

# ***p*-Toluenesulfonic acid catalysed fluorination of $\alpha$ -branched ketones for the construction of fluorinated quaternary carbon centres**

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## 1. General Information

NMR spectra were recorded on a Bruker Avance III 400 MHz NMR Spectrometer or a Varian INOVA 600MHz spectrometer. Chemical shifts of  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR were recorded in parts per million (ppm,  $\delta$ ) and reported relative to tetramethylsilane (TMS, 0.00 ppm) and  $\text{CDCl}_3$  (77.00 ppm), respectively.  $^1\text{H}$  NMR splitting patterns are designated as single (s), double (d), triplet (t), quartet (q), double of doublets (dd), doublet of triplets (dt), triplet of doublets (td), and multiplets (m). Electron ionization mass (EI-MS) spectra were measured on a Shimadzu GCMSQP2010SE spectrometer by direct inlet at 70 eV and the corresponding signals were given in  $m/z$  with relative intensity (%) in brackets. High-resolution mass spectra (HRMS) were measured on a Thermo Scientific Orbitrap Elite Mass Spectrometer by means of the ESI technique. Melting points were determined on a microscopic apparatus and were uncorrected. Optical rotations were detected on RUDOLPH A21202-J APTV/GW using a 0.1 mL cell with 1-cm path length.

Analytical TLC was performed on silica gel GF<sub>254</sub> plates, and the spots were visualized using UV light (254 nm) or phosphomolybdic acid in ethanol (10%). The products were purified by flash column chromatography on silica gel (200-300 mesh).

Unless otherwise noted, commercial reagents were purchased and used directly. The *p*-toluenesulfonic acid was further purified by recrystallization from ethanol. Acetonitrile was purchased from Innochem (extra dry over molecular sieves) and used directly. Dichloromethane (DCM), 1,2-dichloroethane (DCE) and chloroform ( $\text{CHCl}_3$ ) were purified by distillation over the  $\text{CaH}_2$  indicated. Tetrahydrofuran (THF) and toluene were purified by distillation over the Na indicated. All reactions were carried out under argon atmosphere.

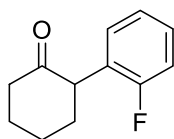
## 2. Preparation of substrates

Substrates **2a**, **2n**, **2q**, **2x**, **2y**, **2aa**, **2ab**, **2ac**, **2ae**, **2af**, **2ag**, and **2ah** were commercial available (**2n** and **2q** were purified by flash column chromatography on silica gel before use). Substrates **2b**, **2c**, **2d**, **2e**, **2f**, **2g**, **2h**, **2i**, **2k**, **2l**, **2m**, **2p**, **2r**, **2ai**, **2aj**, and **2ak** were synthesized according to the literature<sup>1-10</sup> (Method I). Substrate **2w** was synthesized according to the literature<sup>1,5</sup> (Method II). The procedures for the preparation of substrates **2j**, **2o**, **2s**, **2u**, and **2v** were followed as the literature method.<sup>11</sup> Substrates **2t** was prepared according to the literature method.<sup>7,8,12,13</sup> Substrate **2z** was

prepared according to the literature method.<sup>14</sup> Substrate **2ad** was prepared according to the literature method.<sup>15</sup> Substrates **4** and **5** were prepared according to the literature method.<sup>5</sup>

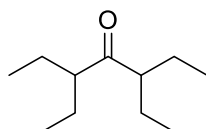
The <sup>1</sup>H NMR spectra data of **2c**,<sup>16</sup> **2d**,<sup>17</sup> **2e**,<sup>18</sup> **2f**,<sup>19</sup> **2g**,<sup>17,19</sup> **2h**,<sup>17,20</sup> **2i**,<sup>17</sup> **2j**,<sup>11</sup> **2k**,<sup>17,19</sup> **2l**,<sup>19</sup> **2m**,<sup>21</sup> **2o**,<sup>11</sup> **2p**,<sup>17,20</sup> **2r**,<sup>19,22</sup> **2s**,<sup>11</sup> **2t**,<sup>7</sup> **2u**,<sup>11</sup> **2v**,<sup>11</sup> **2w**,<sup>20</sup> **2z**<sup>23</sup> are in accordance with the literature, respectively. The NMR and MS spectra data of other substrates (**2b**, **4**, and **5**) are listed below:

#### 2-(2-fluorophenyl)cyclohexan-1-one (**2b**)



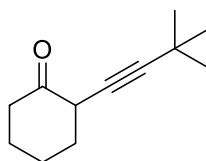
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.27-7.22 (m, 1 H), 7.19-7.10 (m, 2 H), 7.07-7.02 (m, 1 H), 3.85 (dd,  $J$  = 12.8 Hz, 5.2 Hz, 1 H), 2.59-2.46 (m, 2 H), 2.29-2.16 (m, 2 H), 2.08-1.98 (m, 2 H), 1.89-1.77 (m, 2 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  208.4 (s), 160.6 (d,  $J$  = 243 Hz), 129.6 (d,  $J$  = 5 Hz), 128.5 (d,  $J$  = 9 Hz), 126.0 (d,  $J$  = 15 Hz), 123.9 (d,  $J$  = 4 Hz), 115.2 (d,  $J$  = 22 Hz), 51.0 (s), 42.1 (s), 33.6 (s), 27.4 (s), 25.5 (s); **MS** (EI)  $m/z$  (%): 192 (19), 148 (100), 135 (42), 122 (46), 109 (34).

#### 3,5-diethylheptan-4-one (**2ad**)



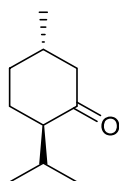
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.45-2.39 (m, 2 H), 1.71-1.60 (m, 4 H), 1.45-1.34 (m, 4 H), 0.86 (t,  $J$  = 7.6 Hz, 12 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  216.4, 54.1, 23.0, 11.7; **HRMS** (ESI)  $m/z$  calculated for C<sub>11</sub>H<sub>23</sub>O [M+H]<sup>+</sup> 171.1743, found 171.1747; **MS** (EI)  $m/z$  (%): 170 (4), 99 (32), 84 (16), 71 (100).

#### 2-(3,3-dimethylbut-1-yn-1-yl)cyclohexan-1-one (**2aj**)



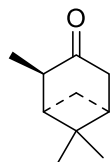
**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  3.25-3.23 (m, 1 H), 2.74-2.70 (m, 1 H), 2.25-2.20 (m, 1 H), 2.03-1.87 (m, 4 H), 1.83-1.76 (m, 1 H), 1.69-1.61 (m, 1 H), 1.22 (s, 9 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  207.8, 94.0, 75.4, 43.9, 39.4, 34.6, 31.1, 27.6, 27.5, 22.6; **HRMS** (ESI)  $m/z$  calculated for C<sub>12</sub>H<sub>19</sub>O [M+H]<sup>+</sup> 179.1430, found 179.1432; **MS** (EI)  $m/z$  (%): 178 (8), 163 (21), 109 (25), 97 (17), 81 (27), 57 (100).

**(2R, 5S)-2-isopropyl-5-methylcyclohexan-1-one (4)**



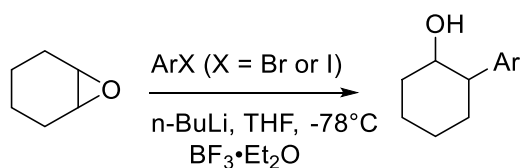
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.37-2.33 (m, 1 H), 2.17-2.12 (m, 1 H), 2.10-2.02 (m, 2 H), 1.97 (d,  $J$  = 12.8 Hz, 1 H), 1.92-1.81 (m, 2 H), 1.41-1.33 (m, 2 H), 1.01 (d,  $J$  = 6.0 Hz, 3 H), 0.91 (d,  $J$  = 6.8 Hz, 3 H), 0.85 (d,  $J$  = 6.8 Hz, 3 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  212.2, 55.8, 50.8, 35.4, 33.8, 27.8, 25.8, 22.2, 21.1, 18.6; **MS** (EI)  $m/z$  (%): 154 (1), 112 (7), 69 (58), 57 (100).

**(1R, 2R, 5S)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one (5)**

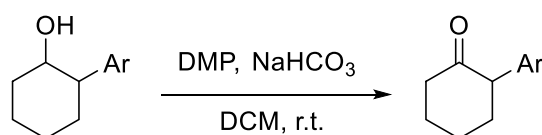


**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  2.66-2.61 (m, 2 H), 2.52 (d,  $J$  = 19.2 Hz, 1 H), 2.46 (q,  $J$  = 7.2 Hz, 1 H), 2.14-2.11 (m, 1 H), 2.06 (td,  $J$  = 6.0 Hz, 1.2 Hz, 1 H), 1.32 (s, 3 H), 1.22-1.19 (m, 1 H), 1.21 (d,  $J$  = 6.0 Hz, 3 H), 0.88 (s, 3 H). **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>):  $\delta$  214.6, 51.2, 45.0, 44.6, 39.1, 39.0, 34.3, 26.9, 21.8, 16.7; **MS** (EI)  $m/z$  (%): 152 (4), 69 (73), 57 (66), 55 (100).

**The preparation of substrates (Method I):**

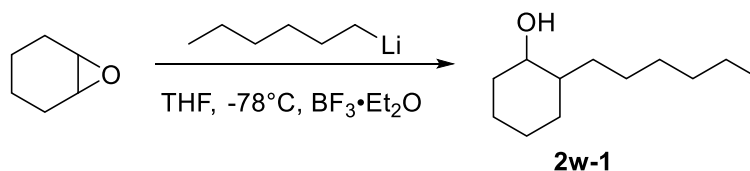


To a solution of ArBr (10 mmol) (or ArI, 10 mmol) in dried THF (40 mL) was added *n*-BuLi dropwise (4.0 mL, 2.5 M in hexane, 10 mmol) at -78 °C under argon atmosphere,, and the resulting mixture was stirred at this temperature for 1 h. Then cyclohexene oxide (5 mmol) was added dropwise to the mixture at -78 °C, followed by addition of BF<sub>3</sub>·Et<sub>2</sub>O (10 mmol) dropwise. The reaction mixture was stirred at this temperature until the consumption of starting material (monitored by TLC), then the reaction was quenched by addition of saturated aqueous NaHCO<sub>3</sub> at -78°C and was allowed to warm to room temperature. The mixture was extracted with ethyl acetate, and the combined organic phase was washed successively with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to provide the desired alcohol.



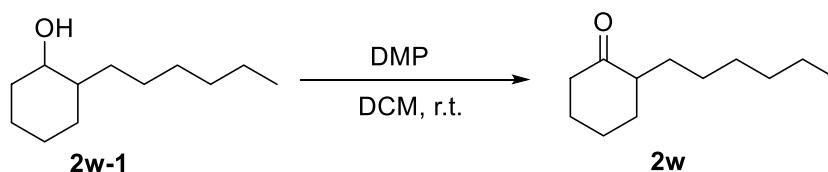
To a stirred solution of alcohol (1.0 equiv.) in DCM were added NaHCO<sub>3</sub> (4.0 eq) and Dess-Martin periodinane (DMP) (2.0 equiv). The reaction mixture was stirred at room temperature until the consumption of starting material (monitored by TLC). The reaction was quenched by addition of saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, then the mixture was extracted with DCM (3×50 mL). The combined organic phase was washed successively with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the expected ketone.

**The preparation of substrate (Method II):**



To a solution of cyclohexene oxide (5 mmol) in THF (30 mL) was added *n*-hexyllithium (4.0 mL, 2.0 M in hexane, 8 mmol) dropwise at -78 °C under an argon atmosphere, then BF<sub>3</sub>·Et<sub>2</sub>O (8 mmol)

was added dropwise. The reaction mixture was stirred at that temperature until the starting material disappeared (monitored by TLC). The reaction was quenched at -78 °C by addition of saturated aqueous NaHCO<sub>3</sub> and was allowed to warm to room temperature. The mixture was extracted with ethyl acetate, and the combined organic phases were washed successively with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to provide the desired alcohol **2w-1**.



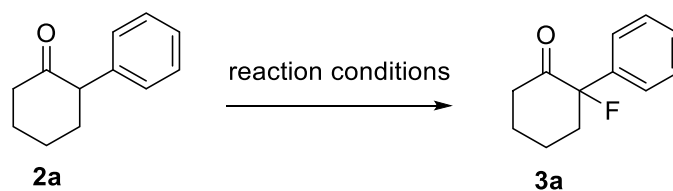
To a solution of alcohol **2w-1** (245.2 mg, 1.33 mmol) in 20 mL DCM was added Dess-Martin periodinane (DMP) (1.128 g, 2.66 mmol). The reaction mixture was stirred at room temperature until the starting material disappeared (monitored by TLC). The reaction was quenched by addition of saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, then the mixture was extracted with DCM, and the combined organic phases were washed successively with water and brine, then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford ketone **2w**.

### 3. Experimental details and characterization data

#### 3.1 General procedure

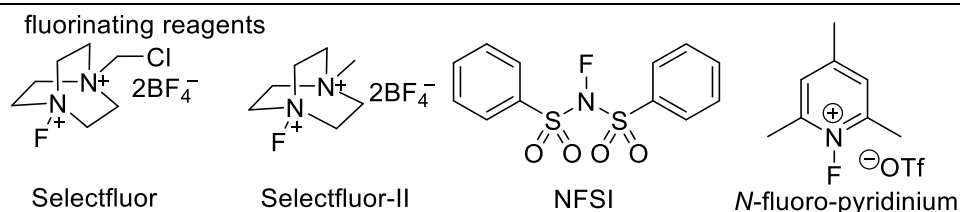
Under argon atmosphere, to a 10 mL reaction tube charged with a magnetic stir bar were added sequentially ketones (0.20 mmol), Selectfluor (0.40 mmol, 141.8 mg), *p*-TsOH (0.04 mmol, 7.6 mg), CH<sub>2</sub>Cl<sub>2</sub> (0.2 mL) and CH<sub>3</sub>CN (0.8 mL). The reaction mixture was stirred at 25 °C until the complete consumption of starting material (monitored by TLC), and the mixture was diluted with ethyl acetate. The resulting organic phase was washed successively with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the fluorinated ketone.

### 3.2 The details for the optimal reaction conditions <sup>a</sup>



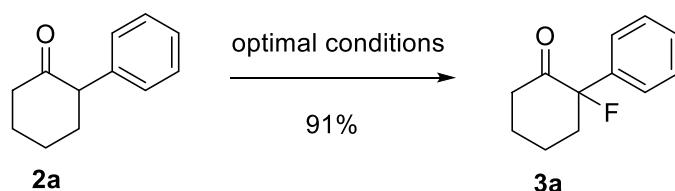
| Entry             | F Reagent (eq)                 | Acid                                       | Solvent (1.0 mL)                                           | Time  | Temp         | Yield (%) <sup>b</sup> | Recovery (%) <sup>c</sup> |
|-------------------|--------------------------------|--------------------------------------------|------------------------------------------------------------|-------|--------------|------------------------|---------------------------|
| 1                 | Selectfluor (2.0) <sup>d</sup> | <i>p</i> -TsOH (20%) <sup>e</sup>          | <b>DCM</b>                                                 | 48 h  | 25 °C        | 18                     | 69                        |
| 2                 | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>DCE</b>                                                 | 48 h  | 25 °C        | 23                     | 66                        |
| 3                 | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>DMSO</b>                                                | 48 h  | 25 °C        | 0                      | 95                        |
| 4                 | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>DME</b>                                                 | 48 h  | 25 °C        | 30                     | 69                        |
| 5                 | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>1,4-Dioxane</b>                                         | 48 h  | 25 °C        | 23                     | 45                        |
| 6                 | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>CHCl<sub>3</sub></b>                                    | 48 h  | 25 °C        | 11                     | 84                        |
| 7 <sup>h</sup>    | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>DMF</b>                                                 | 48 h  | 25 °C        | 47                     | 32                        |
| 8                 | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>THF</b>                                                 | 48 h  | 25 °C        | 18                     | 77                        |
| 9                 | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>Hexane</b>                                              | 48 h  | 25 °C        | 37                     | 36                        |
| 10 <sup>f</sup>   | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>NMP</b>                                                 | 48 h  | 25 °C        | 45                     | 37                        |
| 11 <sup>f</sup>   | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>CH<sub>3</sub>NO<sub>2</sub></b>                        | 12 h  | 25 °C        | 71                     | 0                         |
| 12                | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>Toluene</b>                                             | 48 h  | 25 °C        | 20                     | 71                        |
| 13 <sup>f</sup>   | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>H<sub>2</sub>O</b>                                      | 48 h  | 25 °C        | 0                      | 92                        |
| 14 <sup>f</sup>   | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>CH<sub>3</sub>CN</b>                                    | 9 h   | 25 °C        | 82                     | 0                         |
| 15 <sup>f</sup>   | Selectfluor (2.0)              | <b>H<sub>2</sub>SO<sub>4</sub> (20%)</b>   | CH <sub>3</sub> CN                                         | 12 h  | 25 °C        | 78                     | 0                         |
| 16                | Selectfluor (2.0)              | <b>HCl (20%)</b>                           | CH <sub>3</sub> CN                                         | 12 h  | 25 °C        | 79                     | 0                         |
| 17 <sup>f</sup>   | Selectfluor (2.0)              | <b>HBF<sub>4</sub> (20%)</b>               | CH <sub>3</sub> CN                                         | 24 h  | 25 °C        | 77                     | 0                         |
| 18 <sup>f</sup>   | Selectfluor (2.0)              | <b>H<sub>3</sub>PO<sub>4</sub> (20%)</b>   | CH <sub>3</sub> CN                                         | 48 h  | 25 °C        | 37                     | 56                        |
| 19 <sup>f</sup>   | Selectfluor (2.0)              | <b>CF<sub>3</sub>SO<sub>3</sub>H (20%)</b> | CH <sub>3</sub> CN                                         | 24 h  | 25 °C        | 76                     | 0                         |
| 20                | Selectfluor (2.0)              | -                                          | CH <sub>3</sub> CN                                         | 48 h  | 25 °C        | 0                      | 95                        |
| 21                | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>CH<sub>3</sub>CN:DMSO (4:1)</b>                         | 48 h  | 25 °C        | 0                      | 84                        |
| 22 <sup>f</sup>   | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>CH<sub>3</sub>CN:THF (4:1)</b>                          | 24 h  | 25 °C        | 82                     | 0                         |
| 23 <sup>f</sup>   | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>CH<sub>3</sub>CN:Hexane (4:1)</b>                       | 12 h  | 25 °C        | 80                     | 0                         |
| 24 <sup>f</sup>   | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>CH<sub>3</sub>CN:DMF (4:1)</b>                          | 48 h  | 25 °C        | 51                     | 30                        |
| 25 <sup>f</sup>   | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>CH<sub>3</sub>CN:H<sub>2</sub>O (4:1)</b>               | 48 h  | 25 °C        | 26                     | 73                        |
| 26 <sup>f</sup>   | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>CH<sub>3</sub>CN:DME (4:1)</b>                          | 24 h  | 25 °C        | 84                     | 0                         |
| 27                | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>CH<sub>3</sub>CN:CH<sub>2</sub>Cl<sub>2</sub> (4:1)</b> | 12 h  | 25 °C        | 84                     | 0                         |
| 28                | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | CH <sub>3</sub> CN:CH <sub>2</sub> Cl <sub>2</sub> (4:1)   | 120 h | <b>0 °C</b>  | 82                     | 0                         |
| 29 <sup>f,g</sup> | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | CH <sub>3</sub> CN:CH <sub>2</sub> Cl <sub>2</sub> (4:1)   | 12 h  | <b>40 °C</b> | 74                     | 0                         |
| 30 <sup>f,g</sup> | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | CH <sub>3</sub> CN:CH <sub>2</sub> Cl <sub>2</sub> (4:1)   | 12 h  | <b>60 °C</b> | 45                     | 0                         |
| 31 <sup>f</sup>   | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>CH<sub>3</sub>CN:CH<sub>2</sub>Cl<sub>2</sub> (9:1)</b> | 12 h  | 25 °C        | 84                     | 0                         |
| 32                | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>CH<sub>3</sub>CN:CH<sub>2</sub>Cl<sub>2</sub> (7:3)</b> | 20 h  | 25 °C        | 83                     | 0                         |
| 33                | Selectfluor (2.0)              | <i>p</i> -TsOH (20%)                       | <b>CH<sub>3</sub>CN:CH<sub>2</sub>Cl<sub>2</sub> (3:2)</b> | 24 h  | 25 °C        | 83                     | 0                         |

|                 |                                                     |                      |                                                          |       |       |    |    |
|-----------------|-----------------------------------------------------|----------------------|----------------------------------------------------------|-------|-------|----|----|
| 34 <sup>f</sup> | Selectfluor (2.0)                                   | <i>p</i> -TsOH (10%) | CH <sub>3</sub> CN:CH <sub>2</sub> Cl <sub>2</sub> (4:1) | 24 h  | 25 °C | 83 | 0  |
| 35 <sup>f</sup> | Selectfluor (2.0)                                   | <i>p</i> -TsOH (5%)  | CH <sub>3</sub> CN:CH <sub>2</sub> Cl <sub>2</sub> (4:1) | 120 h | 25 °C | 82 | 0  |
| 36              | <b>Selectfluor (1.0)</b>                            | <i>p</i> -TsOH (20%) | CH <sub>3</sub> CN:CH <sub>2</sub> Cl <sub>2</sub> (4:1) | 24 h  | 25 °C | 74 | 0  |
| 37              | <b>Selectfluor (1.5)</b>                            | <i>p</i> -TsOH (20%) | CH <sub>3</sub> CN:CH <sub>2</sub> Cl <sub>2</sub> (4:1) | 12 h  | 25 °C | 78 | 0  |
| 38              | <b>Selectfluor (2.5)</b>                            | <i>p</i> -TsOH (20%) | CH <sub>3</sub> CN:CH <sub>2</sub> Cl <sub>2</sub> (4:1) | 12 h  | 25 °C | 85 | 0  |
| 39              | <b>Selectfluor II (2.0)<sup>h</sup></b>             | <i>p</i> -TsOH (20%) | CH <sub>3</sub> CN:CH <sub>2</sub> Cl <sub>2</sub> (4:1) | 12 h  | 25 °C | 80 | 0  |
| 40              | <b>NFSI (2.0)<sup>i</sup></b>                       | <i>p</i> -TsOH (20%) | CH <sub>3</sub> CN:CH <sub>2</sub> Cl <sub>2</sub> (4:1) | 48 h  | 25 °C | 23 | 71 |
| 41              | <b><i>N</i>-fluoro-pyridinium (2.0)<sup>j</sup></b> | <i>p</i> -TsOH (20%) | CH <sub>3</sub> CN:CH <sub>2</sub> Cl <sub>2</sub> (4:1) | 48 h  | 25 °C | 0  | 97 |

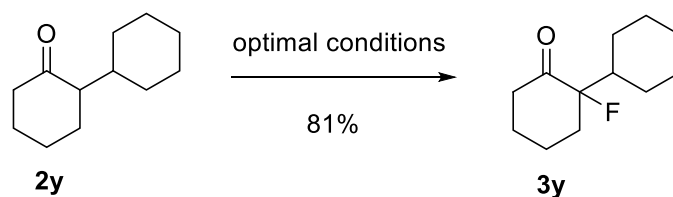


a) Reaction was performed using 2-phenylcyclohexan-1-one (0.2 mmol) in 1.0 mL solvent at noted temperature under an argon atmosphere; b) isolated yield; c) recovery yield of 2-phenylcyclohexan-1-one; d) Selectfluor = 1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) e) *p*-TsOH = *p*-Toluenesulfonic acid; f) The isolated product contains trace unknown impurities; g) The reaction was performed under the sealed tube; h) Selectfluor II = 1-Fluoro-4-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate); i) NFSI = *N*-Fluorobenzenesulfonimide; j) *N*-fluoro-pyridinium = 1-Fluoro-2,4,6-trimethylpyridinium trifluoromethanesulfonate.

### 3.3 Synthesis of products on 1 g-scale



To a 100 mL reaction tube charged with a magnetic stir bar were added sequentially 2-phenylcyclohexan-1-one (5.74 mmol, 1.0 g), Selectfluor (11.48 mmol, 4.07g), *p*-TsOH (1.15 mmol, 218.8 mg), CH<sub>2</sub>Cl<sub>2</sub> (5.7 mL) and CH<sub>3</sub>CN (23.0 mL) under an argon atmosphere. The reaction mixture was stirred at 25 °C until the complete consumption of starting material (monitored by TLC), and the mixture was diluted with ethyl acetate. The resulting organic phase was washed successively with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford compound **3a** (998.5 mg, 91% yield.).



To a 100 mL reaction tube charged with a magnetic stir-bar were added sequentially, [1,1'-bi(cyclohexan)]-2-one (5.55 mmol, 1.0 g), Selectfluor (11.10 mmol, 3.93 g), *p*-TsOH (1.11 mmol, 211.1 mg), CH<sub>2</sub>Cl<sub>2</sub> (5.6 mL) and CH<sub>3</sub>CN (22.2 mL) under an argon atmosphere,. The reaction mixture was stirred at 25 °C until the complete consumption of starting material (monitored by TLC), and the mixture was diluted with ethyl acetate. The resulting organic phase was washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford compound **3y** (891.6 mg, 81% yield.).

### 3.4 Synthesis of fluorinated non-quaternary carbon products

These products (**6a-6f**) were obtained in lower to moderate yield with relatively lower chemical conversion under the optimal reaction conditions. For the details, please see Figure S1.

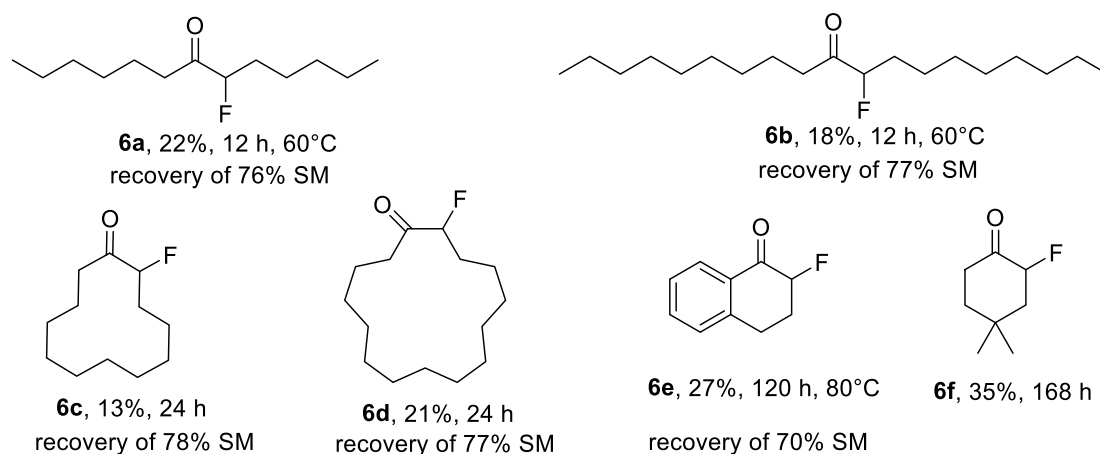
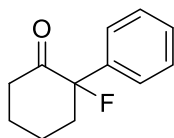


Figure S1 Some fluorinated non-quaternary carbon products.

### 3.5 Characterization data of products

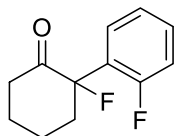
#### 2-fluoro-2-phenylcyclohexan-1-one (3a)<sup>7</sup>



Prepared by the general procedure at 25 °C for 12 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as colorless oil (32.3 mg, 84% yield.).

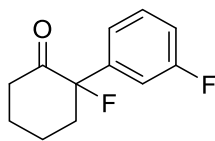
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.45-7.38 (m, 5 H), 2.77-2.60 (m, 2 H), 2.44-2.37 (m, 1 H), 2.35-2.25 (m, 1 H), 2.08-2.03 (m, 1 H), 1.98-1.92 (m, 2 H), 1.85-1.79 (m, 1 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  206.4 (d,  $J$  = 22 Hz), 135.9 (d,  $J$  = 21 Hz), 129.1 (d,  $J$  = 2 Hz), 128.6 (s), 126.3 (d,  $J$  = 6 Hz), 98.2 (d,  $J$  = 183 Hz), 39.9 (s), 37.7 (d,  $J$  = 22 Hz), 27.5 (s), 22.2 (d,  $J$  = 7 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -141.29; **MS** (EI)  $m/z$  (%): 192 (29), 148 (86), 135 (100), 122 (37).

#### 2-fluoro-2-(2-fluorophenyl)cyclohexan-1-one (3b)



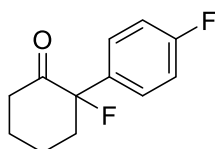
Prepared by the general procedure at 25 °C for 36 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as white foam (37.6 mg, 89% yield.).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.45 (td,  $J$  = 7.6 Hz, 1.6 Hz, 1 H), 7.39-7.34 (m, 1 H), 7.20 (td,  $J$  = 7.6 Hz, 0.8 Hz, 1 H), 7.11-7.06 (m, 1 H), 2.92-2.83 (m, 1 H), 2.61-2.44 (m, 2 H), 2.41-2.31 (m, 1 H), 2.13-2.01 (m, 2 H), 1.92-1.75 (m, 2 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  203.4 (d,  $J$  = 23 Hz), 159.6 (dd,  $J$  = 247 Hz, 5 Hz), 130.5 (d,  $J$  = 9 Hz), 126.7 (dd,  $J$  = 11 Hz, 3 Hz), 124.9 (q,  $J$  = 12 Hz), 124.1 (d,  $J$  = 3 Hz), 116.0 (d,  $J$  = 22 Hz), 96.8 (dd,  $J$  = 181 Hz, 4 Hz), 39.1 (s), 37.8 (dd,  $J$  = 23 Hz, 3 Hz), 27.0 (s), 20.9 (d,  $J$  = 4 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -110.47 (d,  $J$  = 2.63 Hz), -154.31 (d,  $J$  = 3.00 Hz); **HRMS** (ESI)  $m/z$  calculated for C<sub>12</sub>H<sub>12</sub>F<sub>2</sub>ONa [M+Na]<sup>+</sup> 233.0748, found 233.0750; **MS** (EI)  $m/z$  (%): 210 (24), 166 (75), 153 (75), 140 (100), 127 (25), 55 (19).

**2-fluoro-2-(3-fluorophenyl)cyclohexan-1-one (3c)**

Prepared by the general procedure at 25 °C for 18 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as colorless oil (36.3 mg, 86 % yield.).

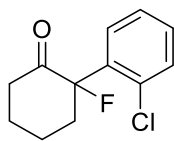
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.39 (dd, *J* = 14 Hz, 8 Hz, 1 H), 7.16-7.06 (m, 3 H), 2.87-2.79 (m, 1 H), 2.55-2.29 (m, 3 H), 2.14-1.98 (m, 2 H), 1.97-1.77 (m, 2 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 205.6 (d, *J* = 23 Hz), 162.7 (d, *J* = 245 Hz), 138.8 (dd, *J* = 22 Hz, 7 Hz), 130.1 (d, *J* = 8 Hz), 121.9 (q, *J* = 3 Hz), 115.8 (d, *J* = 21 Hz), 113.4 (dd, *J* = 24 Hz, 8 Hz), 97.7 (d, *J* = 184 Hz), 39.6 (s), 38.4 (d, *J* = 23 Hz), 27.4 (s), 21.7 (d, *J* = 6 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): δ -112.11, -146.16; **HRMS** (ESI) *m/z* calculated for C<sub>12</sub>H<sub>12</sub>F<sub>2</sub>ONa [M+Na]<sup>+</sup> 233.0748, found 233.0744; **MS** (EI) *m/z* (%): 210 (27), 166 (100), 153 (73), 140 (73), 127 (33), 55 (49).

**2-fluoro-2-(4-fluorophenyl)cyclohexan-1-one (3d)**

Prepared by the general procedure at 25 °C for 18 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as colorless oil (32.5 mg, 77% yield.).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.39-7.35 (m, 2 H), 7.11 (t, *J* = 8.4 Hz, 2 H), 2.83-2.75 (m, 1 H), 2.62-2.49 (m, 1 H), 2.43-2.27 (m, 2 H), 2.12-2.03 (m, 1 H), 2.01-1.87 (m, 2 H), 1.83-1.75 (m, 1 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 206.1 (d, *J* = 22 Hz), 162.9 (dd, *J* = 247 Hz, 3 Hz), 132.0 (dd, *J* = 22 Hz, 3 Hz), 128.3 (dd, *J* = 8 Hz, 6 Hz), 115.5 (d, *J* = 21 Hz), 97.8 (d, *J* = 182 Hz), 39.7 (s), 38.1 (d, *J* = 22 Hz), 27.5 (s), 21.9 (d, *J* = 6 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): δ -112.55 (d, *J* = 4.51 Hz), -142.59; **HRMS** (ESI) *m/z* calculated for C<sub>12</sub>H<sub>12</sub>F<sub>2</sub>ONa [M+Na]<sup>+</sup> 233.0748, found 233.0745. **MS** (EI) *m/z* (%): 210 (24), 166 (73), 153 (100), 140 (35), 127 (13).

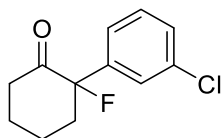
### 2-(2-chlorophenyl)-2-fluorocyclohexan-1-one (3e)



Prepared by the general procedure at 25 °C for 36 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as colorless oil (33.8 mg, 75% yield.).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.55-7.53 (m, 1 H), 7.41-7.39 (m, 1 H), 7.36-7.29 (m, 2 H), 2.92-2.82 (m, 1 H), 2.78-2.59 (m, 2 H), 2.39-2.29 (m, 1 H), 2.16-2.09 (m, 1 H), 2.07-1.99 (m, 1 H), 1.96-1.83 (m, 2 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  202.9 (d,  $J$  = 23 Hz), 136.2 (d,  $J$  = 21 Hz), 131.5 (d,  $J$  = 5 Hz), 130.6 (s), 129.7 (s), 127.0 (d,  $J$  = 14 Hz), 126.8 (d,  $J$  = 2 Hz), 97.3 (d,  $J$  = 178 Hz), 39.1 (d,  $J$  = 2 Hz), 37.1 (d,  $J$  = 24 Hz), 25.8 (s), 20.8 (d,  $J$  = 2 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -152.42; **HRMS** (ESI)  $m/z$  calculated for C<sub>12</sub>H<sub>13</sub>ClFO [M+H]<sup>+</sup> 227.0633, found 227.0629; **MS** (EI)  $m/z$  (%): 228 (3), 226 (11), 184 (15), 182 (49), 169 (36), 156 (41), 115 (15).

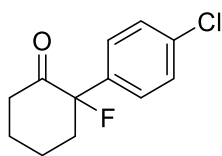
### 2-(3-chlorophenyl)-2-fluorocyclohexan-1-one (3f)



Prepared by the general procedure at 25 °C for 18h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as colorless oil (40.7 mg, 90 % yield.).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.38-7.33 (m, 3 H), 7.26-7.24 (m, 1 H), 2.88-2.80 (m, 1 H), 2.54-2.28 (m, 3 H), 2.13-1.99 (m, 2 H), 1.96-1.89 (m, 1 H), 1.86-1.77 (m, 1 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  205.6 (d,  $J$  = 23 Hz), 138.3 (d,  $J$  = 21 Hz), 134.5 (s), 129.7 (s), 129.0 (d,  $J$  = 1 Hz), 126.3 (d,  $J$  = 8 Hz), 124.4 (d,  $J$  = 7 Hz), 97.7 (d,  $J$  = 183 Hz), 39.6 (s), 38.4 (d,  $J$  = 23 Hz), 27.4 (s), 21.7 (d,  $J$  = 5 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -146.96; **HRMS** (ESI)  $m/z$  calculated for C<sub>12</sub>H<sub>12</sub>ClFONa [M+Na]<sup>+</sup> 249.0453, found 249.0458; **MS** (EI)  $m/z$  (%): 228 (10), 226 (26), 182 (41), 171 (19), 156 (35), 115 (82), 57 (87), 55 (100).

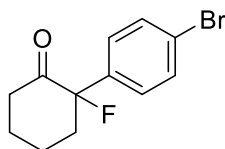
**2-(4-chlorophenyl)-2-fluorocyclohexan-1-one (3g)**<sup>7</sup>



Prepared by the general procedure at 25°C for 18 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as colorless oil (42.8 mg, 94% yield.).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.39 (d,  $J$  = 8.4 Hz, 2 H), 7.32-7.30 (m, 2 H), 2.86-2.78 (m, 1 H), 2.55-2.27 (m, 3 H), 2.13-2.04 (m, 2 H), 1.97-1.91 (m, 1 H), 1.86-1.75 (m, 1 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  205.8 (d,  $J$  = 23 Hz), 134.9 (d,  $J$  = 3 Hz), 134.8 (d,  $J$  = 22 Hz), 128.7 (s), 127.6 (d,  $J$  = 7 Hz), 97.8 (d,  $J$  = 182 Hz), 39.6 (s), 38.3 (d,  $J$  = 22 Hz), 27.5 (s), 21.8 (d,  $J$  = 6 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -145.71; **MS** (EI)  $m/z$  (%): 228 (11), 226 (31), 184 (17), 182 (53), 169 (100), 171 (32), 115 (42).

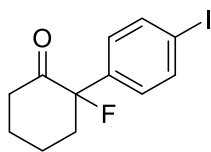
**2-(4-bromophenyl)-2-fluorocyclohexan-1-one (3h)**<sup>7</sup>



Prepared by the general procedure at 25 °C for 18 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as colorless oil (46.0 mg, 85% yield.).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.54 (d,  $J$  = 8 Hz, 2 H), 7.27-7.24 (m, 2 H), 2.87-2.78 (m, 1 H), 2.54-2.28 (m, 3 H), 2.12-1.99 (m, 2 H), 1.94-1.89 (m, 1 H), 1.84-1.76 (m, 1 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  205.8 (d,  $J$  = 24 Hz), 135.3 (d,  $J$  = 22 Hz), 131.6 (s), 127.9 (d,  $J$  = 7 Hz), 123.1 (d,  $J$  = 3 Hz), 97.9 (d,  $J$  = 182 Hz), 39.6 (s), 38.3 (d,  $J$  = 22 Hz), 27.5 (s), 21.7 (d,  $J$  = 6 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -146.30; **MS** (EI)  $m/z$  (%): 272 (24), 270 (26), 228 (62), 226 (65), 202 (20), 200 (22), 134 (100).

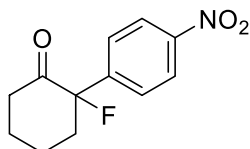
### 2-fluoro-2-(4-iodophenyl)cyclohexan-1-one (3i)



Prepared by the general procedure at 25 °C for 48 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as yellow oil (14.6 mg, 23% yield.).

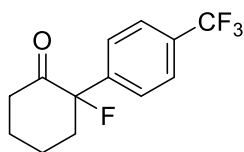
**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.74 (d,  $J$  = 7.8 Hz, 2 H), 7.11 (d,  $J$  = 8.4 Hz, 2 H), 2.85-2.80 (m, 1 H), 2.48-2.39 (m, 2 H), 2.35-2.28 (m, 1 H), 2.10-2.00 (m, 2 H), 1.93-1.87 (m, 1 H), 1.82-1.77 (m, 1 H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>):  $\delta$  205.4 (d,  $J$  = 24 Hz), 137.6 (s), 136.3 (d,  $J$  = 22.5 Hz), 128.0 (d,  $J$  = 7.5 Hz), 97.9 (d,  $J$  = 183 Hz), 94.9 (s), 39.6 (s), 38.5 (d,  $J$  = 22.5 Hz), 27.5 (s), 21.7 (d,  $J$  = 6 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -147.05; **HRMS** (ESI)  $m/z$  calculated for C<sub>12</sub>H<sub>12</sub>FIO<sub>2</sub>Na [M+Na]<sup>+</sup> 340.9809, found 340.9813; **MS** (EI)  $m/z$  (%): 318 (55), 274 (68), 261 (18), 248 (20), 134 (100).

### 2-fluoro-2-(4-nitrophenyl)cyclohexan-1-one (3j)



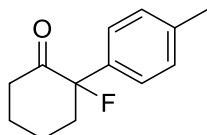
Prepared by the general procedure at 25 °C for 18 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as a yellow crystal (38.3 mg, 81% yield.). m.p. = 60.8-62.4 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.26 (d,  $J$  = 8.4 Hz, 2 H), 7.53 (d,  $J$  = 8.8 Hz, 2 H), 3.04-2.95 (m, 1 H), 2.53-2.46 (m, 1 H), 2.45-2.09 (m, 4 H), 1.95-1.82 (m, 2 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  204.8 (d,  $J$  = 25 Hz), 147.7 (s), 143.8 (d,  $J$  = 22 Hz), 126.8 (d,  $J$  = 8 Hz), 123.3 (s), 98.0 (d,  $J$  = 182 Hz), 39.5 (d,  $J$  = 23 Hz), 39.3 (d,  $J$  = 1 Hz), 27.5 (s), 20.9 (d,  $J$  = 4 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -154.91; **HRMS** (ESI)  $m/z$  calculated for C<sub>12</sub>H<sub>13</sub>FNO<sub>3</sub> [M+H]<sup>+</sup> 238.0874, found 238.0871; **MS** (EI)  $m/z$  (%): 237 (17), 193 (100), 167 (110), 134 (36), 115 (7).

**2-fluoro-2-(4-(trifluoromethyl)phenyl)cyclohexan-1-one (3k)**

Prepared by the general procedure at 25 °C for 18 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as white foam (30.8 mg, 59% yield.).

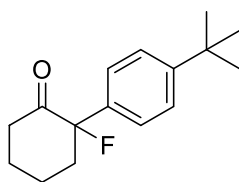
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.67 (d,  $J$  = 8.8 Hz, 2 H), 7.49 (d,  $J$  = 8.4 Hz, 2 H), 2.96-2.87 (m, 1 H), 2.48-2.35 (m, 3 H), 2.17-2.06 (m, 2 H), 1.96-1.78 (m, 2 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  205.4 (d,  $J$  = 25 Hz), 140.5 (d,  $J$  = 22 Hz), 130.7 (q,  $J$  = 32 Hz), 126.4 (d,  $J$  = 8 Hz), 125.3 (q,  $J$  = 4 Hz), 123.9 (q,  $J$  = 271 Hz), 97.9 (d,  $J$  = 182 Hz), 39.5 (d,  $J$  = 1 Hz), 39.0 (d,  $J$  = 22 Hz), 27.5 (s), 21.3 (d,  $J$  = 5 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -62.74, -151.10; **HRMS** (ESI)  $m/z$  calculated for C<sub>13</sub>H<sub>12</sub>F<sub>4</sub>ONa [M+Na]<sup>+</sup> 283.0716, found 283.0709. **MS** (EI)  $m/z$  (%): 260 (18), 216 (51), 203 (35), 190 (43), 147 (100), 115 (31), 55 (24).

**2-fluoro-2-(p-tolyl)cyclohexan-1-one (3l)<sup>7</sup>**

Prepared by the general procedure at 25 °C for 18 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as a white crystal (31.5 mg, 76% yield.). m.p. = 52.4-53.4 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.30-7.28 (m, 2 H), 7.23 (d,  $J$  = 8.4 Hz, 2 H), 2.74-2.64 (m, 2 H), 2.43-2.35 (m, 1 H), 2.37 (d,  $J$  = 1.6 Hz, 3 H), 2.31-2.21 (m, 1 H), 2.08-2.00 (m, 1 H), 1.96-1.89 (m, 2 H), 1.84-1.74 (m, 1 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  206.6 (d,  $J$  = 22 Hz), 139.2 (d,  $J$  = 3 Hz), 132.8 (d,  $J$  = 22 Hz), 129.4 (s), 126.4 (d,  $J$  = 5 Hz), 98.2 (d,  $J$  = 182 Hz), 39.9 (s), 37.4 (d,  $J$  = 23 Hz), 27.5 (s), 22.3 (d,  $J$  = 7 Hz), 21.2 (s); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -139.05; **MS** (EI)  $m/z$  (%): 206 (20), 162 (16), 149 (100), 136 (24), 115 (30), 91 (12).

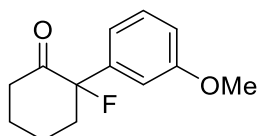
### 2-(4-(tert-butyl)phenyl)-2-fluorocyclohexan-1-one (3m)



Prepared by the general procedure at 25 °C for 18 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as a white crystal (41.9 mg, 84% yield.). m.p. = 55.5-56.2 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.43 (d, *J* = 8.0 Hz, 2 H), 7.33 (dd, *J* = 8.4 Hz, 1.2 Hz, 2 H), 2.75-2.65 (m, 2 H), 2.44-2.37 (m, 1 H), 2.32-2.22 (m, 1 H), 2.07-2.00 (m, 1 H), 1.96-1.89 (m, 2 H), 1.86-1.76 (m, 1 H), 1.32 (s, 9 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 206.6 (d, *J* = 22 Hz), 152.2 (d, *J* = 3 Hz), 132.8 (d, *J* = 22 Hz), 126.2 (d, *J* = 5 Hz), 125.7 (s), 98.1 (d, *J* = 183 Hz), 39.9 (s), 37.5 (d, *J* = 22 Hz), 34.6 (s), 31.2 (s), 27.5 (s), 22.4 (d, *J* = 8 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): δ -138.63; **HRMS** (ESI) *m/z* calculated for C<sub>16</sub>H<sub>21</sub>FONa [M+Na]<sup>+</sup> 271.1469, found 271.1476; **MS** (EI) *m/z* (%): 248 (32), 205 (100), 204 (19), 115 (16), 57 (29).

### 2-fluoro-2-(3-methoxyphenyl)cyclohexan-1-one (3n)<sup>7</sup>

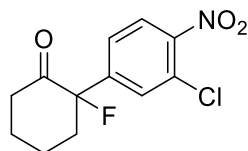


Prepared by the general procedure at 25 °C for 18 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as white foam (40.5 mg, 91% yield.).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.34 (td, *J* = 8.4 Hz, 0.8 Hz, 1 H), 7.00-6.97 (m, 1 H), 6.94-6.91 (m, 2 H), 3.82 (s, 3 H), 2.77-2.59 (m, 2 H), 2.44-2.37 (m, 1 H), 2.33-2.23 (m, 1 H), 2.09-2.01 (m, 1 H), 1.98-1.91 (m, 2 H), 1.87-1.78 (m, 1 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 206.2 (d, *J* = 22 Hz), 159.7 (s), 137.4 (d, *J* = 21 Hz), 129.7 (s), 118.6 (d, *J* = 6 Hz), 114.4 (d, *J* = 3 Hz), 112.2 (d, *J* = 6 Hz), 98.1 (d, *J* = 183 Hz), 55.3 (s), 39.9 (s), 37.7 (d, *J* = 22 Hz), 27.4 (s), 22.2 (d, *J* = 7 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): δ -141.29; **MS** (EI) *m/z* (%): 222 (46), 178 (30), 165 (44), 152 (28), 70 (44), 57 (93),

55 (100).

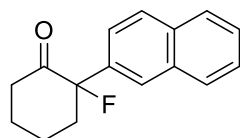
**2-(3-chloro-4-nitrophenyl)-2-fluorocyclohexan-1-one (3o)**



Prepared by the general procedure at 25 °C for 30 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as a white crystal (43.8 mg, 81% yield.). m.p. = 96.8-97.4 °C.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.91 (d,  $J$  = 8.4 Hz, 1 H), 7.54 (d,  $J$  = 1.2 Hz, 1 H), 7.37 (dd,  $J$  = 8.4 Hz, 1.8 Hz, 1 H), 3.03-2.96 (m, 1 H), 2.51 (dt,  $J$  = 13.2 Hz, 3.6 Hz, 1 H), 2.45-2.39 (m, 1 H), 2.28-2.11 (m, 3 H), 1.91-1.83 (m, 2 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  204.2 (d,  $J$  = 25 Hz), 147.3 (s), 143.0 (d,  $J$  = 22 Hz), 129.3 (d,  $J$  = 10 Hz), 127.0 (d,  $J$  = 1 Hz), 125.2 (s), 125.1 (d,  $J$  = 9 Hz), 97.5 (d,  $J$  = 183 Hz), 39.6 (d,  $J$  = 23 Hz), 39.1 (d,  $J$  = 2 Hz), 27.4 (s), 20.8 (d,  $J$  = 3 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -156.09; **HRMS** (ESI)  $m/z$  calculated for C<sub>12</sub>H<sub>12</sub>ClFNO<sub>3</sub> [M+H]<sup>+</sup> 272.0484, found 272.0487; **MS** (EI)  $m/z$  (%): 271 (39), 227 (91), 201 (9), 55 (33).

**2-fluoro-2-(naphthalen-2-yl)cyclohexan-1-one (3p)<sup>7</sup>**

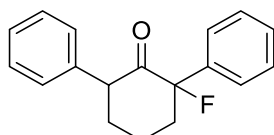


Prepared by the general procedure at 25 °C for 18 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as a white crystal (36.3 mg, 75% yield.). m.p. = 67.5-69.0 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.91-7.84 (m, 4 H), 7.54-7.50 (m, 2 H), 7.46 (dd,  $J$  = 8.8 Hz, 1.6 Hz, 1 H), 2.85-2.74 (m, 2 H), 2.46-2.33 (m, 2 H), 2.14-2.07 (m, 1 H), 2.01-1.94 (m, 2 H), 1.92-1.84 (m, 1 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  206.5 (d,  $J$  = 22 Hz), 133.4 (d,  $J$  = 21 Hz), 133.3 (d,  $J$  =

2 Hz), 132.9 (s), 128.5 (s), 128.4 (s), 127.6 (s), 126.9 (s), 126.5 (s), 125.9 (d,  $J = 8$  Hz), 123.8 (d,  $J = 5$  Hz), 98.4 (d,  $J = 184$  Hz), 40.0 (s), 37.8 (d,  $J = 22$  Hz), 27.5 (s), 22.3 (d,  $J = 6$  Hz);  **$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -141.03; **MS** (EI)  $m/z$  (%): 242 (69), 214 (25), 198 (29), 185 (100), 172 (24), 165 (56).

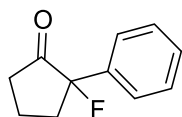
### 2-fluoro-2,6-diphenylcyclohexan-1-one (3q)



Prepared by the general procedure at 25 °C for 120 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as a white crystal (37.1 mg, 69% yield.). m.p. = 116.6-117.6 °C.

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.35-7.30 (m, 7 H), 7.26-7.18 (m, 3 H), 4.49-4.42 (m, 1 H), 2.58-2.51 (m, 1 H), 2.41-2.33 (m, 2 H), 2.32-2.25 (m, 1 H), 2.15-2.08 (m, 1 H), 1.93-1.89 (m, 1 H);  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  204.9 (d,  $J = 28$  Hz), 137.4 (s), 137.1 (d,  $J = 21$  Hz), 128.7 (s), 128.2 (s), 128.1 (s), 127.8 (s), 127.1 (s), 125.7 (d,  $J = 9$  Hz), 99.4 (d,  $J = 179$  Hz), 53.7 (s), 40.1 (d,  $J = 24$  Hz), 35.8 (s), 20.7 (d,  $J = 3$  Hz);  **$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -156.81; **HRMS** (ESI)  $m/z$  calculated for  $\text{C}_{18}\text{H}_{17}\text{FONa}$   $[\text{M}+\text{Na}]^+$  291.1156, found 291.1155; **MS** (EI)  $m/z$  (%): 268 (11), 248 (36), 144 (100), 77 (13).

### 2-fluoro-2-phenylcyclopentan-1-one (3r)

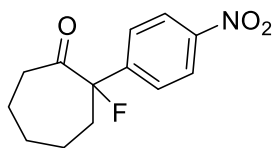


Prepared by the general procedure at 25 °C for 36 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as white foam (10.5 mg, 29% yield.).

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.43-7.38 (m, 5 H), 2.63-2.49 (m, 3 H), 2.47-2.36 (m, 1 H), 2.27-

2.16 (m, 1 H), 2.08-1.97 (m, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  211.6 (d,  $J = 19$  Hz), 135.8 (d,  $J = 23$  Hz), 128.9 (d,  $J = 2$  Hz), 128.5 (s), 125.7 (d,  $J = 6$  Hz), 97.3 (d,  $J = 183$  Hz), 36.0 (d,  $J = 22$  Hz), 35.5 (s), 17.5 (d,  $J = 4$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -149.78; HRMS (ESI)  $m/z$  calculated for  $\text{C}_{11}\text{H}_{12}\text{FO}$   $[\text{M}+\text{H}]^+$  179.0867, found 179.0856; MS (EI)  $m/z$  (%): 178 (20), 122 (100), 77 (8).

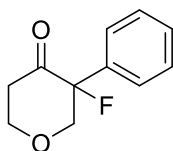
### 2-fluoro-2-(4-nitrophenyl)cycloheptan-1-one (3s)



Prepared by the general procedure at 25 °C for 168 h and. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as a yellow crystal (41.2 mg, 82% yield.). 110.6-112.4 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.24 (d,  $J = 8.8$  Hz, 2 H), 7.70-7.67 (m, 2 H), 2.93-2.86 (m, 1 H), 2.63-2.55 (m, 1 H), 2.30-2.14 (m, 2 H), 2.04-1.92 (m, 3 H), 1.87-1.70 (m, 2 H), 1.43 (q,  $J = 12.4$  Hz, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  207.6 (d,  $J = 26$  Hz), 147.6 (s), 145.4 (d,  $J = 23$  Hz), 126.3 (d,  $J = 10$  Hz), 123.4 (s), 101.0 (d,  $J = 188$  Hz), 40.2 (s), 37.1 (d,  $J = 23$  Hz), 27.7 (s), 24.4 (d,  $J = 1$  Hz), 24.3 (d,  $J = 2$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -159.04; HRMS (ESI)  $m/z$  calculated for  $\text{C}_{13}\text{H}_{14}\text{FNO}_3\text{Na}$   $[\text{M}+\text{Na}]^+$  274.0850, found 274.2734; MS (EI)  $m/z$  (%): 251 (8), 167 (37), 134 (100), 84 (22), 55 (37).

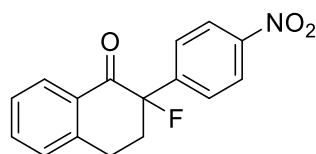
### 3-fluoro-3-phenyltetrahydro-4H-pyran-4-one (3t)<sup>7</sup>



Prepared by the general procedure at 25 °C for 72 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as colorless oil (28.3 mg, 73% yield.).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.63-7.61 (m, 2 H), 7.45-7.39 (m, 3 H), 4.59-4.55 (m, 1 H), 4.27-4.21 (m, 1 H), 3.99-3.91 (m, 2 H), 2.75-2.60 (m, 2 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  201.3 (d,  $J$  = 20 Hz), 134.9 (d,  $J$  = 22 Hz), 129.4 (d,  $J$  = 2 Hz), 128.7 (s), 126.1 (d,  $J$  = 6 Hz), 94.8 (d,  $J$  = 189 Hz), 74.2 (d,  $J$  = 29 Hz), 68.5 (s), 40.7 (s); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -156.46; **MS** (EI)  $m/z$  (%): 194 (3), 112 (100), 77 (8), 55 (30).

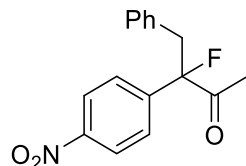
**2-fluoro-2-(4-nitrophenyl)-3,4-dihydronaphthalen-1(2H)-one (3u)<sup>24</sup>**



Prepared by the general procedure at 100 °C for 48 h using a sealed tube. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as a yellow crystal (36.7 mg, 64% yield.). m. p. = 119.0-120.0 °C.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.23 (d,  $J$  = 8.4 Hz, 2 H), 8.14 (d,  $J$  = 7.8 Hz, 1 H), 7.59 (td,  $J$  = 7.8 Hz, 1.2 Hz, 1 H), 7.54 (d,  $J$  = 8.4 Hz, 2 H), 7.42 (t,  $J$  = 7.8 Hz, 1 H), 7.31 (d,  $J$  = 7.8 Hz, 1 H), 3.29 (dt,  $J$  = 17.4 Hz, 6 Hz, 1 H), 2.89 (dt,  $J$  = 17.4 Hz, 6.6 Hz, 1 H), 2.75-2.65 (m, 2 H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>):  $\delta$  191.4 (d,  $J$  = 19.5 Hz), 148.1 (s), 144.8 (d,  $J$  = 22.5 Hz), 143.1 (s), 134.7 (s), 131.4 (s), 128.9 (s), 128.6 (s), 127.5 (s), 126.8 (d,  $J$  = 7.5 Hz), 123.6 (s), 95.0 (d,  $J$  = 183 Hz), 35.8 (d,  $J$  = 24 Hz), 25.4 (d,  $J$  = 7.5 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -154.22; **MS** (EI)  $m/z$  (%): 285 (31), 118 (100), 99 (45).

**3-fluoro-3-(4-nitrophenyl)-4-phenylbutan-2-one (3v)**

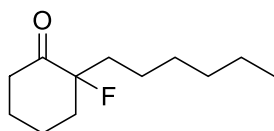


Prepared by the general procedure at 80 °C for 60 h using a sealed tube. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the

residue by flash column chromatography afforded the product as a yellow crystal (52.5 mg, 91% yield.). m. p. = 100.5-101.5 °C.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 8.20 (d, *J* = 8.4 Hz, 2 H), 7.65 (d, *J* = 9 Hz, 2 H), 7.23-7.21 (m, 3 H), 7.10-7.08 (m, 2 H), 3.56 (dd, *J* = 27.6 Hz, 14.4 Hz, 1 H), 3.32 (dd, *J* = 24 Hz, 14.4 Hz, 1 H), 2.10 (d, *J* = 6 Hz, 3 H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>): δ 206.5 (d, *J* = 31.5 Hz), 147.9 (s), 144.0 (d, *J* = 22.5 Hz), 133.4 (s), 130.5 (s), 128.3 (s), 127.3 (s), 125.7 (d, *J* = 10.5 Hz), 123.6 (s), 101.9 (d, *J* = 192 Hz), 44.4 (d, *J* = 22.5 Hz), 26.0 (s); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): δ -164.01; **HRMS** (ESI) *m/z* calculated for C<sub>16</sub>H<sub>15</sub>FNO<sub>3</sub> [M+H]<sup>+</sup> 288.1030, found 288.1033; **MS** (EI) *m/z* (%): 287 (1), 196 (18), 165 (16), 91 (100), 77 (16).

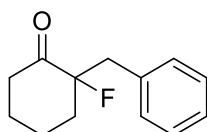
### 2-fluoro-2-hexylcyclohexan-1-one (3w)



Prepared by the general procedure at 25 °C for 48 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as colorless oil (25.6 mg, 64% yield.).

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 2.66-2.61(m, 1 H), 2.39-2.34 (m, 1 H), 2.08-2.02 (m, 1 H), 1.99-1.86 (m, 4 H), 1.85-1.79 (m, 1 H), 1.75-1.65 (m, 2 H), 1.47-1.41 (m, 1 H), 1.33-1.21 (m, 7 H), 0.88 (t, *J* = 6.6 Hz, 3 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 208.1 (d, *J* = 20 Hz), 98.9 (d, *J* = 183 Hz), 39.6 (s), 38.1 (d, *J* = 22 Hz), 34.6 (d, *J* = 23 Hz), 31.5 (s), 29.4 (s), 27.4 (s), 22.5 (s), 22.3 (d, *J* = 3 Hz), 22.1 (d, *J* = 8 Hz), 14.0 (s); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): δ -158.04; **HRMS** (ESI) *m/z* calculated for C<sub>12</sub>H<sub>21</sub>FONa [M+Na]<sup>+</sup> 223.1469, found 223.1472; **MS** (EI) *m/z* (%): 200 (1), 116 (100), 85 (7), 55 (31).

### 2-benzyl-2-fluorocyclohexan-1-one (3x)<sup>25</sup>

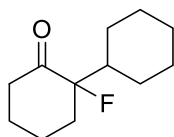


Prepared by the general procedure at 25 °C for 18 h. The reaction mixture was diluted with ethyl

acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as a white crystal (37.5 mg, 91% yield.). m. p. = 95.9-97.8 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.33-7.22 (m, 5 H), 3.23 (dd,  $J$  = 20.4 Hz, 14.8 Hz, 1 H), 3.02 (dd,  $J$  = 30.4 Hz, 14.4 Hz, 1 H), 2.77-2.71 (m, 1 H), 2.50-2.43 (m, 1 H), 2.01-1.69 (m, 6 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  207.7 (d,  $J$  = 21 Hz), 134.6 (s), 130.5 (s), 128.2 (s), 126.9 (s), 97.8 (d,  $J$  = 183 Hz), 39.8 (d,  $J$  = 23 Hz), 39.5 (s), 36.9 (d,  $J$  = 23 Hz), 27.4 (s), 21.5 (d,  $J$  = 6 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -156.34; **MS** (EI)  $m/z$  (%): 206 (1), 186 (40), 129 (31), 115 (46), 91 (100), 77 (13).

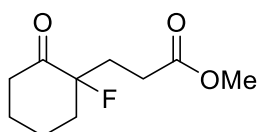
#### 1-fluoro-[1,1'-bi(cyclohexan)]-2-one (3y)



Prepared by the general procedure at 25 °C for 18 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as a white crystal (36.2 mg, 91% yield.). m. p. = 63.7-64.6 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.60-2.53 (m, 1 H), 2.43-2.36 (m, 1 H), 2.31-2.23 (m, 1 H), 2.02-1.66 (m, 10 H), 1.40-1.37 (m, 1 H), 1.33-1.10 (m, 5 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  208.7 (d,  $J$  = 18 Hz), 100.8 (d,  $J$  = 189 Hz), 40.0 (s), 39.7 (d,  $J$  = 22 Hz), 34.7 (d,  $J$  = 22 Hz), 27.3 (s), 26.2 (d,  $J$  = 2 Hz), 25.9 (d,  $J$  = 2 Hz), 24.9 (d,  $J$  = 4 Hz), 22.0 (d,  $J$  = 10 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -168.08; **HRMS** (ESI)  $m/z$  calculated for C<sub>12</sub>H<sub>19</sub>FONa [M+Na]<sup>+</sup> 221.1312, found 221.1308; **MS** (EI)  $m/z$  (%): 198 (1), 178 (2), 154 (5), 116 (100), 55 (13).

#### methyl 3-(1-fluoro-2-oxocyclohexyl)propanoate (3z)<sup>26</sup>

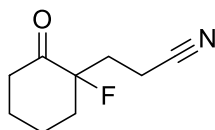


Prepared by the general procedure at 25 °C for 48 h. The reaction mixture was diluted with ethyl

acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as colorless oil (27.0 mg, 67% yield.).

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 3.68 (s, 3 H), 2.72-2.67 (m, 1 H), 2.49-2.28 (m, 4 H), 2.14-2.01 (m, 2 H), 1.95-1.82 (m, 4 H), 1.74-1.68 (m, 1 H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>): δ 207.2 (d, *J* = 21 Hz), 173.3 (s), 97.7 (d, *J* = 183 Hz), 51.7 (s), 39.4 (s), 38.4 (d, *J* = 22.5 Hz), 29.7 (d, *J* = 22.5 Hz), 27.5 (d, *J* = 4.5 Hz), 27.4 (s), 21.6 (d, *J* = 6 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): δ -160.39; **MS** (EI) *m/z* (%): 202 (1), 171 (22), 158 (29), 132 (19), 55 (100).

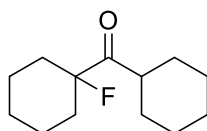
### 3-(1-fluoro-2-oxocyclohexyl)propanenitrile (3aa)<sup>26</sup>



Prepared by the general procedure at 25 °C for 96 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as a yellow crystal (27.7 mg, 82% yield.). m. p. = 72.6-73.3 °C.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 2.84-2.78 (m, 1 H), 2.48 (t, *J* = 7.2 Hz, 2 H), 2.41-2.29 (m, 2 H), 2.26-2.22 (m, 1 H), 2.05-1.94 (m, 3 H), 1.81-1.69 (m, 3 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 206.8 (d, *J* = 23 Hz), 119.2 (s), 96.7 (d, *J* = 181 Hz), 39.1 (s), 38.3 (d, *J* = 22 Hz), 30.3 (d, *J* = 22 Hz), 27.6 (s), 20.8 (d, *J* = 5 Hz), 11.3 (d, *J* = 7 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>): δ -162.96; **MS** (EI) *m/z* (%): 169 (7), 125 (100), 99 (7), 55 (100).

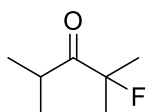
### cyclohexyl(1-fluorocyclohexyl)methanone (3ab)



Prepared by the general procedure at 60 °C for 96 h using a sealed tube. The reaction mixture was diluted with dichloromethane, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as colorless oil (27.0 mg, 64% yield.).

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  3.02-2.94 (m, 1 H), 1.80-1.56 (m, 14 H), 1.37-1.19 (m, 6 H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>):  $\delta$  214.8 (d,  $J$  = 28.5 Hz), 100.3 (d,  $J$  = 183 Hz), 44.9 (s), 32.2 (d,  $J$  = 22.5 Hz), 28.5 (s), 25.8 (s), 25.7 (s), 24.6 (s), 20.9 (s); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -168.92; **HRMS** (ESI)  $m/z$  calculated for C<sub>13</sub>H<sub>15</sub>FONa [M+Na]<sup>+</sup> 229.0999, found 229.1005; **MS** (EI)  $m/z$  (%): 212 (1), 129 (11), 111 (21), 83 (42), 57 (100).

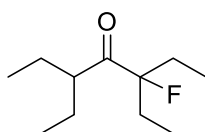
### 2-fluoro-2,4-dimethylpentan-3-one (3ac)



Prepared by the general procedure at 60 °C for 40 h using a sealed tube and CD<sub>3</sub>CN/CD<sub>2</sub>Cl<sub>2</sub> (v/v = 4/1) as a mixture solvent. After the reaction was completed, the reaction mixture was diluted with CDCl<sub>3</sub>, and its chemical yield (82%) was obtained using CH<sub>2</sub>Br<sub>2</sub> as NMR internal standard.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.25-3.20 (m, 1 H), 1.46 (dd,  $J$  = 21.2 Hz, 2.0 Hz, 6 H), 1.11 (dd,  $J$  = 6.8 Hz, 2.0 Hz, 6 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  215.6 (d,  $J$  = 27 Hz), 98.8 (d,  $J$  = 178 Hz), 34.5 (s), 24.4 (d,  $J$  = 24 Hz), 18.0 (d,  $J$  = 2 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -150.68; **MS** (EI)  $m/z$  (%): 132 (11), 89 (13), 71 (100), 61 (13).

### 3, 5-diethyl-3-fluoroheptan-4-one (3ad)

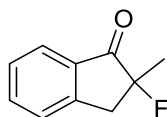


Prepared by the general procedure at 60 °C for 60 h using a sealed tube. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as colorless oil (14.2 mg, 38% yield.).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.92-2.86 (m, 1 H), 1.92-1.77 (m, 2 H), 1.77-1.64 (m, 4 H), 1.48-1.37 (m, 2 H), 0.89 (t,  $J$  = 7.6 Hz, 6 H), 0.86 (t,  $J$  = 7.6 Hz, 6 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  214.9 (d,  $J$  = 28 Hz), 104.0 (d,  $J$  = 185 Hz), 49.1 (s), 28.4 (d,  $J$  = 22 Hz), 22.4 (d,  $J$  = 1 Hz), 11.5 (s), 7.4 (d,  $J$  = 5 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -170.12; **HRMS** (ESI)  $m/z$  calculated for

C<sub>11</sub>H<sub>21</sub>FO<sub>2</sub>Na [M+Na]<sup>+</sup> 211.1469, found 211.1470; MS (EI) *m/z* (%): 188 (1), 169 (5), 99 (23), 84 (16), 71 (100).

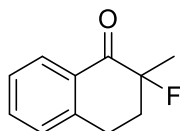
**2-fluoro-2-methyl-2,3-dihydro-1H-inden-1-one (3ae)<sup>27</sup>**



Prepared by the general procedure at 25 °C for 40 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as colorless oil (23.8 mg, 72% yield.).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.81 (d, *J* = 7.8 Hz, 1 H), 7.66 (t, *J* = 7.8 Hz, 1 H), 7.43 (q, *J* = 7.8 Hz, 2 H), 3.45 (dd, *J* = 22.8 Hz, 17.4 Hz, 1 H), 3.30 (dd, *J* = 17.4 Hz, 11.4 Hz, 1 H), 1.62 (d, *J* = 22.8 Hz, 3 H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 200.9 (d, *J* = 19.5 Hz), 150.0 (d, *J* = 3 Hz), 136.2 (s), 133.7 (s), 128.3 (s), 126.7 (s), 125.2 (d, *J* = 6 Hz), 95.7 (d, *J* = 183 Hz), 40.5 (d, *J* = 24 Hz), 21.6 (d, *J* = 27 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -152.19; MS (EI) *m/z* (%): 164 (100), 149 (92).

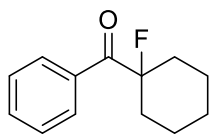
**2-fluoro-2-methyl-3,4-dihydronaphthalen-1(2H)-one (3af)<sup>27</sup>**



Prepared by the general procedure at 25 °C for 96 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as colorless oil (31.5 mg, 88% yield.).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.07 (dd, *J* = 7.6 Hz, 0.8 Hz, 1 H), 7.52 (td, *J* = 7.6 Hz, 1.6 Hz, 1 H), 7.35 (t, *J* = 7.6 Hz, 1 H), 7.26 (d, *J* = 7.6 Hz, 1 H), 3.21-3.14 (m, 1 H), 3.05-2.97 (m, 1 H), 2.54-2.45 (m, 1 H), 2.33-2.23 (m, 1 H), 1.60 (d, *J* = 22 Hz, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 194.2 (d, *J* = 18 Hz), 142.7 (s), 134.0 (s), 130.7 (s), 128.7 (s), 128.3 (s), 127.1 (s), 93.7 (d, *J* = 179 Hz), 35.0 (d, *J* = 23 Hz), 26.2 (d, *J* = 9 Hz), 20.9 (d, *J* = 25 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -152.70; MS (EI) *m/z* (%): 178 (27), 158 (15), 118 (100), 60 (25).

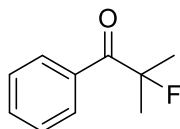
**(1-fluorocyclohexyl)(phenyl)methanone (3ag)**<sup>28</sup>



Prepared by the general procedure at 100 °C for 96 h using a sealed tube. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as colorless oil (23.2 mg, 56% yield.).

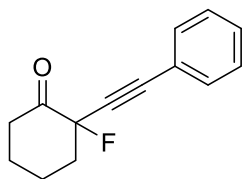
**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  8.05 (d,  $J$  = 7.8 Hz, 2 H), 7.54 (t,  $J$  = 7.8 Hz, 1 H), 7.43 (t,  $J$  = 7.8 Hz, 2 H), 2.09-2.06 (m, 2 H), 1.98-1.87 (m, 2 H), 1.74-1.70 (m, 5 H), 1.38-1.34 (m, 1 H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>):  $\delta$  201.3 (d,  $J$  = 27 Hz), 134.9 (d,  $J$  = 3 Hz), 132.8 (s), 129.8 (d,  $J$  = 7.5 Hz), 128.2 (s), 100.9 (d,  $J$  = 183 Hz), 33.2 (d,  $J$  = 22.5 Hz), 24.8 (s), 21.1 (d,  $J$  = 1.5 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -161.73; **MS** (EI)  $m/z$  (%): 206 (8), 105 (100), 77 (24).

**2-fluoro-2-methyl-1-phenylpropan-1-one (3ah)**<sup>29</sup>



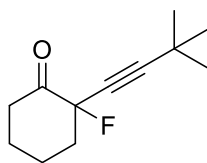
Prepared by the general procedure at 80 °C for 120 h using a sealed tube. The reaction mixture was diluted with dichloromethane, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as colorless oil (24.5 mg, 74% yield.).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.07 (d,  $J$  = 8.4 Hz, 2 H), 7.56 (t,  $J$  = 7.6 Hz, 1 H), 7.45 (t,  $J$  = 7.6 Hz, 2 H), 1.70 (d,  $J$  = 21.6 Hz, 6 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  200.9 (d,  $J$  = 26 Hz), 134.2 (d,  $J$  = 4 Hz), 133.1 (s), 129.9 (d,  $J$  = 8 Hz), 128.3 (s), 99.9 (d,  $J$  = 180 Hz), 25.7 (d,  $J$  = 24 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -143.56; **MS** (EI)  $m/z$  (%): 166 (6), 105 (95), 77 (55), 57 (100).

**2-fluoro-2-(phenylethynyl)cyclohexan-1-one (3ai)**<sup>7</sup>

Prepared by the general procedure at 25 °C for 5 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as colorless oil (17.1 mg, 40% yield.).

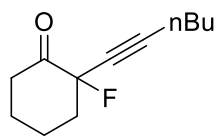
**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.49-7.48 (m, 2 H), 7.40-7.38 (m, 1 H), 7.36-7.33 (m, 2 H), 2.86 (td,  $J$  = 13.2 Hz, 6.0 Hz, 1 H), 2.60-2.52 (m, 2 H), 2.14-1.97 (m, 4 H), 1.77-1.70 (m, 1 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  201.6 (d,  $J$  = 19 Hz), 131.9 (d,  $J$  = 2 Hz), 129.5 (s), 128.4 (s), 121.1 (d,  $J$  = 3 Hz), 92.0 (d,  $J$  = 188 Hz), 91.3 (d,  $J$  = 9 Hz), 83.3 (d,  $J$  = 31 Hz), 40.4 (d,  $J$  = 23 Hz), 38.8 (s), 27.0 (s), 22.8 (d,  $J$  = 7 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -146.36; MS (EI)  $m/z$  (%): 216 (58), 172 (100), 159 (85), 146 (69), 133 (48), 115 (28), 57 (15).

**2-(3,3-dimethylbut-1-yn-1-yl)-2-fluorocyclohexan-1-one (3aj)**

Prepared by the general procedure at 25 °C for 5 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as colorless oil (13.8 mg, 35% yield.).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.78 (td,  $J$  = 13.6 Hz, 6.0 Hz, 1 H), 2.51-2.45 (m, 1 H), 2.41-2.37 (m, 1 H), 2.07-1.88 (m, 4 H), 1.71-1.62 (m, 1 H), 1.25 (s, 9 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  202.3 (d,  $J$  = 19 Hz), 101.1 (d,  $J$  = 9 Hz), 91.7 (d,  $J$  = 186 Hz), 73.9 (d,  $J$  = 30 Hz), 40.5 (d,  $J$  = 22 Hz), 38.6 (s), 30.5 (s), 27.6 (s), 27.0 (s), 23.0 (d,  $J$  = 8 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -146.02; **HRMS** (ESI)  $m/z$  calculated for C<sub>12</sub>H<sub>17</sub>FO<sup>+</sup>Na [M+Na]<sup>+</sup> 219.1156, found 219.1159; MS (EI)  $m/z$  (%): 196 (2), 181 (30), 115 (11), 81 (25), 57 (100).

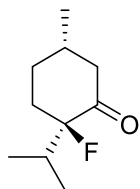
**2-fluoro-2-(hex-1-yn-1-yl)cyclohexan-1-one(3ak)<sup>7</sup>**



Prepared by the general procedure at 25 °C for 5 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as colorless oil (15.7 mg, 40% yield.).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.78 (td,  $J$  = 13.2 Hz, 6.0 Hz, 1 H), 2.50 (dq,  $J$  = 12.4 Hz, 4.0 Hz, 1 H), 2.41-2.36 (m, 1 H), 2.30 (q,  $J$  = 6.8 Hz, 2 H), 2.06-1.89 (m, 4 H), 1.73-1.62 (m, 1 H), 1.55-1.50 (m, 2 H), 1.46-1.37 (m, 2 H), 0.92 (t,  $J$  = 7.2 Hz, 3 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  202.2 (d,  $J$  = 19 Hz), 93.1 (d,  $J$  = 9 Hz), 91.9 (d,  $J$  = 186 Hz), 75.1 (d,  $J$  = 30 Hz), 40.4 (d,  $J$  = 23 Hz), 38.6 (s), 30.2 (s), 27.0 (s), 22.8 (d,  $J$  = 8 Hz), 21.9 (s), 18.5 (s), 13.5 (s); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -145.36; MS (EI)  $m/z$  (%): 196 (6), 123 (71), 109 (76), 105 (37), 97 (100), 81 (38).

**(2S, 5S)-2-fluoro-2-isopropyl-5-methylcyclohexan-1-one (4a)**

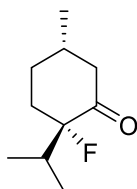


Prepared by the general procedure at 25 °C for 48 h. The reaction mixture was diluted with dichloromethane, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product **4a** as a colorless oil (19.8 mg, 57% yield.), along with the product **4b** as colorless oil (10.8 mg, 31% yield.).

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  2.48 (dddd,  $J$  = 13.2 Hz, 4.8 Hz, 4.8 Hz, 2.2 Hz, 1 H), 2.35-2.22 (m, 2 H), 2.15 (dd,  $J$  = 12.2 Hz, 12.2 Hz, 1 H), 1.99-1.92 (m, 1 H), 1.88-1.83 (m, 1 H), 1.77 (ddd,  $J$  = 13.2 Hz, 13.2 Hz, 4.2 Hz, 1 H), 1.41 (ddd,  $J$  = 14.4 Hz, 14.4 Hz, 3.6 Hz, 1 H), 1.05 (d,  $J$  = 6.0 Hz, 3 H), 1.04 (d,  $J$  = 6.6 Hz, 3 H), 0.88 (d,  $J$  = 6.6 Hz, 3 H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>):  $\delta$  207.6 (d,  $J$  = 12 Hz), 100.3 (d,  $J$  = 192 Hz), 47.9 (s), 34.9 (s), 33.8 (d,  $J$  = 21 Hz), 30.5 (d,  $J$  = 10.5 Hz), 30.2 (d,  $J$  = 22.5 Hz), 21.5 (s), 15.9 (d,  $J$  = 3 Hz), 14.9 (d,  $J$  = 3 Hz); **<sup>19</sup>F**

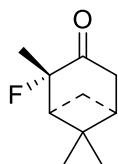
**NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -175.73; **HRMS** (ESI)  $m/z$  calculated for C<sub>10</sub>H<sub>17</sub>FONa [M+Na]<sup>+</sup> 195.1156, found 195.1156; **MS** (EI)  $m/z$  (%): 172 (6), 128 (67), 84 (18), 69 (31), 57 (100).  $[\alpha]_D^{27} = -111.5$  (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>).

**(2R, 5S)-2-fluoro-2-isopropyl-5-methylcyclohexan-1-one (4b)**



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.52 (ddd,  $J = 12.4$  Hz, 10.0 Hz, 6.4 Hz, 1 H), 2.37 (dd,  $J = 12.4$  Hz, 4.4 Hz, 1 H), 2.31-2.15 (m, 2 H), 2.04-1.96 (m, 1 H), 1.78-1.61 (m, 3 H), 1.04 (d,  $J = 6.6$  Hz, 3 H), 0.97 (d,  $J = 7.2$  Hz, 3 H), 0.94 (d,  $J = 7.2$  Hz, 3 H); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -168.78; **HRMS** (ESI)  $m/z$  calculated for C<sub>10</sub>H<sub>17</sub>FONa [M+Na]<sup>+</sup> 195.1156, found 195.1159; **MS** (EI)  $m/z$  (%): 172 (1), 84 (13), 69 (31), 57 (100).  $[\alpha]_D^{27} = 27.6$  (c 1.1, CH<sub>2</sub>Cl<sub>2</sub>). 84 (13), 69 (31), 57 (100).  $[\alpha]_D^{27} = 27.6$  (c 1.1, CH<sub>2</sub>Cl<sub>2</sub>).

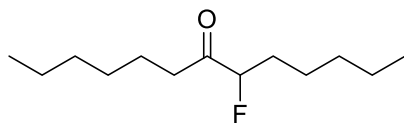
**(1S, 2S, 5S)-2-fluoro-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one (5a)**



Prepared by the general procedure at 25 °C for 96 h. The reaction mixture was diluted with dichloromethane, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product **4a** as colorless oil (13.9 mg, 41% yield.). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.660-2.656 (m, 2 H), 2.53-2.47 (m, 1 H), 2.32 (ddd,  $J = 6.0$  Hz, 6.0 Hz, 4.0 Hz, 1 H), 2.18-2.14 (m, 1 H), 1.68 (dd,  $J = 11.2$  Hz, 1.2 Hz, 1 H), 1.49 (d,  $J = 25.2$  Hz, 3 H), 1.39 (d,  $J = 0.8$  Hz, 3 H), 0.87 (s, 3 H); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -133.51; **HRMS** (ESI)  $m/z$  calculated for C<sub>10</sub>H<sub>16</sub>FO [M+H]<sup>+</sup> 171.1180, found 171.0995; **MS** (EI)  $m/z$  (%): 170 (2), 69 (64), 57 (100), 55 (85).  $[\alpha]_D^{27} = -47.1$  (c 1.2, CH<sub>2</sub>Cl<sub>2</sub>).

### Other fluorinated non-quaternary carbon products:

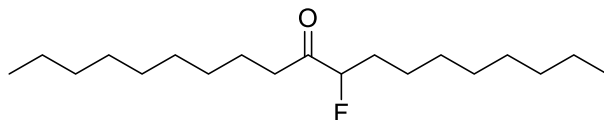
#### 6-fluorotridecan-7-one (6a)



Prepared by the general procedure at 60 °C for 12 h under the refluxed conditions. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as white foam (9.6 mg, 22% yield.). (30.1 mg starting material (76%) was recovered.).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  4.73 (ddd,  $J$  = 50.4 Hz, 8.0 Hz, 4.4 Hz, 1 H), 2.66-2.51 (m, 2 H), 1.88-1.70 (m, 2 H), 1.62-1.54 (m, 2 H), 1.48-1.40 (m, 2 H), 1.36-1.24 (m, 10 H), 0.91-0.87 (m, 6 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  210.5 (d,  $J$  = 25 Hz), 96.1 (d,  $J$  = 183 Hz), 38.0, 32.0 (d,  $J$  = 21 Hz), 31.6, 31.3, 28.8, 24.20, 24.17, 22.63, 22.61, 22.5, 22.4, 14.0, 13.9; **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -191.88; **HRMS** (ESI)  $m/z$  calculated for C<sub>13</sub>H<sub>25</sub>FONa [M+Na]<sup>+</sup> 239.1782, found 239.1786; **MS** (EI)  $m/z$  (%): 216 (2), 113 (100), 85 (13), 71 (3).

#### 9-fluorononadecan-10-one (6b)

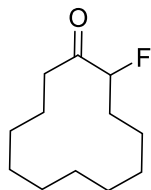


Prepared by the general procedure at 60 °C for 12 h under the refluxed conditions. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as white foam (11.1 mg, 18% yield.). (43.6mg starting material (77%) was recovered.).

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  4.72 (ddd,  $J$  = 50.4 Hz, 8.4 Hz, 4.2 Hz, 1 H), 2.63-2.52 (m, 2 H), 1.85-1.69 (m, 2 H), 1.59-1.57 (m, 2 H), 1.45-1.40 (m, 2 H), 1.32-1.27 (m, 22 H), 0.88 (t,  $J$  = 7.2 Hz, 6 H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>):  $\delta$  210.3 (d,  $J$  = 22.5 Hz), 96.1 (d,  $J$  = 181.5 Hz), 38.0, 32.1 (d,  $J$  = 21.0 Hz), 31.9, 31.8, 29.41, 29.37, 29.3, 29.24, 29.18, 29.1, 24.54, 24.52, 22.7, 22.63, 22.61, 14.0; **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -191.86; **HRMS** (ESI)  $m/z$  calculated for C<sub>19</sub>H<sub>37</sub>FONa [M+Na]<sup>+</sup> 323.2721, found 323.2722; **MS** (EI)  $m/z$  (%): 300 (1), 155 (6), 127 (10), 85 (44), 71 (60),

57 (100).

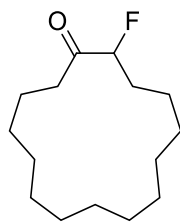
**2-fluorocyclododecan-1-one (6c)**



Prepared by the general procedure at 25 °C for 24 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as white foam (5.3 mg, 13% yield.). (28.5 mg starting material (78%) was recovered.).

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  4.87 (ddd,  $J$  = 49.2 Hz, 6.6 Hz, 4.2 Hz, 1 H), 2.79-2.75 (m, 1 H), 2.50-2.45 (m, 1 H), 2.01-1.94 (m, 2 H), 1.81-1.72 (m, 2 H), 1.43-1.22 (m, 14 H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>):  $\delta$  208.9 (d,  $J$  = 22.5 Hz), 95.7 (d,  $J$  = 183.0 Hz), 34.4, 29.7 (d,  $J$  = 21.0 Hz), 26.5, 26.2, 23.9, 23.4, 23.1, 22.5, 20.8, 19.5; **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -189.33; **HRMS** (ESI)  $m/z$  calculated for C<sub>12</sub>H<sub>21</sub>FONa [M+Na]<sup>+</sup> 223.1469, found 223.1471; **MS** (EI)  $m/z$  (%): 200 (11), 126 (16), 112 (39), 98 (100), 85 (52), 70 (23).

**2-fluorocyclopentadecan-1-one (6d)**

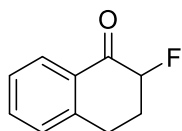


Prepared by the general procedure at 25 °C for 24 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as white foam (10.4 mg, 21% yield.). (34.5 mg starting material (77%) was recovered.).

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  4.81 (dt,  $J$  = 49.8 Hz, 5.4 Hz, 1 H), 2.82-2.76 (m, 1 H), 2.45-2.40 (m, 1 H), 1.94-1.85 (m, 2 H), 1.83-1.76 (m, 1 H), 1.60-1.54 (m, 1 H), 1.43-1.20 (m, 20 H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>):  $\delta$  210.5 (d,  $J$  = 25.5 Hz), 95.7 (d,  $J$  = 183.0 Hz), 37.4, 31.7 (d,  $J$  = 19.5

Hz), 27.4, 27.3, 26.8, 26.6, 26.5, 26.4, 26.30, 26.27, 26.2, 22.34, 22.31, 21.6; **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -191.12; **HRMS** (ESI)  $m/z$  calculated for C<sub>15</sub>H<sub>27</sub>FONa [M+Na]<sup>+</sup> 265.1938, found 265.1942; MS (EI)  $m/z$  (%): 242 (3), 112 (37), 98 (100), 84 (37).

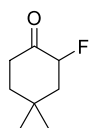
#### 2-fluoro-3,4-dihydronaphthalen-1(2H)-one (6e)



Prepared by the general procedure at 80 °C for 120 h using a sealed tube. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as white foam (8.9 mg, 27% yield.). (20.4 mg starting material (70%) was recovered.).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.06 (dd,  $J$  = 8.0 Hz, 1.2 Hz, 1 H), 7.54 (td,  $J$  = 8.8 Hz, 1.6 Hz, 1 H), 7.36 (t,  $J$  = 7.6 Hz, 1 H), 7.28 (d,  $J$  = 7.2 Hz, 1 H), 5.17 (ddd,  $J$  = 48.0 Hz, 12.8 Hz, 5.2 Hz, 1 H), 3.16-3.13 (m, 2 H), 2.64-2.55 (m, 1 H), 2.42-2.29 (m, 1 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  193.4 (d,  $J$  = 14 Hz), 142.9, 134.1, 131.1, 128.6, 127.7 (d,  $J$  = 3 Hz), 127.1, 91.2 (d,  $J$  = 187 Hz), 30.1 (d,  $J$  = 19 Hz), 27.0 (d,  $J$  = 11 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -190.29; MS (EI)  $m/z$  (%): 164 (74), 118 (100), 90 (77).

#### 2-fluoro-4,4-dimethylcyclohexan-1-one (6f)



Prepared by the general procedure at 25 °C for 168 h. The reaction mixture was diluted with ethyl acetate, and washed, dried, filtered, and concentrated. The purification of the residue by flash column chromatography afforded the product as a white crystal (10.1 mg, 35% yield.). m. p. = 80.2-81.2 °C.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>):  $\delta$  5.02 (ddd,  $J$  = 48.0 Hz, 12.0 Hz, 6.6 Hz, 1 H), 2.51 (td,  $J$  = 13.8 Hz, 6.0 Hz, 1 H), 2.46-2.41 (m, 1 H), 2.21-2.16 (m, 1 H), 1.81-1.59 (m, 3 H), 1.24 (s, 3 H), 1.10 (s, 3 H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  205.9 (d,  $J$  = 14 Hz), 90.2 (d,  $J$  = 188 Hz), 46.1 (d,  $J$  = 16 Hz), 39.1, 36.4, 32.2 (d,  $J$  = 10 Hz), 31.0, 24.6; **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>):  $\delta$  -193.50; **HRMS** (ESI)

$m/z$  calculated for  $C_8H_{13}FONa$   $[M+Na]^+$  167.0843, found 167.0846; MS (EI)  $m/z$  (%): 144 (40), 125 (5), 55 (100).

### 3.6 The detailed structural determination of products (4a, 4b, and 5a)

In order to determine the stereochemistry of three products (4a, 4b, and 5a), some 1D and 2D NMR experiments were conducted. For the details, please see below:

For products 4a and 4b:

Product 4a:

In order to rapidly identify the configuration of tri-substituted 2-fluoro cyclohexanones, Solladie-Cavallo and coworker extensively investigated the NMR data of these compounds,<sup>30</sup> resulting in the unambiguous assignment of the axial or equatorial position of the fluoro atom by the proton non-equivalence, the F-H and F-C coupling constants, and the values of  $^3J_{FH}$  and  $^4J_{FH}$ .

Generally, the four following conclusions could be applied for the determination of the configuration of tri-substituted 2-fluoro cyclohexanones.<sup>30</sup>

#### Rule 1:

*“The geometrical dependence of  $^3J_{FH}$ :  $^3J_{FH}$  axial/axial = 35-40 Hz (fluorine axial) >  $^3J_{FH}$  equatorial/axial = 13-13.5 Hz (fluorine equatorial) >  $^3J_{FH}$  axial/equatorial = 10-12 Hz (fluorine axial) >>  $^3J_{FH}$  (equatorial/equatorial) = 3-4 Hz (fluorine equatorial).”*

#### Rule 2:

*“The non-equivalence  $\Delta\delta_{6e-6a}$  (between H6e and H6a):  $\Delta\delta_{6e-6a}$  is positive when the fluorine atom is equatorial (+0.24 to +0.52 ppm) but negative when the fluorine atom is axial (-0.17 to -0.77 ppm).”*

#### Rule 3:

*“The tri-substituted ketones exhibit clear geometrical dependence of  $^4J_{FH}$  between F*

and protons H6 (with significantly different values of  $^4J_{FH}$ ):  $^4J_{FH}$  axial/axial = 6 Hz >  $^4J_{FH}$  equatorial/equatorial = 3-4 Hz >  $^4J_{FH}$  axial/equatorial = 1.5 Hz >  $^4J_{FH}$  equatorial/axial = 0 Hz.”

**Rule 4:**

“The one-bond coupling constant between F and C2 ( $^1J_{FC2}$ ) reflects the equatorial or axial position of C-F with a 10-14 Hz smaller value when the fluorine is axial ( $^1J_{FC2}$  = 171-172 Hz) than when the fluorine is equatorial ( $^1J_{FC2}$  = 182-186 Hz), .... , Similarly the two-bonds coupling constant between F and C1 ( $^2J_{FC1}$ ) reflects also the equatorial or axial position of C-F with a smaller value of  $^2J_{FC1}$  (16-18 Hz) when the fluorine is equatorial than when the fluorine is axial (24-25 Hz).”

According to the four conclusions deduced by Solladie-Cavallo, and the combination of the NMR spectra of products (**4a** and **4b**) and the fact that C-5 was not involved in the current fluorinated process, so the stereochemistry of products **4a** and **4b** were shown in Figure S2.

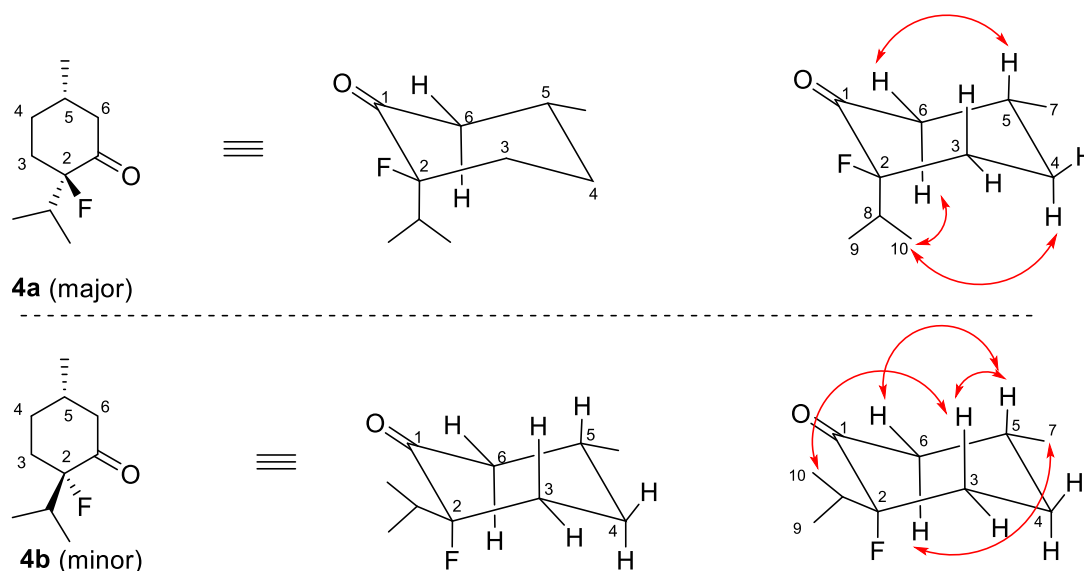


Figure S2 The chemical structures of products (**4a** and **4b**) and the corresponding NOE experiments

The detailed analyses of product **4a** were described as followed:

The corresponding NMR spectroscopic analysis of product **4a** ( $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, DEPT, COSY, HSQC, HMBC etc.) was carried out, and the chemical shifts of protons H-3 — H-10 and the  $J$  values were listed as follows:

H-3e (1.88-1.83, m), H-3a (1.41, ddd,  $J = 14.4$  Hz, 14.4 Hz, 3.6 Hz);

H-4a (2.35-2.29, m), H-4e (1.77, ddd,  $J = 13.2$  Hz, 13.2 Hz, 4.2 Hz);

H-5a (1.99-1.92, m);

H-6e (2.48, dddd,  $J = 13.2$  Hz, 4.8 Hz, 4.8 Hz, 2.2 Hz), H-6a (2.15, dd,  $J = 12.2$  Hz, 12.2 Hz);

H-7 (1.05, d,  $J = 6.0$  Hz);

H-8 (2.27-2.22, m);

H-9 (1.04, d,  $J = 6.6$  Hz);

H-10 (0.88, d,  $J = 6.6$  Hz);

The F atom is equatorial based on the following analyses.

- ① The value of  $^3J_{\text{FH}}$  of H-3 is 14.4 Hz, indicating that the F should be equatorial (Rule 1).
- ② The value of  $\Delta\delta$  (6e-6a) is  $0.32 > 0$ , indicating that the fluorine atom should be equatorial (Rule 2).
- ③ The value of  $^4J_{\text{FH-6}} = 0$  Hz, indicating that the fluorine atom should be equatorial (Rule 3).
- ④ From the  $J$  values ( $^1J_{\text{FC2}} = 191$  Hz and  $^2J_{\text{FC1}} = 10$  Hz of product **4a**), we could deduced that F should be equatorial (Rule 4), and this conclusion is further confirmed by the  $^1J_{\text{FC2}} = 181$  Hz and  $^2J_{\text{FC1}} = 24$  Hz of product **4b** (Rule 4).

Therefore, the isopropyl group at C-2 position should be axial.

Importantly, the NOE experiments was used to further assign the configuration of C-2

of product **4a**. The positive correlation between both H-6a/H-10 and H-4a/H-10 were observed, and the correlation between H-6e/H-5 was also observed. These experimental results indicated that the isopropyl group should be axial, which further confirmed the abovementioned conclusion.

As discussed above, the chemical structure of product **4a** is elucidated as shown in Figure S2.

**As a consequence, another isomer 4b should be assigned as shown in Figure S2.**

Actually, the similar analytical process of product **4b** have also been performed.

Based on the 1DNMR and 2DNMR, the chemical shifts of protons (H-3-H-10) and the *J* values of product **4b** were listed as follows:

H-3e (2.20-2.15, m), H-3a (1.78-1.63, m);

H-4 (1.78-1.61, m, 2 H);

H-5 (2.04-1.96, m);

H-6a (2.52, ddd, *J* = 12.4 Hz, 10.0 Hz, 6.4 Hz); H-6e (2.37, dd, *J* = 12.4 Hz, 4.4 Hz);

H-7 (1.04, d, *J* = 6.6 Hz);

H-8 (2.29-2.19, m);

H-9 (0.97, d, *J* = 7.2 Hz);

H-10 (0.94, d, *J* = 7.2 Hz);

The F atom is axial based on the following analyses.

- ① The combination of *J* value of H6a (12.4 Hz, 10.0 Hz, 6.4 Hz) and *J* value of H6e (12.4 Hz, 4.4 Hz.) could be concluded that the fluorine atom is axial (Rule 1). Moreover, the value of  $^4J_{\text{FH6}} = 6.4$  Hz is also in accordance with the above conclusion (Rule 3).
- ② The non-equivalence  $\Delta\delta_{\text{6e-6a}} = -0.16 < 0$ , indicating that the fluorine atom should be axial (Rule 2).
- ③ The combination of *J* values ( $^1J_{\text{FC2}} = 181$  Hz and  $^2J_{\text{FC1}} = 24$  Hz) could be determined

that F should be in axial (Rule 4).

④ Additionally, the NOE experiments of product **4b** were also used to further assign the configuration of C-2 of product **4b**. The positive correlation between H-6a/H-7 was observed, indicating that H-5 should be axial. Importantly, the NOE correlation of both H-5a/H-3a and H-3a/H-10 could be concluded that isopropyl group should be axial.

For product **5a**:

Because the stereocenters at C-3 and C-5 position of the starting material **5** is not involved in the current fluorinated process, the stereochemistry of C-2 was proposed as followed:

In principle, the relative stereochemistry of C-2 of the compound **5a** might be elucidated in terms of the coupling constant between H-3 and F-2 as well as the NOE experiments.

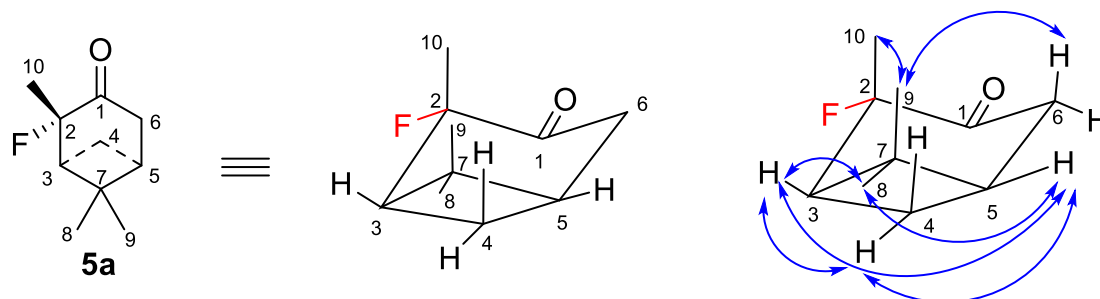


Figure S3. The chemical structures of product **5a** and the corresponding NOE experiments

The corresponding NMR spectroscopic analysis of product **5a** ( $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, DEPT, COSY, HSQC, HMBC etc.) was carried out first, and the chemical shifts of protons (H-2 - H-10) and the J values of compound **5a** were listed as follows:

H-3 (2.32, ddd,  $J = 6.0$  Hz, 6.0 Hz, 4.0 Hz).

H-4a (1.68, dd,  $J = 11.2$  Hz, 1.2 Hz); H-4e (2.53-2.47, m);

H-5 (2.18-2.14, m);

H-6 (2.660-2.656, m, 2H)

H-8 (1.39, d,  $J = 0.8$  Hz);

H-9 (0.87, s);

H-10 (1.49, d,  $J = 25.2$  Hz).

① Apparently, it can be seen that the  $^3J$  (H-F) was less than 8.0 Hz, implying the cis configuration between H-3 and F-2 as shown in Figure S3 (Note: Generally,  $^3J_{a,e}$  (H-F) more than 10 Hz in cyclohexane ring system). If the F-2 stereochemistry was reversed, the value of  $^3J$  (H3-F2) would be usually more than 10 Hz in the more favorable conformation (Note:  $^3J_{a,e} > 10$  Hz in cyclohexane ring system). So, we can conclude a cis-configuration at F-2 and H-3 in compound **5a**.

② In addition, the NOE experiment was used to further assign the stereochemistry of C-2.

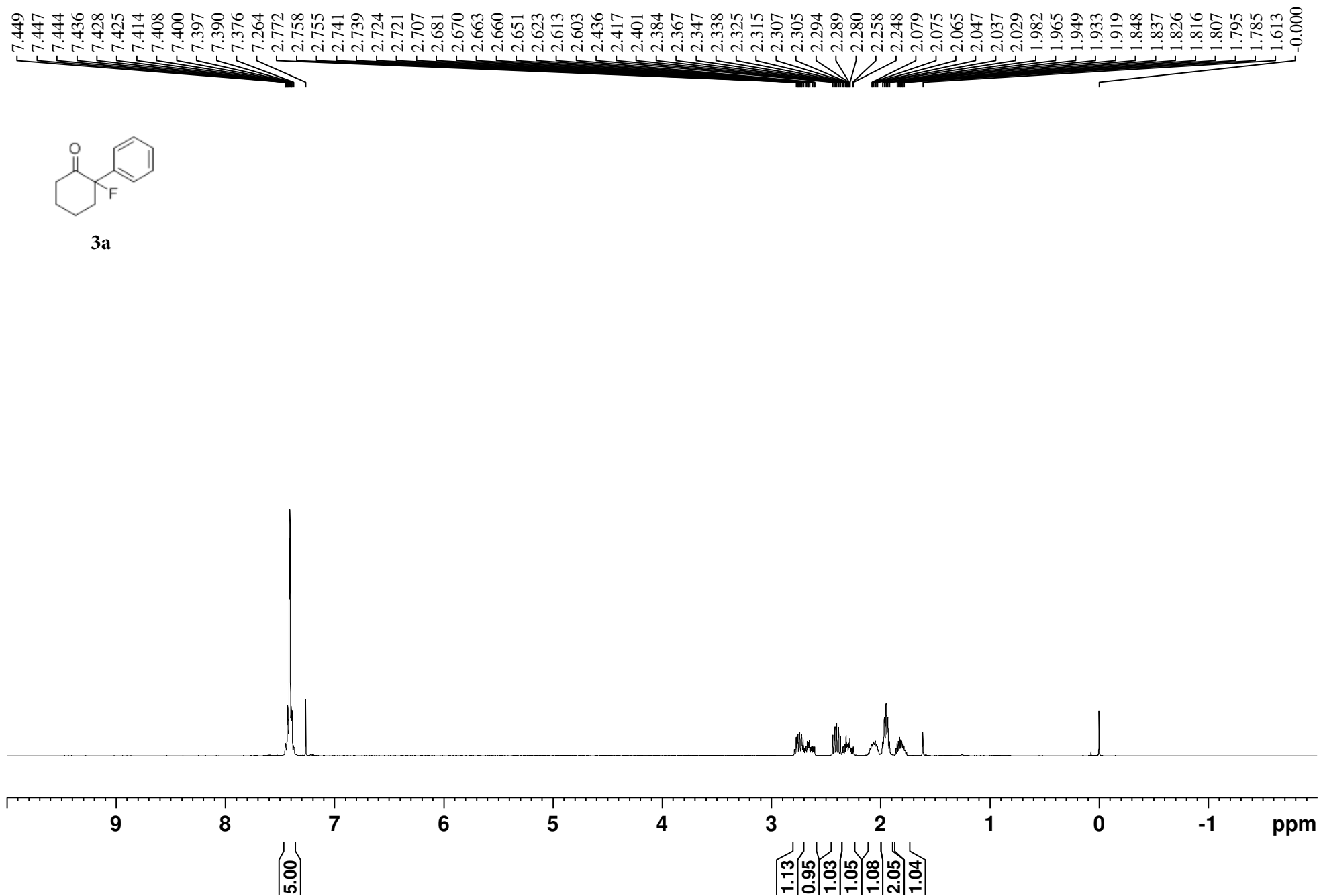
a) The obvious NOEs between H8/H-3, H8/H-5 and H8/H4 were observed for product **5a**, and these results indicate CH<sub>3</sub>-8 should be equatorial, therefore CH<sub>3</sub>-9 should be axial.

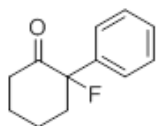
b) The obvious NOEs between H-9/H-10 and H-10/H-6 were observed in product **5a**, and these results indicate CH<sub>3</sub>-10 should be axial.

In all, the structural identification of product **5a** based on NOE experiments is also consistent with the assignment of stereochemistry at C-2 using  $J$  value.

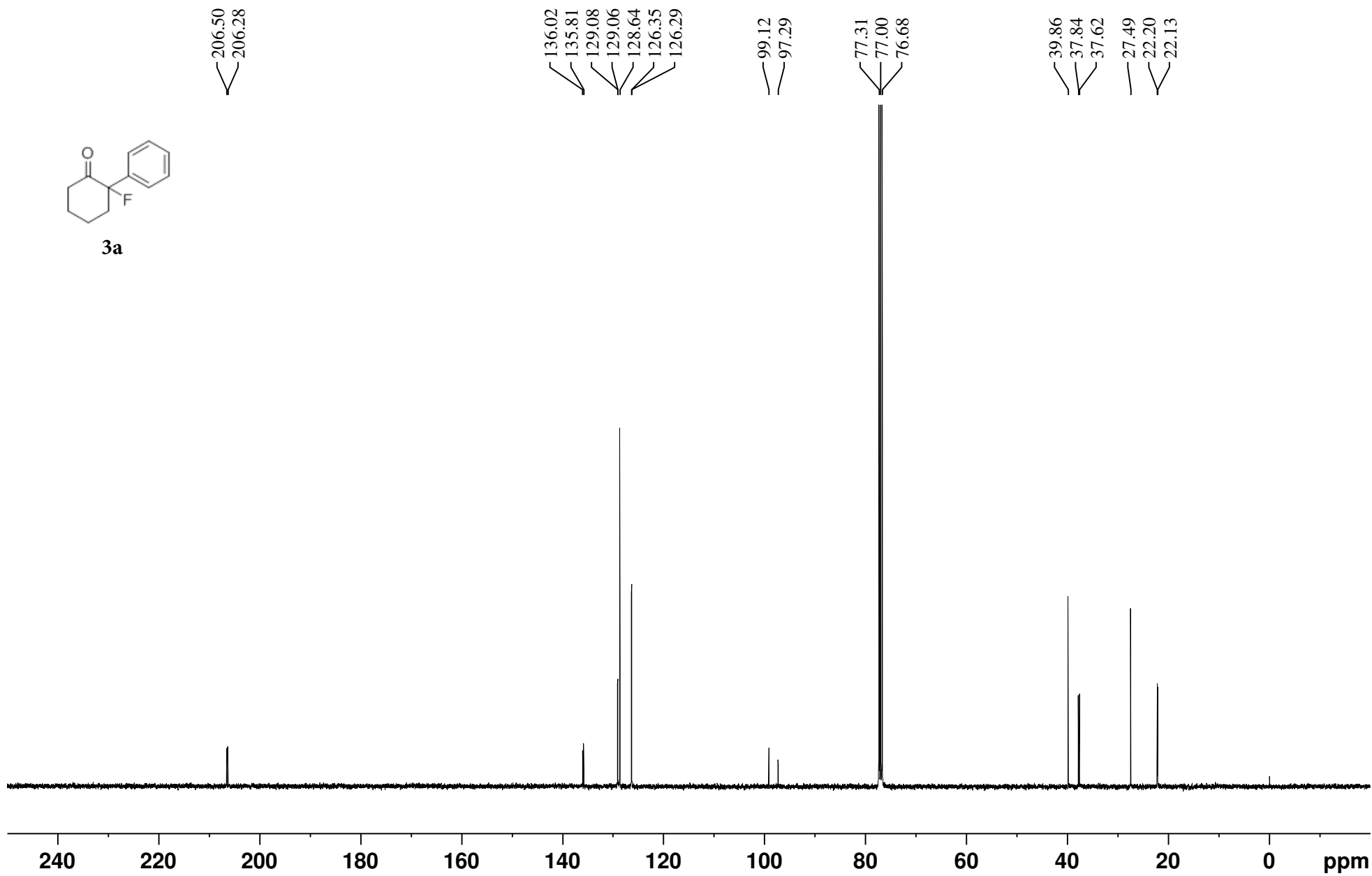
#### 4. References

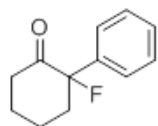
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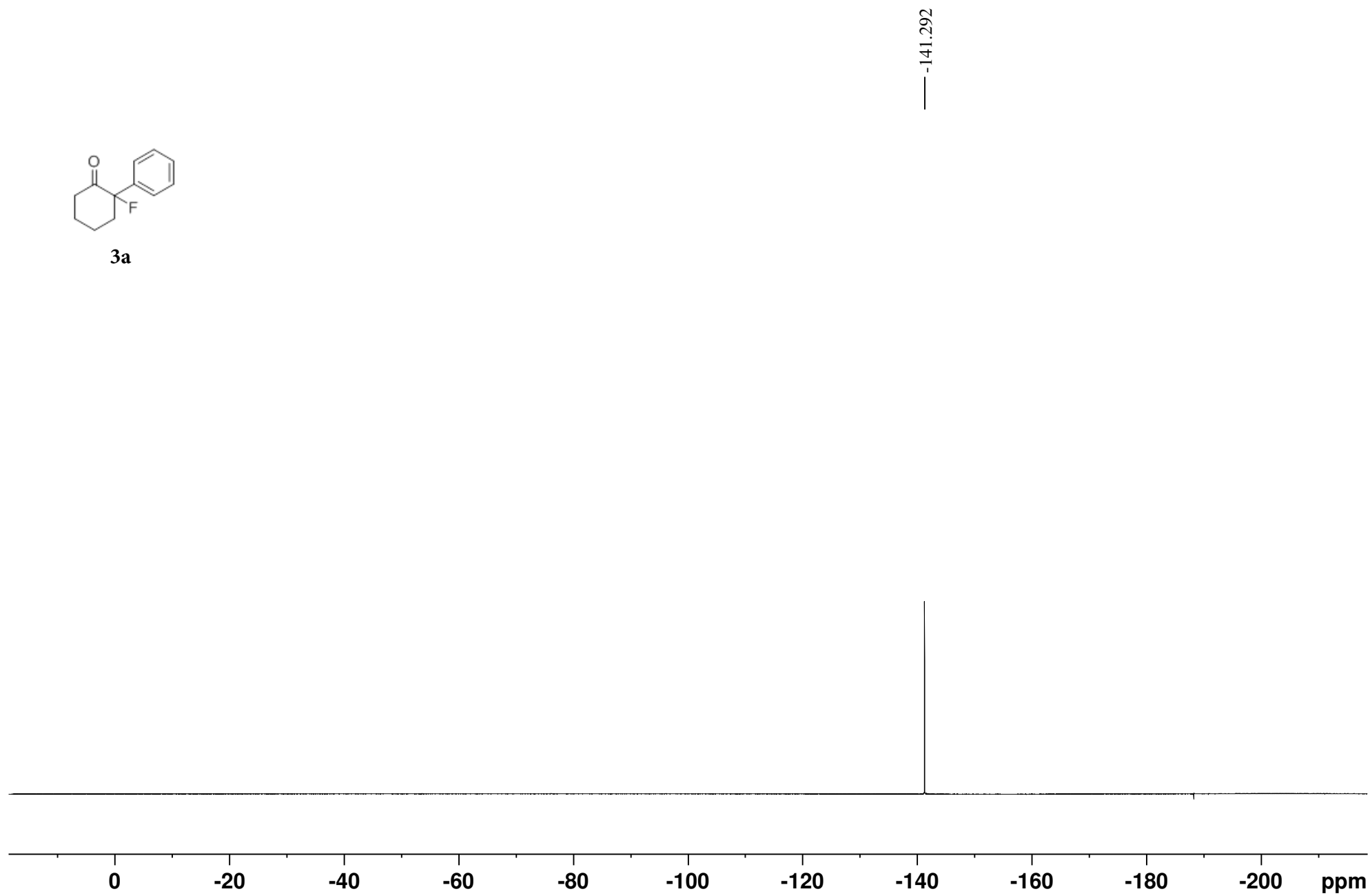


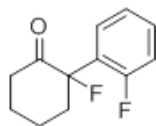
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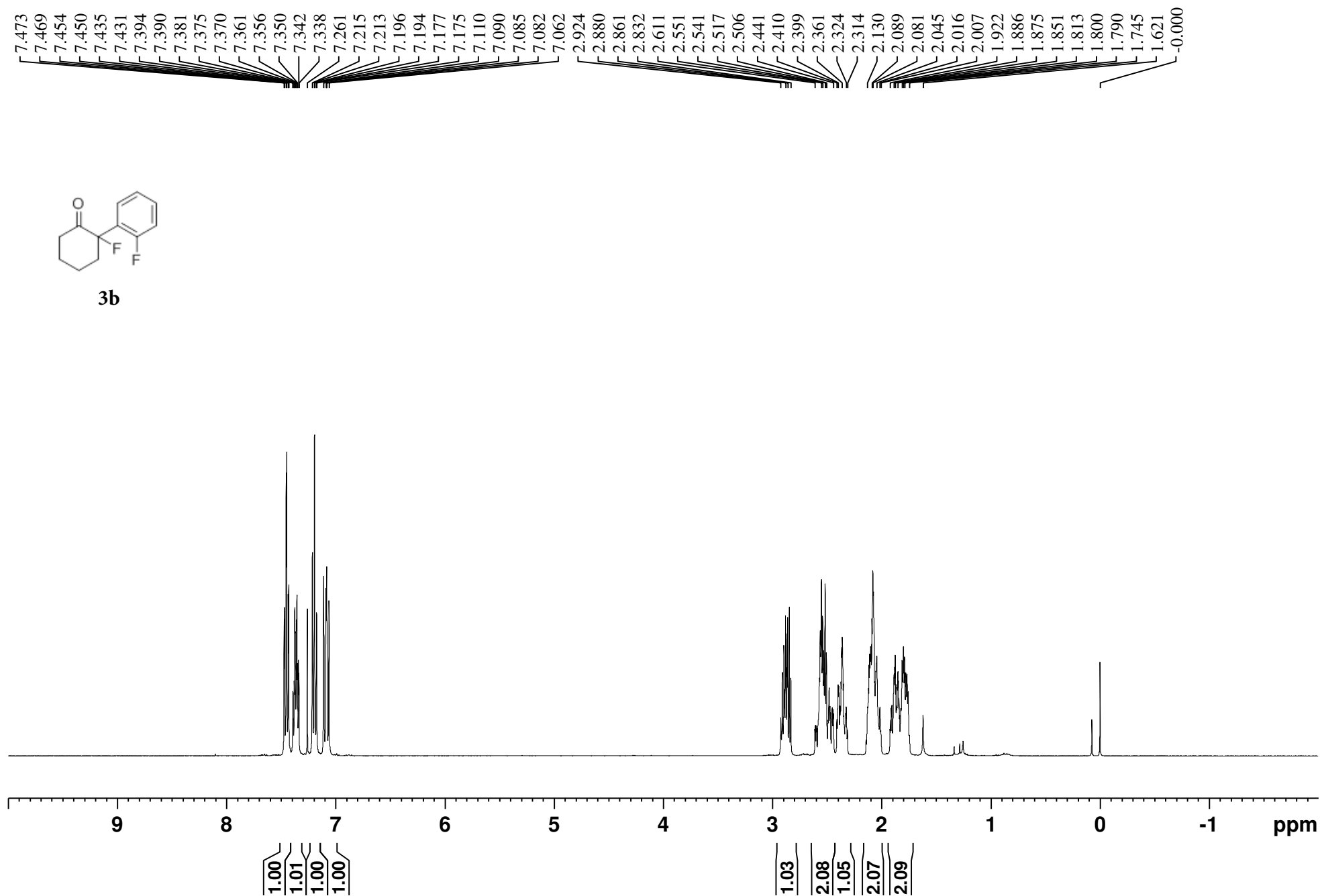


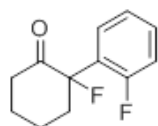
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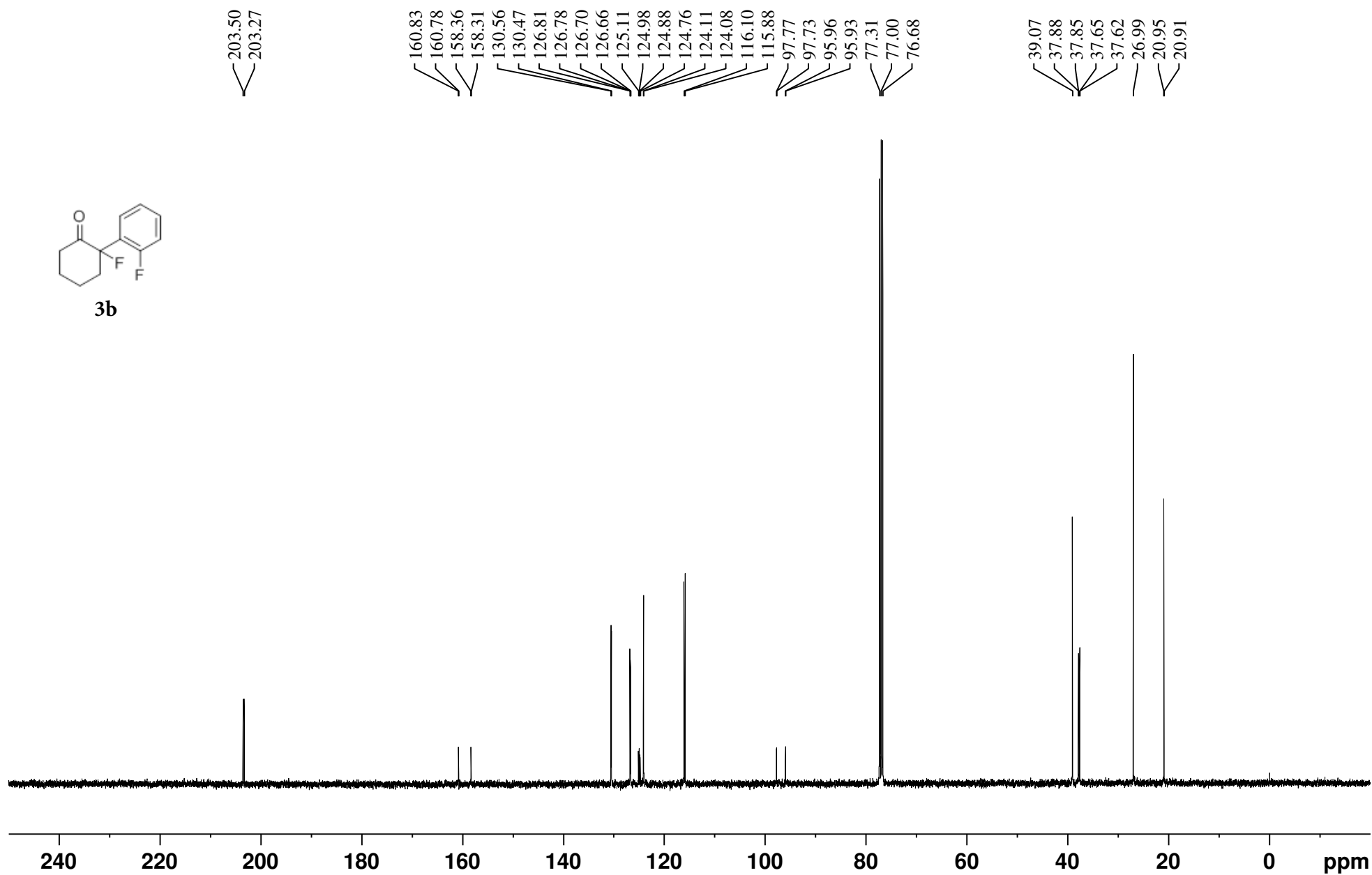


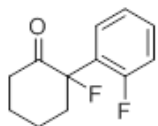
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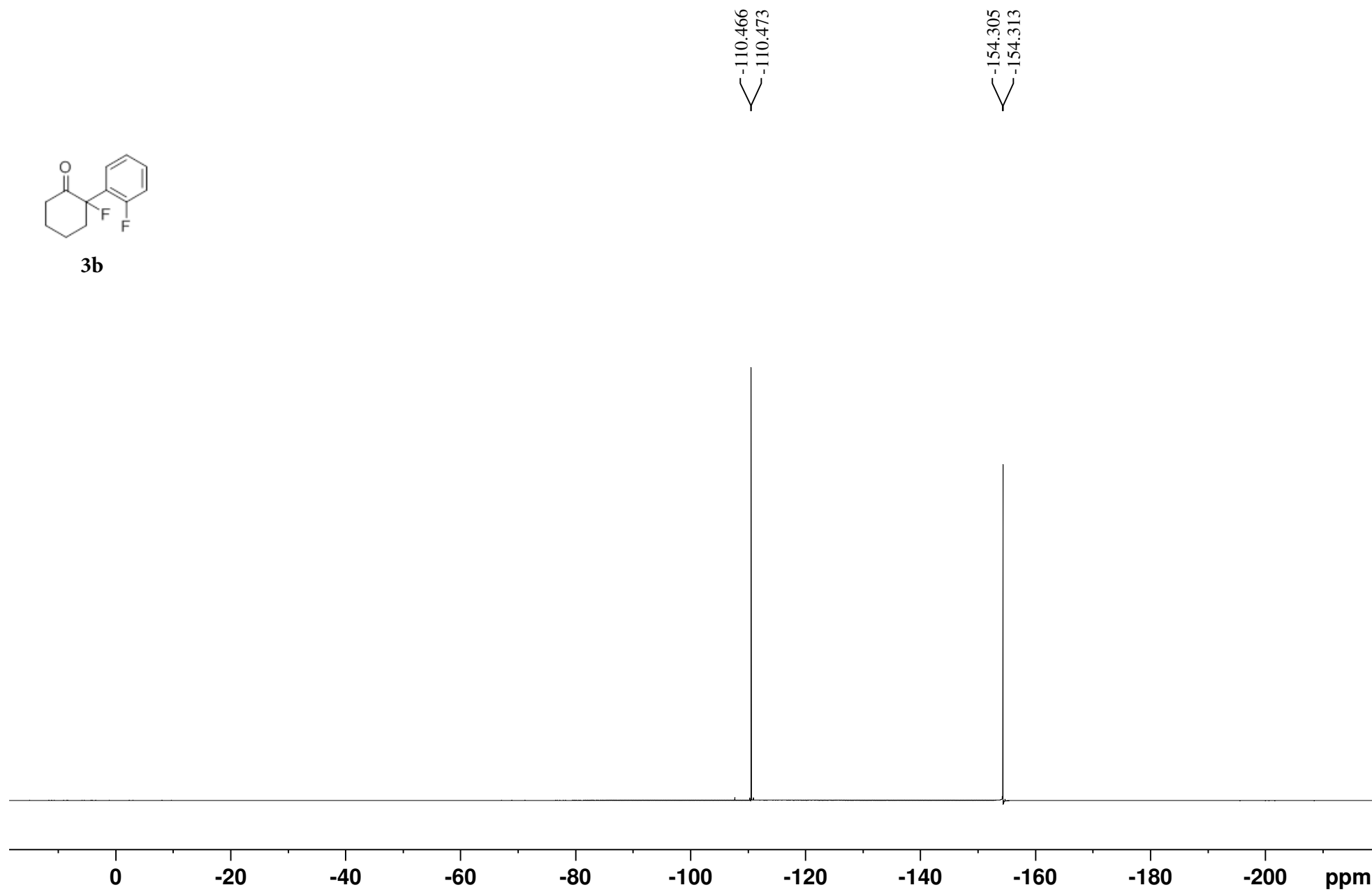


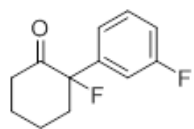
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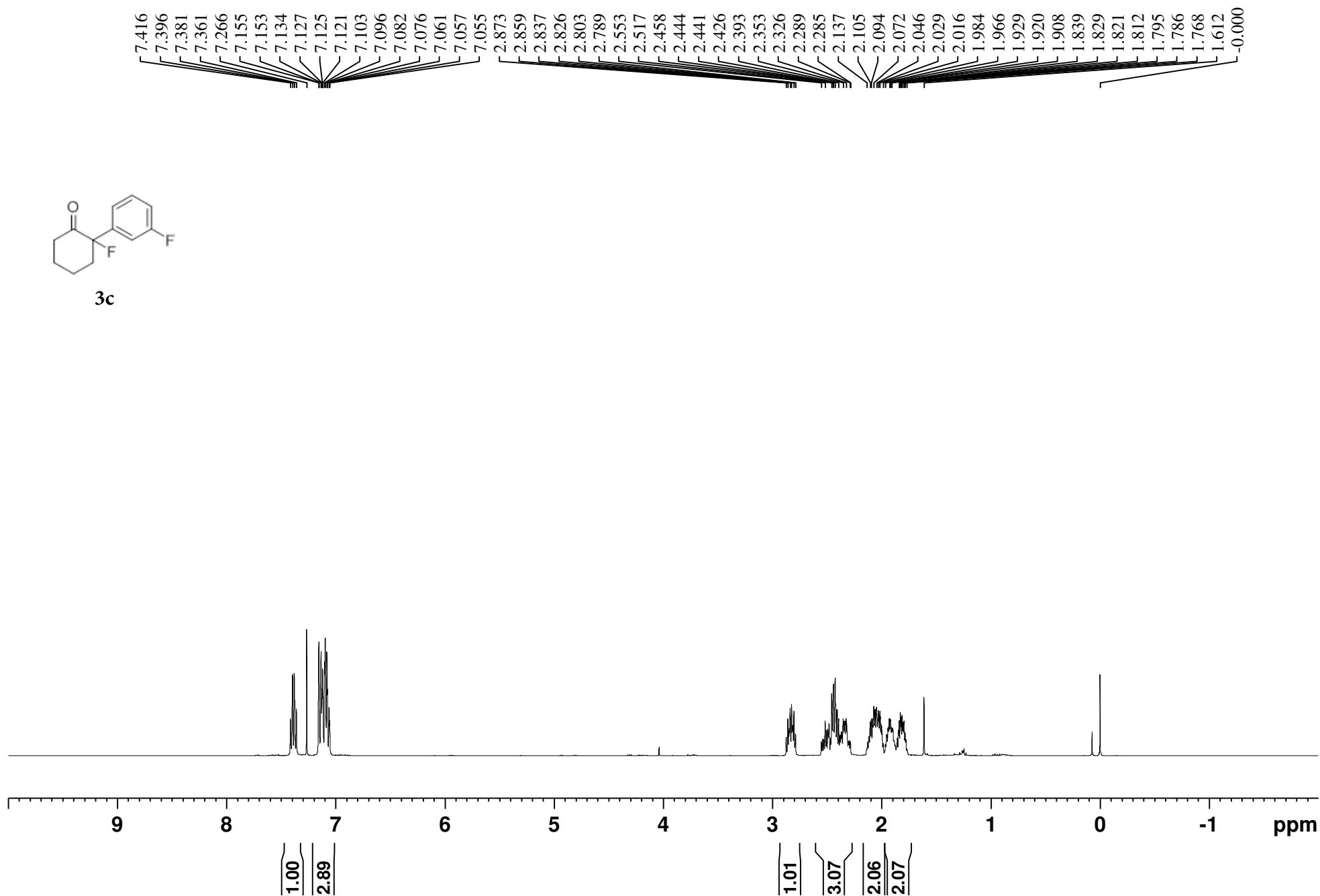


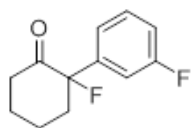
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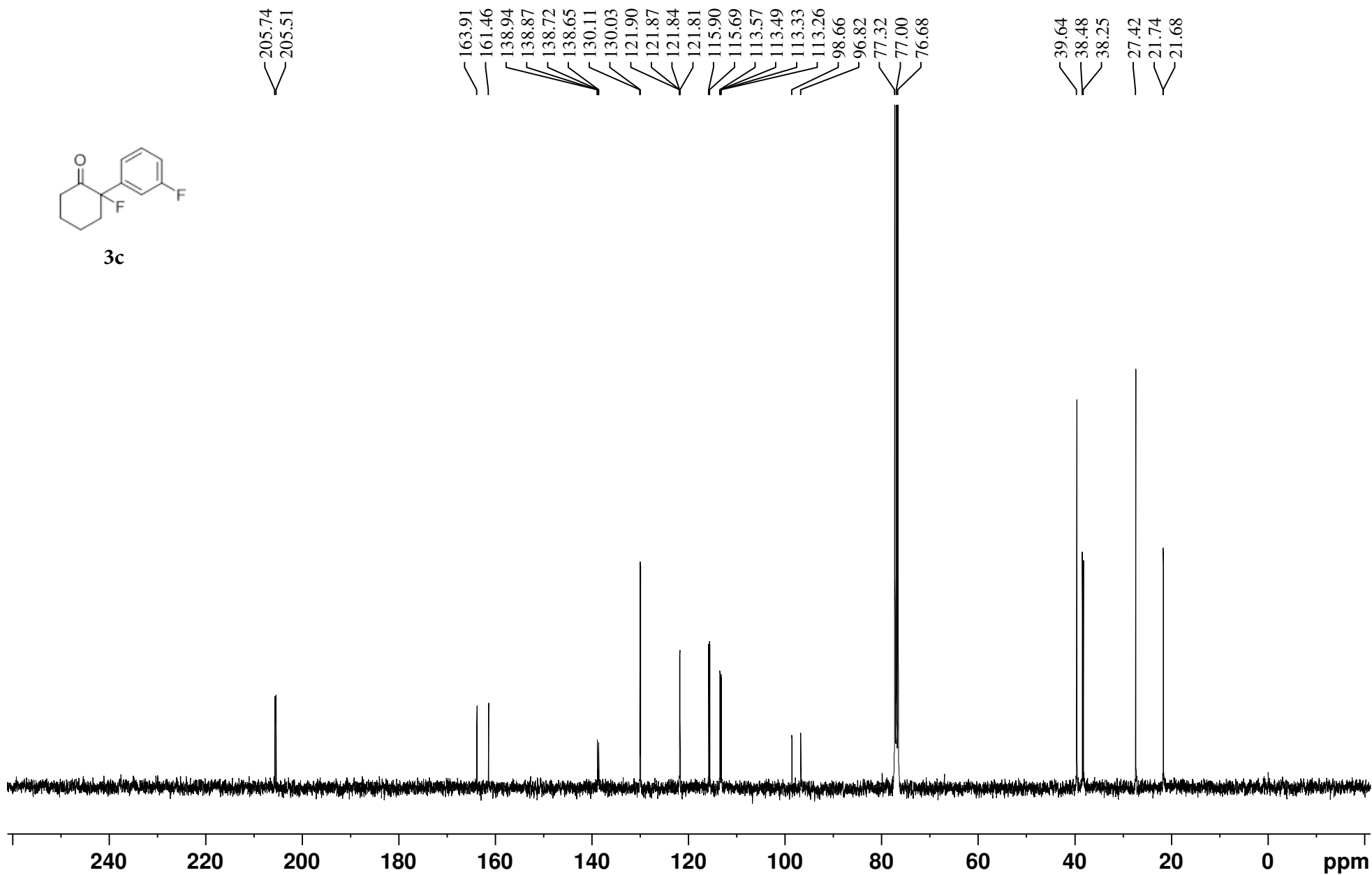


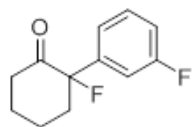
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3c

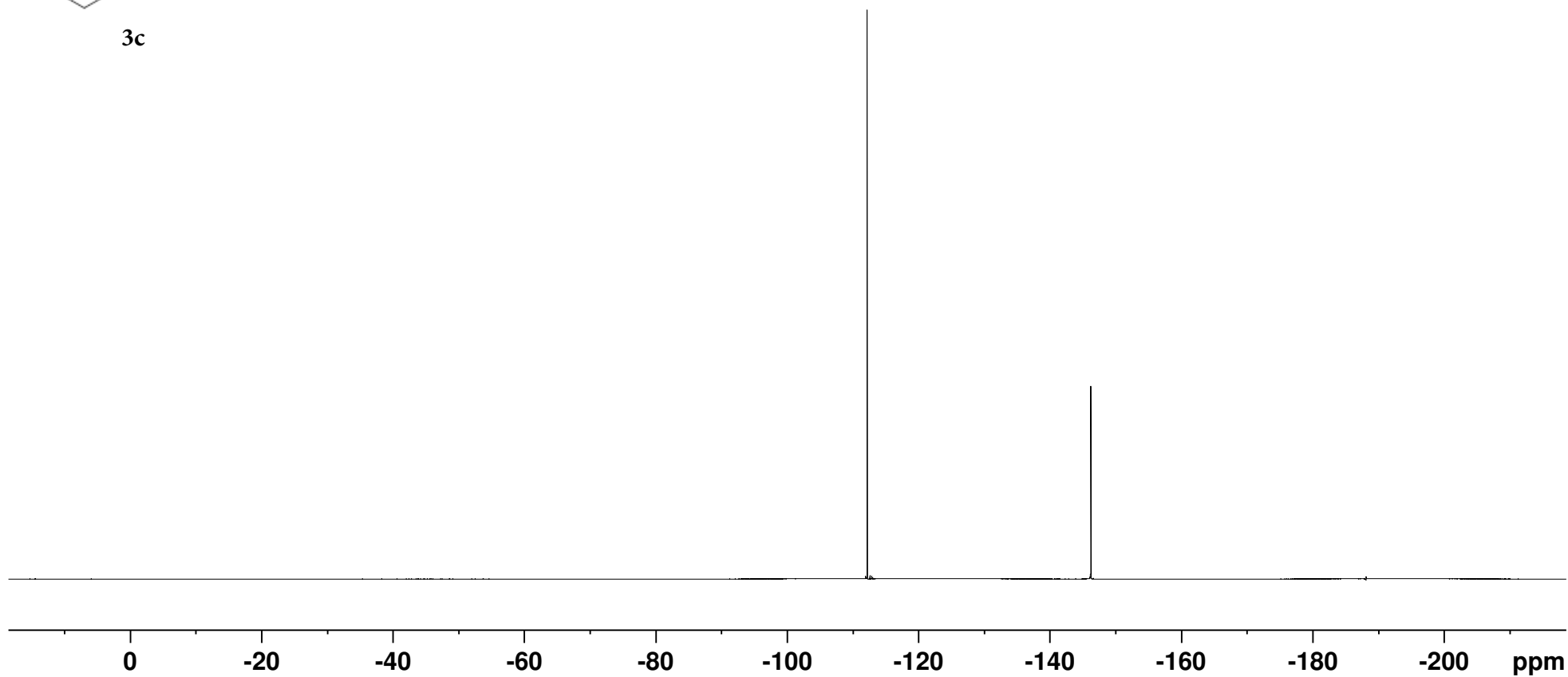


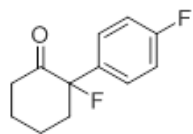


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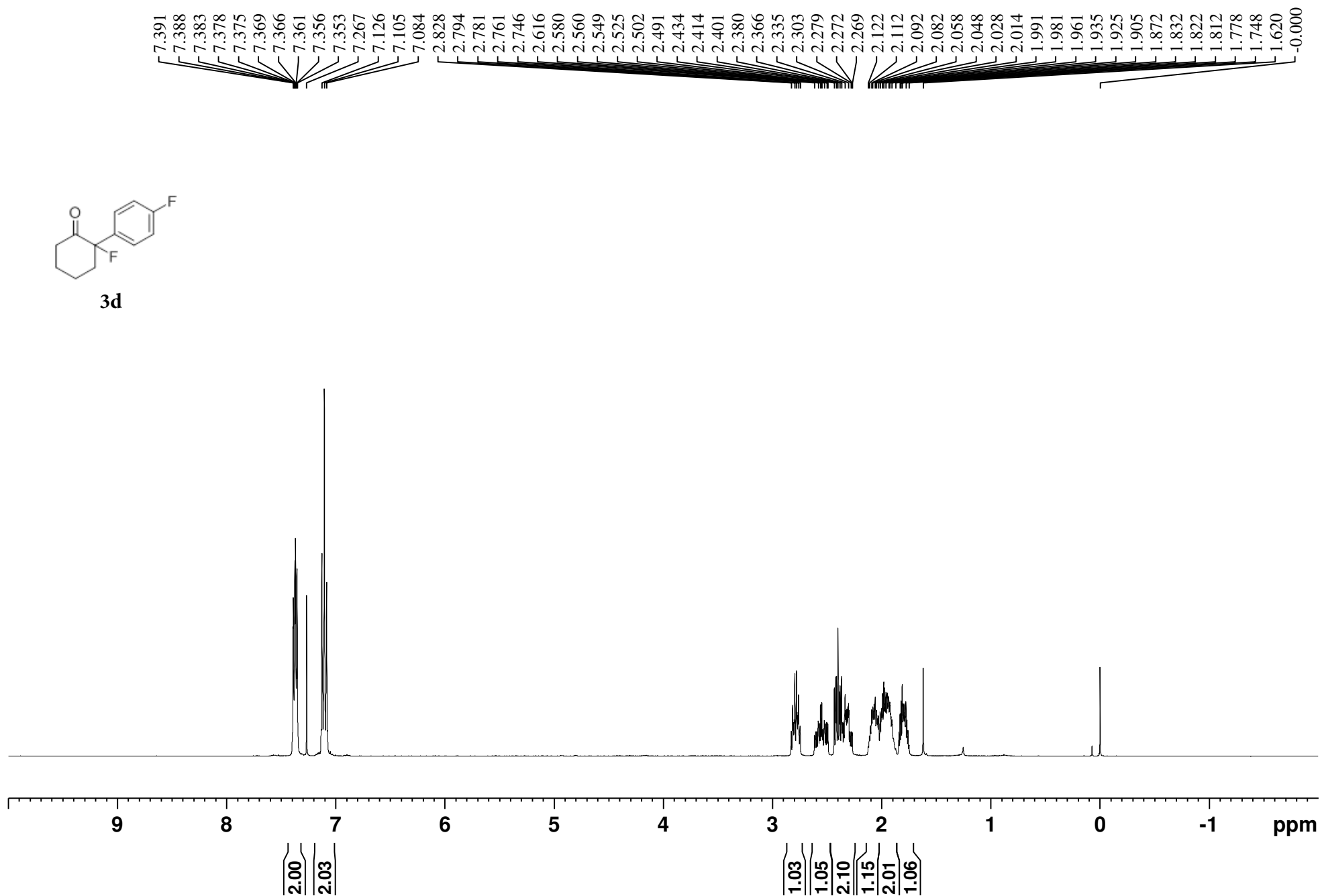
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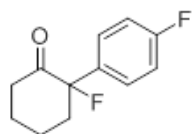
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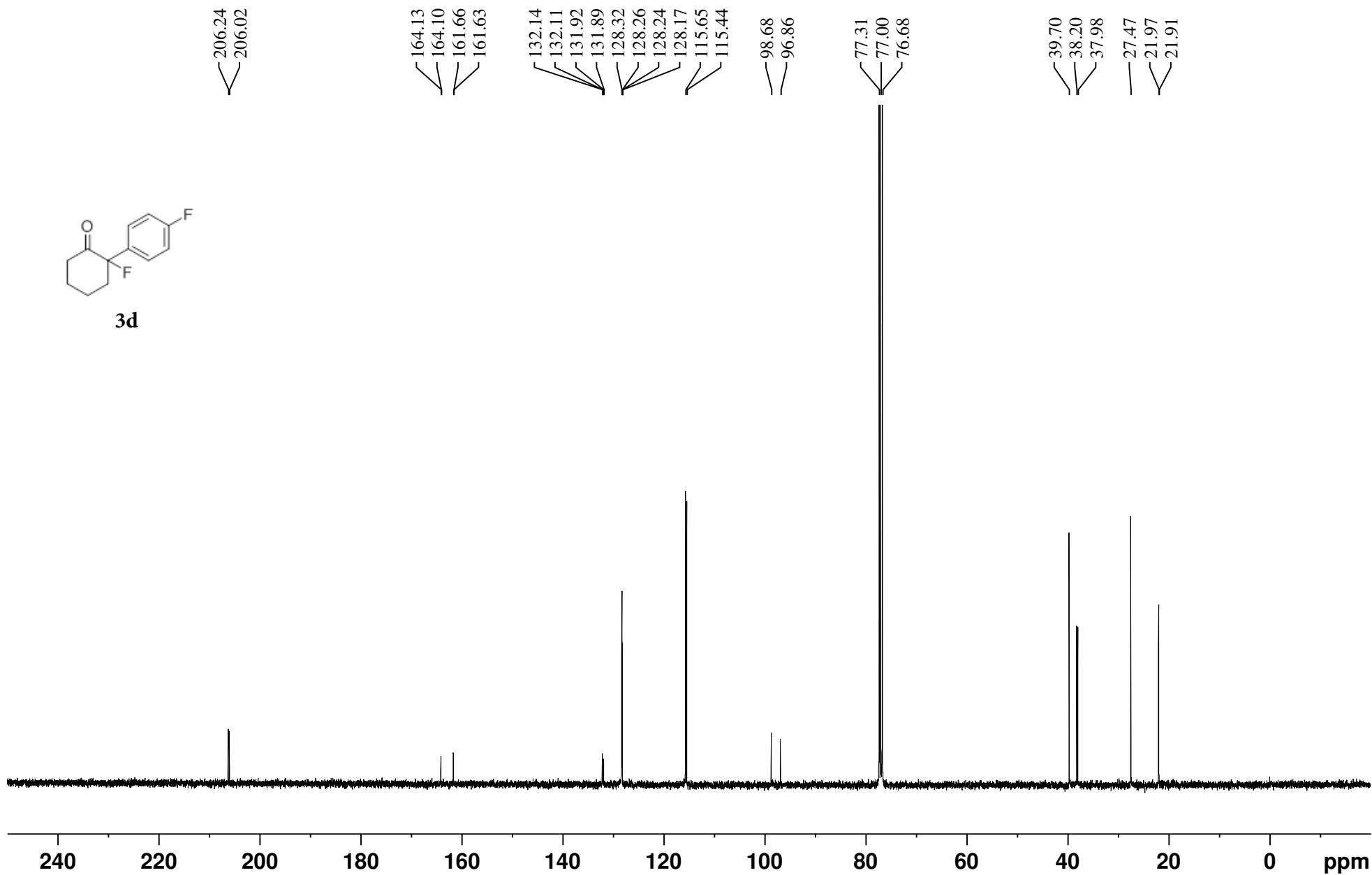


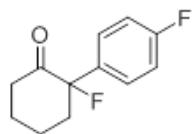
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**3d**

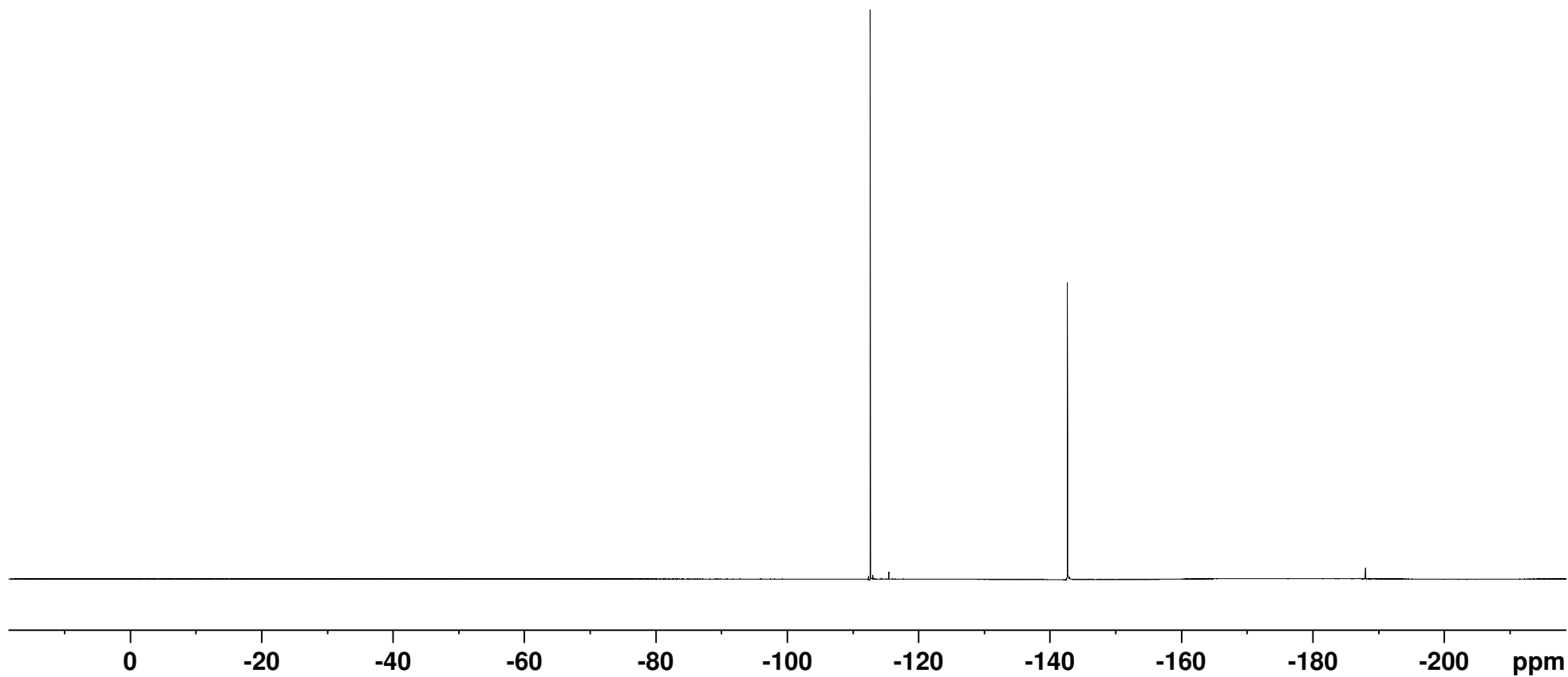


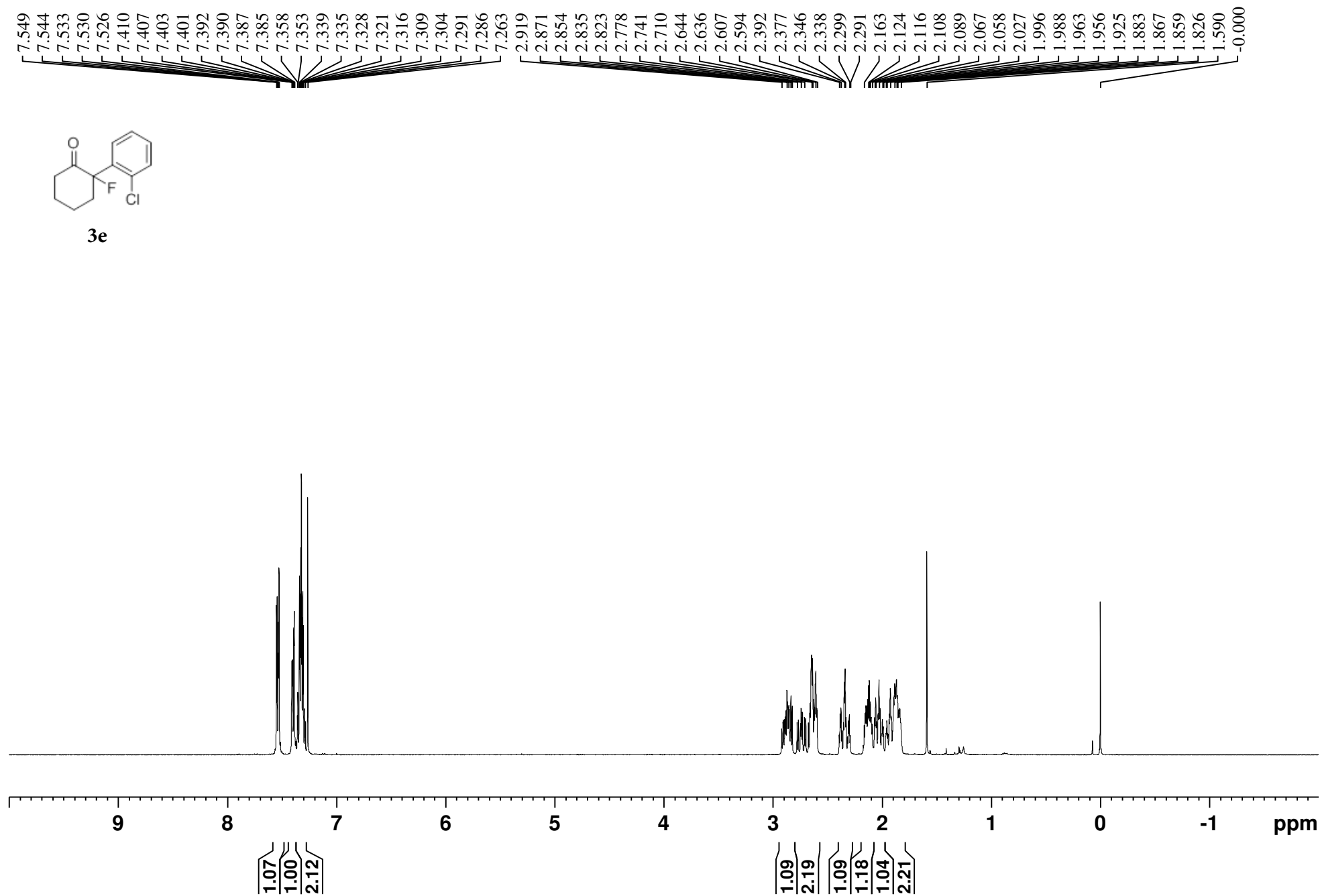


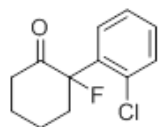
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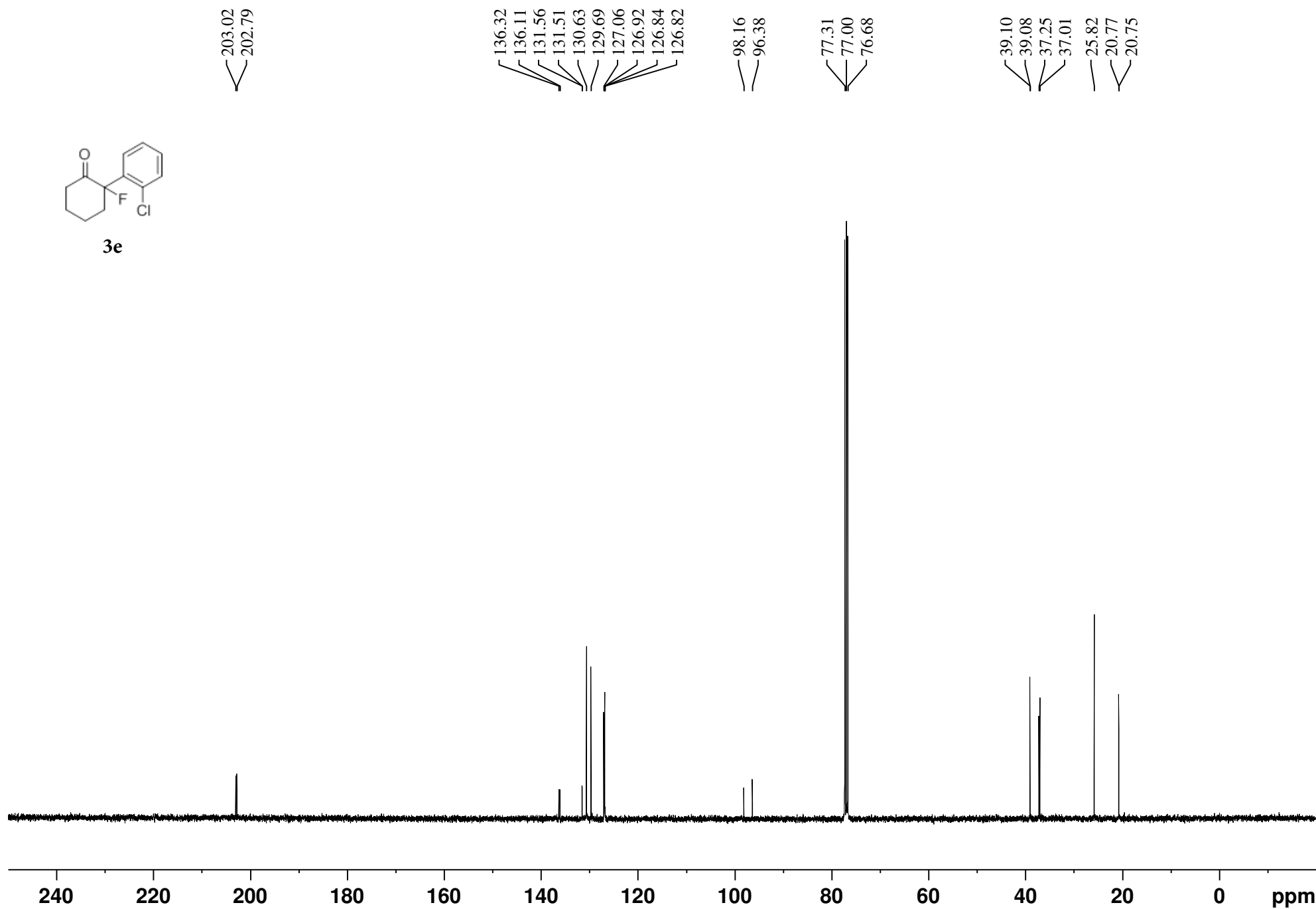
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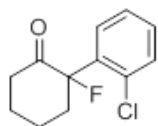




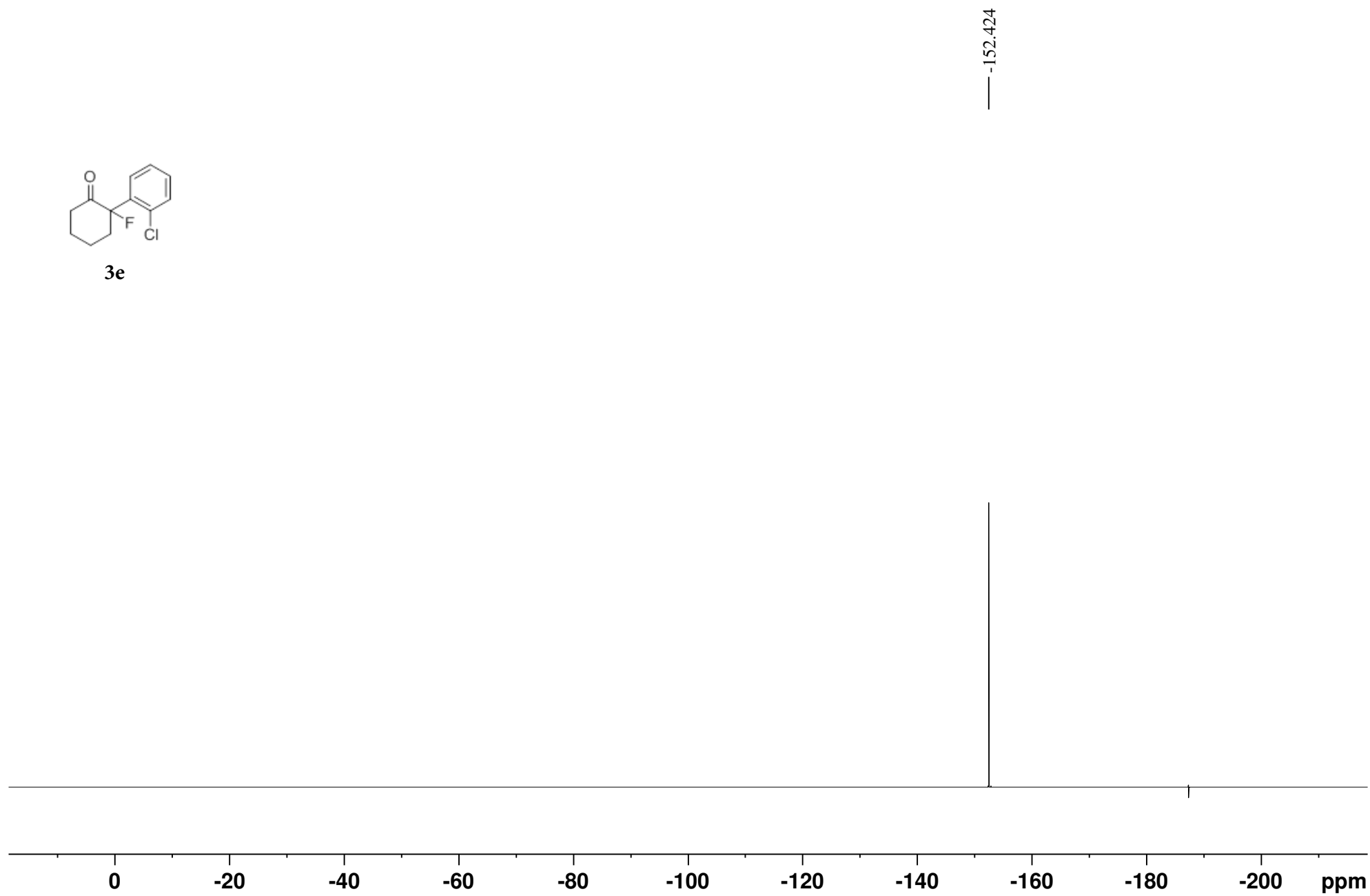


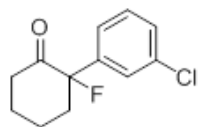
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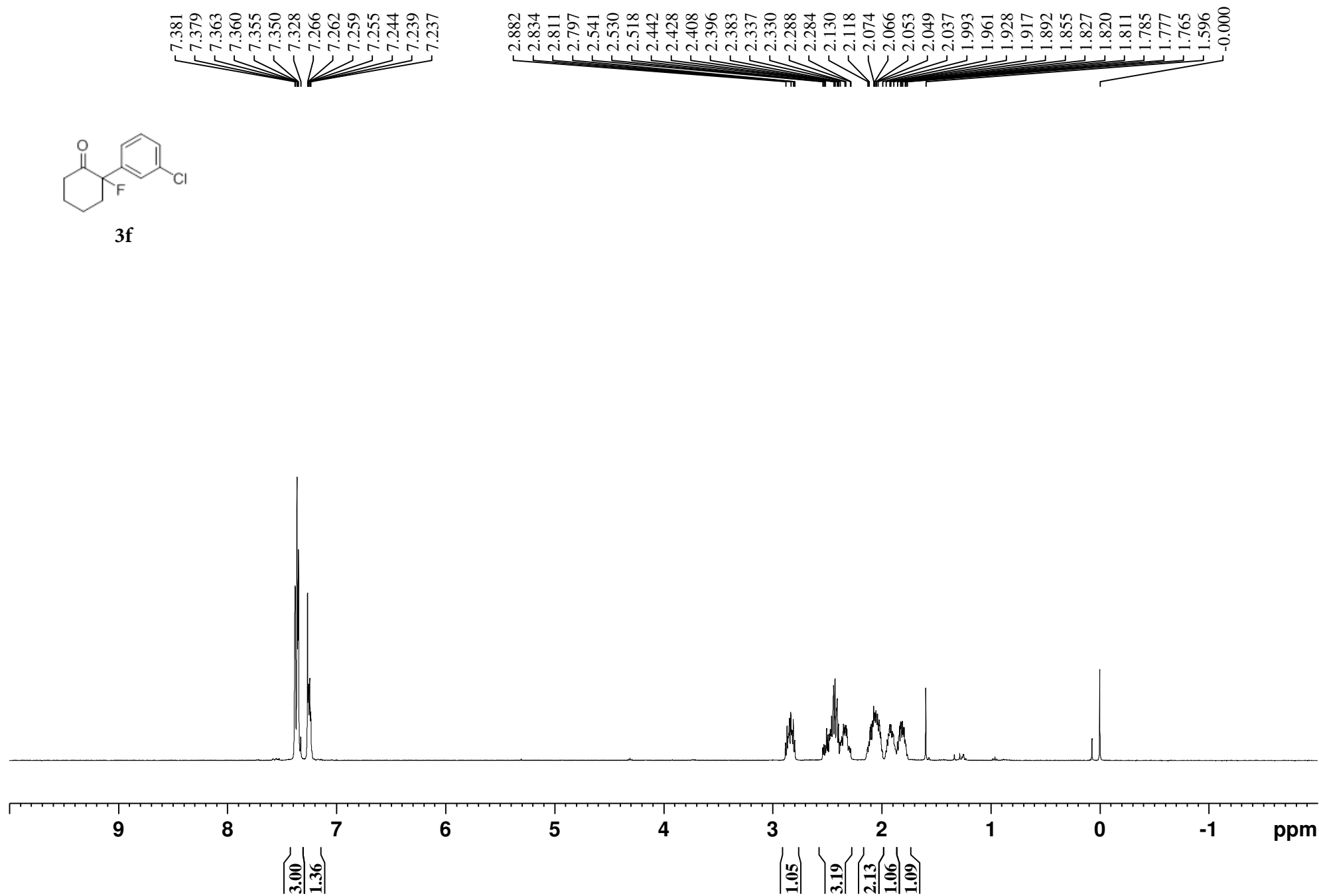


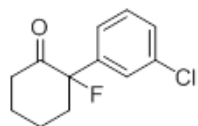
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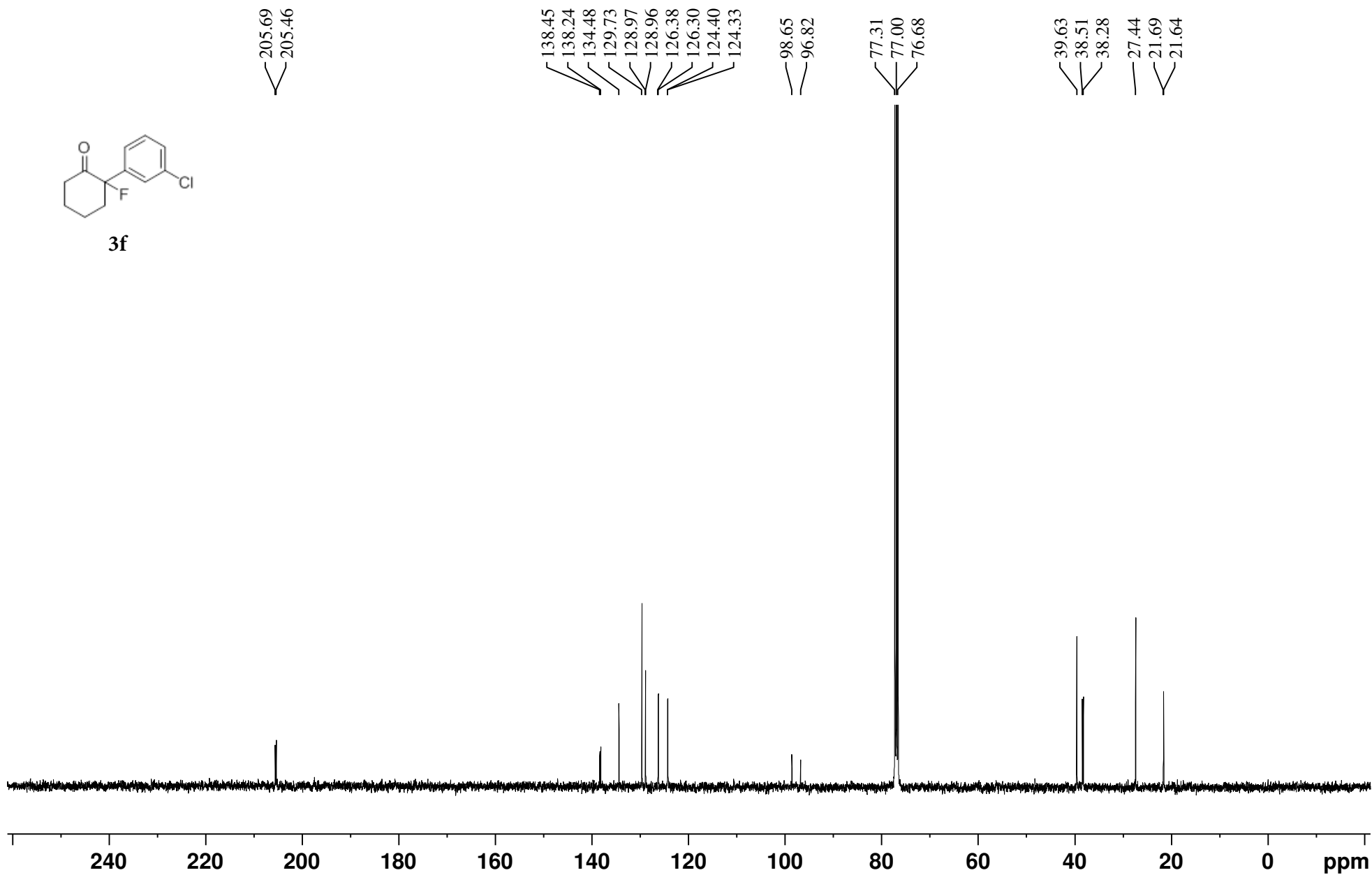


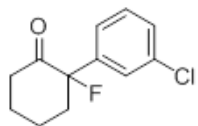
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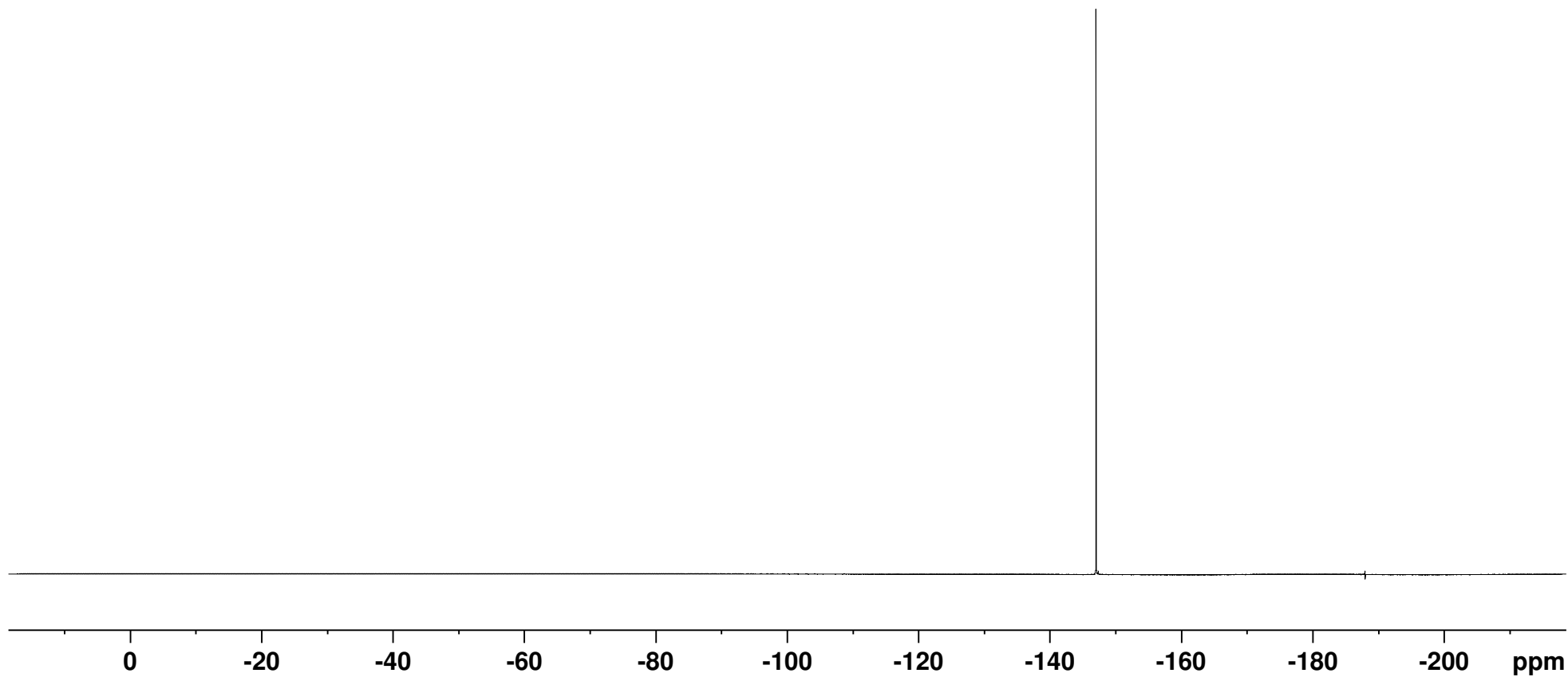
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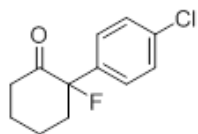




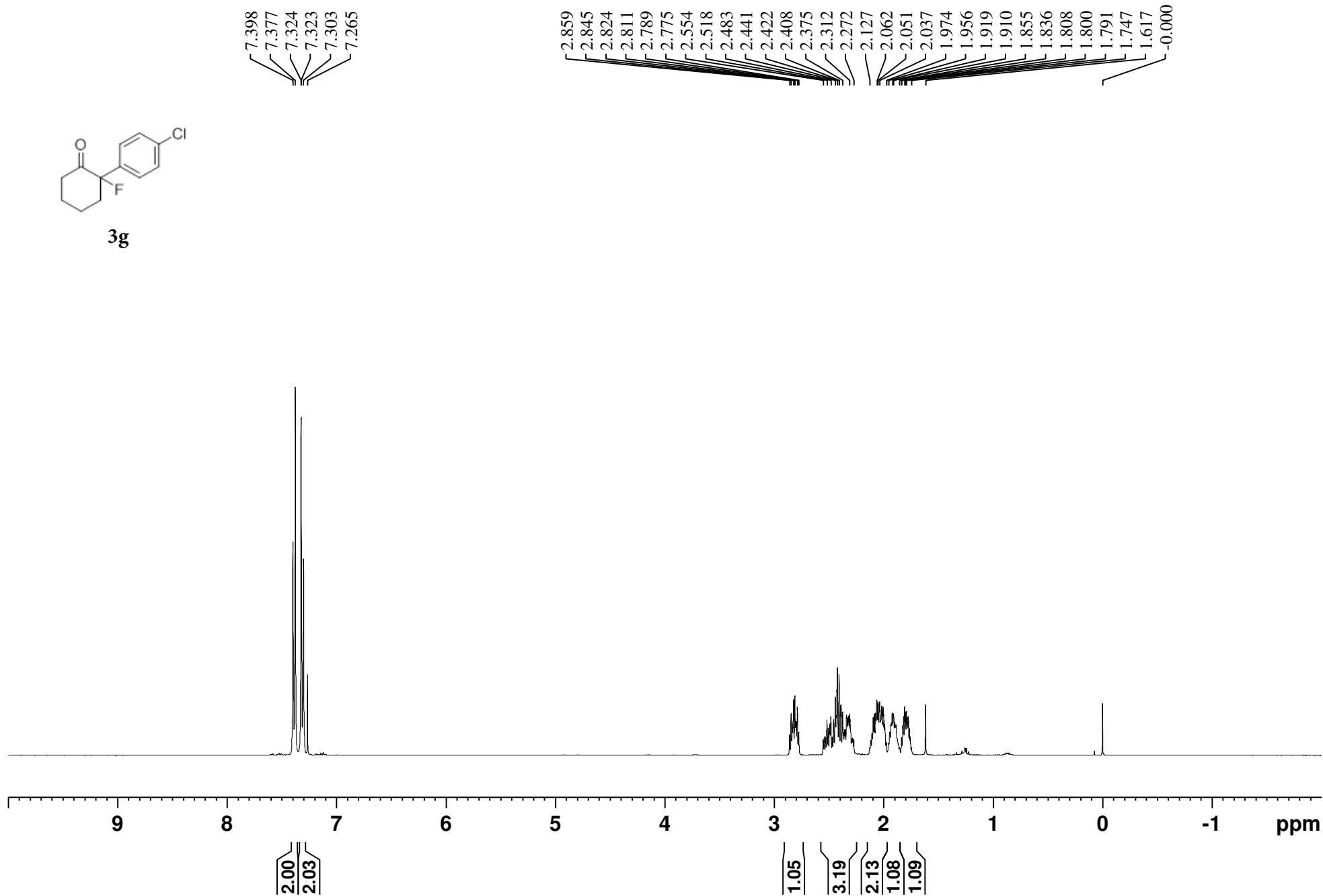
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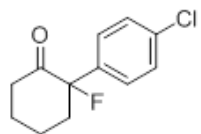
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3g





3g

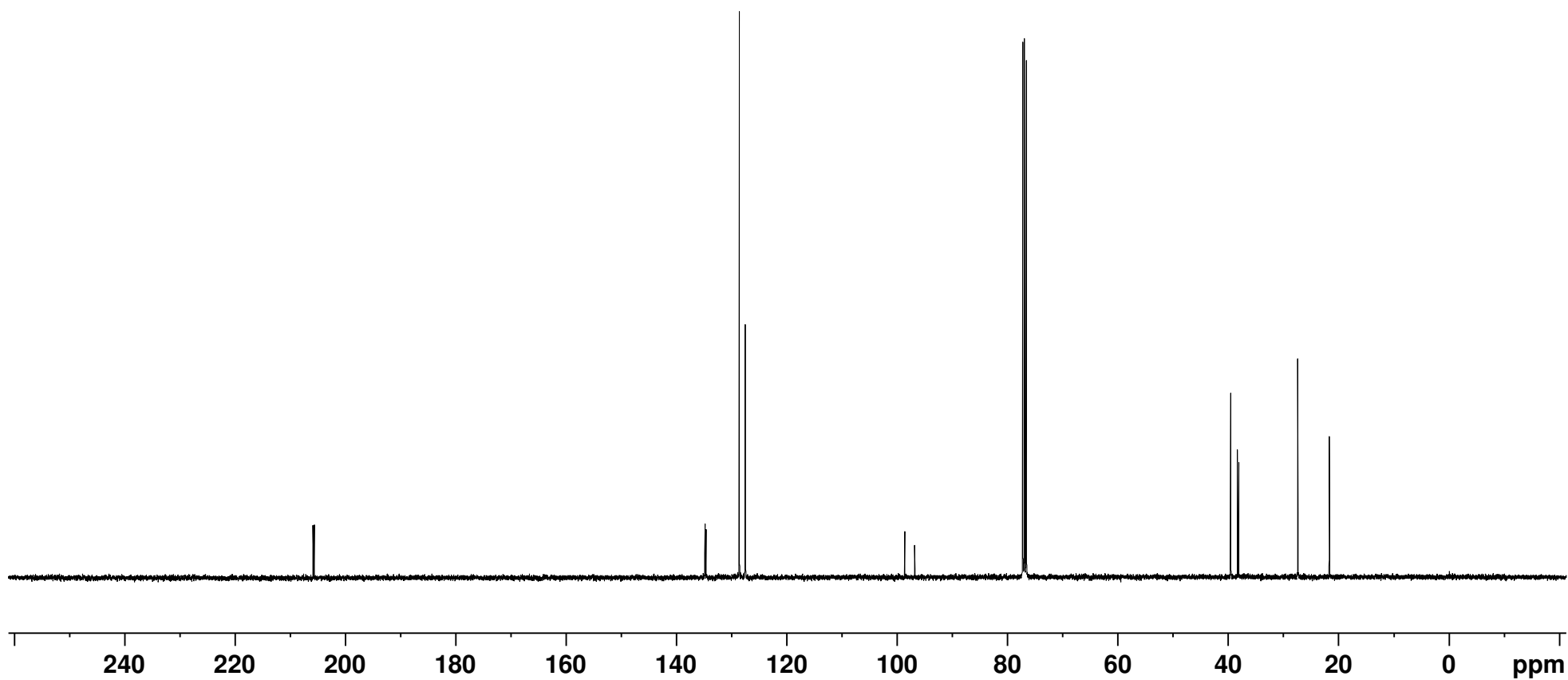
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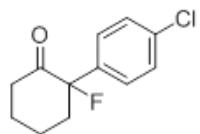
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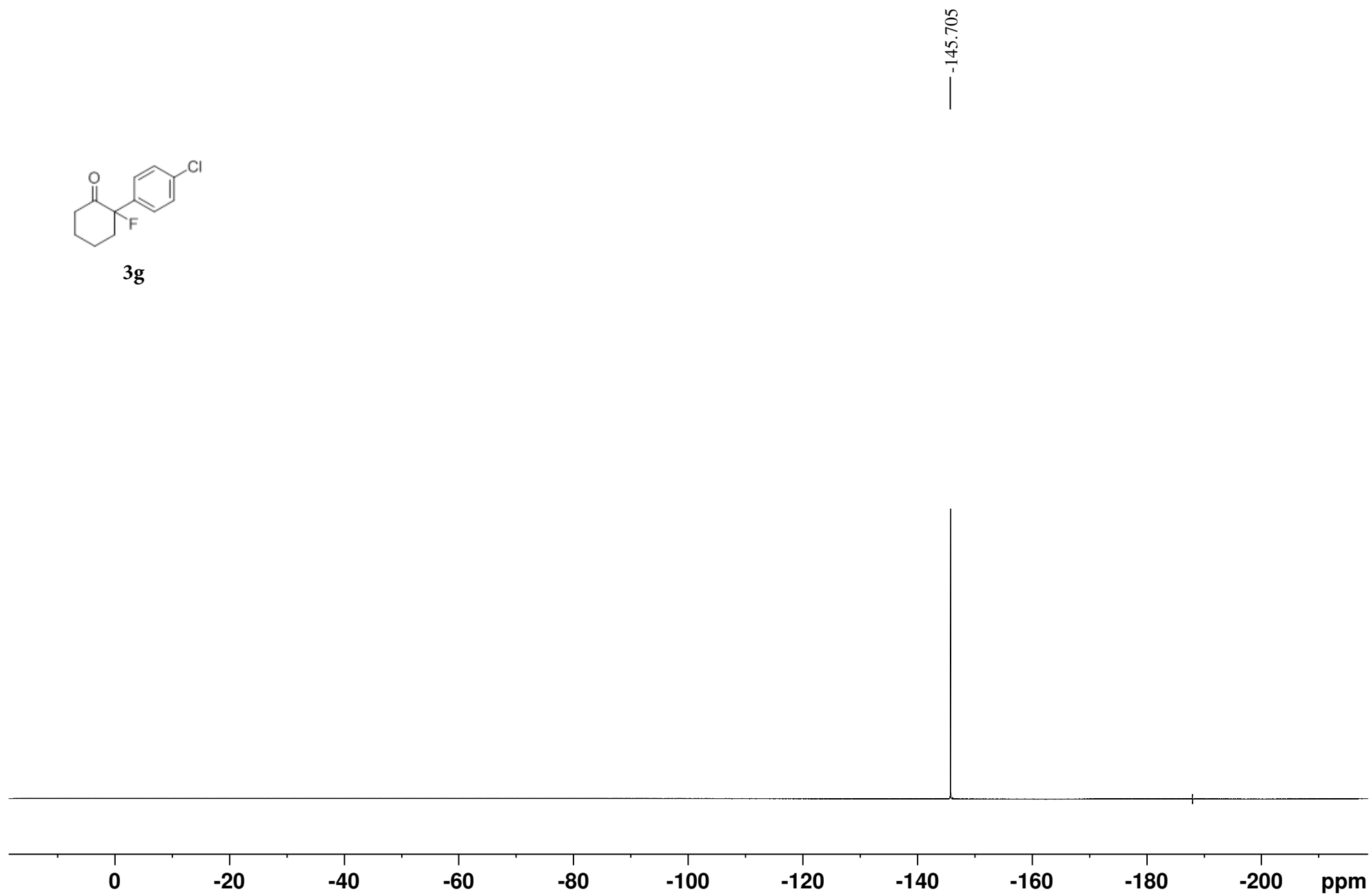
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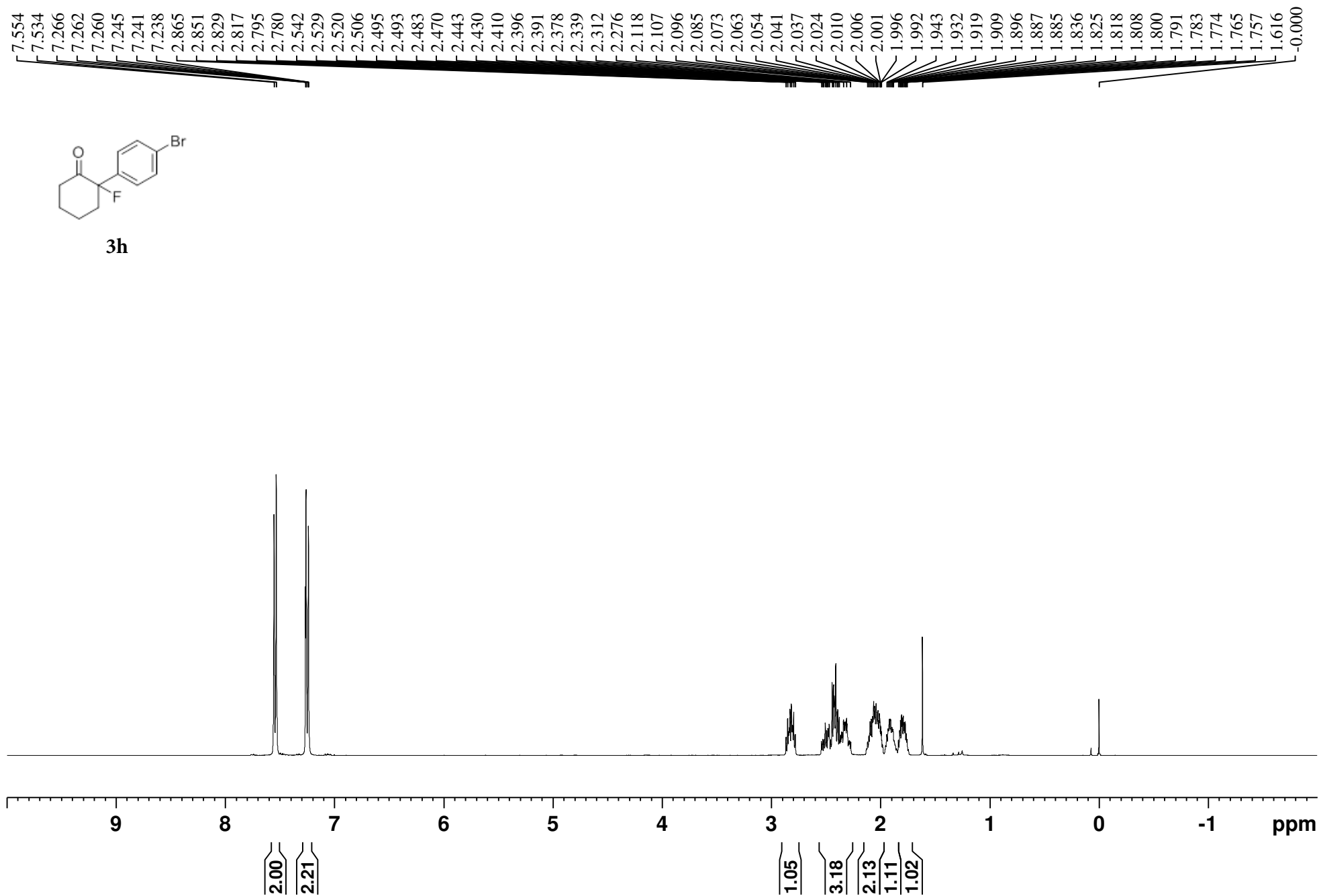
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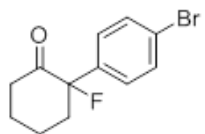




**3g**







**3h**

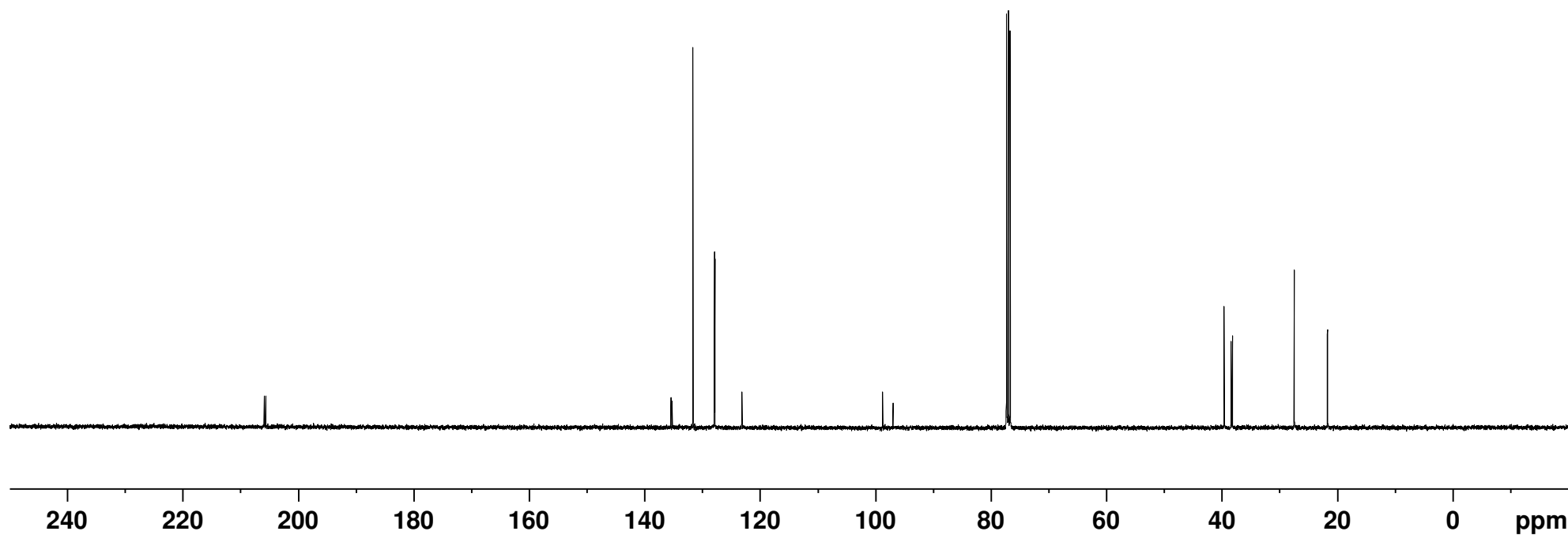
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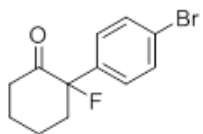
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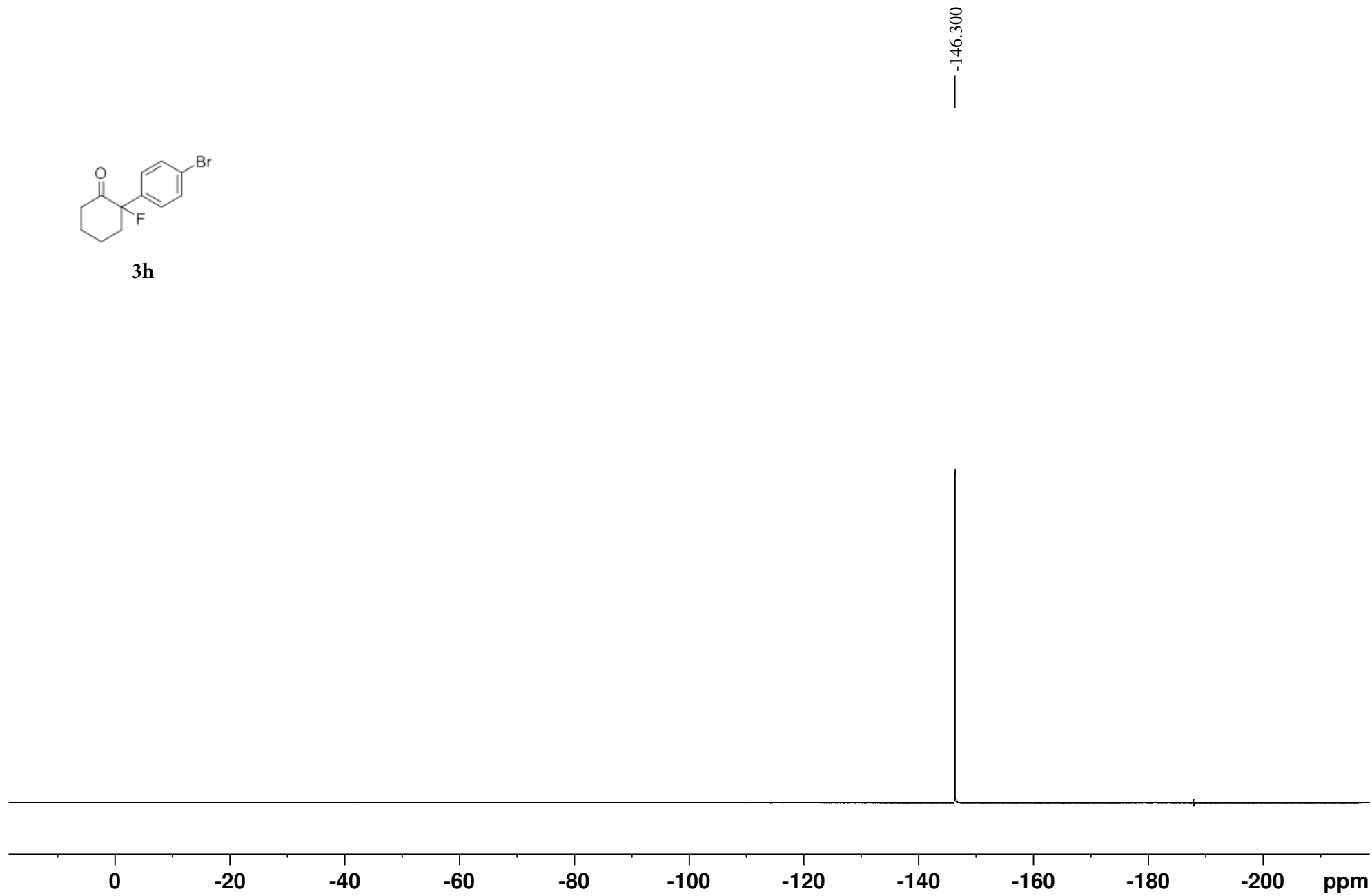
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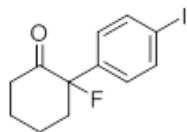
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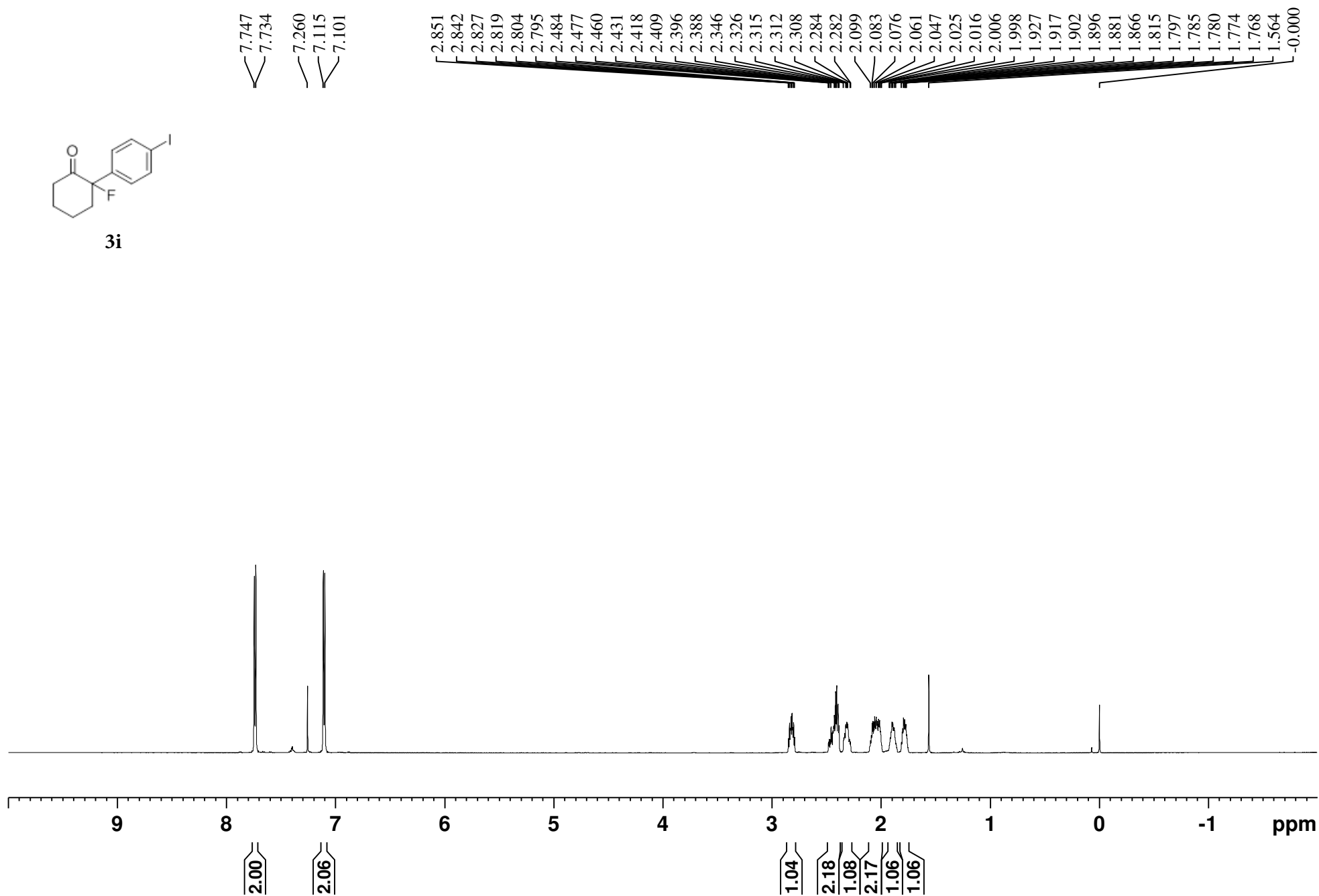


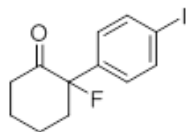
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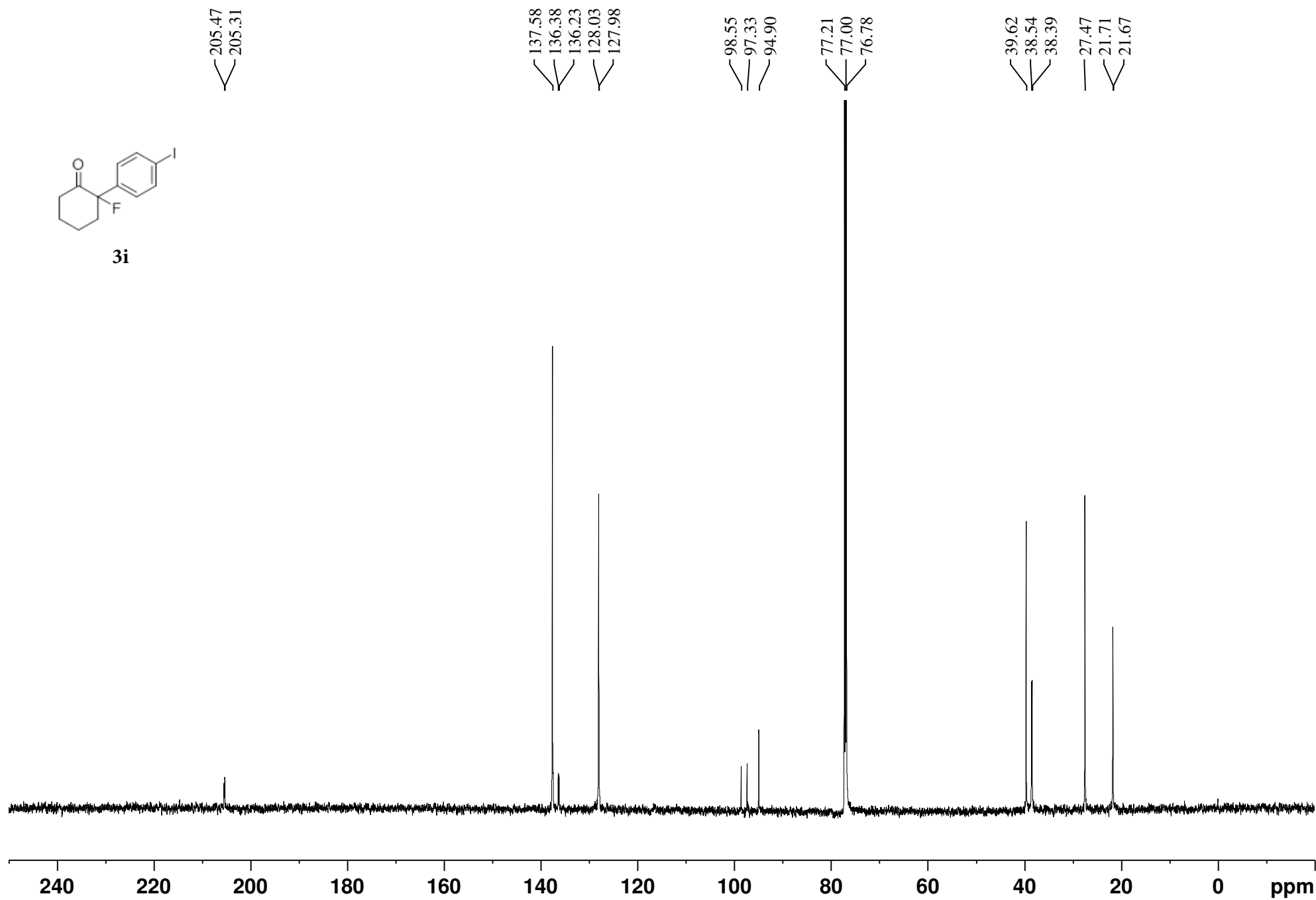


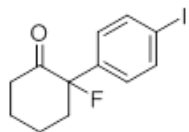
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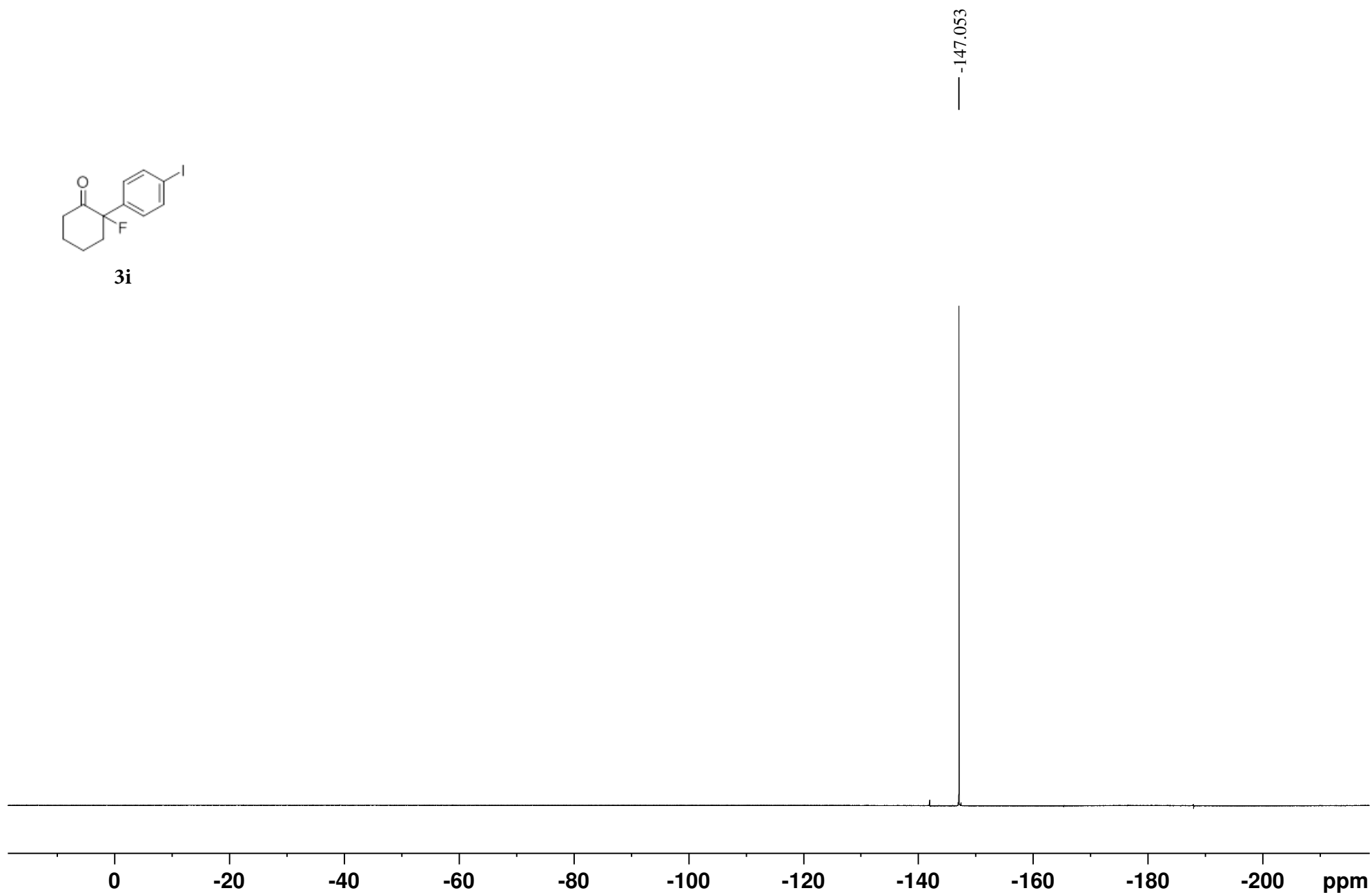


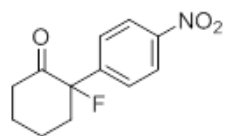
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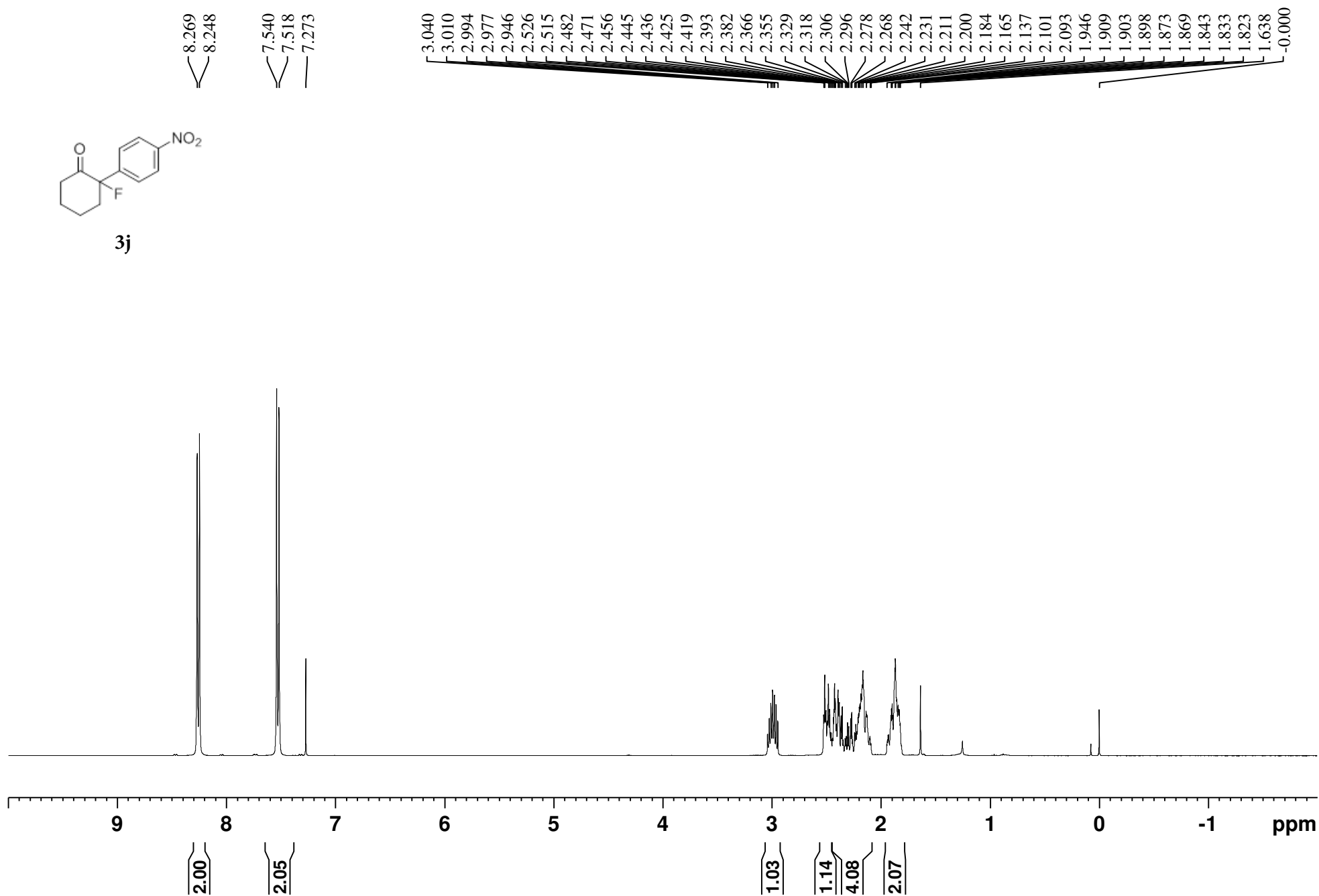


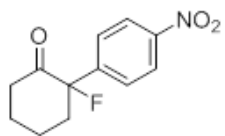
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3j





3j

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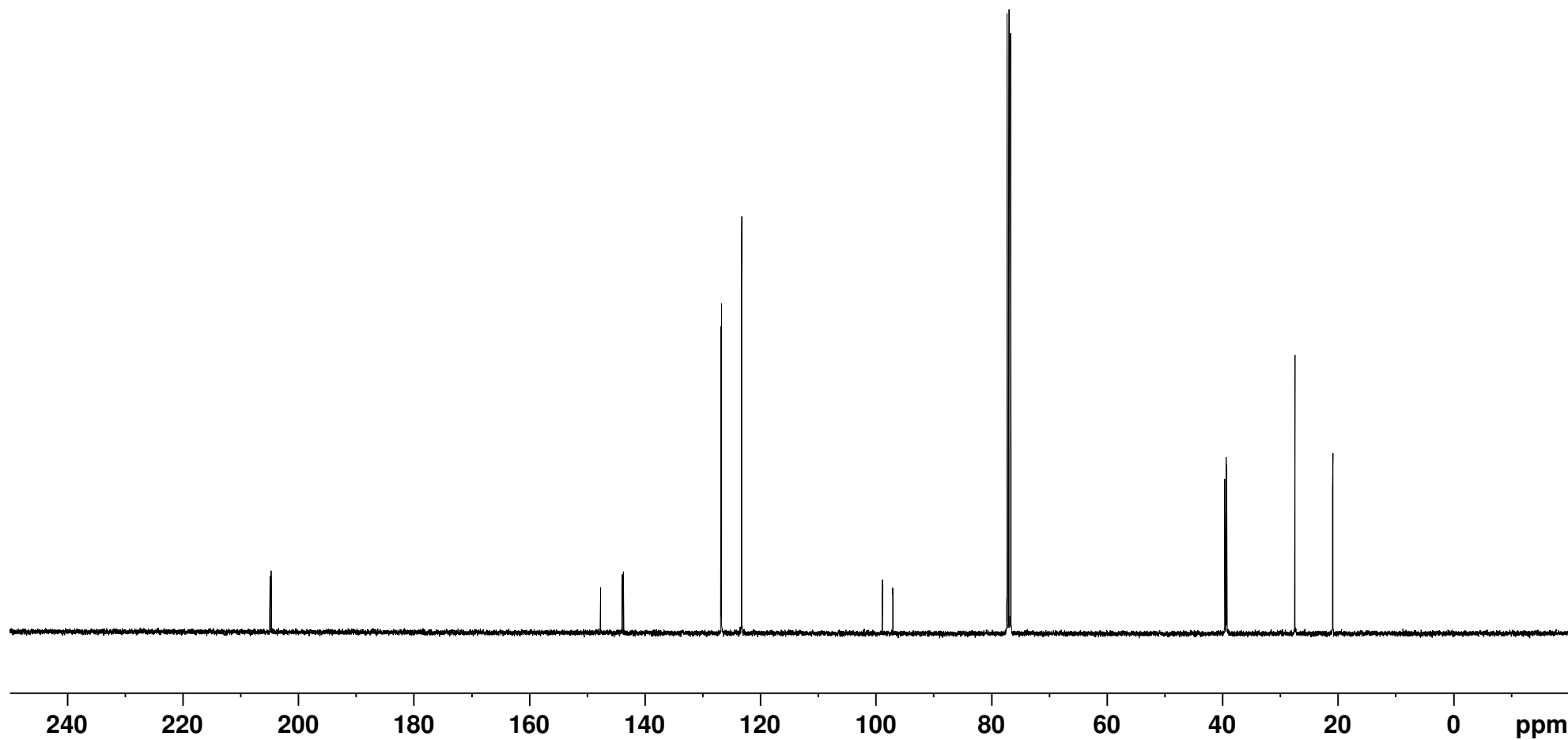
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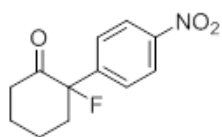
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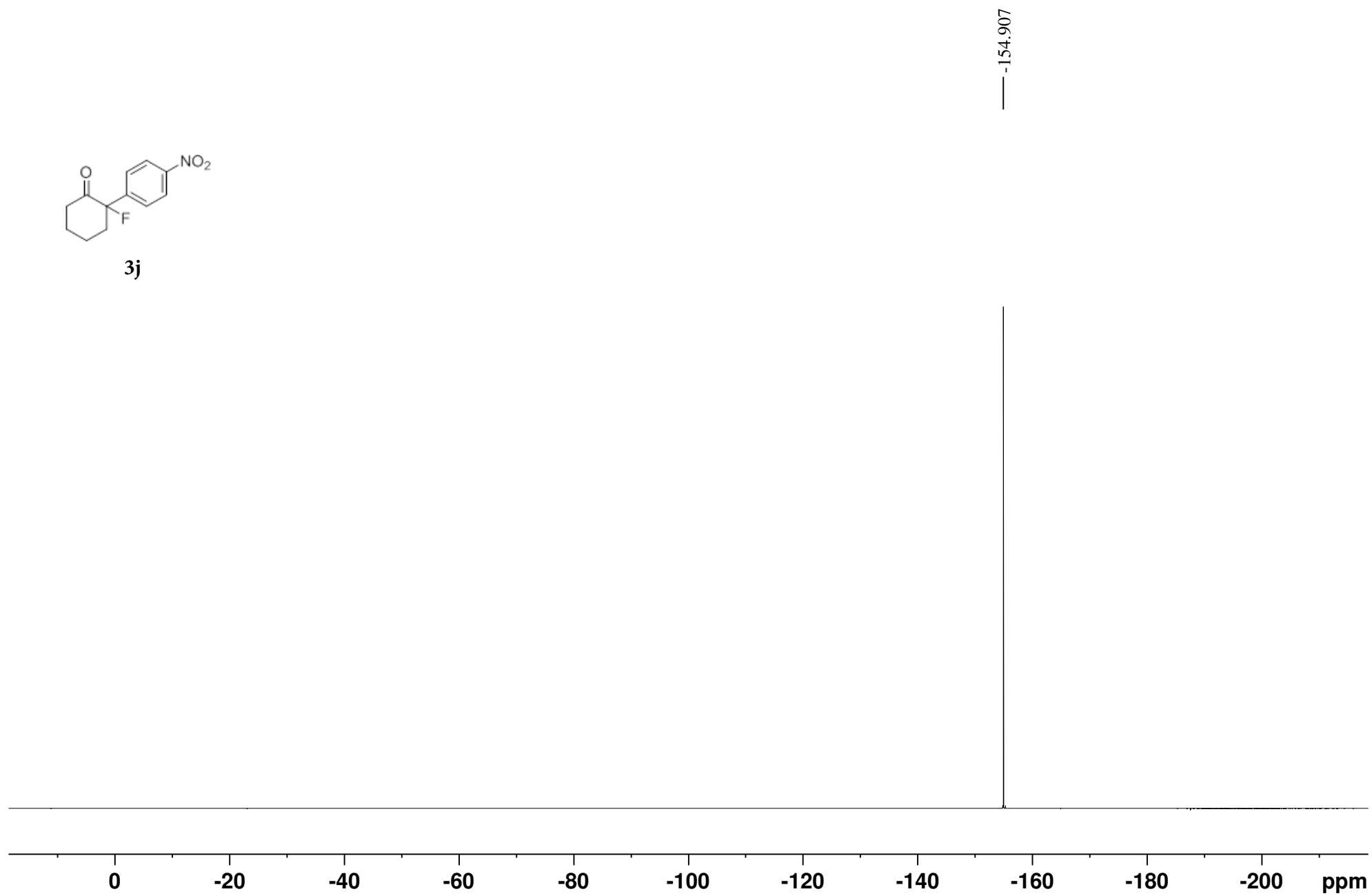
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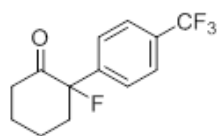
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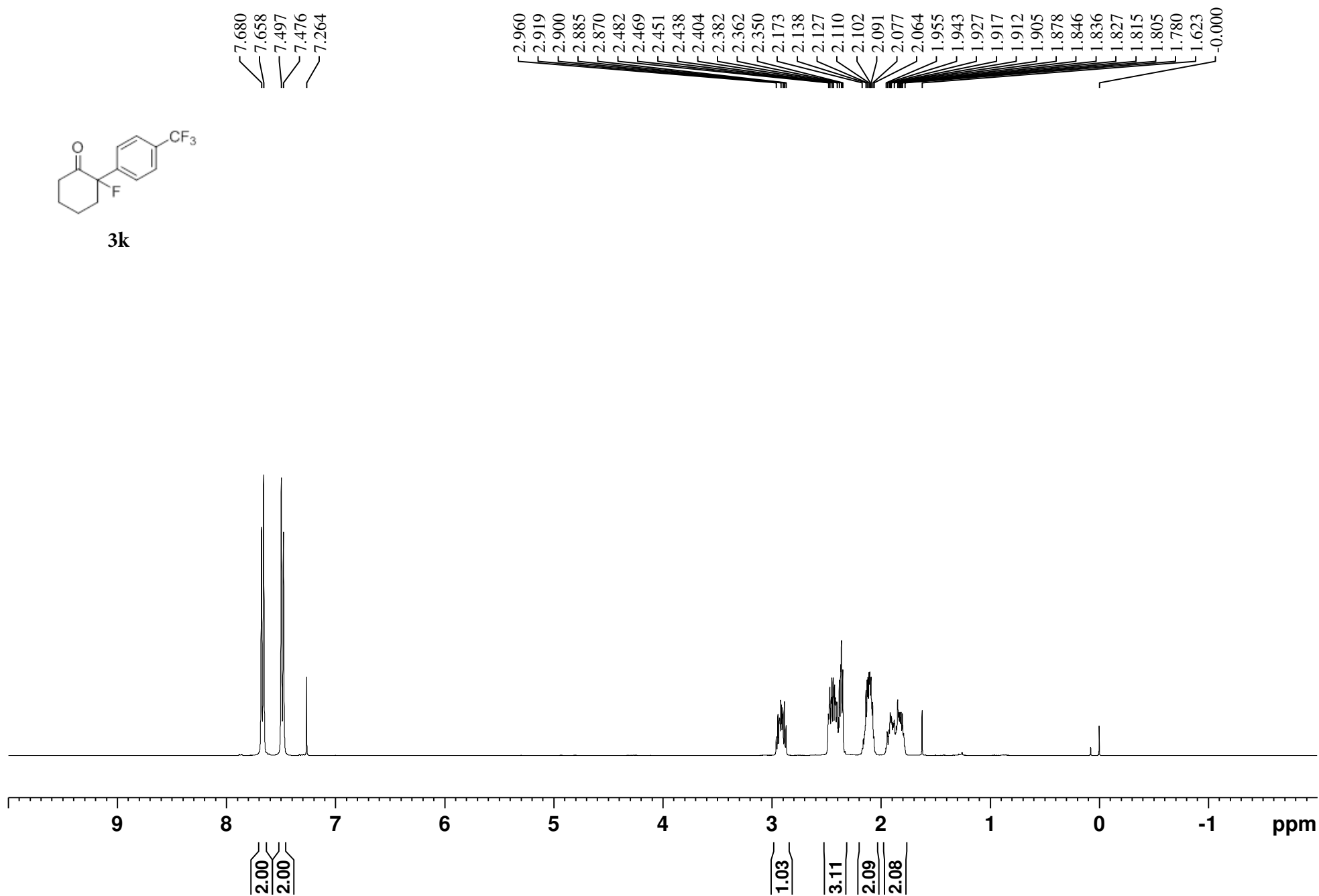


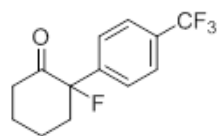
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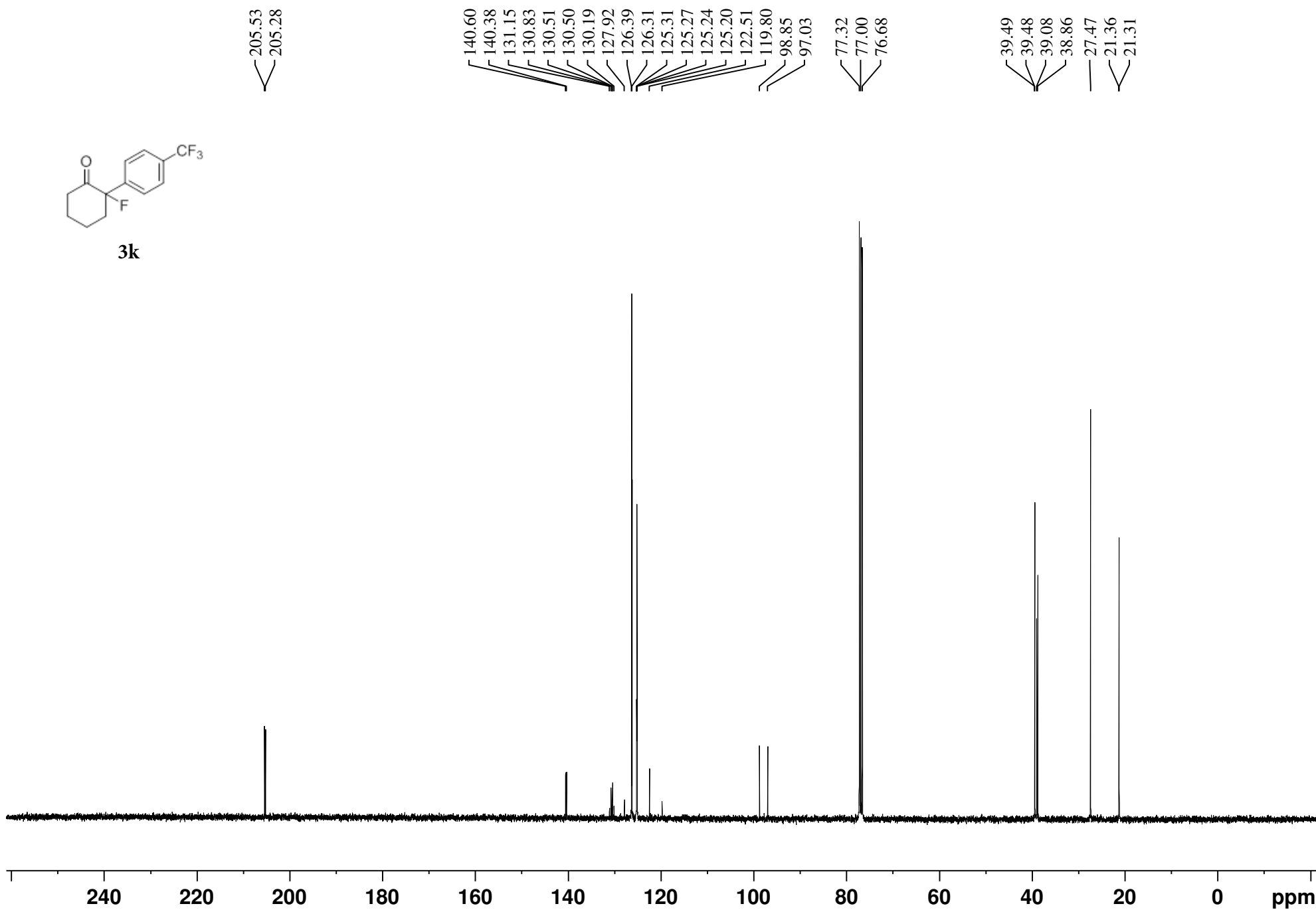


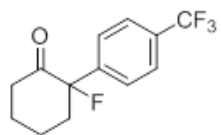
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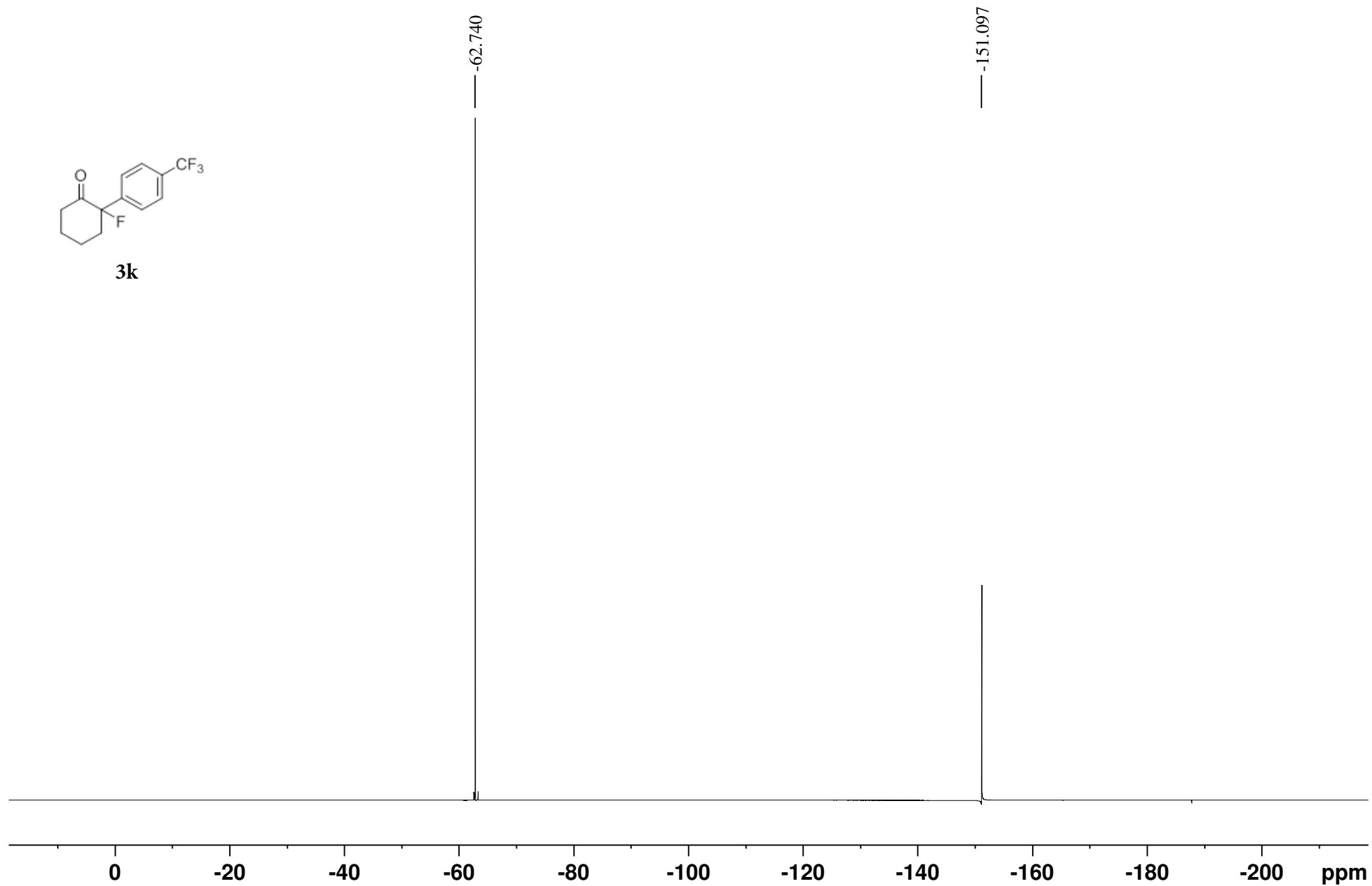


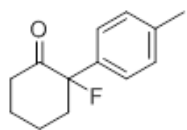
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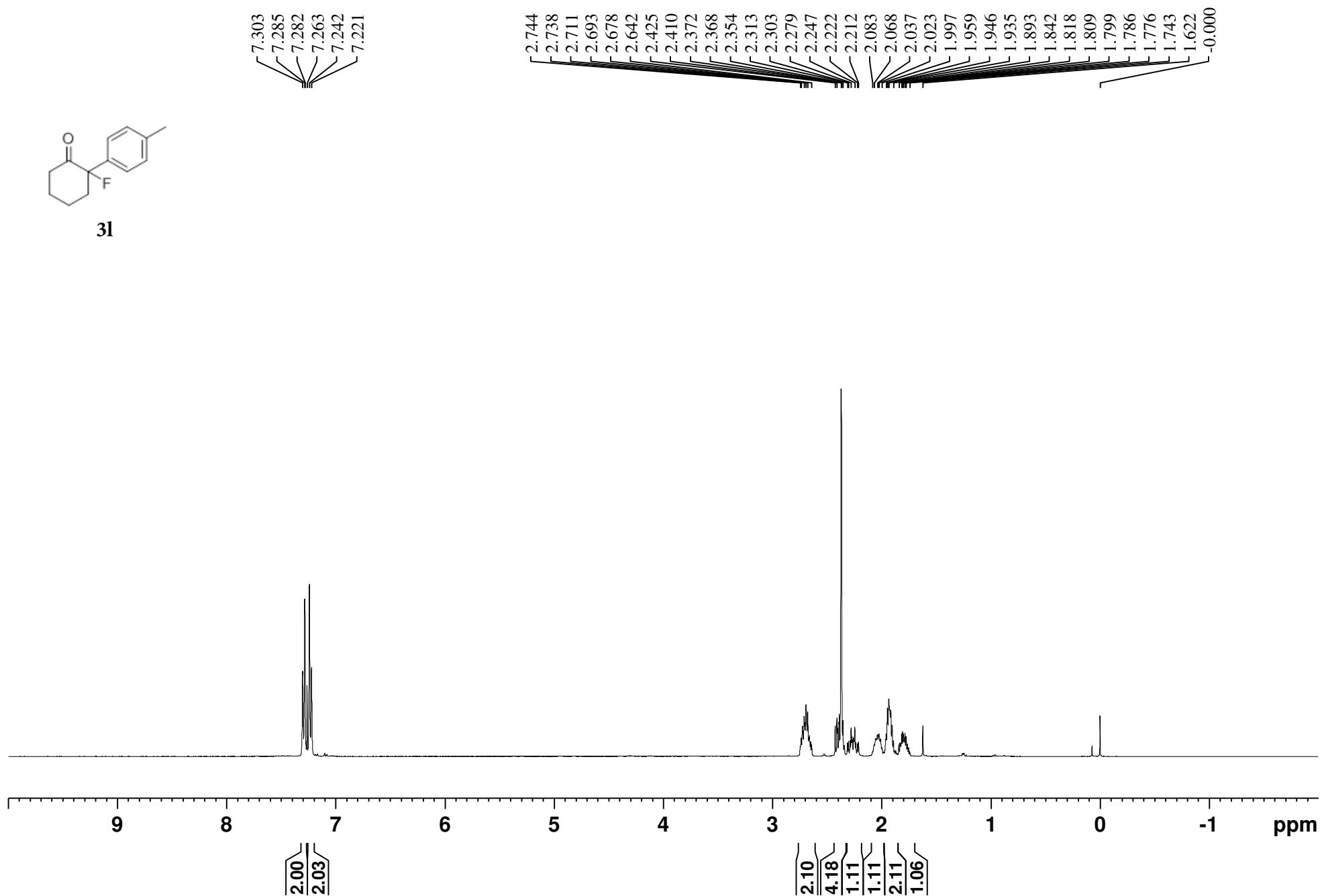


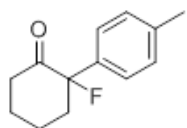
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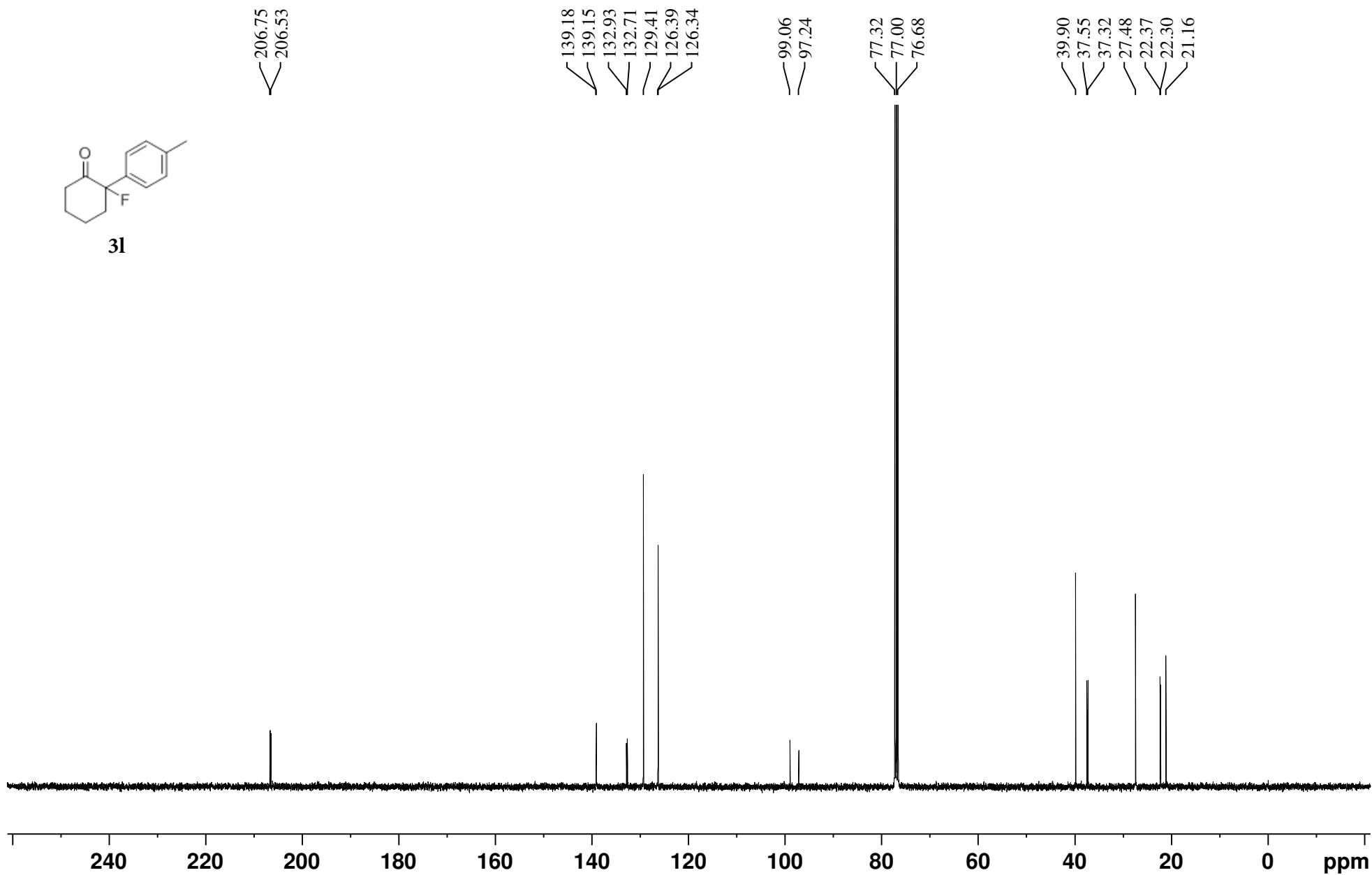


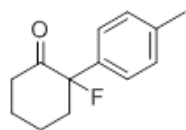
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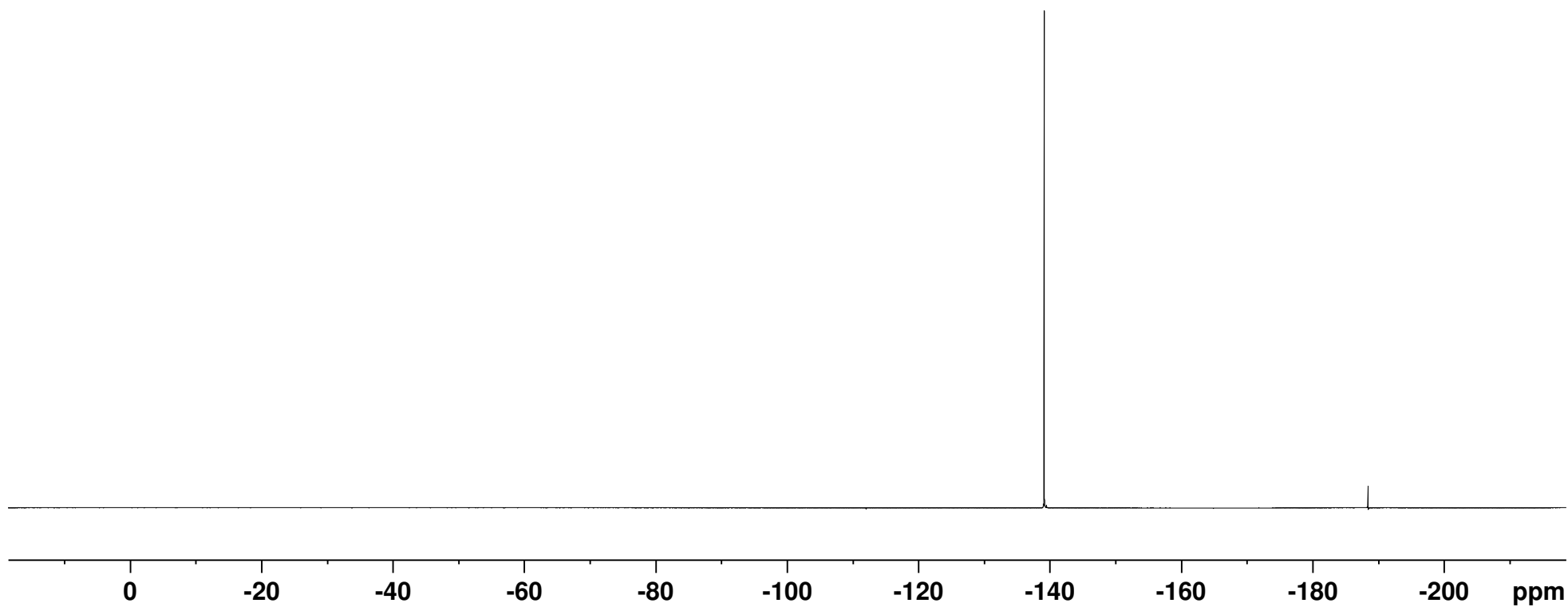
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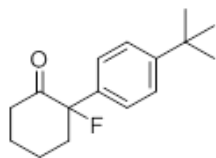




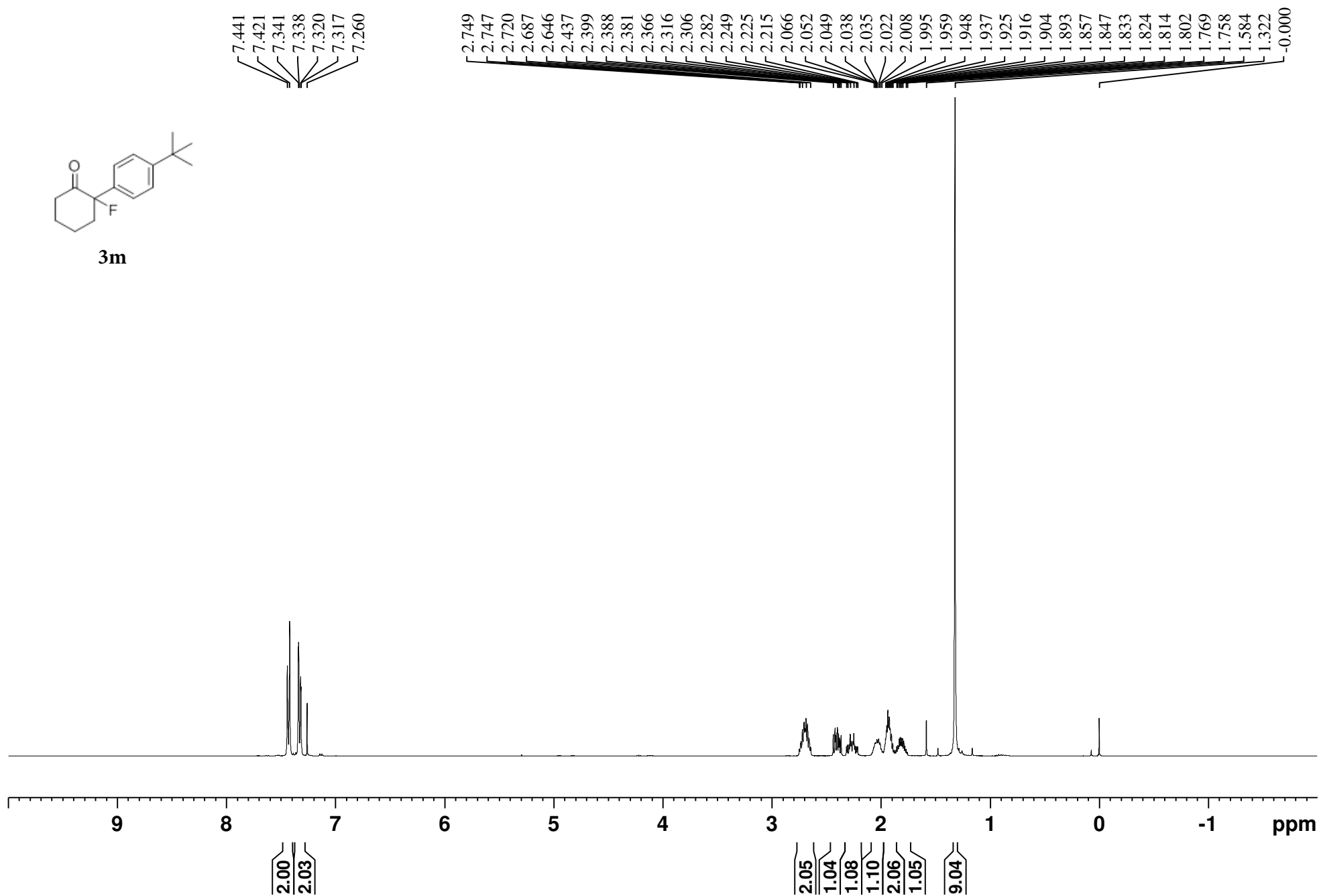
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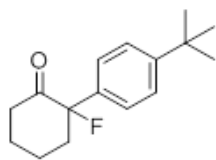
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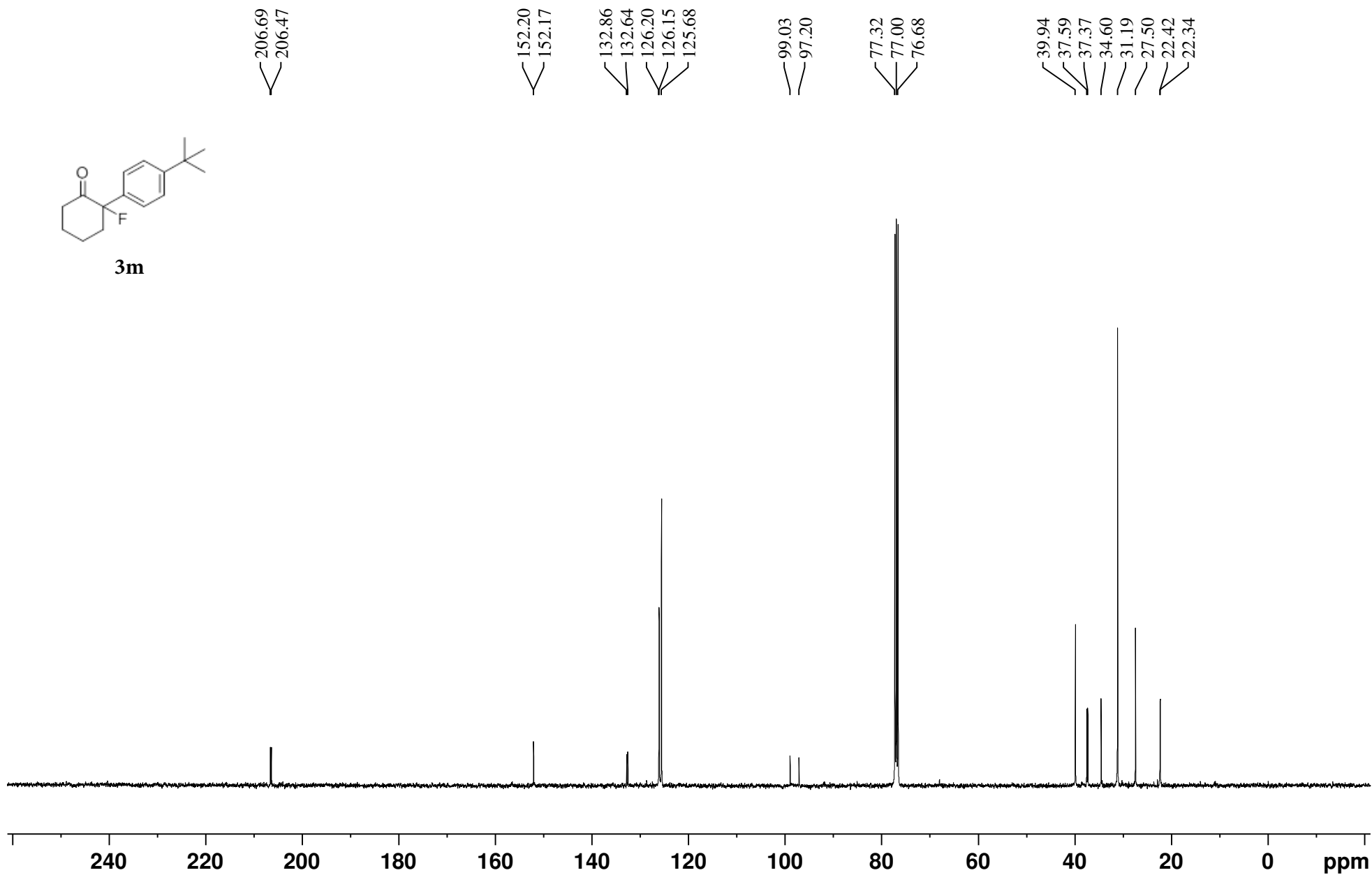


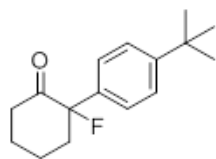
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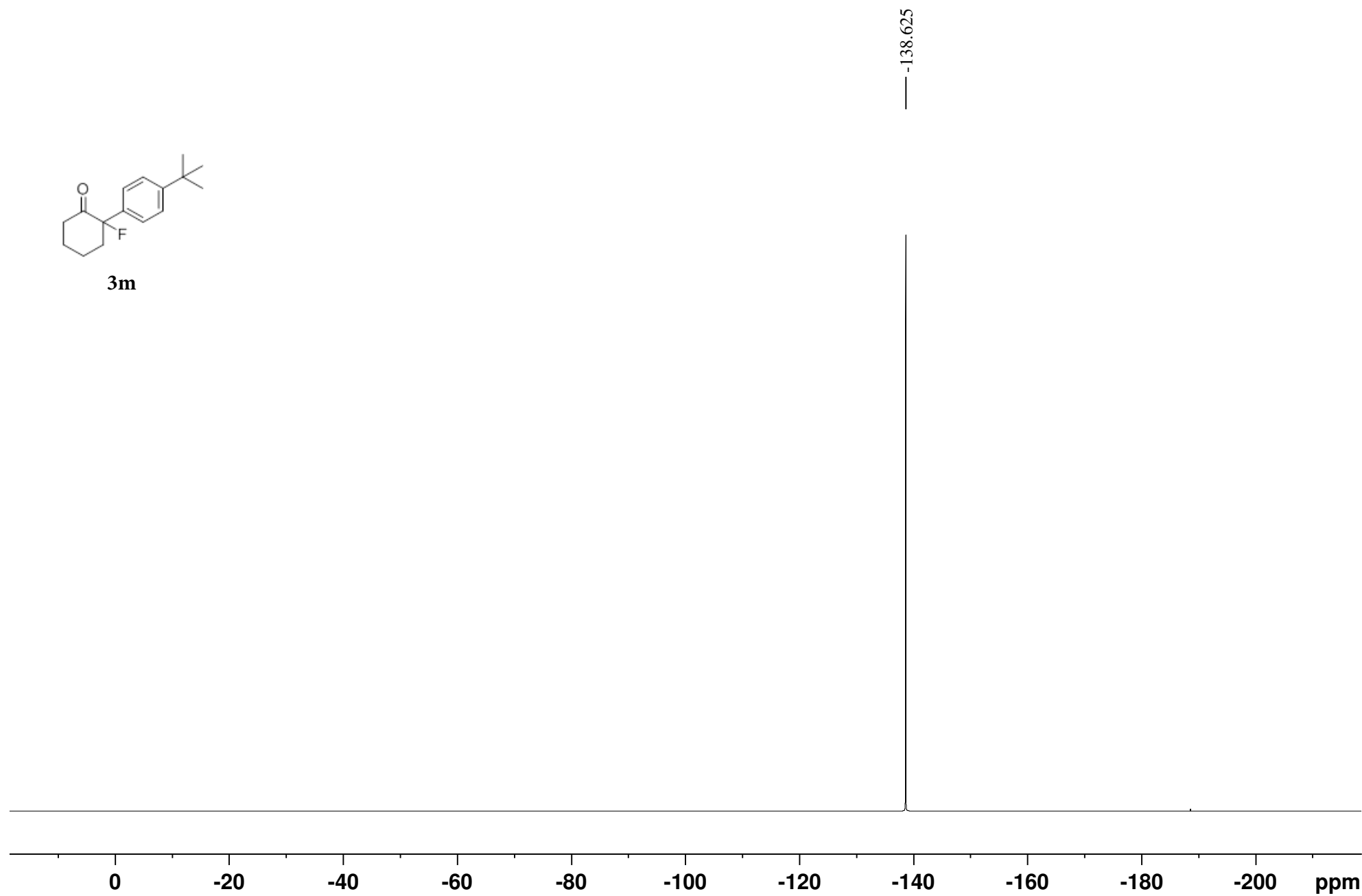


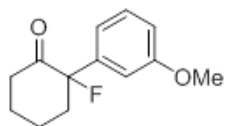
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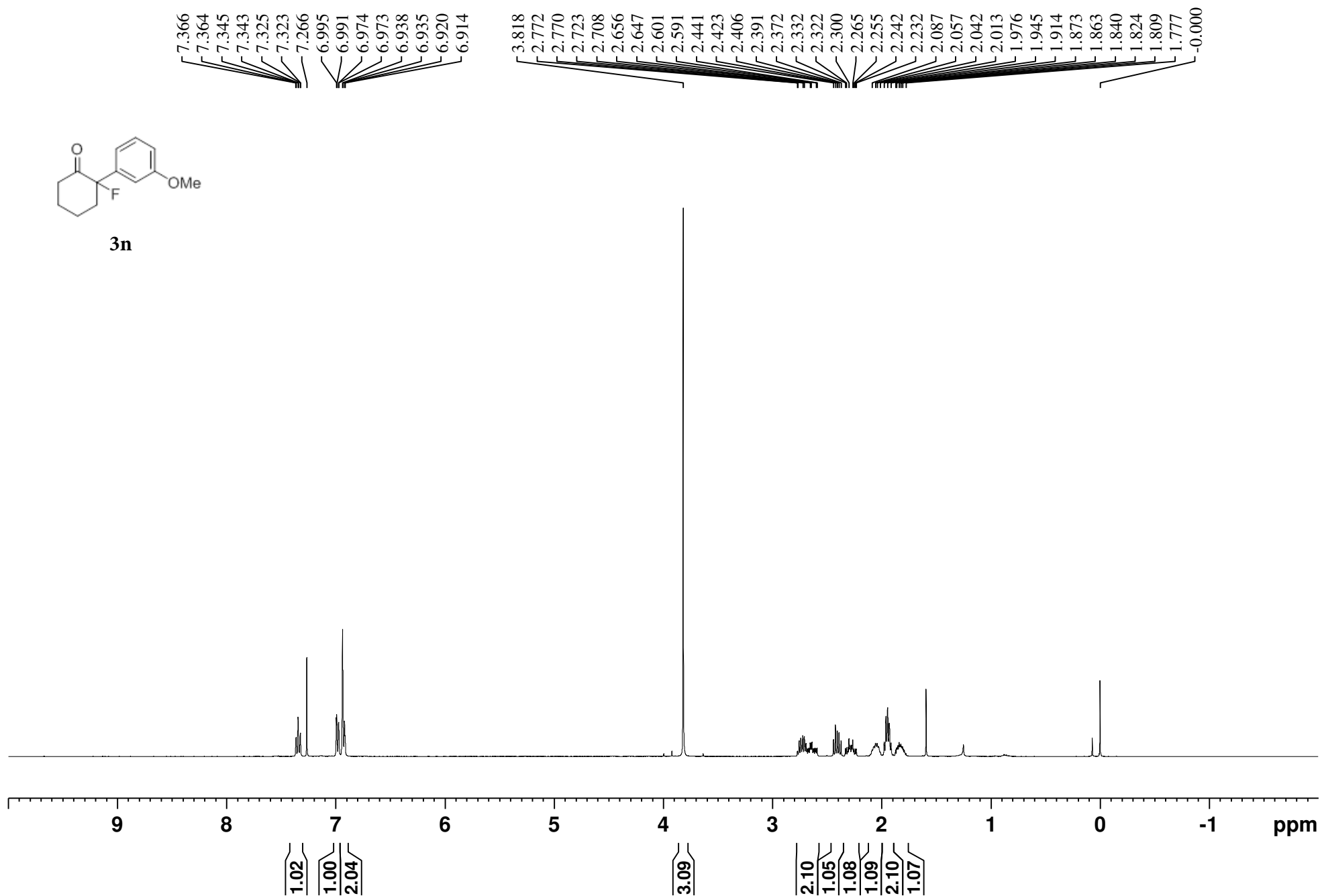


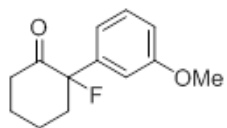
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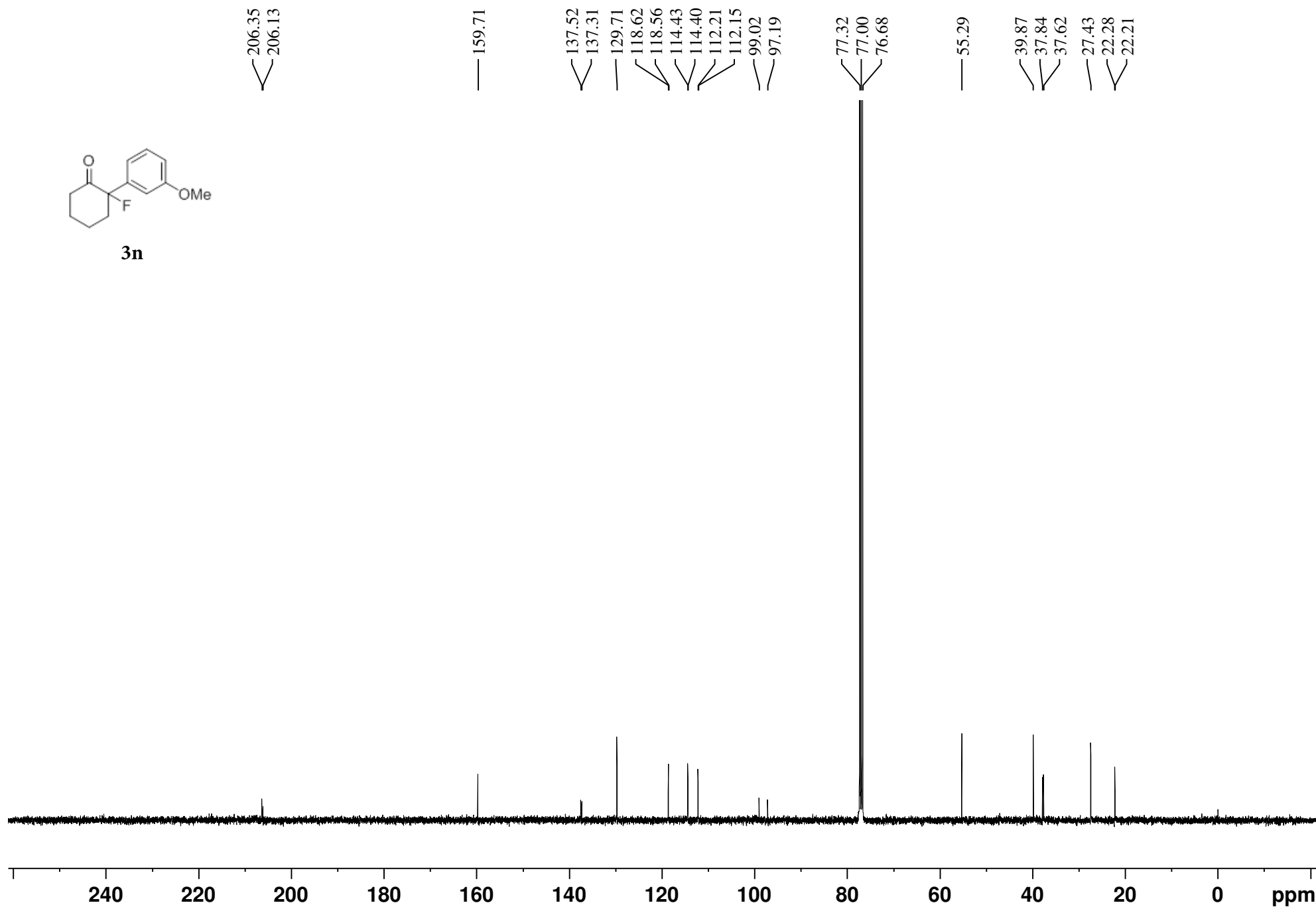


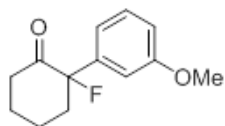
**3n**



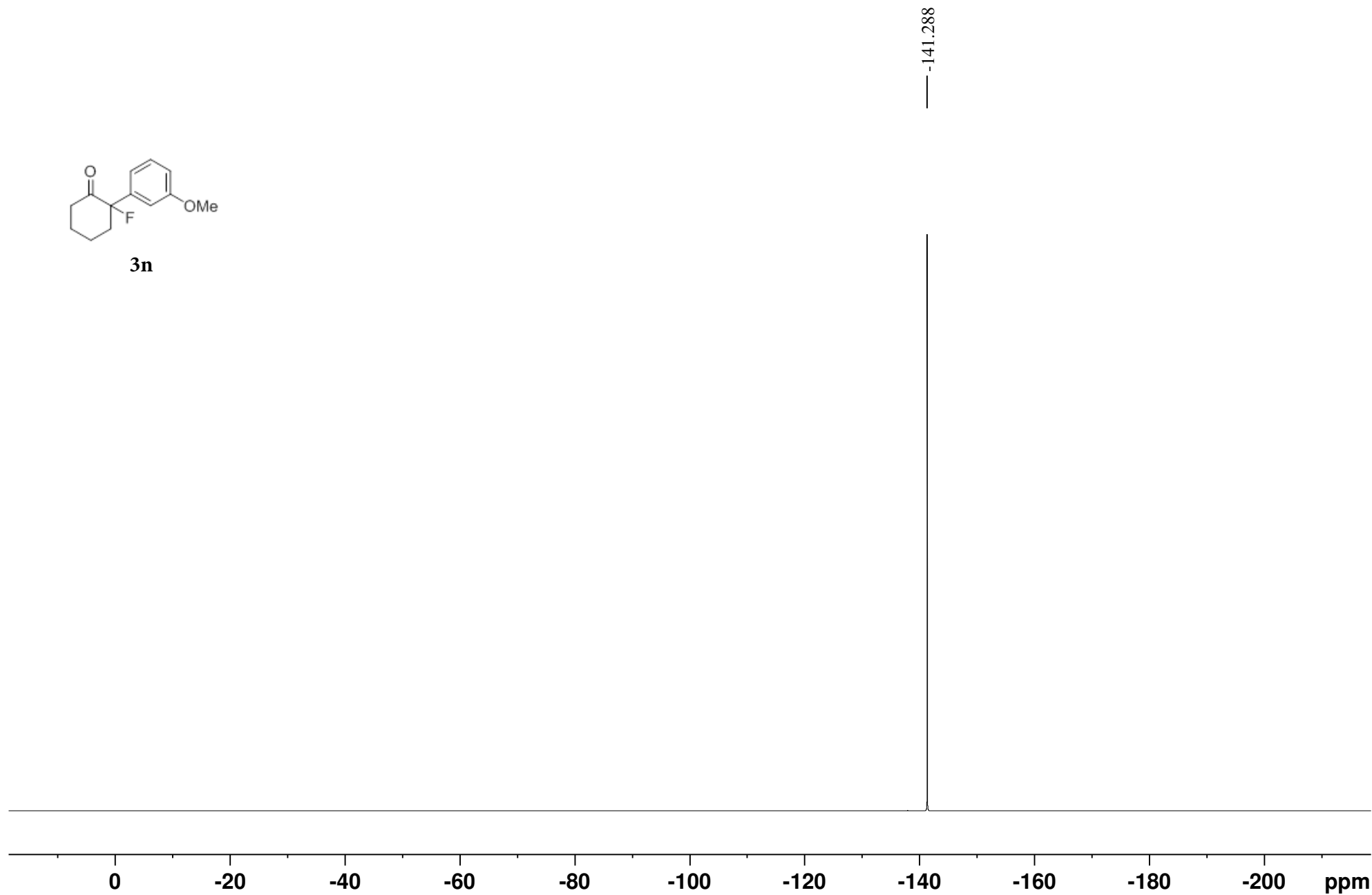


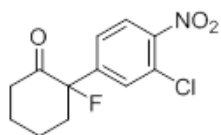
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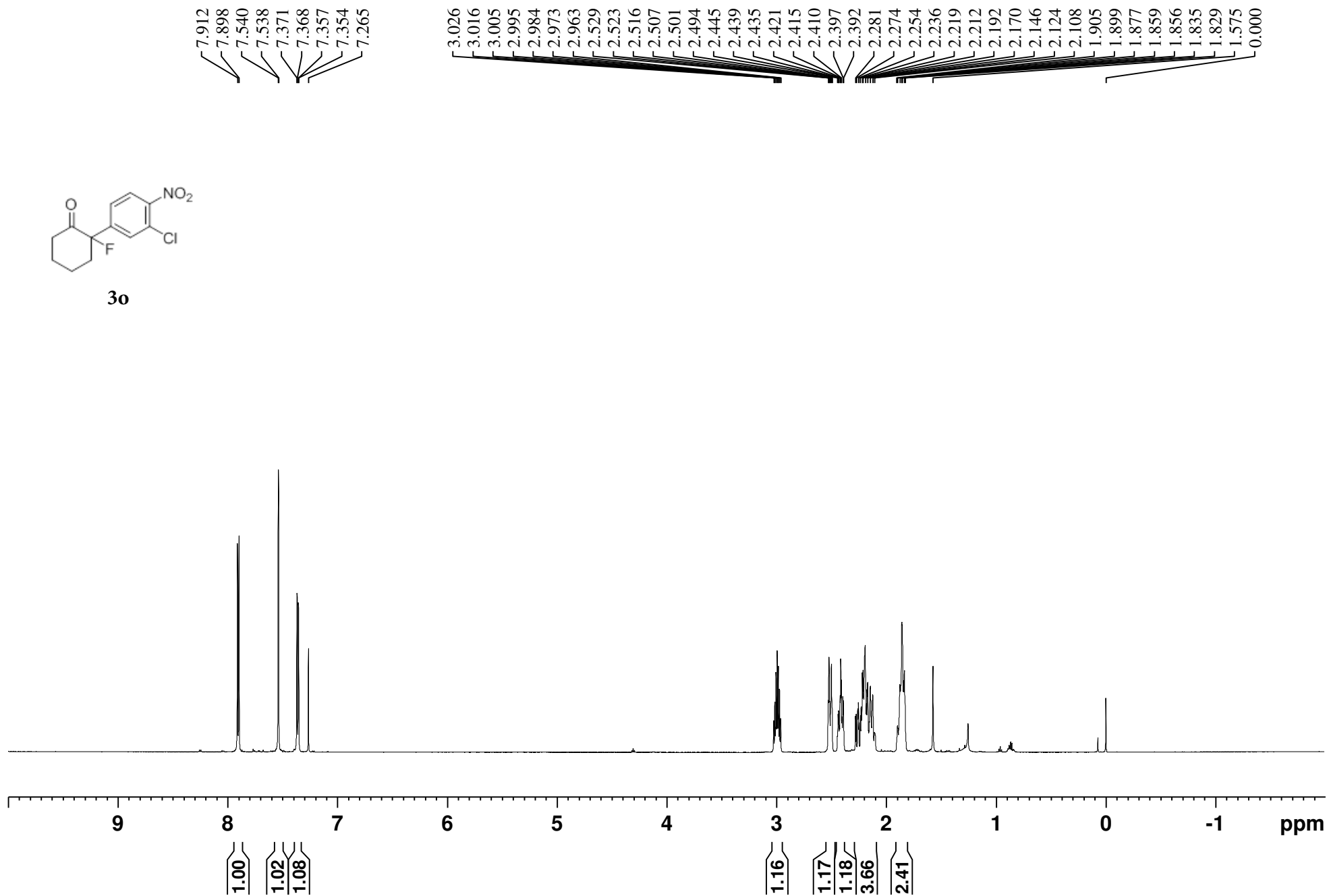


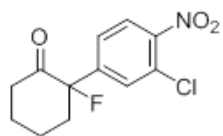
**3n**





**3o**





**3o**

204.29  
204.04

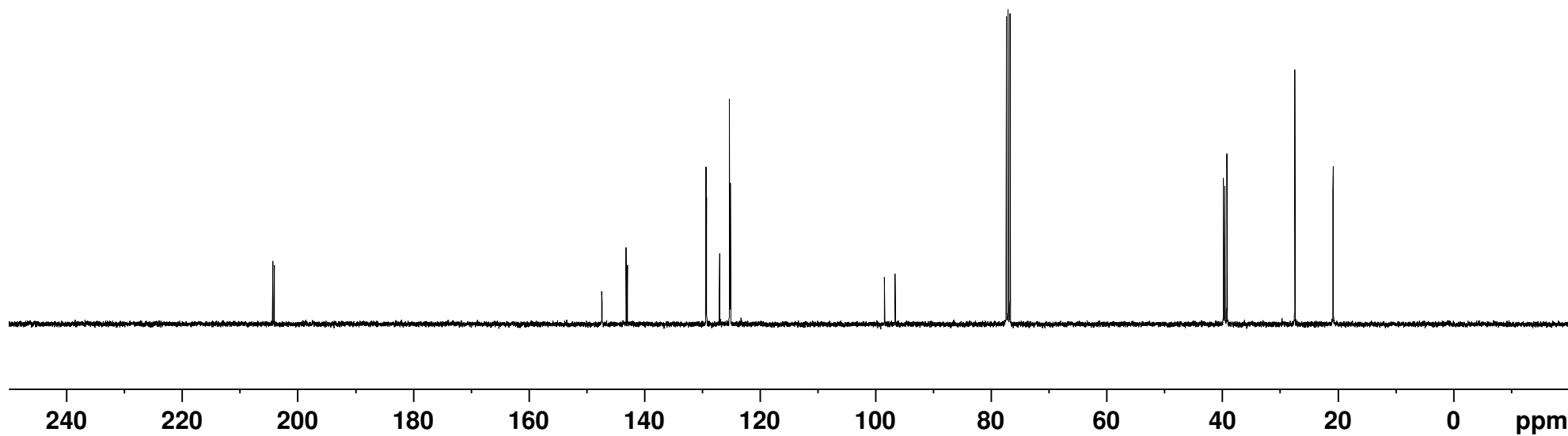
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142.90  
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129.22  
126.96  
126.95  
125.24  
125.15  
125.06

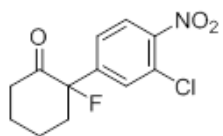
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77.31  
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76.68

39.72  
39.49  
39.15  
39.13

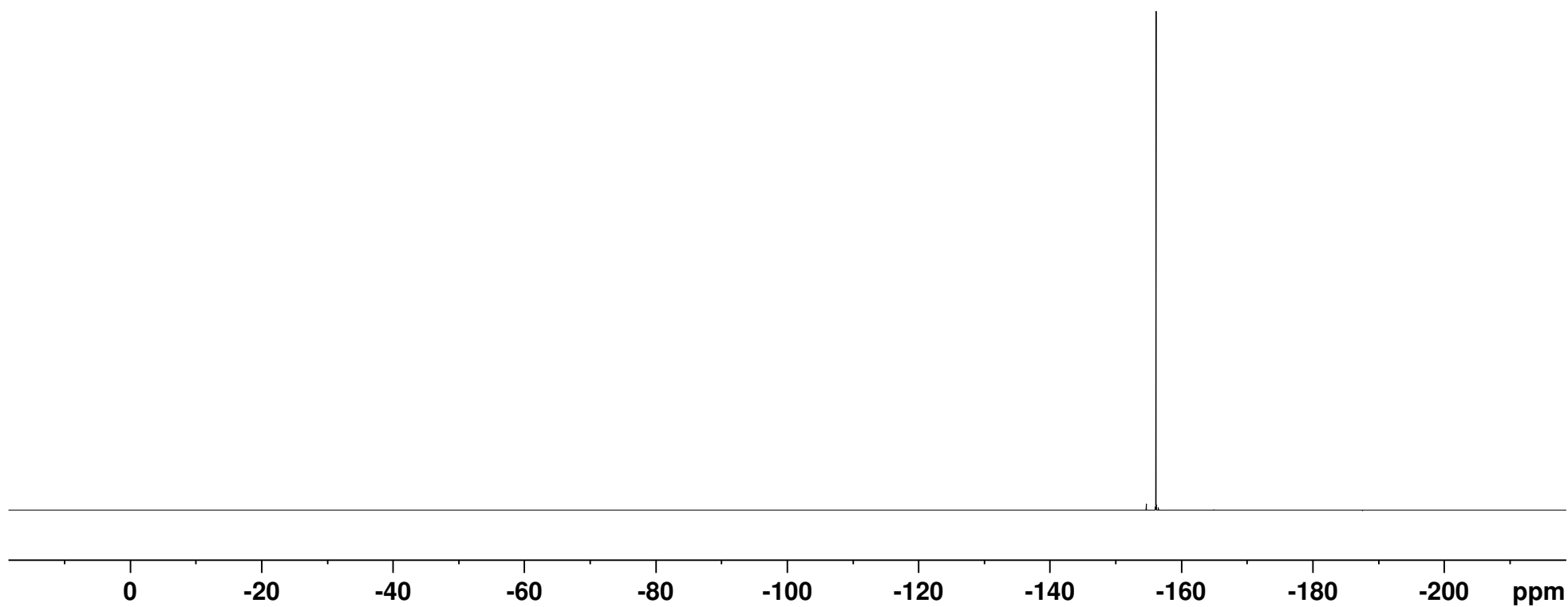
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20.74

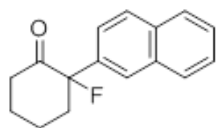




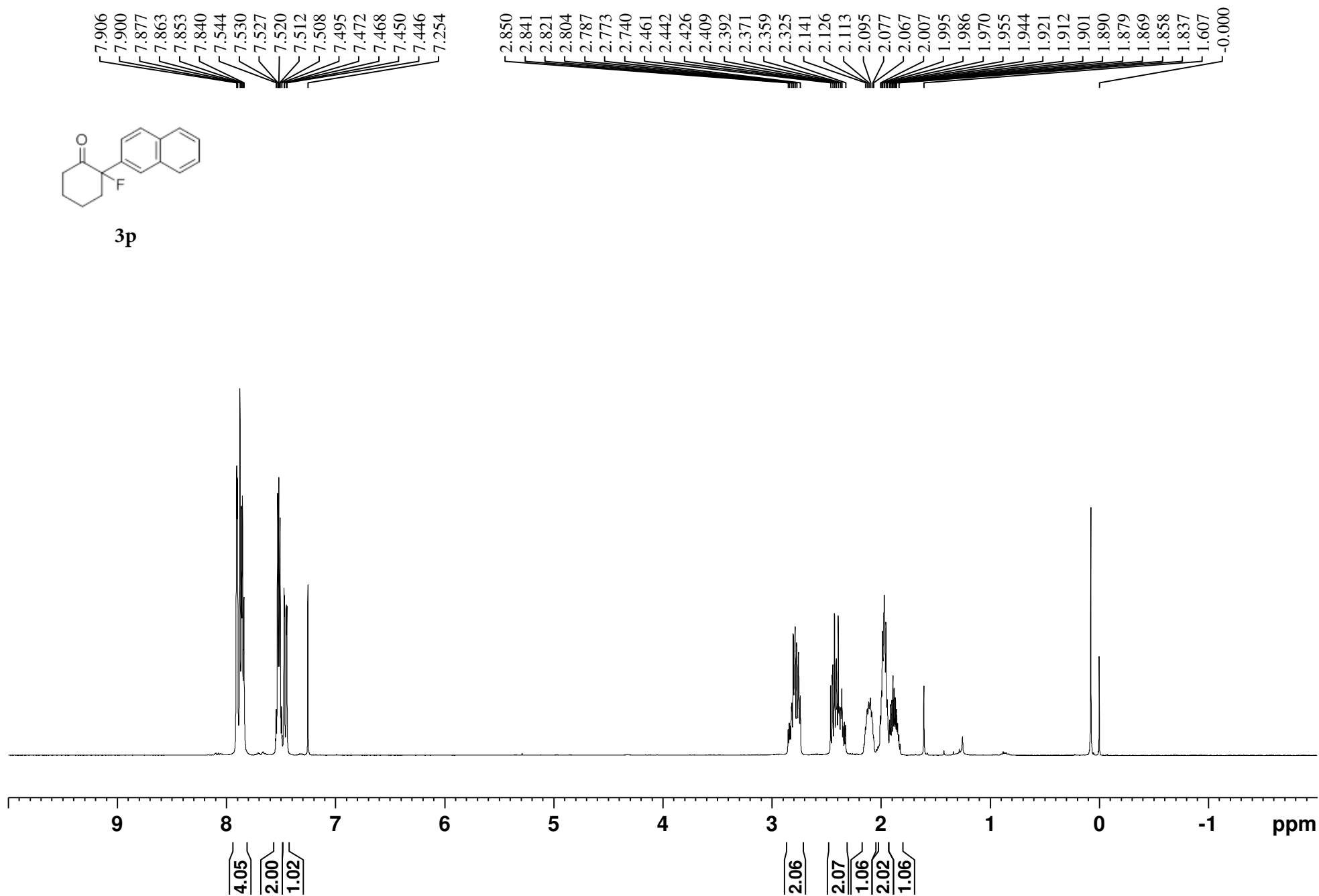
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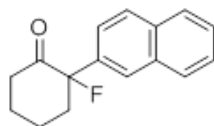
— -156.090





3p





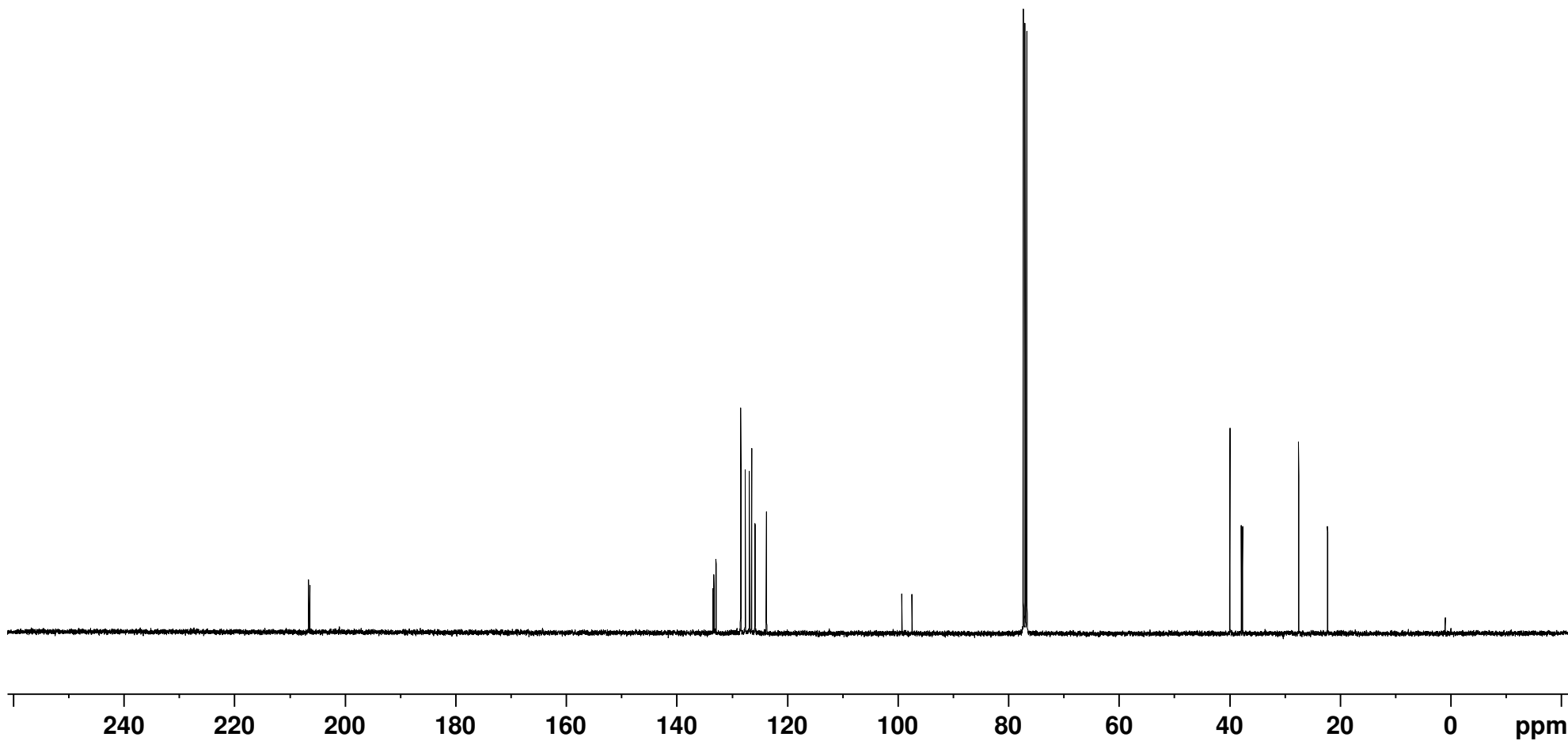
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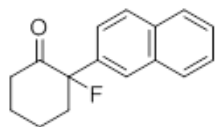
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133.46  
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133.28  
133.25  
132.89  
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126.87  
126.45  
125.89  
125.81  
123.80  
123.75  
99.28  
97.44

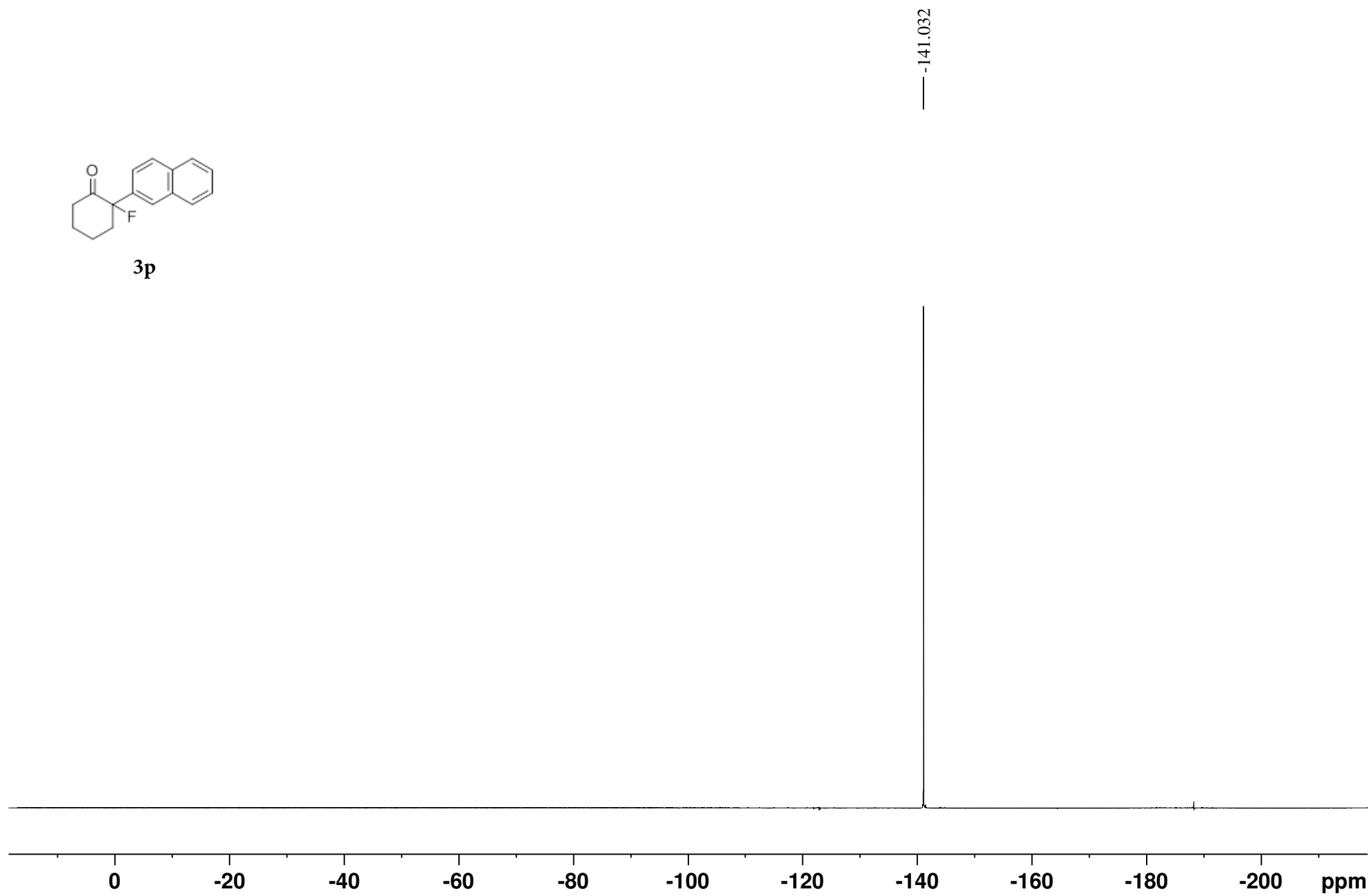
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76.68

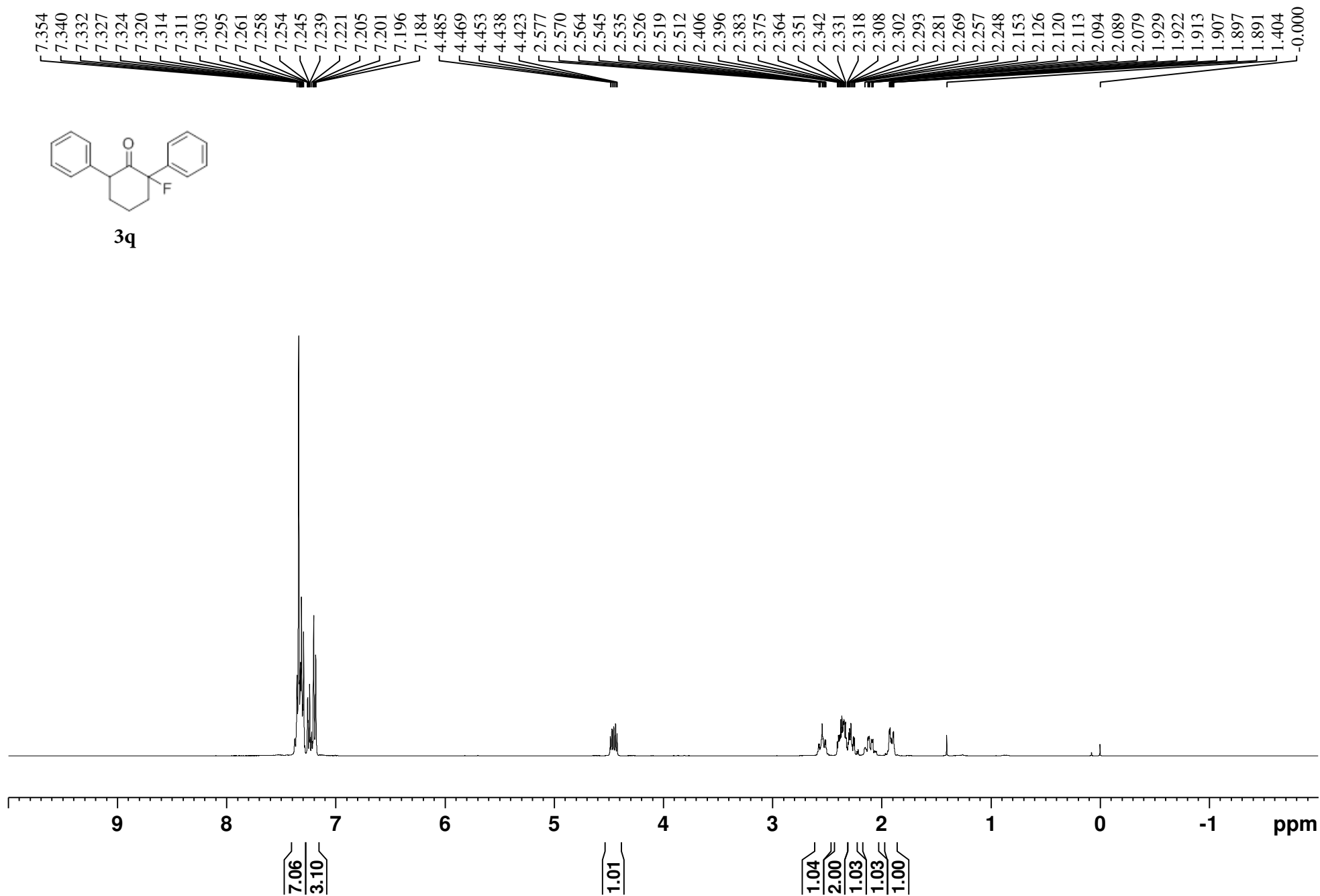
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22.25

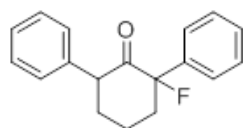




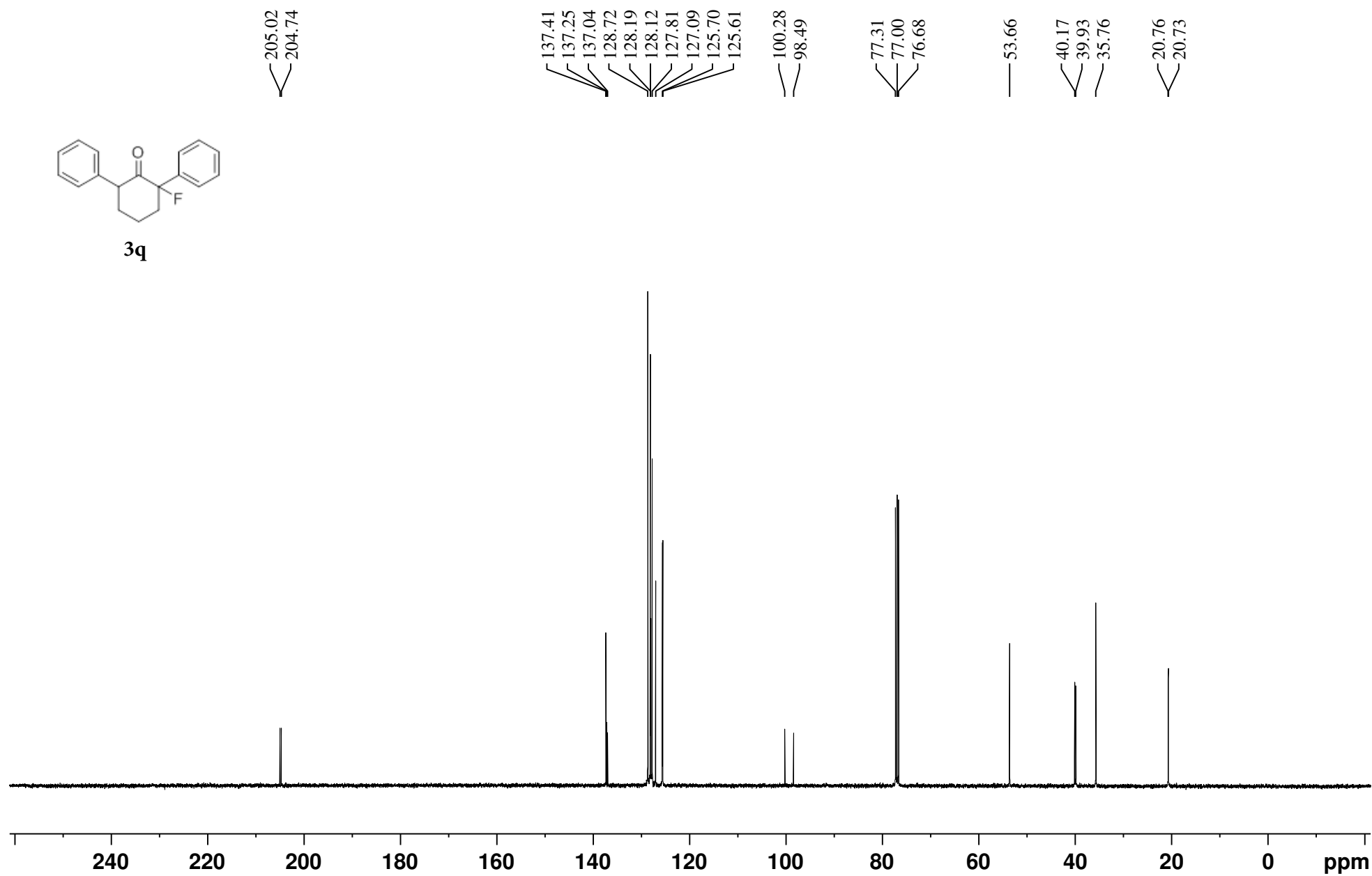
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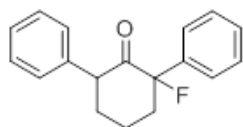




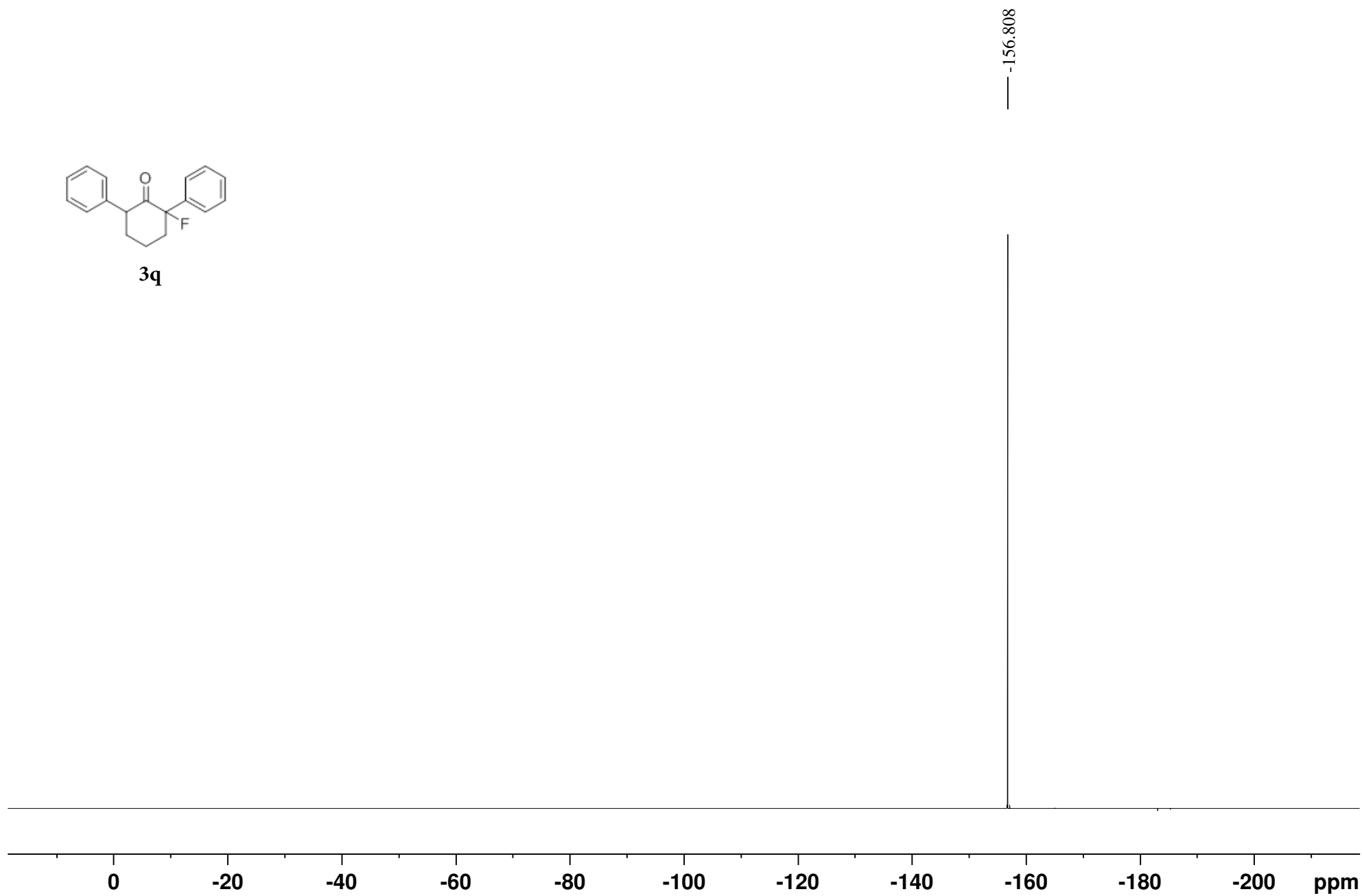


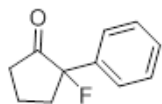
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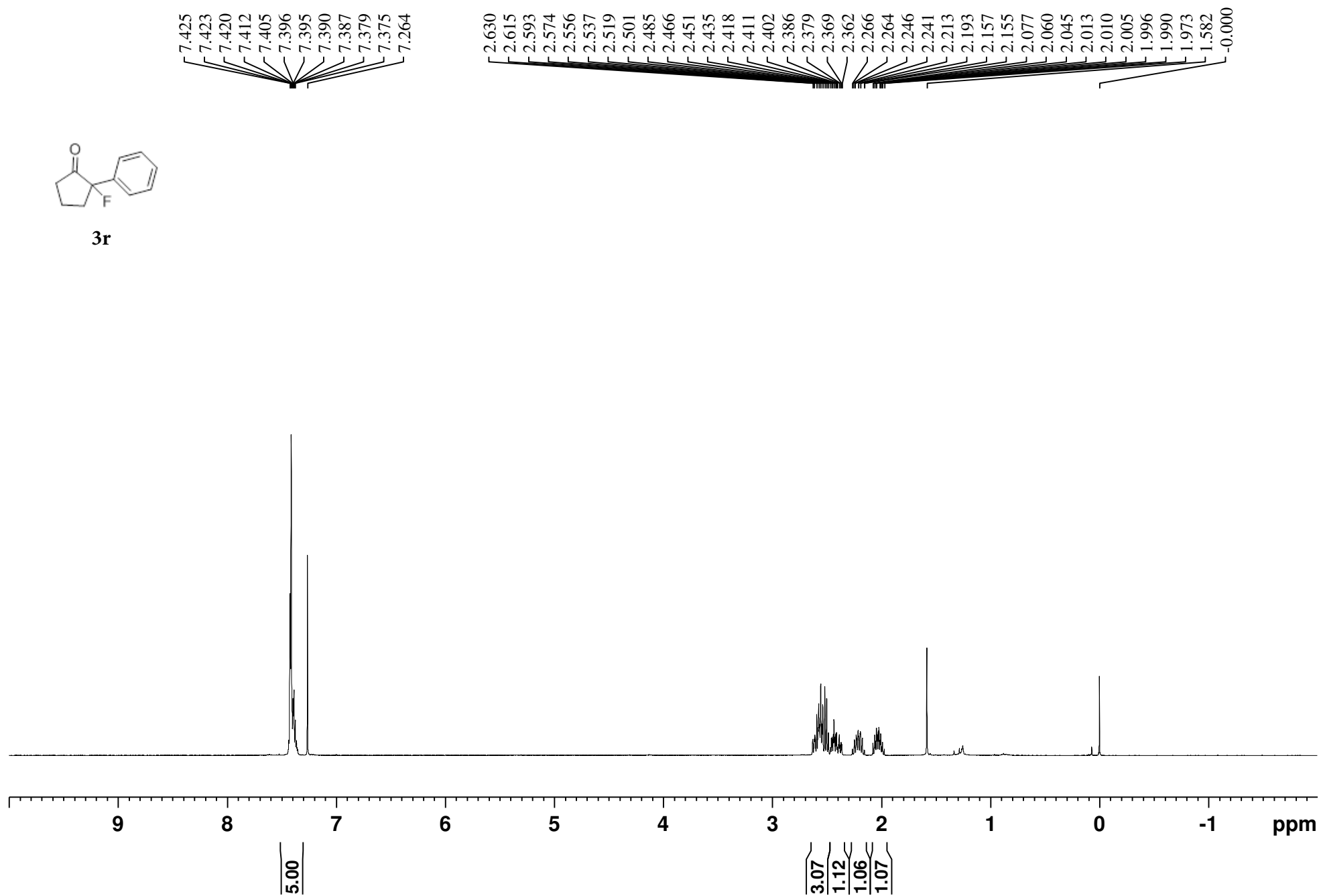


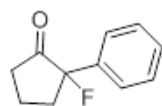
**3q**



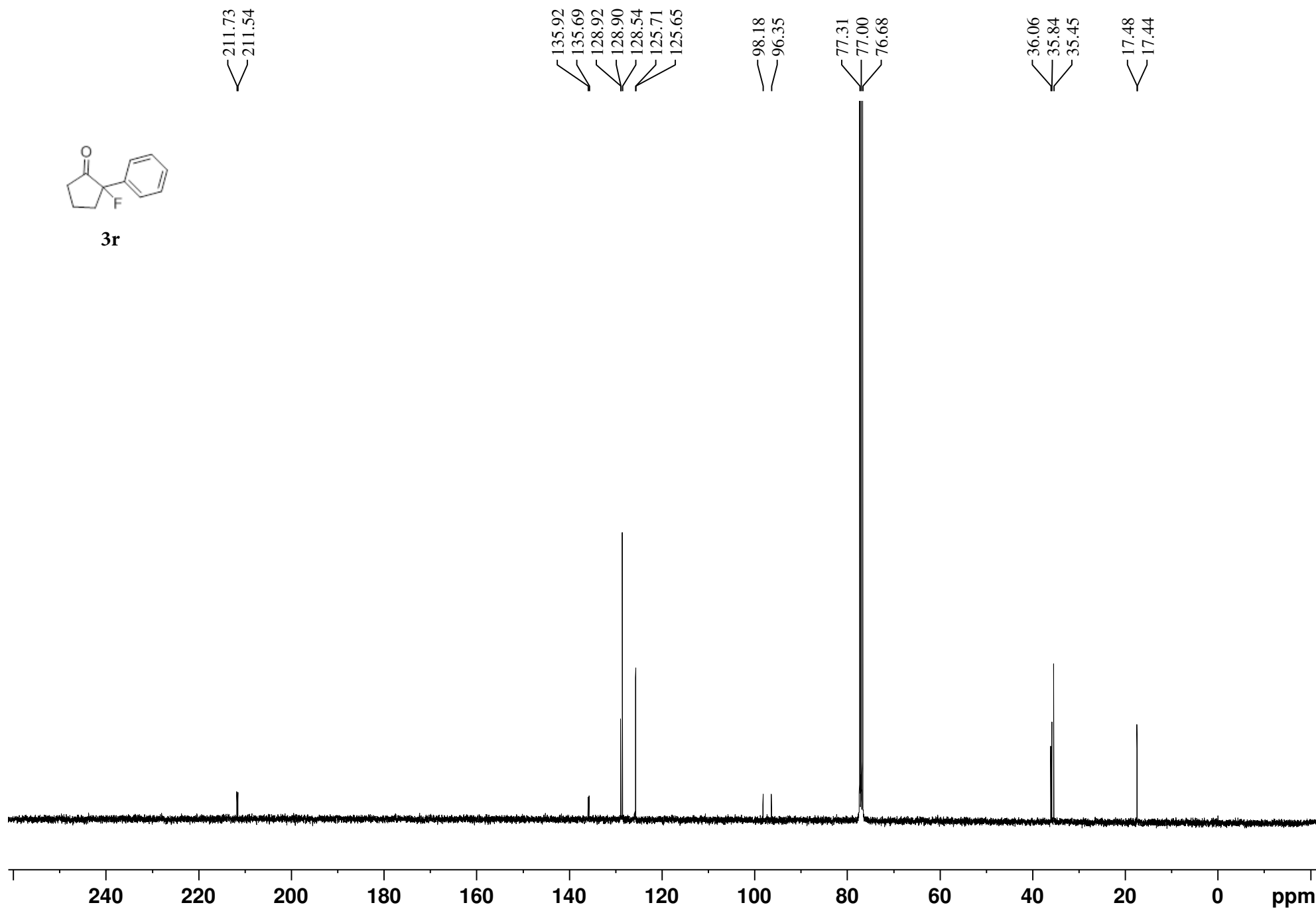


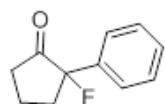
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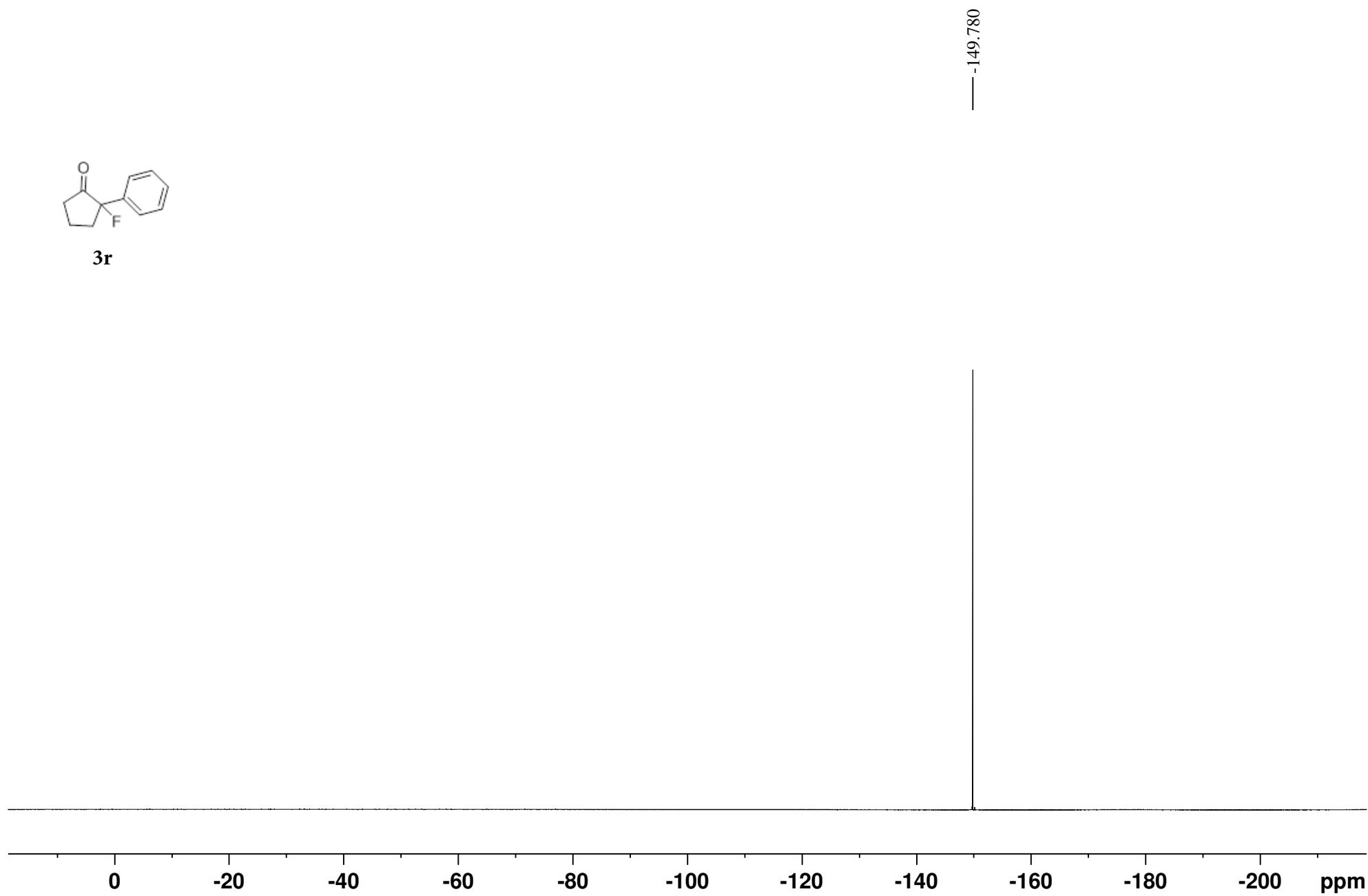


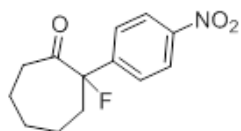
**3r**





**3r**



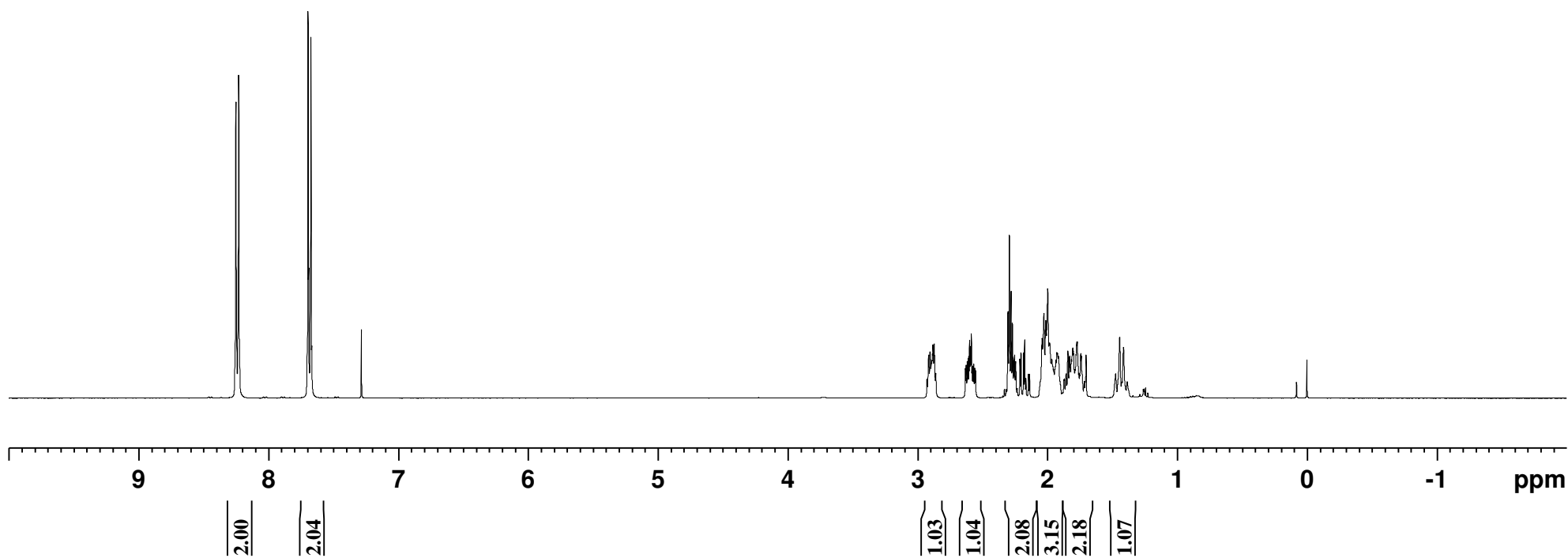


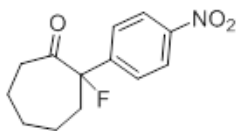
3s

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7.695  
7.690  
7.677  
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7.667  
7.284

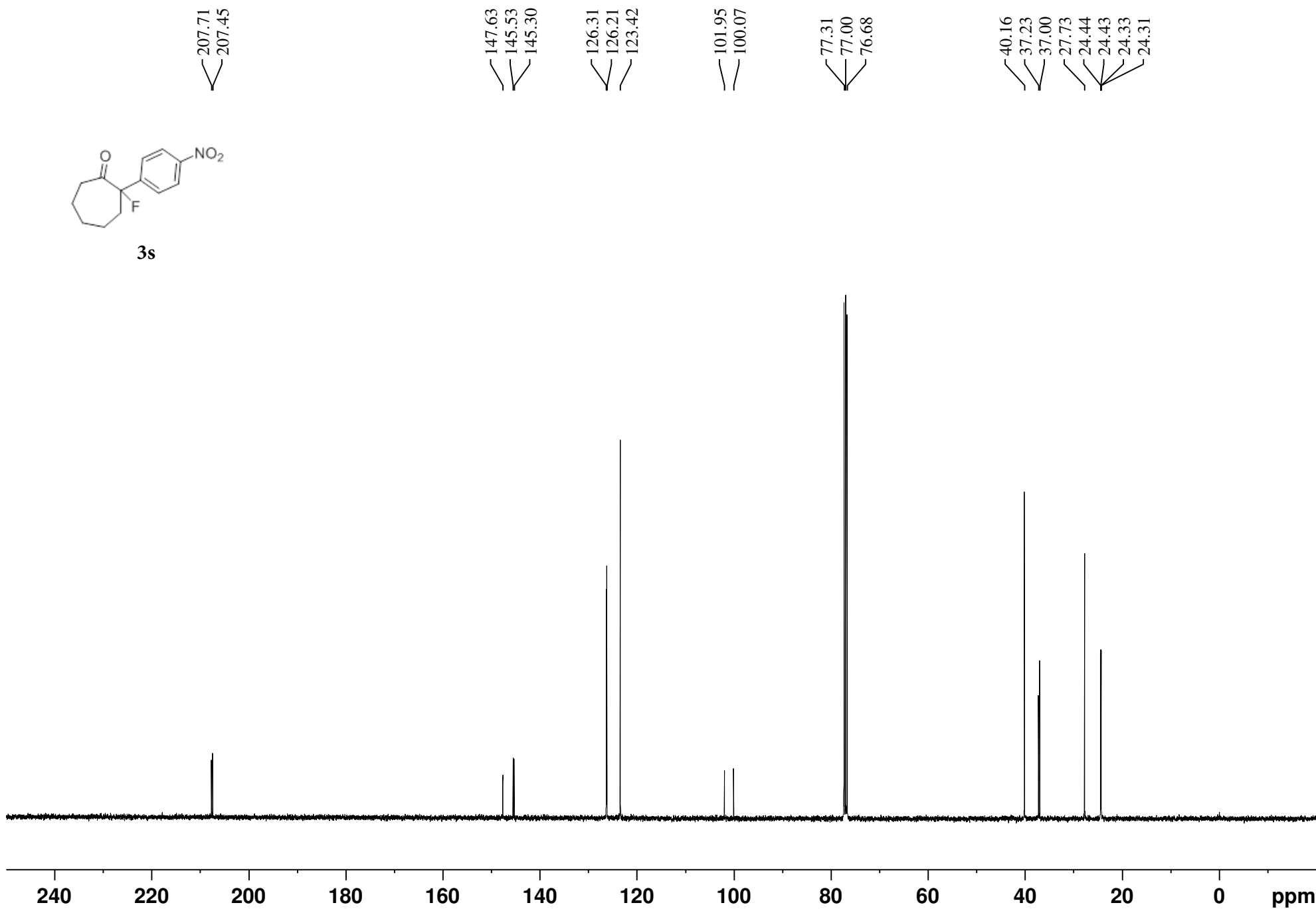
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2.303  
2.292  
2.145  
2.137  
2.040  
1.997  
1.934  
1.928  
1.925  
1.919  
1.915  
1.871  
1.868  
1.804  
1.800  
1.701  
1.474  
1.443  
1.414  
1.385  
-0.000

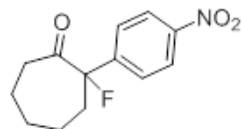
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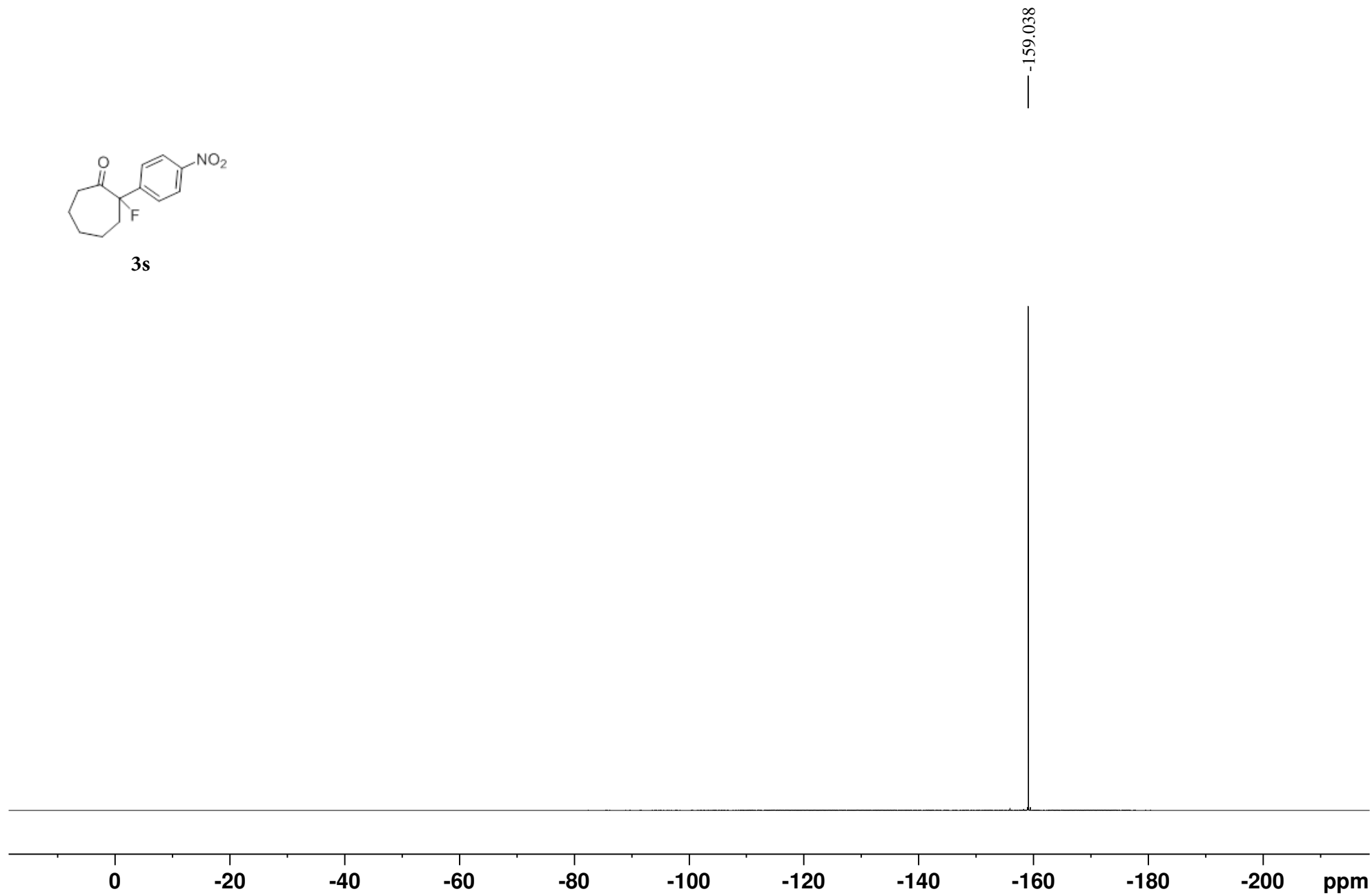


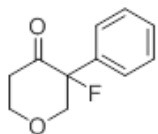
3s



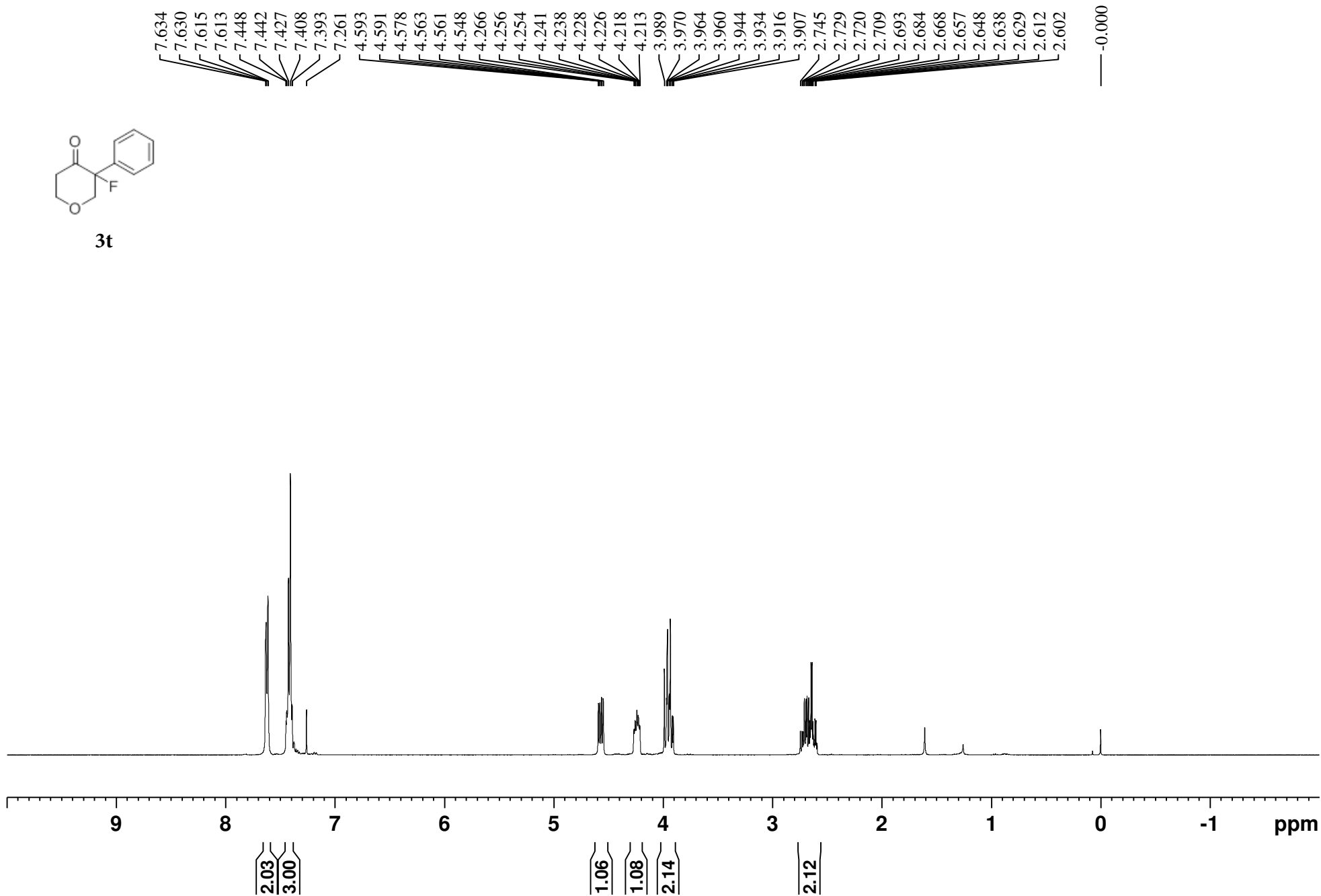


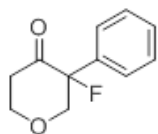
**3s**





**3t**





**3t**

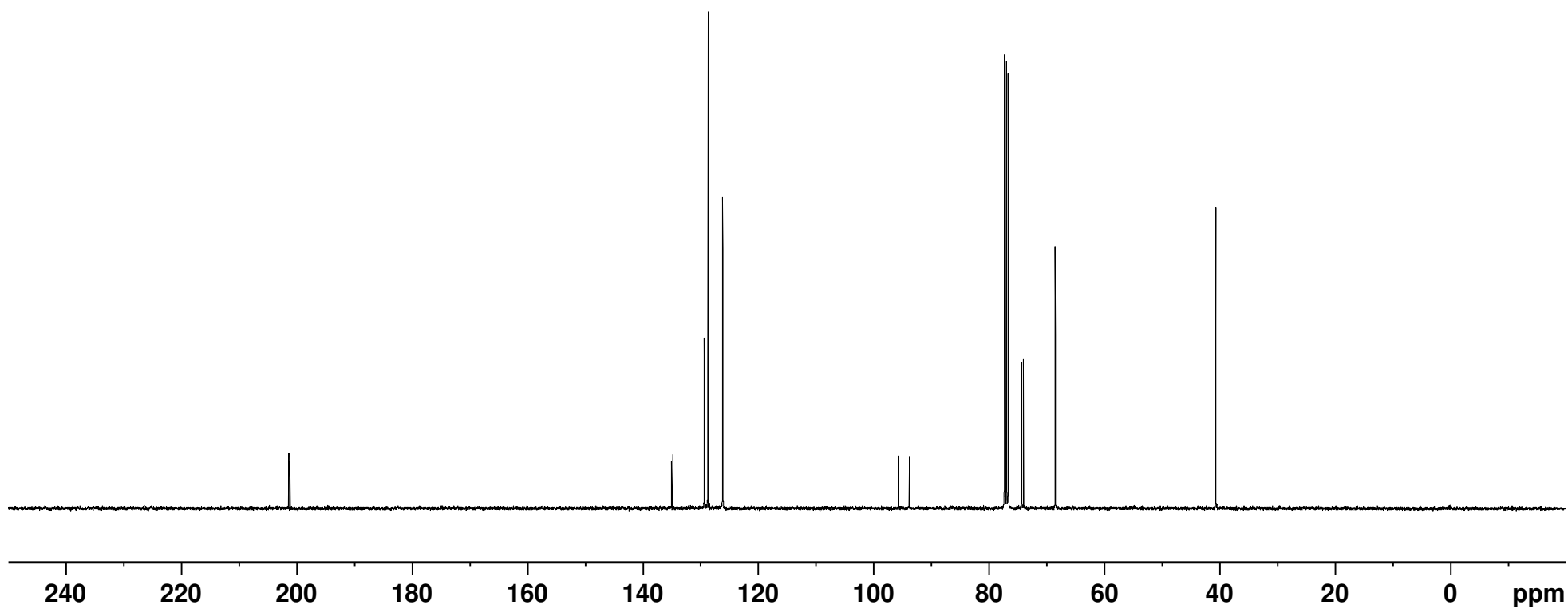
201.36  
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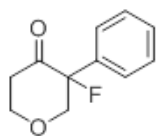
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134.81  
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129.34  
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126.17  
126.11

95.71  
93.82

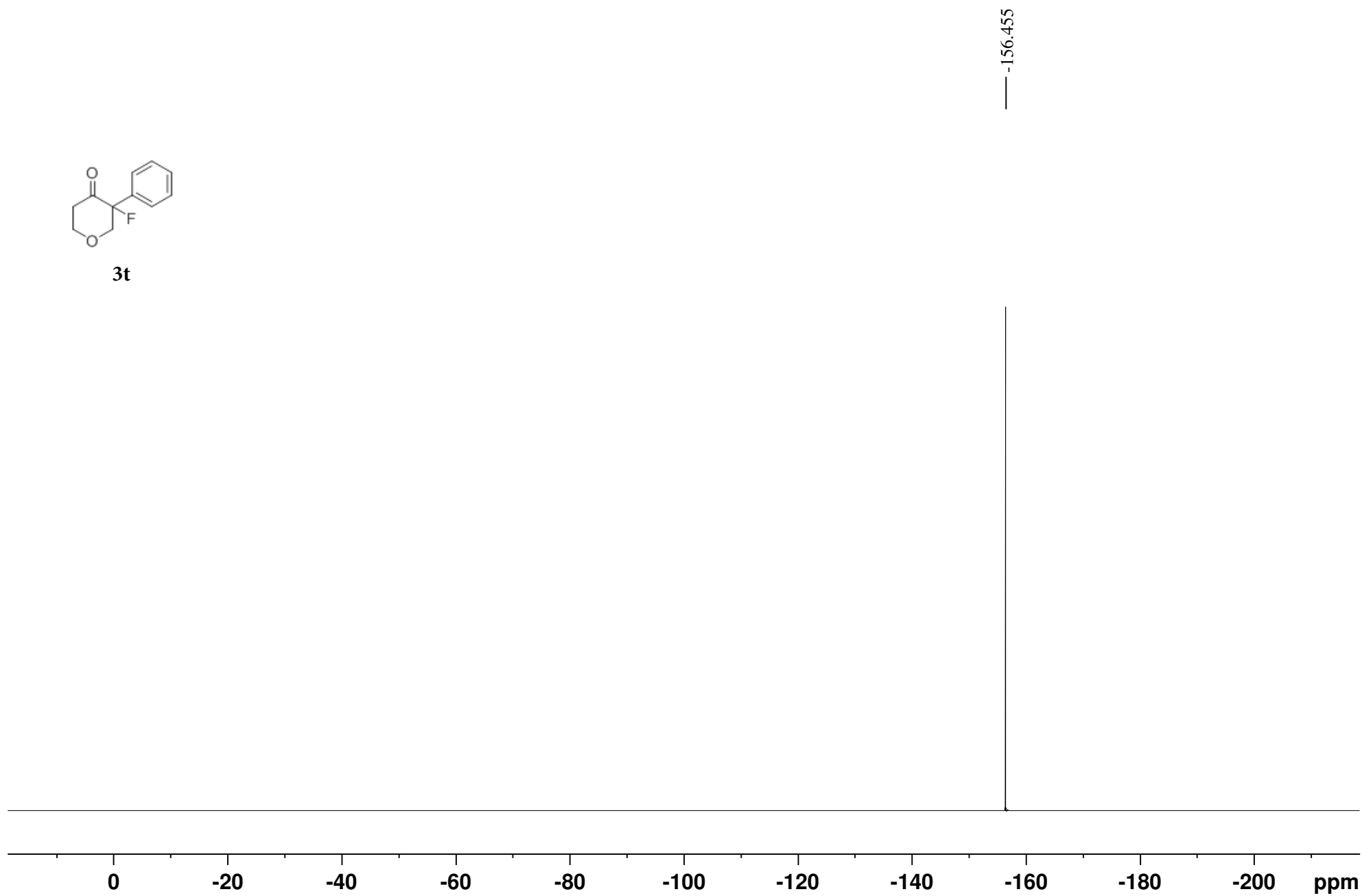
77.32  
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74.03  
68.52

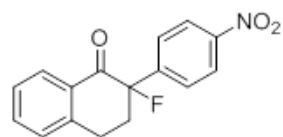
40.71





**3t**

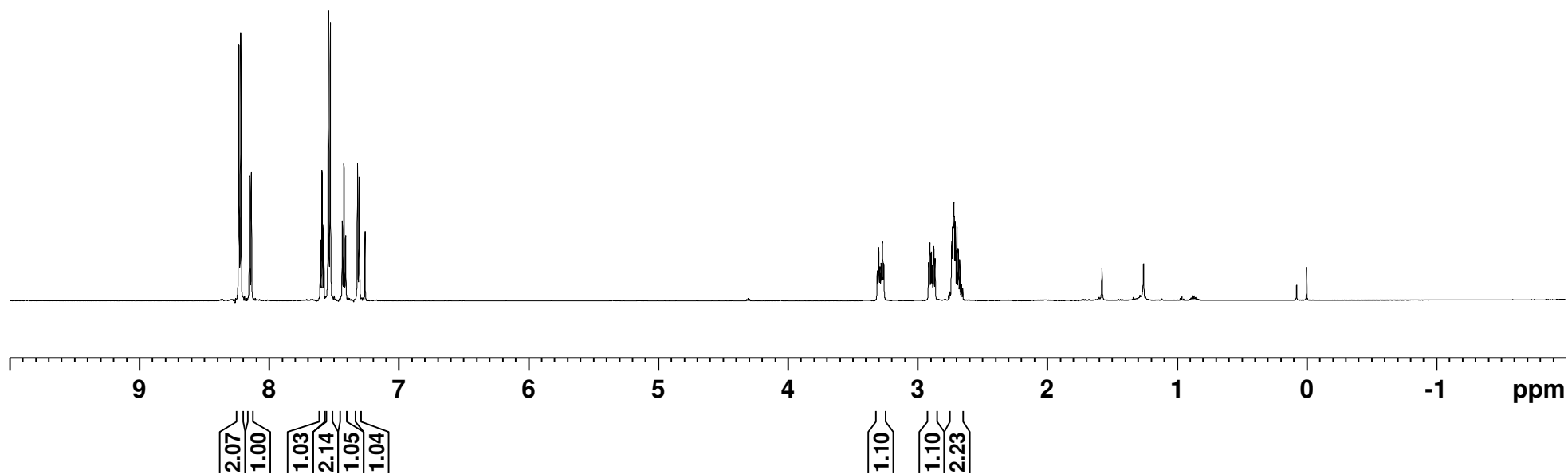


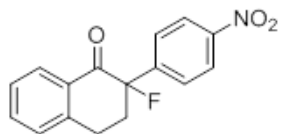


**3u**

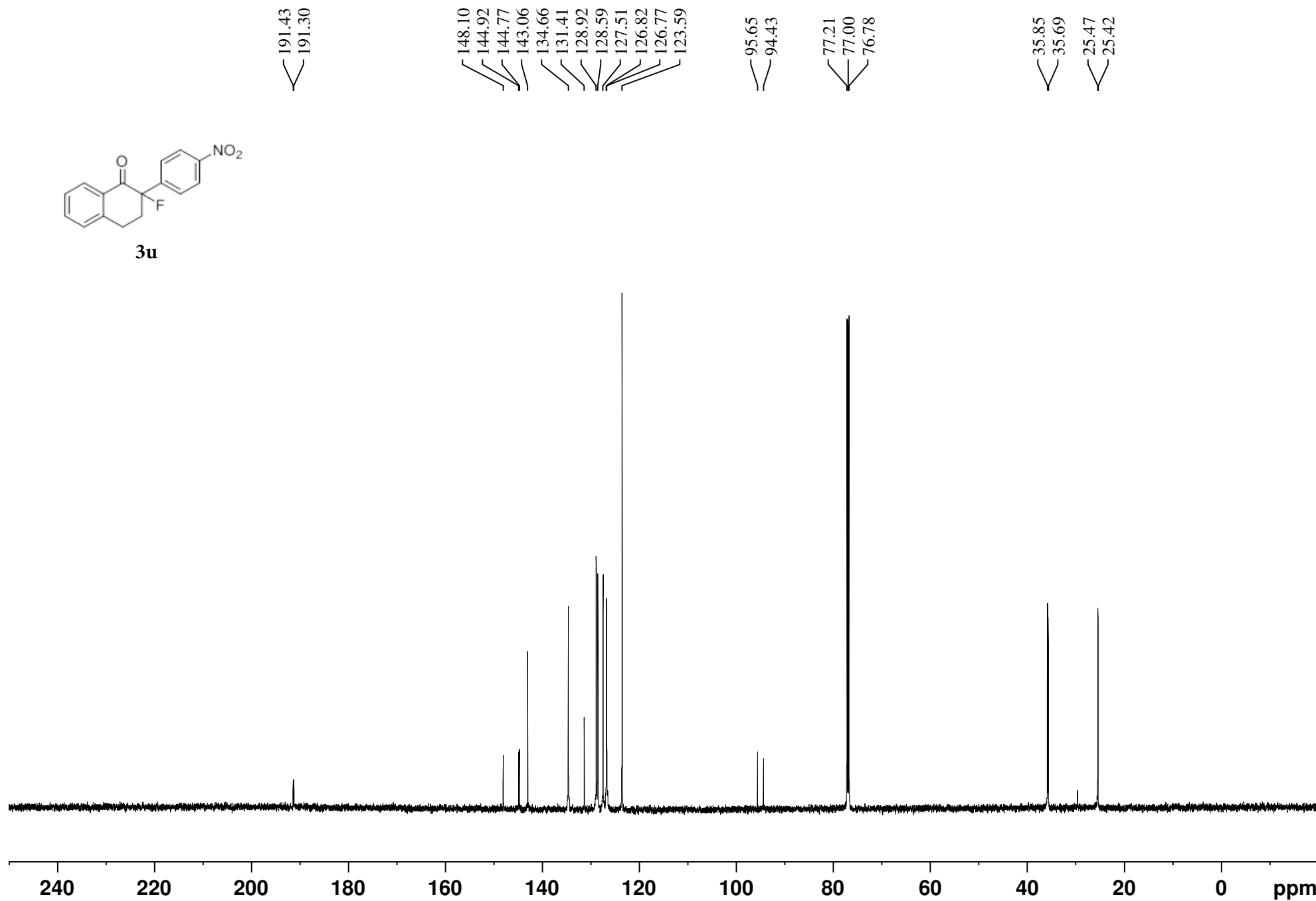
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7.592  
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7.529  
7.436  
7.423  
7.411  
7.319  
7.306  
7.261

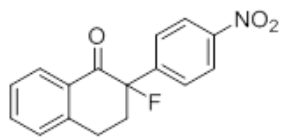
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2.894  
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2.876  
2.865  
2.751  
2.736  
2.732  
2.728  
2.725  
2.720  
2.718  
2.710  
2.705  
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2.684  
2.675  
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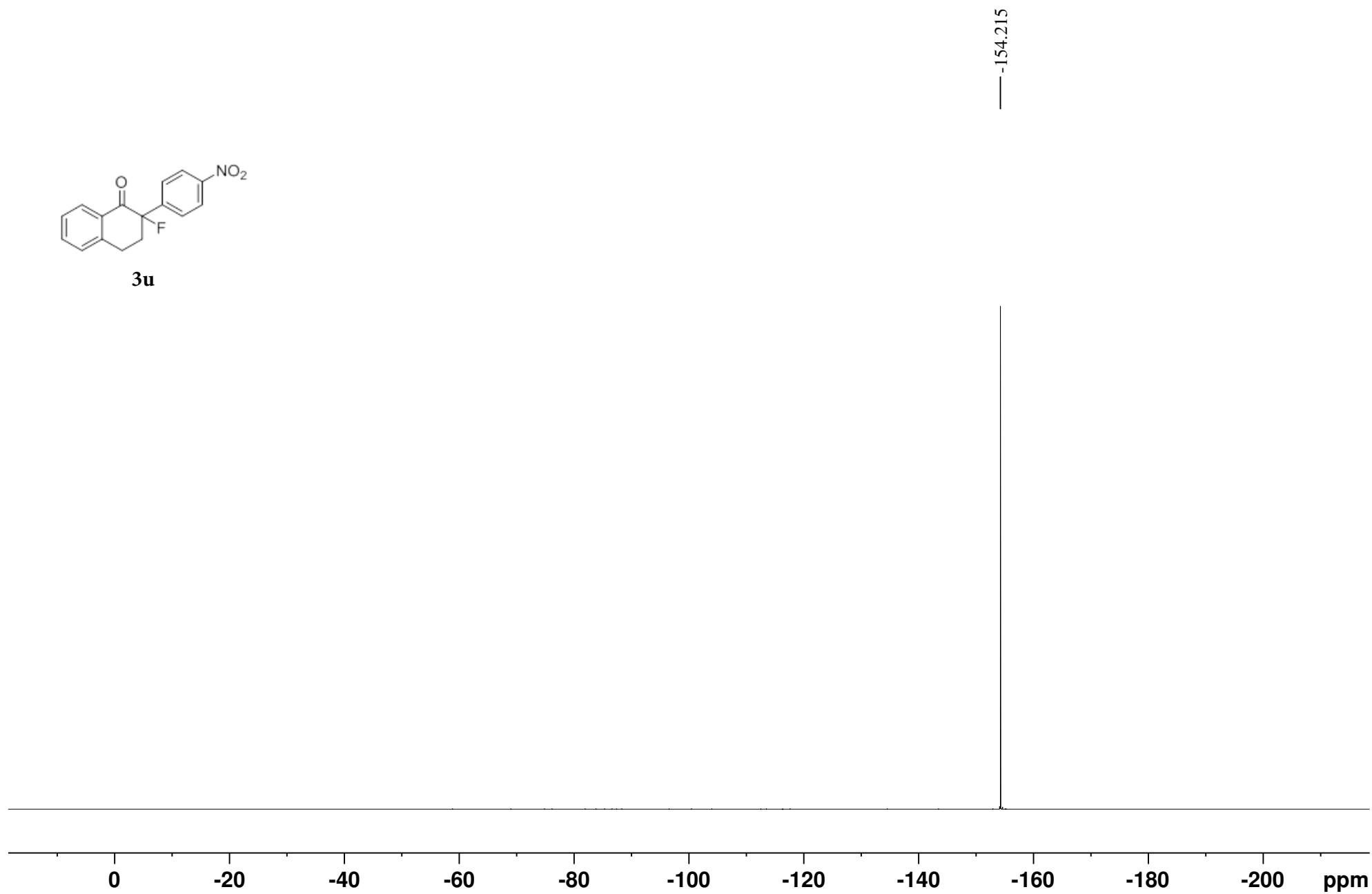


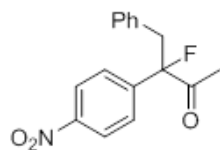
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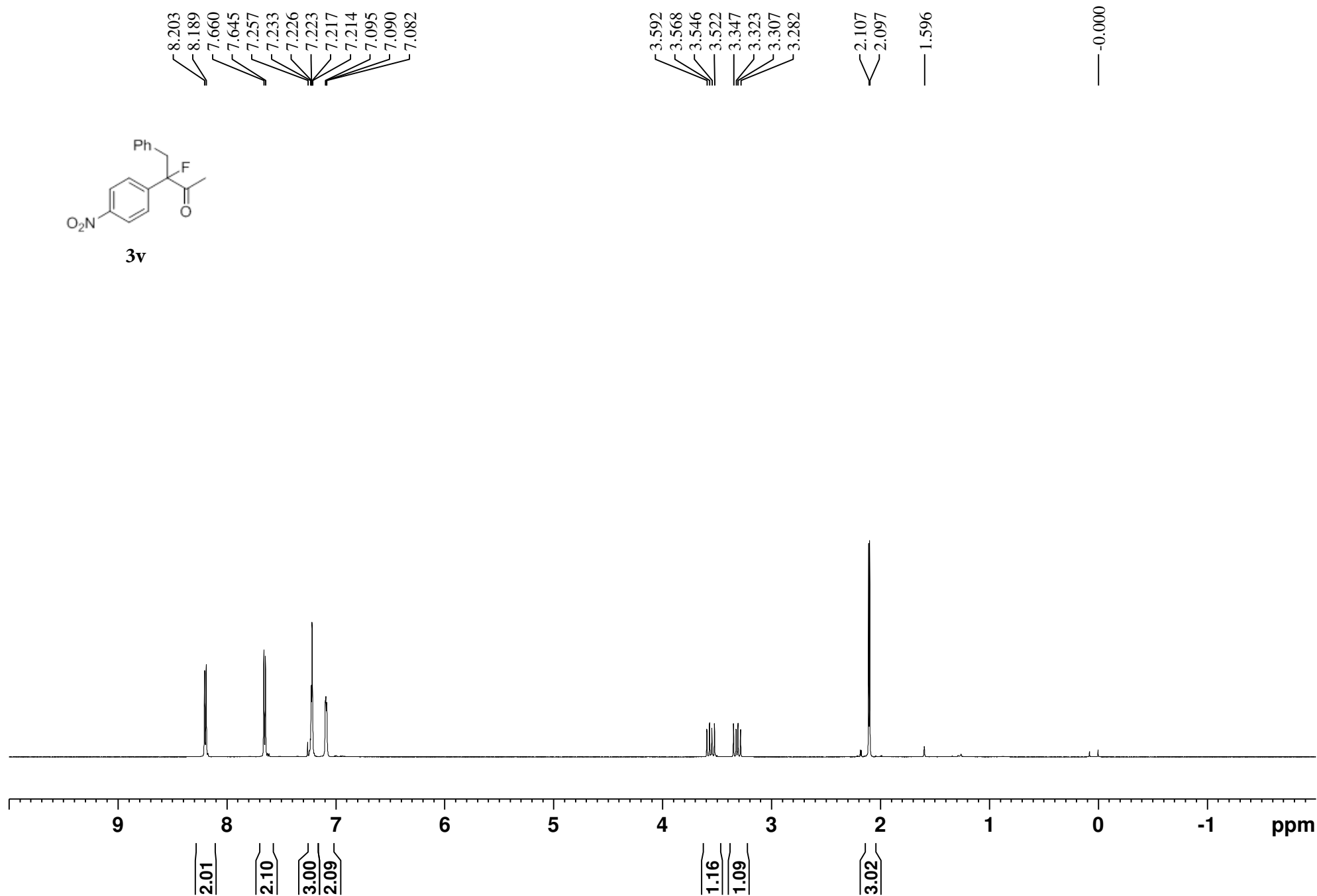


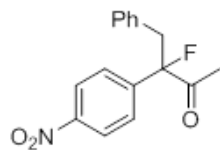
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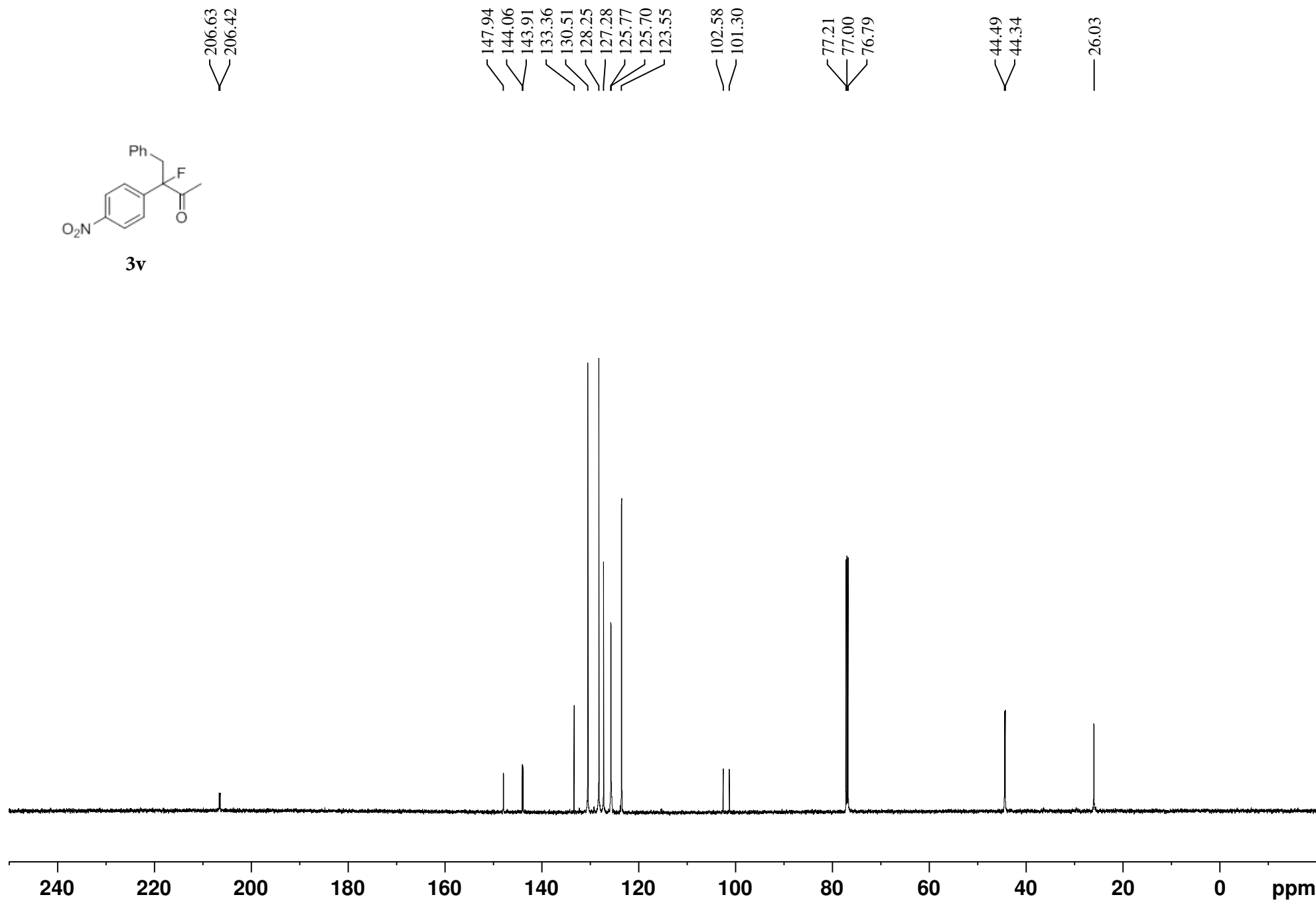


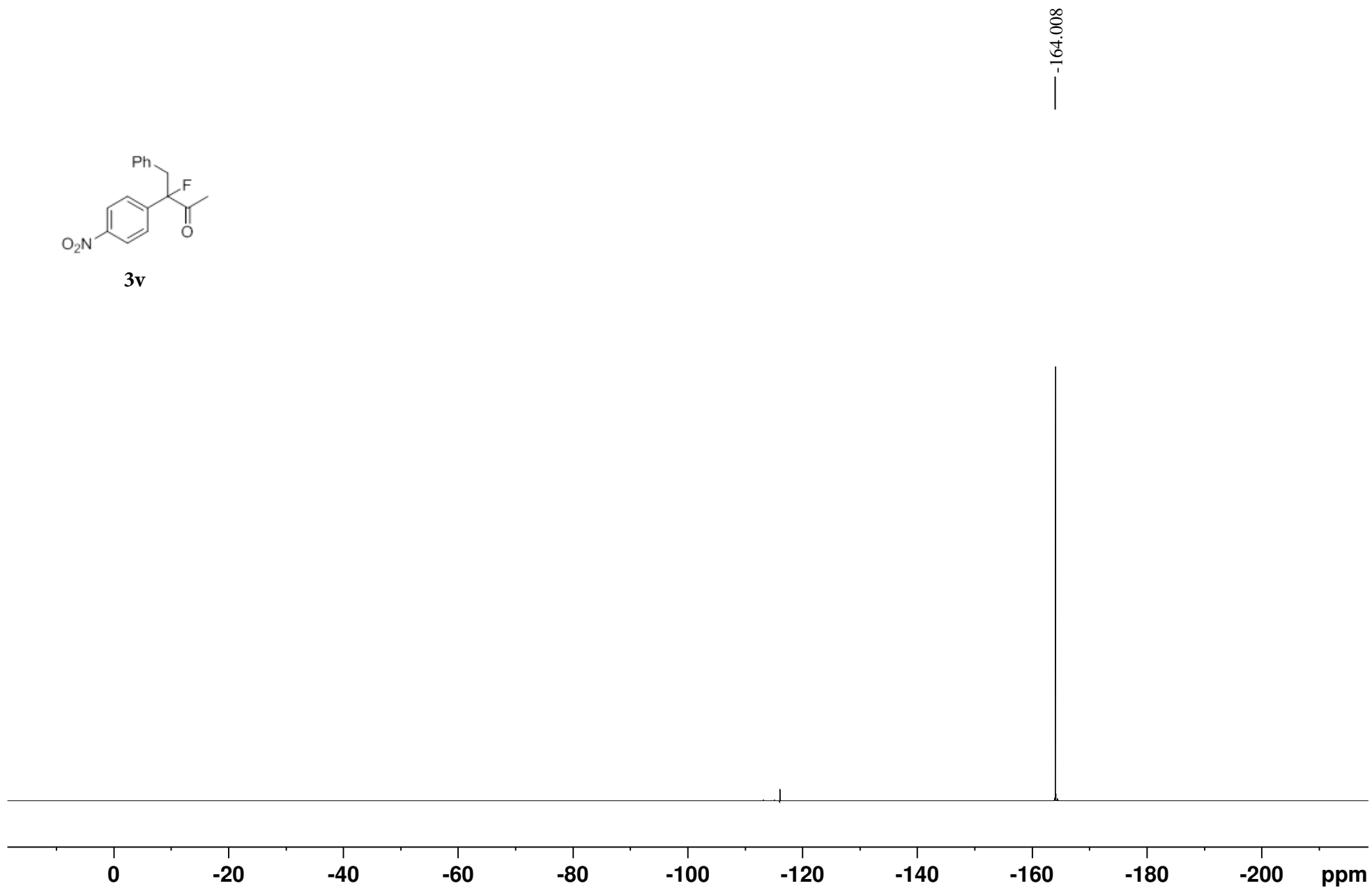
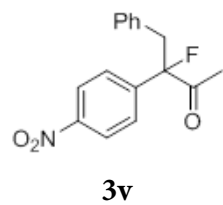
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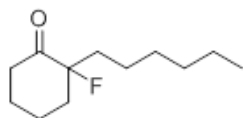




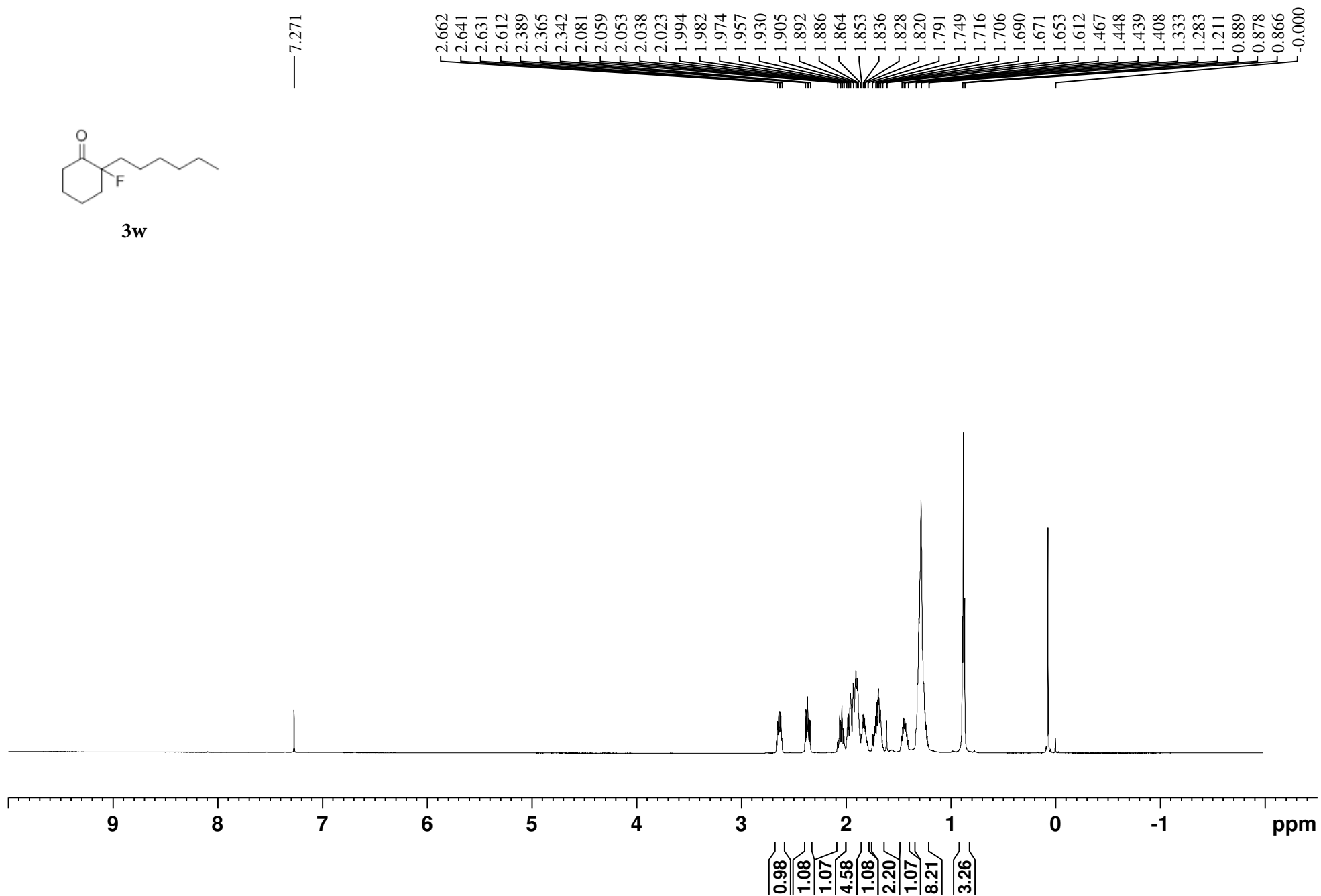
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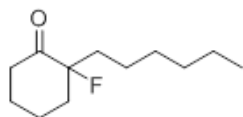






3w





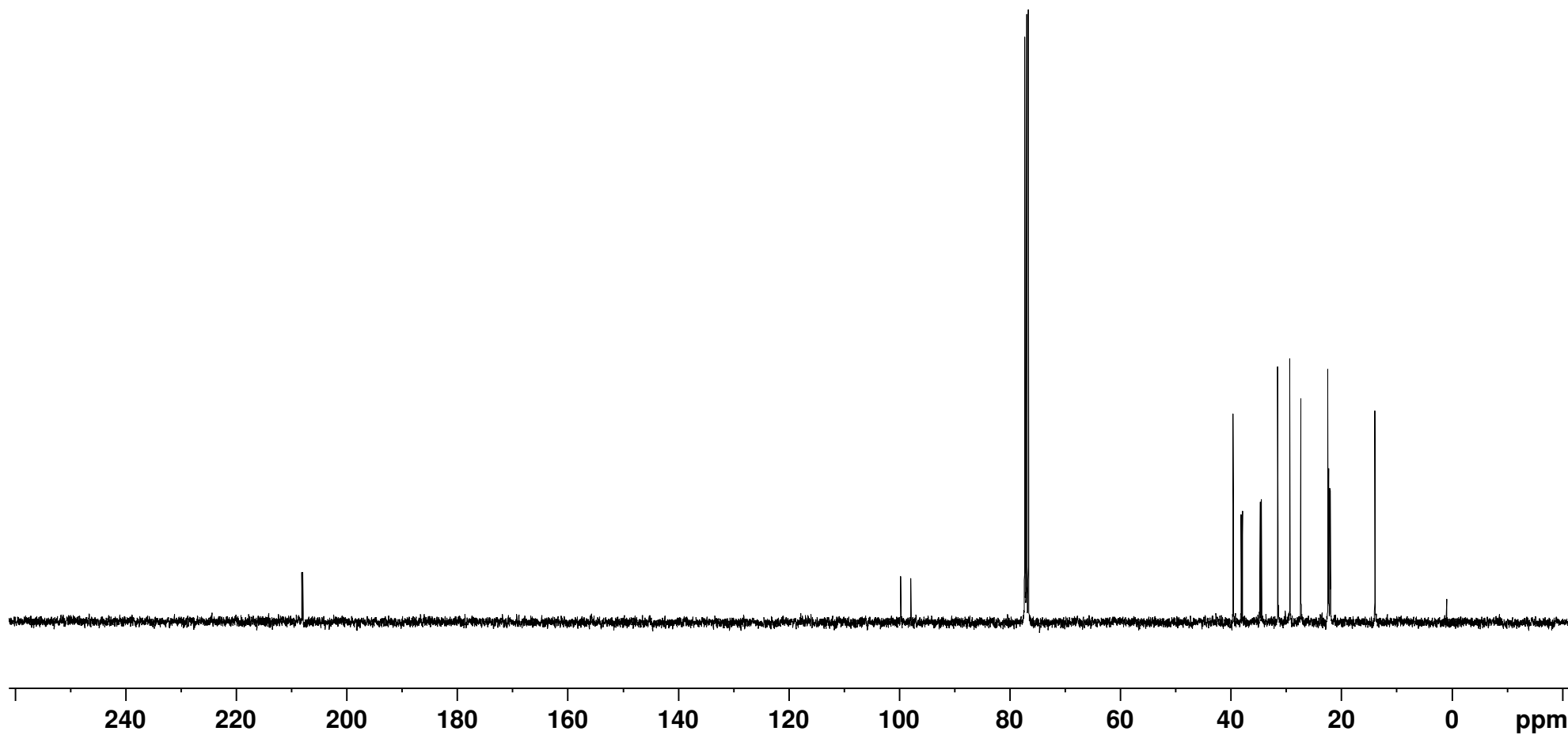
3w

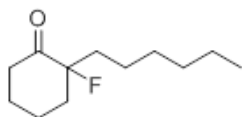
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207.98

99.78  
97.95

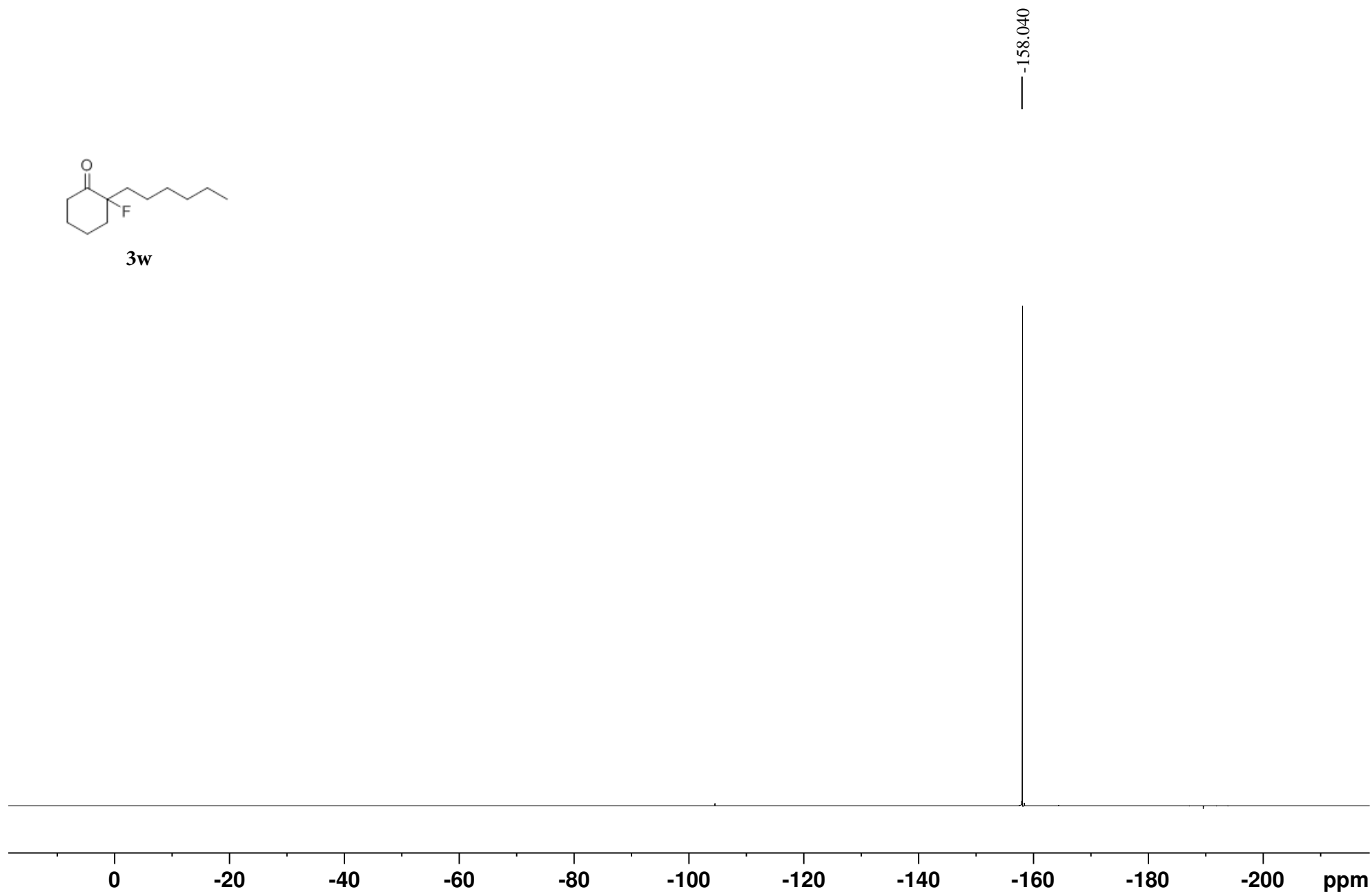
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76.99  
76.68

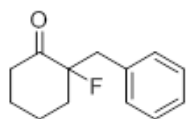
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34.73  
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22.48  
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22.32  
22.10  
22.02  
13.97



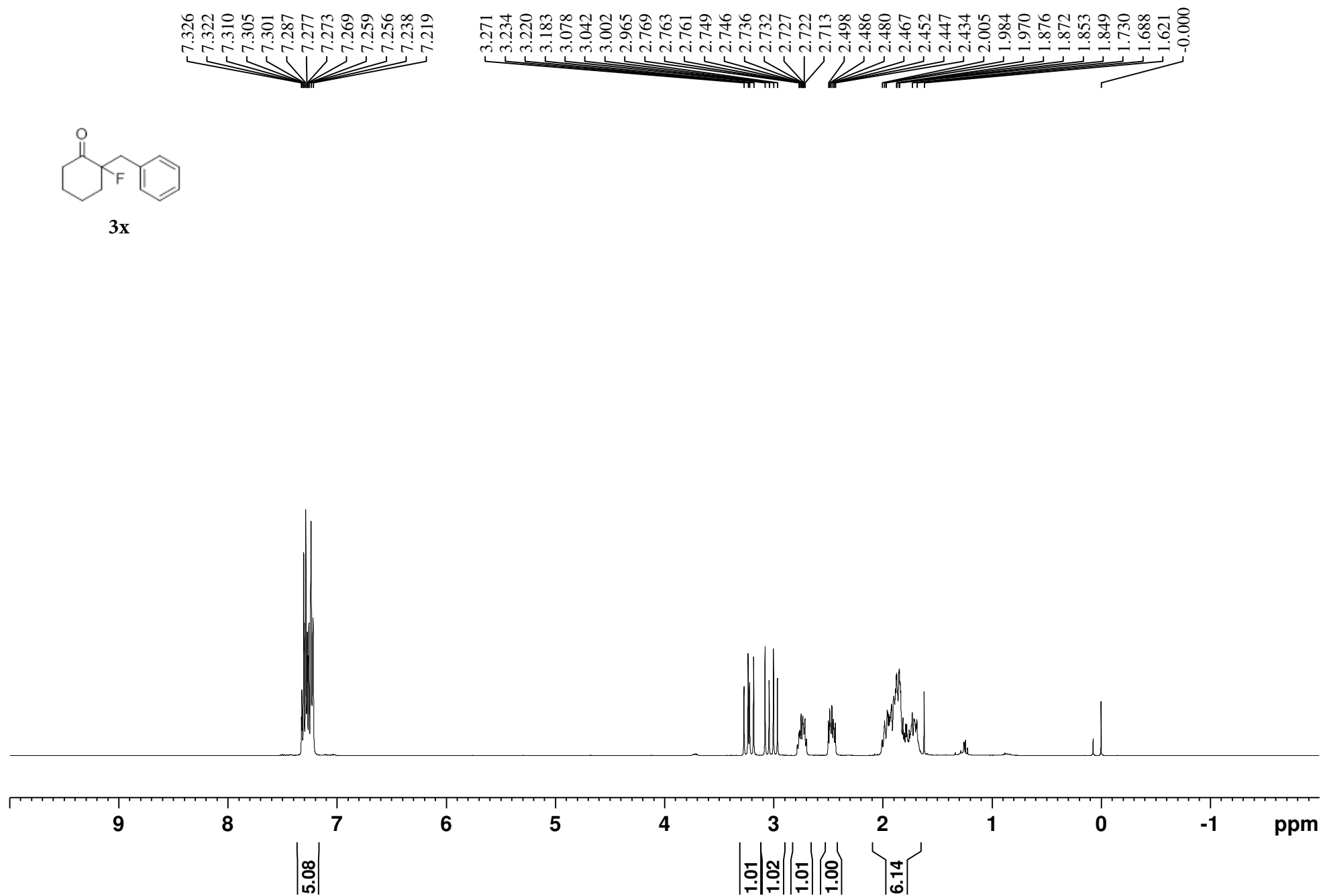


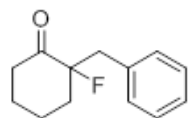
**3w**





**3x**





3x

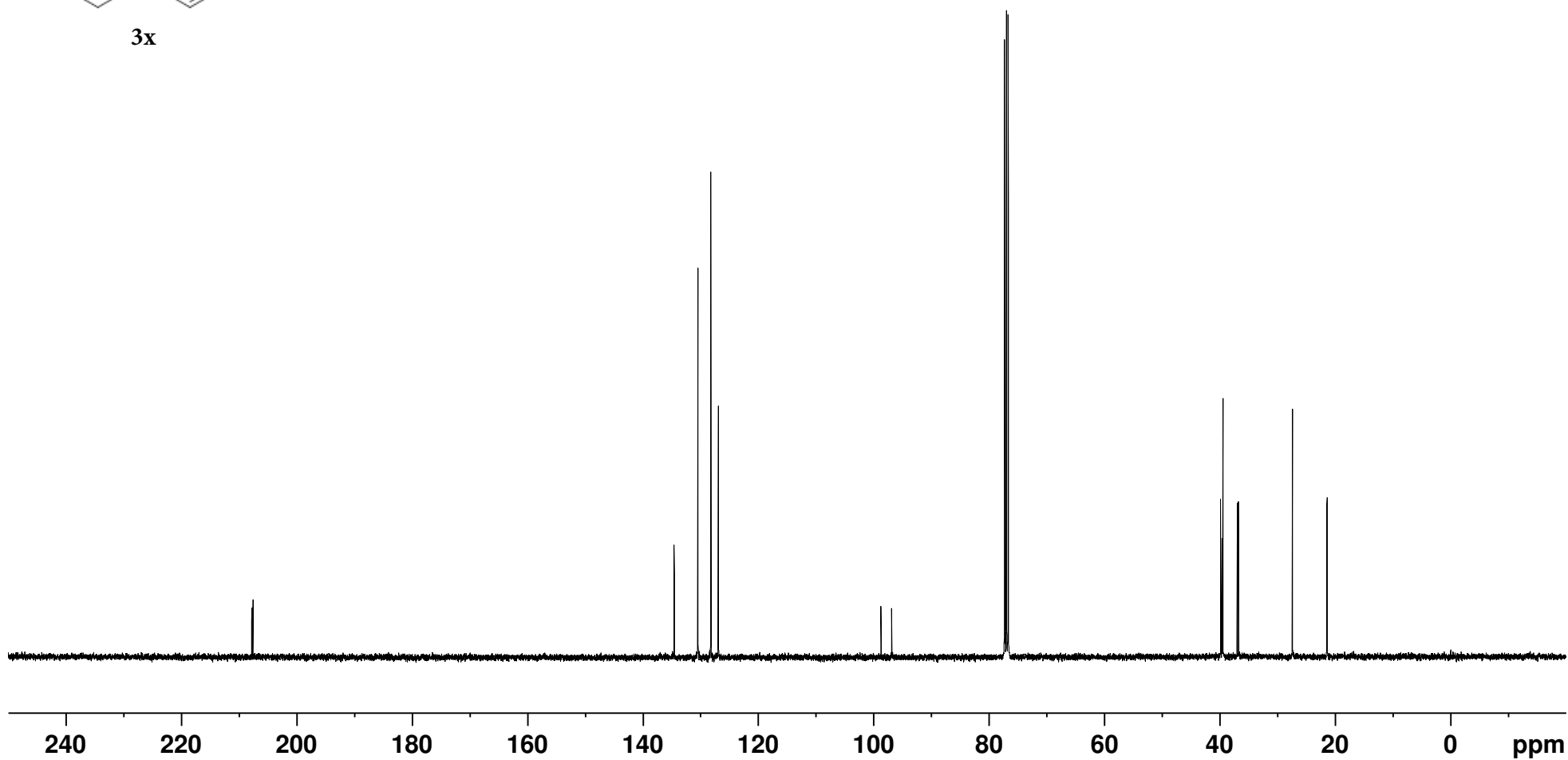
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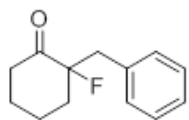
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98.72  
96.89

77.31  
77.00  
76.68

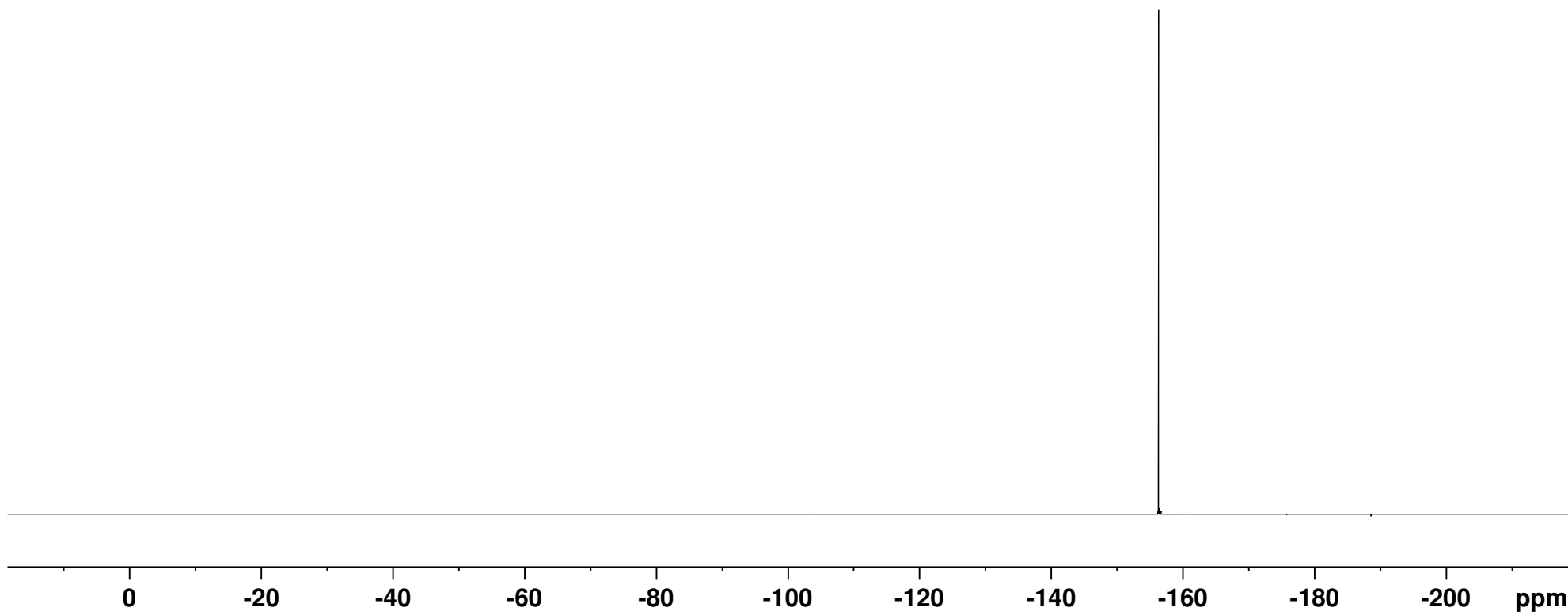
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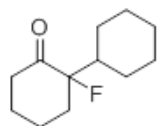




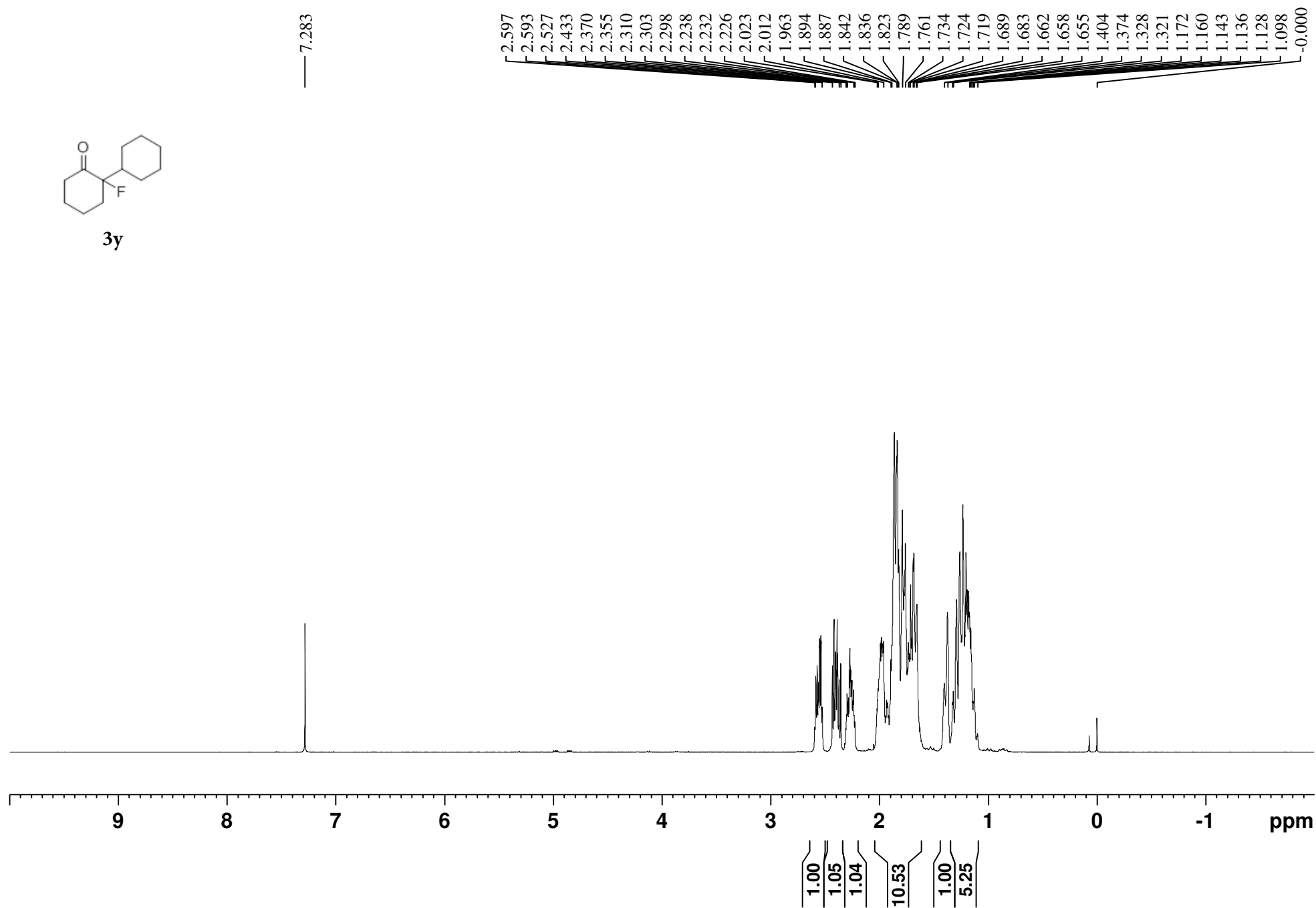
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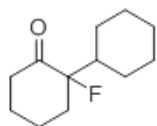
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3y





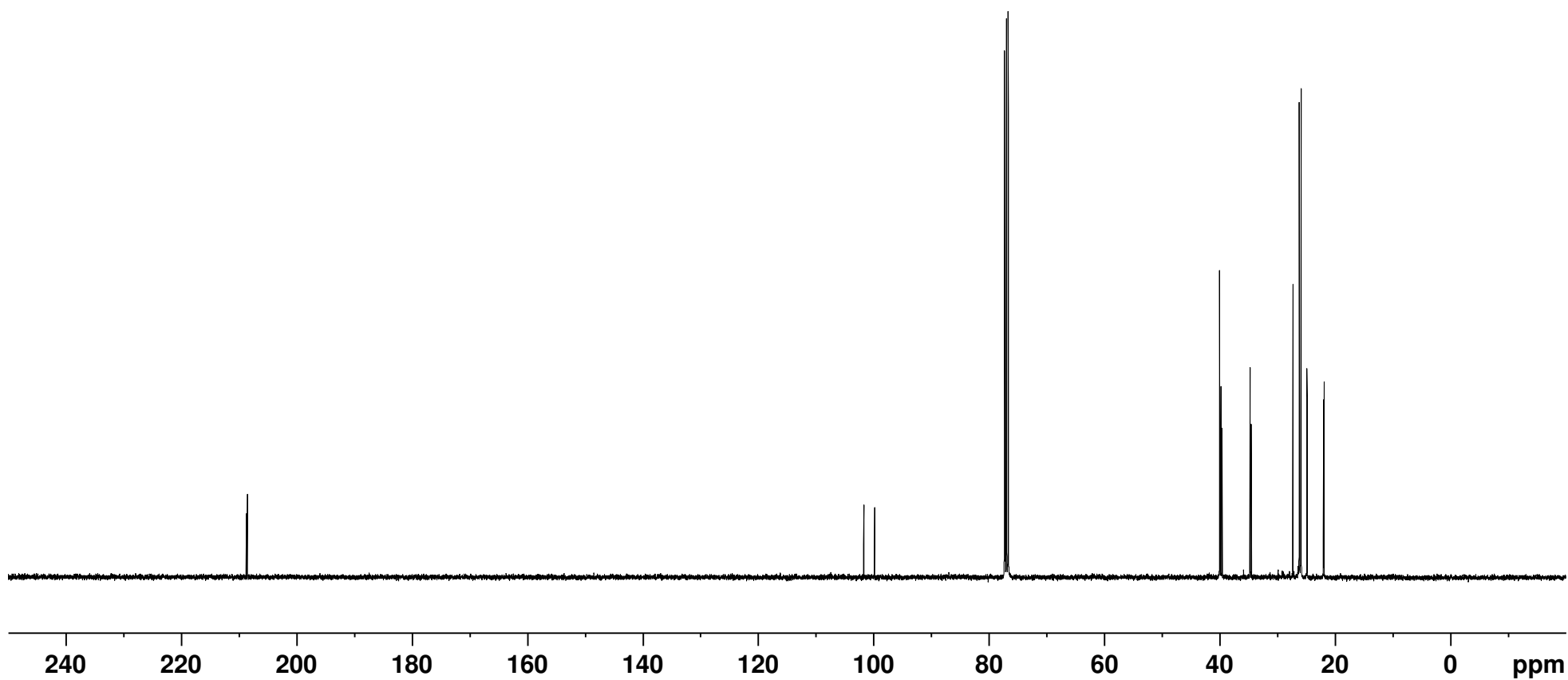
**3y**

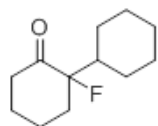
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101.72  
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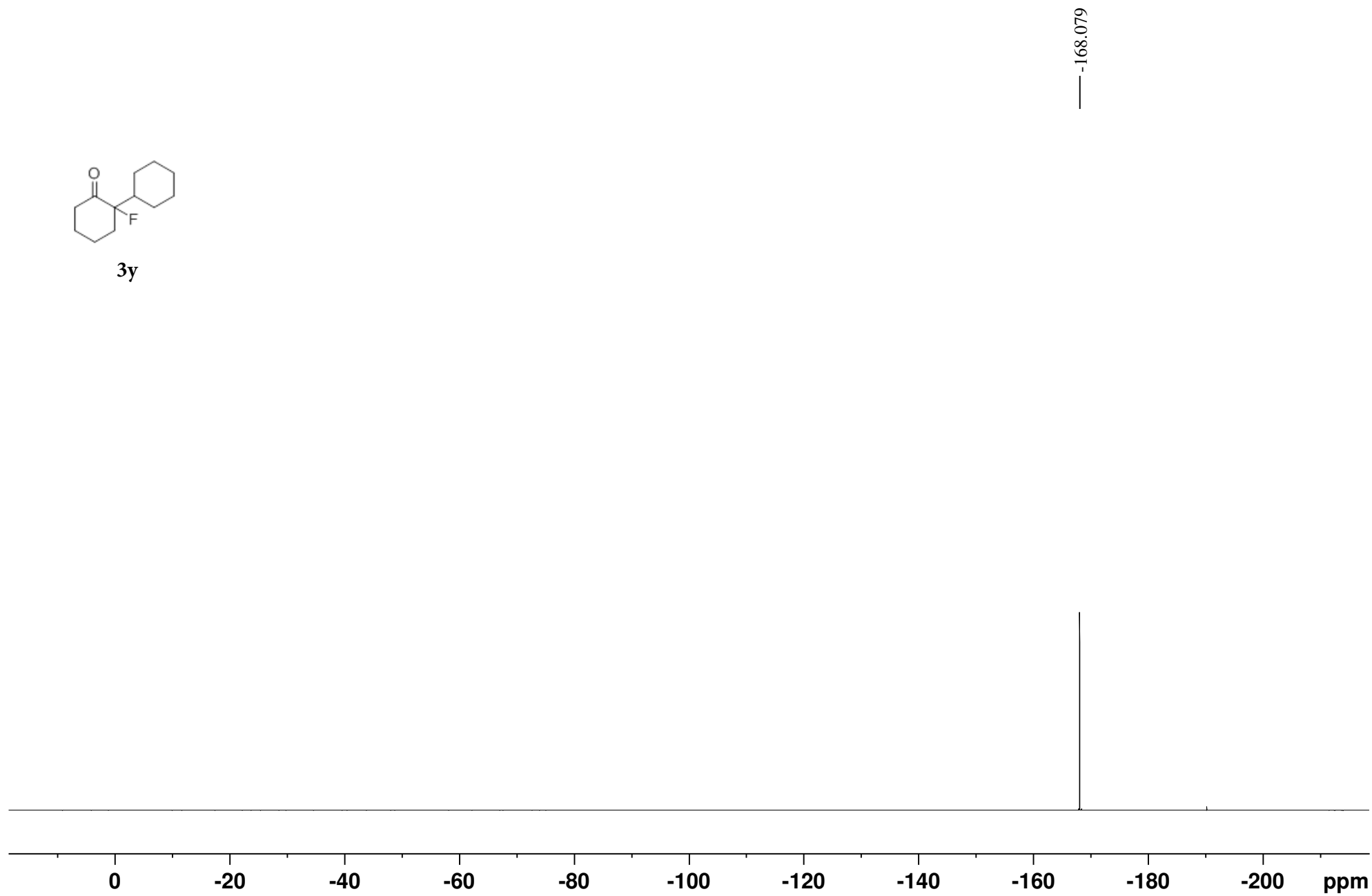
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77.00  
76.68

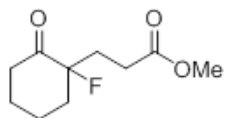
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39.82  
39.60  
34.76  
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25.94  
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24.91  
24.87  
22.04  
21.94



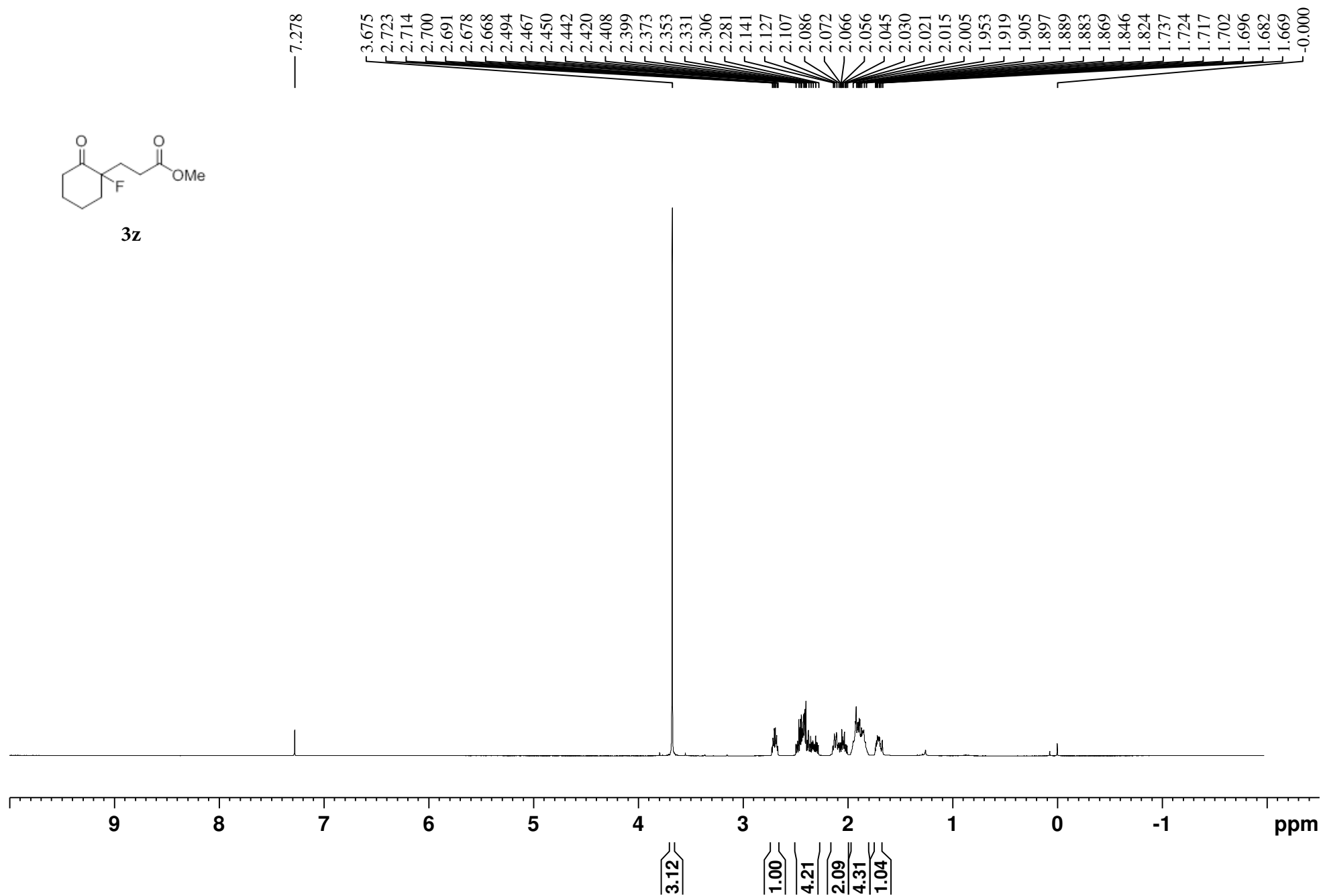


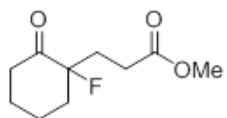
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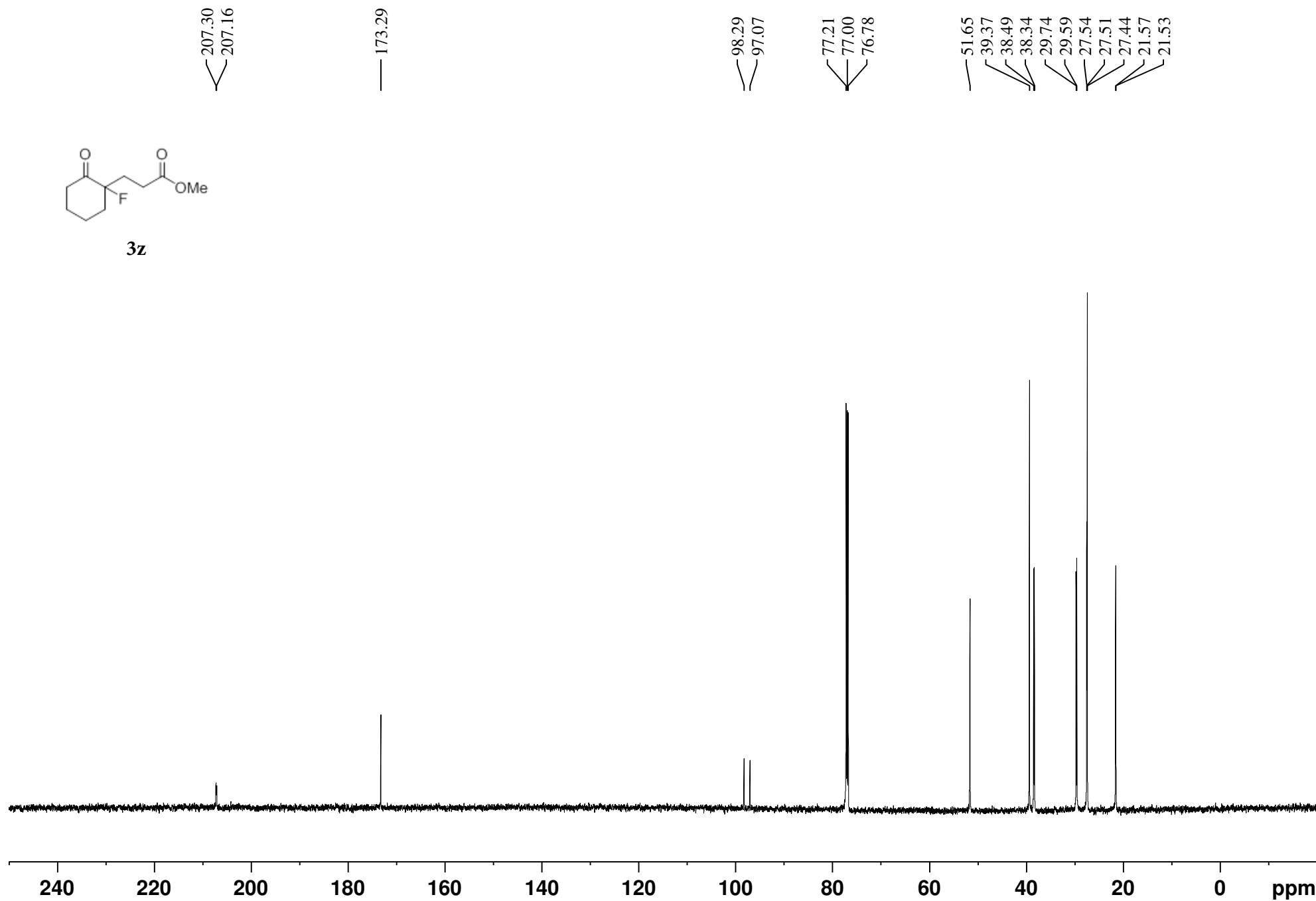


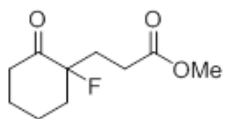
**3z**





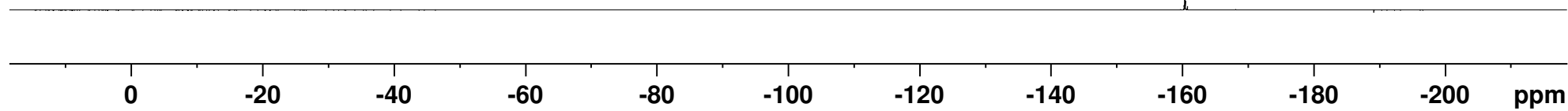
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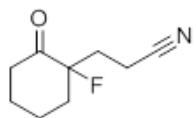




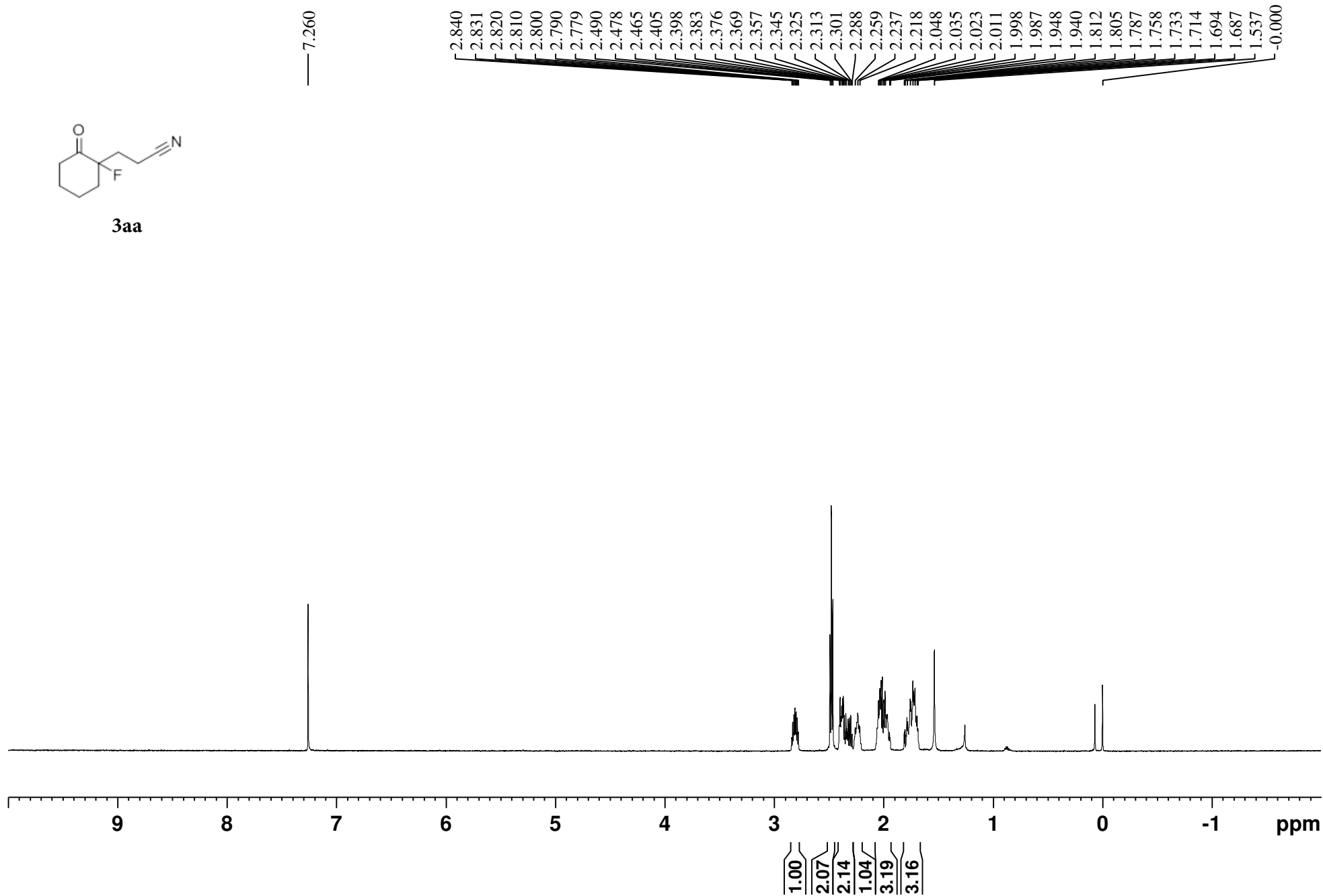
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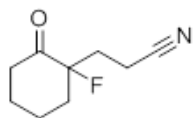
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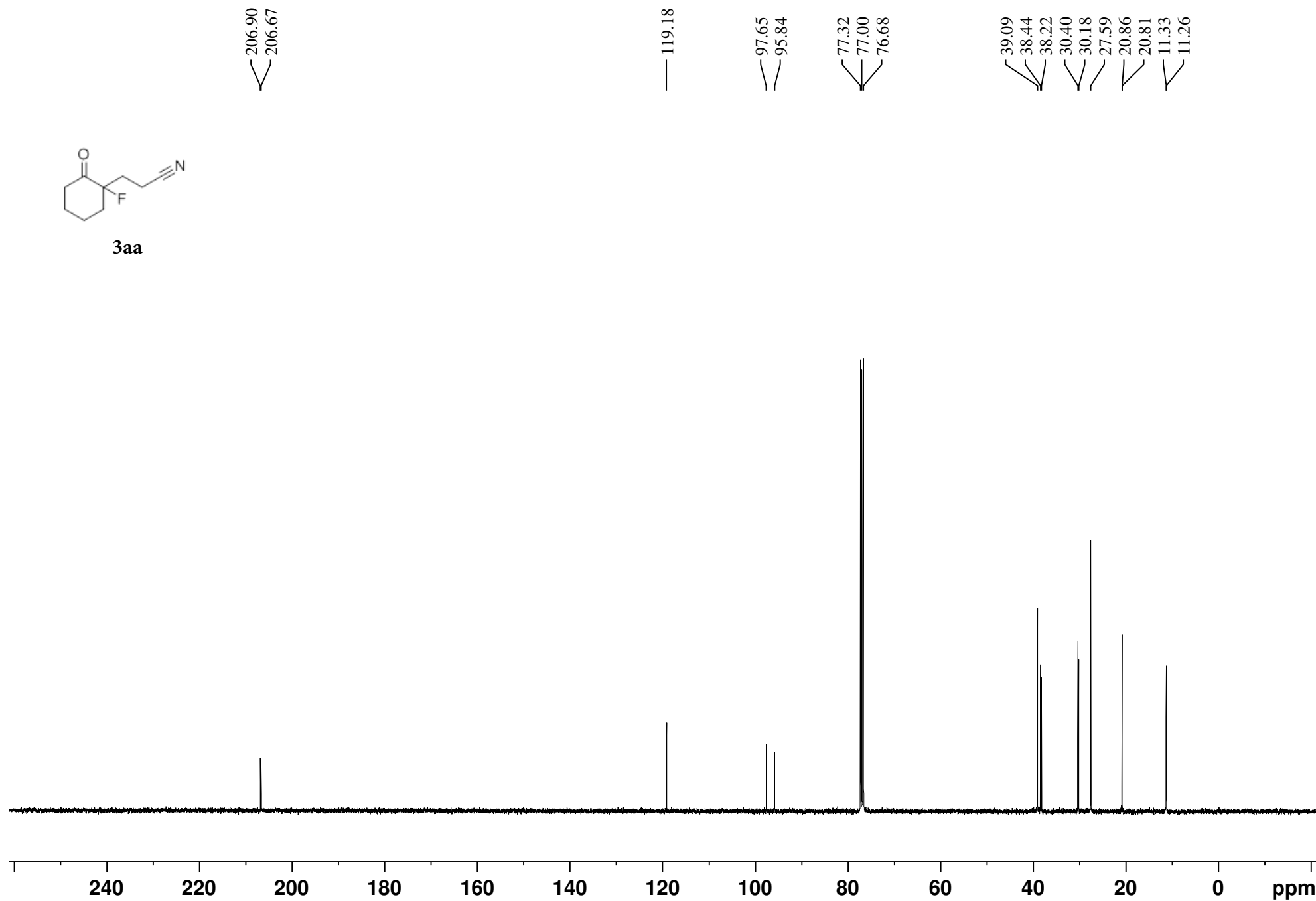


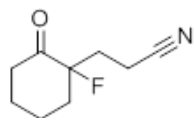
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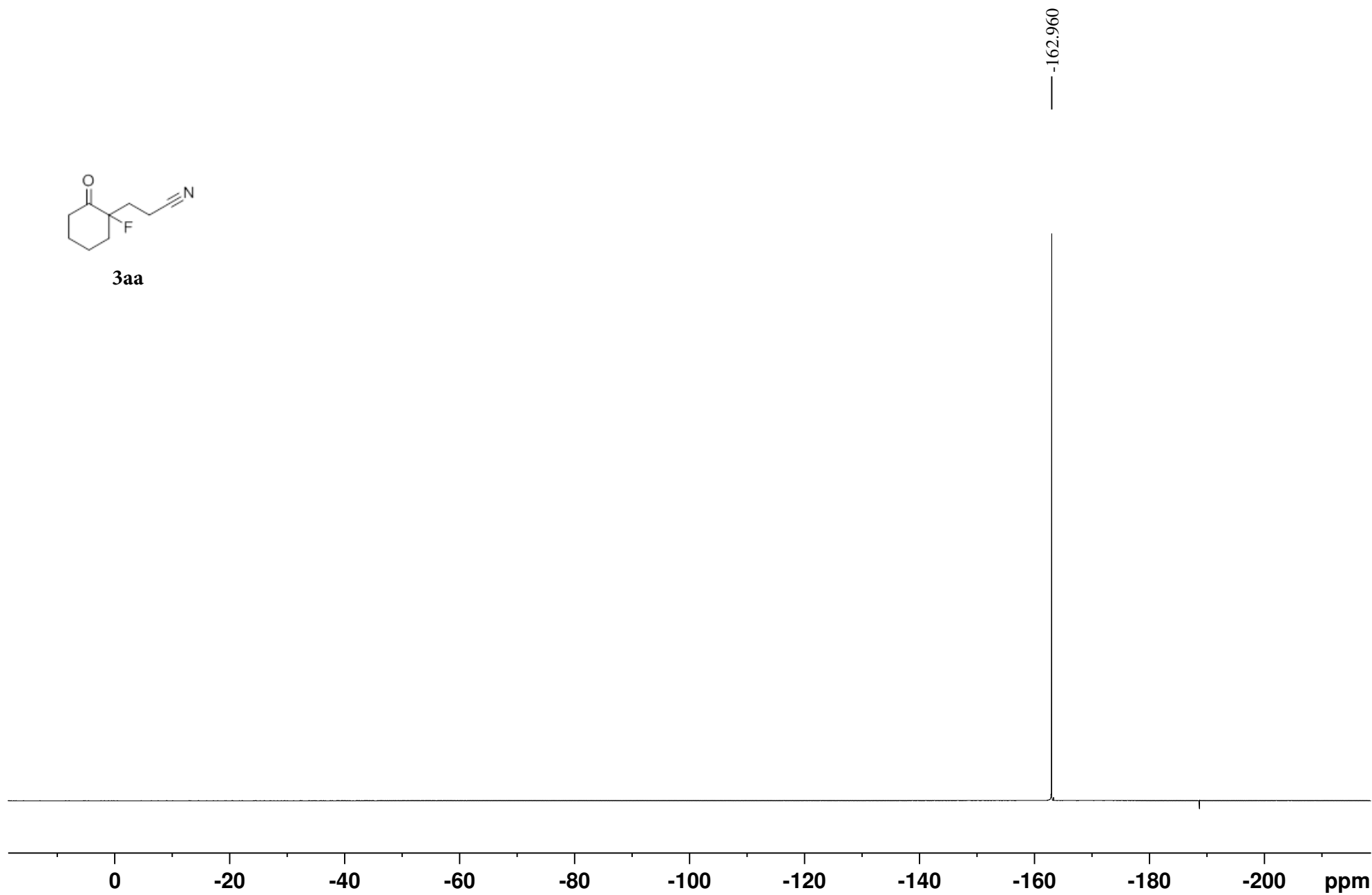


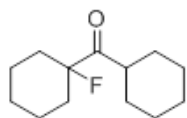
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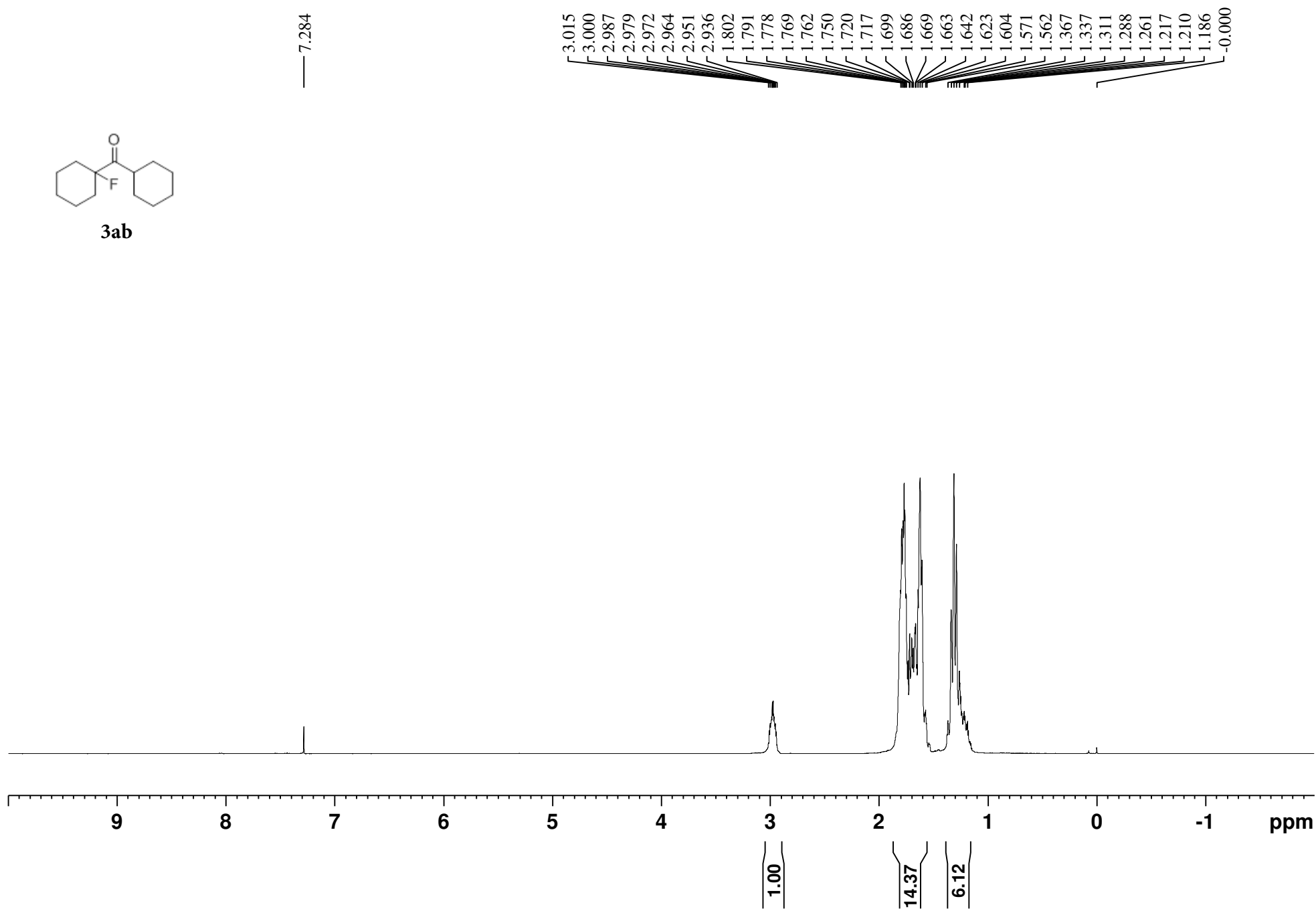


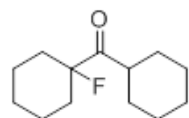
**3aa**





**3ab**





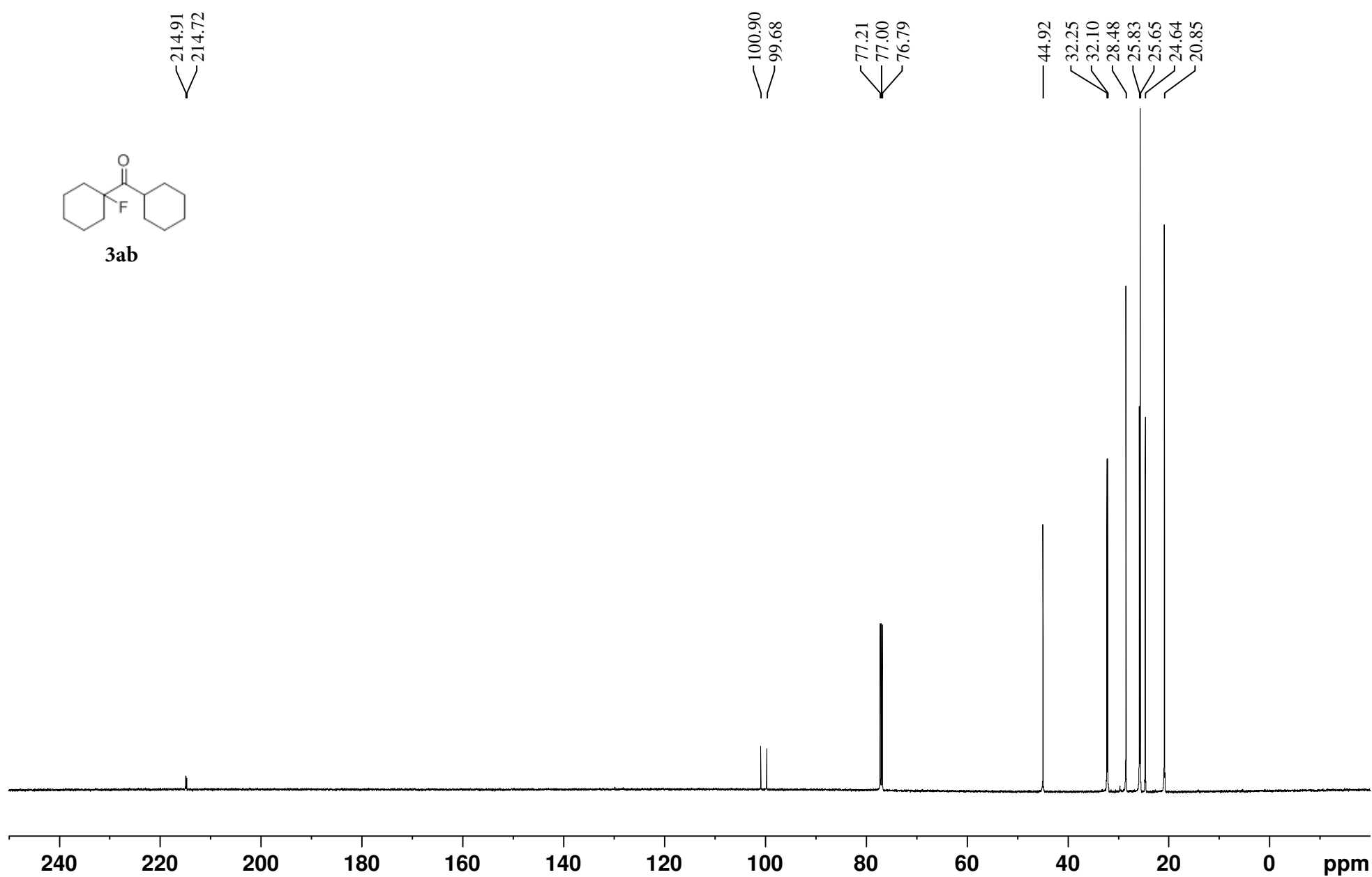
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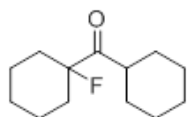
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214.72

100.90  
99.68

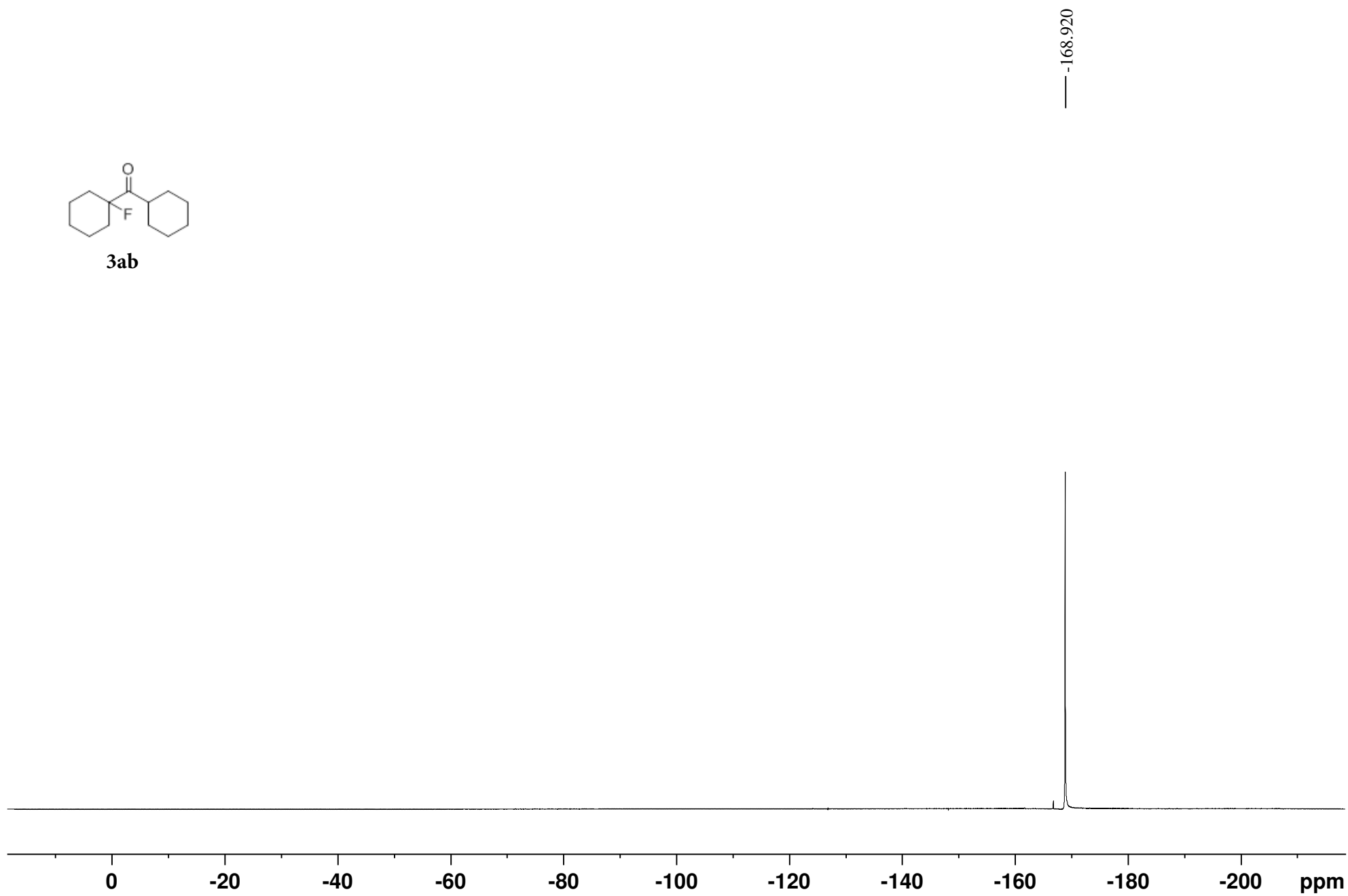
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76.79

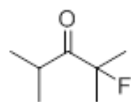
44.92  
32.25  
32.10  
28.48  
25.83  
25.65  
24.64  
20.85



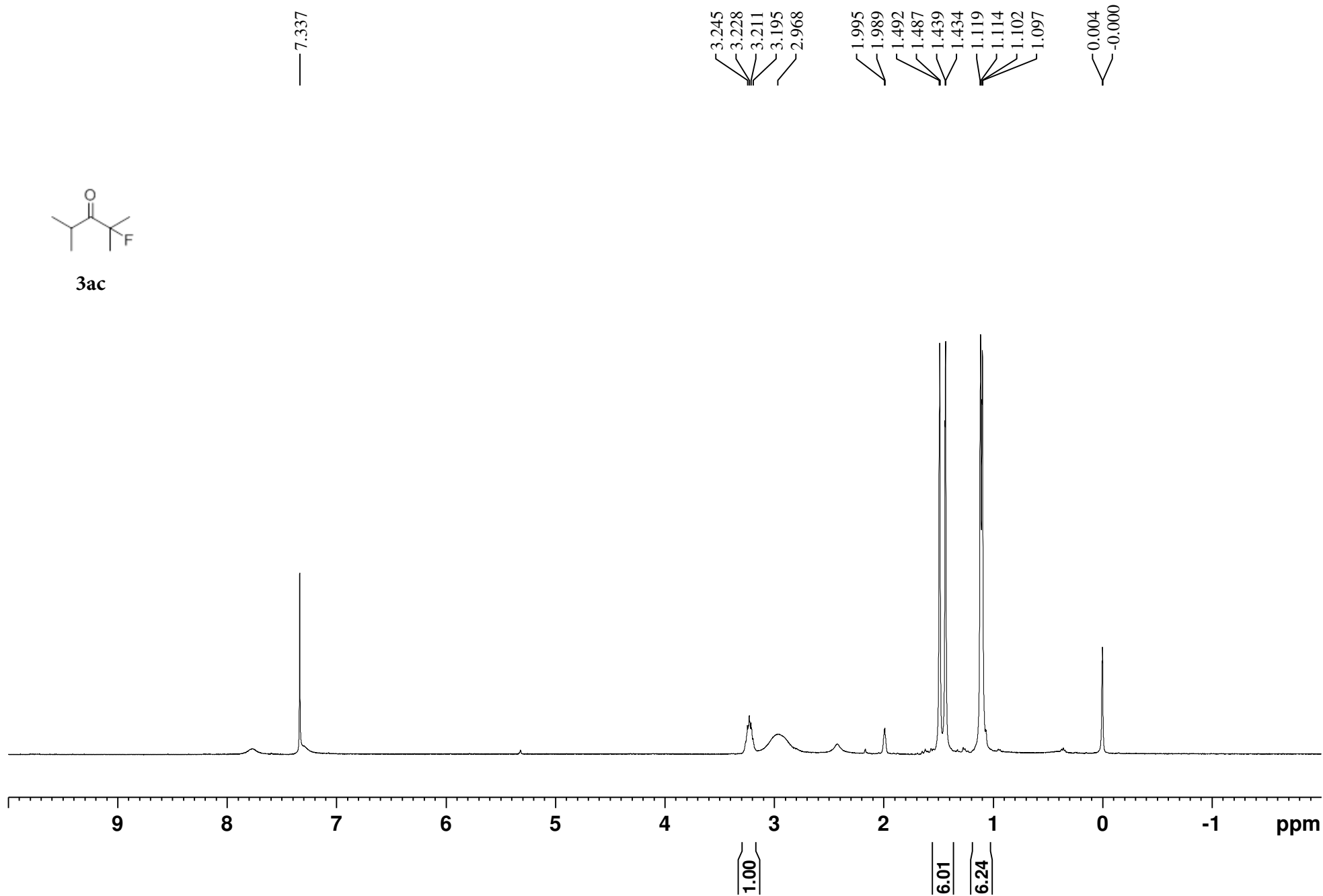


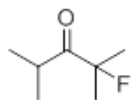
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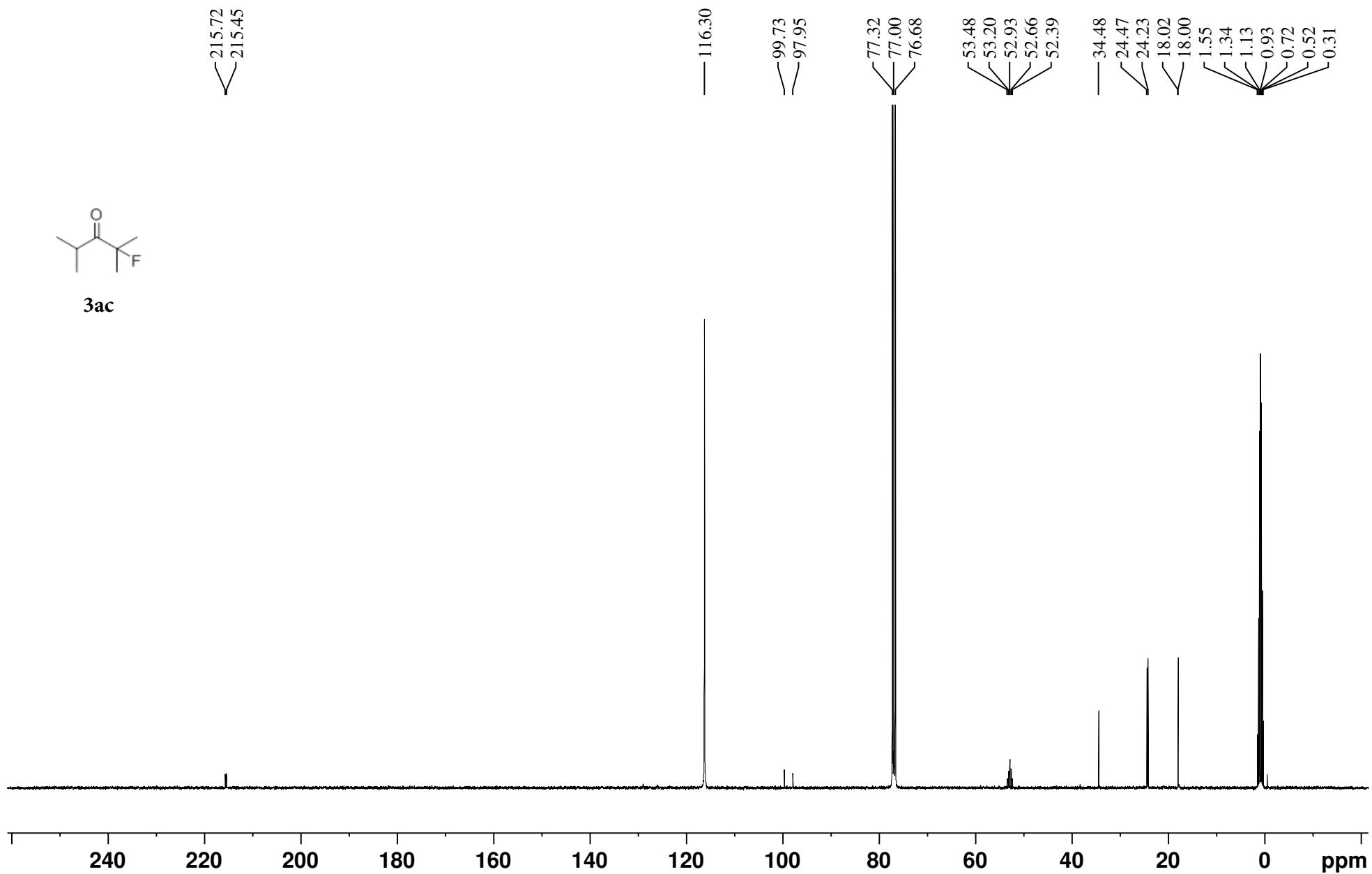


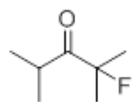
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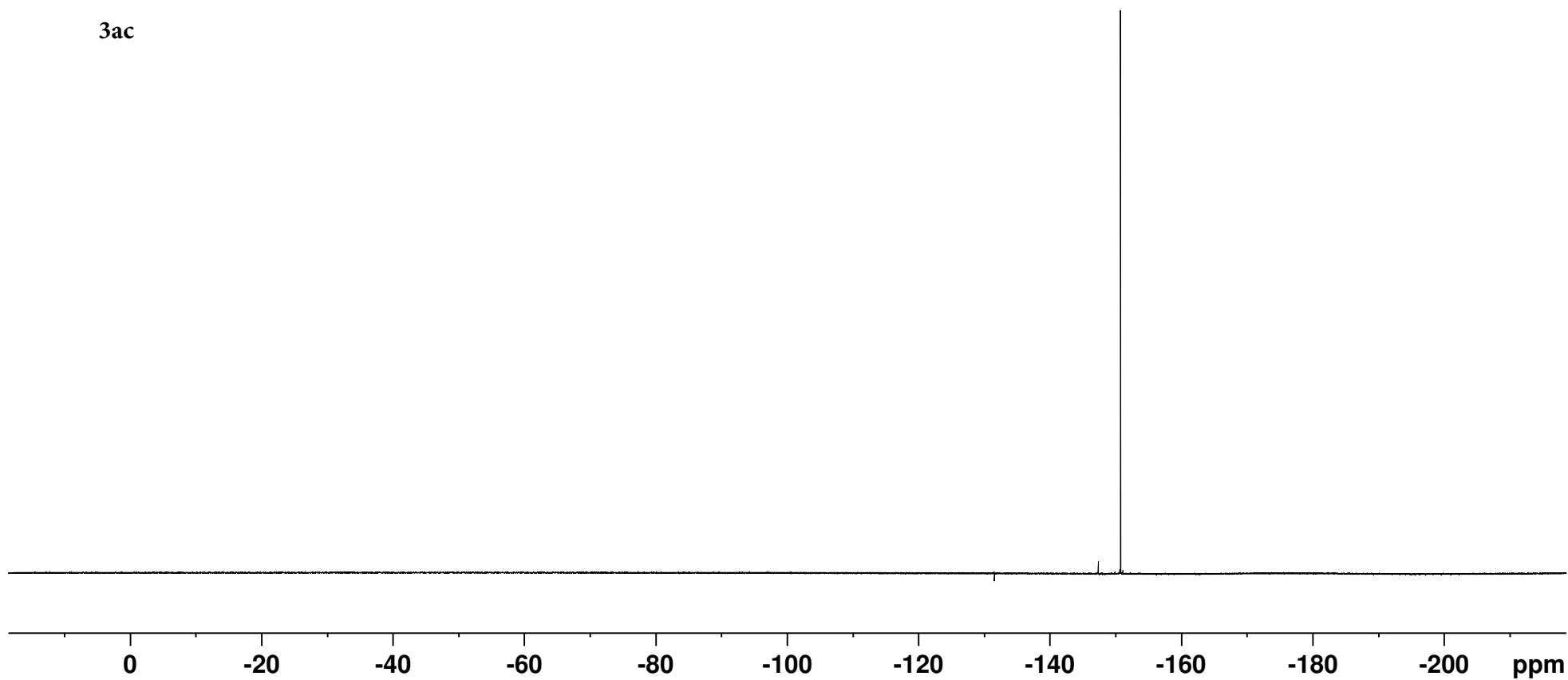
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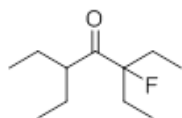




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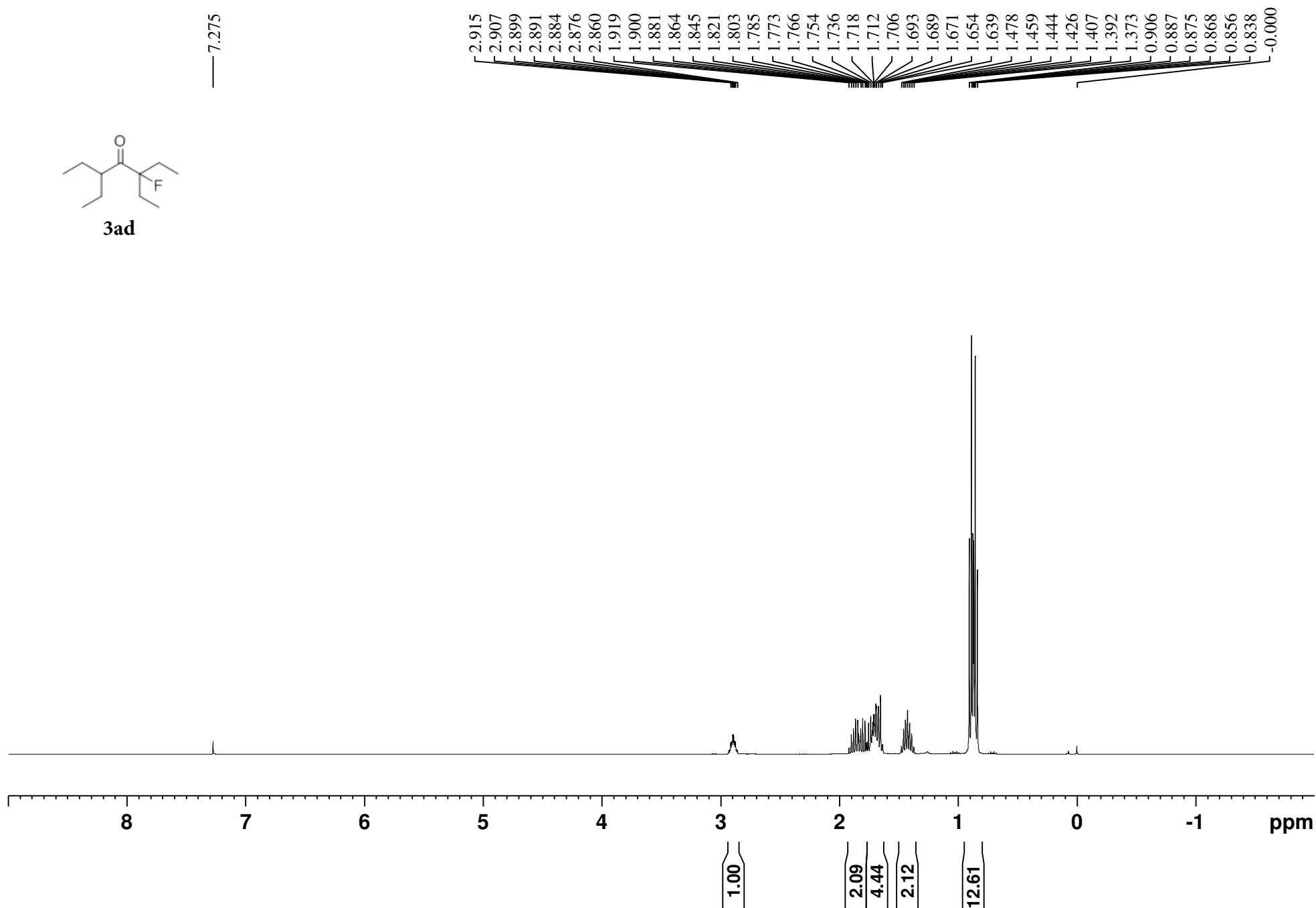
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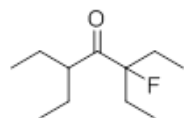




**3ad**

— 7.275





**3ad**

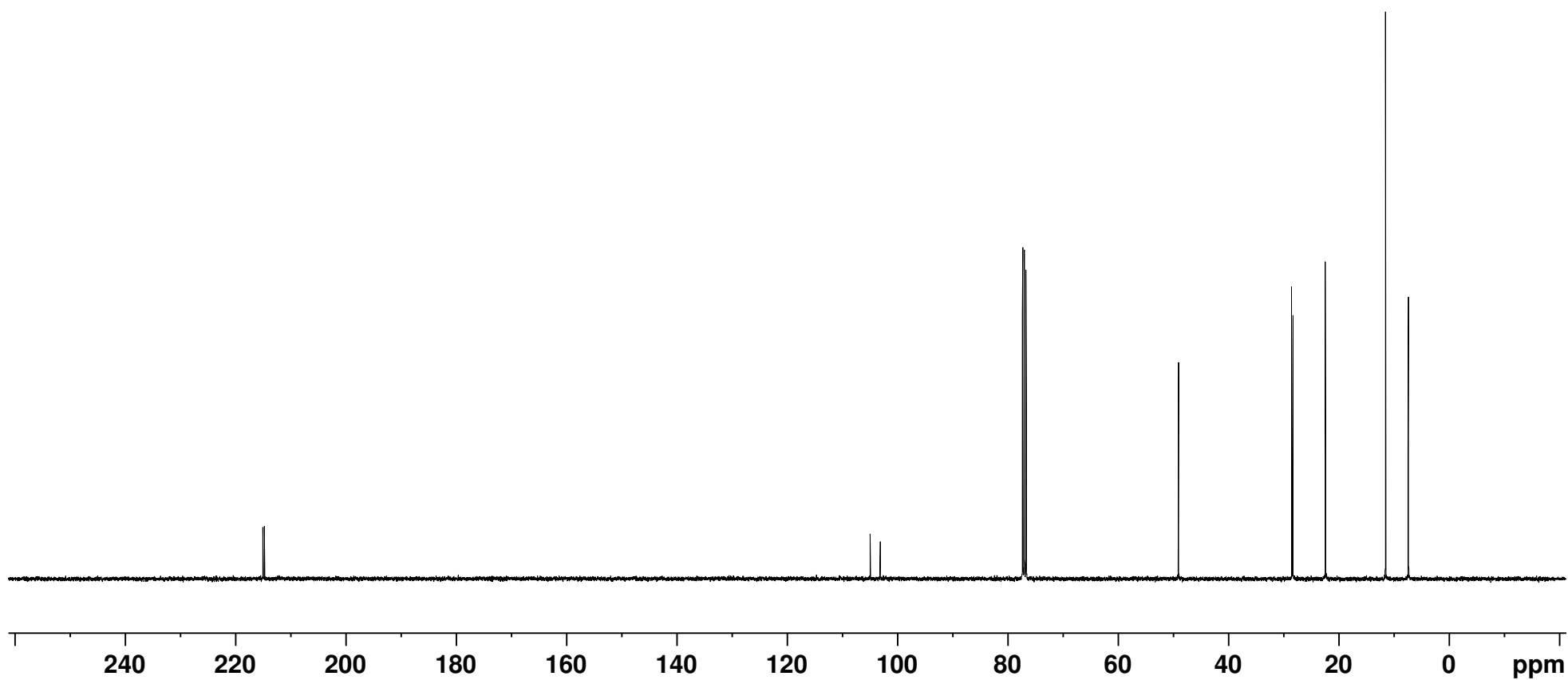
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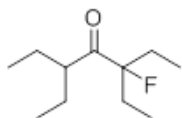
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76.68

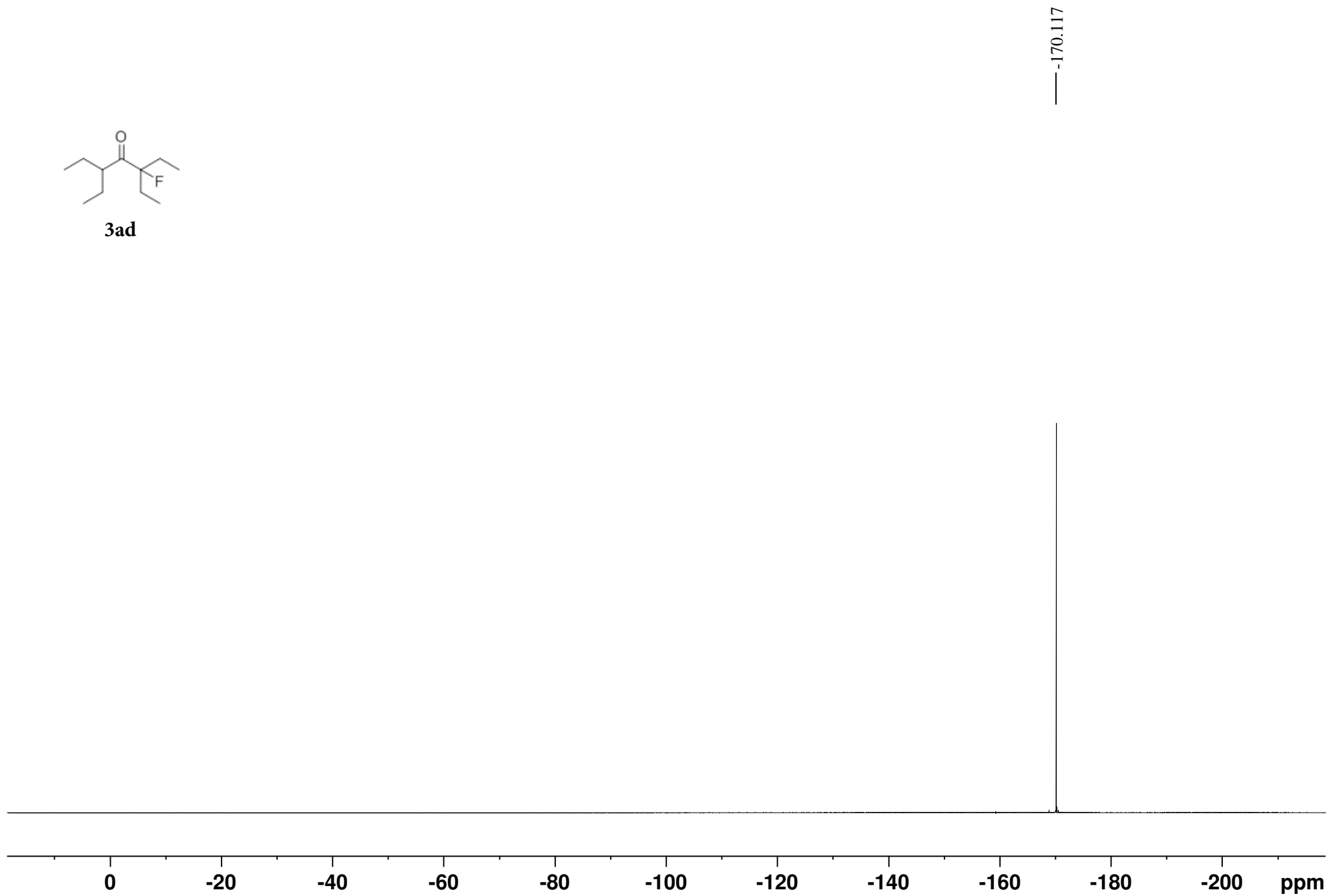
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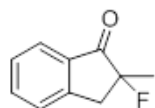
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11.54  
7.42  
7.37



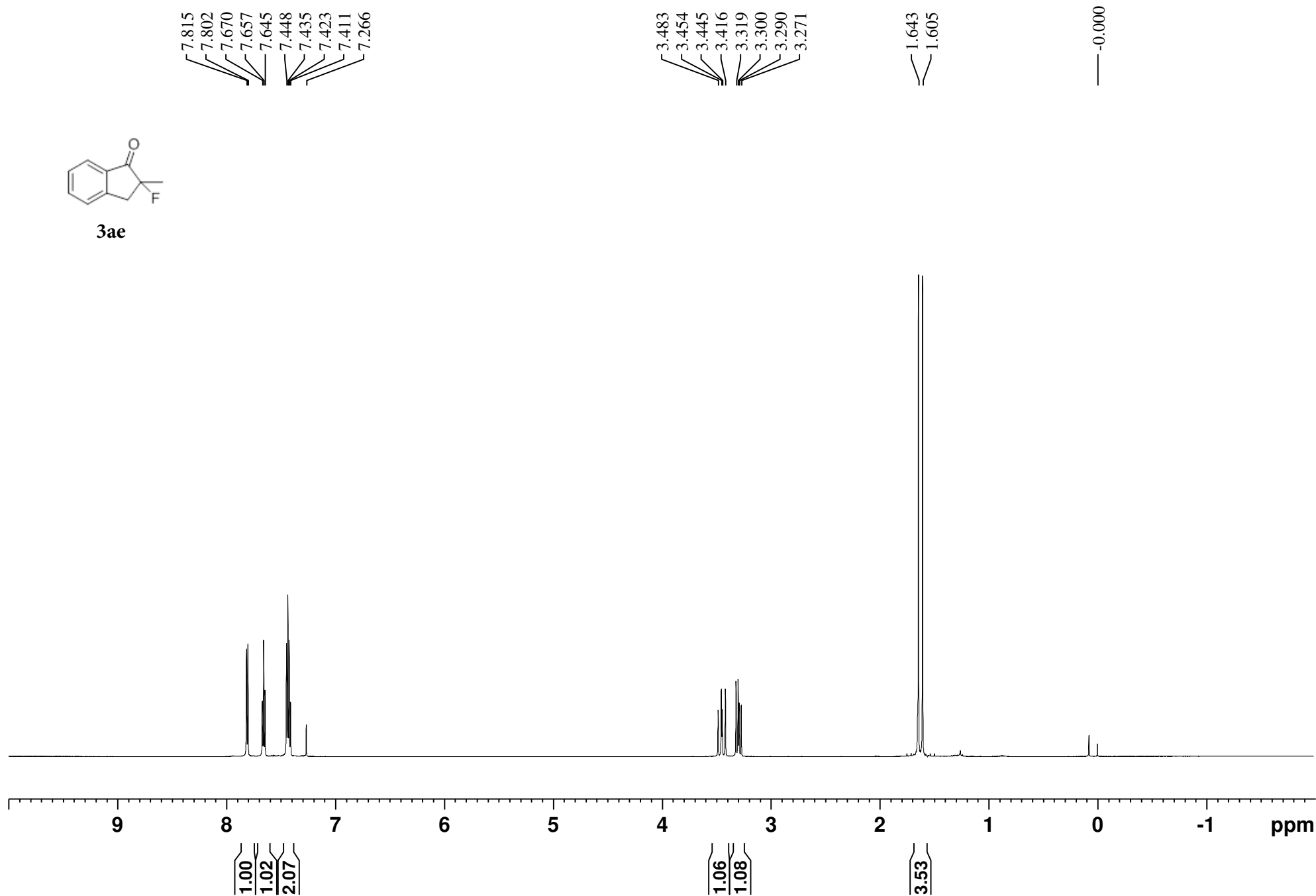


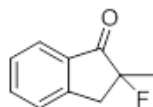
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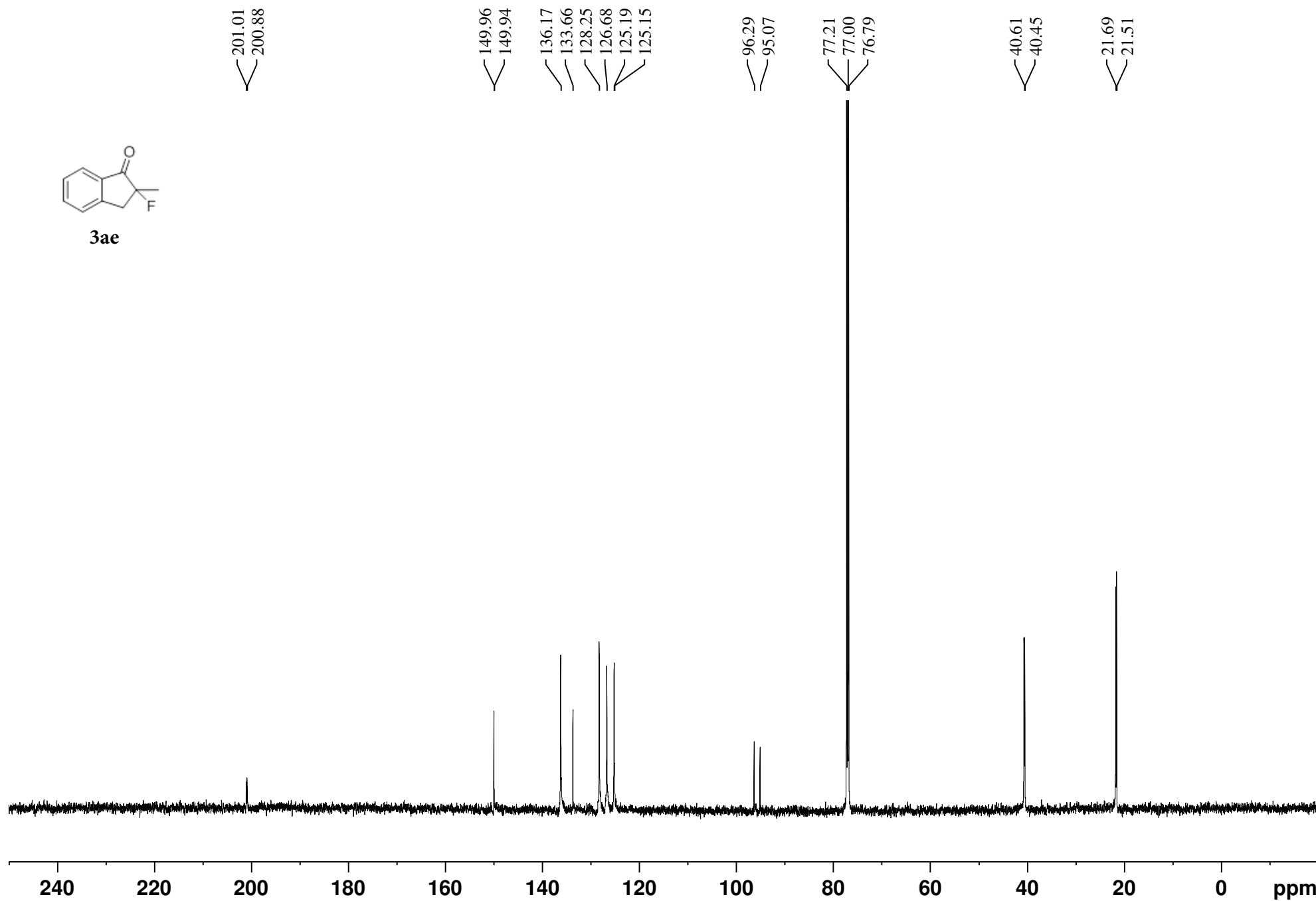


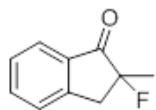
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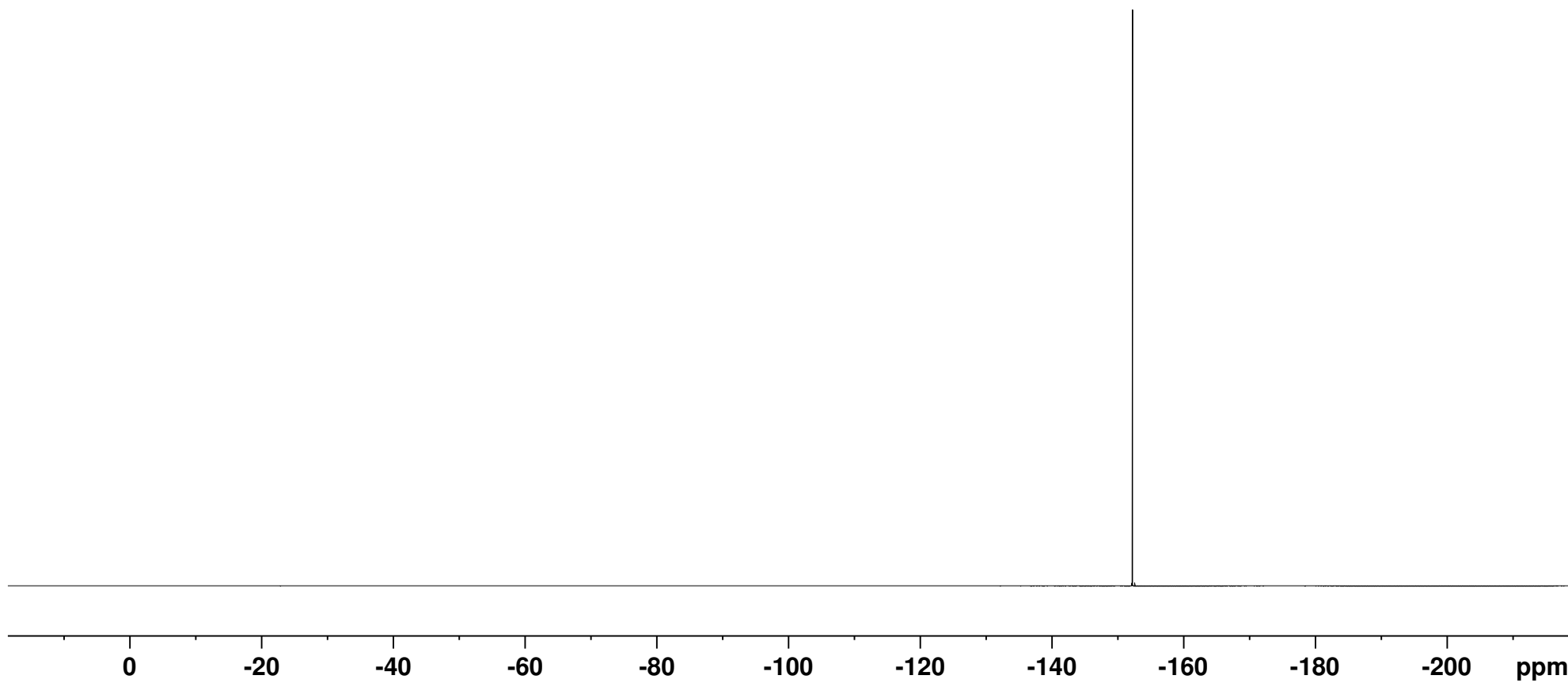
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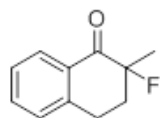




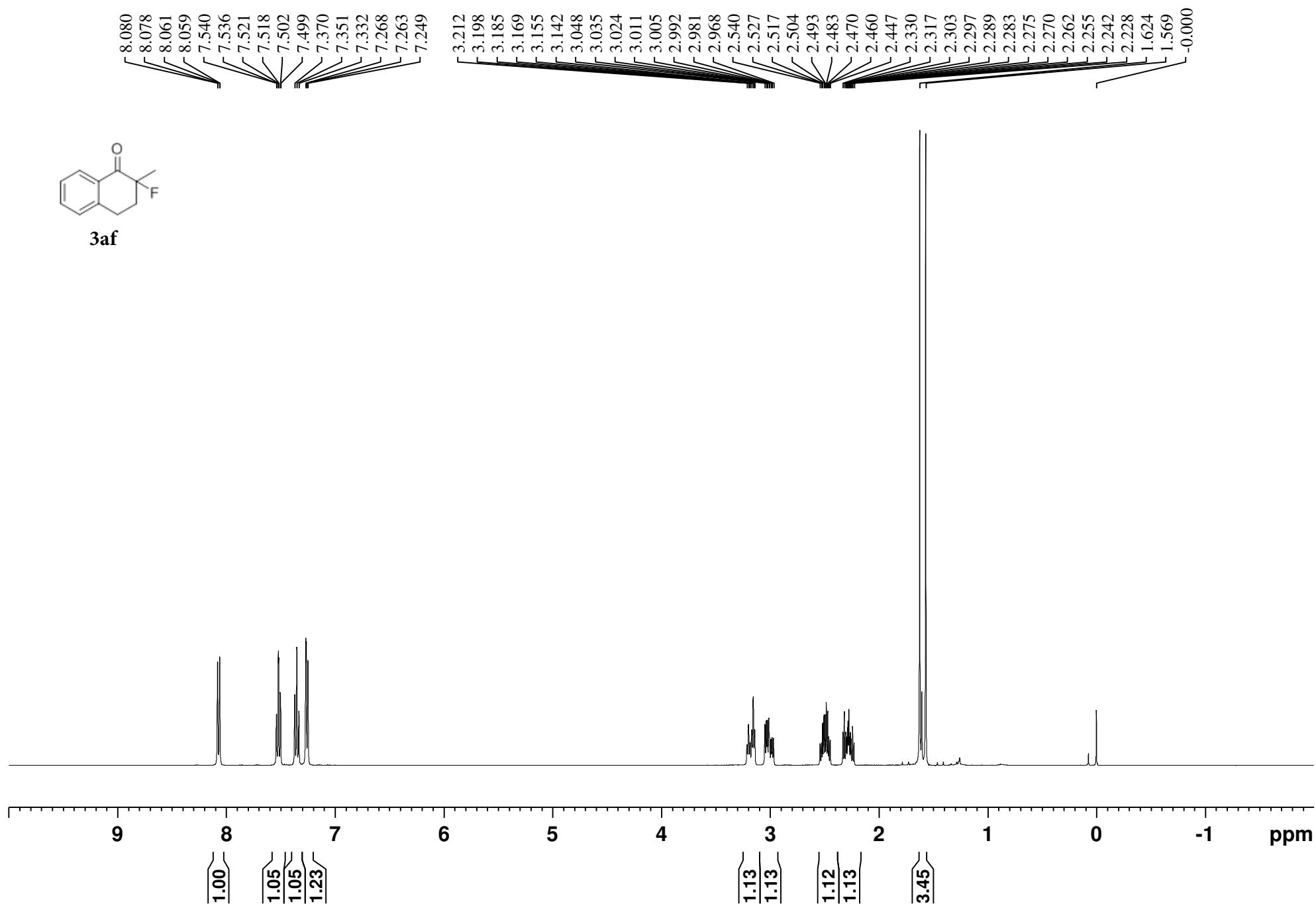
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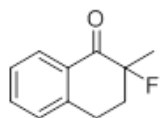
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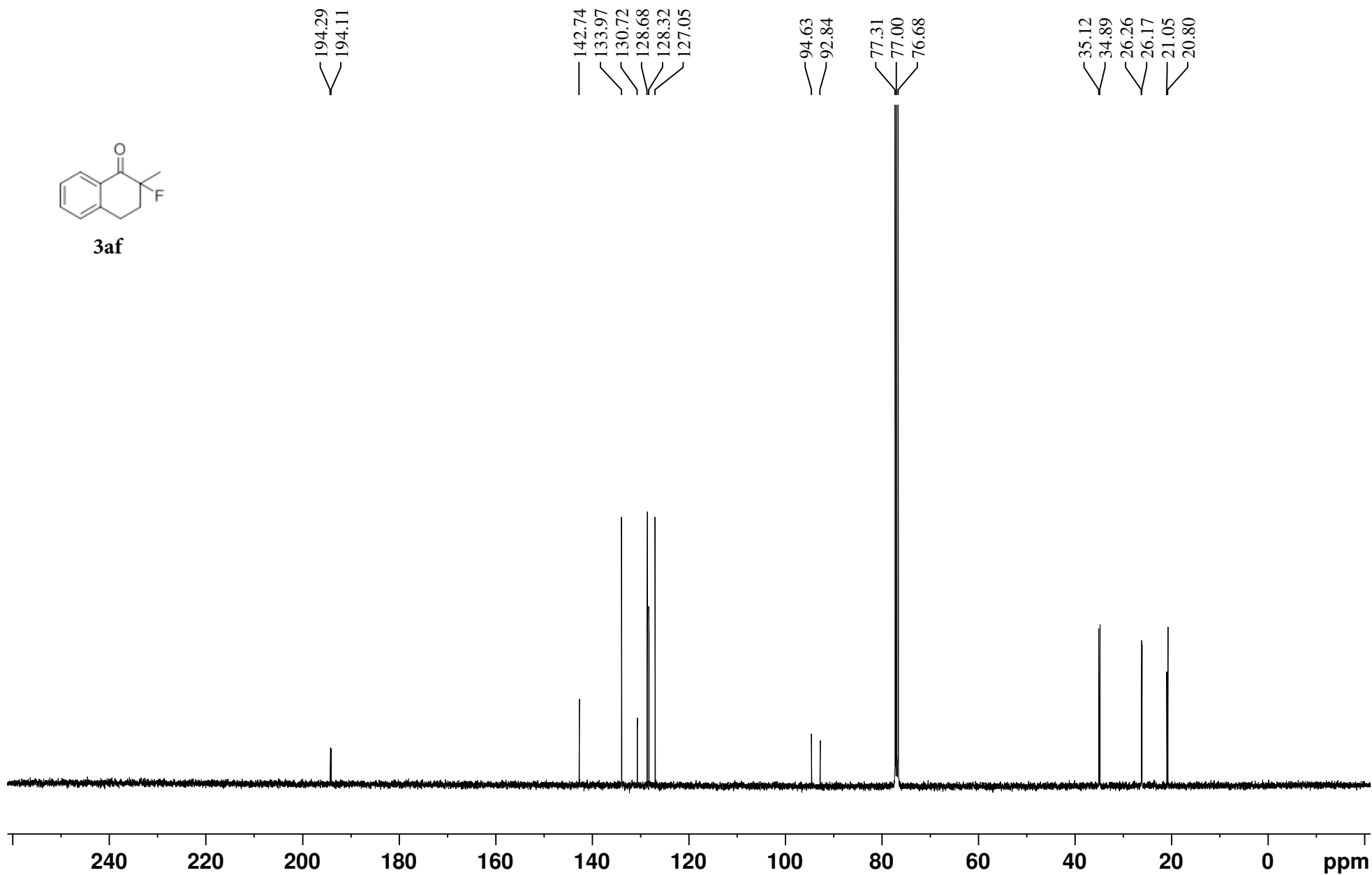


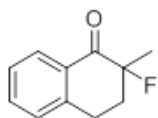
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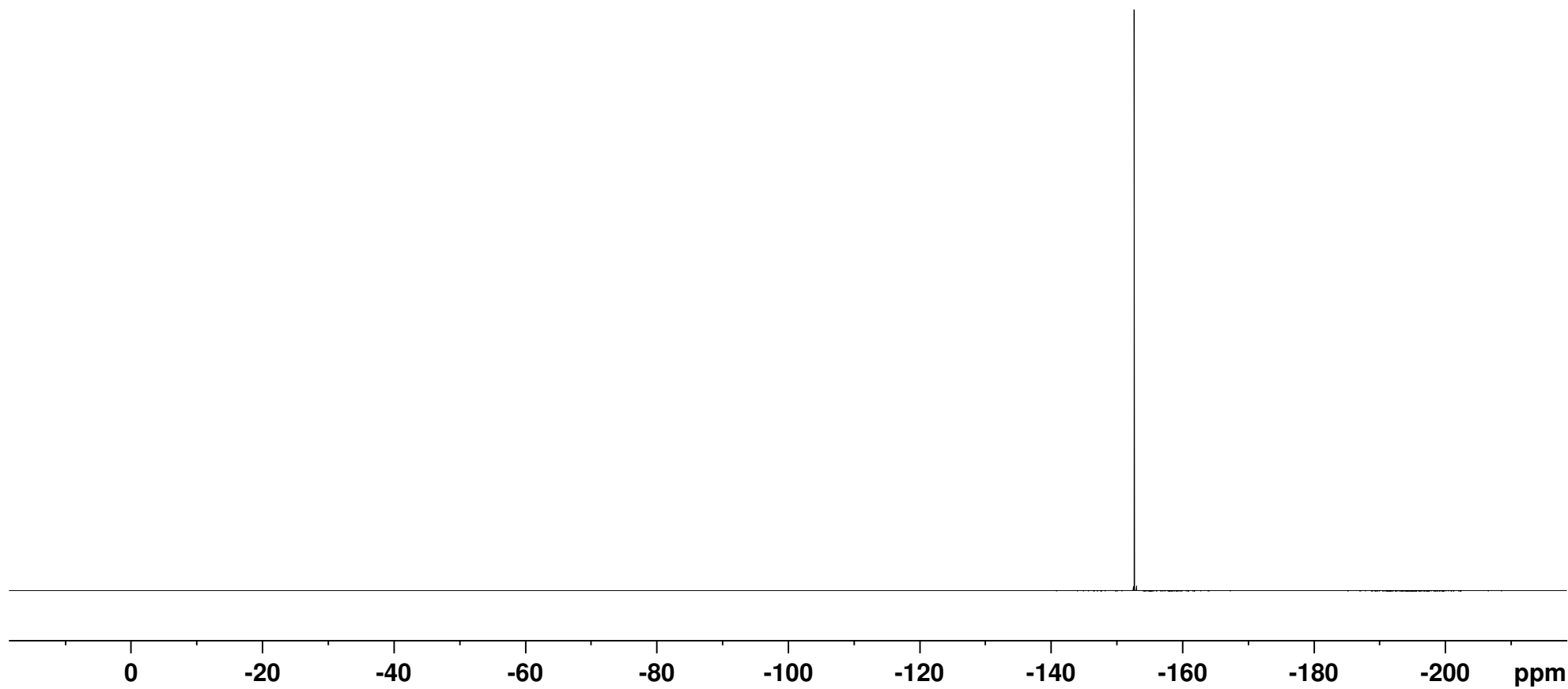
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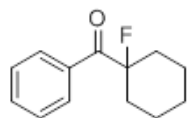




**3af**

— -152.699

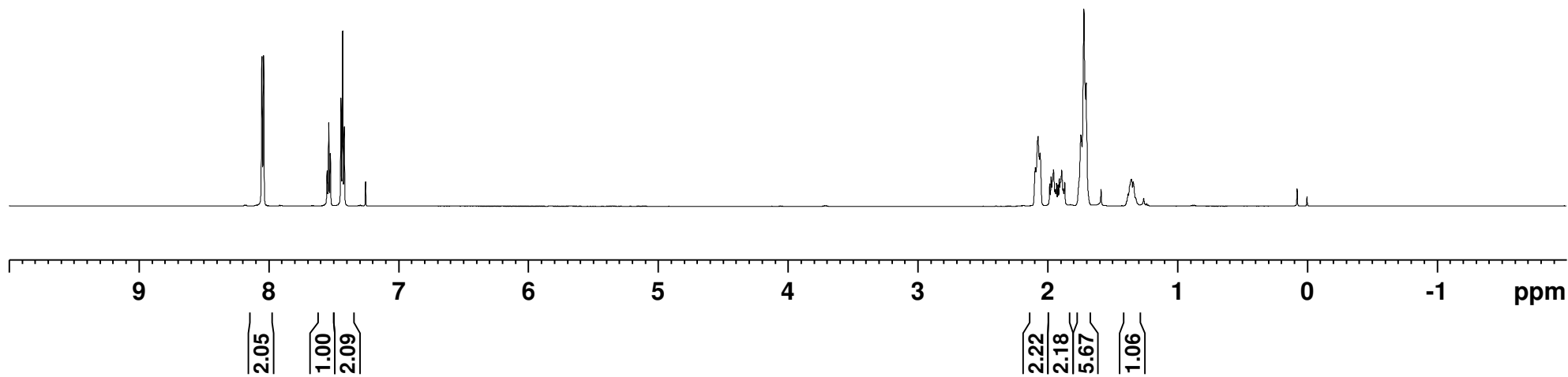


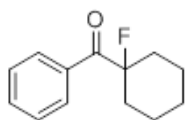


**3ag**

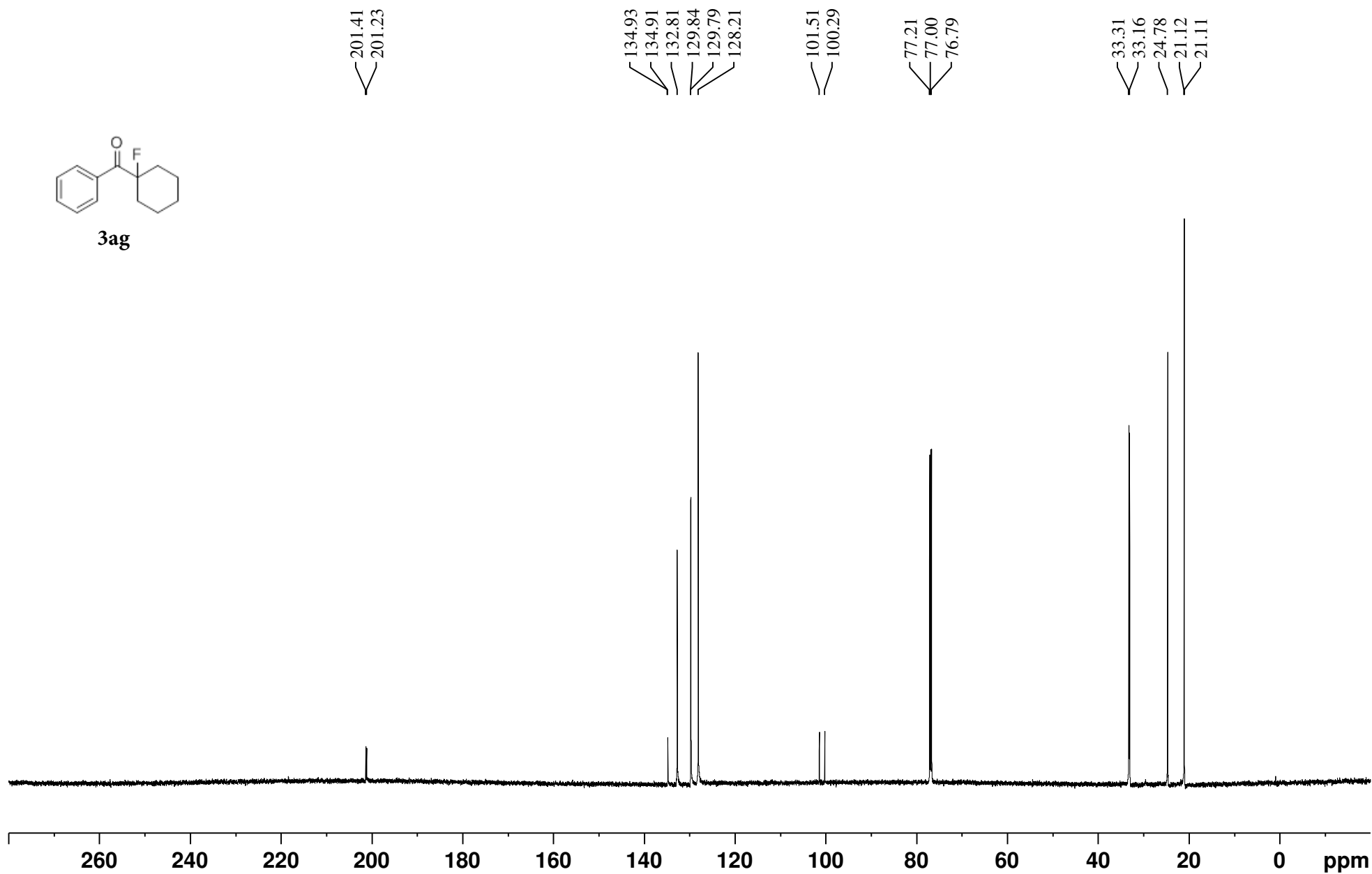
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7.525  
7.443  
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7.417  
7.253

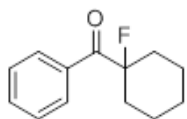
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2.057  
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1.972  
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1.953  
1.941  
1.930  
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1.908  
1.900  
1.890  
1.878  
1.867  
1.743  
1.737  
1.719  
1.708  
1.702  
1.587  
1.379  
1.353  
1.340  
-0.000



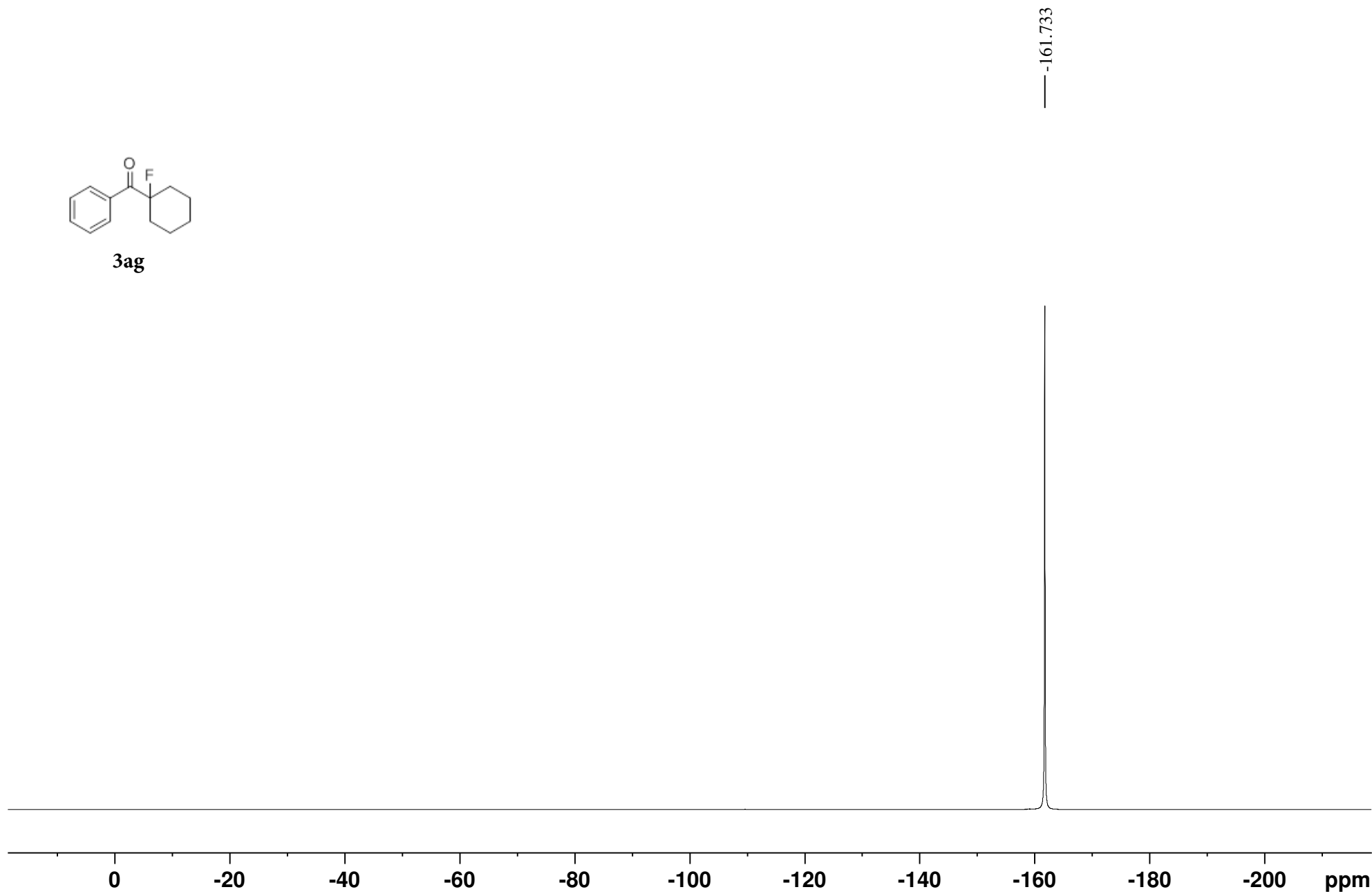


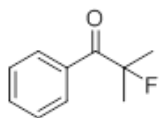
**3ag**





**3ag**

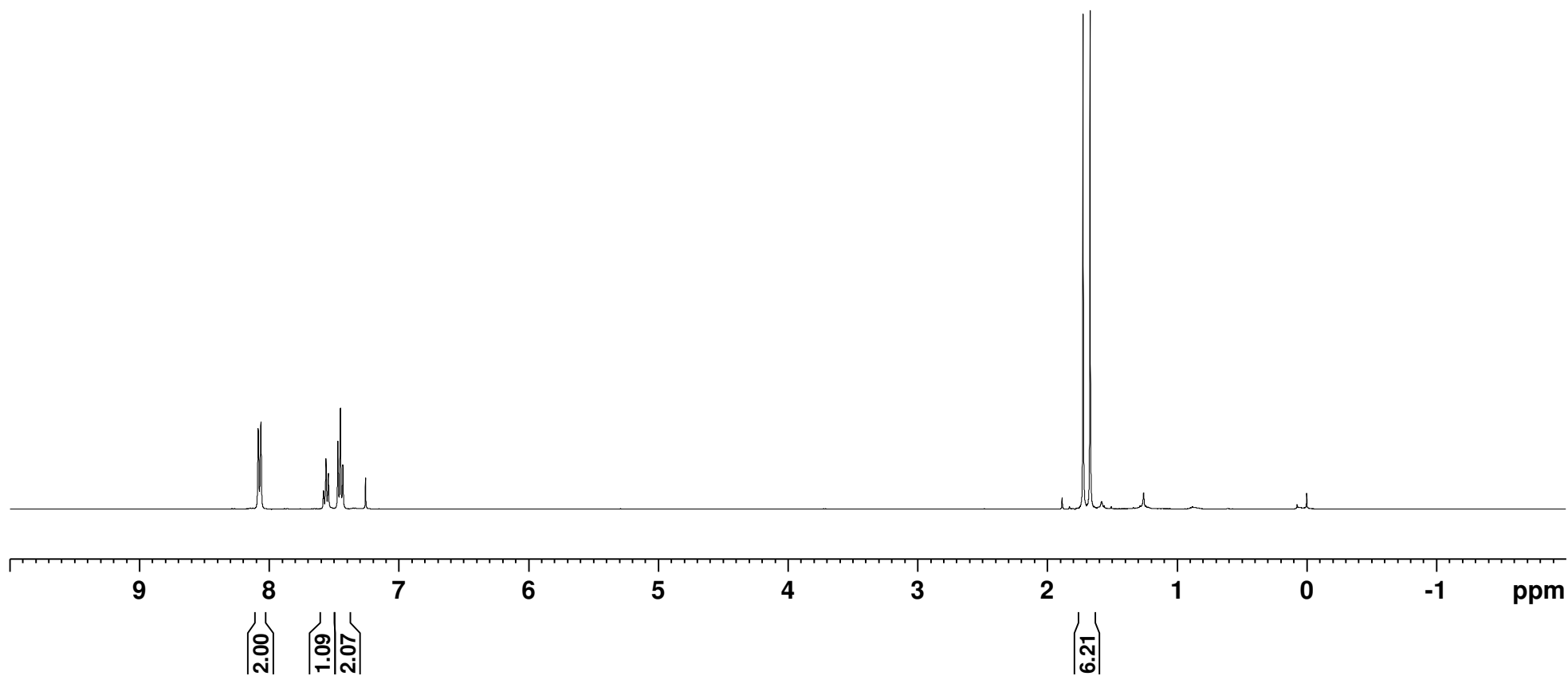


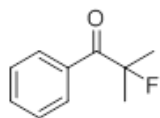


**3ah**

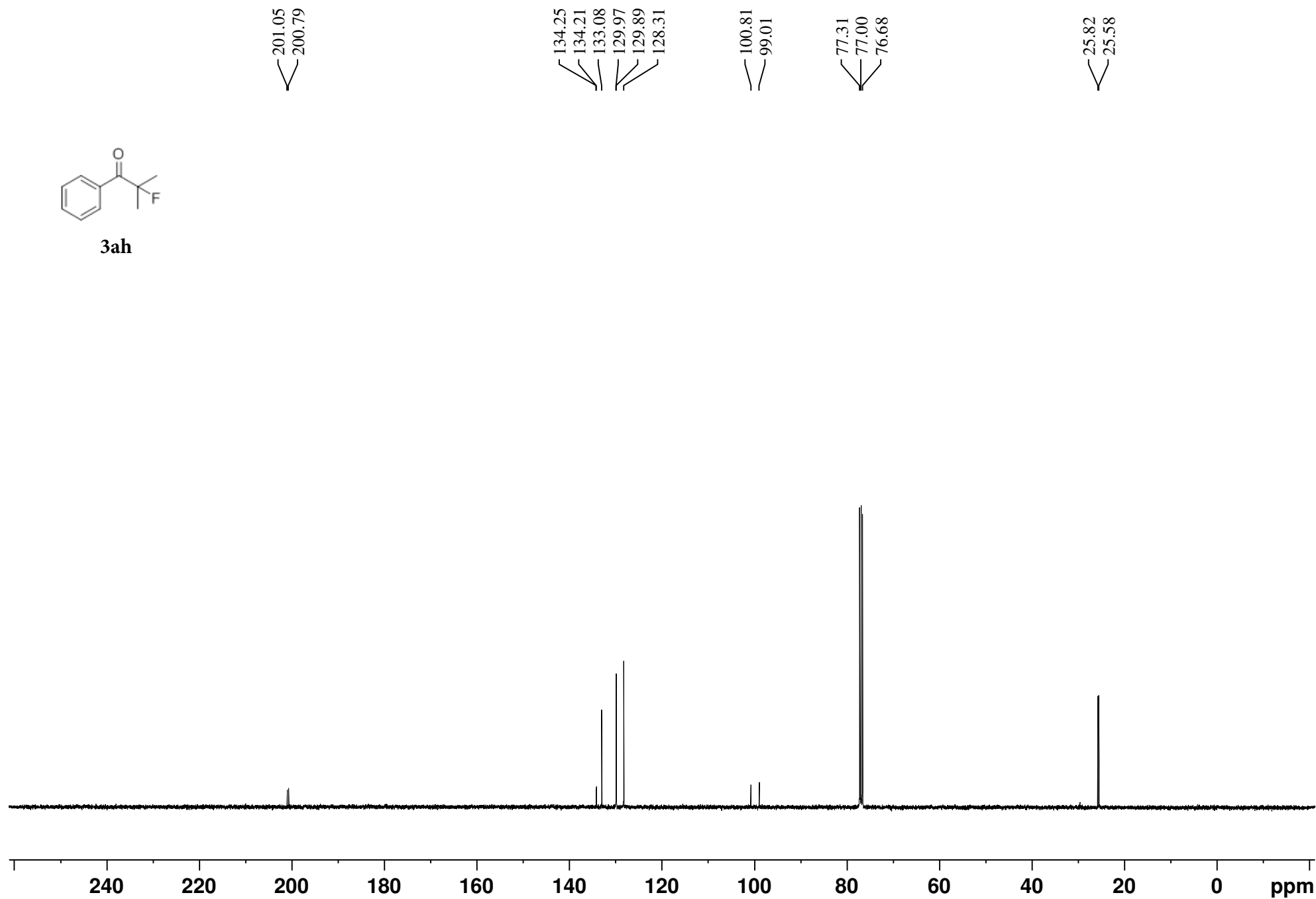
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7.470  
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7.432  
7.257

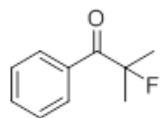
1.724  
1.670



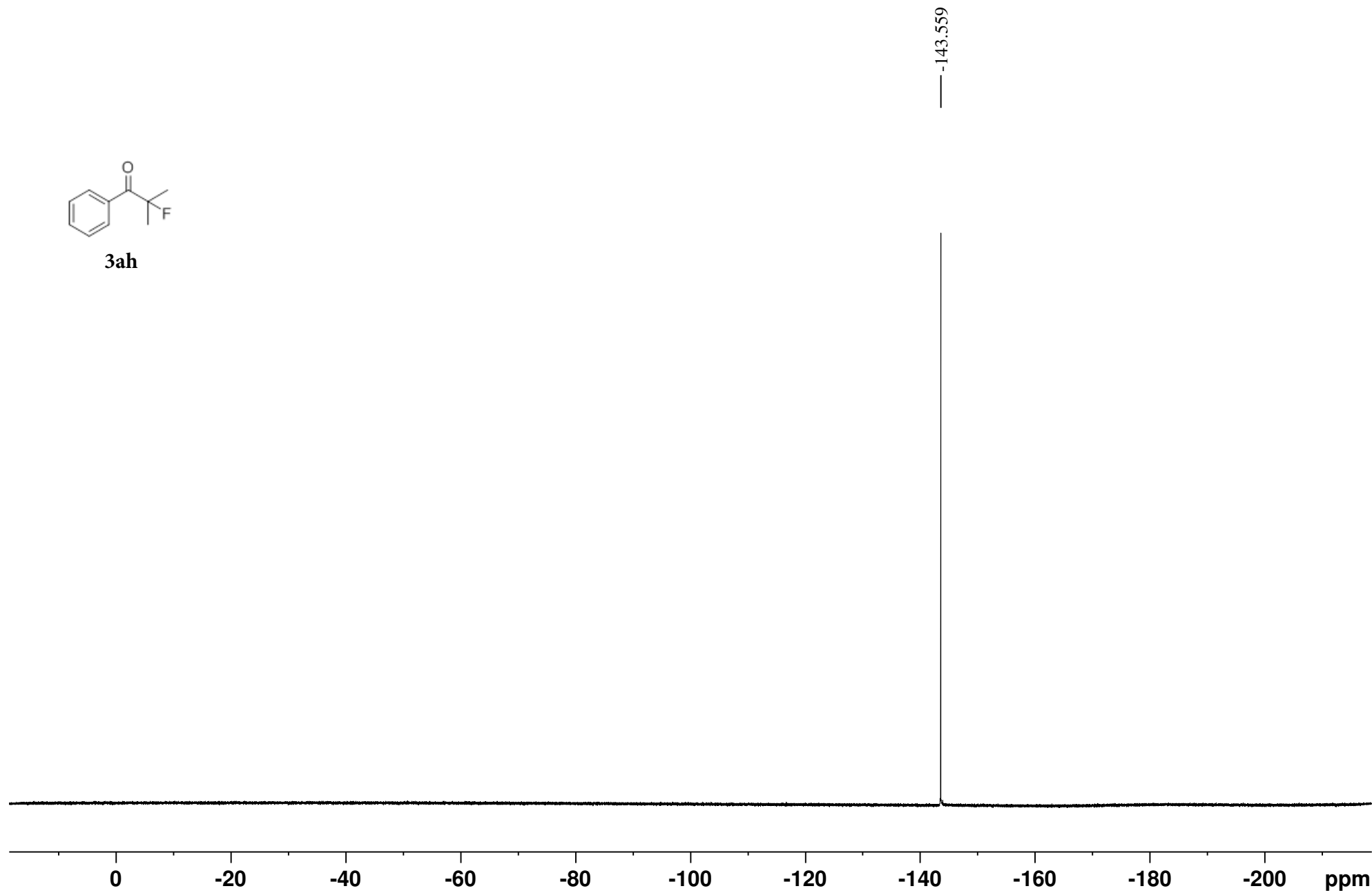


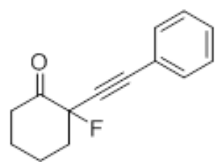
**3ah**





**3ah**

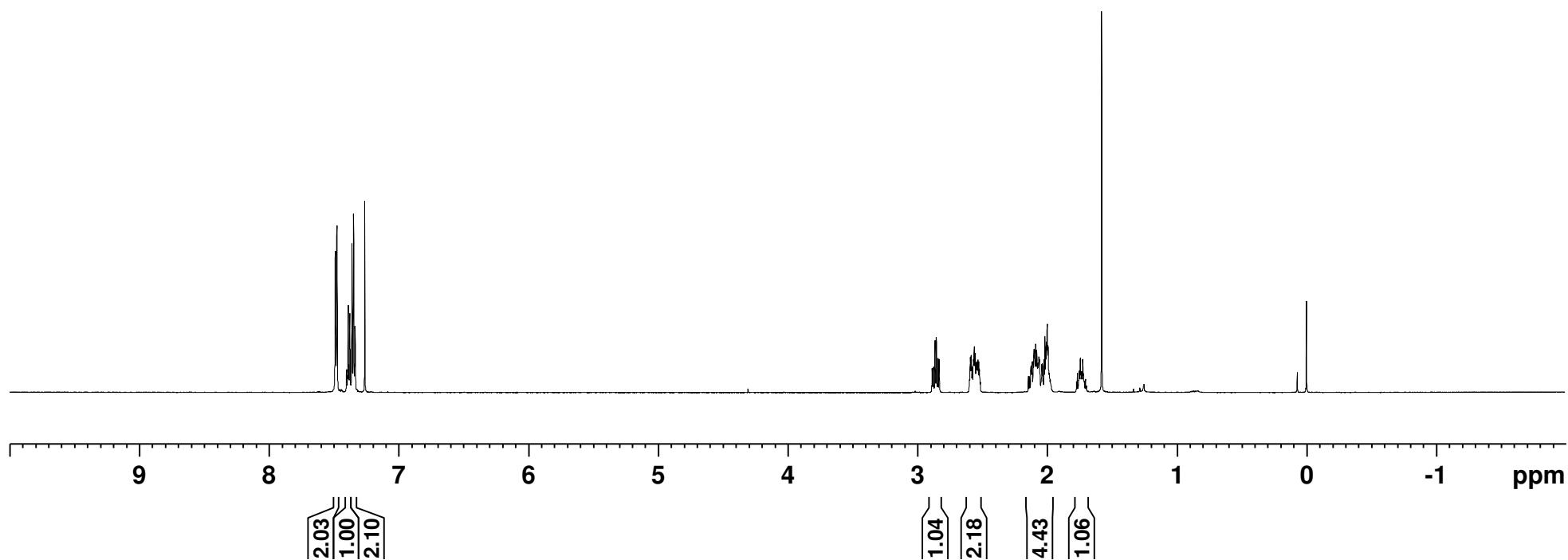


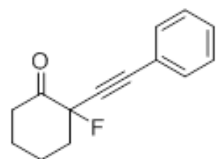


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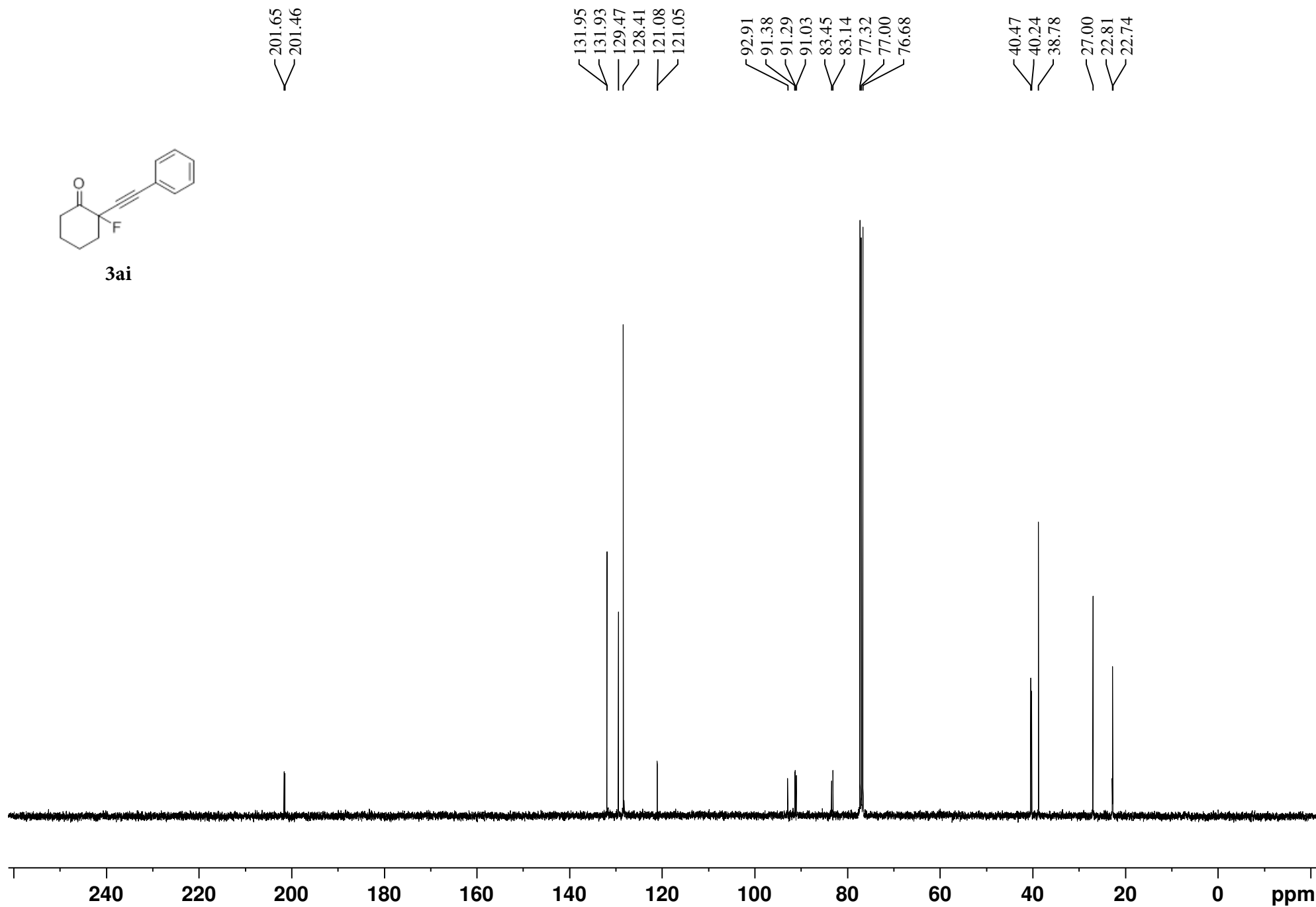
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7.378  
7.361  
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7.339  
7.337  
7.334  
7.262

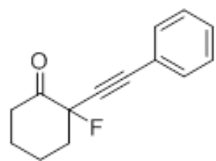
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2.586  
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2.554  
2.537  
2.527  
2.516  
2.144  
2.117  
2.101  
2.096  
2.088  
2.080  
2.063  
2.041  
2.035  
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1.999  
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-0.000



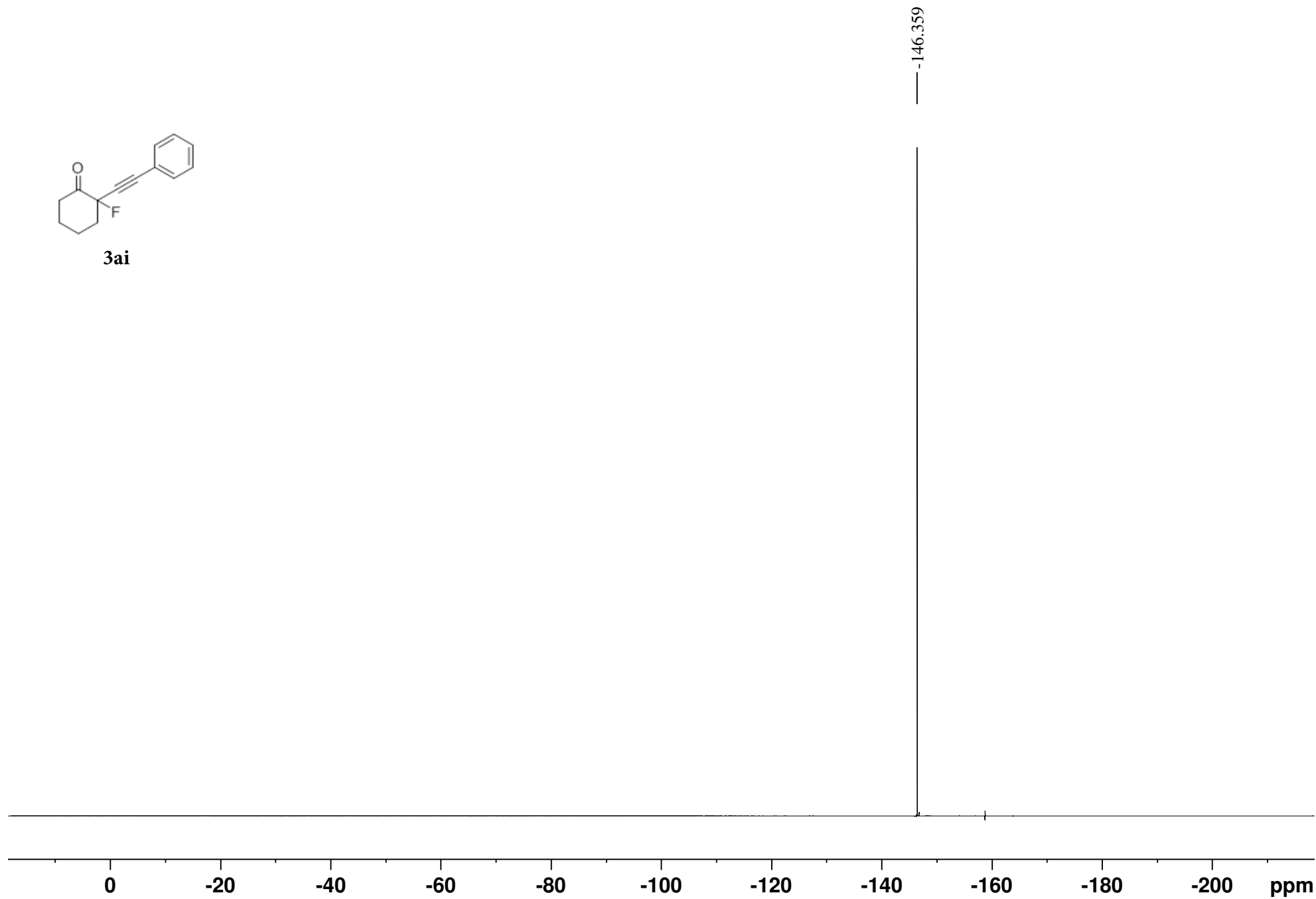


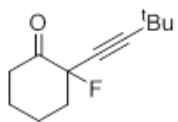
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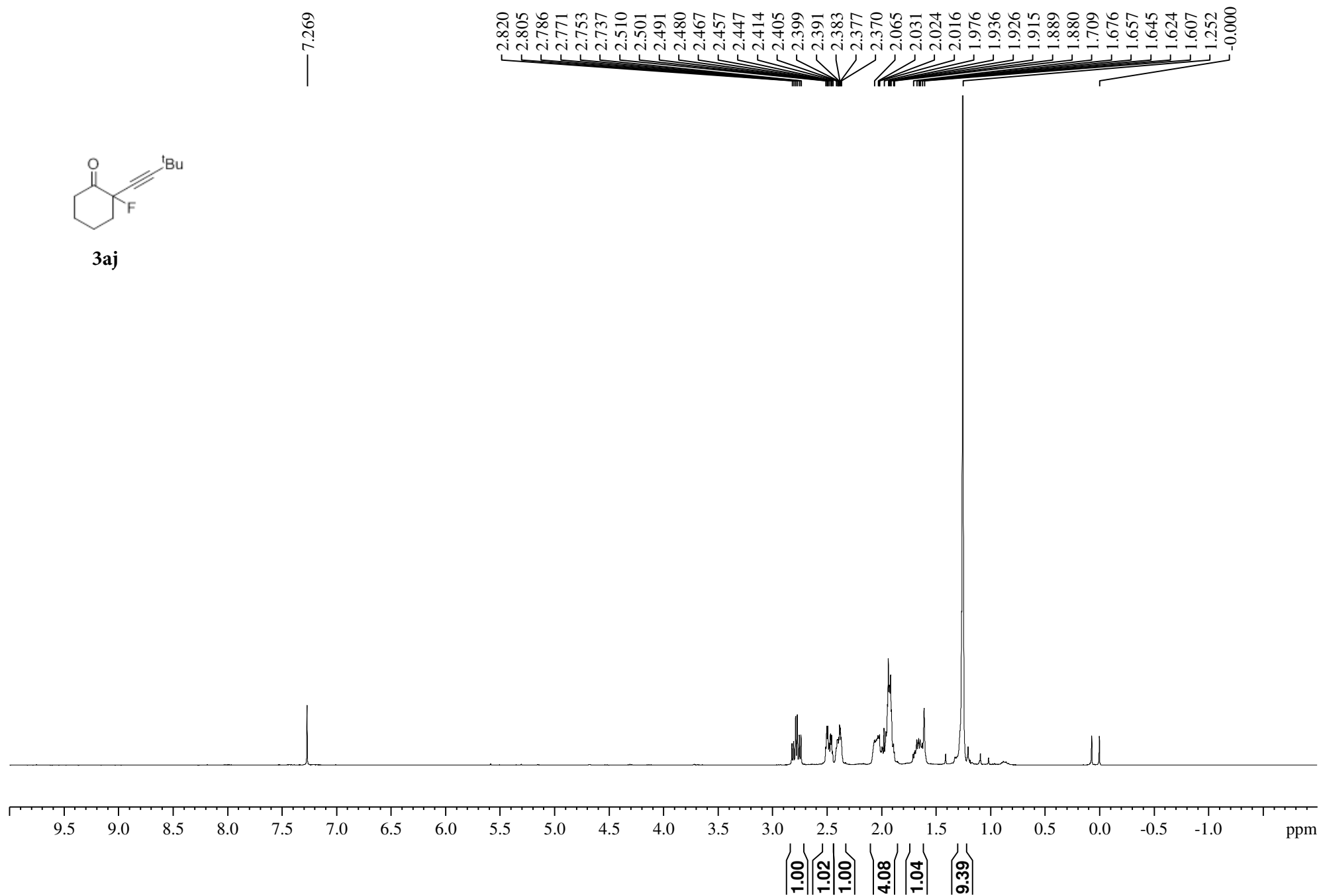


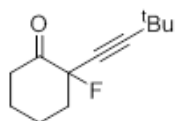
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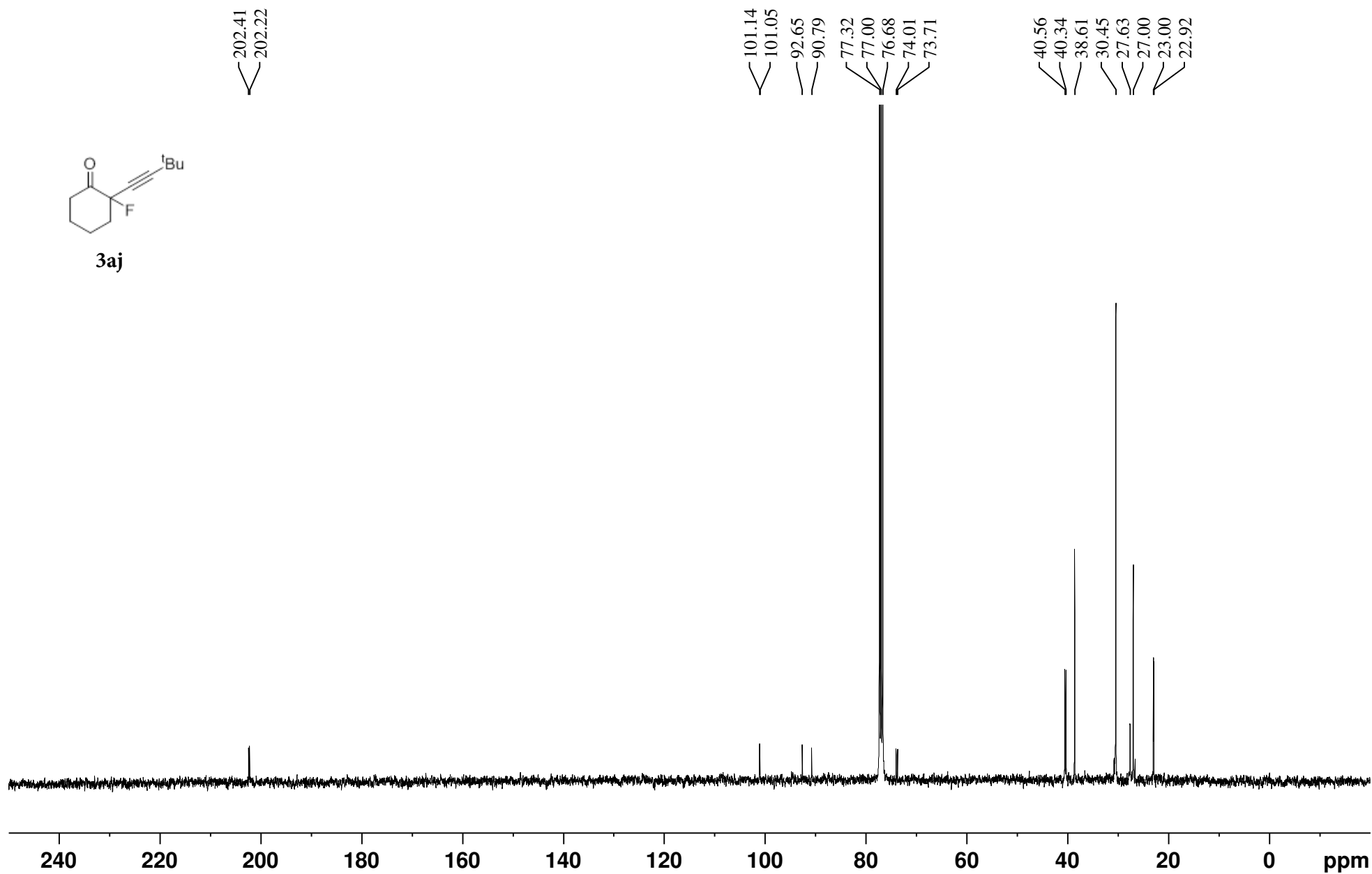


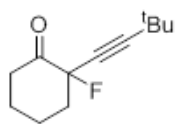
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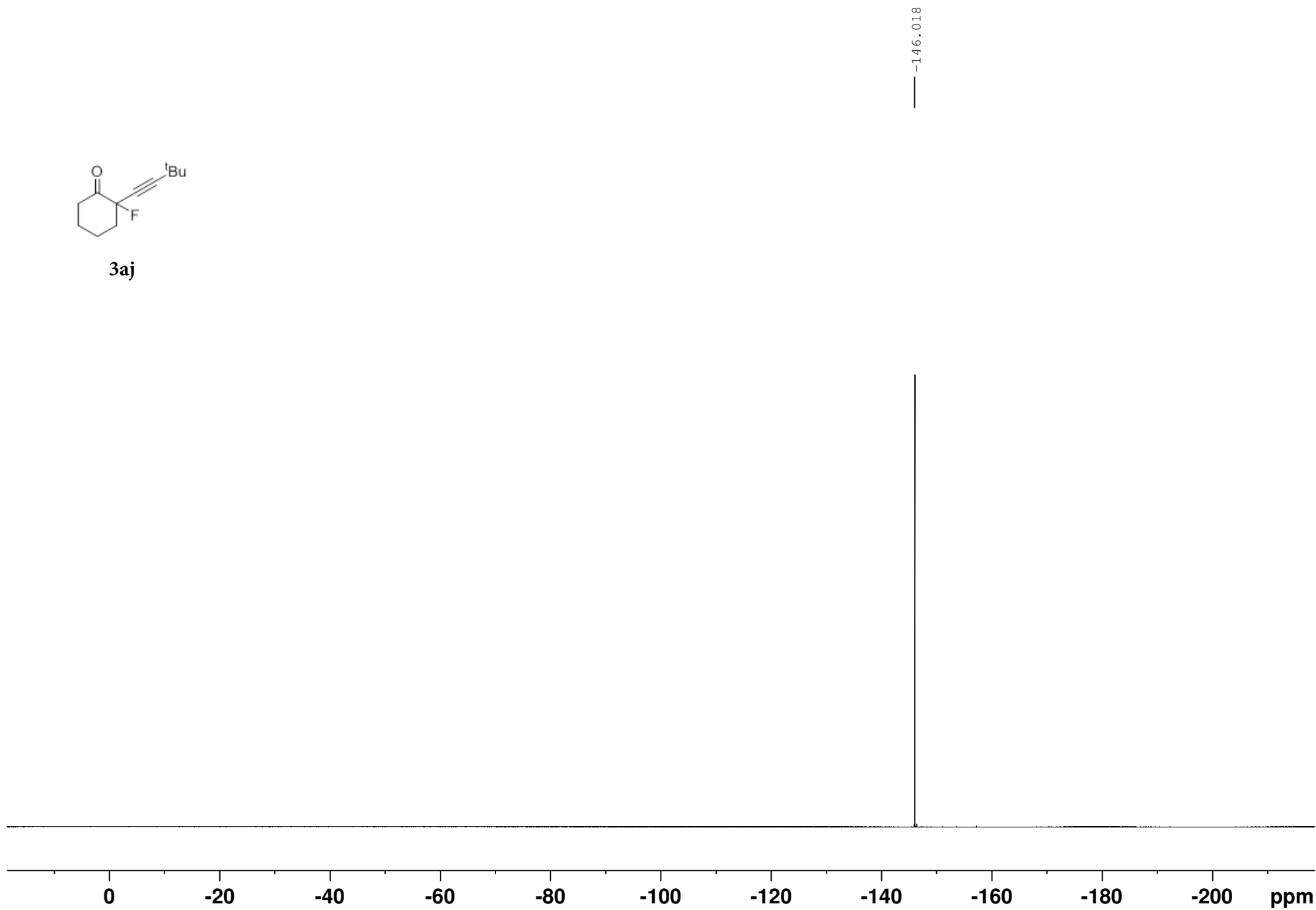


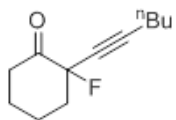
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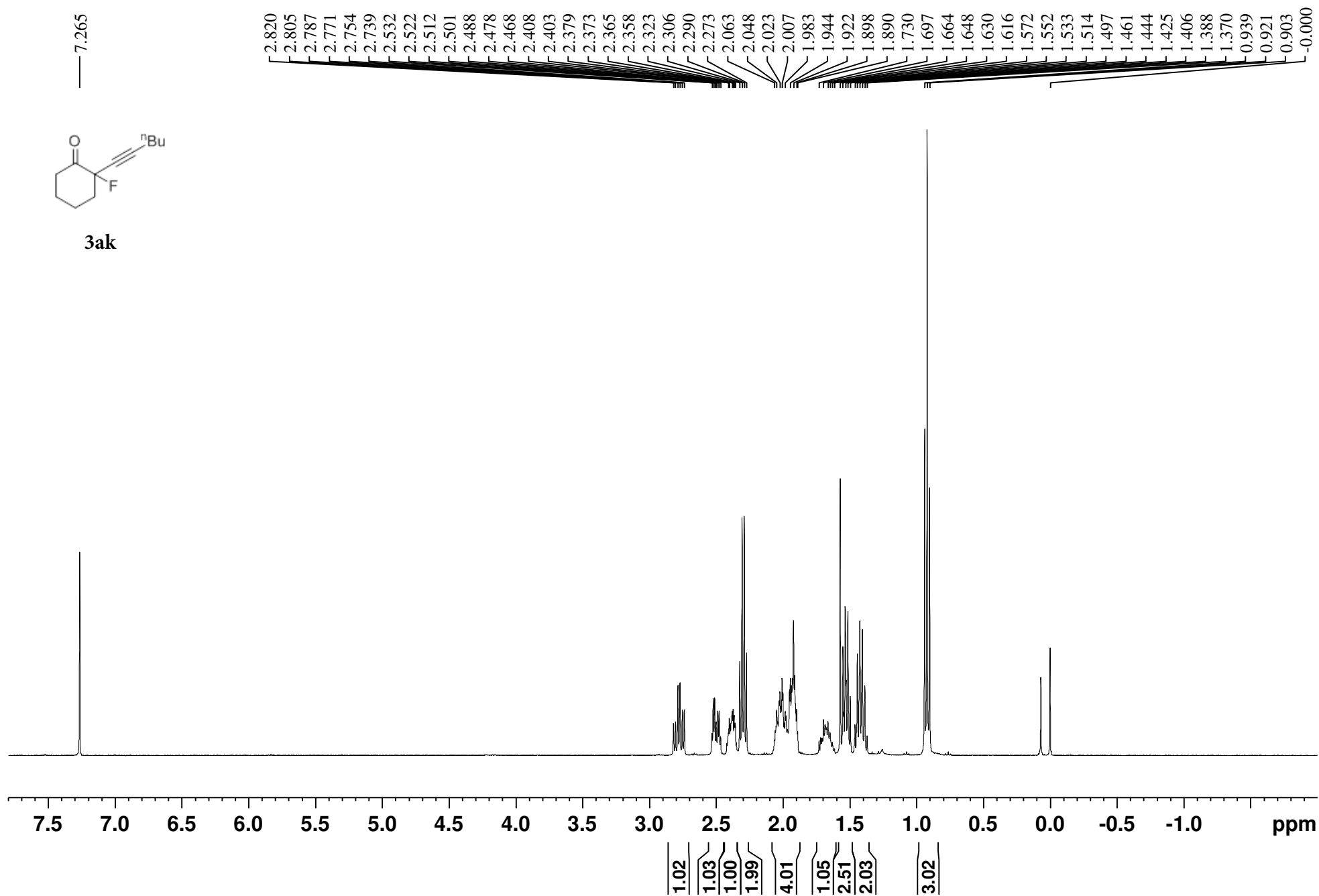


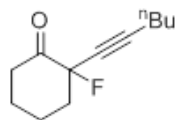
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**3ak**



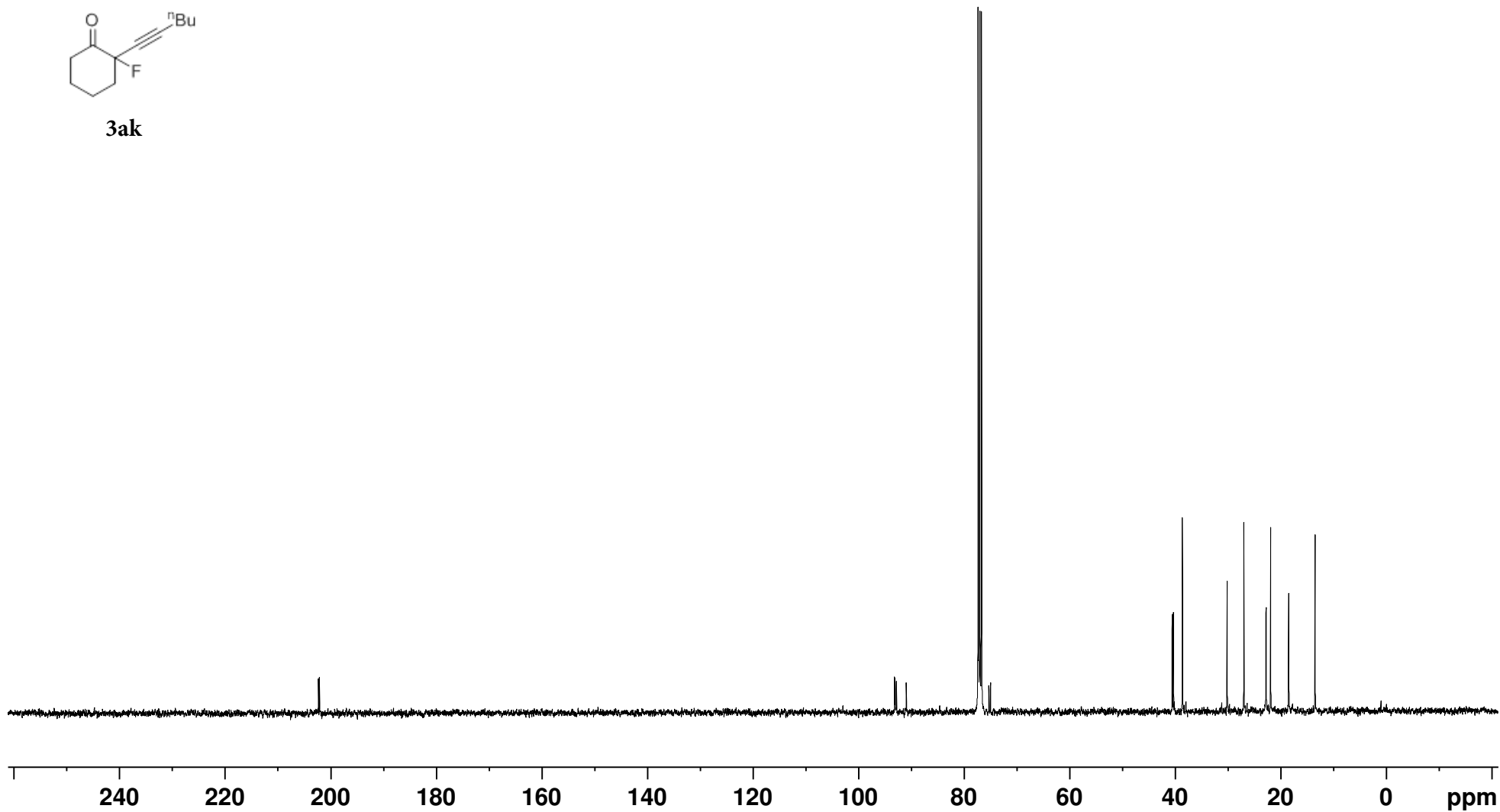


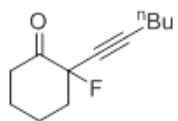
**3ak**

202.31  
202.12

93.14  
93.05  
92.79  
90.93  
77.32  
77.00  
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75.29  
74.99

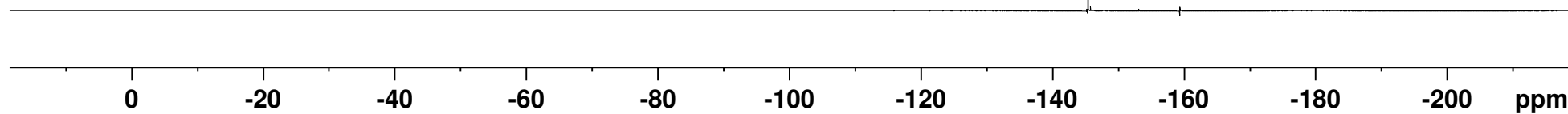
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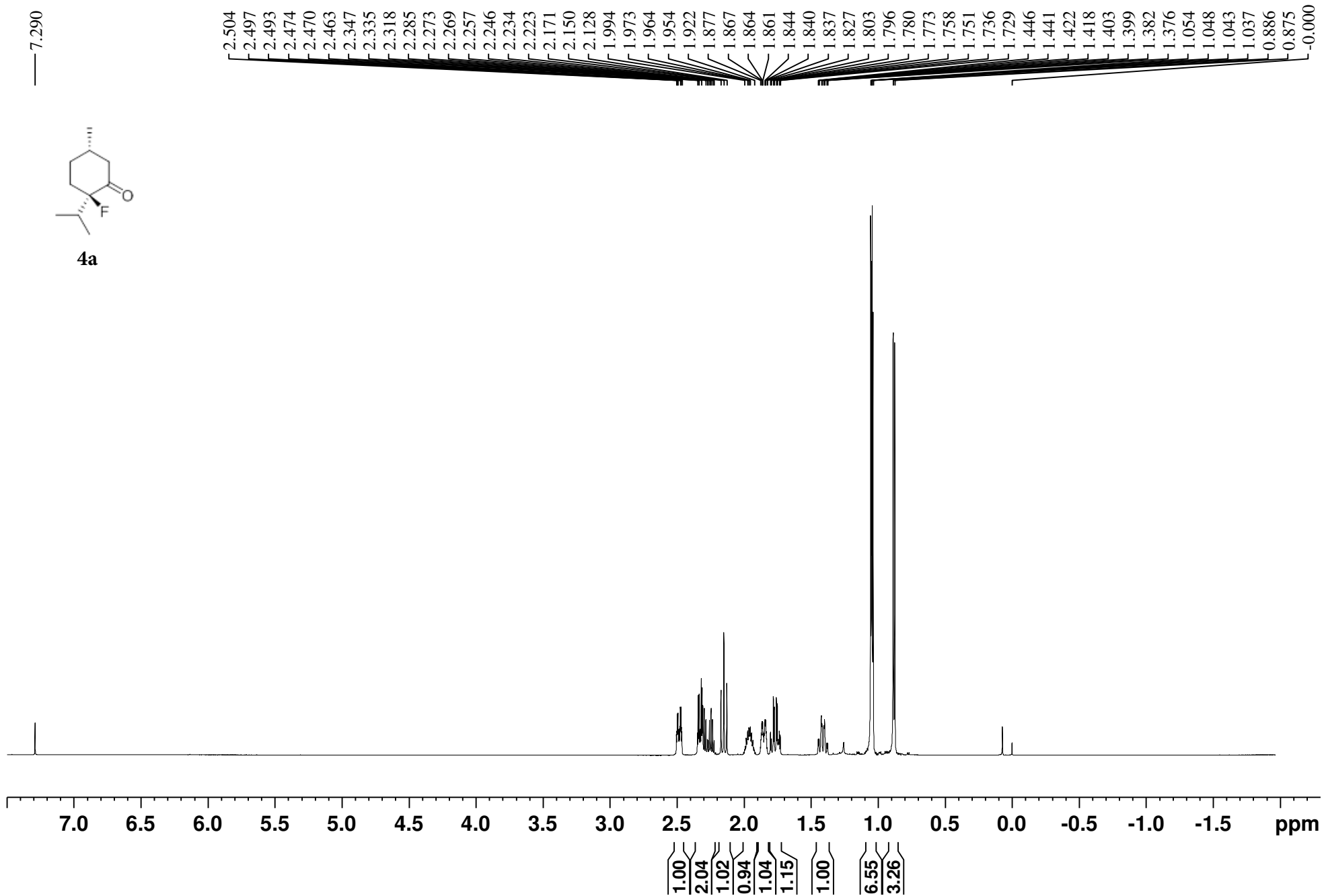


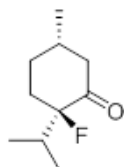


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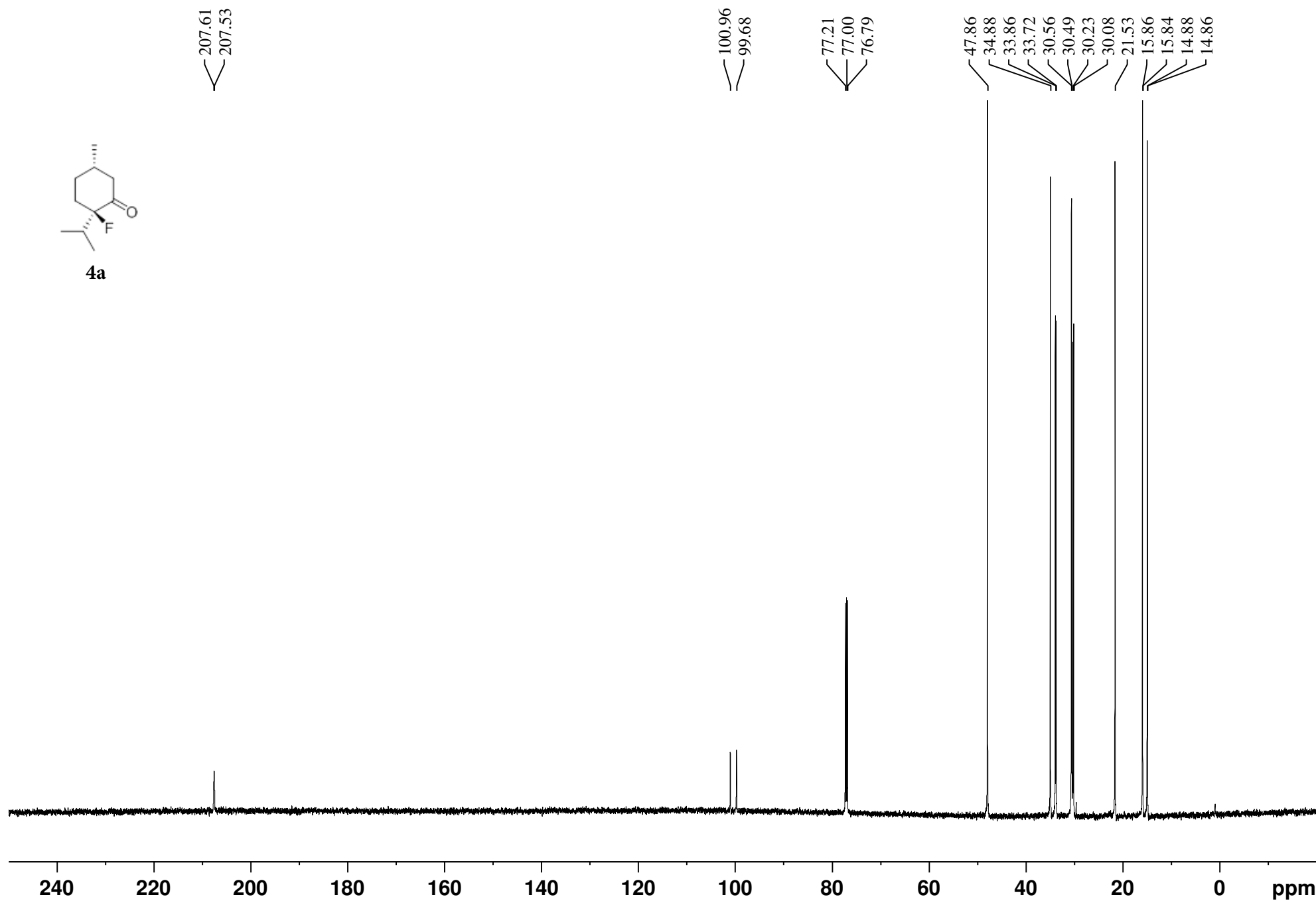
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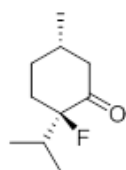




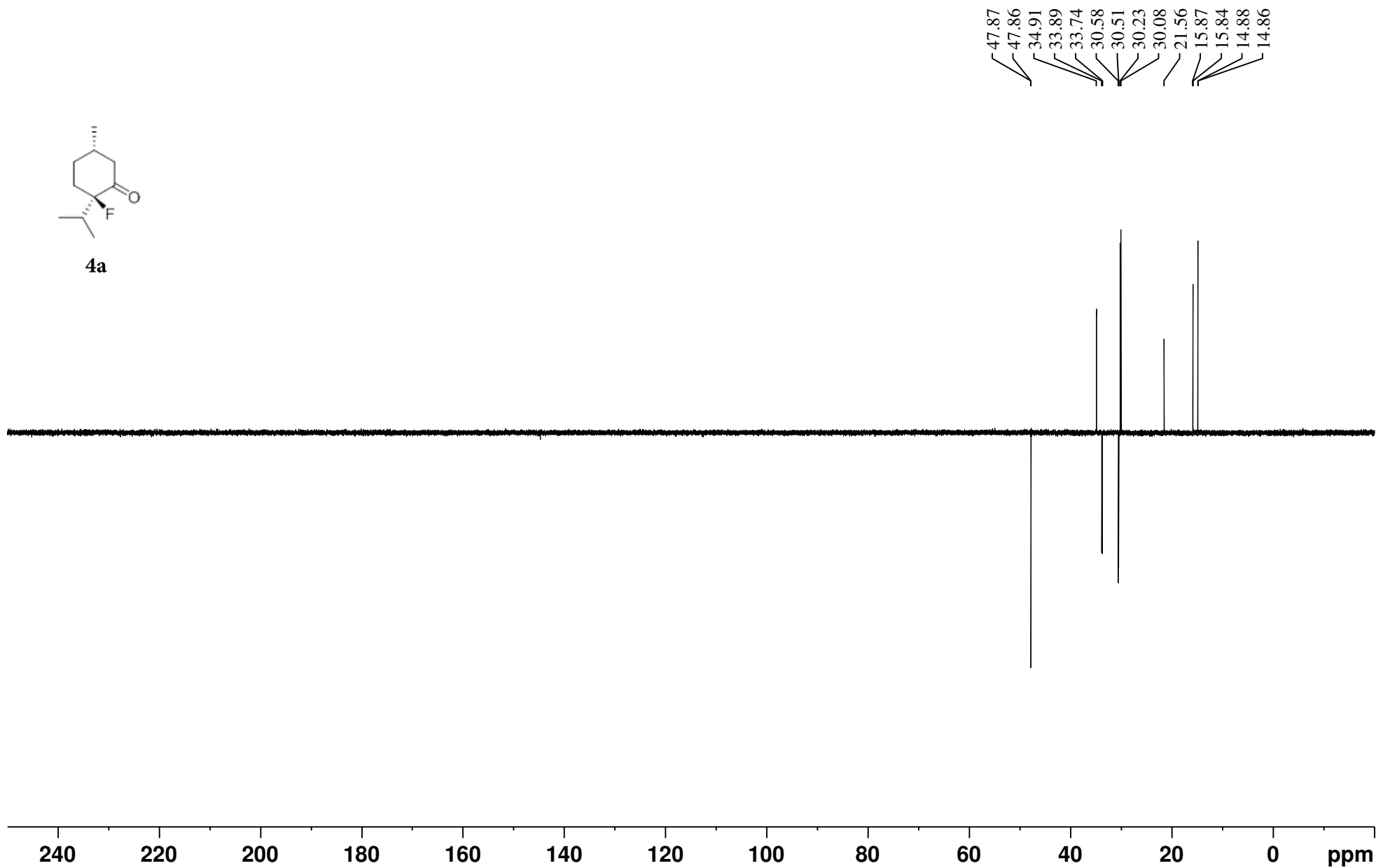


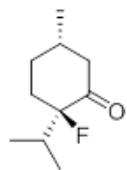
**4a**



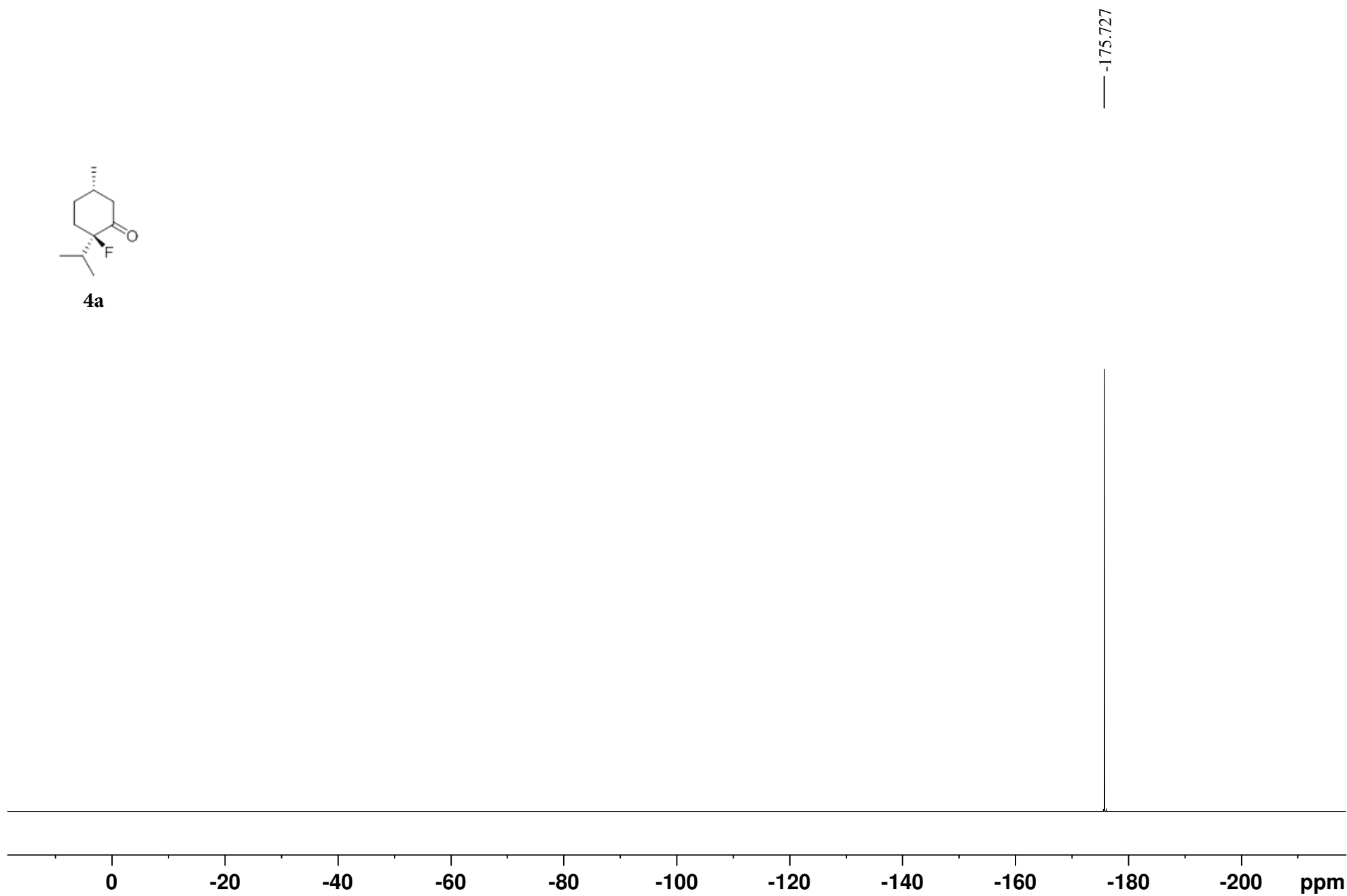


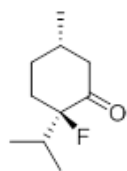
**4a**



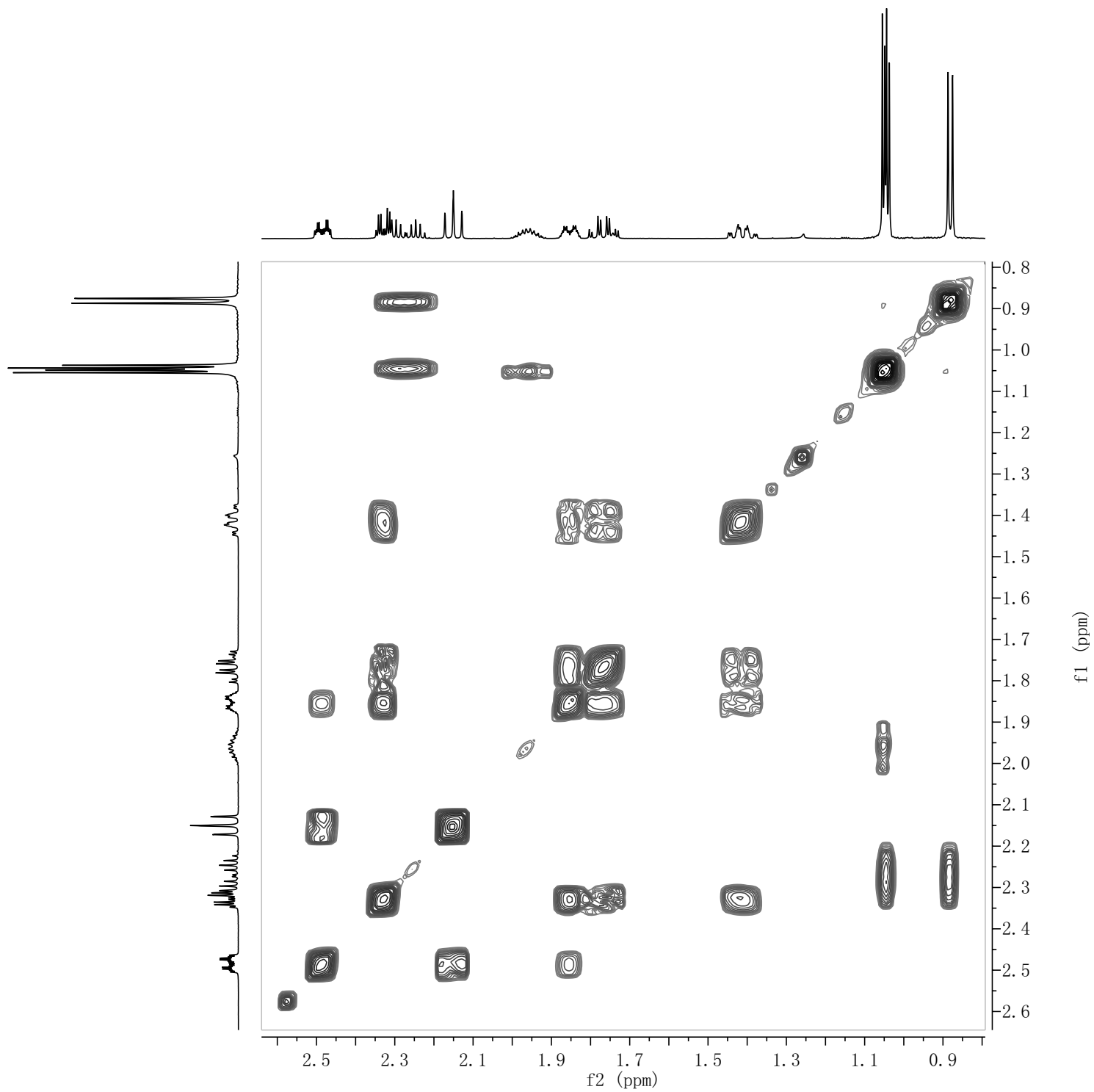


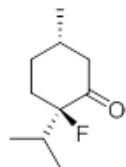
**4a**



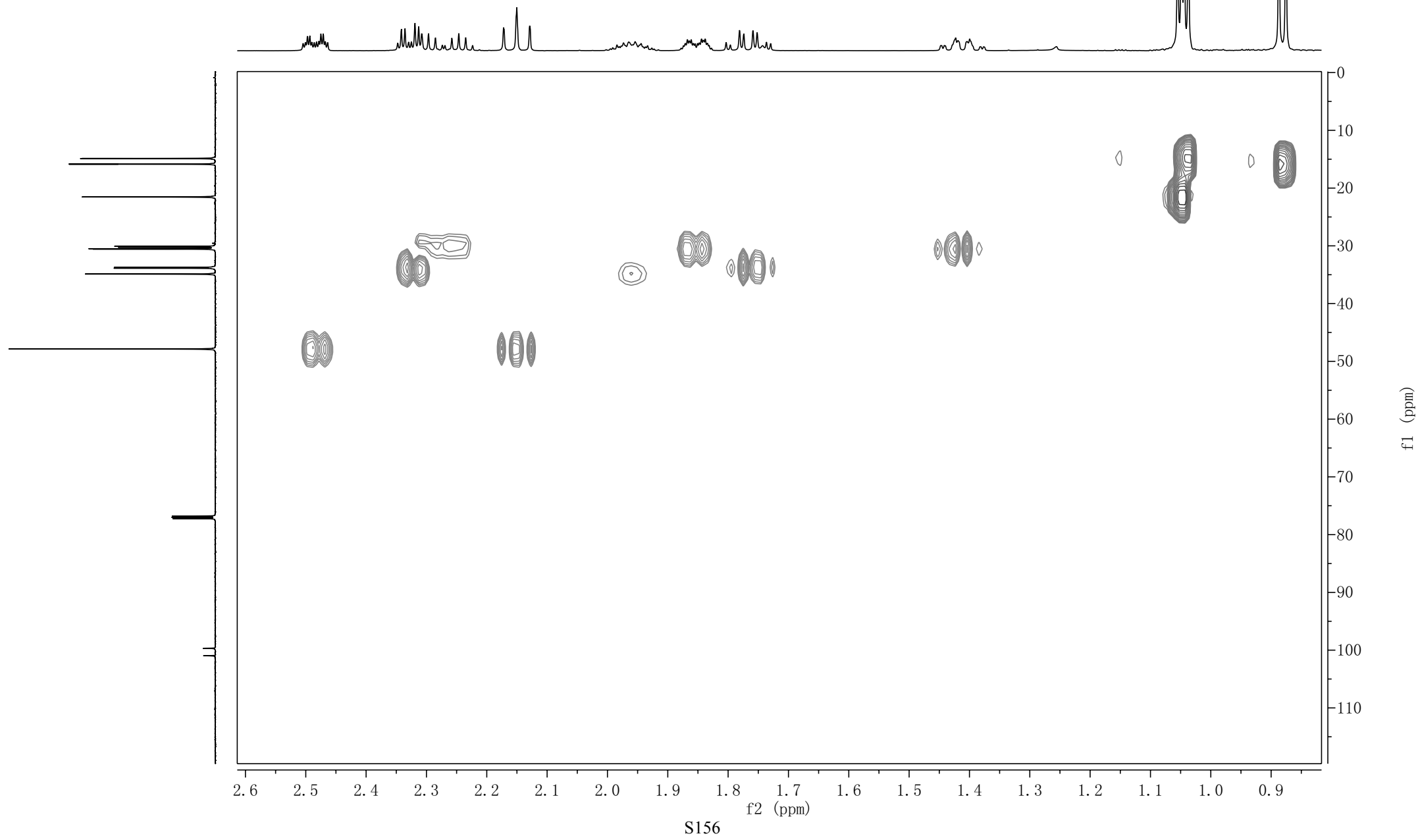


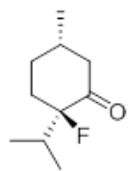
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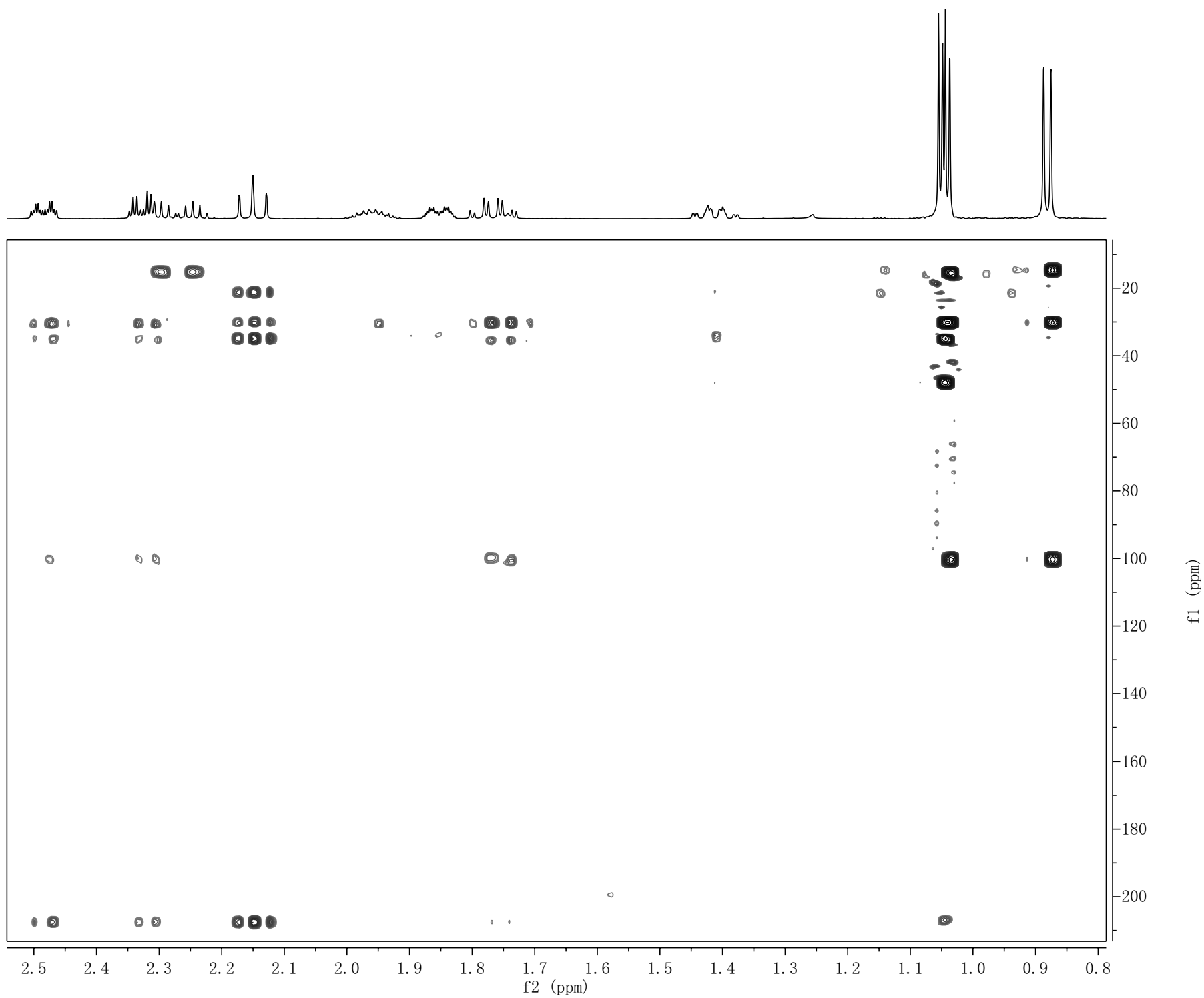


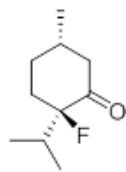
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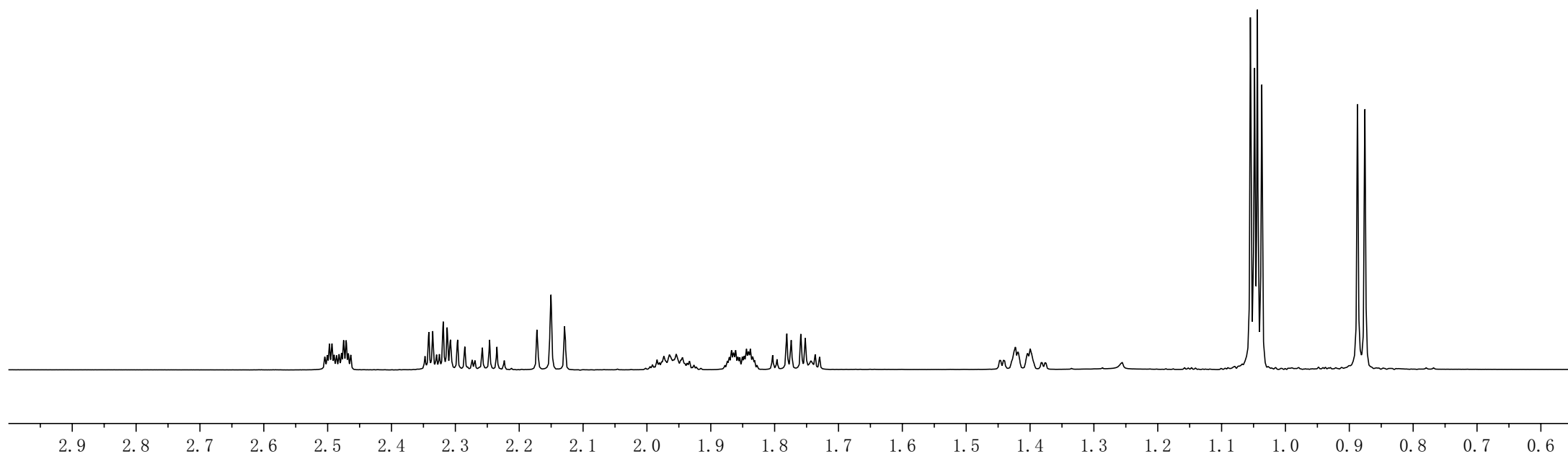
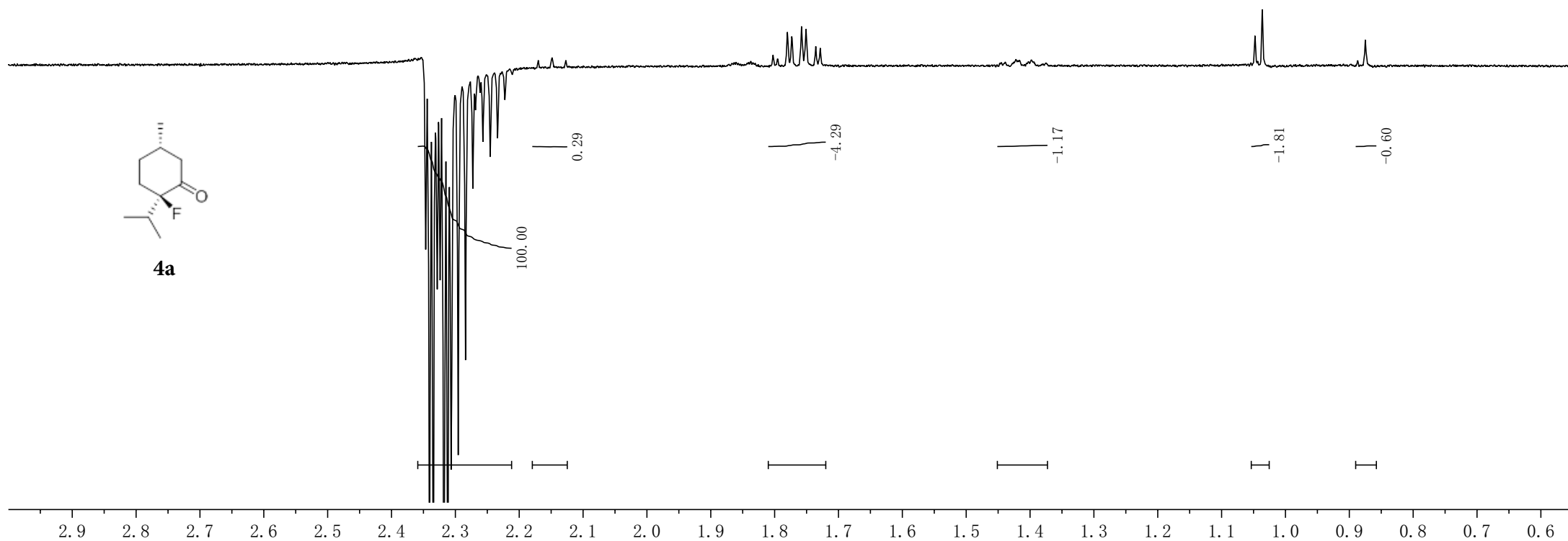


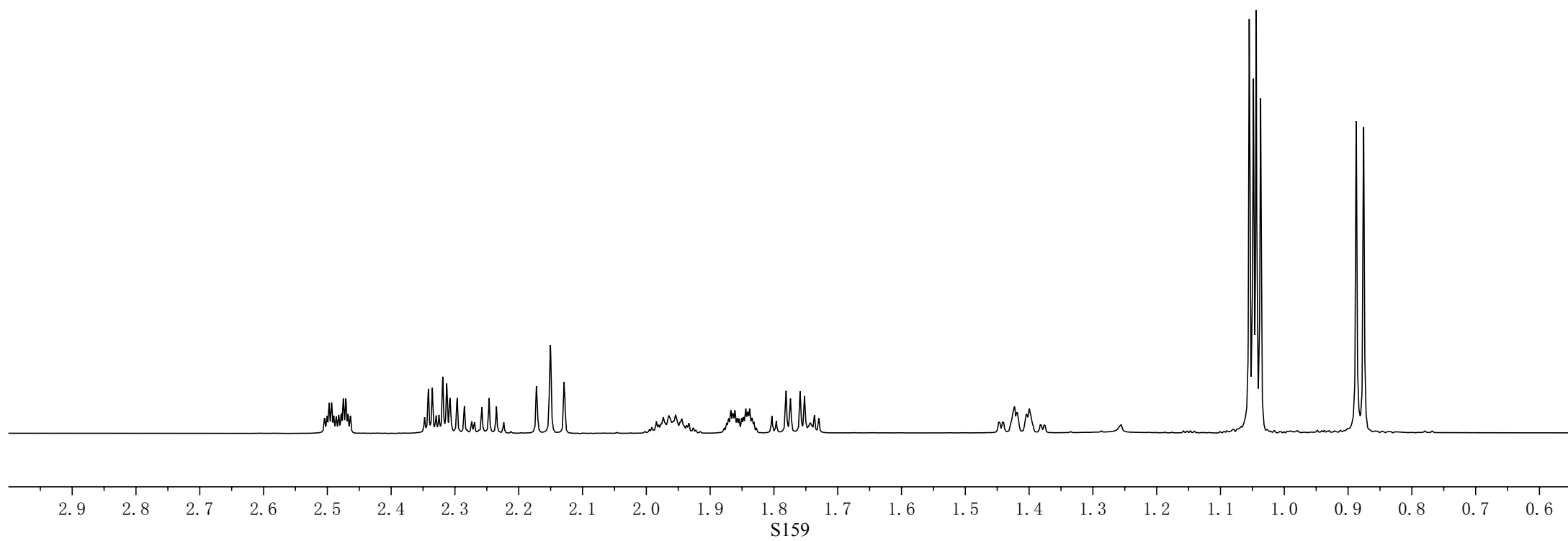
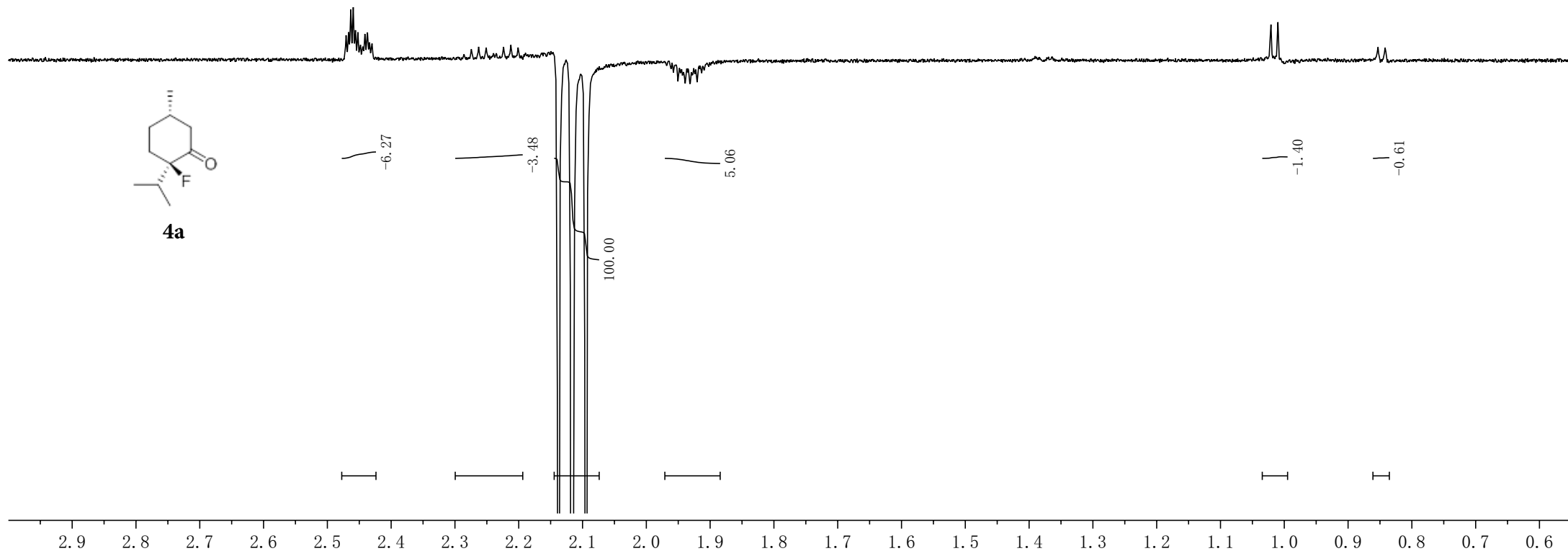
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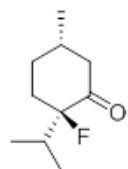




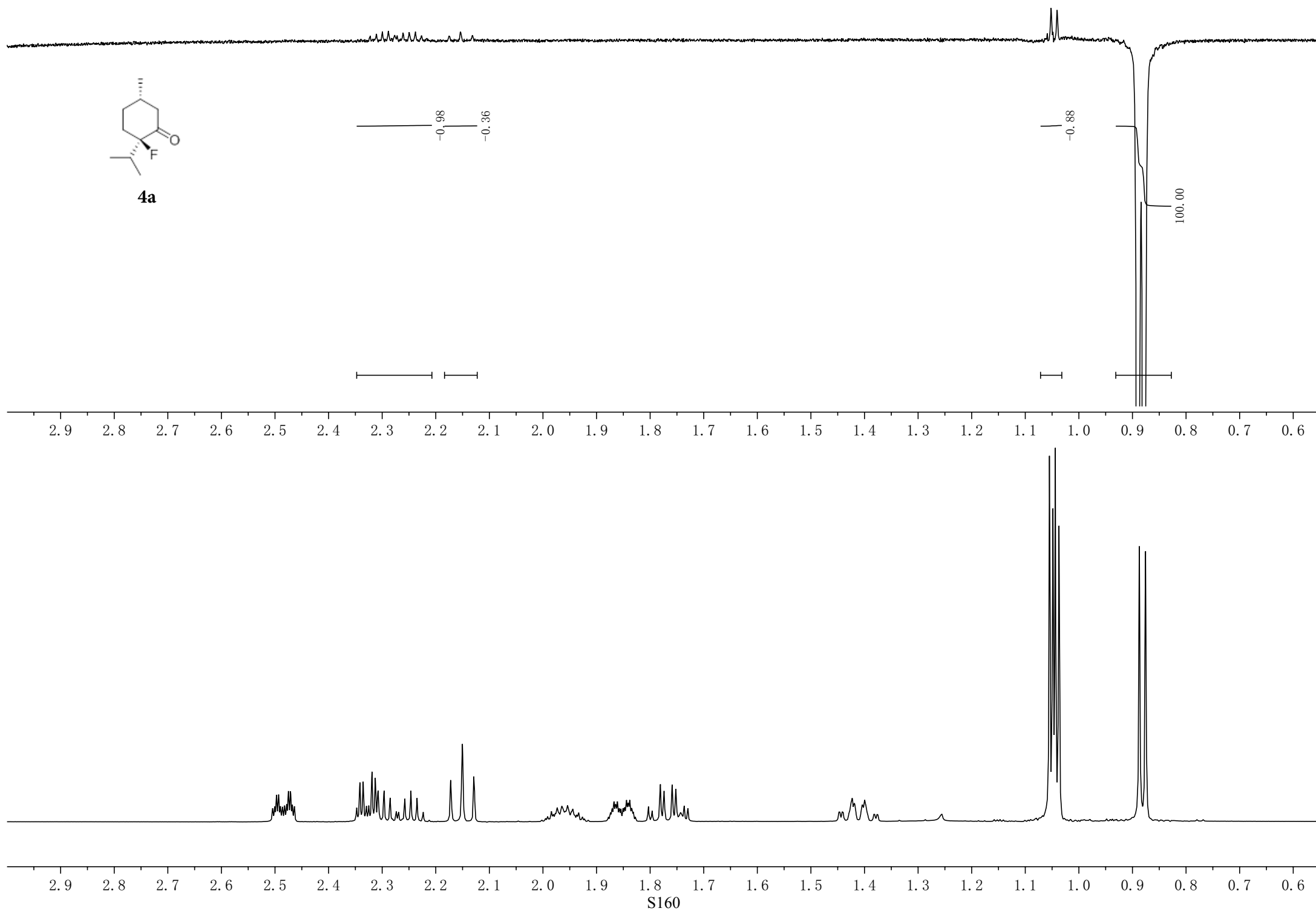
**4a**

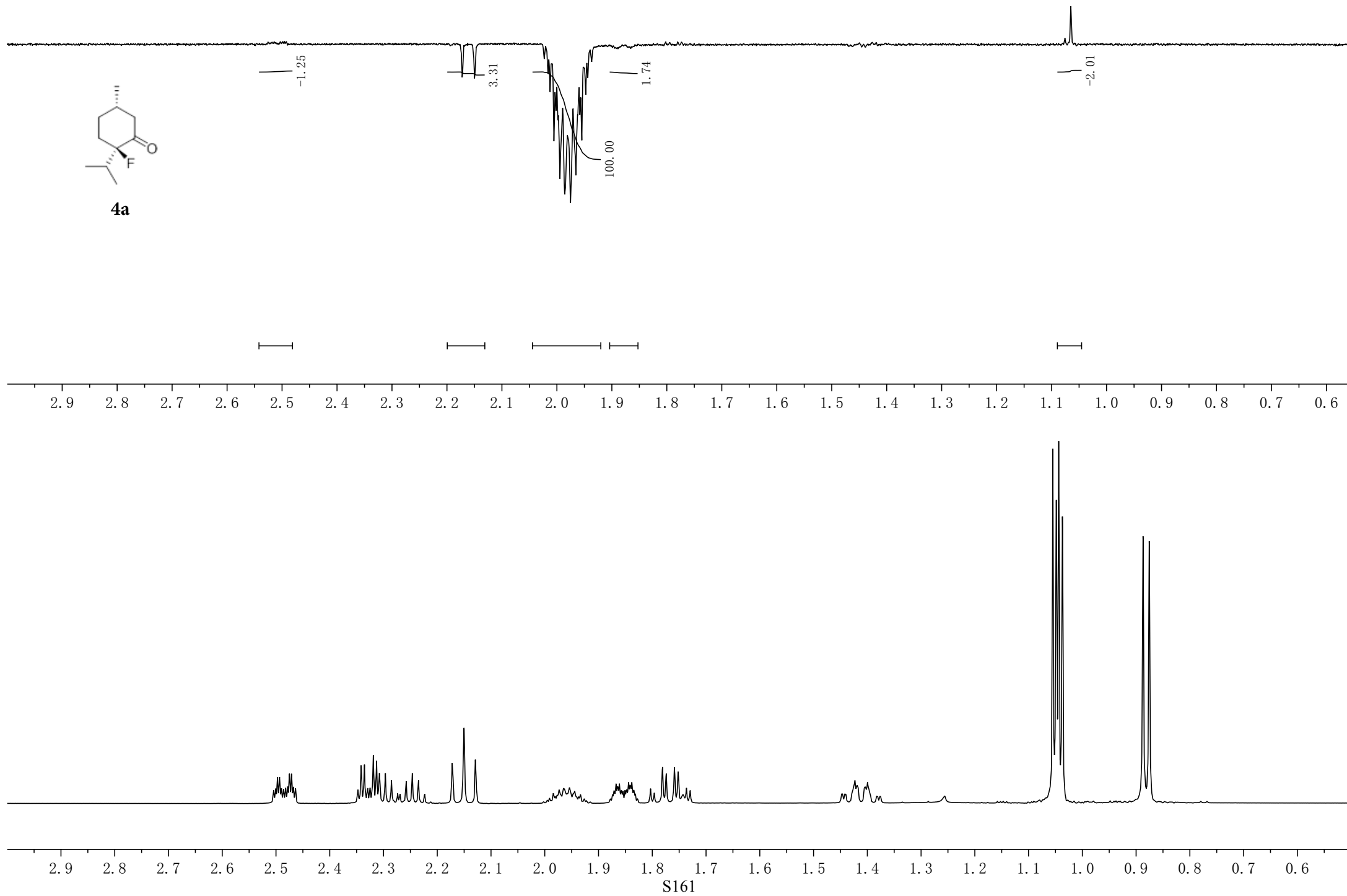


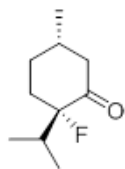




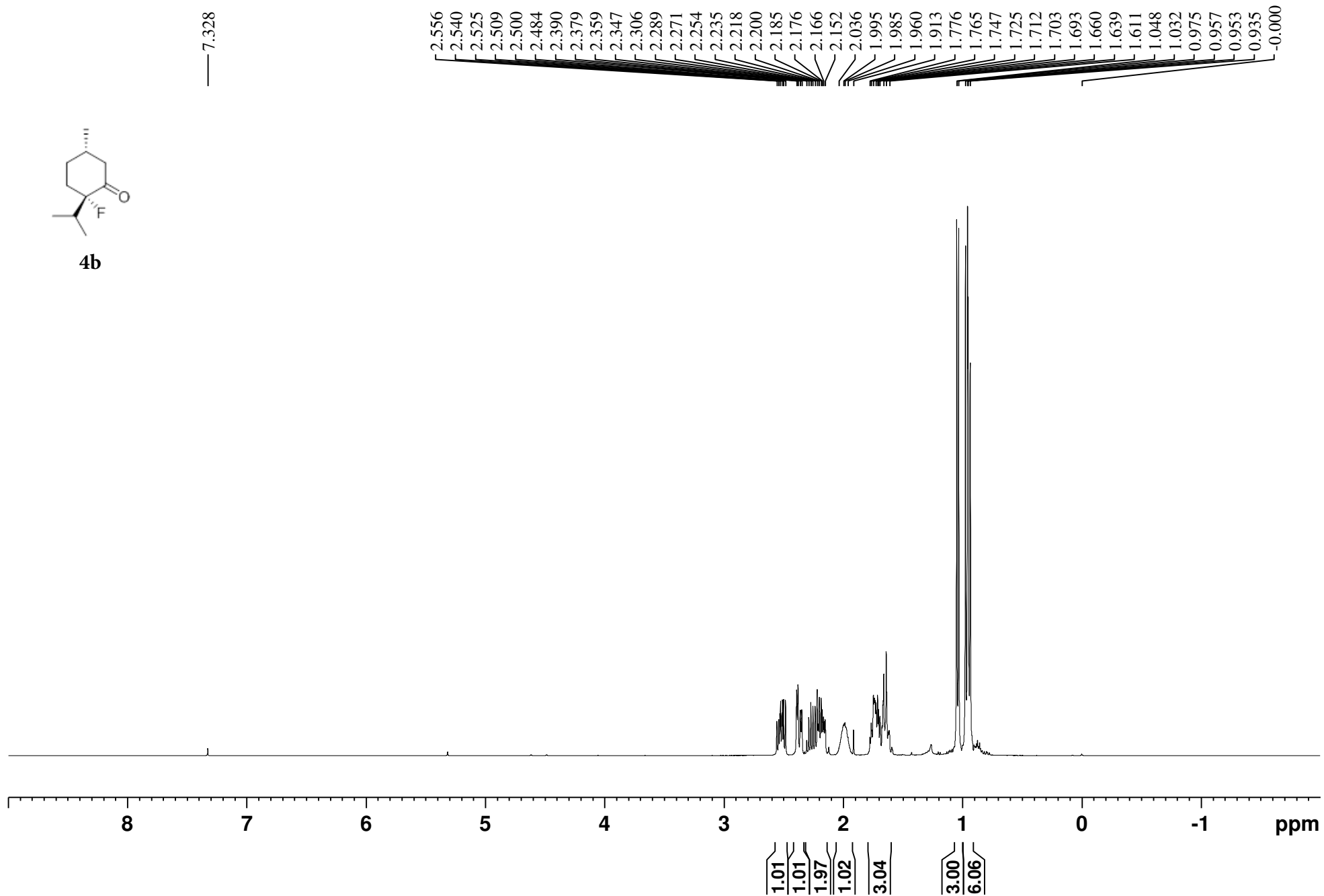
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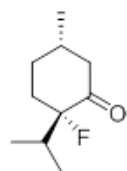




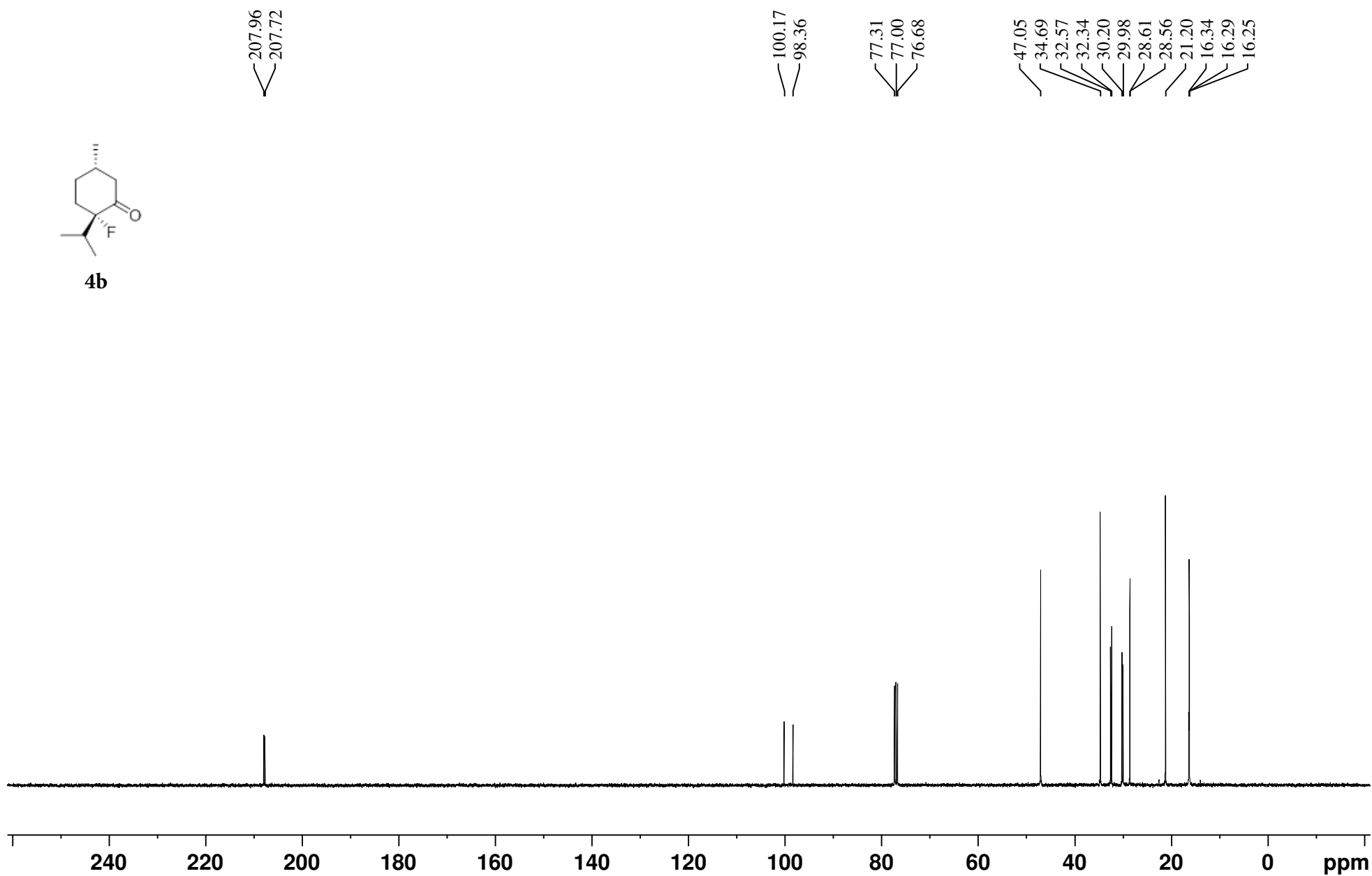


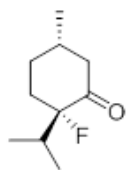
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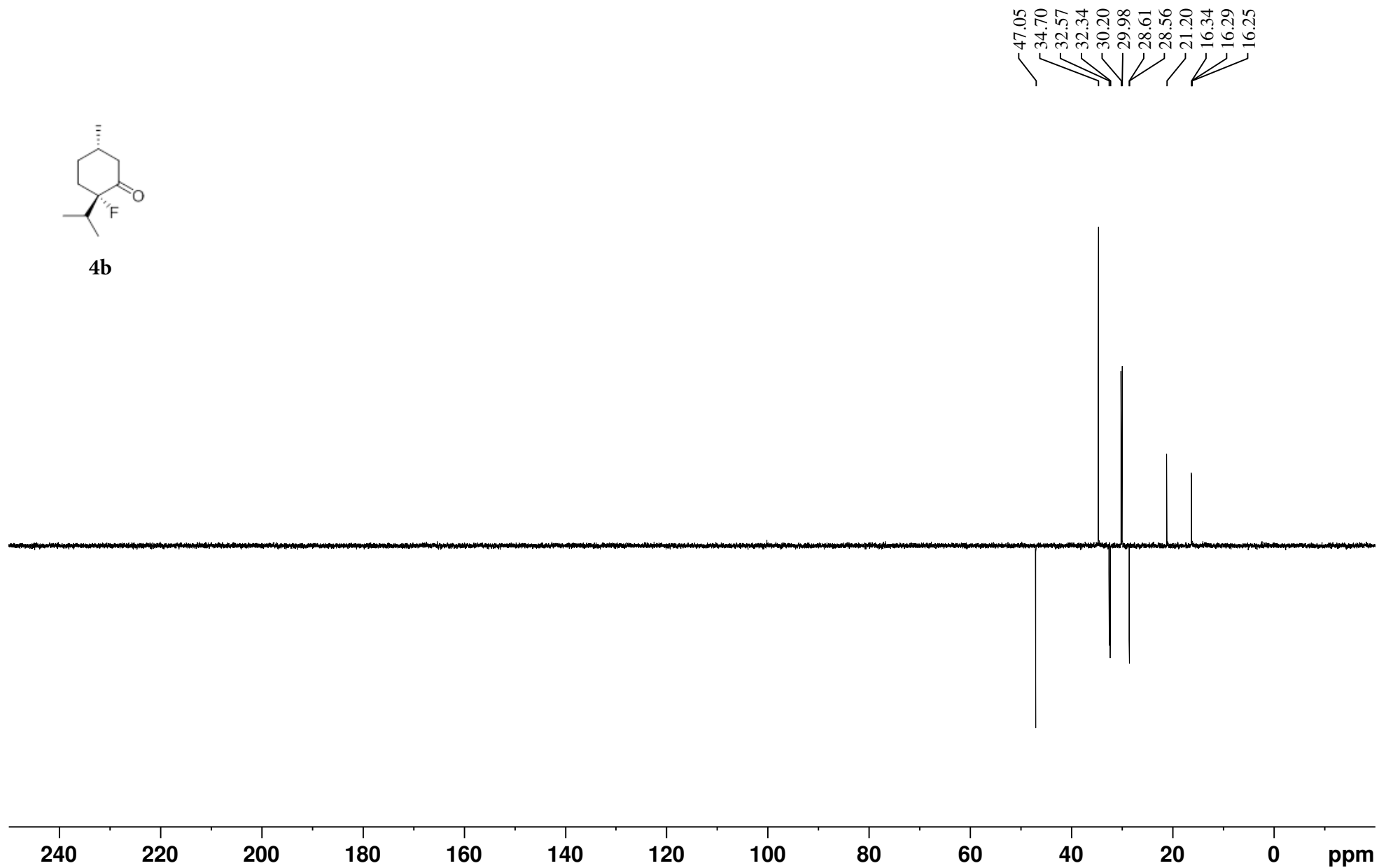


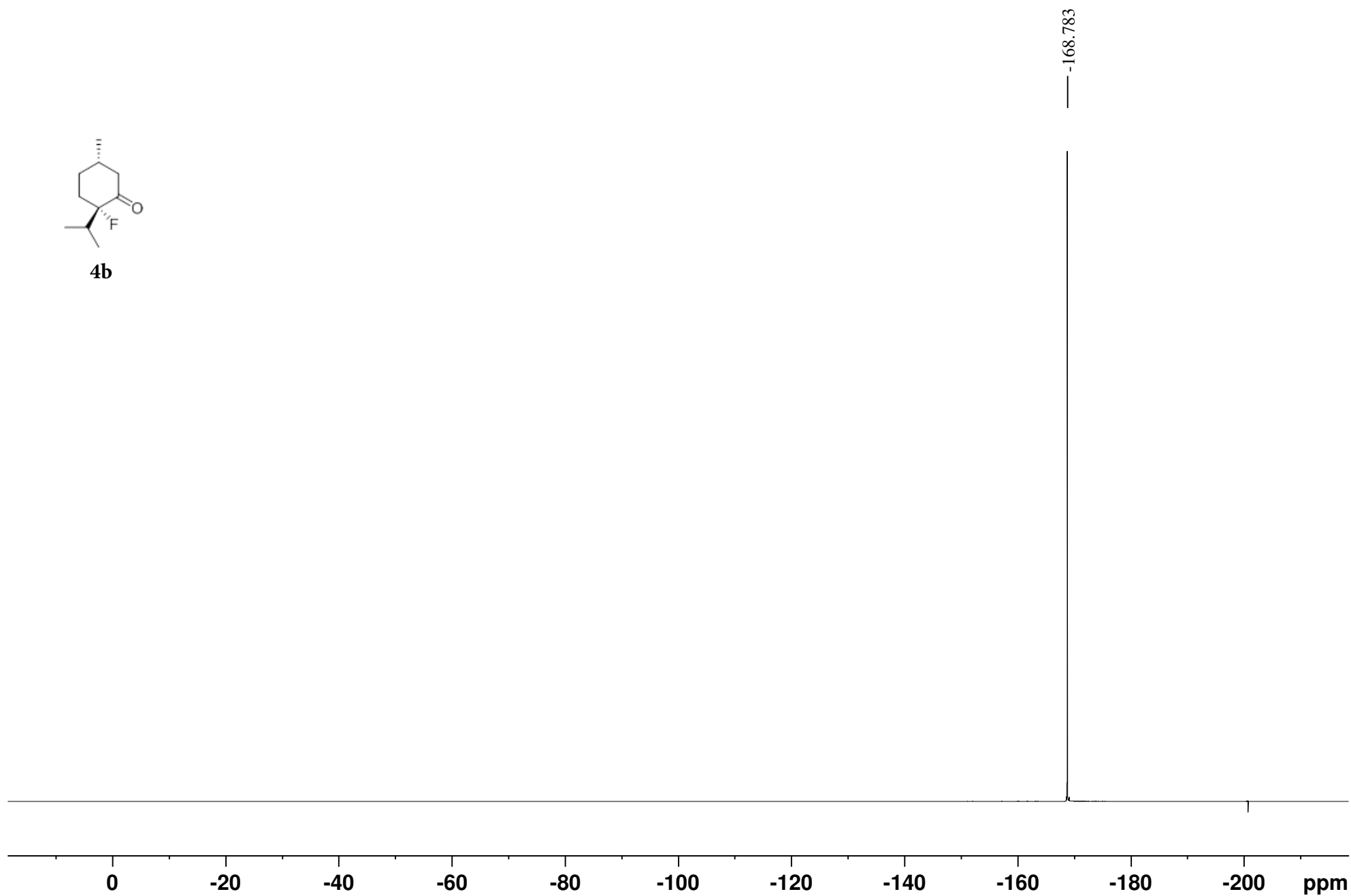
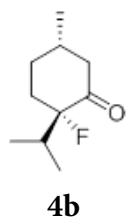
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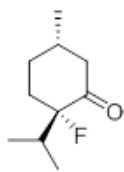




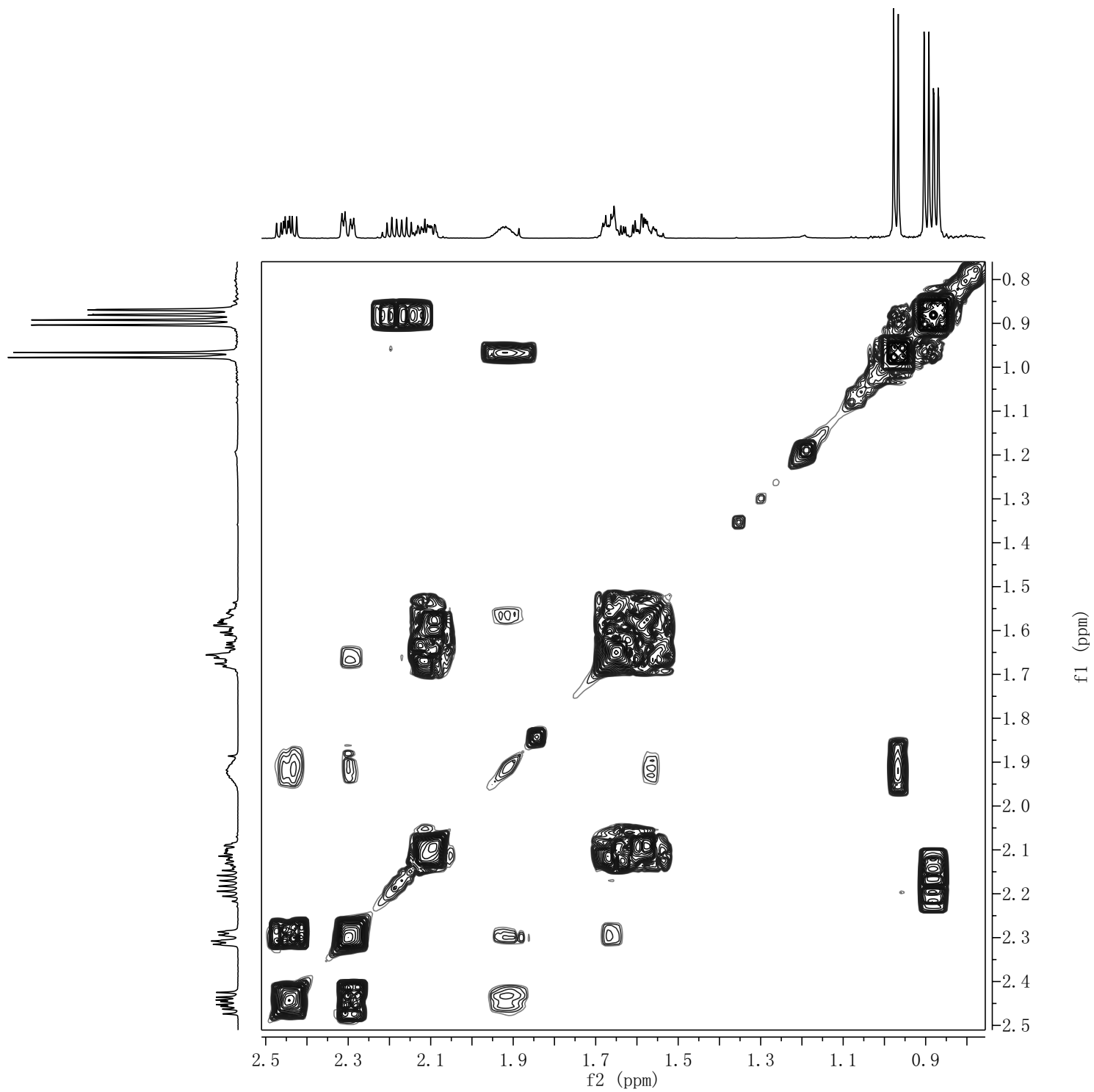
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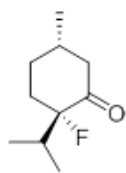




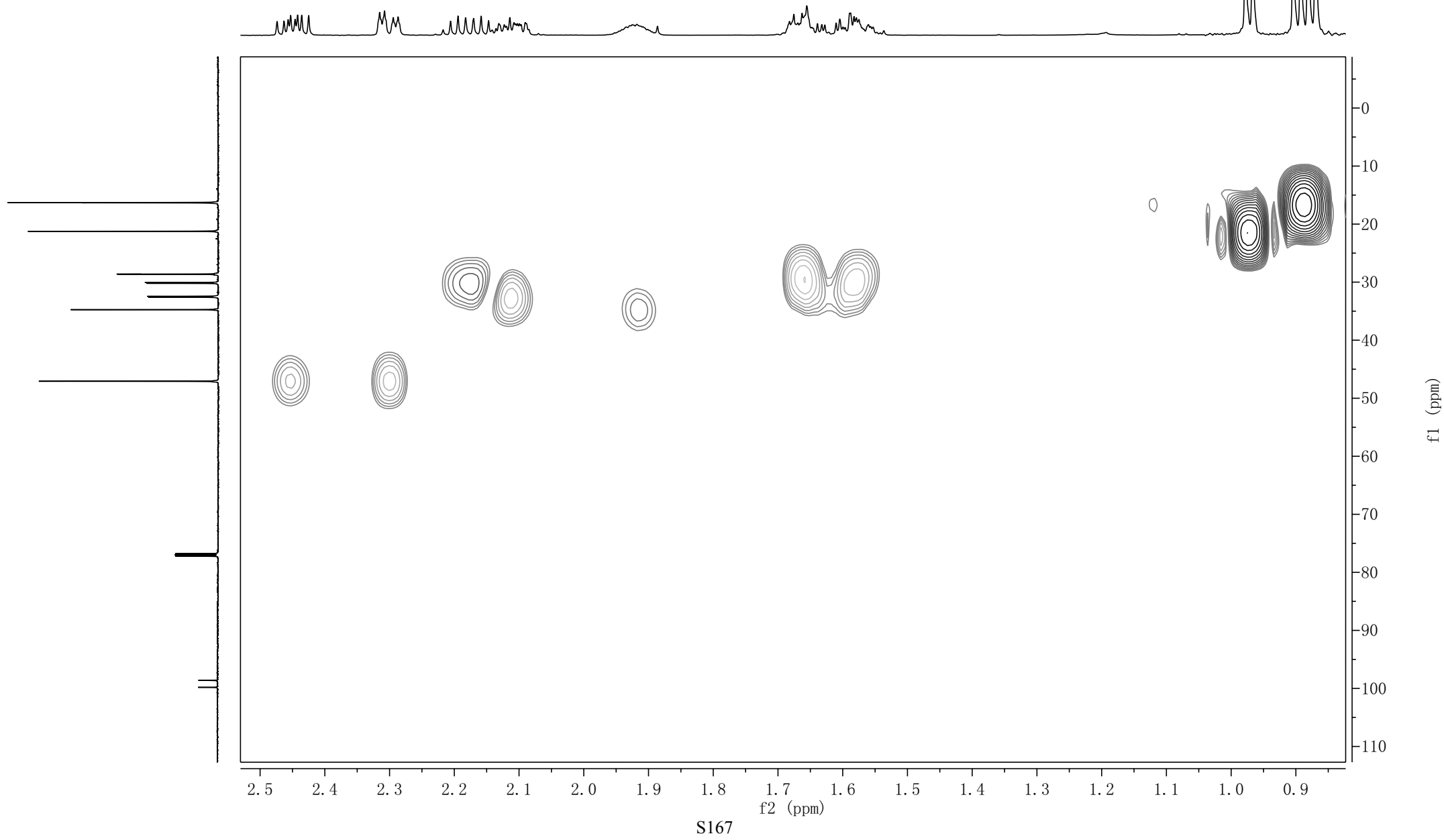


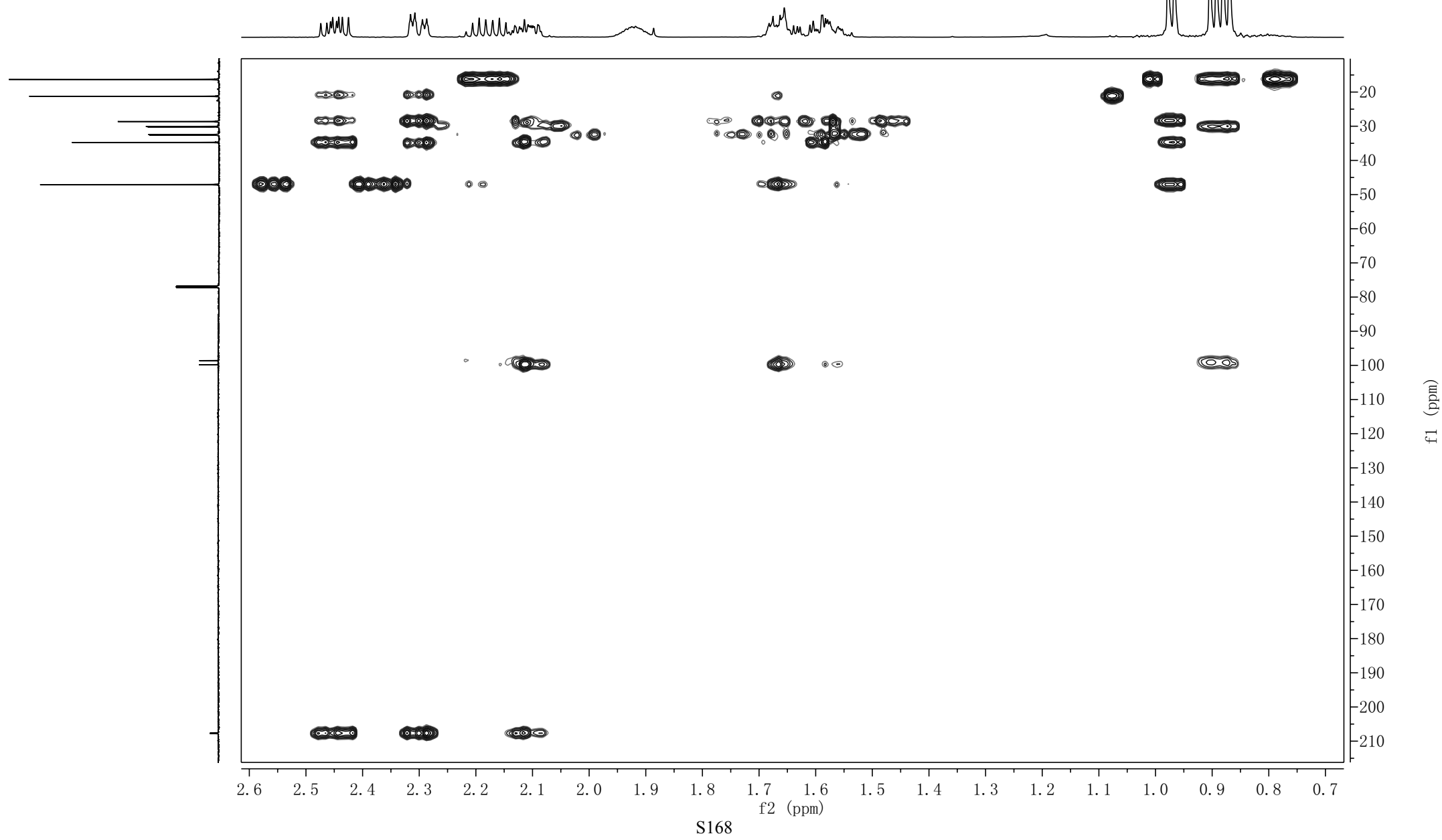
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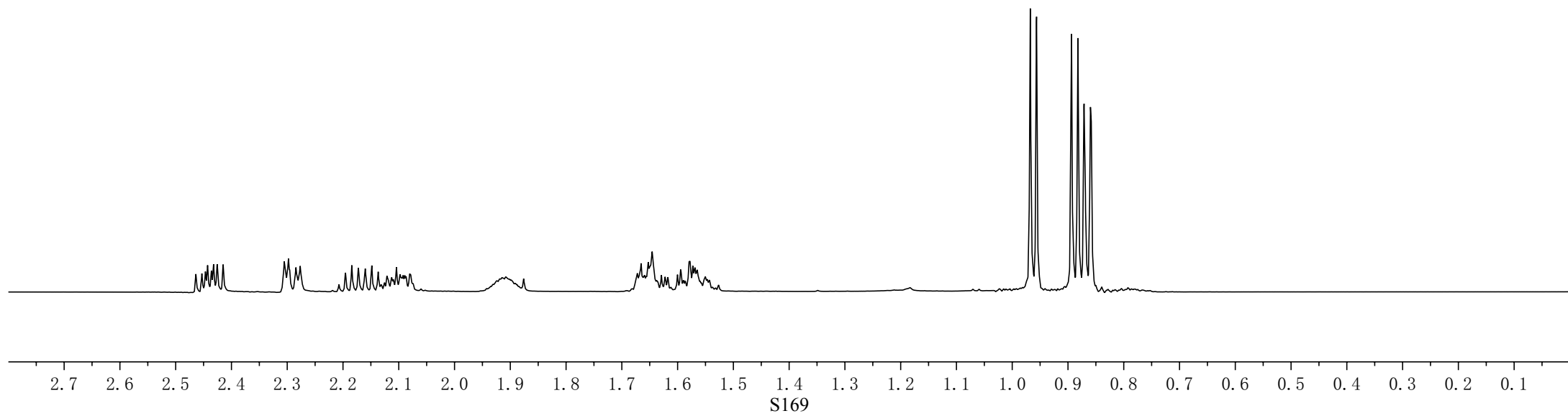
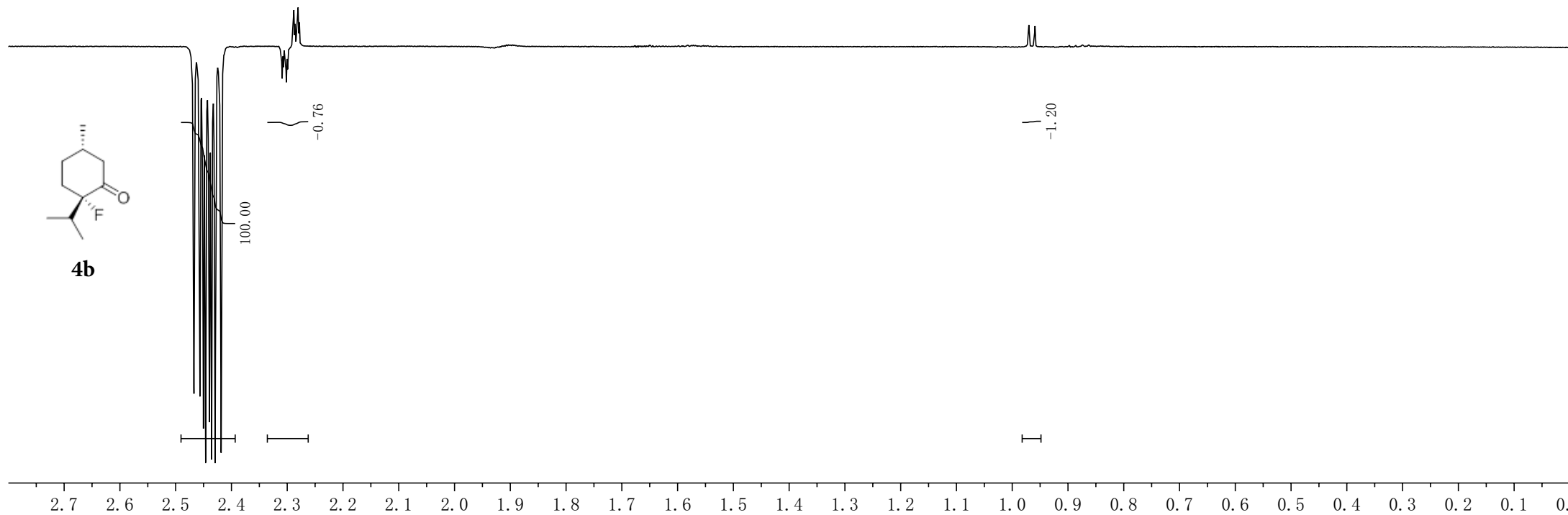


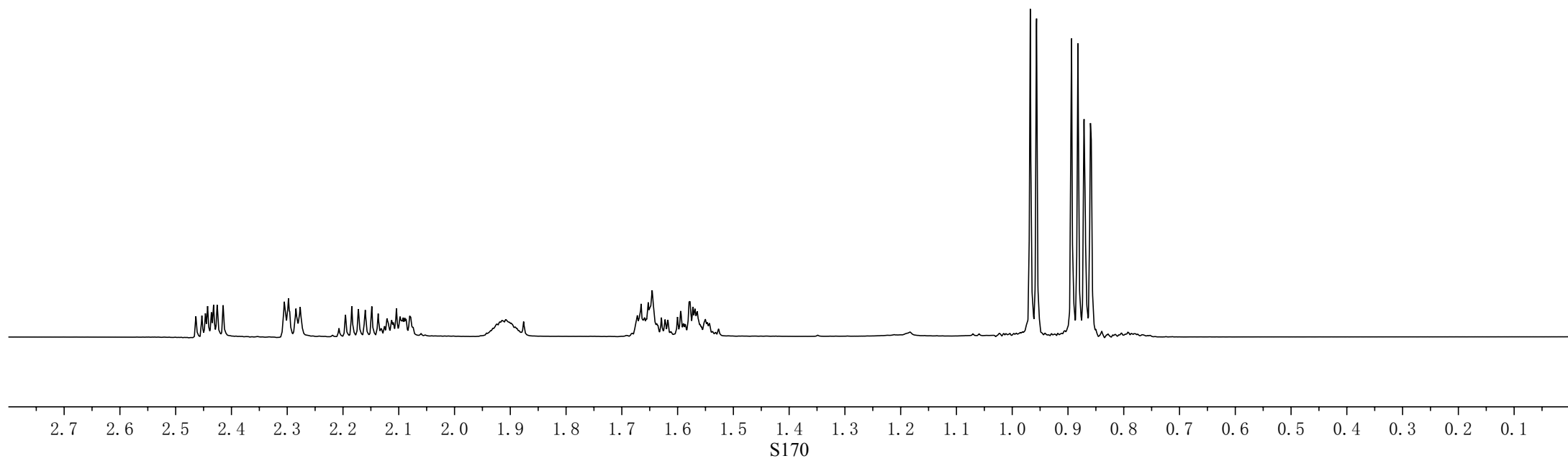
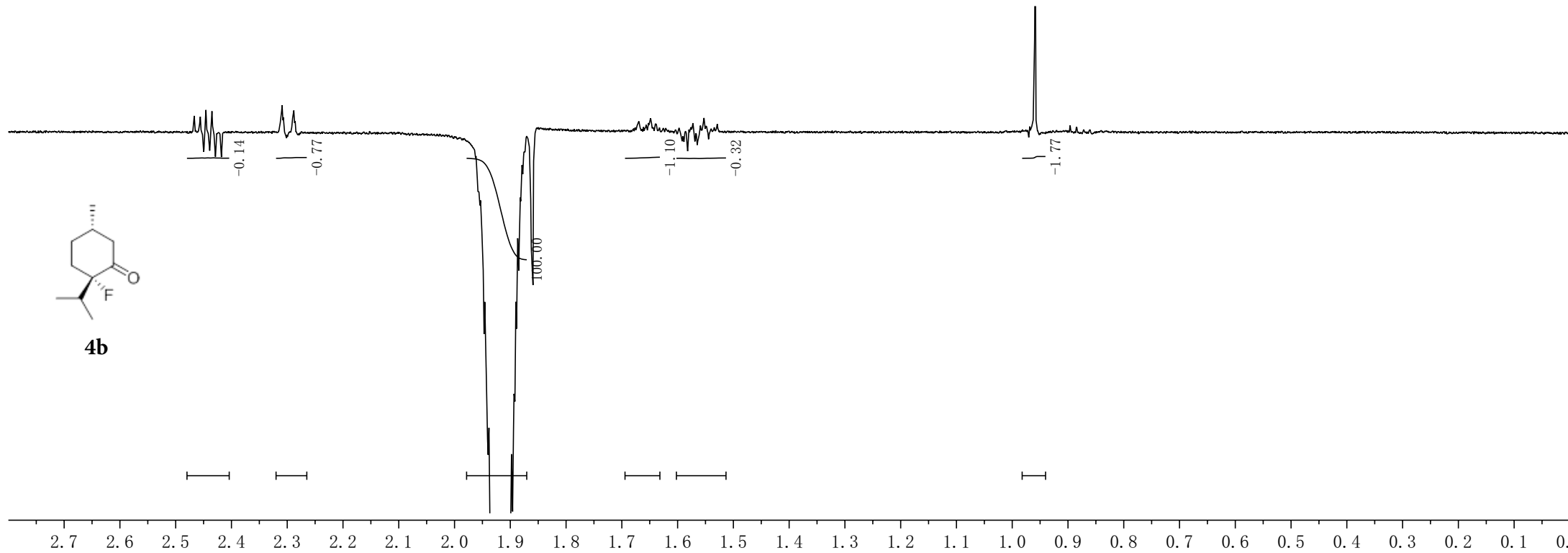


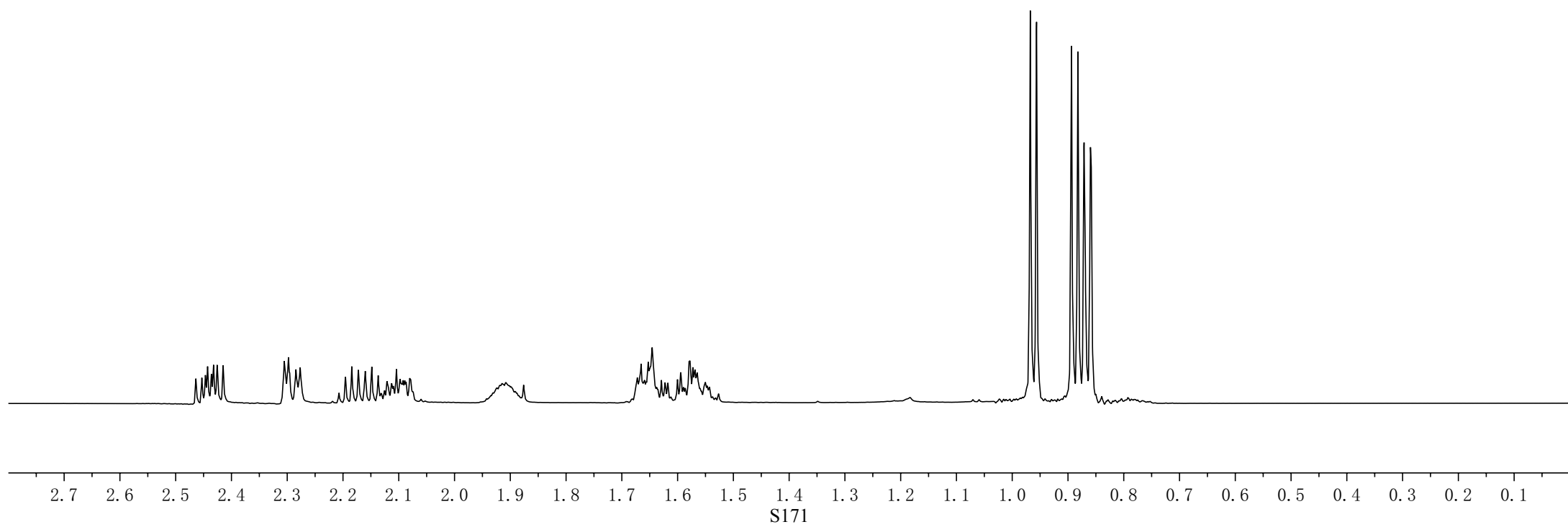
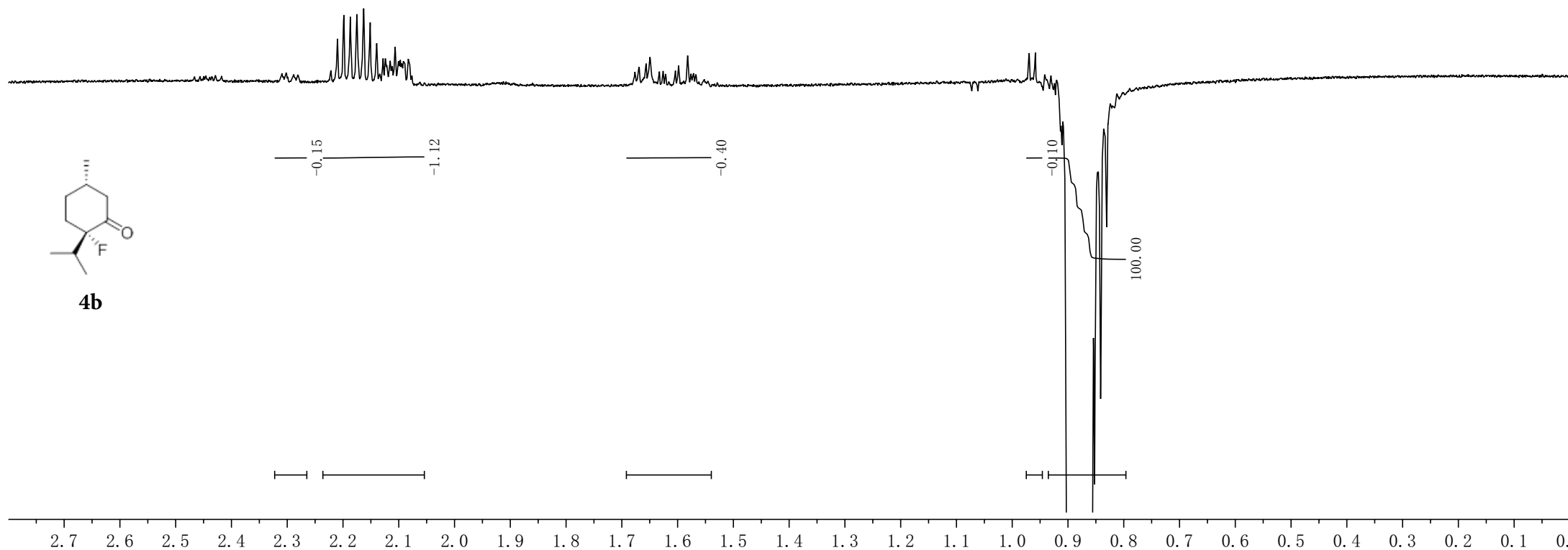
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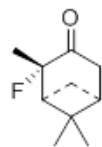




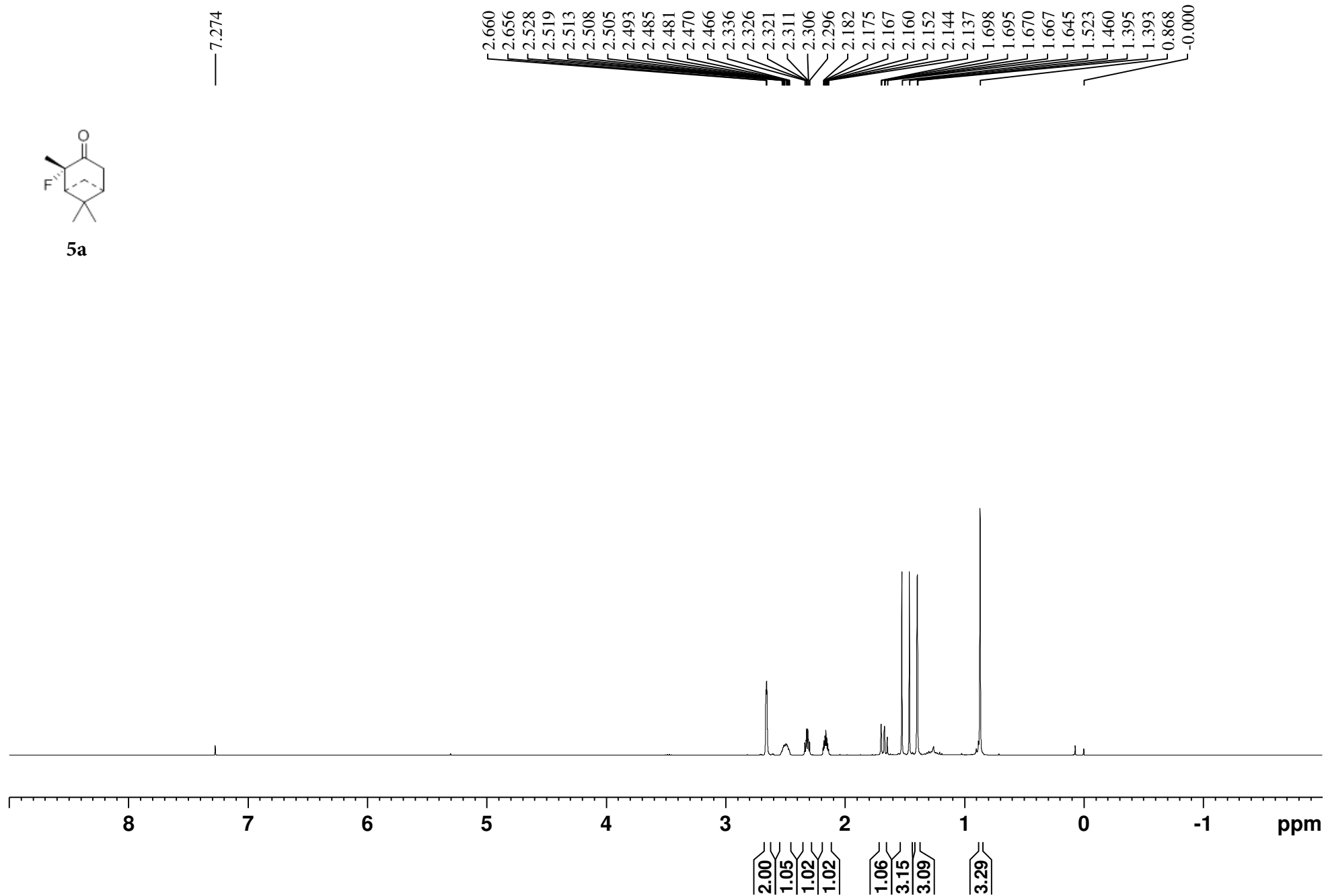


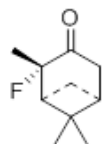




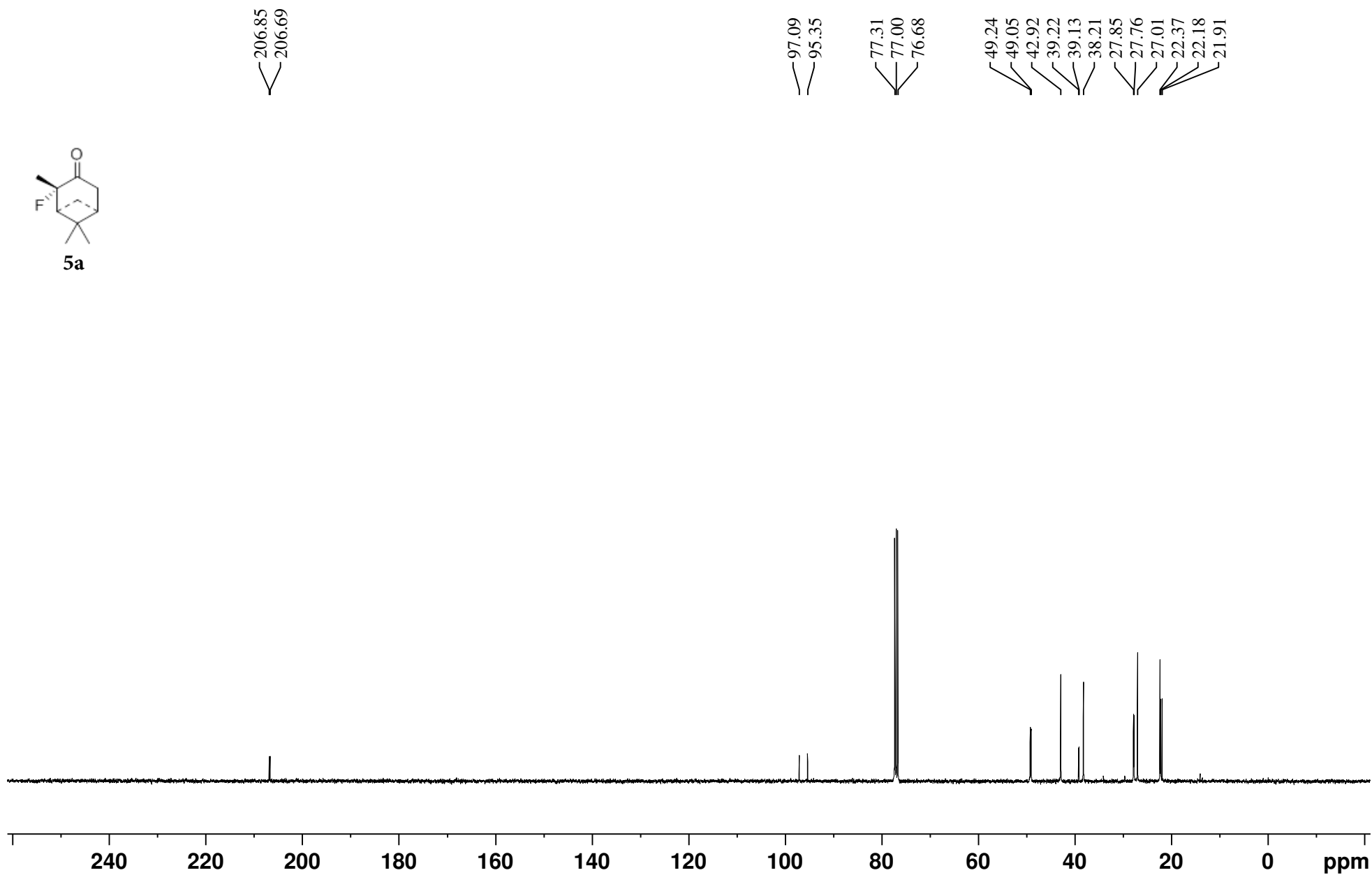


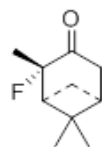
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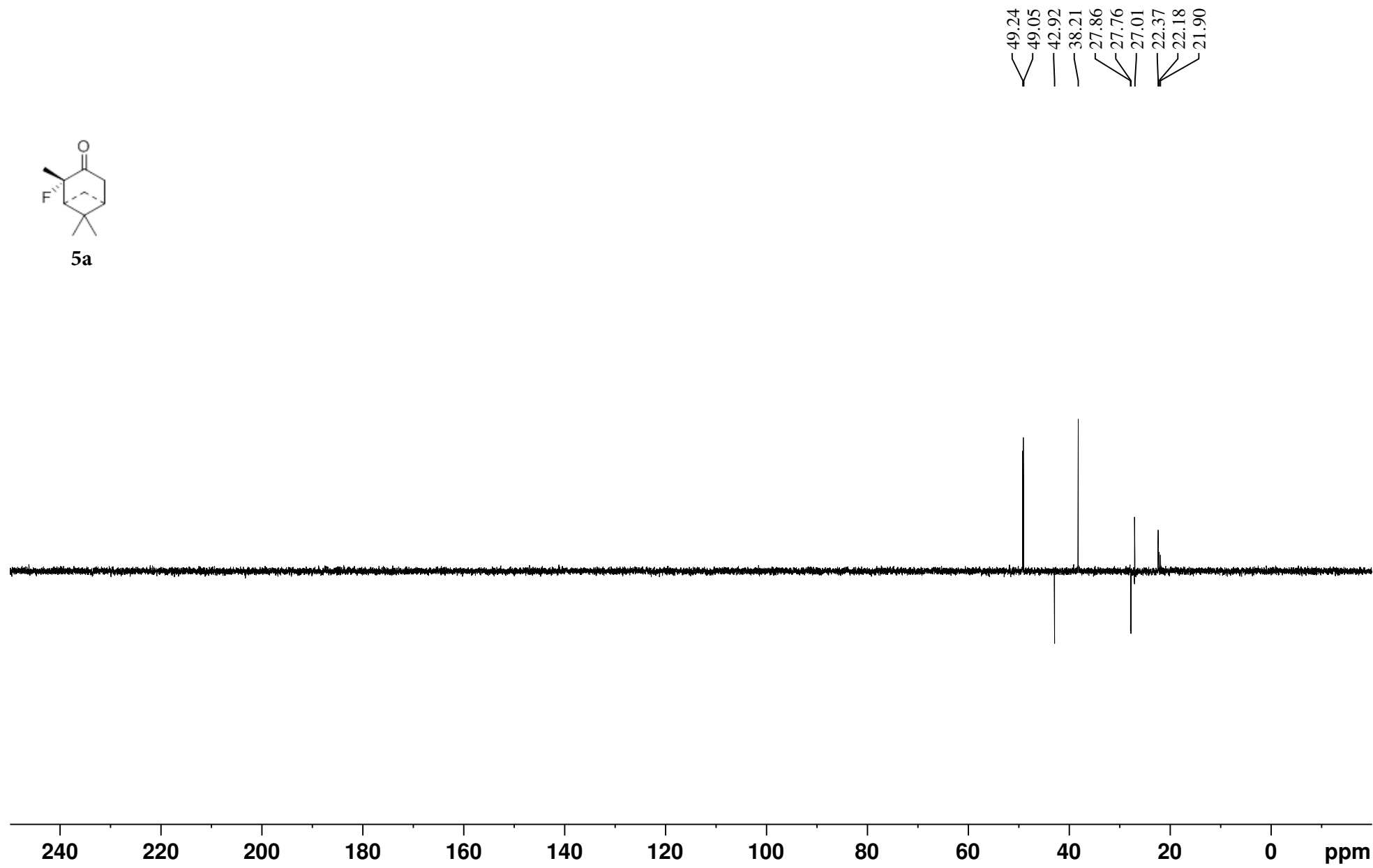


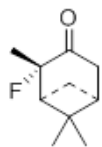
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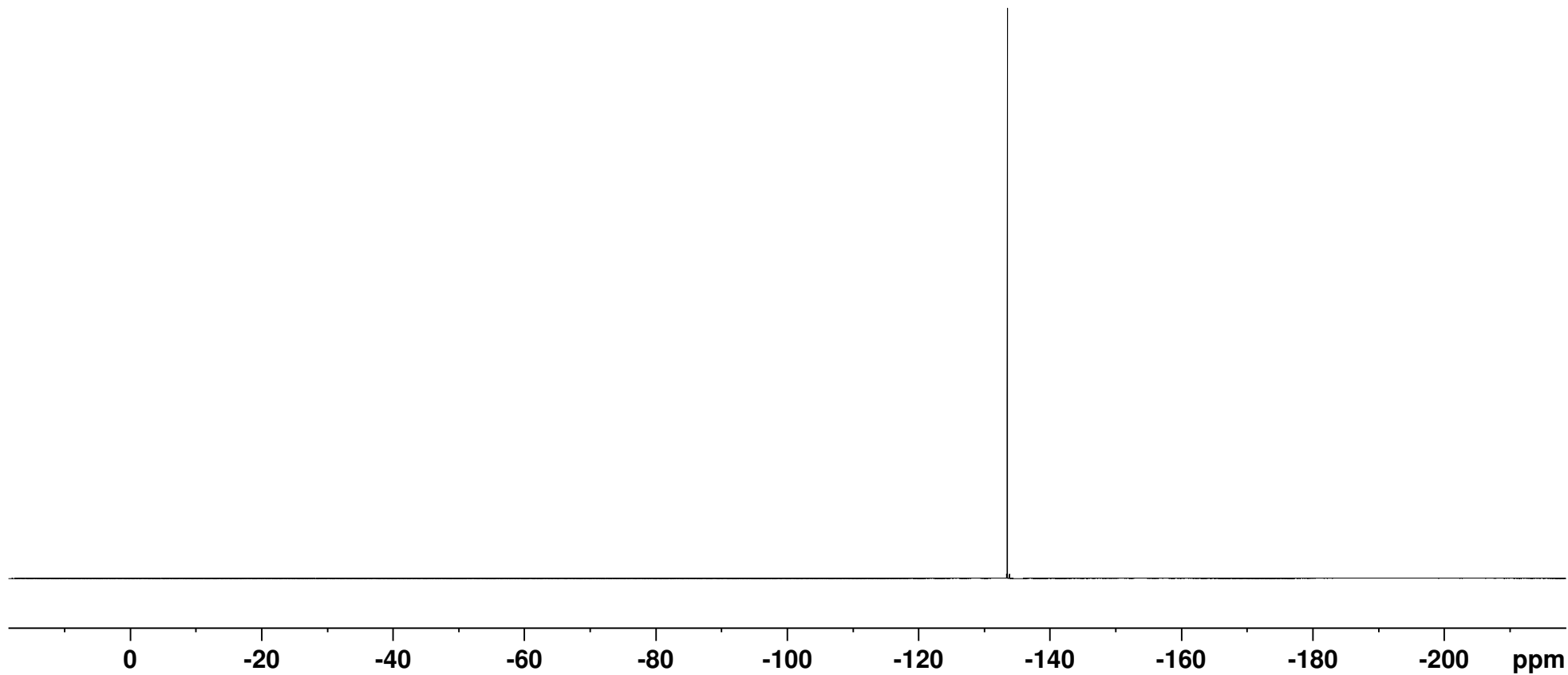
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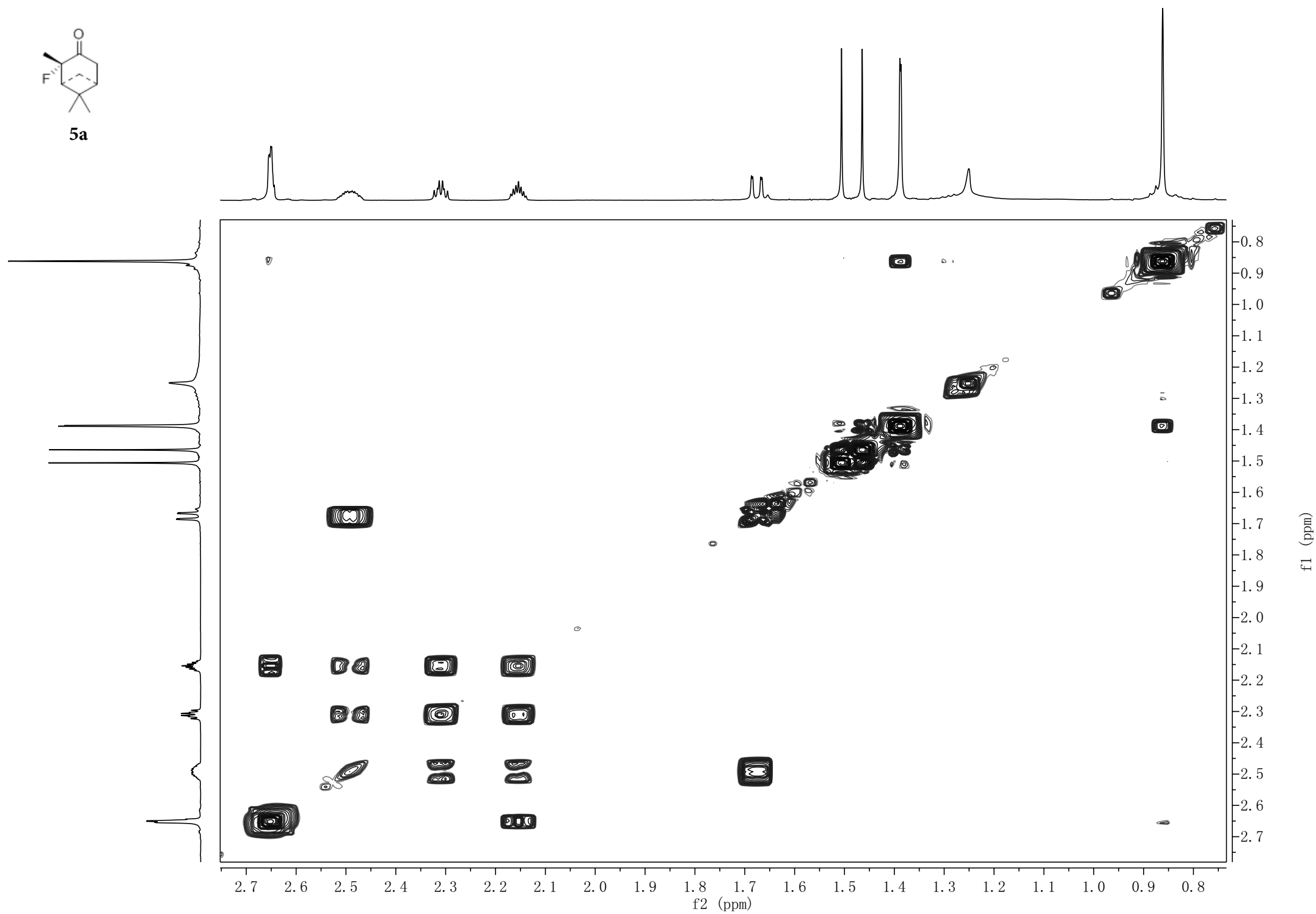
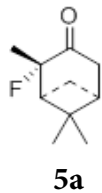


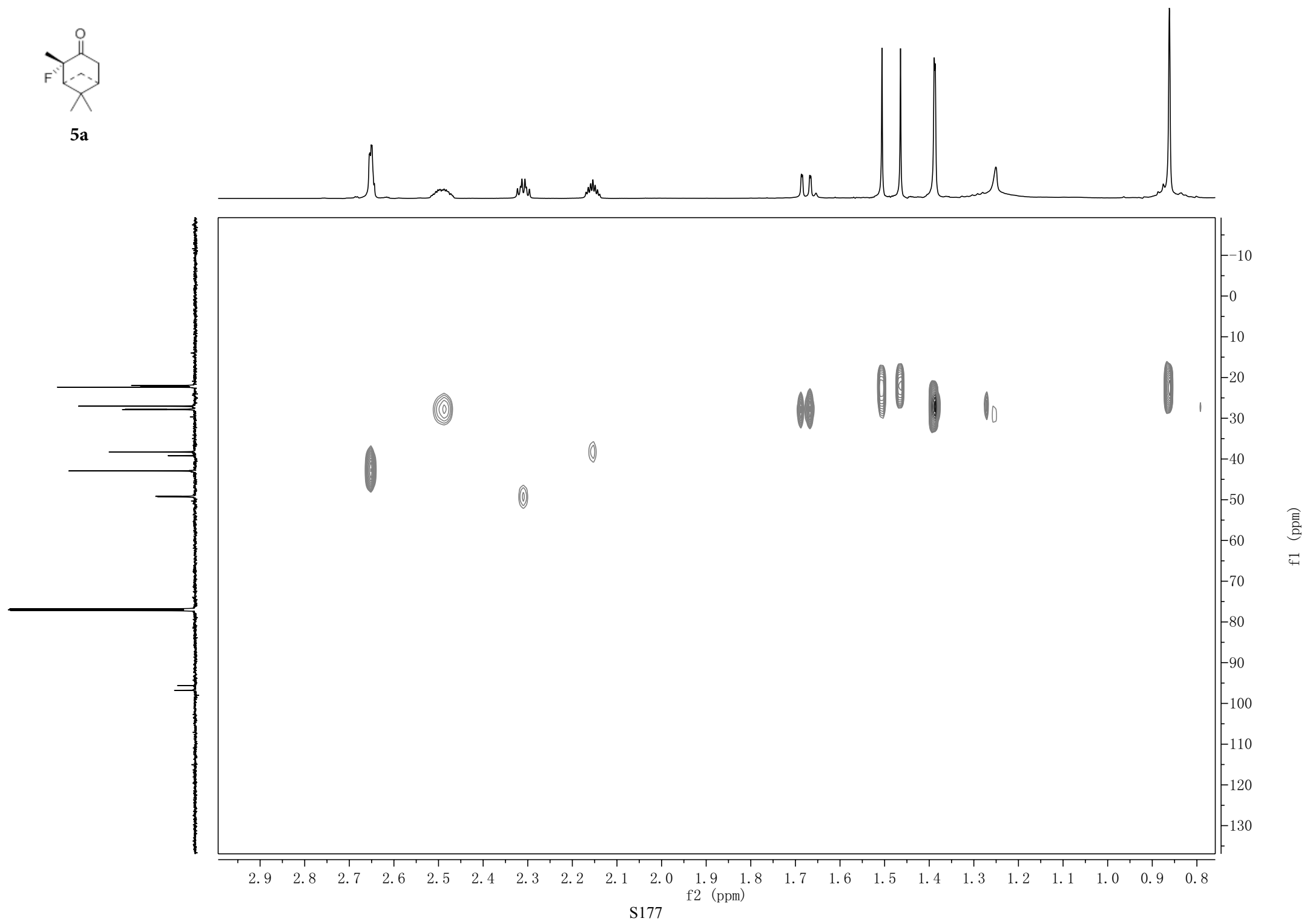
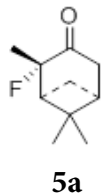


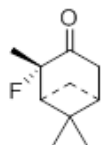
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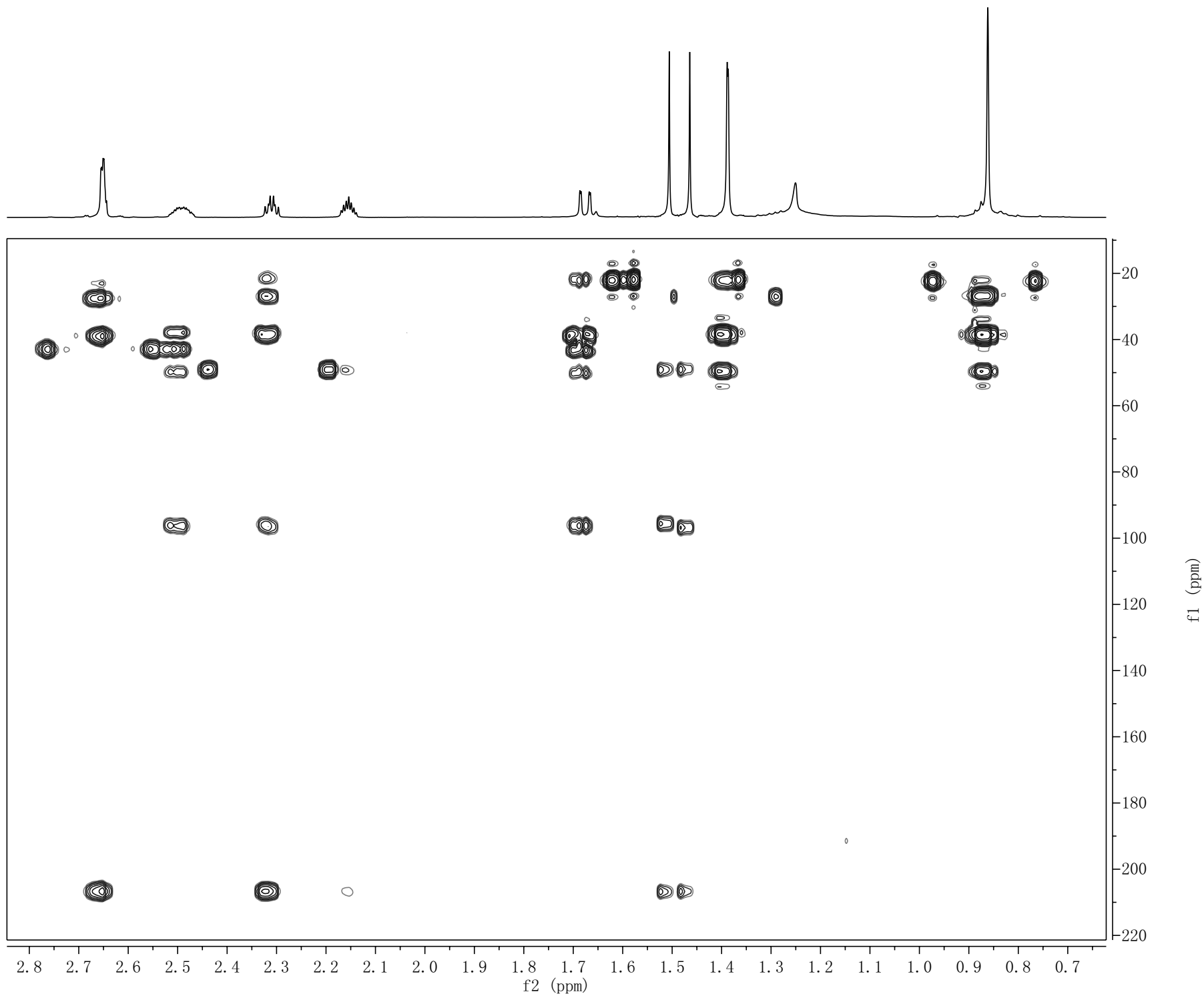


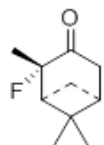






5a





5a

0.02

0.07

-0.54

-6.13

-1.75

100.00

2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0.0 -0.1

f1 (ppm)

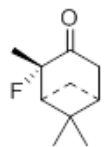
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1.00

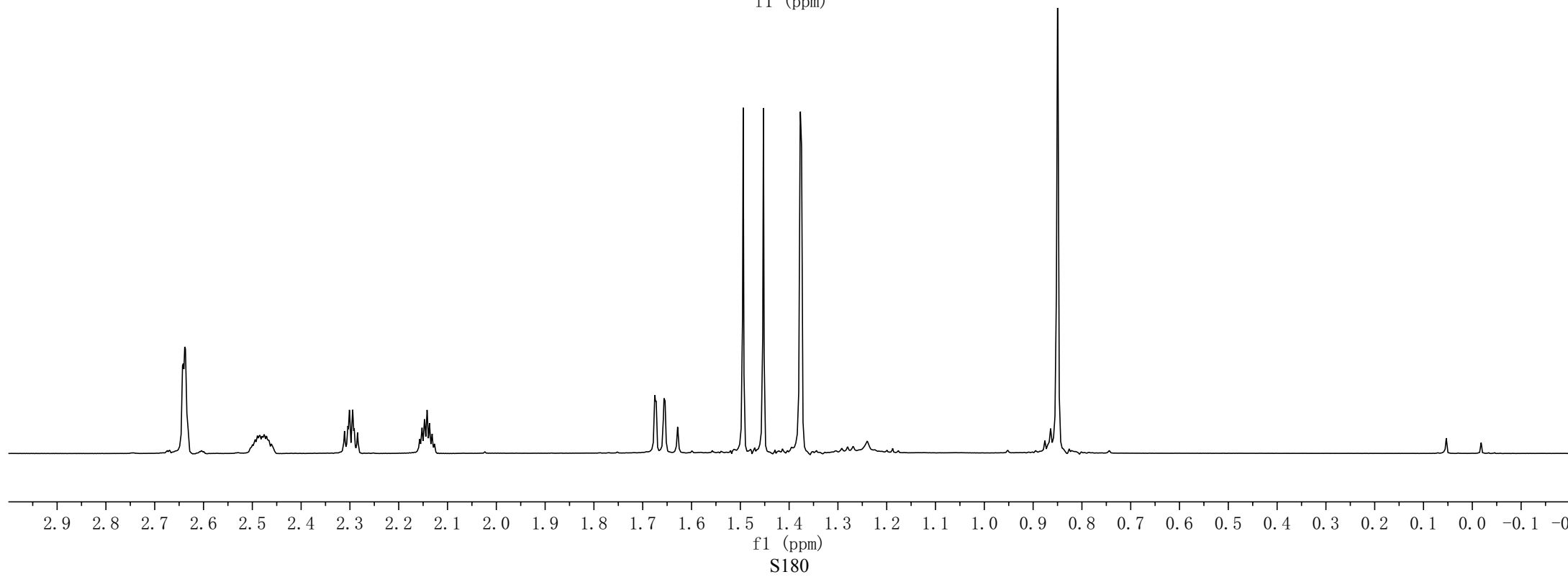
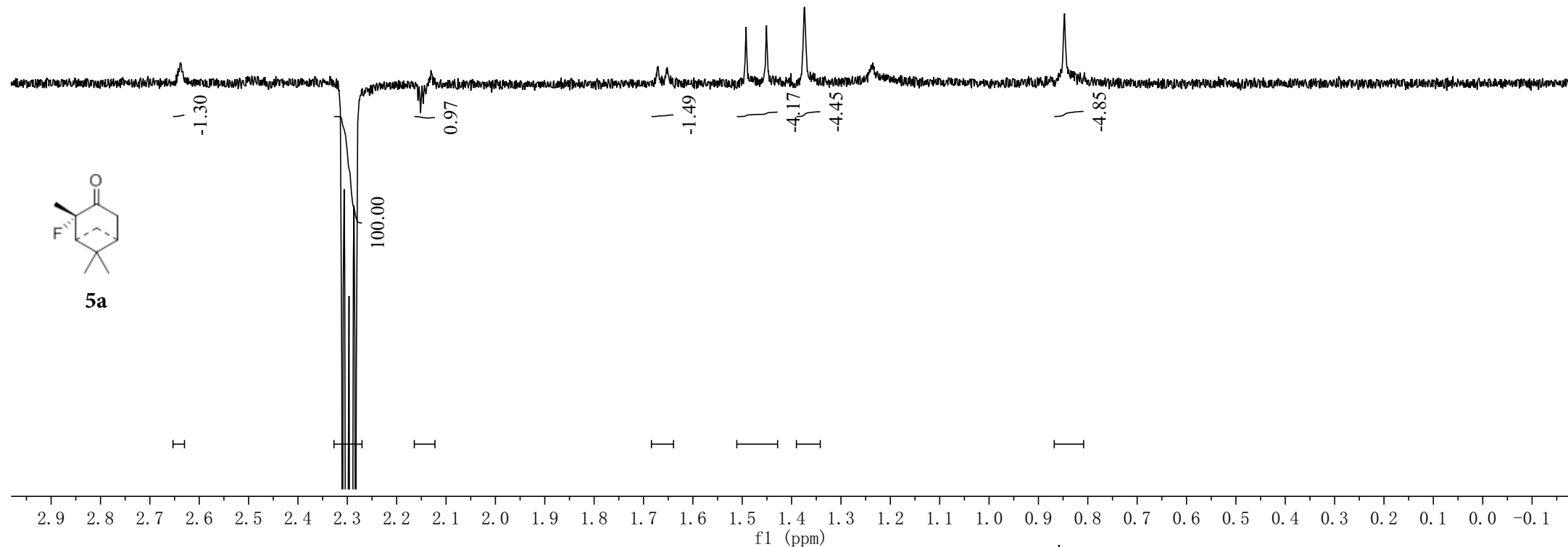
2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0.0 -0.1

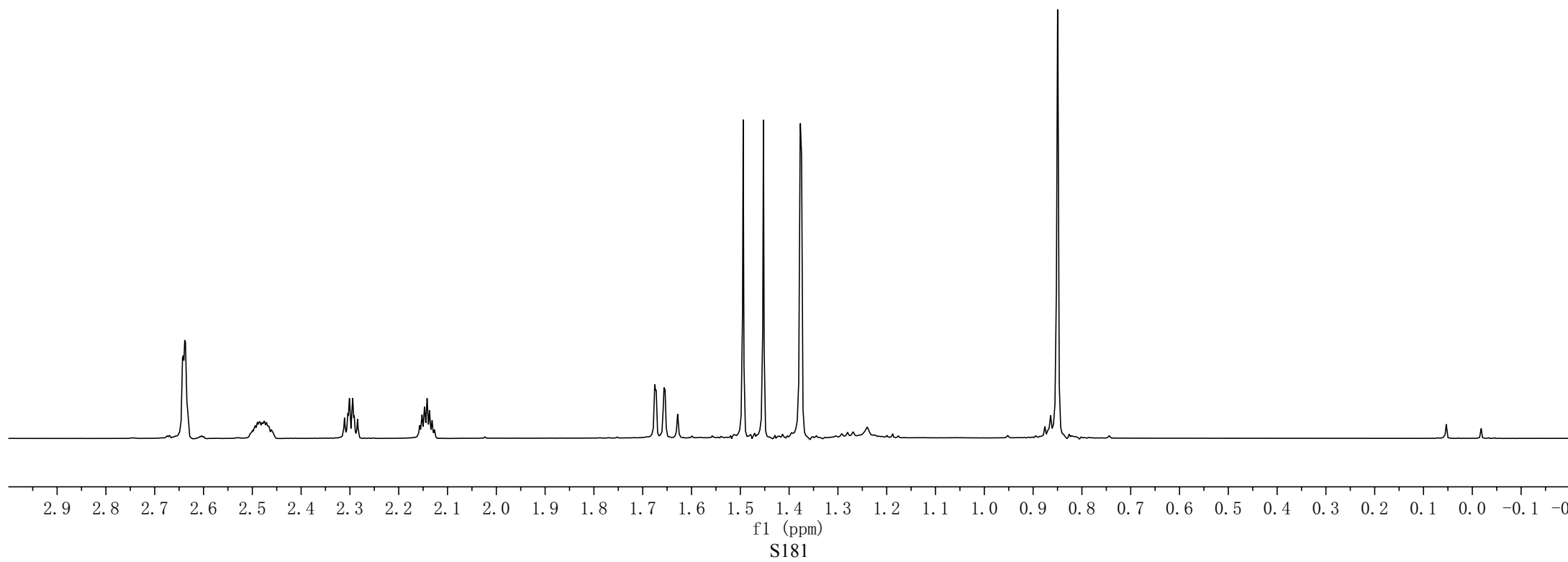
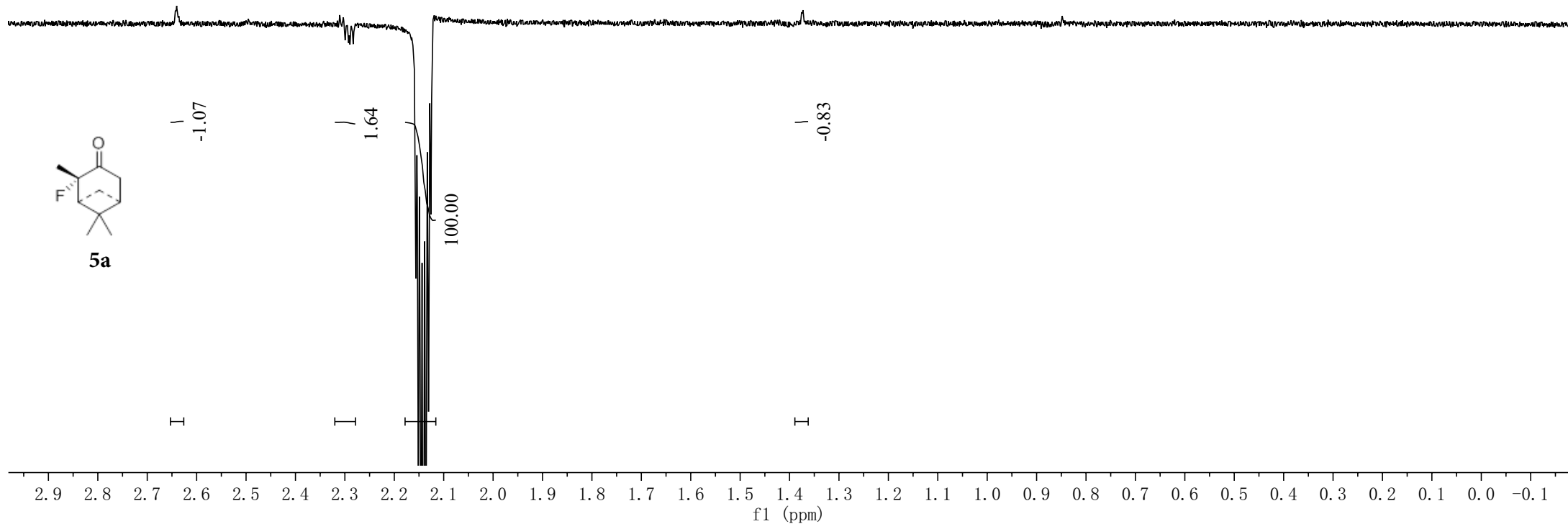
f1 (ppm)

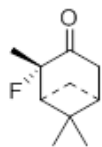
S179



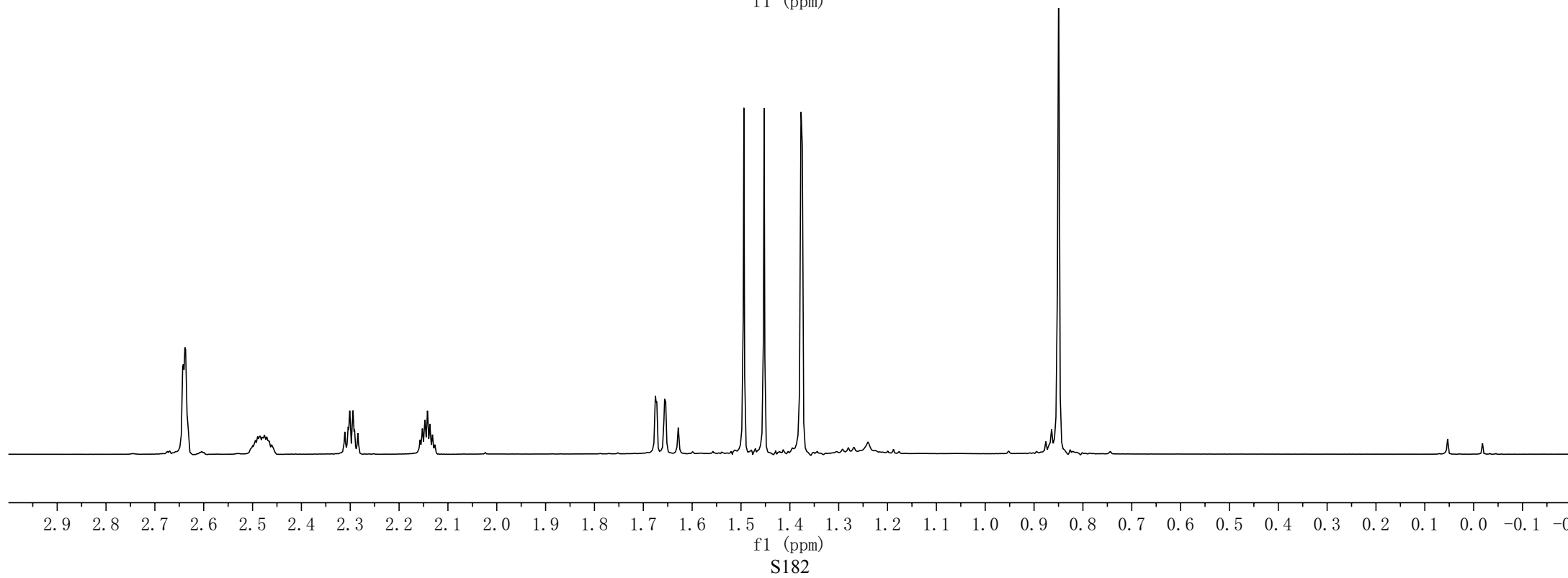
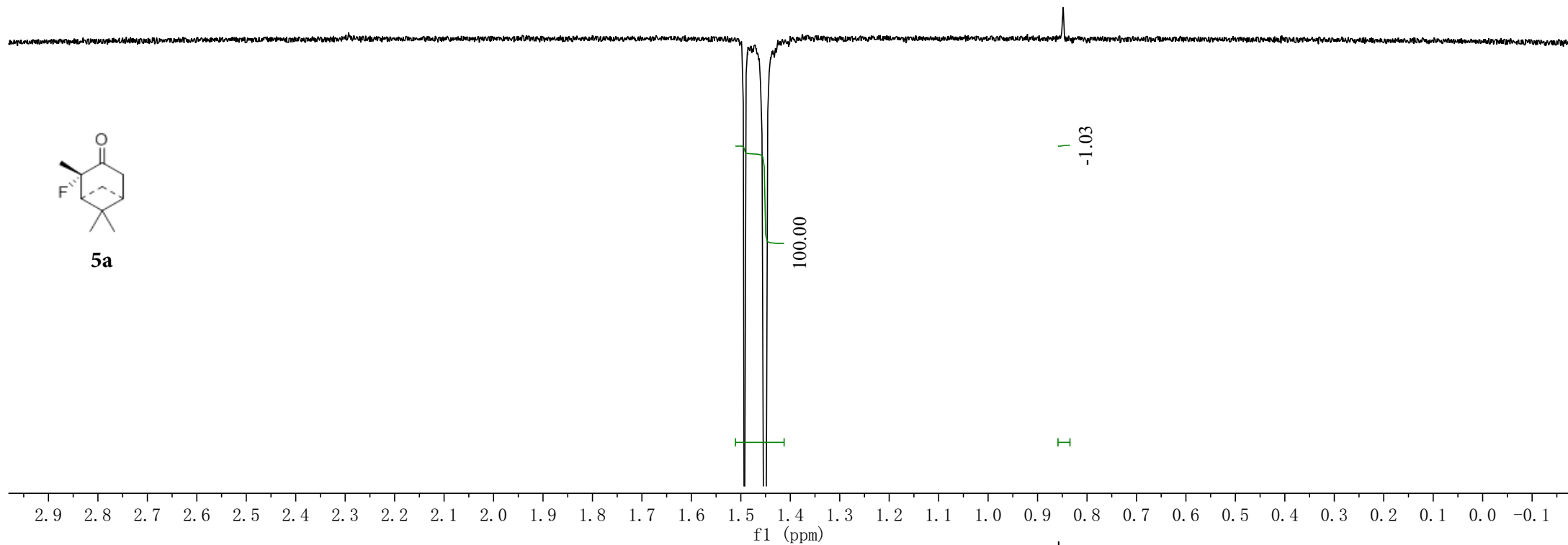
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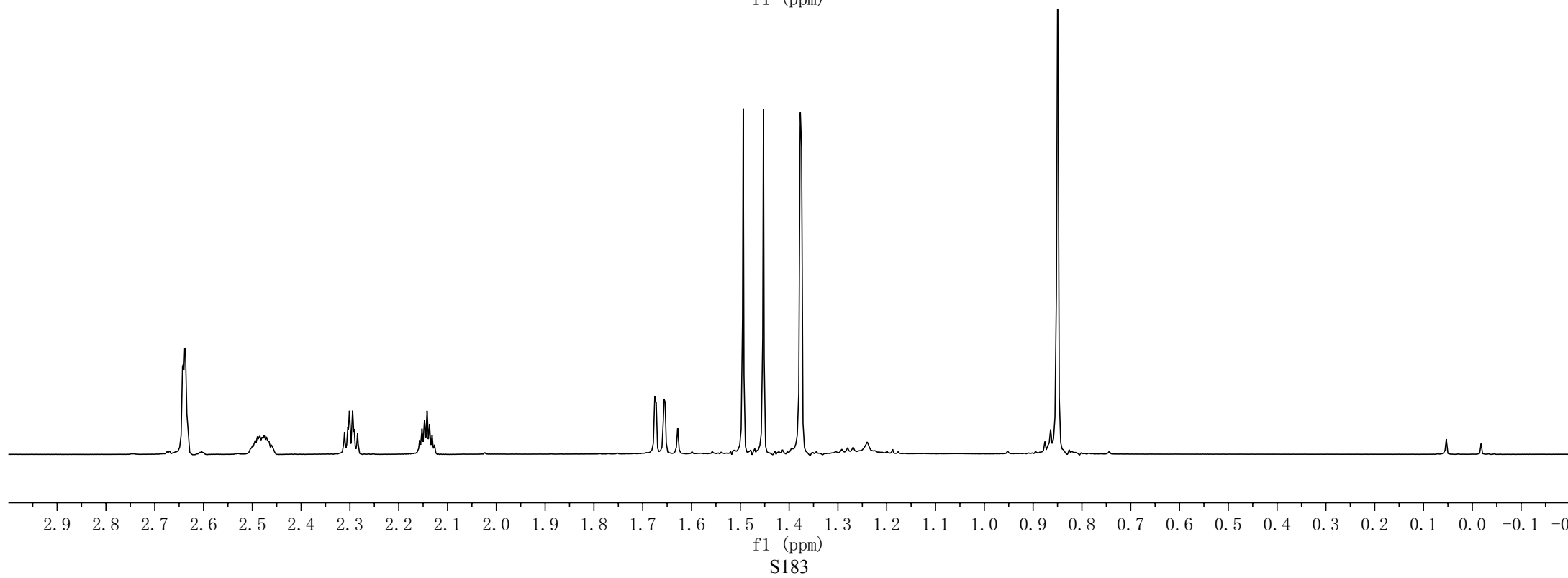
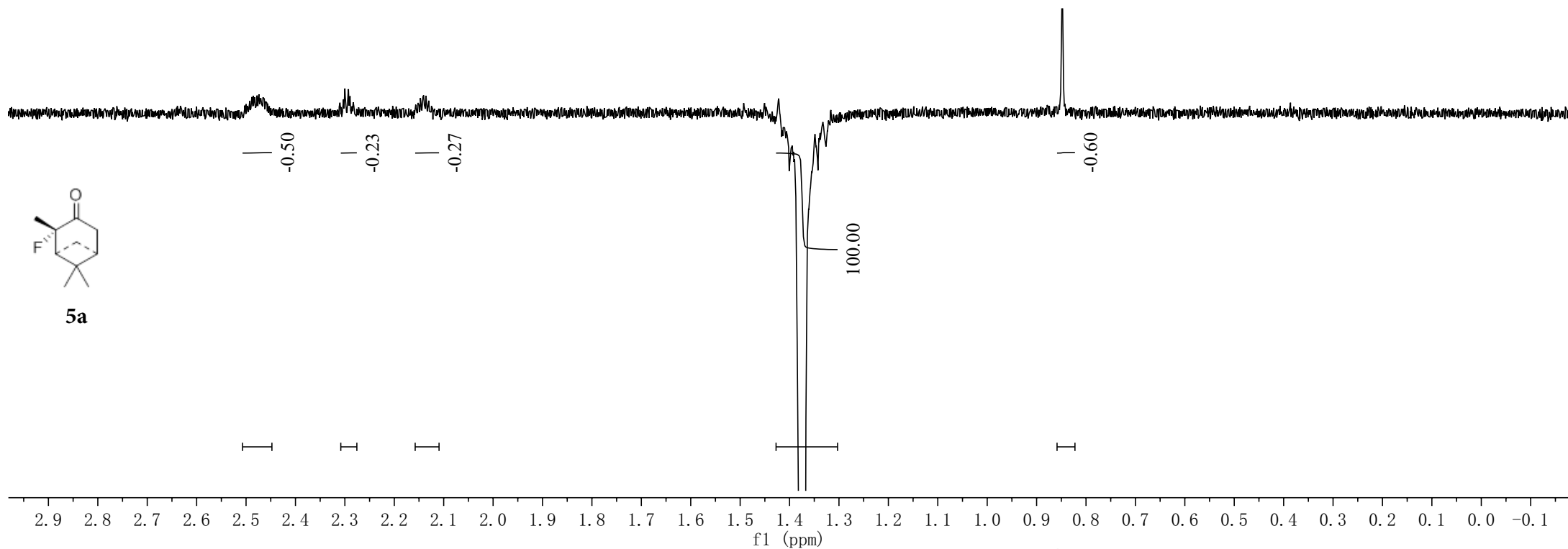


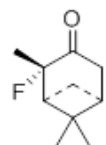




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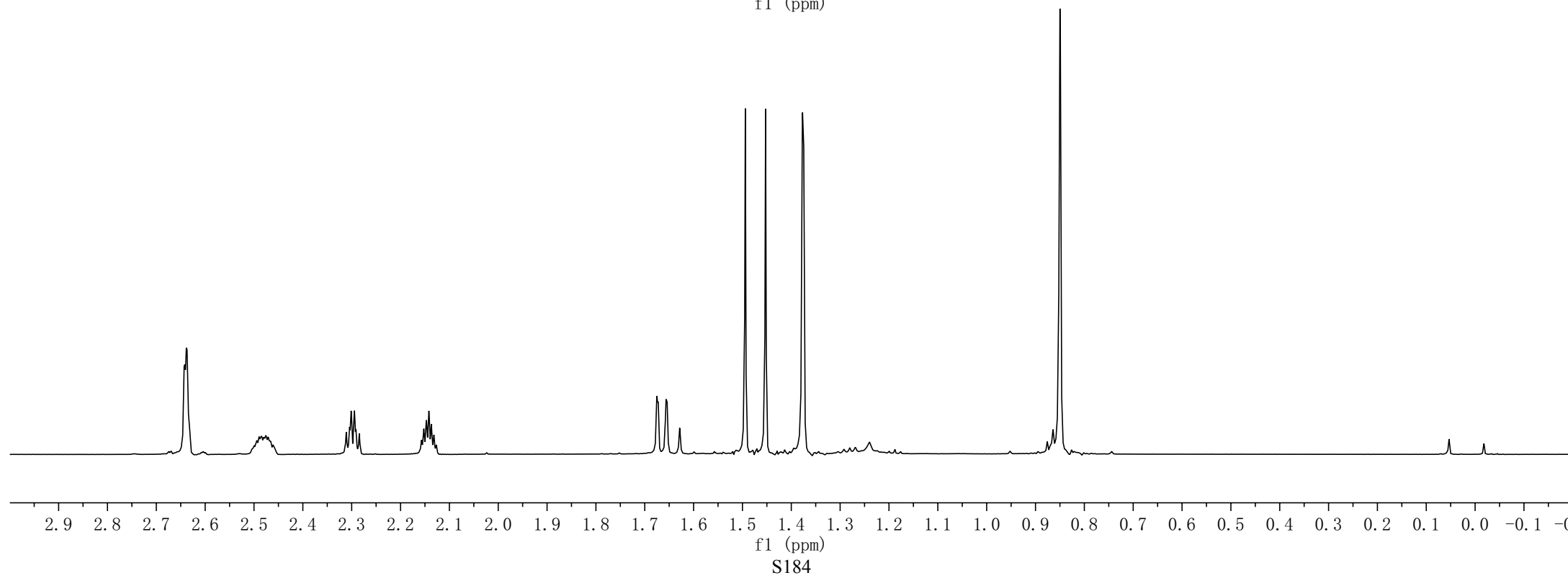
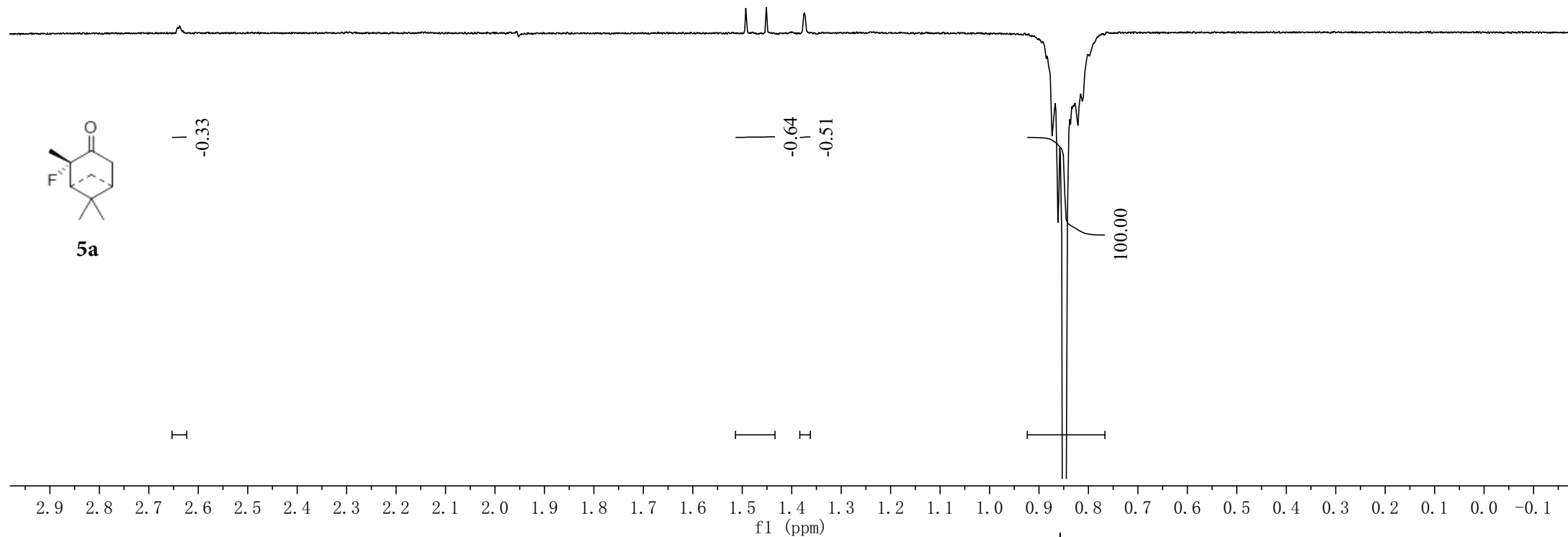


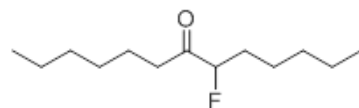
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-0.33

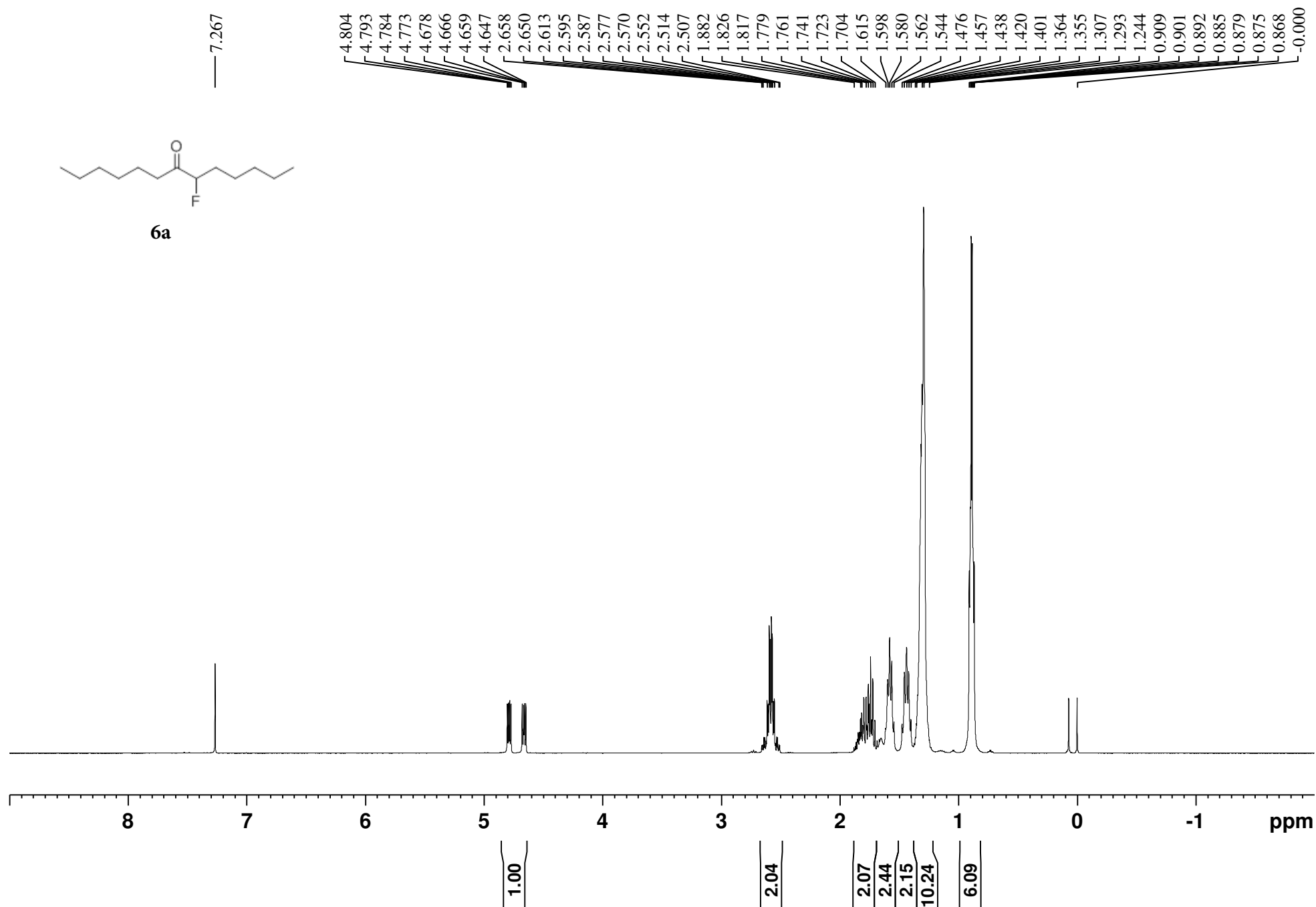
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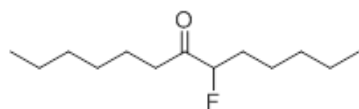
100.00





**6a**





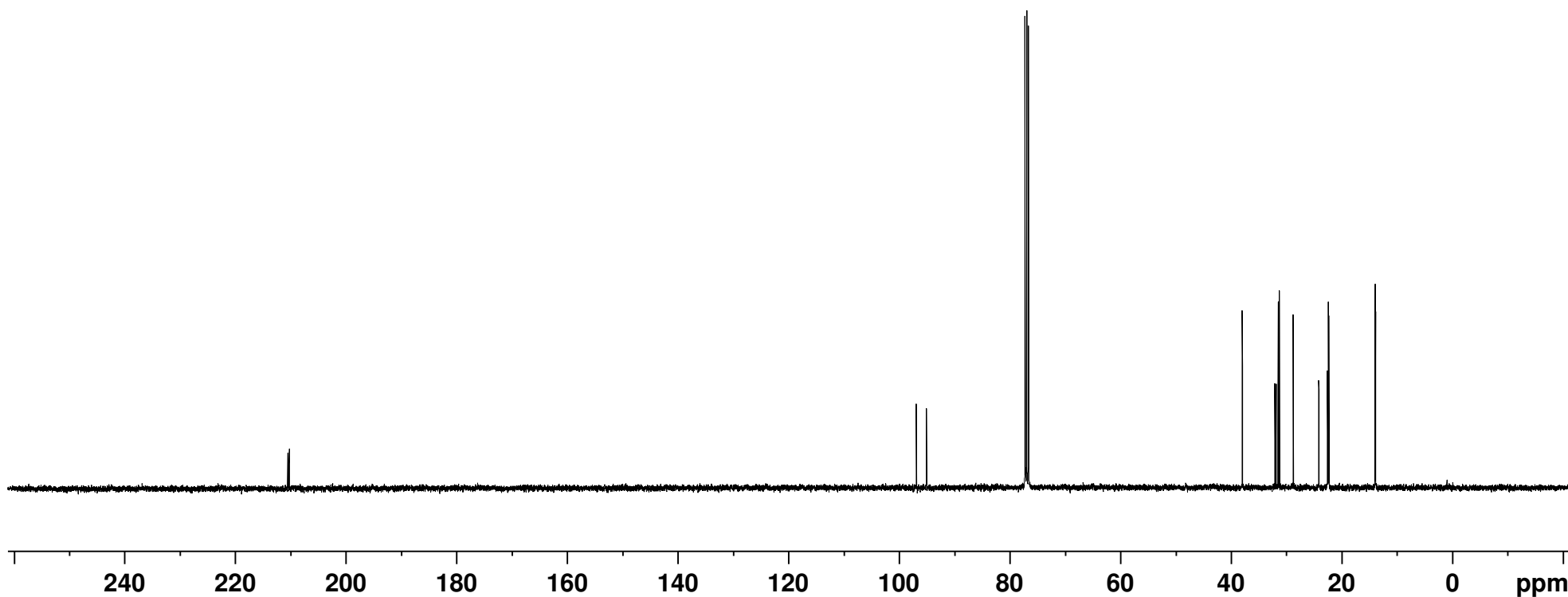
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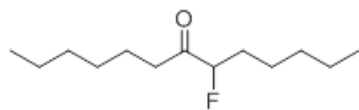
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210.35

96.97  
95.14

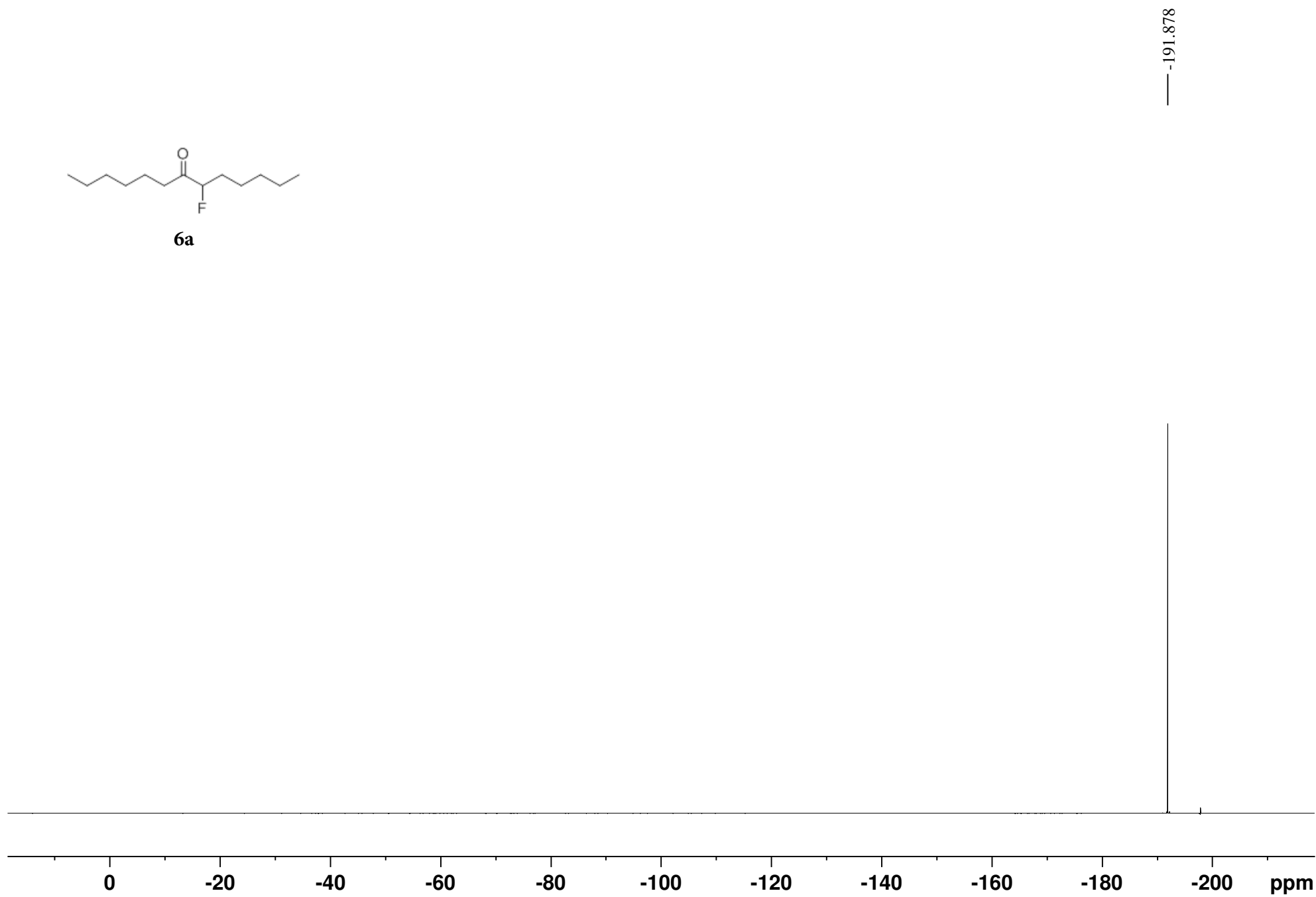
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77.00  
76.68

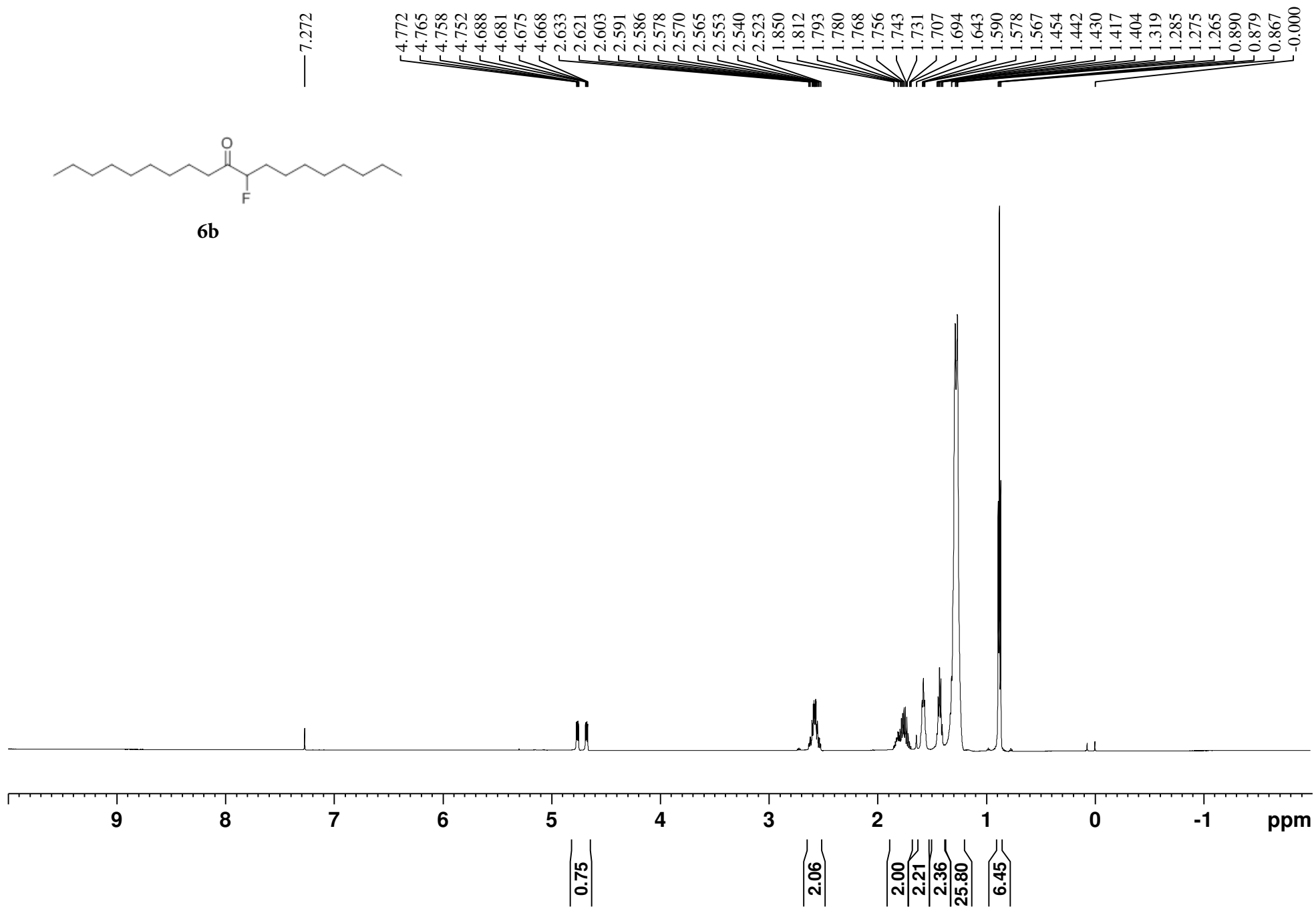
38.01  
32.11  
31.90  
31.55  
31.32  
28.81  
24.20  
24.17  
22.63  
22.61  
22.46  
22.36  
13.99  
13.90

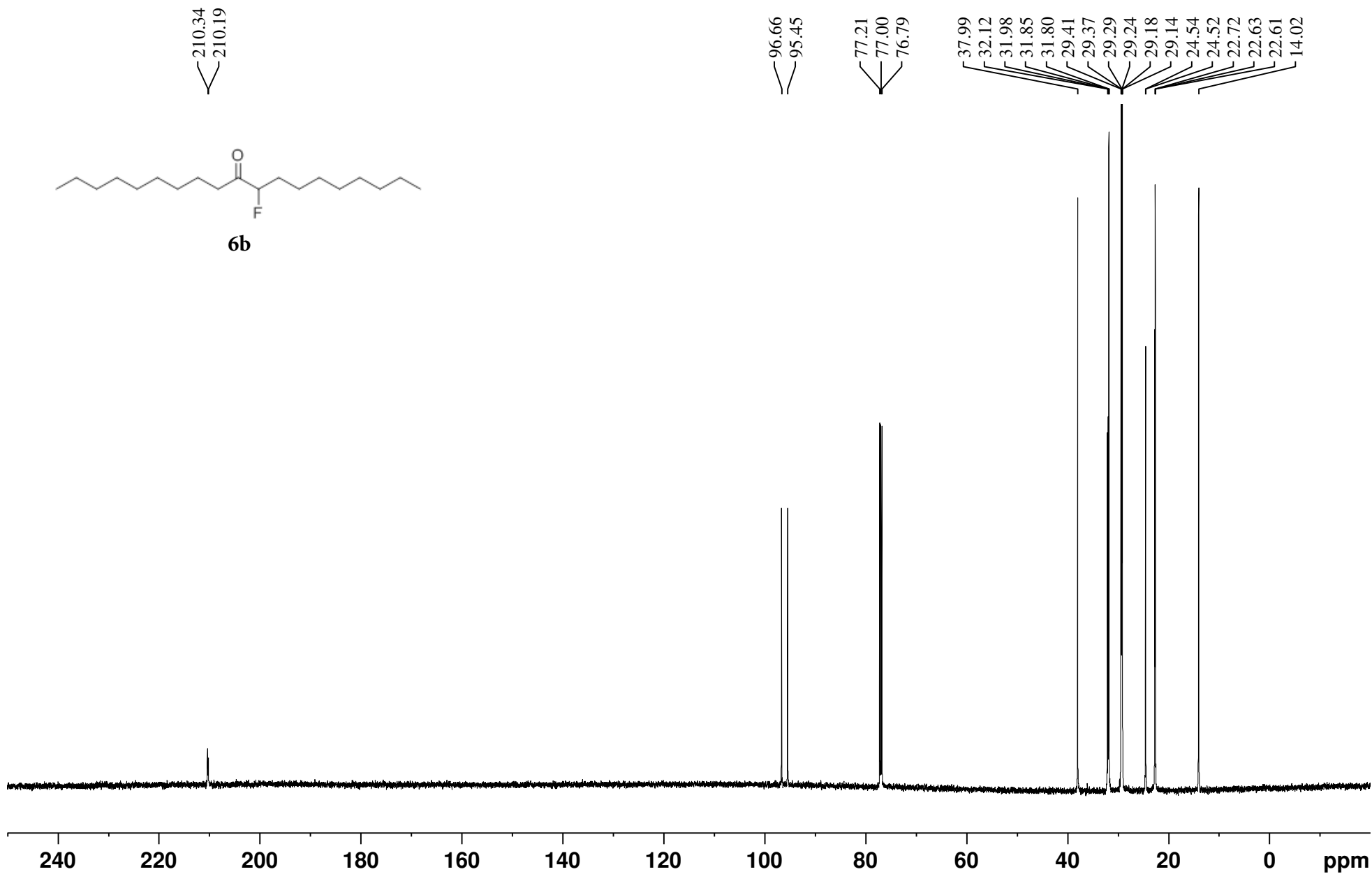
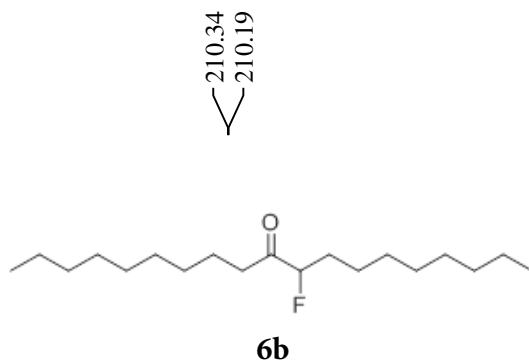


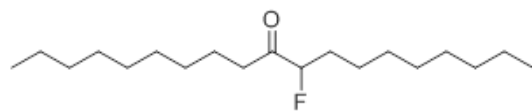


**6a**



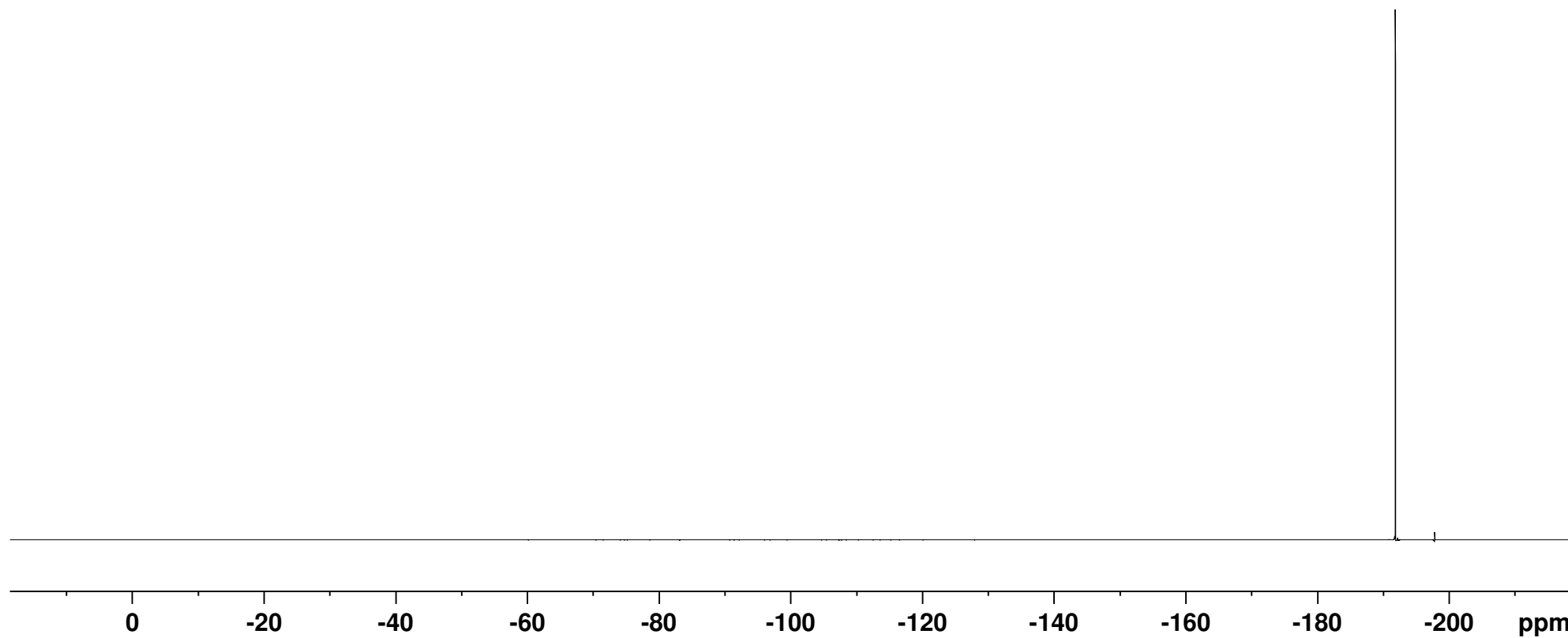


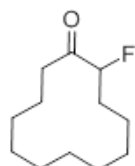




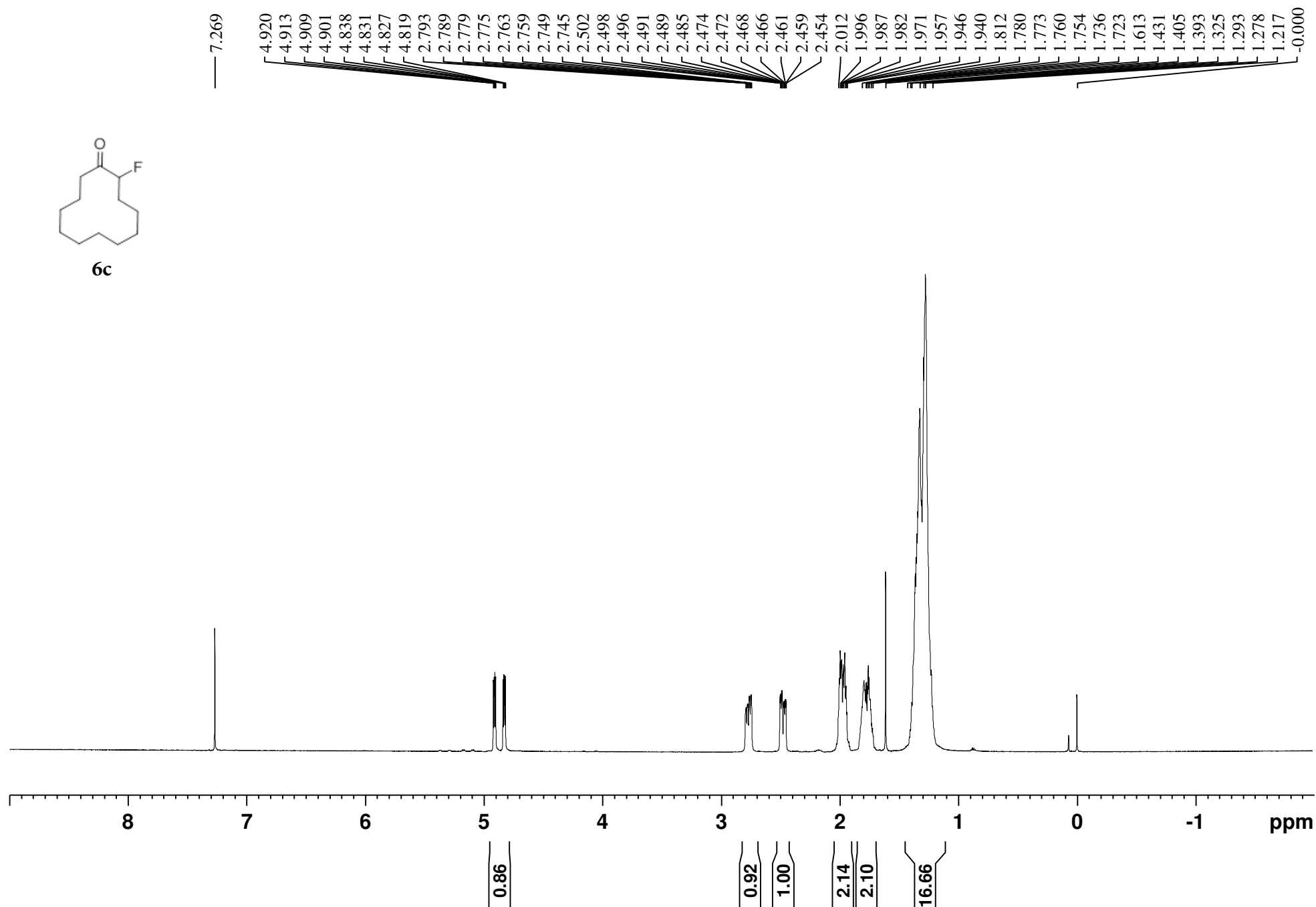
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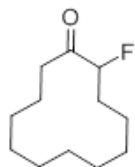
— -191.856





6c





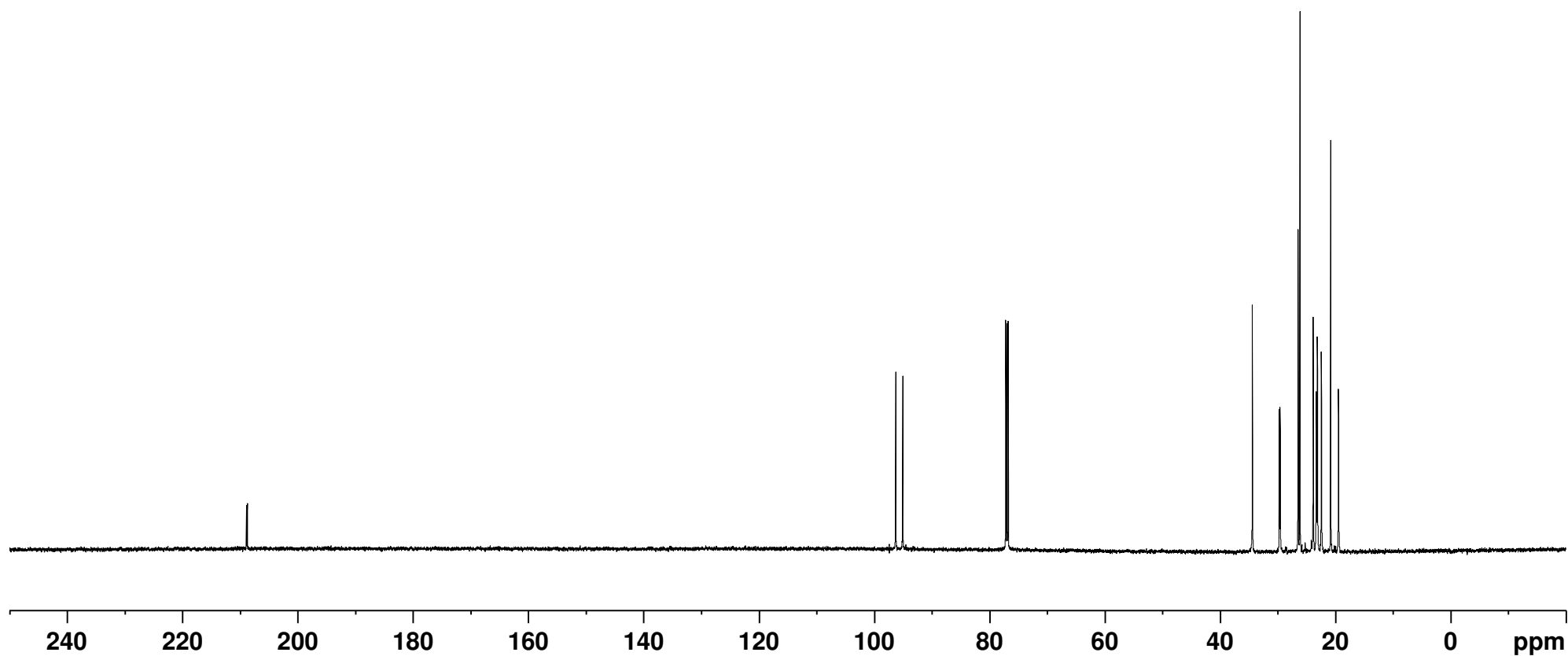
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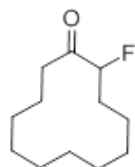
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208.81

96.30  
95.08

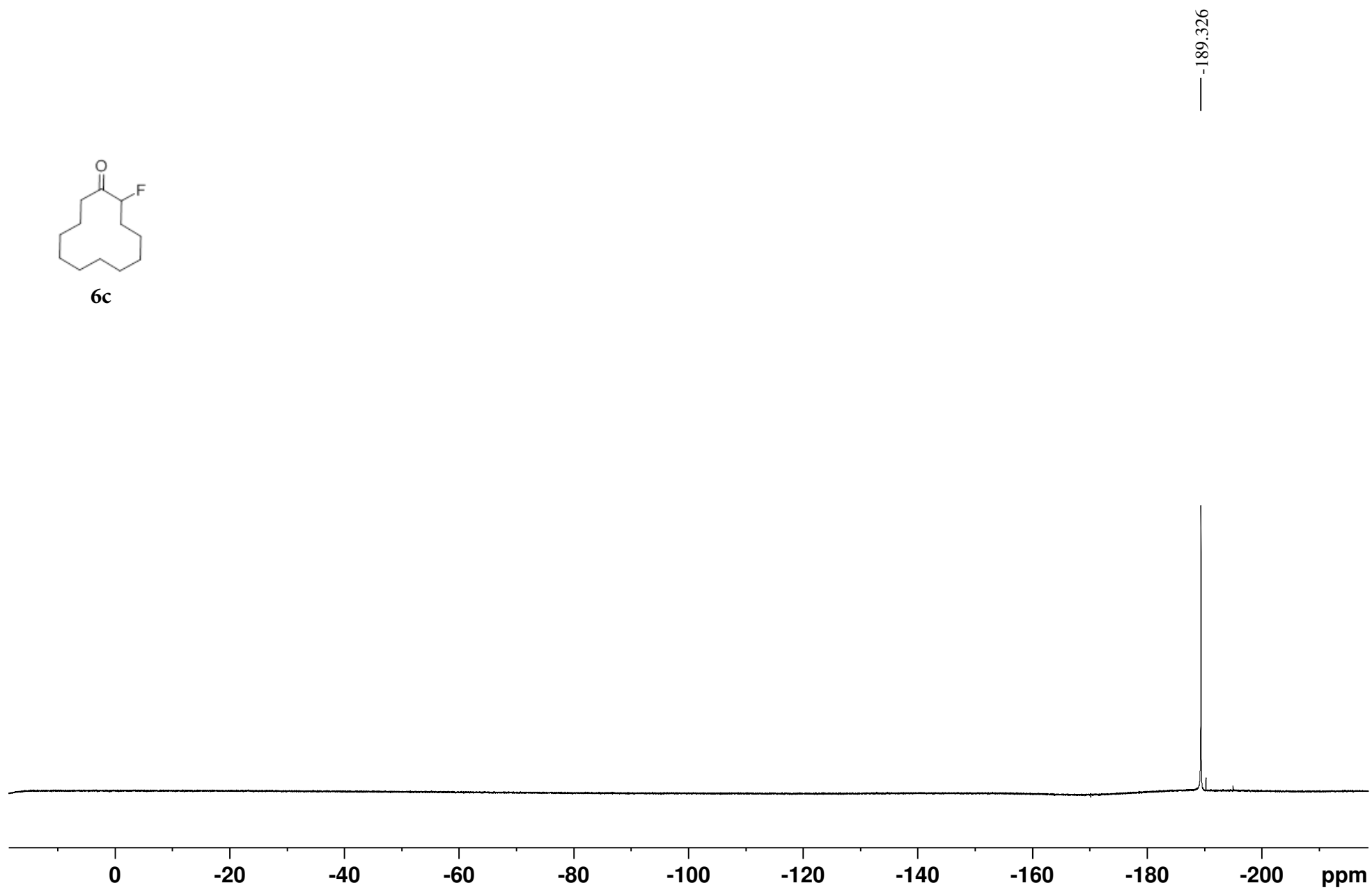
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77.00  
76.78

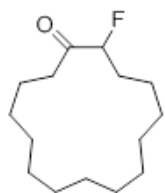
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29.61  
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26.17  
23.89  
23.36  
23.14  
22.47  
20.83  
19.48



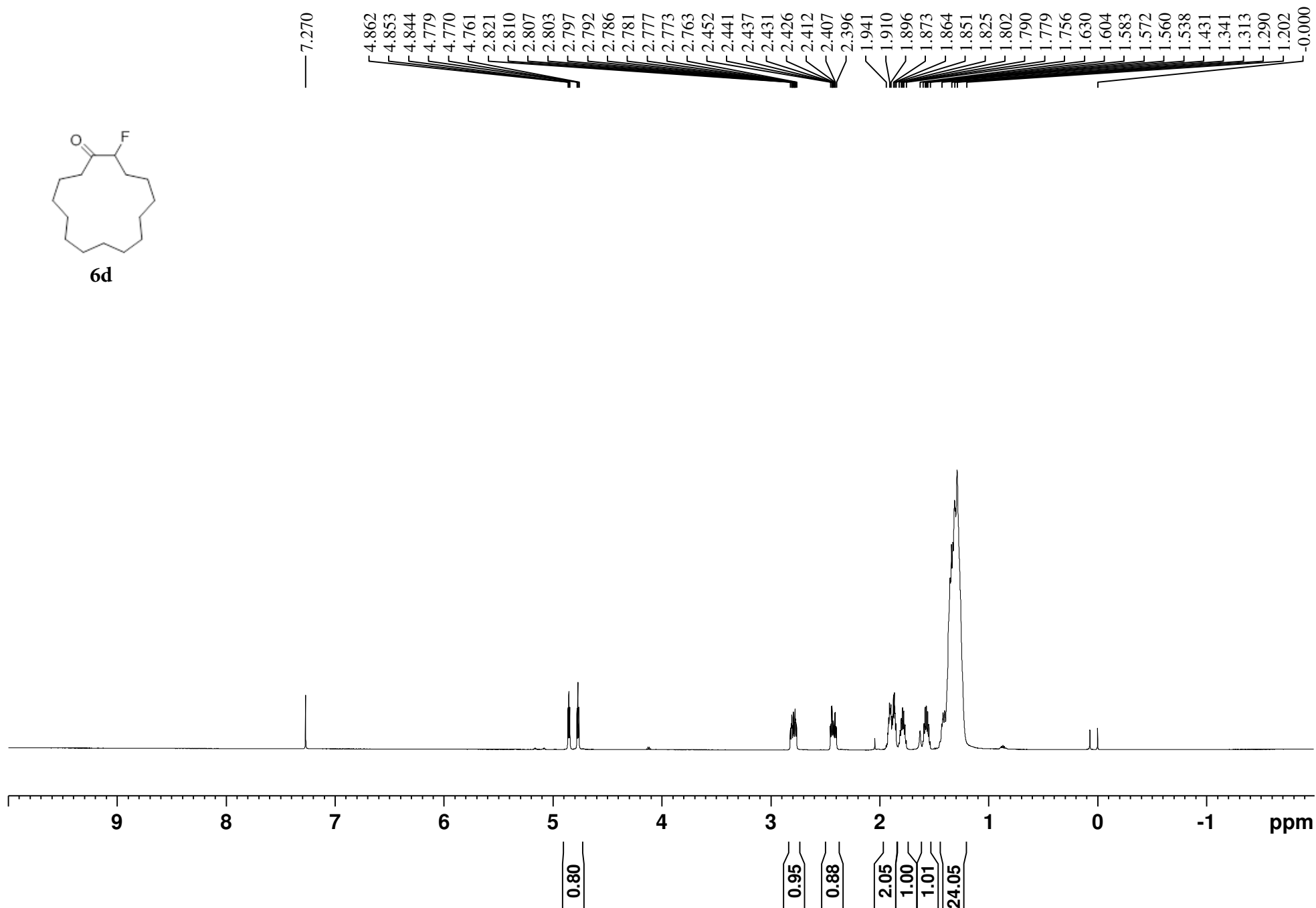


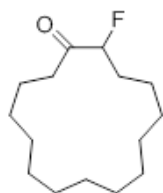
**6c**





6d





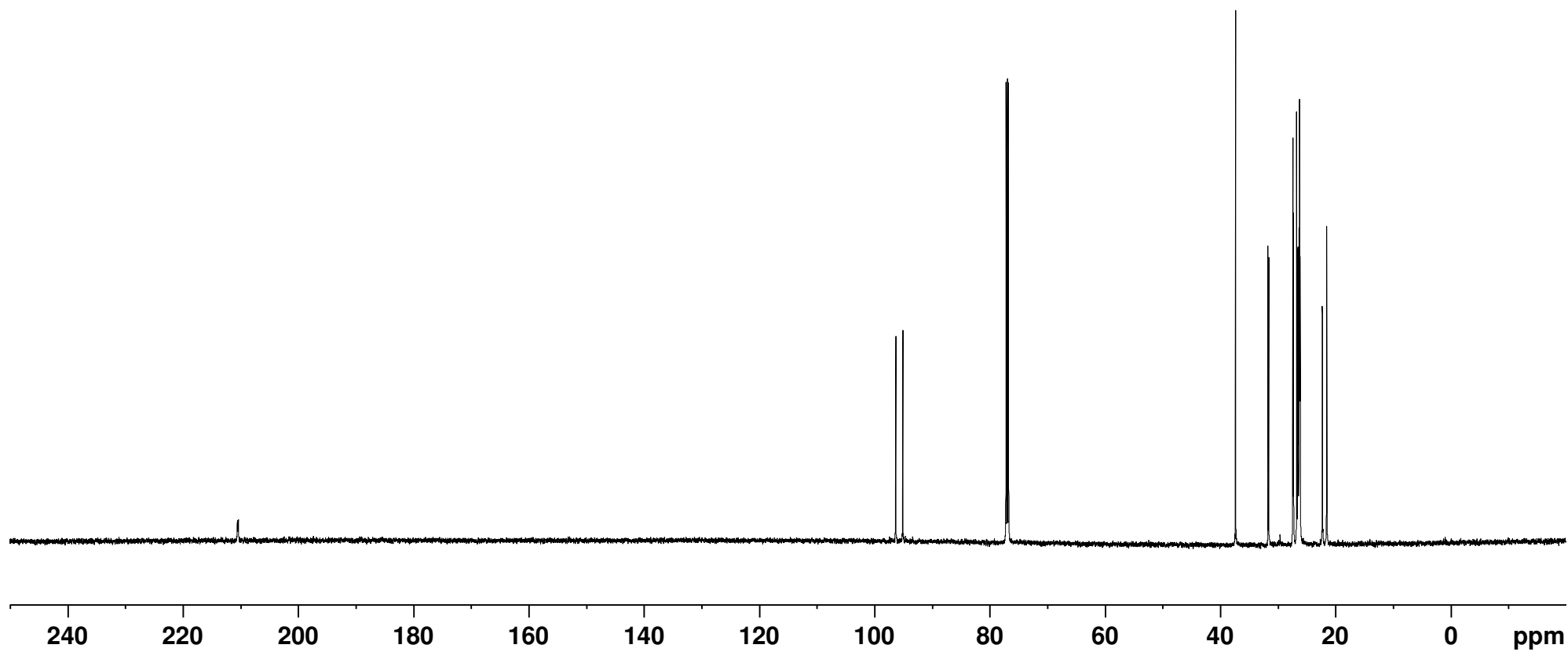
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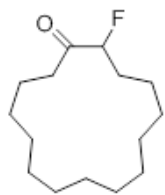
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210.42

96.35  
95.13

77.21  
77.00  
76.79

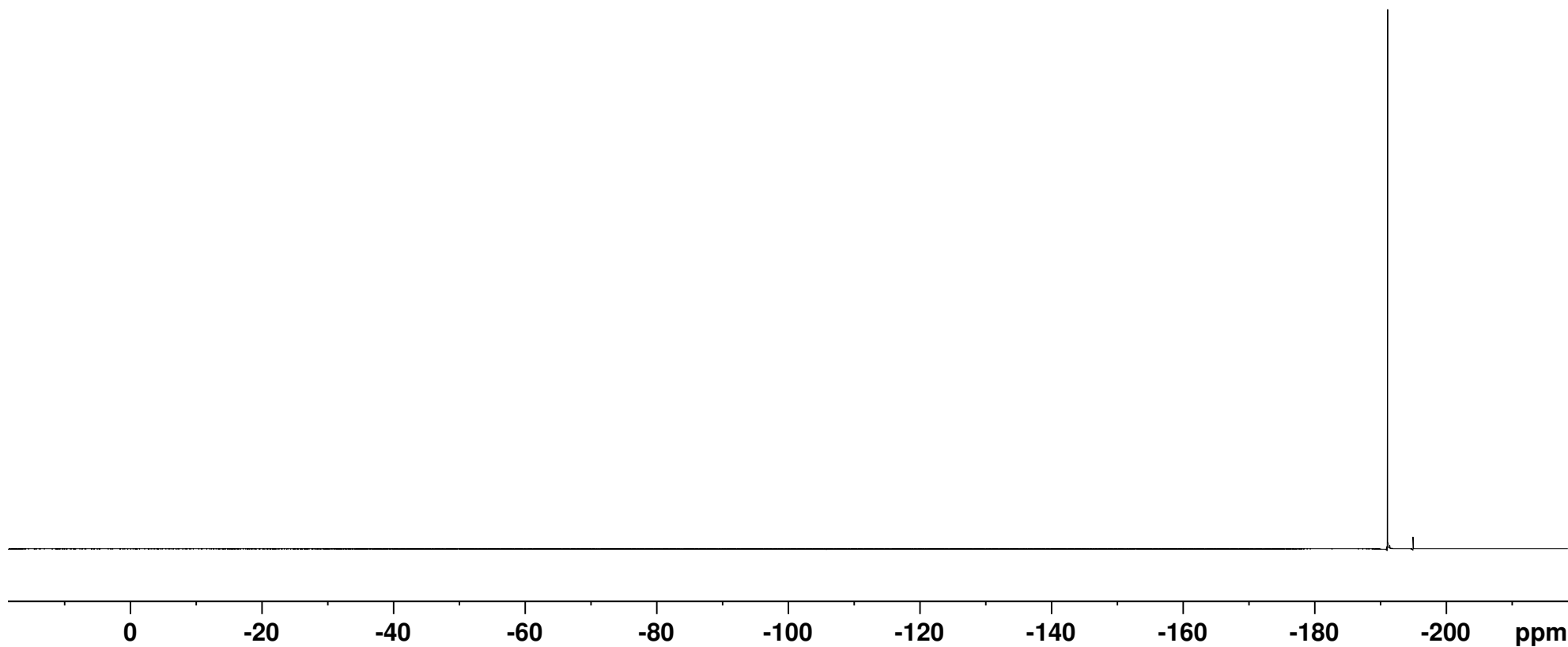
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31.62  
27.44  
27.34  
26.79  
26.61  
26.53  
26.38  
26.30  
26.27  
26.20  
22.34  
22.31  
21.57

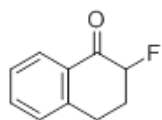




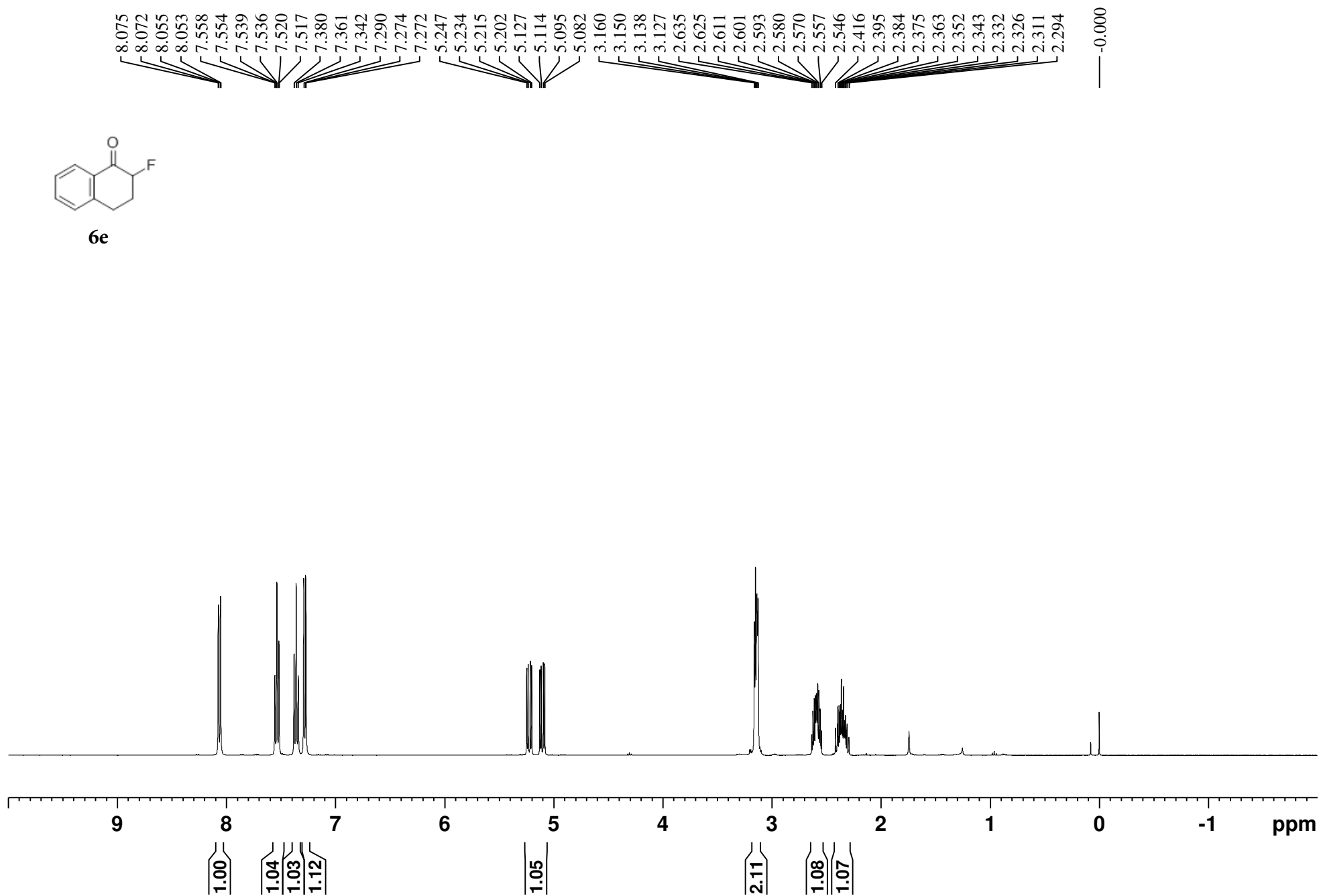
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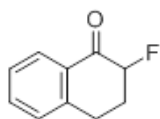
— -191.123



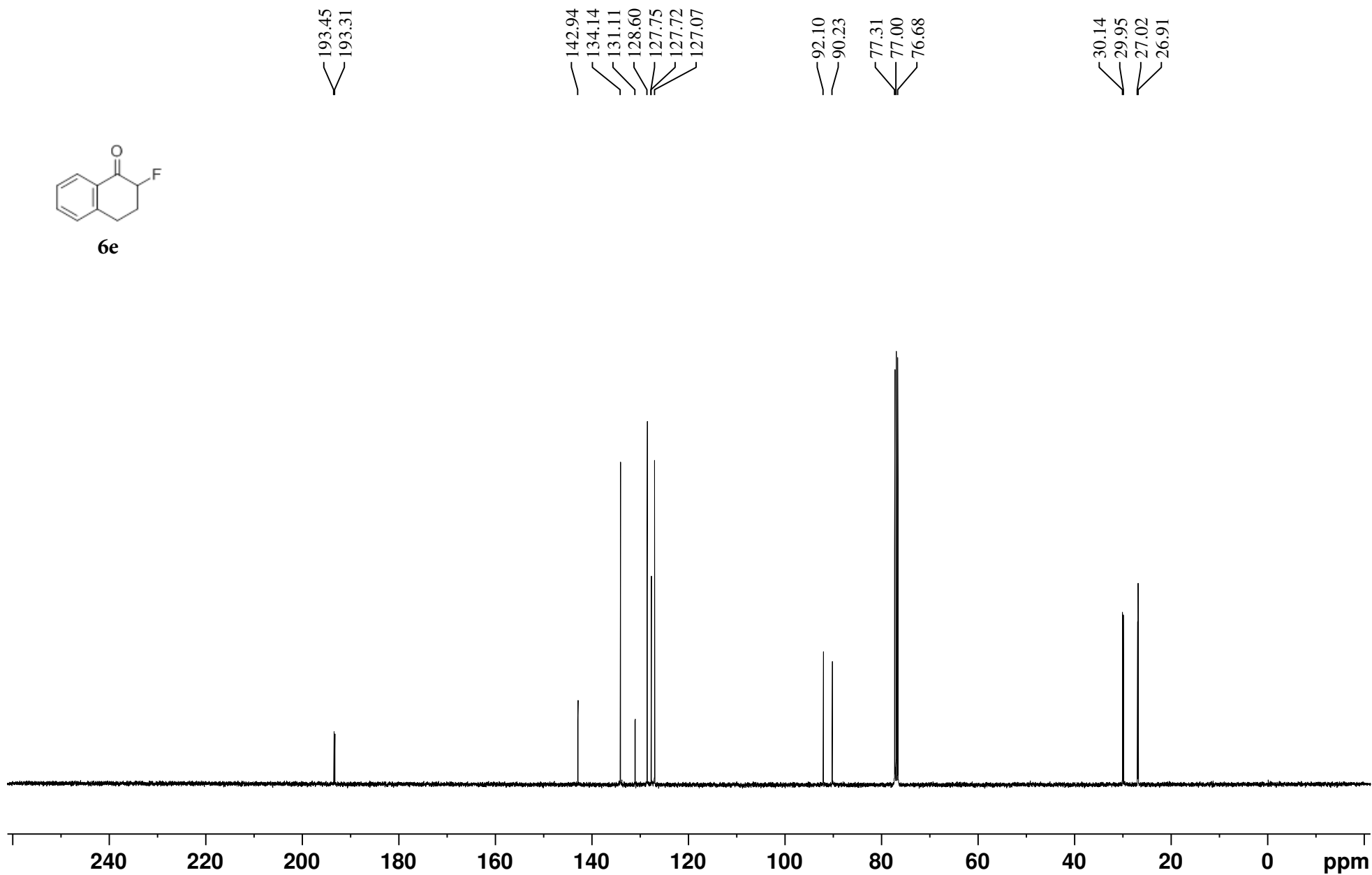


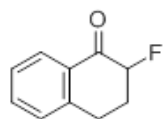
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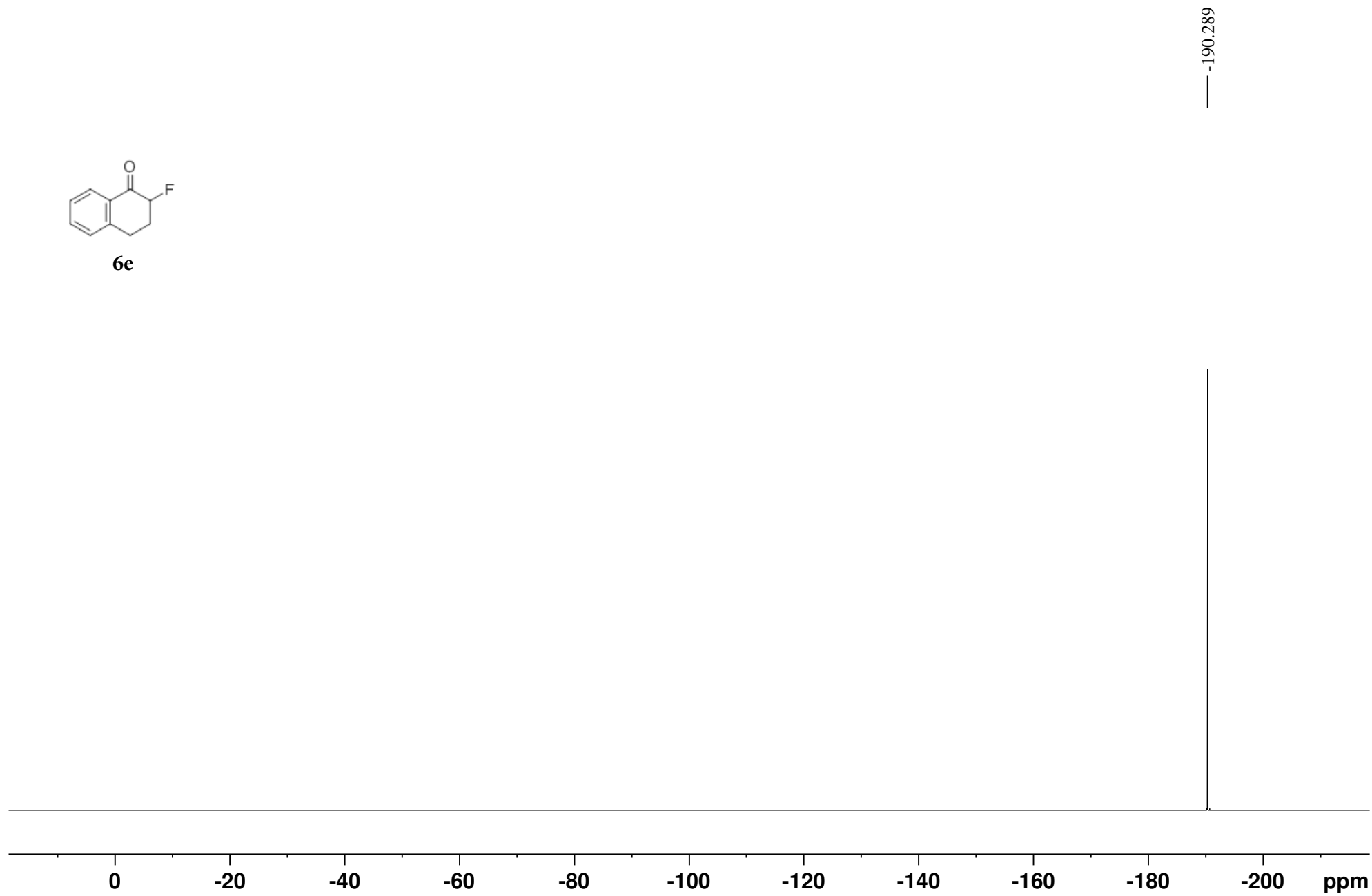


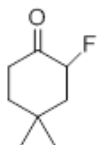
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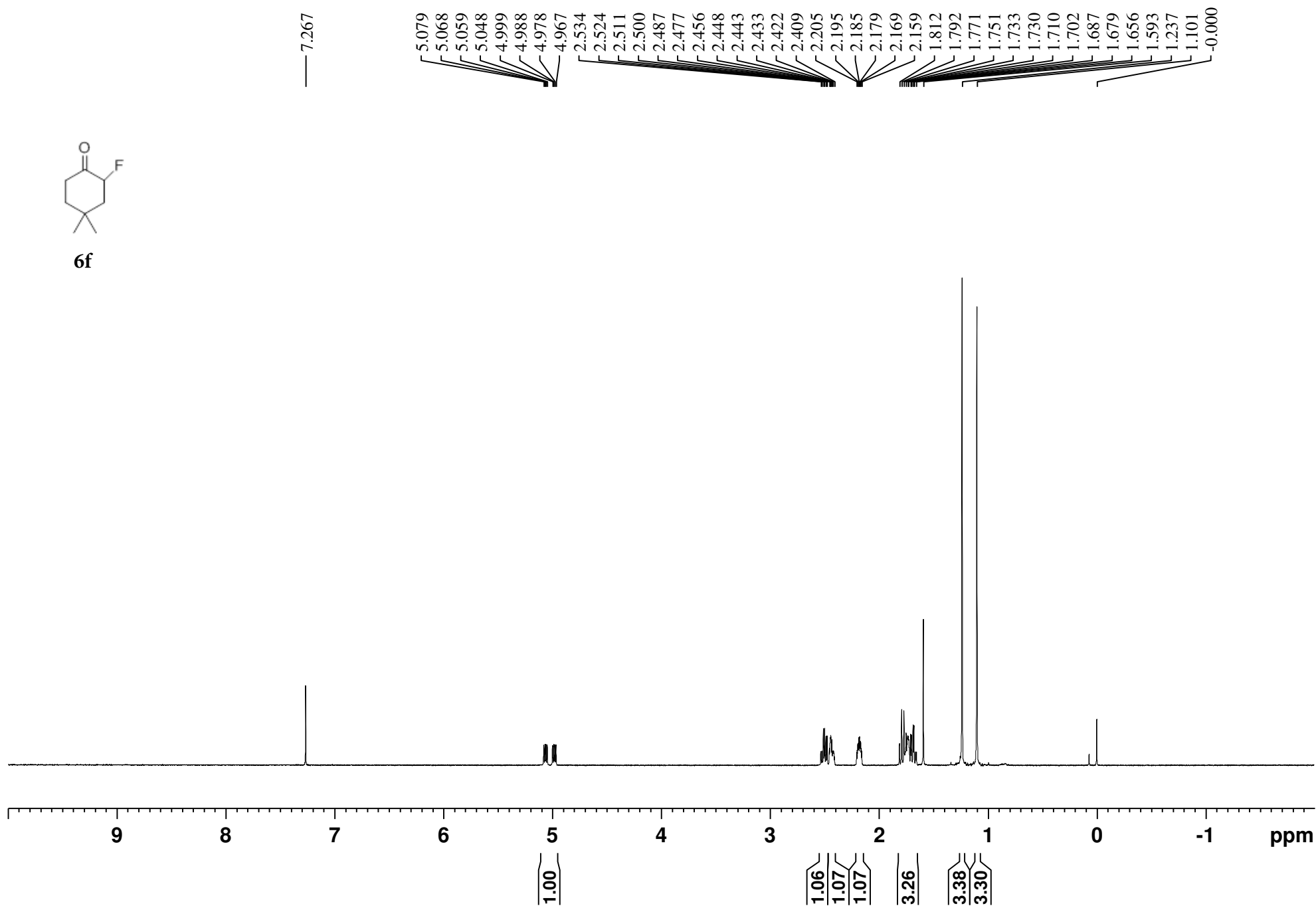


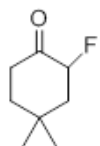
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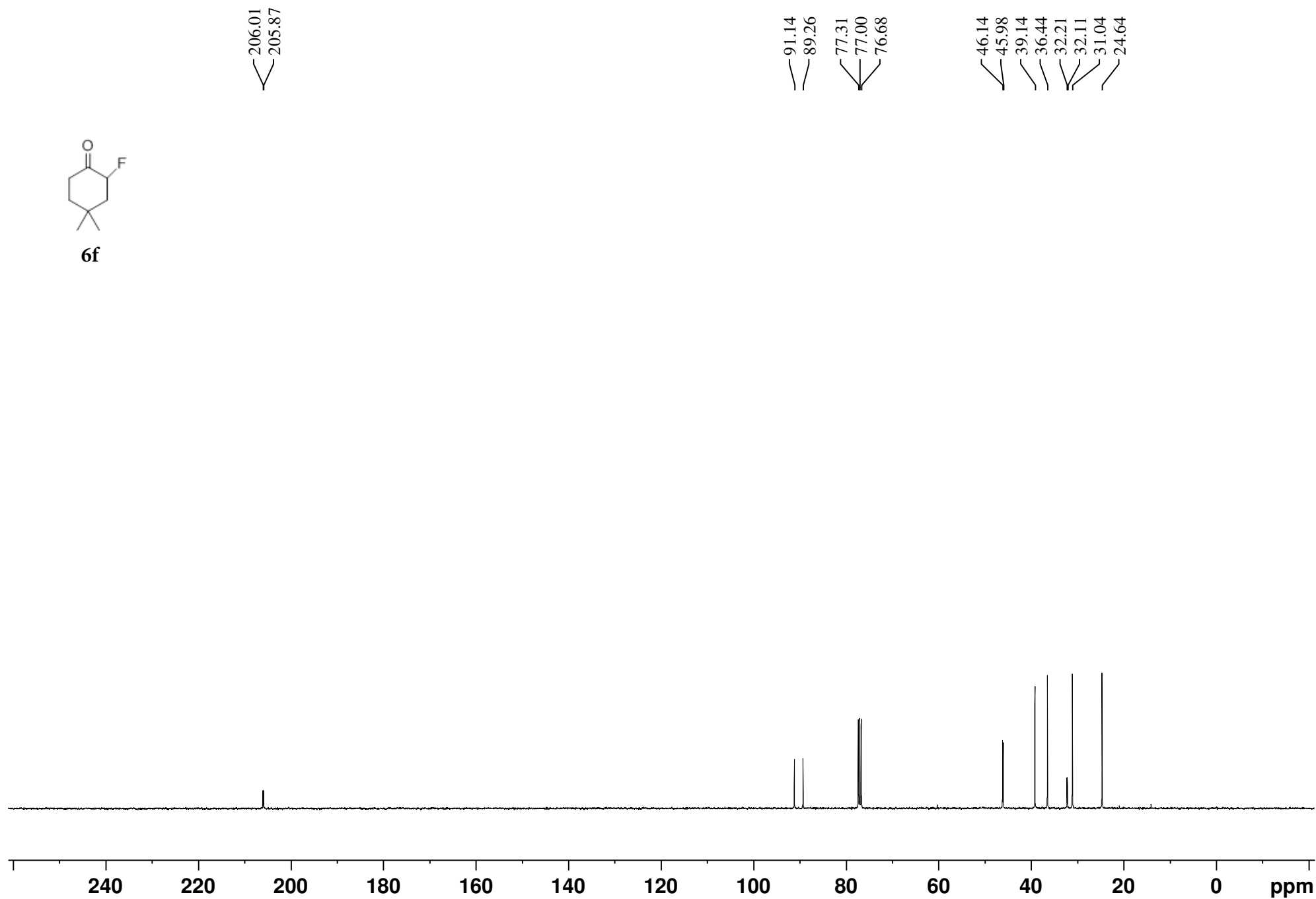


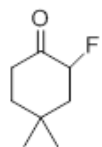
6f





**6f**





**6f**

— -193,496

