Supporting Information for

PEG-400 as carbon synthon: highly selective synthesis of quinolines and methylquinolines under metal-free conditions

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(1)General Information:

All reagents and solvents were purchased from commercial sources and used directly without further purification. Substituted substrates **1** were obtained according to the literature reports. Reactions were monitored by analytical thin-layer chromatography (TLC). ^{1}H NMR spectra were measured at 400 or 500 MHz and ^{13}C NMR spectra were run in the same instrument at 101 or 126 MHz. Unless otherwise stated, deuterochloroform ($CDCl_3$) was used as a solvent and tetramethylsilane (TMS) as internal standard. Mass spectra were measured using the STA-FTIR- GC/MS at Shandong University. High-resolution mass spectra were measured on a time-of-flight(Q-TOF) instrument in positive-ion mode with an ESI ion source.

(2) Mechanistic studies:

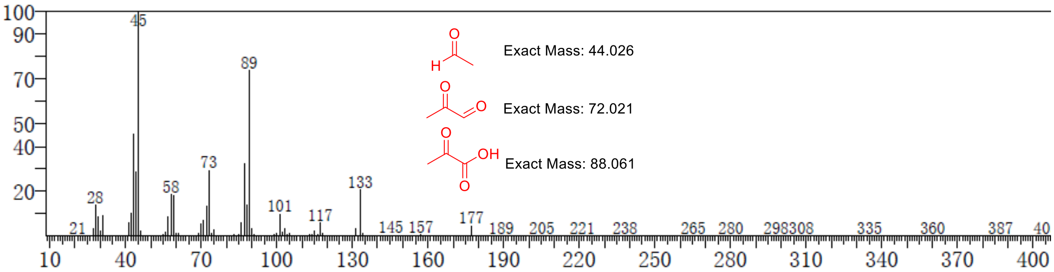


Fig 1: GC-MS for reaction without starting material under 130 °C.

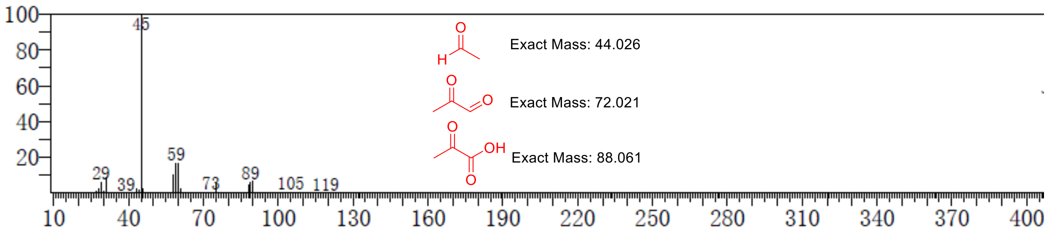


Fig 2: GC-MS for reaction without starting material under 90 °C.

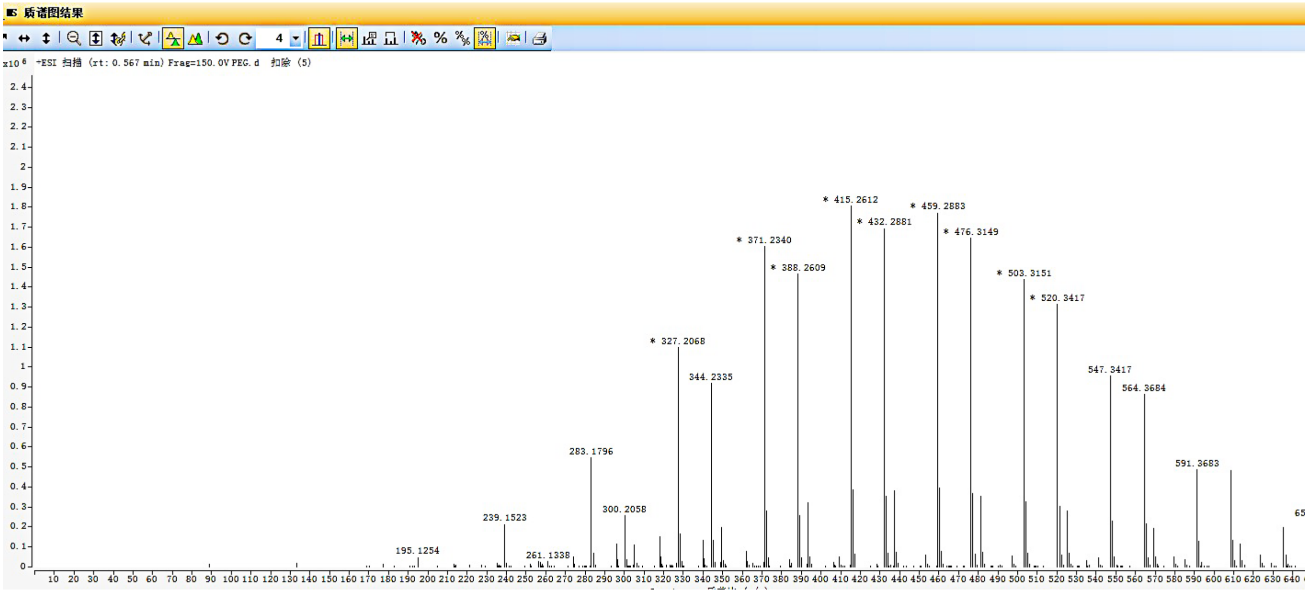


Fig 3: LC-MS for PEG-400.

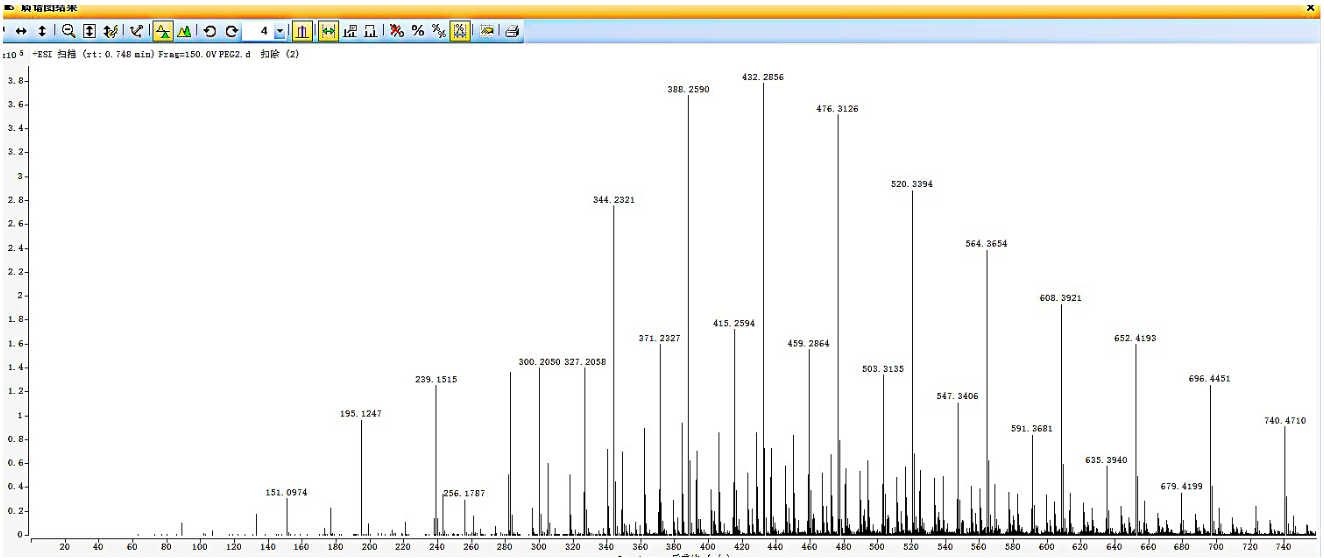
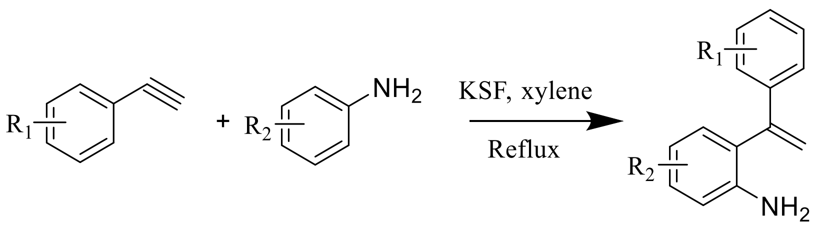


Fig 4: LC-MS for reaction without starting material under 130 °C(reaction time: 0.5 h).

(3)Experimental Procedures:

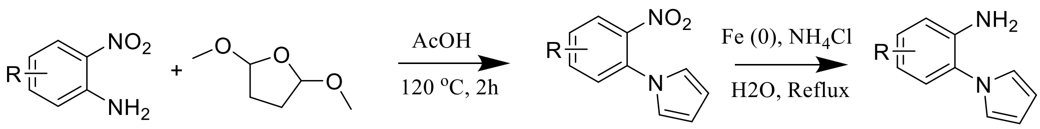
3.1: General Experimental Procedure for the Synthesis of 2-(1-substituted vinyl) anilines.



Substrates **1a-1u** were synthesized according to Method A:[1]

A mixture of anilines (9.0 mmol), phenylacetylenes (9.0 mmol), and 0.9 g of montmorillonite KSF were added to a round-bottomed flask. Then xylene (9 mL) was added. The resulting mixture was stirred in an oil bath preheated to 140 °C, under a reflux condenser (running cold water as the coolant). After 5 hours, the reaction mixture was cooled to room temperature, the reaction mixture was filtered, the solvent was removed in vacuum. The residue was purified using flash column chromatography (silica gel) with petroleum ether/ethyl acetate to obtain 2-(1-phenylvinyl) aniline derivative.

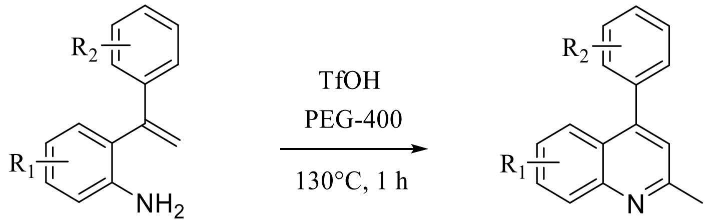
3.2: General Experimental Procedure for the Synthesis of 2-(1*H*-pyrrol-1-yl) anilines.



Substrates **1a-1u** were synthesized according to Method B:[2]

2-nitroaniline (10 mmol) and 2,5-dimethoxytetrahydrofuran (10 mmol) and acetic acid (50 mL) were taken in an oven-dried reaction tube. The reaction mixture was refluxed for 2 h with vigorous stirring and then cooled to room temperature. The reaction mixture was poured into water (150 mL) and extracted with ethyl acetate (3×30 mL). The combined organic layer was dried over anhydrous sodium sulfate and evaporated to dryness under reduced pressure to afford a residue. The residue was added to iron powder (40.0 mmol), NH_4Cl (5.0 mmol) in H_2O (10 mL) and heated to 100 ºC for 4h. After completion of the reaction, the mixture was cooled to room temperature. The reaction mixture was poured into water (150 mL) and extracted with ethyl acetate (3×30 mL). The combined organic layer was dried over anhydrous sodium sulfate and evaporated to dryness under reduced pressure to afford a residue. The residue was purified by column chromatography (silica gel) with petroleum ether/ethyl acetate to obtain the desired product.

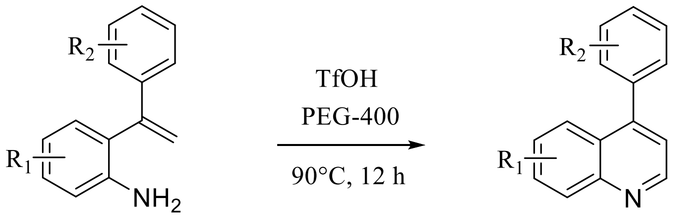
3.3: General Experimental Procedure for the Synthesis of 2-methylquinolines.



1 **2**

A 25 mL round-bottom flask equipped with a magnetic stirring bar was charged with 2-styrylaniline **1** (0.03 mmol), PEG-400 (1.2ml), and TfOH (0.03 mmol). The reaction mixture was allowed to stir at 110ºC until the completion of reaction (1 ~ 3 h) by TLC. After completion of the reaction, the mixture was cooled to room temperature and diluted with 20mL of water. The water layer was extracted with (3X20mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X20mL). The combined organic layer was dried over anhydrous sodium sulfate and evaporated under vacuum to get the crude compound. the resulting residue was purified by column chromatography (silica gel) with petroleum ether/ethyl acetate to obtain the desired product.

3.4: General Experimental Procedure for the Synthesis of quinolines.

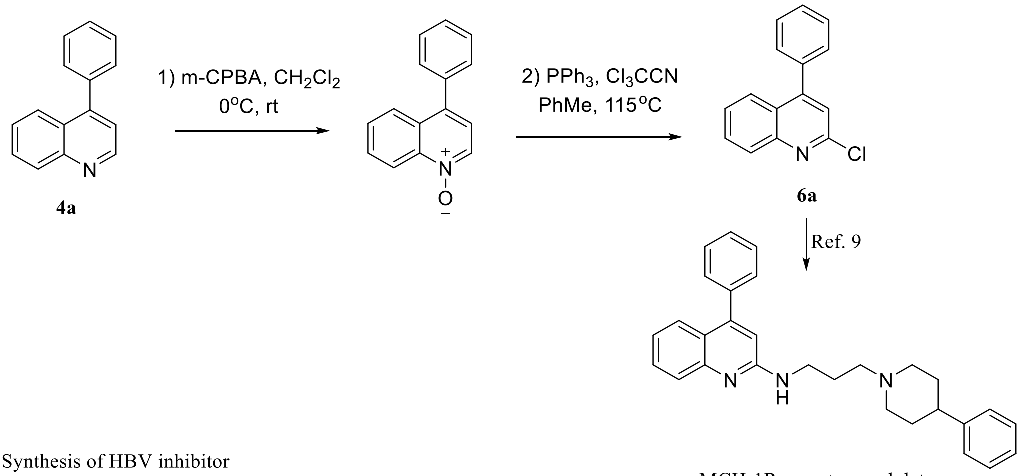


1 **4**

A 25 mL two-neck round-bottom flask equipped with a magnetic stirring bar was charged with 2-styrylaniline **1** (0.03 mmol), PEG-400 (1.2ml), and TfOH (0.03 mmol). The reaction mixture was allowed to stir at 90ºC under an oxygen balloon until the completion of reaction by TLC. After completion of the reaction, the mixture was cooled to room temperature and diluted with 20mL of water. The water layer was extracted with (3X20mL) of ethyl acetate and the combined ethyl acetate layer was given brine wash (1X20mL). The combined organic layer was dried over anhydrous sodium sulfate and evaporated under vacuum to get the crude compound. the resulting residue was purified by column chromatography (silica gel) with petroleum ether/ethyl acetate to obtain the desired product.

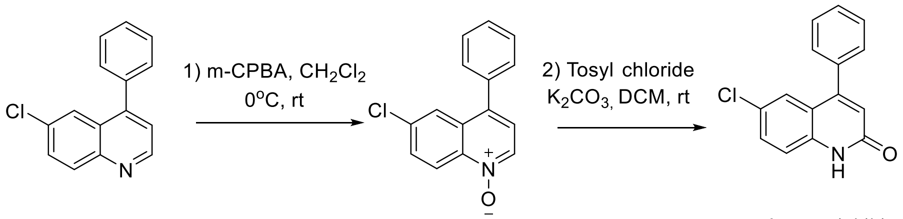
(4) The Application of the Reaction:

(**A**)Synthesis of MCH-1R receptor modulator



MCH-1R receptor modulator

(**B**) Synthesis of HBV inhibitor



6c HBV inhibitor

4.1: Synthesis of 6a

A 50 mL round-bottom flask equipped with a magnetic stirring bar was charged with **4a** (2 mmol) and CH_2Cl_2 (5 ml), 3-chloroperbenzoic acid (m-CPBA) (345 mg, 2 mmol) in CH_2Cl_2 (5 mL) was dropped into the round-bottom flask at 0 ^{O}C. After the addition is complete, the reaction mixture was allowed up to stir at room temperature overnight. An aqueous saturated $NaHCO_3$ solution was added to the reaction mixture. The mixture was extracted with CH_2Cl_2 (3X20mL). The combined organic layer was dried over anhydrous sodium sulfate and evaporated under vacuum to get the crude compound. the resulting residue was purified by column chromatography (silica gel) with petroleum ether/ethyl acetate to obtain the desired product.

A 25 mL Schlenk tube equipped with a magnetic stir bar was sequentially charged with N-oxide (0.25 mmol, 55.3 mg), PPh_3 (0.5 mmol, 131.2 mg), Cl_3CCN (0.5 mmol, 72.2 mg) and toluene (1 mL). The Schlenk tube was capped and placed in a preheated oil bath at 140 °C for 4 h. Once the reaction was completed, the reaction mixture was cooled down to room temperature. Then diluted with ethyl acetate and filter out the solids. The Schlenk tube and solid was wished with ethyl acetate. The filtrate was concentrated under vacuum, the crude was purified by column chromatography (silica gel) with petroleum ether/ethyl acetate to obtain desired product **6a**.

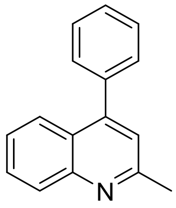
4.2: Synthesis of 6c

A 50 mL round-bottom flask equipped with a magnetic stirring bar was charged with **4c** (2 mmol) and CH_2Cl_2 (5 ml), 3-chloroperbenzoic acid (m-CPBA) (345 mg, 2 mmol) in CH_2Cl_2 (5 mL) was dropped into the round-bottom flask at 0 ^{O}C. After the addition is complete, the reaction mixture was allowed up to stir at room temperature overnight. An aqueous saturated $NaHCO_3$ solution was added to the reaction mixture. The mixture was extracted with CH_2Cl_2 (3X20mL). The combined organic layer was dried over anhydrous sodium sulfate and evaporated under vacuum to get the crude compound. the resulting residue was purified by column chromatography (silica gel) with petroleum ether/ethyl acetate to obtain the desired product.

Tosyl chloride(0.375 mmol) was added at room temperature to a solution of quinoline N-oxide (0.3 mmol)in a 10 % K_2CO_3 solution (0.75 ml)and DCM (0.75ml) and the mixture was stirred at room temperature for one night. After completion of the reaction, the mixture was cooled to room temperature. The reaction mixture was poured into water (150 mL) and extracted with ethyl acetate (3×30 mL). The combined organic layer was dried over anhydrous sodium sulfate and evaporated to dryness under reduced pressure to afford a residue. The residue was purified by column chromatography (silica gel) with petroleum ether/ethyl acetate to obtain the desired product.

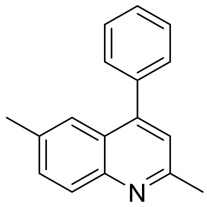
(5) Characterization Data:

2-methyl-4-phenylquinoline (2a)[3]



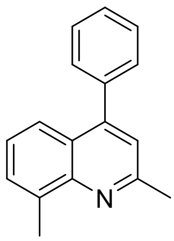
white solid in 72% yield, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 1H), 7.86 (dd, *J* = 8.5, 0.5 Hz, 1H), 7.70 – 7.67 (m, 1H), 7.54 – 7.47 (m, 5H), 7.45 – 7.42 (m, 1H), 7.24 (s, 1H), 2.78 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.50, 148.58, 148.38, 138.17, 129.50, 129.33, 129.00, 128.53, 128.33, 125.75, 125.65, 125.11, 122.23, 25.33. **HRMS** (ESI) calculated for $C_{16}H_{13}N$ $(M+H)^+$220.1118; found: 220.1123.

2,6-dimethyl-4-phenylquinoline(2b)[3]



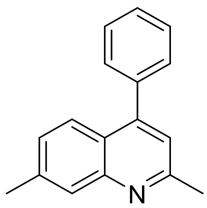
white solid in 81% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.60 (s, 1H), 7.53 – 7.48 (m, 6H), 7.19 (s, 1H), 2.76 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.41, 148.06, 146.76, 138.34, 135.63, 131.61, 129.49, 128.60, 128.54, 128.26, 125.03, 124.45, 122.31, 25.14, 21.73. **HRMS** (ESI) calculated for $C_{17}H_{15}N$ $(M+H)^+$234.1274; found: 234.1281.

2,8-dimethyl-4-phenylquinoline(2c)[4]



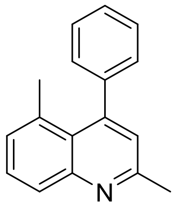
Yellow solid in 78% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 1H), 7.53 – 7.45 (m, 6H), 7.29 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.22 – 7.16 (m, 1H), 2.84 (s, 3H), 2.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.28, 148.56, 147.49, 138.76, 136.82, 129.60, 129.44, 128.44, 128.14, 125.23, 124.97, 123.68, 121.97, 25.69, 18.52. **HRMS** (ESI) calculated for $C_{17}H_{15}N$ $(M+H)^+$234.1274; found: 234.1279.

2,7-dimethyl-4-phenylquinoline(2d)



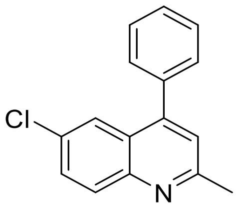
Yellow solid in 43% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.75 (d, *J* = 8.8Hz, 1H), 7.52 – 7.47 (m, 5H), 7.27 (dd, *J* = 8.4, 2 Hz, 1H), 7.17 (s, 1H), 2.76 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.37, 148.52, 148.41, 139.71, 138.27, 129.48, 128.52, 128.32, 128.02, 127.96, 125.34, 123.07, 121.47, 25.23, 21.76. **HRMS** (ESI) calculated for $C_{17}H_{15}N$ $(M+H)^+$234.1274; found: 234.1256.

2,5-dimethyl-4-phenylquinoline(2e)



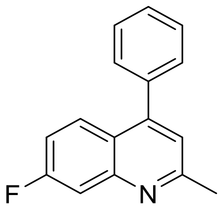
Yellow solid in 73% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.56 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.43 – 7.42 (m, 3H), 7.32 – 7.31 (m, 2H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.10 (s, 1H), 2.73 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.05, 149.42, 149.07, 142.55, 135.51, 129.09, 128.97, 128.73, 127.90, 127.86, 127.69, 124.58, 124.42, 24.83, 24.48. **HRMS** (ESI) calculated for $C_{17}H_{15}N$ $(M+H)^+$234.1274; found: 234.1289.

6-chloro-2-methyl-4-phenylquinoline(2f)[5]



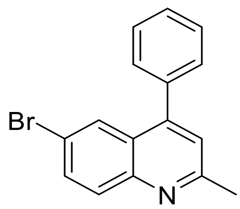
Yellow solid in 74% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 2.4 Hz, 1H), 7.63 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.56 – 7.46 (m, 5H), 7.26 (s, 1H), 2.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.80, 148.04, 146.57, 137.40, 131.73, 130.49, 130.32, 129.38, 128.78, 125.87, 124.53, 123.03, 25.20. **HRMS** (ESI) calculated for $C_{16}H_{12}ClN$ $(M+H)^+$254.0728; found: 254.0742.

7-fluoro-2-methyl-4-phenylquinoline(2g)



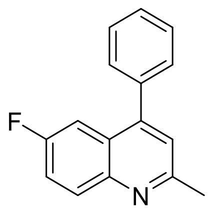
Yellow solid in 52% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 9.2, 6.4 Hz, 1H), 7.74 (dd, *J* = 10.4, 2.4 Hz, 1H), 7.55 – 7.46 (m, 5H), 7.24 – 7.19 (m, 2H), 2.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.32, 161.84, 159.79, 149.3 (d, *J* = 12.1 Hz), 148.90, 137.82, 129.41, 128.66, 128.60, 128.0 (d, *J* = 2.8 Hz), 122.18, 121.6 (d, *J* = 2.0 Hz), 116.0 (d, *J* = 24.2 Hz), 112.5 (d, *J* = 20.2 Hz), 25.24. **HRMS** (ESI) calculated for $C_{16}H_{12}FN$ $(M+H)^+$238.1024; found: 238.1036.

6-bromo-2-methyl-4-phenylquinoline(2h)[5]



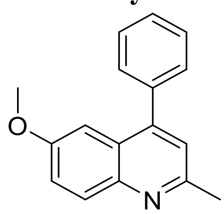
Yellow solid in 69% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.95 (m, 1H), 7.75 (dd, J = 8.8, 2.4 Hz, 1H), 7.56 – 7.46 (m, 3H), 7.25 (s, 1H), 2.76 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.98, 147.88, 146.86, 137.39, 132.84, 130.70, 129.39, 128.79, 128.70, 127.81, 126.39, 123.01, 119.86, 25.29. **HRMS** (ESI) calculated for $C_{16}H_{12}BrN$ $(M+H)^+$298.0223; found: 298.0241.

6-fluoro-2-methyl-4-phenylquinoline (2i)[5]



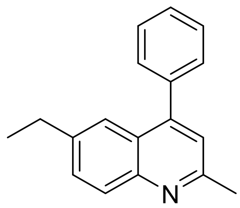
Yellow solid in 84% yield,^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.8, 5.6 Hz, 1H), 7.55 – 7.43 (m, 7H), 7.26 (s, 1H), 2.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.23 (d, *J* = 246.41 Hz), 157.80 (d, *J* = 2.0 Hz), 148.17 (d, *J* = 5.1 Hz), 145.38, 137.67, 131.30 (d, *J* = 9.1 Hz), 129.30, 128.74, 128.61, 125.82 (d, *J* = 9.1 Hz), 122.83, 119.40 (d, *J* = 25.3 Hz), 109.11 (d, *J* = 23.2 Hz), 25.15. **HRMS** (ESI) calculated for $C_{16}H_{12}FN$ $(M+H)^+$238.1024; found: 238.1012.

6-methoxy-2-methyl-4-phenylquinoline(2j)[3]



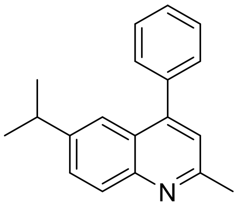
Yellow solid in 82% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 9.2 Hz, 1H), 7.55 – 7.48 (m, 5H), 7.36 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.19 (s, 1H), 7.16 (d, *J* = 2.8 Hz, 1H), 3.77 (s, 3H), 2.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.34, 155.82, 147.55, 144.15, 138.41, 130.25, 129.29, 128.65, 128.33, 125.89, 122.58, 121.53, 103.91, 55.44, 24.88. **HRMS** (ESI) calculated for $C_{17}H_{15}NO$ $(M+H)^+$250.1224; found: 250.1206.

6-ethyl-2-methyl-4-phenylquinoline(2k)



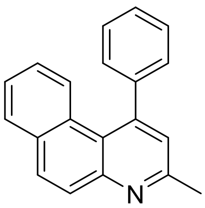
Yellow solid in 71% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 1.2 Hz, 1H), 7.58 – 7.46 (m, 6H), 7.20 (s, 1H), 2.76 – 2.71 (m, 5H), 1.24 (t, *J* = 7.2 Hz, 3H).;^{13}C NMR (101 MHz, $CDCl_3$) δ 157.46, 148.21, 146.96, 141.92, 138.36, 130.46, 129.50, 128.75, 128.54, 128.27, 125.03, 123.28, 122.30, 29.05, 25.14, 15.63. **HRMS** (ESI) calculated for $C_{18}H_{17}N$ (M+H)$^+$248.1431; found: 248.1446.

6-isopropyl-2-methyl-4-phenylquinoline(2l)



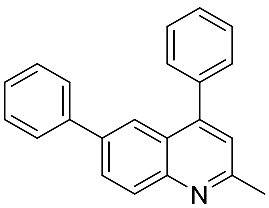
Yellow solid in 69% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.8 Hz, 1H), 7.65 (d, *J* = 1.6 Hz, 1H) 7.62 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 7.55 – 7.47 (m, 5H), 7.20 (s, 1H), 3.00 – 3.04 (m, 1H), 2.76 (s, 3H), 1.26 (d, *J* = 6.8 Hz, 6H);^{13}C NMR (101 MHz, $CDCl_3$) δ 157.50, 148.34, 147.09, 146.41, 138.36, 129.50, 128.87, 128.79, 128.54, 128.29, 124.95, 122.29, 121.95, 34.28, 25.13, 23.93. **HRMS** (ESI) calculated for $C_{19}H_{19}N$ (M+H)$^+$262.1587; found: 262.1596.

3-methyl-1-phenylbenzo[f]quinoline (2m)[6]



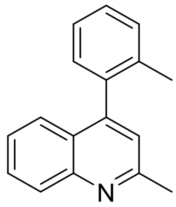
White solid in 68% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (m, 2H), 7.85 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.50 – 7.39 (m, 6H), 7.23 (s, 1H), 7.11 – 7.16 (m, 1H), 2.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.07, 157.07, 149.31, 148.70, 142.80, 132.65, 131.39, 129.80, 129.18, 128.59 , 128.32, 128.28, 128.07, 127.87, 126.22, 125.48, 124.94, 121.88 , 24.59. **HRMS** (ESI) calculated for $C_{20}H_{15}N$ (M+H)$^+$270.1274; found: 270.1291.

2-methyl-4,6-diphenylquinoline(2n)[4]



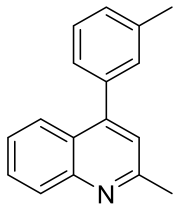
Yellow solid in 77% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.8Hz, 1H), 8.05 (d, *J* = 2.0 Hz, 1H), 7.95 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.60 – 7.47 (m, 7H), 7.43 – 7.40 (m, 2H), 7.35 – 7.31 (m, 1H), 7.25 (s, 1H), 2.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.50, 148.80, 147.75, 140.72, 138.57, 138.12, 129.53, 129.46, 129.08, 128.89, 128.68, 128.45, 127.50, 127.44, 125.25, 123.50, 122.72, 25.36. **HRMS** (ESI) calculated for $C_{12}H_{17}N$ (M+H)$^+$296.1431; found: 296.1438.

2-methyl-4-(o-tolyl)quinoline(2o)[4]



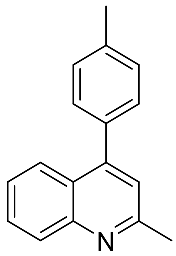
White solid in 71% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 8.4 Hz, 1H), 7.44 – 7.29 (m, 5H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.17 (s, 1H), 2.78 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.60, 148.69, 147.98, 137.63, 136.06, 130.15, 129.54, 129.43, 128.88, 128.35, 125.81, 125.77, 125.62, 122.33, 25.41, 20.01. **HRMS** (ESI) calculated for $C_{17}H_{15}N$ $(M+H)^{+}$234.1274; found: 234.1259.

2-methyl-4-(m-tolyl)quinoline(2p)[4]



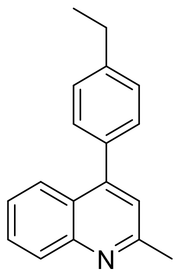
Yellow oil in 58% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.88(d, *J* = 8.4 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.46 – 7.24 (m, 6H), 2.79 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.25, 138.36, 137.85, 130.13, 129.70, 129.25, 128.46, 128.38, 126.61, 125.99, 125.85, 125.20, 122.25, 24.94, 21.50. **HRMS** (ESI) calculated for $C_{17}H_{15}N$ $(M+H)^{+}$234.1274; found: 234.1262.

2-methyl-4-(p-tolyl)quinoline (2q)[3]



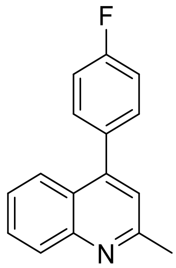
Yellow solid in 82% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.89 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.44 – 7.38 (m, 3H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.22 (s, 1H), 2.77 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.48, 148.70, 148.30, 138.29, 135.18, 129.44, 129.34, 129.27, 128.91, 125.75, 125.70, 125.20, 122.22, 25.34, 21.34. **HRMS** (ESI) calculated for $C_{17}H_{15}N$ $(M+H)^{+}$234.1274; found: 234.1292.

4-(4-ethylphenyl)-2-methylquinoline(2r)[4]



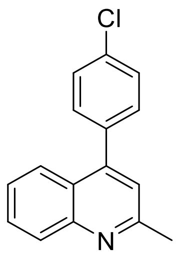
Yellow solid in 79% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 1H), 7.90 (dd, J = 8.4, 0.8 Hz, 1H), 7.65 – 7.69 (m, 1H), 7.33 – 7.44 (m, 5H), 7.22 (s, 1H), 2.78 – 2.73 (m, 5H), 1.32 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.48, 148.68, 148.38, 144.57, 135.42, 129.52, 129.29, 128.96, 128.06, 125.79, 125.66, 125.21, 122.22, 28.70, 25.35, 15.57. **HRMS** (ESI) calculated for $C_{18}H_{17}N$ $(M+H)^+$248.1431; found: 248.1450.

4-(4-fluorophenyl)-2-methylquinoline(2s)[6]



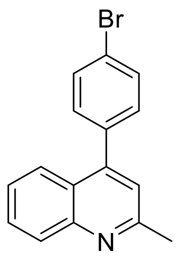
White solid in 71% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.48 – 7.42 (m, 3H), 7.24 – 7.19 (m, 3H), 2.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9(d, *J* = 248.5 Hz), 158.5, 148.3, 147.6, 134.1 (d, *J* = 4.0 Hz), 131.2 (d, *J* = 8.1 Hz), 129.5, 129.0, 125.7 (d, *J* = 56.6 Hz, 1H), 125.1, 122.3, 115.6 (d, *J* = 22.2 Hz), 25.3. **HRMS** (ESI) calculated for $C_{16}H_{12}FN$ $(M+H)^+$238.1024; found: 238.1011.

4-(4-chlorophenyl)-2-methylquinoline(2t)[6]



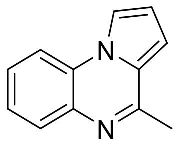
White solid in 69% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.51 – 7.41 (m, 5H), 7.20 (s, 1H), 2.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.49, 148.28, 147.35, 136.52, 134.58, 130.81, 129.55, 129.07, 128.83, 126.02, 125.29, 124.84, 122.17, 25.31. **HRMS** (ESI) calculated for $C_{16}H_{12}ClN$ $(M+H)^+$254.0728; found: 254.0729.

4-(4-bromophenyl)-2-methylquinoline(2u)[6]



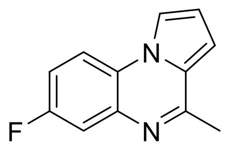
Yellow solid in 69% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.72 – 7.65 (m, 3H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.21 (s, 1H), 2.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.47, 148.16, 147.47, 136.96, 131.80, 131.10, 129.63, 128.98, 126.09, 125.29, 124.78, 122.79, 122.11, 25.25. **HRMS** (ESI) calculated for $C_{16}H_{12}BrN$ $(M+H)^+$298.0223; found: 298.0239.

4-methylpyrrolo[1,2-*a*]quinoxaline(3a)[7]



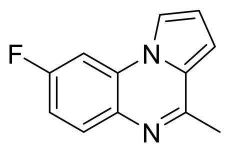
Yellow solid in 68% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.91 (m, 2H), 7.83 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.80 – 7.41 (m, 2H), 6.92 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.86 (dd, *J* = 4.0, 2.8 Hz, 1H), 2.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.63, 135.59, 129.08, 127.27, 127.04, 126.22, 125.22, 114.48, 113.68, 113.66, 106.87, 21.86. **HRMS** (ESI) calculated for $C_{12}H_{10}N_2$ $(M+H)^+$183.0914; found: 183.0923.

7-fluoro-4-methylpyrrolo[1,2-*a*]quinoxaline(3b)[7]



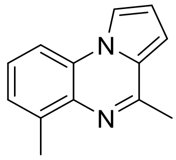
Yellow solid in 69% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.80 – 7.76 (m, 1H), 7.60 (dd, *J* = 9.6, 2.0 Hz, 1H), 7.21 (td, *J* = 8.4, 2.4 Hz, 1H), 6.93 (d, *J* = 3.6 Hz, 1H), 6.86 – 6.85 (m, 1H), 2.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.83 (d, *J* = 244.4 Hz), 154.89, 136.87, 136.70, 125.97, 123.91, 114.89 (d, *J* = 10.1 Hz), 114.64 (d, *J* = 10.1 Hz), 114.34, 113.81, 107.30, 21.86. **HRMS** (ESI) calculated for $C_{12}H_9FN_2$ $(M+H)^+$201.0820; found: 201.0831.

8-fluoro-4-methylpyrrolo[1,2-*a*]quinoxaline(3c)[7]



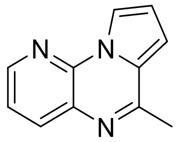
Yellow solid in 76% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 9.2, 5.6 Hz, 1H), 7.78 – 7.77 (m, 1H), 7.48 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.14 (td, *J* = 8.8, 2.4 Hz, 1H), 6.90 – 6.86 (m, 2H), 2.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.05 (d, *J* = 247.5 Hz), 152.76, 132.31, 130.88 (d, *J* = 10.1 Hz), 127.89 (d, *J* = 11.1 Hz), 125.95, 114.53, 114.07, 112.97 (d, J = 23.2 Hz), 106.94, 100.49 (d, J = 27.3 Hz), 21.74. **HRMS** (ESI) calculated for $C_{12}H_9FN_2$ $(M+H)^+$201.0820; found: 201.0839.

4,6-dimethylpyrrolo[1,2-*a*]quinoxaline(3d)



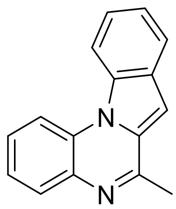
Yellow solid in 75% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.36 – 7.25 (m, 2H), 6.85 – 6.82 (m, 2H), 2.76 (s, 3H), 2.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.19, 137.73, 127.14, 126.29, 126.21, 114.20, 113.42, 111.46, 105.99, 22.24, 18.32. **HRMS** (ESI) calculated for $C_{13}H_{12}N_2$ $(M+H)^+$197.1070; found: 197.1085.

6-methylpyrido[3,2-e]pyrrolo[1,2-*a*]pyrazine(3e)



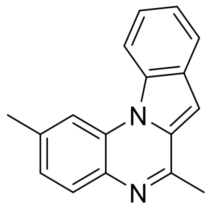
Yellow solid in 68% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, J = 4.8, 1.6 Hz, 1H), 8.37 – 8.36 (m, 1H), 8.20 (dd, J = 7.6, 1.6 Hz, 1H), 7.42 (dd, J = 8.0, 4.8 Hz, 1H), 6.98 (dd, J = 4.0, 1.2 Hz, 1H), 6.90 – 6.88 (m, 1H), 2.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.72, 146.24, 139.43, 136.32, 130.47, 127.58, 121.50, 115.81, 114.14, 108.40, 21.74. **HRMS** (ESI) calculated for $C_{11}H_9N_3$ $(M+H)^+$184.0866; found: 184.0879.

6-methylindolo[1,2-*a*]quinoxaline(3f)[2a]



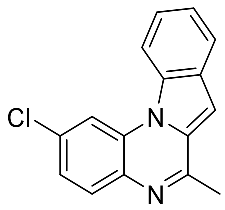
Yellow solid in 72% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 – 8.37 (m, 2H), 7.94 – 7.91 (m, 2H), 7.56 – 7.48 (m, 2H), 7.43 – 7.37 (m, 2H), 7.11 (s, 1H), 2.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.22, 135.62, 132.88, 130.19, 129.66, 129.44, 128.96, 127.78, 124.21, 123.99, 122.63, 122.55, 100.08, 22.28. **HRMS** (ESI) calculated for $C_{16}H_{12}N_2$ $(M+H)^+$233.1070; found: 233.1056.

2,6-dimethylindolo[1,2-*a*]quinoxaline(3g)



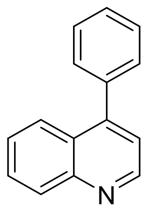
Yellow solid in 68% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 8.8 Hz, 1H), 8.21 (s, 1H), 7.92 (dt, J = 8.0, 1.0 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.44 – 7.40 (m, 1H), 7.21 (dd, J = 8.1, 1.0 Hz, 1H), 7.09 (s, 1H), 2.77 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.09, 138.13, 133.66, 132.86, 130.06, 129.84, 129.15, 129.04, 125.05, 123.98, 122.56, 122.48, 114.91, 114.66, 114.64, 99.75, 22.22, 22.12. **HRMS** (ESI) calculated for $C_{17}H_{14}N_2$ $(M+H)^+$247.1227; found: 247.1210.

2-chloro-6-methylindolo[1,2-*a*]quinoxaline(3h)



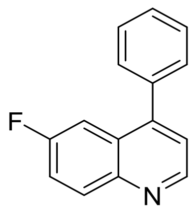
Yellow solid in 74% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 2.1 Hz, 1H), 8.19 (d, J = 8.9 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.5 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.42 – 7.38 (m, 1H), 7.30 (dd, J = 8.5, 2.1 Hz, 1H), 7.04 (s, 1H), 2.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.35, 134.21, 133.03, 132.71, 130.56, 130.30, 129.27, 129.02, 124.64, 124.13, 122.94, 122.75, 114.60, 114.22, 100.66, 22.24. **HRMS** (ESI) calculated for $C_{16}H_{11}ClN_2$ $(M+H)^+$267.0681; found: 267.0699.

4-phenylquinoline(4a)[8]



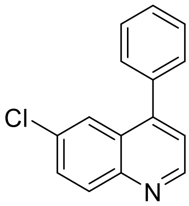
Yellow oil in 61% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J = 4.4 Hz, 1H), 8.20 (d, J = 8.4 Hz, 1H), 7.93 (dd, J =8.8 Hz, 0.8 Hz, 1H), 7.76 – 7.72 (m, 1H), 7.56 – 7.48 (m, 6H), 7.35 (d, J = 4.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.84, 148.72, 148.51, 137.96, 129.73, 129.57, 129.45, 128.61, 128.50, 126.80, 126.72, 125.92, 121.36. **HRMS** (ESI) calculated for $C_{15}H_{11}N$ $(M+H)^+$206.0961; found: 206.0954.

6-fluoro-4-phenylquinoline(4b)[8]



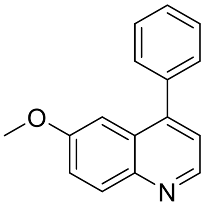
White solid in 49% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, J = 4.0 Hz, 1H), 8.20 (dd, J = 9.2, 5.6 Hz, 1H), 7.58 – 7.48 (m, 7H), 7.38 (d, J = 4.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.95, 159.48, 149.12 (d, J = 1.01 Hz), 148.26(d, J = 6.1 Hz), 145.63, 137.50, 132.23 (d, J = 9.09 Hz), 129.36, 128.82, 128.75, 127.64 (d, J = 9.09 Hz), 121.88, 119. 74 (d, J = 25.3 Hz), 109. 28 (d, J = 23.2 Hz) **HRMS** (ESI) calculated for $C_{15}H_{10}FN$ $(M+H)^+$224.0867; found: 224.0856.

6-chloro-4-phenylquinoline(4c)[8]



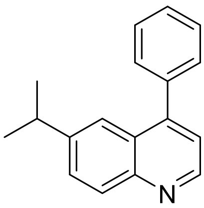
White solid in 50% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, J = 4.0 Hz, 1H), 8.12 (d, J = 8.8 Hz, 1H), 7.88 (d, J = 2.0 Hz, 1H), 7.66 (dd, J = 9.2, 2.4 Hz, 1H), 7.57 – 7.48 (m, 5H), 7.36 (d, J = 4.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.82, 148.24, 146.68, 137.21, 132.84, 131.23, 130.54, 129.44, 128.87, 127.54, 124.75, 122.11. **HRMS** (ESI) calculated for $C_{15}H_{10}ClN$ $(M+H)^+$240.0572; found: 240.0558.

6-methoxy-4-phenylquinoline(4d)[8]



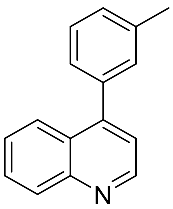
White solid in 67% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 3.2 Hz, 1H), 8.09 (d, *J* = 9.2 Hz, 1H), 7.56 – 7.48 (m, 5H), 7.39 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.29 (d, *J* = 4.4 Hz, 1H), 7.20 (d, *J* = 2.4 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.92, 147.43, 147.26, 144.67, 138.32, 131.19, 129.33, 128.71, 128.42, 127.73, 121.88, 121.72, 103.68, 55.46. **HRMS** (ESI) calculated for $C_{16}H_{13}NO$ $(M+H)^+$236.1067; found: 236.1082.

6-isopropyl-4-phenylquinoline(4e)



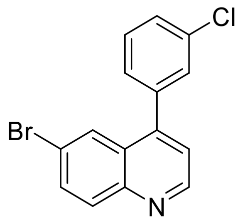
White solid in 55% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 4.4 Hz, 1H), 8.13 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 2.0 Hz, 1H), 7.66 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.57 – 7.49 (m, 5H), 7.30 (d, *J* = 4.4 Hz, 1H), 3.06 – 3.00 (m, 1H), 1.27 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.10, 148.16, 147.52, 147.35, 138.24, 129.71, 129.56, 128.93, 128.60, 128.38, 126.67, 122.09, 121.43, 34.39, 23.91. **HRMS** (ESI) calculated for $C_{18}H_{17}N$ $(M+H)^+$248.1431; found: 248.1435.

4-(m-tolyl)quinoline(4f)



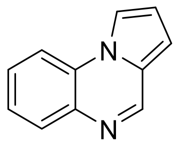
Yellow solid in 52% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, *J* = 4.4 Hz, 1H), 8.18 (dd, *J* = 8.4, 0.4 Hz, 1H), 7.94 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.71 – 7.75 (m, 1H), 7.52 – 7.48 (m, 1H), 7.44 – 7.30 (m, 1H), 7.34 – 7.30 (m, 4H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.91, 148.81, 148.57, 138.34, 137.93, 130.21, 129.76, 129.36, 129.20, 128.48, 126.85, 126.68, 126.62, 126.02, 121.31, 21.53. **HRMS** (ESI) calculated for $C_{16}H_{13}N$ $(M+H)^+$220.1118; found: 220.1132.

6-bromo-4-(3-chlorophenyl)quinoline(4g)



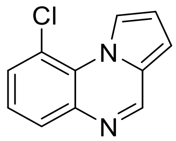
White solid in 54% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, *J* = 4.4 Hz, 1H), 8.10 (d, *J* = 8.8 Hz, 1H), 7.99 (d, *J* = 2.0 Hz, 1H), 7.83 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.52 – 7.47 (m, 3H), 7.38 – 7.36 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.95, 159.48, 149.12, 148.29, 148.23, 145.63, 137.50, 132.27, 132.18, 129.35, 128.82, 128.75, 127.68, 127.59, 121.88, 119.86, 119.61, 109.39, 109.16. **HRMS** (ESI) calculated for $C_{15}H_9BrClN$ $(M+H)^+$317.9677; found: 317.9692.

pyrrolo[1,2-*a*]quinoxaline(5a)[2b]



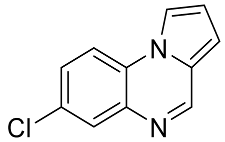
Yellow solid in 46% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.94 (dd, J = 8.0, 1.6 Hz, 1H), 7.88 (dd, J = 2.8, 1.2 Hz, 1H), 7.80 (dd, J = 8.0, 1.6 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.43 – 7.39 (m, 1H), 6.88 – 6.84 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.72, 135.70, 130.03, 127.80, 125.17, 114.25, 114.10, 113.79, 107.39. **HRMS** (ESI) calculated for $C_{11}H_8N_2$ $(M+H)^+$169.0757; found: 169.0739.

9-chloropyrrolo[1,2-*a*]quinoxaline(5b)



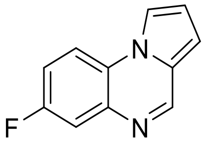
Yellow solid in 46% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.01 (d, *J* = 2.0 Hz, 1H), 7.88 – 7.87 (m, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.54 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.94 – 6.90 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.88, 134.55, 131.37, 128.83, 128.50, 126.30, 121.11, 117.00, 114.73, 114.62, 108.16. **HRMS** (ESI) calculated for $C_{11}H_7ClN_2$ $(M+H)^+$203.0368; found: 203.0382.

7-chloropyrrolo[1,2-*a*]quinoxaline(5c)[7]



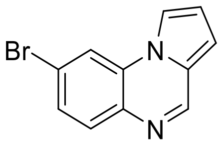
Yellow solid in 44% yield, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.91 (s, 1H), 8.50 – 8.49 (m, 1H), 8.31 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 2.4 Hz, 1H), 7.62 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.06 (dd, *J* = 4.0, 1.2 Hz, 1H), 6.94 (dd, *J* = 4.0, 2.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.01, 135.94, 129.73, 128.39, 128.14, 126.94, 126.09, 117.85, 117.43, 115.39, 109.84. **HRMS** (ESI) calculated for $C_{11}H_7ClN_2$ $(M+H)^+$203.0368; found: 203.0362.

6-fluoropyrrolo[1,2-*a*]quinoxaline(5d)[2b]



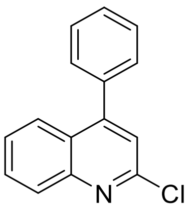
Yellow solid in 59% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 7.90 (d, *J* = 2.4 Hz, 1H), 7.83 (dd, *J* = 8.8, 4.8 Hz, 1H), 7.65 (dd, *J* = 9.6, 2.8 Hz, 1H), 7.29 – 7.24 (m, 1H), 6.94 (dd, *J* = 4.0, 0.8 Hz, 1H), 6.89 (dd, *J* = 4.0, 2.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.00, 158.58, 146.68, 136.85 (d, *J* = 12.1 Hz), 126.22, 124.67 (d, *J* = 2.02 Hz), 115.6 (d, *J* = 25.3 Hz), 115.33 (d, *J* = 22.2 Hz), 115. 03 (d, *J* = 15.2 Hz), 114.63, 114.30, 108.06. **HRMS** (ESI) calculated for $C_{11}H_7FN_2$ $(M+H)^+$187.0663; found: 187.0669.

8-bromopyrrolo[1,2-*a*]quinoxaline(5e)



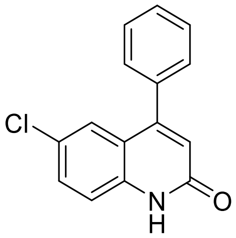
Yellow solid in 48% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.01 (d, *J* = 2.0 Hz, 1H), 7.88 – 7.87 (m, 1H), 7.82 (d, *J* = 8.4Hz, 1H), 7.54 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.94 – 6.90 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.88, 134.55, 131.37, 128.83, 128.50, 126.30, 121.11, 117.00, 114.73, 114.62, 108.16. **HRMS** (ESI) calculated for $C_{11}H_7BrN_2$ $(M+H)^+$246.9863; found: 246.9871.

2-chloro-4-phenylquinoline(6a)[1b]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 8.4, 1.2 Hz, 1H), 7.88 (dd, J = 8.4, 1.6 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.55 – 7.49 (m, 6H), 7.35 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.76, 150.34, 148.34, 136.77, 130.51, 129.42, 128.99, 128.95, 128.76, 127.01, 126.00, 125.66, 122.15. **HRMS** (ESI) calculated for $C_{15}H_{10}ClN$ $(M+H)^+$240.0572; found: 240.0582.

6-chloro-4-phenylquinolin-2(1H)-one(6c)[1b]



^1H NMR (400 MHz, DMSO-d_6) δ 12.06 (s, 1H), 7.62 – 7.54 (m, 4H), 7.50 – 7.47 (m, 2H), 7.42 (d, J = 8.8 Hz, 1H), 7.27 (d, J = 2.3 Hz, 1H), 6.47 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.53, 150.86, 138.53, 136.48, 130.98, 129.51, 129.33, 129.08, 126.25, 125.42, 122.90, 120.09, 118.23. **HRMS** (ESI) calculated for $C_{15}H_{10}ClNO$ $(M+H)^+$256.0521; found: 256.0529.

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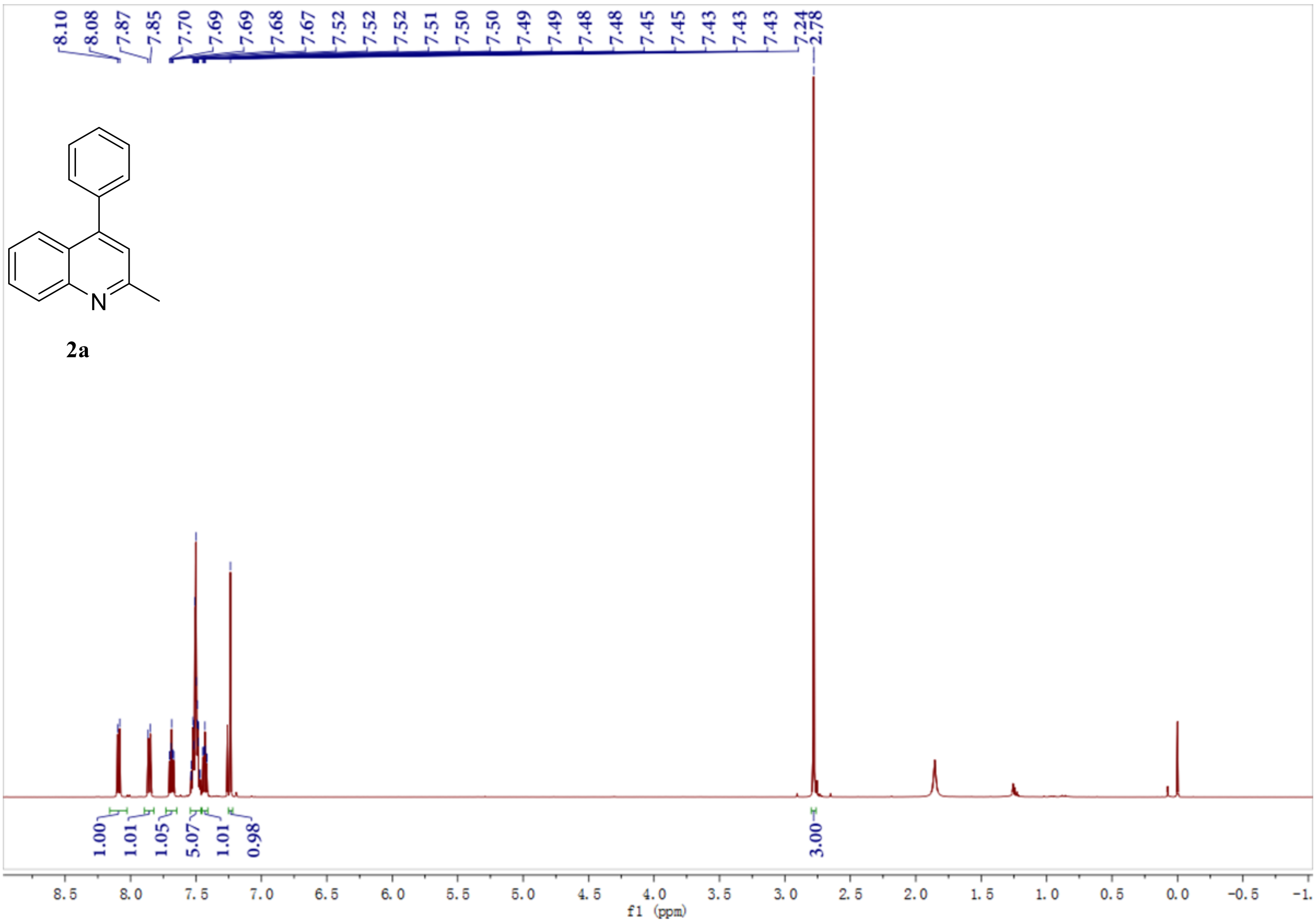
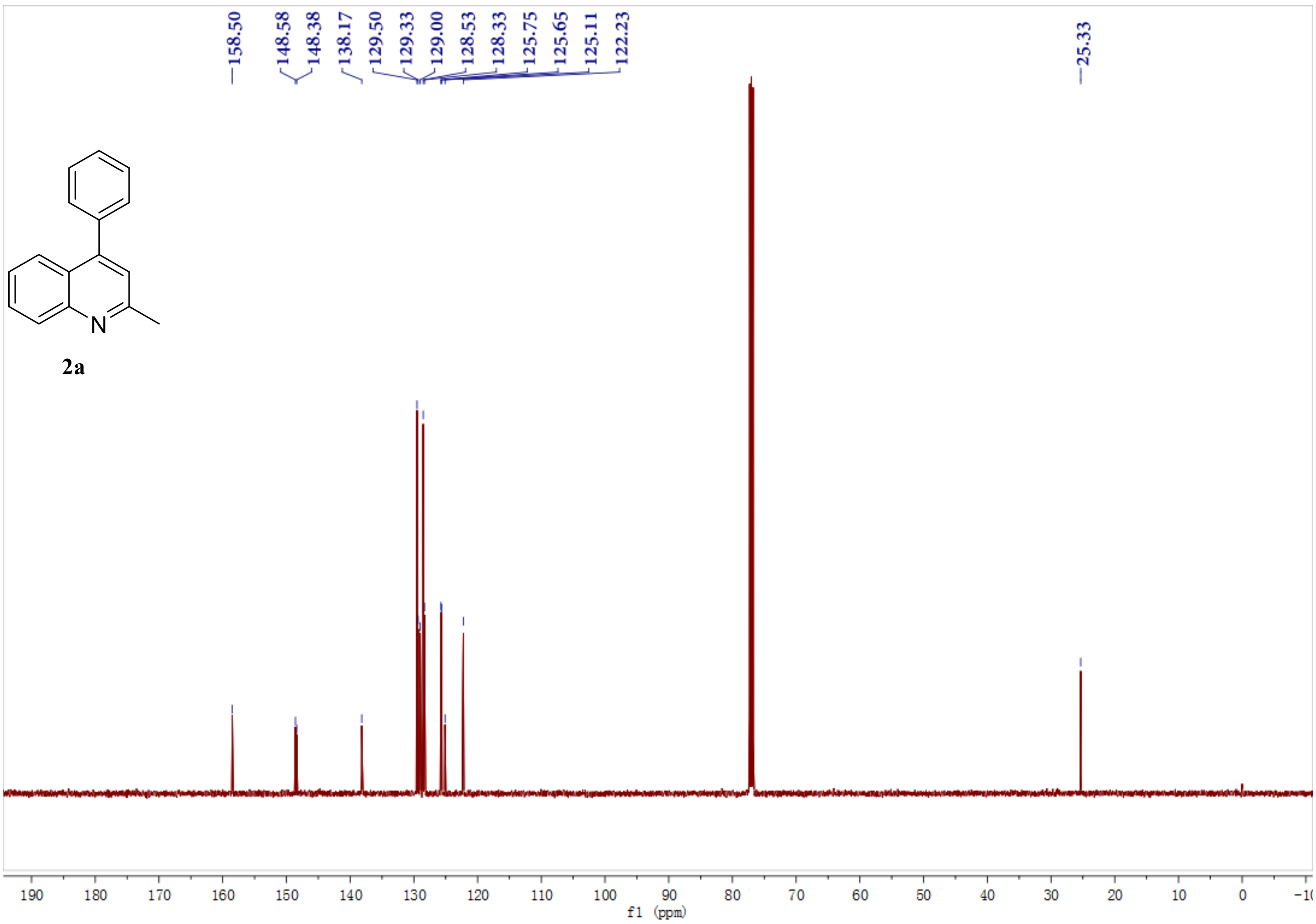
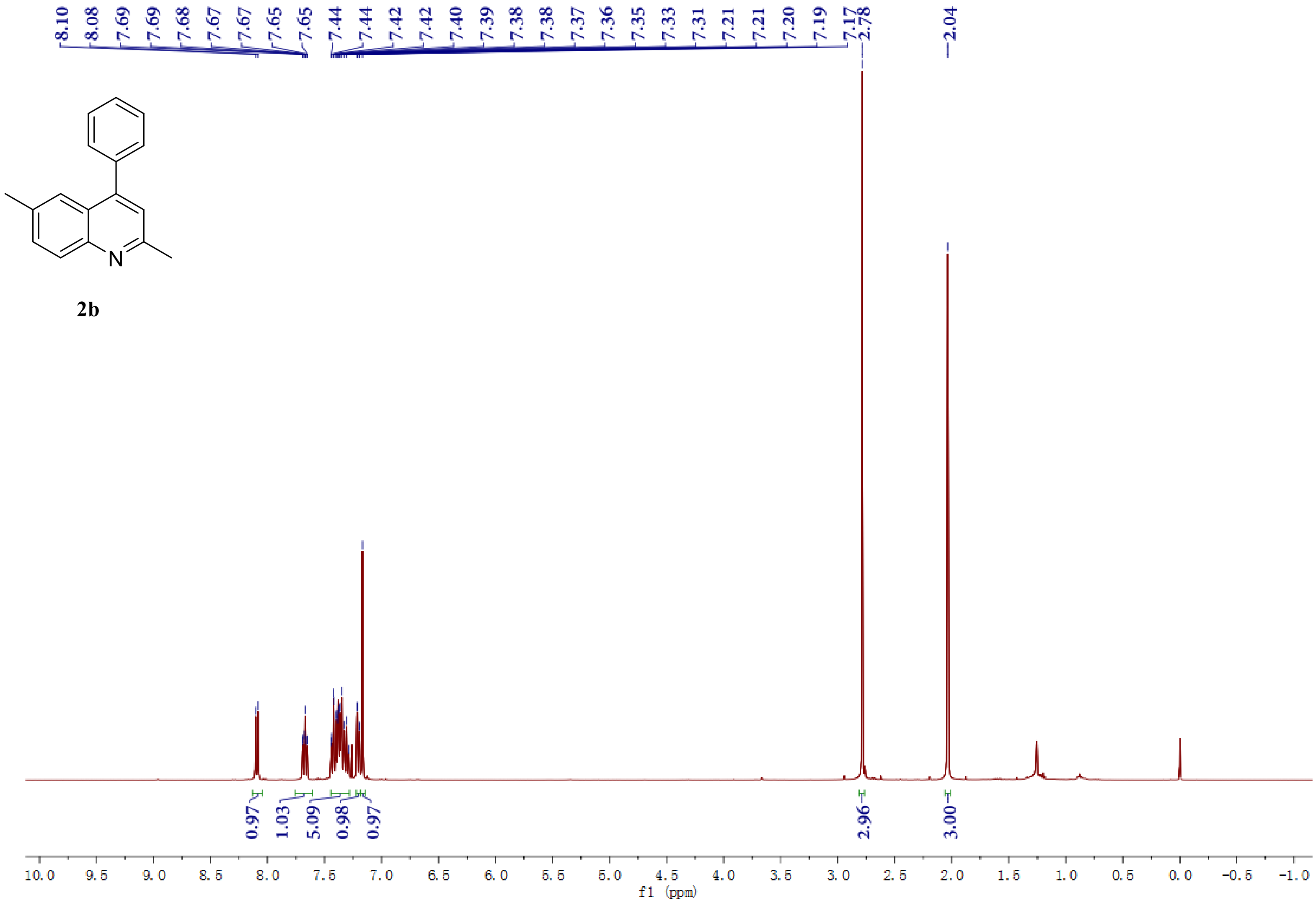
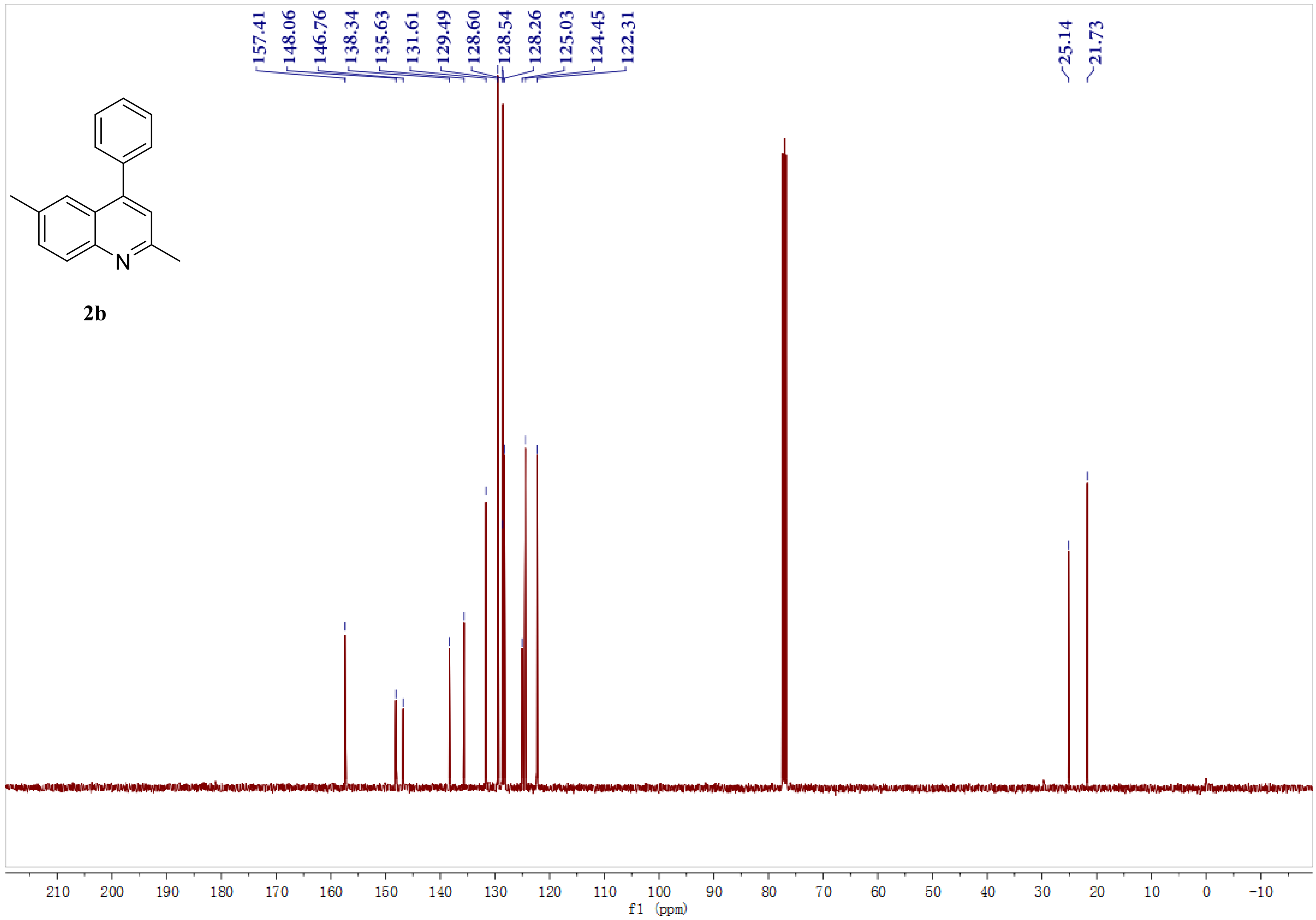
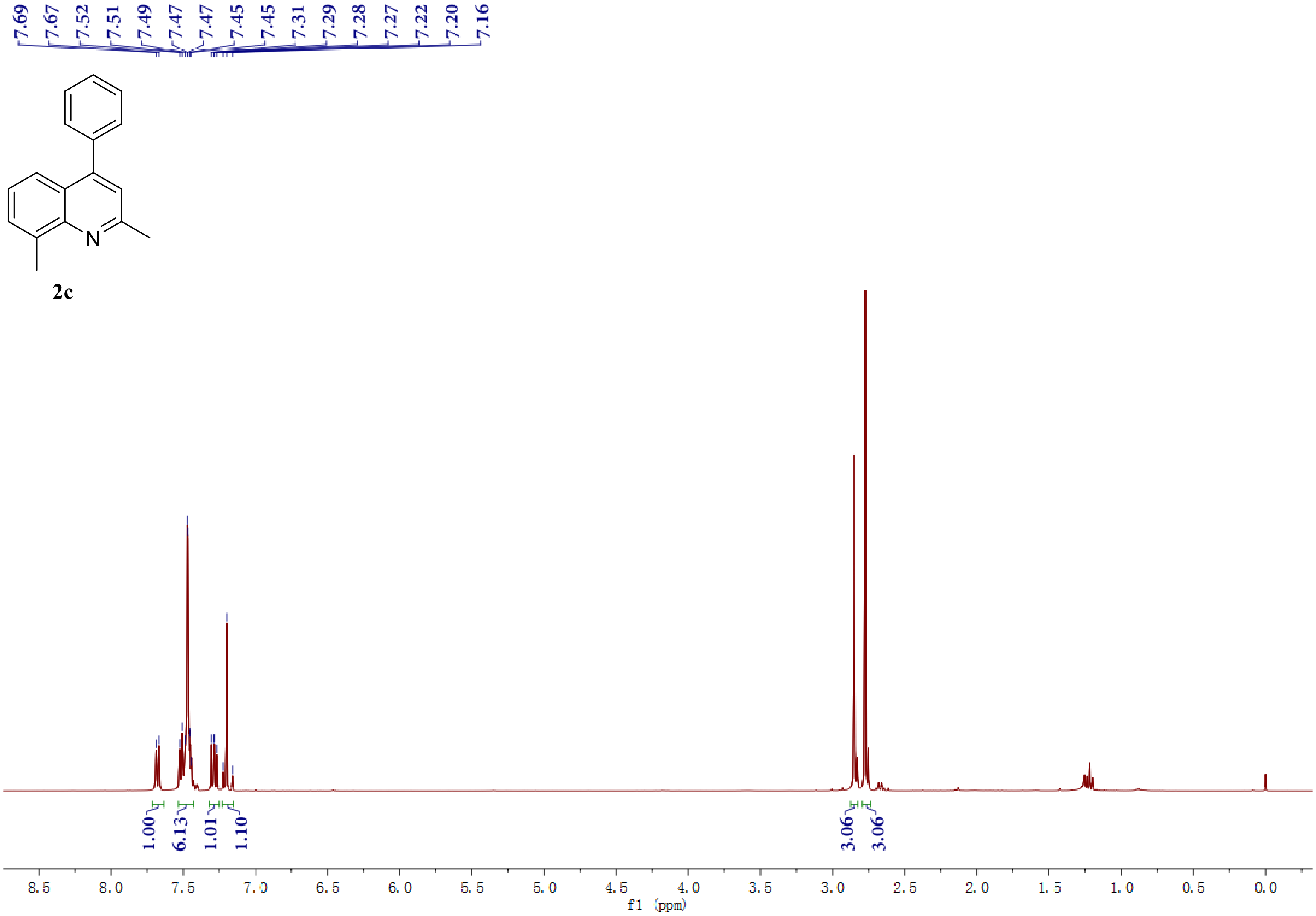
(7) Copies of 1H &13C:

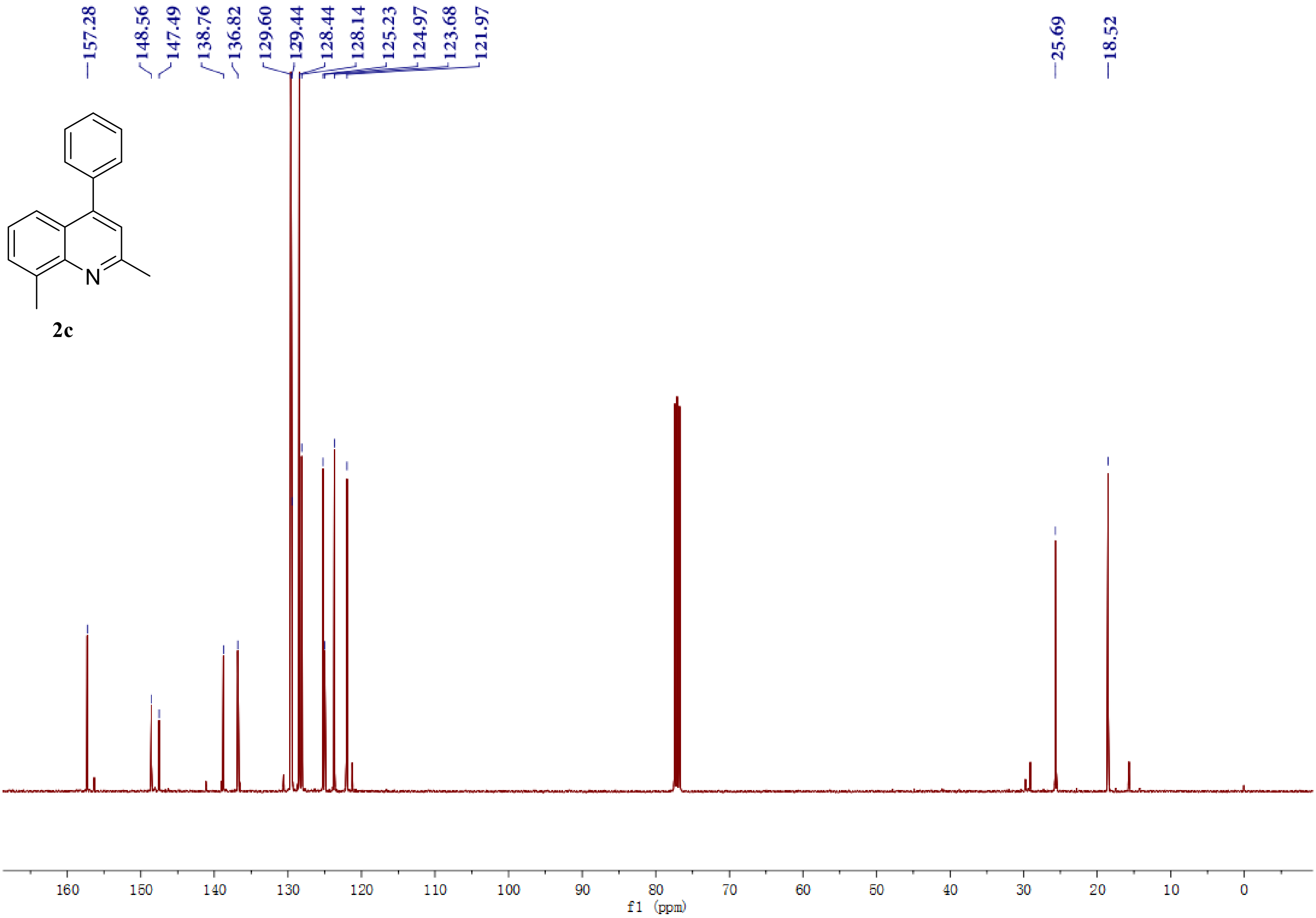





8.10 8.08 7.69 7.69 7.68 7.67 7.67 7.65 7.65 7.44 7.44 7.42 7.42 7.40 7.39 7.38 7.38 7.37 7.36 7.35 7.33 7.31 7.21 7.21 7.20 7.19 7.17 2.78
2.04
N
2b
0.97 1.03 5.09 0.98 0.97
2.96
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


157.41 148.06 146.76 138.34 135.63 131.61 129.49 128.60 128.54 128.26 125.03 124.45 122.31
25.14
21.73
N
2b
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)


7.69
7.67
7.52
7.51
7.49
7.47
7.47
7.45
7.45
7.31
7.29
7.28
7.27
7.22
7.20
7.16
N
2c
1.00
6.13
1.01
1.10
3.06
3.06
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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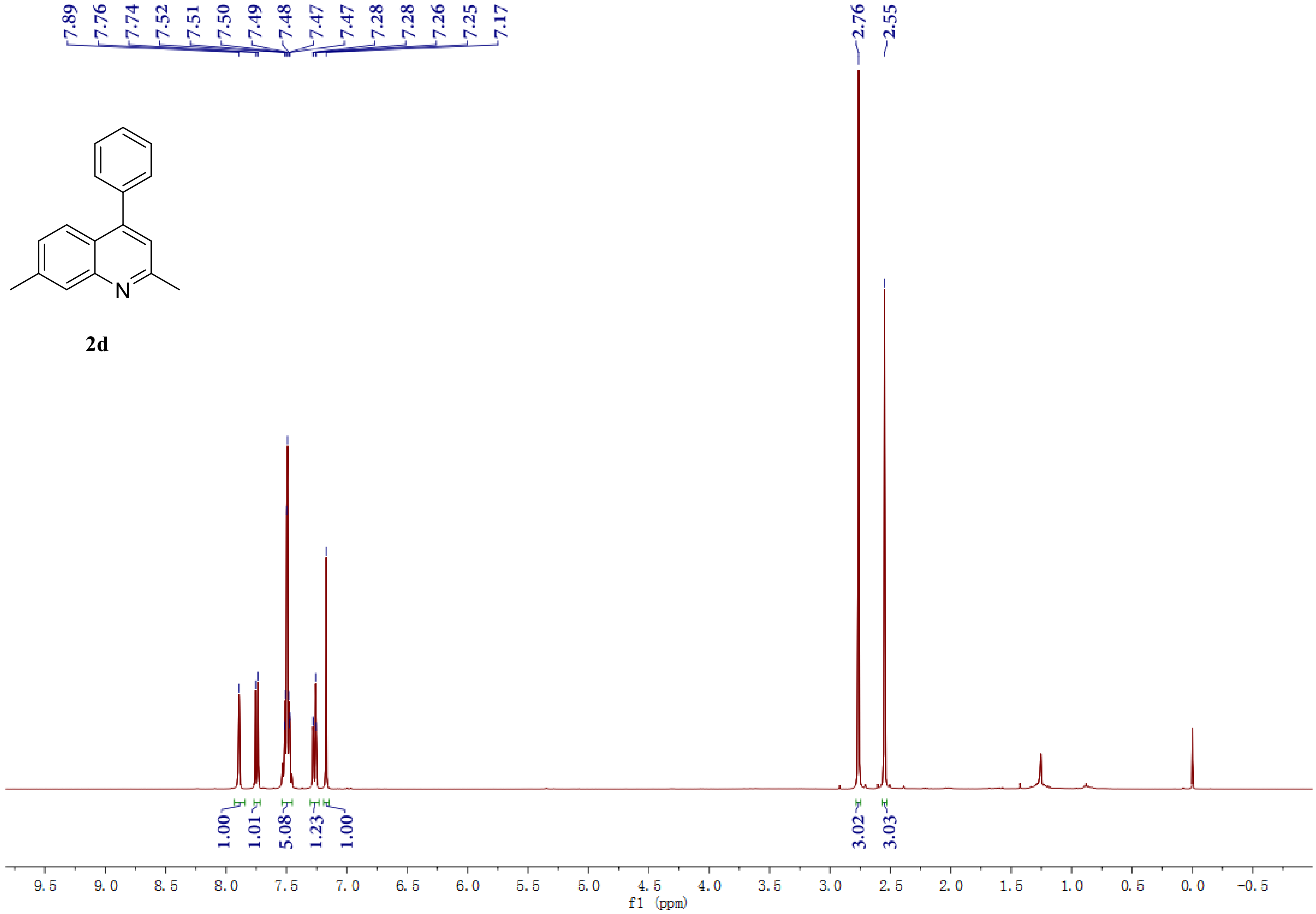
148.56
147.49
138.76
136.82
129.60
129.44
128.44
128.14
125.23
124.97
123.68
121.97
25.69
18.52
N
2c
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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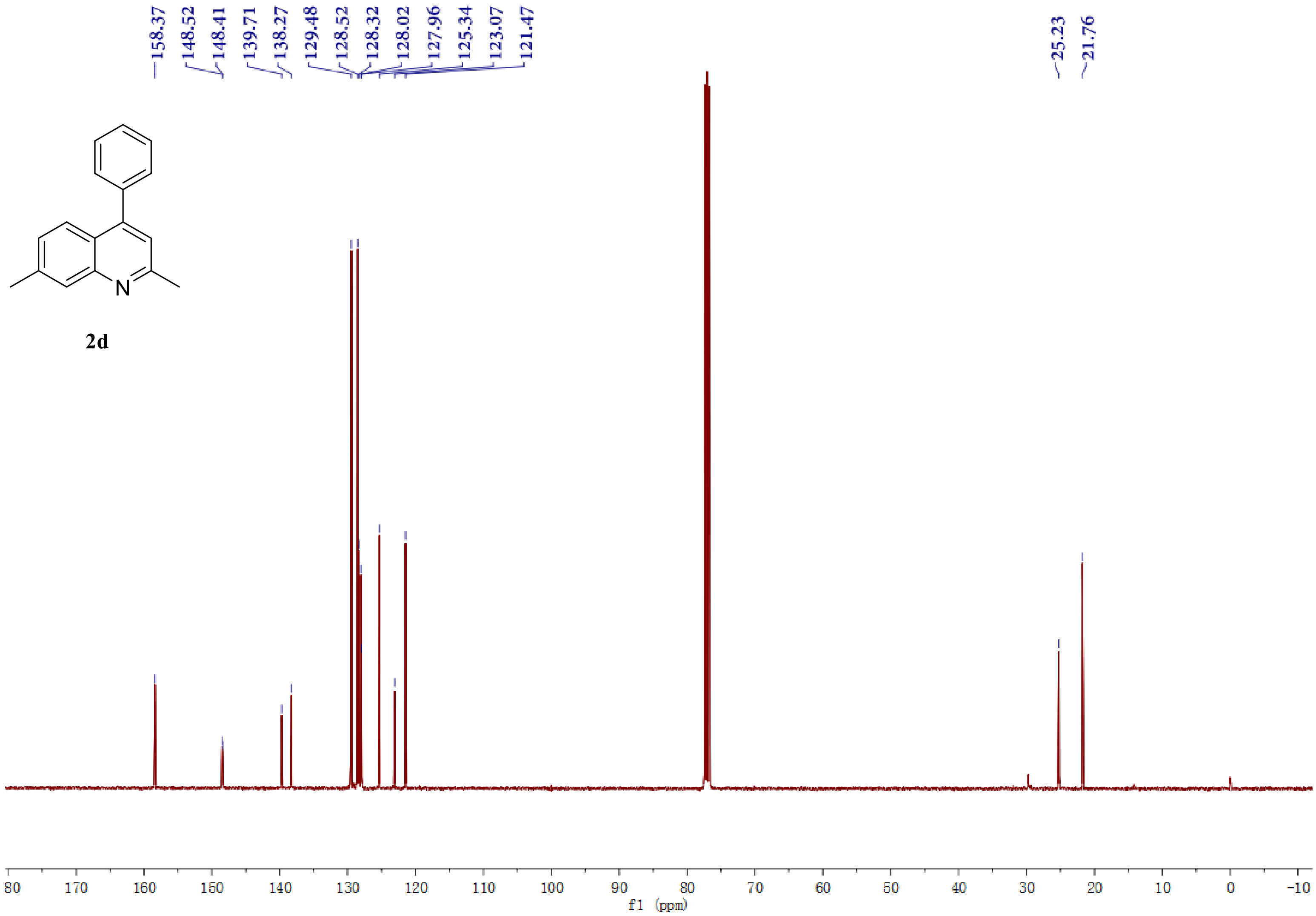
7.74
7.52
7.51
7.50
7.49
7.48
7.47
7.47
7.28
7.28
7.26
7.25
7.17
2.76
2.55
N
1.00
1.01
5.08
1.23
1.00
3.02
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

2d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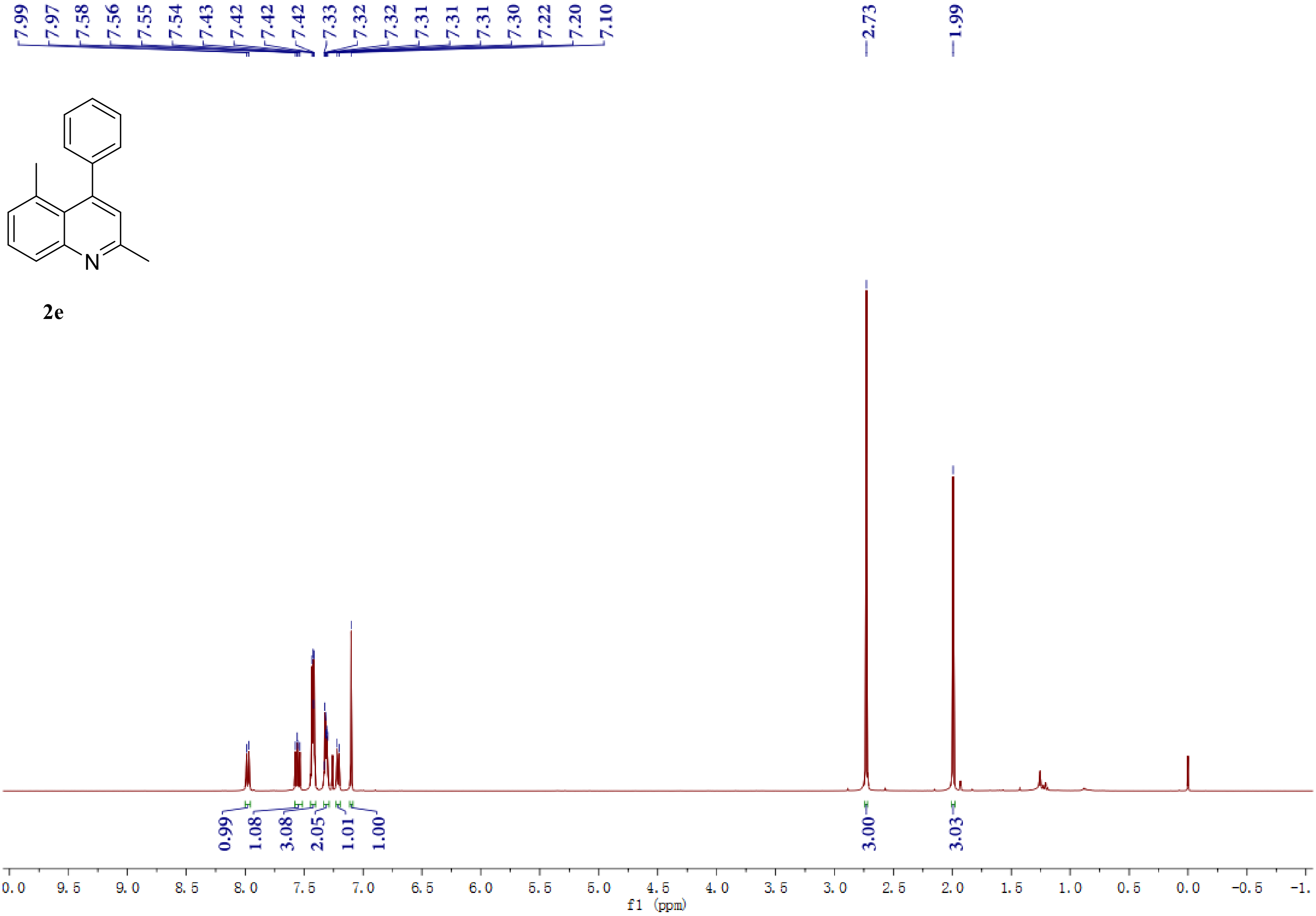
148.52
148.41
139.71
138.27
129.48
128.52
128.32
128.02
127.96
125.34
123.07
121.47
25.23
21.76
N
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2d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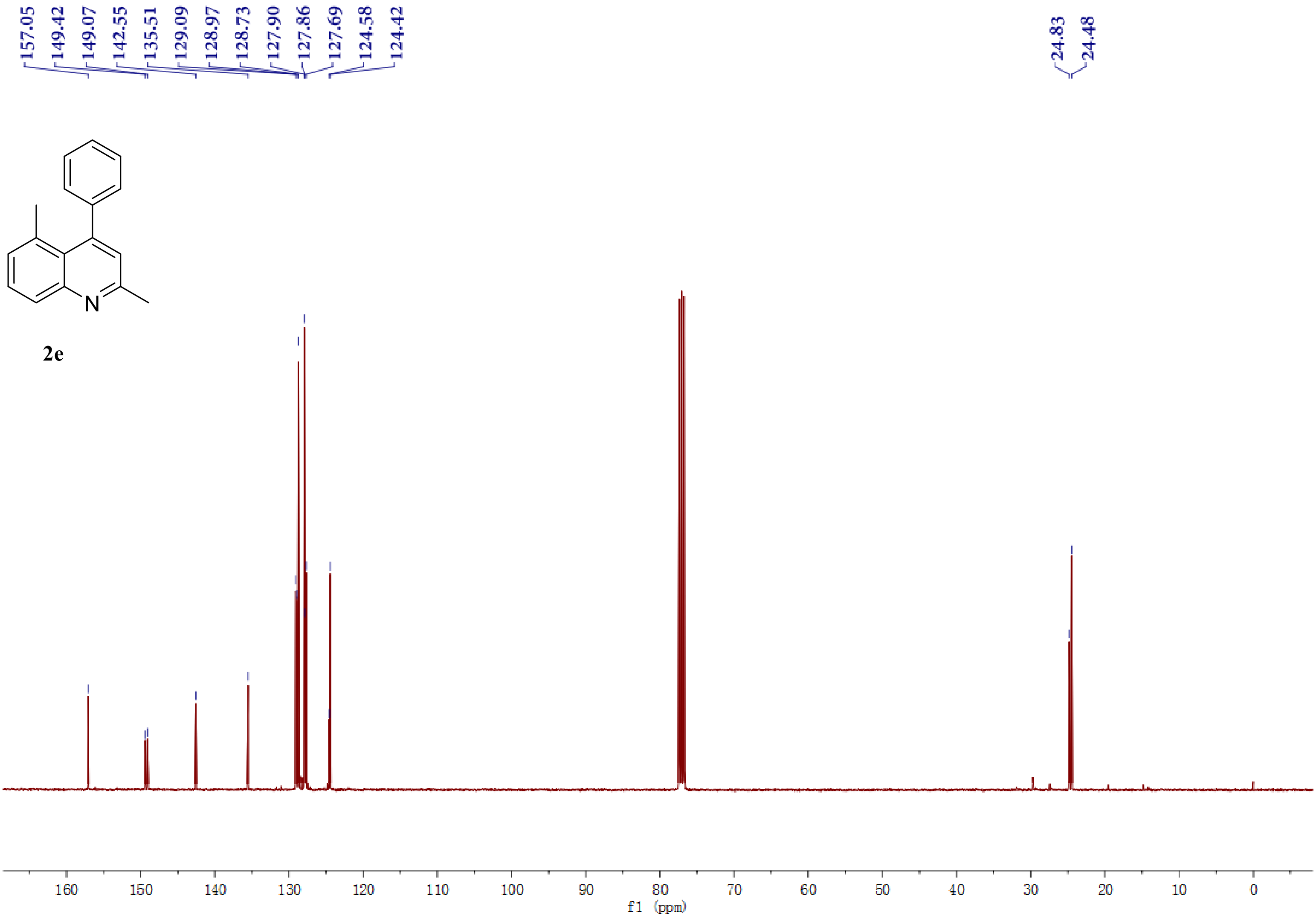
2.73
1.99
N
2e
0.99 1.08 3.08 2.05 1.01 1.00
3.00
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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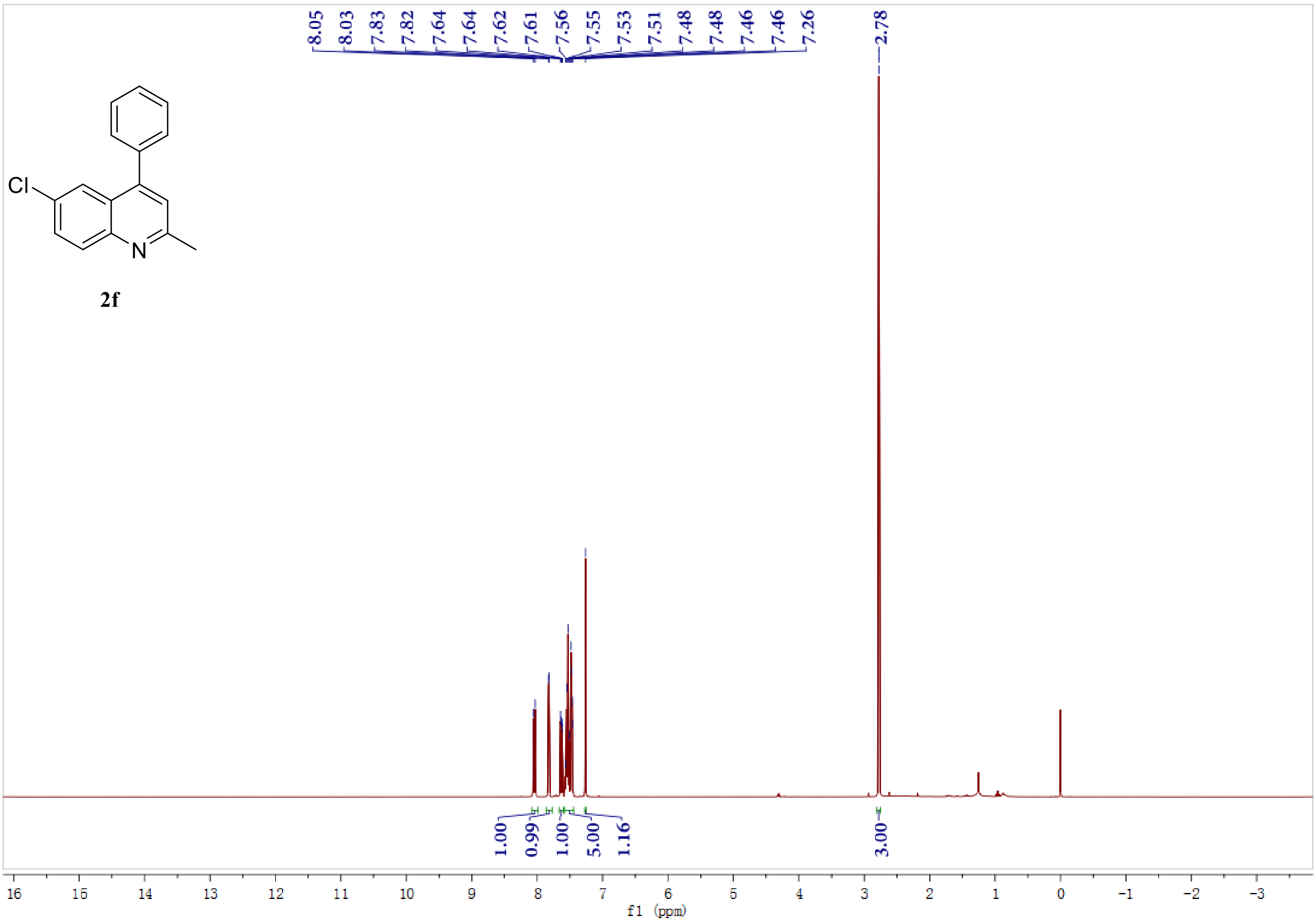
24.83 24.48
N
2e
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.05
8.03
7.83
7.82
7.64
7.64
7.62
7.61
7.56
7.55
7.53
7.51
7.48
7.48
7.46
7.46
7.26
2.78
Cl
N
2f
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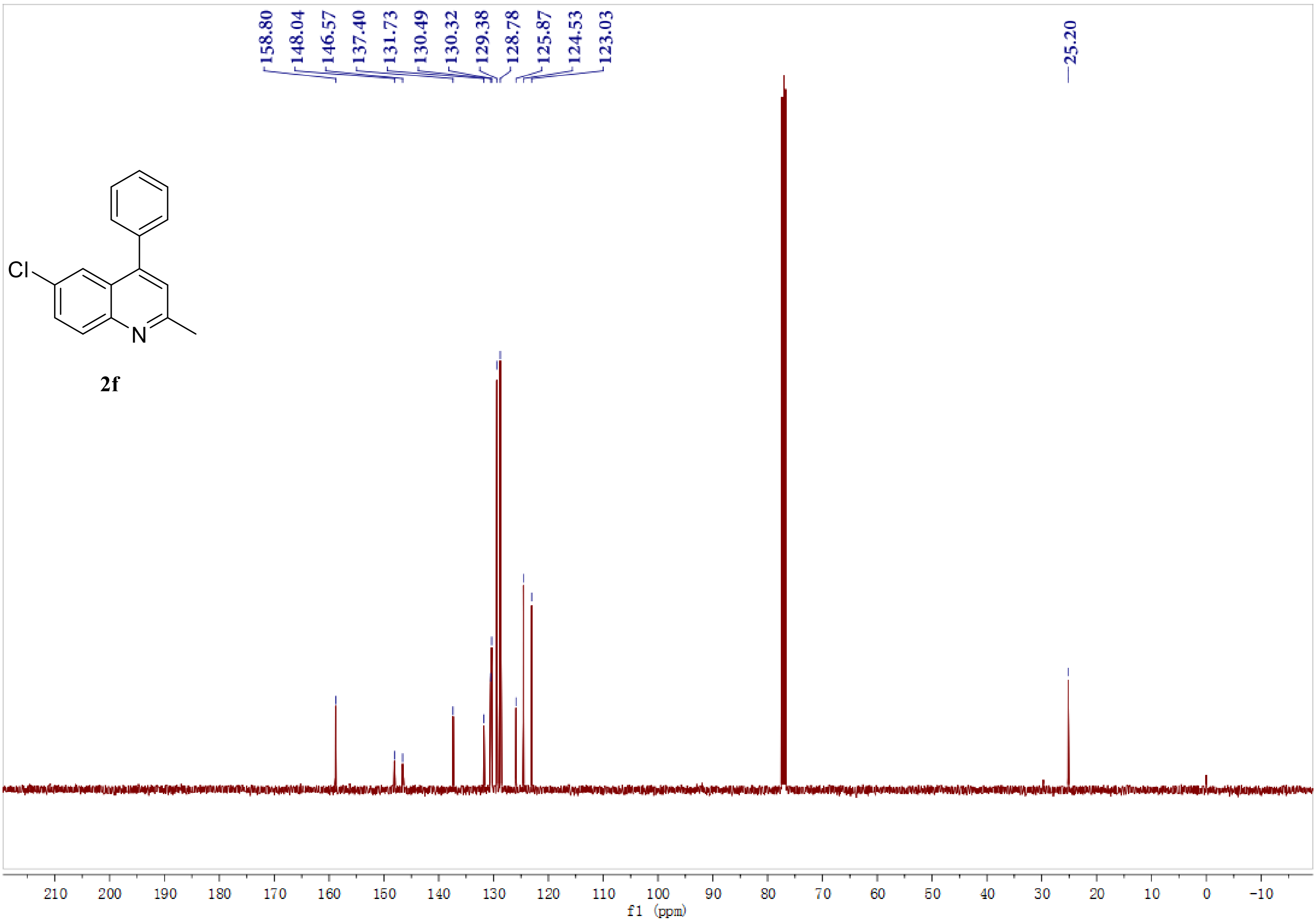
0.99
1.00
5.00
1.16
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)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130.49
130.32
129.38
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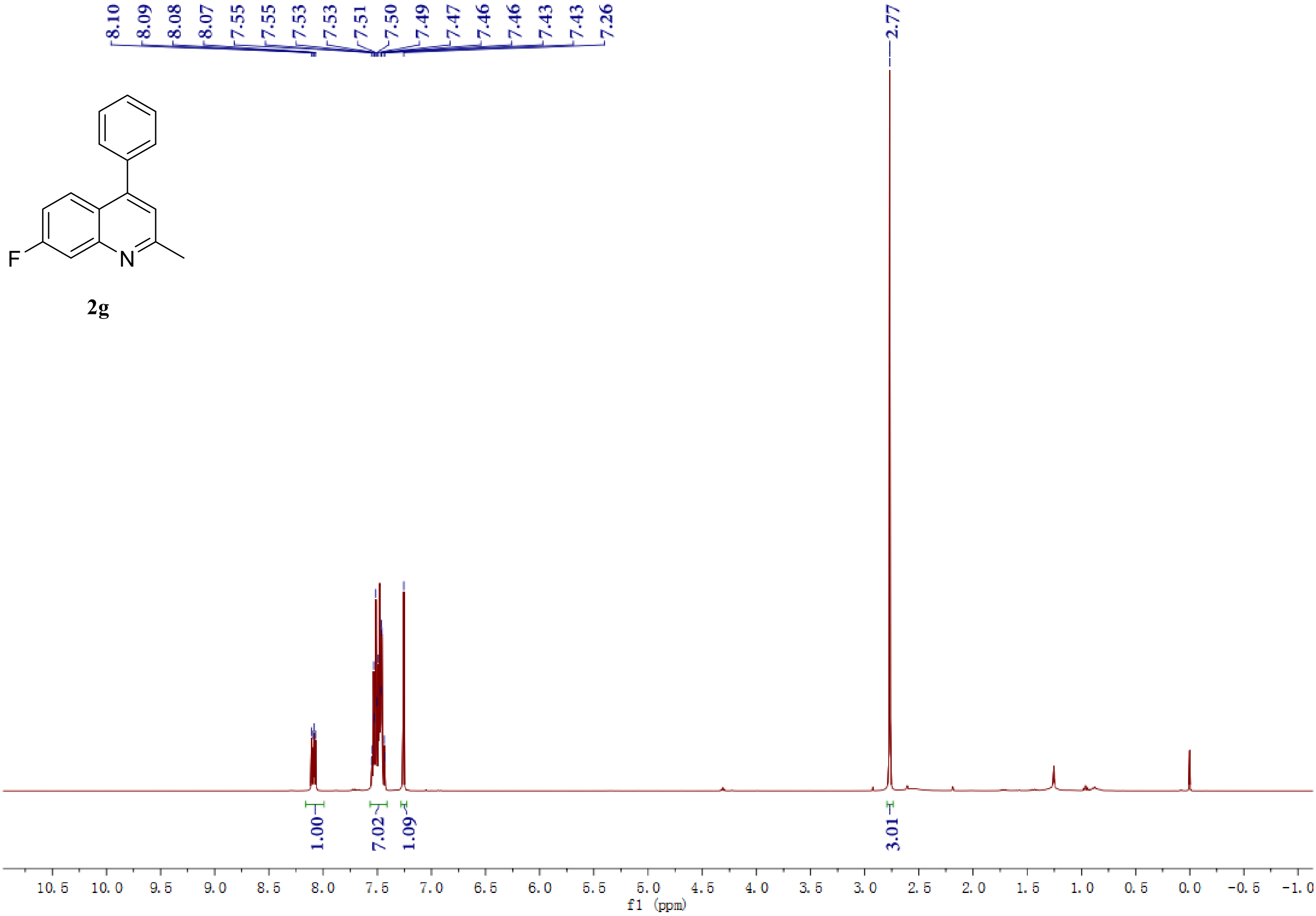
25.20
Cl
N
2f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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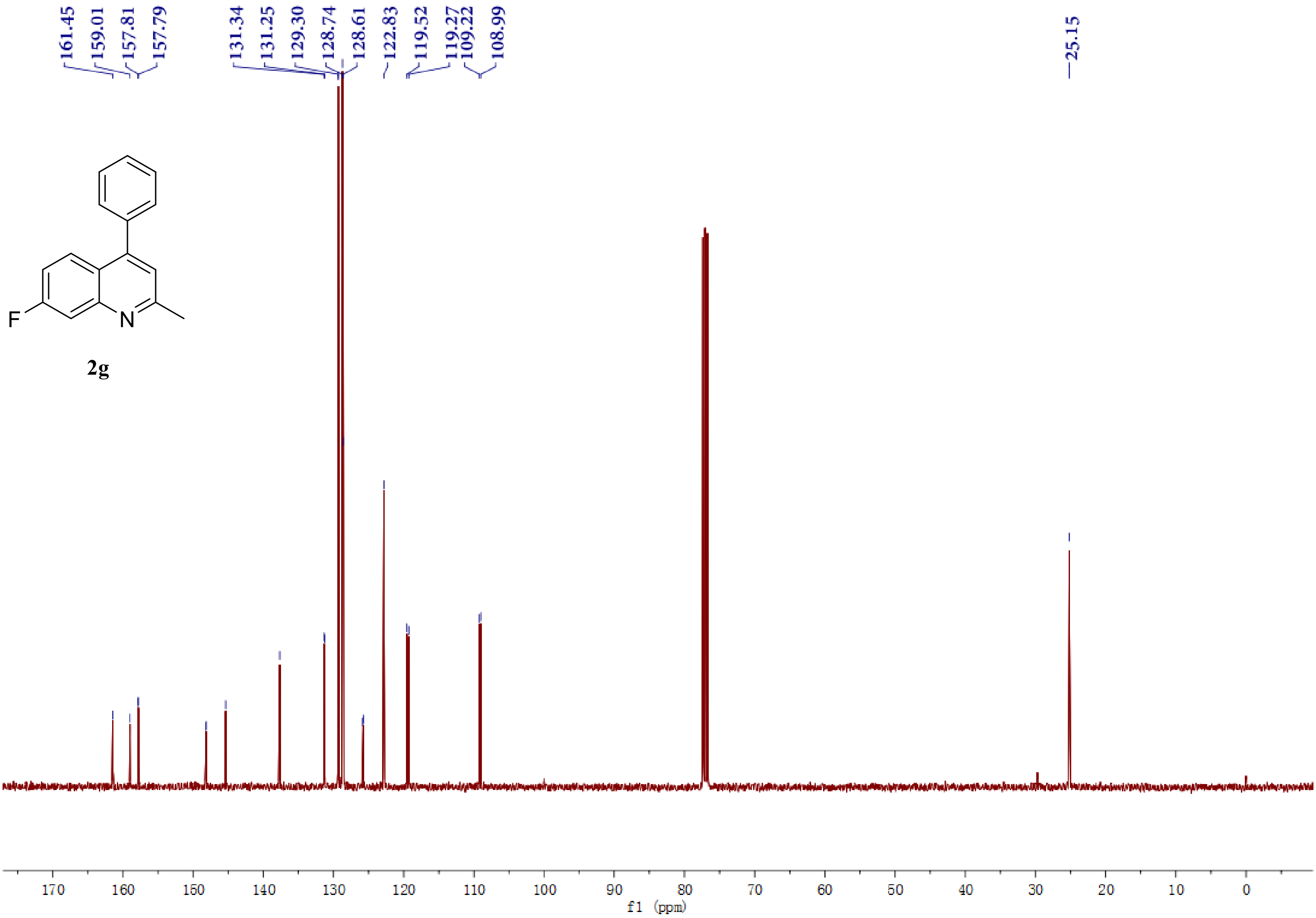
2.77
F
N
2g
1.00
7.02
1.09
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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131.34 131.25 129.30 128.74 128.61 122.83 119.52 119.27 109.22 108.99
25.15
F
N
2g
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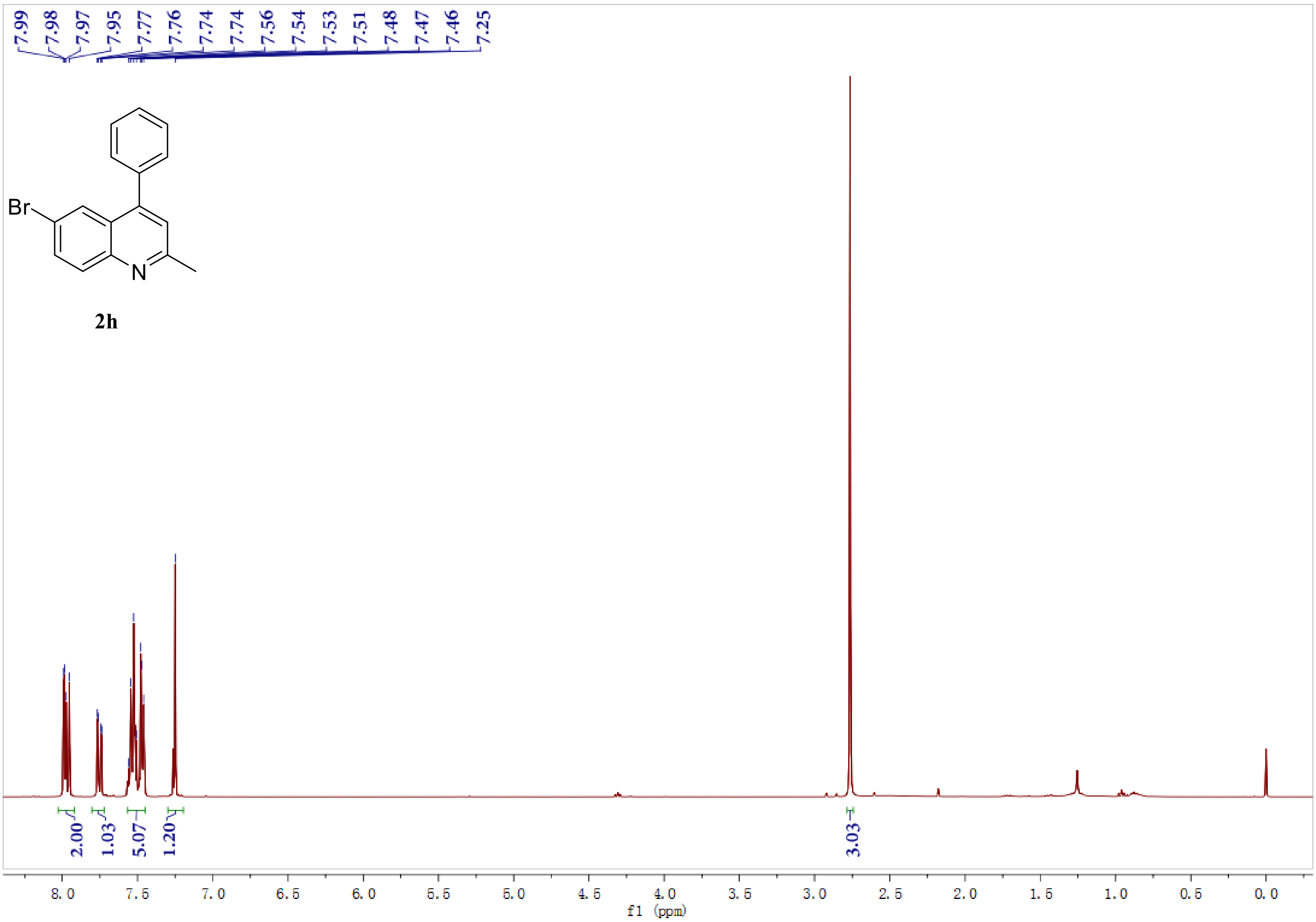
f1 (ppm)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7.74
7.74
7.56
7.54
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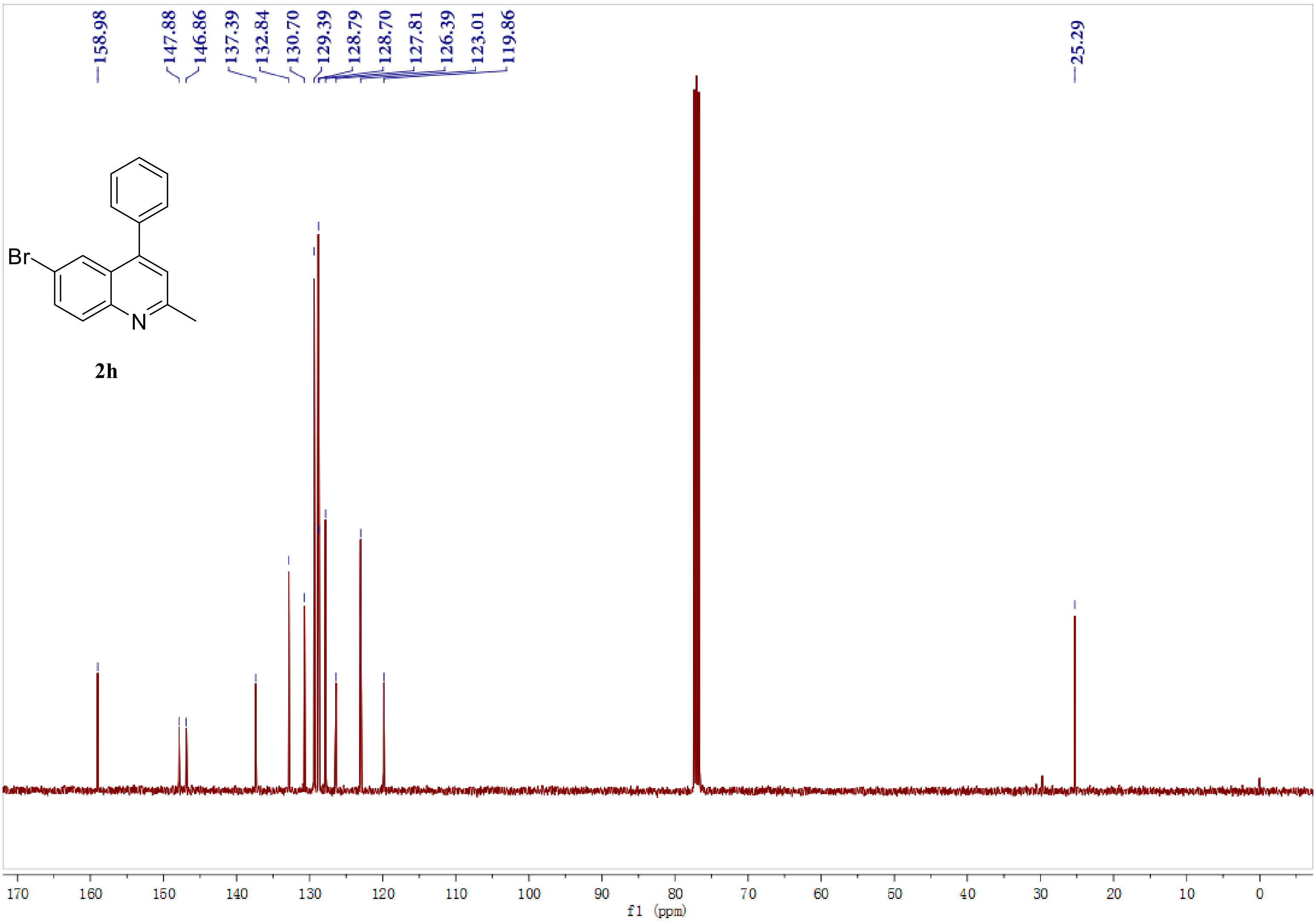
7.51
7.48
7.47
7.46
7.25
Br
N
2h
2.00
1.03
5.07
1.20
3.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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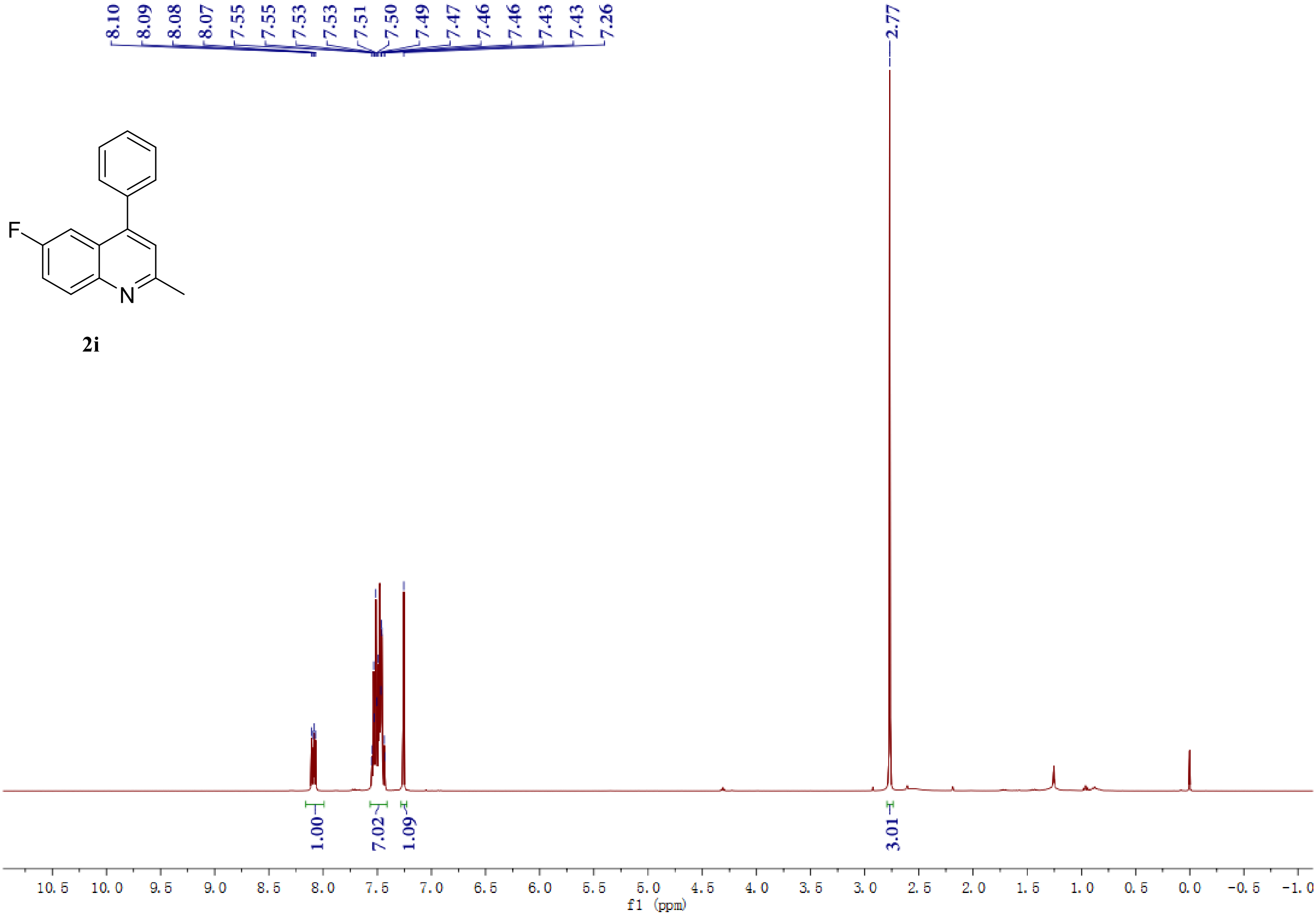
129.39
128.79
128.70
127.81
126.39
123.01
119.86
25.29
Br
N
2h
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.10 8.09 8.08 8.07 7.55 7.55 7.53 7.53 7.51 7.50 7.49 7.47 7.46 7.46 7.43 7.43 7.26
2.77
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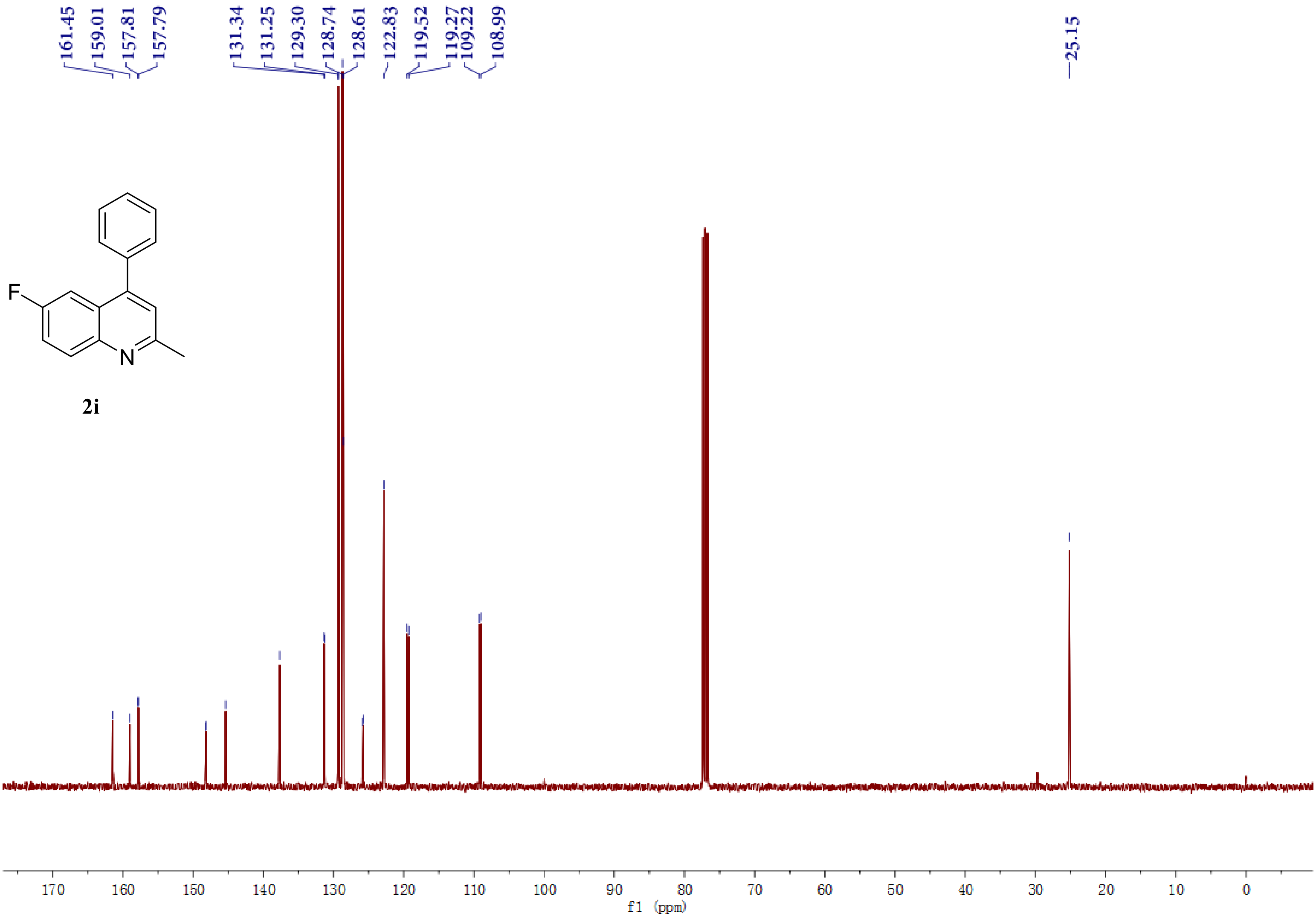
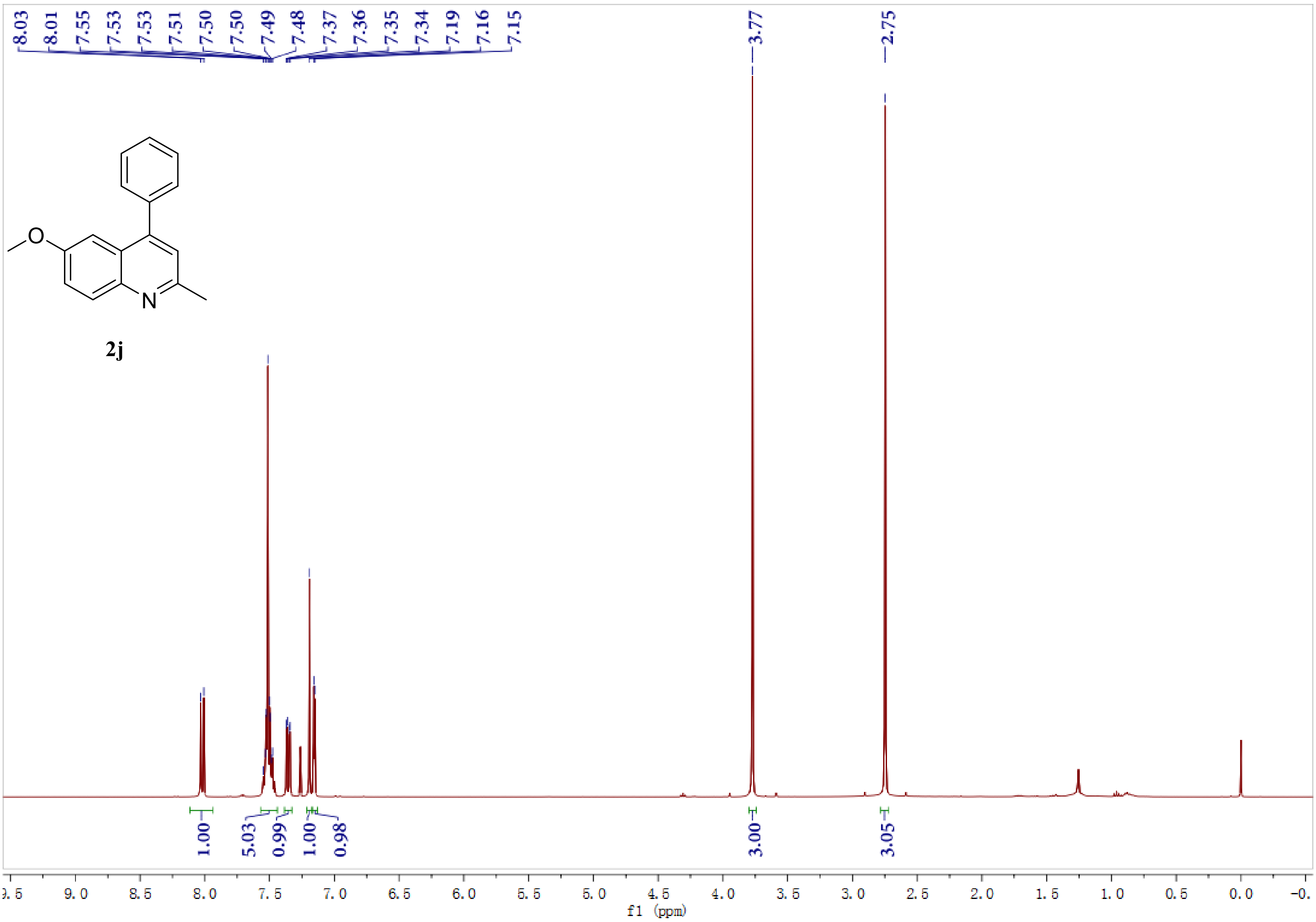
N
2i
1.00
7.02
1.09
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


161.45 159.01 157.81 157.79
131.34 131.25 129.30 128.74 128.61 122.83 119.52 119.27 109.22 108.99
25.15
F
N
2i
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.03
8.01
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7.53
7.53
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7.50
7.50
7.49
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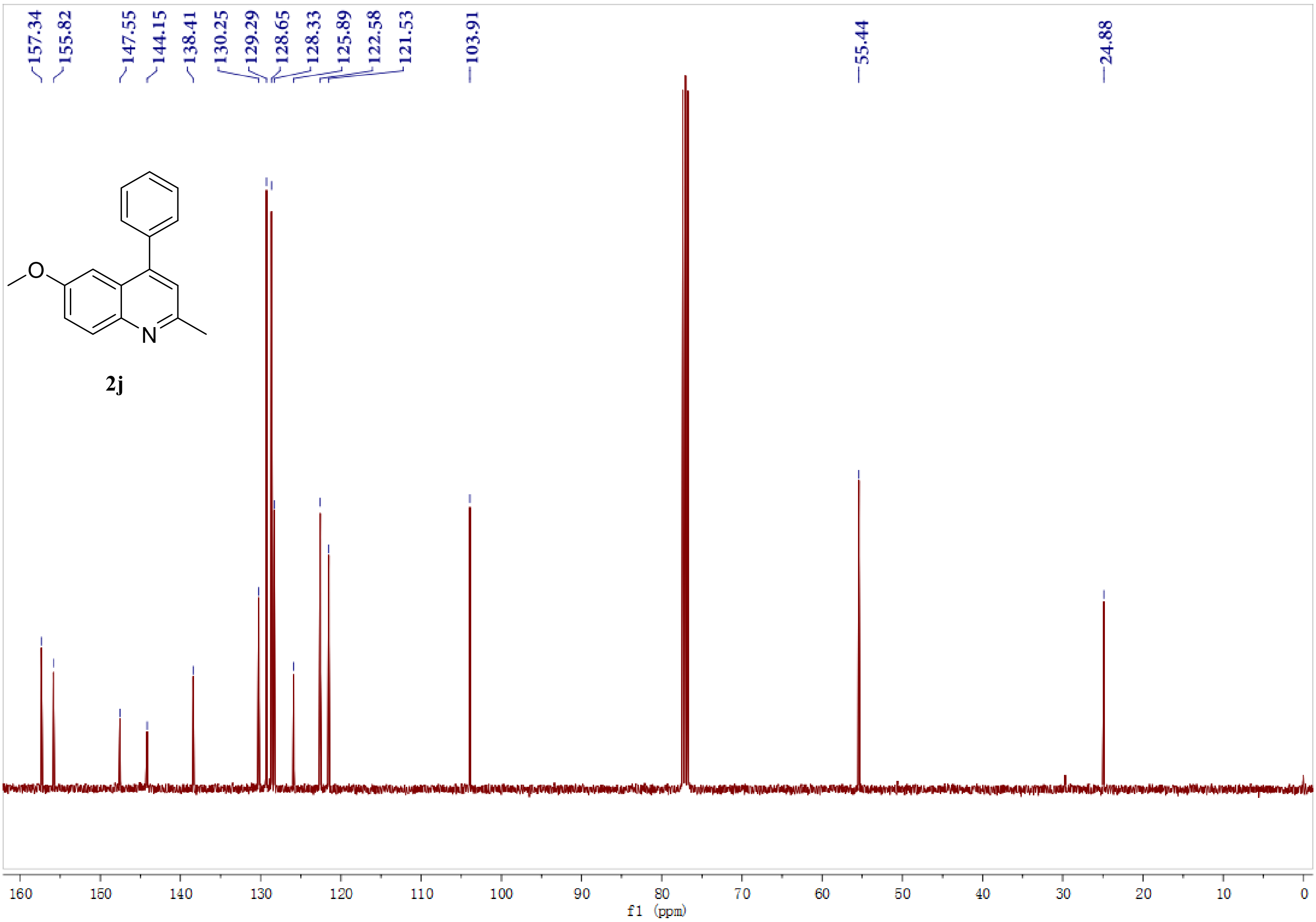
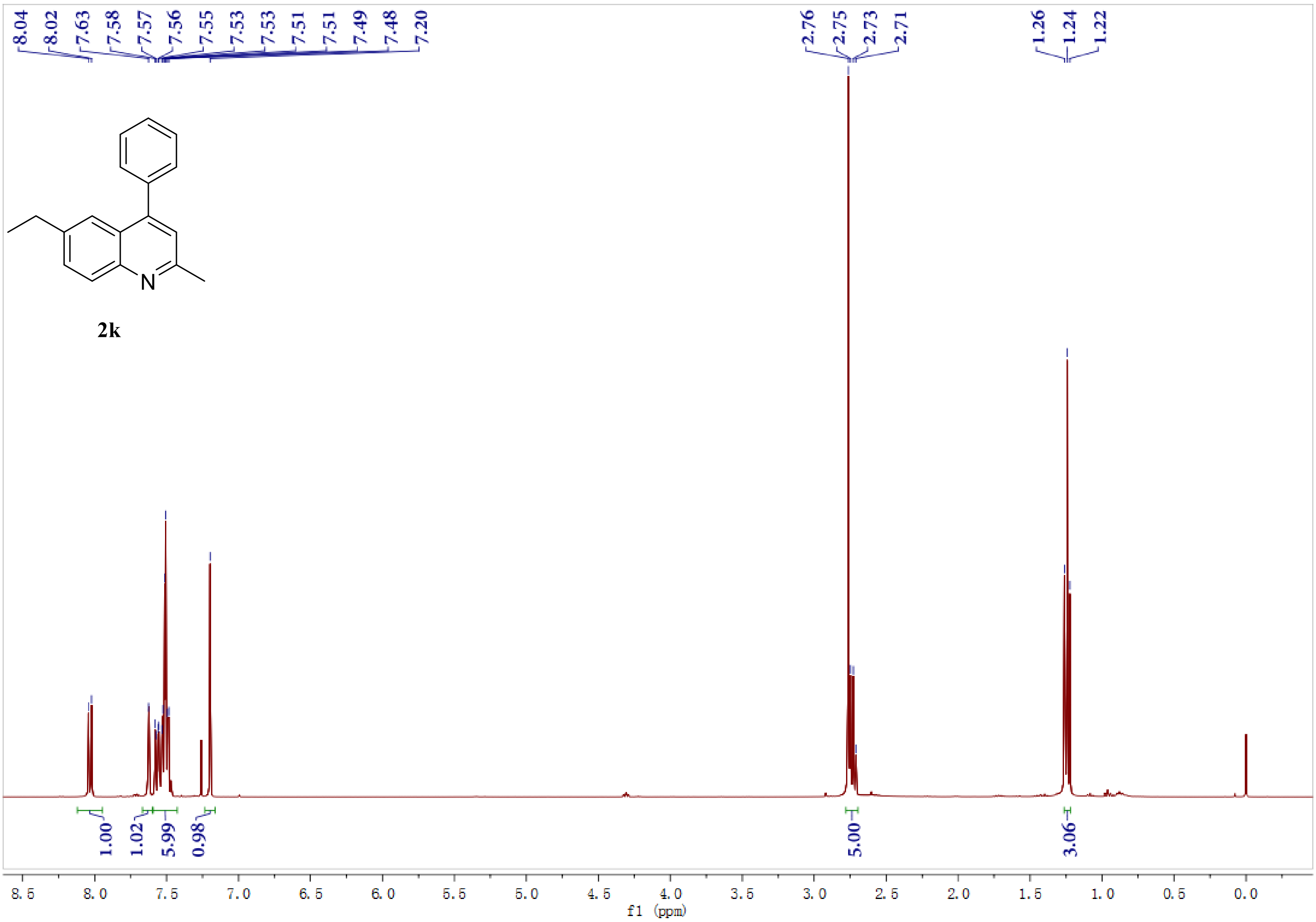
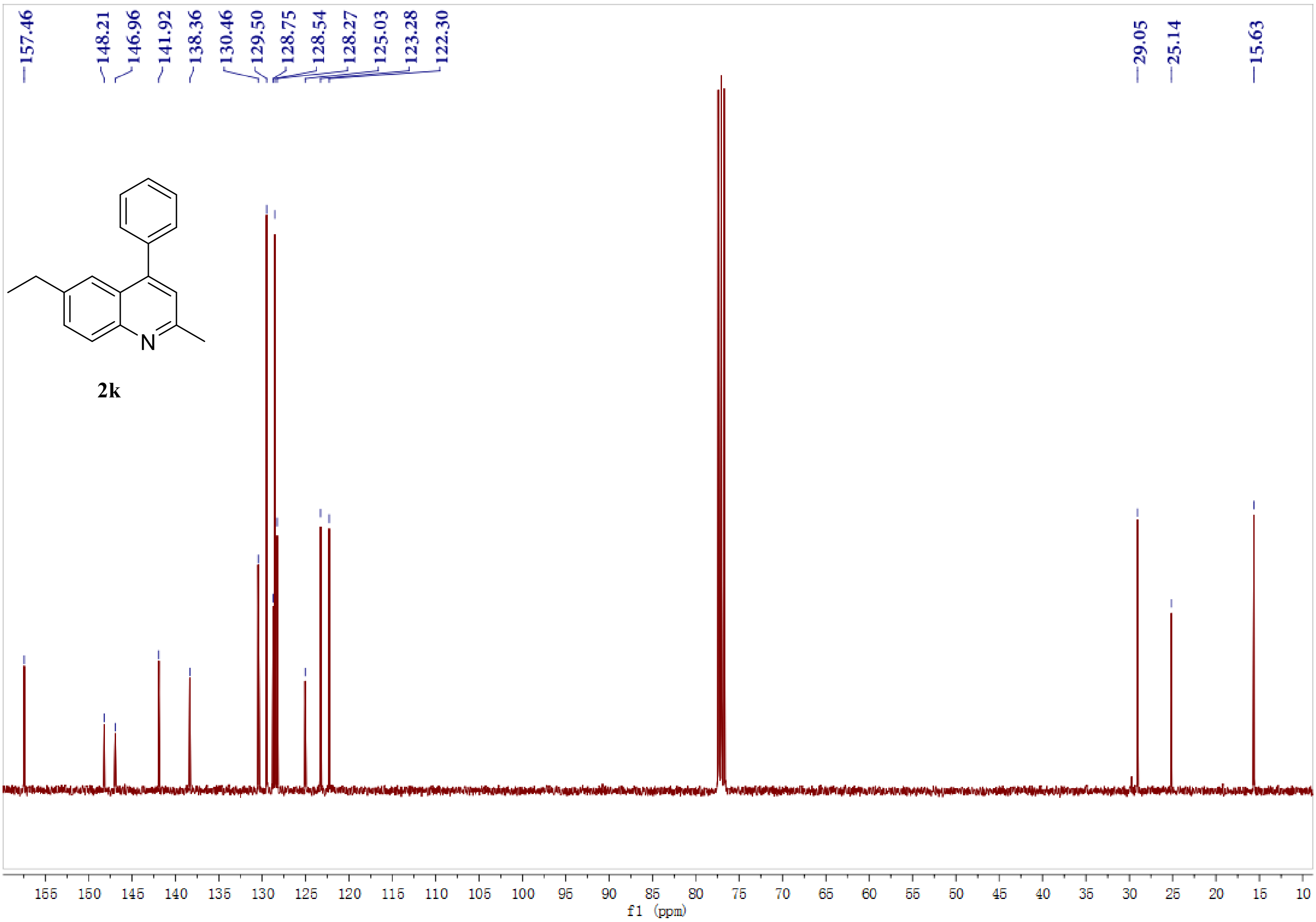
7.35
7.34
7.19
7.16
7.15
3.77
2.75
O
N
2j
1.00
5.03
0.99
1.00
0.98
3.00
3.05
f1 (ppm)


157.34
155.82
147.55
144.15
138.41
130.25
129.29
128.65
128.33
125.89
122.58
121.53
103.91
55.44
24.88
O
N
2j
f1 (ppm)


8.04
8.02
7.63
7.58
7.57
7.56
7.55
7.53
7.53
7.51
7.51
7.49
7.48
7.20
2.76
2.75
2.73
2.71
1.26
1.24
1.22
N
2k
1.00
1.02
5.99
0.98
5.00
3.06
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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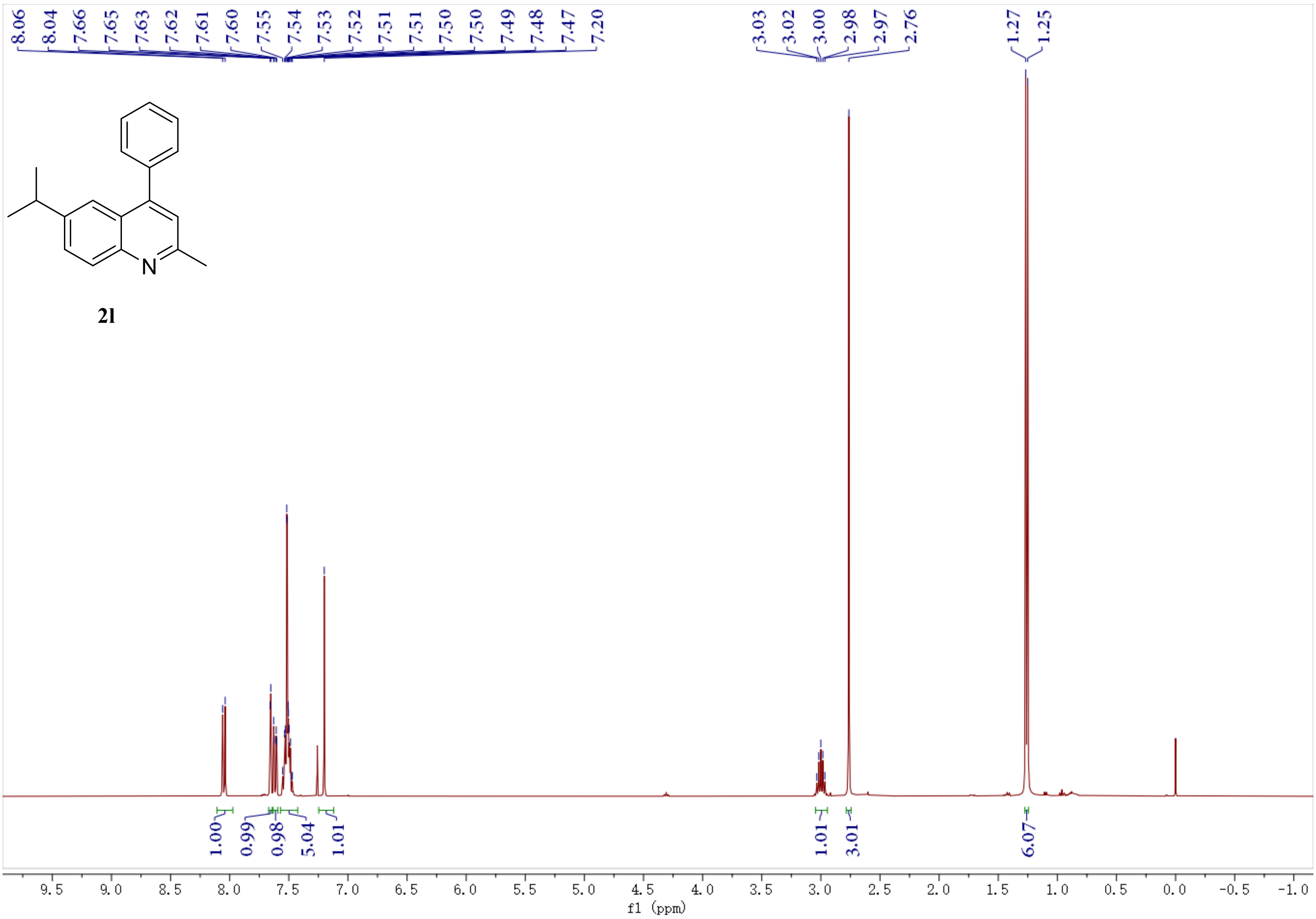
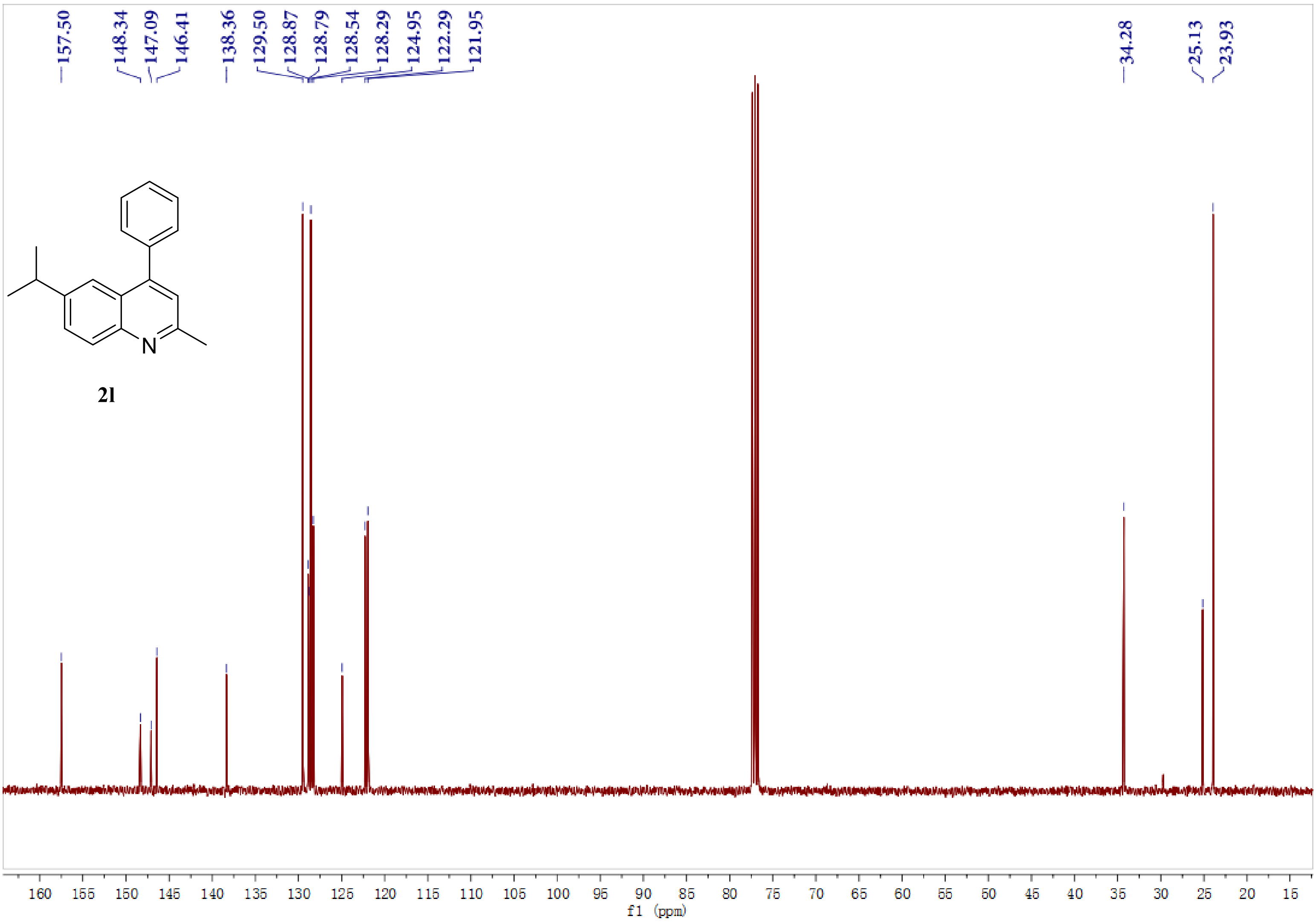
148.21
146.96
141.92
138.36
130.46
129.50
128.75
128.54
128.27
125.03
123.28
122.30
29.05
25.14
15.63
N
2k
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)


8.06
8.04
7.66
7.65
7.63
7.62
7.61
7.60
7.55
7.54
7.53
7.52
7.51
7.51
7.50
7.50
7.49
7.48
7.47
7.20
3.03
3.02
3.00
2.98
2.97
2.76
1.27
1.25
N
2l
1.00
0.99
0.98
5.04
1.01
1.01
3.01
6.07
f1 (ppm)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128.87
128.79
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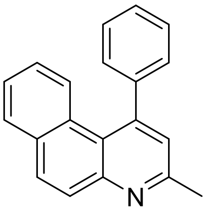
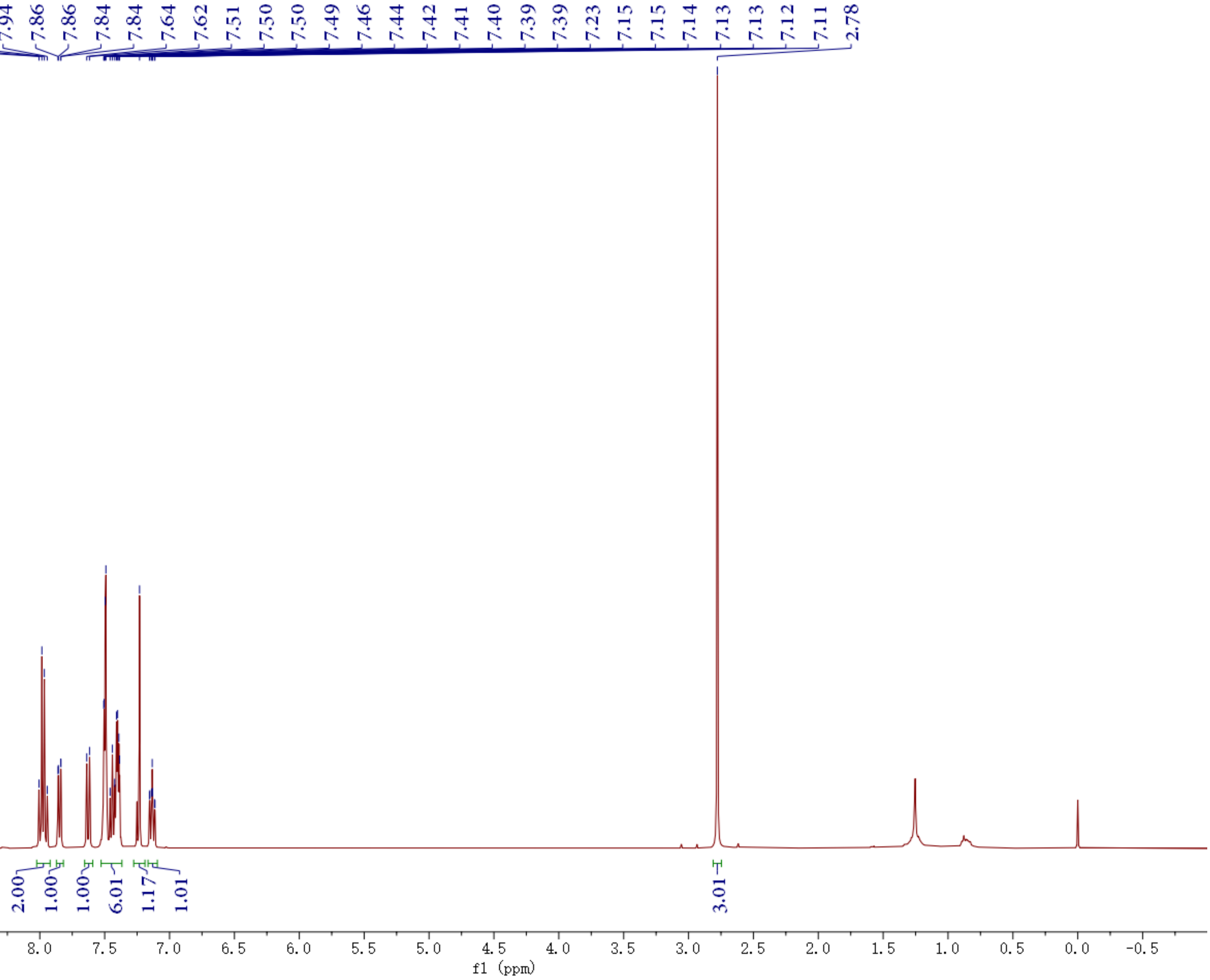
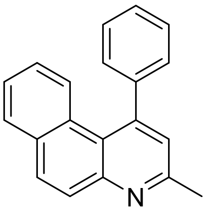
128.29
124.95
122.29
121.95
34.28
25.13
23.93
N
2l
f1 (ppm)



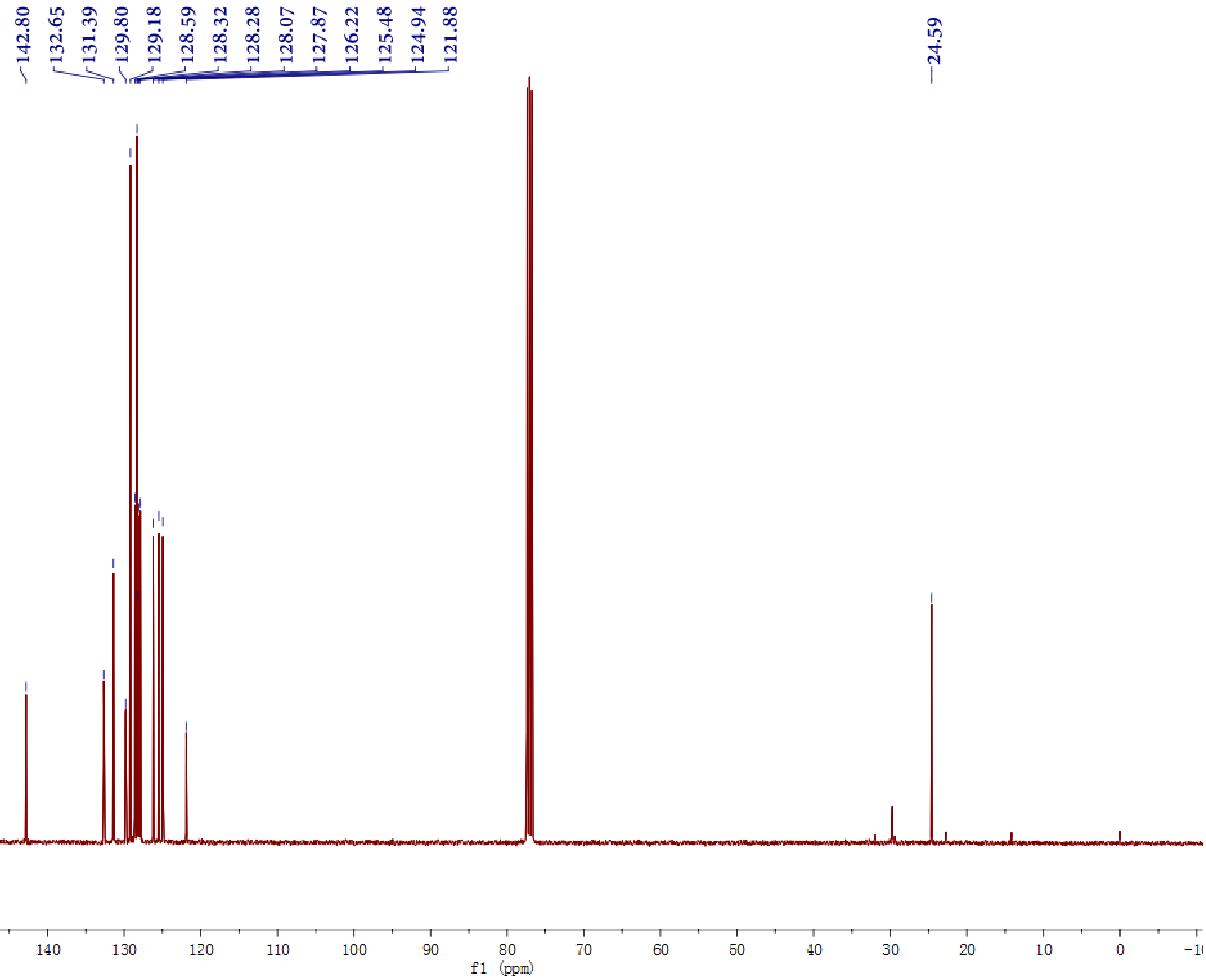
2m



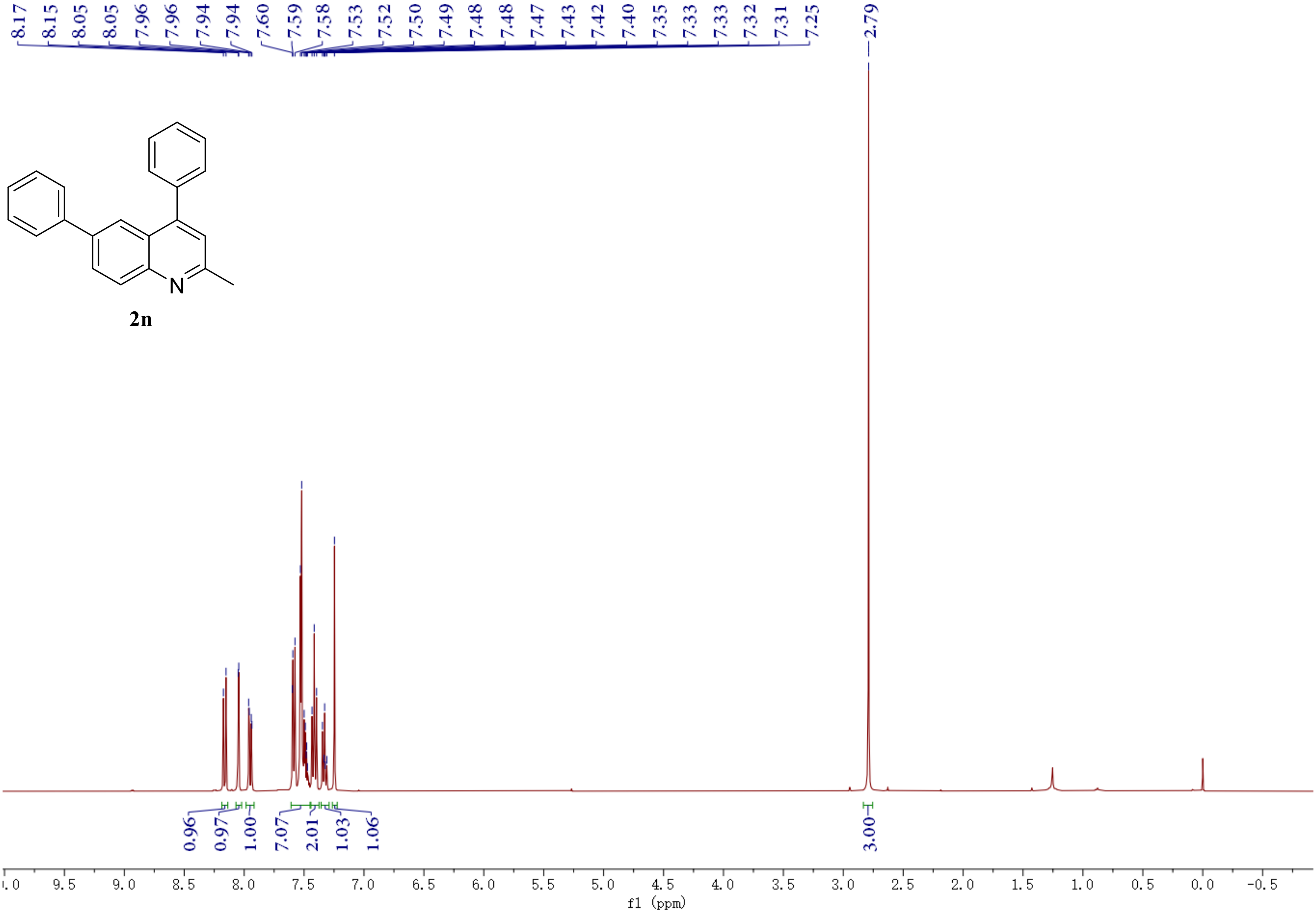
8.01
7.98
7.97
7.94
7.86
7.86
7.84
7.84
7.64
7.62
7.51
7.50
7.50
7.49
7.46
7.44
7.42
7.41
7.40
7.39
7.39
7.23
7.15
7.15
7.14
7.13
7.13
7.12
7.11
2.78
2.00
1.00
1.00
6.01
1.17
1.01
3.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

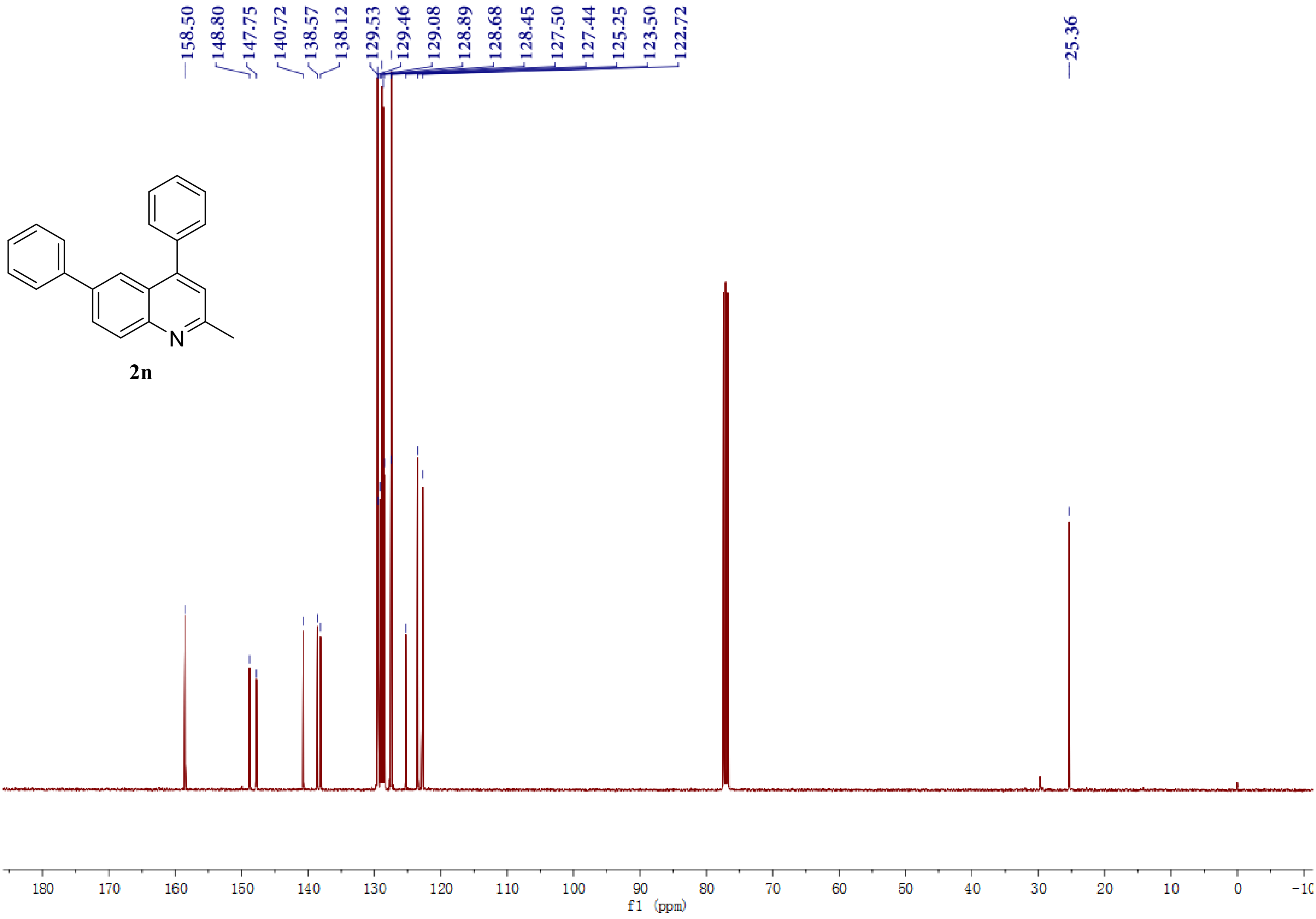


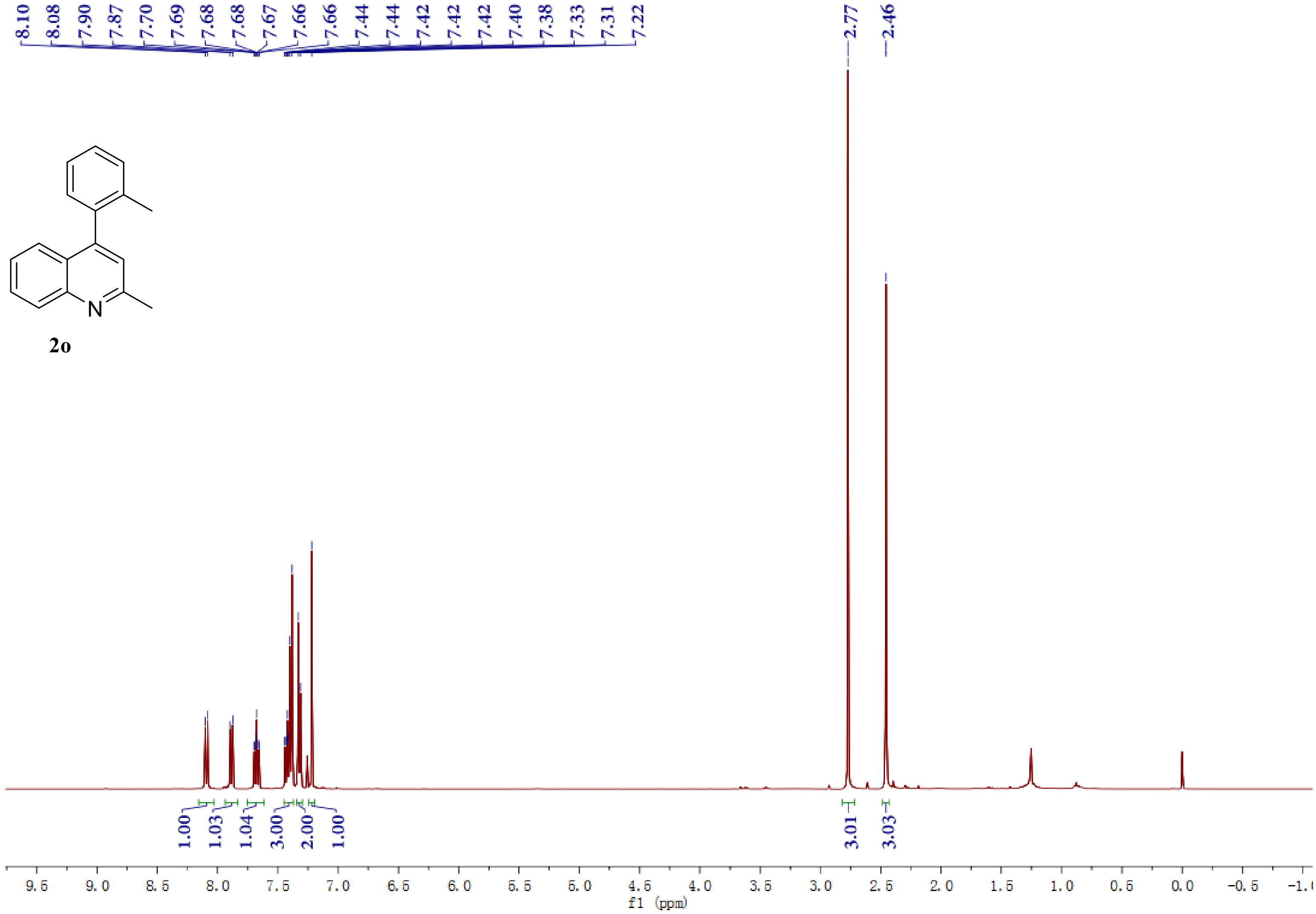
2m

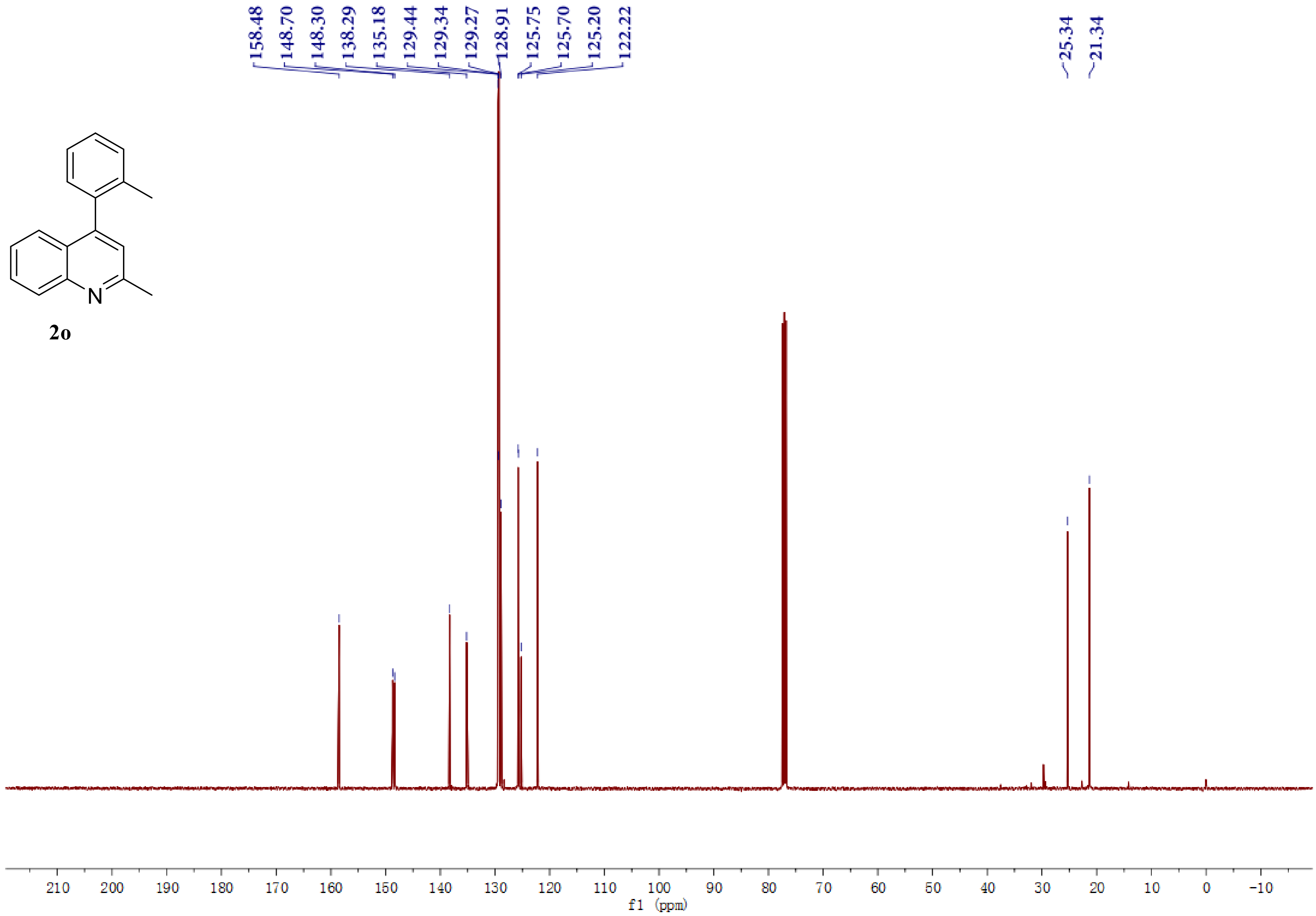


157.07
149.31
148.70
142.80
132.65
131.39
129.80
129.18
128.59
128.32
128.28
128.07
127.87
126.22
125.48
124.94
121.88
24.59
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.17 8.15 8.05 8.05 7.96 7.96 7.94 7.94 7.60 7.59 7.58 7.53 7.52 7.50 7.49 7.48 7.48 7.47 7.43 7.42 7.40 7.35 7.33 7.33 7.32 7.31 7.25
2.79
N
2n
0.96 0.97 1.00 7.07 2.01 1.03 1.06
3.00
f1 (ppm)


158.50 148.80 147.75 140.72 138.57 138.12 129.53 129.46 129.08 128.89 128.68 128.45 127.50 127.44 125.25 123.50 122.72
25.36
N
2n
f1 (ppm)


8.10
8.08
7.90
7.87
7.70
7.69
7.68
7.68
7.67
7.66
7.66
7.44
7.44
7.42
7.42
7.42
7.40
7.38
7.33
7.31
7.22
2.77
2.46
N
2o
1.00
1.03
1.04
3.00
2.00
1.00
3.01
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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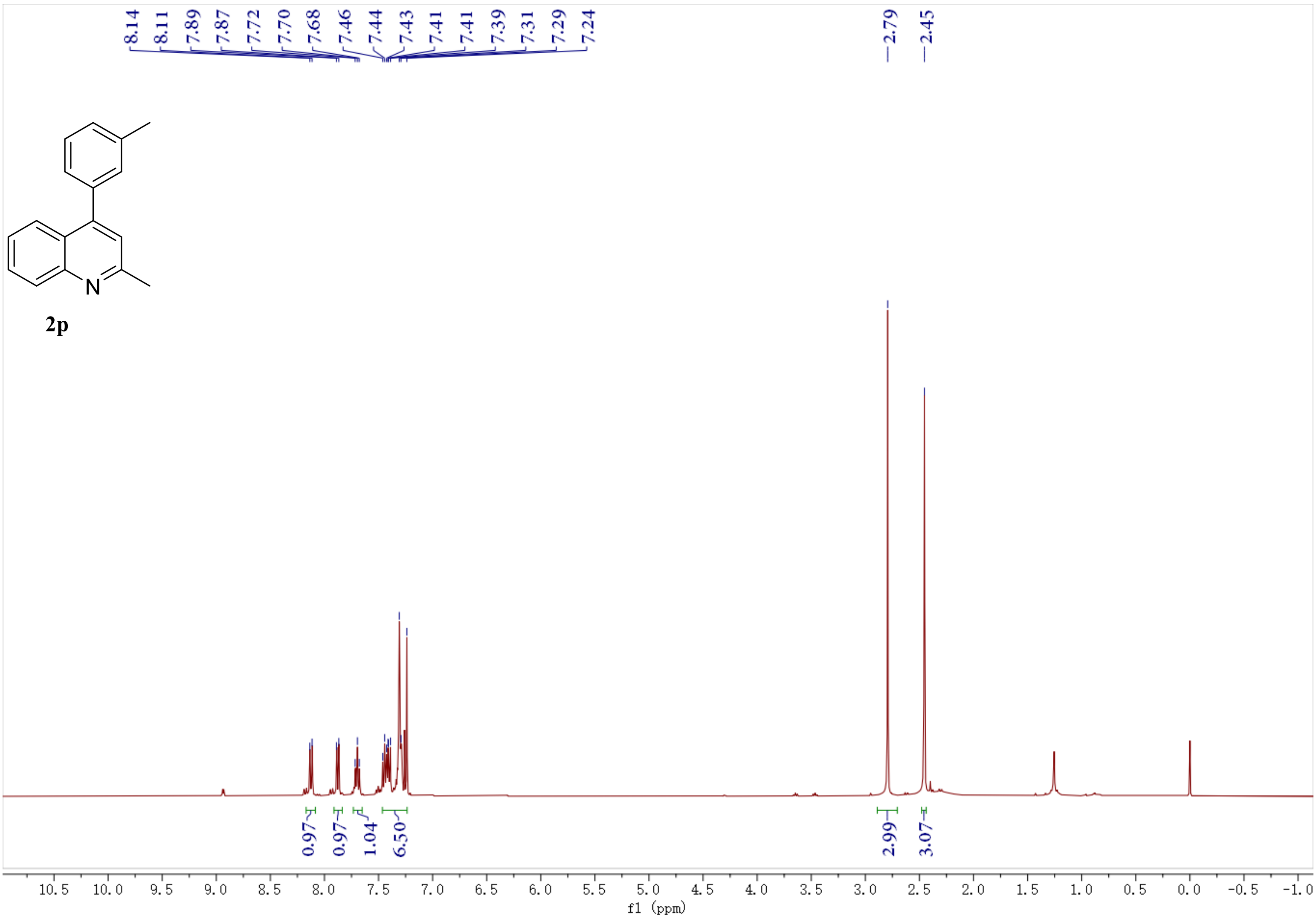
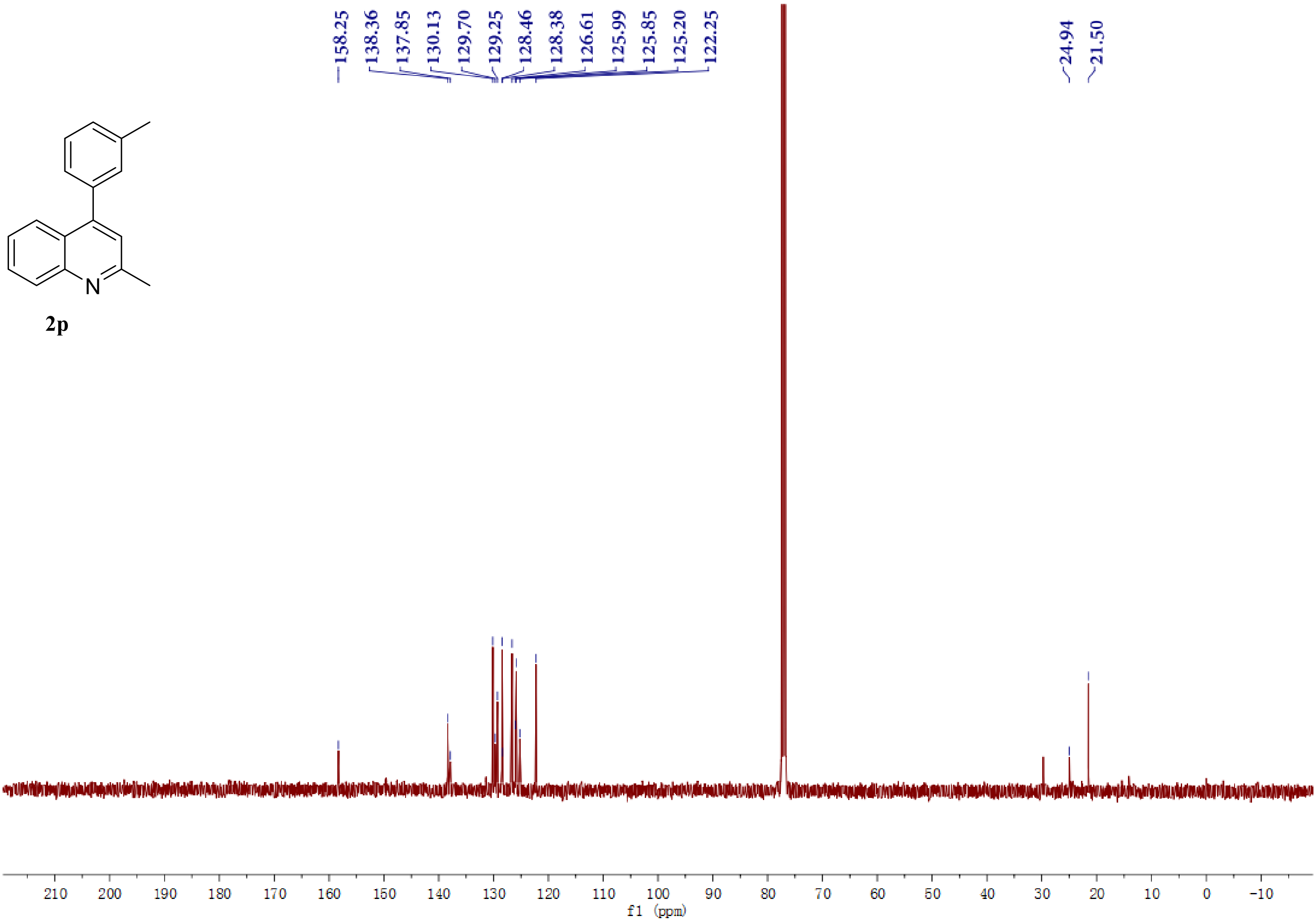
148.70
148.30
138.29
135.18
129.44
129.34
129.27
128.91
125.75
125.70
125.20
122.22
25.34
21.34
N
2o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.14
8.11
7.89
7.87
7.72
7.70
7.68
7.46
7.44
7.43
7.41
7.41
7.39
7.31
7.29
7.24
2.79
2.45
N
2p
0.97
0.97
1.04
6.50
2.99
3.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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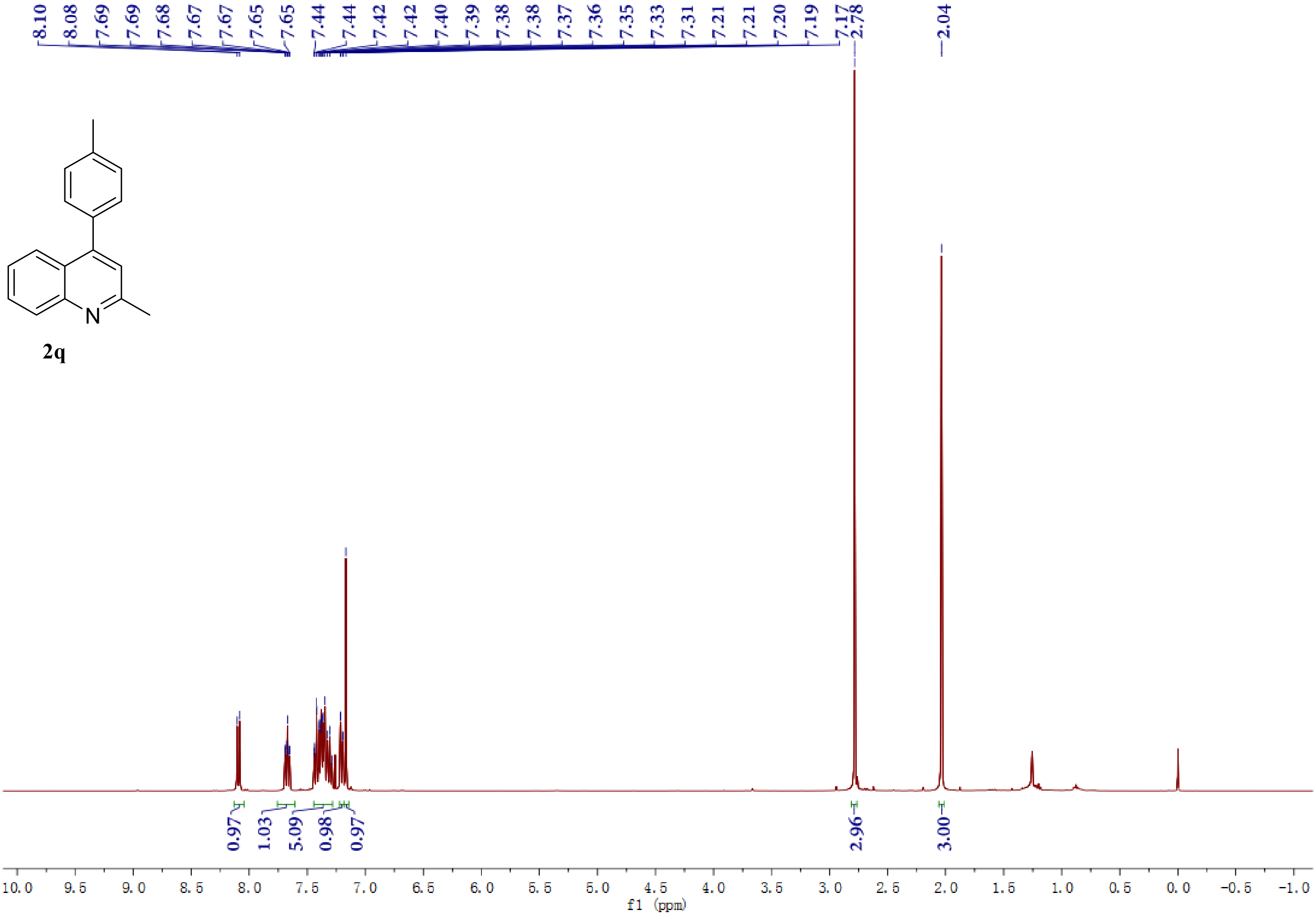
138.36
137.85
130.13
129.70
129.25
128.46
128.38
126.61
125.99
125.85
125.20
122.25
24.94
21.50
N
2p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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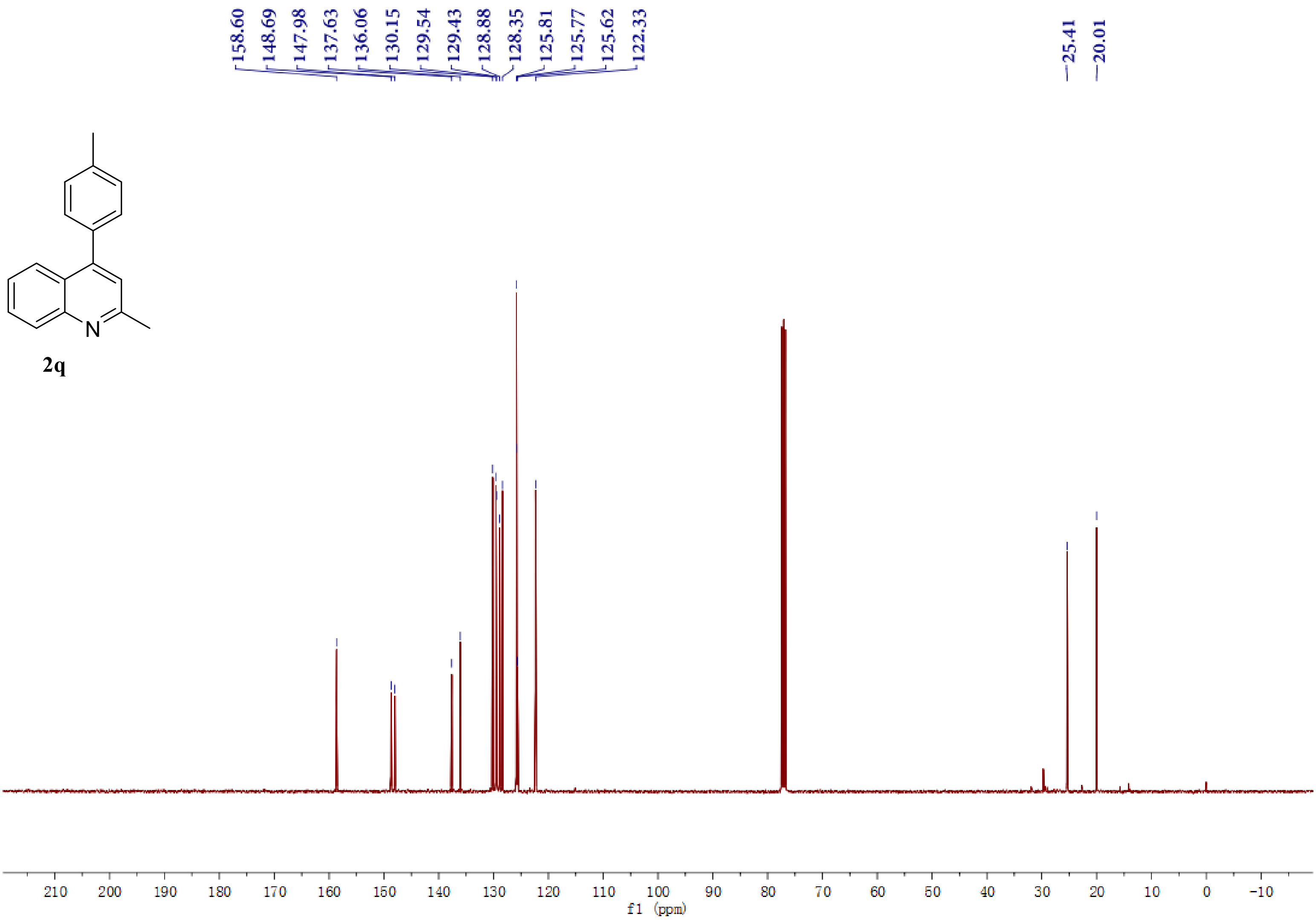
8.08
7.69
7.69
7.68
7.67
7.67
7.65
7.65
7.44
7.44
7.42
7.42
7.40
7.39
7.38
7.38
7.37
7.36
7.35
7.33
7.31
7.21
7.21
7.20
7.19
7.17
2.78
2.04
N
2q
0.97
1.03
5.09
0.98
0.97
2.96
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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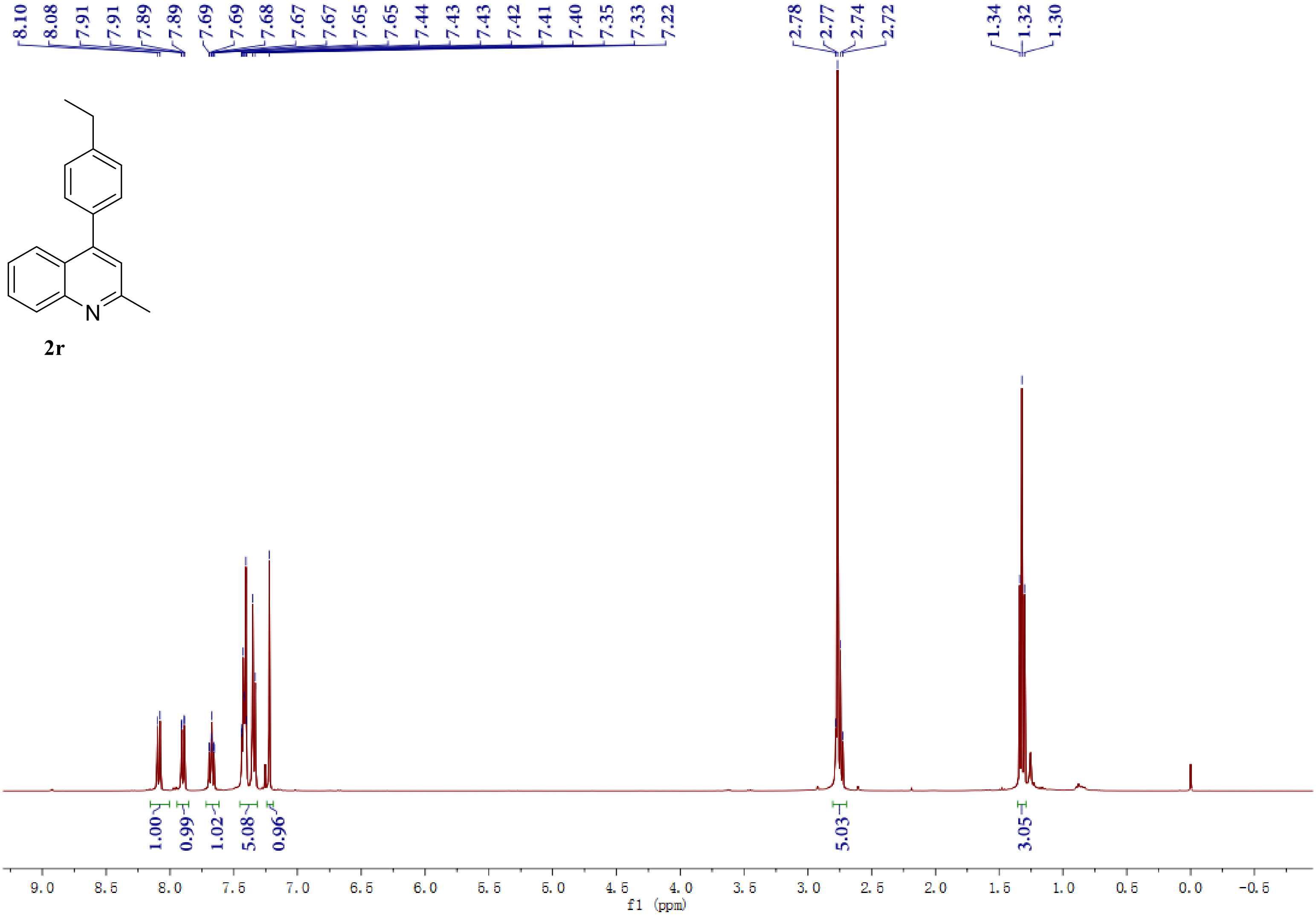
136.06
130.15
129.54
129.43
128.88
128.35
125.81
125.77
125.62
122.33
25.41
20.01
N
2q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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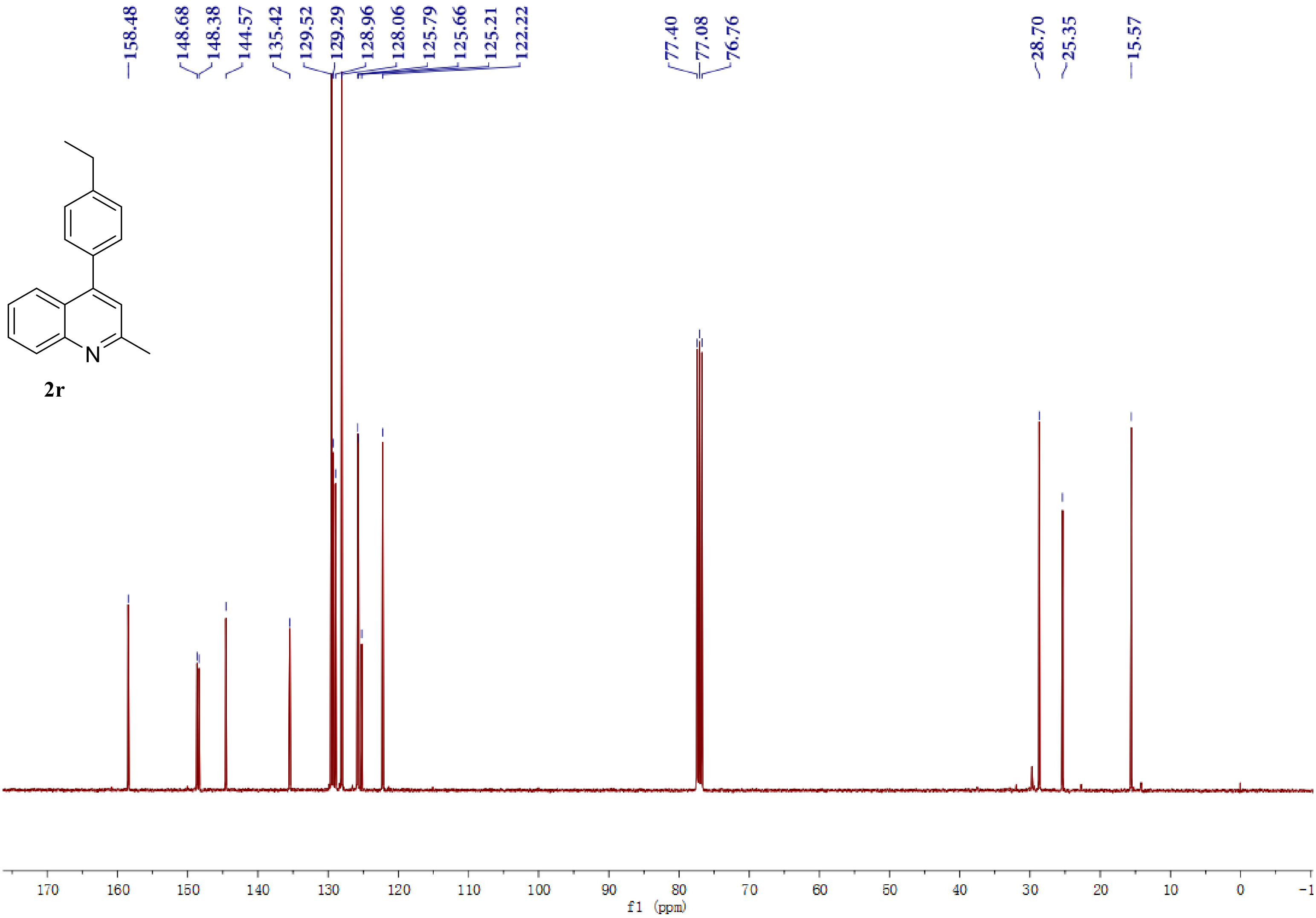
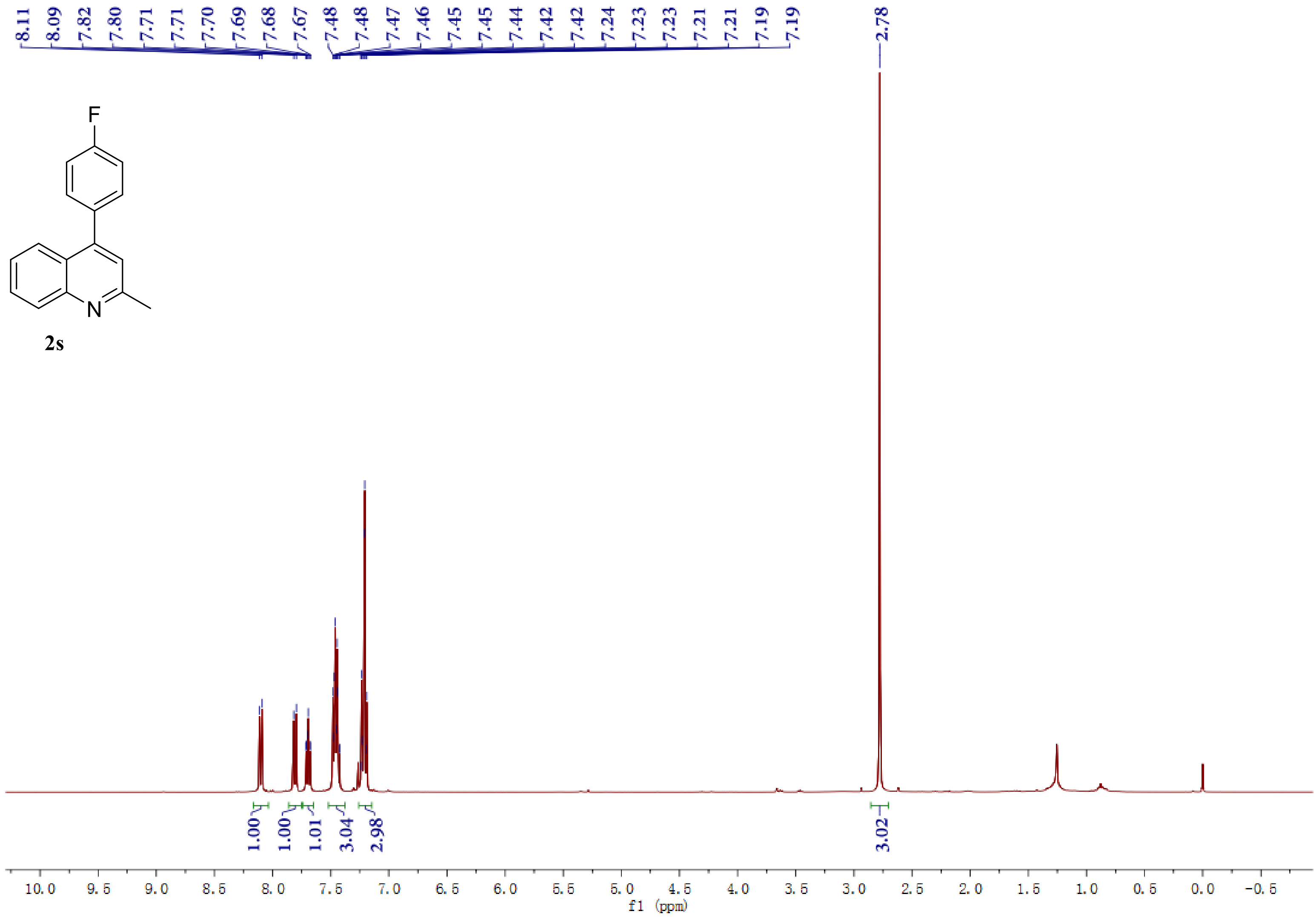
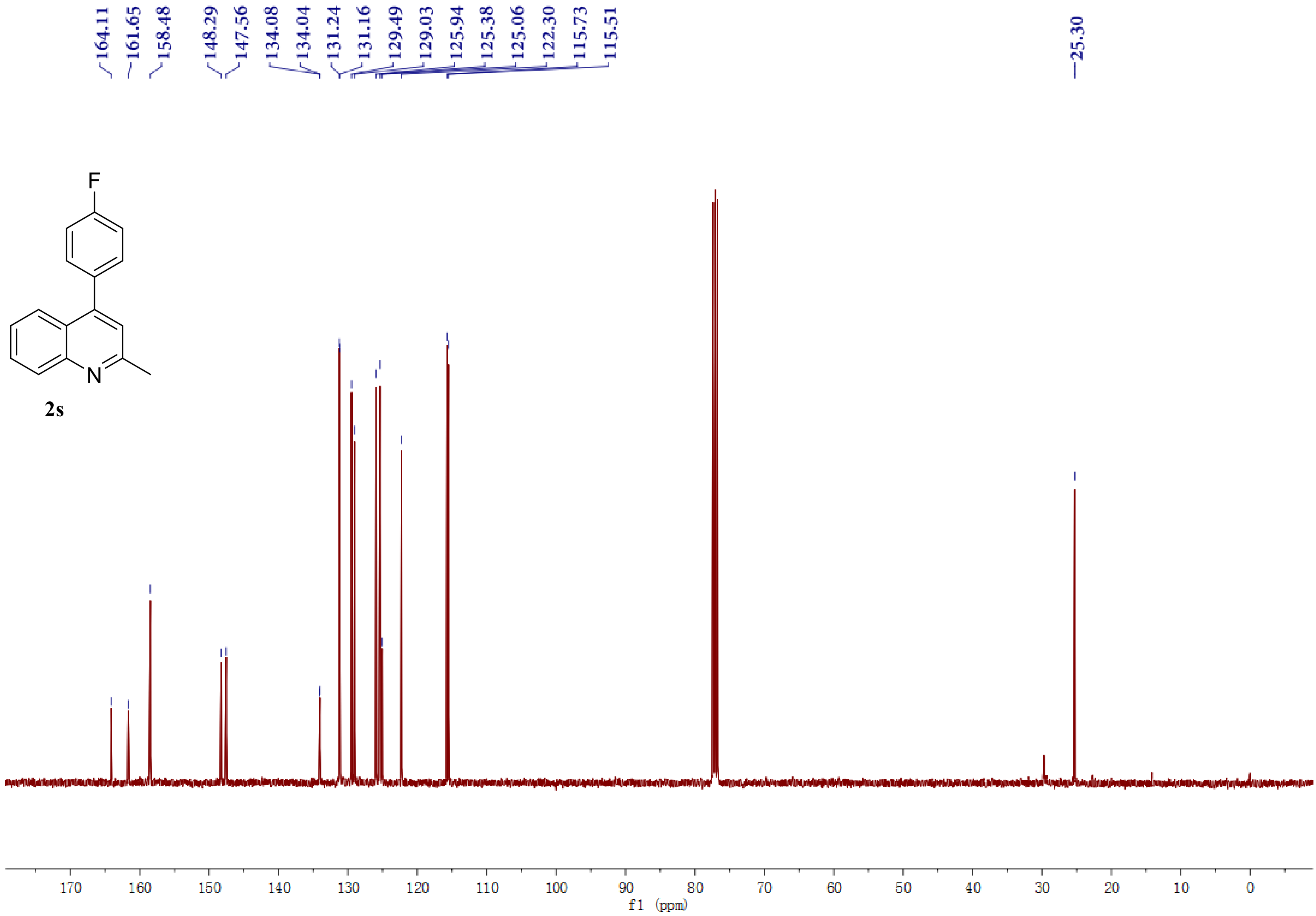
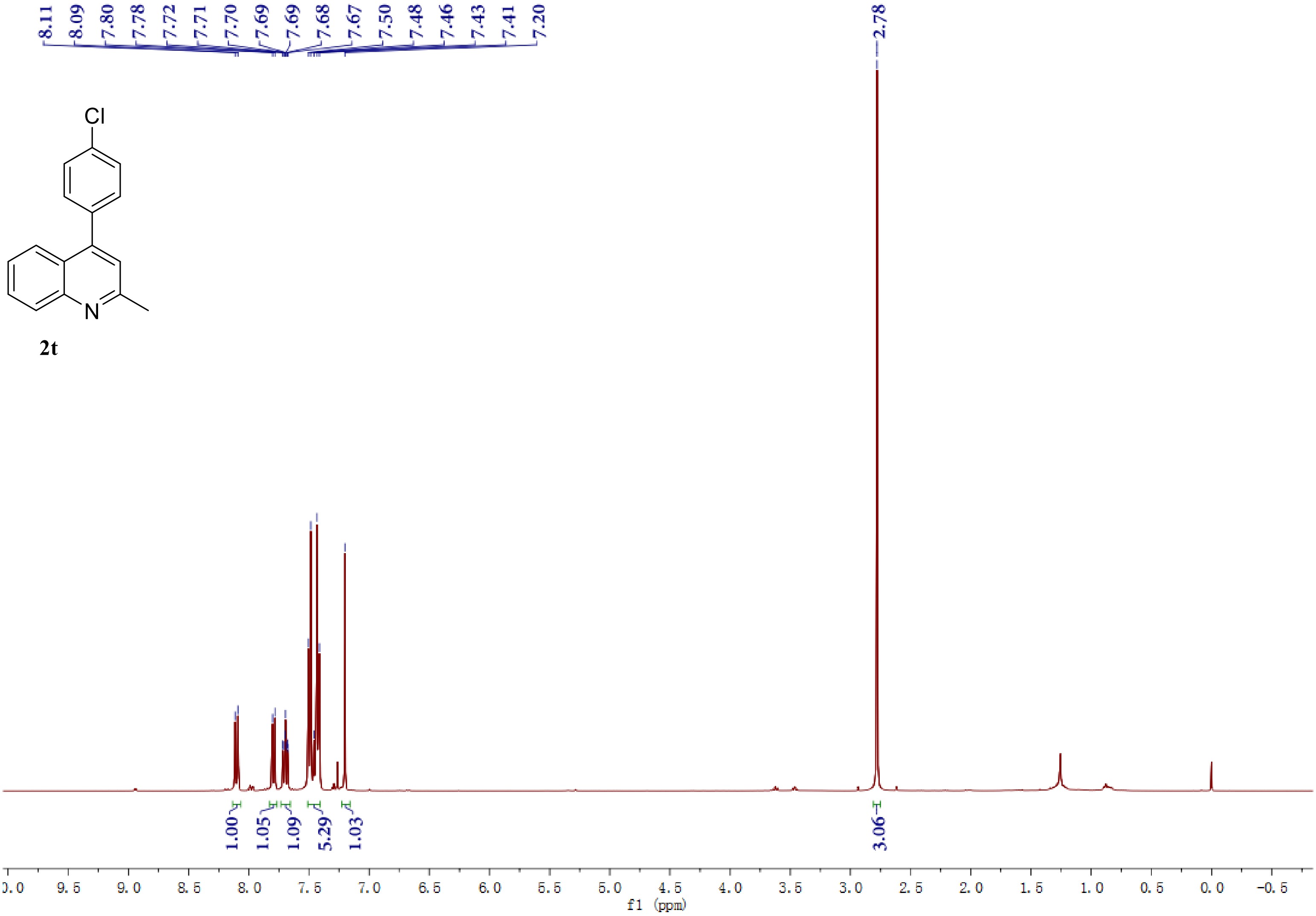
2.78 2.77 2.74 2.72
1.34 1.32 1.30
N
2r
1.00 0.99 1.02 5.08 0.96
5.03
3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


158.48
148.68 148.38 144.57 135.42 129.52 129.29 128.96 128.06 125.79 125.66 125.21 122.22
77.40 77.08 76.76
28.70 25.35 15.57
N
2r
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


8.11 8.09 7.82 7.80 7.71 7.71 7.70 7.69 7.68 7.67 7.48 7.48 7.47 7.46 7.45 7.45 7.44 7.42 7.42 7.24 7.23 7.23 7.21 7.21 7.19 7.19
2.78
F
N
2s
1.00 1.00 1.01 3.04 2.98
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


164.11 161.65 158.48 148.29 147.56 134.08 134.04 131.24 131.16 129.49 129.03 125.94 125.38 125.06 122.30 115.73 115.51
25.30
F
N
2s
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.11 8.09 7.80 7.78 7.72 7.71 7.70 7.69 7.69 7.68 7.67 7.50 7.48 7.46 7.43 7.41 7.20
2.78
Cl
N
2t
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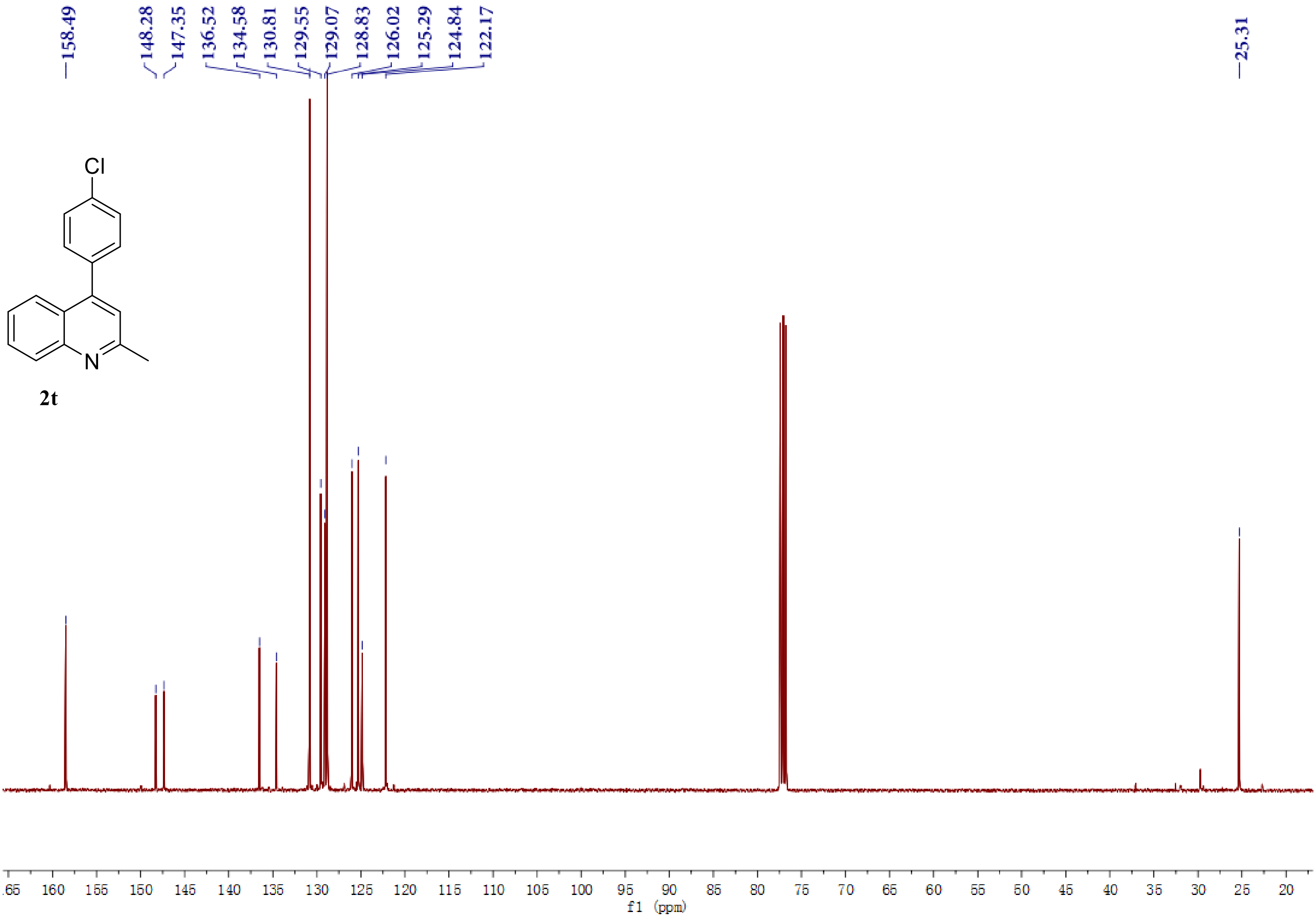
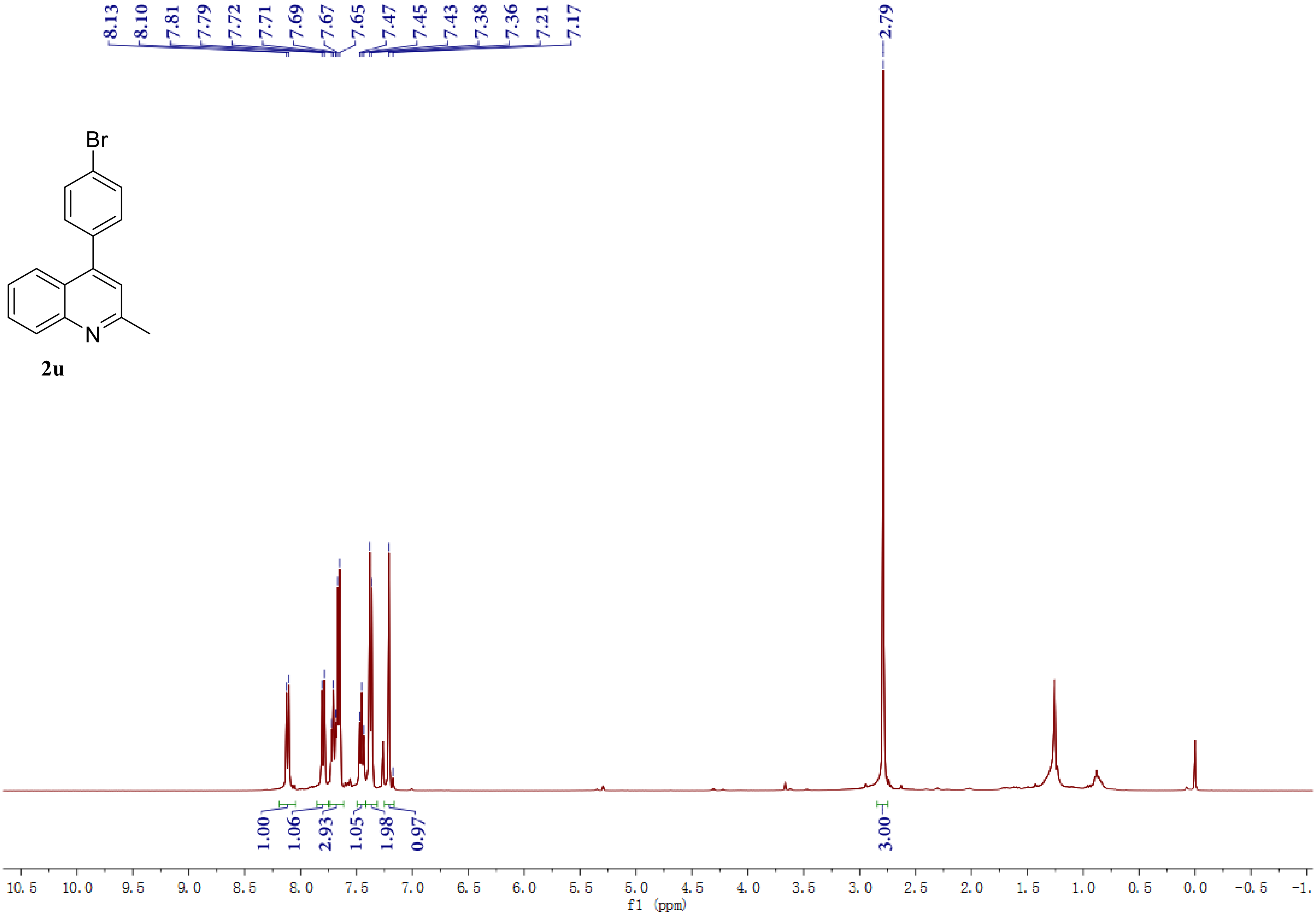
3.06
f1 (ppm)


158.49
148.28 147.35 136.52 134.58 130.81 129.55 129.07 128.83 126.02 125.29 124.84 122.17
25.31
Cl
N
2t
f1 (ppm)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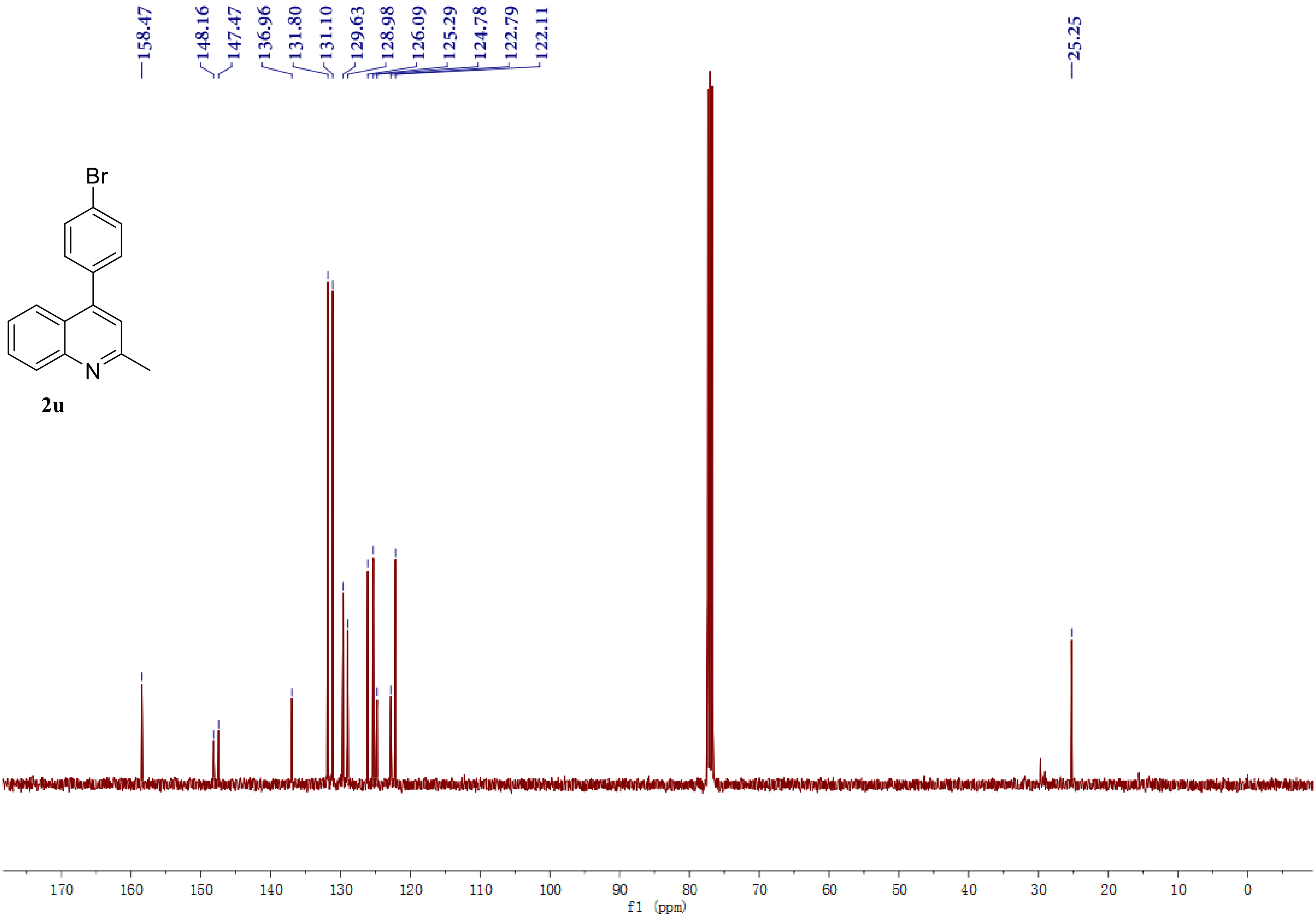
2.79
Br
N
2u
1.00 1.06 2.93 1.05 1.98 0.97
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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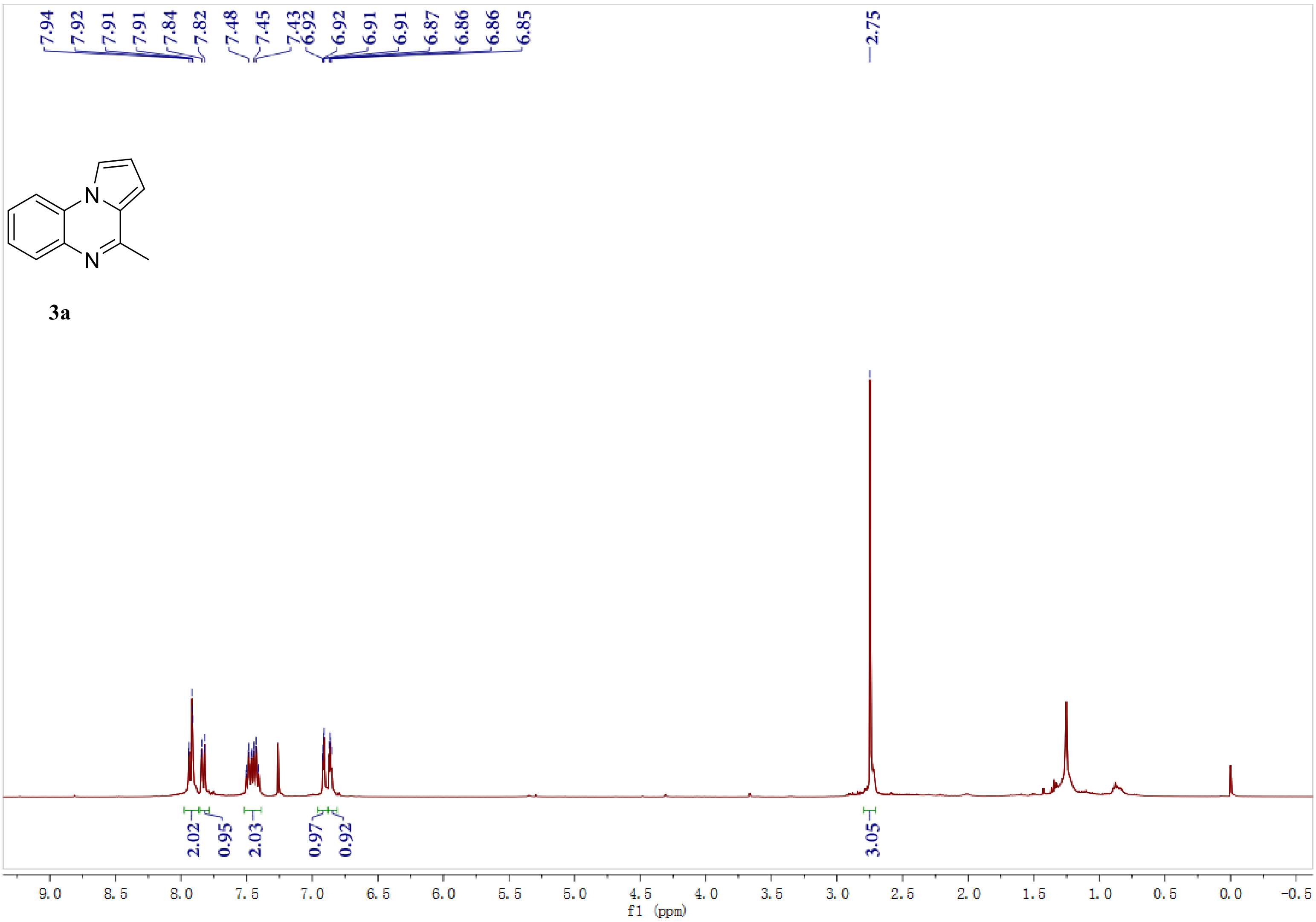
148.16 147.47 136.96 131.80 131.10 129.63 128.98 126.09 125.29 124.78 122.79 122.11
25.25
Br
N
2u
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.92
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7.91
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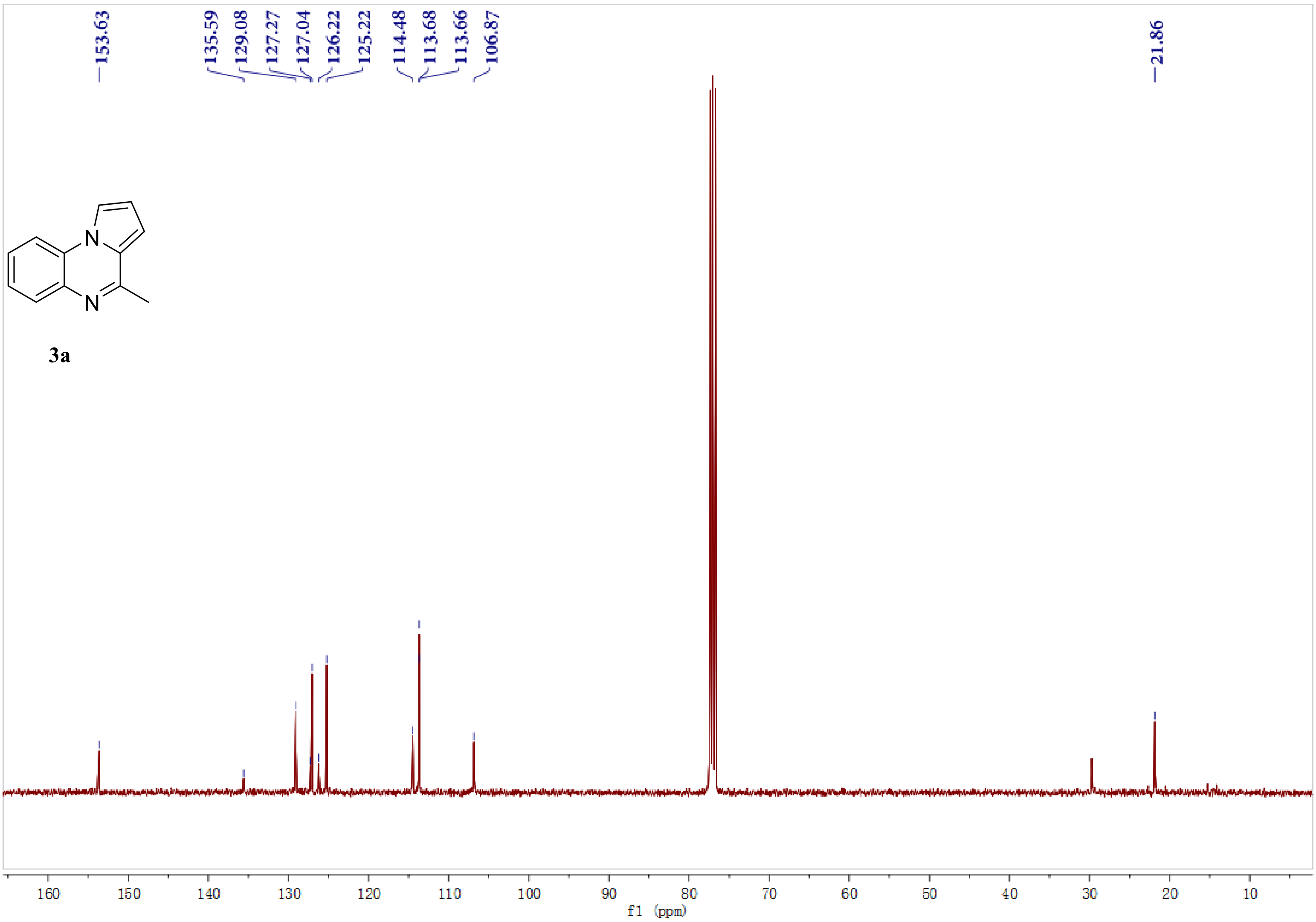
6.92
6.92
6.91
6.91
6.87
6.86
6.86
6.85
2.75
N
N
3a
2.02
0.95
2.03
0.97
0.92
3.05
f1 (ppm)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135.59
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127.04
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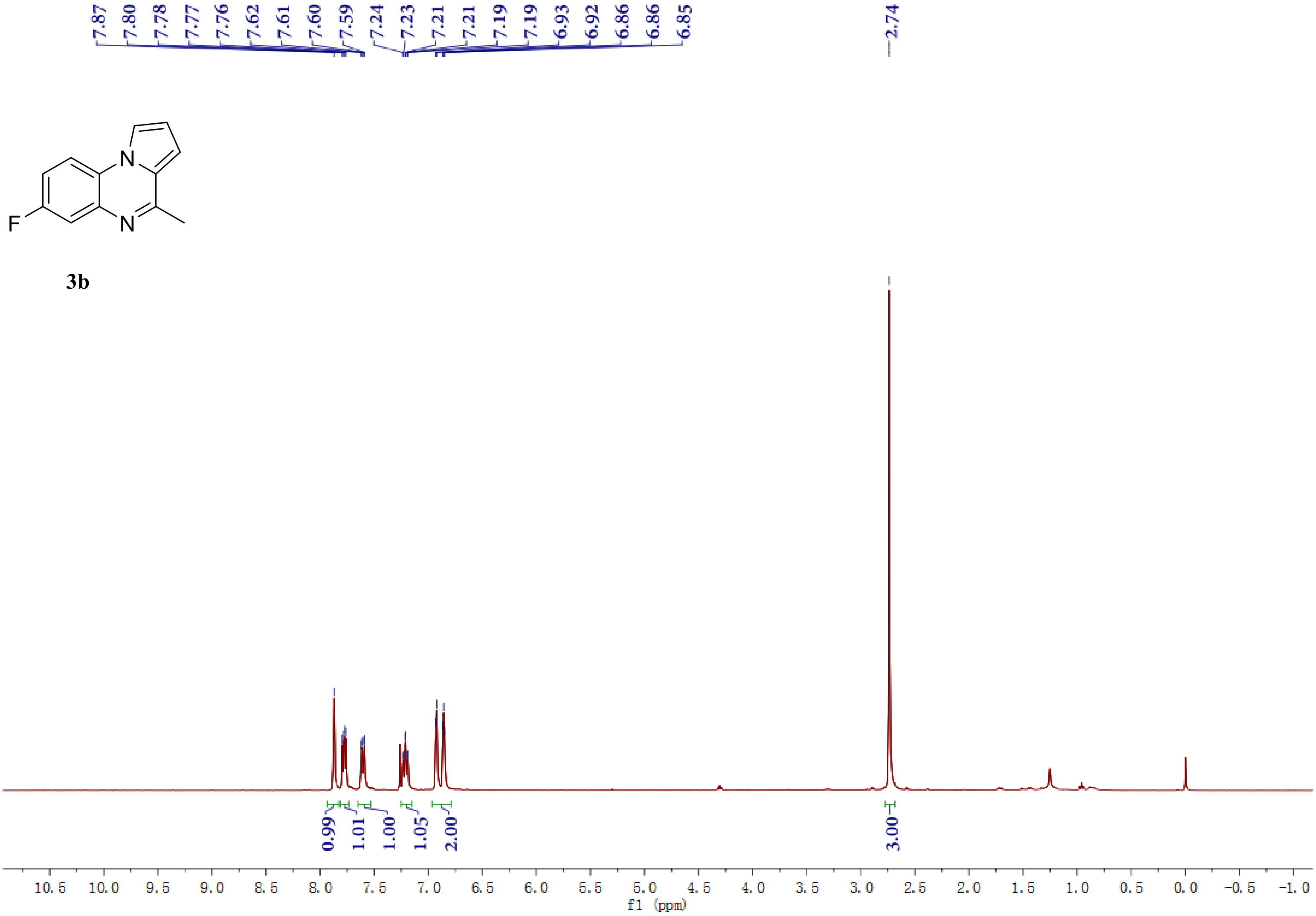
125.22
114.48
113.68
113.66
106.87
21.86
N
N
3a
f1 (ppm)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7.80
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7.77
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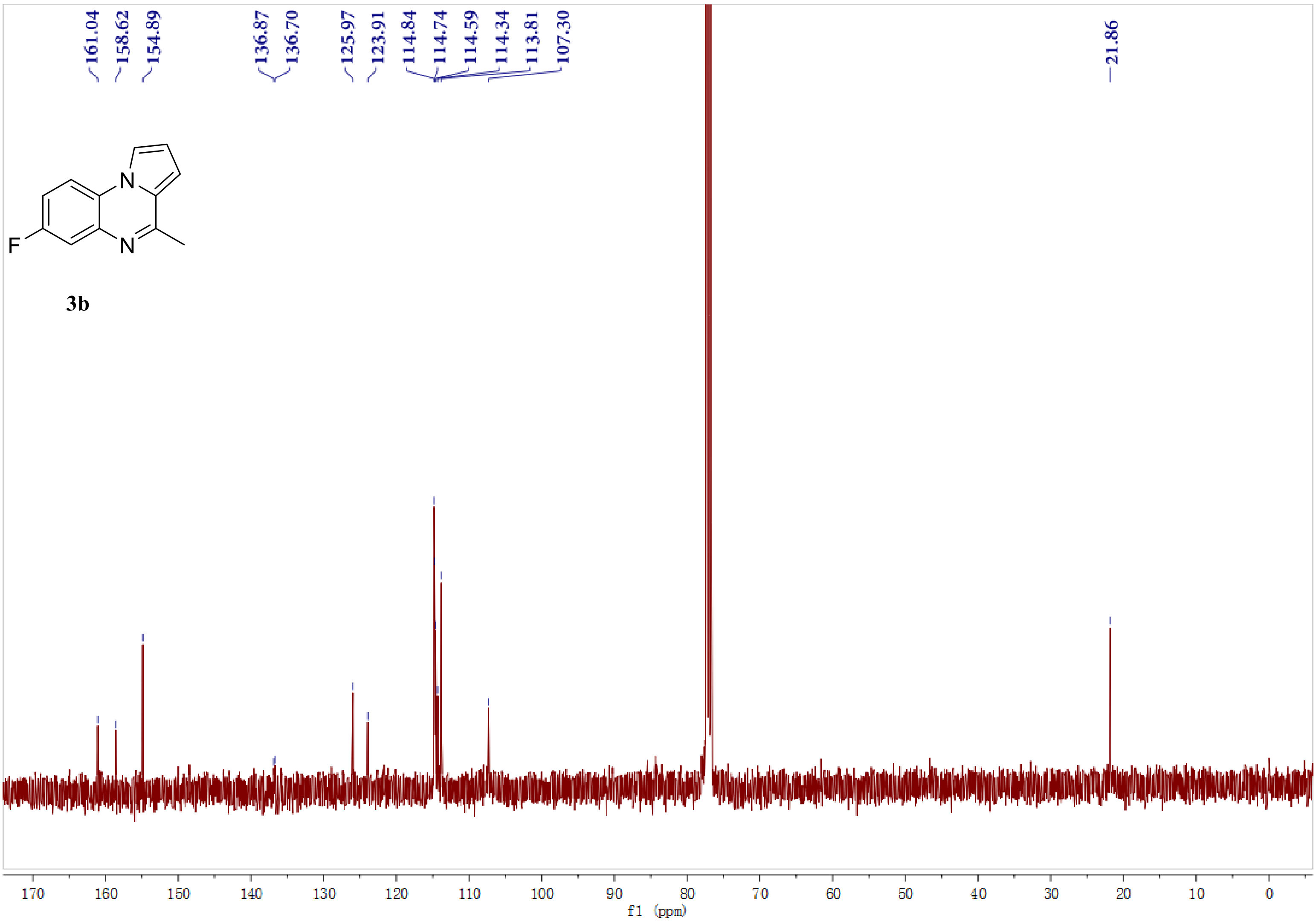
7.62
7.61
7.60
7.59
7.24
7.23
7.21
7.21
7.19
7.19
6.93
6.92
6.86
6.86
6.85
2.74
F
N
N
3b
0.99
1.01
1.00
1.05
2.00
3.00
f1 (ppm)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154.89
136.87
136.70
125.97
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114.84
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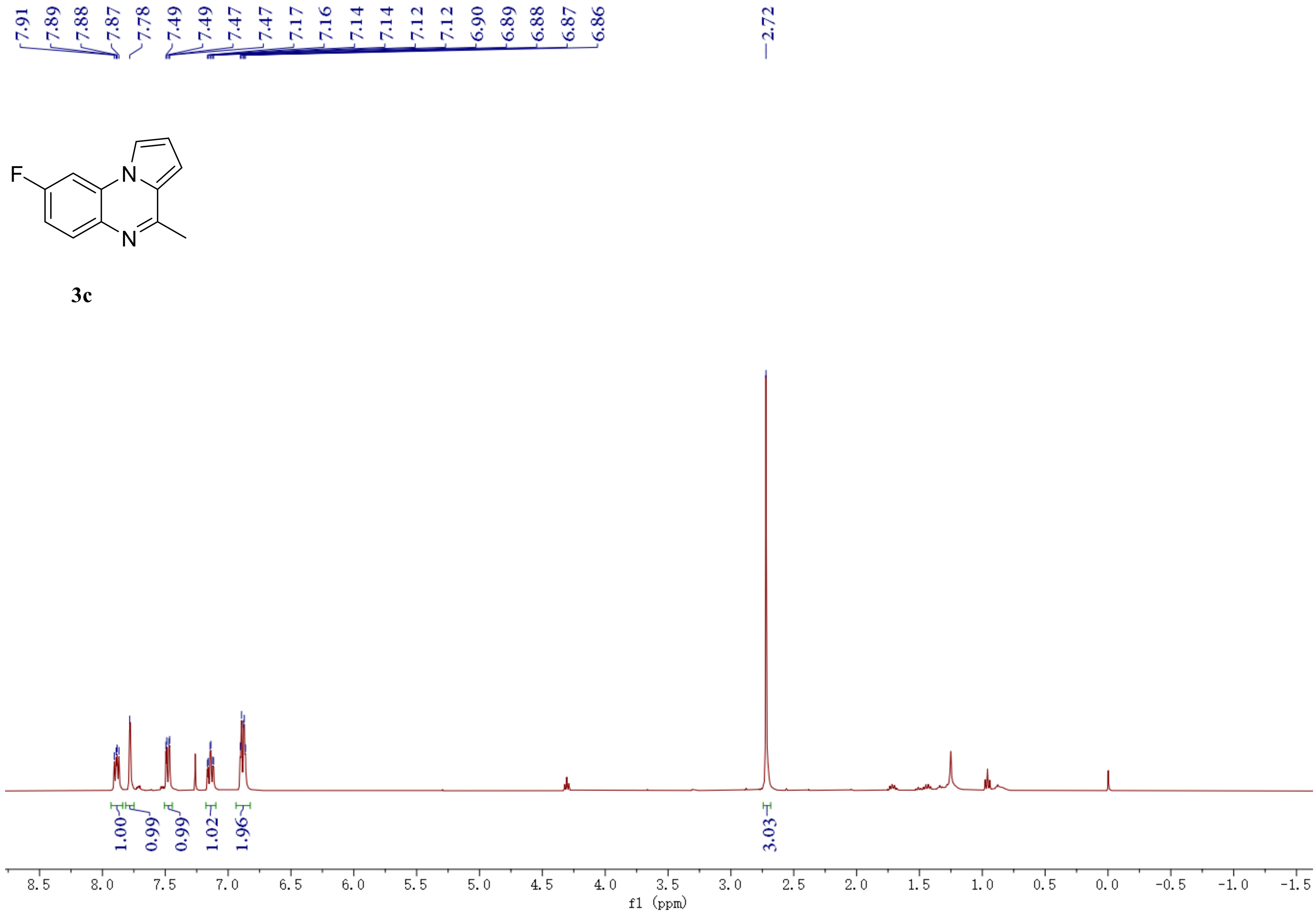
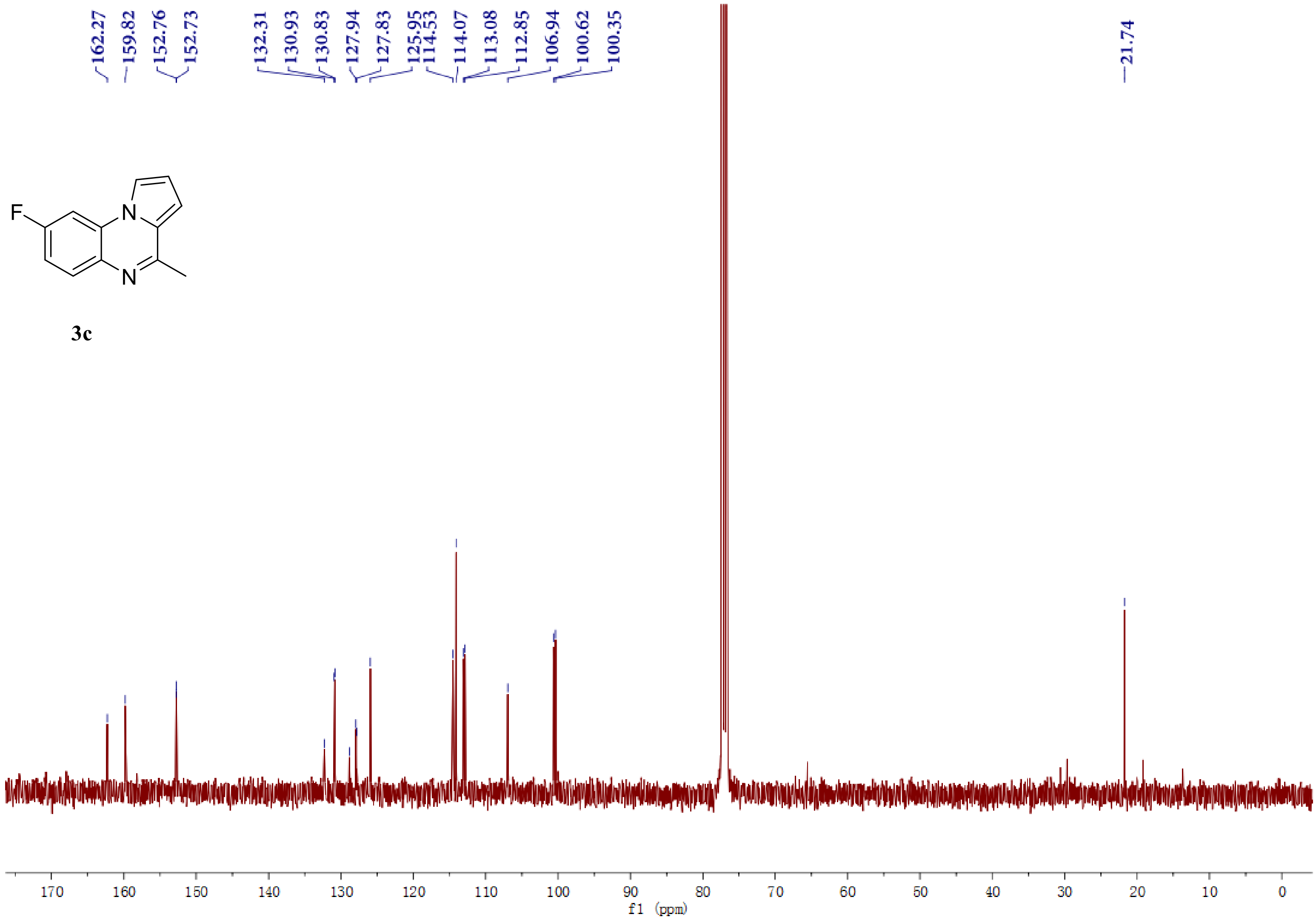
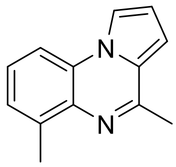
113.81
107.30
21.86
F
N
N
3b
f1 (ppm)



7.91 7.89 7.88 7.87 7.78 7.49 7.49 7.47 7.47 7.17 7.16 7.14 7.14 7.12 7.12 6.90 6.89 6.88 6.88 6.87 6.86
2.72
F
N
N
3c
1.00 0.99 0.99 1.02 1.96
3.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

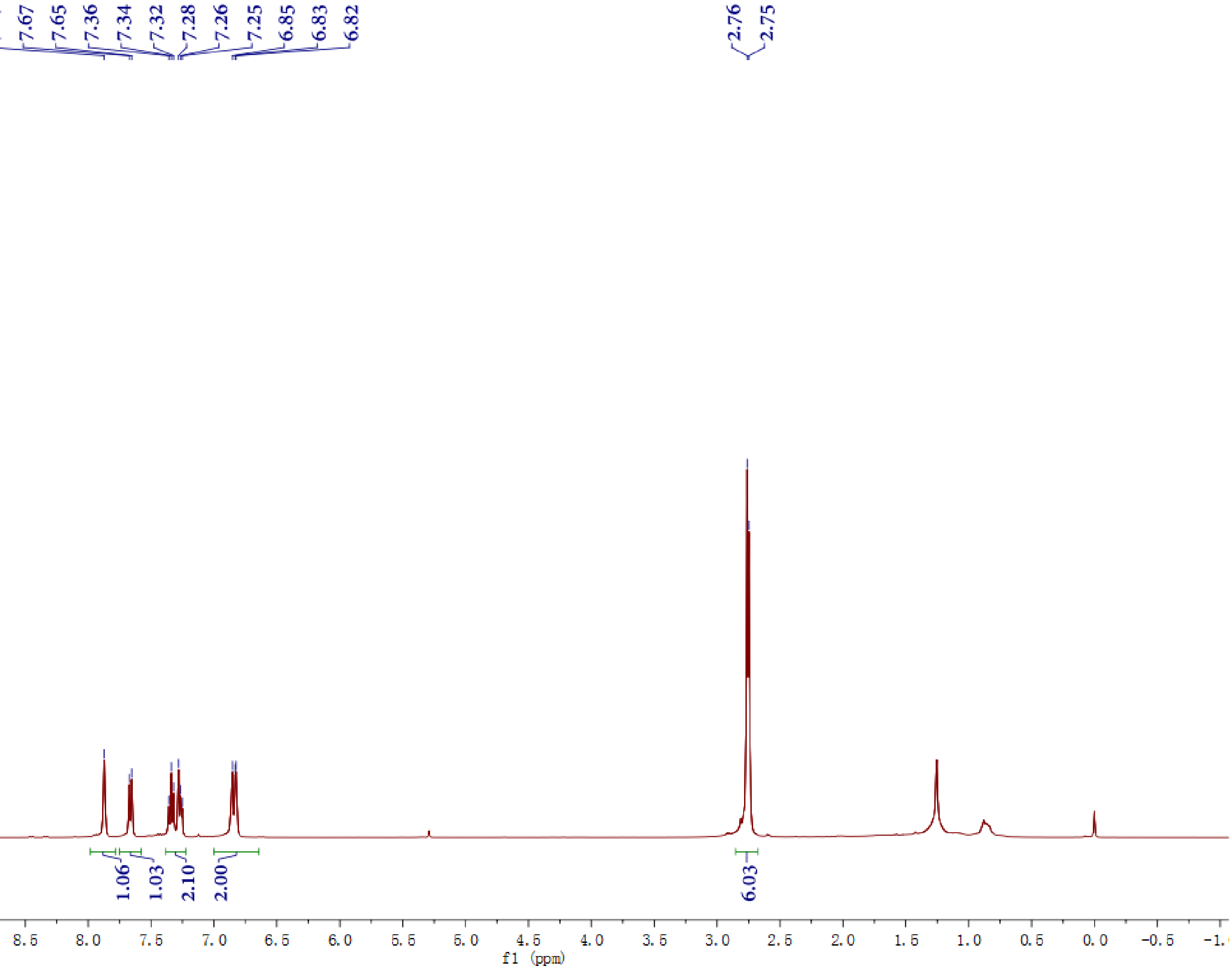


162.27 159.82 152.76 152.73
132.31 130.93 130.83 127.94 127.83 125.95 114.53 114.07 113.08 112.85 106.94 100.62 100.35
21.74
F
N
N
3c
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

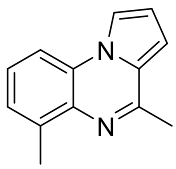


N
N

3d

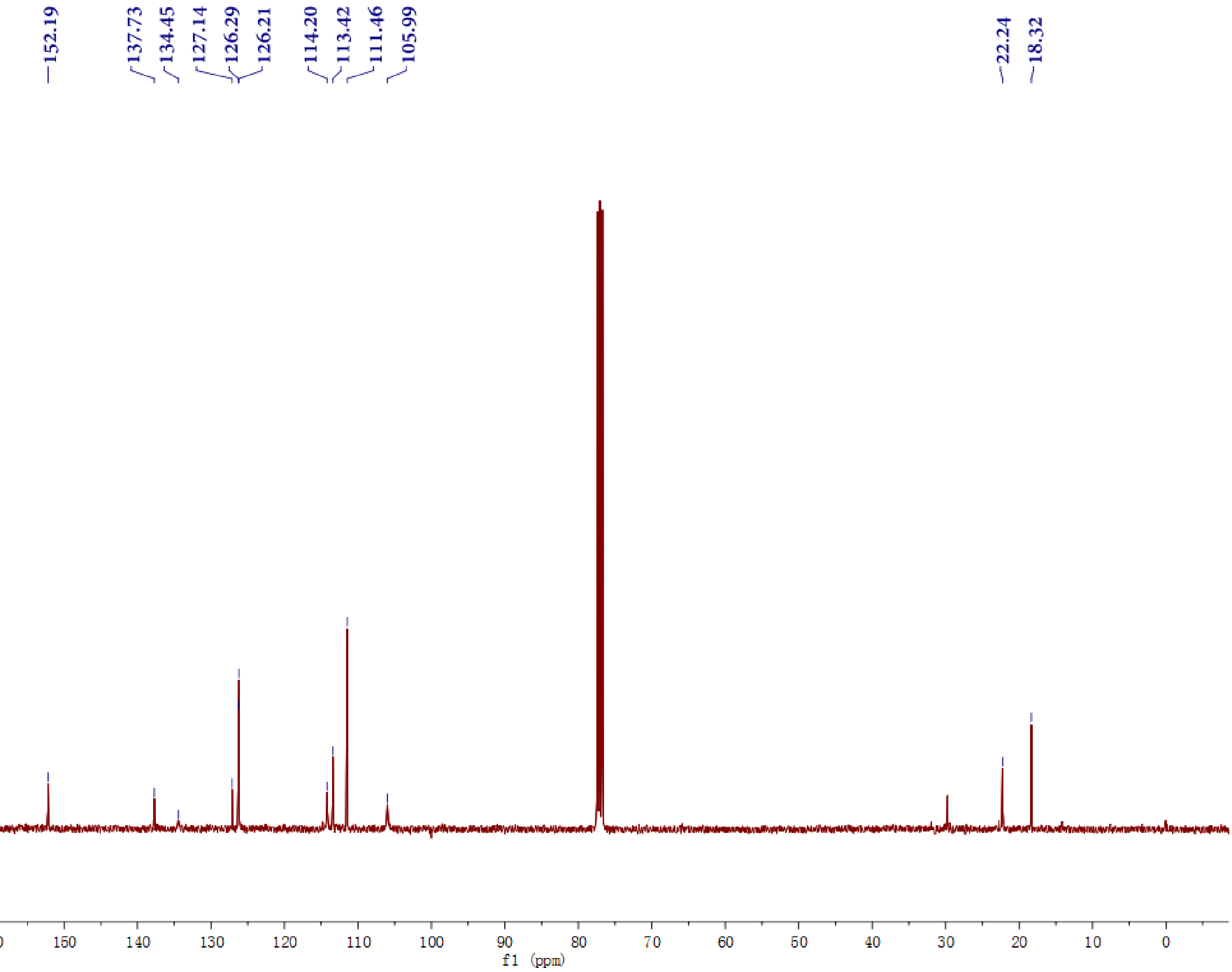


7.87
7.67
7.65
7.36
7.34
7.32
7.28
7.26
7.25
6.85
6.83
6.82
2.76
2.75
1.06
1.03
2.10
2.00
6.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



N
N

3d



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137.73
134.45
127.14
126.29
126.21
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113.42
111.46
105.99
22.24
18.32
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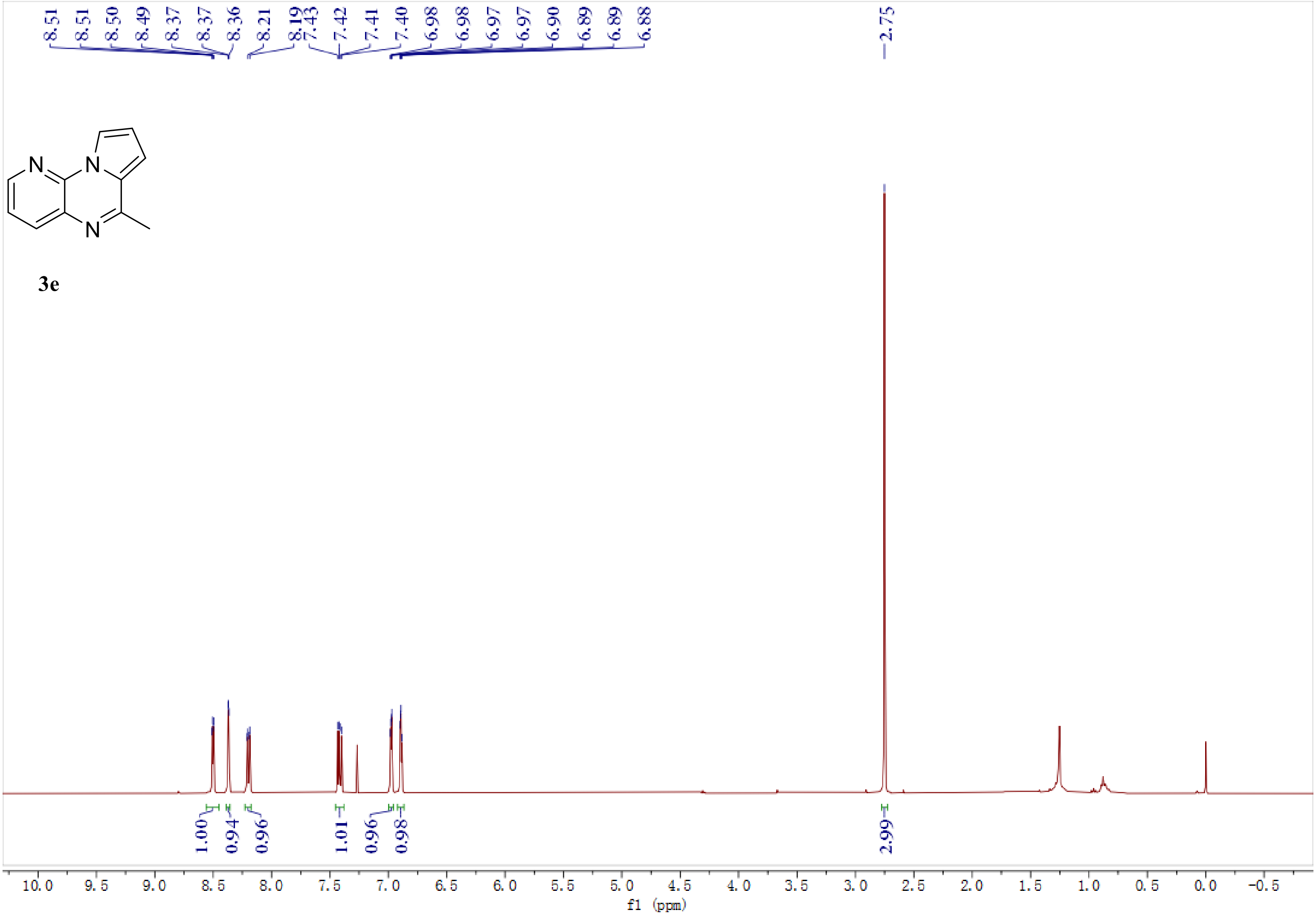
f1 (ppm)


8.51
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8.49
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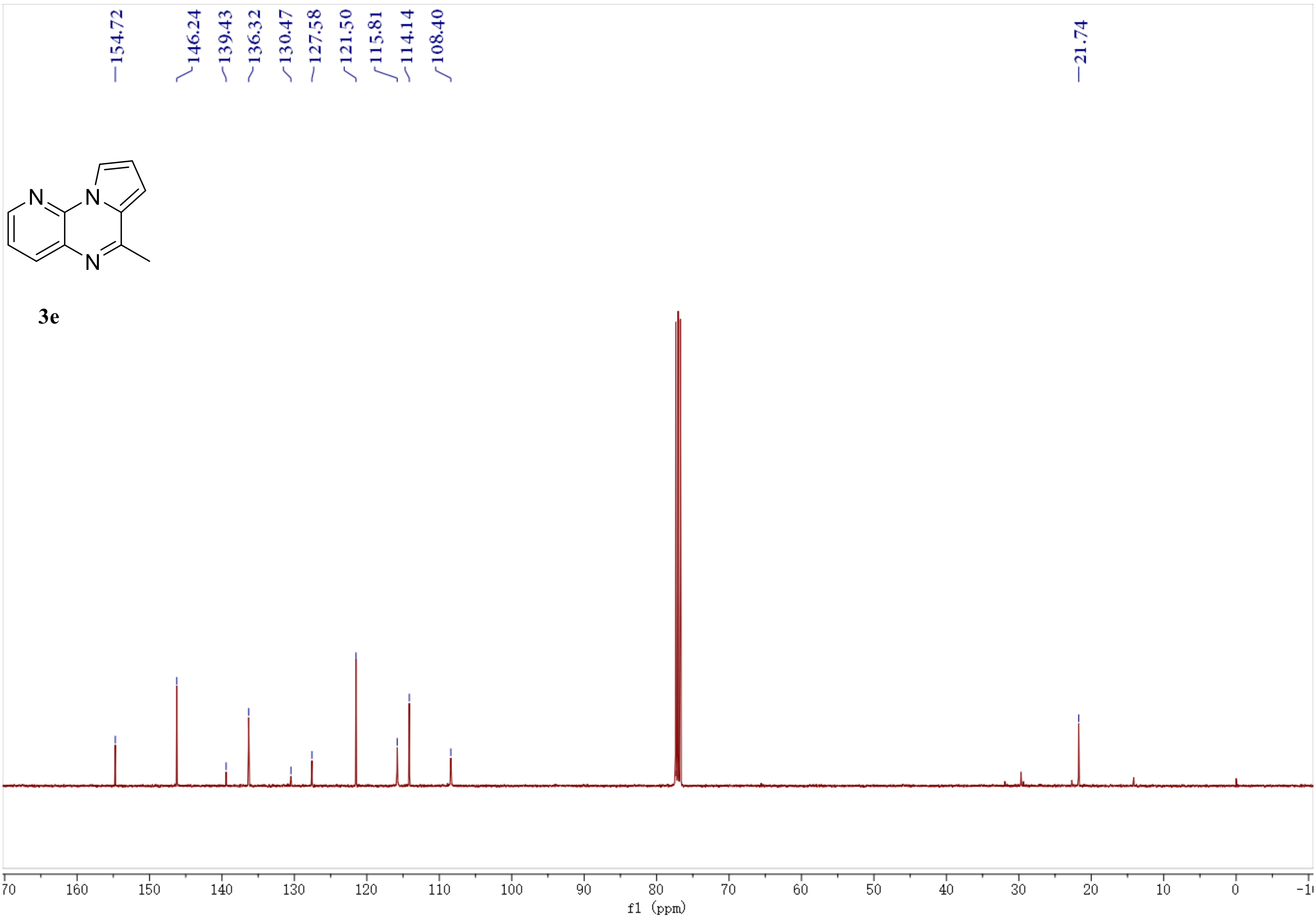
8.37
8.36
8.21
8.19
7.43
7.42
7.41
7.40
6.98
6.98
6.97
6.97
6.90
6.89
6.89
6.88
2.75
1.00
0.94
0.96
1.01
0.96
0.98
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

3e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21.74
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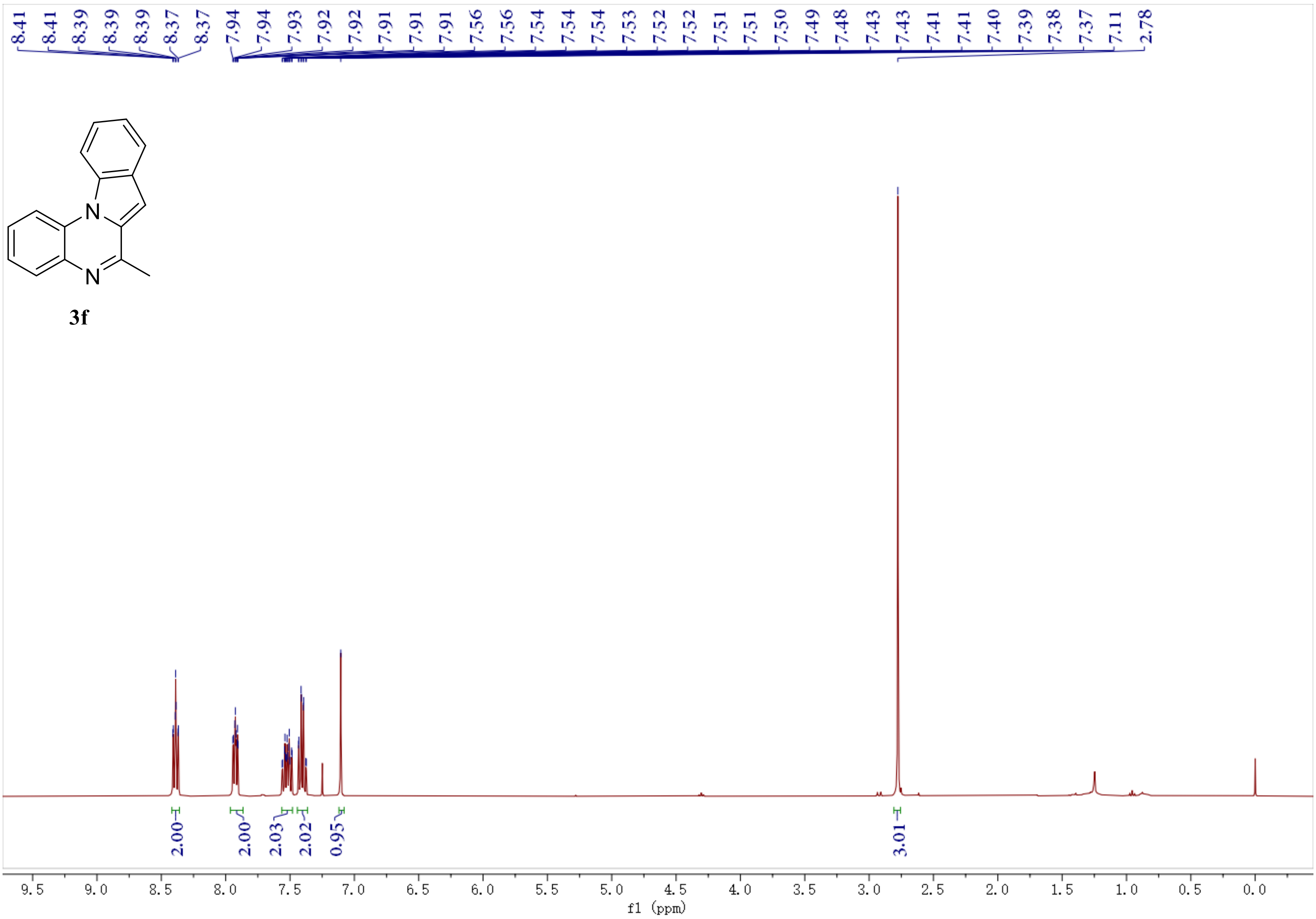
f1 (ppm)

3e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N
N
3f
2.00
2.00
2.03
2.02
0.95
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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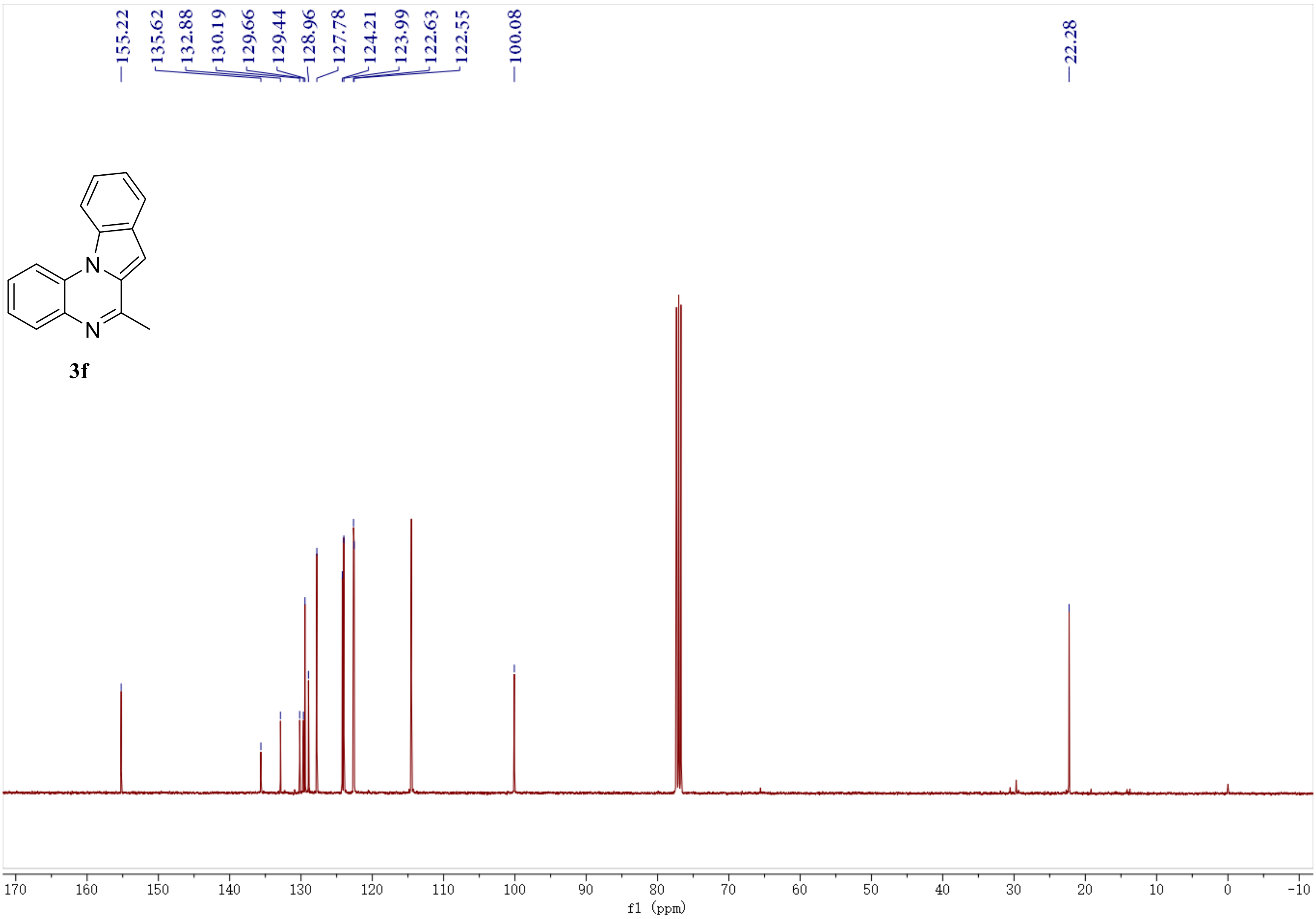
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100.08
22.28
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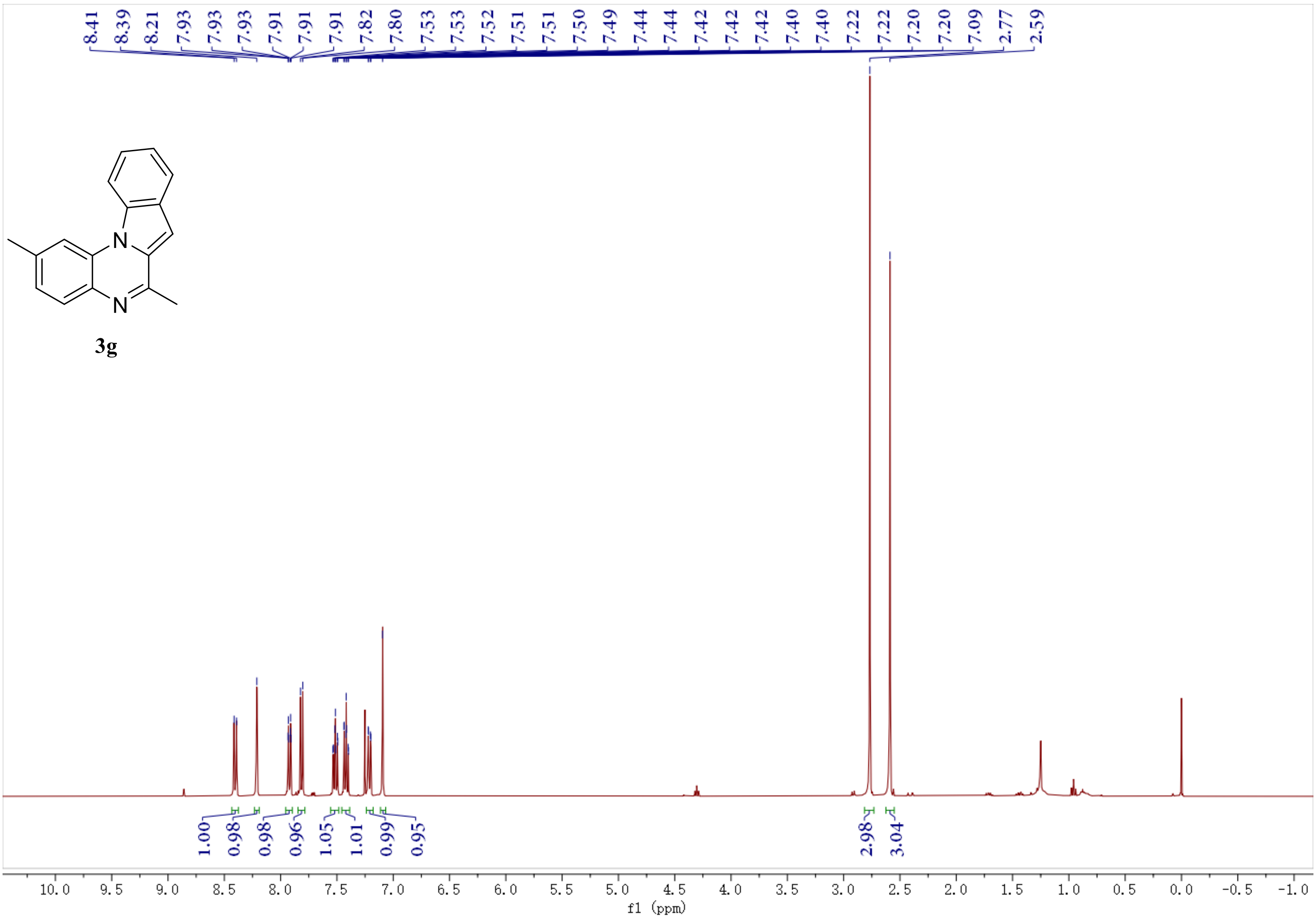
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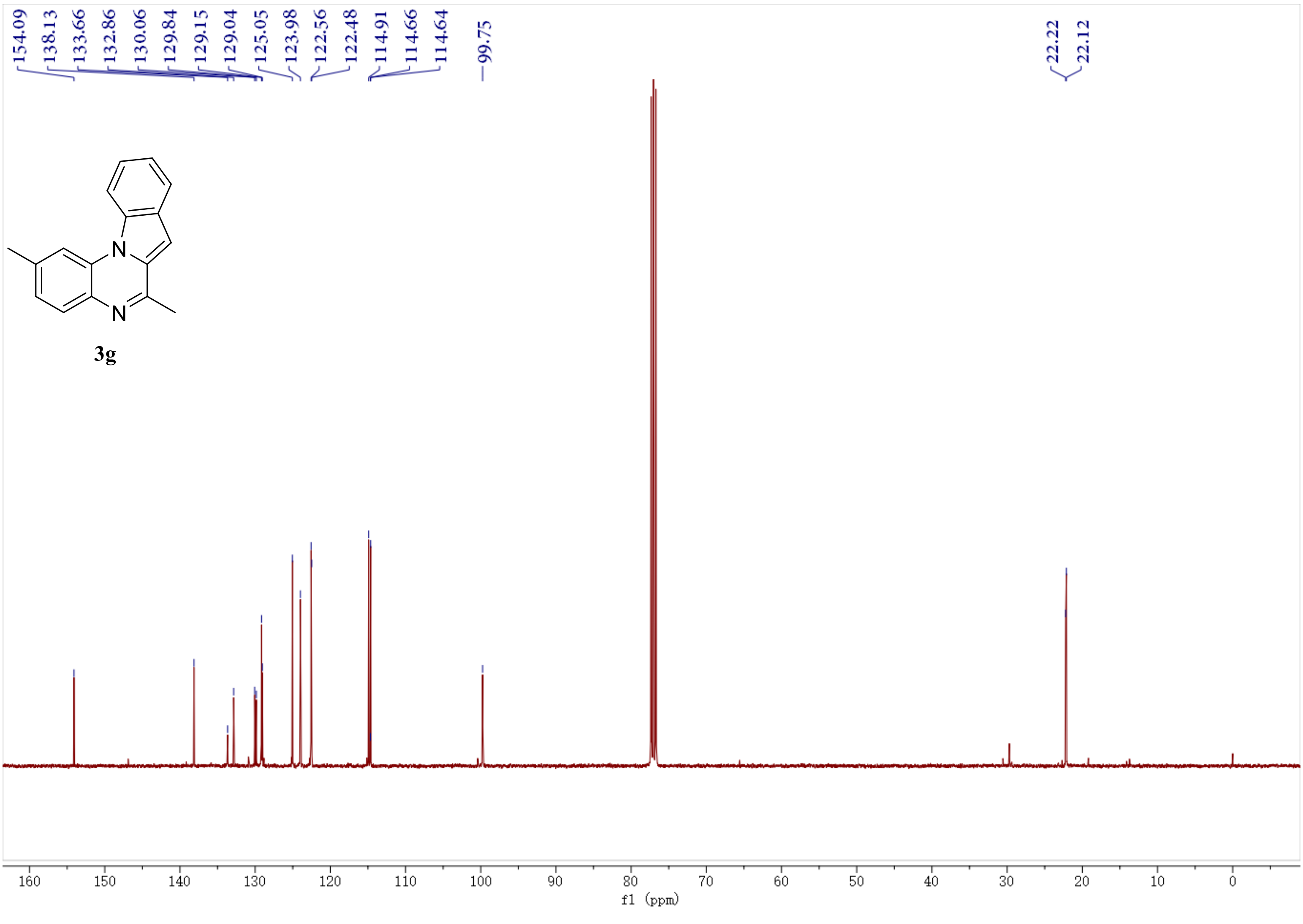
N
N
3g
1.00 0.98 0.98 0.96 1.05 1.01 0.99 0.95 2.98 3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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N
N
3g
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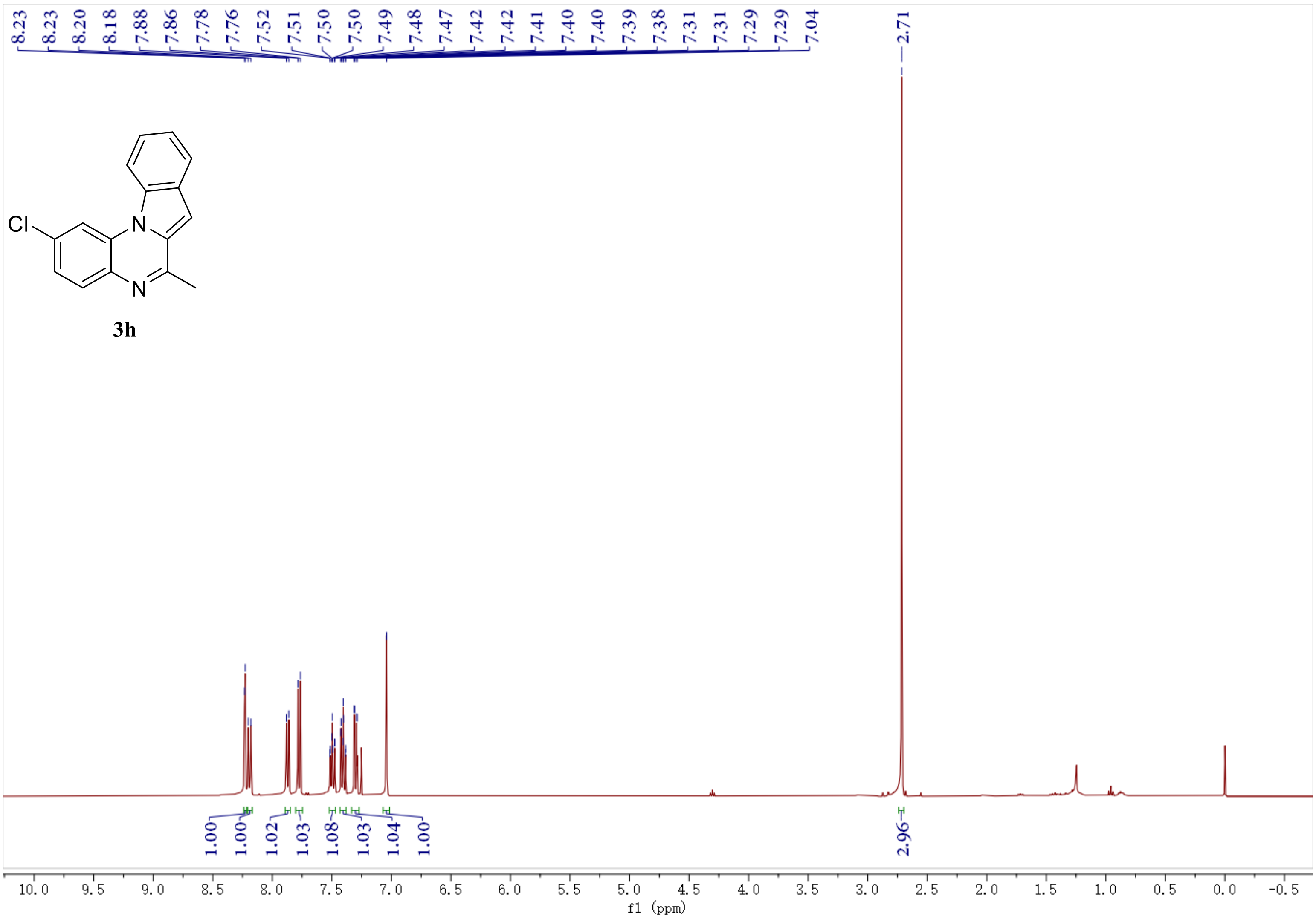
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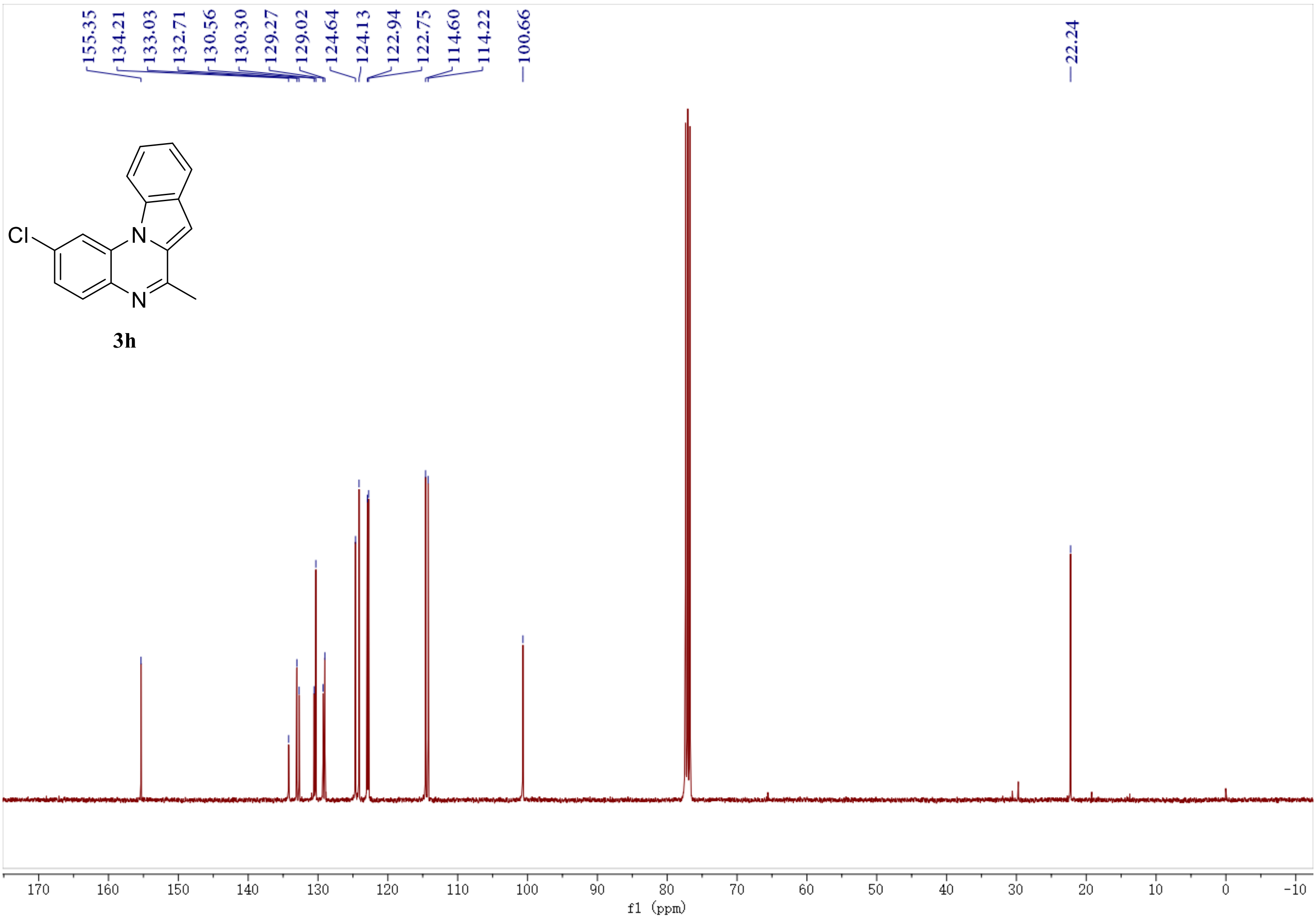
2.71
Cl
N
N
3h
1.00 1.00 1.02 1.03 1.08 1.03 1.04 1.00
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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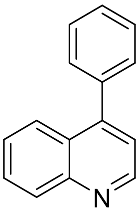
f1 (ppm)



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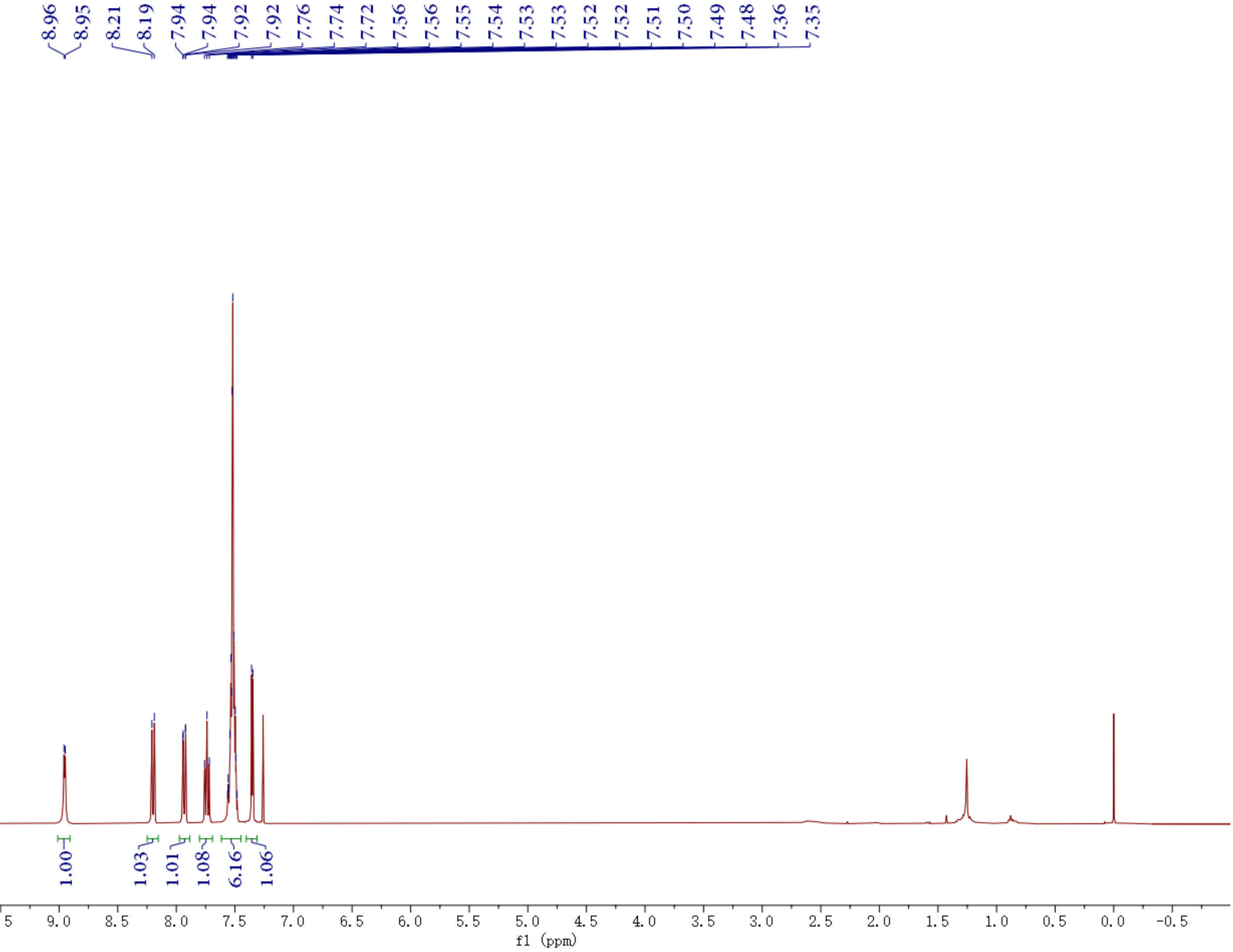
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7.94
7.92
7.92
7.76
7.74
7.72
7.56
7.56
7.55
7.54
7.53
7.53
7.52
7.52
7.51
7.50
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7.36
7.35
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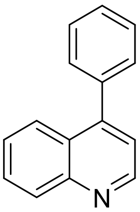
1.03
1.01
1.08
6.16
1.06
f1 (ppm)



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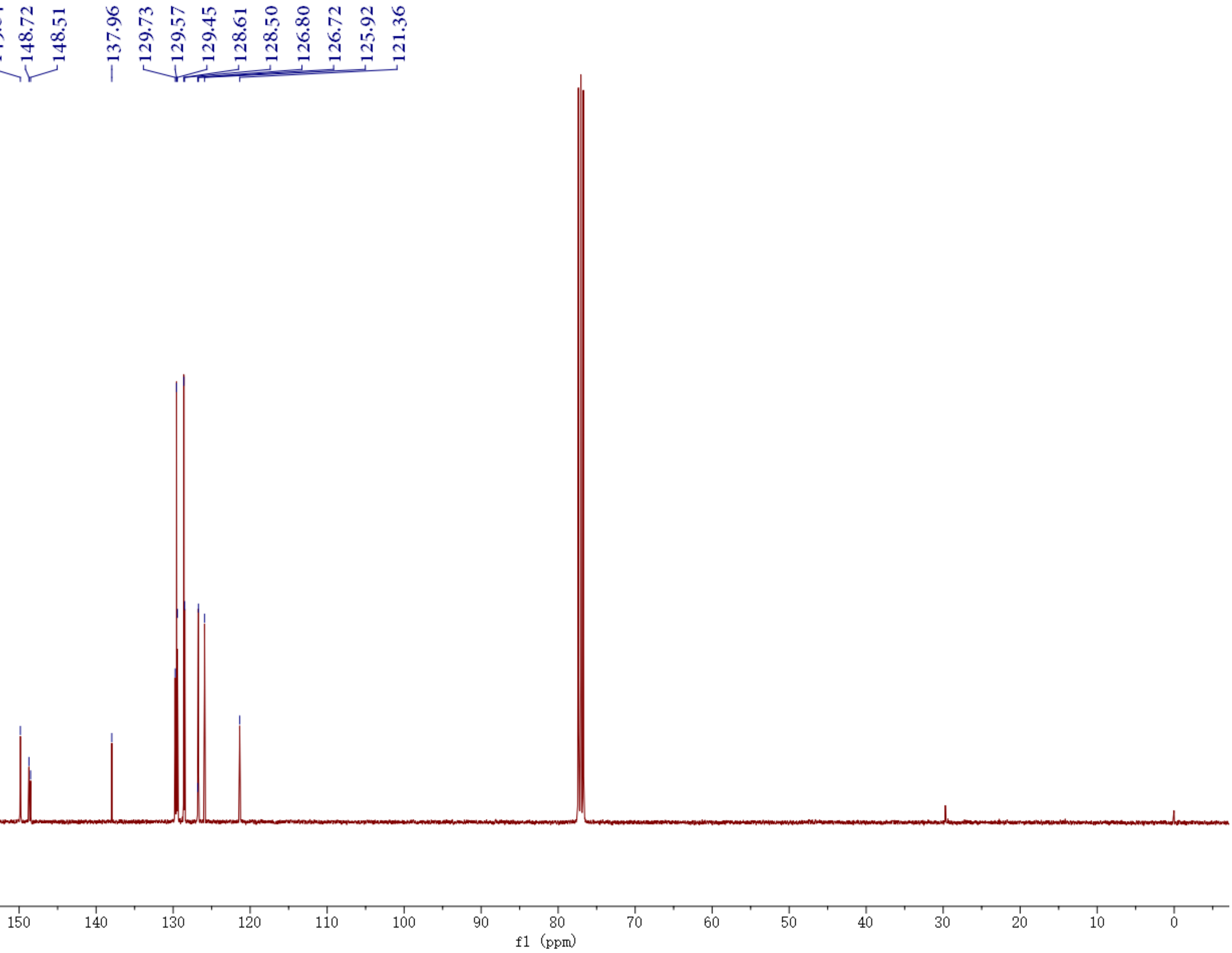
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128.61
128.50
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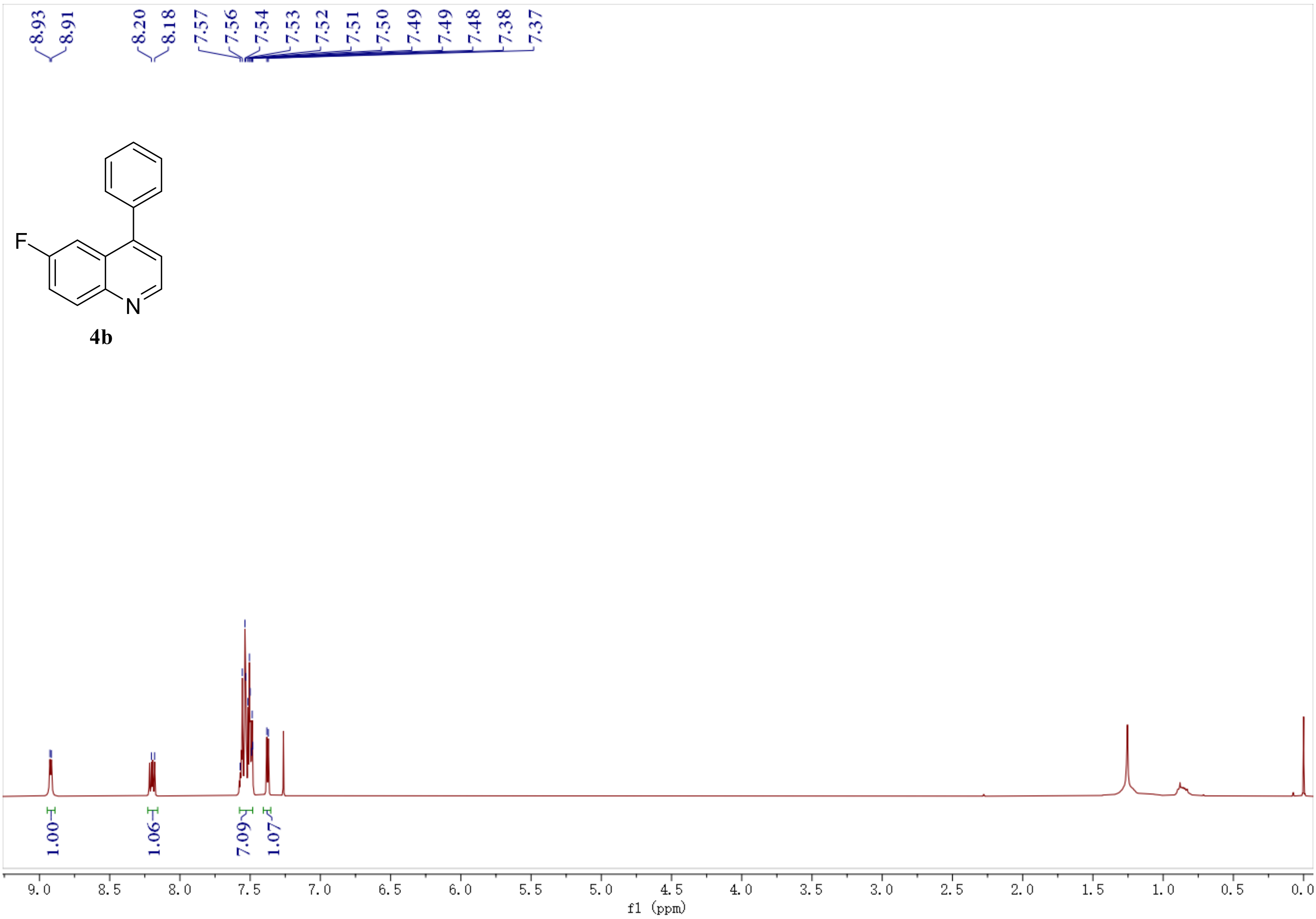
126.72
125.92
121.36
f1 (ppm)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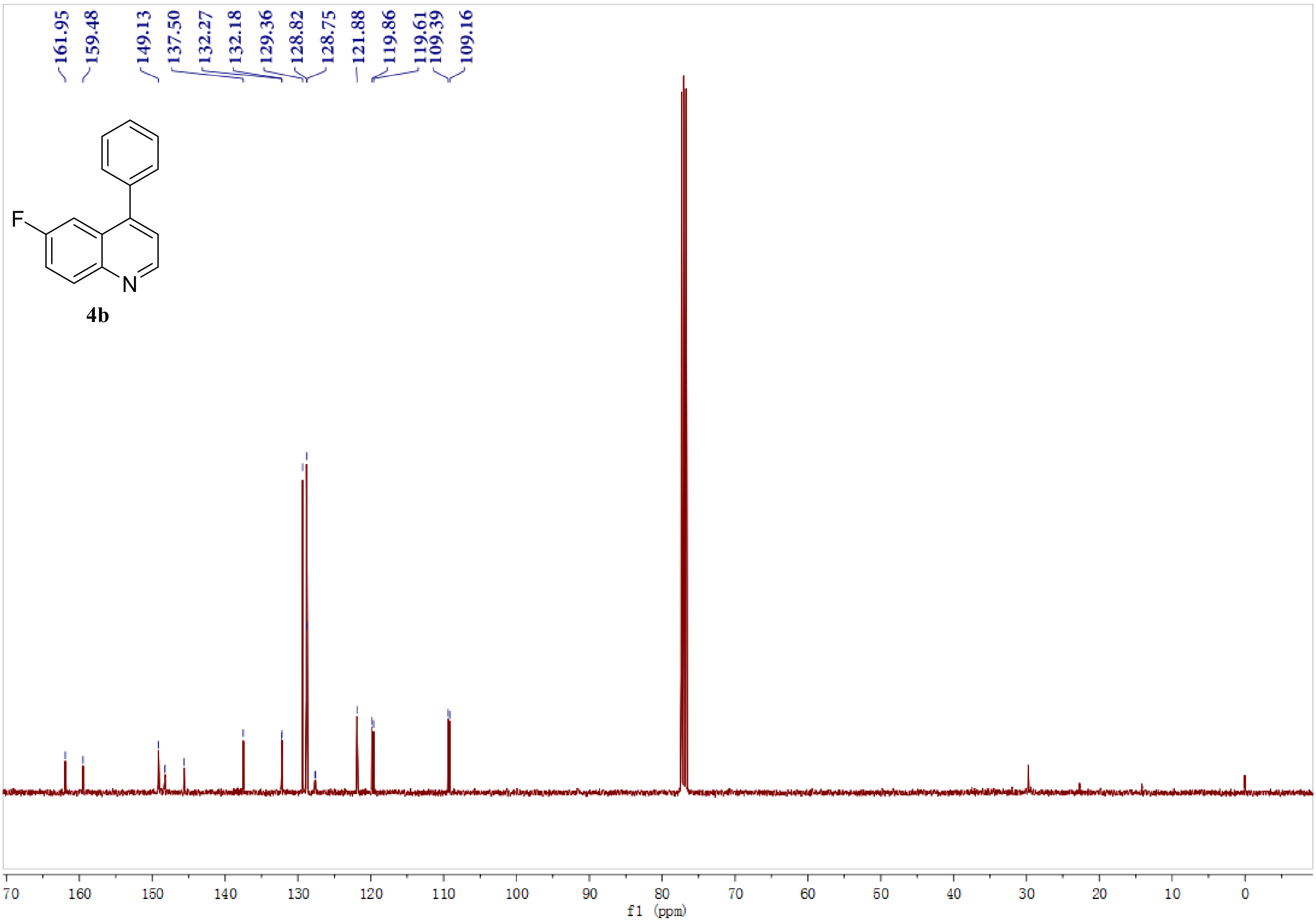
7.53
7.52
7.51
7.50
7.49
7.49
7.48
7.38
7.37
F
N
4b
1.00
1.06
7.09
1.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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132.27
132.18
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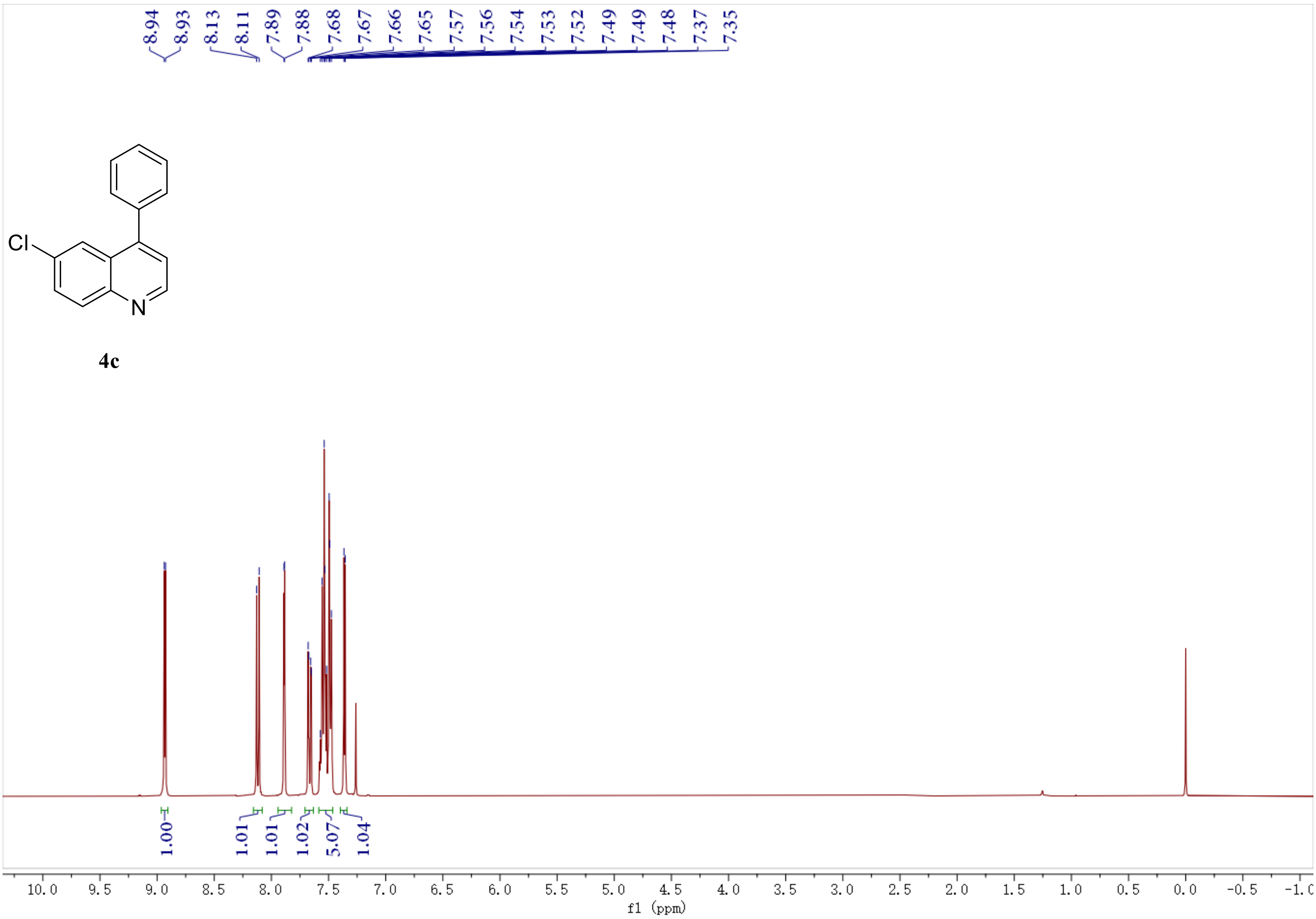
109.39
109.16
F
N
4b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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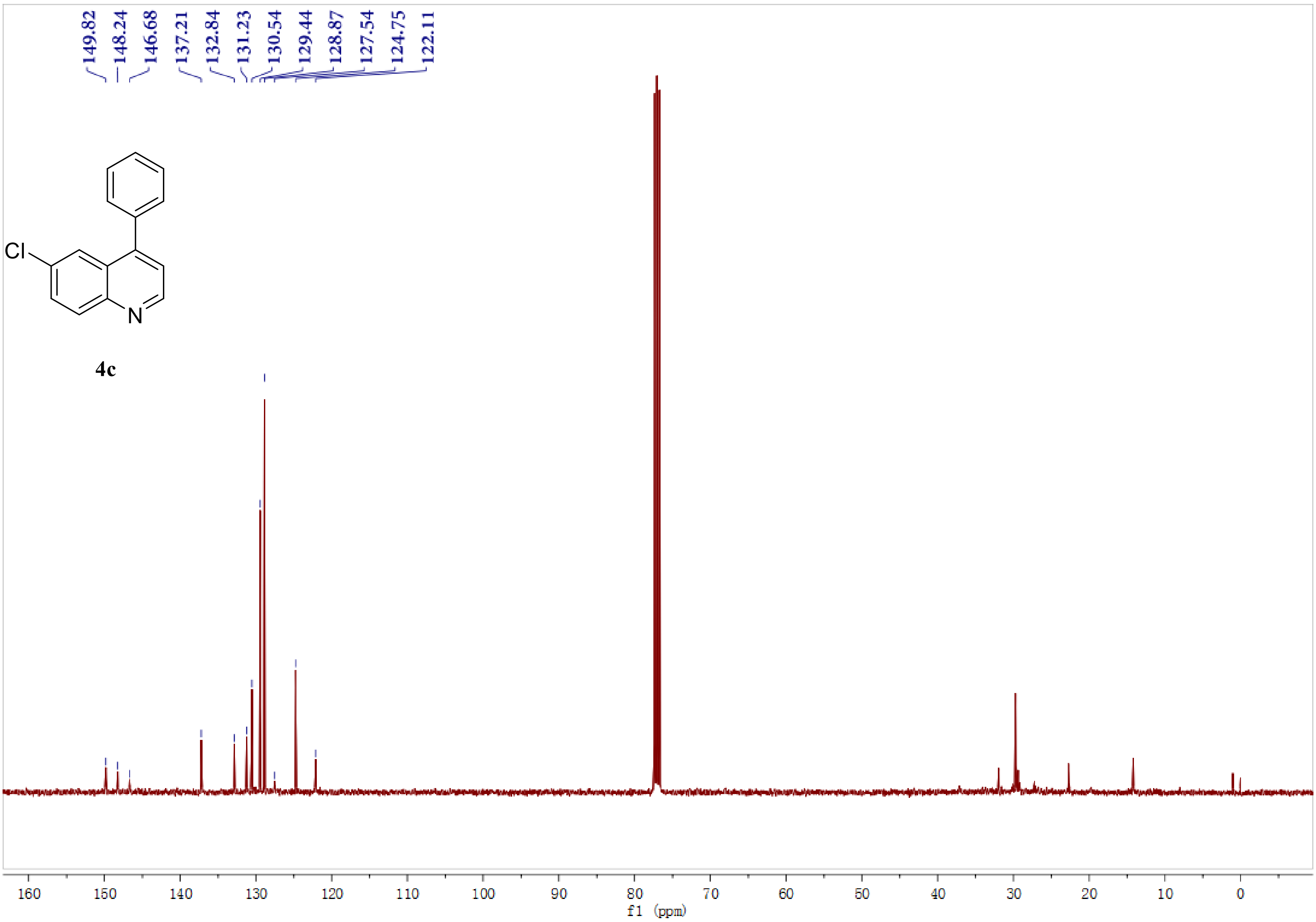
7.57
7.56
7.54
7.53
7.52
7.49
7.49
7.48
7.37
7.35
Cl
N
4c
1.00
1.01
1.01
1.02
5.07
1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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Cl
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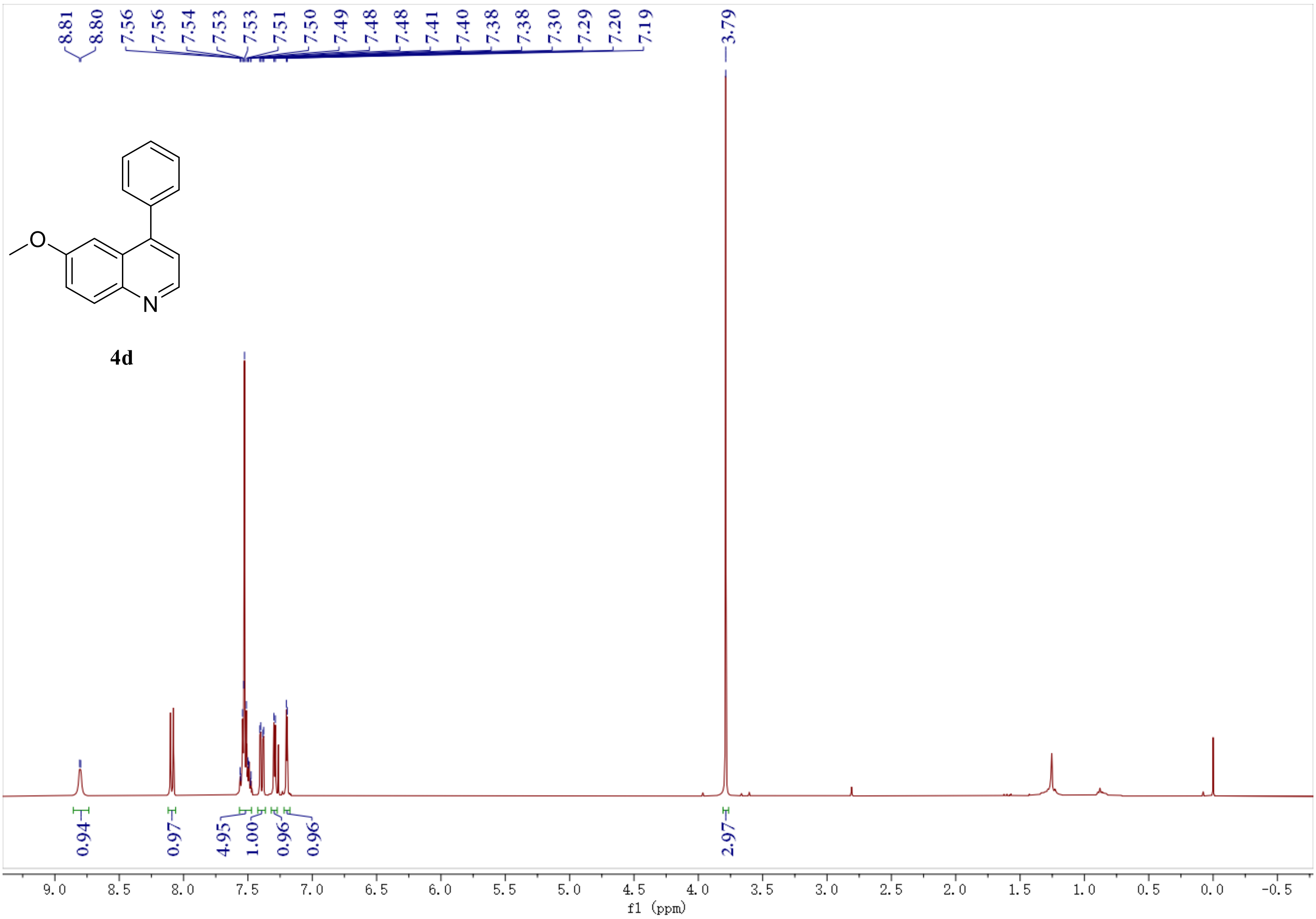
f1 (ppm)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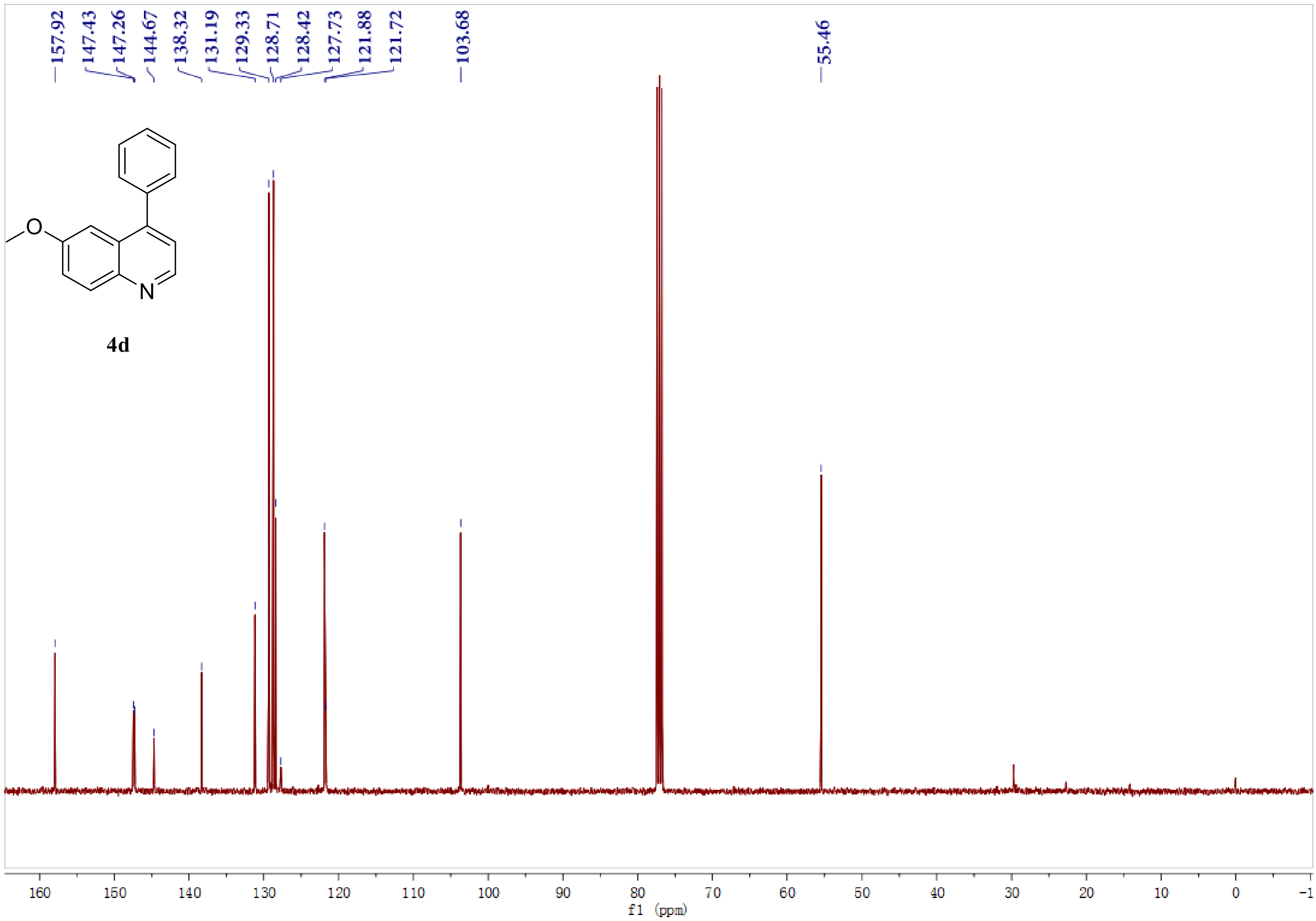
7.41
7.40
7.38
7.38
7.30
7.29
7.20
7.19
3.79
O
N
4d
0.94
0.97
4.95
1.00
0.96
0.96
2.97
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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55.46
O
N
4d
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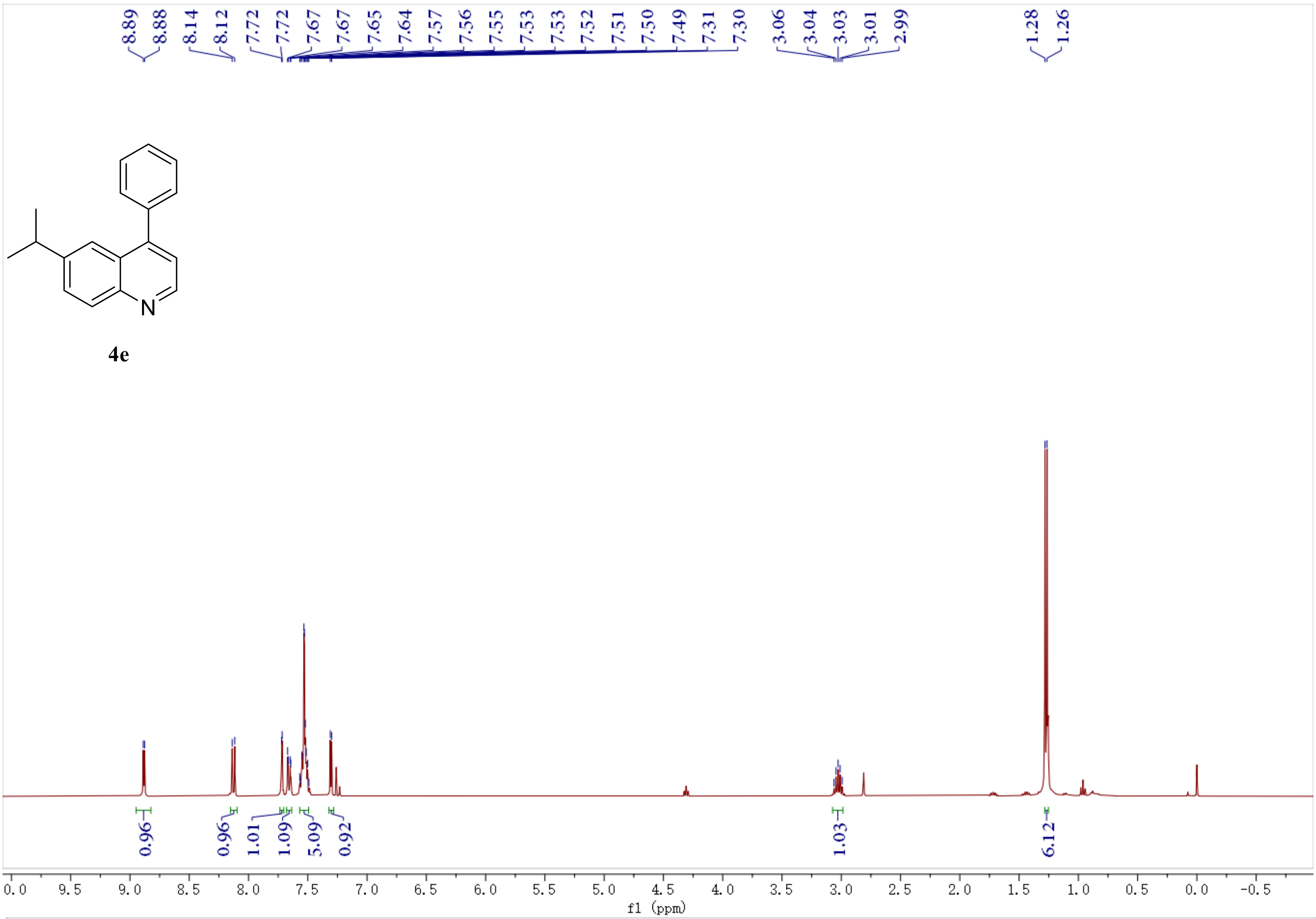
f1 (ppm)



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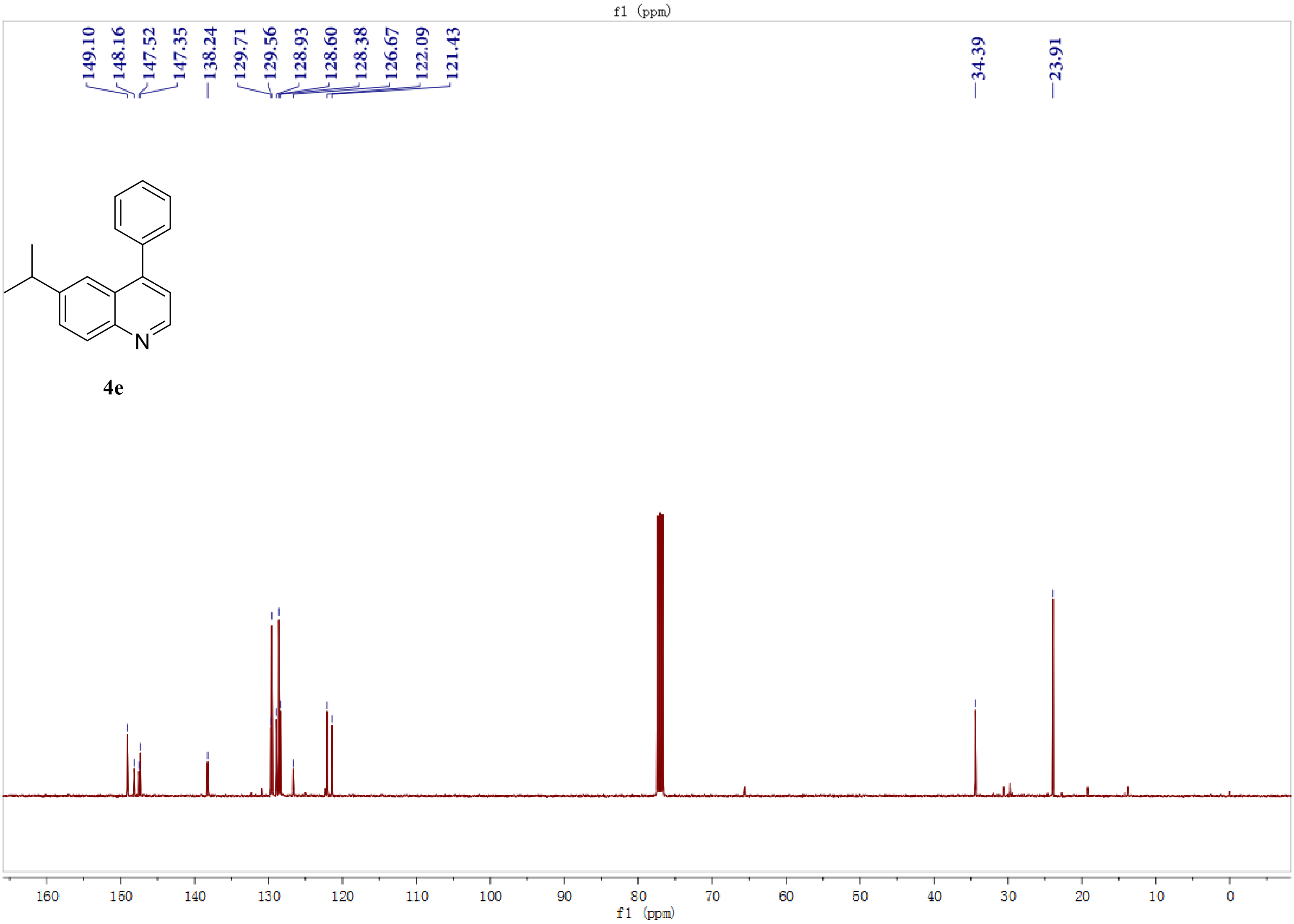

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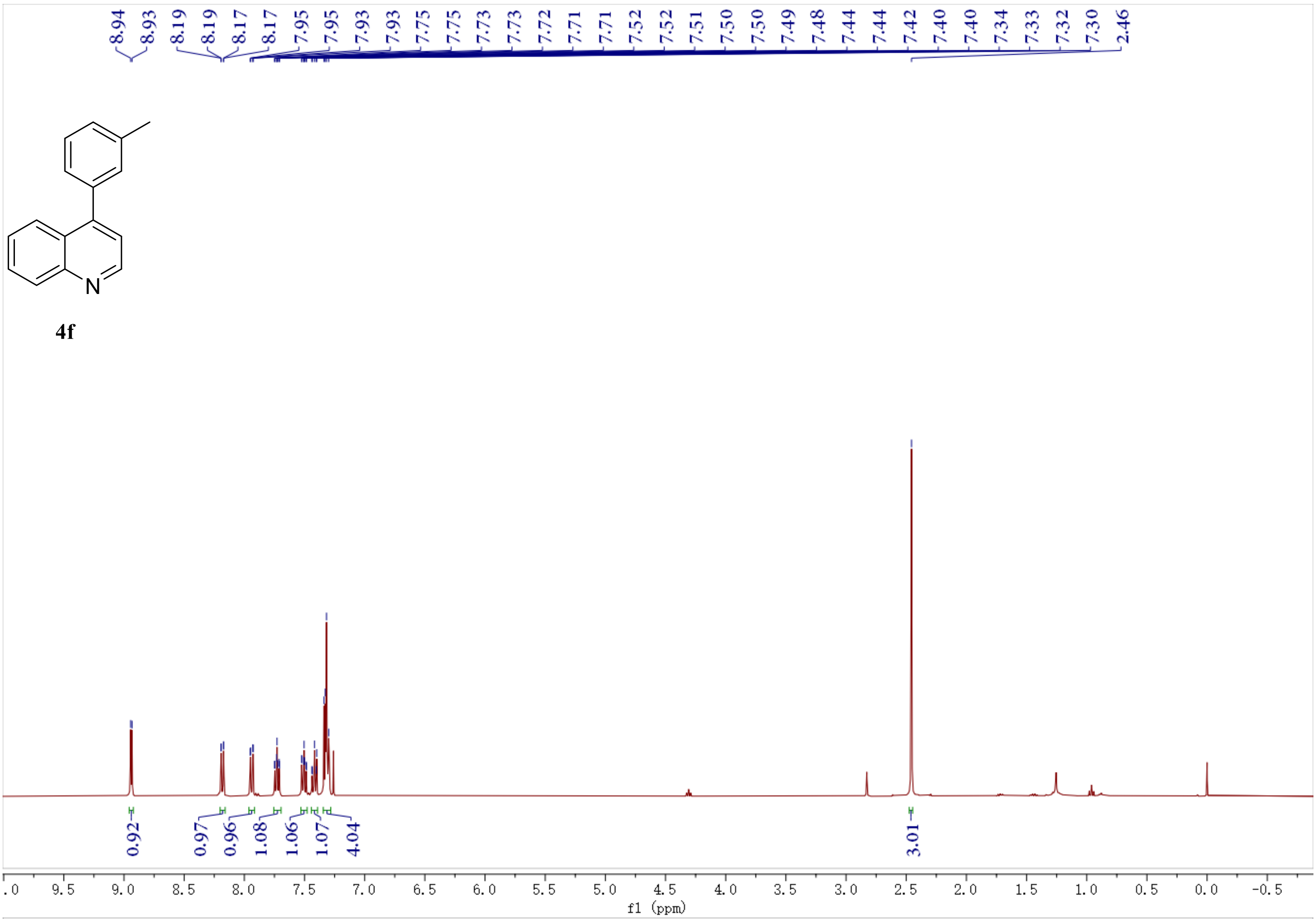
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7.48
7.44
7.44
7.42
7.40
7.40
7.34
7.33
7.32
7.30
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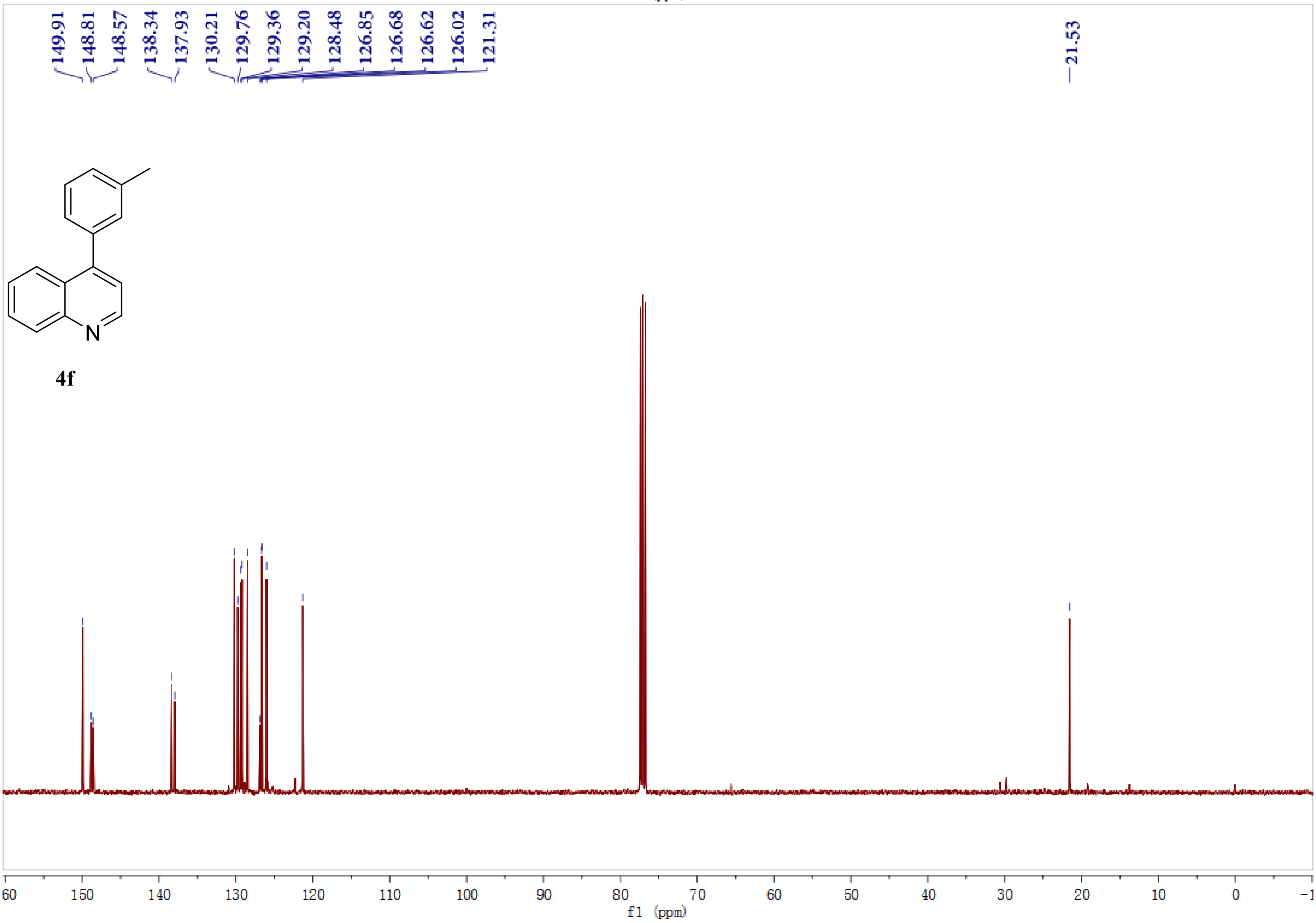
1.08
1.06
1.07
4.04
3.01
f1 (ppm)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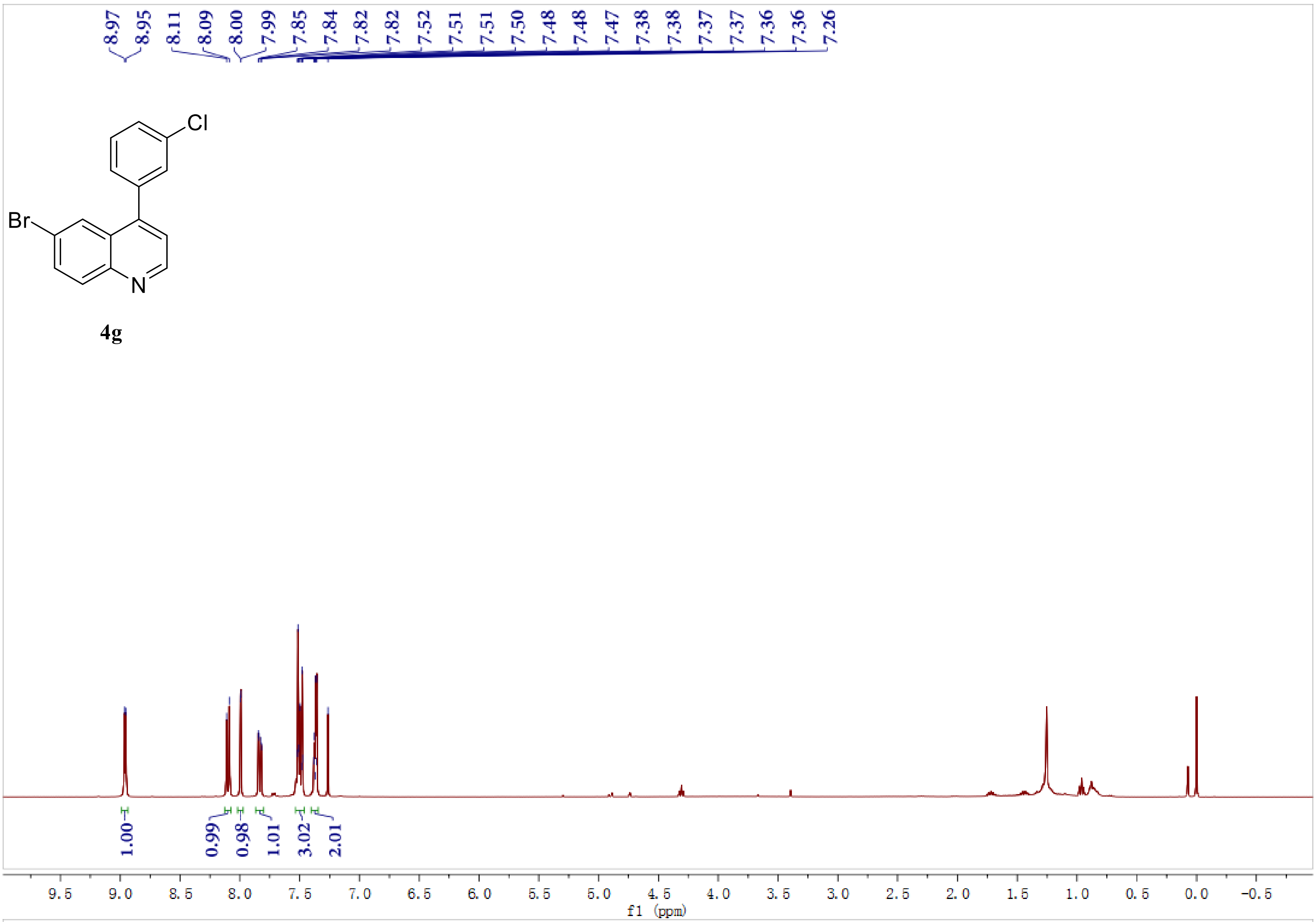
4f
f1 (ppm)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7.51
7.50
7.48
7.48
7.47
7.38
7.38
7.37
7.37
7.36
7.36
7.26
Cl
Br
N
4g
1.00
0.99
0.98
1.01
3.02
2.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
2.5
2.0
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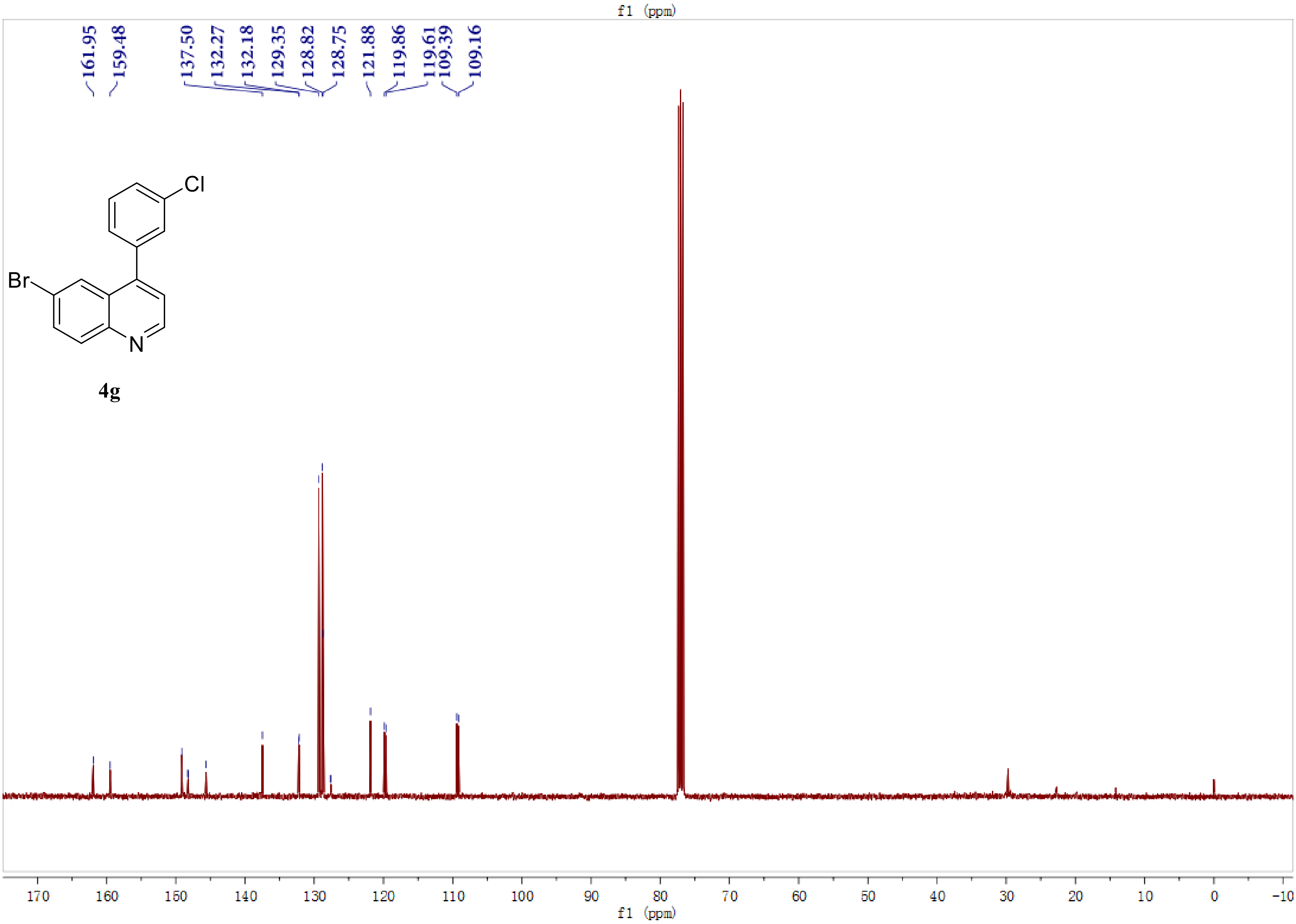
f1 (ppm)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109.16
Cl
Br
N
4g
170
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100
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80
70
60
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40
30
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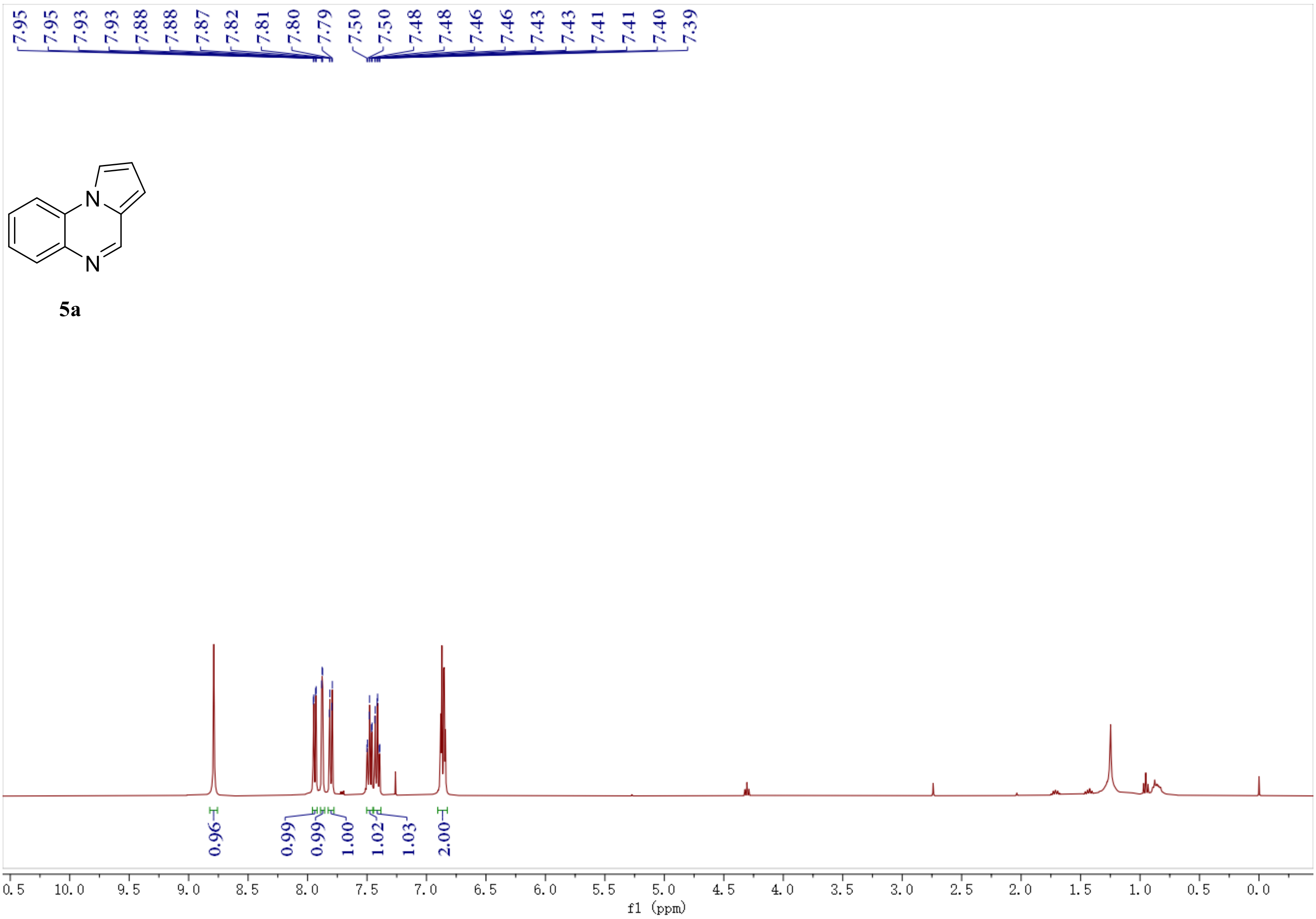
0
-10
f1 (ppm)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7.48
7.48
7.46
7.46
7.43
7.43
7.41
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7.40
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5a
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0.99
0.99
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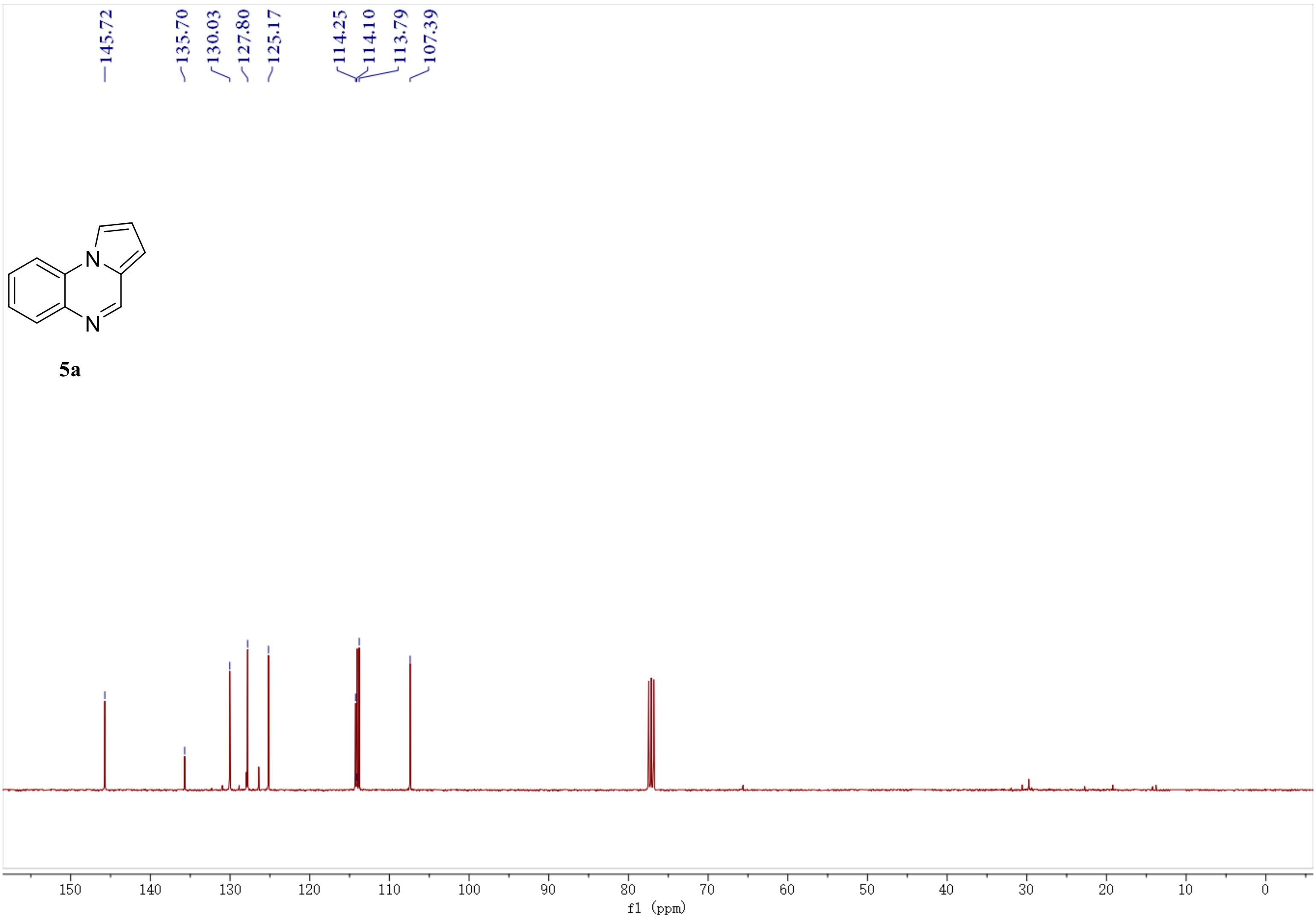
1.02
1.03
2.00
f1 (ppm)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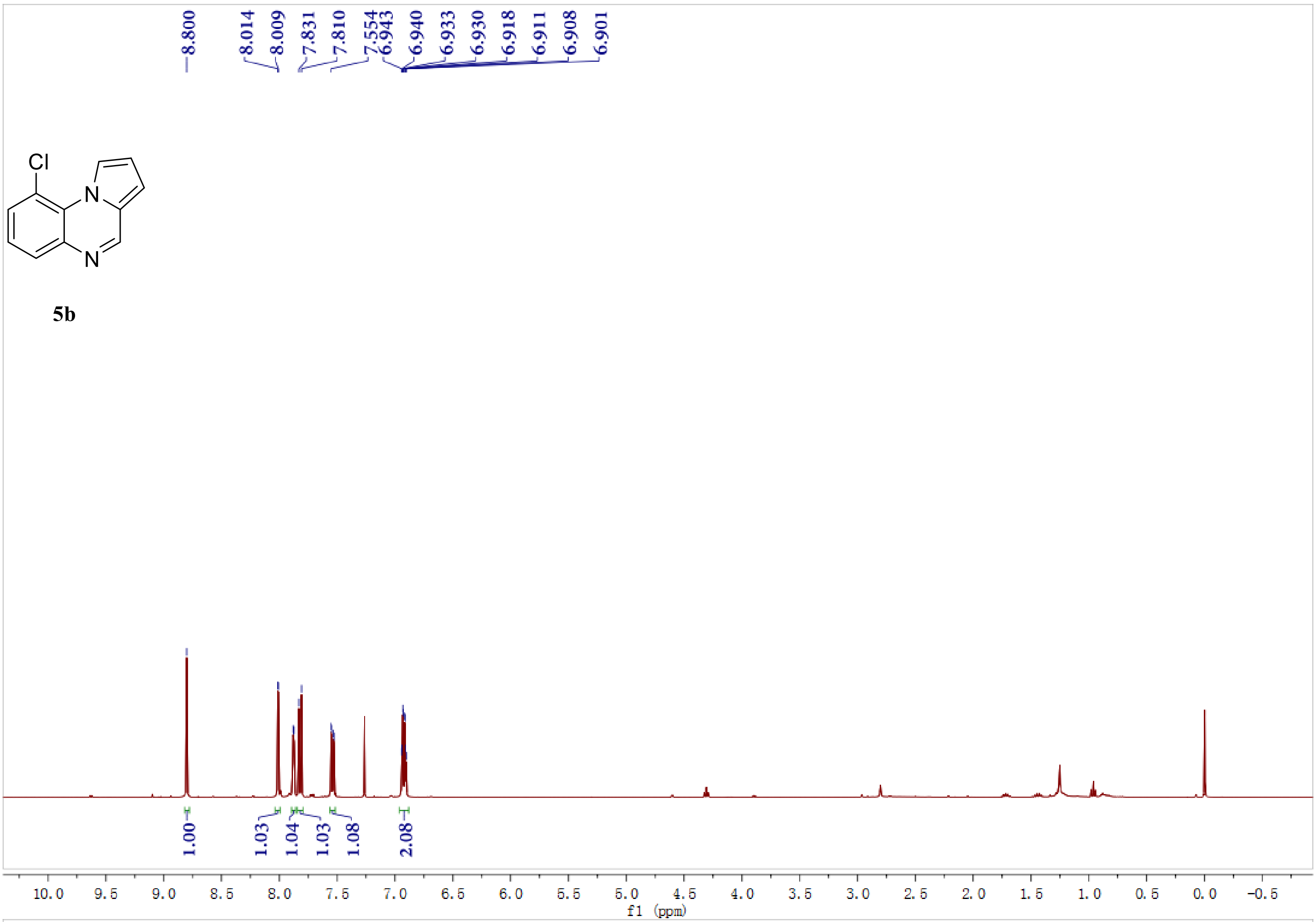
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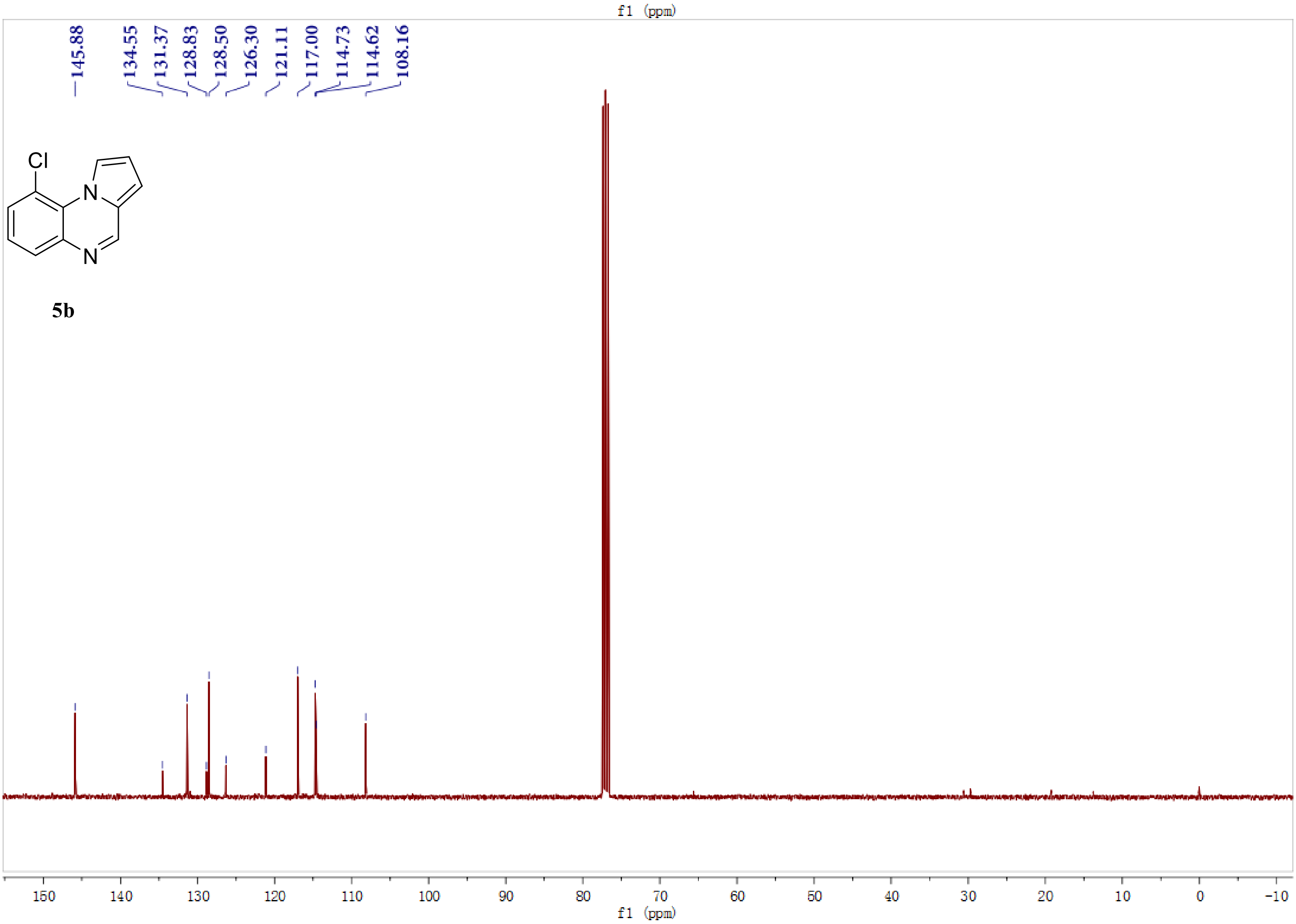
6.911
6.908
6.901
Cl
N
N
5b
1.00
1.03
1.04
1.03
1.08
2.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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126.30
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108.16
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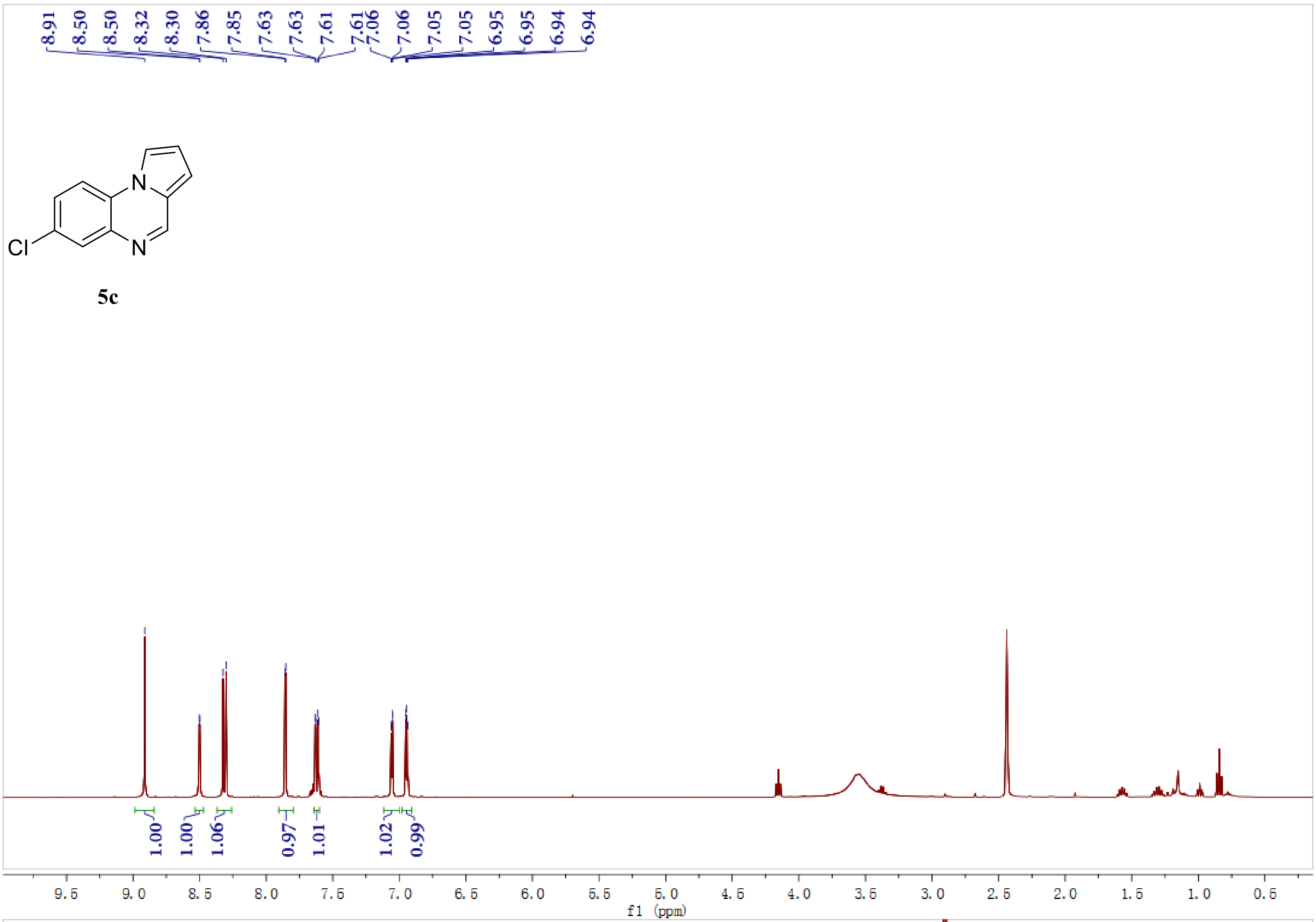
f1 (ppm)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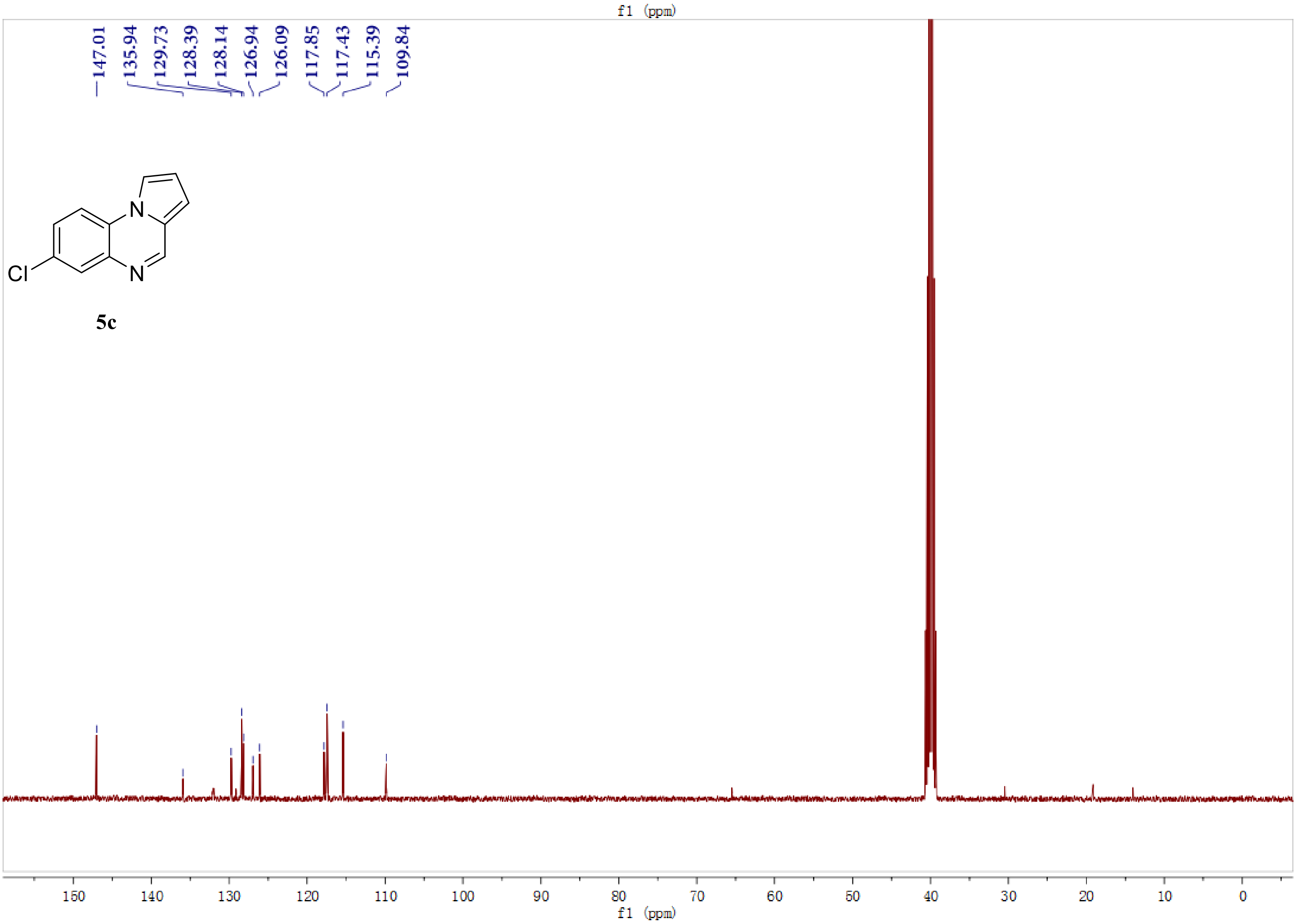
7.05
7.05
6.95
6.95
6.94
6.94
N
N
Cl
5c
1.00
1.00
1.06
0.97
1.01
1.02
0.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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Cl
5c
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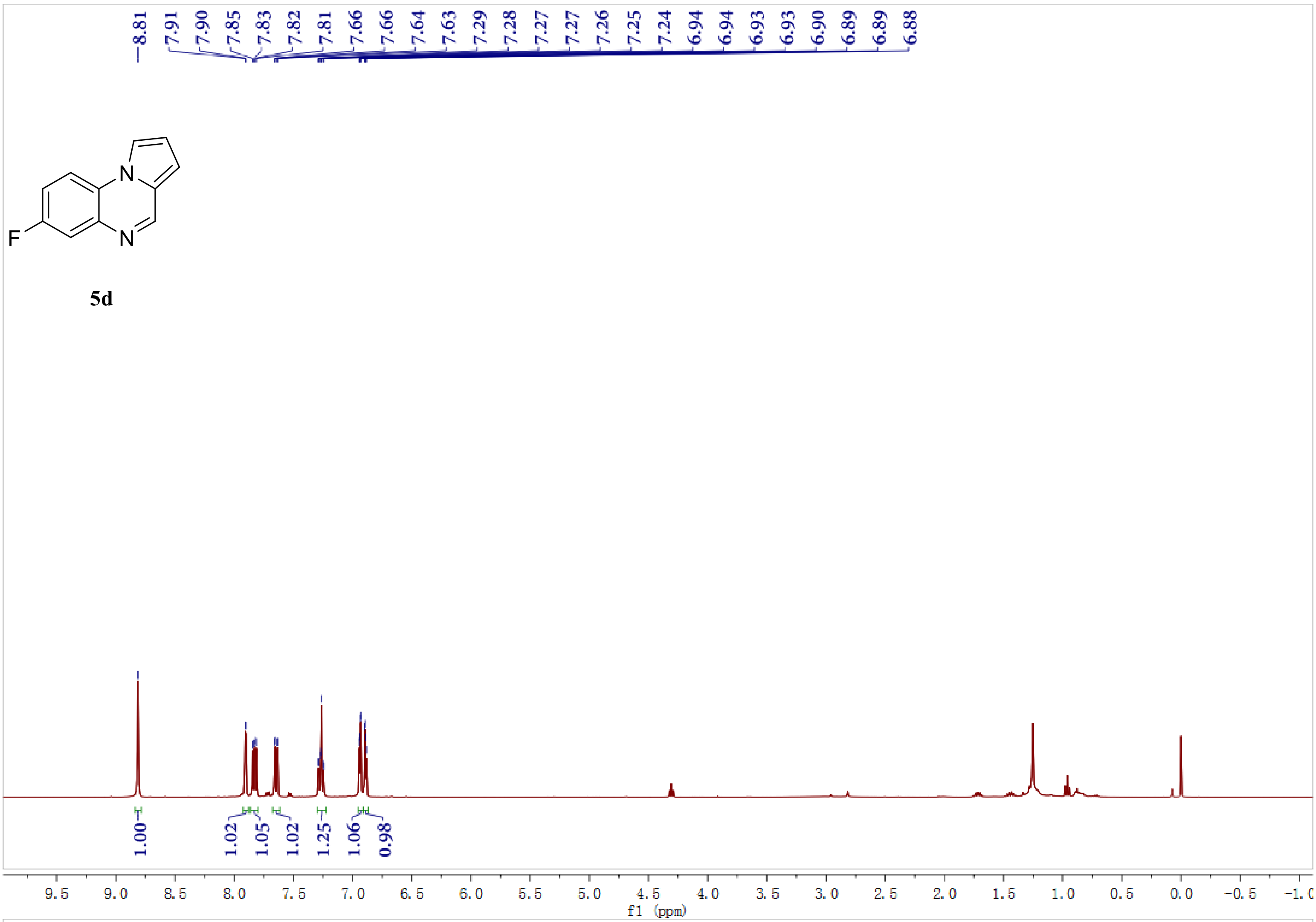
f1 (ppm)



5d
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7.83
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7.66
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7.29
7.28
7.27
7.27
7.26
7.25
7.24
6.94
6.94
6.93
6.93
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1.05
1.02
1.25
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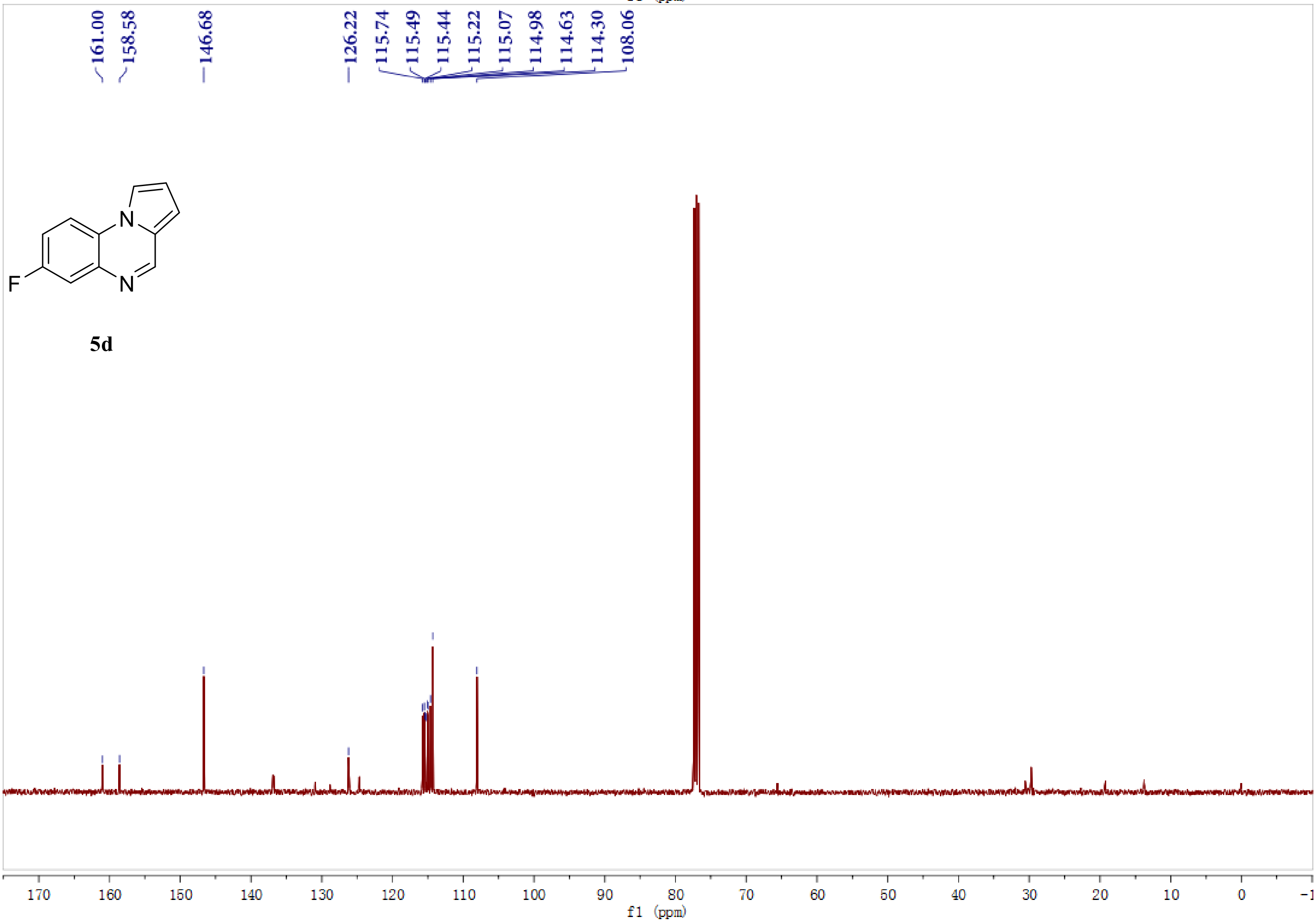
0.98
f1 (ppm)



5d
161.00
158.58
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115.44
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115.07
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114.63
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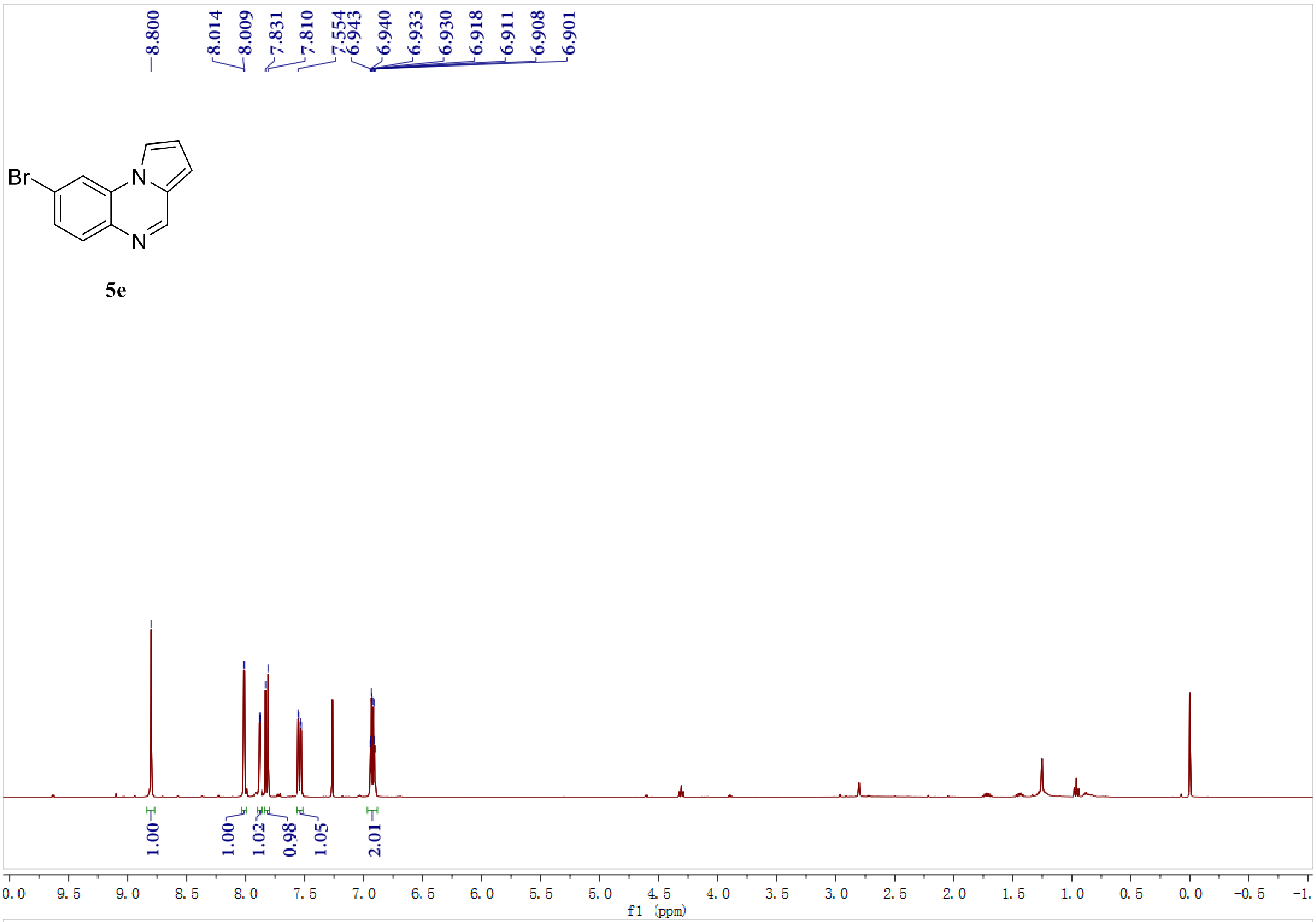
108.06
f1 (ppm)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6.940
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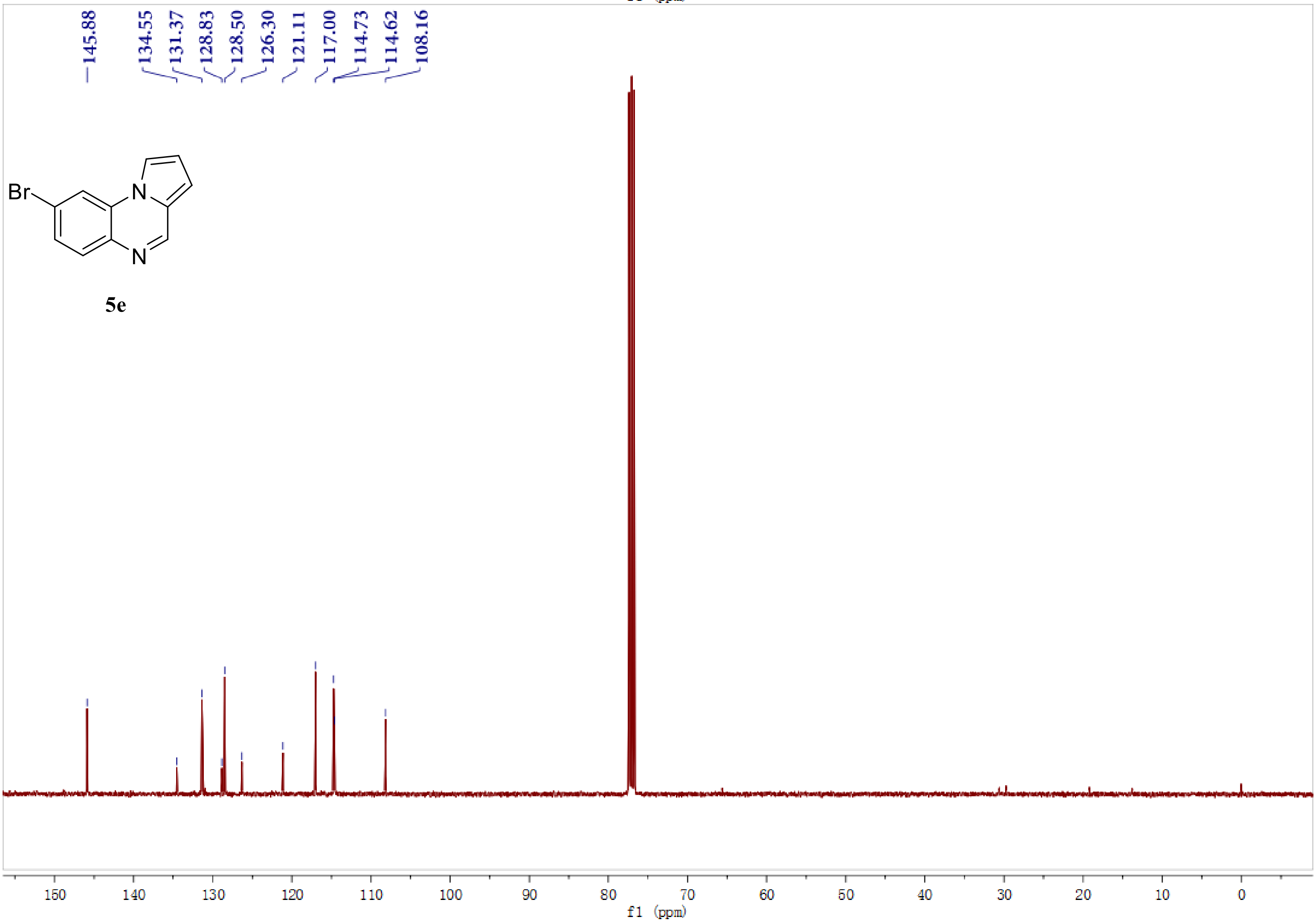
6.911
6.908
6.901
Br
N
N
5e
1.00
1.00
1.02
0.98
1.05
2.01
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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128.83
128.50
126.30
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108.16
Br
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N
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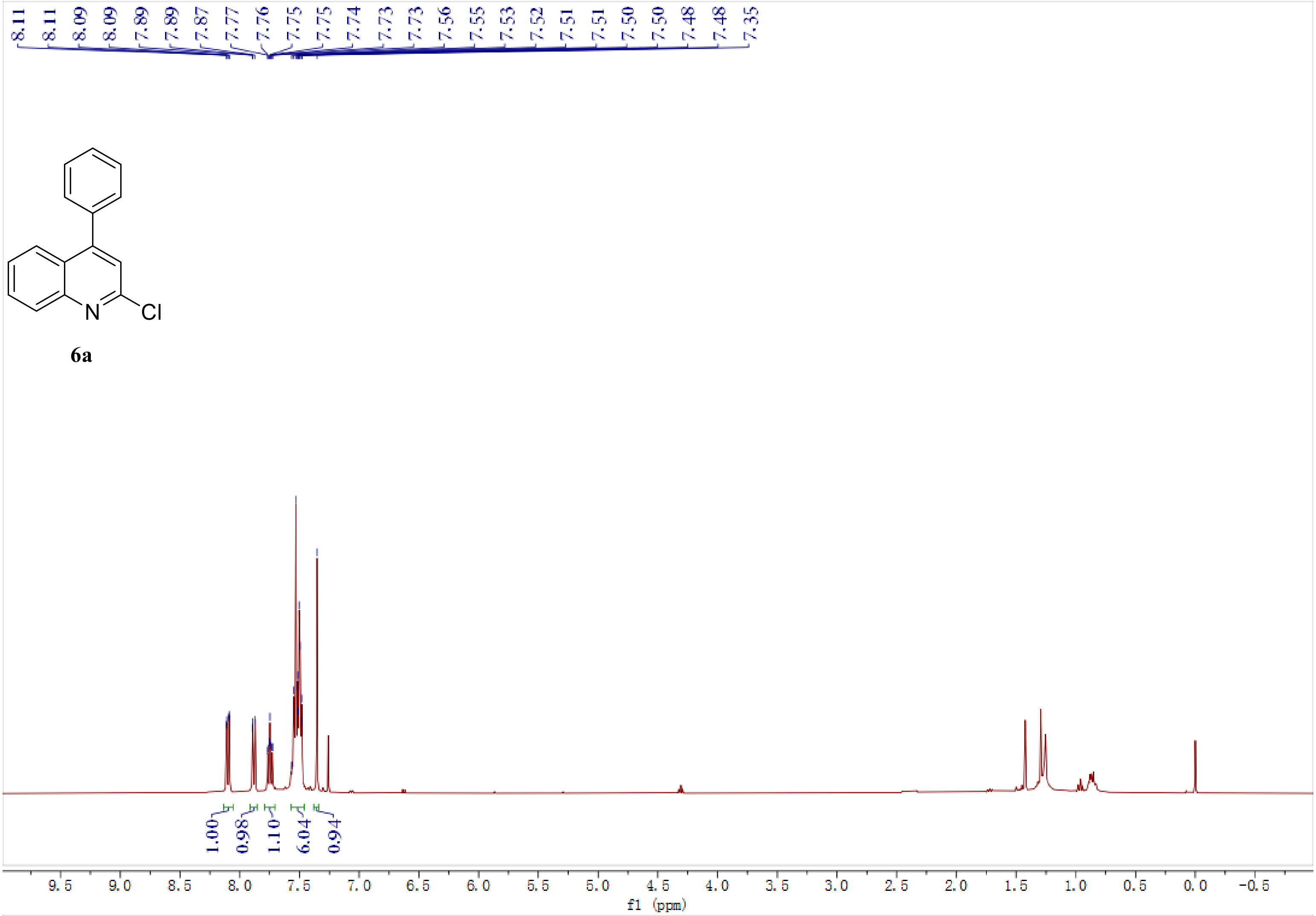
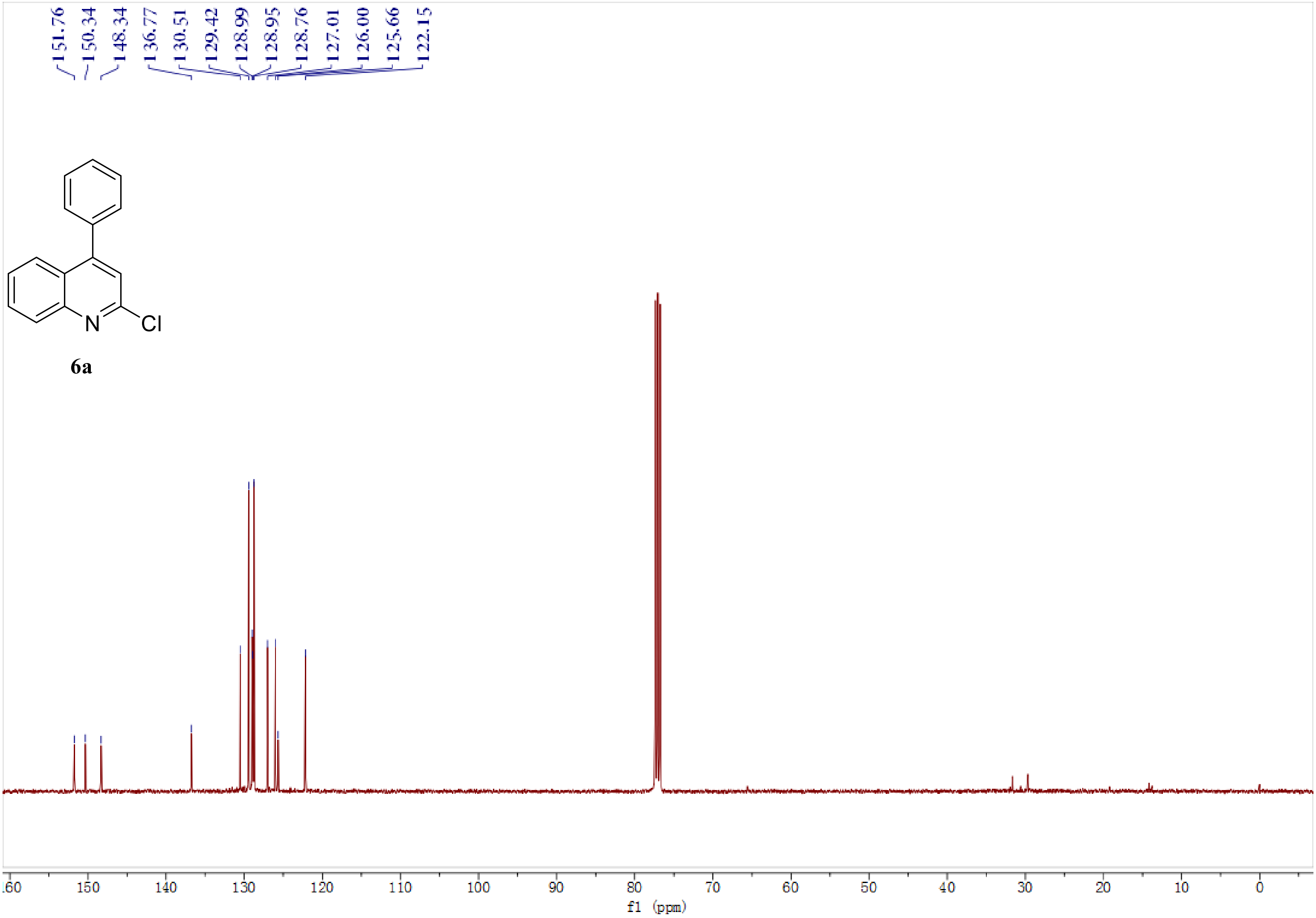
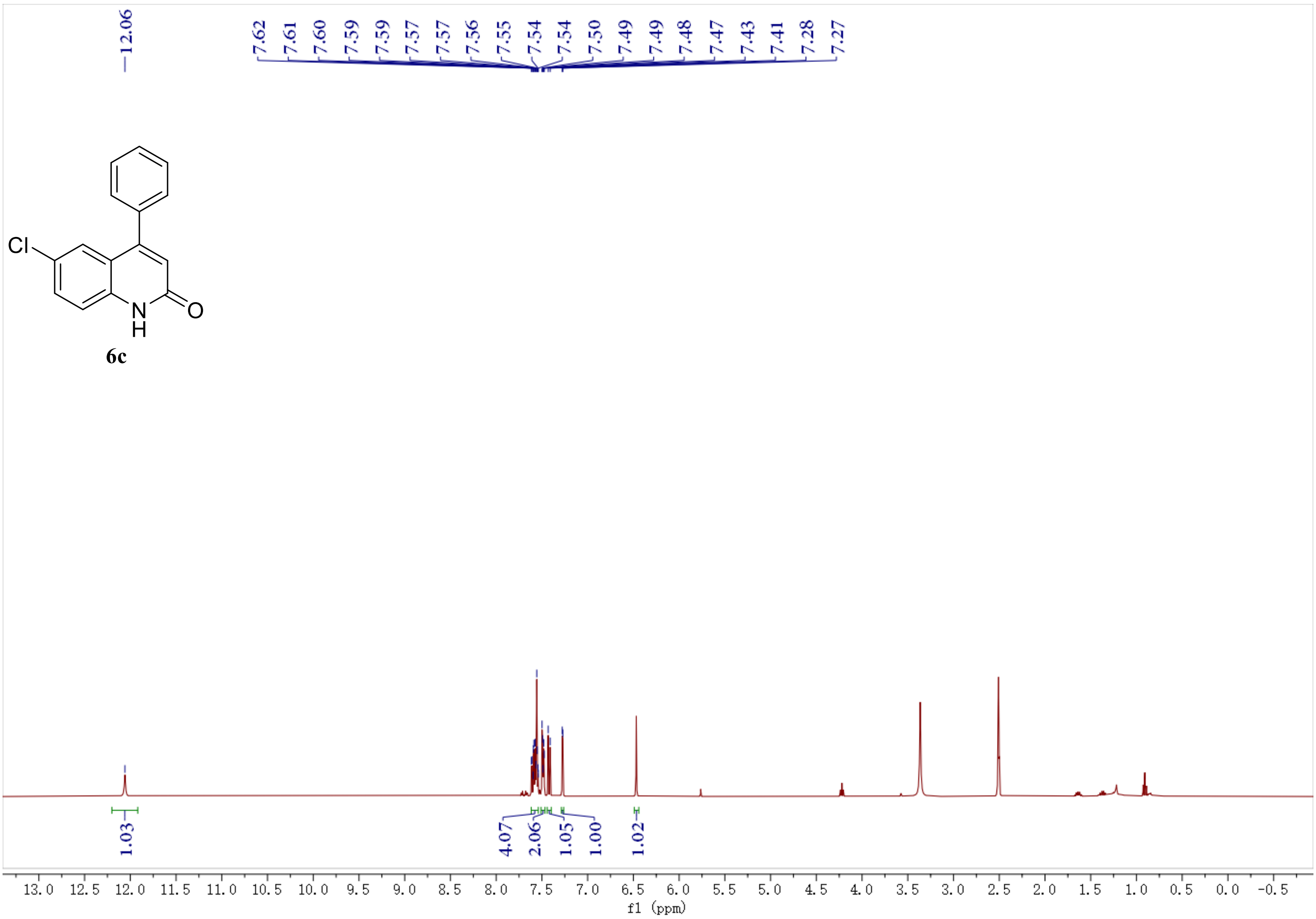
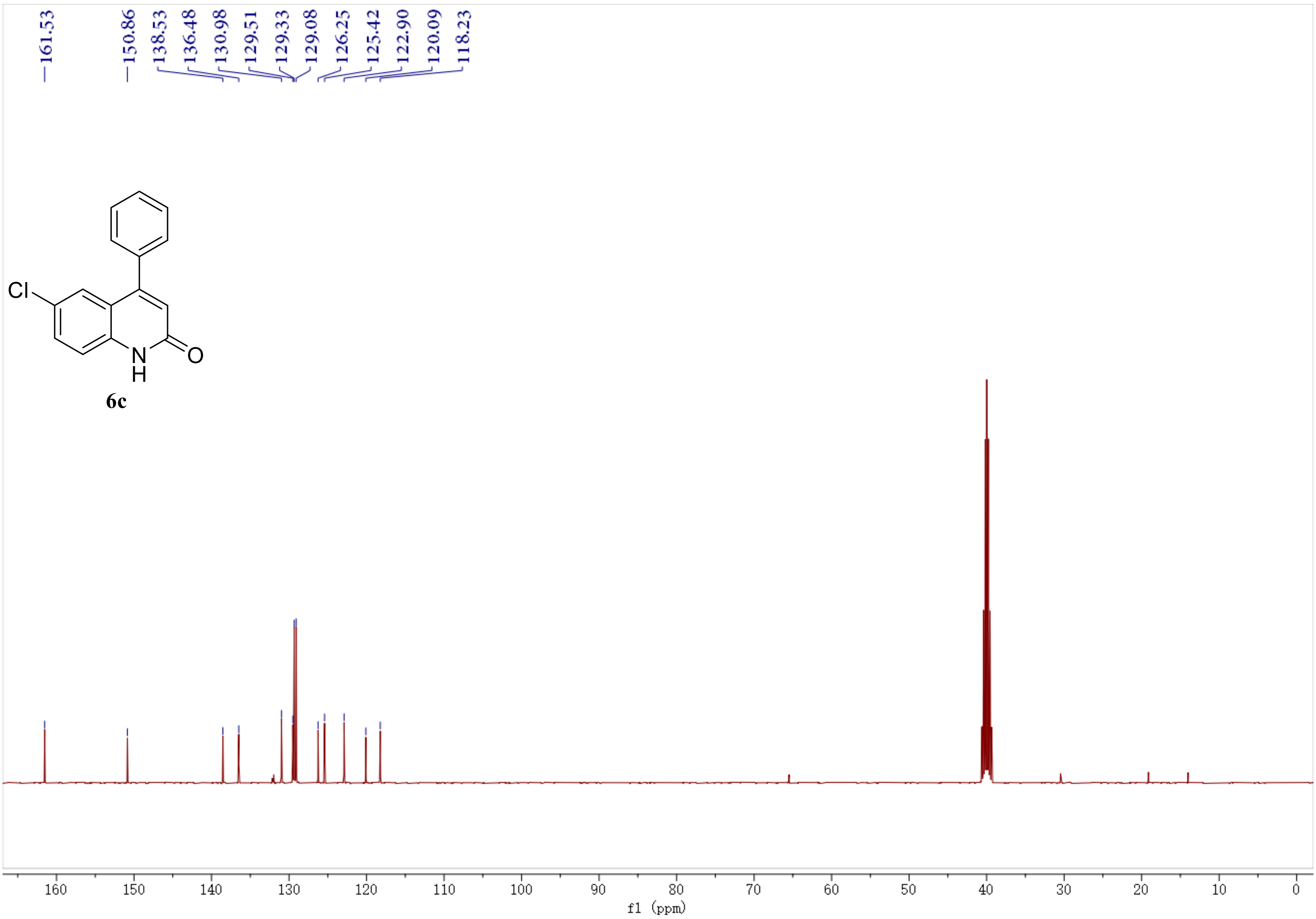
f1 (ppm)


8.11 8.11 8.09 8.09 7.89 7.89 7.87 7.77 7.76 7.75 7.75 7.74 7.73 7.73 7.56 7.55 7.53 7.52 7.51 7.51 7.50 7.50 7.48 7.48 7.35
N
Cl
6a
1.00 0.98 1.10 6.04 0.94
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


151.76 150.34 148.34 136.77 130.51 129.42 128.99 128.95 128.76 127.01 126.00 125.66 122.15
N
Cl
6a
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


12.06
7.62 7.61 7.60 7.59 7.59 7.57 7.57 7.56 7.55 7.54 7.54 7.50 7.49 7.49 7.48 7.47 7.43 7.41 7.28 7.27
Cl
N
H
O
6c
1.03
4.07 2.06 1.05 1.00
1.02
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


161.53
150.86 138.53 136.48 130.98 129.51 129.33 129.08 126.25 125.42 122.90 120.09 118.23
Cl
N
H
O
6c
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)