

## Radical-mediated Sulfonylative/Thiolative Cyclization of Biaryl Enones to Phenanthrone Derivatives

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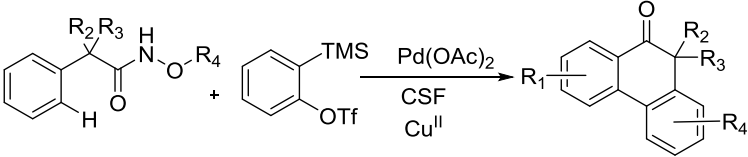
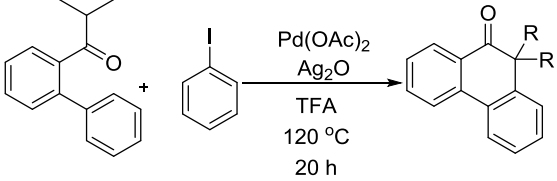
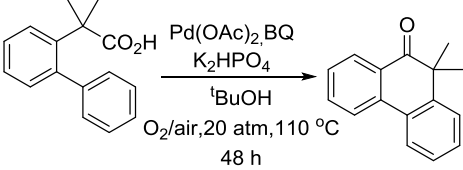
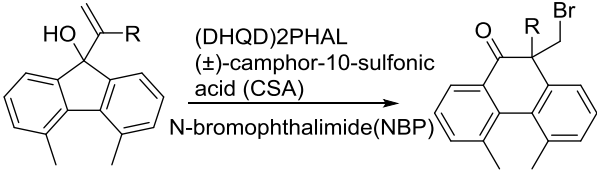
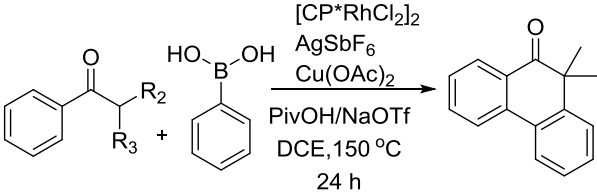
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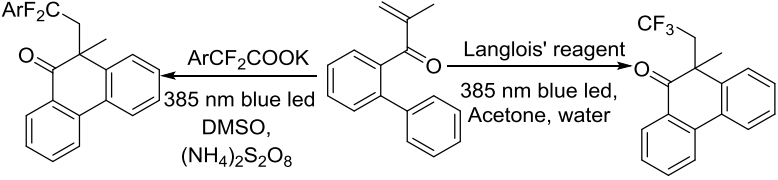
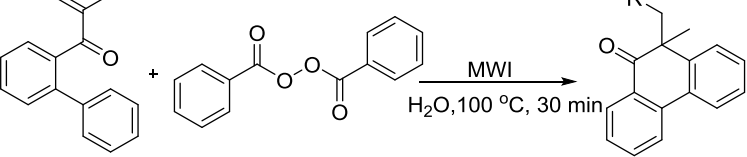
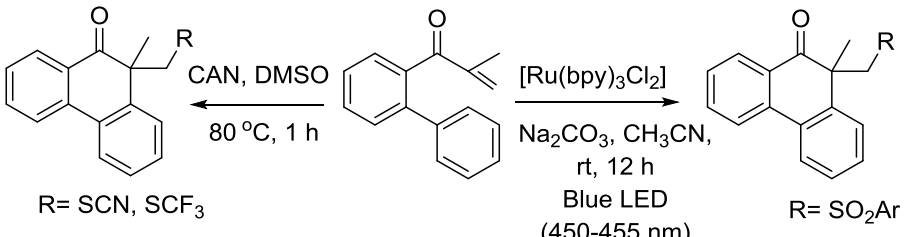
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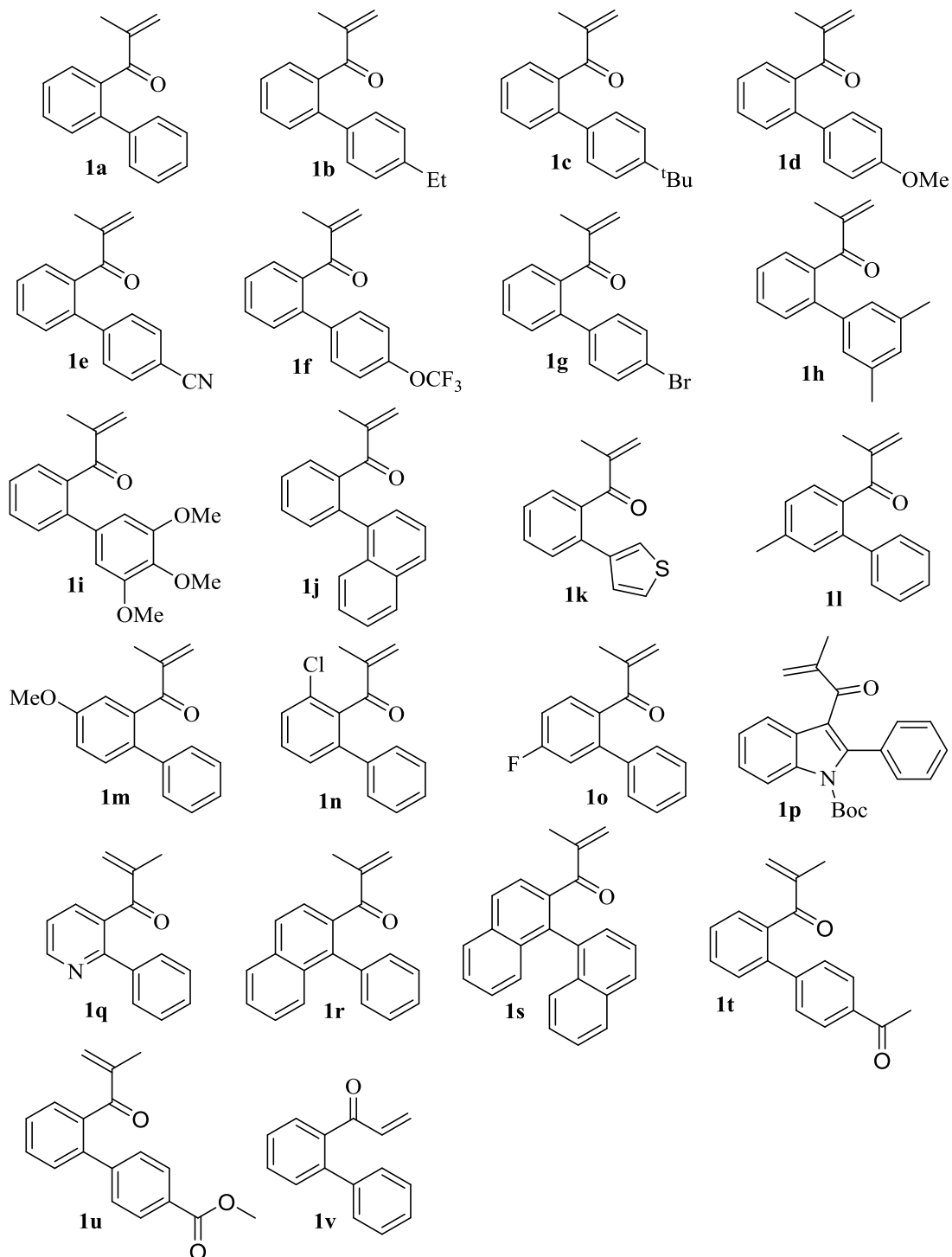
**Table S1: Comparison table between literature approaches for the synthesis of phenanthrone derivatives and this strategy**

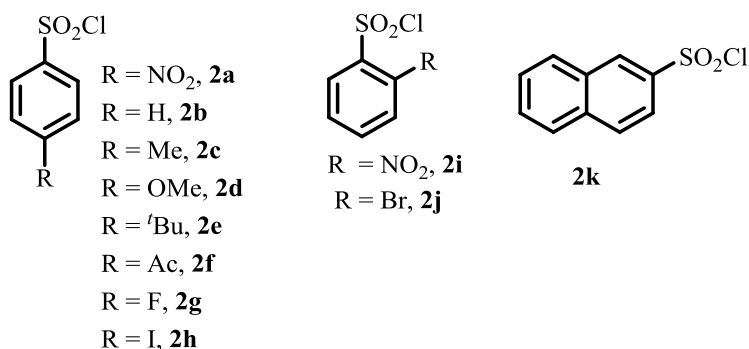
Reaction and reference	Remarks
<p><b>Previous Approaches:</b></p>  <p>Z. Chen, B. Tang &amp; Co-workers, <i>Org. Lett.</i> 2022, <b>24</b>, 2087–2092</p>	<p>R<sub>2</sub>, R<sub>3</sub> = alkyl or cycloalkyl -Cu-salts needed along with the metal catalyst &amp; -Reaction proceeds at higher temperature</p>
 <p>C. -H. Cheng &amp; Co-workers, <i>J. Am. Chem. Soc.</i> 2010, <b>132</b>, 8569–8571</p>	<p>R = Me, cycloalkyl  It requires metal catalyst along with the oxidant at higher temperatures.</p>
 <p>J. -Q. You &amp; Co-workers, <i>J. Am. Chem. Soc.</i>, 2008, <b>130</b>, 17676–17677</p>	<p>R = Me  Metal catalyst along with the oxidant in Oxygen atmosphere is obligatory, also higher temperatures and long-time span for the reaction to proceed.</p>
 <p>Y. -Y. Yeung &amp; Co-workers, <i>ACS Catal.</i> 2017, <b>7</b>, 4435–4440</p>	<p>R = Me, Aryl, Naphthyl  Substituted 9-fluorenones are needed to prepare the starting materials</p>
 <p>Z. Bin, J. You &amp; Co-workers, <i>Chem. Sci.</i>, 2023, <b>14</b>, 5125-5131</p>	<p>R<sub>2</sub>, R<sub>3</sub> = Me, Aryl and cyclo alkyl  Oxidant, metal catalyst as well as additives are needed</p>

 <p>P. Li &amp; Co-workers, <i>Asian J. Org. Chem.</i>, 2022, <b>11</b>, e202200269</p>	<p>Langlois' reagent in presence of molecular oxygen (O<sub>2</sub>) in air is essential</p>
 <p>P. Li &amp; Co-workers, <i>Org. Biomol. Chem.</i>, 2023, <b>21</b>, 4018-4021</p>	<p>R= alkyl, aryl Microwave accelerated transformation at higher temperature</p>
<p><b>THIS WORK:</b></p>	
 <p>R= SCN, SCF<sub>3</sub></p> <p>R= SO<sub>2</sub>Ar</p>	<p>-Oxidant at 80 °C -Photocatalyst at Room temperature Unprecedented Thiofunctionalized phenanthrones</p>

## 2. Structures of starting materials 1 and 2

All the Starting materials (**1a**, **1c**, **1d**, **1g**, **1j**, **1u**, **1v**)<sup>8(a,b),17</sup> were prepared based on literature reports, and the spectral data was compared.





- **Visual representation of the reaction set-up:**

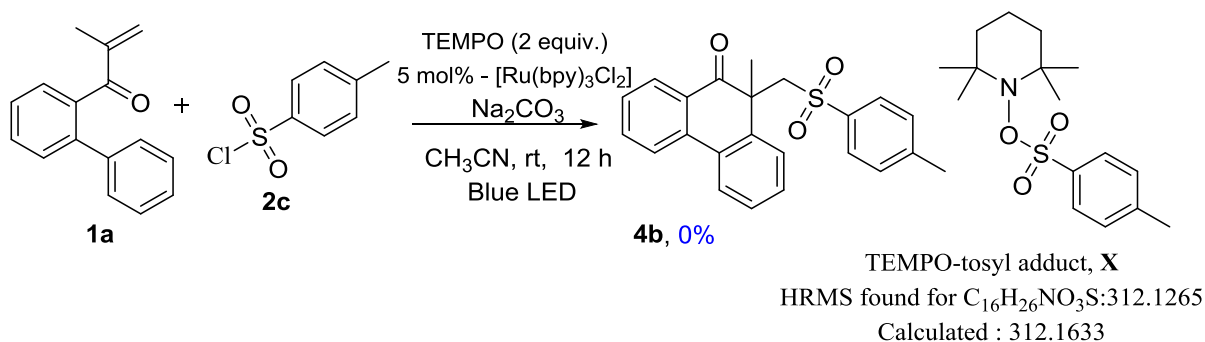


**Figure S1:** Blue LED reactor with magnetic stirring plate

**3. Control experiments:**

**A. Radical trapping reaction with 2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO):**

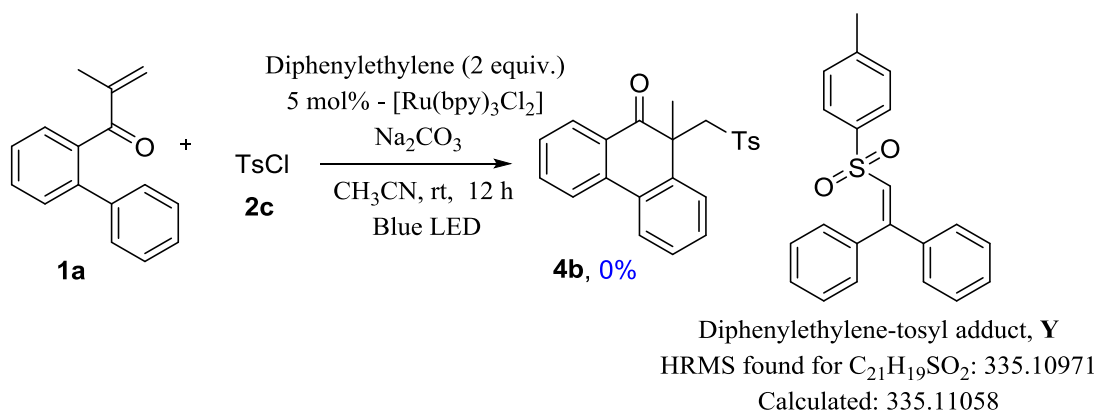
Biaryl enone (**1a**, 0.3 mmol), 4-nitro benzenesulfonyl chloride (**2c**, 0.6 mmol),  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  (5 mol %),  $\text{Na}_2\text{CO}_3$  (0.3 mmol), 2,2,6,6-tetramethylpiperidin-1-yl) oxidanyl (TEMPO) (0.6 mmol) were taken in a reaction vial and solvent anhydrous  $\text{CH}_3\text{CN}$  was added. The reaction mixture was stirred under blue LED at room temperature and the progress of the reaction was monitored by TLC and found that the reaction inhibited.



**B. Radical trapping reaction with 1,1-Diphenyl ethylene:**

Biaryl enone (0.3 mmol), 4-nitro benzenesulfonyl chloride (0.6 mmol),  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  (5 mol %),  $\text{Na}_2\text{CO}_3$  (0.3 mmol), 1,1-Diphenyl ethylene (0.6 mmol) were taken in a reaction vial and solvent anhydrous  $\text{CH}_3\text{CN}$  was added. The reaction mixture was stirred under blue LED at

room temperature and the progress of the reaction was monitored by TLC was found to be inhibited.

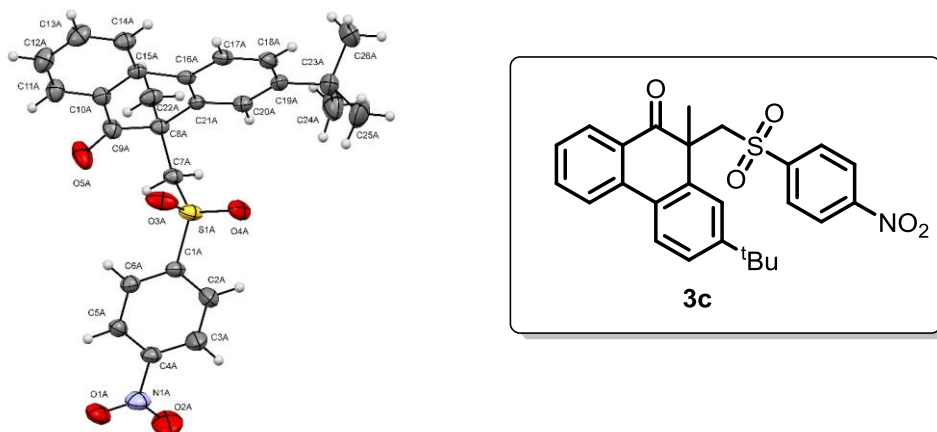


#### 4. X-ray Crystallography:

X-ray data for the compounds KB11 and KB328 were collected at room temperature on a Bruker D8 QUEST instrument with an I $\mu$ S Mo microsource ( $\lambda = 0.7107$  Å) and a PHOTON-III detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [1]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [2] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. The atoms C24A/C25A/C26A/O4A and C3B/N1B/C24B/C25B/C26B of KB11 were disordered over two positions and their site occupation factors were refined into 0.724(5)/0.276(5) and 0.538(6)/0.462(6), respectively. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms].

##### A. Crystal structure determination of **3c**:

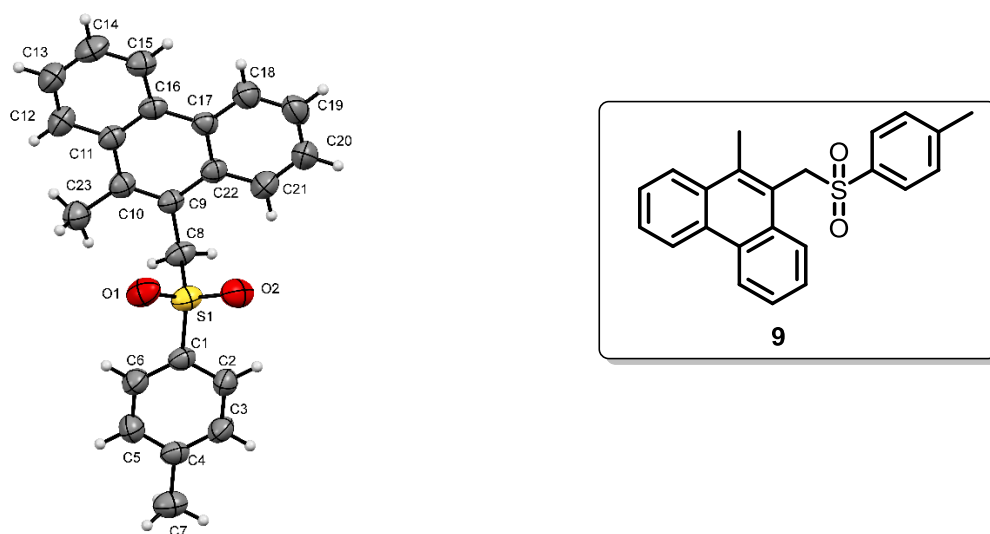
**Crystal Data** for C<sub>26</sub>H<sub>25</sub>NO<sub>5</sub>S ( $M = 463.53$  g/mol): triclinic, space group P-1 (no. 2),  $a = 9.7342(7)$  Å,  $b = 12.3271(9)$  Å,  $c = 21.0097(15)$  Å,  $\alpha = 98.273(2)^\circ$ ,  $\beta = 95.450(2)^\circ$ ,  $\gamma = 104.946(2)^\circ$ ,  $V = 2387.3(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 294.15$  K,  $\mu(\text{MoK}\alpha) = 0.172$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.290$  g/cm<sup>3</sup>, 43584 reflections measured ( $3.956^\circ \leq 2\theta \leq 52.784^\circ$ ), 9745 unique ( $R_{\text{int}} = 0.0672$ ,  $R_{\text{sigma}} = 0.0703$ ) which were used in all calculations. The final  $R_1$  was 0.0641 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1715 (all data). **CCDC 2278957** deposition numbers contains the supplementary crystallographic data for this paper which can be obtained free of charge at <https://www.ccdc.cam.ac.uk/structures/>.



**Figure S2:** ORTEP diagram of compound **3c** with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius. Only molecule A was shown for a better view. The minor disordered atom components were omitted for clarity

### B. Crystal structure determination of **9**:

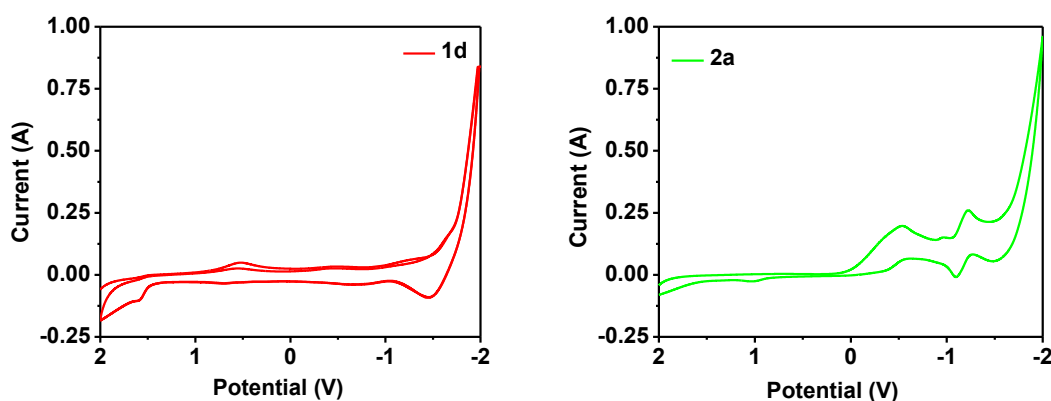
**Crystal Data** for  $C_{23}H_{20}O_2S$  ( $M = 360.480$  g/mol): monoclinic, space group  $P2_1/c$  (no. 14),  $a = 14.441(4)$  Å,  $b = 4.9171(15)$  Å,  $c = 25.385(7)$  Å,  $\beta = 103.485(9)^\circ$ ,  $V = 1752.9(9)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 294.15$  K,  $\mu(\text{Mo K}\alpha) = 0.199$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.366$  g/cm<sup>3</sup>, 18591 reflections measured ( $4.88^\circ \leq 2\theta \leq 52.48^\circ$ ), 3520 unique ( $R_{\text{int}} = 0.1265$ ,  $R_{\text{sigma}} = 0.1348$ ) which were used in all calculations. The final  $R_1$  was 0.0774 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.2415 (all data). **CCDC 2278958** deposition numbers contains the supplementary crystallographic data for this paper which can be obtained free of charge at <https://www.ccdc.cam.ac.uk/structures/>.



**Figure S3:** ORTEP diagram of compound **9** with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

## 5. Electrochemical studies:

Cyclic voltammetry experiments of **1d** and **2a** were carried out on a PC-controlled CH instruments model CHI 620C electrochemical analyser in acetonitrile at a scan rate of 200 mV/s using 0.1 mM concentration of tetrabutylammonium hexafluorophosphate (NBu<sub>4</sub>PF<sub>6</sub>) as supporting electrolyte. The working electrode is glassy carbon, saturated calomel electrode (SCE) is reference electrode, and platinum wire is auxiliary electrode. Then, the spectro electrochemistry of both the substrates was measured using this cyclic voltammetric technique and evaluated the maximum oxidation and reduction potentials of the individual substrates. Substrate **1d** shows oxidation potentials at 1.82 V, 1.57 V and reduction potentials at -1.46 V, -1.21 V. whereas **2a** shows the oxidation potential at 1.01 V, 1.79 V and reduction potentials at -1.21 V, -1.09 V.

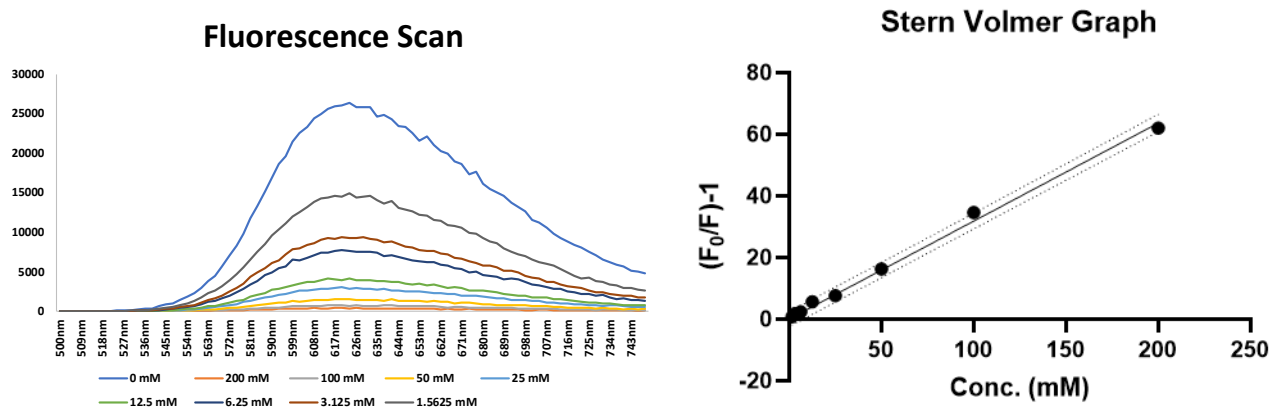


**Fig. S4:** (a) Cyclic voltammogram of **1d** recorded using tetrabutylammonium hexafluorophosphate (NBu<sub>4</sub>PF<sub>6</sub>) as supporting electrolyte. (b) Cyclic voltammogram of **1d** and **2a** in CH<sub>3</sub>CN recorded using tetrabutylammonium hexafluorophosphate (NBu<sub>4</sub>PF<sub>6</sub>) as supporting electrolyte.

## 6. Stern-Volmer Quenching Experiment:

All spectroscopic measurements were carried out in TECAN Infinite M200 PRO spectrophotometer. The excitation of Ru(bpy)<sub>3</sub>Cl<sub>2</sub> catalyst at 455 nm and emission was recorded from 500 nm to 750 nm. The substrate 4-nitrobenzene sulfonyl chloride (**2a**) was serially diluted (200 mM- 1.5625 mM) in degassed acetonitrile. The photocatalyst concentration at 10 mM in degassed acetonitrile was incubated with serially diluted 4-nitrobenzene sulfonyl chloride and the corresponding fluorescence was recorded. The experiments were performed in replicates. The Stern Volmer graph was plotted in Graph Pad Prism 8.0.2 software by using values at the emission maxima of 620 nm. Stern Volmer constant ( $K_{SV}$ ) was calculated to be  $3.18 \times 10^{-2} \text{ M}^{-1}$ .

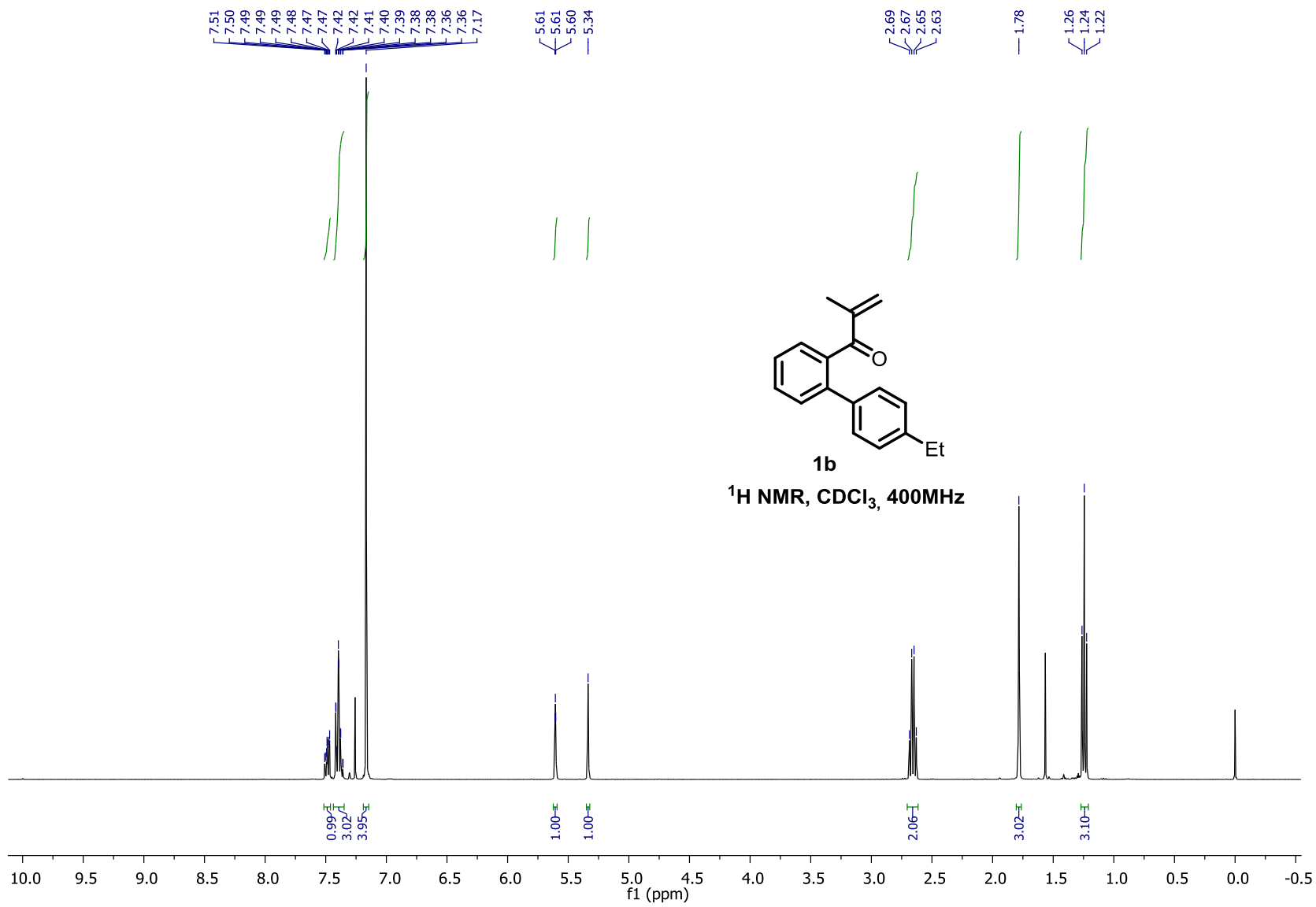


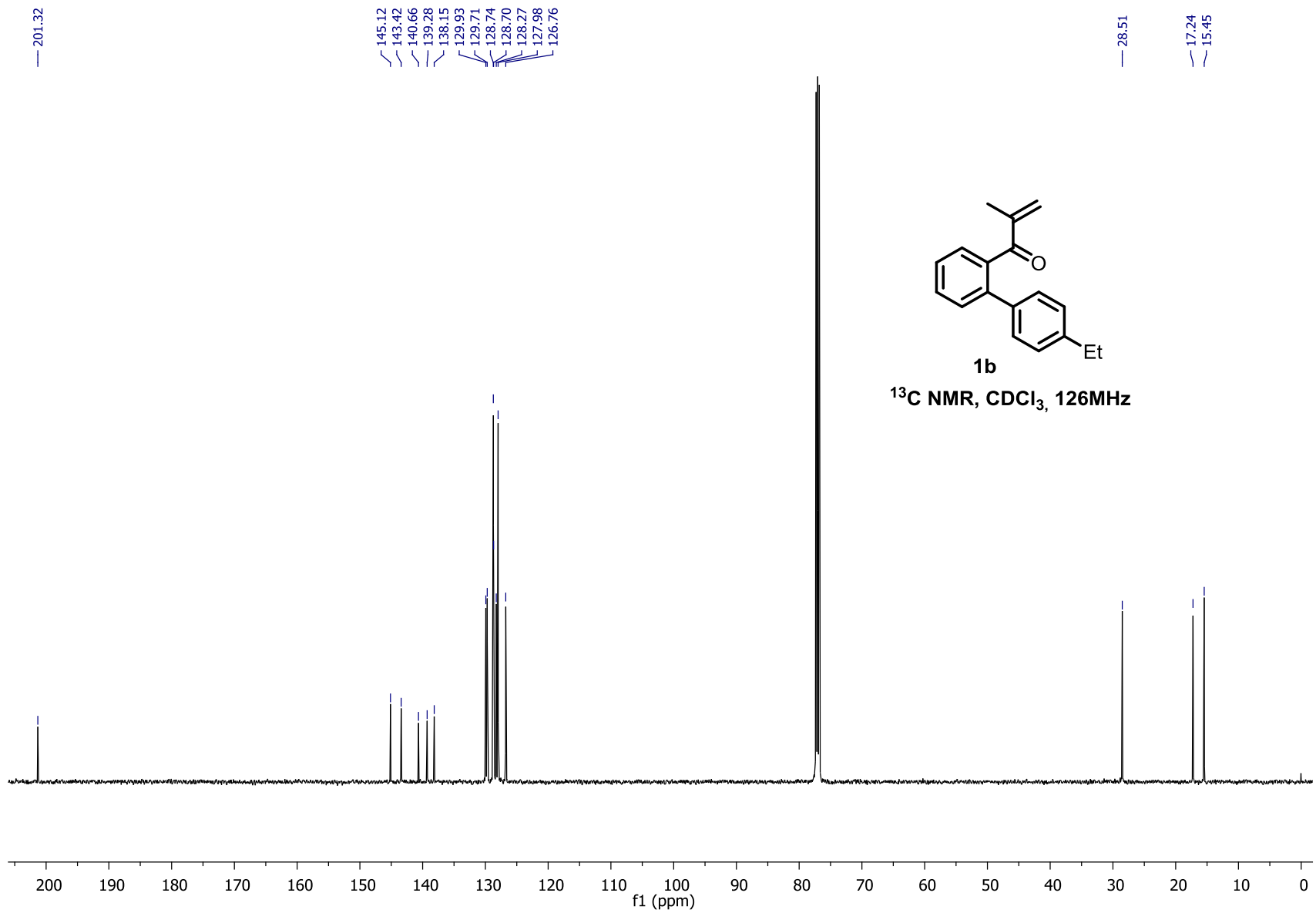


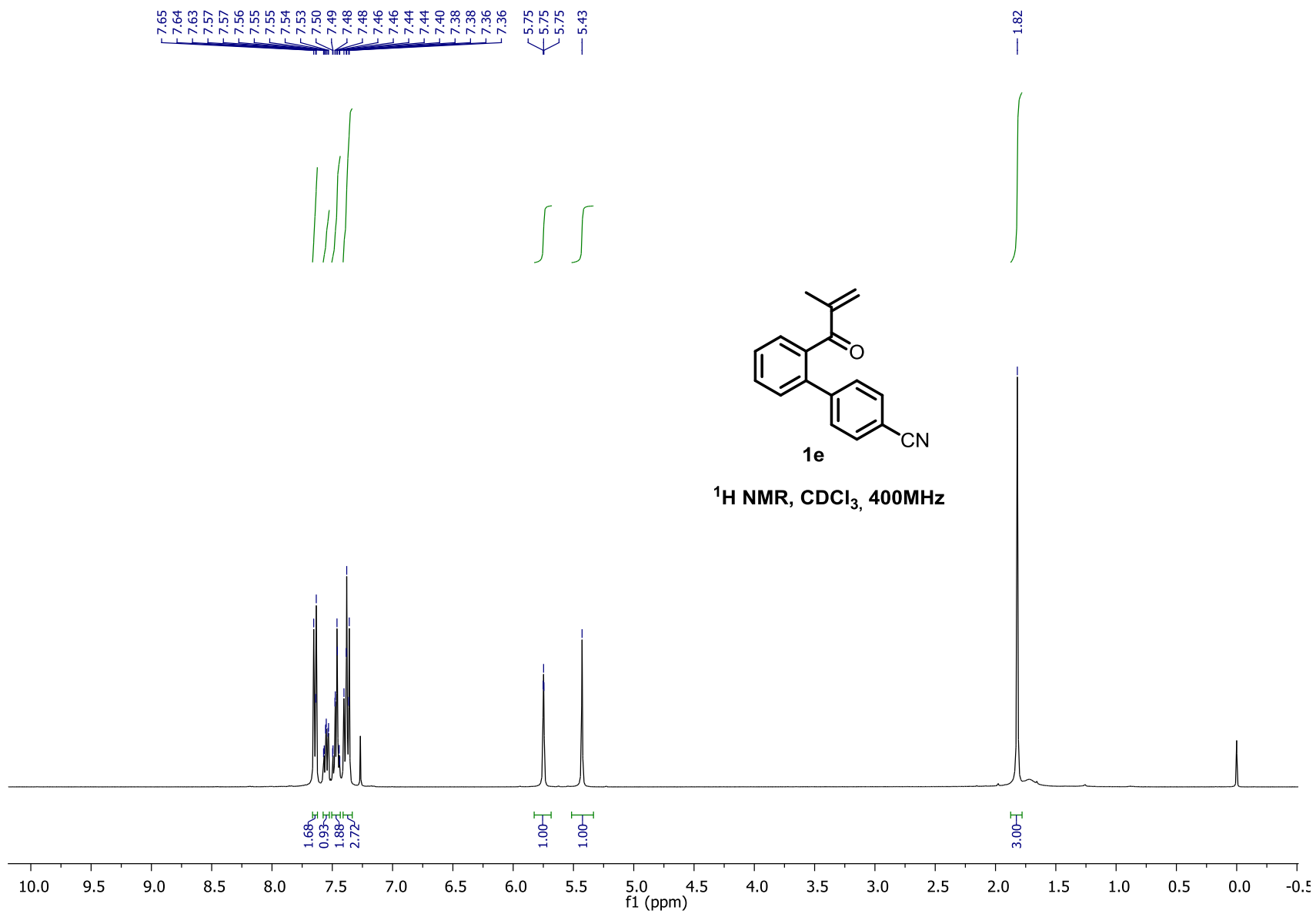
**Fig. S5:** (a) Fluorescence spectrum showing quenching of  $[\text{Ru}(\text{bpy})_3]^{2+}$  (Ex = 455 nm, Em = 620 nm) with increasing concentrations of 4-nitrobenzenesulfonyl chloride (0- 200 mM); (b) Corresponding Stern–Volmer plot.

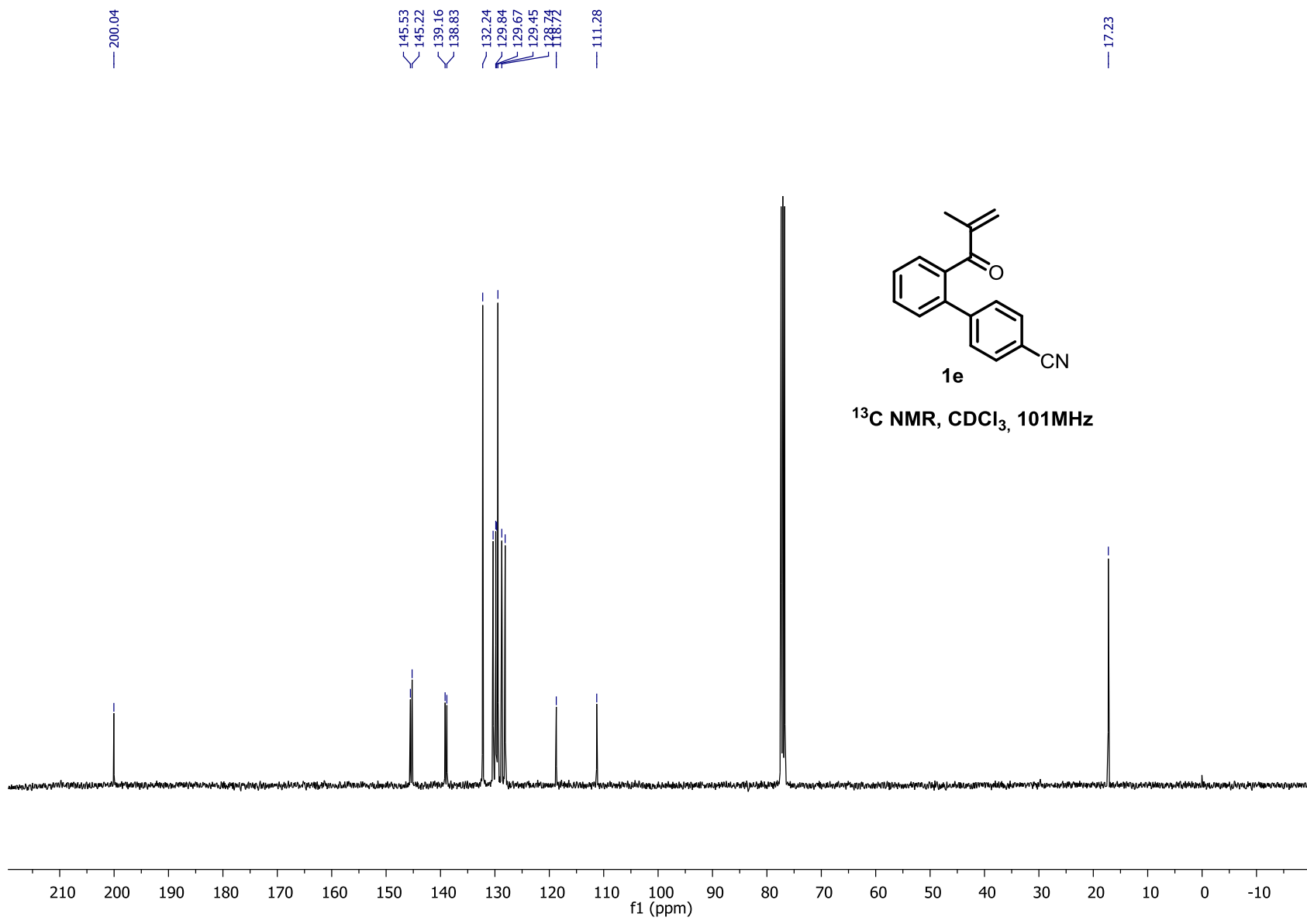
## 7. References:

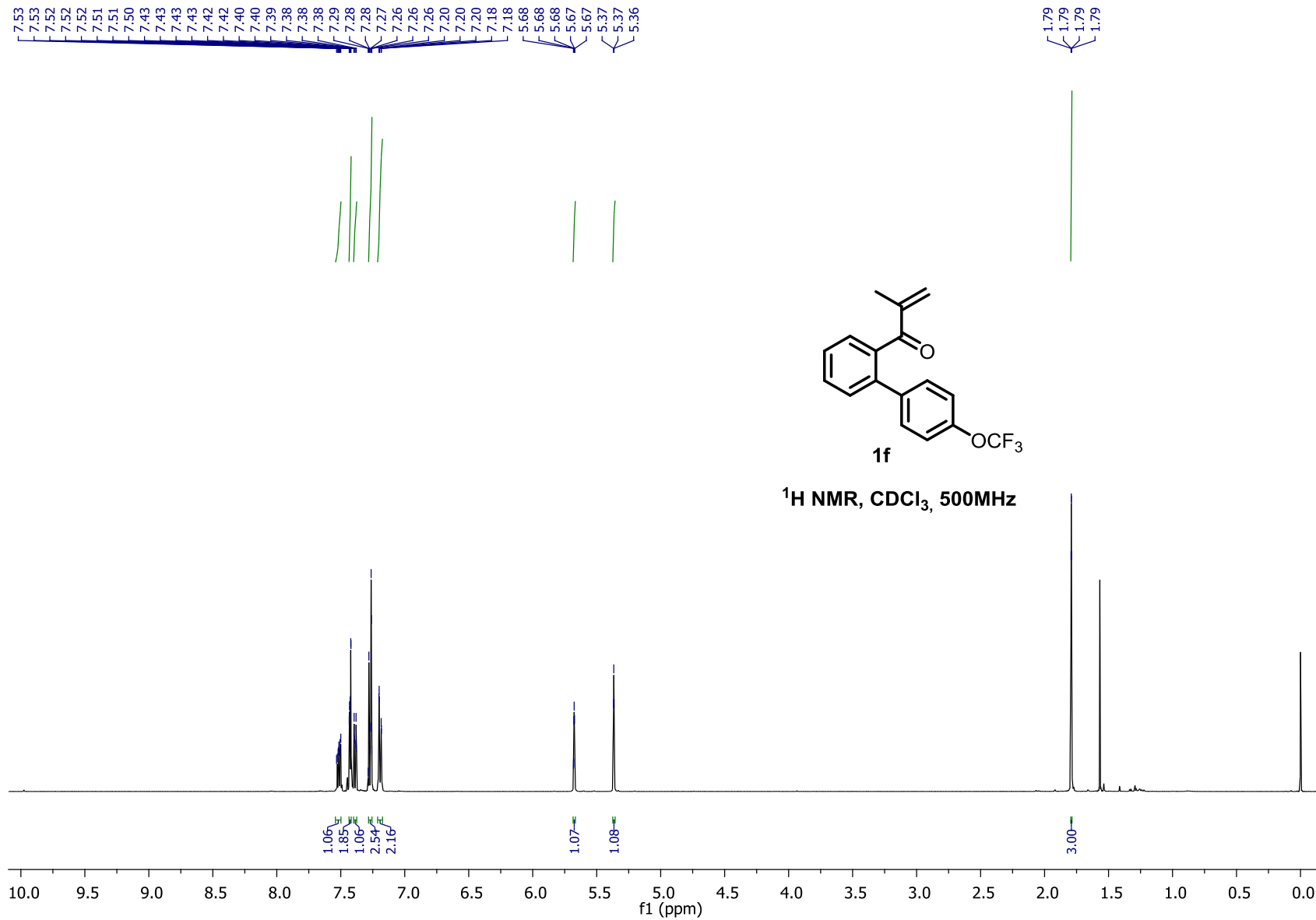
- (a) X. Yang, J. Liu, Y. Gao, L. Wang, Y. Zhang, and P. Li, *Asian J. Org. Chem.* 2022, 11, e202200269 (b) X. Yang, G.Zhang, J. Zhou, C. Zhou, L. Wang and P. Li, *Org. Biomol. Chem.*, 2023, 21, 4018-4021.
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- Sheldrick G. M. (2015). *Acta Crystallogr C* 71: 3-8.

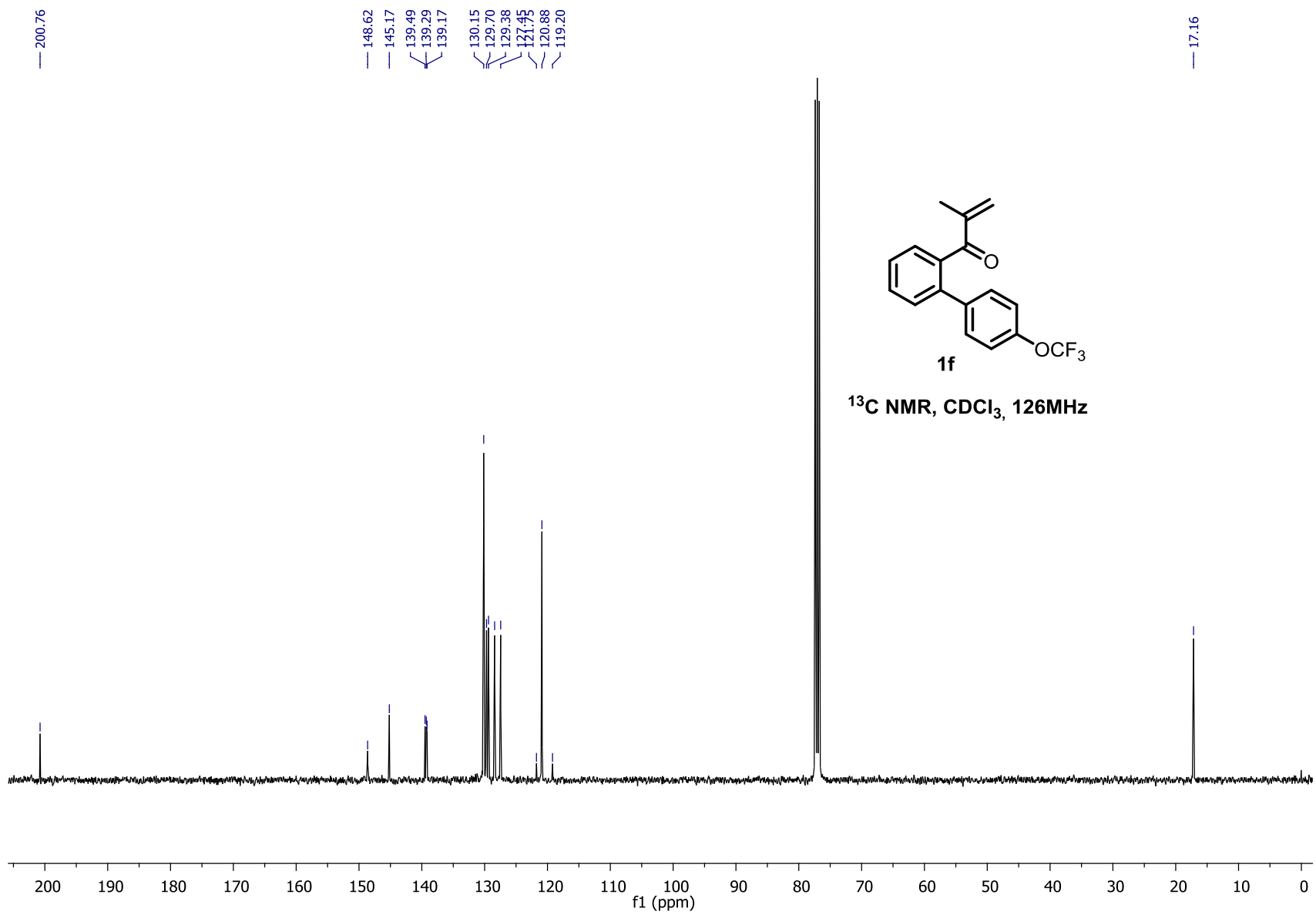


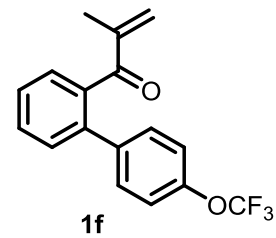




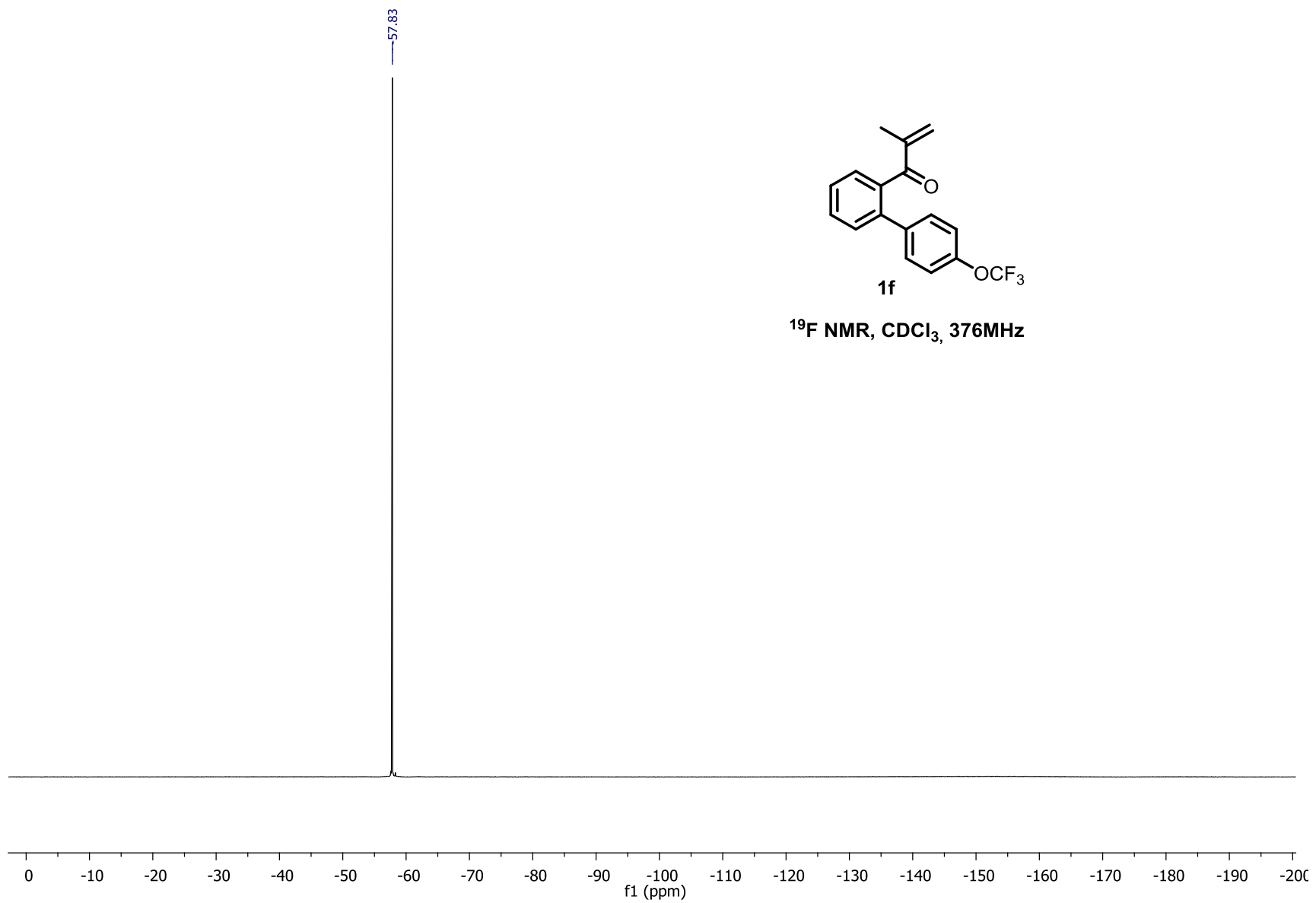




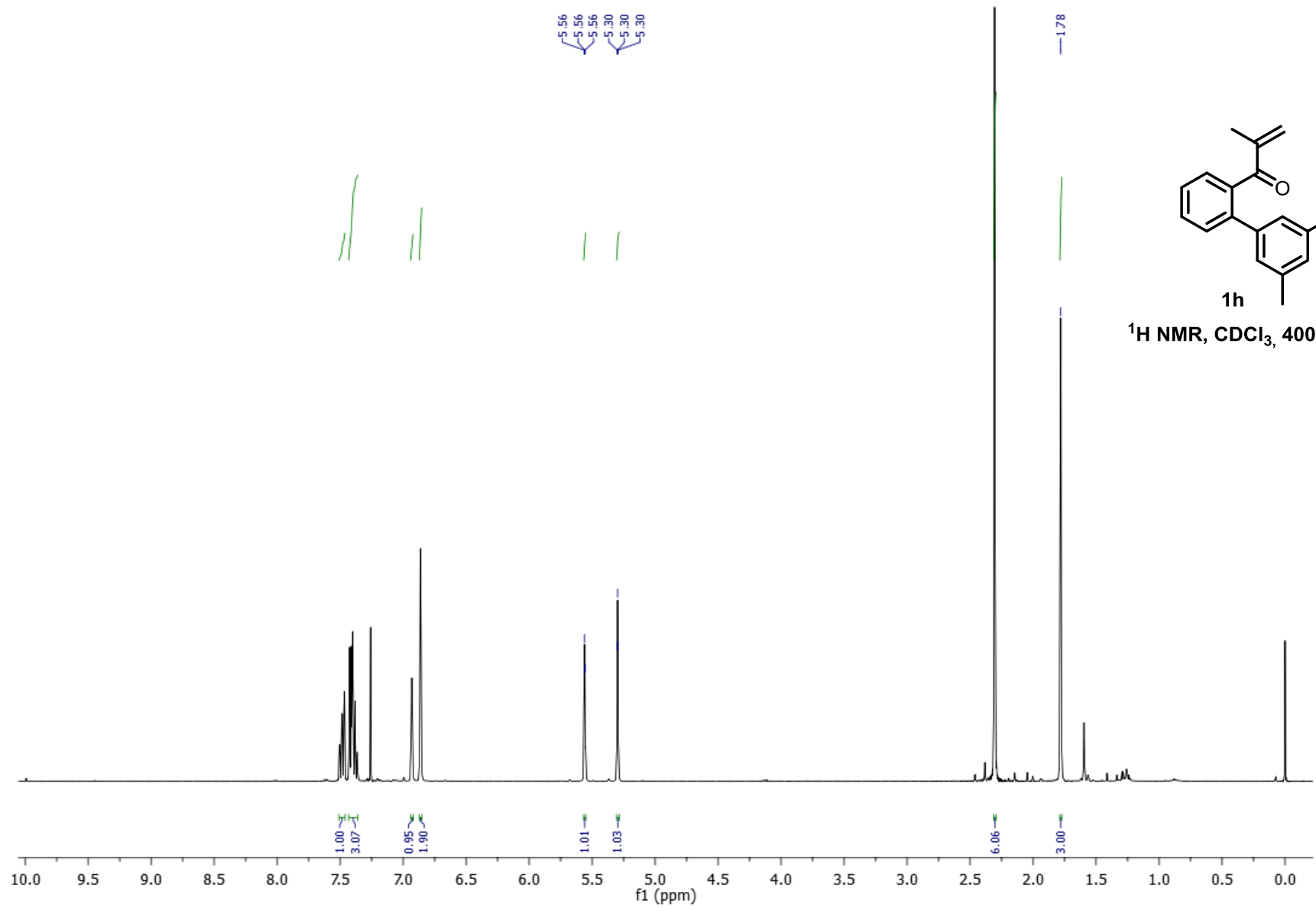


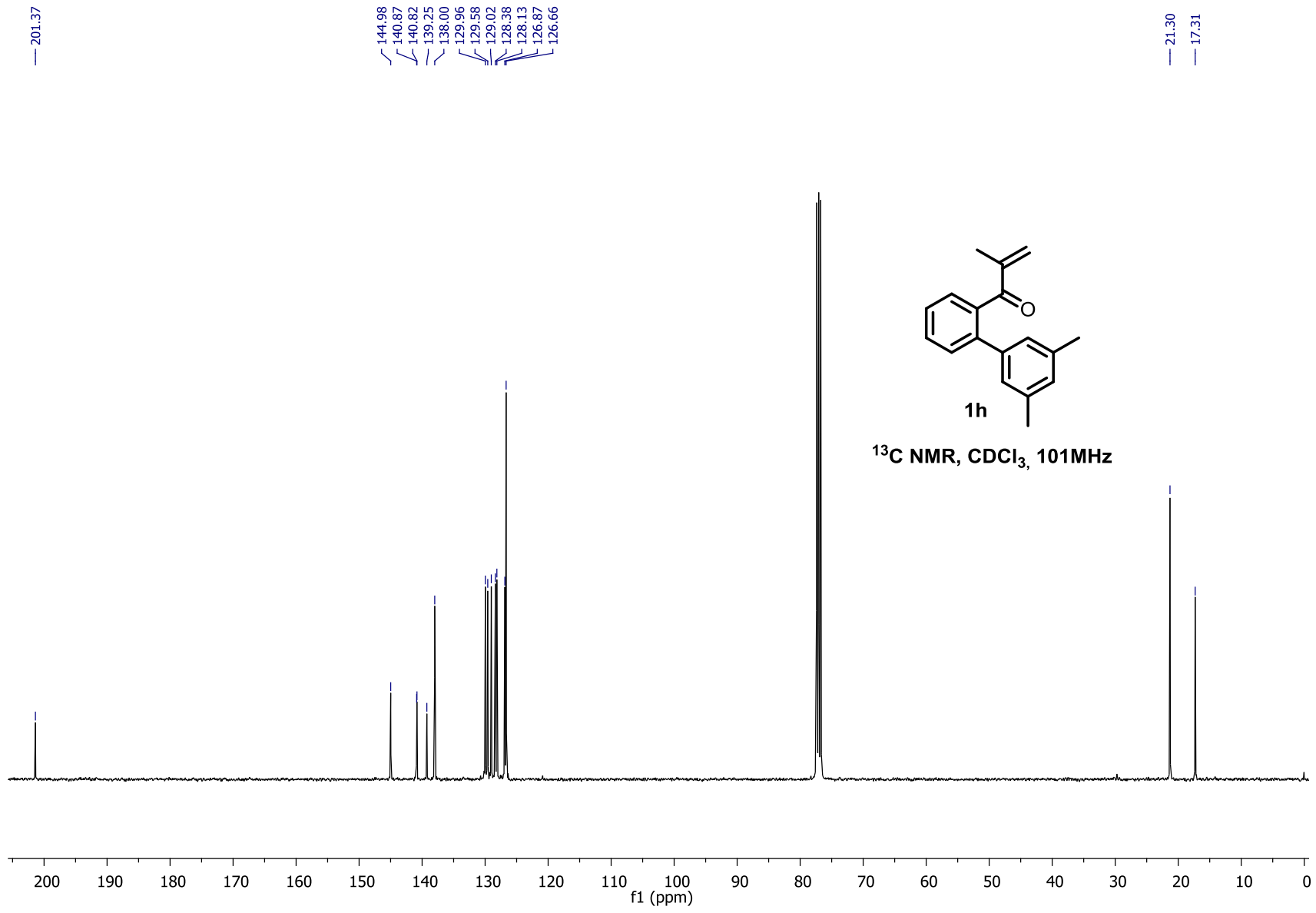


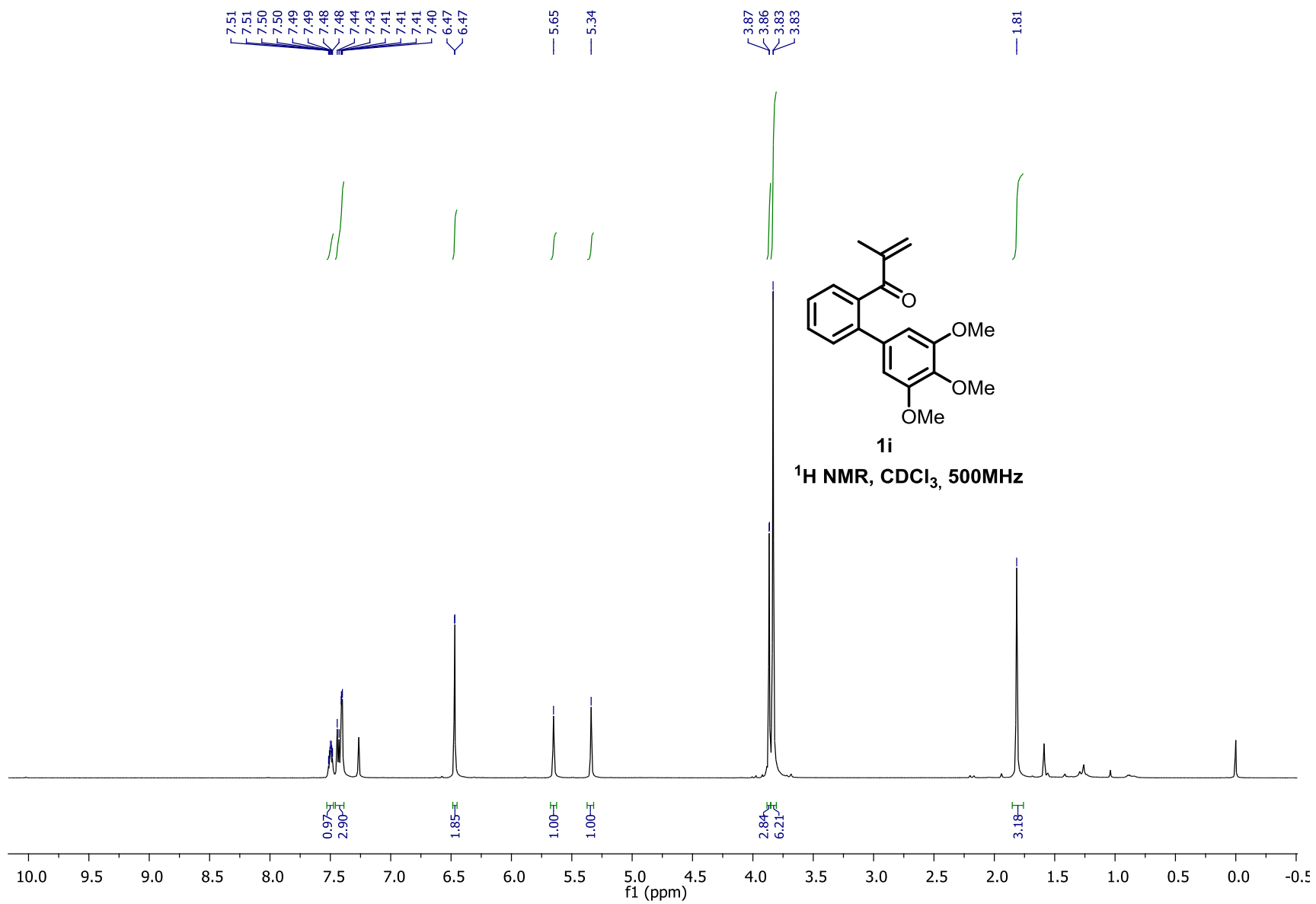
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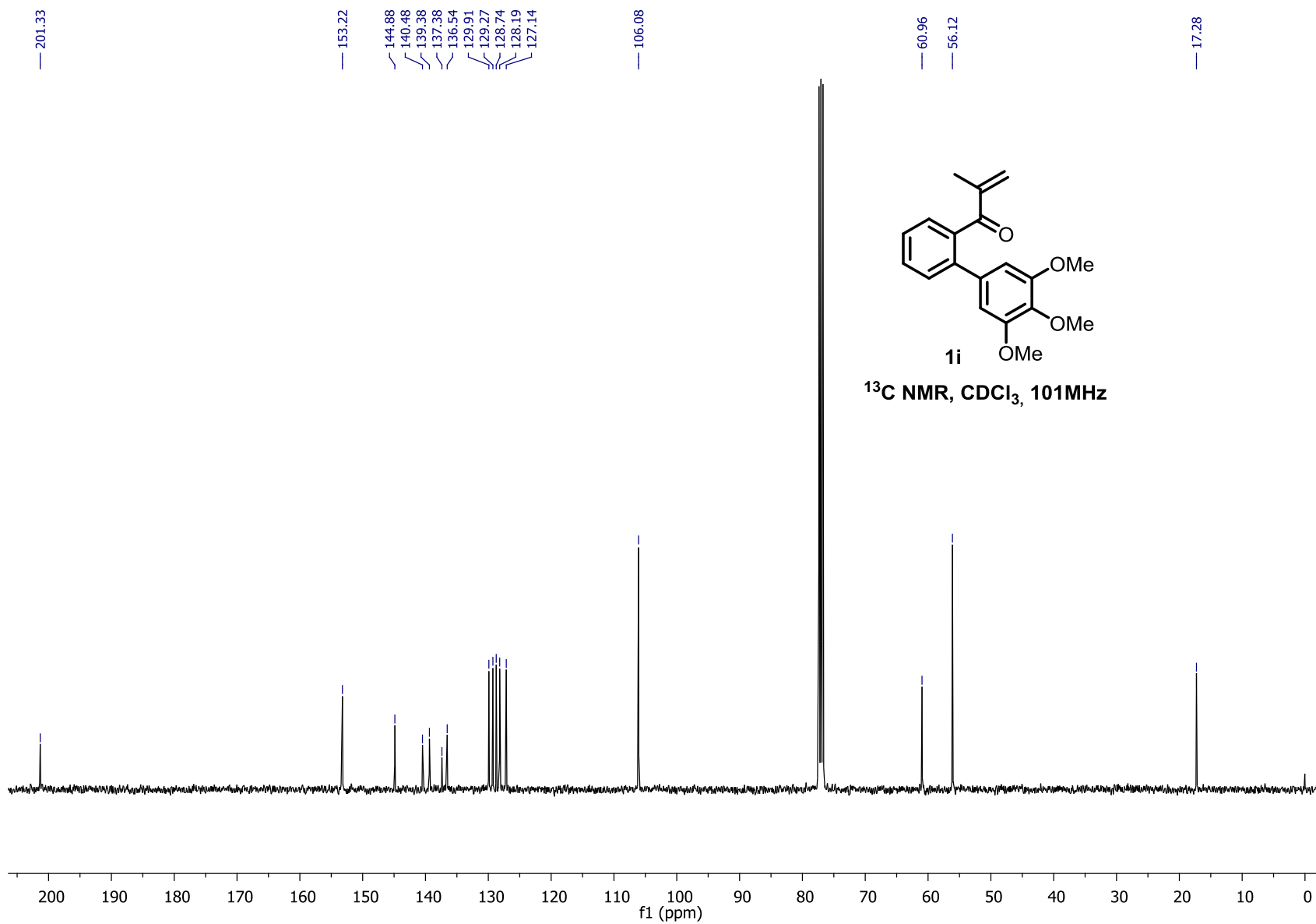


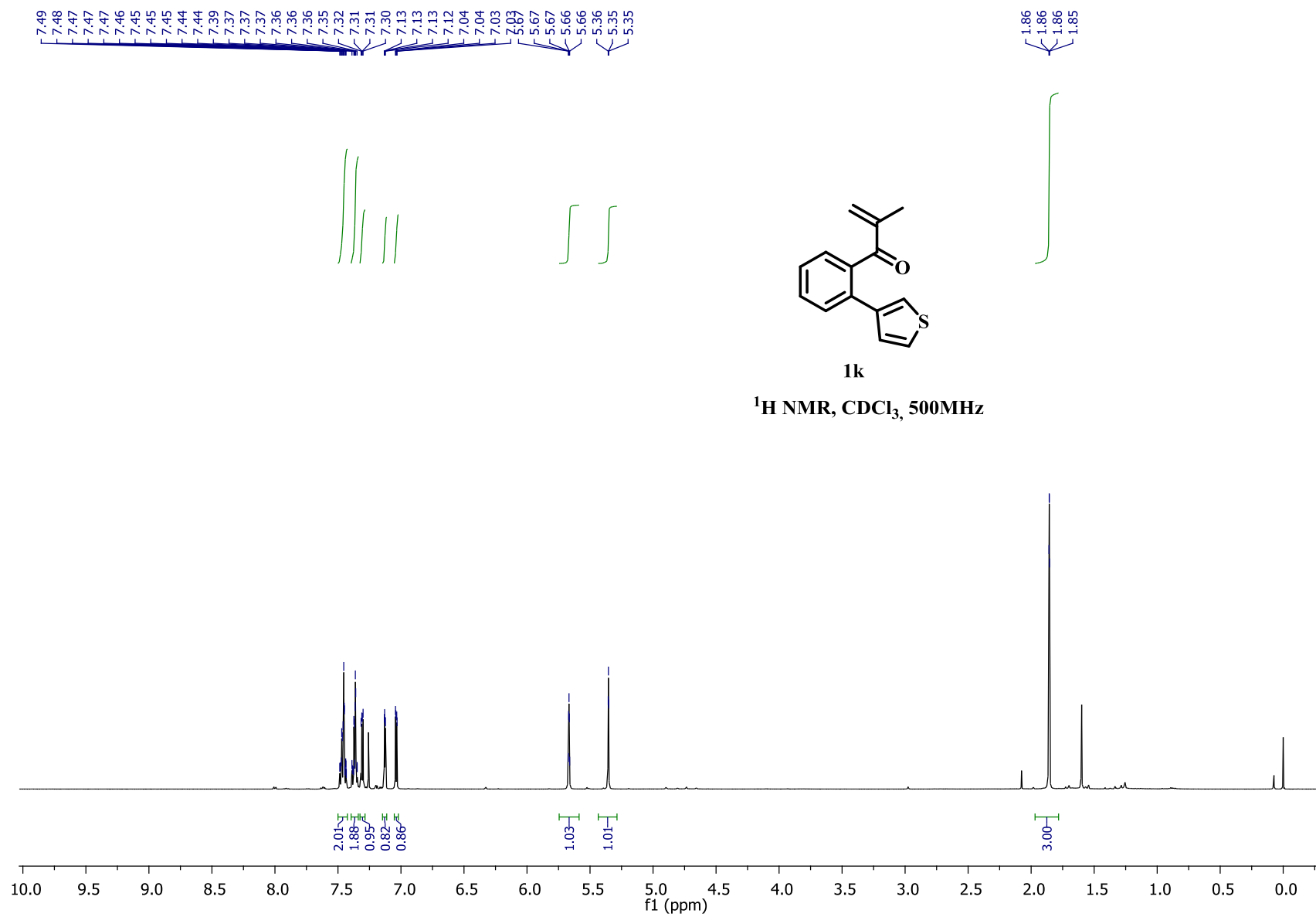


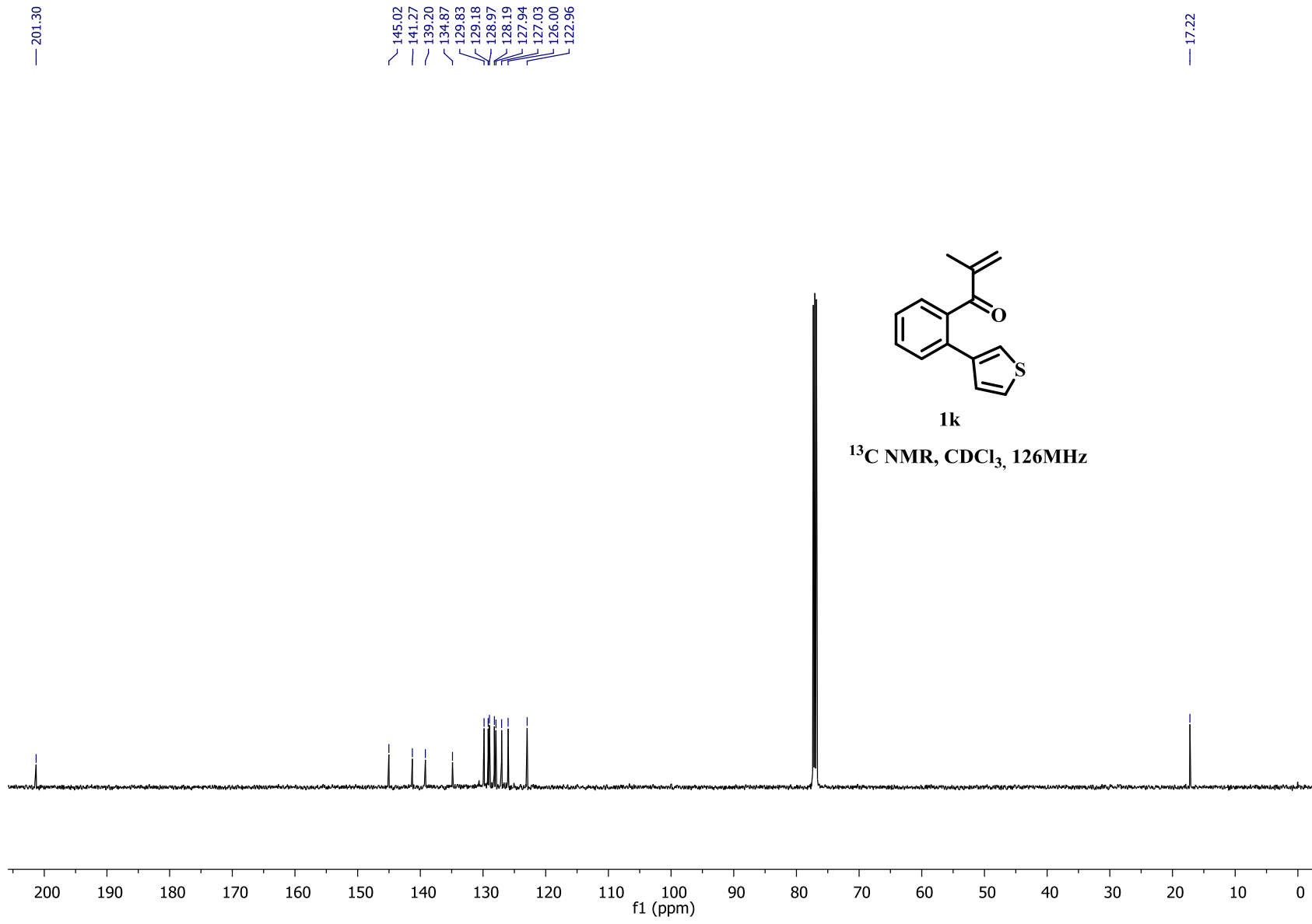


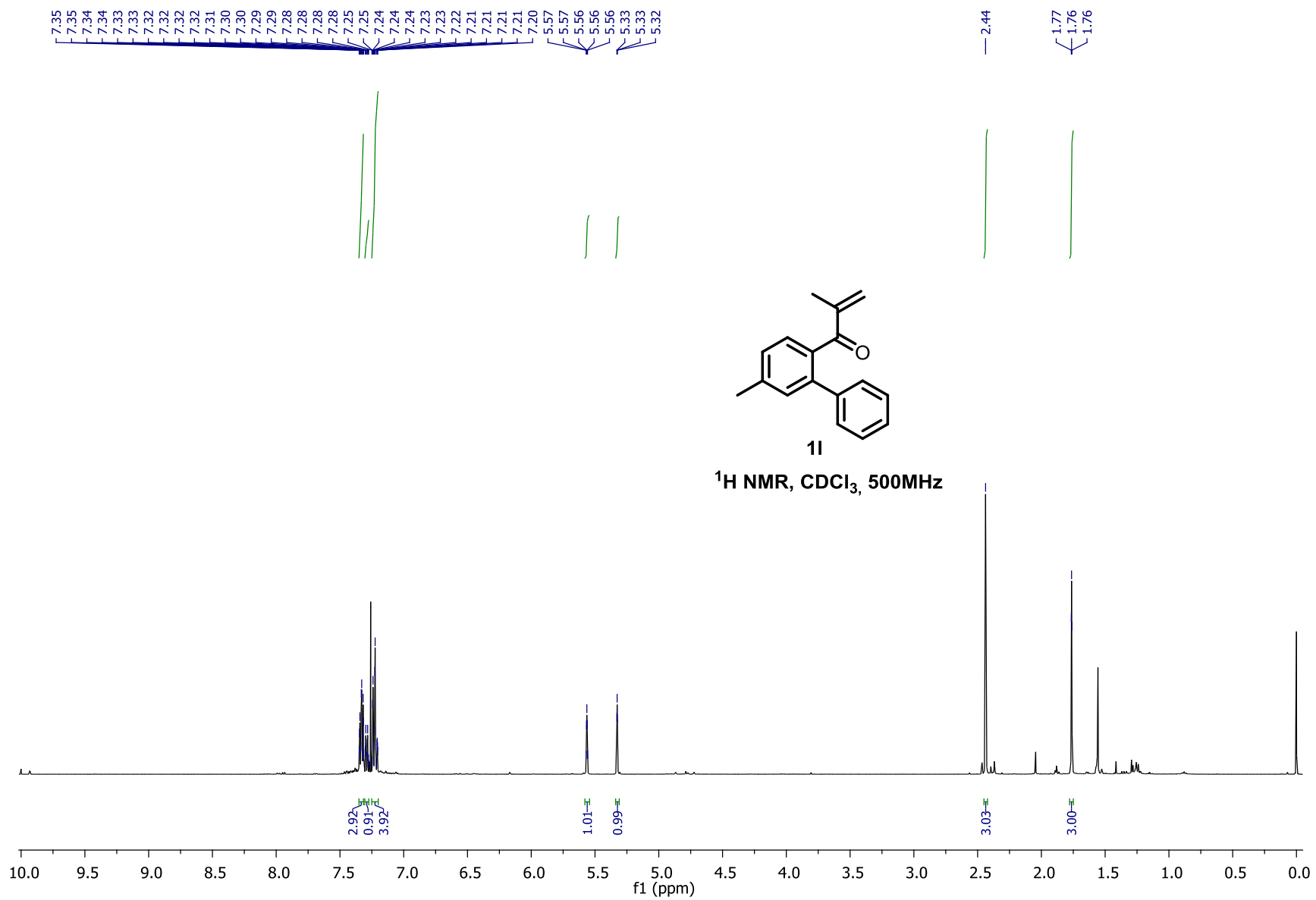








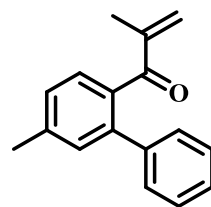




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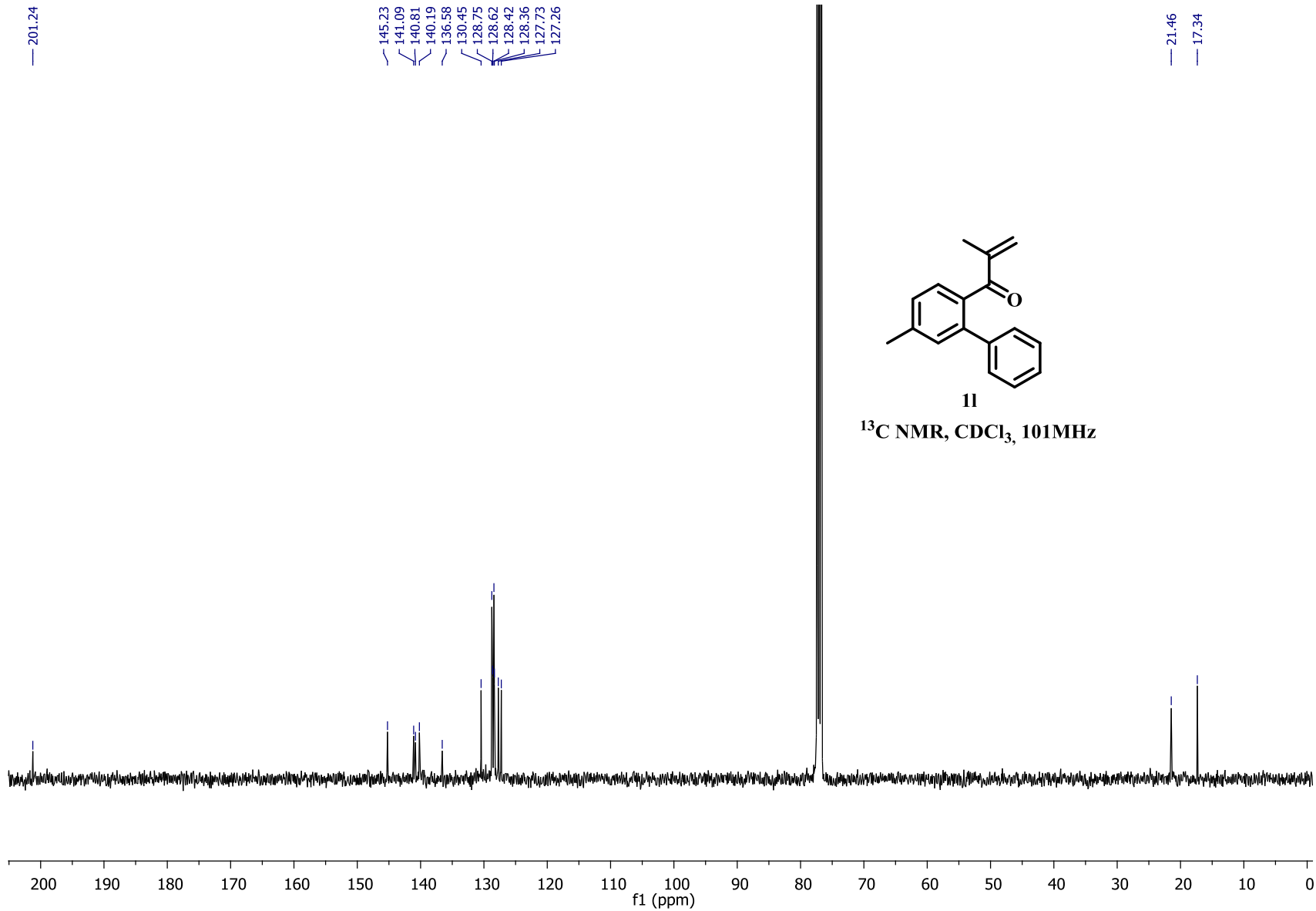
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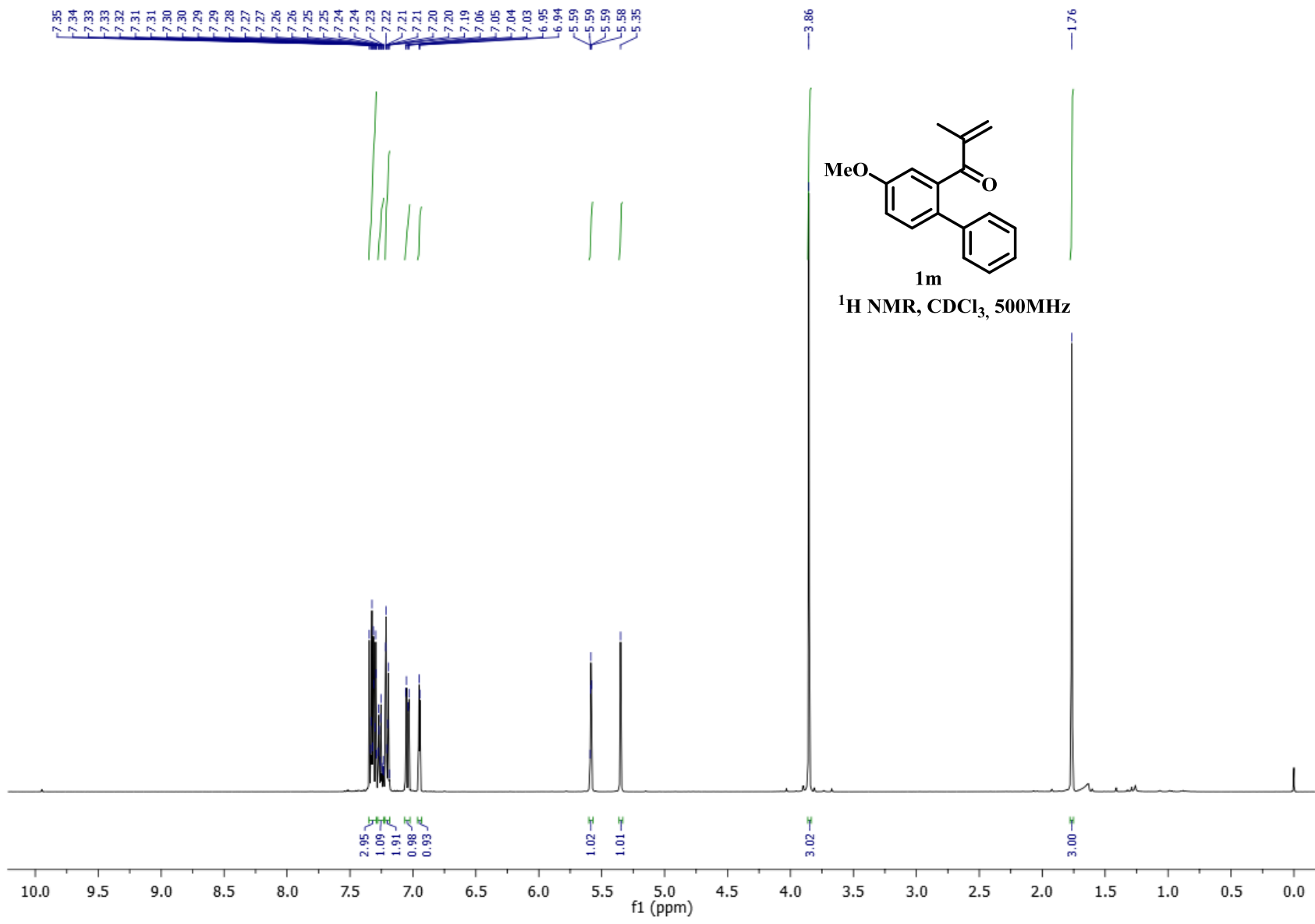


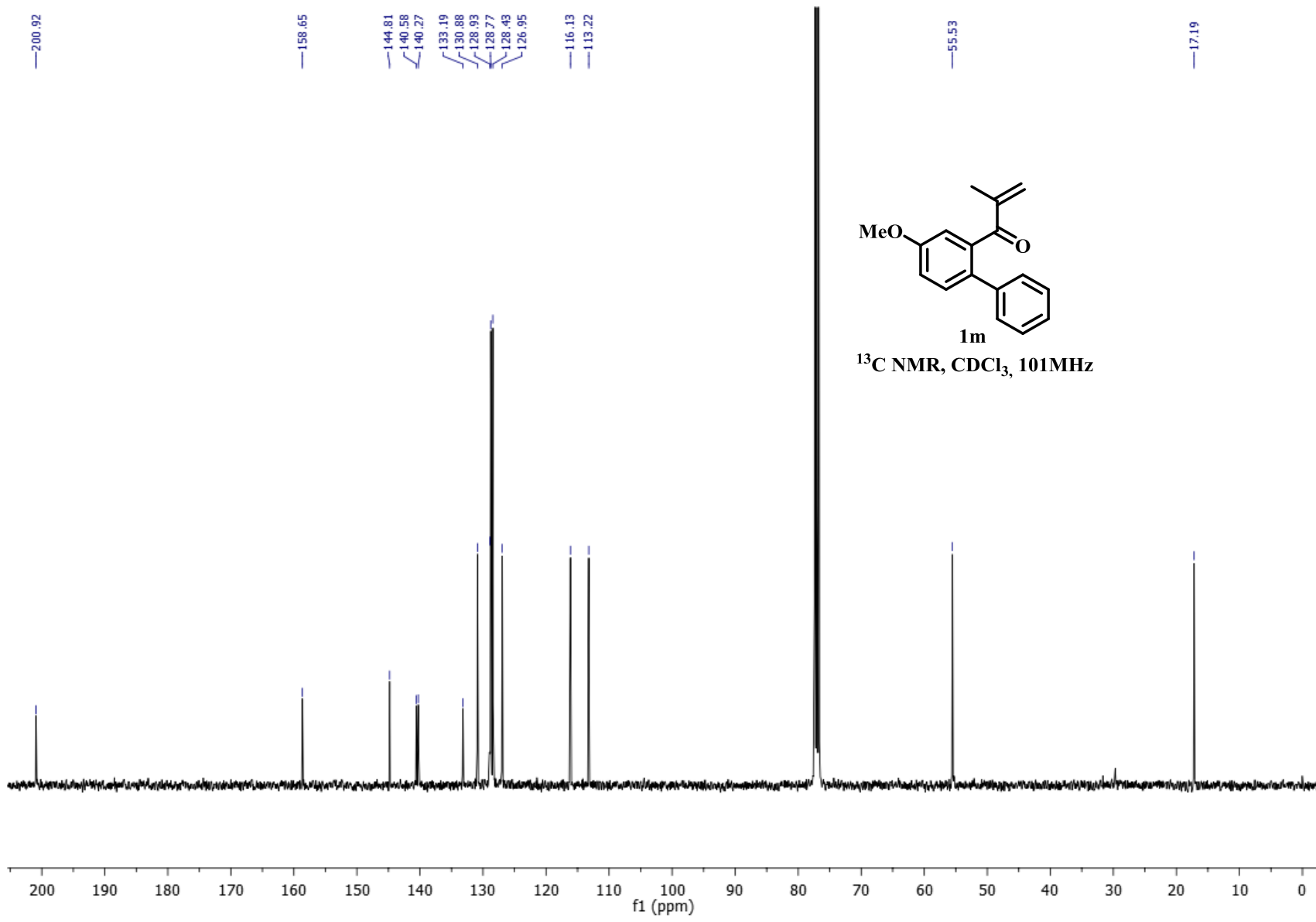
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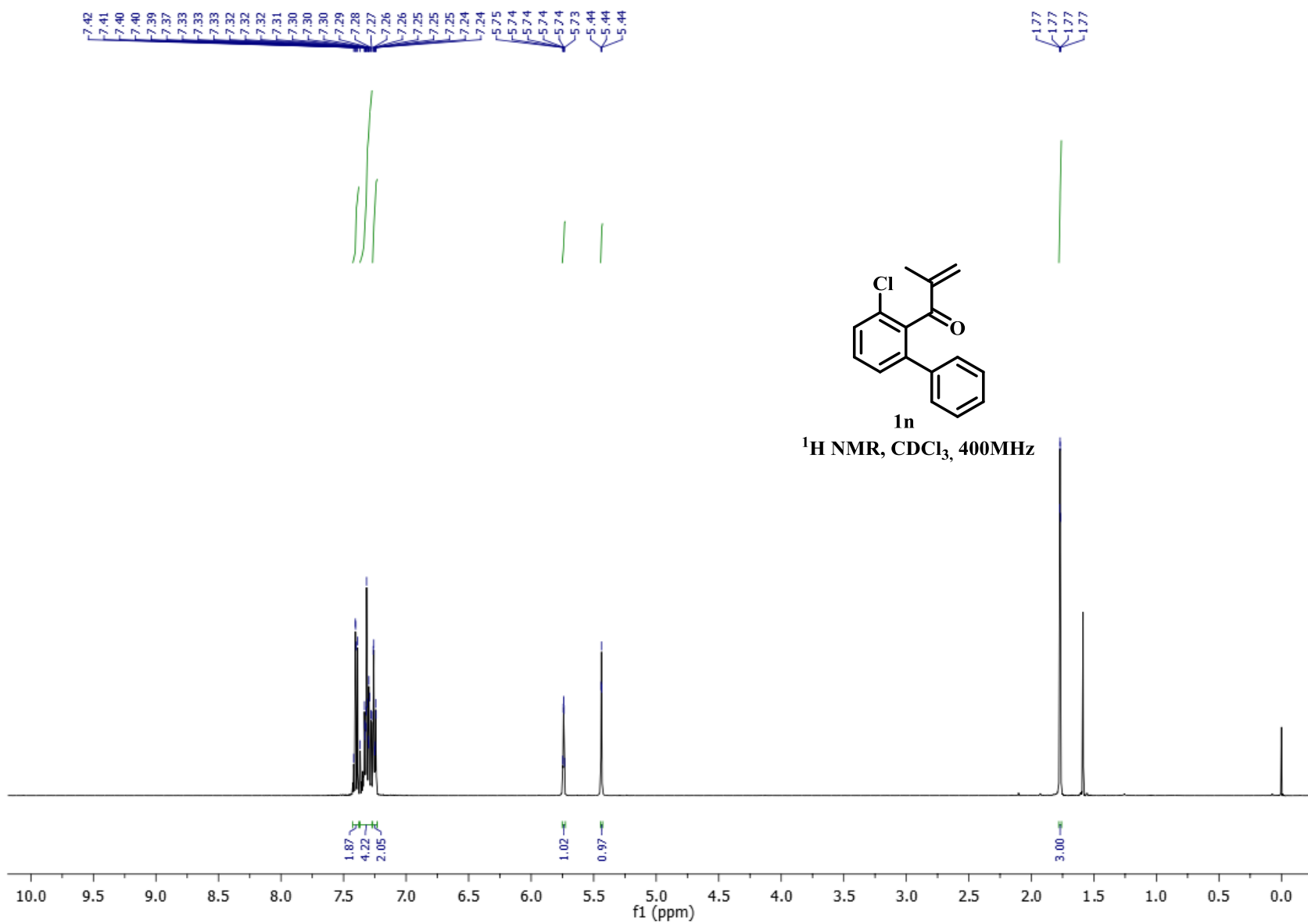
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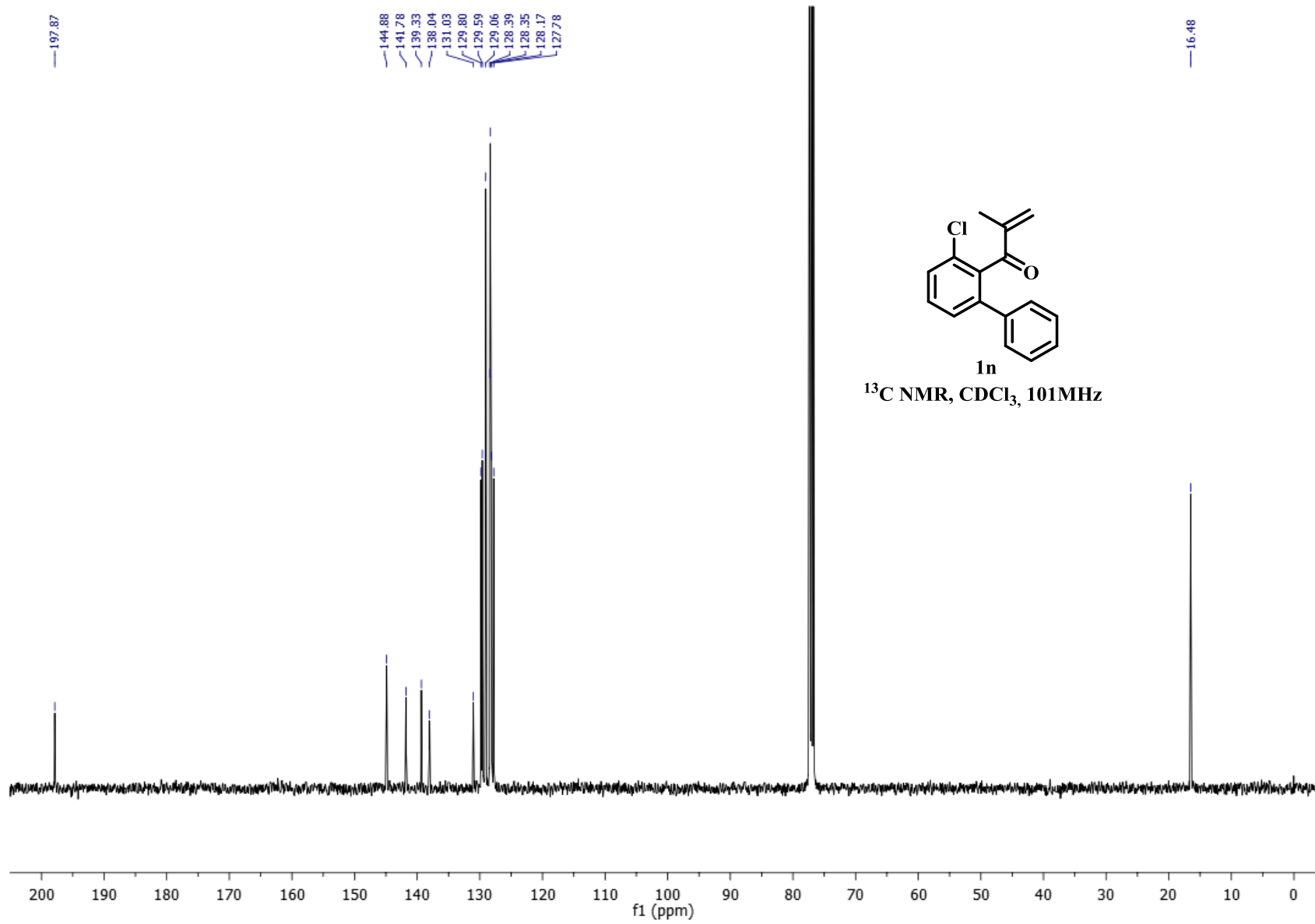


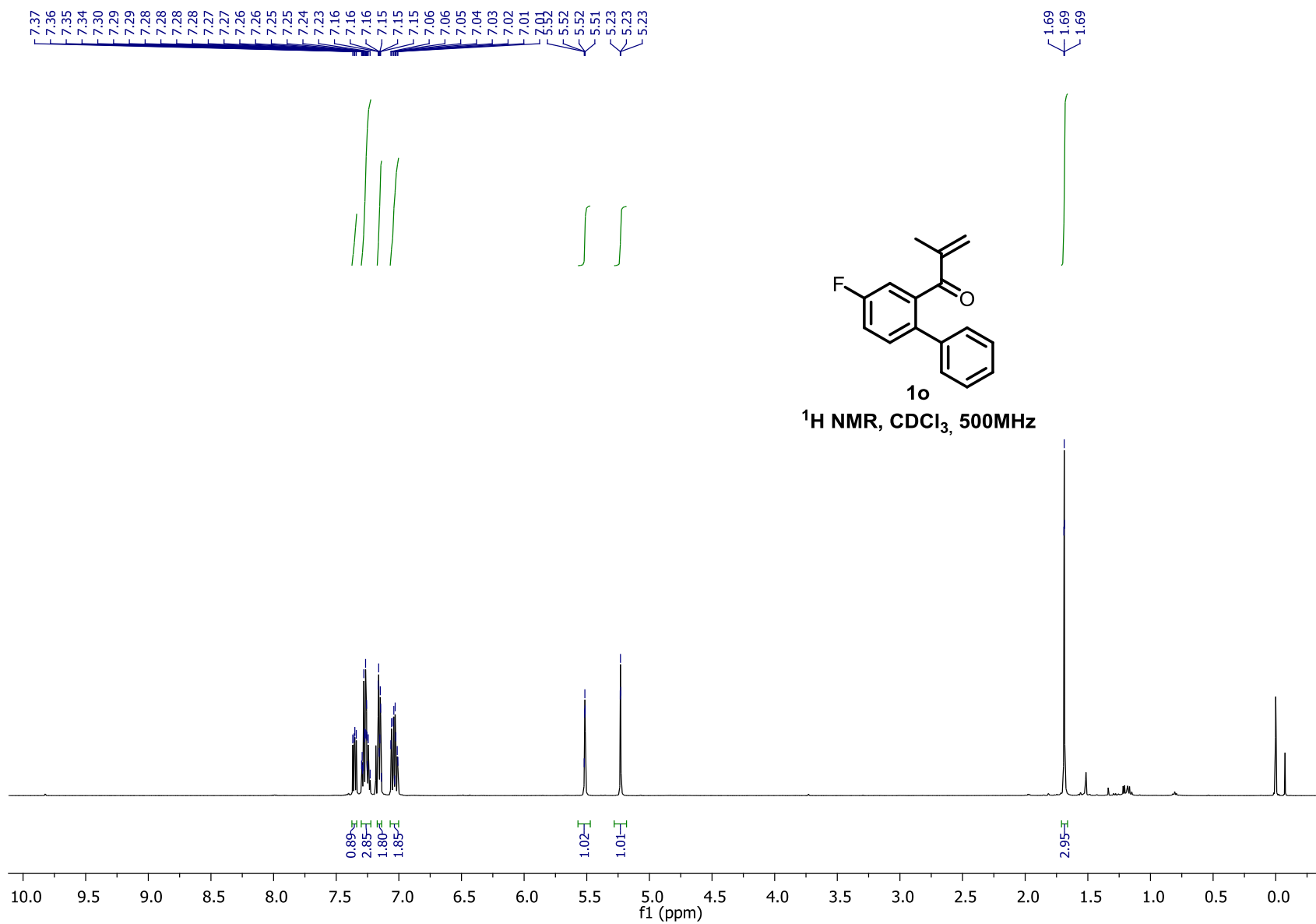


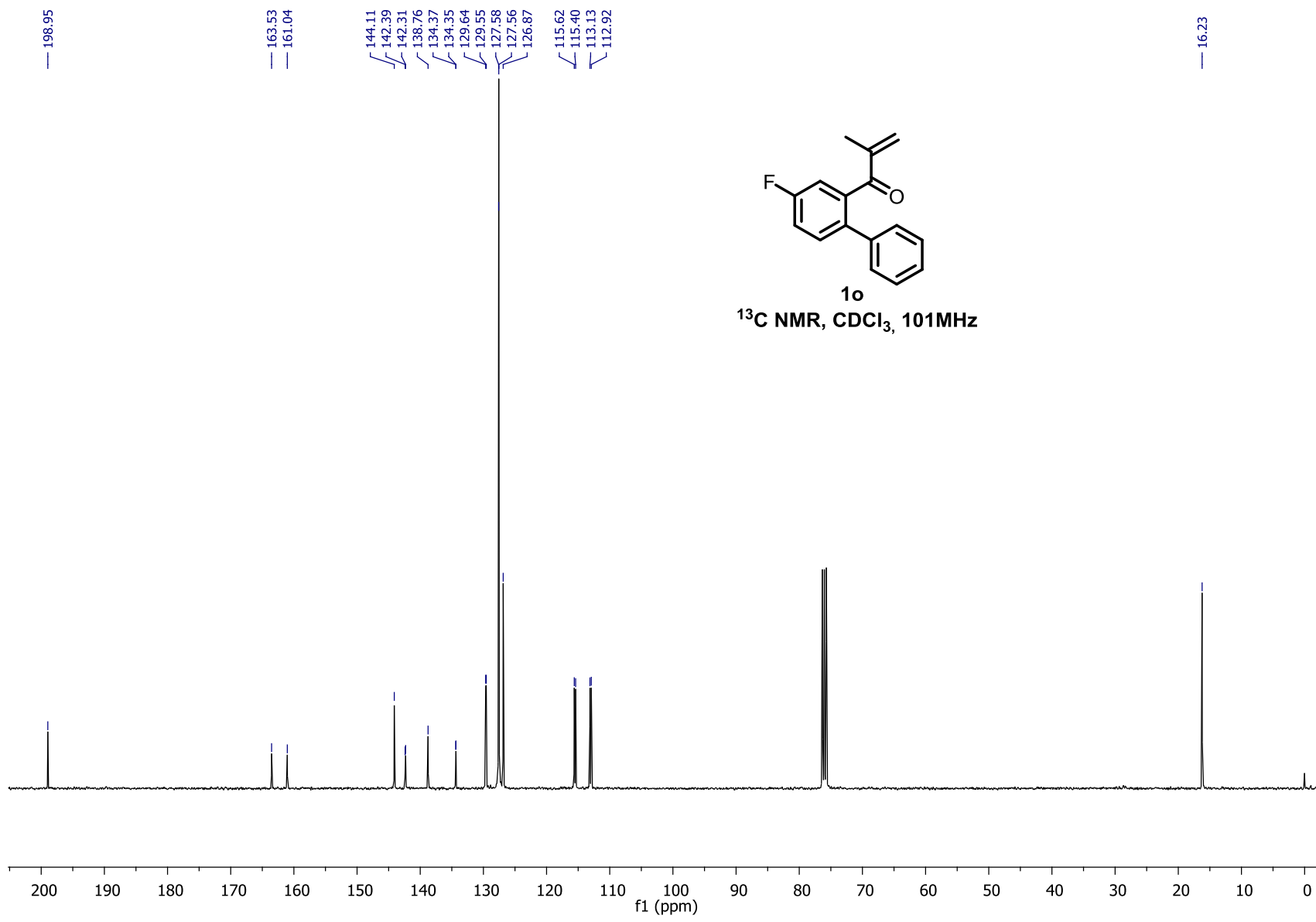


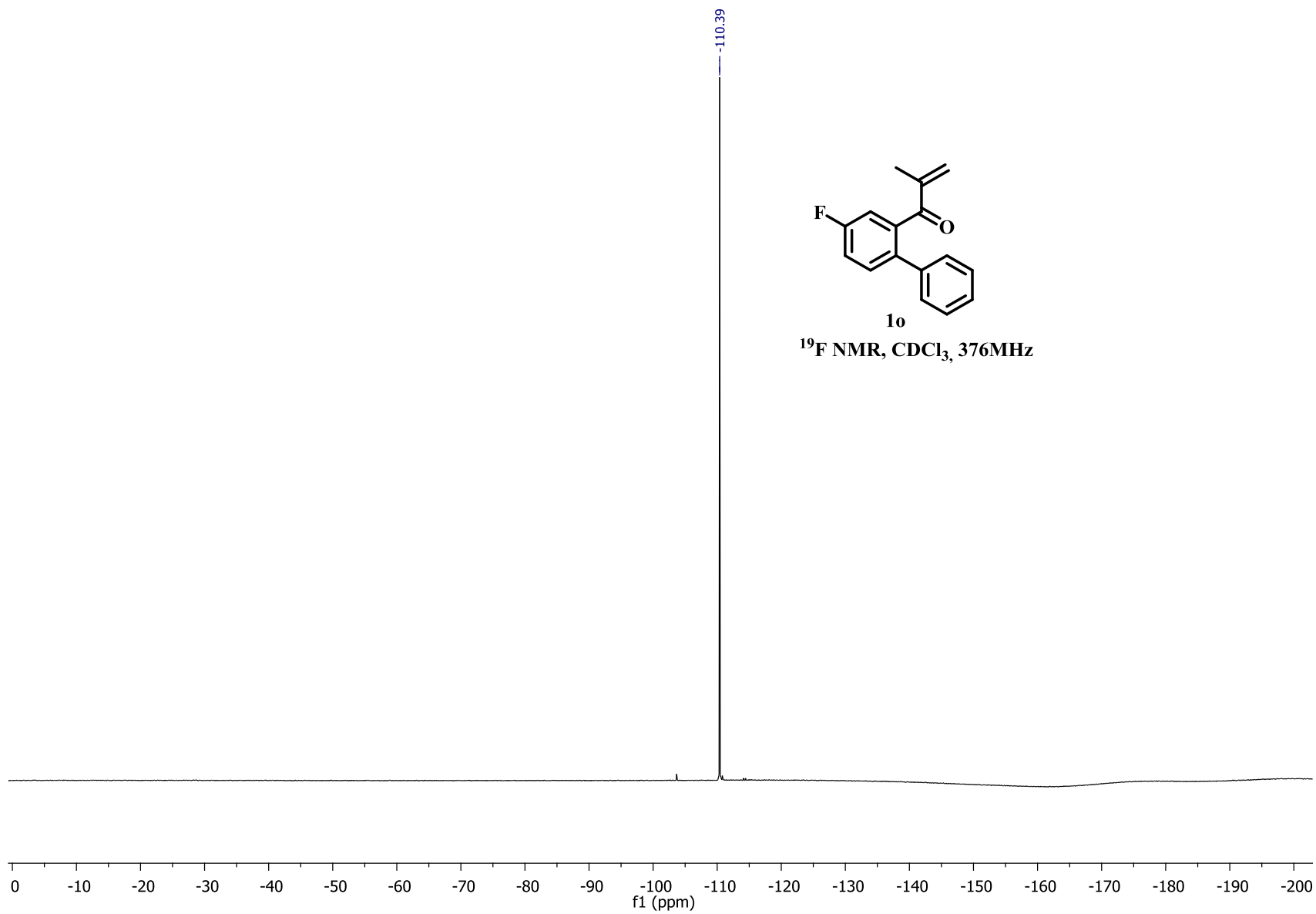


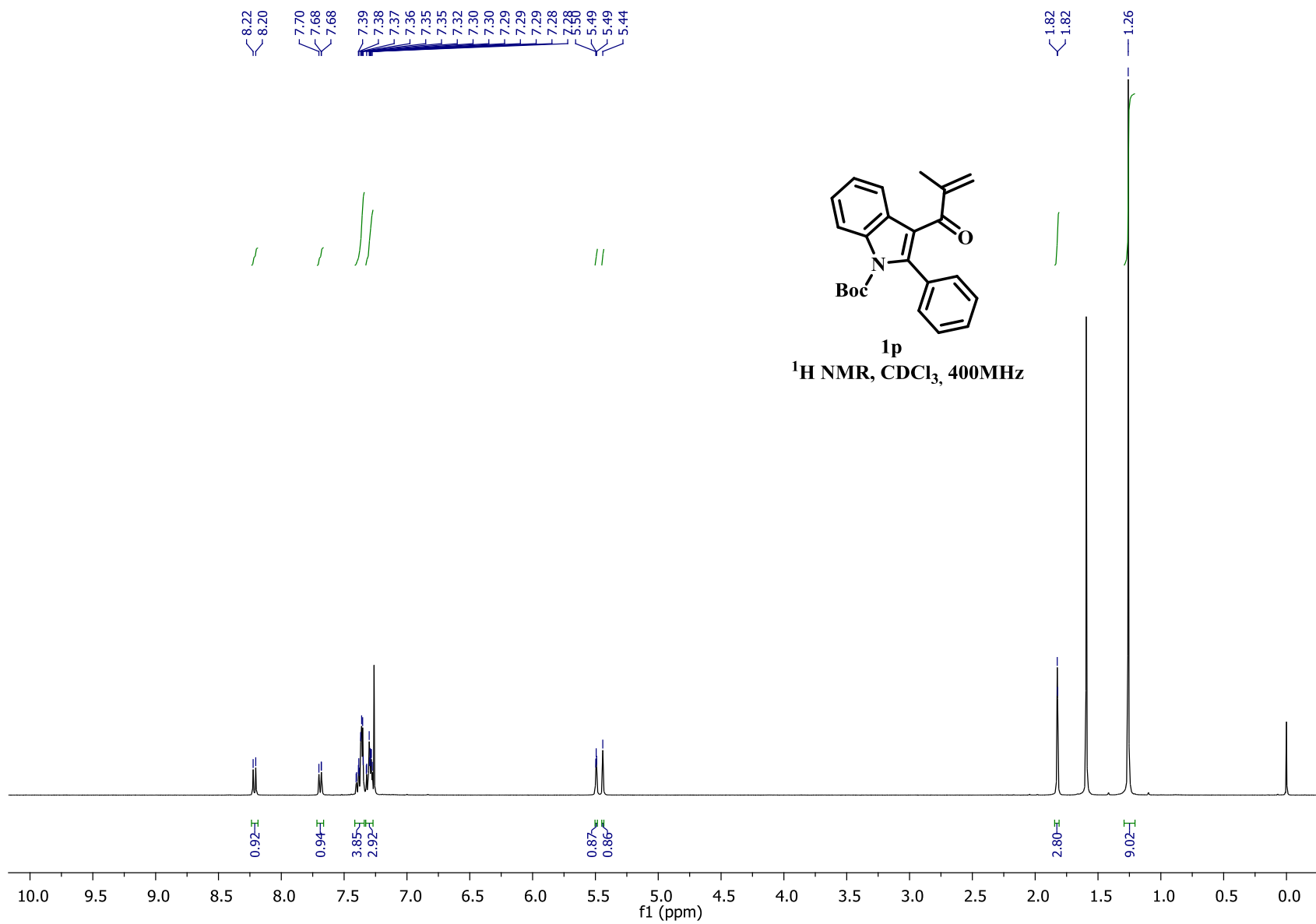




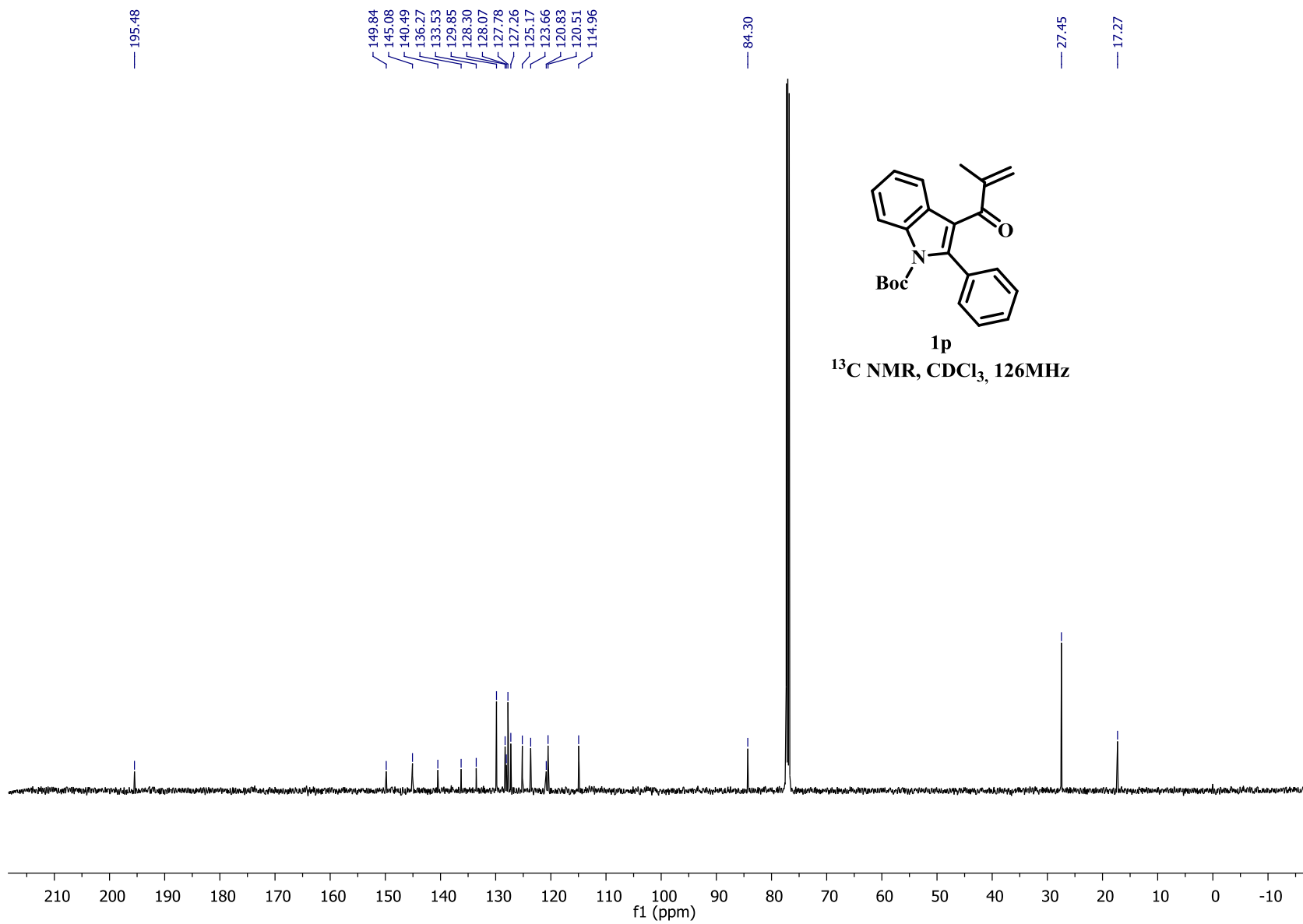


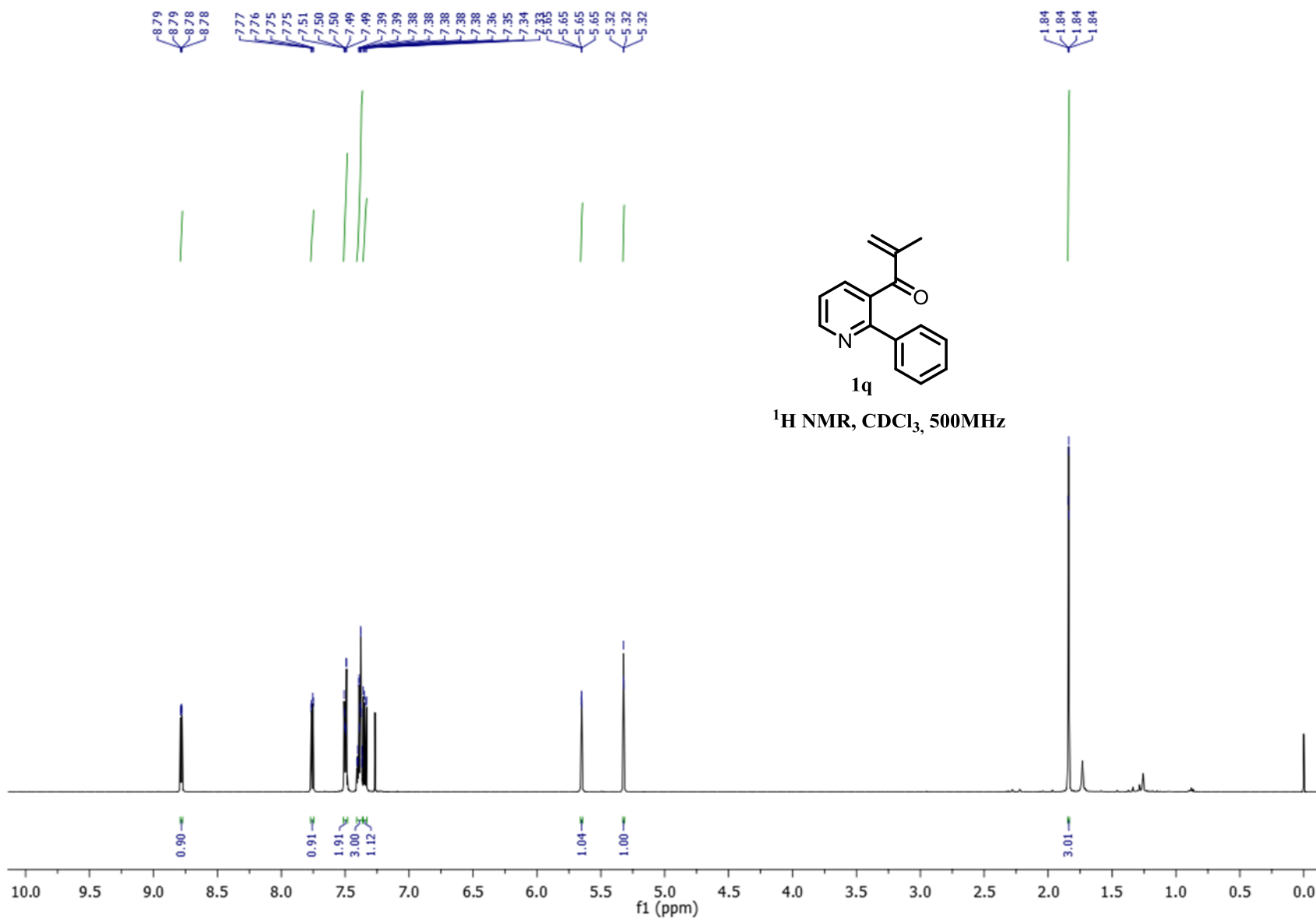


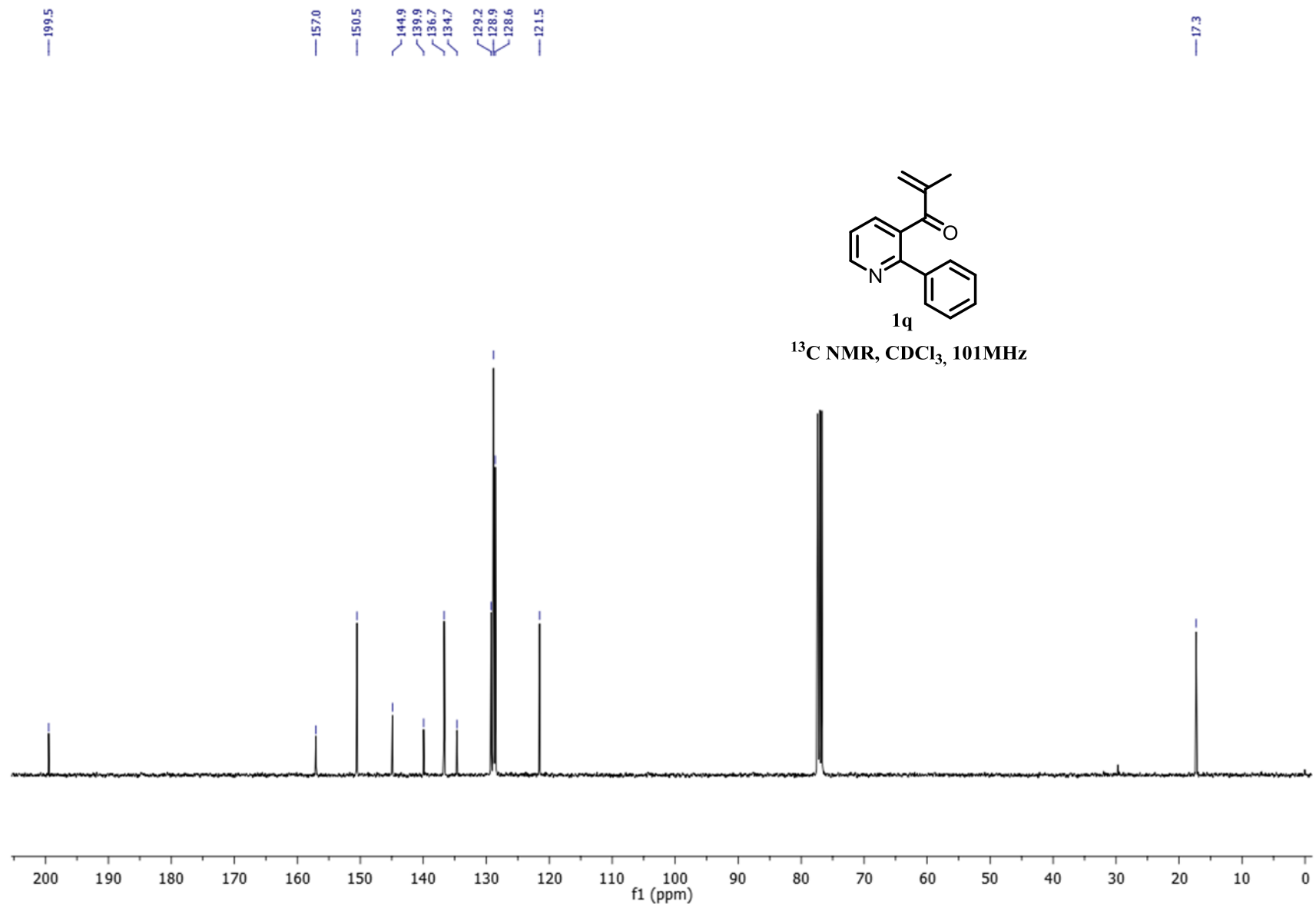


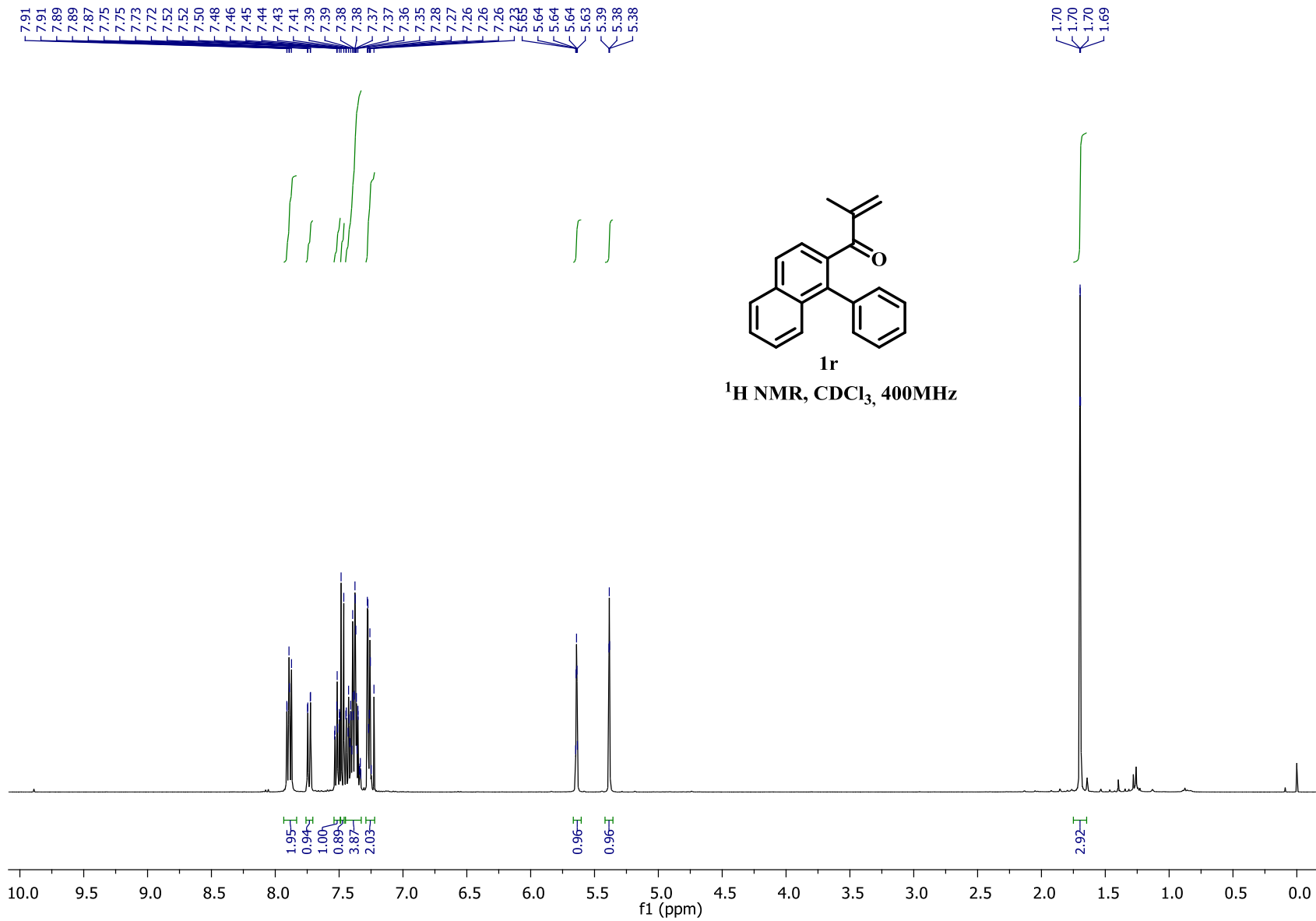


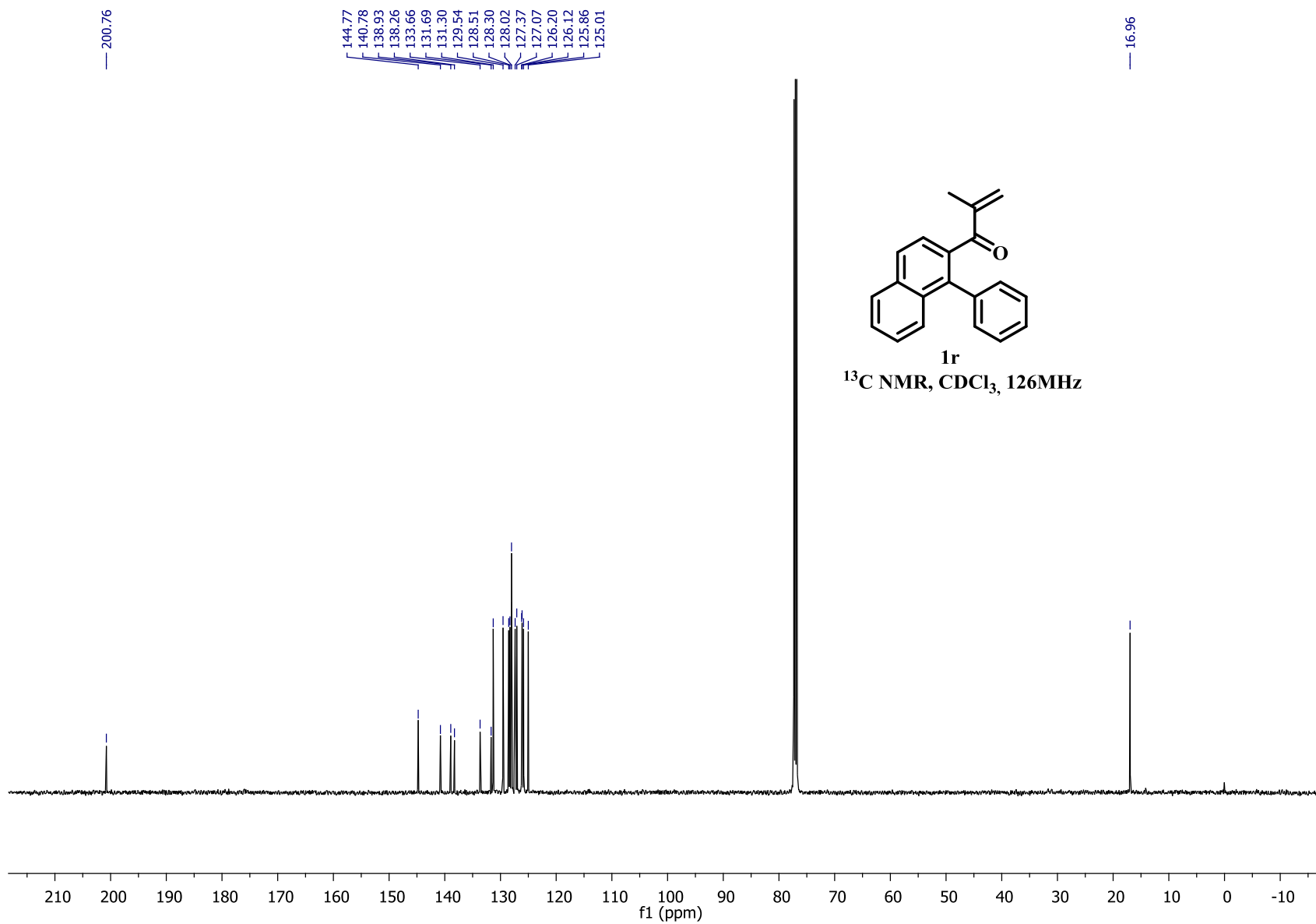


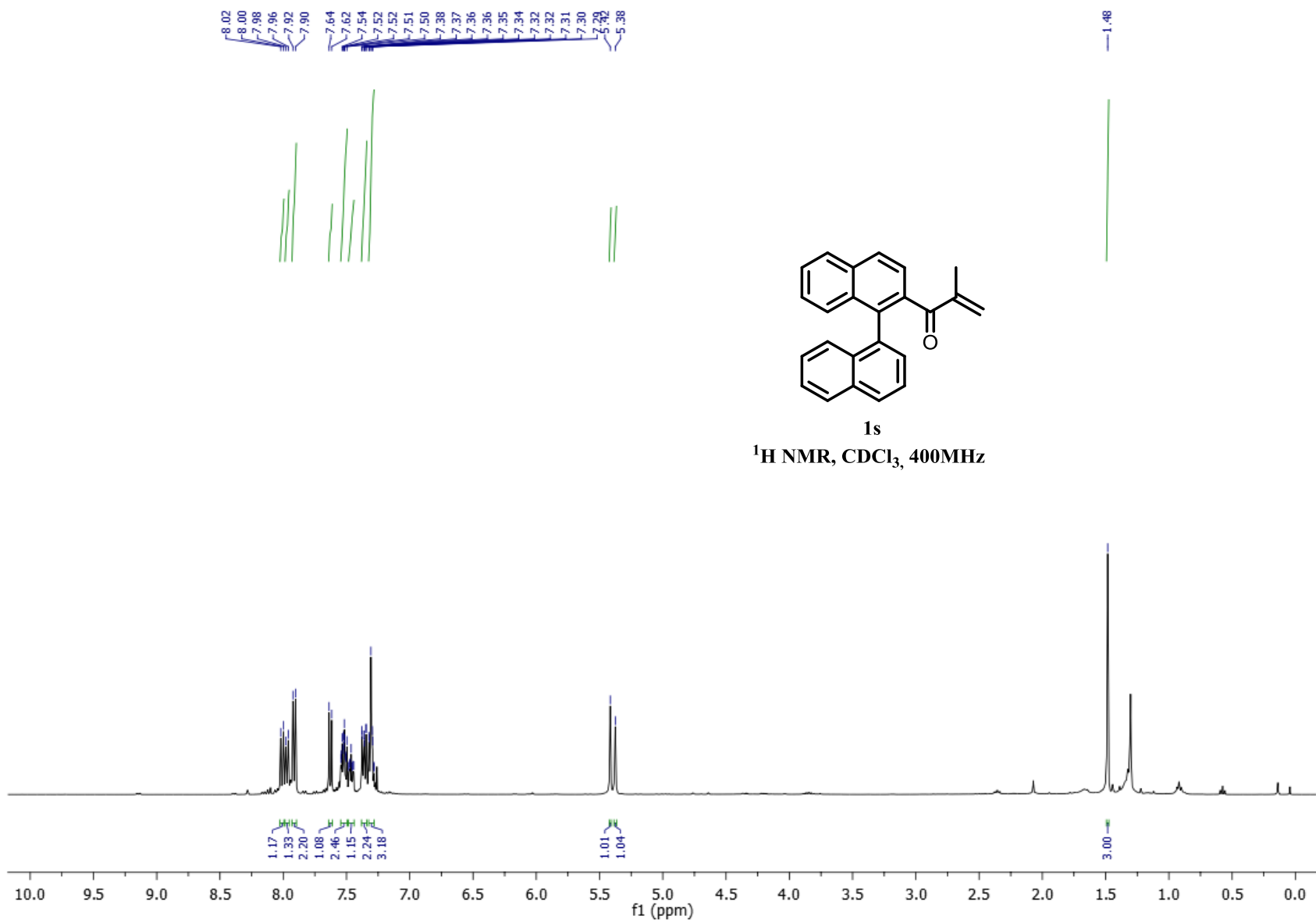








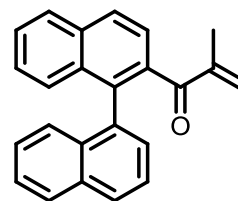




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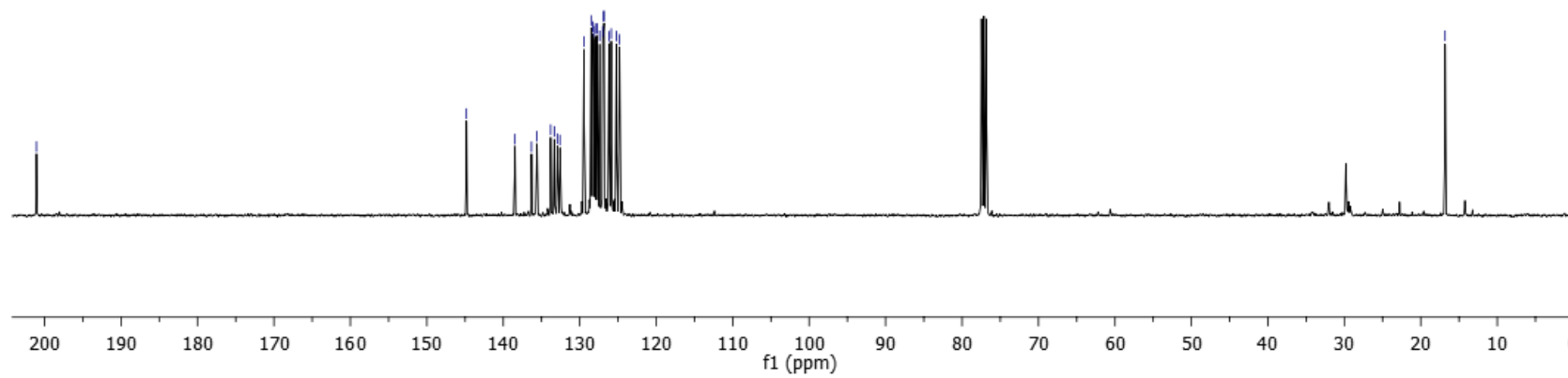
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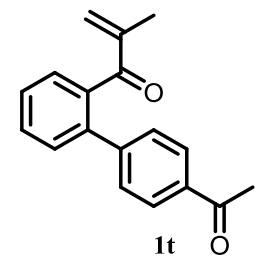
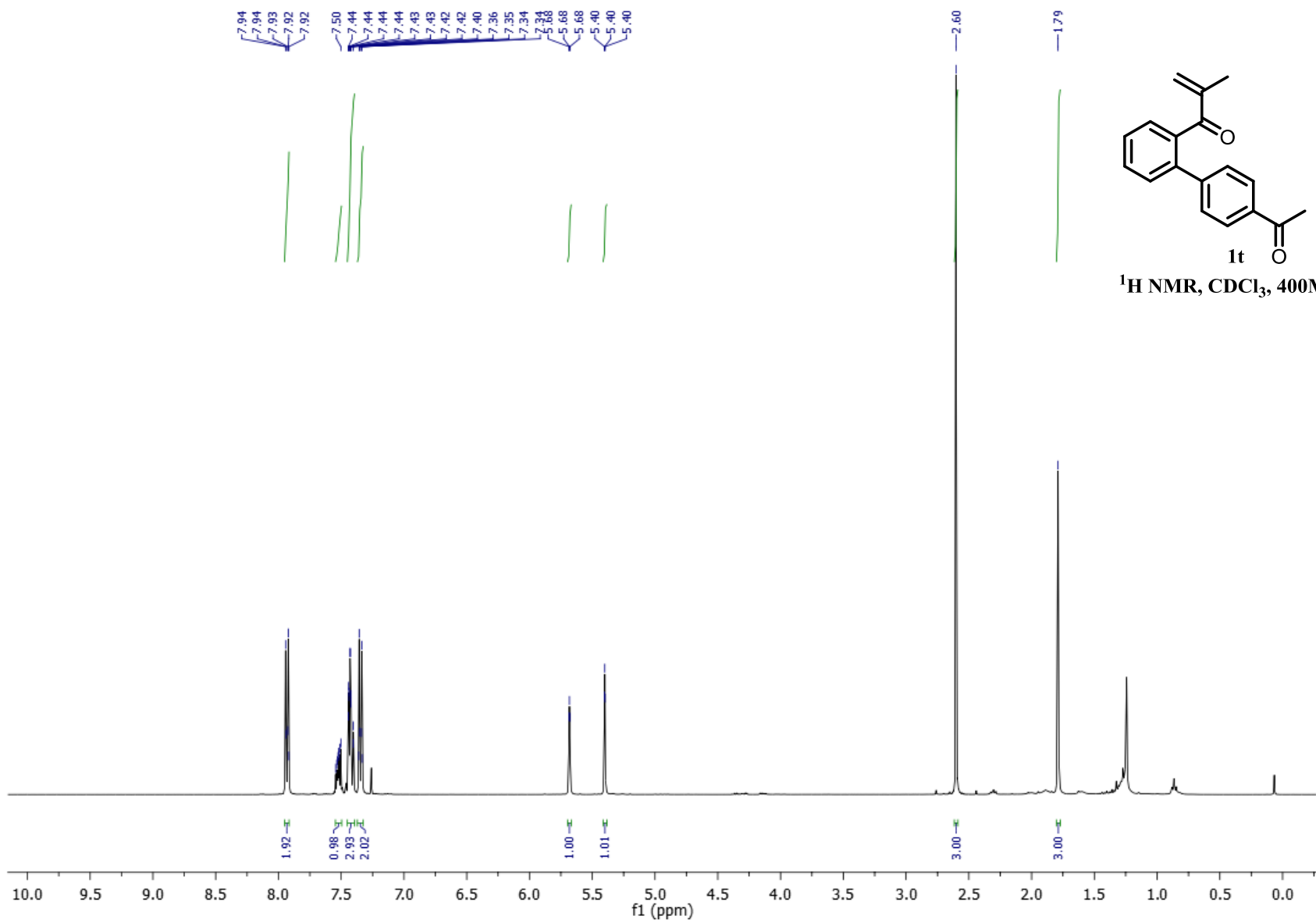
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1s

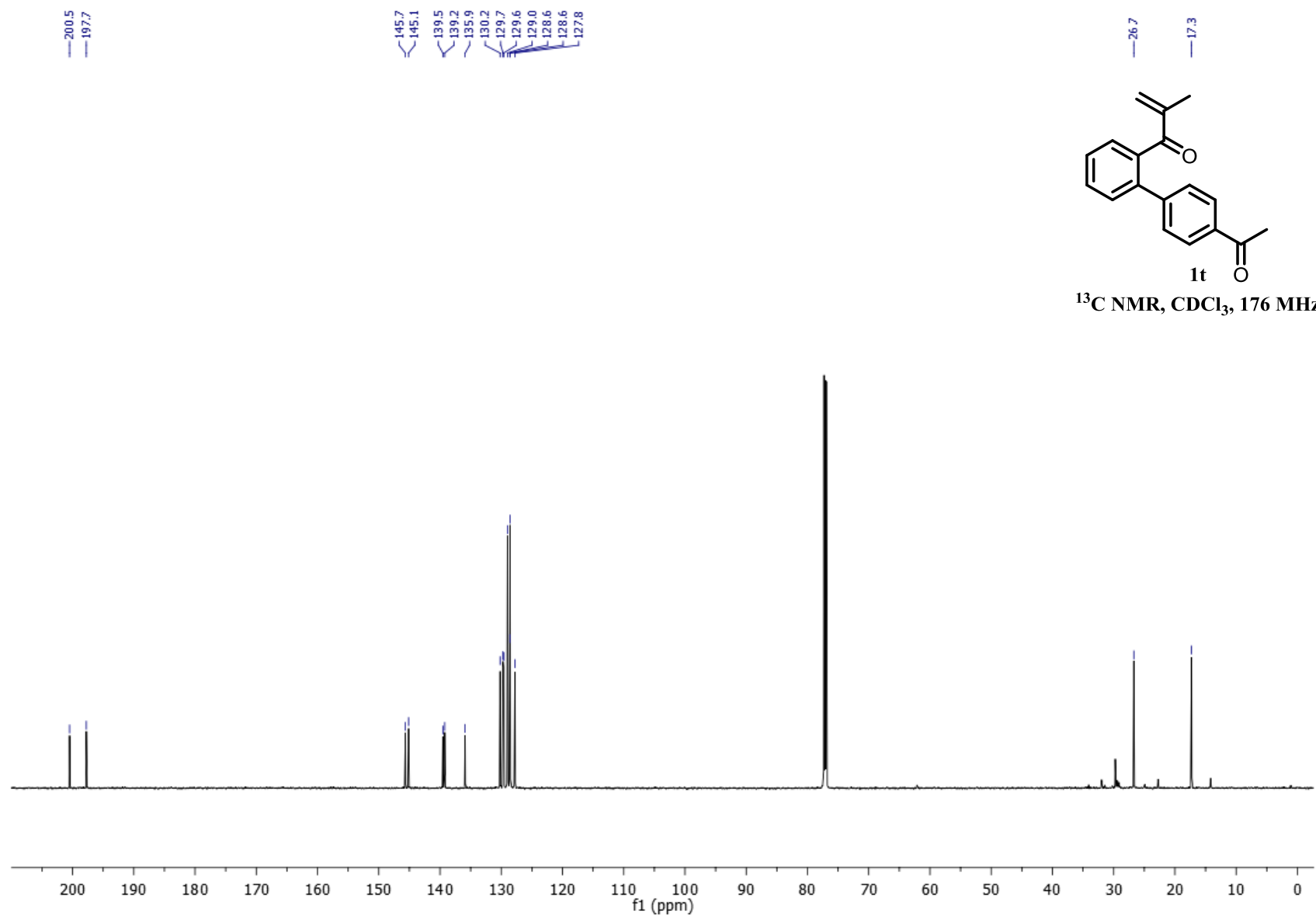
<sup>13</sup>C NMR, CDCl<sub>3</sub>, 101MHz

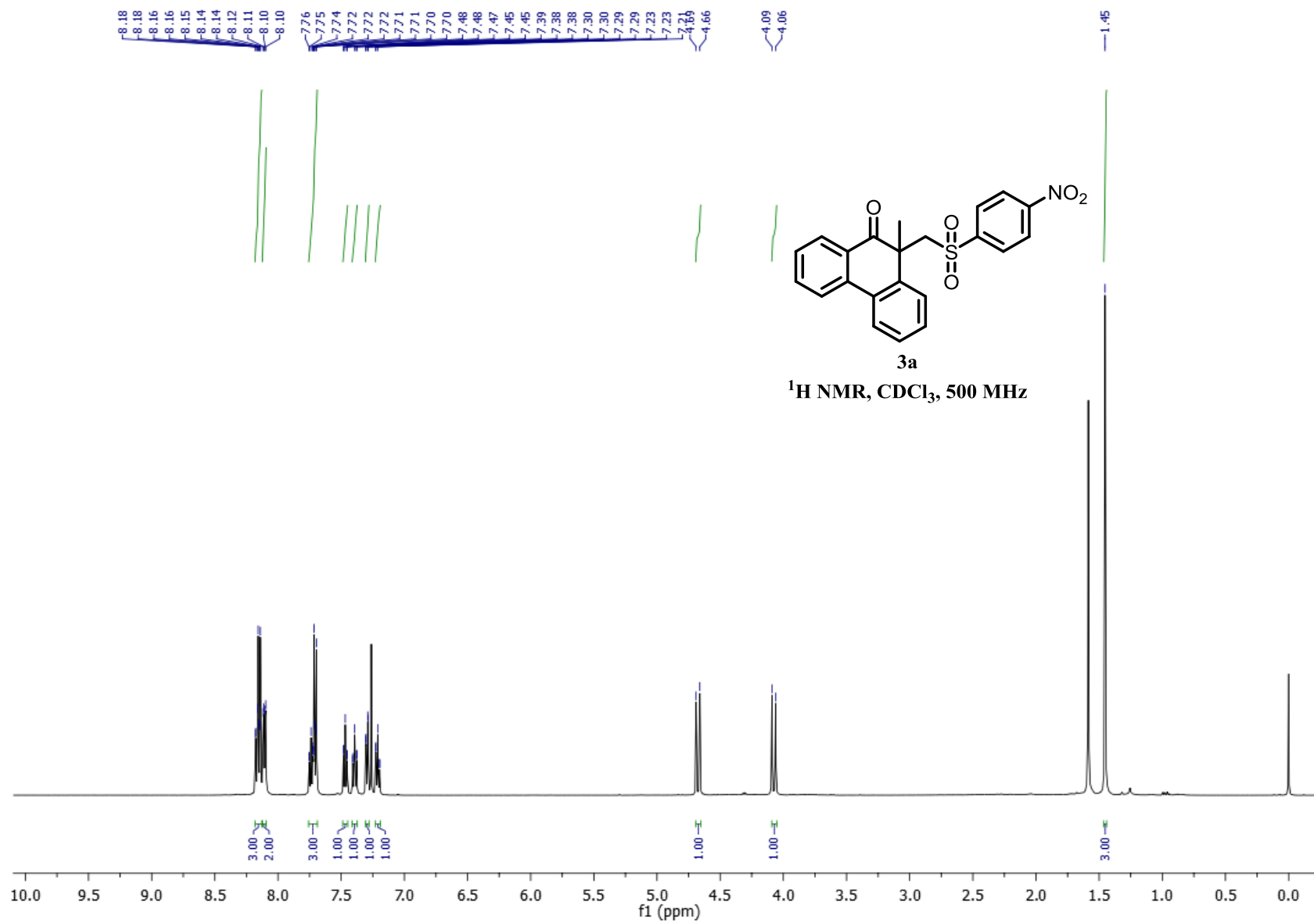


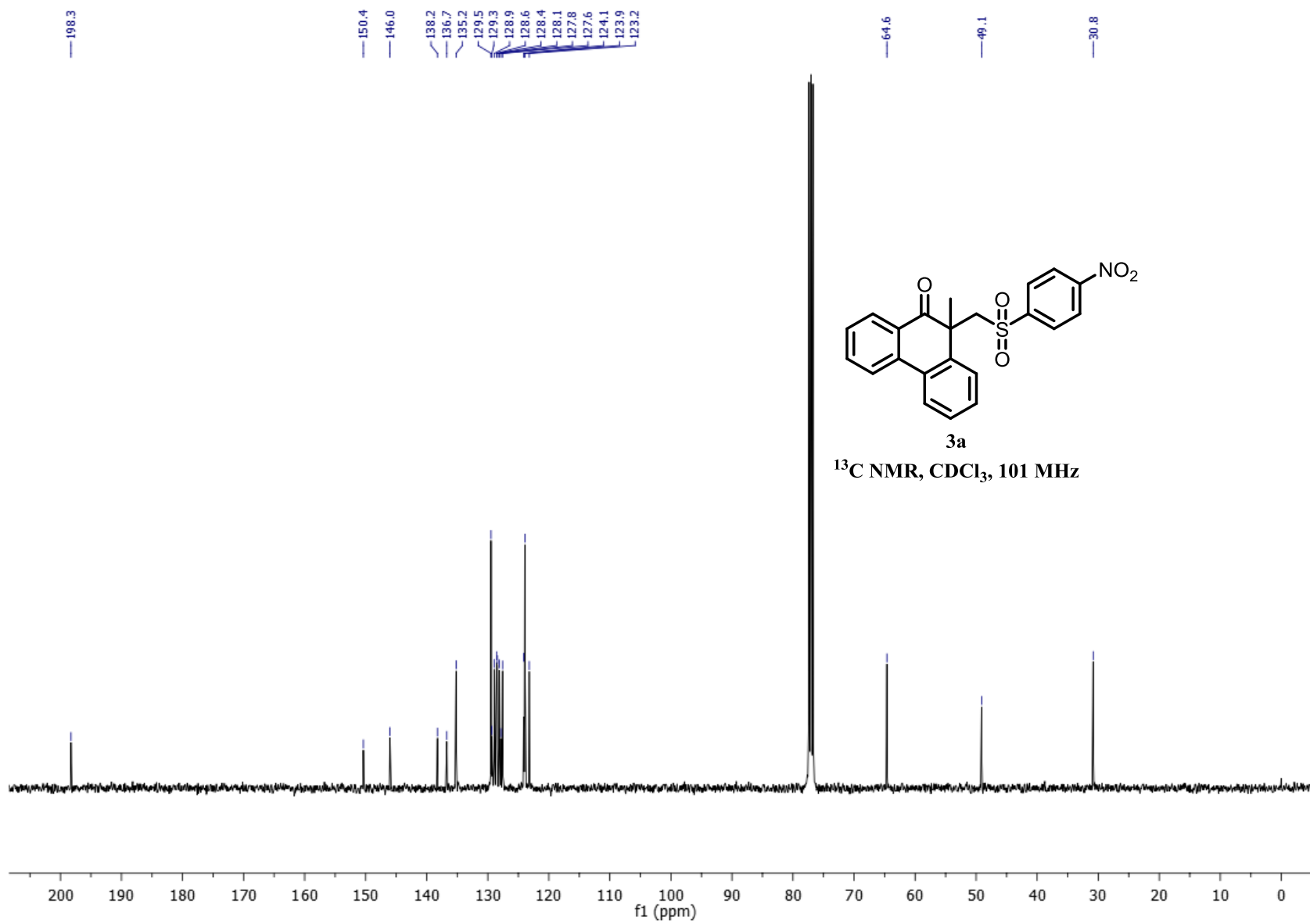


$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400MHz

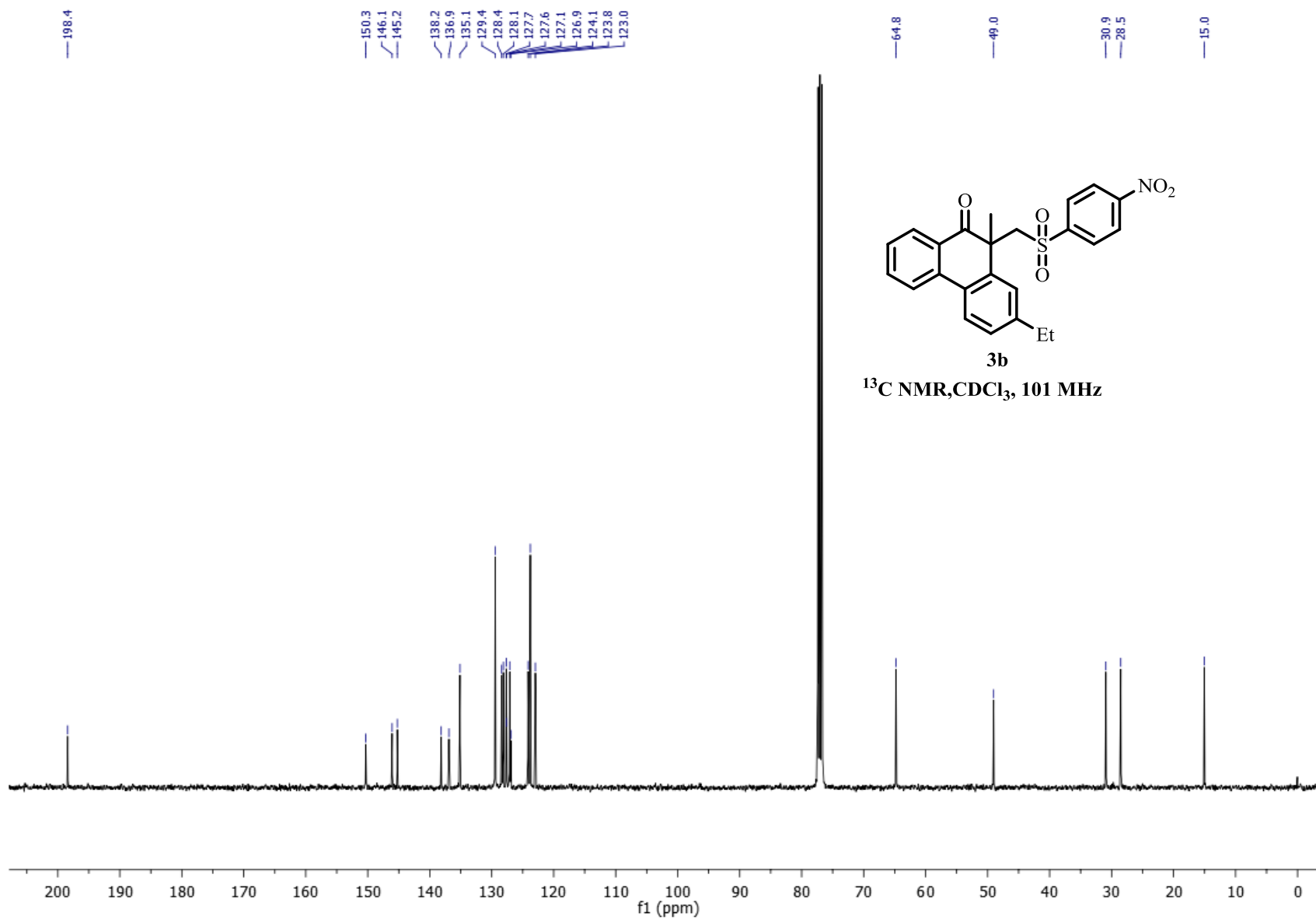


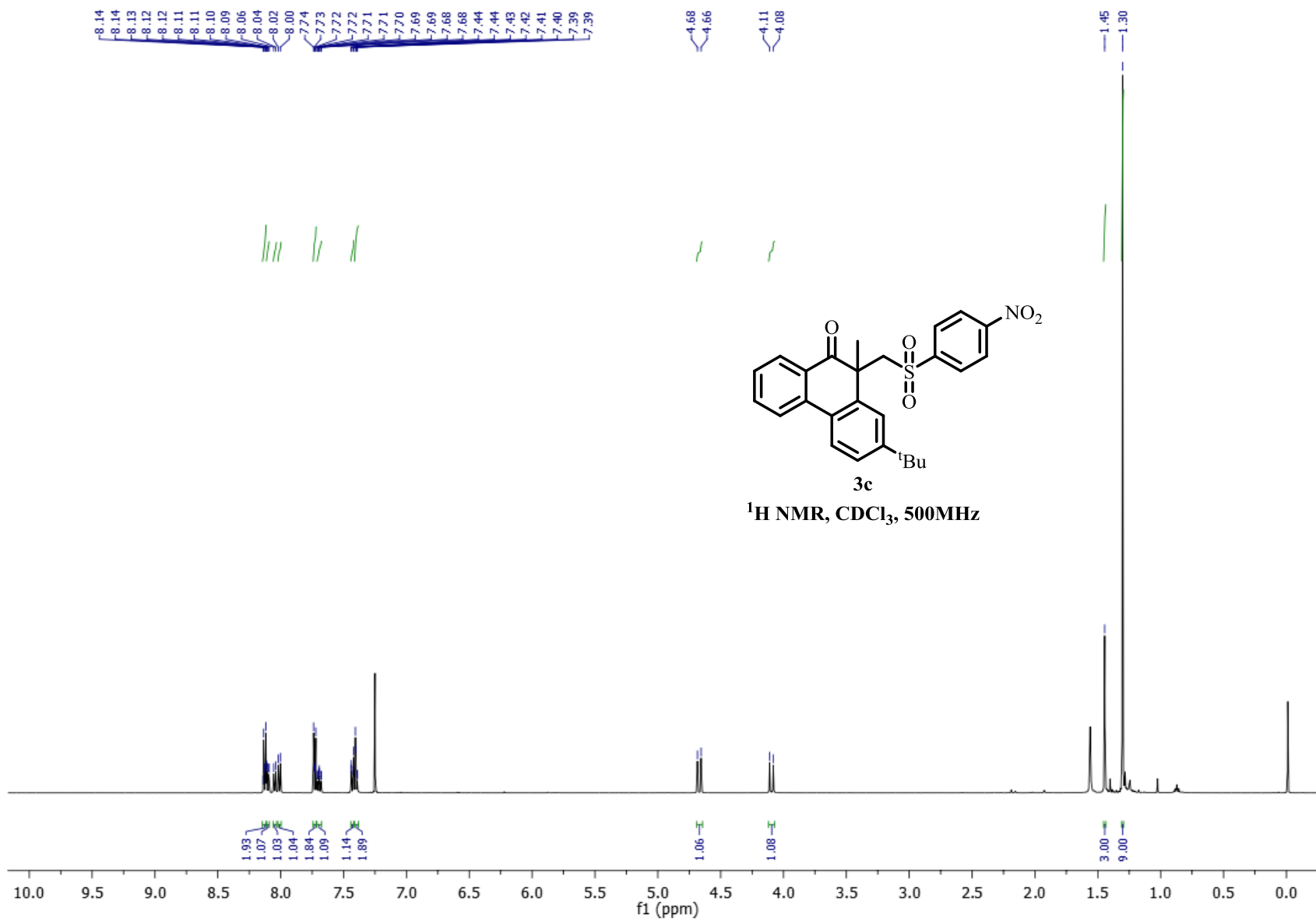


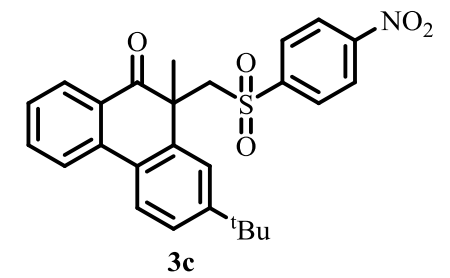
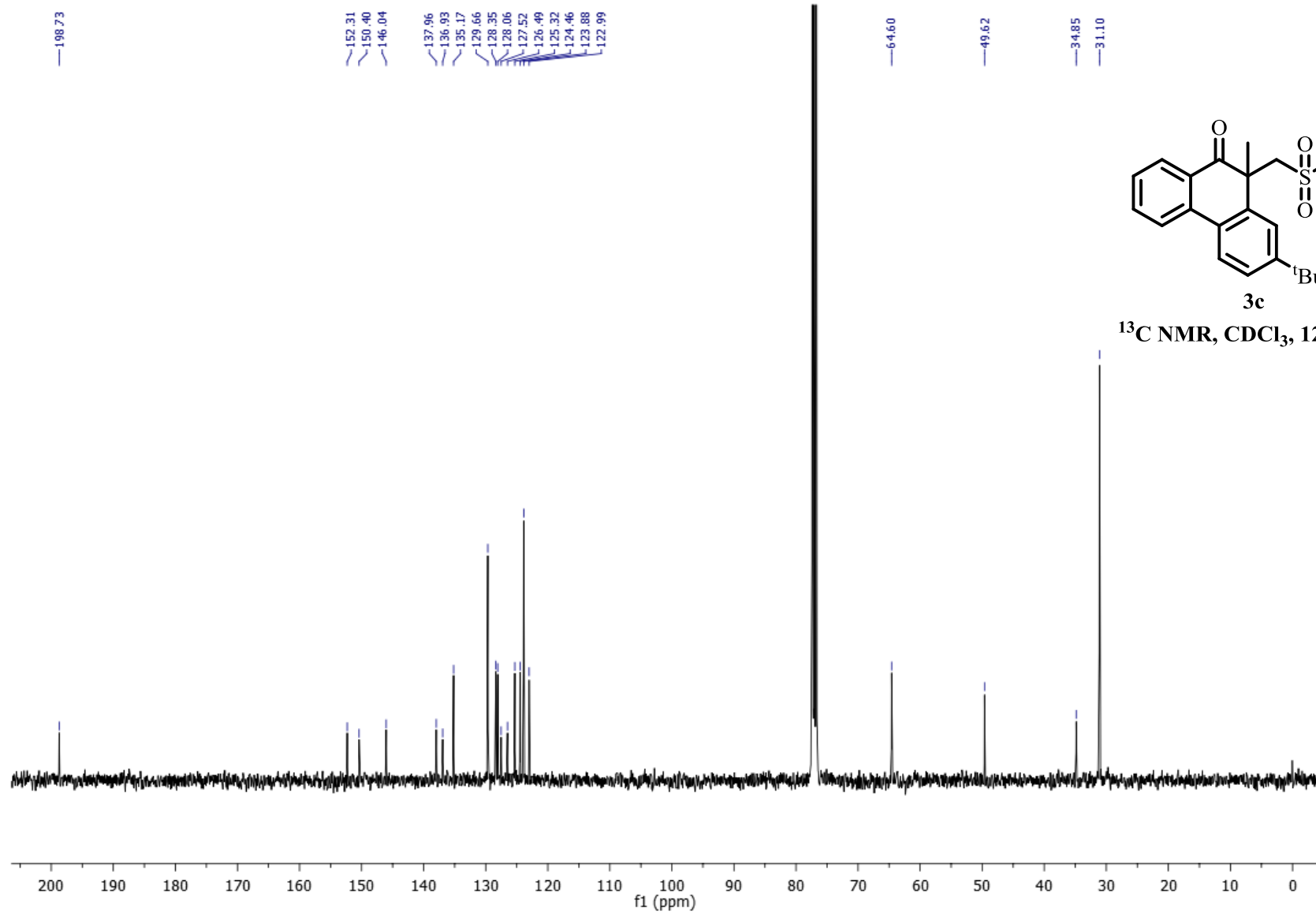




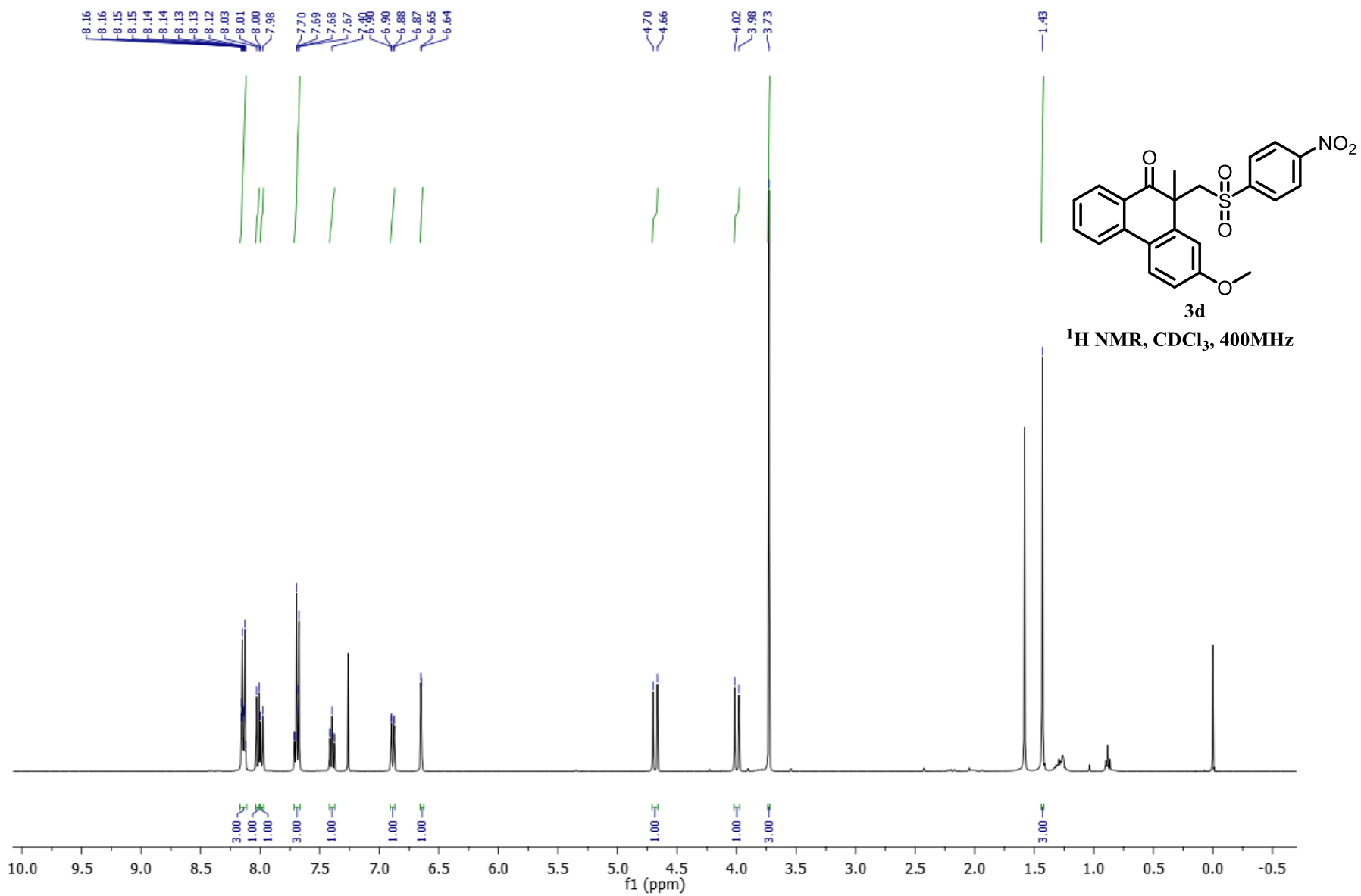




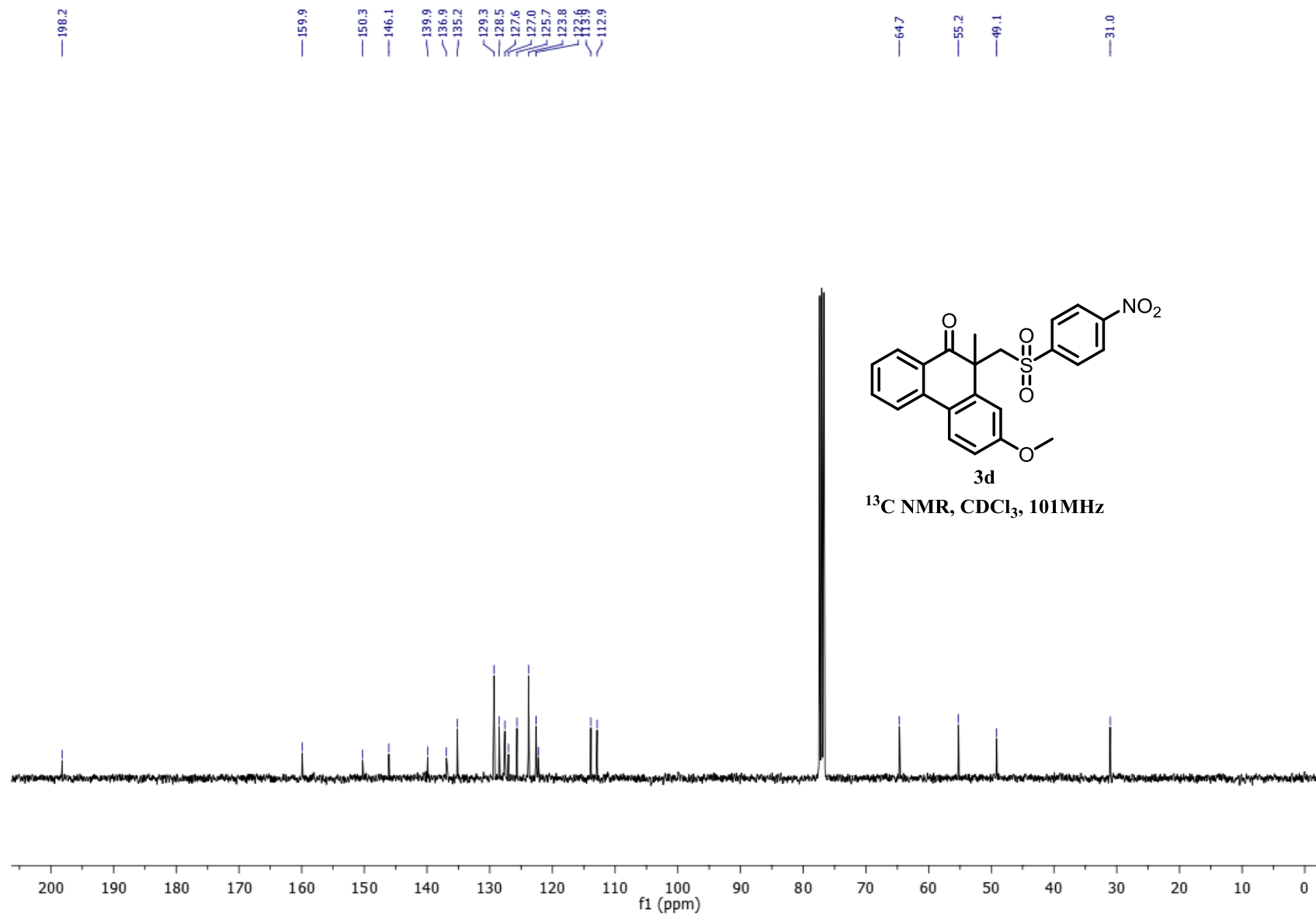


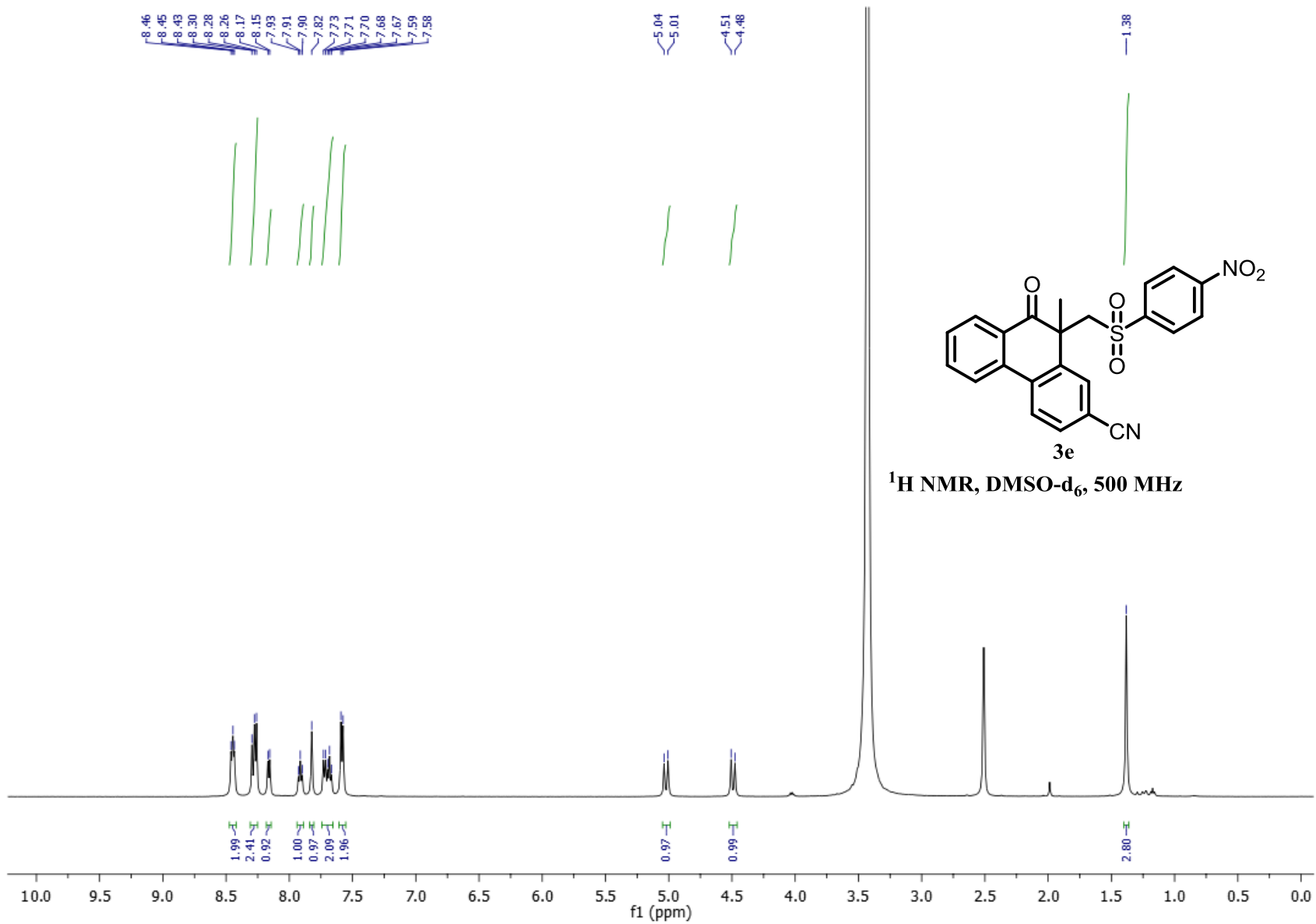


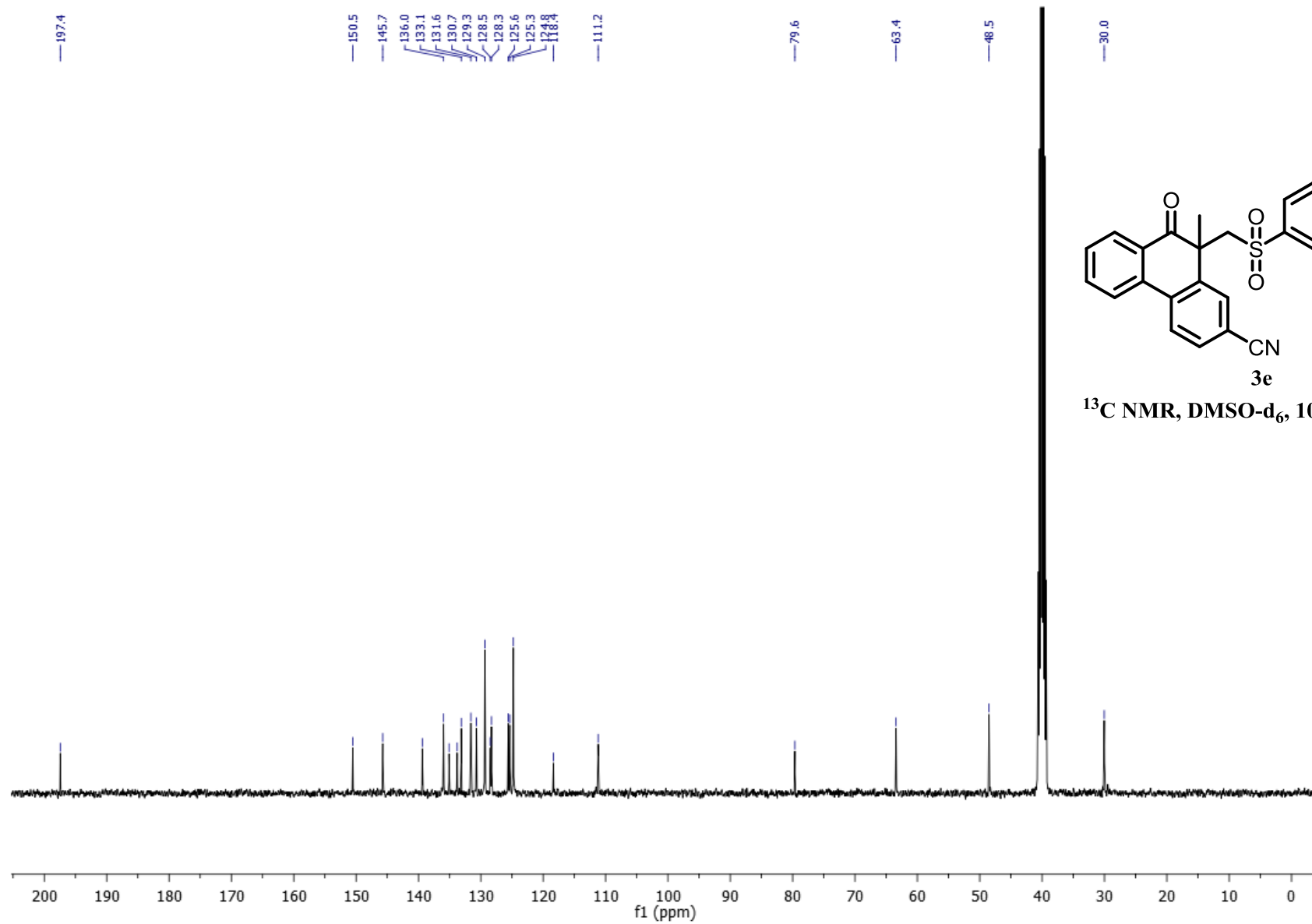
<sup>13</sup>C NMR, CDCl<sub>3</sub>, 126 MHz

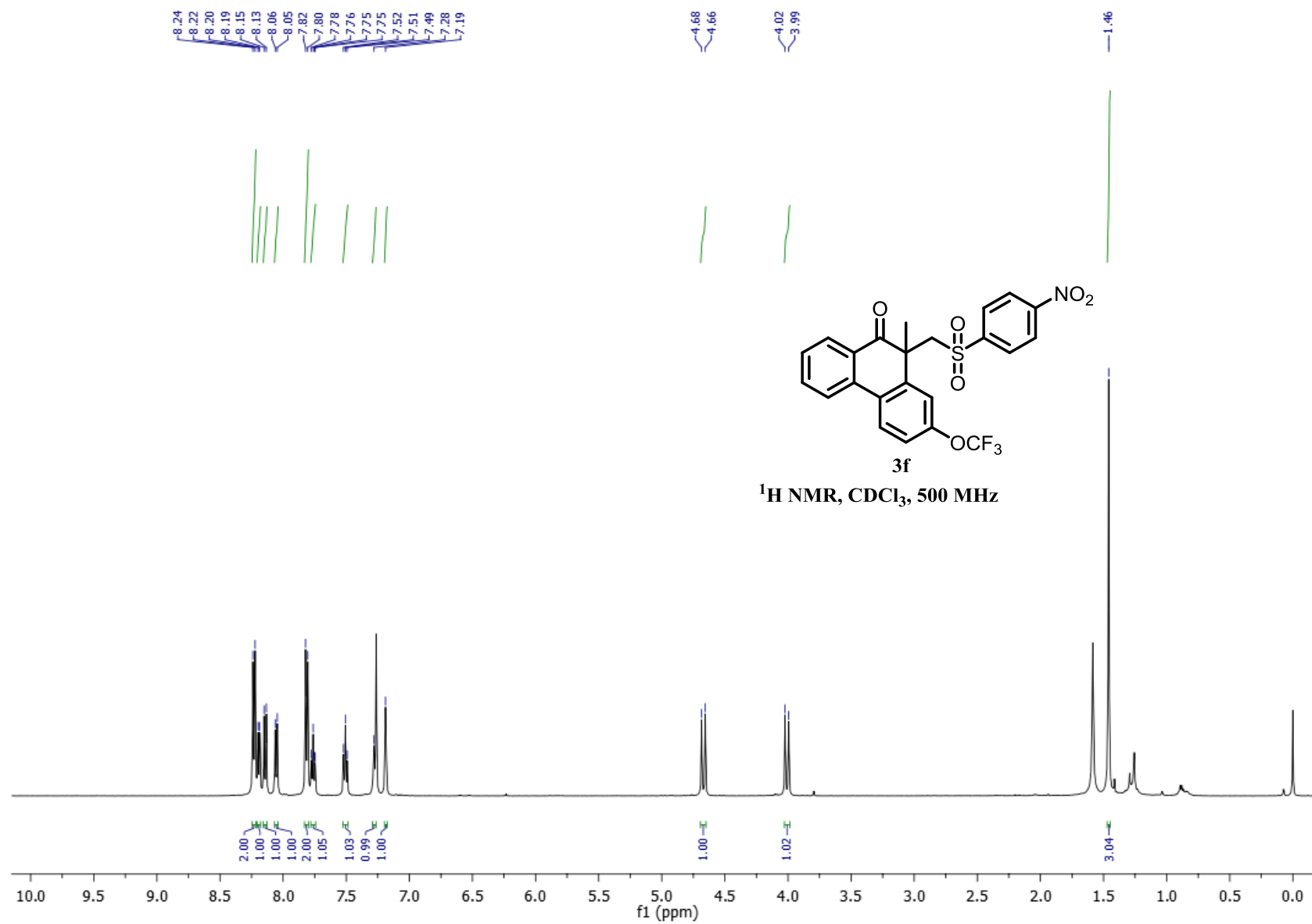


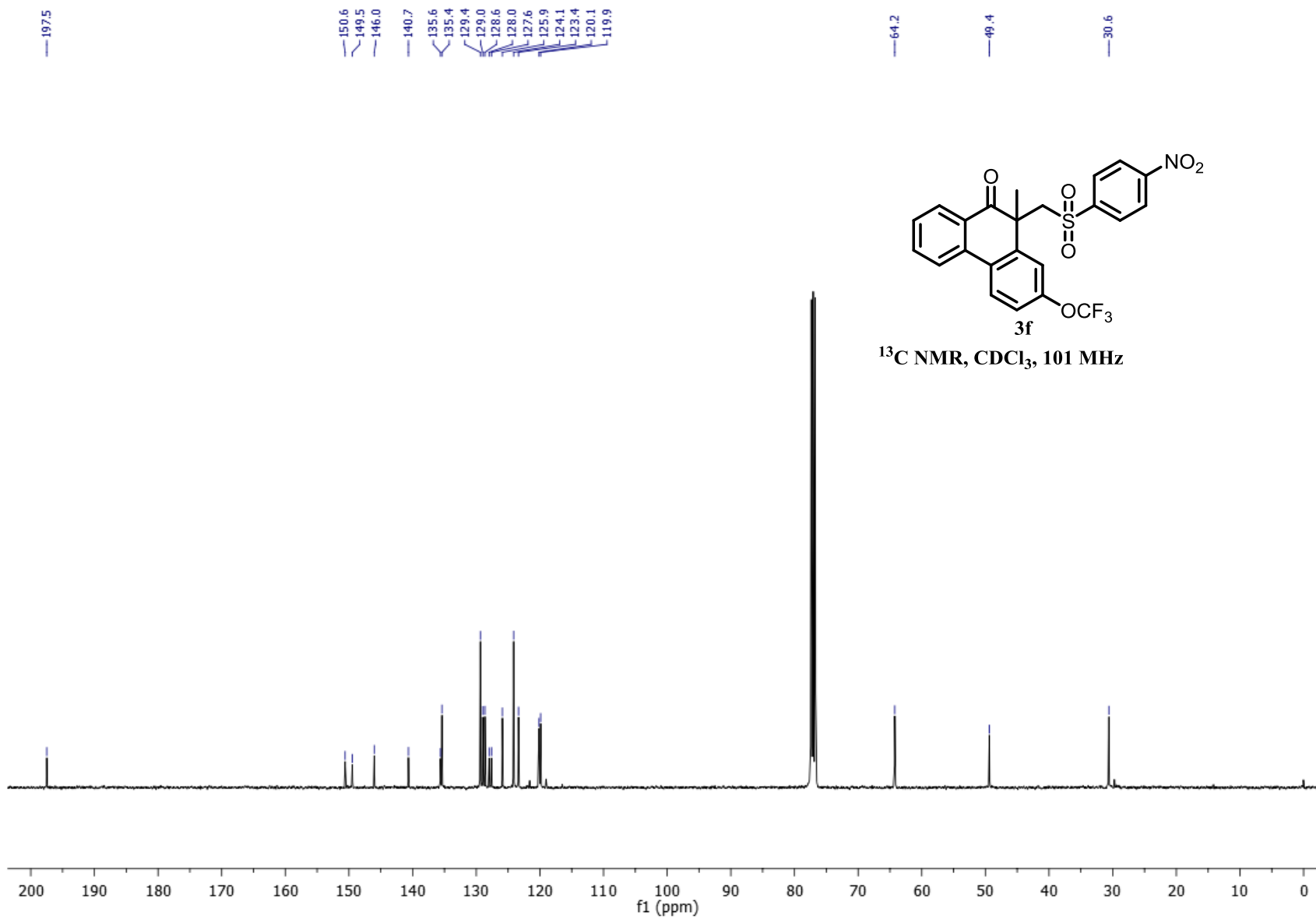


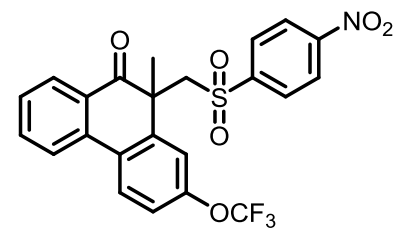






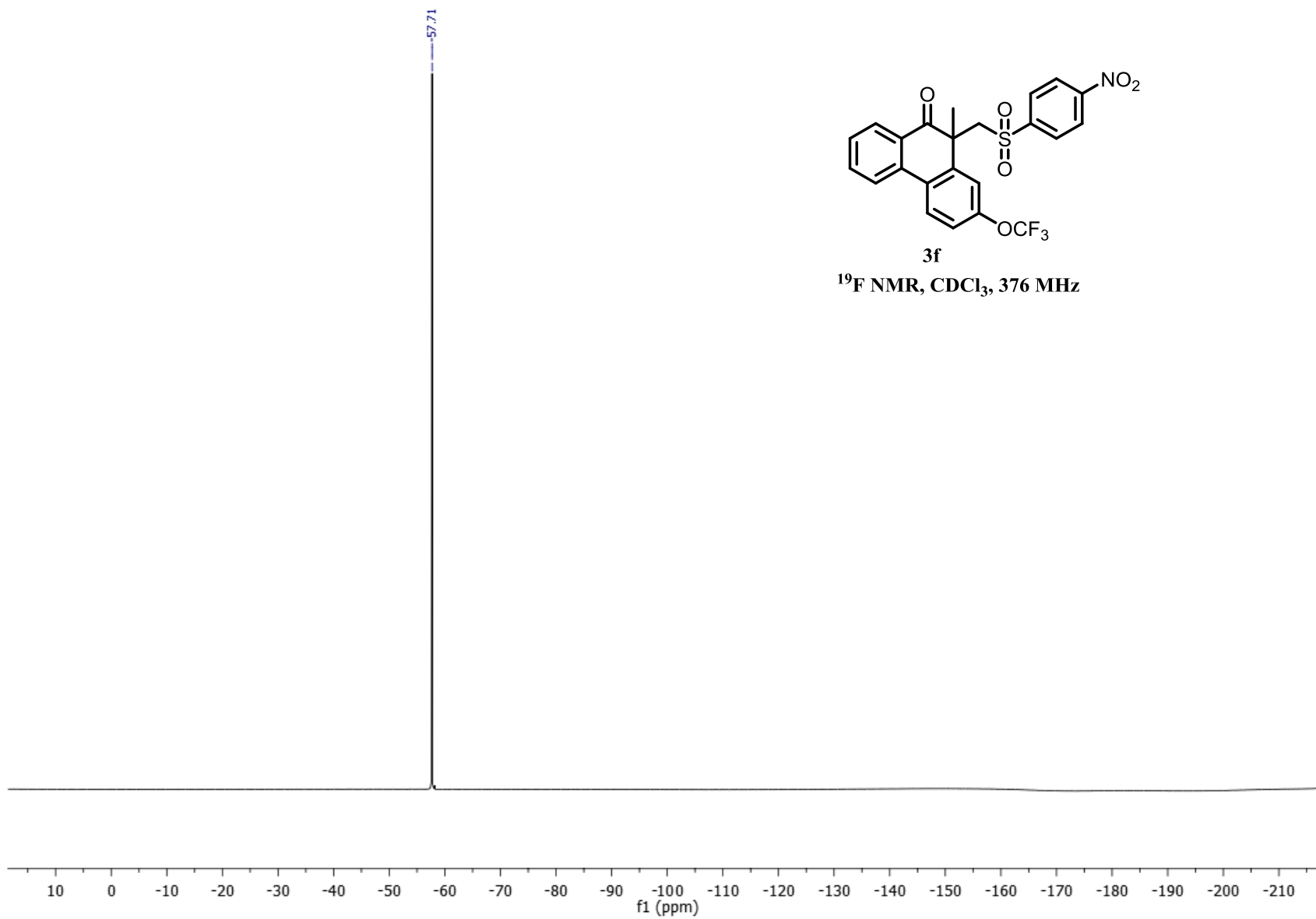


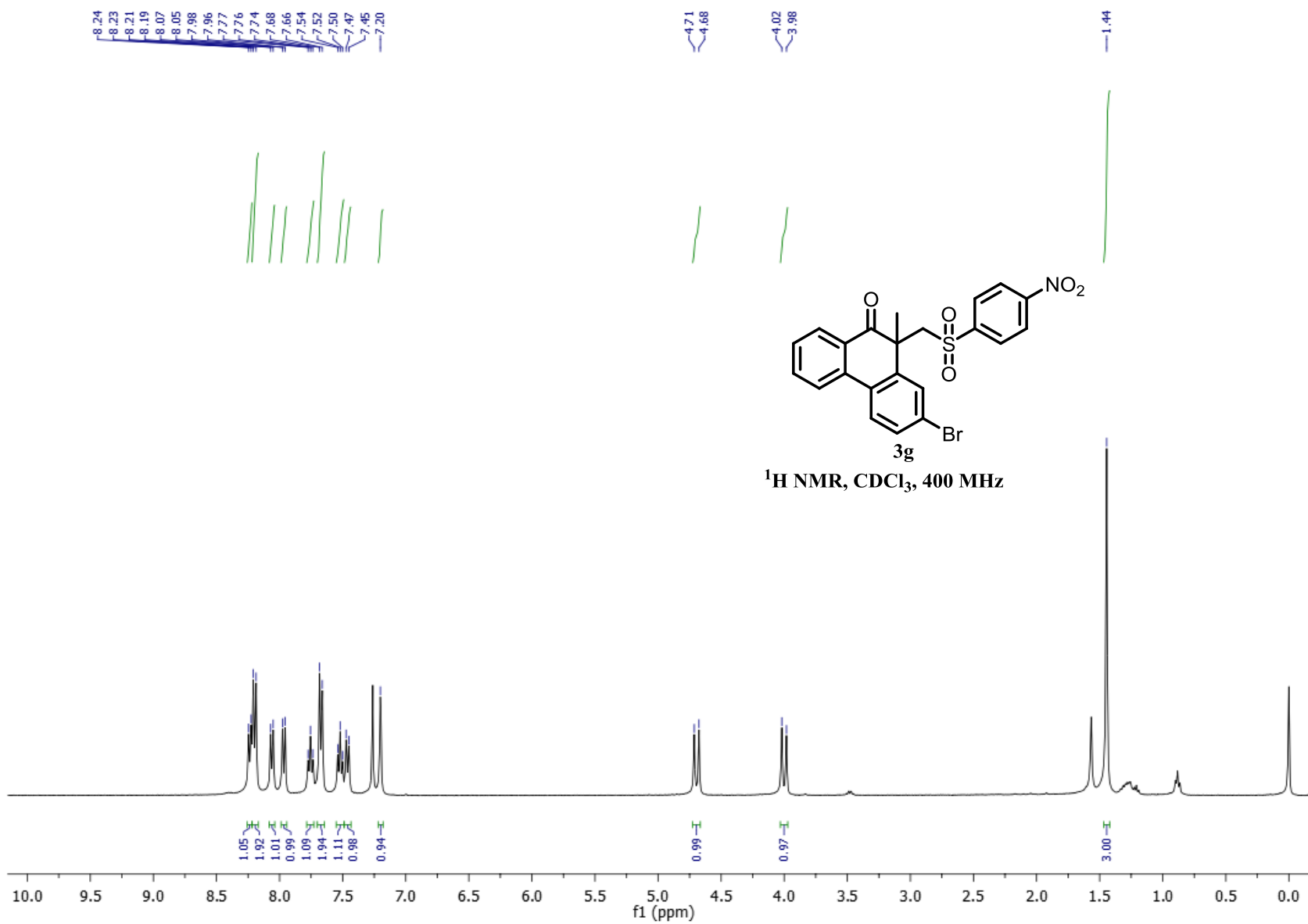


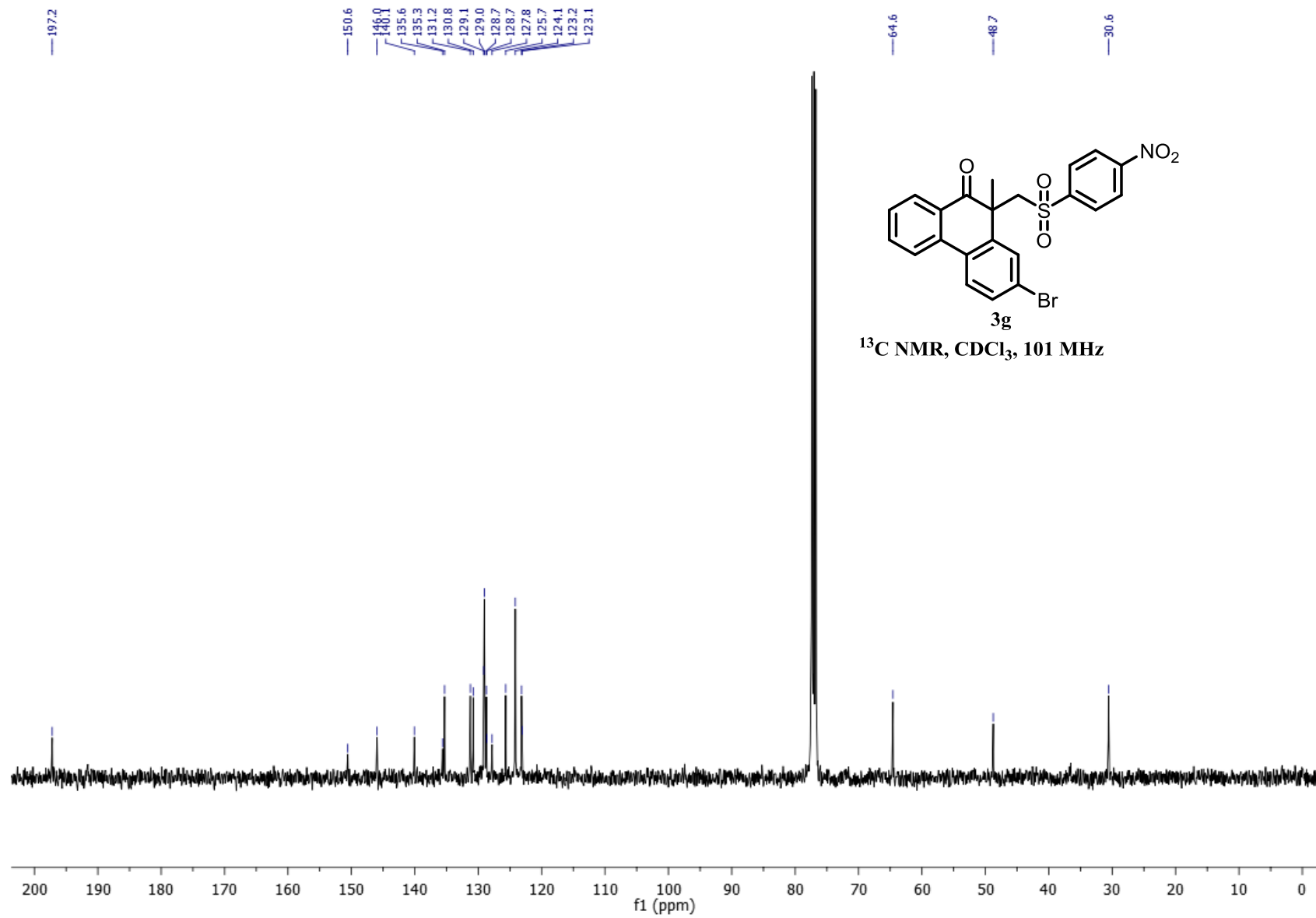


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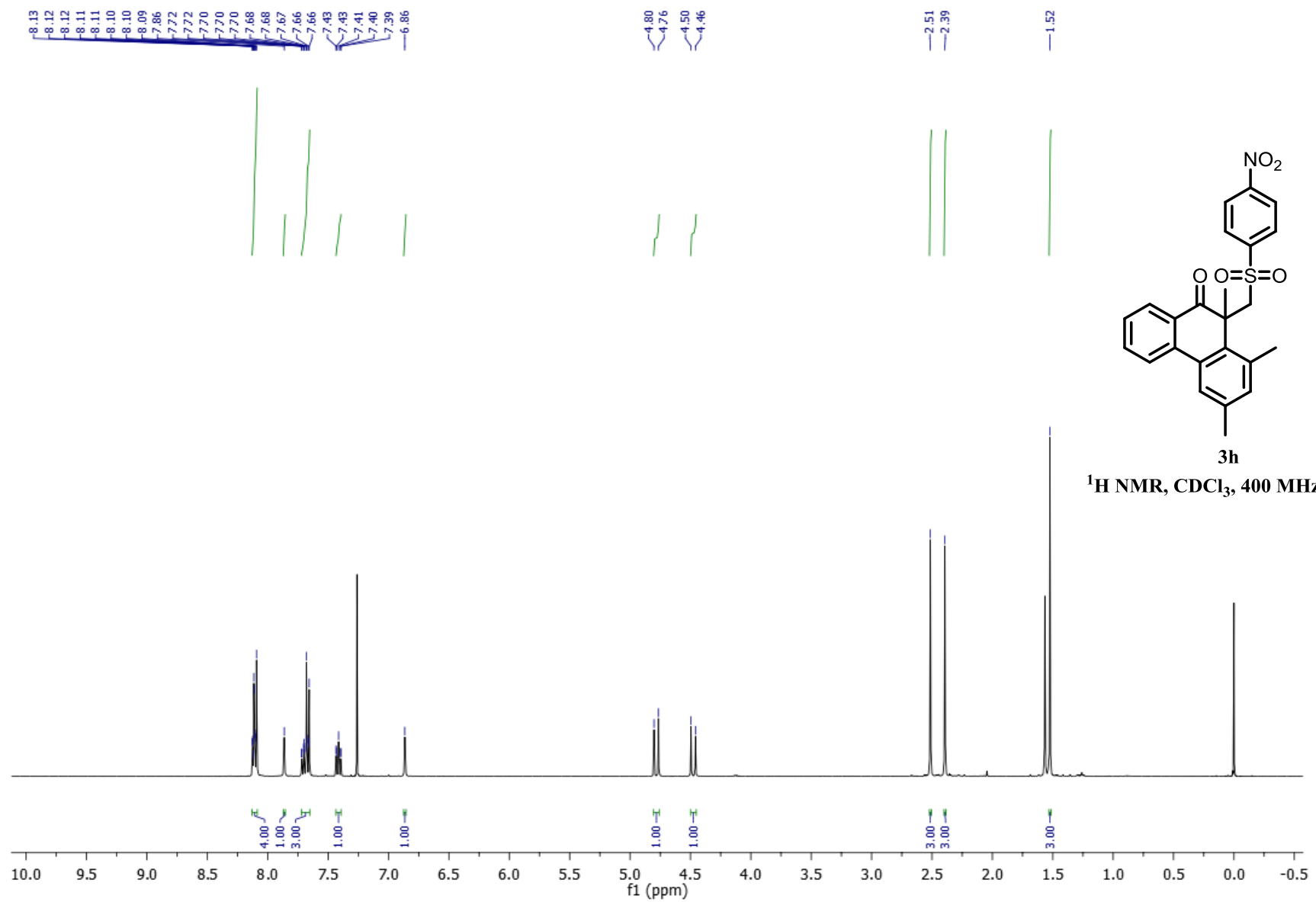
<sup>19</sup>F NMR, CDCl<sub>3</sub>, 376 MHz

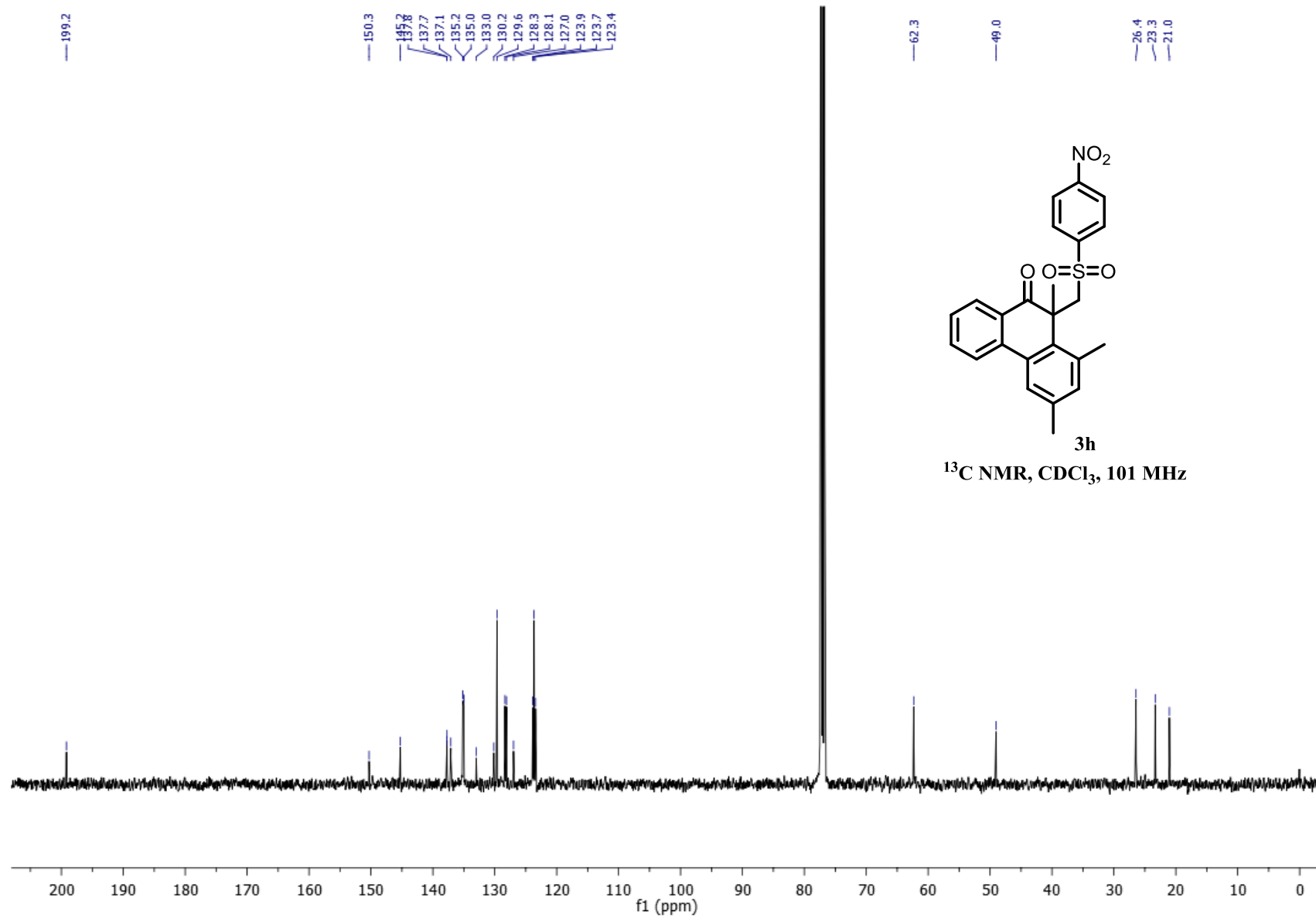


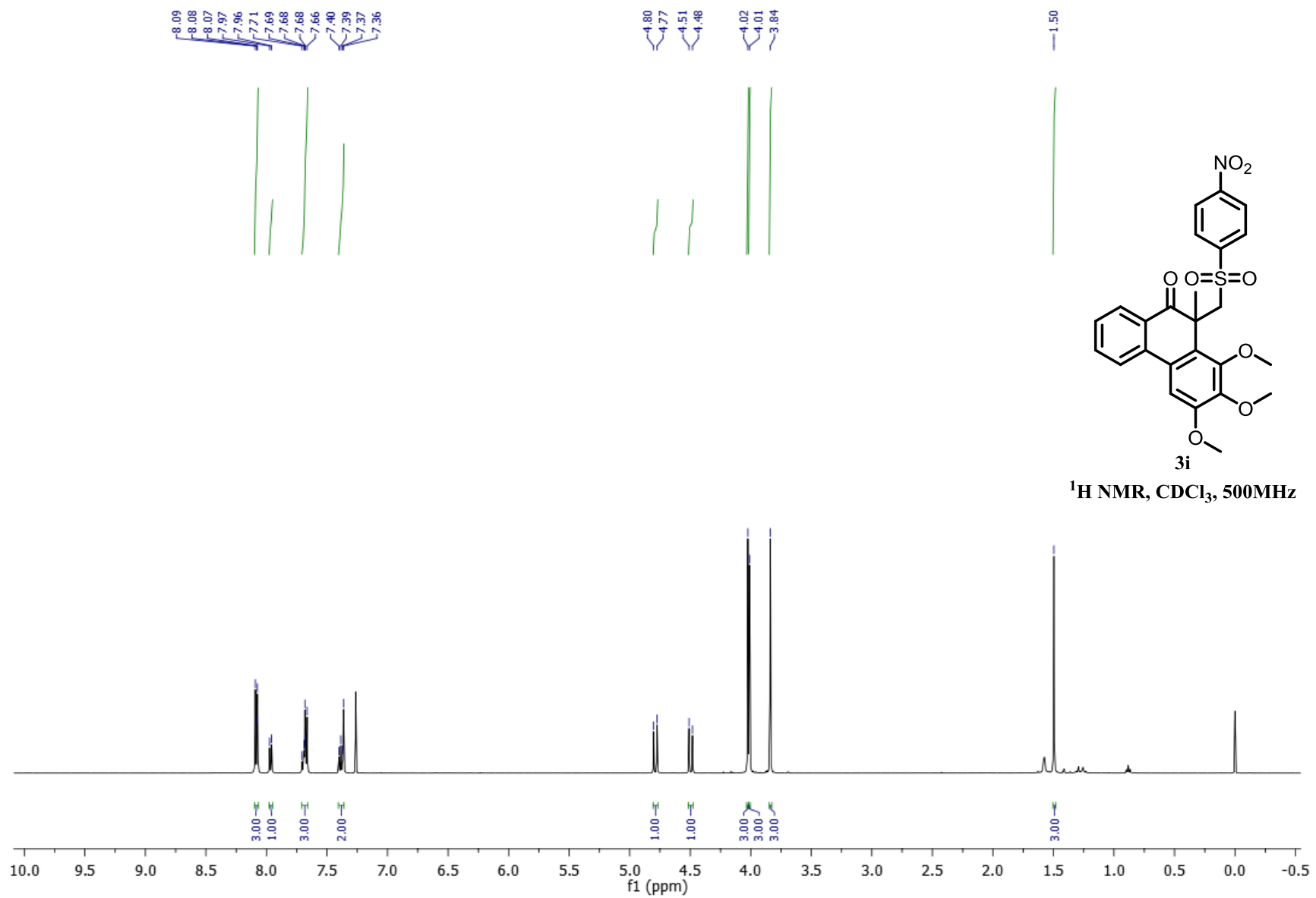


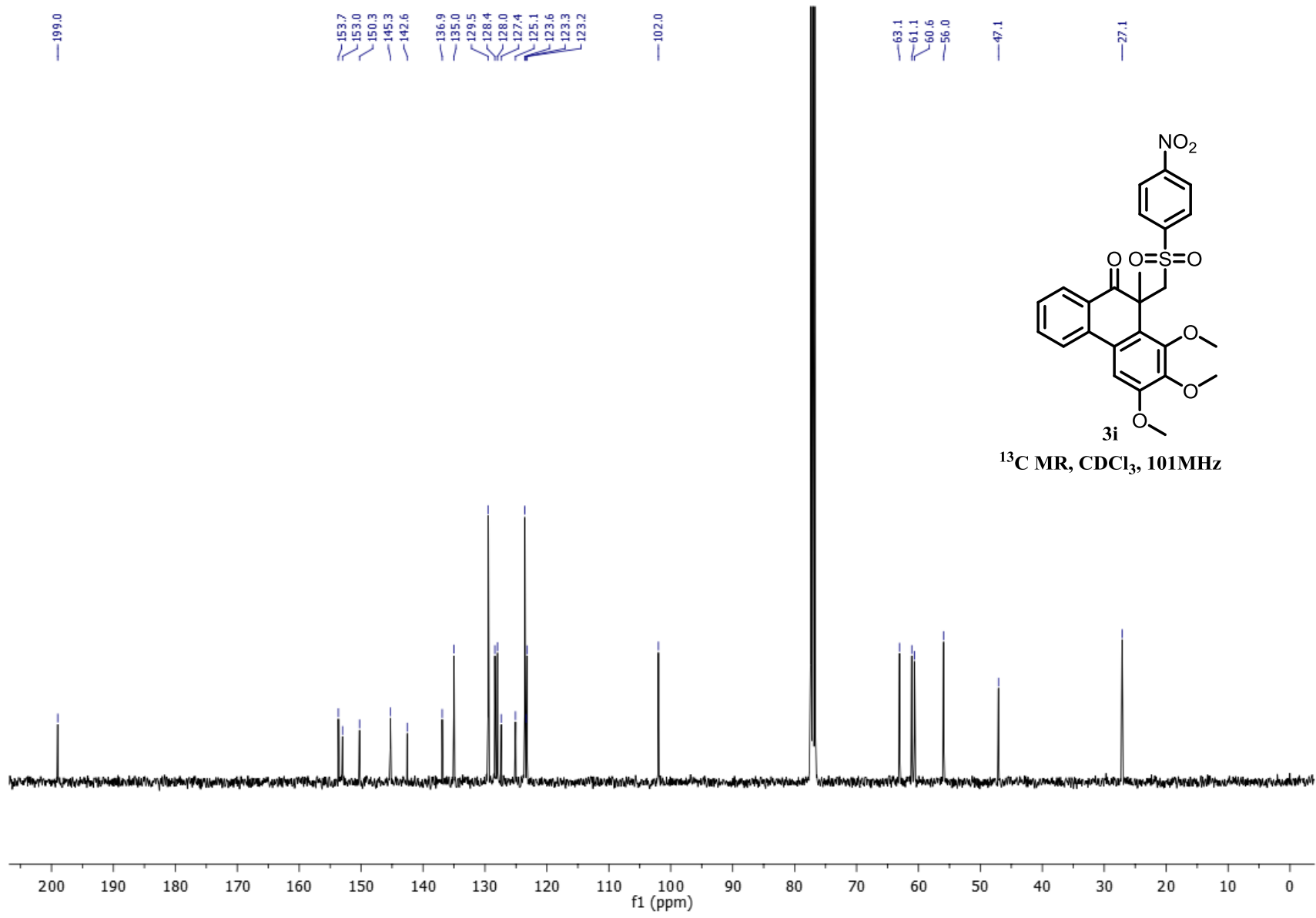


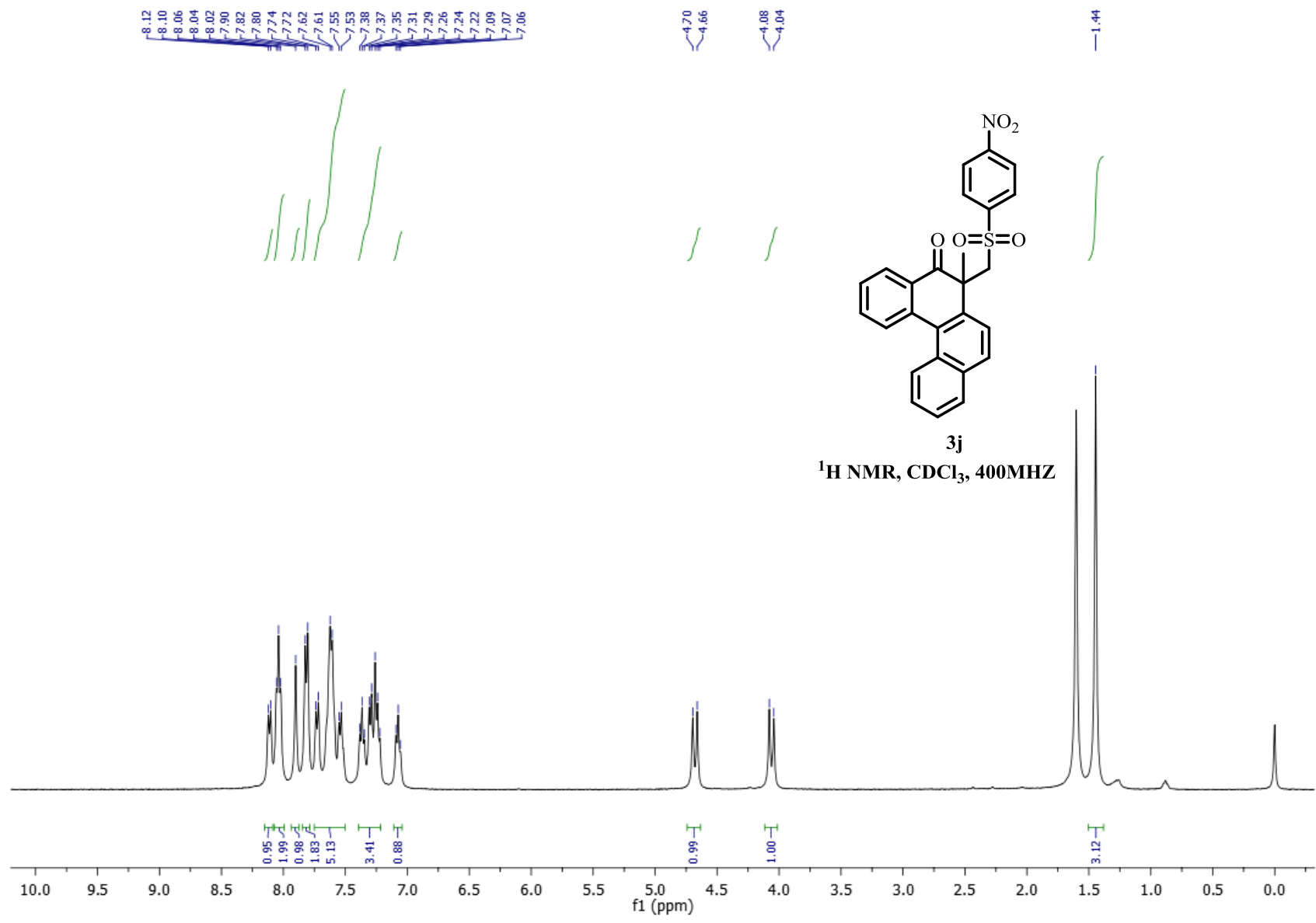


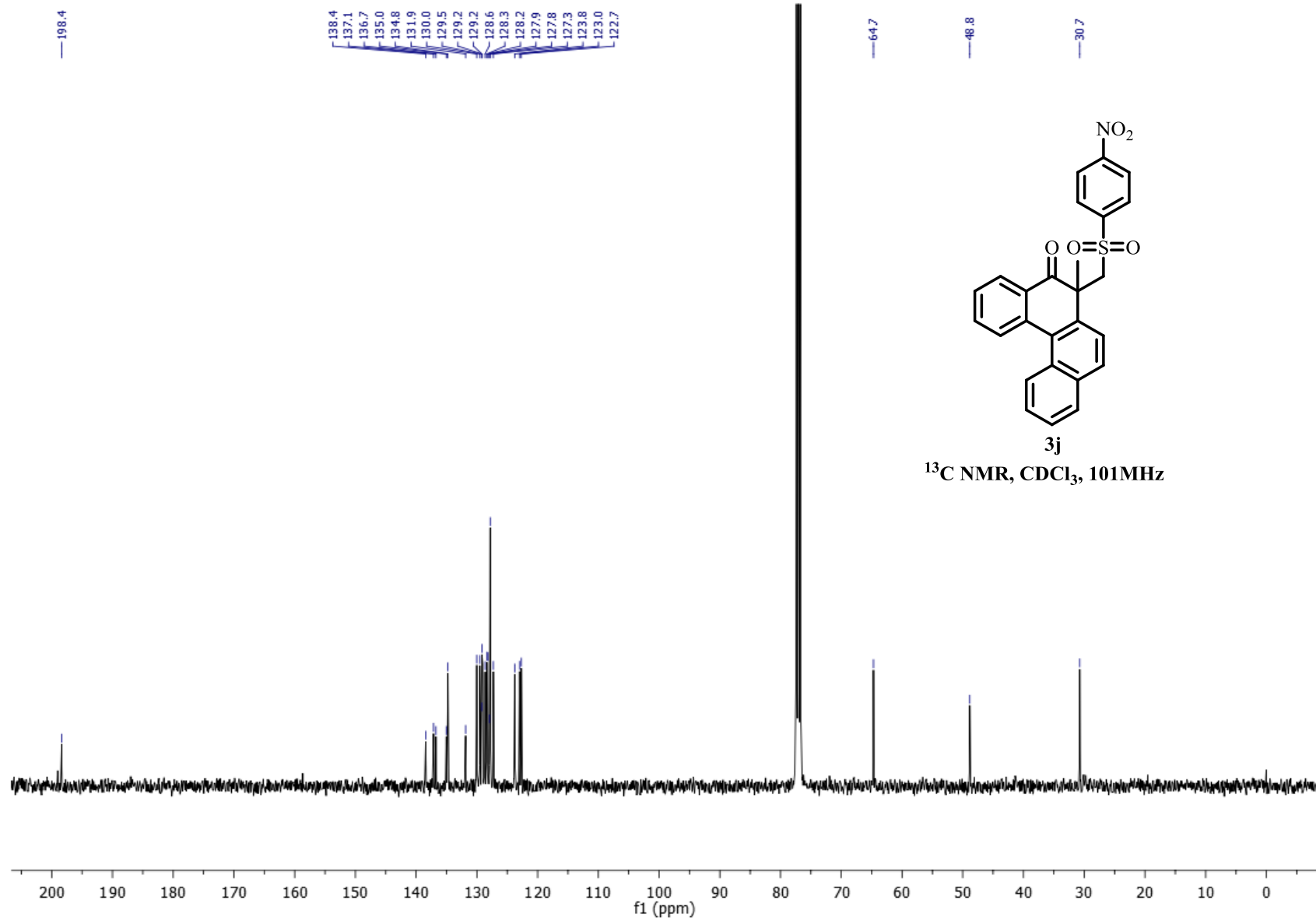










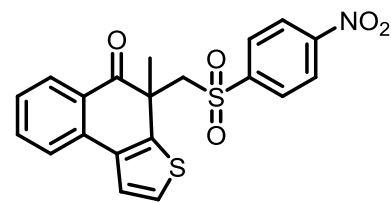


8.17  
8.14  
8.12  
8.10  
7.74  
7.73  
7.71  
7.70  
7.69  
7.69  
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7.42  
7.40  
7.39  
7.38  
7.29  
7.27

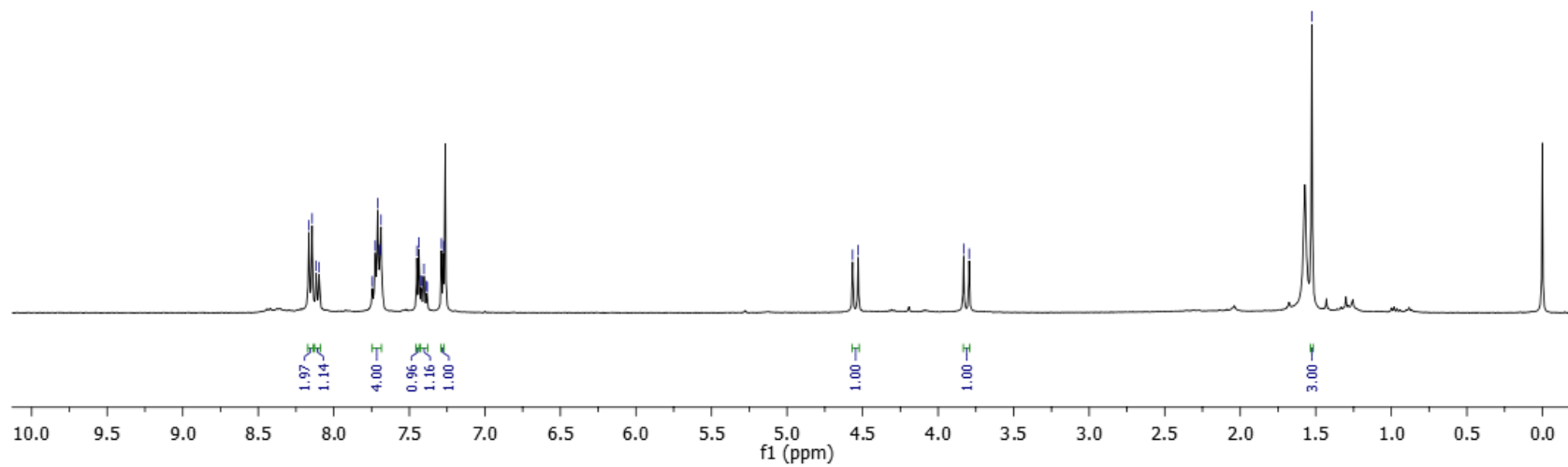
4.57  
4.53

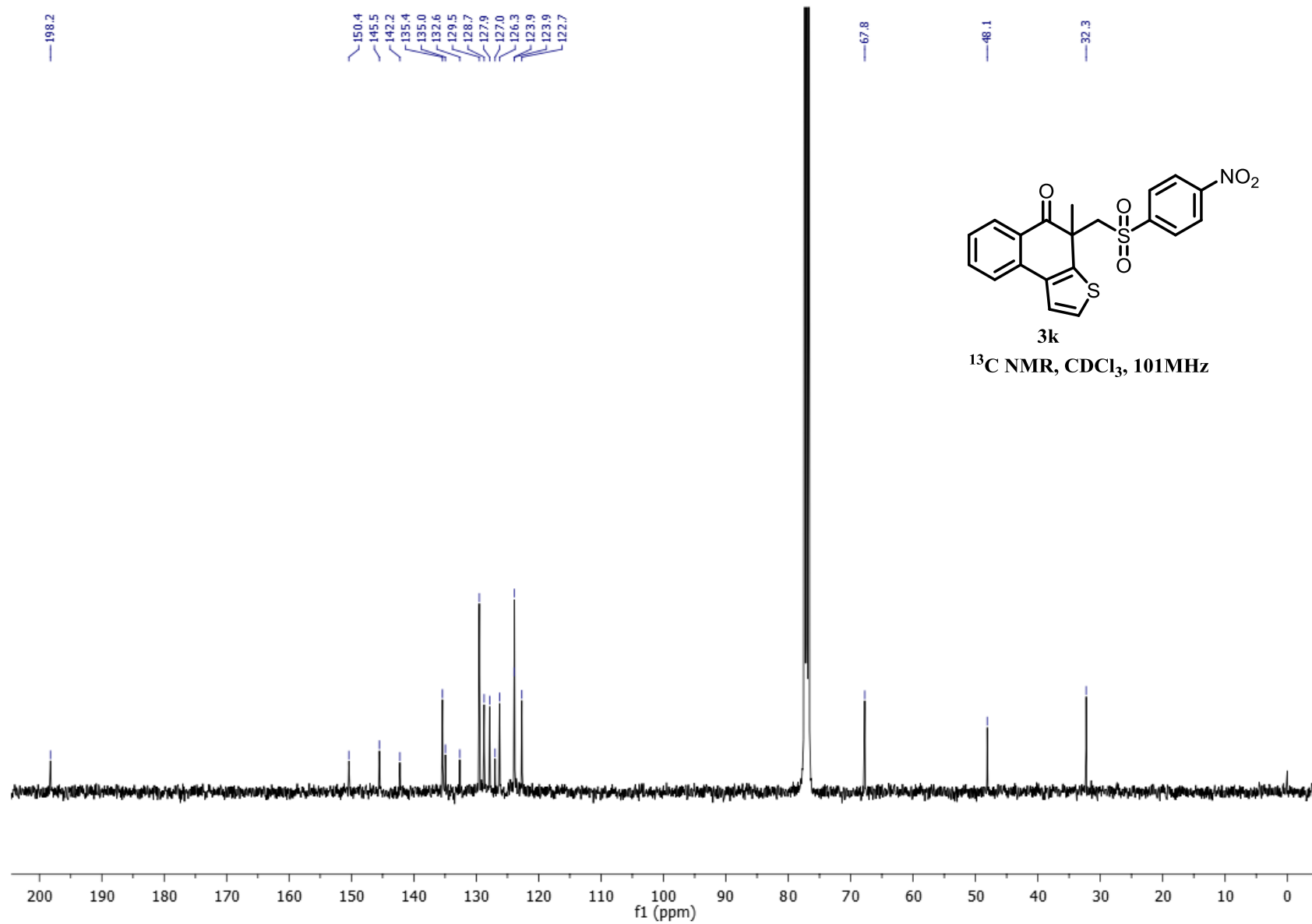
3.83  
3.79

1.53

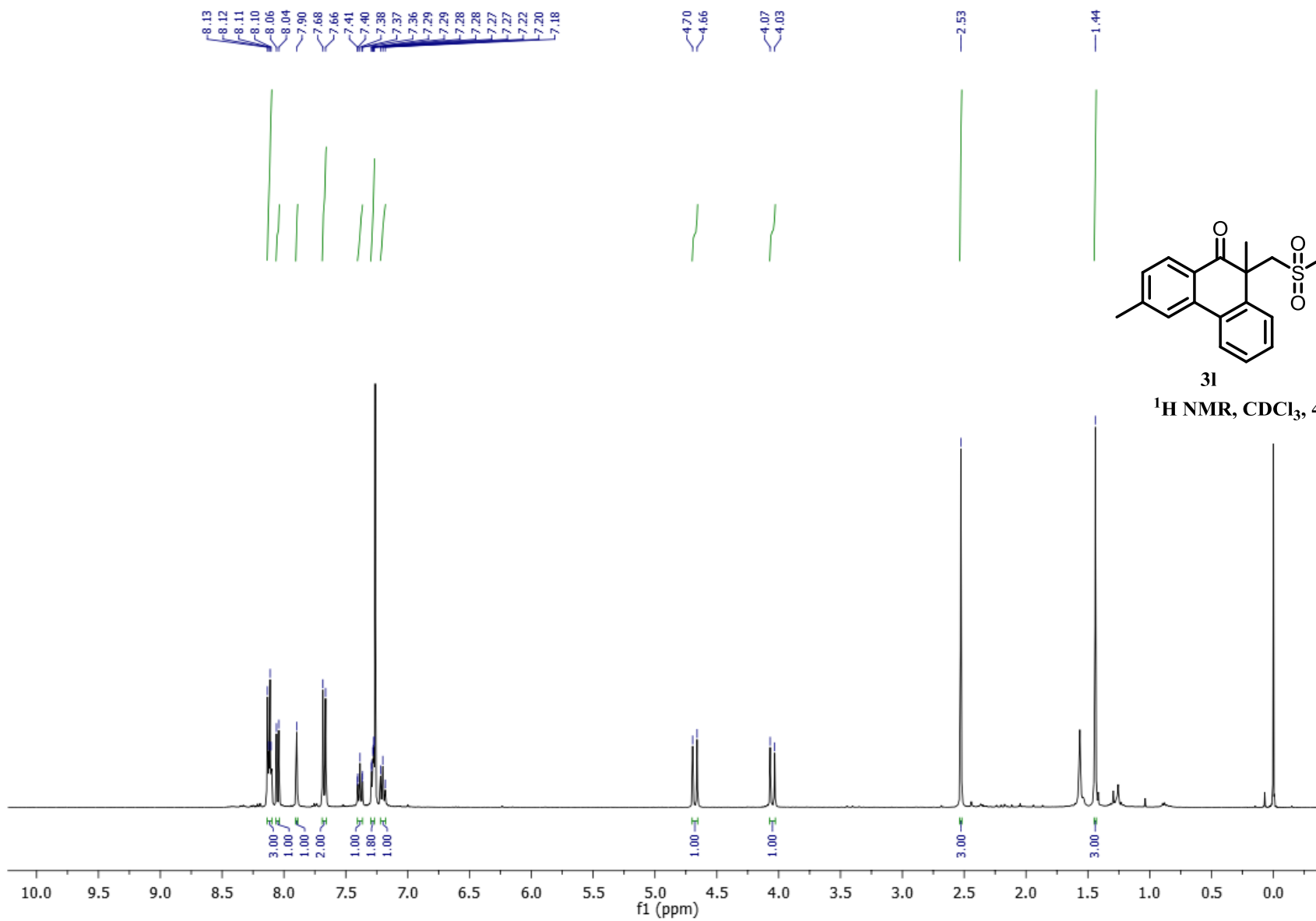


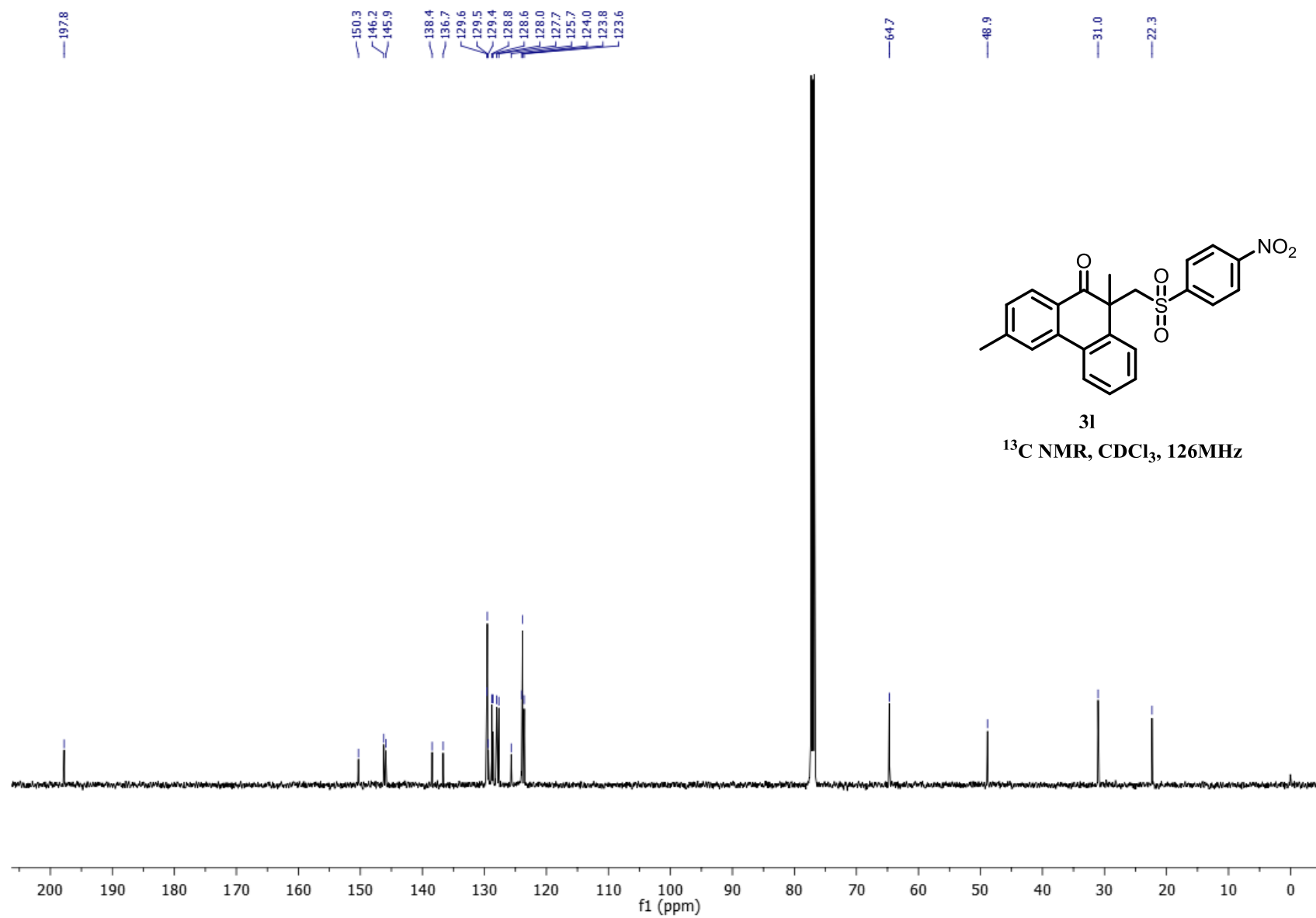
<sup>1</sup>H NMR, CDCl<sub>3</sub>, 400MHz

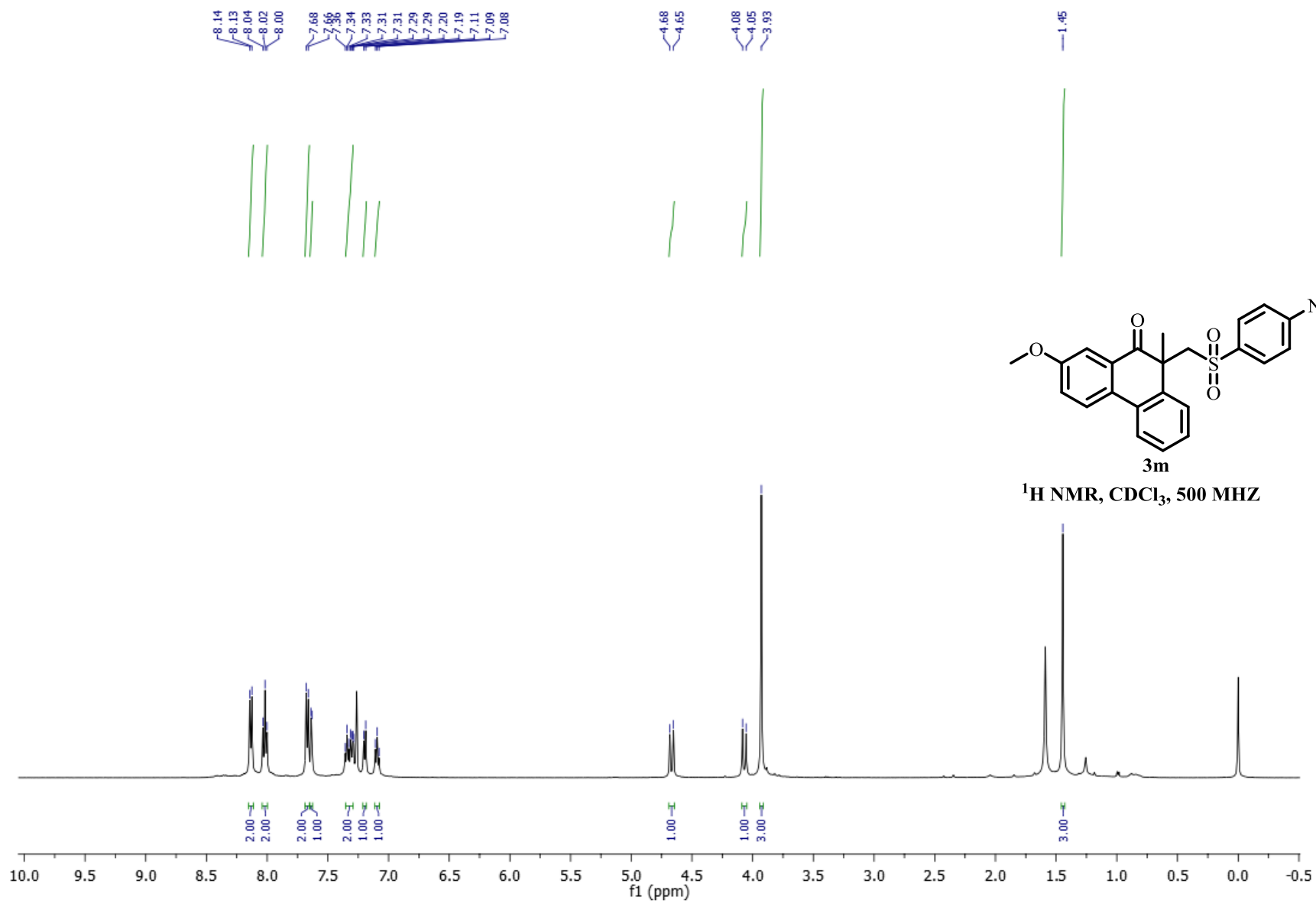


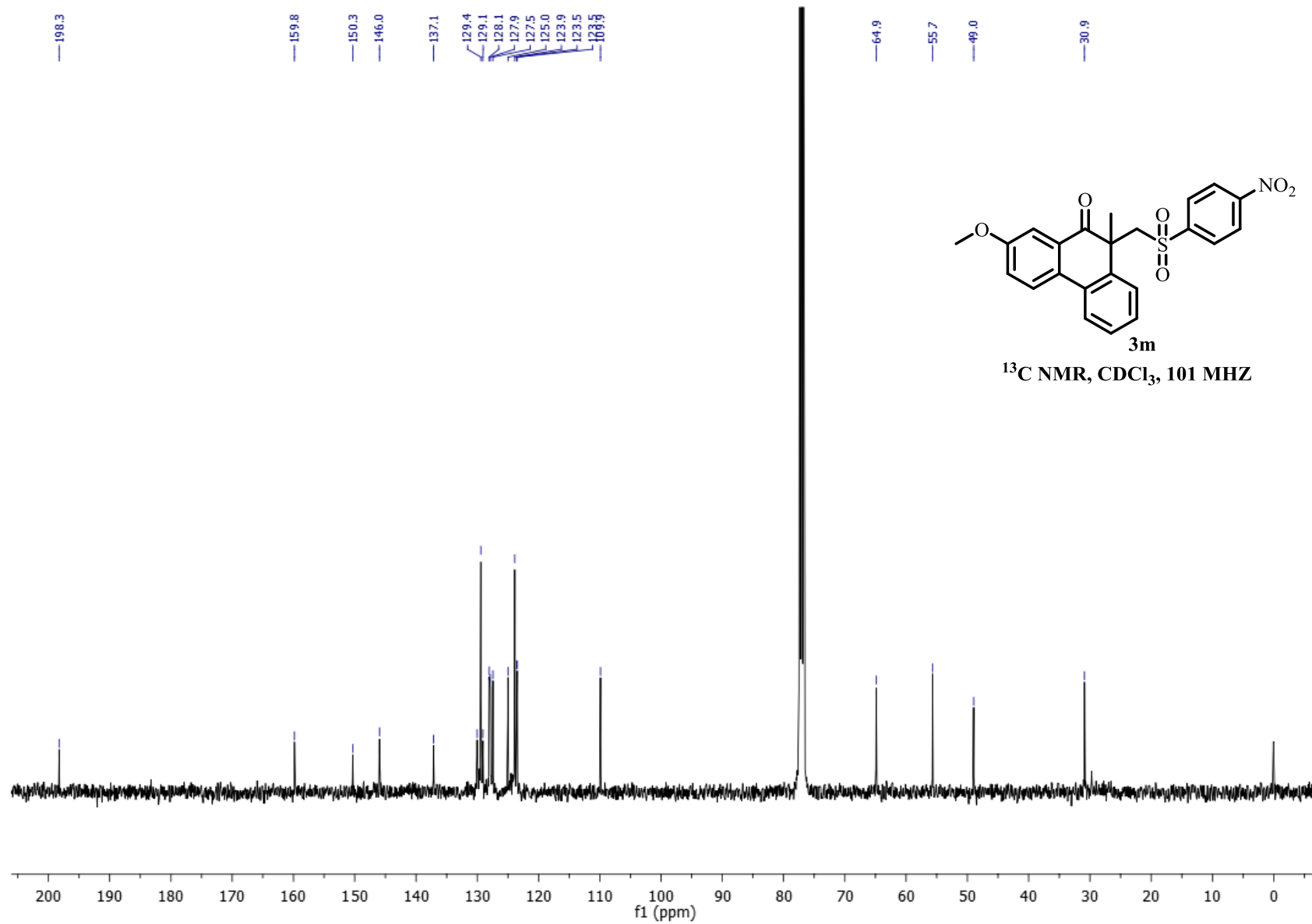


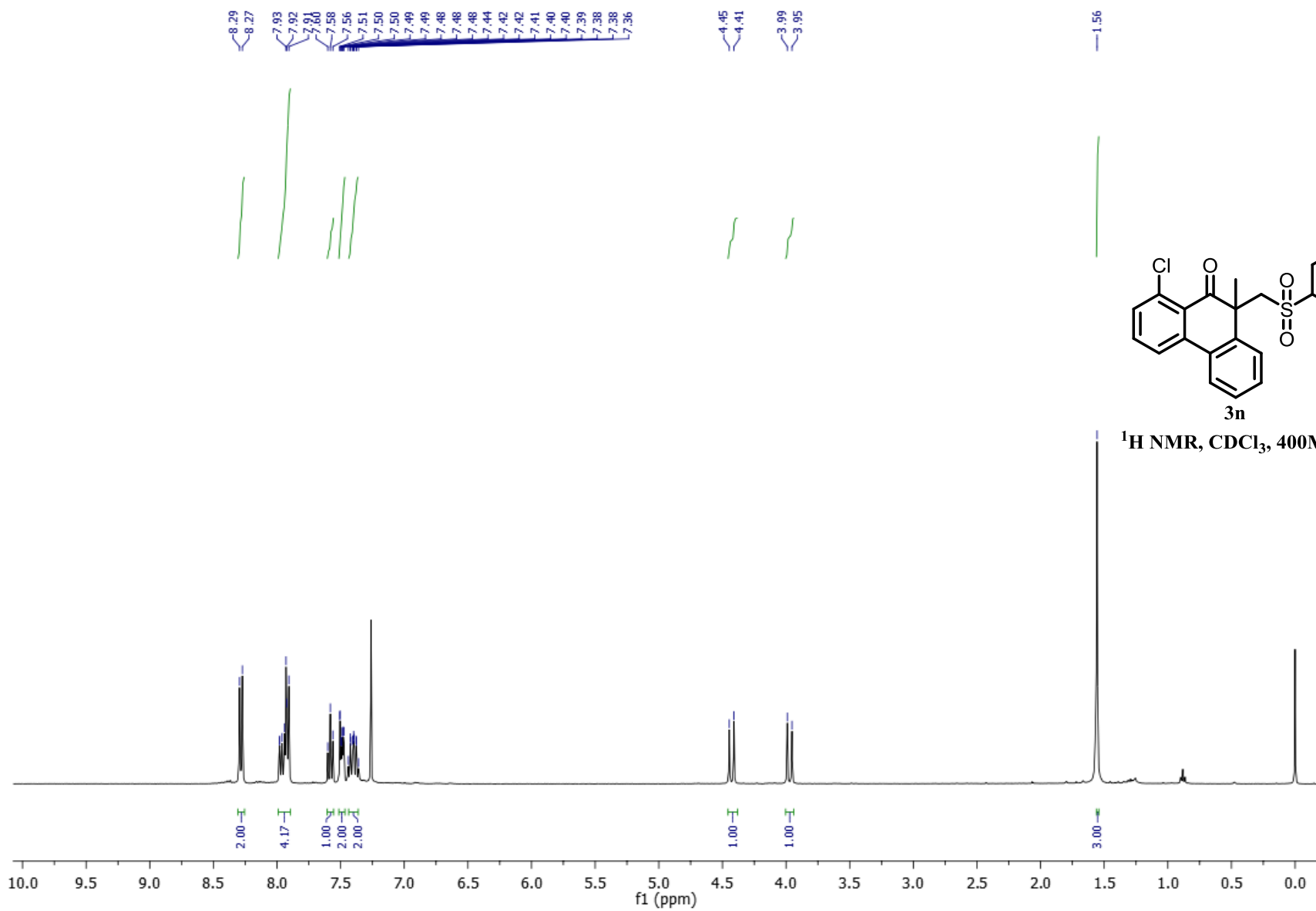


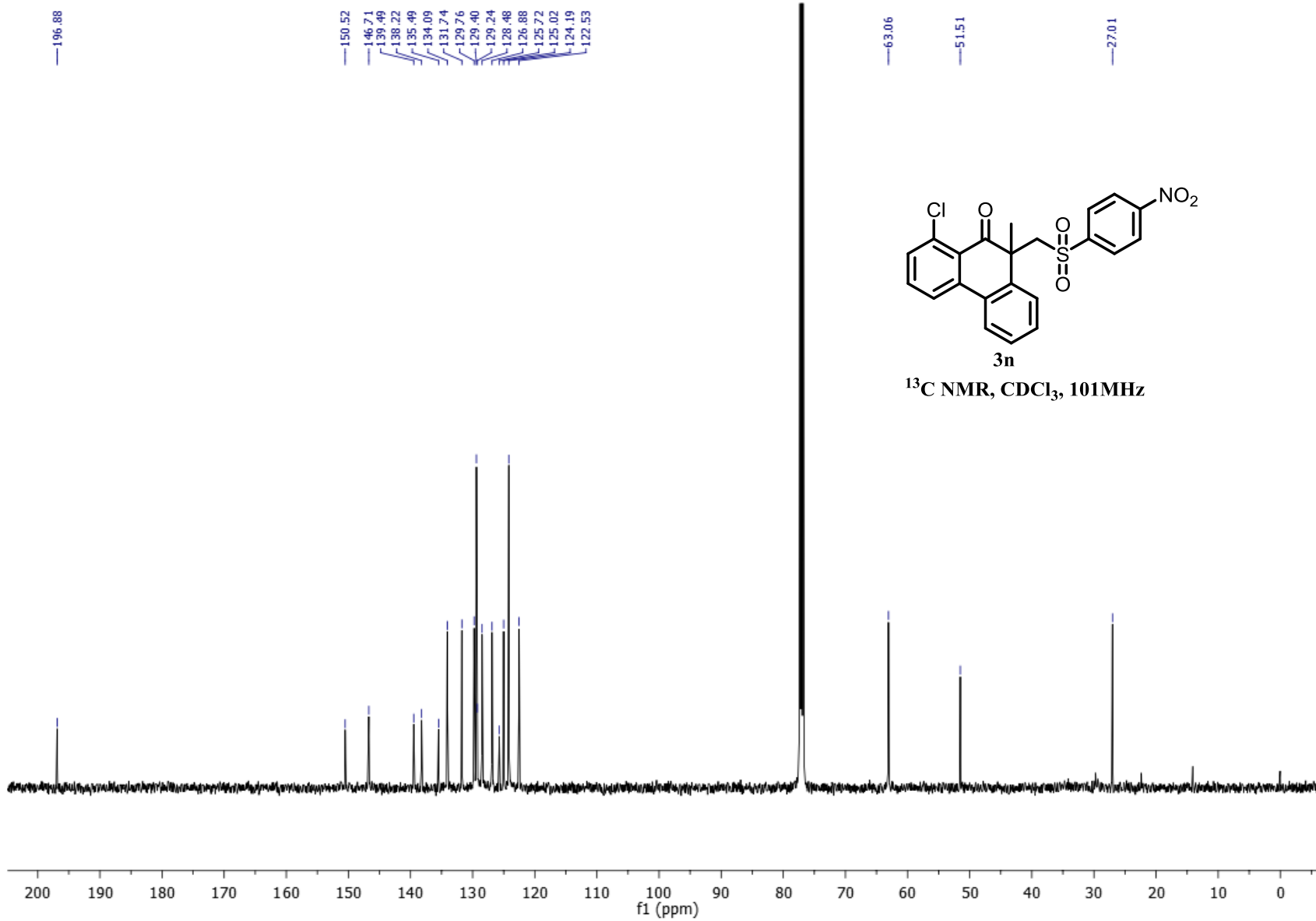


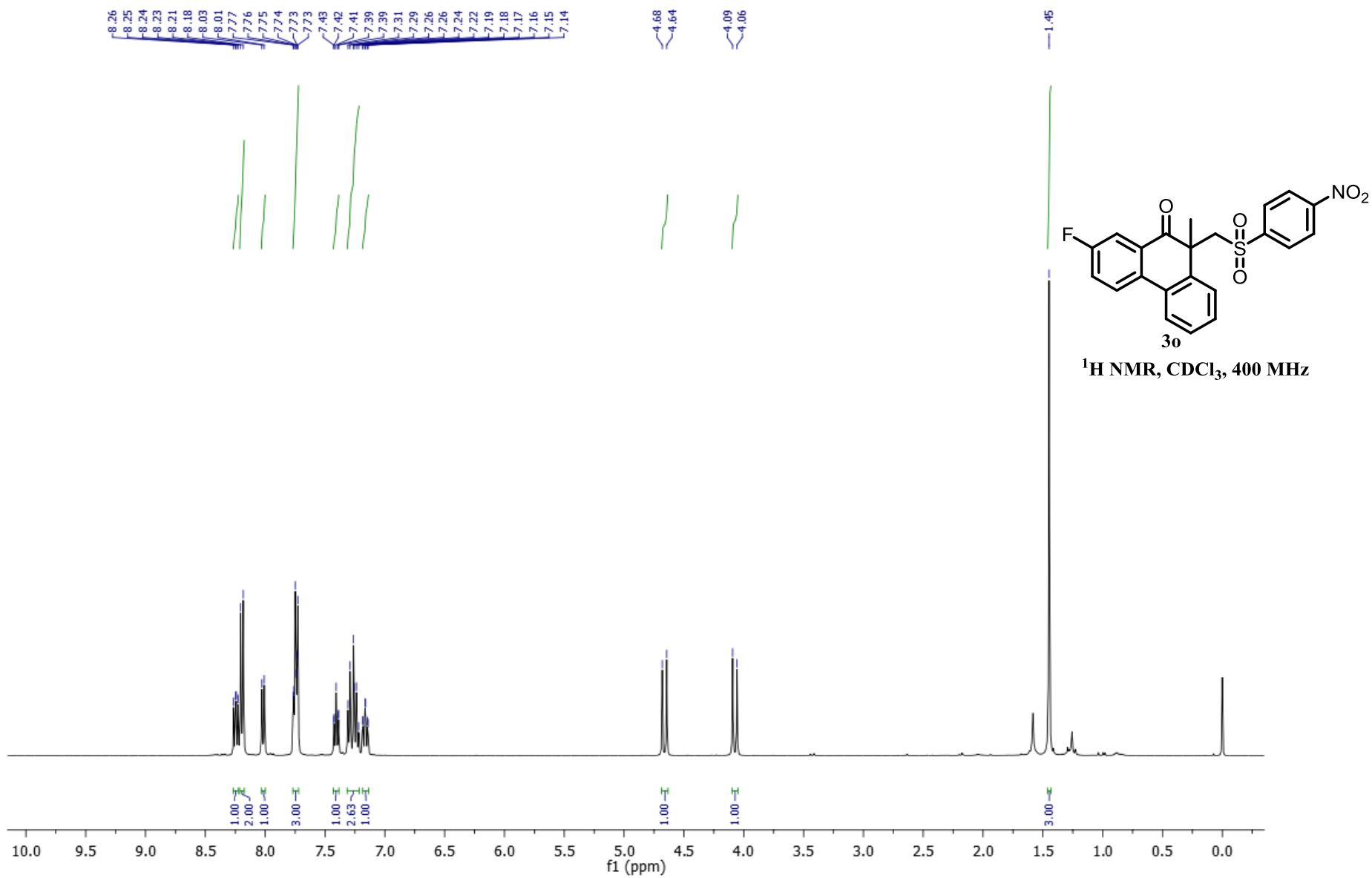


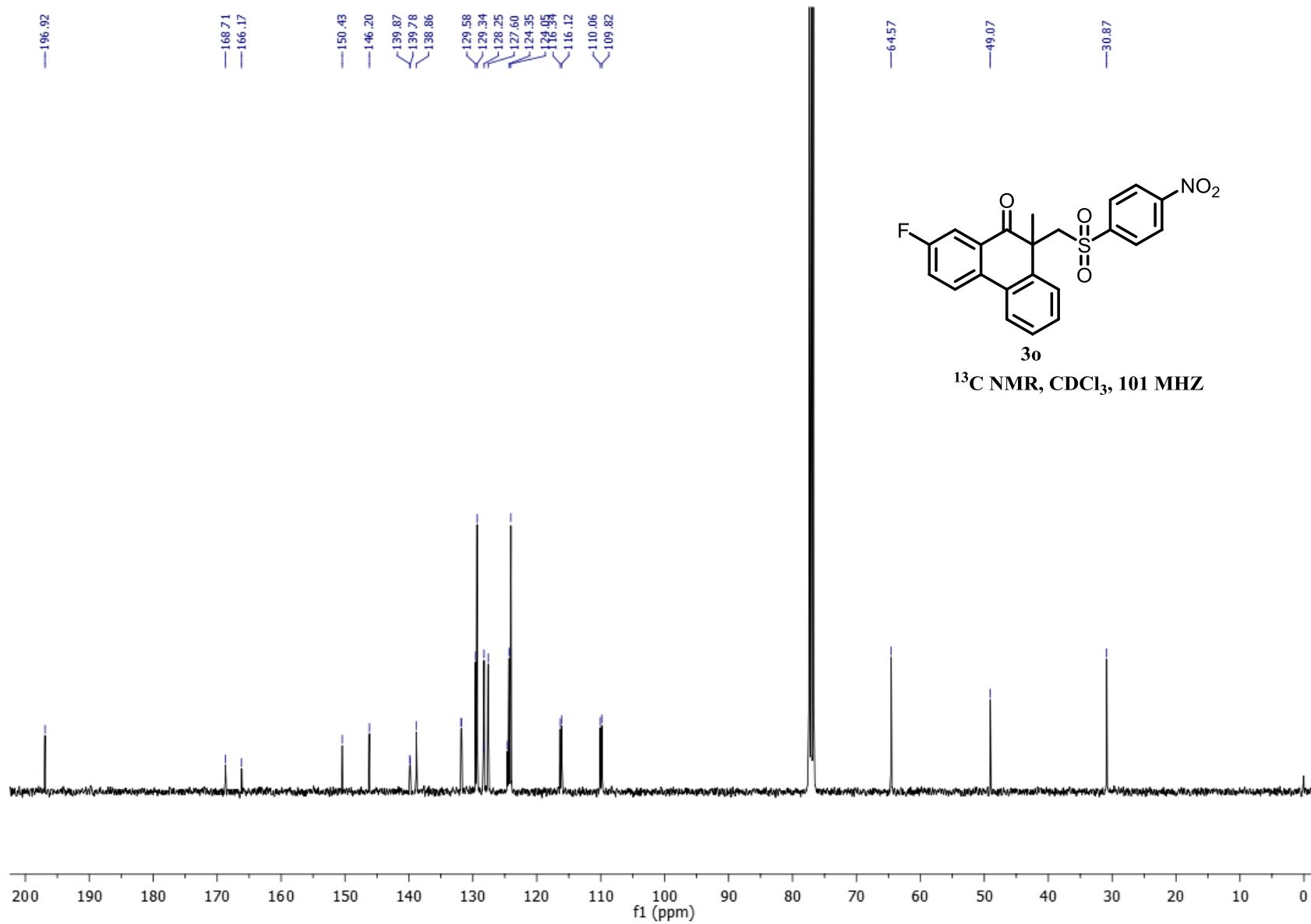




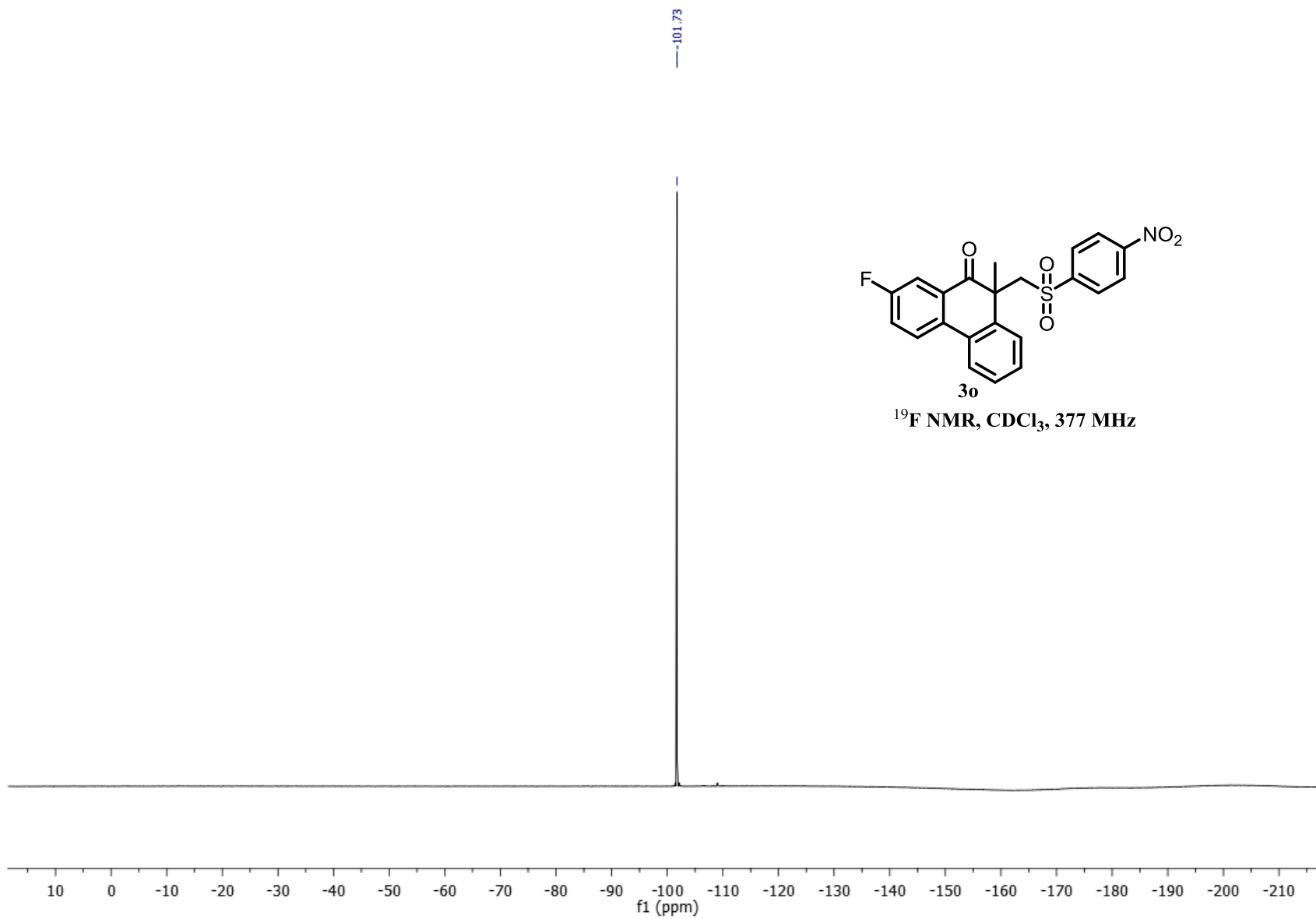


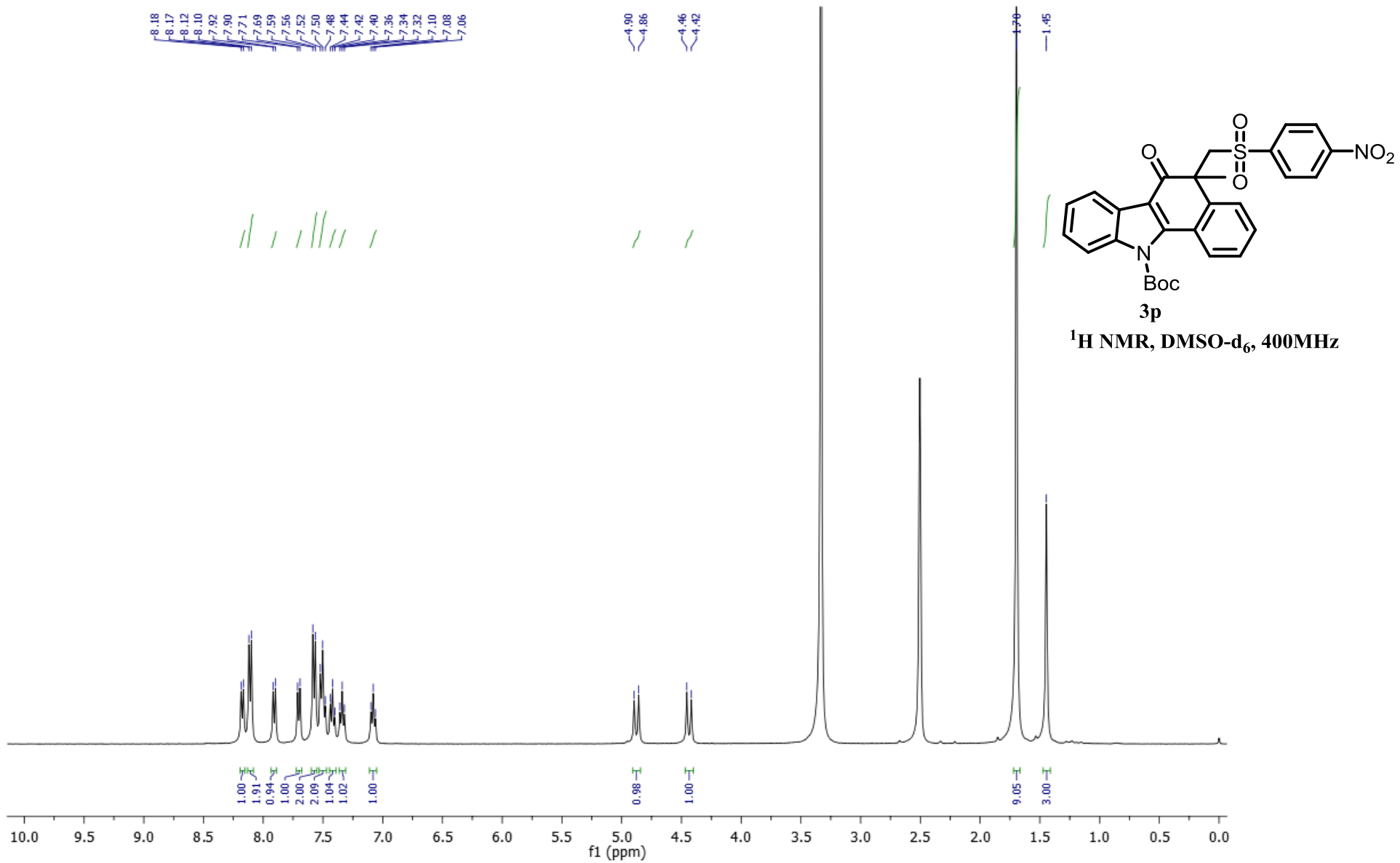


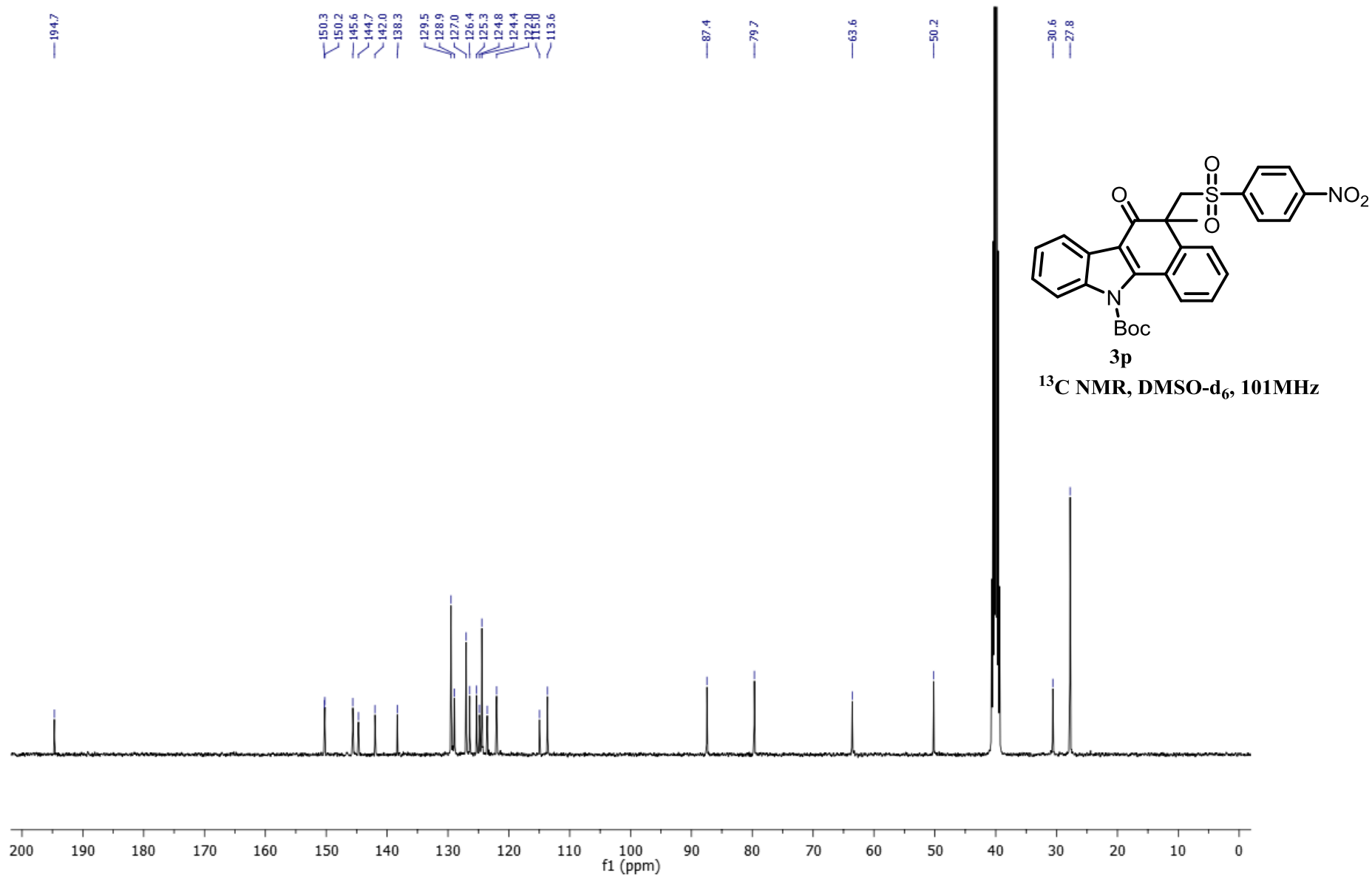


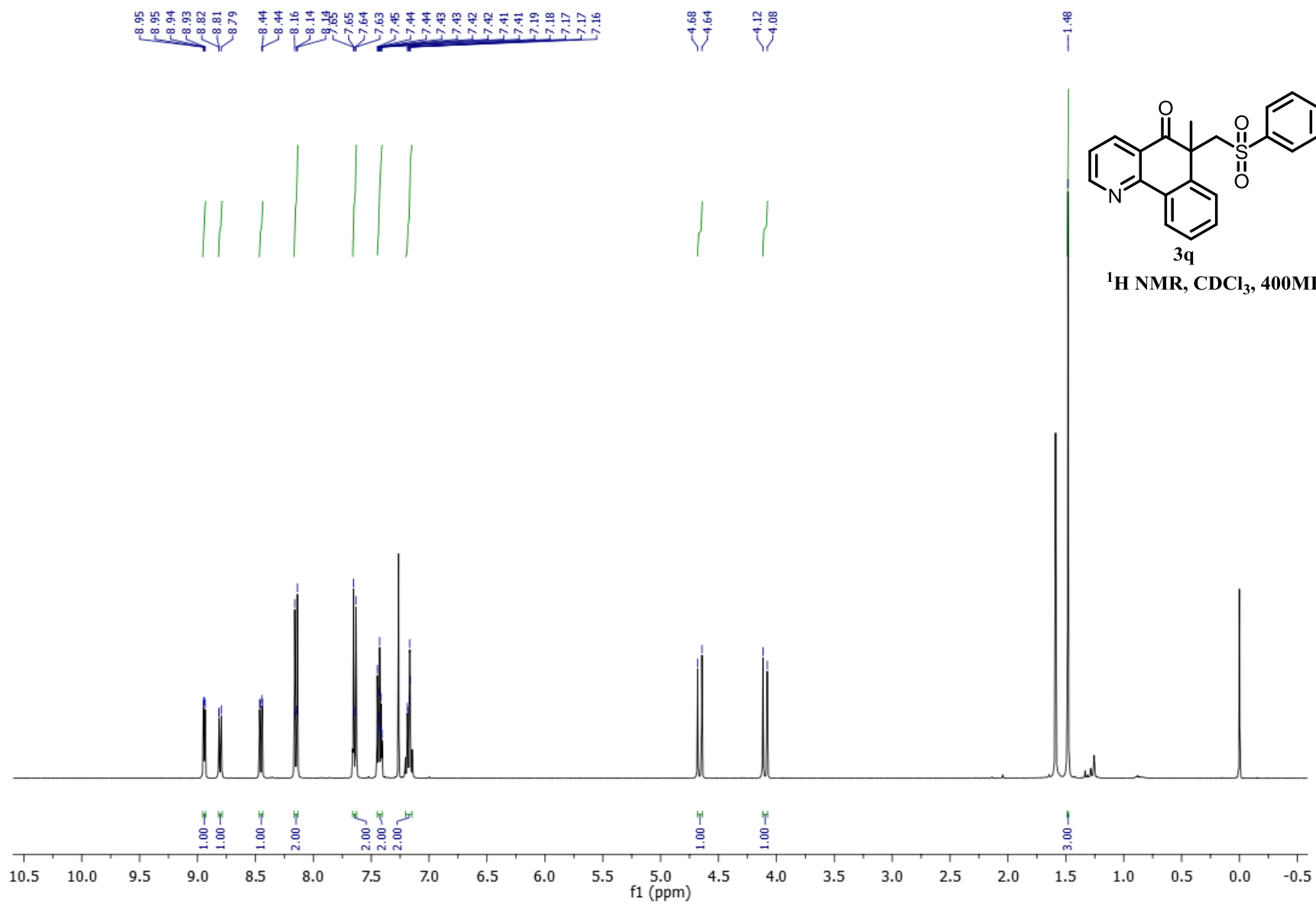


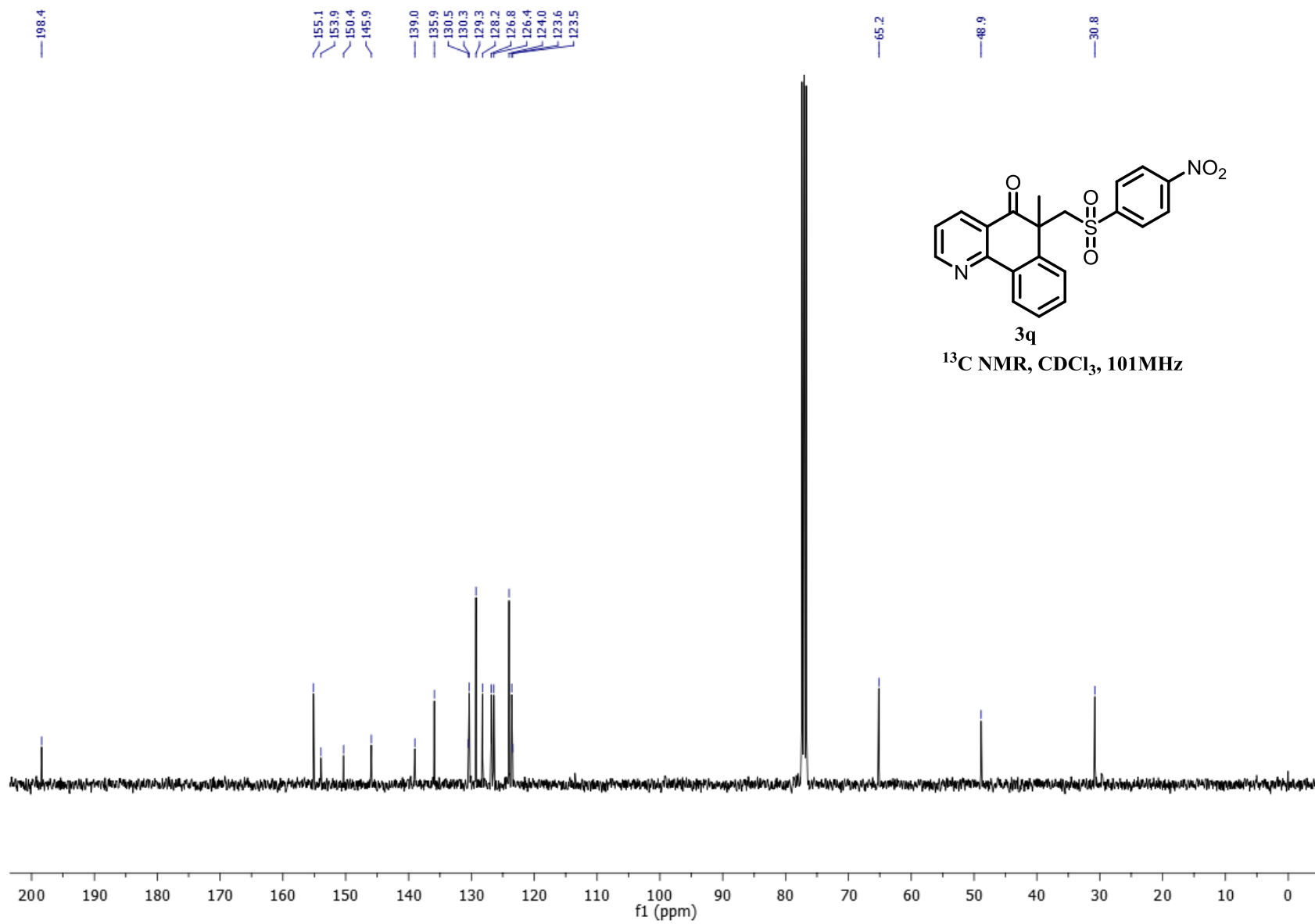


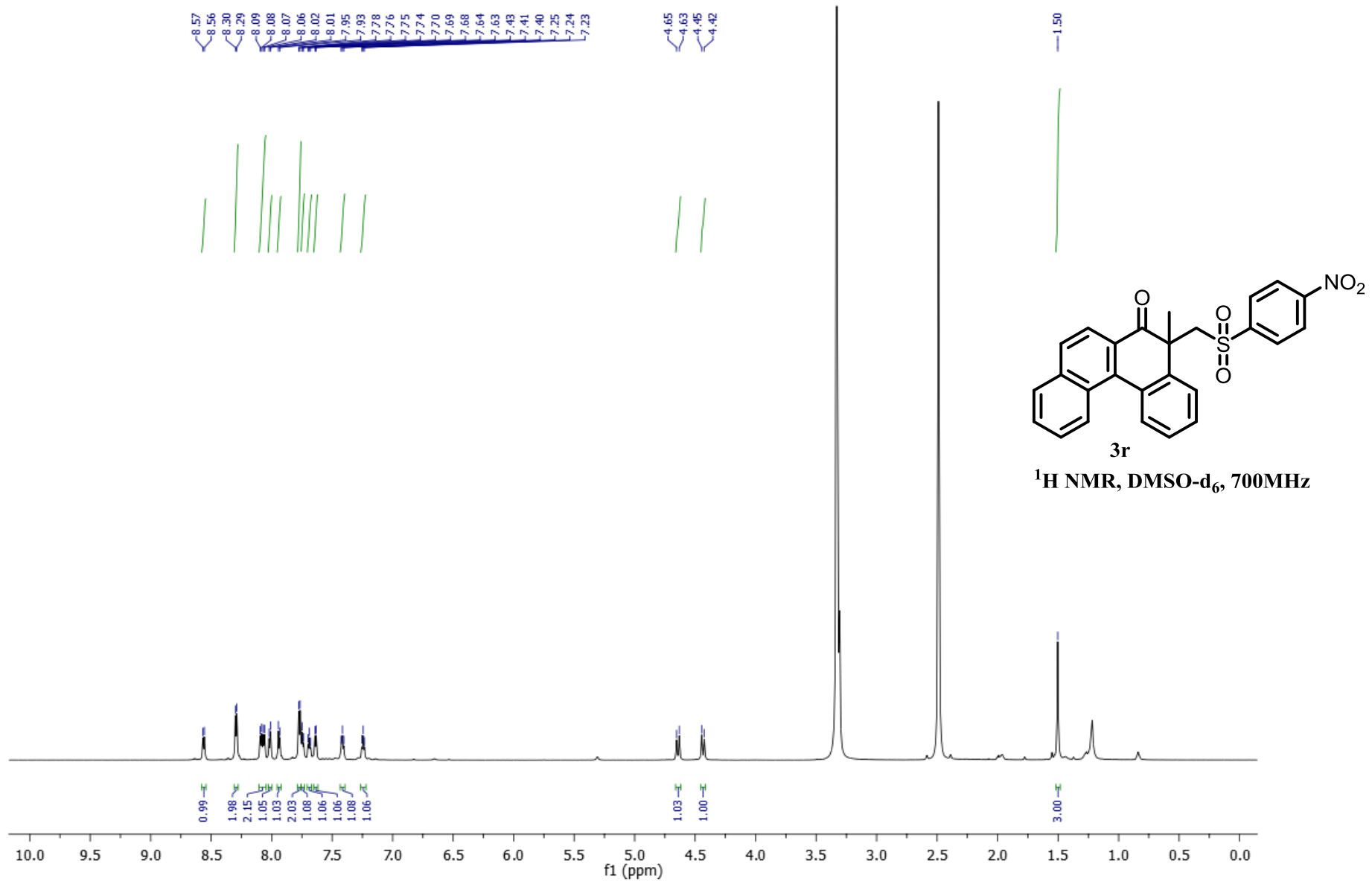


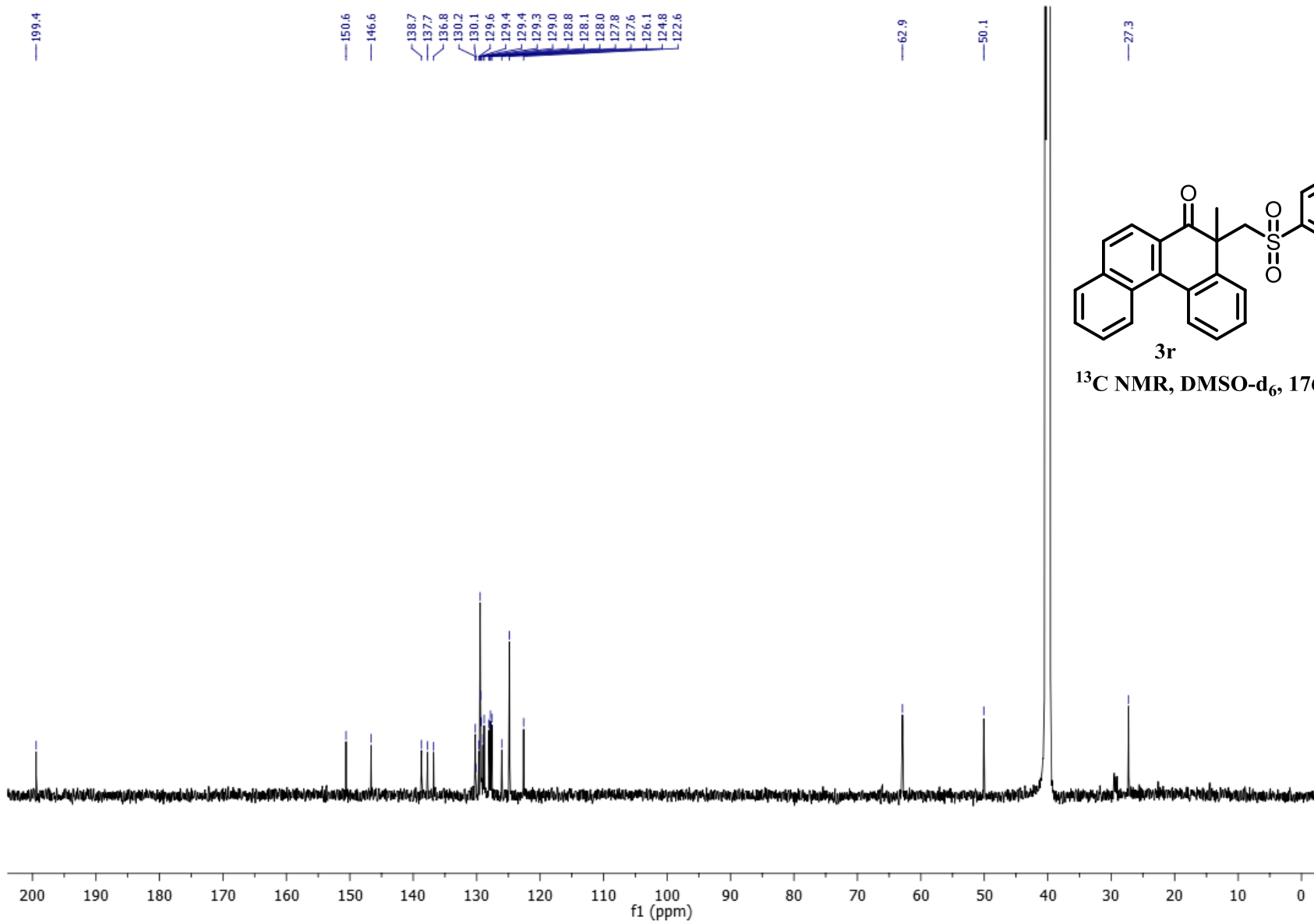


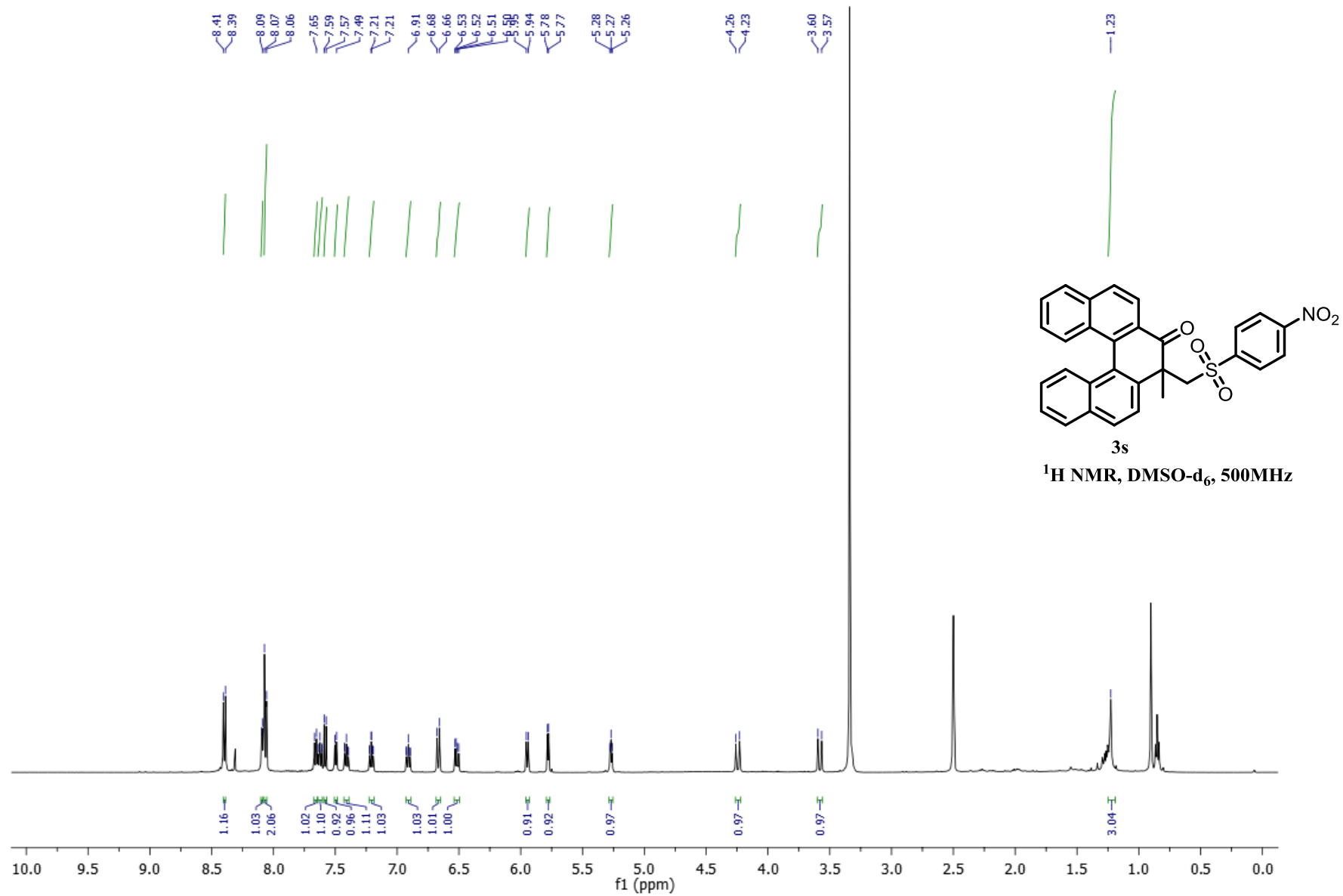




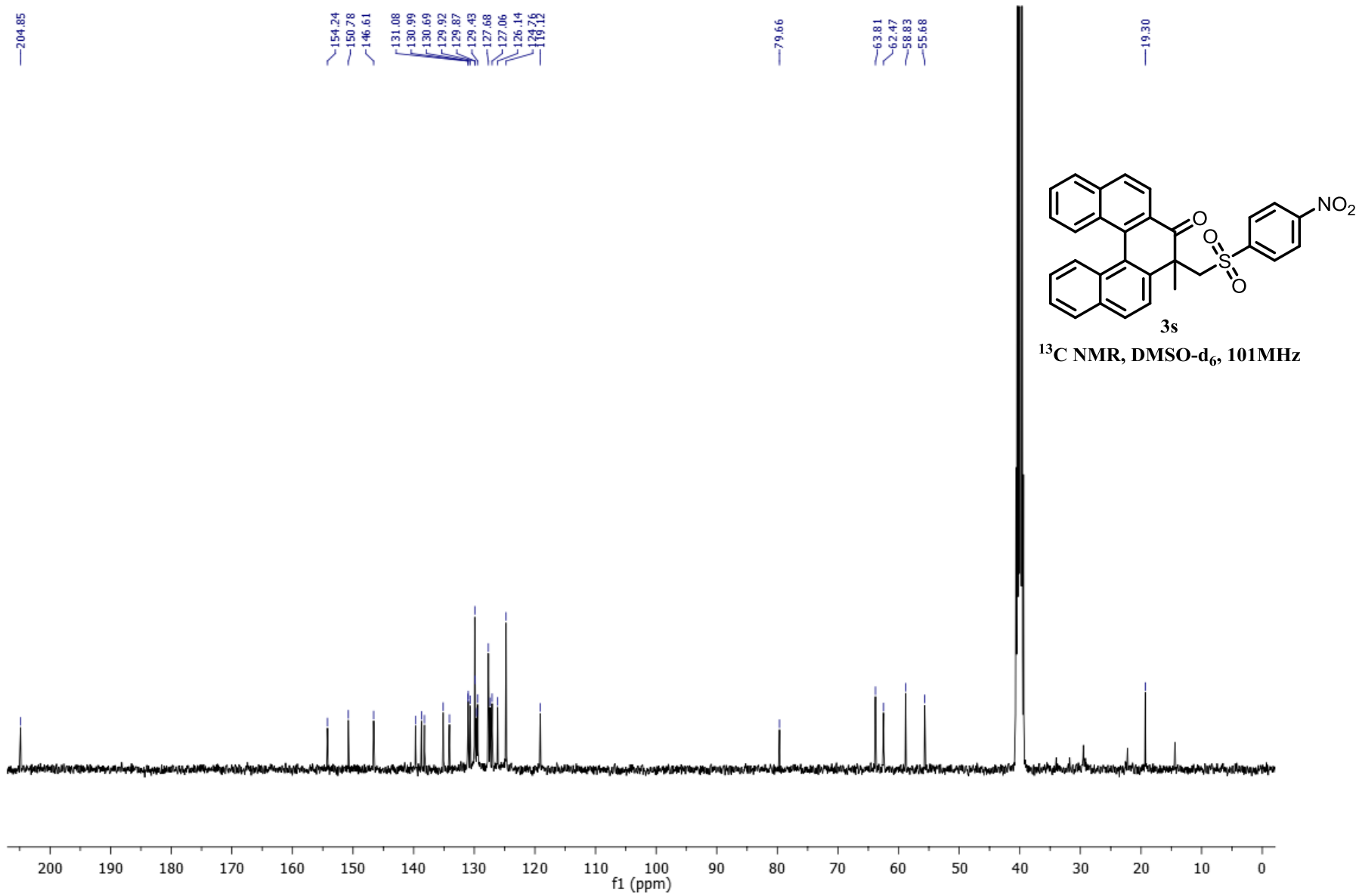


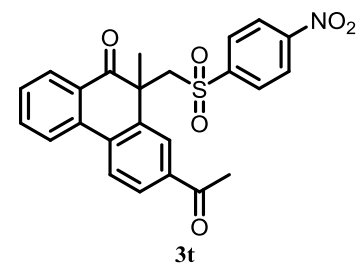
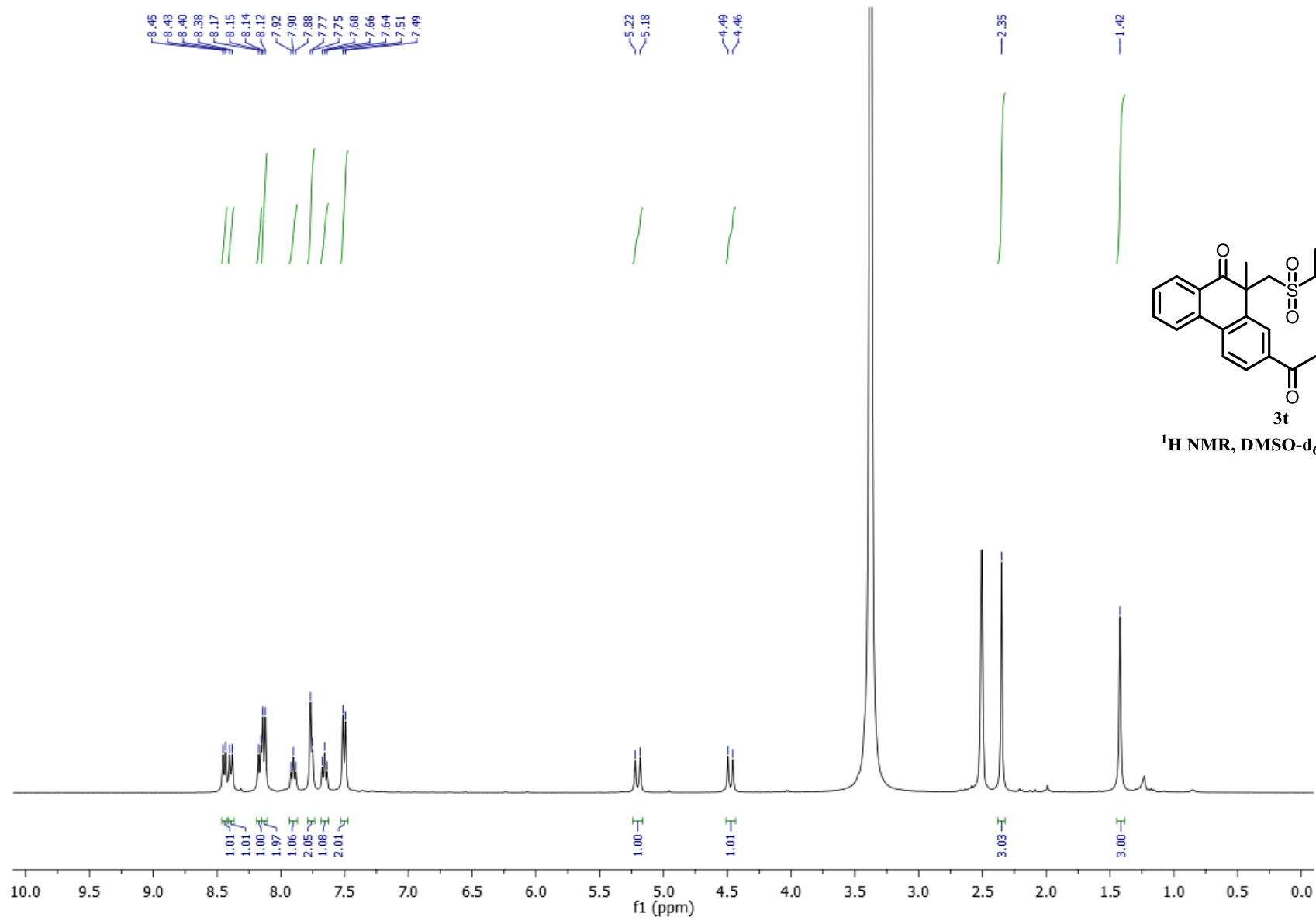




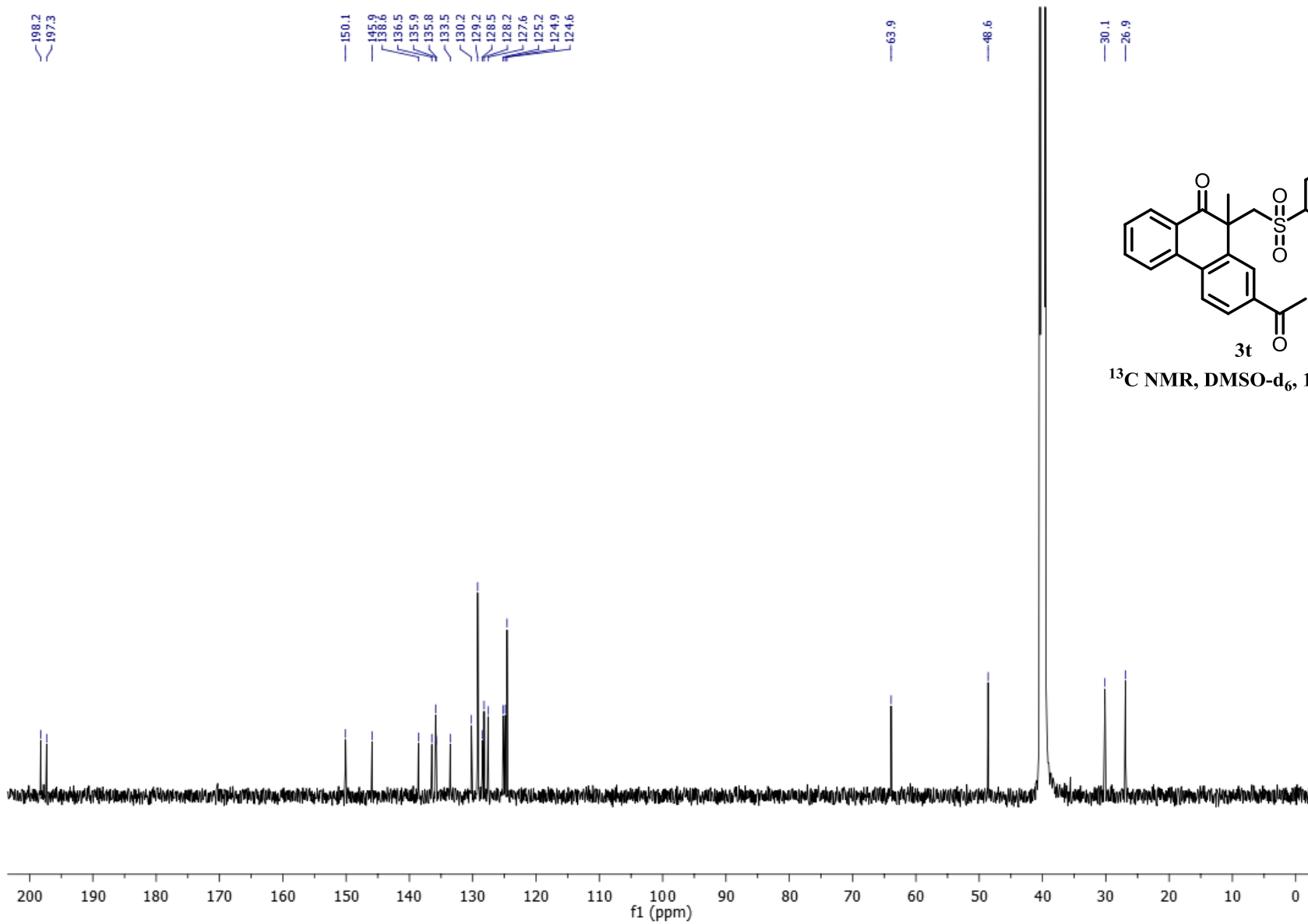


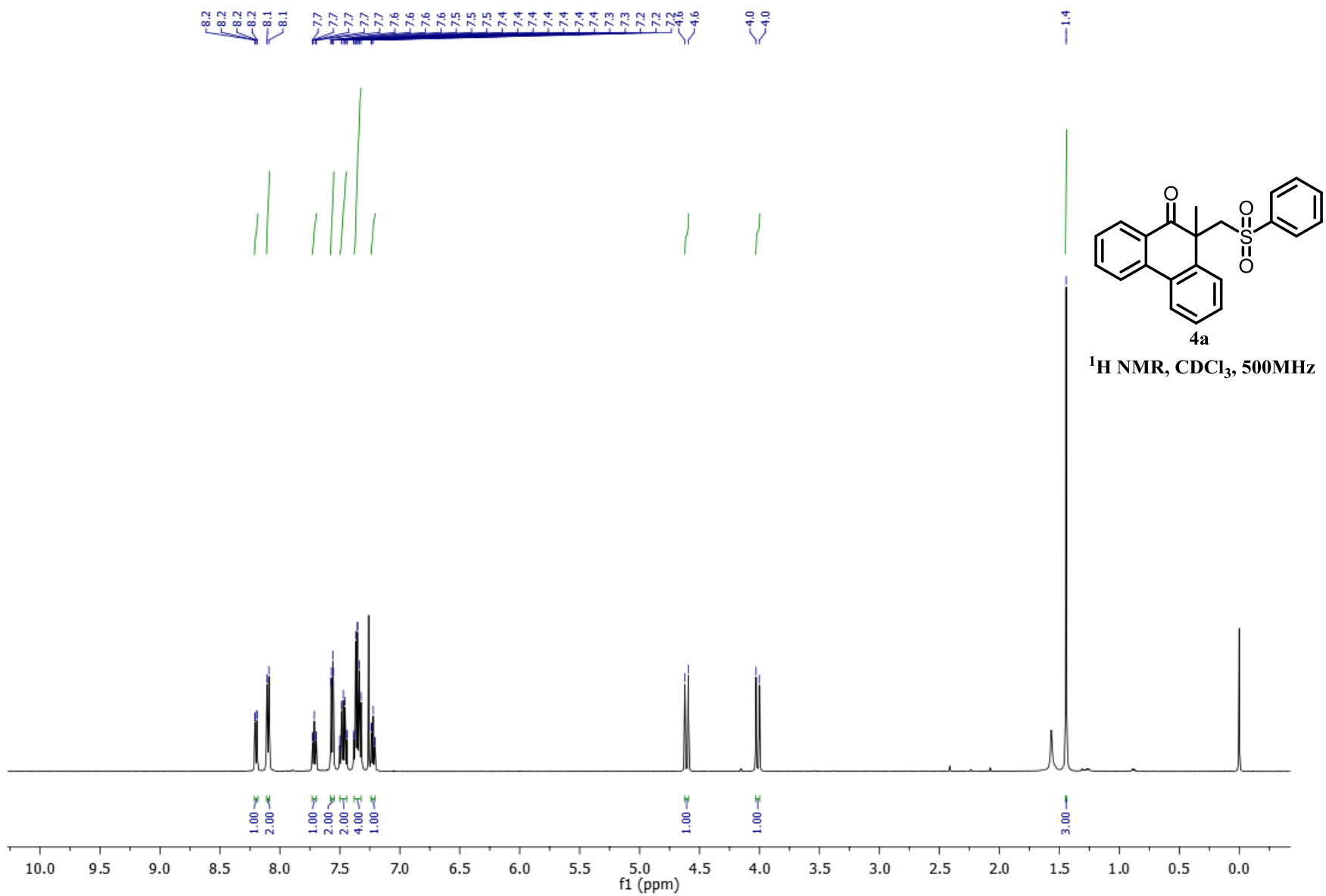


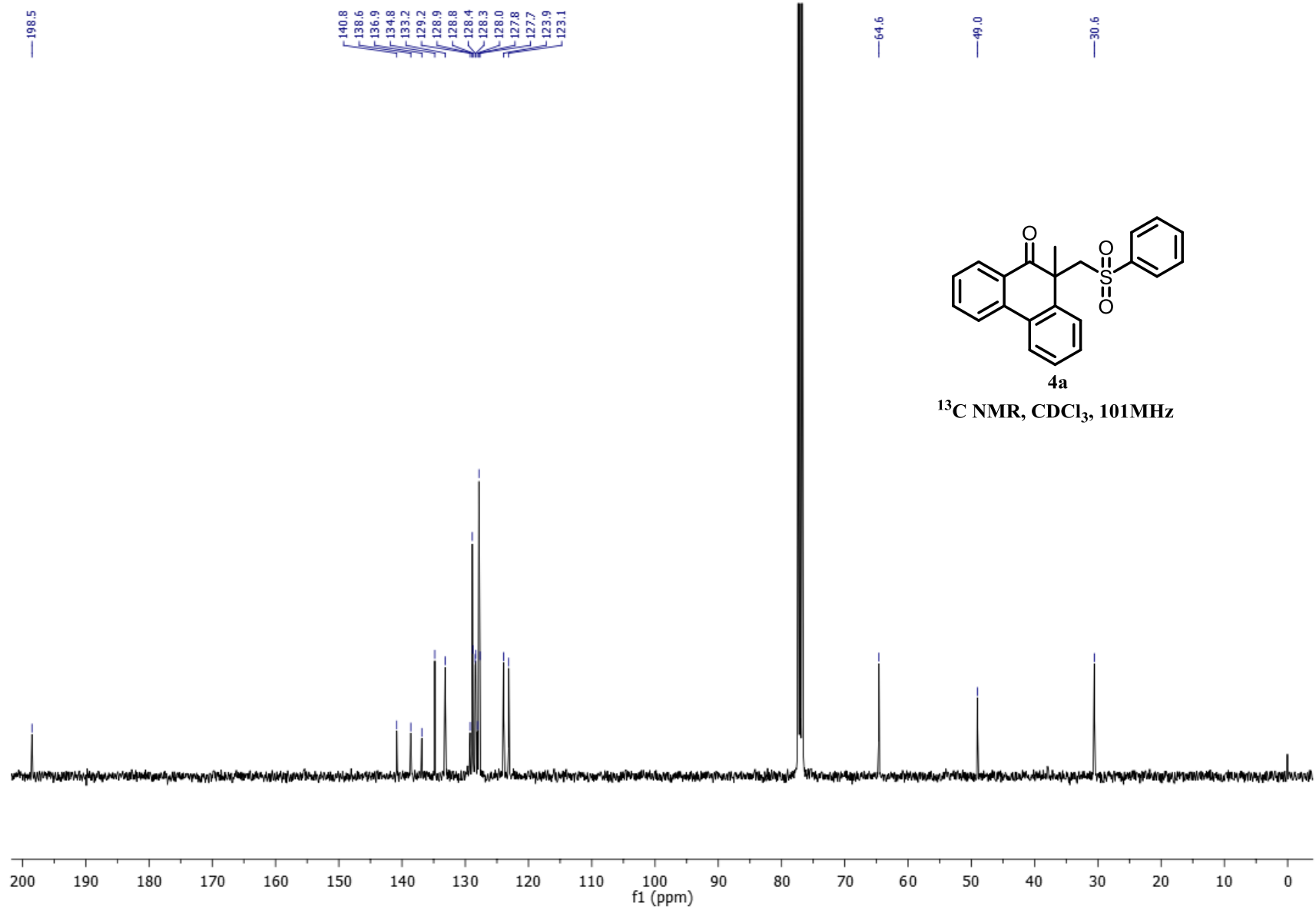


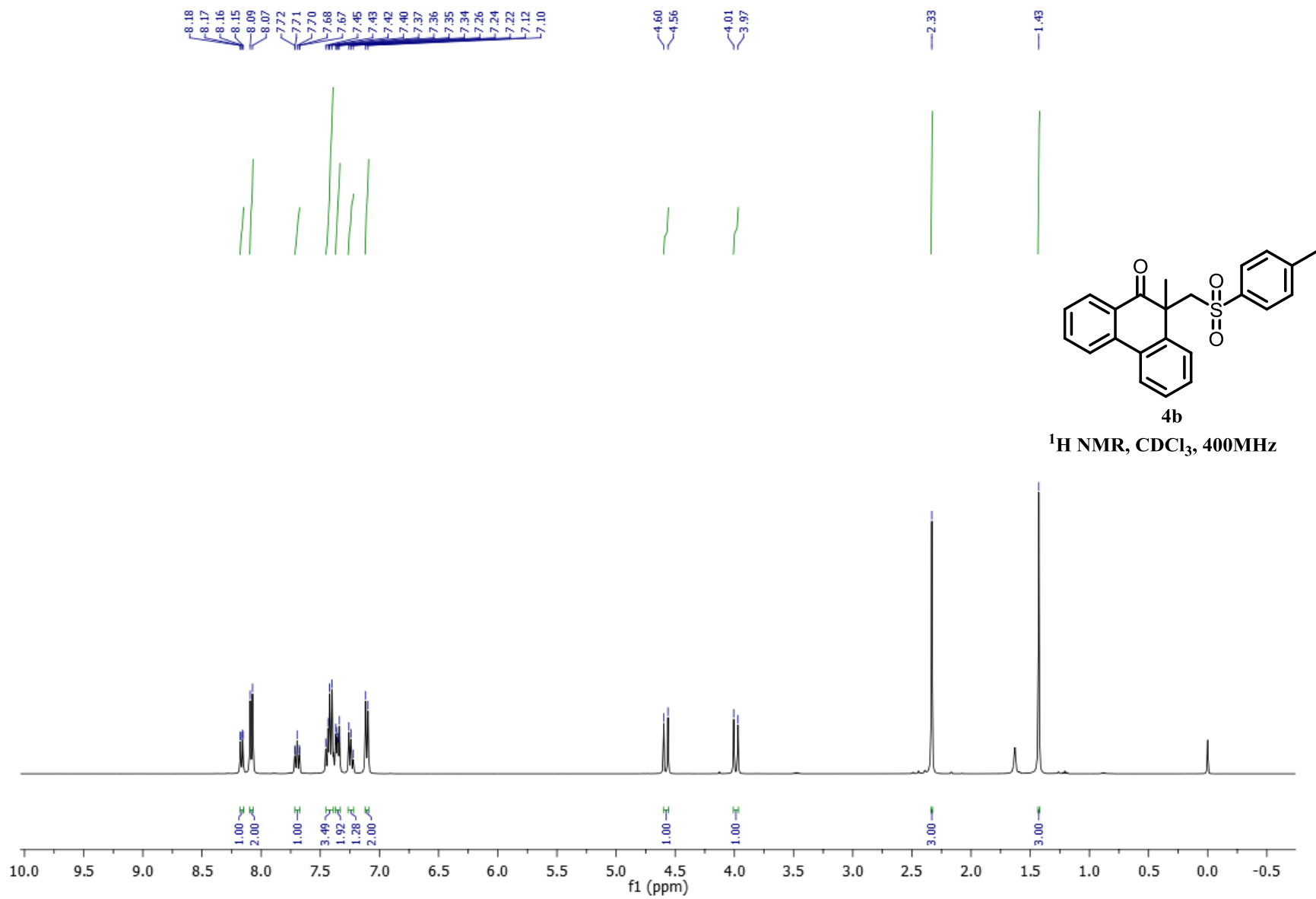


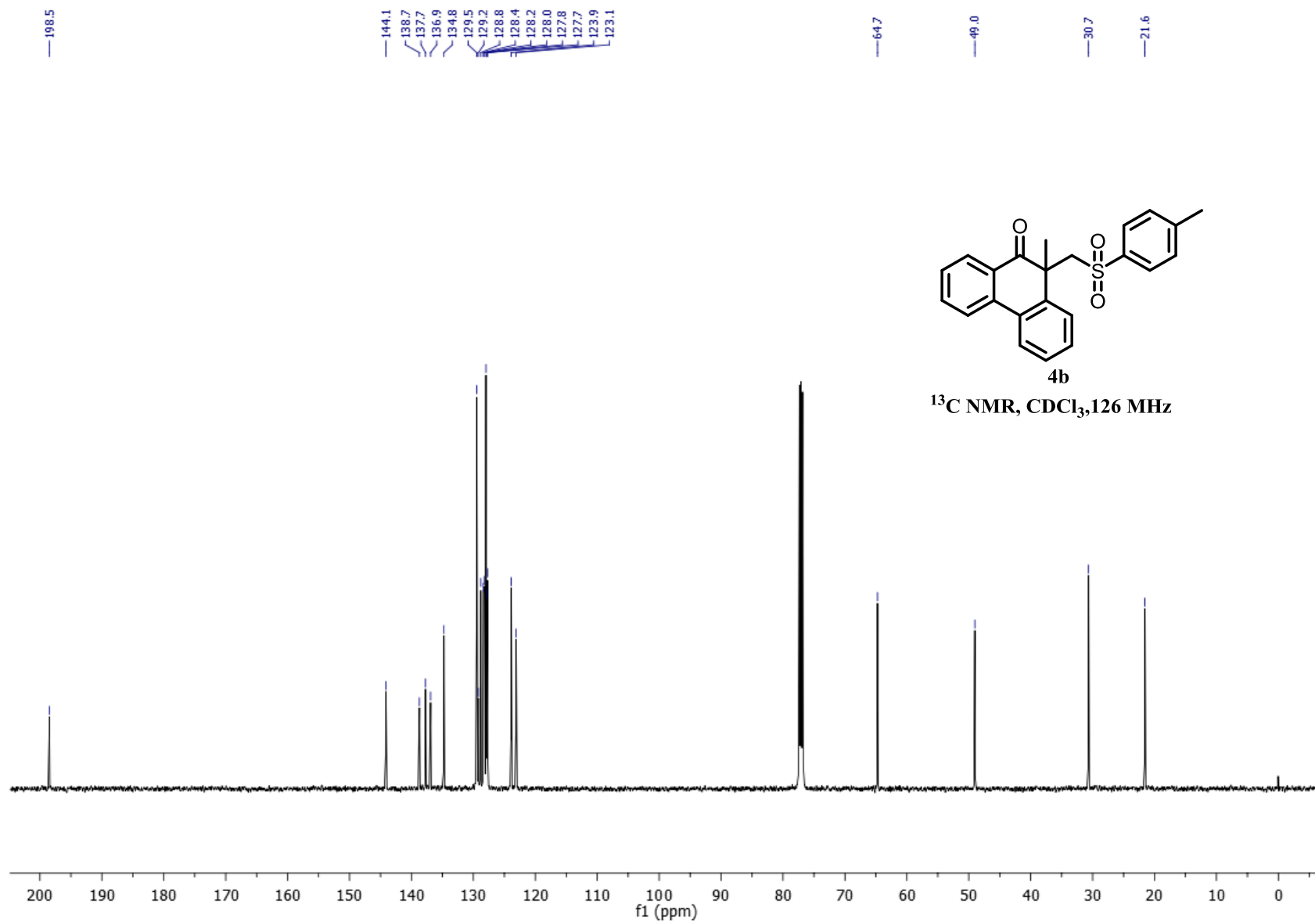
<sup>1</sup>H NMR, DMSO-d<sub>6</sub>, 400 MHz

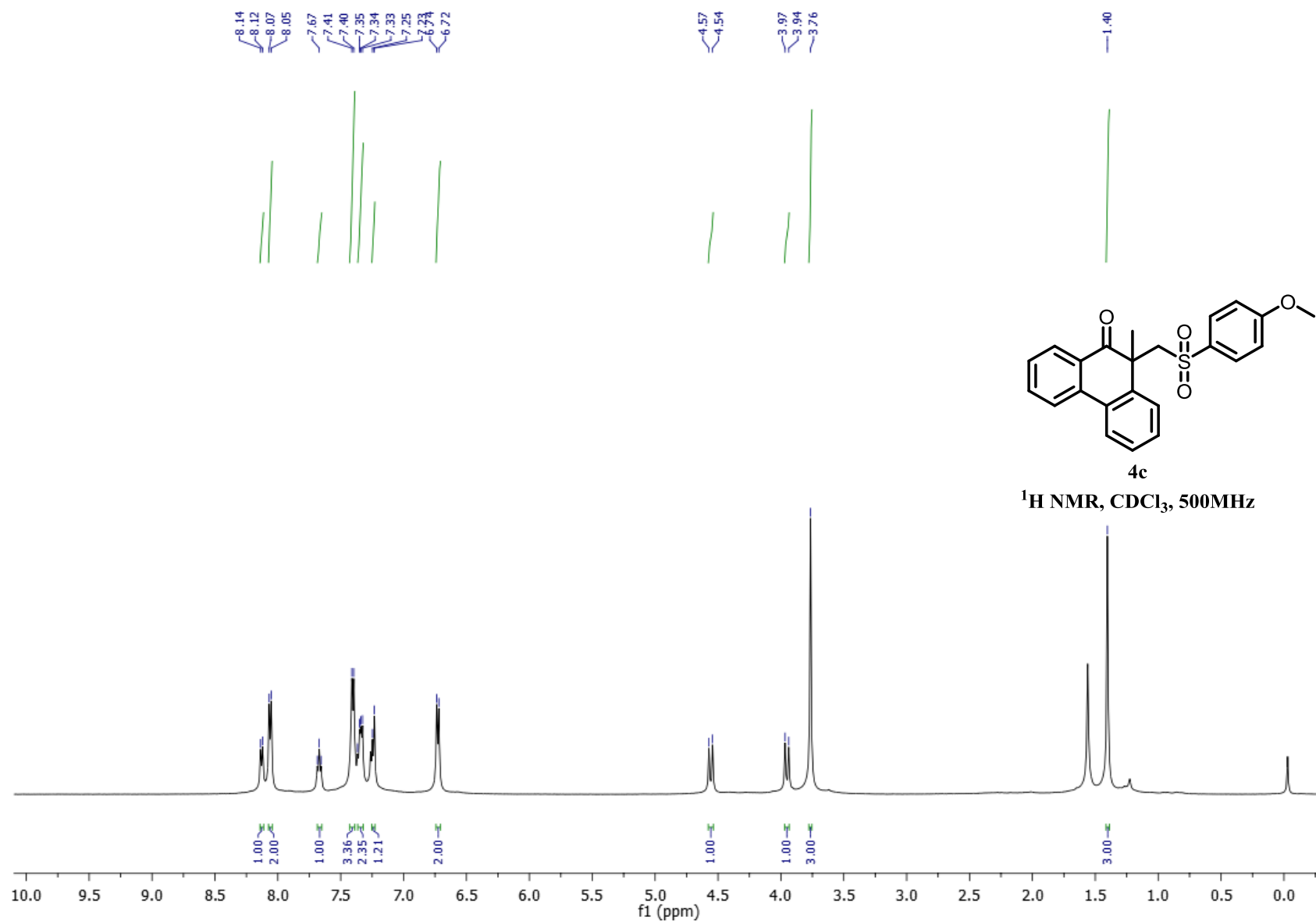




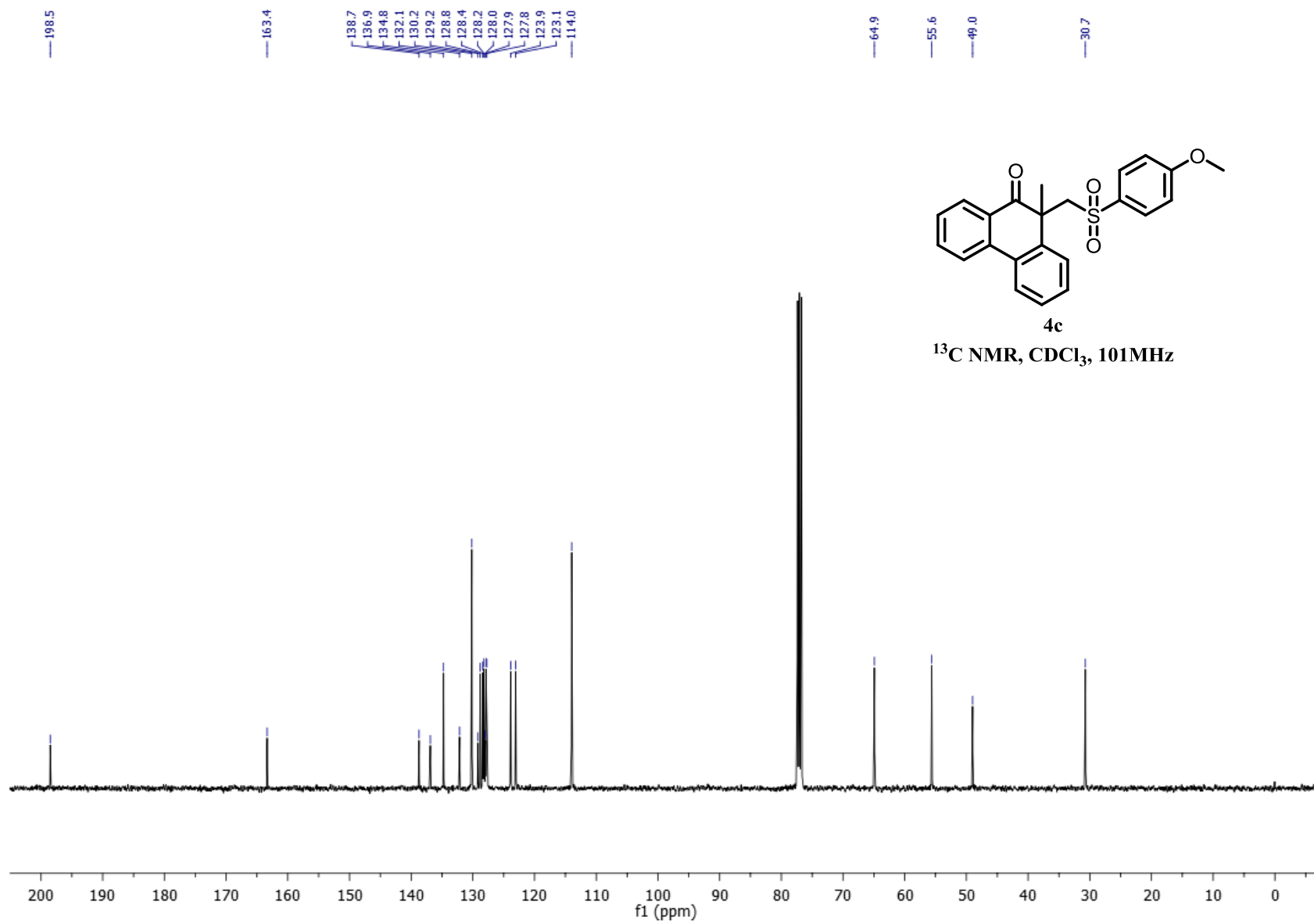


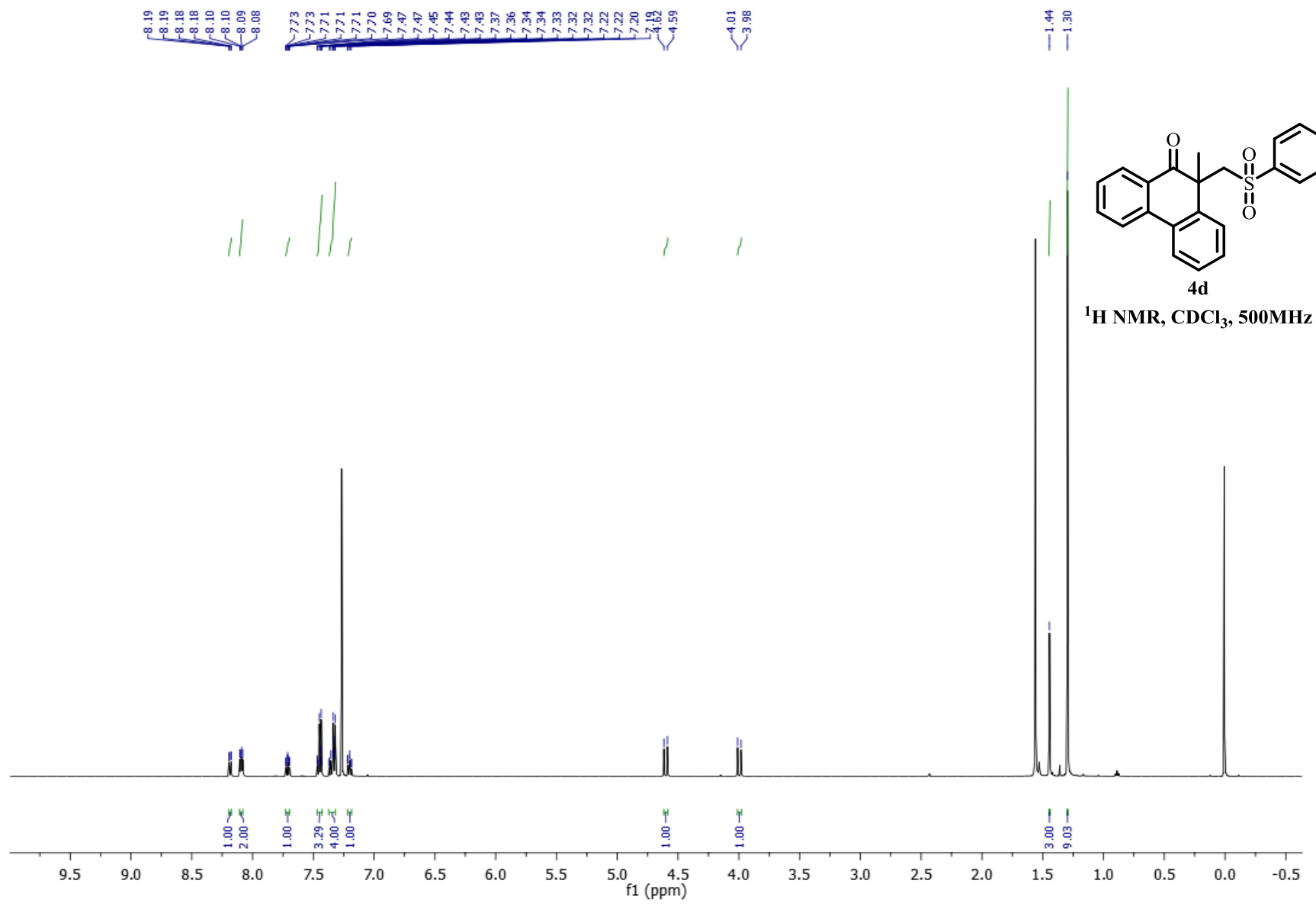


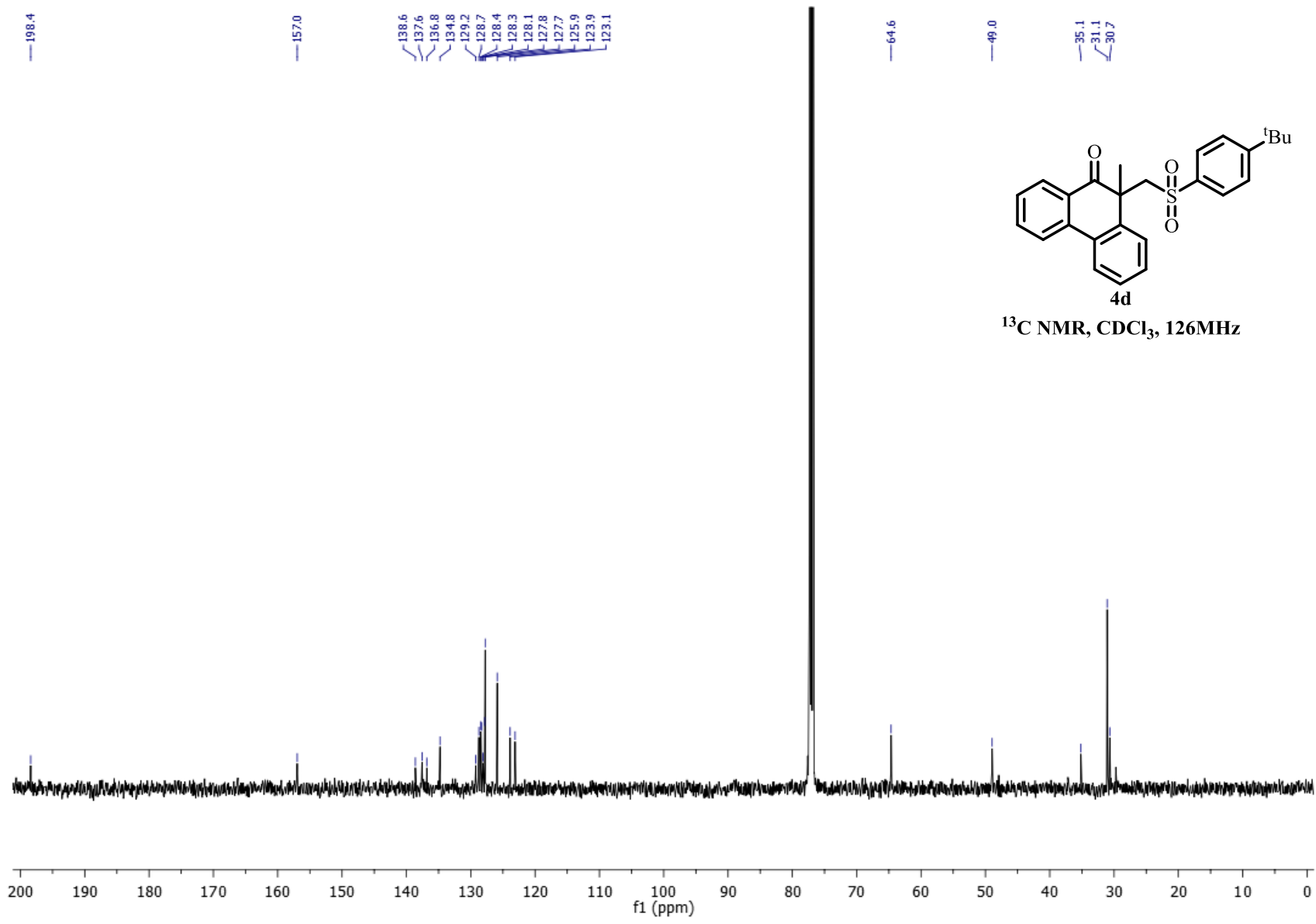


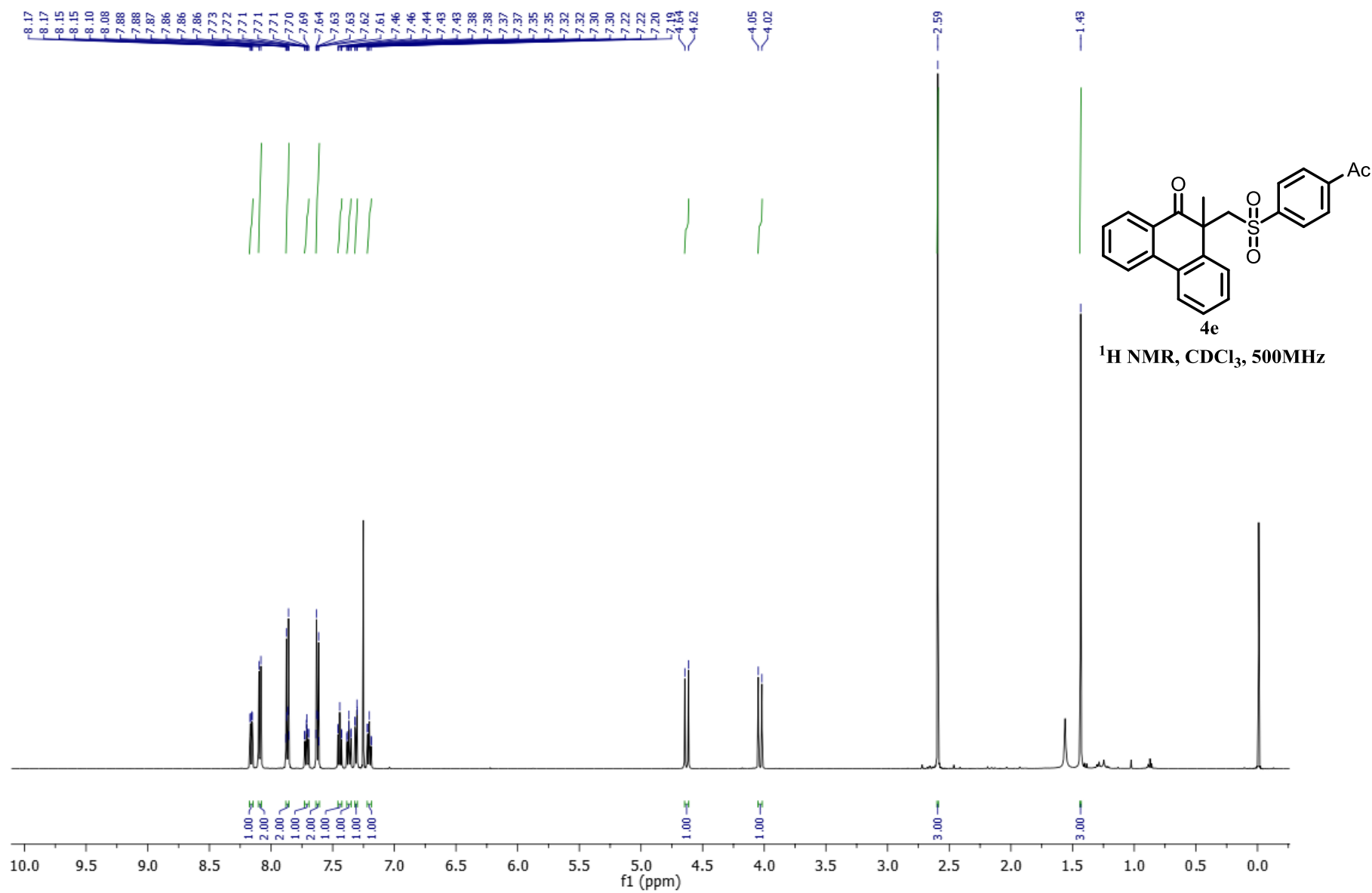


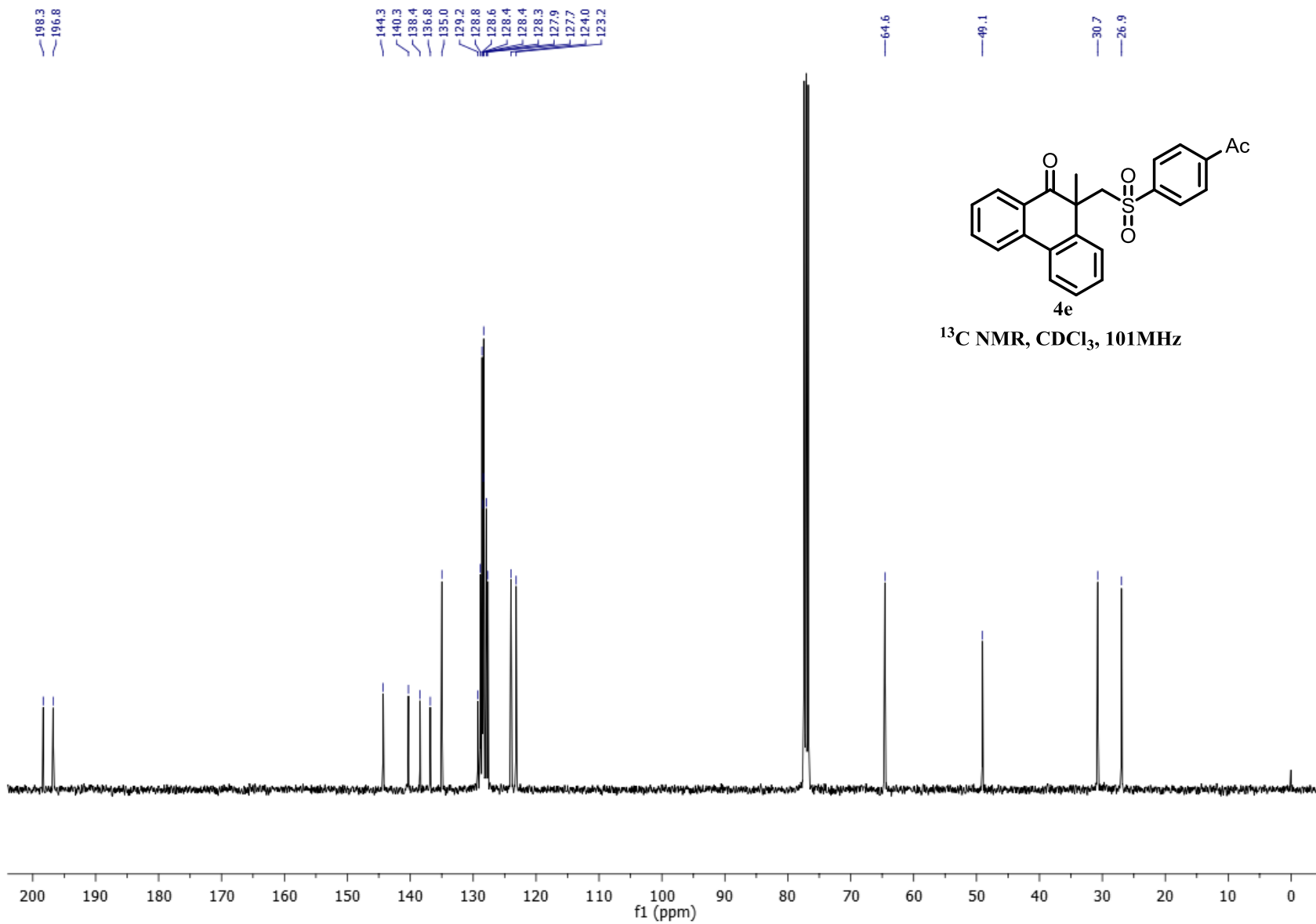


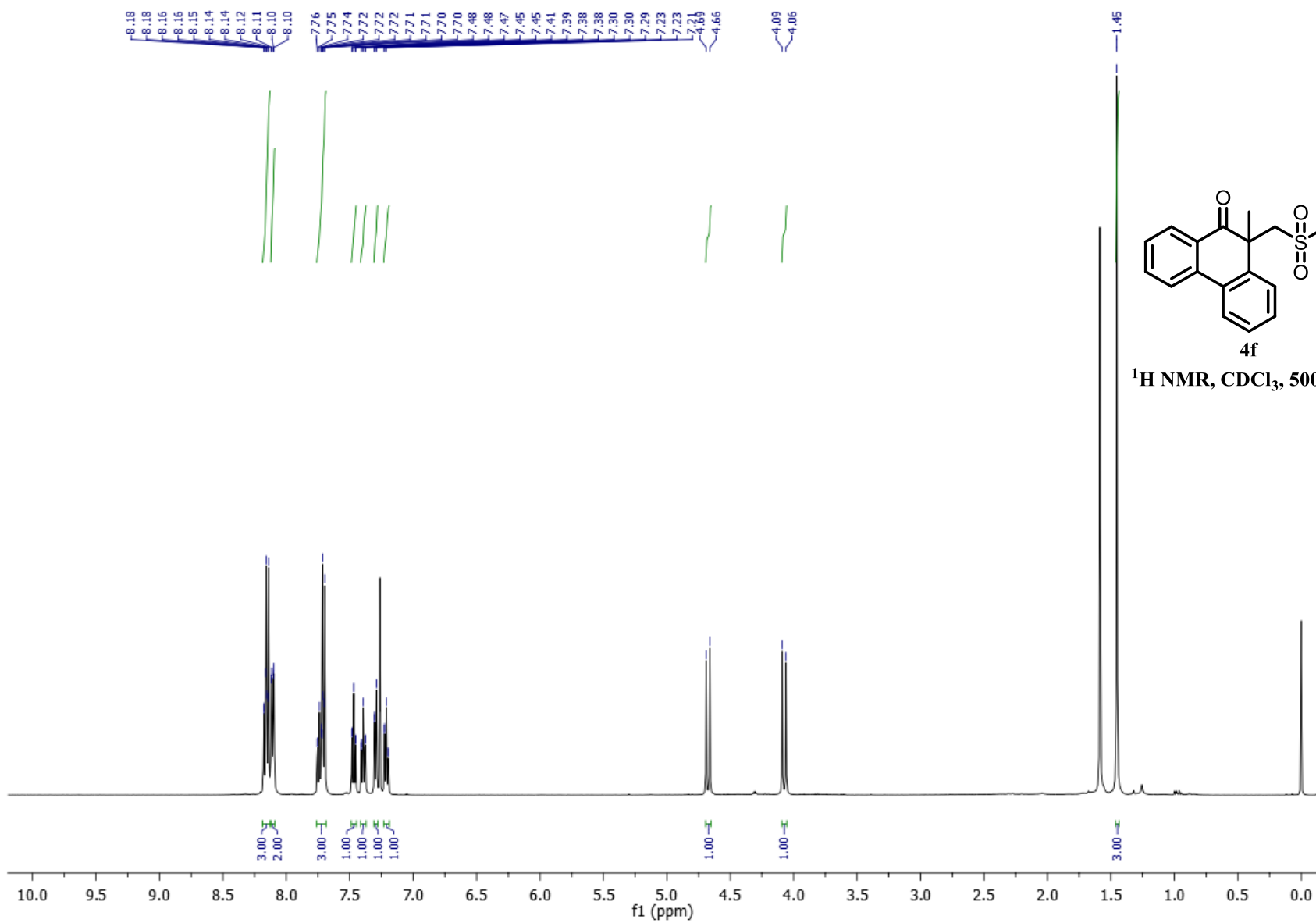


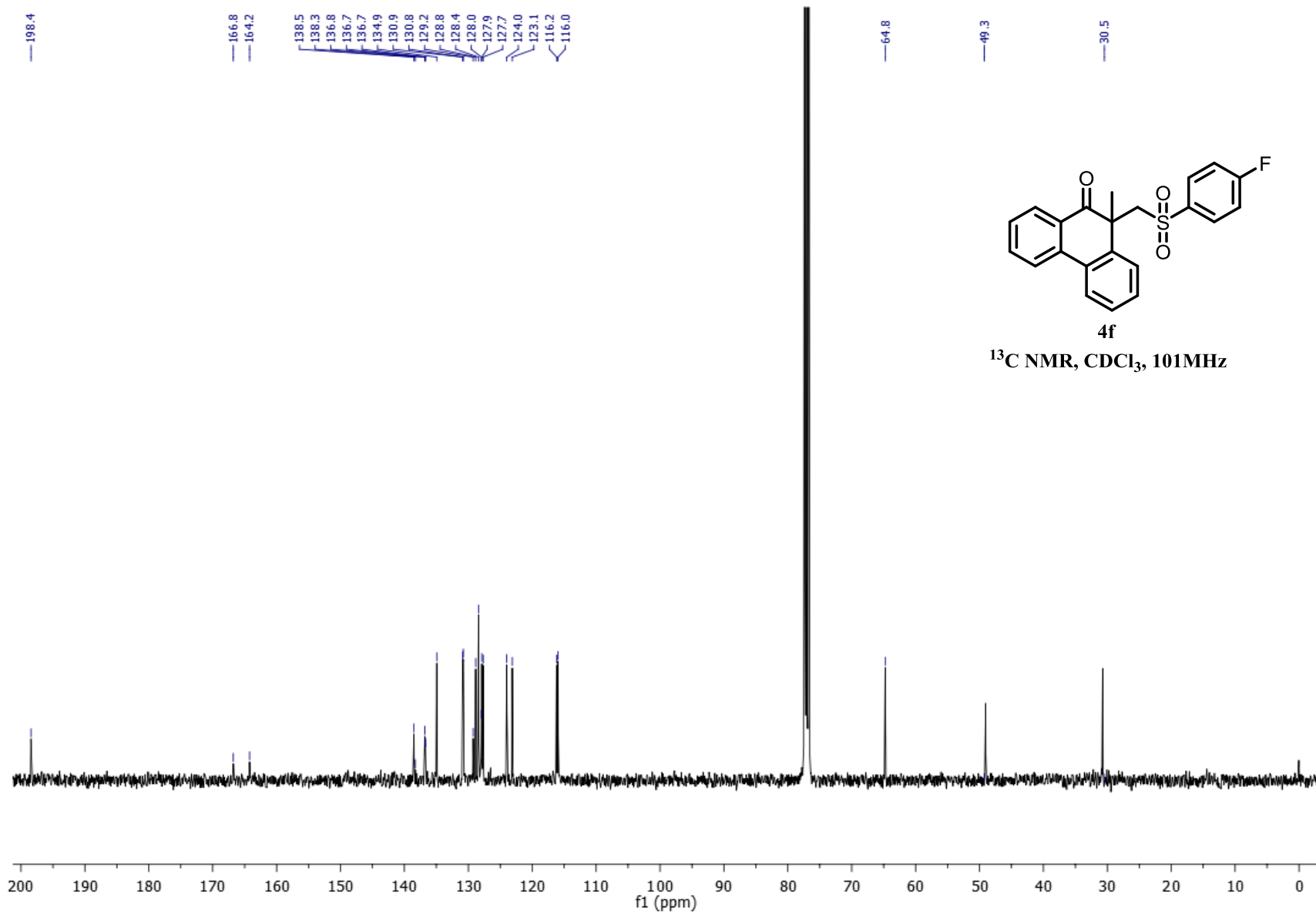


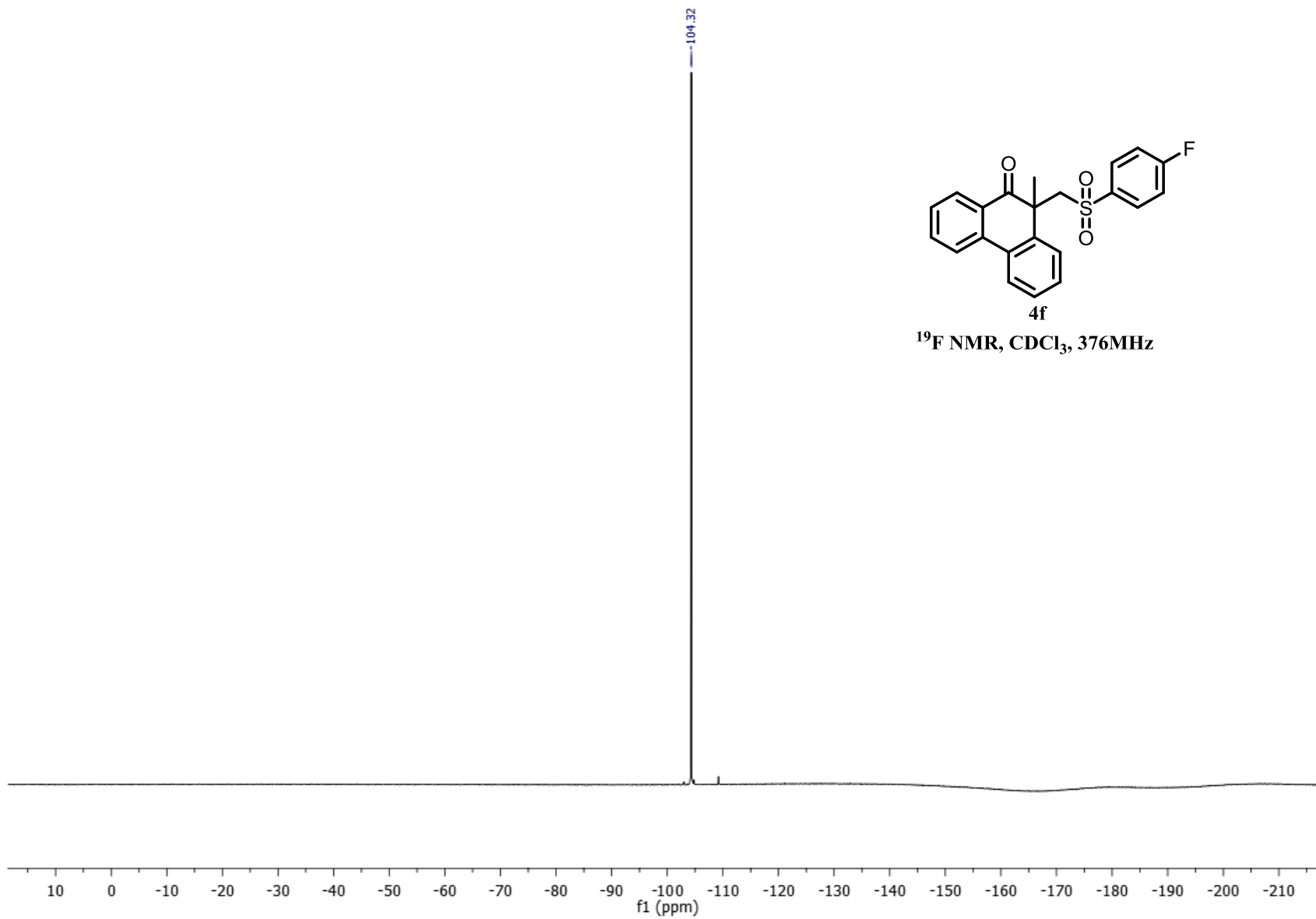




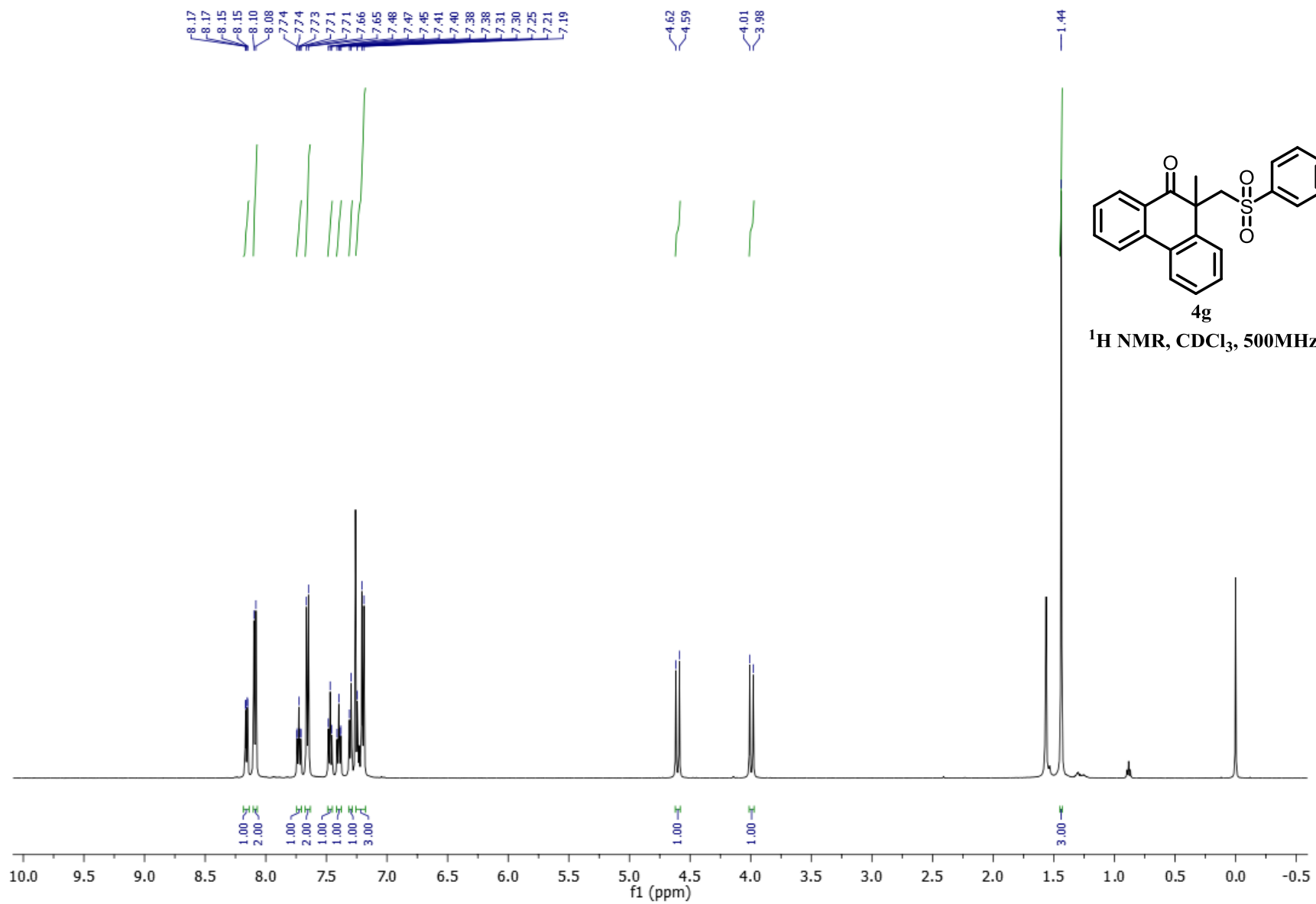


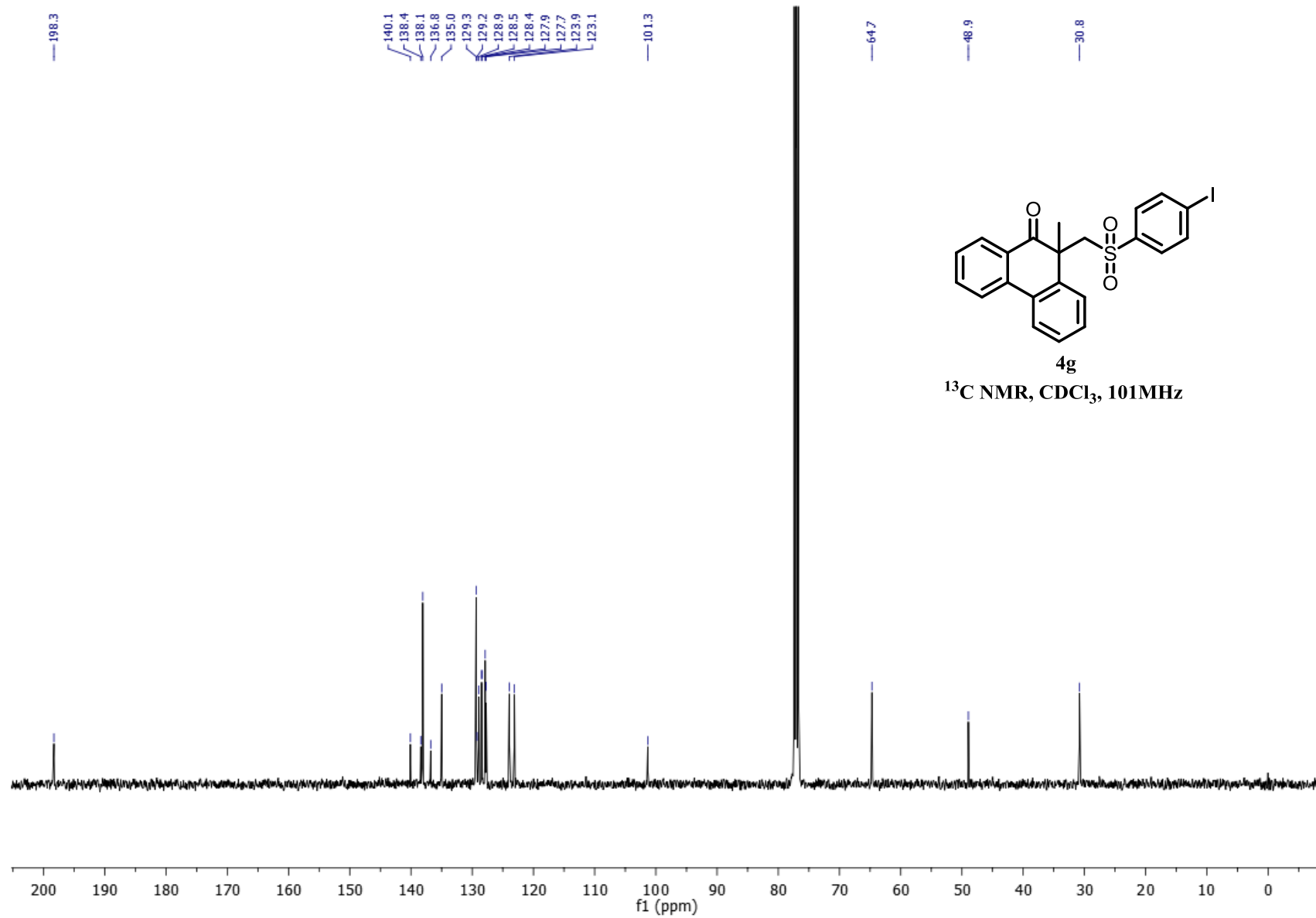


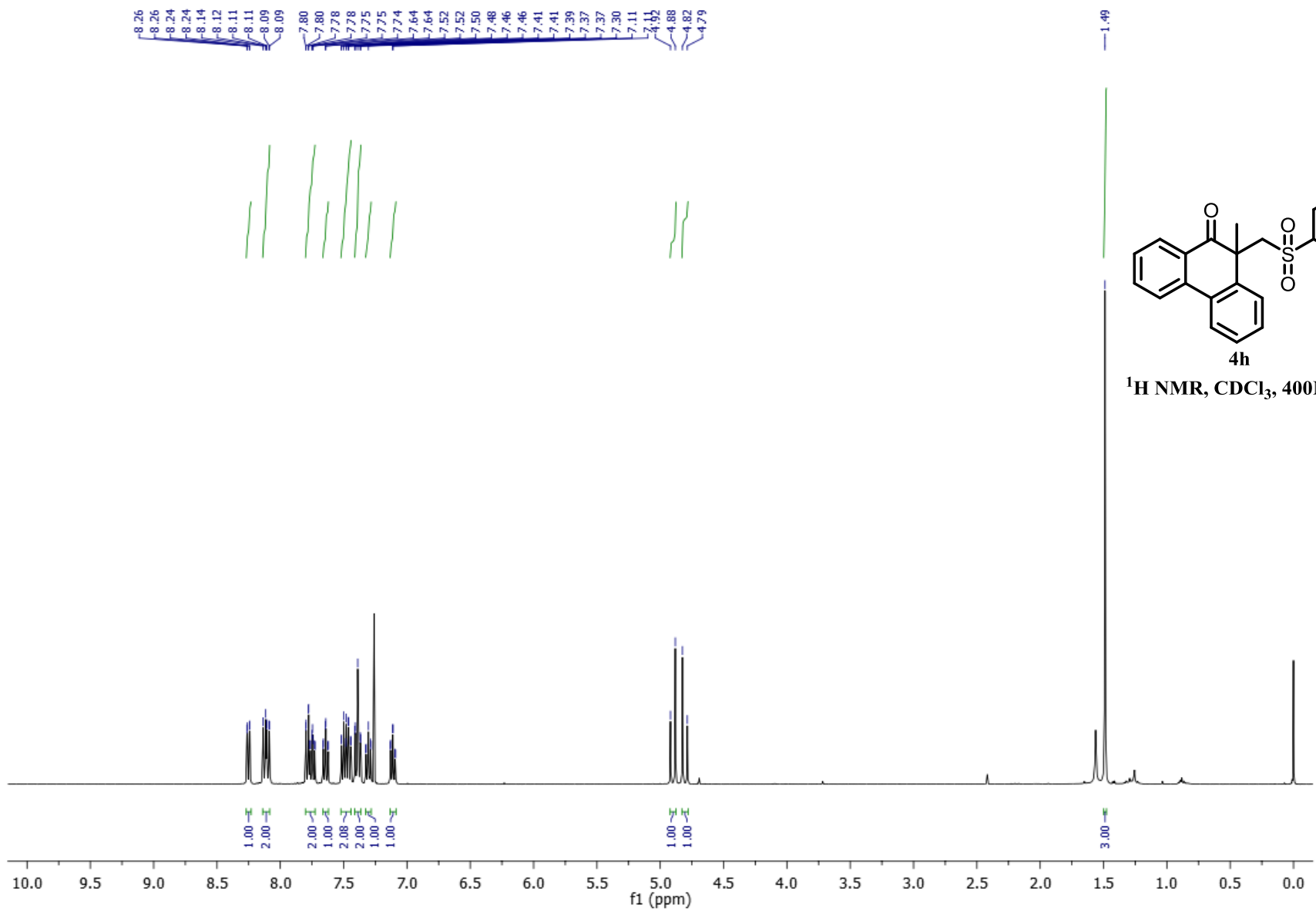


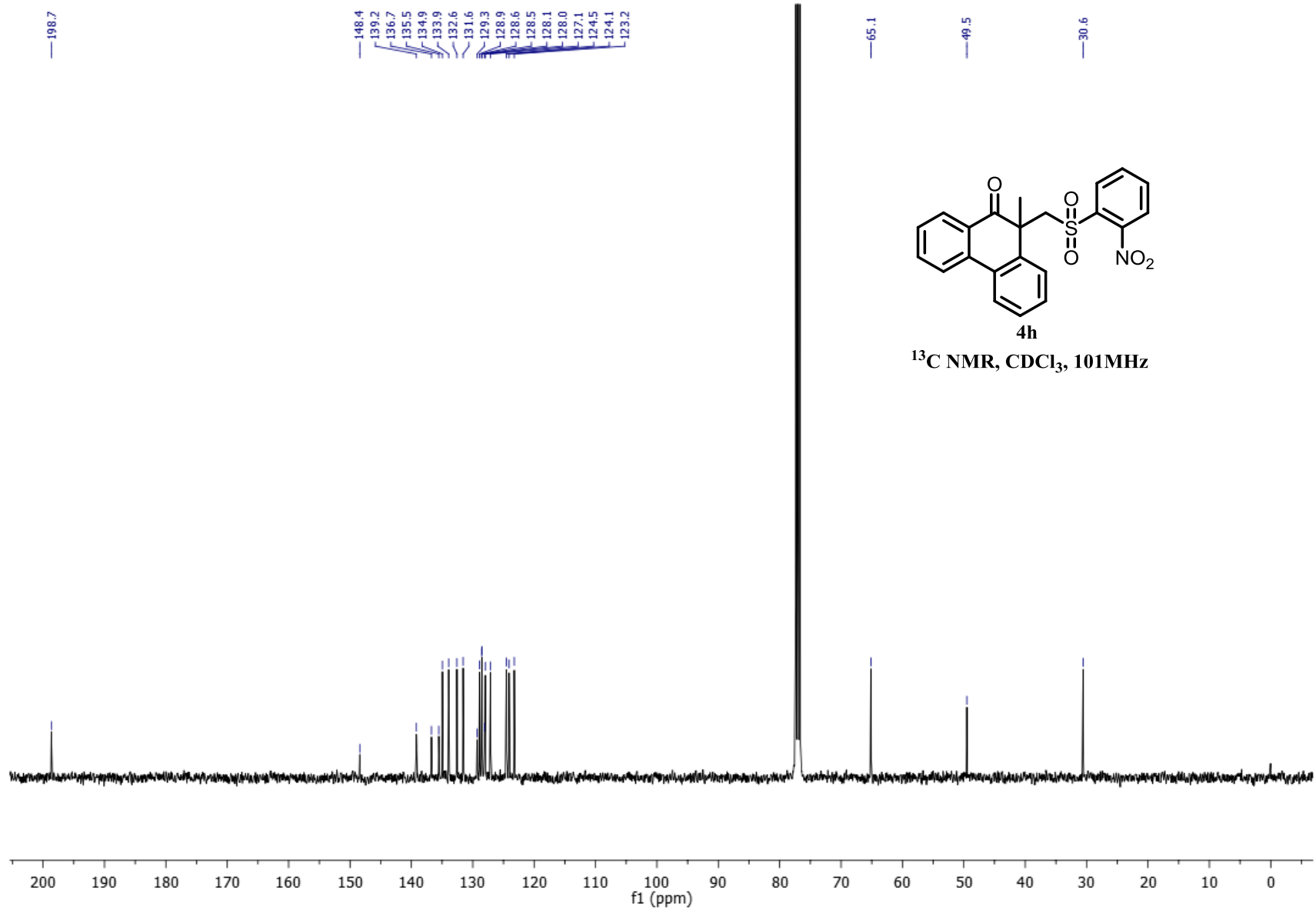


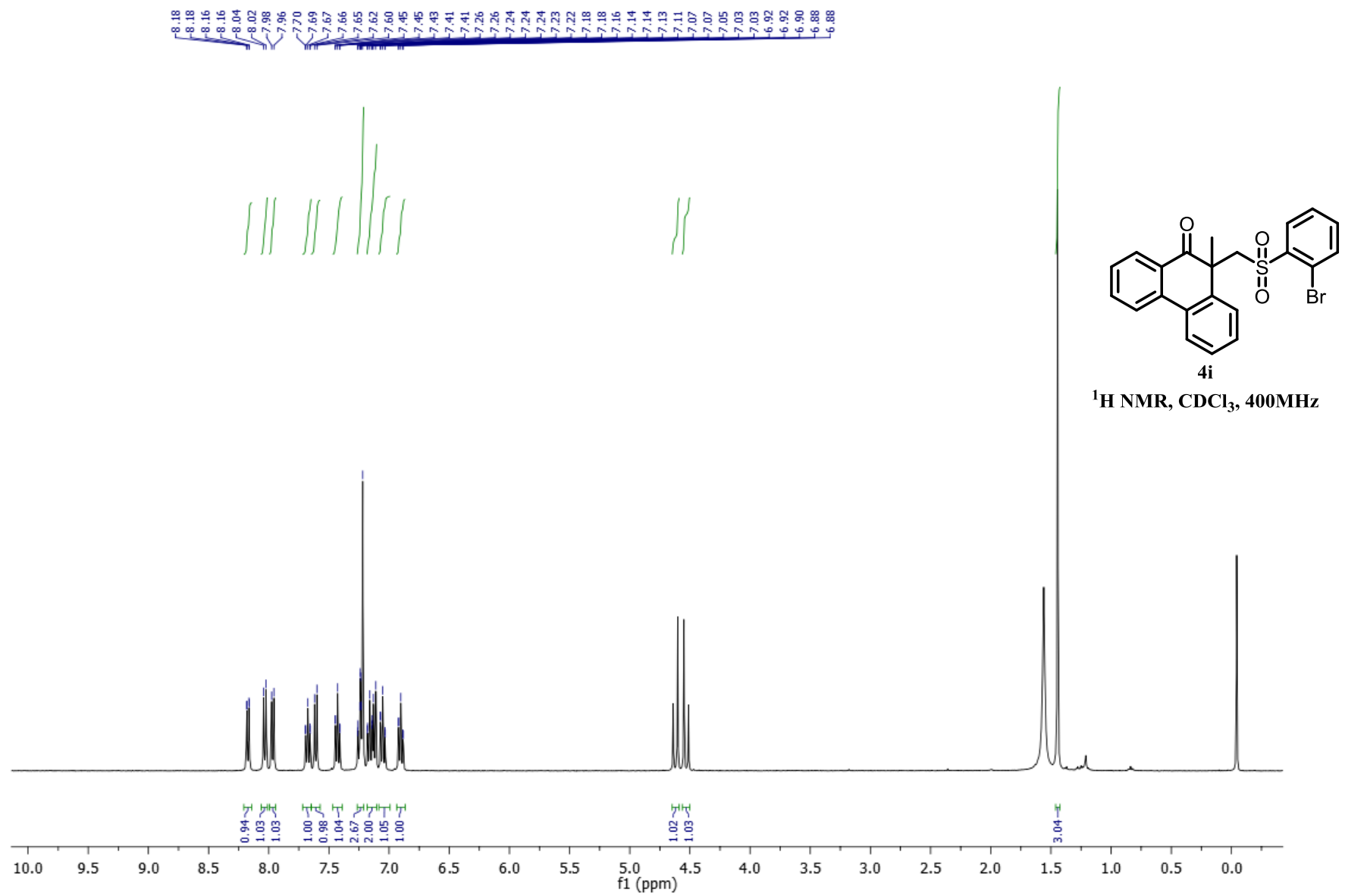


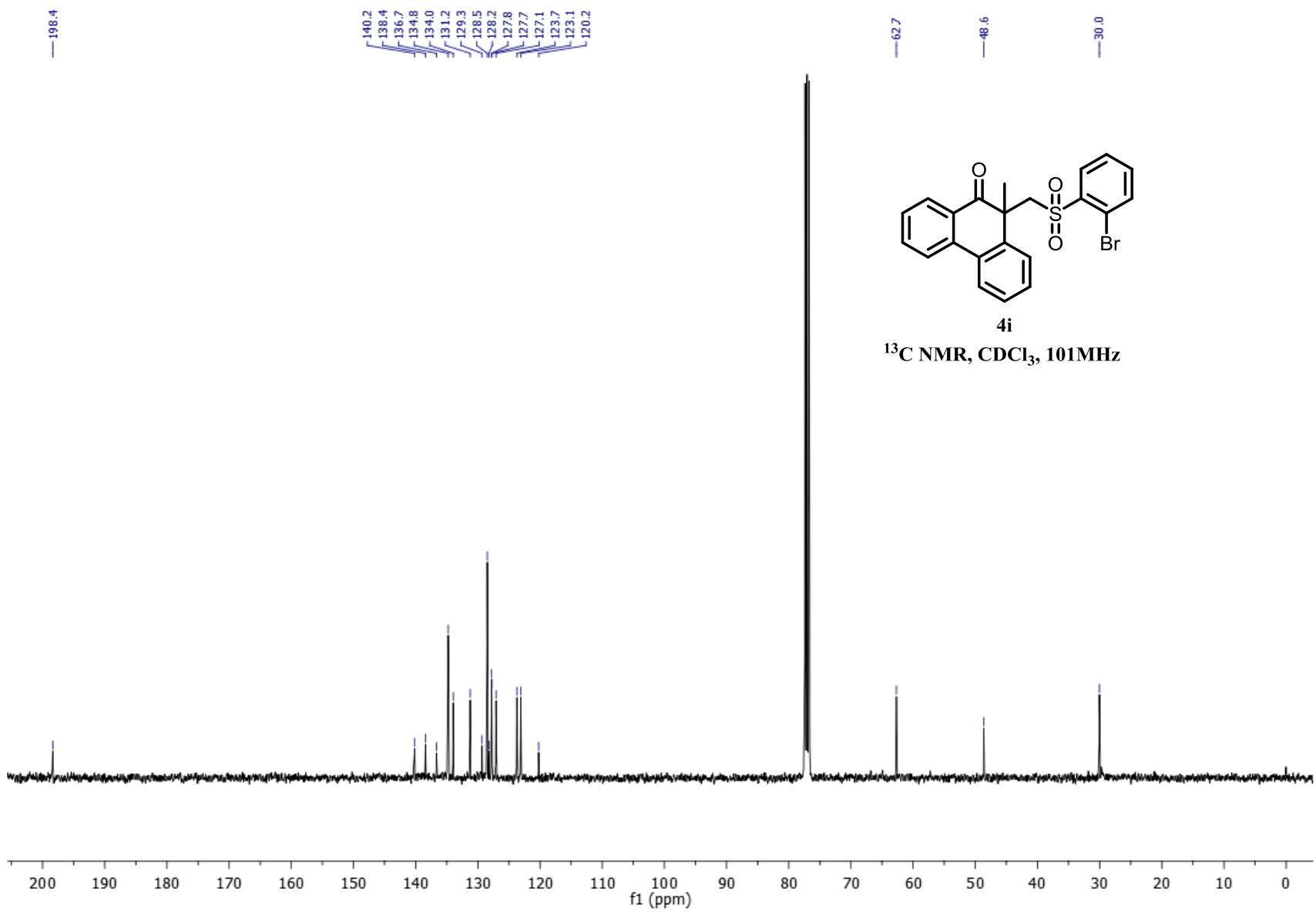


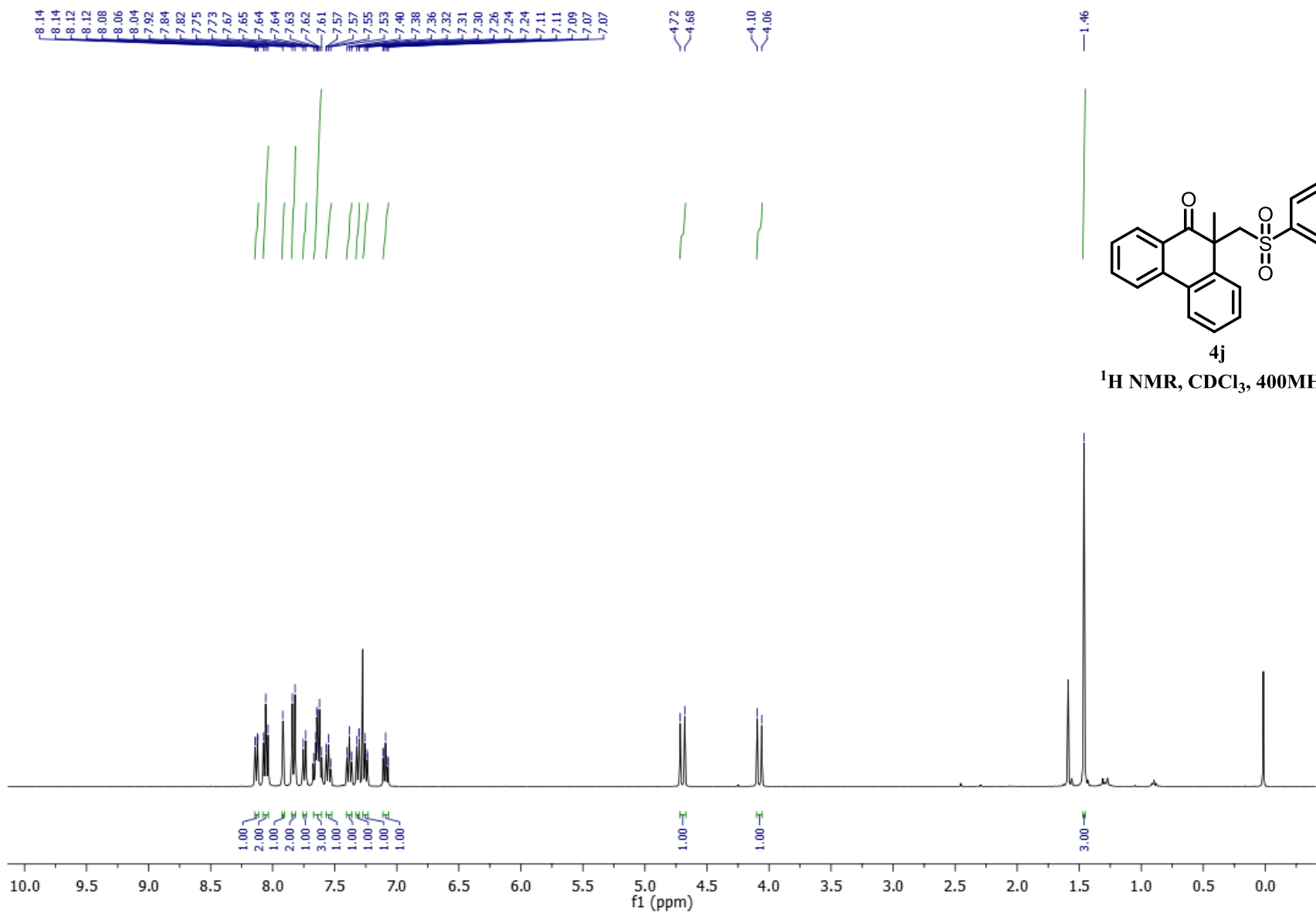


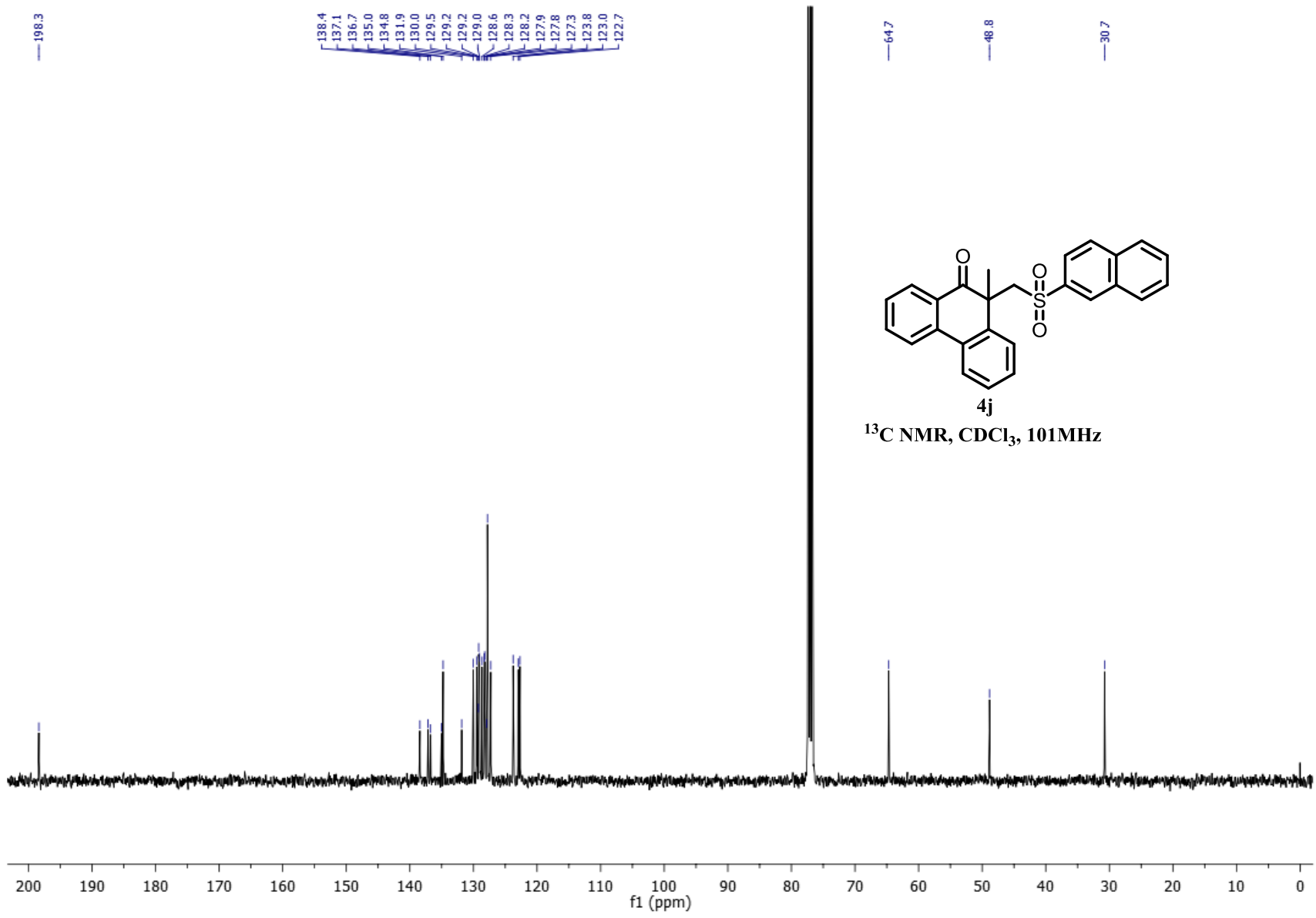




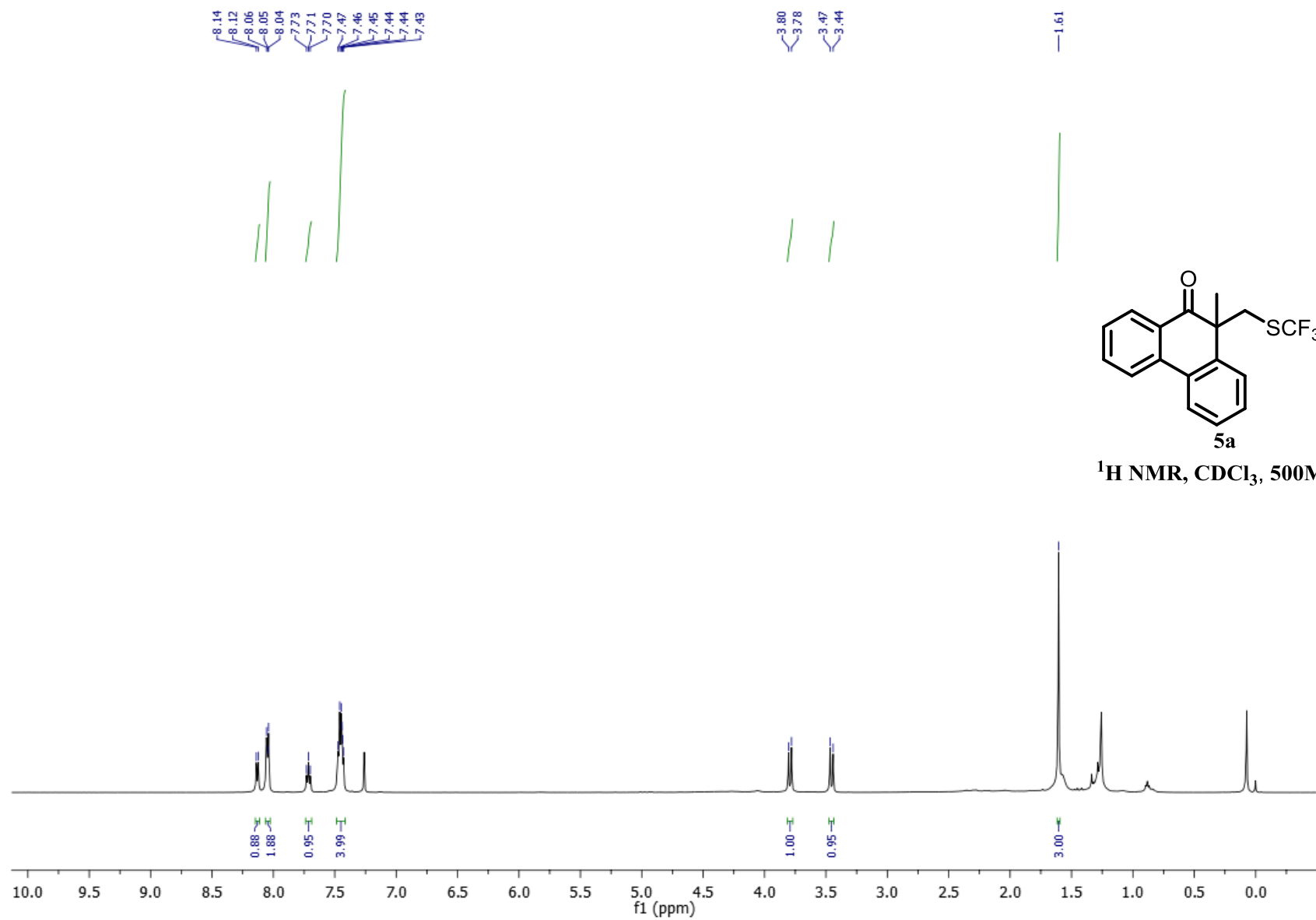


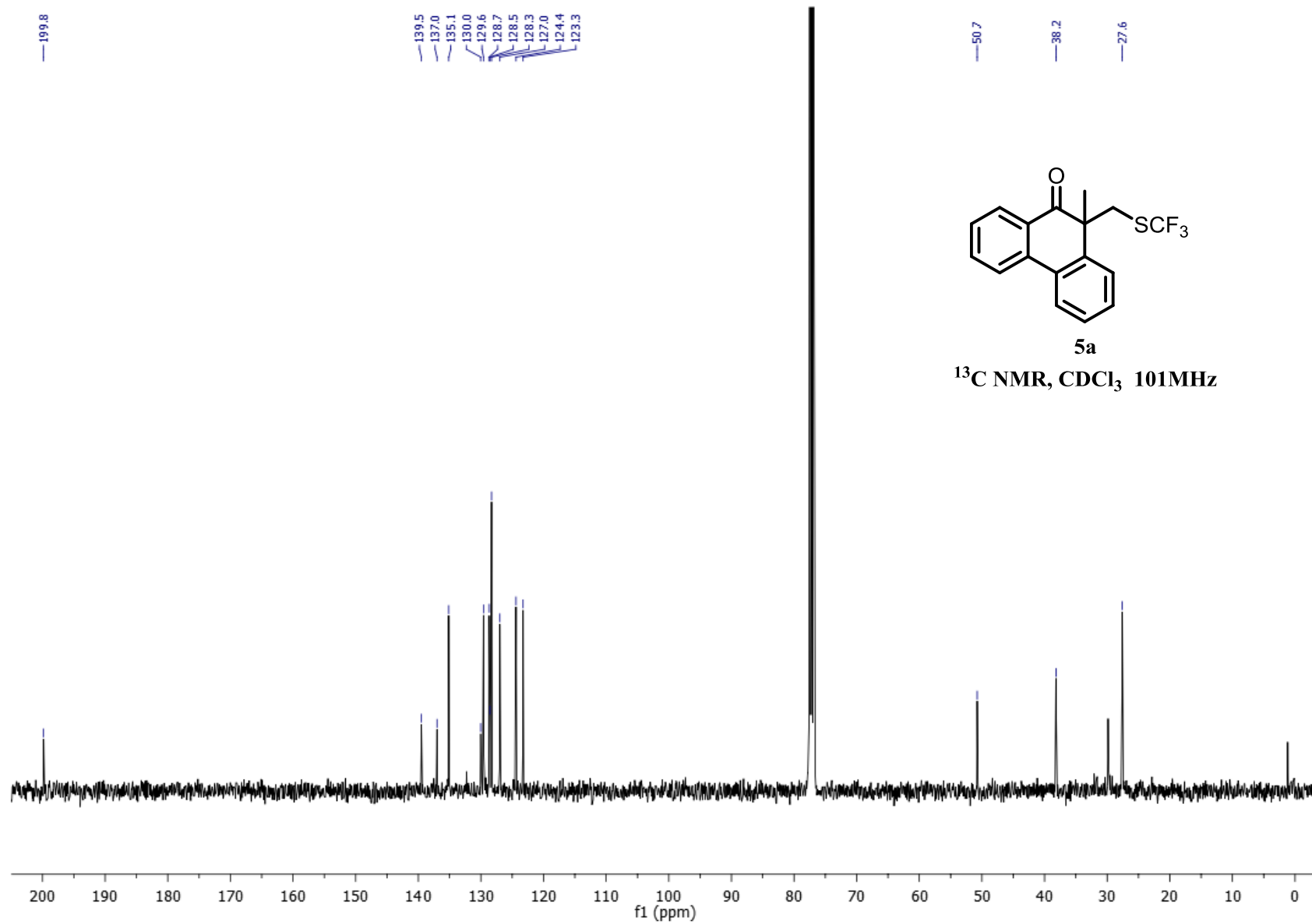


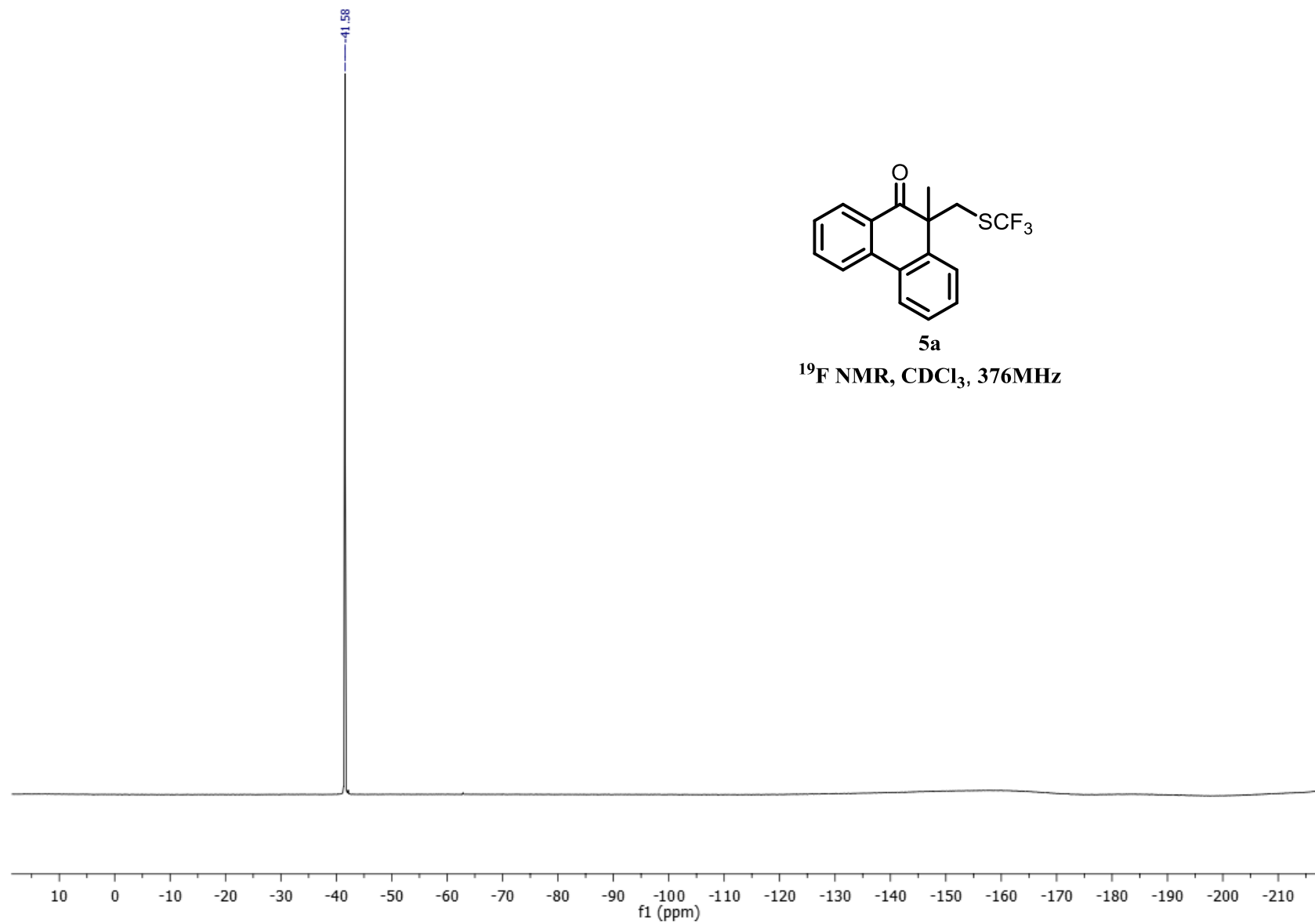


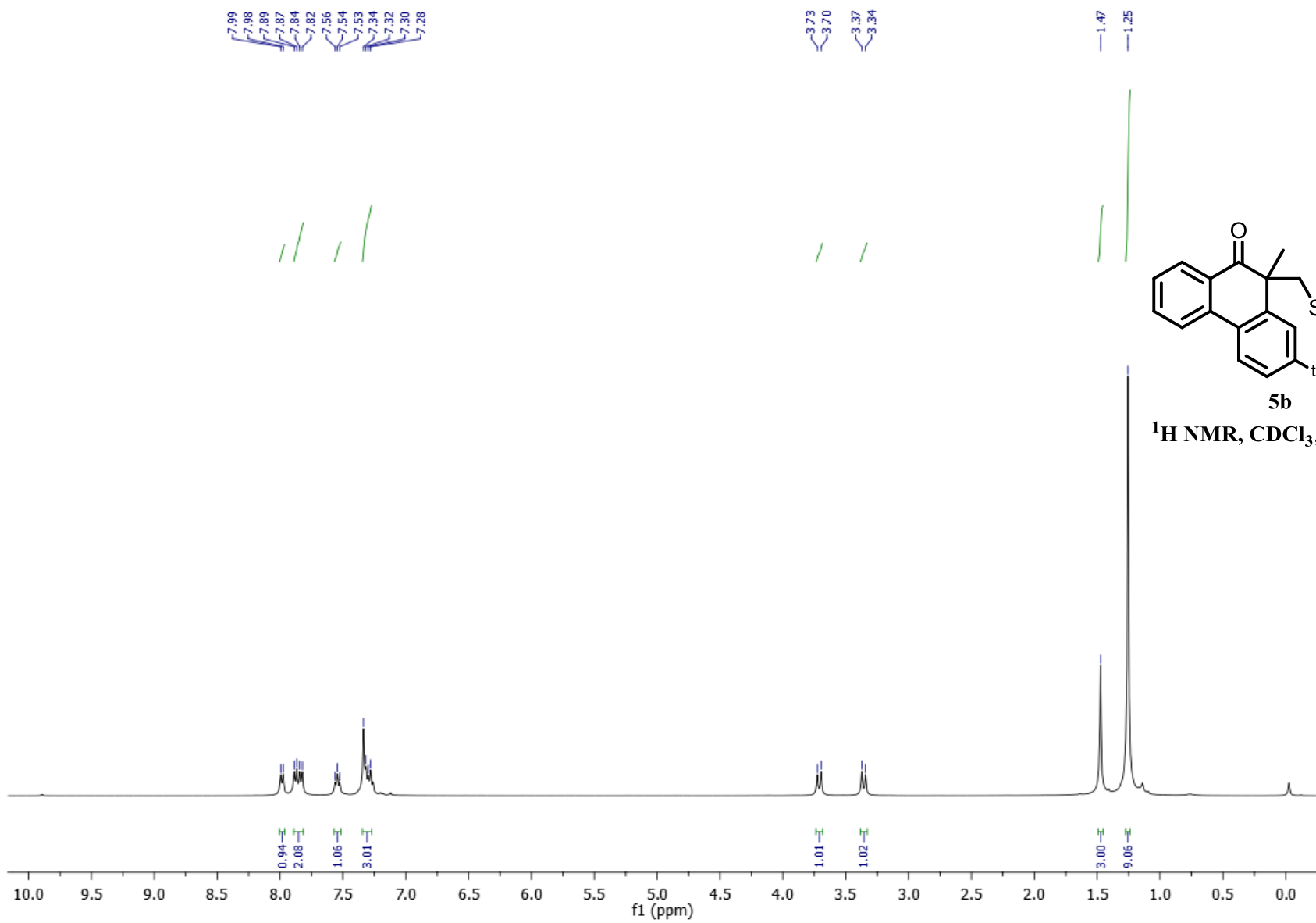


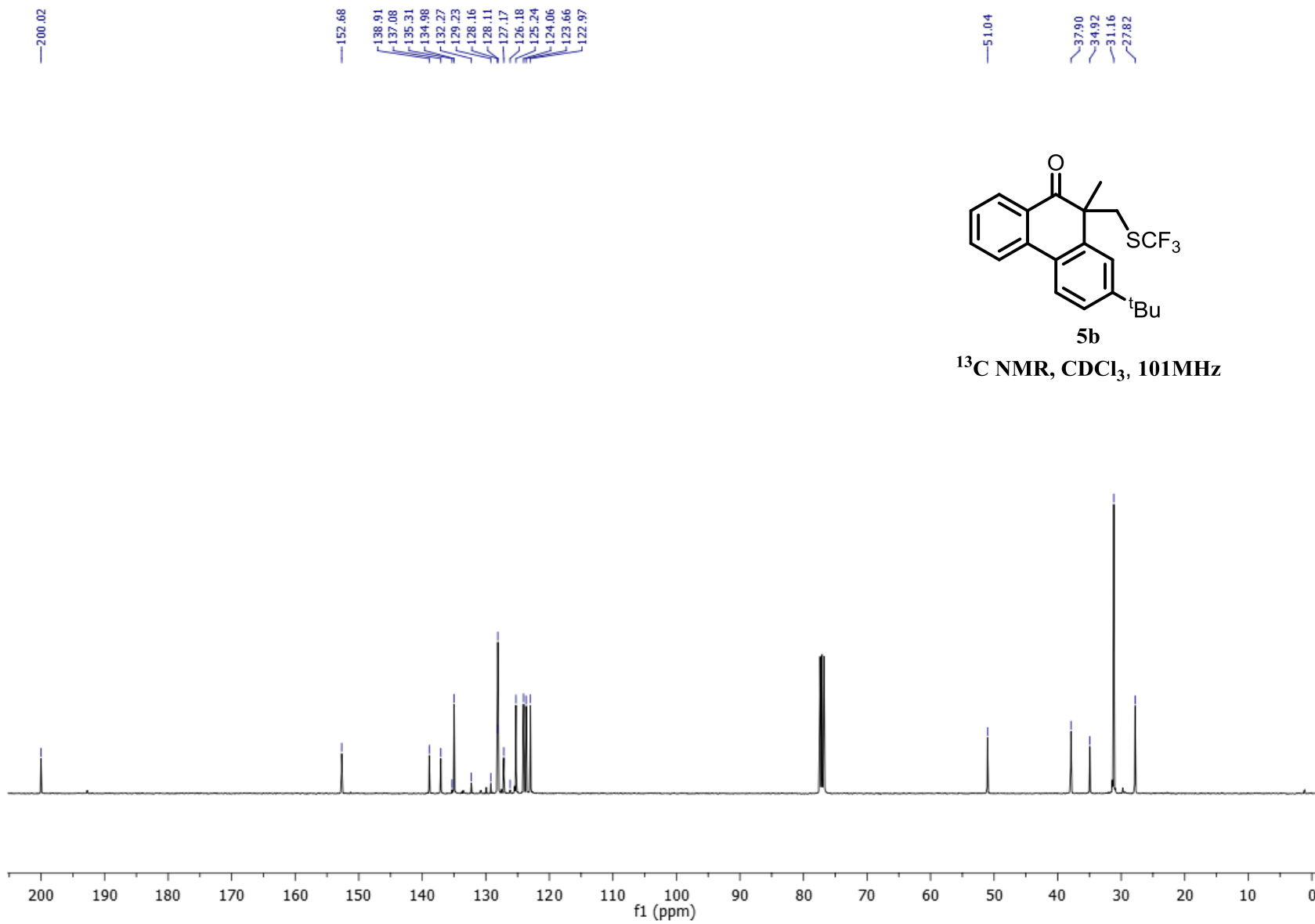


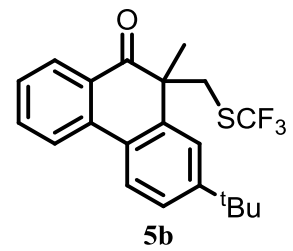




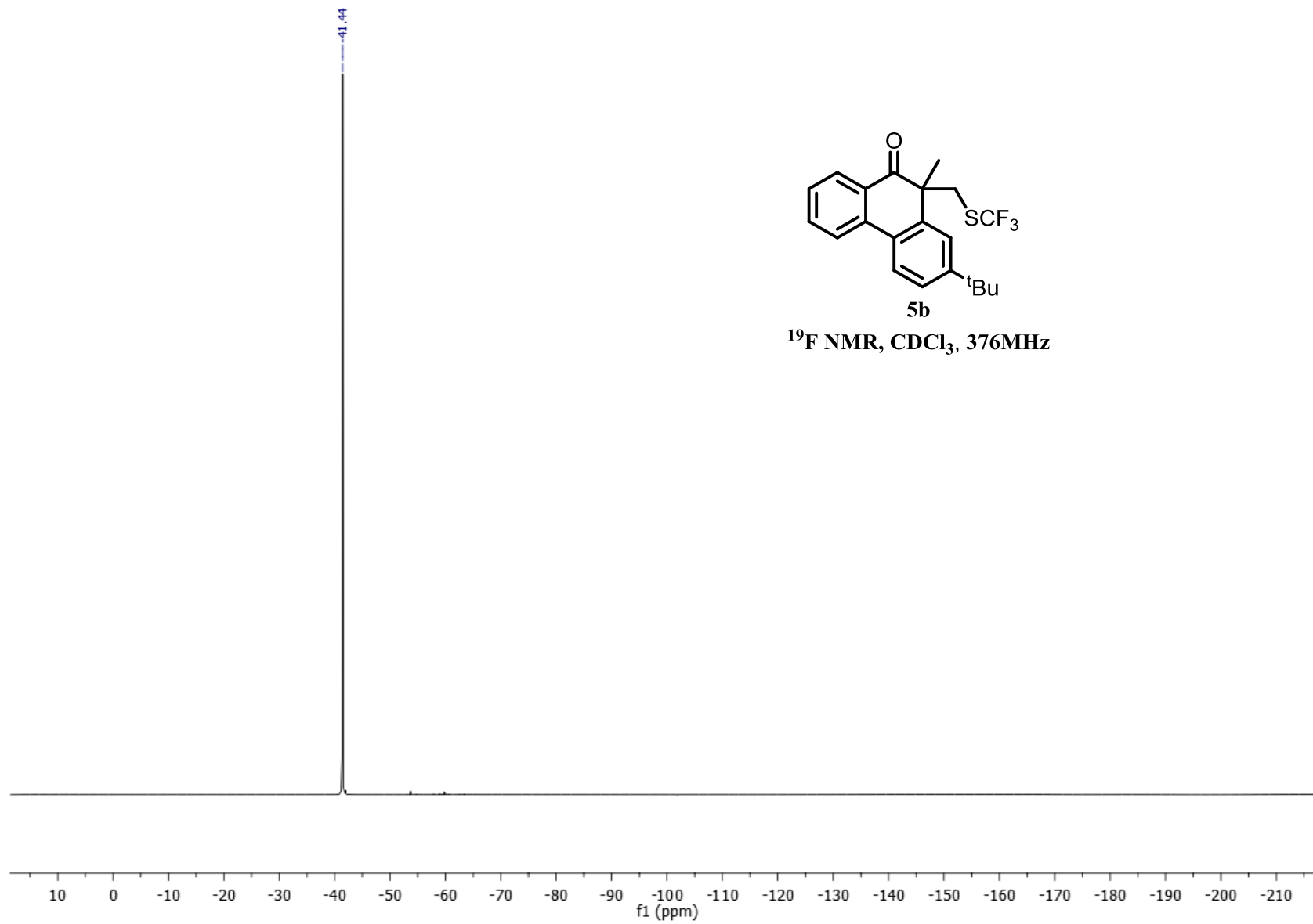


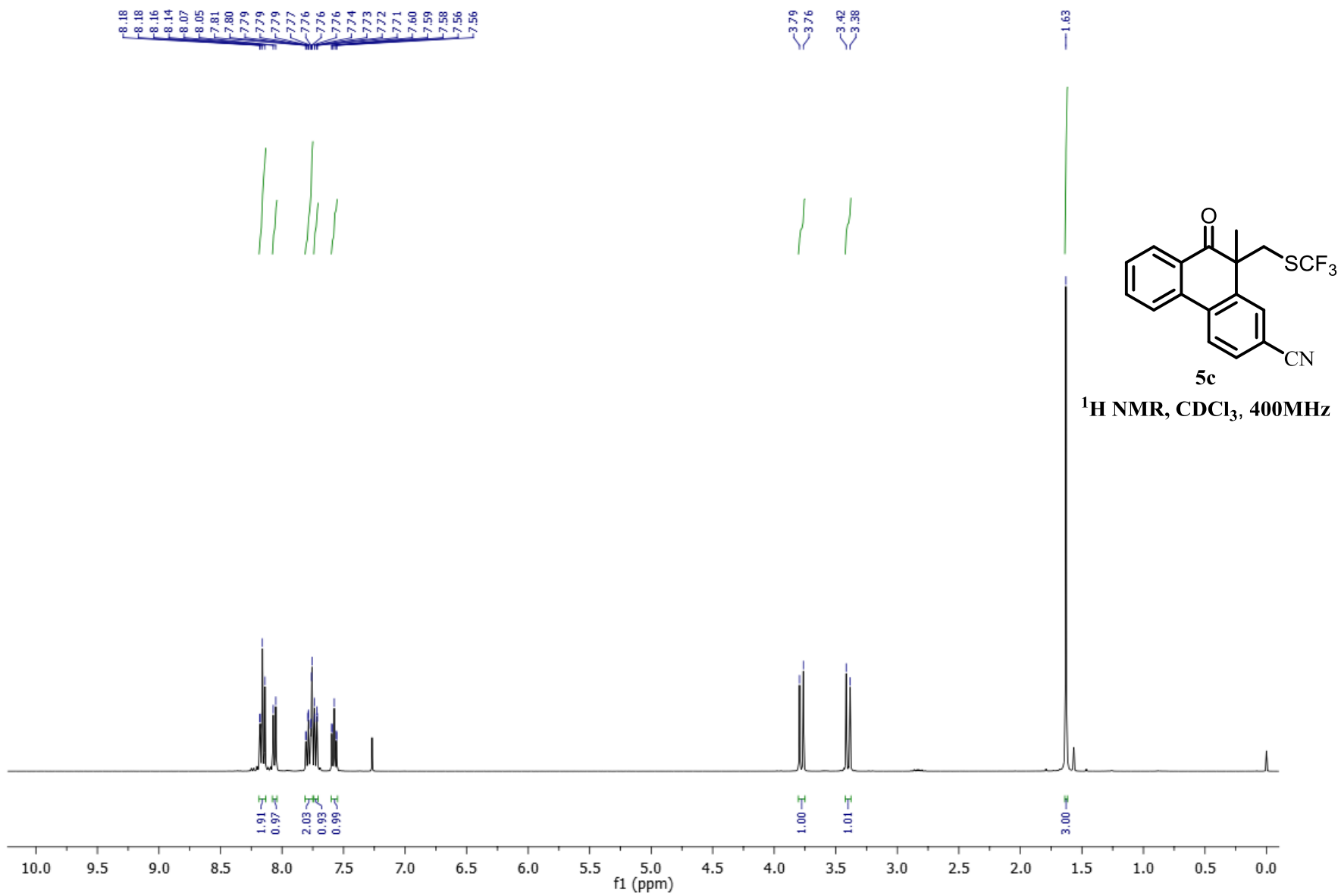


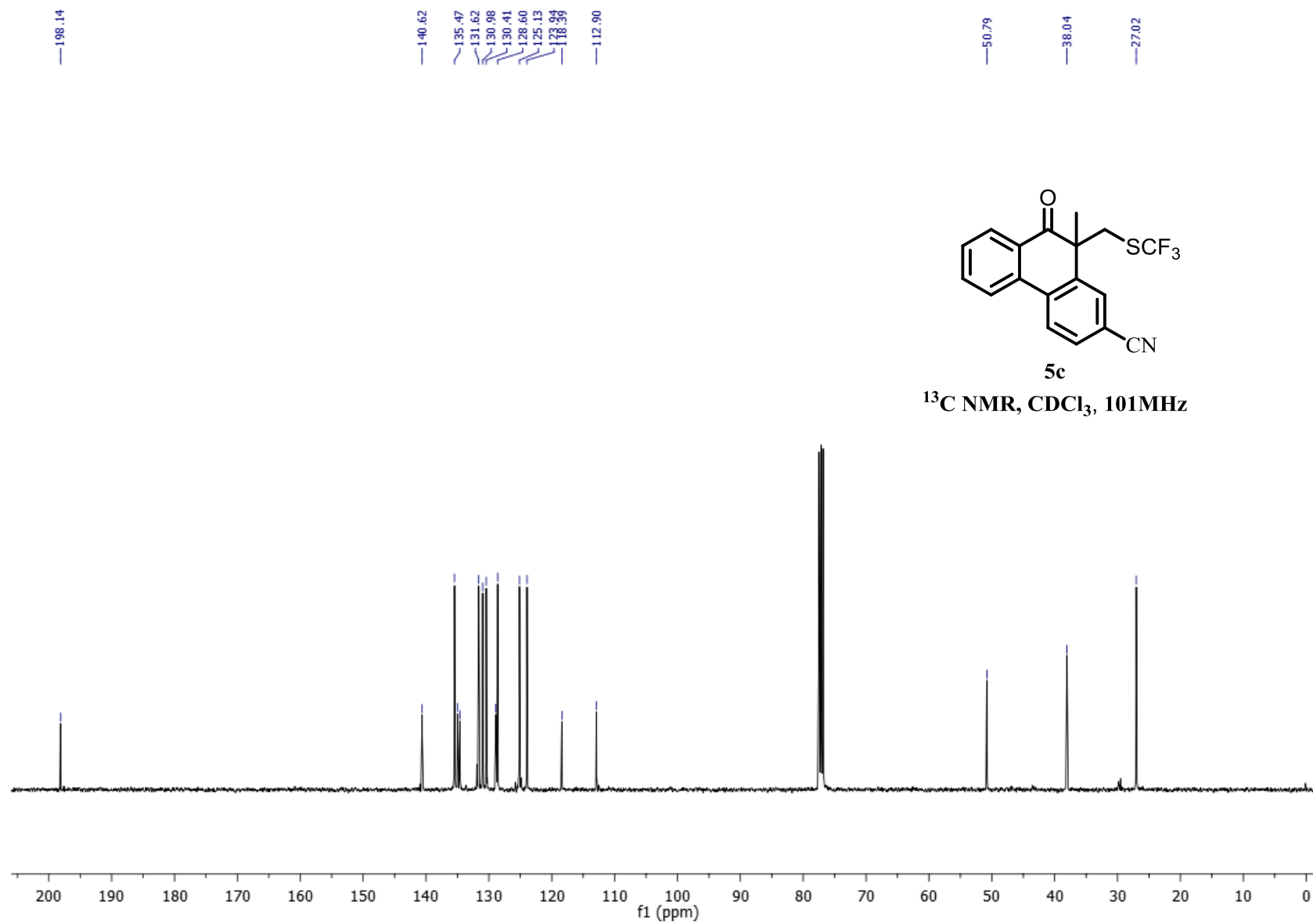




<sup>19</sup>F NMR, CDCl<sub>3</sub>, 376MHz

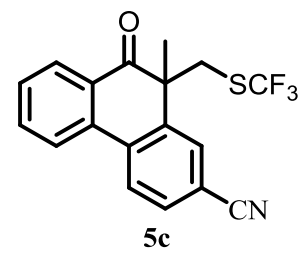




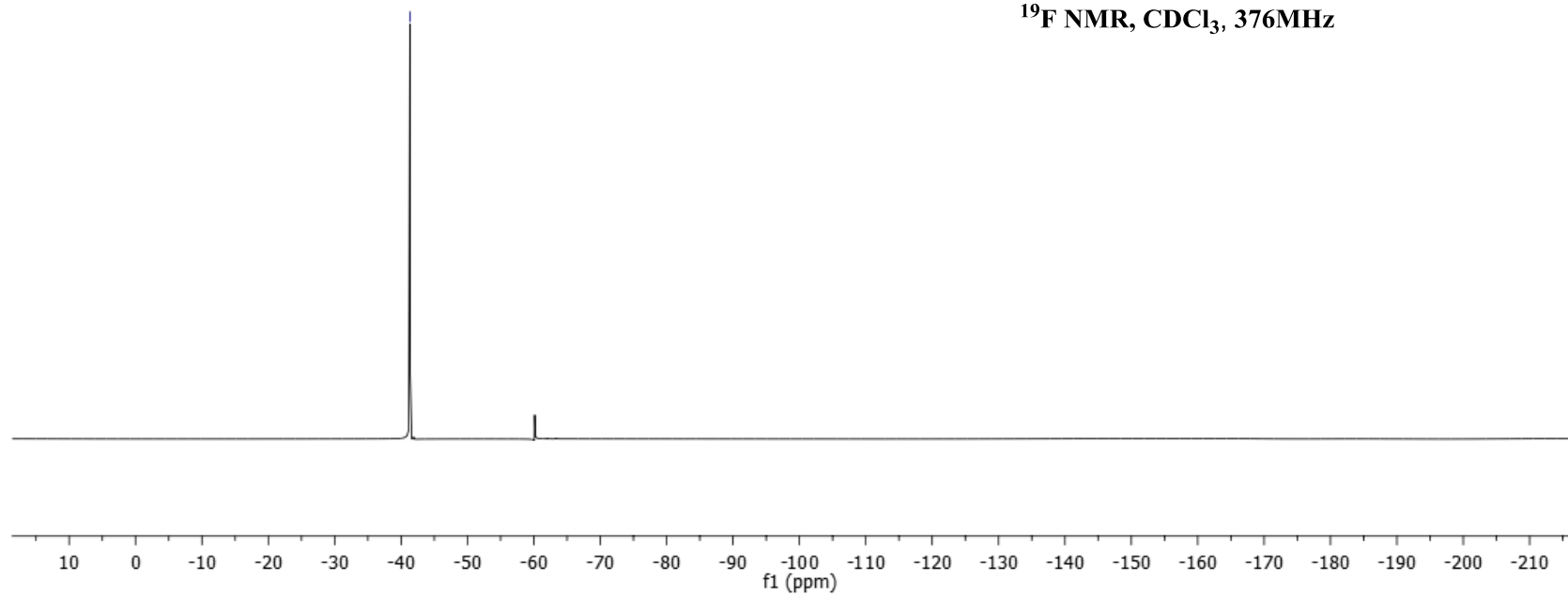


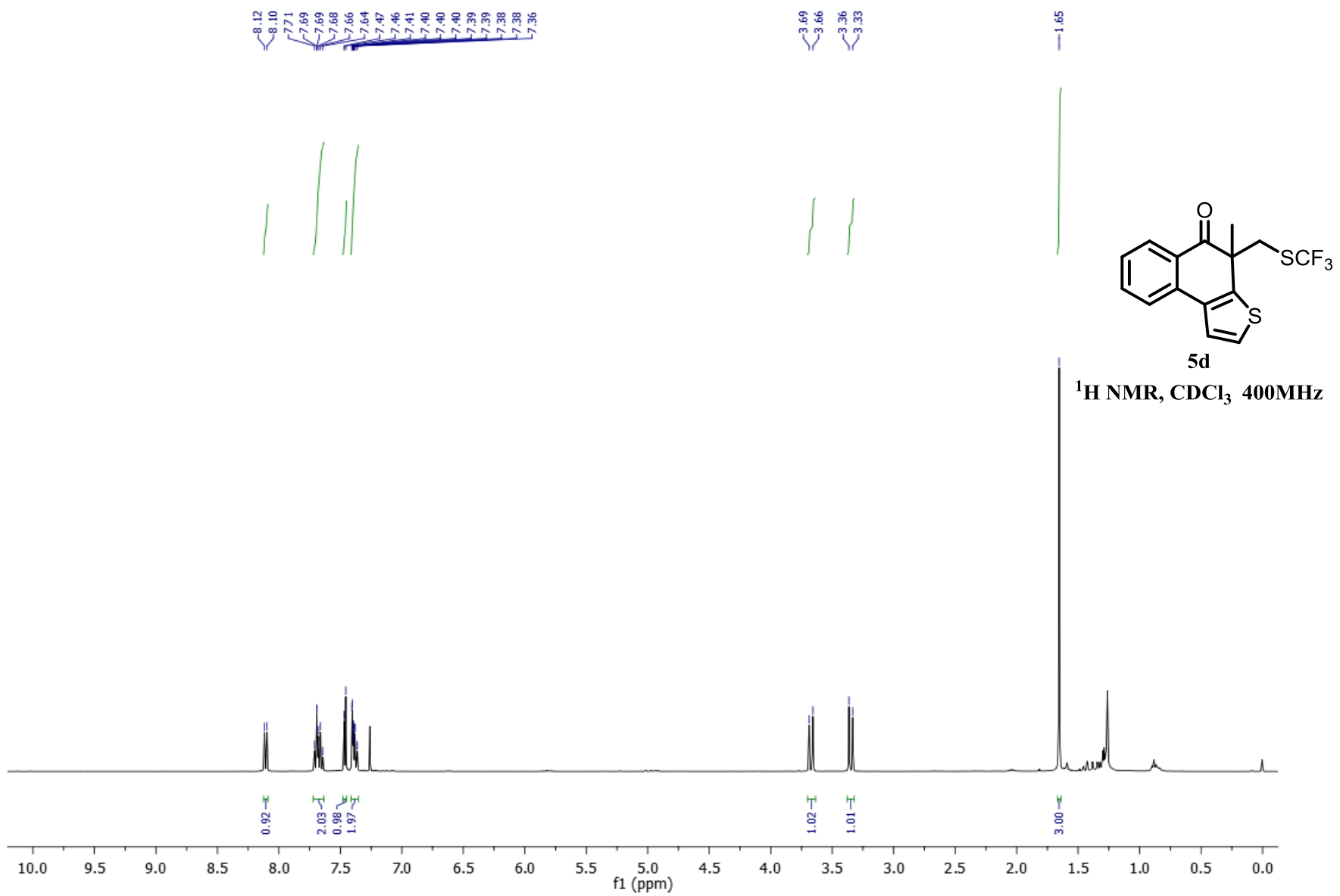


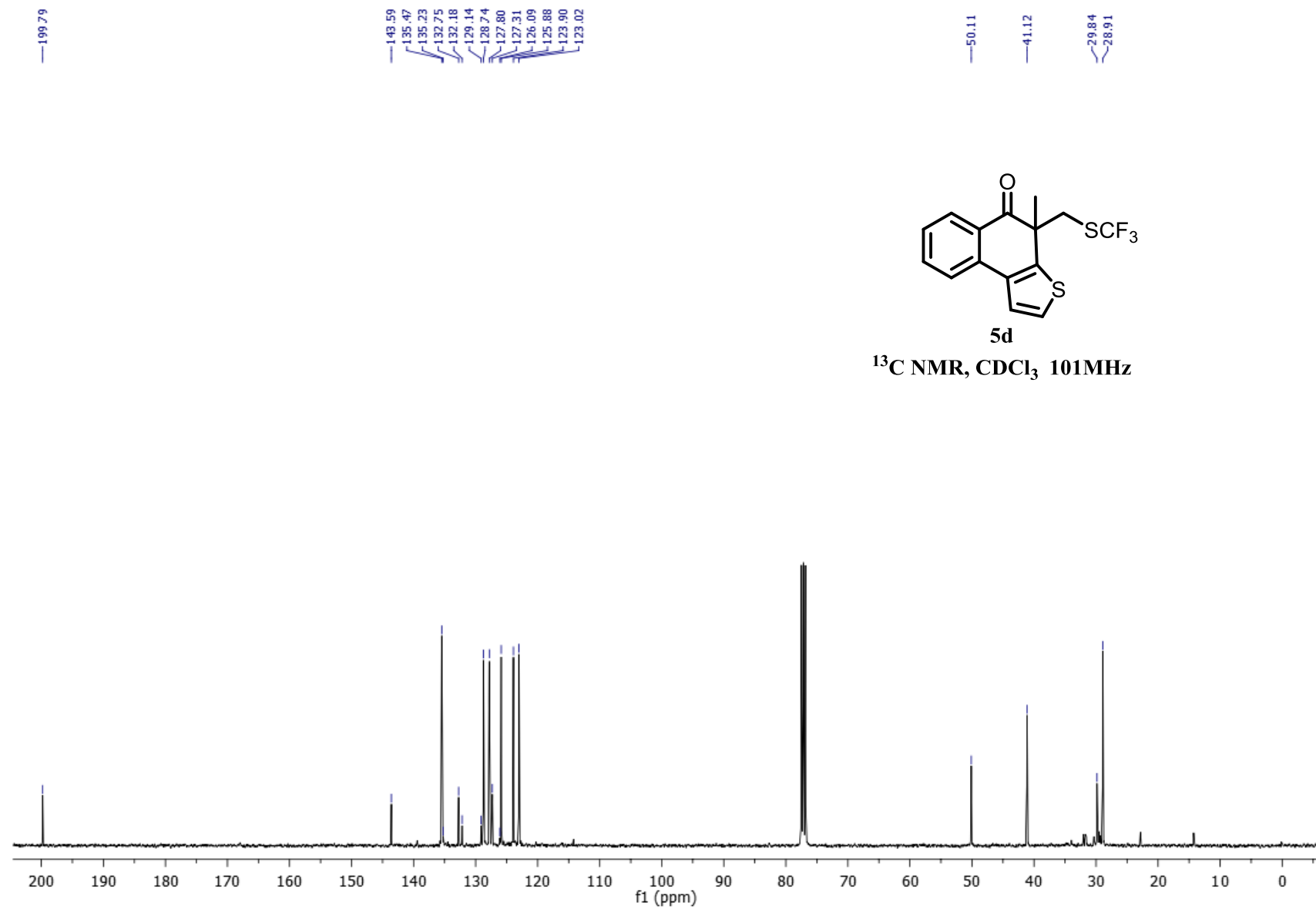
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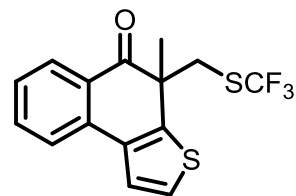
<sup>19</sup>F NMR, CDCl<sub>3</sub>, 376MHz





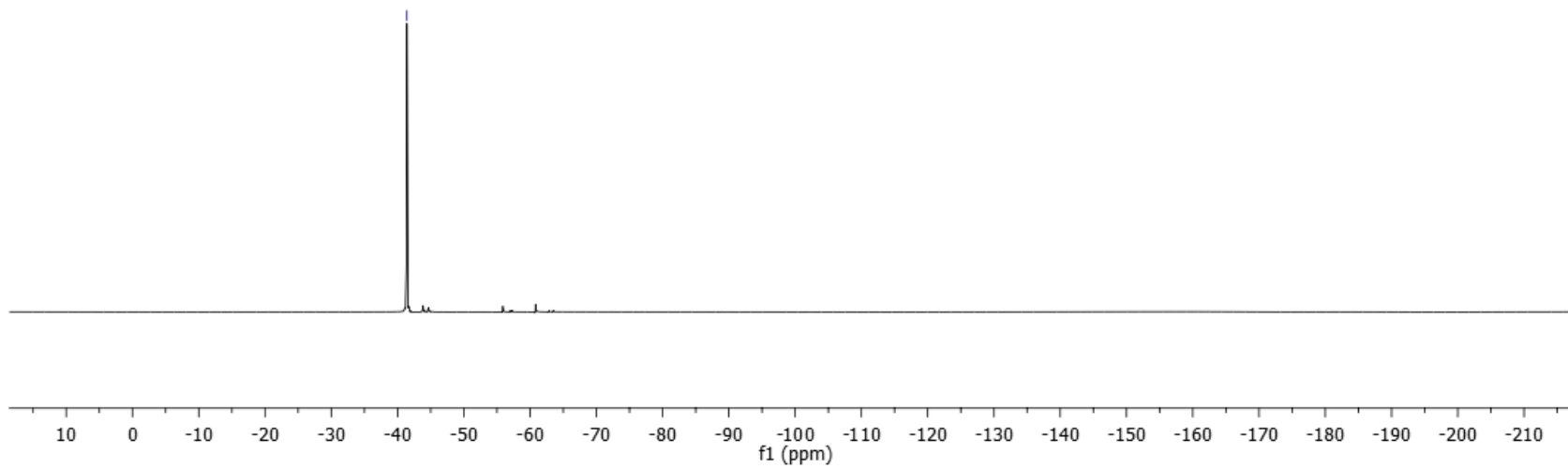


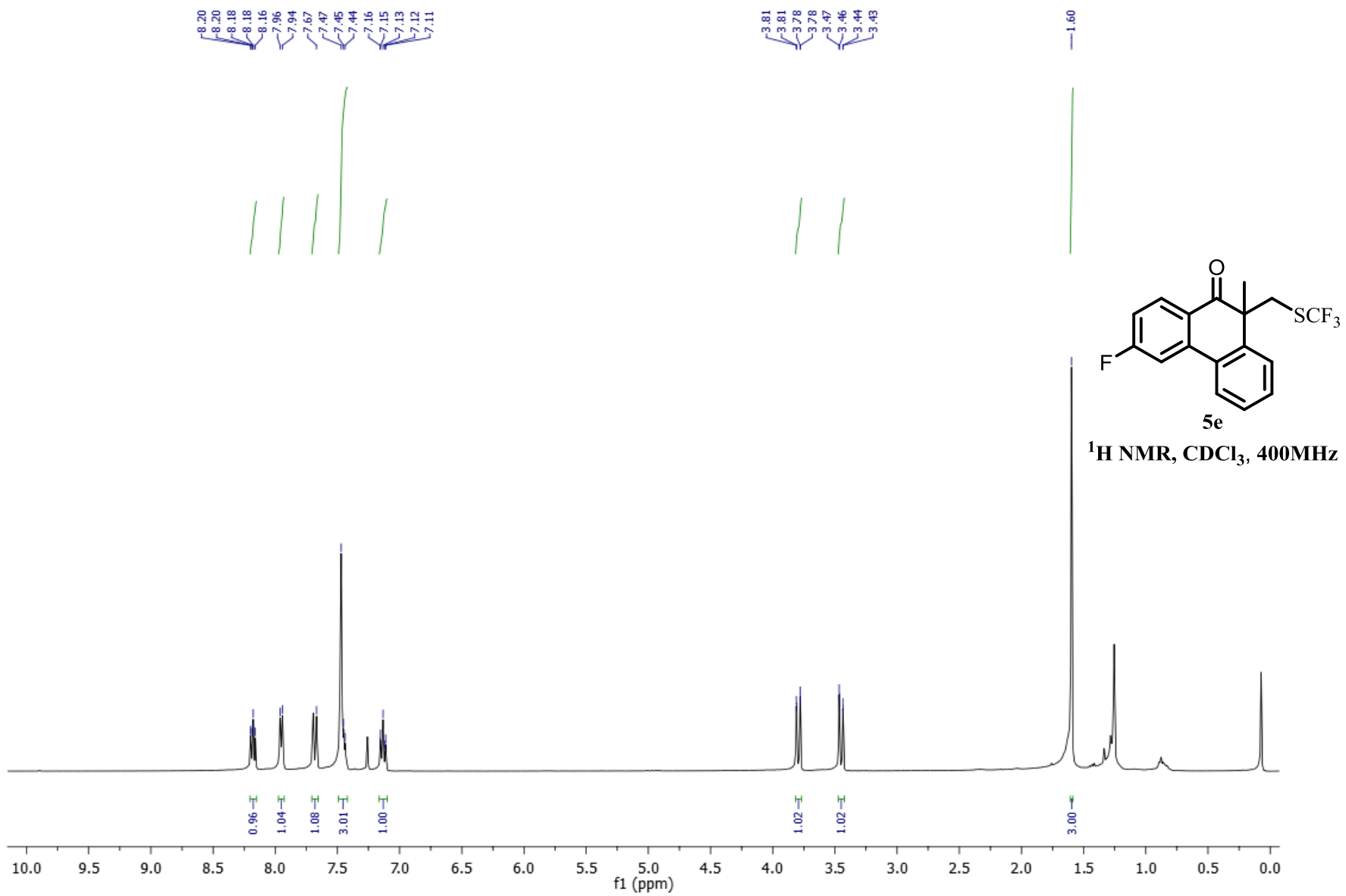
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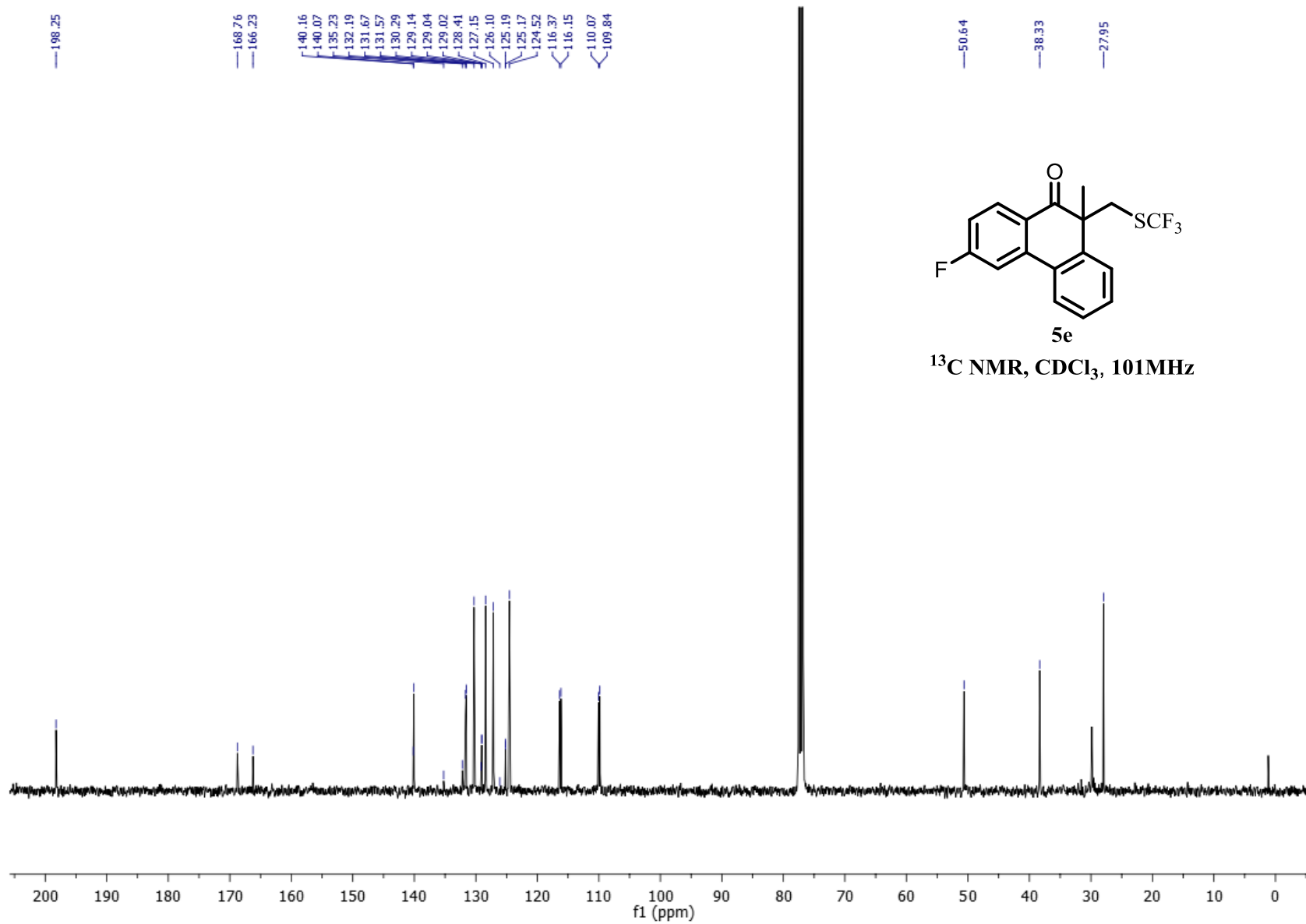


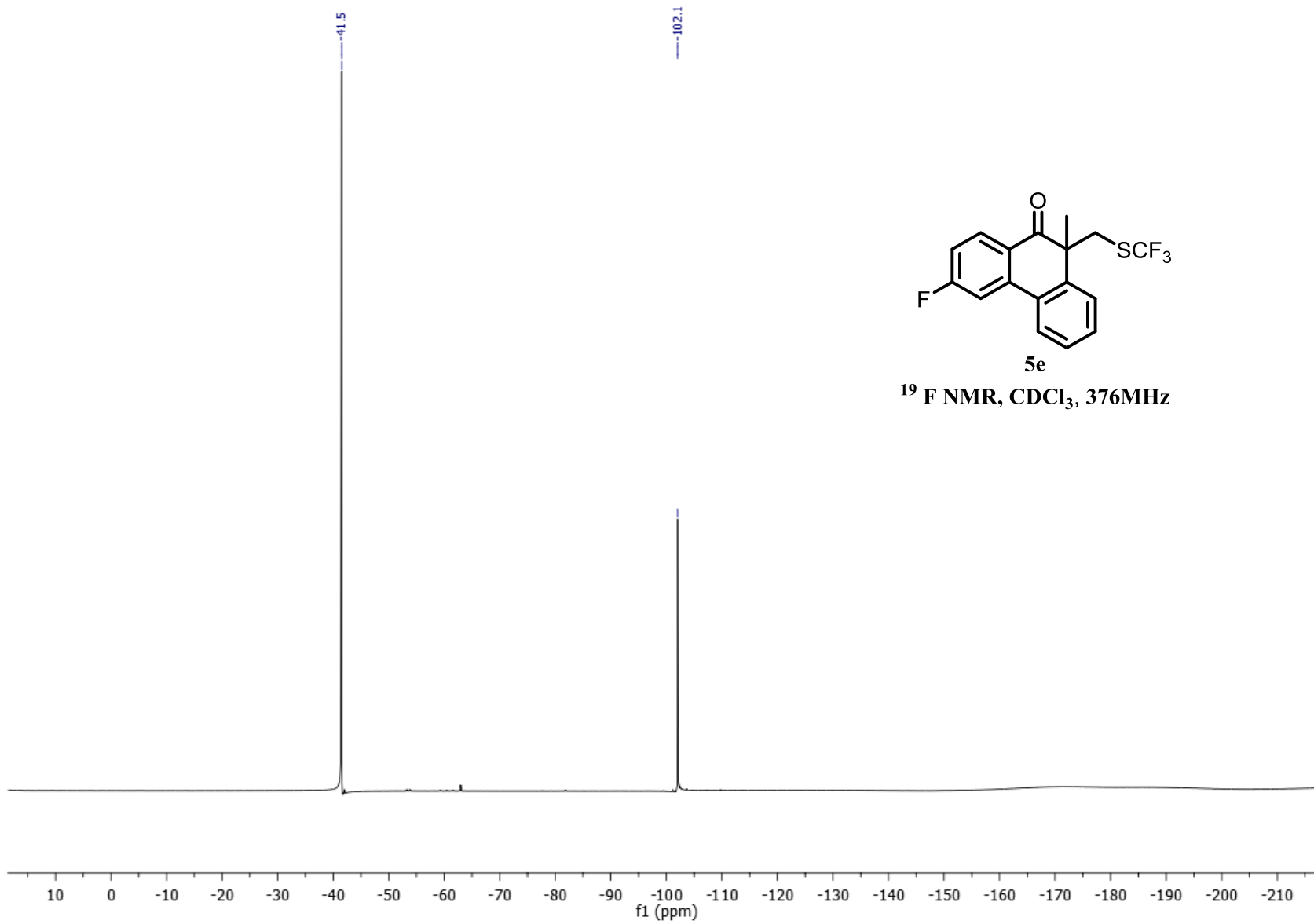
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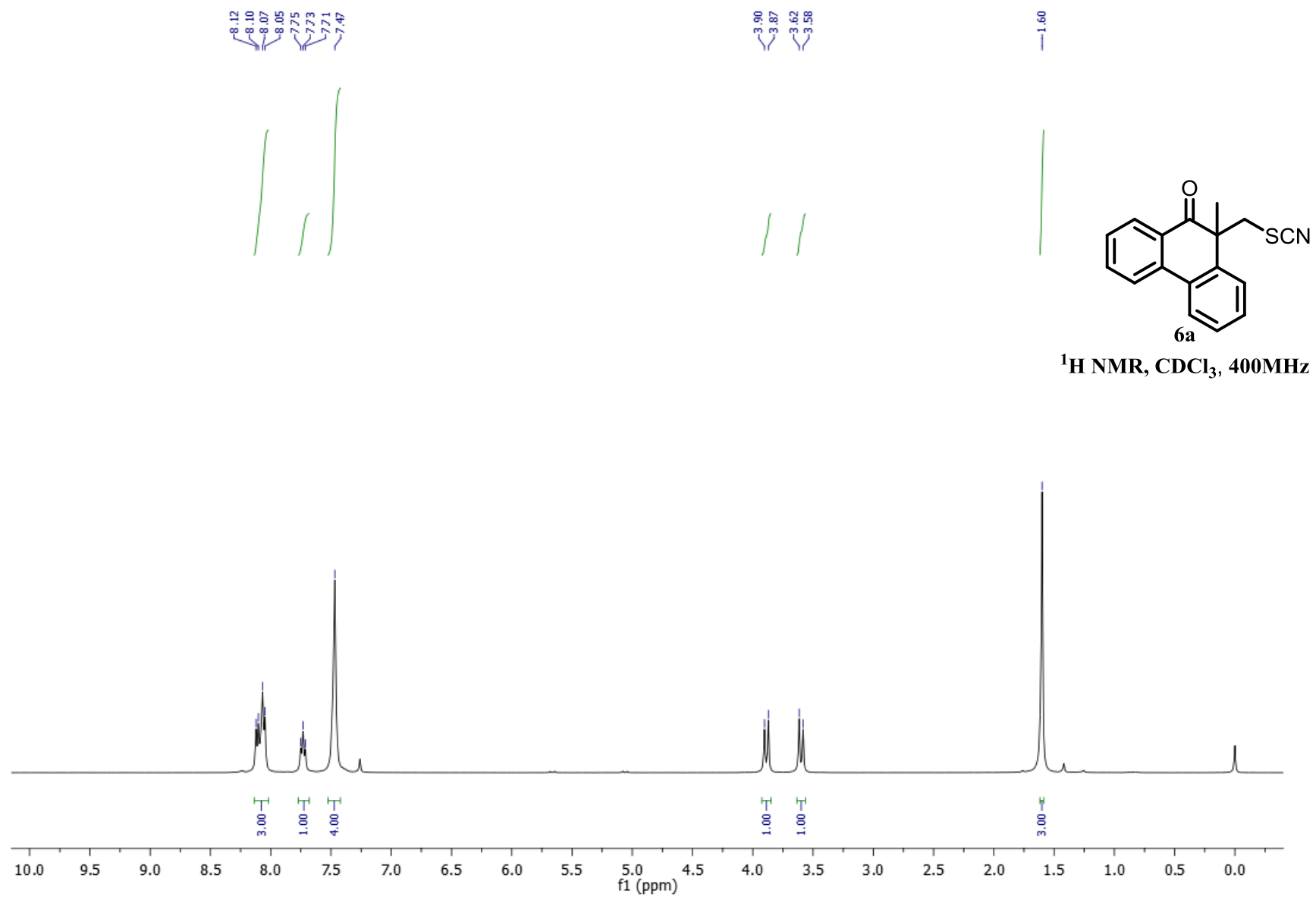
$^{19}\text{F}$  NMR,  $\text{CDCl}_3$ , 376MHz



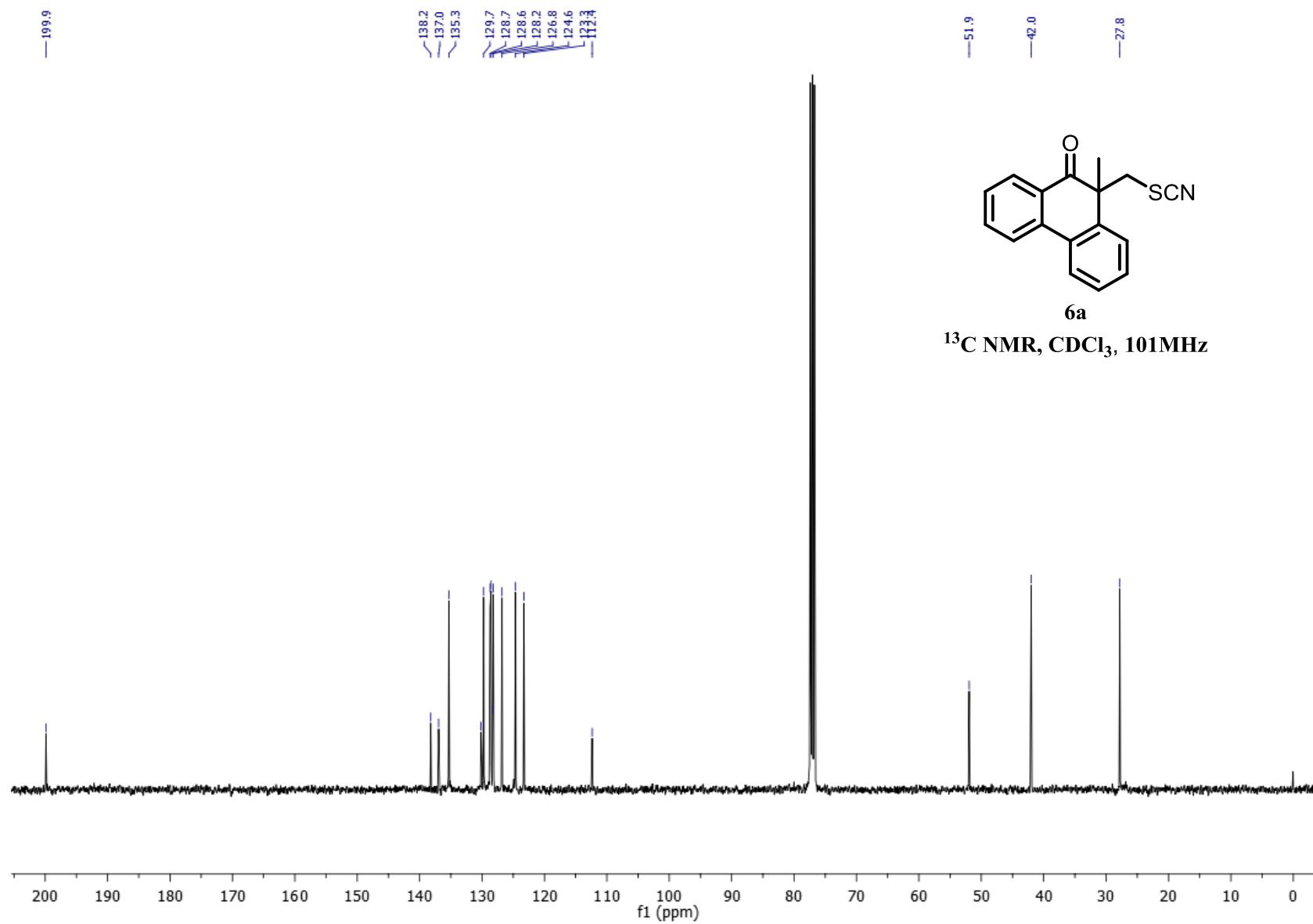


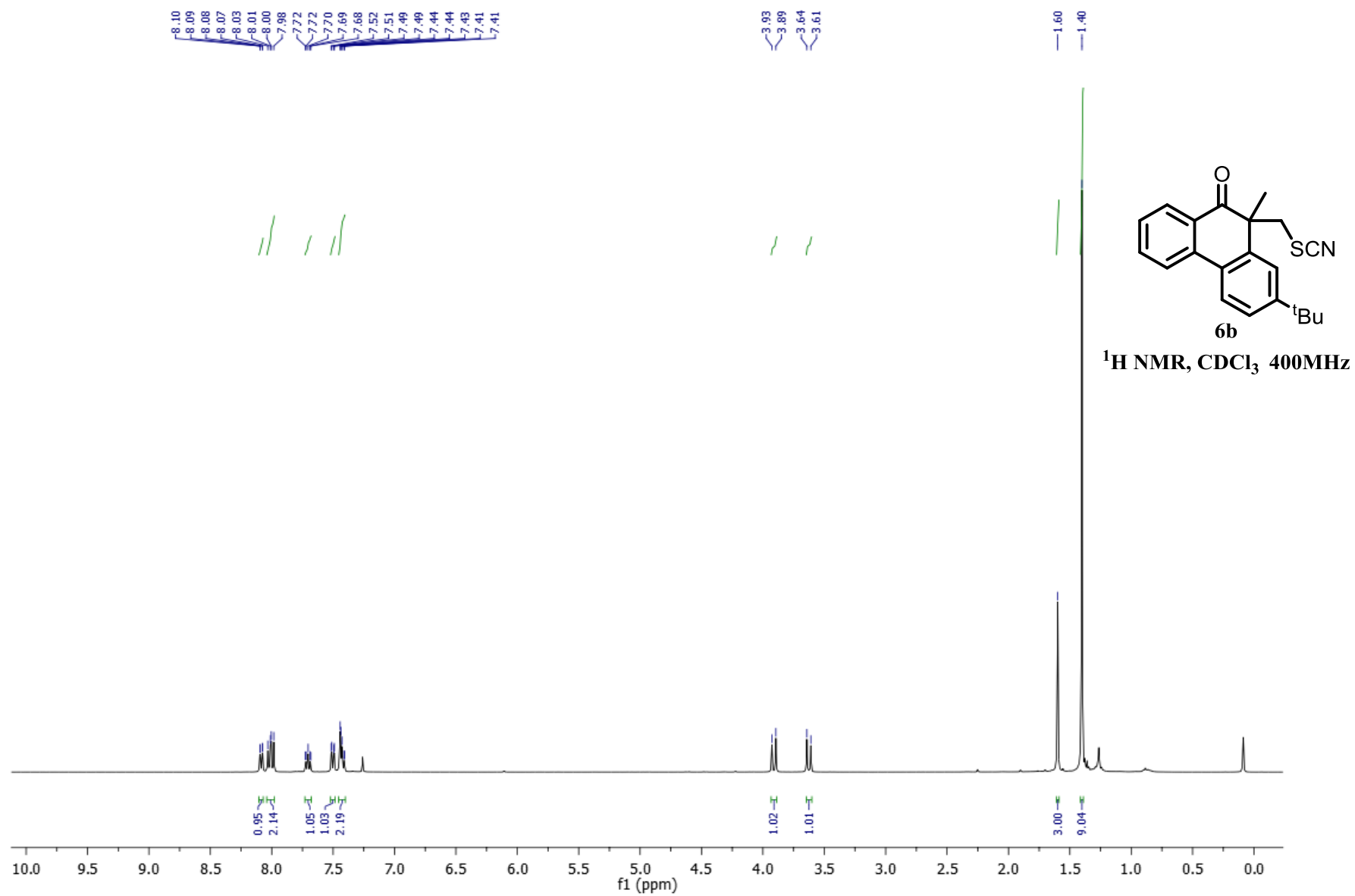


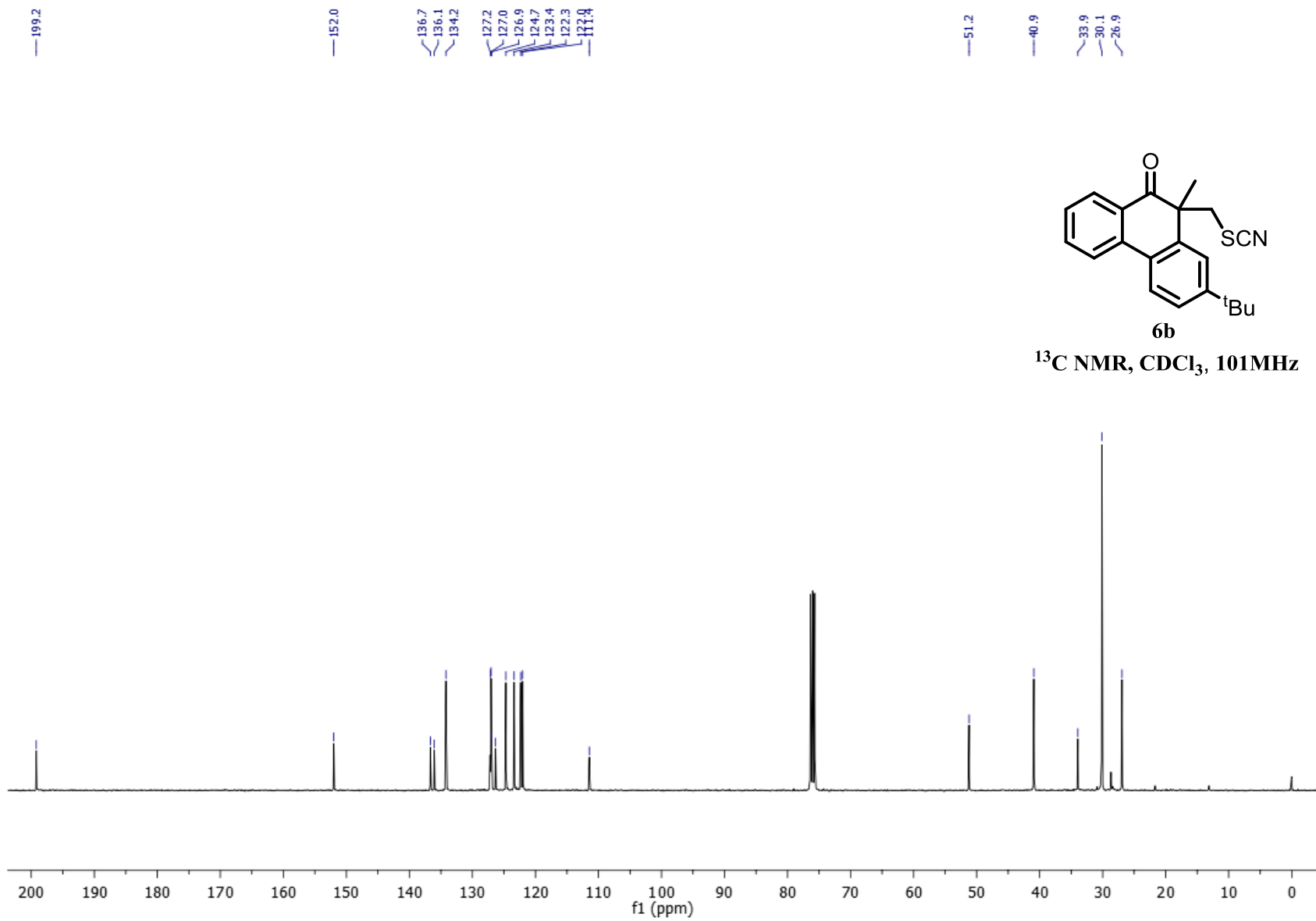


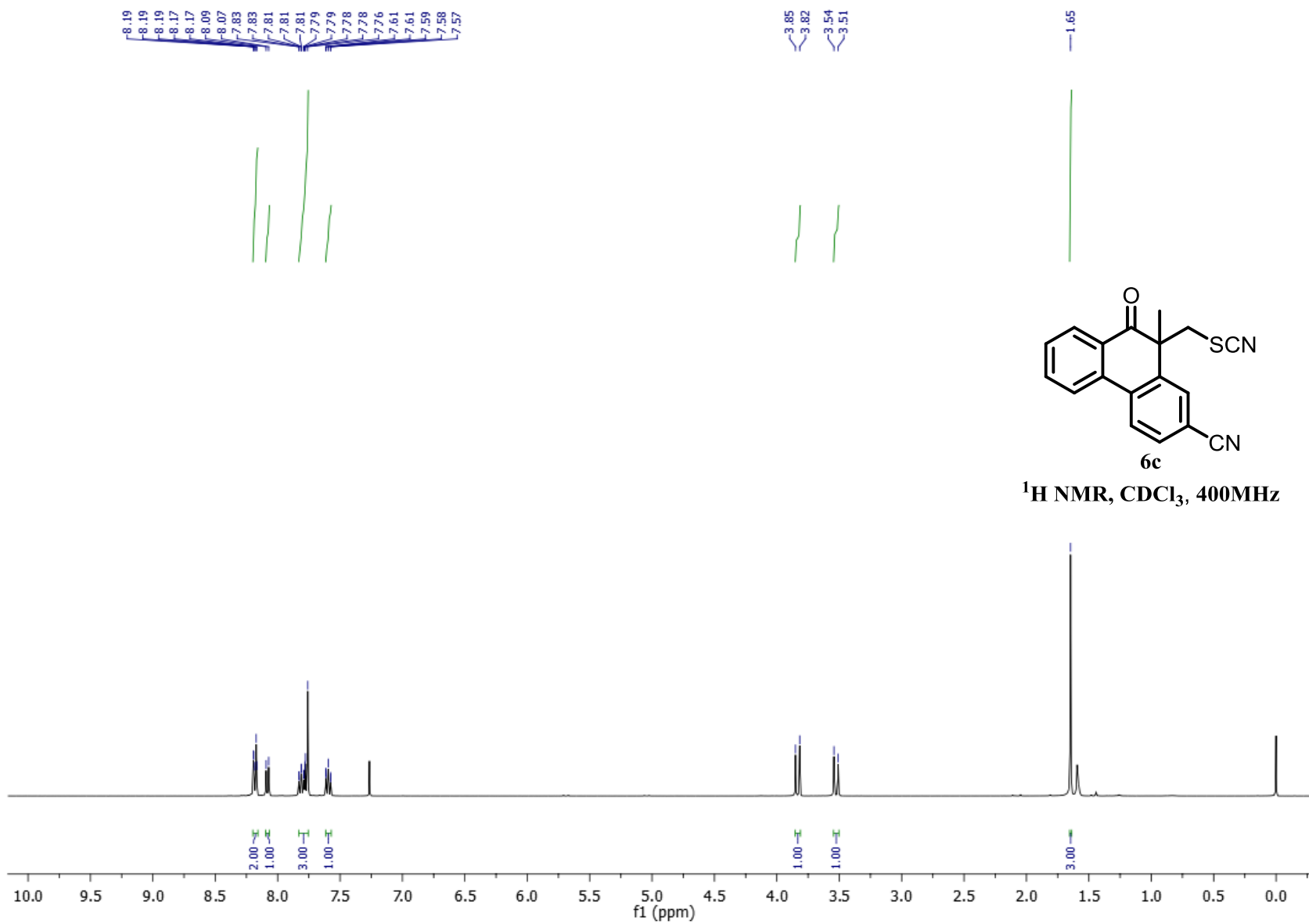


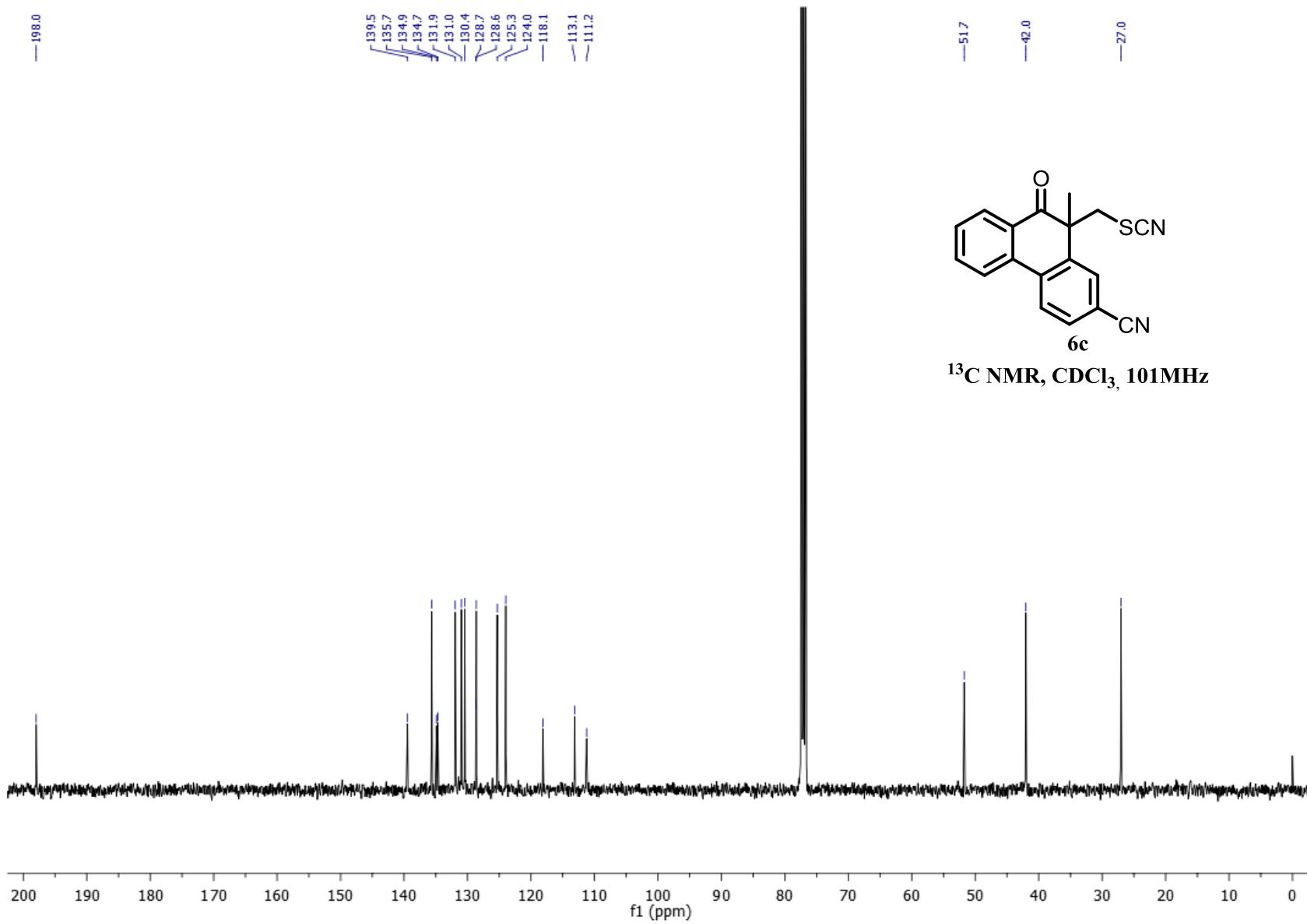


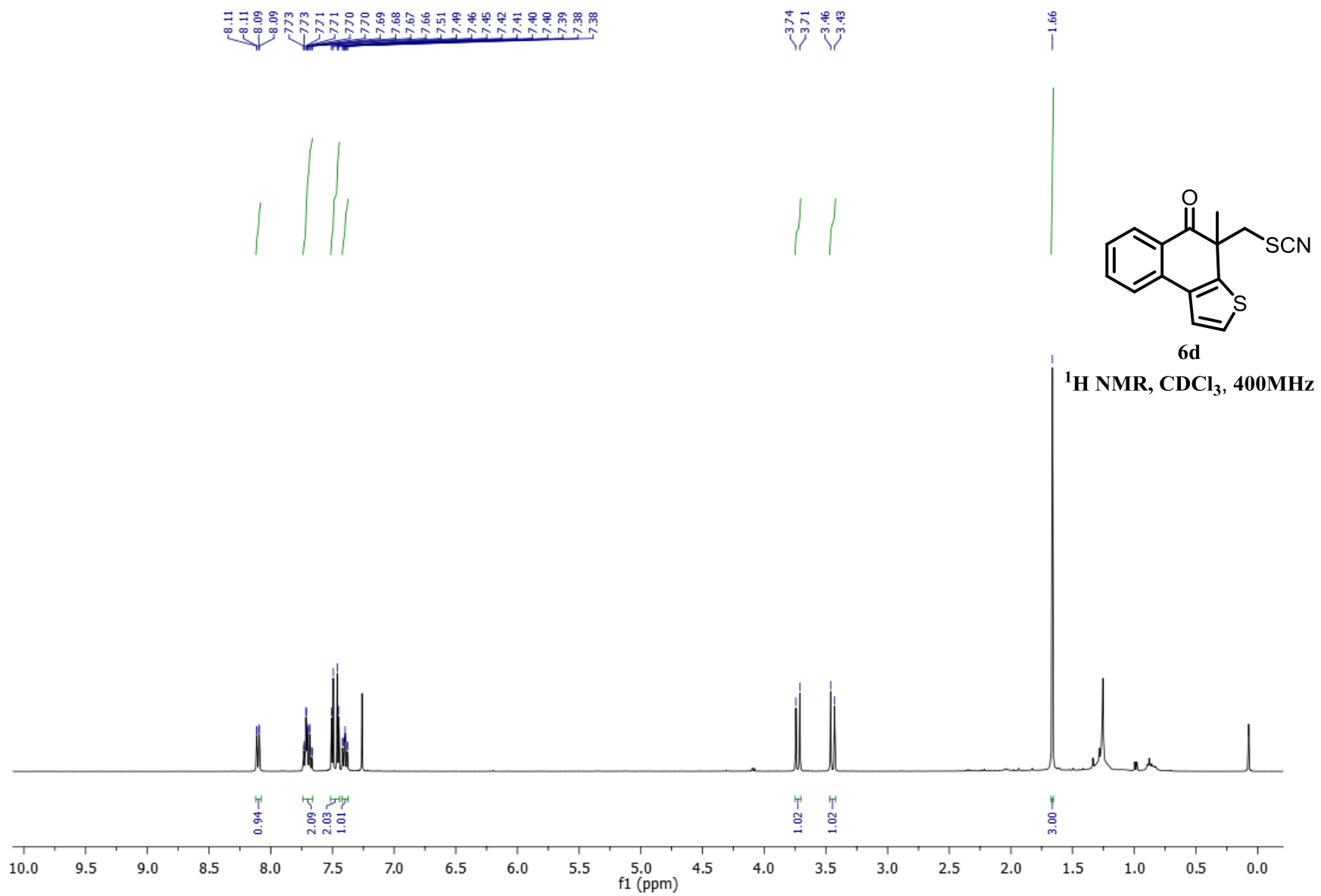


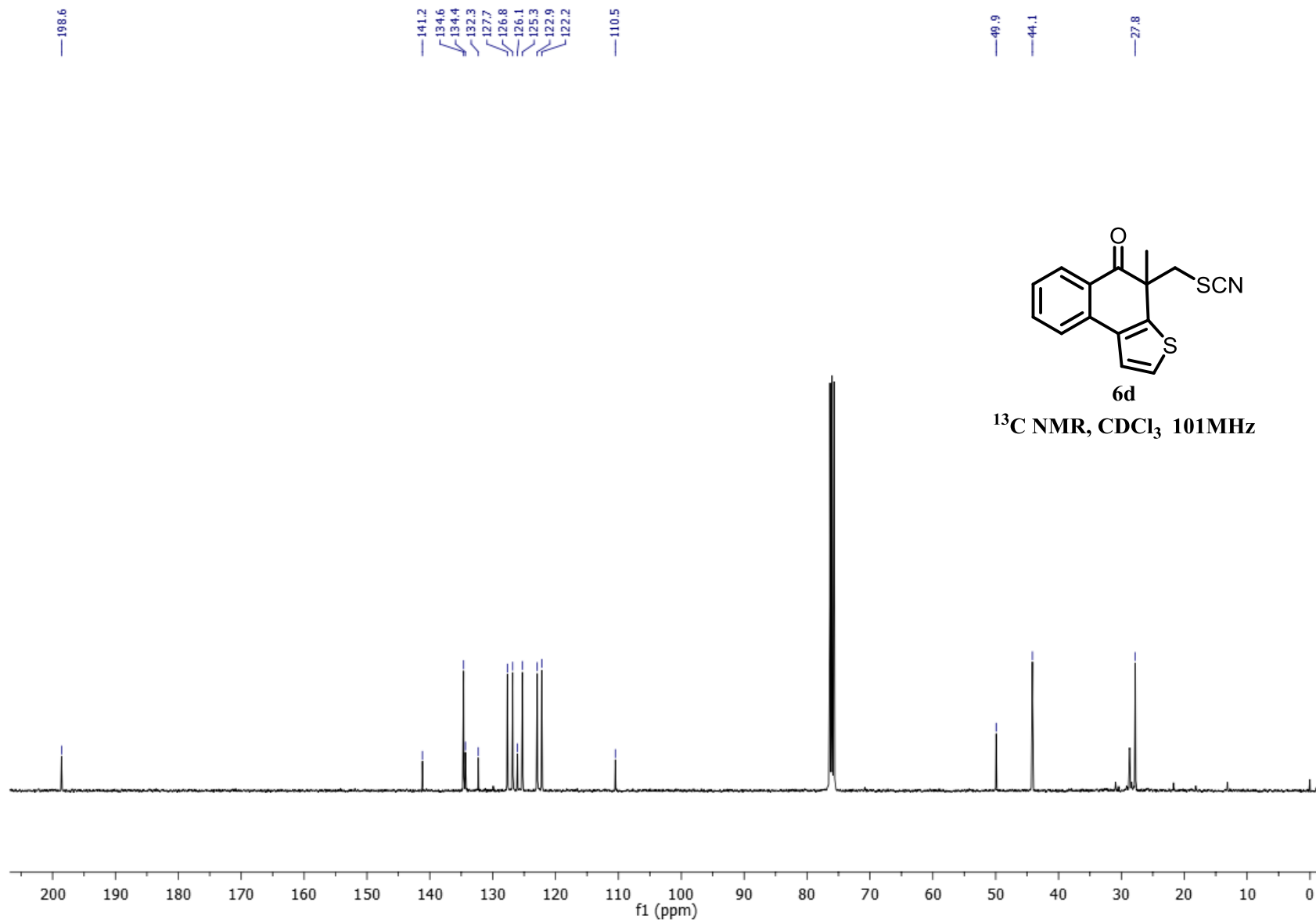


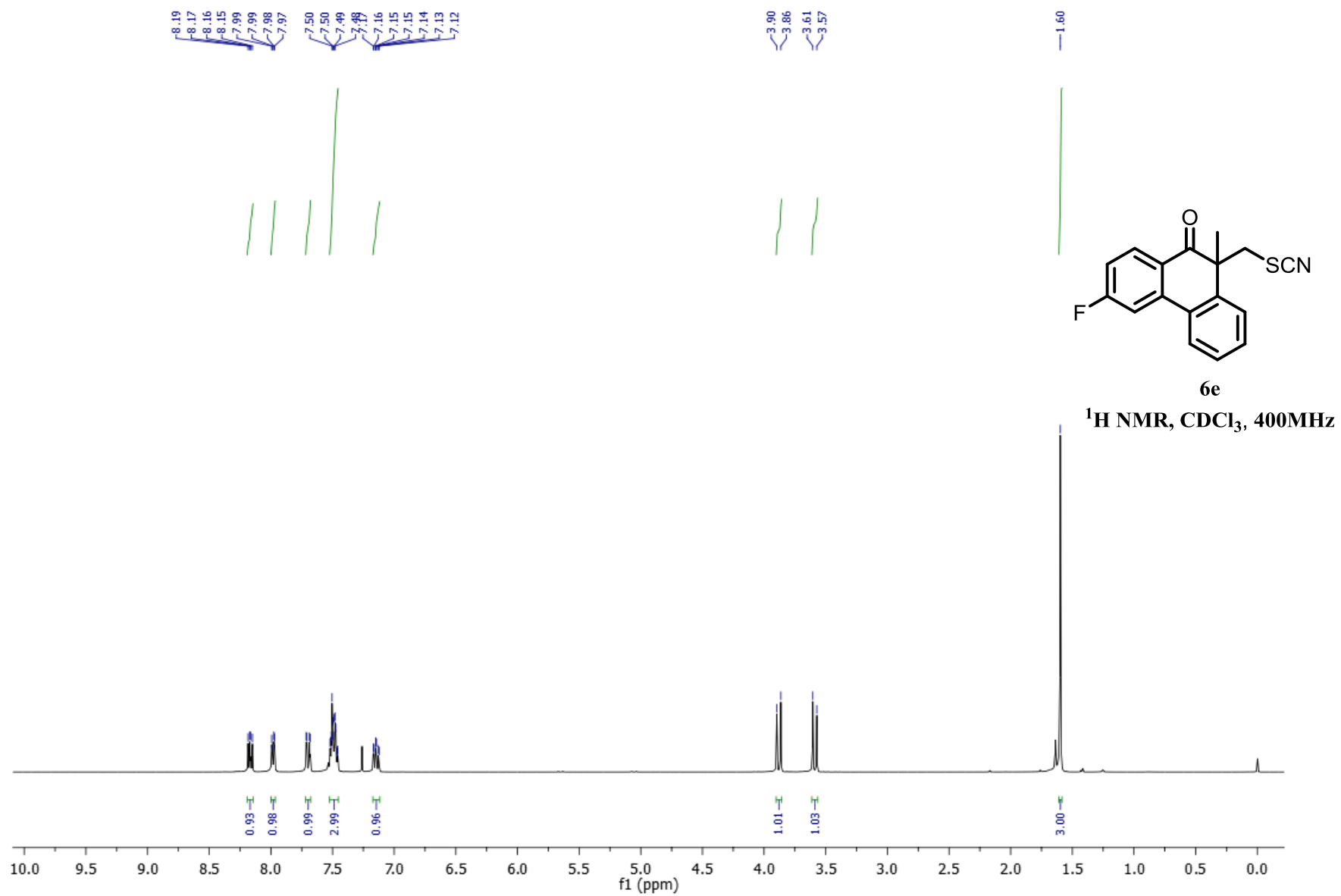




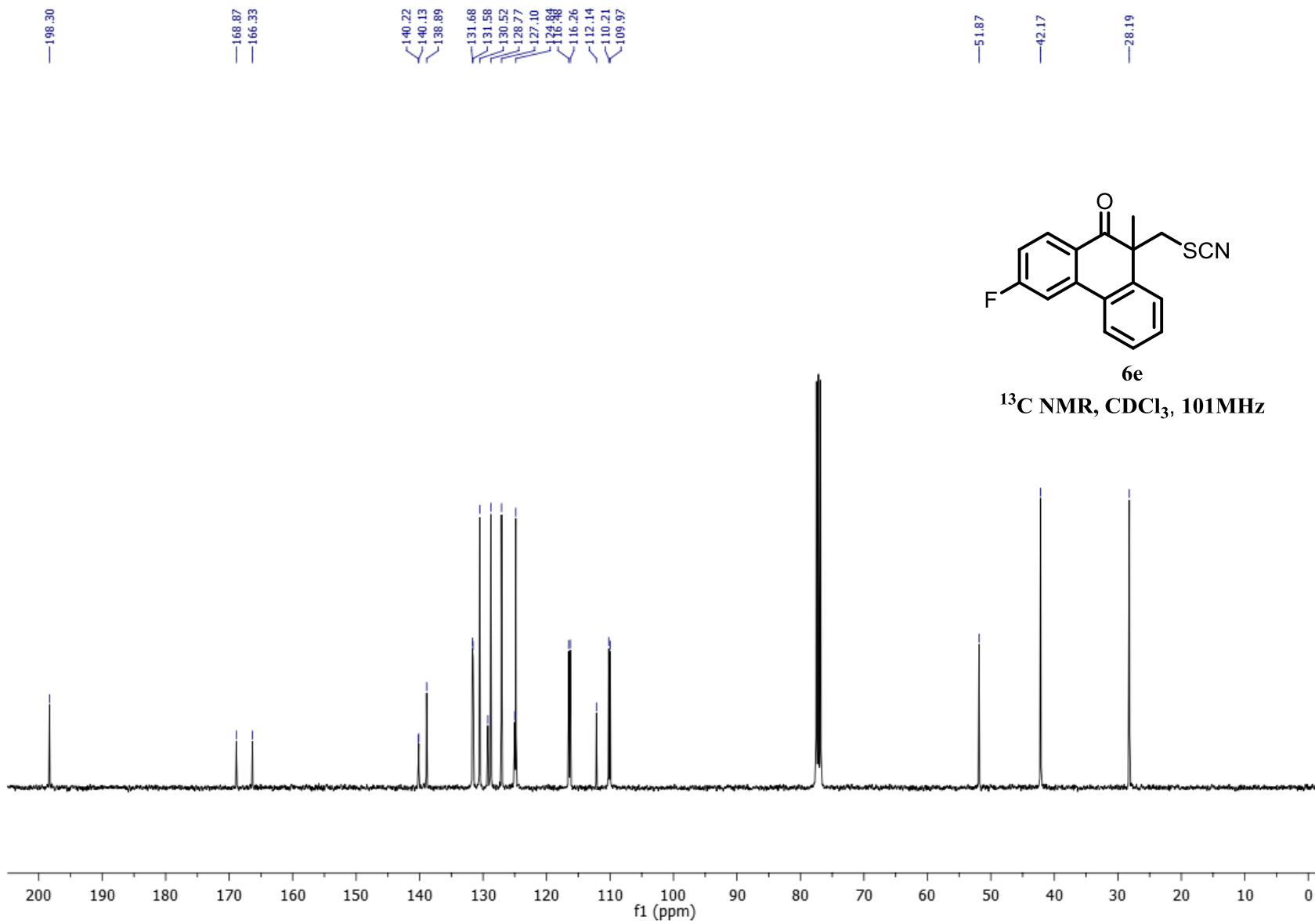




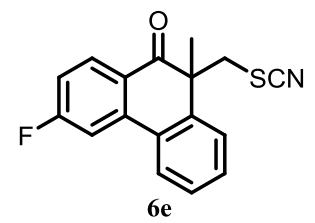








-101.39



<sup>19</sup>F NMR, CDCl<sub>3</sub>, 377MHz

