

Supporting Information

Regio- and Stereoselective Selenium Dioxide Allylic Oxidation of (*E*)-Dialkyl Alkylidenesuccinates to (*Z*)- Allylic Alcohols: Synthesis of Natural and Unnatural Butenolides

Ramesh M. Patel,^a Vedavati G. Puranik^b and Narshinha P. Argade^{*,a}

^a *Division of Organic Chemistry and* ^b *Centre for Material Characterization, National
Chemical Laboratory (CSIR), Pune 411 008, India*

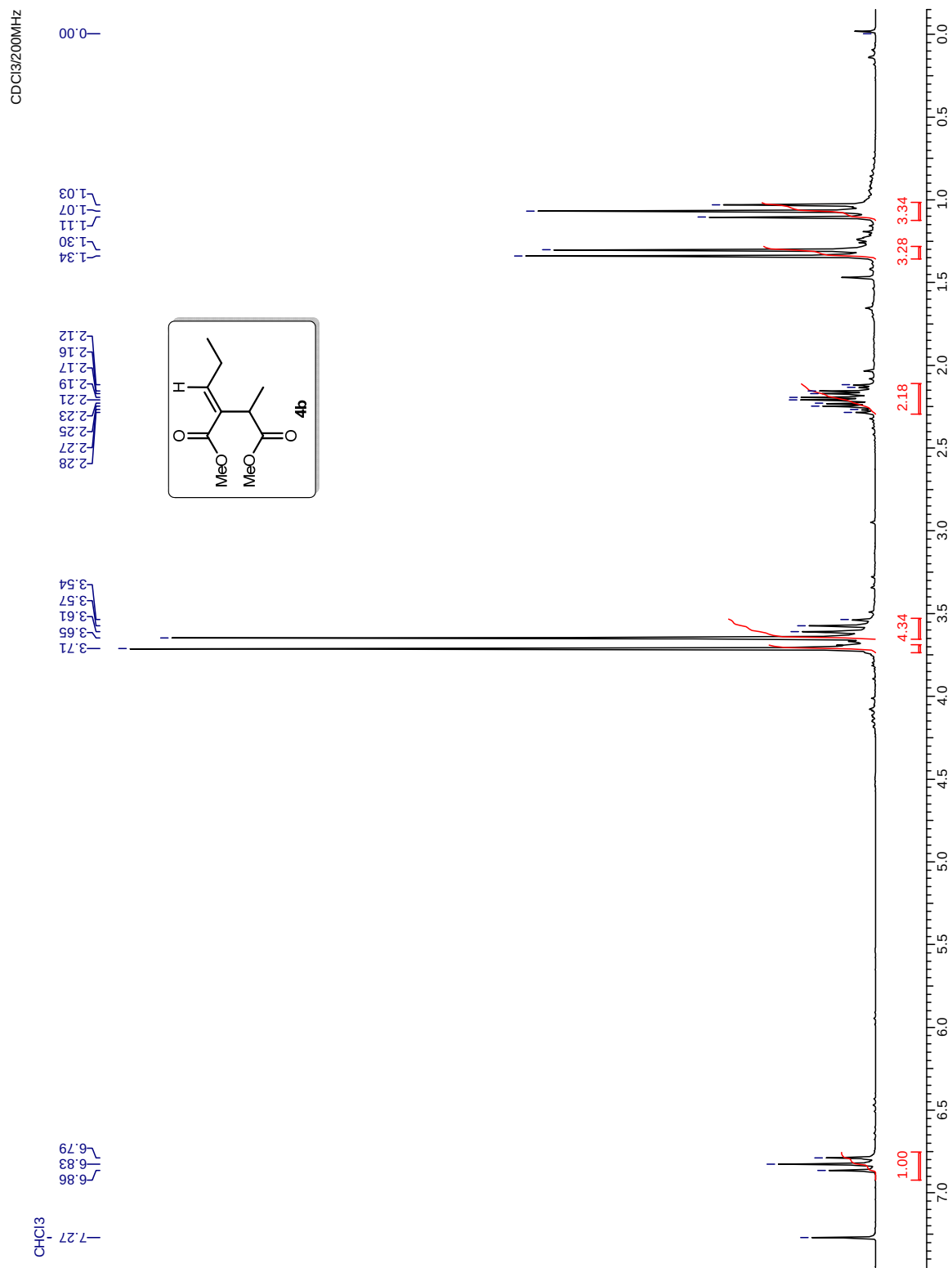
E-mail: np.argade@ncl.res.in

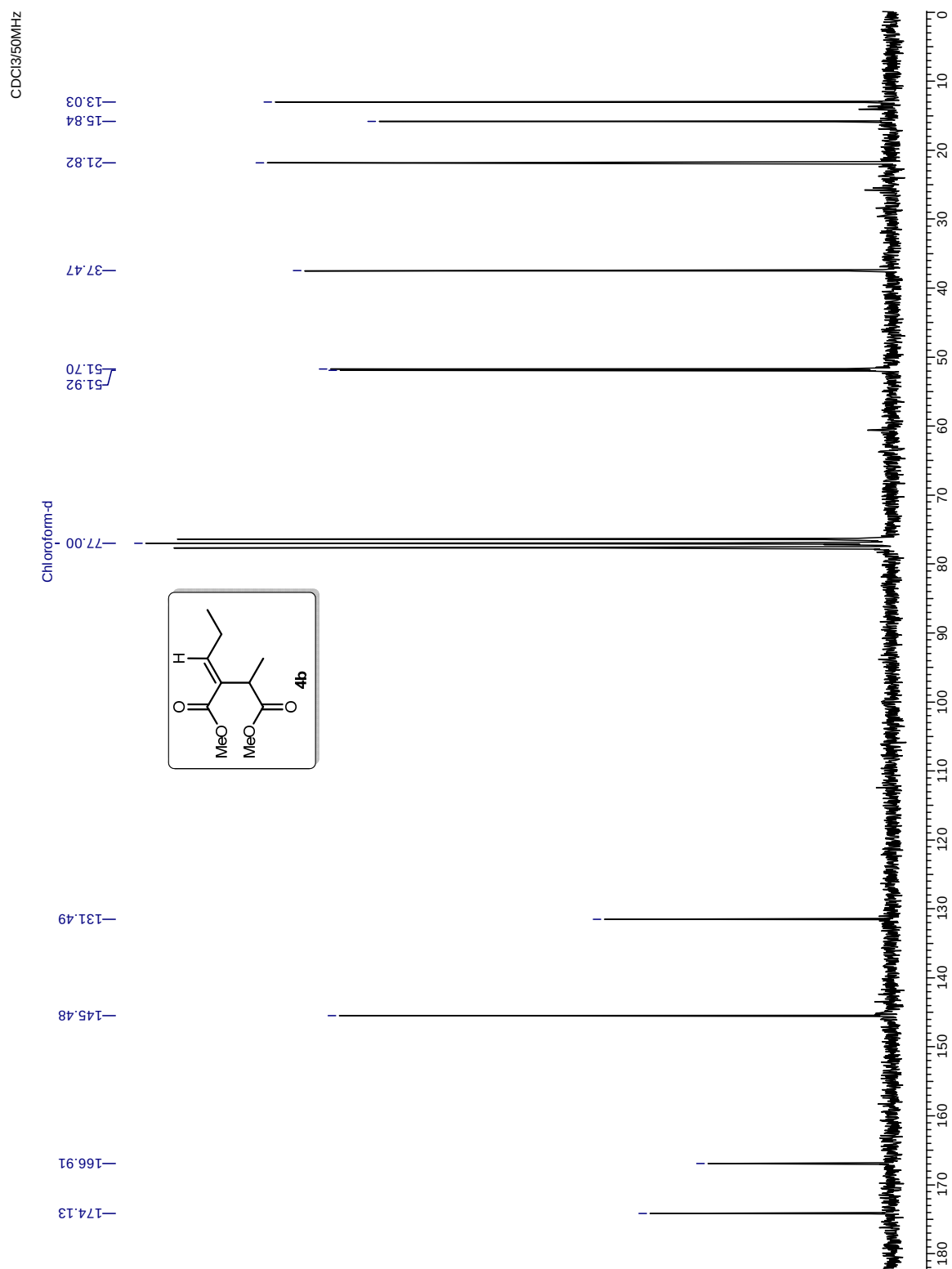
Table of Contents

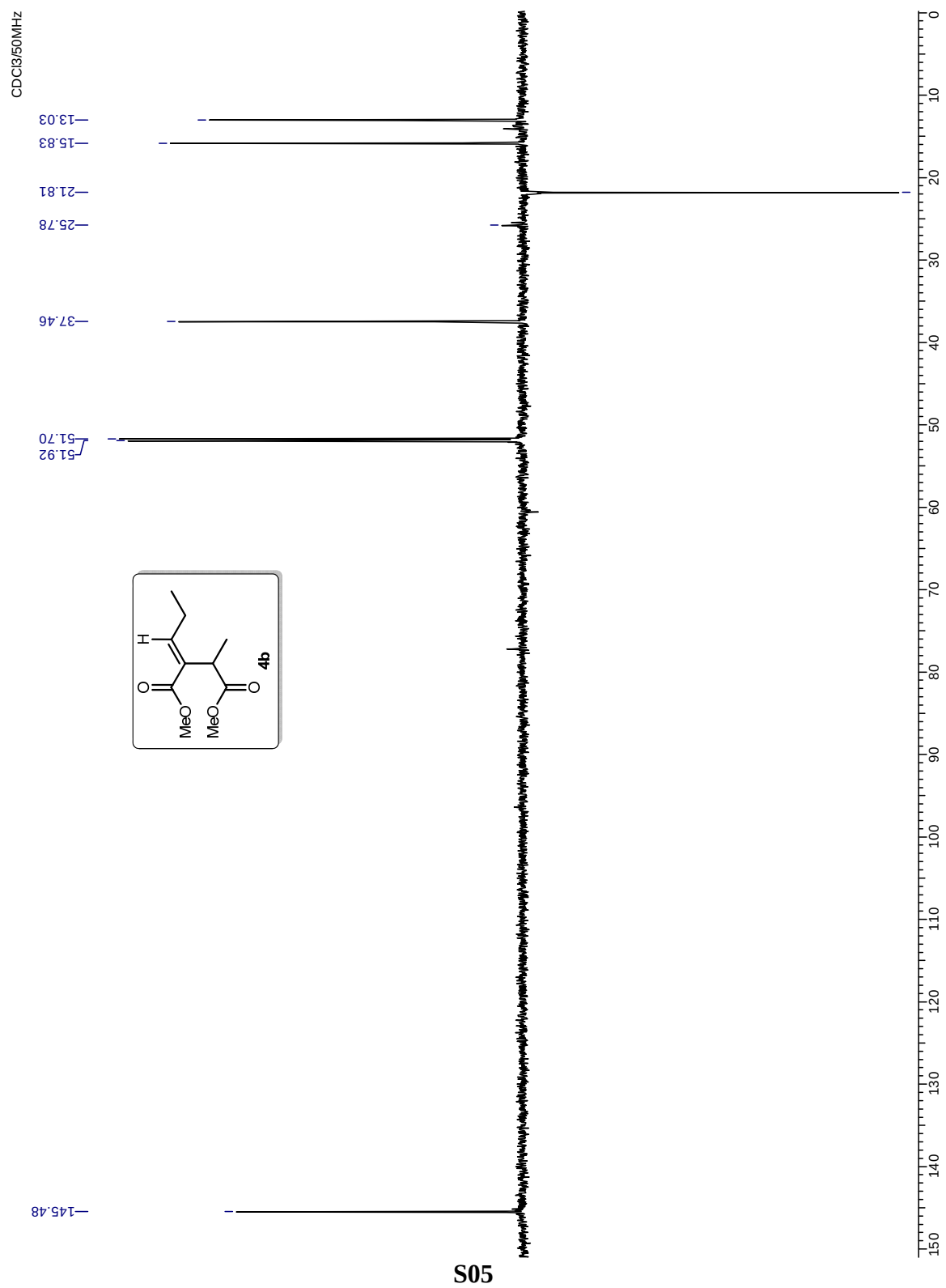
1. General Experimental Description	S02
2. Copies of ^1H NMR and ^{13}C NMR Spectra	S03
3. ORTEP diagrams of compounds 8, 19, 24 and 28	S100

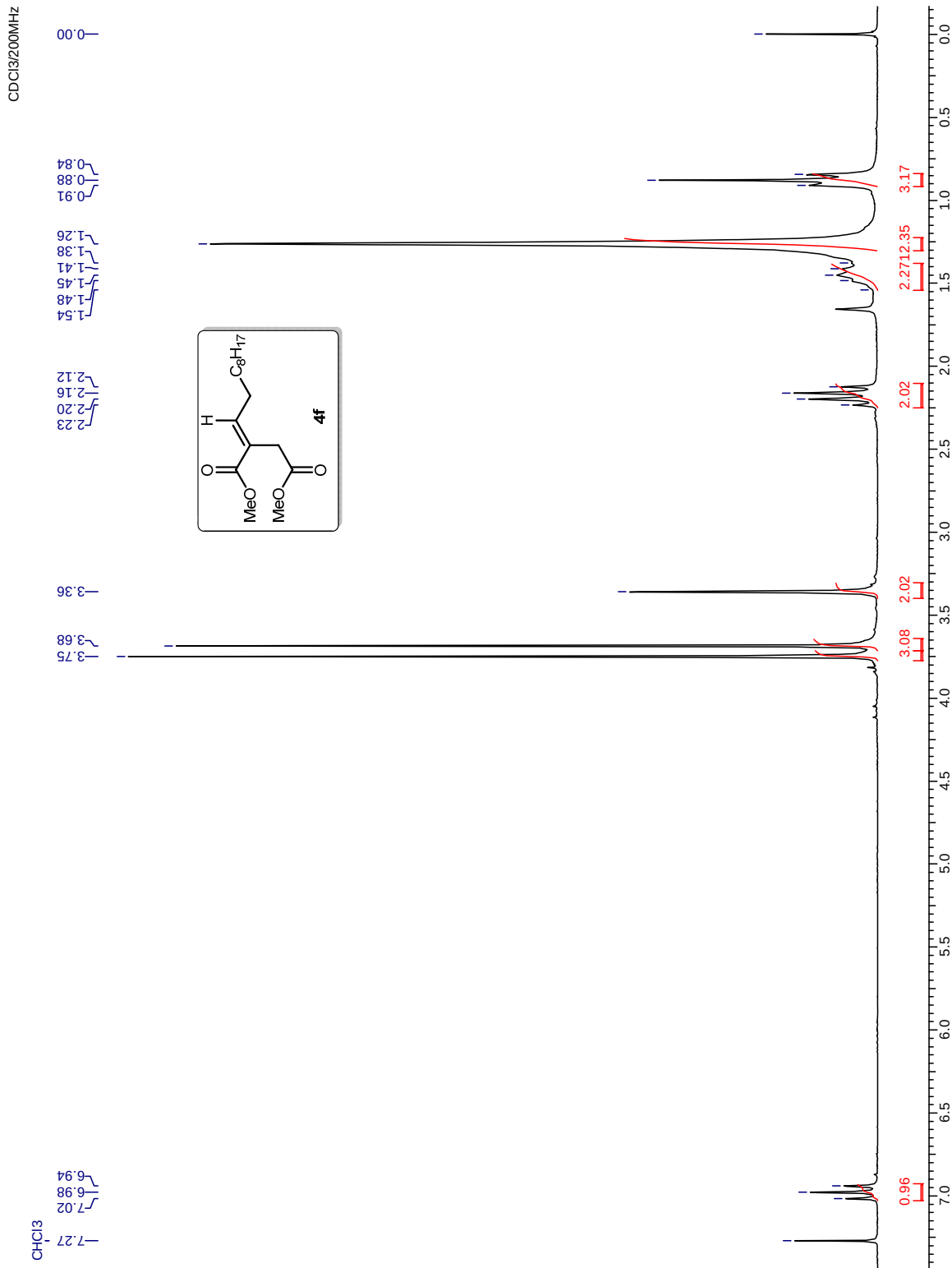
Experimental: General Description

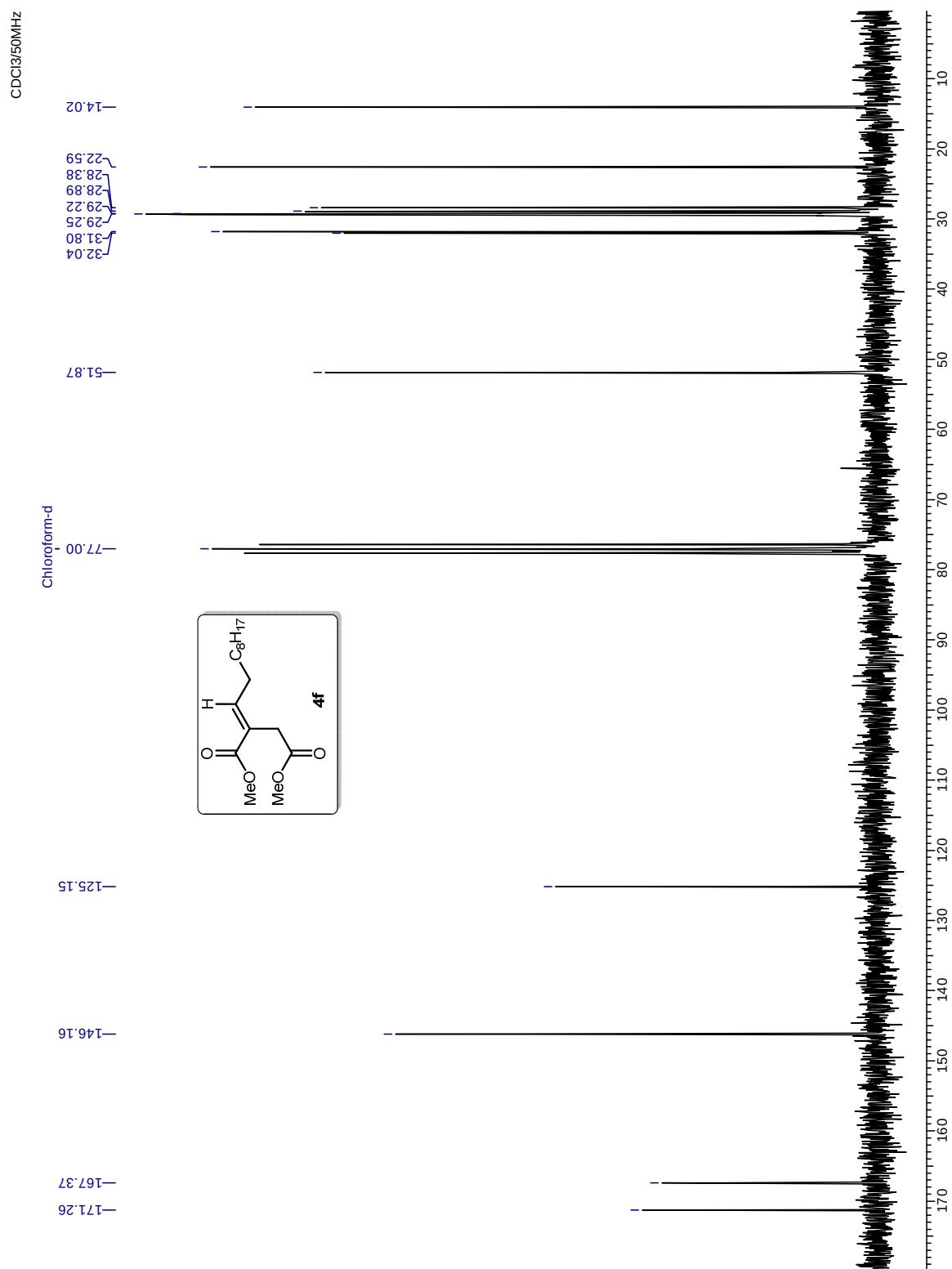
The ^1H NMR spectra were recorded on 200 MHz NMR spectrometer, 400 MHz NMR and 500 MHz NMR spectrometer using TMS as an internal standard. The ^{13}C NMR spectra were recorded on 200 NMR spectrometer (50 MHz), 400 NMR spectrometer (100 MHz) and 500 NMR spectrometer (125 MHz). Mass spectra were taken on MS-TOF mass spectrometer. The IR spectra were recorded on an FT-IR spectrometer. HRMS were taken on ESI mass spectrometer. Column chromatographic separations were carried out on silica gel (60-120 mesh). Commercially available dimethyl succinate, diethyl succinate, dimethyl methylsuccinate, propanal, butanal, hexanal, decanal, cyclohexanone, 4-methylcyclohexanone, *tert*-butylcyclohexanone, cycloheptanone, α -tetralone, selenium dioxide, sodium methoxide, trifluoroacetic acid, ethanethiol, *N*-ethyl *N'*-(3-dimethylpropyl)carbodiimide (EDCI), triethylsilane, lead tetraacetate, cupric acetate, DMAP, 10% Pd/C, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and potassium *tert*-butoxide were used. $\text{HRh}(\text{PPh}_3)_4$ was prepared using the known procedure (Levison J. J.; Robinson, S. D. *J. Chem. Soc. A*, **1970**, 2947).

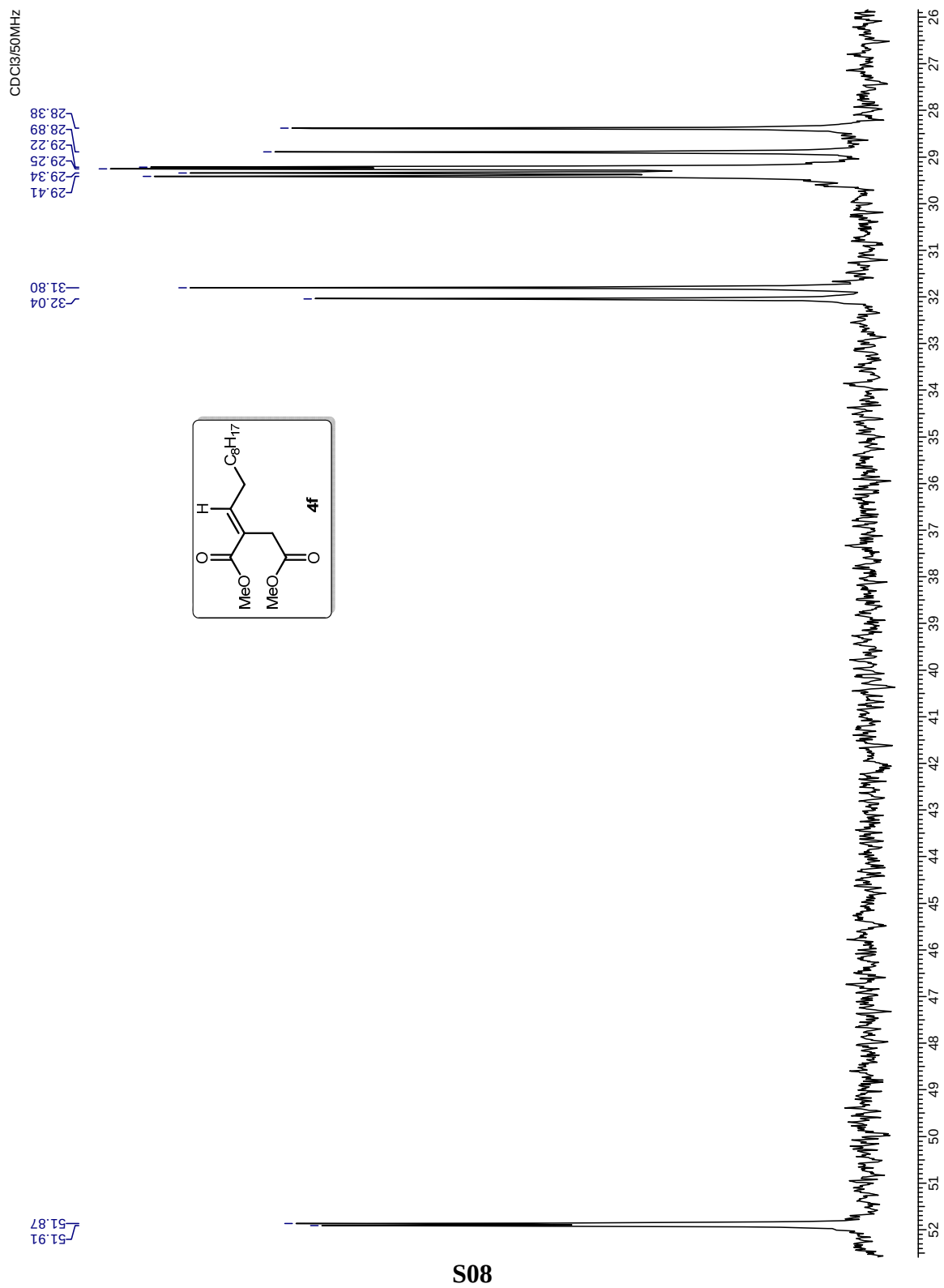


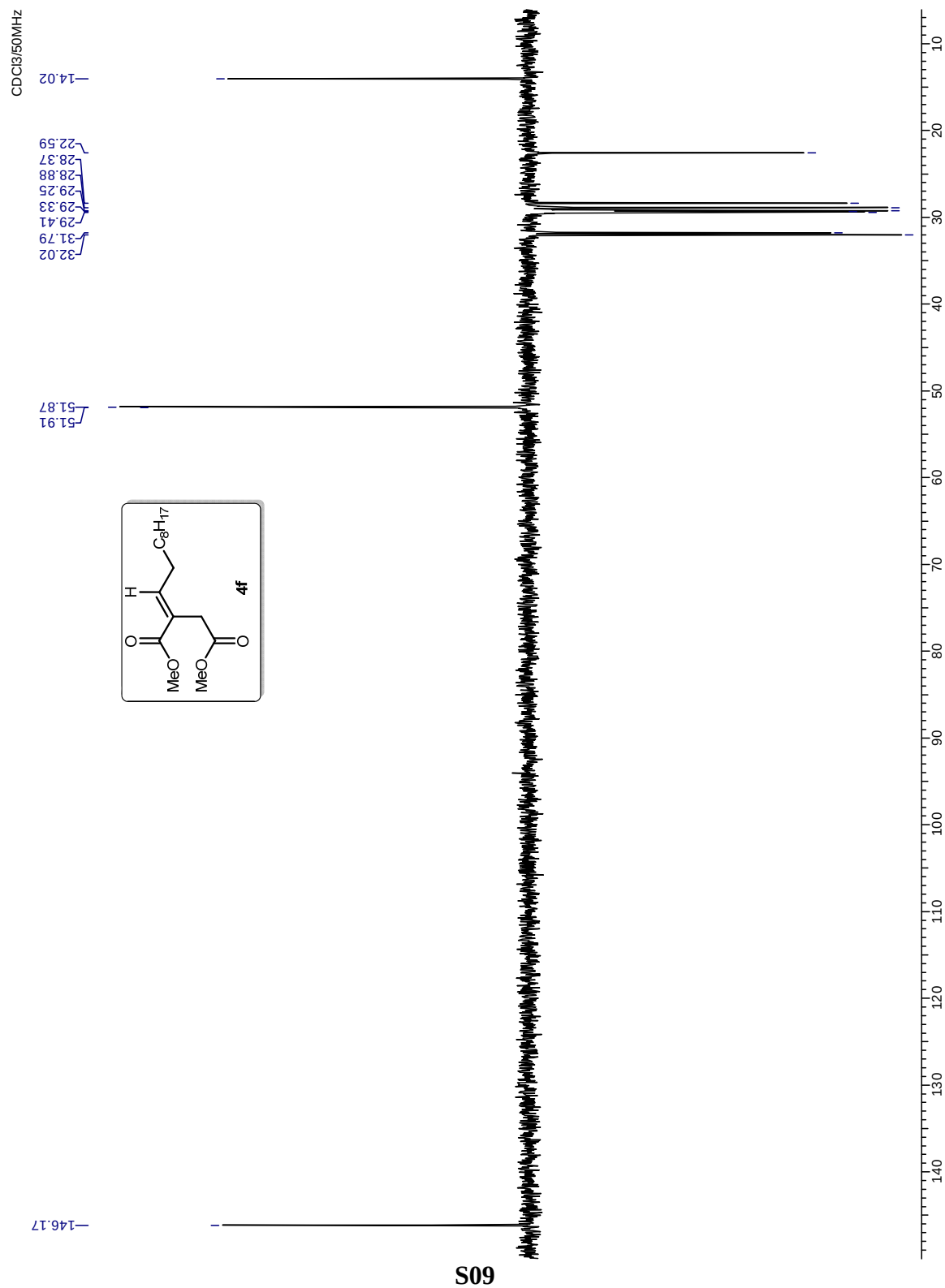


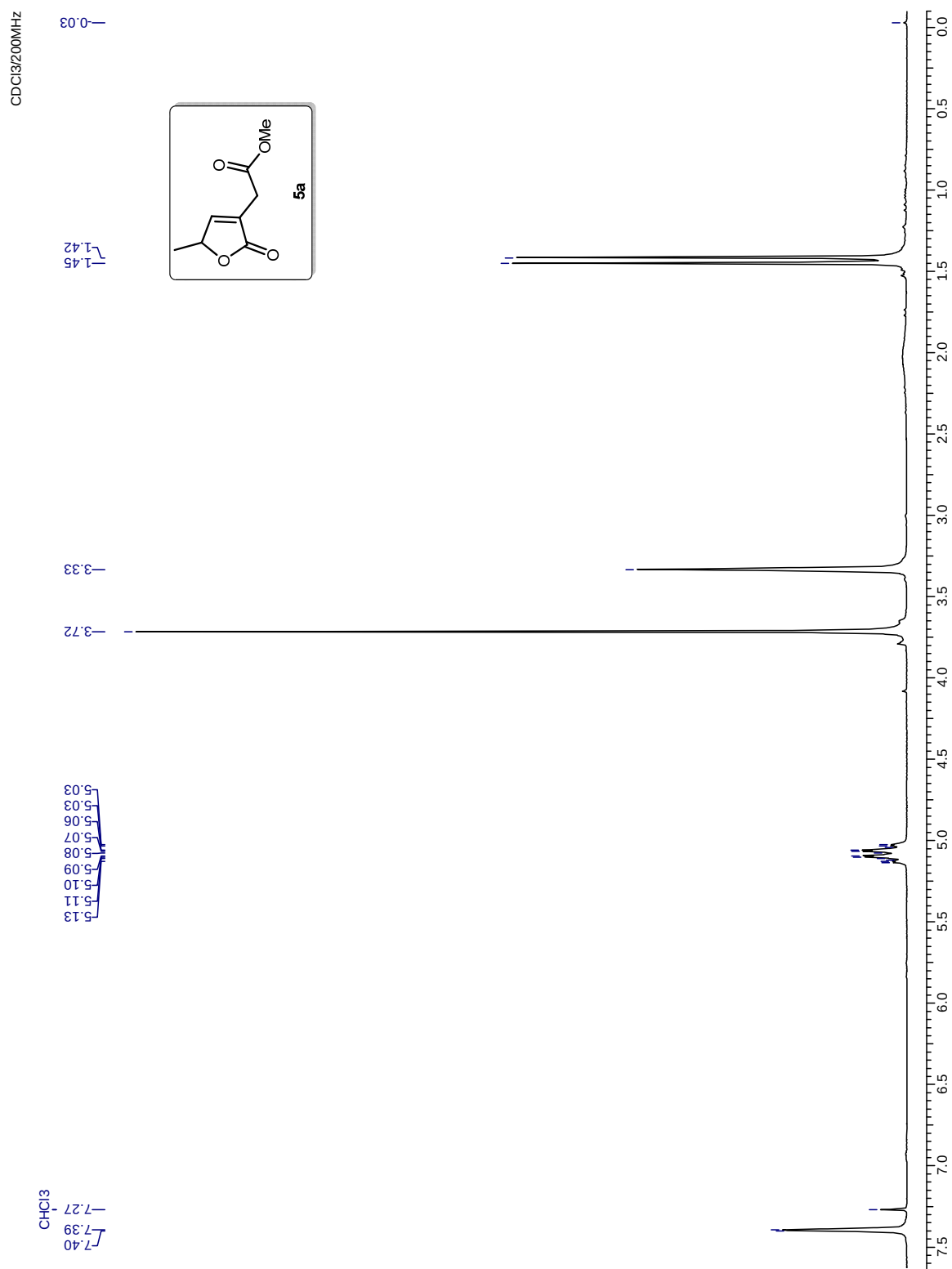


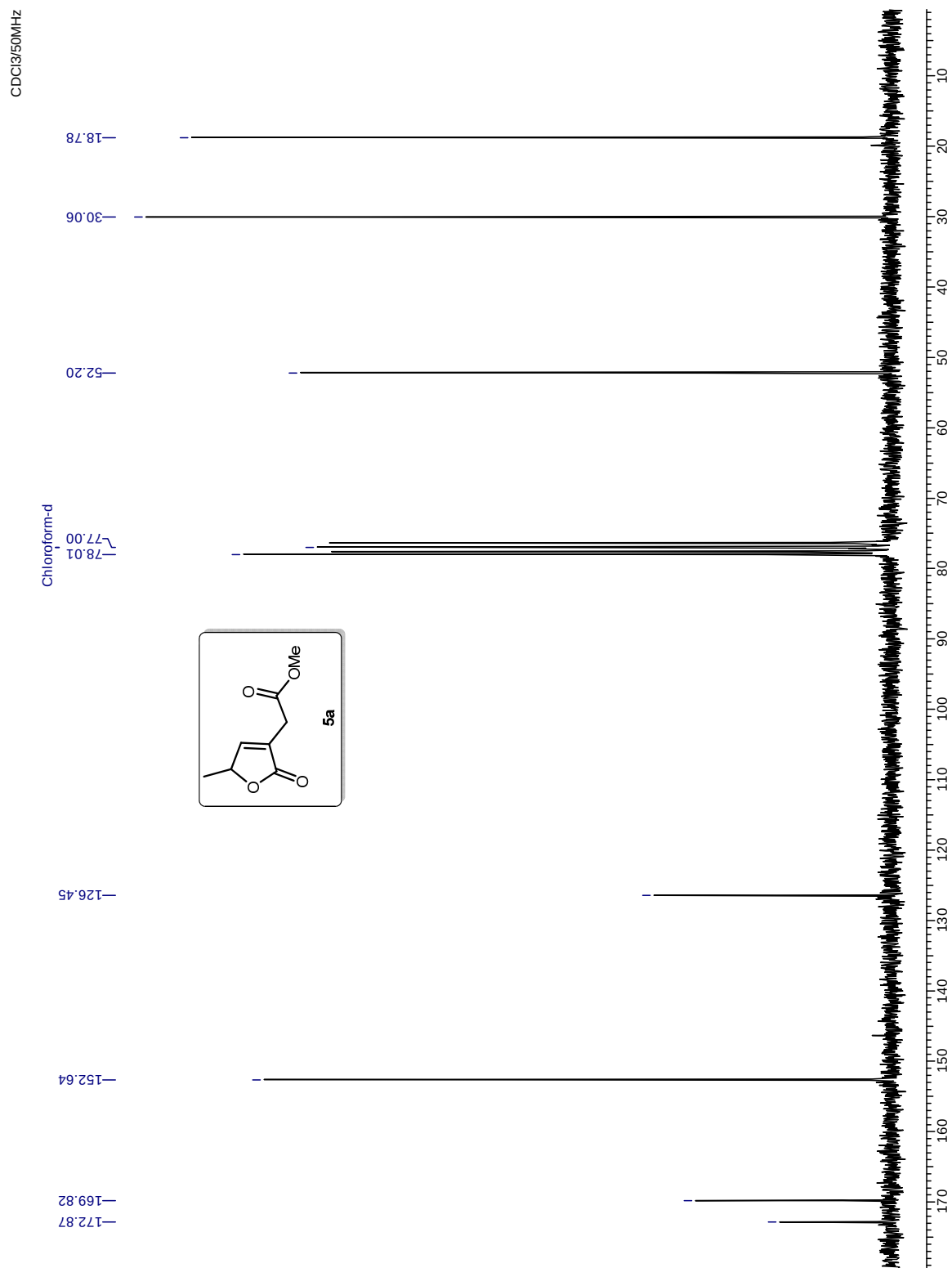


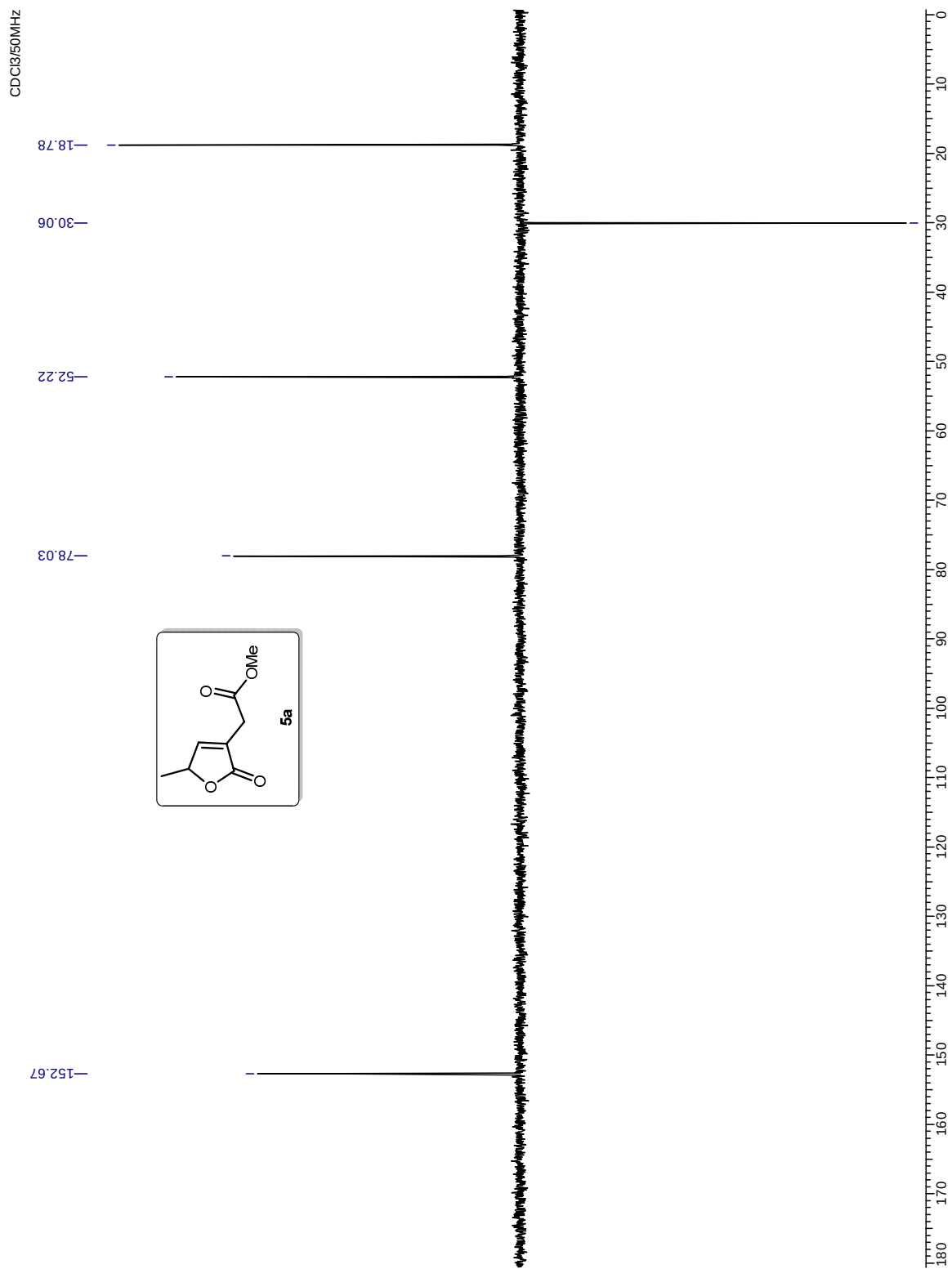


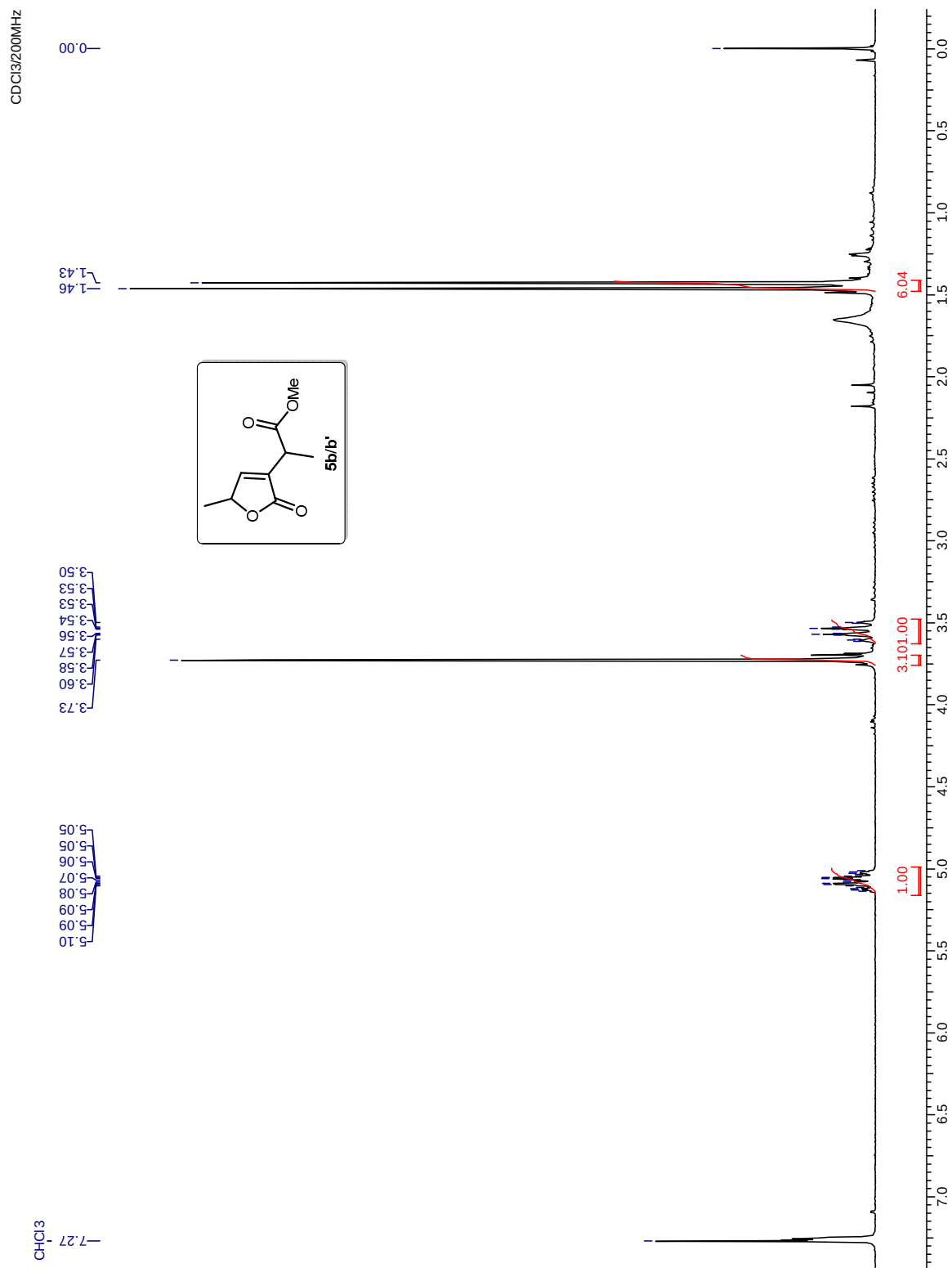


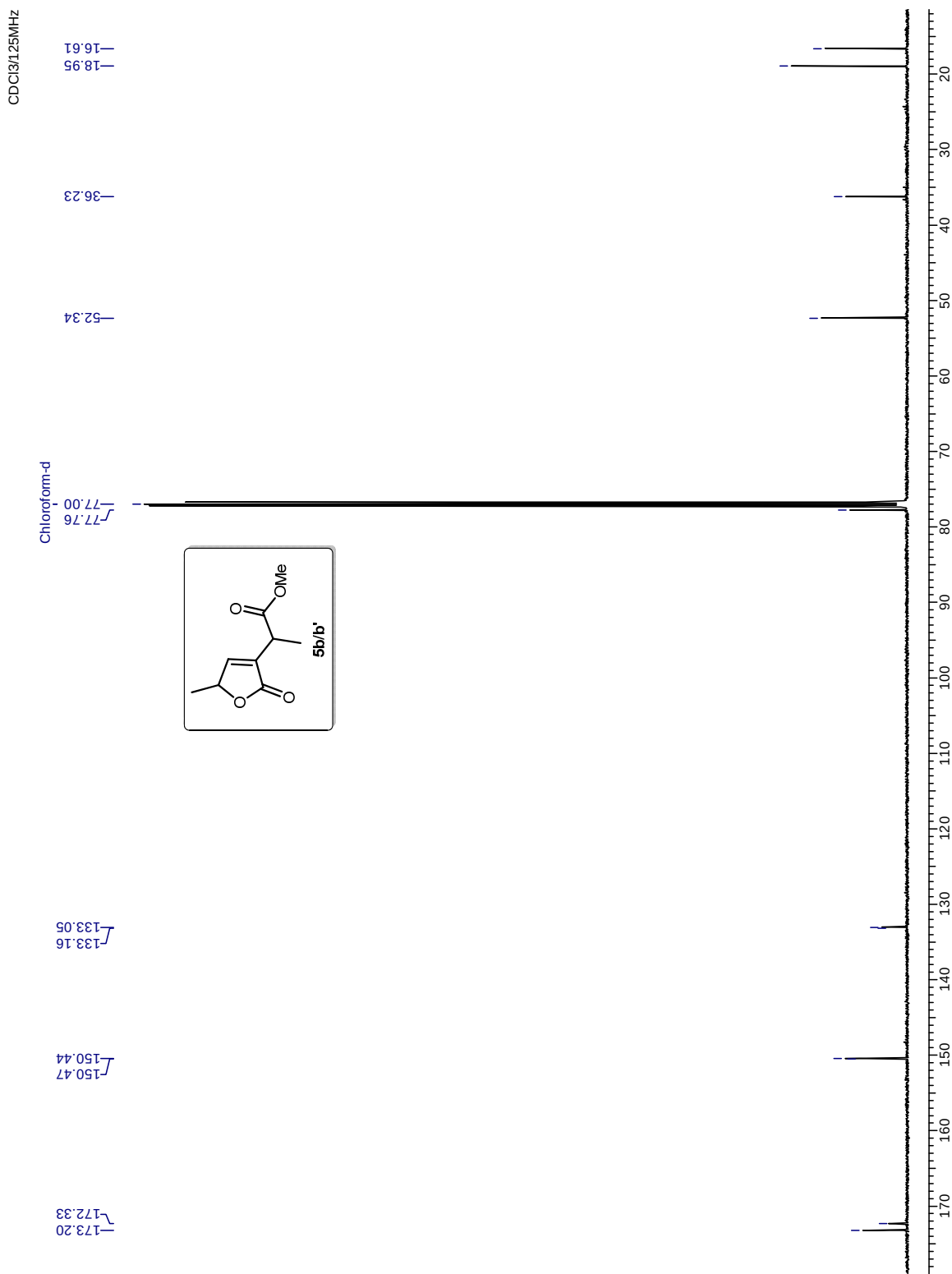


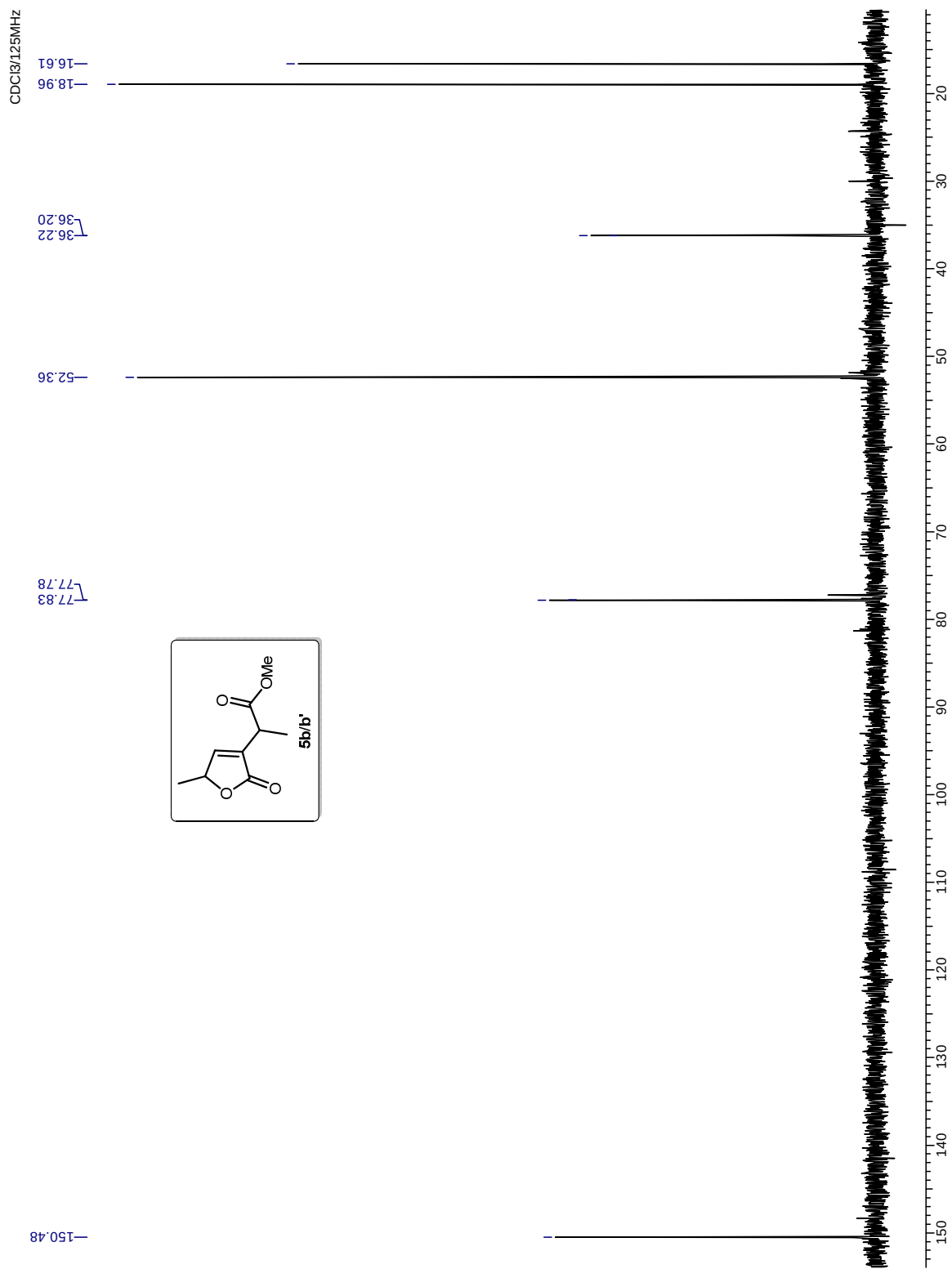


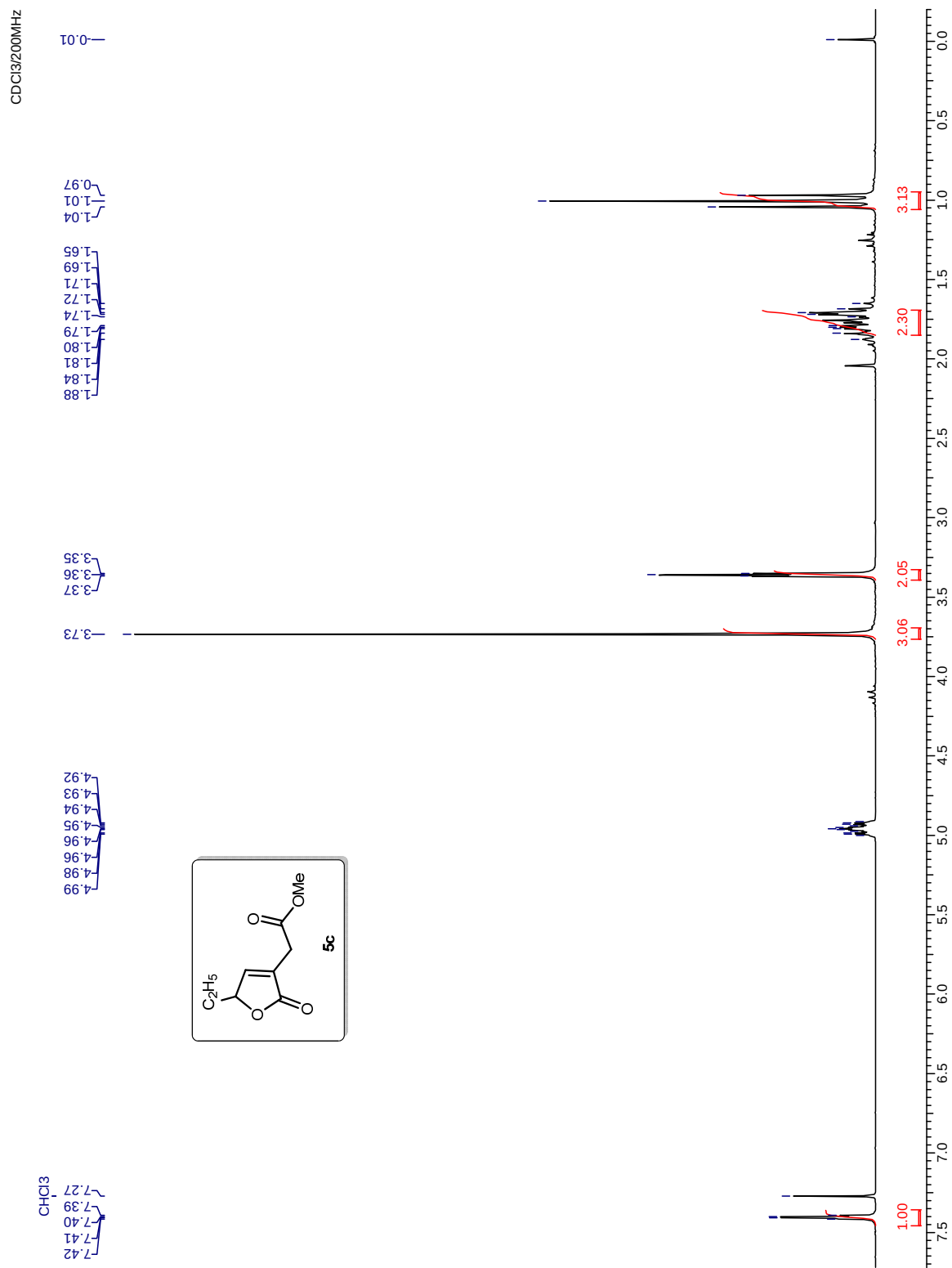


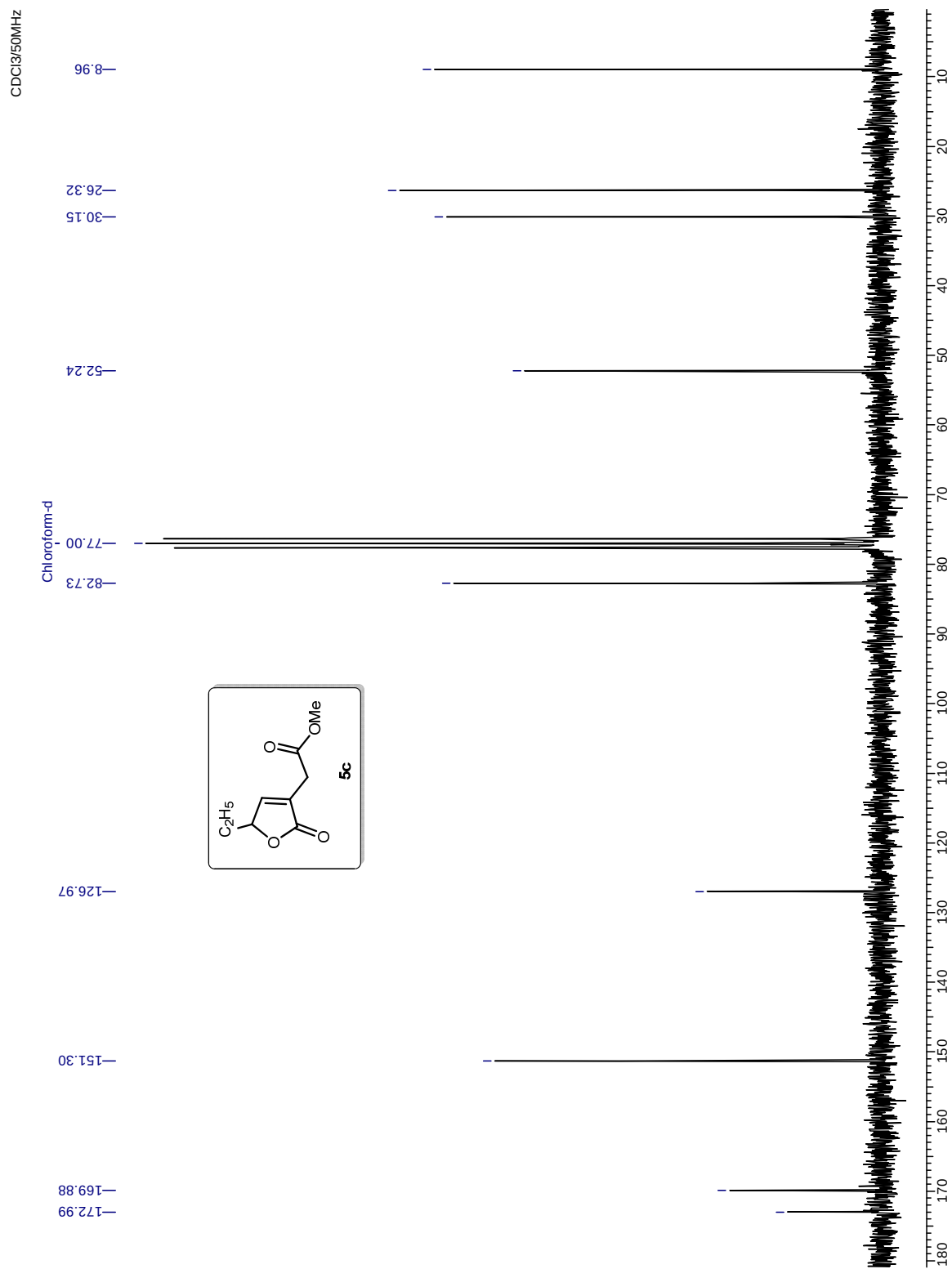


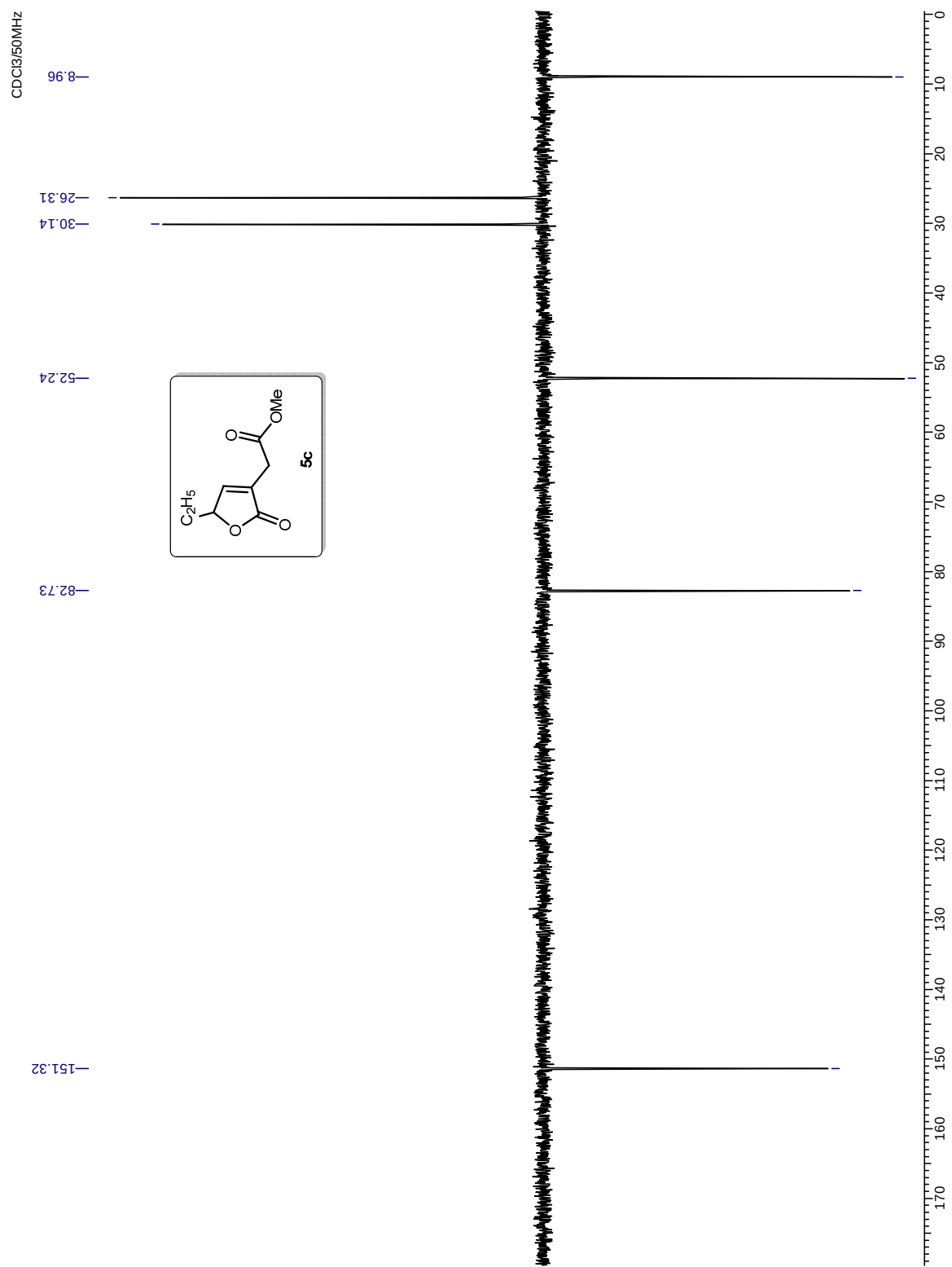


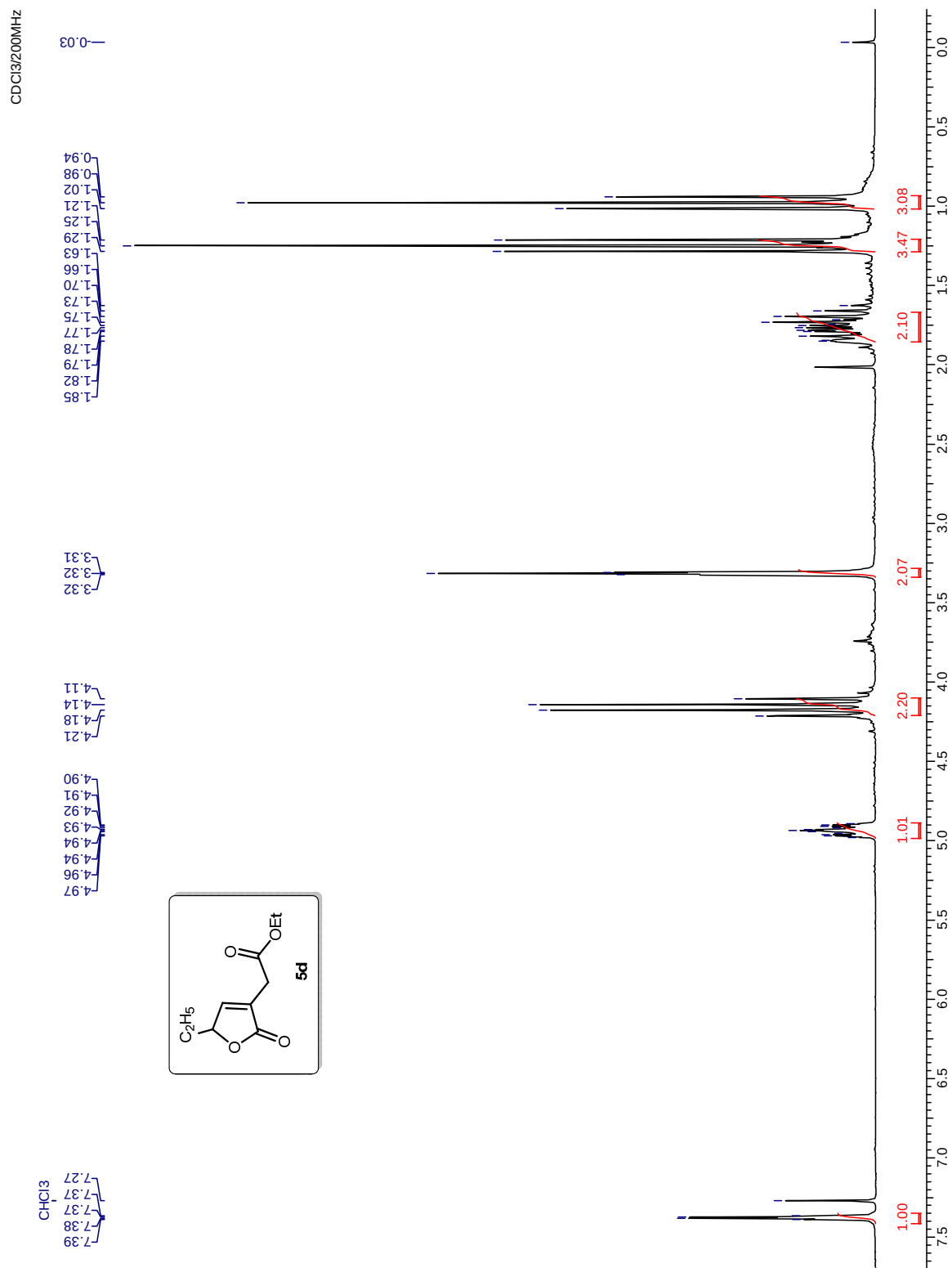


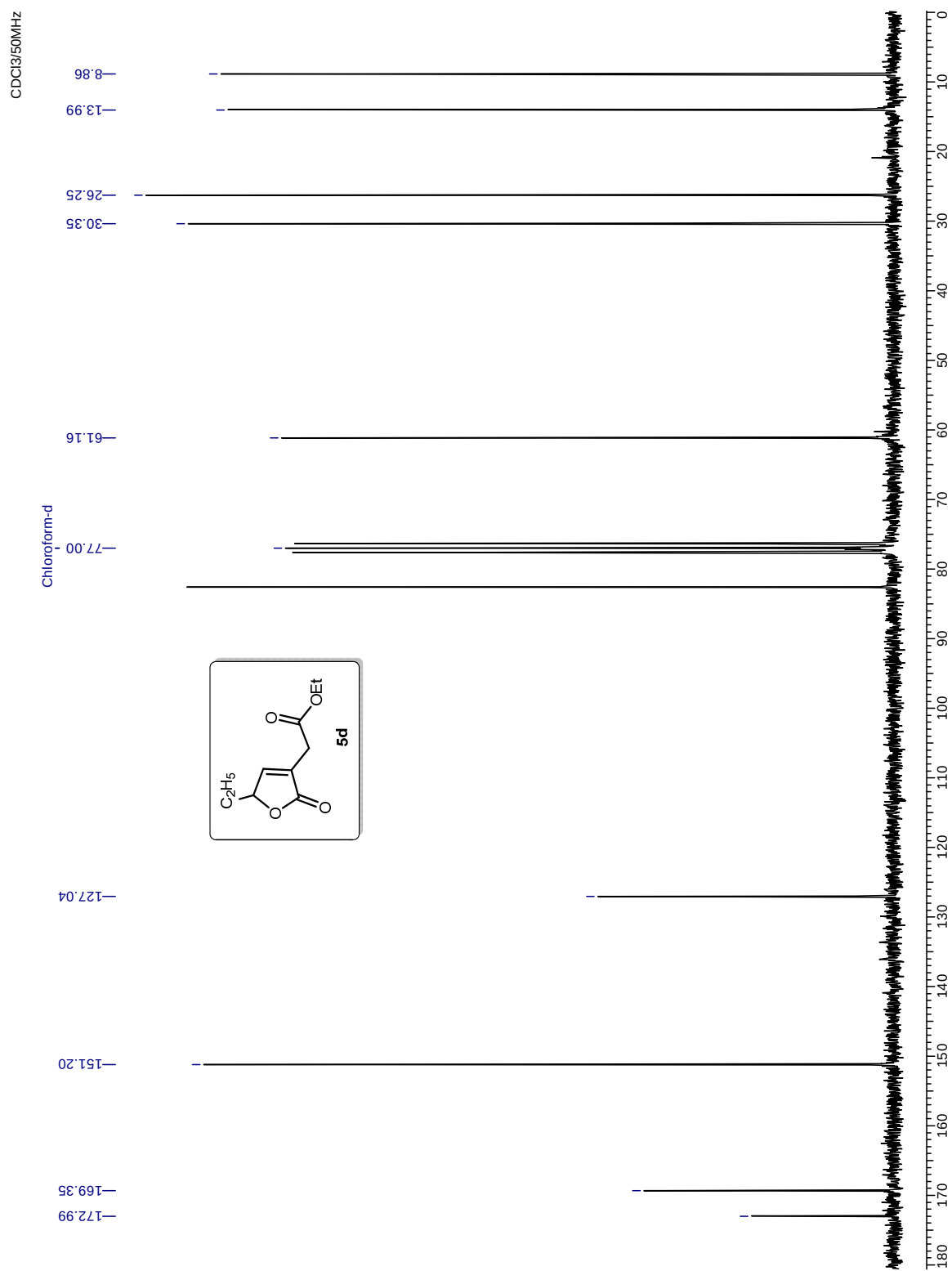


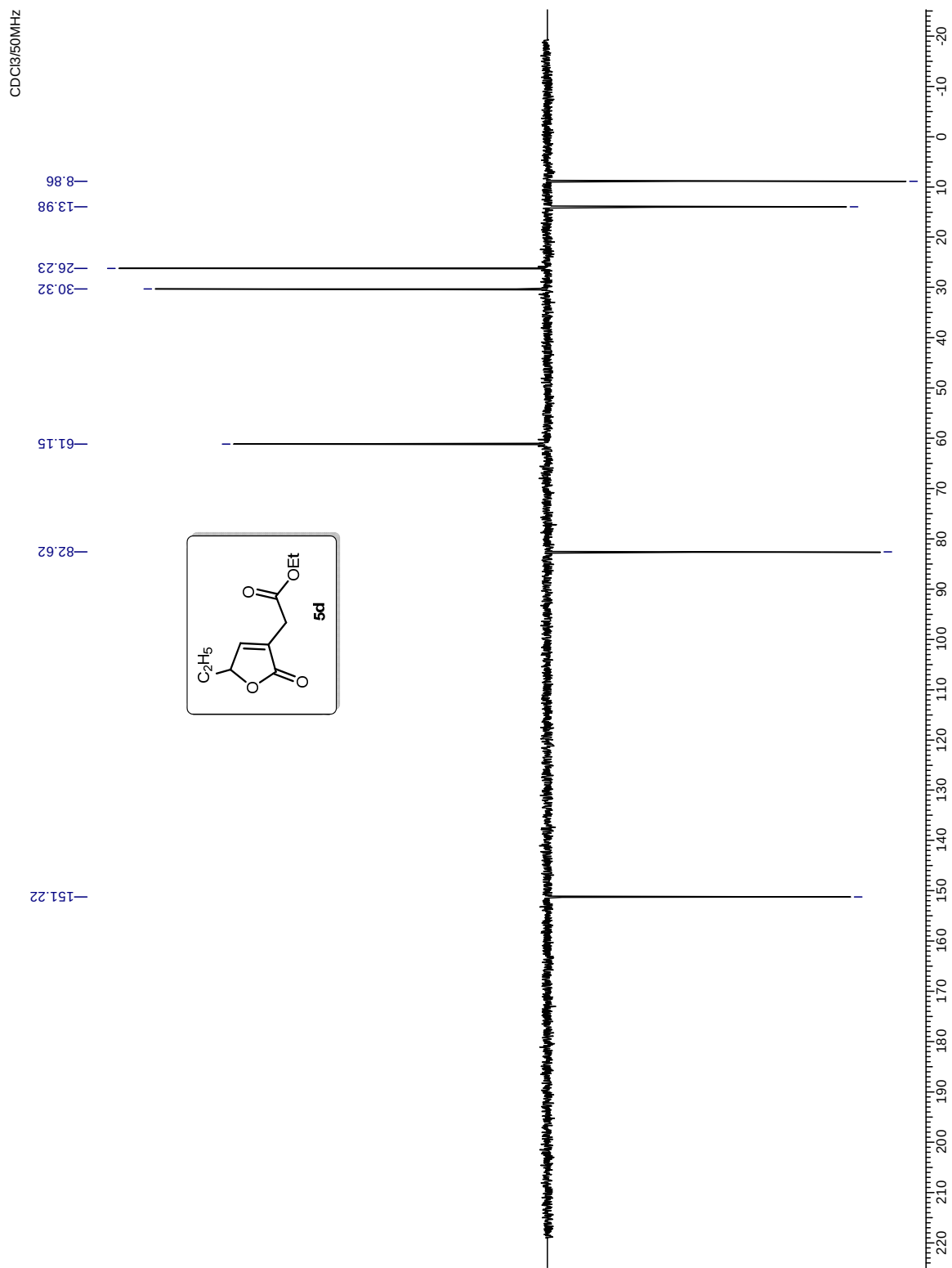


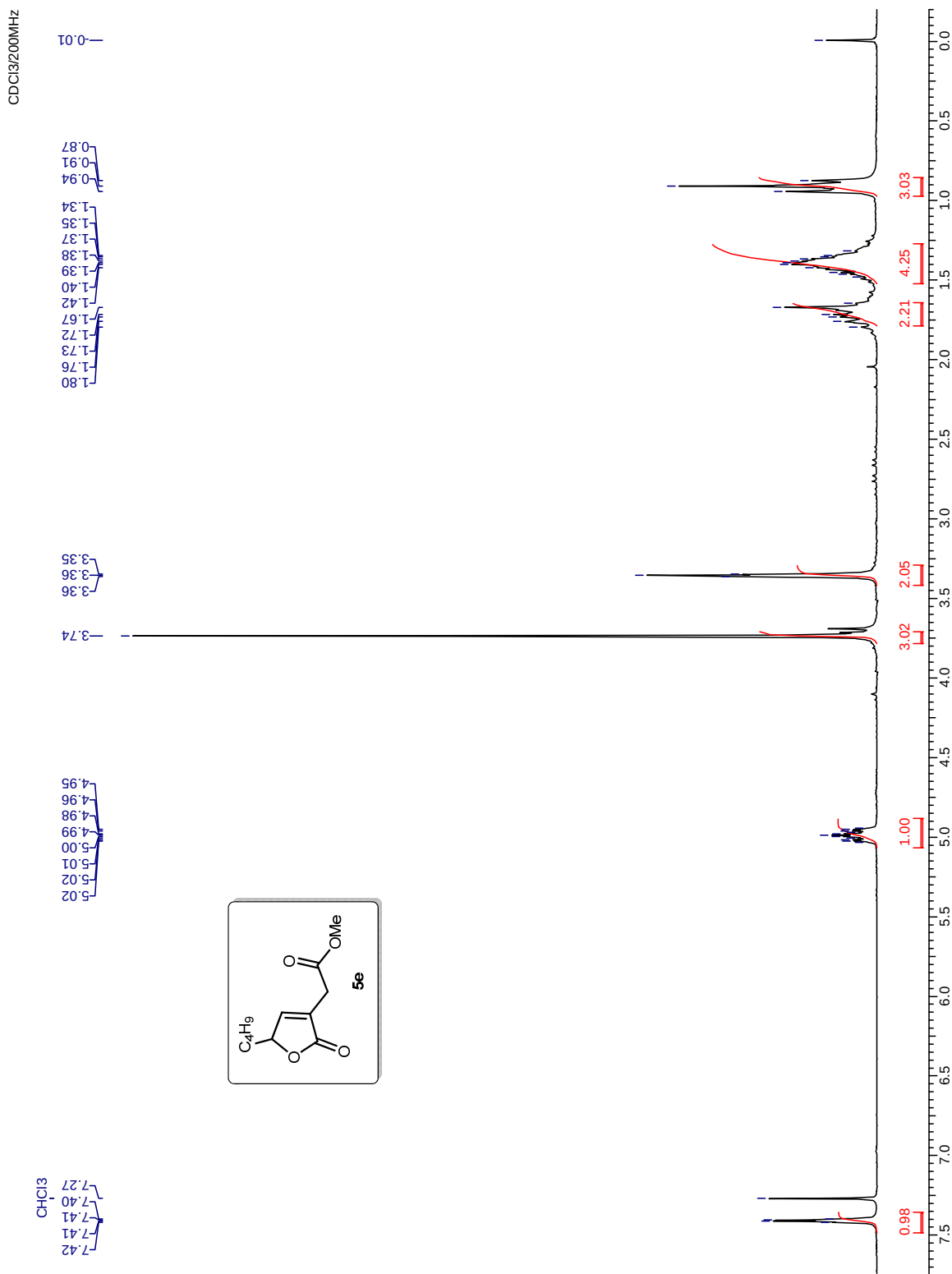


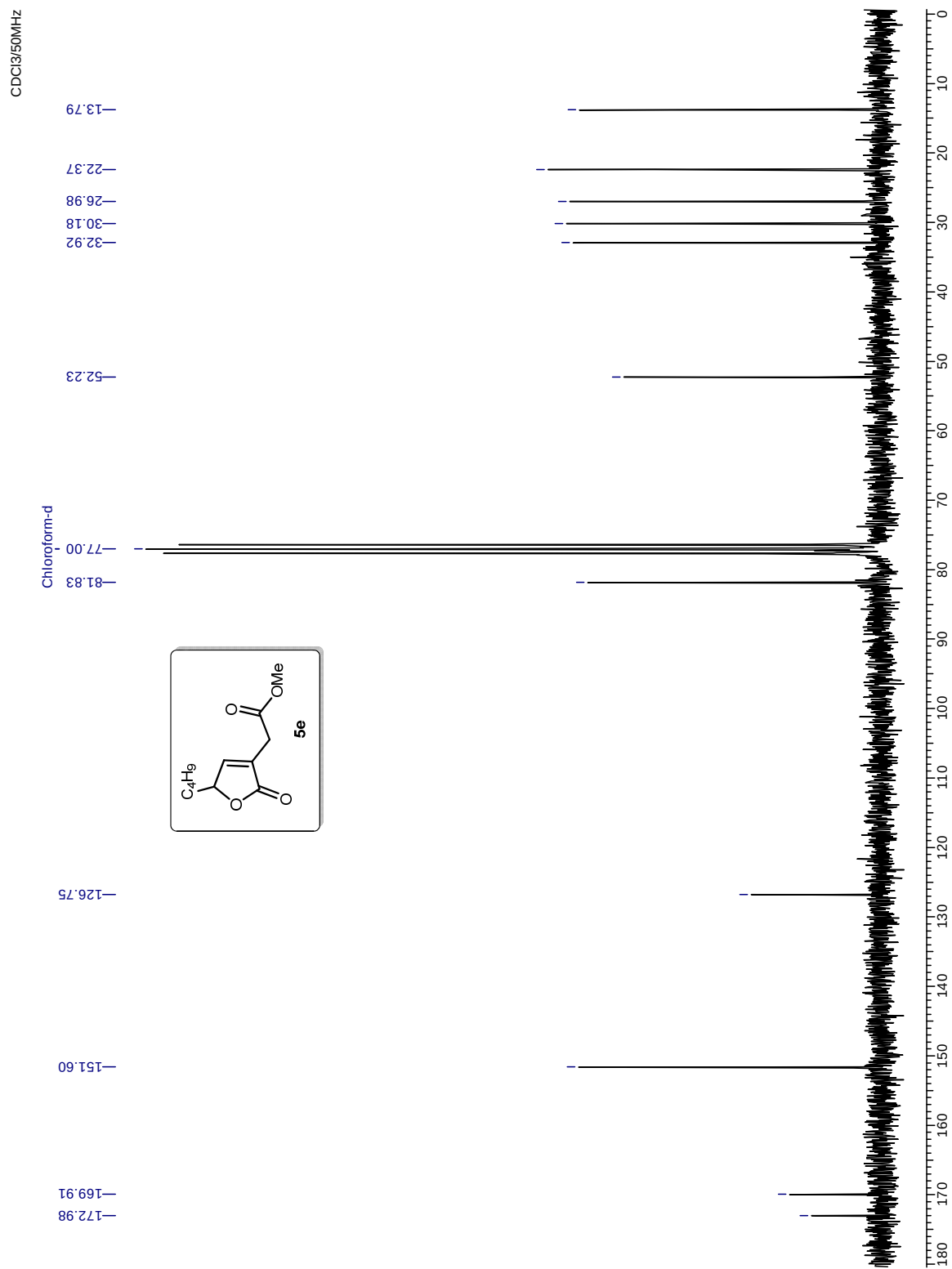


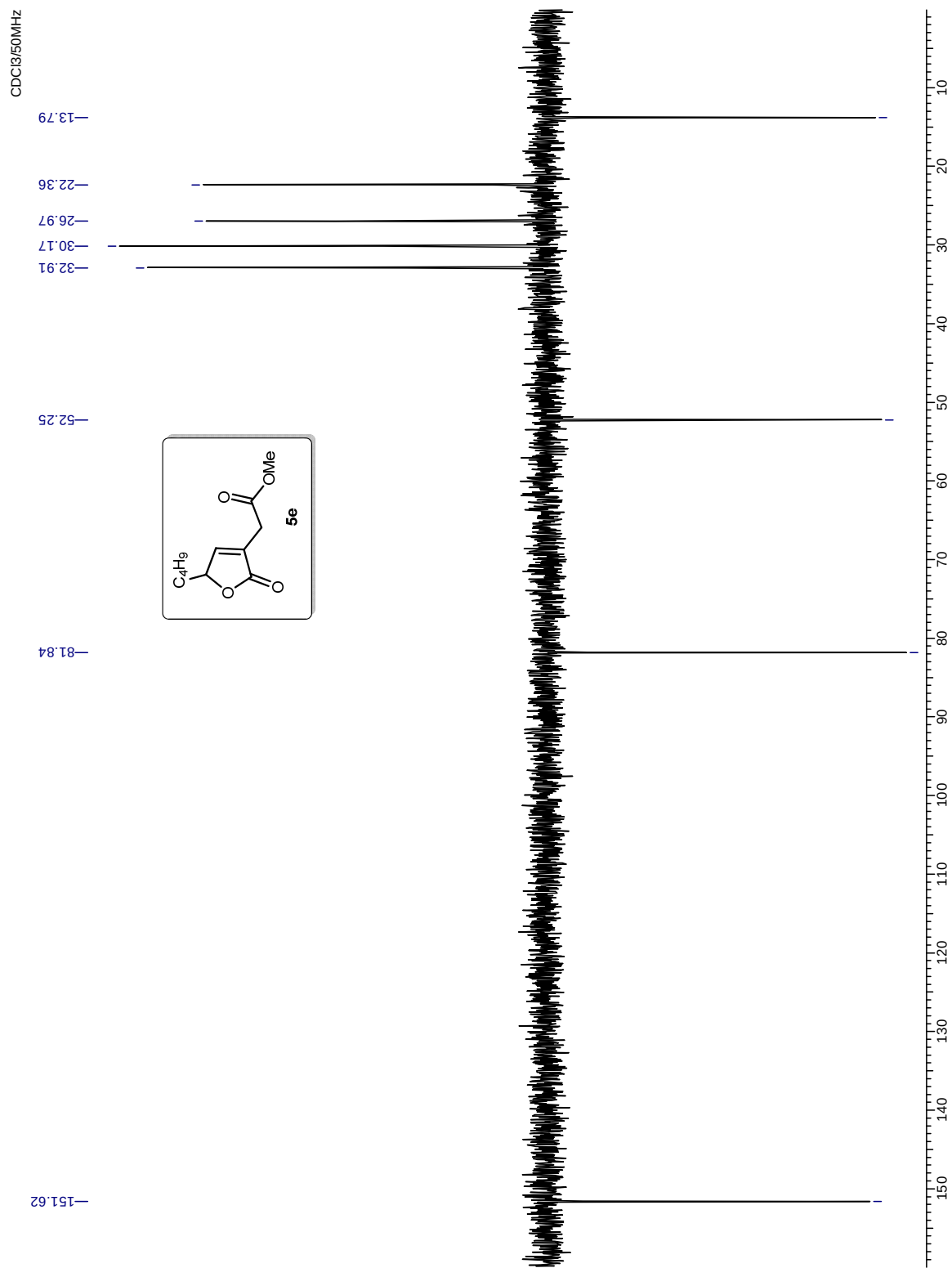


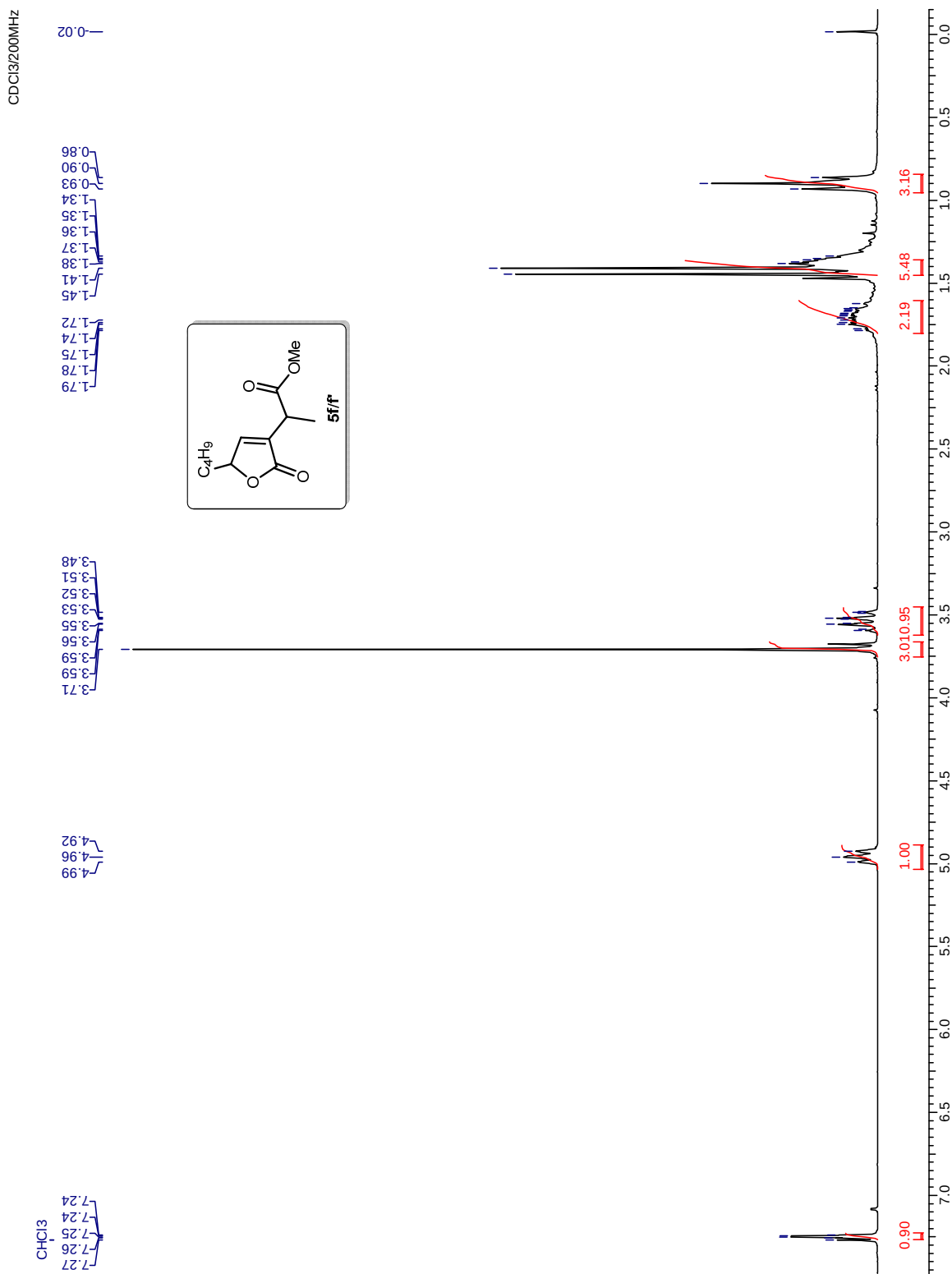


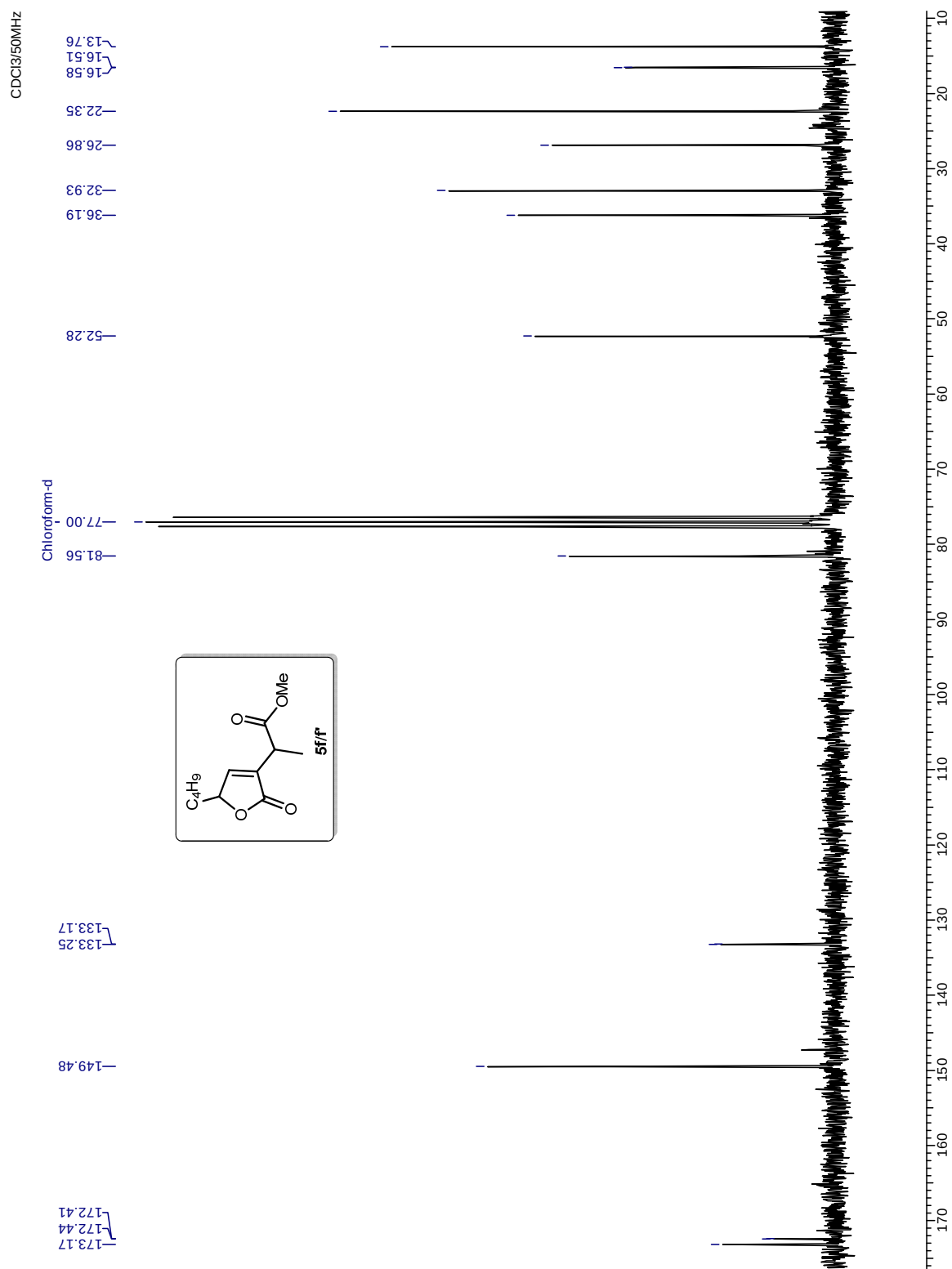


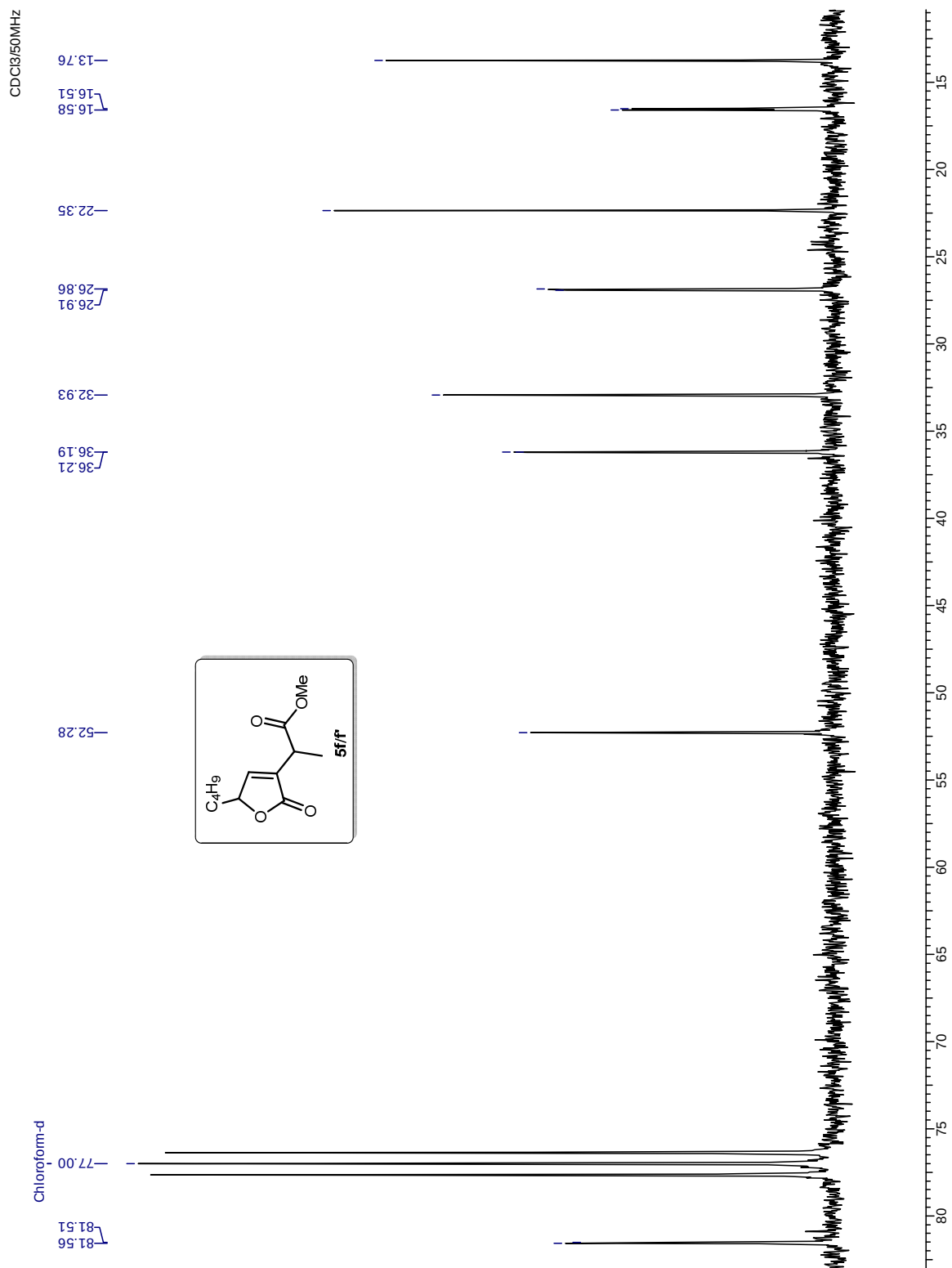


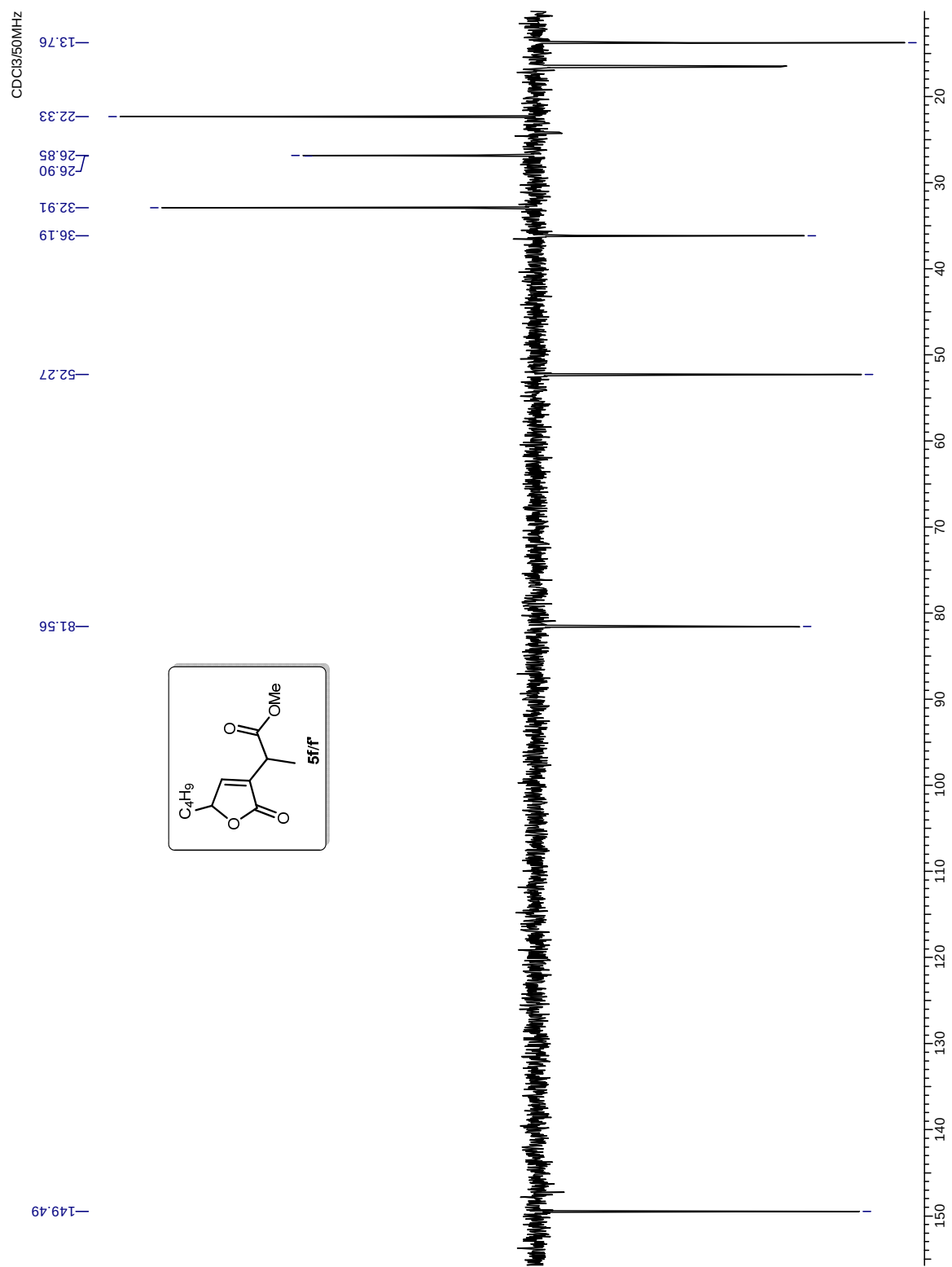


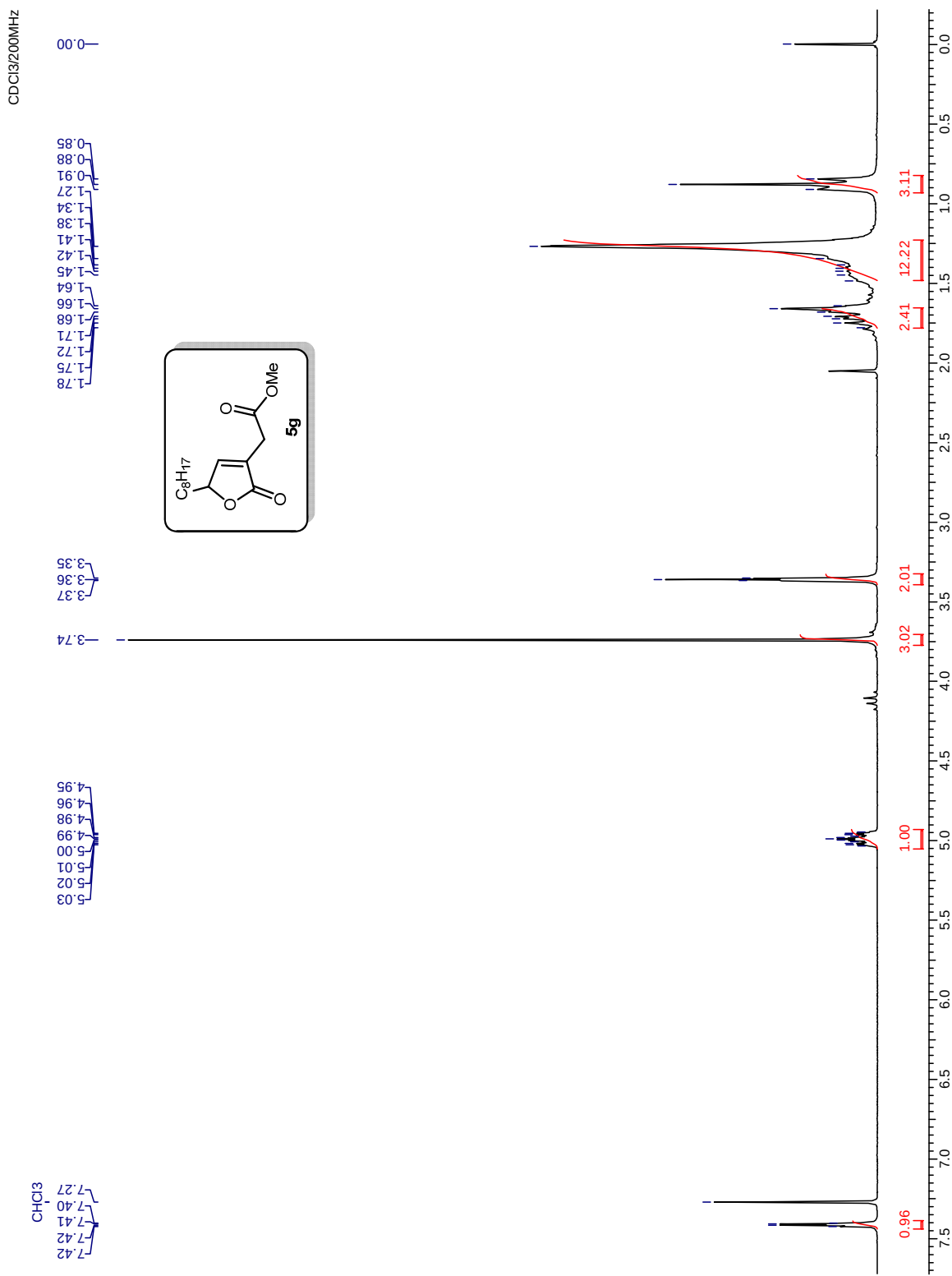


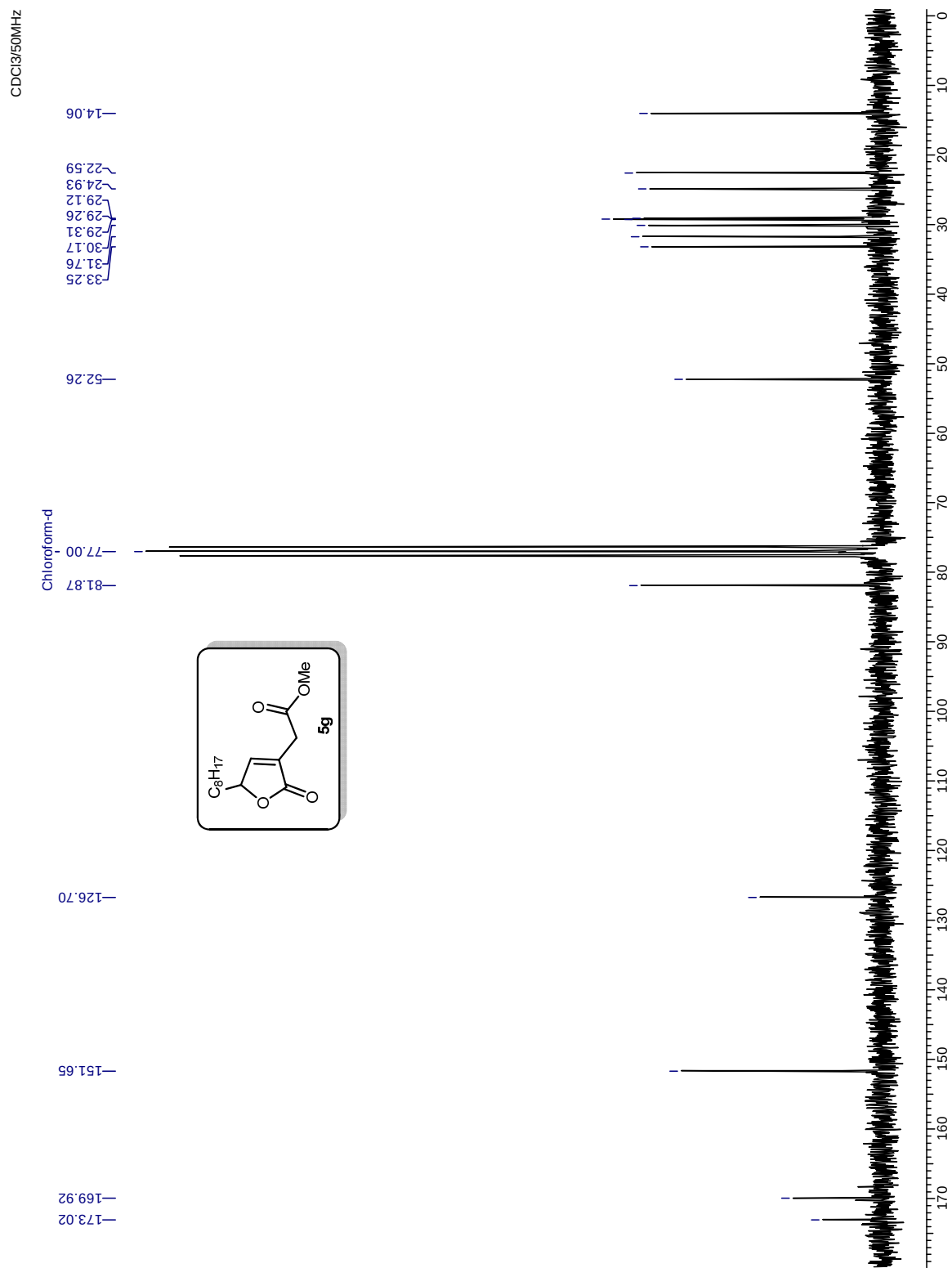


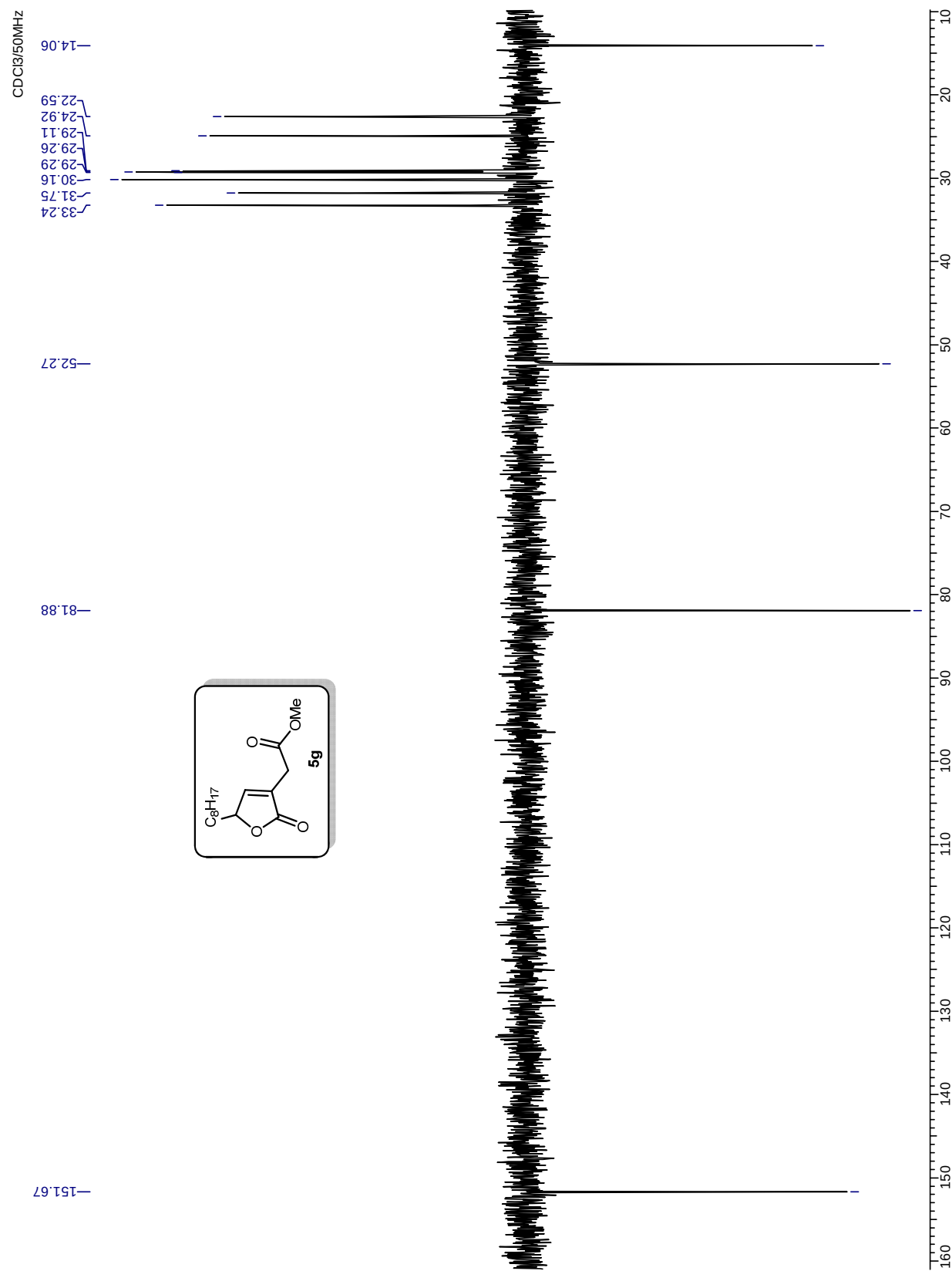


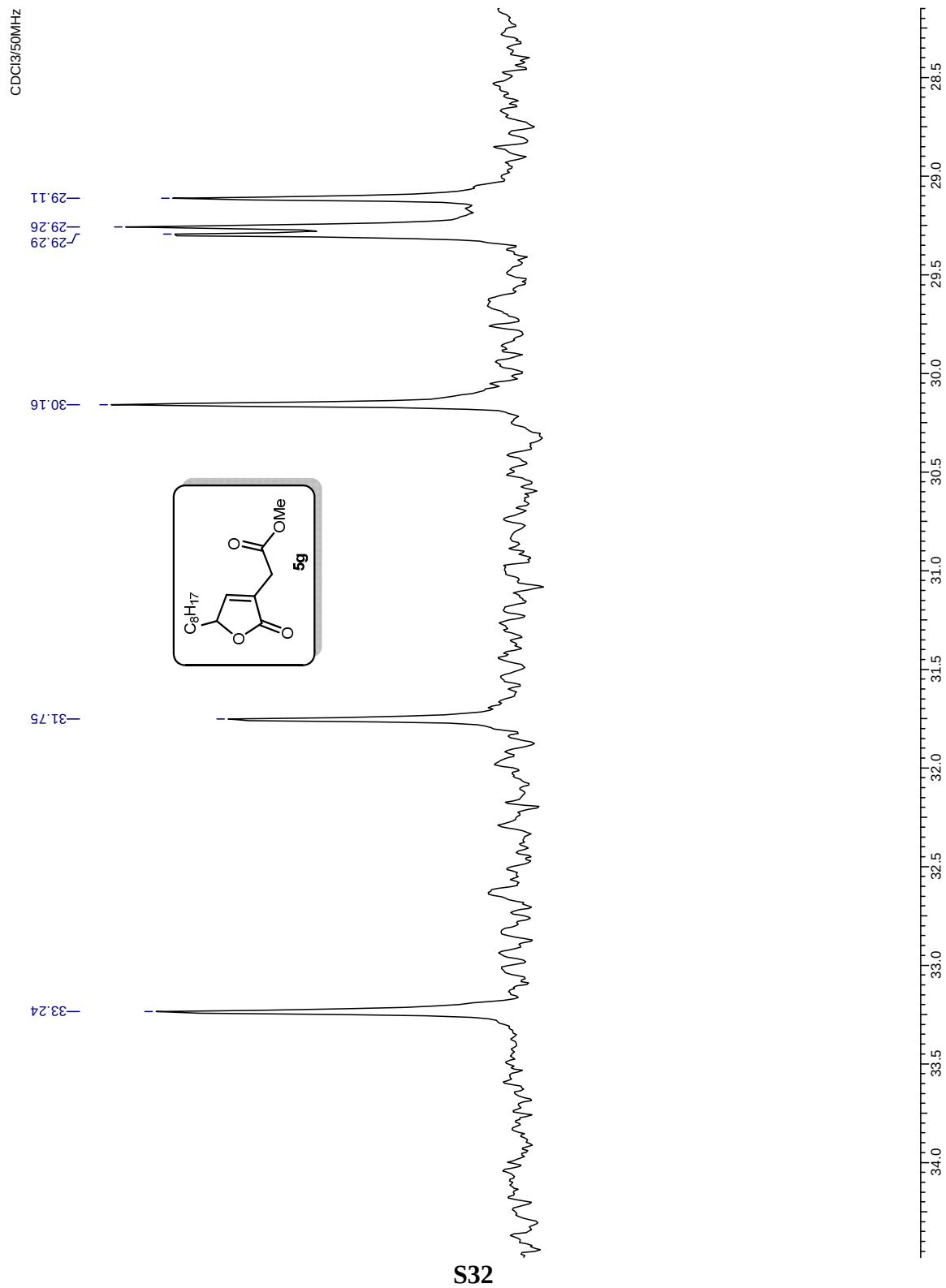


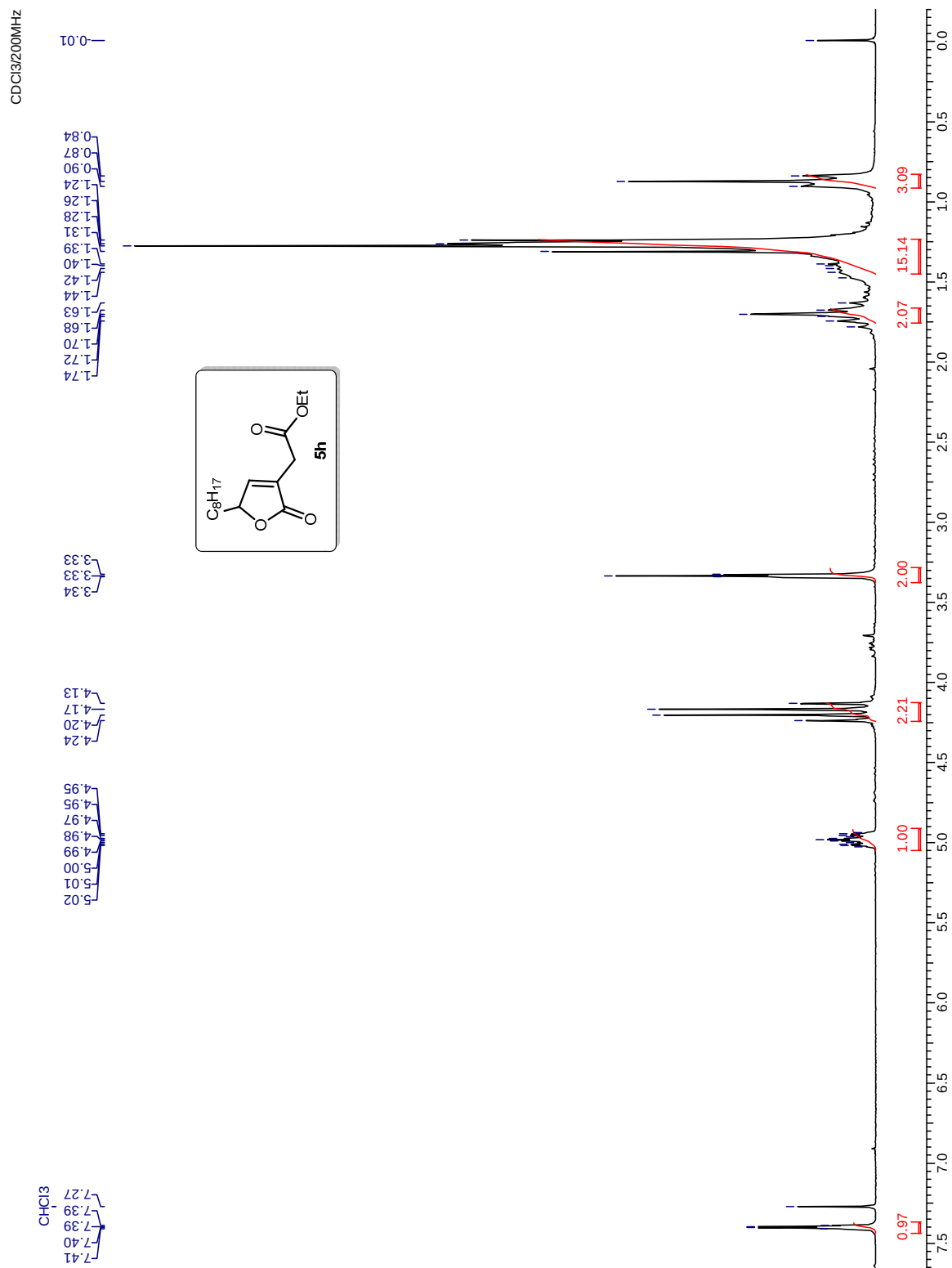


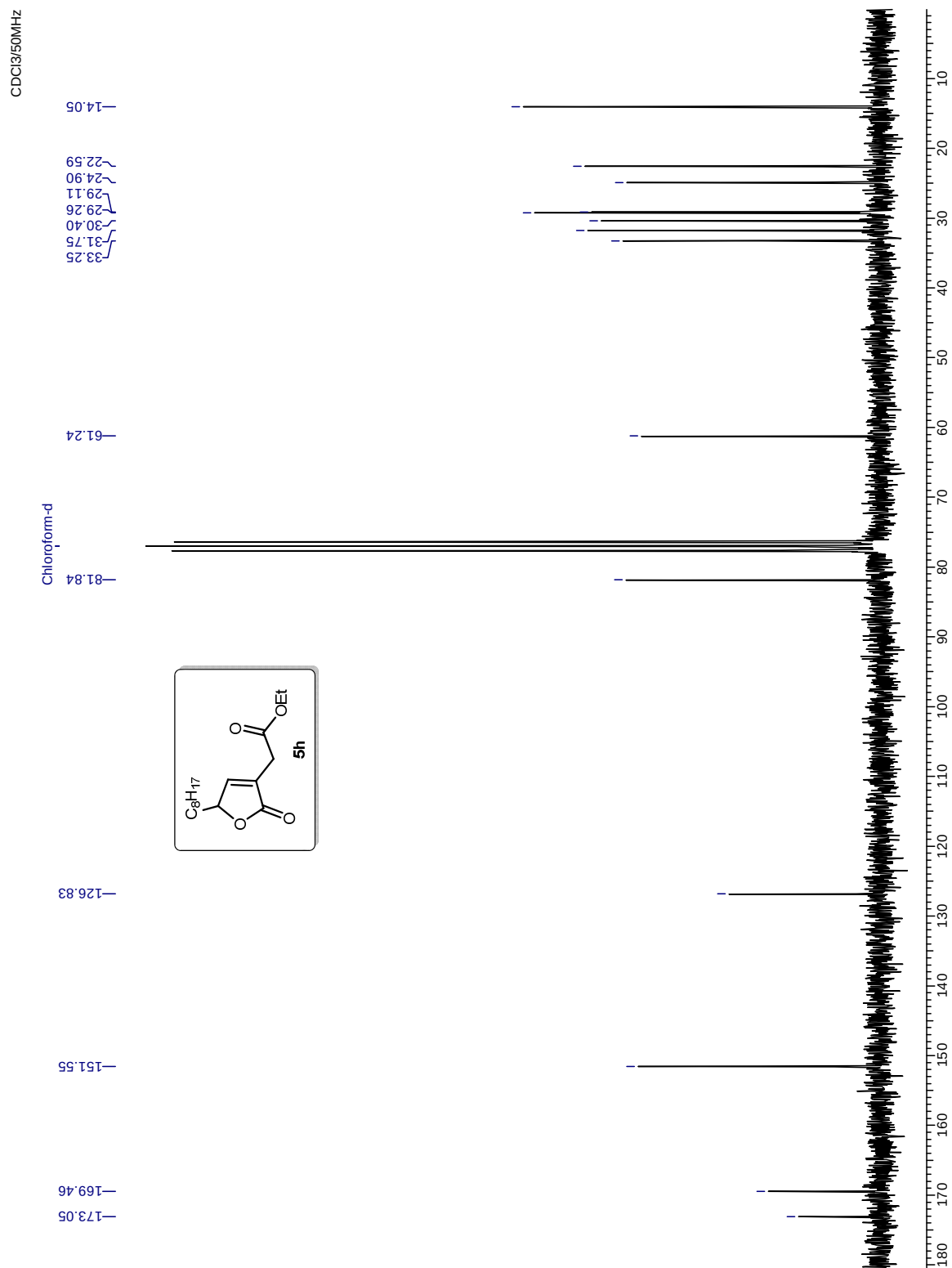


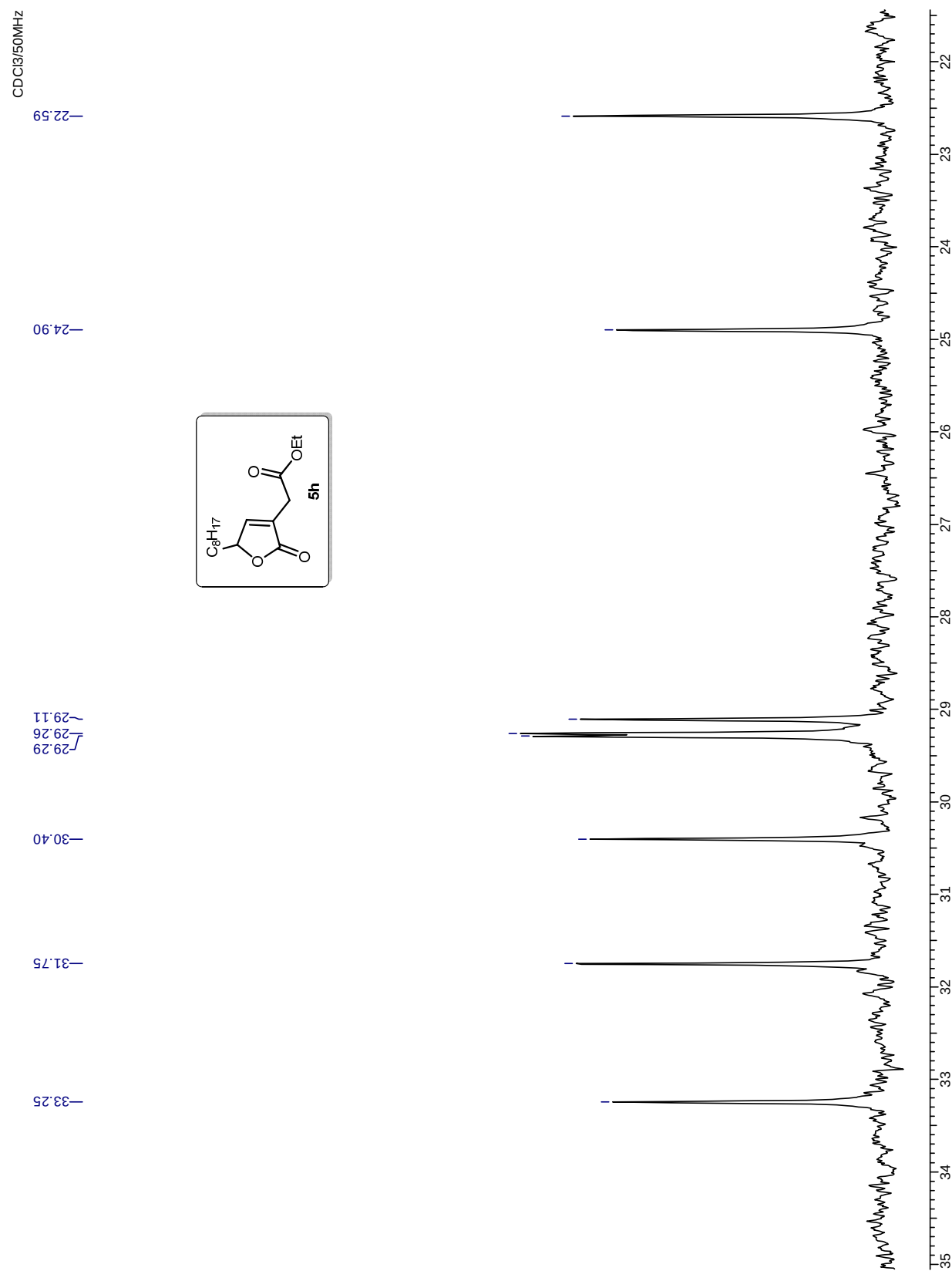


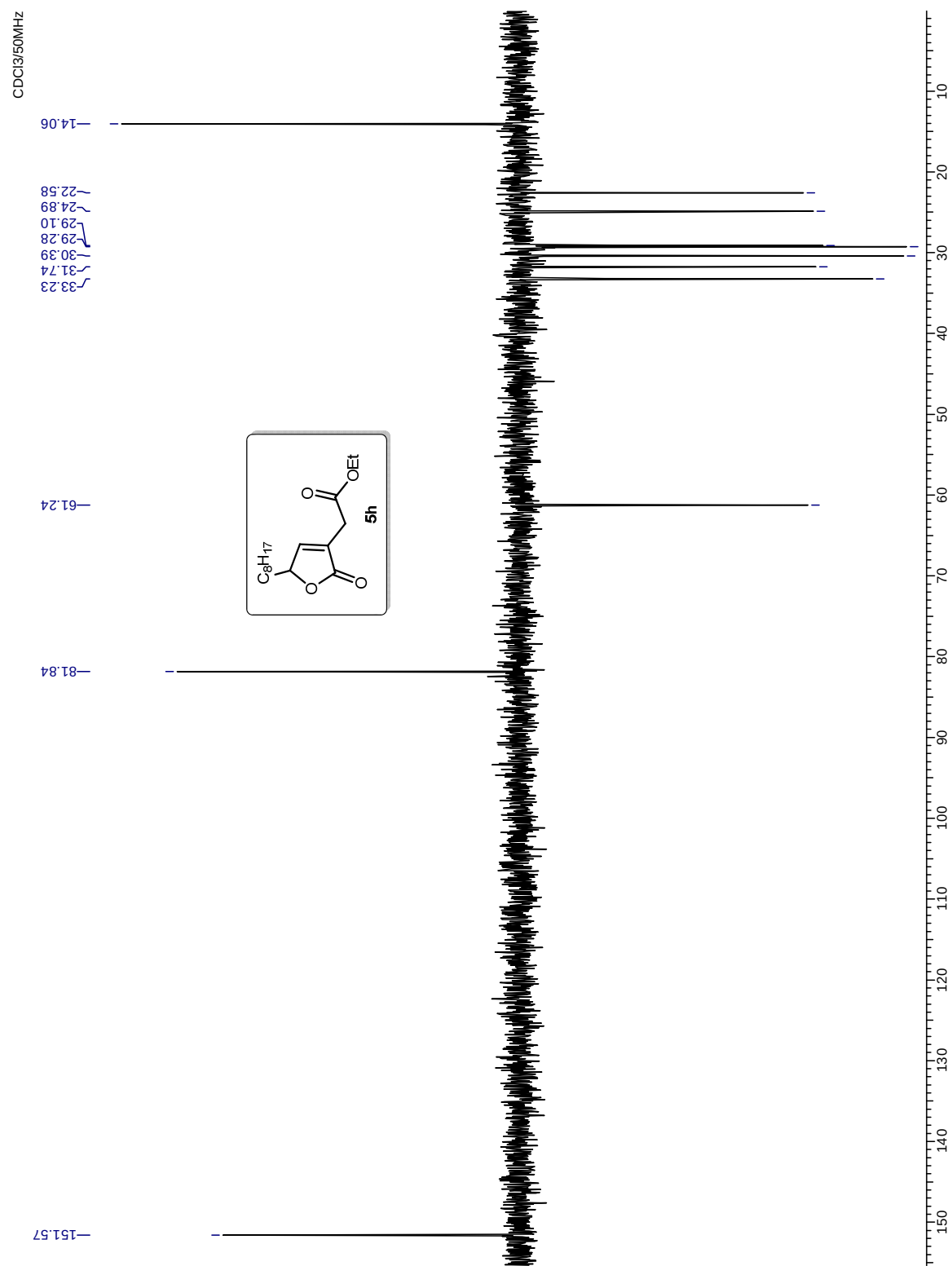


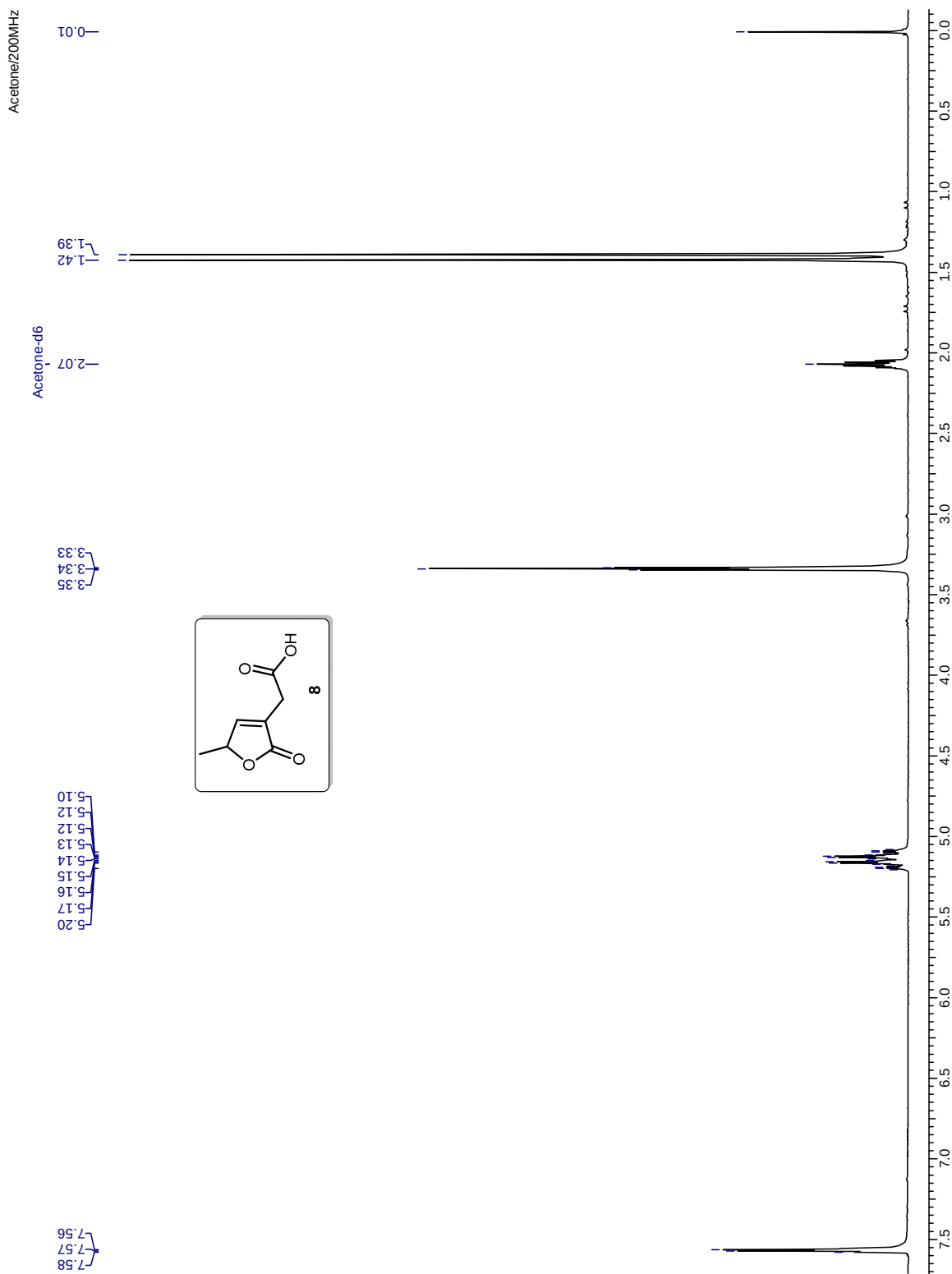


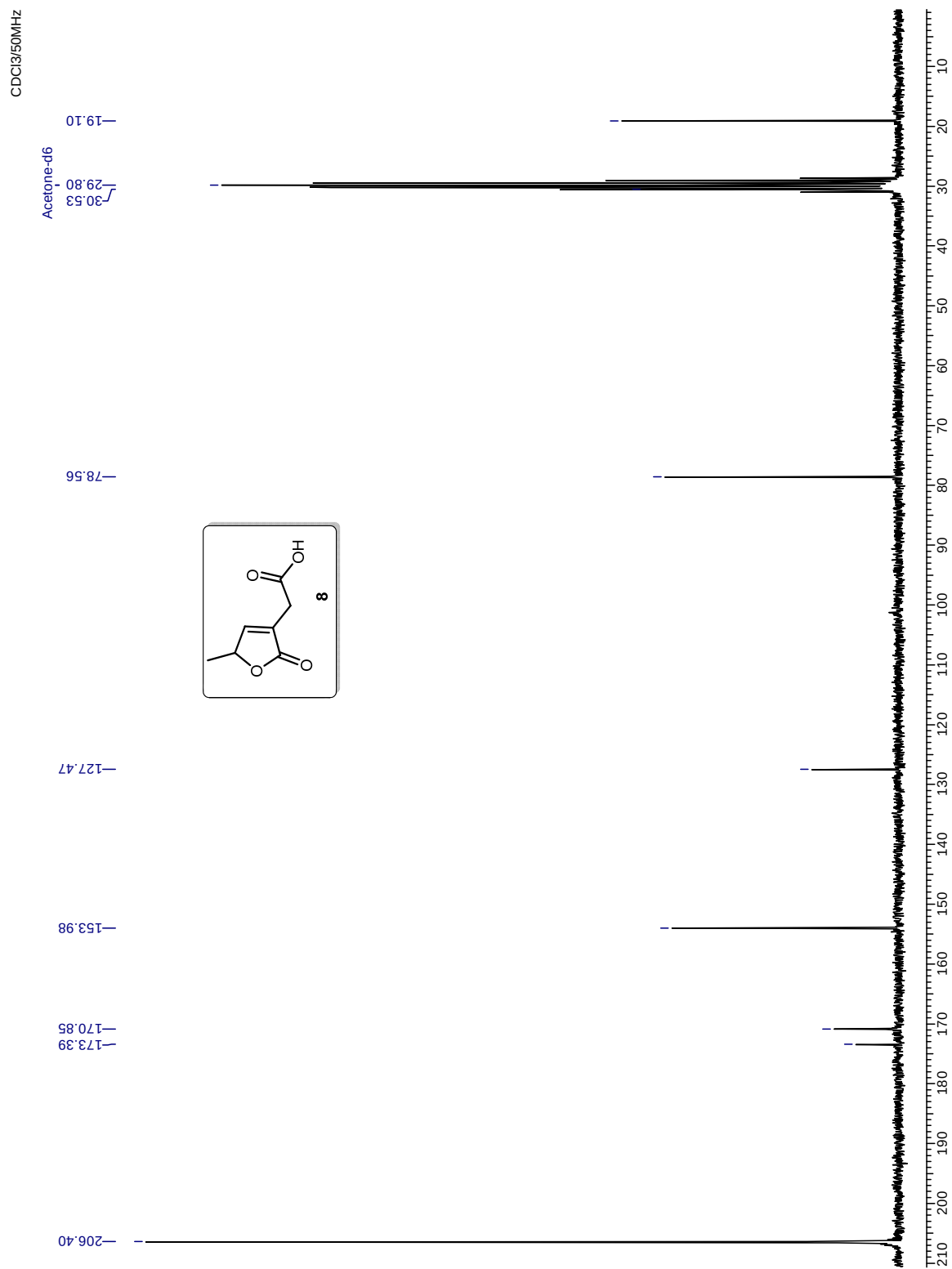


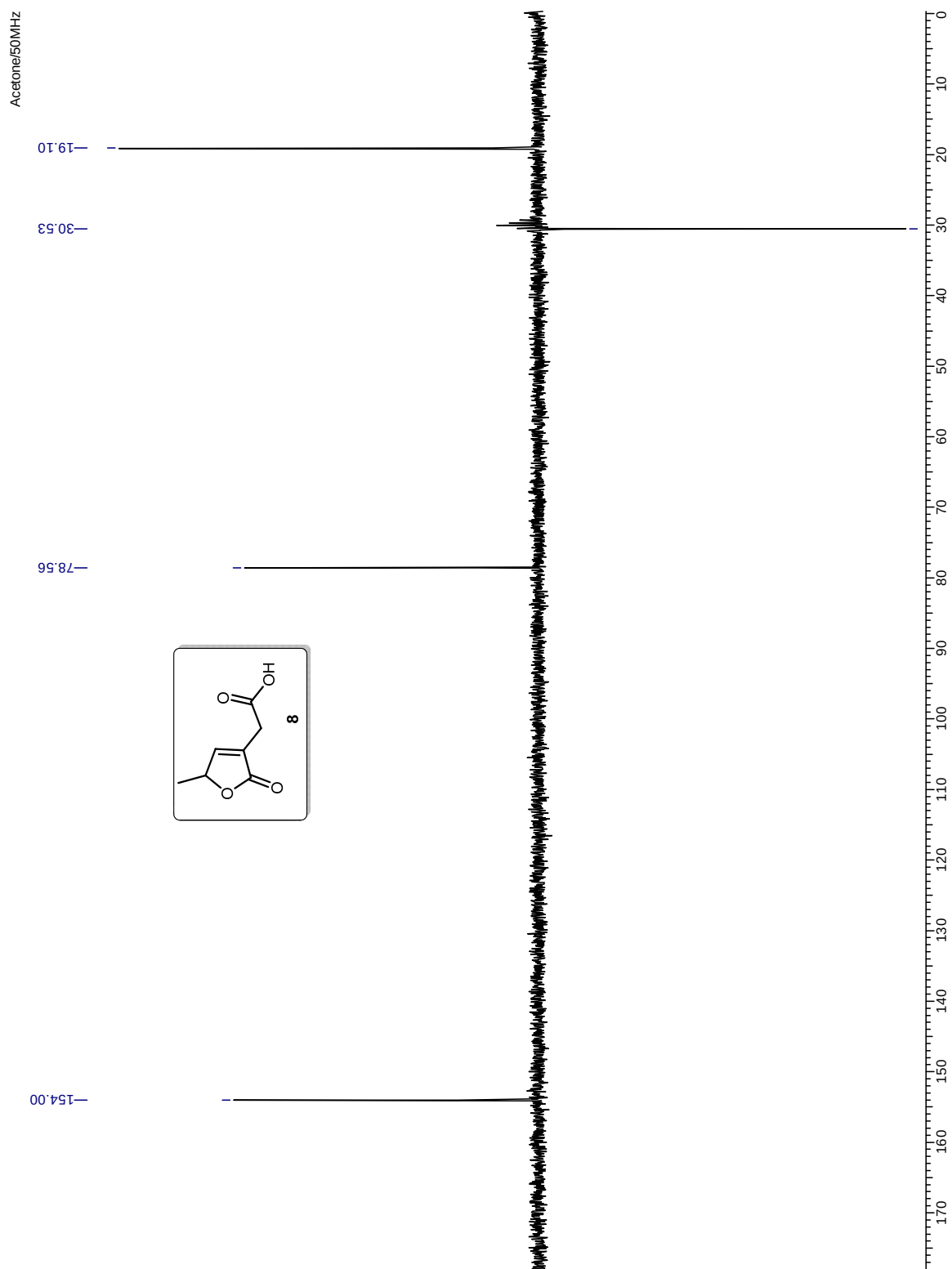


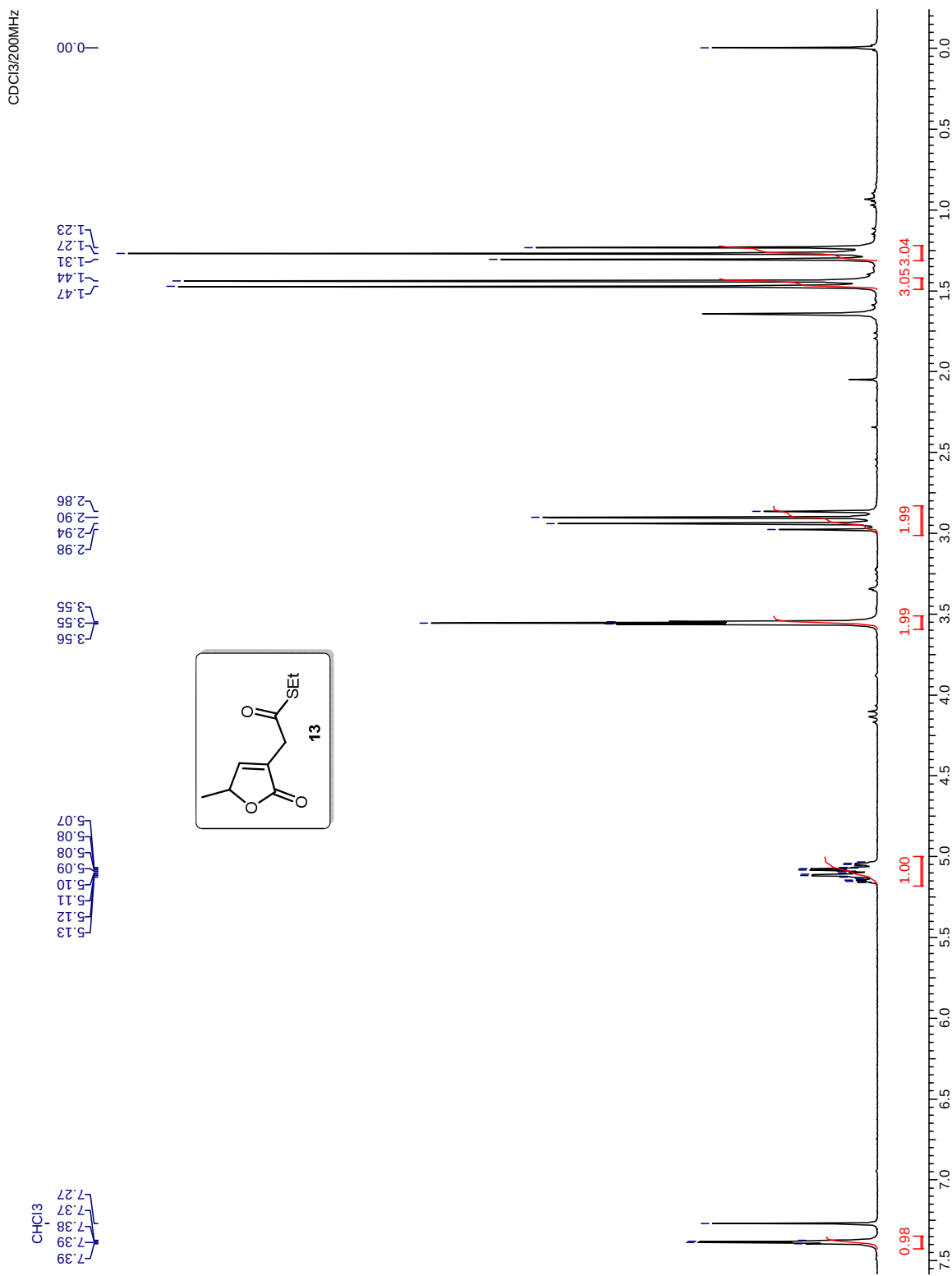


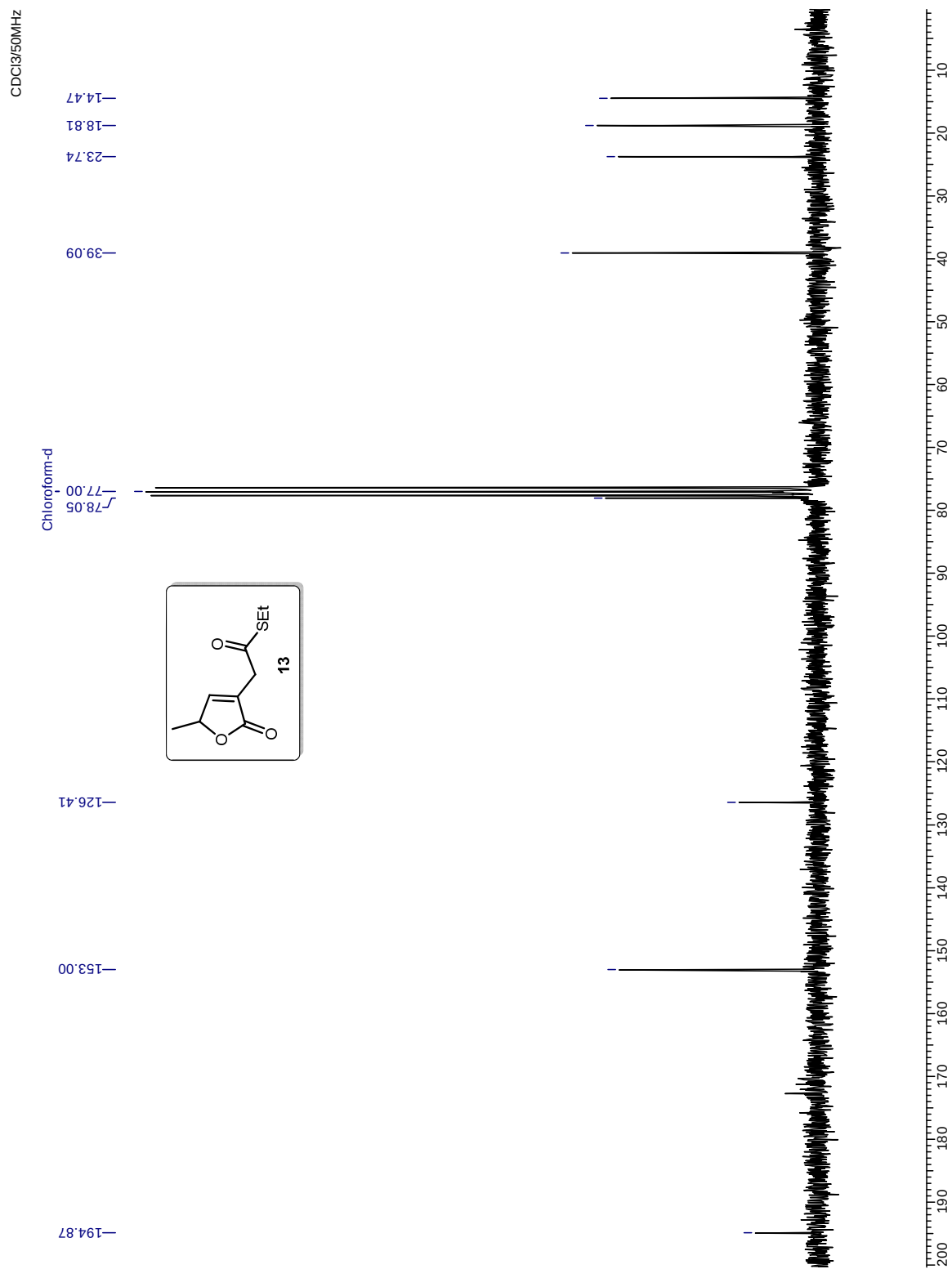


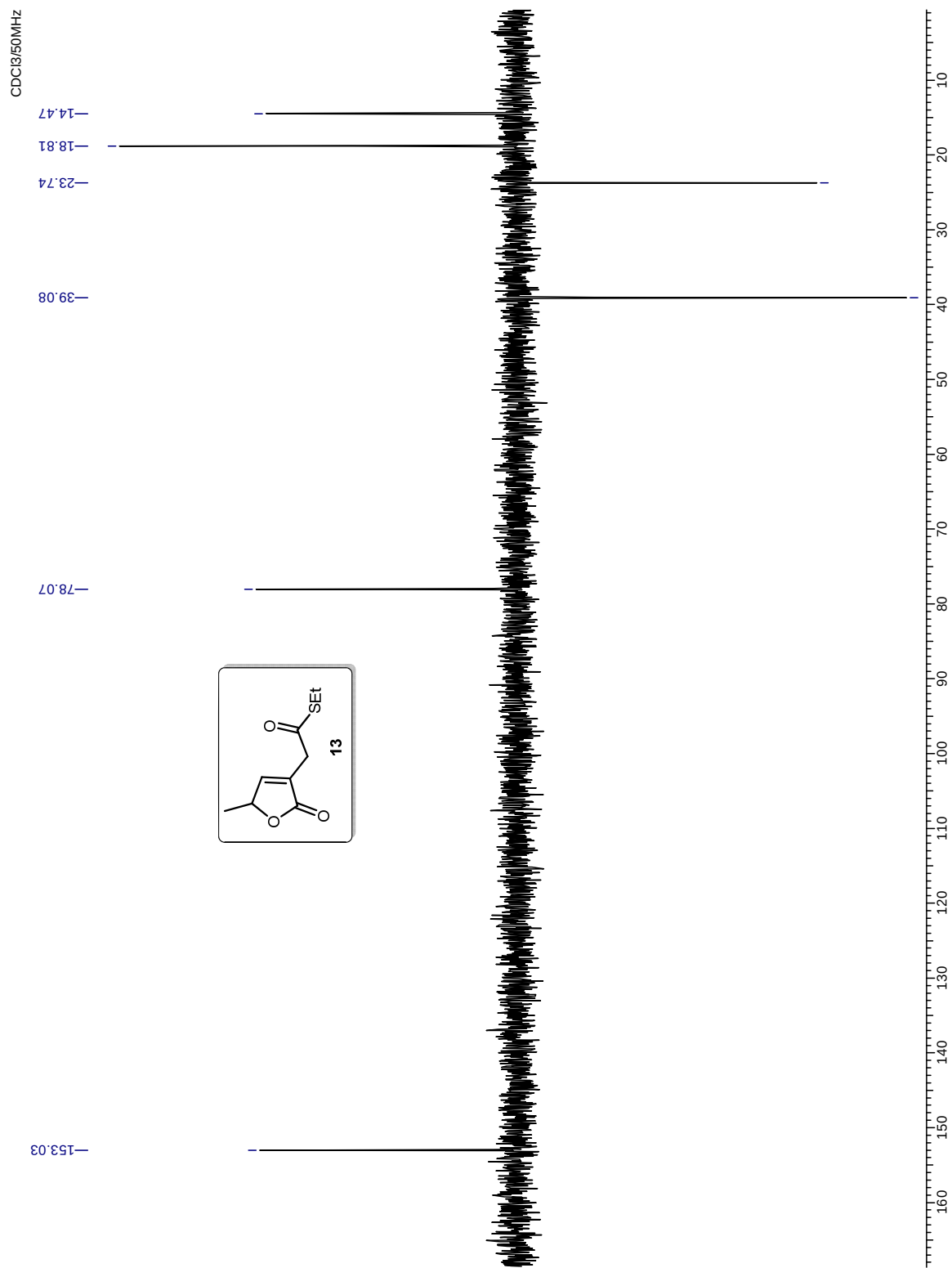


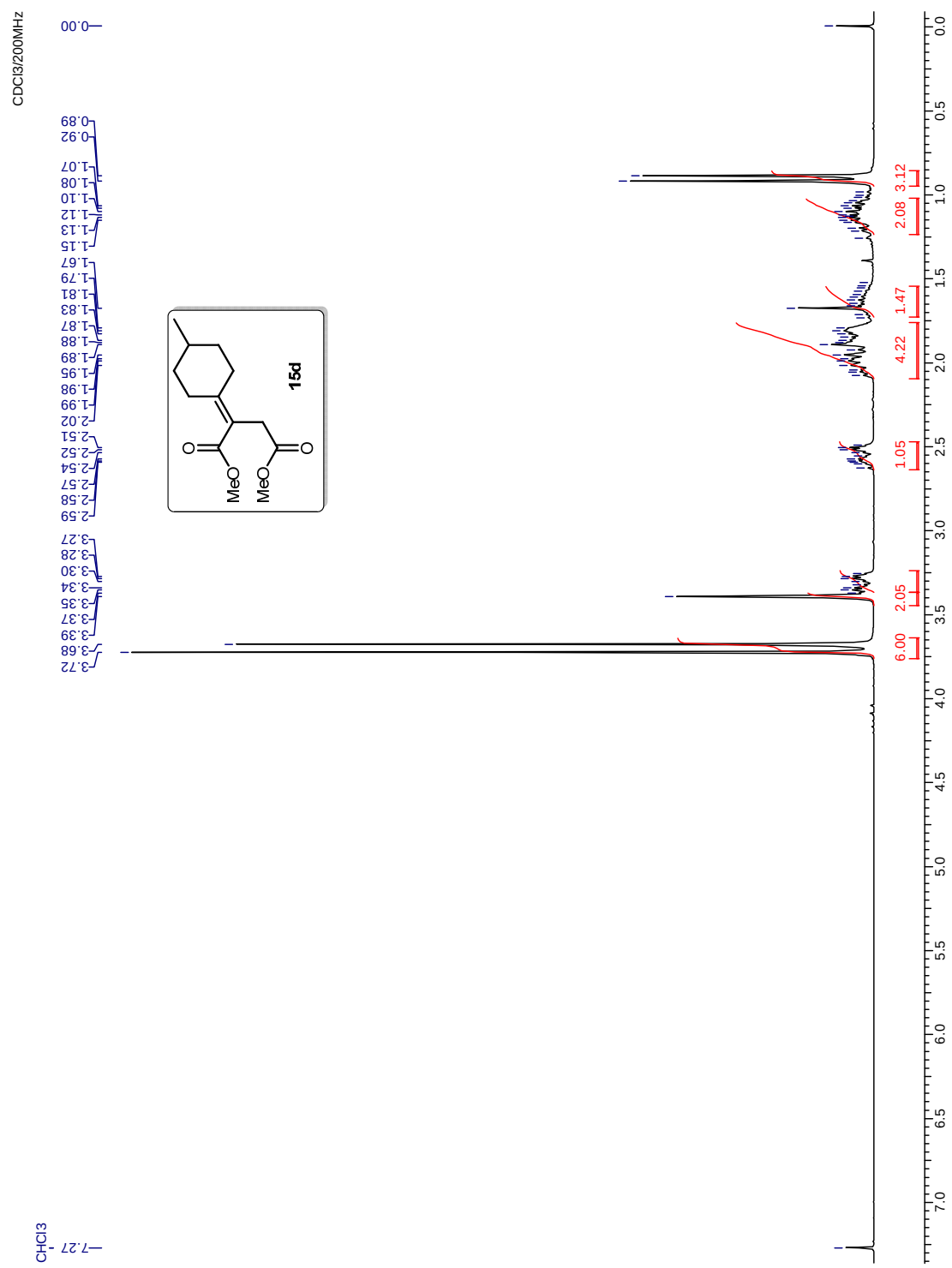


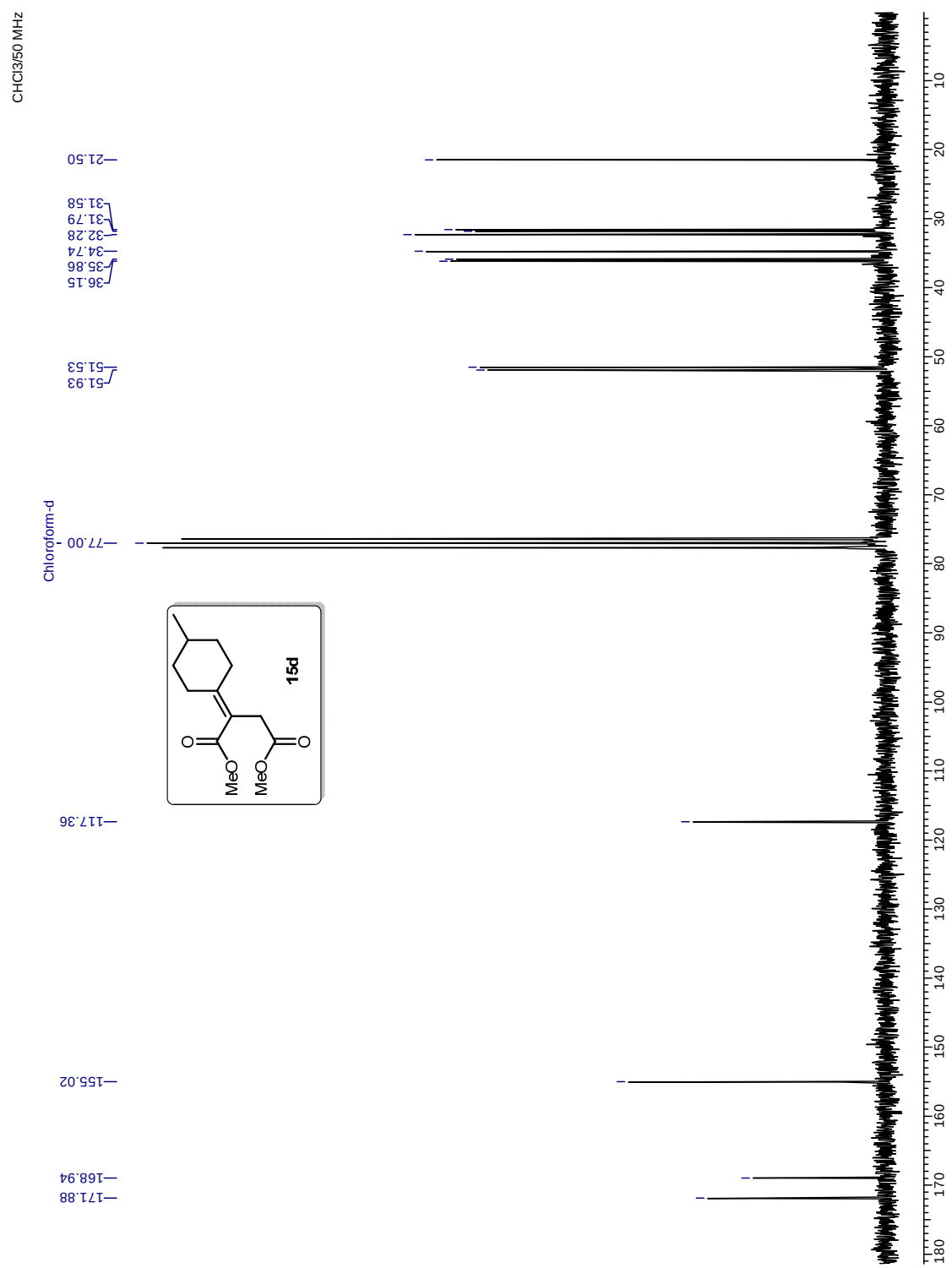


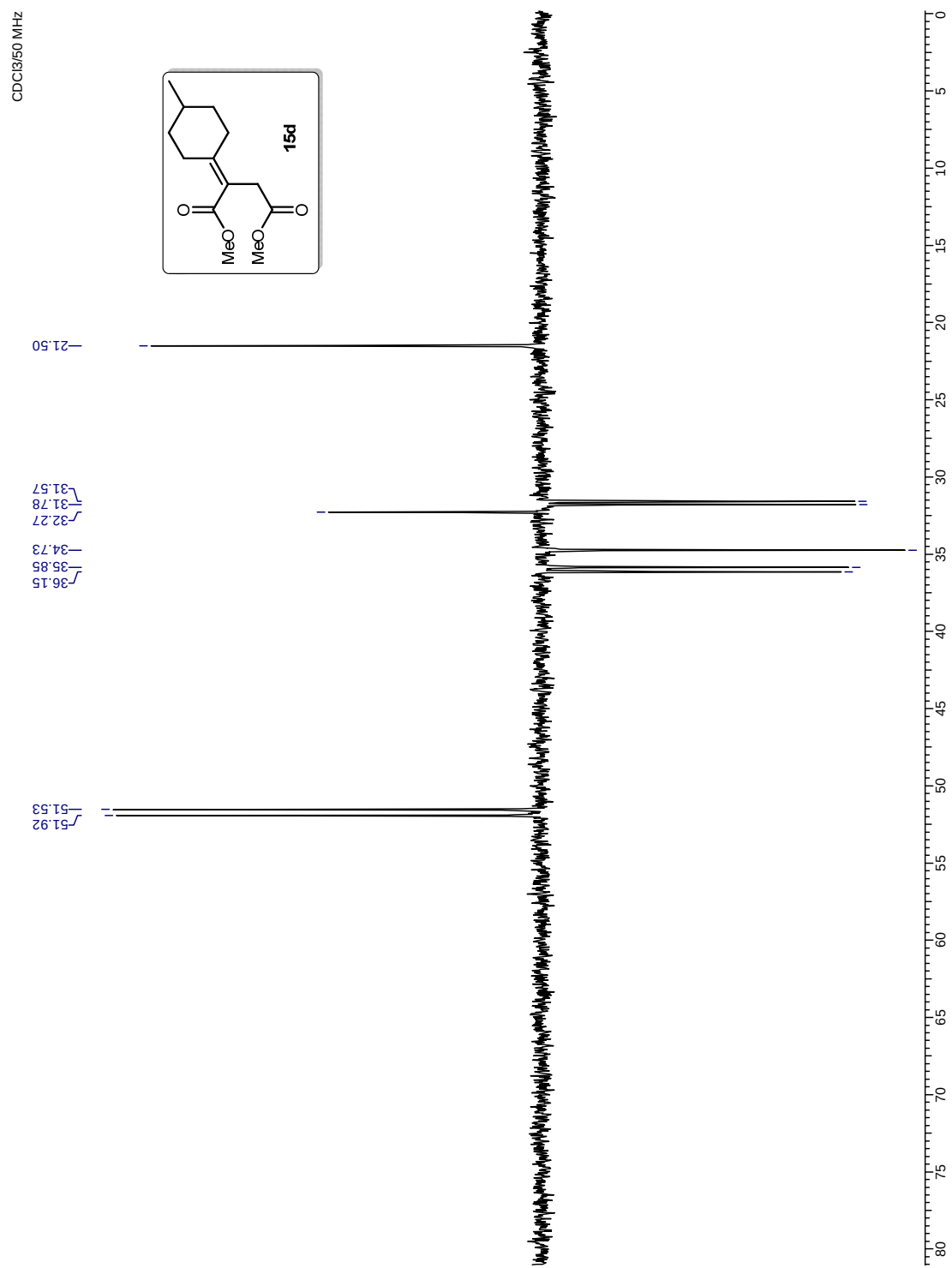


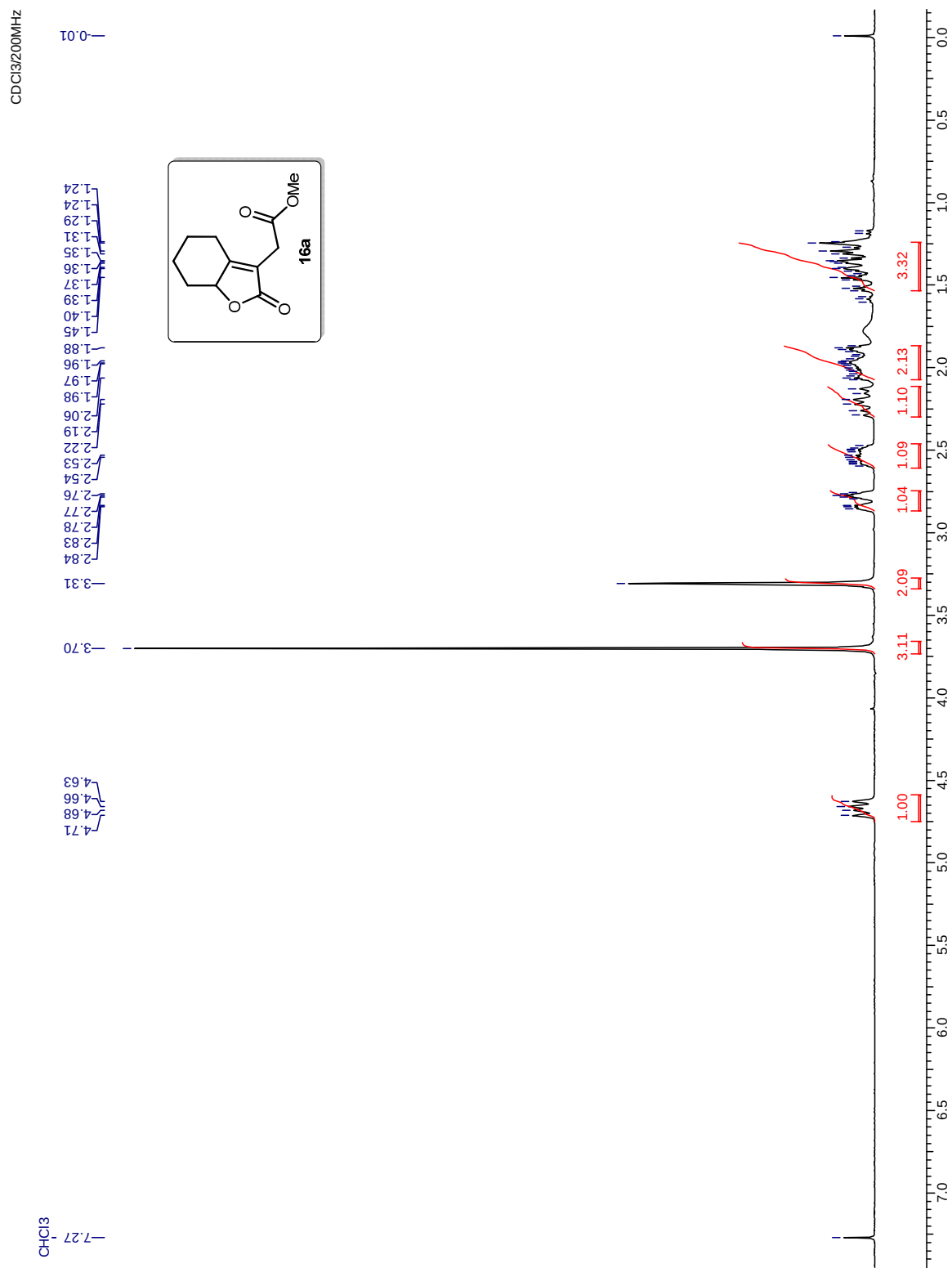


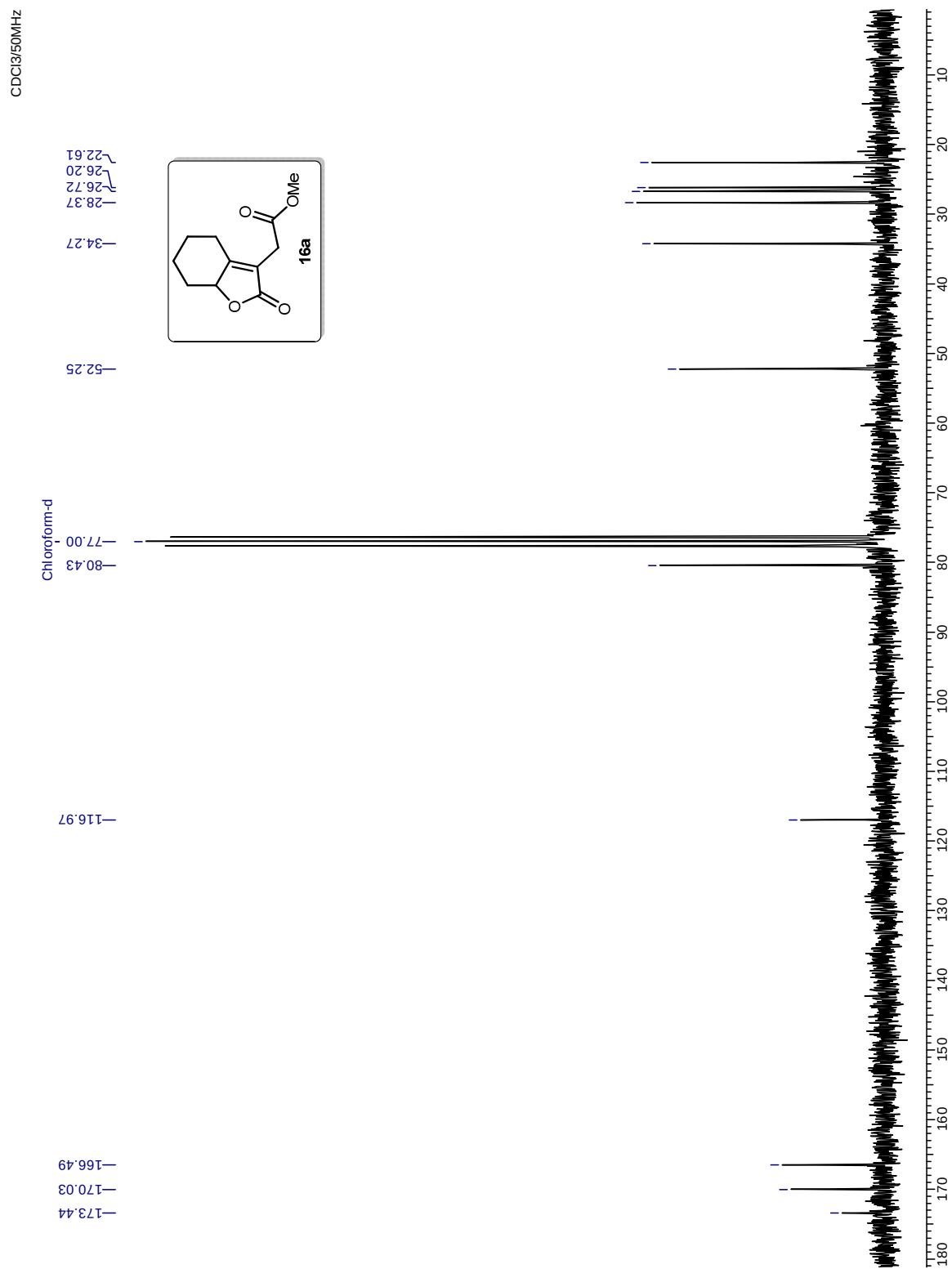


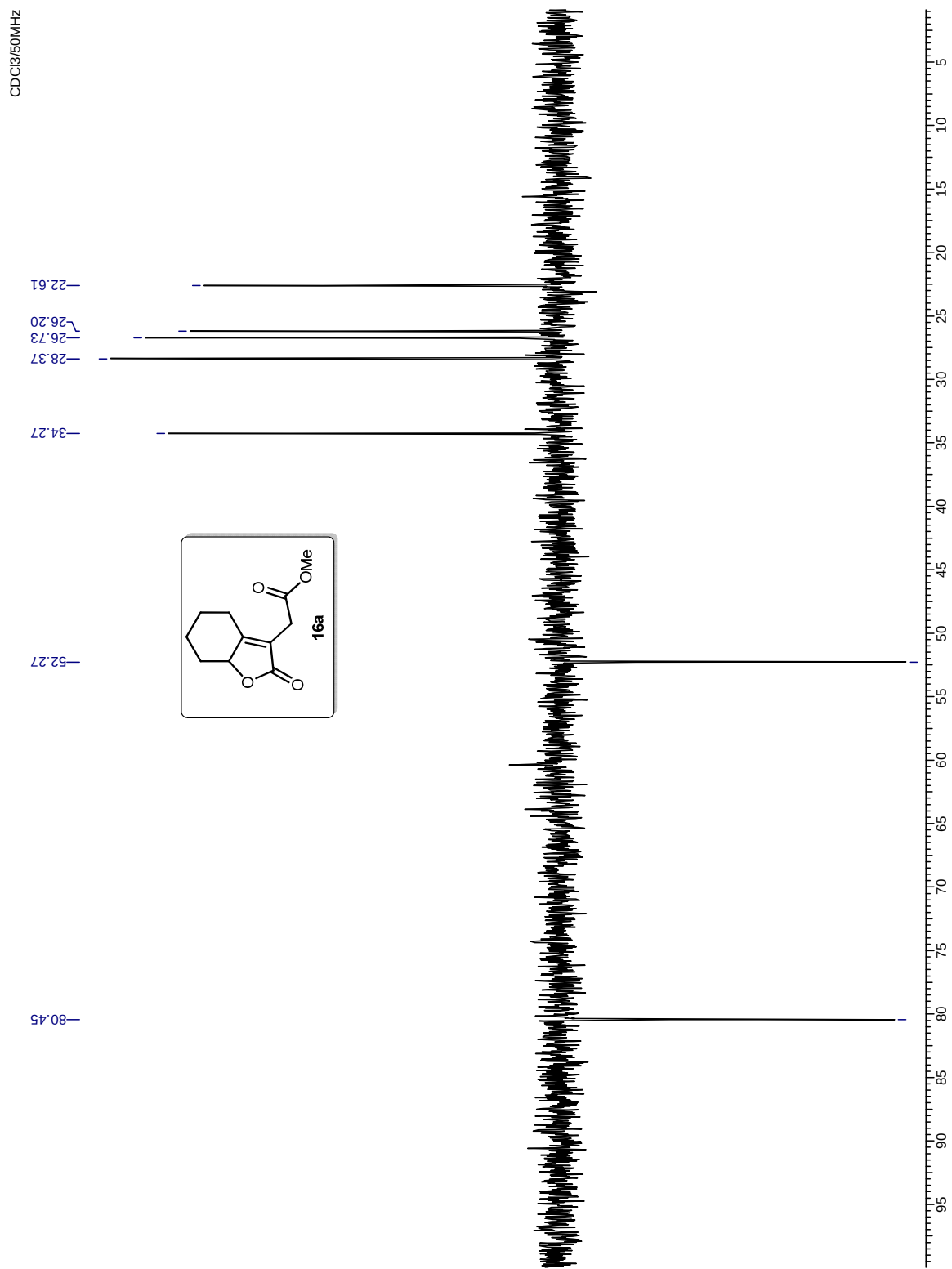


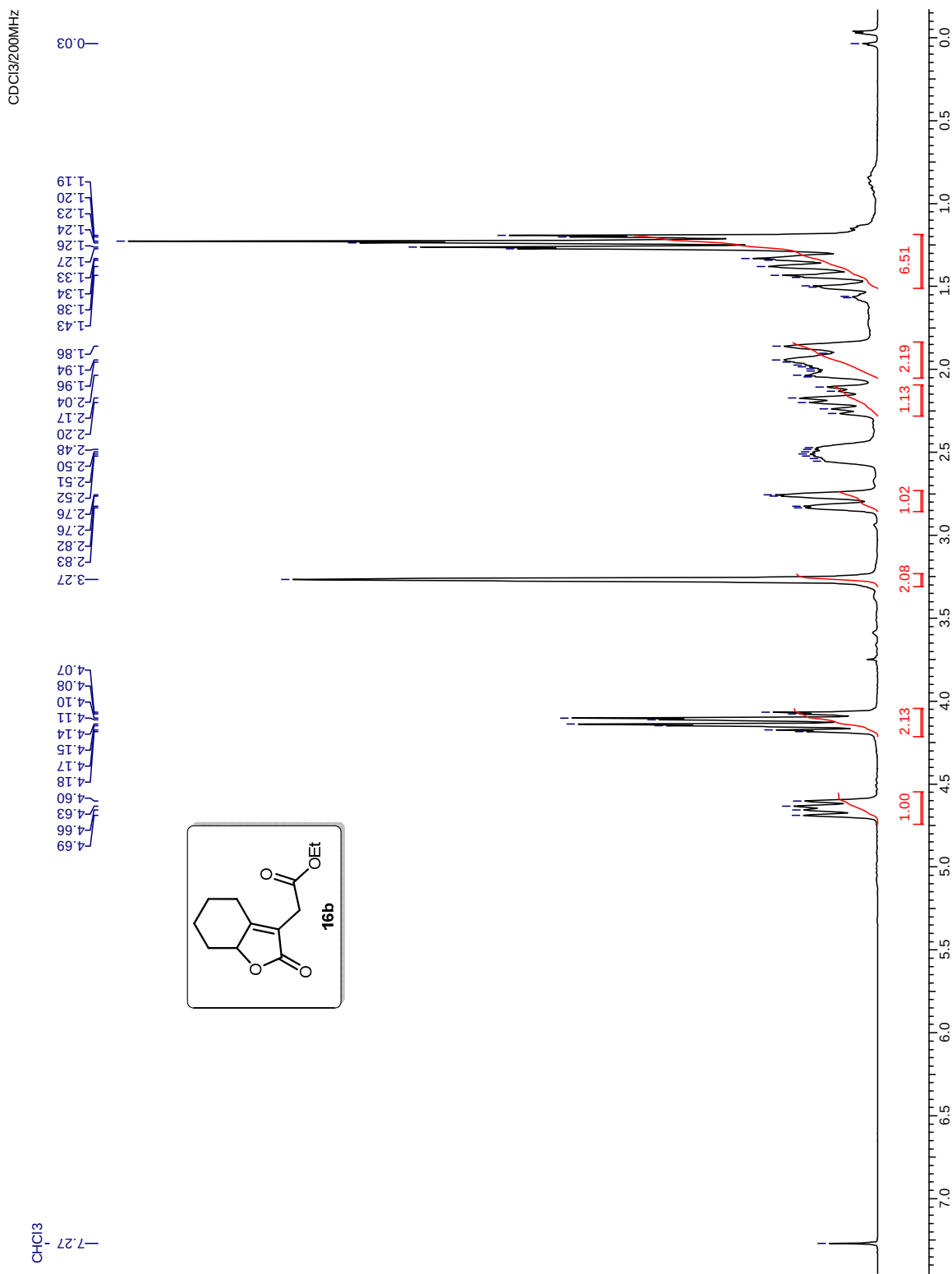


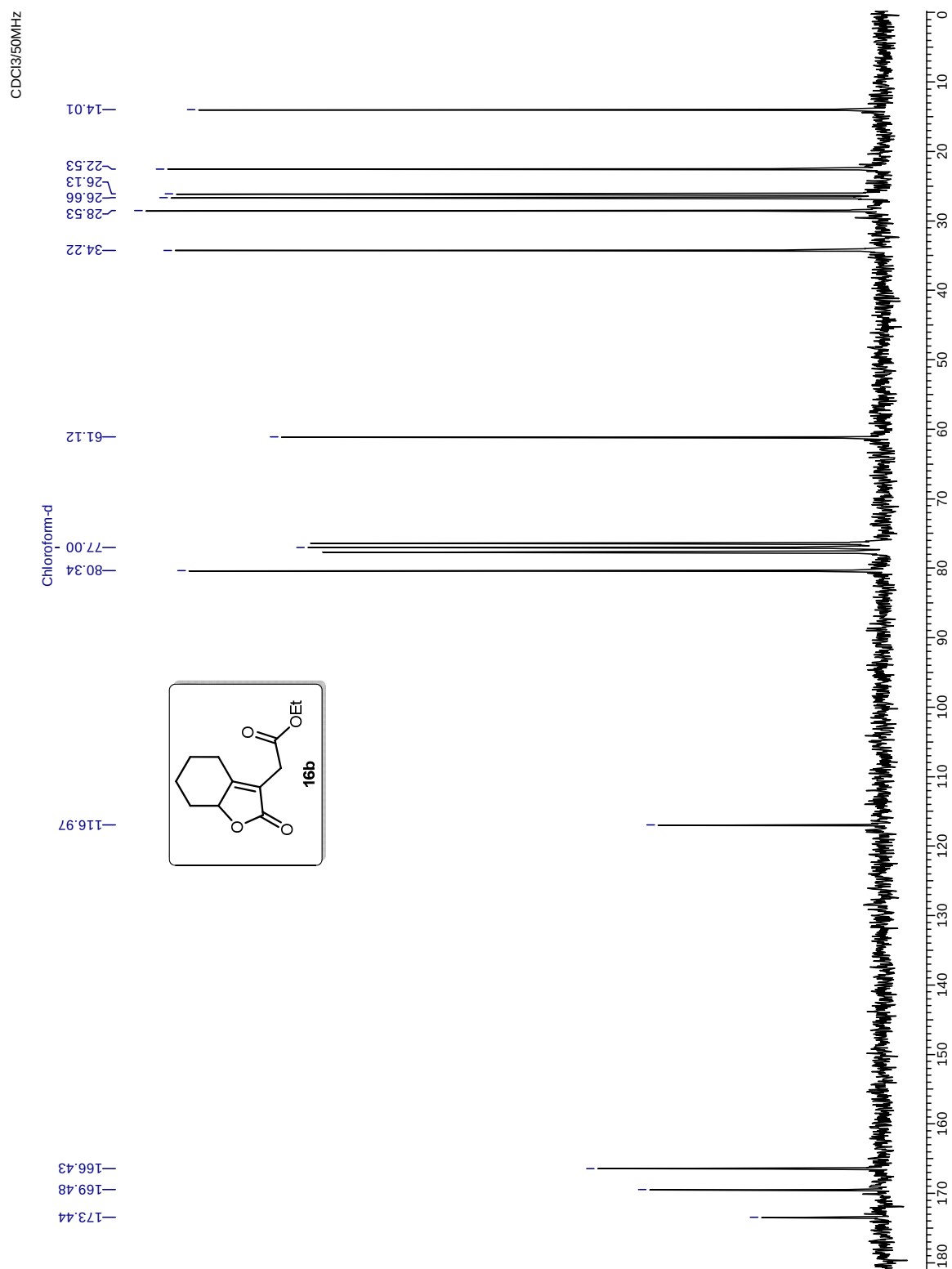


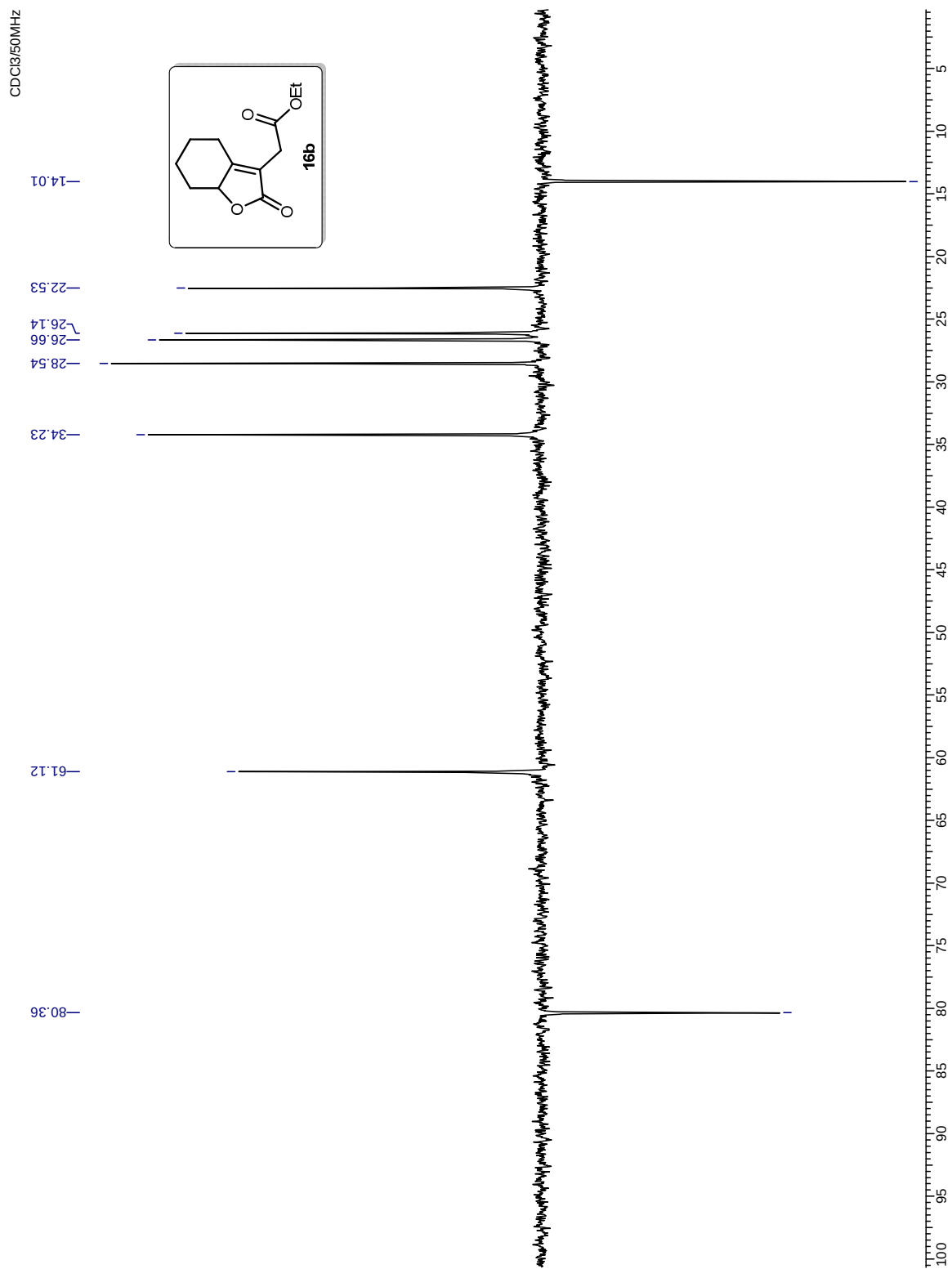


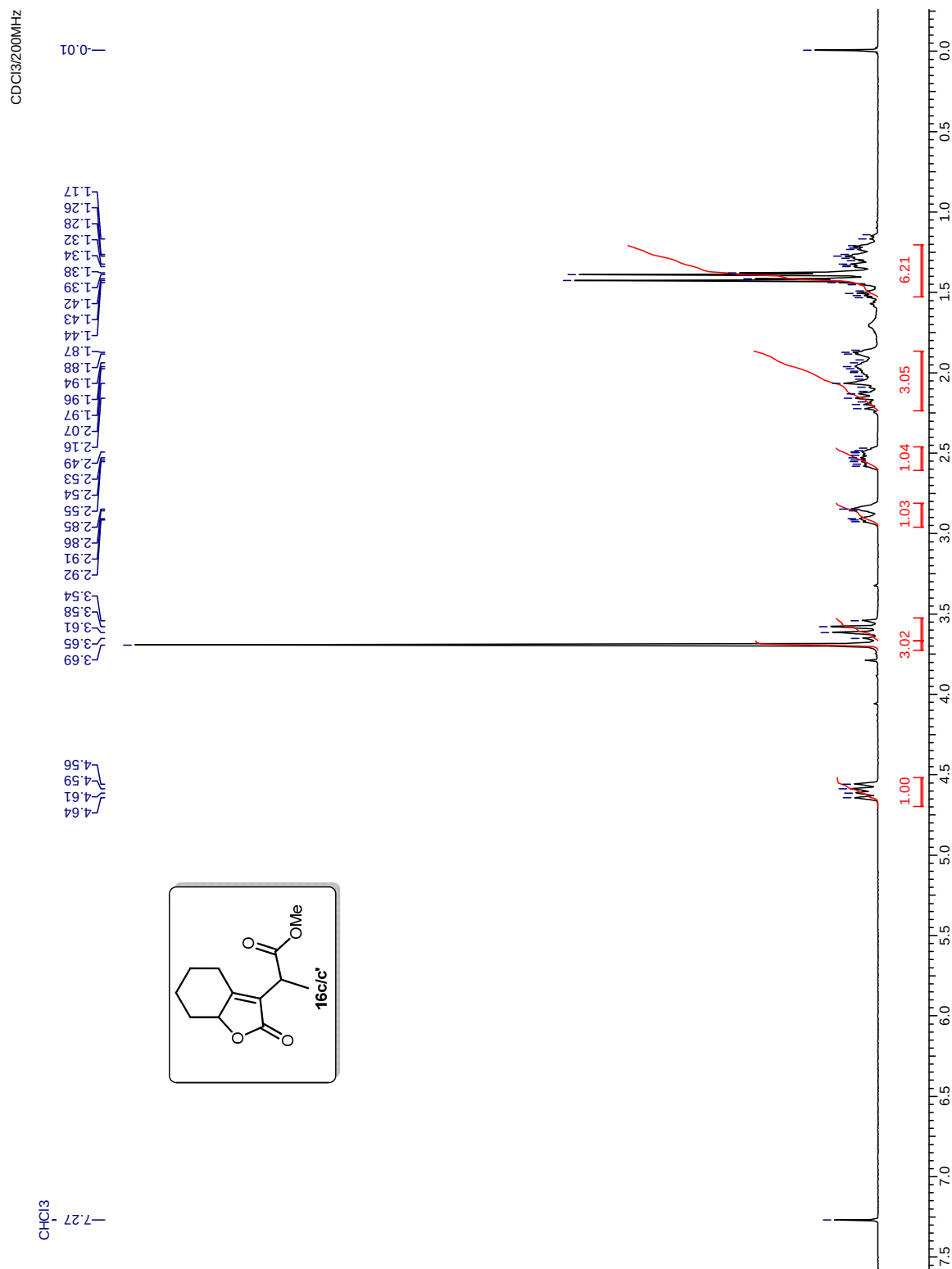


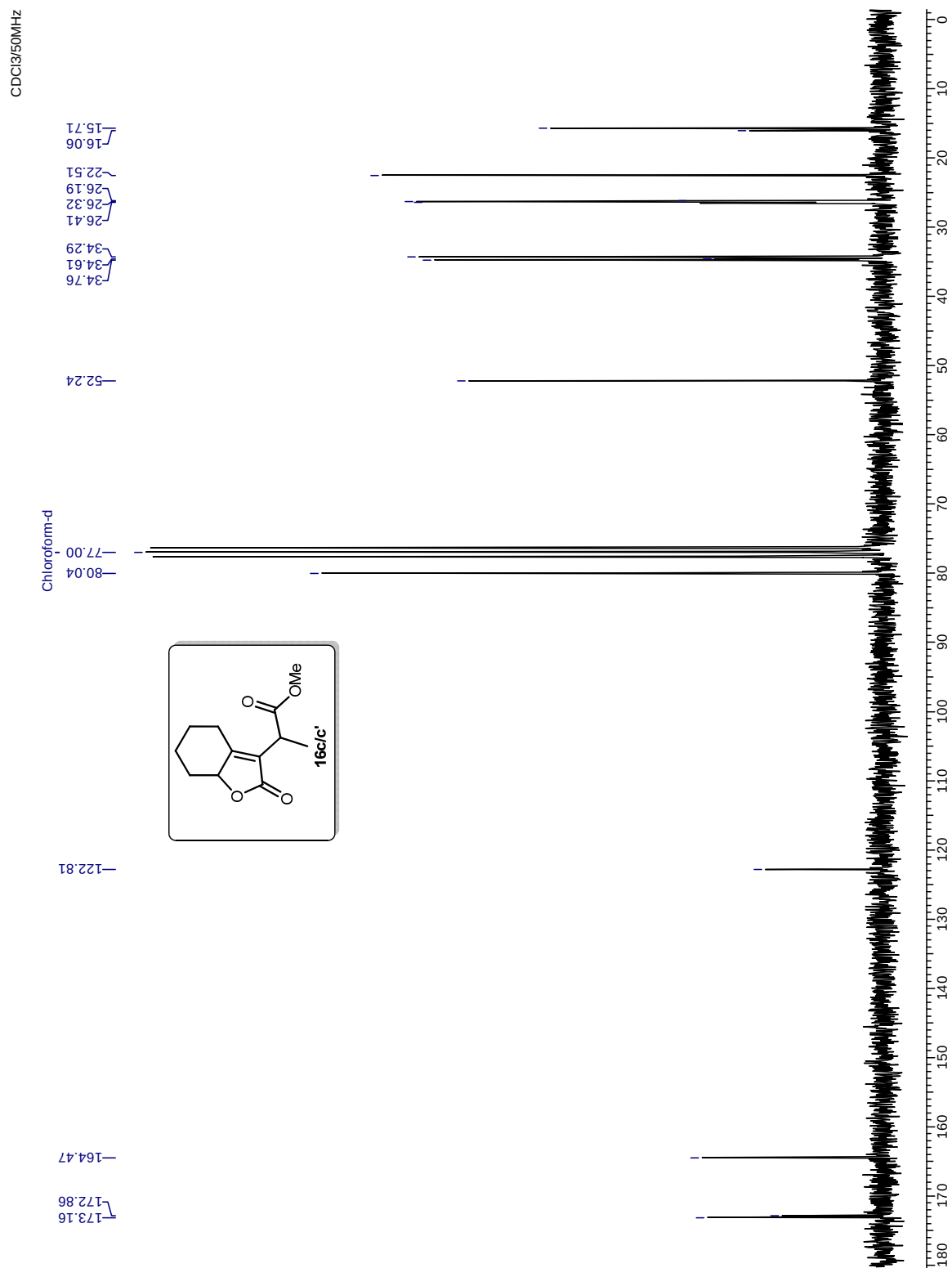


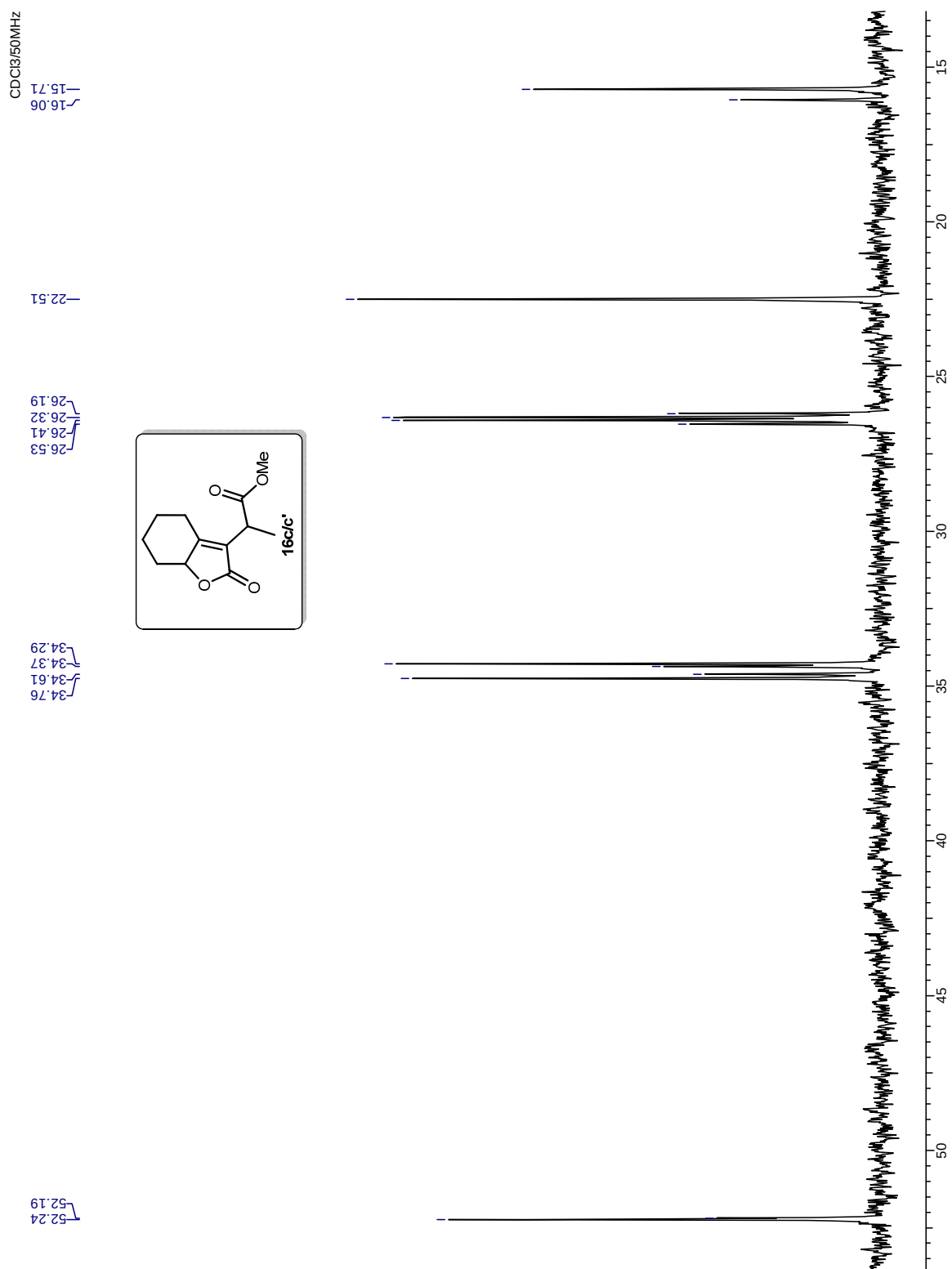


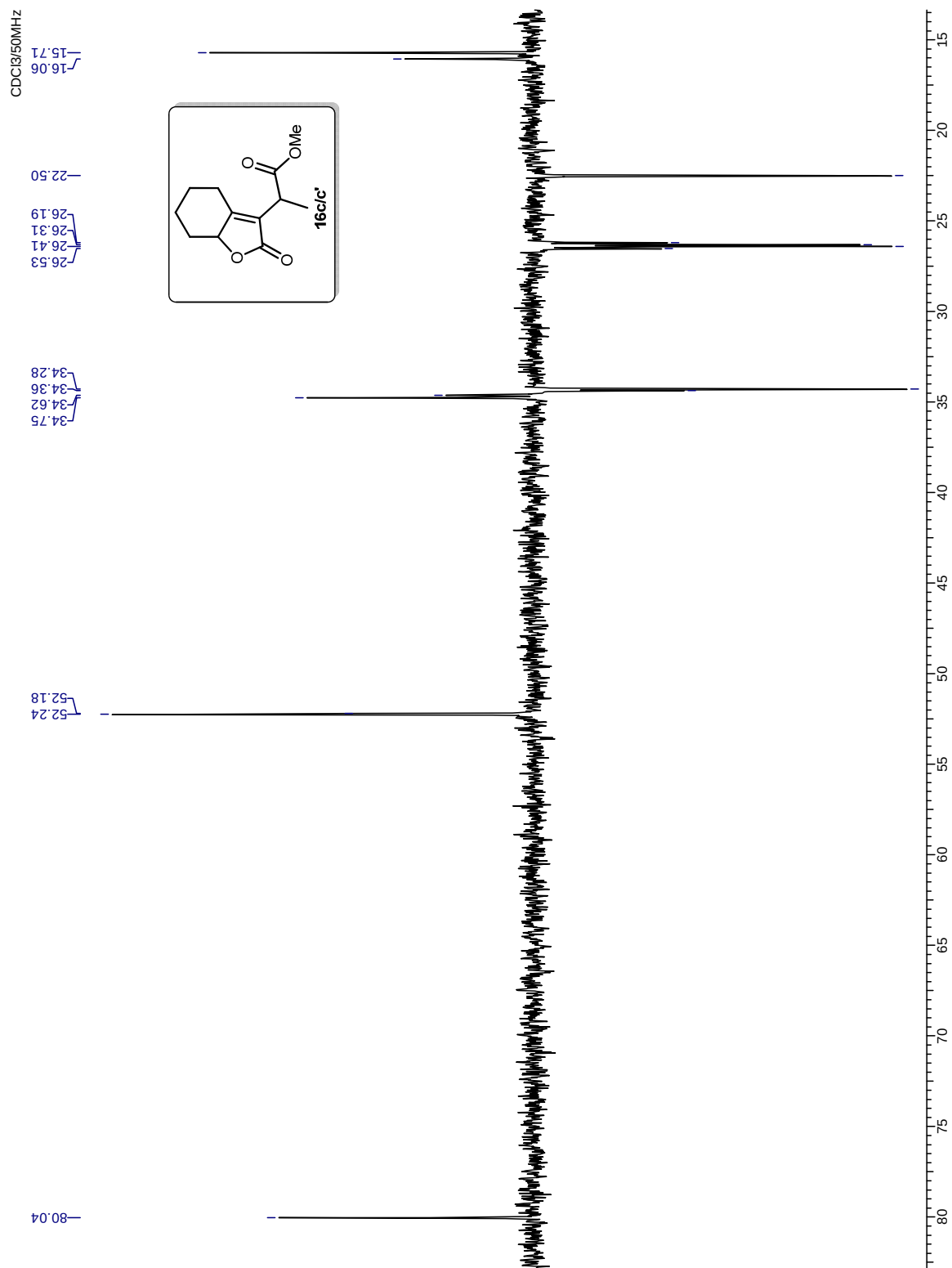


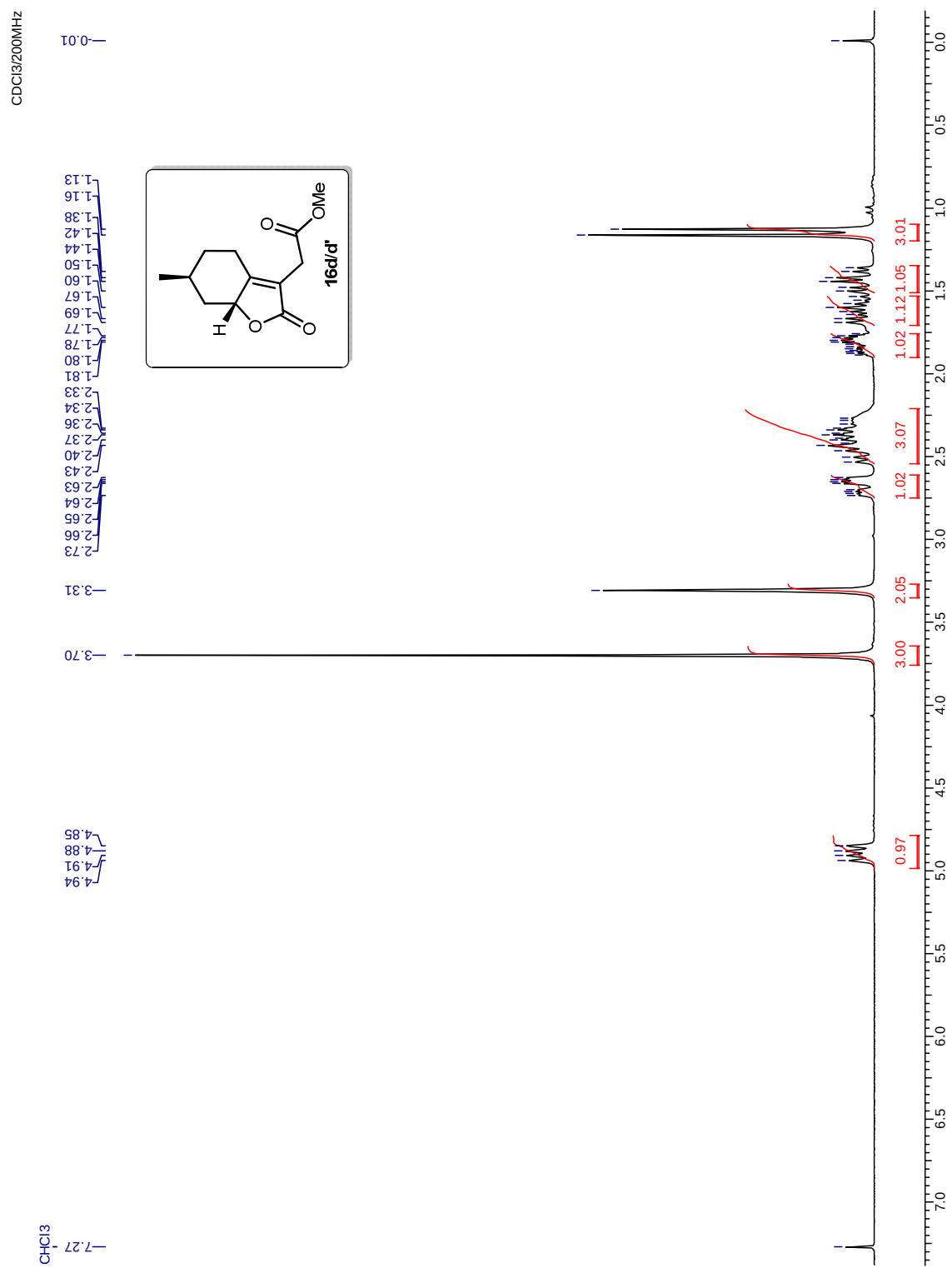


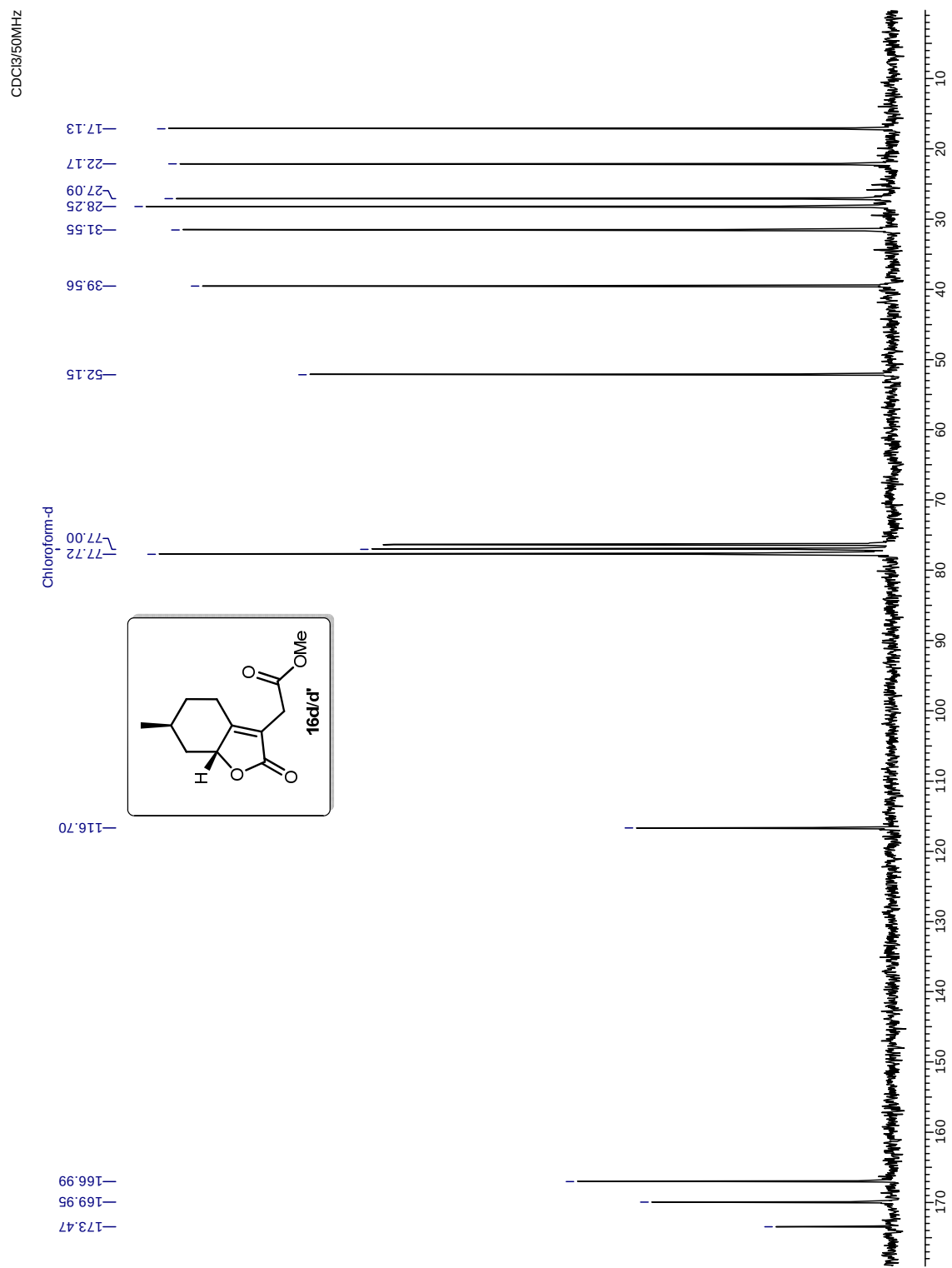


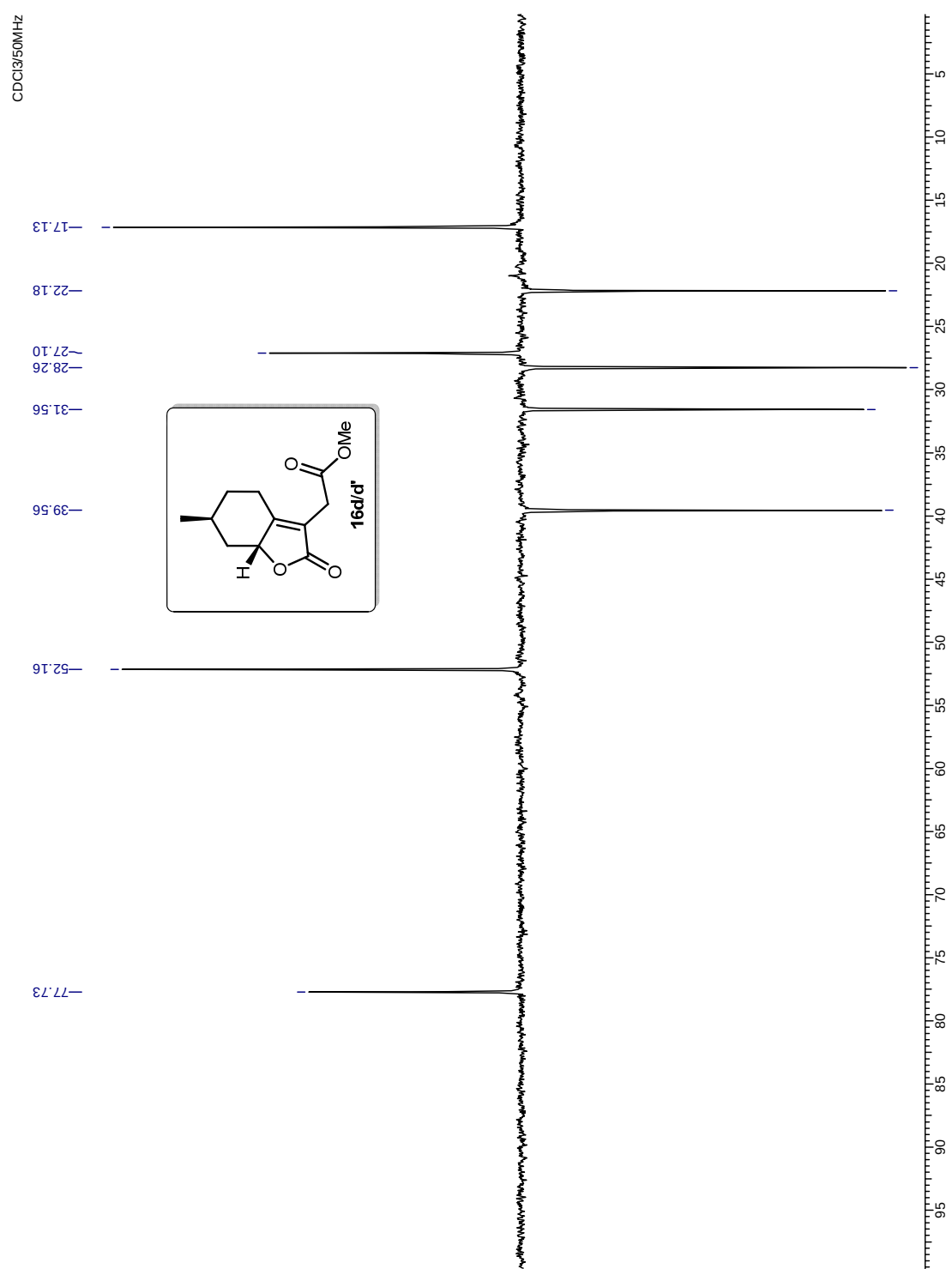


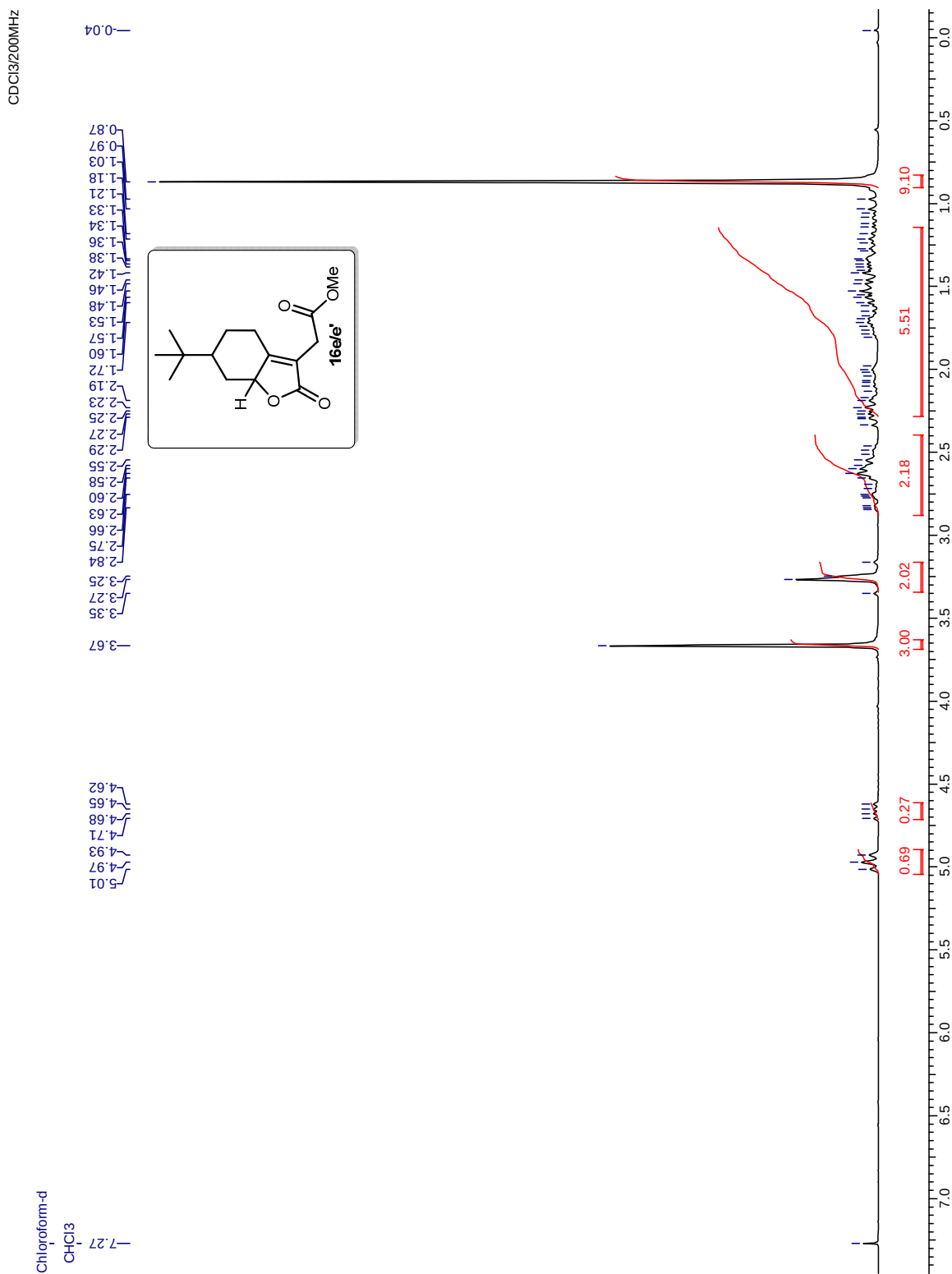


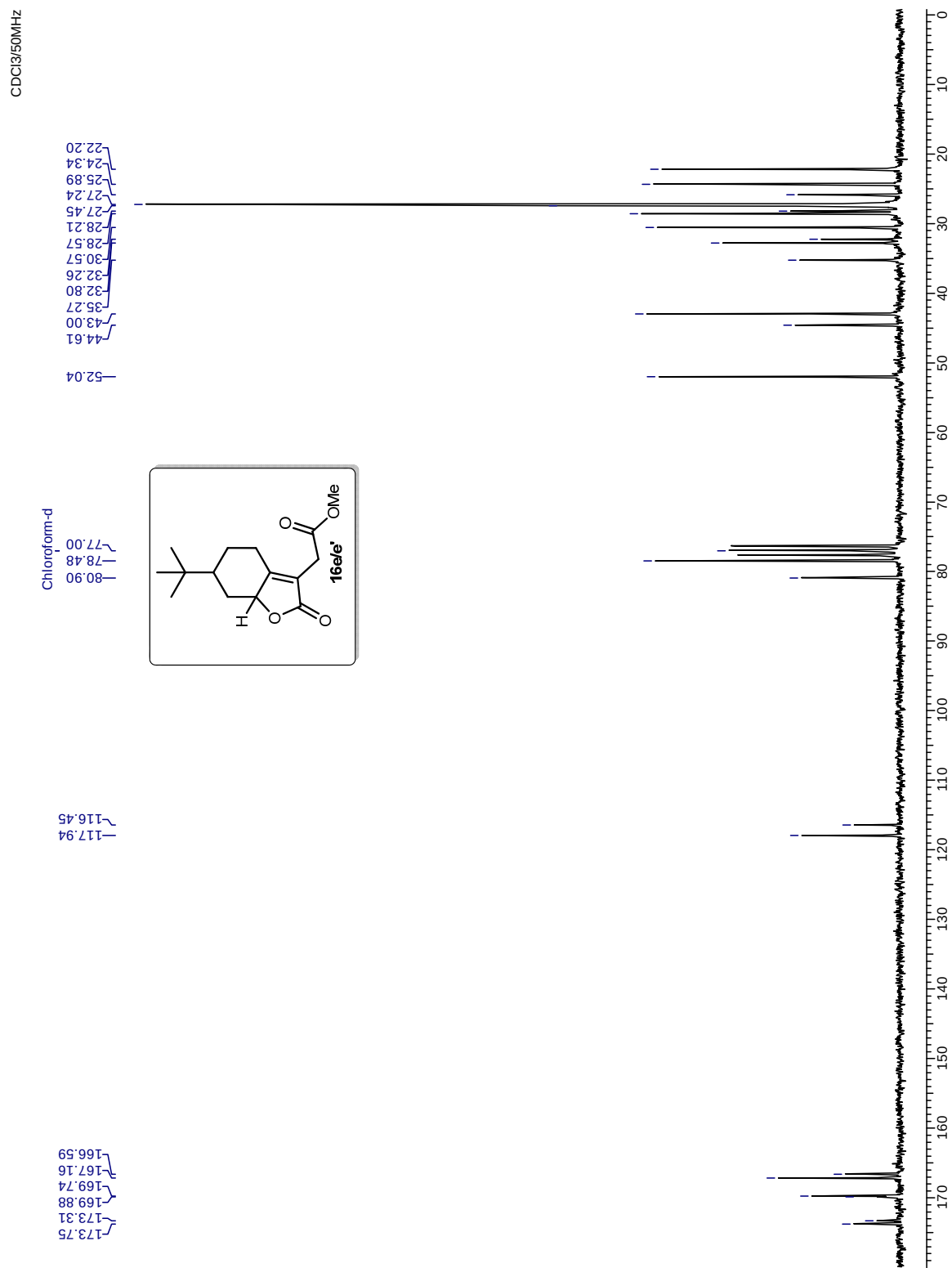


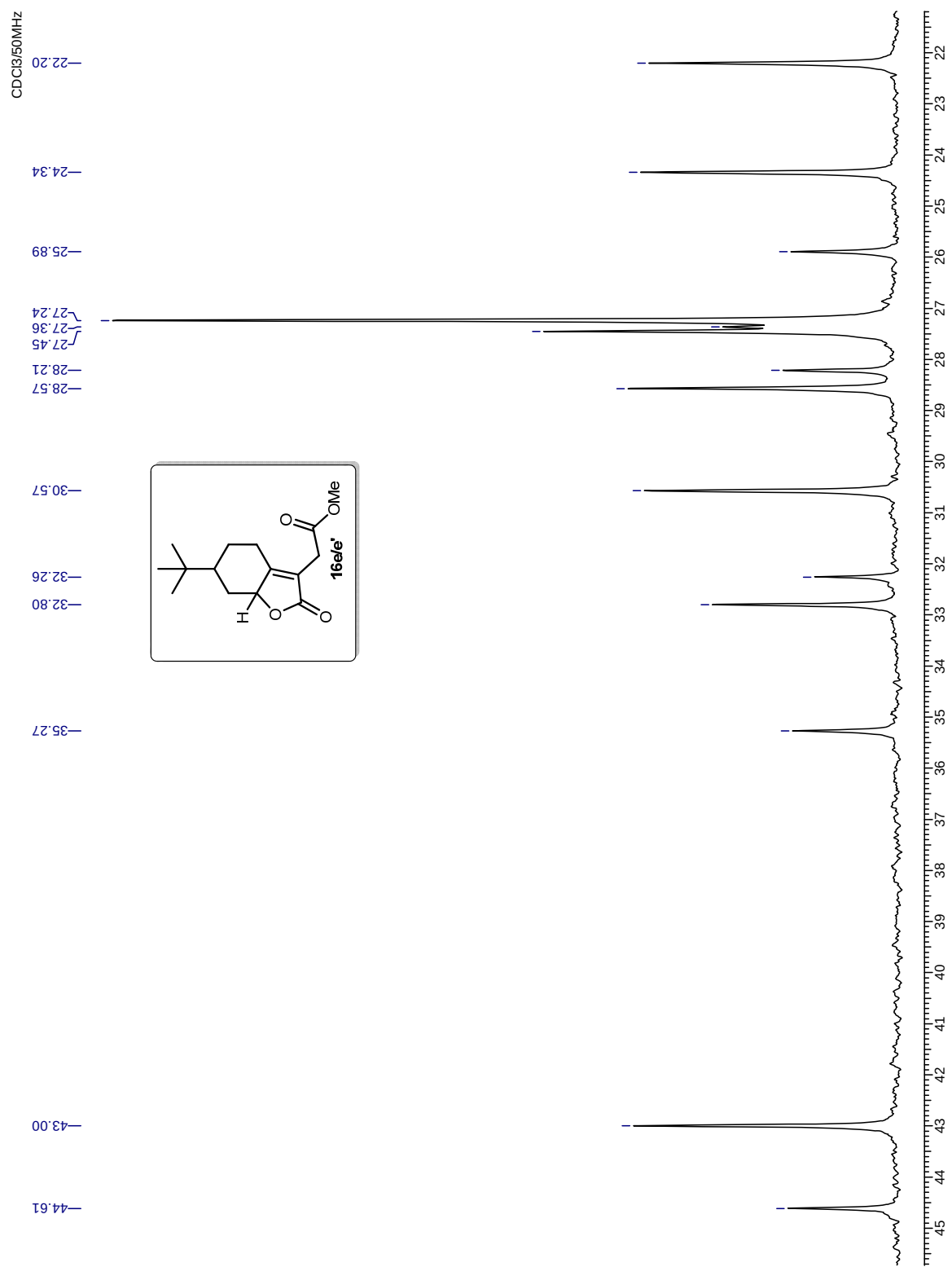




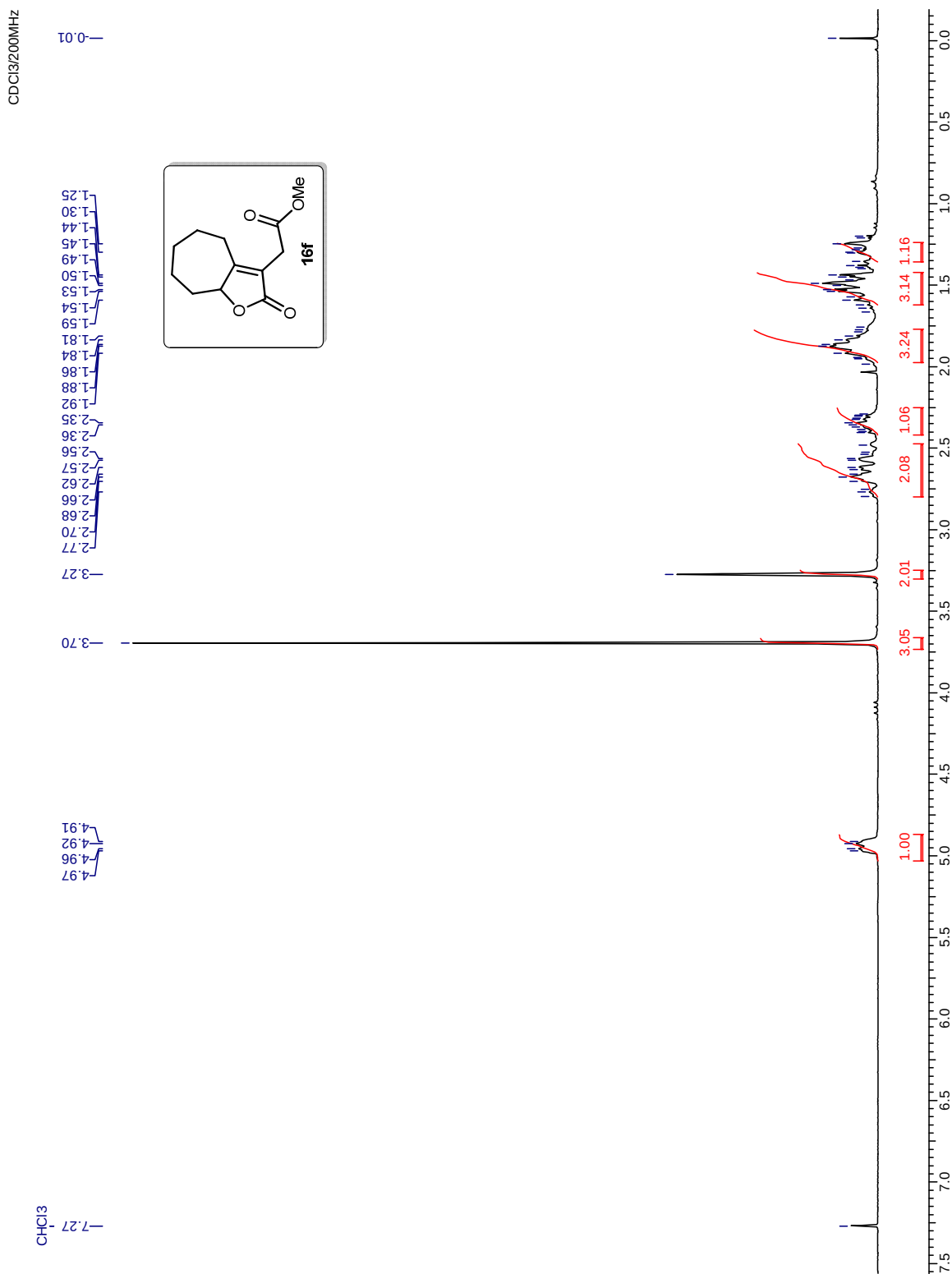


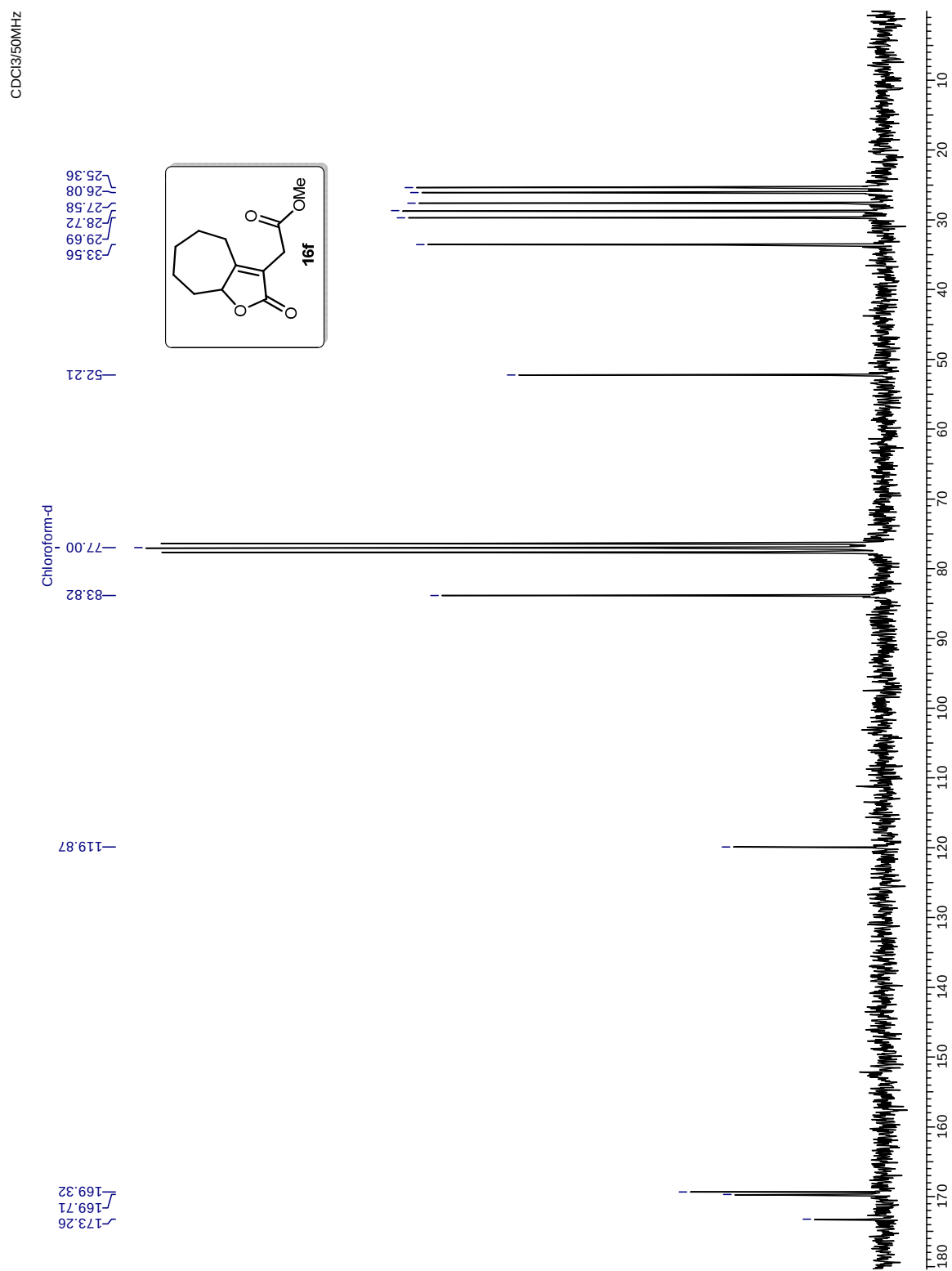


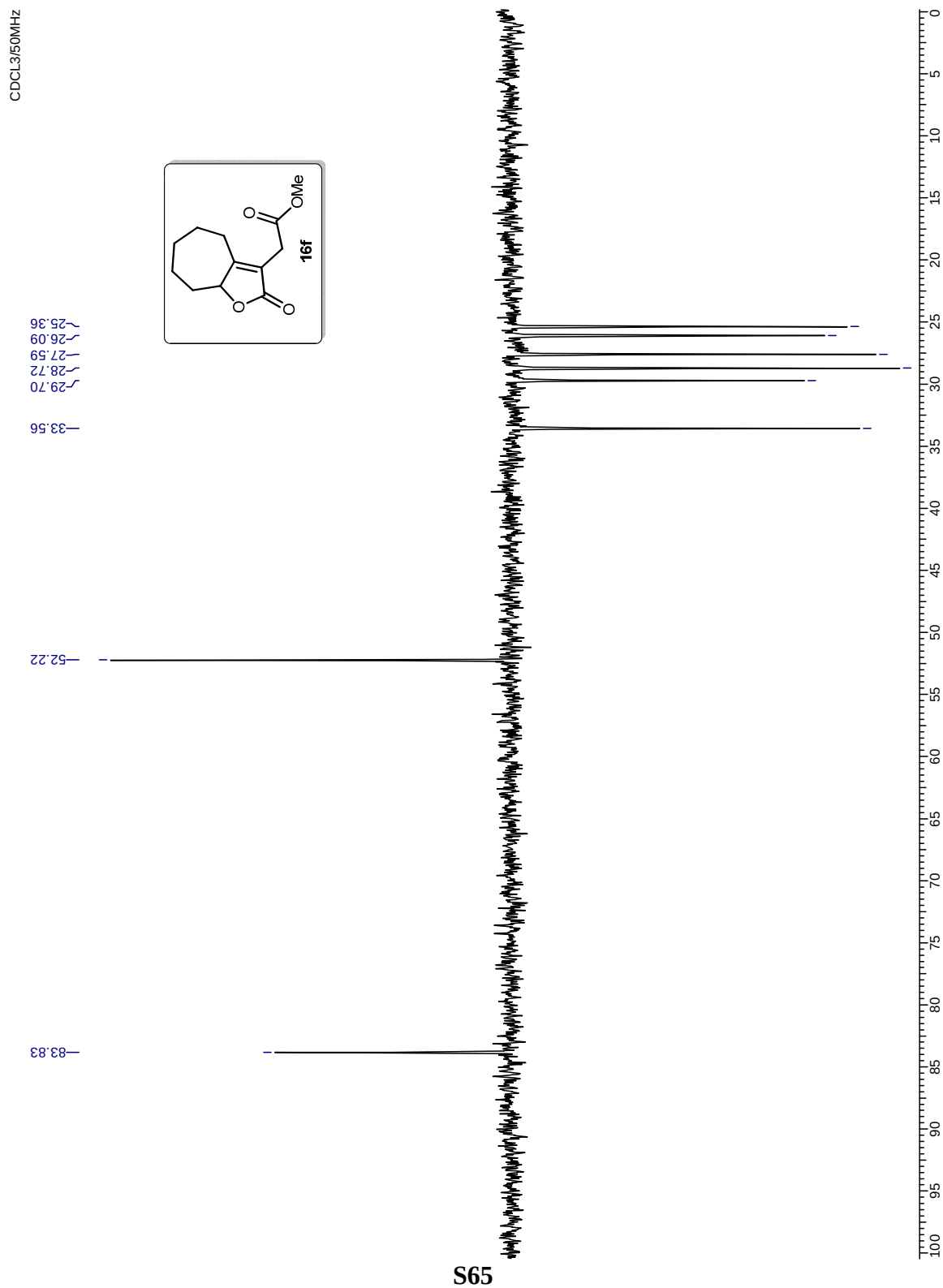


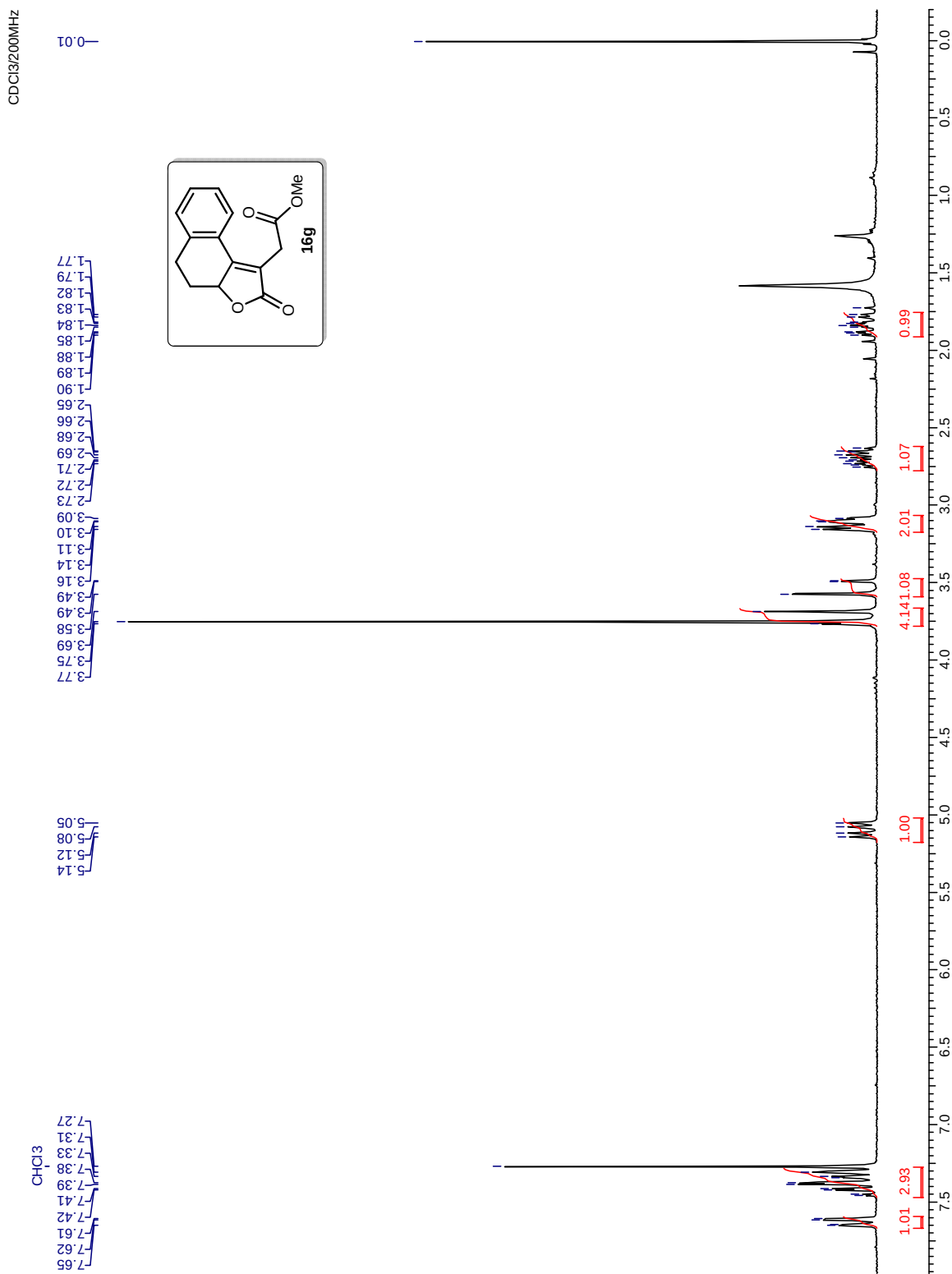


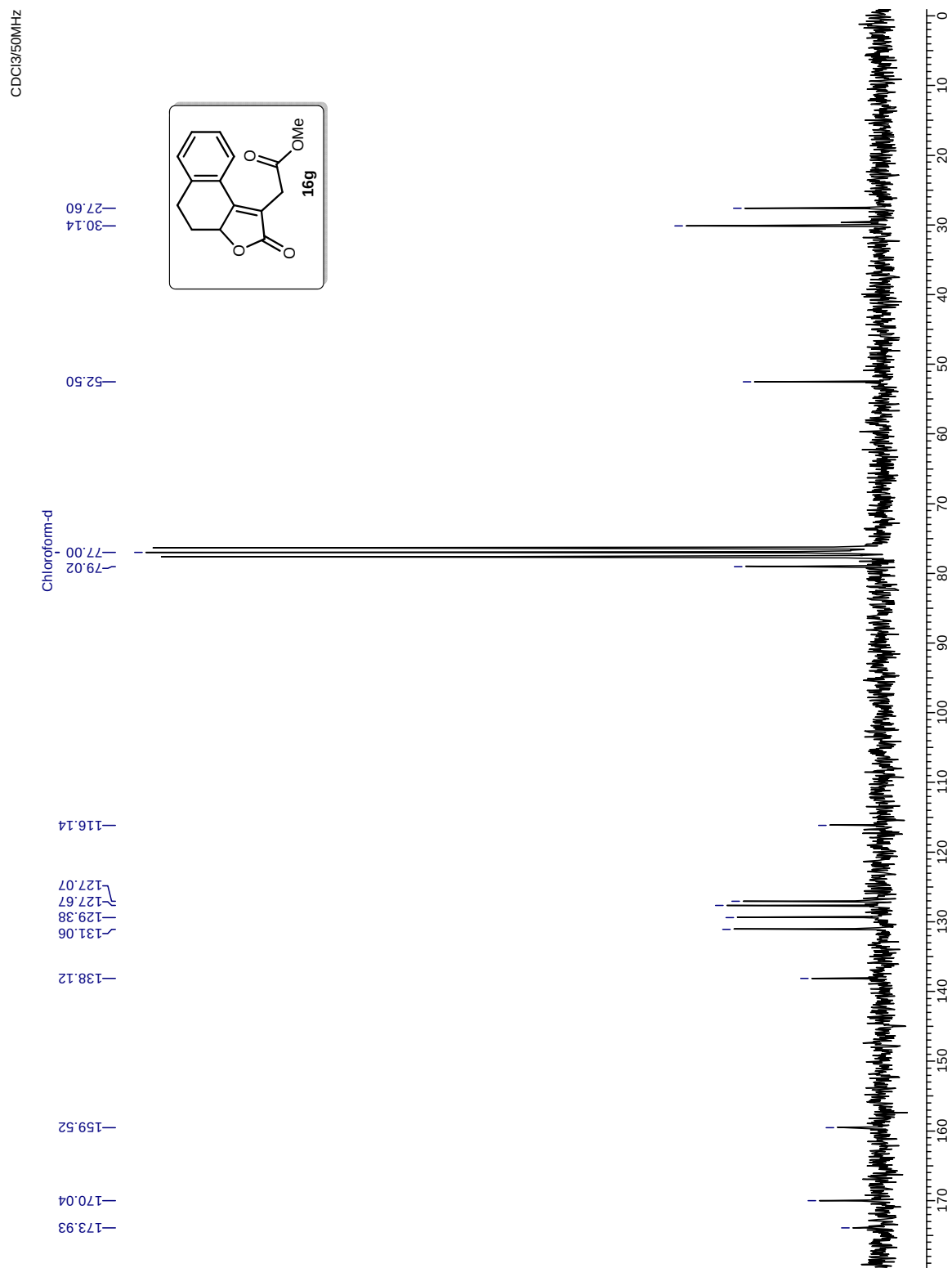


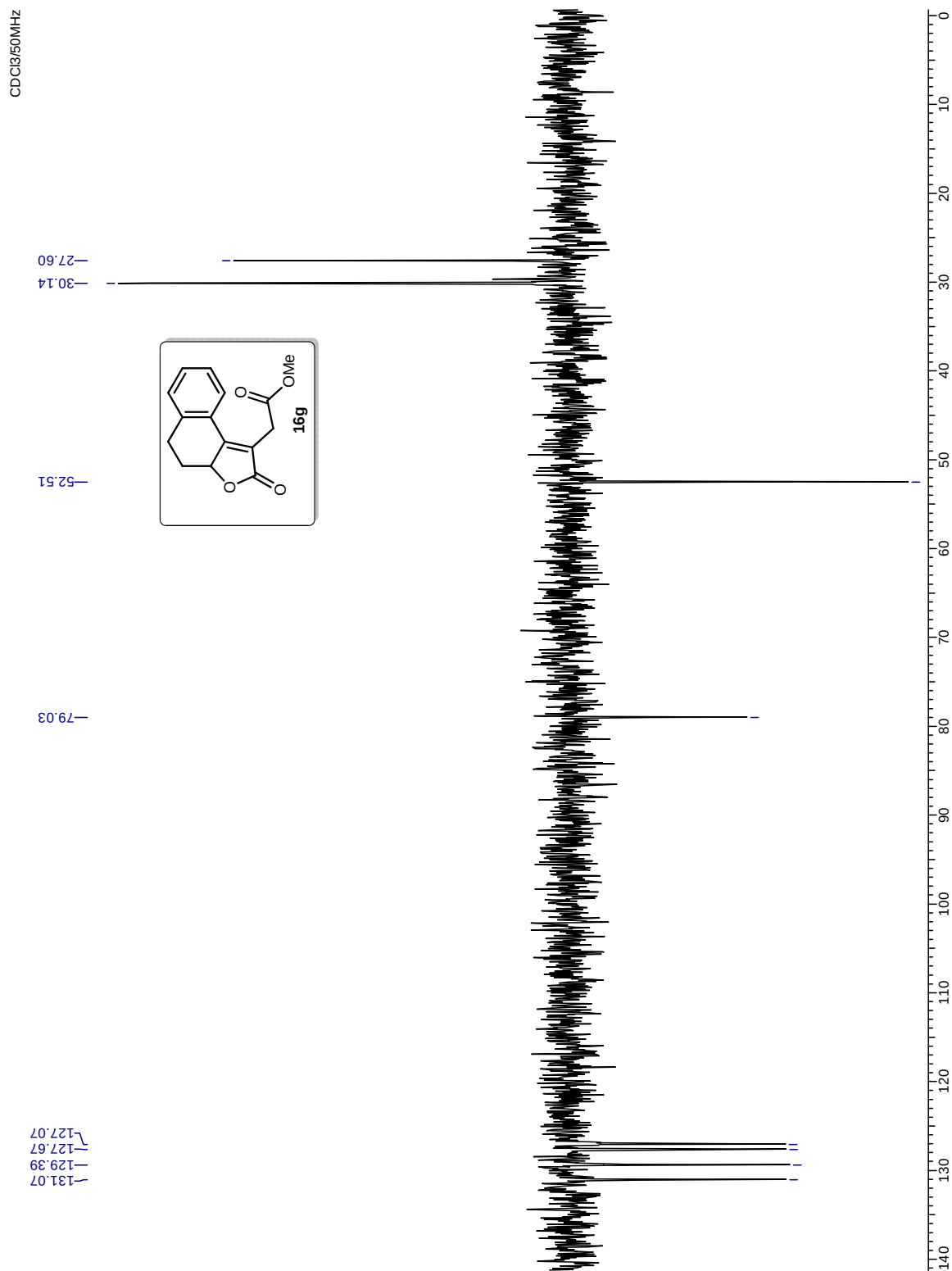


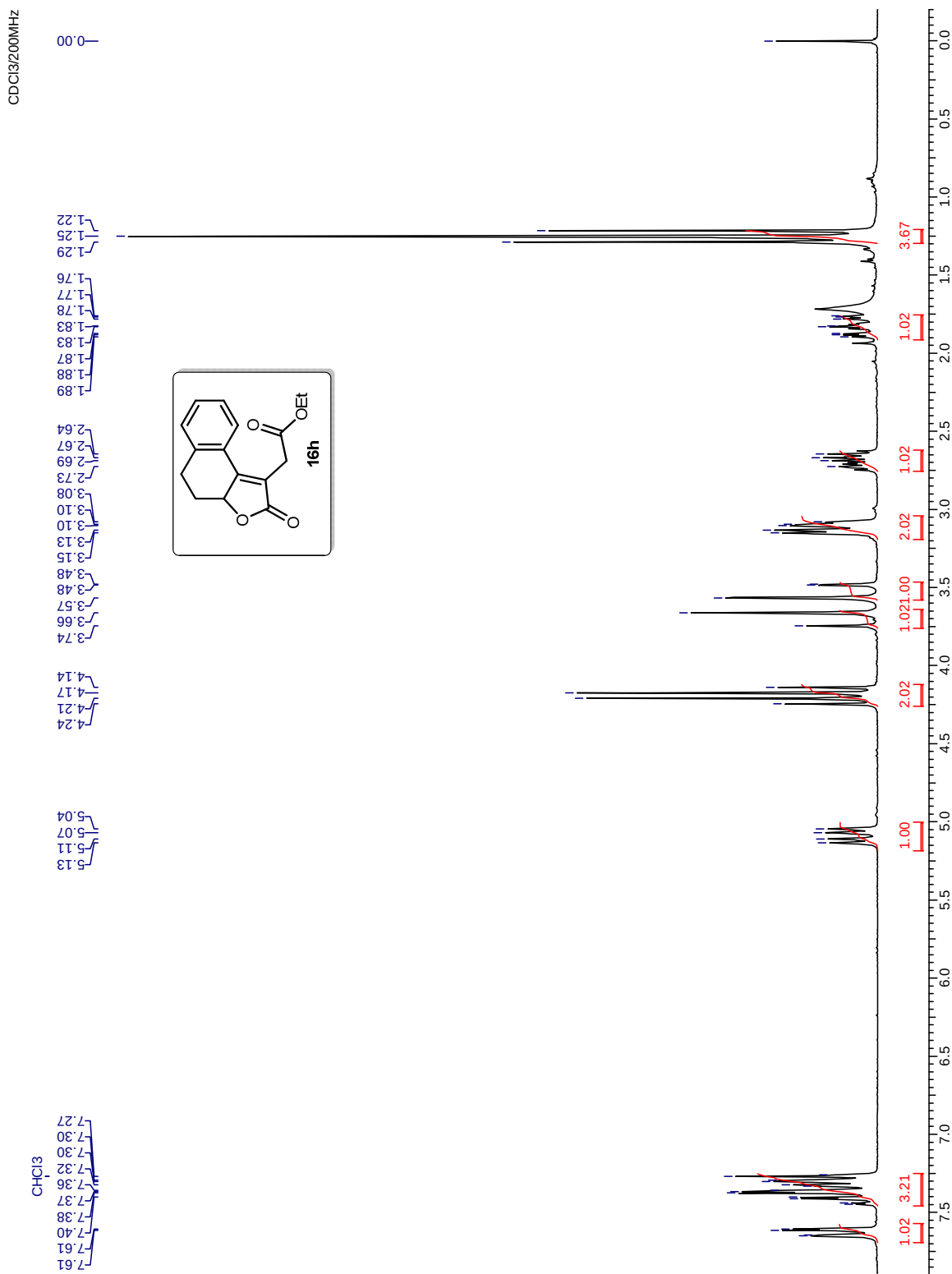


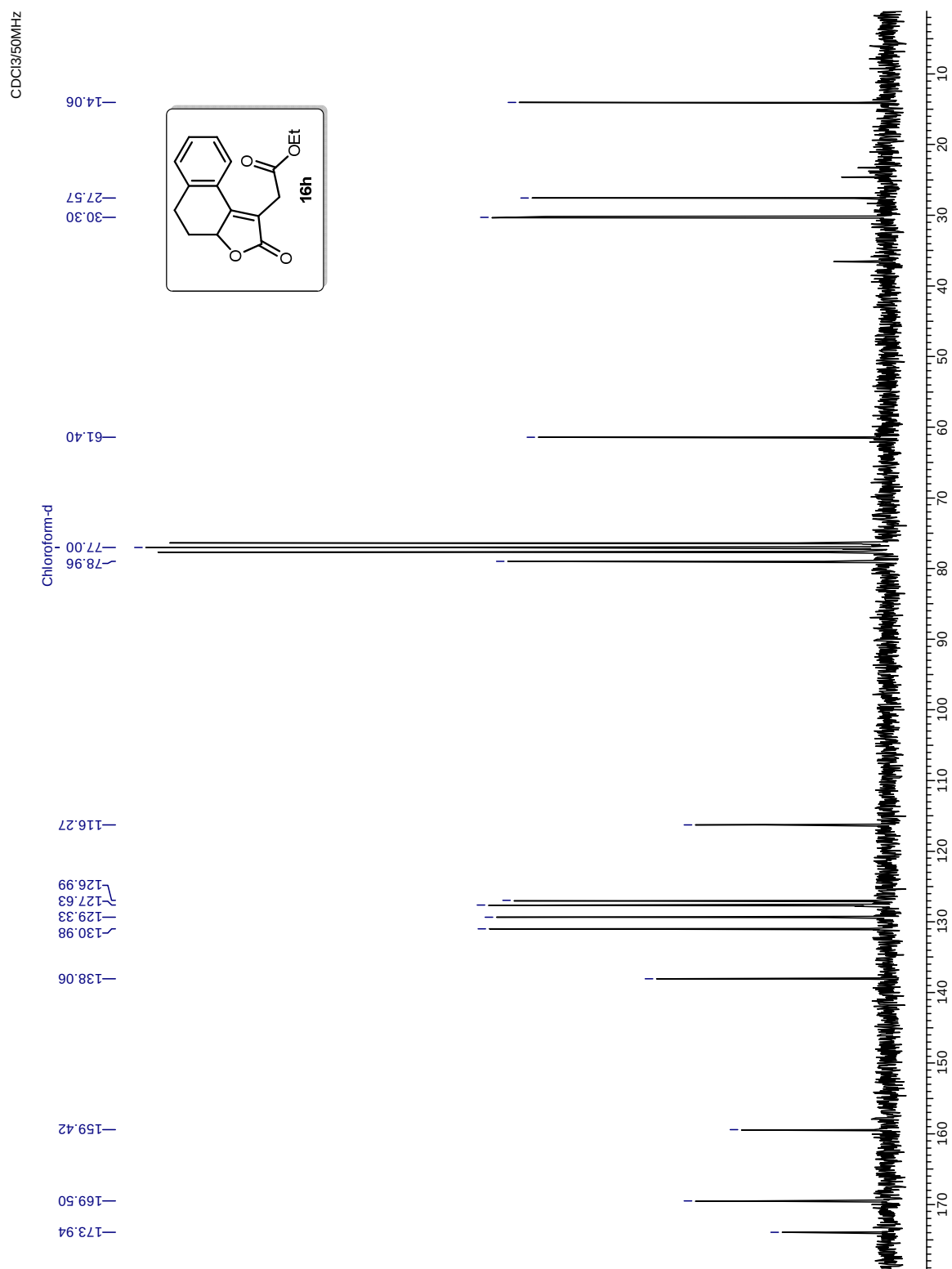


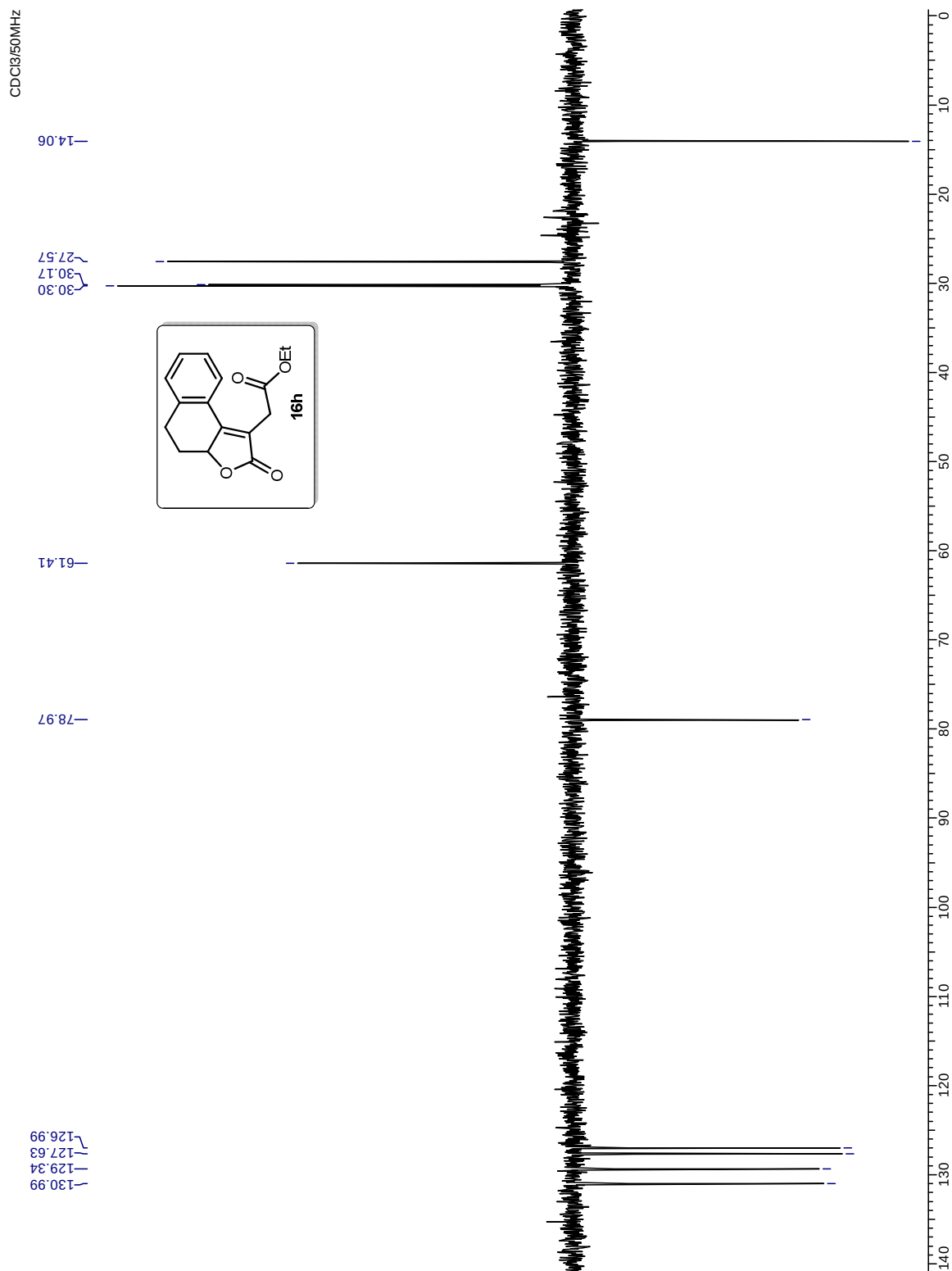


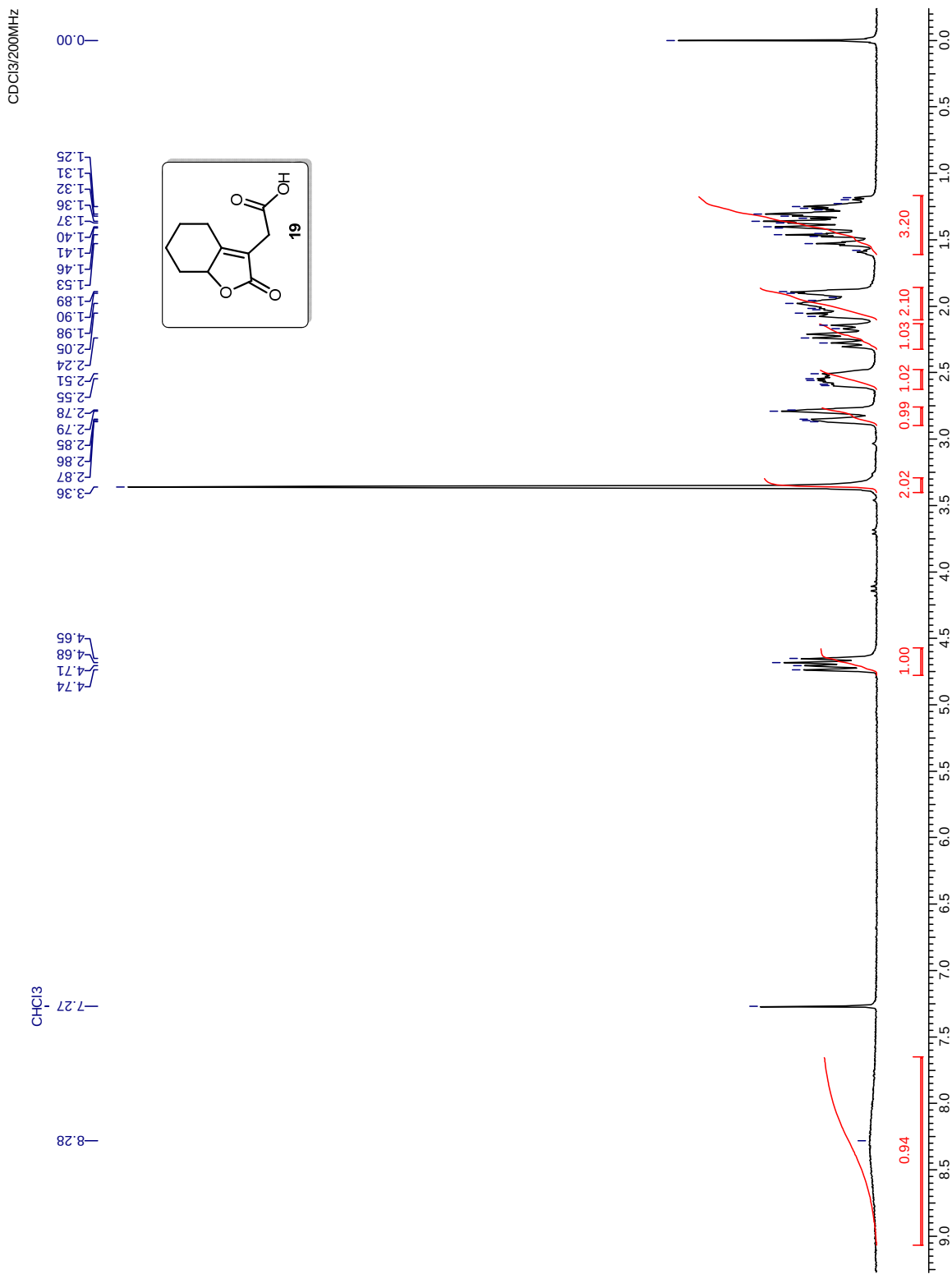


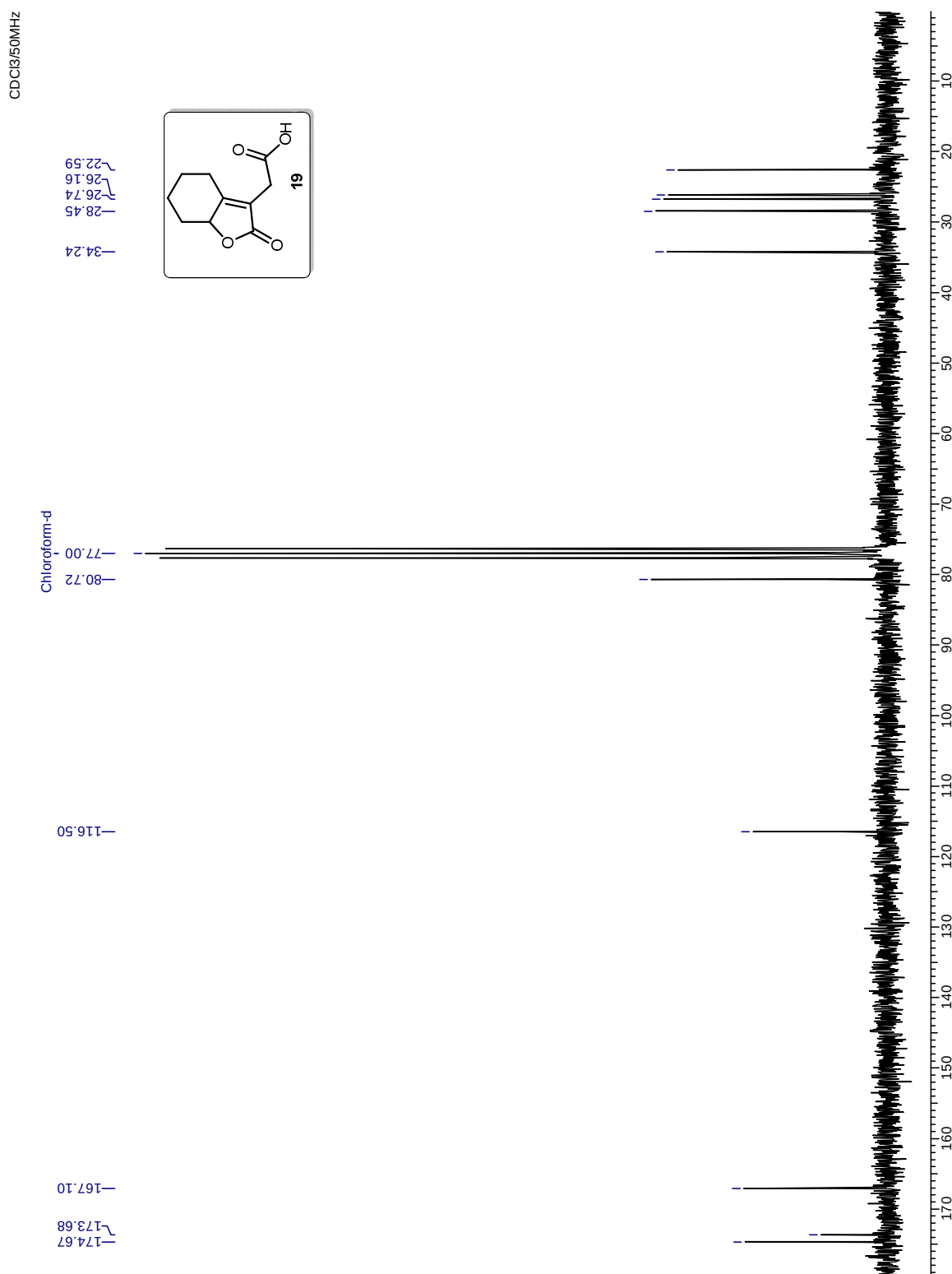


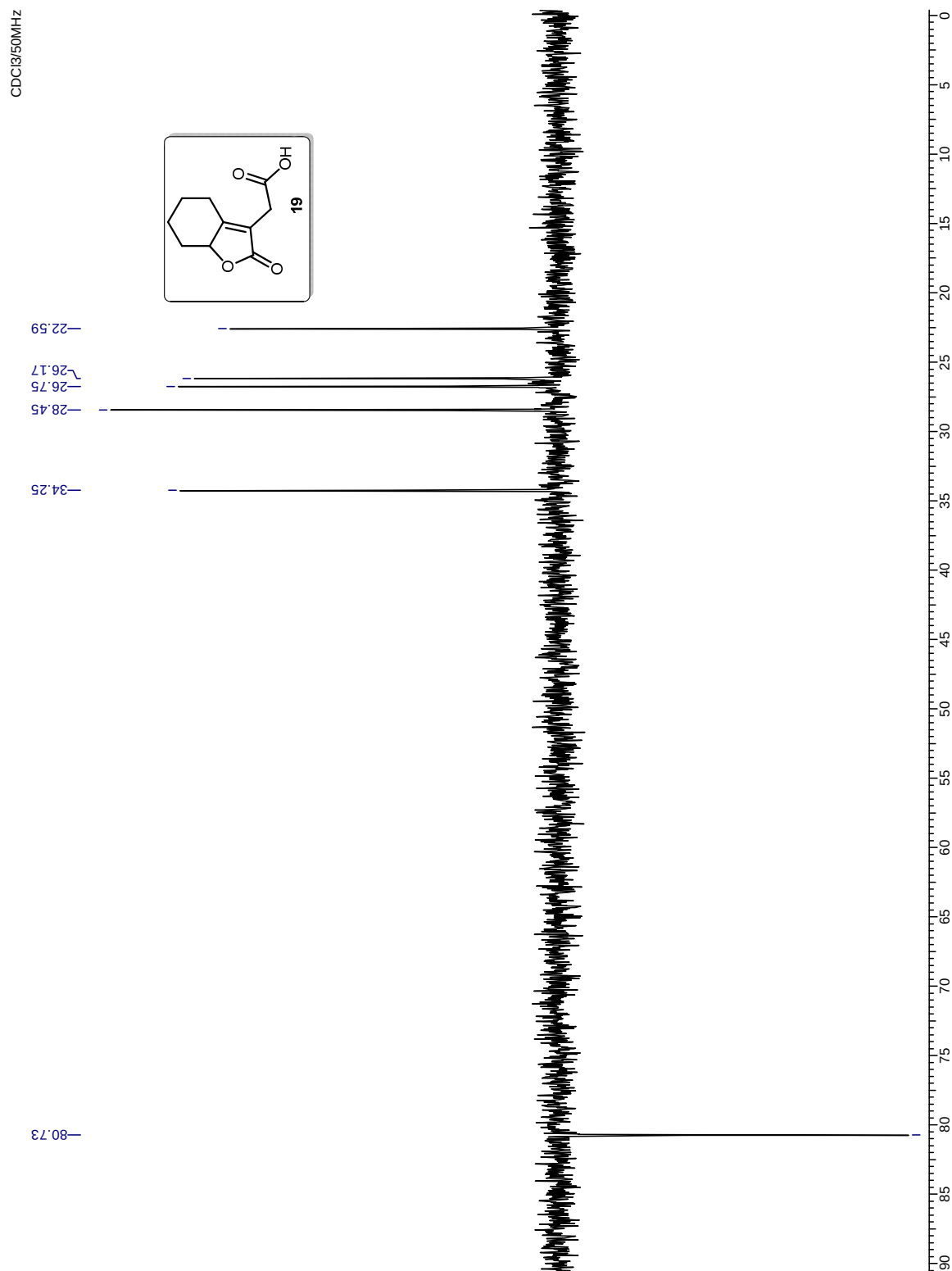


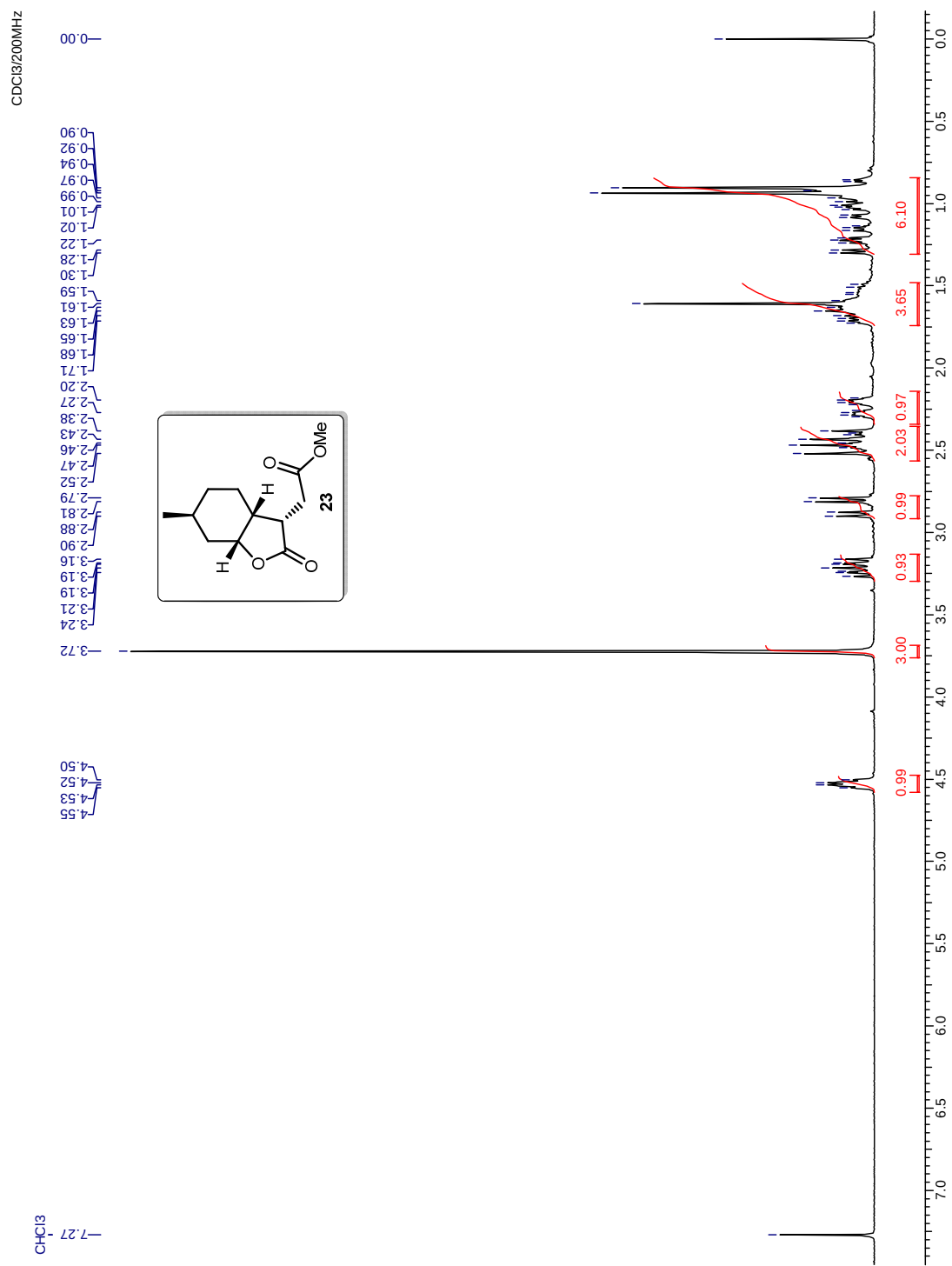


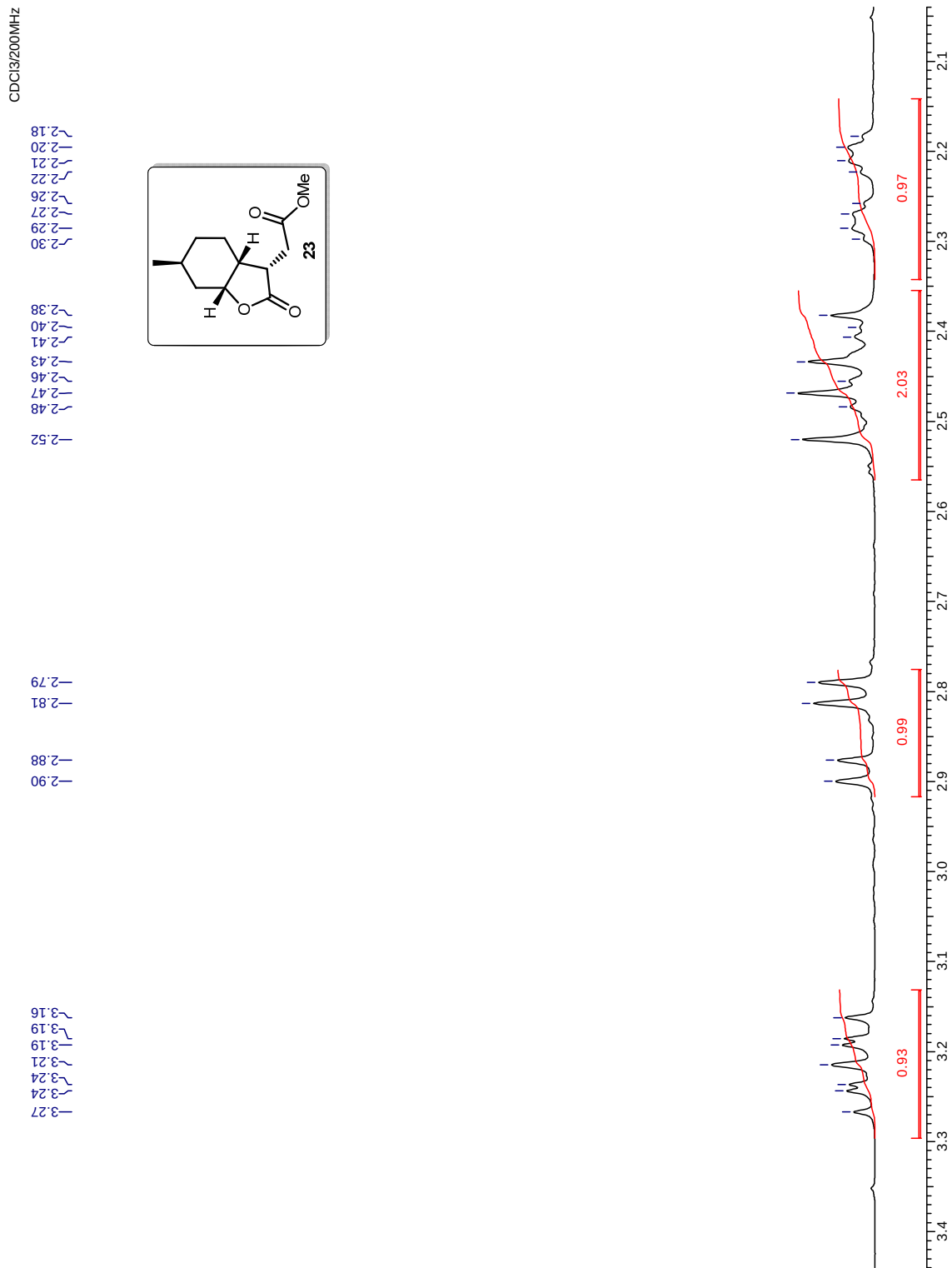


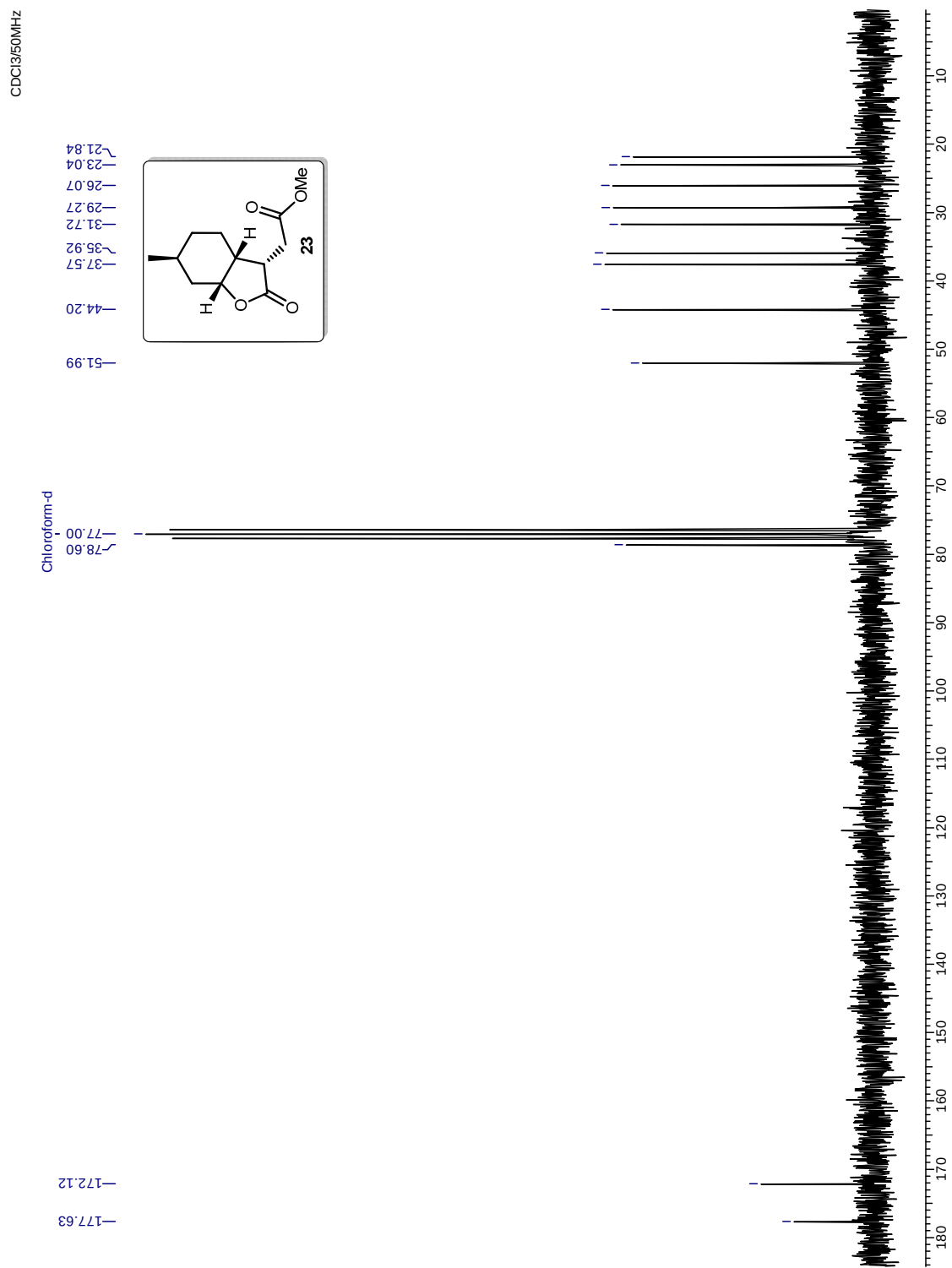


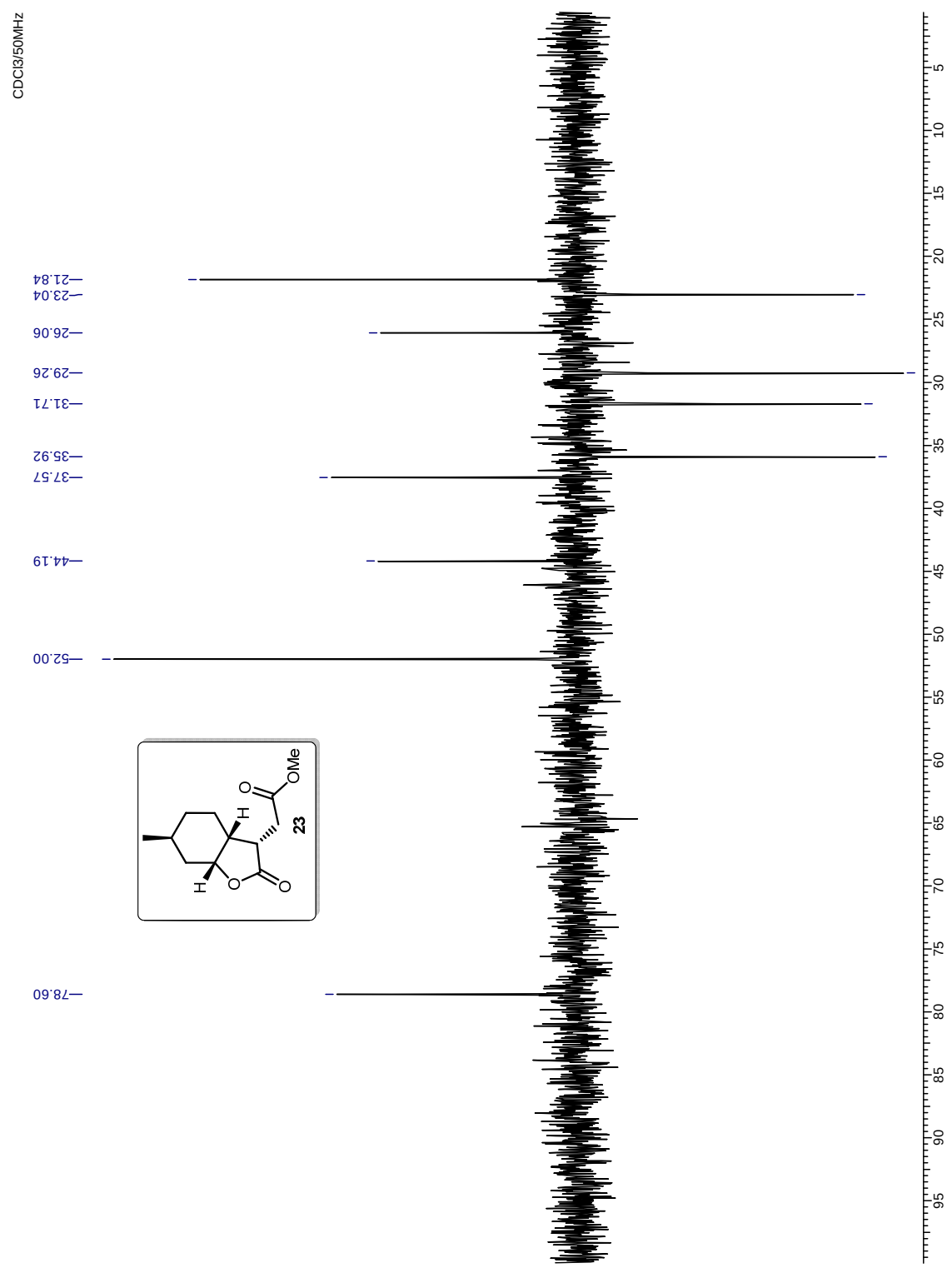


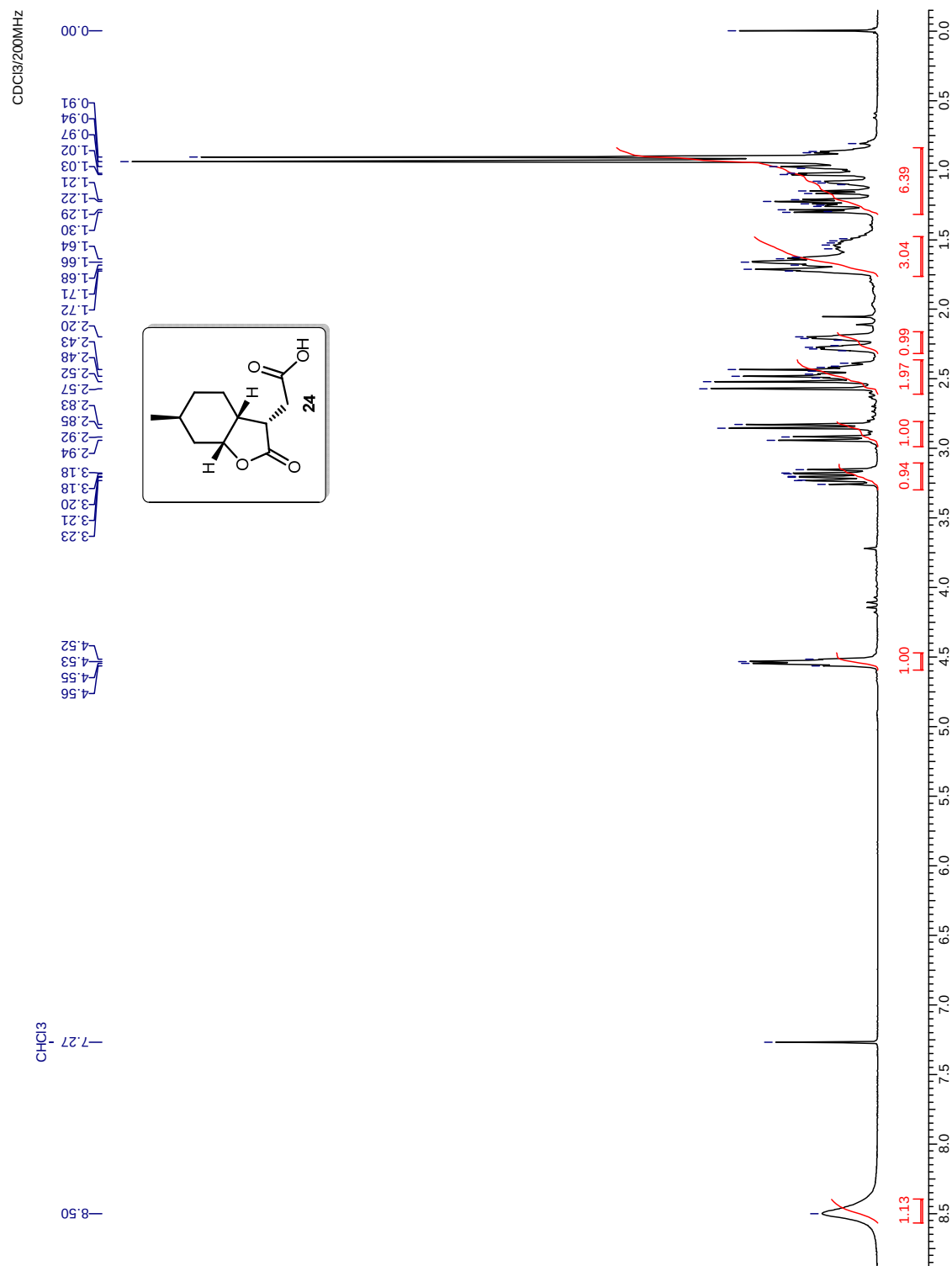


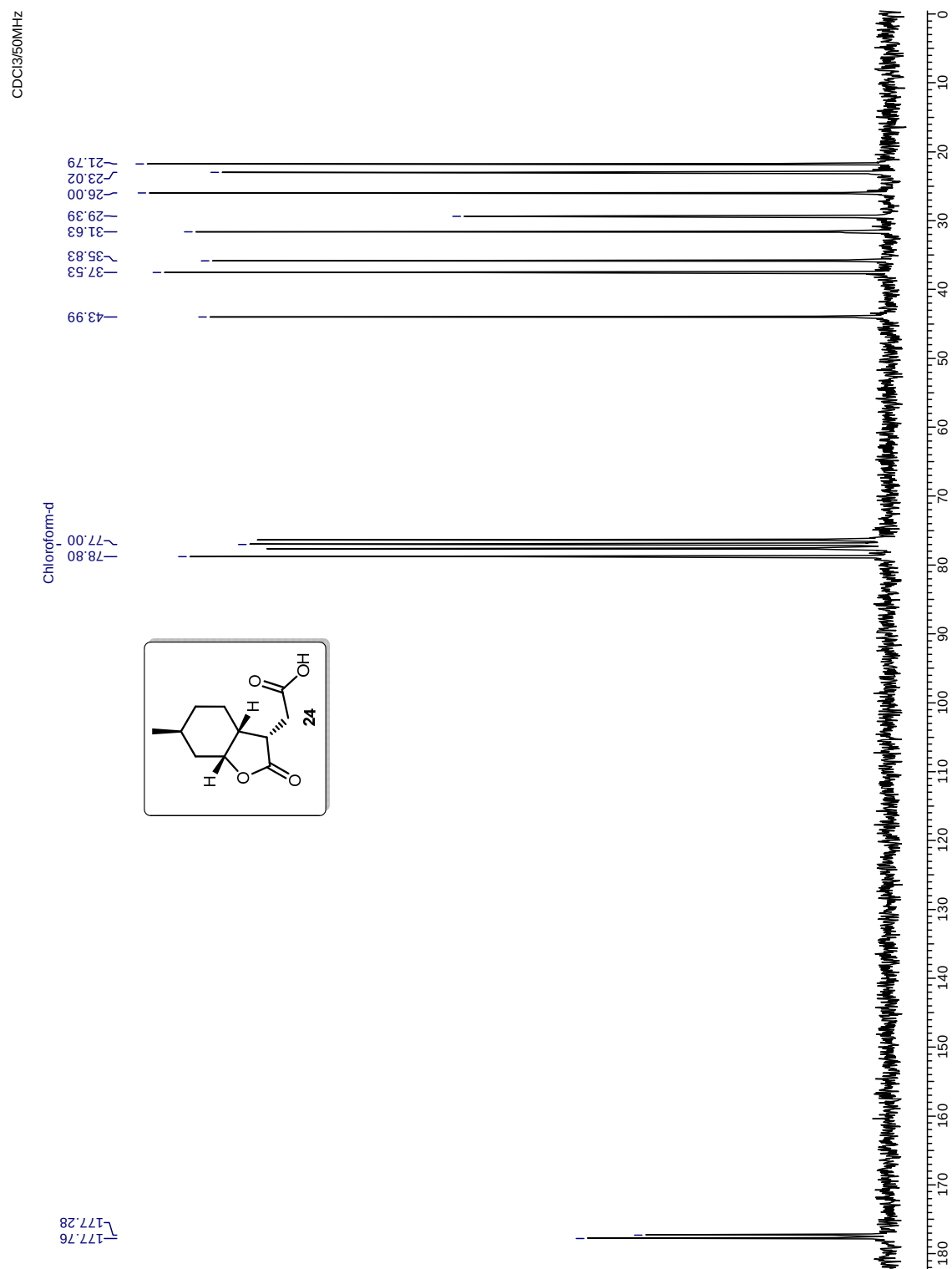


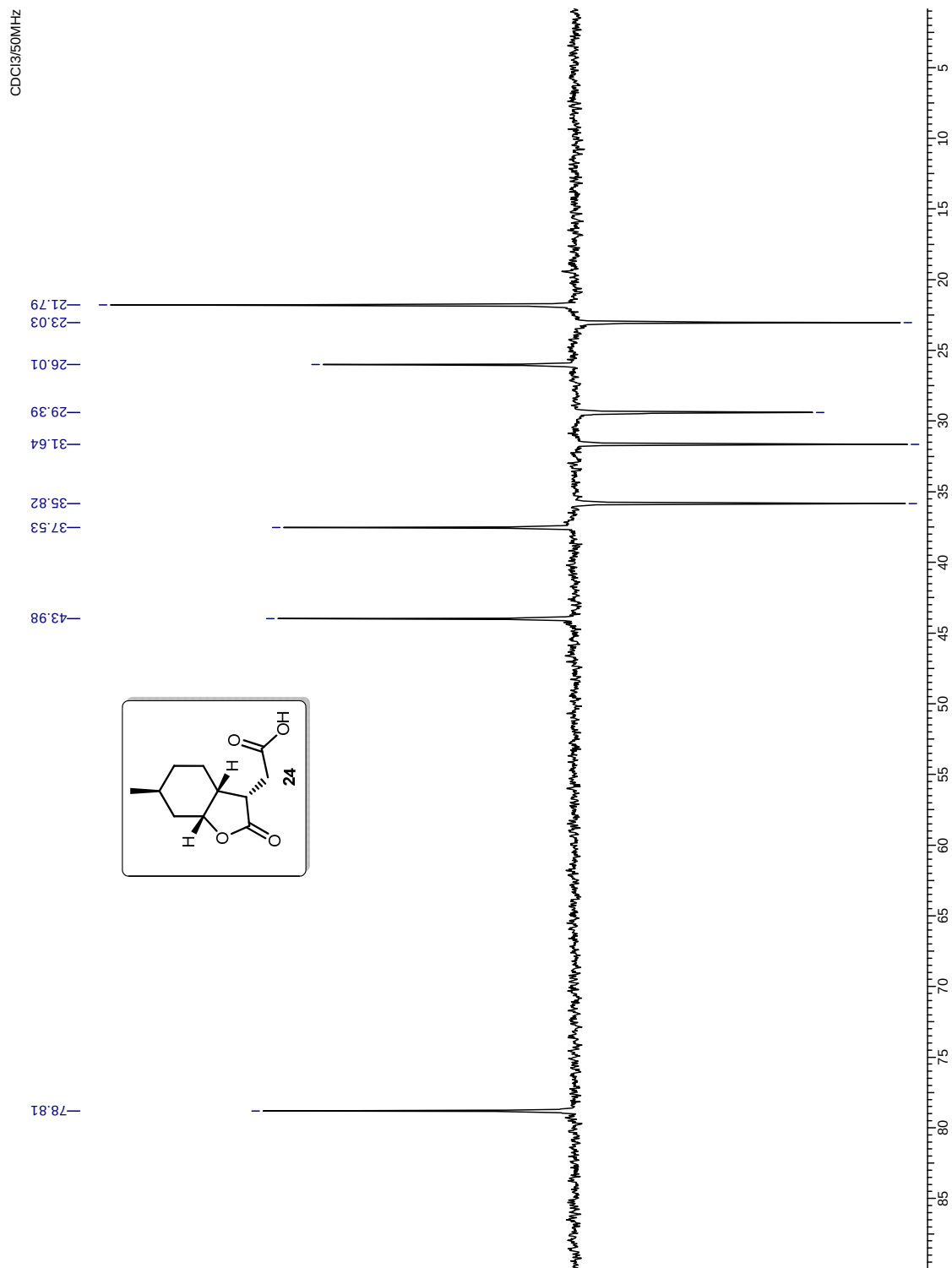


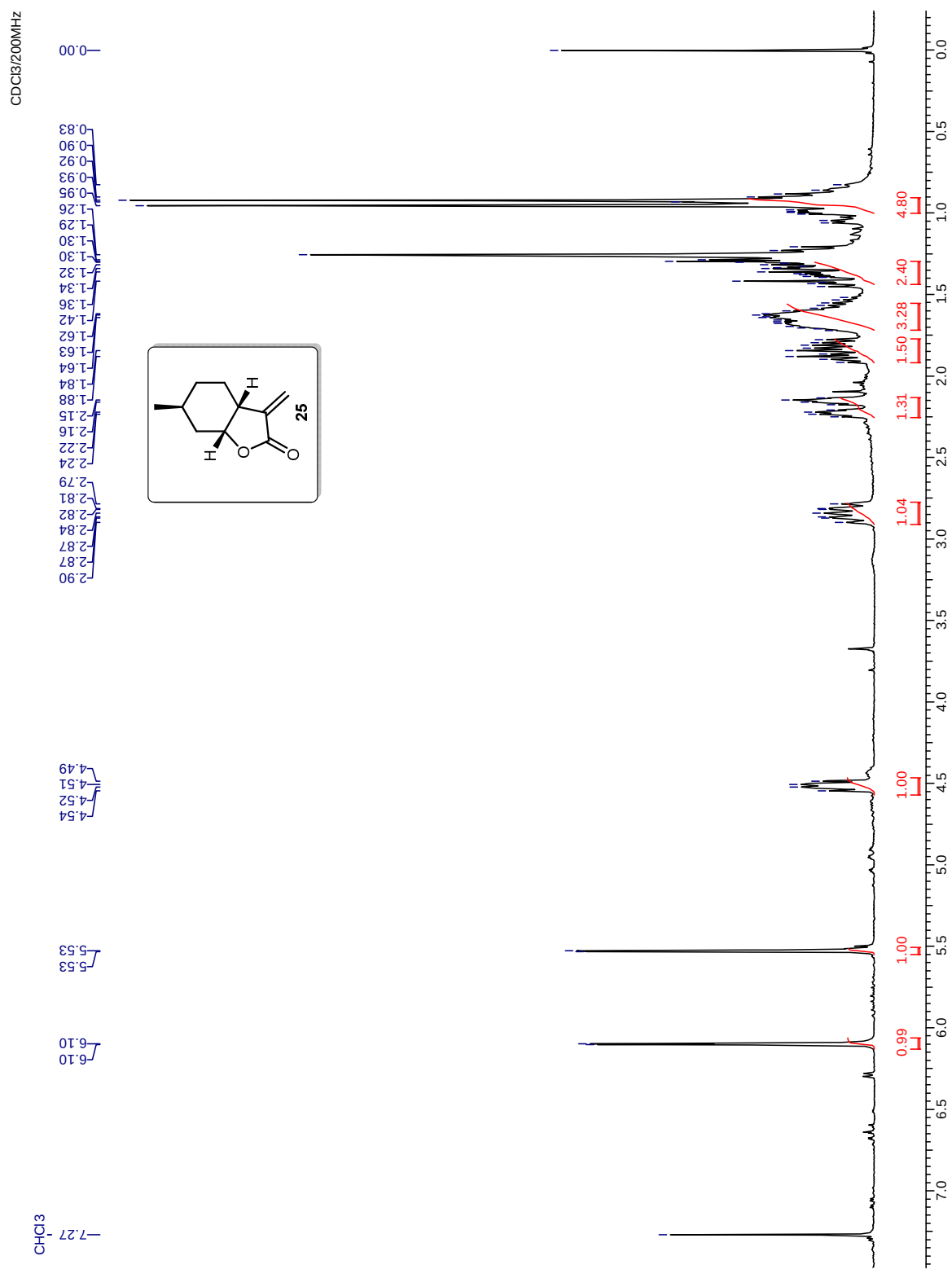


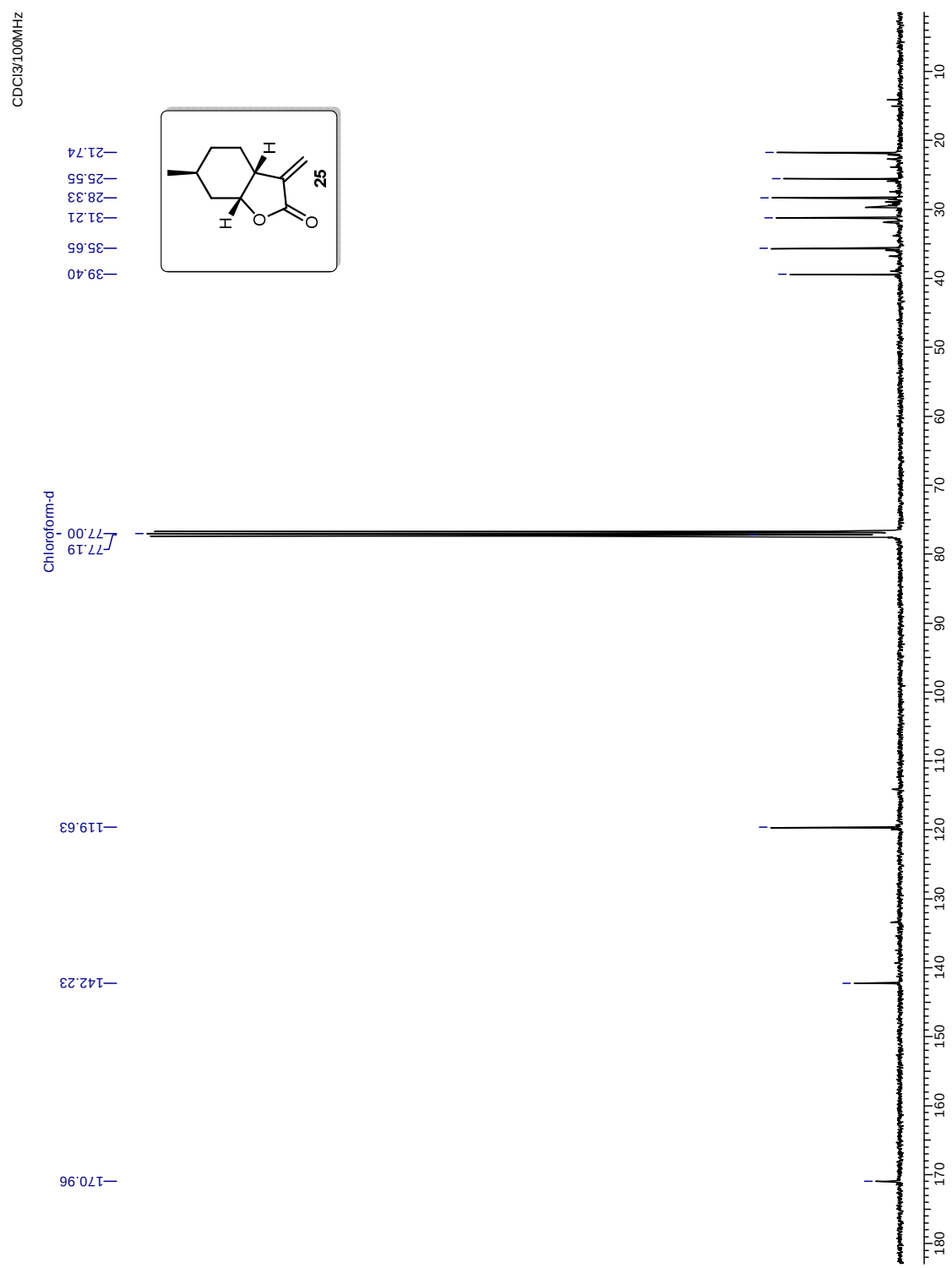


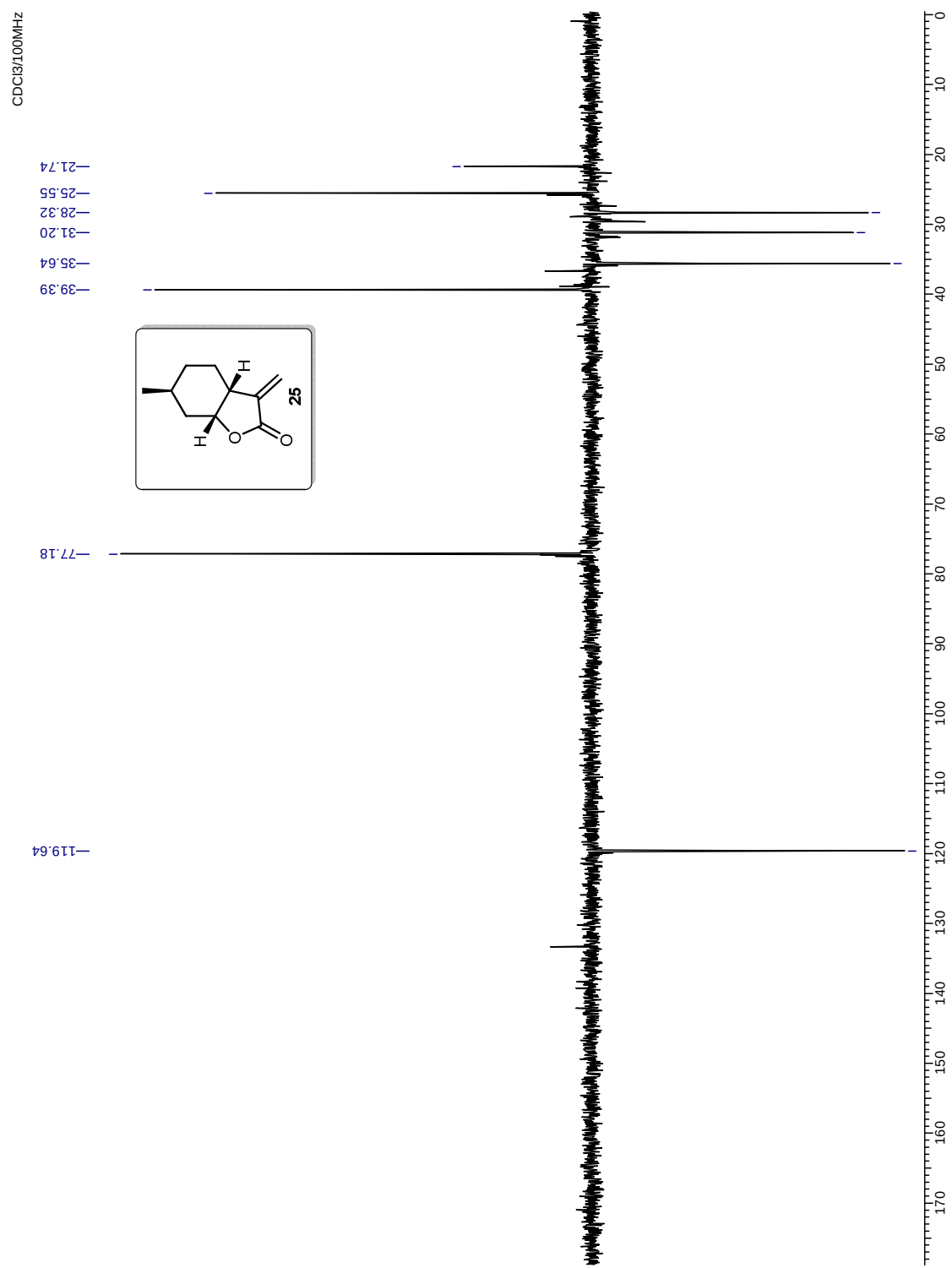


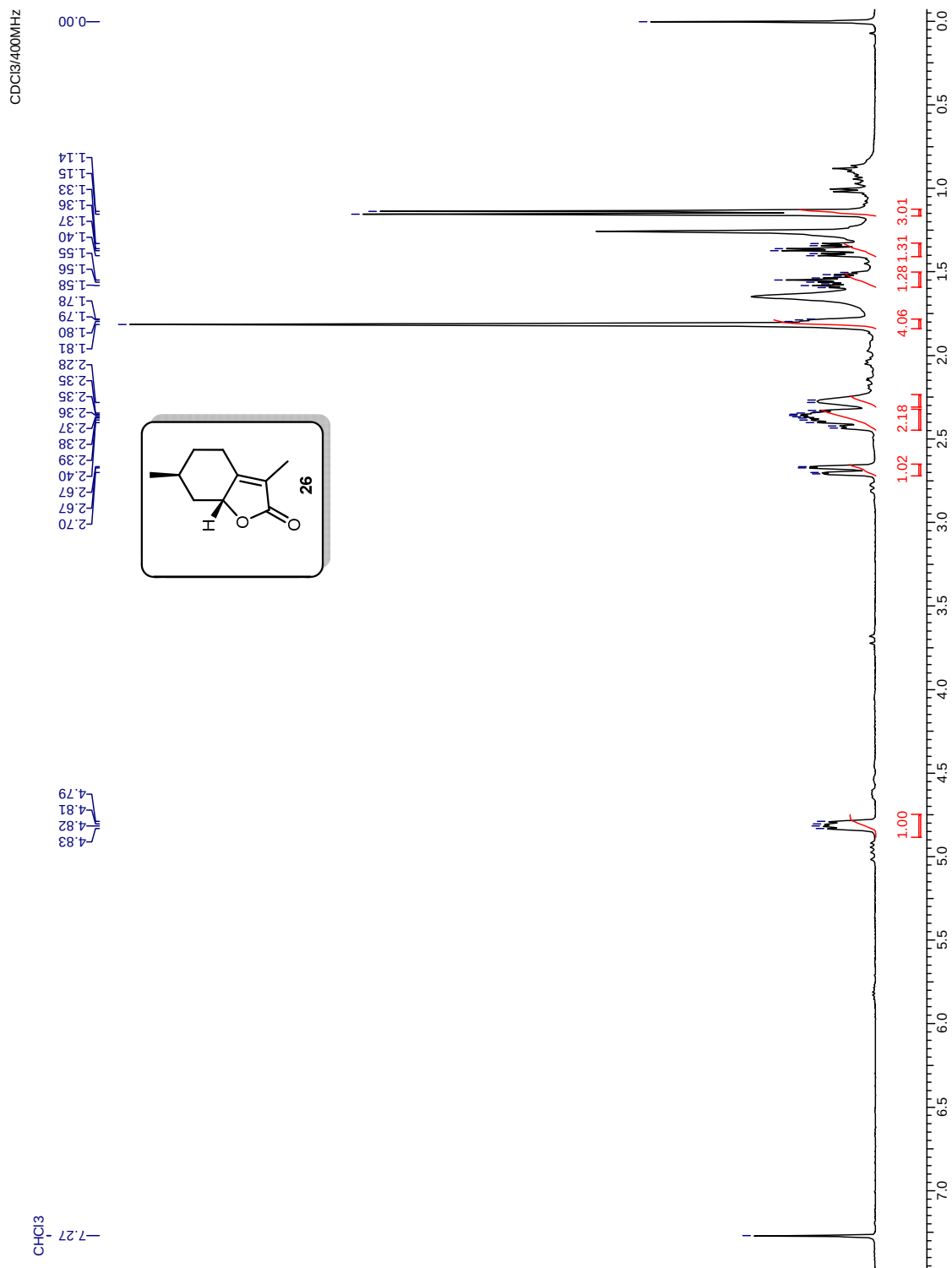


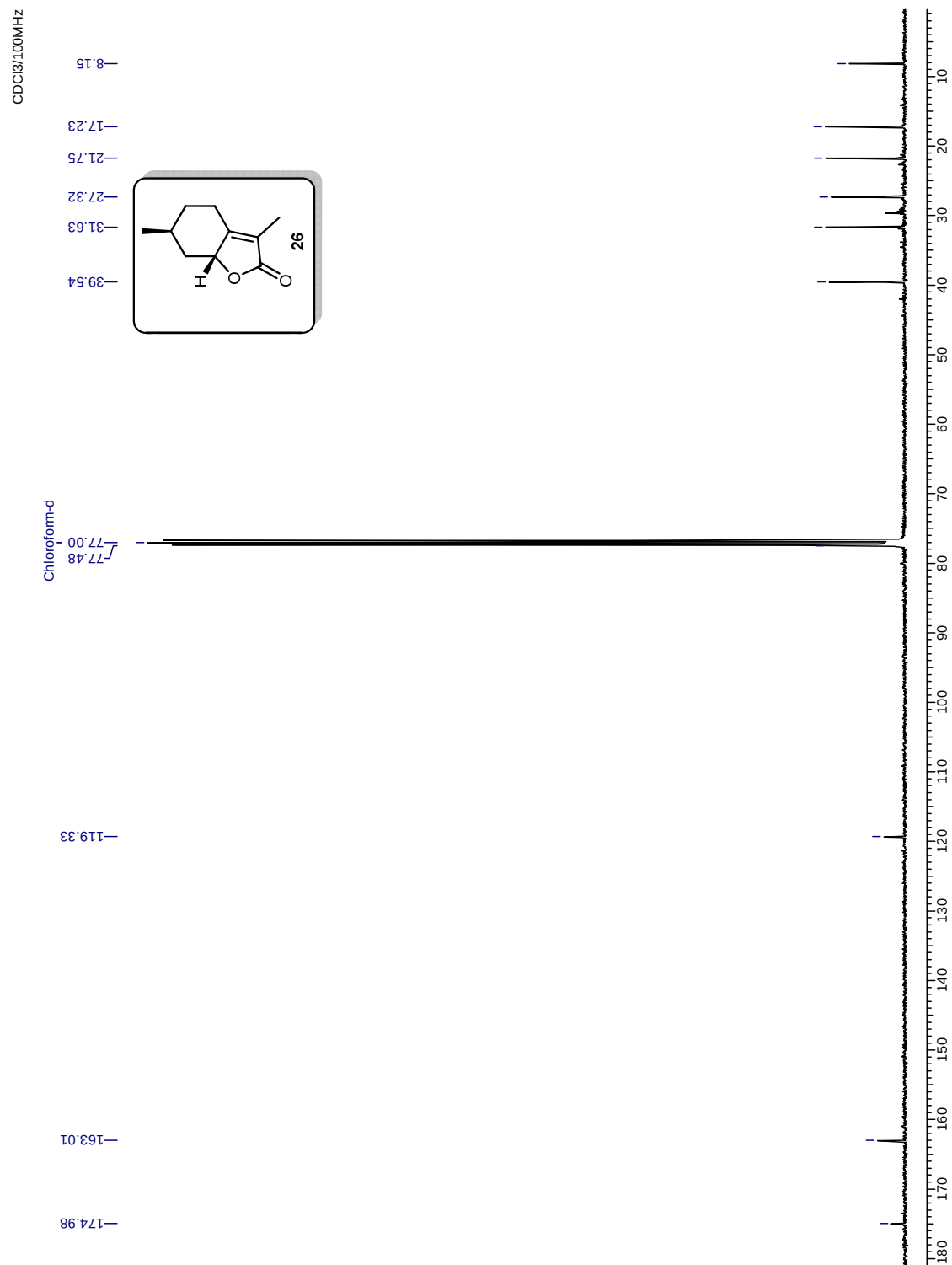


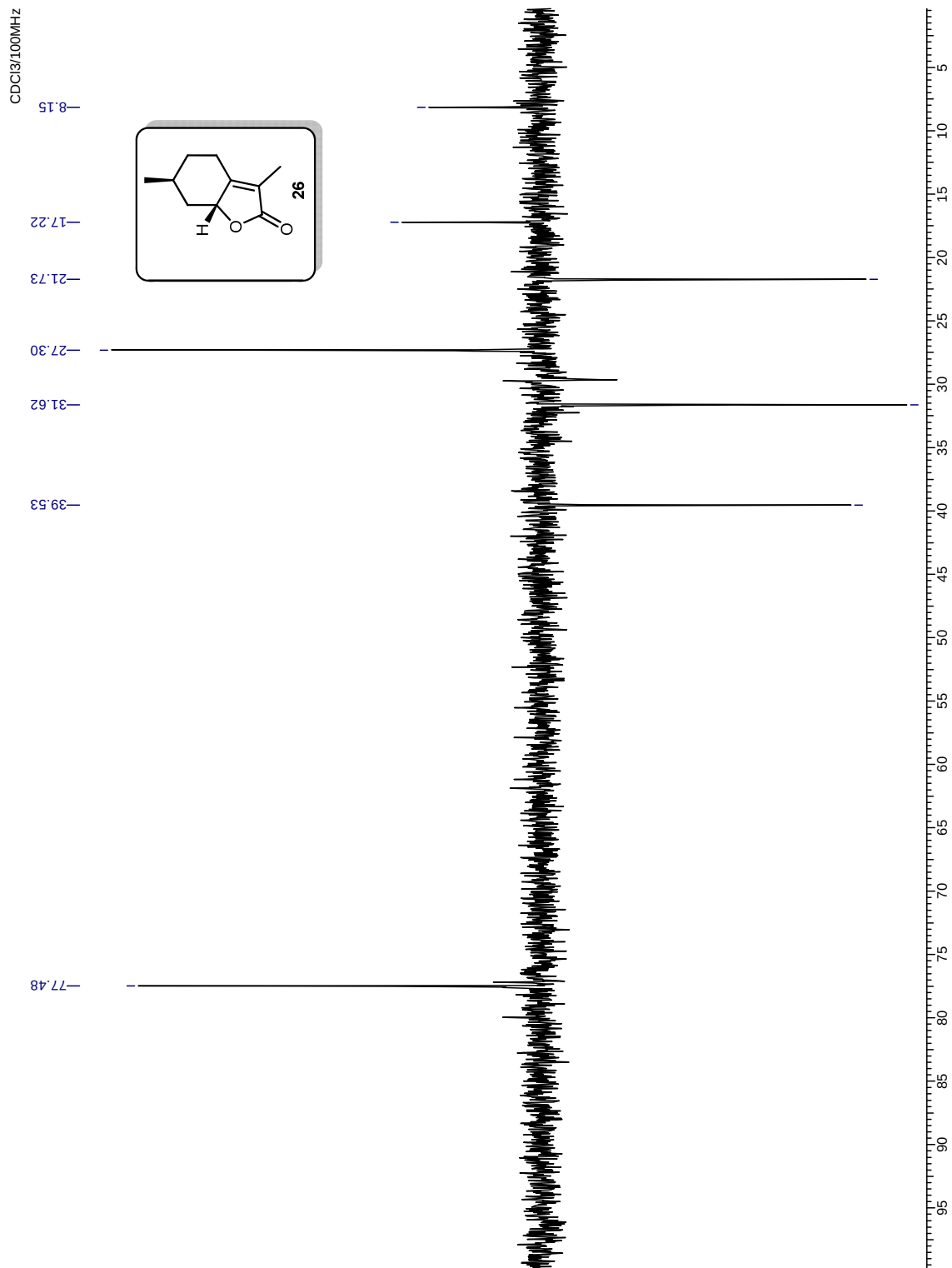


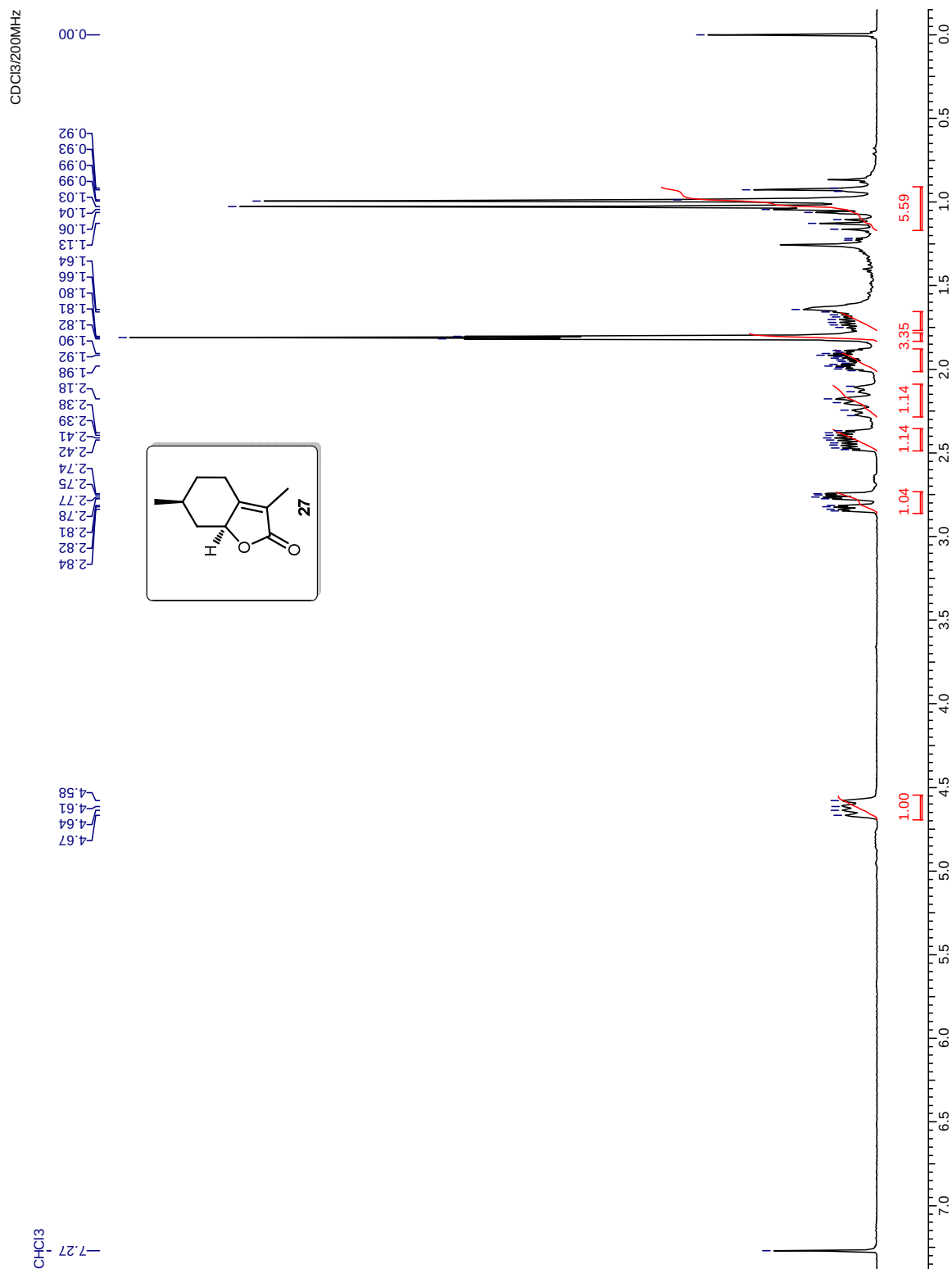


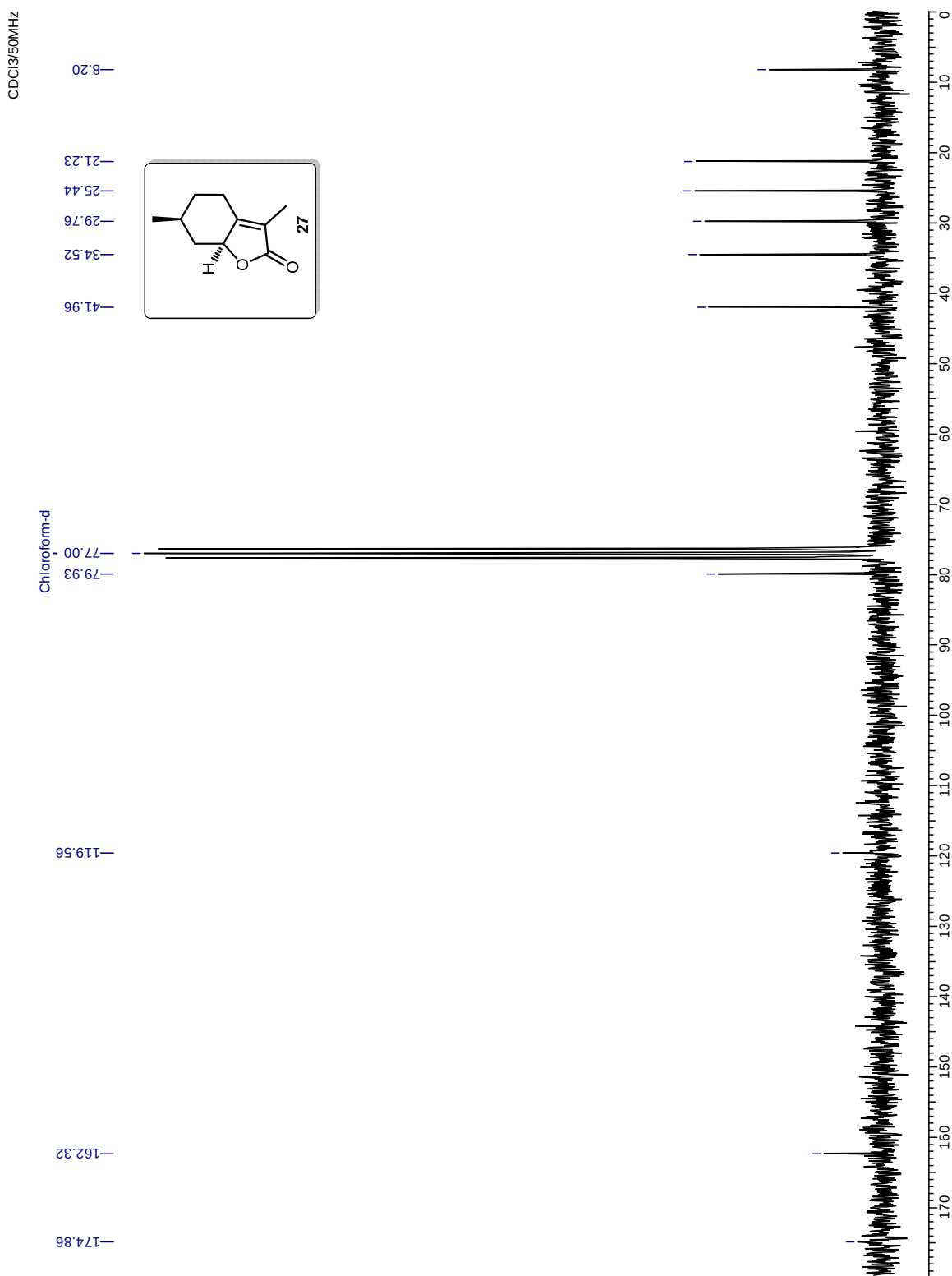


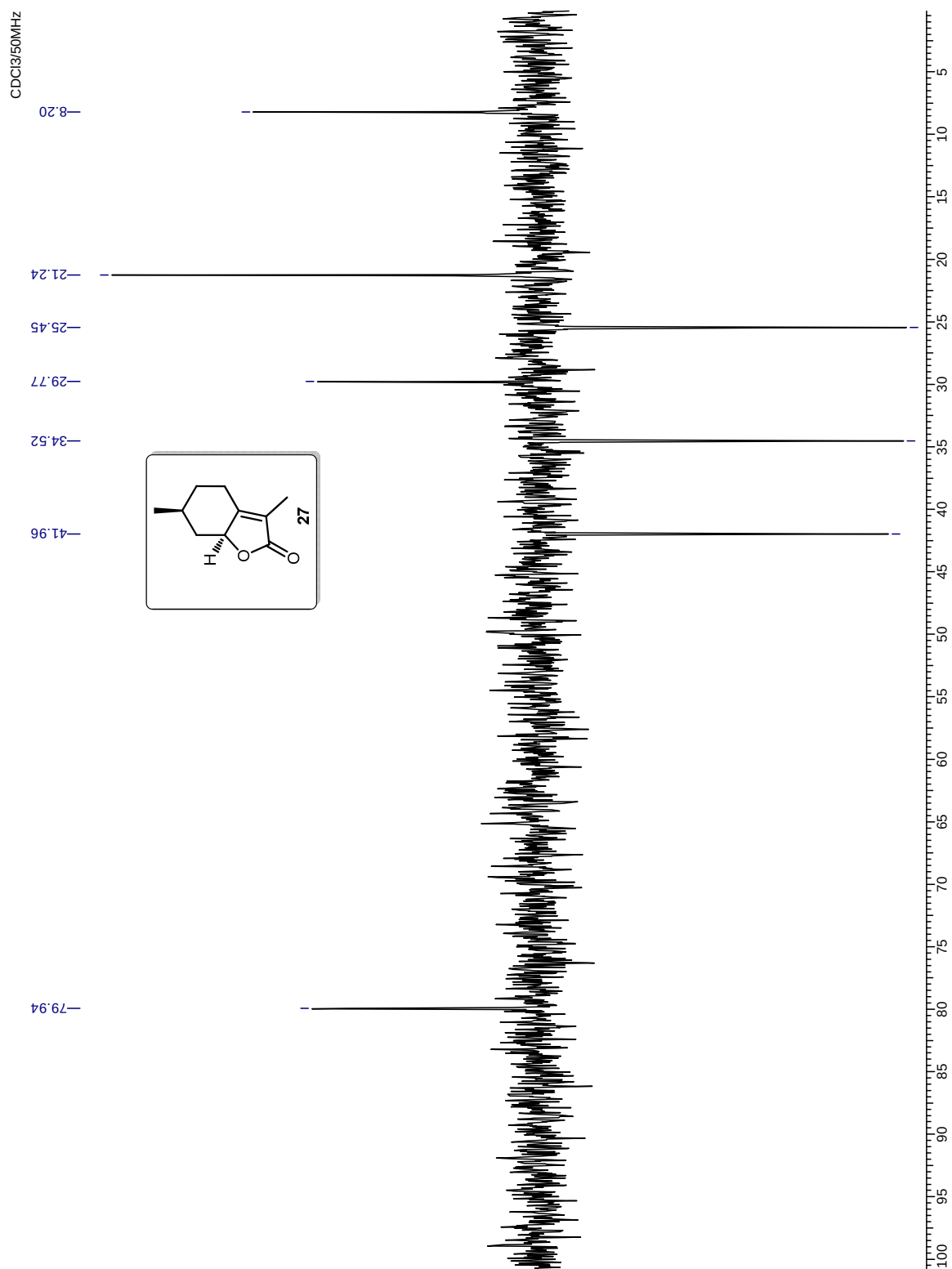


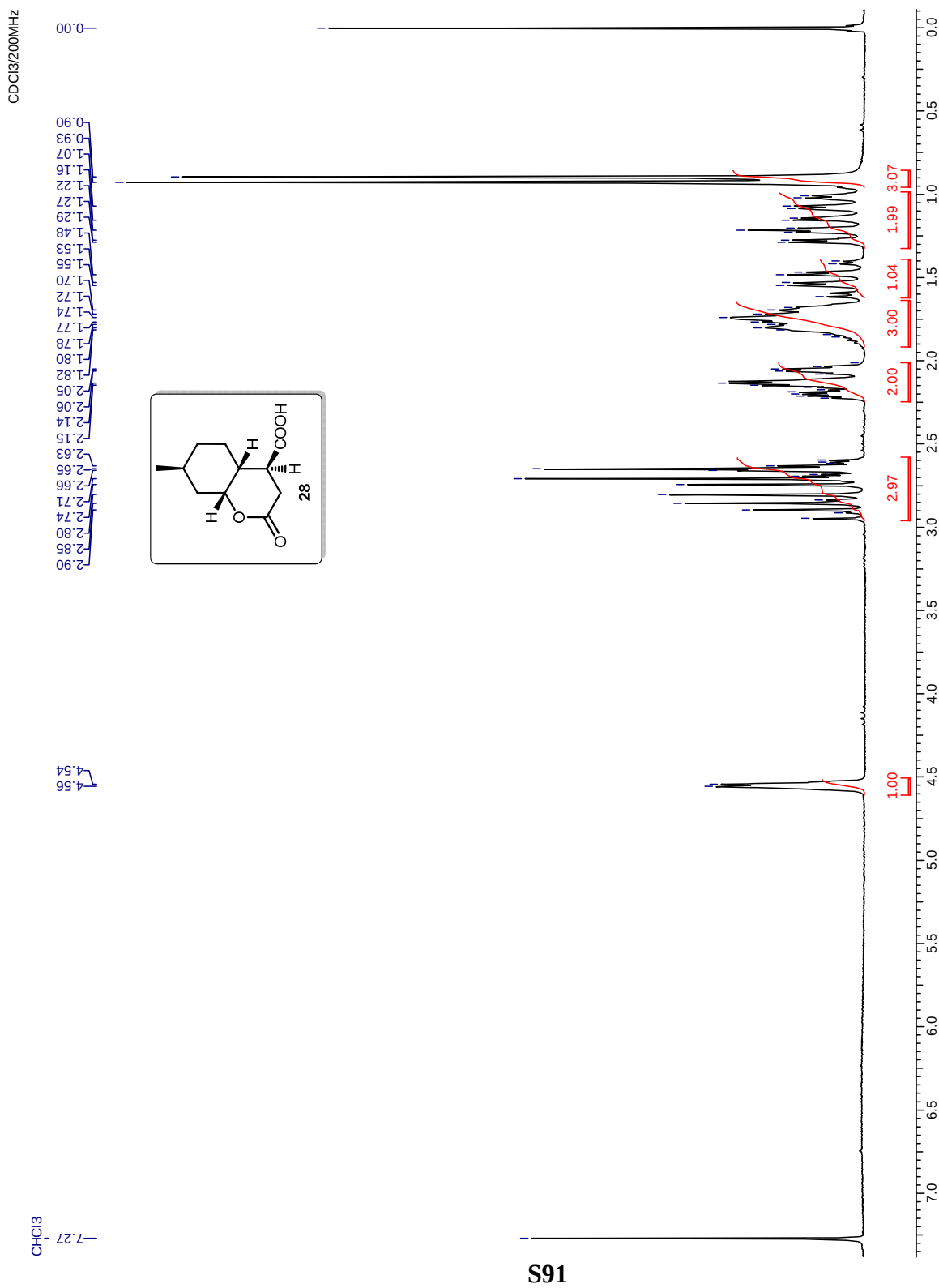




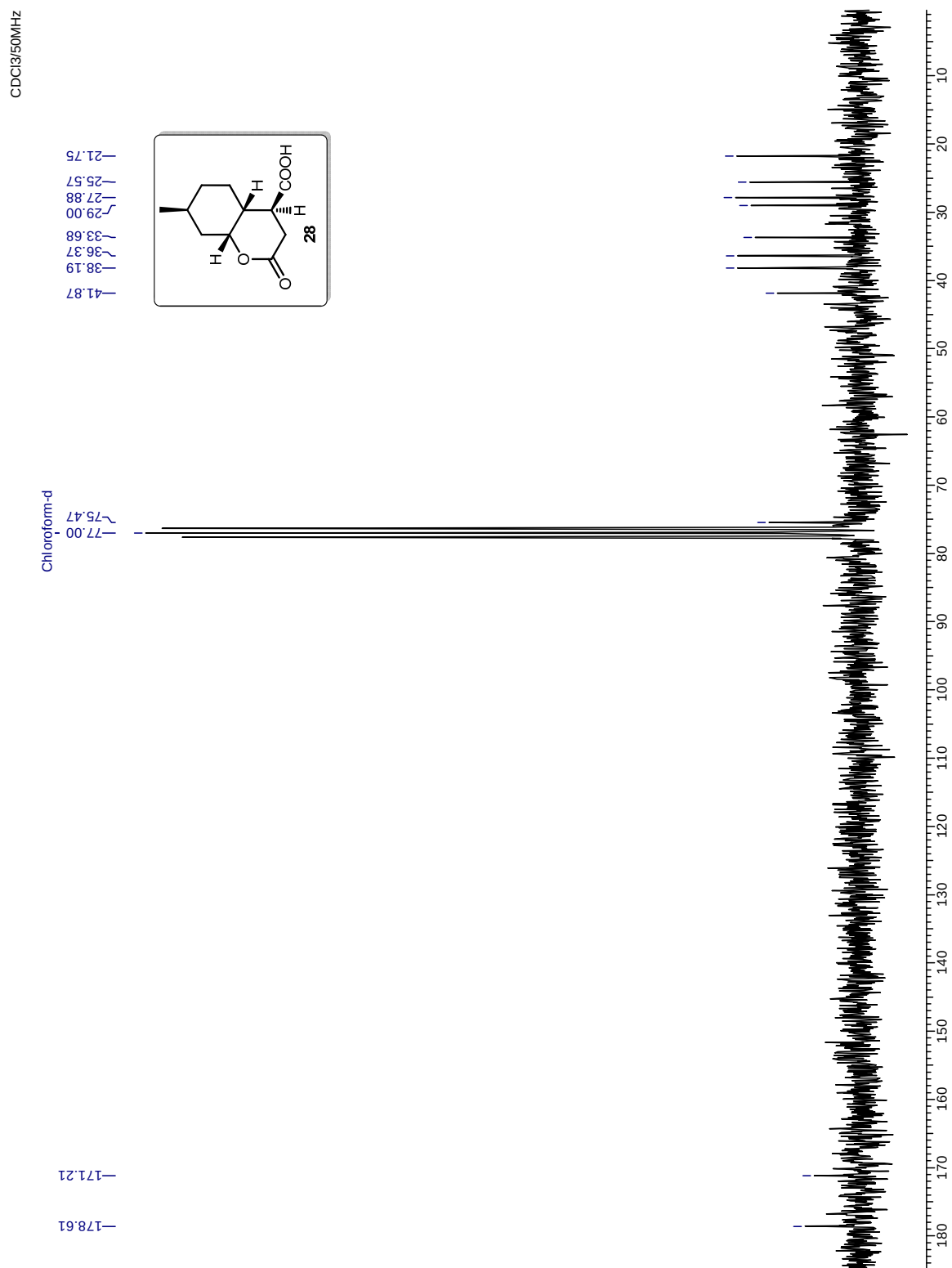


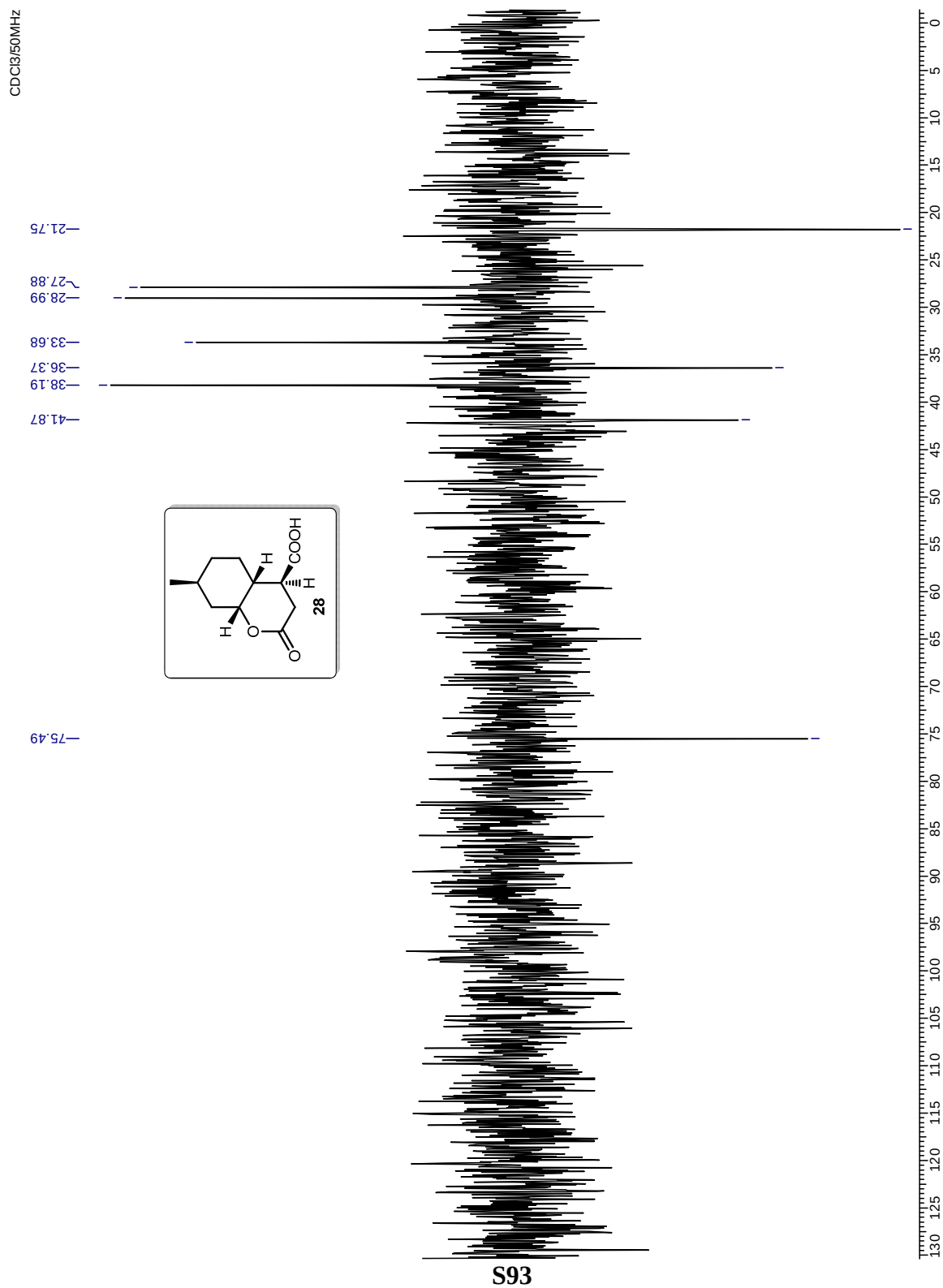


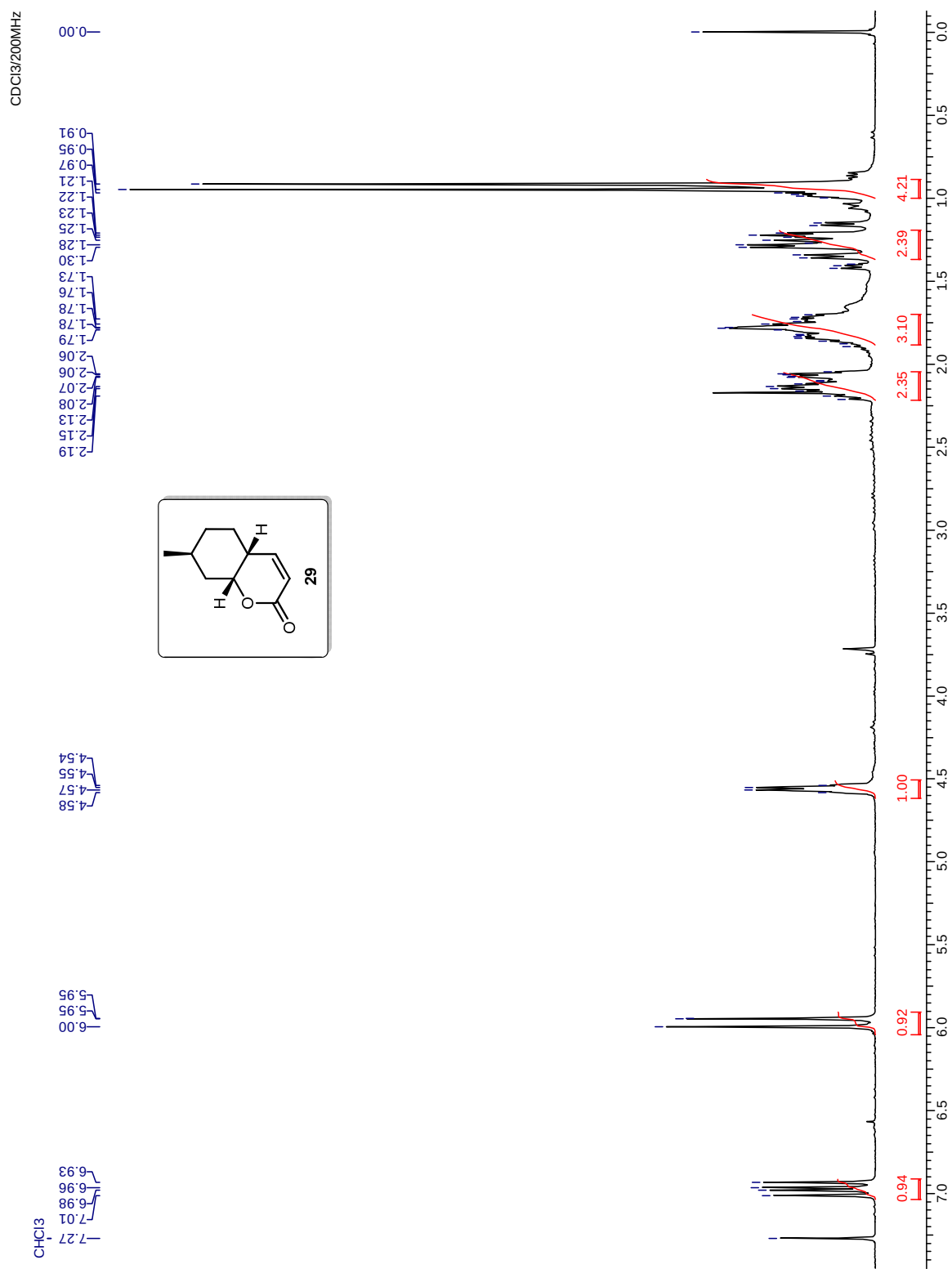


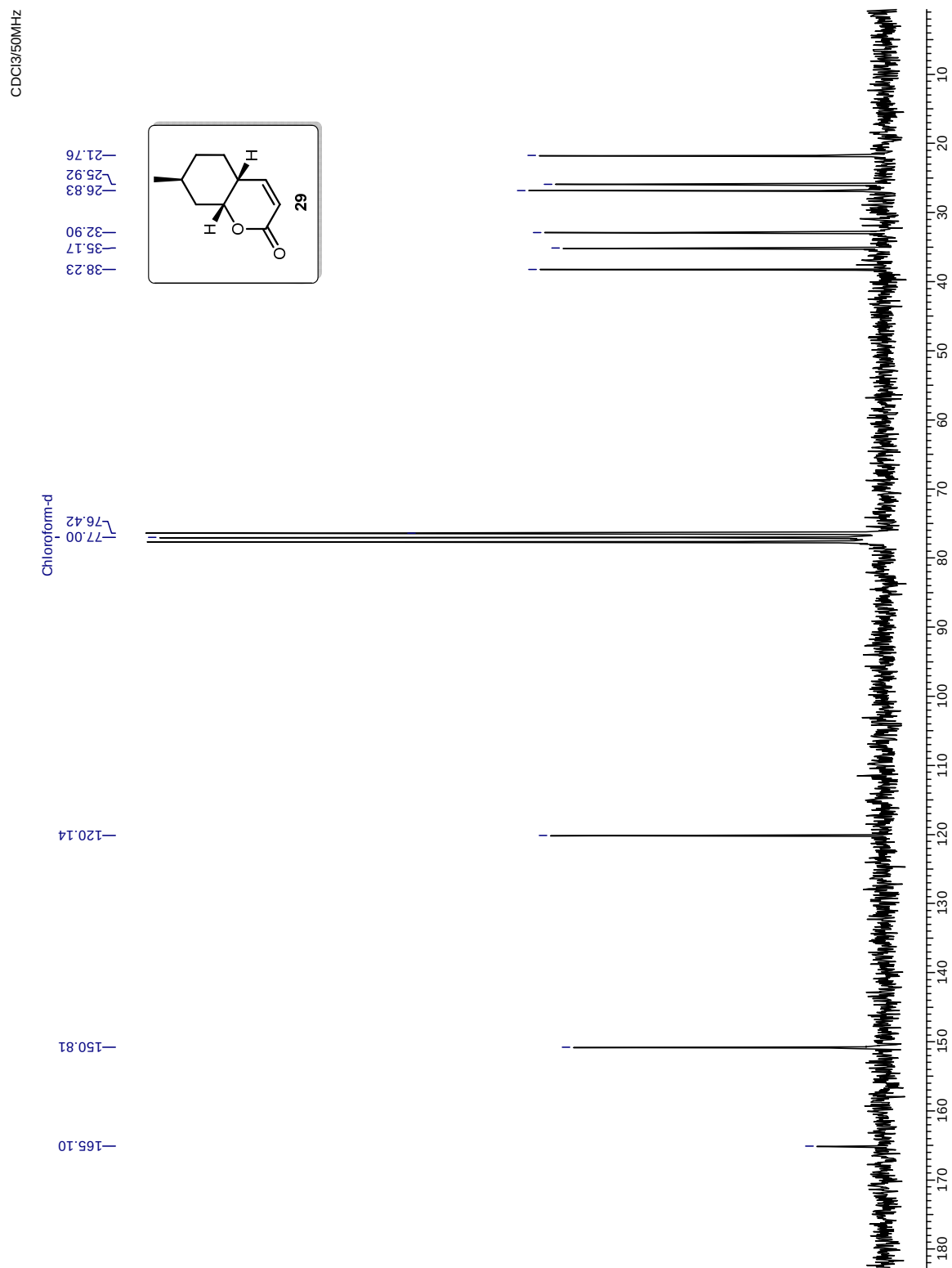


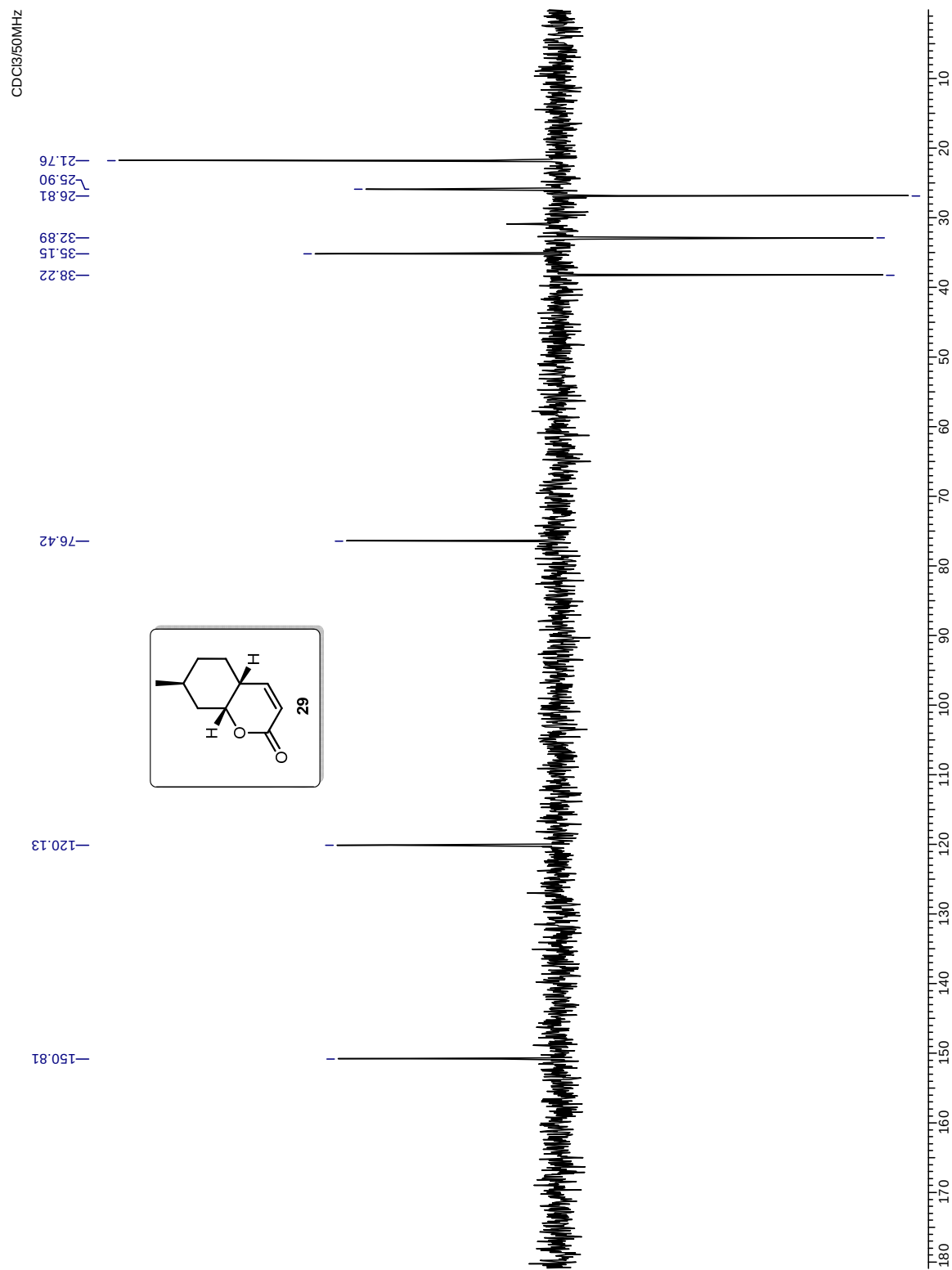
S91

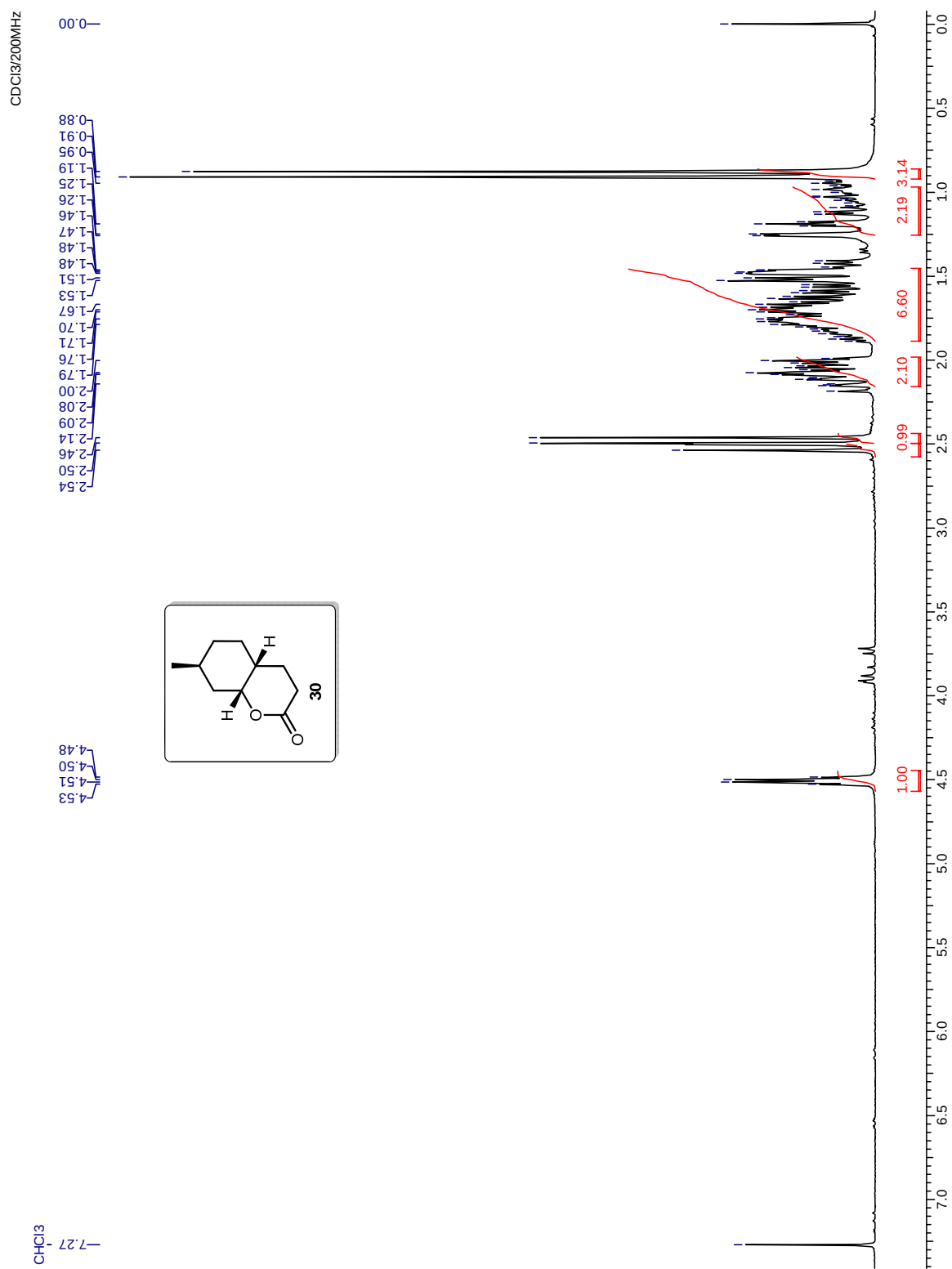


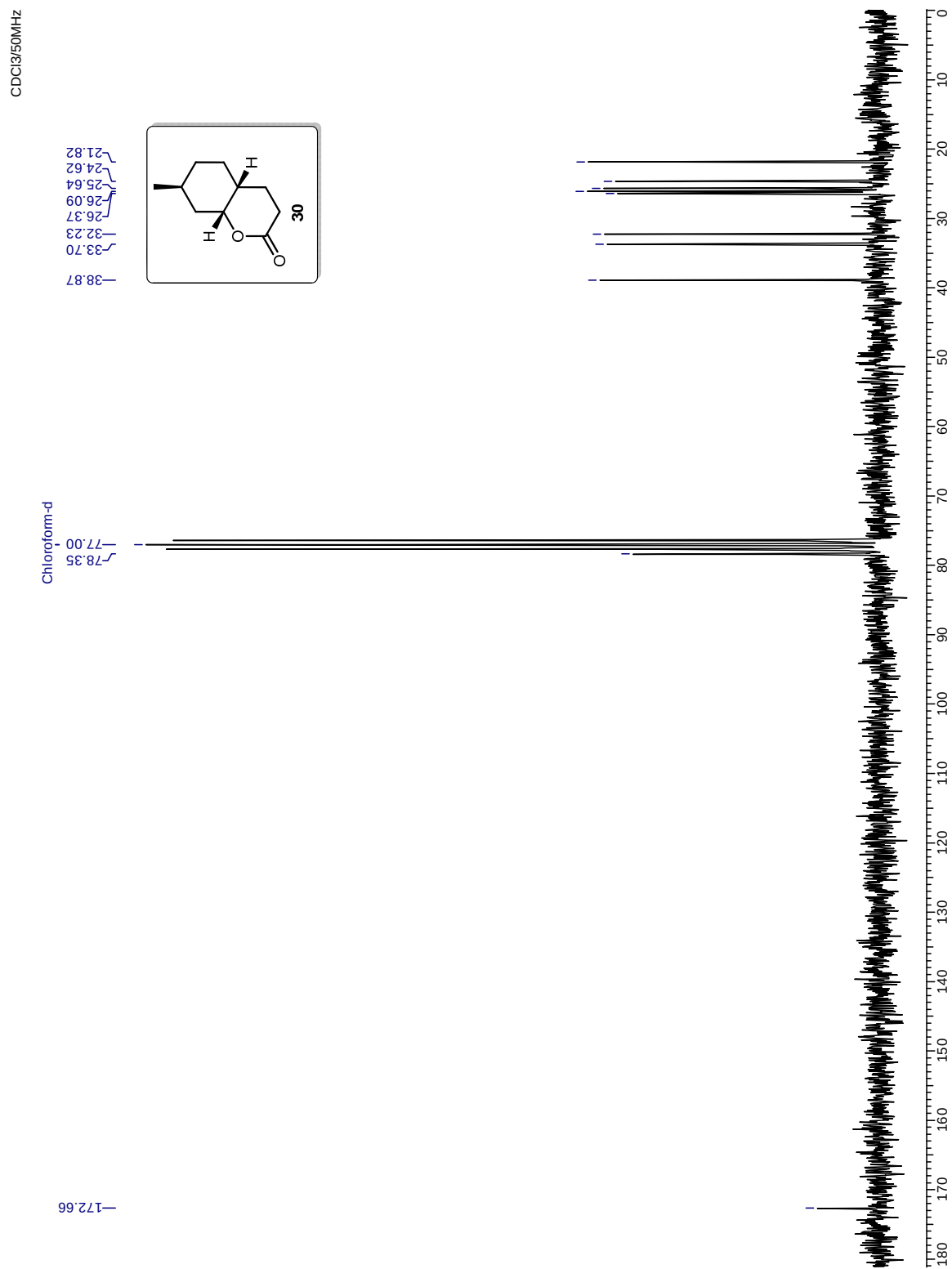


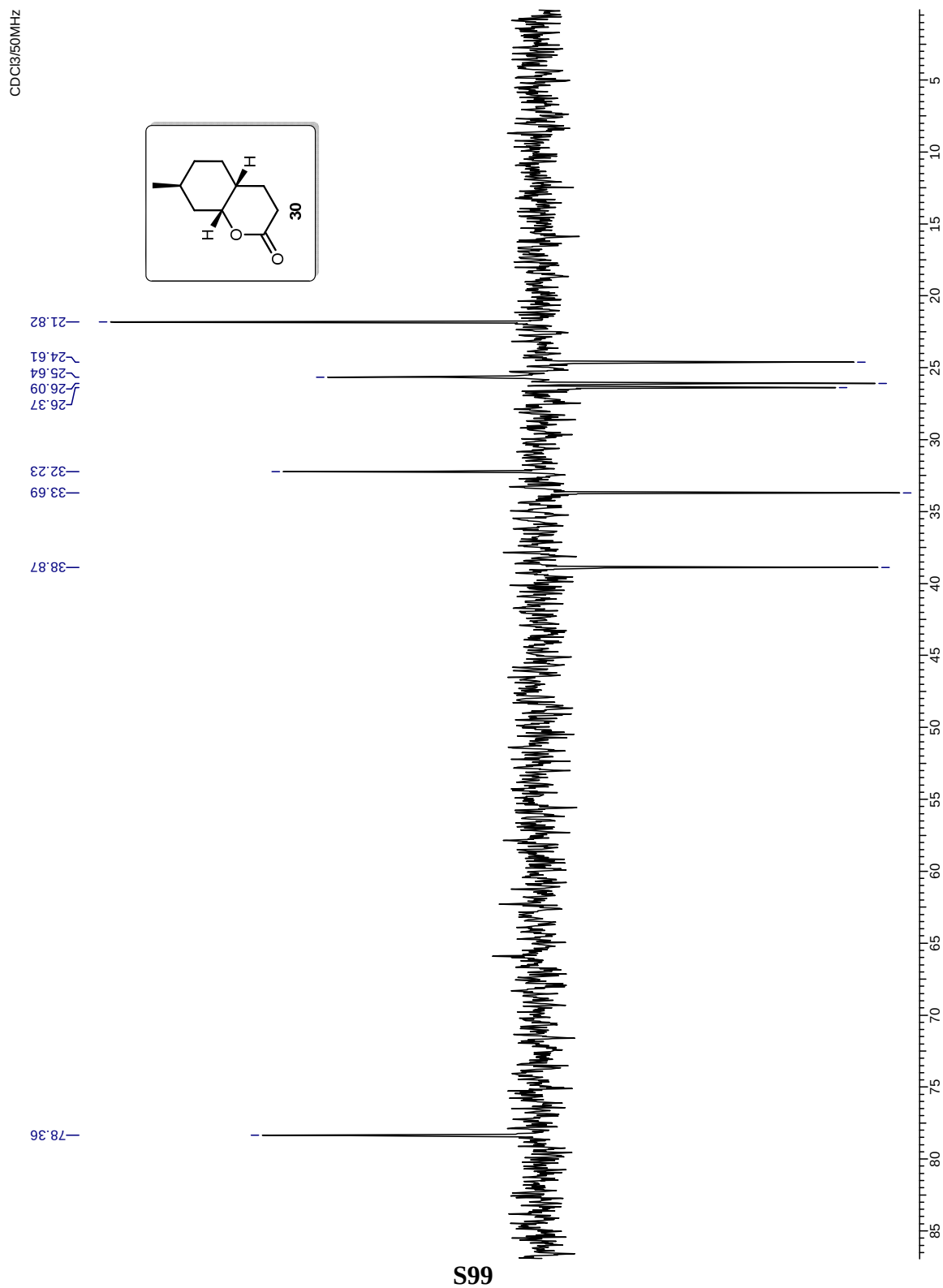










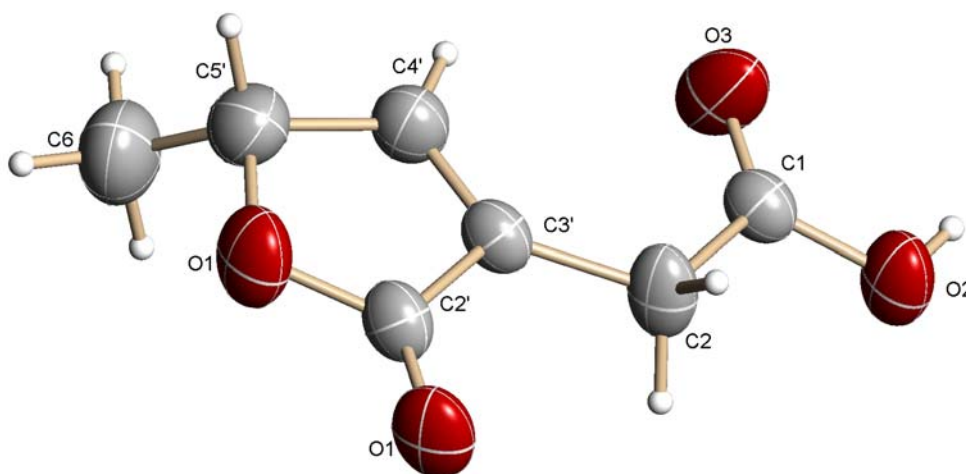


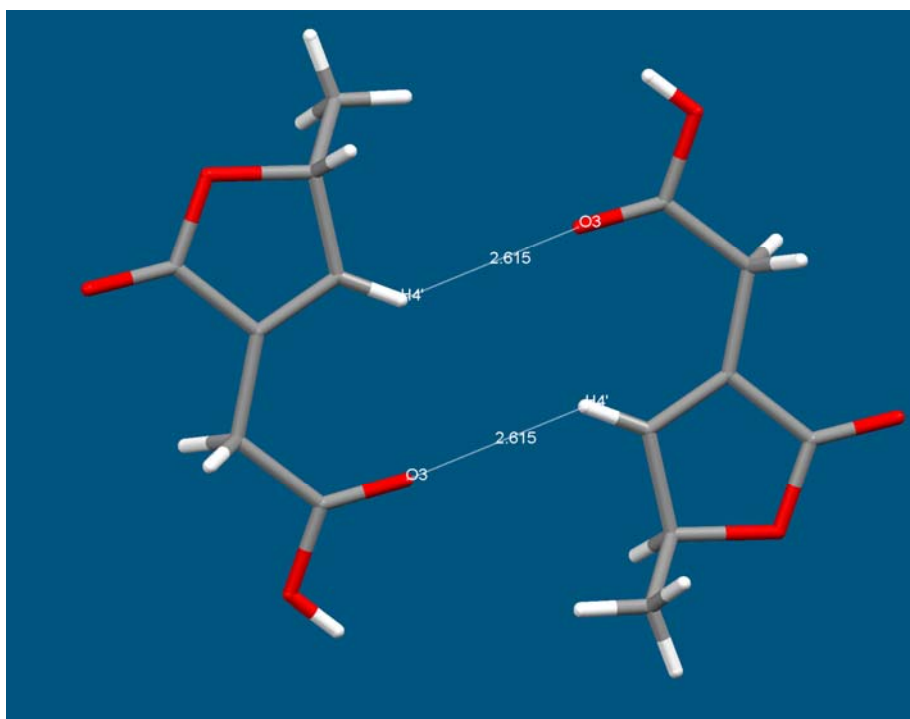
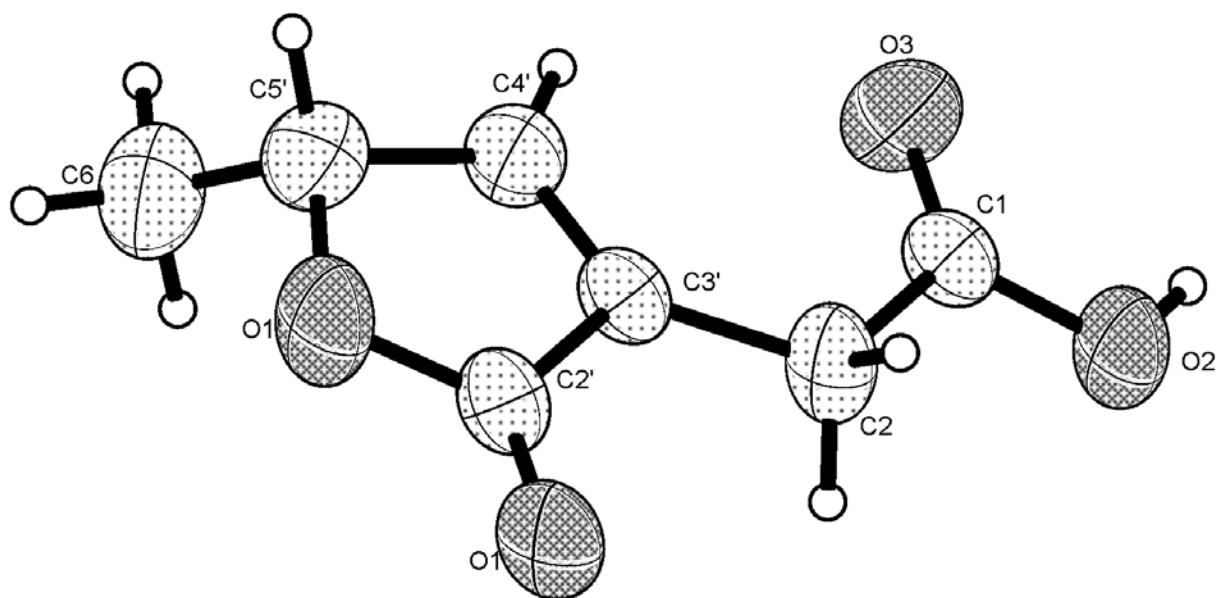
X-ray Crystal Structure Analysis For ramargd

Crystal Data: Data for all the four compounds were collected at $T = 293$ K, on SMART APEX CCD Single Crystal X-ray diffractometer using Mo-K α radiation ($\lambda = 0.7107$ Å) to a maximum θ range of 25.00° . Crystal to detector distance 6.05 cm, 512 x 512 pixels / frame, Oscillation / frame -0.3° , exposure / frame = 5.0 sec / frame, maximum detector swing angle = -30.0° , beam center = (260.2, 252.5), in plane spot width = 1.24, SAINT integration and SADABS correction applied. The structures were solved by direct methods using SHELXTL. All the data were corrected for Lorentzian, polarisation and absorption effects. SHELX-97 (ShelxTL)^{ref} was used for structure solution and full matrix least squares refinement on F^2 . Hydrogen atoms were included in the refinement as per the riding model. The refinements were carried out using SHELXL-97.

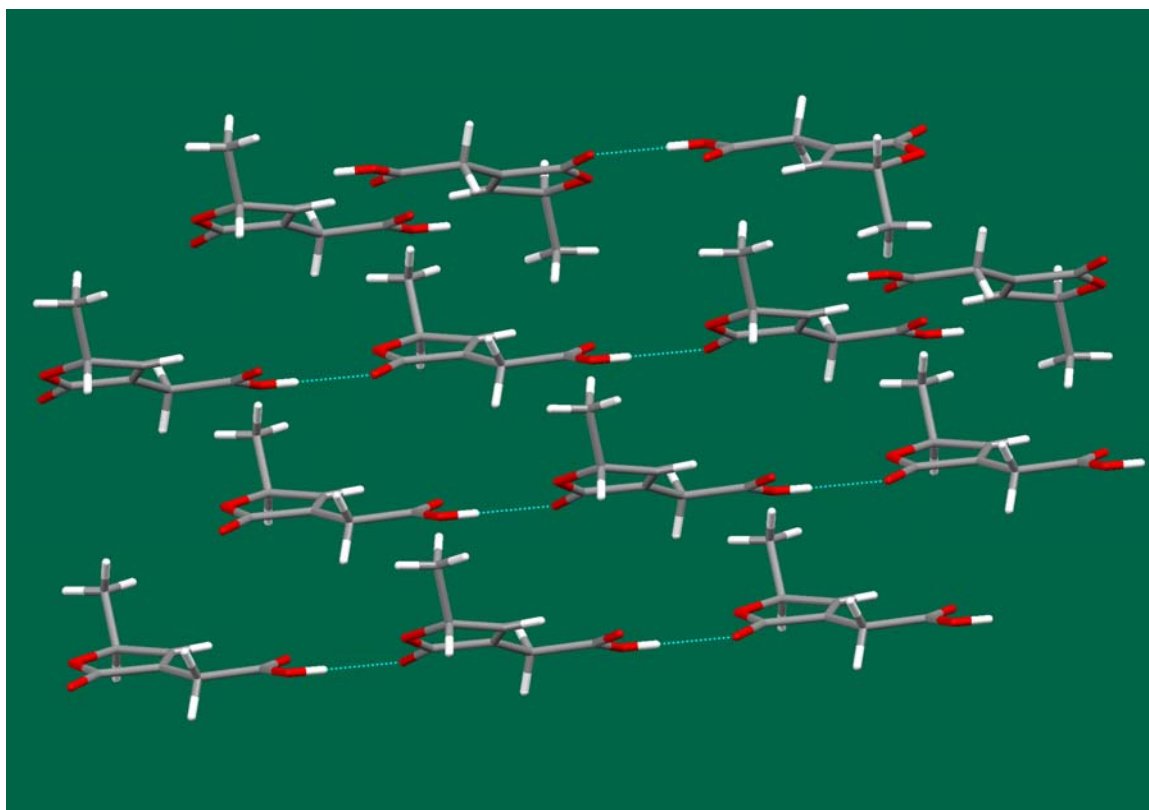
2-(5-Methyl-2-oxo-2,5-dihydrofuran-3-yl)acetic acid (8): Single crystals of the compound were grown by slow evaporation of the solution in chloroform. Colourless needle of approximate size $0.08 \times 0.02 \times 0.01$ mm, was used for data collection. Quadrant data acquisition. Total scans = 4, total frames = 2424, θ range = 2.45 to 25.00° , completeness to θ of 25.0° is 100.0 %, $C_7H_8O_4$, $M = 156.13$. Crystals belong to Monoclinic, space group $P2_1/c$, $a = 5.0397(3)$, $b = 14.351(1)$, $c = 10.3160(7)$ Å, $\beta = 98.118(1)^\circ$, $V = 738.64(8)$ Å³, $Z = 4$, $D_c = 1.404$ g /cc, μ (Mo-K α) = 0.117 mm⁻¹, 6969 reflections measured, 1291 unique [$I > 2\sigma(I)$], R value 0.0658, $wR2 = 0.1684$. Largest diff. peak and hole 0.503 and -0.163 e. Å⁻³.

The compound was confirmed to have a five membered γ -lactone ring.





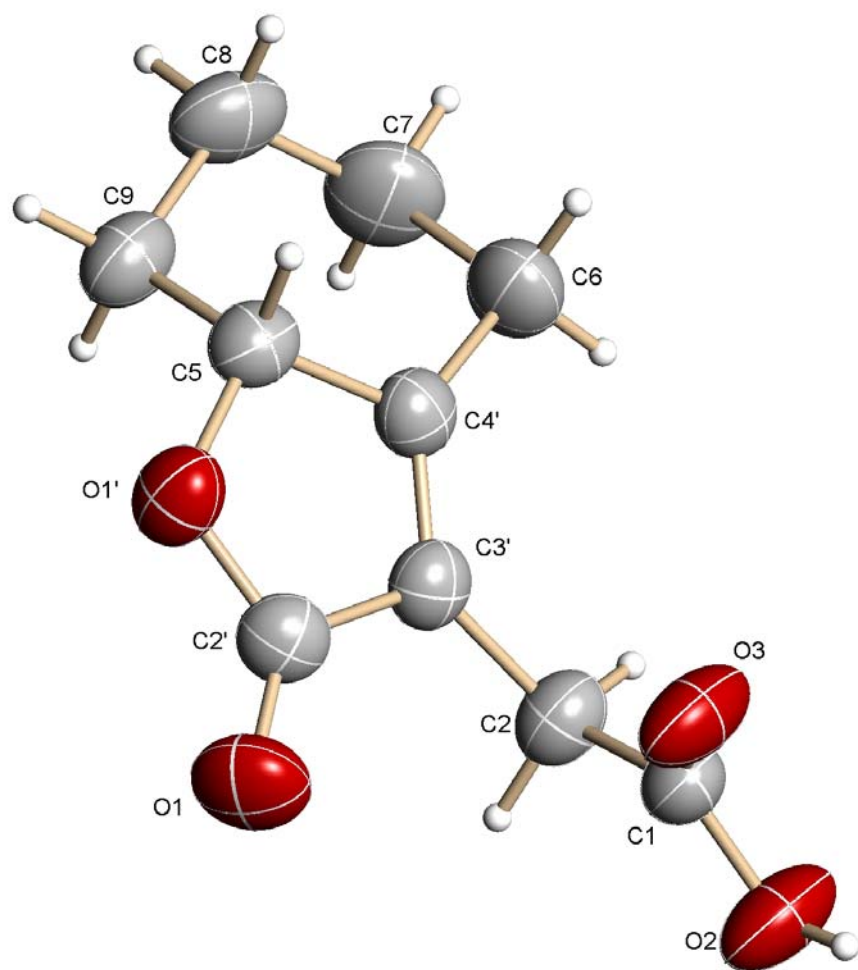
The molecules forms weak hydrogen bonded dimers via $\text{C}=\text{O}^3 \cdots \text{H}^{4'}$ interactions.

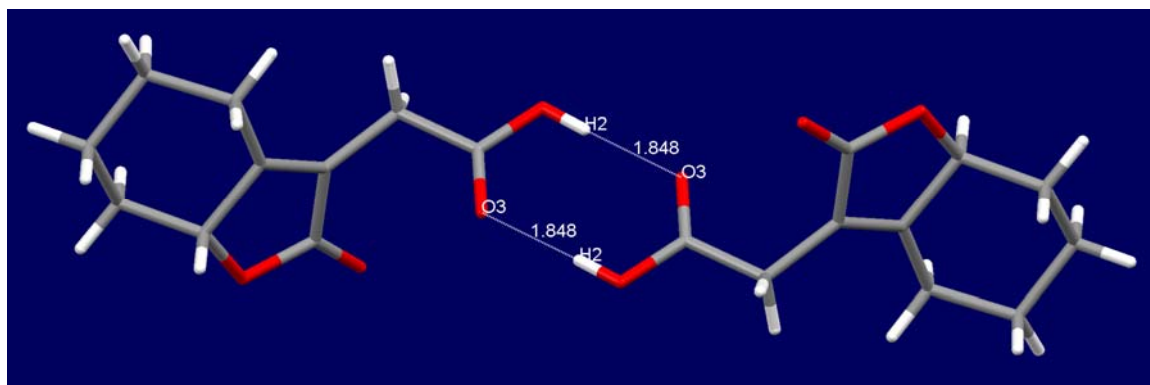
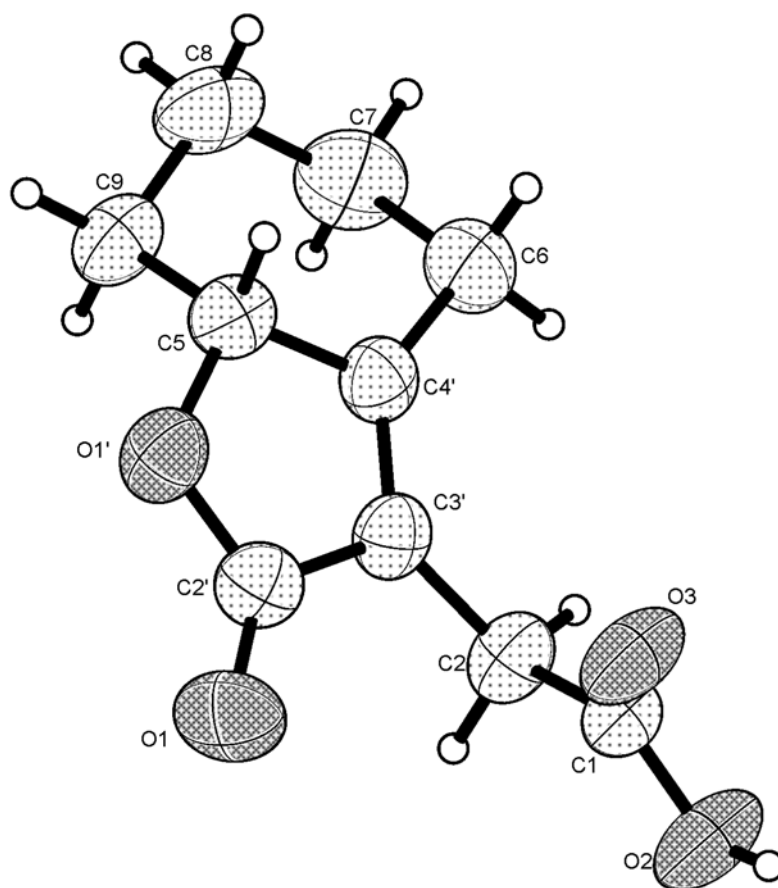


The packing of the molecules viewed down “b” axis with the H-bonding.

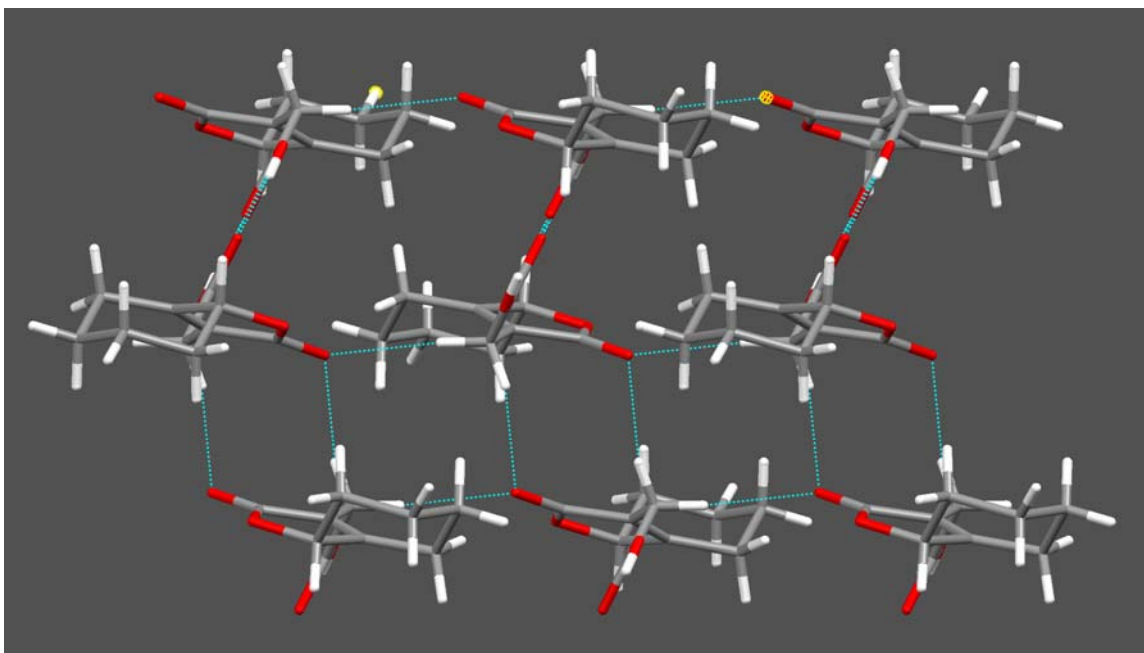
2-(2-Oxo-2,4,5,6,7,7a-hexahydrobenzofuran-3-yl)acetic acid (19): Single crystals of the compound were grown by slow evaporation of the solution mixture of ethylacetate and pet-ether. Colourless plate of approximate size 0.35 x 0.34 x 0.06 mm, was used for data collection. Hemisphere data acquisition. Total scans = 3, total frames = 1271, θ range = 2.34 to 25.00 °, completeness to θ of 25.0 ° is 99.6 %, $C_{10}H_{12}O_4$, $M = 196.20$. Crystals belong to Monoclinic, space group C2/c, $a = 18.725(1)$, $b = 10.4070(9)$, $c = 12.115(1)\text{\AA}$, $\beta = 122.302(1)^\circ$, $V = 1995.5(3)\text{\AA}^3$, $Z = 8$, $D_c = 1.306\text{ g/cc}$, $\mu(\text{Mo-K}\alpha) = 0.101\text{ mm}^{-1}$, 4885 reflections measured, 1753 unique [$I > 2\sigma(I)$], R value 0.0483, $wR2 = 0.1156$. Largest diff. peak and hole 0.203 and -0.185 e. $\text{\AA}^{-3}$.

The compound was confirmed to have a five membered fused γ -lactone ring. The fused six membered ring has chair conformation.





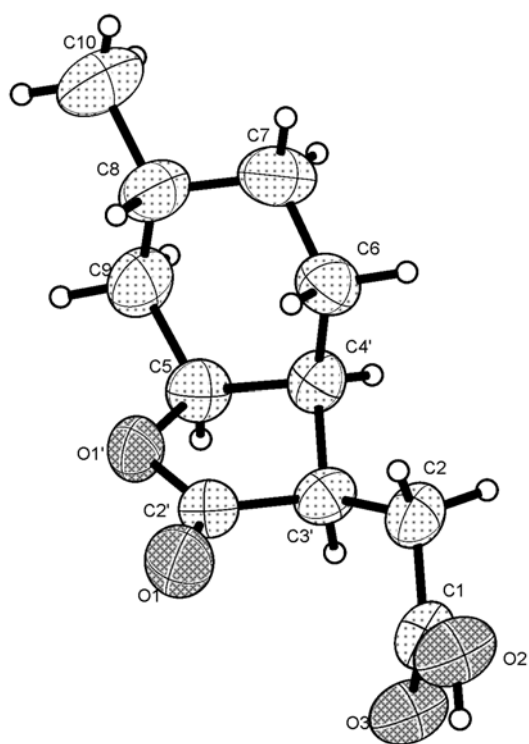
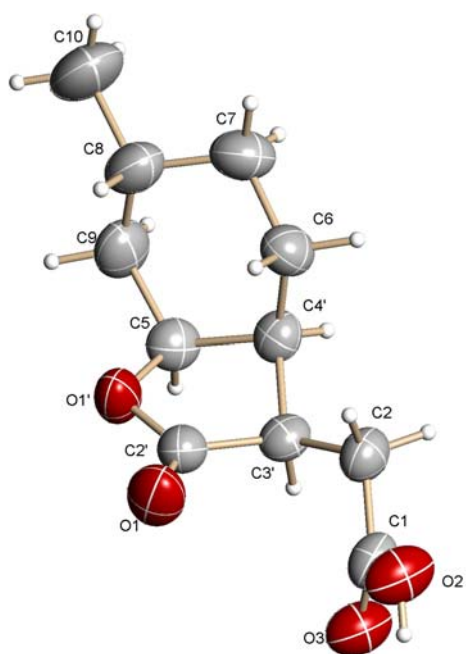
The molecules forms strong hydrogen bonded dimers via $\text{C}=\text{O}^3 \cdots \text{H}^2$ interactions.

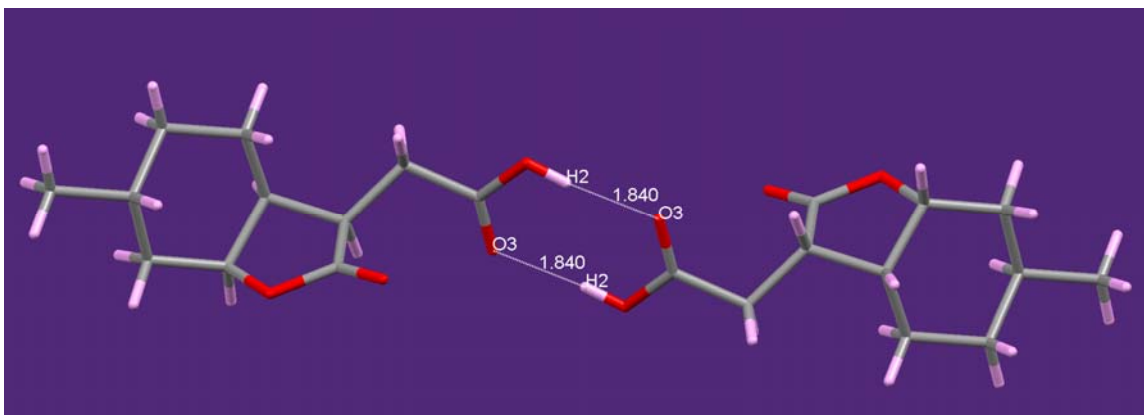


The packing of the molecules viewed down “b” axis with the H-bonding.

2-((±)-6-Methyl-2-oxo-octahydrobenzofuran-3-yl)acetic acid (24): Single crystals of the compound were grown by slow evaporation of the solution mixture of ethylacetate and pet-ether. Colourless needle of approximate size 0.38 x 0.08 x 0.05 mm, was used for data collection. Hemisphere data acquisition. Total scans = 3, total frames = 1271, θ range = 1.78 to 25.00 °, completeness to θ of 25.0 ° is 99.5 %, $C_{11}H_{16}O_4$, $M = 212.24$. Crystals belong to Monoclinic, space group $P2_1/n$, $a = 6.1283(7)$, $b = 8.099(1)$, $c = 22.952(3)$ Å, $\beta = 92.622(2)^\circ$, $V = 1138.0(2)$ Å³, $Z = 4$, $D_c = 1.239$ g /cc, μ (Mo– K_α) = 0.094 mm⁻¹, 5472 reflections measured, 1990 unique [$I > 2\sigma(I)$], R value 0.0617, wR2 = 0.1502. Largest diff. peak and hole 0.151 and -0.171 e. Å⁻³.

The compound was confirmed to have a five membered fused γ -lactone ring. The fused six membered ring has chair conformation. The relative stereochemistry at C6, C7 and C11 is found to be cis as shown below.

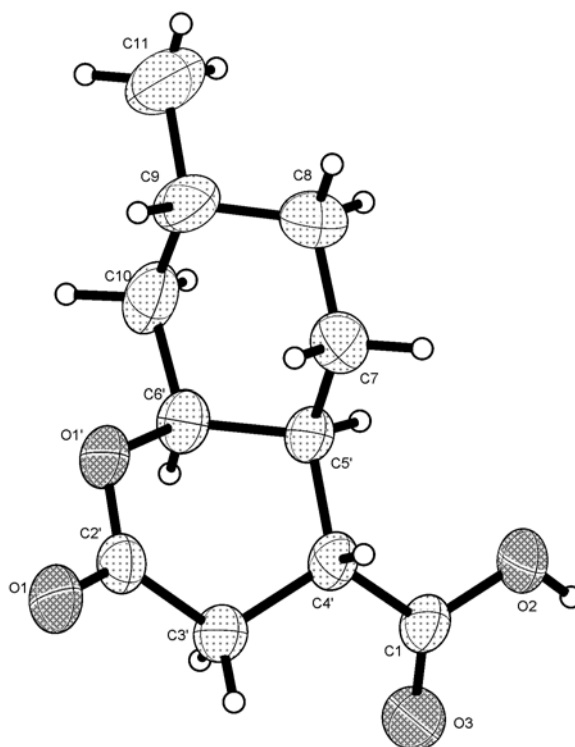
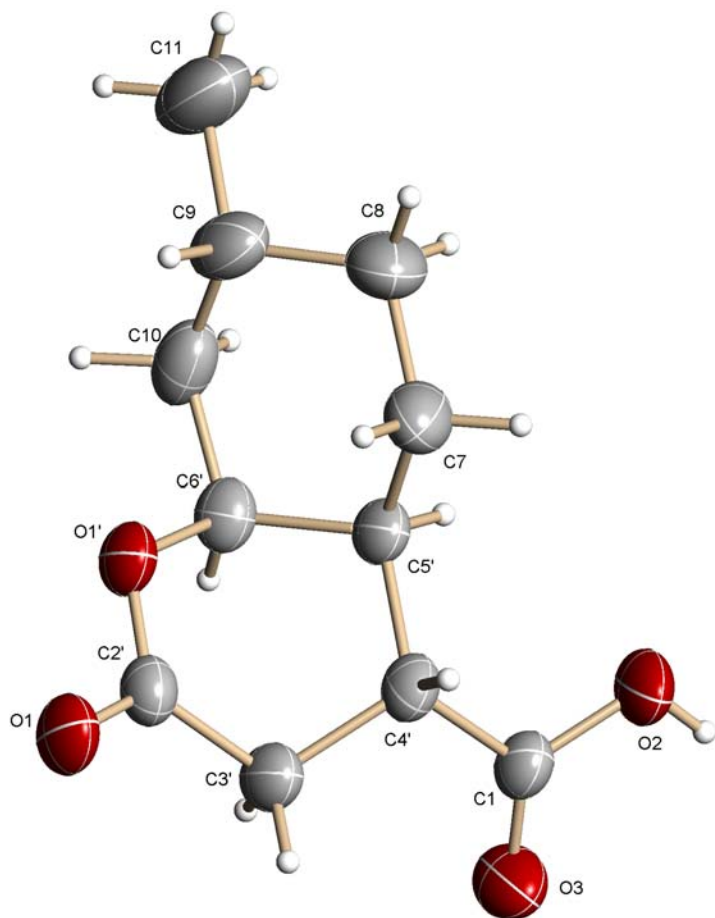




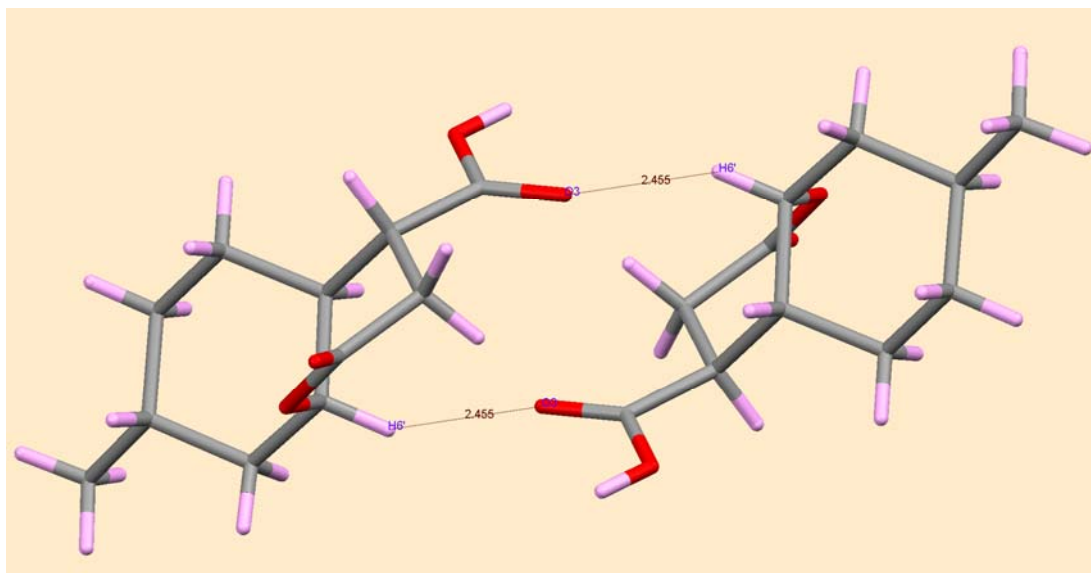
The molecules forms strong hydrogen bonded dimers via $\text{C}=\text{O}^3 \cdots \text{H}^2$ interactions.

(±)-7-Methyl-2-oxo-octahydro-2H-chromene-4-carboxylic acid (28): Single crystals of the compound were grown by slow evaporation of the solution mixture of ethylacetate and pet-ether. Colourless needle of approximate size 0.33 x 0.14 x 0.08 mm, was used for data collection. Hemisphere data acquisition. Total scans = 3, total frames = 1271, θ range = 2.08 to 24.99 °, completeness to θ of 24.99 ° is 99.7 %, $\text{C}_{11}\text{H}_{16}\text{O}_4$, $M = 212.24$. Crystals belong to Monoclinic, space group $\text{P2}_1/\text{c}$, $a = 10.4595(10)$, $b = 8.2649(8)$, $c = 13.482(1)$ Å, $\beta = 110.602(2)$ °, $V = 1090.95(18)$ Å³, $Z = 4$, $D_c = 1.292$ g /cc, μ (Mo- $\text{K}\alpha$) = 0.098 mm⁻¹, 5199 reflections measured, 1916 unique [$I > 2\sigma(I)$], R value 0.0395, wR2 = 0.0998. Largest diff. peak and hole 0.169 and - 0.119 e. Å⁻³.

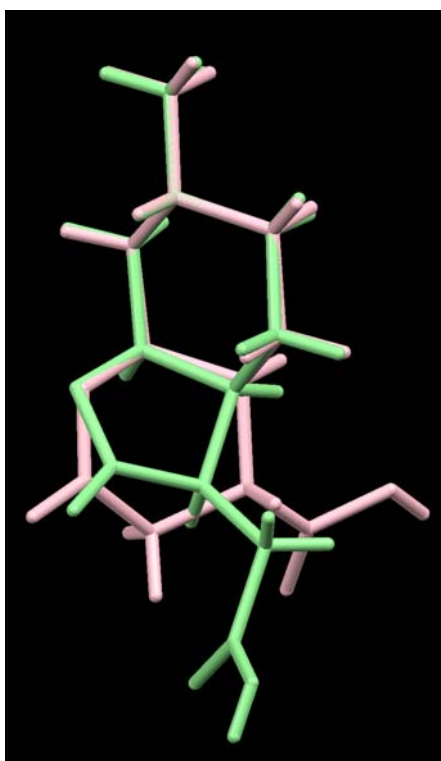
The compound was confirmed to have a six membered fused lactone ring. The fused six membered ring has chair conformation while the lactone ring has a boat conformation.



S108



The molecules forms weak hydrogen bonded dimers via $\text{C}=\text{O}\cdots\text{H}^6$ interactions.



The overlapping of the molecules 24 and 28 shows the conformational changes by base catalyzed hydrolysis.

Caption to Figures

Fig 1.: ORTEP diagram of the molecule compound 2-(5-Methyl-2-oxo-2,5-dihydrofuran-3-yl)acetic acid (**8**) Ellipsoids are drawn at 50% probability.

Fig 2.: ORTEP diagram of the molecule compound 2-(2-Oxo-2,4,5,6,7,7a-hexahydrobenzofuran-3-yl)acetic acid (**19**) Ellipsoids are drawn at 50% probability.

Fig 3.: ORTEP diagram of the molecule compound 2-((±)-6-Methyl-2-oxo-octahydrobenzofuran-3-yl)acetic acid (**24**) Ellipsoids are drawn at 50% probability.

Fig 4.: ORTEP diagram of the molecule compound (±)-7-Methyl-2-oxo-octahydro-2*H*-chromene-4-carboxylic acid (**28**) Ellipsoids are drawn at 50% probability.

Reference

G. M. Sheldrick, SHELX-97 program for crystal structure solution and refinement, University of Gottingen, Germany, 1997