

## Supporting Information for

# Pd-Diimine: A Highly Selective Catalyst System for the Base-free Oxidative Heck Reaction.

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## Contents

No.	Entry	Page No.
1.	General	S2
2.	Synthesis of Bis(aryl)acenaphthequinonediimine (BIAN) ( <b>3</b> )	S3
3.	Synthesis of <b>7a</b> , <b>7b</b> , <b>8a</b> , <b>8b</b>	S4
4.	General procedure oxidative Heck reaction	S5
5.	Time Profile of Reaction with <b>7a</b> , <b>7b</b> , <b>8a</b> , <b>8b</b>	S6
6.	Preparation of 3-phenylcyclohex-2-enone ( <b>6</b> )	S7
7.	Preparation of 3-p-tolylcyclohex-2-enone ( <b>9a</b> )	S7
8.	3-(4-fluorophenyl)cyclohex-2-enone ( <b>9b</b> )	S8
9.	Preparation of 3-(4-(trifluoromethyl)phenyl)cyclohex-2-enone ( <b>9c</b> )	S9
10.	Preparation of 4'-nitro-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one ( <b>9d</b> )	S9
11.	Preparation of 3-(4-chlorophenyl)cyclohex-2-enone ( <b>9e</b> )	S10
12.	Preparation of 3-m-tolylcyclohex-2-enone ( <b>9f</b> )	S11
13.	Preparation of 3-(3-fluorophenyl)cyclohex-2-enone ( <b>9g</b> )	S11
14.	Preparation of 3-(3-methoxyphenyl)cyclohex-2-enone ( <b>9h</b> )	S12
15.	Preparation of 3-(3-nitrophenyl)cyclohex-2-enone ( <b>9i</b> )	S13
16.	Preparation of 3-(3-chlorophenyl)cyclohex-2-enone ( <b>9j</b> )	S13
17.	Preparation of 2'-methyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one ( <b>9k</b> )	S14
18.	Preparation of 3-(2-fluorophenyl)cyclohex-2-enone ( <b>9l</b> )	S15
19.	Preparation of 3-(2-methoxyphenyl)cyclohex-2-enone ( <b>9m</b> )	S15
20.	Preparation of 2',6'-dimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one ( <b>9n</b> )	S16
21.	Preparation of butyl cinnamate ( <b>10a</b> )	S17
22.	Preparation of <i>tert</i> -butyl cinnamate ( <b>10b</b> )	S17
23.	Preparation of (E)-4-phenylbut-3-en-2-one ( <b>10c</b> )	S18
24.	Preparation of <i>tert</i> -butyl 4-oxo-6-phenyl-3,4-dihydropyridine-1(2H)-carboxylate ( <b>10d</b> )	S18
25.	Preparation of 3,3-diphenylacrylaldehyde ( <b>10e</b> )	S19
26.	NMR Spectra	S20-65
27.	References	S67

## General

All reactions were performed under an atmosphere of oxygen unless specified, in oven-dried glassware, using standard Schlenk techniques. The oxygen atmosphere was maintained by connecting the Schlenk tubes to an oxygen filled balloon and flushing with oxygen before capping.

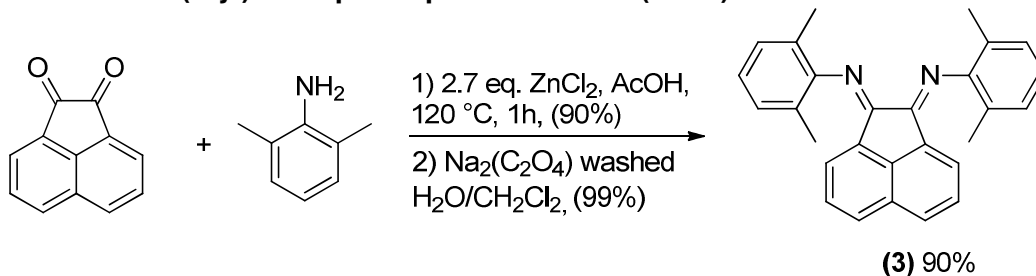
All the chemicals, except BIAN (see synthesis below) were sourced from commercial sources, and were used without further purification. 2,9-dimethyl-1,10-phenanthroline (dmphen) was recrystallized before use. Methanol was distilled prior to use and mixed in 9:1 (v/v) ratio with water.

## Analysis

TLC was performed using pre-coated silica gel plates (0.25 mm thick, 60 F254). The compounds were visualized under UV light (254 nm) or by staining with Seebach Stain (25 g phosphomolybdic acid, 7.5 g cerium (IV) sulfate, 500 ml H<sub>2</sub>O, 25 ml H<sub>2</sub>SO<sub>4</sub>) or a KMnO<sub>4</sub> dip.

Gas Chromatography (GC) analyses were performed, with dodecane as internal standard, and conversions were calculated from multi-point calibration curves.

### Synthesis of Bis(aryl)acenaphthequinonediimine (BIAN)<sup>1</sup>



The reaction was done under an atmosphere of nitrogen. To a 100 ml, oven-dried, double-necked, round-bottom flask containing a magnetic stirring bar was added acenaphthoquinone **1** (500 mg, 2.74 mmol, 1.0 eq.) and dry zinc chloride (1000 mg, 7.34 mmol, 2.7 eq.). These compounds were suspended in glacial acetic acid (20 ml) turning the reaction yellow. After 5 minutes of stirring at 60 °C, 2,6-dimethylaniline **2** (0.75 ml, 6.30 mmol, 2.3 eq.) was added and the mixture was stirred at reflux for 1 hour. During this time the reaction changed from yellow to red and back again. The mixture was then vacuum filtered while still hot and the residue was washed with ether (2 x 10 ml) to provide the zinc chloride complex (1300 mg, 2.47 mmol, 90%) as a yellow solid. The zinc chloride complex was suspended in CH<sub>2</sub>Cl<sub>2</sub> (40 ml) in a 100 ml separatory funnel. A solution of sodium oxalate (453 mg, 3.38 mmol, 1.25 eq.) in water (20 ml) was added. After washing for 5 minutes a white precipitate was formed in the water layer. The layers were separated and the organic layer was washed with water (2 x 10 ml), dried over MgSO<sub>4</sub> and concentrated *in vacuo*. The obtained red oil was further dried under reduced pressure. The desired product **3** (0.95 g, 2.44 mmol, 99%) was obtained as a red foamy solid in an overall yield: 90%

**<sup>1</sup>H-NMR:** (400 MHz, CDCl<sub>3</sub>) δ  
7.90 (d, *J* = 8.3 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.21 – 6.96 (m, 6H),  
6.72 (d, *J* = 7.2 Hz, 2H), 2.14 (s, 12H).

**<sup>13</sup>C-NMR:** (101 MHz, CDCl<sub>3</sub>) δ  
161.2, 149.5, 140.9, 131.3, 129.8, 129.3, 128.5, 128.6, 125.0, 124.0,  
122.8, 18.1.

**HRMS:** Calculated for [M+H]<sup>+</sup> : 389.1939  
Found [M+H]<sup>+</sup> : 389.1996

**TLC:** R<sub>f</sub> 0.5 (5:1 pentane/ether)



## General procedure oxidative Heck reaction

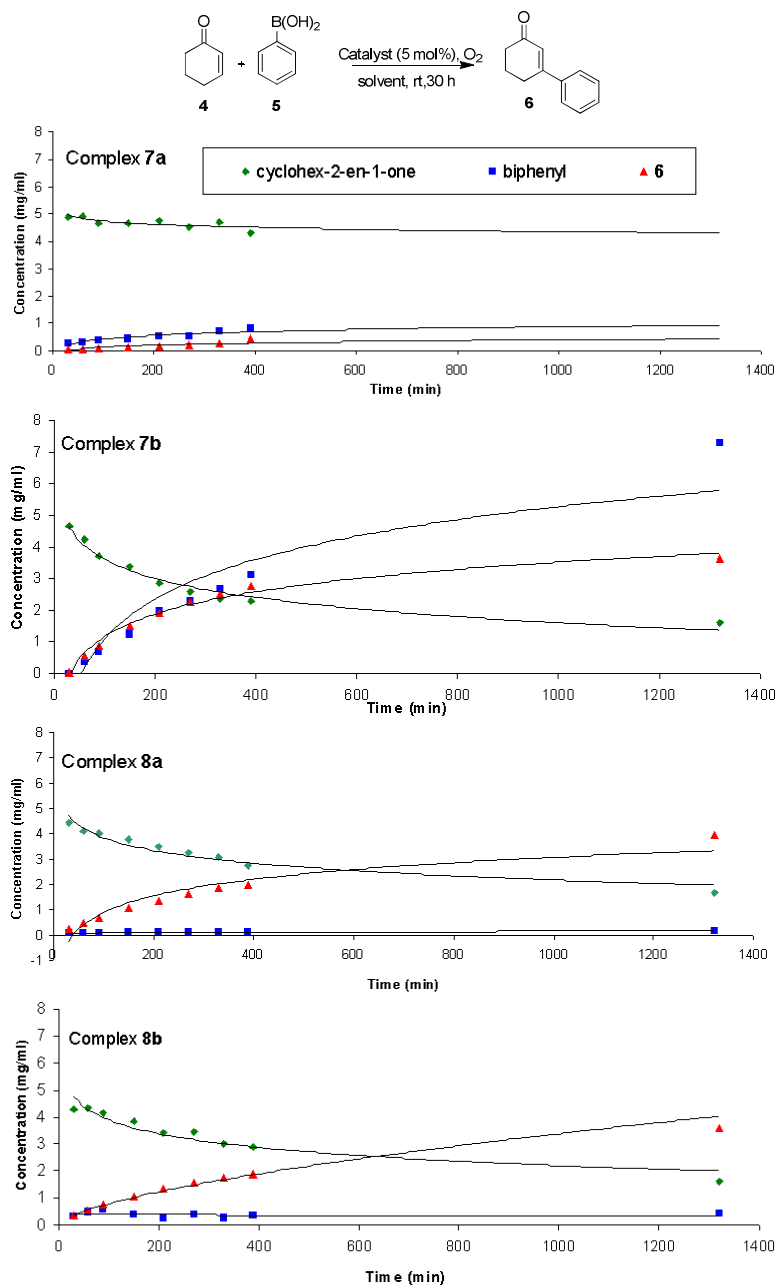
### General procedure A

To a Schlenk tube equipped with a magnetic stirring bar and a septum was added palladium acetate (11 mg, 5 mol%, 0.05 equiv), and BIAN (28 mg, 7 mol%, 0.07 equiv). The mixture was dissolved in 2 ml of a solution of MeOH/H<sub>2</sub>O (9:1) and stirred for 30 minutes at 20 °C, followed by the addition of the olefin (1.0 equiv) and the boronic acid (1.5 equiv). The Schlenk tube was equipped with an oxygen balloon on the side arm, and oxygen was flushed through the flask. Upon addition of the oxygen the reaction mixture turned dark red/black. The reaction mixture was allowed to stir at 20 °C. When the reaction was judged complete (by TLC, GC), the reaction was stopped. The reaction mixture was concentrated *in vacuo* and loaded directly on the column, and the desired product was isolated.

### General procedure B

To a Schlenk tube equipped with a magnetic stirring bar and a septum was added palladium acetate (11 mg, 5 mol%, 0.05 equiv), and BIAN (28 mg, 7 mol%, 0.07 equiv). The mixture was dissolved in 2 ml of a solution of MeOH/H<sub>2</sub>O (9:1) and stirred for 30 minutes at 20 °C, followed by the addition of the olefin (1.0 equiv) and the boronic acid (1.5 equiv). The Schlenk tube was equipped with an oxygen balloon on the side arm, and oxygen was flushed through the flask. Upon addition of the oxygen the reaction mixture turned dark red/black. The reaction mixture was allowed to stir at 80 °C. When the reaction was judged complete (by TLC, GC), the reaction was stopped. The reaction mixture was concentrated *in vacuo* and loaded directly on the column, and the desired product was isolated.

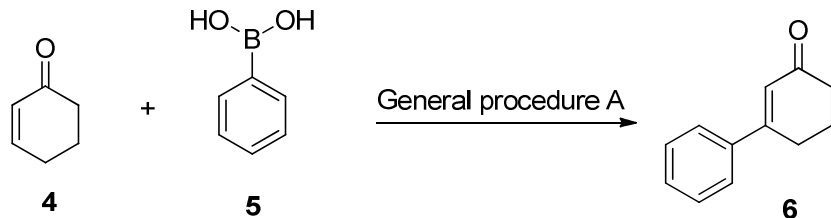
## Time Profile of reaction with complexes 7a, 8a, 8b, 8c



Reaction conditions: Catalyst (5 mol%), 9:1 (v/v) MeOH/H<sub>2</sub>O (3 ml), rt, O<sub>2</sub>.

**FIGURE .** Time-profile of reaction 1 with 7a, 7b, 8a, 8b.

## Preparation of 3-phenylcyclohex-2-enone (**6**)



The title compound was prepared from cyclohexenone **4** (97  $\mu$ l, 1.0 mmol, 1.0 eq.) and phenylboronic acid (183 mg, 1.5 mmol, 1.5 eq.) according to general procedure **A**. The reaction mixture was purified by flash column chromatography (pentane/ether 5:1) to yield 3-phenylcyclohex-2-enone **6** (147 mg, 0.85 mmol, 85%) as a yellow/white solid.

### Data for 3-phenylcyclohex-2-enone

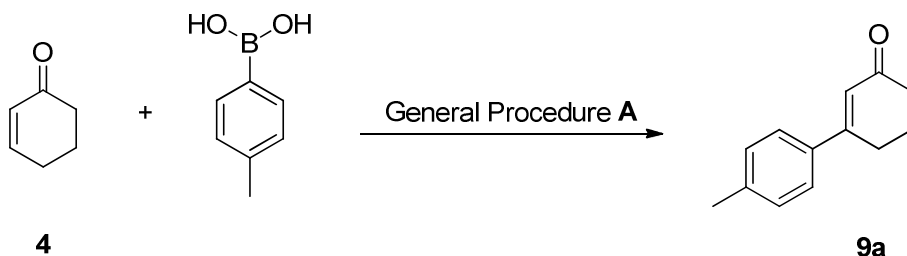
$^1\text{H-NMR}$ : (300 MHz,  $\text{CDCl}_3$ )  $\delta$   
7.54 – 7.34 (m, 5H), 6.38 (s, 1H), 2.73 (t,  $J = 6.0$  Hz, 2H), 2.44 (t,  $J = 6.7$  Hz, 2H), 2.10 (t,  $J = 6.3$  Hz, 2H).

$^{13}\text{C-NMR}$ : (101 MHz,  $\text{CDCl}_3$ )  $\delta$   
199.8, 159.8, 138.8, 130.0, 128.8, 126.1, 125.4, 37.3, 28.1, 22.1.

HRMS: Calculated for  $[\text{M}+\text{H}]^+$  : 173.0961  
Found  $[\text{M}+\text{H}]^+$  : 173.0960

TLC:  $R_f$  0.25 (5:1 pentane/ether)

## Preparation of 3-*p*-tolylcyclohex-2-enone (**9a**)



The title compound was prepared from cyclohexenone **4** (97  $\mu$ l, 1.0 mmol, 1.0 eq.) and *p*-tolylboronic acid (204 mg, 1.5 mmol, 1.5 equiv) according to general procedure **A**. The reaction mixture was purified by flash column chromatography (pentane/ether 5:1) to yield 3-*p*-tolylcyclohex-2-enone **9a** (151 mg, 0.81 mmol, 81%) as a yellow oil.

### Data for 3-*p*-tolyl-cyclohex-2-enone:

$^1\text{H-NMR}$ : (400 MHz,  $\text{CDCl}_3$ )  $\delta$   
7.37 (d,  $J = 8.0$  Hz, 2H), 7.14 (d,  $J = 7.7$  Hz, 2H), 6.35 (s, 1H), 2.68 (t,  $J = 5.8$  Hz, 2H), 2.40 (t,  $J = 6.6$  Hz, 2H), 2.31 (s, 3H), 2.11 – 2.02 (m, 2H).

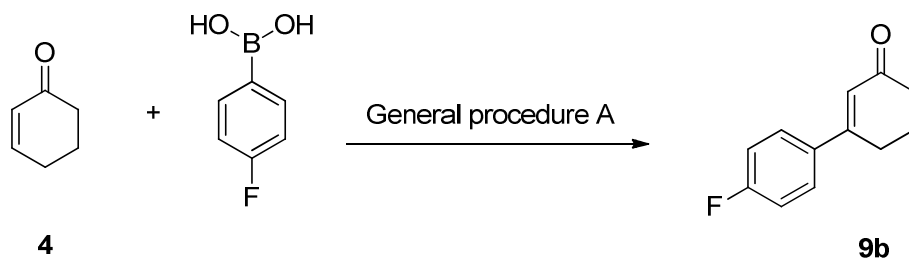
$^{13}\text{C-NMR}$ : (101 MHz,  $\text{CDCl}_3$ )  $\delta$

199.4, 159.3, 140.0, 135.4, 129.2, 125.7, 124.2, 37.0, 27.6, 22.5, 21.0.

MS: Calculated for  $[M+H]^+$  : 187.1117  
Found  $[M+H]^+$  : 187.1116

TLC:  $R_f$  0.25 (5:1 pentane/ether)

### Preparation of 3-(4-fluorophenyl)cyclohex-2-enone (**9b**)



The title compound was prepared from cyclohexenone **4** (97  $\mu$ l, 1.0 mmol, 1.0 eq.) and 4-fluorophenylboronic acid (210 mg, 1.5 mmol, 1.5 eq.) according to general procedure **A**. The reaction mixture was purified by flash column chromatography (pentane/ether 5:1) to yield 3-(4-fluorophenyl)cyclohex-2-enone **9b** (175 mg, 0.91 mmol, 91%) as a off-white solid.

#### Data for 3-(4-fluorophenyl)cyclohex-2-enone

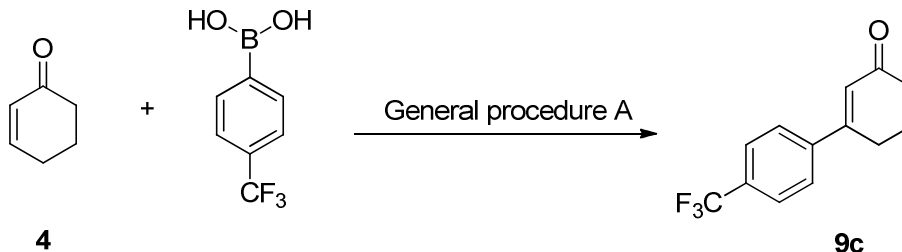
$^1\text{H-NMR}$ : (400 MHz,  $\text{CDCl}_3$ )  $\delta$   
7.49 – 7.42 (m, 2H), 7.06 – 6.99 (m, 2H), 6.30 (s, 1H), 2.68 (t,  $J = 6.6$  Hz, 2H), 2.41 ( $J = 6.73$  Hz, 2H), 2.08 (q,  $J = 6.2$  Hz, 2H).

$^{13}\text{C-NMR}$ : (101 MHz,  $\text{CDCl}_3$ )  $\delta$   
199.5, 163.5 (d,  $J_{\text{C-F}} = 250$  Hz), 158.3, 134.5 (d,  $J_{\text{C-F}} = 3$  Hz), 127.8 (d,  $J_{\text{C-F}} = 8$  Hz), 124.9 (d,  $J_{\text{C-F}} = 1$  Hz), 115.5 (d,  $J = 21$  Hz), 36.9, 27.8, 22.5.

HRMS: Calculated for  $[M+H]^+$  : 191.0867  
Found  $[M+H]^+$  : 191.0865

TLC:  $R_f$  0.25 (5:1 pentane/ether)

### Preparation of 3-(4-(trifluoromethyl)phenyl)cyclohex-2-enone (**9c**)



The title compound was prepared from cyclohexenone **4** (97  $\mu$ l, 1.0 mmol, 1.0 eq.) and 4-trifluoromethylphenylboronic acid (285 mg, 1.5 mmol, 1.5 eq.) according to general procedure **A**. The reaction mixture was purified by flash column chromatography (pentane/ether 5:1) to yield 3-(4-(trifluoromethyl)phenyl)cyclohex-2-enone **9c** (180 mg, 0.75 mmol, 75%) as a colorless liquid

#### Data for 3-(4-(trifluoromethyl)phenyl)cyclohex-2-enone

<sup>1</sup>H-NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$   
7.60 (q,  $J$  = 8.5 Hz, 4H), 6.38 (s, 1H), 2.74 (t,  $J$  = 6.7 Hz, 2H), 2.47 (t,  $J$  = 6.7 Hz, 2H), 2.14 (q,  $J$  = 6.2 Hz, 2H).

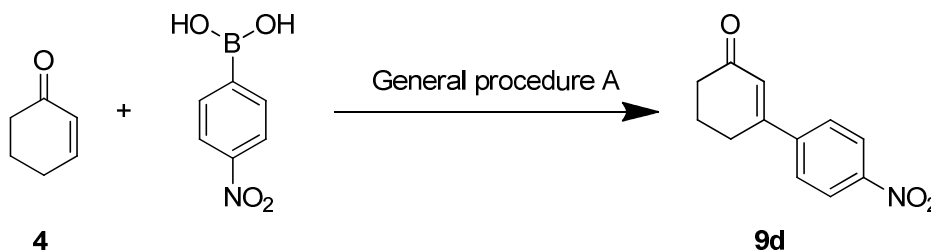
<sup>13</sup>C-NMR: (101 MHz, CDCl<sub>3</sub>)  $\delta$   
199.7, 158.3, 142.5, 127.0, 126.7, 126.3, 125.7, 125.6, 37.1

<sup>19</sup>F-NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$  -62.89.

TLC: R<sub>f</sub> 0.2 (5:1 pentane/ether)

All characterization data match completely with literature<sup>3</sup>.

### Preparation of 4'-nitro-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (**9d**)



The title compound was prepared from Cyclohexenone **4** (97  $\mu$ l, 1.0 mmol, 1.0 eq.) and 4-nitrophenylboronic acid (251 mg, 1.5 mmol, 1.5 eq.) according to general procedure **A**. The reaction mixture was purified by flash column chromatography (pentane/ether 2:1) to yield 4'-nitro-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one **9d** (115 mg, 0.55 mmol, 55%) as a yellow solid.

#### Data for 4'-nitro-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one

<sup>1</sup>H-NMR: (400 MHz, CDCl<sub>3</sub>)  $\delta$

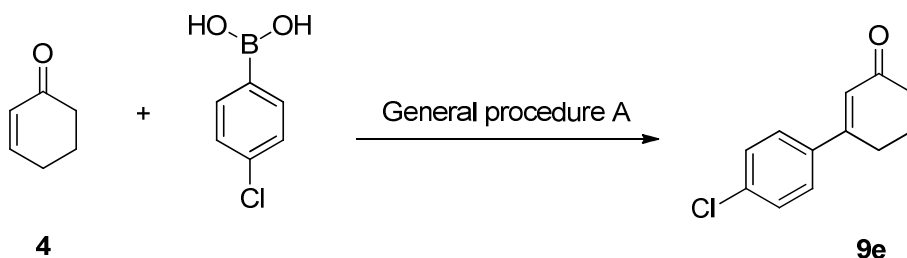
8.28 (d,  $J = 9.0$  Hz, 2H), 7.68 (d,  $J = 9.0$  Hz, 2H), 6.45 (t,  $J = 1.5$  Hz, 1H), 2.80 (td,  $J = 6.1, 1.5$  Hz, 2H), 2.58 – 2.50 (m, 2H), 2.21 (dt,  $J = 12.3, 6.2$  Hz, 2H).

**<sup>13</sup>C-NMR:** (100 MHz, CDCl<sub>3</sub>) δ  
199.2, 157.0, 148.3, 145.2, 127.8, 127.0, 123.9, 37.1, 28.1, 22.6.

**MS:** Calculated for [M+H]<sup>+</sup> :218.0817  
Found [M+H]<sup>+</sup> :218.0813

**TLC:** R<sub>f</sub> 0.15 (5:1 pentane/ether)

### Preparation of 3-(4-chlorophenyl)cyclohex-2-enone (9e)



The title compound was prepared from Cyclohexenone **4** (97 μl, 1.0 mmol, 1.0 eq.) and *p*-Chlorophenylboronic acid (235 mg, 1.5 mmol, 1.5 eq.) according to general procedure **A**. The reaction mixture was purified by flash column chromatography (pentane/ether 5:1) to yield 3-(4-chlorophenyl)cyclohex-2-enone **9e** (189 mg, 0.92 mmol, 92%) as a off-white solid.

#### Data for 3-(4-chlorophenyl)cyclohex-2-enone

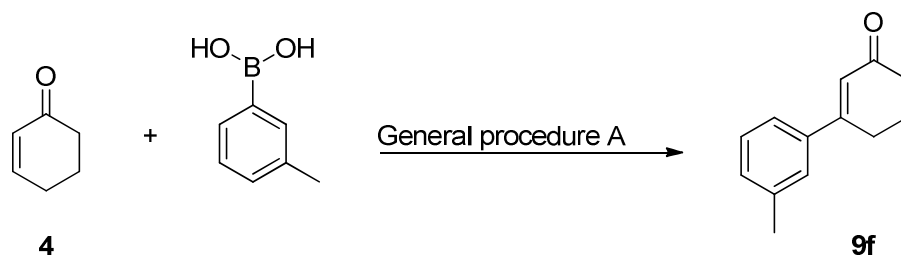
**<sup>1</sup>H-NMR:** (400 MHz, CDCl<sub>3</sub>) δ  
7.42 (d,  $J = 8.6$  Hz, 2H), 7.32 (d,  $J = 8.7$  Hz, 2H), 6.33 (s, 1H), 2.69 (t,  $J = 6.6$  Hz, 2H), 2.43 (t,  $J = 6.7$  Hz, 2H), 2.11 (t,  $J = 6.2$  Hz, 2H).

**<sup>13</sup>C-NMR:** (100 MHz, CDCl<sub>3</sub>) δ  
199.5, 158.2, 137.1, 135.9, 128.9, 127.3, 125.5, 37.1, 27.9, 22.7.

**HRMS:** Calculated for [M+H]<sup>+</sup> : 207.0571  
Found [M+H]<sup>+</sup> : 207.0572

**TLC:** R<sub>f</sub> 0.25 (5:1 pentane/ether)

### Preparation of 3-*m*-tolylcyclohex-2-enone (**9f**)



The title compound was prepared from Cyclohexenone **4** (97  $\mu$ l, 1.0 mmol, 1.0 eq.) and *m*-Tolylboronic acid (204 mg, 1.5 mmol, 1.5 equiv.) according to general procedure **A**. The reaction mixture was purified by flash column chromatography (pentane/ether 5:1) to yield 3-*m*-tolylcyclohex-2-enone **9f** (172 mg, 0.92 mmol, 92%) as a yellow oil.

#### Data for 3-*m*-tolylcyclohex-2-enone

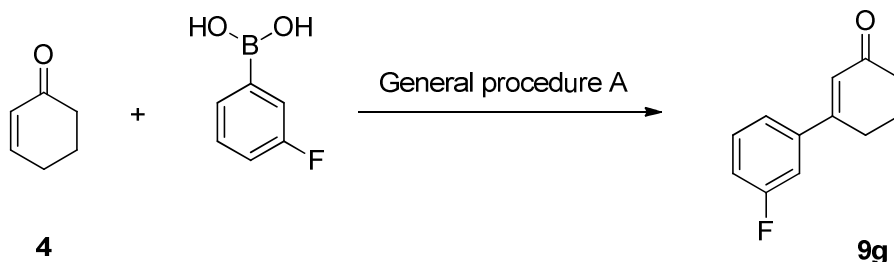
**<sup>1</sup>H-NMR:** (400 MHz, CDCl<sub>3</sub>)  $\delta$   
7.30 – 7.11 (m, 4H), 6.33 (s, 1H), 2.67 (t,  $J$ =6.5 Hz, 2H), 2.40 (t,  $J$ =6.7 Hz, 2H), 2.31 (s, 3H), 2.06 (q,  $J$ =6.4 Hz, 2H)

**<sup>13</sup>C-NMR:** (101 MHz, CDCl<sub>3</sub>)  $\delta$   
199.6, 159.9, 138.7, 138.3, 130.7, 128.6, 126.7, 125.2, 123.2, 37.2, 28.1, 22.8, 21.4

**MS:** Calculated for [M+H]<sup>+</sup> : 209.0942  
Found [M+Na]<sup>+</sup> : 209.0936

**TLC:** R<sub>f</sub> 0.25 (5:1 pentane/ether)

### Preparation of 3-(3-fluorophenyl)cyclohex-2-enone (**9g**)



The title compound was prepared from Cyclohexenone **4** (97  $\mu$ l, 1.0 mmol, 1.0 eq.) and 3-Fluorophenylboronic acid (210 mg, 1.5 mmol, 1.5 eq.) according to general procedure **A**. The reaction mixture was purified by flash column chromatography (pentane/ether 5:1) to yield 3-(3-fluorophenyl)cyclohex-2-enone **9g** (99 mg, 0.52 mmol, 52%) as a off-white solid.

#### Data for 3-(3-fluorophenyl)cyclohex-2-enone

**<sup>1</sup>H-NMR:** (400 MHz, CDCl<sub>3</sub>)  $\delta$

7.43 – 7.30 (m, 3H), 7.25 – 7.19 (m, 1H), 7.10 (tdd,  $J = 3.6, 2.5, 1.0$  Hz, 1H), 6.40 (br s, 1H), 2.75 (td,  $J = 6.2, 1.4$  Hz, 2H), 2.55 – 2.45 (m, 2H), 2.16 (dt,  $J = 12.4, 6.2$  Hz, 2H).

**<sup>13</sup>C-NMR:** (101 MHz, CDCl<sub>3</sub>) δ  
199.5, 162.9 (d,  $J_{C-F} = 246$  Hz), 158.1 (d,  $J_{C-F} = 2$  Hz), 141.1 (d,  $J_{C-F} = 7$  Hz), 130.3 (d,  $J_{C-F} = 8$  Hz), 126.1, 121.7 (d,  $J_{C-F} = 3$  Hz), 116.7 (d,  $J_{C-F} = 21$  Hz), 113.0 (d,  $J_{C-F} = 22$  Hz), 37.2, 28.0, 22.7.

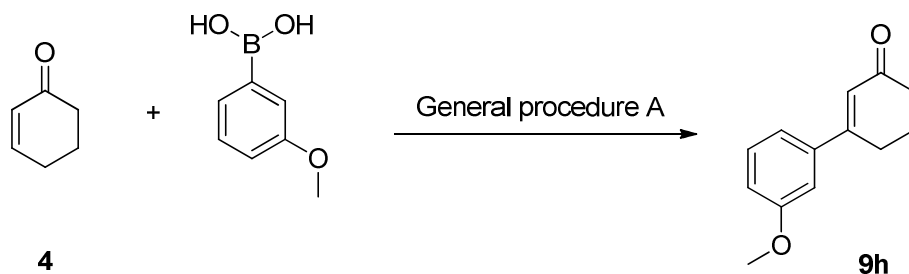
**<sup>19</sup>F-NMR** -112.28.

**HRMS:** Calculated for [M+H]<sup>+</sup> :191.0870

Found [M+H]<sup>+</sup>: :191.0867

**TLC:** R<sub>f</sub> 0.25 (5:1 pentane/ether)

### Preparation of 3-(3-methoxyphenyl)cyclohex-2-enone (9h)



The title compound was prepared from Cyclohexenone **4** (97 μl, 1.0 mmol, 1.0 eq.) and 3-Methoxyphenylboronic acid (228 mg, 1.5 mmol, 1.5 equiv) according to general procedure **A**. The reaction mixture was purified by flash chromatography (pentane/ether gradient 5:1 to 5:3) to yield 3-(3-methoxyphenyl)cyclohex-2-enone **9h** (186 mg, 0.92 mmol, 92%) as a white solid.

#### Data for 3-(3-methoxyphenyl)cyclohex-2-enone

**<sup>1</sup>H-NMR:** (400 MHz, CDCl<sub>3</sub>) δ  
7.23 (t,  $J = 8.0$  Hz, 1H), 7.05 – 6.84 (m, 3H), 6.32 (s, 1H), 3.74 (s, 3H), 2.66 (t,  $J = 5.3$  Hz, 2H), 2.39 (t,  $J = 6.7$  Hz, 2H), 2.05 (t,  $J = 6.4$  Hz, 2H)

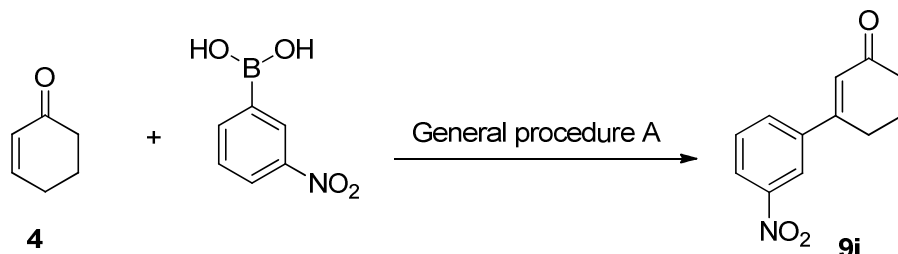
**<sup>13</sup>C-NMR:** (101 MHz, CDCl<sub>3</sub>) δ  
199.7, 159.7, 159.7, 140.2, 129.7, 125.4, 118.5, 115.3, 111.7, 55.2, 37.2, 28.1, 22.7

**HRMS:** Calculated for [M+Na]<sup>+</sup> : 225.0886

Found [M+Na]<sup>+</sup> : 225.0885

**TLC:** R<sub>f</sub> 0,15 (5:1 pentane/ether)

### Preparation of 3-(3-nitrophenyl)cyclohex-2-enone (**9i**)



The title compound was prepared from Cyclohexenone **4** (97  $\mu$ l, 1.0 mmol, 1.0 eq.) and 3-Nitrophenylboronic acid (251 mg, 1.5 mmol, 1.5 eq.) according to general procedure **A**. The reaction mixture was purified by flash column chromatography (pentane/ether gradient 5:1 to 1:1) to yield 3-(3-nitrophenyl)cyclohex-2-enone **9i** (206 mg, 0.95 mmol, 95%) as a yellow foam.

#### Data for 3-(3-nitrophenyl)cyclohex-2-enone

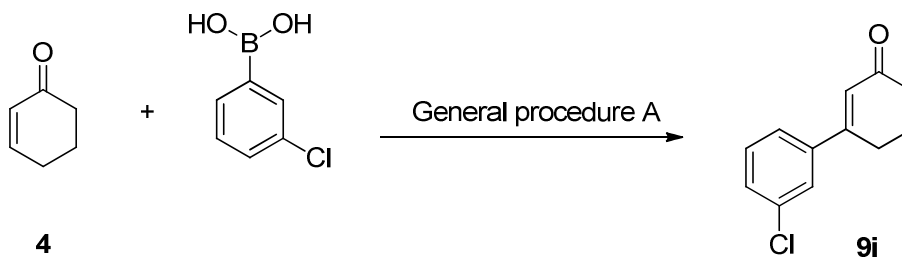
**<sup>1</sup>H-NMR:** (400 MHz, CDCl<sub>3</sub>)  $\delta$   
8.38 (s, 1H), 8.27 (d,  $J$  = 8.4 Hz, 1H), 7.86 (d,  $J$  = 7.7 Hz, 1H), 7.61 (t,  $J$  = 8.0 Hz, 1H), 6.47 (s, 1H), 2.81 (t,  $J$  = 5.6 Hz, 2H), 2.56 – 2.50 (m, 2H), 2.26 – 2.17 (m, 2H).

**<sup>13</sup>C-NMR:** (101 MHz, CDCl<sub>3</sub>)  $\delta$   
199.3, 156.5, 144.5, 141.0, 131.8, 129.9, 127.2, 124.4, 121.0, 37.1, 28.1, 22.6.

**HRMS:** Calculated for [M+H]<sup>+</sup> : 218.0812  
Found [M+H]<sup>+</sup> : 218.0812

**TLC:** R<sub>f</sub> 0,15 (5:1 pentane/ether)

### Preparation of 3-(3-chlorophenyl)cyclohex-2-enone (**9j**)



The title compound was prepared from Cyclohexenone **4** (97  $\mu$ l, 1.0 mmol, 1.0 eq.) and 3-Chlorophenylboronic acid (235 mg, 1.5 mmol, 1.5 eq.) according to general procedure **A**. The reaction mixture was purified by flash column chromatography (pentane/ether 5:1) to yield 3-(3-chlorophenyl)cyclohex-2-enone **9j** (175 mg, 0.85 mmol, 85%) as a off-white solid.

#### Data for 3-(3-chlorophenyl)cyclohex-2-enone

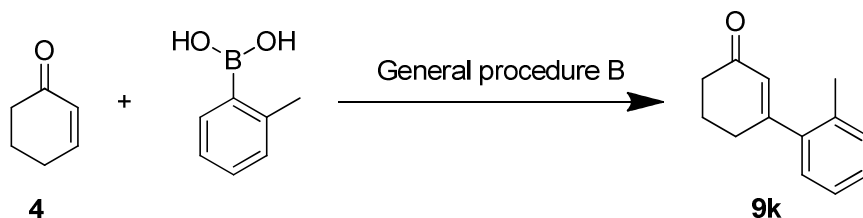
**<sup>1</sup>H-NMR:** (400 MHz, CDCl<sub>3</sub>) δ  
7.43 – 7.18 (m, 4H), 6.28 (s, 1H), 2.64 (t, *J* = 6.6 Hz, 2H), 2.38 (t, *J* = 6.6 Hz, 2H), 2.10 (q, *J* = 6.3 Hz, 2H).

**<sup>13</sup>C-NMR:** (50 MHz, CDCl<sub>3</sub>) δ  
199.4, 158.1, 140.6, 134.7, 130.0, 129.7, 126.1, 126.0, 124.1, 37.1, 27.9, 22.6.

**HRMS:** Calculated for [M+H]<sup>+</sup> : 207.0571  
Found [M+H]<sup>+</sup> : 207.0572

**TLC:** R<sub>f</sub> 0,25 (5:1 pentane/ether)

### Preparation of 2'-methyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (**9k**)



The title compound was prepared from Cyclohexenone **4** (97 μl, 1.0 mmol, 1.0 eq.) and 2-methylphenylboronic acid (204 mg, 1.5 mmol, 1.5 eq.) according to general procedure **B**. The reaction mixture was purified by flash column chromatography (pentane/ether 10:1) to yield 2'-methyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one **9k** (81 mg, 0.45 mmol, 45%) as a yellow oil.

#### Data for yield 2'-methyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one

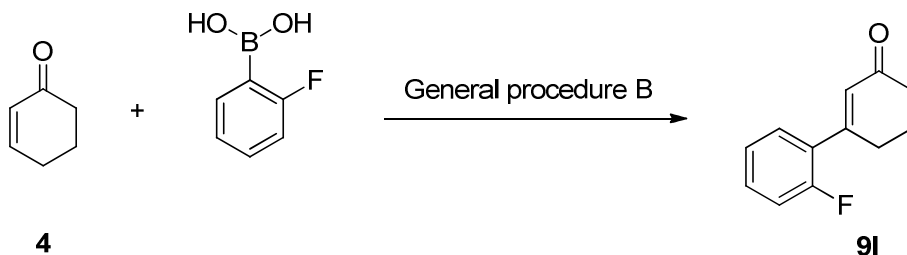
**<sup>1</sup>H-NMR:** (400 MHz, CDCl<sub>3</sub>) δ  
7.25 – 7.14 (m, 3H), 7.13 – 7.03 (m, 1H), 5.99 (t, *J* = 1.5 Hz, 1H), 2.59 (td, *J* = 6.1, 1.6 Hz, 2H), 2.53 – 2.48 (m, 2H), 2.31 (s, 3H), 2.16 (dq, *J* = 12.3, 6.2 Hz, 2H).

**<sup>13</sup>C-NMR:** 100 MHz, CDCl<sub>3</sub>) δ  
199.6, 163.6, 140.7, 133.9, 130.7, 128.6, 128.3, 126.9, 125.9, 37.3, 31.2, 23.2, 20.0.

**HRMS:** Calculated for [M+H]<sup>+</sup> : 187.1123  
Found [M+H]<sup>+</sup> : 187.1117

**TLC:** R<sub>f</sub> 0.25 (5:1 pentane/ether)

### Preparation of 3-(2-fluorophenyl)cyclohex-2-enone (9I)



The title compound was prepared from Cyclohexenone **4** (97  $\mu$ l, 1.0 mmol, 1.0 eq.) and 2-Fluorophenylboronic acid (210 mg, 1.5 mmol, 1.5 eq.) according to general procedure **B**. The reaction mixture was purified by flash column chromatography (pentane/ether 5:1) to yield 3-(2-fluorophenyl)cyclohex-2-enone **9I** (141 mg, 0.74 mmol, 74%) as a off-white solid.

#### Data for 3-(2-fluorophenyl)cyclohex-2-enone

**<sup>1</sup>H-NMR:** (400 MHz, CDCl<sub>3</sub>)  $\delta$   
7.40 – 7.31 (m, 2H), 7.20 – 7.15 (m, 1H), 7.11 (dd,  $J = 11.1, 8.2$  Hz, 1H), 6.28 (br s, 1H), 2.76 (ddd,  $J = 7.8, 3.3, 1.7$  Hz, 2H), 2.54 – 2.46 (m, 2H), 2.15 (dt,  $J = 12.3, 6.2$  Hz, 2H).

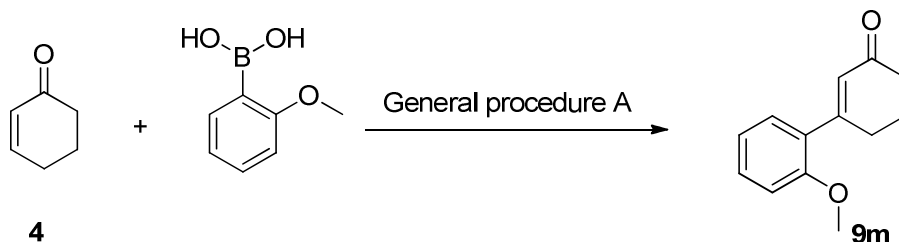
**<sup>13</sup>C-NMR:** (101 MHz, CDCl<sub>3</sub>)  $\delta$   
199.5, 159.9 (d,  $J_{C-F} = 251$  Hz), 157.11 (d,  $J_{C-F} = 2$  Hz), 130.9 (d,  $J_{C-F} = 9$  Hz), 128.8 (d,  $J_{C-F} = 3$  Hz), 127.7 (d,  $J_{C-F} = 13$  Hz), 124.4 (d,  $J_{C-F} = 4$  Hz), 116.3 (d,  $J_{C-F} = 22$  Hz), 37.37, 29.6 (d,  $J_{C-F} = 4$  Hz), 23.10.

**<sup>19</sup>F-NMR** -112.66

**HRMS:** Calculated for [M+H]<sup>+</sup> : 191.0867  
Found [M+H]<sup>+</sup> : 191.0870

**TLC:** R<sub>f</sub> 0.25 (5:1 pentane/ether)

### Preparation of 3-(2-methoxyphenyl)cyclohex-2-enone (9m)



The title compound was prepared from Cyclohexenone **4** (97  $\mu$ l, 1.0 mmol, 1.0 eq.) and 2-Methoxyphenylboronic acid (228 mg, 1.5 mmol, 1.5 eq.) according to general procedure **A**. The reaction mixture was purified by flash column chromatography

(pentane/ether gradient 5:1 to 5:3) to yield 3-(2-methoxyphenyl)cyclohex-2-enone **9m** (156 mg, 0.77 mmol, 77%) as a white solid.

Data for 3-(2-methoxyphenyl)cyclohex-2-enone

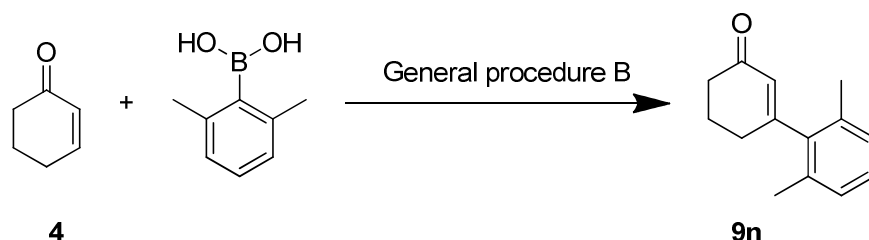
<sup>1</sup>H-NMR: (400 MHz, CDCl<sub>3</sub>) δ  
7.34 – 7.28 (m, 1H), 7.17 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.99 – 6.86 (m, 2H),  
6.17 (s, 1H), 3.80 (s, 3H), 2.71 (t, *J* = 6.0 Hz, 2H), 2.50 – 2.39 (m, 2H),  
2.11 – 2.03 (m, 2H).

<sup>13</sup>C-NMR: (101 MHz, CDCl<sub>3</sub>) δ  
199.9, 161.5, 156.4, 130.2, 129.4, 128.5, 128.0, 120.6, 111.0, 55.3,  
37.4, 29.9, 23.2.

MS: Calculated for [M+H]<sup>+</sup> : 203.1067  
Found [M+H]<sup>+</sup> : 203.1066

TLC: R<sub>f</sub> 0,15 (5:1 pentane/ether)

**Preparation of 2',6'-dimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (9n)**



The title compound was prepared from Cyclohexenone **4** (97 μl, 1.0 mmol, 1.0 eq.) and 2,6-dimethylphenylboronic acid (225 mg, 1.5 mmol, 1.5 eq.) according to general procedure **B**. The reaction mixture was purified by flash column chromatography (pentane/ether 10:1) to yield 2',6'-dimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one **9n** (71 mg, 0.35 mmol, 35%) as a yellow oil.

Data for 2',6'-dimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one

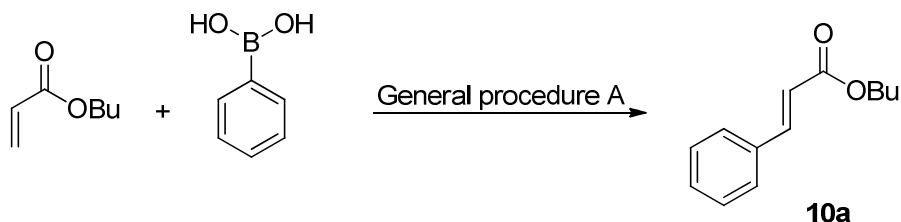
<sup>1</sup>H-NMR: (400 MHz, CDCl<sub>3</sub>) δ  
7.13 – 7.05 (m, 3H), 5.91 (*J* = 1.6 Hz, 1H), 2.54 – 2.51 (m, 2H), 2.47  
(dd, *J* = 8.5, 3.4 Hz, 2H), 2.21 (s, 6H), 2.18 (dd, *J* = 12.1, 5.9 Hz, 2H).

<sup>13</sup>C-NMR: (101 MHz, CDCl<sub>3</sub>) δ  
199.6, 163.9, 140.3, 133.4, 129.0, 127.6, 127.6, 37.4, 30.6, 23.03, 19.7.

HRMS: Calculated for [M+H]<sup>+</sup> : 203.1067  
Found [M+H]<sup>+</sup> : 203.1066

TLC: R<sub>f</sub> 0,15 (5:1 pentane/ether)

## Preparation of butyl cinnamate (10a)



The title compound was synthesized from Butyl acrylate (128 mg, 1.0 mmol, 1.0 eq.) and phenyl boronic acid (183 mg, 1.5 mmol, 1.5 eq.) using general procedure **A**. The reaction mixture was purified by flash column chromatography (pentane/ether 10:1) to yield butyl cinnamate **10a** (174 mg, 0.85 mmol, 85%) as a colorless oil.

### Data for butyl cinnamate

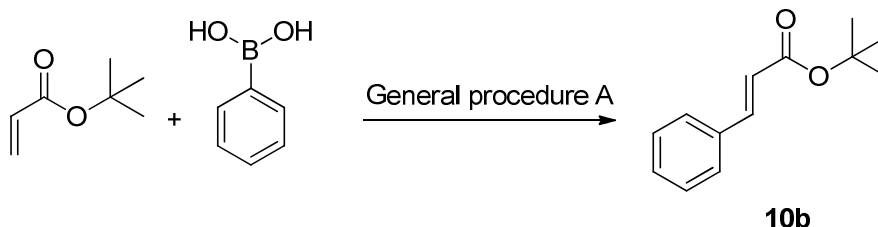
**<sup>1</sup>H-NMR:** (200 MHz, CDCl<sub>3</sub>) δ  
7.69 (d, *J* = 16.0 Hz, 1H), 7.58 – 7.46 (m, 2H), 7.41 – 7.34 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.22 (t, *J* = 6.6 Hz, 2H), 1.81 – 1.59 (m, 2H), 1.57 – 1.32 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H).

**<sup>13</sup>C-NMR:** (101 MHz, CDCl<sub>3</sub>) δ  
167.1, 144.5, 134.5, 130.2, 128.8, 128.0, 118.3, 64.4, 30.8, 19.2, 13.7.

**HRMS:** Calculated for [M+H]<sup>+</sup> : 205.1223  
Found [M+H]<sup>+</sup> : 205.1223

**TLC:** R<sub>f</sub> 0.8 (5:1 pentane/ether)

## Preparation of *tert*-butyl cinnamate (10b)



The title compound was prepared from *Tert*-butyl acrylate (148 μl, 1.0 mmol, 1.0 equiv.) and Phenyl boronic acid (183 mg, 1.5 mmol, 1.5 equiv.) according to general procedure **A**. The reaction mixture was purified by flash column chromatography (pentane/ether 10:1) to yield *tert*-butyl cinnamate **10b** (173 mg, 0.85 mmol, 85%) as a colorless oil.

### Data for *tert*-butyl cinnamate

**<sup>1</sup>H-NMR:** (400 MHz, CDCl<sub>3</sub>) δ  
7.59 (d, *J* = 16.0 Hz, 1H), 7.51 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.37 (dd, *J* =

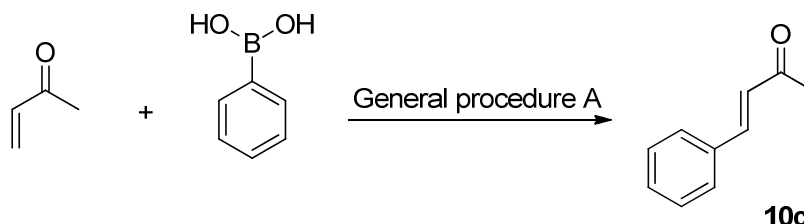
5.0, 1.9 Hz, 3H), 6.37 (d,  $J = 16.0$  Hz, 1H), 1.54 (s, 9H).

**<sup>13</sup>C-NMR:** (101 MHz, CDCl<sub>3</sub>)  $\delta$   
166.2, 143.5, 134.7, 127.9, 120.2, 80.4, 28.2

**HRMS:** Calculated for [M+H]<sup>+</sup> : 205.1223  
Found [M+H]<sup>+</sup> : 205.1222

**TLC:** R<sub>f</sub> 0.8 (10:1 pentane/ether)

### Preparation of (*E*)-4-phenylbut-3-en-2-one (**10c**)



The title compound was prepared from Methyl vinyl ketone (170  $\mu$ l, 2.0 mmol, 5.0 eq.) and Phenyl boronic acid (121 mg, 1.0 mmol, 1.0 eq.) according to general procedure **A**. Methyl vinyl ketone was taken in an excess due to its high volatility. Phenyl boronic acid (121 mg, 1.0 mmol, 1.0 eq.) The reaction mixture was purified by flash column chromatography (pentane/ether 3:1) to yield (*E*)-4-phenylbut-3-en-2-one **10c** (127 mg, 0.87 mmol, 87%) as a red-brown solid.

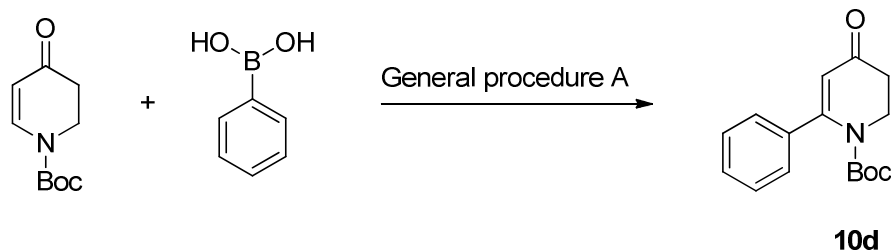
### Data for (*E*)-4-phenylbut-3-en-2-one

**<sup>1</sup>H-NMR:** (400 MHz, CDCl<sub>3</sub>)  $\delta$   
7.59 – 7.31 (m, 6H), 6.67 (d,  $J = 16.3$  Hz, 1H), 2.33 (s, 3H)

**<sup>13</sup>C-NMR:** (101 MHz, CDCl<sub>3</sub>)  $\delta$   
198.3, 143.4, 134.4, 130.5, 128.9, 128.2, 127.1, 27.5

**TLC:** R<sub>f</sub> 0.45 (3:1 pentane/ether)

### Preparation of *tert*-butyl 4-oxo-6-phenyl-3,4-dihydropyridine-1(2H)-carboxylate (**10d**)



The title compound was prepared from *tert*-butyl 4-oxo-3,4-dihydropyridine-1(2H)-carboxylate (197 mg, 1.0 mmol, 1.0 eq.) and Phenyl boronic acid (183 mg, 1.5 mmol, 1.5 eq.) according to general procedure **A**. The reaction mixture was purified by flash column chromatography (pentane/ether 3:1) to yield *tert*-butyl 4-oxo-6-phenyl-3,4-dihydropyridine-1(2H)-carboxylate **10d** (202 mg, 0.74 mmol, 74%) as a yellow/white solid.

#### Data for *tert*-butyl 4-oxo-6-phenyl-3,4-dihydropyridine-1(2H)-carboxylate

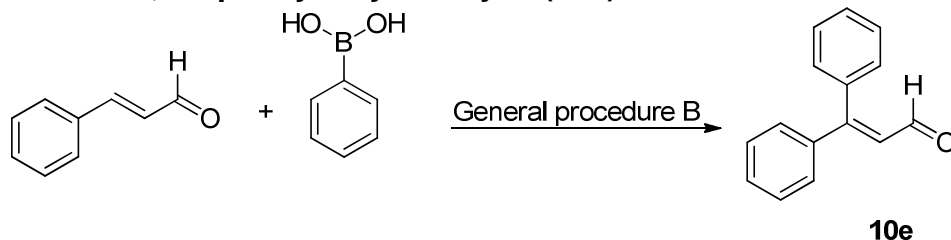
**<sup>1</sup>H-NMR:** (400 MHz, CDCl<sub>3</sub>) δ  
7.41 – 7.30 (m, 5H), 5.59 (s, 1H), 4.19 (t, *J*=5.9 Hz, 2H), 2.58 (t, *J*=6.2 Hz, 2H), 1.05 (s, 9H).

**<sup>13</sup>C-NMR:** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ  
194.9, 157.7, 152.3, 137.8, 129.8, 128.2, 126.4, 113.2, 82.4, 46.2, 37.9, 27.3.

**MS:** Calculated for [M+Na]<sup>+</sup> : 296.1263  
Found [M+Na]<sup>+</sup> : 296.1258

**TLC:** R<sub>f</sub> 0.3 (3:1 pentane/ether)

### Preparation of 3,3-diphenylacrylaldehyde (**10e**)



The title compound was prepared from Cinnamaldehyde (132 mg, 1.0 mmol, 1.0 eq.) and Phenyl boronic acid (183 mg, 1.5 mmol, 1.5 eq.) according to general procedure **B**. The reaction mixture was purified by flash column chromatography (pentane/ether 3:1) to yield 3,3-diphenylacrylaldehyde **10e** (174 mg, 0.85 mmol, 85%) as a off-white solid.

#### Data for 3,3-diphenylacrylaldehyde

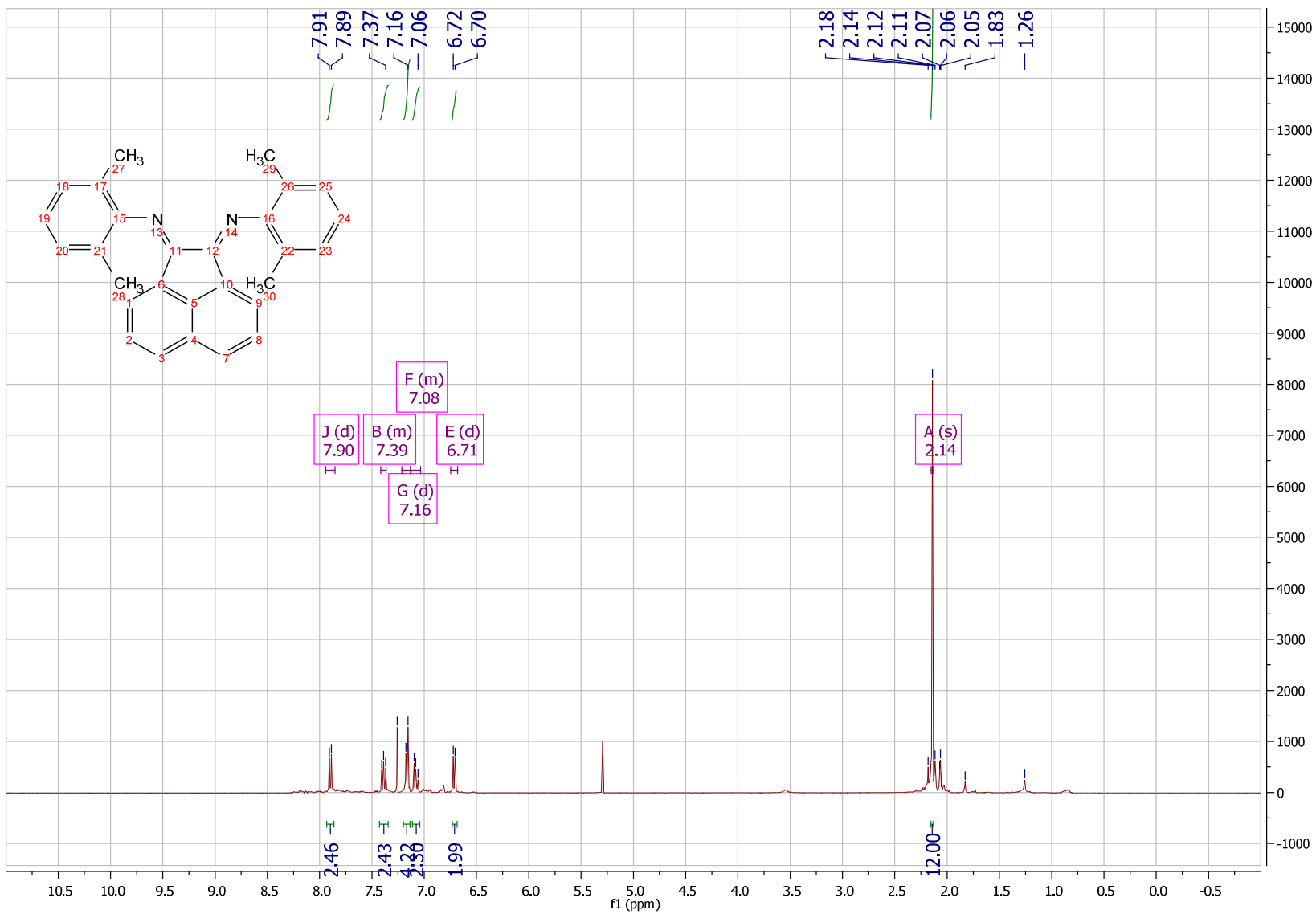
<sup>1</sup>H-NMR: (400 MHz, CDCl<sub>3</sub>) δ  
9.78 (s, 1H), 7.51 – 7.12 (m, 11H).

<sup>13</sup>C-NMR: (101 MHz, CDCl<sub>3</sub>) δ  
193.7, 150.1, 130.7, 130.2, 129.3, 128.9, 128.5, 128.3, 77.3, 77.0, 76.7.

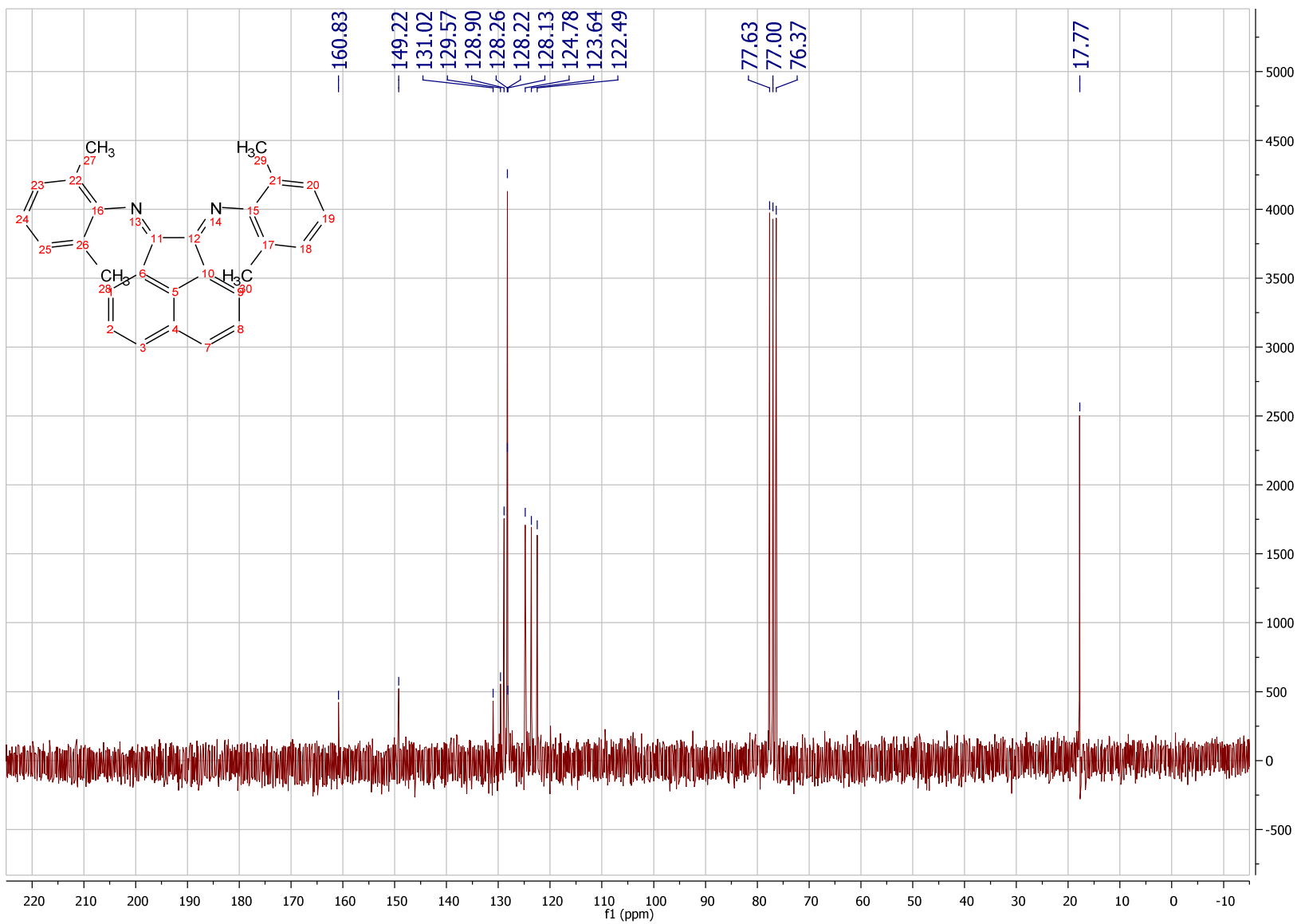
MS: Calculated for [M+H]<sup>+</sup> : 209.0966  
Found [M+H]<sup>+</sup> : 209.0961

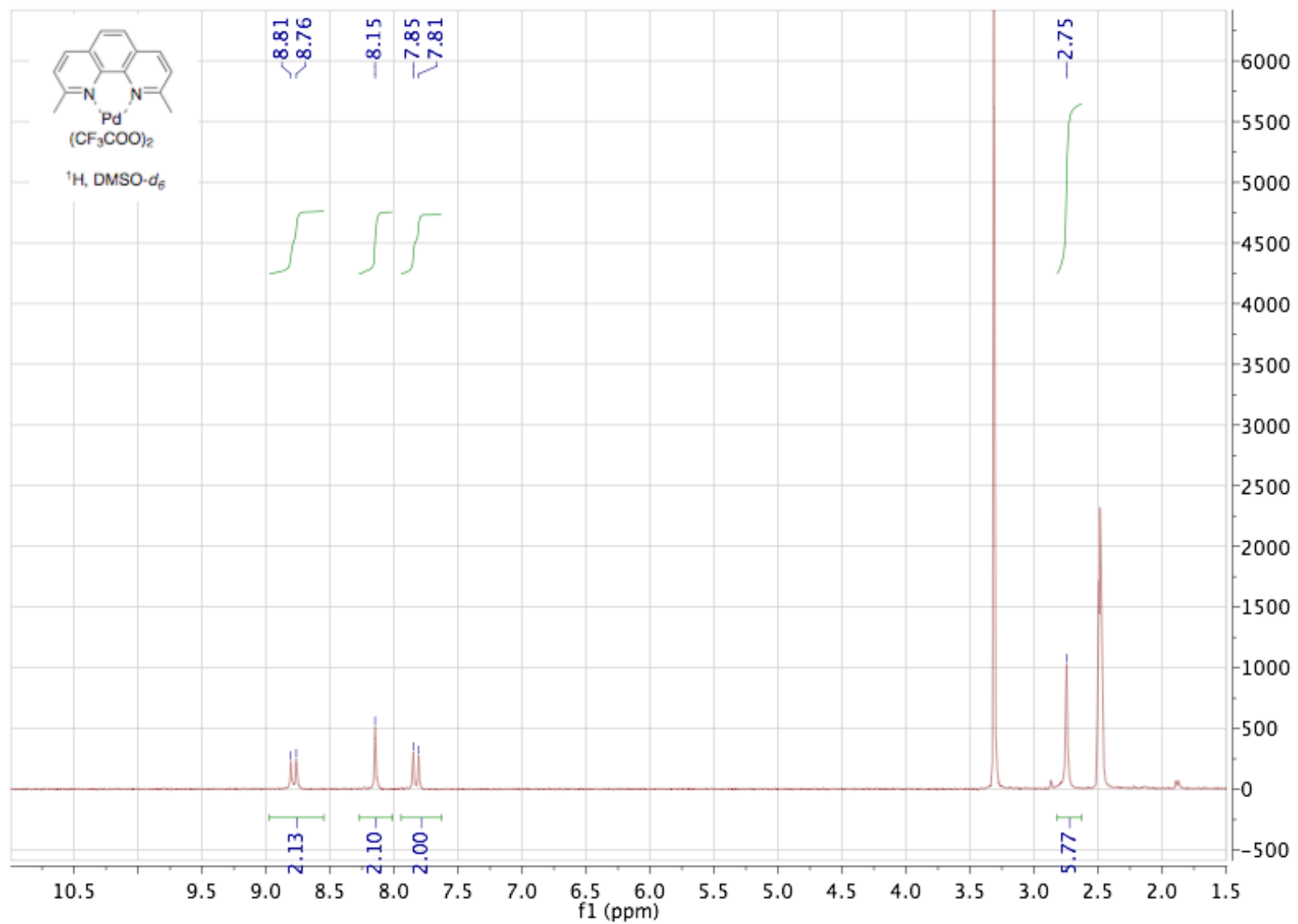
TLC: R<sub>f</sub> 0.3 (5:1 pentane/ether)

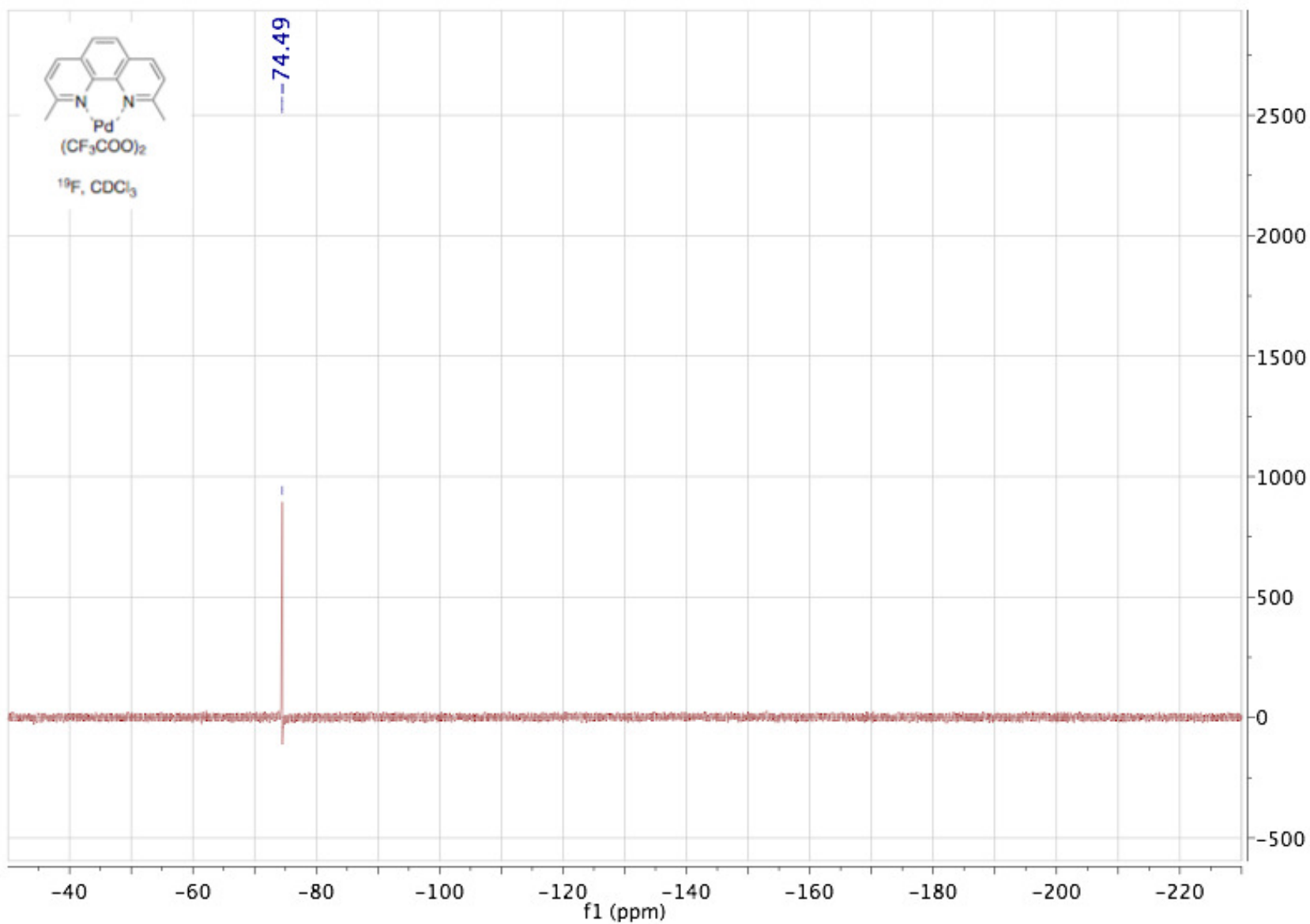
Bis(aryl)acenaphthequinonediimine (BIAN) (3)



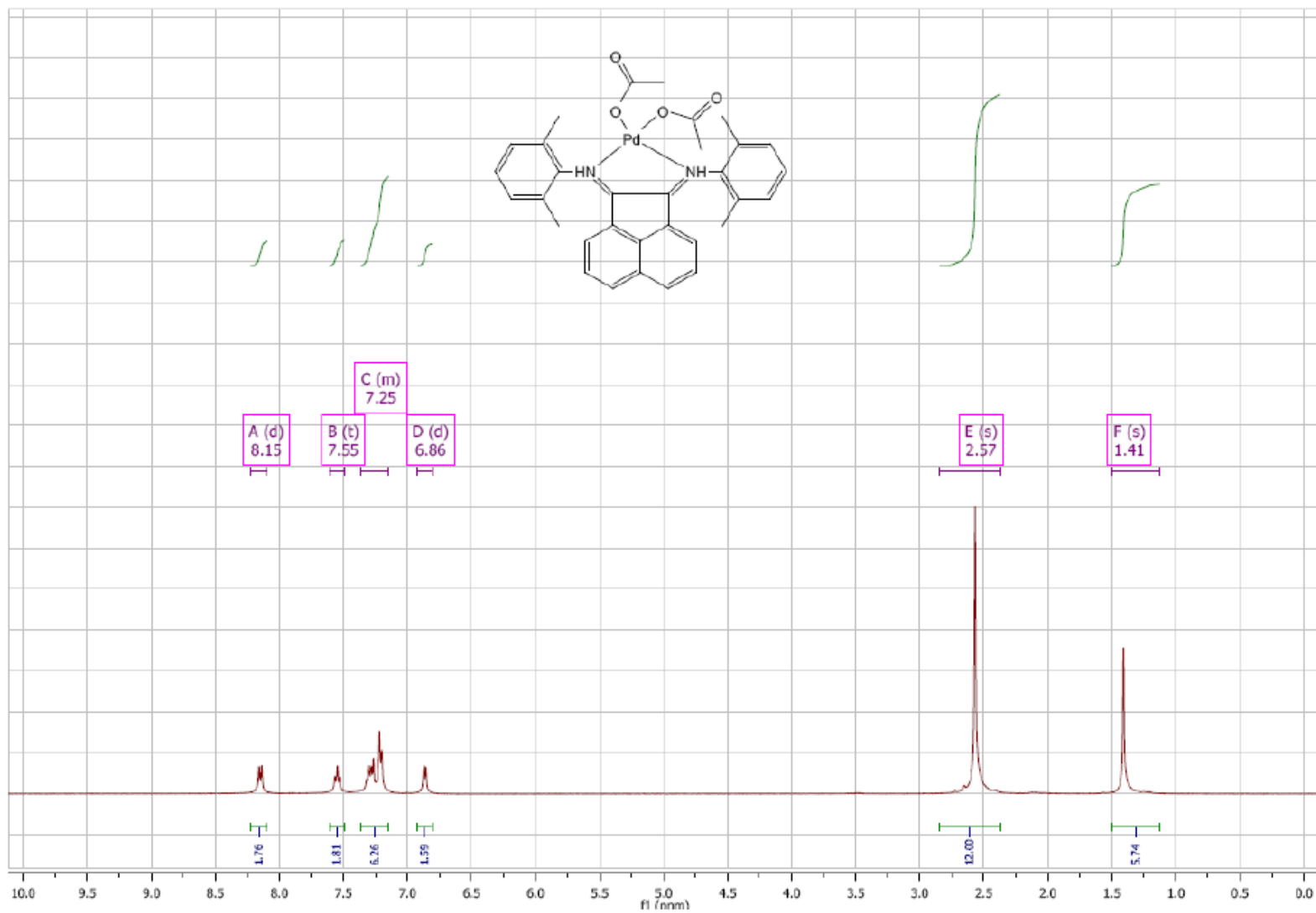
Bis(aryl)acenaphthequinonediimine (BIAN) (3)



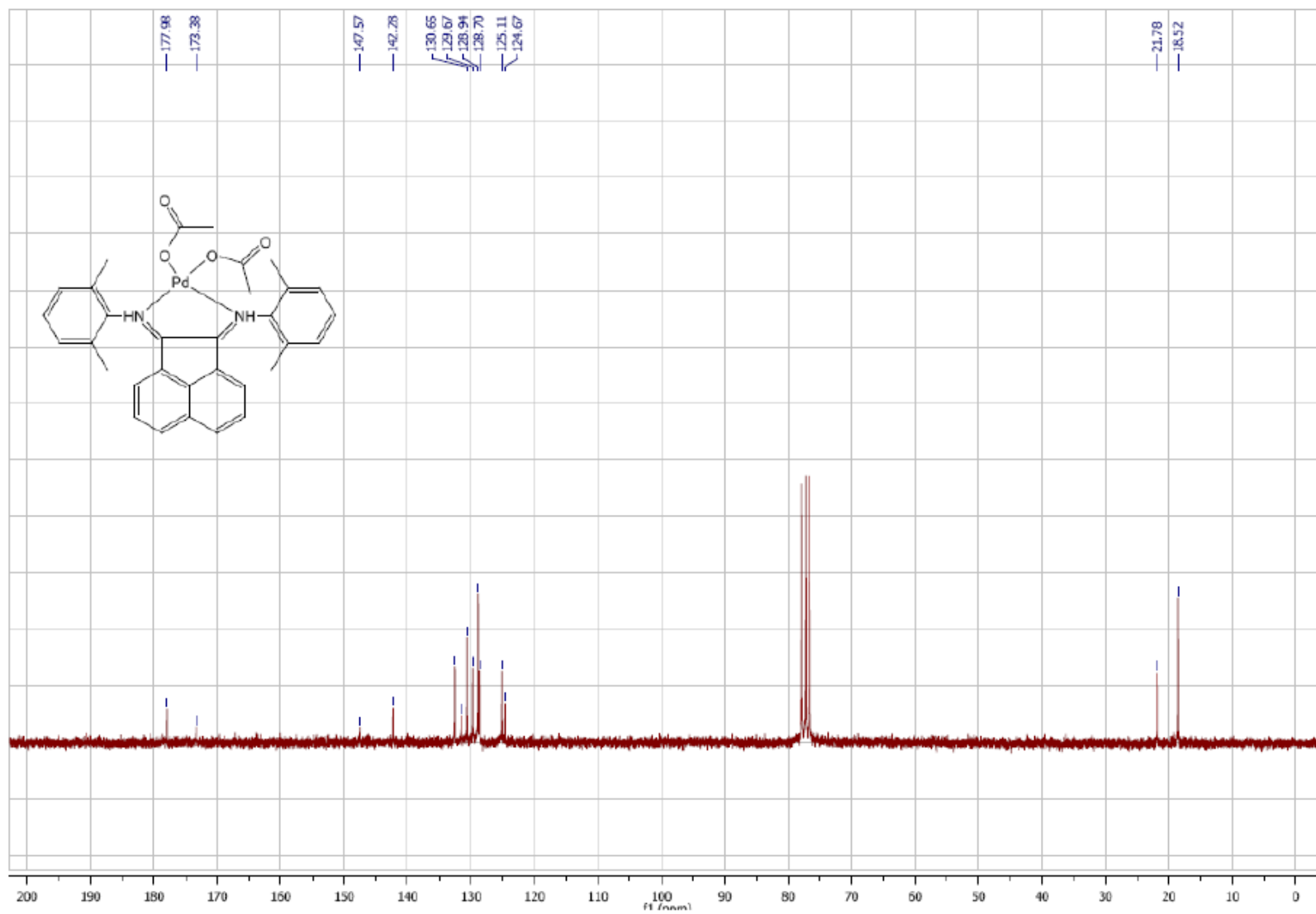




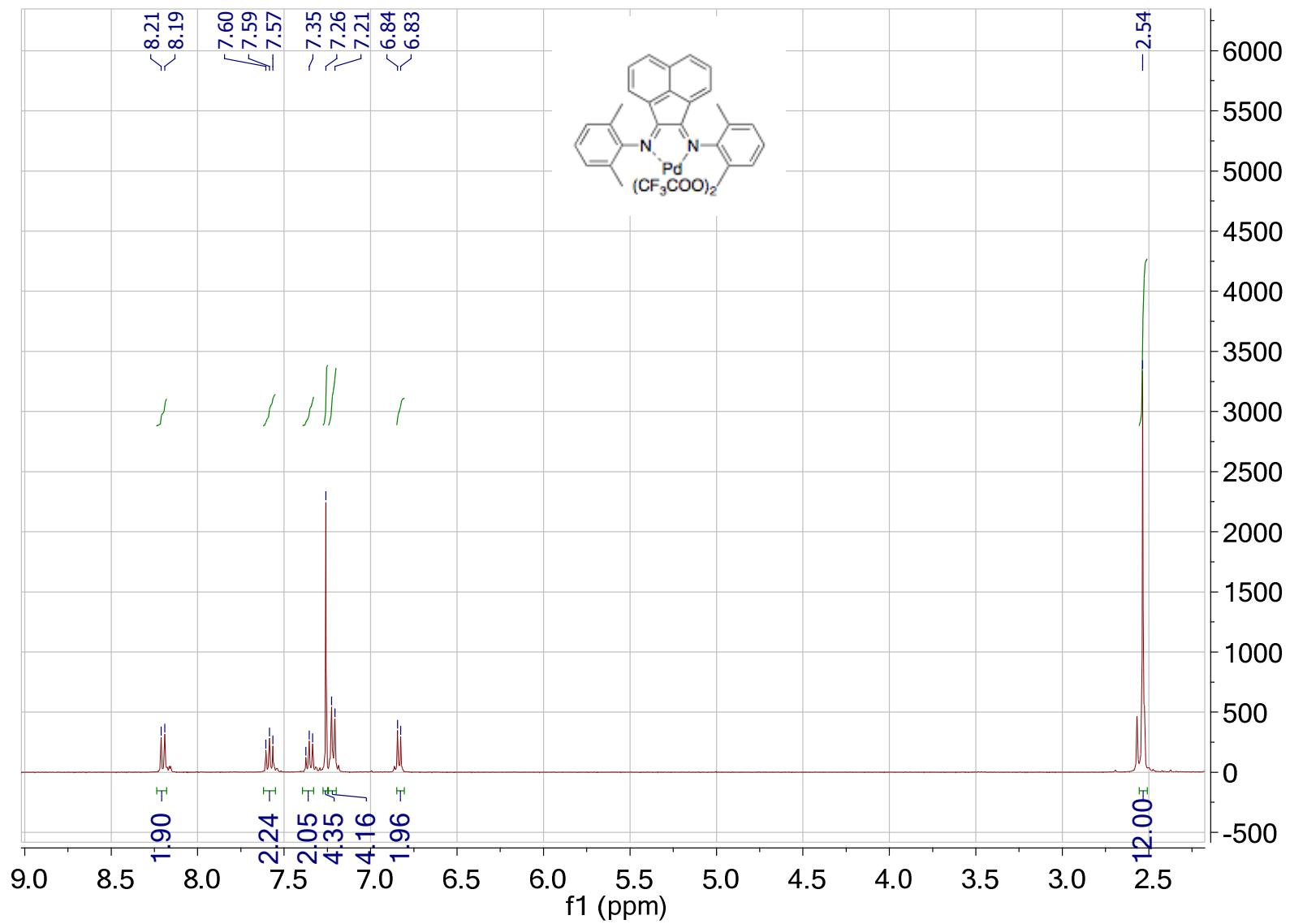
Complex 7b



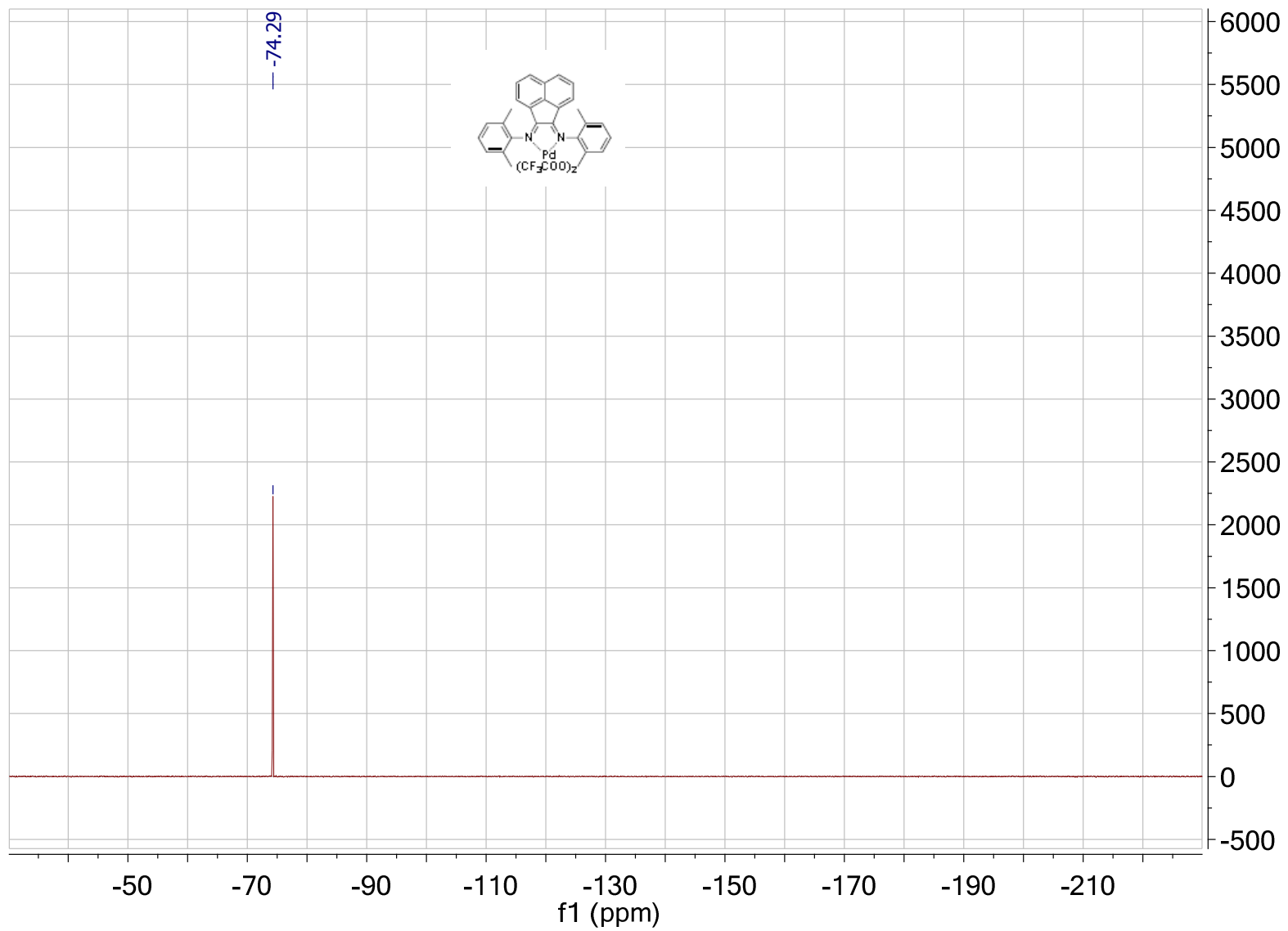
Complex 8a

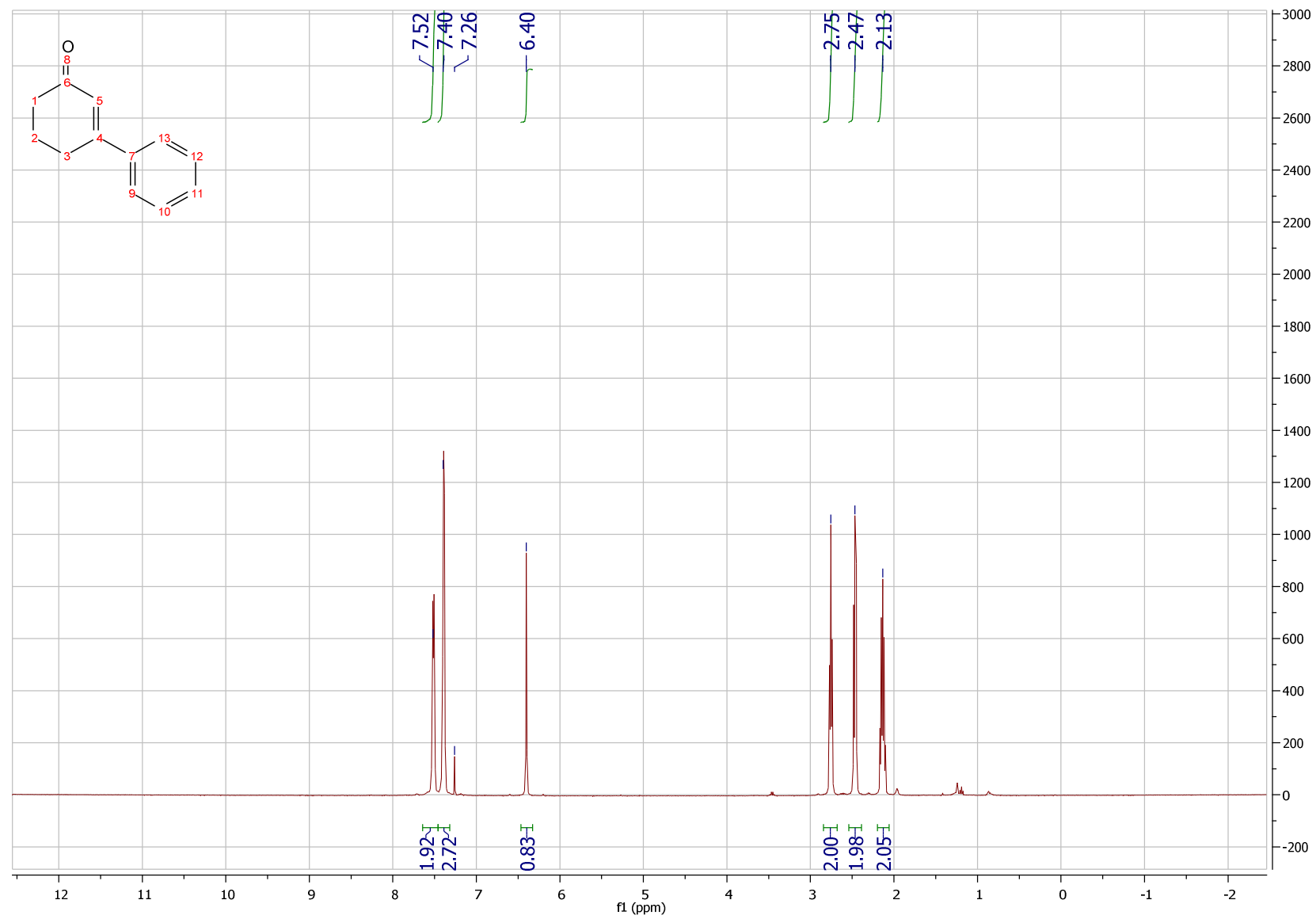


Complex 8a



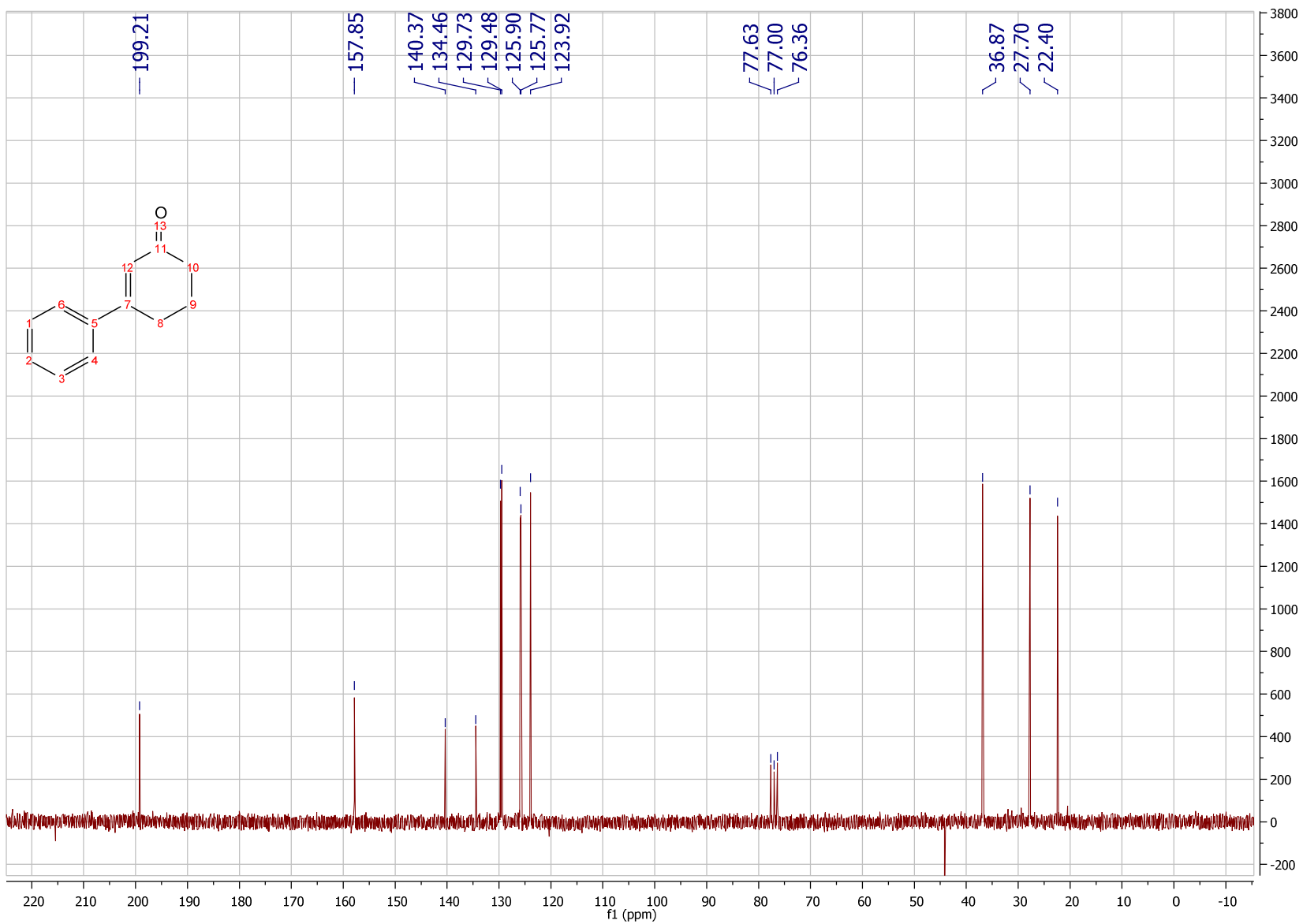
Complex 8b



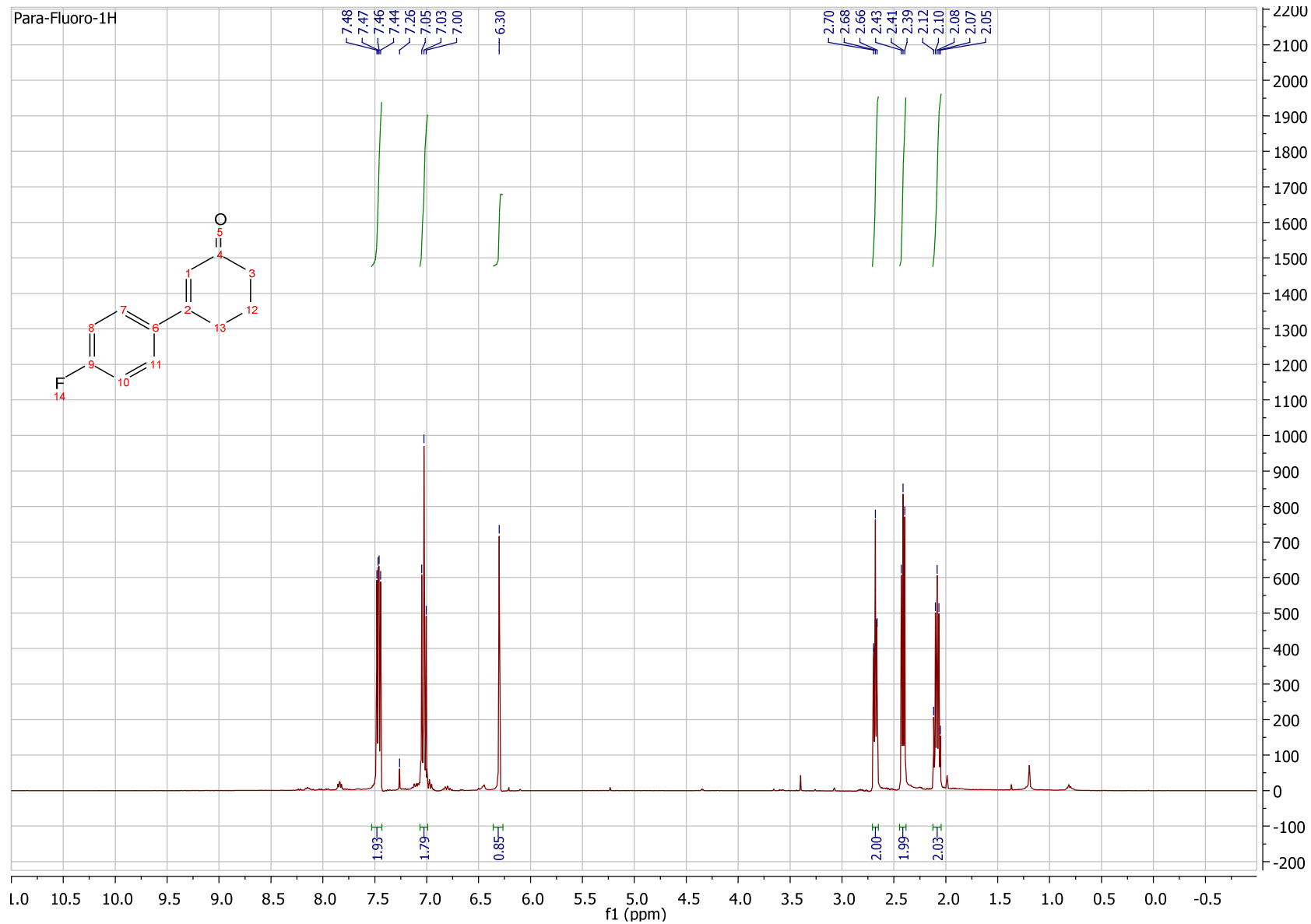


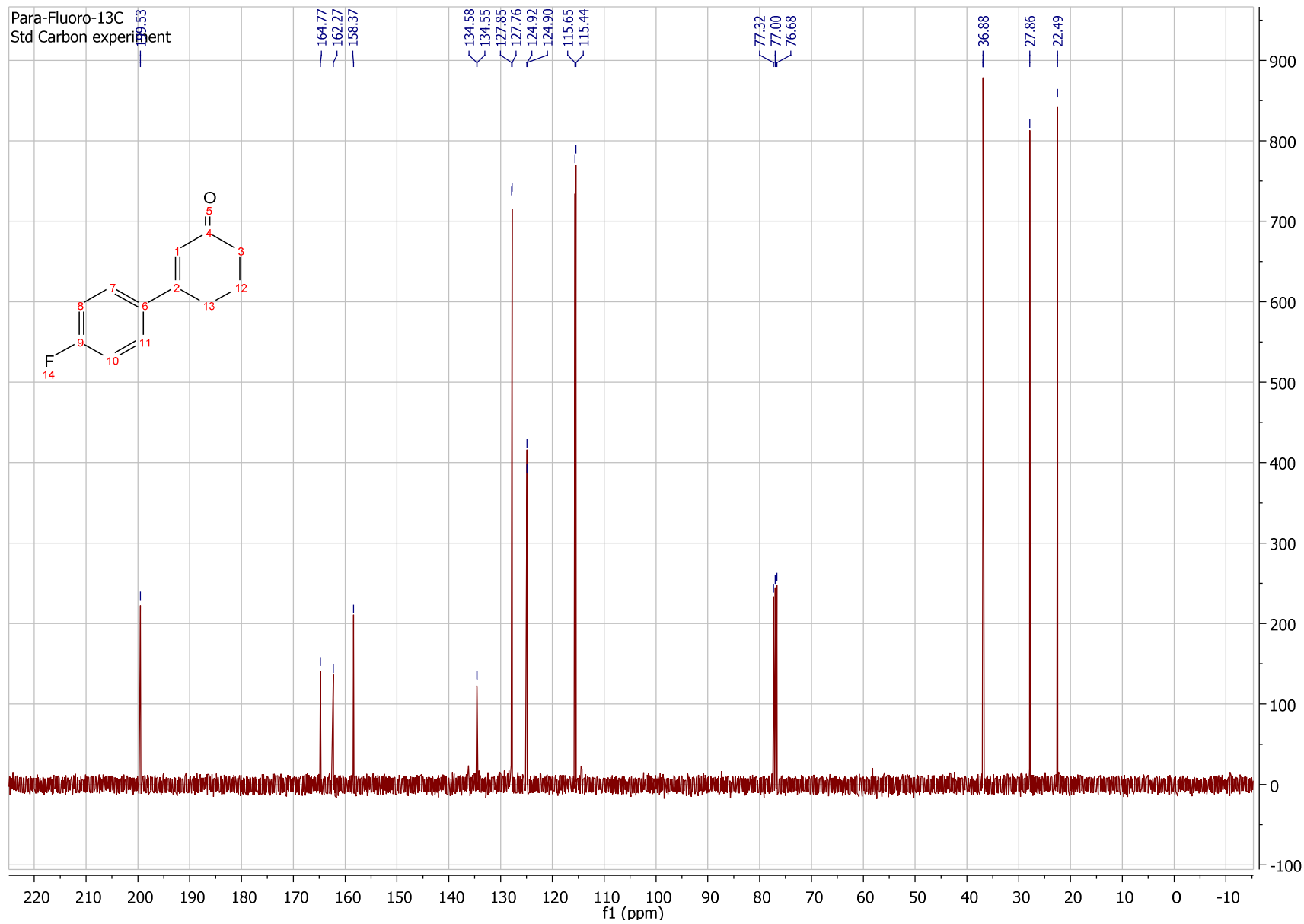
3-phenylcyclohex-2-enone (9a)

3-phenylcyclohex-2-enone (9a)



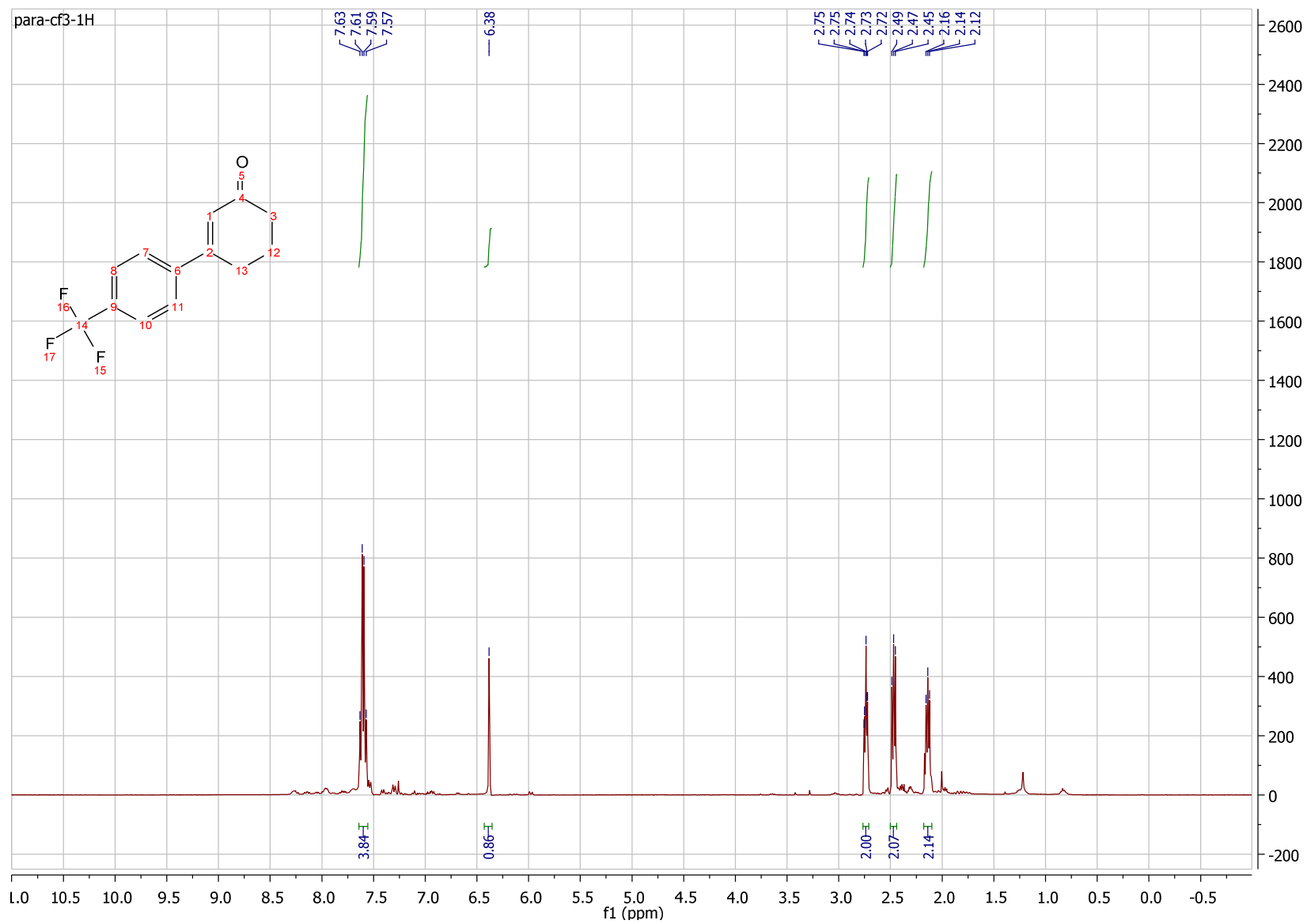
3-(4-fluorophenyl)cyclohex-2-enone (9b)



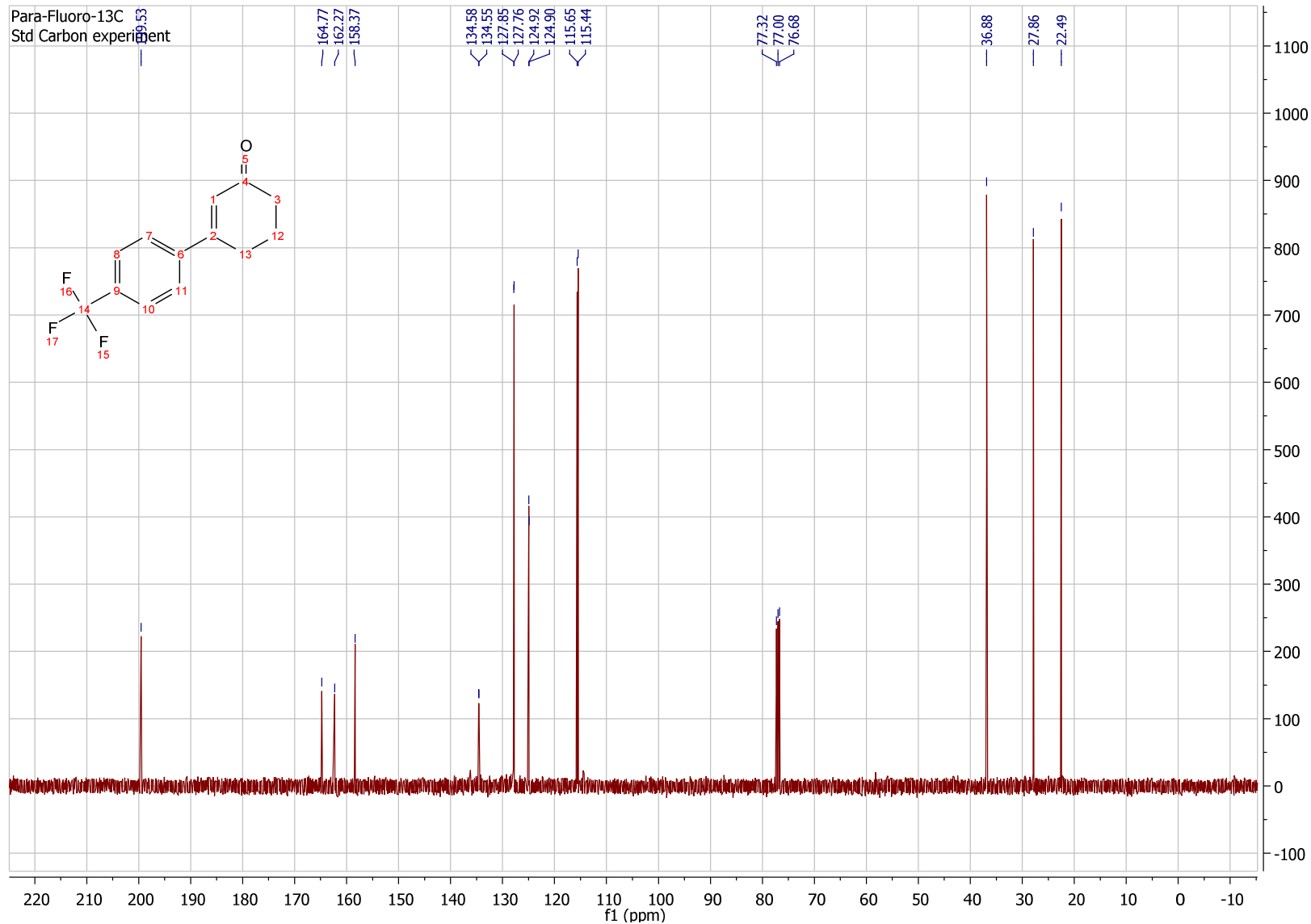


3-(4-fluorophenyl)cyclohex-2-enone (9b)

3-(4-(trifluoromethyl)phenyl)cyclohex-2-enone (9c)

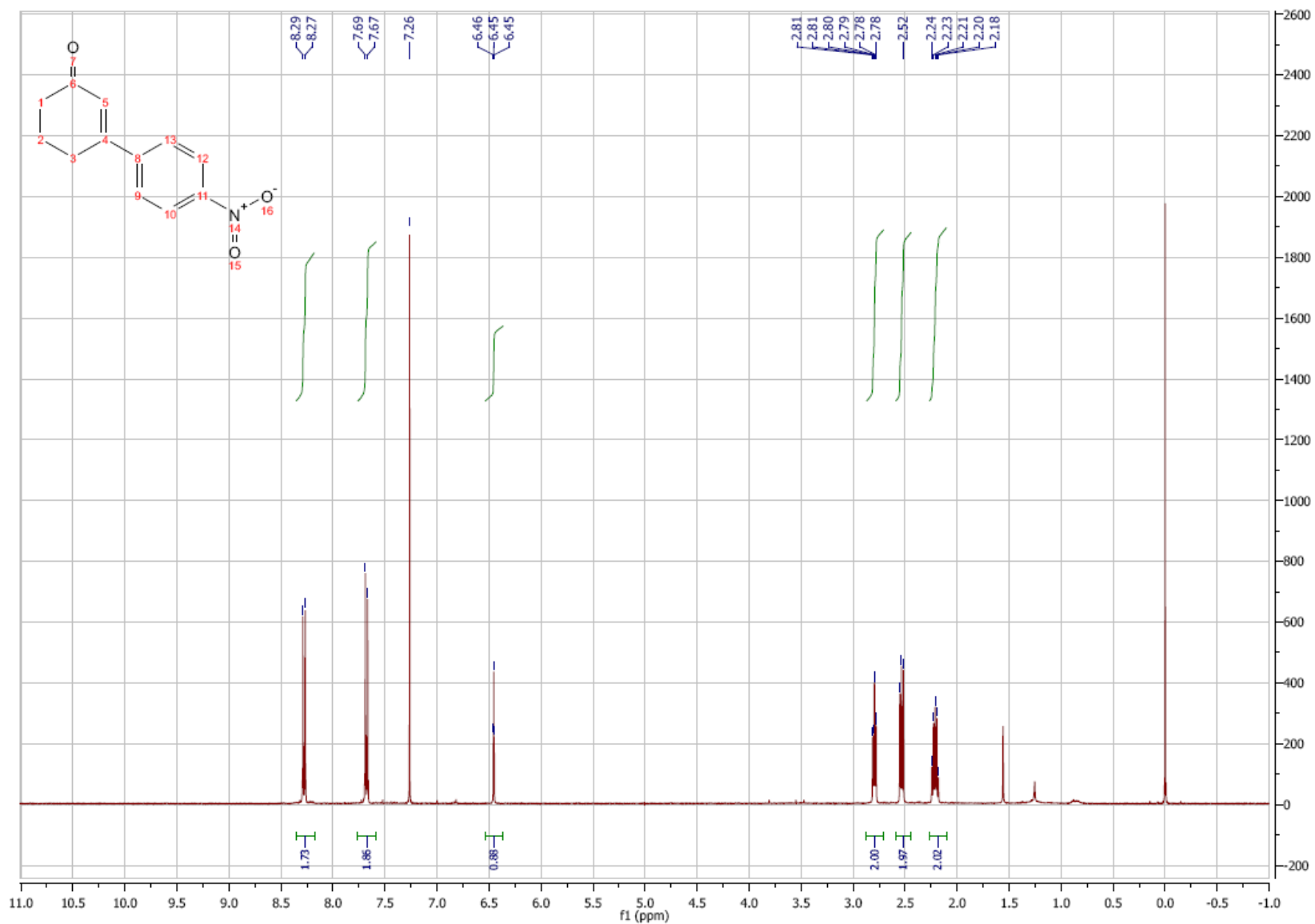


Para-Fluoro-13C  
Std Carbon experiment

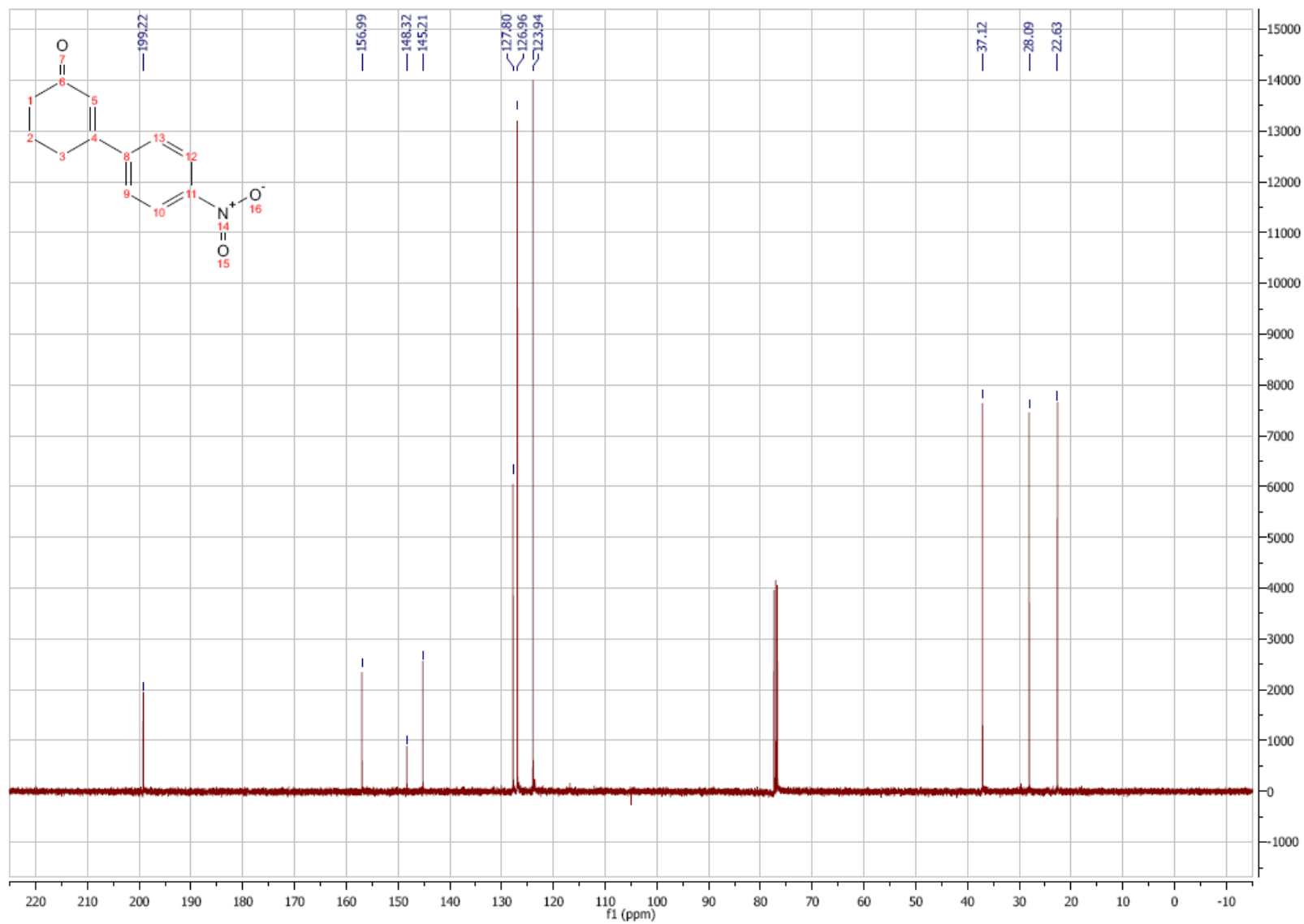


3-(4-(trifluoromethyl)phenyl)cyclohex-2-enone (9c)

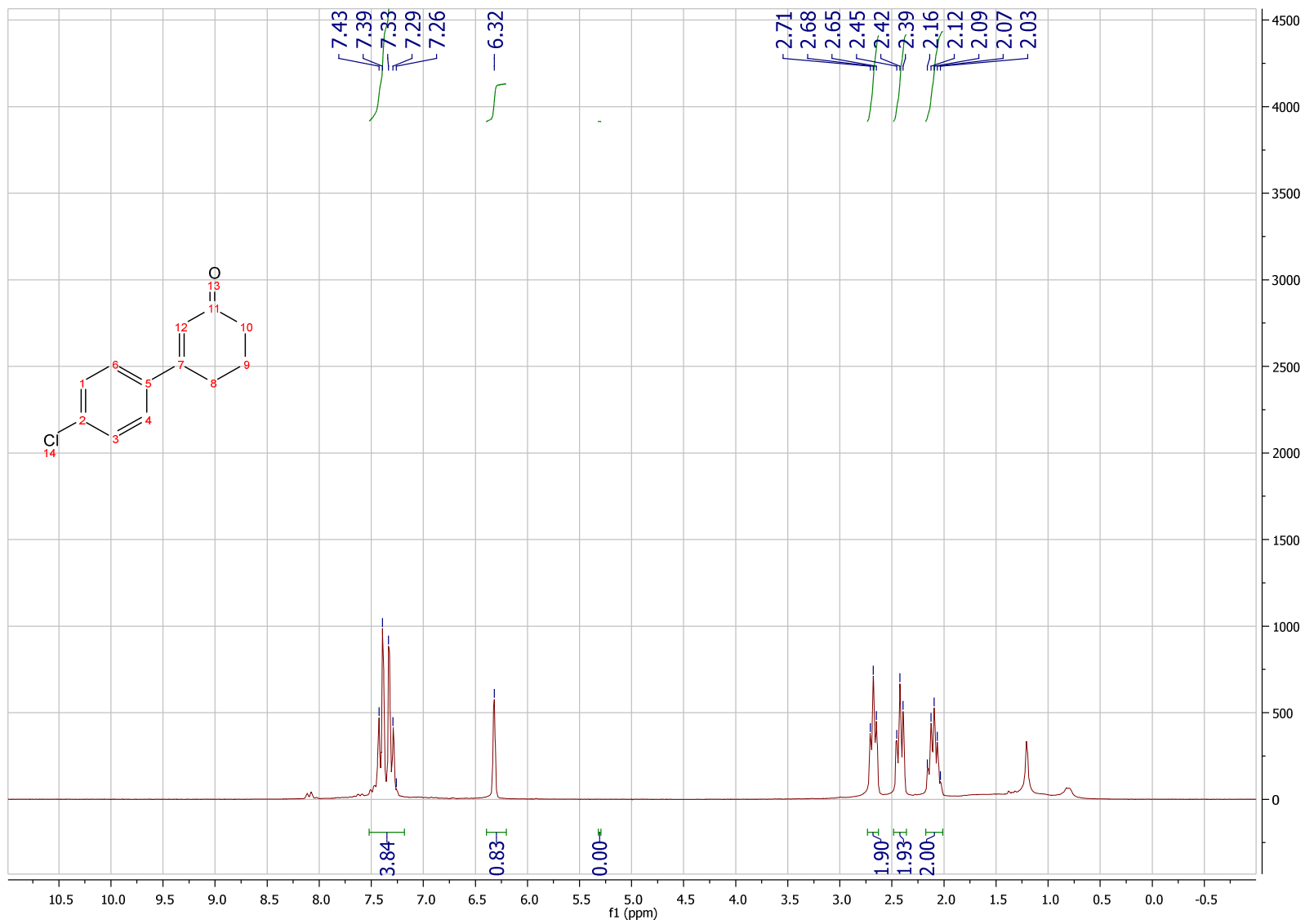
4-nitro-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (9d)

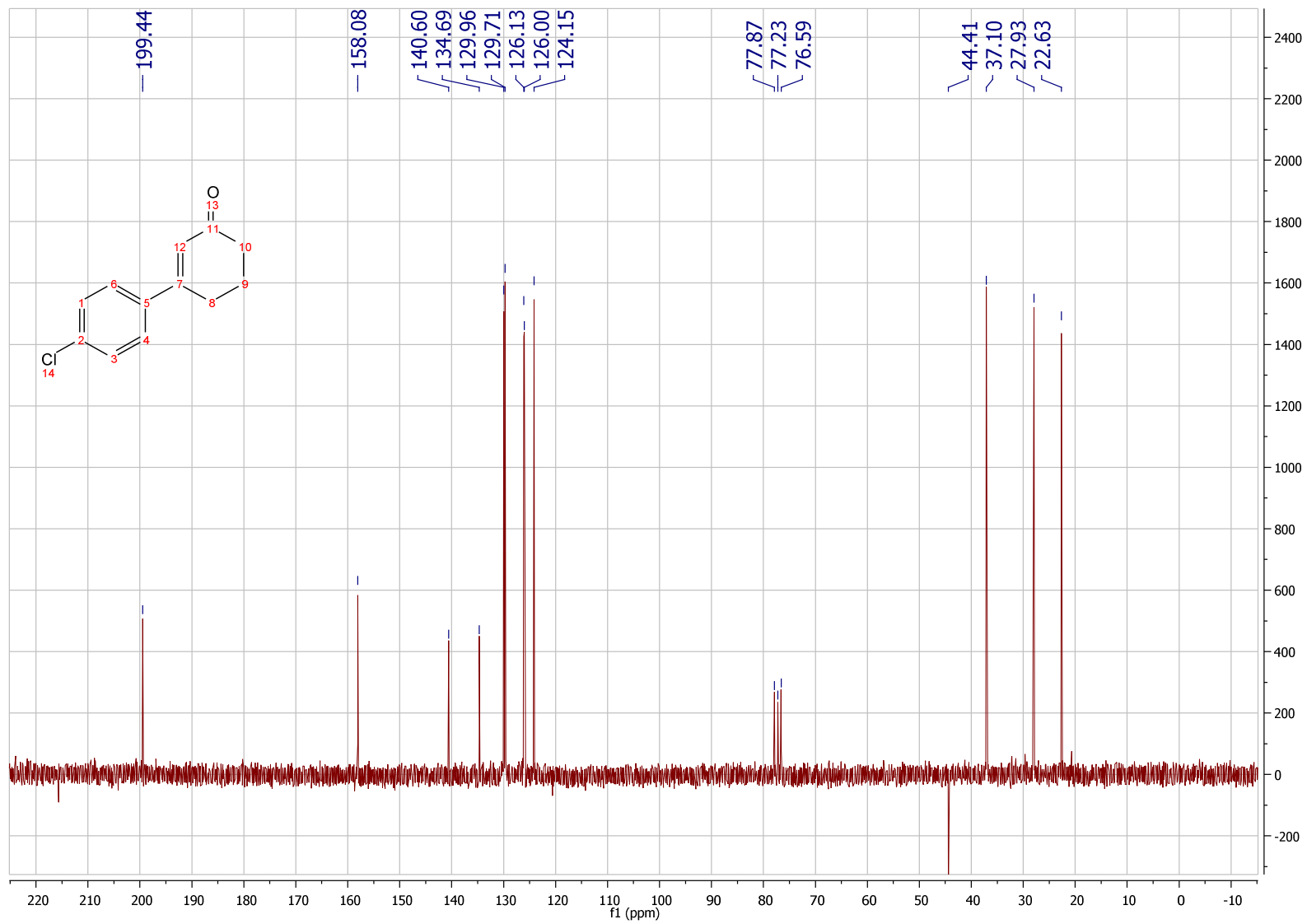


4'-nitro-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (9d)

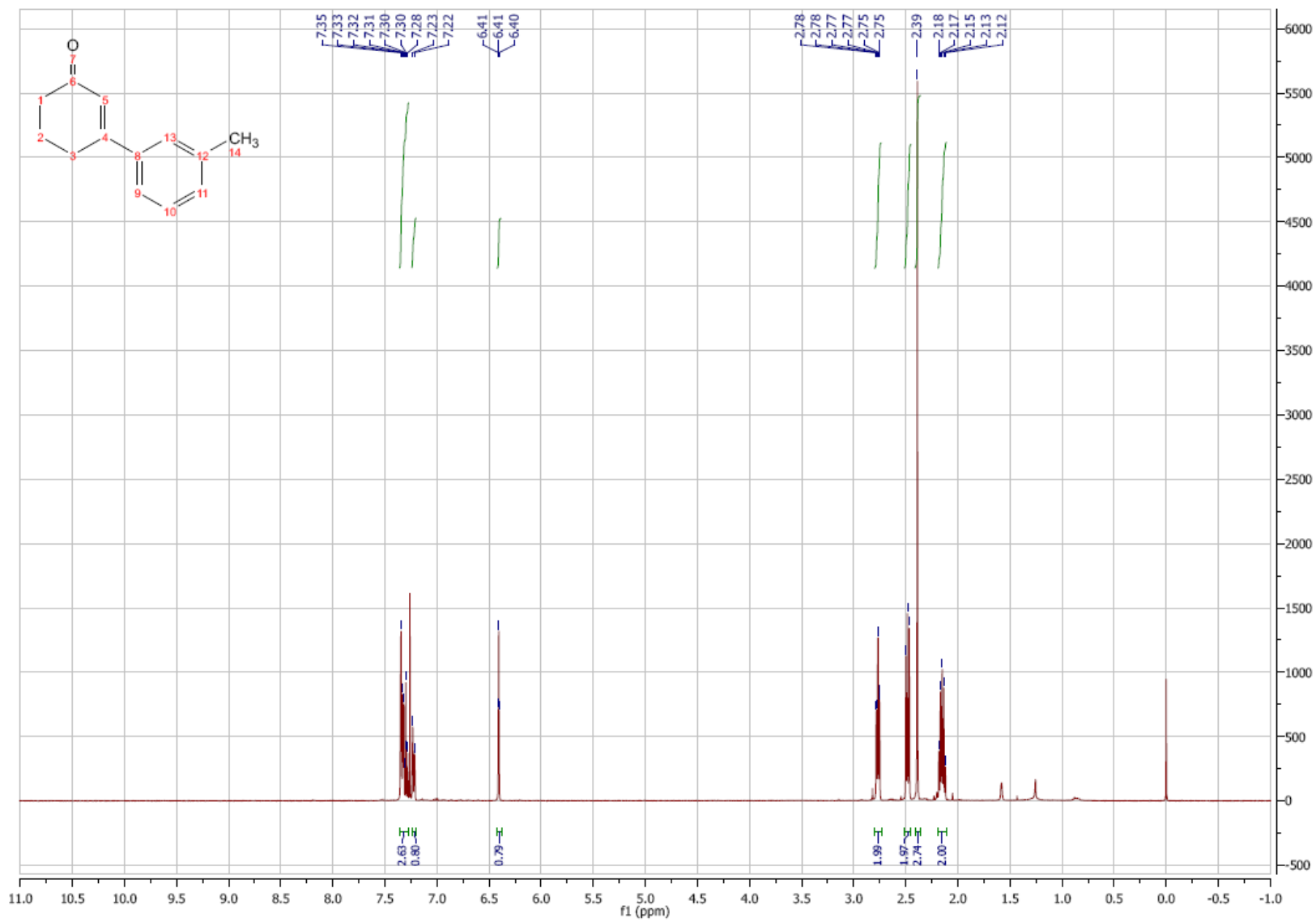


3-(4-chlorophenyl)cyclohex-2-enone (9e)

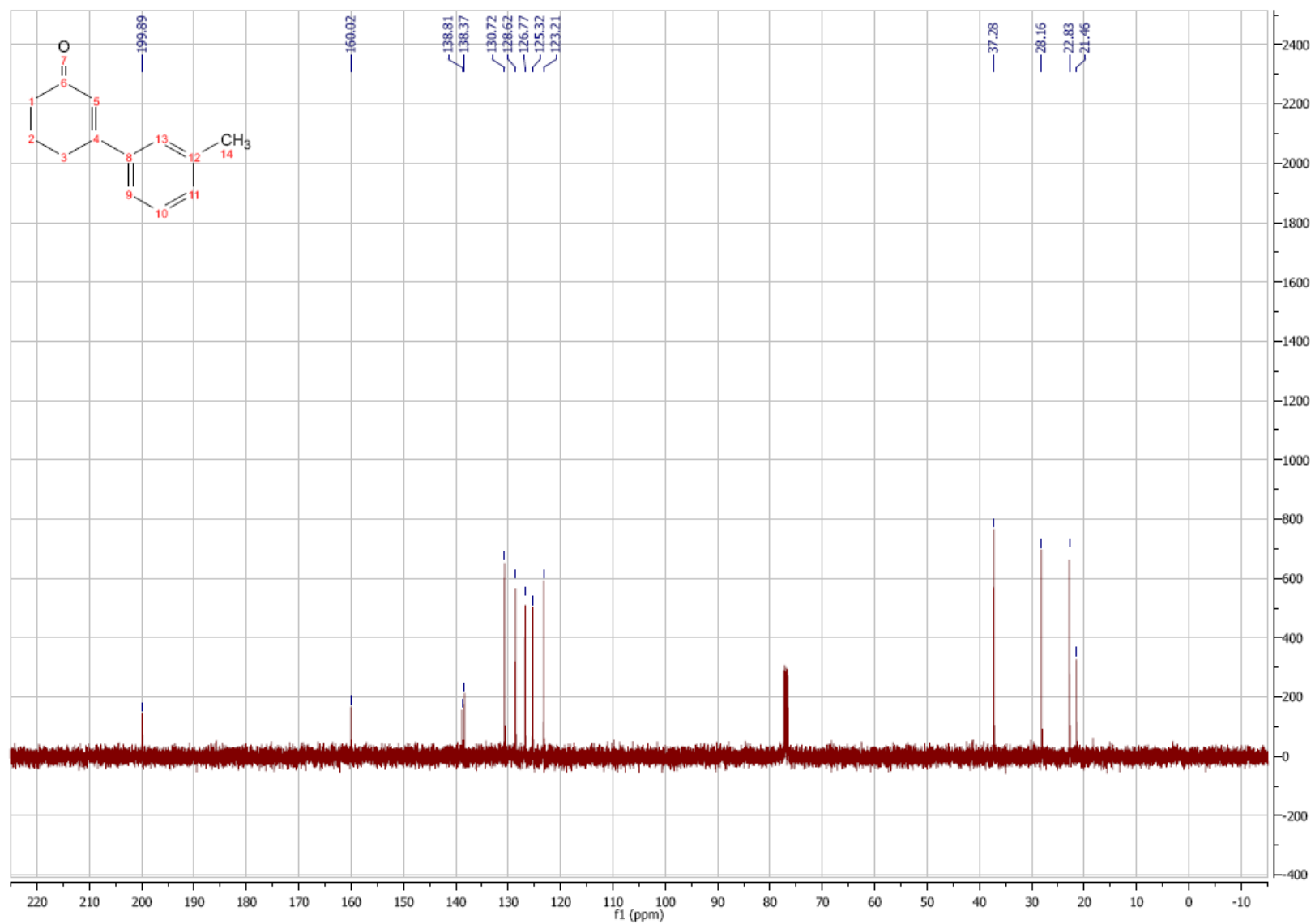




3-(4-chlorophenyl)cyclohex-2-enone (9e)

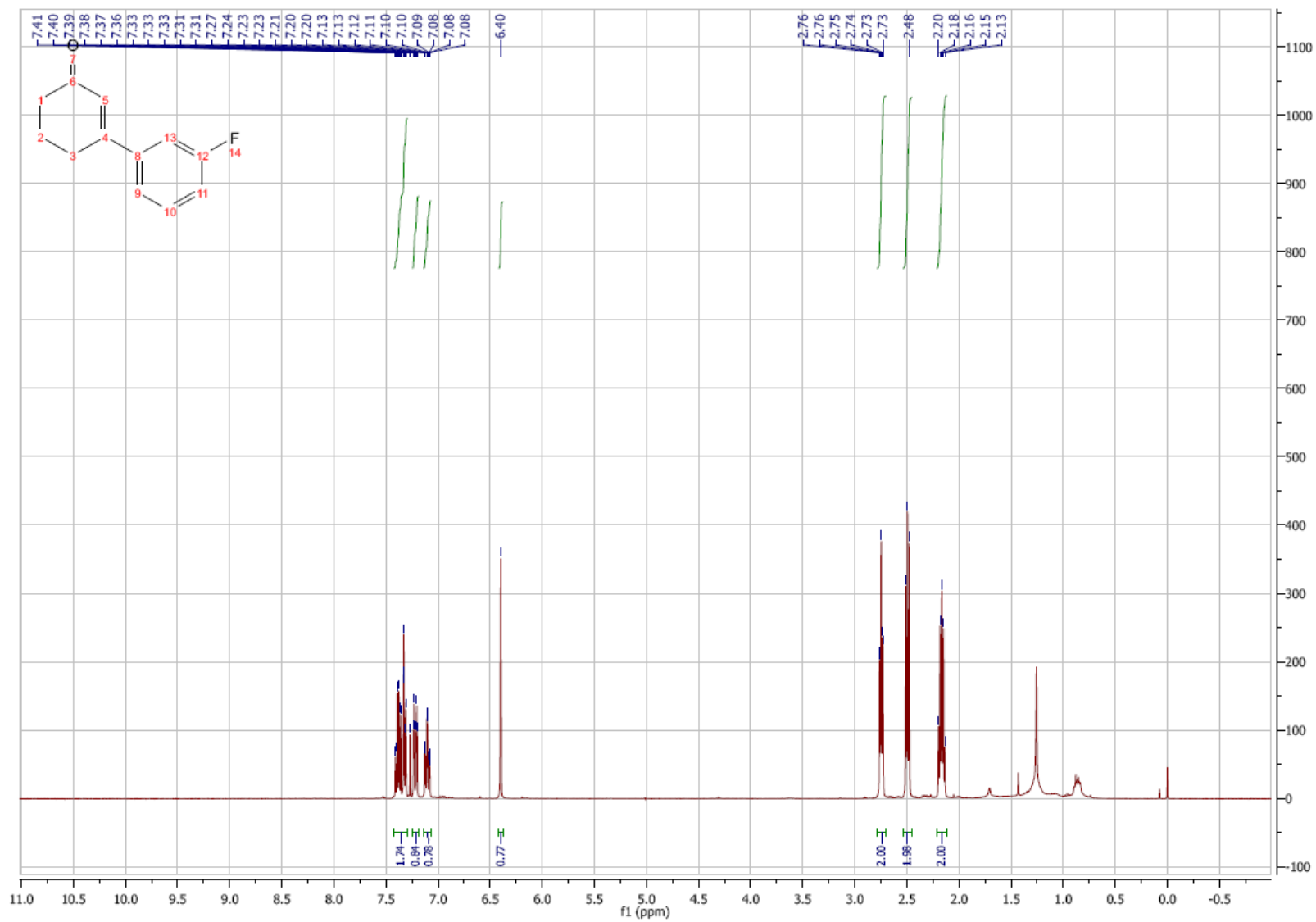


3-methyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (9f)

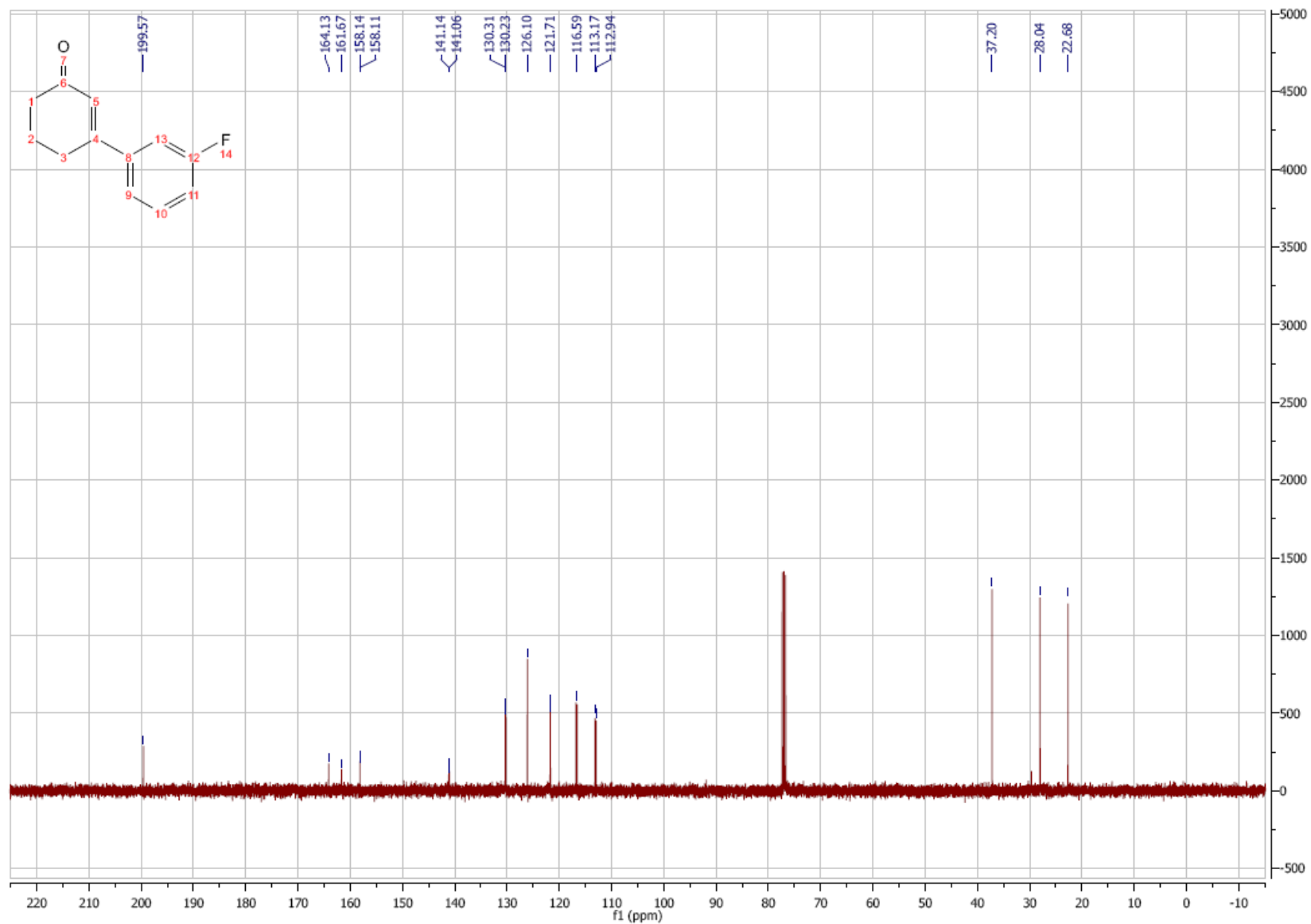


3'-methyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (9f)

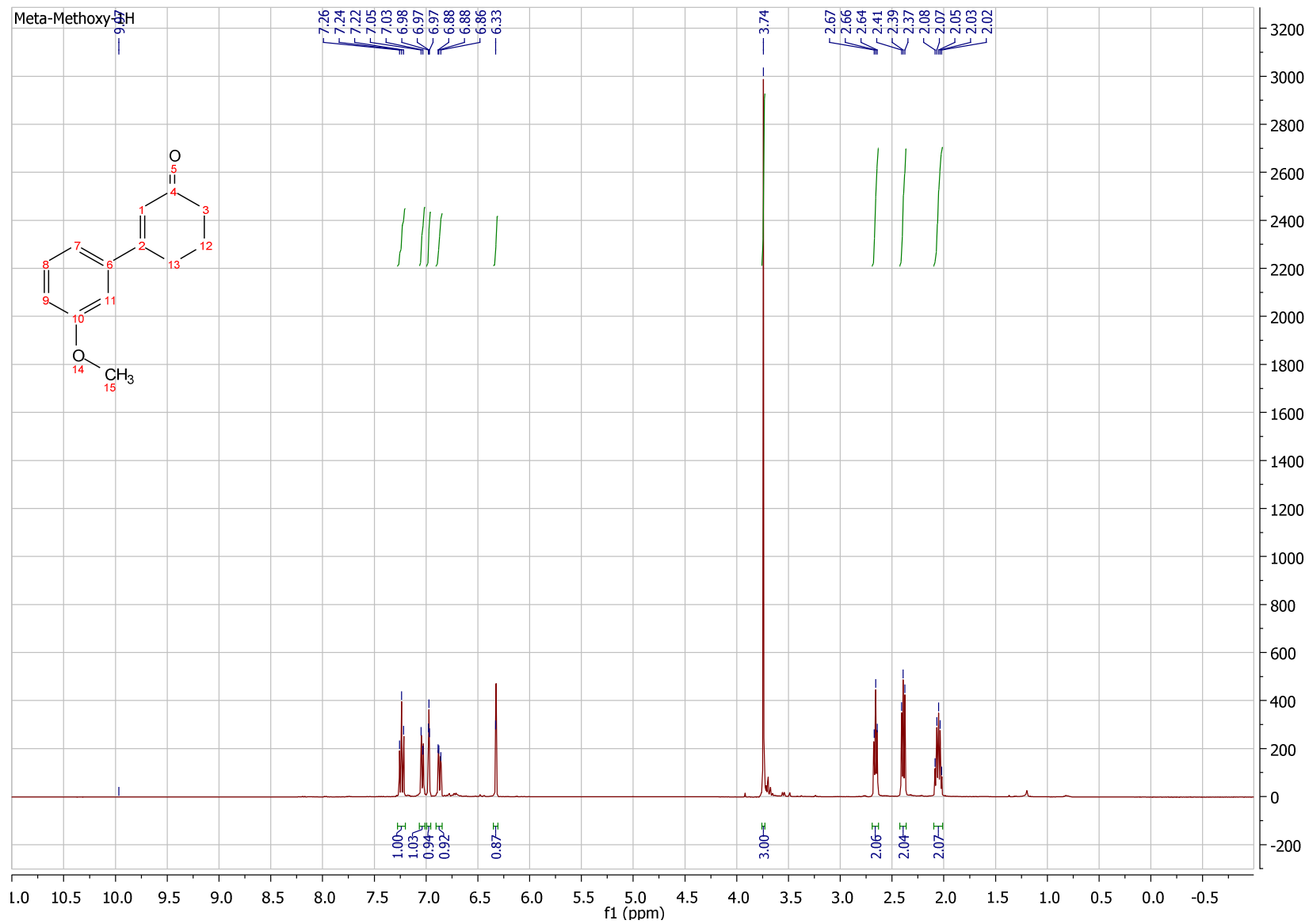
3'-fluoro-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (9g)



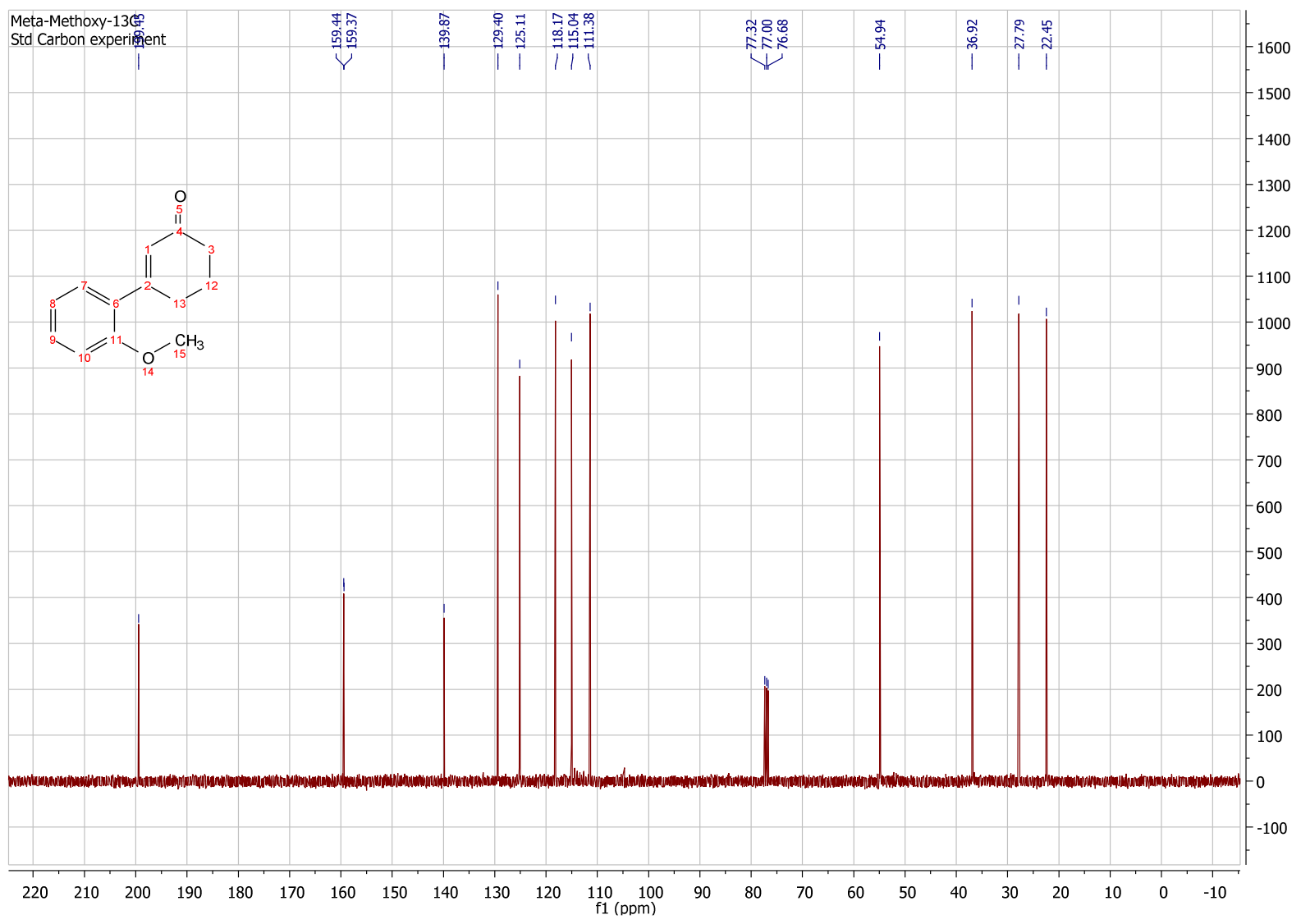
3'-fluoro-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (9g)



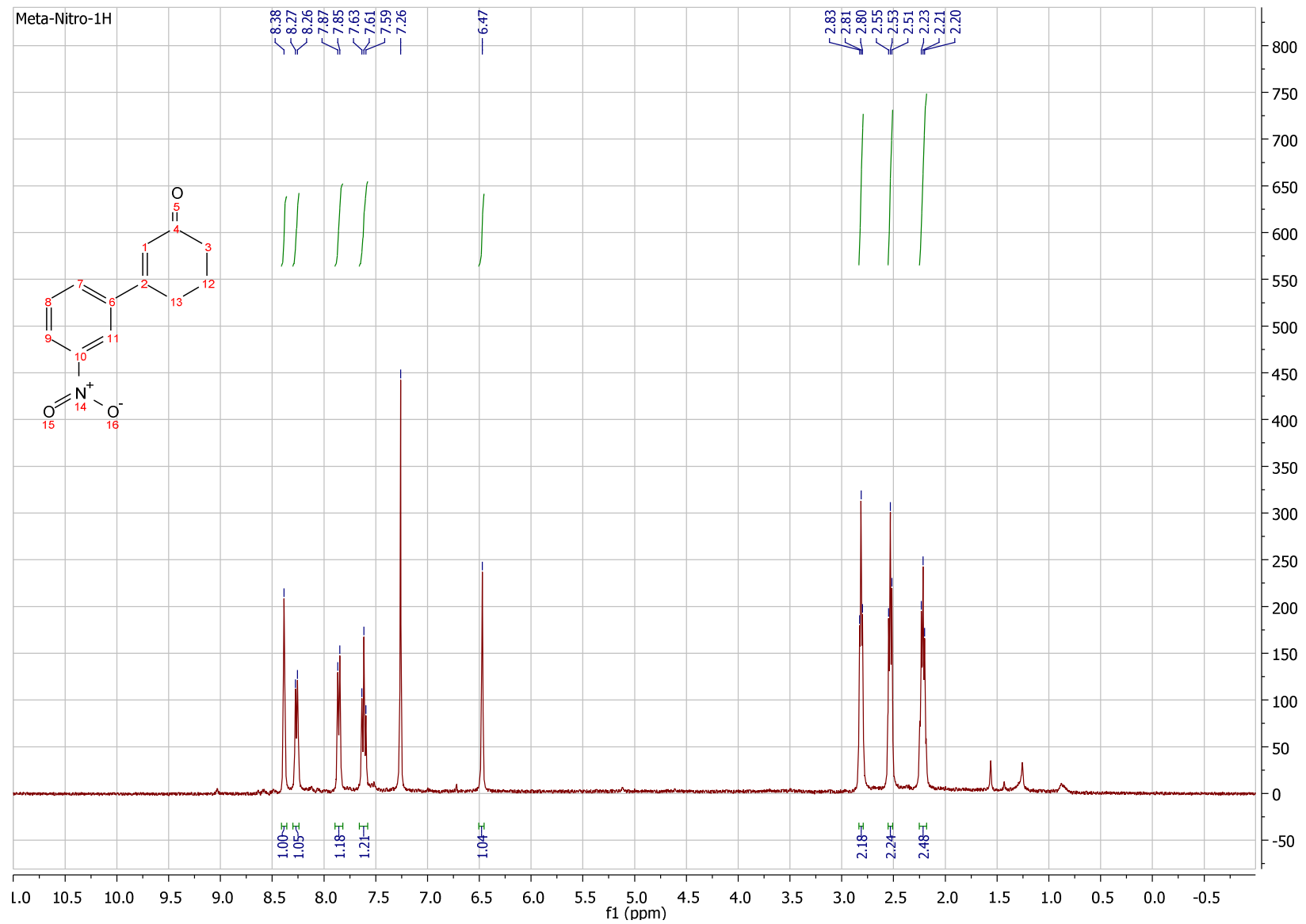
3-(3-methoxyphenyl)cyclohex-2-enone (9h)



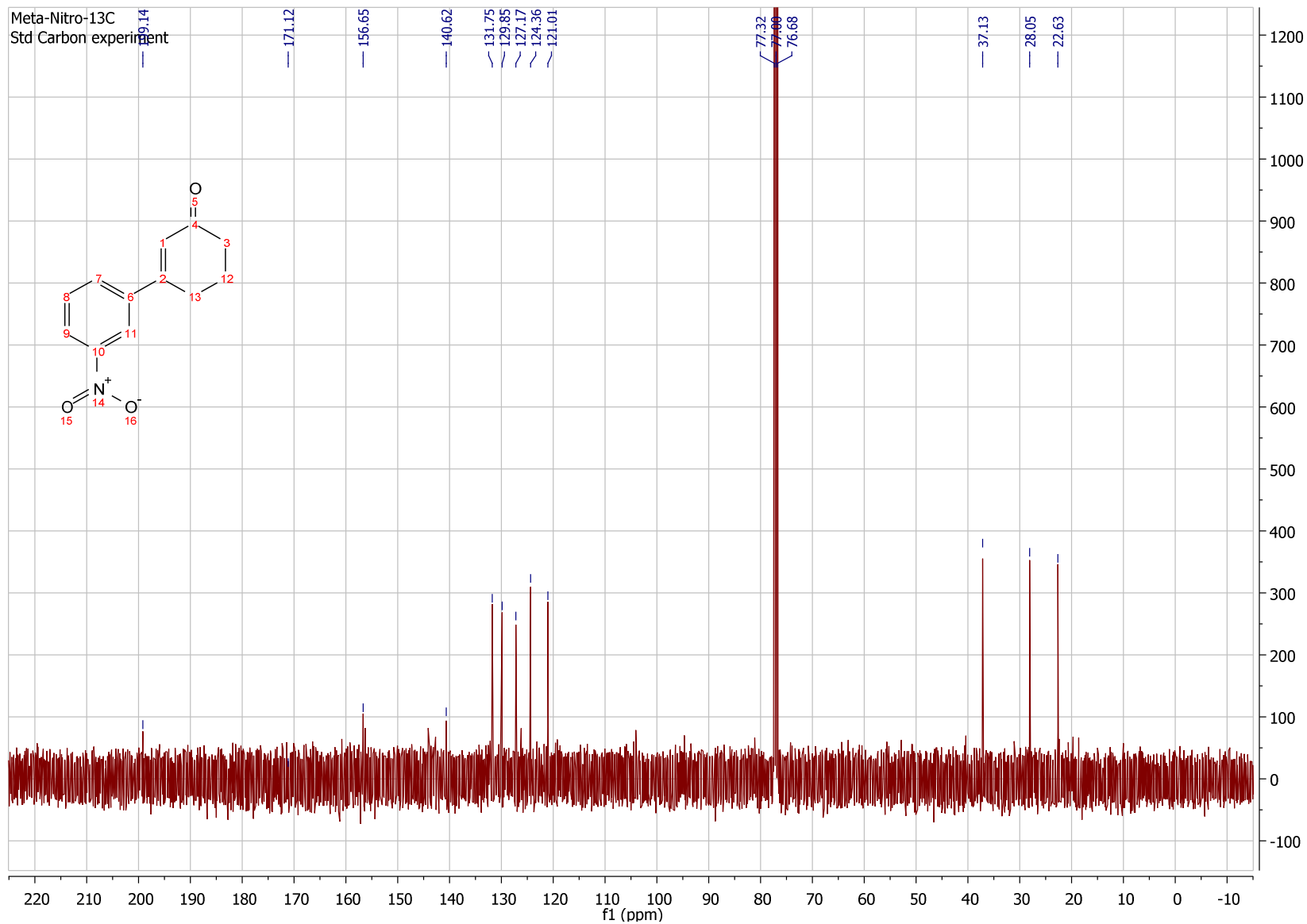
3-(3-methoxyphenyl)cyclohex-2-enone (9h)



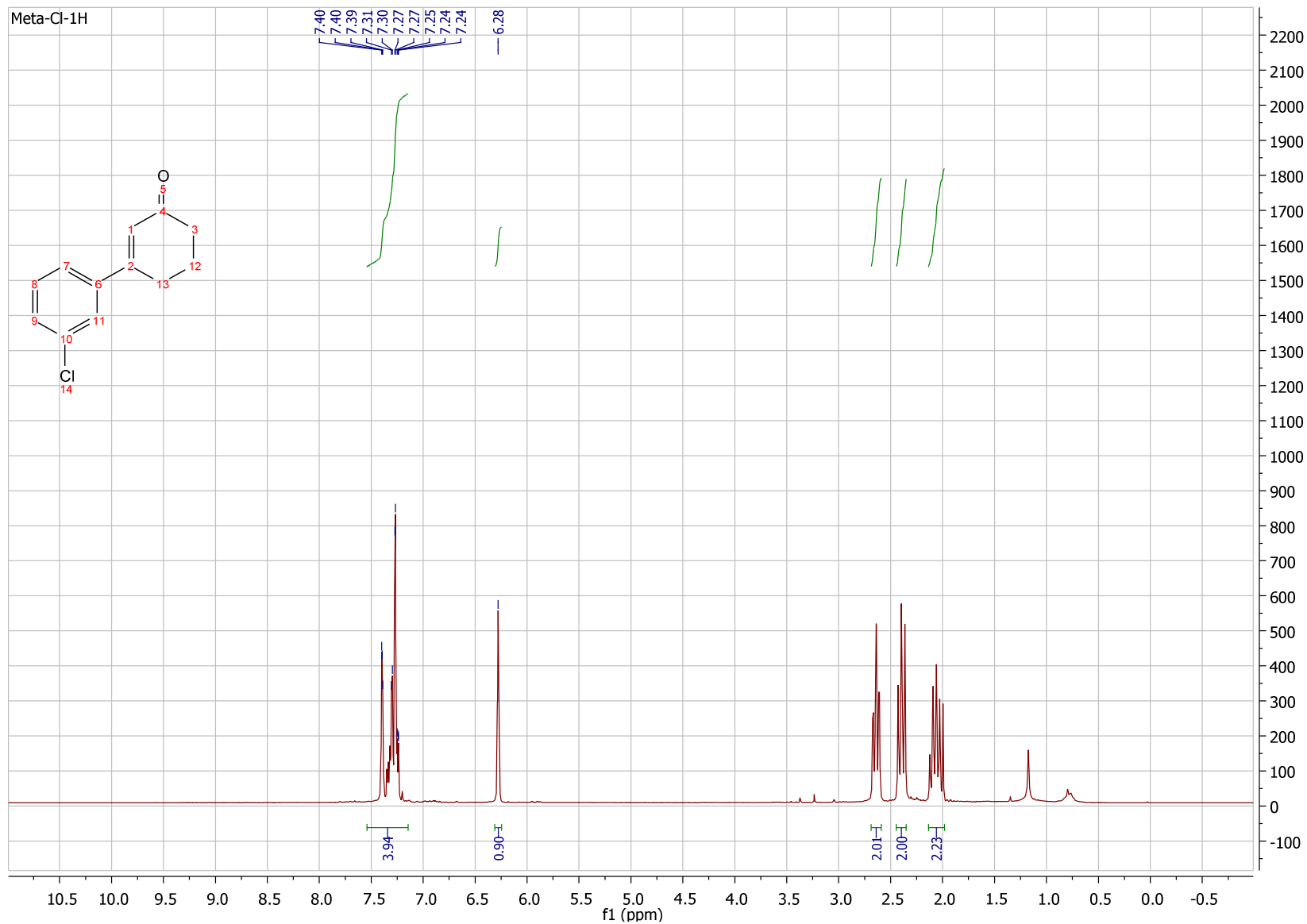
3-(3-nitrophenyl)cyclohex-2-enone (9i)



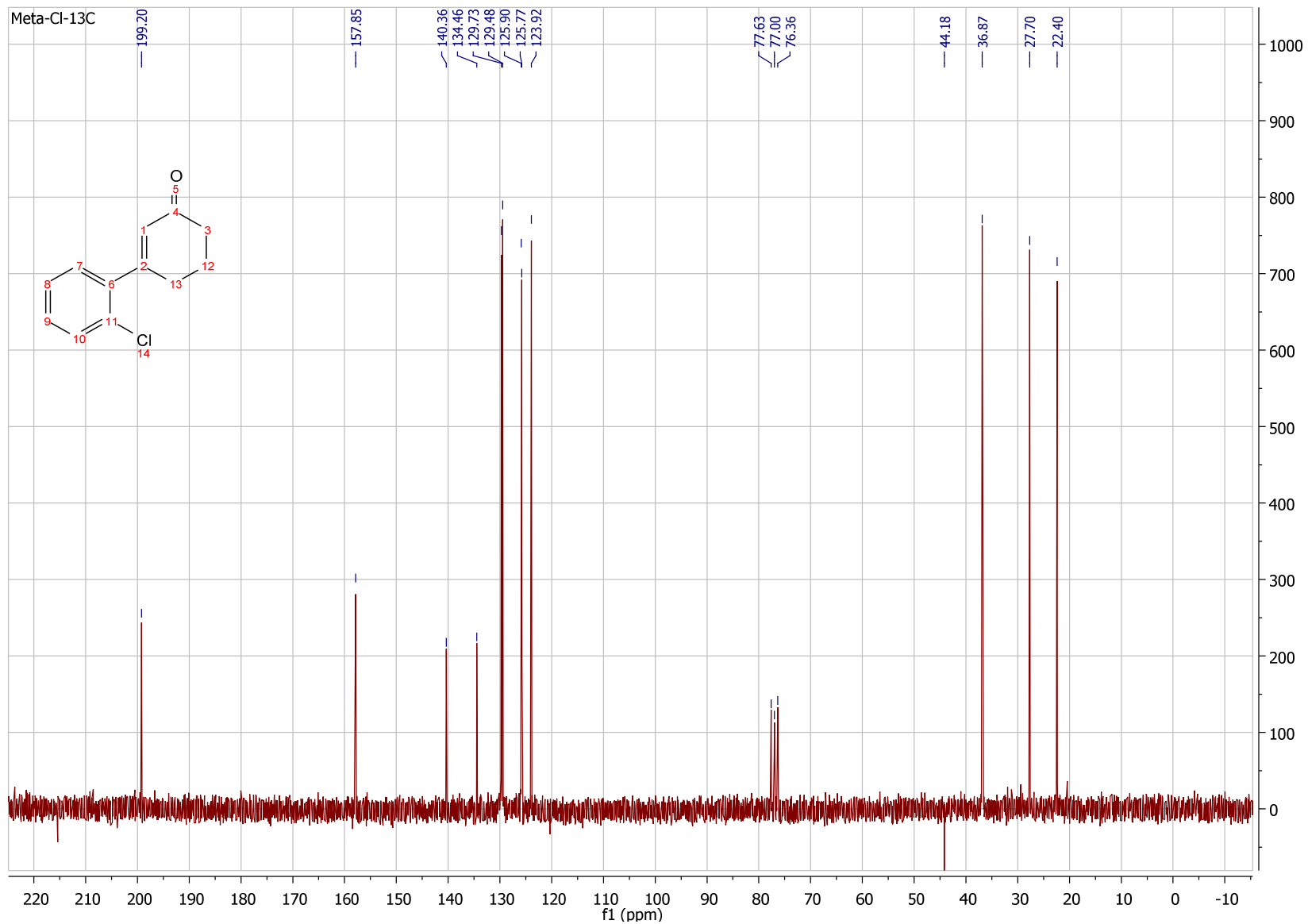
3-(3-nitrophenyl)cyclohex-2-enone (9i)



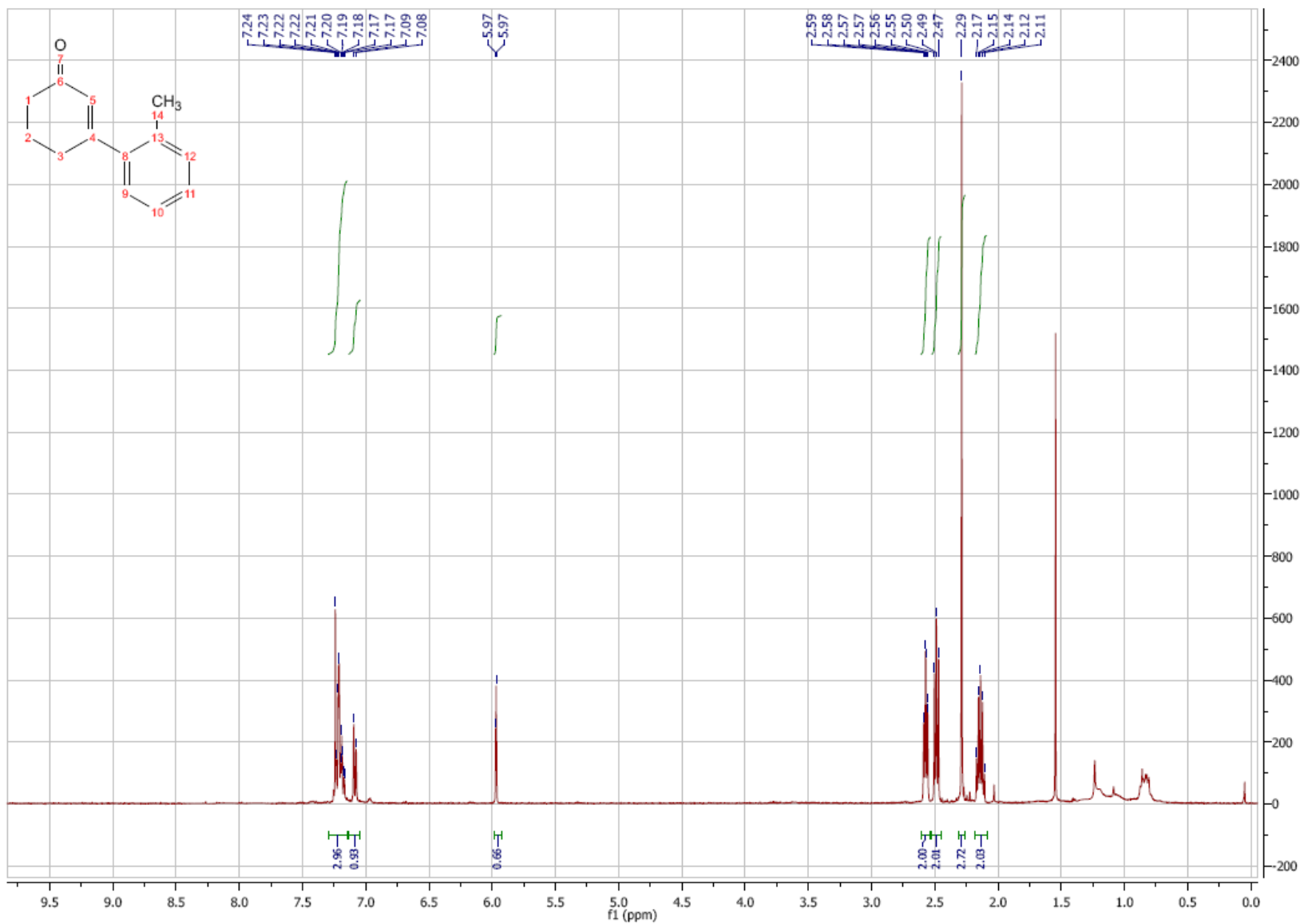
3-(3-chlorophenyl)cyclohex-2-enone (9)



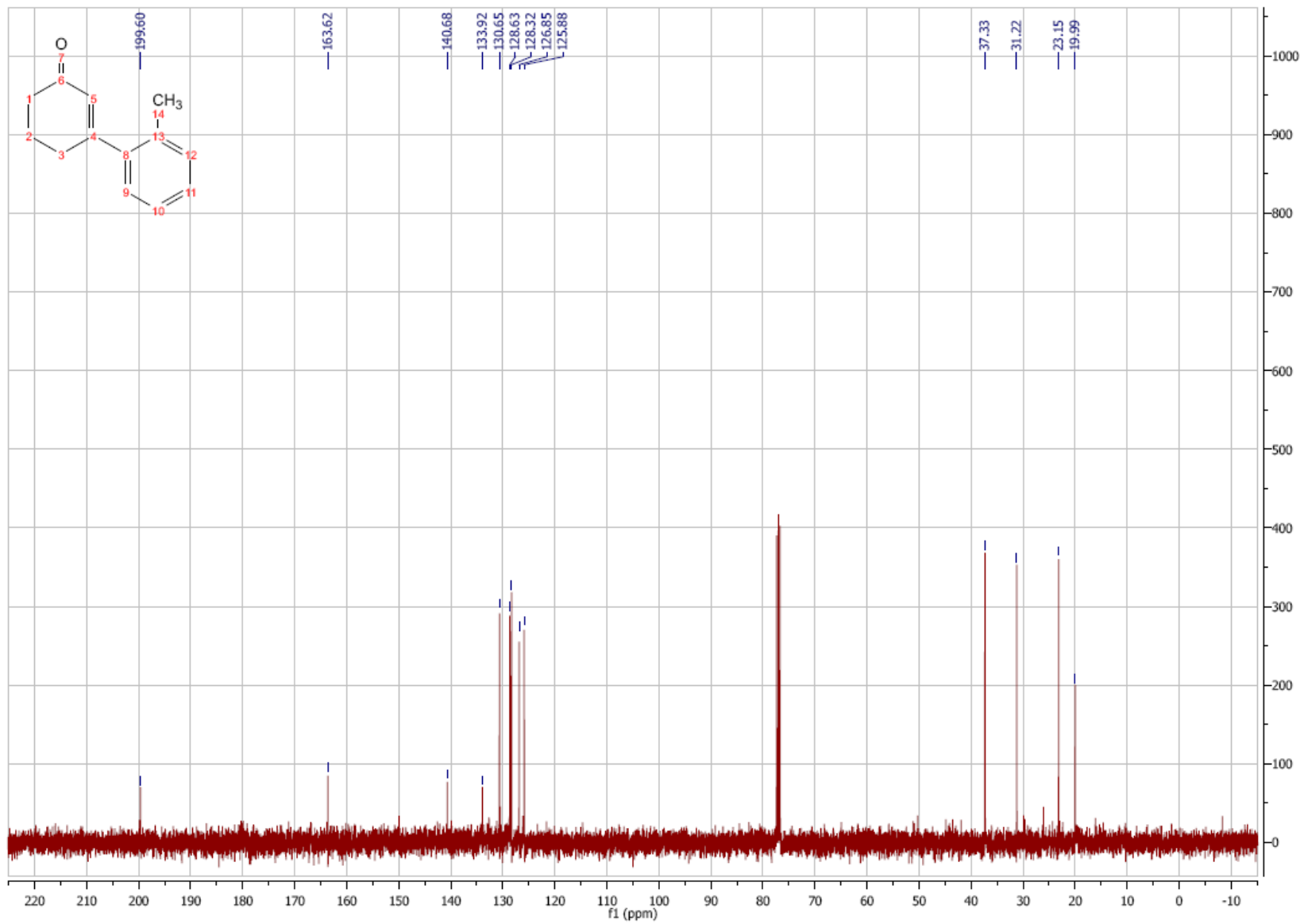
3-(3-chlorophenyl)cyclohex-2-enone (9j)

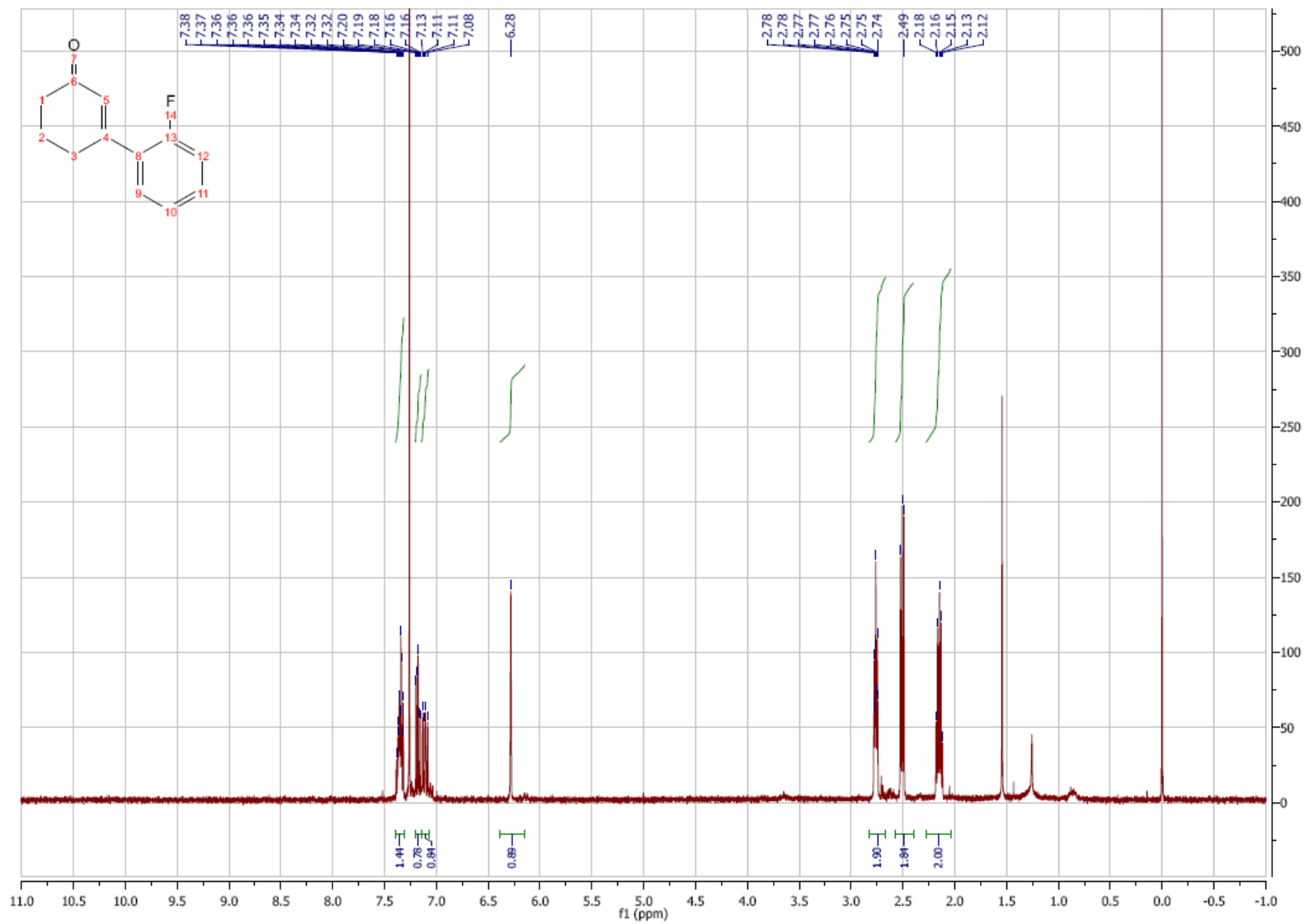


2'-methyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (9k)

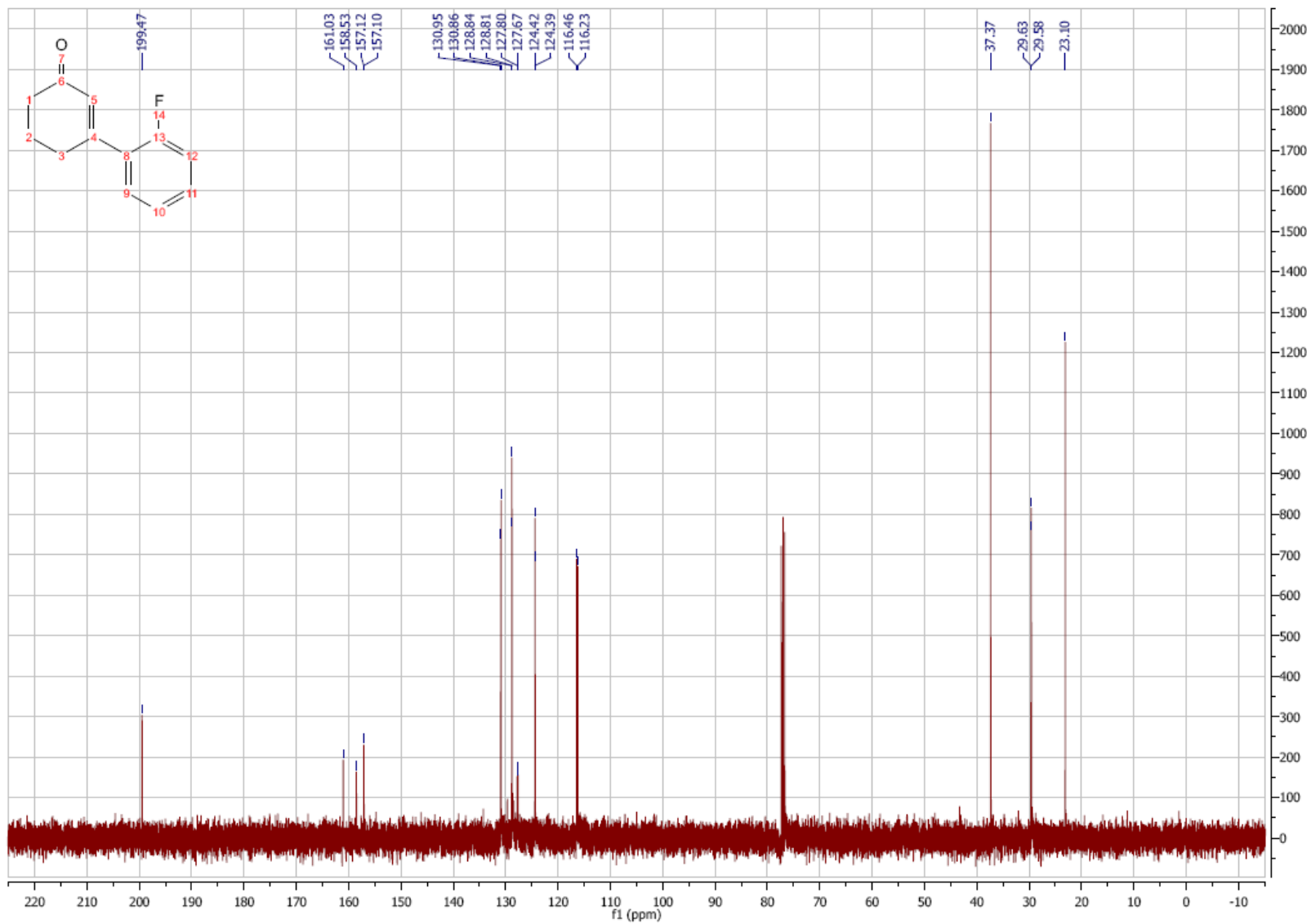


2'-methyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (9k)



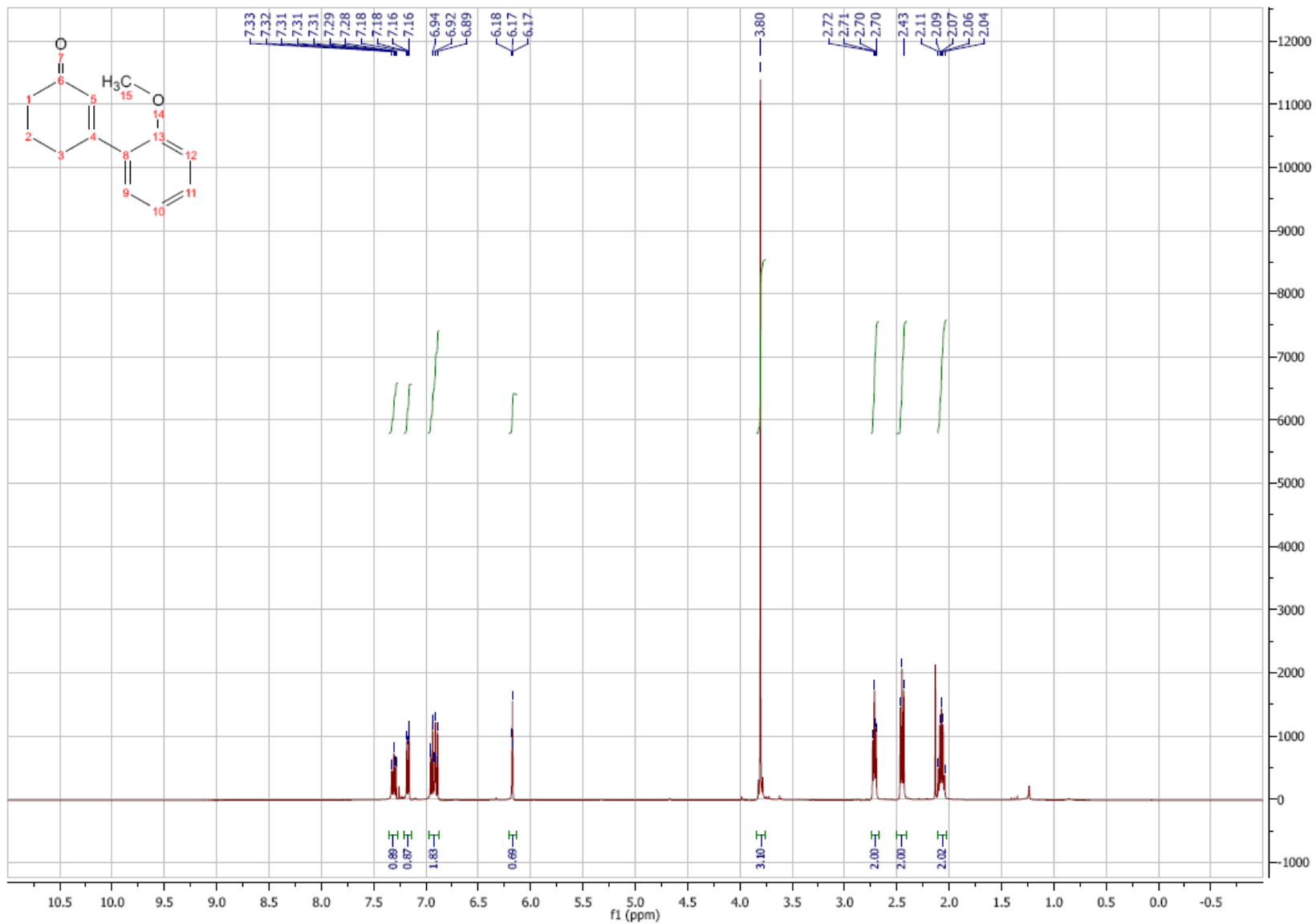


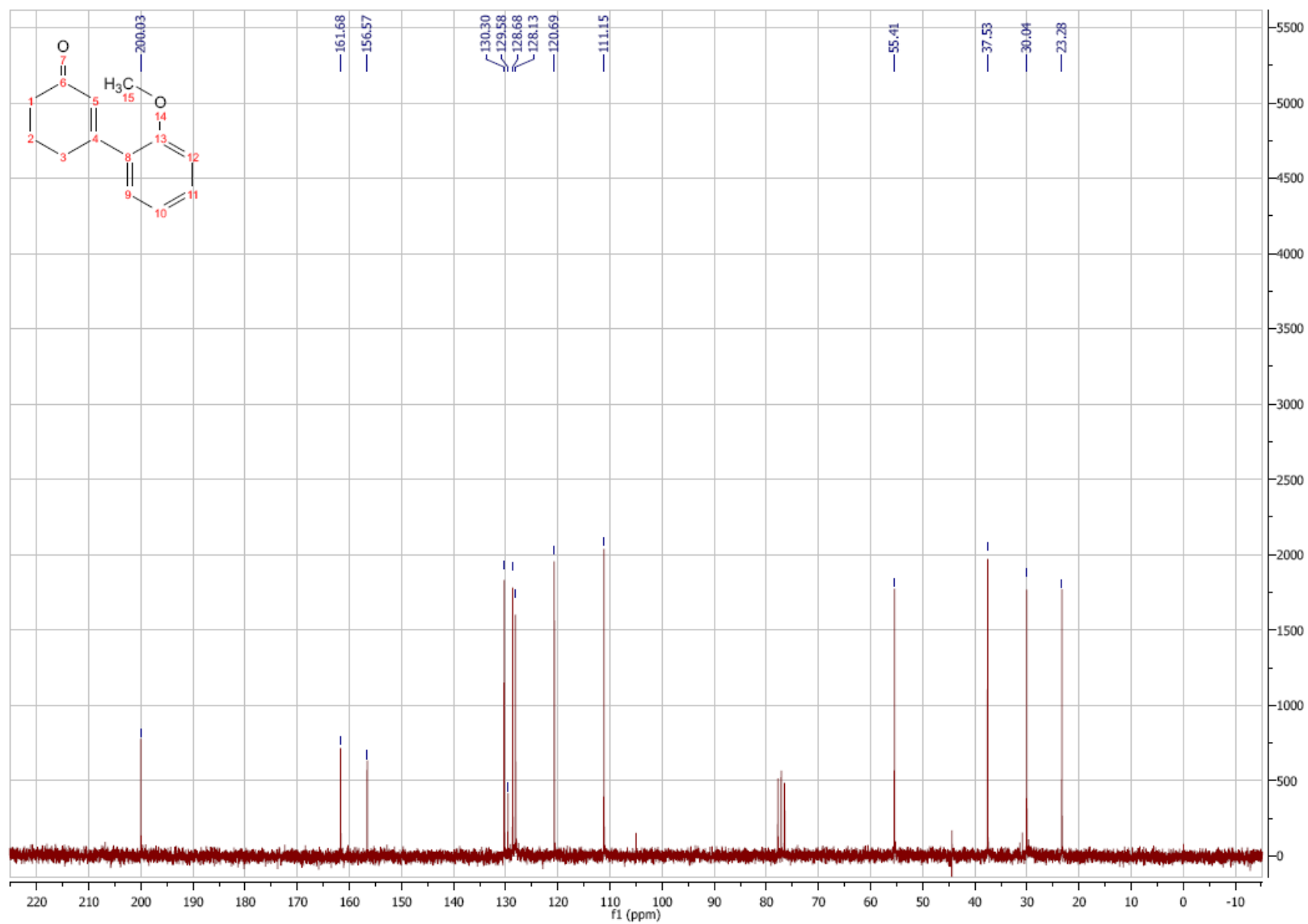
3-(2-fluorophenyl)cyclohex-2-enone (9l)



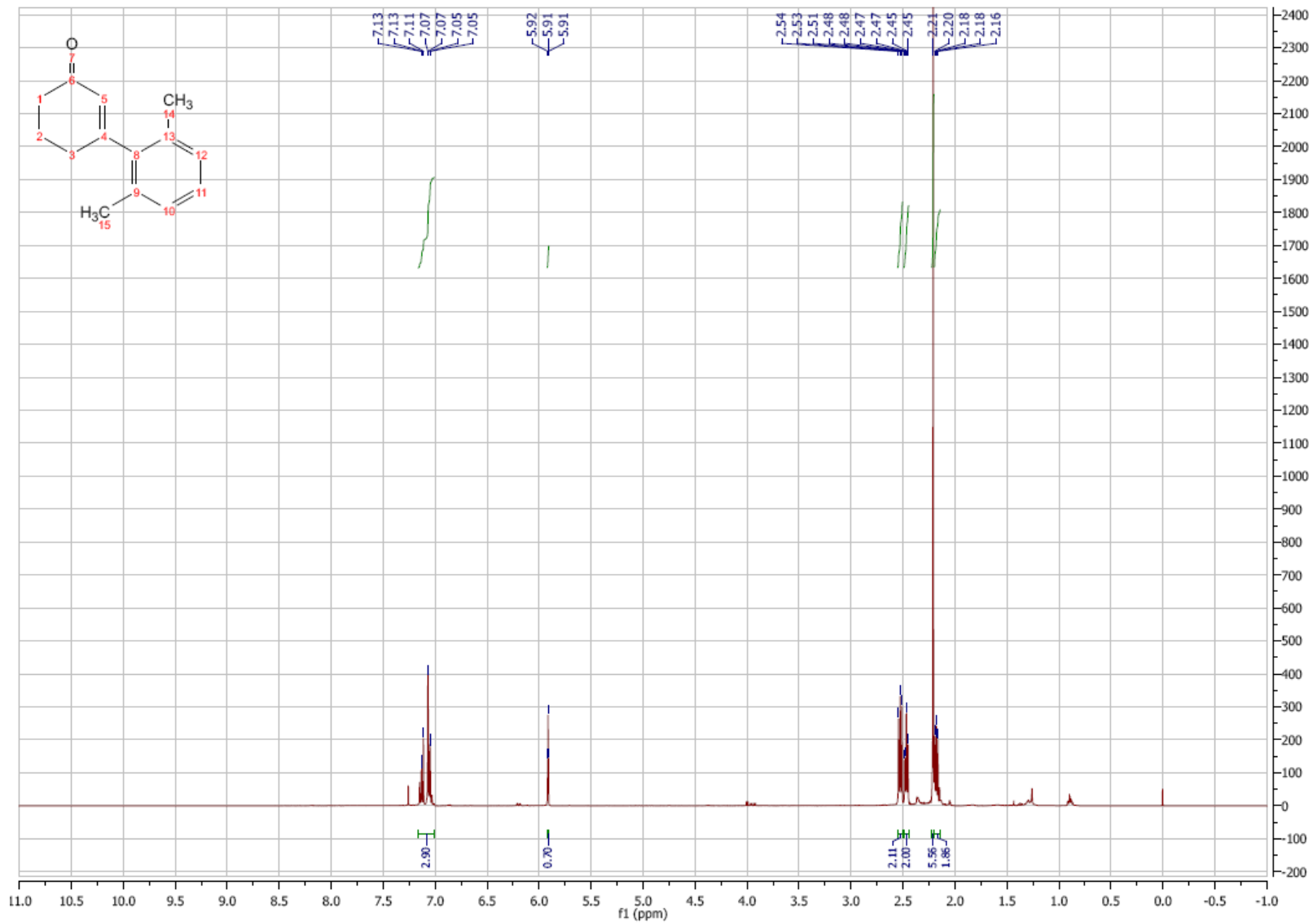
3-(2-fluorophenyl)cyclohex-2-enone (9l)

3-(2-methoxyphenyl)cyclohex-2-enone (9m)



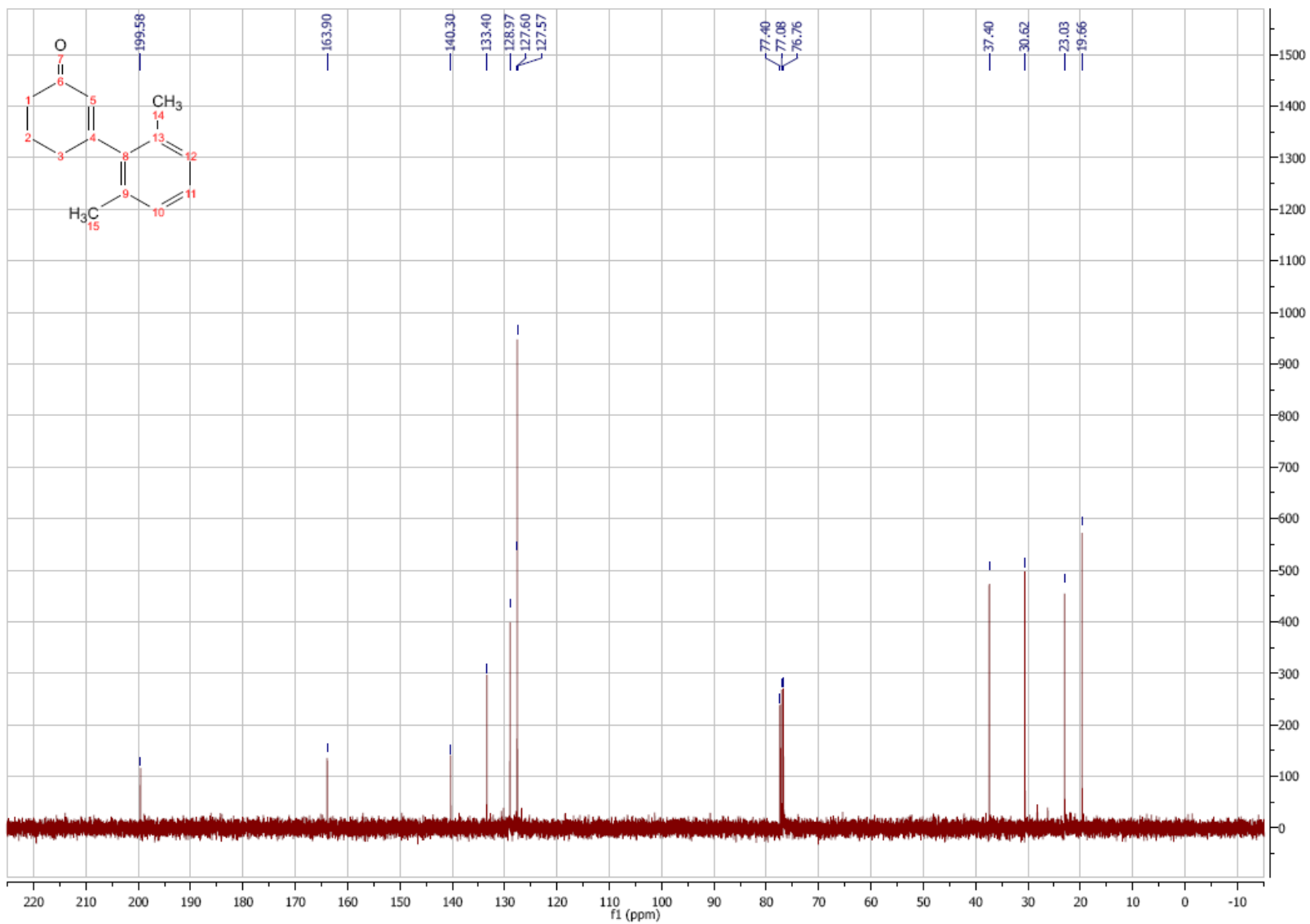


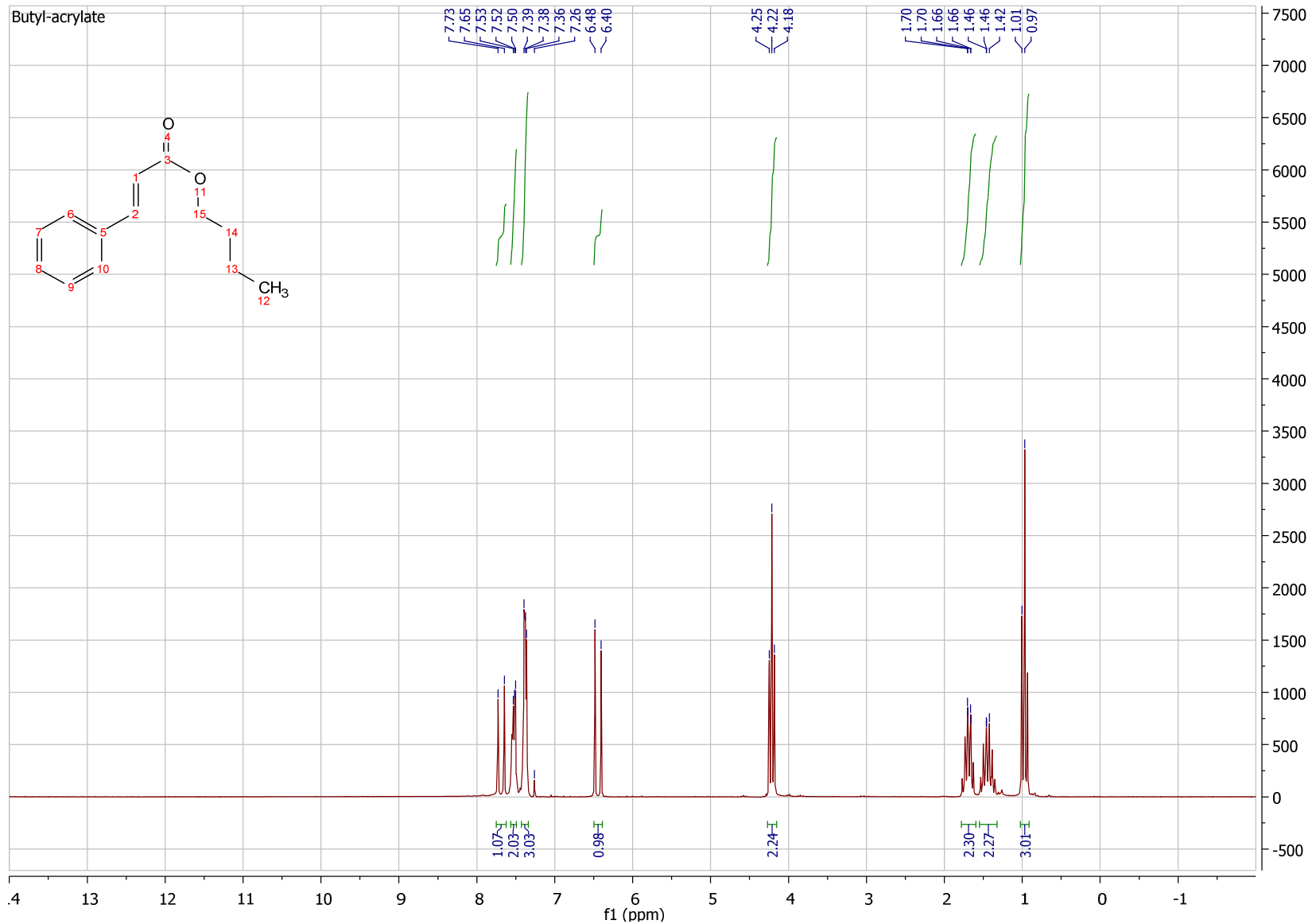
3-(2-methoxyphenyl)cyclohex-2-enone (9m)



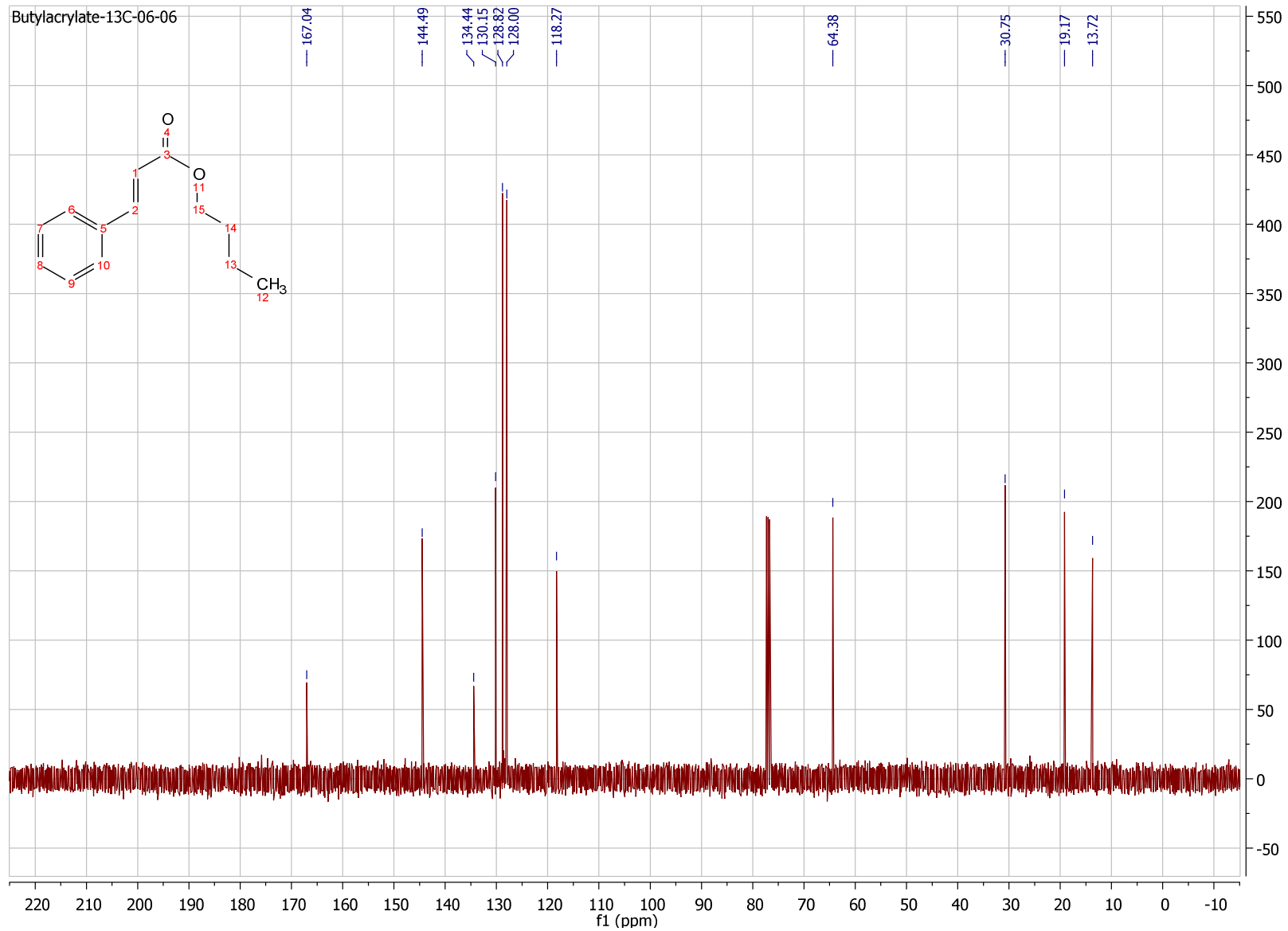
2',6'-dimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (9n)

2',6'-dimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (9n)

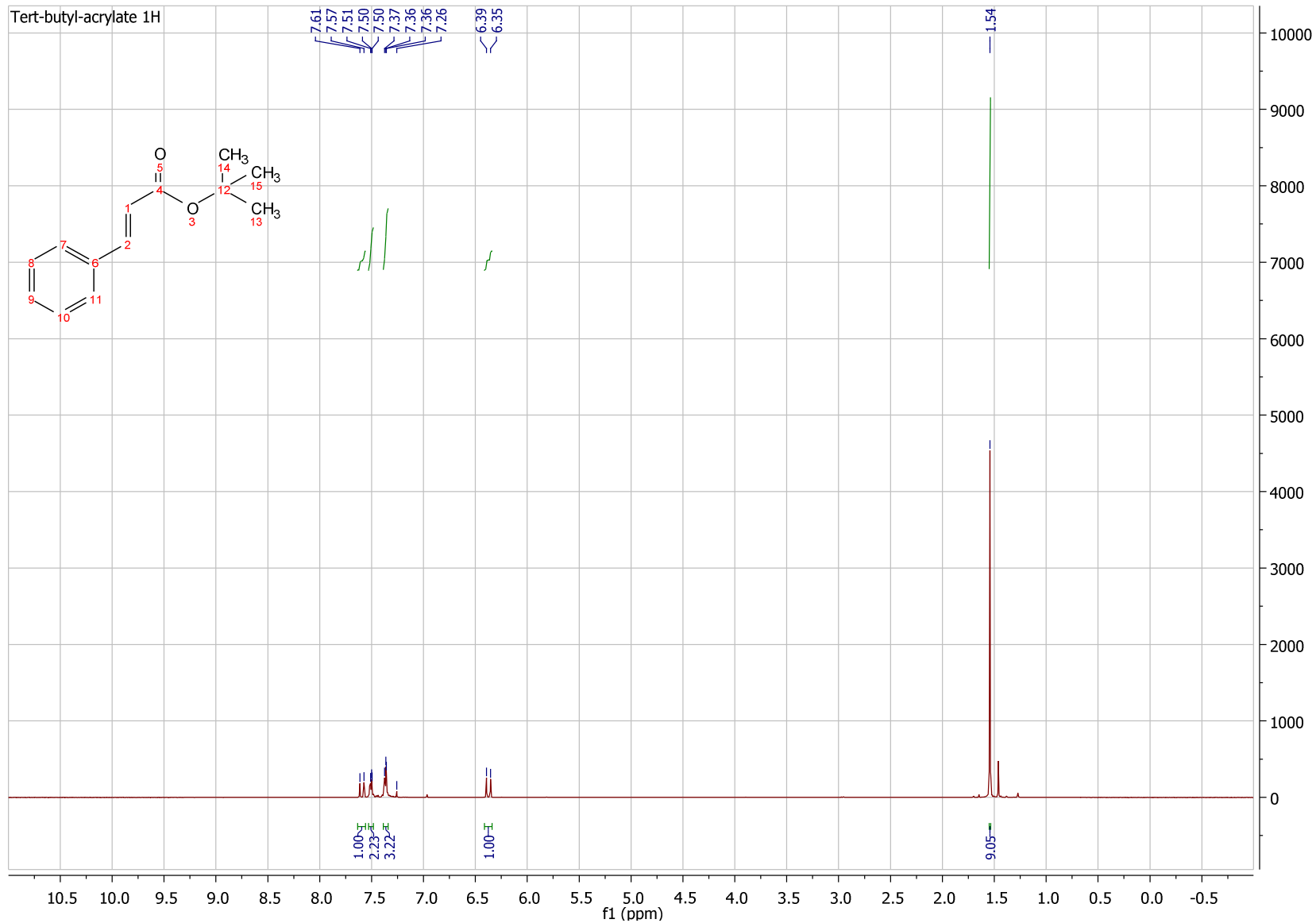




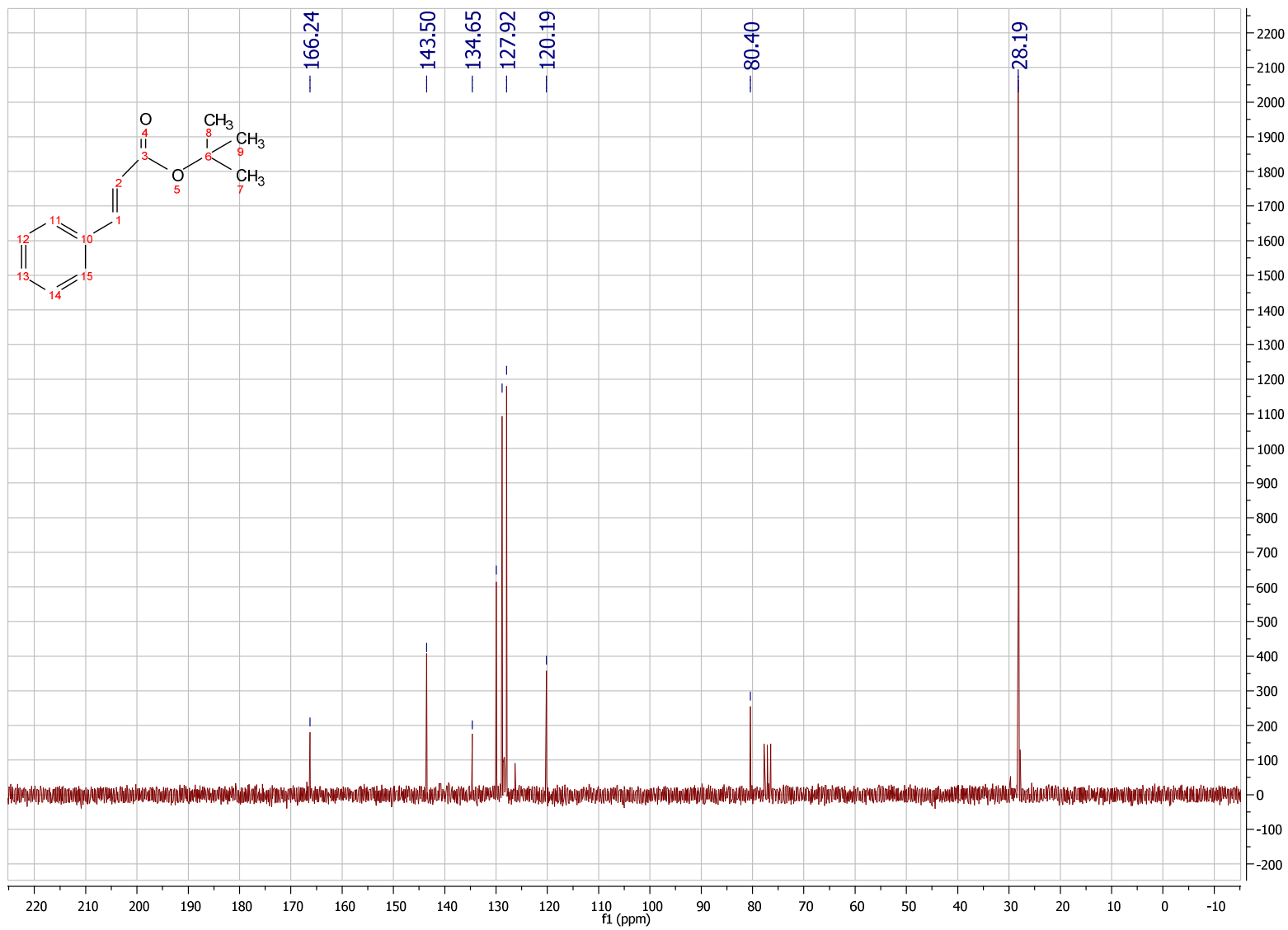
*n*-butyl cinnamate (10a)



*n*-butyl cinnamate (10a)

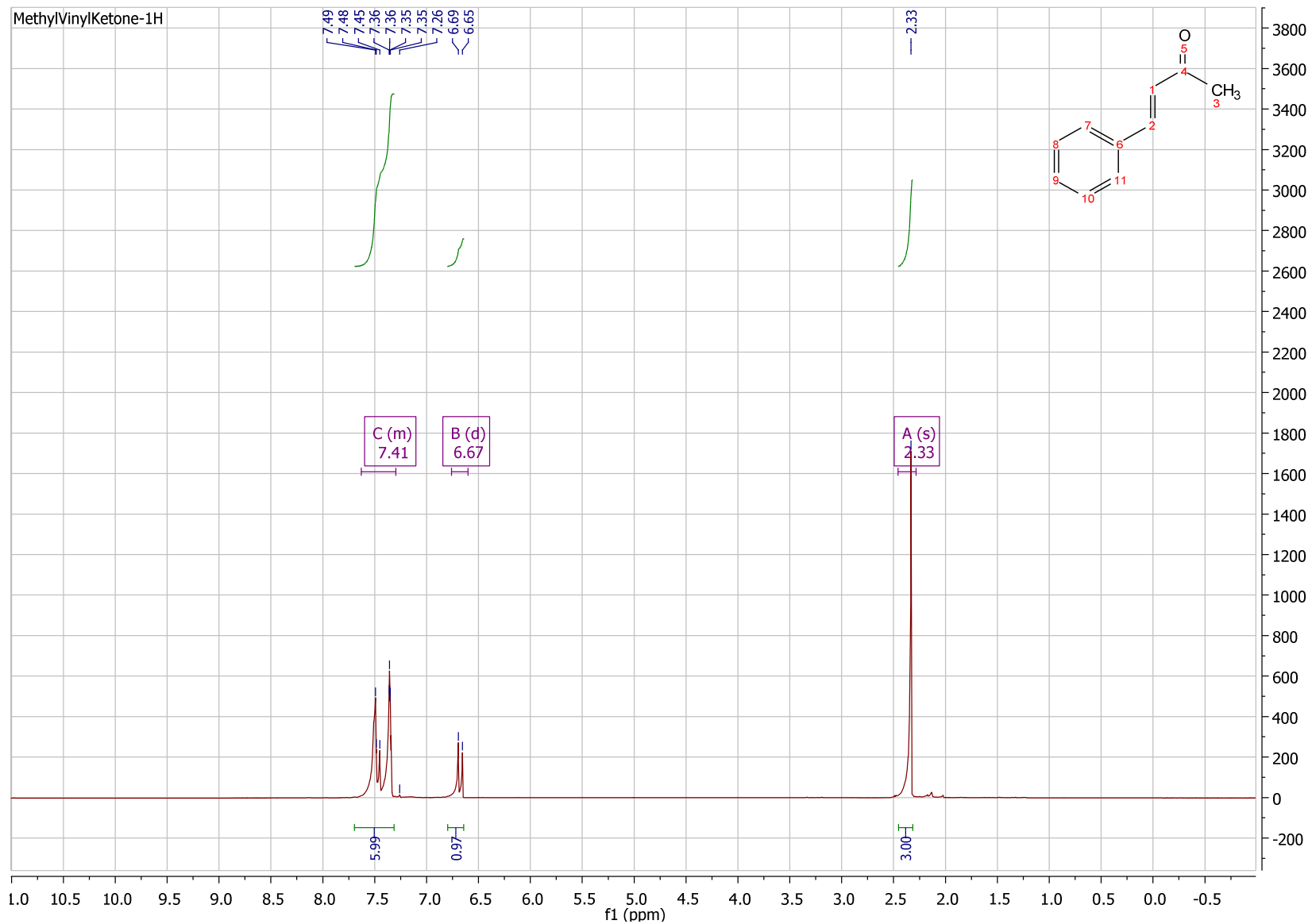


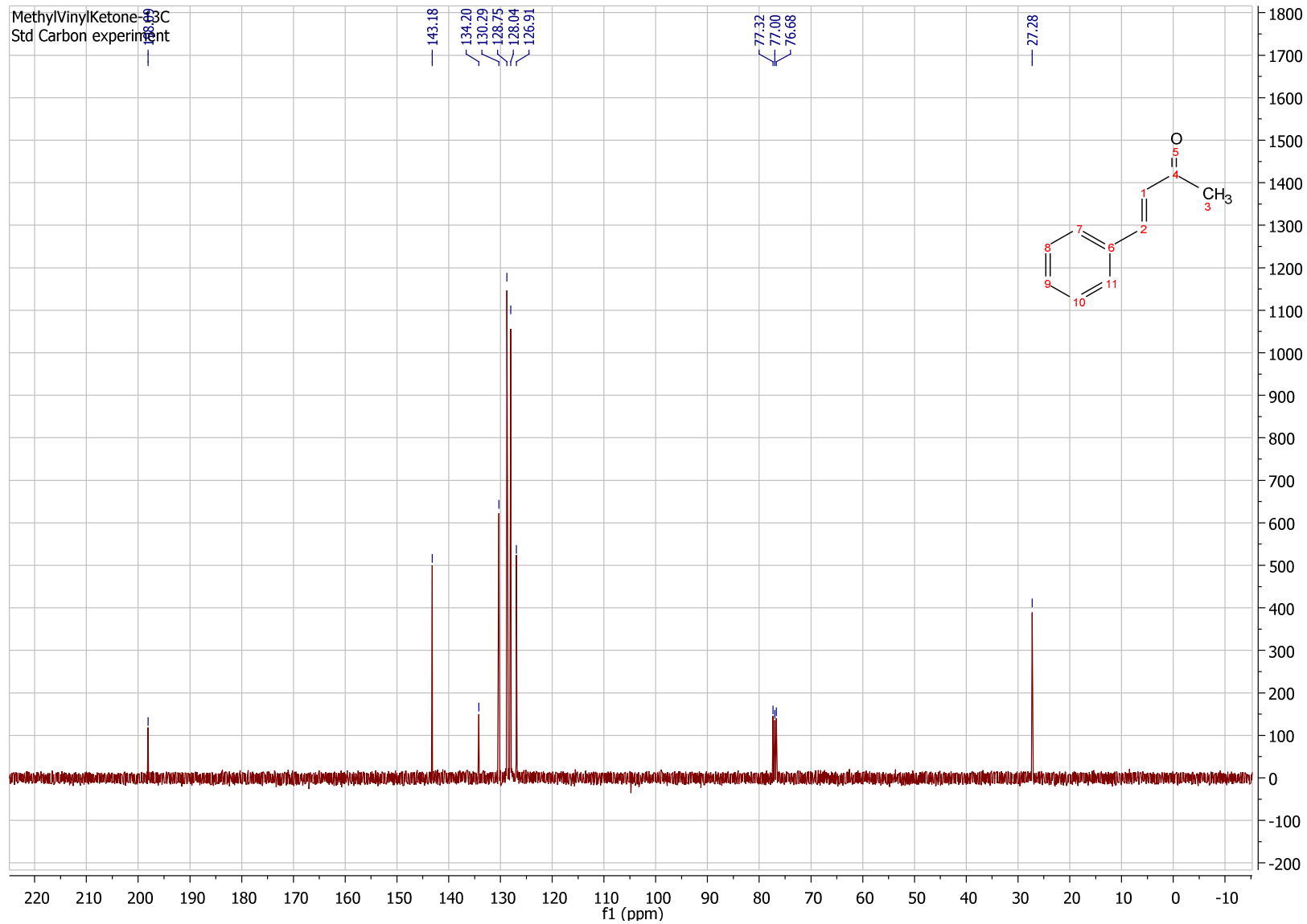
*tert*-butyl cinnamate (10b)



*tert*-butyl cinnamate (10b)

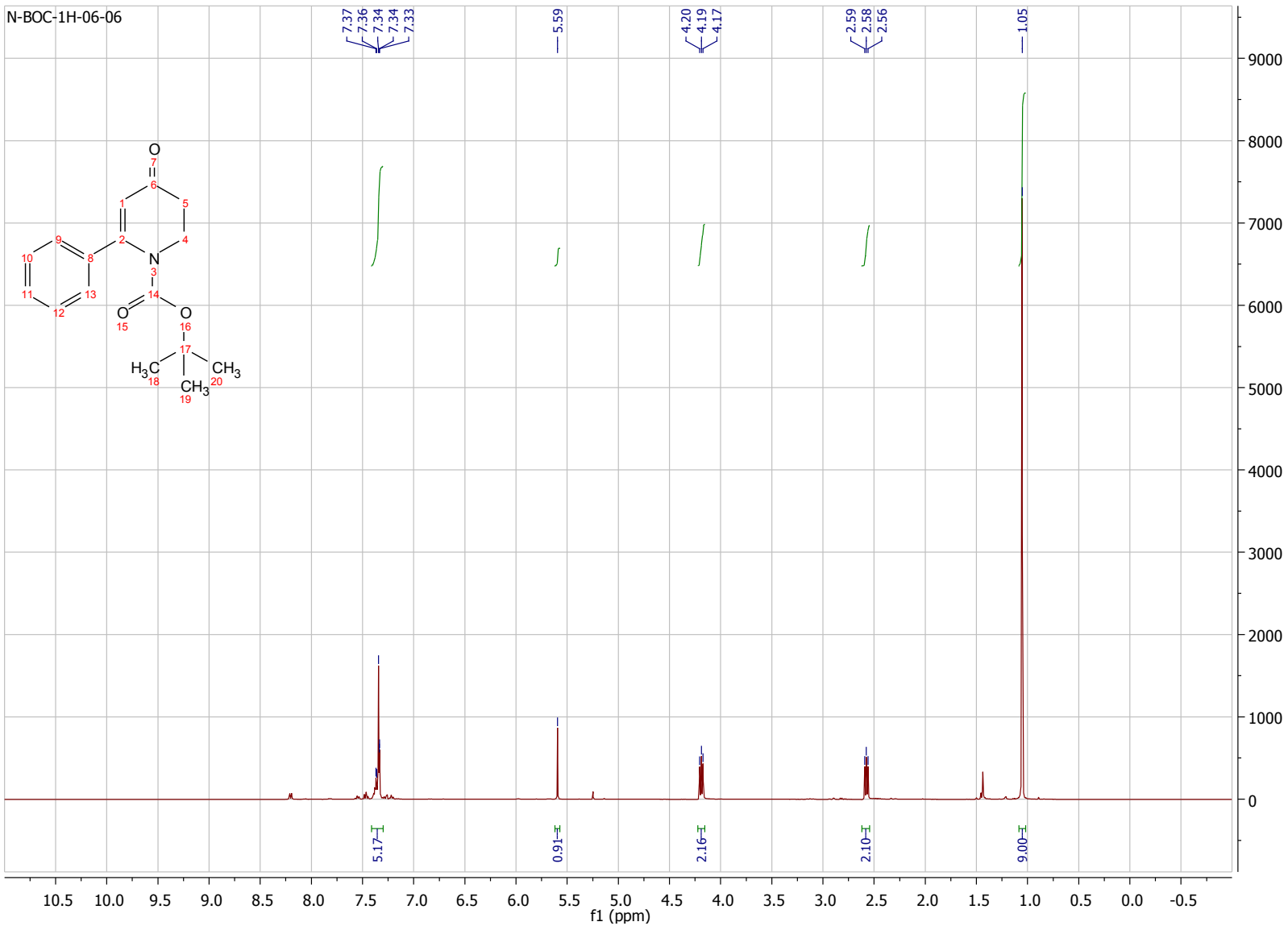
*(E)*-4-phenylbut-3-en-2-one (10c)





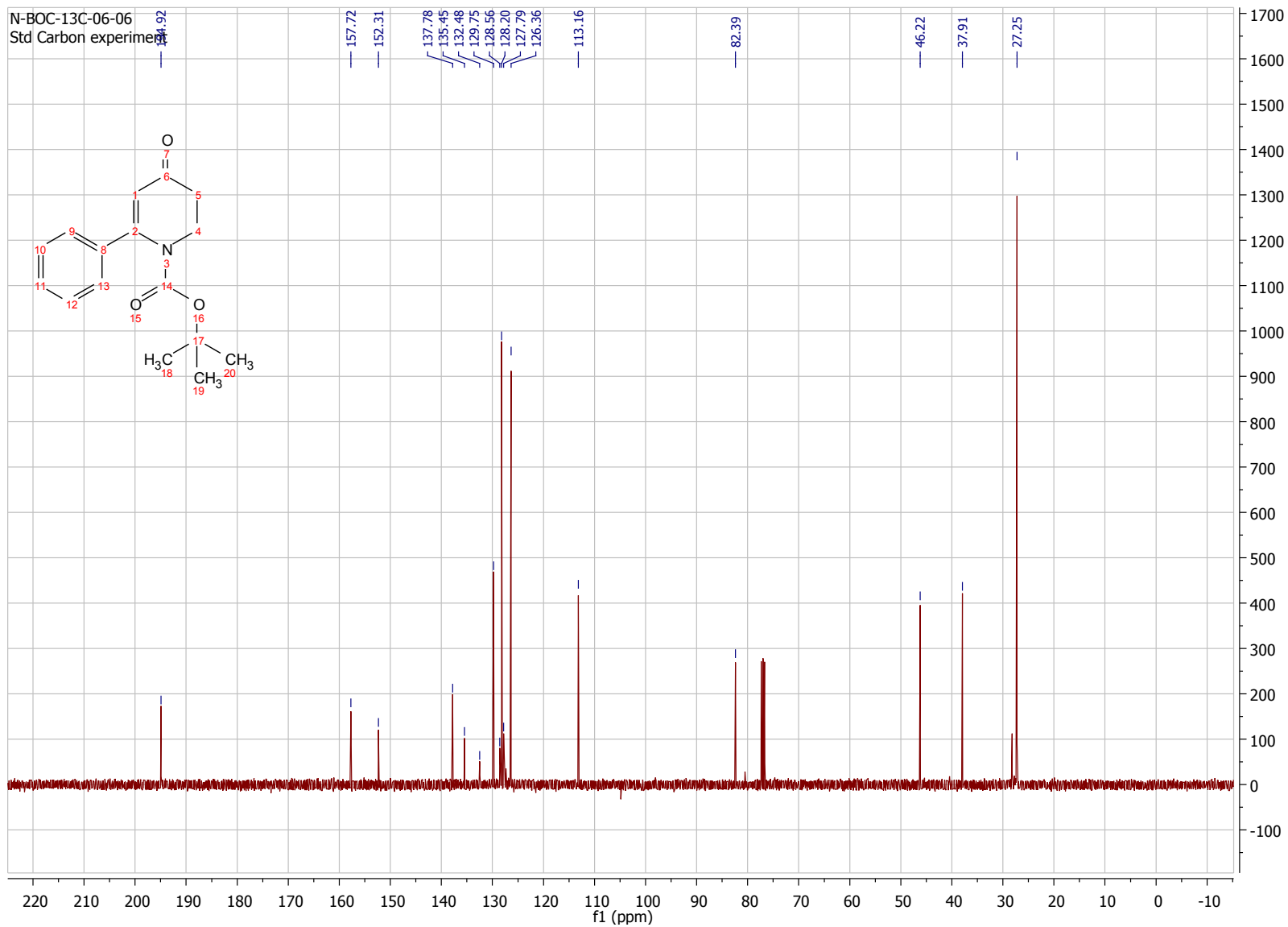
(E)-4-phenylbut-3-en-2-one (10c)

N-BOC-1H-06-06

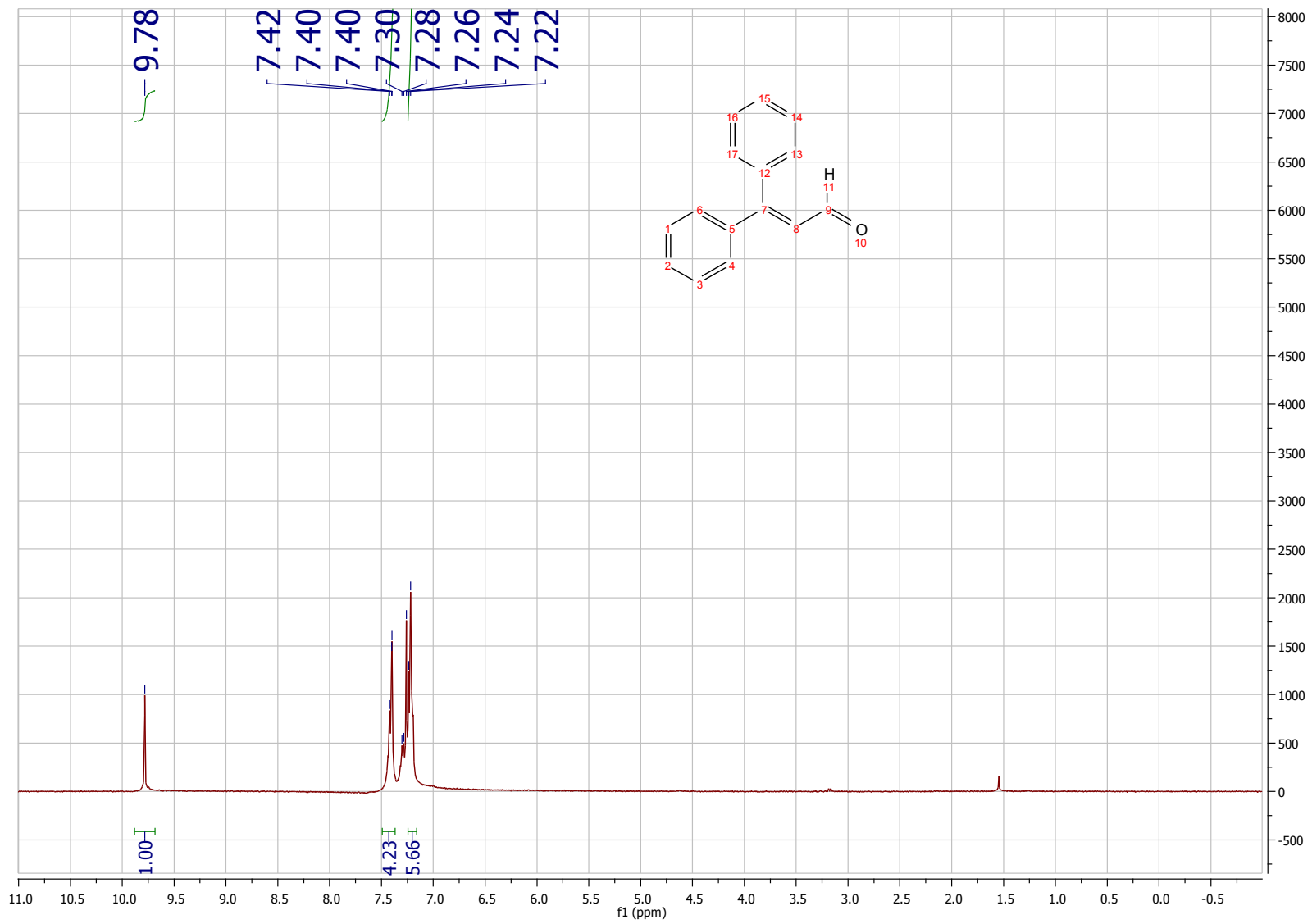


*tert*-butyl 4-oxo-6-phenyl-3,4-dihydropyridine-1(2H)-carboxylate (10d)

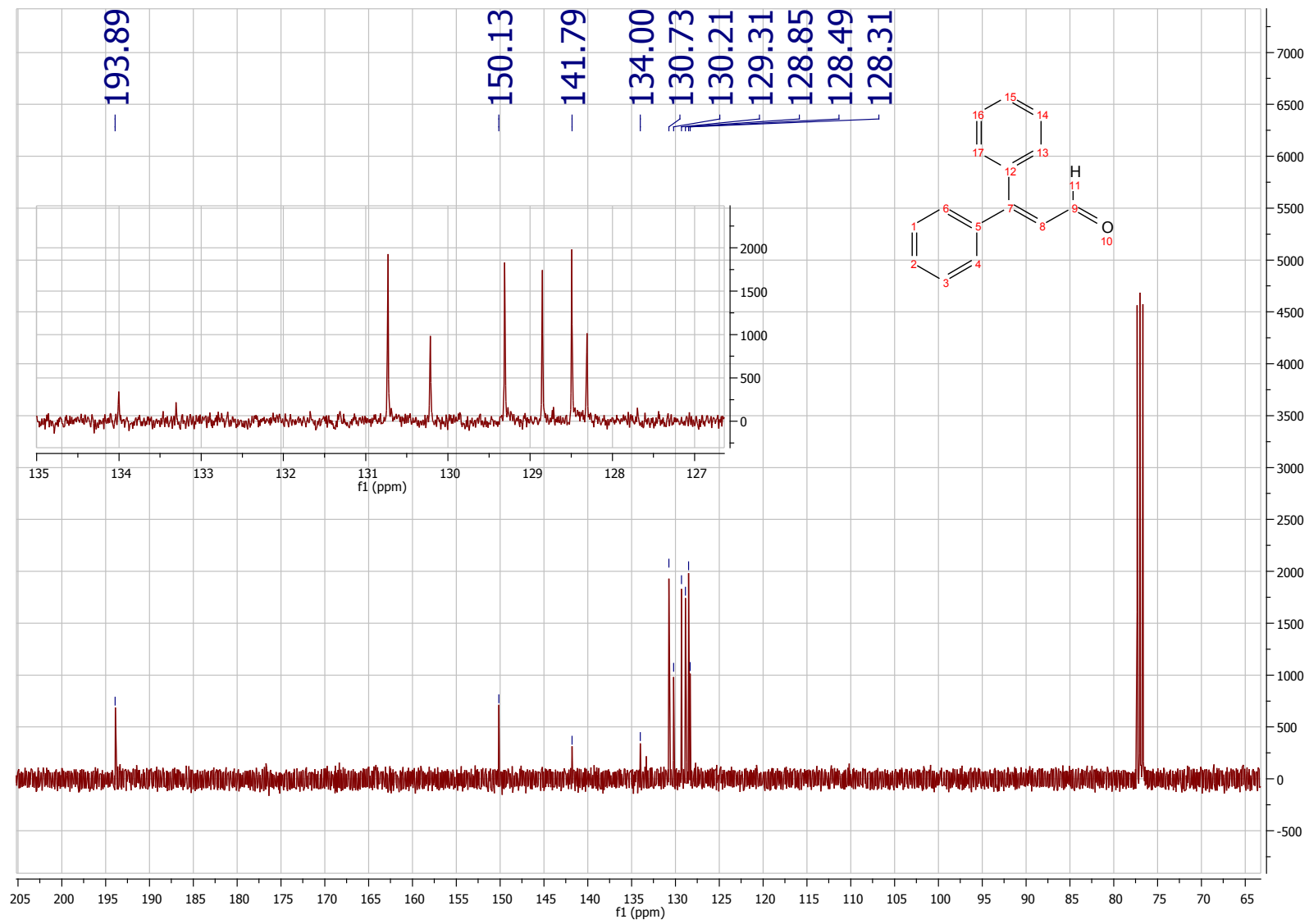
***tert*-butyl 4-oxo-6-phenyl-3,4-dihydropyridine-1(2H)-carboxylate (10d)**



3,3-diphenylacrylaldehyde (10e)



3,3-diphenylacrylaldehyde (10e)



## References:

- (1) El-Ayaan, U.; Murata, F.; El-Derby, S.; Fukuda, Y. *J. Mol. Struct.* **2004**, *692*, 209.
- (2) ten Brink, G. J.; Arends, I.; Hoogenraad, M.; Verspui, G.; Sheldon, R. A. *Adv. Synth. Catal.* **2003**, *345*, 1341.
- (3) Palais, L.; Alexakis, A. *Chem. Eur. J.* **2009**, *15*, 10473.