

# Supporting Information

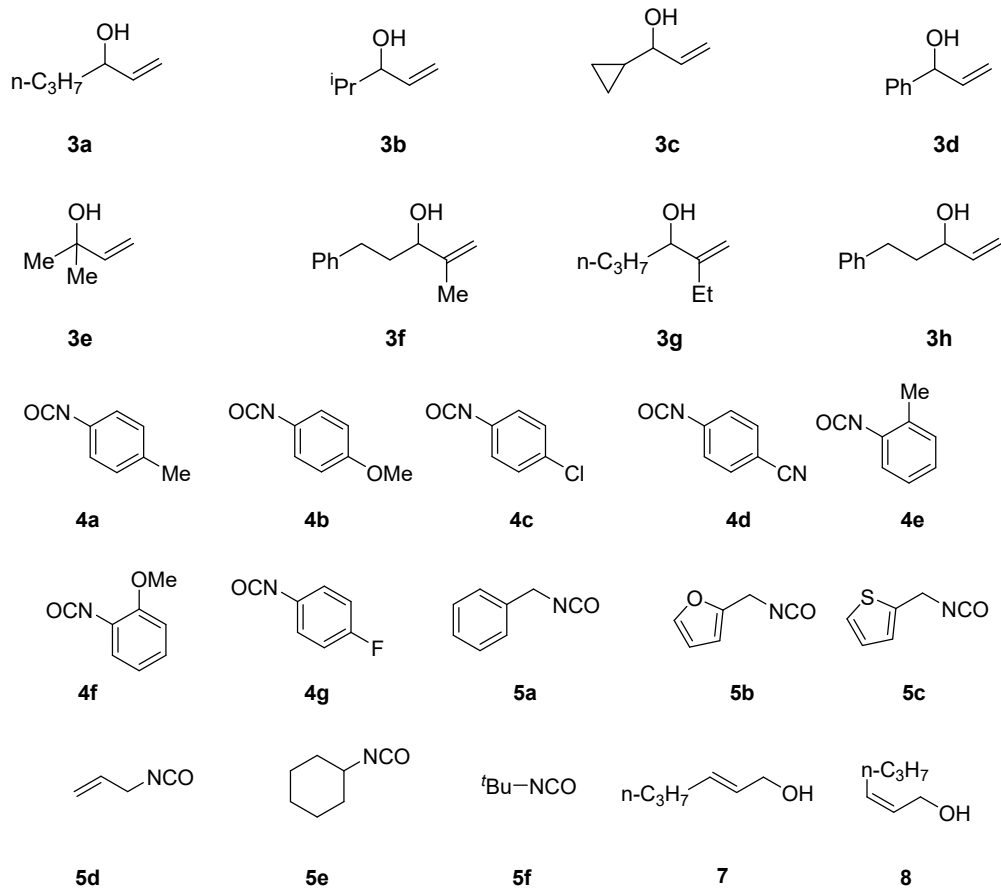
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## 1. General Information.

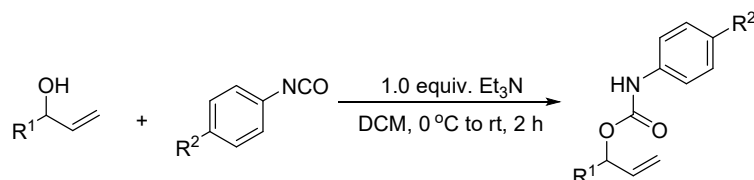
Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under dry argon atmosphere. All reagents and solvents were purchased from commercial suppliers without further purification. Column chromatography was performed using 200-300 mesh silica gels. The NMR spectra were recorded on a Bruker-400 instrument (400 MHz,  $^1\text{H}$ ; 101 MHz,  $^{13}\text{C}$ ), spectrometer with chemical shifts reported in ppm relative to the residual deuterated solvent and the internal standard tetramethylsilane.  $^{19}\text{F}$  NMR spectra were recorded on a Bruker-400 (376 MHz, respectively) and referenced relative to  $\text{PhCF}_3$ . Data for  $^1\text{H}$  NMR are recorded as follows: chemical shift ( $\delta$ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). High-resolution mass spectra (HRMS) were performed at Instrumental Analysis Center of Jilin institute of Chemical Technology with electrospray spectrometer Waters Micromass Q-TOF Premier Mass Spectrometer.



## 2. Synthesis of allylic alcohols.

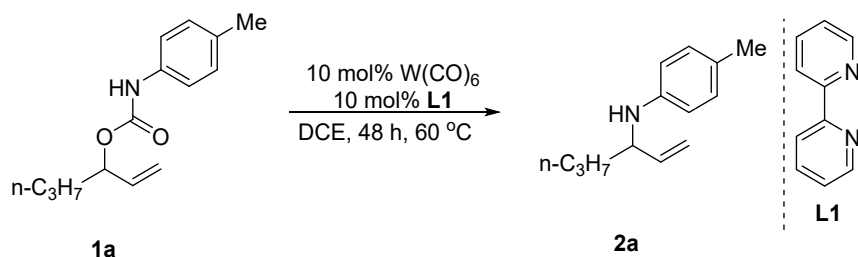
The allylic alcohols **3b-3d**, **3h**<sup>[1]</sup>, **3f-3g**<sup>[2]</sup> were prepared according to the literature.

## 3. General procedure for the synthesis of racemic allylic carbamates.



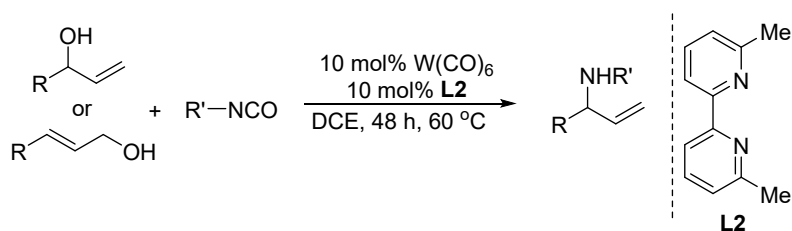
To a round-bottomed flask charged with the allylic alcohol (15 mmol, 1.0 equiv.) and isocyanate (15 mol, 1.0 equiv.) under an argon atmosphere was added DCM (20 mL). The flask was cooled to 0 °C in an ice/water bath for 20 minutes. Triethylamine (15 mmol, 1.0 equiv.) was added dropwise. After it was stirred at the same temperature for 30 minutes, the reaction mixture was brought to room temperature over 2 hours. After that, the reaction mixture was concentrated under reduced pressure. The resulting residue was subjected to flash column chromatography to furnish the title compound.

## 4. General procedure for regioselective W-catalyzed decarboxylative allylic amination of allylic carbamates.



A pressure tube equipped with a magnetic stir bar was charged with  $\text{W(CO)}_6$  (10 mol%), **L1** (10 mol%). The tube was purged with argon for 3 minutes. DCE (2 mL) was added followed by the allylic carbamate **1a** (0.4 mmol, 1.0 equiv.). The tube was sealed with a PTFE lined cap and was stirred in an oil bath at 60 °C for 48 hours. After cooled down, the crude reaction mixture was directly subjected to flash column chromatography.

## 5. General procedure for regioselective W-catalyzed decarboxylative allylic amination of allylic alcohols with isocyanates.



A pressure tube equipped with a magnetic stir bar was charged with  $W(CO)_6$  (10 mol%), **L2** (10 mol%). The tube was purged with argon for 3 minutes. DCE (2 mL) was added followed by the corresponding allylic alcohol (0.6 mmol, 1.5 equiv.) and isocyanate (0.4 mmol, 1.0 equiv.). The tube was sealed with a PTFE lined cap and was stirred in an oil bath at 60 °C for 48 hours. After cooled down, the crude reaction mixture was directly subjected to flash column chromatography.

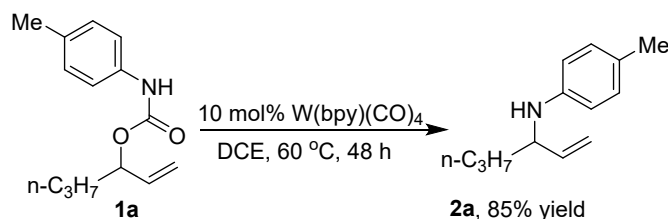
## 6. Mechanistic experiments.

### 6.1 Synthesis of $[W(2,2'\text{-bipyridine})(CO)_4]$ complex.

A pressure tube equipped with a magnetic stir bar was charged with  $W(CO)_6$  (351.9 mg, 1.0 mmol), 2,2'-bipyridine (156.1 mg, 1.0 mmol, 1.0 equiv.). The tube was purged with argon for 3 minutes. Benzene (5 mL) was added to the tube. The tube was sealed with a PTFE lined cap and was stirred at 80 °C for 12 hours. The suspension was filtered to remove the solvent. The solid was washed with 5 mL hexane for three times and dried in vacuo to afford the  $[W(2,2'\text{-bipyridine})(CO)_4]$  complex as a dark red solid (352.6 mg, 78%).

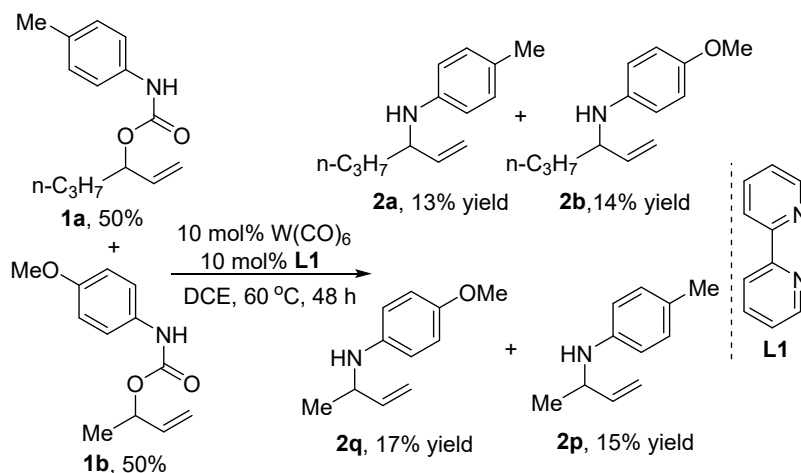
Dark red solid. mp. 168 °C (decomposed).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.70 (m, 2H), 8.41 (dt,  $J = 8.0, 1.0$  Hz, 2H), 7.84 (td,  $J = 7.8, 1.8$  Hz, 2H), 7.33 (m, 2H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  201.0, 156.2, 149.2, 136.9, 136.9, 123.7, 123.7, 121.1.

### 6.2 Reaction procedure with $[W(2,2'\text{-bipyridine})(CO)_4]$ as a catalyst.



A pressure tube equipped with a magnetic stir bar was charged with  $[W(2,2'\text{-bipyridine})(CO)_4]$  (10 mol%). The tube was purged with argon for 3 minutes. DCE (2 mL) was added followed by the allylic carbamate **1a** (0.4 mmol, 1.0 equiv). The tube was sealed with a PTFE lined cap and stirred in an oil bath at 60 °C for 48 hours. After cooled down, the crude reaction mixture was directly subjected to flash column chromatography.

### 6.3 Procedure for $W(0)$ -catalyzed crossover experiment.

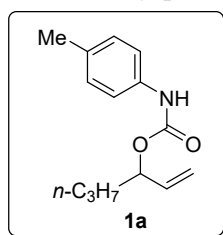


A pressure tube equipped with a magnetic stir bar was charged with  $W(CO)_6$  (10 mol%), **L1** (10

mol%). The tube was purged with argon for 3 minutes. DCE (2 mL) was added, followed by the allylic carbamate **1a** (0.2 mmol, 0.5 equiv) and **1b** (0.2 mmol, 0.5 equiv). The tube was sealed with a PTFE lined cap and was stirred in an oil bath at 60 °C for 48 hours. After cooled down, the crude reaction mixture was directly subjected to flash column chromatography.

## 7. Spectral data of allylic carbamates and allylic amines.

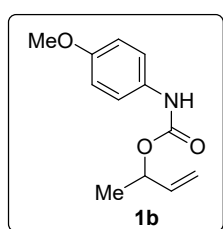
### hex-1-en-3-yl *p*-tolylcarbamate.



Colorless solid, 78 °C, Yield 3.2 g, 92%. TLC  $R_f$  = 0.5 (PE:EA 10:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J$  = 7.2 Hz, 2H), 7.10 (d,  $J$  = 8.2 Hz, 2H), 6.89 (s, 1H), 5.88 – 5.80 (m, 1H), 5.33 – 5.29 (m, 2H), 5.18 (d,  $J$  = 7.0 Hz, 1H), 2.31 (s, 3H), 1.74 – 1.56 (m, 2H), 1.45 – 1.38 (m, 2H), 0.96 (t,  $J$  = 7.3 Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.6, 137.2, 135.8, 133.0, 129.7, 119.1, 116.7, 75.7, 36.8, 21.0, 18.6, 14.1. **HRMS** (ESI-TOF)  $m/z$ : ([M+H]) calcd for  $\text{C}_{14}\text{H}_{19}\text{NO}_2\text{H}$ :

234.1489; Found: 234.1493

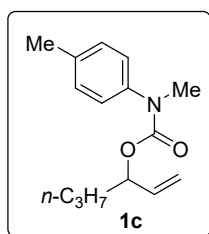
### but-3-en-2-yl (4-methoxyphenyl)carbamate.



White solid, 82 °C, 3.2 g, 95%. TLC  $R_f$  = 0.2 (PE:EA 10:1).  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.31 – 7.25 (m, 2H), 6.84 (d,  $J$  = 8.6 Hz, 2H), 6.58 (br, 1H), 5.92 – 5.85 (m, 1H), 5.34 – 5.31 (m, 1H), 5.28 (dd,  $J$  = 17.4, 1.5 Hz, 1H), 5.15 (dd,  $J$  = 10.6, 1.5 Hz, 1H), 3.77 (s, 3H), 1.36 (d,  $J$  = 6.5 Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.9, 153.3, 138.0, 131.0, 120.6, 115.8, 114.2, 71.8, 55.5, 20.2. **HRMS** (ESI-TOF)  $m/z$ : ([M+H]) Calcd for  $\text{C}_{12}\text{H}_{15}\text{NO}_3\text{H}$ : 222.1125; Found:

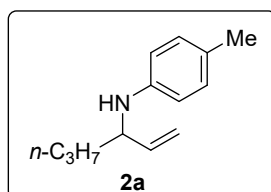
222.1129.

### hex-1-en-3-yl methyl(*p*-tolyl)carbamate.



Colorless oil, 454 mg, 92%. TLC  $R_f$  = 0.2 (PE:EA 10:1).  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.14 – 7.09 (m, 4H), 5.80 – 5.71 (m, 1H), 5.21 – 5.15 (m, 2H), 5.11 – 5.09 (m, 1H), 3.27 (s, 3H), 2.33 (s, 3H), 1.58 – 1.52 (m, 2H), 1.50 – 1.31 (m, 2H), 0.89 (t,  $J$  = 7.4 Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.3, 140.9, 137.2, 135.7, 129.4, 125.6, 115.9, 37.8, 36.5, 21.0, 18.3, 13.9. **HRMS** (ESI-TOF)  $m/z$ : ([M+H]) Calcd for  $\text{C}_{15}\text{H}_{21}\text{NO}_2\text{H}$ : 248.1645.; Found: 248.1655.

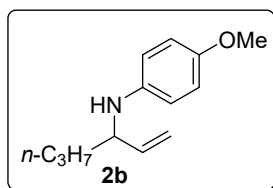
### *N*-(hex-1-en-3-yl)-4-methylaniline.



Colorless oil, Yield 62.0 mg, 82%. TLC  $R_f$  = 0.5 (PE:EA 100:1)  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.05 (d,  $J$  = 8.1 Hz, 2H), 6.61 (d,  $J$  = 8.4 Hz, 2H), 5.84 – 5.76 (m, 1H), 5.29 – 5.25 (m, 1H), 5.19 – 5.16 (m, 1H), 3.88 – 3.83 (m, 1H), 3.51 (br, 1H), 2.30 (s, 3H), 1.67 – 1.61 (m, 2H), 1.54 – 1.46 (m, 2H), 1.02 (t,  $J$  = 7.3 Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.4,

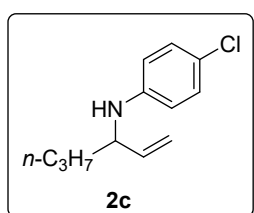
140.5, 129.7, 126.3, 114.9, 113.6, 56.1, 38.1, 20.4, 19.2, 14.1. **HRMS** (ESI-TOF)  $m/z$ : ([M+H]) Calcd for  $\text{C}_{13}\text{H}_{19}\text{NH}$ : 190.1590; Found: 190.1598.

#### *N*-(hex-1-en-3-yl)-4-methoxyaniline<sup>[3]</sup>.



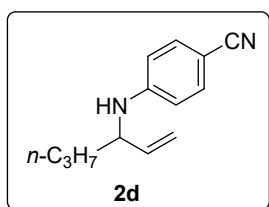
Colorless oil, Yield 61.5 mg, 75%; TLC  $R_f$  = 0.3 (PE:EA 100:1). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  6.80 (d,  $J$  = 8.9 Hz, 2H), 6.62 (d,  $J$  = 8.9 Hz, 2H), 5.80 – 5.71 (m, 1H), 5.23 (dt,  $J$  = 17.2, 1.4 Hz, 1H), 5.14 (dt,  $J$  = 10.4, 1.3 Hz, 1H), 3.77 (s, 4H), 3.21 (br, 1H), 1.64 – 1.55 (m, 2H), 1.51 – 1.42 (m, 2H), 0.98 (t,  $J$  = 7.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  151.9, 141.8, 140.6, 115.0, 114.8, 114.7, 56.8, 55.8, 38.0, 19.1, 14.0. HRMS (ESI-TOF)  $m/z$ : ([M+H]) Calcd for C<sub>13</sub>H<sub>19</sub>NOH: 206.1539; Found: 206.1532.

#### 4-chloro-*N*-(hex-1-en-3-yl)aniline.



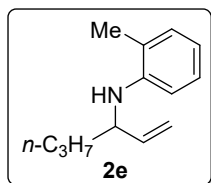
Colorless oil, Yield 51.9 mg, 62%; TLC  $R_f$  = 0.8 (PE:EA 100:1). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.10 (d,  $J$  = 8.8 Hz, 2H), 6.52 (d,  $J$  = 8.8 Hz, 2H), 5.76 – 5.66 (m, 1H), 5.22 – 5.17 (m, 1H), 5.15 – 5.12 (m, 1H), 3.79 – 3.75 (m, 1H), 3.65 (br, 1H), 1.60 – 1.55 (m, 2H), 1.50 – 1.41 (m, 2H), 0.96 (t,  $J$  = 7.3 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  146.3, 140.0, 129.1, 121.8, 115.4, 114.6, 56.1, 38.2, 19.3, 14.2. HRMS (ESI-TOF)  $m/z$ : ([M+Na]) Calcd for C<sub>12</sub>H<sub>16</sub>ClNNa: 232.0863; Found: 232.0869.

#### 4-(hex-1-en-3-ylamino)benzonitrile<sup>[4]</sup>.



Colorless oil, Yield 50.4 mg, 63%; TLC  $R_f$  = 0.3 (PE:EA 20:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 (d,  $J$  = 8.7 Hz, 2H), 6.54 (d,  $J$  = 8.8 Hz, 2H), 5.70 (ddd,  $J$  = 16.7, 10.3, 6.1 Hz, 1H), 5.16 (dd,  $J$  = 13.7, 12.7 Hz, 2H), 4.26 (d,  $J$  = 6.2 Hz, 1H), 3.85 – 3.82 (m, 1H), 1.59 (dd,  $J$  = 14.6, 7.0 Hz, 2H), 1.43 (dd,  $J$  = 12.6, 7.2 Hz, 2H), 0.94 (t,  $J$  = 7.3 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  151.1, 138.8, 133.8, 120.8, 115.9, 112.9, 98.5, 55.5, 37.9, 19.3, 14.1. HRMS (ESI-TOF)  $m/z$ : ([M+H]) Calcd for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>H: 201.1386; Found: 201.1389.

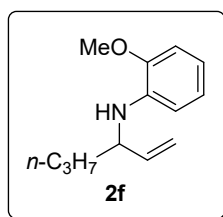
#### *N*-(hex-1-en-3-yl)-2-methylaniline<sup>[3]</sup>.



Colorless oil, Yield 37.8 mg, 50%; TLC  $R_f$  = 0.8 (PE:EA 100:1). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.14 – 7.08 (m, 2H), 6.68 – 6.62 (m, 2H), 5.84 – 5.76 (m, 1H), 5.26 – 5.22 (m, 1H), 5.17 – 5.14 (m, 1H), 3.91 (d,  $J$  = 6.6 Hz, 1H), 3.51 (s, 1H), 2.20 (s, 3H), 1.69 – 1.63 (m, 2H), 1.57 – 1.45 (m, 2H), 1.00 (t,  $J$  = 7.3 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  145.7, 140.6, 130.3, 127.2, 121.8, 116.8, 115.1, 110.9, 55.8, 38.4, 19.4, 17.9, 14.3. HRMS (ESI-TOF)  $m/z$ : ([M+H]) Calcd for C<sub>13</sub>H<sub>19</sub>NH: 190.1590; Found: 190.1593.

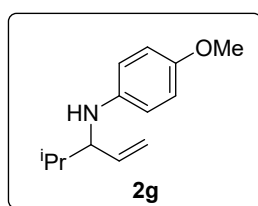


#### *N*-(hex-1-en-3-yl)-2-methoxyaniline.



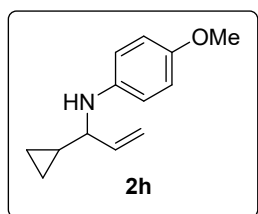
Colorless oil, Yield 42.6 mg, 52%; TLC  $R_f$  = 0.5 (PE:EA 50:1).  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  6.90 – 6.86 (m, 1H), 6.82 (dd,  $J$  = 7.9, 1.4 Hz, 1H), 6.71 – 6.64 (m, 2H), 5.84 – 5.75 (m, 1H), 5.27 – 5.23 (m, 1H), 5.17 – 5.14 (m, 1H), 4.32 (br, 1H), 3.90 (s, 3H), 3.87 – 3.85 (m, 1H), 1.71 – 1.64 (m, 2H), 1.54 – 1.47 (m, 2H), 1.00 (t,  $J$  = 7.3 Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.7, 140.4, 137.6, 121.2, 116.1, 114.8, 110.8, 109.4, 55.6, 55.4, 38.1, 19.2, 14.1. **HRMS** (ESI-TOF)  $m/z$ : ([ $M+H$ ]) Calcd for  $\text{C}_{13}\text{H}_{19}\text{NOH}$ : 206.1539; Found: 206.1533.

#### 4-methoxy-*N*-(4-methylpent-1-en-3-yl)aniline<sup>[4]</sup>.



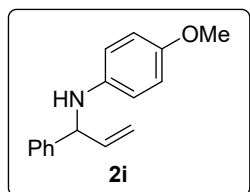
Colorless oil, Yield 47.6 mg, 58%; TLC  $R_f$  = 0.3 (PE:EA 20:1).  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  6.83 (d,  $J$  = 8.9 Hz, 2H), 6.64 (d,  $J$  = 8.9 Hz, 2H), 5.82 – 5.73 (m, 1H), 5.27 – 5.21 (m, 2H), 3.79 (s, 3H), 3.64 – 3.61 (m, 1H), 3.47 (br, 1H), 1.96 – 1.88 (m, 1H), 1.05 (dd,  $J$  = 14.2, 6.8 Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.9, 142.1, 138.3, 116.1, 114.8, 114.7, 62.5, 55.8, 32.5, 19.0, 18.6. **HRMS** (ESI-TOF)  $m/z$ : ([ $M+H$ ]) Calcd for  $\text{C}_{13}\text{H}_{19}\text{NOH}$ : 206.1539; Found: 206.1549.

#### *N*-(1-cyclopropylallyl)-4-methoxyaniline<sup>[4]</sup>.



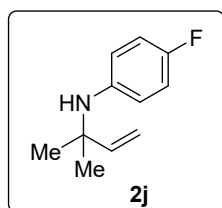
Colorless oil, Yield 48.7 mg, 60%; TLC  $R_f$  = 0.2 (PE:EA 100:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.82 – 6.80 (m, 2H), 6.64 – 6.62 (m, 2H), 5.91 – 5.82 (m, 1H), 5.29 (dt,  $J$  = 17.2, 1.4 Hz, 1H), 5.18 (dd,  $J$  = 10.3, 1.2 Hz, 1H), 3.78 (s, 3H), 3.22 (dd,  $J$  = 7.4, 6.4 Hz, 1H), 1.10-1.02 (m, 1H), 0.62 – 0.58 (m, 2H), 0.41 – 0.38 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.1, 142.1, 139.2, 115.2, 114.9, 114.7, 61.2, 55.8, 16.8, 3.4, 2.5. **HRMS** (ESI) calcd for  $\text{C}_{13}\text{H}_{17}\text{NOH}$ ([ $M+H$ ]): 204.1383. Found: 204.1386

#### 4-methoxy-*N*-(1-phenylallyl)aniline<sup>[4]</sup>.



Colorless oil, Yield 68.8 mg, 72%; TLC  $R_f$  = 0.3 (PE:EA 50:1).  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.41 – 7.30 (m, 4H), 7.30 – 7.26 (m, 1H), 6.74 – 6.59 (m, 2H), 6.63 – 6.46 (m, 2H), 6.09 – 6.01 (m, 1H), 5.31 – 5.27 (m, 1H), 5.23 (dt,  $J$  = 10.2, 1.3 Hz, 1H), 4.87 (d,  $J$  = 6.0 Hz, 1H), 3.83 (s, 1H), 3.73 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  152.4, 142.3, 141.6, 139.7, 128.9, 127.3, 116.1, 115.1, 114.9, 62.0, 56.0. **HRMS** (ESI-TOF)  $m/z$ : ([ $M+H$ ]) Calcd for  $\text{C}_{16}\text{H}_{17}\text{NOH}$ : 240.1383; Found: 240.1387.

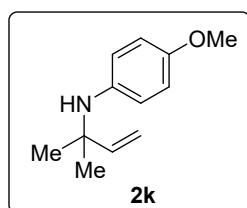
#### 4-fluoro-*N*-(2-methylbut-3-en-2-yl)aniline



Colorless oil, Yield 41.5 mg, 58%; TLC  $R_f$  = 0.8 (PE:EA 100:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.88 – 6.84 (m, 2H), 6.71 – 6.67 (m, 2H), 6.02 (dd,  $J$  = 17.5, 10.7 Hz, 1H), 5.15 (ddd,  $J$  = 13.4, 10.7, 9.0 Hz, 2H), 1.38 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  157.41, 157.39, 155.07, 155.05, 146.18, 142.81, 142.79, 117.59, 117.55, 117.52, 117.48, 115.24, 115.23, 115.03, 115.02, 112.81, 112.79, 54.98,

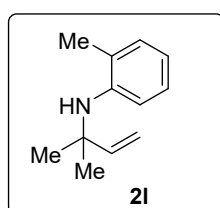
28.17.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -127.34. HRMS (ESI-TOF)  $m/z$ : ( $[\text{M}+\text{H}]$ ) Calcd for  $\text{C}_{11}\text{H}_{14}\text{NFH}$ : 180.1183; Found: 180.1189.

#### 4-methoxy-*N*-(2-methylbut-3-en-2-yl)aniline



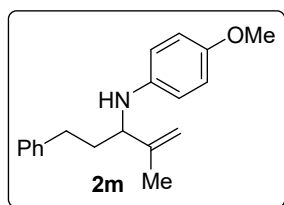
Colorless oil, Yield 42.0 mg, 55%; TLC  $R_f$ = 0.3 (PE:EA 50:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.75 (s, 4H), 6.04 (dd,  $J$  = 17.5, 10.7 Hz, 1H), 5.19 – 5.14 (m, 1H), 5.12 – 5.09 (m, 1H), 3.77 (s, 3H), 1.36 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.0, 146.6, 140.2, 119.2, 114.2, 112.4, 55.6, 55.2, 28.2. HRMS (ESI-TOF)  $m/z$ : ( $[\text{M}+\text{H}]$ ) Calcd for  $\text{C}_{12}\text{H}_{17}\text{NOH}$ : 192.1383; Found: 192.1389.

#### 2-methyl-*N*-(2-methylbut-3-en-2-yl)aniline



Colorless oil, Yield 36.4 mg, 52%; TLC  $R_f$ = 0.8 (PE:EA 50:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.05 (dd,  $J$  = 13.0, 7.2 Hz, 2H), 6.86 (d,  $J$  = 8.1 Hz, 1H), 6.64 (t,  $J$  = 7.2 Hz, 1H), 6.05 (dd,  $J$  = 17.5, 10.7 Hz, 1H), 5.18 (dd,  $J$  = 29.6, 14.0 Hz, 2H), 2.17 (s, 3H), 1.46 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.3, 144.5, 130.2, 126.3, 116.7, 113.5, 112.7, 54.5, 31.5, 28.5. HRMS (ESI-TOF)  $m/z$ : ( $[\text{M}+\text{H}]$ ) Calcd for  $\text{C}_{12}\text{H}_{17}\text{NH}$ : 176.1434; Found: 176.1435.

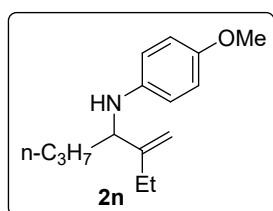
#### 4-methoxy-*N*-(2-methyl-5-phenylpent-1-en-3-yl)aniline<sup>[2]</sup>



Yellow oil; Yield 56.2 mg, 50%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 – 7.31 (m, 2H), 7.25 – 7.22 (m, 3H), 6.79 (d,  $J$  = 8.9 Hz, 2H), 6.56 (d,  $J$  = 8.9 Hz, 2H), 4.99 – 4.96 (m, 2H), 3.82 – 3.67 (m, 4H), 2.78 – 2.66 (m, 2H), 1.96 (d,  $J$  = 7.7 Hz, 2H), 1.71 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.9, 145.6, 141.8, 128.5, 128.4, 125.9, 114.7, 112.7, 60.0, 55.8, 36.0, 32.7, 17.7. HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{23}\text{NOH}$  ( $[\text{M}+\text{H}]$ ): 282.1852. Found:

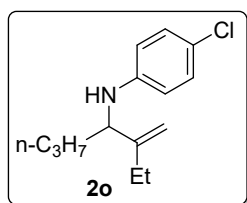
282.1859.

#### 4-methoxy-*N*-(3-methyleneheptan-4-yl)aniline<sup>[2]</sup>



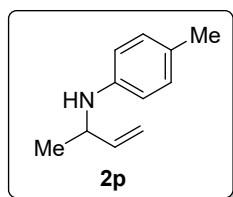
Yellow oil; Yield 48.4 mg, 52%.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  6.78 (d,  $J$  = 8.9 Hz, 2H), 6.56 (d,  $J$  = 8.9 Hz, 2H), 5.02 (s, 1H), 4.89 (d,  $J$  = 1.5 Hz, 1H), 3.75 (s, 3H), 3.72 (t,  $J$  = 6.8 Hz, 1H), 2.06 – 2.00 (m, 2H), 1.65 – 1.54 (m, 2H), 1.46 – 1.36 (m, 2H), 1.07 (t,  $J$  = 7.4 Hz, 3H), 0.96 (t,  $J$  = 7.3 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.1, 142.6, 138.2, 126.5, 114.9, 114.8, 55.8, 50.5, 29.5, 23.0, 22.0, 13.9, 13.3. HRMS (ESI) calcd for  $\text{C}_{15}\text{H}_{23}\text{NOH}$  ( $[\text{M}+\text{H}]$ ): 234.1852. Found: 234.1859.

#### 4-chloro-*N*-(3-methyleneheptan-4-yl)aniline<sup>[2]</sup>



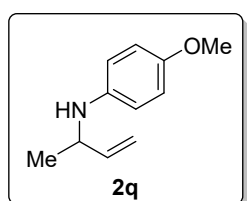
Yellow oil; Yield 50.2 mg, 53%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.07 (d,  $J$  = 9.1 Hz, 2H), 6.48 (d,  $J$  = 8.5 Hz, 2H), 4.98 (s, 1H), 4.88 (s, 1H), 3.71 (t,  $J$  = 6.4 Hz, 2H), 2.01 – 1.96 (m, 2H), 1.65 – 1.48 (m, 2H), 1.47 – 1.28 (m, 2H), 1.04 (t,  $J$  = 7.4 Hz, 3H), 0.93 (t,  $J$  = 7.3 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  151.2, 146.4, 128.9, 121.4, 114.2, 109.5, 59.2, 37.2, 23.8, 19.6, 14.0, 12.1. HRMS (ESI) calcd for C<sub>14</sub>H<sub>20</sub>ClNH ([M+H]): 238.1357. Found: 238.1365.

#### *N*-(but-3-en-2-yl)-4-methylaniline



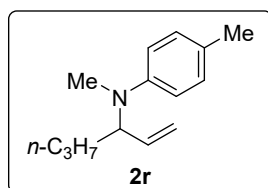
Colorless oil, 12.2 mg, 15%; TLC  $R_f$  = 0.3 (PE:EA 100:1). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  6.96 (d,  $J$  = 8.1 Hz, 2H), 6.53 (d,  $J$  = 8.5 Hz, 2H), 5.86 – 5.78 (m, 1H), 5.22 – 5.18 (m, 1H), 5.08 – 5.05 (m, 1H), 3.98 – 3.91 (m, 1H), 2.22 (s, 3H), 1.29 (dd,  $J$  = 6.7, 1.0 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  145.1, 141.5, 129.6, 126.5, 114.0, 113.7, 51.4, 21.7, 20.4. HRMS (ESI-TOF)  $m/z$ : ([M+H]) Calcd for C<sub>11</sub>H<sub>15</sub>NH: 162.1277; Found: 162.1277.

#### *N*-(but-3-en-2-yl)-4-methoxyaniline<sup>[6]</sup>.



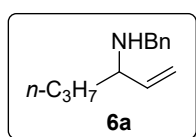
Colorless oil, 14.9 mg, 17%; TLC  $R_f$  = 0.5 (PE:EA 50:1). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  6.82 (d,  $J$  = 8.9 Hz, 2H), 6.64 (d,  $J$  = 8.9 Hz, 2H), 5.92 – 5.84 (m, 1H), 5.28 – 5.23 (m, 1H), 5.13 (dt,  $J$  = 10.3, 1.4 Hz, 1H), 4.06 – 3.87 (m, 1H), 3.79 (s, 3H), 1.34 (d,  $J$  = 6.7 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.1, 141.7, 141.6, 115.0, 114.8, 114.1, 55.8, 52.1, 21.7.

#### *N*-(hex-1-en-3-yl)-*N*,4-dimethylaniline.



Colorless oil, 59.3 mg, 73%; TLC  $R_f$  = 0.3 (PE:EA 100:1). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.01 (d,  $J$  = 8.1 Hz, 2H), 6.69 (d,  $J$  = 8.0 Hz, 2H), 5.83 – 5.75 (m, 1H), 5.11 – 5.05 (m, 2H), 4.24 – 4.19 (m, 1H), 2.70 (s, 3H), 2.23 (s, 3H), 1.71 – 1.52 (m, 2H), 1.38 – 1.24 (m, 2H), 0.90 (t,  $J$  = 8.0 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  148.6, 137.7, 129.6, 125.6, 115.3, 113.3, 60.2, 34.1, 31.5, 20.2, 20.0, 14.1. HRMS (ESI-TOF)  $m/z$ : ([M+H]) Calcd for C<sub>14</sub>H<sub>21</sub>NH: 204.1747; Found: 204.1759.

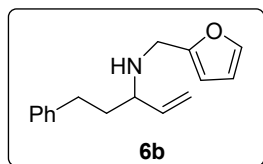
#### *N*-benzylhex-1-en-3-amine<sup>[4]</sup>.



Colorless oil, Yield 45.4 mg, 60%; TLC  $R_f$  = 0.3 (PE:EA 20:1). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.32 (d,  $J$  = 4.9 Hz, 4H), 7.25 – 7.22 (m, 1H), 5.66 – 5.57 (m, 1H), 5.16 – 5.09 (m, 2H), 3.83 (d,  $J$  = 13.1 Hz, 1H), 3.64 (d,  $J$  = 13.2 Hz, 1H), 3.05 – 3.00 (m, 1H), 1.50 – 1.40 (m, 2H), 1.37 – 1.26 (m, 2H), 0.89 (t,  $J$  = 7.2 Hz,

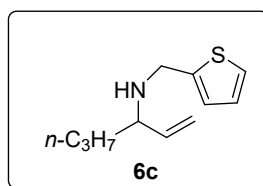
3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.4, 140.8, 128.4, 128.2, 126.8, 115.9, 61.0, 51.3, 38.0, 19.1, 14.1. HRMS (ESI) calcd for  $\text{C}_{13}\text{H}_{19}\text{NH}$  ( $[\text{M}+\text{H}]$ ): 190.1590. Found: 190.1596.

#### *N*-(furan-2-ylmethyl)-5-phenylpent-1-en-3-amine<sup>[4]</sup>



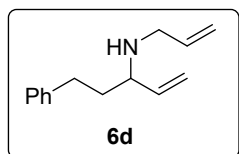
Colorless oil, Yield 58.8 mg, 61%; TLC  $R_f$  = 0.2 (PE:EA 10:1).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.38 (d,  $J$  = 1.9 Hz, 1H), 7.30 (t,  $J$  = 7.4 Hz, 2H), 7.20 (t,  $J$  = 8.4 Hz, 3H), 6.33 (dd,  $J$  = 3.2, 1.9 Hz, 1H), 6.17 (d,  $J$  = 3.2 Hz, 1H), 5.72 – 5.63 (m, 1H), 5.26 – 5.18 (m, 2H), 3.85 (d,  $J$  = 14.4 Hz, 1H), 3.69 (d,  $J$  = 14.3 Hz, 1H), 3.11 – 3.06 (m, 1H), 2.73 – 2.59 (m, 2H), 1.91 – 1.75 (m, 2H), 1.56 (br, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.1, 142.1, 141.8, 140.6, 128.5, 128.4, 125.8, 117.1, 110.1, 106.9, 60.5, 43.6, 37.3, 32.2. HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{19}\text{NOH}$  ( $[\text{M}+\text{H}]$ ): 242.1539. Found: 242.1541.

#### *N*-(thiophen-2-ylmethyl)hex-1-en-3-amine<sup>[4]</sup>



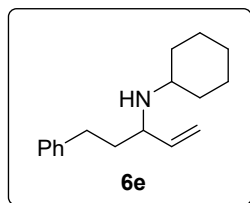
Colorless oil, Yield 42.9 mg, 55%; TLC  $R_f$  = 0.2 (PE:EA 5:1).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.20 – 7.18 (m, 1H), 6.95 – 6.91 (m, 2H), 5.64 – 5.55 (m, 1H), 5.17 – 5.10 (m, 2H), 4.01 (d,  $J$  = 14.1 Hz, 1H), 3.87 (d,  $J$  = 14.1 Hz, 1H), 3.10 – 3.05 (m, 1H), 1.59 – 1.19 (m, 5H), 0.90 (t,  $J$  = 7.2 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.7, 141.1, 126.6, 124.6, 124.1, 116.2, 60.6, 45.7, 37.9, 19.1, 14.1. HRMS (ESI) calcd for  $\text{C}_{11}\text{H}_{17}\text{NSH}$  ( $[\text{M}+\text{H}]$ ): 196.1154. Found: 196.1162.

#### *N*-allyl-5-phenylpent-1-en-3-amine<sup>[4]</sup>



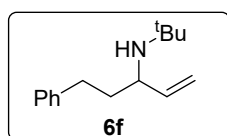
Colorless oil, Yield 41.8 mg, 52%; TLC  $R_f$  = 0.2 (PE:EA 5:1).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.30 – 7.26 (m, 2H), 7.20 – 7.18 (m, 3H), 5.95 – 5.85 (m, 1H), 5.67 – 5.58 (m, 1H), 5.20 – 5.16 (m, 2H), 5.13 – 5.07 (m, 2H), 3.31 – 3.26 (m, 1H), 3.15 – 3.04 (m, 2H), 2.82 – 2.42 (m, 2H), 2.06 – 1.58 (m, 2H), 1.31 (br, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.2, 140.9, 137.0, 128.4, 128.3, 125.8, 116.5, 115.7, 60.9, 49.8, 37.3, 32.2. HRMS (ESI) calcd for  $\text{C}_{14}\text{H}_{19}\text{NH}$  ( $[\text{M}+\text{H}]$ ): 202.1590. Found: 202.1599.

#### *N*-(5-phenylpent-1-en-3-yl)cyclohexanamine



Colorless oil, Yield 42.8 mg, 44%; TLC  $R_f$  = 0.2 (PE:EA 5:1).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.32 – 7.29 (m, 2H), 7.23 – 7.19 (m, 3H), 5.70 – 5.61 (m, 1H), 5.17 – 5.11 (m, 2H), 3.26 – 3.20 (m, 1H), 2.74 – 2.60 (m, 2H), 2.55 – 2.48 (m, 1H), 1.95 – 1.69 (m, 5H), 1.67 – 1.59 (m, 1H), 1.53 – 1.12 (m, 5H), 1.10 – 0.93 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.3, 141.8, 128.4, 128.3, 125.7, 115.6, 58.0, 53.3, 37.7, 34.8, 33.2, 32.3, 26.3, 25.4, 25.0. HRMS (ESI-TOF)  $m/z$ : ( $[\text{M}+\text{H}]$ ) Calcd for  $\text{C}_{17}\text{H}_{25}\text{NH}$ : 244.2060; Found: 244.2069.

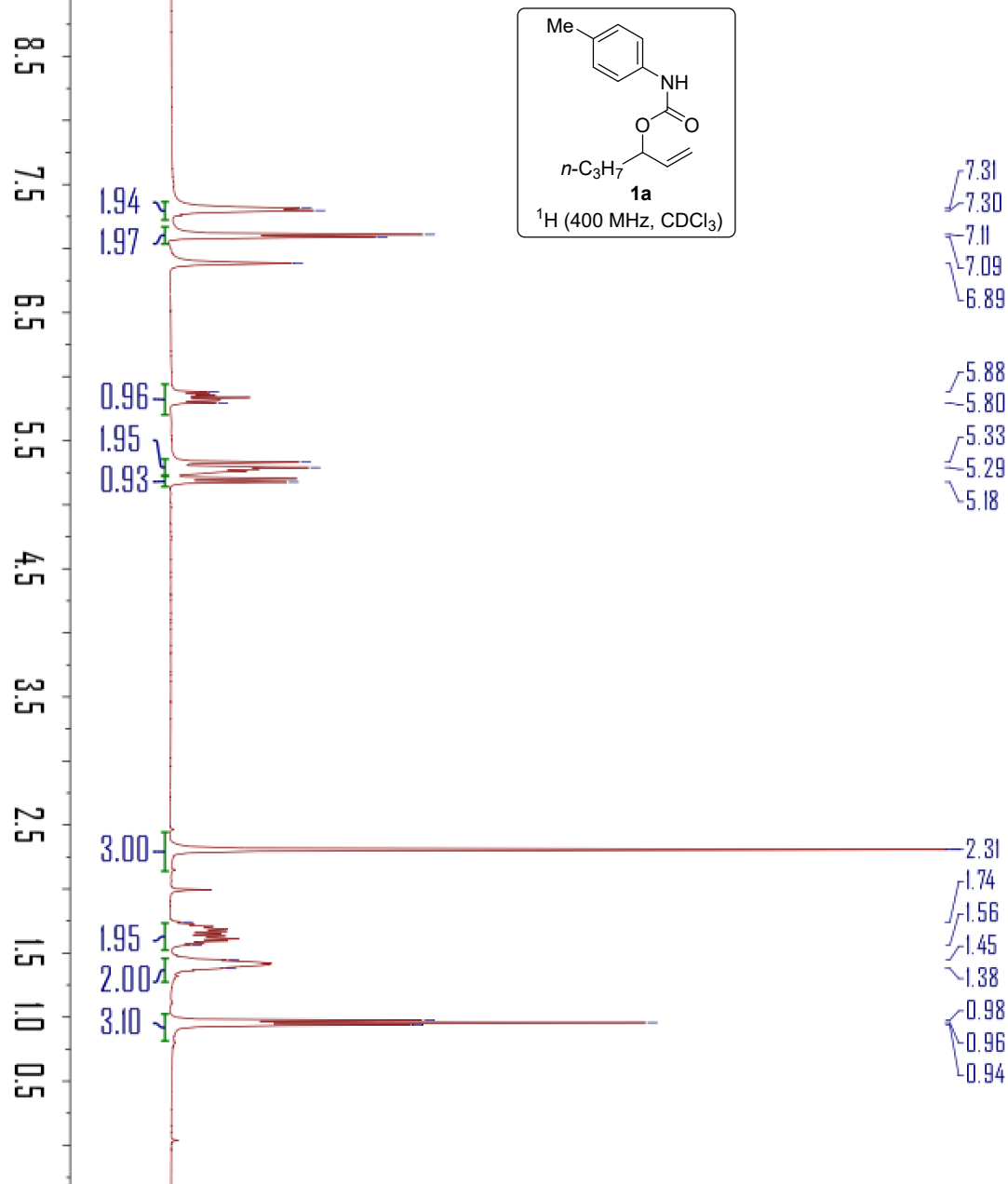
#### *N*-(tert-butyl)-5-phenylpent-1-en-3-amine

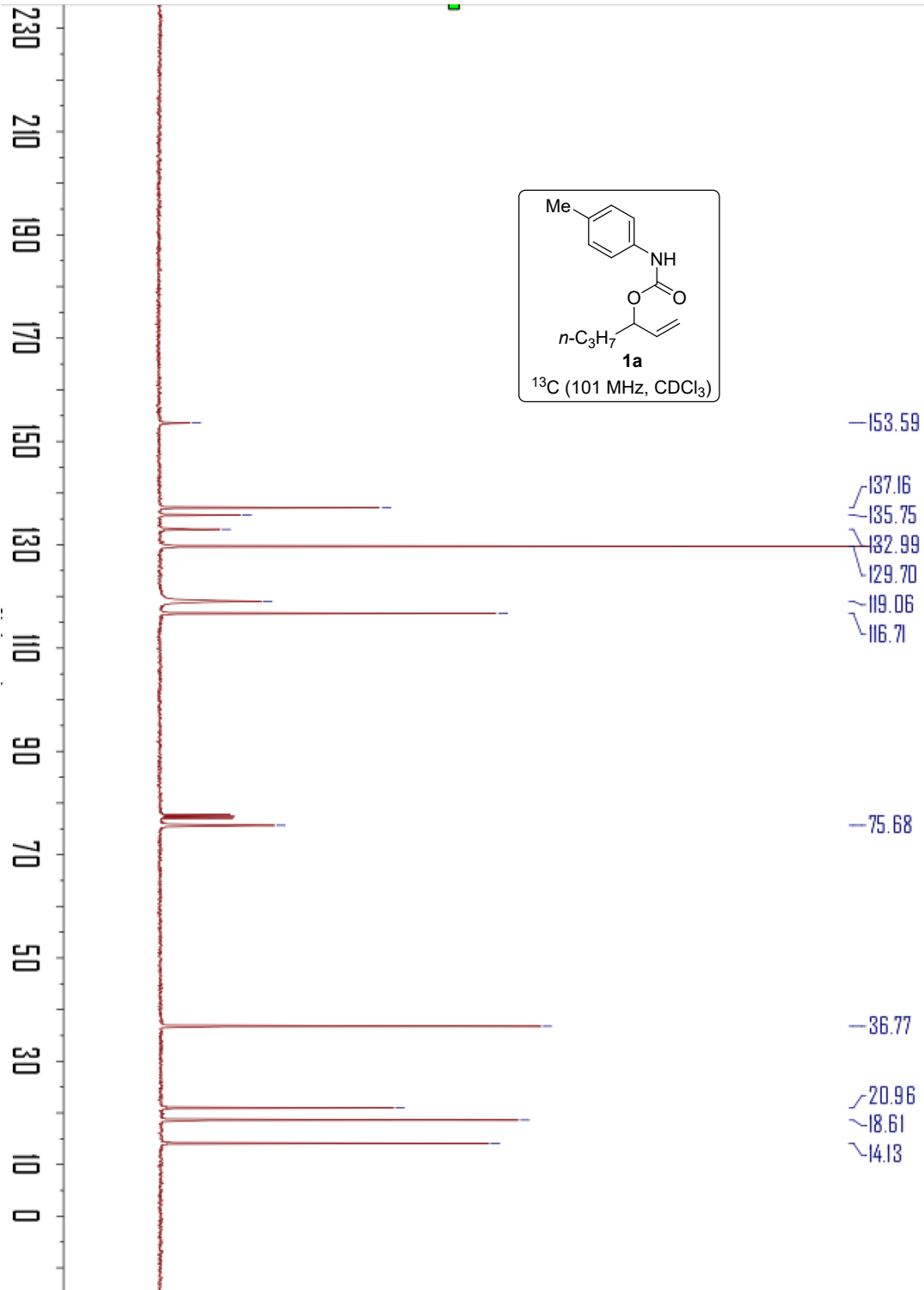


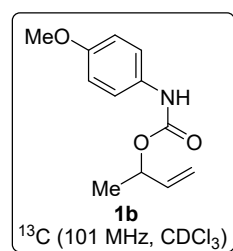
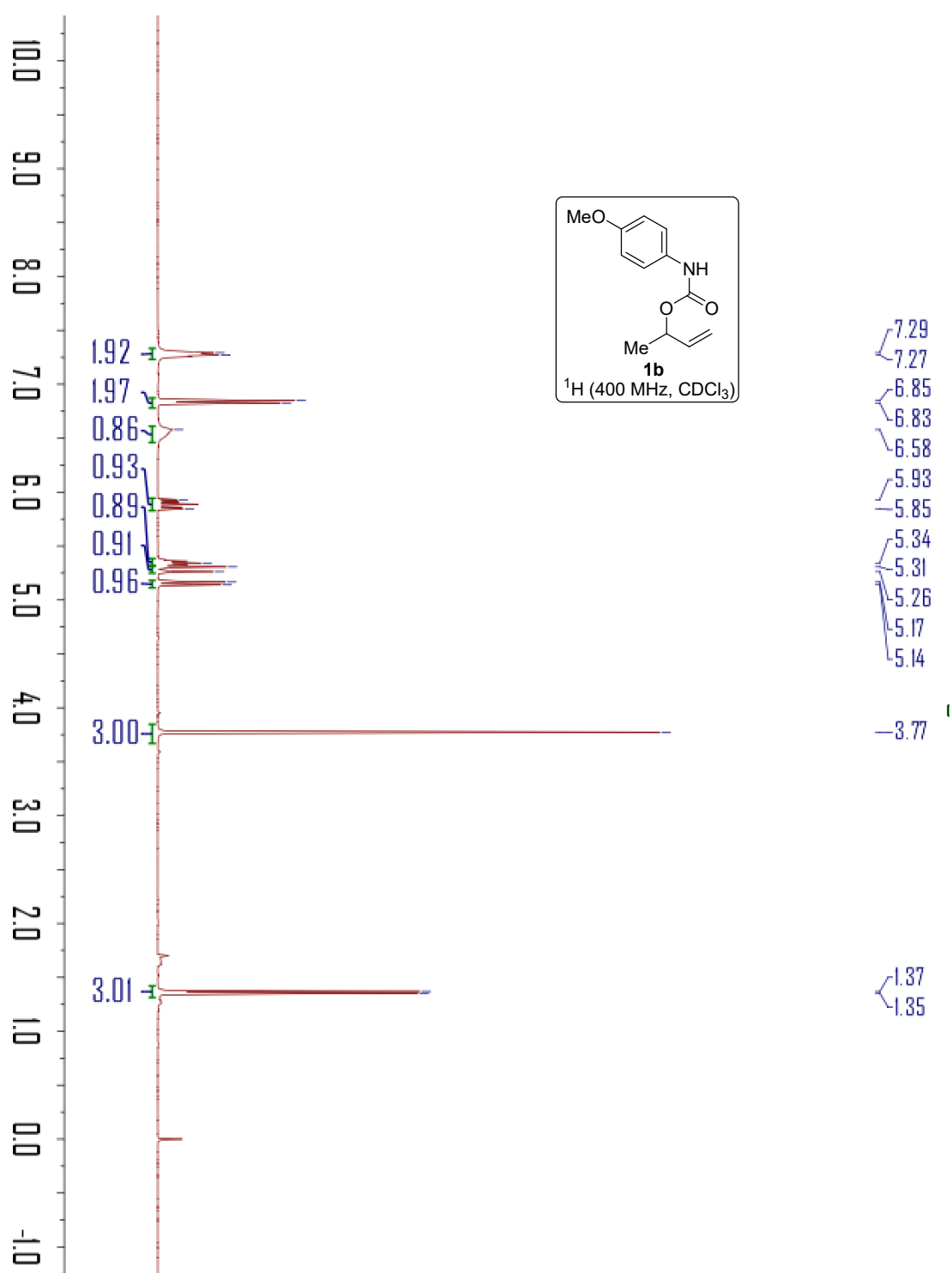
Colorless oil, Yield 30.3 mg, 35%; TLC  $R_f$  = 0.1 (PE:EA 3:1).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.33 – 7.29 (m, 2H), 7.23 – 7.19 (m, 3H), 5.84 – 5.75 (m,

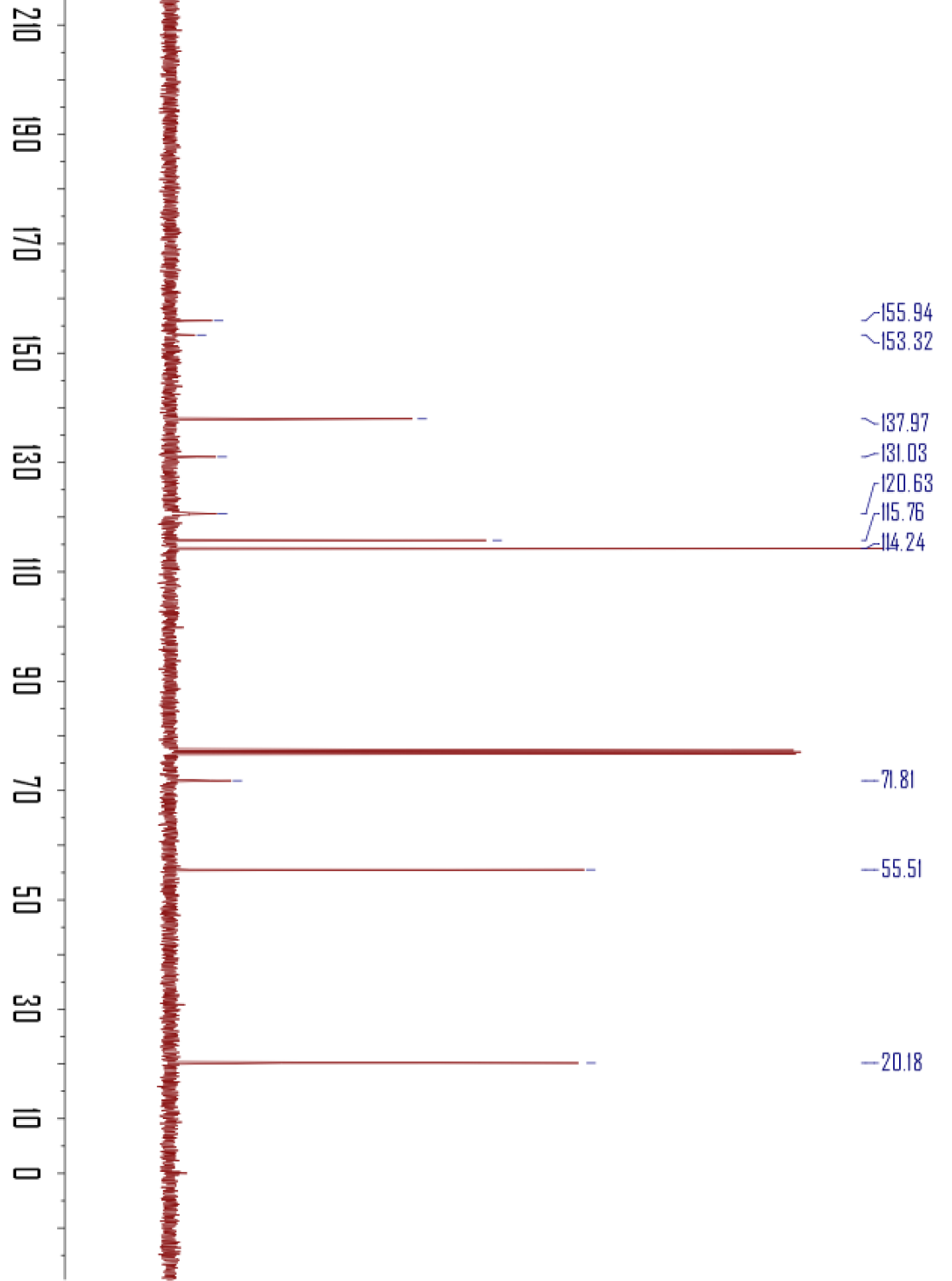
1H), 5.14 – 5.10 (m, 1H), 5.00, 5.06 (m, 1H), 2.20, 2.22 (m, 1H), 2.72, 2.50 (m, 2H), 1.81, 1.71 (m, 2H), 1.12 (s, 9H).  
 39.4, 32.5, 30.3. **H**

**8. NMR spectra c**

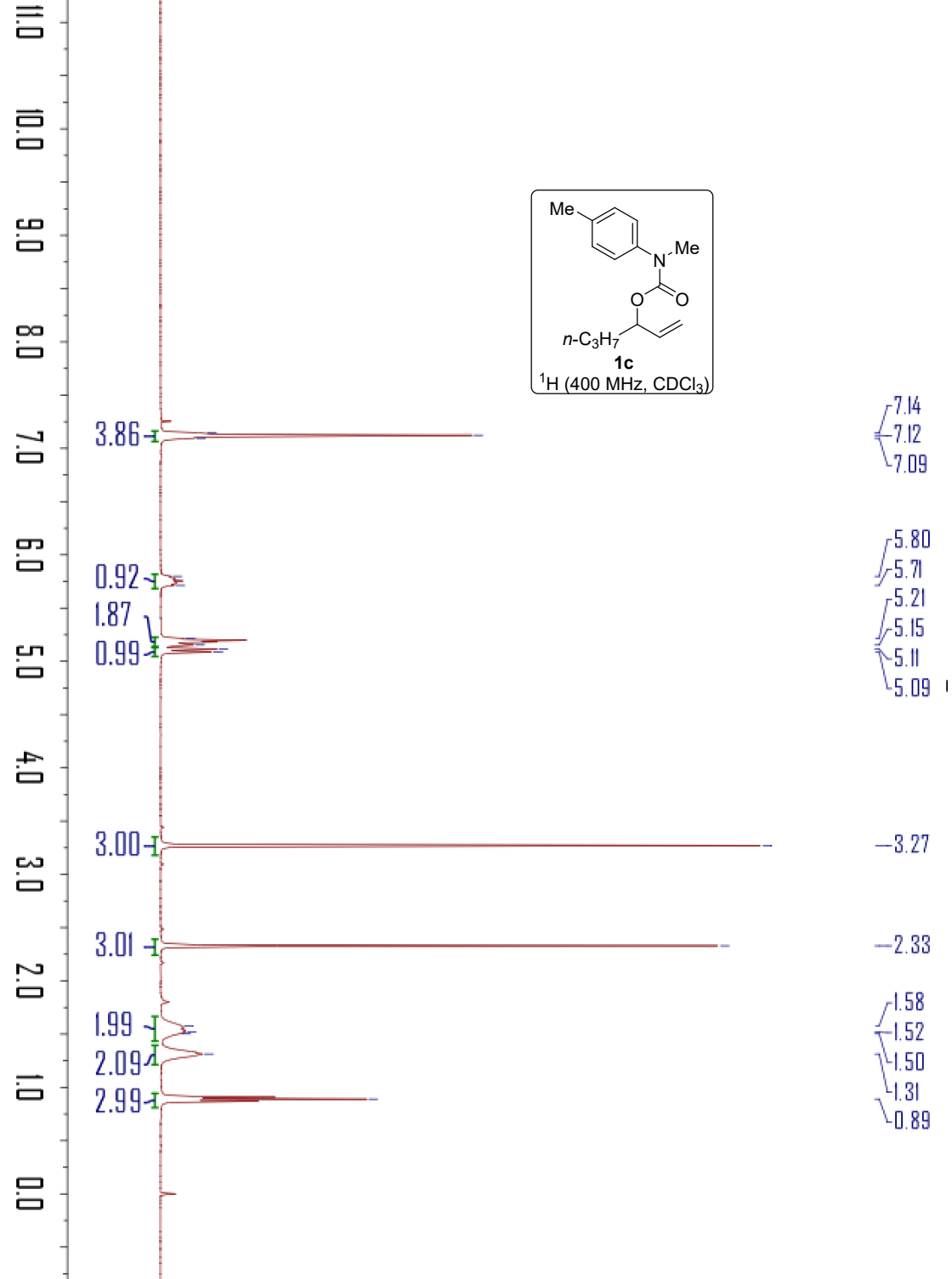


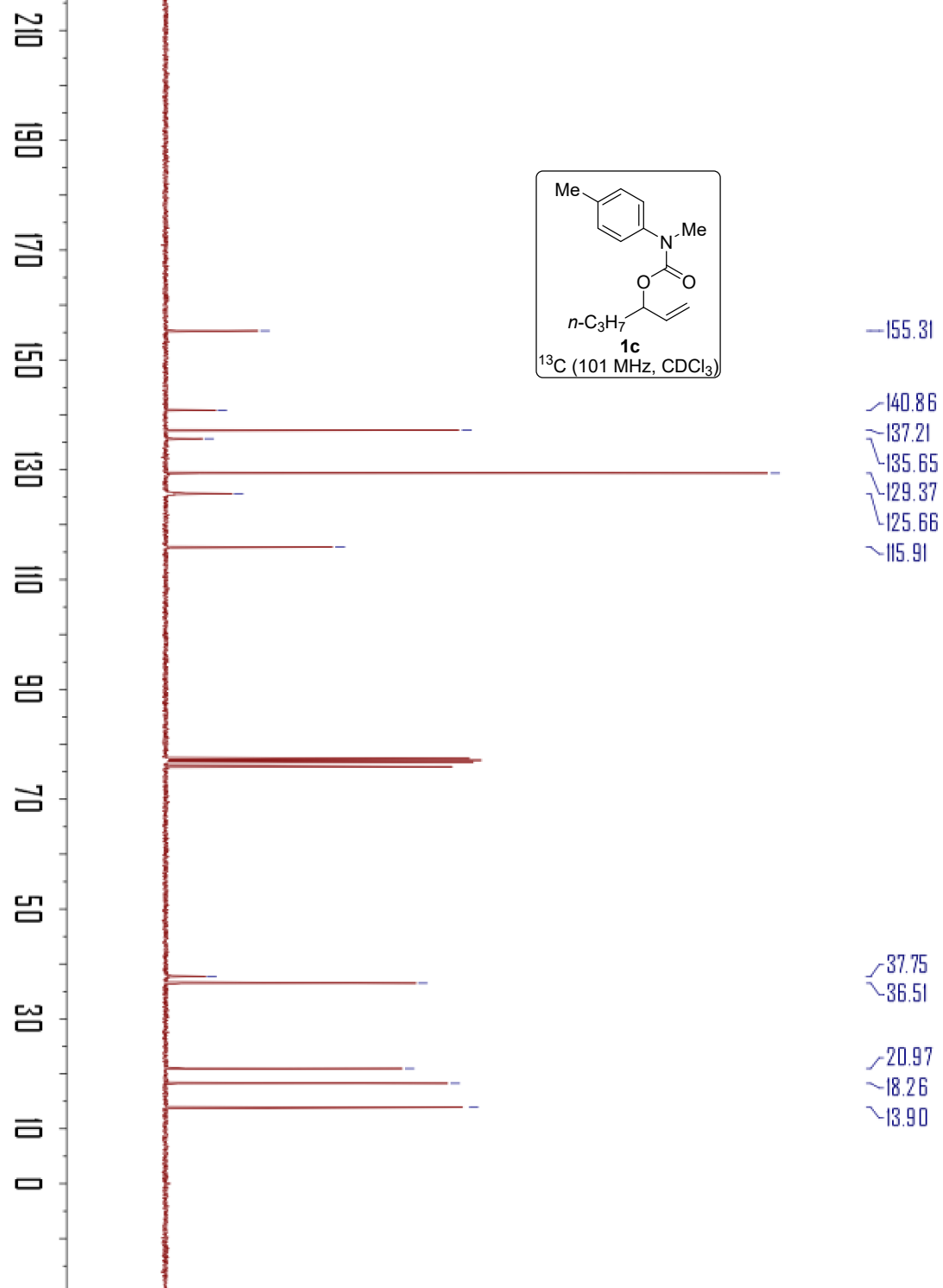


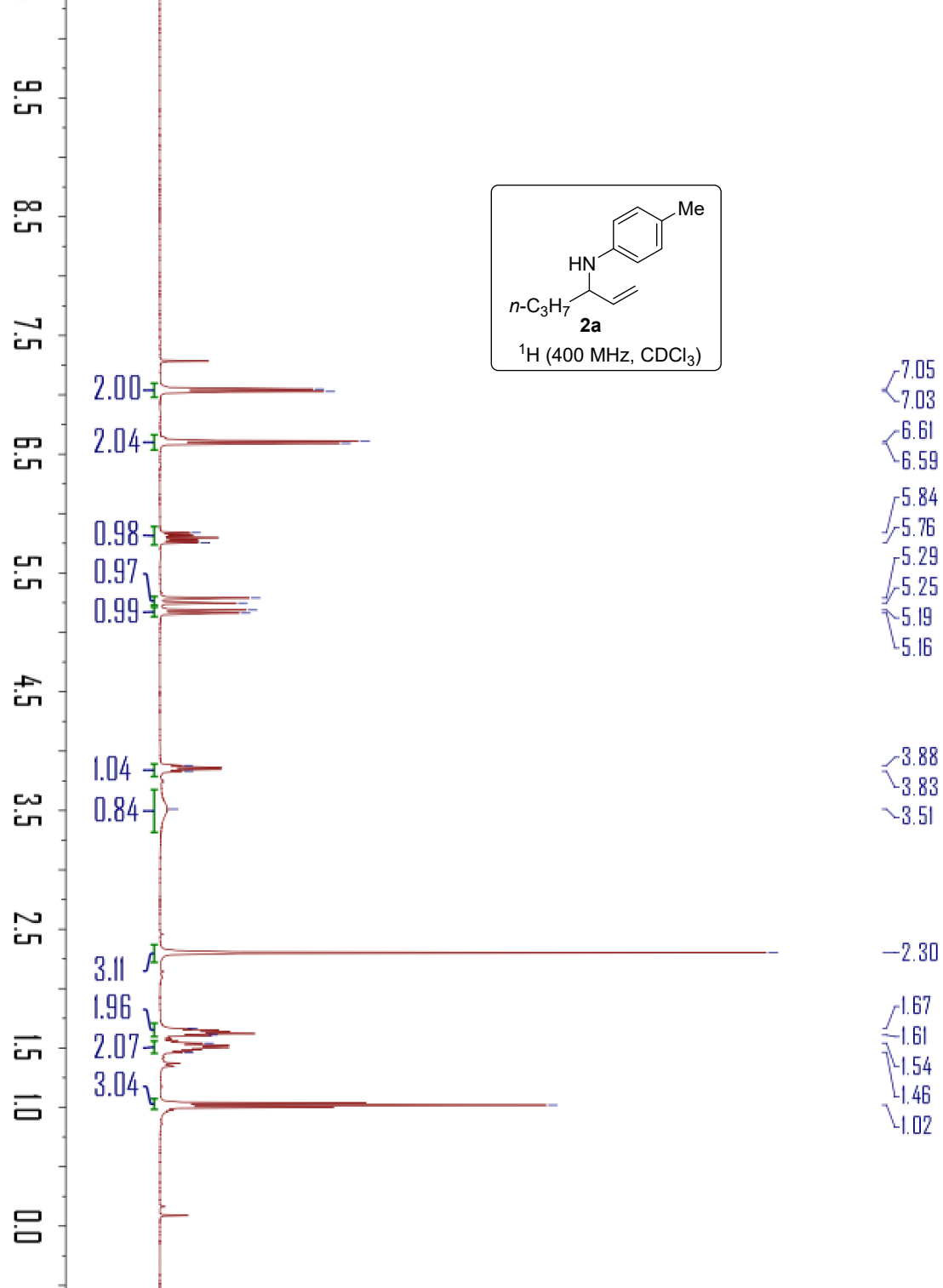


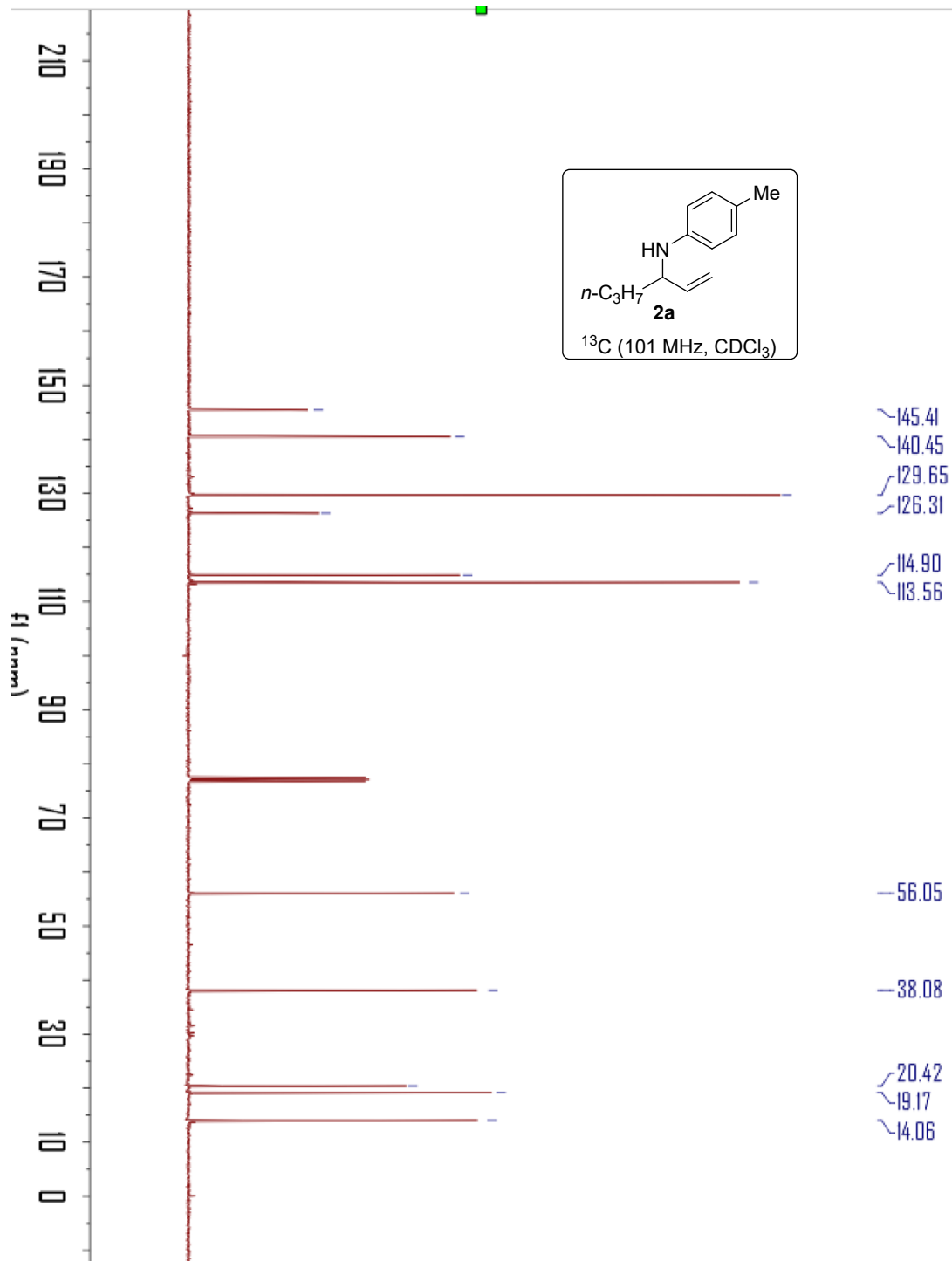


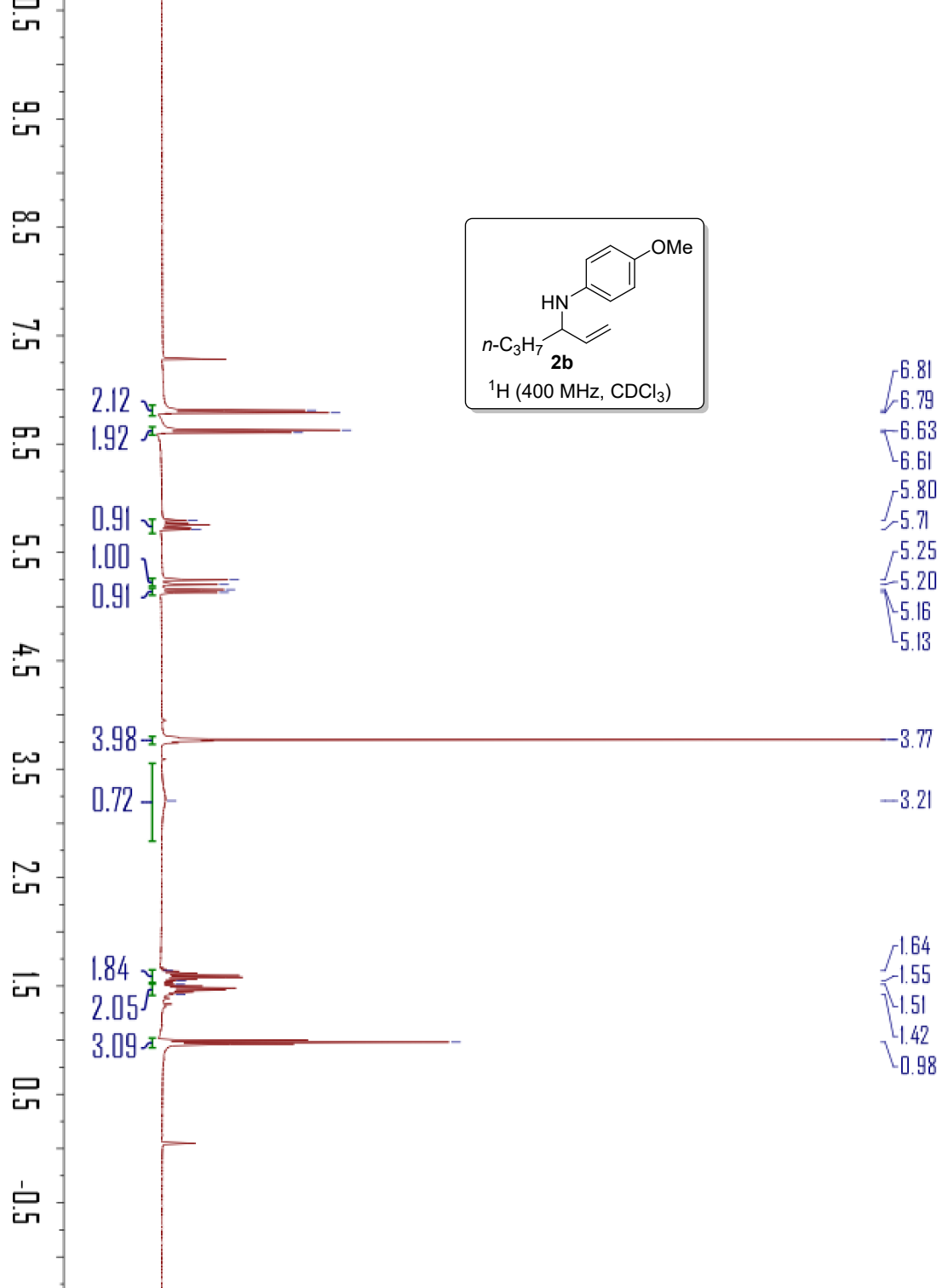


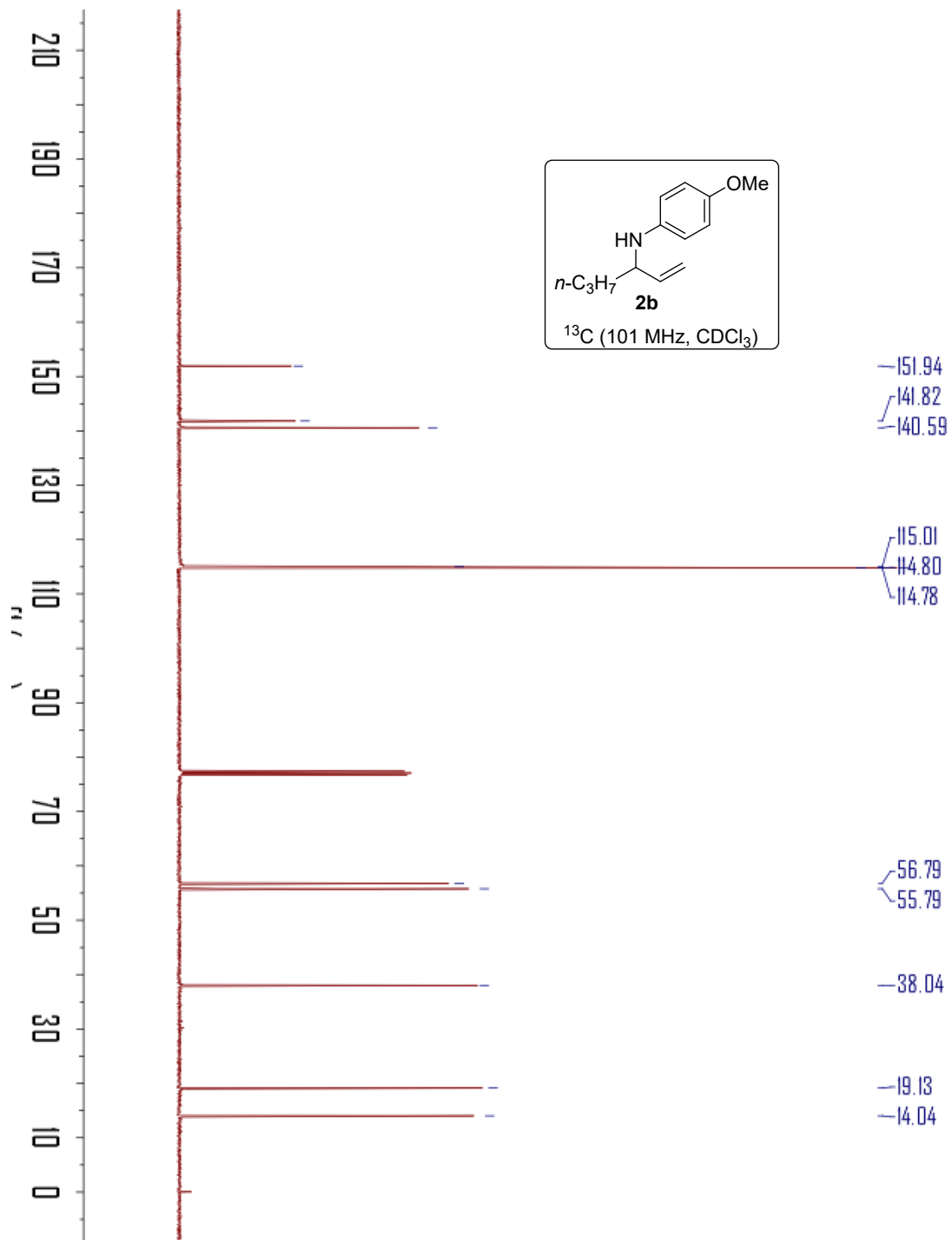


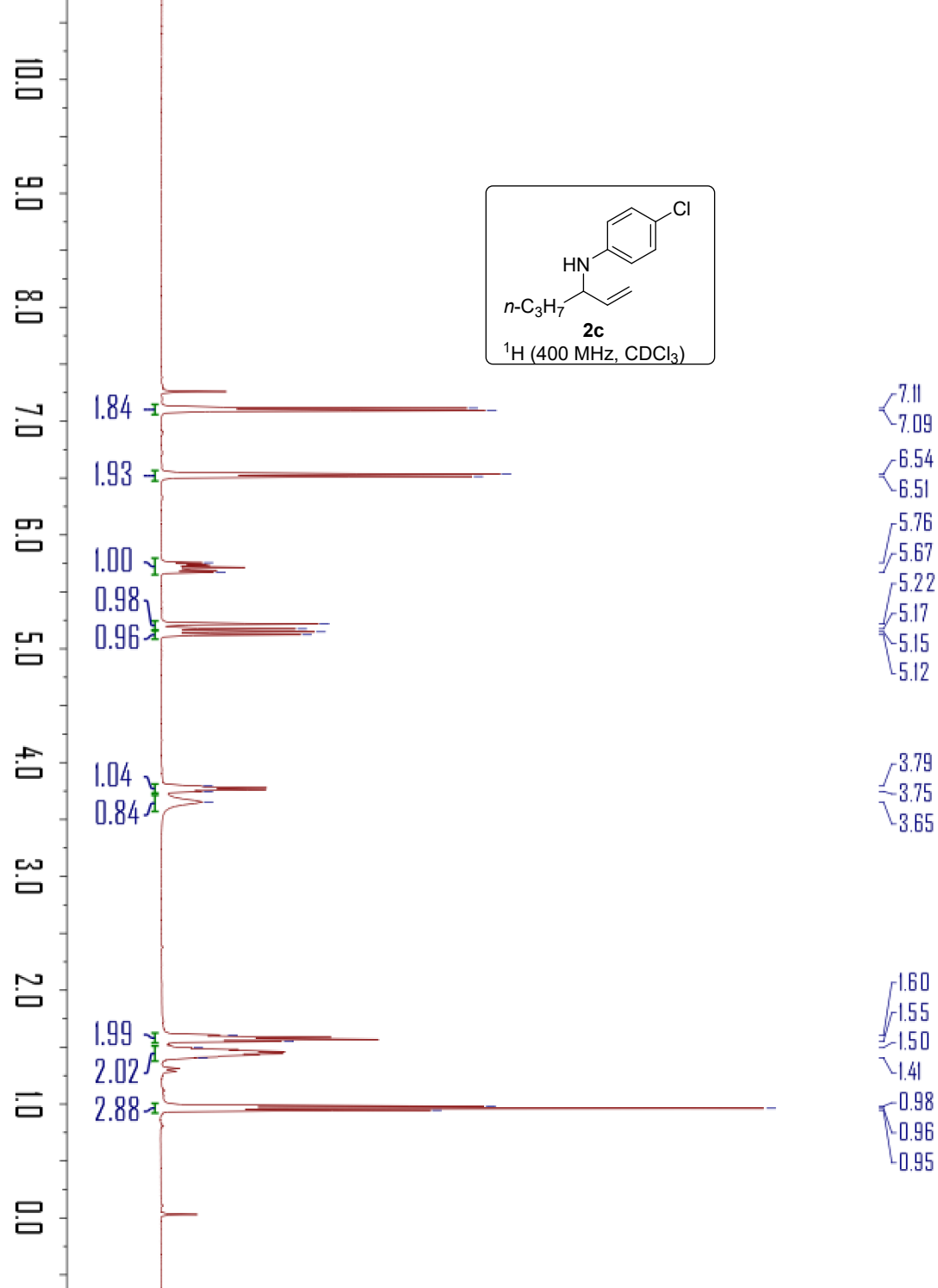


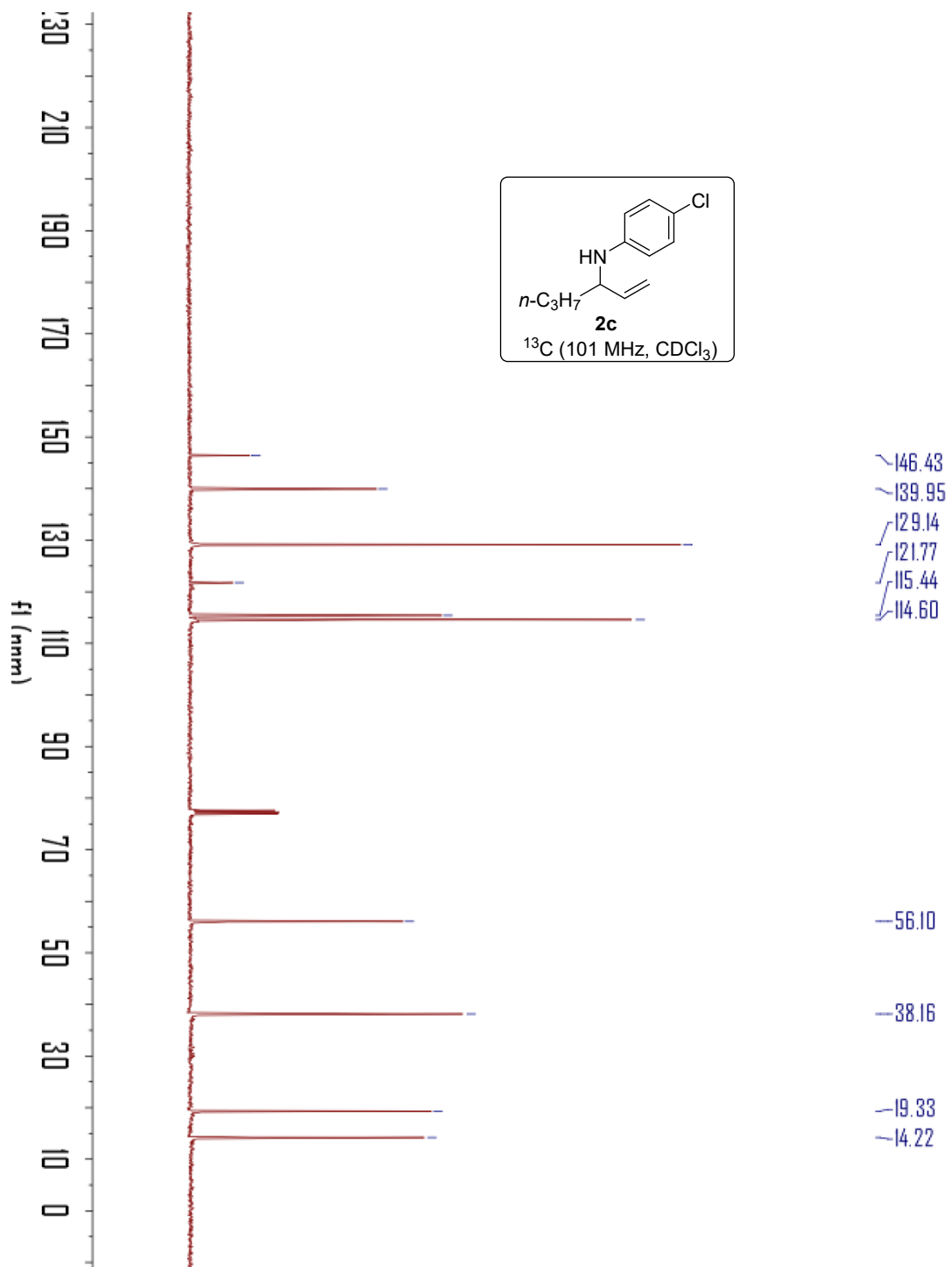




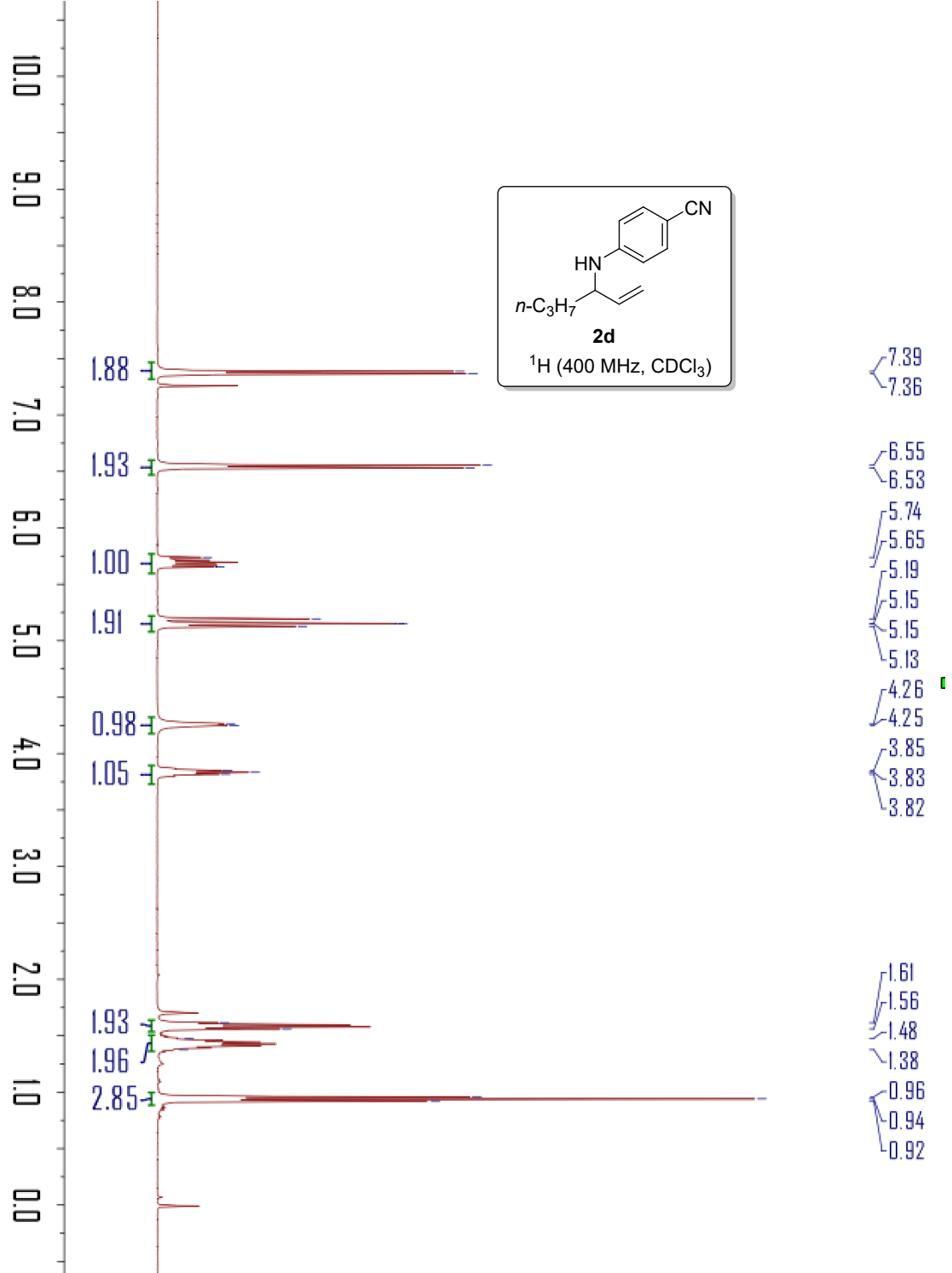


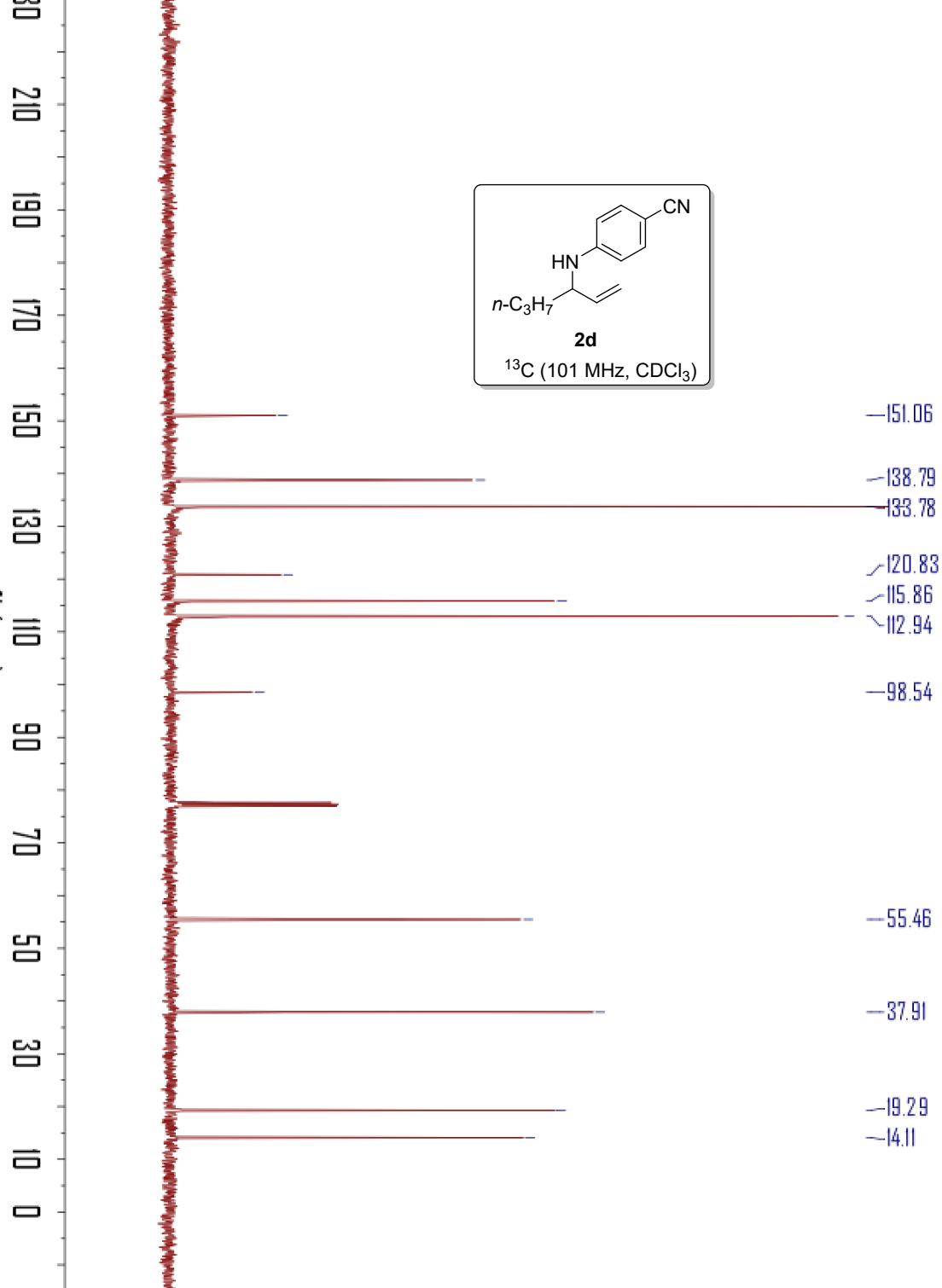


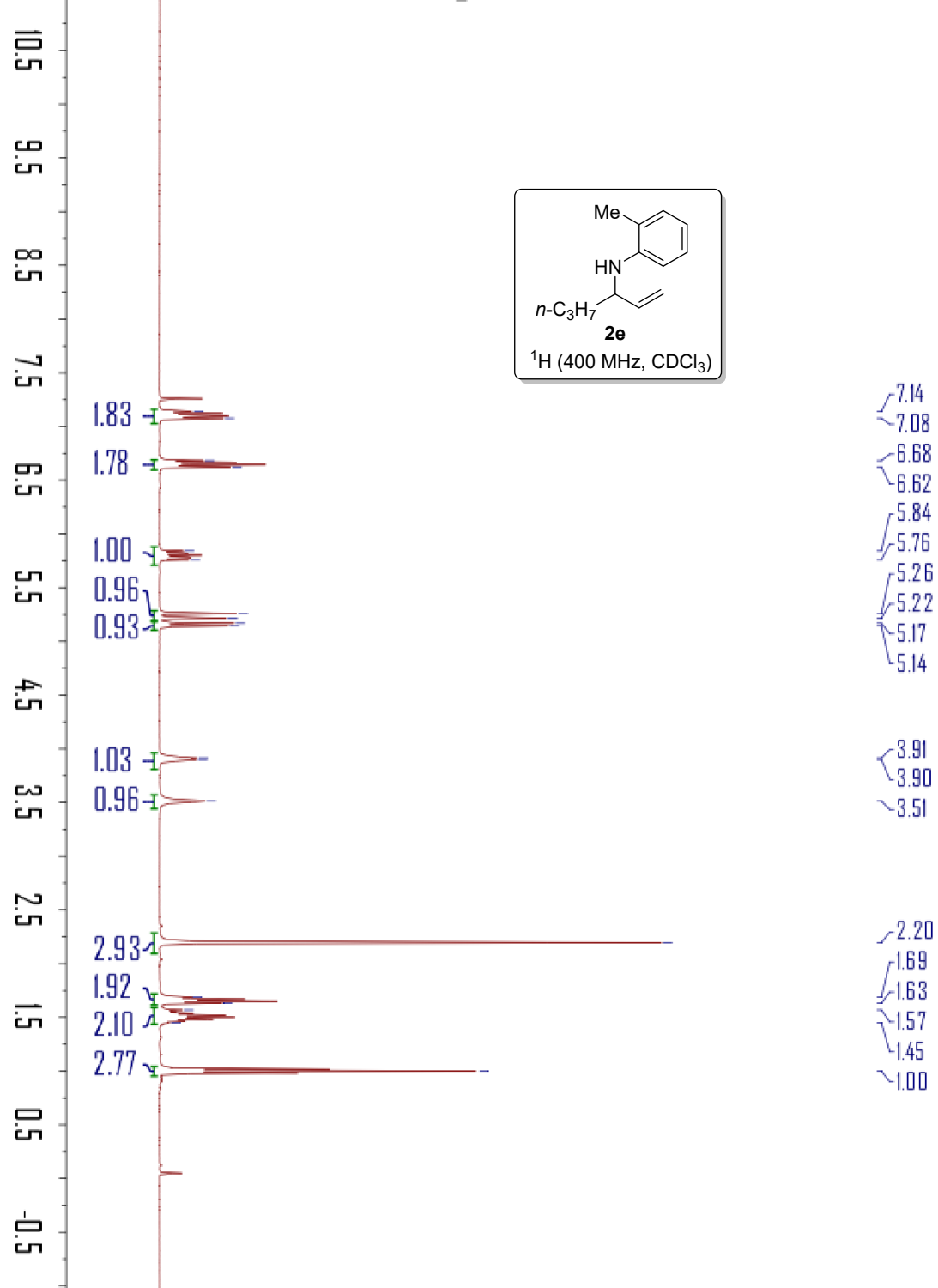


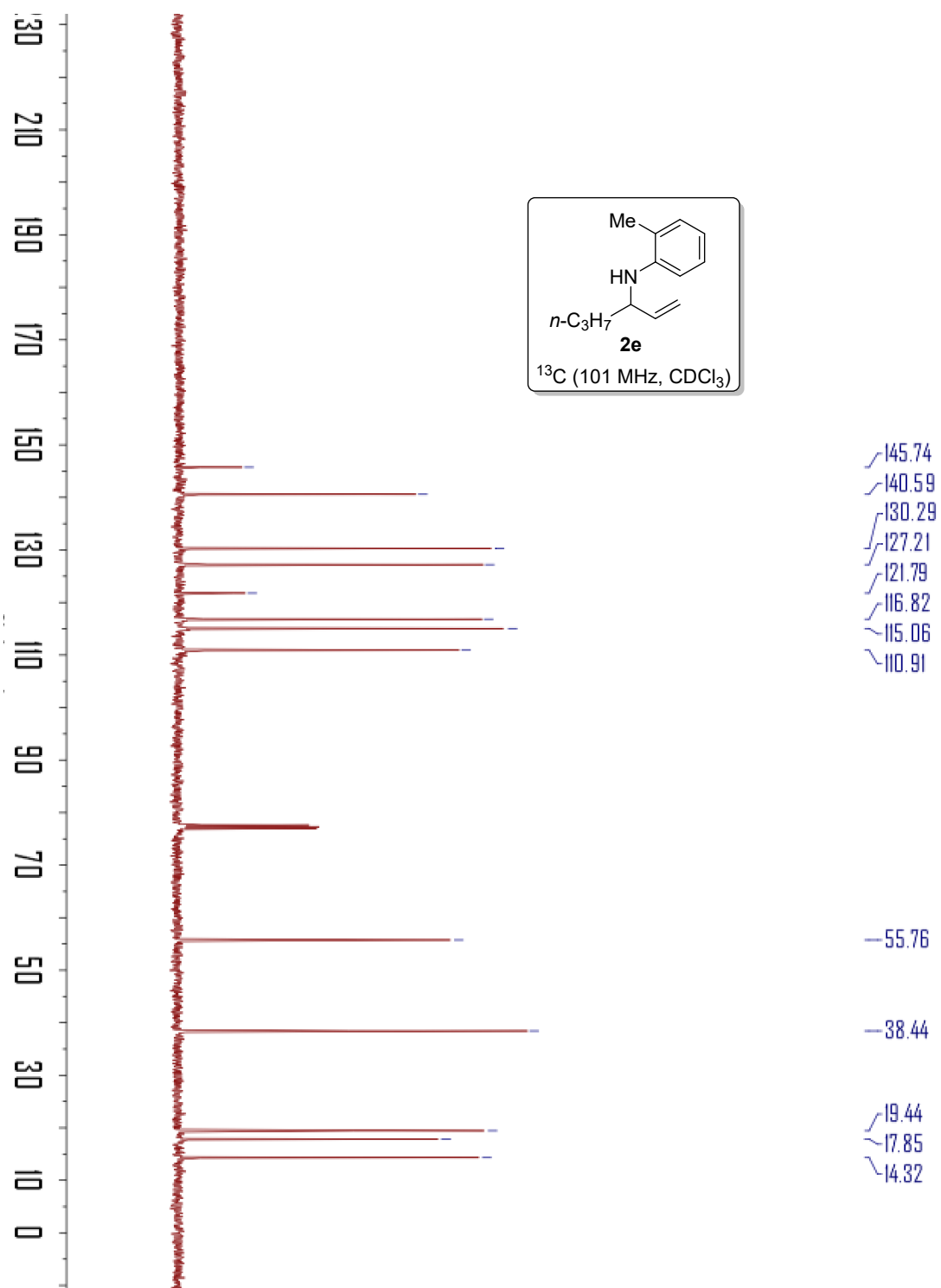


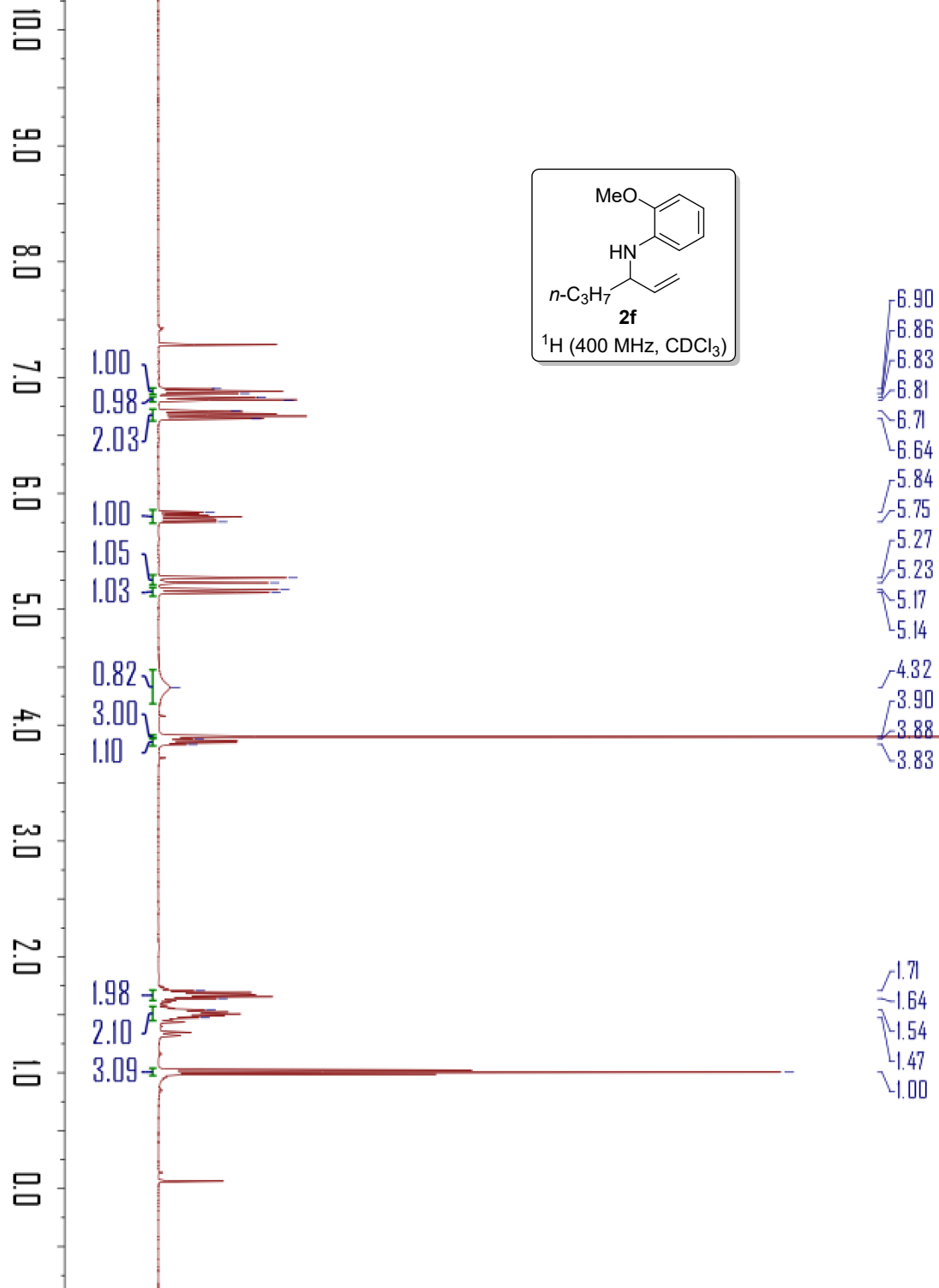


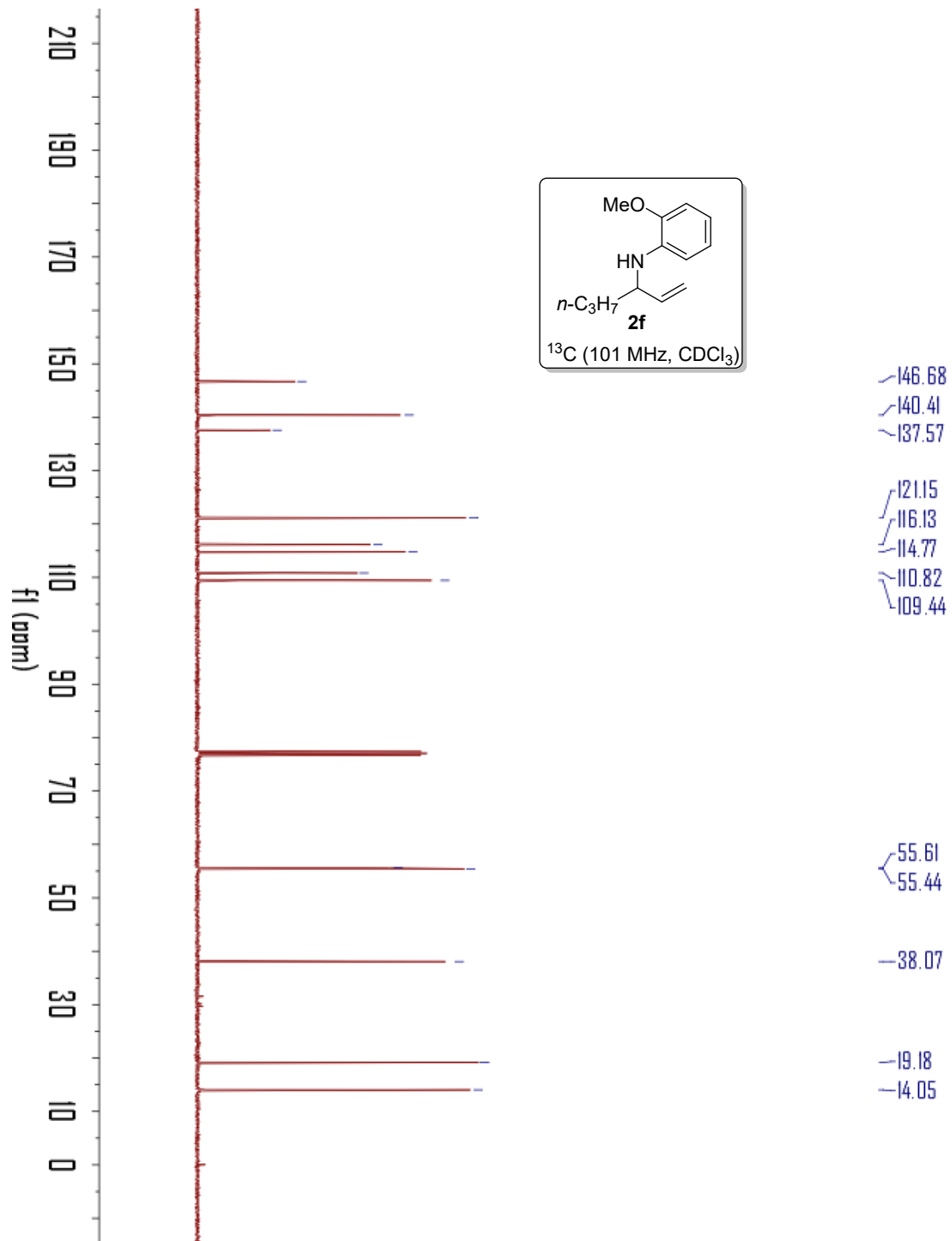


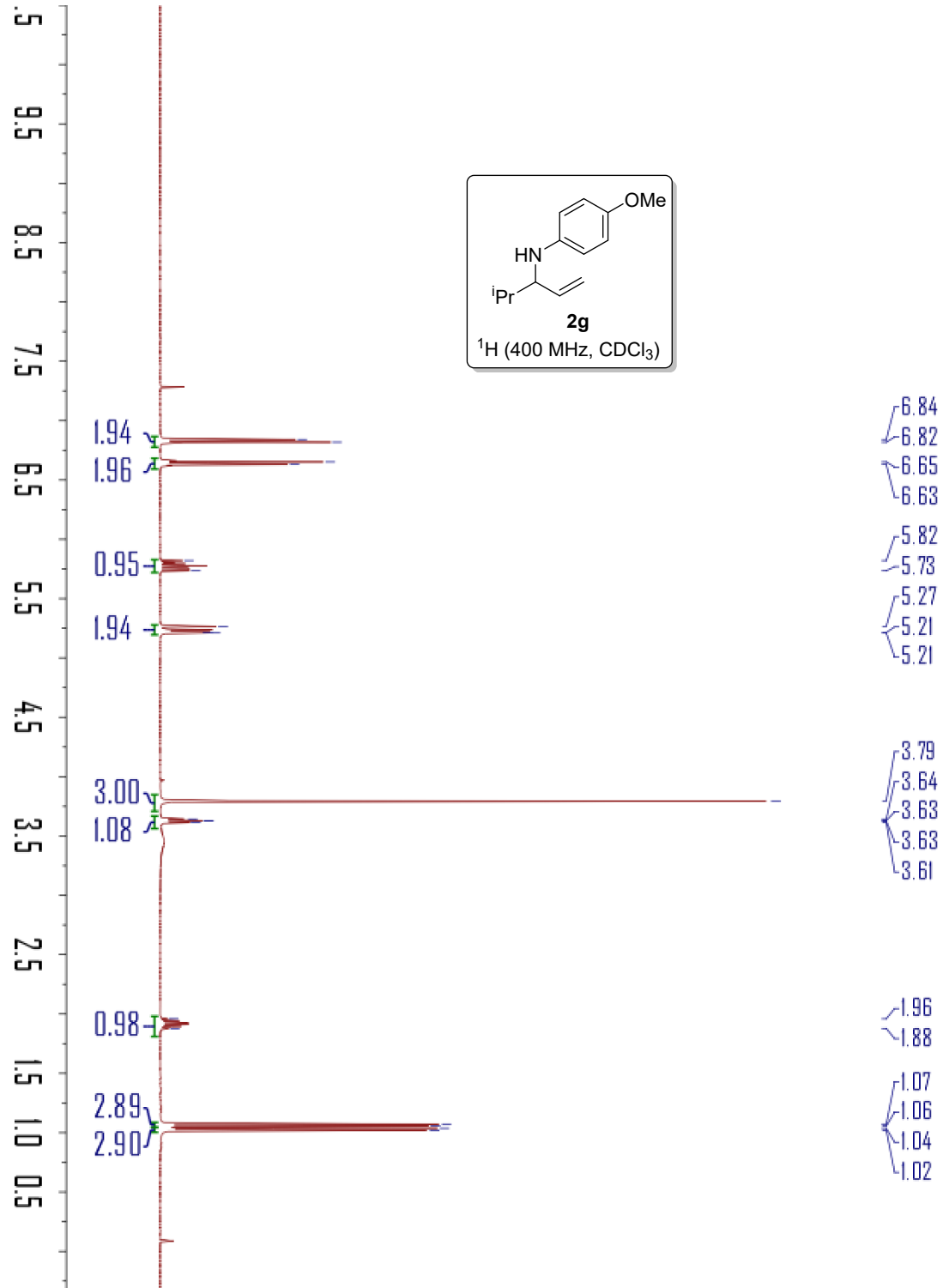


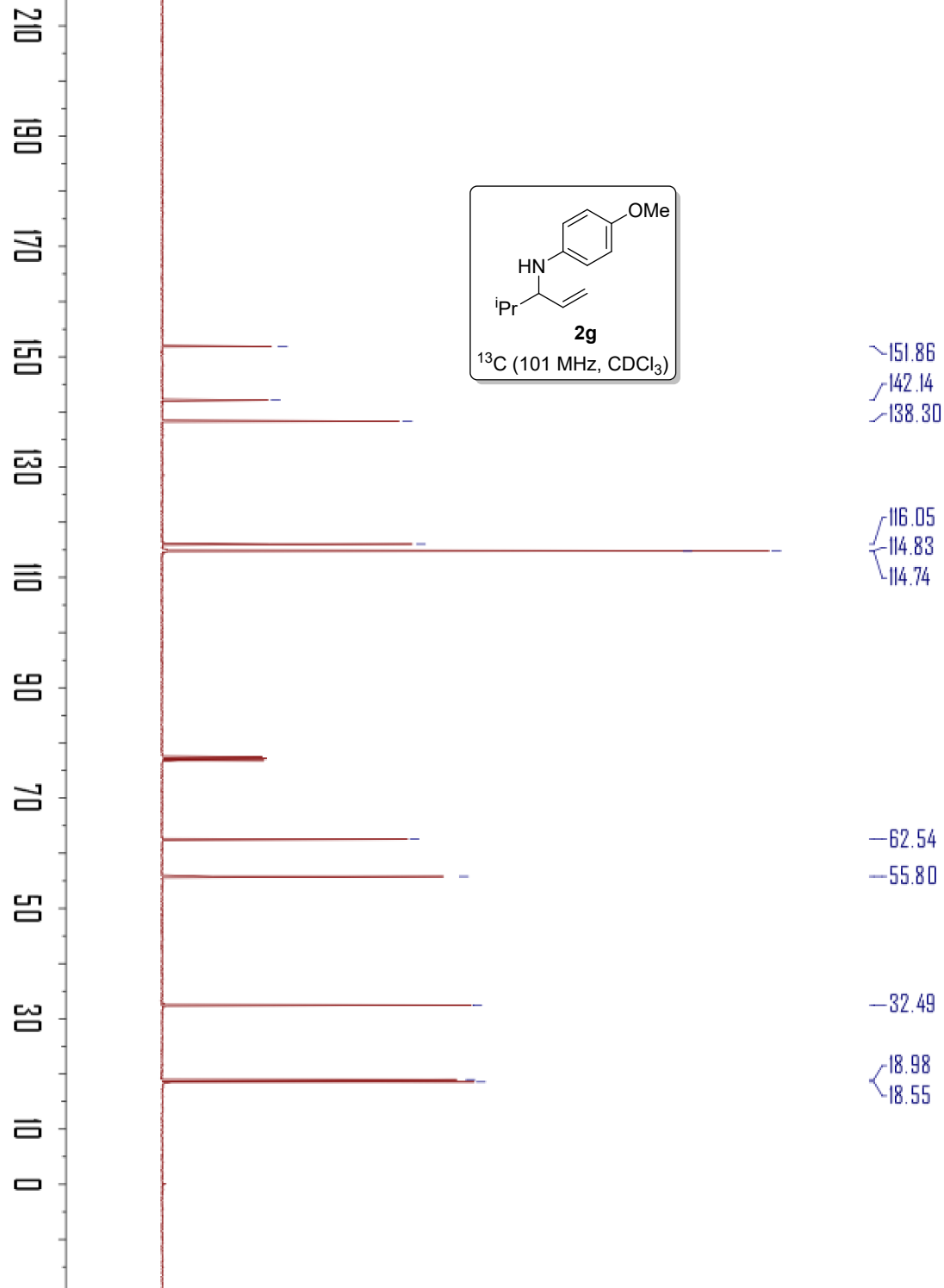




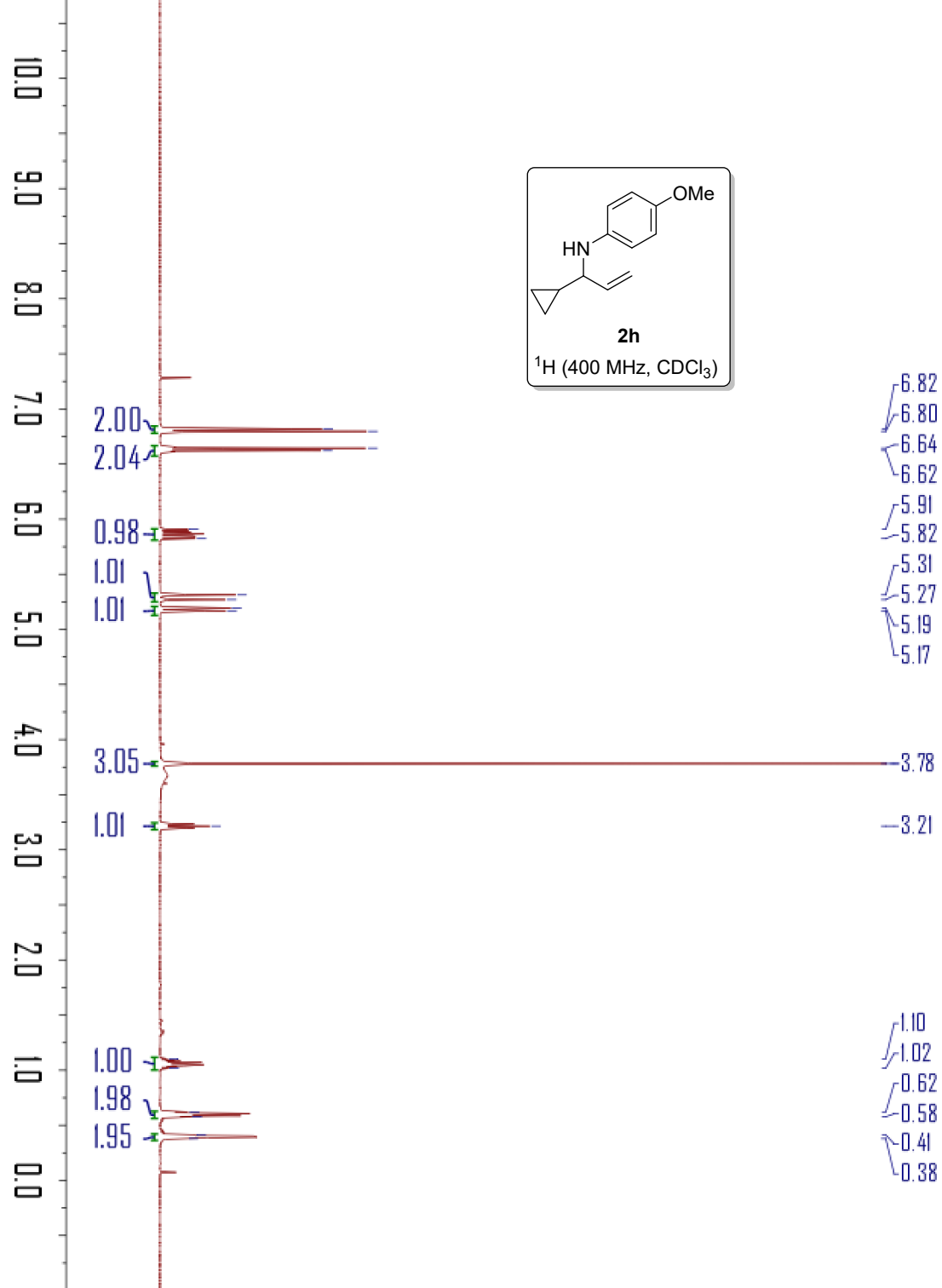


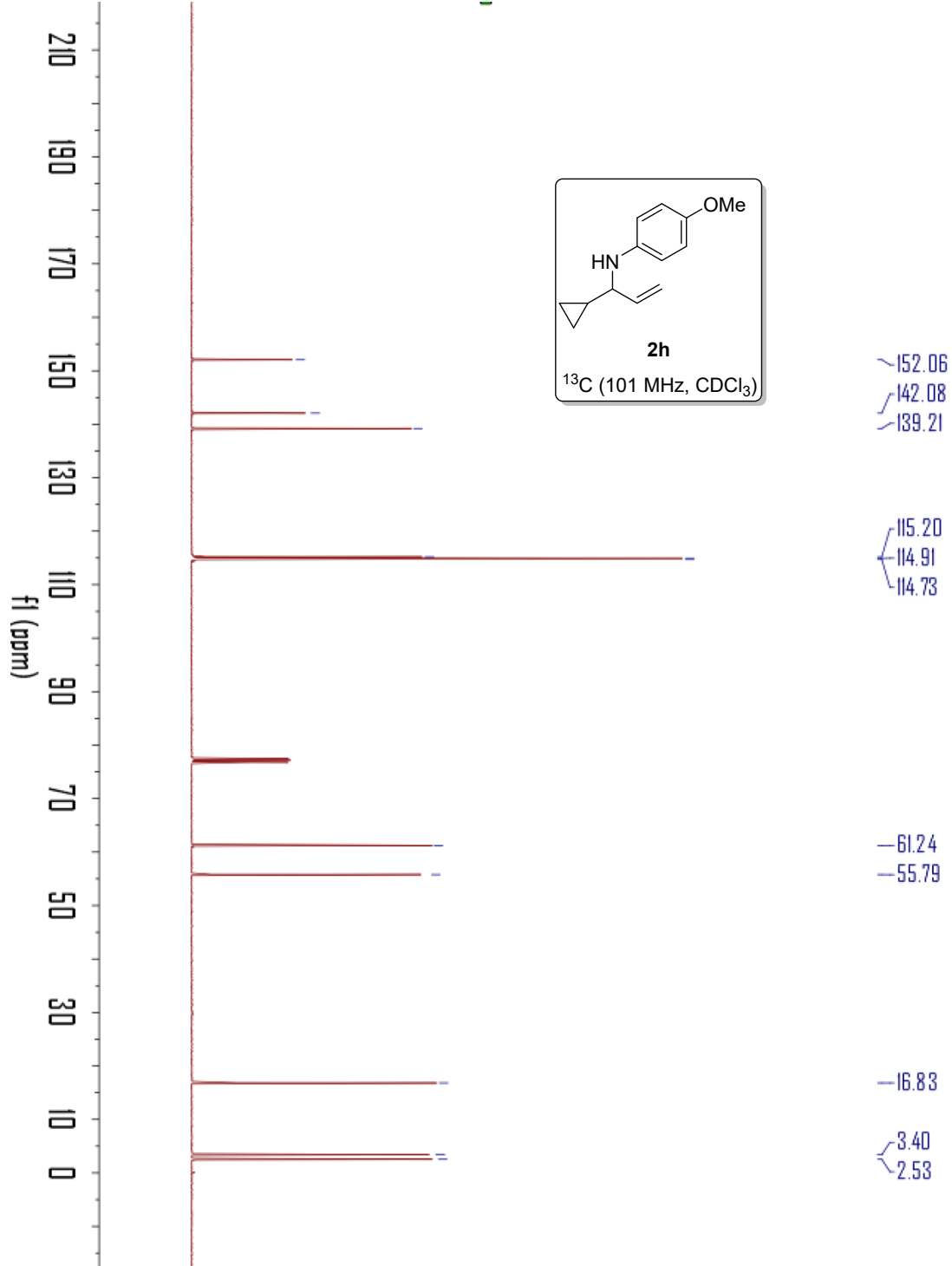


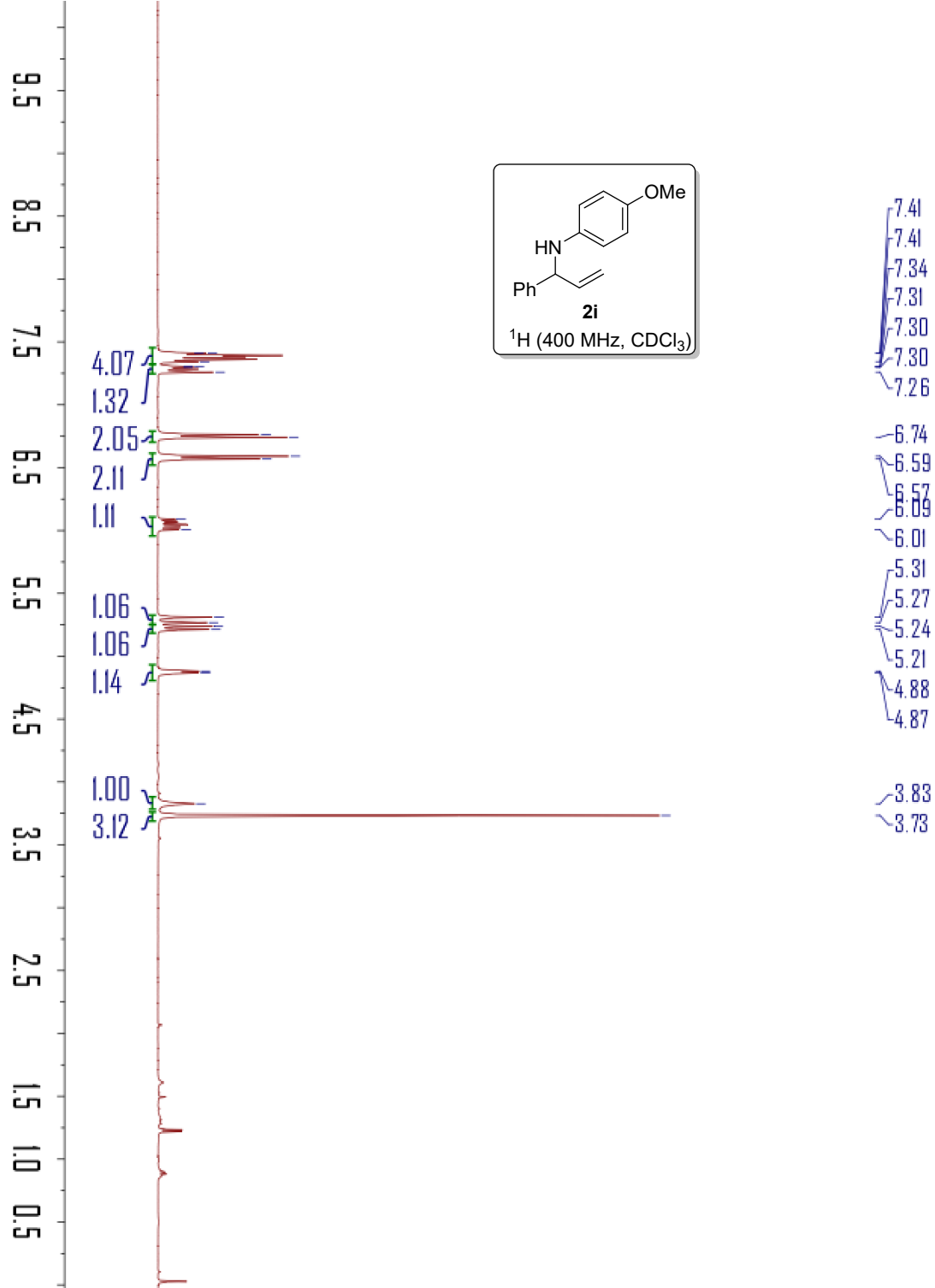


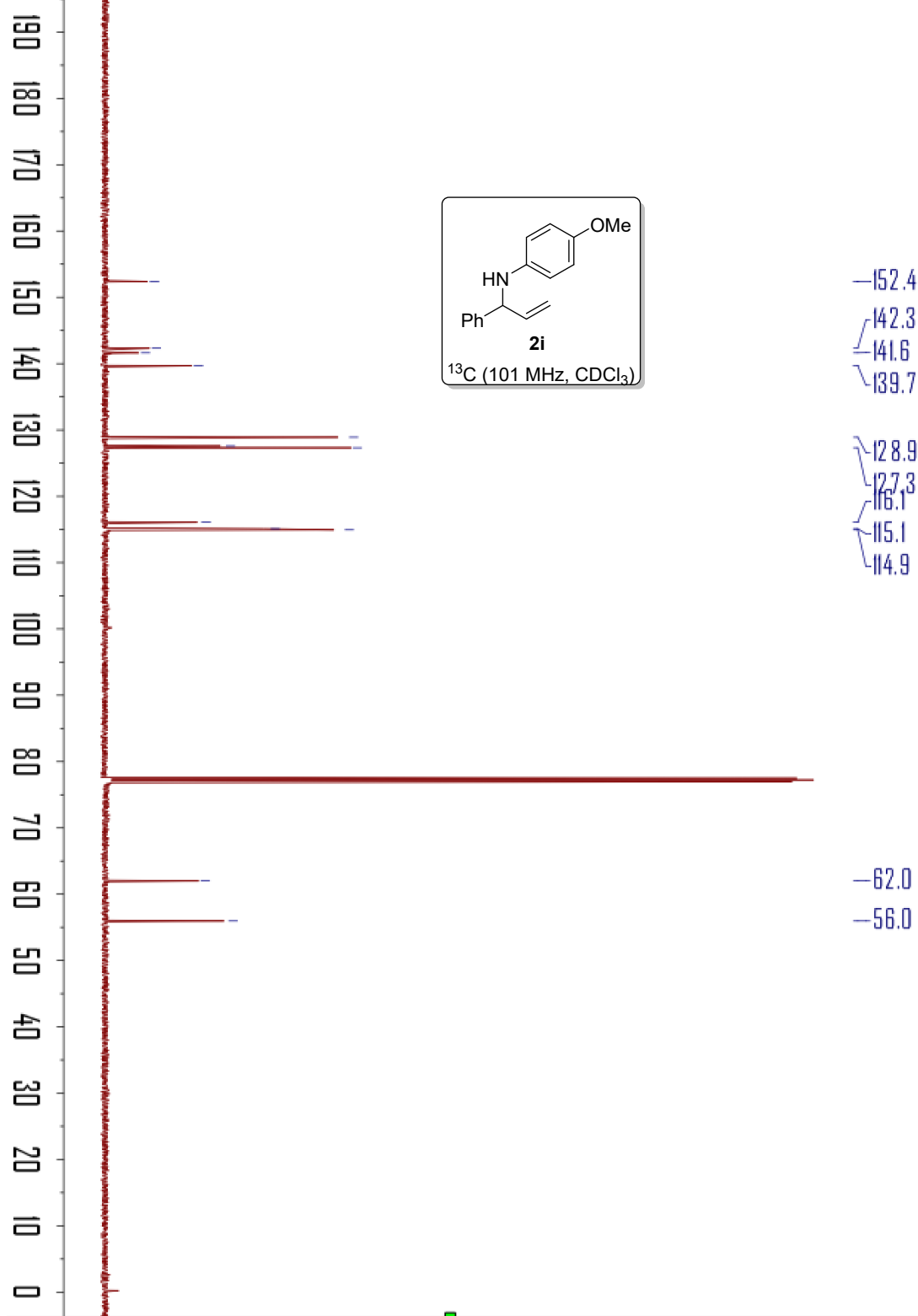


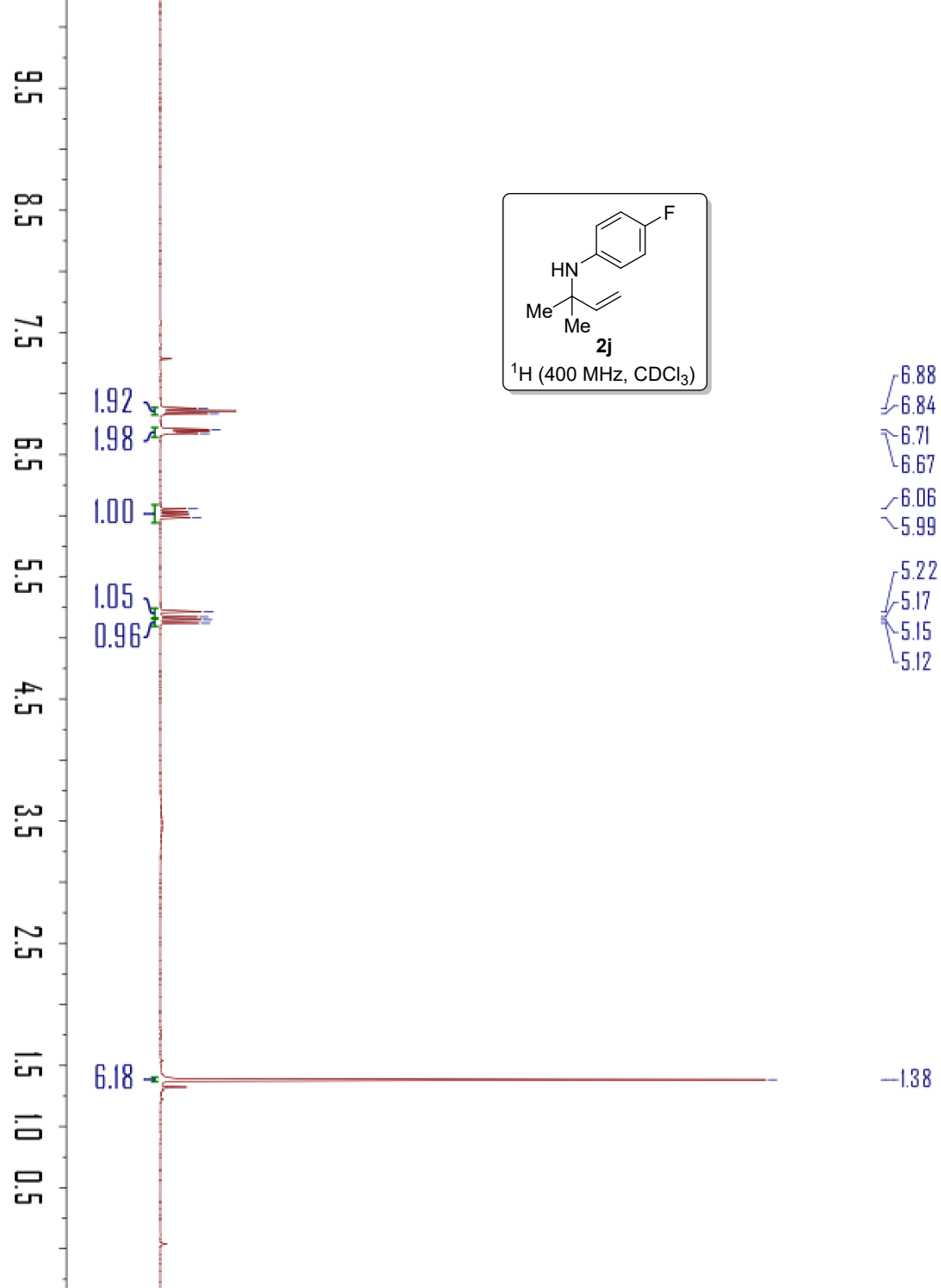


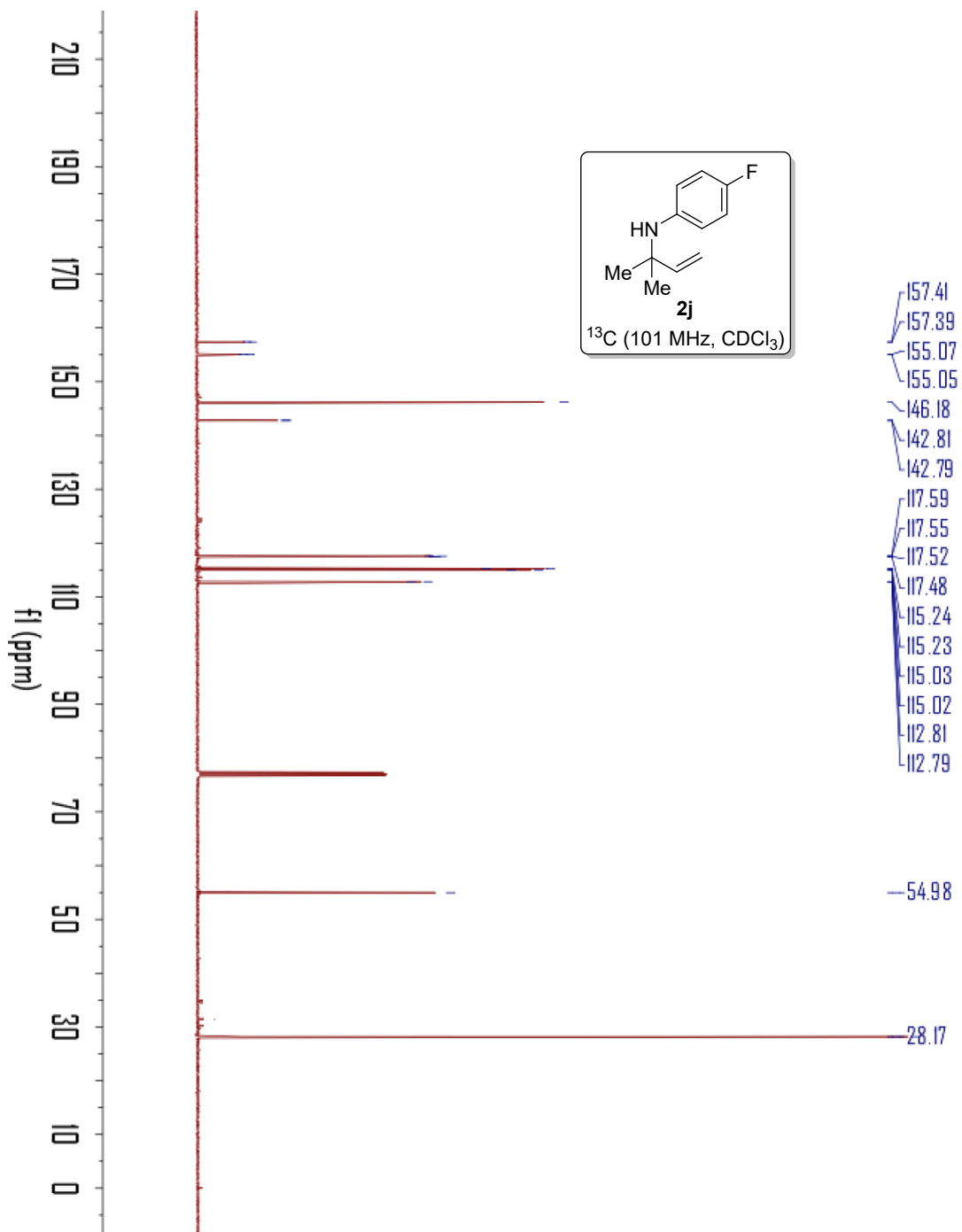


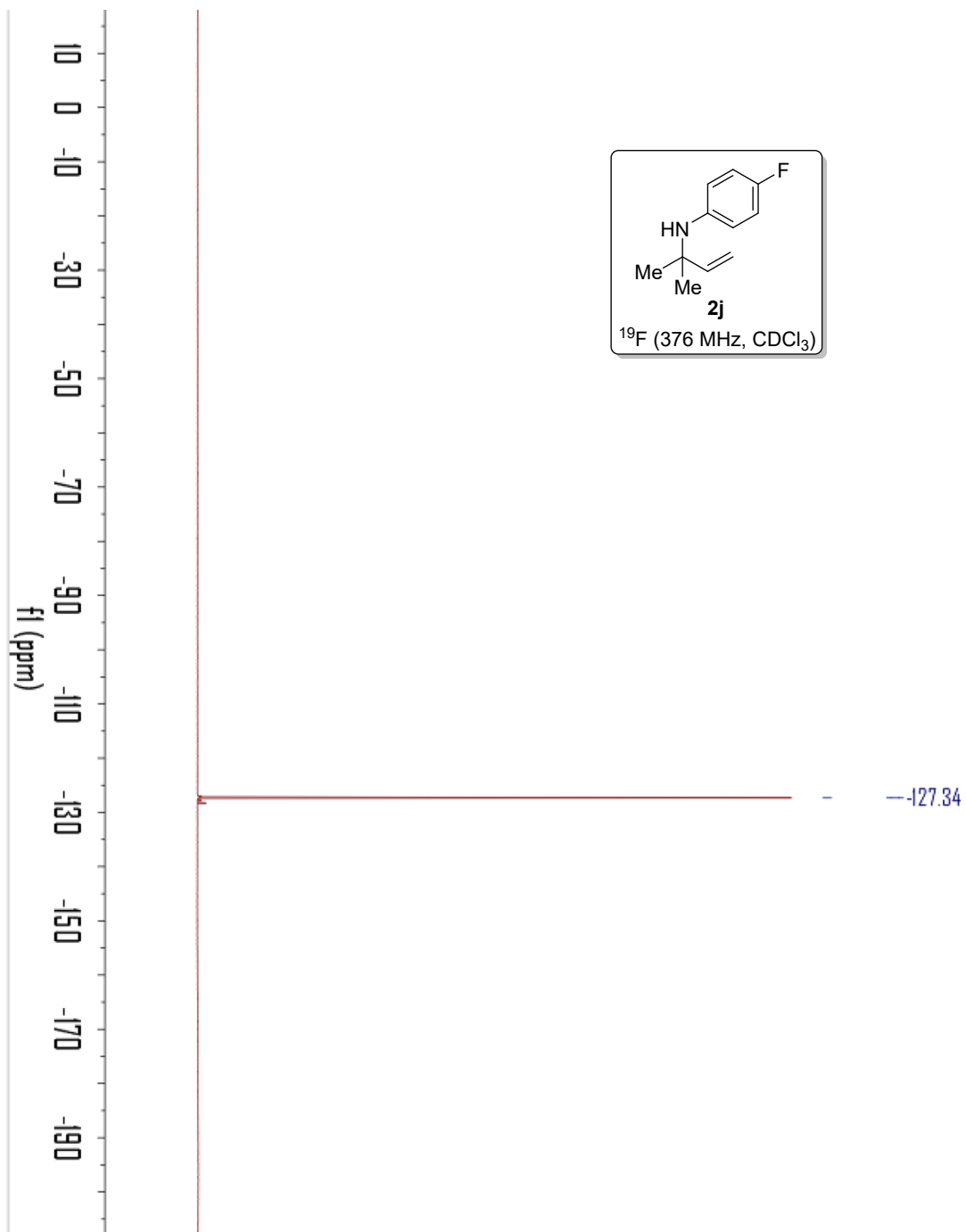


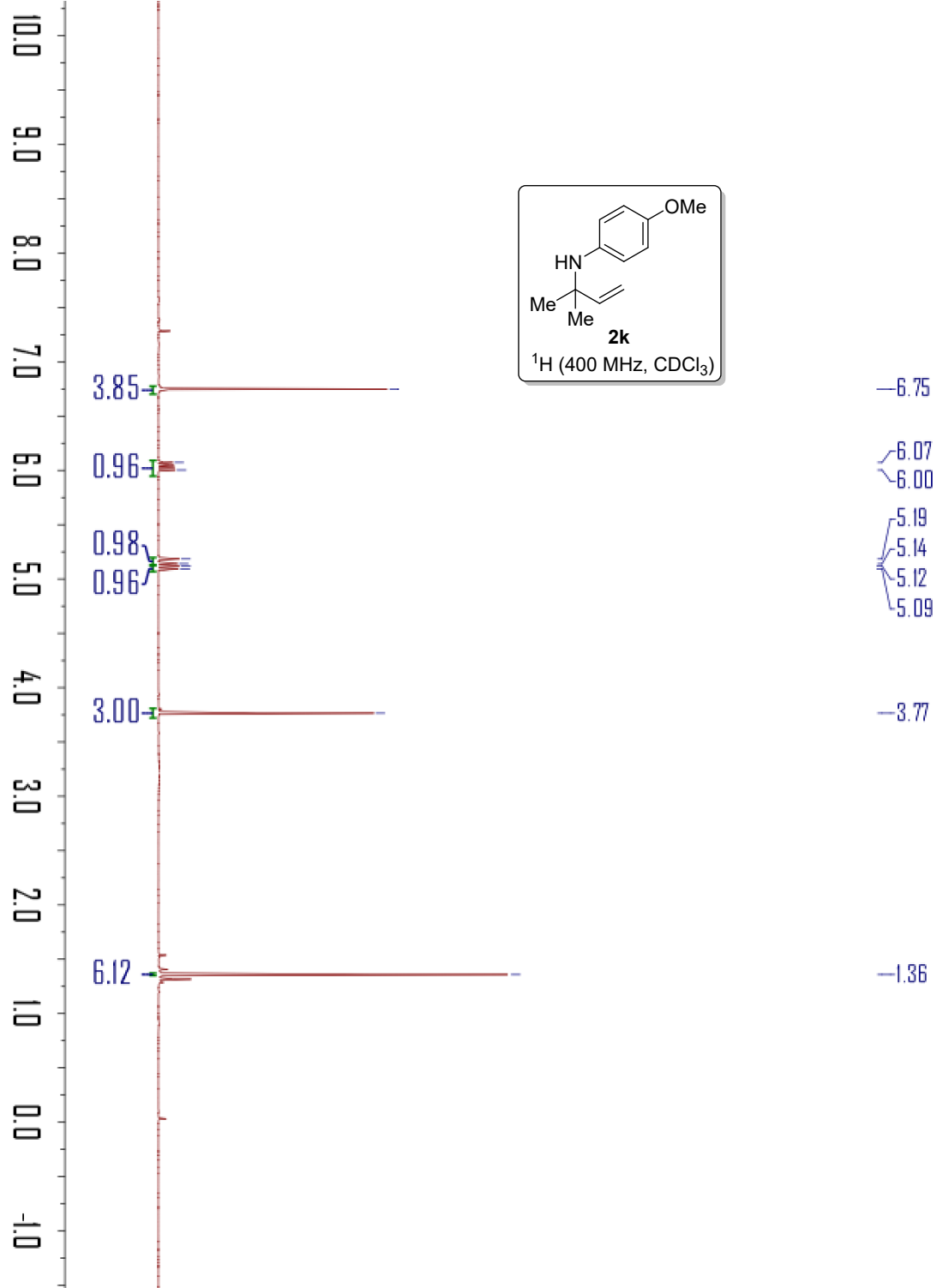




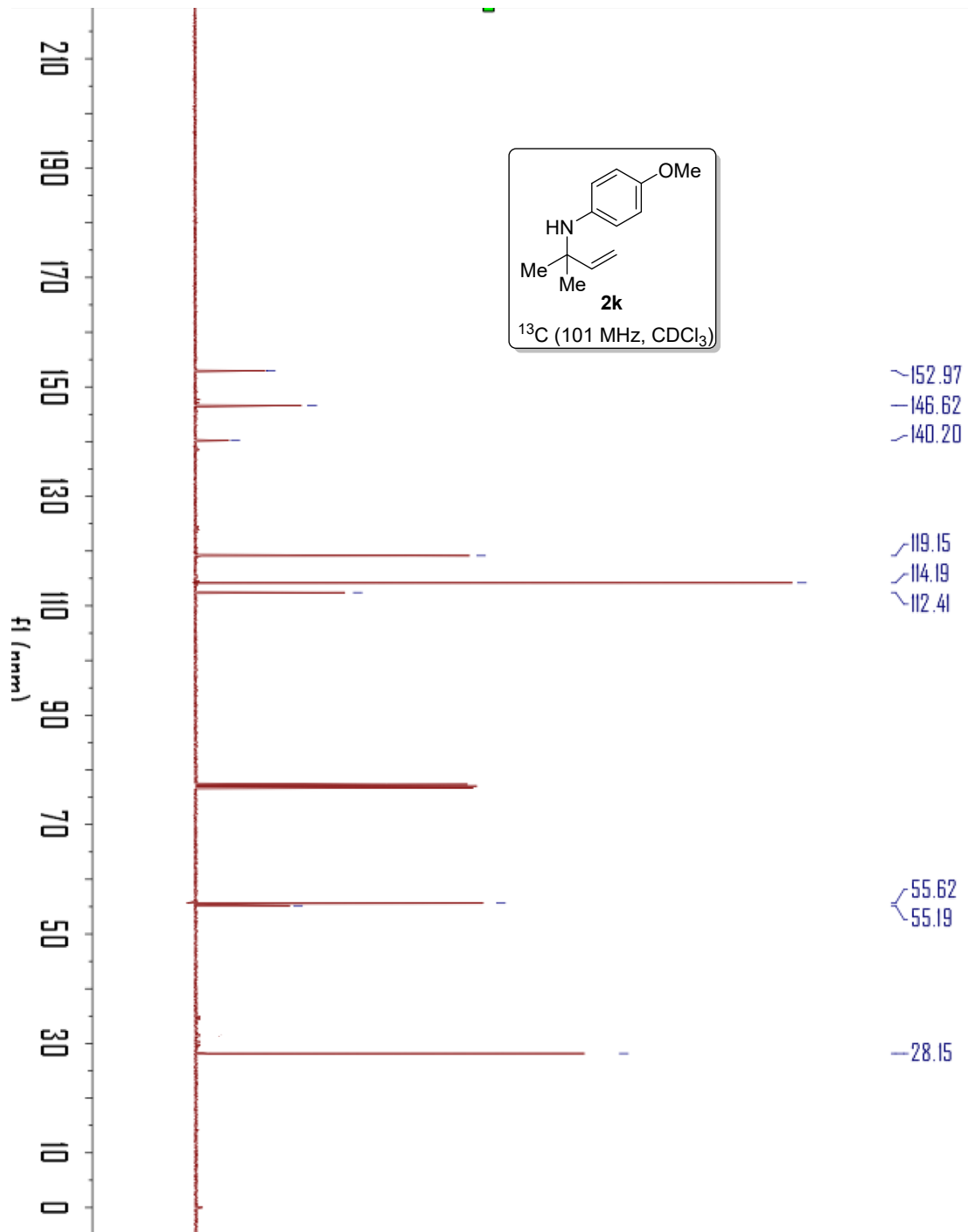


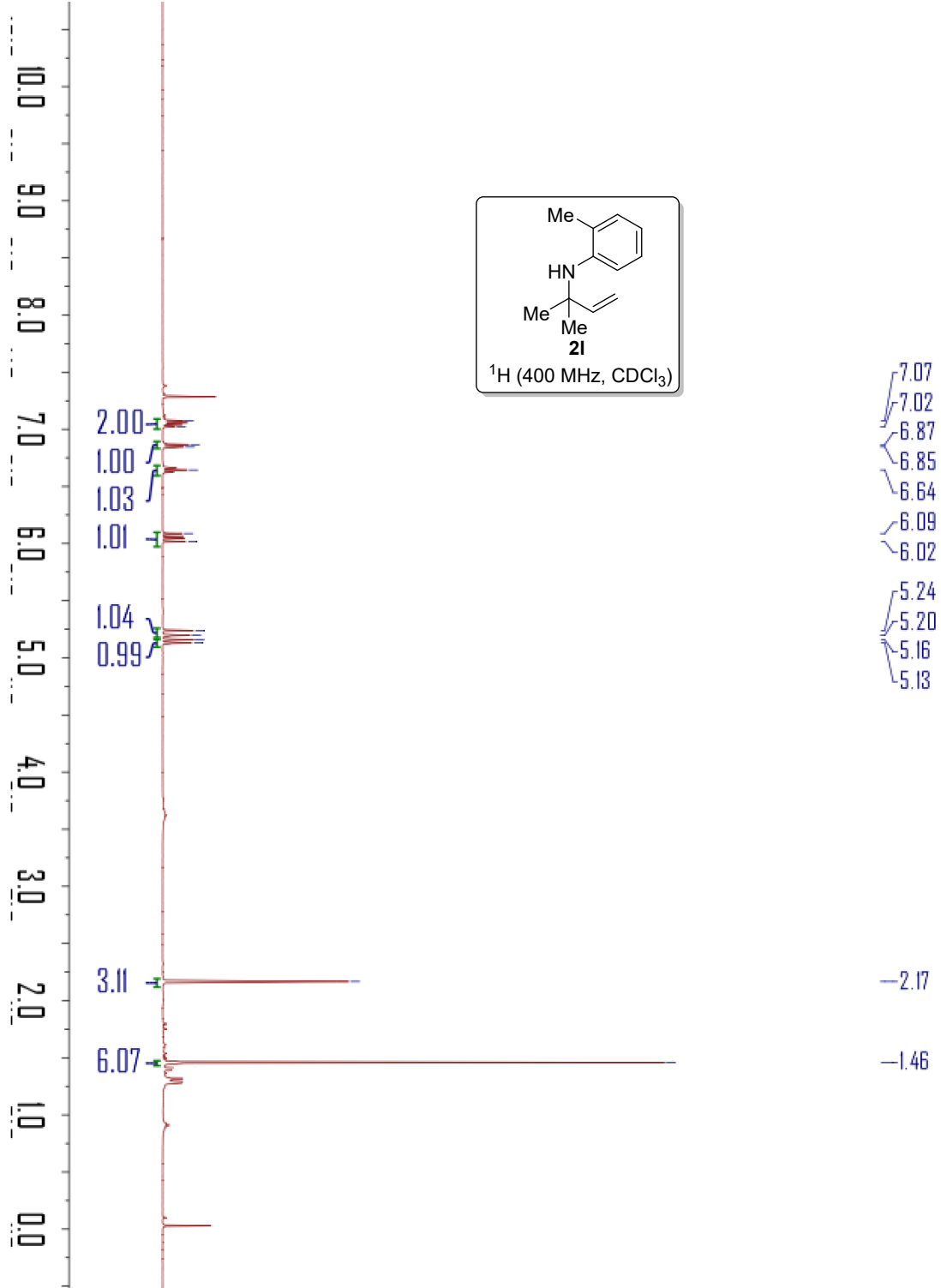


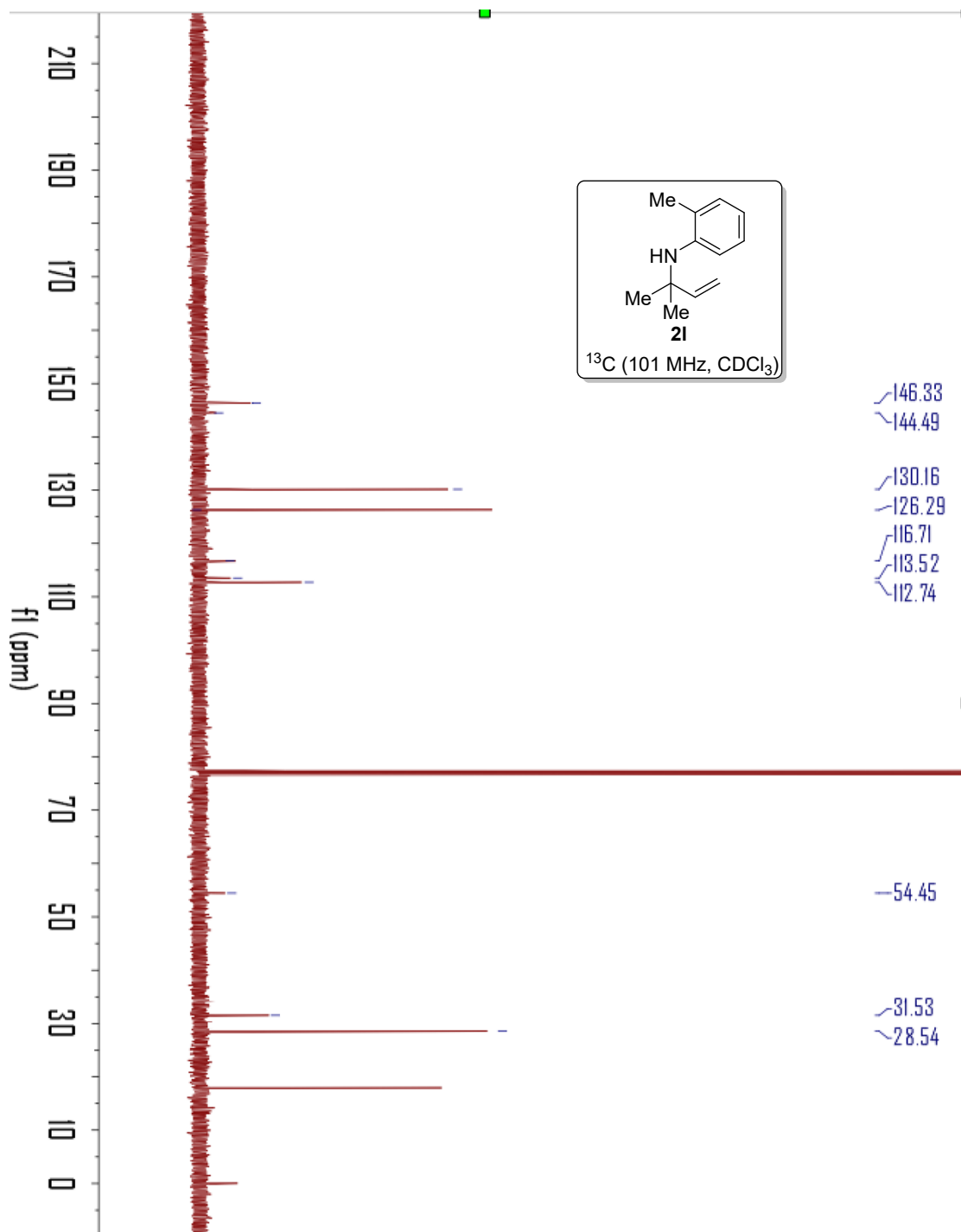


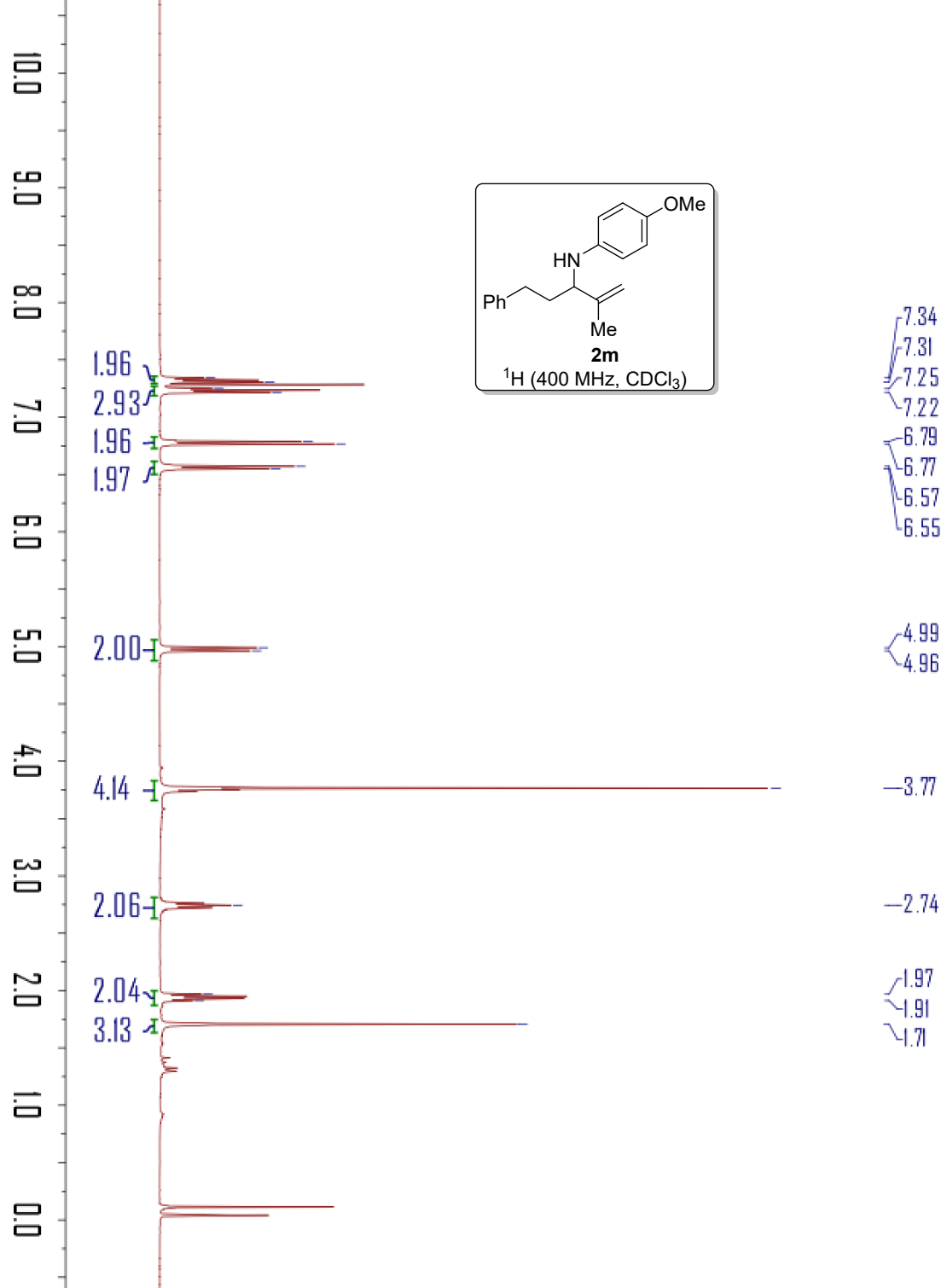


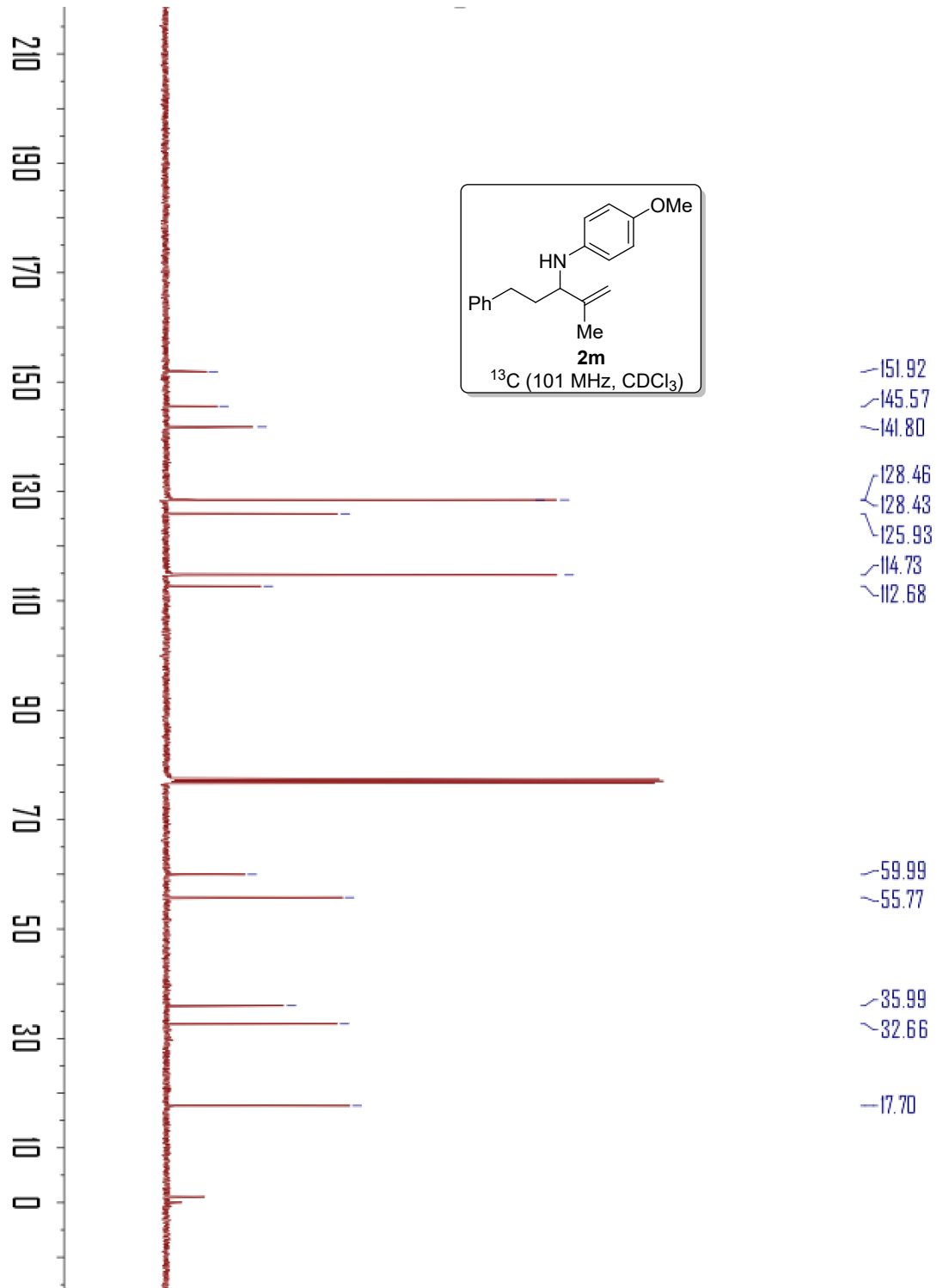


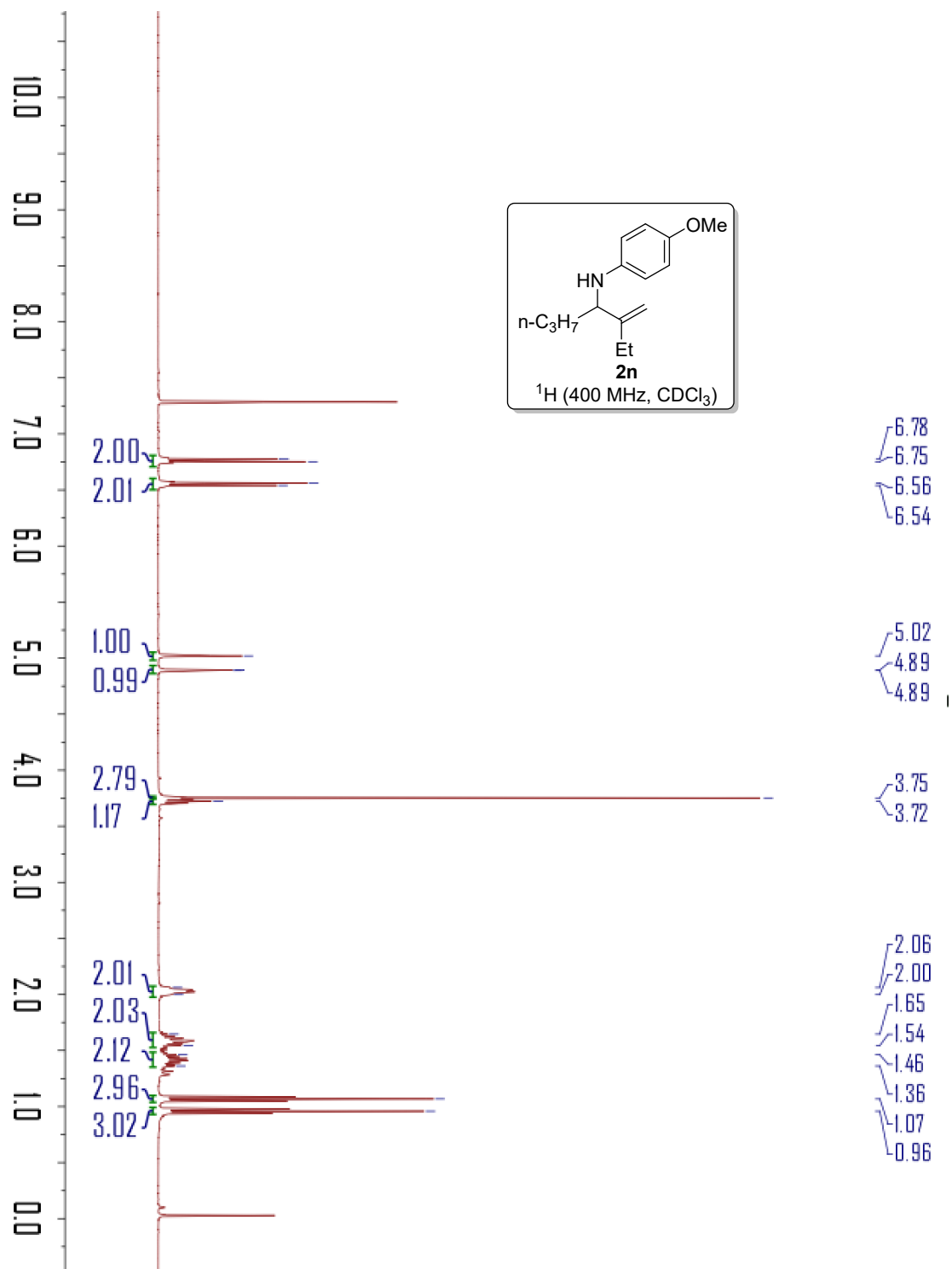


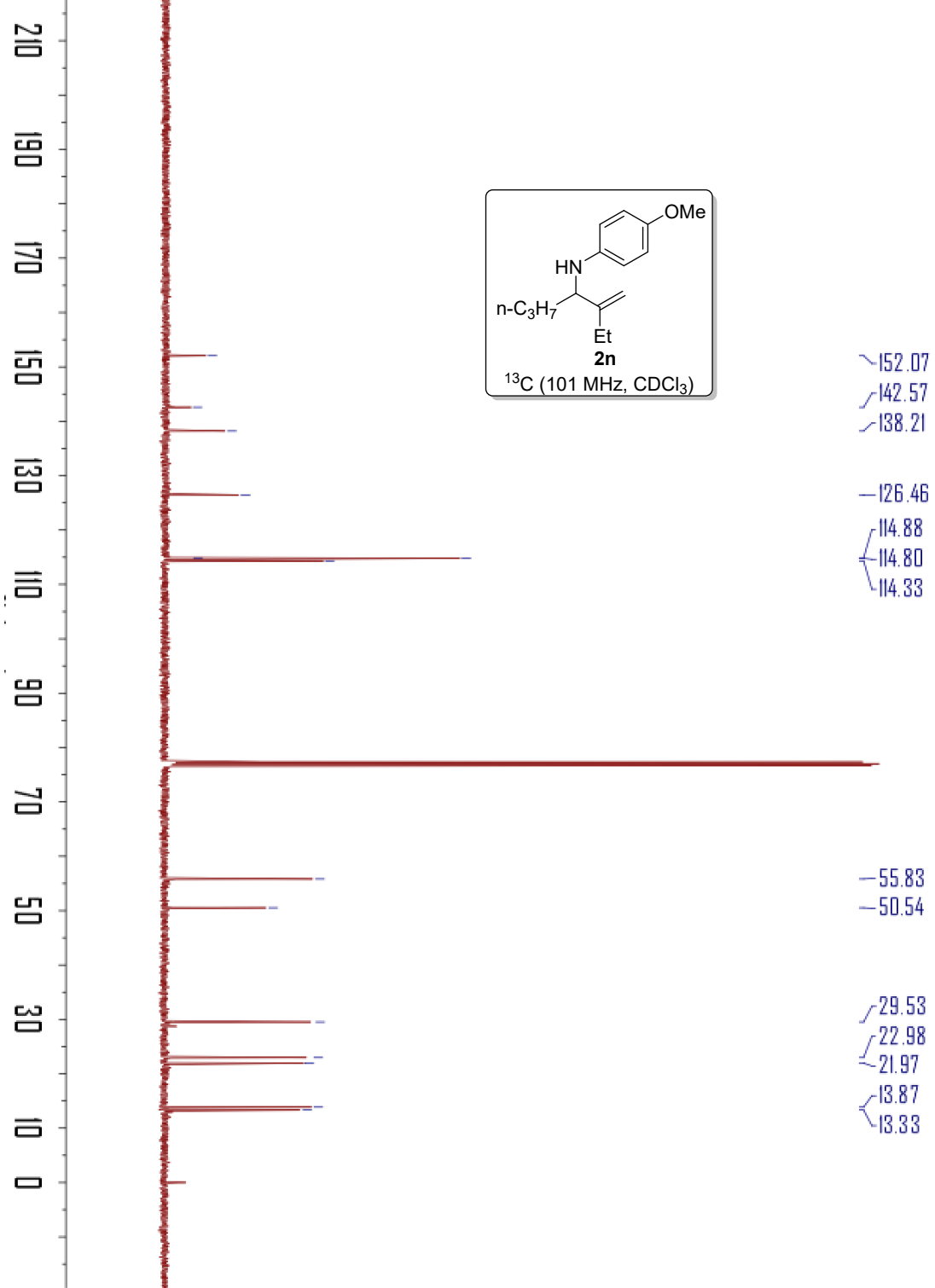


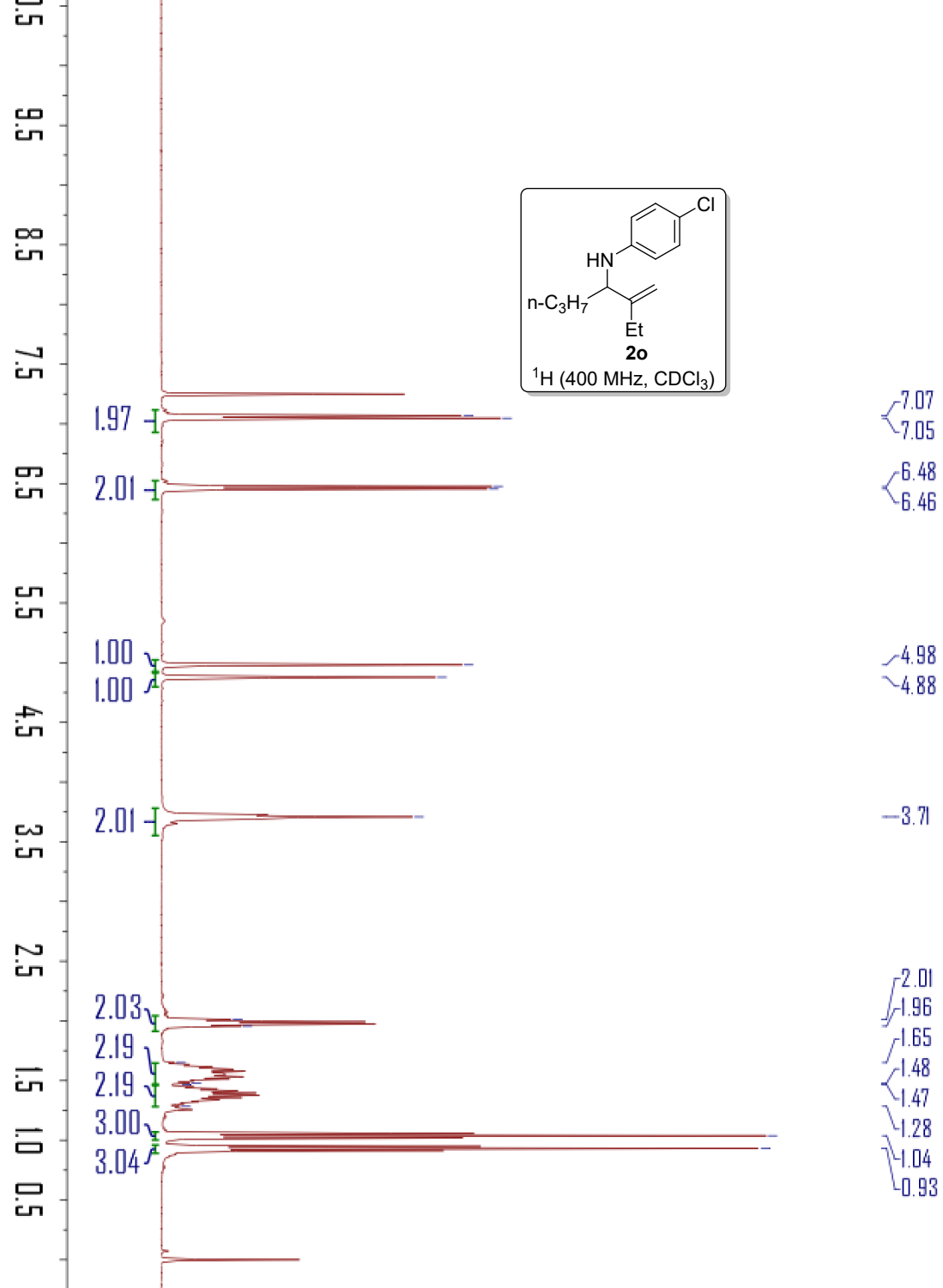




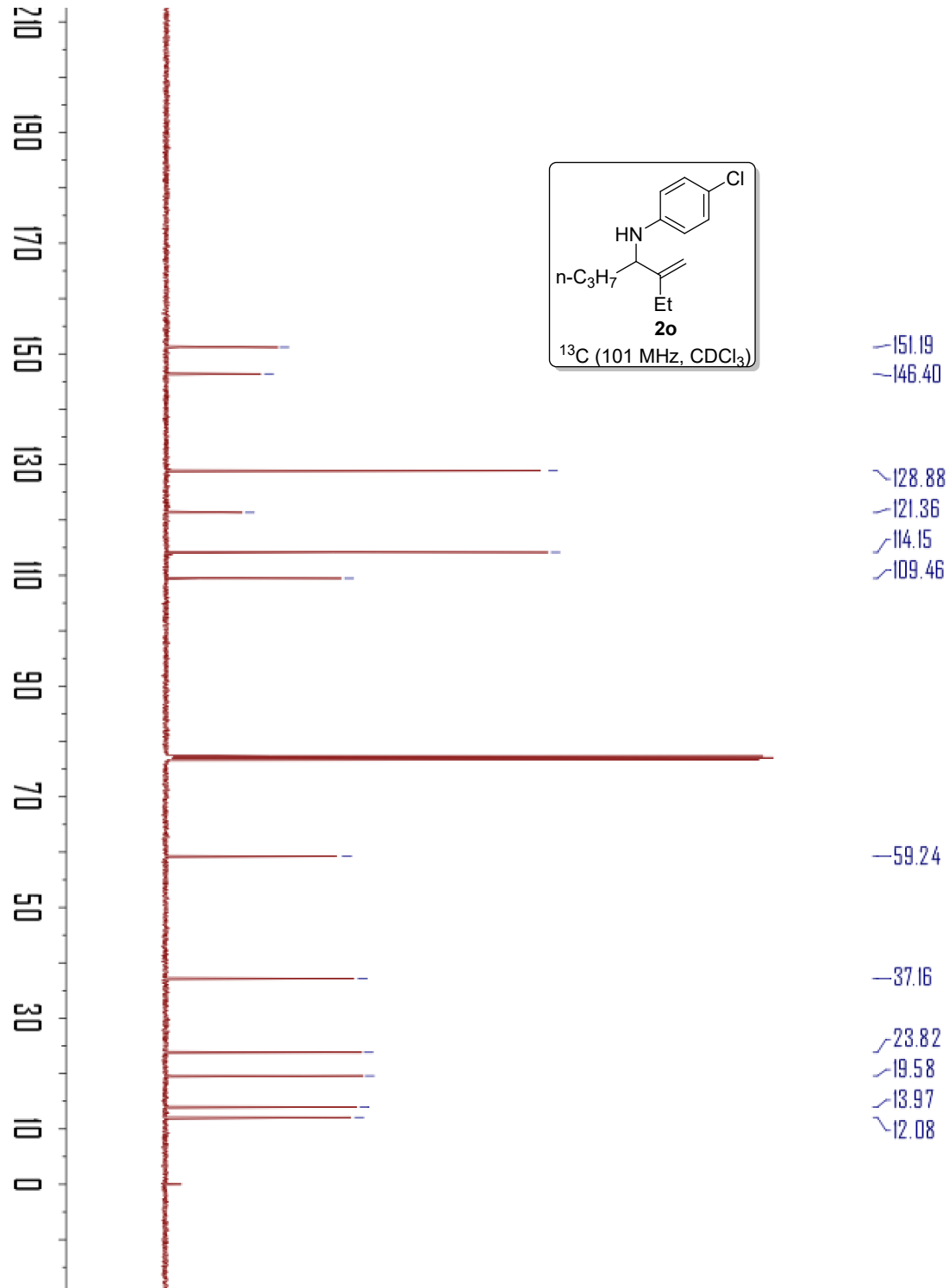


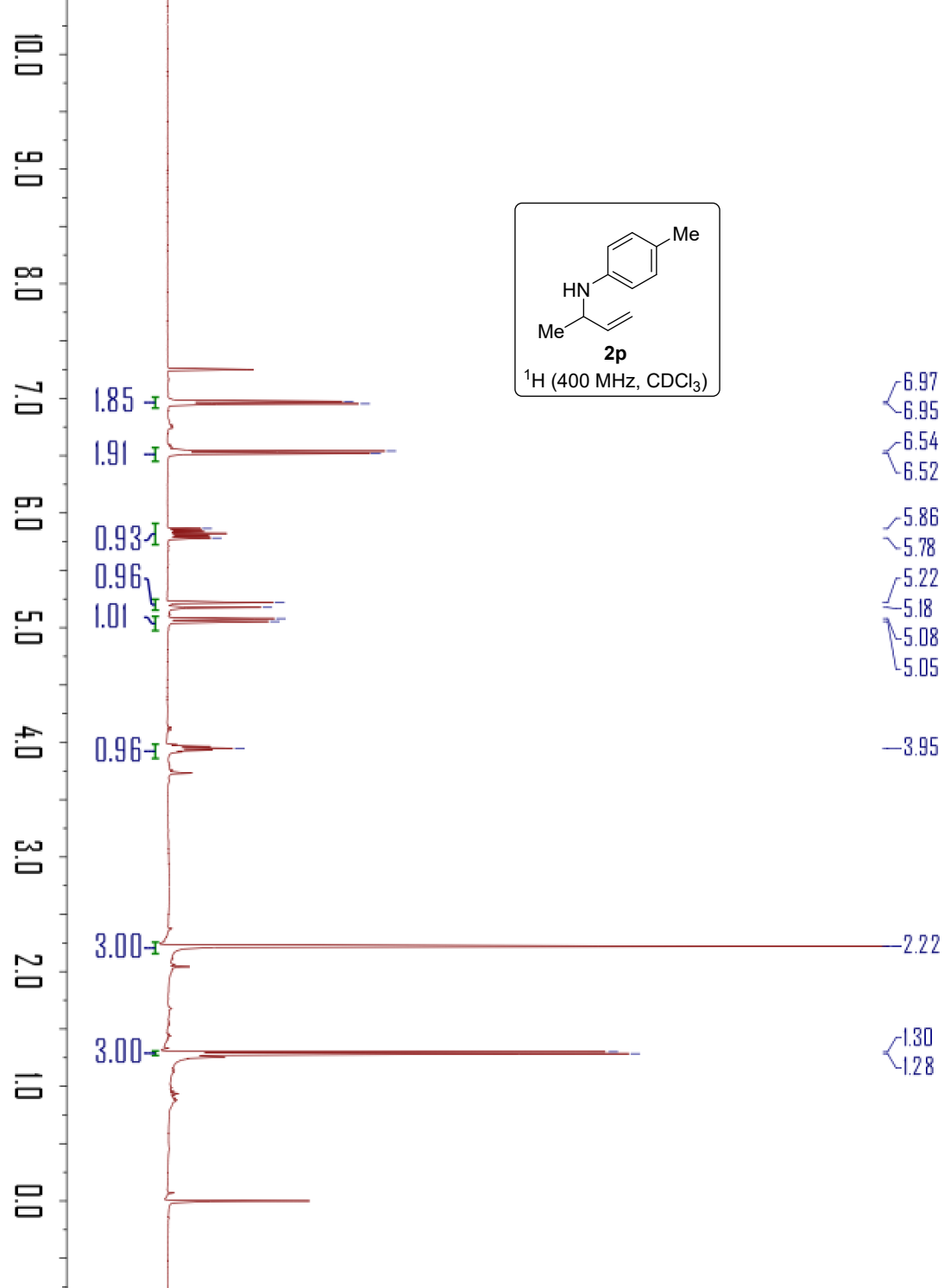


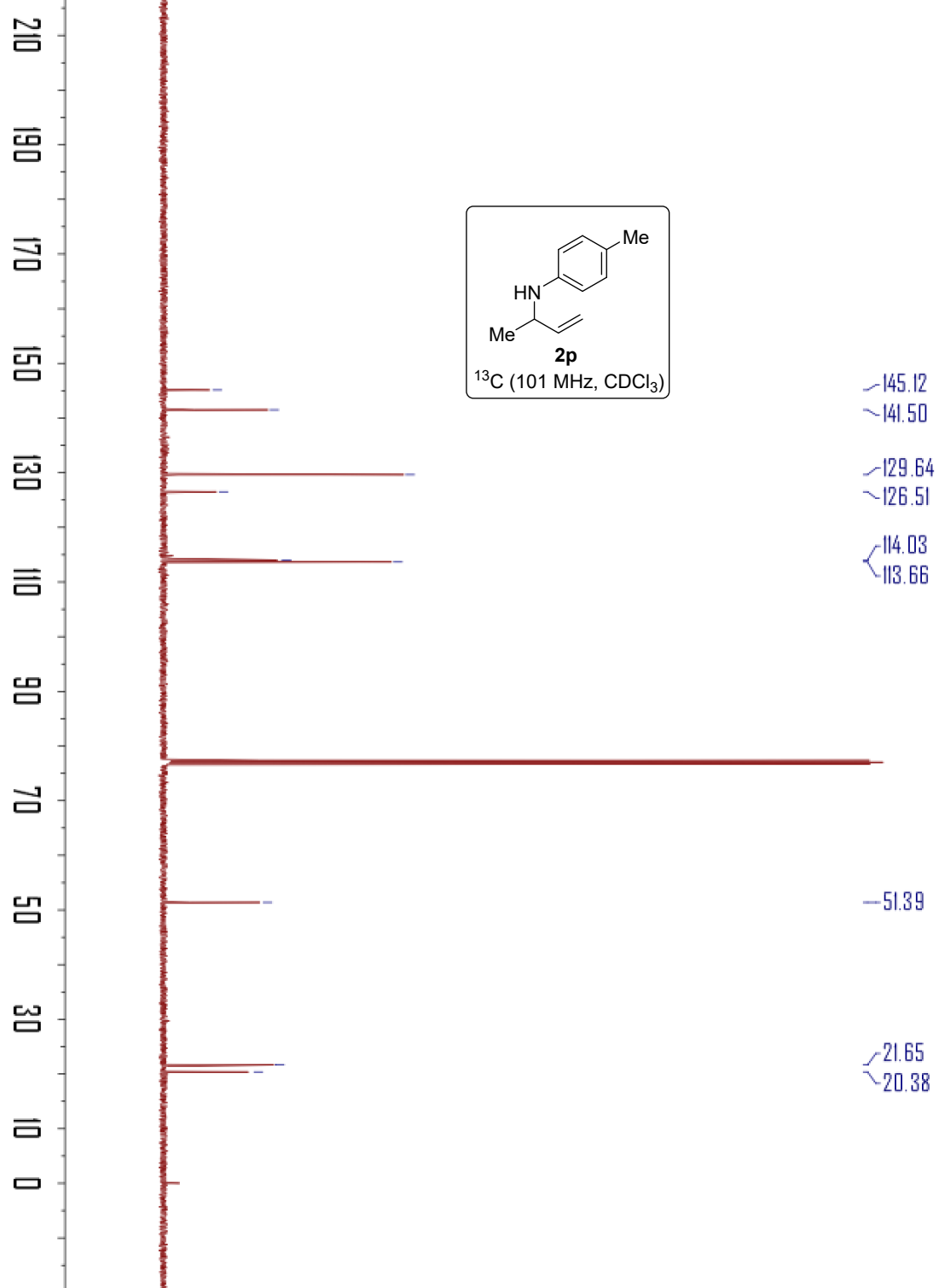


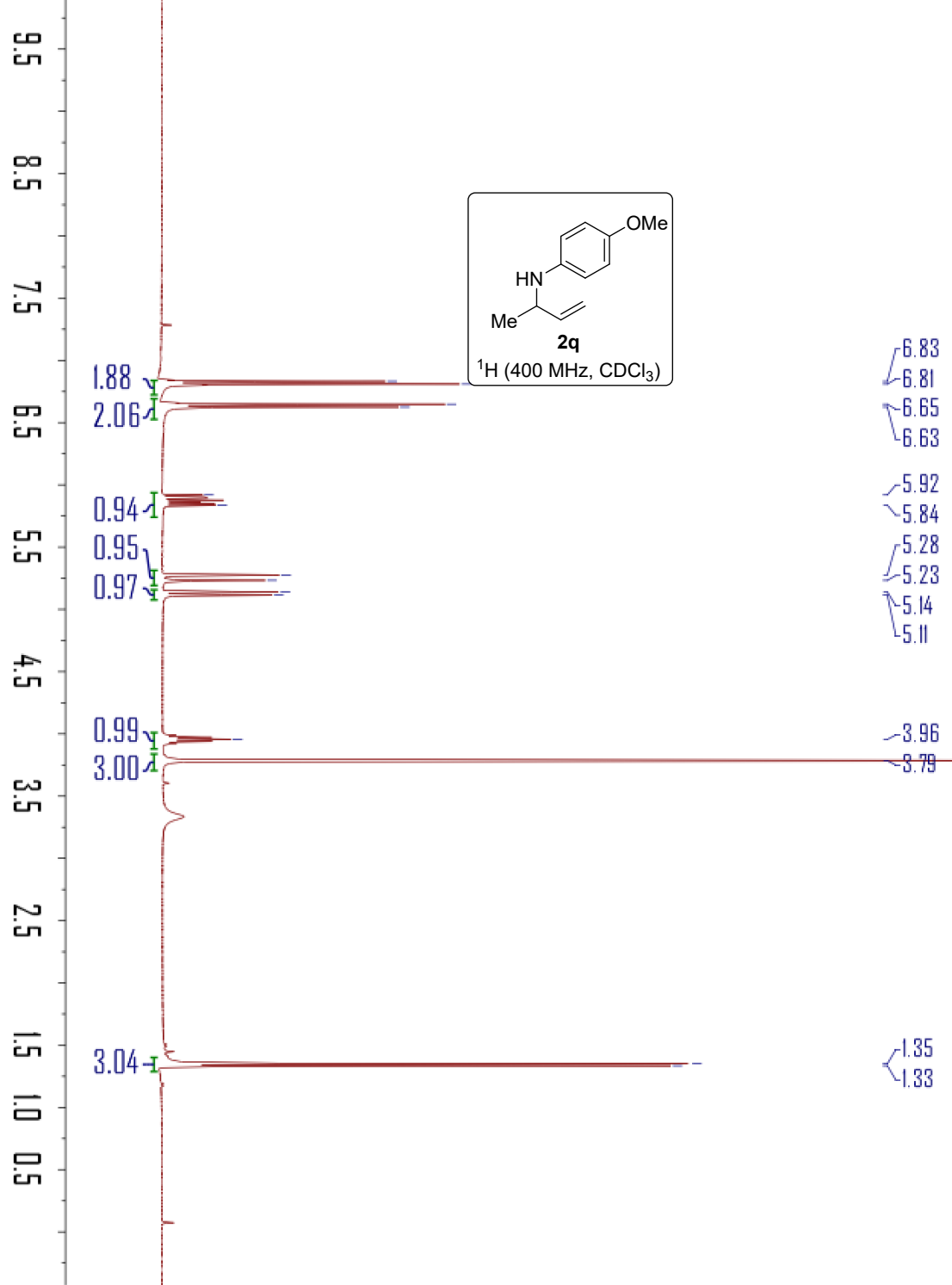


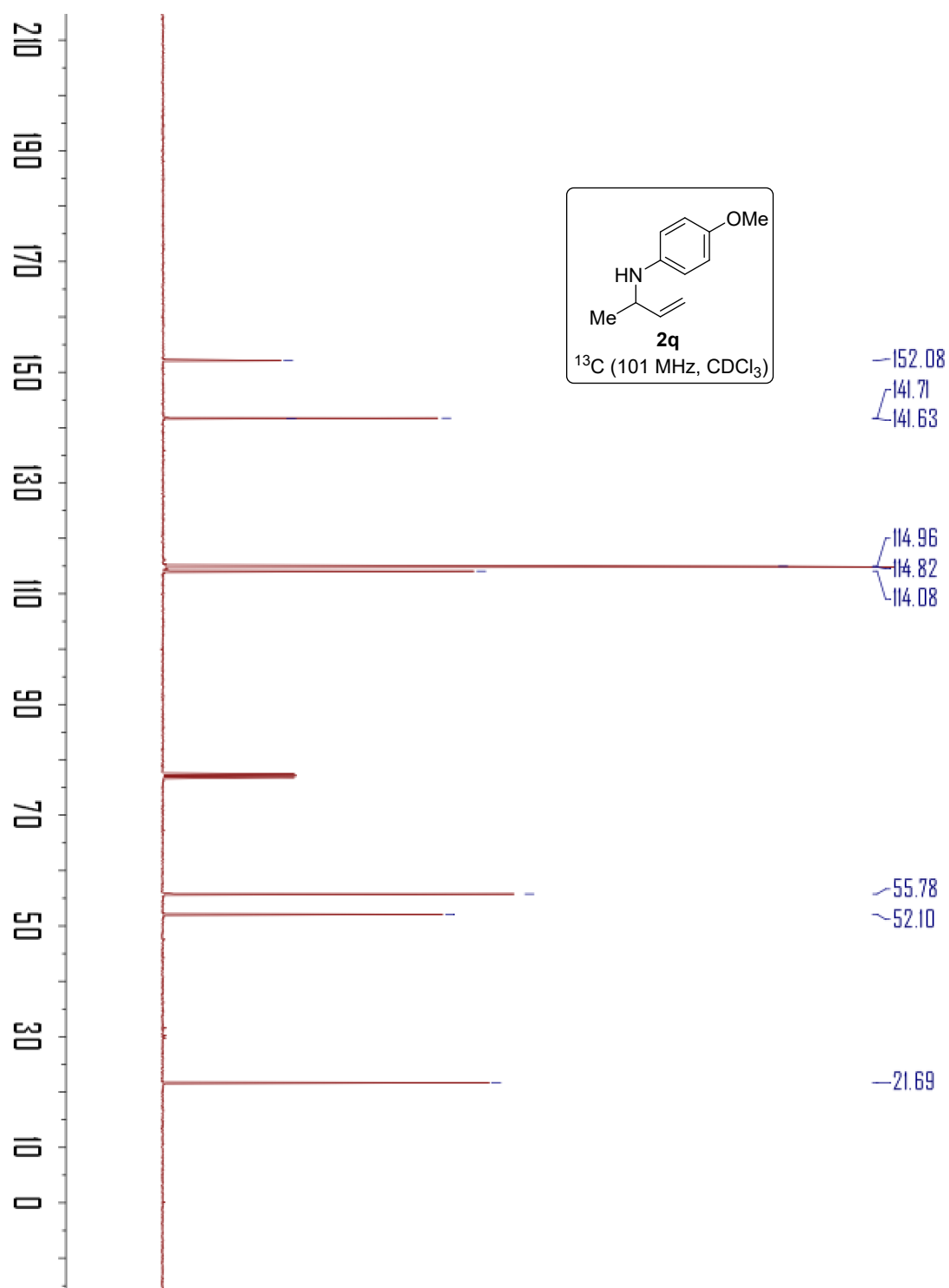


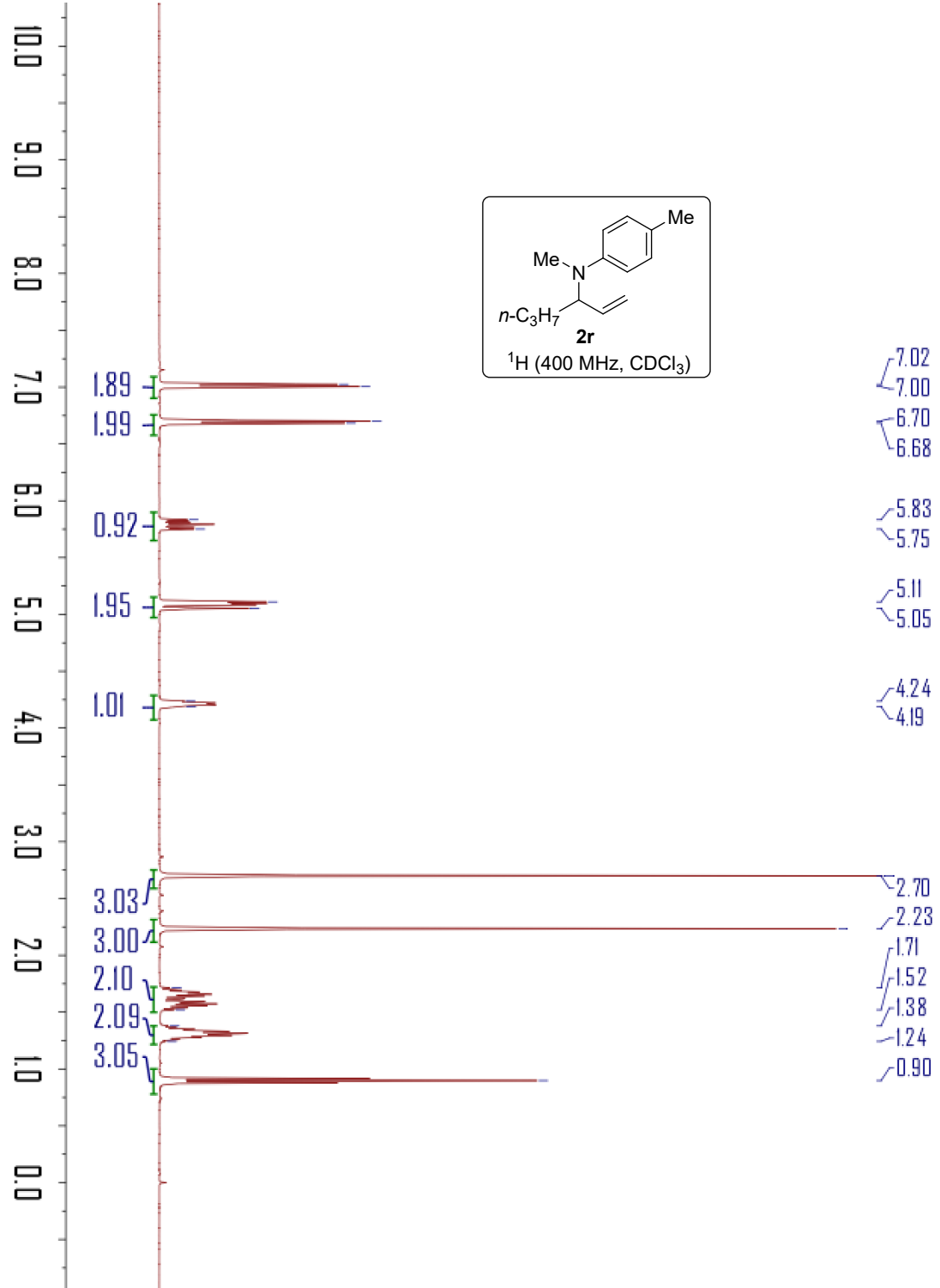


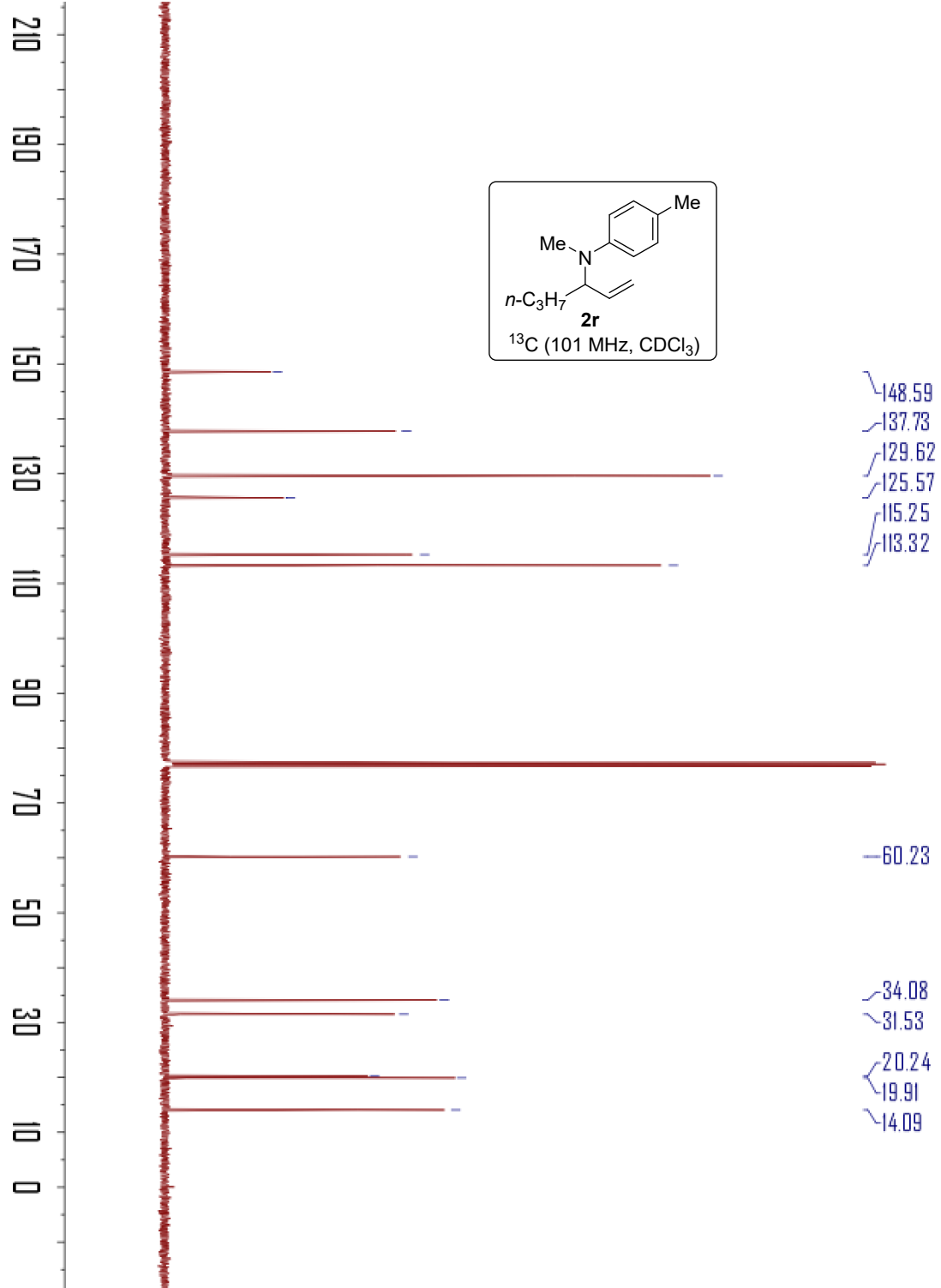


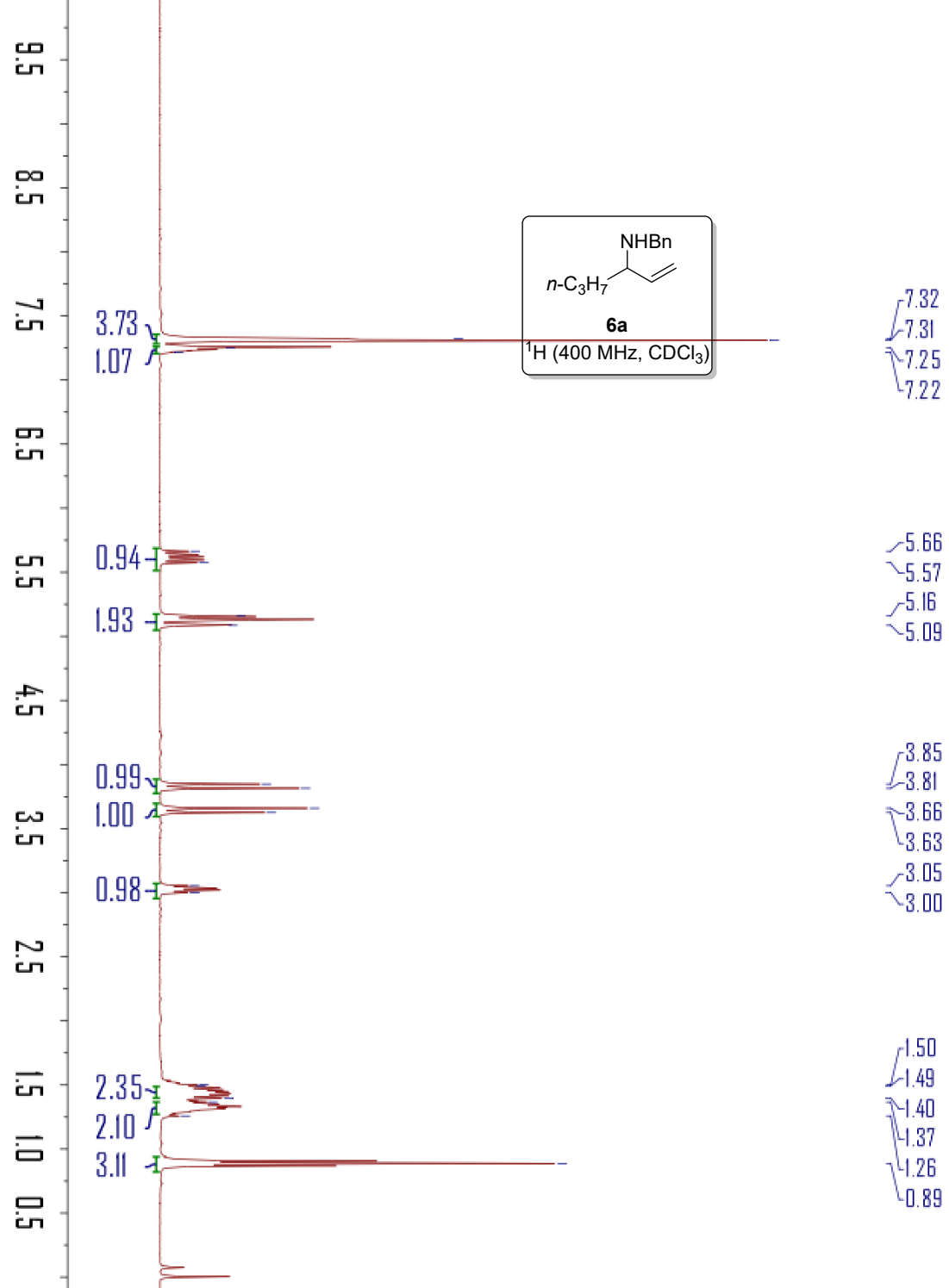




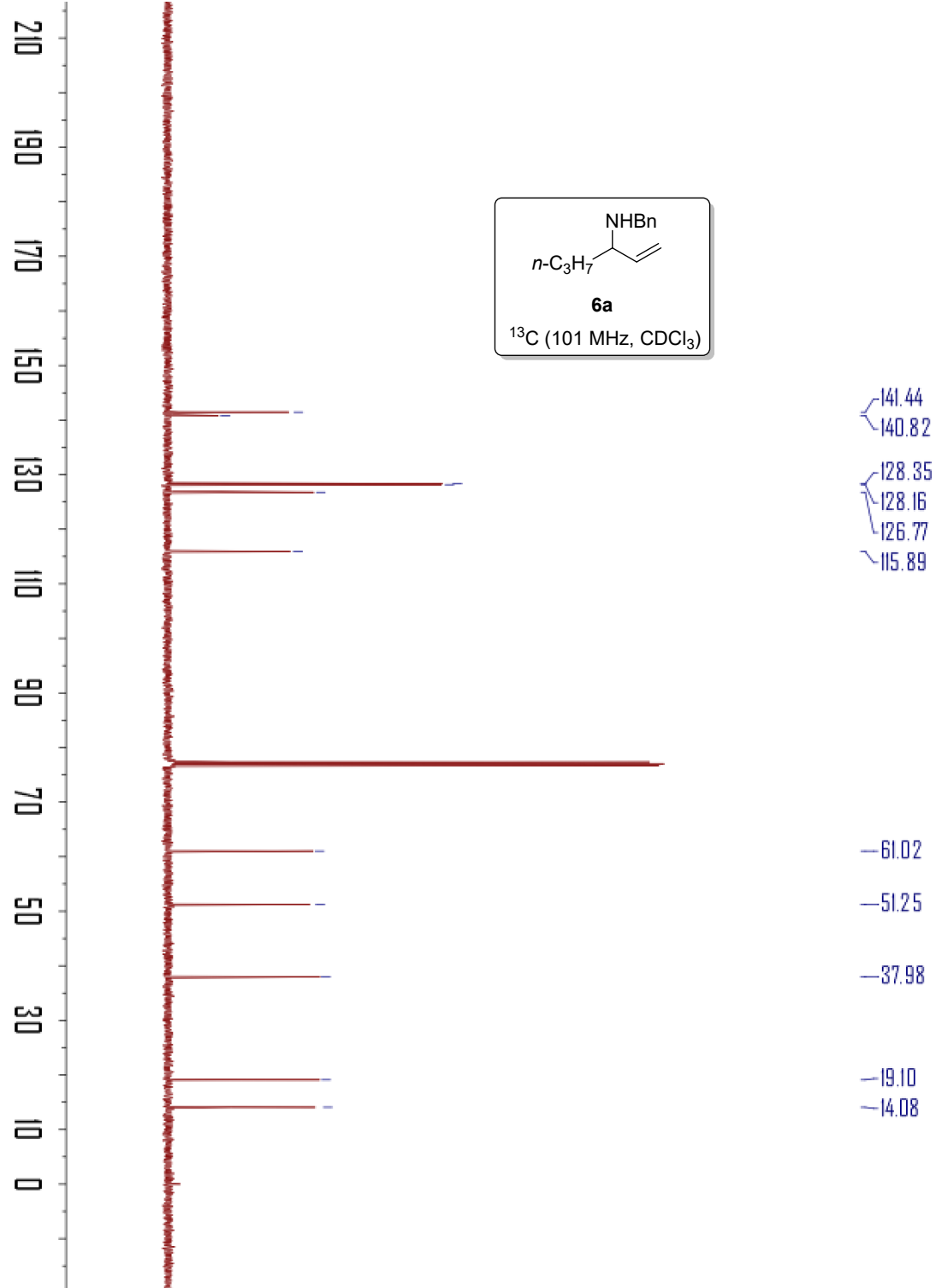


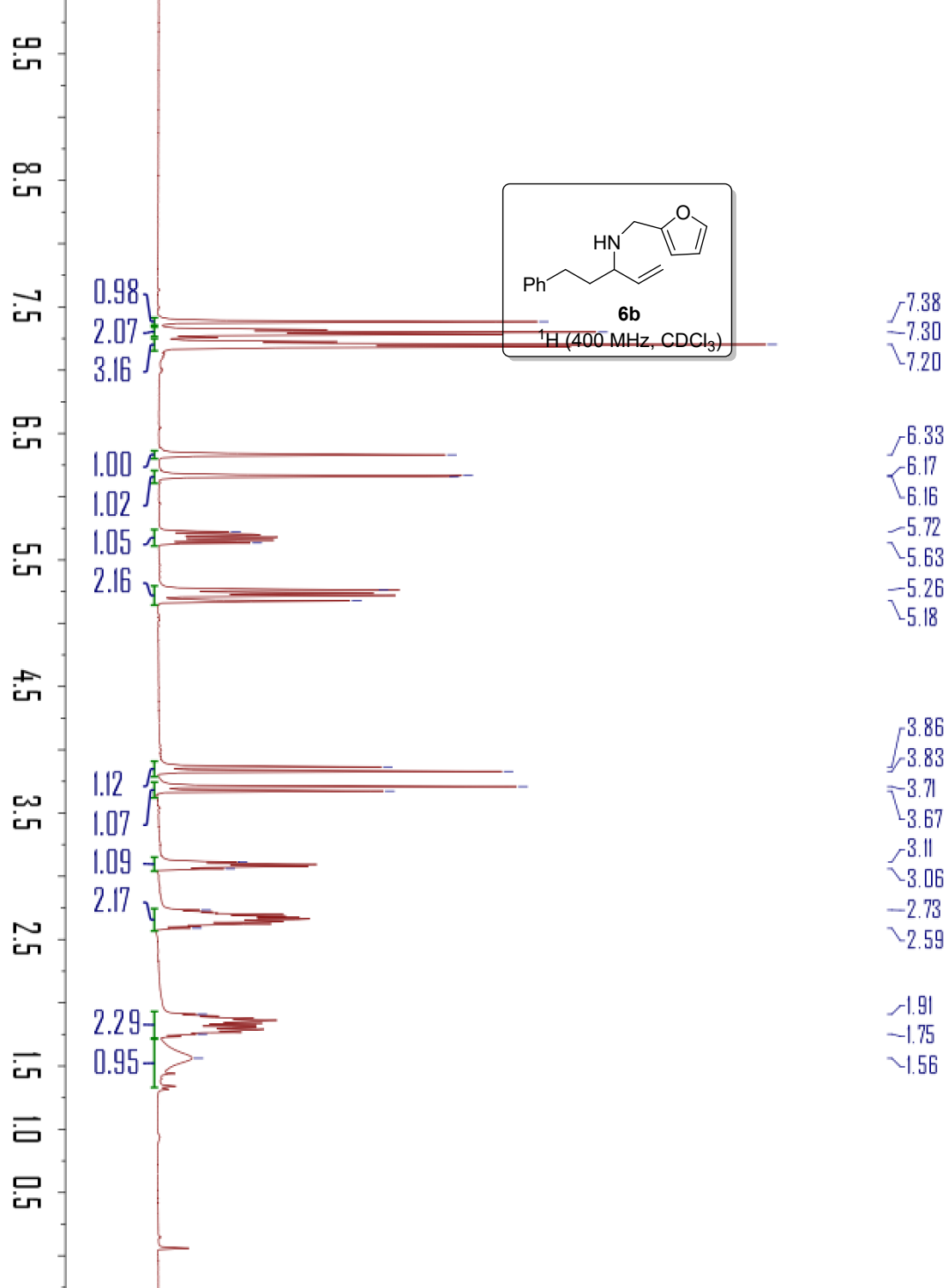


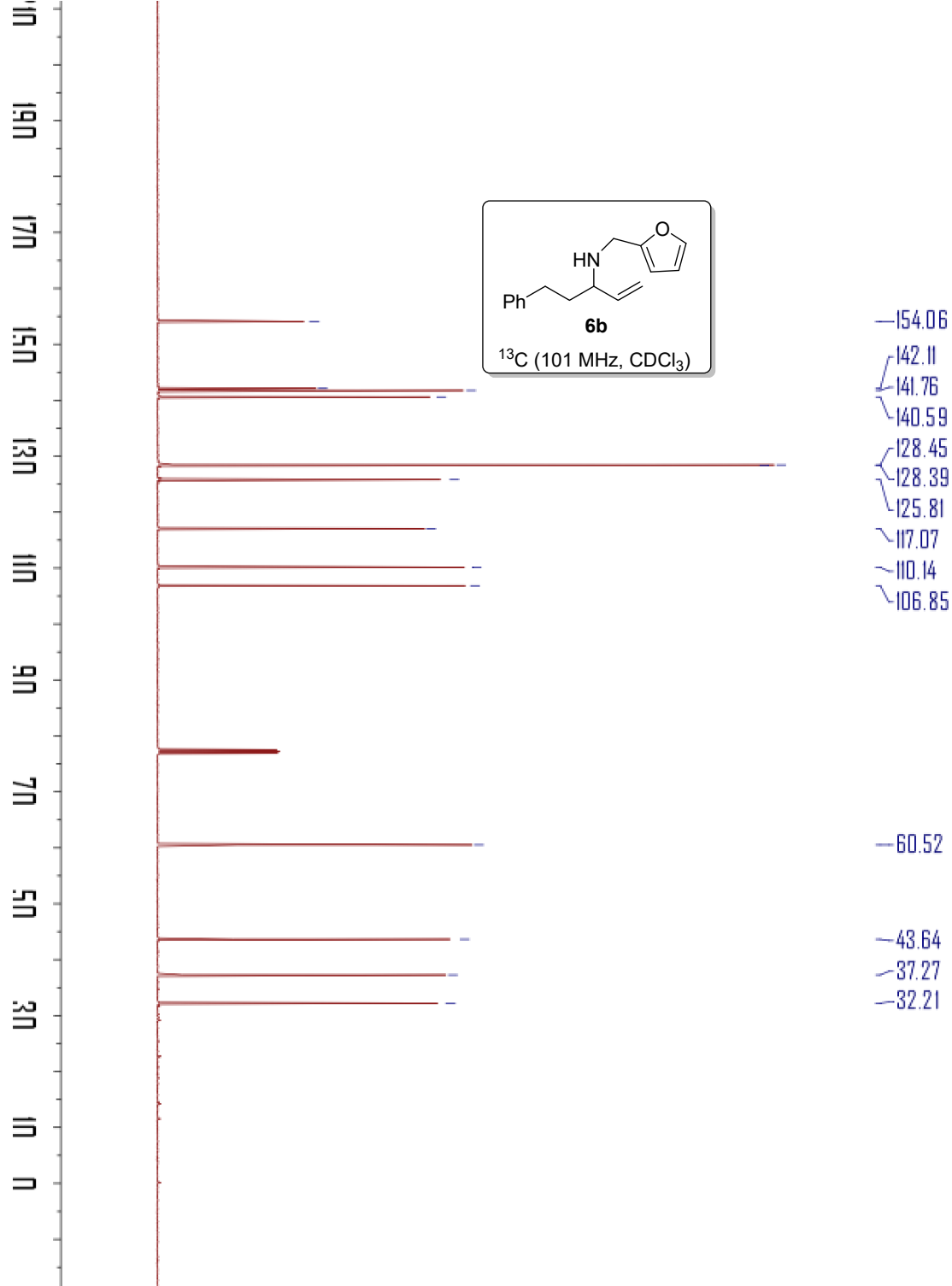


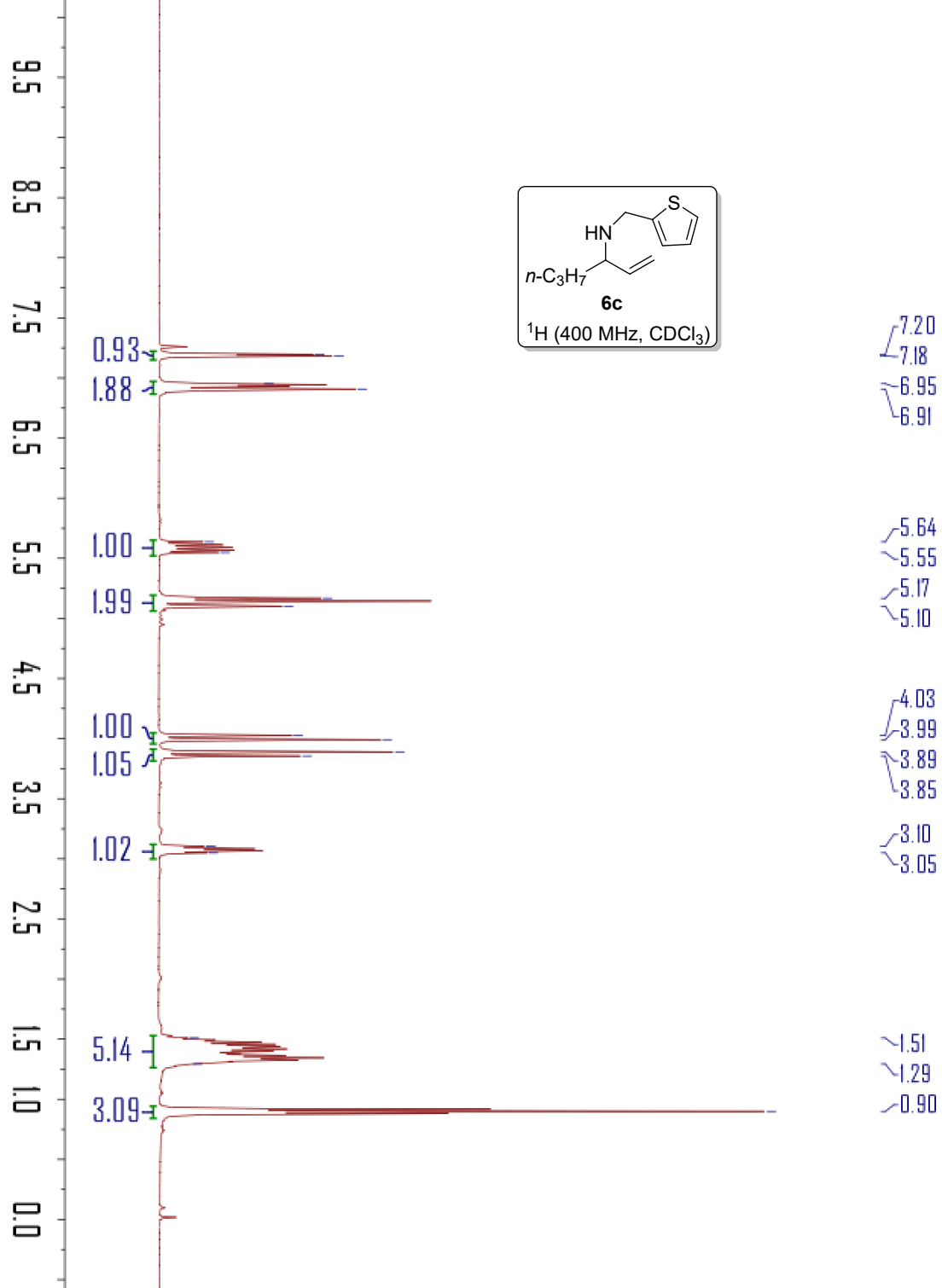


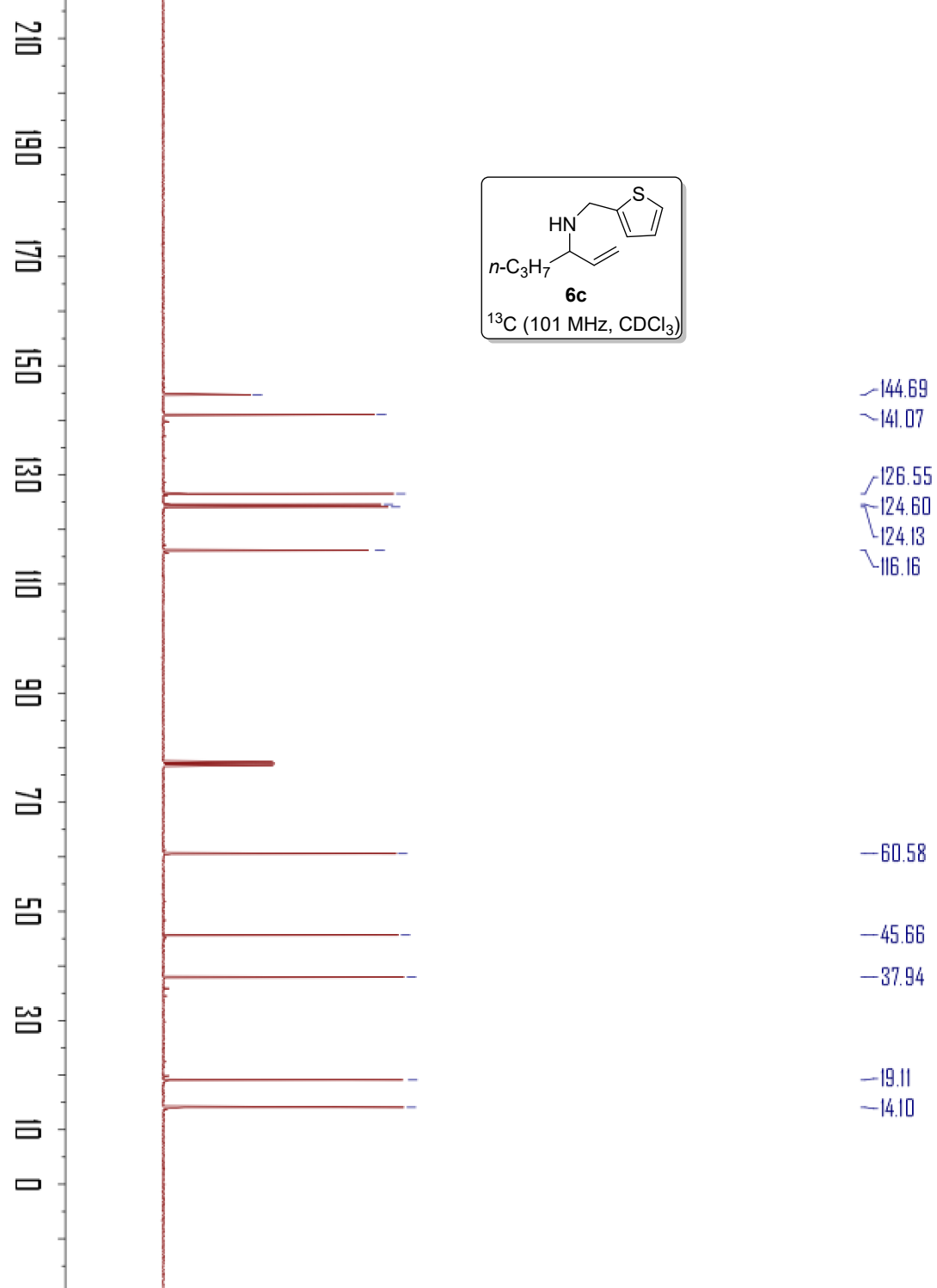


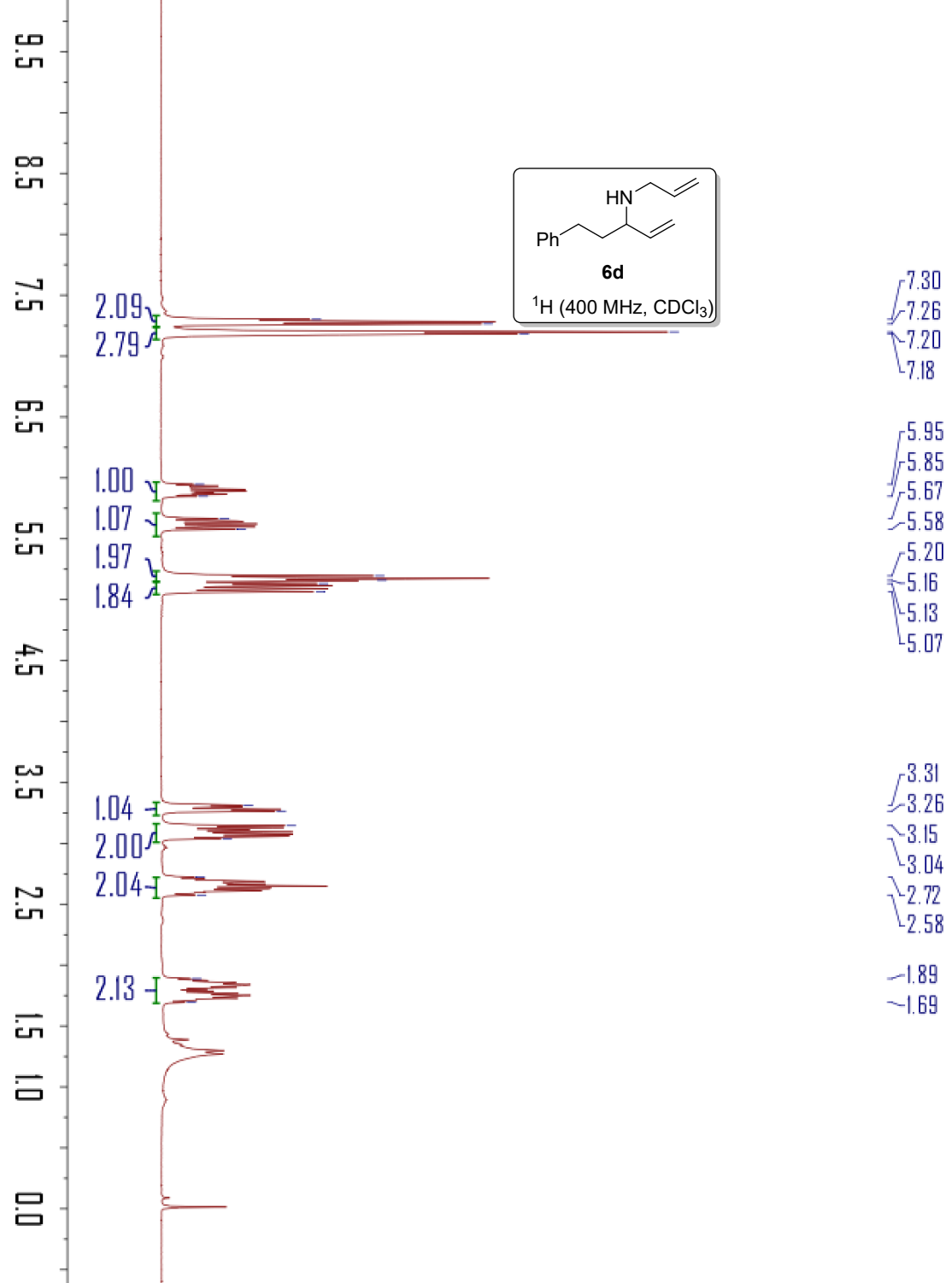


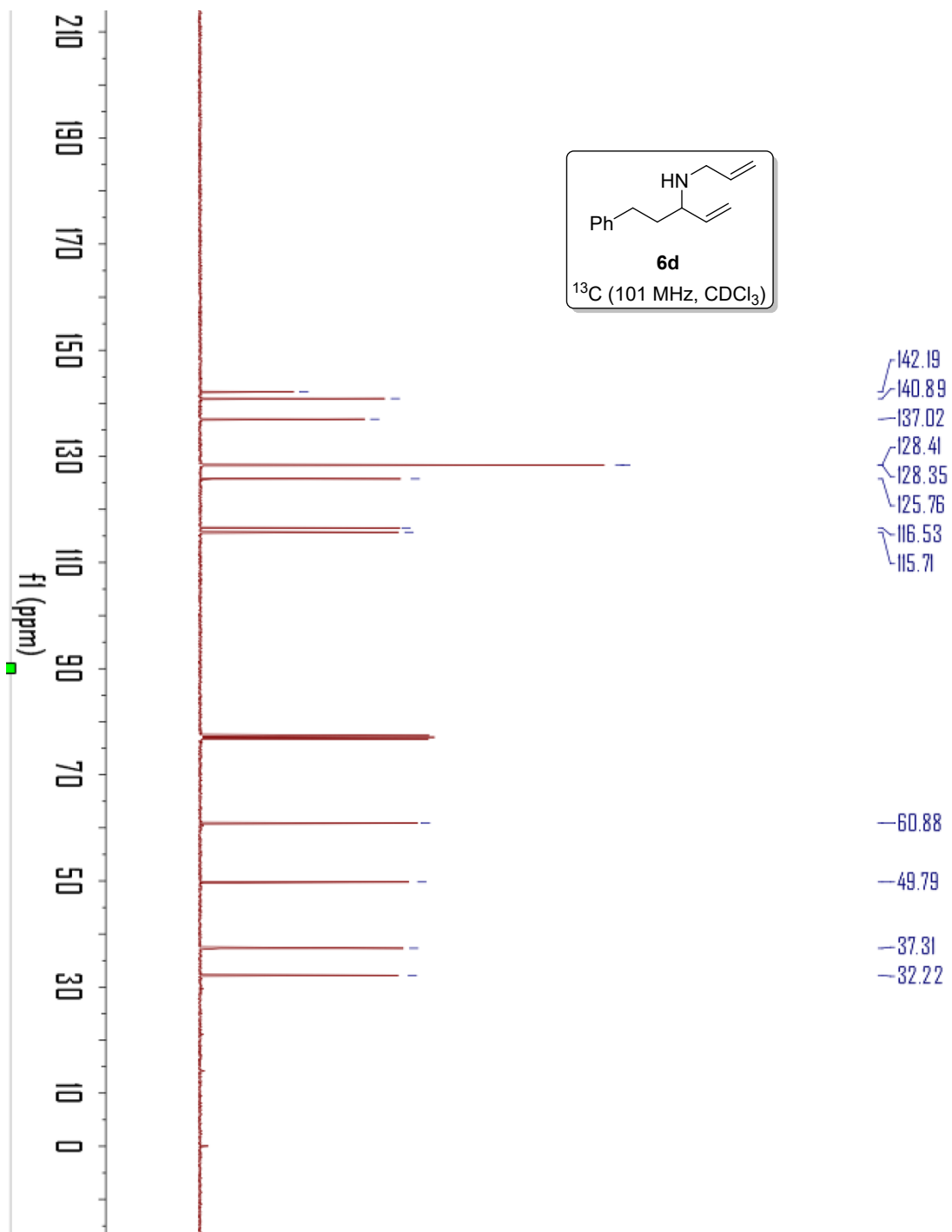


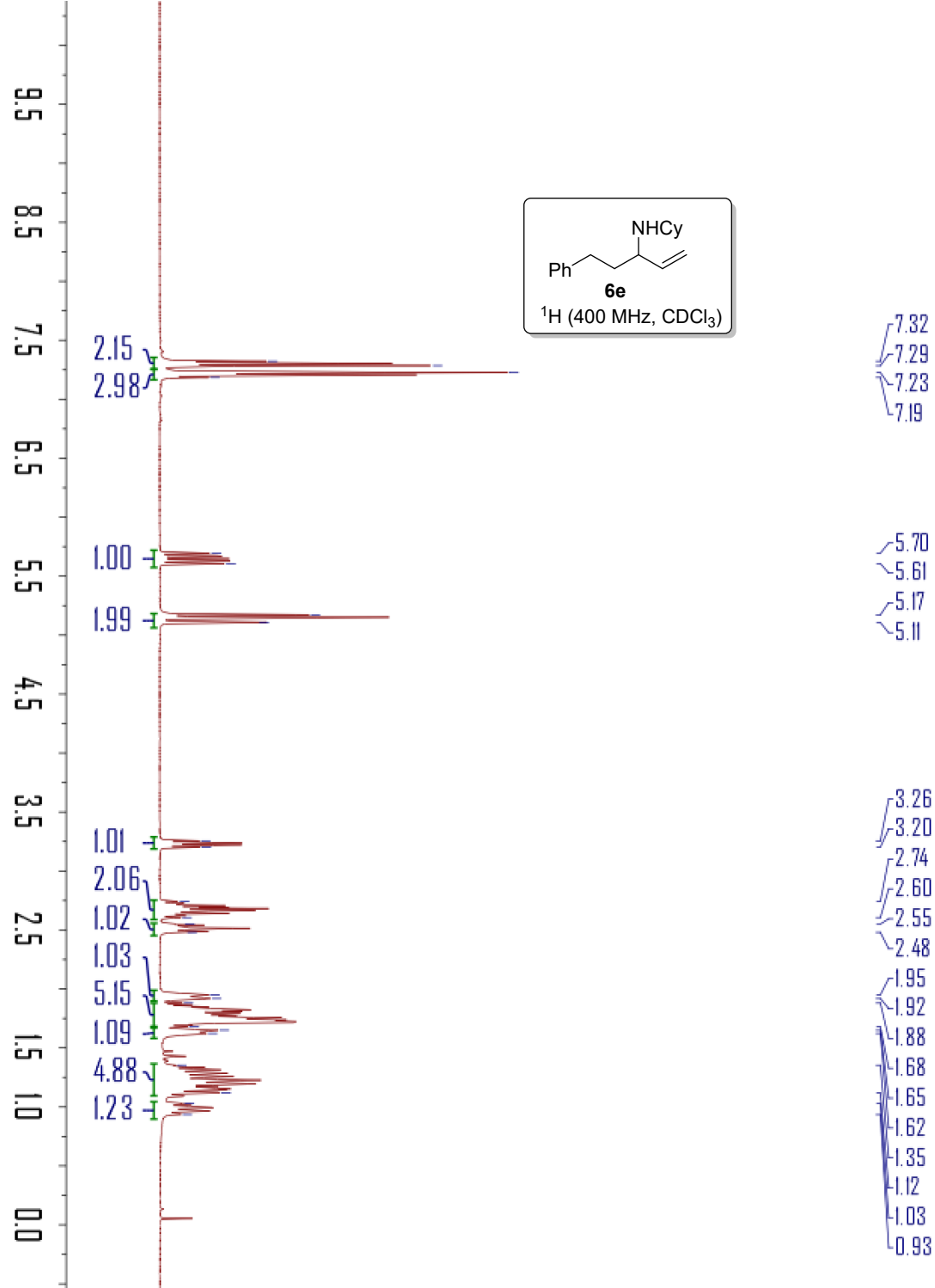




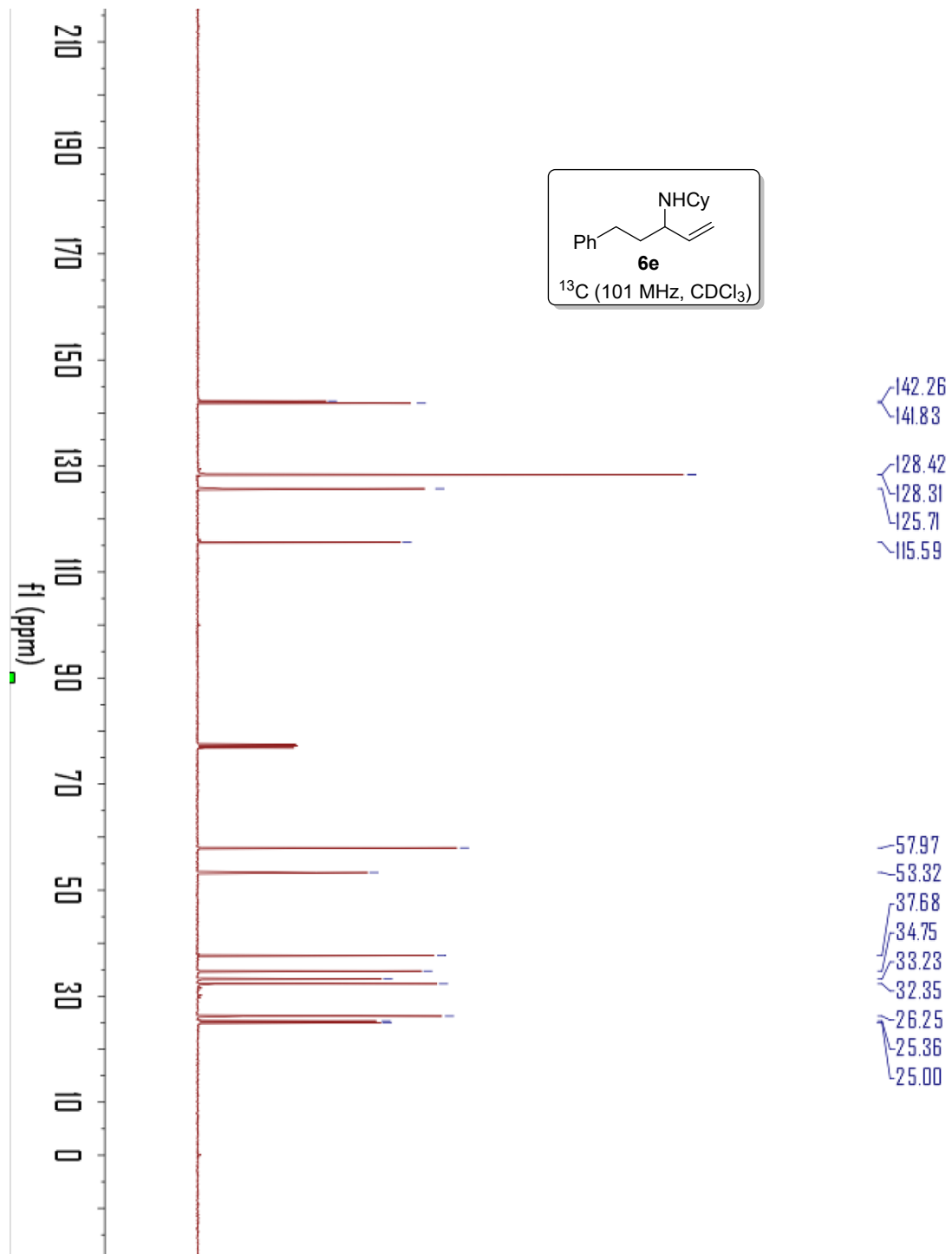


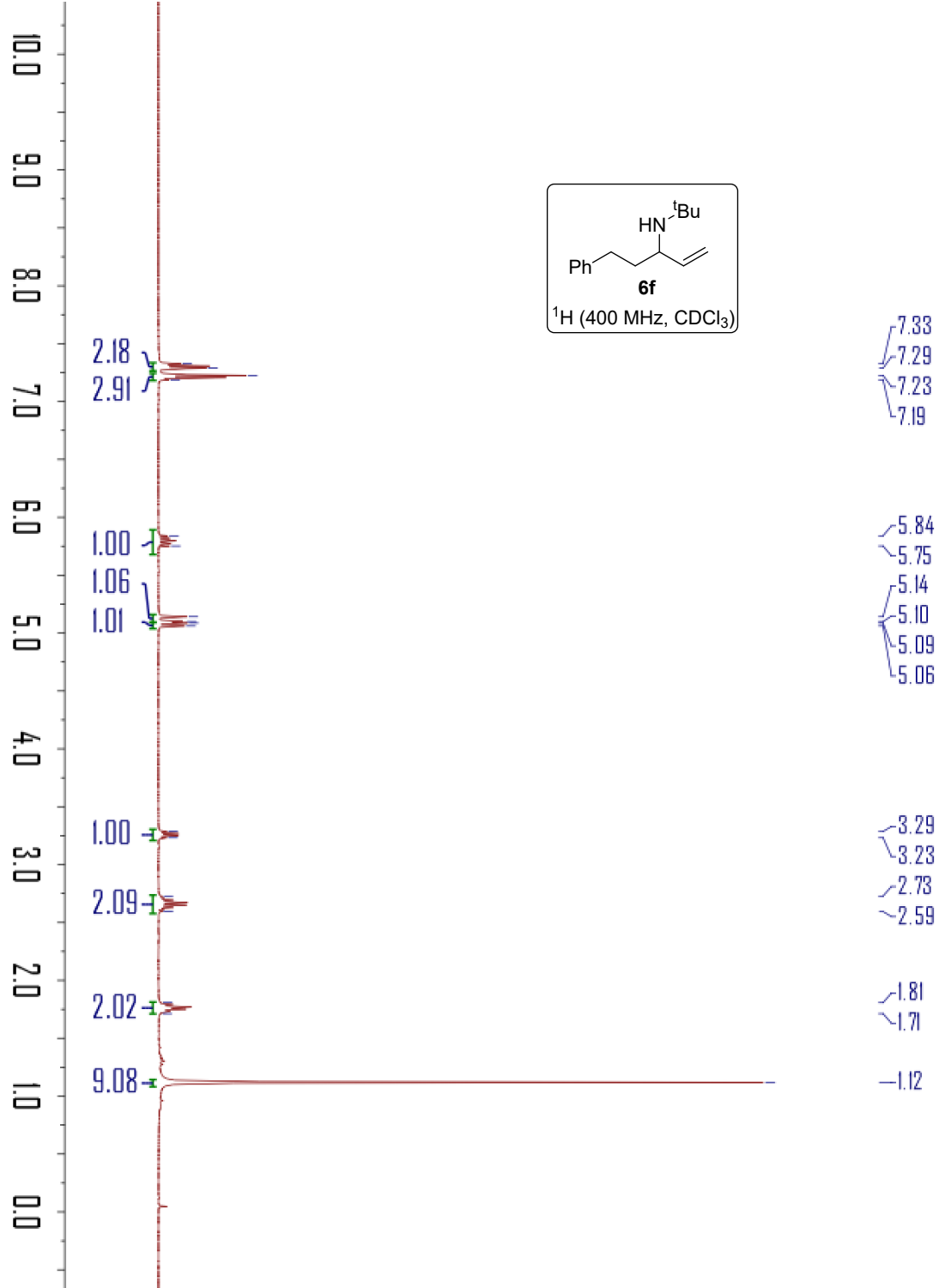


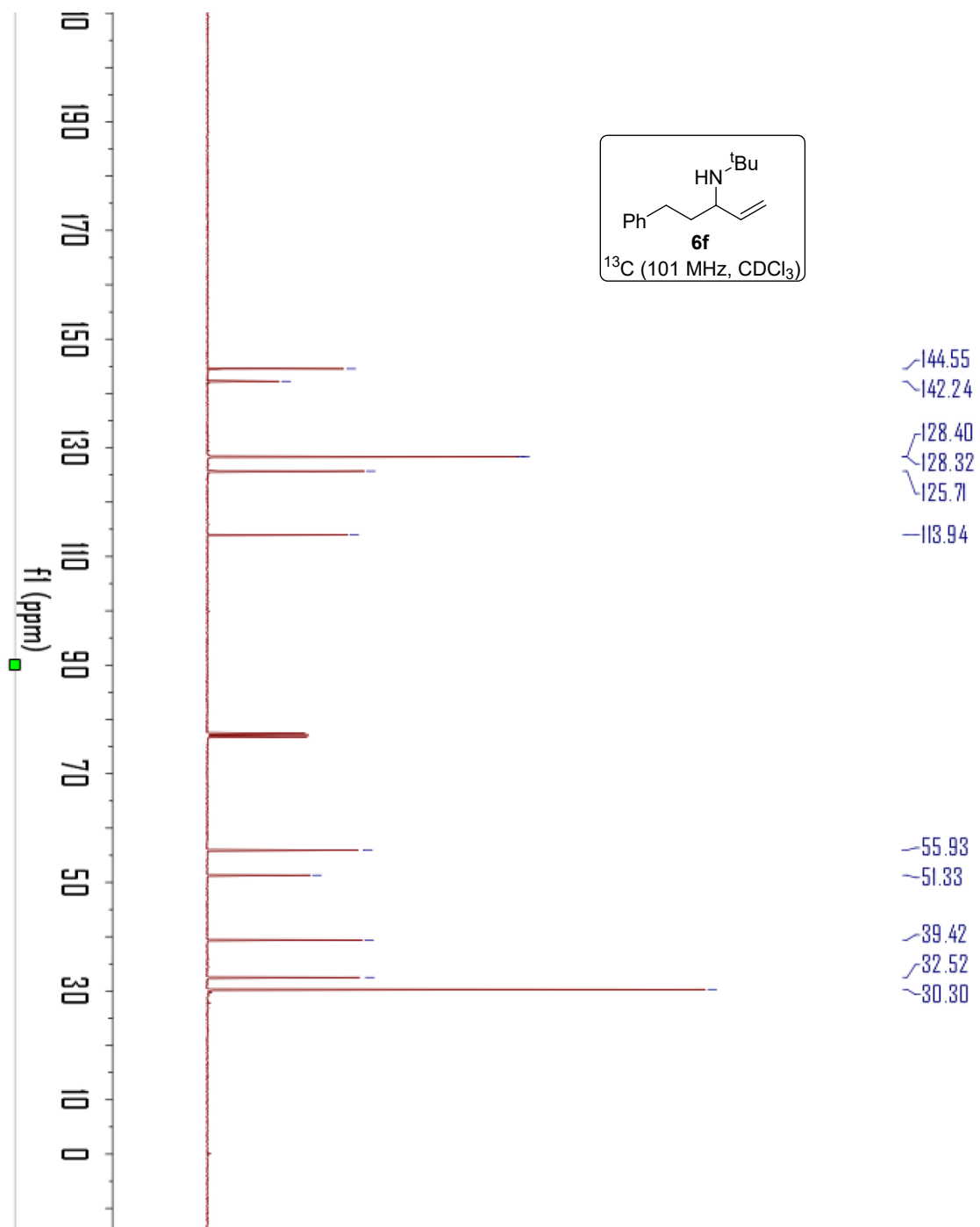


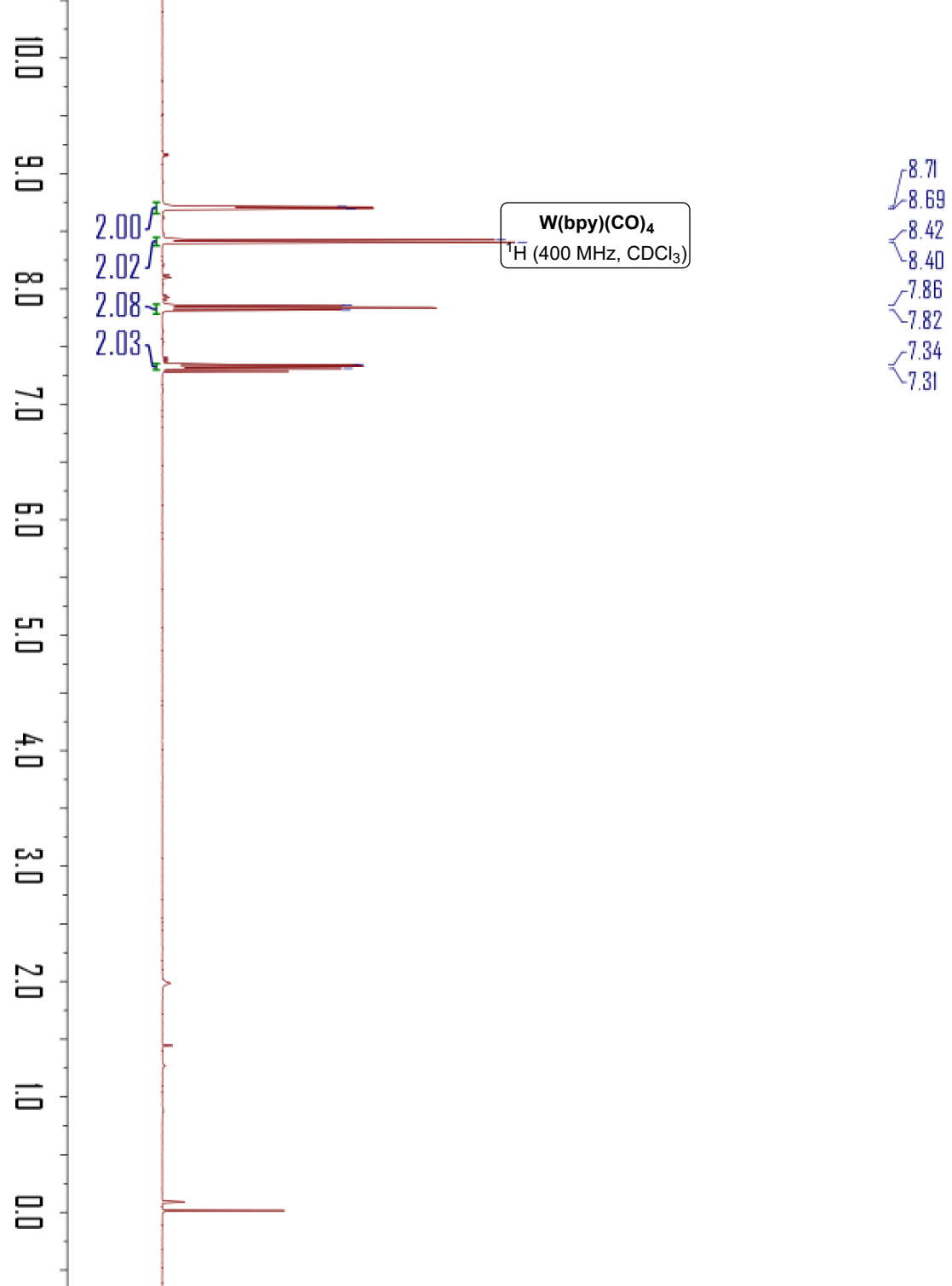


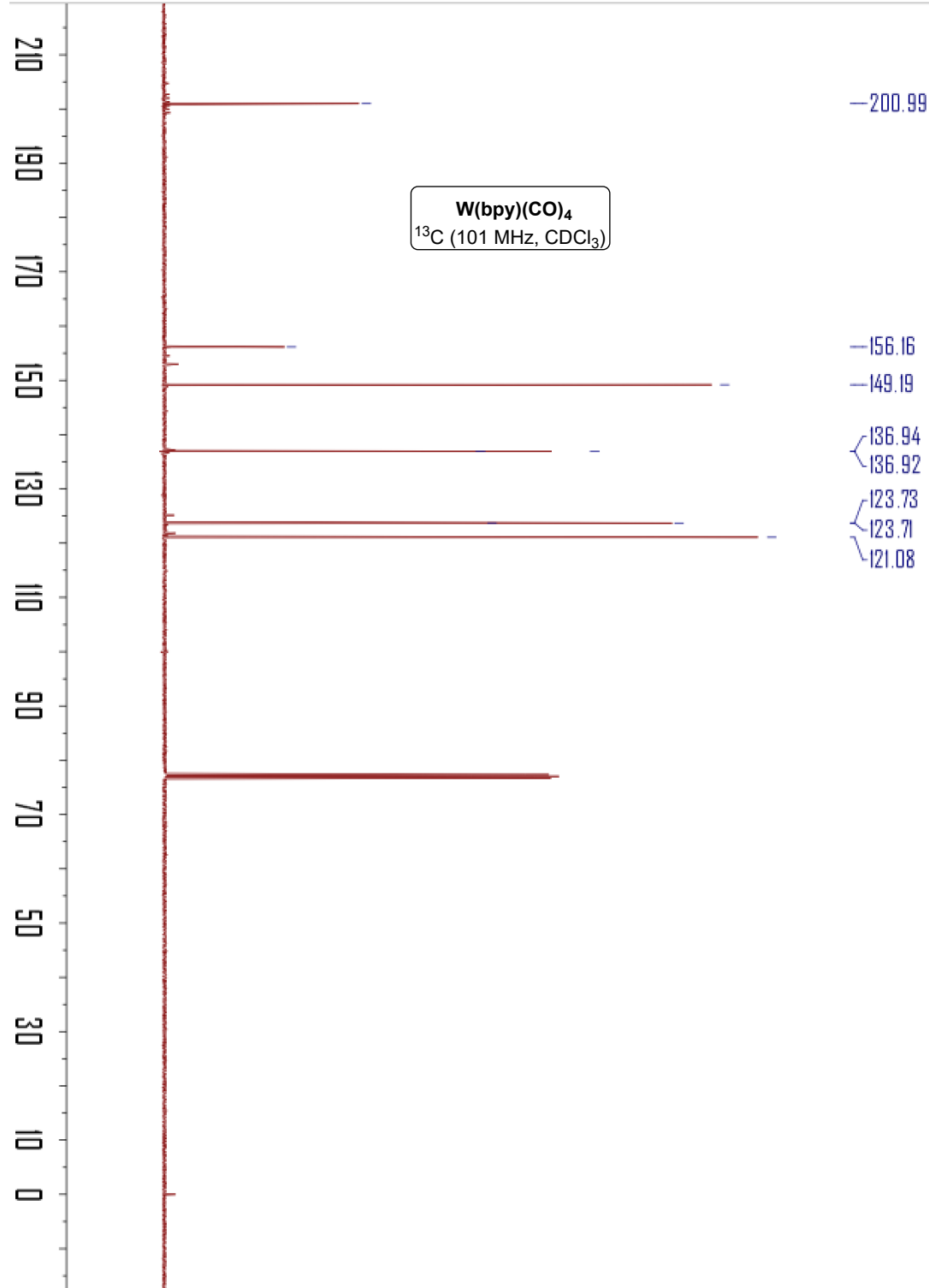












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