

# Supporting Information

## Highly Diastereo- and Enantioselective Ir-catalyzed Hydrogenation of 2,3-Disubstituted Quinolines with Structurally Fine-Tuned Phosphine-Phosphoramidite Ligands

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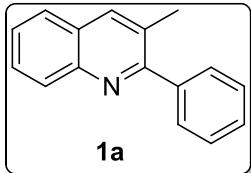
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## I. General Methods

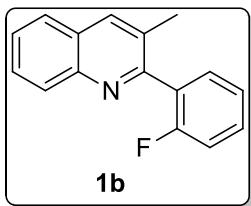
All reactions and manipulations were performed in a nitrogen-filled glove box or under nitrogen using Schlenk techniques unless otherwise noted. Solvents were purified by standard procedure before use. Commercial reagents were used without further purification. Flash chromatography was performed on silica gel 60 (40-63 $\mu$ m, 60 $\text{\AA}$ ). Thin layer chromatography (TLC) was performed on glass plates coated with silica gel 60 with F254 indicator. Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ( $\text{CHCl}_3 = \delta 7.26$  or  $\text{DMSO} = \delta 2.50$ ). Carbon nuclear magnetic resonance ( $^{13}\text{C}$  NMR) spectra were recorded on a Bruker 100 MHz spectrometer. Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ( $\text{CDCl}_3 = \delta 77.23$  or  $\text{DMSO} = \delta 39.60$ ). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. Only the most important and relevant frequencies are reported. Enantiomeric ratios were determined by chiral HPLC with hexane and *i*-PrOH as solvents. Optical rotations were recorded on a JASCO P-1020 polarimeter. 2-Phenylquinoline **1x-4** was purchased from Acros.

## II. General Procedure for the Preparation of Quinolines

**Representative procedure for the synthesis of 3-Methyl-2-phenylquinoline (1a).**<sup>1,2</sup> To a solution of 2-aminobenzyl alcohol (1.23 g, 10 mmol) in 1,4-dioxane (30 mL) were added the propiophenone (1.34 g, 10 mmol), benzophenone (1.82 g, 10 mmol), and potassium tertbutoxide (1.12 g, 10 mmol) under an argon atmosphere. The resulting mixture was heated at 90 °C in oil bath with stirring overnight. Then, the reaction was cooled to room temperature and filtered through Celite. The resulting solution was removed in vacuo. Yellow solid was obtained in 76% yield (1.67 g) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 38-40 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J = 8.5$  Hz, 1H), 7.84 (s, 1H), 7.62 (d,  $J = 8.1$  Hz, 1H), 7.57 – 7.49 (m, 1H), 7.49 – 7.43 (m, 2H), 7.40 – 7.26 (m, 4H), 2.31 (s, 3H).

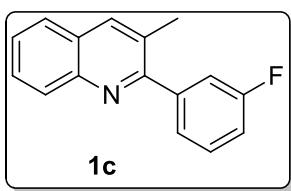


**2-(2-Fluorophenyl)-3-methylquinoline (1b).** Yellow solid was obtained in 56% yield (1.33 g) after



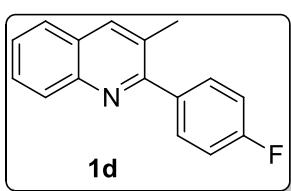
purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 64-66 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 (d,  $J$  = 8.5 Hz, 1H), 7.99 (s, 1H), 7.77 (d,  $J$  = 8.1 Hz, 1H), 7.65 (ddd,  $J$  = 8.4, 7.0, 1.3 Hz, 1H), 7.54 – 7.36 (m, 3H), 7.32 – 7.22 (m, 1H), 7.21 – 7.10 (m, 1H), 2.36 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.85 (d,  $J$  = 246.6 Hz), 156.25 (s), 146.60 (s), 136.12 (s), 131.16 (d,  $J$  = 3.7 Hz), 130.49 (s), 130.35 (s), 130.27 (s), 129.32 (s), 128.83 (s), 128.71 (d,  $J$  = 16.7 Hz), 127.92 (s), 126.80 (d,  $J$  = 11.4 Hz), 124.56 (d,  $J$  = 3.5 Hz), 115.71 (d,  $J$  = 21.9 Hz), 19.26 (d,  $J$  = 4.0 Hz). HRMS calcd for  $\text{C}_{16}\text{H}_{13}\text{FN}$  [M+H] $^+$ : 238.1027, found: 238.1028.

**2-(3-Fluorophenyl)-3-methylquinoline (1c).** Yellow liquid was obtained in 63% yield (1.49 g) after



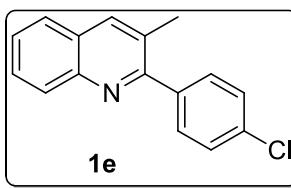
purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (d,  $J$  = 8.6 Hz, 1H), 7.89 (s, 1H), 7.68 (d,  $J$  = 8.1 Hz, 1H), 7.61 (ddd,  $J$  = 8.4, 6.9, 1.4 Hz, 1H), 7.49 – 7.25 (m, 4H), 7.09 (tdd,  $J$  = 8.7, 2.6, 1.2 Hz, 1H), 2.37 (d,  $J$  = 0.8 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.71 (d,  $J$  = 246.3 Hz), 158.97 (d,  $J$  = 2.2 Hz), 146.60 (s), 143.03 (d,  $J$  = 7.4 Hz), 137.04 (s), 129.91 (d,  $J$  = 8.2 Hz), 129.31 (s), 128.96 (s), 128.91 (s), 127.70 (s), 126.80 (s), 126.69 (s), 124.74 (d,  $J$  = 3.0 Hz), 116.13 (d,  $J$  = 22.1 Hz), 115.17 (d,  $J$  = 21.1 Hz), 20.47 (s). HRMS calcd for  $\text{C}_{16}\text{H}_{13}\text{FN}$  [M+H] $^+$ : 238.1027, found: 238.1034.

**2-(4-Fluorophenyl)-3-methylquinoline (1d).** Yellow solid was obtained in 67% yield (1.59 g) after



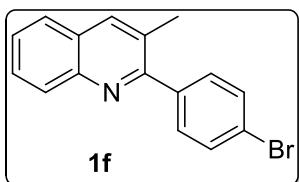
purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 64-66 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (d,  $J$  = 8.5 Hz, 1H), 7.96 (s, 1H), 7.74 (d,  $J$  = 8.1 Hz, 1H), 7.64 (ddd,  $J$  = 8.4, 6.9, 1.4 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.49 (ddd,  $J$  = 8.1, 6.9, 1.1 Hz, 1H), 7.21 – 7.10 (m, 2H), 2.42 (d,  $J$  = 0.7 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.83 (d,  $J$  = 247.3 Hz), 159.40 (s), 146.65 (s), 136.95 (s), 130.81 (d,  $J$  = 8.2 Hz), 129.25 (s), 129.07 (s), 128.83 (d,  $J$  = 14.6 Hz), 127.62 (s), 126.84 (s), 126.77 (s), 126.56 (s), 115.29 (d,  $J$  = 21.5 Hz), 20.64 (s). HRMS calcd for  $\text{C}_{16}\text{H}_{13}\text{FN}$  [M+H] $^+$ : 238.1027, found: 238.1027.

**2-(4-Chlorophenyl)-3-methylquinoline (1e).<sup>2</sup>** Yellow solid was obtained in 70% yield (1.78 g) after



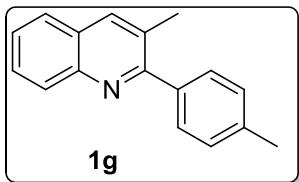
purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 84-86 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 (d,  $J$  = 8.5 Hz, 1H), 7.99 (s, 1H), 7.76 (d,  $J$  = 8.1 Hz, 1H), 7.65 (ddd,  $J$  = 8.4, 7.0, 1.3 Hz, 1H), 7.59 – 7.39 (m, 5H), 2.44 (s, 3H).

**2-(4-Bromophenyl)-3-methylquinoline (1f).**<sup>2</sup> Yellow solid was obtained in 60% yield (1.79 g) after



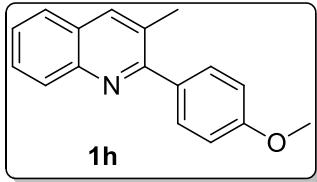
purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 90-92 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.10 (d, *J* = 8.5 Hz, 1H), 8.01 (s, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.71 – 7.58 (m, 3H), 7.56 – 7.41 (m, 3H), 2.45 (s, 3H).

**2-(4-Methylphenyl)-3-methylquinoline (1g).**<sup>1,2</sup> Yellow solid was obtained in 75% yield (1.75 g) after



purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 54-56 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12 (d, *J* = 8.3 Hz, 1H), 7.99 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.56 – 7.45 (m, 3H), 7.29 (d, *J* = 7.8 Hz, 2H), 2.47 (d, *J* = 0.6 Hz, 3H), 2.43 (s, 3H).

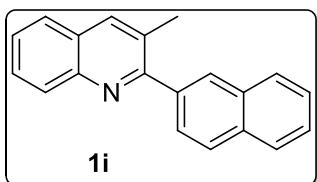
**2-(4-Methoxyphenyl)-3-methylquinoline (1h).**<sup>1,2</sup> Yellow solid was obtained in 68% yield (1.70 g) after



purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 68-70 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.11 (d, *J* = 8.5 Hz, 1H), 7.90 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.61 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.48 – 7.40 (m, 1H), 7.05 – 6.92 (m, 2H), 3.81 (s, 3H), 2.43 (s, 3H).

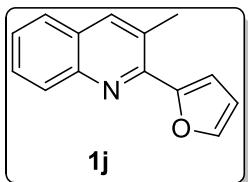
3H).

**3-Methyl-2-(naphthalen-2-yl)quinoline (1i).** Yellow solid was obtained in 56% yield (1.51 g) after



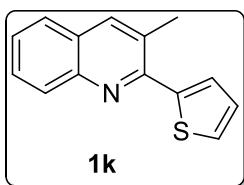
purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 86-88 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16 (d, *J* = 8.4 Hz, 1H), 8.06 (s, 1H), 8.02 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.89 (dd, *J* = 9.2, 4.4 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.71 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.69 – 7.63 (m, 1H), 7.55 – 7.45 (m, 3H), 2.48 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.46 (s), 146.75 (s), 138.35 (s), 136.88 (s), 133.19 (d, *J* = 15.1 Hz), 129.40 (d, *J* = 8.9 Hz), 128.87 (s), 128.37 (d, *J* = 18.3 Hz), 127.98 (s), 127.72 (d, *J* = 8.7 Hz), 126.78 (d, *J* = 3.6 Hz), 126.62 – 126.19 (m), 20.74 (s). HRMS calcd for C<sub>16</sub>H<sub>17</sub>BrN [M+H]<sup>+</sup>: 302.0539, found: 302.0534. HRMS calcd for C<sub>20</sub>H<sub>16</sub>N [M+H]<sup>+</sup>: 270.1277, found: 270.1284.

**2-(Furan-2-yl)-3-methylquinoline (1j).**<sup>2</sup> Yellow solid was obtained in 50% yield (1.05 g) after



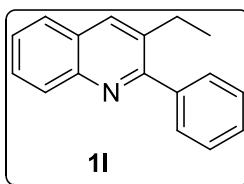
purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 50-52 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13 (d, *J* = 8.5 Hz, 1H), 7.90 (s, 1H), 7.72 – 7.58 (m, 3H), 7.44 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.10 (dd, *J* = 3.4, 0.6 Hz, 1H), 6.57 (dd, *J* = 3.4, 1.8 Hz, 1H), 2.66 (d, *J* = 0.7 Hz, 3H).

**3-Methyl-2-(thiophen-2-yl)quinoline (1k).**<sup>2</sup> Yellow solid was obtained in 46% yield (1.04 g) after



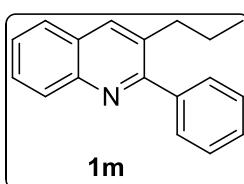
purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 64-66 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.88 (s, 1H), 7.71 – 7.52 (m, 3H), 7.49 – 7.38 (m, 2H), 7.13 (dd, *J* = 5.1, 3.7 Hz, 1H), 2.65 (d, *J* = 0.6 Hz, 3H).

**3-Ethyl-2-phenylquinoline (1l).**<sup>2</sup> Yellow solid was obtained in 76% yield (1.77 g) after purification with



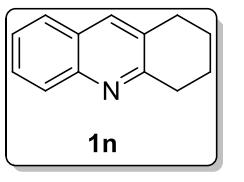
column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 52-54 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13 (d, *J* = 8.5 Hz, 1H), 8.04 (s, 1H), 7.80 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.65 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.59 – 7.39 (m, 6H), 2.79 (q, *J* = 7.4 Hz, 2H), 1.19 (t, *J* = 7.5 Hz, 3H).

**2-Phenyl-3-propylquinoline (1m).**<sup>2</sup> Yellow liquid was obtained in 74% yield (1.83 g) after purification



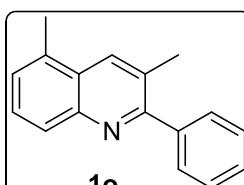
with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13 (d, *J* = 8.5 Hz, 1H), 8.00 (s, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.64 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.58 – 7.37 (m, 6H), 2.83 – 2.62 (m, 2H), 1.68 – 1.45 (m, 2H), 0.94 – 0.73 (m, 3H).

**1,2,3,4-Tetrahydroacridine (1n).**<sup>3</sup> Yellow solid was obtained in 56% yield (1.03 g) after purification with



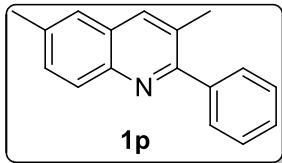
column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 46-48 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.60 – 7.37 (m, 3H), 7.30 (dd, *J* = 10.8, 3.9 Hz, 1H), 3.02 (q, *J* = 6.1 Hz, 2H), 2.68 (q, *J* = 6.5 Hz, 2H), 1.88 – 1.76 (m, 2H), 1.75 – 1.62 (m, 2H).

**3,5-Dimethyl-2-phenylquinoline (1o).** Yellow solid was obtained in 66% yield (1.54 g) after purification



with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 72-74 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 (s, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.55 – 7.38 (m, 4H), 7.31 (d, *J* = 7.0 Hz, 1H), 2.66 (s, 3H), 2.47 (d, *J* = 0.7 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.95 (s), 146.90 (s), 140.96 (s), 133.49 (d, *J* = 16.9 Hz), 128.94 (s), 128.73 (s), 128.32 (t, *J* = 14.4 Hz), 127.65 (s), 126.88 (d, *J* = 2.6 Hz), 20.94 (s), 18.69 (s). HRMS calcd for C<sub>17</sub>H<sub>16</sub>N [M+H]<sup>+</sup>: 234.1277, found: 234.1275.

**3,6-Dimethyl-2-phenylquinoline (1p).** Yellow solid was obtained in 78% yield (1.82 g) after purification



with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 66-68 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.01 (d, *J* = 8.5 Hz, 1H), 7.86 (s, 1H), 7.61 – 7.53 (m, 2H), 7.50 – 7.34 (m, 5H), 2.50 (s, 3H), 2.40 (d, *J* = 0.5 Hz, 3H).

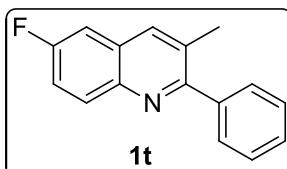
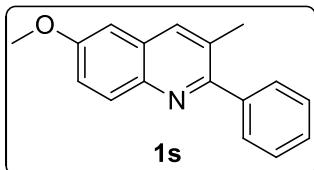
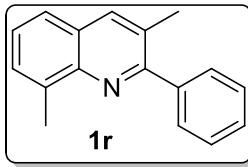
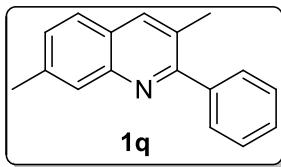
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.62 (s), 145.30 (s), 141.04 (s), 136.17 (d, *J* = 8.0 Hz), 131.07 (s), 129.22 – 128.84 (m), 128.30 (s), 128.09 (s), 127.66 (s), 125.58 (s), 21.68 (s), 20.66 (s). HRMS calcd for C<sub>17</sub>H<sub>16</sub>N [M+H]<sup>+</sup>: 234.1277, found: 234.1278.

**3,7-Dimethyl-2-phenylquinoline (1q).** Yellow solid was obtained in 75% yield (1.75 g) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 74-76 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (d, *J* = 12.2 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.58 (dd, *J* = 7.0, 1.3 Hz, 2H), 7.52 – 7.38 (m, 3H), 7.34 (dd, *J* = 8.3, 1.1 Hz, 1H), 2.54 (s, 3H), 2.44 (d, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.43 (s), 146.90 (s), 141.08 (s), 138.88 (s), 136.50 (s), 128.89 (s), 128.68 (s), 128.24 (dd, *J* = 13.5, 11.1 Hz), 126.37 (s), 125.66 (s), 21.89 (s), 20.57 (s). HRMS calcd for C<sub>17</sub>H<sub>16</sub>N [M+H]<sup>+</sup>: 234.1277, found: 234.1282.

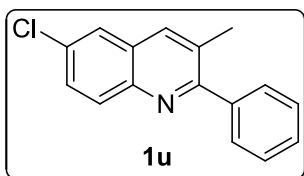
**3,8-Dimethyl-2-phenylquinoline (1r).** Yellow solid was obtained in 45% yield (1.05 g) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 38-40 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (s, 1H), 7.74 – 7.64 (m, 2H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.54 – 7.34 (m, 5H), 2.81 (s, 3H), 2.50 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.74 (s), 145.82 (s), 141.32 (s), 137.37 (s), 137.12 (s), 129.43 (s), 128.73 (d, *J* = 6.7 Hz), 128.10 (s), 127.46 (s), 126.16 (s), 124.66 (s), 20.77 (s), 17.98 (s). HRMS calcd for C<sub>17</sub>H<sub>16</sub>N [M+H]<sup>+</sup>: 234.1277, found: 234.1275.

**6-Methoxy-3-methyl-2-phenylquinoline (1s).** Yellow solid was obtained in 60% yield (1.50 g) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 80-82 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 (d, *J* = 9.2 Hz, 1H), 7.89 (s, 1H), 7.63 – 7.53 (m, 2H), 7.51 – 7.37 (m, 3H), 7.31 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.02 (d, *J* = 2.7 Hz, 1H), 3.91 (s, 3H), 2.43 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.03 (s), 157.79 (s), 142.74 (s), 140.95 (s), 135.68 (s), 130.77 (s), 129.46 (s), 128.95 (s), 128.57 (s), 128.28 (s), 128.00 (s), 121.45 (s), 104.24 (s), 55.53 (s), 20.62 (s). HRMS calcd for C<sub>17</sub>H<sub>16</sub>NO [M+H]<sup>+</sup>: 250.1226, found: 250.1221.

**6-Fluoro-3-methyl-2-phenylquinoline (1t).** Yellow solid was obtained in 70% yield (1.66 g) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 66-68 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.11 (dd, *J* = 9.2, 5.4 Hz, 1H), 7.94 (s, 1H), 7.61 – 7.54 (m, 2H), 7.52 – 7.33 (m, 5H), 2.45 (d, *J* = 0.7 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.82 (d, *J* = 187.9 Hz), 159.29 (s), 143.72 (s), 140.56 (s), 136.11 (d, *J* = 5.4 Hz), 131.80 (d, *J* = 9.2 Hz), 130.20 (s), 128.84

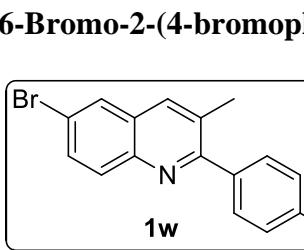


(s), 128.37 (s), 128.31 (s), 128.18 (d,  $J$  = 10.1 Hz), 118.96 (d,  $J$  = 25.8 Hz), 109.64 (d,  $J$  = 21.6 Hz), 20.64 (s). HRMS calcd for  $C_{16}H_{13}FN$  [M+H]<sup>+</sup>: 238.1027, found: 238.1032.



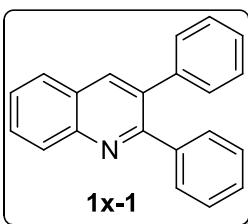
**6-Chloro-3-methyl-2-phenylquinoline (1u).** Yellow solid was obtained in 68% yield (1.72 g) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 74-76 °C. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.03 (d,  $J$  = 9.0 Hz, 1H), 7.84 (s, 1H), 7.69 (d,  $J$  = 2.3 Hz, 1H), 7.62 – 7.52 (m, 3H), 7.51 – 7.38 (m, 3H), 2.42 (d,  $J$  = 0.7 Hz, 3H). <sup>13</sup>C NMR (101 MHz,  $CDCl_3$ )  $\delta$  160.78 (s), 145.00 (s), 140.48 (s), 135.78 (s), 132.03 (s), 130.97 (s), 130.34 (s), 129.65 (s), 128.85 (s), 128.40 (d,  $J$  = 3.3 Hz), 128.15 (s), 125.37 (s), 20.70 (s). HRMS calcd for  $C_{16}H_{13}ClN$  [M+H]<sup>+</sup>: 254.0731, found: 254.0727.

**6-Bromo-3-methyl-2-phenylquinoline (1v).** Yellow solid was obtained in 78% yield (2.32 g) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 84-86 °C. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.98 (d,  $J$  = 9.0 Hz, 1H), 7.94 – 7.86 (m, 2H), 7.70 (dd,  $J$  = 8.9, 2.2 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.53 – 7.39 (m, 3H), 2.45 (d,  $J$  = 0.7 Hz, 3H). <sup>13</sup>C NMR (101 MHz,  $CDCl_3$ )  $\delta$  160.94 (s), 145.19 (s), 140.46 (s), 135.69 (s), 132.21 (s), 131.09 (s), 130.35 (s), 128.90 – 128.59 (m), 128.41 (d,  $J$  = 4.5 Hz), 120.23 (s), 77.39 (s), 77.07 (s), 76.76 (s), 20.71 (s). HRMS calcd for  $C_{16}H_{13}BrN$  [M+H]<sup>+</sup>: 298.0226, found: 298.0226.



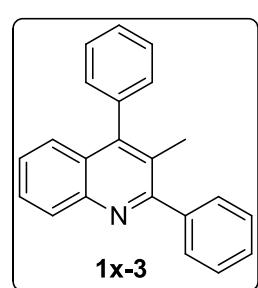
**6-Bromo-2-(4-bromophenyl)-3-methylquinoline (1w).** Yellow solid was obtained in 77% yield (2.90 g) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 190-192 °C. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.01 – 7.86 (m, 3H), 7.72 (dd,  $J$  = 8.9, 1.8 Hz, 1H), 7.63 (d,  $J$  = 8.3 Hz, 2H), 7.47 (d,  $J$  = 8.3 Hz, 2H), 2.46 (s, 3H). <sup>13</sup>C NMR (101 MHz,  $CDCl_3$ )  $\delta$  159.62 (s), 145.21 (s), 139.33 (s), 135.93 (s), 132.42 (s), 131.56 (s), 131.04 (s), 130.57 (s), 130.04 (s), 128.75 (d,  $J$  = 6.0 Hz), 122.86 (s), 120.50 (s), 99.99 (s), 20.63 (s). HRMS calcd for  $C_{16}H_{12}Br_2N$  [M+H]<sup>+</sup>: 375.9331, found: 375.9339.

**2,3-diphenylquinoline (1x-1).**<sup>4</sup> Yellow solid was obtained in 67% yield (1.88 g) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 66-68 °C. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.11 (d,  $J$  = 8.4 Hz, 1H), 8.05 (s, 1H), 7.75 (d,  $J$  = 8.0 Hz, 1H), 7.62 (t,  $J$  = 7.5 Hz, 1H), 7.44 (t,  $J$  = 7.4 Hz, 1H), 7.36 (d,  $J$  = 3.2 Hz, 2H), 7.16 (d,  $J$  = 10.1 Hz, 8H).



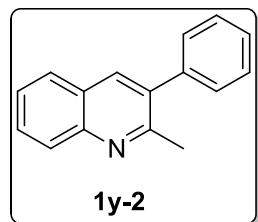
**3-isopropyl-2-phenylquinoline (1x-2).**<sup>4</sup> Yellow solid was obtained in 52% yield (1.28 g) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 50-52 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12 (d, *J* = 6.1 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 7.3 Hz, 1H), 7.58 – 7.35 (m, 6H), 3.25 (dt, *J* = 13.7, 6.8 Hz, 1H), 1.25 (d, *J* = 6.8 Hz, 6H).

**3-methyl-2,4-diphenylquinoline (1x-3).**<sup>2</sup> Yellow solid was obtained in 46% yield (1.36 g) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 140-142 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.70 – 7.58 (m, 3H), 7.57 – 7.35 (m, 8H), 7.31 (d, *J* = 7.3 Hz, 2H), 2.15 (s, 3H).

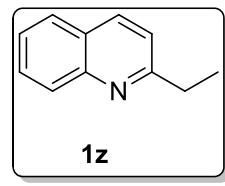


**2,3-dimethylquinoline (1y-1).**<sup>3</sup> Yellow solid was obtained in 40% yield (0.63 g) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 50-52 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.80 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 2.68 (s, 3H), 2.42 (s, 3H).

**2-methyl-3-phenylquinoline (1y-2).**<sup>5</sup> Yellow liquid was obtained in 42% yield (0.92 g) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.07 (d, *J* = 8.5 Hz, 1H), 7.92 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.54 – 7.31 (m, 7H), 2.66 (s, 3H).



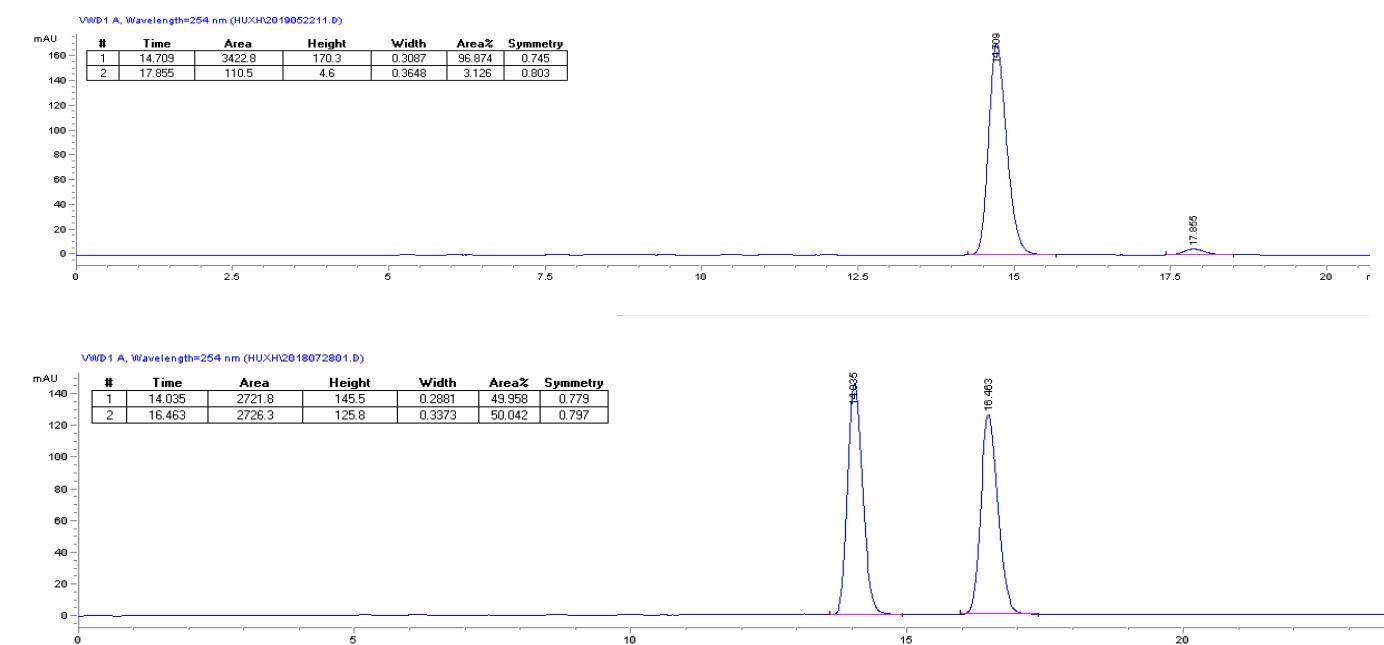
**2-ethylquinoline (1z).**<sup>3</sup> Yellow liquid was obtained in 38% yield (0.60 g) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.11 – 7.94 (m, 2H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 3.00 (q, *J* = 7.6 Hz, 2H), 1.39 (t, *J* = 7.6 Hz, 3H).



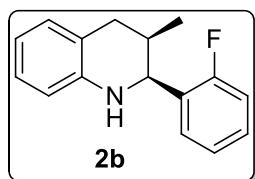
**III. Representative procedure for asymmetric hydrogenation of 2,3-disubstituted quinolones (1a) (Table 2, entry1):** In a nitrogen-filled glovebox, a mixture of [Ir(COD)Cl]<sub>2</sub> (1.3 mg, 0.0020 mmol) and (*R<sub>c</sub>,S<sub>a</sub>*)-**L3b** (3.2 mg, 0.0044 mmol) were dissolved in 2 mL of degassed dioxane in a

Schlenk tube under N<sub>2</sub>. After stirring at room temperature for 1 h, To each of the vial, 2,3-disubstituted quinoline substrate **1a** (87.7 mg, 0.4 mmol, S/C = 100) in 2 mL of degassed dioxane were then added to the catalyst solution and the resulting mixture was transferred to an autoclave which was charged with H<sub>2</sub> (10 bar). The hydrogenation was performed at room temperature (25 °C) for 24 h. After carefully releasing the hydrogen gas, the solvent was removed under reduced pressure. The crude product was purified through a silica gel plug (eluting with a mixture of hexanes/ethyl acetate = 20/1) to afford the corresponding 2,3-disubstituted tetrahydroquinoline *cis*-**2a** as a yellow solid. The enantiomeric excess was determined by chiral HPLC under conditions in the following.

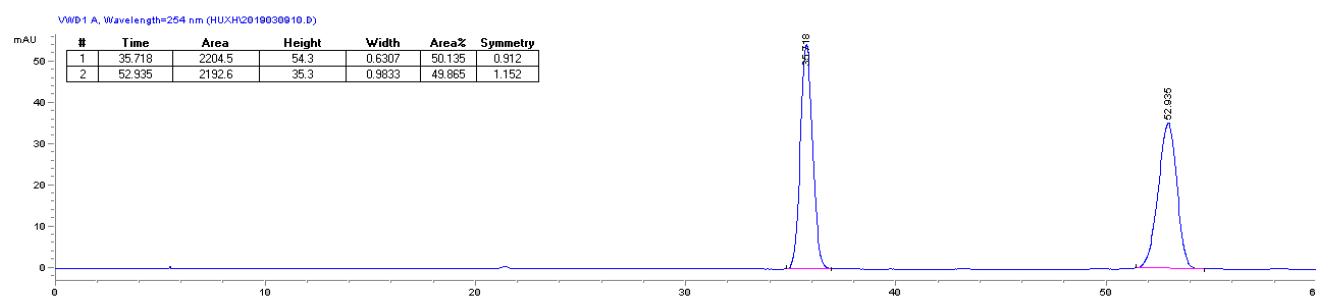
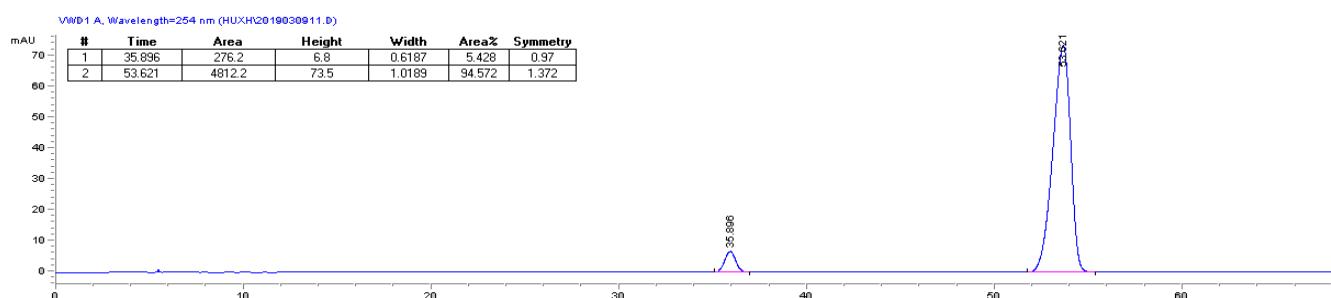
**(2S,3R)-3-Methyl-2-phenyl-1,2,3,4-tetrahydroquinoline (2a).**<sup>2</sup> Yellow solid was obtained in 96% yield (85.8 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 20/1). M.p.: 34–36 °C. 94% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 70/30, 0.8 mL/min, 254 nm, 40 °C): *t*<sub>R</sub> (major) = 14.7 min, *t*<sub>R</sub> (minor) = 17.9 min. [α]<sup>25</sup><sub>D</sub> = 17.8 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30 – 7.14 (m, 5H), 6.93 (dd, *J* = 14.5, 7.4 Hz, 2H), 6.57 (t, *J* = 7.4 Hz, 1H), 6.46 (d, *J* = 7.9 Hz, 1H), 4.42 (d, *J* = 3.5 Hz, 1H), 4.02 (bs, 1H), 2.88 (dd, *J* = 16.1, 4.9 Hz, 1H), 2.42 (dd, *J* = 16.1, 6.7 Hz, 1H), 2.22 (dt, *J* = 10.9, 5.8 Hz, 1H), 0.74 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.12 (s), 141.89 (s), 128.67 (s), 127.08 (s), 126.10 (d, *J* = 5.9 Hz), 125.84 (s), 118.98 (s), 116.04 (s), 112.63 (s), 58.32 (s), 32.34 (s), 30.85 (s), 14.11 (s).



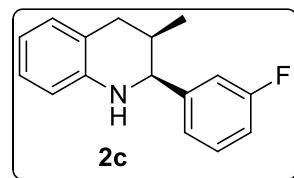
**(2S,3R)-2-(2-Fluorophenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (2b).** Yellow liquid was obtained in



95% yield (91.6 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). 89% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, 0.6 mL/min, 254 nm, 40 °C): *t<sub>R</sub>* (minor) = 35.9 min, *t<sub>R</sub>* (major) = 53.6 min.  $[\alpha]^{25}_D$  = 38.2 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39 (td, *J* = 7.6, 1.7 Hz, 1H), 7.22 (tdd, *J* = 7.2, 5.3, 1.8 Hz, 1H), 7.08 (td, *J* = 7.5, 1.0 Hz, 1H), 7.05 – 6.97 (m, 3H), 6.66 (td, *J* = 7.4, 1.1 Hz, 1H), 6.55 (dd, *J* = 7.9, 0.8 Hz, 1H), 4.90 (d, *J* = 3.7 Hz, 1H), 4.01 (bs, 1H), 2.93 (dd, *J* = 16.1, 4.7 Hz, 1H), 2.49 (dd, *J* = 16.1, 7.3 Hz, 1H), 2.43 – 2.32 (m, 1H), 0.84 (dd, *J* = 6.9, 1.7 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.05 (d, *J* = 245.7 Hz), 144.07 (s), 130.16 (d, *J* = 12.8 Hz), 129.73 (s), 128.49 (d, *J* = 2.6 Hz), 128.43 (d, *J* = 1.2 Hz), 126.94 (s), 124.00 (d, *J* = 3.5 Hz), 120.10 (s), 117.20 (s), 114.97 (d, *J* = 22.4 Hz), 113.72 (s), 51.75 (d, *J* = 2.8 Hz), 32.95 (s), 30.59 (s), 15.12 (s). HRMS calcd for C<sub>16</sub>H<sub>17</sub>FN [M+H]<sup>+</sup>: 242.1340, found: 242.1338.

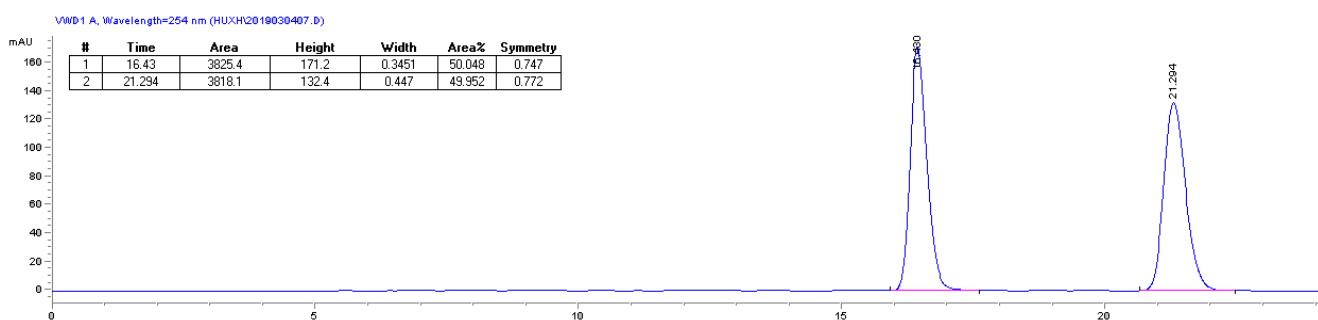
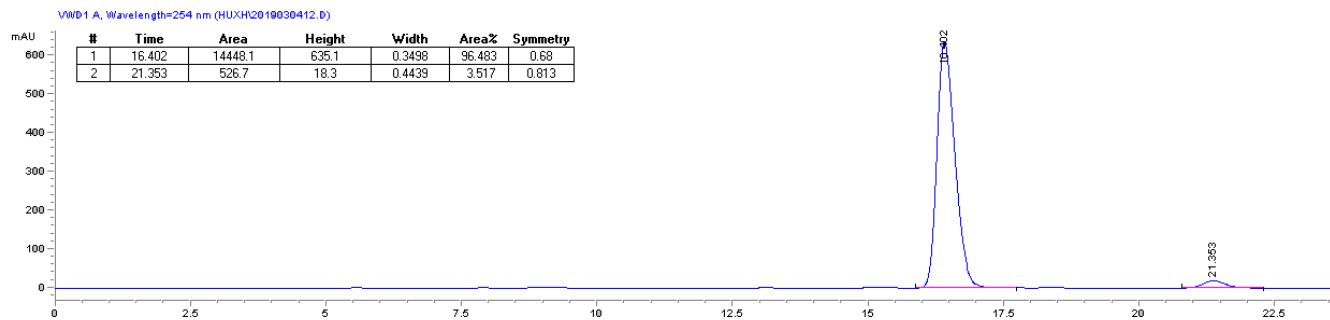


**(2S,3R)-2-(3-Fluorophenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (2c).** Yellow liquid was obtained in

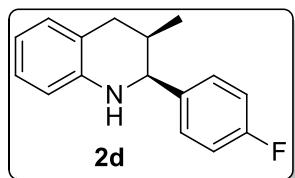


96% yield (92.5 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). 93% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, 0.6 mL/min, 254 nm, 40 °C): *t<sub>R</sub>* (major) = 16.4 min, *t<sub>R</sub>* (minor) = 21.3 min.  $[\alpha]^{25}_D$  = 17.8 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 – 7.22 (m, 1H), 7.09 – 6.88 (m, 5H), 6.65 (t, *J* = 7.4 Hz, 1H), 6.54 (d, *J* = 7.9 Hz, 1H), 4.48 (d, *J* = 3.5 Hz, 1H), 3.99 (bs, 1H), 2.96 (dd, *J* = 16.2, 4.9 Hz, 1H), 2.48 (dd, *J* = 16.2, 6.6 Hz, 1H), 2.35 – 2.20 (m, 1H), 0.81 (dd, *J* = 6.9, 1.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.83 (d, *J* = 245.4 Hz),

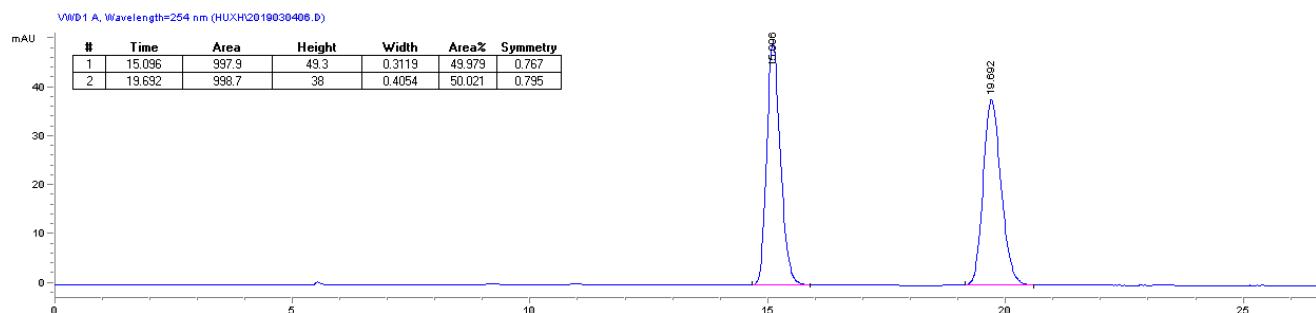
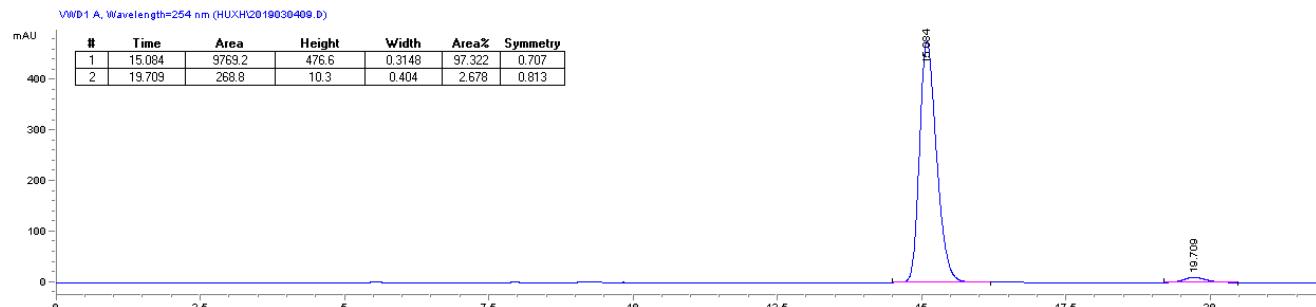
145.78 (d,  $J = 6.4$  Hz), 143.80 (s), 129.79 (s), 129.61 (d,  $J = 8.2$  Hz), 127.01 (s), 122.81 (d,  $J = 2.7$  Hz), 119.95 (s), 117.45 (s), 114.21 (s), 114.04 (d,  $J = 9.8$  Hz), 113.87 (s), 59.04 (s), 33.36 (s), 31.93 (s), 15.12 (s). HRMS calcd for  $C_{16}H_{17}FN$  [M+H]<sup>+</sup>: 242.1340, found: 242.1342.



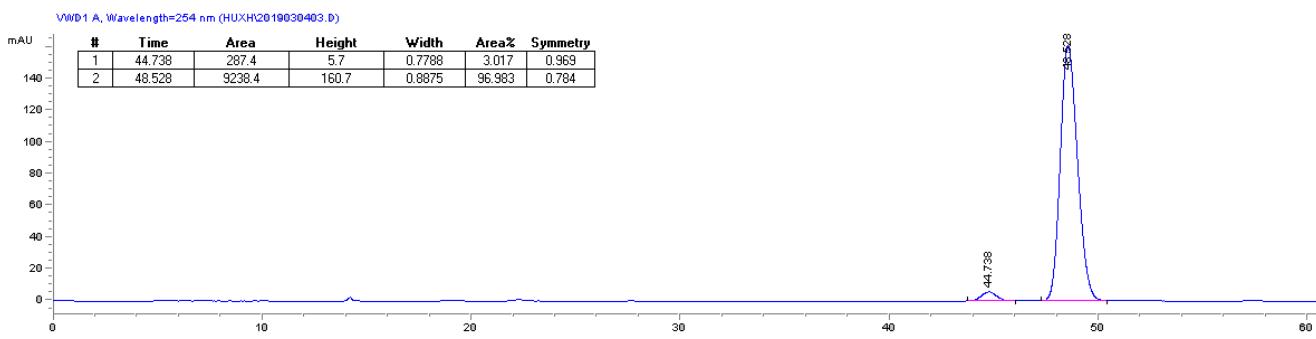
**(2S,3R)-2-(4-fluorophenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (2d).** Yellow liquid was obtained in 96% yield (92.3 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate,

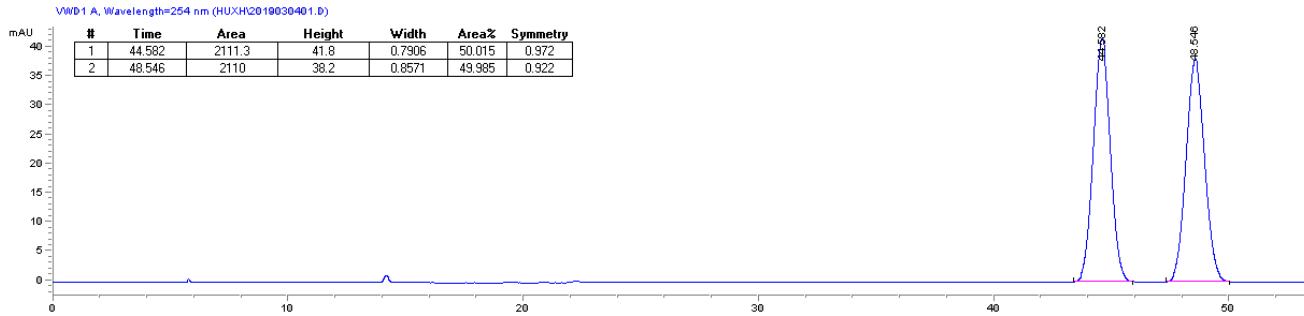


10/1). 95% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, 0.6 mL/min, 254 nm, 40 °C):  $t_R$  (major) = 15.1 min,  $t_R$  (minor) = 19.7 min.  $[\alpha]^{25}_D = 11.7$  (c 1.0,  $CH_2Cl_2$ ). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.27 – 7.17 (m, 2H), 7.06 – 6.91 (m, 4H), 6.65 (dd,  $J = 10.7, 4.0$  Hz, 1H), 6.53 (d,  $J = 7.9$  Hz, 1H), 4.46 (d,  $J = 3.5$  Hz, 1H), 4.05 (bs, 1H), 2.93 (dd,  $J = 16.2, 4.9$  Hz, 1H), 2.46 (dd,  $J = 16.2, 6.9$  Hz, 1H), 2.32 – 2.16 (m, 1H), 0.79 (d,  $J = 6.9$  Hz, 3H). <sup>13</sup>C NMR (101 MHz,  $CDCl_3$ )  $\delta$  162.03 (d,  $J = 245.1$  Hz), 143.98 (s), 138.67 (d,  $J = 3.1$  Hz), 129.78 (s), 128.70 (d,  $J = 7.9$  Hz), 127.02 (s), 120.00 (s), 117.32 (s), 114.96 (d,  $J = 21.2$  Hz), 113.80 (s), 58.80 (s), 33.23 (s), 31.94 (s), 15.24 (s). HRMS calcd for  $C_{16}H_{17}FN$  [M+H]<sup>+</sup>: 242.1340, found: 242.1345.

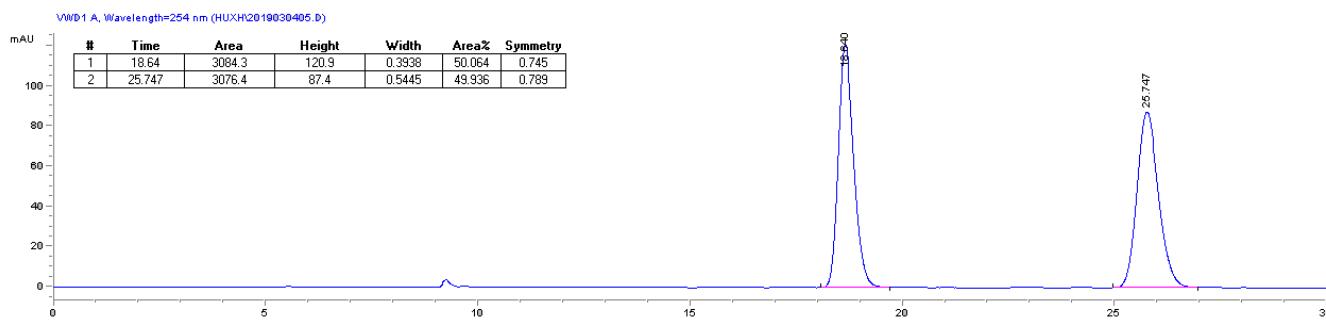
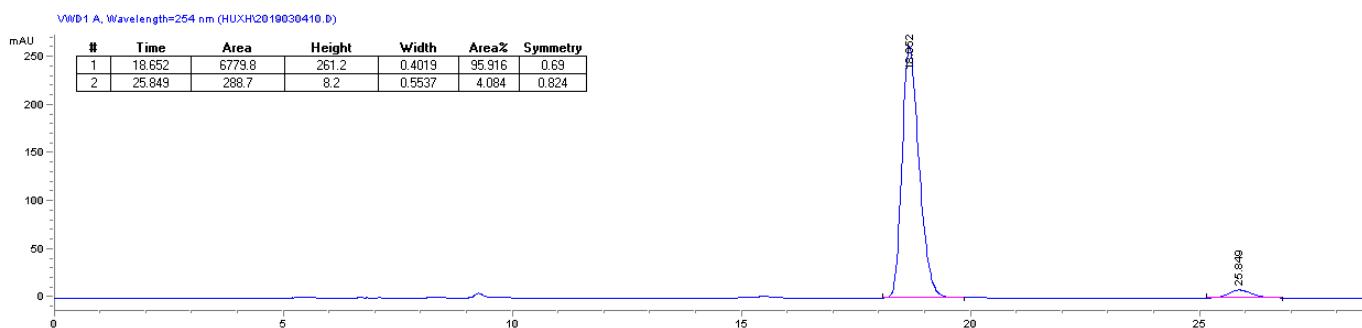


**(2S,3R)-2-(4-Chlorophenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (2e).**<sup>2</sup> Yellow solid was obtained in 97% yield (100.0 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 50-52 °C. 94% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, 0.6 mL/min, 254 nm, 40 °C): *t*<sub>R</sub> (minor) = 44.7 min, *t*<sub>R</sub> (major) = 48.5 min. [α]<sup>25</sup><sub>D</sub> = 22.0 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.29 – 7.23 (m, 2H), 7.19 (dd, *J* = 6.1, 4.2 Hz, 2H), 7.05 – 6.92 (m, 2H), 6.65 (td, *J* = 7.4, 1.1 Hz, 1H), 6.52 (dd, *J* = 7.9, 0.7 Hz, 1H), 4.44 (d, *J* = 3.6 Hz, 1H), 4.02 (bs, 1H), 2.92 (dd, *J* = 16.2, 4.9 Hz, 1H), 2.44 (dd, *J* = 16.2, 6.9 Hz, 1H), 2.30 – 2.18 (m, 1H), 0.78 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.89 (s), 141.51 (s), 132.84 (s), 129.79 (s), 128.61 (s), 128.31 (s), 127.99 (s), 127.12 (d, *J* = 12.6 Hz), 119.98 (s), 117.39 (s), 113.84 (s), 58.87 (s), 33.21 (s), 31.88 (s), 15.27 (s).

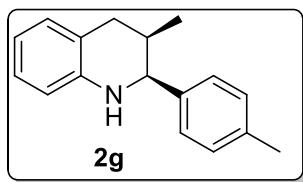




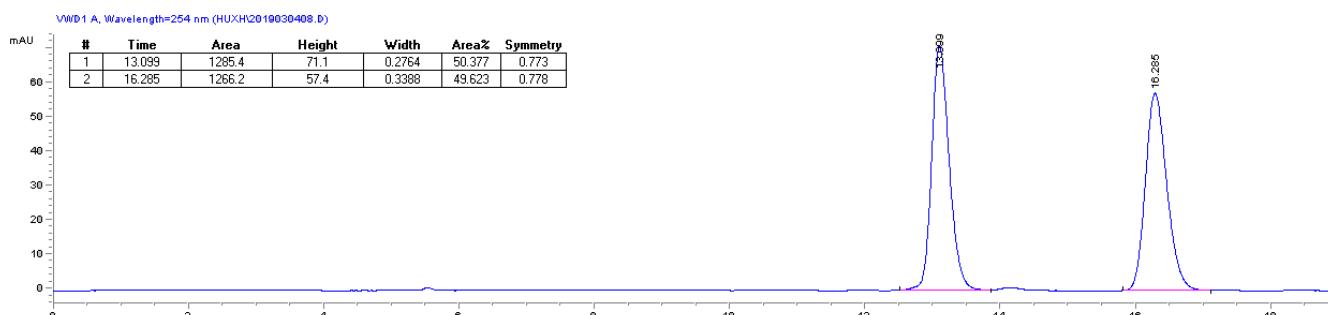
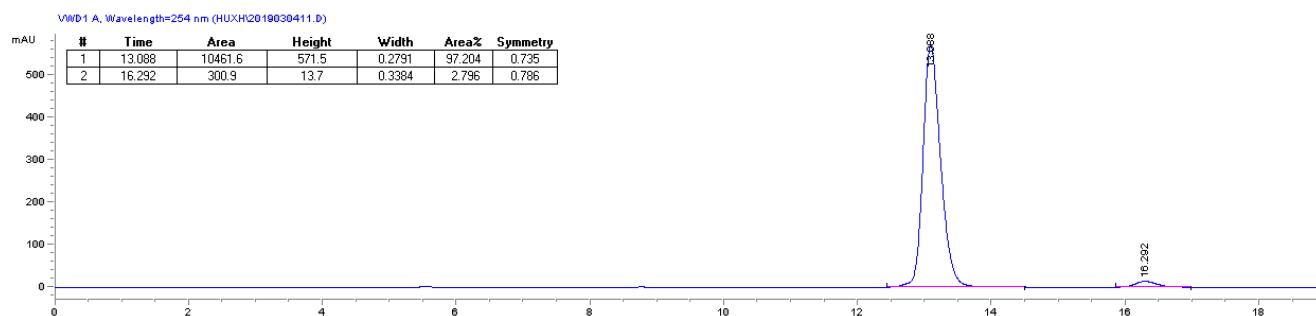
**(2S,3R)-2-(4-Bromophenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (2f).**<sup>2</sup> Yellow solid was obtained in 97% yield (117.5 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 60-62 °C. 92% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, 0.6 mL/min, 254 nm, 40 °C): *t*<sub>R</sub> (major) = 18.6 min, *t*<sub>R</sub> (minor) = 25.8 min. [α]<sup>25</sup><sub>D</sub> = 20.5 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.00 (dd, *J* = 16.9, 7.8 Hz, 2H), 6.65 (td, *J* = 7.4, 0.9 Hz, 1H), 6.53 (d, *J* = 7.9 Hz, 1H), 4.44 (d, *J* = 3.6 Hz, 1H), 4.04 (bs, 1H), 2.93 (dd, *J* = 16.2, 4.8 Hz, 1H), 2.45 (dd, *J* = 16.2, 6.8 Hz, 1H), 2.34 – 2.17 (m, 1H), 0.79 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.84 (s), 142.01 (s), 131.24 (s), 129.78 (s), 128.97 (s), 127.04 (s), 120.93 (s), 119.96 (s), 117.39 (s), 113.82 (s), 58.91 (s), 33.18 (s), 31.81 (s), 15.25 (s).



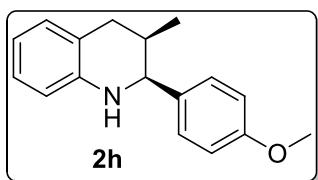
**(2S,3R)-3-Methyl-2-(p-tolyl)-1,2,3,4-tetrahydroquinoline (2g).**<sup>2</sup> Yellow solid was obtained in 96% yield



(90.8 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 54-56 °C. 94% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, 0.6 mL/min, 254 nm, 40 °C): *t*<sub>R</sub> (major) = 13.1 min, *t*<sub>R</sub> (minor) = 16.3 min. [α]<sup>25</sup><sub>D</sub> = 21.8 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.16 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.99 (dd, *J* = 14.4, 7.2 Hz, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 7.9 Hz, 1H), 4.44 (d, *J* = 3.2 Hz, 1H), 4.03 (bs, 1H), 2.93 (dd, *J* = 16.1, 4.7 Hz, 1H), 2.48 (dd, *J* = 16.1, 6.7 Hz, 1H), 2.32 (s, 3H), 2.26 (tdd, *J* = 8.8, 6.0, 3.1 Hz, 1H), 0.90 – 0.73 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.30 (s), 139.99 (s), 136.75 (s), 129.78 (s), 128.88 (s), 127.16 (s), 126.94 (s), 120.12 (s), 117.09 (s), 113.74 (s), 59.21 (s), 33.47 (s), 31.98 (s), 21.15 (s), 15.25 (s).

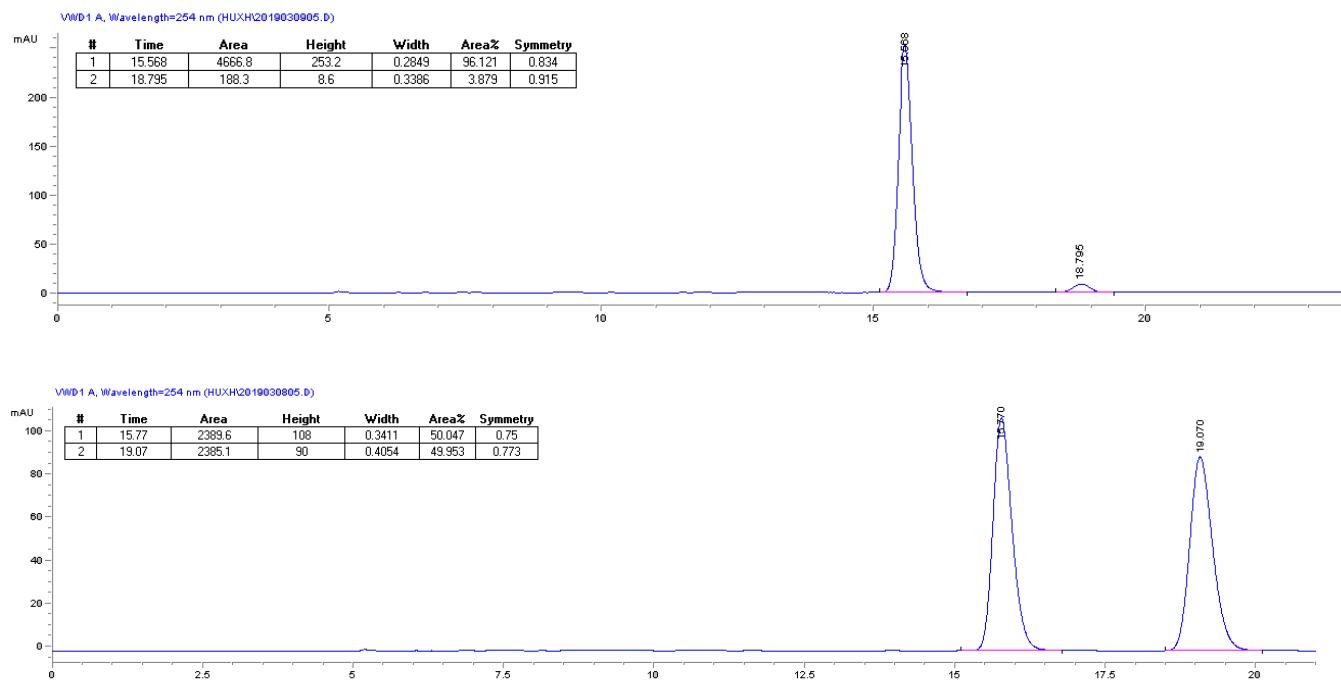


**(2S,3R)-2-(4-Methoxyphenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (2h).**<sup>2</sup> White solid was obtained in

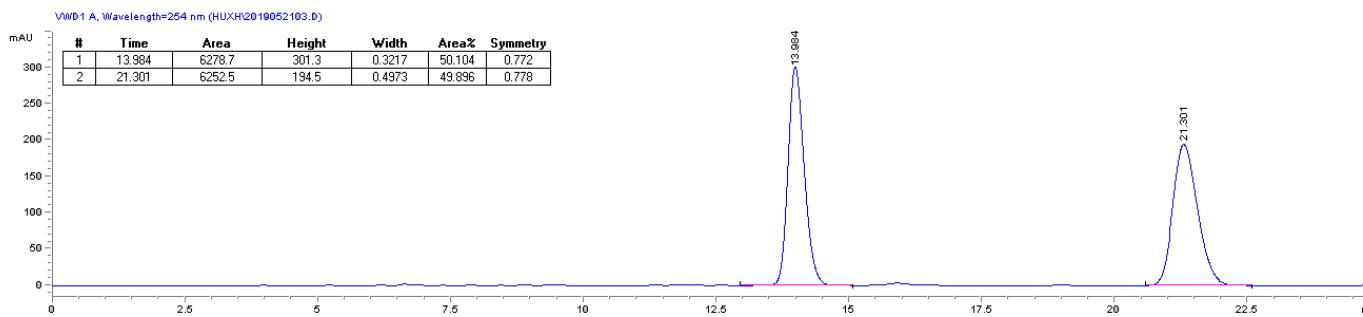
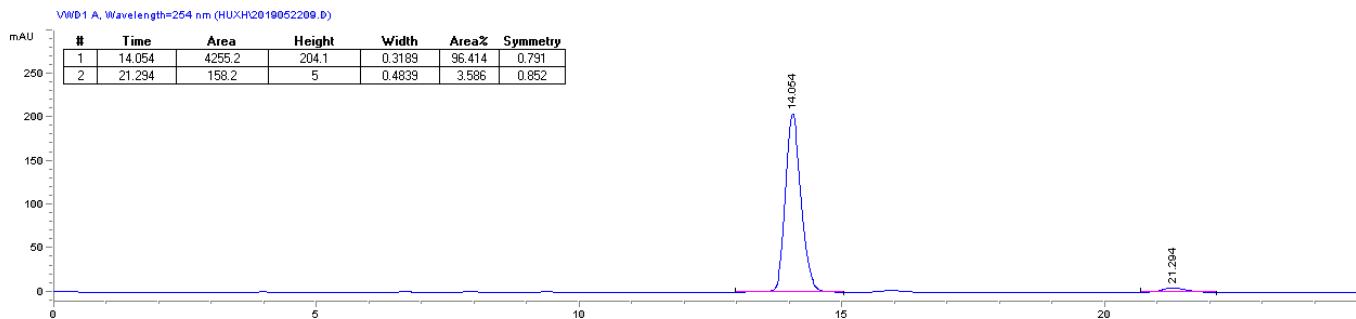


99% yield (100.2 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 108-110 °C. 92% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, 0.6 mL/min, 254 nm, 40 °C): *t*<sub>R</sub> (major) = 15.6 min, *t*<sub>R</sub> (minor) = 18.8 min. [α]<sup>25</sup><sub>D</sub> = 18.3 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.24 – 7.15 (m, 2H), 7.00 (dd, *J* = 14.3, 7.3 Hz, 2H), 6.84 (d, *J* = 8.2 Hz, 2H), 6.64 (t, *J* = 7.4 Hz, 1H), 6.53 (d, *J* = 7.9 Hz, 1H), 4.44 (d, *J* = 3.5 Hz, 1H), 4.07 (bs, 1H), 3.78 (s, 3H), 2.93 (dd, *J* = 16.1, 4.9 Hz, 1H), 2.47 (dd, *J* = 16.1, 6.8 Hz, 1H), 2.25 (ddd, *J* = 11.0, 7.0, 4.2 Hz, 1H), 0.81 (dd, *J* = 6.8, 0.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.75 (s), 144.24 (s), 135.06 (s),

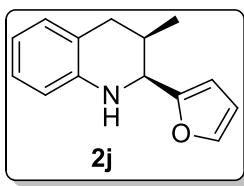
129.73 (s), 128.25 (s), 126.91 (s), 120.11 (s), 117.06 (s), 113.61 (d,  $J$  = 20.0 Hz), 58.85 (s), 55.30 (s), 33.34 (s), 32.01 (s), 15.28 (s).



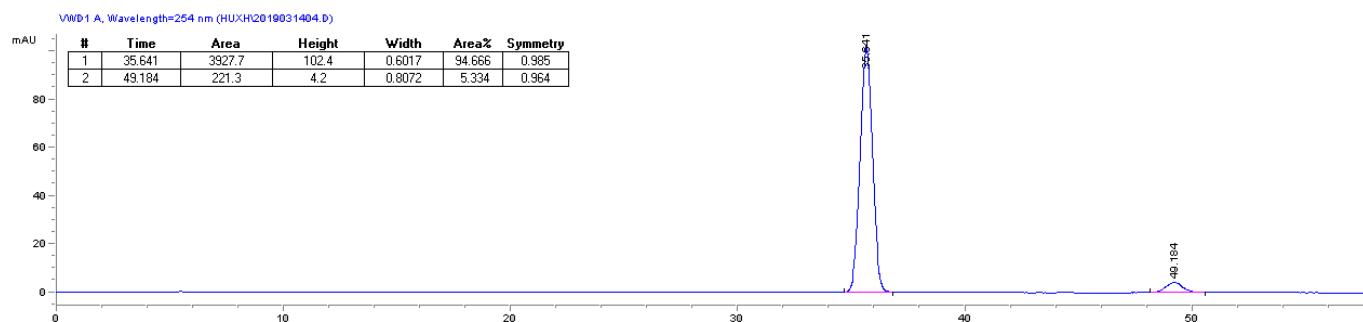
**(2S,3R)-3-Methyl-2-(naphthalen-2-yl)-1,2,3,4-tetrahydroquinoline (2i).** Yellow liquid was obtained in 95% yield (103.9 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). 93% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm, 40 °C):  $t_R$  (major) = 14.0 min,  $t_R$  (minor) = 21.3 min.  $[\alpha]^{25}_D$  = -17.3 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.77 (ddd,  $J$  = 20.4, 10.9, 5.5 Hz, 4H), 7.50 – 7.32 (m, 3H), 7.08 – 6.94 (m, 2H), 6.67 (td,  $J$  = 7.4, 1.1 Hz, 1H), 6.57 (dd,  $J$  = 7.9, 0.8 Hz, 1H), 4.62 (d,  $J$  = 3.5 Hz, 1H), 4.14 (bs, 1H), 3.00 (dd,  $J$  = 16.1, 5.0 Hz, 1H), 2.53 (dd,  $J$  = 16.1, 6.2 Hz, 1H), 2.35 (tdd,  $J$  = 6.4, 5.1, 3.7 Hz, 1H), 0.81 (d,  $J$  = 6.9 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.23 (s), 140.57 (s), 133.28 (s), 132.83 (s), 129.89 (s), 128.09 – 127.60 (m), 127.01 (s), 126.16 (s), 125.78 (d,  $J$  = 9.1 Hz), 125.50 (s), 120.15 (s), 117.32 (s), 113.90 (s), 59.49 (s), 33.75 (s), 32.11 (s), 15.05 (s). HRMS calcd for C<sub>20</sub>H<sub>20</sub>N [M+H]<sup>+</sup>: 274.1590, found: 274.1596.

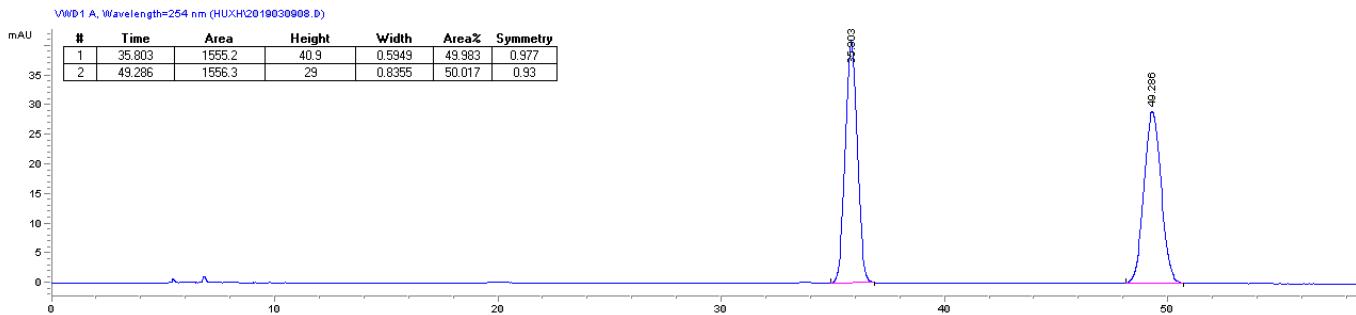


**(2S,3R)-2-(furan-2-yl)-3-methyl-1,2,3,4-tetrahydroquinoline (2j).**<sup>2</sup> Colorless liquid was obtained in 94%

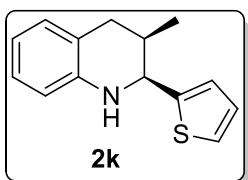


yield (80.6 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 20/1). 89% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, 0.6 mL/min, 254 nm, 40 °C): *t*<sub>R</sub> (major) = 35.6 min, *t*<sub>R</sub> (minor) = 49.2 min. [α]<sup>25</sup><sub>D</sub> = 95.1 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33 (d, *J* = 0.8 Hz, 1H), 6.99 (dd, *J* = 13.5, 7.3 Hz, 2H), 6.65 (t, *J* = 7.4 Hz, 1H), 6.52 (d, *J* = 7.9 Hz, 1H), 6.35 – 6.23 (m, 1H), 6.12 (d, *J* = 3.2 Hz, 1H), 4.50 (d, *J* = 3.6 Hz, 1H), 4.04 (bs, 1H), 2.87 (dd, *J* = 16.1, 4.9 Hz, 1H), 2.53 (dd, *J* = 16.1, 8.0 Hz, 1H), 2.45 – 2.28 (m, 1H), 0.92 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 156.18 (s), 143.24 (s), 141.41 (s), 129.62 (s), 126.85 (s), 120.49 (s), 117.57 (s), 114.12 (s), 110.16 (s), 106.16 (s), 54.01 (s), 32.86 (s), 30.51 (s), 16.08 (s).

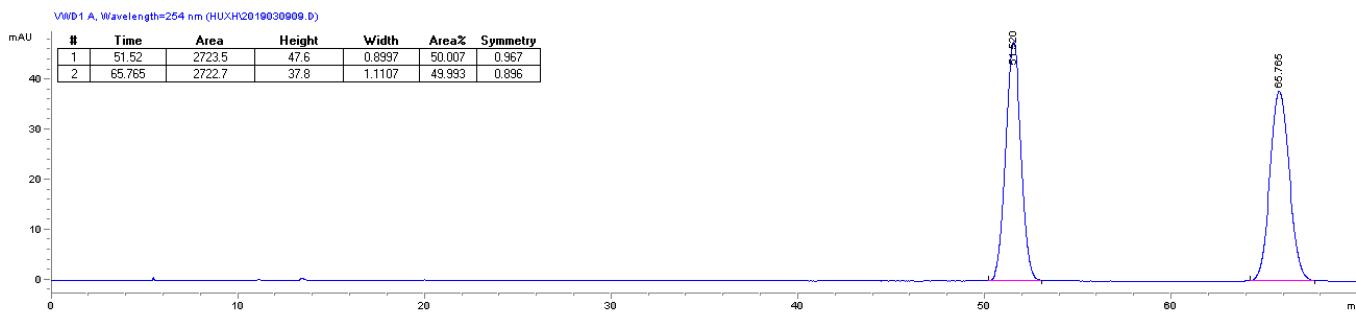
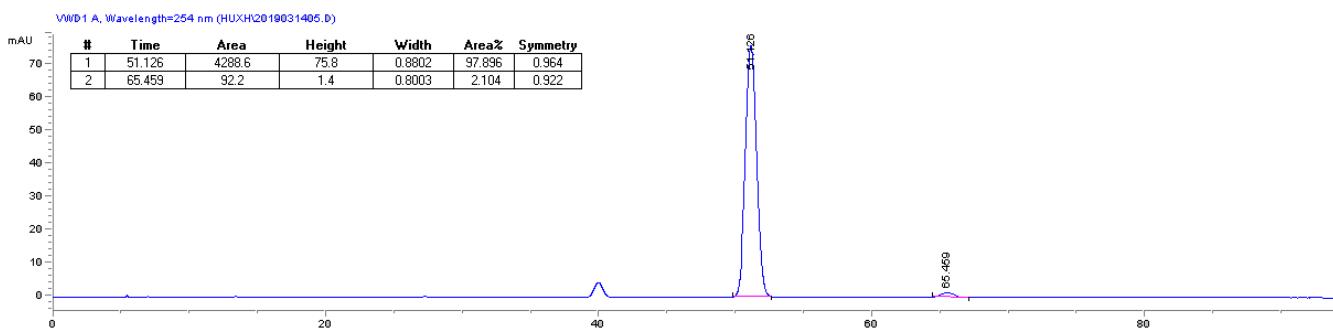




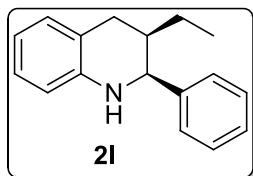
**(2S,3R)-3-Methyl-2-(thiophen-2-yl)-1,2,3,4-tetrahydroquinoline (2k).**<sup>2</sup> Colorless liquid was obtained in



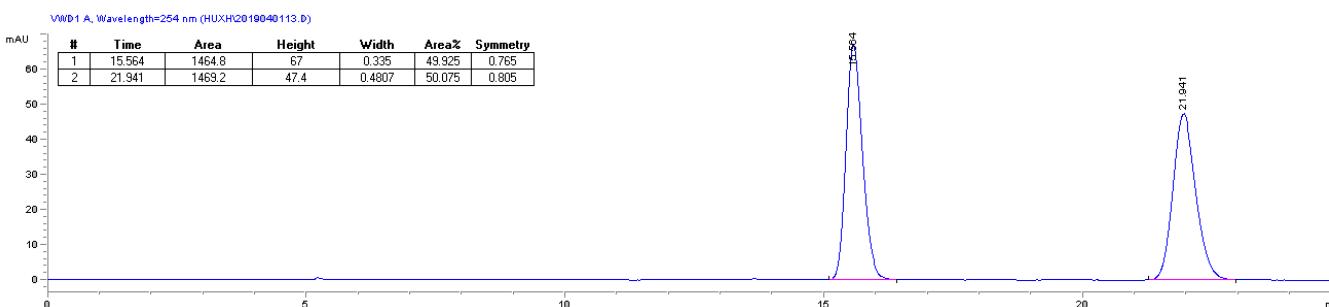
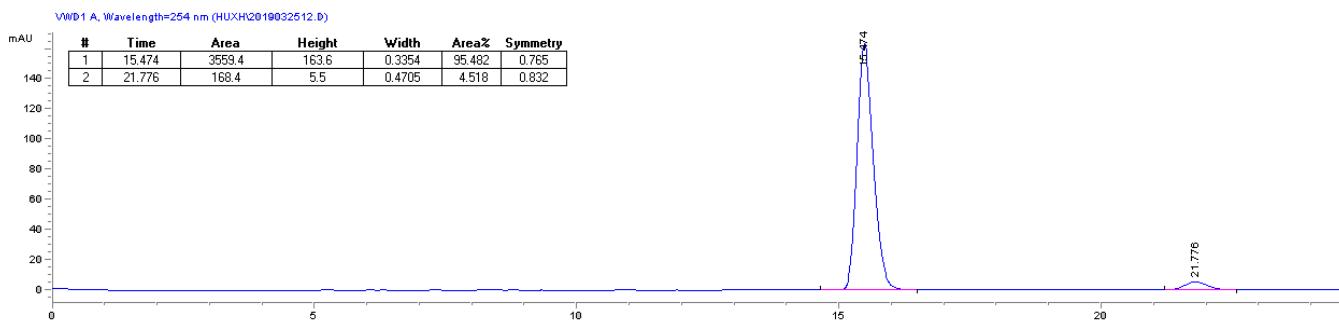
95% yield (87.5 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). 95% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, 0.6 mL/min, 254 nm, 40 °C): *t*<sub>R</sub> (major) = 51.1 min, *t*<sub>R</sub> (minor) = 65.4 min. [α]<sup>25</sup><sub>D</sub> = 105.7 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.17 (d, *J* = 5.0 Hz, 1H), 7.06 – 6.89 (m, 4H), 6.73 – 6.60 (m, 1H), 6.52 (d, *J* = 7.9 Hz, 1H), 4.73 (d, *J* = 3.4 Hz, 1H), 4.17 (bs, 1H), 2.93 (dd, *J* = 16.3, 5.0 Hz, 1H), 2.57 (dd, *J* = 16.3, 7.6 Hz, 1H), 2.41 – 2.23 (m, 1H), 0.92 (dd, *J* = 6.9, 1.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.12 (s), 143.27 (s), 129.69 (s), 126.96 (s), 126.55 (s), 124.33 (s), 123.93 (s), 120.37 (s), 117.79 (s), 114.31 (s), 55.89 (s), 32.87 (s), 32.18 (s), 16.03 (s).



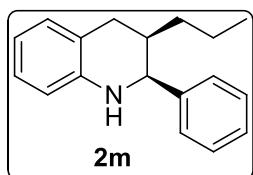
**(2S,3R)-3-Ethyl-2-phenyl-1,2,3,4-tetrahydroquinoline (2l).**<sup>2</sup> Colorless liquid was obtained in 96% yield



(91.5 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 20/1). 91% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, 0.6 mL/min, 254 nm, 40 °C): *t<sub>R</sub>* (major) = 15.5 min, *t<sub>R</sub>* (minor) = 21.8 min. [α]<sup>25</sup><sub>D</sub> = 59.2 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 – 7.19 (m, 5H), 7.07 – 6.92 (m, 2H), 6.64 (td, *J* = 7.4, 1.1 Hz, 1H), 6.52 (d, *J* = 7.9 Hz, 1H), 4.52 (d, *J* = 3.8 Hz, 1H), 4.19 (bs, 1H), 2.86 (dd, *J* = 16.3, 4.7 Hz, 1H), 2.53 (dd, *J* = 16.3, 8.6 Hz, 1H), 2.05 (dq, *J* = 13.0, 4.4 Hz, 1H), 1.28 (dtd, *J* = 12.1, 7.3, 5.0 Hz, 1H), 1.02 (ddt, *J* = 13.8, 8.8, 7.1 Hz, 1H), 0.89 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.40 (s), 143.20 (s), 129.71 (s), 128.16 (s), 127.41 – 126.96 (m), 120.25 (s), 116.99 (s), 113.62 (s), 58.91 (s), 38.90 (s), 29.56 (s), 22.57 (s), 12.10 (s).

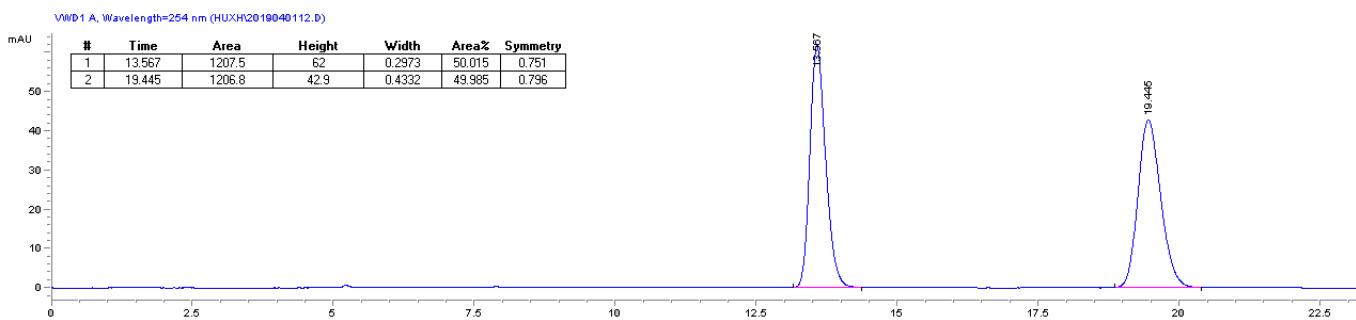
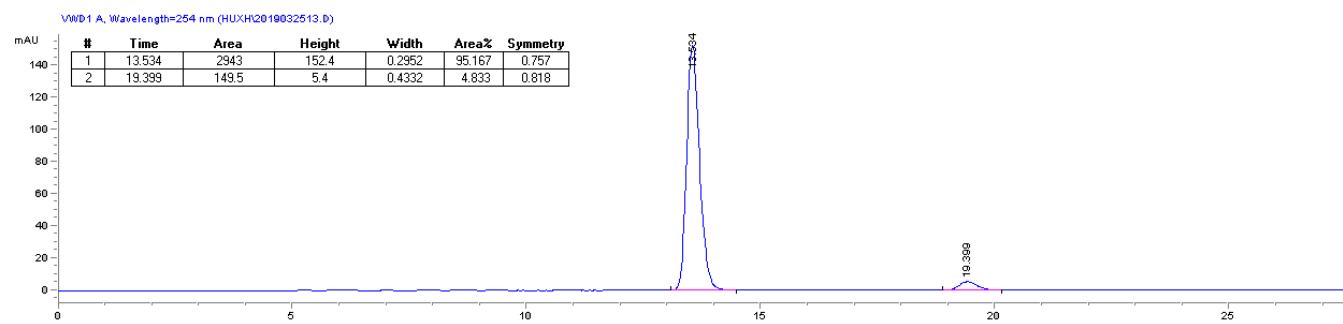


**(2S,3R)-2-phenyl-3-propyl-1,2,3,4-tetrahydroquinoline (2m).**<sup>2</sup> Colorless liquid was obtained in 97%

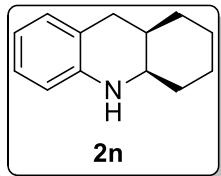


yield (97.4 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 20/1). 90% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, 0.6 mL/min, 254 nm, 40 °C): *t<sub>R</sub>* (major) = 13.5 min, *t<sub>R</sub>* (minor) = 19.4 min. [α]<sup>25</sup><sub>D</sub> = 66.9 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32 – 7.19 (m, 5H), 7.06 – 6.93 (m, 2H), 6.64 (td, *J* = 7.4, 1.1 Hz, 1H), 6.56 – 6.46 (m, 1H), 4.50 (d, *J* = 3.8 Hz, 1H), 4.18 (bs, 1H), 2.84 (dd, *J* = 16.2, 4.7 Hz, 1H), 2.53 (dd, *J* = 16.2, 8.6 Hz, 1H), 2.22 – 2.09 (m, 1H), 1.48 – 1.31 (m, 1H), 1.31 – 1.14 (m, 2H), 1.08 – 0.93 (m, 1H), 0.81 (t, *J* = 7.2 Hz,

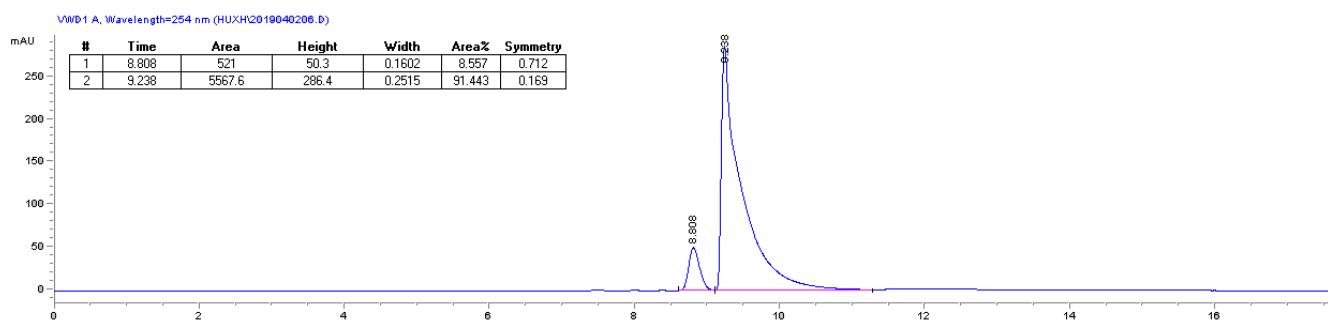
3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.39 (s), 143.19 (s), 129.71 (s), 128.17 (s), 127.42 – 126.97 (m), 120.34 (s), 117.00 (s), 113.64 (s), 59.00 (s), 36.71 (s), 31.97 (s), 30.04 (s), 20.57 (s), 14.25 (s).

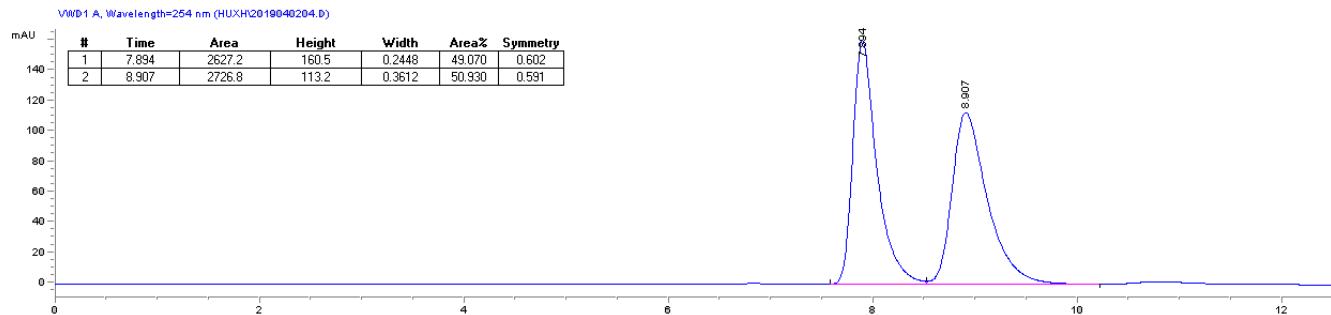


**(4a*R*,9a*R*)-1,2,3,4,4a,9,9a,10-Octahydroacridine (2n).**<sup>3</sup> White solid was obtained in 97% yield (72.6 mg)

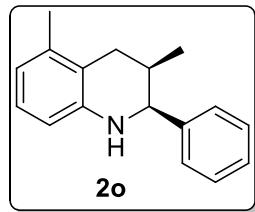


after purification with column chromatography on silica gel (hexanes/ethyl acetate, 20/1). M.p.: 62–64 °C. 83% ee was determined by chiral HPLC (Chiralpak AS-H, *n*-hexane/*i*-PrOH = 99.5/0.5, 0.6 mL/min, 254 nm, 40 °C):  $t_R$  (minor) = 8.8 min,  $t_R$  (major) = 9.2 min.  $[\alpha]^{25}_D = 26.6$  (c 1.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.93 (dd,  $J$  = 13.1, 6.9 Hz, 2H), 6.56 (t,  $J$  = 7.3 Hz, 1H), 6.43 (d,  $J$  = 7.9 Hz, 1H), 3.49 (d,  $J$  = 2.9 Hz, 2H), 2.89 (dd,  $J$  = 16.3, 5.5 Hz, 1H), 2.51 (dd,  $J$  = 16.2, 3.5 Hz, 1H), 1.95 (dt,  $J$  = 8.8, 4.2 Hz, 1H), 1.64 (ddd,  $J$  = 23.5, 11.8, 6.1 Hz, 4H), 1.51 – 1.19 (m, 4H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.95 (s), 129.75 (s), 126.62 (s), 119.32 (s), 116.44 (s), 113.29 (s), 50.06 (s), 33.00 (s), 32.59 (s), 31.81 (s), 27.31 (s), 24.80 (s), 20.77 (s).

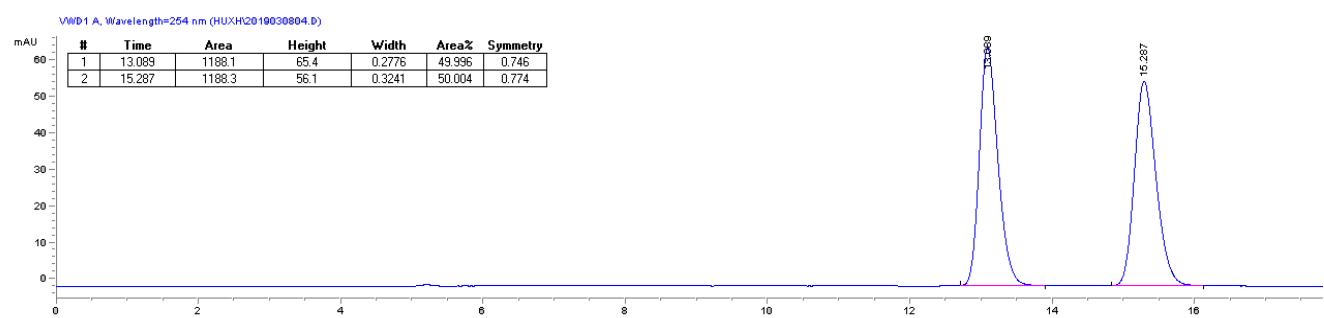
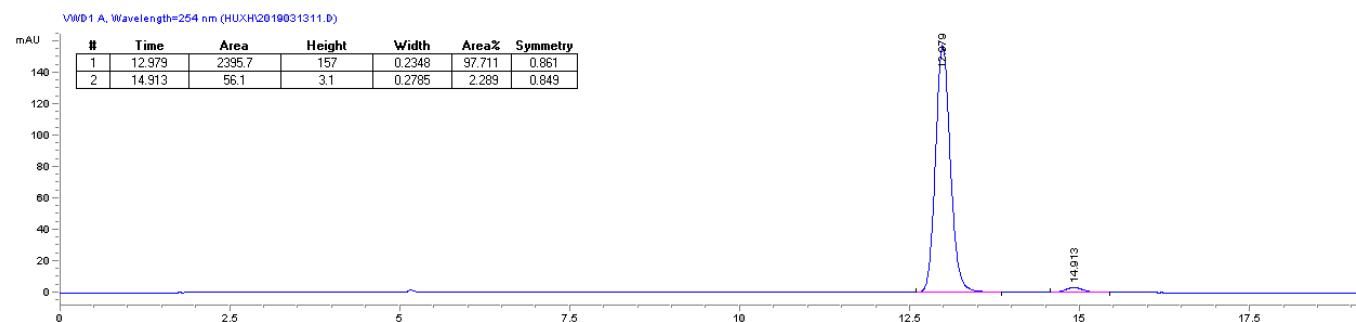




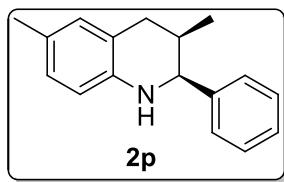
**(2S,3R)-3,5-Dimethyl-2-phenyl-1,2,3,4-tetrahydroquinoline (2o).** Colorless liquid was obtained in 68%



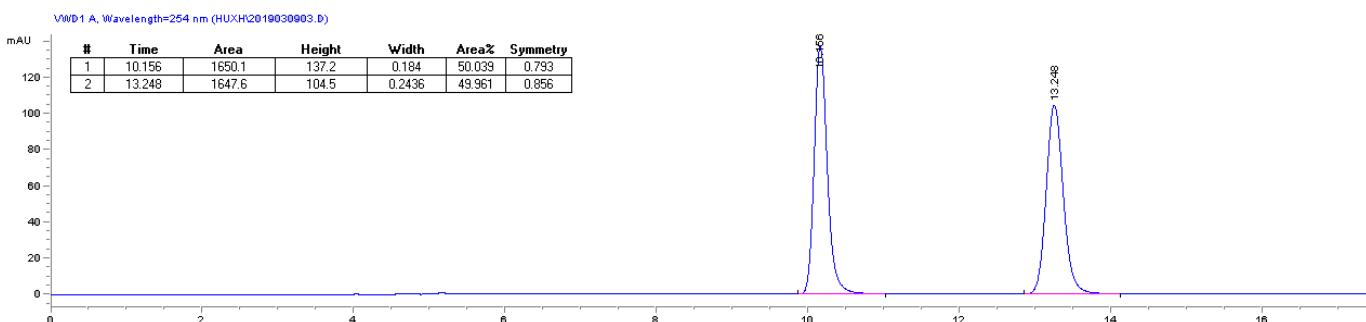
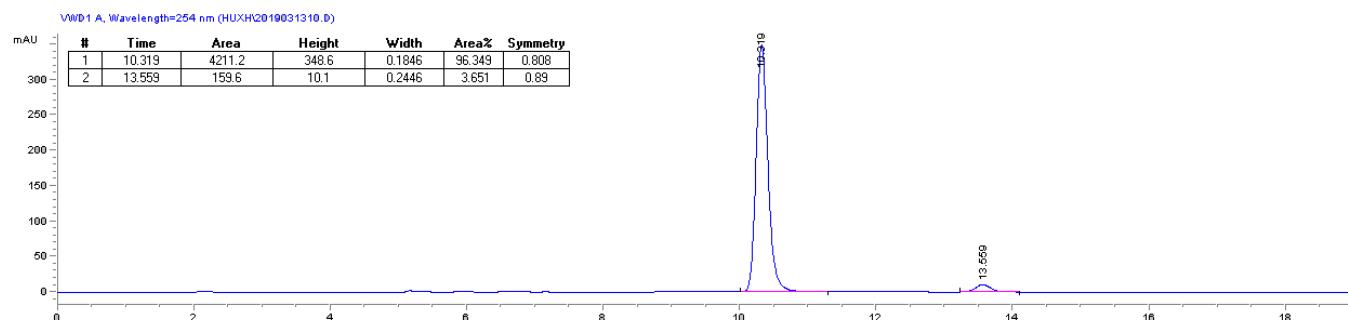
yield (64.8 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 20/1). 95% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, 0.6 mL/min, 254 nm, 40 °C): *t*<sub>R</sub> (major) = 13.0 min, *t*<sub>R</sub> (minor) = 14.9 min. [α]<sup>25</sup><sub>D</sub> = 33.5 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35 – 7.20 (m, 5H), 6.93 (t, *J* = 7.7 Hz, 1H), 6.55 (d, *J* = 7.4 Hz, 1H), 6.43 (d, *J* = 8.0 Hz, 1H), 4.45 (d, *J* = 3.2 Hz, 1H), 4.10 (bs, 1H), 2.91 – 2.72 (m, 1H), 2.41 – 2.27 (m, 2H), 2.18 (d, *J* = 10.9 Hz, 3H), 0.83 (d, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.26 (s), 143.06 (s), 137.32 (s), 128.16 (s), 127.16 (d, *J* = 12.5 Hz), 126.42 (s), 118.90 (d, *J* = 15.9 Hz), 111.95 (s), 59.01 (s), 32.12 (s), 30.69 (s), 19.57 (s), 15.73 (s). HRMS calcd for C<sub>17</sub>H<sub>20</sub>N [M+H]<sup>+</sup>: 238.1590, found: 238.1591.



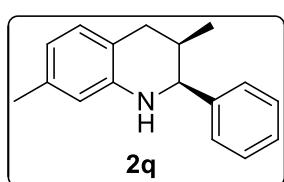
**(2S,3R)-3,6-Dimethyl-2-phenyl-1,2,3,4-tetrahydroquinoline (2p).** Colorless liquid was obtained in 95%



yield (90.1 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 20/1). 93% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, 0.6 mL/min, 254 nm, 40 °C): *t<sub>R</sub>* (major) = 10.3 min, *t<sub>R</sub>* (minor) = 13.6 min.  $[\alpha]^{25}_D = 19.2$  (c 2.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 – 7.19 (m, 5H), 6.82 (d, *J* = 10.3 Hz, 2H), 6.46 (d, *J* = 7.7 Hz, 1H), 4.45 (s, 1H), 3.91 (s, 1H), 2.93 (d, *J* = 16.2 Hz, 1H), 2.45 (dd, *J* = 16.0, 5.7 Hz, 1H), 2.32 – 2.24 (m, 1H), 2.24 – 2.17 (m, 3H), 0.85 – 0.68 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.17 (s), 141.86 (s), 130.31 (s), 128.16 (s), 127.52 (s), 127.17 (d, *J* = 10.9 Hz), 126.33 (s), 120.12 (s), 113.92 (s), 59.54 (s), 33.56 (s), 32.17 (s), 20.55 (s), 15.10 (s). HRMS calcd for C<sub>17</sub>H<sub>20</sub>N [M+H]<sup>+</sup>: 238.1590, found: 238.1588.

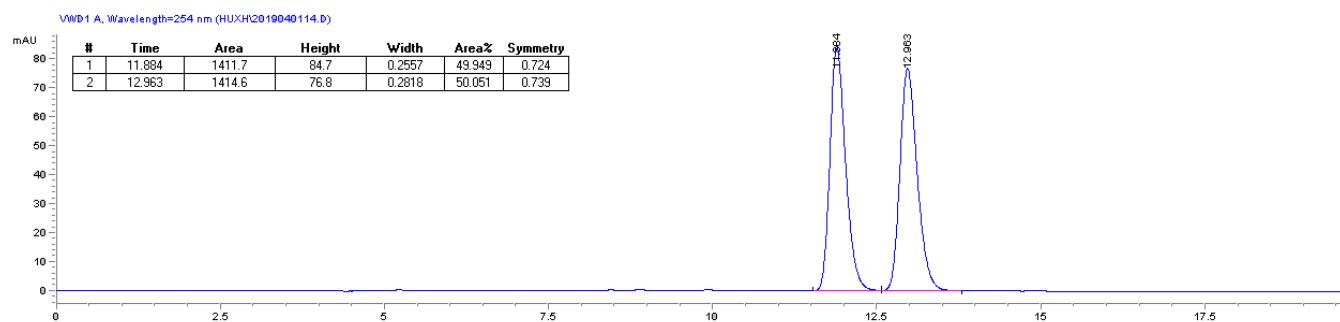
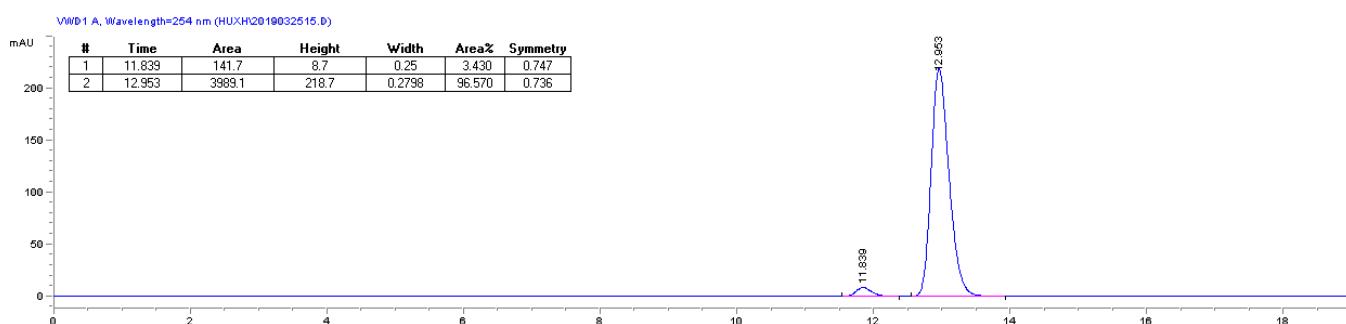


**(2S,3R)-3,7-Dimethyl-2-phenyl-1,2,3,4-tetrahydroquinoline (2q).** Yellow liquid was obtained in 95%

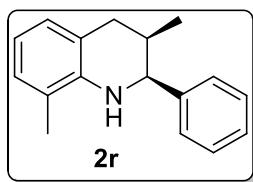


yield (90.3 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 20/1). 93% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, 0.6 mL/min, 254 nm, 40 °C): *t<sub>R</sub>* (minor) = 11.8 min, *t<sub>R</sub>* (major) = 12.9 min.  $[\alpha]^{25}_D = 0$  (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35 – 7.20 (m, 5H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.48 (dd, *J* = 7.5, 0.9 Hz, 1H), 6.37 (s, 1H), 4.46 (d, *J* = 3.6 Hz, 1H), 4.03 (bs, 1H), 2.91 (dd, *J* = 16.0, 4.9 Hz, 1H), 2.44 (dd, *J* = 16.0, 6.7 Hz, 1H), 2.32 – 2.25 (m, 1H), 2.24 (s, 3H), 0.80 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.04 (s), 143.09 (s),

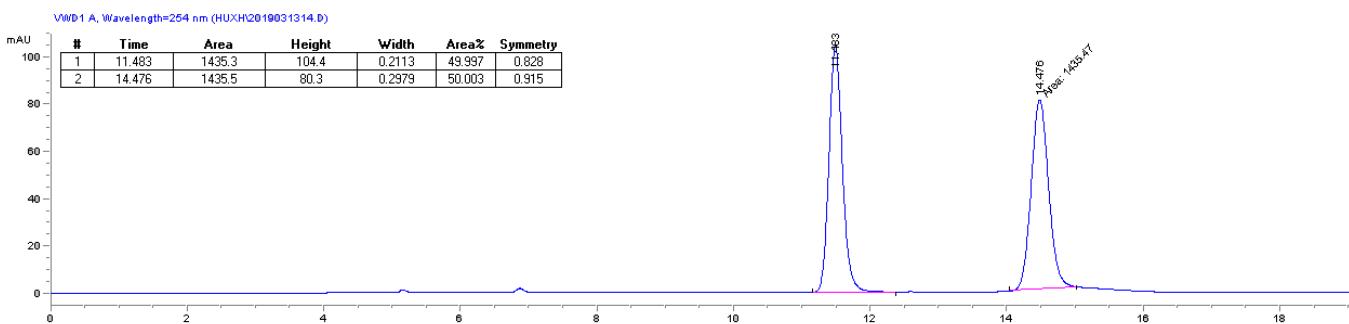
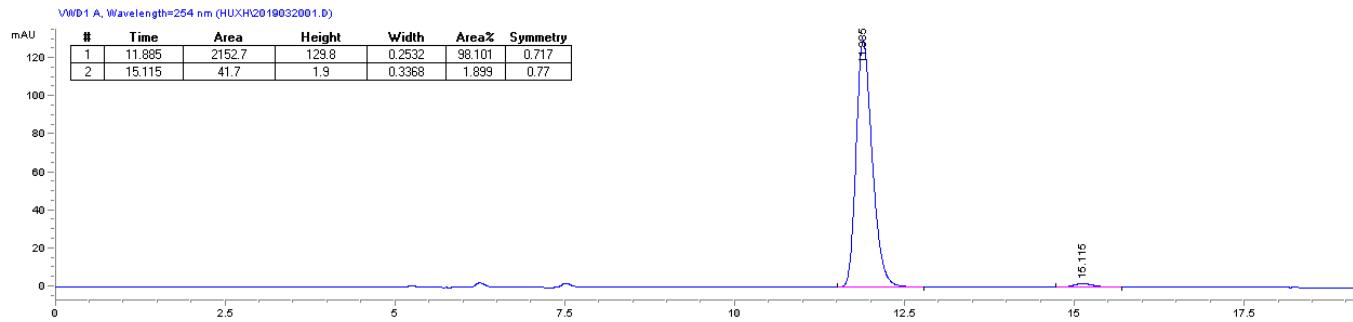
136.59 (s), 129.65 (s), 128.18 (s), 127.20 (d,  $J$  = 10.6 Hz), 118.19 (s), 117.20 (s), 114.35 (s), 59.46 (s), 33.09 (s), 32.15 (s), 21.29 (s), 15.23 (s). HRMS calcd for  $C_{17}H_{20}N$  [M+H]<sup>+</sup>: 238.1590, found: 238.1594.



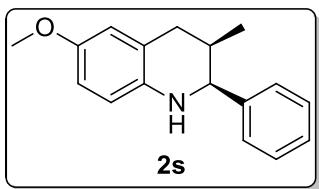
**(2S,3R)-3,8-dimethyl-2-phenyl-1,2,3,4-tetrahydroquinoline (2r).** White solid was obtained in 95% yield



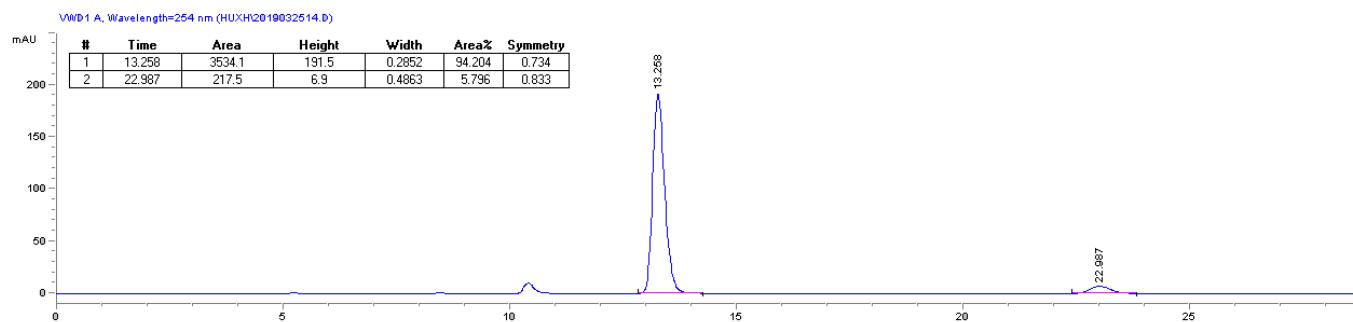
(90.1 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 20/1). M.p.: 44-46 °C. 96% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, 0.6 mL/min, 254 nm, 40 °C):  $t_R$  (major) = 11.9 min,  $t_R$  (minor) = 15.1 min.  $[\alpha]^{25}_D$  = -22.9 (c 2.0,  $CH_2Cl_2$ ). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.29 – 7.13 (m, 5H), 6.85 (d,  $J$  = 7.3 Hz, 1H), 6.81 (d,  $J$  = 7.4 Hz, 1H), 6.52 (t,  $J$  = 7.4 Hz, 1H), 4.50 (d,  $J$  = 3.6 Hz, 1H), 3.88 (bs, 1H), 2.91 (dd,  $J$  = 16.1, 4.9 Hz, 1H), 2.44 (dd,  $J$  = 16.2, 6.5 Hz, 1H), 2.22 (tdd,  $J$  = 6.8, 4.9, 3.8 Hz, 1H), 2.05 (s, 3H), 0.73 (d,  $J$  = 6.9 Hz, 3H). <sup>13</sup>C NMR (101 MHz,  $CDCl_3$ )  $\delta$  143.29 (s), 142.15 (s), 128.13 (d,  $J$  = 18.0 Hz), 127.63 (s), 127.20 (d,  $J$  = 1.8 Hz), 120.70 (s), 119.46 (s), 116.58 (s), 59.62 (s), 33.71 (s), 31.82 (s), 17.31 (s), 15.11 (s). HRMS calcd for  $C_{17}H_{20}N$  [M+H]<sup>+</sup>: 238.1590, found: 238.1586.

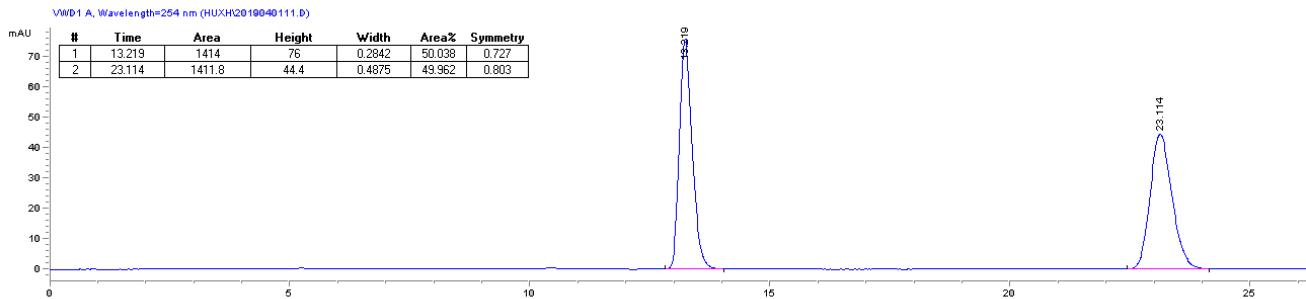


**(2S,3R)-6-Methoxy-3-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline (2s).** Yellow liquid was obtained in

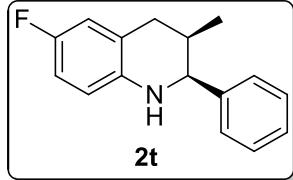


94% yield (95.1 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 20/1). 88% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, 0.6 mL/min, 254 nm, 40 °C): *t*<sub>R</sub> (major) = 13.3 min, *t*<sub>R</sub> (minor) = 23.0 min. [α]<sup>25</sup><sub>D</sub> = 4.2 (c 4.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 – 7.27 (m, 4H), 7.27 – 7.21 (m, 1H), 6.64 (dd, *J* = 8.6, 2.9 Hz, 1H), 6.60 (d, *J* = 2.8 Hz, 1H), 6.50 (d, *J* = 8.6 Hz, 1H), 4.45 (d, *J* = 3.3 Hz, 1H), 3.82 (bs, 1H), 3.73 (s, 3H), 3.00 (dd, *J* = 16.3, 5.1 Hz, 1H), 2.47 (dd, *J* = 16.3, 6.0 Hz, 1H), 2.28 (dtd, *J* = 9.4, 6.0, 3.5 Hz, 1H), 0.81 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 151.88 (s), 143.16 (s), 138.30 (s), 128.16 (s), 127.13 (d, *J* = 5.9 Hz), 121.30 (s), 114.98 (d, *J* = 19.4 Hz), 113.05 (s), 59.61 (s), 55.81 (s), 34.03 (s), 32.21 (s), 14.83 (s). HRMS calcd for C<sub>17</sub>H<sub>20</sub>NO [M+H]<sup>+</sup>: 254.1539, found: 254.1539.

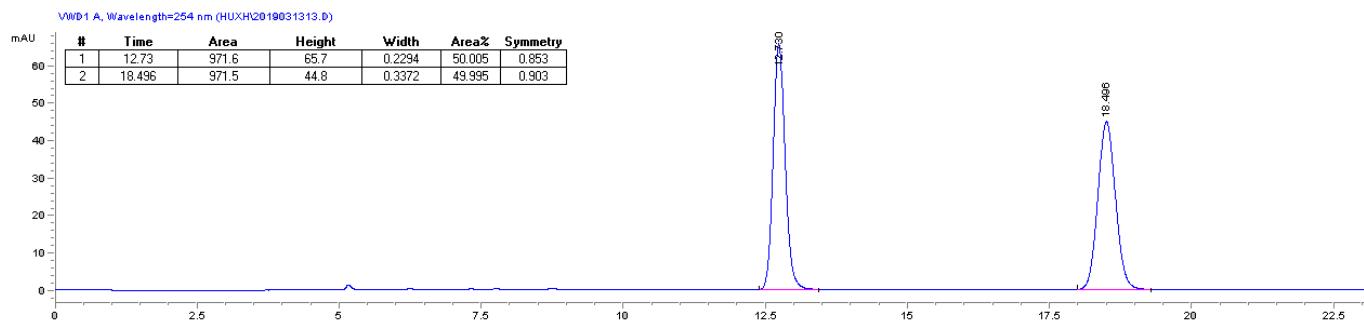
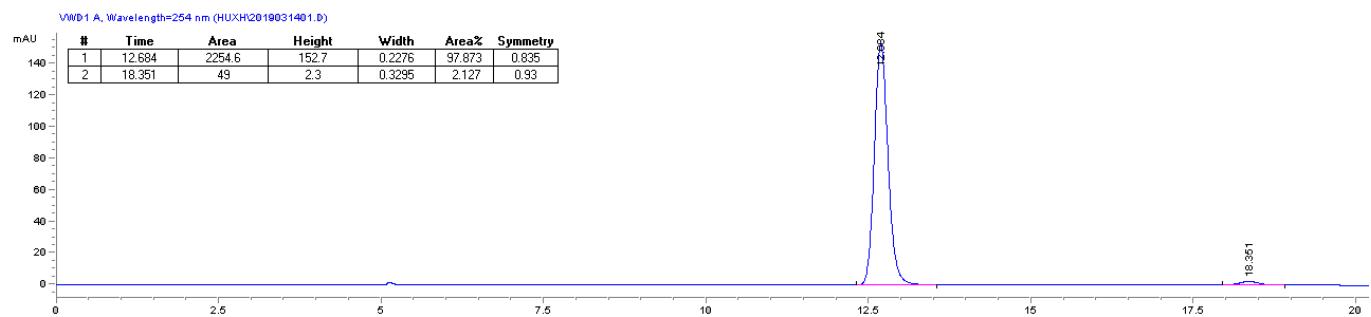




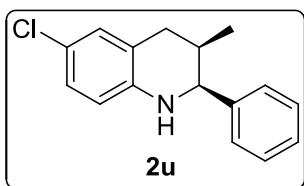
**(2S,3R)-6-Fluoro-3-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline (2t).** Colorless liquid was obtained in



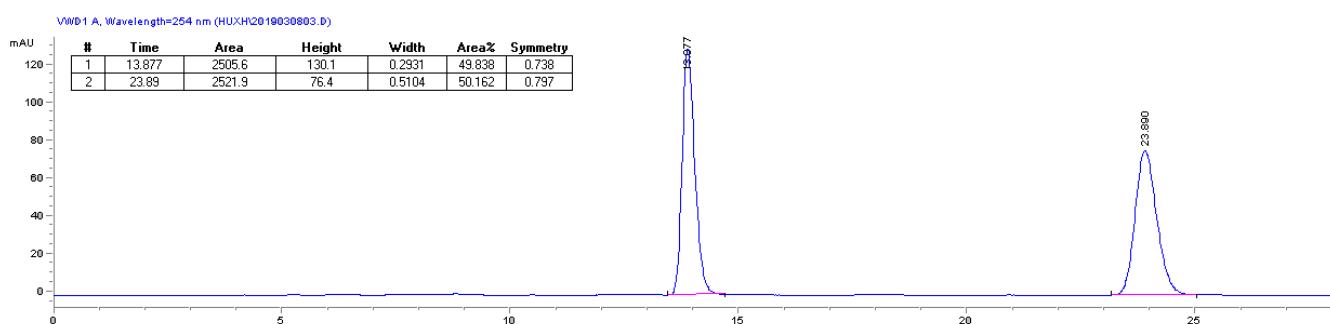
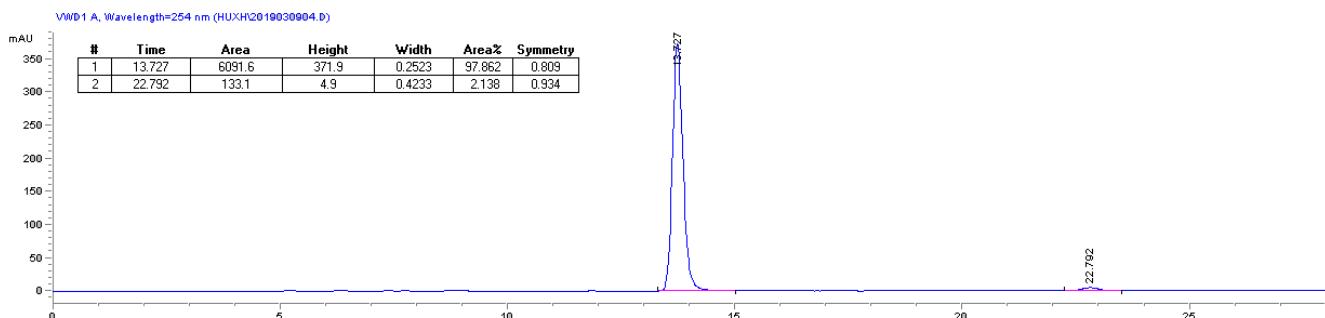
95% yield (91.6 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 20/1). 96% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, 0.6 mL/min, 254 nm, 40 °C): *t*<sub>R</sub> (major) = 12.7 min, *t*<sub>R</sub> (minor) = 18.4 min. [α]<sup>25</sup><sub>D</sub> = -5.9 (c 2.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37 – 7.23 (m, 5H), 6.74 (dd, *J* = 13.1, 5.2 Hz, 2H), 6.50 – 6.41 (m, 1H), 4.47 (d, *J* = 2.7 Hz, 1H), 3.91 (bs, 1H), 2.97 (dd, *J* = 16.4, 4.6 Hz, 1H), 2.47 (dd, *J* = 16.4, 6.0 Hz, 1H), 2.28 (ddd, *J* = 6.3, 3.2, 1.6 Hz, 1H), 0.85 – 0.66 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.58 (d, *J* = 234.5 Hz), 142.79 (s), 140.36 (s), 128.22 (s), 127.24 (s), 127.12 (s), 121.33 (d, *J* = 6.7 Hz), 115.85 (d, *J* = 21.4 Hz), 114.37 (d, *J* = 7.5 Hz), 113.45 (d, *J* = 22.5 Hz), 59.45 (s), 33.71 (s), 31.82 (s), 14.86 (s). HRMS calcd for C<sub>16</sub>H<sub>17</sub>FN [M+H]<sup>+</sup>: 242.1340, found: 242.1346.



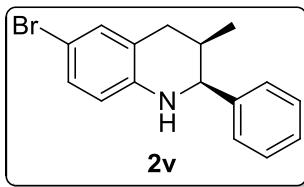
**(2S,3R)-6-Chloro-3-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline (2u).** Yellow solid was obtained in



97% yield (100.0 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 52-54 °C. 96% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, 0.6 mL/min, 254 nm, 40 °C):  $t_R$  (major) = 13.7 min,  $t_R$  (minor) = 22.8 min.  $[\alpha]^{25}_D$  = 48.6 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43 – 7.17 (m, 5H), 7.05 – 6.88 (m, 2H), 6.53 – 6.37 (m, 1H), 4.47 (d, *J* = 3.5 Hz, 1H), 4.08 (bs, 1H), 2.90 (dd, *J* = 16.3, 4.9 Hz, 1H), 2.45 (dd, *J* = 16.3, 6.8 Hz, 1H), 2.34 – 2.15 (m, 1H), 0.79 (dd, *J* = 6.9, 1.6 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 142.77 (s), 142.51 (s), 129.29 (s), 128.24 (s), 127.23 (d, *J* = 17.6 Hz), 126.77 (s), 121.62 (s), 121.40 (s), 114.71 (s), 59.35 (s), 33.24 (s), 31.59 (s), 15.12 (s). HRMS calcd for C<sub>16</sub>H<sub>17</sub>ClN [M+H]<sup>+</sup>: 258.1044, found: 258.1047.

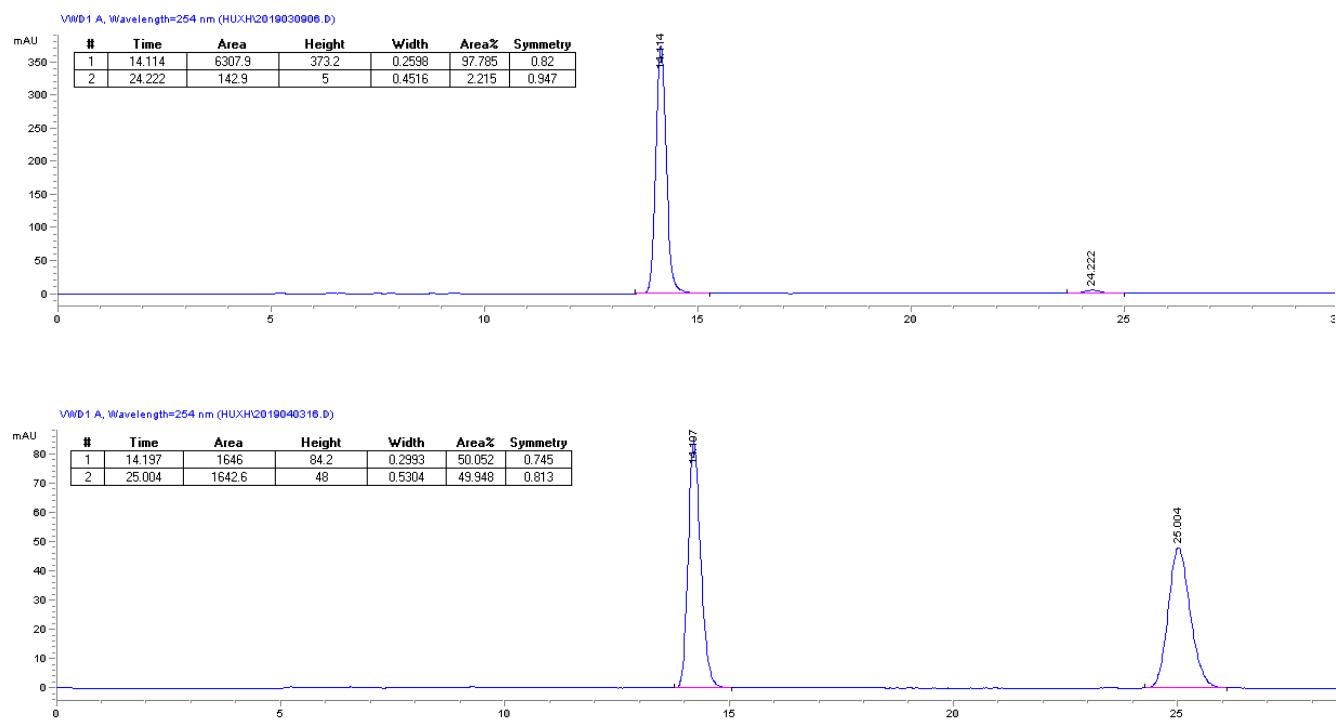


**(2S,3R)-6-Bromo-3-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline (2v).** Yellow solid was obtained in 98%

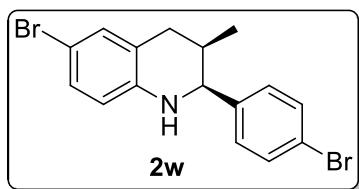


yield (118.4 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 54-56 °C. 96% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, 0.6 mL/min, 254 nm, 40 °C):  $t_R$  (major) = 14.1 min,  $t_R$  (minor) = 24.2 min.  $[\alpha]^{25}_D$  = 52.9 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36 – 7.18 (m, 5H), 7.08 (d, *J* = 7.2 Hz, 2H), 6.41 (d, *J* = 8.9 Hz, 1H), 4.46 (d, *J* = 3.6 Hz, 1H), 3.99 (bs, 1H), 2.89 (dd, *J* = 16.3, 4.9 Hz, 1H), 2.45 (dd, *J* = 16.3, 6.9 Hz, 1H), 2.31 – 2.16 (m, 1H), 0.79 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.21 (s), 142.43 (s),

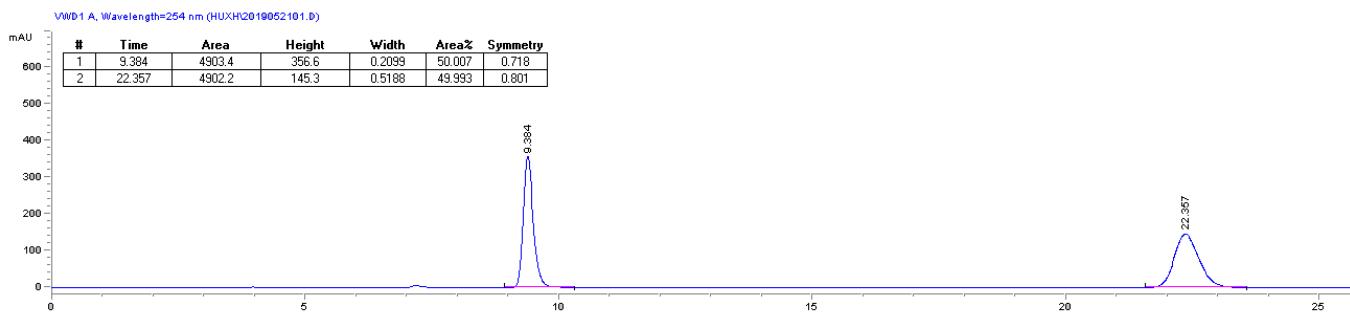
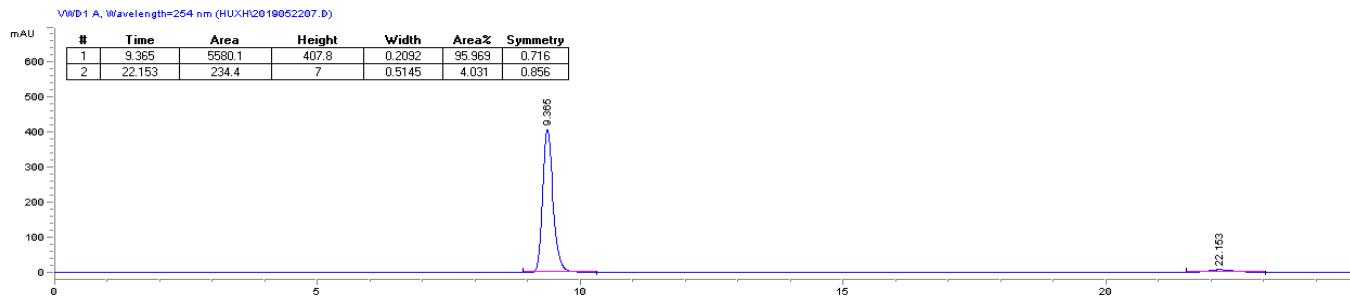
132.12 (s), 129.61 (s), 128.24 (s), 127.23 (d,  $J$  = 18.7 Hz), 122.17 (s), 115.15 (s), 108.45 (s), 59.30 (s), 33.14 (s), 31.52 (s), 15.16 (s). HRMS calcd for  $C_{16}H_{17}BrN$  [M+H]<sup>+</sup>: 302.0539, found: 302.0546.



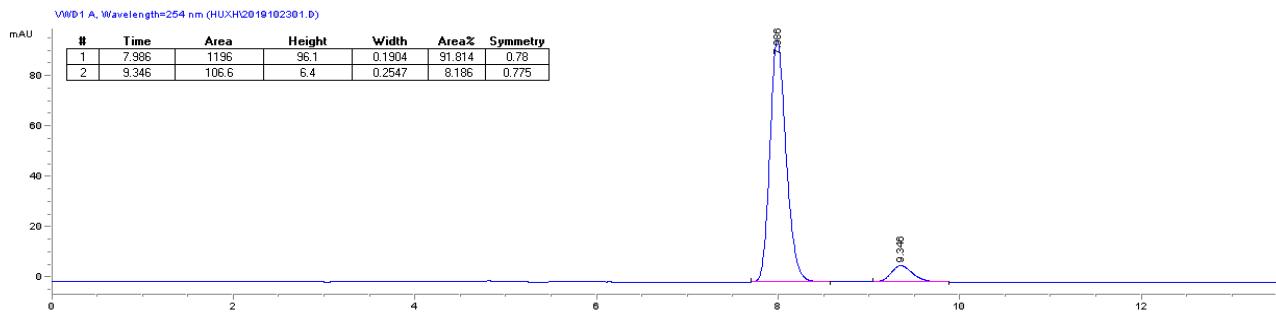
**(2S,3R)-6-Bromo-2-(4-bromophenyl)-3-methyl-1,2,3,4-tetrahydroquinoline (2w).** White solid was

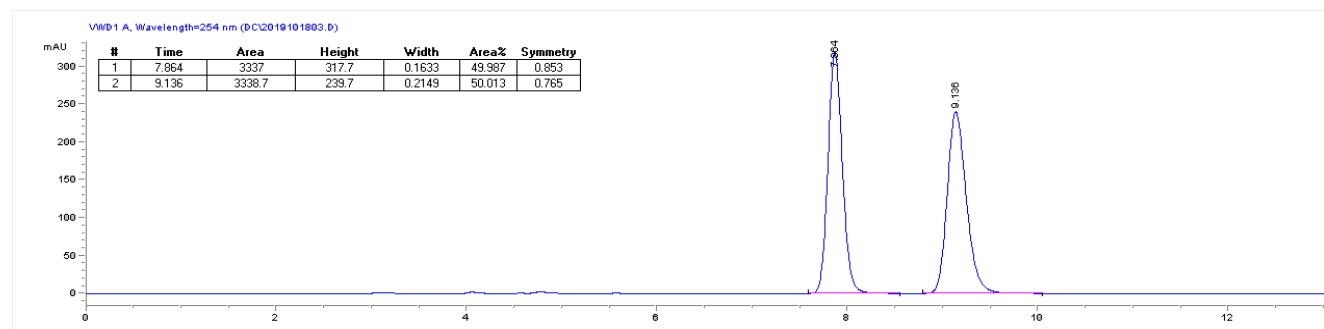


obtained in 97% yield (147.8 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 20/1). M.p.: 86-88 °C. 92% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm, 40 °C):  $t_R$  (major) = 9.4 min,  $t_R$  (minor) = 22.2 min.  $[\alpha]^{25}_D$  = 49.2 (c 2.0,  $CH_2Cl_2$ ).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.49 – 7.36 (m, 2H), 7.18 – 7.02 (m, 4H), 6.49 – 6.37 (m, 1H), 4.44 (s, 1H), 4.11 (bs, 1H), 2.90 (dd,  $J$  = 16.3, 4.8 Hz, 1H), 2.43 (dd,  $J$  = 16.3, 7.0 Hz, 1H), 2.33 – 2.16 (m, 1H), 0.78 (d,  $J$  = 6.9 Hz, 3H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  142.84 (s), 141.44 (s), 132.12 (s), 131.30 (s), 129.70 (s), 128.83 (s), 122.01 (s), 121.09 (s), 115.22 (s), 108.72 (s), 58.78 (s), 32.91 (s), 31.40 (s), 15.11 (s). HRMS calcd for  $C_{16}H_{16}Br_2N$  [M+H]<sup>+</sup>: 379.9644, found: 379.9652.

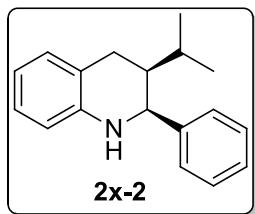


**(2S,3S)-2,3-diphenyl-1,2,3,4-tetrahydroquinoline (2x-1).** White solid was obtained in 95% yield (108.4 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 108-110 °C. 84% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm, 40 °C): *t*<sub>R</sub> (major) = 8.0 min, *t*<sub>R</sub> (minor) = 9.3 min. [α]<sup>25</sup><sub>D</sub> = 143.1 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.12 – 6.92 (m, 8H), 6.77 – 6.65 (m, 4H), 6.62 (t, *J* = 7.4 Hz, 1H), 6.51 (d, *J* = 7.9 Hz, 1H), 4.61 (d, *J* = 3.8 Hz, 1H), 4.20 (bs, 1H), 3.43 (dd, *J* = 11.0, 7.0 Hz, 1H), 2.97 (d, *J* = 2.5 Hz, 1H), 2.96 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.40 (s), 141.83 (s), 141.30 (s), 129.58 (s), 128.84 (s), 127.74 (d, *J* = 16.8 Hz), 127.22 (d, *J* = 9.6 Hz), 126.55 (s), 120.62 (s), 117.33 (s), 113.74 (s), 60.37 (s), 43.47 (s), 29.70 (s). HRMS calcd for C<sub>21</sub>H<sub>20</sub>N [M+H]<sup>+</sup>: 286.1590, found: 286.1591.

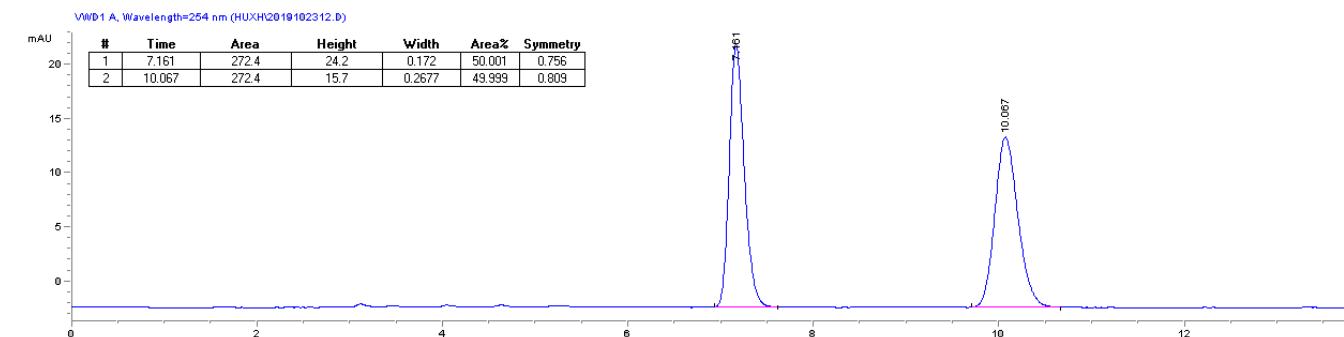
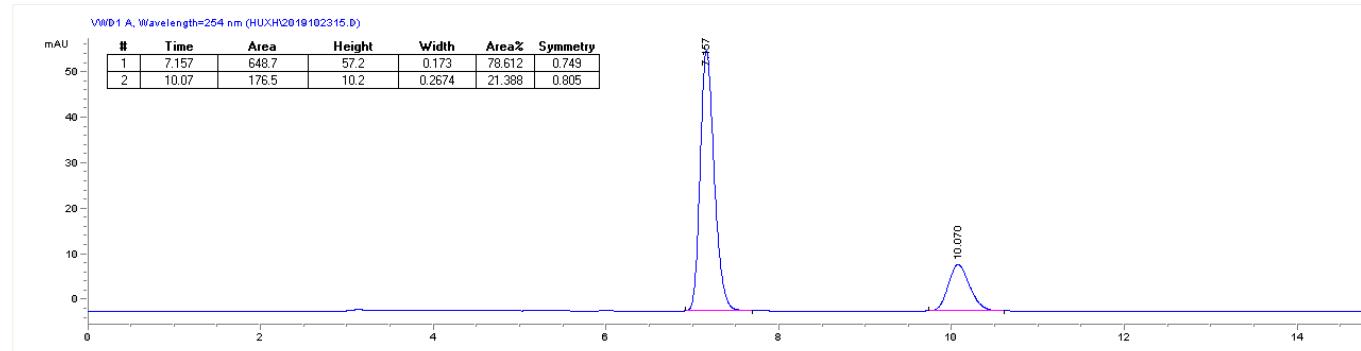




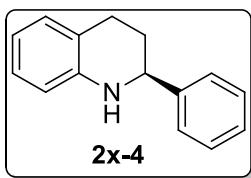
**(2S,3S)-3-isopropyl-2-phenyl-1,2,3,4-tetrahydroquinoline (2x-2).** White solid was obtained in 85%



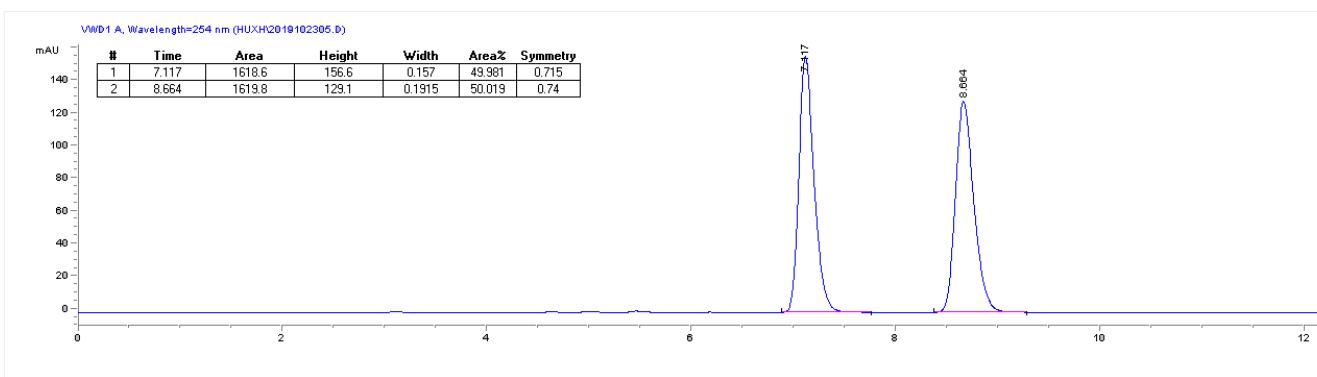
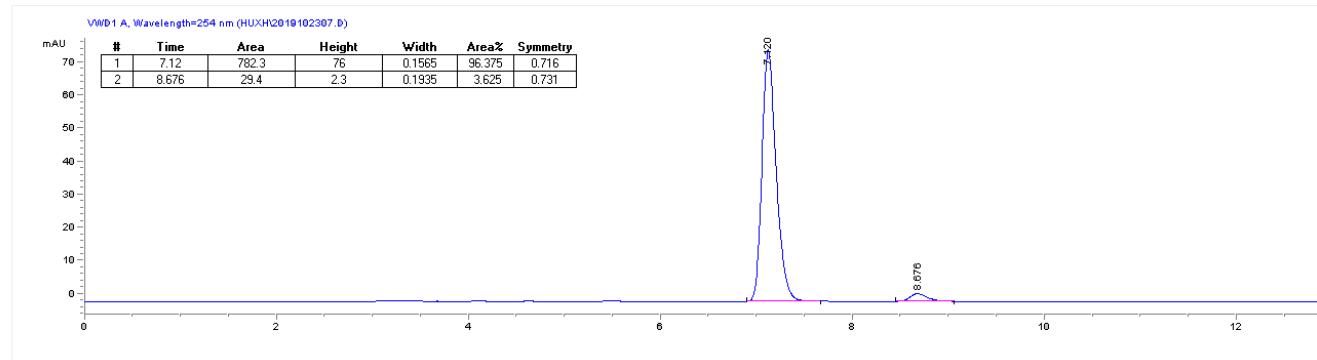
yield (85.4 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). M.p.: 52-54 °C. 57% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm, 40 °C): *t*<sub>R</sub> (major) = 7.2 min, *t*<sub>R</sub> (minor) = 10.0 min.  $[\alpha]^{25}_D = 118.4$  (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.15 (t, *J* = 6.5 Hz, 5H), 6.93 (t, *J* = 7.3 Hz, 2H), 6.56 (t, *J* = 7.3 Hz, 1H), 6.42 (d, *J* = 8.0 Hz, 1H), 4.54 (d, *J* = 3.7 Hz, 1H), 4.27 (bs, 1H), 2.74 (dd, *J* = 16.3, 4.4 Hz, 1H), 2.43 (dd, *J* = 16.1, 12.5 Hz, 1H), 2.02 – 1.74 (m, 1H), 1.26-1.16 (m, 1H), 1.01 (d, *J* = 6.4 Hz, 3H), 0.76 (d, *J* = 6.6 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  143.02 (s), 142.75 (s), 128.48 (s), 127.11 (s), 126.47 (s), 126.05 (d, *J* = 2.6 Hz), 119.70 (s), 115.62 (s), 112.27 (s), 55.71 (s), 42.45 (s), 27.27 (s), 25.70 (s), 21.11 (s), 19.17 (s). HRMS calcd for C<sub>18</sub>H<sub>22</sub>N [M+H]<sup>+</sup>: 252.1747, found: 252.1746.



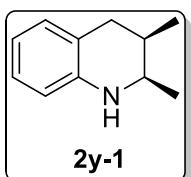
**(S)-2-phenyl-1,2,3,4-tetrahydroquinoline (2x-4).**<sup>6</sup> Yellow liquid was obtained in 96% yield (80.4 mg)



after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). 93% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm, 40 °C): *t*<sub>R</sub> (major) = 7.1 min, *t*<sub>R</sub> (minor) = 8.7 min. [α]<sup>25</sup><sub>D</sub> = -44.3 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.25 (dt, *J* = 14.9, 7.3 Hz, 4H), 7.17 (t, *J* = 6.9 Hz, 1H), 6.90 (t, *J* = 7.7 Hz, 2H), 6.54 (t, *J* = 7.4 Hz, 1H), 6.40 (d, *J* = 7.9 Hz, 1H), 4.30 (dd, *J* = 9.2, 3.0 Hz, 1H), 3.88 (bs, 1H), 2.80 (ddd, *J* = 16.1, 10.6, 5.4 Hz, 1H), 2.61 (dt, *J* = 16.3, 4.7 Hz, 1H), 2.00 (ddd, *J* = 12.9, 8.5, 4.5 Hz, 1H), 1.94 – 1.80 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.89 (d, *J* = 10.6 Hz), 129.40 (s), 128.68 (s), 127.54 (s), 127.01 (s), 126.66 (s), 120.96 (s), 117.26 (s), 114.09 (s), 56.34 (s), 31.09 (s), 26.48 (s).

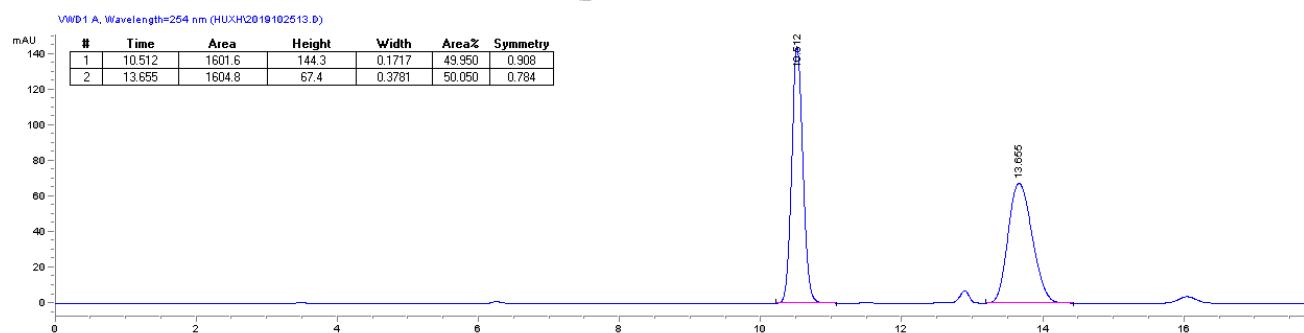
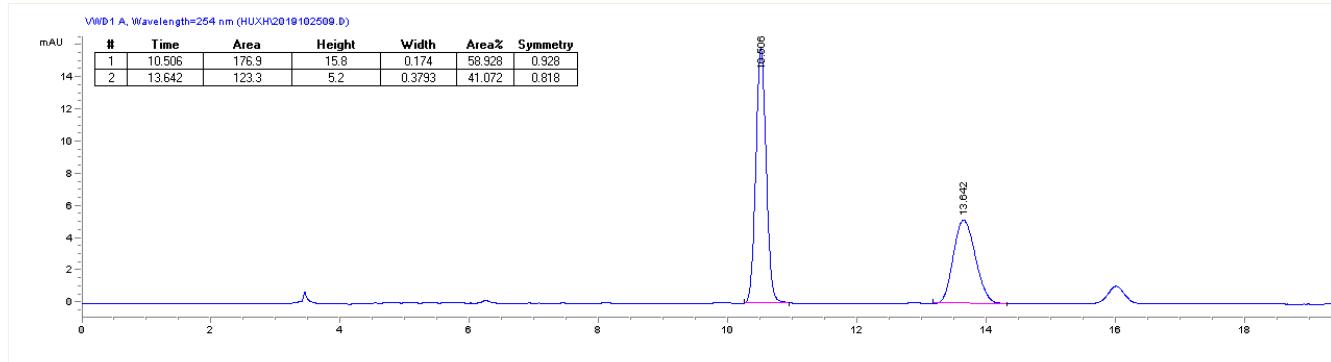


**(2*R*,3*R*)-2,3-dimethyl-1,2,3,4-tetrahydroquinoline (2y-1).**<sup>3</sup> Yellow liquid was obtained in 90% yield

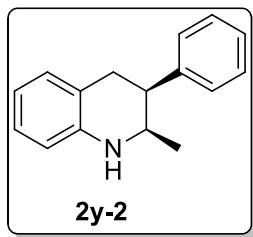


(58.1 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). 18% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, 254 nm, 40 °C): *t*<sub>R</sub> (major) = 10.5 min, *t*<sub>R</sub> (minor) = 13.6 min. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.88 (t, *J* = 7.8 Hz, 2H), 6.52 (t, *J* = 7.3 Hz, 1H), 6.39 (d, *J* = 7.8 Hz, 1H), 3.59 (bs, 1H), 3.38 (qd, *J* = 6.5, 3.0 Hz, 1H), 2.82 (dd, *J* = 16.2, 5.3 Hz, 1H), 2.40 (dd, *J* = 16.2, 5.9 Hz, 1H), 1.95 (dt, *J* = 8.8, 6.3 Hz, 1H), 1.03 (d, *J* = 6.5 Hz, 3H), 0.86 (d, *J* = 6.9 Hz,

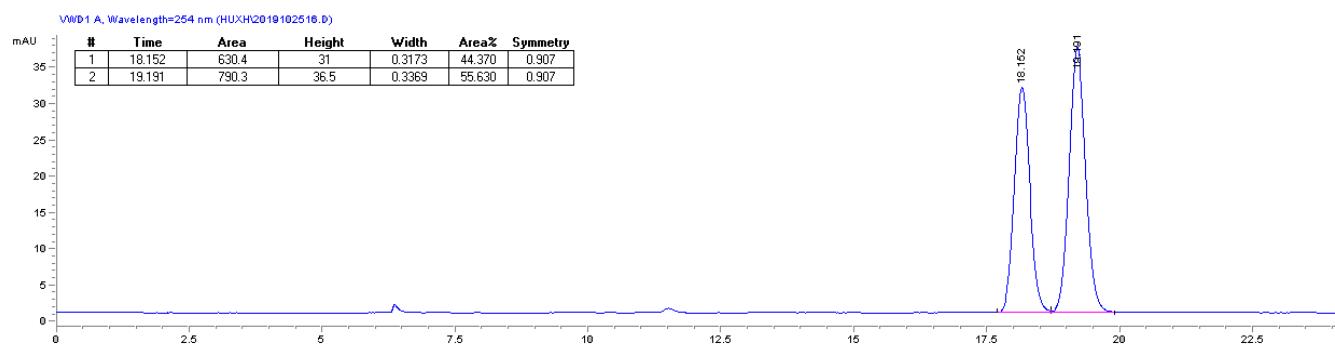
3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.95 (s), 129.81 (s), 126.60 (s), 120.04 (s), 116.90 (s), 113.83 (s), 49.95 (s), 33.84 (s), 30.54 (s), 18.11 (s), 14.39 (s).

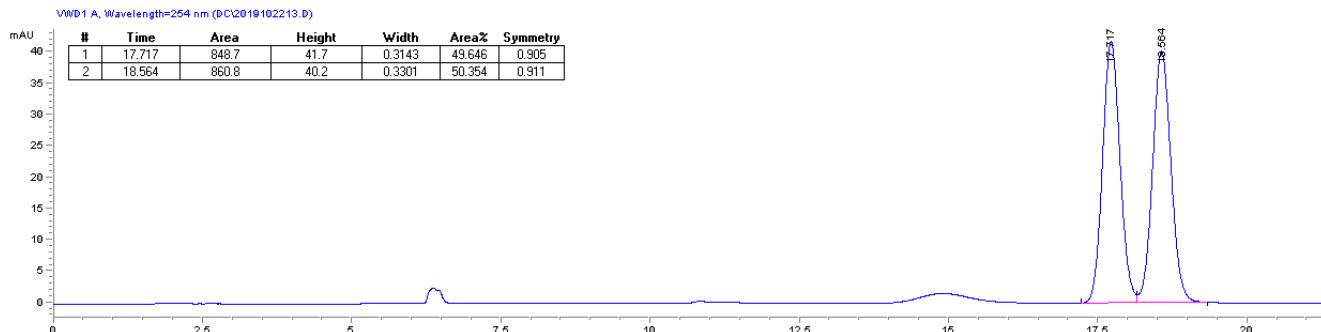


**(2*R*,3*S*)-2-methyl-3-phenyl-1,2,3,4-tetrahydroquinoline (2y-2).** Colourless liquid was obtained in 86%

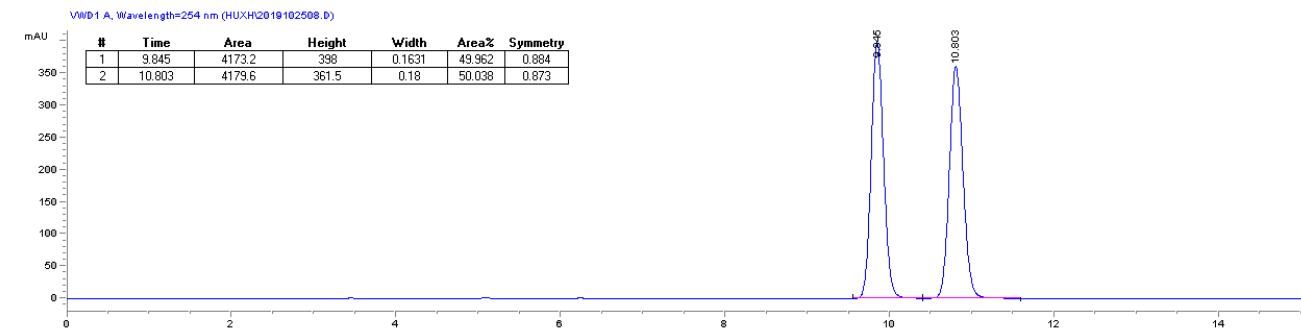
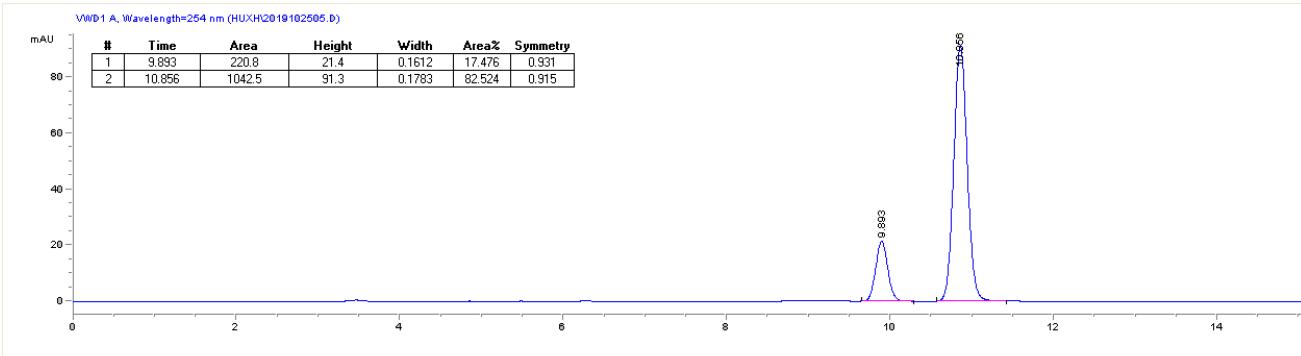
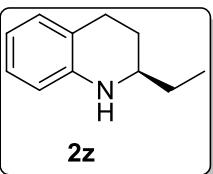


yield (76.8 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). 11% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 93.5/6.5, 0.5 mL/min, 254 nm, 40 °C):  $t_R$  (minor) = 18.2 min,  $t_R$  (major) = 19.2 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 – 7.02 (m, 5H), 6.93 (t,  $J$  = 6.9 Hz, 2H), 6.58 (t,  $J$  = 7.2 Hz, 1H), 6.44 (d,  $J$  = 7.9 Hz, 1H), 3.70 (bs, 1H), 3.59 (td,  $J$  = 9.7, 6.2 Hz, 1H), 3.12 (dd,  $J$  = 9.3, 6.4 Hz, 1H), 3.00 (qd,  $J$  = 16.4, 6.4 Hz, 2H), 0.85 (d,  $J$  = 6.5 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.21 (s), 142.21 (s), 129.67 (s), 128.58 (s), 128.22 (s), 126.95 (s), 126.49 (s), 120.51 (s), 117.47 (s), 114.35 (s), 50.37 (s), 42.26 (s), 30.45 (s), 18.27 (s). HRMS calcd for  $\text{C}_{16}\text{H}_{18}\text{N}$   $[\text{M}+\text{H}]^+$ : 224.1434, found: 224.1439.

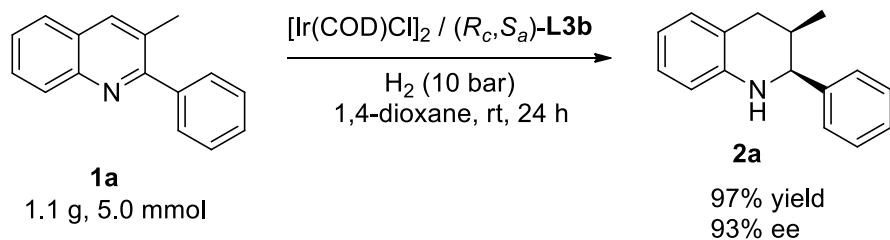




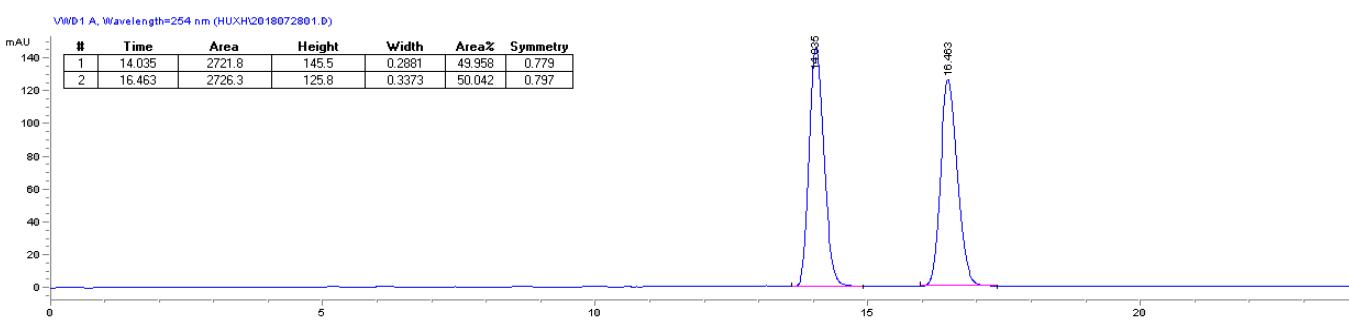
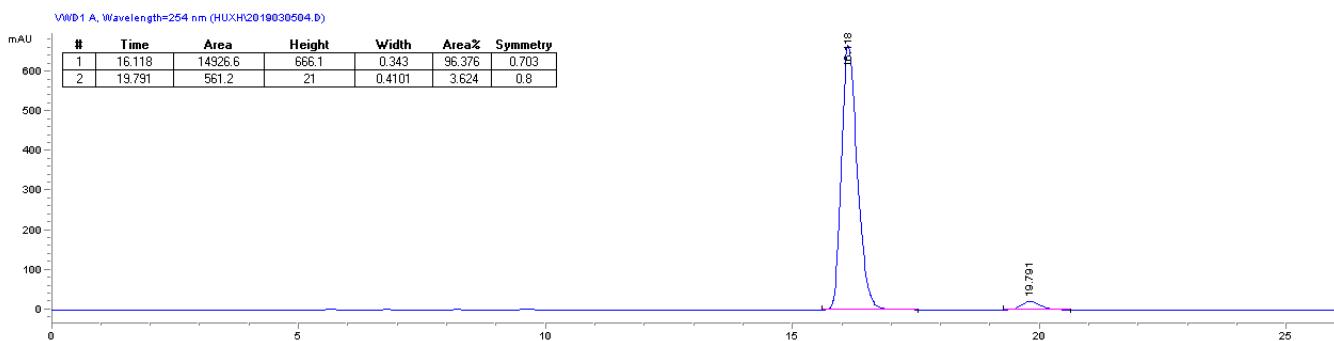
**(R)-2-ethyl-1,2,3,4-tetrahydroquinoline (2z).**<sup>3</sup> Yellow liquid was obtained in 94% yield (60.6 mg) after purification with column chromatography on silica gel (hexanes/ethyl acetate, 10/1). 65% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, 254 nm, 40 °C): *t*<sub>R</sub> (minor) = 9.9 min, *t*<sub>R</sub> (major) = 10.9 min. [α]<sup>25</sup><sub>D</sub> = 48.9 (c 1.8, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.86 (t, *J* = 7.5 Hz, 2H), 6.50 (t, *J* = 7.3 Hz, 1H), 6.37 (d, *J* = 8.1 Hz, 1H), 3.64 (s, 1H), 3.15 – 2.94 (m, 1H), 2.77 – 2.46 (m, 2H), 1.86 (dtd, *J* = 6.6, 5.5, 3.9 Hz, 1H), 1.56 – 1.46 (m, 1H), 1.46 – 1.37 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.85 (s), 129.32 (s), 126.80 (s), 121.45 (s), 116.95 (s), 114.11 (s), 53.12 (s), 29.50 (s), 27.68 (s), 26.53 (s), 10.16 (s).



## IV. Gram-scale reaction

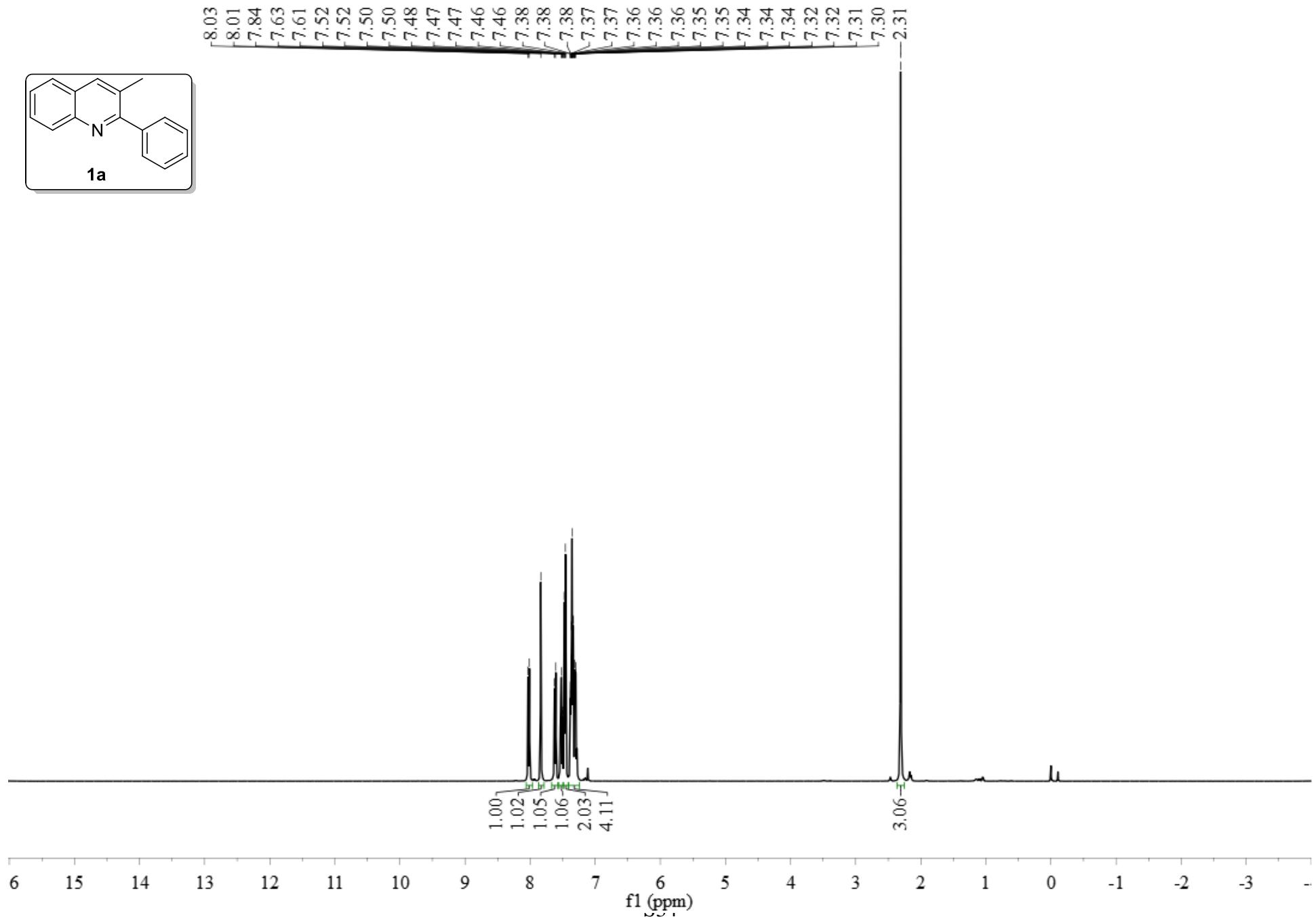
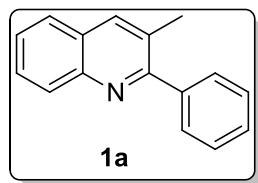


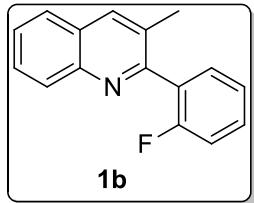
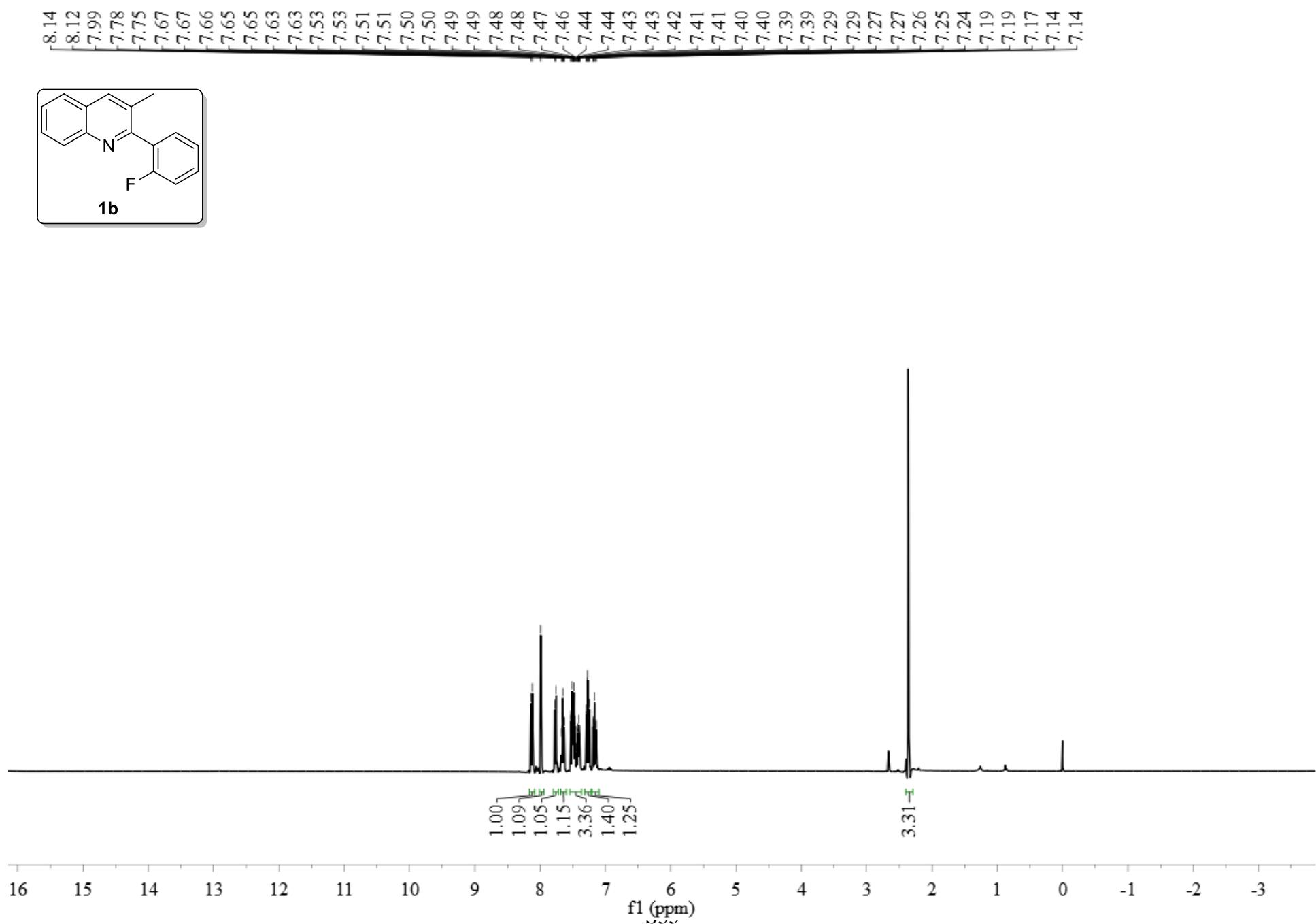
In a nitrogen-filled glovebox, a mixture of  $[\text{Ir}(\text{COD})\text{Cl}]_2$  (16.8 mg, 0.025 mmol) and  $(R_c, S_a)\text{-L3b}$  (36.8 mg, 0.055 mmol) were dissolved in 10 mL of degassed dioxane in a Schlenk tube under  $\text{N}_2$ . After stirring at room temperature for 1 h, 2,3-disubstituted quinoline substrate **1a** (1.1 g, 5 mmol, S/C = 100) in 40 mL of degassed dioxane were then added to the catalyst solution and the resulting mixture was transferred to an autoclave which was charged with  $\text{H}_2$  (10 bar). The hydrogenation was performed at room temperature (25 °C) for 24 h. After carefully releasing the hydrogen gas, the solvent was removed under reduced pressure. The crude product was purified through a silica gel plug (eluting with a mixture of hexanes/ethyl acetate = 20/1) to afford the corresponding 2,3-disubstituted tetrahydroquinoline *cis*-**2a** as a yellow solid (1.09 g, 97% yield, 93% ee).

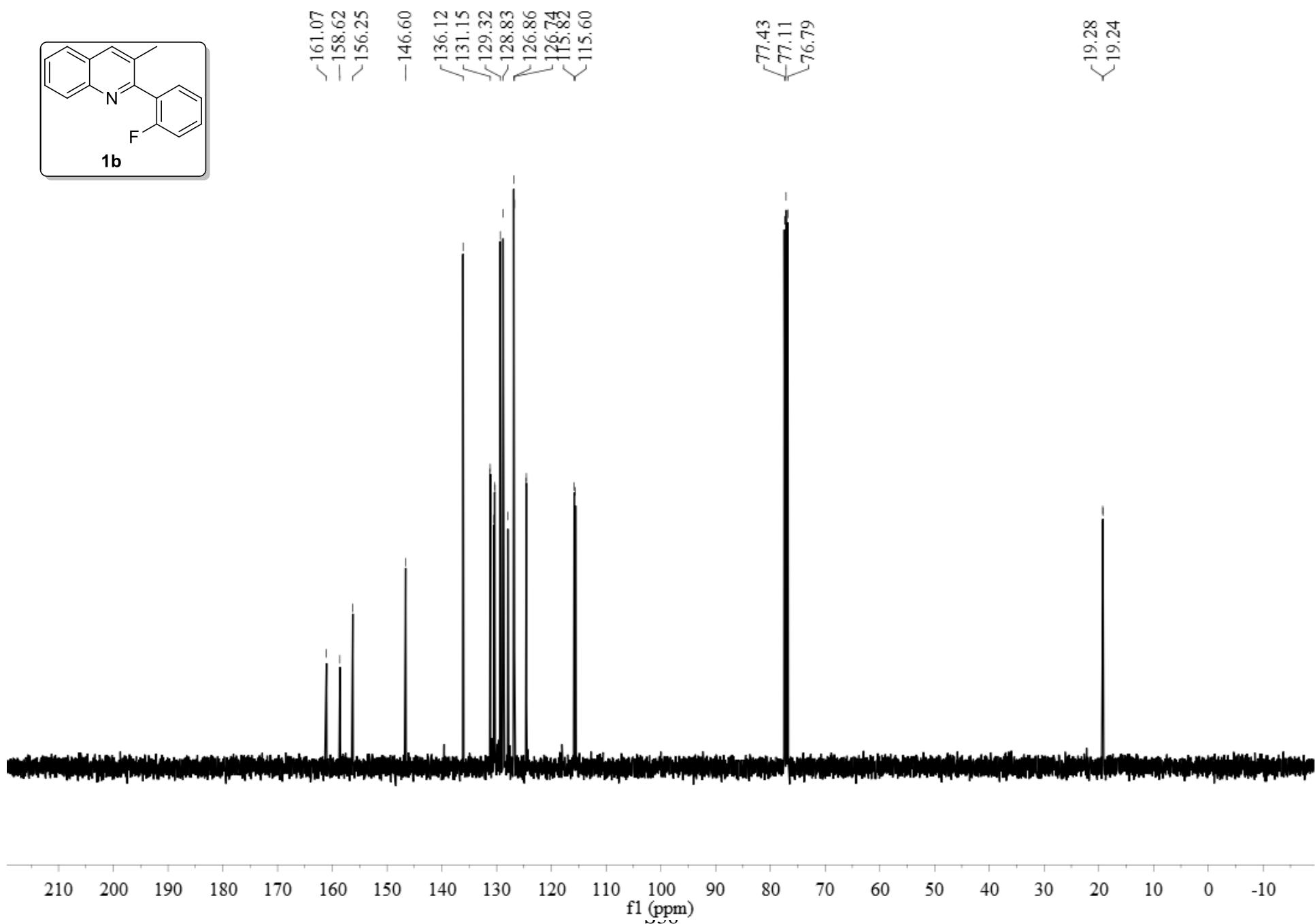
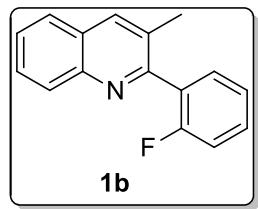


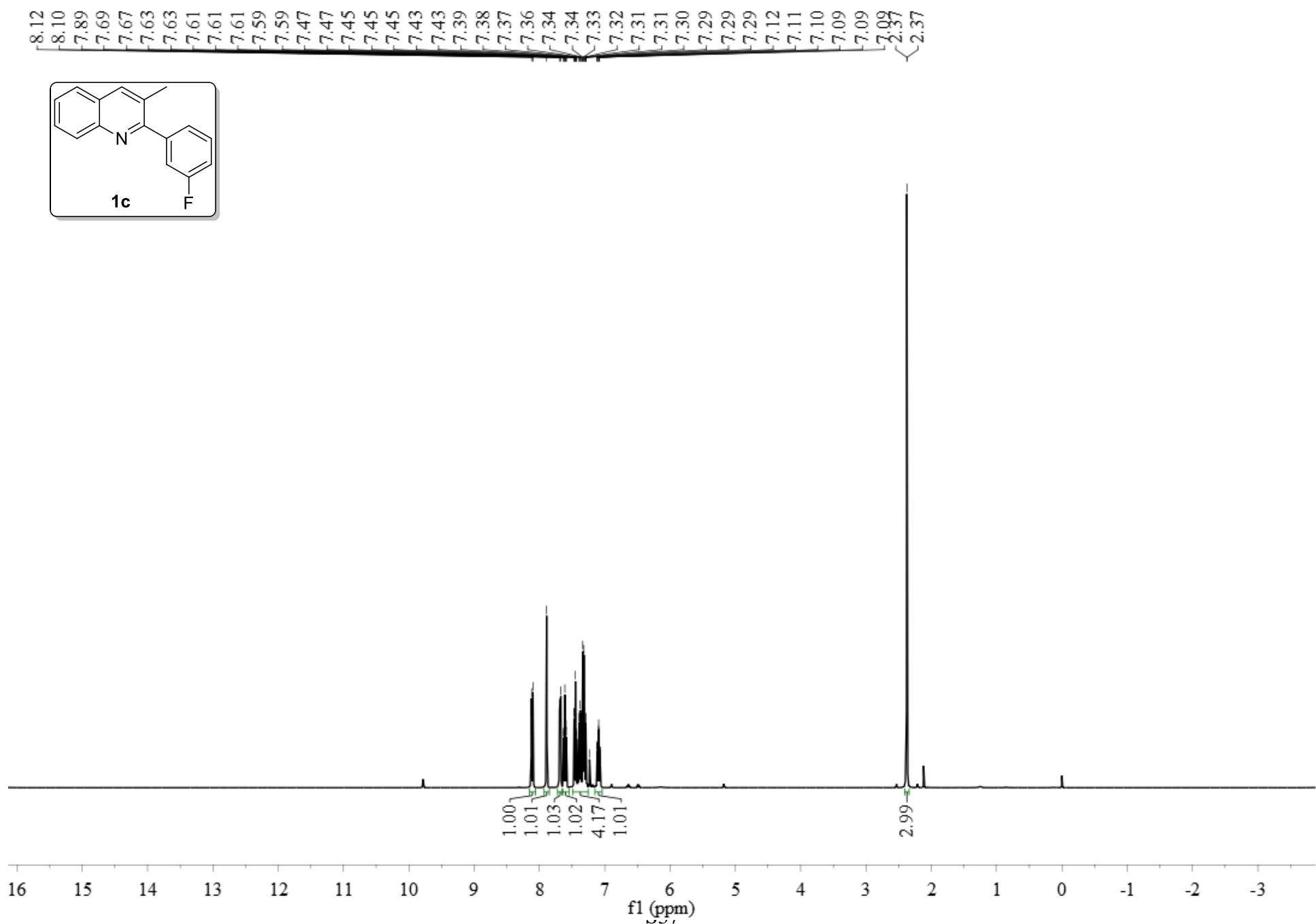
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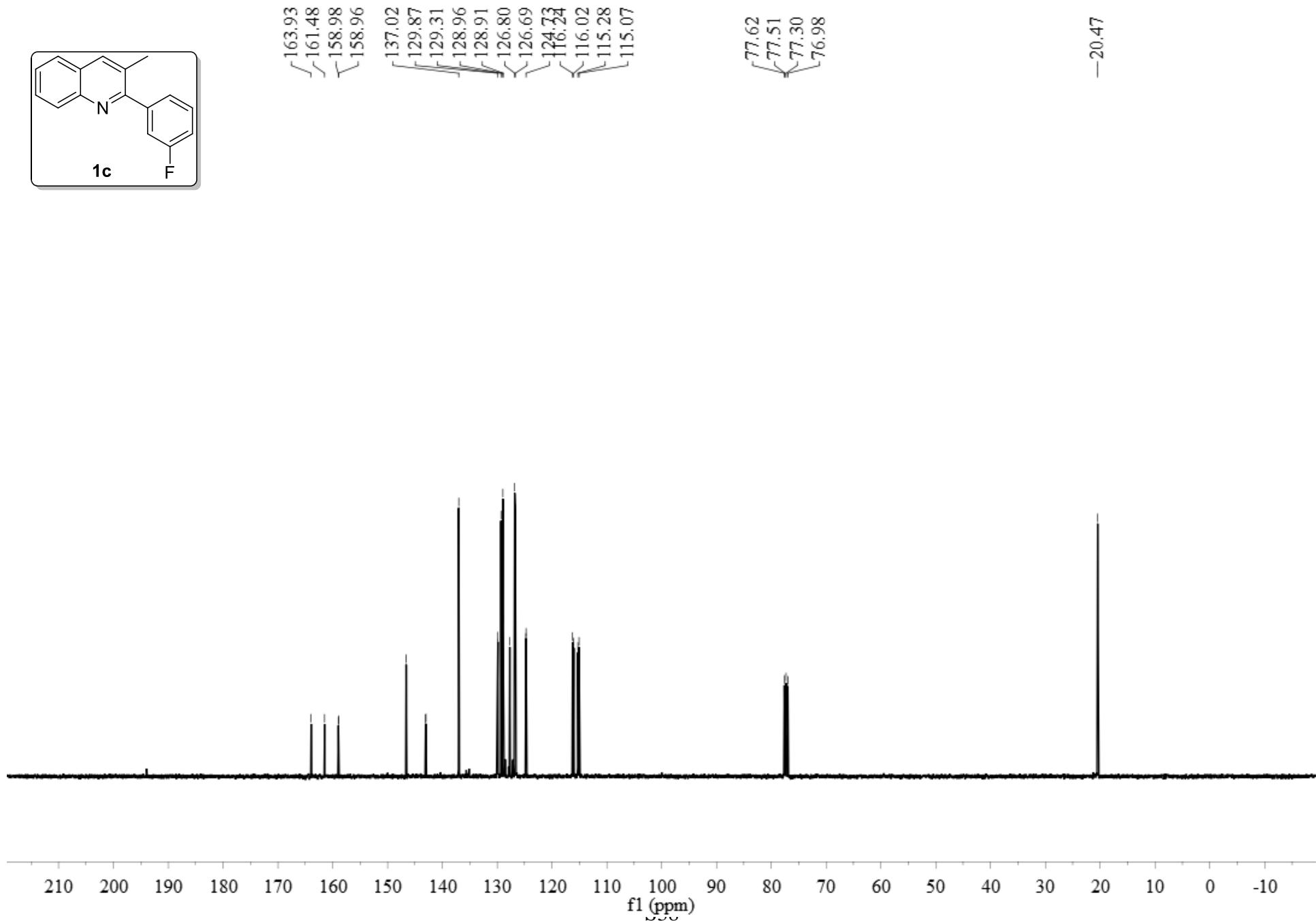
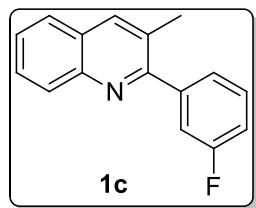
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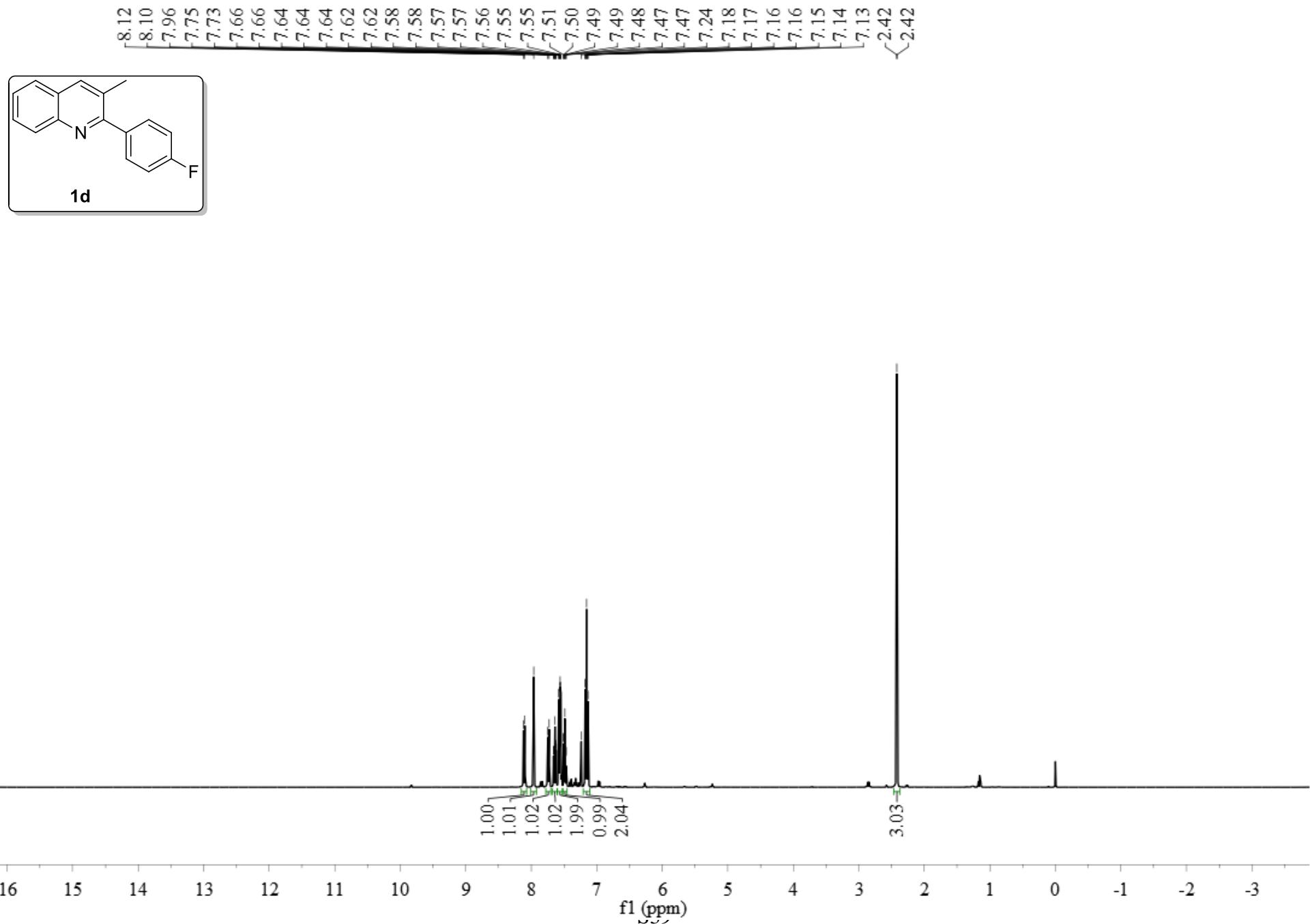


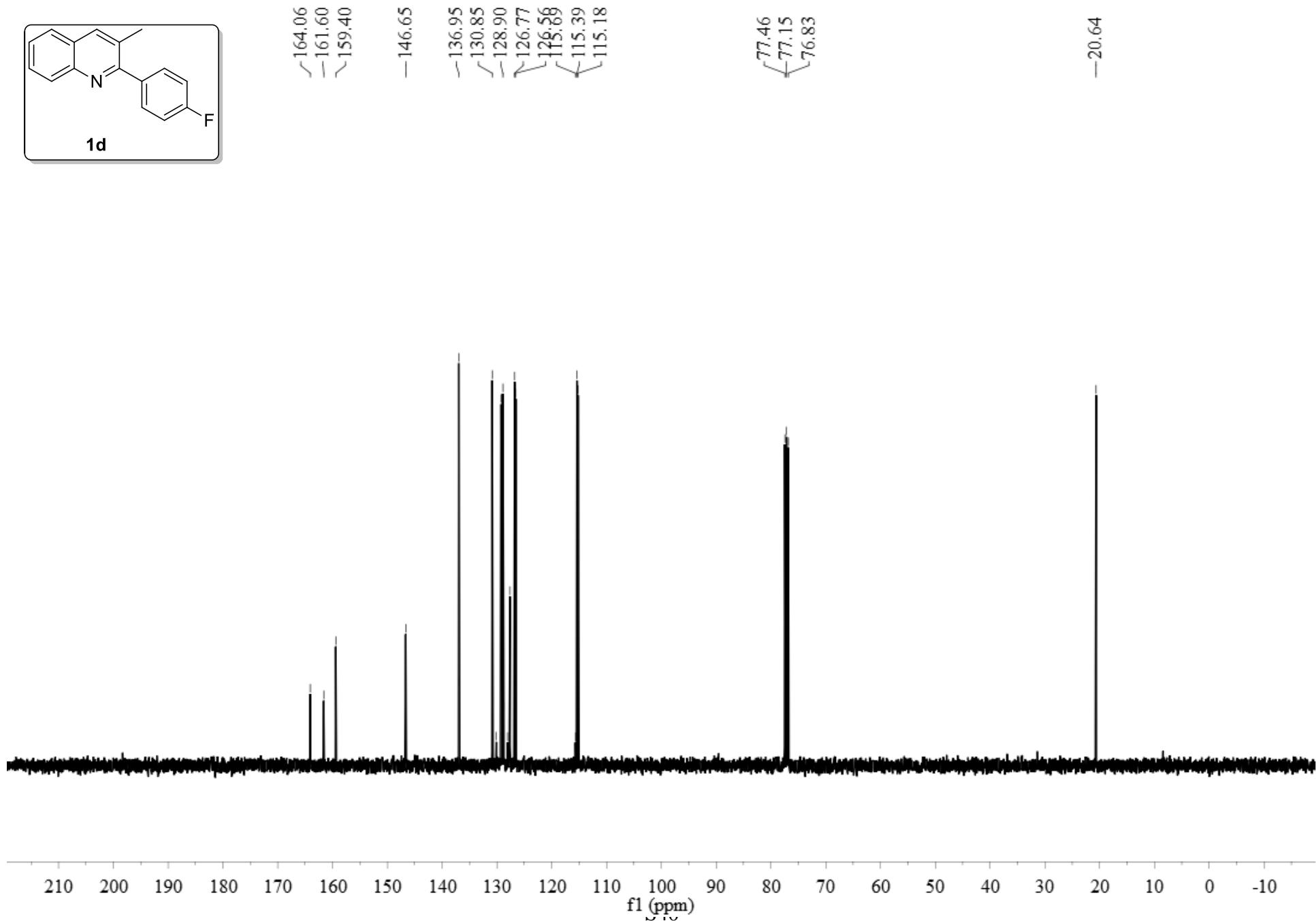
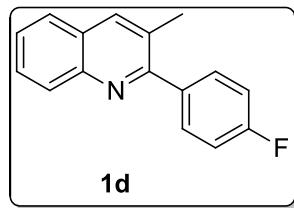


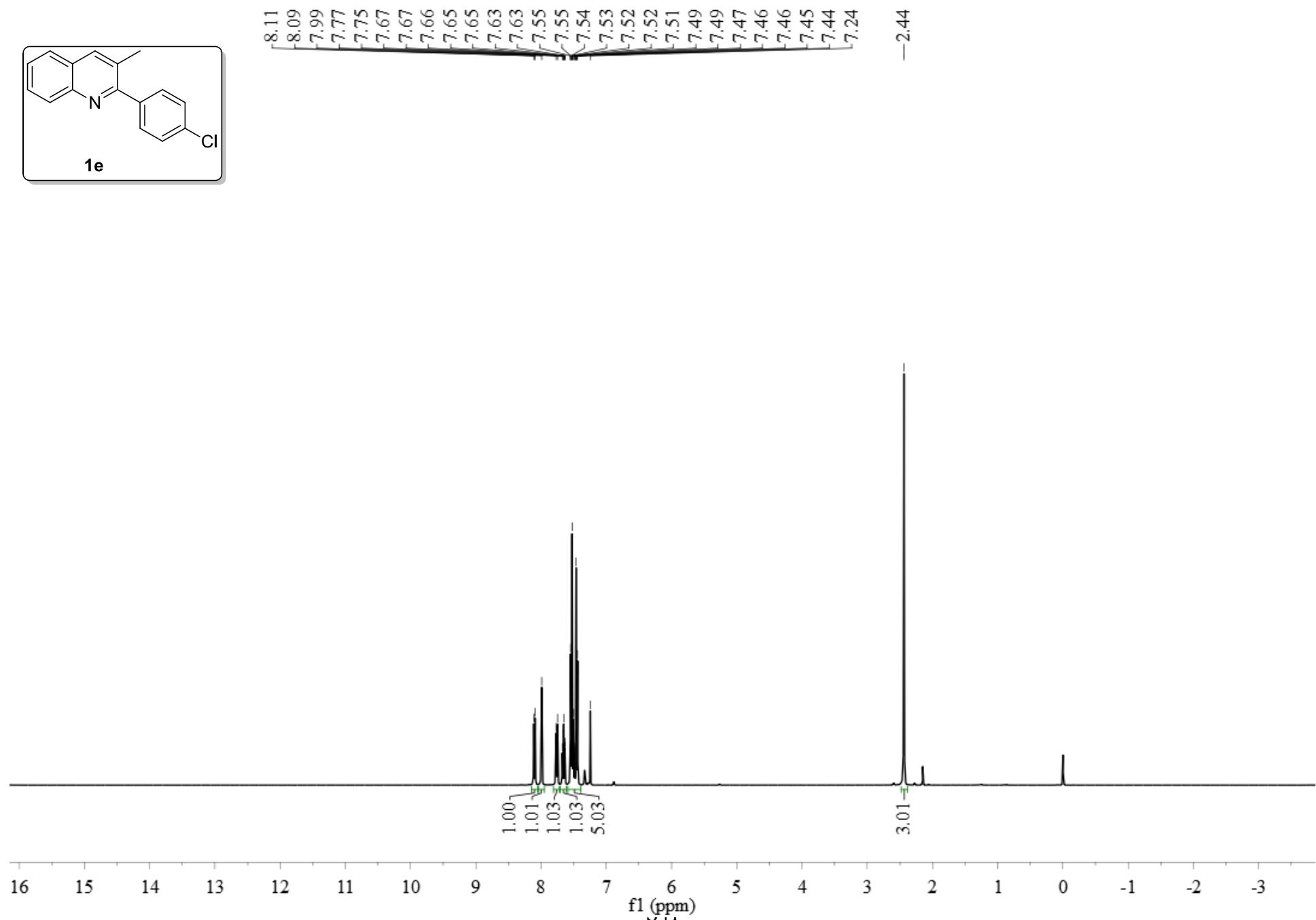
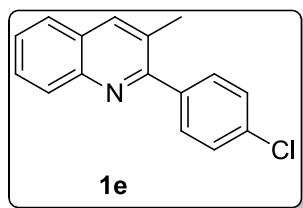


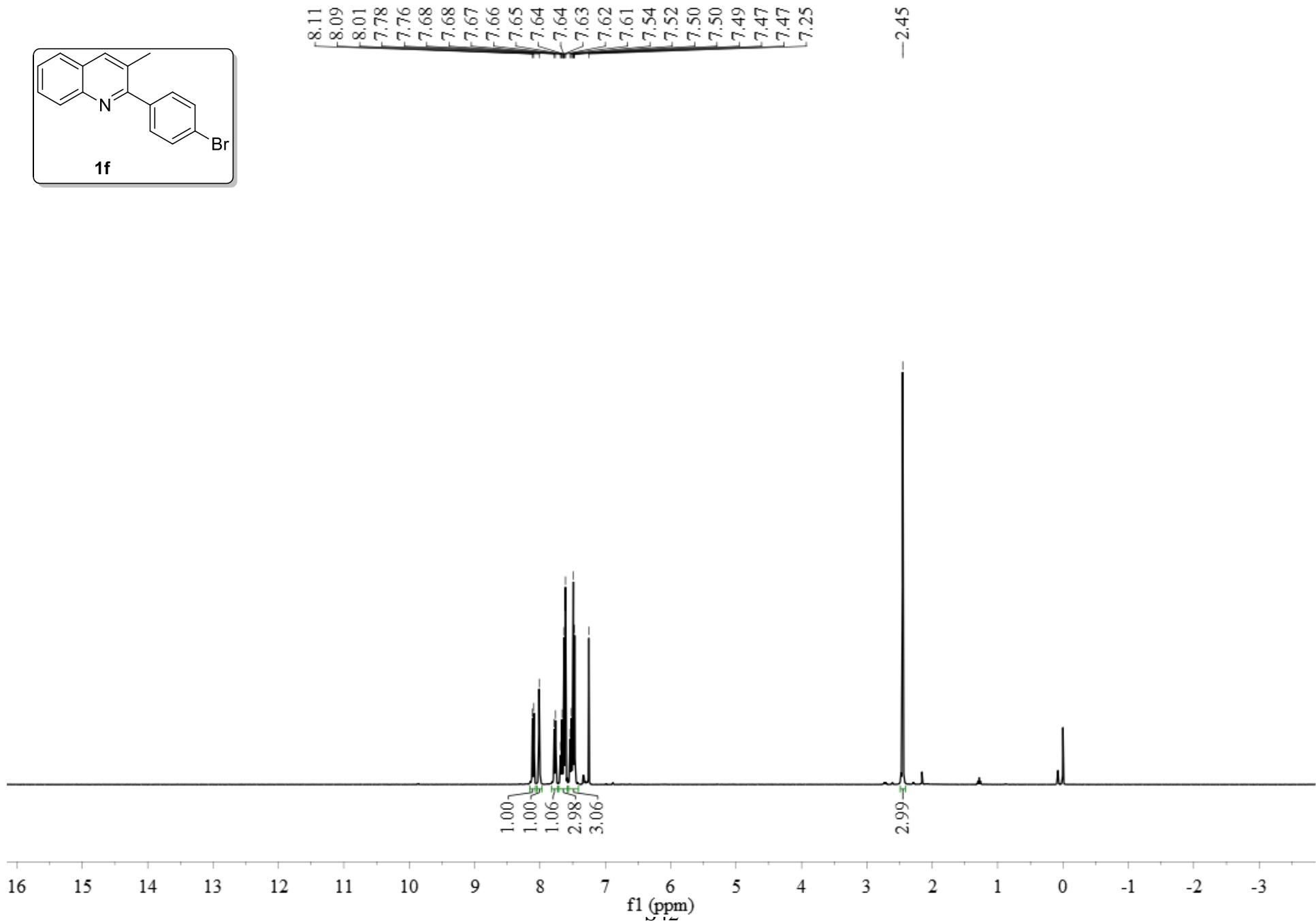
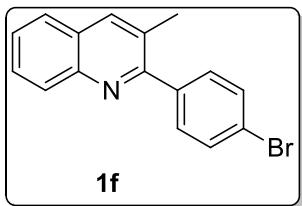


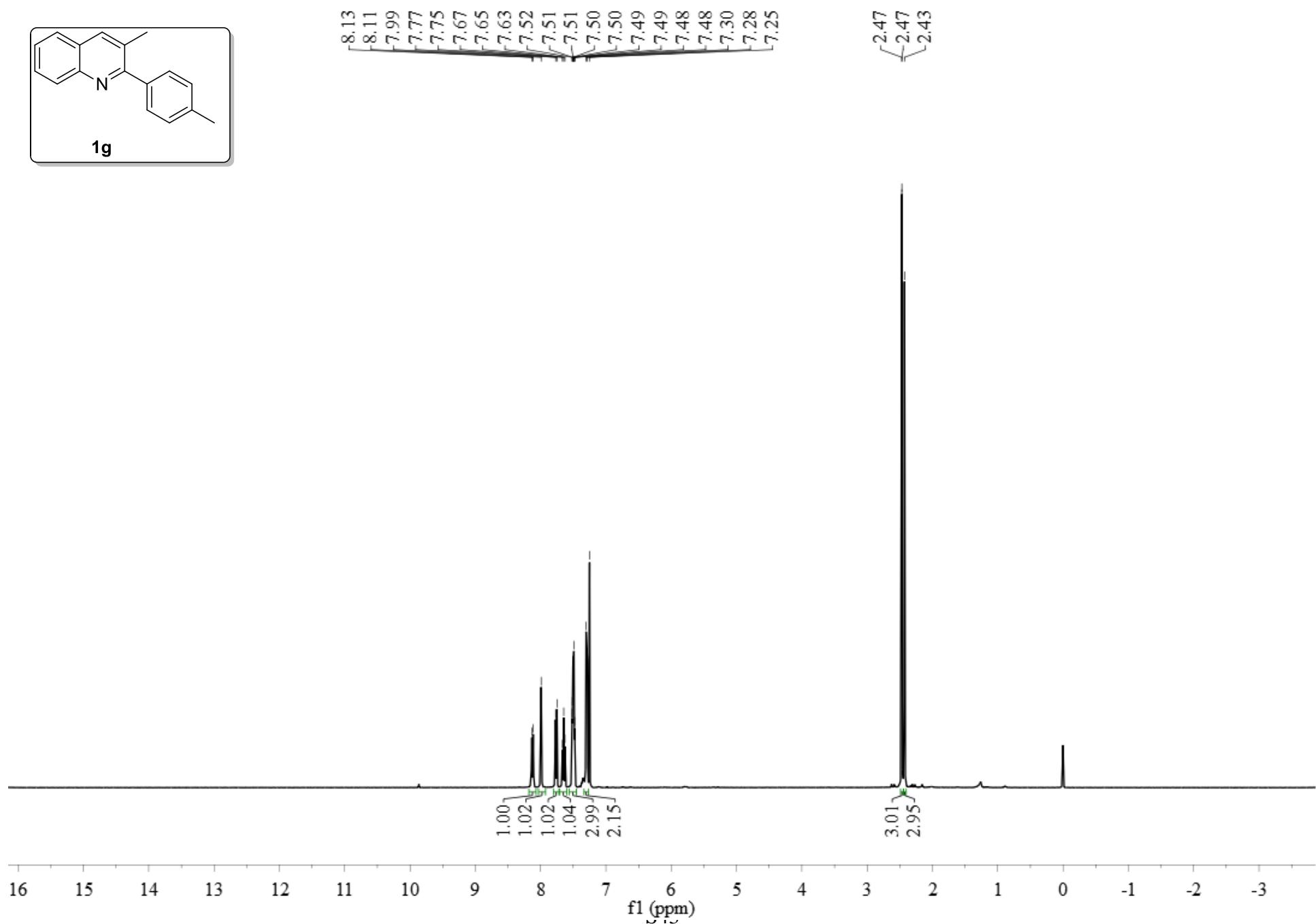
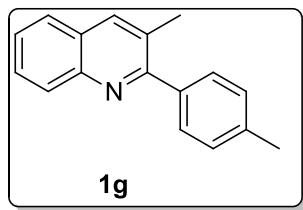


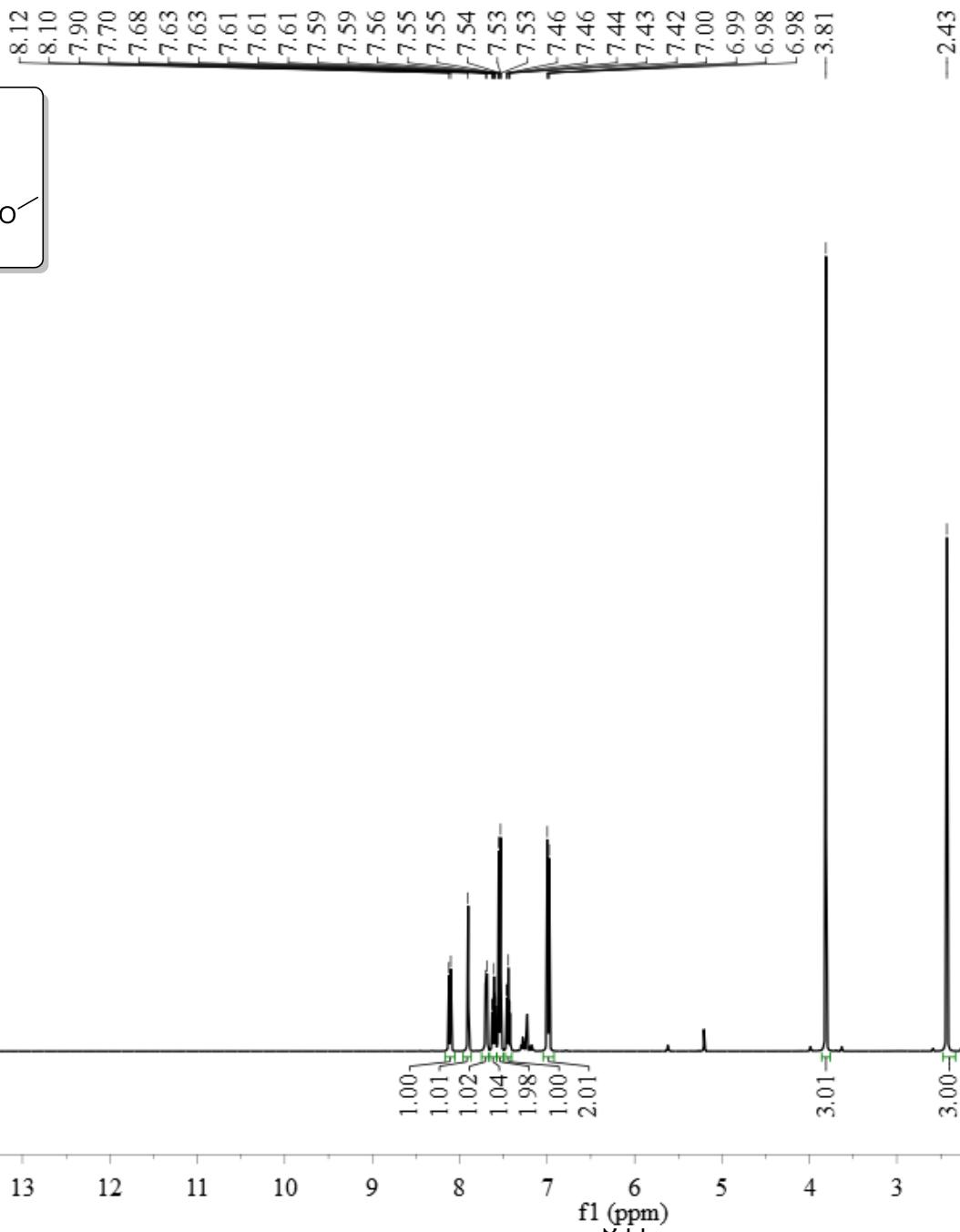
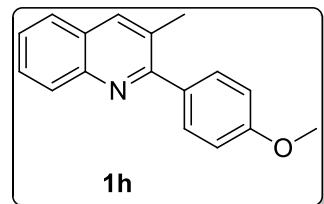


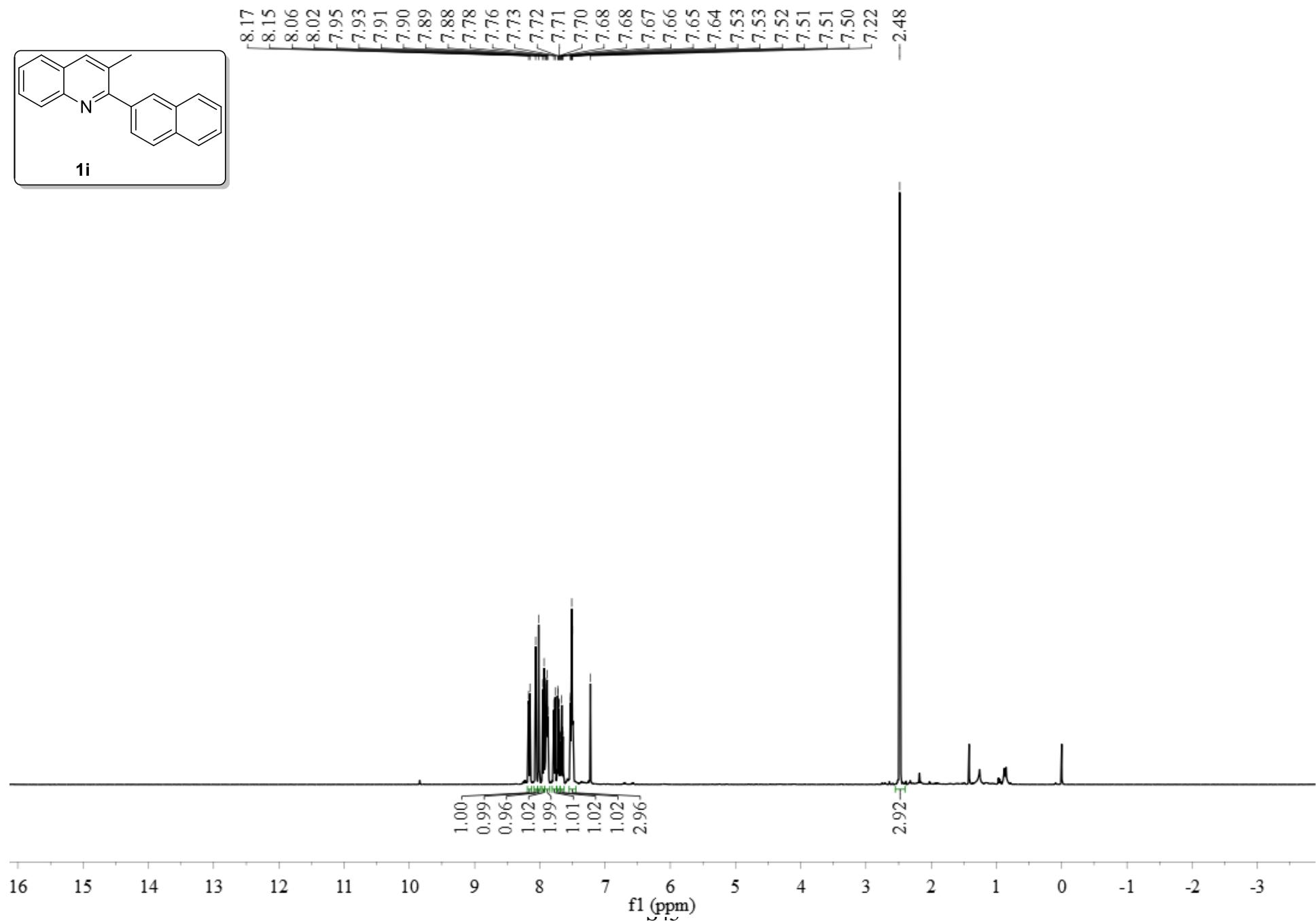
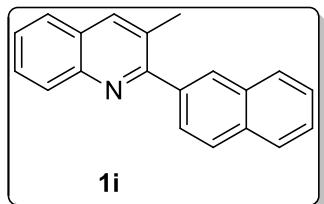


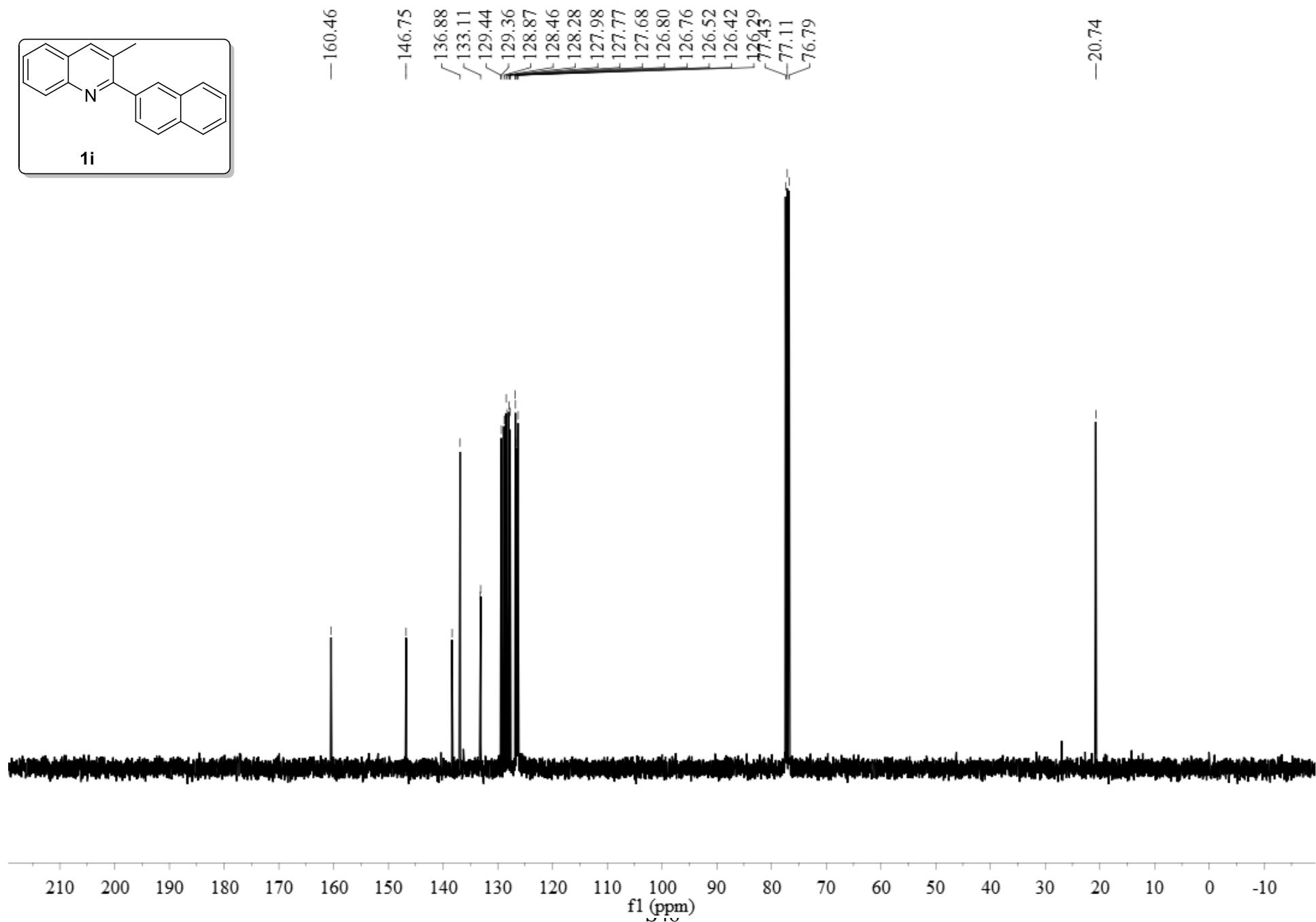
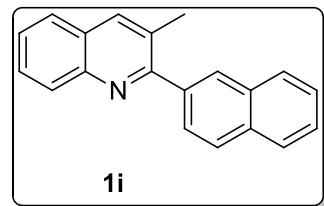


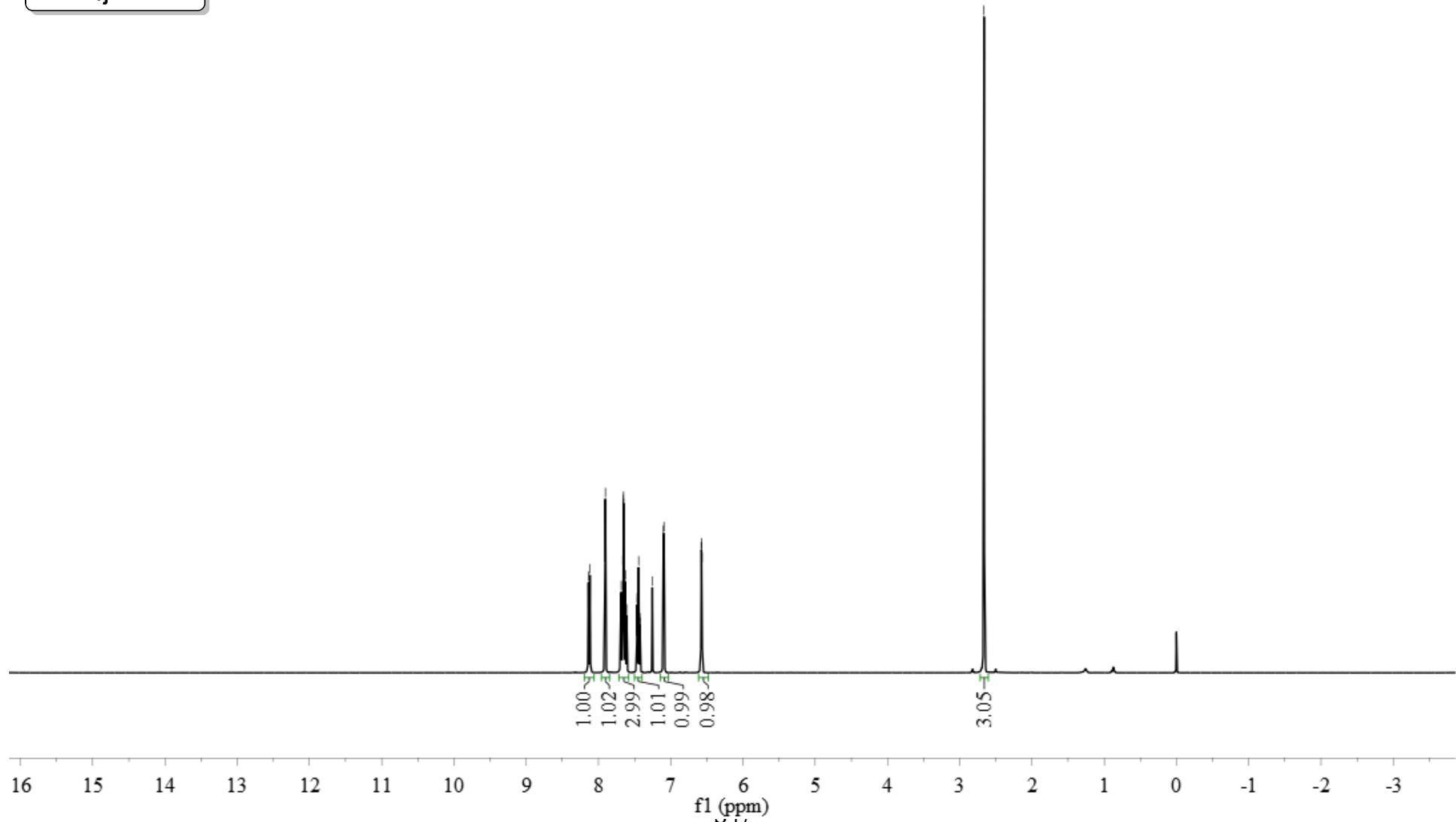
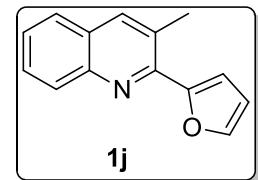


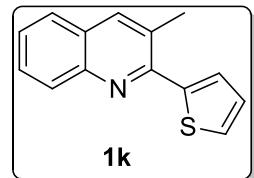




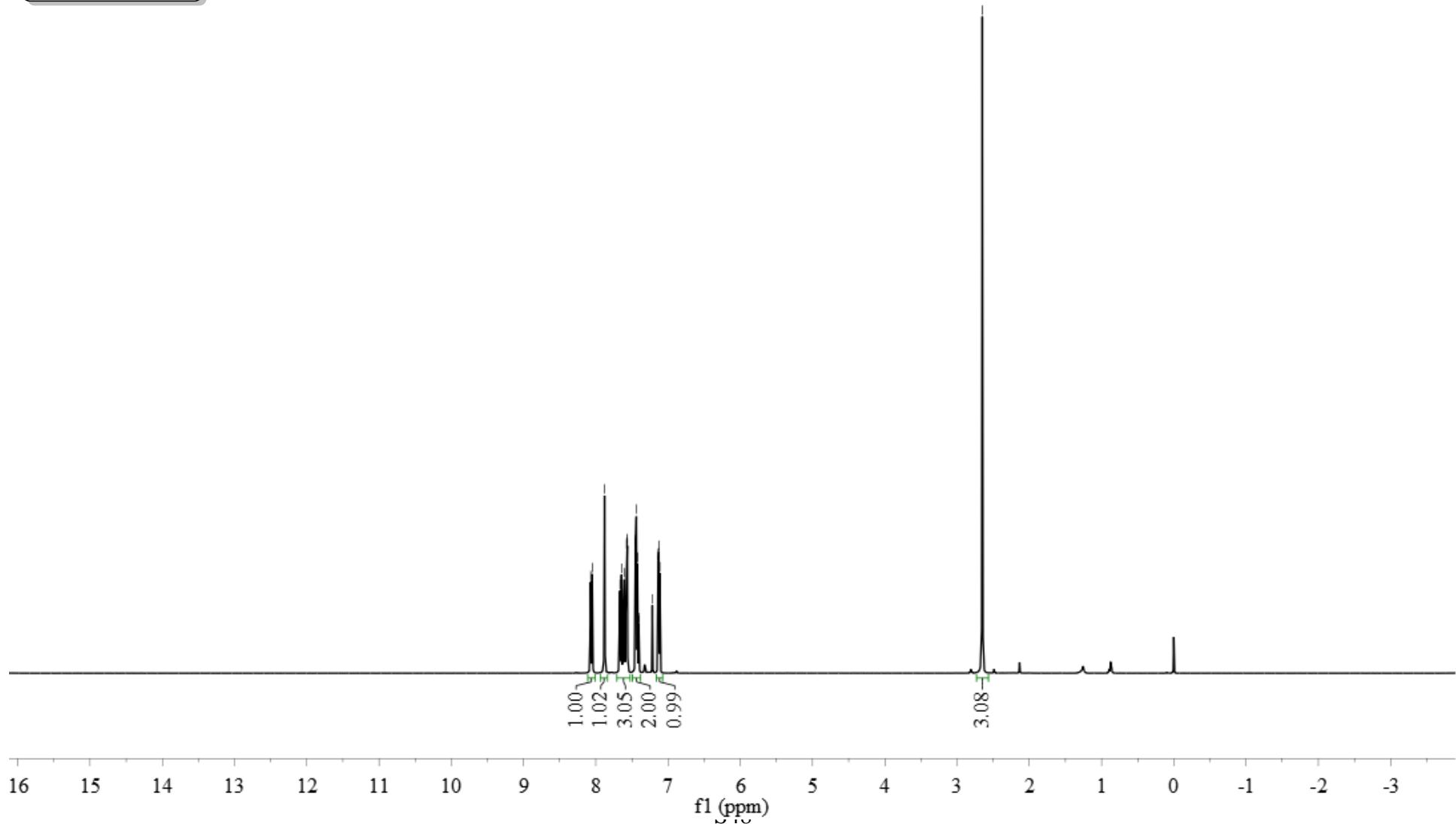


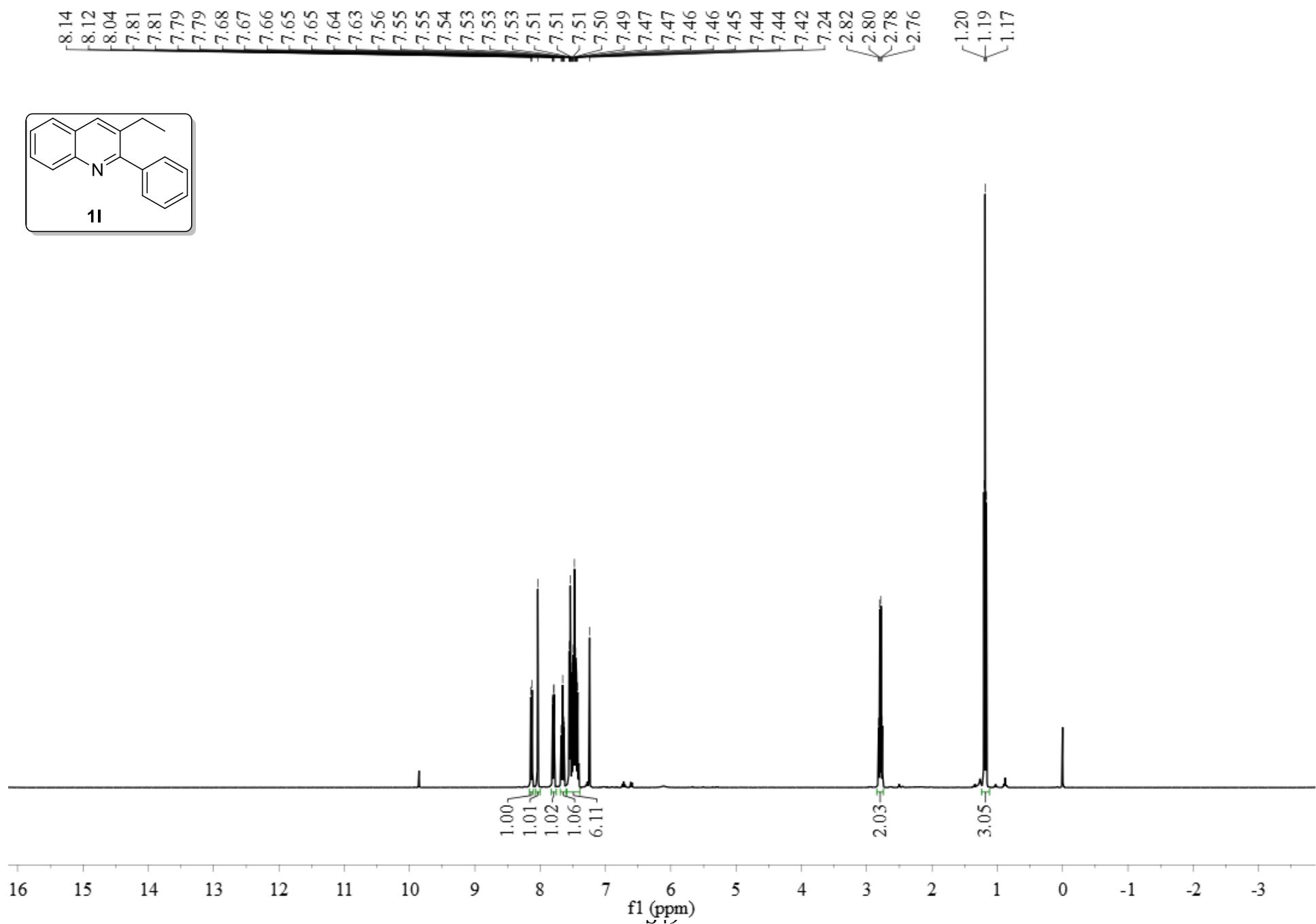


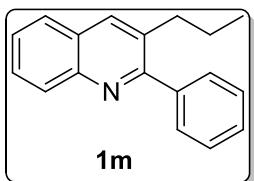
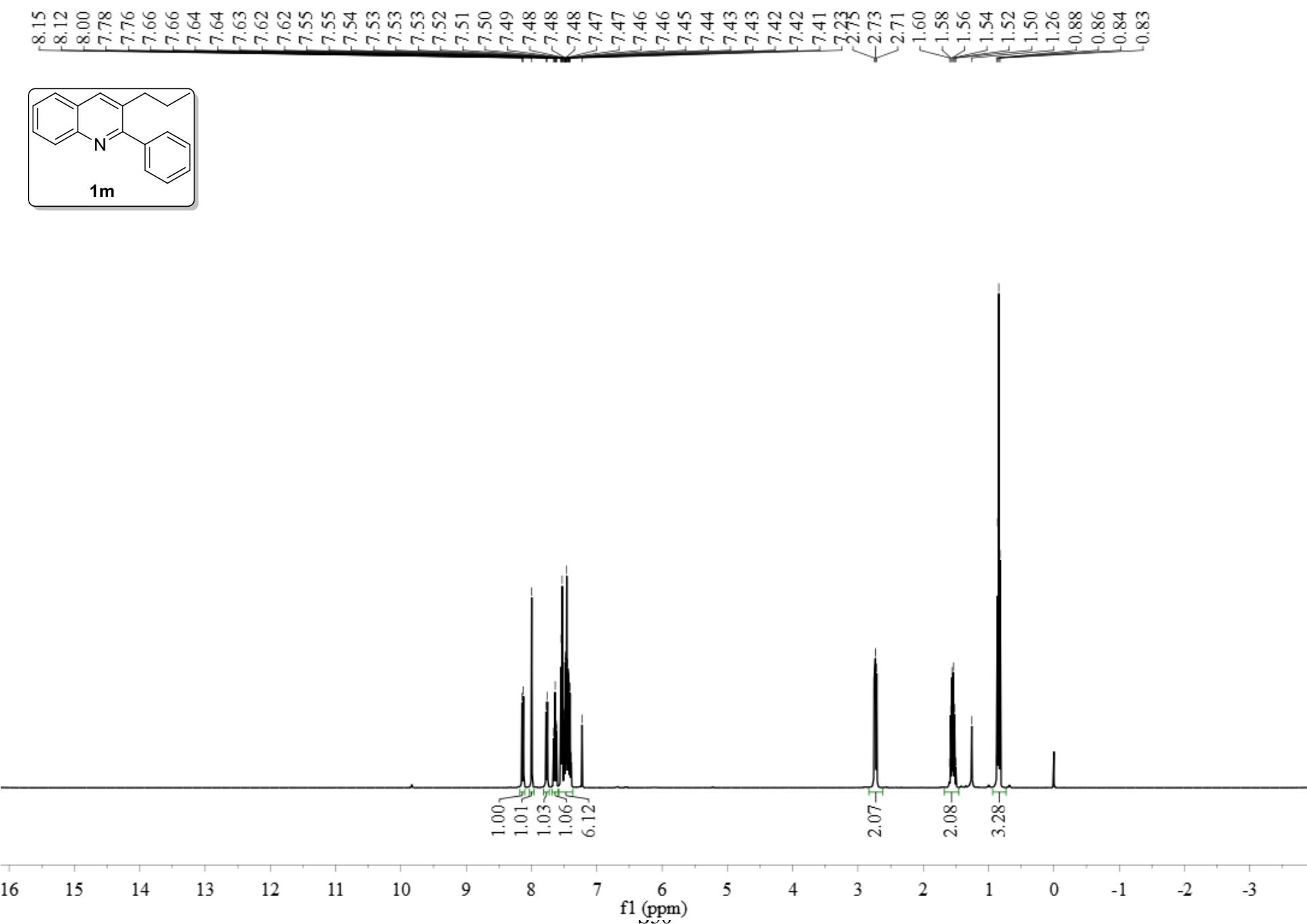


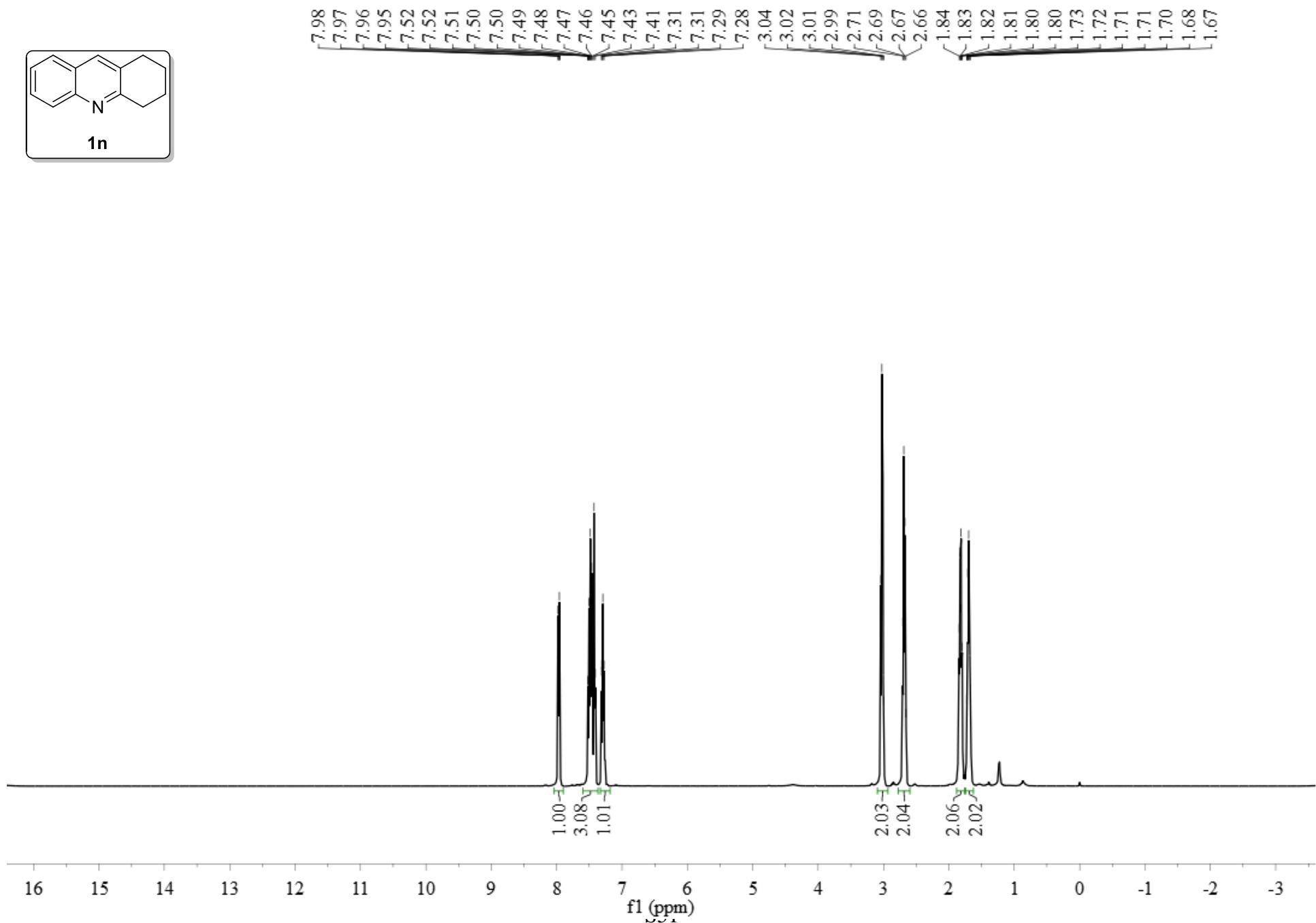
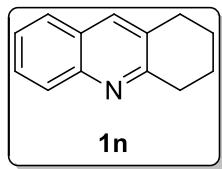


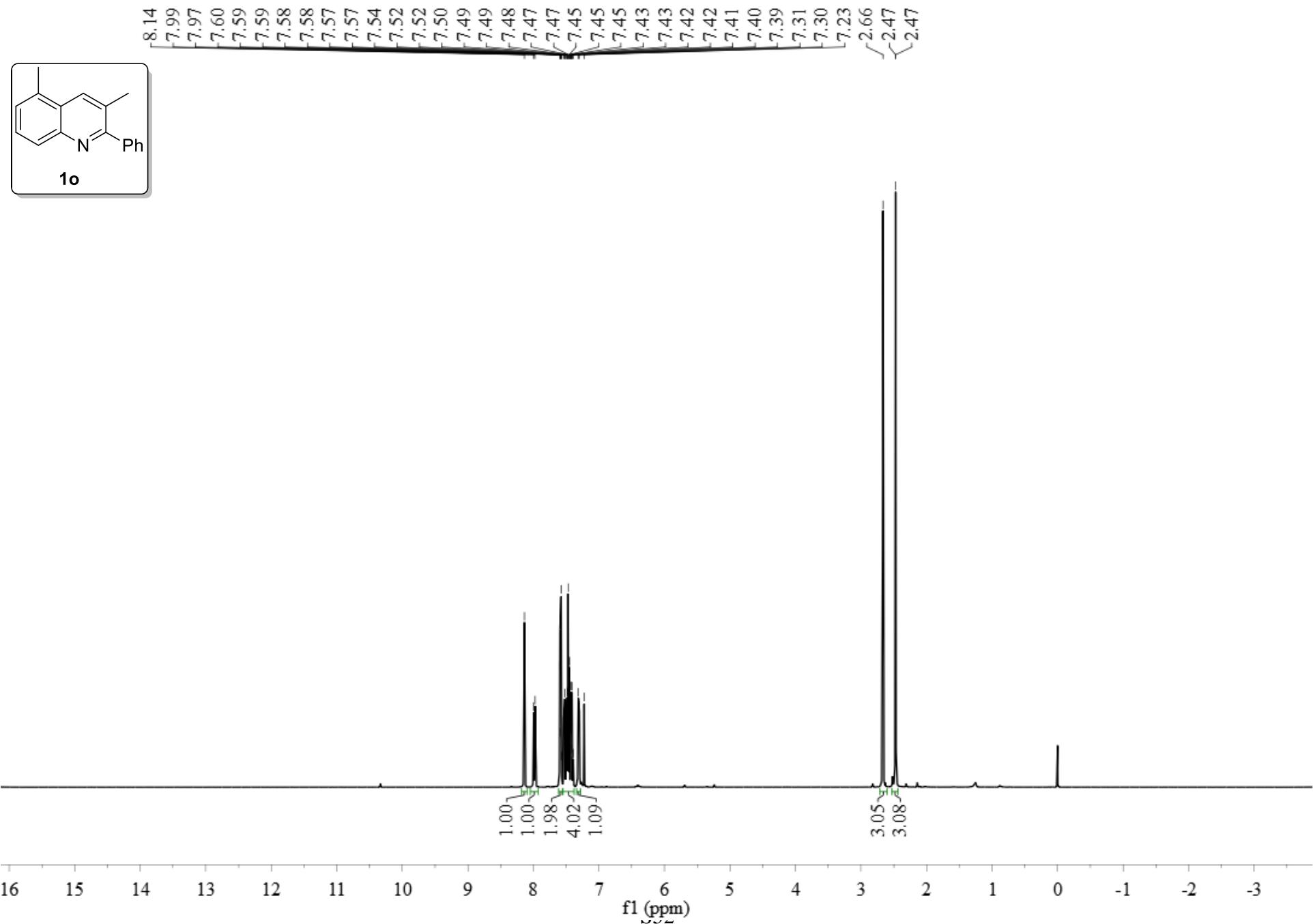
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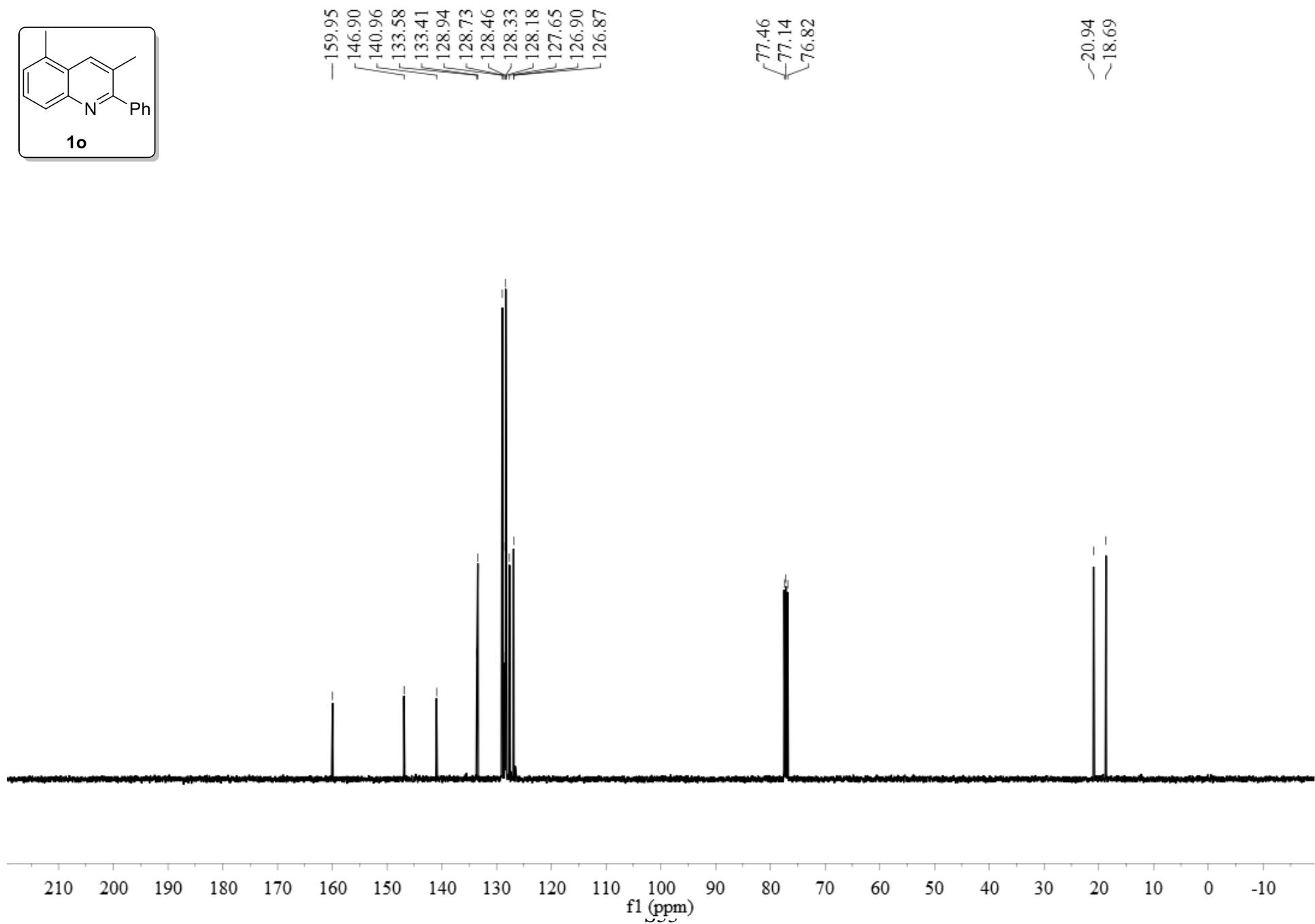
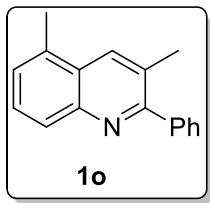


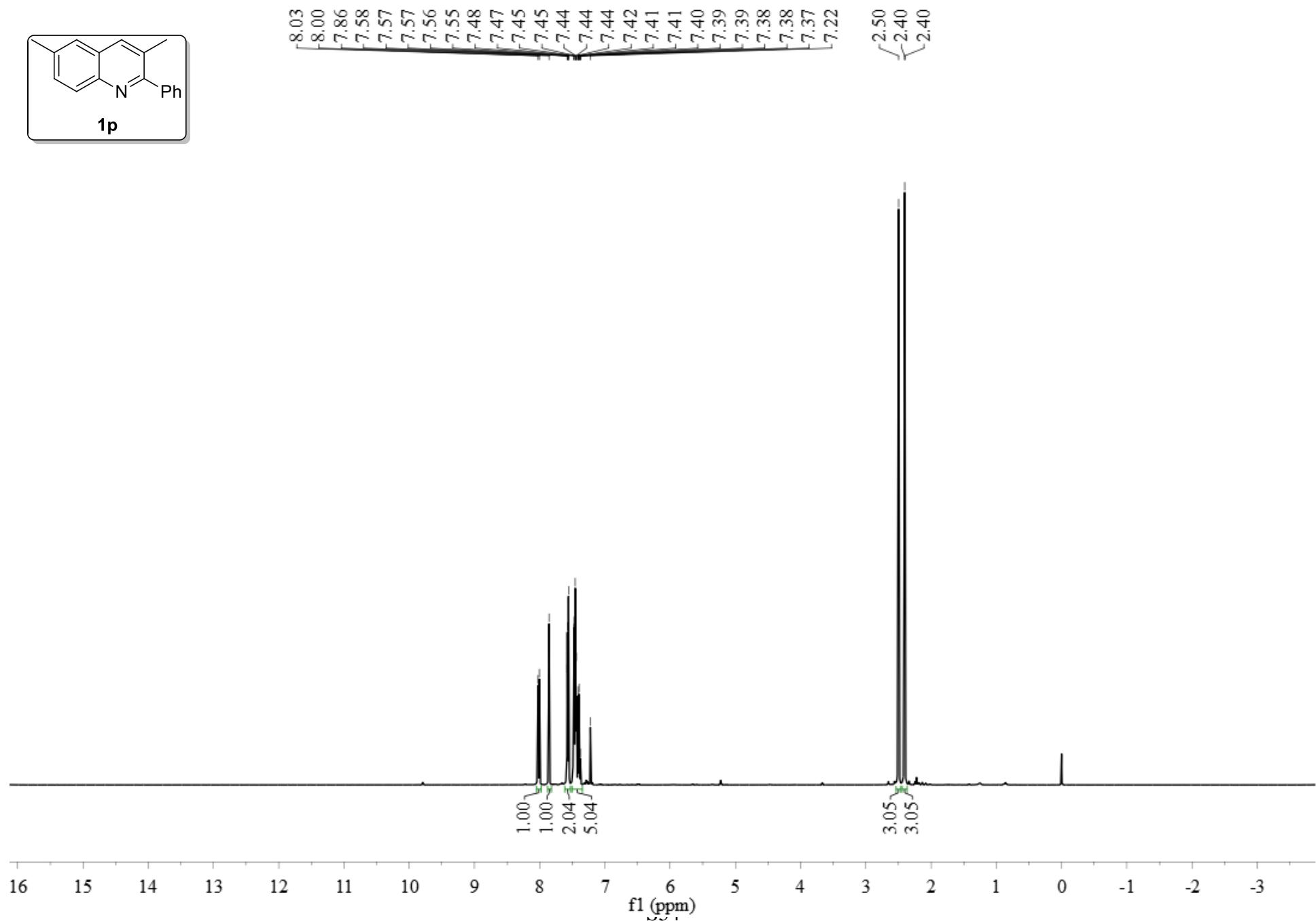
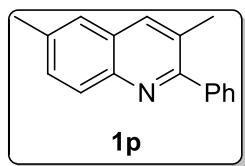


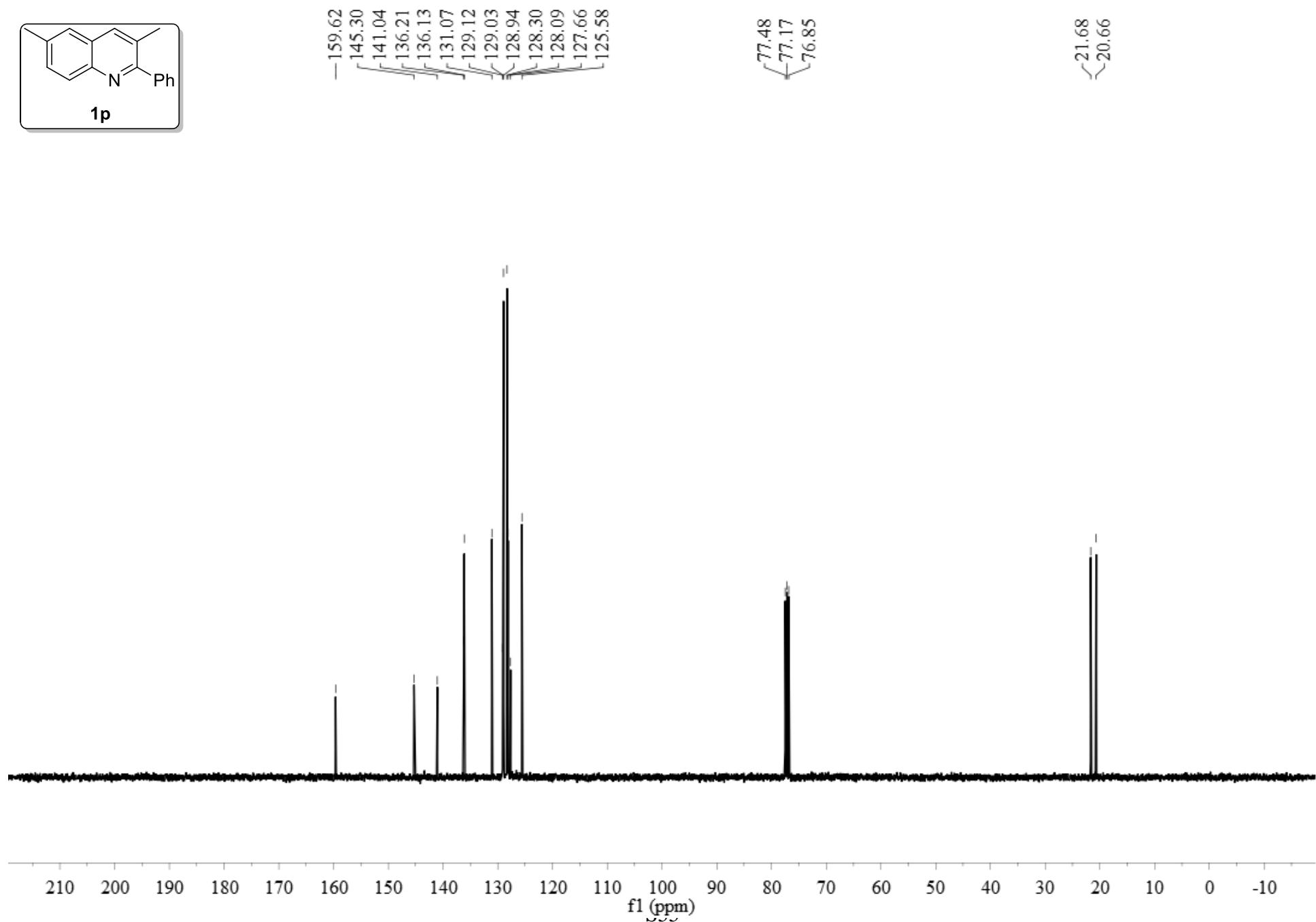
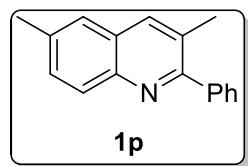


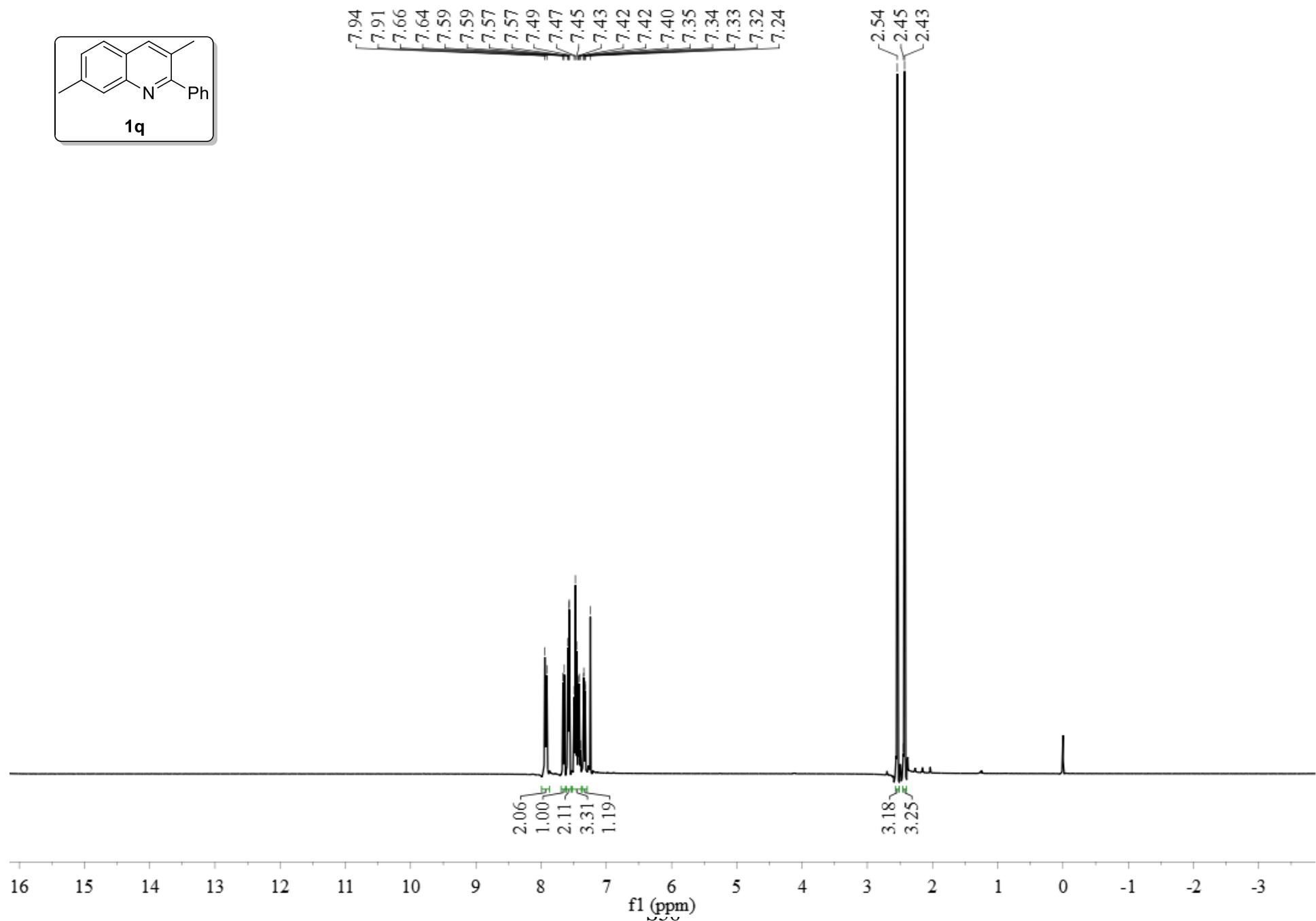
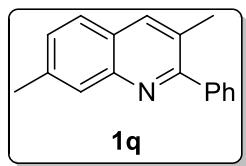


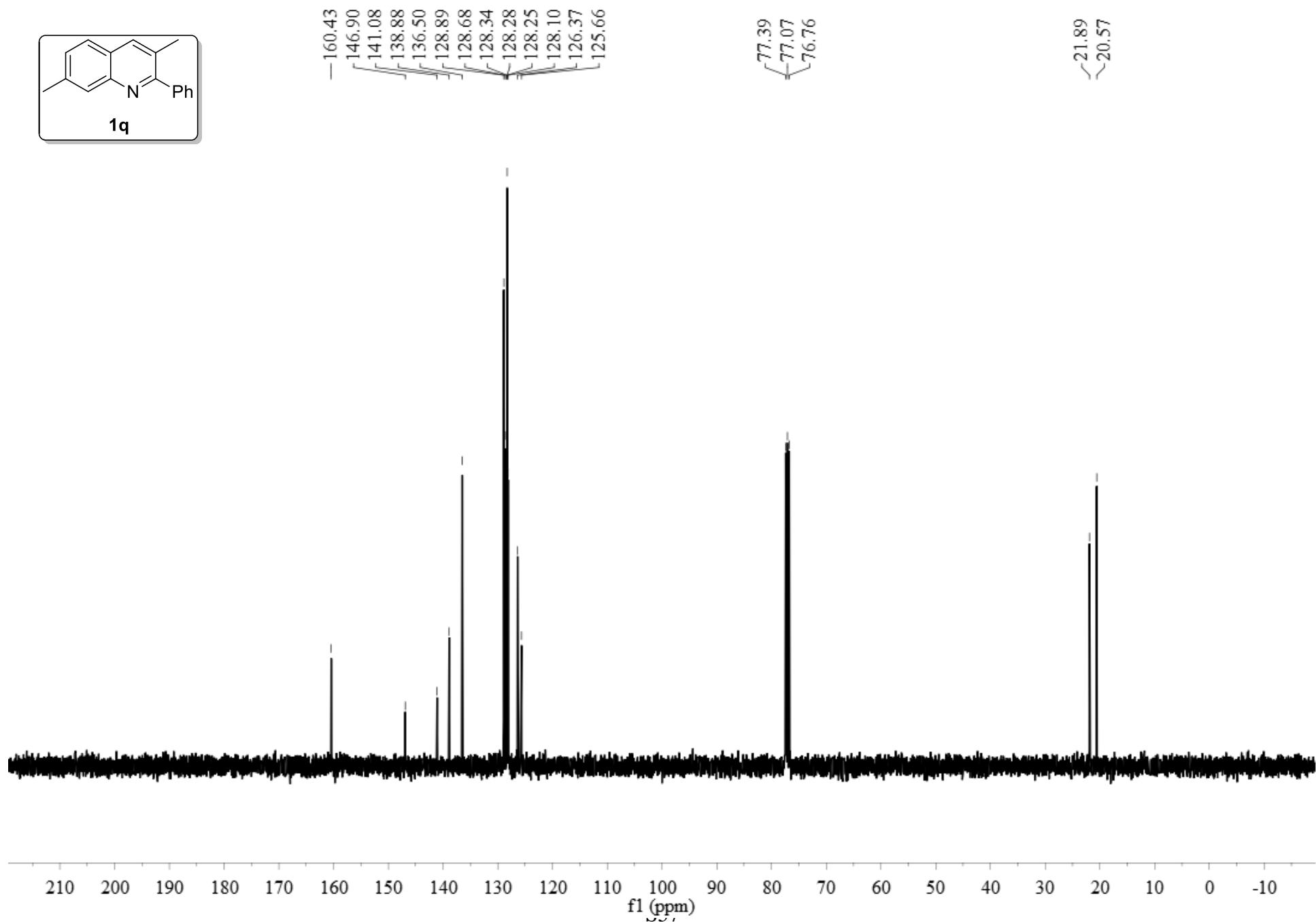
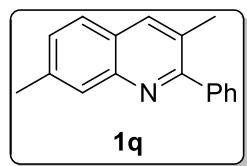


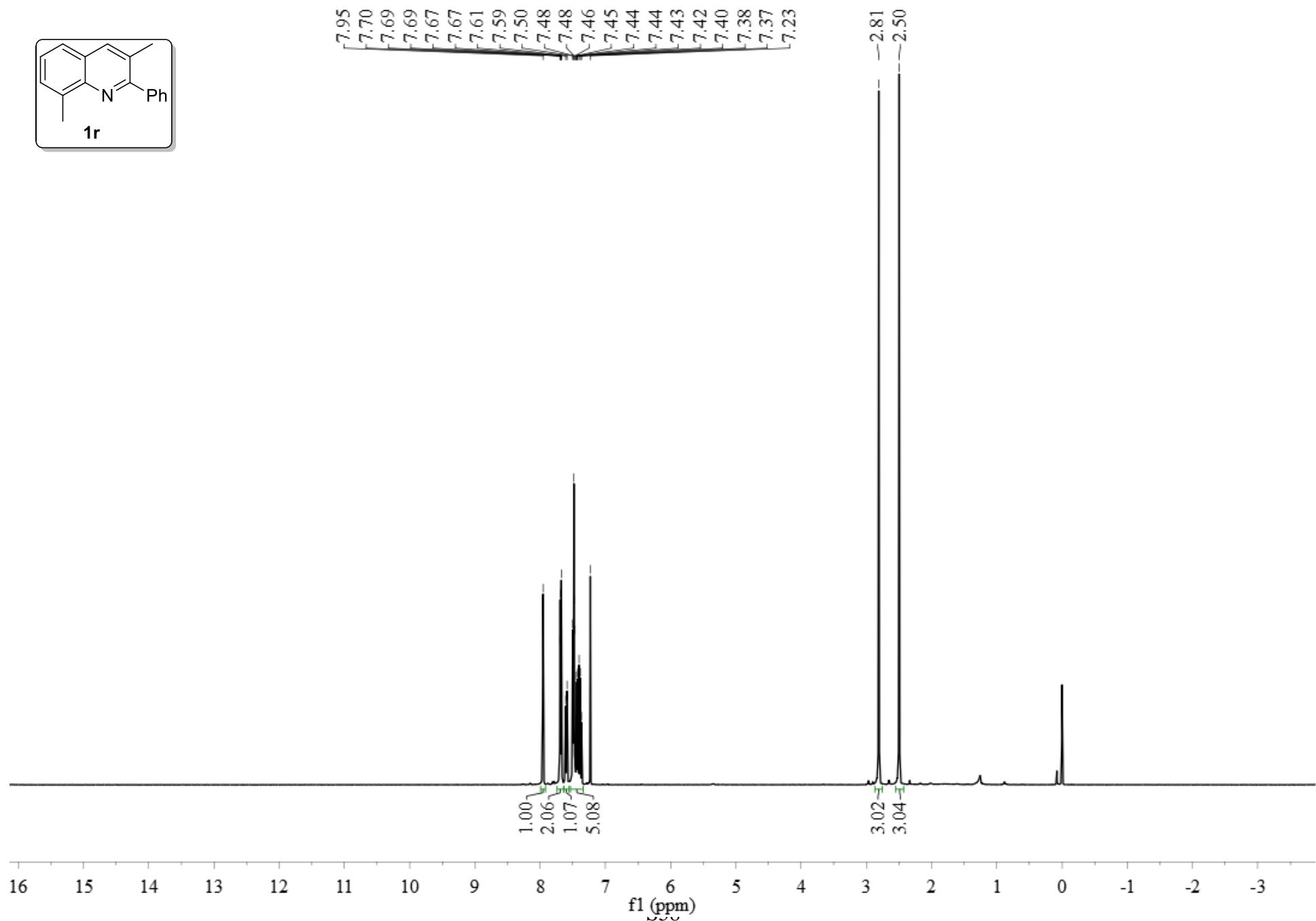
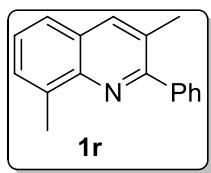


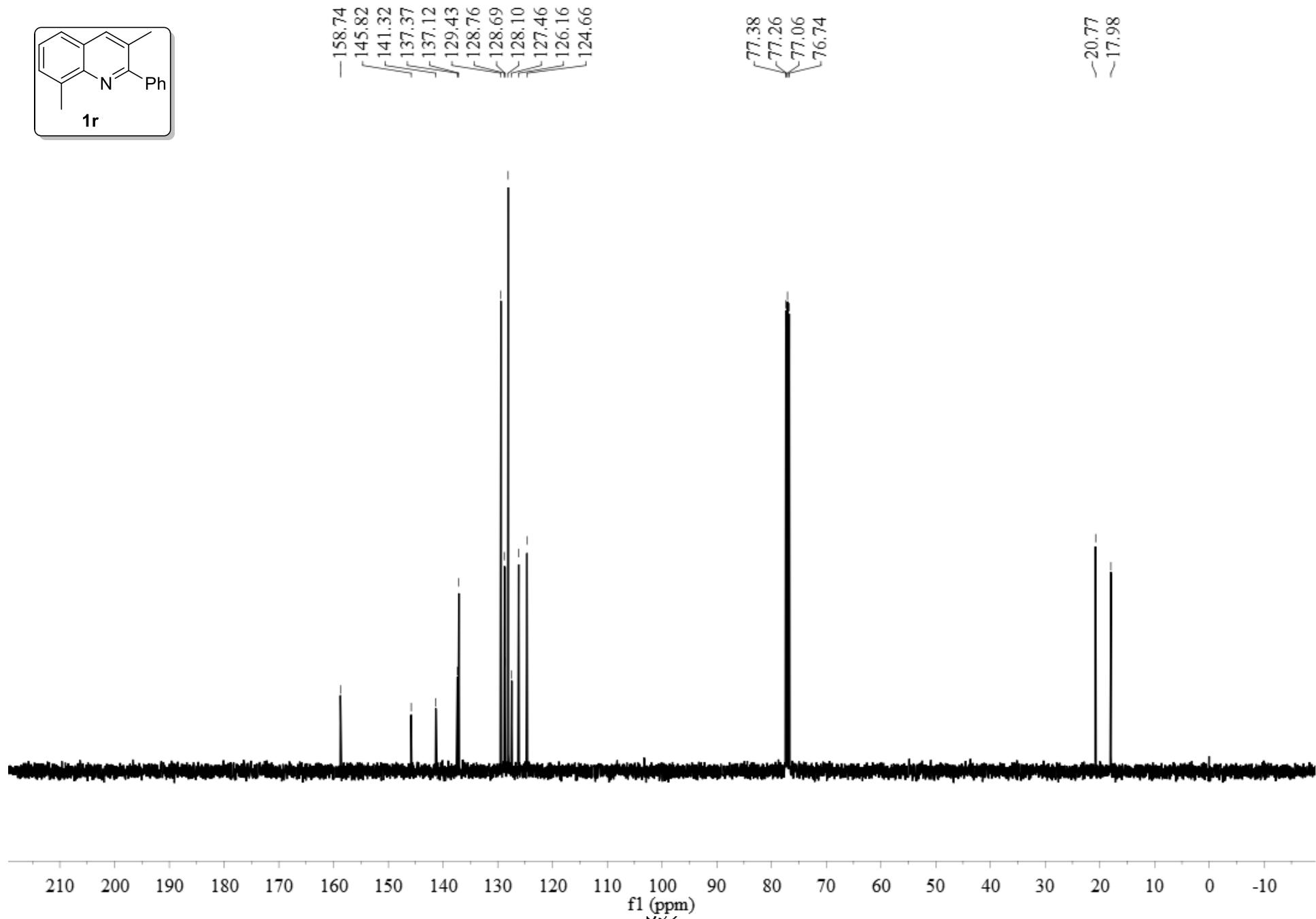
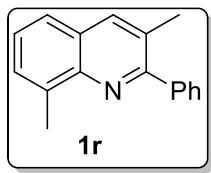


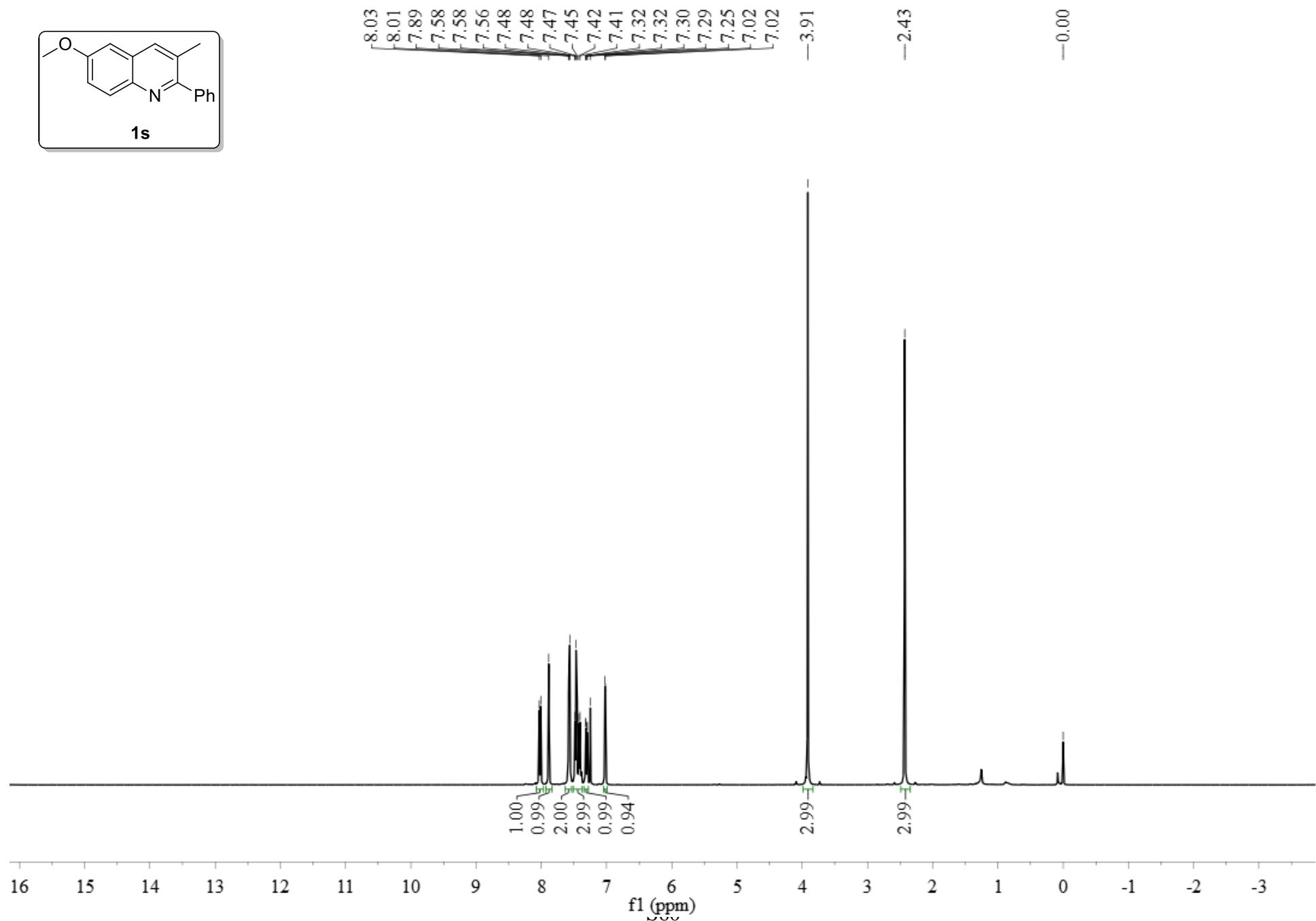
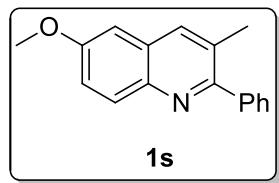


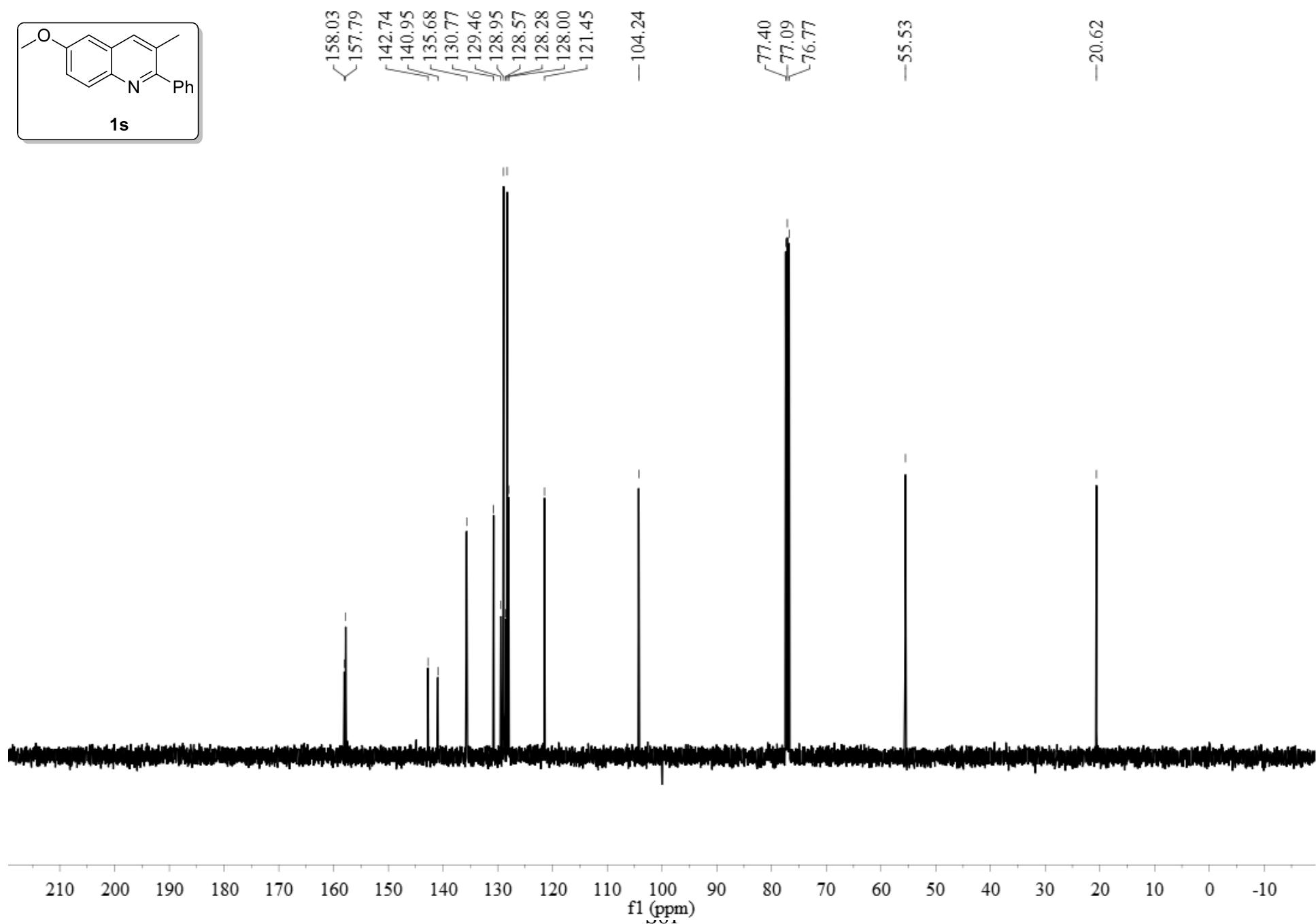
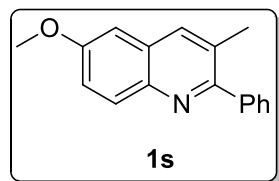


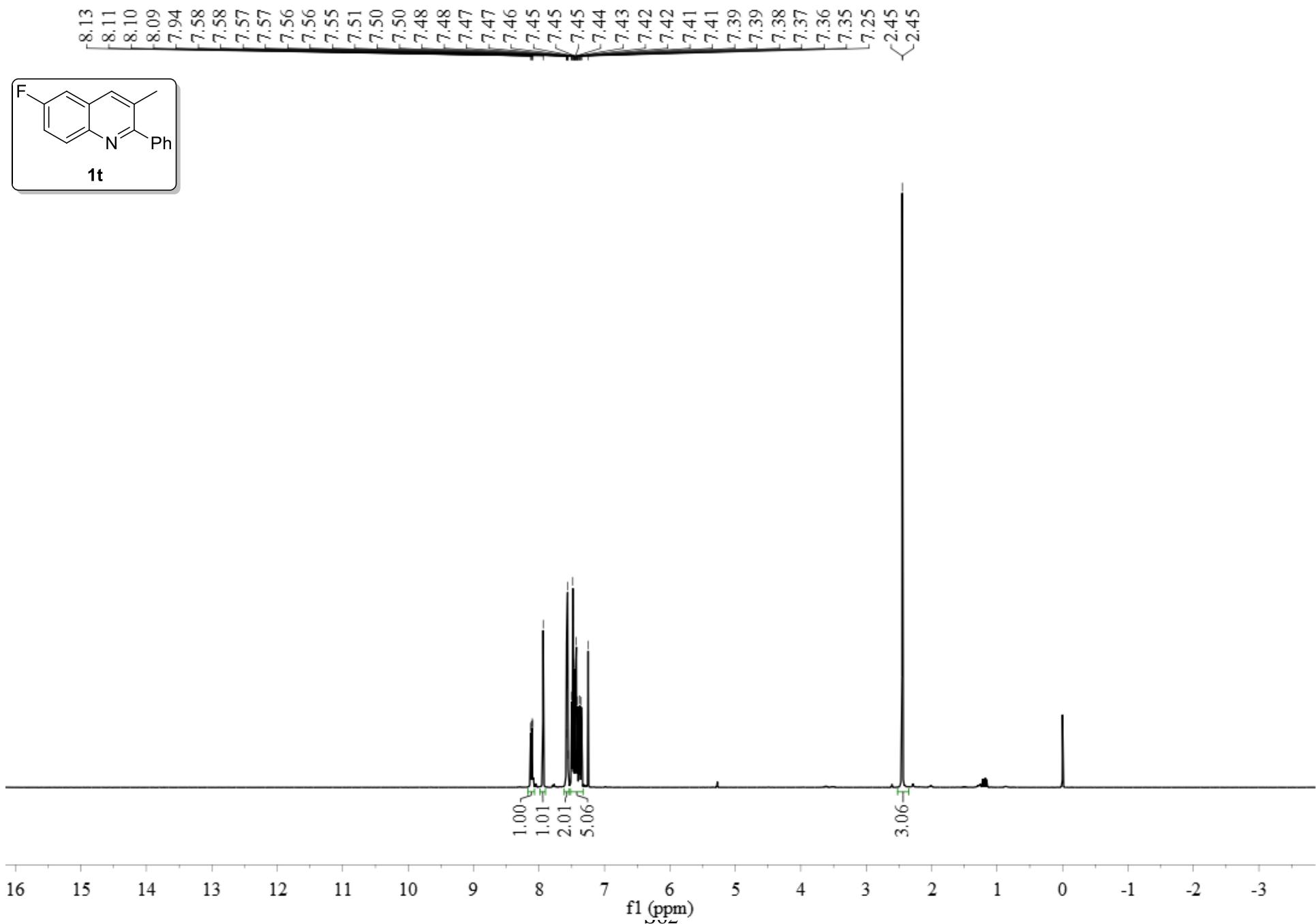


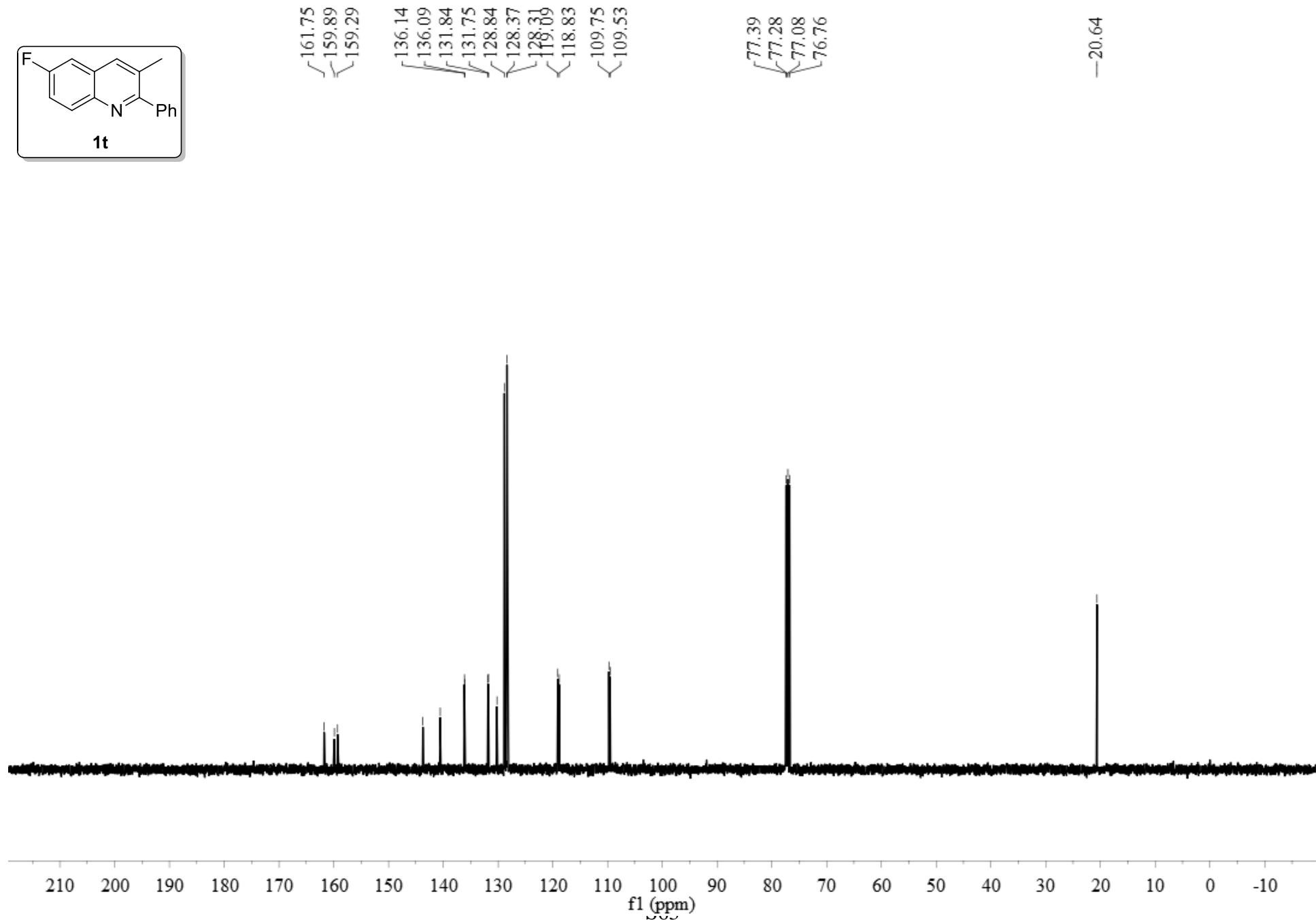
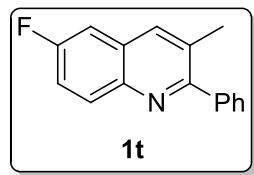


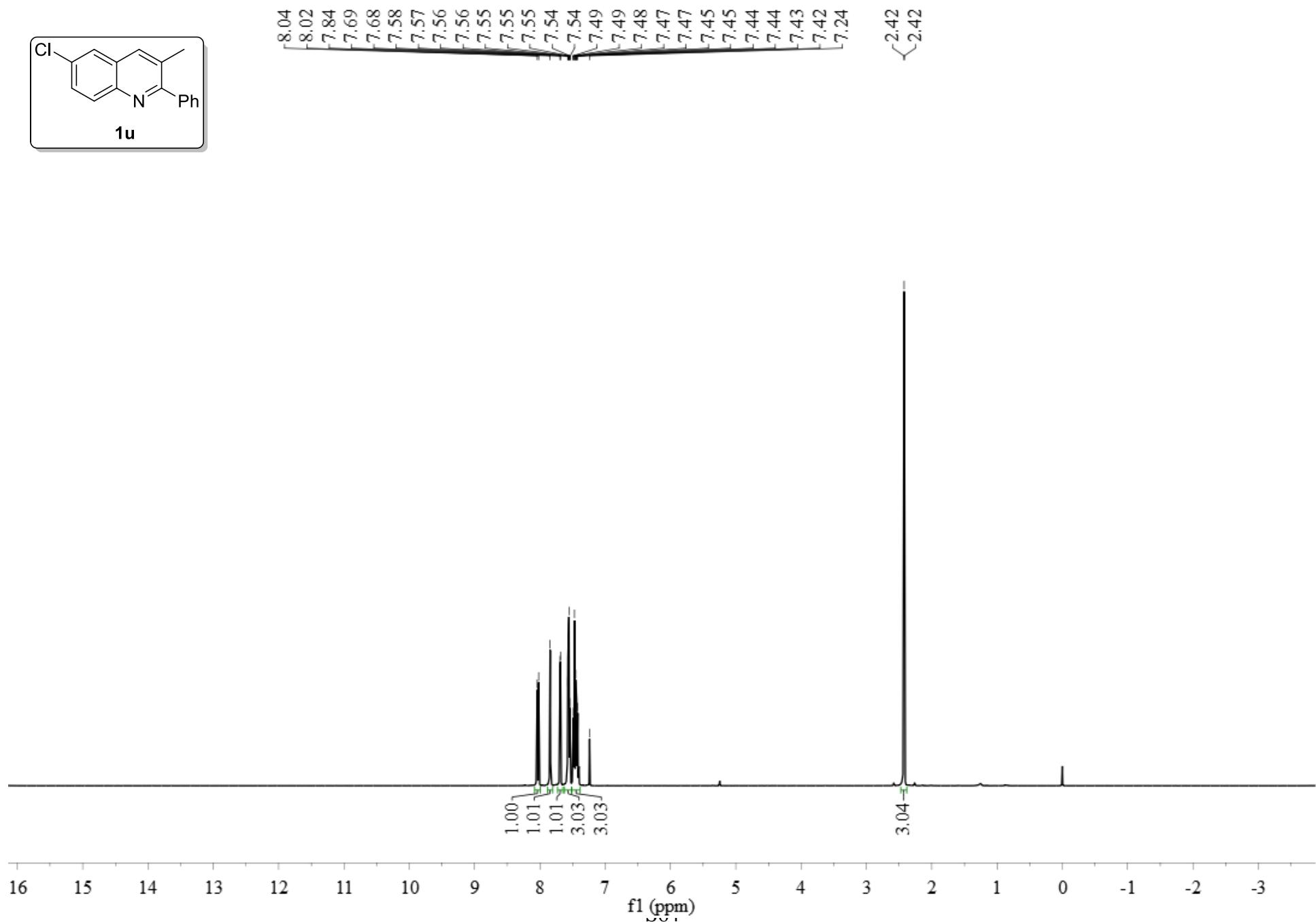
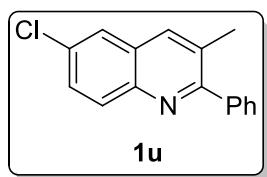


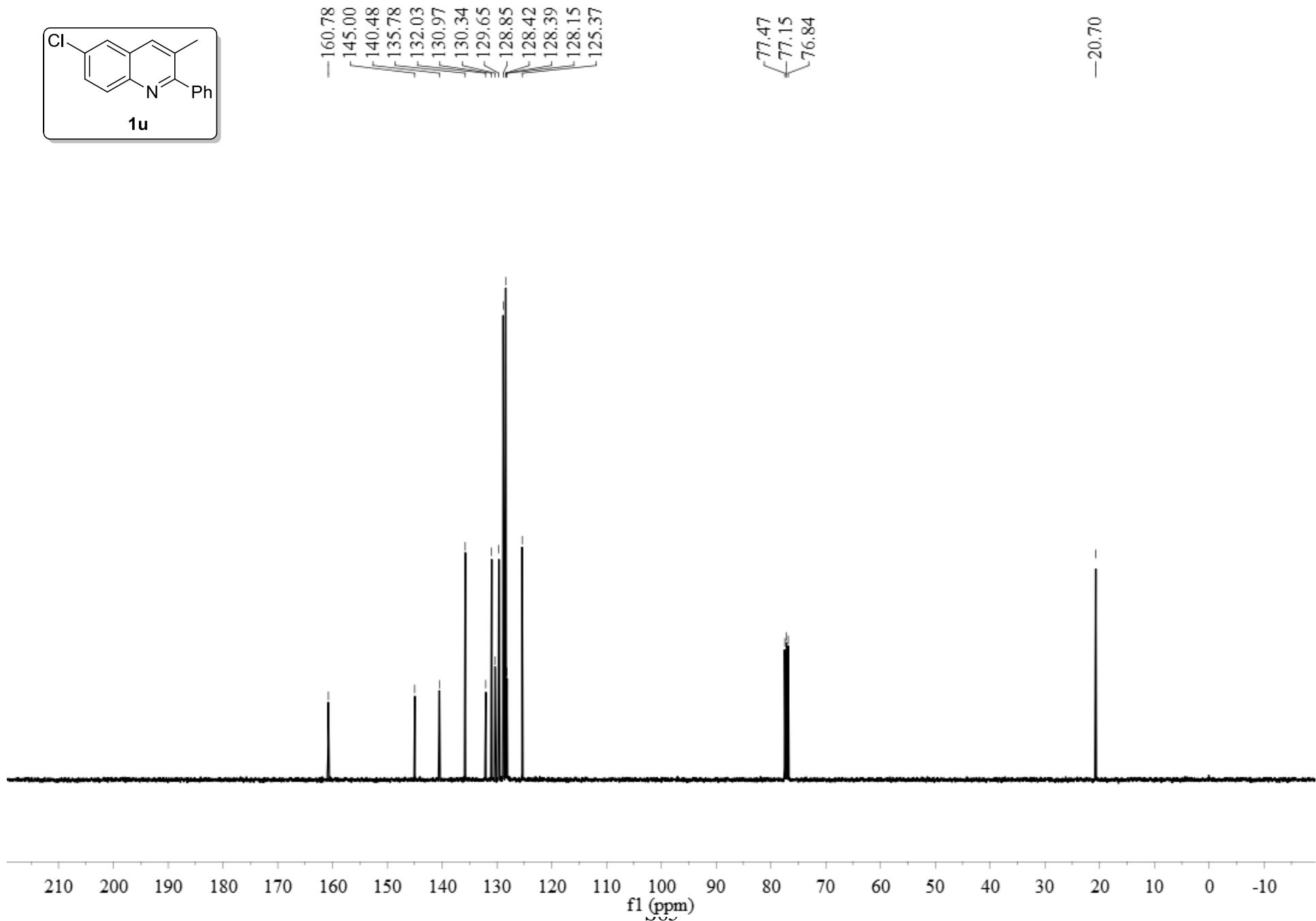
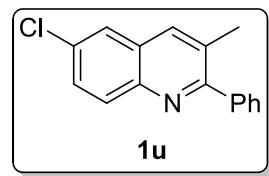


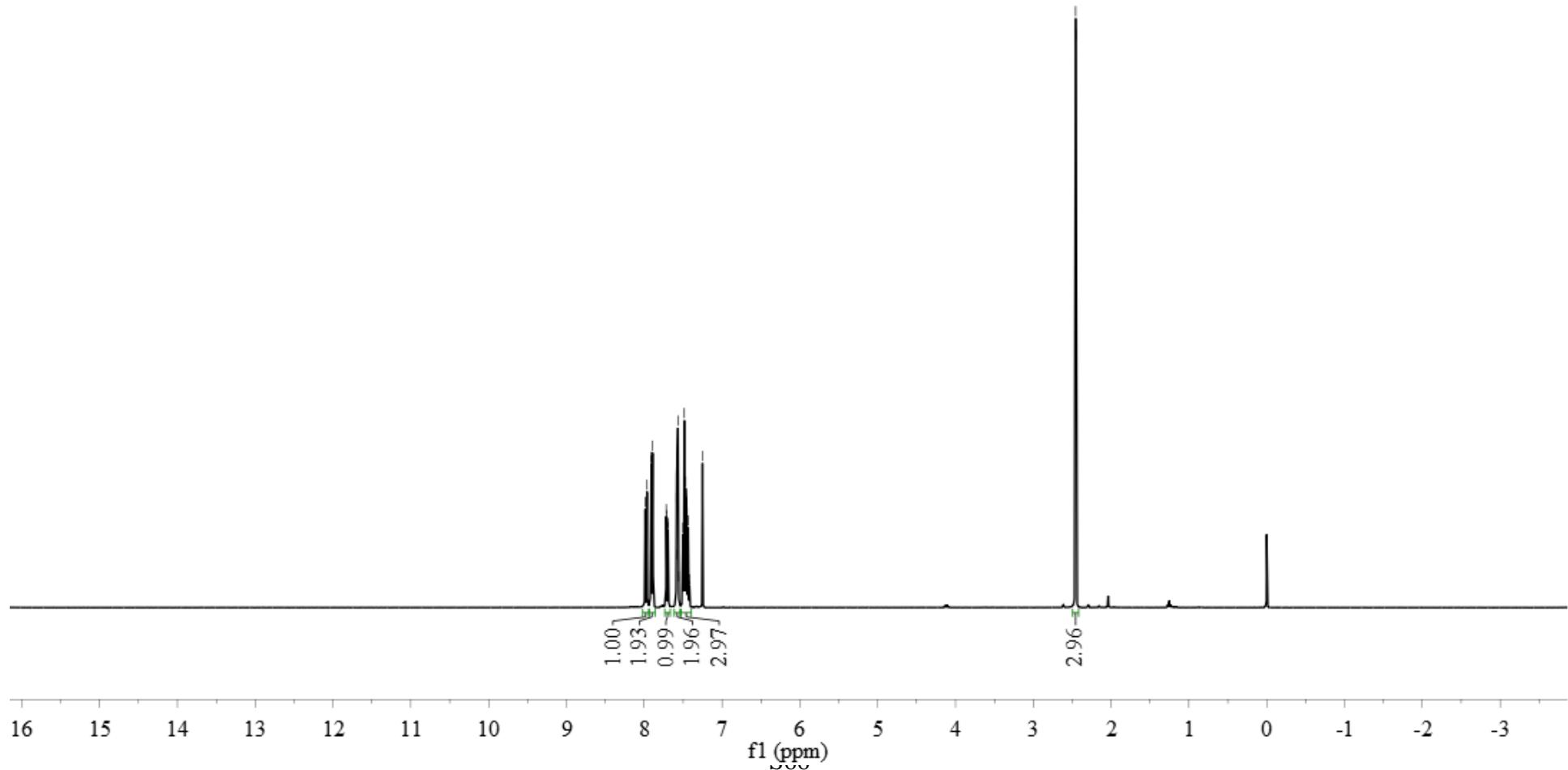
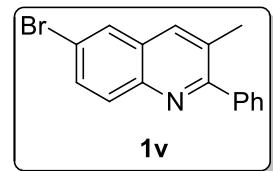


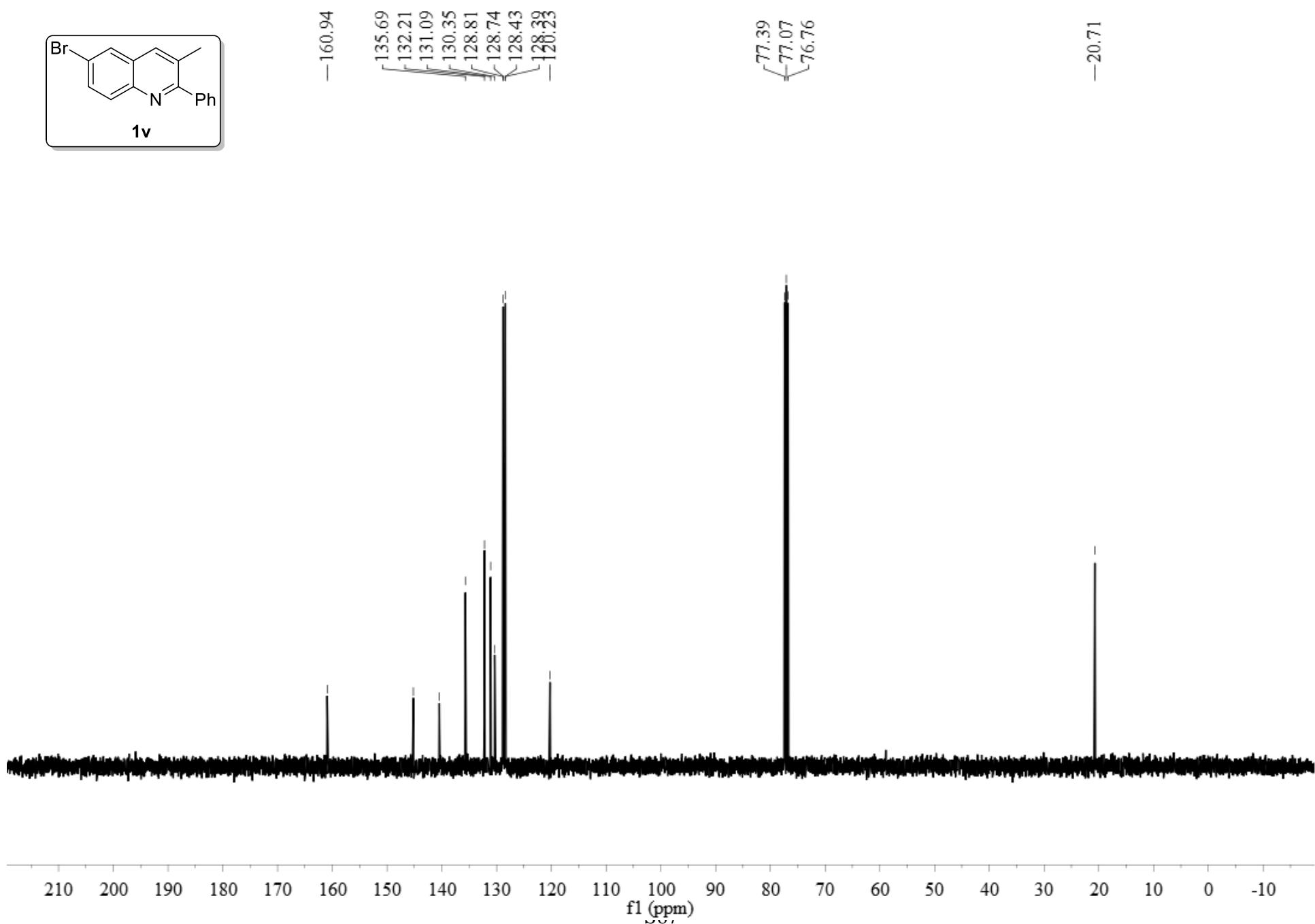
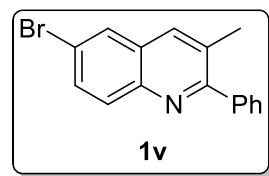


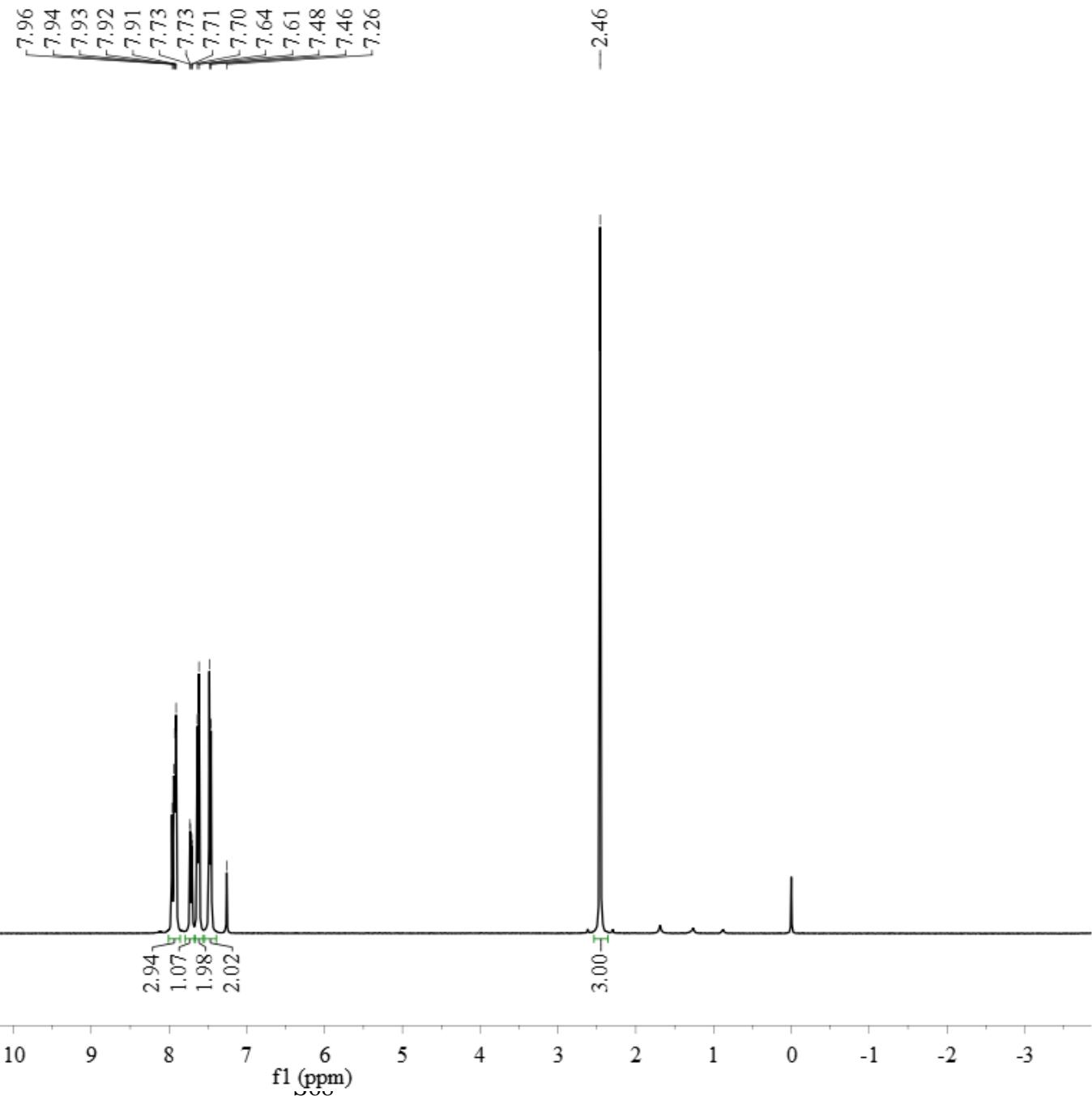
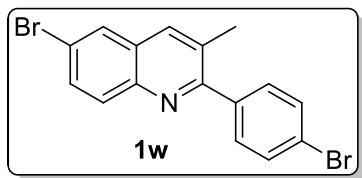


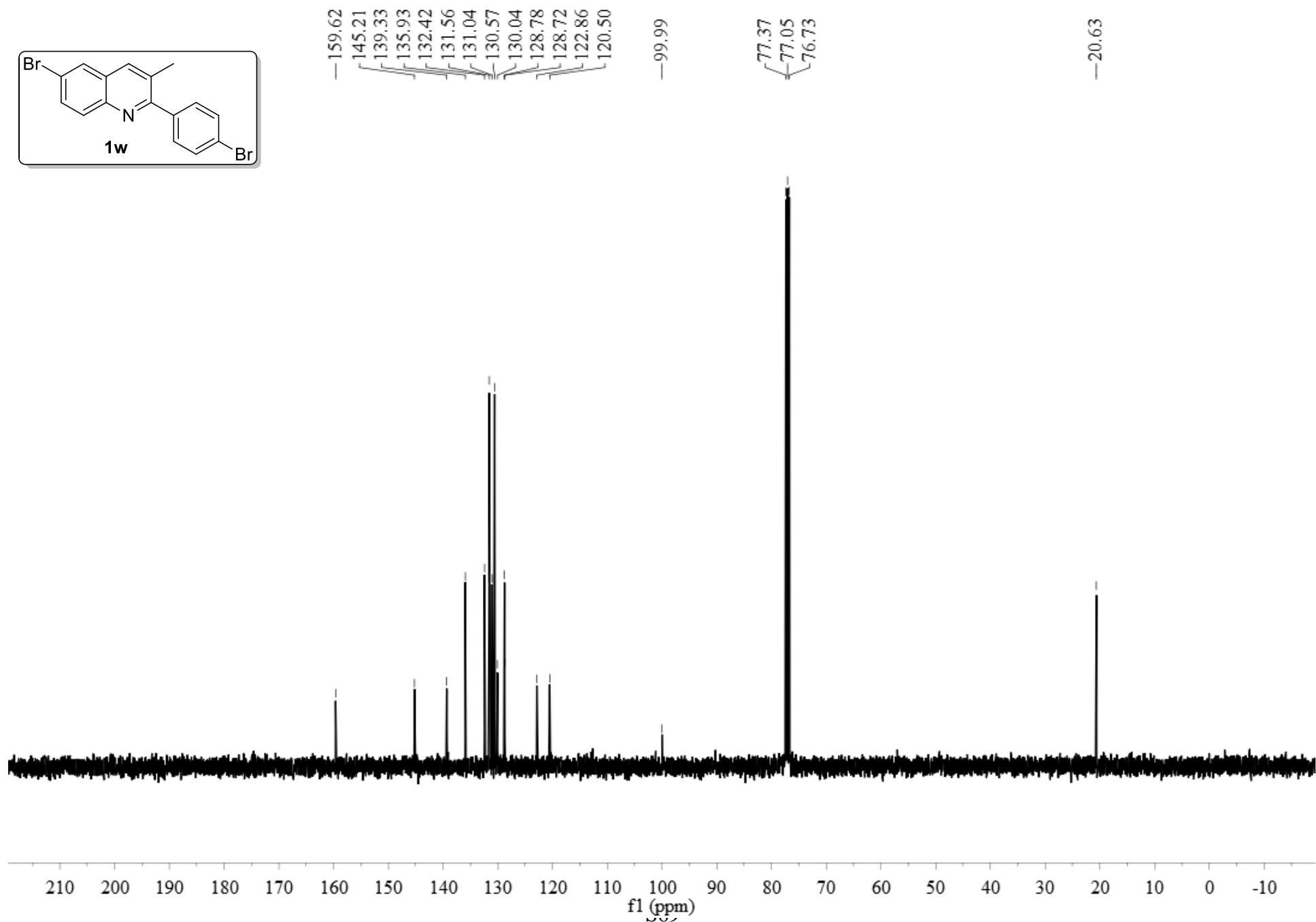
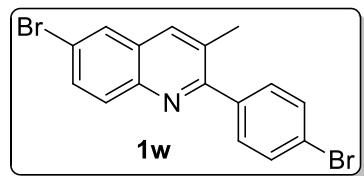


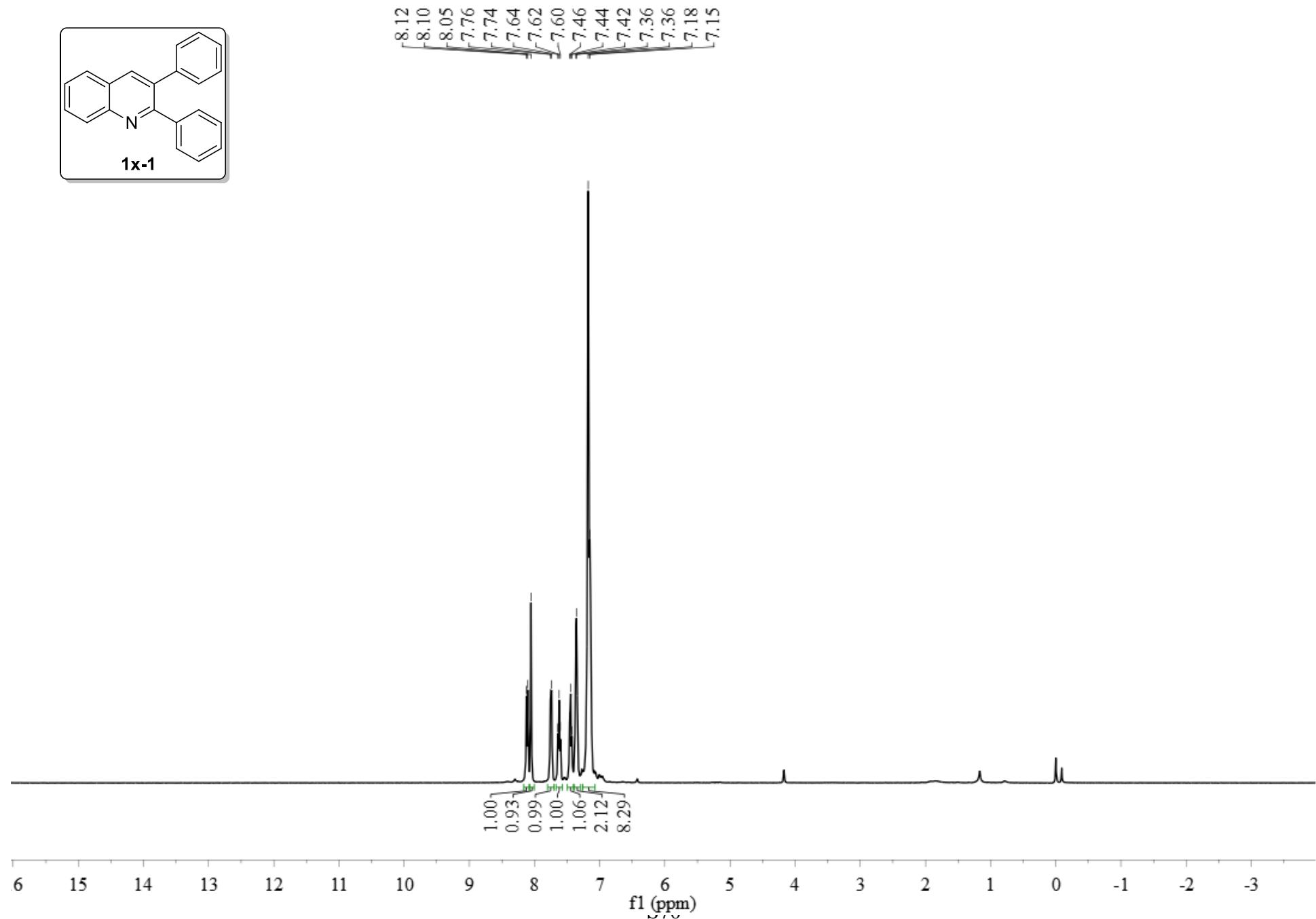
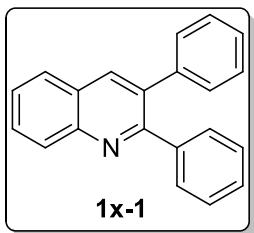


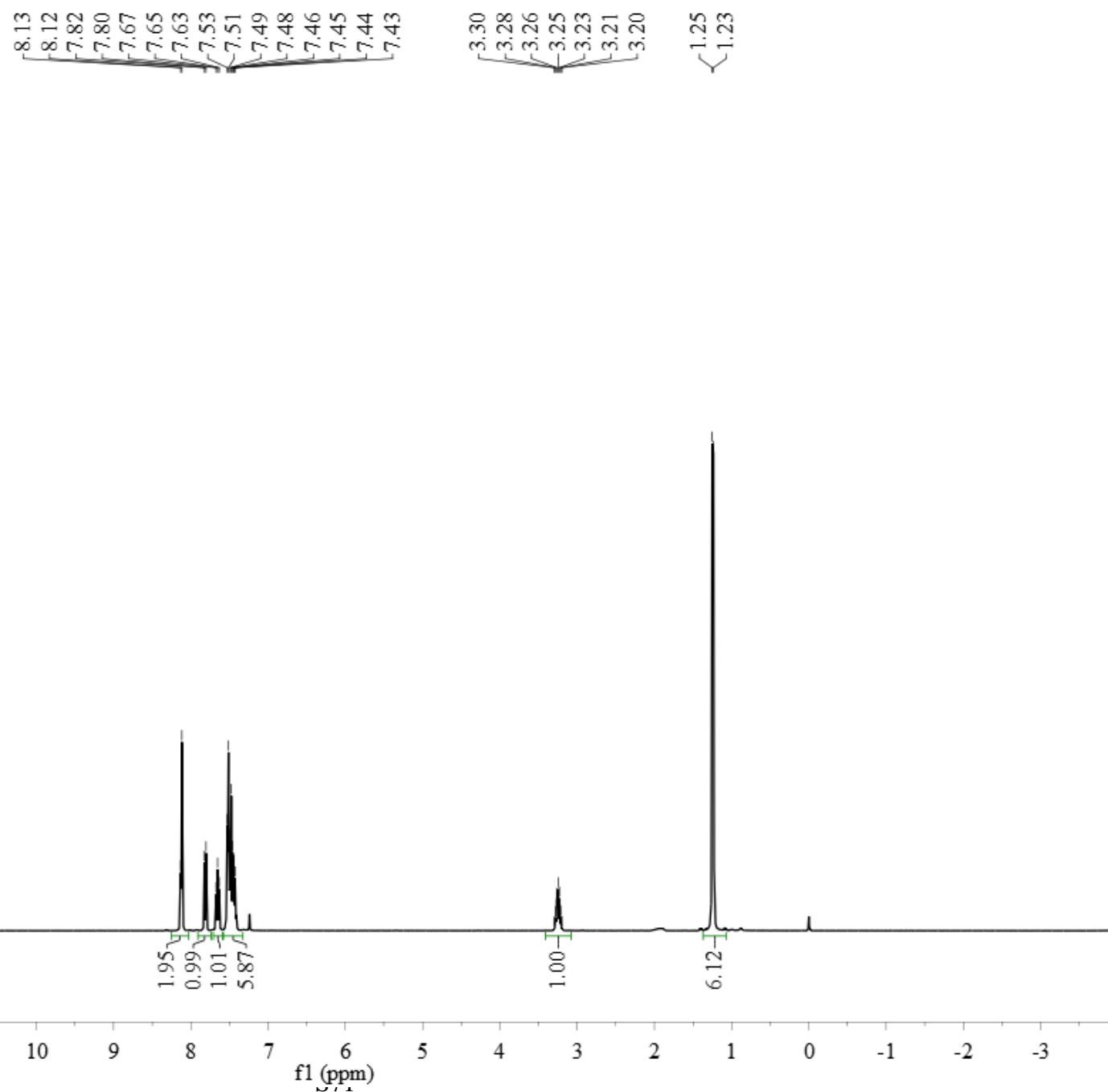
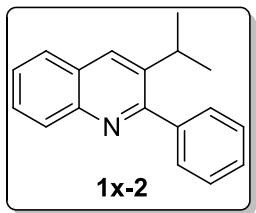


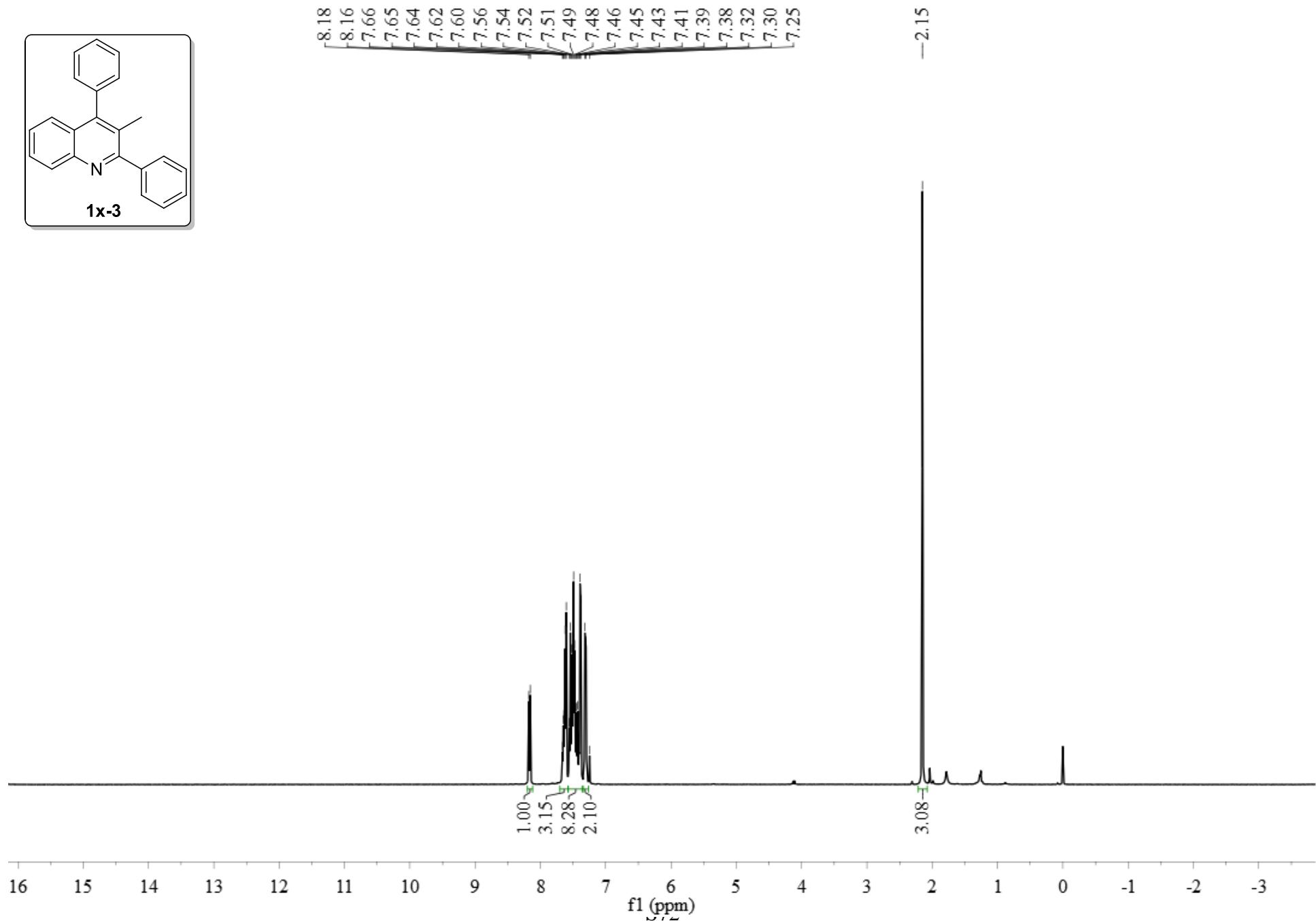
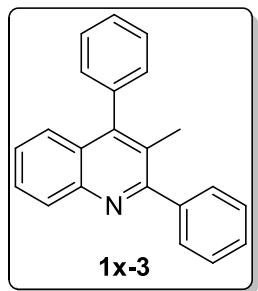


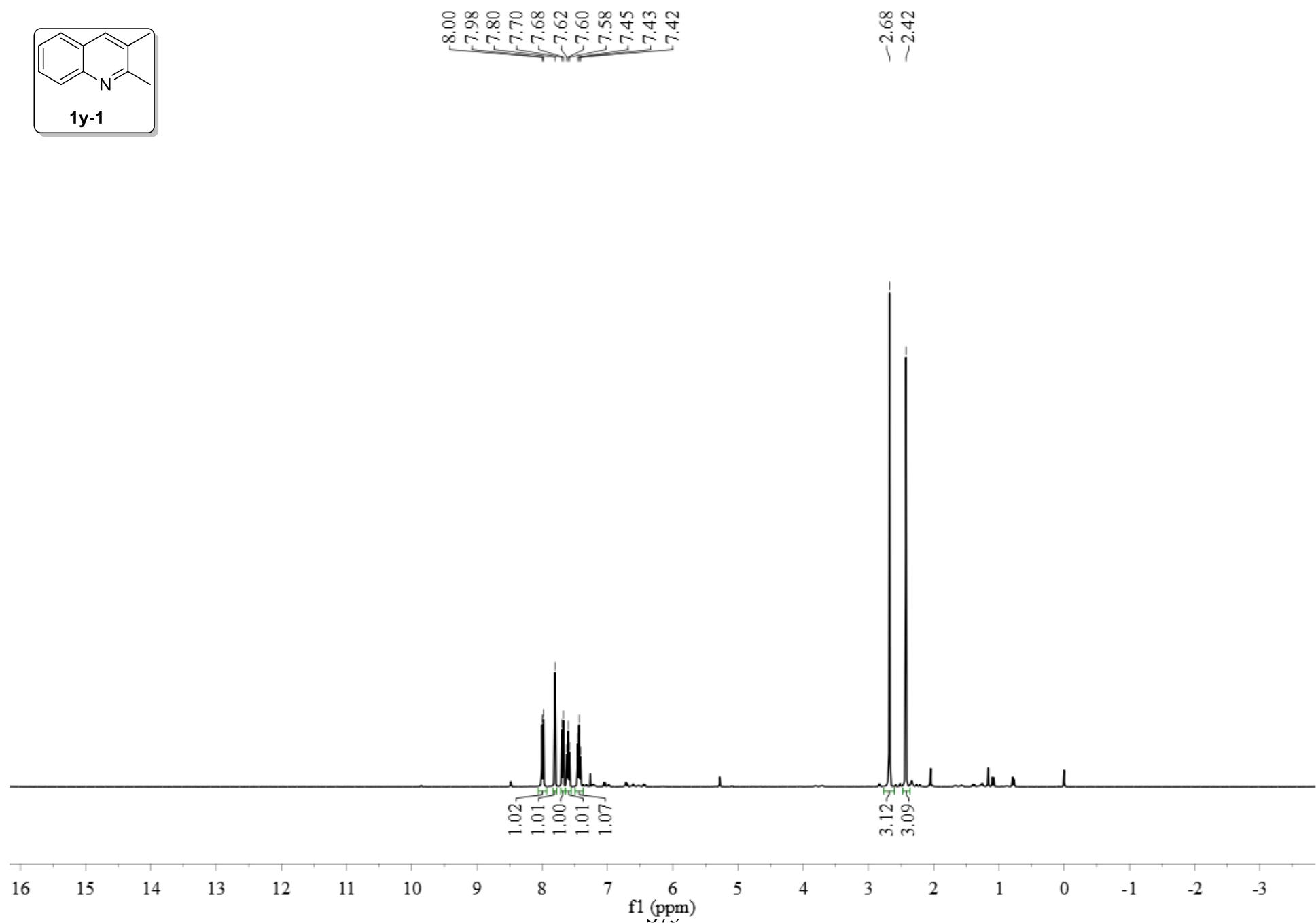
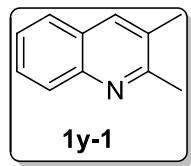


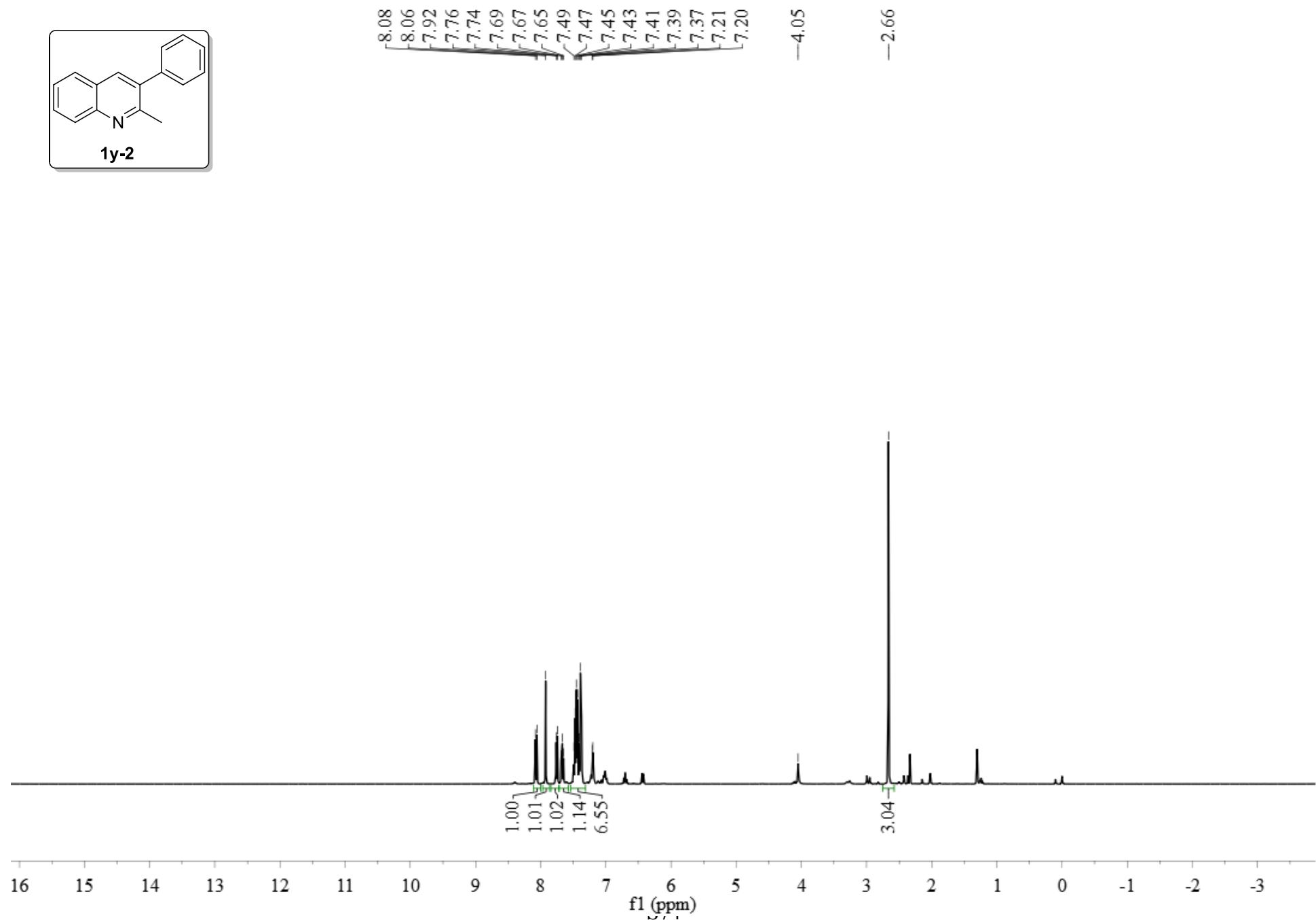
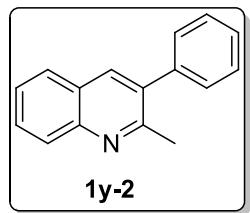


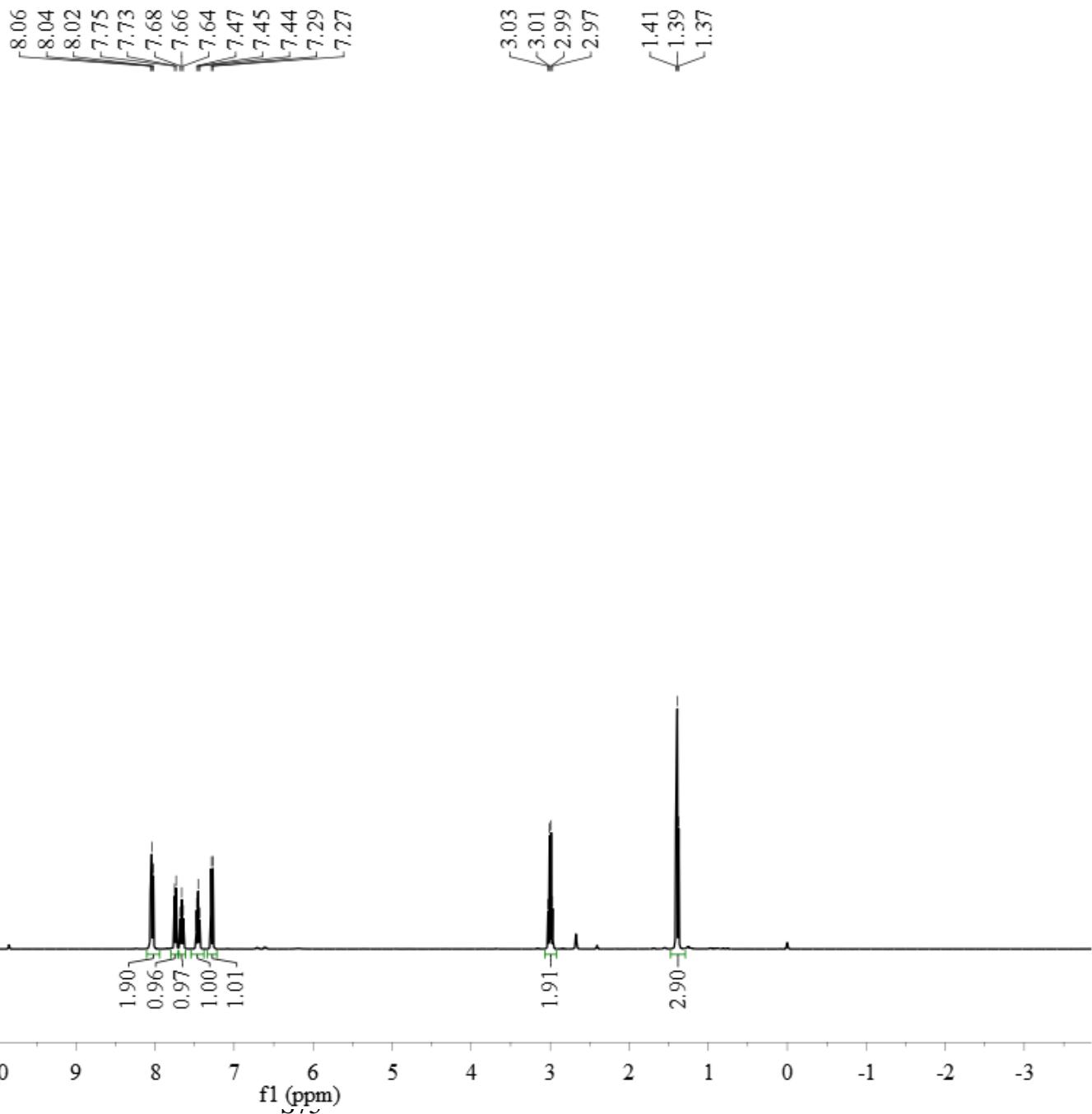
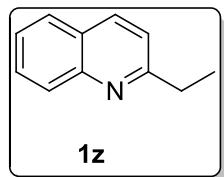


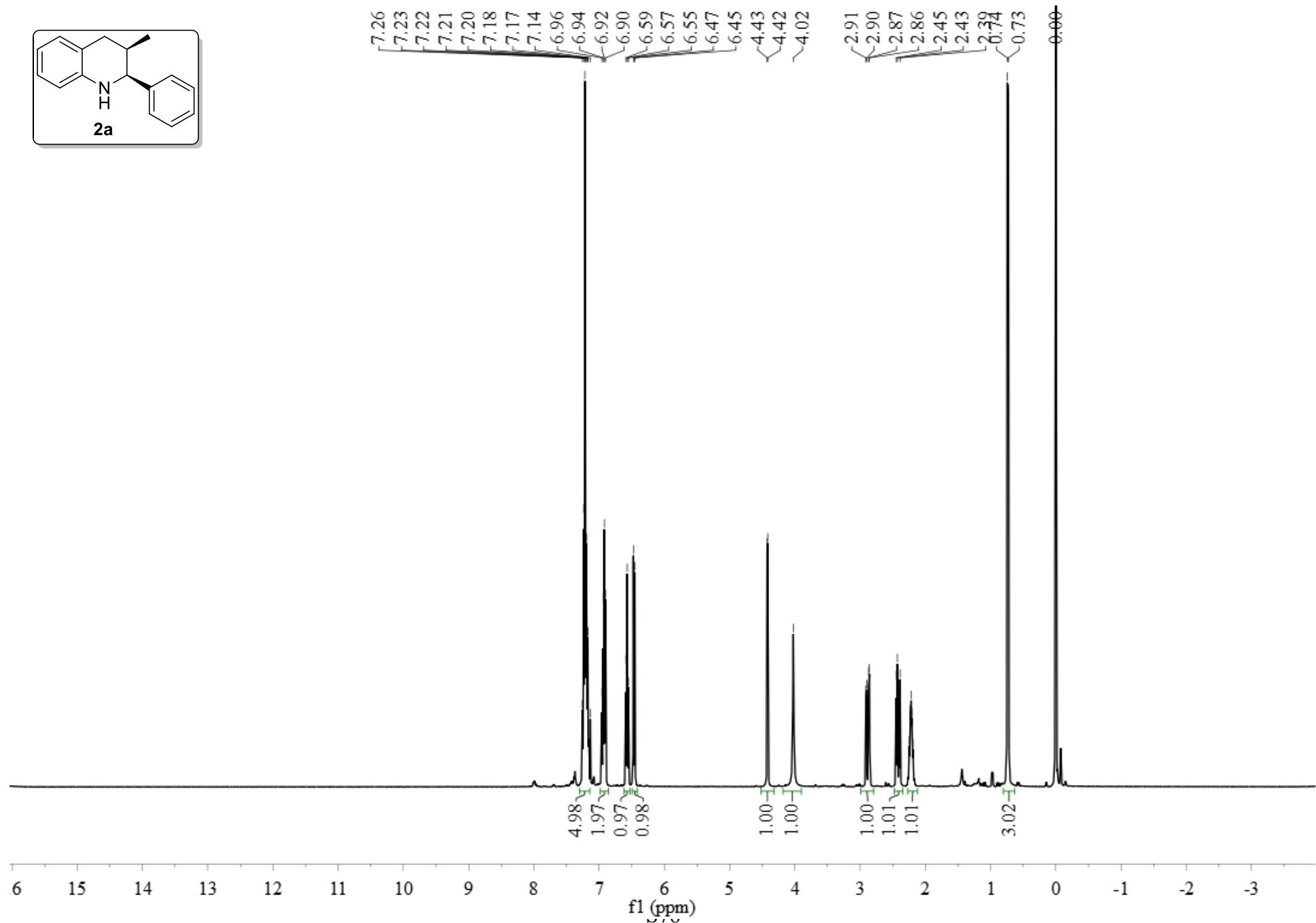
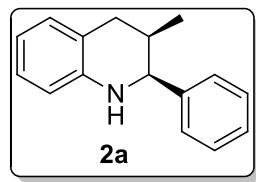


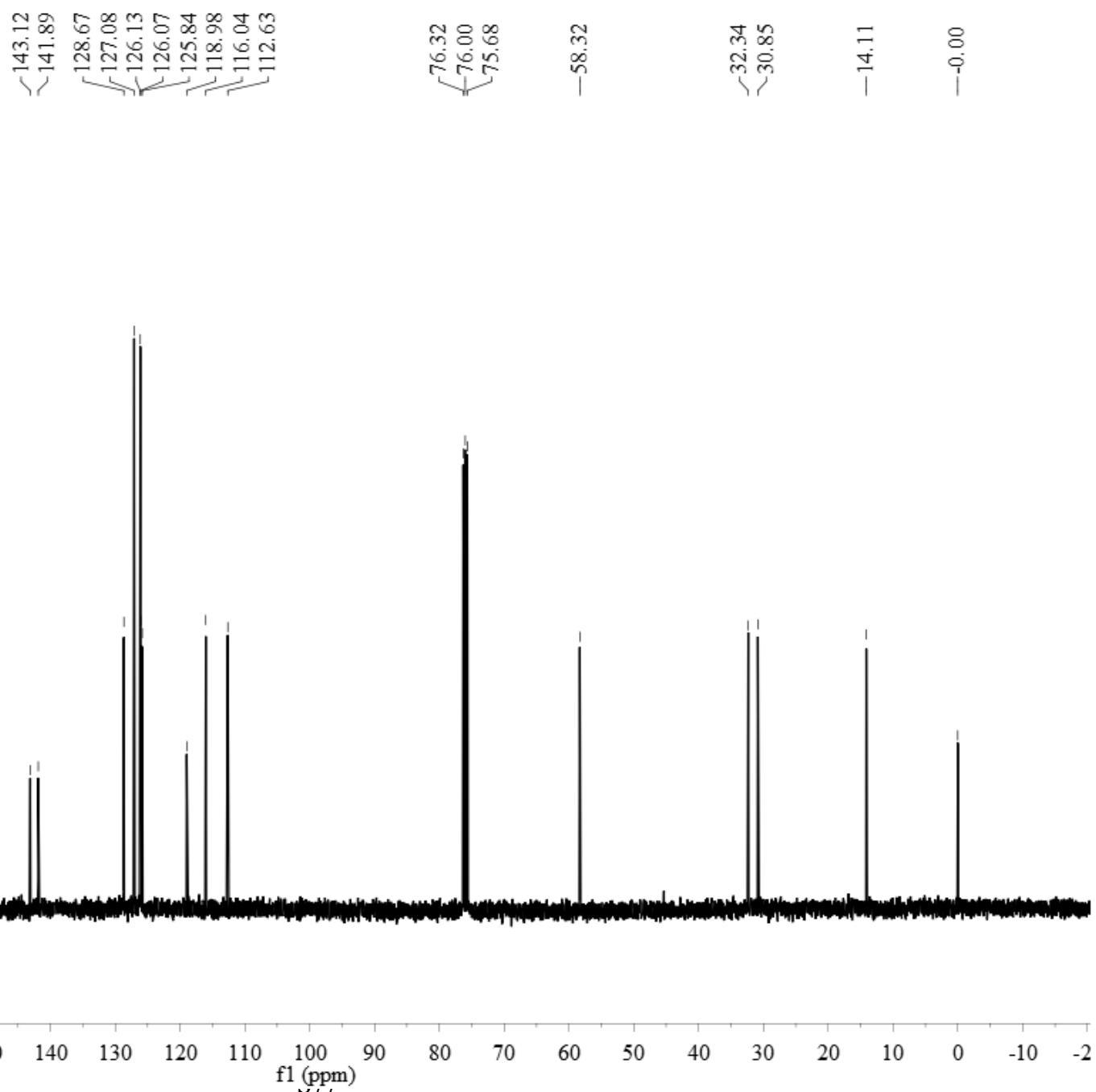
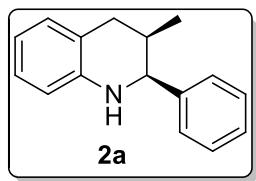


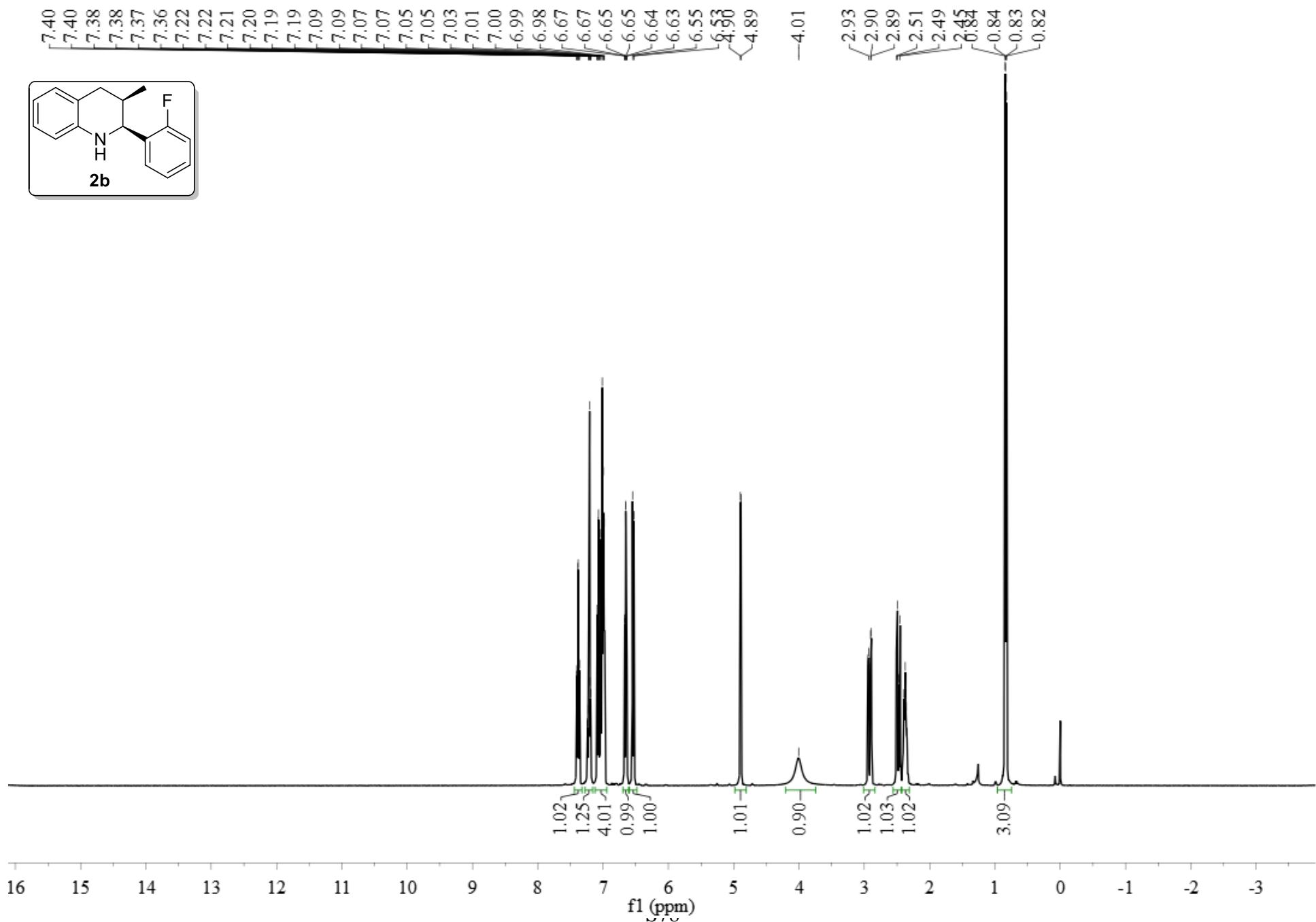


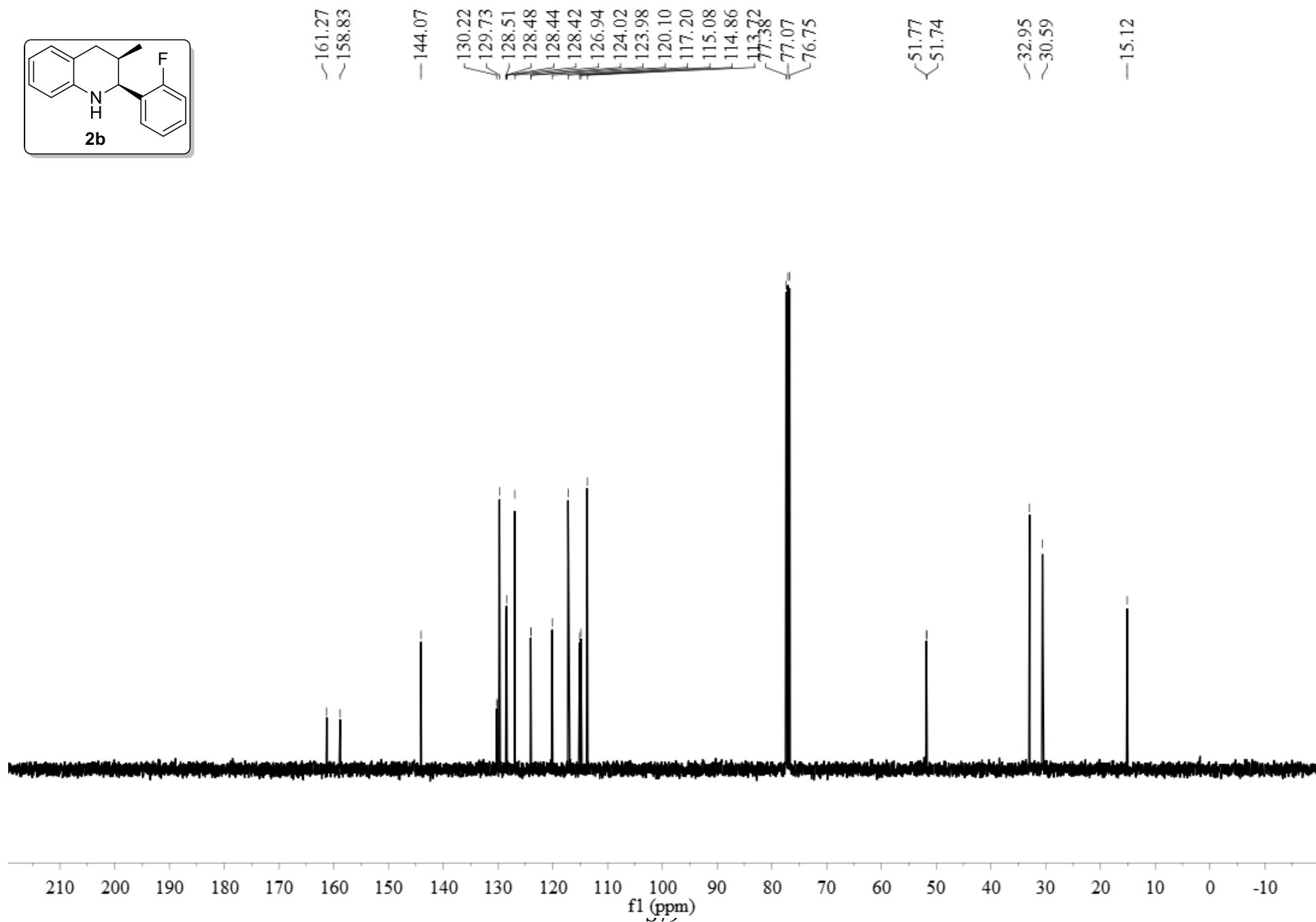
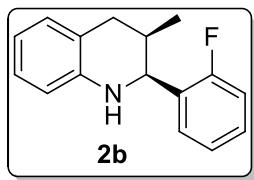


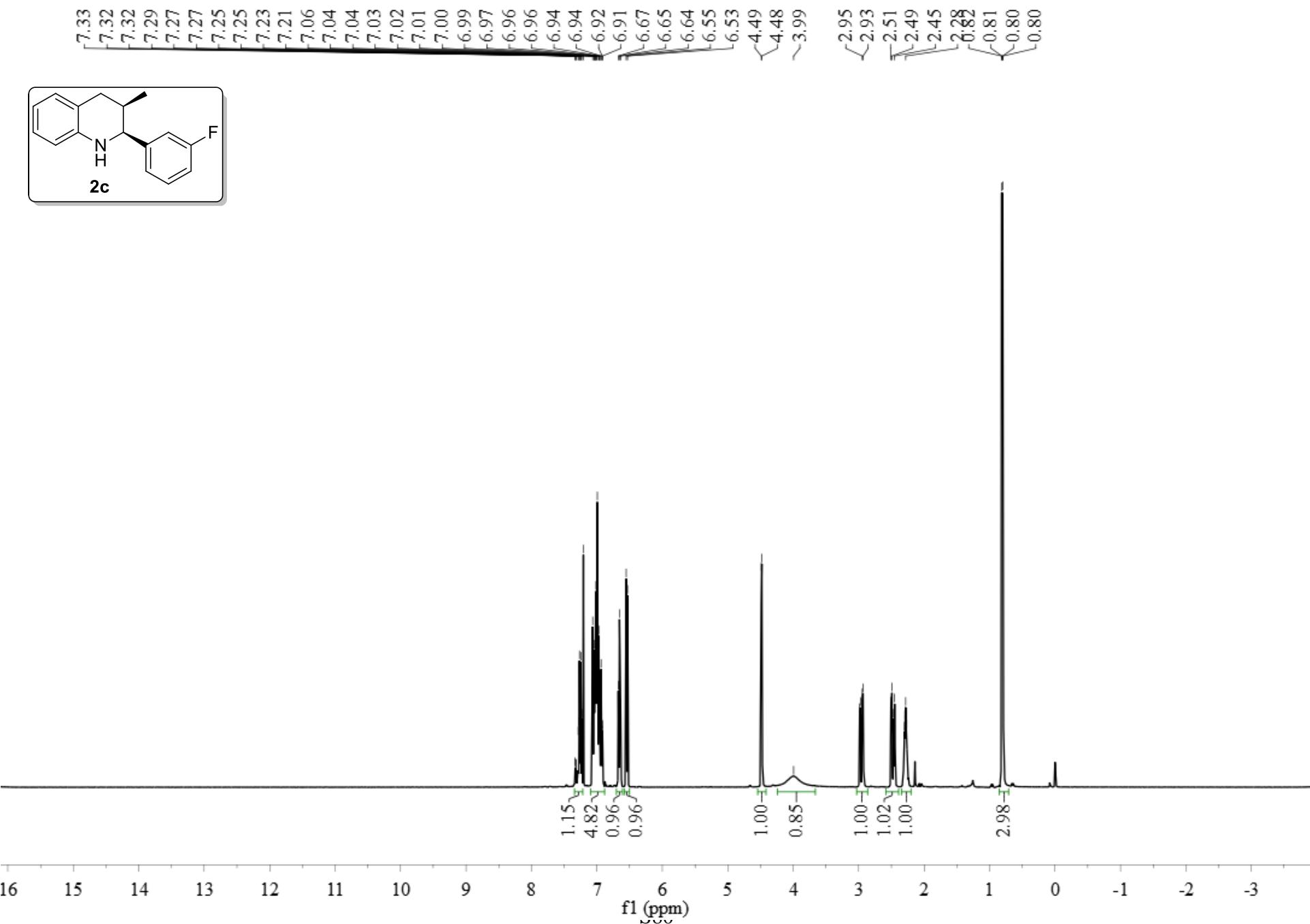


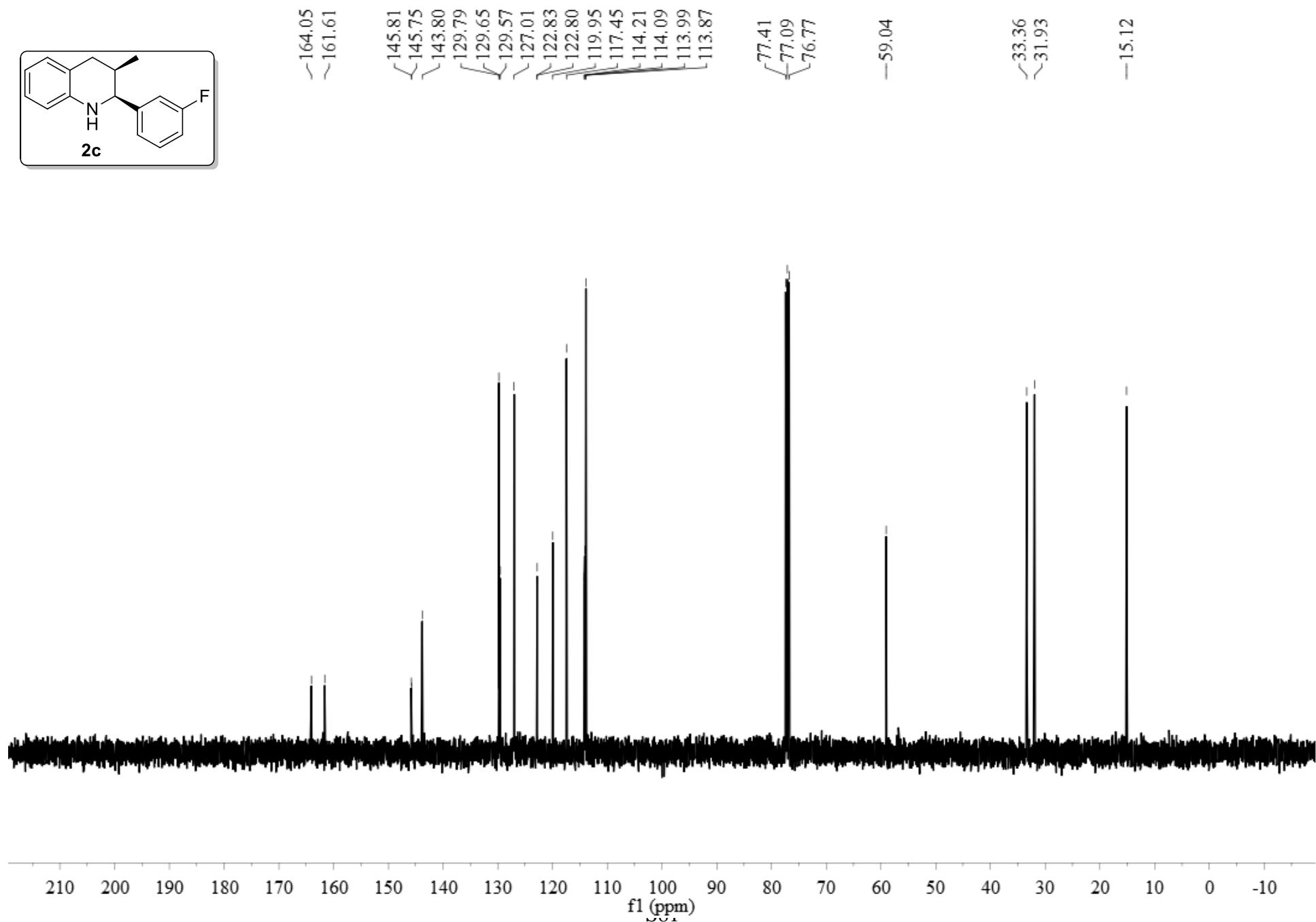
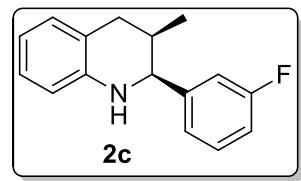


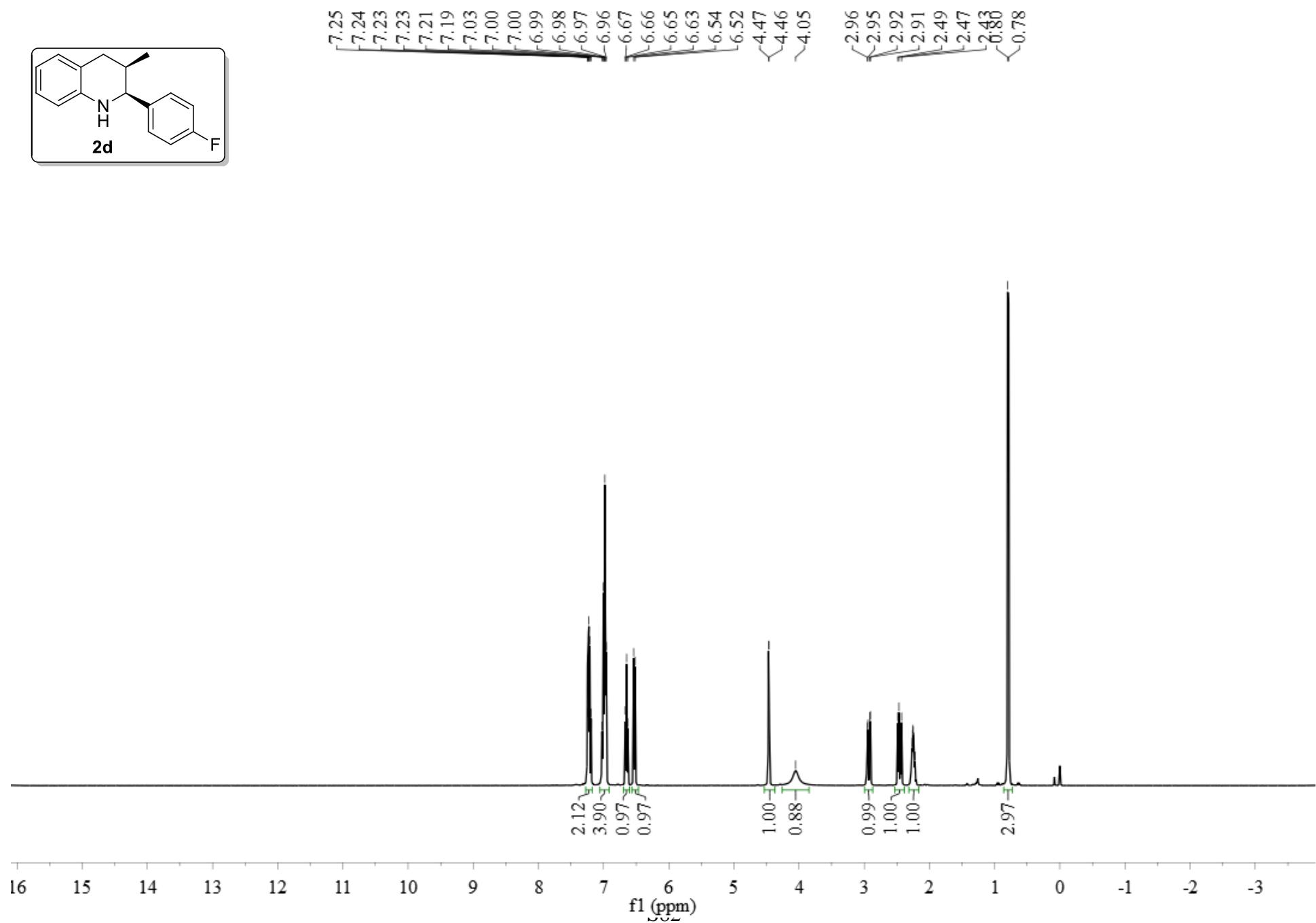
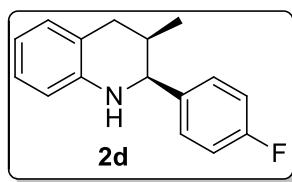


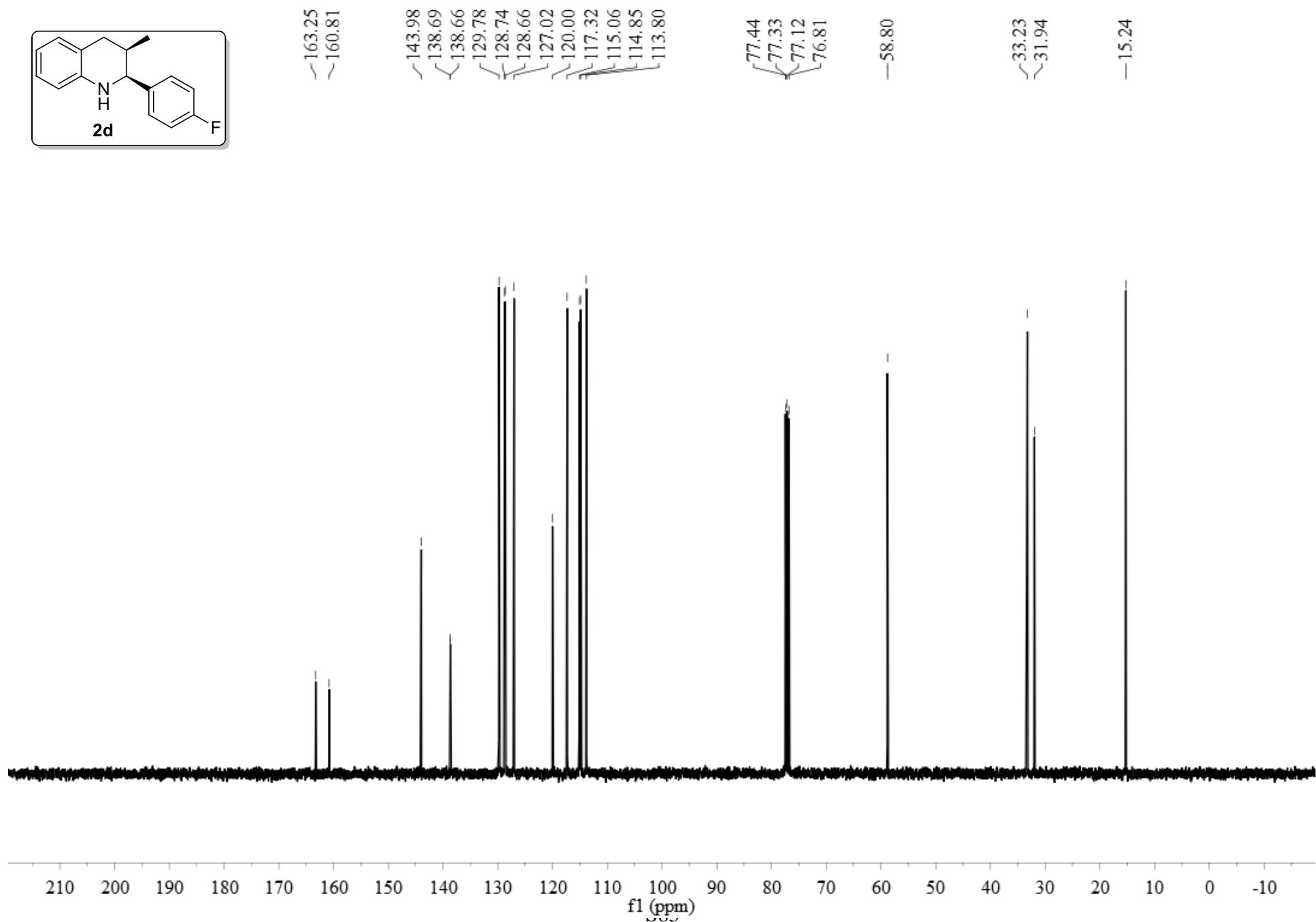
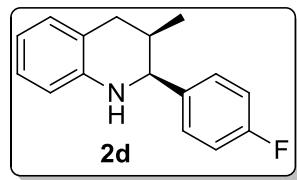


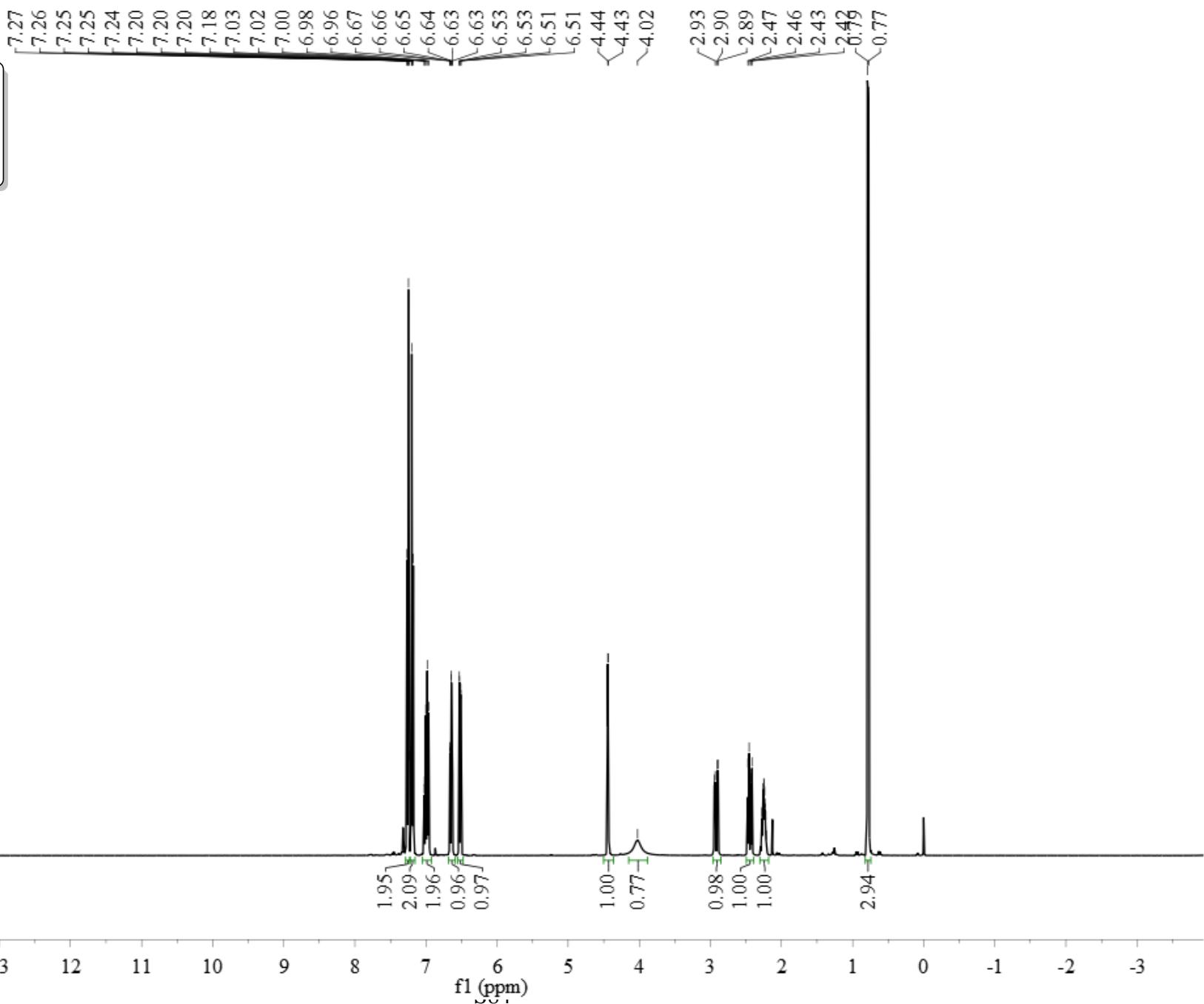
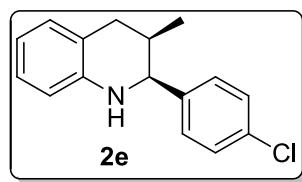


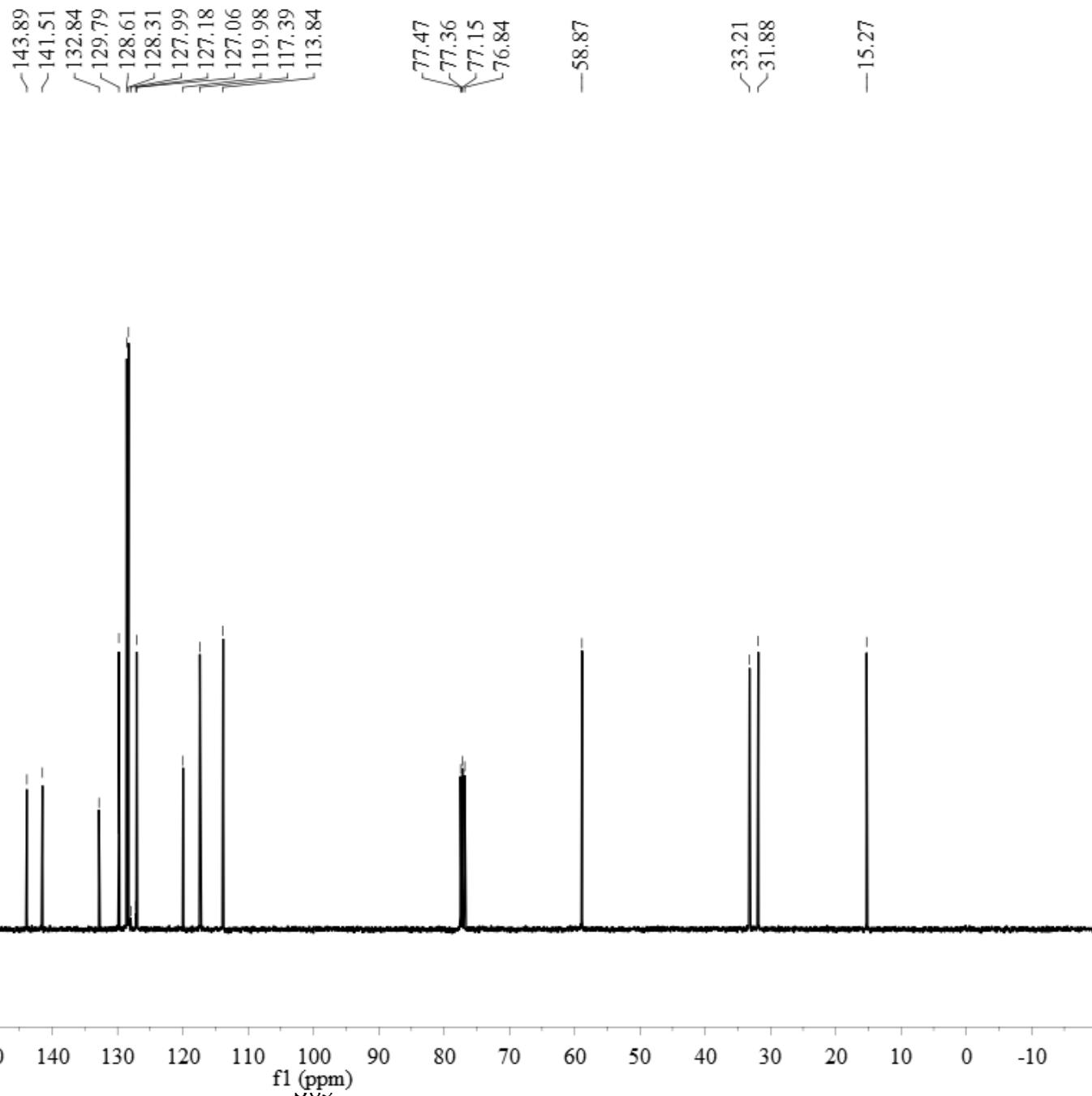
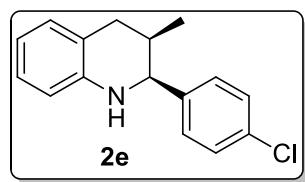


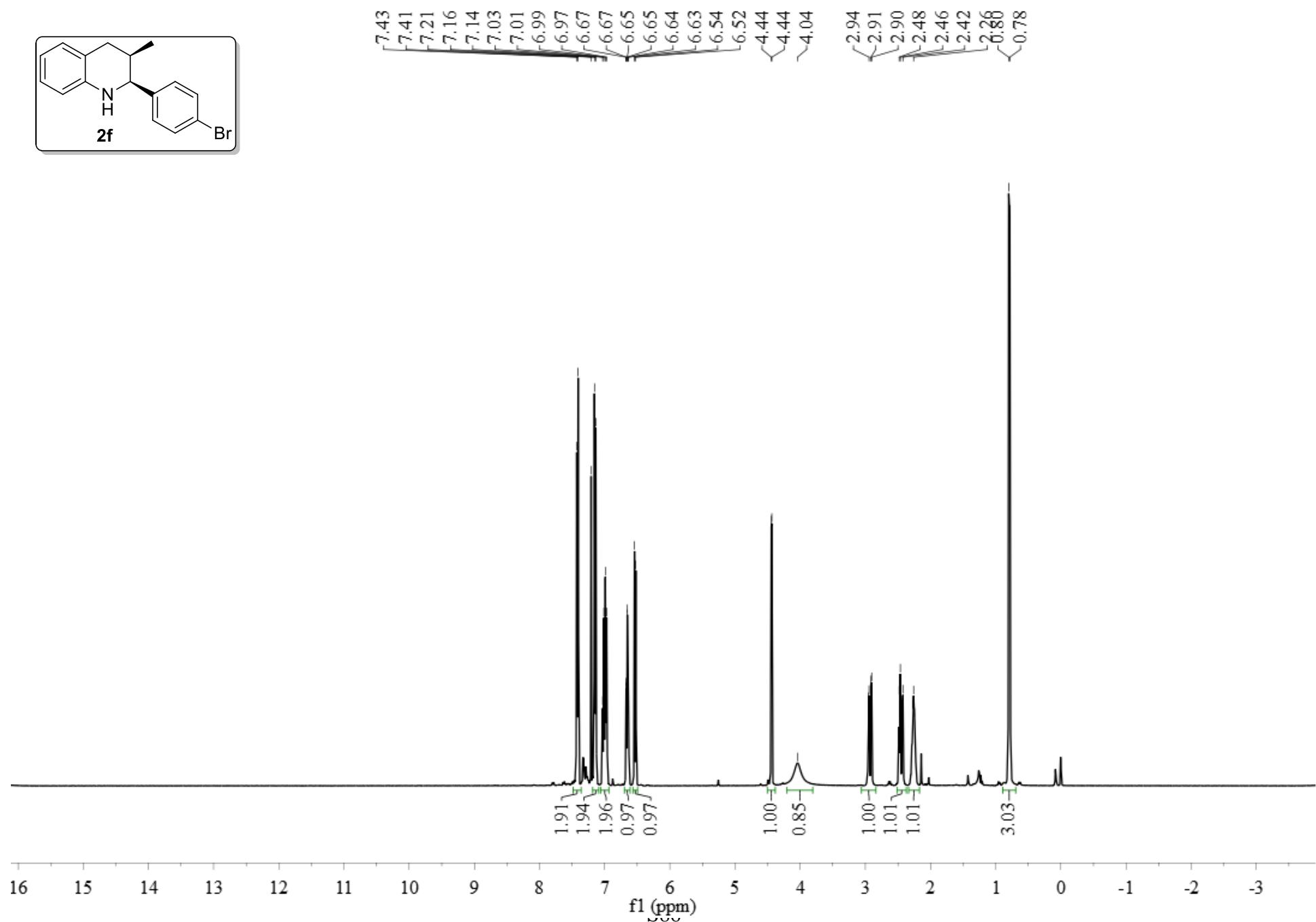
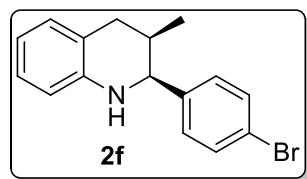


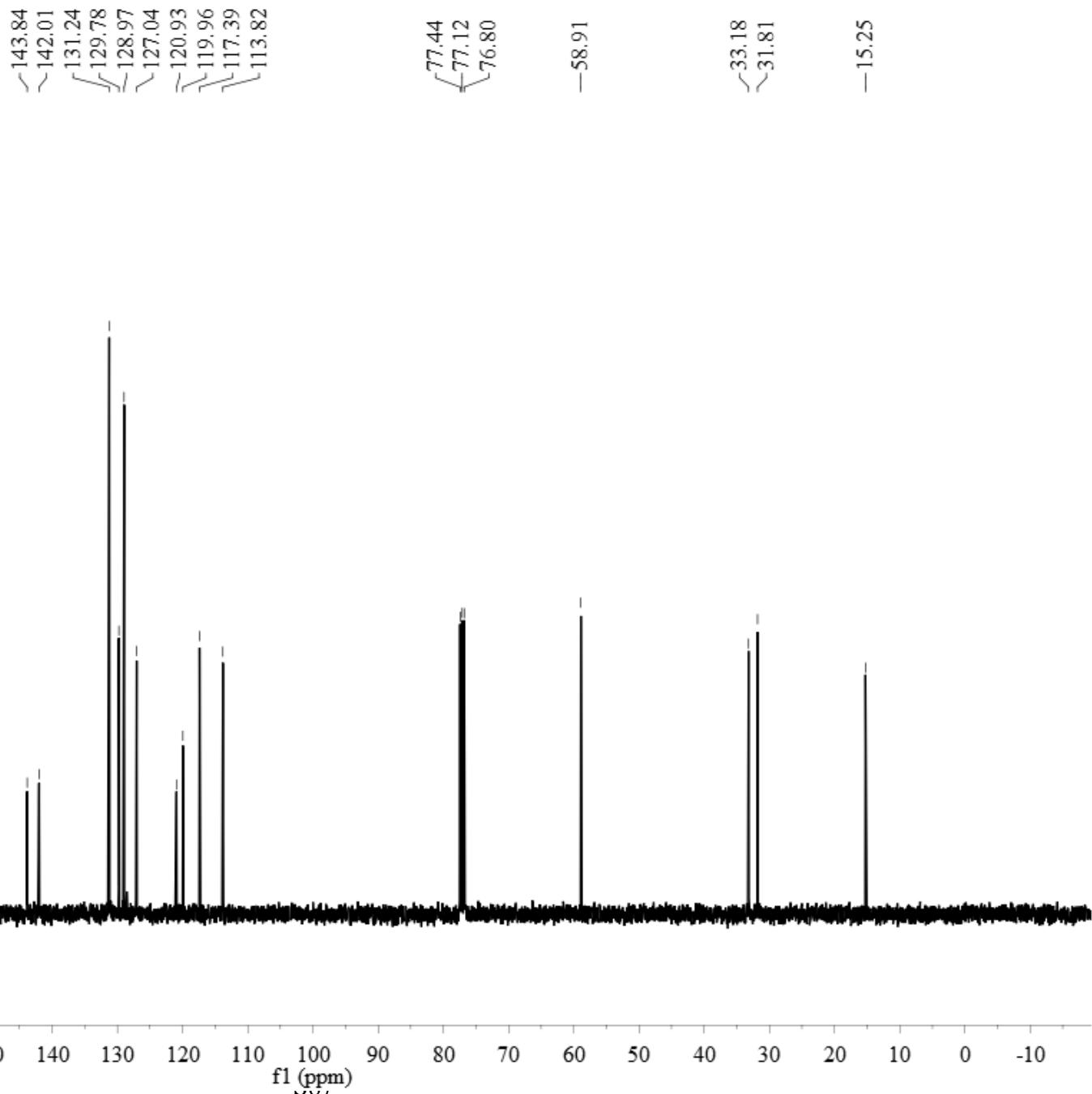
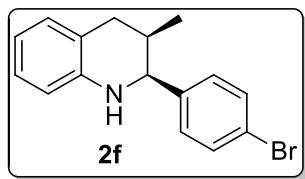


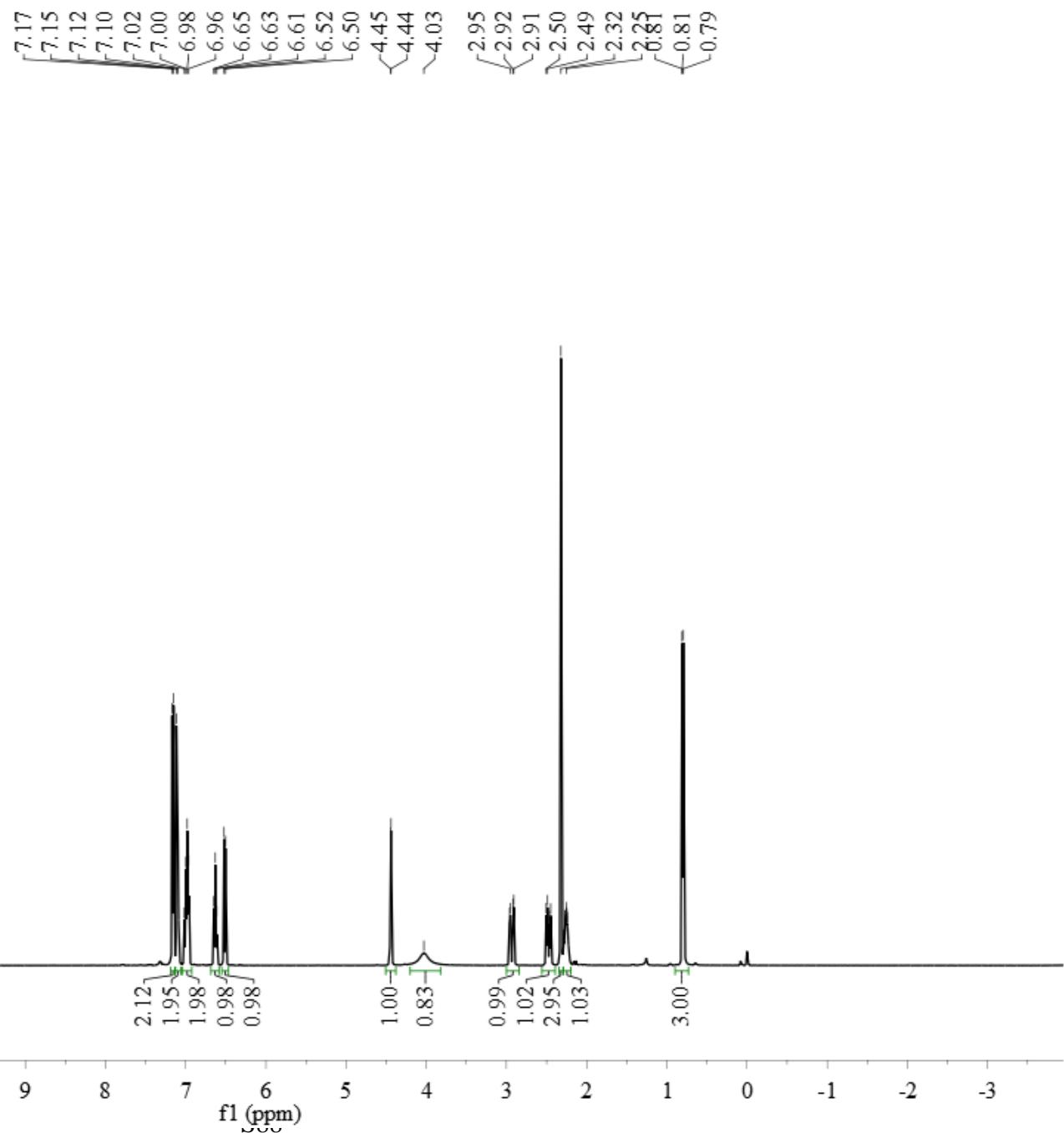
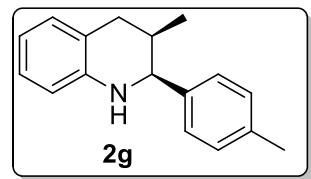


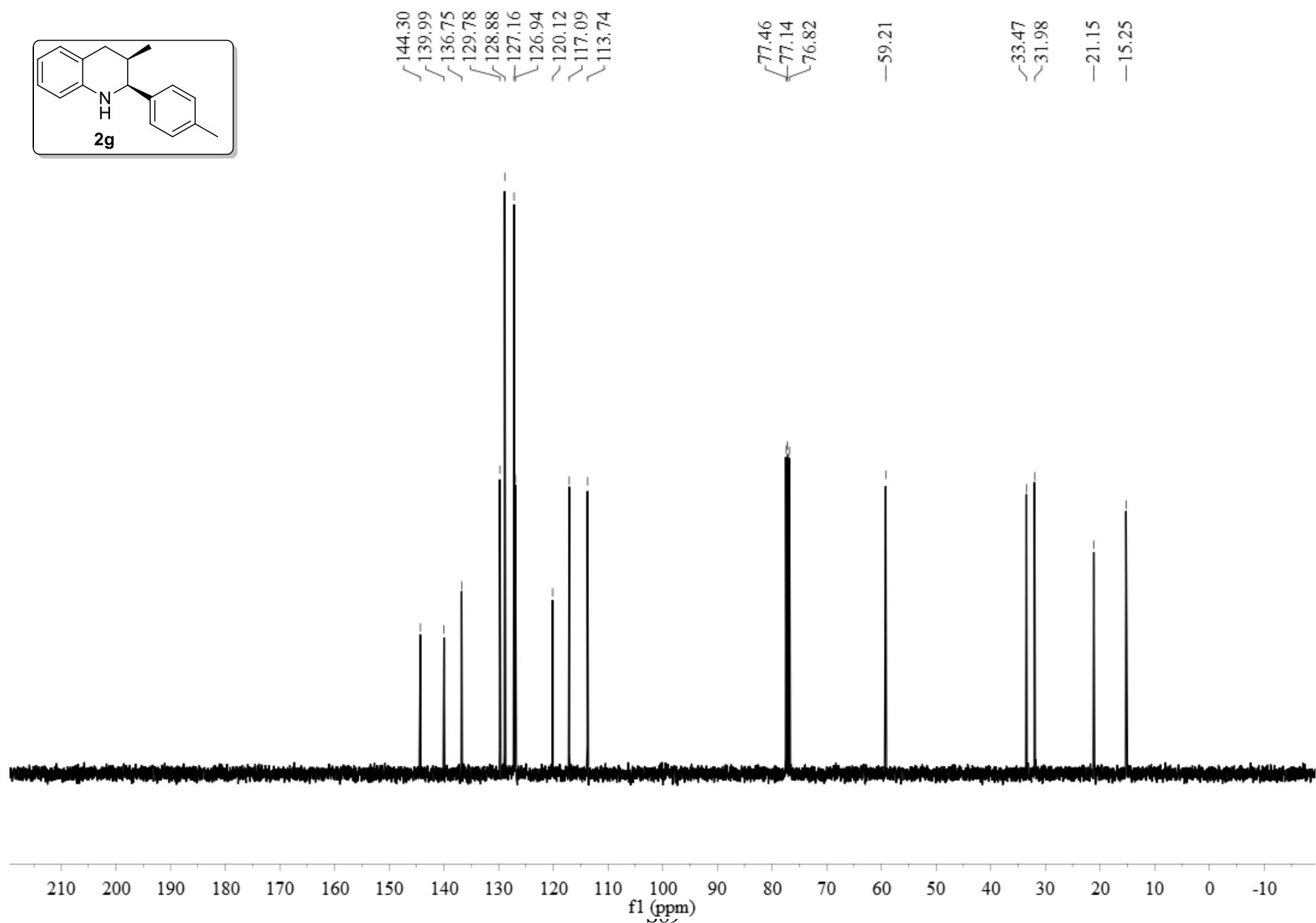
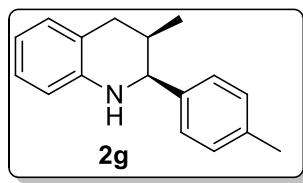


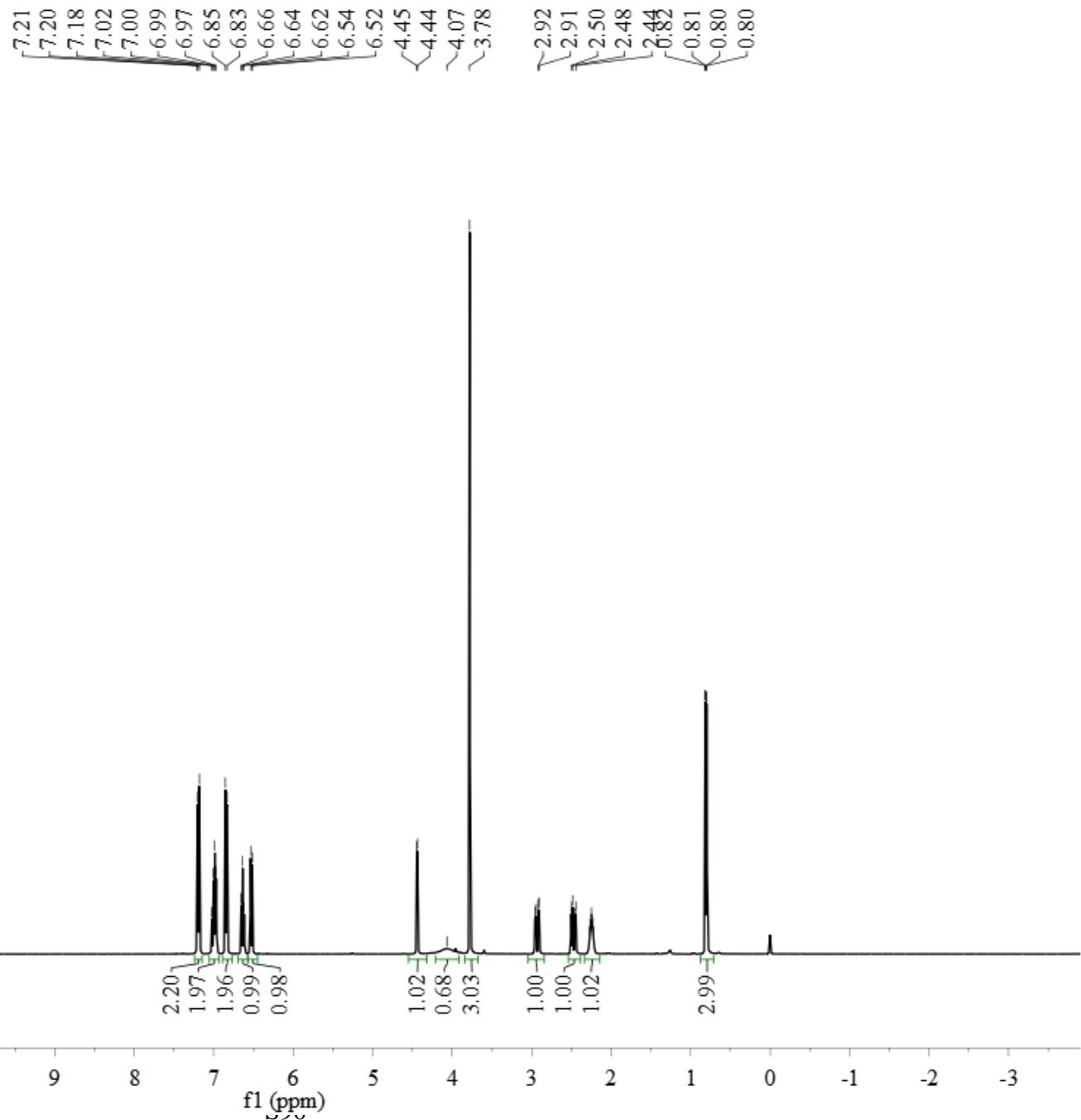
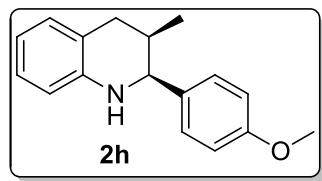


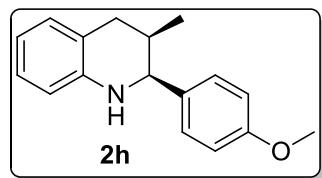












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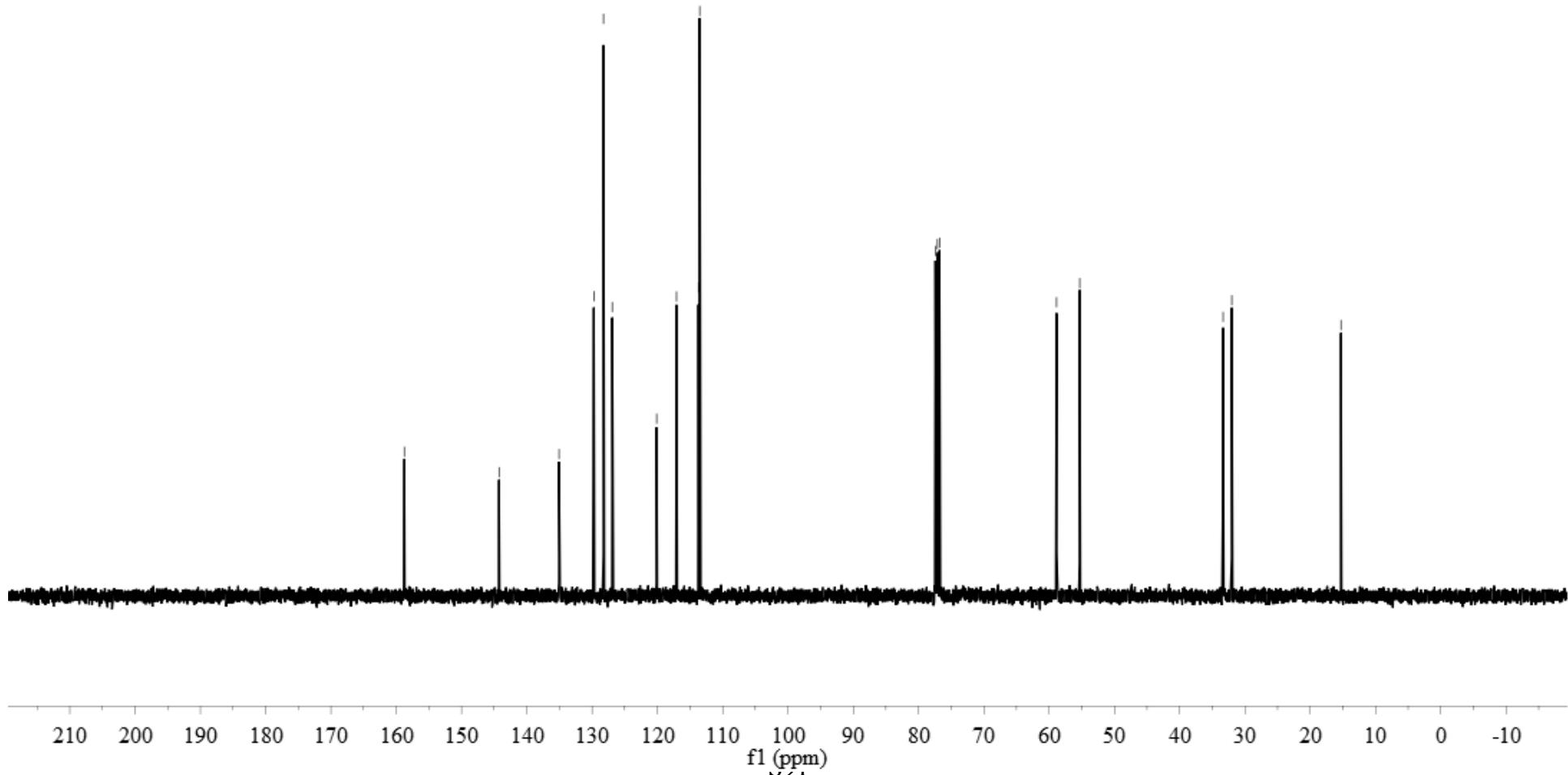
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~ 126.91  
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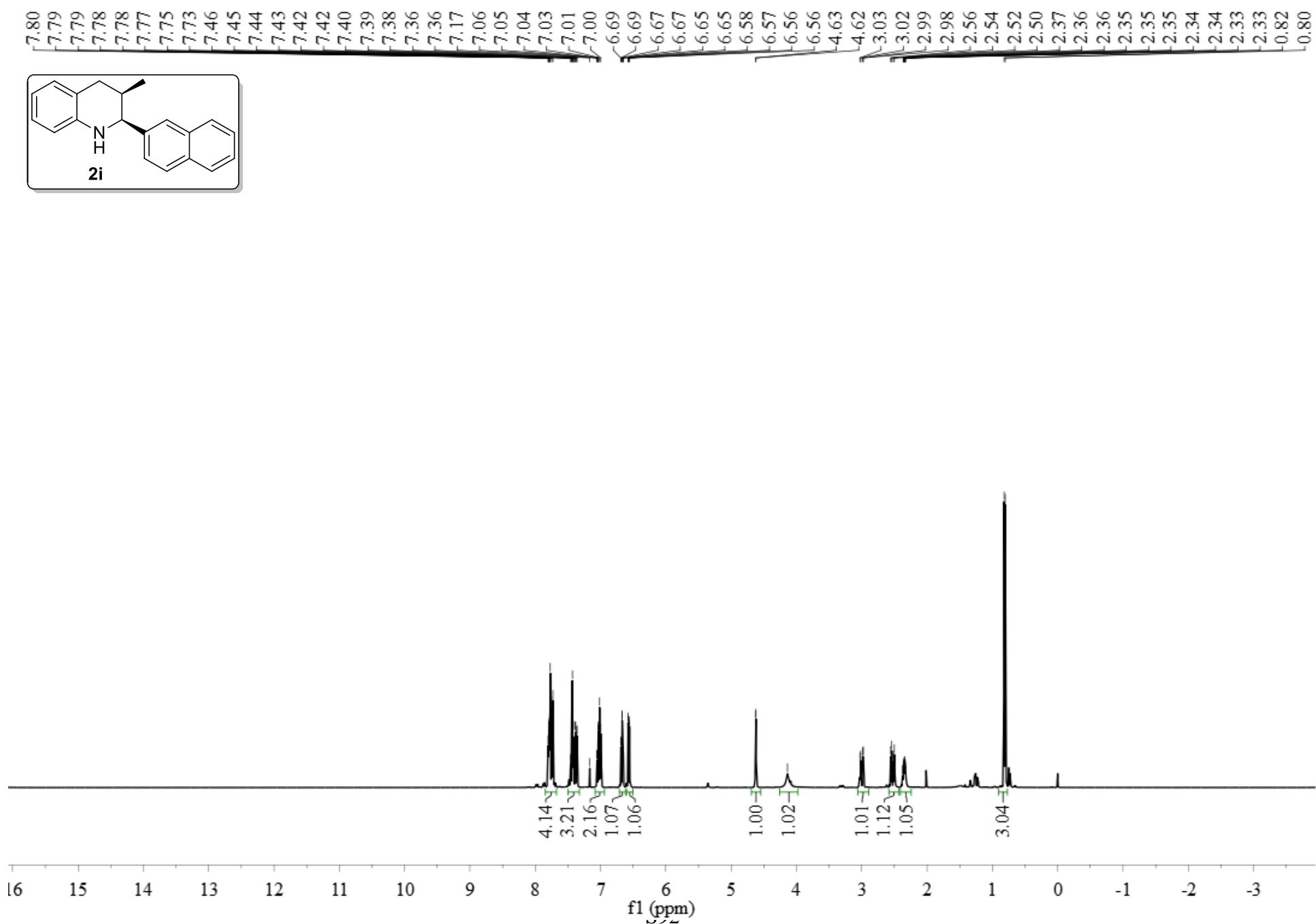
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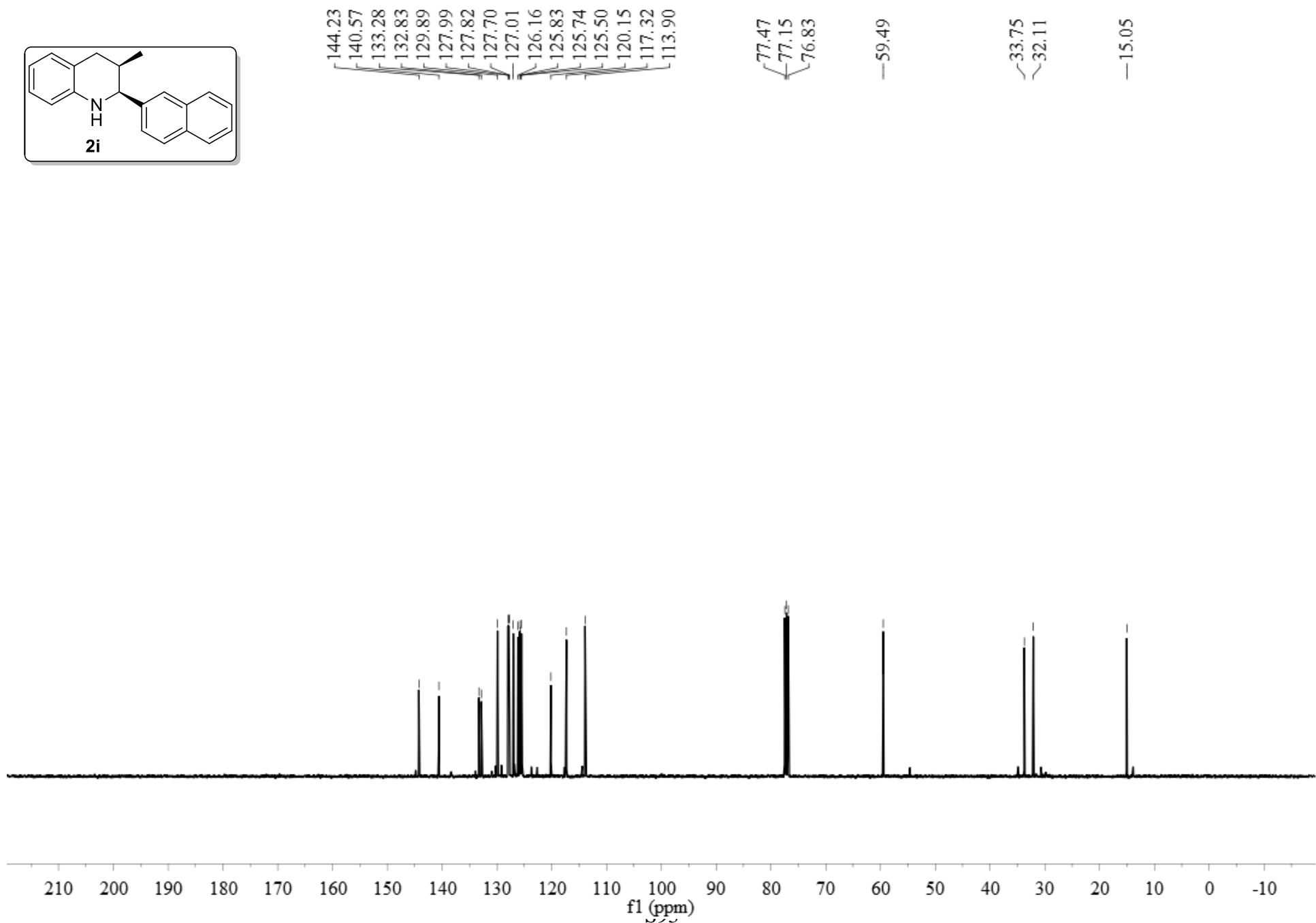
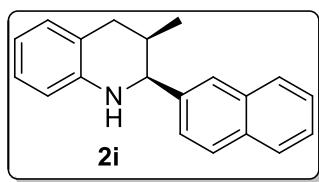
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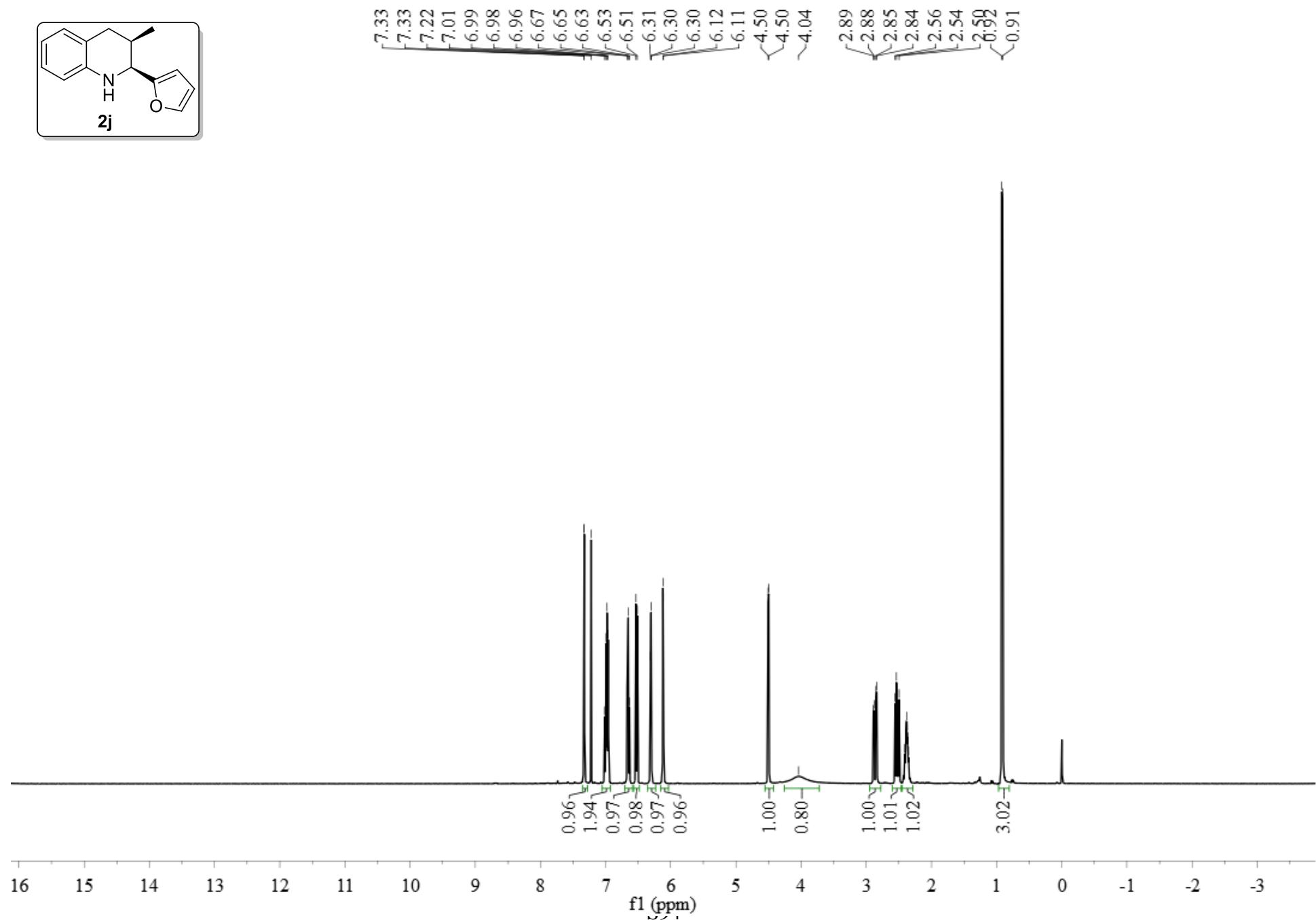
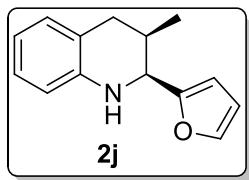
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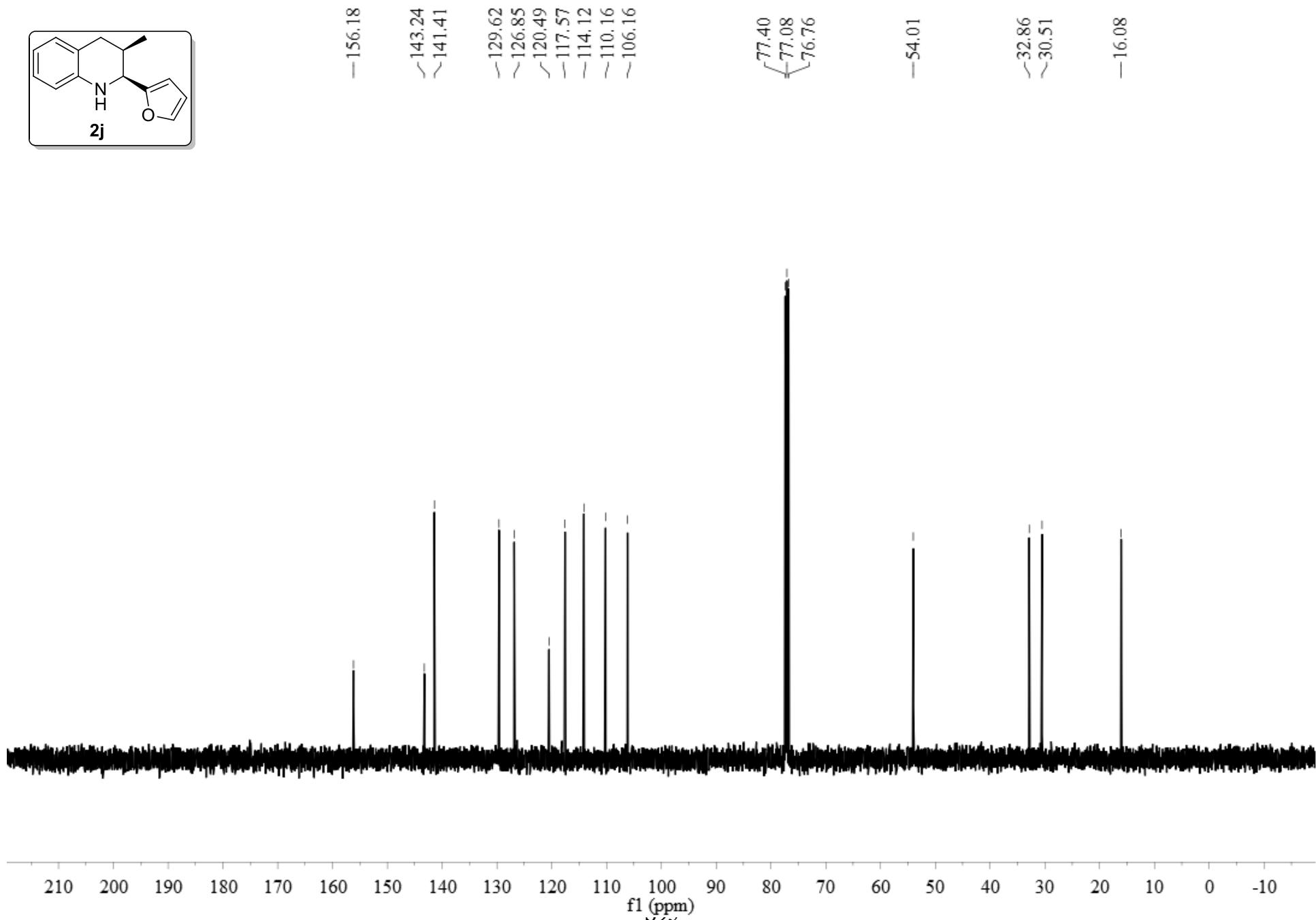
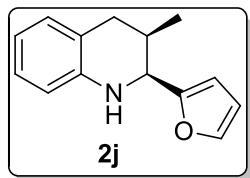
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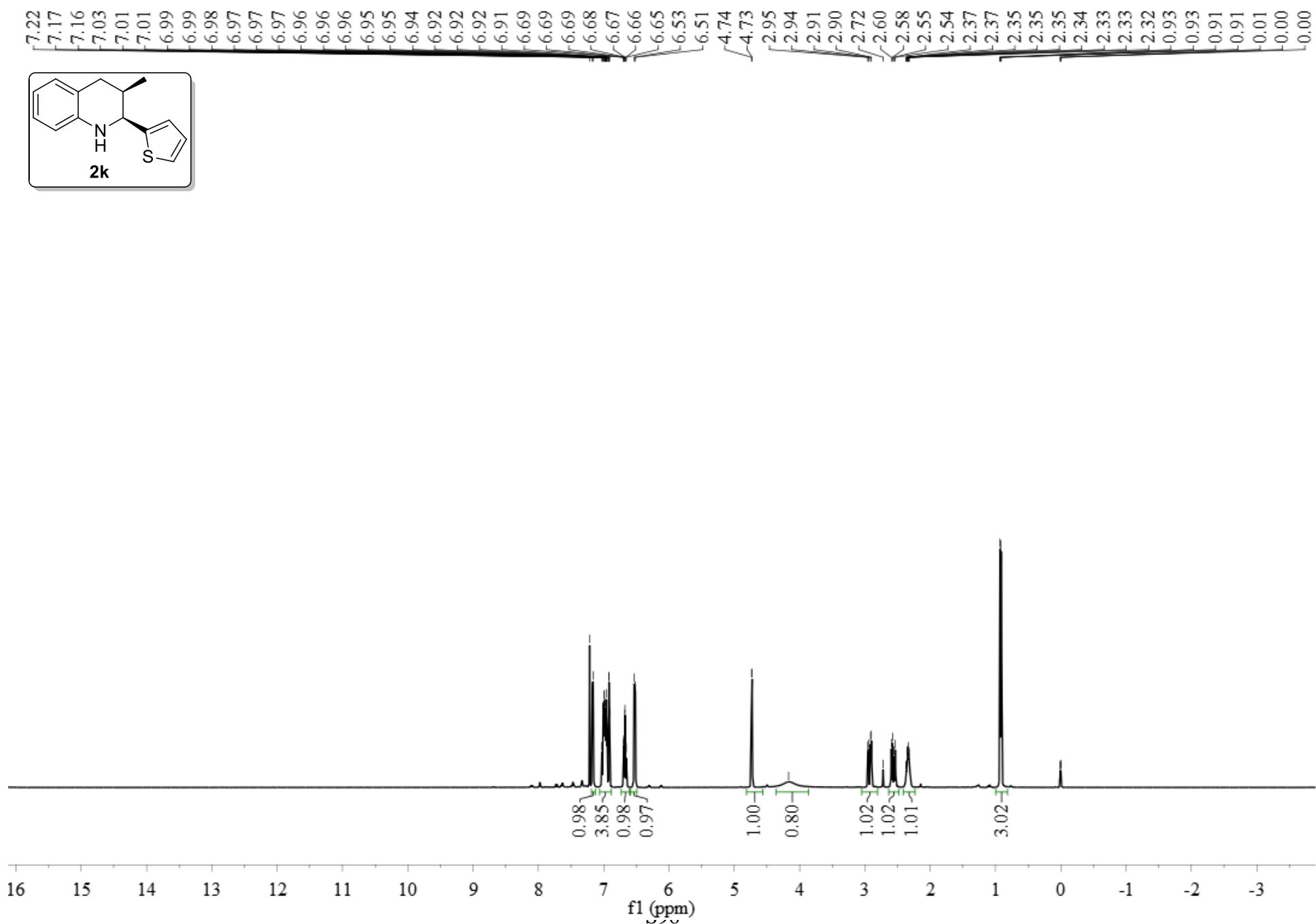


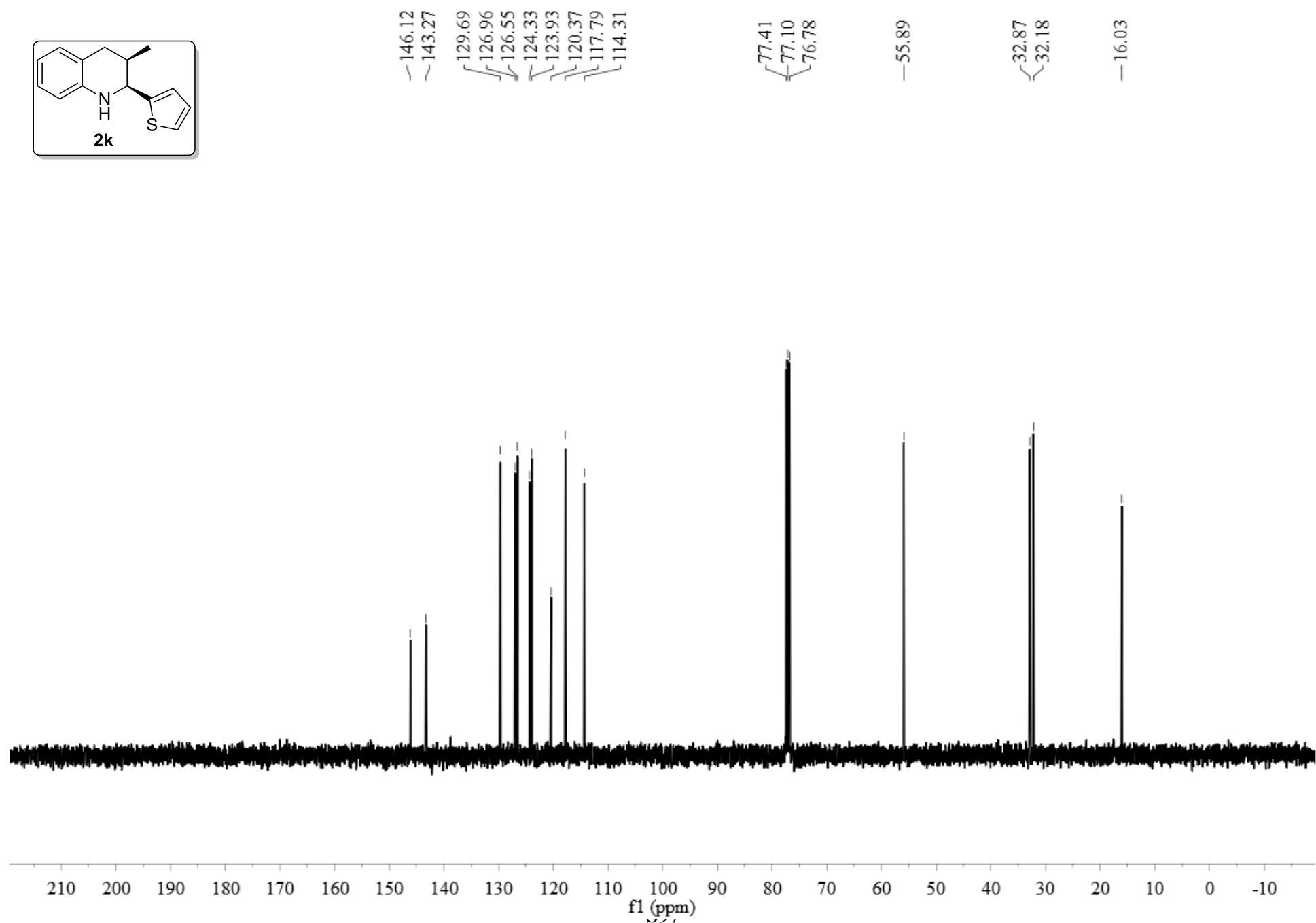
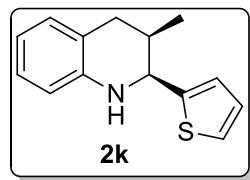


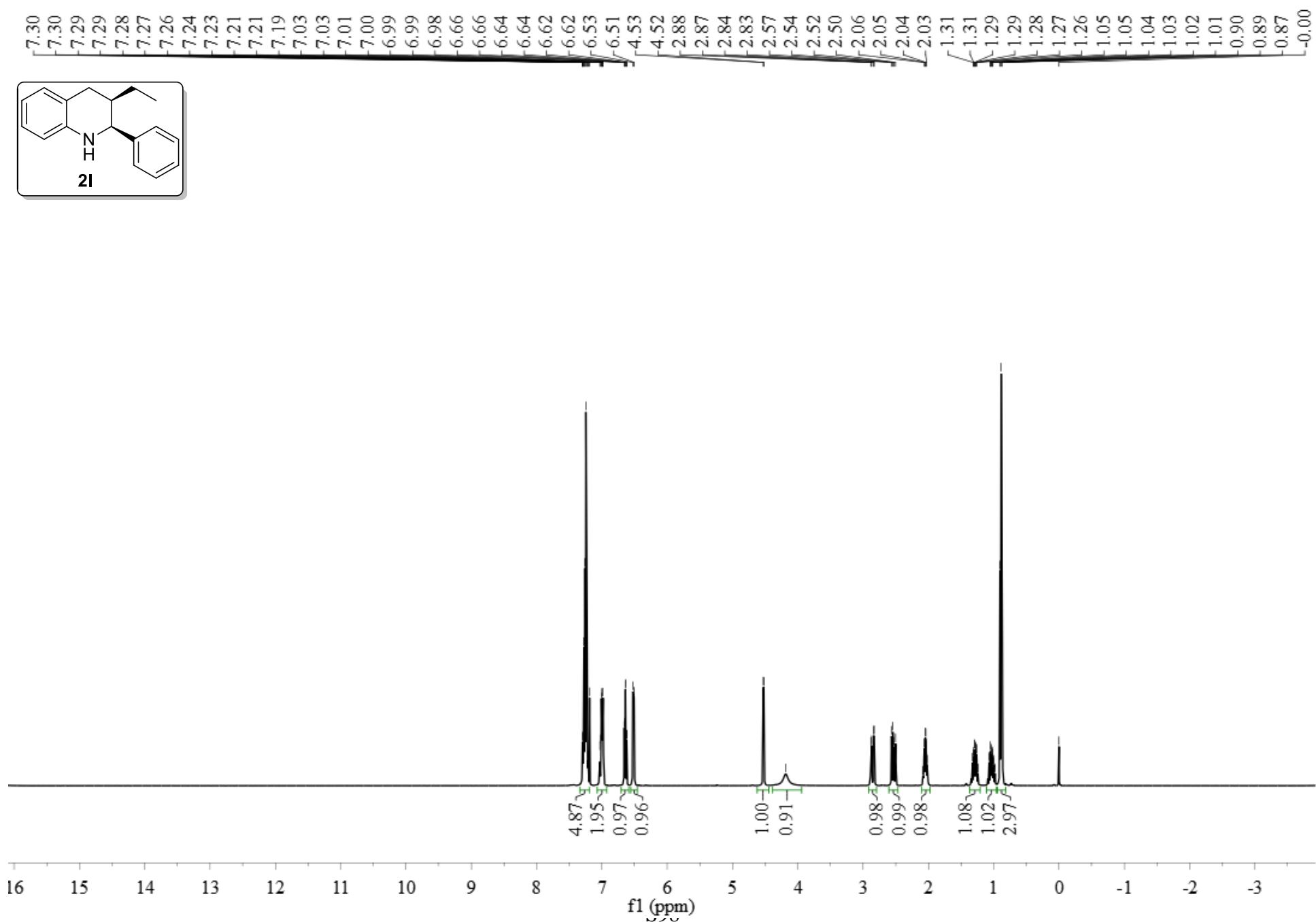


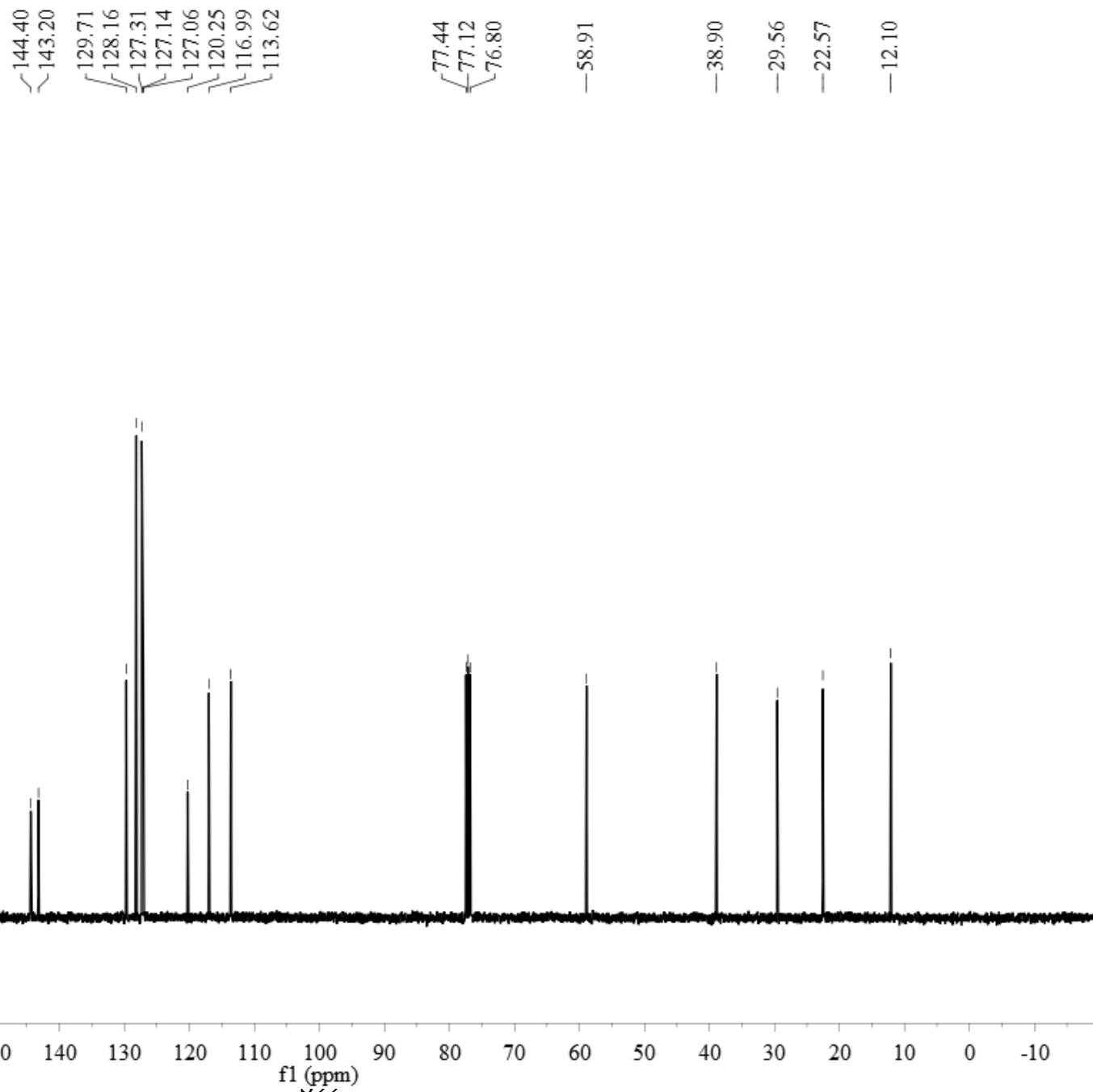
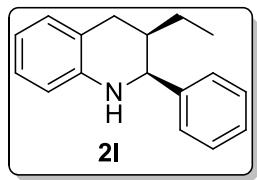


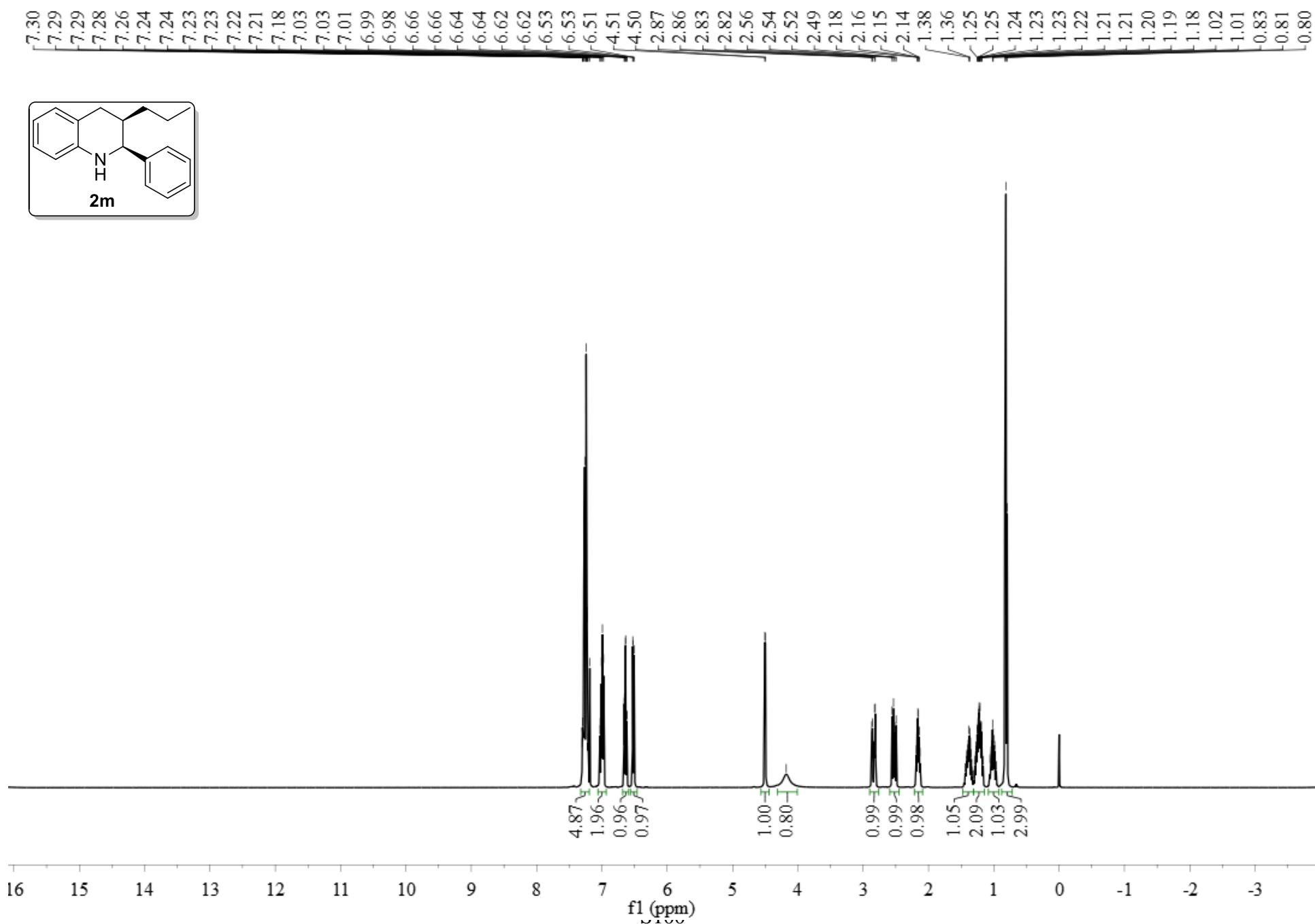


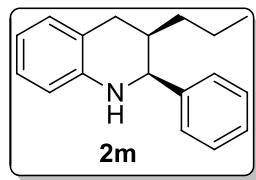












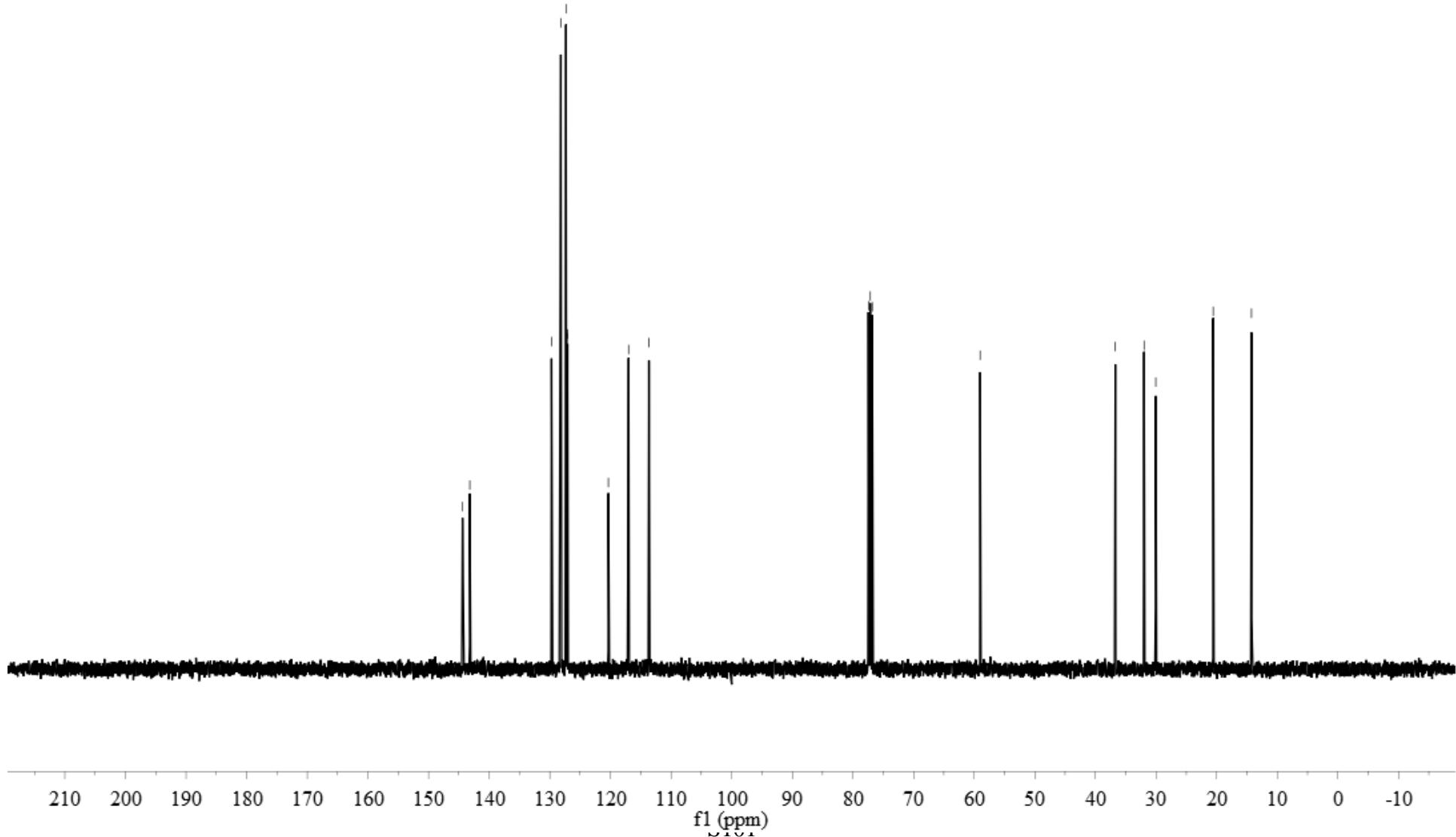
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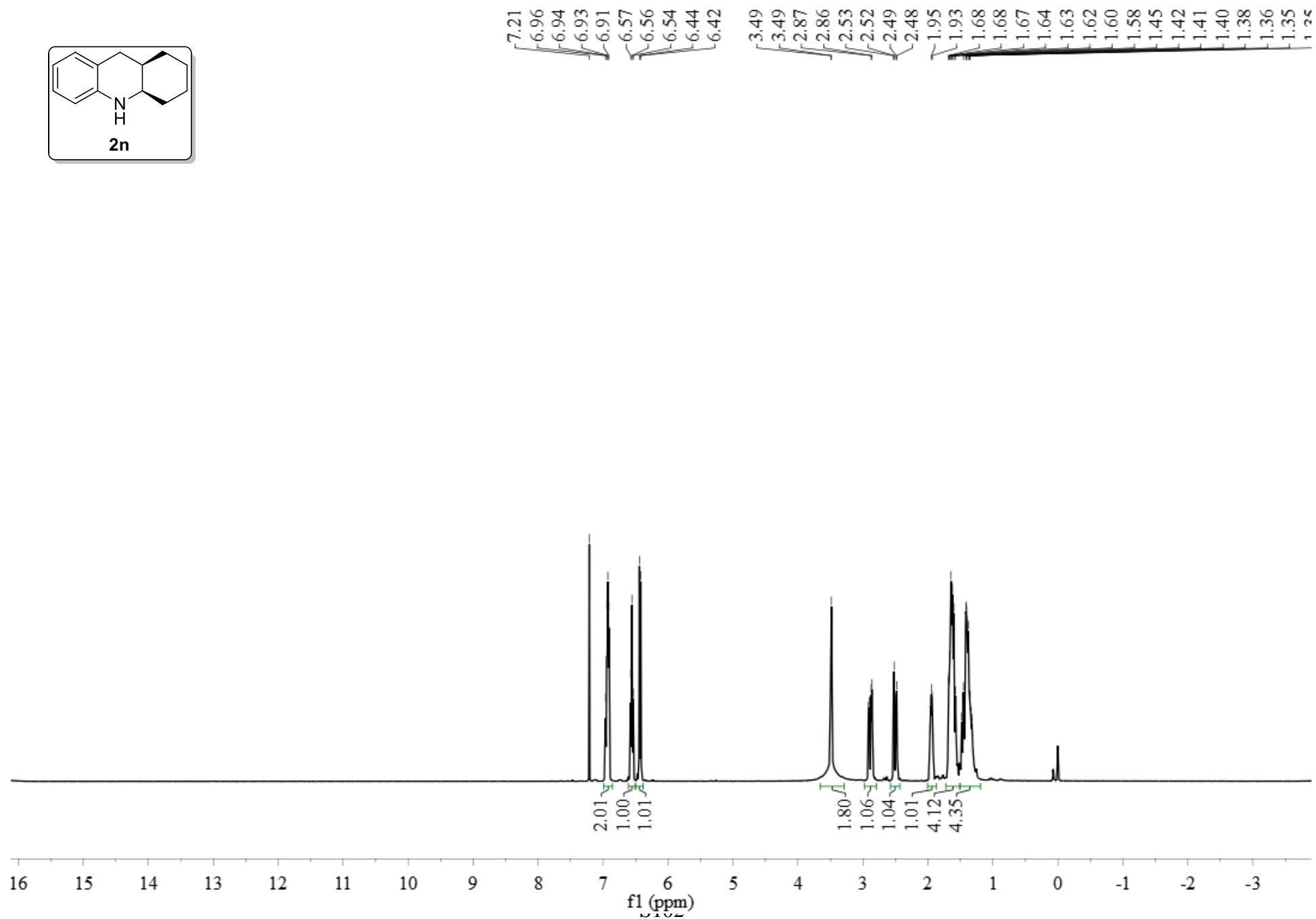
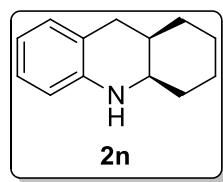
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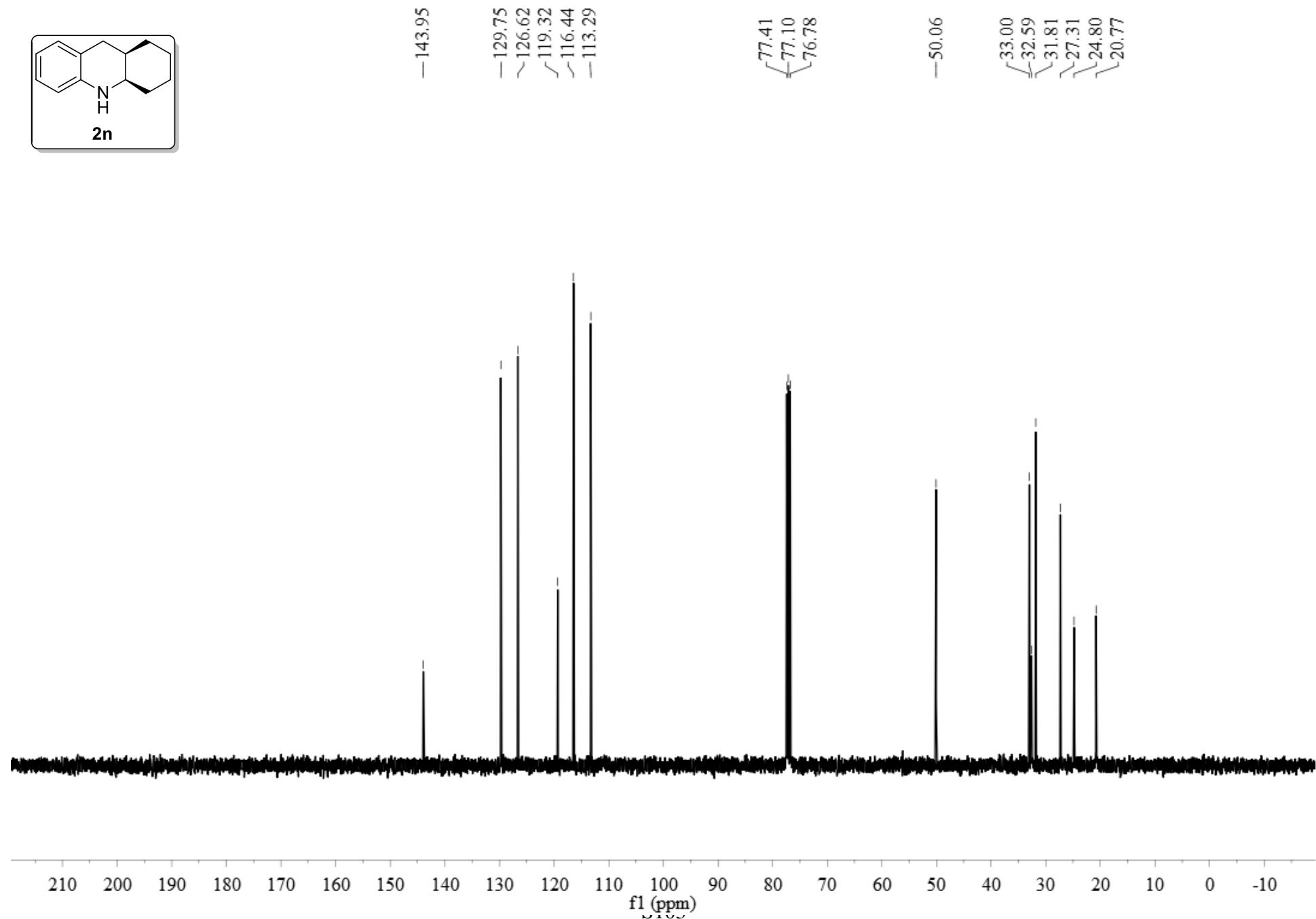
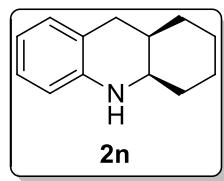
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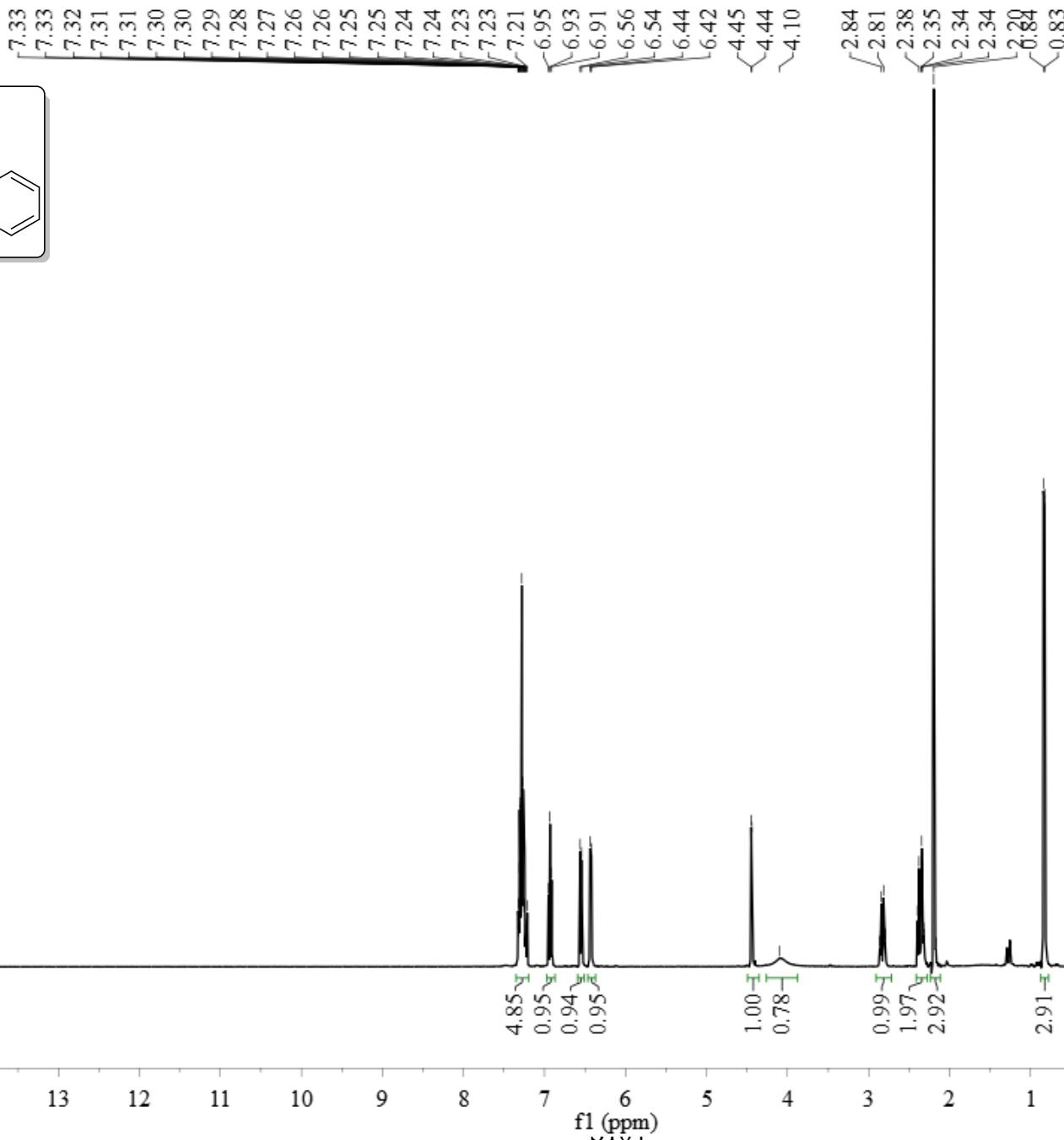
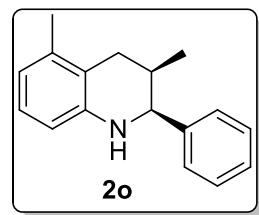
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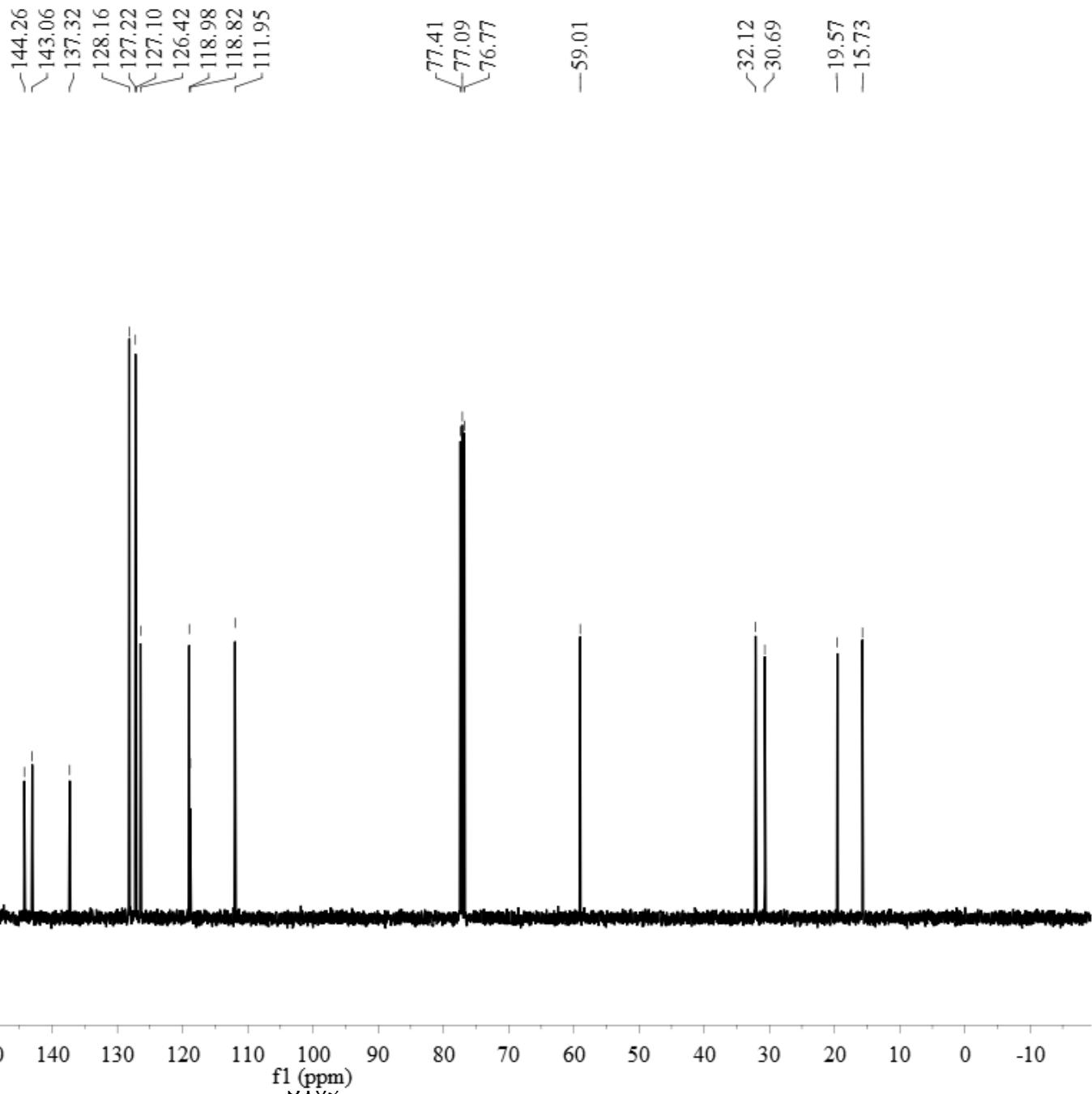
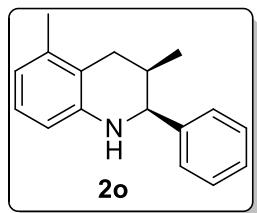
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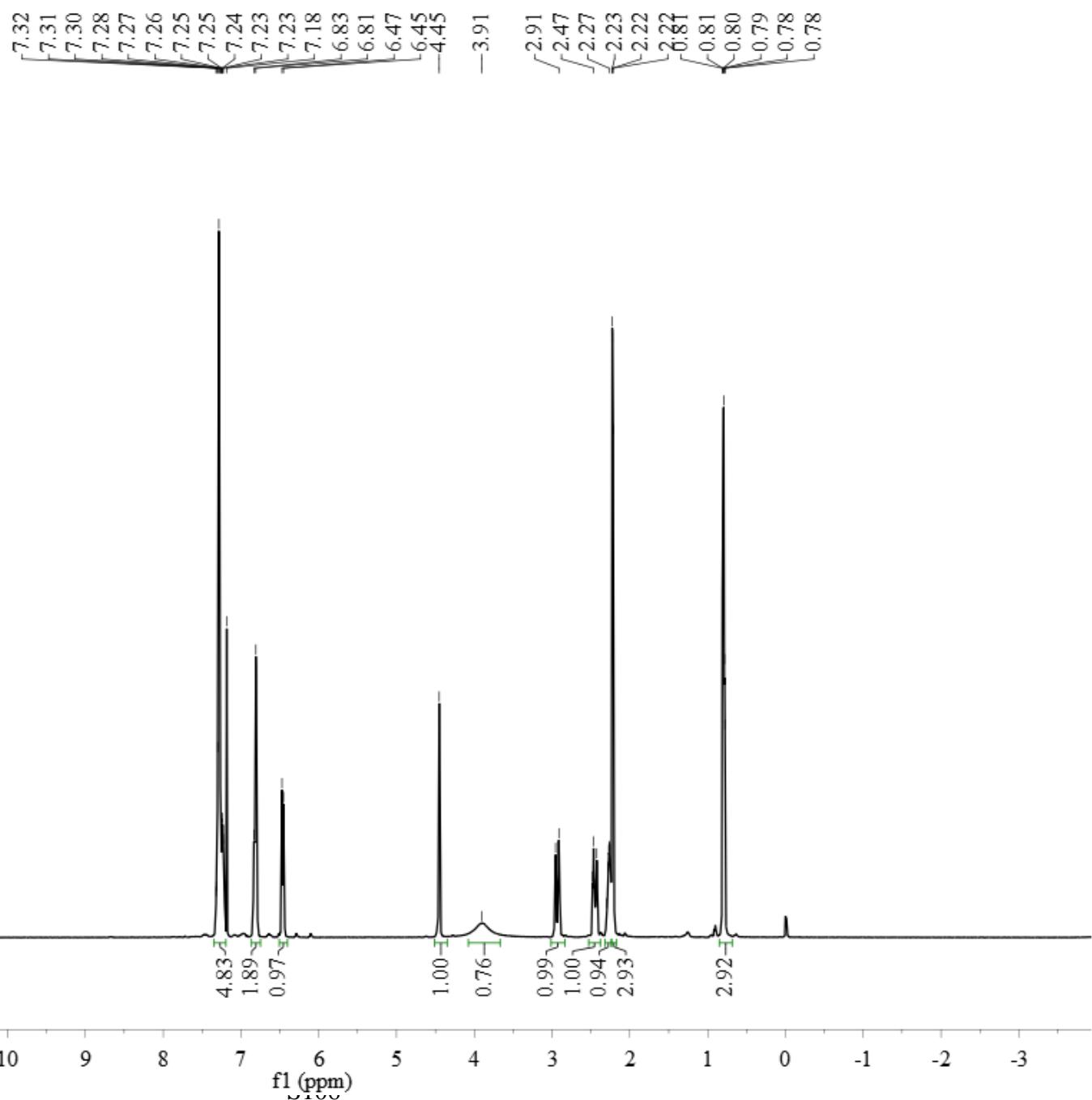
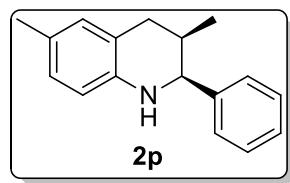


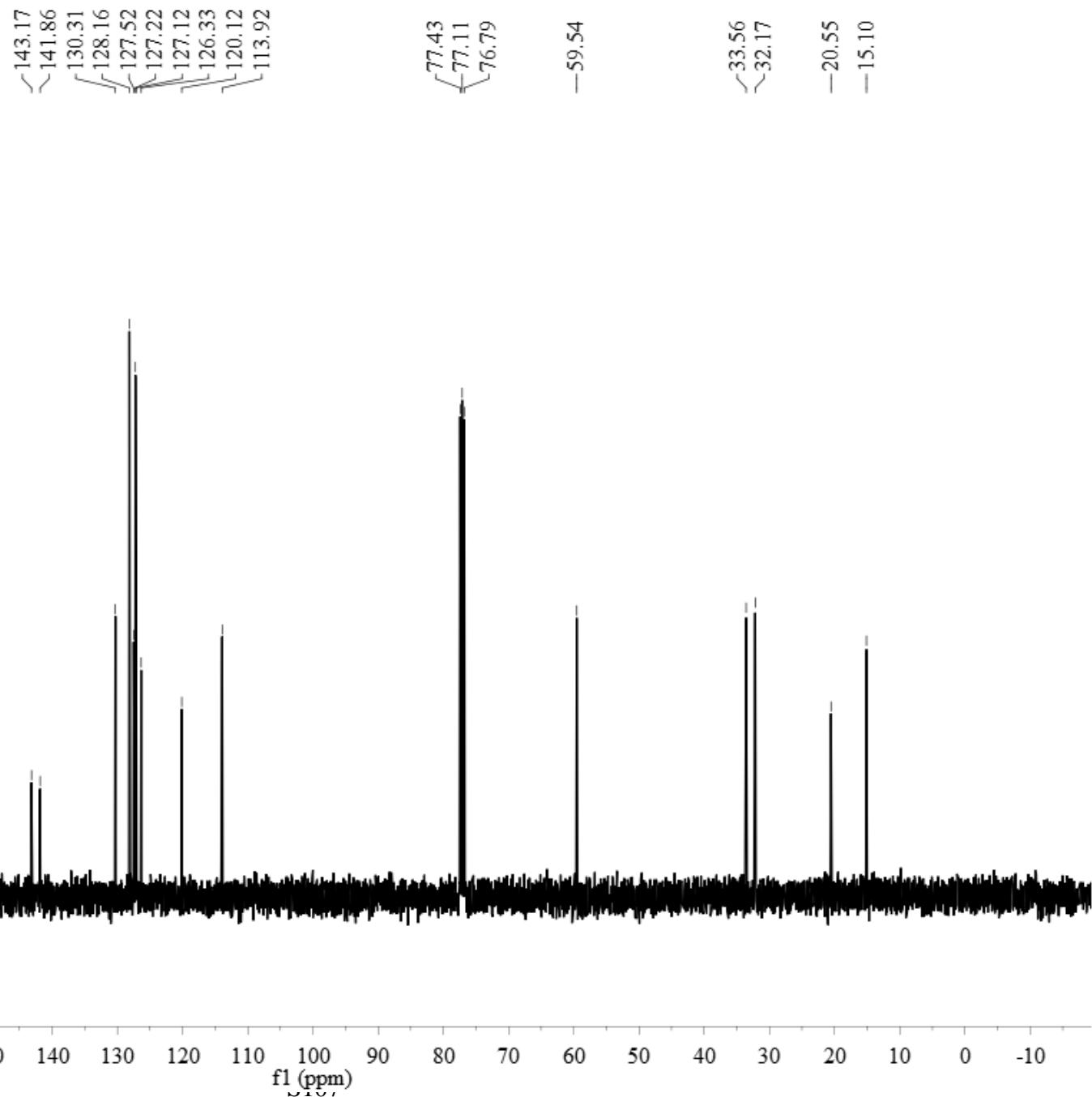
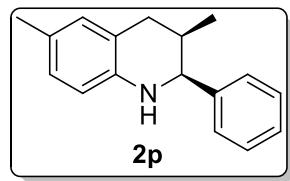


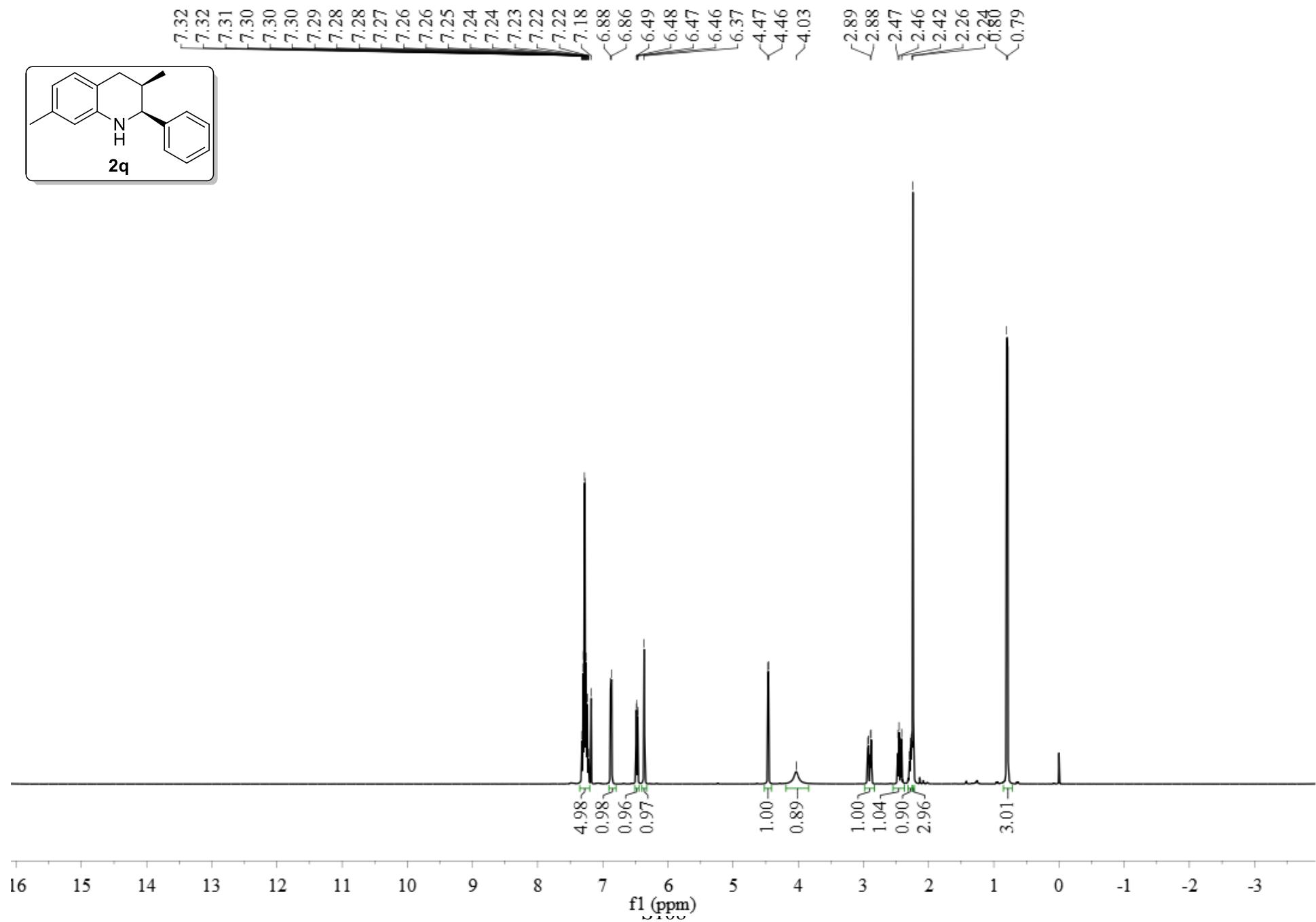
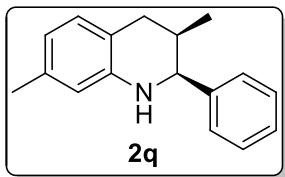


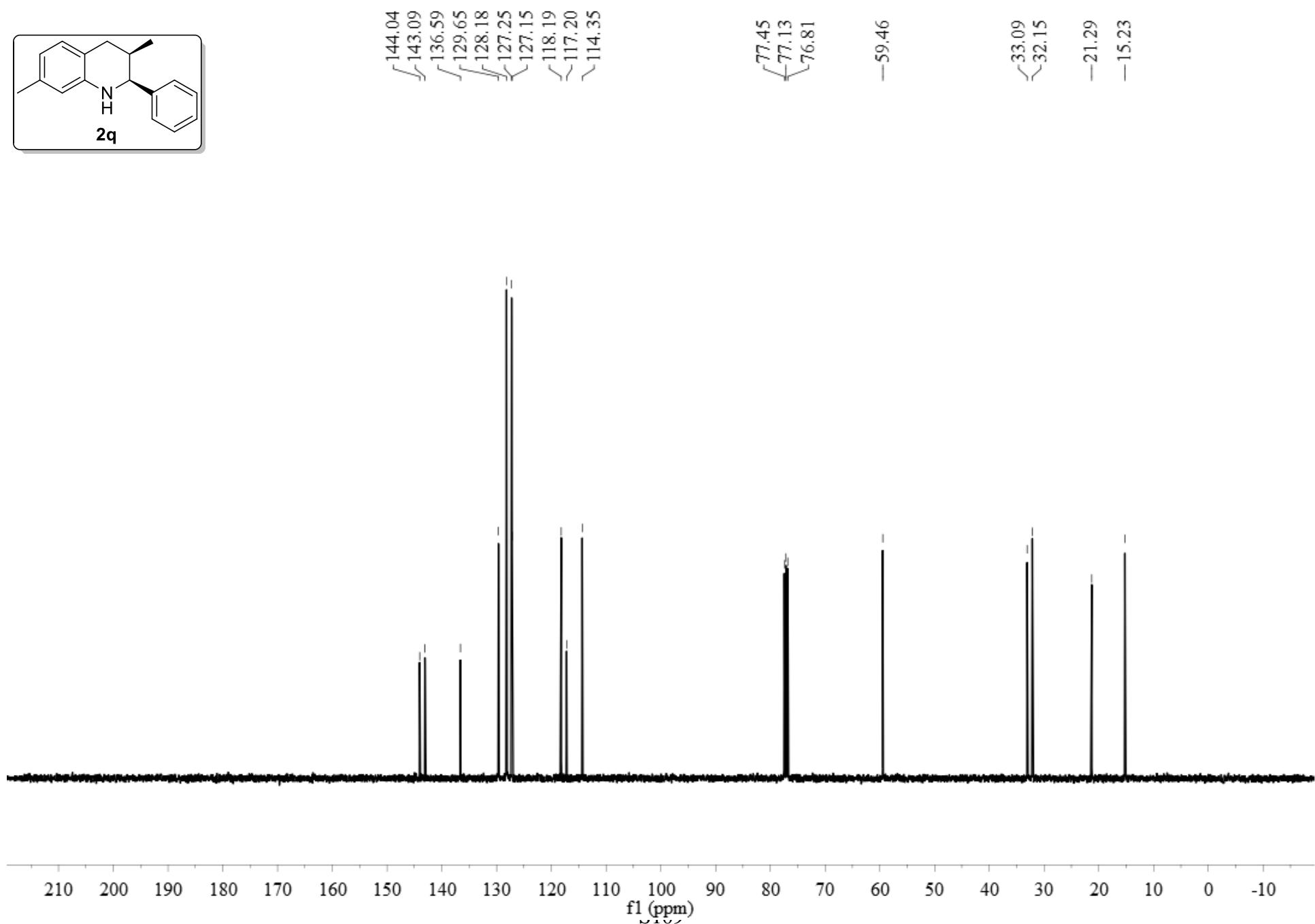
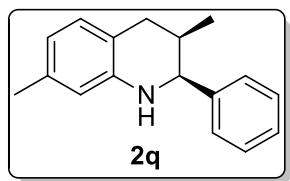


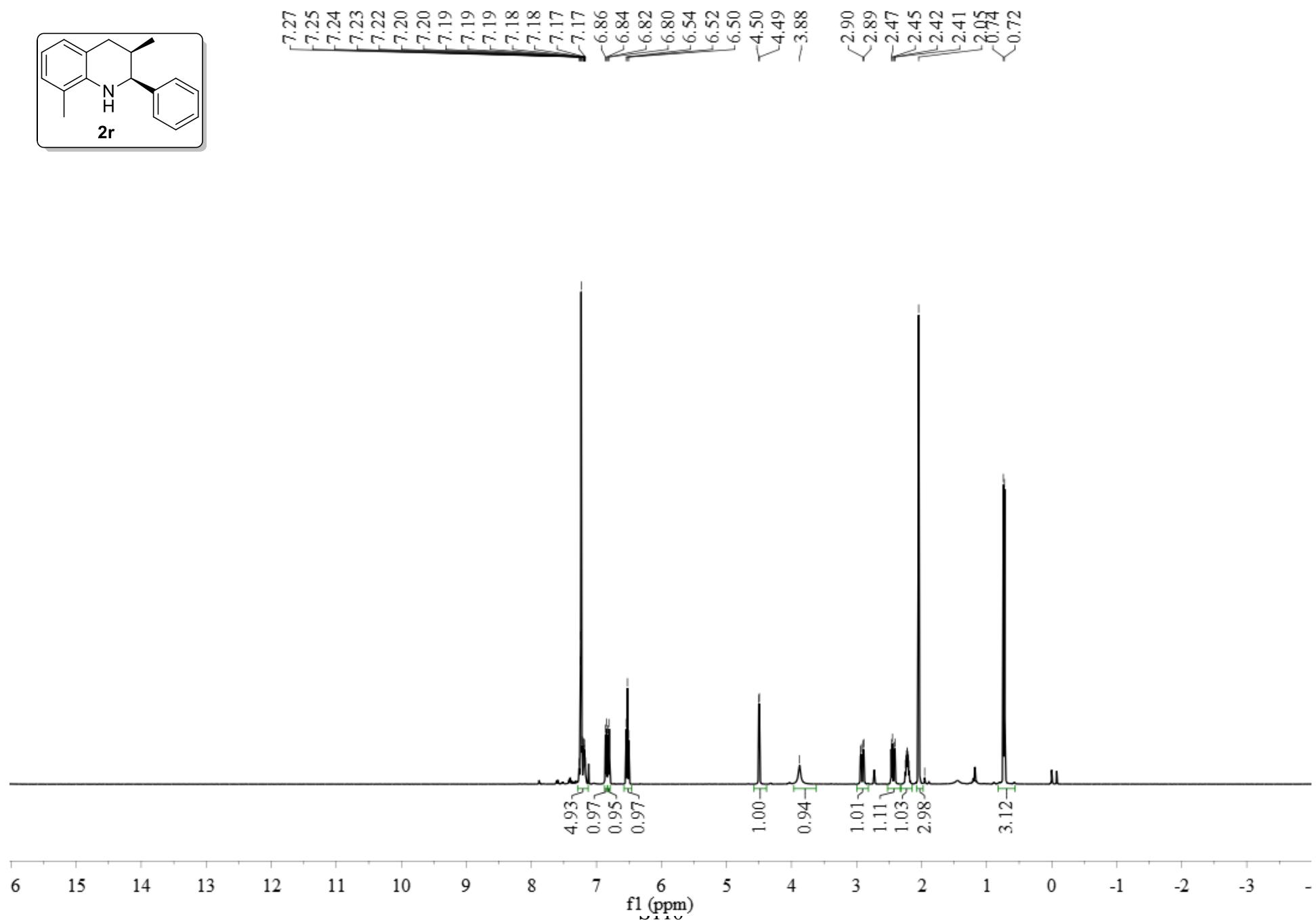
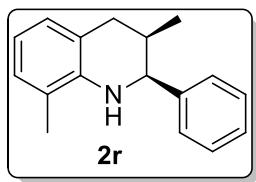


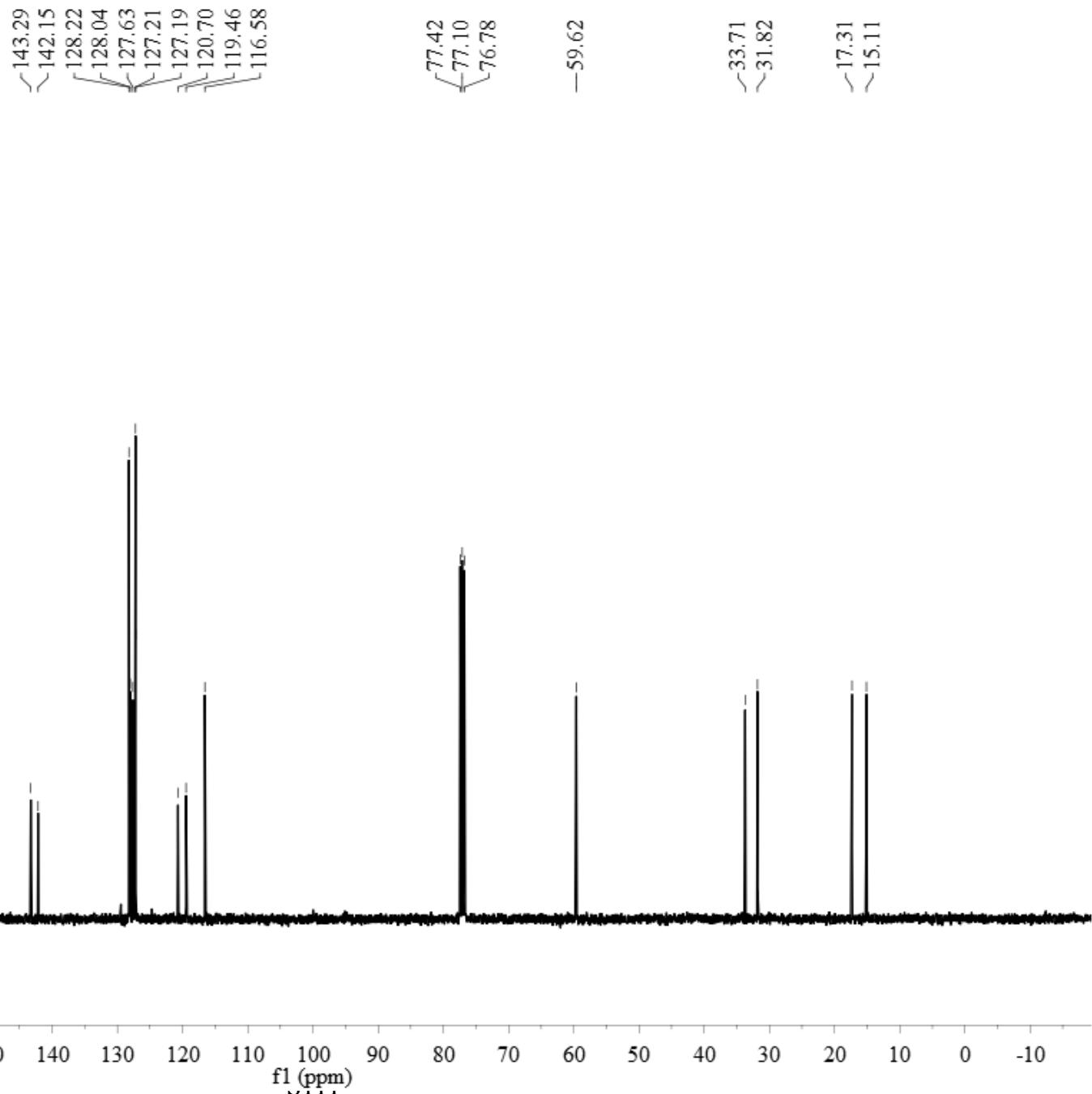
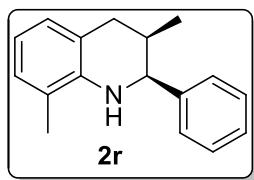


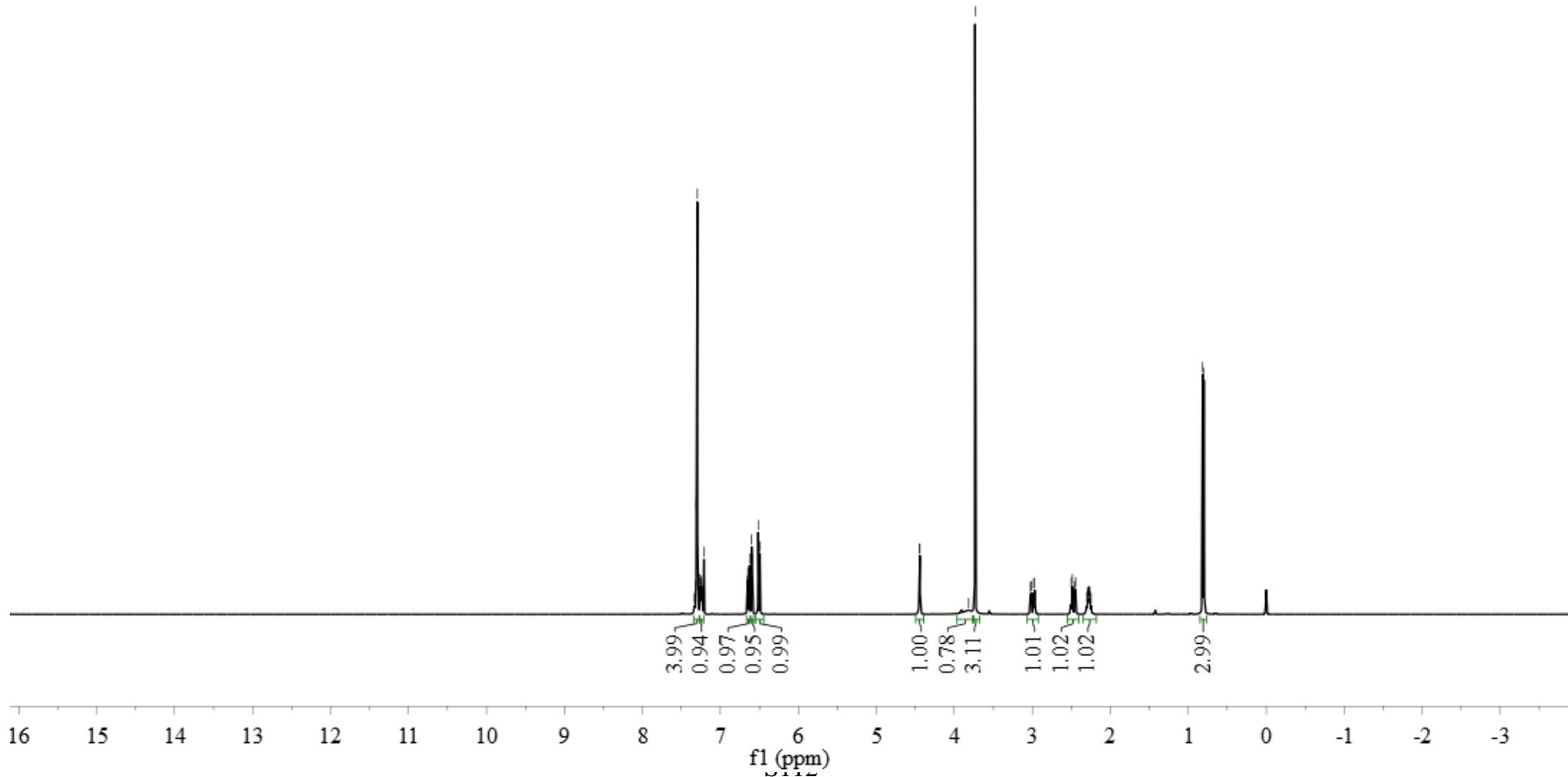
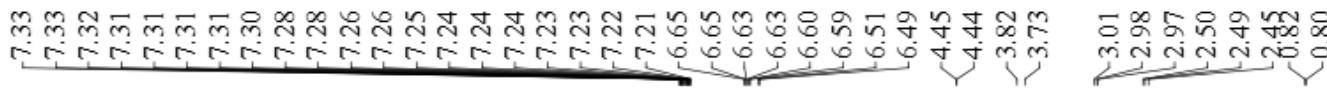
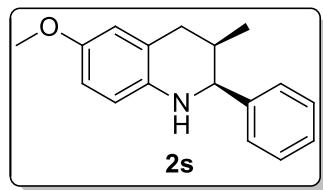


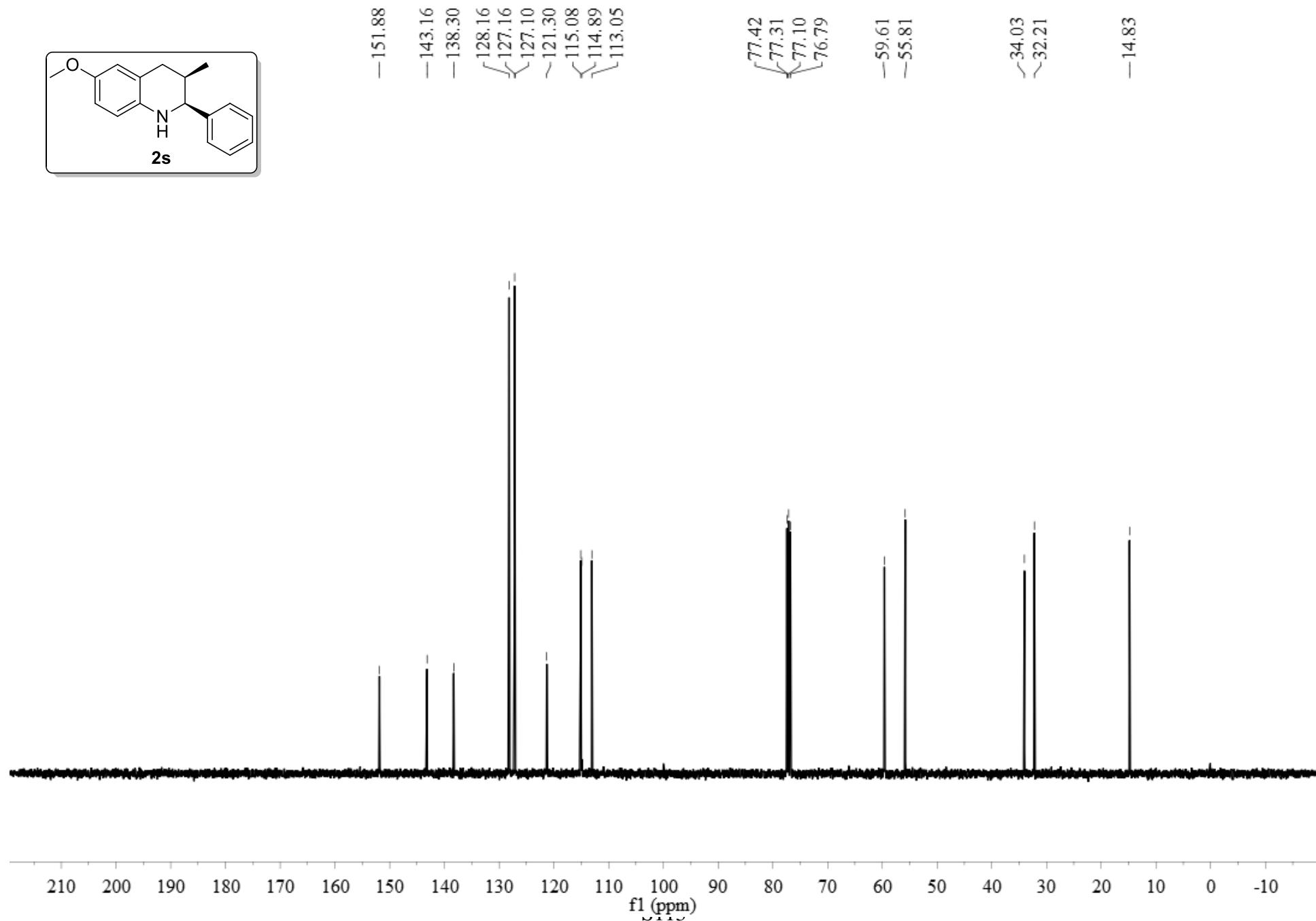
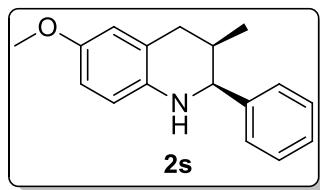


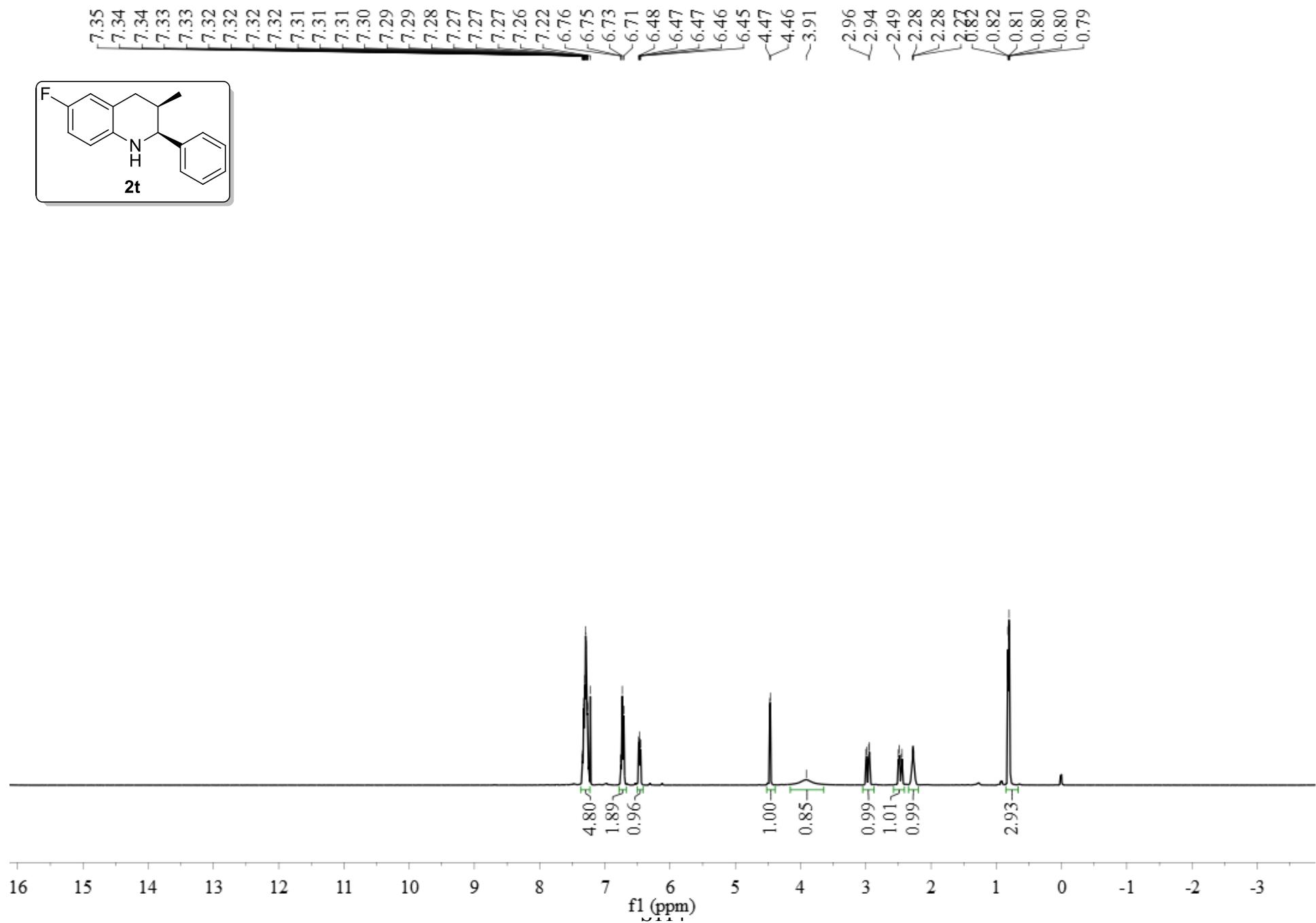
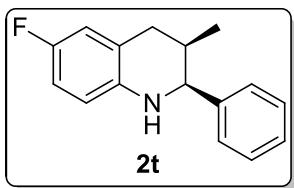


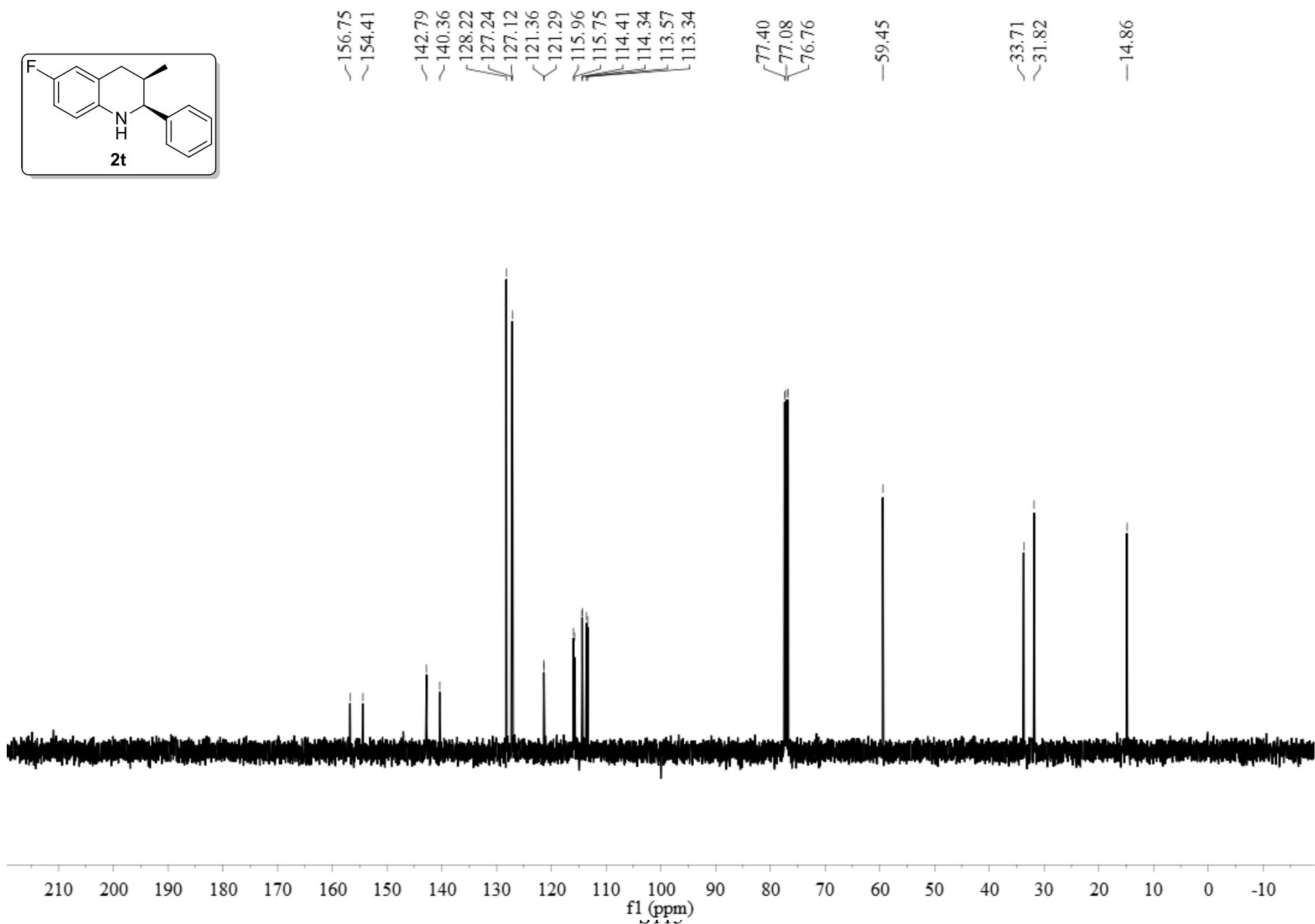
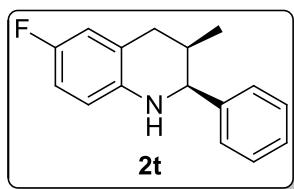


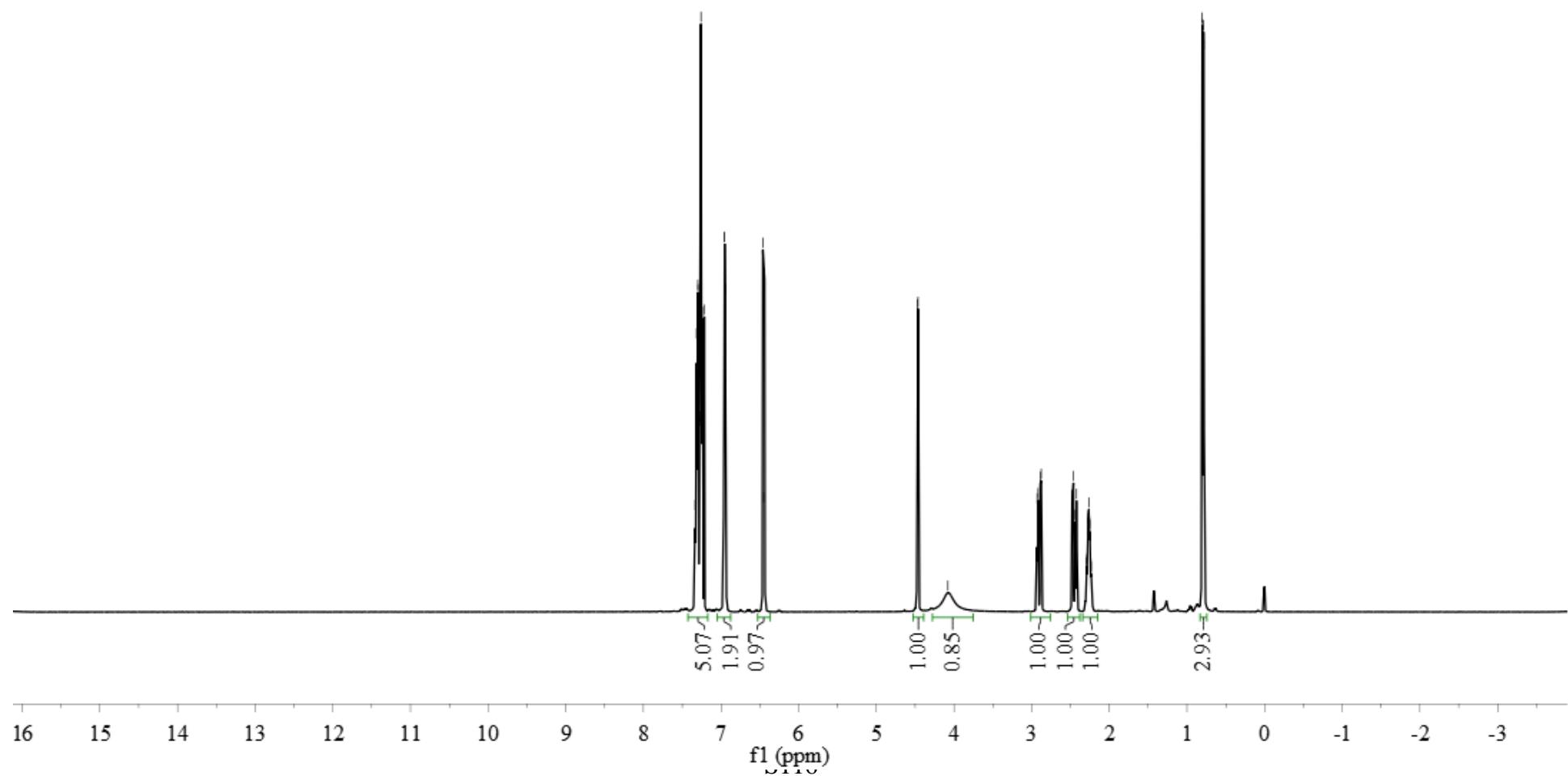
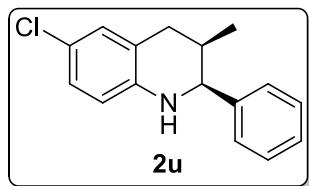


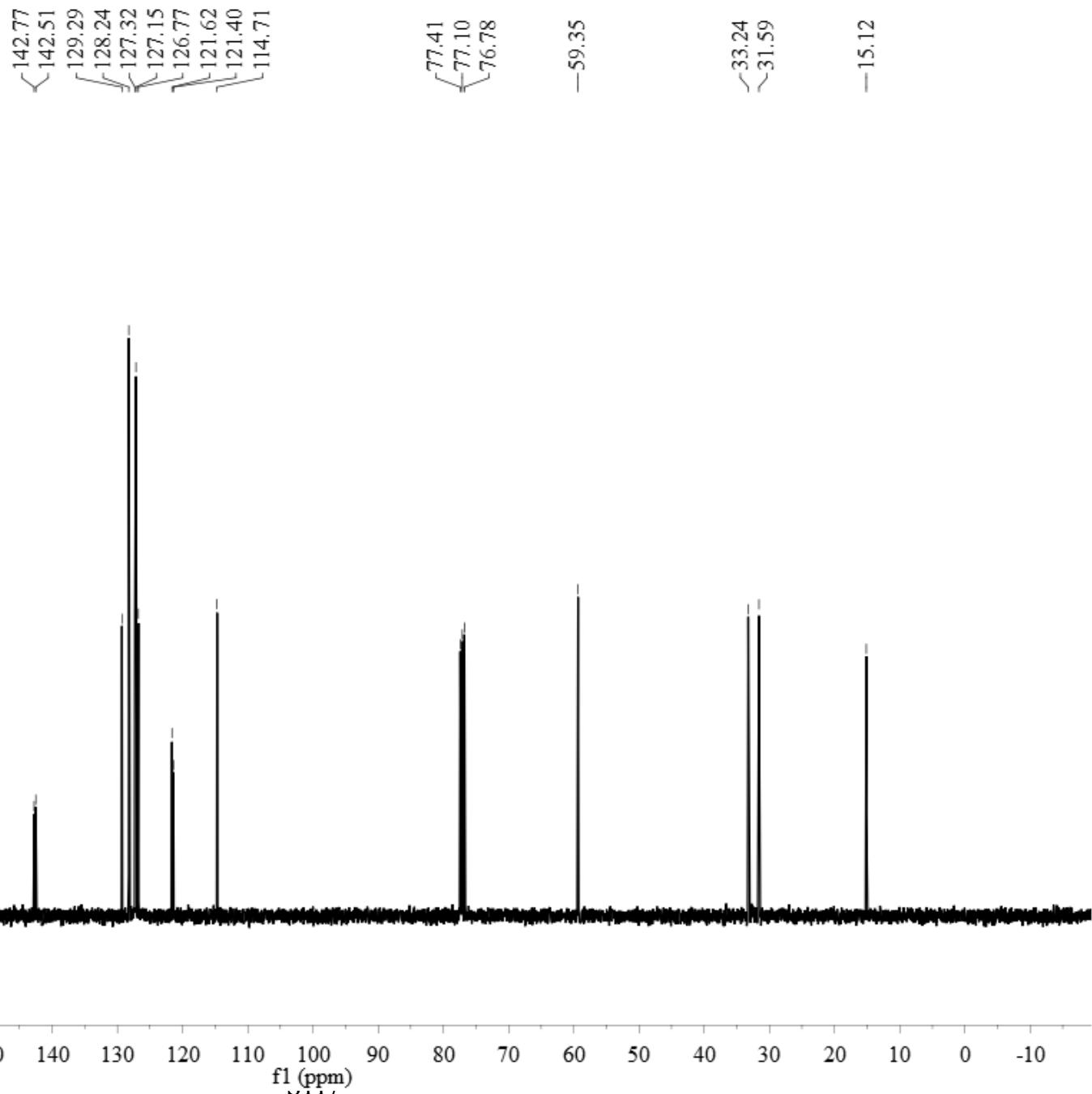
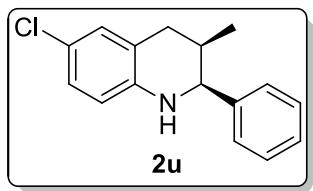


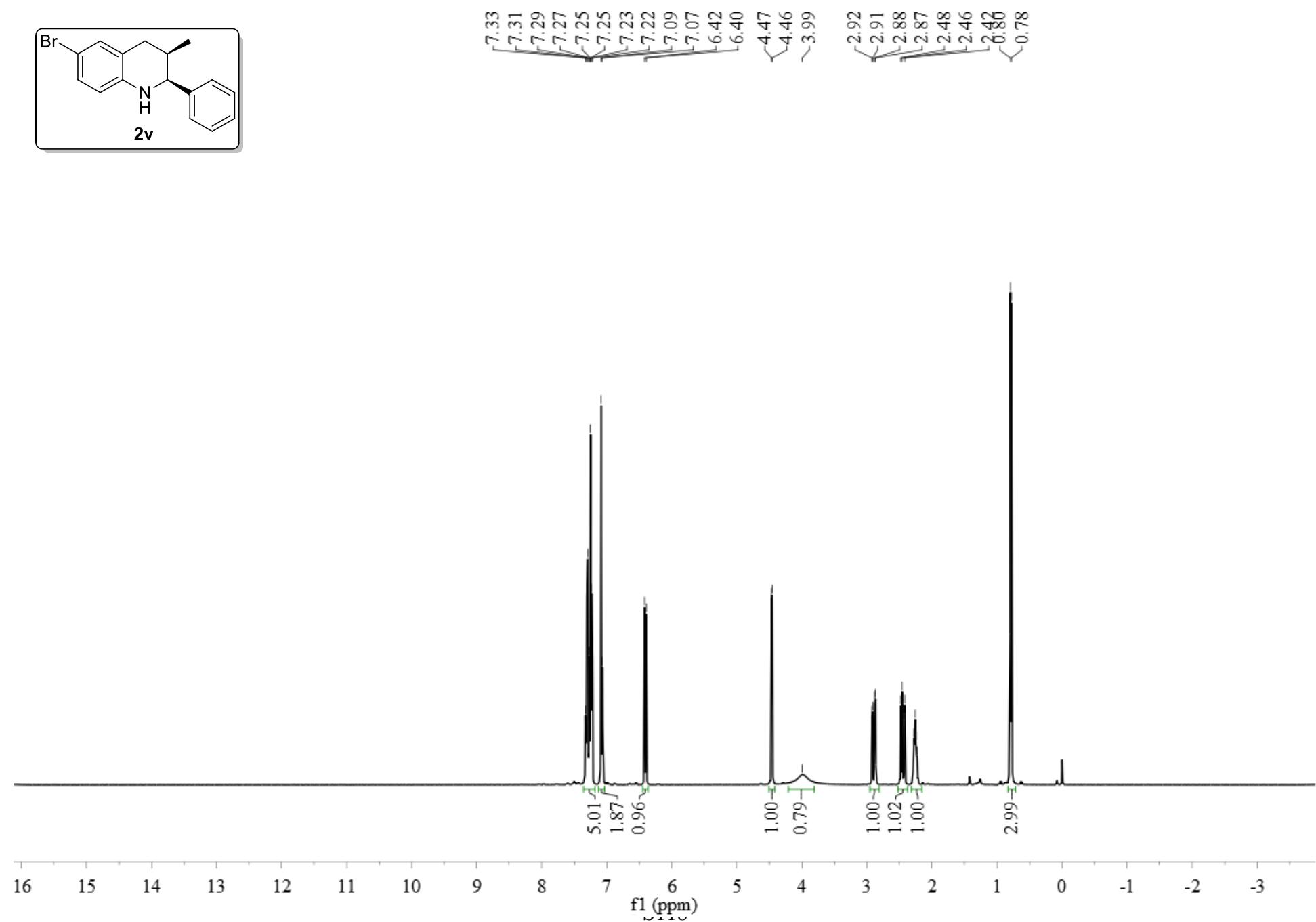
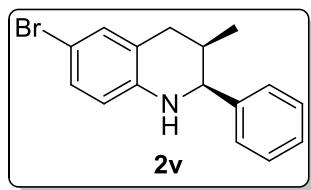


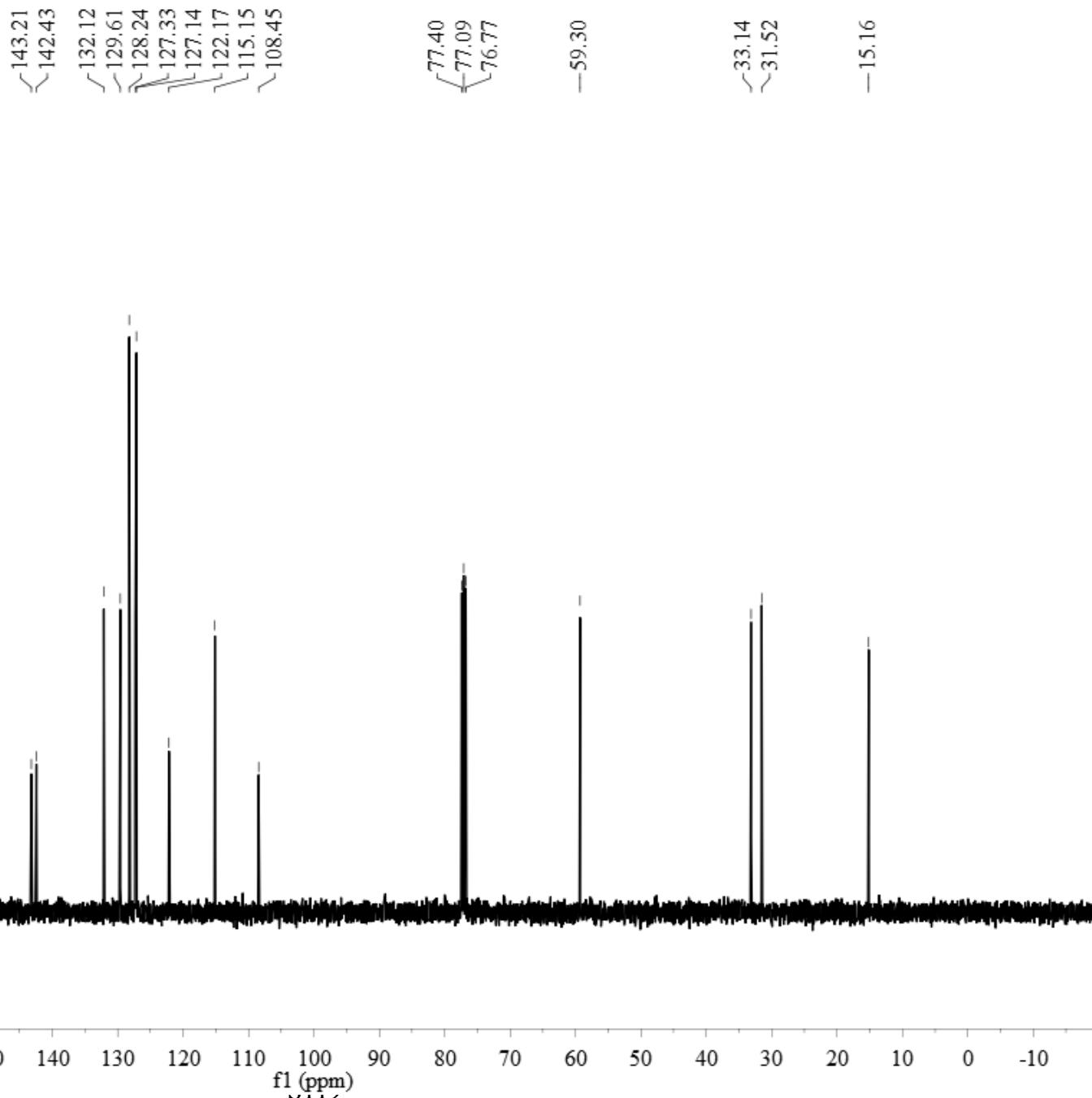
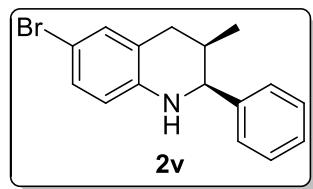


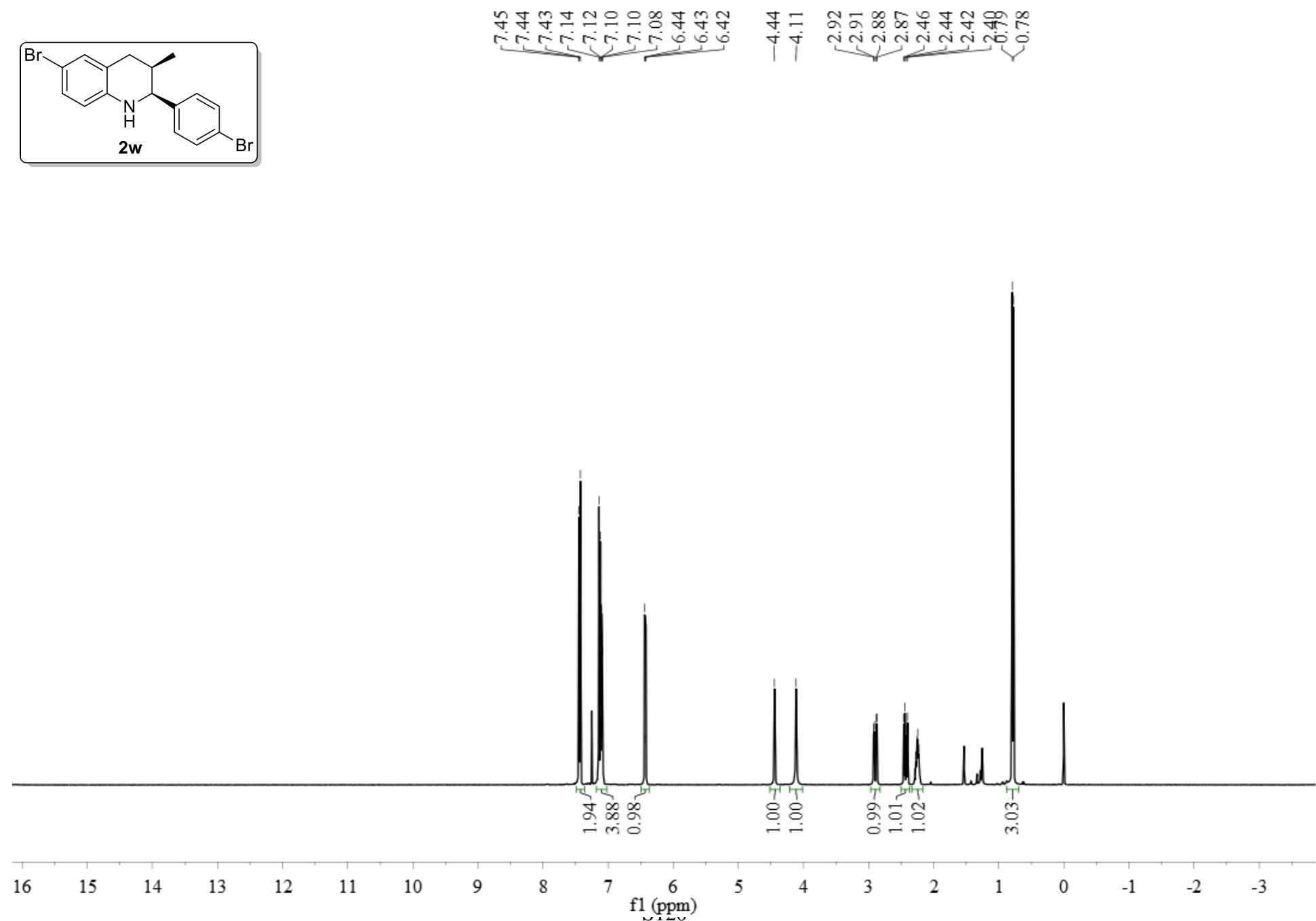
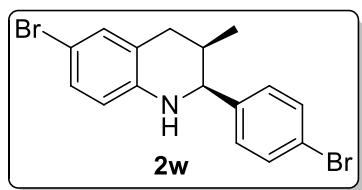


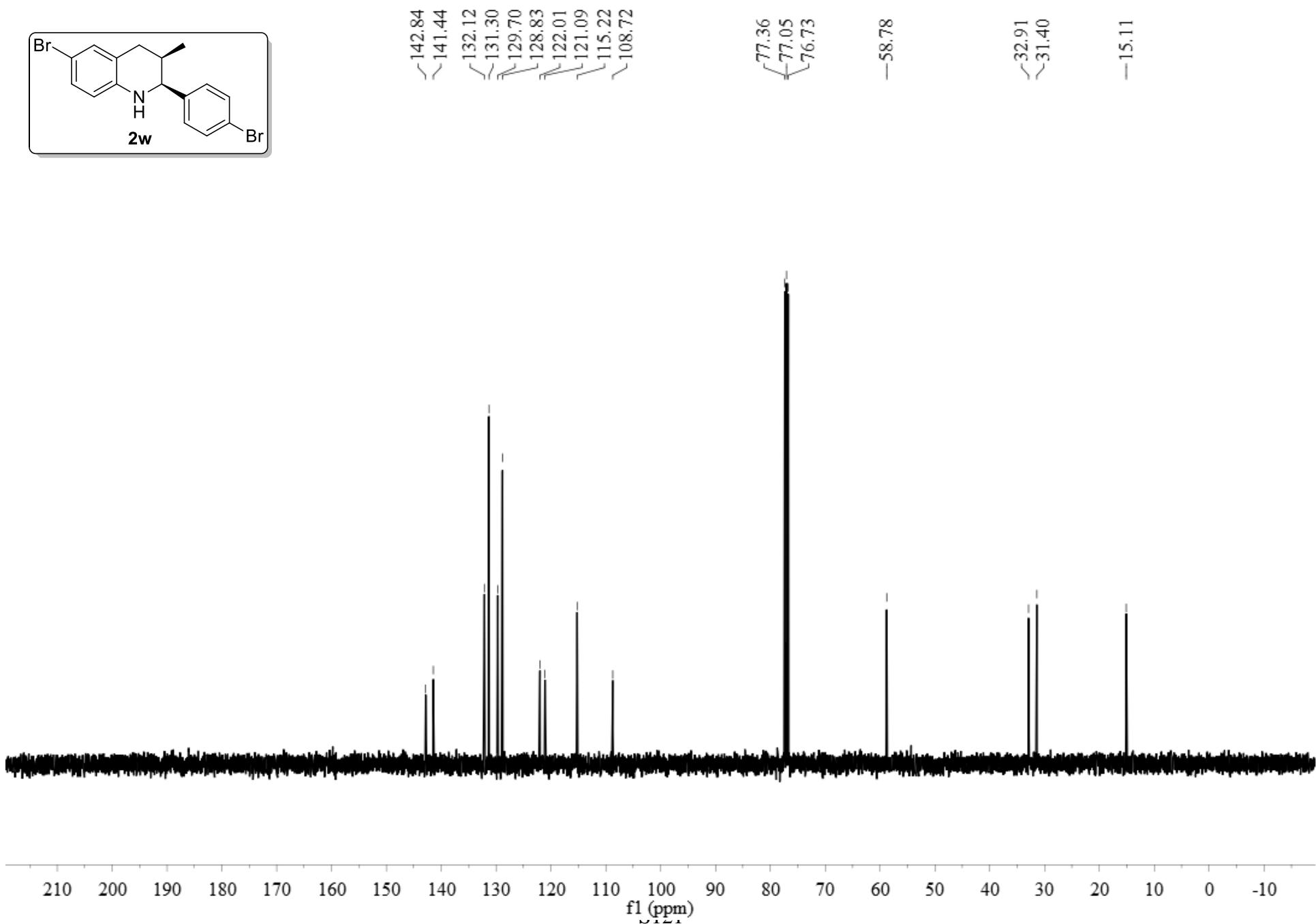
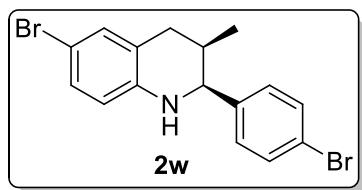


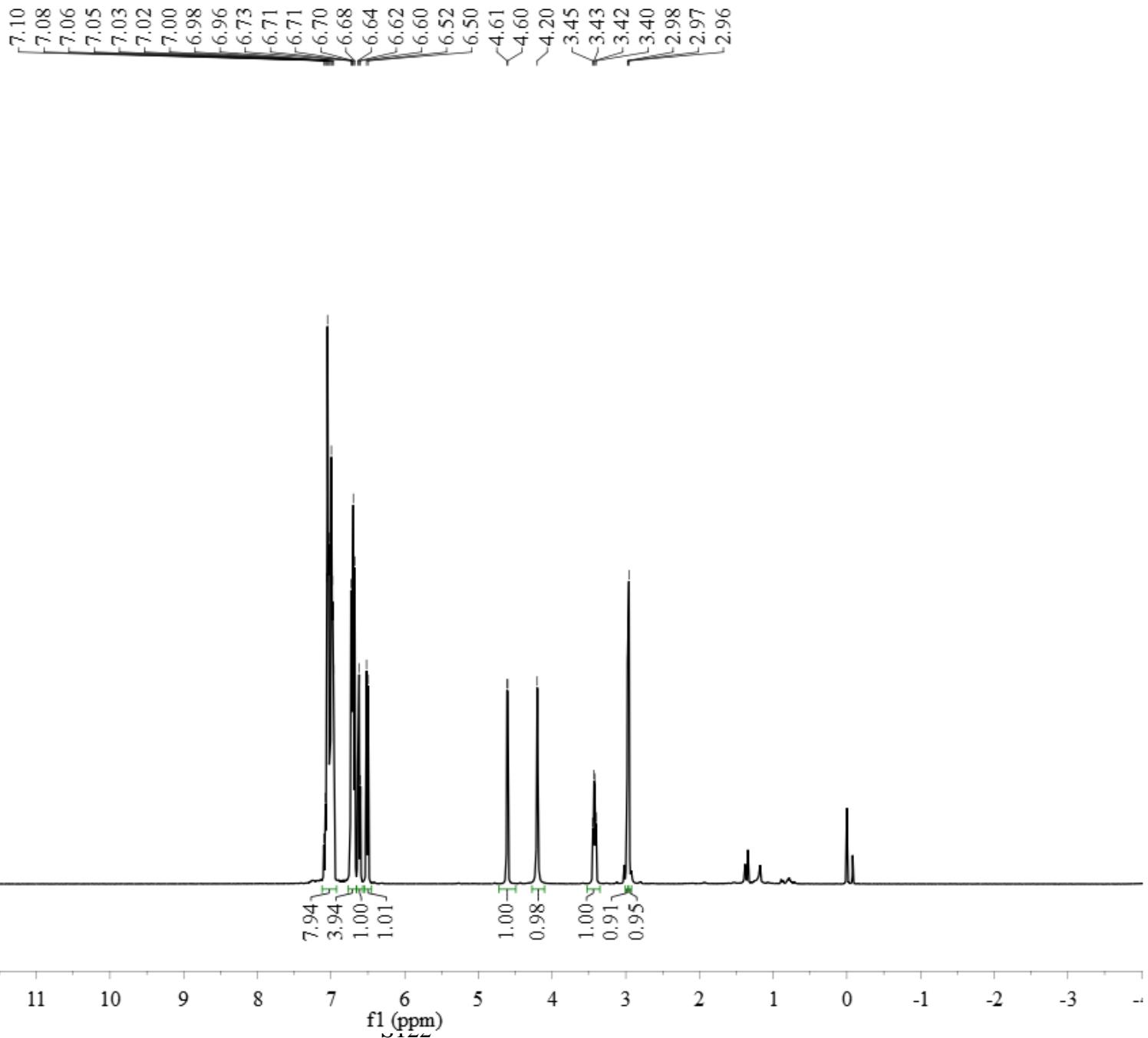
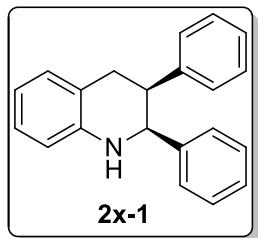


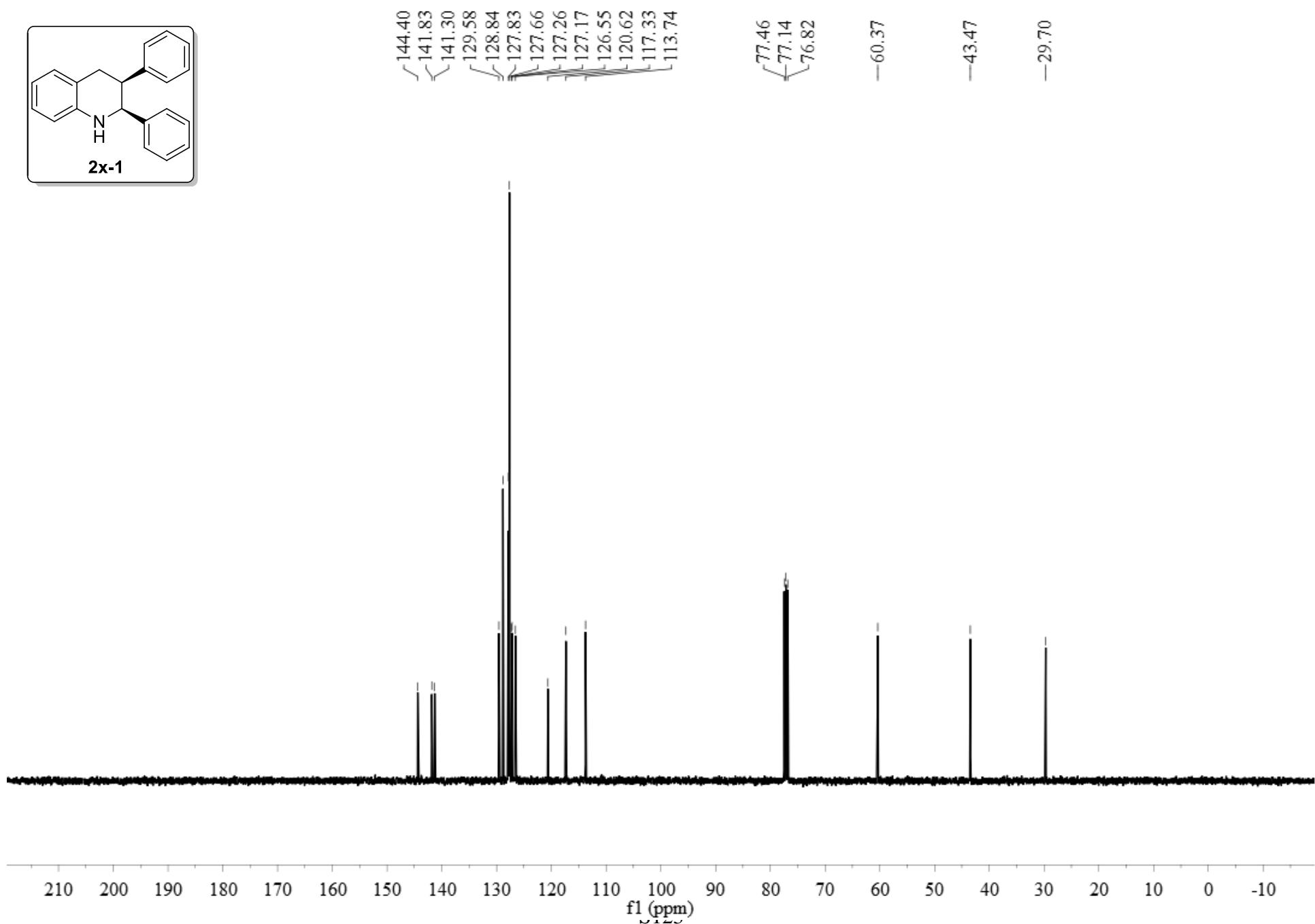
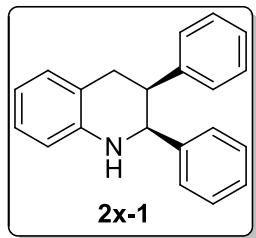


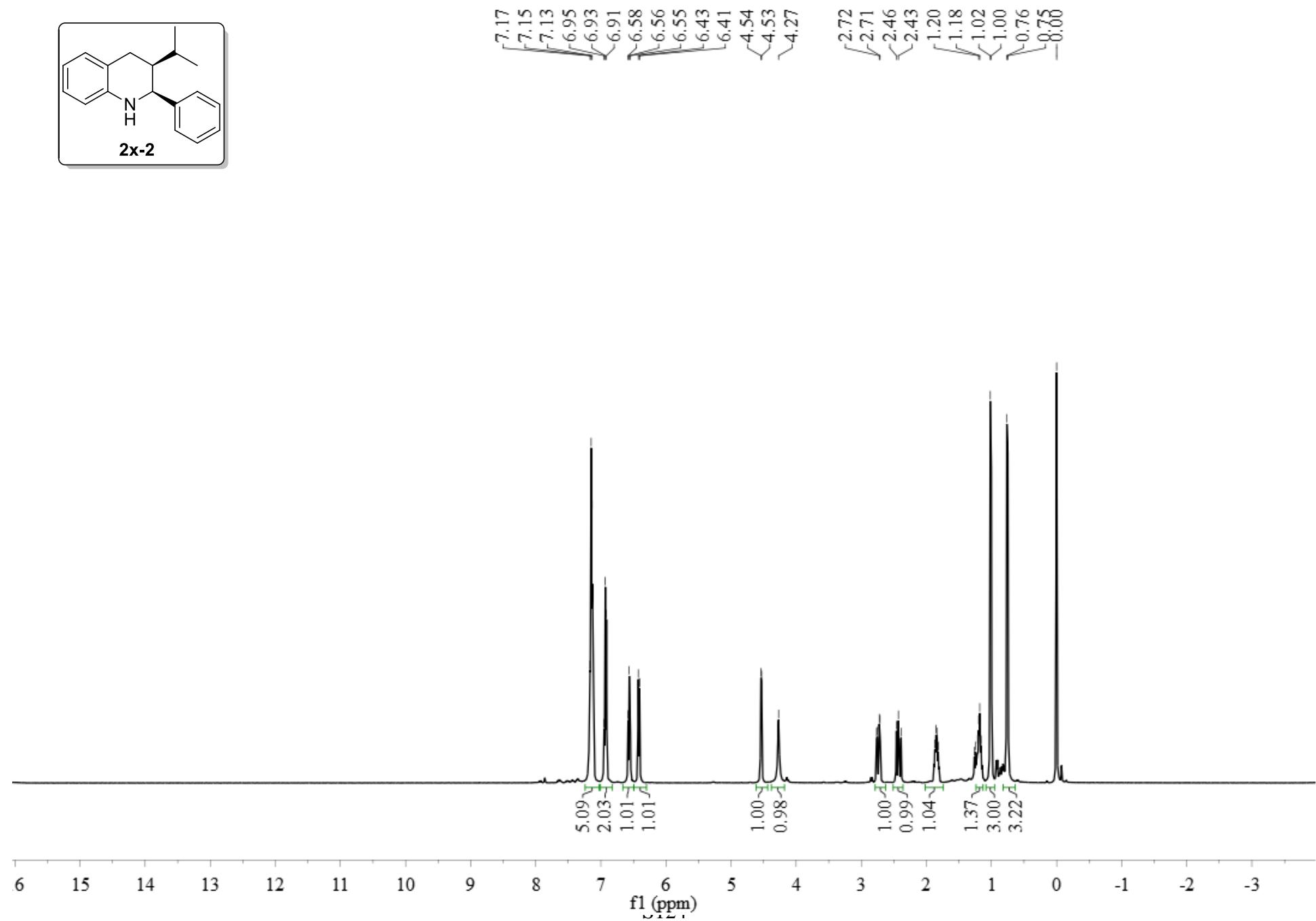
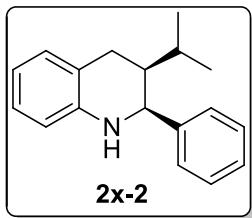


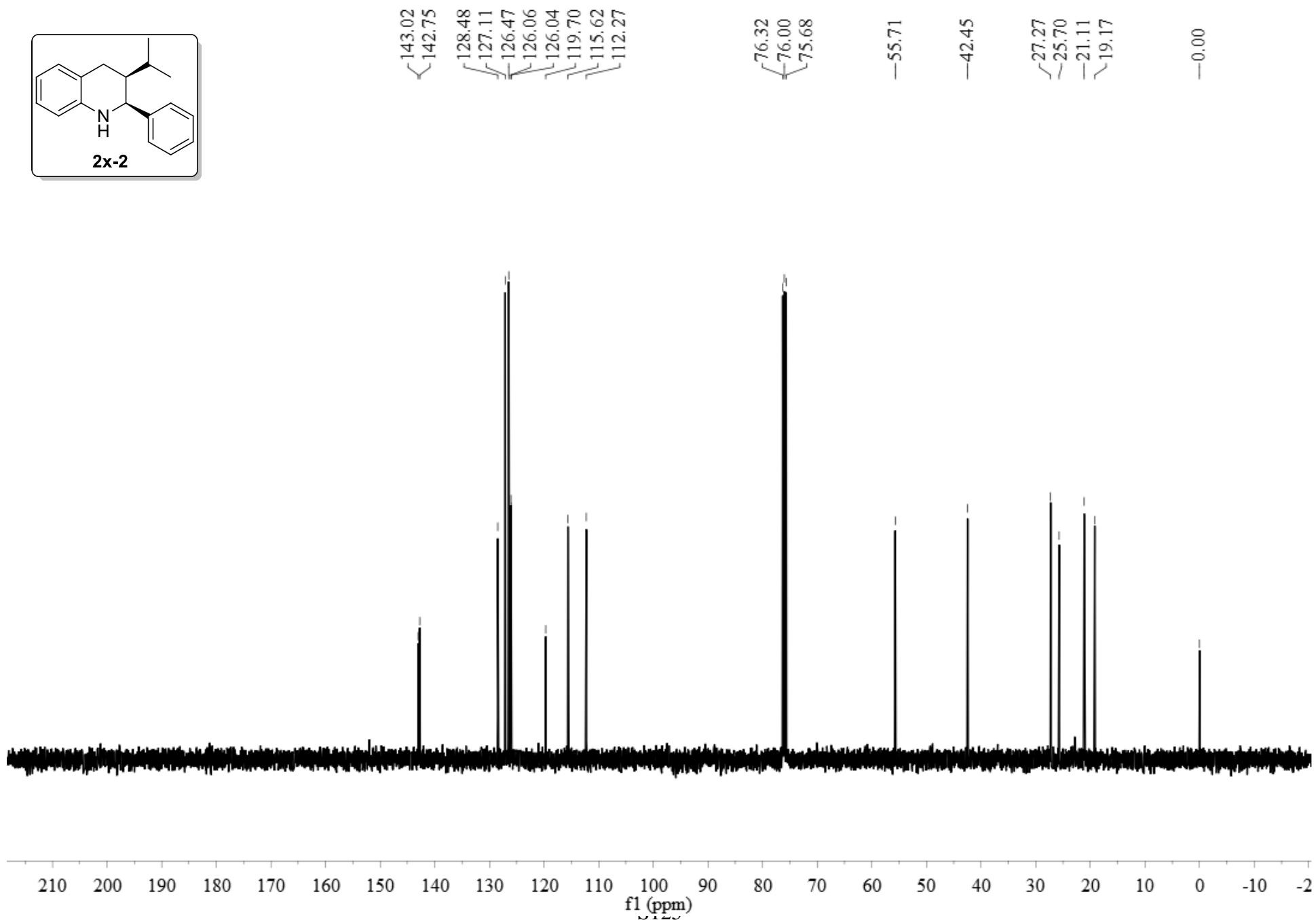
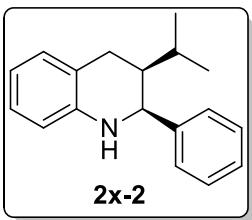


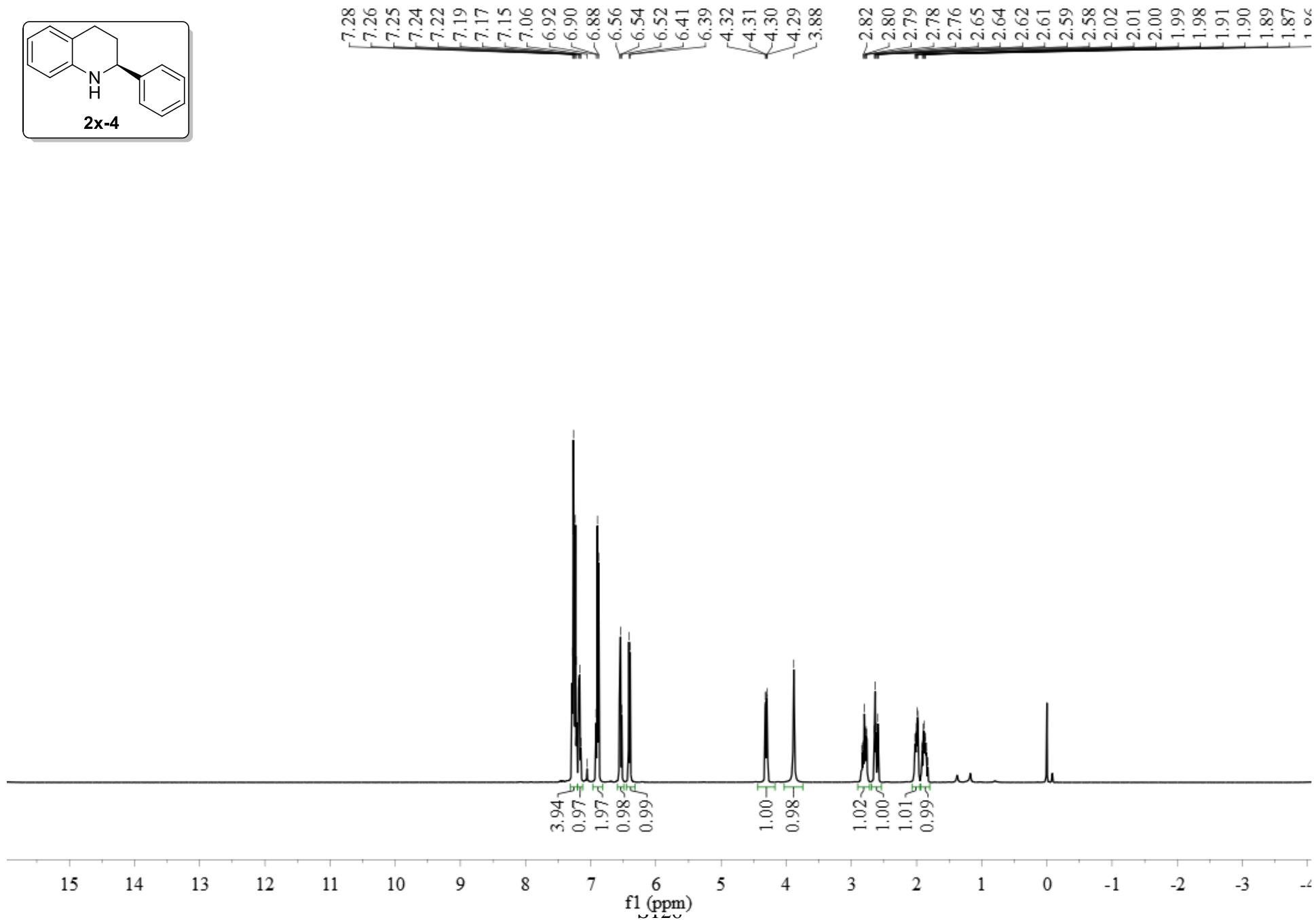
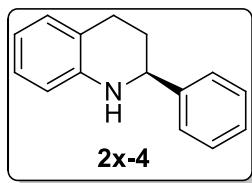


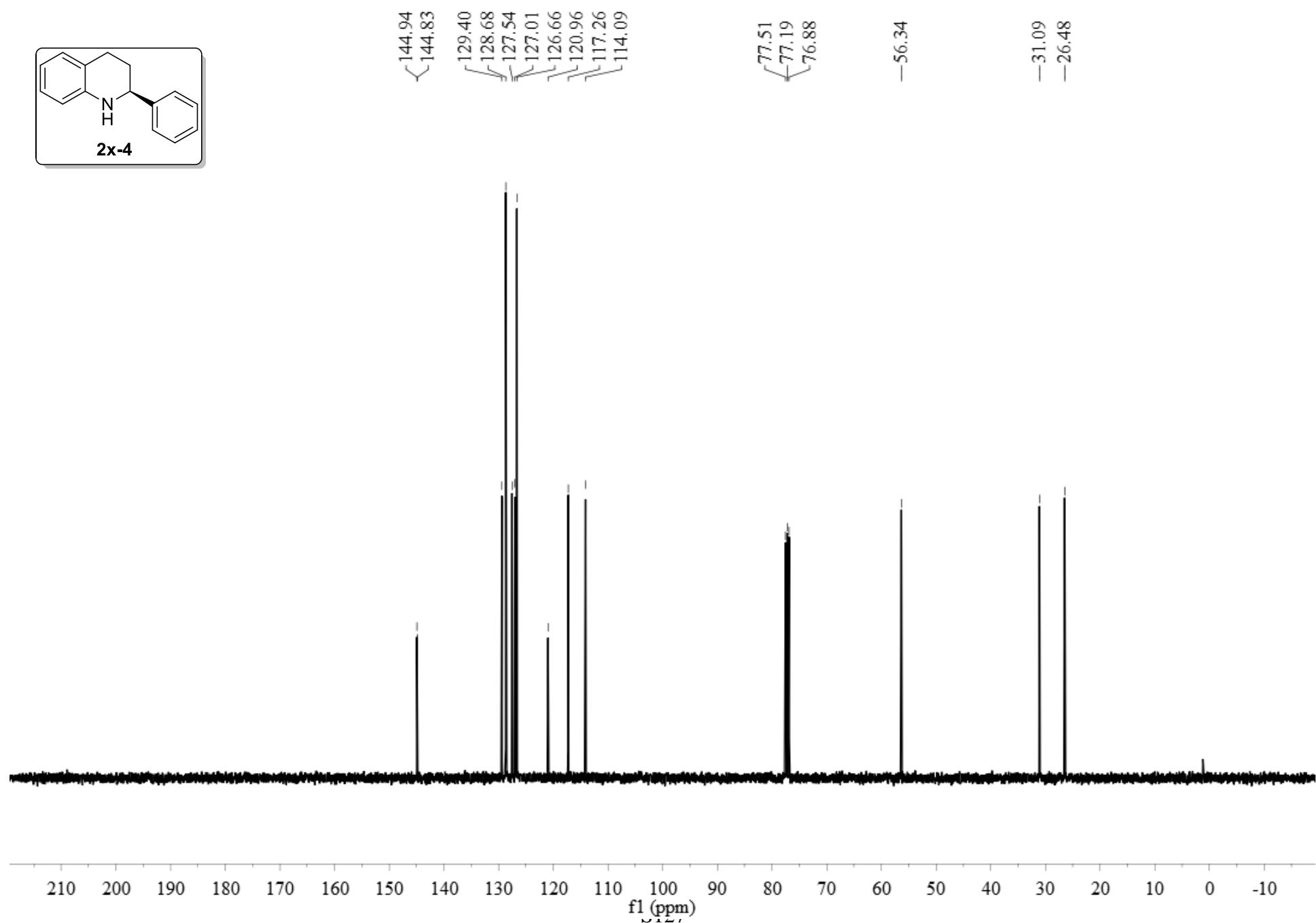
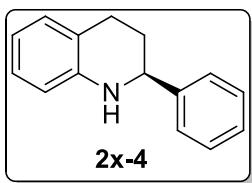


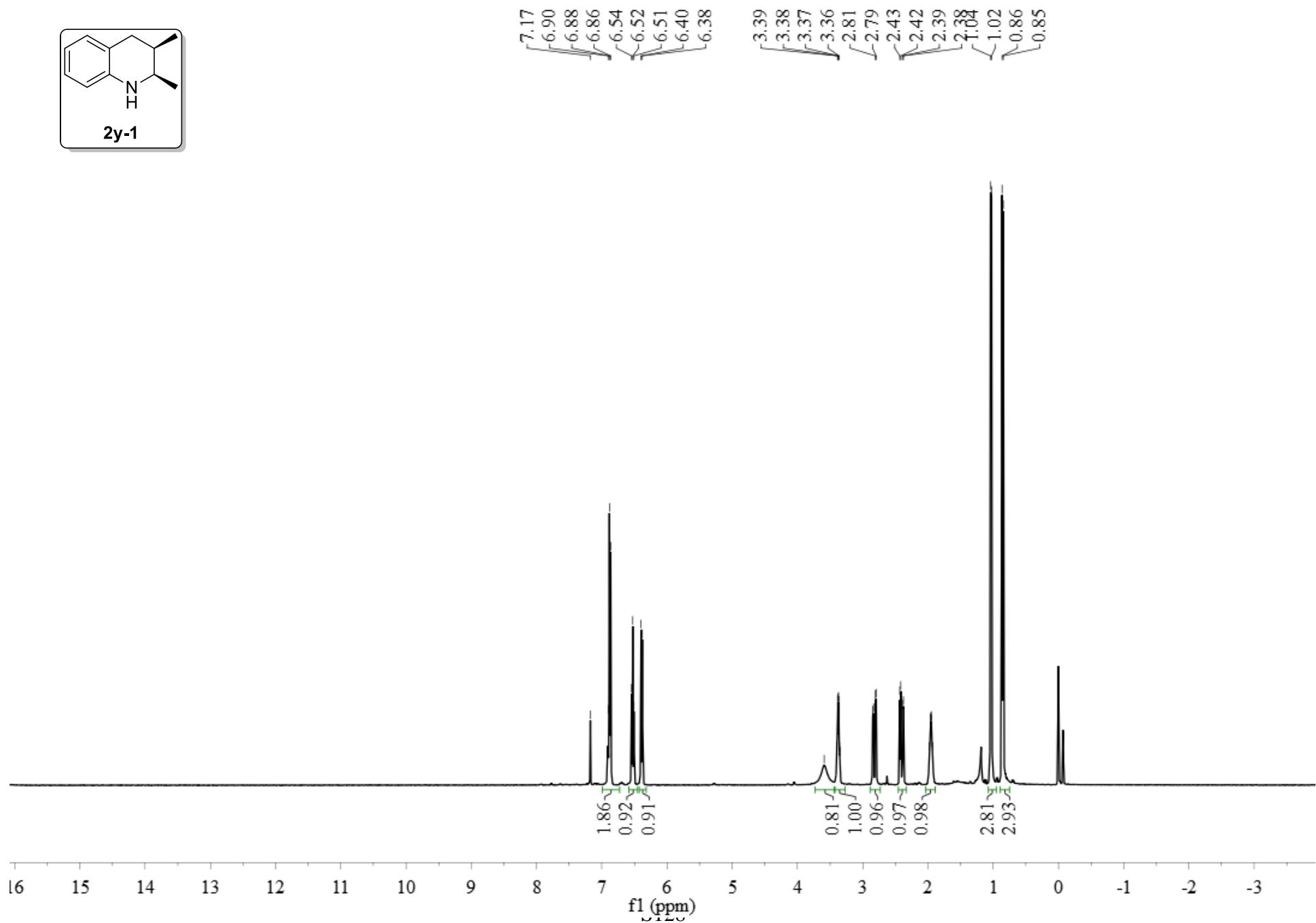
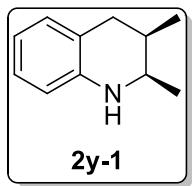


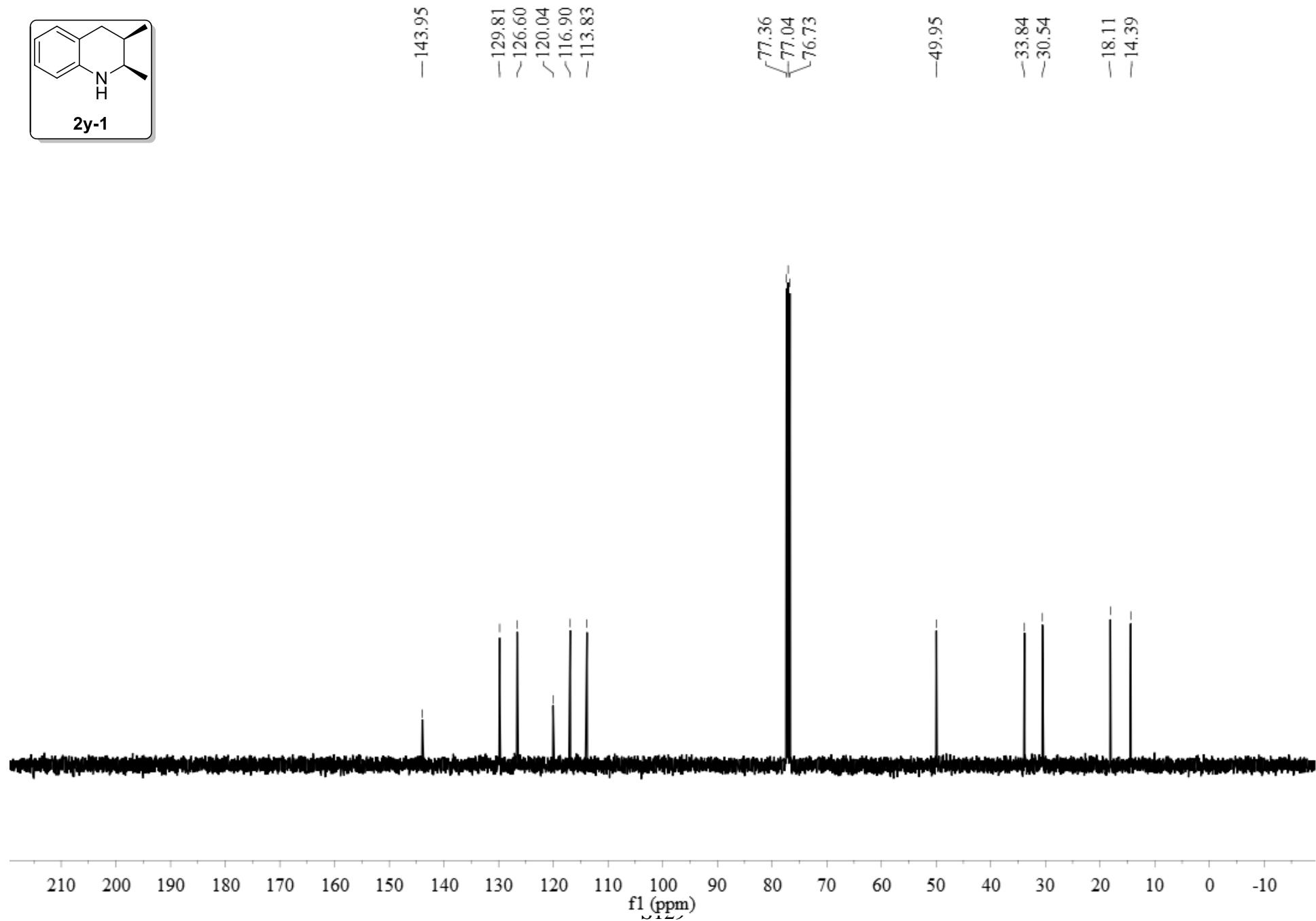
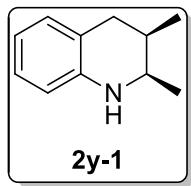


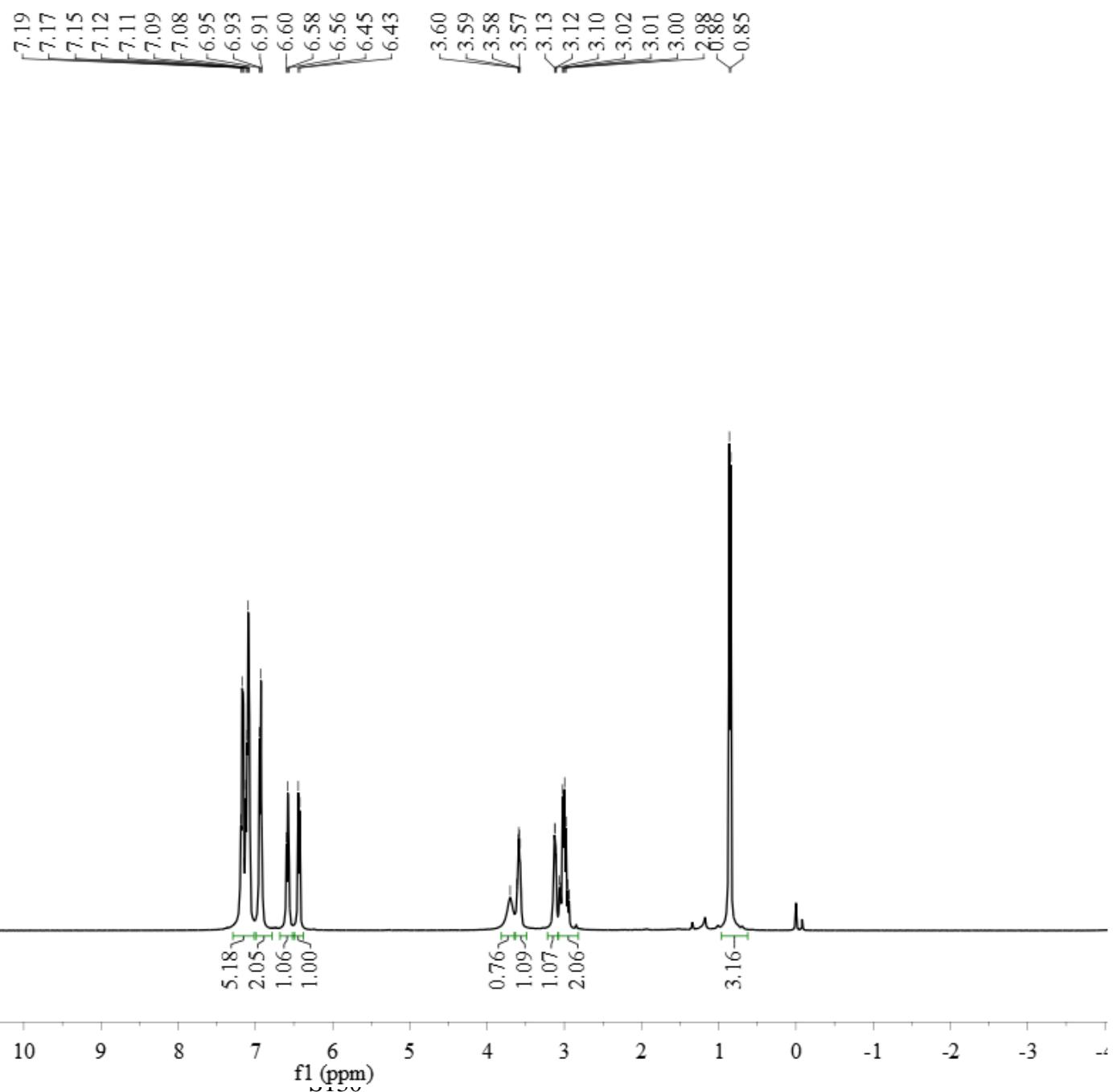
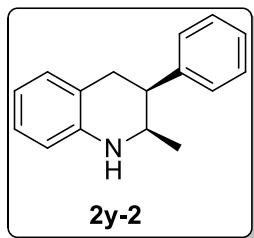


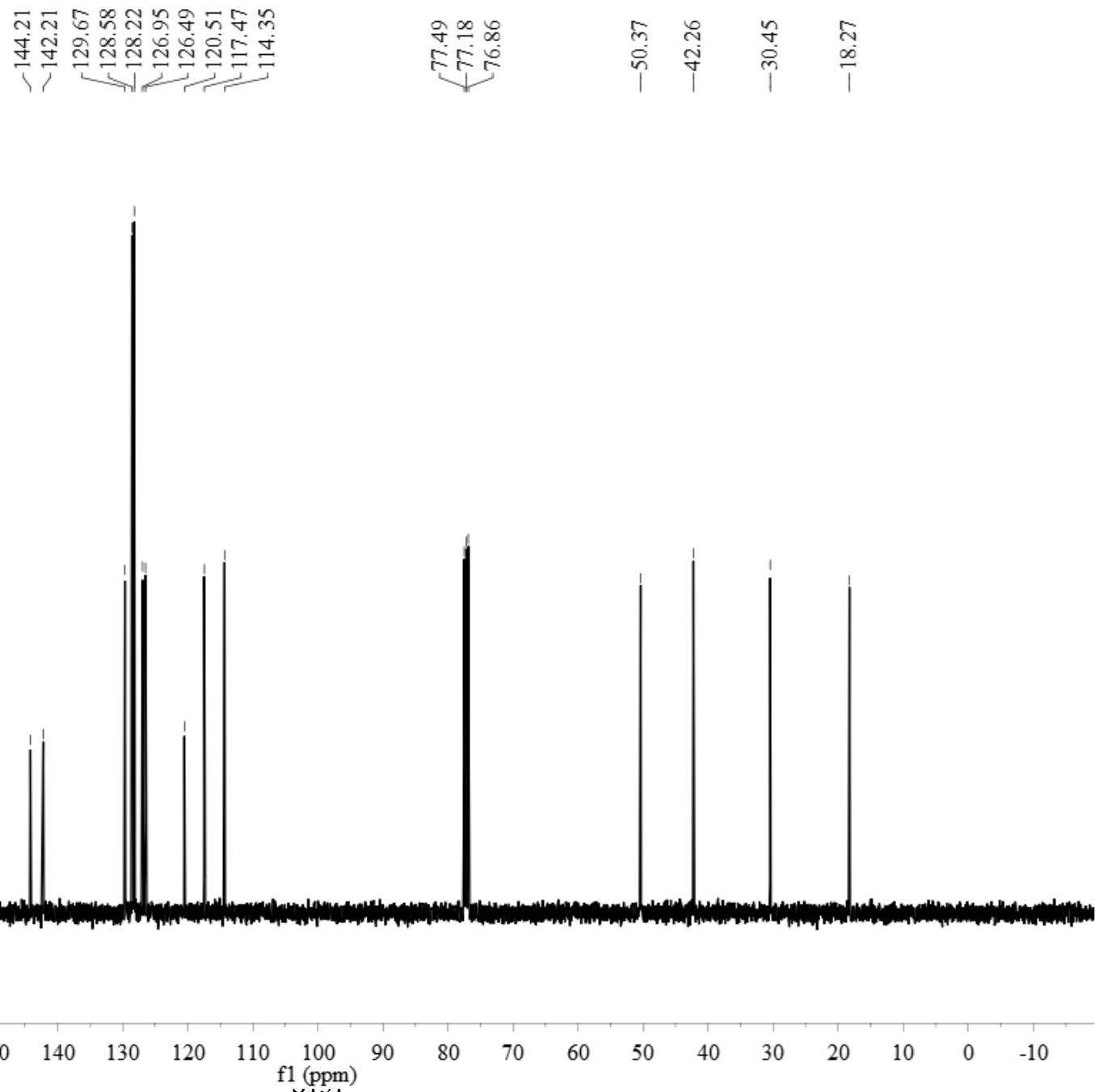
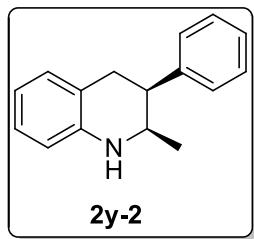


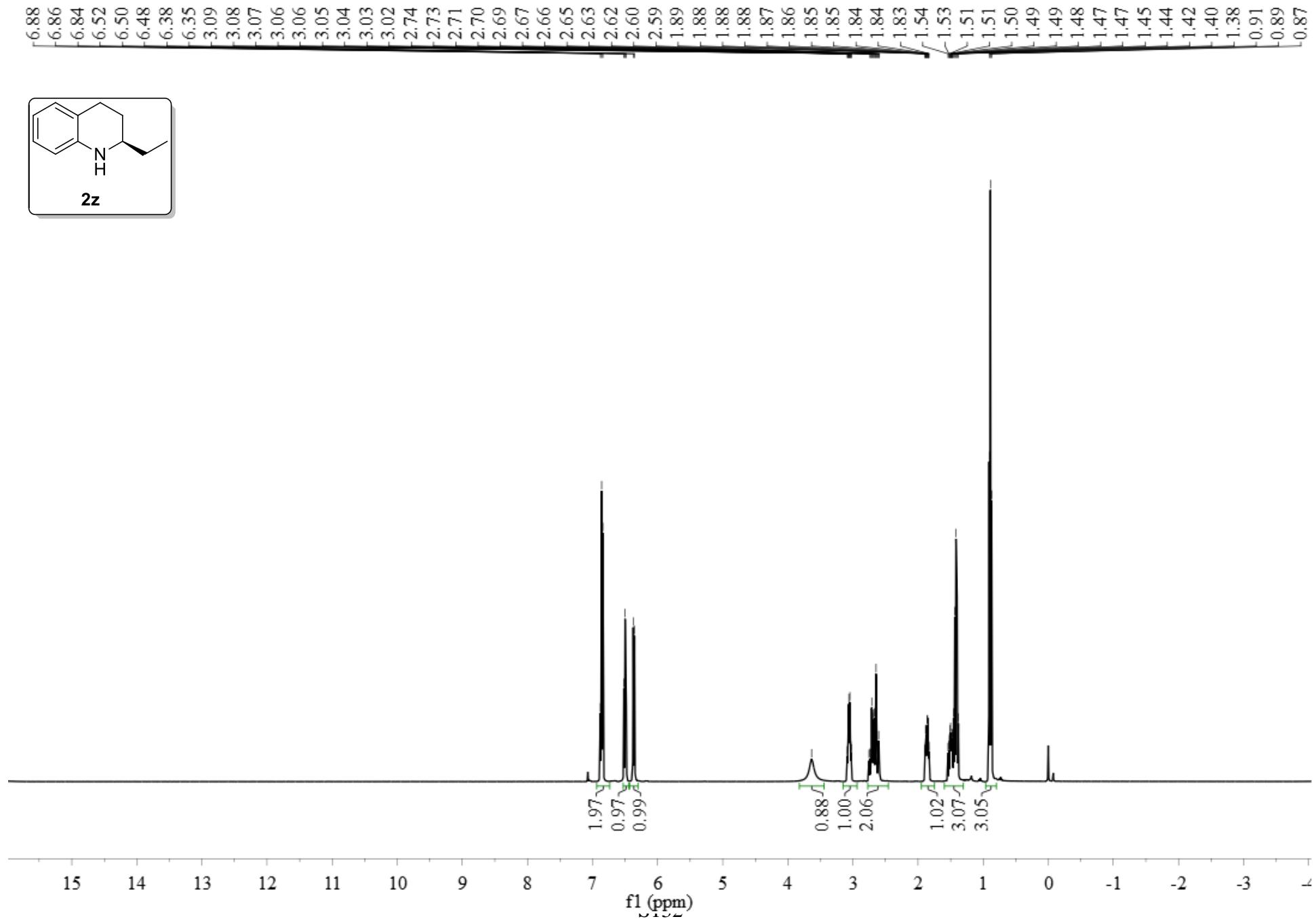


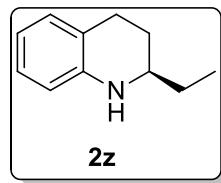












—144.85

—129.32  
~126.80  
—121.45  
~116.95  
~114.11

77.53  
77.21  
76.89

—53.12

29.50  
—27.68  
~26.53

—10.16

