

## Dipyrazolodioxadiazocines as shelf-stable "ready-to-use" precursors for an in situ generation of enolate-iminium 1,4-dipoles: a straightforward atom-economical approach to pyrazolo[5,1-*d*] [1,3,5]dioxazines

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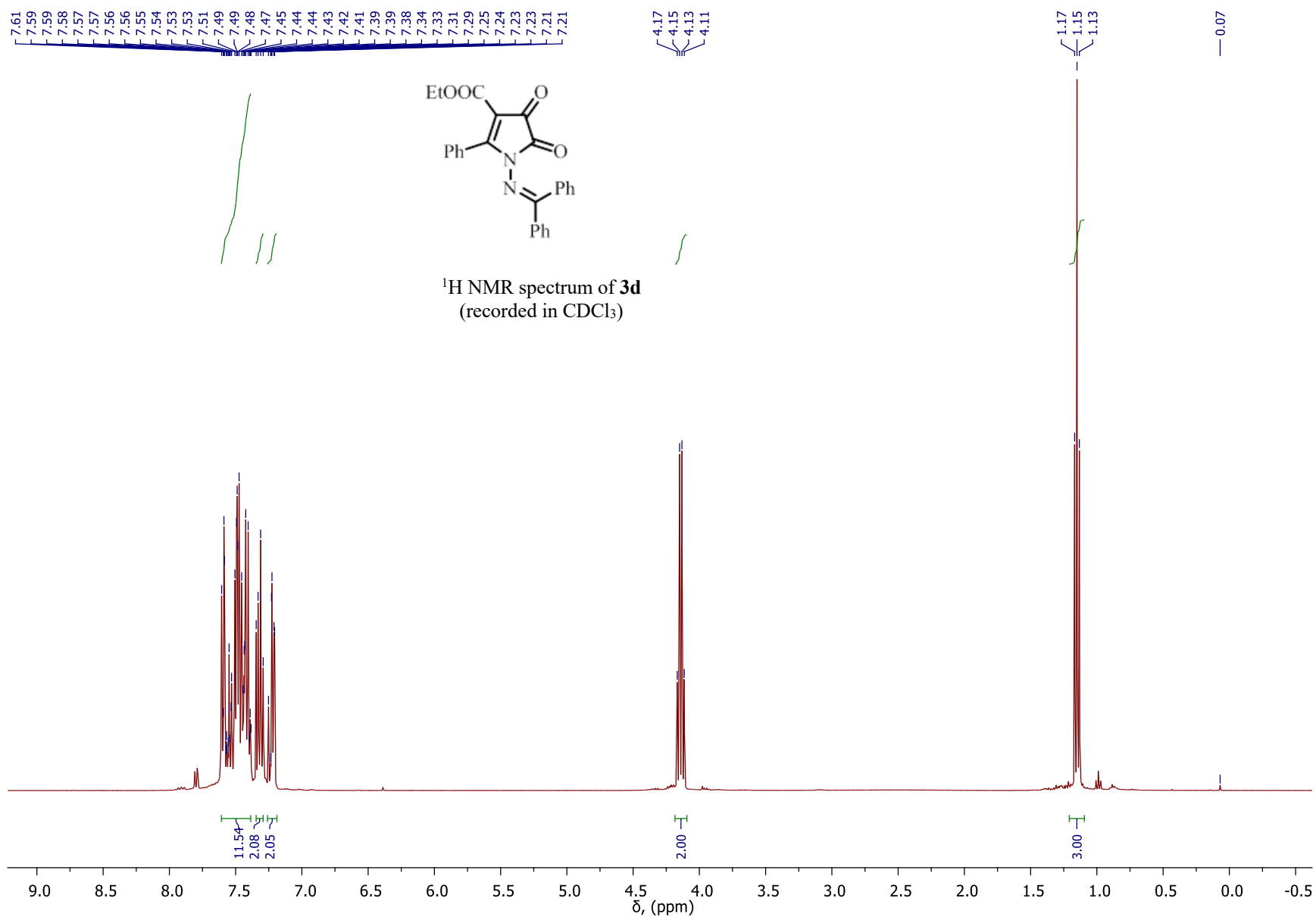
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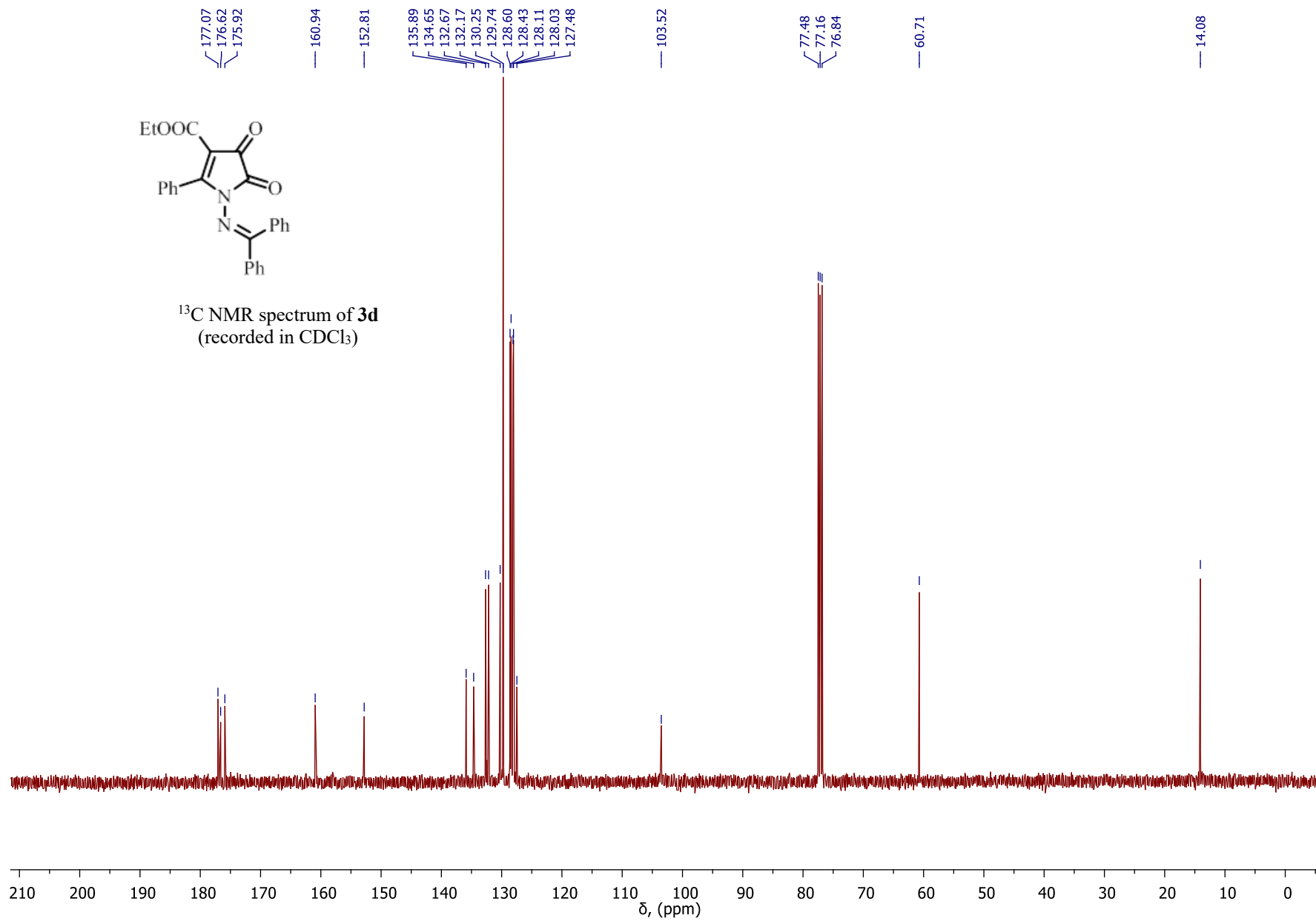
# Supporting Information

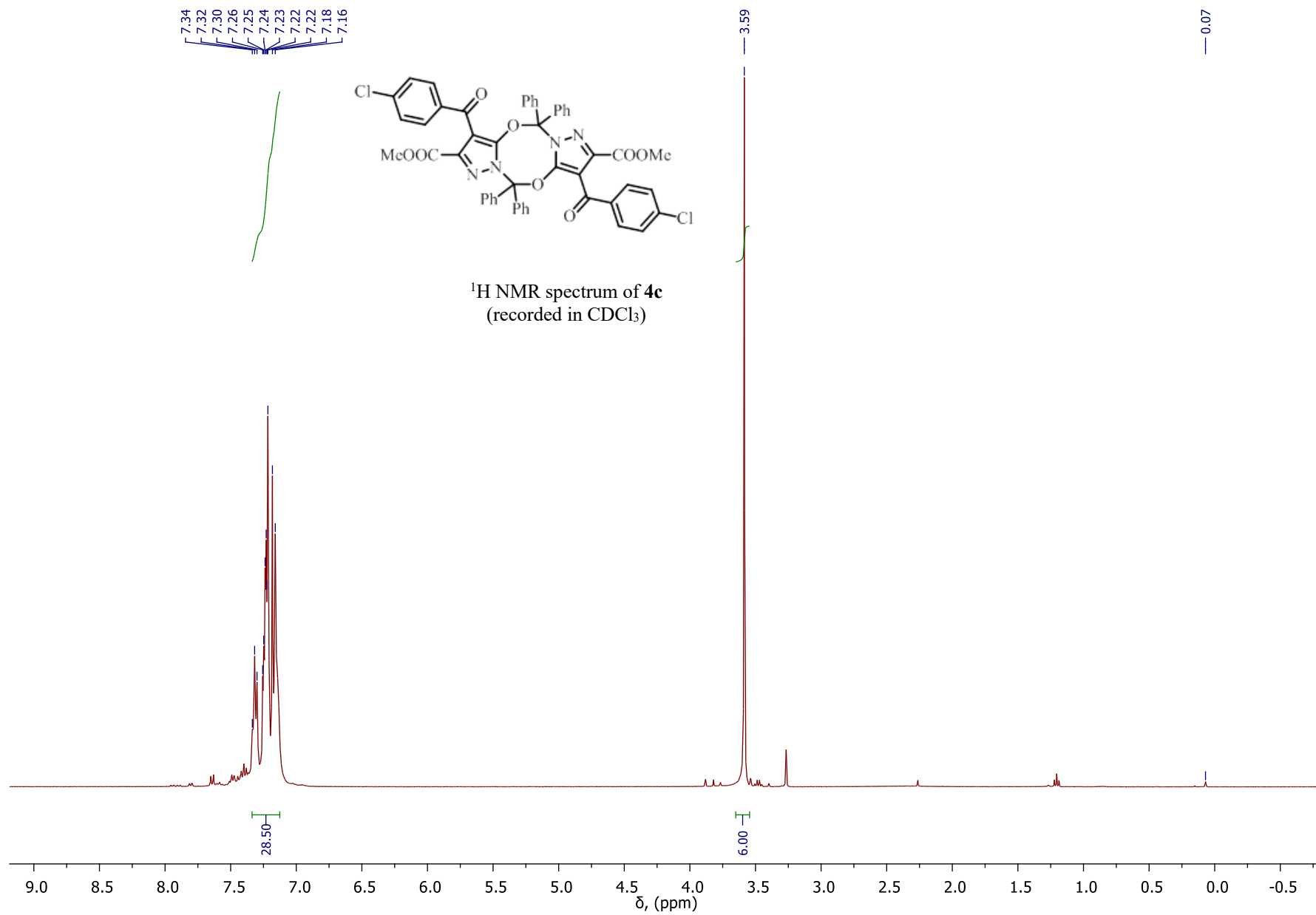
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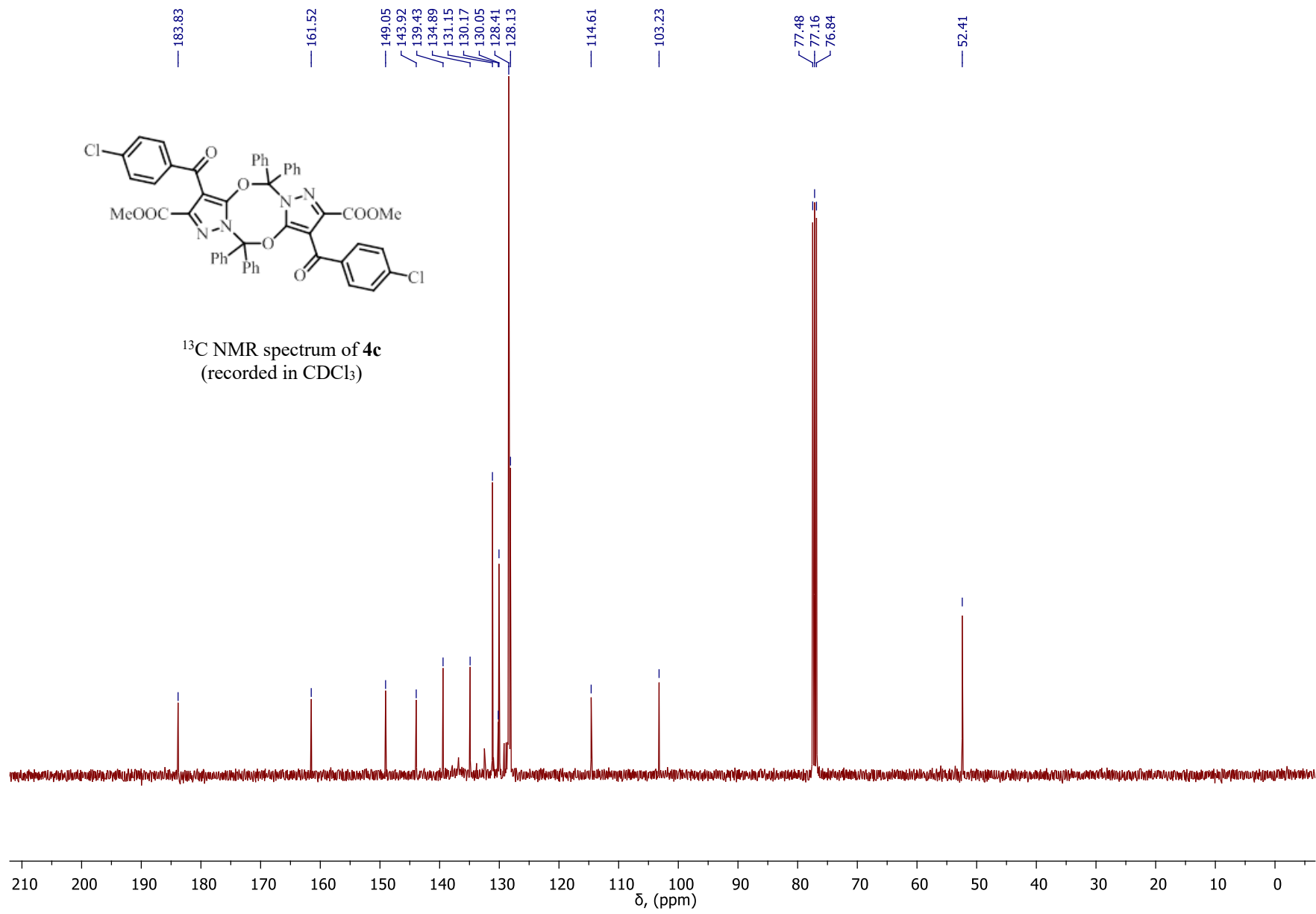
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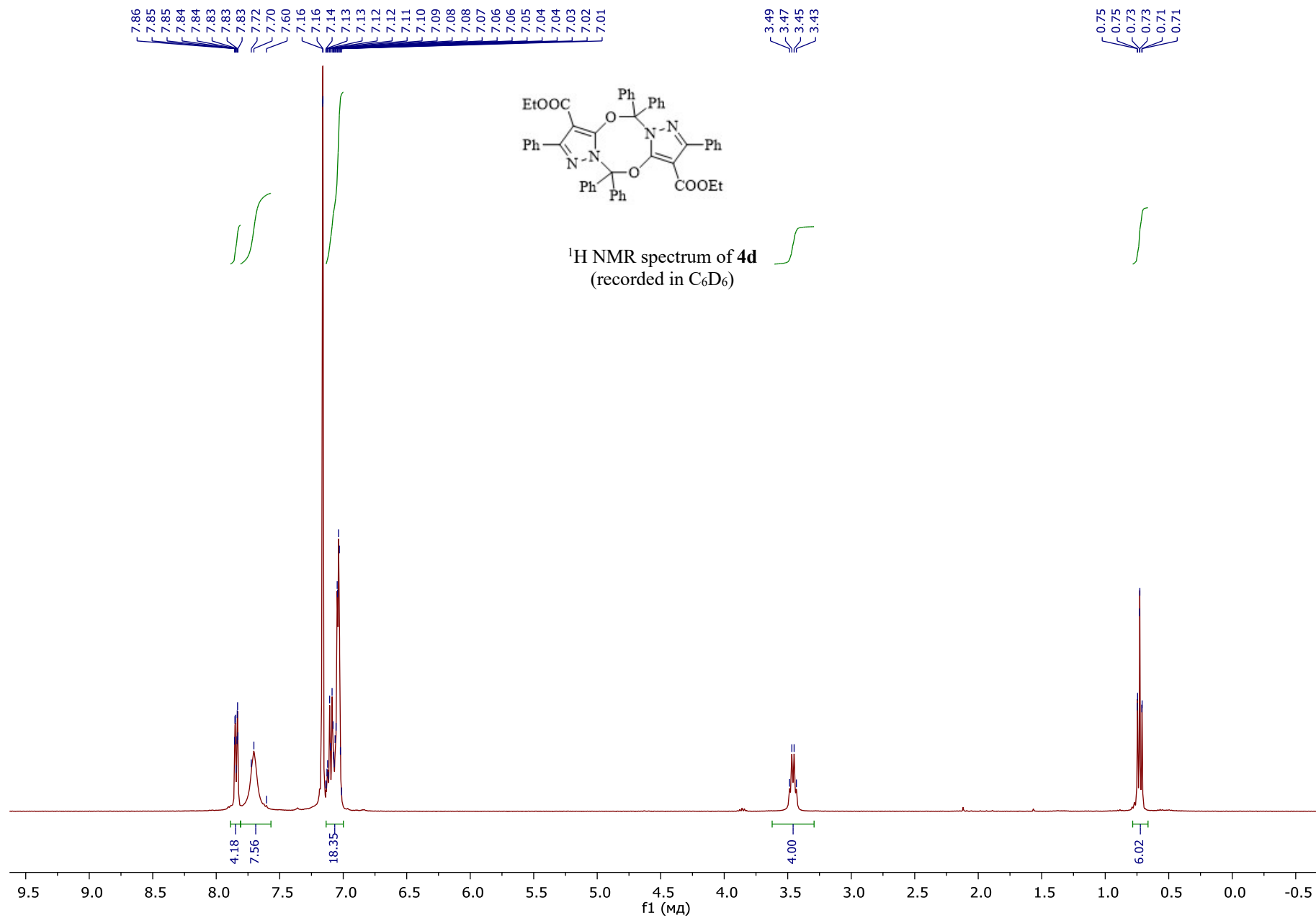
# $^1\text{H}$ and $^{13}\text{C}$ -NMR spectra of the synthesized compounds

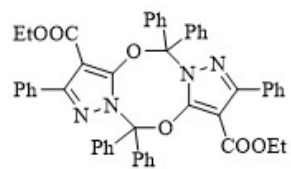




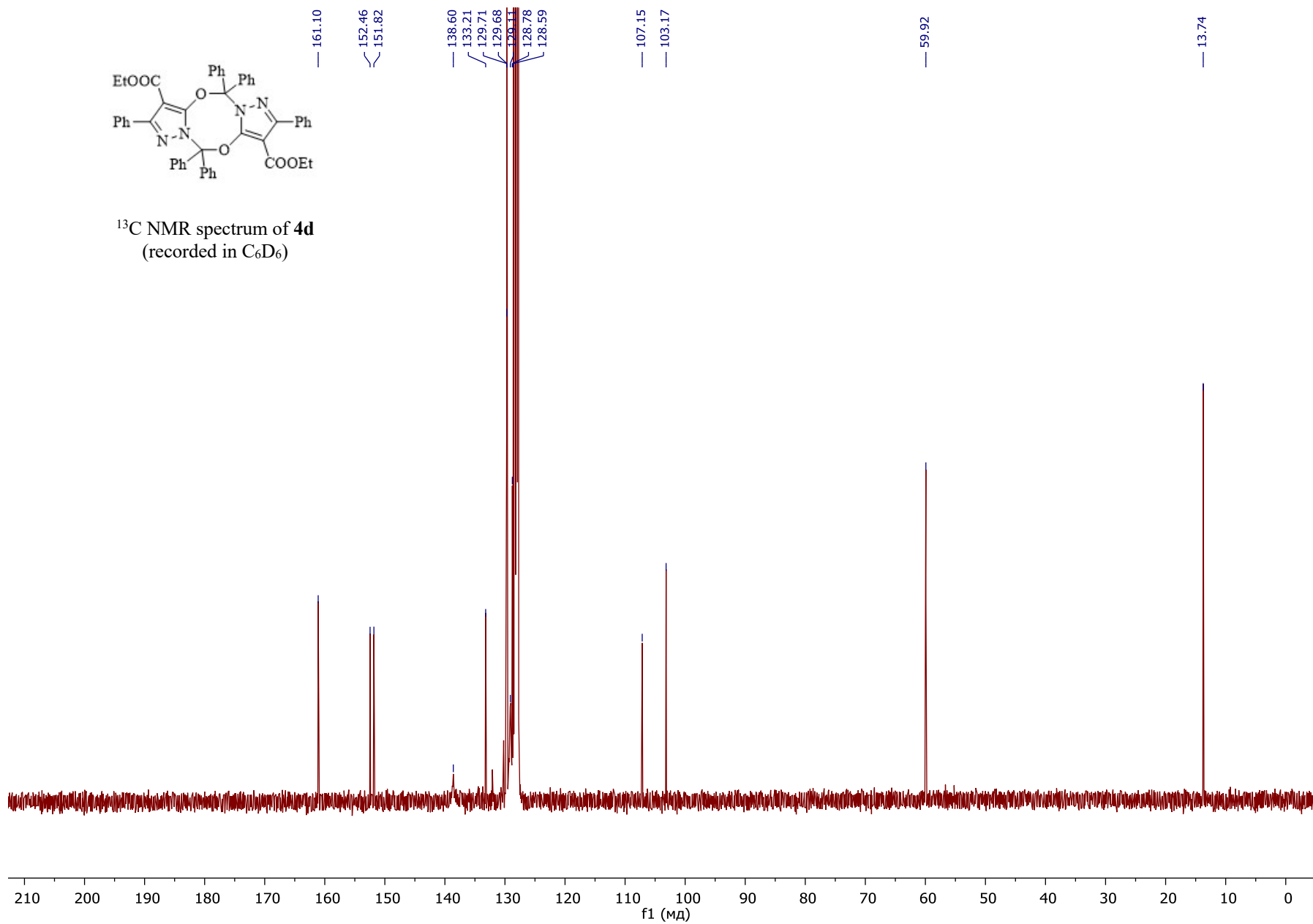


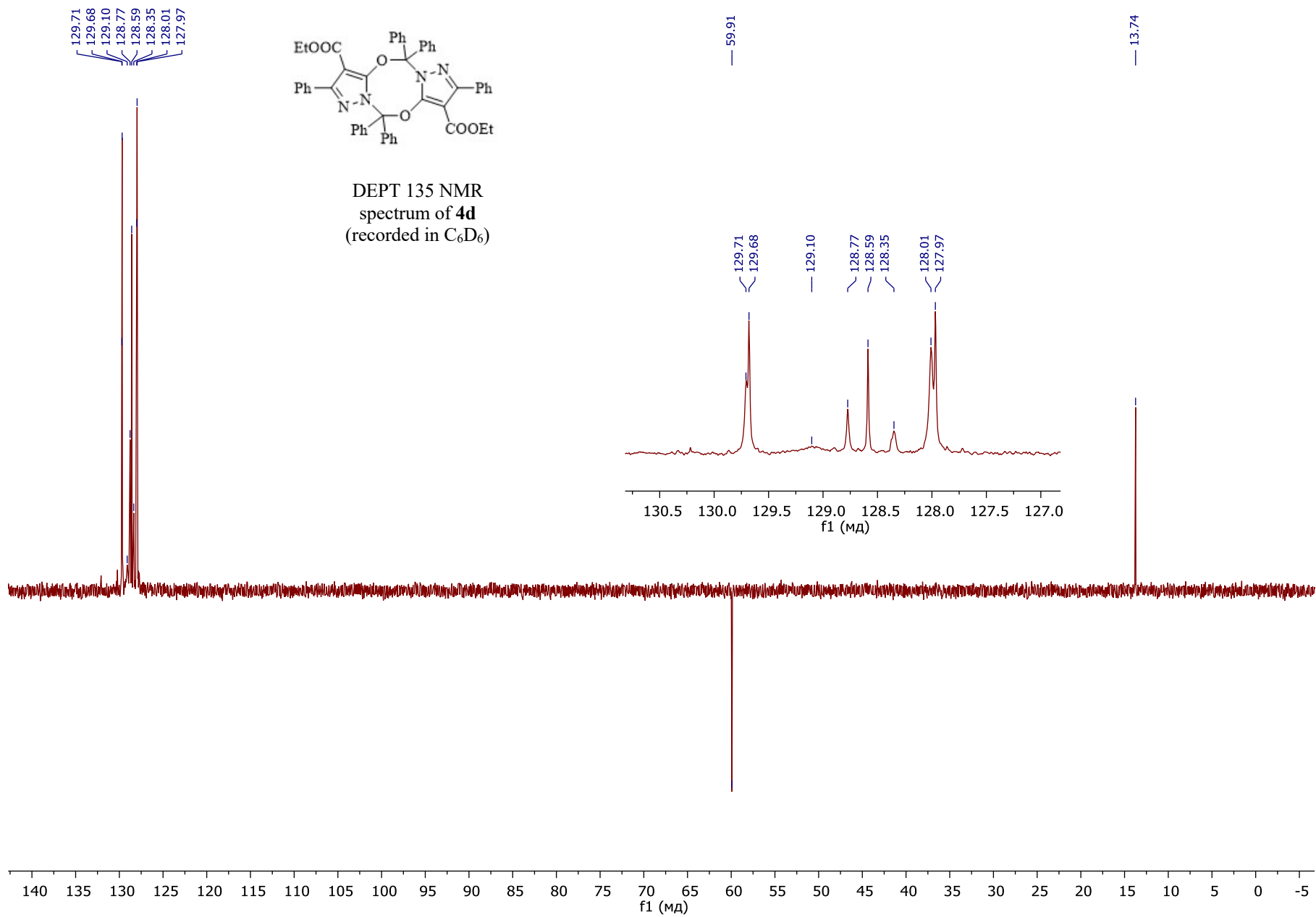




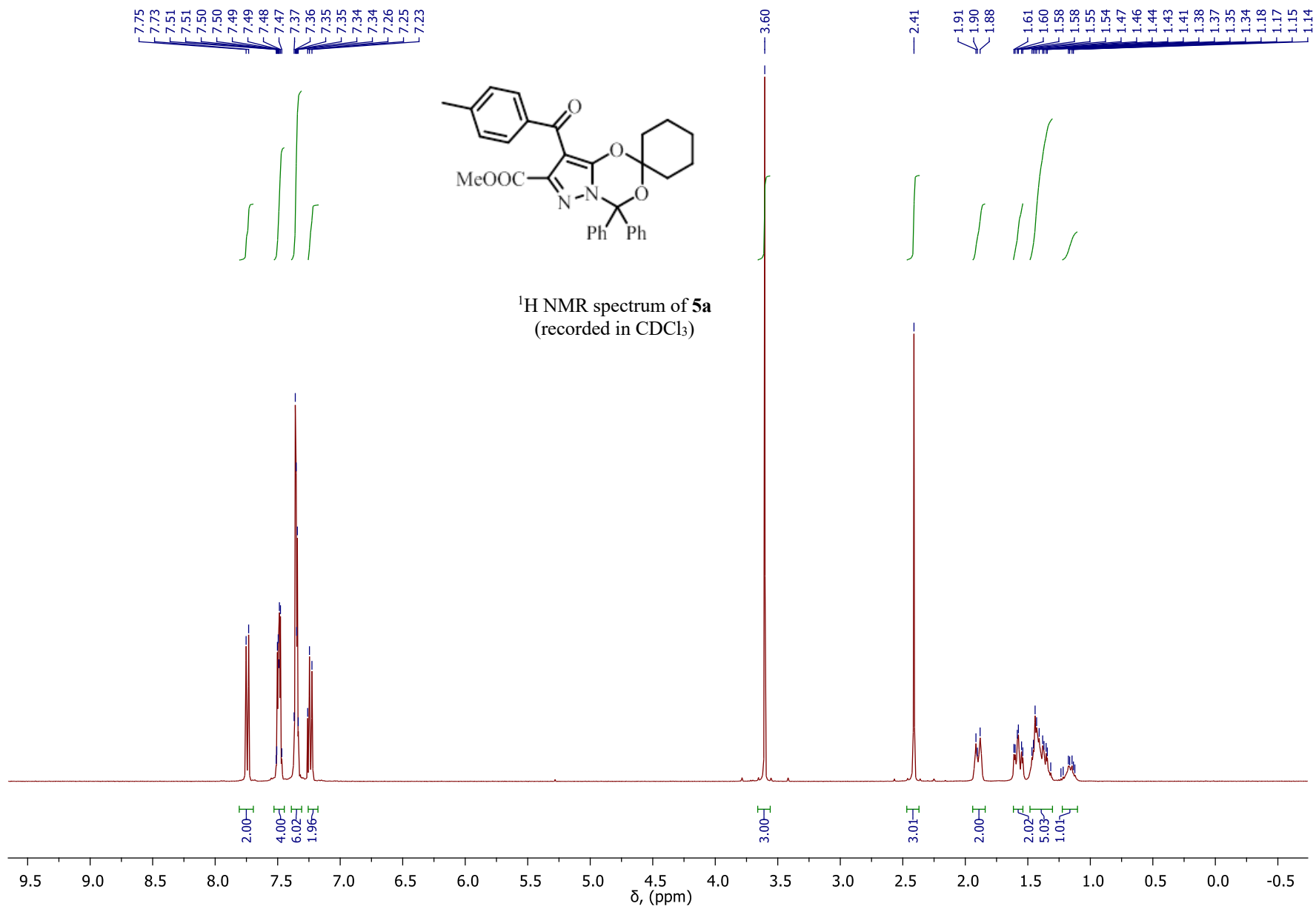


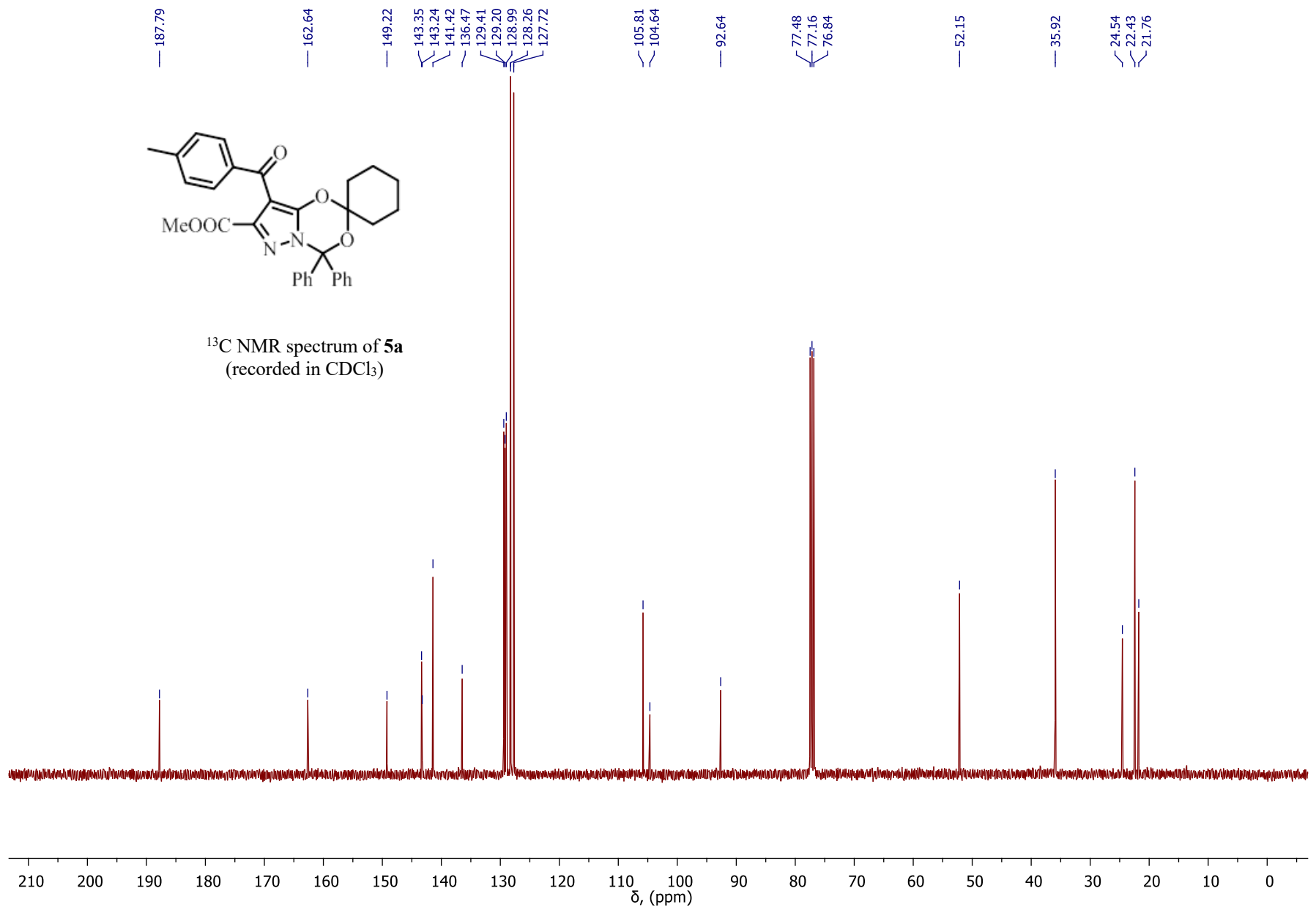
$^{13}\text{C}$  NMR spectrum of **4d**  
(recorded in  $\text{C}_6\text{D}_6$ )

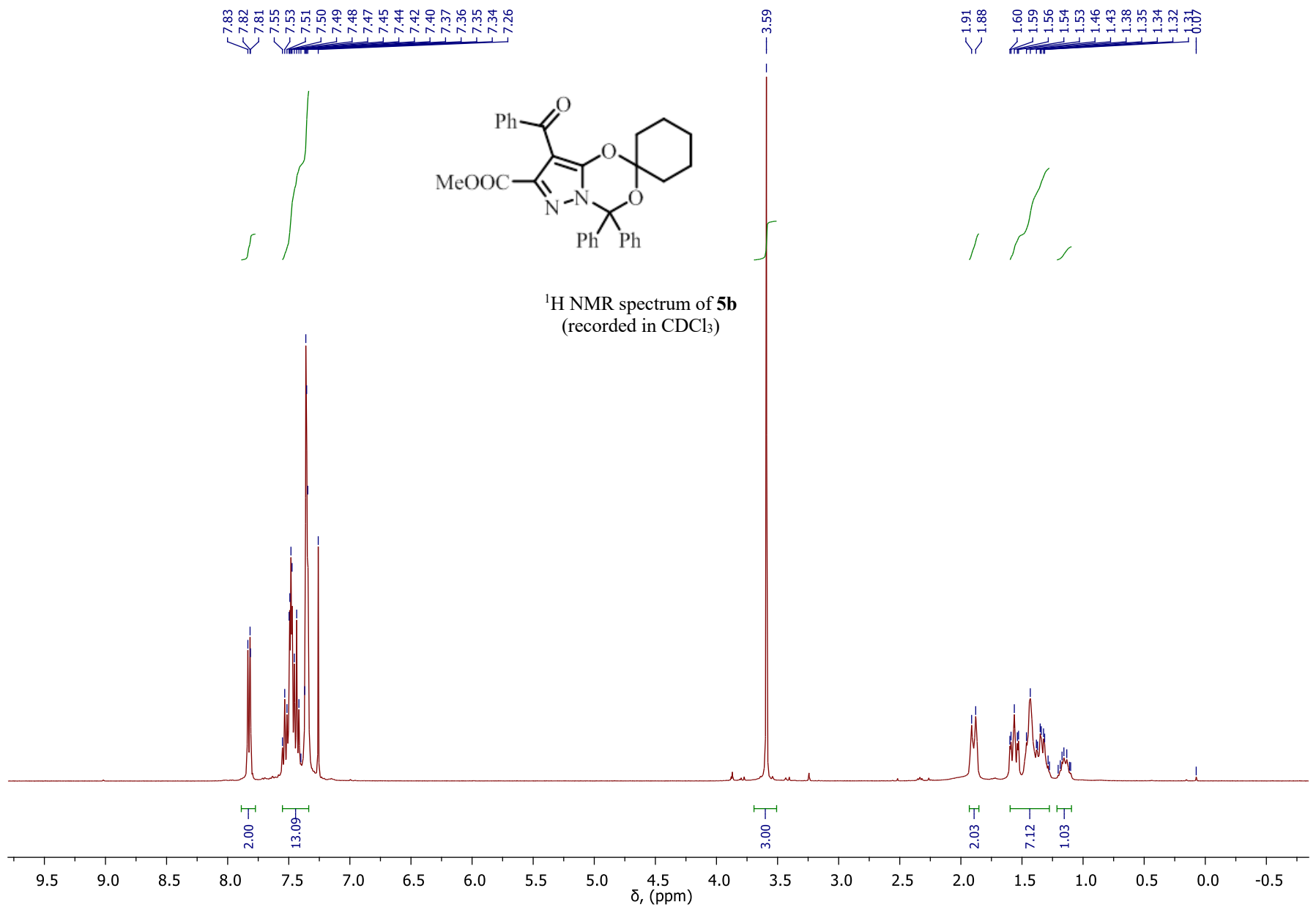


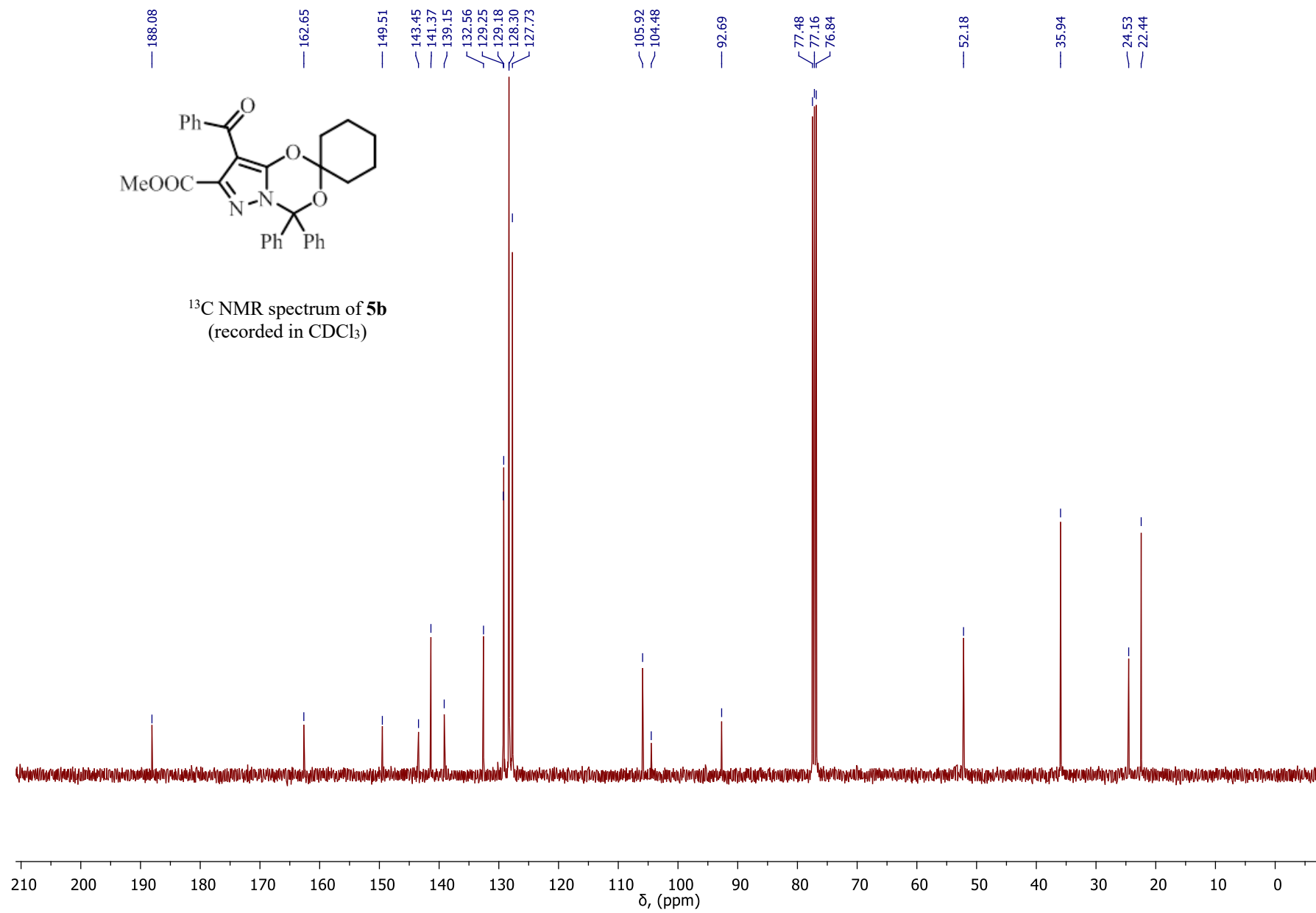


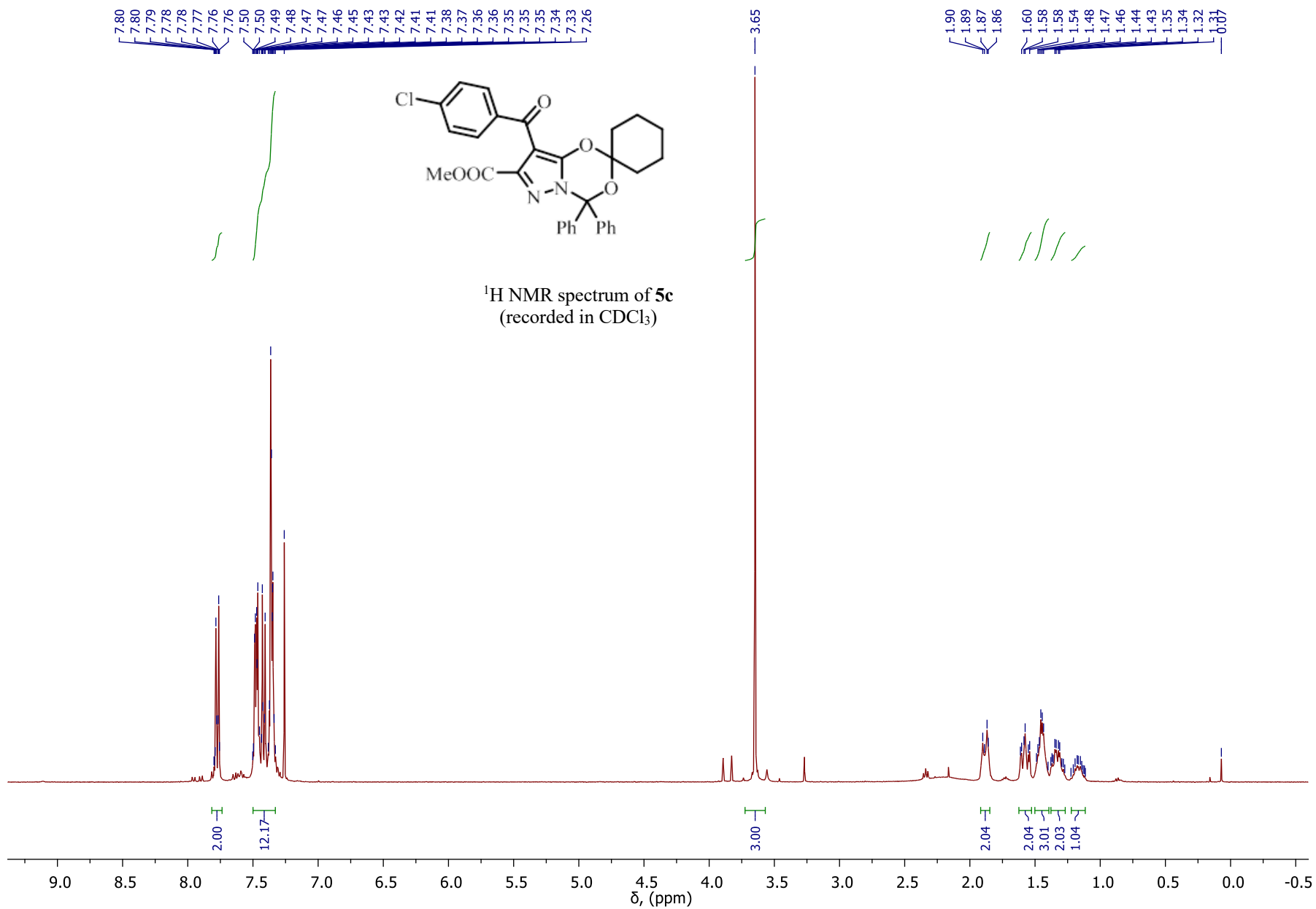


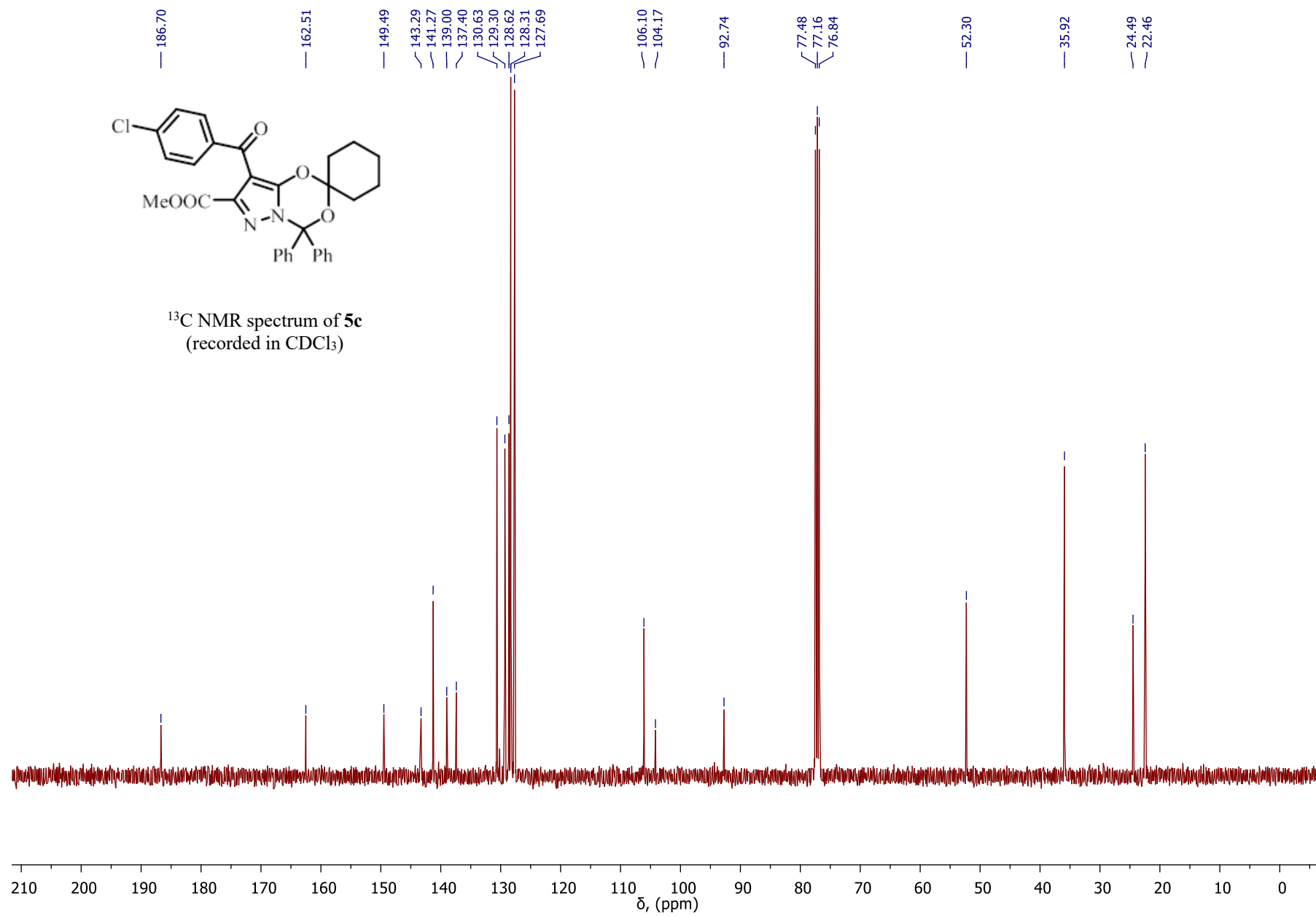


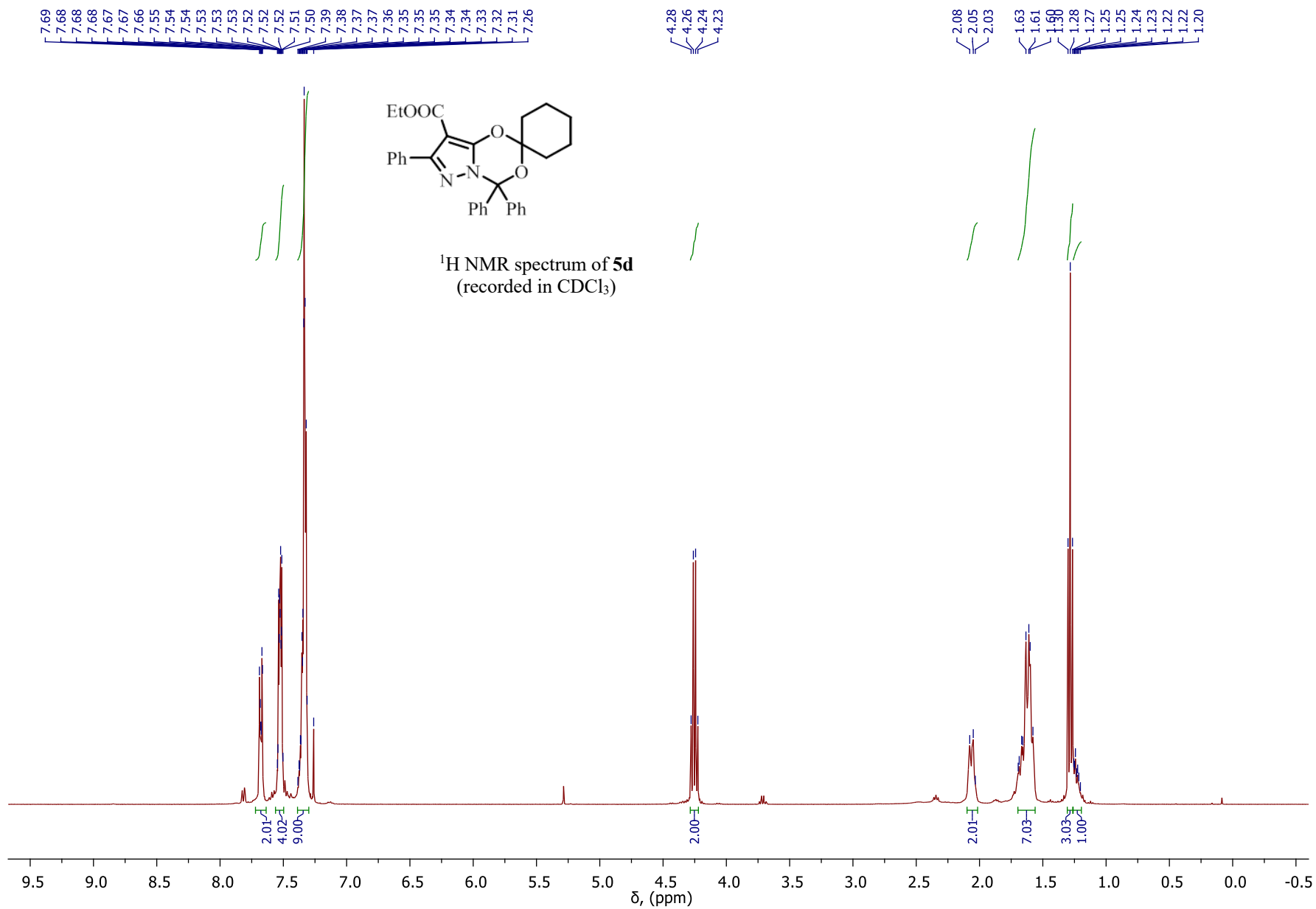


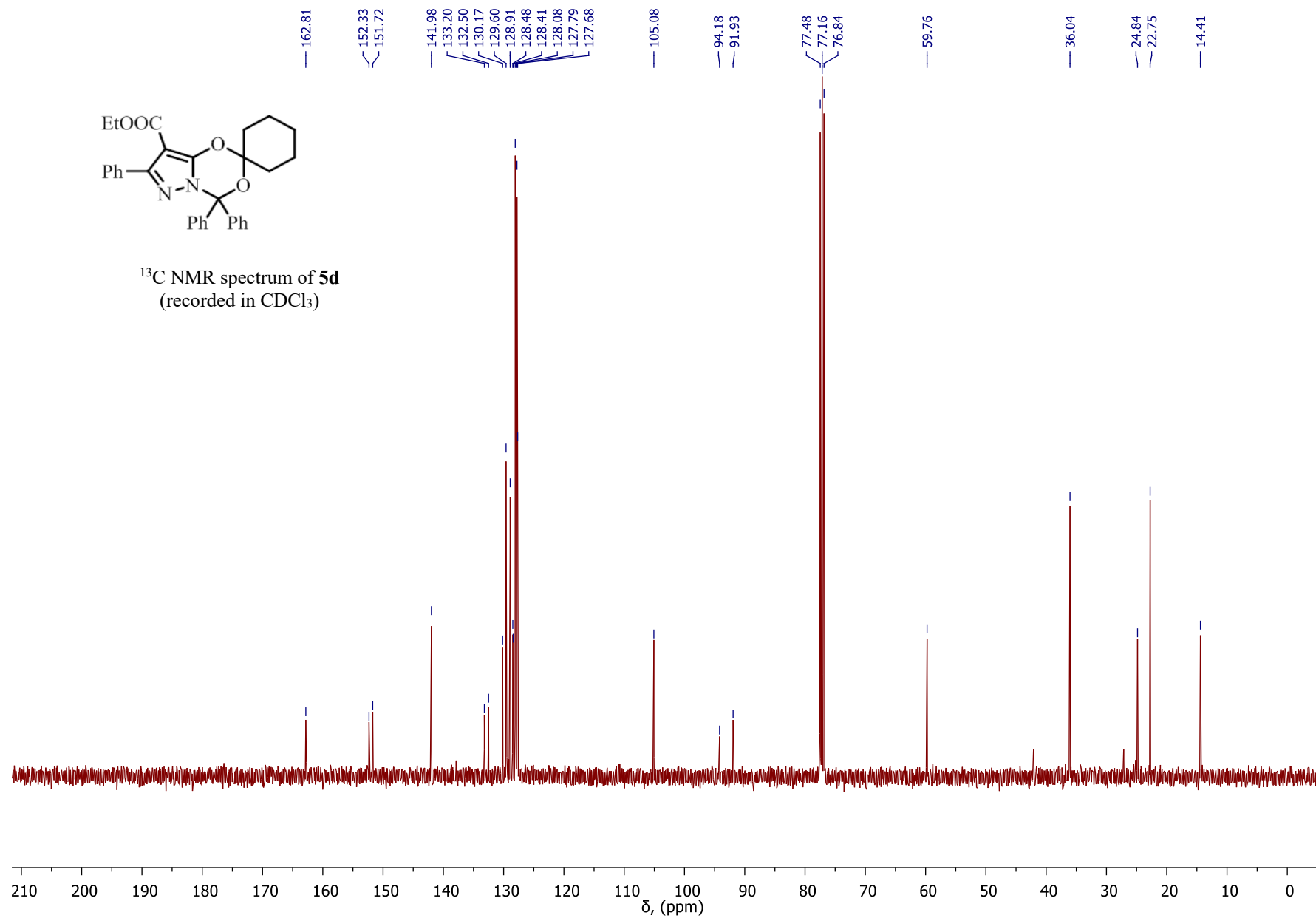




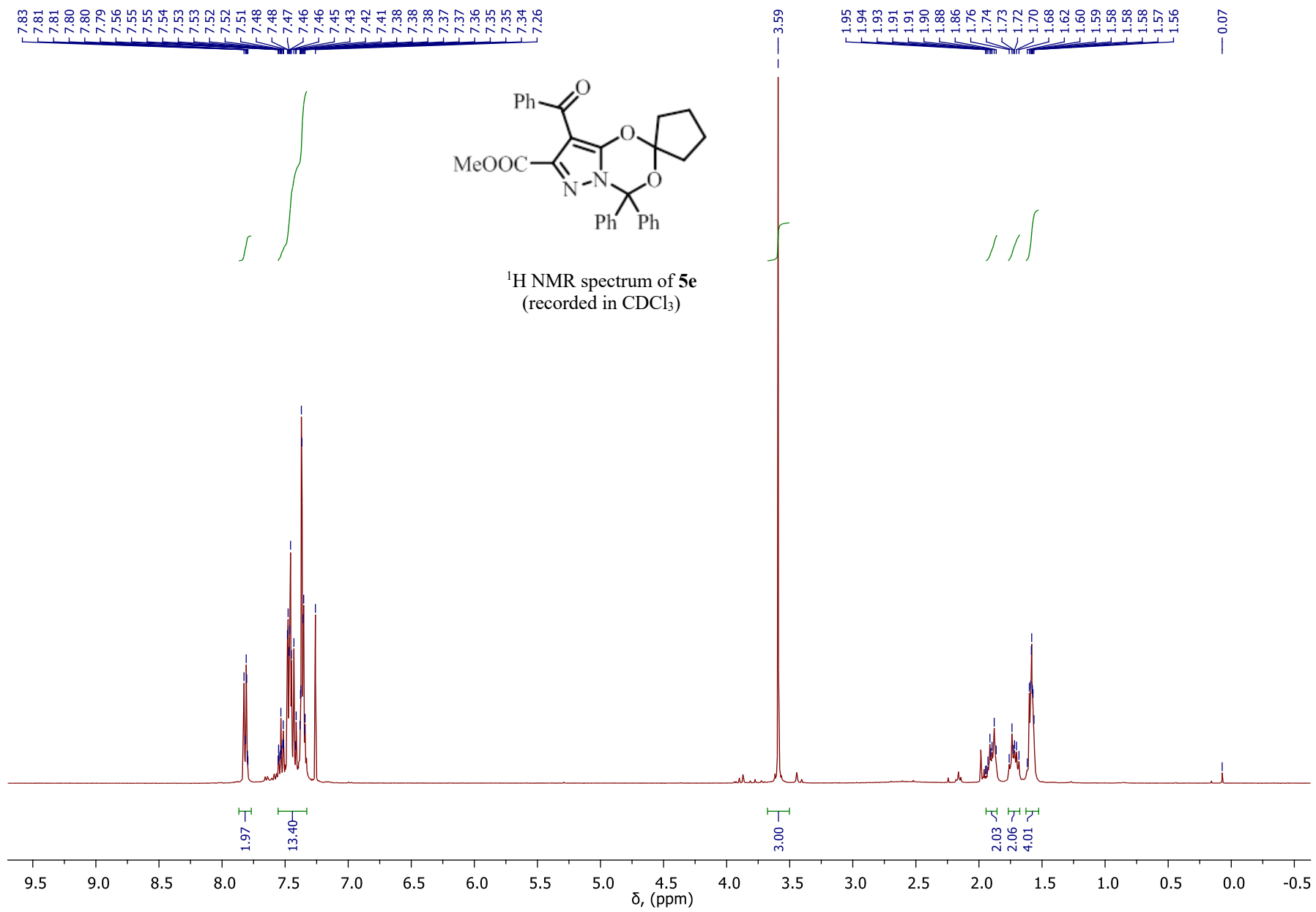


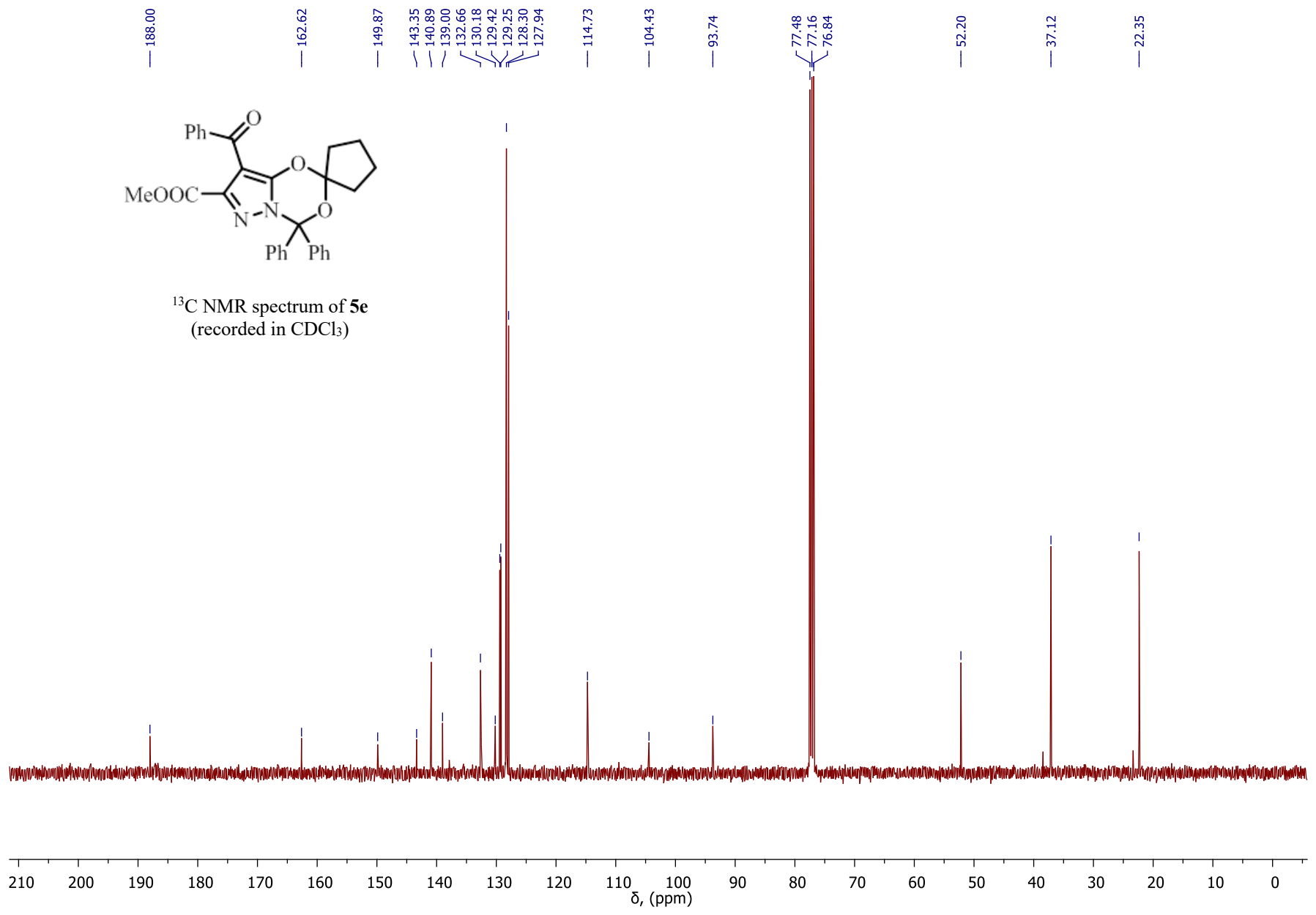


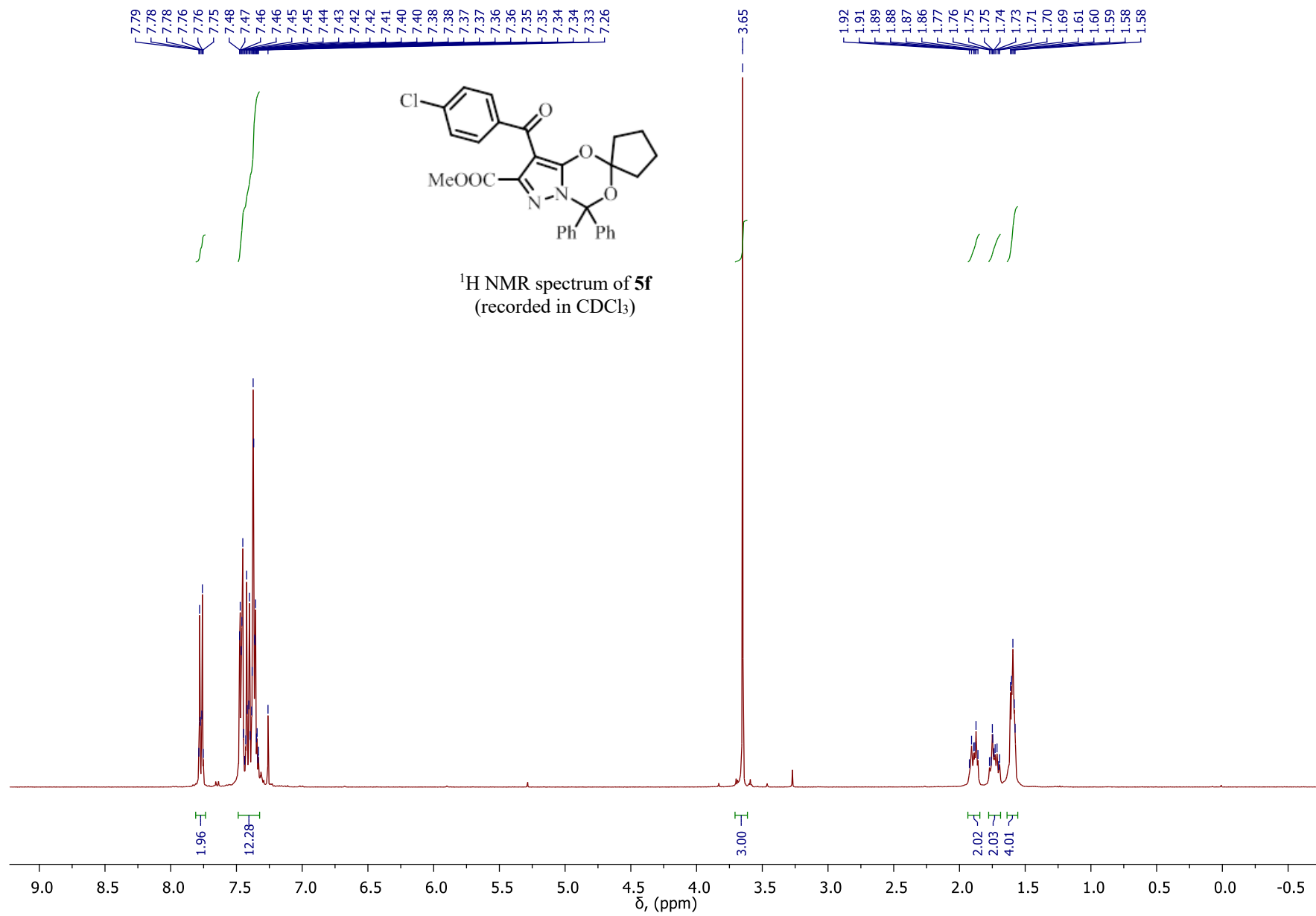


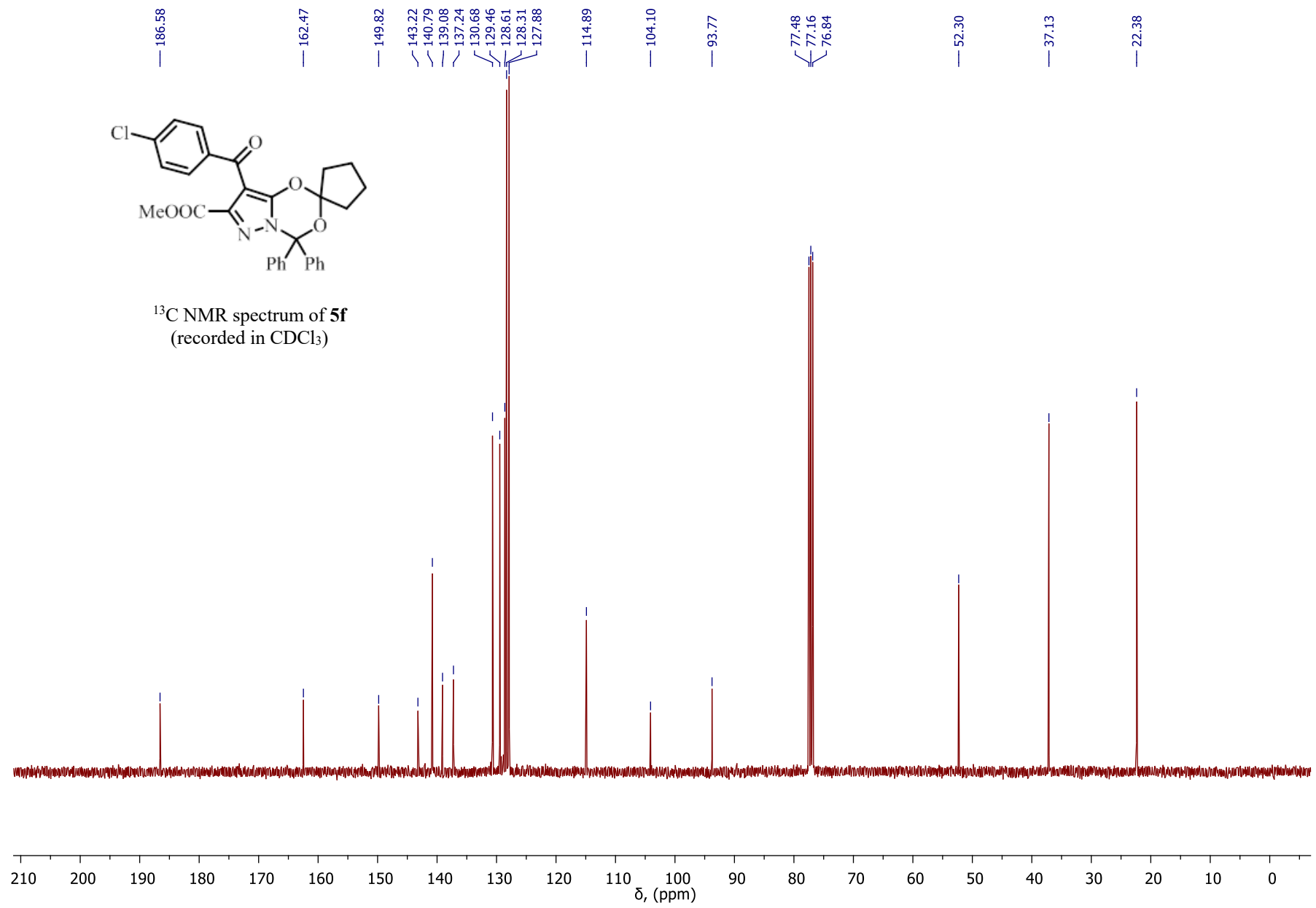


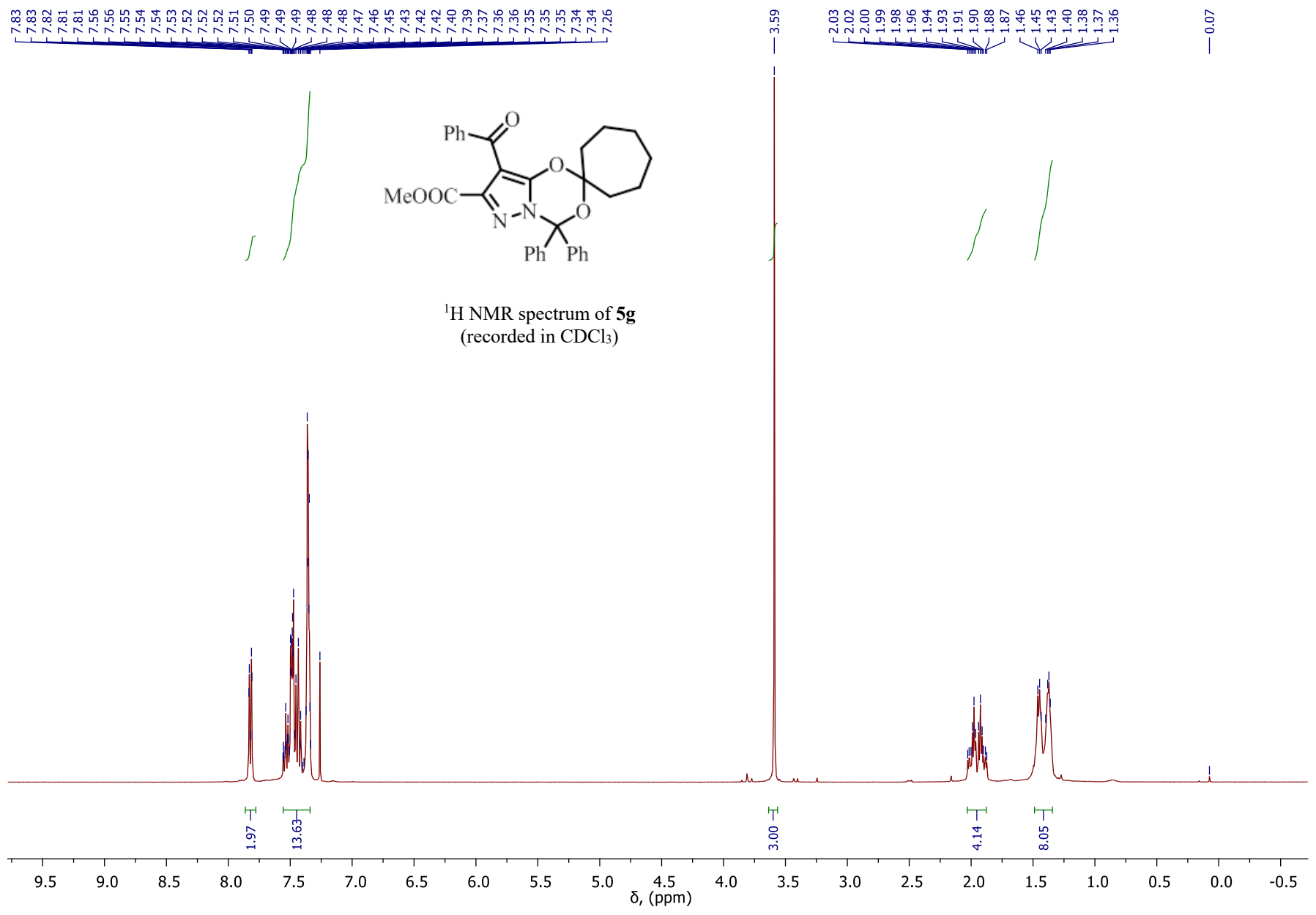


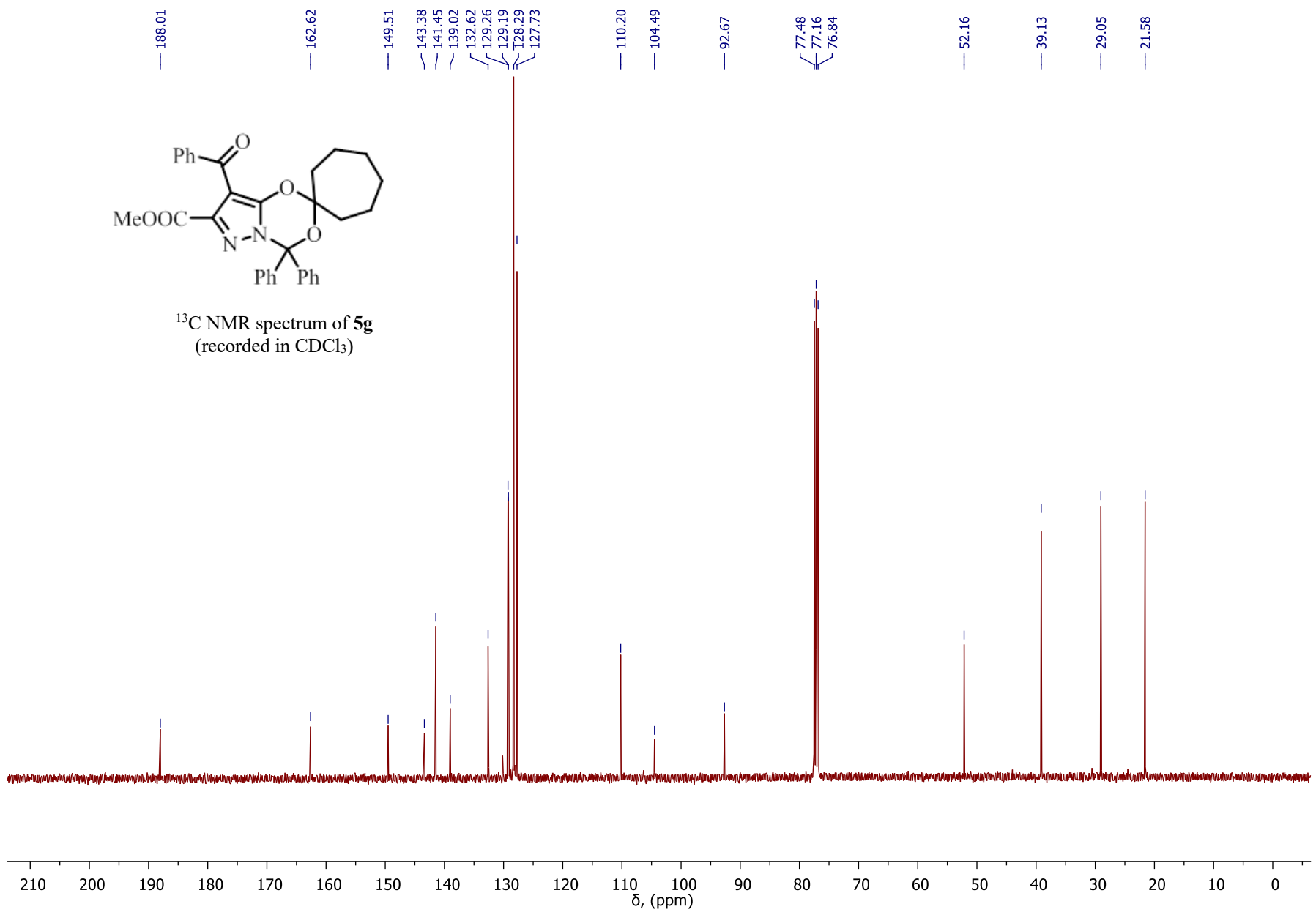


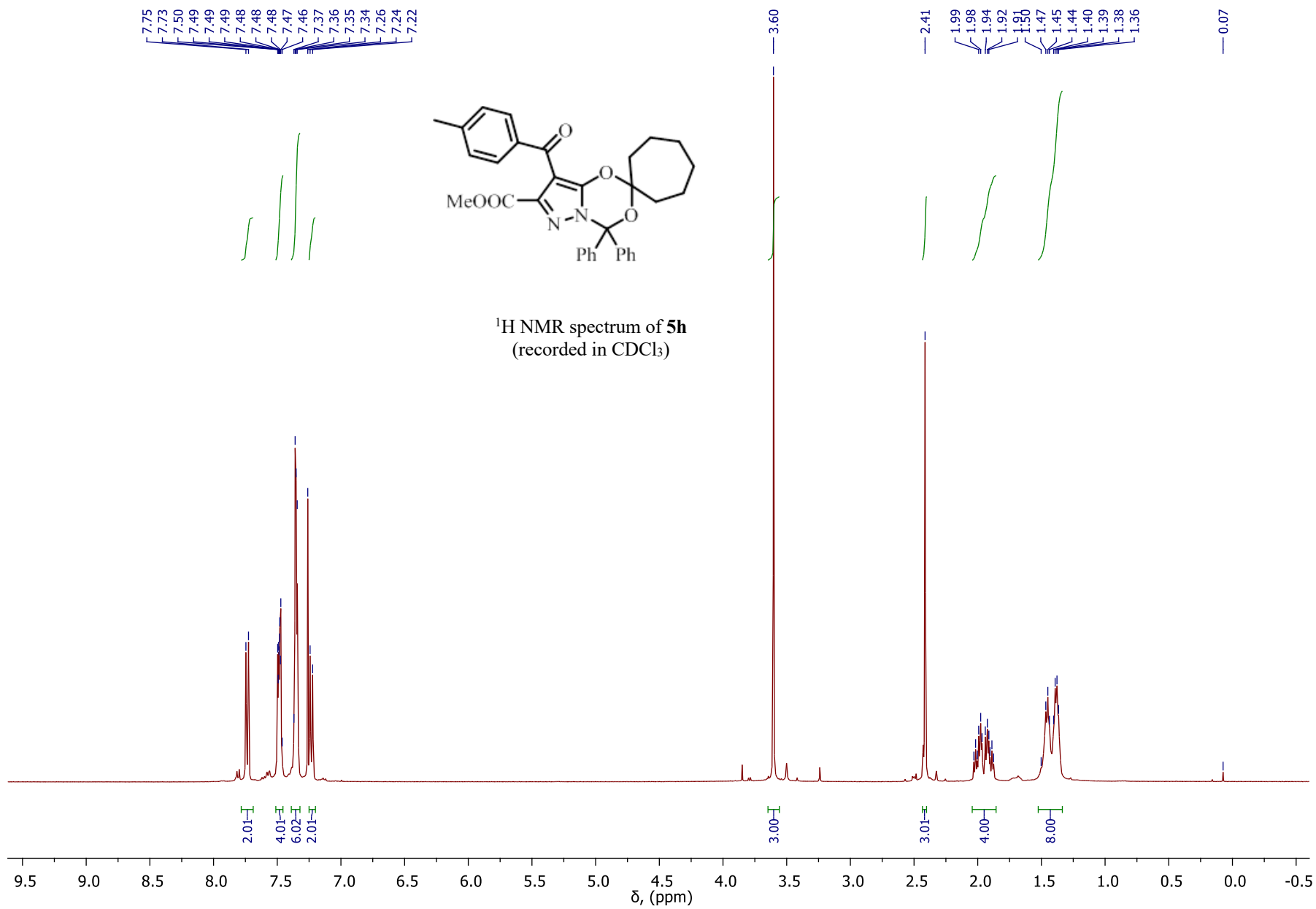


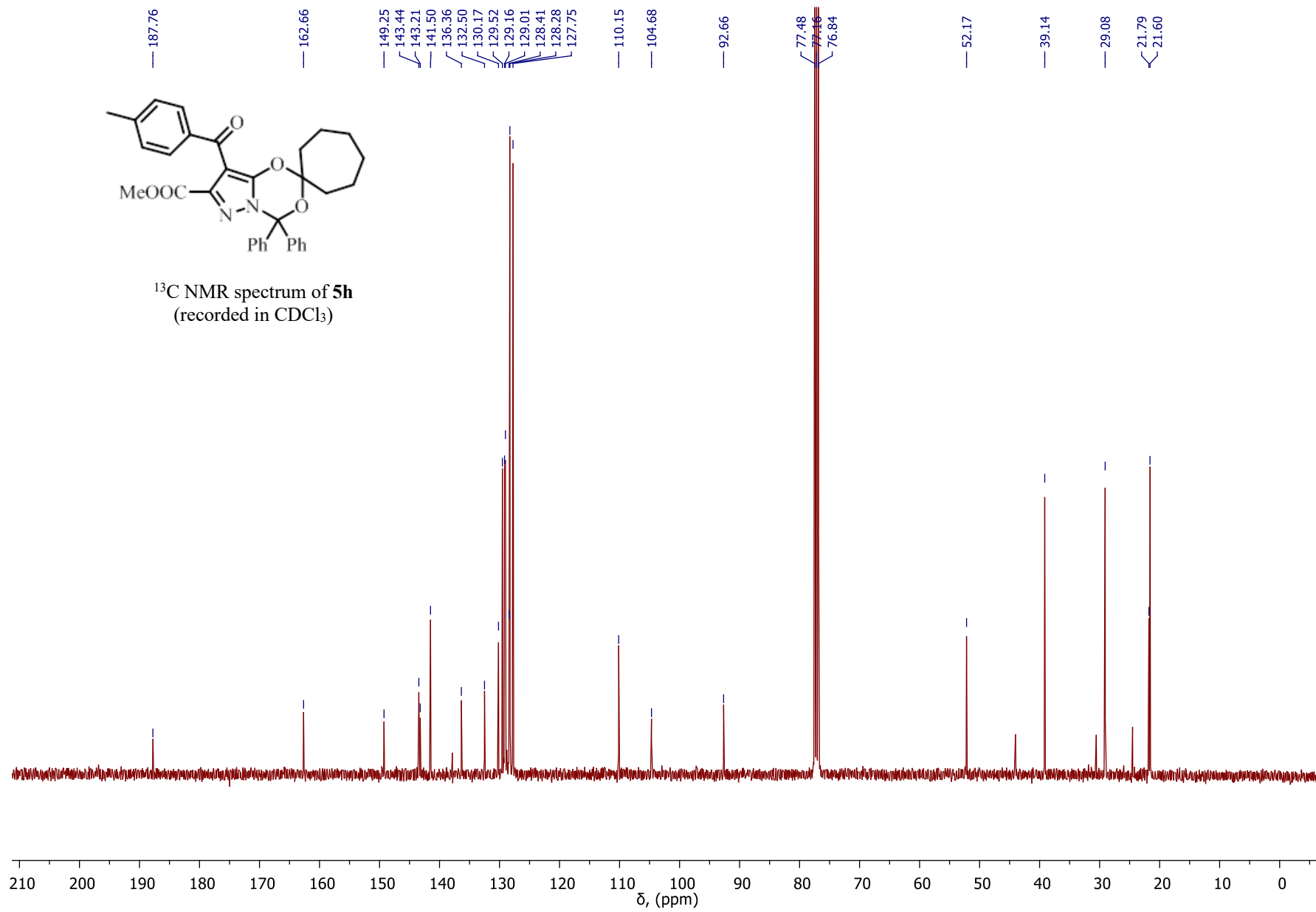




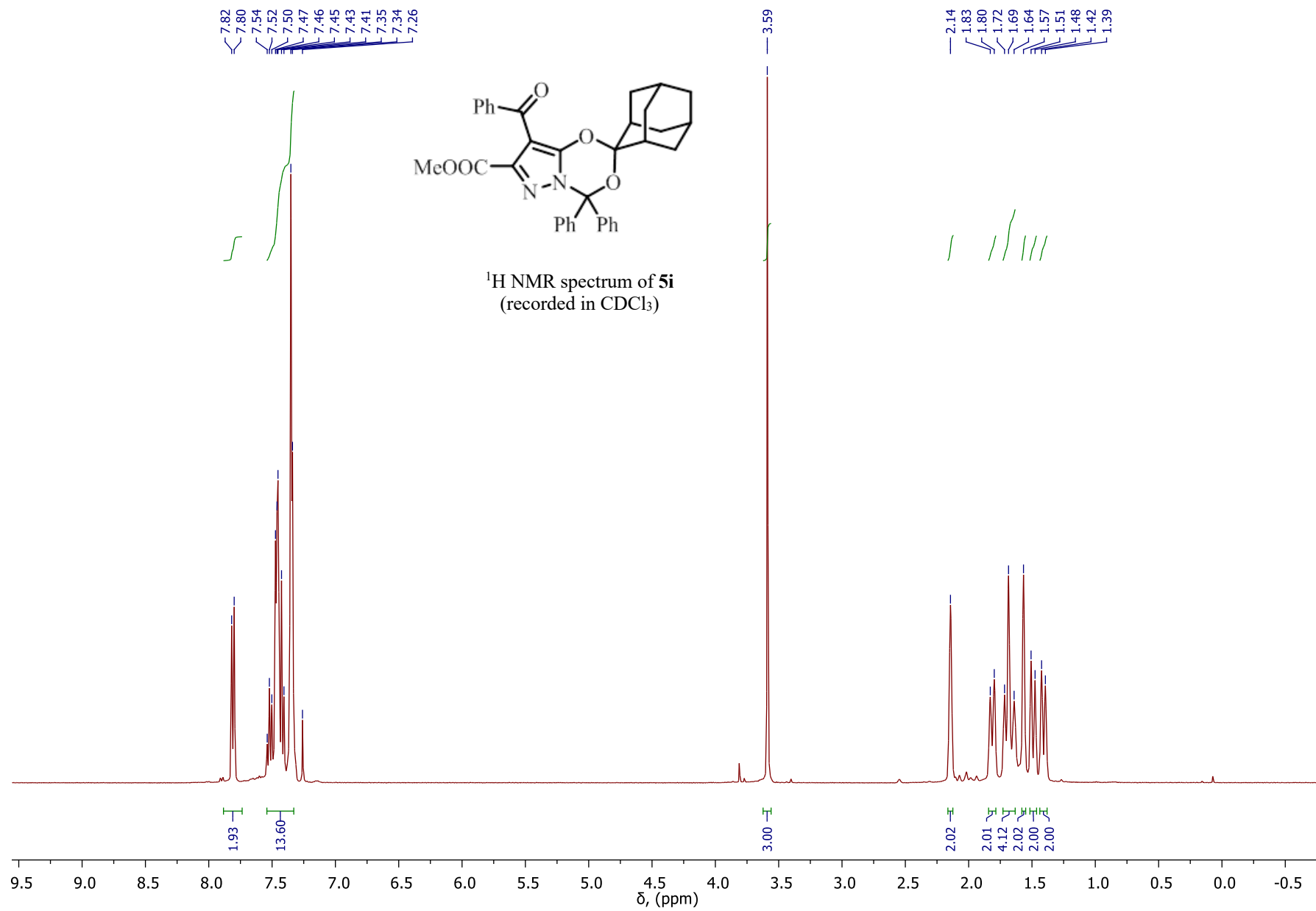


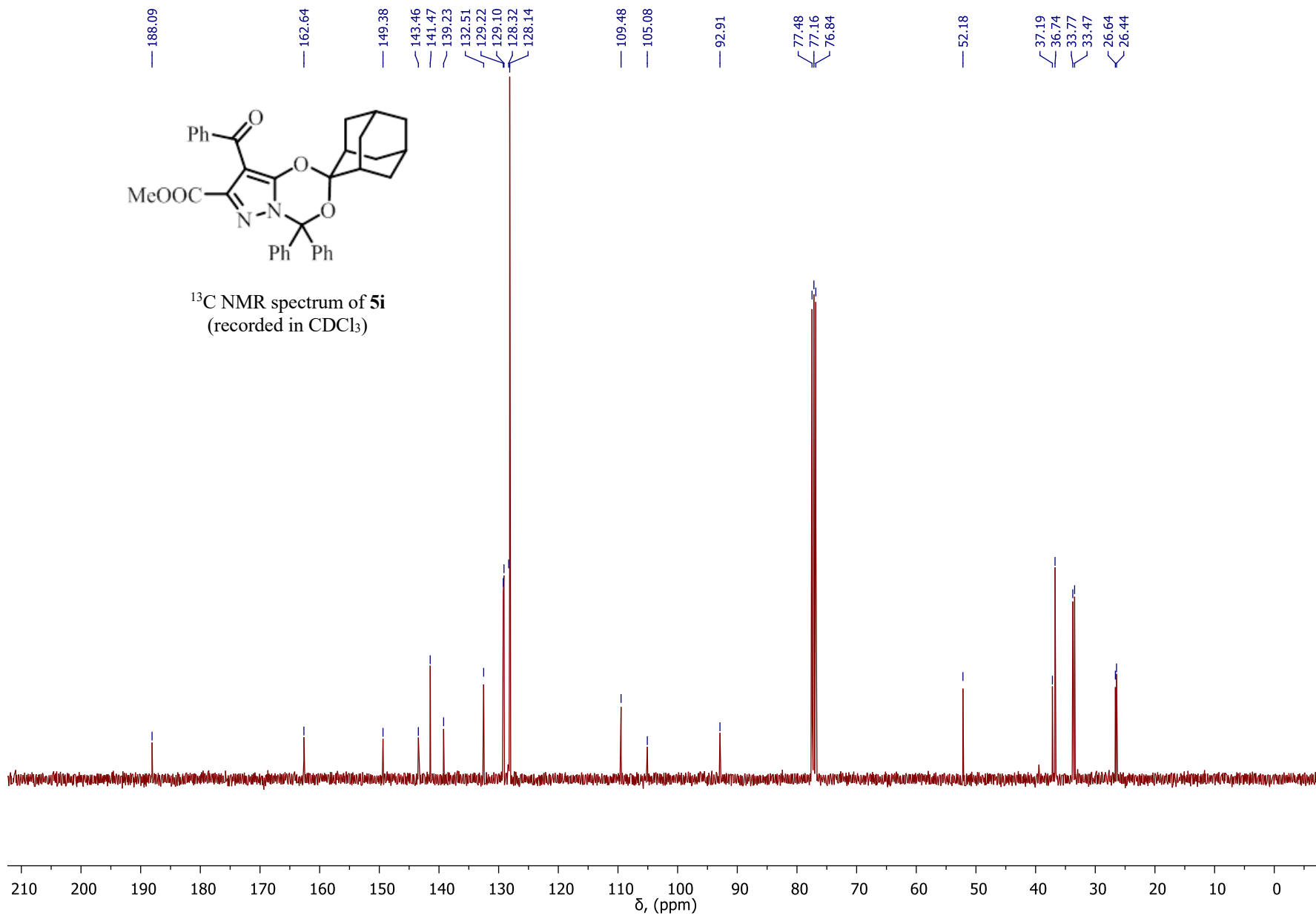


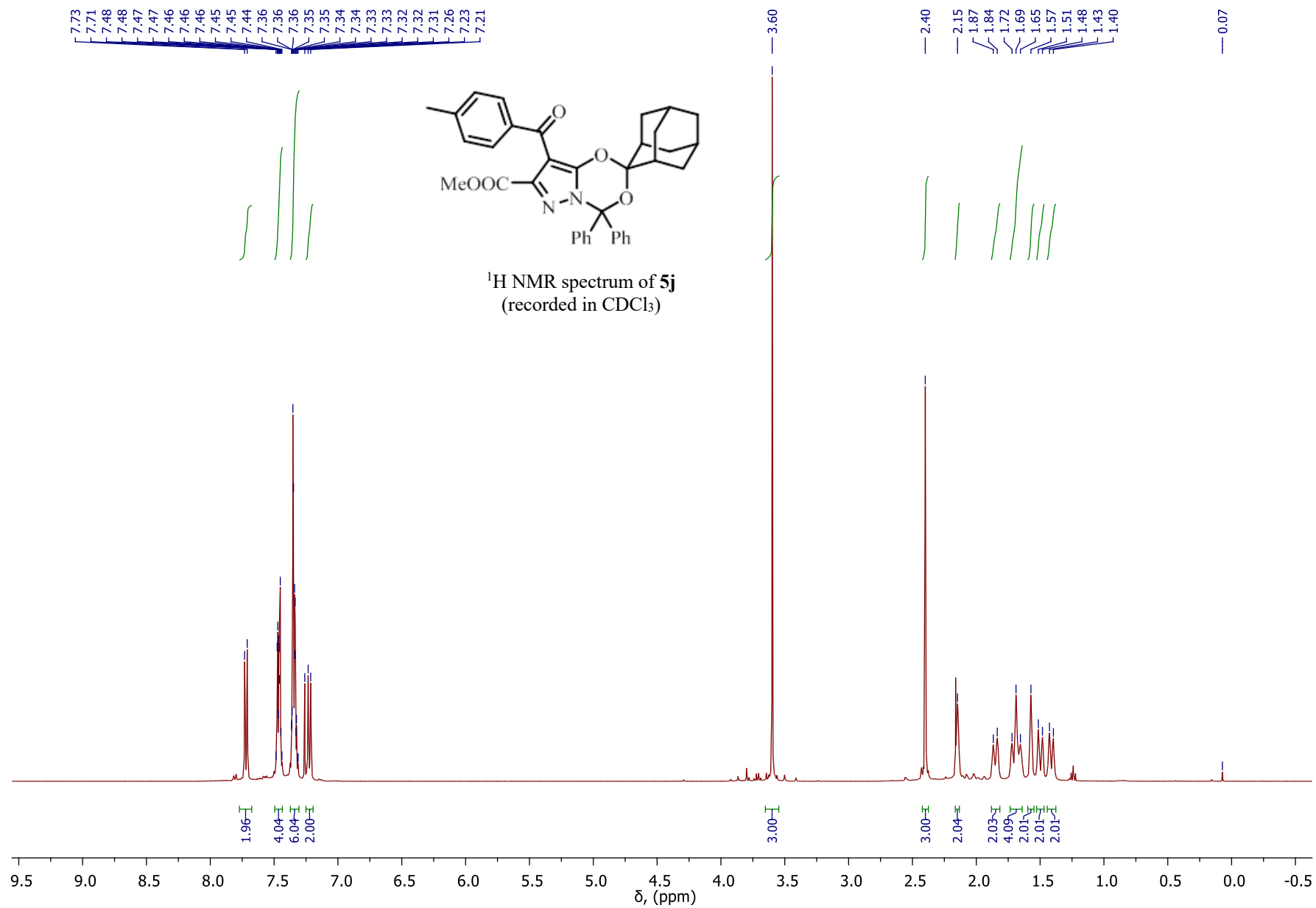


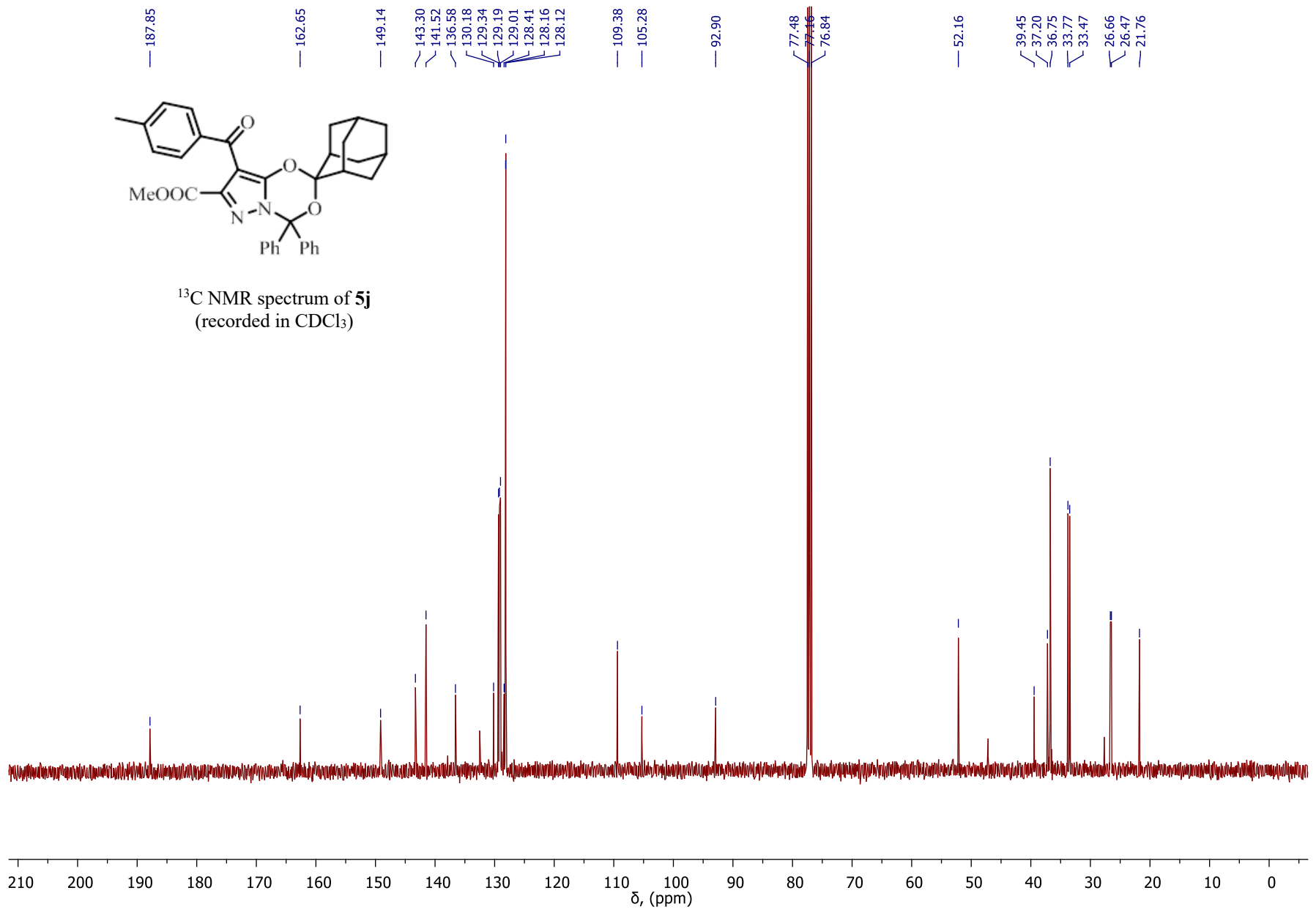


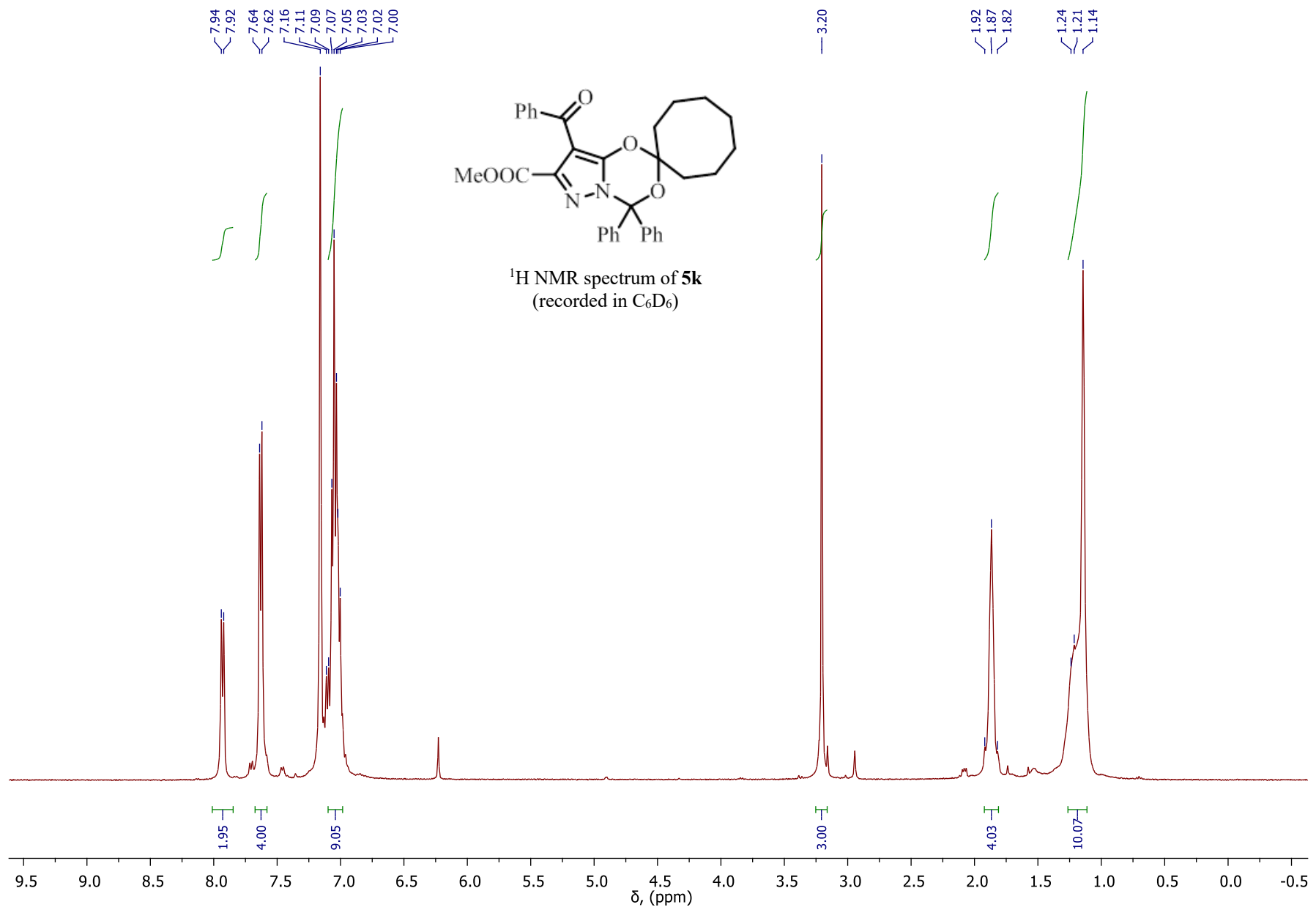


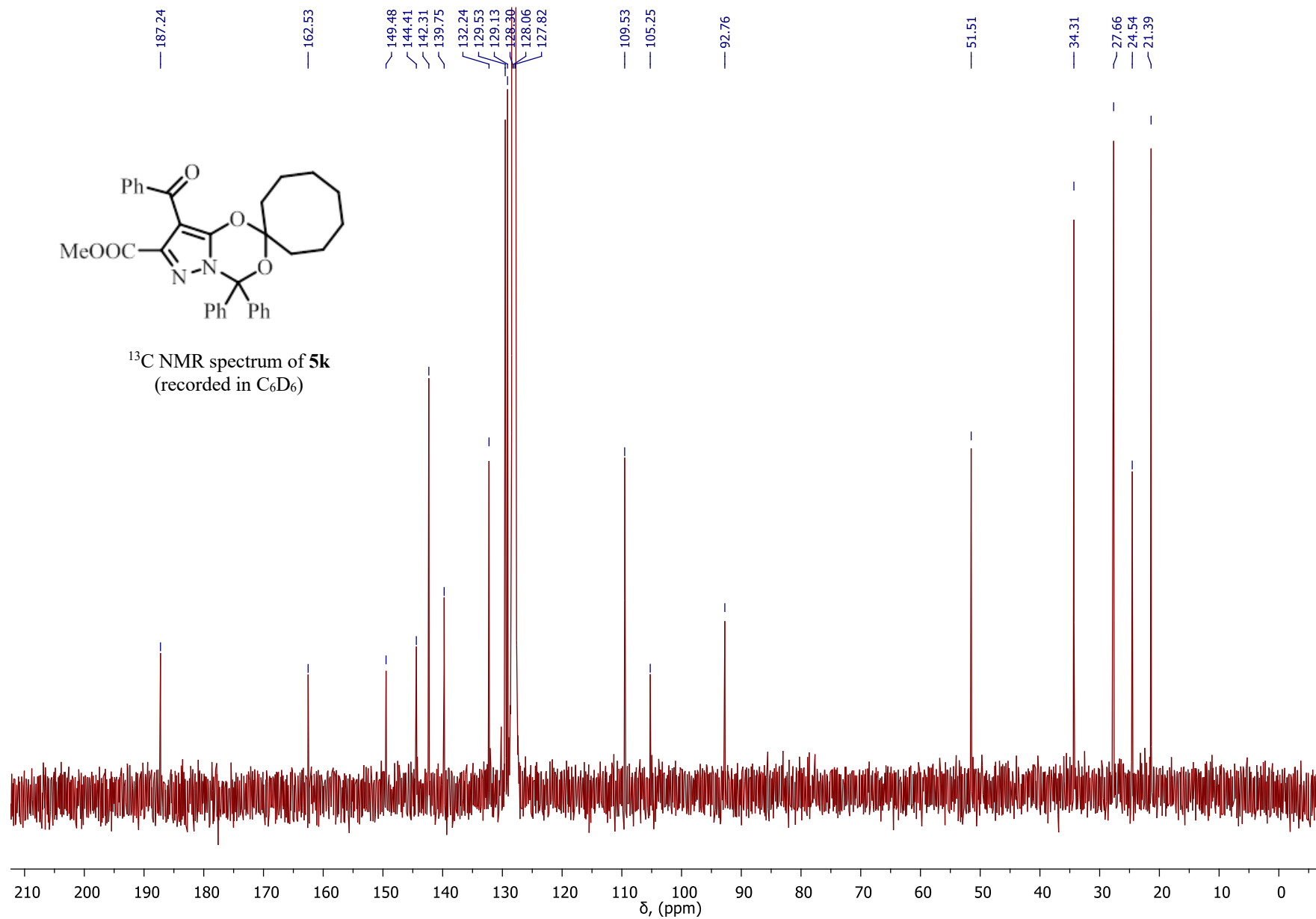


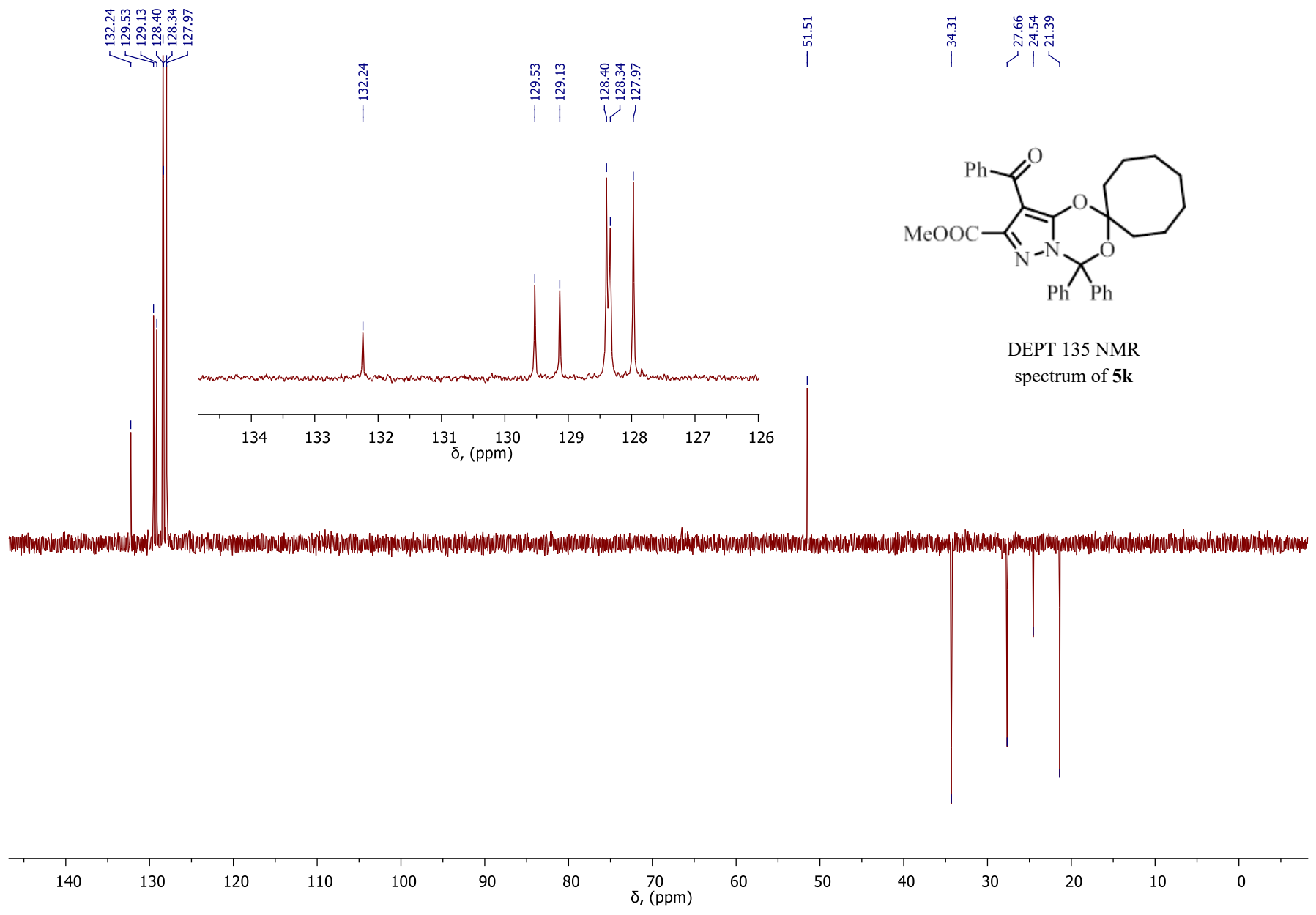


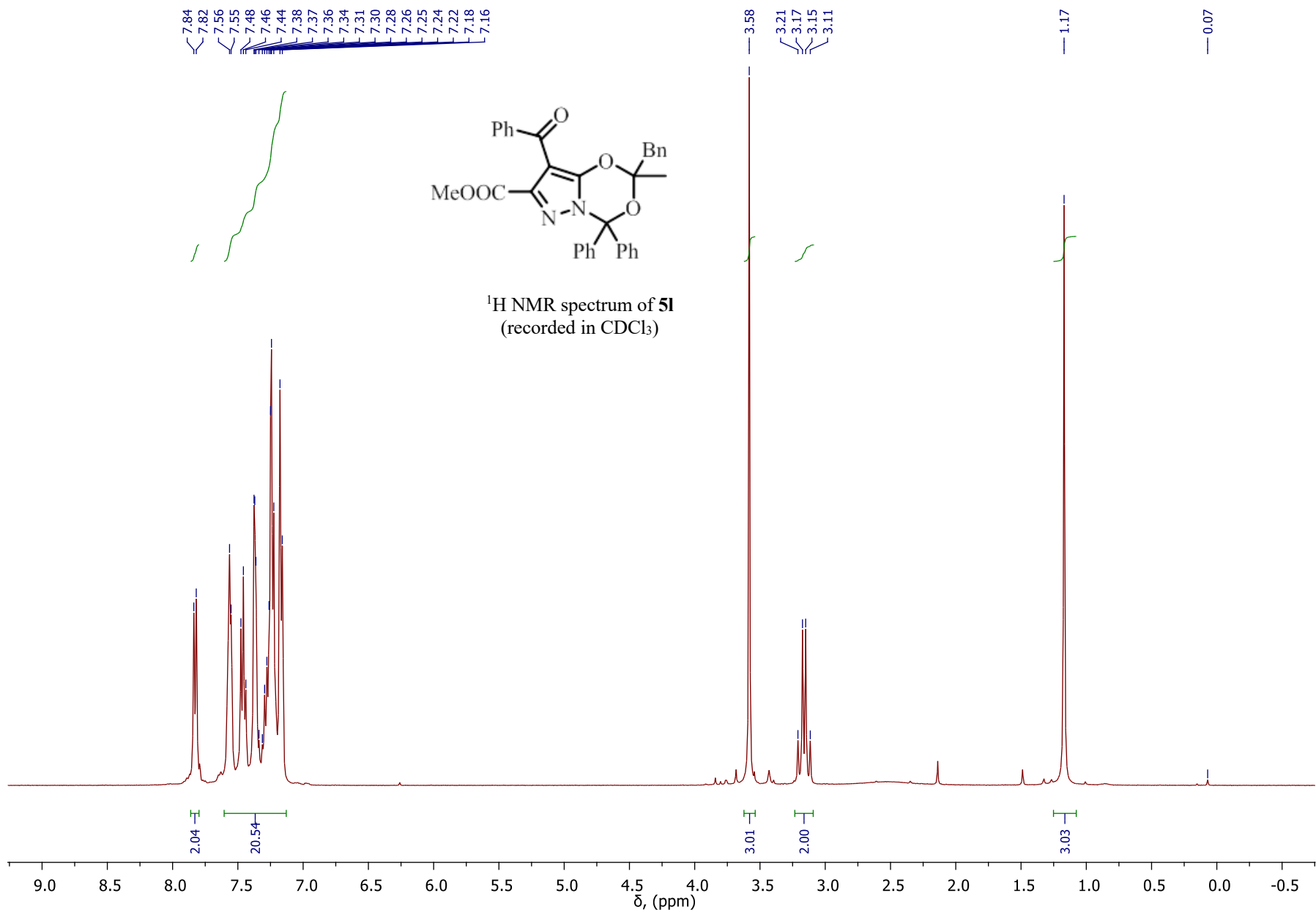




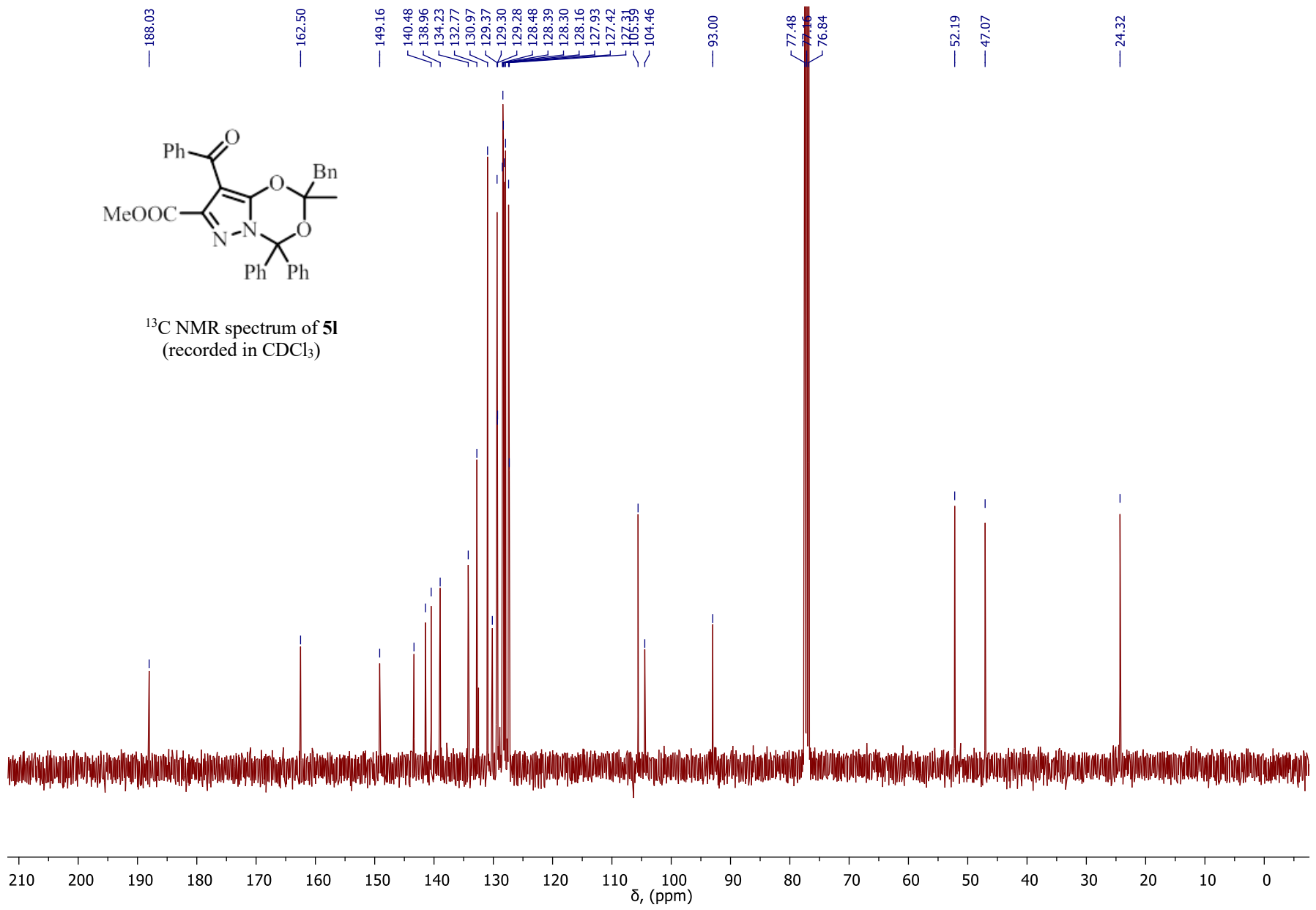


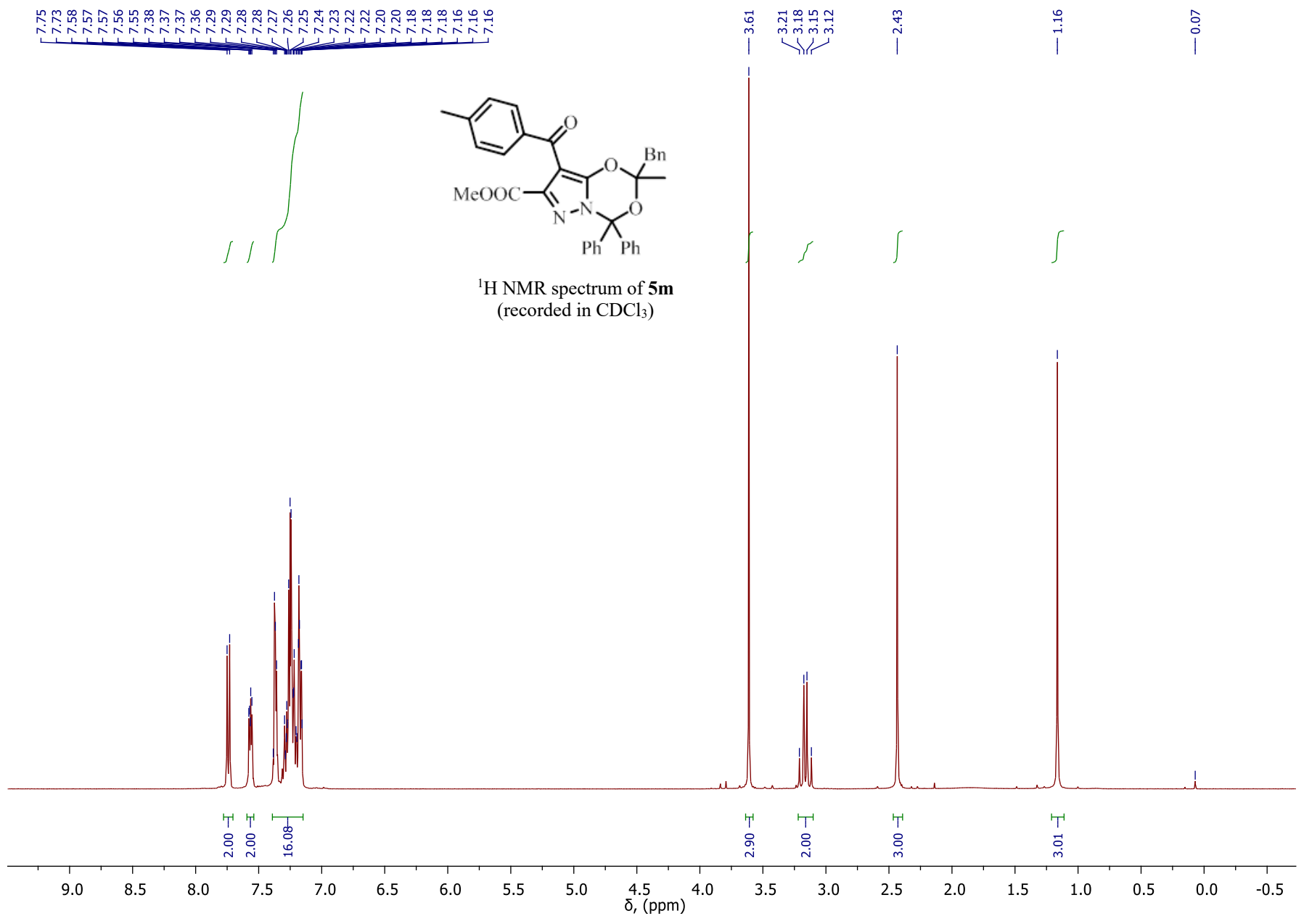


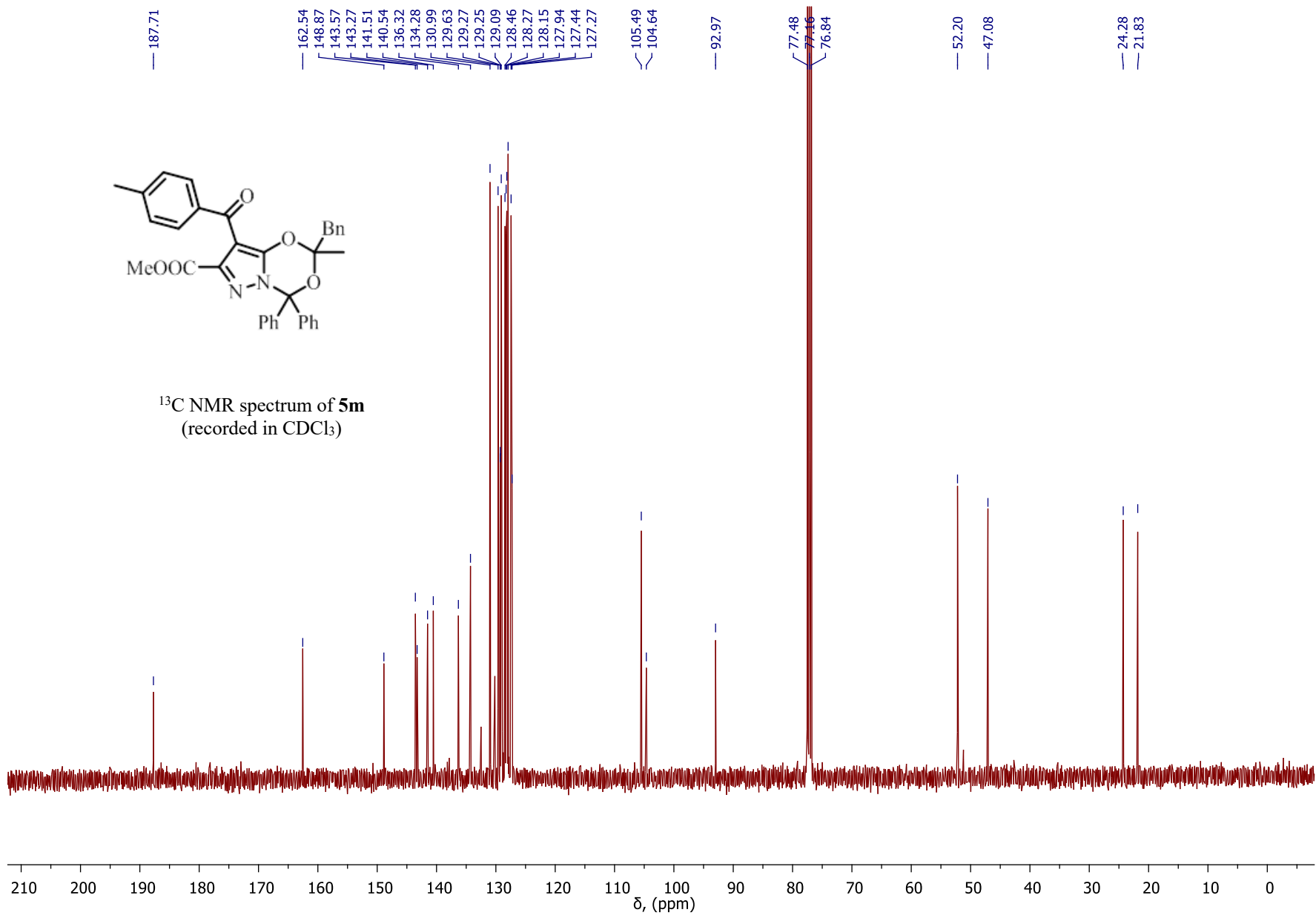


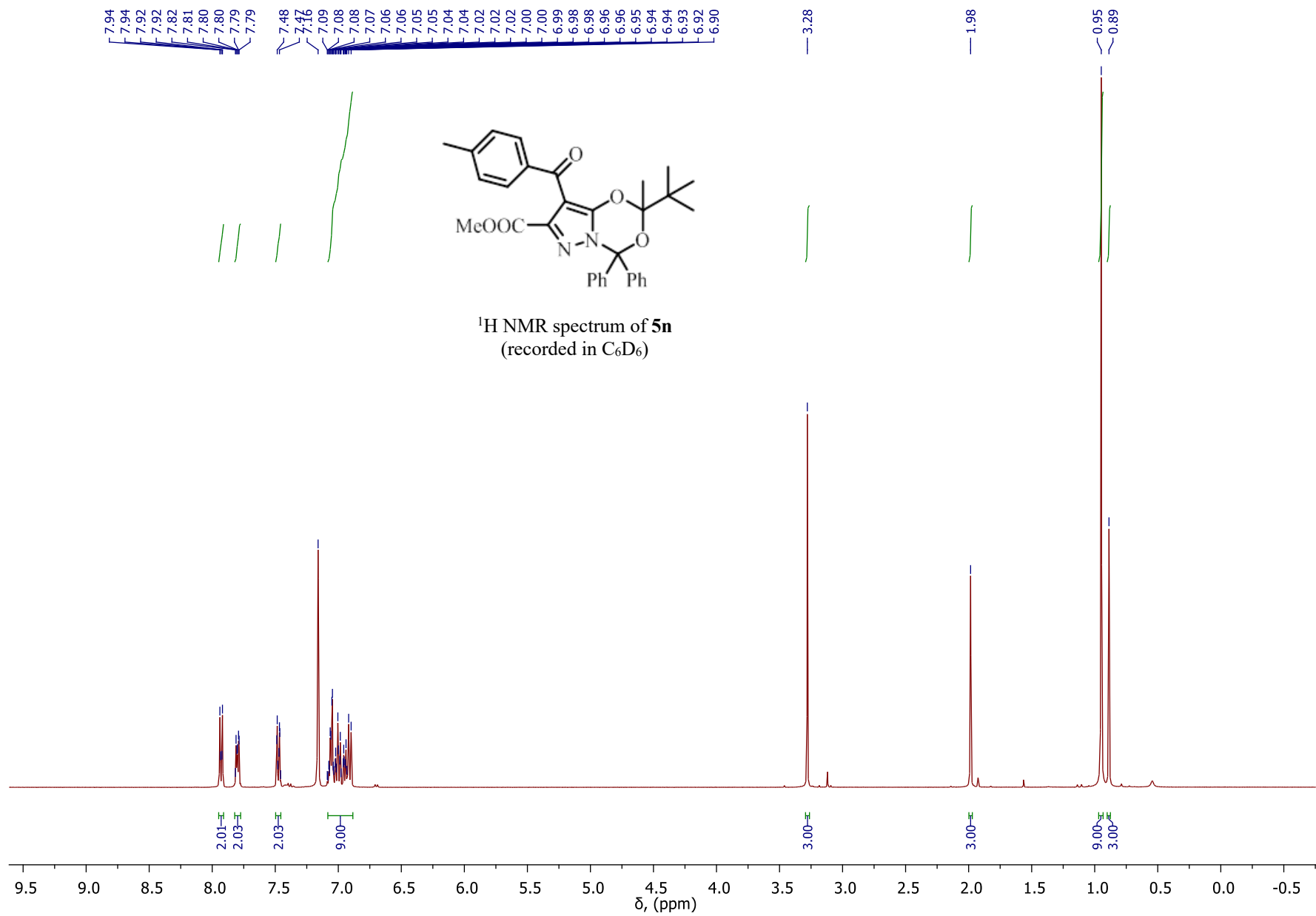


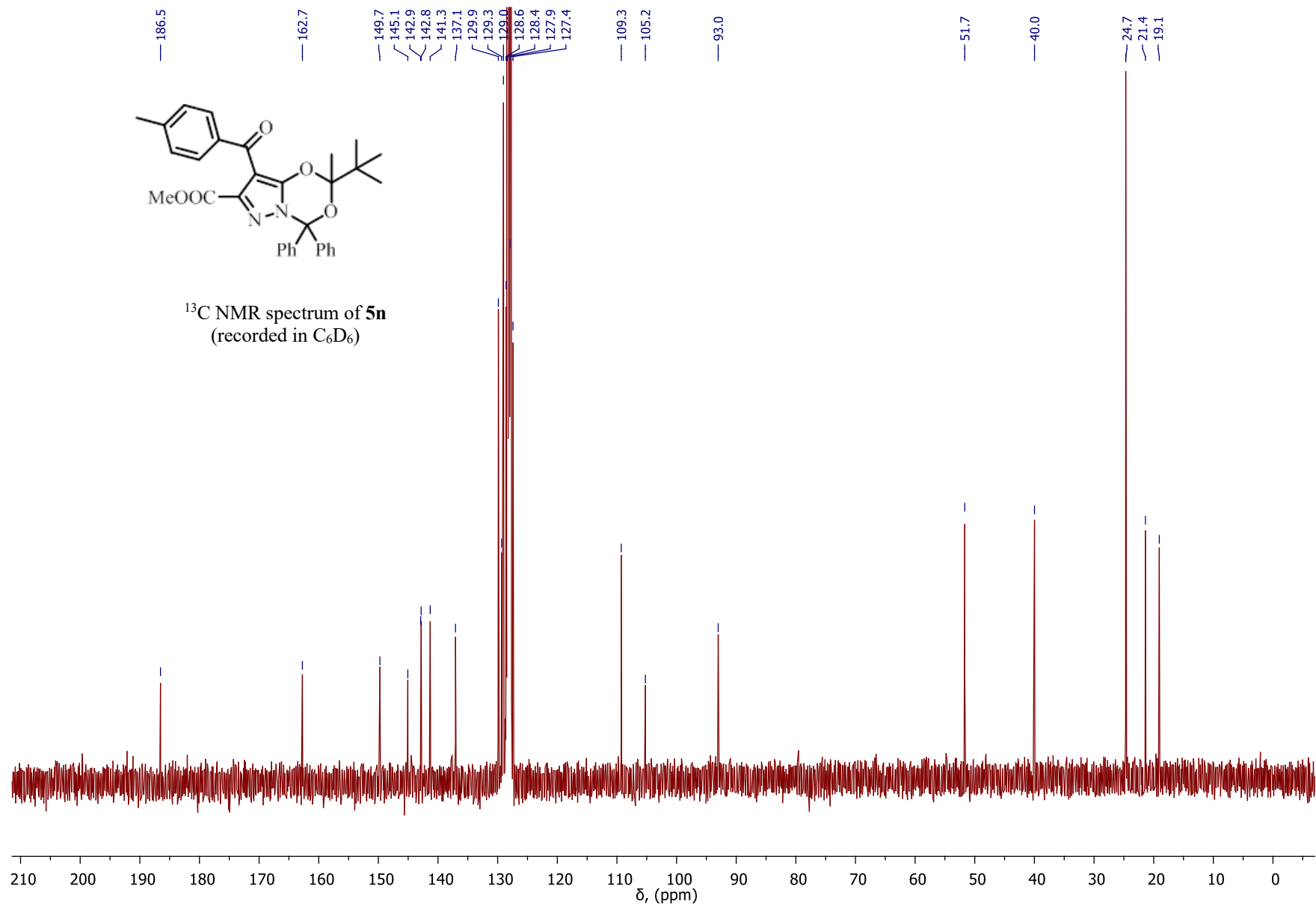


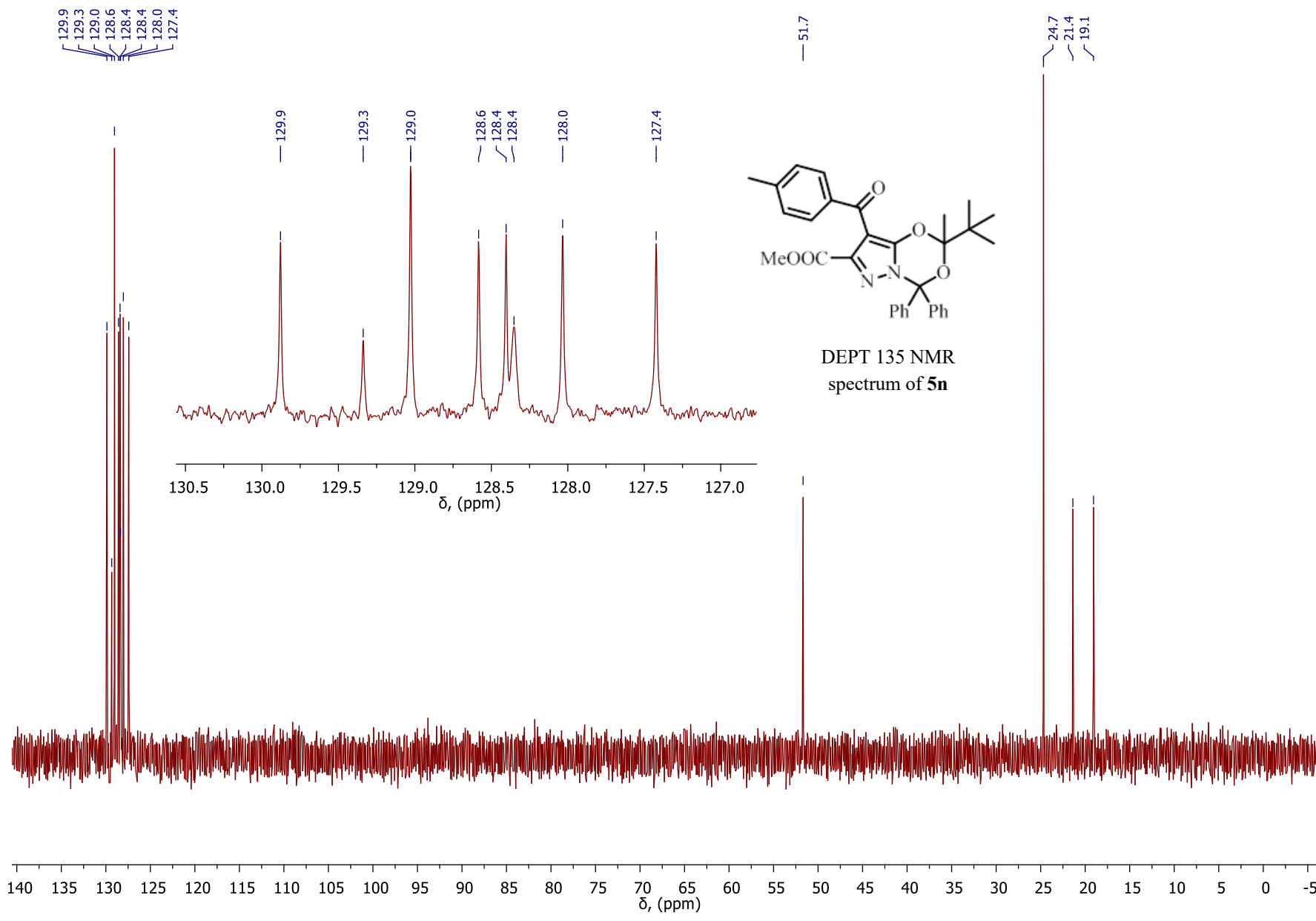


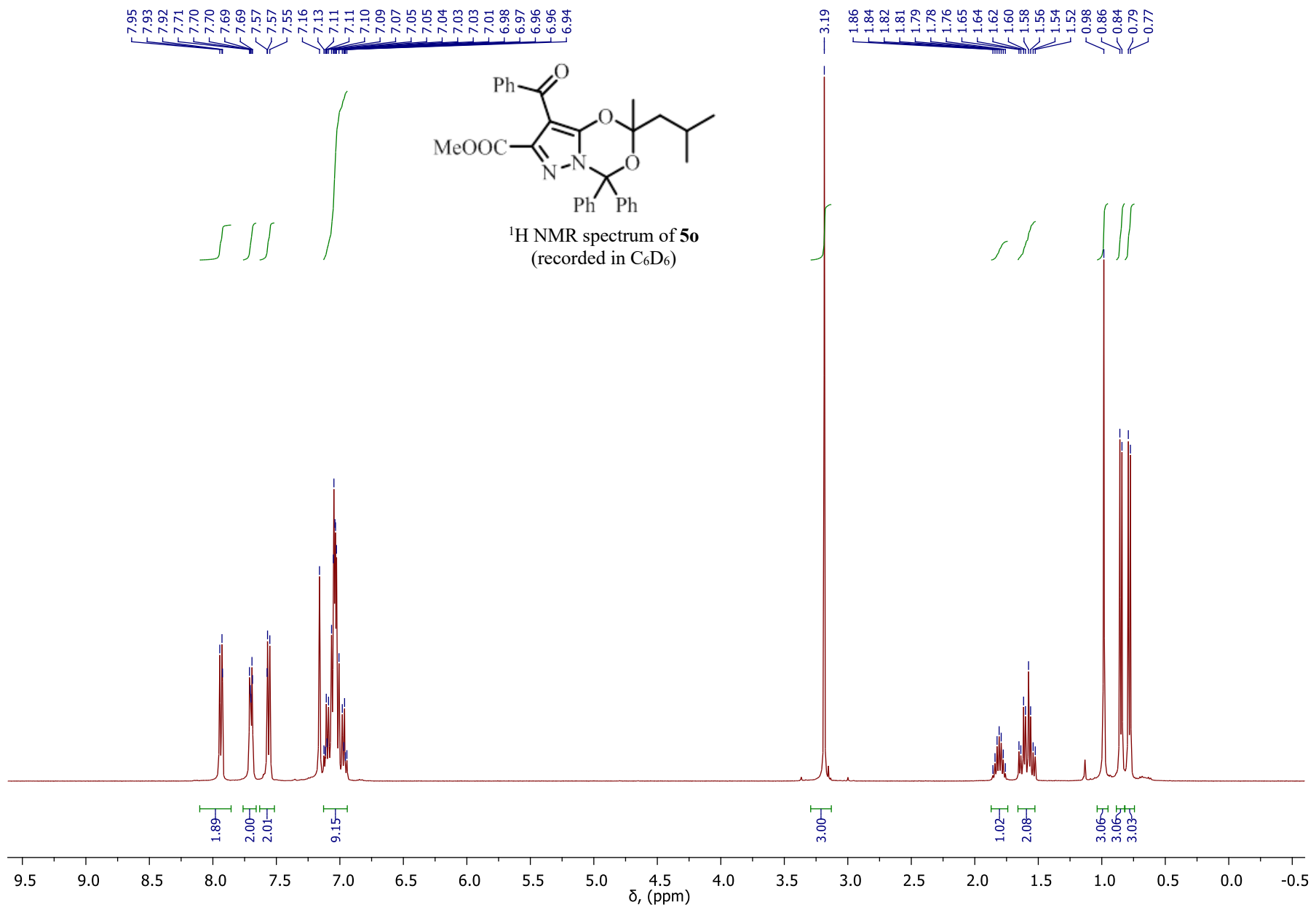


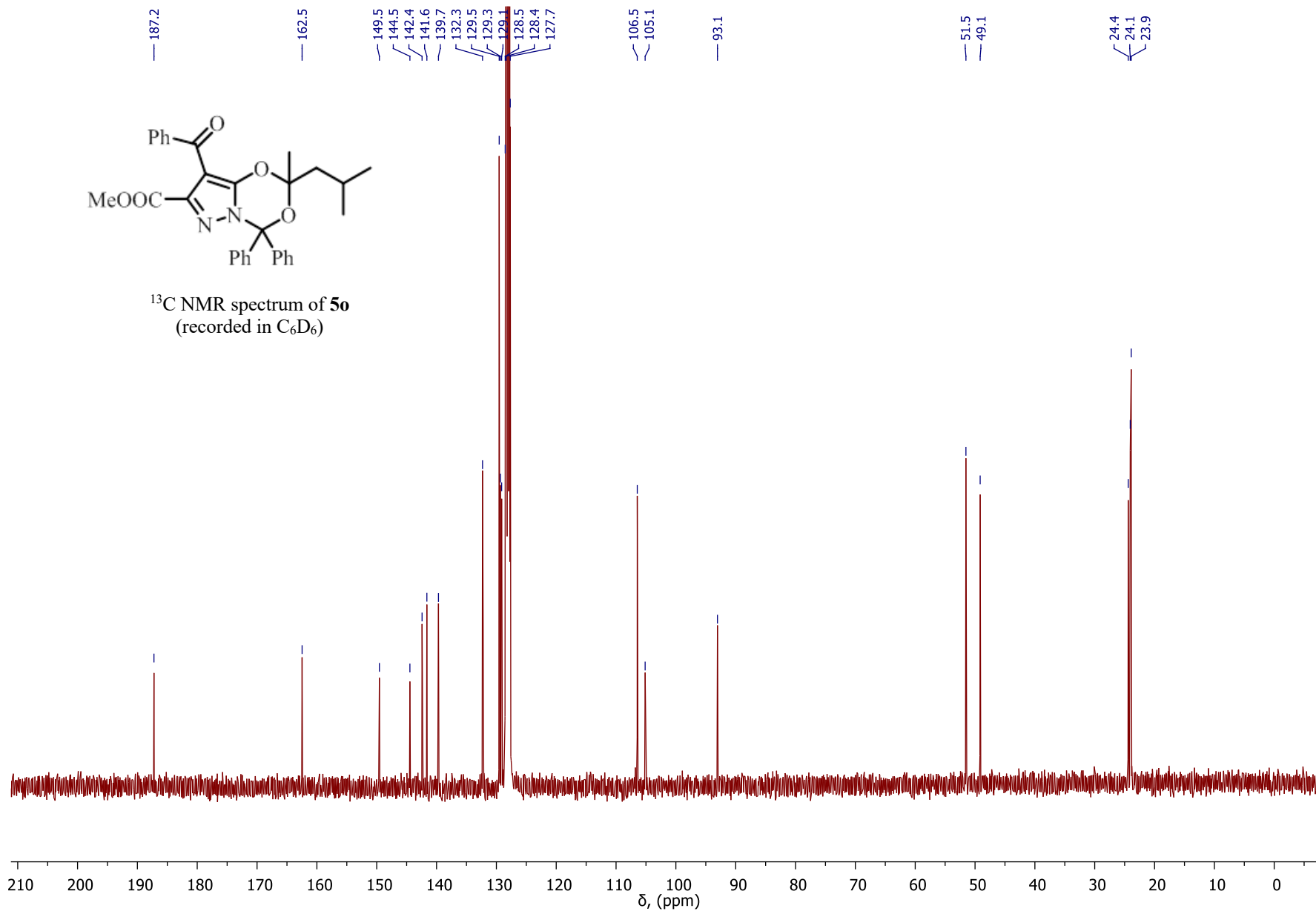




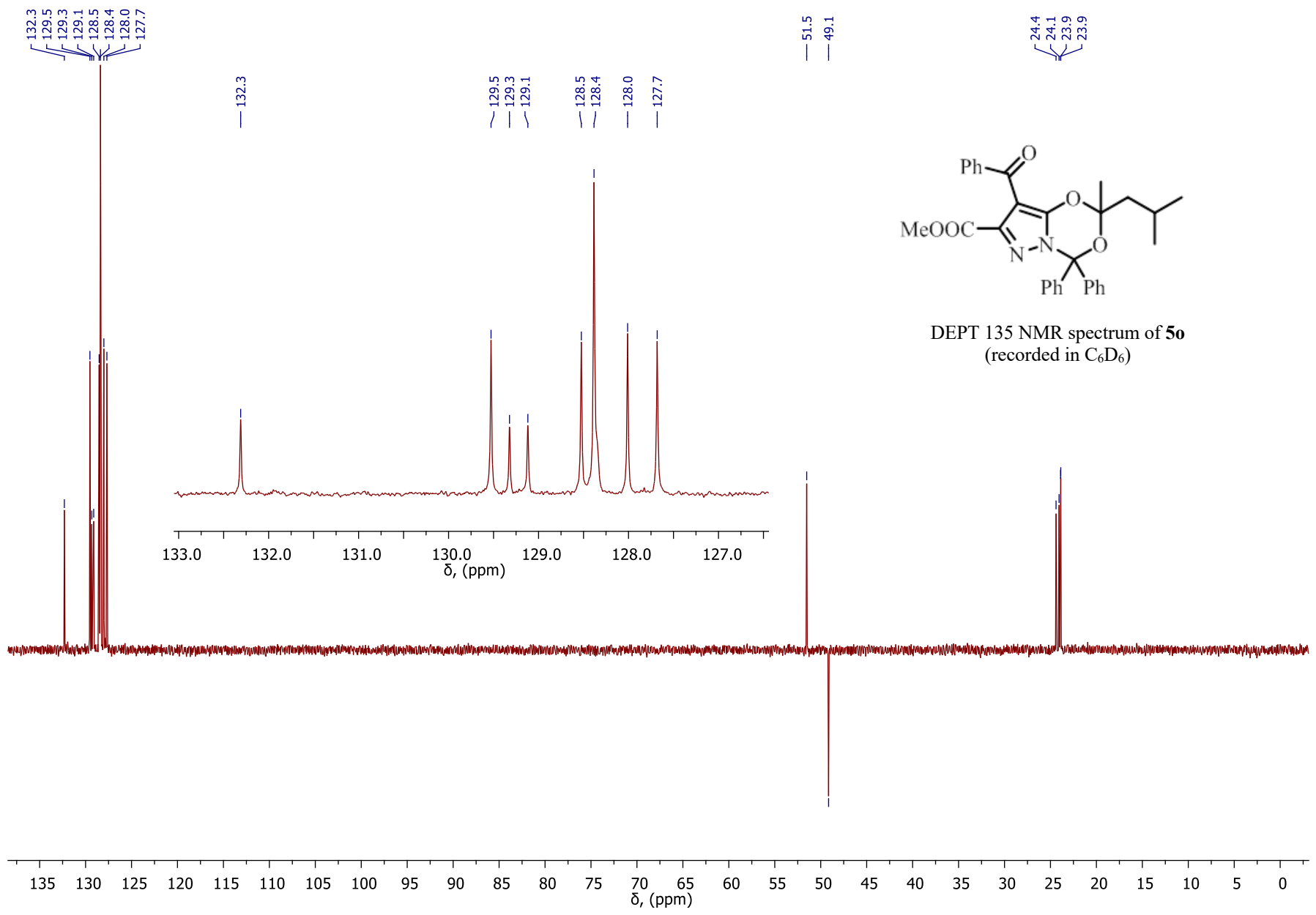


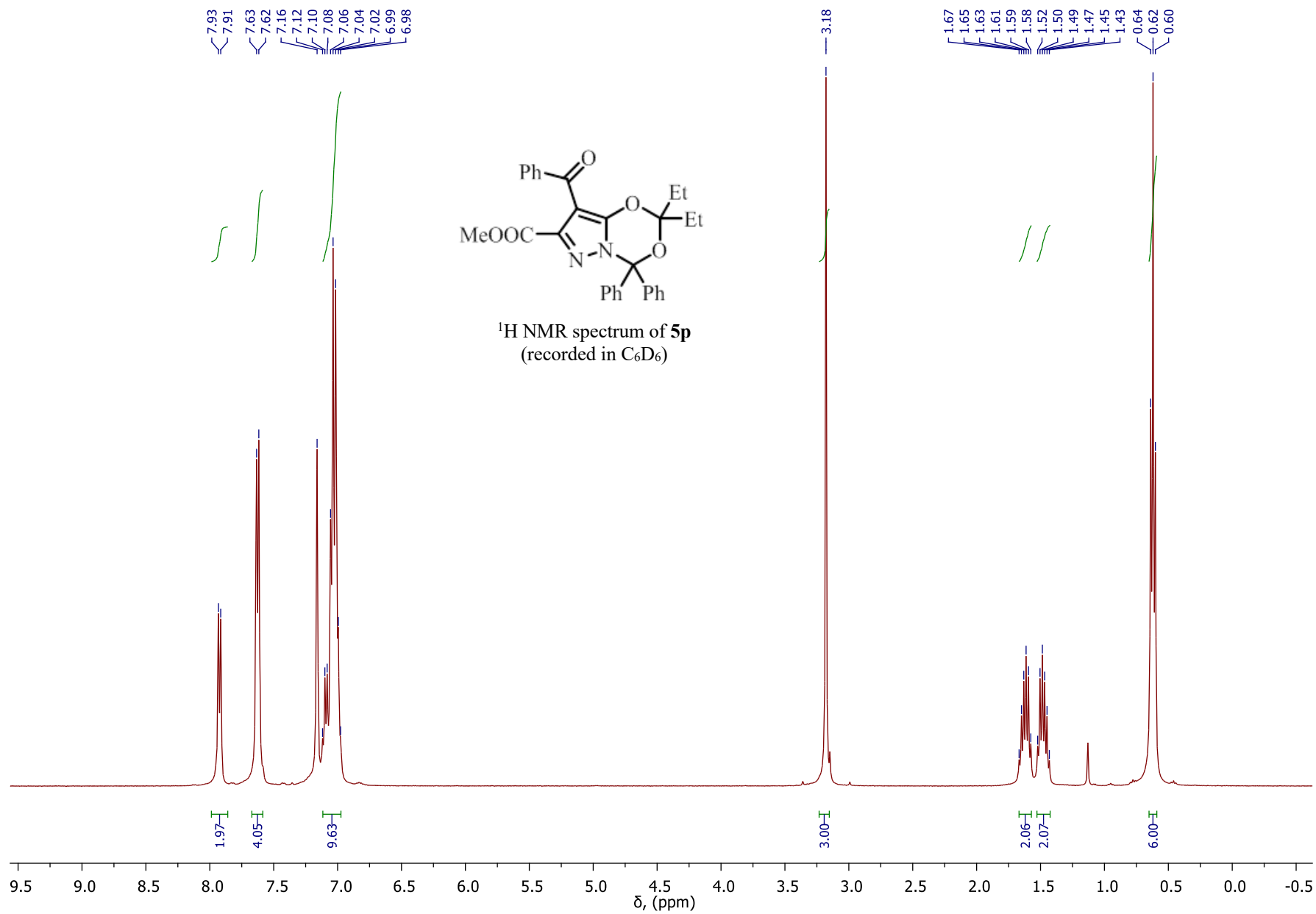


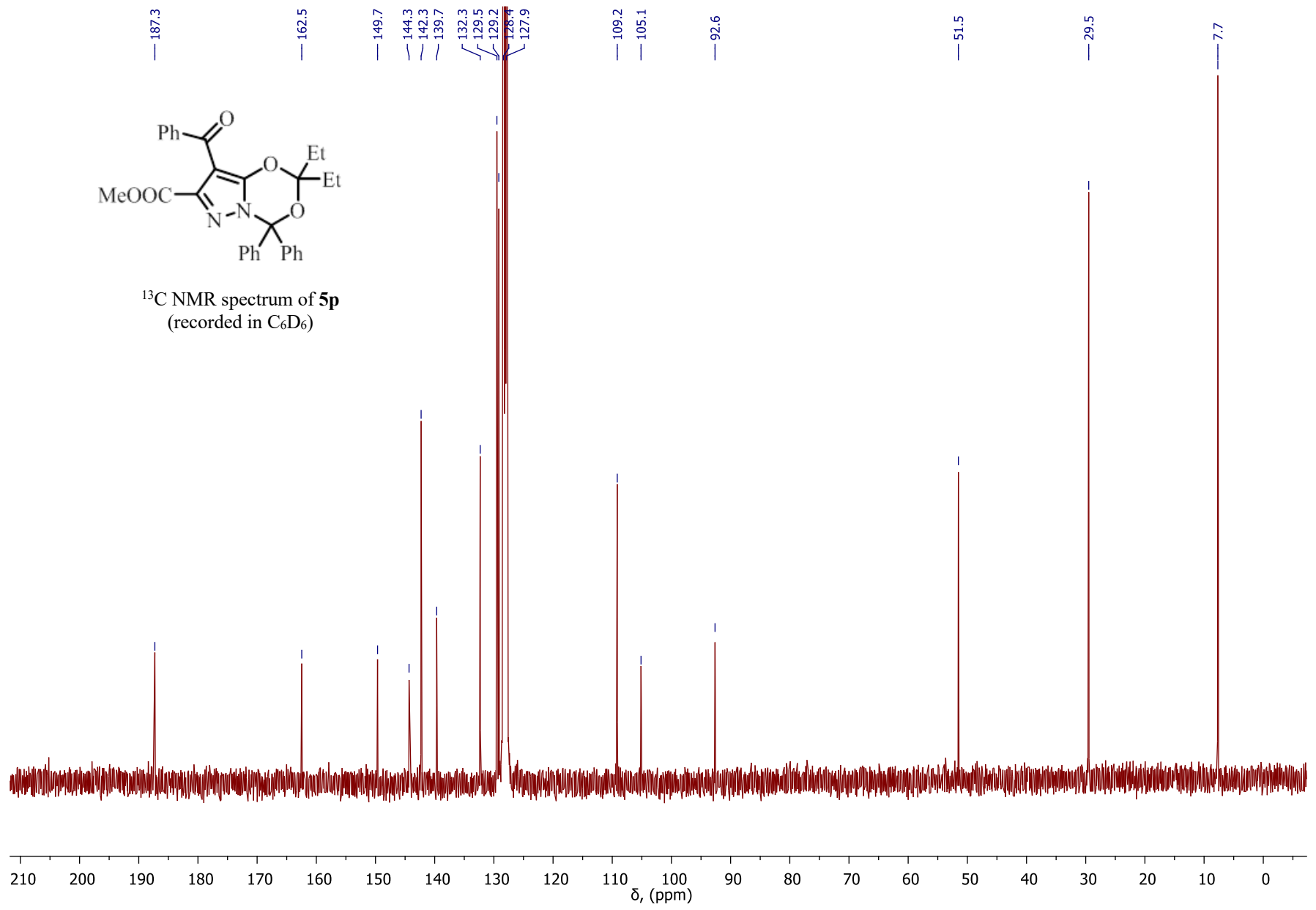


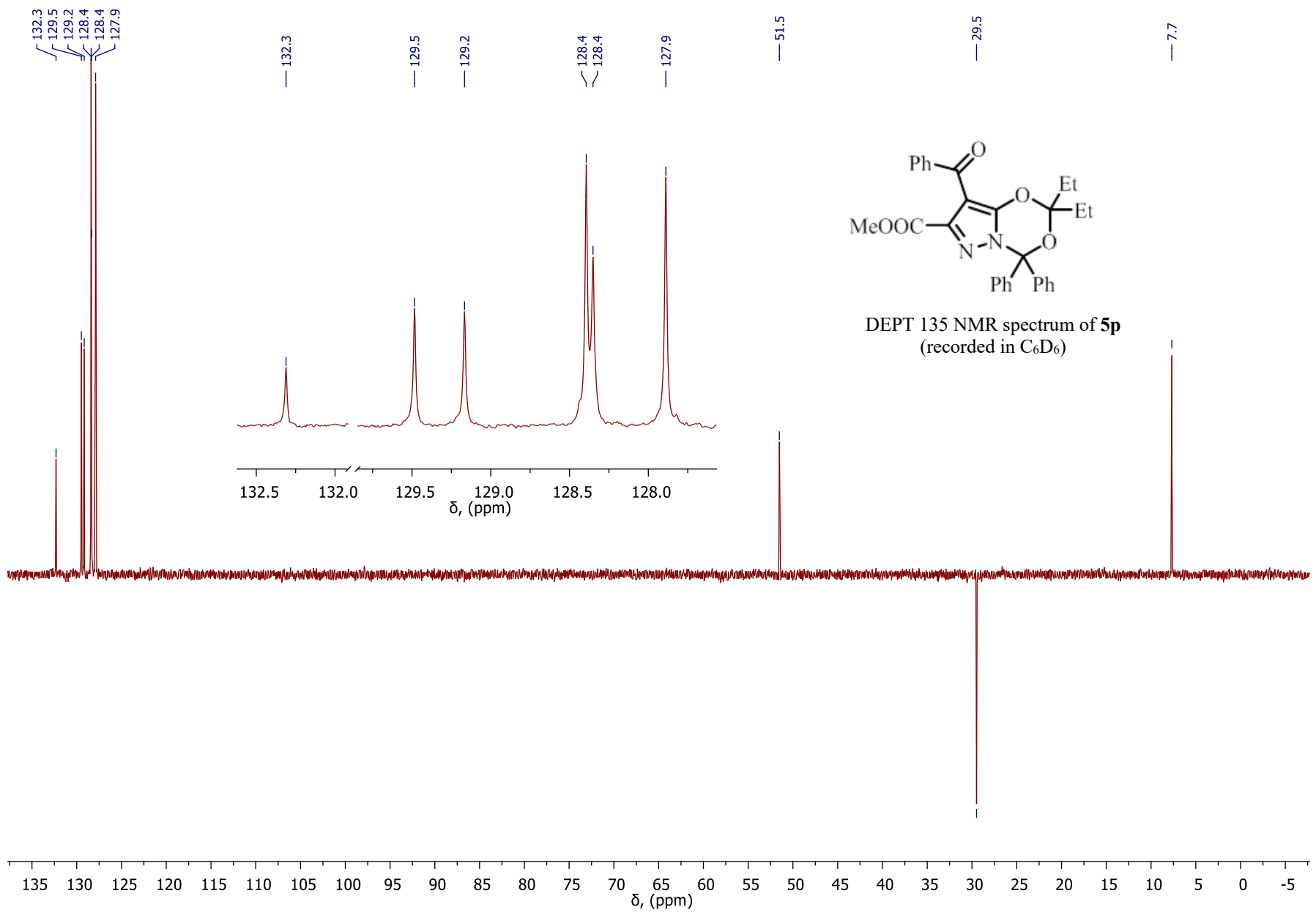


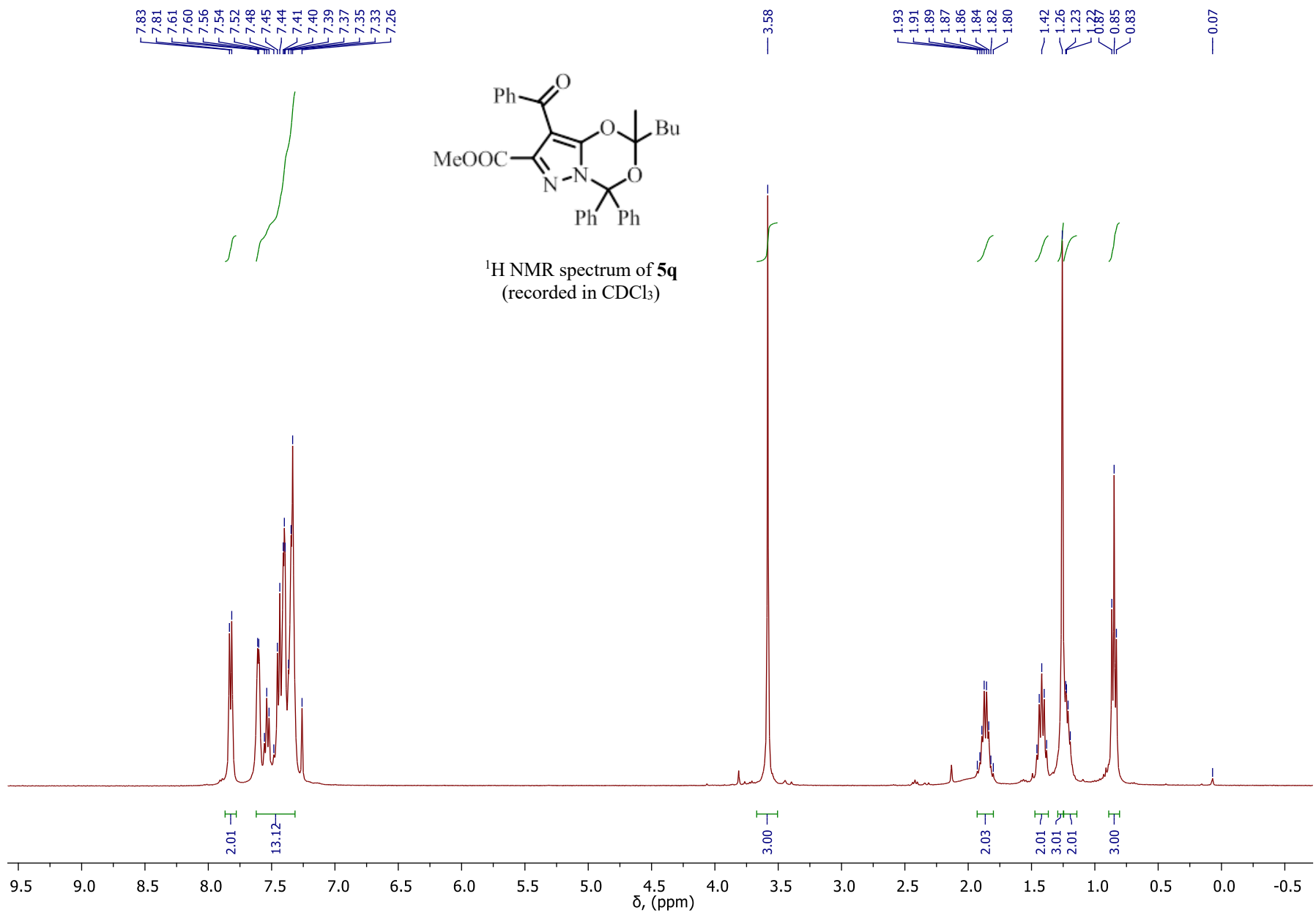


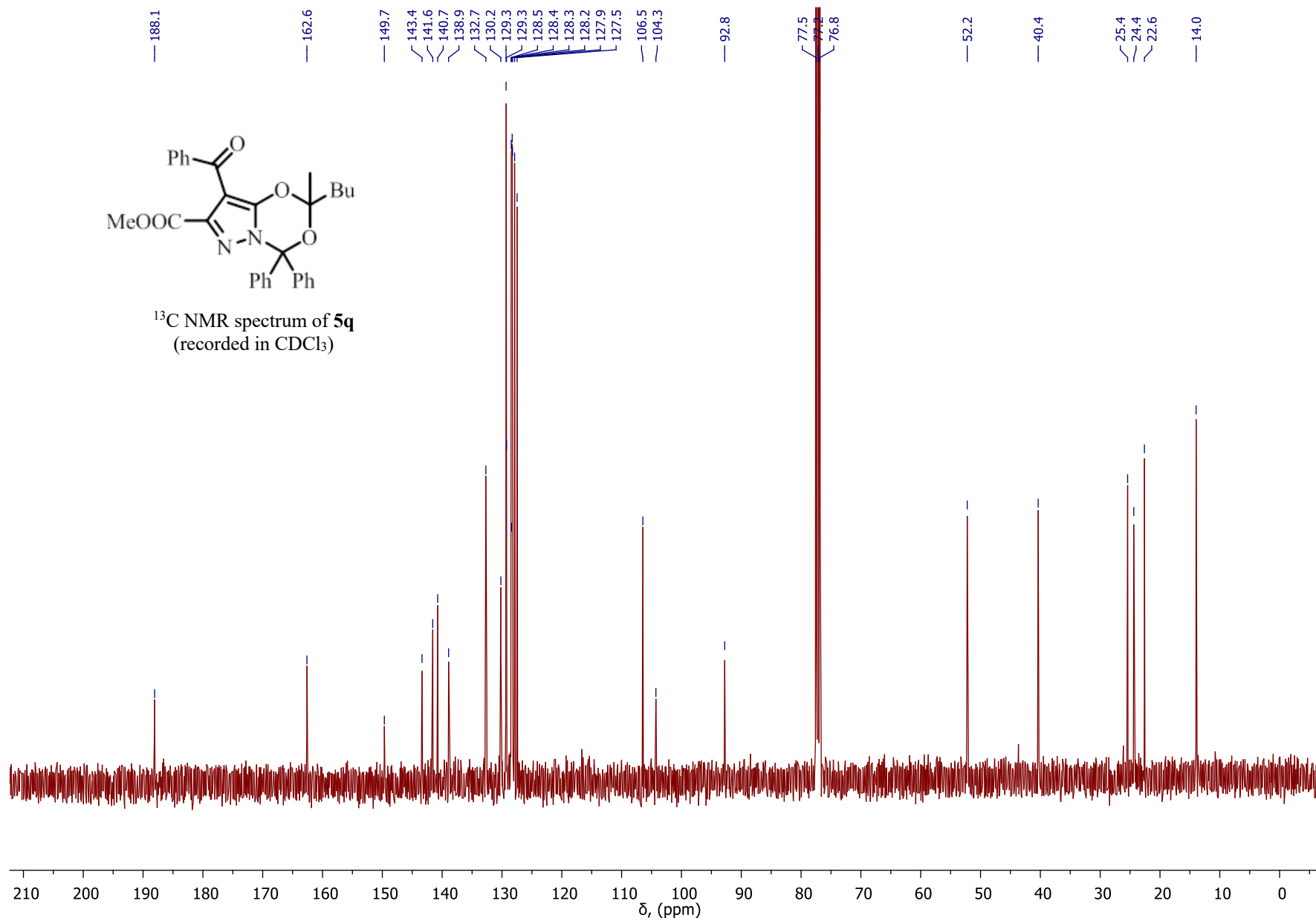


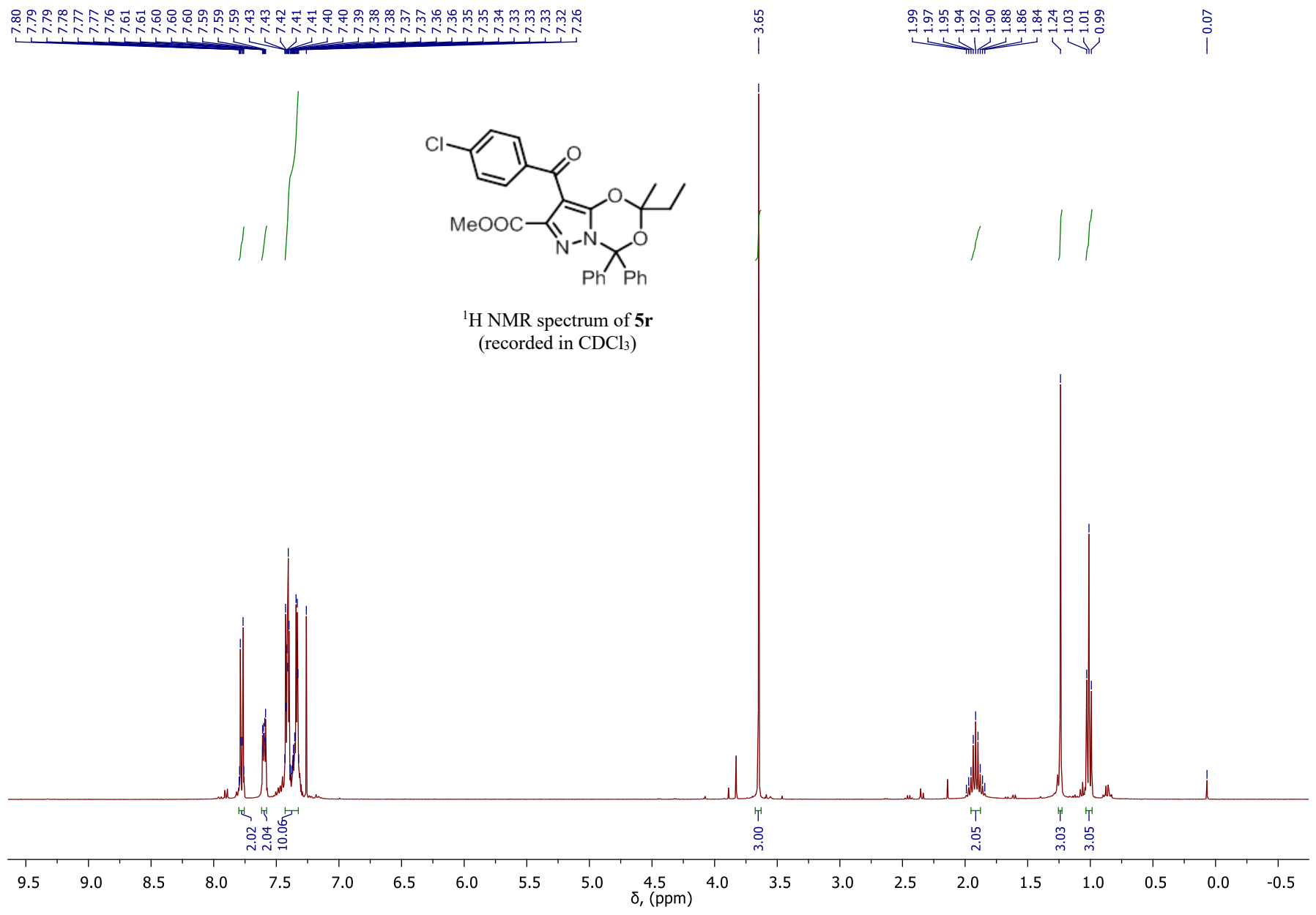


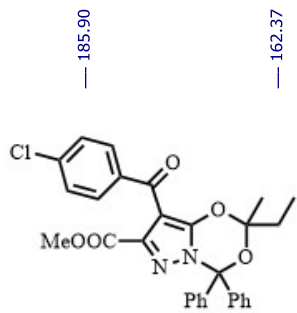




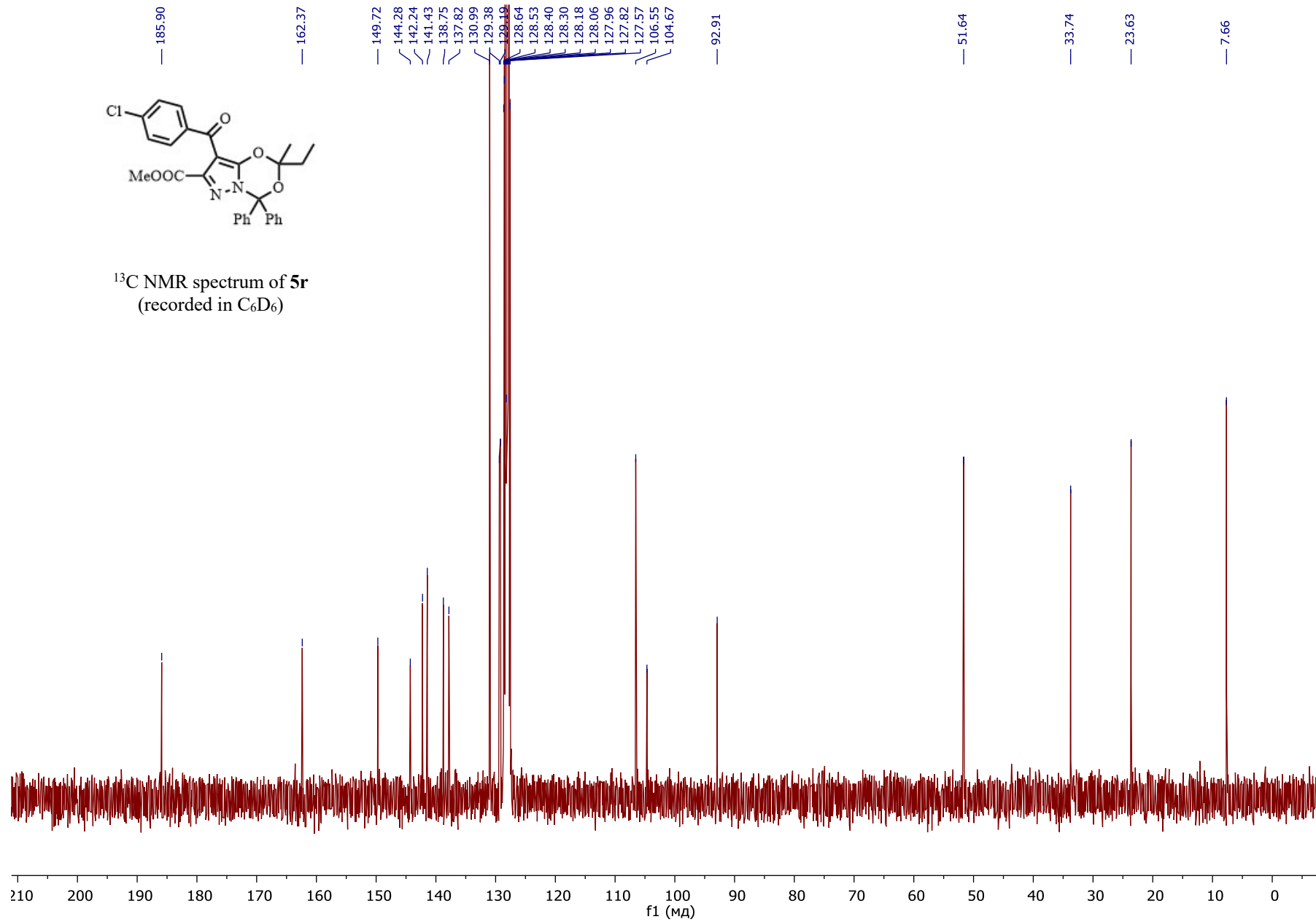




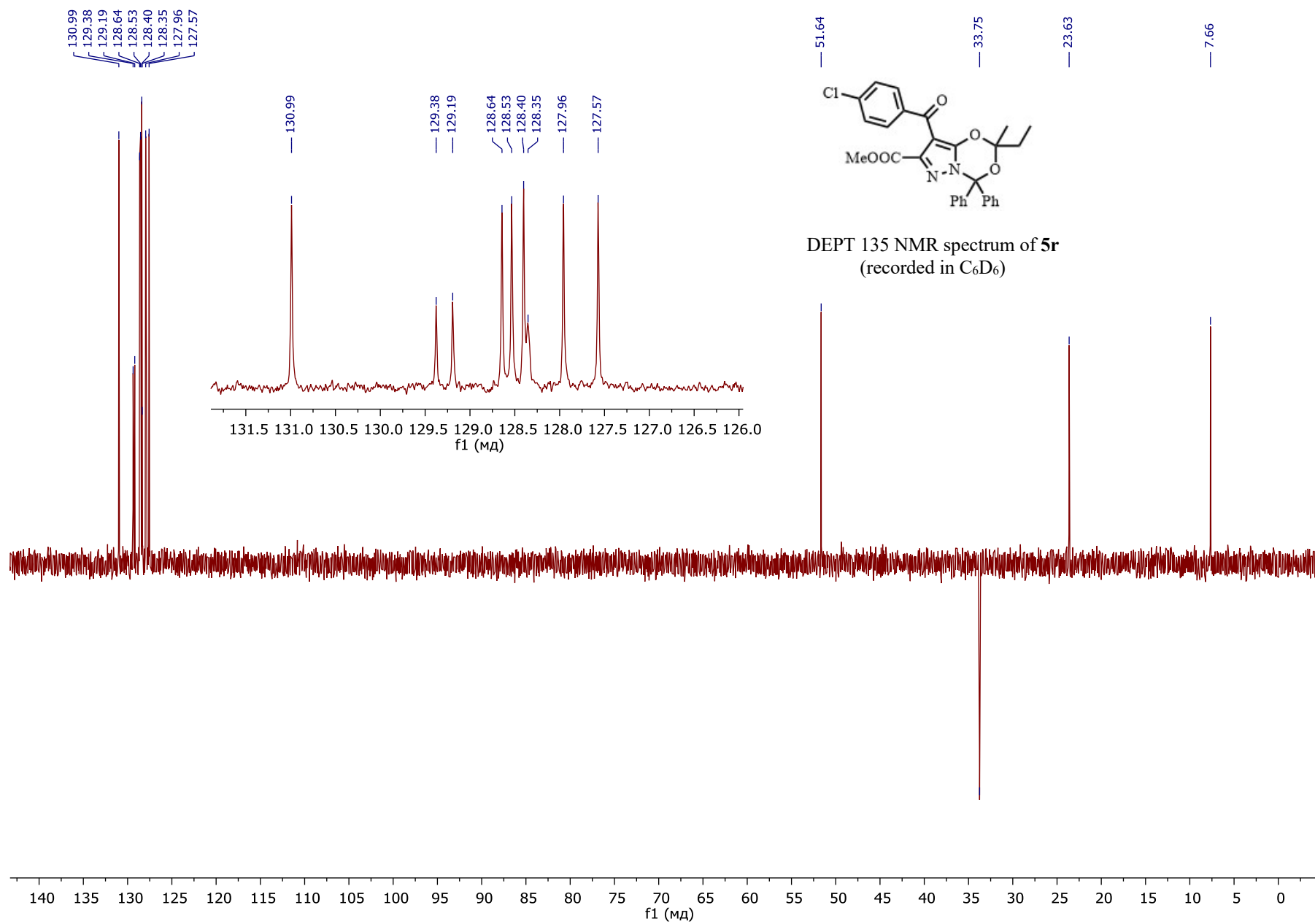


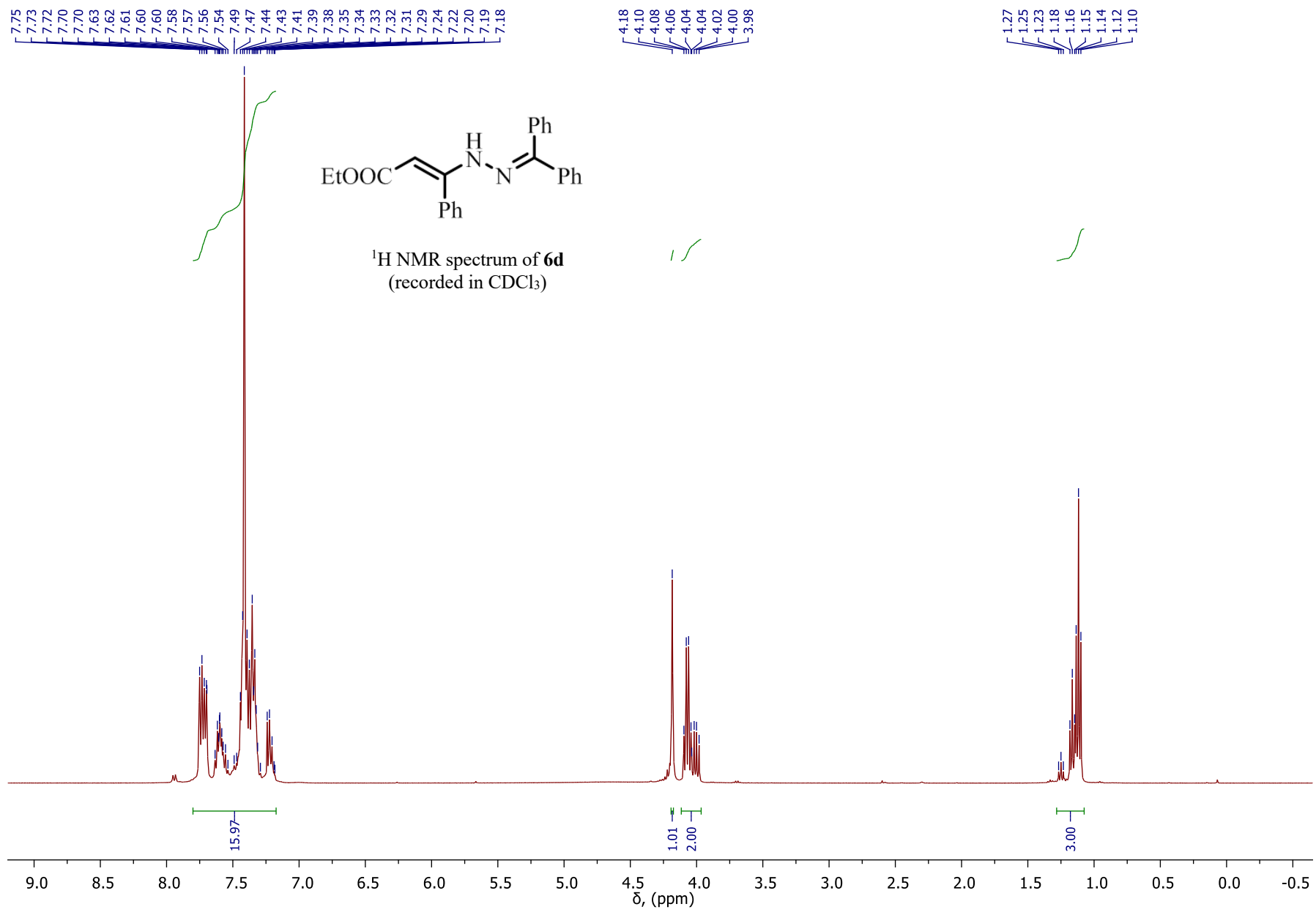


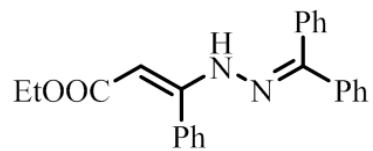
$^{13}\text{C}$  NMR spectrum of **5r**  
(recorded in  $\text{C}_6\text{D}_6$ )



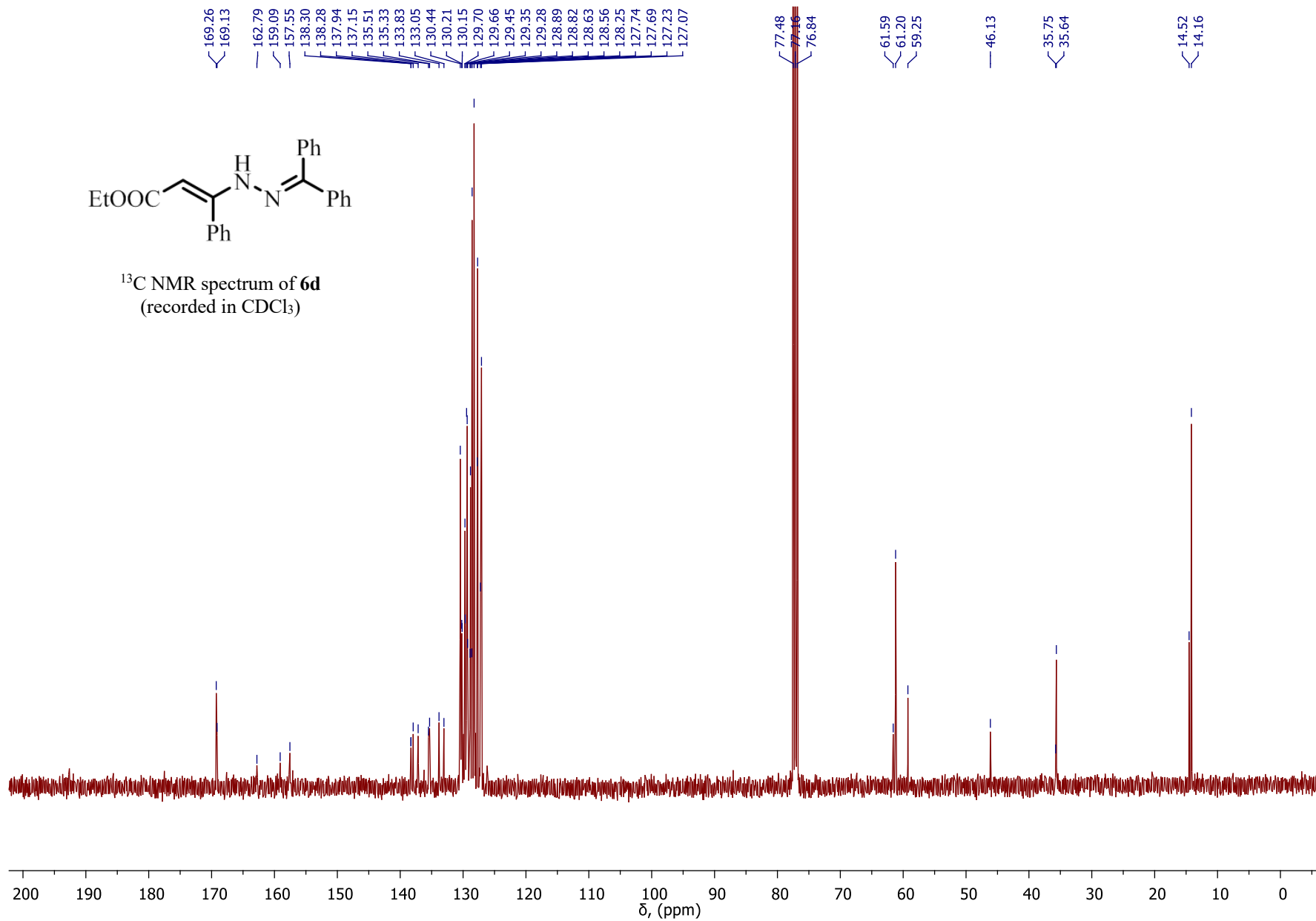






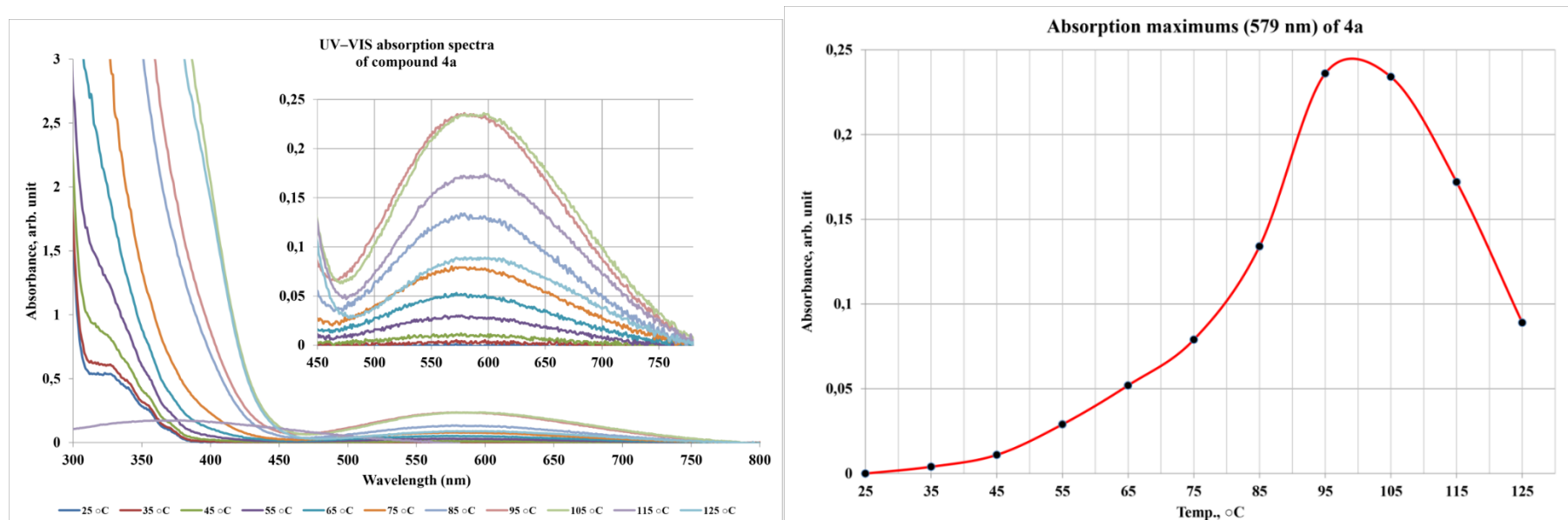


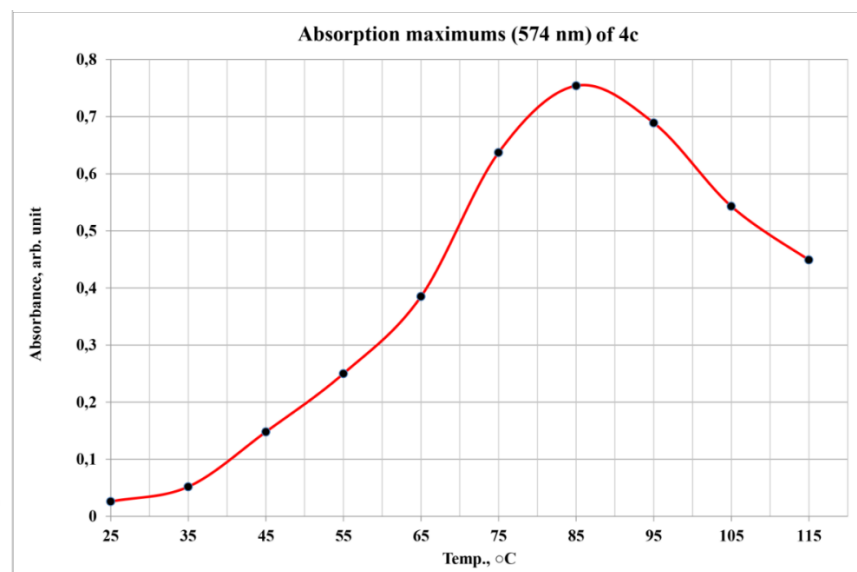
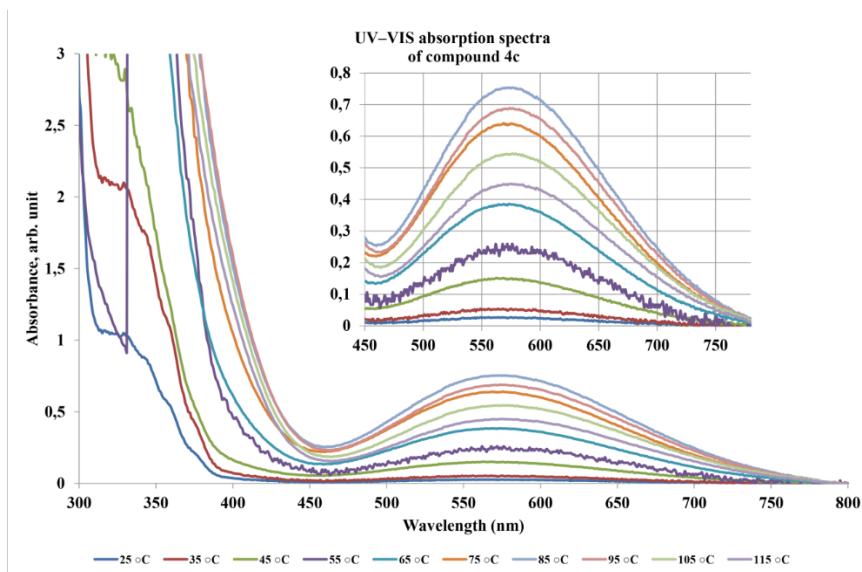
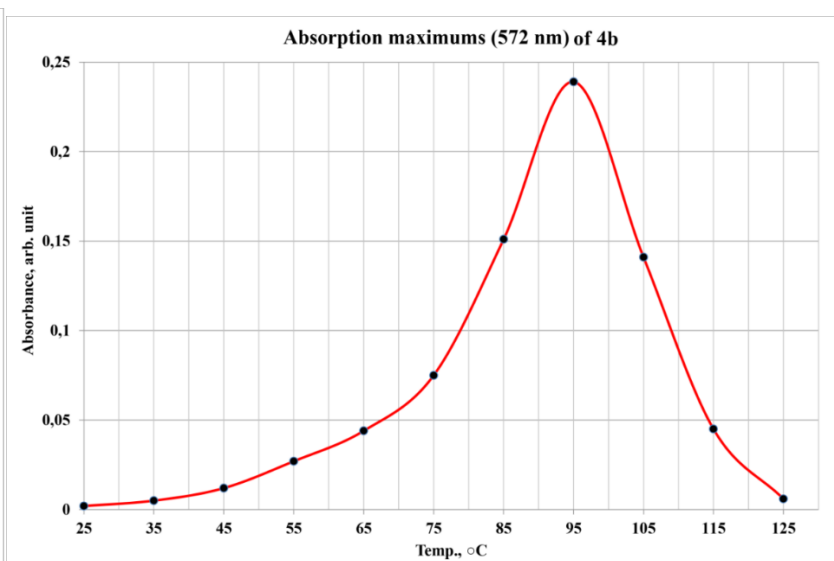
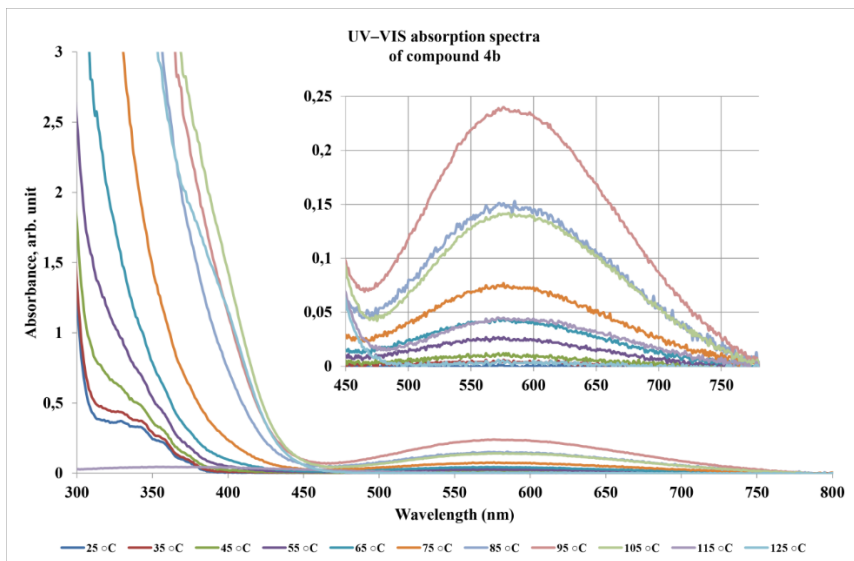
<sup>13</sup>C NMR spectrum of **6d**  
(recorded in CDCl<sub>3</sub>)

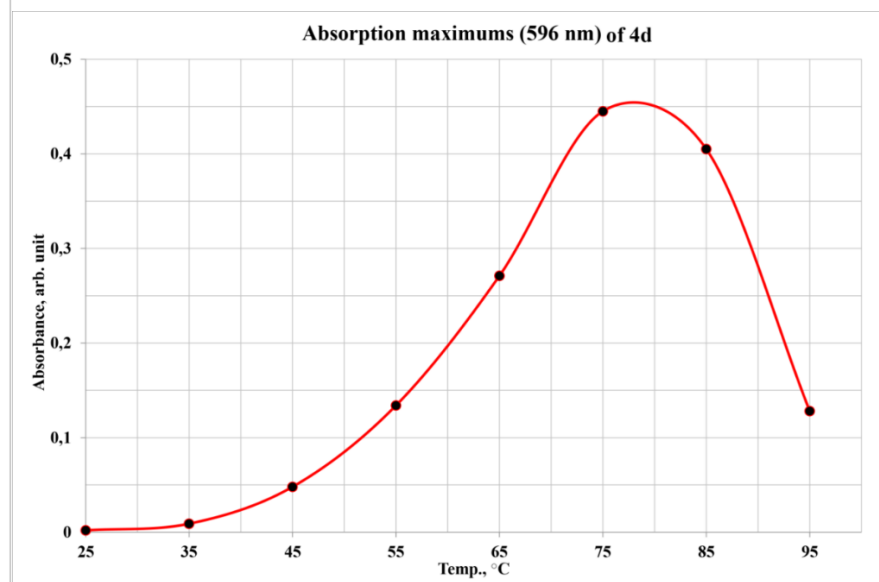
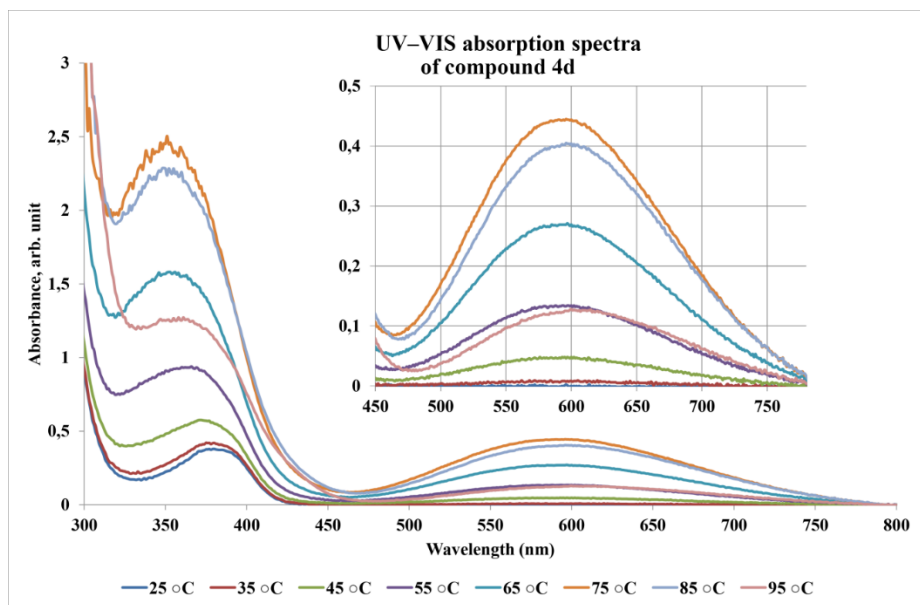


## UV-VIS absorption spectra of compounds 4a-d

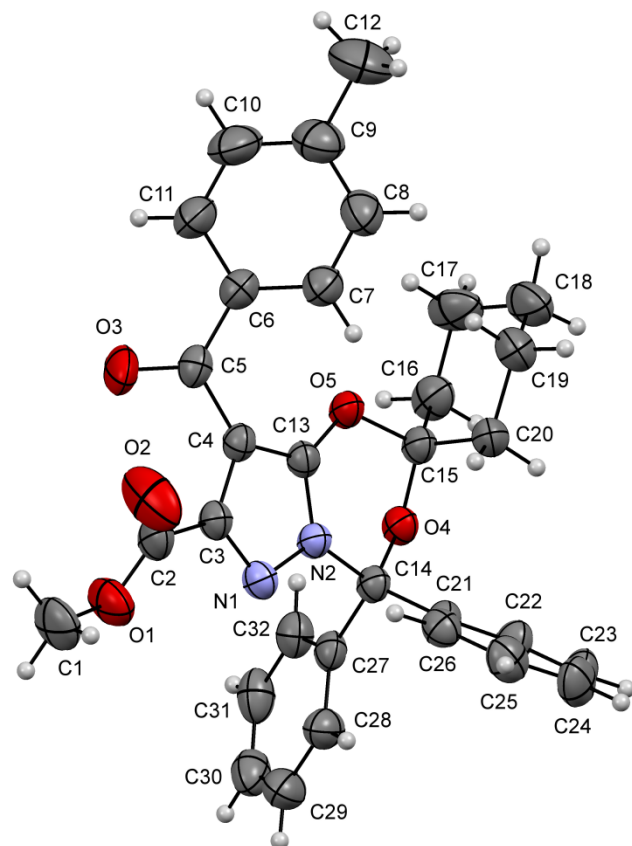
UV-VIS absorption spectra were recorded in 10×10×45 mm cuvettes on a Shimadzu UV-2600 spectrophotometer for dry *o*-xylene solutions of the compounds **4a-d** with the concentration of the solutions  $2 \times 10^{-3}$  mol L<sup>-1</sup>. For graphics and statistical analysis Microsoft Excell Professional 2010 Plus Software was utilized. Spectrophotometric studies were performed by measuring the optical densities of the titled solutions. For this purpose, the hermetically-sealed spectrophotometric cuvettes with the solutions of the appropriate compounds **4a-d** were thermostated in a silicone oil bath equipped with a magnetic stirrer in the temperature range from 25 to 135°C (at 10°C intervals) for 3-5 min, and then were quickly placed in an interchangeable cell compartment for a measurements. The resulting quantitative data were analyzed using a graphical method (absorption – wavelength dependence diagrams (UV-VIS absorption spectra diagrams) were calculated and the absorption maximum wavelength were determined). Then, having determined maximum absorption wavelengths for each of the compounds **4a-d**, absorption – temperature dependence diagrams (at the maximum absorption wavelength) were calculated and the absorption (decomposition) maximum temperatures were determined. As a result of this approach, it was revealed that each of the compounds **4a-d** decompose at an individual temperature (with the average maximum of the decomposition approximately at 80-100°C) and there is no definite correlation between the donor/acceptor substituents in the pyrazole ring and decomposition temperatures of the compounds **4a-d**. The determined decomposition temperatures were successfully utilized in the syntheses of the target compounds **5**.



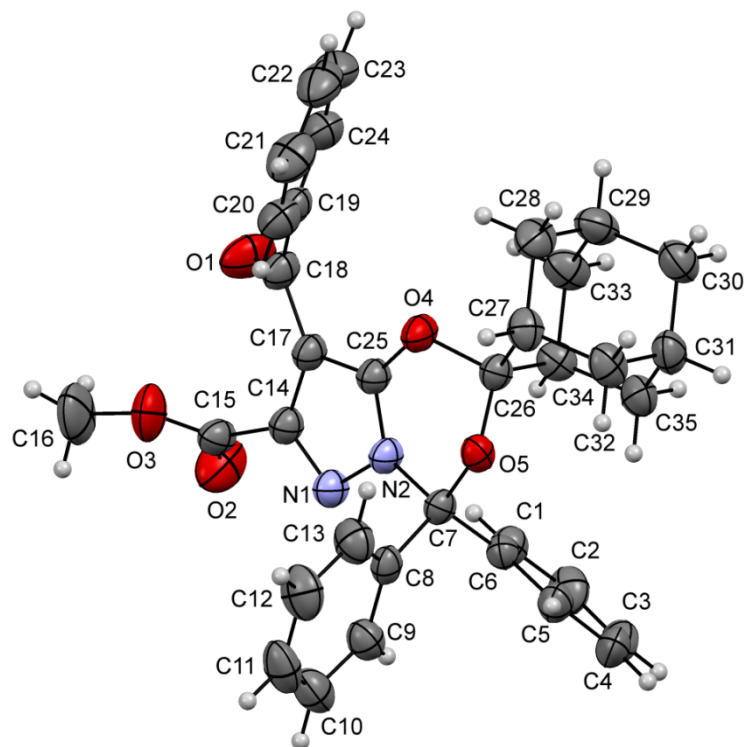




## Single crystal X-ray analysis of compounds **5a**, **i**



**Figure 1.** ORTEP drawing of **5a** (CCDC #1983826), showing atom numbering schemes and 50% probability amplitude displacement ellipsoids. Second molecule of **5a** and solvent molecule were removed for clarity.



**Figure 2.** ORTEP drawing of **5i** (CCDC #1983816), showing atom numbering schemes and 50% probability amplitude displacement ellipsoids.

## Crystal structure determination

The unit cell parameters and the X-ray diffraction intensities were measured on a four-circle Xcalibur Ruby diffractometer. The empirical absorption correction was determined by multi-scan method using SCALE3 ABSPACK algorithm<sup>S1</sup>. The structures were solved by the SHELXS<sup>S2</sup> software and refined by full-matrix least-squares on all  $F^2$  data using SHELXL-97<sup>S3</sup> in conjunction with the WinGX graphical user interface. Hydrogen atoms were located from the Fourier synthesis of the electron density and refined using a riding model.

*Crystal Data of 5a.*  $2(C_{32}H_{30}N_2O_5) \cdot C_2H_6O$ ,  $M = 1091.23$ , triclinic,  $a = 9.2689(14) \text{ \AA}$ ,  $b = 9.7820(12) \text{ \AA}$ ,  $c = 35.199(3) \text{ \AA}$ ,  $V = 2869.5(6) \text{ \AA}^3$ ,  $T = 295(2)$ , space group  $P\bar{1}$ ,  $Z = 2$ ,  $\mu(\text{Mo K}\alpha) = 0.086 \text{ mm}^{-1}$ . The final refinement parameters:  $R1 = 0.0759$ ,  $wR2 = 0.1856$  [for observed 7998 reflections with  $I > 2\sigma(I)$ ];  $R1 = 0.1265$ ,  $wR2 = 0.2195$  (for all independent 28351 reflections,  $R_{\text{int}} = 0.0615$ ),  $S = 1.019$ .

*Crystal Data of 5i.*  $C_{35}H_{32}N_2O_5$ ,  $M = 560.63$ , triclinic,  $a = 10.5718(13) \text{ \AA}$ ,  $b = 10.6288(12) \text{ \AA}$ ,  $c = 13.5806(17) \text{ \AA}$ ,  $\alpha = 100.473(10)^\circ$ ,  $\beta = 97.068(10)^\circ$ ,  $\gamma = 103.526(10)^\circ$ ,  $V = 1436.9(3) \text{ \AA}^3$ ,  $T = 295(2)$ , space group  $P\bar{1}$ ,  $Z = 2$ ,  $\mu(\text{Mo K}\alpha) = 0.087 \text{ mm}^{-1}$ . The final refinement parameters:  $R1 = 0.0523$ ,  $wR2 = 0.1289$  [for observed 5019 reflections with  $I > 2\sigma(I)$ ];  $R1 = 0.0726$ ,  $wR2 = 0.1459$  (for all independent 13186 reflections,  $R_{\text{int}} = 0.0366$ ),  $S = 1.064$ .



CCDC 1983826 (**5a**) and 1983816 (**5i**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk>.

## References

- S1. CrysAlisPro, Agilent Technologies, Version 1.171.37.33
- S2. Sheldrick G.M. *ActaCryst.* **2015**, *A71*, 3.
- S3. Sheldrick, G.M. *ActaCryst.* **2015**, *C71*, 3.