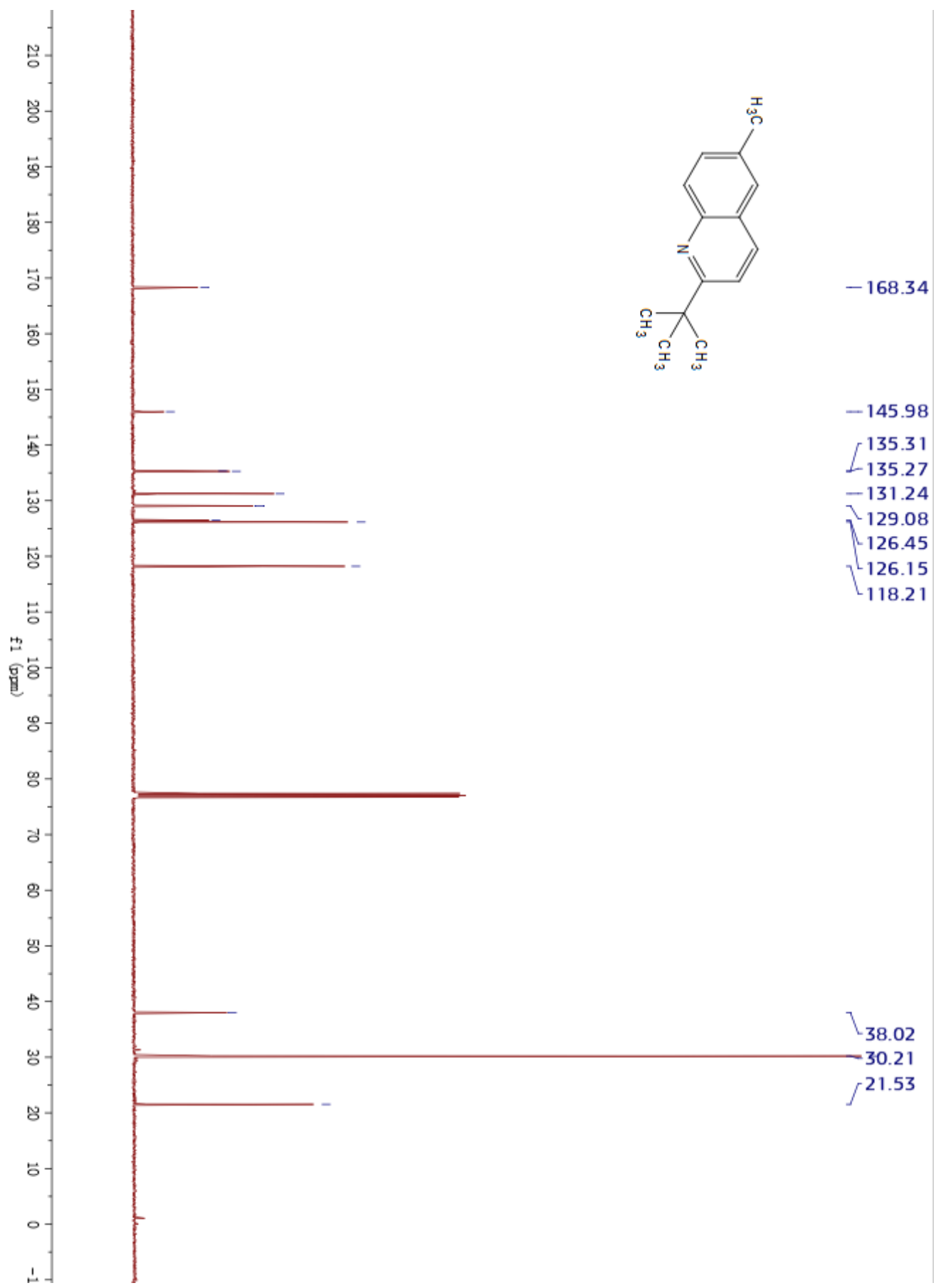
^1H and ^{13}C NMR spectra of **3ae**



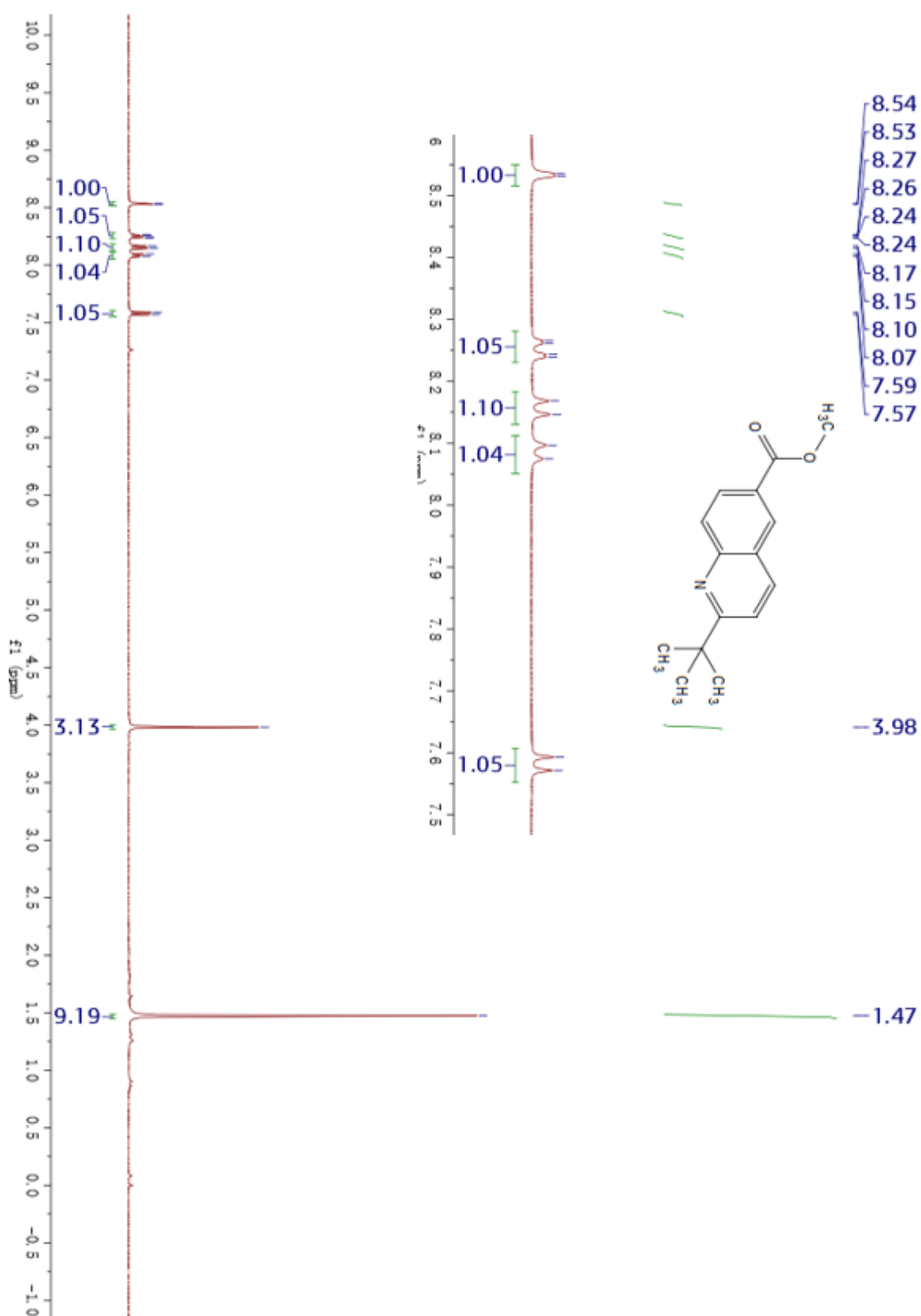


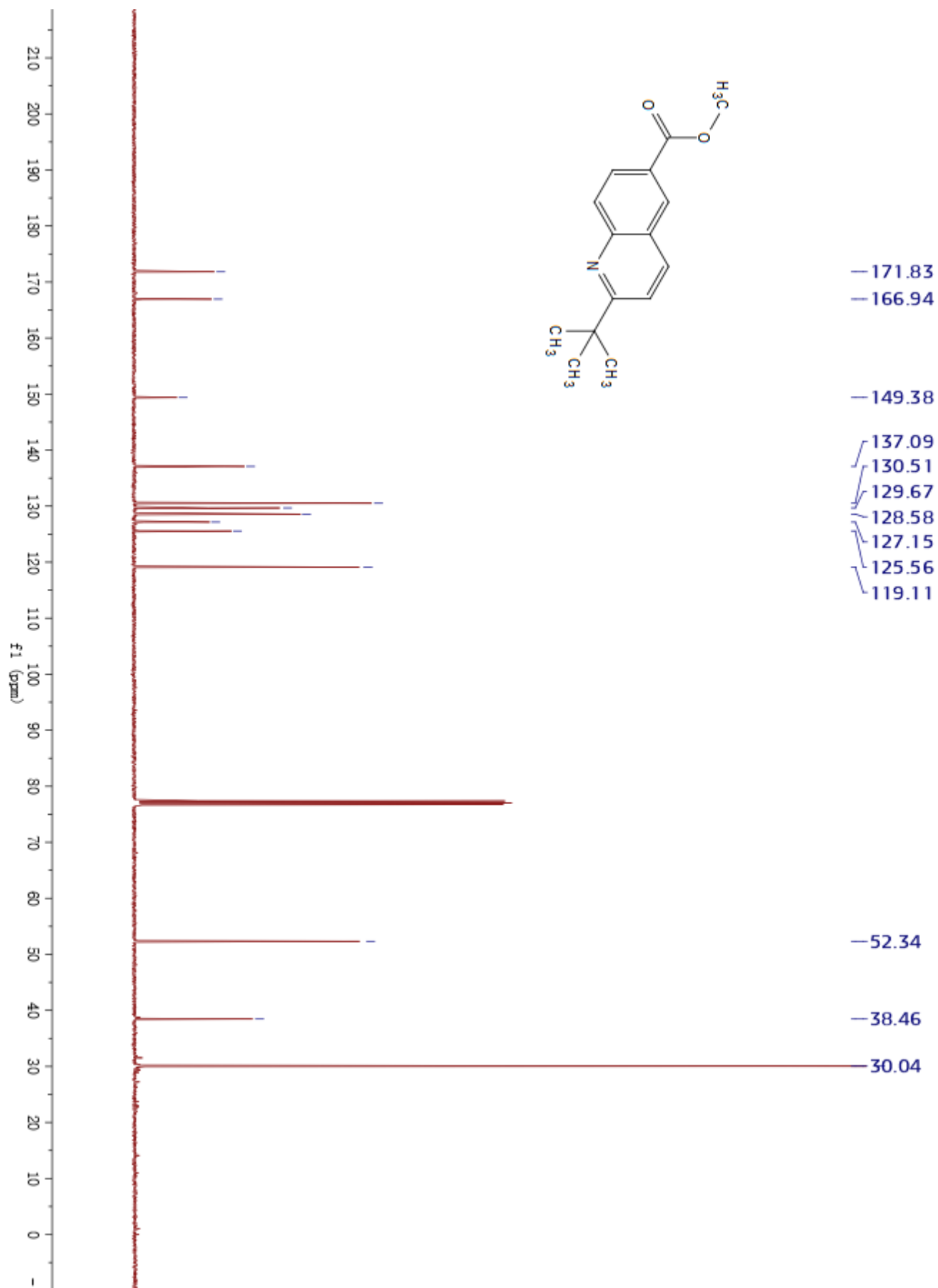
^1H and ^{13}C NMR spectra of **3af**



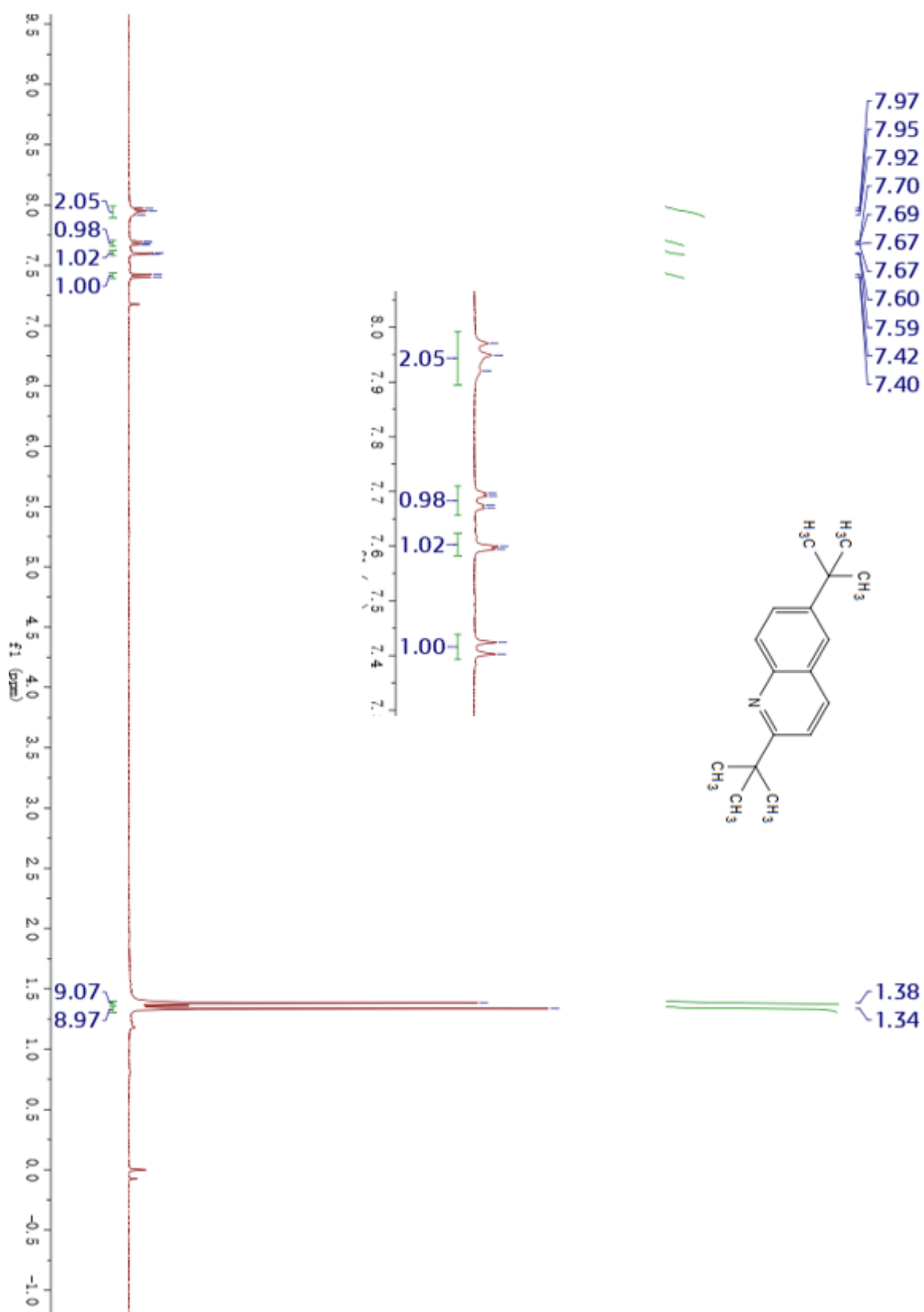


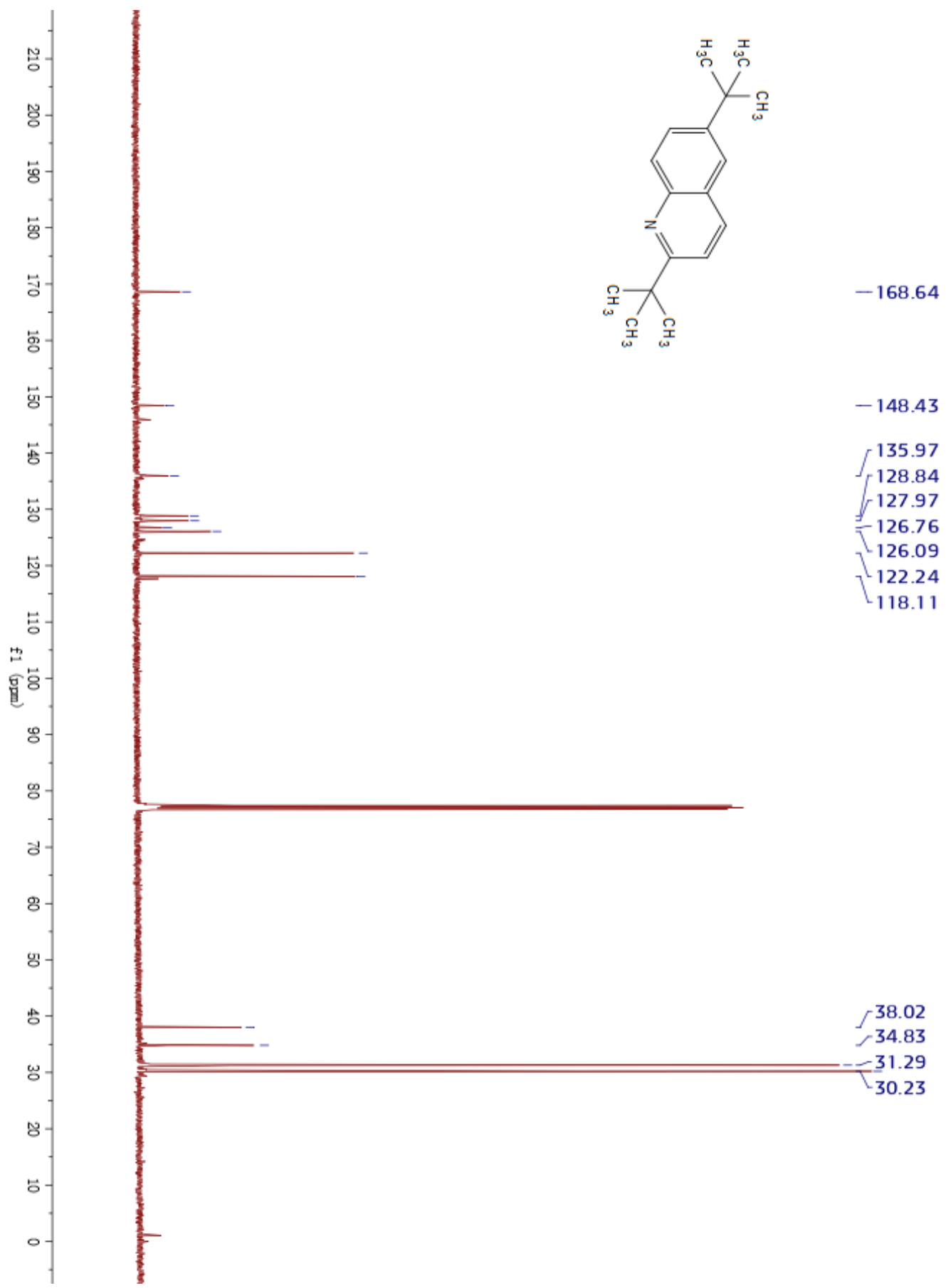
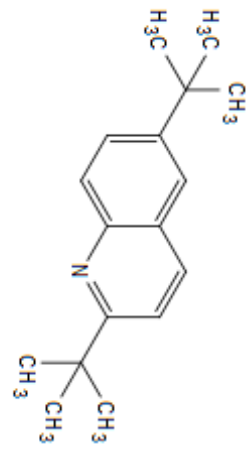
^1H and ^{13}C NMR spectra of **3ag**



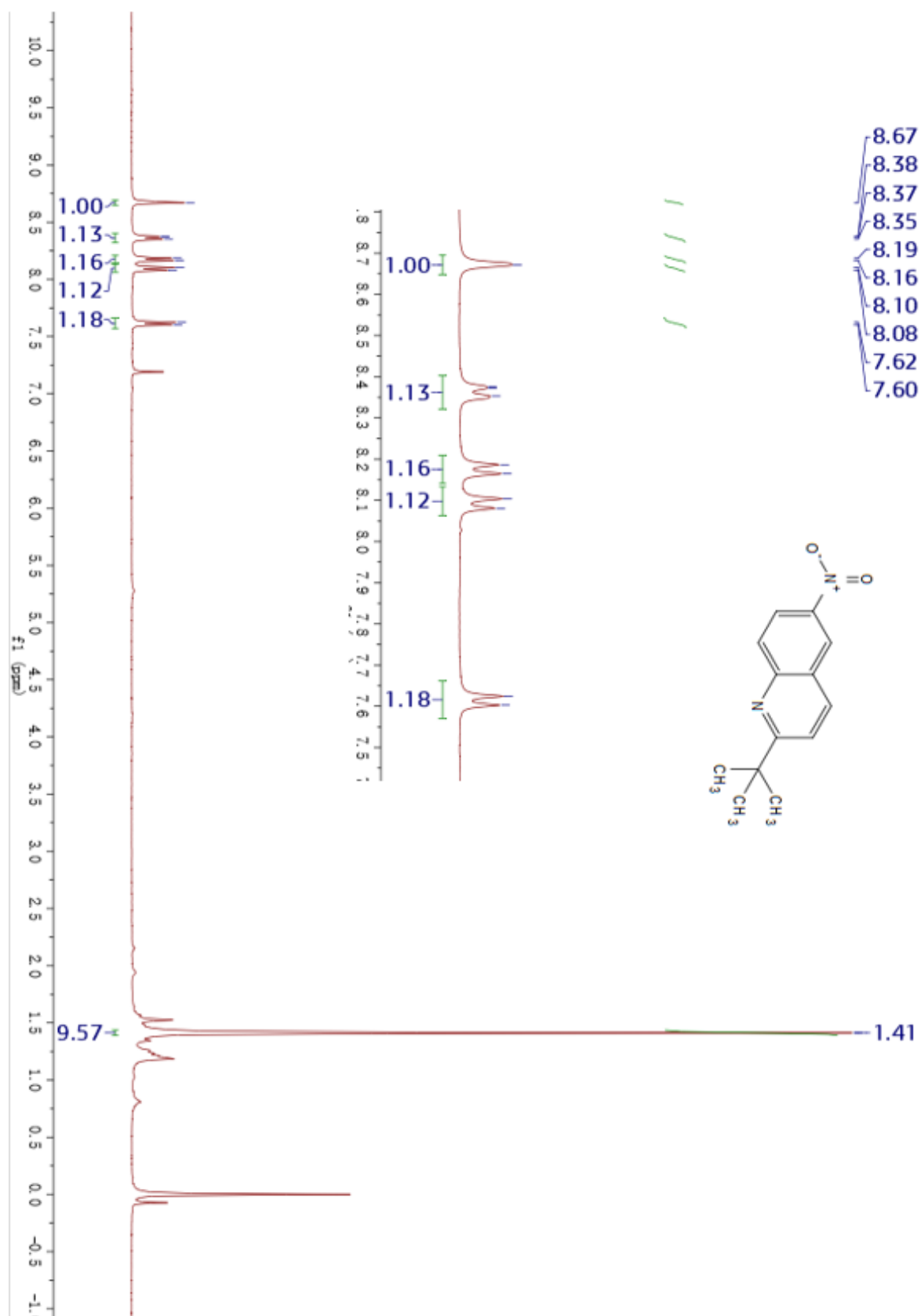


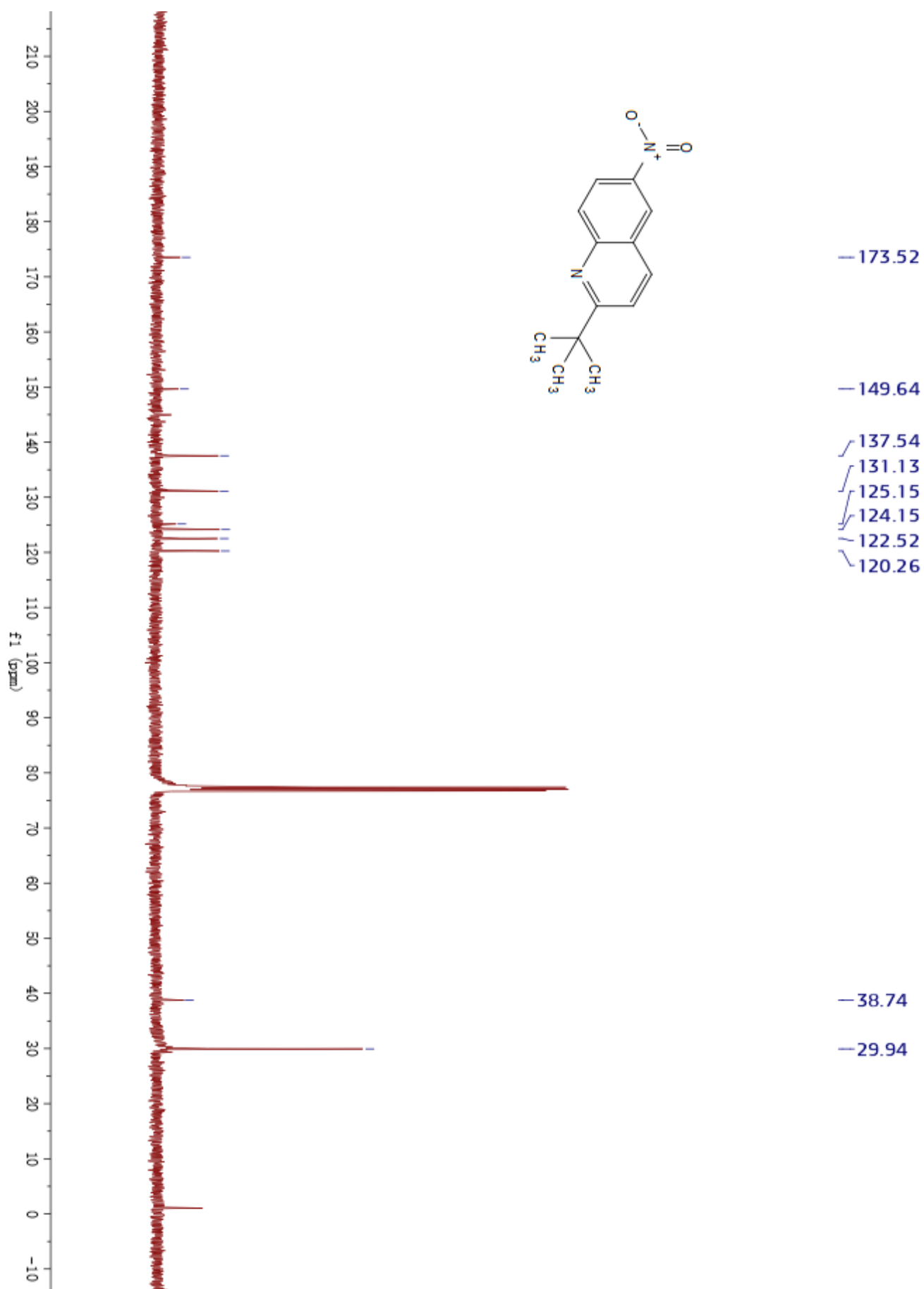
^1H and ^{13}C NMR spectra of **3ah**



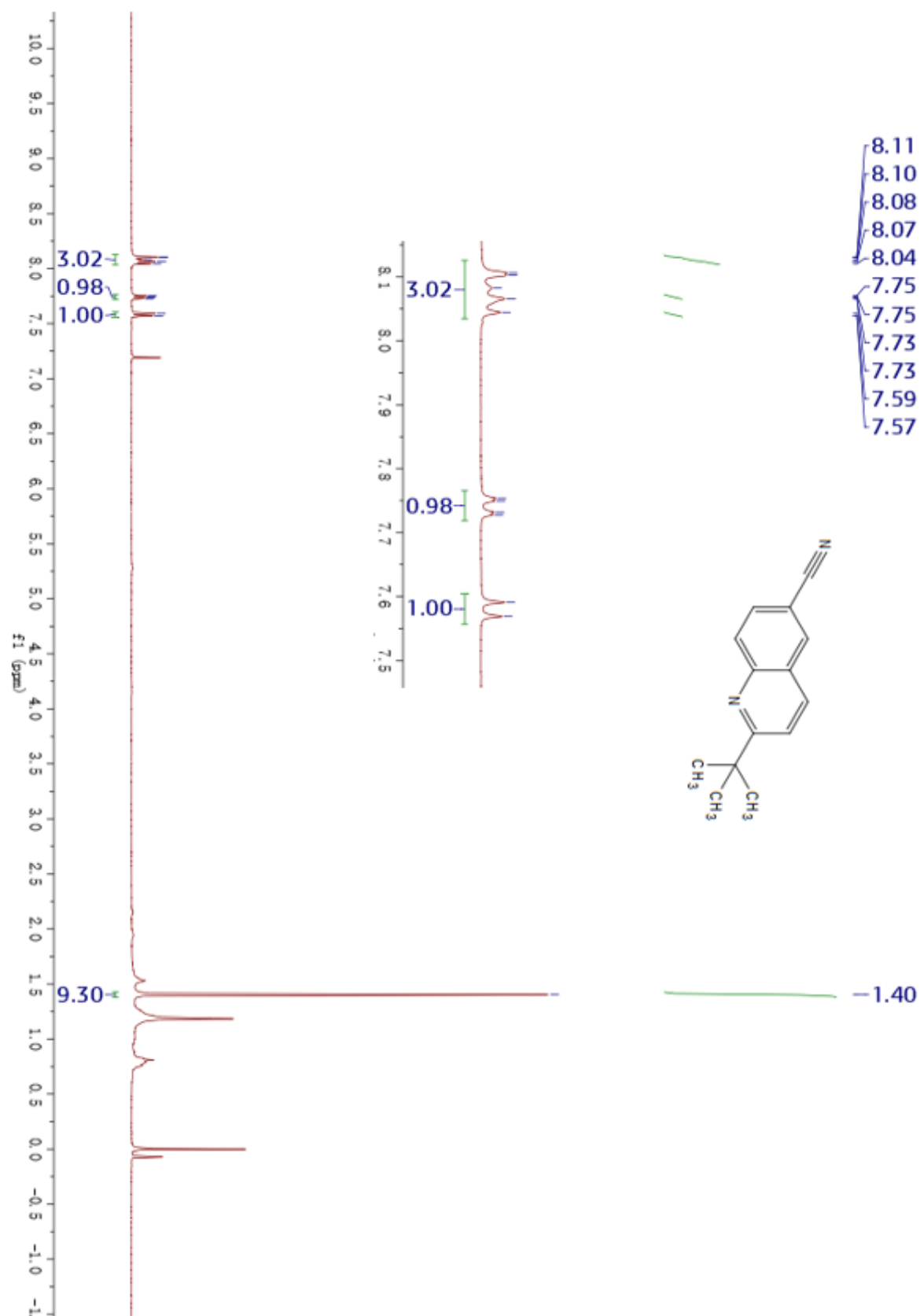


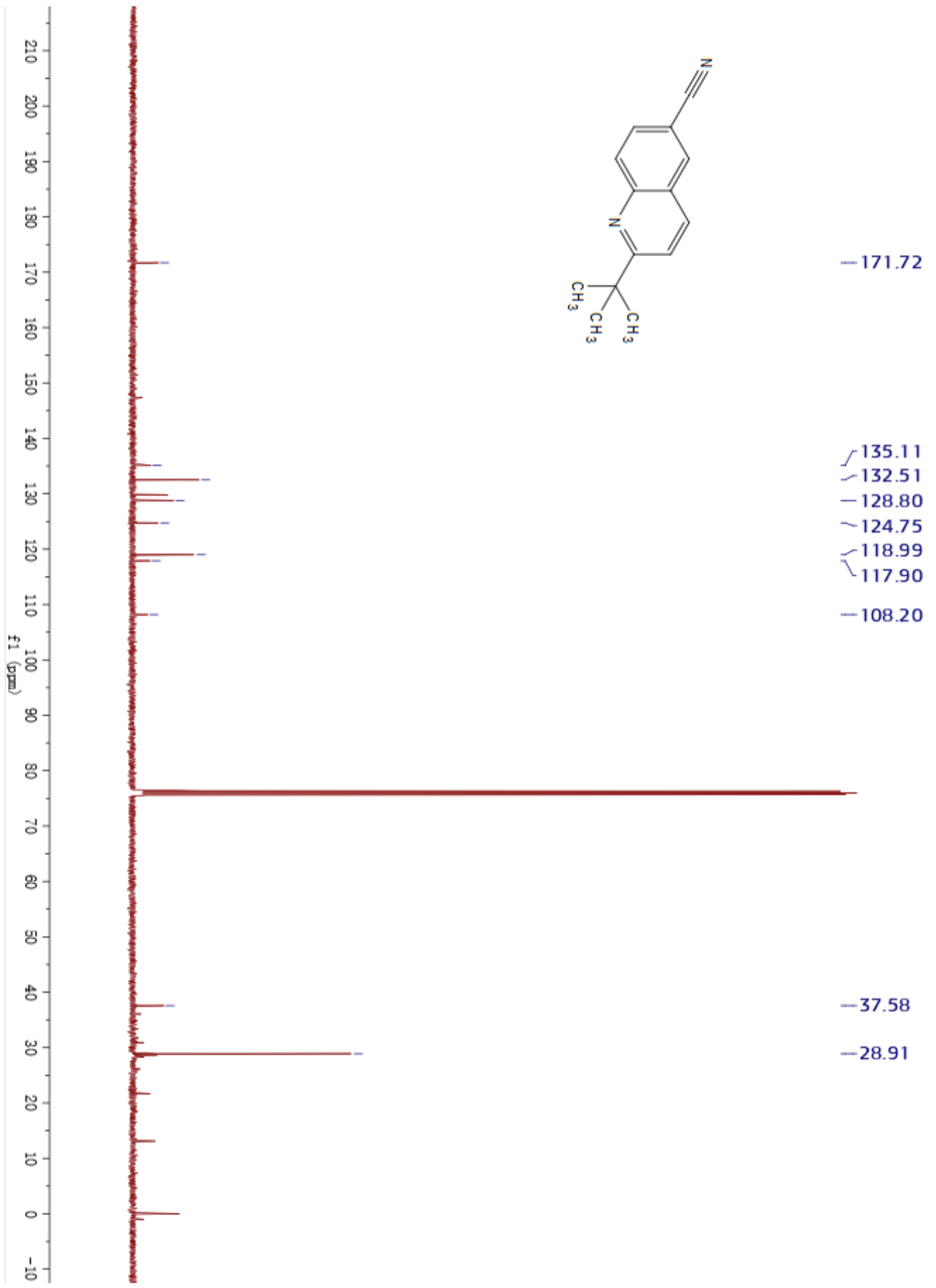
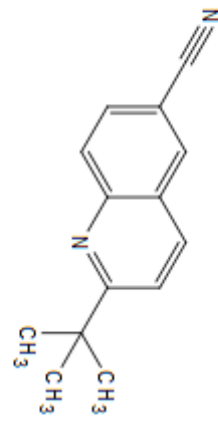
^1H and ^{13}C NMR spectra of **3ai**



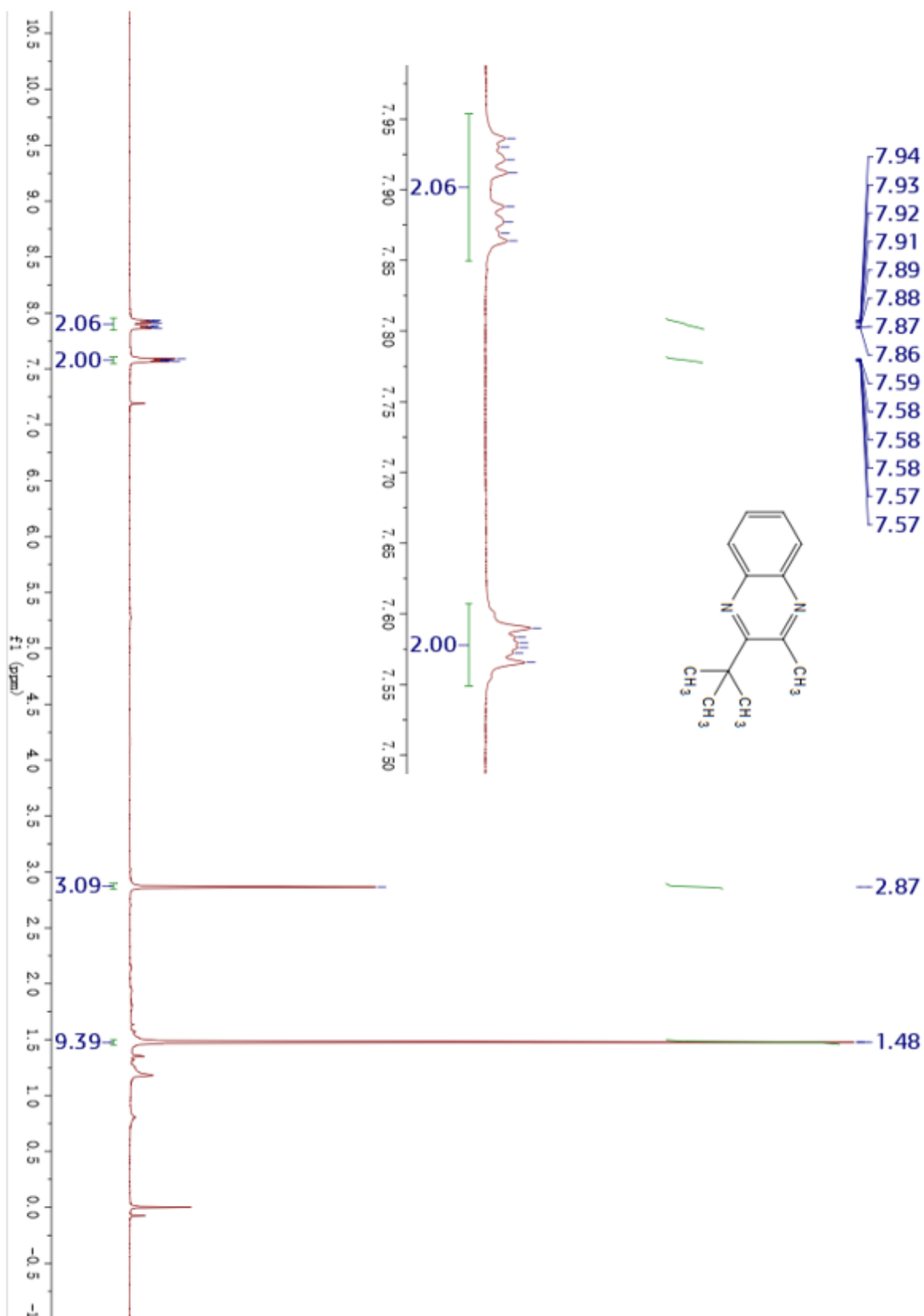


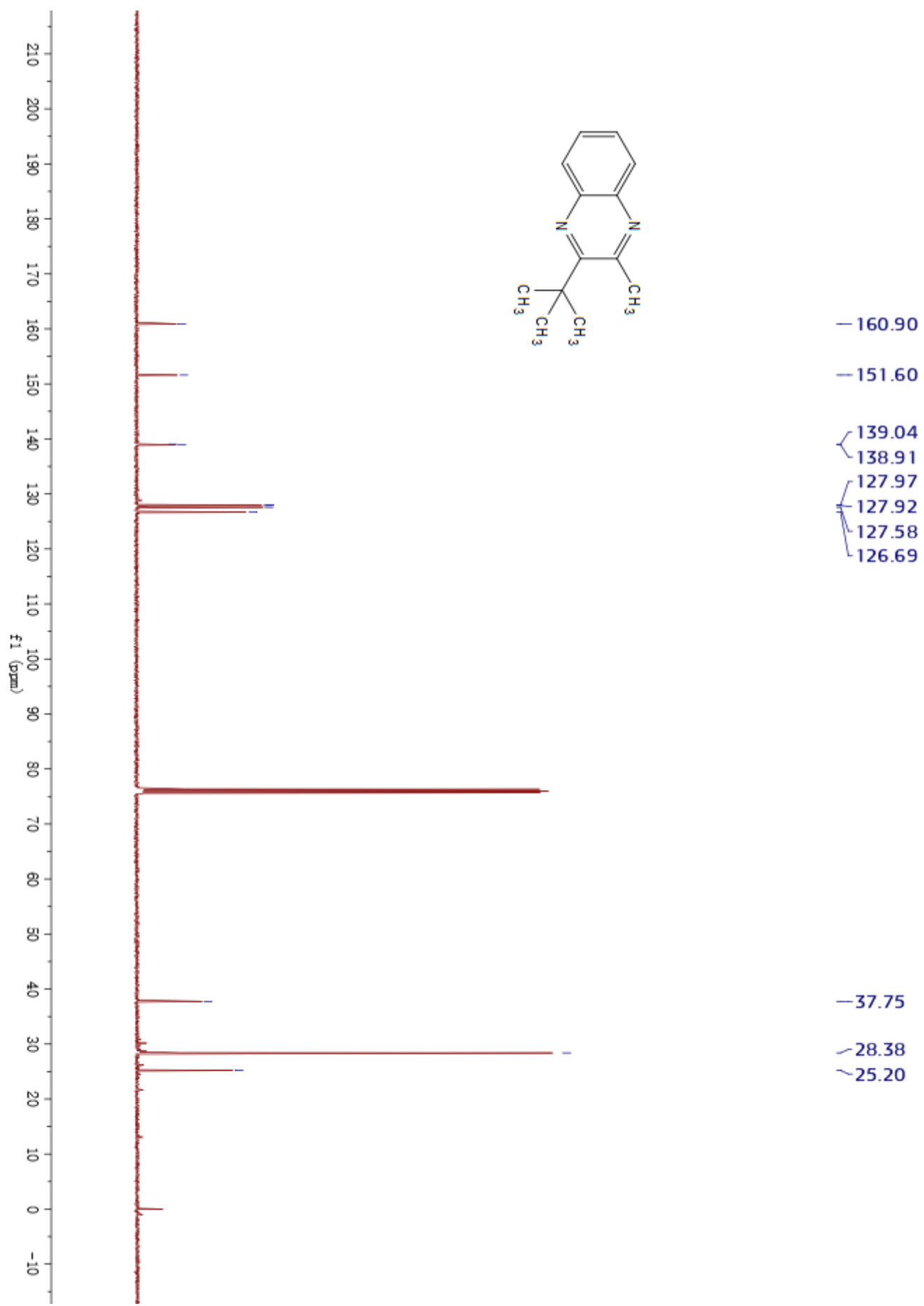
^1H and ^{13}C NMR spectra of **3aj**



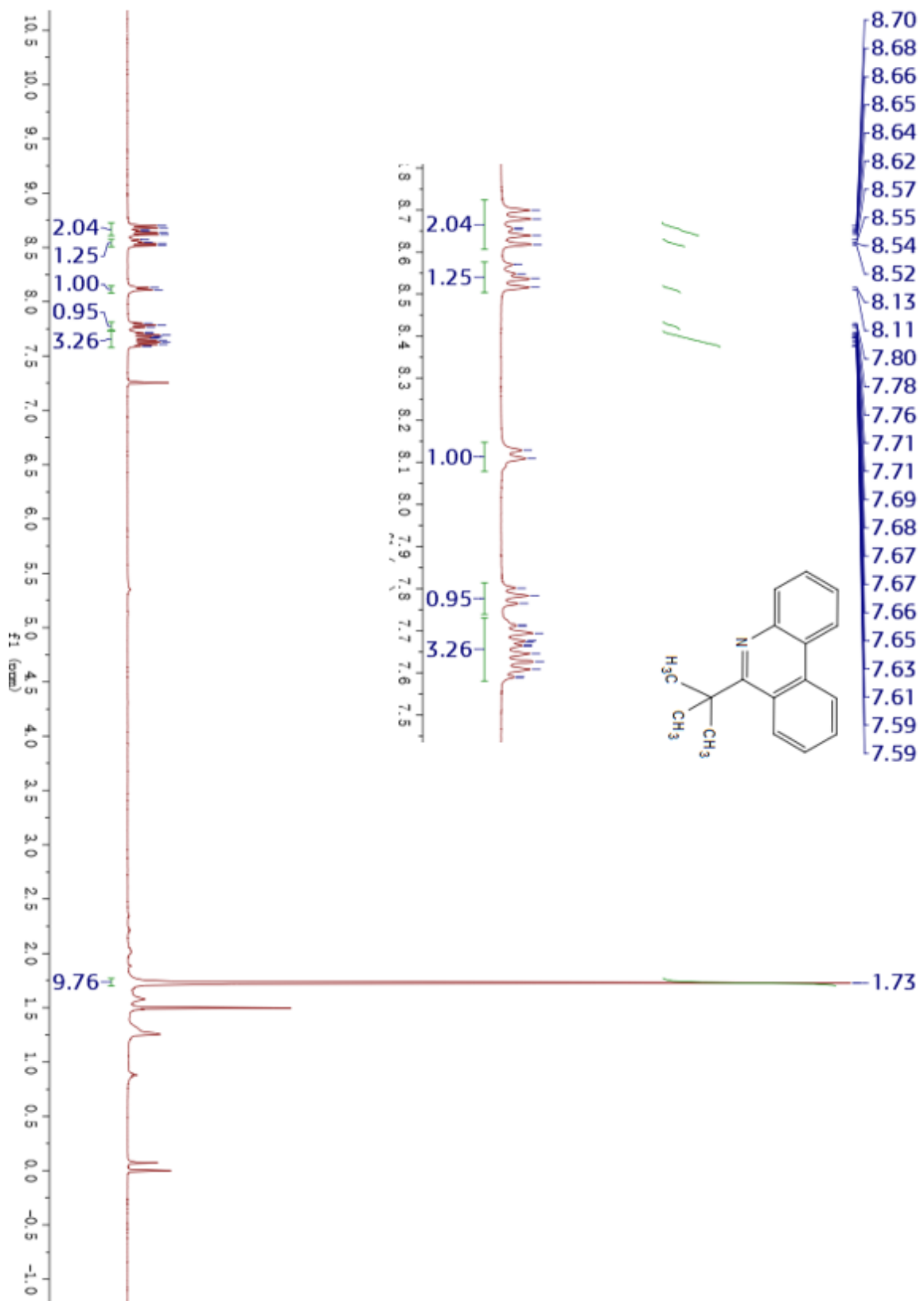


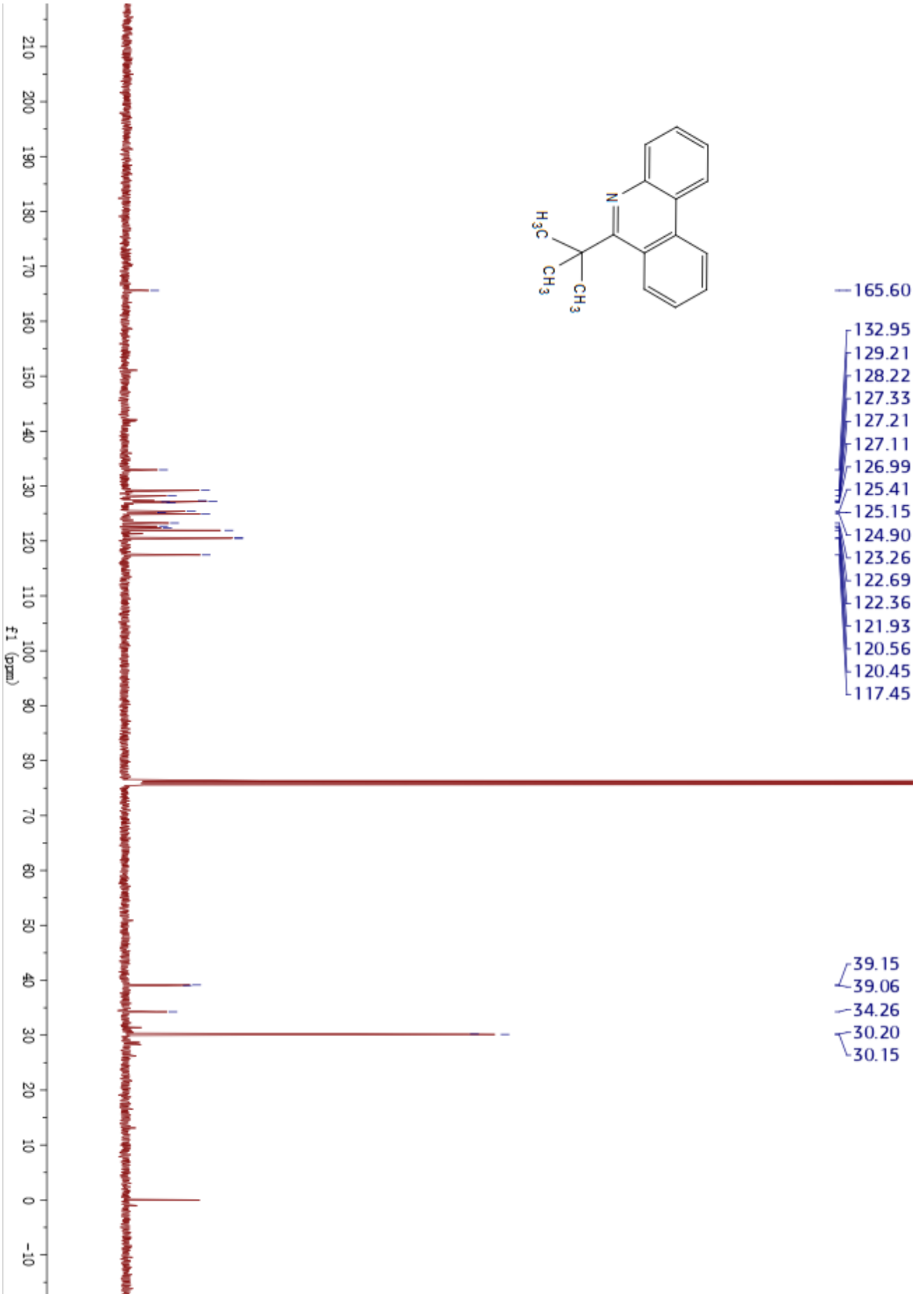
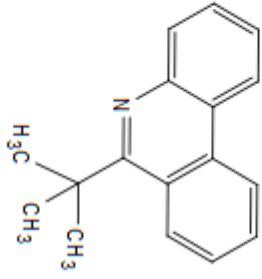
^1H and ^{13}C NMR spectra of **3ak**



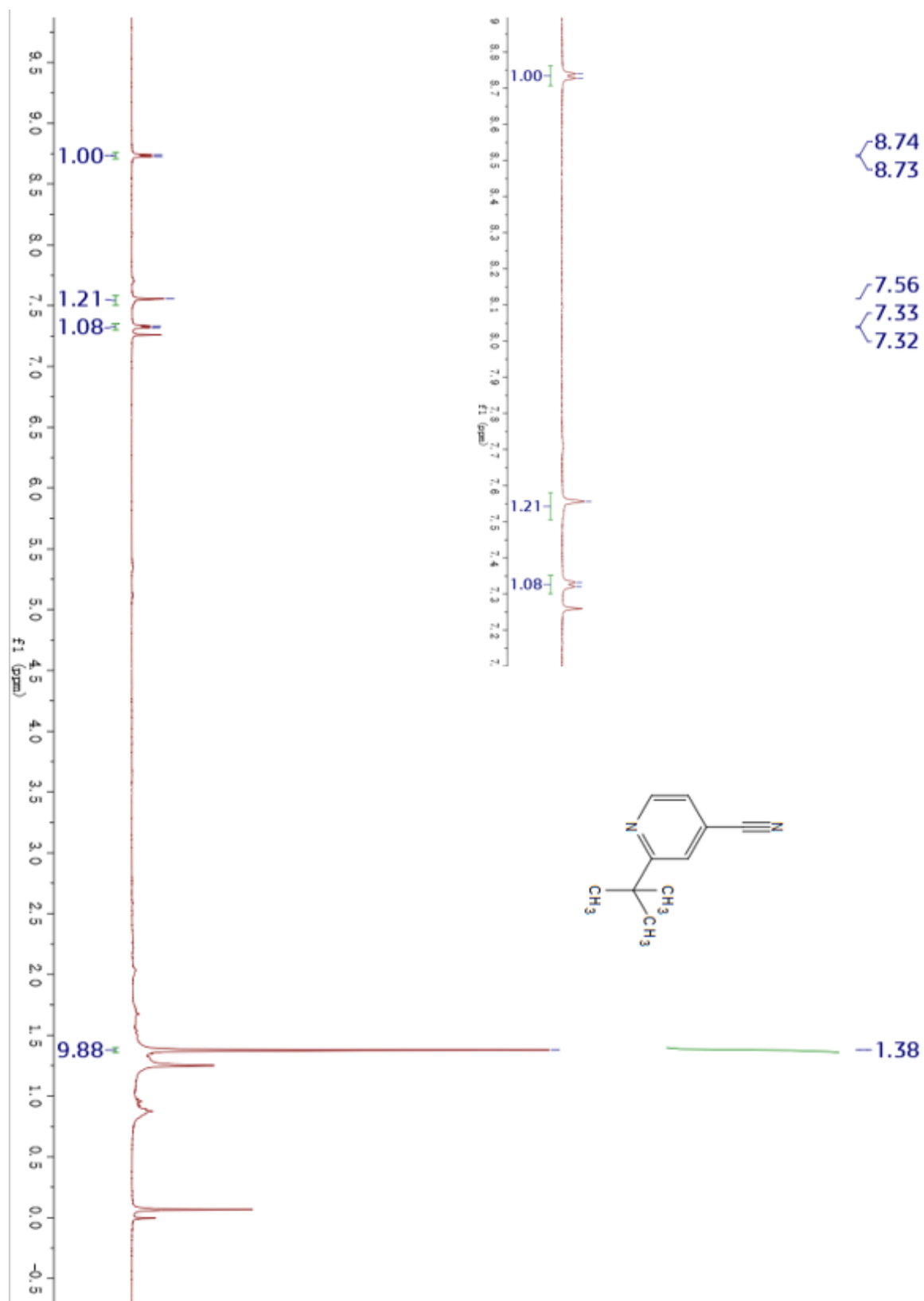


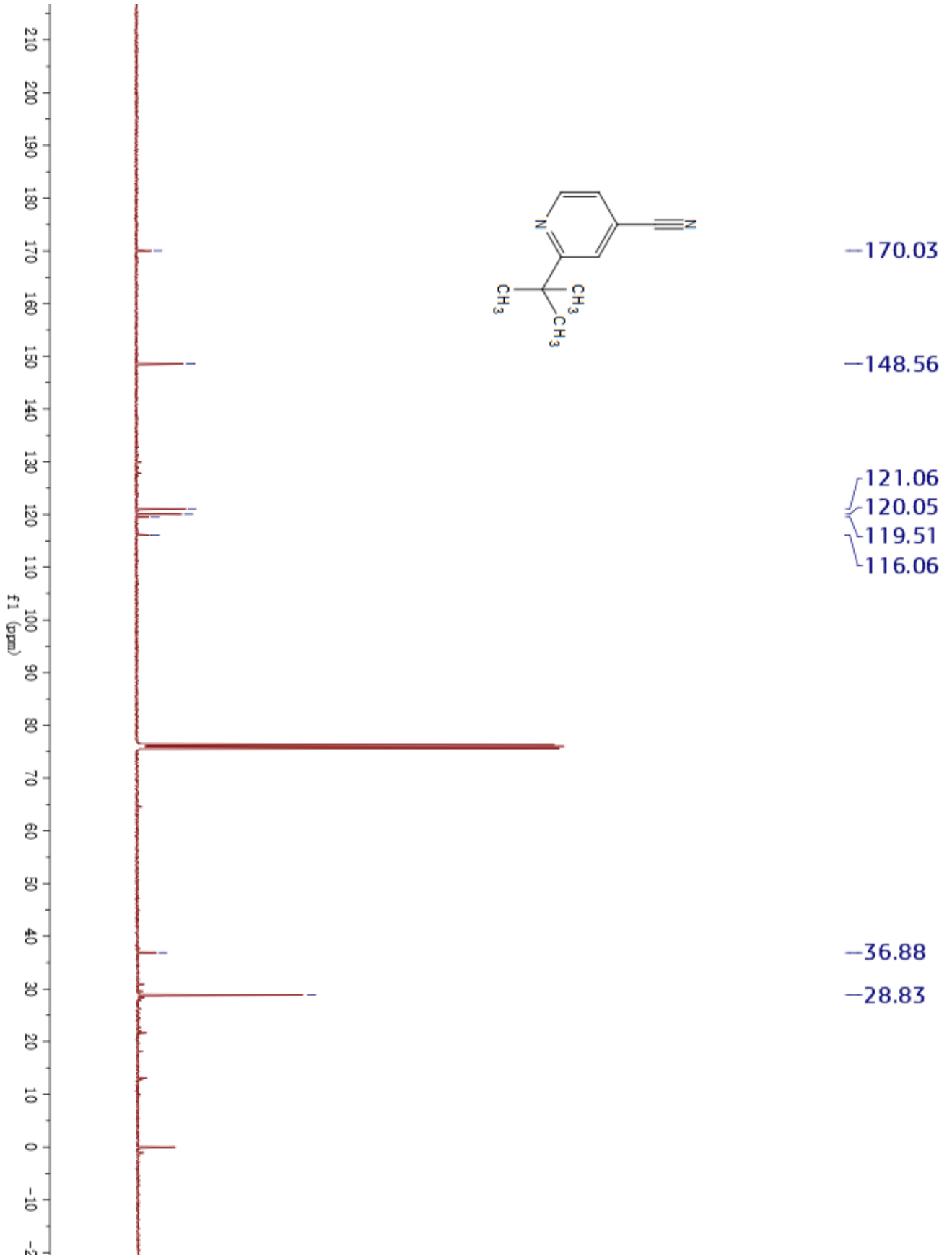
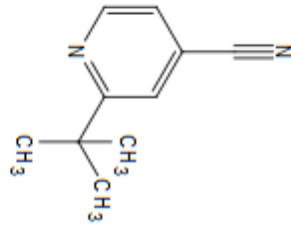
^1H and ^{13}C NMR spectra of **3aI**



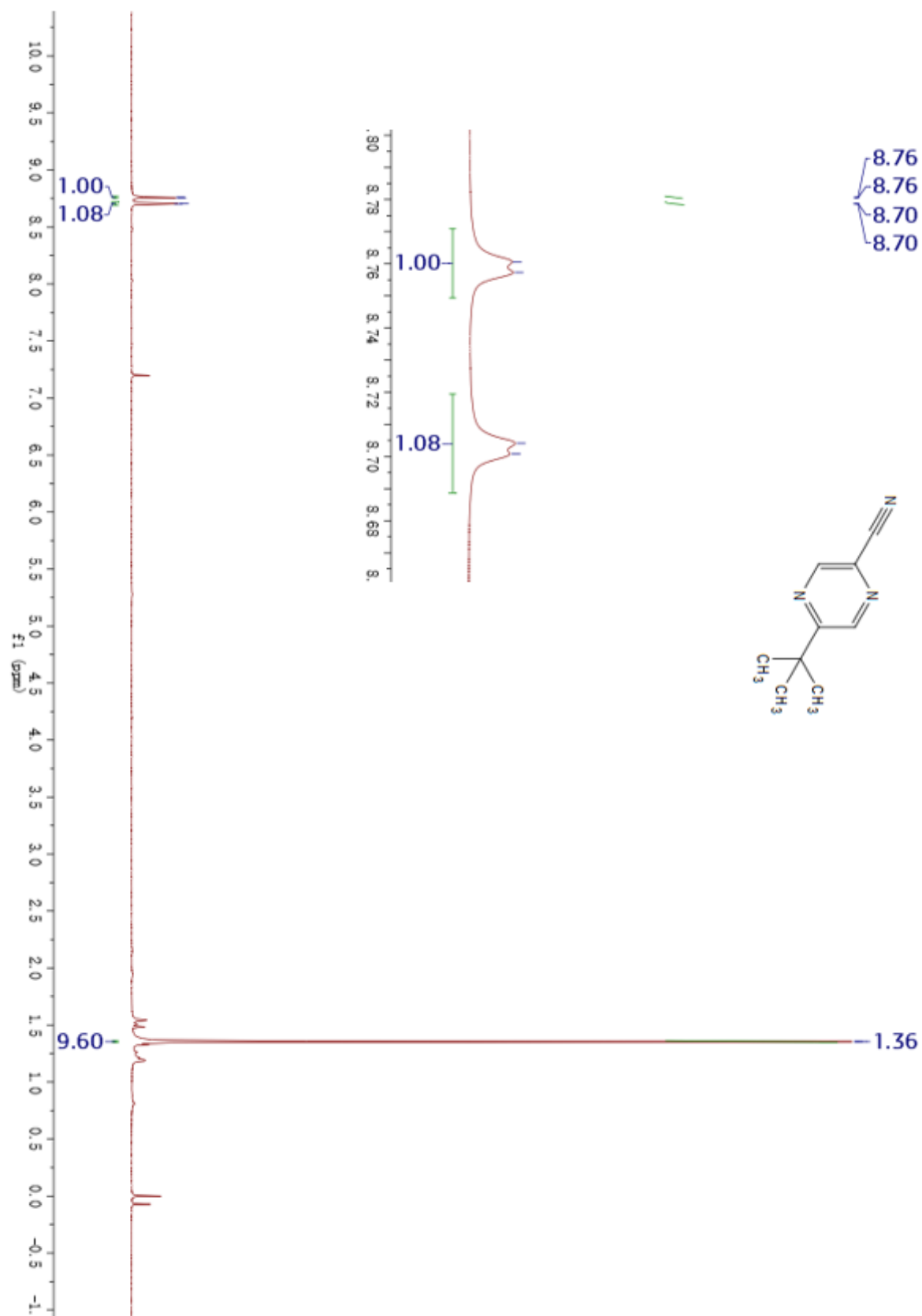


^1H and ^{13}C NMR spectra of **3am**



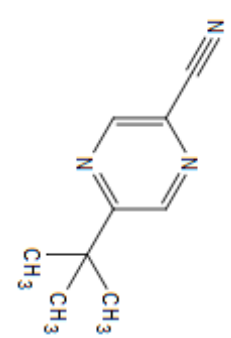
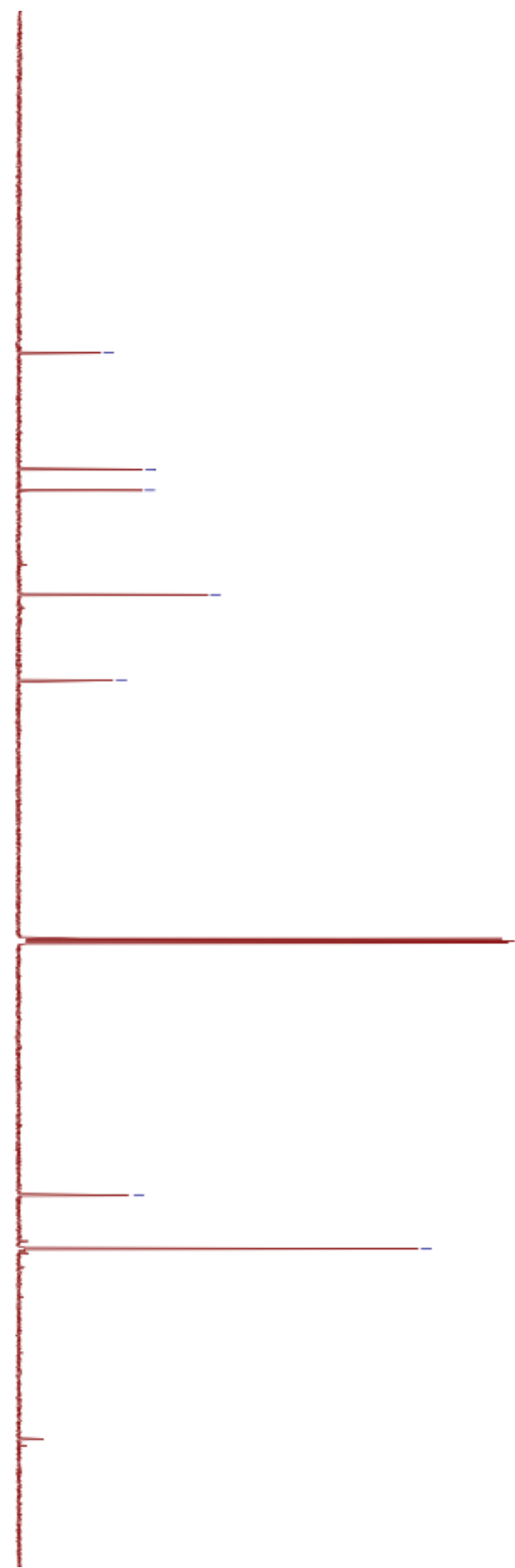


^1H and ^{13}C NMR spectra of **3an**



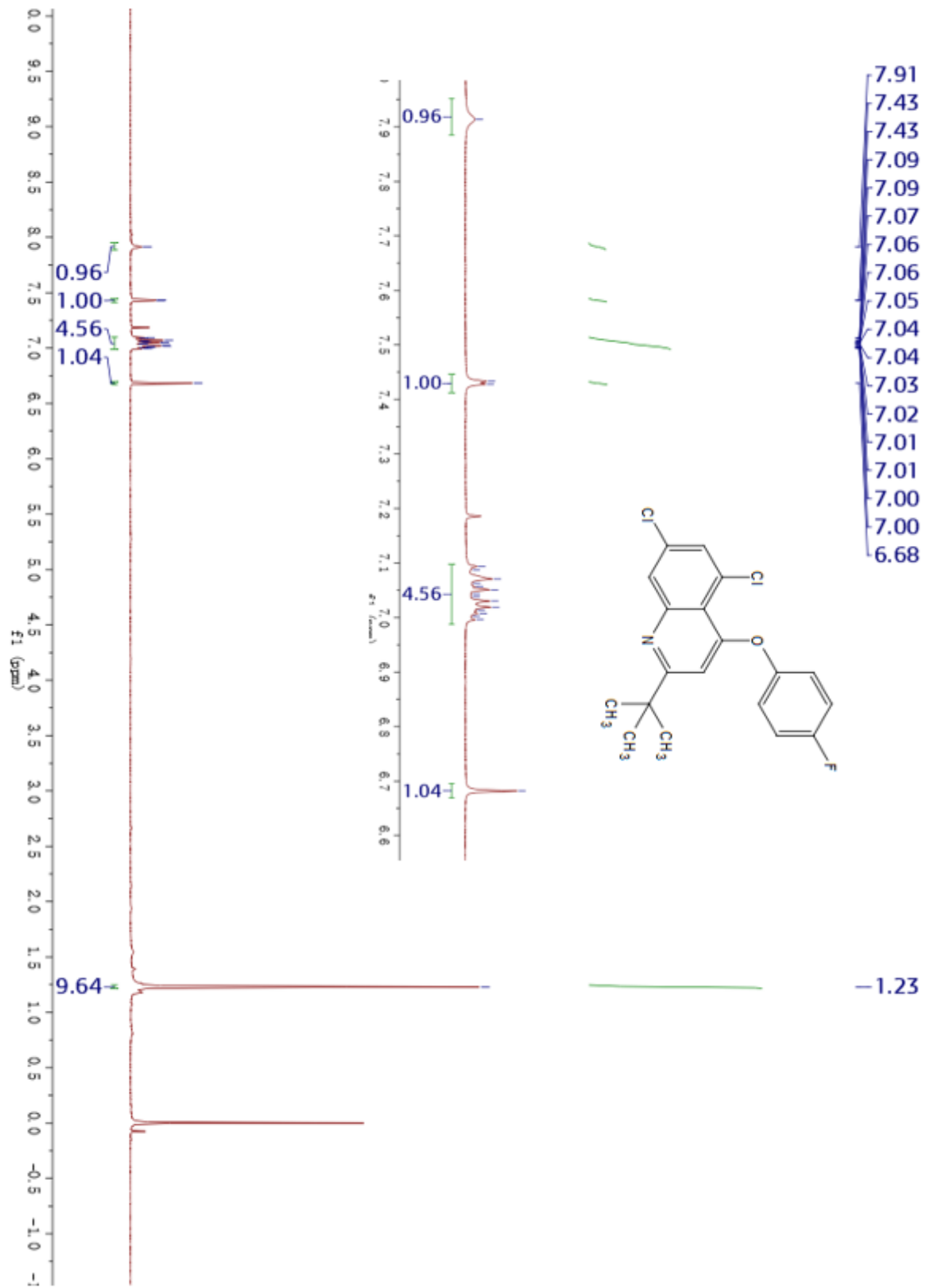
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-

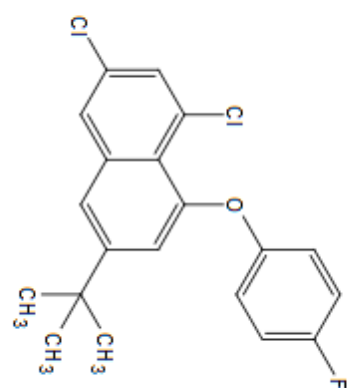
f1 (ppm)



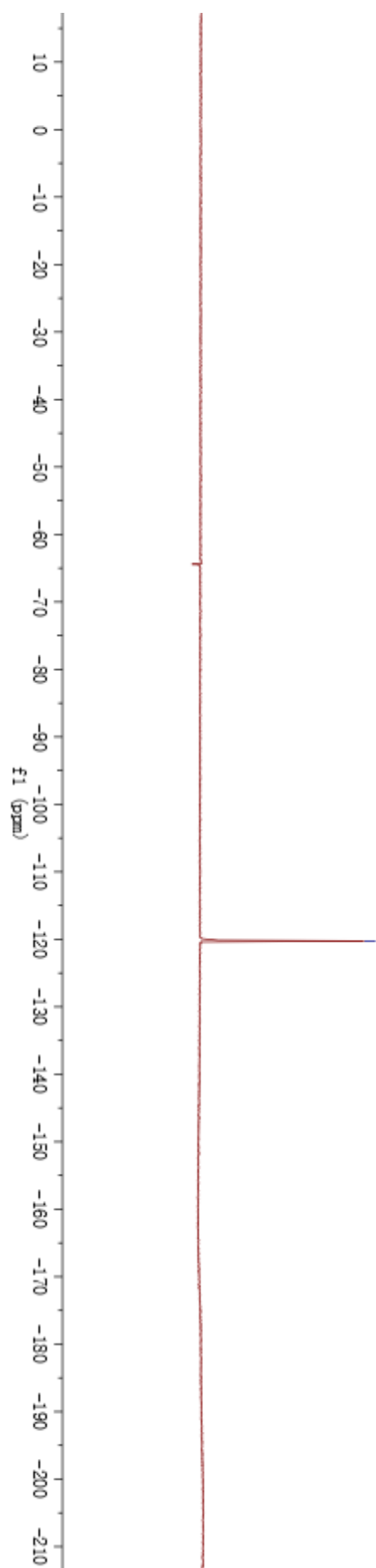
- 166.17
- ~148.38
- ~145.22
- 129.28
- 116.24
- 37.64
- 29.51

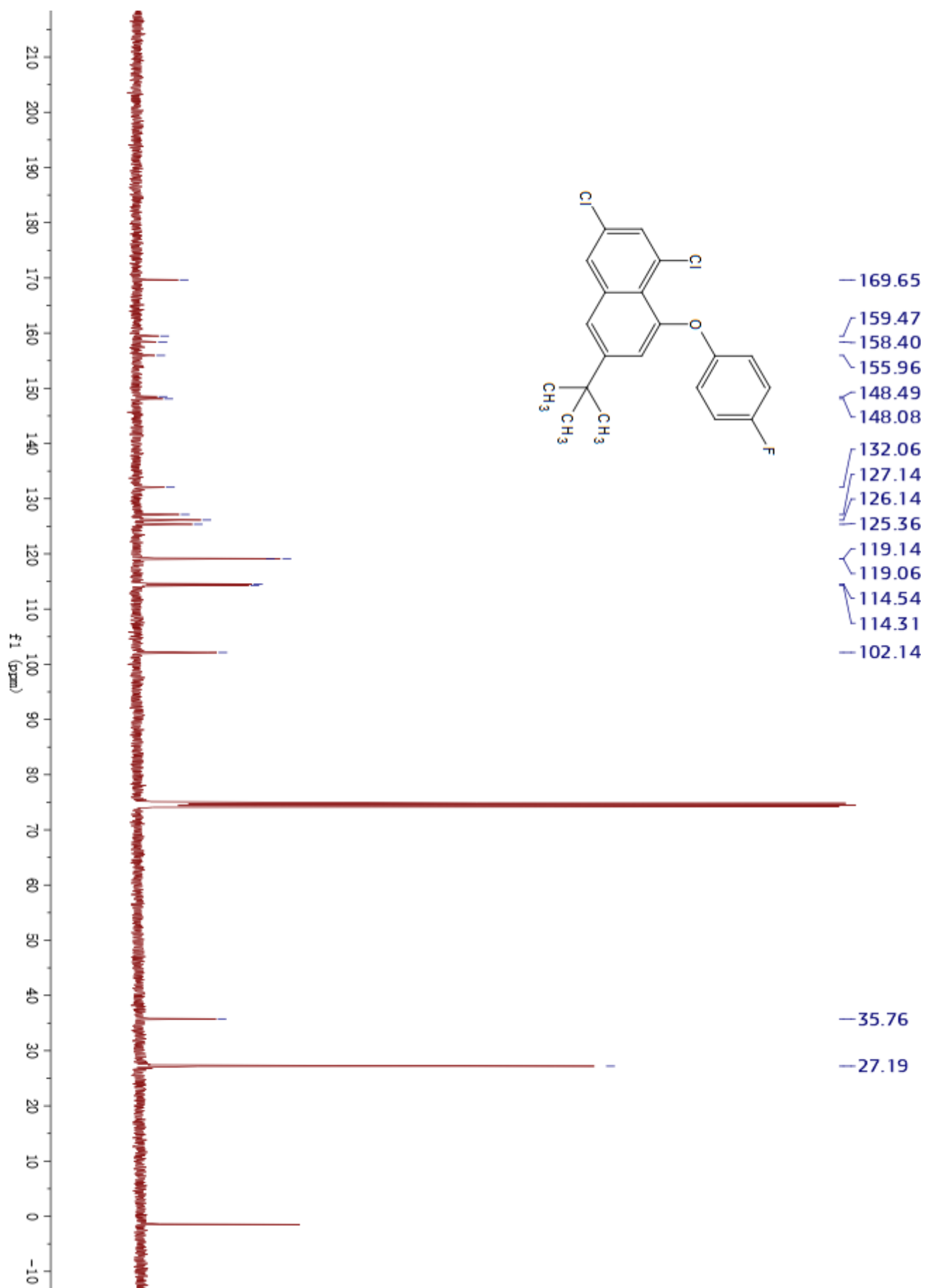
^1H and ^{13}C NMR spectra of **5a**





—120.24





^1H and ^{13}C NMR spectra of **5b**

