Supporting Information

For

Green and sustainable dearomative cycloaddition of arenes via visible-light energy transfer catalysis: an atom economic synthesis of *N*-heterocyclic skeletons

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1. MATERIALS AND METHODS

All air- and moisture-insensitive reactions were carried out under ambient atmosphere and monitored by thin layer chromatography (TLC). Concentration under reduced pressure was performed by rotary evaporation at 35-45 °C at an appropriate pressure. Purified compounds were further dried under high vacuum. Yields refer to purified and spectroscopically pure compounds, unless otherwise stated. Mass spectra and High-Resolution Mass spectral (HRMS) data was carried out using an Agilent6890N GC (JEOL JMS-700) TOF instrument, and the ion source is electrospray ionization (ESI), electronic ionization (EI), CI, and FAB as ion source at National Taiwan Normal University, Taipei City, Taiwan and ESI-TOF(FT-MS solariX) at National Sun Yat-Sen University, Kaohsiung, Taiwan, and LTQ Orbitrap XL (Thermo Fischer Scientific) at National Chung Hsing University. Liquid-chromatography mass spectra (LCMS) were measured using the LC-MS/MS-8045 (Shimadzu Corporation, Japan) at Kaohsiung Medical University, Kaohsiung, Taiwan. Melting points were determined on an EZ-Melt (Automated melting point apparatus).

Solvents

Bottle grade 2-MeTHF, MeOH, DMSO, Anisole and Ethyl acetate were purchased from Alfa acer. All deuterated solvents were purchased from Sigma-Aldrich.

Chromatography

Thin layer chromatography (TLC) was performed using Merck TLC aluminum sheets (silica gel 60 F254) and visualized by fluorescence quenching under UV light. Flash column chromatography was performed using silica gel (40-63 µm particle size) purchased from Merck.

Photochemistry

All reactions with blue light were carried out using 1 x 40 W Kessil Blue LED (Kessil A160WE Controllable LED Aquarium Light) lamp purchased from Amazon (Taiwan) with an output centered at a wavelength of approximately λmax = 456 nm. The reaction vials were cooled with a fan while being irradiated under blue light.

See the following links for more details.

https://www.kessil.com/aquarium/saltwater_A160.php

https://www.kessil.com/support/downloadfiles/aquarium/A160WE_UserManual.pdf

Spectroscopy and Instruments

^{1}H, ^{13}C, and DEPT NMR spectra were recorded on a 400 and 600 MHz Varian Unity Plus or Varian Mercury plus spectrometer or JEOL ECS-400. The chemical shift (δ) values are reported in ppm, and the coupling constants (J) are given in Hz. For ^{1}H NMR: $CDCl_3$, δ 7.26; CD_3CN, δ 1.96; CD_2Cl_2, δ 5.32; $(CD_3)_2SO$, δ 2.50; For ^{13}C NMR: $CDCl_3$, δ 77.16; 1.32; CD_2Cl_2, δ 53.84; $(CD_3)_2SO$, δ 39.52.[1] The abbreviations used are as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of doublet of doublet, dt = doublet of triplets, td = triplet of doublet, m = multiplet, br = broad; coupling constants in Hz; integration.

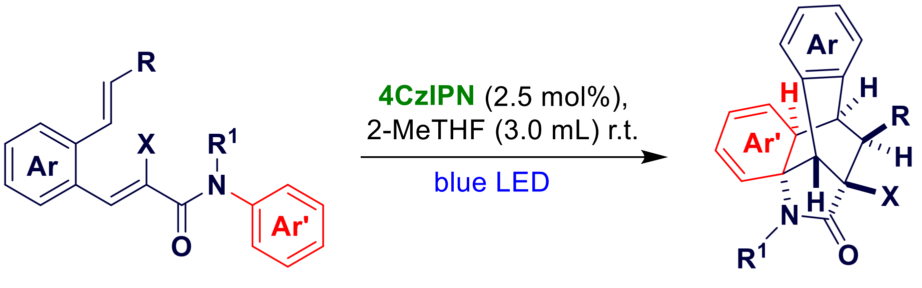
Starting materials

All substrates were used as received from commercial suppliers, or prepared according to published procedures, respectively, unless otherwise stated. Photocatalysts were purchased from Sigma Aldrich, TCI and Alfa Aesar, and stored in an under vacuum/dark hood cabinet. Aldehydes, Alkenes, *N*-substituted amines were purchased from Sigma-Aldrich, Acros, TCI, or Alfa Aesar.

2. EXPERIMENTAL DATA

General procedure and reaction condition optimization for cascade dearomatization

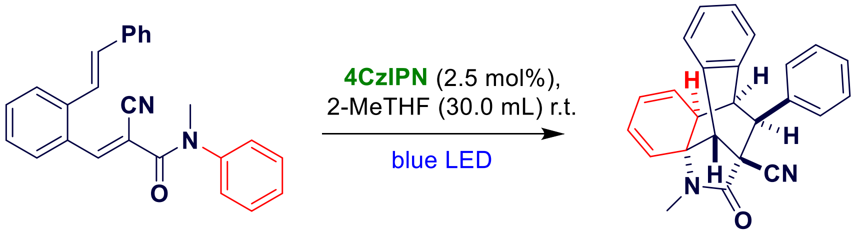
a) General procedure for dearomatization



1 **2-42**

A clean vial (5 mL) equipped with a magnetic stir bar were added to **3** (0.2 mmol) 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 40 W blue LED lamp, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **2-42** derivatives.

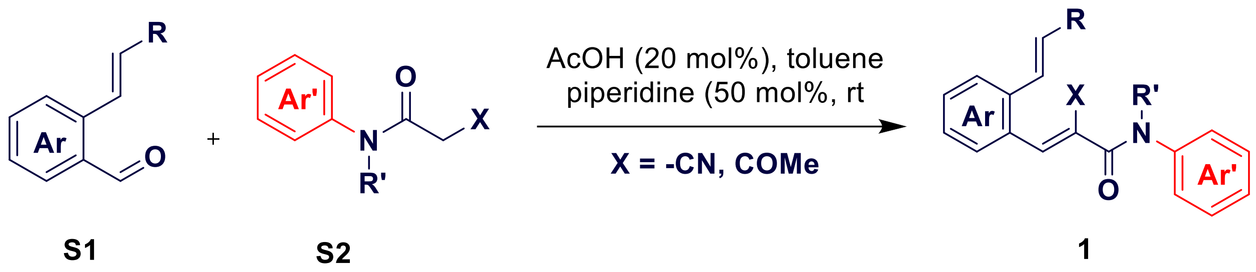
b) General procedure for gram scale synthesis of 2.



1a, 1.1 gm **2,** 803 mg, 73% yield

A clean vial (5 mL) equipped with a magnetic stir bar were added to **1a** (3.0 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (30.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 40 W blue LED lamp, and the solution was stirred at room temperature under visible-light irradiation for 24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **2** derivatives in 73% (803 mg) yield.

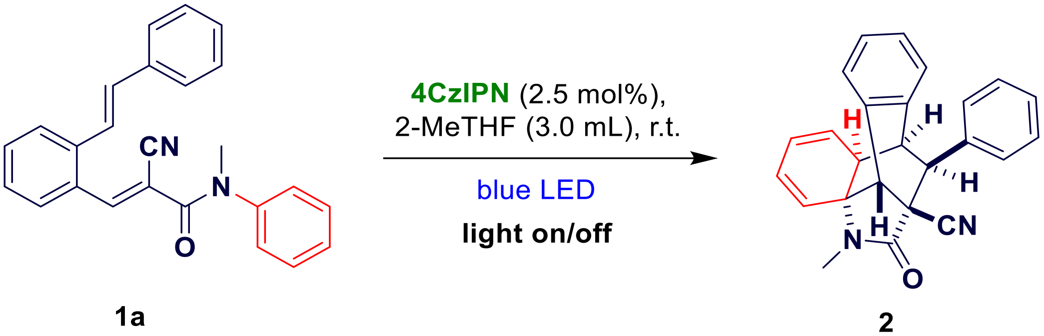
c. General Procedure for the Synthesis of analogous (1).[1]



A reaction tube was charged with (*E*)-1-Formyl-2-(2-aryl-(alkene) alkenyl) benzene (**S1**) (1.0 equiv), **S2** derivatives (1.2 equiv), acetic acid (20 mol%) and piperidine (20 mol%), in 3.0 mL of toluene. The reaction suspension was stirred at room temperature and progress of reaction was monitored by TLC. Upon completion water was added to quench the reaction mixture and then extracted with the ethyl acetate (3 × 20 mL). Finally combined organic layer was dried over sodium sulphate, filtered and concentrated in vacuum. The residue was purified by column chromatography on silica gel to afford the corresponding **1** derivative.

3. CONTROL STUDIES

a) Light On-Off Experiment



A light on/off experiment was performed separately by using the model reaction of **1a** irradiated under the standard catalytic system respectively. The reaction proceeded over a period of time under alternating cycles of irradiation and darkness (0-240 minutes for product **2**), and the progress was monitored by TLC analysis. As shown in Figure S1, cyclization product **2** was only formed under irradiation with blue LED.

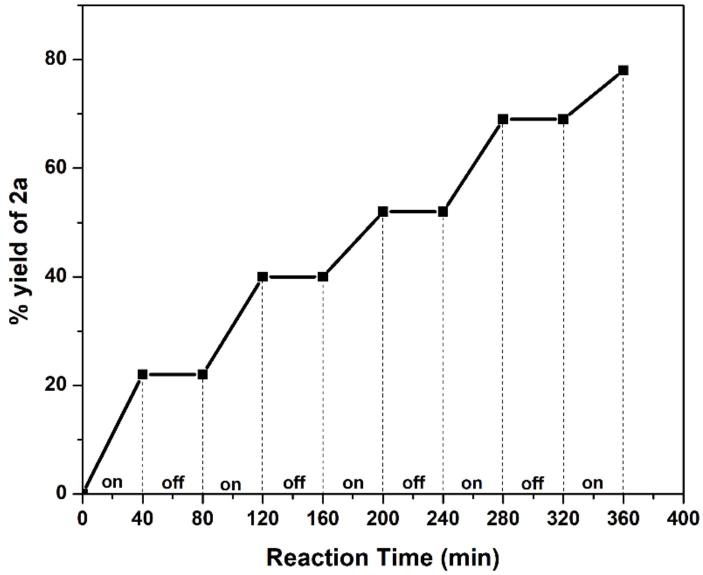


Figure S1. Visible-light Irradiation ON/OFF Experiments for product **2** respectively.

b. Fluorescence Quenching Study

A solution of 4CzIPN in acetonitrile at 25 °C was excited at 320 nm and the intensity of emission spectrum was measured at 480 nm (emission maximum). The fluorescence quenching experiments demonstrated that substrates **1a** efficiently quenches the excited state of the 4CzIPN photocatalyst under the standard reaction conditions respectively (Figure S2).

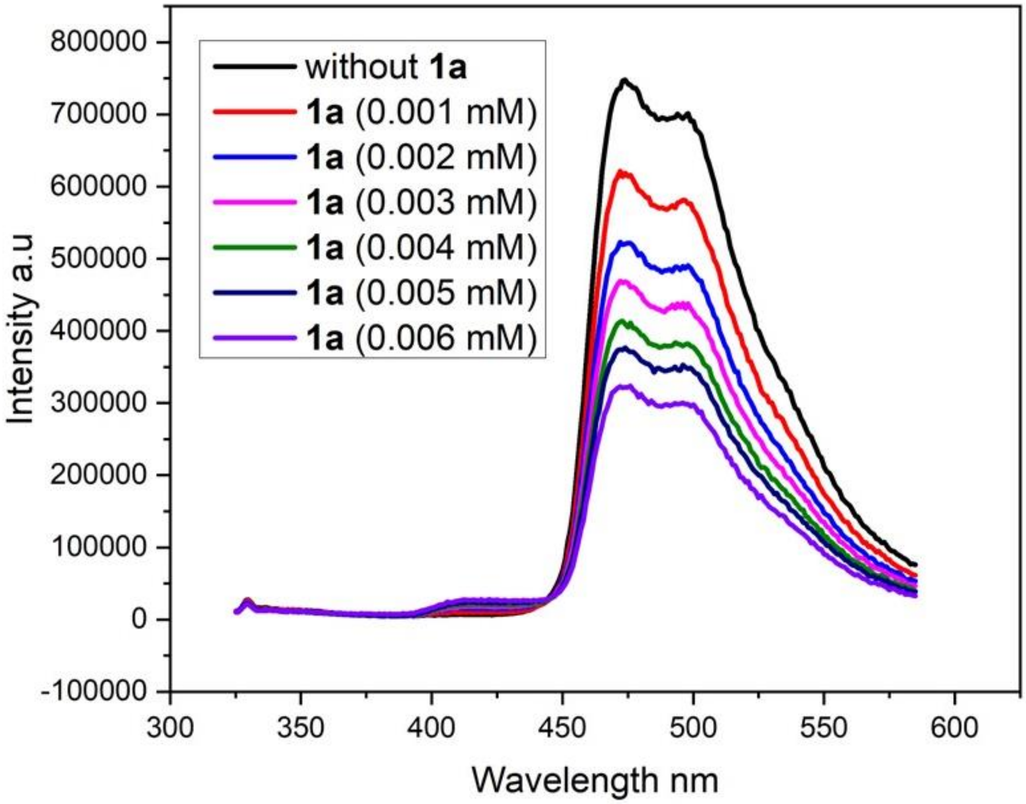


Figure S2. Fluorescence quenching of 4CzIPN (0.05 mM) of **1a** in acetonitrile.

4. Evaluation of Green Metrics of the Process.

Atom economy defined as “how much of the reactants remain in the final desired product"

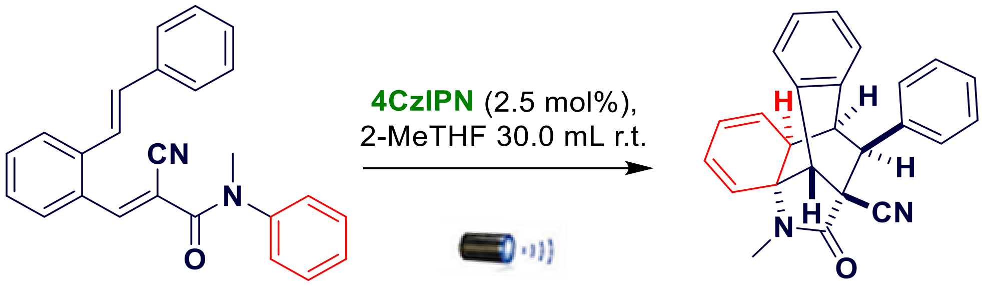
$$\text{Atom economy (AE)} = \frac{\text{Molecular mass of desired product}}{\text{Molecular mass of all reactants}} \times 100$$

Reaction mass efficiency (RME) defined as “the percentage of the mass of the reactants that remain in the product”

$$\underset{\text{(RME)}}{\text{Reaction mass efficiency}} = \frac{\text{mass of desired product}}{\text{mass of all reactants}} \times 100$$

Evaluation of Green metrics for the current process

Reaction Scheme



1a, 1.1 gm

2, 0.803 gm

Total = 364.16

Product yield 73%

Reactant 1	((*E*)-2-cyano-N-methyl-N-phenyl-3-(2-((*E*)-styryl)phenyl)acrylamide (**1a**)	1.1 gm	0.003021 mol	FW 364.16
Auxiliary	4CzIPN	0.0596 gm	0.00000755 mol	788.89
Product	3-methyl-2-oxo-13-phenyl-2,3,8,12*b*-tetrahydro-1,8-methanodibenzo[*e*,*h*]indole-1(7a*H*)-carbonitrile (**2**)	0.803 gm	0.002205 mol	FW 364.16

$$\text{E-factor} = \frac{1.1\text{ gm} + 0.0596\text{ gm} - 0.803\text{ gm}}{0.803} = 0.444\text{ kg waste / 1 kg product}$$

$$\text{Atom economy} = \frac{364.16}{364.16} \times 100 = 100\%$$

$$\text{Atom efficiency} = \frac{73 \times 100}{100} = 73\%$$

$$\text{Carbon efficiency} = \frac{25}{25} = 100\%$$

$$\text{Reaction mass efficiency} = \frac{0.803\text{ gm}}{1.1\text{ gm}} \times 100 = 73\%$$

5. Computational Methods

The DFT calculations were done by using the Gaussian 16 package.[2] The M06-2X functional[3] in combination with the double-zeta quality basis sets Def2-SVP was adopted for geometry optimization and vibrational frequency calculations. Additional single-point-energy calculations with the triple-zeta quality basis sets Def2-TZVP were performed to provide more accurate electronic energies. All the calculations include the solvent effect (solvent = N,N-dimethylacetamide) treated by the SMD solvation model.[4] The open-shell singlet diradical states involved in the reaction mechanism were tackled by the broken-symmetry approach. The free energies were evaluated at the standard conditions of 1 atm and 298.15 K. The values of spin density were provided by the natural population analysis (NPA).

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1a-singlet

O	10.45060900	5.02438900	3.24119800
N	10.24144700	6.83693500	1.89644200
N	7.42451000	3.18433100	2.74029300
C	9.74120400	5.79249400	2.61960700
C	8.24072800	5.64455500	2.70757500
C	7.40576500	6.68917900	2.87415900
H	7.85106200	7.68690100	2.80502600
C	9.52750800	7.48456300	0.84445400
C	8.88320200	6.73245900	-0.14249700
H	8.93820700	5.64239000	-0.11020300
C	8.17248700	7.37664900	-1.15440400
H	7.66553600	6.78342300	-1.91740300
C	8.12251000	8.77038700	-1.20130200
H	7.57181600	9.27257900	-1.99828600
C	8.78580400	9.51980100	-0.22766400
H	8.75252100	10.61022900	-0.25803200
C	9.48315800	8.88155700	0.79643900
H	9.98586300	9.46213500	1.57256300
C	5.86908800	4.98144200	4.93508500
H	5.44201600	3.98481200	5.08964900
C	5.22548500	5.79559100	3.88576900
C	3.82580800	5.75756900	3.78312400
H	3.27239900	5.08300600	4.43999700
C	3.13831700	6.57762000	2.89375100
H	2.04910100	6.53189200	2.84391400
C	3.84265700	7.46886200	2.08242500
H	3.31280500	8.12726600	1.39249200
C	5.23126400	7.50687500	2.15155500
H	5.79267100	8.18511700	1.50396300
C	5.93819900	6.65368500	3.01544900
C	6.87465500	5.40688100	5.71628400
H	7.23588700	6.43553300	5.60689700
C	7.55620200	4.60142200	6.74213800
C	8.32161300	5.24798300	7.72569300
H	8.39984000	6.33756500	7.70797700

C	8.97096600	4.51847200	8.72024700
H	9.55720400	5.03903400	9.47979300
C	8.87415800	3.12685300	8.74246800
H	9.38486400	2.55308600	9.51788400
C	8.13038300	2.47013000	7.75840300
H	8.06505500	1.38047400	7.75988600
C	7.48108900	3.19774900	6.76491200
H	6.92894400	2.67144700	5.98352900
C	7.78277600	4.28315000	2.73393600
C	11.67940700	7.06816500	1.99777800
H	11.90629200	8.07570100	1.63344400
H	12.23904000	6.33353900	1.39778400
H	11.99388500	6.97811900	3.04381600

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TS1-singlet

O	10.41756800	4.52828100	3.33950800
N	9.78561900	6.53796300	2.54240400
N	8.14267500	2.11198900	3.26286900
C	9.53039900	5.25147900	2.92054800
C	8.11548600	4.68698400	2.88702000
C	7.02207400	5.05756400	2.04010200
H	6.77473300	4.34225200	1.24699900
C	8.91525200	7.37685700	1.77821600
C	8.76687700	7.16023200	0.40592300
H	9.28741800	6.32181000	-0.06158100
C	7.95123100	8.00664200	-0.34363300
H	7.82880800	7.83324000	-1.41425800
C	7.29528600	9.07374200	0.27352400
H	6.65453700	9.73337600	-0.31449400
C	7.45677400	9.29616000	1.64184200
H	6.94561100	10.12997400	2.12640600
C	8.27091000	8.45049600	2.39562400
H	8.40601000	8.61331000	3.46752800
C	6.33446900	6.05386100	4.71582300
H	5.70986600	5.92333400	5.60595800
C	5.70514600	6.53217000	3.55986500
C	4.48654300	7.28798400	3.68616900
H	4.19057900	7.60383400	4.68865300
C	3.73936600	7.64237200	2.60160800
H	2.84325800	8.25221000	2.72878600
C	4.10992200	7.19436800	1.29541800
H	3.49287800	7.46305300	0.43641900
C	5.21566700	6.41520400	1.13021100
H	5.48685200	6.04257600	0.14013000
C	6.07931400	6.07170400	2.23291900
C	7.68342200	5.66125400	4.77480000
H	8.38120100	6.40579200	4.39395900
C	8.19976000	4.83676500	5.88157000
C	9.50286600	5.03831300	6.36127200
H	10.12073700	5.82055400	5.91447100
C	9.99972400	4.25843500	7.40342900
H	11.01143700	4.42928000	7.77556600
C	9.20579300	3.25876100	7.96886600
H	9.59686800	2.64527700	8.78262300
C	7.91376000	3.03843000	7.48610100
H	7.29574300	2.24940500	7.91826100
C	7.41485000	3.81800300	6.44508800
H	6.41201200	3.63148700	6.05280500
C	8.19072900	3.24893900	3.05631300
C	11.15761900	7.01486200	2.69597400

H	11.14102900	8.10779700	2.78278200
H	11.77678000	6.73433000	1.82838200
H	11.60055100	6.58128800	3.59923600

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A-singlet

O	10.05950200	4.03534200	3.08618500
N	9.93169800	6.23617900	2.60122900
N	7.15868900	2.40378500	3.29194600
C	9.37902900	5.02016400	2.88113400
C	7.84055700	4.93916900	3.08108200
C	7.00116900	5.45186800	1.92349000
H	7.37626200	5.27819000	0.91408900
C	9.24887100	7.35005600	2.00818800
C	9.02979300	7.36635100	0.62764600
H	9.35632400	6.51559200	0.02584100
C	8.37862900	8.44880000	0.03921400
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H	7.44839500	10.37053200	0.36488200
C	8.22287400	9.52845000	2.19595700
H	7.91777700	10.37718000	2.81018000
C	8.87526100	8.44720500	2.78788800
H	9.09281800	8.44736500	3.85798900
C	5.99281300	5.85157600	4.55958900
H	5.58306900	5.93982400	5.56920400
C	5.19255400	6.03841800	3.48697600
C	3.77810700	6.37353000	3.61896400
H	3.35312200	6.39756000	4.62483600
C	3.03148600	6.67696200	2.53591500
H	1.97957000	6.94480100	2.64888900
C	3.61211600	6.66623300	1.19826400
H	2.97874000	6.93322300	0.35033300
C	4.90292100	6.32356100	0.99915200
H	5.33429600	6.29844000	-0.00407500
C	5.75860400	5.94454800	2.11988600
C	7.47971900	5.67622700	4.41406300
H	7.89504700	6.69058800	4.29437100
C	8.15544600	5.05045000	5.61609900
C	9.42366100	5.49181200	6.01306400
H	9.90347200	6.30639900	5.46319000
C	10.07214600	4.90497700	7.09911300
H	11.05893300	5.26212800	7.39924500
C	9.45846200	3.86756700	7.80252600
H	9.96377500	3.40898700	8.65443300
C	8.19424600	3.42223800	7.41532900
H	7.70680600	2.61343300	7.96265900
C	7.54649000	4.01059900	6.32879500
H	6.55623400	3.65701300	6.03095800
C	7.50422800	3.50100100	3.20614600
C	11.39049500	6.31440600	2.60699900
H	11.68289100	7.35673500	2.78157000
H	11.81411000	5.97697000	1.64732800
H	11.78655700	5.68115500	3.40899200

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TS2-singlet

O	11.24397900	4.96192300	3.04214500
N	10.07776200	6.53897200	1.86720200
N	9.00522600	2.44830400	3.71008500
C	10.20357200	5.48246400	2.70391400
C	8.82072100	5.02257400	3.22830300

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C                  7.79323700    5.19689100    2.12946300
H                  8.01186100    4.65276800    1.20637400
C                  8.80498500    7.18255900    1.71199100
C                  8.27990100    7.35245300    0.38966600
H                  8.67427000    6.72028200   -0.40921900
C                  7.26473500    8.23720100    0.16326400
H                  6.82311400    8.32039200   -0.83124700
C                  6.81849500    9.11208400    1.21001800
H                  6.04593300    9.85227200    0.99307300
C                  7.41388700    9.07996200    2.43849900
H                  7.13598500    9.80161700    3.21000600
C                  8.38647900    8.07688800    2.75396000
H                  9.09426100    8.27243500    3.56193300
C                  7.35195000    6.83812300    4.26444900
H                  7.21215700    7.59160800    5.04481900
C                  6.24401700    6.45785200    3.50477200
C                  4.96286500    7.07755300    3.63691600
H                  4.79447900    7.75726800    4.47541800
C                  3.96172000    6.80694600    2.74189600
H                  2.97747300    7.26169500    2.86761800
C                  4.19481500    5.93905500    1.63195000
H                  3.38590900    5.74563400    0.92518100
C                  5.42351900    5.36697800    1.44239000
H                  5.61425600    4.71985000    0.58337900
C                  6.48267900    5.58831800    2.38372800
C                  8.48019600    5.86339900    4.52585900
H                  9.38164000    6.43301400    4.79092300
C                  8.15529200    5.01166300    5.74578200
C                  9.04895600    4.99210400    6.82113200
H                  9.96106000    5.59161000    6.77161600
C                  8.78753300    4.21403000    7.95067700
H                  9.49468600    4.21161800    8.78218900
C                  7.62791600    3.44362300    8.01431200
H                  7.42081700    2.83451700    8.89605000
C                  6.73160700    3.45405600    6.94287700
H                  5.82313600    2.85042100    6.98350200
C                  6.99129100    4.23405500    5.81830900
H                  6.28546800    4.23005900    4.98446800
C                  8.93984100    3.58484500    3.52373300
C                 11.25651400    7.21423800    1.34959500
H                 11.14524600    7.39007000    0.27118200
H                 12.12891400    6.57623200    1.52833100
H                 11.40165500    8.18152300    1.85551800
                          48
                      2a-singlet
O                 11.29198800    4.80257500    2.72854700
N                 10.05951500    6.43853300    1.67580900
N                  8.69915900    2.37115600    3.22527900
C                 10.24883200    5.35262700    2.45783400
C                  8.85362600    4.97035300    3.00880900
C                  7.91822600    5.54469800    1.90779300
H                  7.97354700    4.92589500    1.00275700
C                  8.66454500    6.89554000    1.66009800
C                  8.29181800    7.46252100    0.31863800
H                  8.56465700    6.85560800   -0.54924900
C                  7.60966900    8.60630100    0.18269300
H                  7.32147800    8.95176700   -0.81230900
C                  7.23397800    9.42528700    1.34319000
H                  6.66043700   10.33808200    1.17212400
C                  7.60567500    9.07672500    2.58084200
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H                   7.34626100    9.70493200    3.43821600
C                   8.41336100    7.84496200    2.87939900
H                   9.39916100    8.17988400    3.24696700
C                   7.75797900    7.02042100    4.02276800
H                   7.66407000    7.63889700    4.92550500
C                   6.42067500    6.54461200    3.53297000
C                   5.17843600    6.80728900    4.10339100
H                   5.10755800    7.42663200    5.00051200
C                   4.03032600    6.25941900    3.52362100
H                   3.05244700    6.45587700    3.96720900
C                   4.12628300    5.45965000    2.38271300
H                   3.22412500    5.03499000    1.93886600
C                   5.37255700    5.20109400    1.80498800
H                   5.45428400    4.57622300    0.91292600
C                   6.51553100    5.74757500    2.38425800
C                   8.64801400    5.78241400    4.34964500
H                   9.63526300    6.16606200    4.64492300
C                   8.11382700    5.00729200    5.53746700
C                   8.74564500    5.17163900    6.77662900
H                   9.62863700    5.81184000    6.84381600
C                   8.26581200    4.53268400    7.92016400
H                   8.77565000    4.67546100    8.87469000
C                   7.14202800    3.71144700    7.84029800
H                   6.76454200    3.20678700    8.73148100
C                   6.50483700    3.53537100    6.61122700
H                   5.62630600    2.89184300    6.53731300
C                   6.98348800    4.17787500    5.46977300
H                   6.46759000    4.02218800    4.52002400
C                   8.76500500    3.52037200    3.14897400
C                  11.14468300    7.25484200    1.18308300
H                  11.11670200    8.25587700    1.64264100
H                  11.08903400    7.36622500    0.09123300
H                  12.08873100    6.76365800    1.44745400
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                    1a-triplet
O                   9.54383700    3.86908900    3.18301900
N                   9.69396200    6.09609500    2.75975400
N                   6.72034000    2.45529900    1.81106400
C                   9.05866800    4.88750200    2.71791300
C                   7.68152000    4.82826900    2.12621300
C                   6.78493500    5.91325800    1.69357200
H                   6.98593800    6.32922500    0.70113200
C                   9.35181000    7.17957300    1.89350700
C                   9.55261300    7.05322500    0.51627700
H                   9.96591200    6.12301100    0.11978000
C                   9.20031700    8.10128200   -0.33360300
H                   9.34349200    7.99723800   -1.41049300
C                   8.66894000    9.27943700    0.19307100
H                   8.39157000   10.09846300   -0.47266700
C                   8.50037800    9.41463900    1.57321800
H                   8.09120300   10.33771600    1.98703400
C                   8.84545400    8.36836400    2.42636900
H                   8.70847300    8.45659900    3.50637100
C                   5.91493800    5.16596900    4.54108800
H                   5.49744900    4.34380700    5.13240000
C                   5.03824200    5.75757900    3.52447900
C                   3.68097800    5.92049600    3.83655700
H                   3.31215100    5.51252100    4.78037600
C                   2.82008400    6.63249700    3.00734800
H                   1.77390400    6.76193500    3.28843300
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C	3.31139500	7.20153900	1.82184400
H	2.64918200	7.77953400	1.17508800
C	4.62927300	7.00385200	1.45707300
H	5.00215000	7.40310200	0.51126700
C	5.52070000	6.23623300	2.26139400
C	7.13093100	5.66472400	4.84136900
H	7.46997600	6.56086300	4.31032300
C	8.05974500	5.15157200	5.85406500
C	9.13067100	5.96460200	6.25712600
H	9.24066700	6.95692000	5.81205800
C	10.04387600	5.52125300	7.21269700
H	10.86940800	6.16745200	7.51694000
C	9.90386800	4.25185500	7.77400100
H	10.61932100	3.89914500	8.51901000
C	8.84719800	3.42878000	7.37227900
H	8.74120600	2.43012000	7.80000200
C	7.93536500	3.87037900	6.41879800
H	7.12984400	3.20854300	6.09416100
C	7.18795100	3.50776000	1.95848700
C	11.00450800	6.15674700	3.39472200
H	11.15799400	7.16439400	3.80187000
H	11.80490800	5.94148300	2.66738300
H	11.04876100	5.42005600	4.20383400

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TS1-triplet

O	9.76141100	3.92667200	3.25380200
N	9.84496800	6.13278500	2.75952900
N	6.67936600	2.53657900	3.02562700
C	9.18608700	4.93490000	2.87250900
C	7.69923800	4.89524300	2.68706800
C	6.86125000	5.80639400	1.89715000
H	7.22613000	6.14912400	0.92857400
C	9.38277000	7.23756400	1.97766500
C	9.51120100	7.19811900	0.58612500
H	9.94854300	6.31443400	0.11623600
C	9.05145400	8.26536300	-0.18395700
H	9.13667400	8.22628000	-1.27126900
C	8.48038200	9.37903900	0.43527900
H	8.11488600	10.21149800	-0.16845900
C	8.38803300	9.43315300	1.82703200
H	7.95472500	10.30840900	2.31384200
C	8.84811300	8.36801800	2.60091800
H	8.78722000	8.40166800	3.69082900
C	5.78345600	5.42031300	4.62592600
H	5.32165800	4.79565400	5.39629800
C	4.95469300	5.87052600	3.53455100
C	3.57320900	6.05271400	3.72633000
H	3.14184700	5.79078500	4.69504200
C	2.77623300	6.60303400	2.73202700
H	1.71062800	6.75691400	2.90759600
C	3.35154200	6.97736900	1.50374000
H	2.73025200	7.42566700	0.72646800
C	4.69551000	6.75668500	1.26598400
H	5.13213300	7.00873900	0.29692300
C	5.52940400	6.15776900	2.24834400
C	7.14112700	5.71943000	4.69049200
H	7.47191600	6.65309000	4.22697100
C	8.04706100	5.15396500	5.69445800
C	9.20875000	5.85997800	6.04842800
H	9.40310300	6.83119200	5.58642900

C	10.10160200	5.33302300	6.97858400
H	10.99730700	5.89433700	7.25085700
C	9.85189900	4.08743200	7.55820500
H	10.55283500	3.67165900	8.28429800
C	8.70655000	3.37085900	7.20238600
H	8.51513200	2.39226700	7.64616900
C	7.81149500	3.89548900	6.27396000
H	6.93179500	3.31802900	5.98113200
C	7.17592100	3.57010100	2.85857400
C	11.25254100	6.16171800	3.13671400
H	11.51487800	7.18449900	3.43664100
H	11.90299200	5.85823400	2.29932700
H	11.41608400	5.47728100	3.97664600

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A-triplet

O	10.15977100	4.05546500	3.12912800
N	9.93007700	6.22810800	2.55014300
N	7.28584600	2.33012800	3.37155400
C	9.43801600	5.00368300	2.89541400
C	7.90274700	4.87288500	3.10431500
C	7.08112500	5.34400700	1.93505400
H	7.43023000	5.07649300	0.93813500
C	9.16792200	7.31268900	2.00105900
C	8.88902400	7.33712100	0.62987900
H	9.23180800	6.51201300	0.00225700
C	8.16216400	8.39350500	0.08608300
H	7.93297900	8.40054600	-0.98087300
C	7.72878800	9.43887200	0.90501600
H	7.15332300	10.26297300	0.47996300
C	8.04747700	9.43785600	2.26282500
H	7.73102100	10.26402800	2.90153700
C	8.77876700	8.38293400	2.81063900
H	9.04969600	8.38564700	3.86840100
C	6.02742100	5.77275400	4.54800500
H	5.58285100	5.85061600	5.54138100
C	5.23279900	6.11189100	3.40132500
C	3.93365900	6.61601600	3.52299100
H	3.50642300	6.73806500	4.52076100
C	3.18744900	6.97555500	2.39042200
H	2.17784100	7.37143700	2.51201100
C	3.73467000	6.82881800	1.12049000
H	3.15969900	7.10980100	0.23672000
C	5.02630300	6.30336500	0.97232200
H	5.45061900	6.16306500	-0.02461100
C	5.78543700	5.93332000	2.08954000
C	7.50633900	5.61605300	4.43837700
H	7.93312300	6.62561900	4.31487000
C	8.16513100	5.00079200	5.65521600
C	9.43048600	5.44480200	6.05833800
H	9.91820200	6.24919500	5.50009100
C	10.06557600	4.87504300	7.16113200
H	11.05016400	5.23429000	7.46592400
C	9.44073200	3.85164600	7.87518900
H	9.93520900	3.40613700	8.74032600
C	8.18002800	3.40251800	7.48074000
H	7.68522200	2.60322100	8.03542900
C	7.54612900	3.97340800	6.37681400
H	6.56017900	3.61507000	6.07106800
C	7.60708000	3.43336700	3.26326500
C	11.38228100	6.37615500	2.50125700

H	11.63286500	7.42996300	2.67229100
H	11.78329200	6.06537700	1.52316100
H	11.83801900	5.75768600	3.28262700

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TS2-triplet

O	10.51847400	4.47328700	3.49599600
N	9.89153300	6.32313900	2.30879400
N	7.63614700	2.40716000	3.35190900
C	9.66405100	5.20149900	3.04035700
C	8.15373800	4.97821700	3.28256700
C	7.42470200	5.55981400	2.09703000
H	7.64043300	5.04444900	1.15747300
C	8.82617100	7.13249300	1.76882900
C	8.71365400	7.21810800	0.34363800
H	9.18828000	6.44273200	-0.26207200
C	7.95571400	8.21369800	-0.24119900
H	7.83184400	8.22840000	-1.32562900
C	7.36529600	9.21814600	0.54503400
H	6.76864500	10.00185400	0.07631300
C	7.59751100	9.23826800	1.92649300
H	7.20458800	10.05639700	2.53316600
C	8.36505800	8.25318200	2.52707200
H	8.60524000	8.31587900	3.58973900
C	6.32788600	6.05491400	4.69344300
H	5.89363700	6.24808400	5.67614000
C	5.55496300	6.35374200	3.53696600
C	4.25520900	6.89281500	3.64209000
H	3.84493800	7.08527700	4.63587100
C	3.50343500	7.18065900	2.50461900
H	2.50339500	7.60491800	2.61002100
C	4.02166900	6.91656500	1.23547900
H	3.43023000	7.13035200	0.34391300
C	5.30173300	6.36237100	1.10838800
H	5.70580000	6.13635700	0.11896500
C	6.07951300	6.08960200	2.23449600
C	7.76926800	5.66700100	4.64663200
H	8.36249900	6.59852100	4.66342400
C	8.21264700	4.86781900	5.85874700
C	9.45577000	5.11956600	6.44902600
H	10.09722300	5.90089900	6.03496200
C	9.87672500	4.38679400	7.55850300
H	10.84737300	4.59745300	8.01117900
C	9.05683400	3.39122100	8.09086700
H	9.38396000	2.81867100	8.96074200
C	7.81425900	3.13406800	7.50980800
H	7.16609200	2.35894000	7.92272100
C	7.39458700	3.86919500	6.40151100
H	6.42003900	3.66481000	5.95071700
C	7.88901200	3.53323400	3.33887900
C	11.25138600	6.78860500	2.08676100
H	11.38274600	7.79187200	2.51859100
H	11.47034400	6.83470700	1.01027600
H	11.94175500	6.08824100	2.56874700

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B-triplet

O	10.56573300	4.62273100	3.59078900
N	9.78907600	6.33983200	2.27735500
N	7.57639800	2.49331200	3.31003700
C	9.66929900	5.26888800	3.09497700
C	8.16231200	5.04466600	3.34363800

C	7.51984200	5.75033000	2.13197900
H	7.58002700	5.04974000	1.28611200
C	8.53135200	6.91297000	1.77008600
C	8.58164400	7.06281900	0.27310000
H	8.89659000	6.17635800	-0.28404800
C	8.21974500	8.20655800	-0.37401000
H	8.24496900	8.23581000	-1.46521500
C	7.82217100	9.36304300	0.34506100
H	7.53252400	10.26932800	-0.18633800
C	7.85212100	9.34200500	1.76296900
H	7.60124800	10.24936900	2.31623200
C	8.20617400	8.21863400	2.45054200
H	8.24819600	8.24095000	3.54137300
C	6.32096400	6.03612900	4.76527700
H	5.86393800	6.17189900	5.74720500
C	5.54527900	6.31262500	3.61350600
C	4.19253700	6.73168600	3.73615400
H	3.76704000	6.83460800	4.73672700
C	3.42733200	7.00971600	2.61624900
H	2.39207900	7.33538100	2.73276500
C	3.97653000	6.86562800	1.33436600
H	3.37229500	7.07458100	0.45040000
C	5.29987900	6.44117600	1.19136000
H	5.72576300	6.31092200	0.19341600
C	6.09127400	6.17382400	2.30589800
C	7.77382700	5.68542800	4.72445700
H	8.35392500	6.62423100	4.78235300
C	8.21660700	4.84823600	5.91234600
C	9.44910900	5.09741700	6.52580400
H	10.08331800	5.90165100	6.14656300
C	9.86979600	4.33171800	7.61265700
H	10.83215300	4.54099400	8.08333900
C	9.06091400	3.30404000	8.09919900
H	9.38828100	2.70494600	8.95093200
C	7.82891500	3.04922000	7.49554600
H	7.18873800	2.24949900	7.87250800
C	7.40886700	3.81811700	6.41028700
H	6.44178900	3.61483500	5.94339800
C	7.84489900	3.61508200	3.33169300
C	11.06399300	6.94549900	1.96536000
H	11.05028500	8.01411900	2.22817100
H	11.29750600	6.84692600	0.89492200
H	11.83874800	6.43652200	2.55050000

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TS3-triplet

O	11.27115700	4.91258100	2.96815500
N	10.06083600	6.44513800	1.74971400
N	8.68297600	2.43376500	3.34880200
C	10.23079100	5.42426900	2.62258900
C	8.82232100	5.03680400	3.14863100
C	7.91625200	5.57835700	2.02248400
H	8.01118400	4.93575100	1.13739300
C	8.67566300	6.92774900	1.68949500
C	8.24157800	7.35546300	0.32531900
H	8.51047900	6.69773400	-0.50379500
C	7.34415500	8.43225100	0.13308100
H	6.90758000	8.58219000	-0.85621600
C	7.03944400	9.28343600	1.16290000
H	6.34482800	10.11184300	1.01884000
C	7.74857200	9.15133100	2.43347200

H	7.71618200	9.98054100	3.14321900
C	8.48073500	8.02177300	2.74423000
H	9.29913100	8.12660900	3.46305400
C	7.51537300	6.90989900	4.26283800
H	7.43223100	7.62712800	5.08441800
C	6.29423600	6.54184100	3.56973600
C	4.99880900	6.93806000	3.93195100
H	4.84634300	7.53501900	4.83365500
C	3.91549900	6.55061100	3.14418200
H	2.90507400	6.84951300	3.42982900
C	4.11150300	5.78116900	1.99303100
H	3.25622200	5.48281800	1.38453000
C	5.40338100	5.40724700	1.61121900
H	5.56893000	4.83364200	0.69619100
C	6.48872400	5.79365300	2.39271900
C	8.55624800	5.82181200	4.49237300
H	9.49924900	6.31308500	4.77307400
C	8.16089000	4.96099300	5.68304400
C	8.95828900	4.97847800	6.83264400
H	9.86596300	5.58650000	6.84545700
C	8.60743700	4.22928600	7.95705100
H	9.24266900	4.25462500	8.84438500
C	7.45147100	3.45069400	7.94436700
H	7.17485800	2.86325900	8.82171700
C	6.64914800	3.42484800	6.80118100
H	5.74389100	2.81529400	6.78181700
C	6.99833500	4.17507200	5.68022900
H	6.36373400	4.14032900	4.79153600
C	8.74611500	3.58376800	3.28173400
C	11.16051300	7.22450700	1.22913500
H	11.17226300	8.23109800	1.67724900
H	11.07959700	7.32406500	0.13770800
H	12.09514000	6.70809700	1.47763300

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2a-triplet

O	11.28656500	4.76092100	2.73149200
N	10.08386100	6.43100700	1.70066000
N	8.65510700	2.36686800	3.20332300
C	10.25269800	5.33112500	2.46423200
C	8.85204100	4.96484500	3.00667000
C	7.92432800	5.55691400	1.90662000
H	7.97620000	4.94267400	0.99879900
C	8.69274700	6.90900600	1.66084100
C	8.36766300	7.49051200	0.33300400
H	8.72924500	6.94973600	-0.54296100
C	7.49600800	8.64110600	0.17468000
H	7.16322200	8.90729400	-0.82974400
C	7.12374300	9.37926300	1.24884900
H	6.47639400	10.24950700	1.12495700
C	7.56900500	9.03547000	2.58323100
H	7.23968000	9.63955100	3.43037600
C	8.42461900	7.85145600	2.88174100
H	9.41366900	8.19311500	3.23861000
C	7.78084300	7.01709300	4.03017800
H	7.69364000	7.63423300	4.93451300
C	6.43760400	6.55534100	3.54032000
C	5.19728400	6.82485800	4.11266500
H	5.13220400	7.43541300	5.01627300
C	4.04402900	6.29728500	3.52489800
H	3.06775300	6.50010300	3.96915700

C	4.13231500	5.51045800	2.37397900
H	3.22581800	5.10203300	1.92379400
C	5.37608300	5.24412500	1.79513000
H	5.45208300	4.62905100	0.89577800
C	6.52484500	5.76924600	2.38371100
C	8.66091400	5.77169000	4.35044400
H	9.65271900	6.14617100	4.64256000
C	8.12448600	4.99895800	5.53883100
C	8.76289600	5.15416000	6.77584100
H	9.65268700	5.78511400	6.84079800
C	8.28108300	4.51786300	7.92001700
H	8.79615400	4.65351900	8.87277800
C	7.14859400	3.70833000	7.84313400
H	6.76947800	3.20585000	8.73485100
C	6.50474400	3.54137900	6.61625600
H	5.61927000	2.90717600	6.54457600
C	6.98524200	4.18149400	5.47423300
H	6.46377800	4.03351000	4.52632200
C	8.74100100	3.51541500	3.13639900
C	11.18520200	7.23034800	1.21526800
H	11.11354400	8.25705000	1.60787300
H	11.19383700	7.27223100	0.11712800
H	12.11907200	6.77413300	1.56491400

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B-BS-singlet

O	10.55469700	4.59861400	3.57920600
N	9.78400600	6.31761500	2.26476600
N	7.54710600	2.49263900	3.32436900
C	9.66047700	5.25037700	3.08676800
C	8.15353000	5.03941600	3.34562100
C	7.50884200	5.74521600	2.13546800
H	7.56116400	5.04238700	1.29107300
C	8.52858300	6.90084400	1.76402100
C	8.56979600	7.04591300	0.26680800
H	8.87763700	6.15672800	-0.28996300
C	8.20548700	8.18860300	-0.38116300
H	8.22179400	8.21416900	-1.47263300
C	7.81809700	9.34861900	0.33739700
H	7.52630300	10.25400100	-0.19437400
C	7.86232300	9.33272600	1.75509300
H	7.62124500	10.24332100	2.30740100
C	8.21874700	8.21043500	2.44318300
H	8.27196100	8.23654900	3.53340100
C	6.33086000	6.05595600	4.77455300
H	5.88238200	6.20345200	5.75874900
C	5.54846400	6.32803400	3.62662400
C	4.19883000	6.75558000	3.75579700
H	3.78100000	6.86799300	4.75857700
C	3.42740600	7.02993800	2.63941500
H	2.39477400	7.36207100	2.76084000
C	3.96698200	6.87452900	1.35459100
H	3.35781900	7.08138200	0.47351800
C	5.28686500	6.44196100	1.20521800
H	5.70529700	6.30311700	0.20526100
C	6.08439500	6.17693400	2.31611200
C	7.77963800	5.68896000	4.72661200
H	8.37101000	6.62102700	4.77873500
C	8.21891800	4.85017400	5.91475900
C	9.45738100	5.08675400	6.52110700
H	10.09904400	5.88224600	6.13607400

C	9.87453400	4.31962500	7.60834200
H	10.84169100	4.51903100	8.07344200
C	9.05600500	3.30327700	8.10243900
H	9.38053500	2.70318600	8.95455600
C	7.81804000	3.06102100	7.50581300
H	7.17038400	2.27019300	7.88870400
C	7.40163200	3.83124300	6.42012500
H	6.42989700	3.63786300	5.95869300
C	7.82468300	3.61227400	3.34074800
C	11.06214700	6.91179000	1.94371000
H	11.06053600	7.98030100	2.20729100
H	11.28660800	6.81178900	0.87148300
H	11.83644400	6.39512400	2.52267400

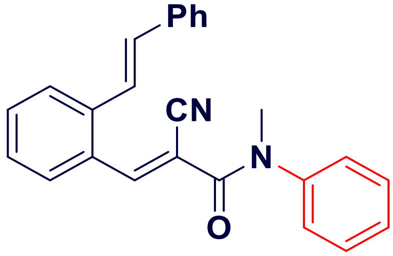
48

TS3-BS-singlet

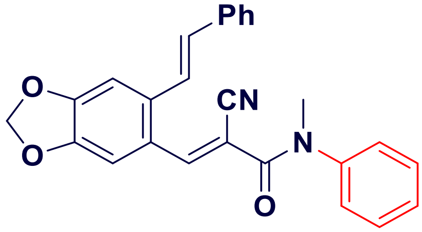
O	11.03374100	4.86398100	3.34612000
N	10.03079600	6.44241100	2.00443500
N	8.21222000	2.54593100	3.51048400
C	10.05903200	5.42197200	2.89314000
C	8.59528900	5.12495400	3.28762100
C	7.81479400	5.67428900	2.08008600
H	7.96320700	4.99805000	1.22758400
C	8.69724700	6.98380700	1.73473600
C	8.44727500	7.27978300	0.28811800
H	8.89623200	6.60160200	-0.44198900
C	7.56418900	8.24144600	-0.07313700
H	7.29596500	8.36713800	-1.12412900
C	7.00828300	9.14068800	0.90089200
H	6.29134500	9.89895700	0.58400200
C	7.51033900	9.14467000	2.20024500
H	7.23696600	9.95000100	2.88585300
C	8.39137300	8.15988000	2.62439100
H	8.97435400	8.28602100	3.53634700
C	7.06478700	6.79287500	4.48111000
H	6.86381800	7.45686800	5.32561000
C	6.03191300	6.56363200	3.53267500
C	4.69908000	7.00223900	3.72001300
H	4.43388300	7.52111900	4.64378300
C	3.73886900	6.74786300	2.75248000
H	2.70905300	7.07205400	2.91412600
C	4.07835000	6.07262600	1.56934100
H	3.31471500	5.87194000	0.81640200
C	5.39713100	5.68085800	1.34776400
H	5.67914700	5.18966200	0.41337900
C	6.37584700	5.92865500	2.31303100
C	8.27684400	5.91361000	4.62085300
H	9.14294300	6.56419800	4.81703300
C	8.18795400	4.99046700	5.83016200
C	9.36012500	4.64963100	6.51507500
H	10.31237200	5.07810000	6.19346900
C	9.31897800	3.76260900	7.59020700
H	10.24001500	3.50532400	8.11662100
C	8.10318200	3.20919200	7.99426400
H	8.06947600	2.51666400	8.83728000
C	6.93083300	3.54607800	7.31679300
H	5.97662000	3.11663900	7.62747100
C	6.97230600	4.43174300	6.23963800
H	6.05080800	4.68509600	5.70997000
C	8.38846500	3.68290000	3.42699300
C	11.22310500	7.14216500	1.58089000

H	11.23675000	8.16548800	1.98791100
H	11.27139800	7.19602900	0.48426800
H	12.09458200	6.59209500	1.95459200

6. SPECTRAL CHARACTERIZATION

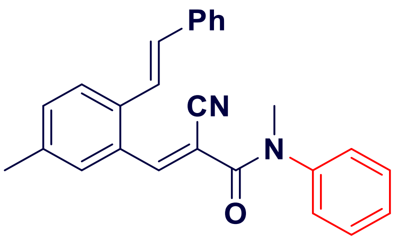


(*E/Z*)-2-cyano-N-methyl-*N*-phenyl-3-(2-((*E*)-styryl)phenyl)acrylamide (1a): A reaction tube was charged with respective styryl aldehyde (1.0 equiv), 2-cyano-*N*-methyl-*N*-phenylacetamide (1.5 equiv), AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the **1a** (10.9:1) as a mixture of E/Z isomers. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.31 (s, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.61-7.52 (m, 3H), 7.47-7.25 (m, 11H), 7.19 (d, *J* = 16.0 Hz, 1H), 6.93 (d, *J* = 16.0 Hz, 1H), 6.62 (d, *J* = 6.8 Hz, 1H), 3.47 (s, 3H), 3.24 (s, 1H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 163.11, 151.71, 142.68, 138.48, 136.70, 134.37, 133.84, 131.43, 130.75, 130.32, 129.85, 129.12, 128.76, 128.69, 128.54, 128.38, 128.20, 127.86, 127.62, 127.20, 127.02, 126.89, 126.63, 125.94, 124.89, 124.62, 114.60, 109.68, 38.87. Yield: 94%, pale yellow solid, m.p. 109-111 °C; **HRMS-EI (m/z):** [M+Na]$^+$ calcd. for C$_{25}$H$_{20}$N$_2$O 387.1473 found 387.1471.

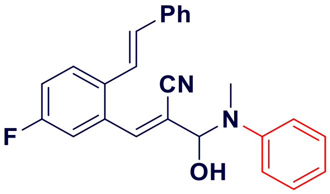


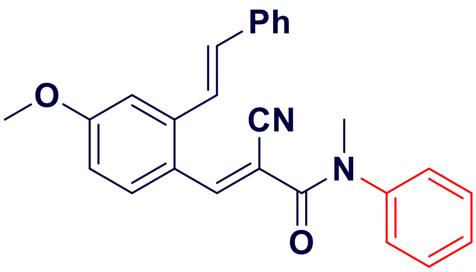
(*E/Z*)-2-cyano-*N*-methyl-*N*-phenyl-3-(6-((*E*)-styryl)benzo[*d*][1,3]dioxol-5-yl)acrylamide (1b): A reaction tube was charged with respective styryl aldehyde (1.0 equiv), 2-cyano-*N*-methyl-*N*-phenylacetamide (1.5 equiv), AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the **1b** as a mixture of E/Z isomers. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.28 (s, 1H), 7.49 (dd, *J* = 16.2, 7.8 Hz, 4H), 7.41 (ddd, *J* = 7.2, 6.0, 2.5 Hz, 4H), 7.37-7.29 (m, 4H), 7.27-7.21 (m, 5H), 7.15 (d, *J* = 12.2 Hz, 1H), 7.05 (s, 1H), 6.94 (d, *J* = 5.8 Hz, 1H), 6.83 (d, *J* = 15.9 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.06 (s, 1H), 5.99 (d, *J* = 0.9 Hz, 2H), 3.45 (s, 3H), 3.31 (d, *J* = 4.7 Hz, 3H), 3.22 (s, 2H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 163.51, 150.88, 150.38, 147.36, 144.99, 142.83, 142.29, 136.59, 135.49, 133.40, 132.99, 130.40, 129.76, 129.12, 128.97, 128.72, 128.65, 128.26, 128.20, 128.00, 127.93, 126.96, 126.94, 126.77, 126.50, 126.00, 124.38, 124.29, 124.22, 115.06, 114.05, 108.12, 107.48, 106.68, 106.57, 101.90, 38.91, 37.84, 37.25, 33.85, 25.35. Yield: 87%, yellow solid, m.p. 151-153 °C; **HRMS-EI (m/z):** [M+Na]$^+$ calcd. for C$_{26}$H$_{20}$N$_2$O$_3$ 431.1372 found 431.1368.

(*E*/*Z*)-2-cyano-*N*-methyl-3-(5-methyl-2-((*E*)-styryl)phenyl)-N-phenylacrylamide (1d): A reaction tube was charged with respective styryl aldehyde (1.0 equiv), 2-cyano-*N*-methyl-*N*-phenylacetamide (1.5 equiv), AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the **1d** as a mixture of E/Z isomers (8:2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.57-7.50 (m, 2H), 7.45-7.29 (m, 7H), 7.28-7.23 (m, 2H), 7.19 (d, *J* = 16.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 16.0 Hz, 1H), 3.46 (d, *J* = 2.2 Hz, 3H), 3.24 (d, *J* = 5.4 Hz, 1H), 2.38 (s, 3H), 2.32 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.38, 151.43, 142.82, 142.15, 138.67, 136.76, 134.15, 129.80, 128.73, 128.55, 128.46, 128.30, 128.07, 127.82, 127.64, 127.00, 126.86, 124.95, 114.92, 108.35, 38.88, 21.58; . Yield: 91%, yellow solid, m.p. 114-115 °C; **HRMS-EI (m/z):** $[M+Na]^+$ calcd. for $C_{26}H_{22}N_2O$ 401.1629 found 401.1629.

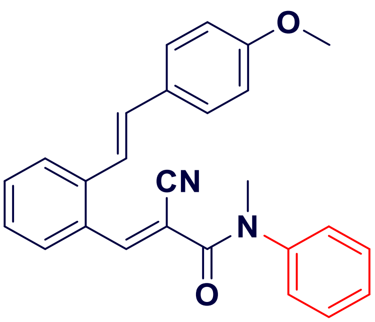


(*E*/*Z*)-2-cyano-3-(5-fluoro-2-((*E*)-styryl)phenyl)-*N*-methyl-*N*-phenylacrylamide (1e): A reaction tube was charged with respective styryl aldehyde (1.0 equiv), 2-cyano-*N*-methyl-*N*-phenylacetamide (1.5 equiv), AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the **1e** as a mixture of E/Z isomers (7:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29-8.21 (m, 1H), 7.74 (dd, *J* = 8.8, 5.7 Hz, 1H), 7.58-7.50 (m, 3H), 7.46-7.23 (m, 10H), 7.18 – 7.07 (m, 2H), 7.00-6.92 (m, 1H), 6.86 (d, *J* = 16.0 Hz, 1H), 6.69 (td, J = 8.8, 4.3 Hz, 1H), 6.32 (dd, *J* = 16.6, 10.1 Hz, 1H), 3.46 (s, 3H), 3.26 (d, *J* = 12.3 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.56, 163.05, 162.92, 162.73, 162.59, 160.25, 150.31, 150.18, 150.15, 142.64, 142.47, 141.33, 141.24, 136.53, 136.18, 135.29, 134.75, 134.72, 134.28, 134.26, 131.79, 131.71, 130.85, 130.75, 129.90, 129.86, 129.26, 129.18, 129.09, 129.01, 128.80, 128.77, 128.70, 128.42, 128.37, 128.23, 128.02, 127.04, 127.00, 126.83, 126.78, 126.58, 126.51, 126.48, 125.91, 123.86, 123.68, 123.65, 123.56, 118.68, 118.47, 115.11, 115.02, 114.88, 114.80, 114.55, 113.99, 113.76, 113.54, 110.85, 109.38, 38.89, 38.86; Yield: 80%, light brown solid, m.p. 125-127 °C; **HRMS-EI (m/z):** $[M+Na]^+$ calcd. for $C_{25}H_{19}FN_2O$ 403.1565 found 403.1561.



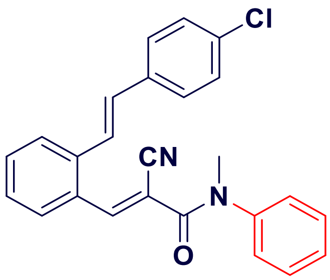


(*E*/*Z*)-2-cyano-3-(4-methoxy-2-((*E*)-styryl)phenyl)-N-methyl-N-phenylacrylamide (1g): A reaction tube was charged with respective styryl aldehyde (1.0 equiv), 2-cyano-*N*-methyl-*N*-phenylacetamide (1.5 equiv), AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the **1g** as a mixture of E/Z isomers (2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.51 (dd, J = 8.1, 3.1 Hz, 3H), 7.44 – 7.24 (m, 11H), 7.21 – 7.10 (m, 2H), 7.03 – 6.93 (m, 2H), 6.82 (d, J = 16.0 Hz, 1H), 6.67 (d, J = 7.0 Hz, 1H), 6.20 (dd, J = 134.6, 16.1 Hz, 1H), 3.84 (s, 1H), 3.76 (s, 3H), 3.46 (s, 3H), 3.25 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.99, 162.26, 158.65, 151.22, 145.35, 142.64, 141.75, 136.92, 136.54, 132.42, 132.10, 131.97, 131.32, 131.03, 130.09, 129.77, 129.14, 128.65, 128.58, 128.42, 128.14, 127.96, 127.92, 127.90, 126.96, 126.62, 126.35, 125.95, 124.35, 124.23, 118.78, 117.99, 116.78, 114.64, 112.37, 112.04, 111.17, 109.45, 55.51, 55.38, 38.81, 37.10; Yield: 91%, yellow solid, m.p. 100-102 °C; **HRMS-EI (m/z):** $[M+Na]^+$ calcd. for $C_{26}H_{22}N_2O_2Na$ 417.1578 found 417.1575.

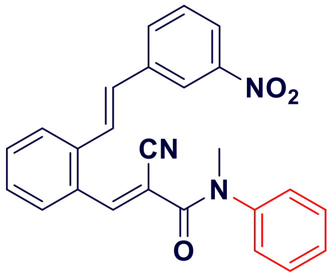


(*E*/*Z*)-2-cyano-3-(2-((E)-4-methoxystyryl)phenyl)-*N*-methyl-*N*-phenylacrylamide (1h): A reaction tube was charged with respective styryl aldehyde (1.0 equiv), 2-cyano-*N*-methyl-*N*-phenylacetamide (1.5 equiv), AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the **1h** as a mixture of E/Z isomers (2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.51-7.33 (m, 8H), 7.30-7.20 (m, 6H), 7.15 (ddd, J = 8.5, 7.9, 6.0 Hz, 2H), 7.05 (d, J = 16.0 Hz, 1H), 6.96-6.83 (m, 4H), 6.61 (dd, J = 8.1, 1.3 Hz, 1H), 6.24 (d, J = 16.1 Hz, 1H), 6.09 (d, J = 16.1 Hz, 1H), 3.85 (s, 3H), 3.83 (d, J = 3.0 Hz, 2H), 3.47 (s, 3H), 3.23 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.17, 162.36, 159.84, 159.79, 151.79, 145.67, 142.72, 141.95, 138.84, 137.84, 133.91, 133.39, 132.55, 131.38, 131.04, 130.68, 130.07, 129.82, 129.72, 129.54, 129.14, 129.07, 128.86, 128.49, 128.20, 128.14, 127.94, 127.80, 127.19, 127.01, 126.98, 126.95, 126.84, 125.93, 122.64, 122.43, 116.98, 114.66, 114.38, 114.17, 114.10, 110.85, 109.41, 55.31, 38.83, 37.09; Yield: 94%, yellow solid, m.p. 141-143 °C; **HRMS-EI (m/z):** $[M+Na]^+$ calcd. for $C_{26}H_{22}N_2O_2Na$ 417.1578 found 417.1575.

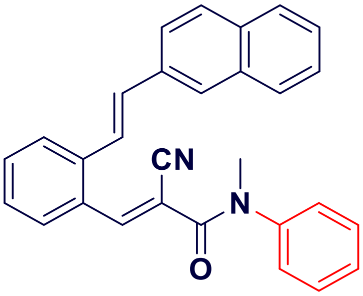
(*E/Z*)-3-(2-((*E*)-4-chlorostyryl)phenyl)-2-cyano-*N*-methyl-*N*-phenylacrylamide (1j): A reaction tube was charged with respective styryl aldehyde (1.0 equiv), 2-cyano-*N*-methyl-*N*-phenylacetamide (1.5 equiv), AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the **1j** as a mixture of E/Z isomers (2:1). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.31 (s, 1H), 7.63 (dd, *J* = 16.4, 7.8 Hz, 2H), 7.43 (ddd, *J* = 10.1, 8.0, 4.4 Hz, 6H), 7.34 (ddd, *J* = 14.1, 6.8, 3.4 Hz, 5H), 7.23-7.07 (m, 4H), 6.87 (d, *J* = 16.1 Hz, 1H), 6.61 (d, *J* = 7.2 Hz, 1H), 6.35 (d, *J* = 16.1 Hz, 1H), 6.12 (d, *J* = 16.2 Hz, 1H), 3.47 (s, 3H), 3.23 (s, 1H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 162.99, 162.17, 151.57, 145.34, 142.61, 141.90, 138.05, 137.02, 135.16, 134.76, 133.97, 132.96, 132.30, 131.42, 131.29, 130.75, 130.33, 129.83, 129.06, 128.94, 128.90, 128.85, 128.57, 128.21, 128.04, 127.80, 127.75, 127.48, 127.18, 127.05, 126.99, 125.93, 125.43, 125.16, 116.84, 114.49, 111.29, 109.82, 38.85, 37.10; Yield: 85%, pale yellow solid, m.p. 121-123 °C; **HRMS-EI (m/z):** [M+Na]$^+$ calcd. for $C_{25}H_{19}ClN_2O$ 421.1084 found 421.1080.



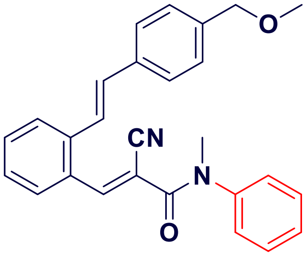
(*E/Z*)-2-cyano-N-methyl-3-(2-((E)-3-nitrostyryl)phenyl)-N-phenylacrylamide (1l): A reaction tube was charged with respective styryl aldehyde (1.0 equiv), 2-cyano-*N*-methyl-*N*-phenylacetamide (1.5 equiv), AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the **1l** as a mixture of E/Z isomers (3:1). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.36 (s, 1H), 8.29 (s, 1H), 8.16 (ddd, *J* = 10.2, 5.1, 4.0 Hz, 2H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.57 (dt, *J* = 15.7, 7.8 Hz, 3H), 7.46 (dt, *J* = 15.0, 6.4 Hz, 4H), 7.41 – 7.15 (m, 7H), 6.96 (d, *J* = 16.1 Hz, 1H), 6.65 (d, *J* = 6.7 Hz, 1H), 6.46 (d, *J* = 16.1 Hz, 1H), 6.20 (d, *J* = 16.1 Hz, 1H), 3.48 (s, 3H), 3.24 (s, 1H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 162.86, 162.05, 151.29, 148.61, 145.09, 142.57, 142.00, 138.42, 138.05, 137.36, 136.34, 132.55, 132.23, 131.87, 131.62, 131.50, 131.00, 130.85, 130.62, 129.87, 129.72, 129.64, 129.20, 129.05, 128.69, 128.41, 128.30, 128.13, 128.07, 127.88, 127.85, 127.55, 127.33, 127.03, 126.03, 122.73, 122.67, 121.40, 121.16, 116.71, 114.41, 111.75, 110.19, 38.88, 37.14; Yield: 70%, yellow solid, m.p. 95-97 °C; **HRMS-EI (m/z)**: [M+Na]$^+$ calcd. for $C_{25}H_{19}N_3O_3Na$ 432.1323 found 432.1323.

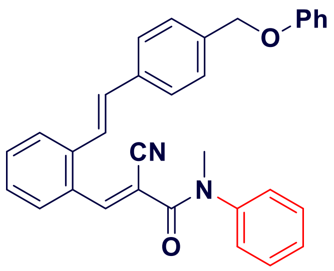


(*E/Z*)-2-cyano-N-methyl-3-(2-((*E*)-2-(naphthalen-2-yl)vinyl)phenyl)-*N*-phenylacrylamide (1m): A reaction tube was charged with respective styryl aldehyde (1.0 equiv), 2-cyano-*N*-methyl-*N*-phenylacetamide (1.5 equiv), AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the **1m** as a mixture of E/Z isomers (3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.91-7.79 (m, 5H), 7.74 (dd, *J* = 12.0, 4.8 Hz, 2H), 7.68-7.60 (m, 1H), 7.54-7.38 (m, 7H), 7.38-7.23 (m, 6H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.14-7.04 (m, 1H), 6.64 (d, *J* = 7.3 Hz, 1H), 6.42 (dd, *J* = 20.6, 16.1 Hz, 1H), 3.47 (s, 3H), 3.24 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.10, 151.61, 145.55, 142.69, 138.47, 137.39, 134.35, 134.16, 133.65, 133.51, 133.42, 133.30, 131.43, 131.32, 130.74, 130.34, 129.84, 129.11, 128.98, 128.57, 128.43, 128.38, 128.17, 128.12, 128.05, 127.88, 127.69, 127.63, 127.41, 127.30, 127.24, 127.14, 127.01, 126.49, 126.44, 126.32, 126.28, 125.96, 125.05, 124.79, 123.49, 123.15, 114.62, 109.76, 38.85, 37.11; Yield: 84%, pale yellow solid, m.p. 119-121 °C; **HRMS-EI (m/z):** $(M)^+$ calcd. for $C_{29}H_{22}N_2O$ 414.1732 found 414.1729.

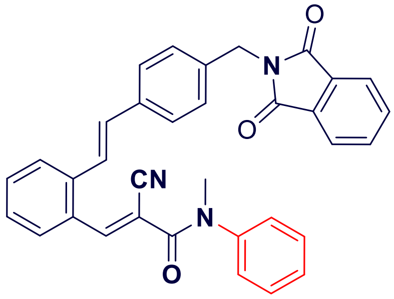


(*E/Z*)-2-cyano-3-(2-((E)-4-(methoxymethyl)styryl)phenyl)-*N*-methyl-*N*-phenylacrylamide (1n): A reaction tube was charged with respective styryl aldehyde (1.0 equiv), 2-cyano-*N*-methyl-*N*-phenylacetamide (1.5 equiv), AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the **1n** as a mixture of E/Z isomers (2.9:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.48 – 7.25 (m, 12H), 7.24 – 7.10 (m, 3H), 6.93 (d, *J* = 16.0 Hz, 1H), 6.65 – 6.58 (m, 1H), 6.37 (d, *J* = 16.1 Hz, 1H), 6.15 (d, *J* = 16.2 Hz, 1H), 4.49 (s, 3H), 3.47 (s, 3H), 3.41 (d, *J* = 1.2 Hz, 3H), 3.24 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.10, 151.67, 145.53, 142.67, 141.90, 138.47, 138.44, 137.43, 136.10, 135.69, 134.01, 133.45, 131.42, 131.25, 130.73, 130.29, 129.84, 129.64, 129.09, 128.91, 128.54, 128.19, 128.07, 128.00, 127.84, 127.60, 127.26, 127.16, 127.10, 127.01, 126.93, 126.66, 125.92, 124.79, 124.52, 116.91, 114.59, 109.67, 74.27, 58.08, 38.86, 37.12; Yield: 75%, yellow liquid; **HRMS-EI (m/z):** $[M+Na]^+$ calcd. for $C_{27}H_{24}N_2O_2Na$ 431.1735 found 431.1735.



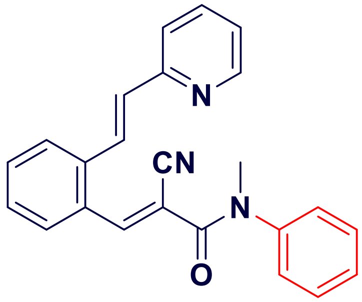


(E/Z)-2-cyano-N-methyl-3-(2-((E)-4-(phenoxymethyl)styryl)phenyl)-N-phenylacrylamide (1o): A reaction tube was charged with respective styryl aldehyde (1.0 equiv), 2-cyano-*N*-methyl-*N*-phenylacetamide (1.5 equiv), AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the **1o** as a mixture of E/Z isomers (4.3:1). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.30 (s, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.56 (dd, *J* = 13.3, 8.0 Hz, 3H), 7.49 – 7.39 (m, 6H), 7.37 – 7.10 (m, 9H), 7.04 – 6.85 (m, 5H), 6.65 – 6.56 (m, 1H), 6.38 (d, *J* = 16.1 Hz, 1H), 6.15 (d, J = 16.1 Hz, 1H), 5.08 (d, *J* = 7.1 Hz, 3H), 3.46 (s, 3H), 3.23 (s, 1H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 163.01, 162.23, 158.54, 151.62, 145.43, 142.63, 141.87, 138.31, 137.31, 137.24, 137.21, 136.33, 135.94, 133.84, 133.27, 131.38, 131.23, 130.70, 130.28, 129.80, 129.42, 129.05, 128.87, 128.51, 128.14, 127.80, 127.76, 127.71, 127.62, 127.28, 127.15, 127.09, 127.04, 126.96, 126.77, 125.88, 125.01, 124.76, 120.95, 120.93, 116.87, 114.77, 114.74, 114.55, 111.09, 109.68, 69.45, 69.41, 38.82, 37.07; Yield: 77%, yellow solid, m.p. 127-129 °C; **HRMS-EI (m/z):** M+Na]$^+$ calcd. for C$_{32}$H$_{26}$N$_2$O$_2$Na 493.1892 found 493.1888.

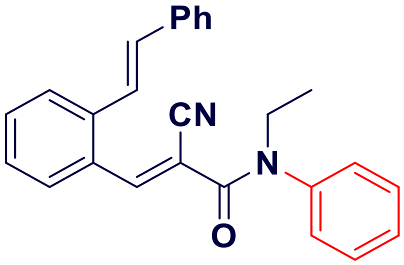


1r

(E/Z)-2-cyano-3-(2-((E)-4-((1,3-dioxoisoindolin-2-yl)methyl)styryl)phenyl)-N-methyl-N-phenylacrylamide (1q): A reaction tube was charged with respective styryl aldehyde (1.0 equiv), 2-cyano-*N*-methyl-*N*-phenylacetamide (1.5 equiv), AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the **1q** as a mixture of E/Z isomers (2.9:1). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.26 (s, 1H), 7.87 (dd, *J* = 5.5, 3.0 Hz, 3H), 7.78 – 7.65 (m, 4H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.51 – 7.46 (m, 4H), 7.42 (ddd, *J* = 9.2, 4.3, 3.0 Hz, 4H), 7.38 – 7.28 (m, 2H), 7.26 – 7.21 (m, 2H), 7.19 – 7.11 (m, 2H), 6.88 (d, *J* = 16.0 Hz, 1H), 6.66 – 6.54 (m, 1H), 6.32 (dd, *J* = 16.1, 8.8 Hz, 1H), 6.09 (dd, *J* = 16.1, 7.6 Hz, 1H), 4.87 (d, *J* = 6.9 Hz, 3H), 3.46 (s, 3H), 3.32 (s, 1H), 3.23 (s, 1H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 167.98, 163.03, 151.64, 145.40, 142.67, 138.33, 136.47, 136.34, 134.04, 134.00, 133.82, 133.25, 132.03, 131.38, 130.72, 130.45, 130.33, 129.84, 129.10, 129.07, 128.96, 128.90, 128.54, 128.18, 127.86, 127.67, 127.33, 127.21, 127.16, 127.00, 126.91, 125.92, 125.25, 124.97, 123.35, 114.57, 109.70, 41.30, 38.86, 37.12; Yield: 74%, yellow solid, m.p. 121-123 °C; **HRMS-EI (m/z):** [M+Na]$^+$ calcd. for C$_{34}$H$_{25}$N$_3$O$_3$Na 546.1794 found 546.1788.

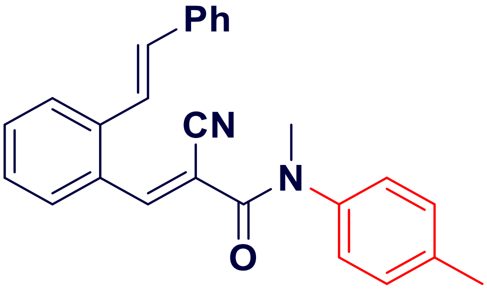


(*E/Z*)-2-cyano-*N*-methyl-*N*-phenyl-3-(2-((*E*)-2-(pyridin-2-yl)vinyl)phenyl)acrylamide (1t): A reaction tube was charged with respective styryl aldehyde (1.0 equiv), 2-cyano-*N*-methyl-*N*-phenylacetamide (1.5 equiv), AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the **1t** as a mixture of E/Z isomers (9:1). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.69 – 8.61 (m, 1H), 8.35 (s, 1H), 7.79 (d, *J* = 15.8 Hz, 1H), 7.75 – 7.60 (m, 3H), 7.48 – 7.25 (m, 8H), 7.21 (ddd, *J* = 7.5, 4.8, 1.0 Hz, 1H), 7.11 (ddd, *J* = 30.4, 13.9, 7.6 Hz, 1H), 6.98 (d, *J* = 15.8 Hz, 1H), 3.47 (s, 3H), 3.24 (s, 1H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 163.01, 154.73, 151.66, 149.71, 145.42, 142.59, 137.67, 136.64, 136.49, 133.24, 133.09, 131.32, 130.83, 130.77, 129.83, 129.10, 128.94, 128.66, 128.54, 128.15, 127.82, 127.71, 127.52, 127.08, 125.82, 122.74, 122.66, 114.48, 110.06, 38.79; Yield: 91%, yellow solid, m.p. 100-102 °C; **HRMS-EI (m/z):** $[M+Na]^+$ calcd. for $C_{24}H_{19}N_3ONa$ 388.1435 found 388.1428.

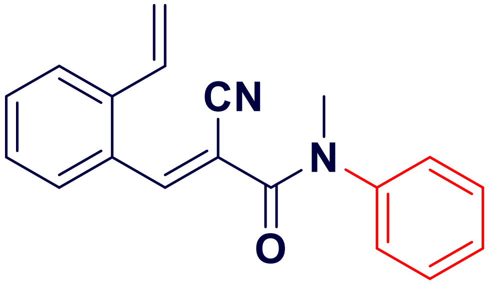


(*E/Z*)-2-cyano-*N*-ethyl-*N*-phenyl-3-(2-((*E*)-styryl)phenyl)acrylamide (1v): A reaction tube was charged with respective styryl aldehyde (1.0 equiv), 2-cyano-*N*-ethyl-*N*-phenylacetamide (1.5 equiv), AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the **1v** as a mixture of E/Z isomers (2.9:1). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.28 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.59-7.44 (m, 4H), 7.44-7.21 (m, 12H), 7.18-7.11 (m, 2H), 6.92 (d, *J* = 16.0 Hz, 1H), 6.60 (dd, *J* = 7.7, 1.8 Hz, 1H), 6.41 (d, *J* = 16.1 Hz, 1H), 6.15 (d, *J* = 16.1 Hz, 1H), 3.92 (q, *J* = 7.1 Hz, 2H), 3.70 (q, *J* = 7.2 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 162.49, 161.67, 151.45, 144.96, 140.85, 140.30, 138.31, 137.32, 136.66, 136.25, 134.20, 133.81, 131.26, 131.19, 130.68, 130.32, 130.00, 129.68, 129.43, 129.14, 129.11, 128.67, 128.61, 128.47, 128.27, 128.21, 128.00, 127.96, 127.51, 127.17, 127.09, 126.92, 126.83, 126.56, 124.86, 124.64, 116.96, 114.63, 111.43, 110.06, 46.04, 44.50, 12.58, 12.34; Yield: 89%, pale yellow solid, m.p. 105-107 °C; **HRMS-EI (m/z):** $[M+Na]^+$ calcd. for $C_{26}H_{22}N_2O$ 378.1732 found 378.1729.

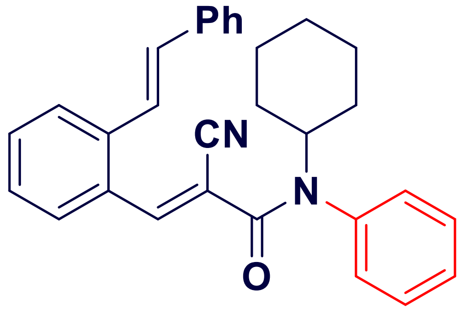
(*E/Z*)-2-cyano-*N*-methyl-3-(2-((*E*)-styryl)phenyl)-*N*-(*p*-tolyl)acrylamide (1w): A reaction tube was charged with respective styryl aldehyde (1.0 equiv), 2-cyano-*N*-methyl-*N*-(*p*-tolyl)acetamide (1.5 equiv), AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the **1w** as a mixture of E/Z isomers (2.6:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.61-7.50 (m, 3H), 7.47-7.25 (m, 9H), 7.15 (ddd, *J* = 11.2, 8.4, 5.4 Hz, 6H), 6.97-6.88 (m, 2H), 6.45 (dd, *J* = 20.1, 12.2 Hz, 1H), 6.14 (d, *J* = 16.2 Hz, 1H), 3.43 (s, 3H), 3.19 (s, 1H), 2.35 (s, 3H), 2.03 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.06, 162.26, 151.35, 145.38, 140.02, 139.29, 138.34, 138.15, 137.94, 137.27, 136.67, 136.26, 134.21, 133.50, 131.35, 131.28, 130.57, 130.38, 130.22, 129.68, 128.93, 128.71, 128.64, 128.50, 128.44, 128.30, 127.90, 127.55, 127.21, 127.11, 127.00, 126.82, 126.74, 126.59, 126.49, 125.65, 124.85, 124.59, 116.91, 114.61, 111.26, 109.88, 38.85, 37.08, 29.60, 21.07, 20.70; Yield: 86%, pale yellow solid, m.p. 72-74 °C. **HRMS-EI (m/z):** $[M+Na]^+$ calcd. for $C_{26}H_{22}N_2ONa$ 378.1732 found 378.1731.



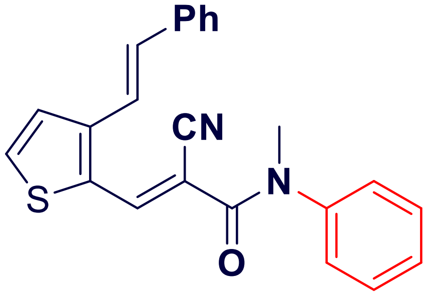
(*E*)-2-cyano-N-methyl-N-phenyl-3-(2-vinylphenyl)acrylamide (1ad): A reaction tube was charged with respective styryl aldehyde (1.0 equiv), 2-cyano-*N*-ethyl-*N*-phenylacetamide (1.5 equiv), AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the **1ad** as a mixture of E/Z isomers (9.7:0.3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.49 – 7.35 (m, 5H), 7.30 – 7.23 (m, 3H), 6.70 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.54 (dd, *J* = 17.3, 1.0 Hz, 1H), 5.43 (dd, *J* = 11.0, 1.0 Hz, 1H), 3.46 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.04, 151.67, 142.73, 138.61, 133.56, 131.27, 130.06, 129.83, 128.25, 128.08, 127.80, 126.97, 126.65, 119.50, 114.53, 109.89, 109.72, 38.79; Yield: 87%, yellow solid, m.p. 100-102 °C; **HRMS-EI (m/z):** $[M+Na]^+$ calcd. for $C_{19}H_{16}N_2ONa$ 311.1160 found 311.1157.



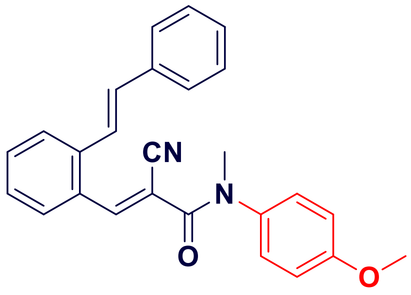
(*E*/*Z*)-2-cyano-N-cyclohexyl-N-phenyl-3-(2-((*E*)-styryl)phenyl)acrylamide (1ag): A reaction tube was charged with respective styryl aldehyde (1.0 equiv), 2-cyano-*N*-hexyl-*N*-phenylacetamide (1.5 equiv), AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the **1ag** as a mixture of E/Z isomers (9.7:0.3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.62 – 7.50 (m, 3H), 7.46 (td, *J* = 7.6, 1.2 Hz, 1H), 7.43 – 7.27 (m, 6H), 7.25 – 7.12 (m, 4H), 7.10 (s, 1H), 6.91 (d, *J* = 16.1 Hz, 1H), 6.55 (d, *J* = 7.1 Hz, 1H), 6.47 (d, *J* = 16.2 Hz, 1H), 6.19 (d, *J* = 16.2 Hz, 1H), 4.67 – 4.46 (m, 1H), 1.94 (d, *J* = 11.3 Hz, 1H), 1.84 – 1.55 (m, 4H), 1.49 – 1.34 (m, 2H), 1.31 – 1.18 (m, 1H), 1.06 – 0.79 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.80, 161.69, 150.74, 143.89, 138.10, 137.61, 137.30, 137.20, 136.73, 136.30, 134.09, 133.96, 131.34, 131.07, 130.96, 130.74, 130.50, 129.43, 129.11, 128.96, 128.88, 128.86, 128.73, 128.66, 128.49, 128.47, 128.31, 128.29, 127.52, 127.31, 127.18, 127.04, 126.83, 126.59, 124.99, 124.80, 117.05, 114.88, 112.02, 110.97, 56.74, 55.44, 31.24, 30.81, 25.71, 25.52, 25.21, 25.09; Yield: 91%, yellow solid, m.p. 100-102 °C; **HRMS-EI (m/z):** (M+Na) calcd. for $C_{30}H_{28}N_2ONa$ 455.2075 found 455.2071.



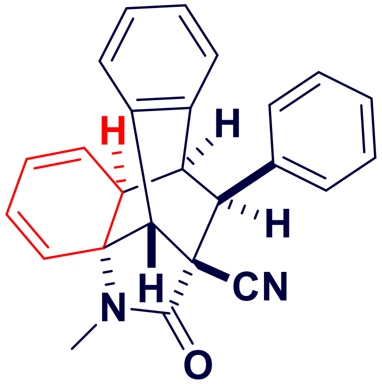
(*E*)-2-cyano-N-methyl-N-phenyl-3-(3-((*E*)-styryl)thiophen-2-yl)acrylamide (1al): A reaction tube was charged with respective styryl aldehyde (1.0 equiv), 2-cyano-*N*-hexyl-*N*-phenylacetamide (1.5 equiv), AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the **1al** as a mixture of E/Z isomers (9.8:0.2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.55 (dd, *J* = 6.0, 3.0 Hz, 3H), 7.47 – 7.30 (m, 9H), 7.28 – 7.22 (m, 2H), 7.11 (d, *J* = 16.0 Hz, 1H), 3.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.50, 146.79, 143.11, 142.88, 136.27, 134.01, 133.70, 132.30, 131.35, 129.81, 129.50, 128.79, 128.66, 128.12, 127.04, 126.90, 126.74, 125.98, 125.62, 119.20, 115.38, 101.85, 39.25; Yield: 80%, yellow solid, m.p. 121-123 °C; **HRMS-EI (m/z):** $[M+Na]^+$ calcd. for $C_{23}H_{18}N_2OSNa$ 393.1017 found 393.1015.



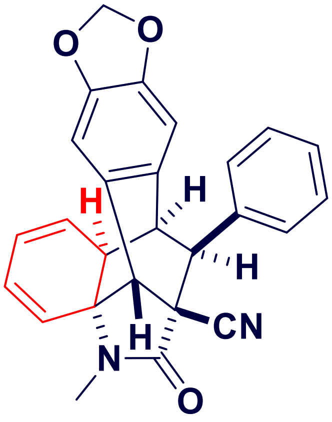
(*E*/*Z*)-2-cyano-N-(4-methoxyphenyl)-N-methyl-3-(2-((*E*)-styryl)phenyl)acrylamide (1aq): A reaction tube was charged with respective styryl aldehyde (1.0 equiv), 2-cyano-*N*-hexyl-*N*-phenylacetamide (1.5 equiv), AcOH (20 mol%) and piperidine (20 mol%) in 5.0 mL of toluene. The reaction suspension was stirred at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, water was added to quench the reaction mixture, which was then extracted with ethyl acetate (3×15 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford the **1aq** as a mixture of E/Z isomers (3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.54 (dd, J = 8.1, 1.0 Hz, 2H), 7.51 – 7.37 (m, 5H), 7.37 – 7.27 (m, 4H), 7.24 (d, *J* = 1.5 Hz, 1H), 7.17 (dt, *J* = 5.7, 4.9 Hz, 3H), 6.98 – 6.88 (m, 3H), 6.65 (d, *J* = 9.1 Hz, 1H), 6.49 (dd, *J* = 25.3, 12.5 Hz, 1H), 6.26 (d, *J* = 16.1 Hz, 1H), 3.80 (s, 3H), 3.47 (s, 1H), 3.42 (s, 3H), 3.20 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.17, 159.25, 158.93, 151.48, 145.27, 138.38, 137.32, 136.71, 136.33, 135.27, 134.64, 134.24, 133.69, 131.34, 130.66, 130.44, 129.01, 128.77, 128.66, 128.57, 128.40, 128.36, 127.62, 127.34, 127.14, 127.09, 127.03, 126.87, 126.63, 124.91, 124.75, 114.95, 114.66, 114.22, 109.94, 55.44, 55.01, 39.08, 37.28, 30.92; Yield: 87%, yellow solid, m.p. = 137-138 °C; **HRMS (EI) m/z:** $[M+Na]^+$ calcd. for $C_{26}H_{22}N_2O_2Na$ 417.1578 found 417.1575.



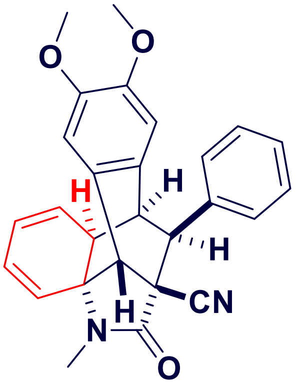
3-methyl-2-oxo-13-phenyl-2,3,8,12*b*-*tetrahydro*-1,8-methanodibenzo[*e*,*h*]indole-1(7*aH*)-carbonitrile (2): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1a** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80;20-60:40 to afford the dearomative cyclization product **2** derivative. **^{1}H NMR** (400 MHz, $CDCl_3$, major isomer) δ 7.47 (d, *J* = 6.8 Hz, 1H), 7.39 (td, *J* = 7.5, 1.3 Hz, 1H), 7.31 (td, *J* = 7.5, 1.3 Hz, 1H), 7.19-7.13 (m, 1H), 7.08 (t, *J* = 7.5 Hz, 2H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.39 (d, *J* = 7.3 Hz, 2H), 5.84 (dd, *J* = 9.8, 5.4 Hz, 1H), 5.48-5.37 (m, 1H), 5.36-5.24 (m, 2H), 3.73 (d, *J* = 2.5 Hz, 1H), 3.59 (s, 1H), 3.40 (t, *J* = 2.8 Hz, 1H), 3.20 (dd, *J* = 5.9, 3.0 Hz, 1H), 2.98 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, major isomer) δ 171.28, 138.31, 137.78, 132.02, 128.97, 128.78, 128.34, 127.94, 127.91, 127.87, 127.77, 127.50, 127.44, 122.40, 120.97, 116.82, 64.98, 53.72, 51.73, 50.87, 47.21, 44.17, 27.49; Yield: 91% d.r. 20:1, White solid, m.p. = 292-294 °C; **HRMS (EI) m/z:** calc'd for $C_{25}H_{20}N_2O$ $[M+Na]^+$, 364.1576; found, 364.1574.



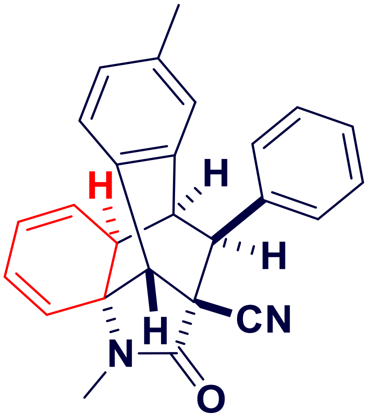
3-methyl-2-oxo-14-phenyl-2,3,8,13*b*-*tetrahydro*-1,8-methano[1,3]dioxolo[4',5':4,5]benzo[1,2-*e*]benzo[*h*]indole-1(7*aH*)-carbonitrile (3): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1b** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **3** derivatives. **^{1}H NMR** (597 MHz, CDCl$_3$, major isomer) δ 7.19 (t, *J* = 7.3 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 2H), 6.95 (s, 1H), 6.51 (d, *J* = 7.4 Hz, 2H), 6.43 (s, 1H), 6.01 (dd, *J* = 14.8, 1.4 Hz, 2H), 5.86 (dd, *J* = 9.8, 5.6 Hz, 1H), 5.50 – 5.43 (m, 1H), 5.32 – 5.22 (m, 2H), 3.68 (d, *J* = 2.1 Hz, 1H), 3.50 (s, 1H), 3.32 (s, 1H), 3.14 (d, *J* = 2.6 Hz, 1H), 2.96 (s, 3H); **^{13}C NMR** (150 MHz, CDCl$_3$, major diastereomer) δ 171.29, 147.95, 146.91, 138.39, 131.61, 129.05, 128.74, 128.05, 127.86, 125.04, 122.51, 121.17, 116.82, 108.86, 108.63, 101.08, 64.98, 54.05, 52.03, 50.83, 47.49, 44.54, 27.56; Yield: 73%, d.r. 20:1 Off-white solid, m.p.= 173-175 °C; **HRMS-EI (m/z):** calc'd for $C_{26}H_{20}N_2O_3Na$ [M+Na]$^+$, 431.1372; found, 431.1370.



10,11-dimethoxy-3-methyl-2-oxo-13-phenyl-2,3,8,12*b*-*tetrahydro*-1,8-methanodibenzo[*e*,*h*]indole-1(7aH)-carbonitrile (4): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1c** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **4** derivatives. **^{1}H NMR** (400 MHz, CDCl$_3$, mixer of diastereomers) δ 7.20-7.14 (m, 1H), 7.10 (t, *J* = 7.4 Hz, 2H), 7.03 (d, *J* = 2.3 Hz, 1H), 6.84 – 6.81 (m, 1H), 6.42 (d, *J* = 7.3 Hz, 2H), 5.85 (dd, *J* = 9.8, 5.8 Hz, 1H), 5.49-5.40 (m, 1H), 5.28 (dd, *J* = 14.7, 6.3 Hz, 2H), 3.88 (s, 3H), 3.71 (d, *J* = 2.4 Hz, 1H), 3.54 (d, *J* = 5.9 Hz, 1H), 3.34 (t, *J* = 2.7 Hz, 1H), 3.17 (d, *J* = 2.8 Hz, 1H), 2.97 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$, mixer of diastereomers) δ 171.44, 159.05, 138.47, 133.19, 129.74, 129.64, 129.07, 129.02, 128.34, 128.12, 127.91, 127.80, 122.36, 120.99, 116.82, 113.92, 113.46, 65.04, 55.35, 54.21, 52.12, 46.59, 44.45, 27.51; Yield: 70%, d.r. 7:1 Off-white solid, m.p.= 142-144 °C; **HRMS-EI (m/z):** calc'd for $C_{27}H_{24}N_2O_3Na$ [M+Na]$^+$ 447.1684; found, 447.1680.

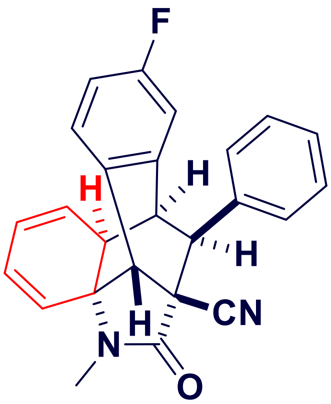


3,11-dimethyl-2-oxo-13-phenyl-2,3,8,12*b-tetrahydro*-1,8-methanodibenzo[*e*,*h*]indole-1(7*aH*)-carbonitrile



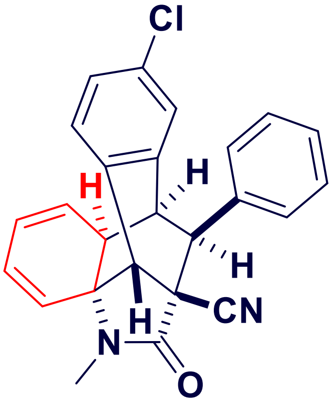
(5): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1d** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **5** derivatives. **^{1}H NMR** (400 MHz, CDCl$_3$, major isomer) δ 7.34 (d, *J* = 7.5 Hz, 1H), 7.21-7.12 (m, 2H), 7.08 (t, *J* = 7.4 Hz, 2H), 6.73 (s, 1H), 6.40 (d, *J* = 7.3 Hz, 2H), 5.83 (dd, *J* = 9.8, 5.7 Hz, 1H), 5.48-5.36 (m, 1H), 5.28 (dd, *J* = 13.5, 6.4 Hz, 2H), 3.70 (d, *J* = 2.3 Hz, 1H), 3.53 (d, *J* = 9.1 Hz, 1H), 3.33 (s, 1H), 3.17 (d, *J* = 2.6 Hz, 1H), 2.97 (s, 3H), 2.32 (s, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$, major isomer) δ 171.43, 138.45, 138.21, 137.59, 129.07, 128.91, 128.65, 128.20, 128.17, 127.89, 127.86, 127.76, 127.66, 127.23, 122.53, 120.98, 116.87, 65.09, 53.56, 51.88, 50.98, 47.27, 46.88, 44.30, 27.50, 21.43; Yield: 84%, d.r. 20:1, White solid, m.p.= 194-196 °C; **HRMS-EI (m/z):** calc'd for $C_{26}H_{22}N_2ONa$ [M+Na]$^+$, 401.1630; found, 401.1625.

11-fluoro-3-methyl-2-oxo-13-phenyl-2,3,8,12*b-tetrahydro*-1,8-methanodibenzo[*e*,*h*]indole-1(7*aH*)-



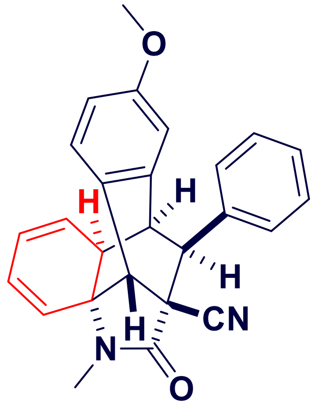
carbonitrile (6): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1e** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **6** derivatives. **^{1}H NMR** (400 MHz, CDCl$_3$, major isomer) δ 7.49-6.99 (m, 6H), 6.77 (ddd, *J* = 10.6, 8.2, 3.8 Hz, 1H), 6.42 (t, *J* = 6.8 Hz, 2H), 5.91 – 5.77 (m, 1H), 5.44 (ddd, *J* = 11.9, 5.8, 3.0 Hz, 1H), 5.36-5.20 (m, 2H), 3.74 (d, *J* = 2.0 Hz, 1H), 3.58 (d, *J* = 9.2 Hz, 1H), 3.40 (s, 1H), 3.19 (d, *J* = 2.8 Hz, 1H), 2.98 (s, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 170.98, 164.18, 163.22, 161.70, (d, J_{C-F} = 245 Hz), 160.77, 140.16 (d, J_{C-F} = 8.7 Hz), 138.10 (d, J_{C-F} = 12 Hz), 137.98, 134.04 (d, J_{C-F} = 8 Hz), 133.96, 133.56 (d, J_{C-F} = 3 Hz), 129.52, 129.44 (d, J_{C-F} = 8 Hz), 128.92, 128.87, 128.66, 128.38, 128.17, 128.10, 128.01, 127.95, 122.37, 122.22 (d, J_{C-F} = 15 Hz), 121.29, 121.17 (d, J_{C-F} = 12 Hz), 116.68, 116.57 (d, J_{C-F} = 11 Hz), 115.47, 115.45 (d, J_{C-F} = 2 Hz), 115.23, 115.05, 114.83, 114.61 (dd, J_{C-F} = 44 Hz), 114.39, 64.84, 53.78, 53.16, 51.78, 51.45, 50.66, 47.52, 46.77, 44.25, 44.11, 27.55, 27.53; Yield: 76%, d.r. 20:1, Off-white solid, m.p.= 298-300 °C; **HRMS-EI (m/z):** calc'd for $C_{25}H_{19}FN_2ONa$ [M+Na]$^+$ 405.1379; found, 405.1376.

11-chloro-3-methyl-2-oxo-13-phenyl-2,3,8,12*b-tetrahydro*-1,8-methanodibenzo[*e*,*h*]indole-1(7*aH*)-carbonitrile (8):



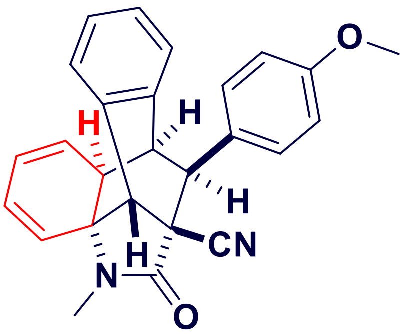
A clean vial (5 mL) equipped with a magnetic stir bar were added to **1f** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **7** derivatives. **^{1}H NMR** (400 MHz, CDCl$_3$, major isomer) δ 7.46 (t, *J* = 16.8 Hz, 1H), 7.39-7.28 (m, 1H), 7.23-7.08 (m, 3H), 6.89 (dd, *J* = 16.8, 4.9 Hz, 1H), 6.43 (d, *J* = 7.3 Hz, 2H), 5.87 (dd, *J* = 9.8, 5.7 Hz, 1H), 5.50-5.40 (m, 1H), 5.34-5.22 (m, 2H), 3.74 (d, *J* = 2.5 Hz, 1H), 3.57 (d, *J* = 10.7 Hz, 1H), 3.39 (dd, *J* = 6.2, 3.5 Hz, 1H), 3.20 (d, *J* = 2.8 Hz, 1H), 2.98 (s, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$, major isomer) δ 170.93, 138.00, 136.42, 133.96, 133.25, 129.17, 128.92, 128.88, 128.67, 128.60, 128.48, 128.43, 128.25, 128.13, 128.08, 128.01, 127.77, 127.57, 122.31, 122.22, 121.39, 121.31, 116.54, 114.08, 64.84, 53.53, 53.26, 51.64, 51.50, 50.67, 47.28, 46.91, 44.21, 44.13, 27.54; Yield: 80%, d.r. 20:1, White solid, m.p.= 241-243 °C; **HRMS-EI (m/z):** calc'd for $C_{25}H_{19}ClN_2ONa$ [M+Na]$^+$ 421.1084; found, 421.1080.

11-methoxy-3-methyl-2-oxo-13-phenyl-2,3,8,12*b-tetrahydro*-1,8-methanodibenzo[*e*,*h*]indole-1(7*aH*)-carbonitrile (8): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1g** (0.2 mmol) 4CzIPN

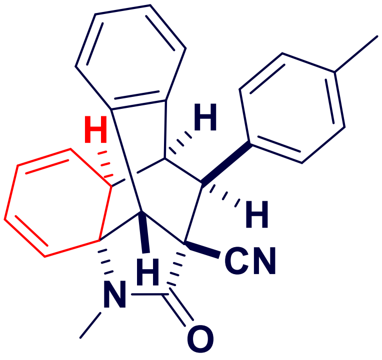


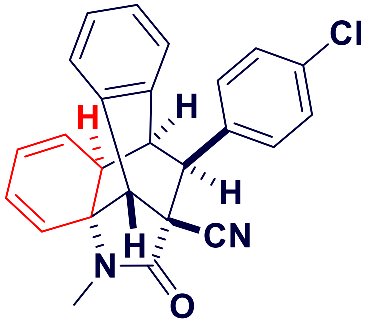
(2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, water was added to quench the reaction mixture, followed by extraction with ethyl acetate (3×10 mL). Finally, the combined organic layer was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **8** derivatives. **^{1}H NMR** (400 MHz, CDCl$_3$, major isomer) δ 7.16 (ddd, *J* = 6.4, 3.7, 1.2 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 2H), 7.03 (d, *J* = 2.3 Hz, 1H), 6.83 (dt, *J* = 14.1, 5.3 Hz, 2H), 6.42 (d, *J* = 7.3 Hz, 2H), 5.85 (dd, *J* = 9.9, 5.7 Hz, 1H), 5.43 (ddd, *J* = 10.1, 5.7, 2.6 Hz, 1H), 5.28 (dd, *J* = 15.4, 6.4 Hz, 2H), 3.86 (d, *J* = 5.7 Hz, 3H), 3.71 (d, *J* = 2.5 Hz, 1H), 3.53 (s, 1H), 3.34 (t, *J* = 2.8 Hz, 1H), 3.19 – 3.15 (m, 1H), 2.97 (s, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$, major isomer) δ 171.32, 159.03, 138.47, 133.18, 130.00, 129.63, 129.05, 128.99, 128.87, 128.69, 128.32, 128.09, 127.88, 127.77, 125.15, 122.32, 120.96, 116.81, 113.90, 113.45, 65.04, 55.33, 54.18, 52.09, 50.90, 46.57, 44.43, 35.97, 27.48; Yield: 85%, d.r. 20:1, White solid, m.p.= 288-290°C; **HRMS-EI (m/z)** calc'd for $C_{26}H_{24}N_2O_2$ [M+H]$^+$ 395.1755; found, 395.1759.

13-(4-methoxyphenyl)-3-methyl-2-oxo-2,3,8,12*b*-*tetrahydro*-1,8-methanodibenzo[*e*,*h*]indole-1(7*aH*)-carbonitrile (9): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1g** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **9** derivatives. **^{1}H NMR** (400 MHz, $CDCl_3$, major isomer) δ 7.46 (d, *J* = 7.0 Hz, 1H), 7.35 (dtd, *J* = 18.4, 7.6, 1.3 Hz, 2H), 6.93 (d, *J* = 6.8 Hz, 1H), 6.60 (d, *J* = 8.9 Hz, 2H), 6.29 (d, *J* = 8.7 Hz, 2H), 5.83 (dd, *J* = 9.9, 5.5 Hz, 1H), 5.45-5.36 (m, 1H), 5.33-5.24 (m, 2H), 3.70 (s, 3H), 3.69 (s, 1H), 3.57 (s, 1H), 3.37 (t, *J* = 2.7 Hz, 1H), 3.18 (dd, *J* = 5.7, 2.8 Hz, 1H), 2.97 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, major isomer) δ 171.35, 158.95, 137.95, 132.10, 130.62, 130.11, 128.86, 128.33, 127.92, 127.49, 127.47, 122.45, 120.94, 116.91, 113.22, 64.98, 55.02, 53.79, 51.20, 51.09, 47.47, 44.21, 27.47; Yield: 83%, d.r. 20:1, White solid, m.p.= 288-290°C; **HRMS-EI (m/z):** calc'd for $C_{26}H_{24}N_2O_2$ $[M+H]^+$ 395.1755; found, 395.1759.

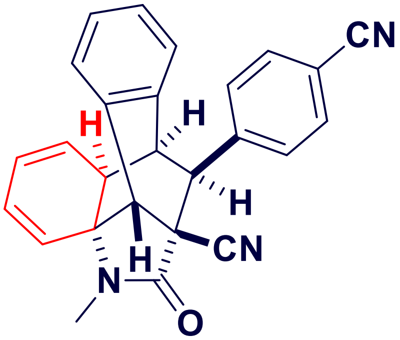


3-methyl-2-oxo-13-(*p*-tolyl)-2,3,8,12*b*-*tetrahydro*-1,8-methanodibenzo[*e*,*h*]indole-1(7*aH*)-carbonitrile (10): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1h** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **10** derivatives. **^{1}H NMR** (597 MHz, $CDCl_3$, major isomer) δ 7.45 (d, *J* = 7.1 Hz, 1H), 7.39-7.35 (m, 1H), 7.30 (td, *J* = 7.5, 1.2 Hz, 1H), 6.94-6.91 (m, 1H), 6.88 (d, *J* = 8.1 Hz, 2H), 6.26 (d, *J* = 8.1 Hz, 2H), 5.82 (dd, *J* = 9.8, 5.6 Hz, 1H), 5.40 (ddd, *J* = 8.9, 5.7, 2.7 Hz, 1H), 5.32-5.26 (m, 2H), 3.69 (d, *J* = 2.5 Hz, 1H), 3.57 (s, 1H), 3.37 (t, *J* = 2.8 Hz, 1H), 3.18 (dd, *J* = 5.9, 3.0 Hz, 1H), 2.97 (s, 3H), 2.22 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$, major isomer) δ 171.36, 137.96, 137.42, 135.43, 132.11, 128.87, 128.85, 128.59, 128.29, 127.91, 127.46, 127.45, 122.48, 120.94, 116.88, 65.00, 53.82, 51.50, 51.05, 47.36, 44.24, 27.46, 20.95; Yield: 82%, d.r. 20:1, White solid, m.p.= 279-281 °C; **HRMS-EI(m/z):** calc'd for $C_{26}H_{22}N_2ONa$ $[M+Na]^+$, 401.1630; found, 401.1625.

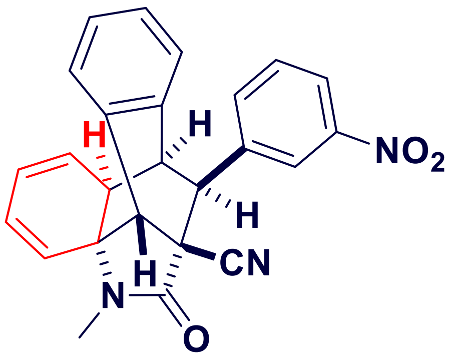




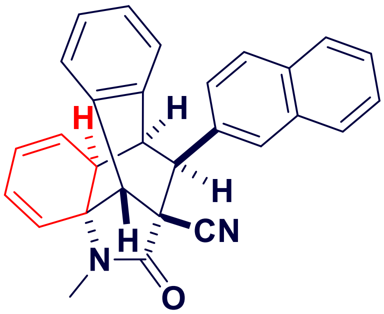
13-(4-chlorophenyl)-3-methyl-2-oxo-2,3,8,12*b-tetrahydro*-1,8-methanodibenzo[*e*,*h*]indole-1(7*aH*)-carbonitrile (11): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1i** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **11** derivatives. **^{1}H NMR** (400 MHz, CDCl$_3$, major isomer) δ 7.47 (d, *J* = 7.1 Hz, 1H), 7.39 (td, *J* = 7.5, 1.1 Hz, 1H), 7.32 (td, *J* = 7.5, 1.2 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.29 (d, *J* = 8.5 Hz, 2H), 5.84 (dd, *J* = 9.7, 5.6 Hz, 1H), 5.46-5.37 (m, 1H), 5.35-5.24 (m, 2H), 3.72 (d, *J* = 2.4 Hz, 1H), 3.59 (s, 1H), 3.35 (t, *J* = 2.6 Hz, 1H), 3.19 (d, *J* = 2.8 Hz, 1H), 2.98 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$, major isomer) δ 171.03, 137.41, 136.80, 133.79, 131.98, 130.31, 128.62, 128.51, 128.11, 128.04, 127.74, 127.51, 122.33, 121.11, 116.69, 64.98, 53.66, 51.09, 50.78, 47.16, 44.15, 27.54; Yield: 75%, d.r. 20:1, Off-white solid, m.p.= 303-305 °C; **HRMS-EI (m/z):** calc'd for C$_{25}$H$_{19}$ClN$_2$ONa [M+Na]$^+$ 421.1084; found, 421.1080.



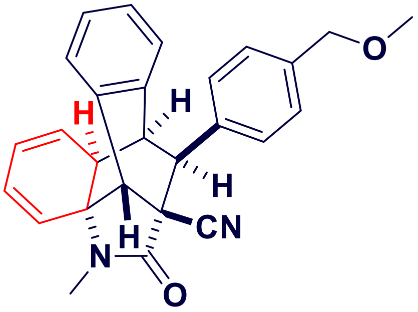
13-(4-cyanophenyl)-3-methyl-2-oxo-2,3,8,12b-*tetrahydro*-1,8-methanodibenzo[*e*,*h*]indole-1(7*aH*)-carbonitrile (12): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1j** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **12** derivatives. **^{1}H NMR** (400 MHz, CDCl$_3$, major isomer) δ 7.49 (d, *J* = 7.1 Hz, 1H), 7.45-7.29 (m, 4H), 6.88 (d, *J* = 7.3 Hz, 1H), 6.48 (d, *J* = 8.3 Hz, 2H), 5.85 (dd, *J* = 9.7, 5.6 Hz, 1H), 5.42 (dd, *J* = 5.7, 2.6 Hz, 1H), 5.36 – 5.21 (m, 2H), 3.80 (d, *J* = 2.4 Hz, 1H), 3.62 (s, 1H), 3.37 (t, *J* = 2.6 Hz, 1H), 3.21 (d, *J* = 2.8 Hz, 1H), 2.98 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$, major isomer) δ 170.64, 143.36, 136.92, 131.87, 131.67, 129.78, 128.68, 128.31, 128.15, 128.01, 127.43, 122.16, 121.29, 118.34, 116.48, 111.79, 64.99, 53.49, 51.49, 50.40, 46.79, 44.10, 27.57; Yield: 73%, d.r. 20:1, Off-white solid, m.p.= 275-277 °C; **HRMS-EI (m/z):** calc'd for C$_{26}$H$_{19}$N$_3$ONa [M+Na]$^+$ 412.1425; found, 412.1418.



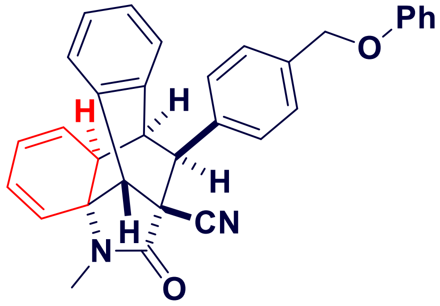
3-methyl-13-(3-nitrophenyl)-2-oxo-2,3,8,12b-*tetrahydro*-1,8-methanodibenzo[*e,h*]indole-1(7*aH*)-carbonitrile (13): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1k** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **13** derivatives. **^{1}H NMR** (400 MHz, CDCl$_3$, major isomer) δ 8.04 (dd, J = 8.2, 1.6 Hz, 1H), 7.53 (d, J = 6.6 Hz, 1H), 7.48-7.41 (m, 2H), 7.35 (td, J = 7.5, 1.3 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 6.89 (d, J = 7.2 Hz, 1H), 6.56 (d, J = 7.6 Hz, 1H), 5.87 (dd, J = 9.8, 5.4 Hz, 1H), 5.50-5.41 (m, 1H), 5.38-5.25 (m, 2H), 3.89 (d, J = 2.0 Hz, 1H), 3.64 (s, 1H), 3.42 (s, 1H), 3.24 (d, J = 2.5 Hz, 1H), 3.00 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$, major isomer) δ 170.64, 147.66, 140.12, 136.79, 135.05, 131.88, 128.82, 128.35, 128.31, 128.19, 127.46, 124.20, 122.92, 122.22, 121.34, 116.44, 65.02, 53.56, 51.19, 50.61, 46.87, 44.12, 27.61; Yield: 60%, d.r. 20:1, Off-white solid, m.p.= 307-309 °C; **HRMS-EI (m/z):** calc'd for $C_{25}H_{19}N_3O_3Na$ $[M+Na]^+$ 432.1323; found, 432.1320.



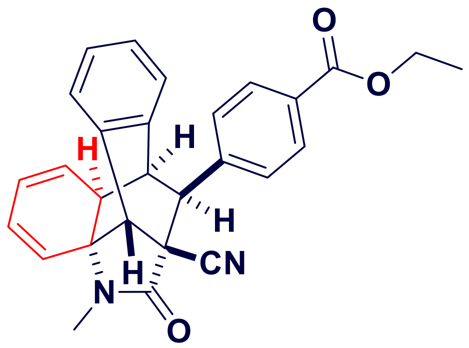
3-methyl-13-(naphthalen-2-yl)-2-oxo-2,3,8,12b-*tetrahydro*-1,8-methanodibenzo[*e,h*]indole-1(7*aH*)-carbonitrile (14): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1l** (0.2 mmol4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **14** derivatives. **^{1}H NMR** (400 MHz, CDCl$_3$, major isomer) δ 7.70 (dd, J = 6.2, 3.1 Hz, 1H), 7.54 (ddd, J = 10.9, 7.6, 4.0 Hz, 3H), 7.46-7.35 (m, 3H), 7.31 (td, J = 7.5, 1.2 Hz, 1H), 7.02 (s, 1H), 6.88 (d, J = 7.3 Hz, 1H), 6.30 (d, J = 7.3 Hz, 1H), 5.85 (dd, J = 9.7, 5.4 Hz, 1H), 5.48-5.39 (m, 1H), 5.38-5.26 (m, 2H), 3.92 (d, J = 2.3 Hz, 1H), 3.64 (s, 1H), 3.45 (s, 1H), 3.24 (d, J = 2.9 Hz, 1H), 3.01 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$, major isomer) δ 171.32, 137.93, 135.87, 132.76, 132.69, 132.16, 128.81, 128.49, 128.43, 128.07, 128.02, 127.97, 127.62, 127.57, 127.40, 127.36, 126.58, 126.07, 125.92, 122.48, 121.08, 116.86, 65.06, 53.86, 51.95, 50.94, 47.46, 44.28, 27.57; Yield: 74%, d.r. 20:1, White solid, m.p.= 318-320 °C; **HRMS-EI (m/z):** calc'd for $C_{29}H_{22}N_2ONa$ $[M+Na]^+$ 437.1630; found, 437.1625.



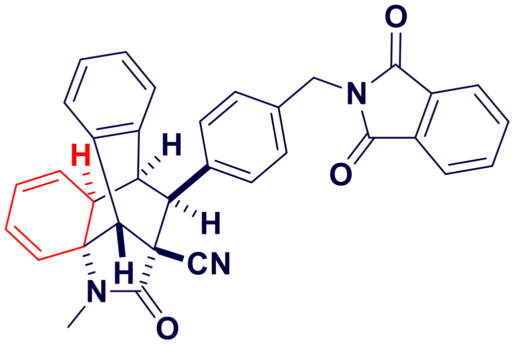
13-(4-(methoxymethyl)phenyl)-3-methyl-2-oxo-2,3,8,12*b-tetrahydro*-1,8-methanodibenzo[*e*,*h*]indole-1(7*aH*)-carbonitrile (15): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1m** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **15** derivatives. **^{1}H NMR** (400 MHz, CDCl$_3$, major isomer) δ 7.45 (s, 1H), 7.38 (d, *J* = 1.2 Hz, 1H), 7.30 (d, *J* = 1.3 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 2H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.36 (d, *J* = 8.2 Hz, 2H), 5.83 (dd, *J* = 9.7, 5.5 Hz, 1H), 5.44 – 5.37 (m, 1H), 5.33 – 5.25 (m, 2H), 4.33 (s, 2H), 3.73 (d, *J* = 2.5 Hz, 1H), 3.58 (s, 1H), 3.37 (t, *J* = 2.8 Hz, 1H), 3.33 (s, 3H), 3.19 (dd, *J* = 5.9, 3.0 Hz, 1H), 2.98 (d, *J* = 3.3 Hz, 3H). **^{13}C NMR** (100 MHz, CDCl$_3$, major isomer) δ 171.29, 137.76, 137.71, 132.03, 129.05, 128.81, 128.38, 127.96, 127.93, 127.53, 127.22, 122.45, 121.00, 116.80, 74.20, 65.01, 58.16, 53.80, 51.56, 50.92, 47.28, 44.22, 27.50. Yield: 79%, d.r. 20:1, White solid, m.p.= 318-320 °C; **HRMS-EI (m/z):** calc'd for $C_{27}H_{25}N_2O_2$ $[M+H]^+$ 431.1735; found, 431.1732.



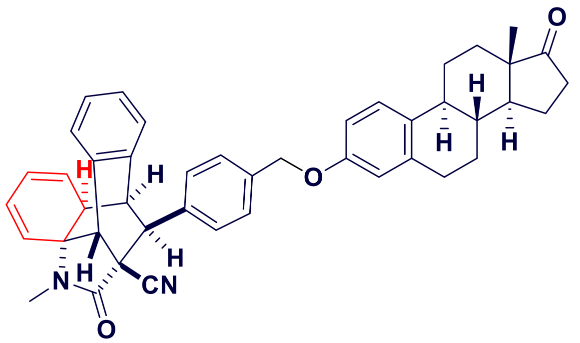
3-methyl-2-oxo-13-(4-(phenoxymethyl)phenyl)-2,3,8,12*b-tetrahydro*-1,8-methanodibenzo[*e*,*h*]indole-1(7*aH*)-carbonitrile (16): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1n** (0.2 mmol), 4CzIPN (2.5 mol%) and 2- MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **16** derivatives. **^{1}H NMR** (400 MHz, CDCl$_3$, major isomer) δ 7.47 (d, *J* = 6.8 Hz, 1H), 7.38 (td, *J* = 7.5, 1.3 Hz, 1H), 7.33 – 7.25 (m, 3H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.98 – 6.88 (m, 4H), 6.40 (d, *J* = 8.2 Hz, 2H), 5.83 (dd, *J* = 9.7, 5.3 Hz, 1H), 5.45 – 5.38 (m, 1H), 5.33 – 5.25 (m, 2H), 4.93 (s, 2H), 3.75 (d, *J* = 2.5 Hz, 1H), 3.59 (s, 1H), 3.39 (t, *J* = 2.8 Hz, 1H), 3.19 (dd, *J* = 5.9, 3.0 Hz, 1H), 2.98 (s, 3H). **^{13}C NMR** (100 MHz, CDCl$_3$, major isomer) δ 171.25, 158.68, 138.02, 137.71, 136.58, 132.03, 129.40, 129.21, 128.77, 128.41, 127.97, 127.95, 127.57, 127.53, 126.98, 122.41, 121.02, 120.89, 116.80, 114.74, 69.43, 65.02, 53.76, 51.54, 50.92, 47.19, 44.22, 27.50; Yield: 80%, d.r. 20:1, White solid, m.p.= 310-312 °C; **HRMS-EI (m/z):** calc'd for $C_{32}H_{26}N_2O_2Na$ $[M+Na]^+$ 493.1889; found, 493.1885.



4-ethyl-1-cyano-3-methyl-2-oxo-1,2,3,7a,8,12*b-hexahydro*-1,8-methanodibenzo[*e,h*]indol-13-yl)benzoate (17): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1o** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **17** derivatives. **^{1}H NMR** (400 MHz, CDCl$_{3,}$ major isomer) δ 7.76 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.40 (td, *J* = 7.5, 1.2 Hz, 1H), 7.31 (td, *J* = 7.5, 1.2 Hz, 1H), 6.87 (d, *J* = 7.3 Hz, 1H), 6.45 (d, *J* = 8.4 Hz, 2H), 5.84 (dd, *J* = 9.7, 5.6 Hz, 1H), 5.47 – 5.38 (m, 1H), 5.36 – 5.24 (m, 2H), 4.30 (qd, *J* = 7.1, 1.9 Hz, 2H), 3.81 (d, *J* = 2.5 Hz, 1H), 3.61 (s, 1H), 3.38 (t, *J* = 2.7 Hz, 1H), 3.25 – 3.17 (m, 1H), 3.00 (d, *J* = 9.8 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, CDCl$_{3,}$ major isomer) δ 170.98, 166.10, 143.08, 137.35, 131.94, 129.87, 129.13, 129.01, 128.57, 128.52, 128.04, 128.03, 127.75, 127.47, 122.31, 121.13, 116.62, 77.31, 76.99, 76.67, 65.00, 60.86, 53.65, 51.53, 50.56, 47.01, 44.13, 27.54, 14.23. Yield: 86%, d.r. 20:1, White solid, m.p.= 318-320 °C; **HRMS-EI (m/z):** calc'd for $C_{28}H_{25}N_2O_3$ [M+H]$^+$ 437.1867; found, 437.1869.

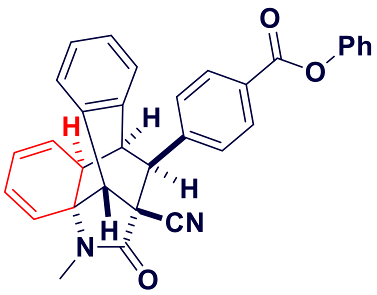


13-(4-((1,3-dioxoisoindolin-2-yl)methyl)phenyl)-3-methyl-2-oxo-2,3,8,12*b-tetrahydro*-1,8-methanodibenzo[*e,h*]indole-1(7*aH*)-carbonitrile (18): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1p** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL)at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **18** derivatives. **^{1}H NMR** (400 MHz, CDCl$_{3,}$ major isomer) δ 7.82 (dt, *J* = 7.0, 3.5 Hz, 2H), 7.70 (td, *J* = 5.3, 2.1 Hz, 2H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.37 (td, *J* = 7.5, 1.2 Hz, 1H), 7.30 (td, *J* = 7.5, 1.3 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 7.0 Hz, 1H), 6.33 (d, *J* = 8.2 Hz, 2H), 5.82 (dd, *J* = 9.8, 5.6 Hz, 1H), 5.45 – 5.35 (m, 1H), 5.33 – 5.20 (m, 2H), 4.72 (q, *J* = 14.7 Hz, 2H), 3.71 (d, *J* = 2.4 Hz, 1H), 3.56 (s, 1H), 3.34 (t, *J* = 2.7 Hz, 1H), 3.20 – 3.14 (m, 1H), 2.95 (d, *J* = 8.5 Hz, 3H); **^{13}C NMR** (100 MHz, CDCl$_{3,}$ major isomer) δ 171.19, 167.91, 137.91, 137.59, 135.80, 133.92, 132.00, 131.91, 129.30, 128.74, 128.47, 128.18, 127.95, 127.91, 127.54, 127.48, 123.30, 122.37, 120.98, 116.72, 64.97, 53.68, 51.43, 50.82, 47.08, 44.16, 41.02, 27.48. Yield: 66%, d.r. 20:1, White solid, m.p.= 281-283 °C; **HRMS-EI (m/z):** calc'd for $C_{34}H_{25}N_3O_3Na$ $[M+Na]^+$ 546.1793; found, 546.1786.



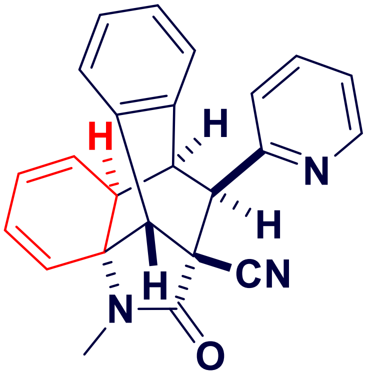
3-methyl-13-(4-((((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)methyl)phenyl)-2-oxo-2,3,8,12b-*tetrahydro*-1,8-methanodibenzo[*e,h*]indole-1(7*aH*)-carbonitrile (19): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1q** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **19** derivatives. **^{1}H NMR** (400 MHz, $CDCl_3$, mixture of diastereomers,) δ 7.47 (d, *J* = 7.4 Hz, 1H), 7.39 (td, *J* = 7.5, 1.3 Hz, 1H), 7.31 (ddd, *J* = 5.4, 4.6, 2.0 Hz, 1H), 7.16 (dd, *J* = 14.4, 8.5 Hz, 3H), 6.93 (d, *J* = 7.3 Hz, 1H), 6.73 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.66 (d, *J* = 2.6 Hz, 1H), 6.40 (d, *J* = 8.2 Hz, 1H), 5.84 (dd, *J* = 9.7, 5.2 Hz, 1H), 5.41 (ddd, *J* = 8.4, 4.2, 1.7 Hz, 1H), 5.35 – 5.25 (m, 2H), 4.91 (s, 2H), 4.12 (d, *J* = 3.0 Hz, 1H), 3.75 (d, *J* = 2.5 Hz, 1H), 3.59 (s, 1H), 3.39 (t, *J* = 2.8 Hz, 1H), 3.20 (d, *J* = 2.9 Hz, 1H), 3.00 (d, *J* = 12.9 Hz, 2H), 2.87 (dd, *J* = 9.7, 5.1 Hz, 2H), 2.56 – 2.32 (m, 2H), 2.24 (s, 1H), 2.18 – 1.88 (m, 6H), 1.66 – 1.38 (m, 11H), 1.31 – 1.24 (m, 6H), 0.90 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, mixture of diastereomers) δ 221.04, 171.29, 156.75, 137.94, 137.74, 137.72, 136.79, 132.28, 132.02, 129.20, 128.78, 128.42, 127.99, 127.96, 127.58, 127.54, 126.93, 126.29, 124.74, 123.97, 123.44, 122.41, 121.03, 116.78, 115.85, 114.75, 112.38, 69.50, 65.04, 53.77, 51.55, 50.94, 50.38, 47.99, 47.21, 44.24, 43.95, 38.29, 35.85, 34.70, 34.27, 31.89, 31.59, 31.54, 30.26, 29.66, 29.62, 29.59, 27.51, 26.49, 25.86, 21.55, 14.09, 13.82. Yield: 57%, d.r. 4;1, White solid, m.p.= 256-258 °C; **HRMS-EI (m/z):** calc'd for $C_{44}H_{42}N_2O_3Na$ $[M+Na]^+$ 669.3085; found, 669.3082.

4-phenyl-1-cyano-3-methyl-2-oxo-1,2,3,7a,8,12*b-hexahydro*-1,8-methanodibenzo[*e,h*]indol-13-yl)benzoate (20): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1r** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **20** derivatives. **^{1}H NMR** (400 MHz, $CDCl_3$, major isomer) δ 7.93 (d,



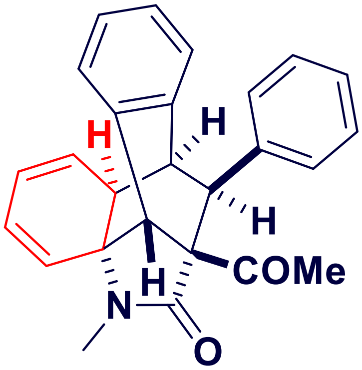
$J = 8.7$ Hz, 2H), 7.50 (d, $J = 6.9$ Hz, 1H), 7.46 – 7.31 (m, 4H), 7.29 – 7.21 (m, 1H), 7.18 – 7.11 (m, 2H), 6.91 (d, $J = 7.3$ Hz, 1H), 6.52 (d, $J = 8.4$ Hz, 2H), 5.86 (dd, $J = 9.8$, 5.4 Hz, 1H), 5.48 – 5.38 (m, 1H), 5.36 – 5.26 (m, 2H), 3.86 (d, $J = 2.5$ Hz, 1H), 3.63 (s, 1H), 3.41 (t, $J = 2.8$ Hz, 1H), 3.23 (dd, $J = 5.9$, 3.0 Hz, 1H), 3.01 (d, $J = 4.1$ Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, major isomer) δ 170.90, 164.67, 150.78, 143.91, 137.27, 131.92, 129.78, 129.42, 129.27, 128.94, 128.61, 128.52, 128.10, 127.86, 127.48, 125.82, 122.28, 121.60, 121.19, 116.64, 77.31, 76.99, 76.67, 65.00, 53.60, 51.55, 50.54, 46.96, 44.13, 27.58; Yield: 84%, d.r. 20:1, White solid, m.p. = 242-244 °C; **HRMS-EI (m/z):** calc'd for $C_{32}H_{24}N_2O_3Na$ $[M+Na]^+$ 507.1684; found, 507.1680.

3-methyl-2-oxo-13-(pyridin-2-yl)-2,3,8,12*b-tetrahydro*-1,8-methanodibenzo[*e,h*]indole-1(7*aH*)-carbonitrile



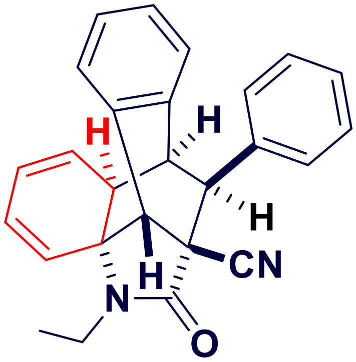
(21): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1s** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80;20-60:40 to afford the dearomative cyclization product **21** derivatives. **^{1}H NMR** (400 MHz, $CDCl_3$, major isomer) δ 8.42 (s, 1H), 7.47 (d, $J = 7.2$ Hz, 1H), 7.40 – 7.23 (m, 3H), 7.08 (dd, $J = 6.8$, 4.8 Hz, 1H), 6.83 (d, $J = 7.3$ Hz, 1H), 5.92 – 5.79 (m, 2H), 5.46 – 5.38 (m, 1H), 5.35 – 5.24 (m, 2H), 4.10 (d, $J = 2.3$ Hz, 1H), 3.60 (s, 1H), 3.51 (t, $J = 2.5$ Hz, 1H), 3.22 (dd, $J = 5.8$, 3.0 Hz, 1H), 2.97 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, major isomer) δ 170.82, 157.45, 148.84, 137.60, 135.54, 132.03, 128.81, 128.28, 128.00, 127.90, 127.51, 127.13, 123.10, 122.61, 122.44, 121.04, 116.96, 65.02, 53.80, 53.40, 49.44, 46.04, 43.79, 27.53; Yield: 64%, d.r. 20:1, Off-White solid, m.p.= 292-294 °C; **HRMS-EI (m/z):** calc'd for $C_{24}H_{20}N_3O$ $[M+H]^+$ 366.4360; found, 366.4362.

1-acetyl-3-methyl-13-phenyl-1,7a,8,12*b-tetrahydro*-1,8-methanodibenzo[*e,h*]indol-2(3*H*)-one (22): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1t** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **22** derivatives. **^{1}H NMR** (400 MHz, $CDCl_3$, mixture of diastereomers) δ 9.33 (s, 1H), 8.03 (d, $J = 7.4$ Hz, 1H), 7.42 (ddd, $J = 8.5$, 6.1, 2.1 Hz, 3H), 7.38 – 7.30 (m, 2H), 7.25 – 7.15 (m, 6H), 7.09 – 6.95 (m, 11H), 6.76 (q, $J = 12.1$ Hz, 2H), 6.59 (d, $J = 12.2$ Hz, 1H),

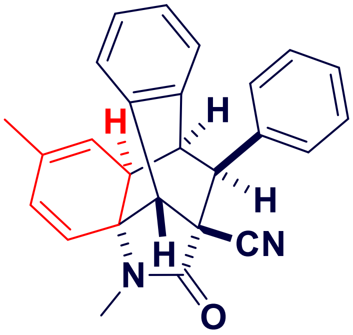


6.48 – 6.40 (m, 2H), 6.32 (d, *J* = 12.1 Hz, 1H), 5.83 (d, *J* = 6.9 Hz, 2H), 4.10 (dd, *J* = 11.2, 6.4 Hz, 1H), 3.62 (s, 3H), 3.22 (dd, *J* = 17.8, 11.3 Hz, 1H), 2.55 (s, 3H), 2.31 (dd, *J* = 18.1, 6.3 Hz, 1H), 1.55 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$, mixture of diastereomers) δ 205.79, 169.16, 162.81, 160.70, 141.28, 138.56, 137.89, 137.75, 136.34, 136.27, 136.04, 136.02, 133.74, 131.81, 131.16, 130.48, 129.91, 129.36, 129.30, 129.03, 128.83, 128.76, 128.68, 128.25, 128.11, 127.69, 127.63, 127.51, 127.45, 127.03, 124.62, 123.46, 120.50, 119.47, 111.21, 65.68, 55.30, 41.50, 38.54, 30.53, 29.33; Yield: 68%, d.r. 1:1, White solid, m.p.= 256-258 °C; **HRMS-EI (m/z):** calc'd for $C_{26}H_{23}NO_2Na$ $[M+Na]^+$ 404.1626; found, 404.1624.

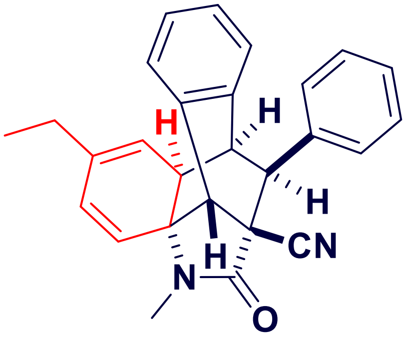
3-ethyl-2-oxo-13-phenyl-2,3,8,12b-tetrahydro-1,8-methanodibenzo[e,h]indole-1(7aH)-carbonitrile (23): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1u** (0.2 mmol), (4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **23** derivatives. **^{1}H NMR** (597 MHz, $CDCl_3$, major isomer) δ 7.45 (d, *J* = 7.3 Hz, 1H), 7.37 (td, *J* = 7.5, 1.1 Hz, 1H), 7.30 (td, *J* = 7.5, 1.2 Hz, 1H), 7.15 (dd, *J* = 10.6, 4.2 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 2H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.39 (d, *J* = 7.4 Hz, 2H), 5.81 (dd, *J* = 9.8, 5.6 Hz, 1H), 5.44-5.37 (m, 1H), 5.35 (d, *J* = 9.8 Hz, 1H), 5.30-5.23 (m, 1H), 3.74 (d, *J* = 2.5 Hz, 1H), 3.59 (s, 1H), 3.54 (dt, *J* = 14.2, 7.1 Hz, 1H), 3.47-3.40 (m, 1H), 3.37 (t, *J* = 2.7 Hz, 1H), 3.24 (dd, *J* = 5.9, 3.0 Hz, 1H), 1.33 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$, major isomer) δ 171.41, 138.43, 137.76, 132.23, 129.00, 128.65, 128.29, 127.89, 127.86, 127.75, 127.71, 127.47, 122.95, 120.82, 116.97, 65.31, 54.25, 51.74, 51.01, 47.41, 46.56, 37.04, 14.79; Yield: 93%, d.r. 20;1, White solid, m.p.= 298-300°C; **HRMS-EI (m/z):** calc'd for $C_{26}H_{22}N_2ONa$ $[M+Na]^+$ 401.1630; found, 401.1628.



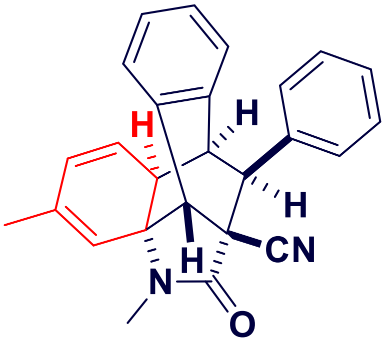
3,6-dimethyl-2-oxo-13-phenyl-2,3,8,12*b-tetrahydro*-1,8-methanodibenzo[*e*,*h*]indole-1(7*aH*)-carbonitrile (24): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1v** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **24** derivatives. **^{1}H NMR** (400 MHz, $CDCl_3$, major isomer) δ 7.44 (d, *J* = 7.1 Hz, 1H), 7.35 (td, *J* = 7.5, 1.2 Hz, 1H), 7.31 – 7.25 (m, 1H), 7.18 – 7.12 (m, 1H), 7.07



(t, J = 7.5 Hz, 2H), 6.89 (d, *J* = 7.2 Hz, 1H), 6.38 (d, *J* = 7.4 Hz, 2H), 5.69 (dd, *J* = 9.8, 1.1 Hz, 1H), 5.31 (d, *J* = 9.8 Hz, 1H), 4.94 (d, *J* = 1.0 Hz, 1H), 3.71 (d, *J* = 2.4 Hz, 1H), 3.57 (s, 1H), 3.34 (t, *J* = 2.7 Hz, 1H), 3.19 – 3.08 (m, 1H), 2.96 (s, 3H), 1.42 (s, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$, major isomer) δ 171.41, 138.46, 137.96, 132.20, 131.90, 129.00, 128.31, 128.29, 127.85, 127.78, 127.72, 127.47, 127.36, 123.08, 122.48, 116.88, 64.65, 53.70, 51.71, 50.99, 47.67, 44.27, 27.44, 21.02; Yield: 89%, d.r. 20:1, White solid, m.p.= 296-298 °C; **HRMS-EI (m/z):** calc'd for C$_{26}$H$_{22}$N$_2$ONa [M+Na]$^+$ 401.1630; found, 401.1625.

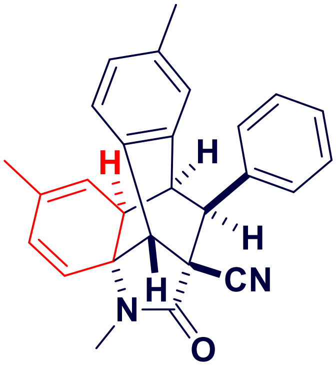


6-ethyl-3-methyl-2-oxo-13-phenyl-2,3,8,12*b-tetrahydro*-1,8-methanodibenzo[*e,h*]indole-1(7*aH*)-carbonitrile (25): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1w** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **25** derivatives. **^{1}H NMR** (400 MHz, CDCl$_3$, , major isomer) δ 7.43 (d, *J* = 7.3 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 7.2 Hz, 1H), 6.41 (d, *J* = 7.5 Hz, 2H), 5.71 (d, *J* = 9.8 Hz, 1H), 5.32 (d, *J* = 9.8 Hz, 1H), 4.89 (s, 1H), 3.72 (d, *J* = 2.4 Hz, 1H), 3.56 (s, 1H), 3.36 (t, *J* = 2.7 Hz, 1H), 3.16 (s, 1H), 2.97 (s, 3H), 1.75 – 1.66 (m, 2H), 0.63 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$, , major isomer) δ 171.45, 138.52, 138.08, 134.32, 131.90, 131.36, 129.03, 128.21, 127.87, 127.73, 127.42, 127.25, 122.64, 121.74, 116.90, 65.01, 53.71, 51.65, 50.97, 47.73, 43.91, 27.99, 27.47, 12.39; Yield: 90%, d.r. 20:1, White solid, m.p.= 298-300°C; **HRMS-EI (m/z):** calc'd for C$_{27}$H$_{24}$N$_2$ONa [M+Na]$^+$ 415.1787; found, 415.1784.

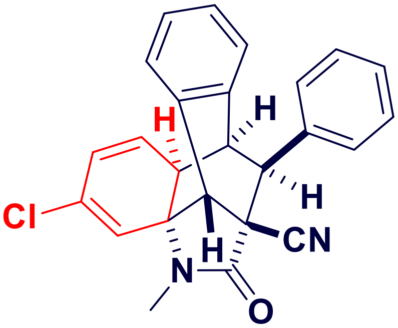


3,5-dimethyl-2-oxo-13-phenyl-2,3,8,12*b-tetrahydro*-1,8-methanodibenzo[*e,h*]indole-1(7*aH*)-carbonitrile (26): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1x** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **26** derivatives. **^{1}H NMR** (597 MHz, CDCl$_3$, , mixture of diastereomers) δ 7.45 (dd, *J* = 16.2, 7.3 Hz, 1H), 7.37 (dtd, *J* = 8.6, 7.5, 1.2 Hz, 1H), 7.30 (tdd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 7.15 (dd, *J* = 15.6, 7.4 Hz, 1H), 7.08 (dd, *J* = 16.0, 8.3 Hz, 2H), 6.96 (d, *J* =

7.3 Hz, 1H), 6.89 (d, *J* = 7.2 Hz, 1H), 6.38 (t, *J* = 8.6 Hz, 2H), 5.79 (dd, *J* = 9.8, 5.9 Hz, 1H), 5.32 – 5.25 (m, 1H), 5.24 – 5.19 (m, 1H), 5.01 (s, 1H), 3.71 (dd, *J* = 14.1, 2.4 Hz, 1H), 3.66-3.61 (m, 1H), 3.54 (s, 1H), 3.38 (t, *J* = 2.5 Hz, 1H), 3.10 (s, 1H), 2.95 (d, *J* = 4.1 Hz, 3H), 1.63 (d, *J* = 1.4 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$, mixture of diastereomers) δ 171.28, 171.11, 138.51, 138.44, 137.74, 137.12, 136.25, 134.68, 132.34, 132.31, 129.02, 128.78, 128.33, 128.30, 128.21, 127.92, 127.88, 127.86, 127.82, 127.74, 127.59, 127.47, 127.37, 126.81, 125.24, 120.43, 118.71, 117.04, 116.92, 116.90, 65.59, 65.45, 54.19, 53.86, 51.85, 51.75, 50.95, 50.26, 48.27, 47.31, 44.28, 43.67, 27.41, 27.39, 21.66, 20.17; Yield: 86%, d.r. 8:1, White solid, m.p.= 234-236 °C; **HRMS-EI (m/z):** calc'd for $C_{26}H_{22}N_2ONa$ $[M+Na]^+$ 401.1630; found, 401.1625.

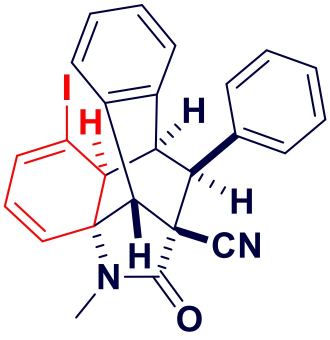


3,6,11-trimethyl-2-oxo-13-phenyl-2,3,8,12*b-tetrahydro*-1,8-methanodibenzo[*e,h*]indole-1(7*aH*)-carbonitrile (27): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1y** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **27** derivatives. **^{1}H NMR** (400 MHz, $CDCl_3$, major isomer) δ 7.43 (d, *J* = 7.3 Hz, 1H), 7.35 (td, *J* = 7.5, 1.3 Hz, 1H), 7.29 (td, *J* = 7.5, 1.4 Hz, 1H), 6.89 (dd, *J* = 11.0, 7.9 Hz, 3H), 6.26 (d, *J* = 8.1 Hz, 2H), 5.68 (dd, *J* = 9.8, 1.3 Hz, 1H), 5.30 (d, *J* = 9.8 Hz, 1H), 4.94 (d, *J* = 1.4 Hz, 1H), 3.67 (d, *J* = 2.5 Hz, 1H), 3.55 (s, 1H), 3.32 (t, *J* = 2.8 Hz, 1H), 3.12 (dd, *J* = 5.5, 2.8 Hz, 1H), 2.95 (s, 3H), 2.22 (s, 3H), 1.45 – 1.40 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$, major isomer) δ 171.50, 138.12, 137.40, 135.54, 132.20, 131.94, 128.88, 128.59, 128.29, 128.26, 127.79, 127.50, 127.32, 123.17, 122.54, 116.96, 64.66, 53.75, 51.45, 51.15, 47.79, 44.30, 27.43, 21.03, 20.97.; Yield: 81%, d.r. 20:1, White solid, m.p.= 298-300°C; **HRMS-EI (m/z):** calc'd for $C_{27}H_{24}N_2ONa$ $[M+Na]^+$, 415.1787; found, 415.1784.

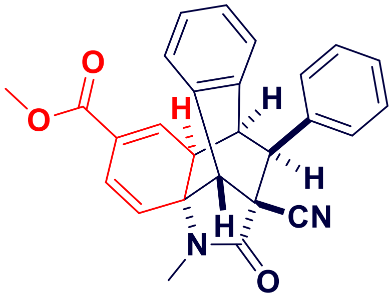


5-chloro-3-methyl-2-oxo-13-phenyl-2,3,8,12*b-tetrahydro*-1,8-methanodibenzo[*e,h*]indole-1(7*aH*)-carbonitrile (28): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1z** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 4-10 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **28** derivatives. **^{1}H**

NMR (400 MHz, $CDCl_3$, mixture of diastereomers) δ 7.49 (dd, *J* = 12.2, 7.3 Hz, 1H), 7.41 (td, *J* = 7.5, 1.3 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.22 – 7.14 (m, 1H), 7.09 (dd, *J* = 14.3, 7.4 Hz, 3H), 6.91 (d, *J* = 7.3 Hz, 1H), 6.39 (dd, *J* = 17.1, 7.4 Hz, 2H), 5.76 (dd, *J* = 9.7, 6.4 Hz, 1H), 5.59 (dd, *J* = 6.3, 2.1 Hz, 1H), 5.45 (s, 1H), 5.41 – 5.36 (m, 1H), 5.35 (s, 1H), 3.94 (t, *J* = 2.7 Hz, 1H), 3.70 (dd, *J* = 11.2, 2.6 Hz, 2H), 3.64 (s, 1H), 3.42 (t, *J* = 2.7 Hz, 1H), 3.19 (dd, *J* = 18.6, 2.7 Hz, 1H), 2.99 (d, *J* = 1.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, mixture of diastereomers) δ 170.90, 138.06, 137.99, 137.24, 136.51, 134.51, 133.15, 131.58, 131.27, 129.00, 128.96, 128.70, 128.67, 128.14, 128.00, 127.96, 127.89, 127.80, 127.62, 127.42, 126.68, 124.24, 121.94, 120.57, 118.28, 116.58, 116.48, 67.02, 66.54, 53.73, 53.62, 51.68, 51.15, 50.69, 50.01, 49.28, 46.91, 44.22, 43.50, 27.63, 27.59; Yield: 70%, d.r. 2:1, Off-white solid, m.p.= 303-305 °C; **HRMS-EI (m/z):** calc'd for $C_{25}H_{19}ClN_2ONa$ [M+Na]$^+$ 421.1084; found, 421.1080.

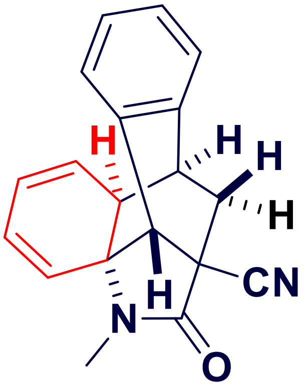


7-iodo-3-methyl-2-oxo-13-phenyl-2,3,8,12*b-tetrahydro*-1,8-methanodibenzo[*e*,*h*]indole-1(7*aH*)-carbonitrile (29): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1aa** (0.2 mmol), 4CzIPN (2.5 mol%) and 2- MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **29** derivatives. **^{1}H NMR** (400 MHz, $CDCl_3$, major isomer) δ 7.56 (d, *J* = 7.3 Hz, 1H), 7.42 (tt, *J* = 3.9, 1.9 Hz, 1H), 7.34 (td, *J* = 7.5, 1.3 Hz, 1H), 7.20 – 7.14 (m, 1H), 7.08 (t, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 6.9 Hz, 1H), 6.53 (d, *J* = 6.2 Hz, 1H), 6.42 – 6.35 (m, 2H), 5.34 (dd, *J* = 9.5, 3.4 Hz, 1H), 5.13 – 5.04 (m, 1H), 4.13 (s, 1H), 3.66 (d, *J* = 2.5 Hz, 1H), 3.39 – 3.30 (m, 2H), 3.07 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, major isomer) δ 171.20, 140.69, 137.95, 137.82, 131.23, 129.38, 129.00, 128.73, 127.99, 127.97, 127.40, 121.76, 116.63, 99.63, 69.93, 52.44, 51.75, 50.37, 47.82, 45.64, 28.05. Yield: 54%, d.r. 20:1, Off-white solid, m.p.= 303-305 °C; **HRMS-EI (m/z):** calc'd for $C_{25}H_{19}IN_2ONa$ [M+Na]$^+$ 513.0440; found, 513.0438.

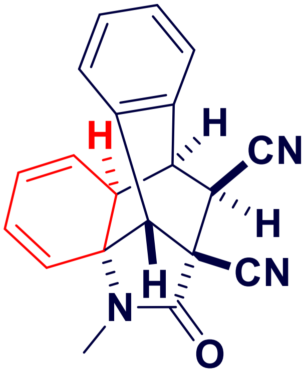


methyl-1-cyano-3-methyl-2-oxo-13-phenyl-1,2,3,7a,8,12*b-hexahydro*-1,8-methanodibenzo[*e*,*h*]indole-6-carboxylate (30): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1ab** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **30** derivatives. **^{1}H NMR** (400 MHz, $CDCl_3$, major isomer) δ 7.97 (d, *J* = 1.4 Hz, 1H), 7.89 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.50 (dd, *J* = 5.6, 3.0 Hz, 1H), 7.46 (dd, *J* = 5.7, 2.9 Hz, 1H), 7.42 – 7.40 (m, 1H), 7.34 – 7.29 (m, 2H), 7.27 – 7.21 (m, 3H), 6.96 (dd, *J* = 7.5, 1.9 Hz, 2H), 6.19 (s, 1H), 4.75 (s, 1H), 4.54 (s, 1H), 3.91 (d, *J* = 1.2 Hz, 1H), 3.88 (s, 3H), 2.80 (t, *J* = 10.4 Hz, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$, major isomer) δ 166.82, 166.30, 144.71, 142.54, 140.28, 139.67, 138.57, 128.84, 128.73, 128.61, 128.17, 128.12, 127.69, 127.17, 126.55, 126.35, 125.68, 123.68, 119.38, 56.32, 53.11, 52.42, 52.09, 49.53, 27.44. Yield: 66%, d.r.20:1, White solid, m.p.= 308-310 °C; **HRMS-EI (m/z):** calc'd for $C_{27}H_{22}N_2O_3Na[M+Na]^+$ 445.1528; found, 445.1526.

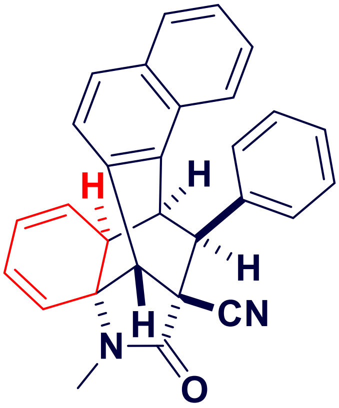
3-methyl-2-oxo-2,3,8,12*b*-*tetrahydro*-1,8-methanodibenzo[*e*,*h*]indole-1(7*aH*)-carbonitrile (31): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1ac** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **31** derivatives. **^{1}H NMR** (400 MHz, CDCl$_3$, mixture of diasteriomers) δ 7.97 (d, *J* = 1.4 Hz, 1H), 7.89 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.55 – 7.37 (m, 4H), 7.34 – 7.30 (m, 2H), 7.29 – 7.21 (m, 4H), 6.96 (dd, *J* = 7.5, 1.9 Hz, 2H), 6.19 (s, 1H), 4.75 (s, 1H), 4.54 (s, 1H), 3.91 (d, *J* = 1.2 Hz, 1H), 3.88 (s, 3H), 2.82 (d, *J* = 4.7 Hz, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$, mixture of diastereomers) δ 166.82, 166.30, 144.71, 142.54, 140.28, 139.67, 138.57, 128.84, 128.73, 128.61, 128.17, 128.12, 127.69, 127.17, 126.55, 126.35, 125.68, 123.68, 119.38, 56.32, 53.11, 52.42, 52.09, 49.53, 27.44. Yield: 55%, d.r. 1:1, White solid, m.p.= 261-263 °C; **HRMS-EI (m/z):** calc'd for $C_{19}H_{16}N_2ONa$ $[M+Na]^+$ 311.1161; found, 311.1157.



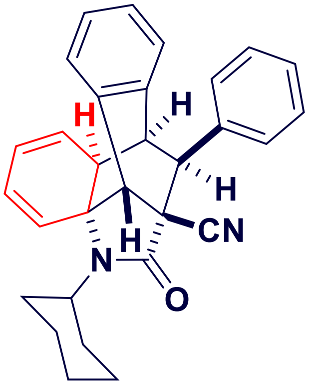
3-methyl-2-oxo-2,3,8,12*b*-*tetrahydro*-1,8-methanodibenzo[*e*,*h*]indole-1,13(7*aH*)-dicarbonitrile (32): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1ad** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **32** derivatives. **^{1}H NMR** (400 MHz, CDCl$_3$, major isomer) δ 7.48 – 7.40 (m, 5H), 7.34 – 7.30 (m, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 5.45 (d, *J* = 10.1 Hz, 1H), 3.75 – 3.67 (m, 1H), 3.46 (s, 1H), 3.42 (s, 3H), 2.85 (dd, *J* = 17.1, 7.5 Hz, 1H), 2.62 (dd, *J* = 17.1, 7.6 Hz, 1H); **^{13}C NMR**



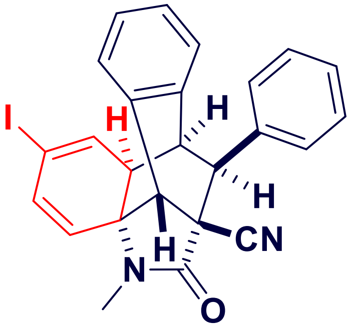
(100 MHz, CDCl$_3$, major isomer) δ 162.18, 141.62, 141.28, 138.78, 137.72, 130.60, 129.87, 129.68, 129.42, 129.18, 127.31, 125.24, 123.61, 117.38, 116.08, 114.72, 55.97, 50.92, 49.86, 40.92, 38.76, 37.07, 21.37; Yield: 53%, d.r. 18:1, White solid, m.p.= 232-234 °C; **HRMS-EI (m/z):** calc'd for $C_{20}H_{15}N_3O$ $[M+H]^+$ 313.1215; found, 314.1420.



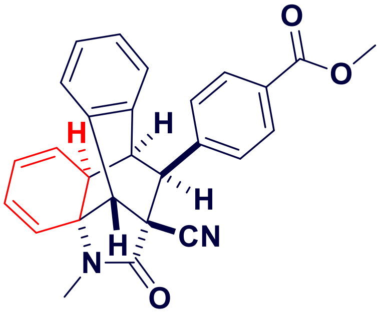
3-methyl-2-oxo-15-phenyl-2,3,8,14*b-tetrahydro*-1,8-methanobenzo[*h*]naphtho[2,1-*e*]indole-1(7*aH*)-carbonitrile (33): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1ae** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **33** derivatives. **^{1}H NMR** (400 MHz, CDCl$_3$, major isomer) δ 7.89 (dd, *J* = 8.2, 4.8 Hz, 2H), 7.58 (dd, *J* = 8.2, 4.8 Hz, 2H), 7.45 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.36 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.05 – 6.98 (m, 1H), 6.88 (t, *J* = 7.8 Hz, 2H), 6.34 (d, *J* = 7.3 Hz, 2H), 5.79 (dd, J = 9.8, 5.1 Hz, 1H), 5.39 (d, J = 9.8 Hz, 1H), 5.29 (dd, *J* = 9.6, 3.1 Hz, 1H), 5.24 (dd, *J* = 5.2, 2.2 Hz, 1H), 4.33 (t, *J* = 2.9 Hz, 1H), 3.89 (d, *J* = 2.6 Hz, 1H), 3.80 (s, 1H), 3.34 (dd, *J* = 5.6, 2.9 Hz, 1H), 3.02 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$, major isomer) δ 171.49, 138.11, 135.14, 133.24, 131.25, 129.72, 129.00, 128.66, 128.04, 128.01, 127.77, 127.55, 126.76, 125.91, 125.54, 122.82, 121.97, 121.37, 116.89, 65.02, 54.56, 52.34, 51.15, 44.94, 42.41, 27.72; Yield: 57%, d.r. 18:1, White solid, m.p.= 215-217 °C; **HRMS-EI (m/z):** calc'd for $C_{29}H_{22}N_2O$ $[M+H]^+$ 437.1630; found, 437.1628.



3-cyclohexyl-2-oxo-13-phenyl-2,3,8,12*b-tetrahydro*-1,8-methanodibenzo[*e*,*h*]indole-1(7*aH*)-carbonitrile (34): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1af** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **34** derivatives. **^{1}H NMR** (400 MHz, CDCl$_3$, major isomer) δ 7.43 (d, *J* = 6.7 Hz, 1H), 7.36 (td, *J* = 7.5, 1.2 Hz, 1H), 7.30 (td, *J* = 7.4, 1.3 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 2H), 6.91 (d, *J* = 7.1 Hz, 1H), 6.41 (d, *J* = 7.4 Hz, 2H), 5.78 (dd, *J* = 9.8, 5.6 Hz, 1H), 5.39 (dd, *J* = 18.1, 5.6 Hz, 2H), 5.25 (d, *J* = 8.7 Hz, 1H), 3.73 (s, 1H), 3.61 – 3.56 (m, 1H), 3.53 (dd, *J* = 7.9, 4.3 Hz, 1H), 3.38 (s, 2H), 2.32 (dt, *J* = 12.4, 8.9 Hz, 1H), 2.11 (tt, *J* = 12.3, 6.3 Hz, 1H), 1.85 (d, *J* = 11.0 Hz, 4H), 1.67 (s, 1H), 1.27 (ddd, *J* = 20.2, 16.6, 13.2 Hz, 3H); **^{13}C NMR** (150 MHz, CDCl$_3$, major isomer) δ 170.87, 138.53, 137.74, 132.35, 129.03, 128.61, 128.21, 127.87, 127.84, 127.71, 127.41, 127.40, 127.13, 123.81, 120.83, 117.07, 66.17, 55.04, 54.46, 51.59, 51.48, 47.32, 46.99, 31.21, 30.80, 26.11, 26.07, 25.08; Yield: 87%, d.r. 20:1, White solid, m.p.= 263-265 °C; **HRMS-EI (m/z):** calc'd for C$_{30}$H$_{28}$N$_2$ONa [M+Na]$^+$ 455.2099; found, 455.2096.

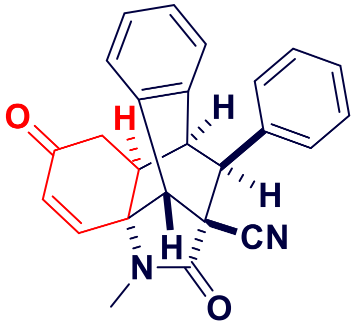


6-iodo-3-methyl-2-oxo-13-phenyl-2,3,8,12*b*-*tetrahydro*-1,8-methanodibenzo[*e*,*h*]indole-1(7*aH*)-carbonitrile (35): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1ag** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **35** derivatives. **^{1}H NMR** (400 MHz, CDCl$_3$, major isomer) δ 7.48 (d, J = 7.3 Hz, 1H), 7.39 (dtd, *J* = 16.6, 7.5, 1.3 Hz, 2H), 7.17 (ddd, *J* = 6.6, 3.9, 1.2 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 2H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.37 (d, *J* = 7.3 Hz, 2H), 5.99 (dd, *J* = 10.0, 1.1 Hz, 1H), 5.89 (d, *J* = 3.5 Hz, 1H), 5.20 (d, *J* = 10.0 Hz, 1H), 3.69 (d, *J* = 2.5 Hz, 1H), 3.62 (s, 1H), 3.39 (t, *J* = 2.8 Hz, 1H), 3.19 (t, *J* = 3.3 Hz, 1H), 2.98 (s, 3H); **^{13}C NMR** (101 MHz, CDCl$_3$, major isomer) δ 171.22, 137.97, 137.27, 136.86, 136.20, 131.46, 129.05, 128.97, 128.12, 128.07, 128.01, 127.46, 124.46, 116.59, 85.72, 63.26, 53.58, 51.35, 50.82, 47.93, 47.04, 27.69; Yield: 75%, d.r. 20:1, White solid, m.p.= 223-225 °C; **HRMS-EI (m/z):** calc'd for C$_{25}$H$_{19}$IN$_2$ONa [M+Na]$^+$ 513.0440; found, 513.0438.

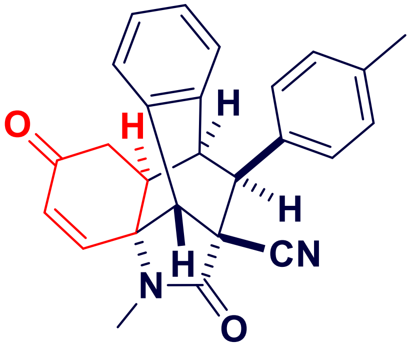


methyl 1-cyano-3-methyl-2-oxo-1,2,3,7a,8,12*b*-*hexahydro*-1,8-methanodibenzo[*e*,*h*]indol-13-yl)benzoate (36): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1ah** (0.2 mmol), (4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **36** derivatives. **^{1}H NMR** (400 MHz, CDCl$_3$, major isomer) δ 7.97 (d, *J* = 1.6 Hz, 1H), 7.90 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.51 (dd, *J* = 5.5, 3.0 Hz, 1H), 7.46 (dd, *J* = 5.7, 3.0 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.32 (ddd, *J* = 9.6, 5.0, 3.0 Hz, 2H), 7.28 – 7.27 (m, 1H), 7.26 – 7.23 (m, 1H), 6.96 (dd, *J* = 7.5, 2.0 Hz, 2H), 6.19 (s, 1H), 4.75 (s, 1H), 4.54 (d, *J* = 1.2 Hz, 1H), 3.90 (d, *J* = 1.4 Hz, 1H), 3.88 (s, 3H), 2.97 – 2.88 (m, 1H), 2.83 (d, *J* = 4.8 Hz, 3H); ^{13}**C NMR** (100 MHz, $CDCl_3$, major isomer) δ 166.84, 166.32, 144.70, 142.55, 140.26, 139.67, 138.54, 128.81, 128.73, 128.64, 128.19, 128.16, 127.71, 127.20, 126.57, 126.39, 125.70, 123.69, 119.40, 56.31, 53.07, 52.48, 52.13, 49.52, 27.47; Yield: 73%, d.r. 20:1, White solid, m.p.= 223-225 °C; **HRMS-EI (m/z):** calc'd for $C_{27}H_{22}N_2O_3Na$ $[M+Na]^+$ 445.1528; found, 445.1526.

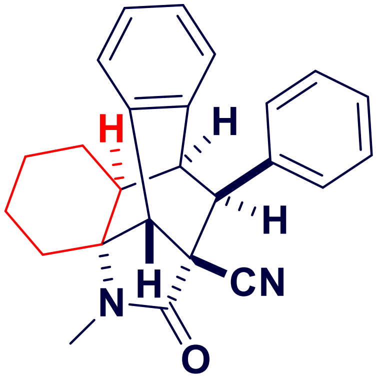
3-methyl-2,6-dioxo-13-phenyl-2,3,7,7a,8,12*b-hexahydro*-1,8-methanodibenzo[*e*,*h*]indole-1(6*H*)-carbonitrile (43): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1ai** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **43** derivatives. ^{1}**H NMR** (597 MHz, $CDCl_3$, major isomers) δ 7.52 (d, *J* = 7.3 Hz, 1H), 7.46 (td, *J* = 7.5, 1.2 Hz, 1H), 7.40 (td, *J* = 7.5, 1.3 Hz, 1H), 7.21-7.16 (m, 1H), 7.10 (t, *J* = 7.7 Hz, 2H), 7.03 (d, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 10.3 Hz, 1H), 6.41 (d, *J* = 7.3 Hz, 2H), 6.16 (d, *J* = 10.3 Hz, 1H), 3.87 (s, 1H), 3.66 (d, *J* = 2.4 Hz, 1H), 3.26 (t, *J* = 2.6 Hz, 1H), 2.91 (s, 3H), 2.81 (ddd, *J* = 10.8, 7.9, 3.0 Hz, 1H), 2.45 (dd, *J* = 16.7, 7.9 Hz, 1H), 1.69 (dd, *J* = 16.7, 10.6 Hz, 1H); ^{13}**C NMR** (150 MHz, $CDCl_3$, major isomers) δ 195.99, 171.04, 143.87, 137.76, 136.98, 134.70, 130.51, 129.33, 129.07, 129.02, 128.59, 128.16, 128.07, 116.29, 62.96, 52.77, 51.13, 51.09, 48.83, 40.31, 40.07, 27.15; Yield: 85%, d.r. 20:1, Off-white solid, m.p.= 201-203 °C; **HRMS-EI (m/z):** calc'd for $C_{25}H_{20}N_2O_2Na$ $[M+Na]^+$ 403.1423; found, 403.1421.



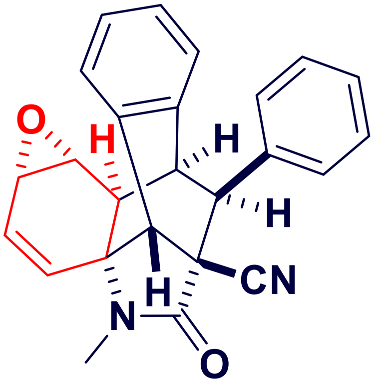
3-methyl-2,6-dioxo-13-(p-tolyl)-2,3,7,7a,8,12*b-hexahydro*-1,8-methanodibenzo[*e*,*h*]indole-1(6*H*)-carbonitrile (43'): A clean vial (5 mL) equipped with a magnetic stir bar were added to **1aj** (0.2 mmol), 4CzIPN (2.5 mol%) and 2-MeTHF (3.0 mL) at room temperature, and then placed at a distance of approx. 3 cm from a 24 W blue LED, and the solution was stirred at room temperature under visible-light irradiation for 6-24 h. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with Hex/EA = 80:20-60:40 to afford the dearomative cyclization product **43**' derivatives. ^{1}**H NMR** (400 MHz, $CDCl_3$, major isomers) δ 7.44 (d, *J* = 7.1 Hz, 1H), 7.33 (dtd, *J* = 25.7, 7.5, 1.2 Hz, 2H), 6.90 (dd, *J* = 10.6, 8.0 Hz, 3H), 6.27 (d, *J* = 8.1 Hz, 2H), 5.69 (dd, *J* = 10.1, 2.1 Hz, 1H), 5.38 (d, *J* = 10.0 Hz, 1H), 4.11 (d, *J* = 2.4 Hz, 1H), 3.68 (d, *J* = 2.5 Hz, 1H), 3.58 (s, 1H), 3.31 (t, *J* = 2.7 Hz, 1H), 3.27 (s, 3H), 2.97 (s, 3H), 2.22 (s, 3H); ^{13}**C NMR** (100 MHz, $CDCl_3$, major



isomers) δ 171.44, 150.50, 138.14, 137.46, 135.51, 131.63, 129.06, 128.91, 128.64, 128.41, 127.91, 127.74, 127.47, 124.97, 116.89, 94.79, 65.08, 54.24, 53.52, 51.30, 51.13, 48.80, 43.35, 27.52, 21.02; Yield: 83%, d.r. 20:1, Off-white solid, m.p.= 205-207 °C; **HRMS-EI (m/z):** calc'd for $C_{26}H_{22}N_2O_2Na$ $[M+Na]^+$ 417.1579; found, 417.1577.



3-methyl-2-oxo-13-phenyl-2,3,5,6,7,7a,8,12*b-octahydro*-1,8-methanodibenzo[*e*,*h*]indole-1(4*H*)-carbonitrile (44): To a 25 mL Schlenk tube with a magnetic bar were added **2** (0.22 mmol) in MeOH (3 mL) was added Pd/C (10 mmol%), the resulted mixture was stirred at room temperature under H_2 (balloon) for 24 hours. The progress of the reaction was monitored by thin layer chromatography. When the reaction was complete, water was added to quench the reaction mixture, followed by extraction with ethyl acetate (3×10 mL). Finally, the combined organic layer was dried over sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography (Hex/EA = 60:40) on silica gel to afford the corresponding **44**. **^{1}H NMR** (400 MHz, $CDCl_3$, mixture of diastereomers) δ 7.50 (d, *J* = 7.3 Hz, 1H), 7.42 (td, *J* = 7.5, 1.2 Hz, 1H), 7.33 (td, *J* = 7.5, 1.3 Hz, 1H), 7.18-7.11 (m, 1H), 7.10-7.03 (m, 2H), 6.95 (d, *J* = 7.3 Hz, 1H), 6.43-6.35 (m, 2H), 6.26-6.09 (m, 1H), 5.40 (dt, *J* = 46.9, 23.4 Hz, 1H), 3.71 (s, 1H), 3.63 (d, *J* = 2.4 Hz, 1H), 3.59 (d, *J* = 2.5 Hz, 1H), 3.55 (s, 1H), 3.14 (t, *J* = 2.7 Hz, 1H), 3.04 (s, 3H), 2.83 (s, 1H), 2.26 (ddd, *J* = 12.6, 5.6, 3.1 Hz, 1H), 2.03 (ddd, *J* = 12.4, 4.6, 3.2 Hz, 1H), 1.88-1.66 (m, 3H), 1.60-1.19 (m, 5H), 0.88 (t, *J* = 7.1 Hz, 1H), 0.60-0.50 (m, 1H), 0.41 (dd, *J* = 12.9, 4.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$, mixture of diastereomers) δ 171.19, 138.63, 138.19, 138.10, 131.70, 131.36, 129.09, 129.03, 128.33, 128.25, 128.04, 127.92, 127.74, 127.67, 127.56, 127.52, 125.73, 117.21, 63.14, 54.23, 53.89, 51.85, 51.80, 51.31, 48.79, 48.67, 43.60, 42.25, 27.10, 26.77, 26.12, 24.91, 22.90, 19.45, 17.39. white solid, 91% yield, d.r. 7:1 m.p.= 261-263 °C; **HRMS-EI (m/z):** calc'd for $C_{25}H_{24}N_2ONa$ $[M+Na]^+$ 391.1787; found, 391.1785.



4-methyl-5-oxo-12-phenyl-4,5,6*a*,11,11a,11*b-hexahydro*-6,11-methanobenzo[*e*]oxireno[2',3':5,6]benzo[1,2-*h*]indole-6(1*aH*)-carbonitrile (45): To a 25 mL Schlenk tube with a magnetic bar were added **2** (1.0 eq, 0.14 mmol) and *m*-CPBA (1.2 eq, 1.2 mmol) in DCM (2.0 mL) at r.t. After the reaction was finished, the reaction mixture was washed with water (3 mL), extracted with DCM (3×10 mL), dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, petroleum ether/EtOAc = 1:1) to afford **45** as off-white solid (92% yield, d.r. 20:1), m.p.= 198-200 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, major isomer) δ 7.49-7.31 (m, 3H), 7.21-7.13 (m, 1H), 7.13-6.98 (m, 3H), 6.38 (d, *J* = 7.3 Hz, 2H), 6.16 (dd, *J* = 10.3, 3.7 Hz, 1H), 5.64 (d, *J* = 10.3 Hz, 1H), 3.69-3.62 (m, 2H), 3.47 (t, *J* = 2.8

Hz, 1H), 2.93 (d, *J* = 3.9 Hz, 1H), 2.85 (s, 3H), 2.72-2.64 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$, major isomer) δ 171.19, 137.75, 136.26, 131.23, 131.20, 129.82, 128.95, 128.90, 128.23, 127.99, 127.96, 127.95, 127.25, 116.73, 63.90, 56.10, 53.56, 51.06, 50.41, 47.14, 45.26, 42.15, 27.10. **HRMS-EI (m/z):** calc'd for $C_{25}H_{20}N_2O_2Na$ $[M+Na]^+$ 403.1423; found, 403.1421.

7. REFERENCES

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(3) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.*, **2008**, *120*, 215-241.

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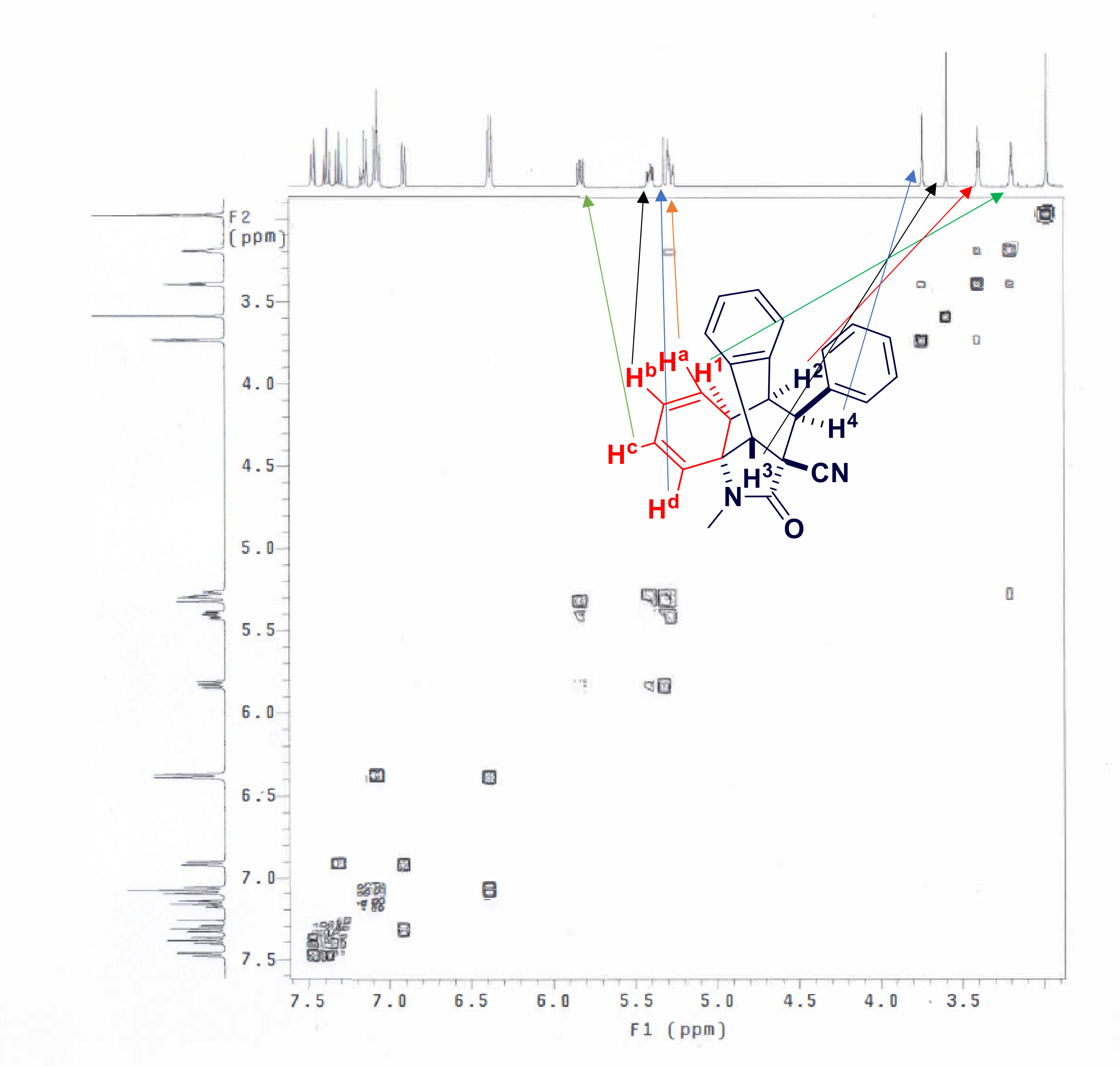
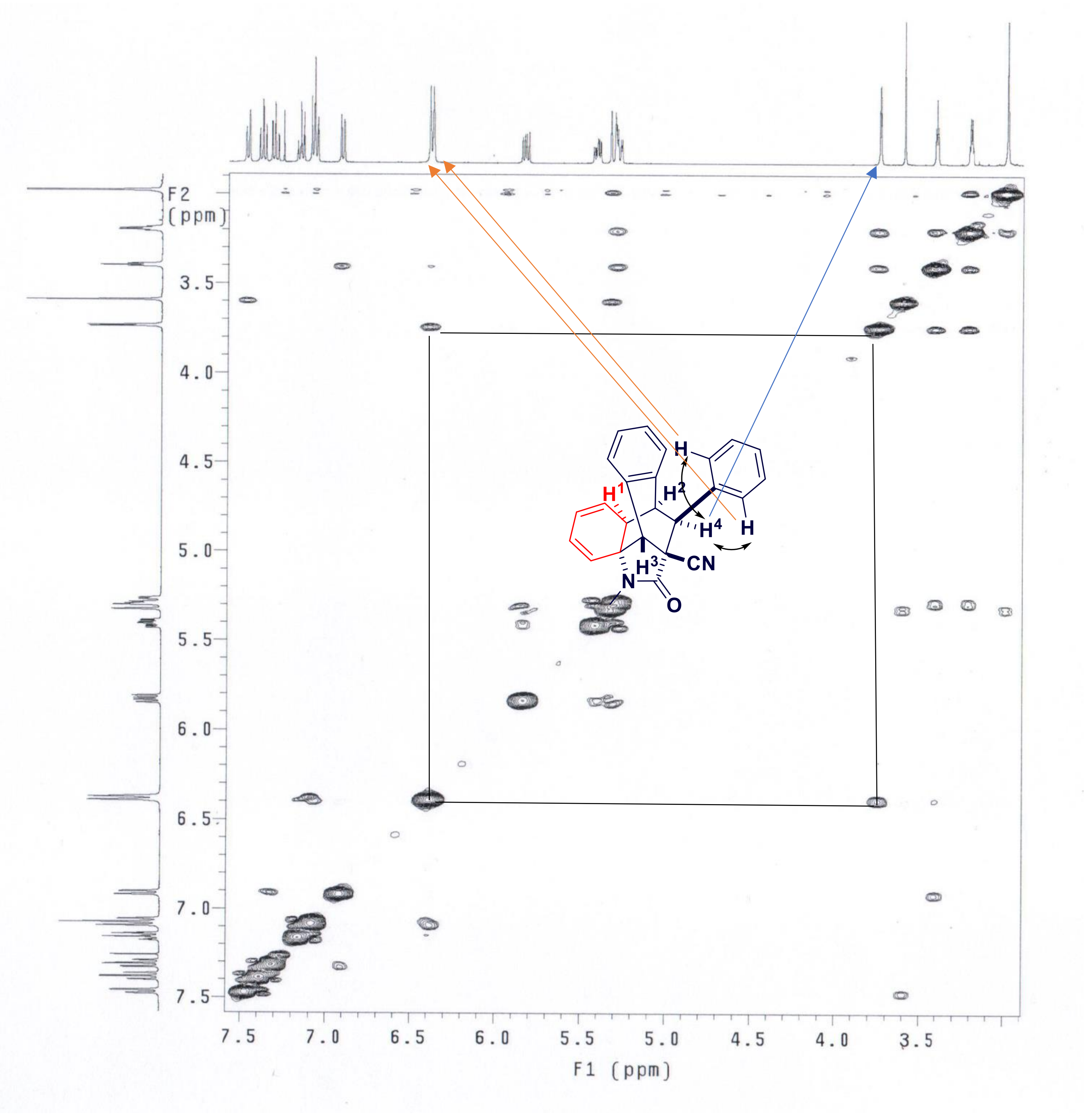
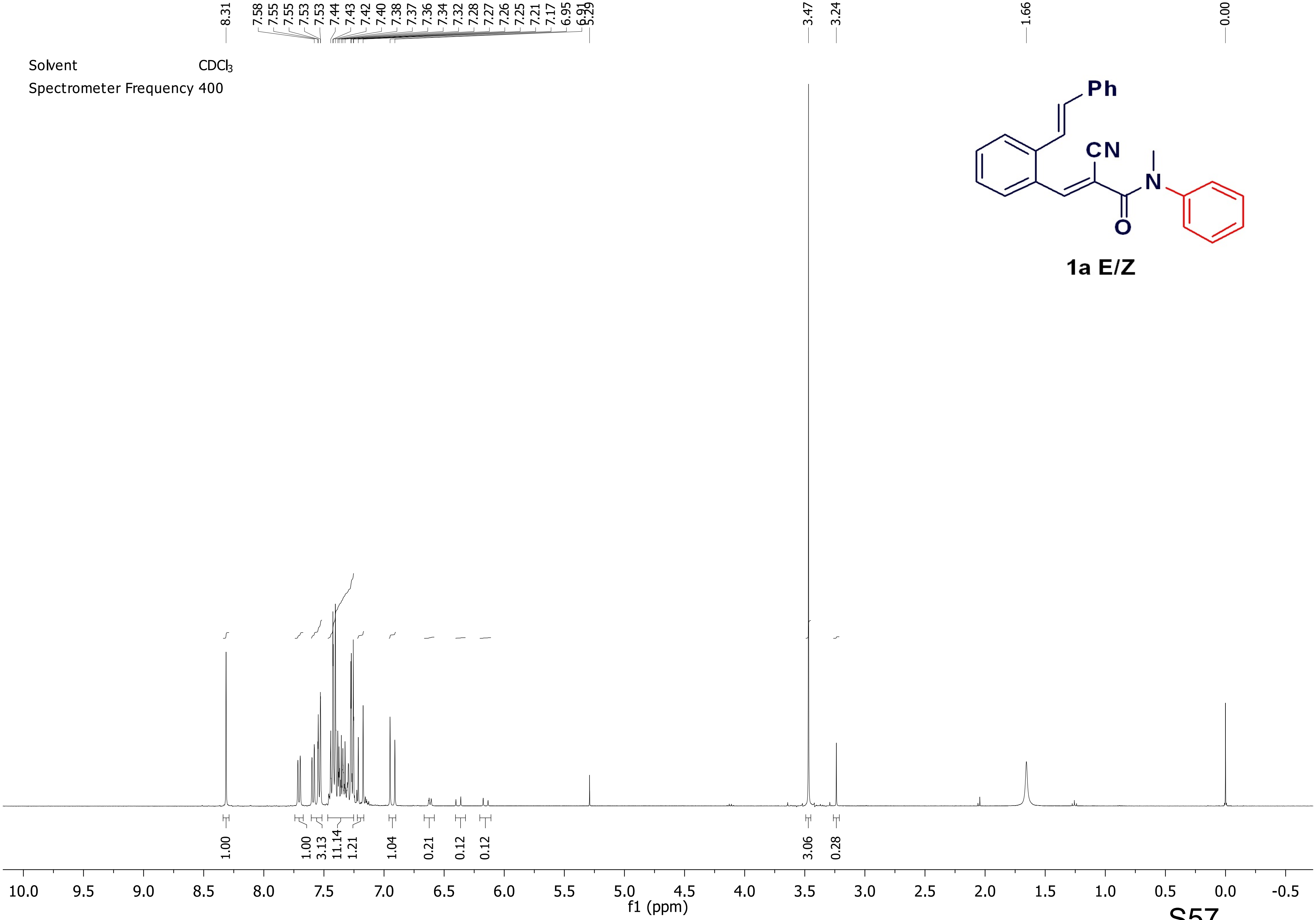
8. COSY and NOESY spectrum of compound of 2



COESY spectrum of compound of 2 (recorded in $CDCl_3$)



NOESY spectrum of compound of 2 (recorded in CDCl$_3$)



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7.28
7.27
7.26
7.25
7.21
7.17
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3.24
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0.12
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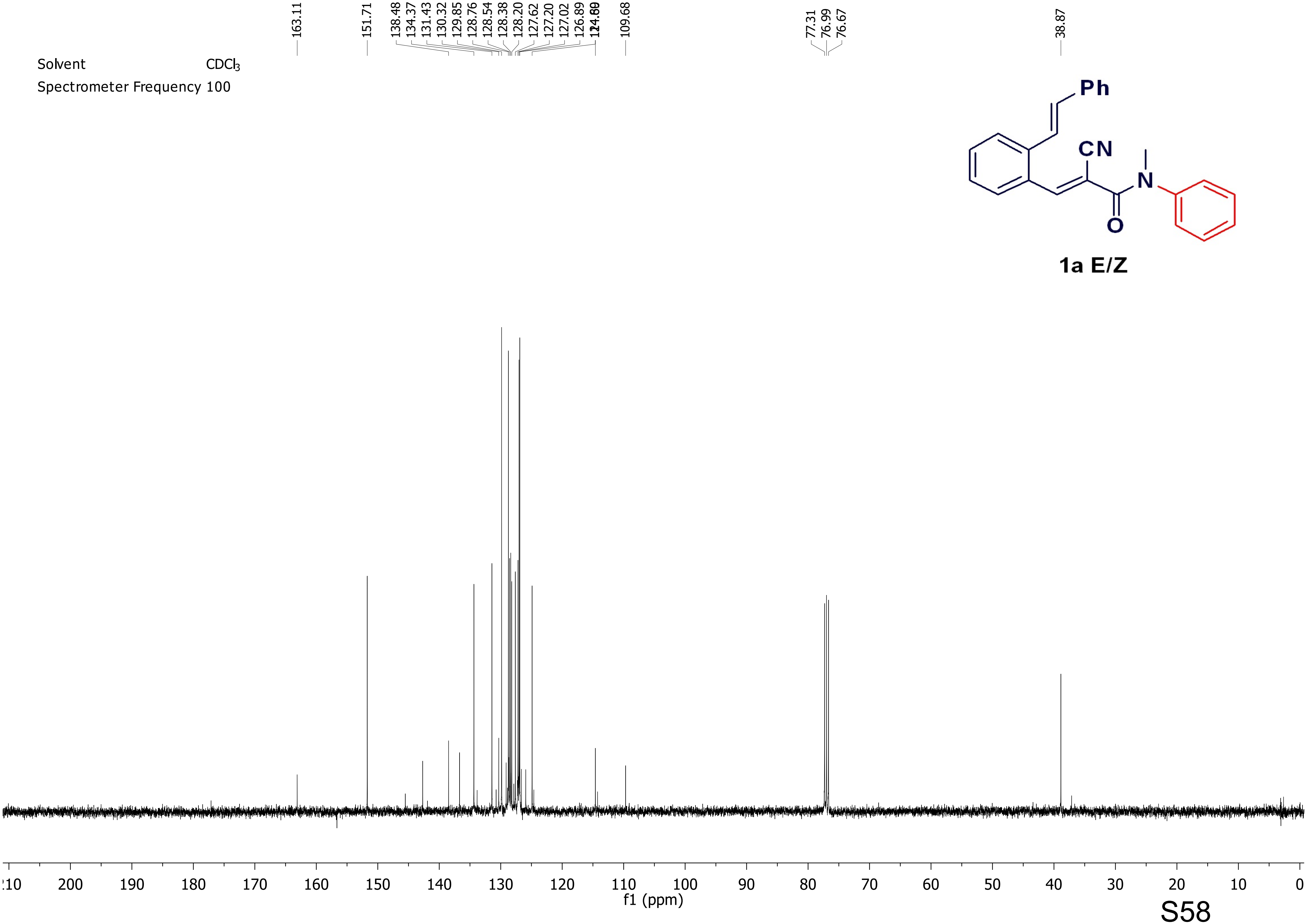
1a E/Z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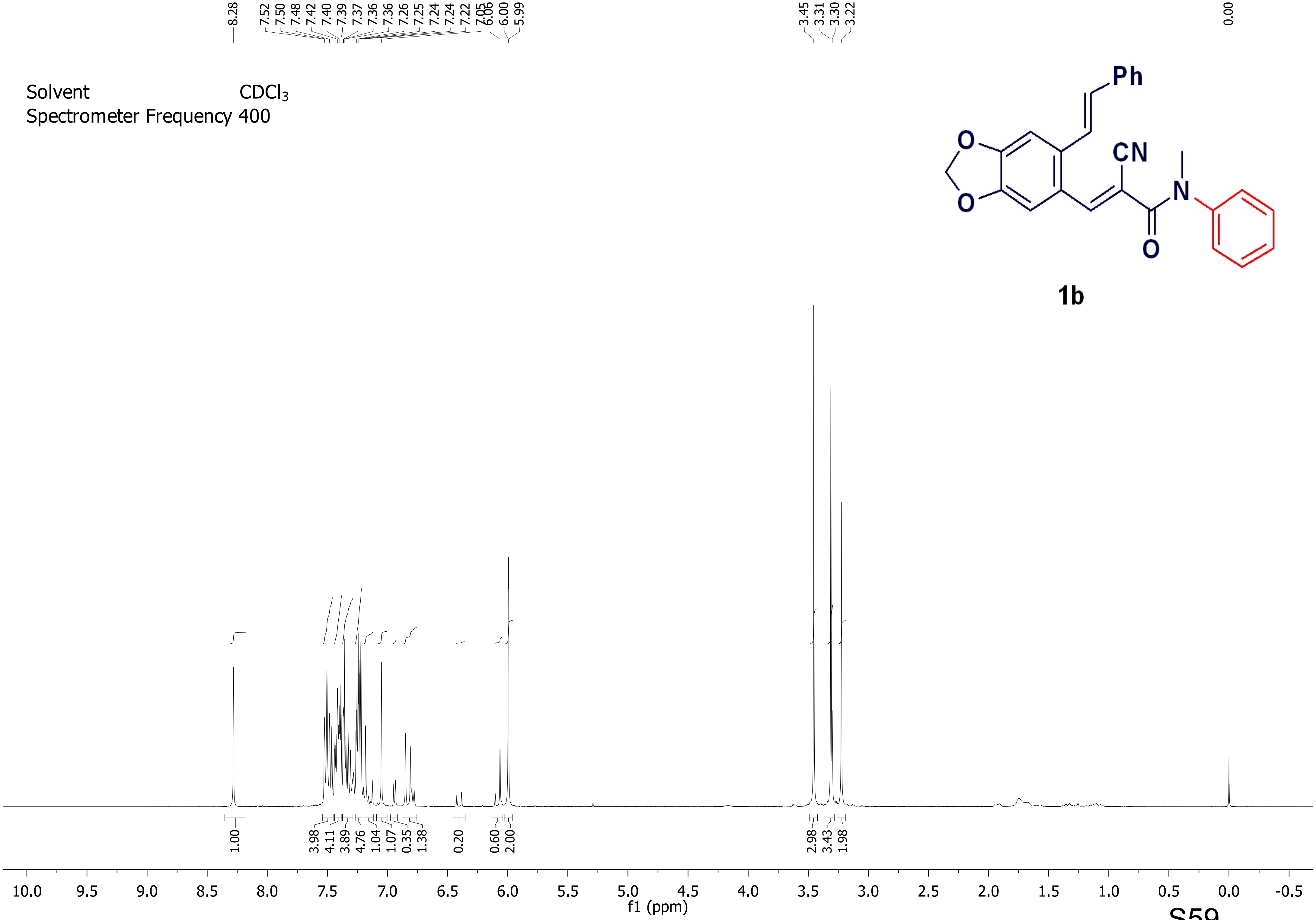
1a E/Z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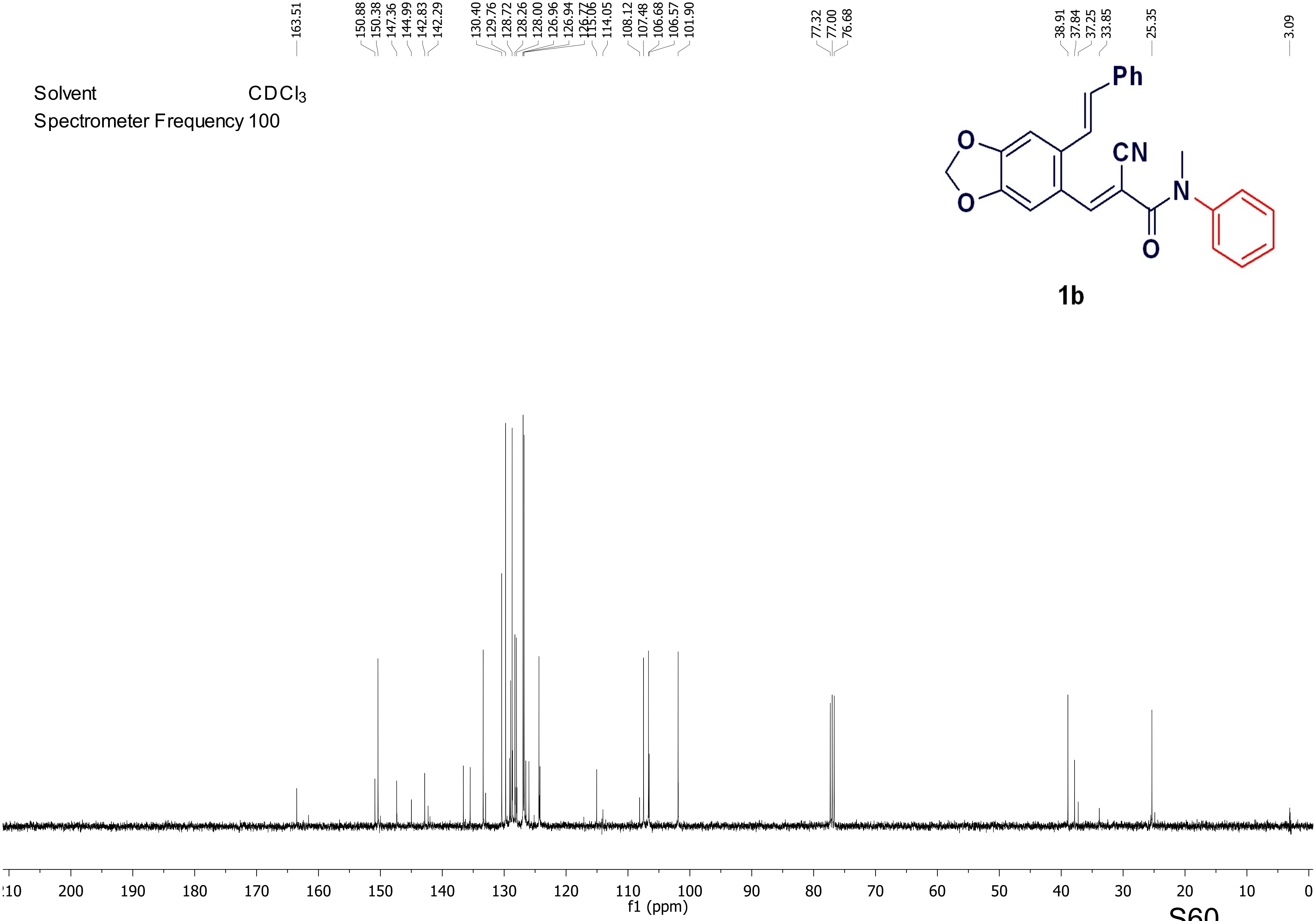
1b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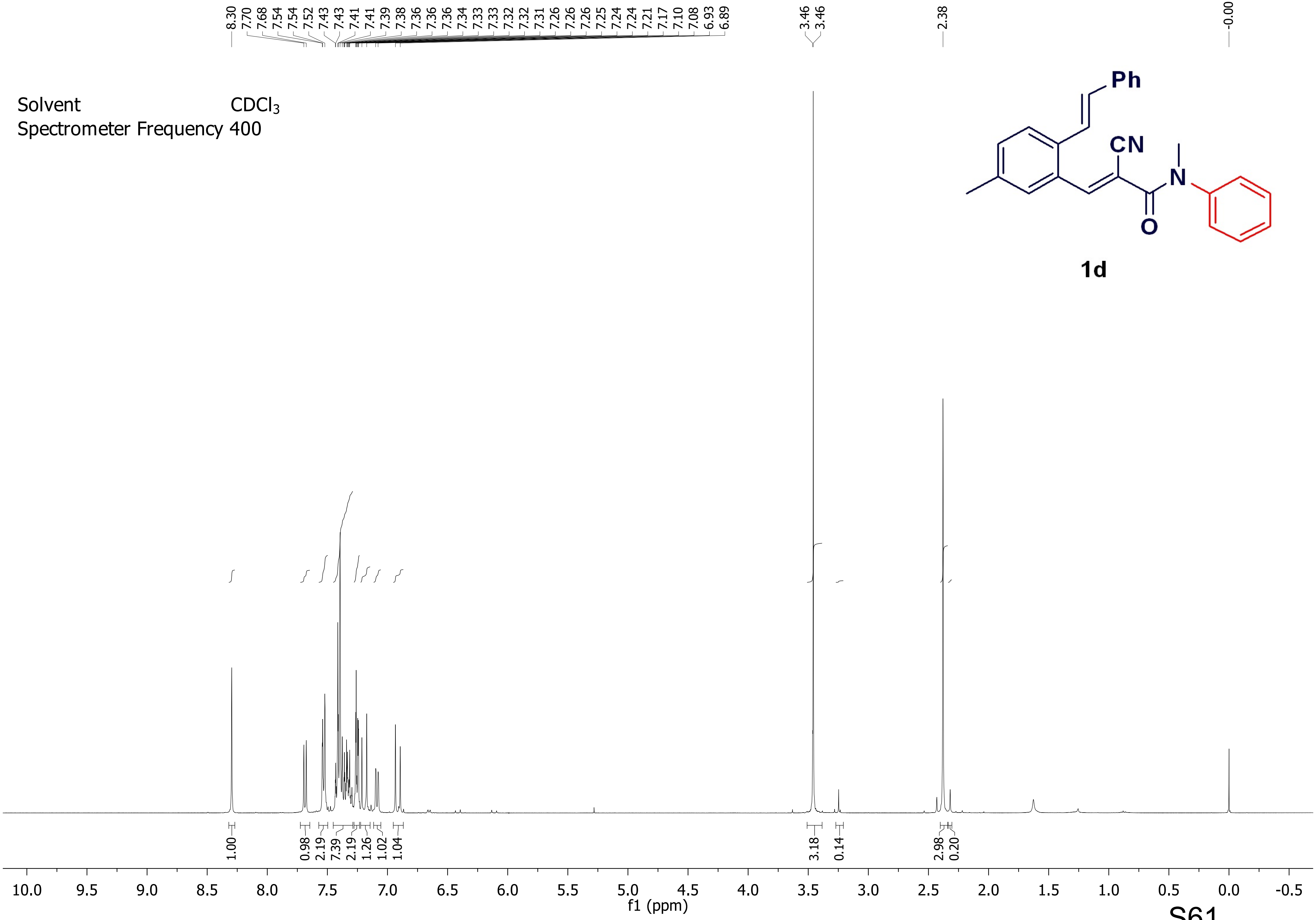
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Solvent CDCl$_3$
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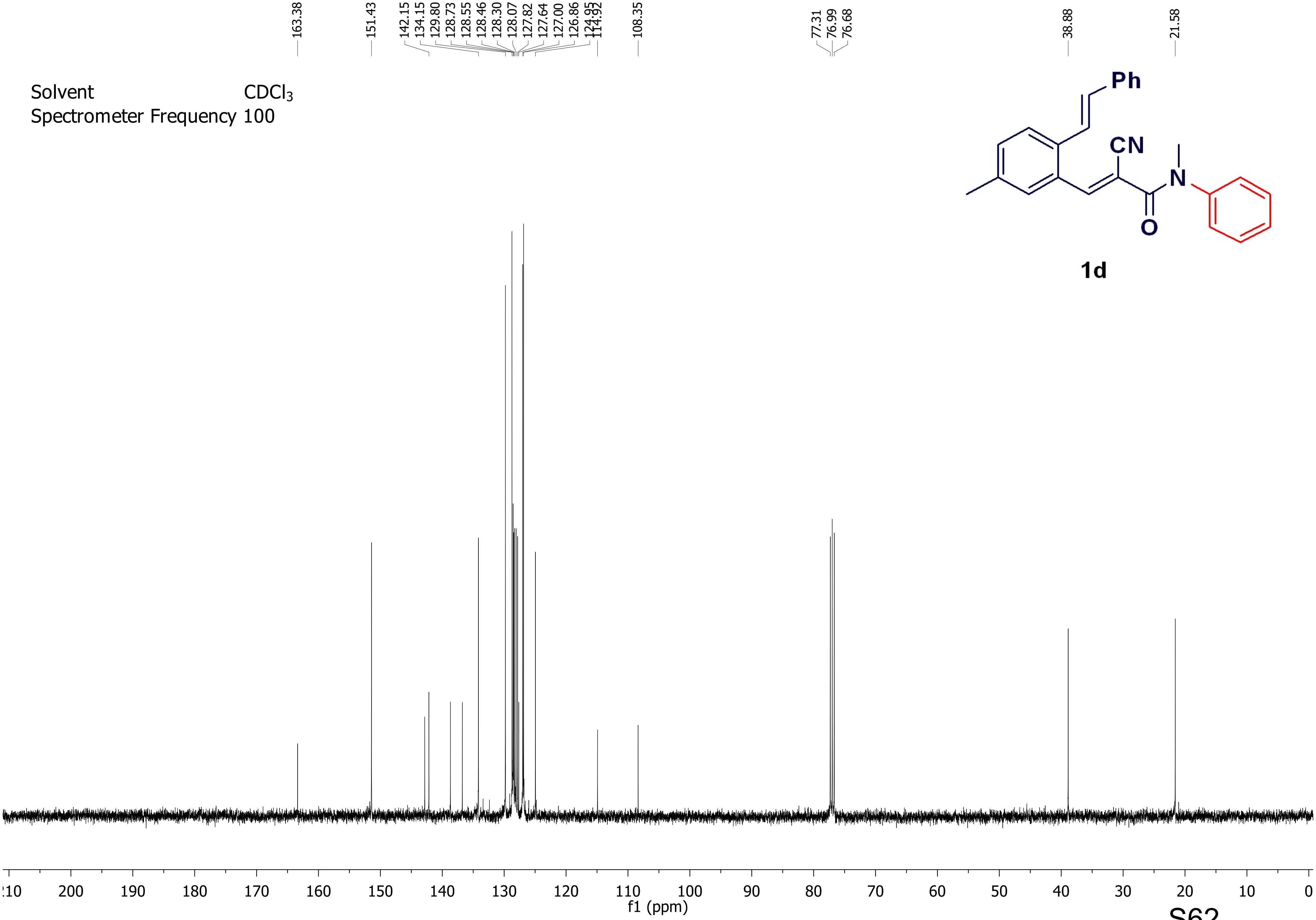

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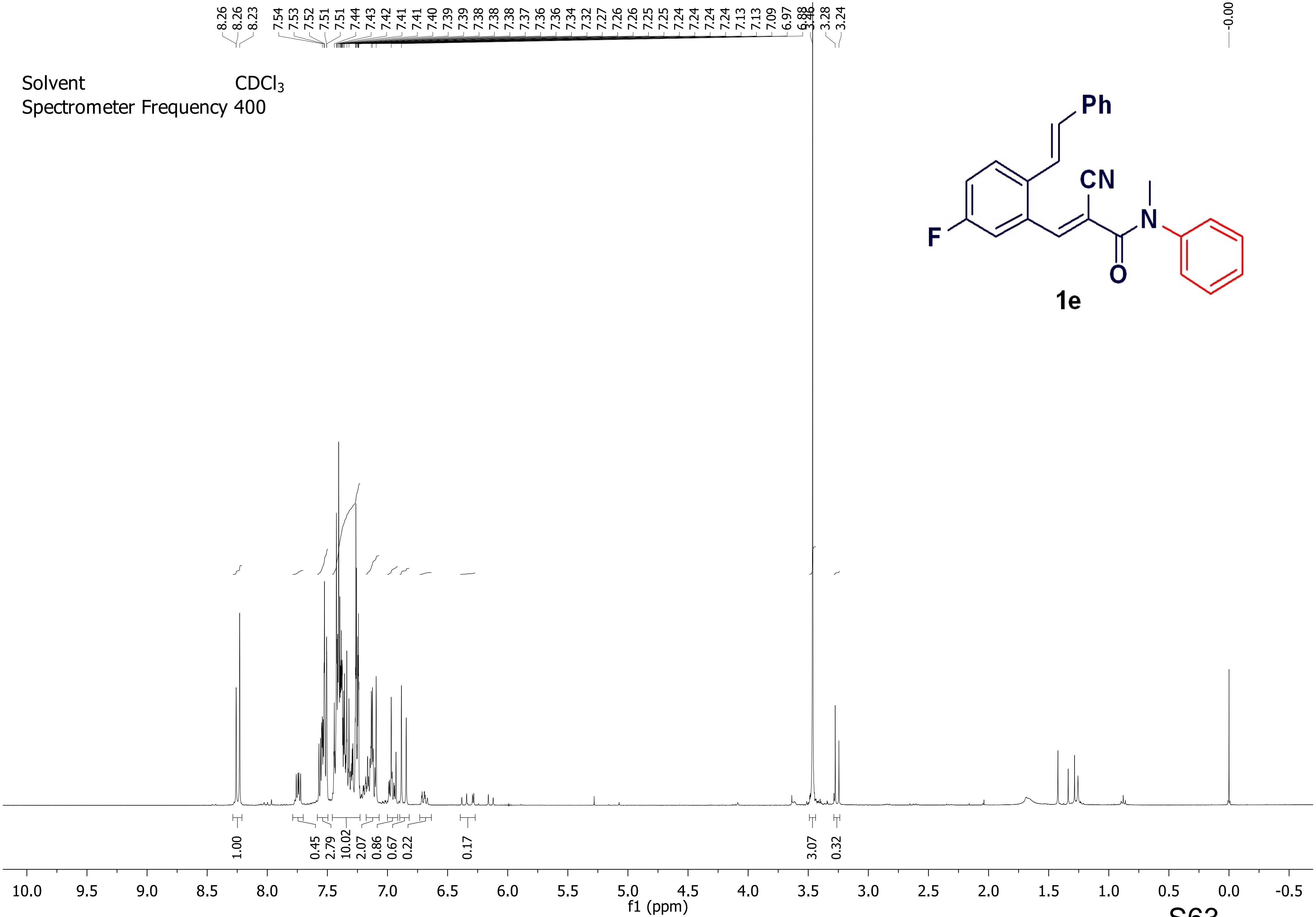
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Ph
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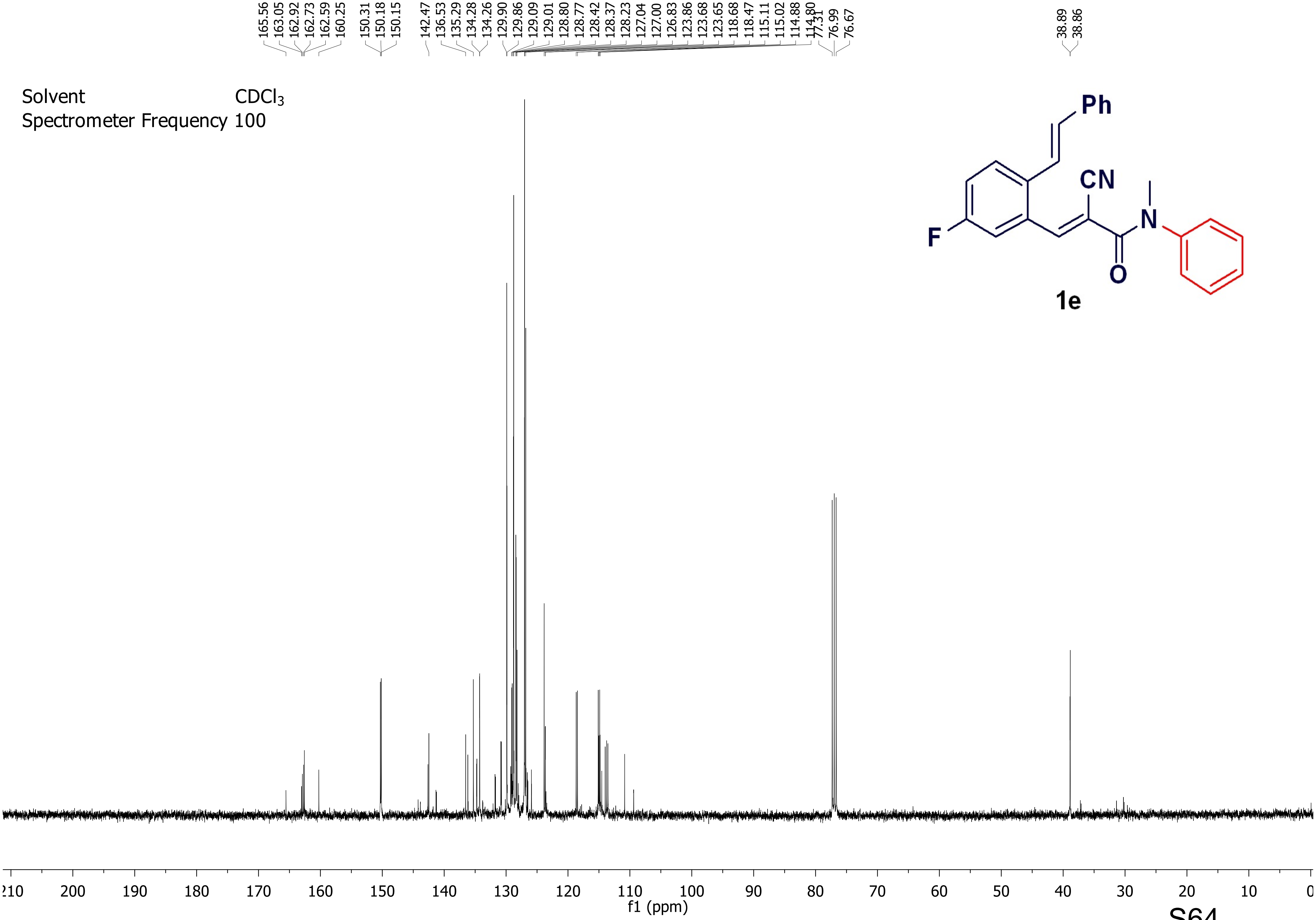
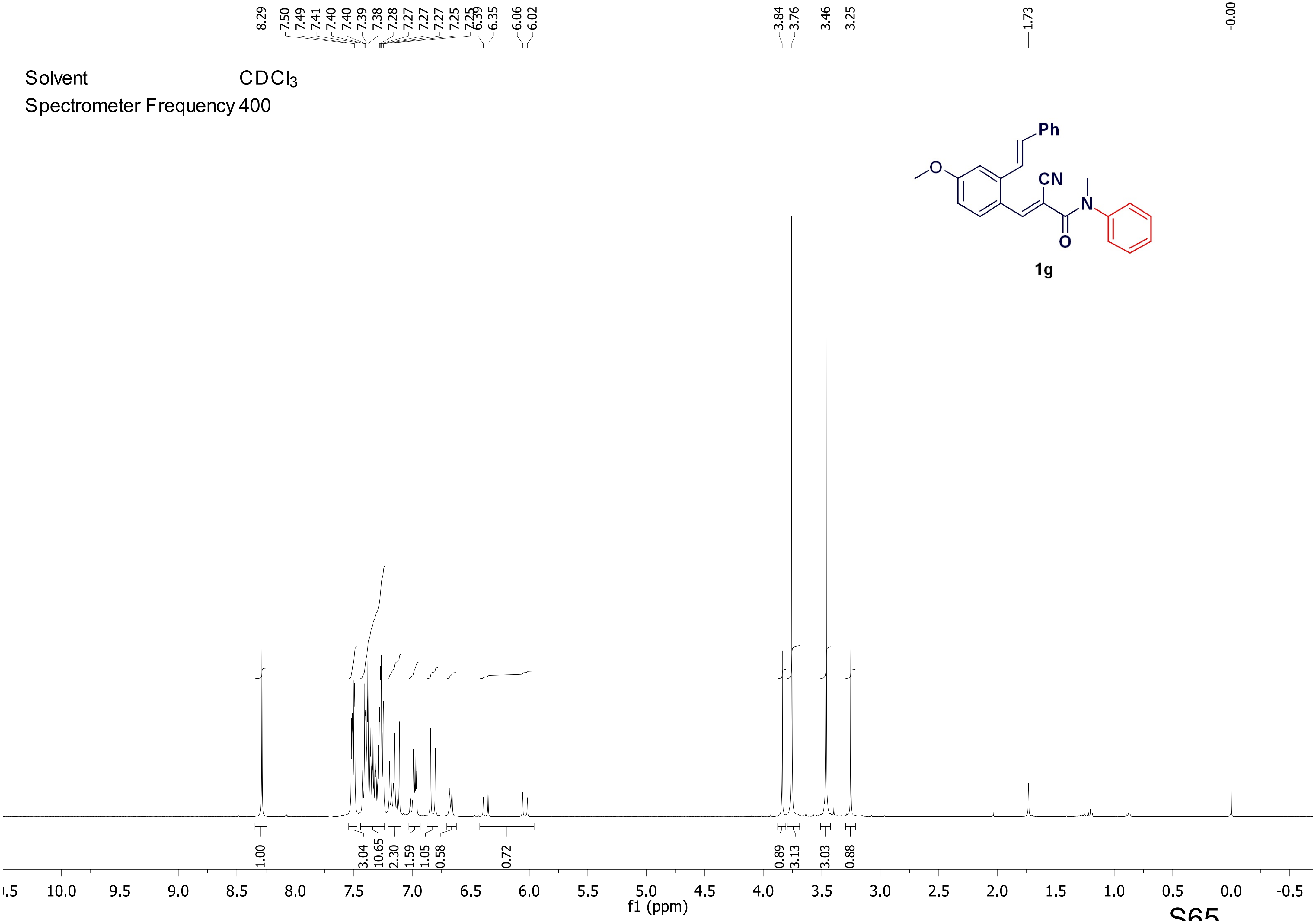
-0.5
f1 (ppm)

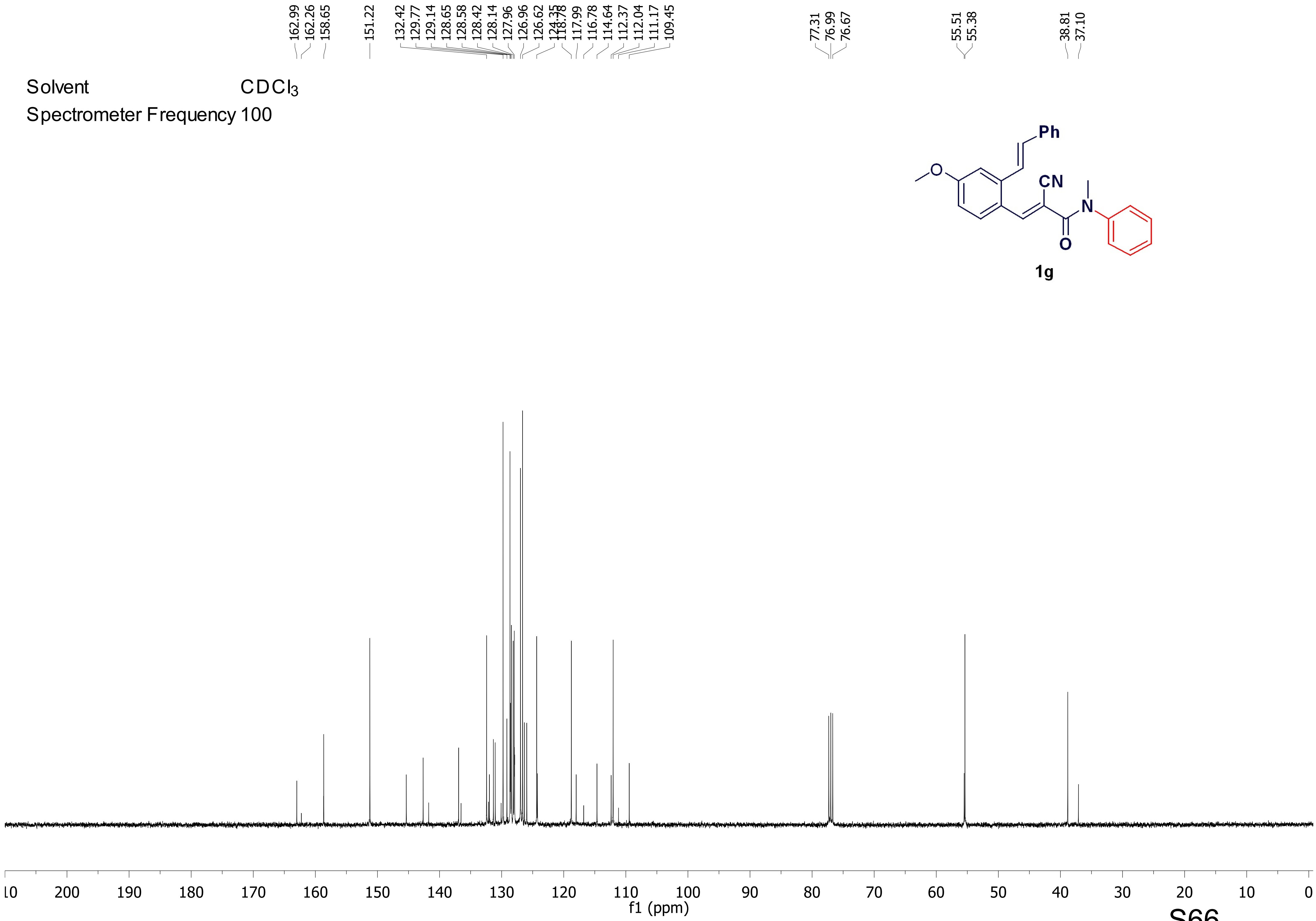

165.56
163.05
162.92
162.73
162.59
160.25
150.31
150.18
150.15
142.47
136.53
135.29
134.28
134.26
129.90
129.86
129.09
129.01
128.80
128.77
128.42
128.37
128.23
127.04
127.00
126.83
123.86
123.68
123.65
118.68
118.47
115.11
115.02
114.88
114.80
77.31
76.99
76.67
38.89
38.86
Solvent CDCl$_3$
Spectrometer Frequency 100
Ph
CN
F
N
O
1e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.29
7.50
7.49
7.41
7.40
7.40
7.39
7.38
7.28
7.27
7.27
7.27
7.25
7.25
6.39
6.35
6.06
6.02
3.84
3.76
3.46
3.25
1.73
-0.00
Solvent CDCl$_3$
Spectrometer Frequency 400
Ph
O
CN
N
O
1.00
3.04
10.65
2.30
1.59
1.05
0.58
0.72
0.89
3.13
3.03
0.88
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

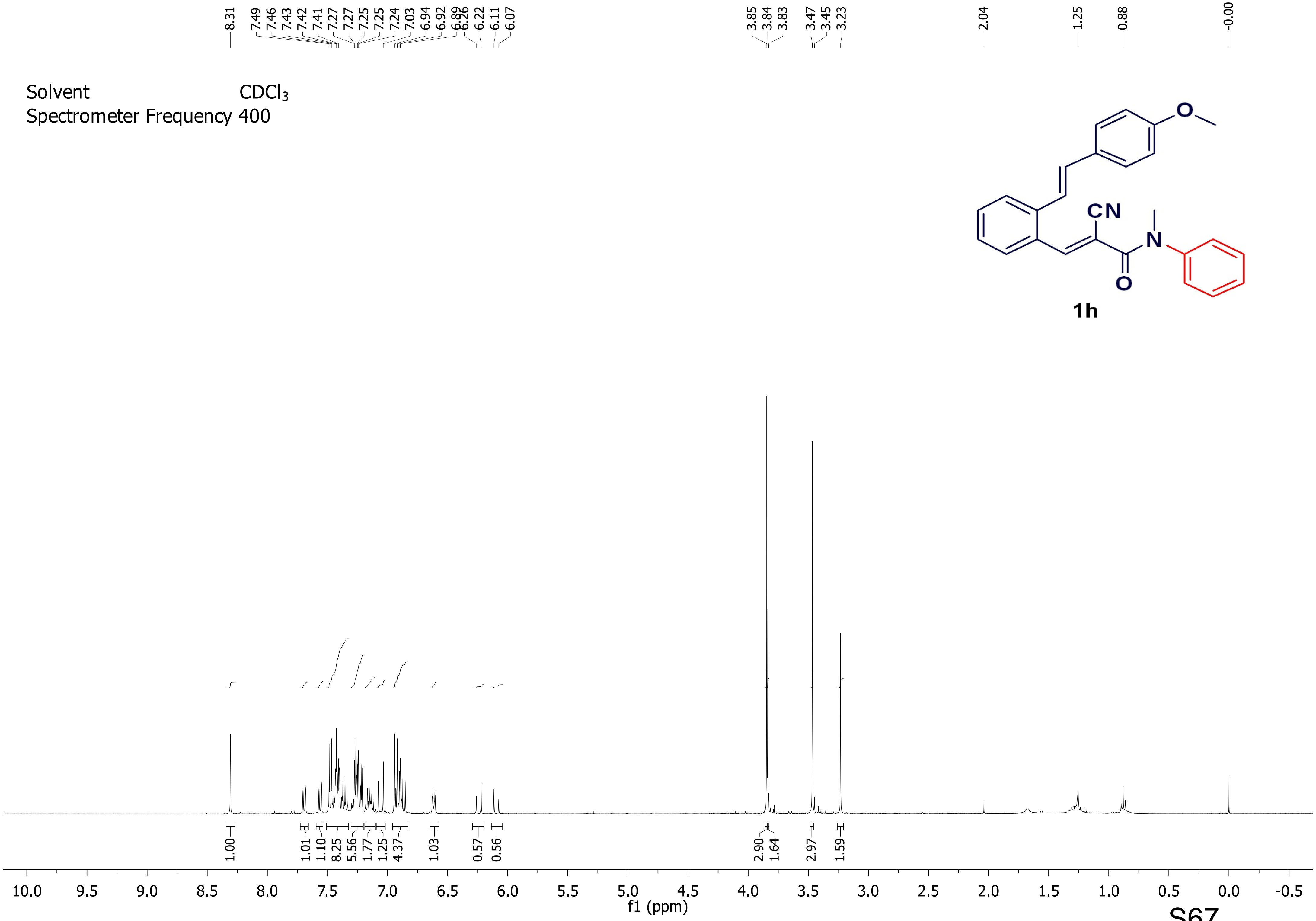
1g

Solvent CDCl$_3$

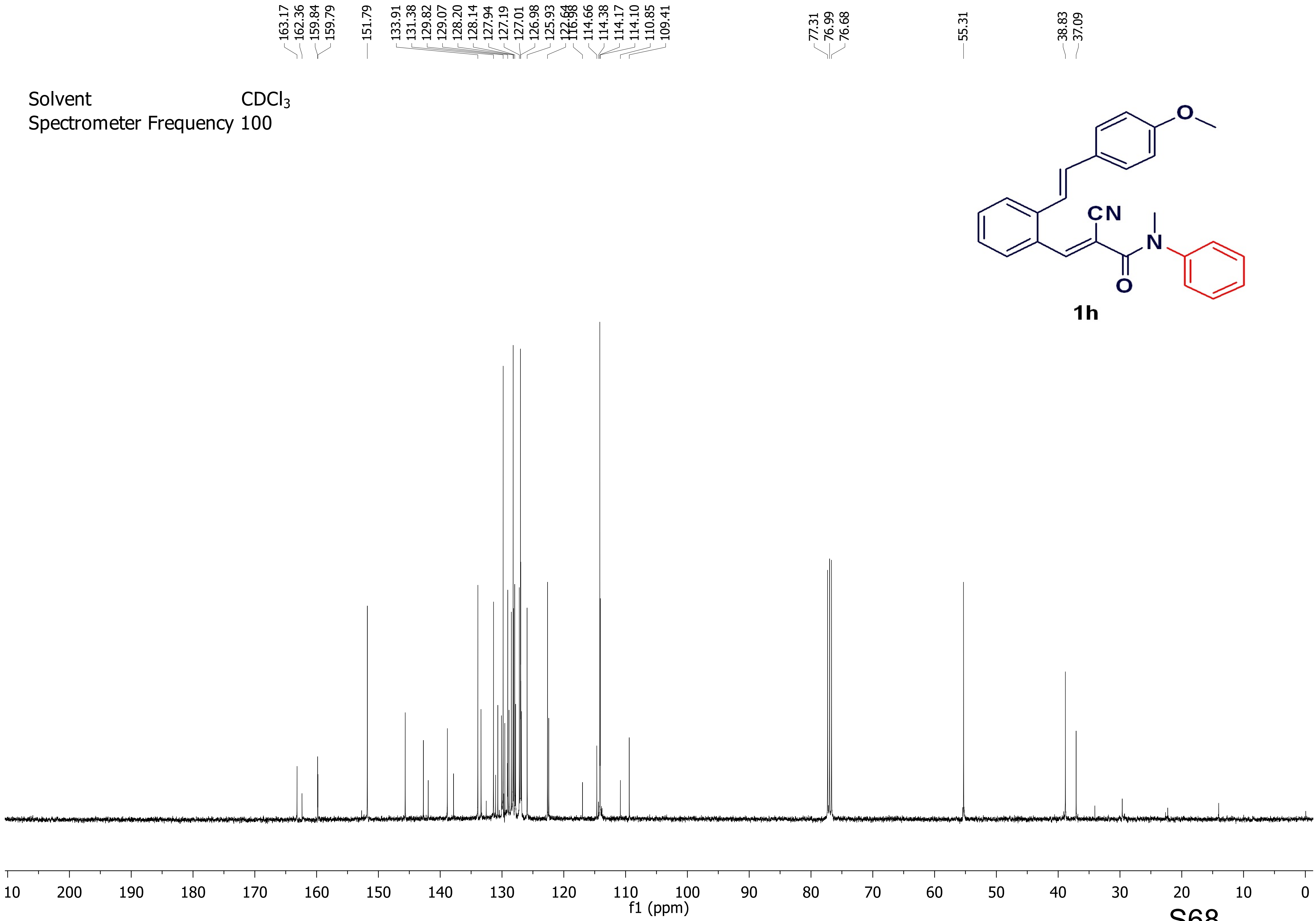
Spectrometer Frequency 100

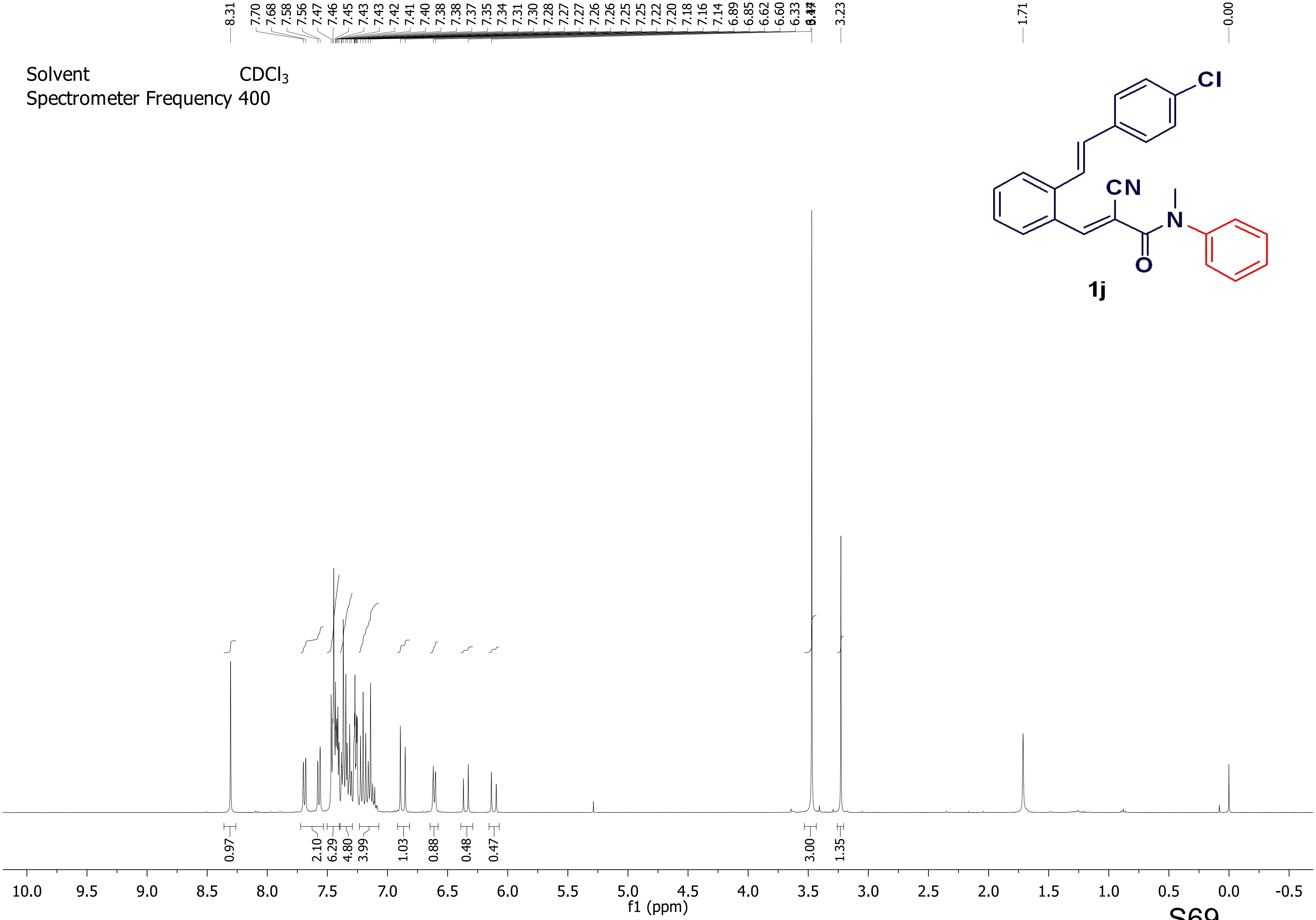


Solvent CDCl$_3$
Spectrometer Frequency 400

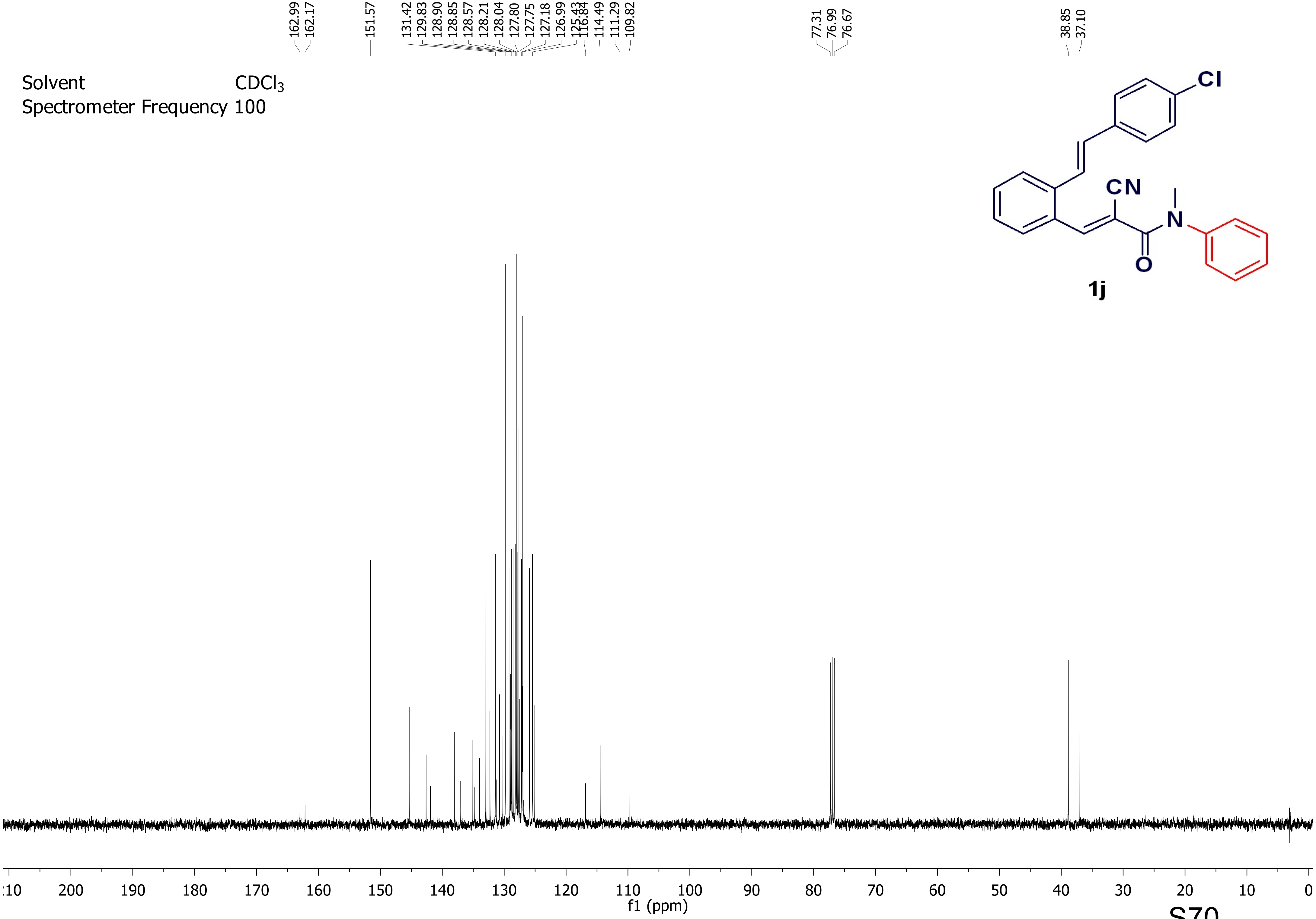


Solvent CDCl$_3$
Spectrometer Frequency 100



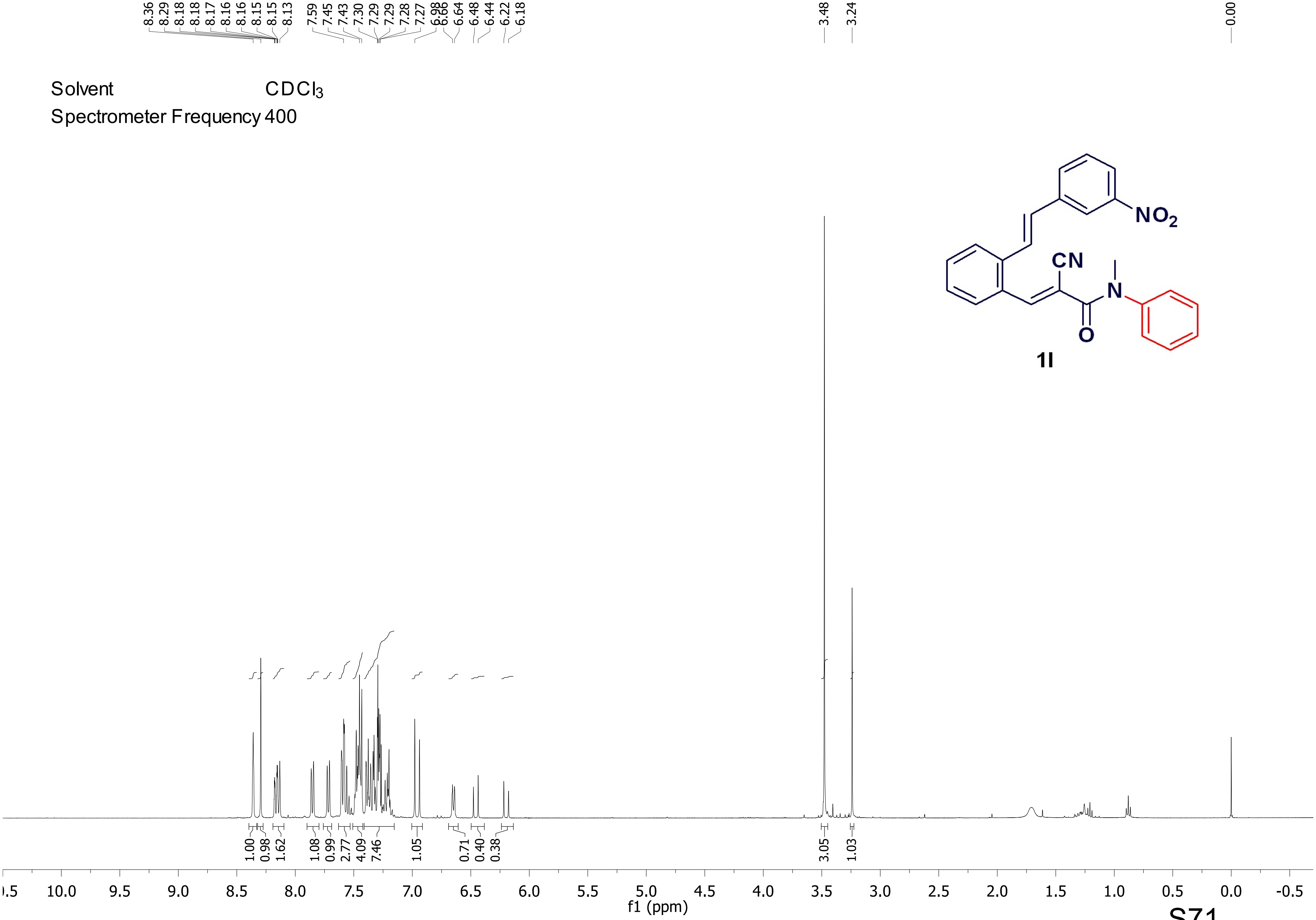


Solvent CDCl$_3$
Spectrometer Frequency 400

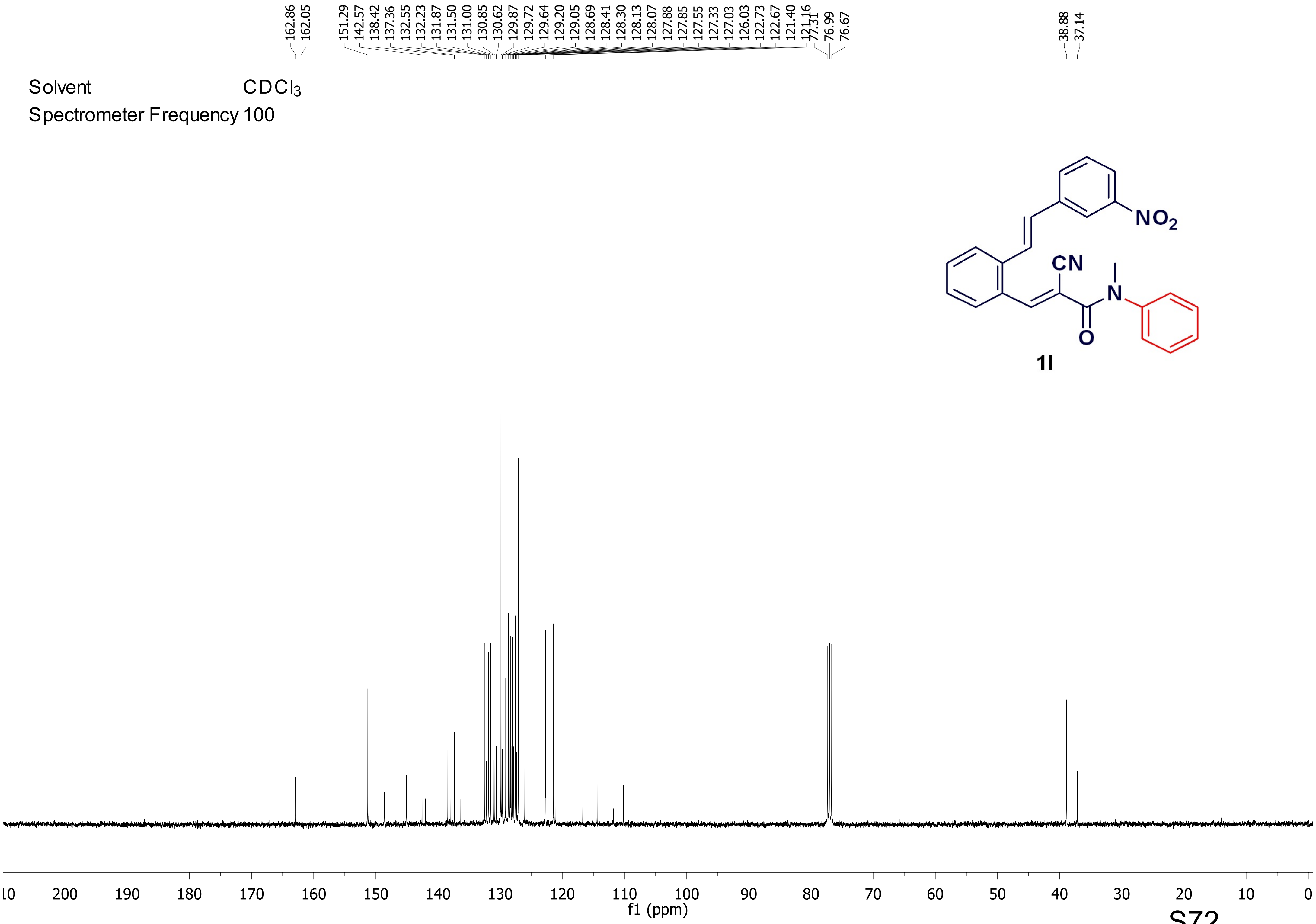

162.99
162.17
151.57
131.42
129.83
128.90
128.85
128.57
128.21
128.04
127.80
127.75
127.18
126.99
125.43
116.84
114.49
111.29
109.82
77.31
76.99
76.67
38.85
37.10
Solvent CDCl$_3$
Spectrometer Frequency 100
Cl
CN
N
O
1j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Solvent CDCl$_3$

Spectrometer Frequency 400



1l


162.86
162.05
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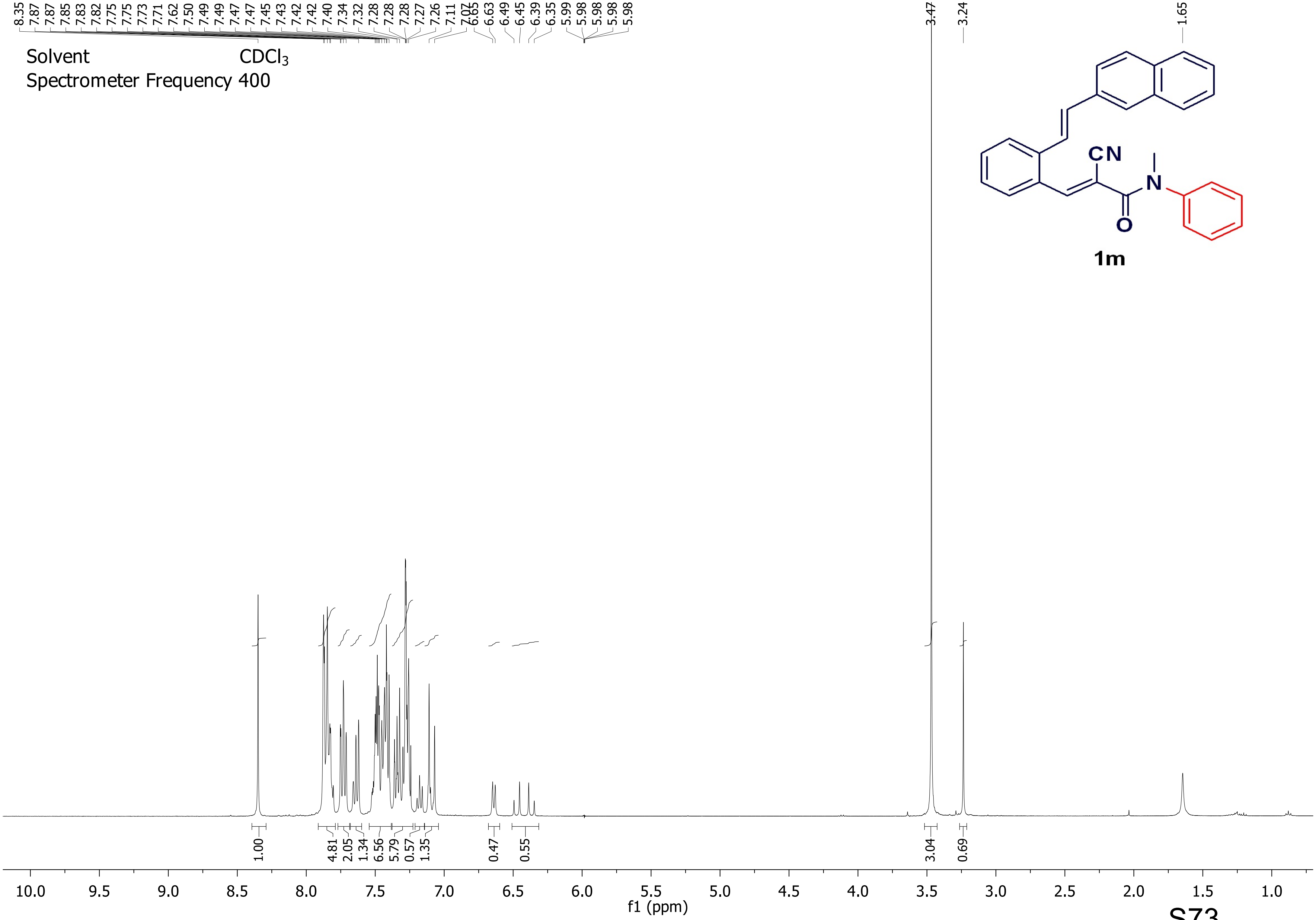
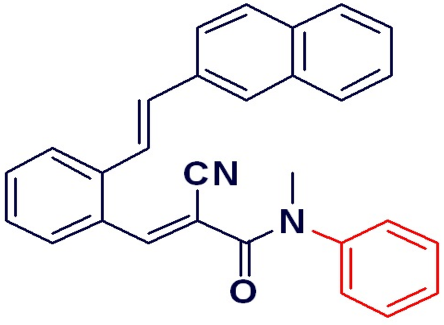
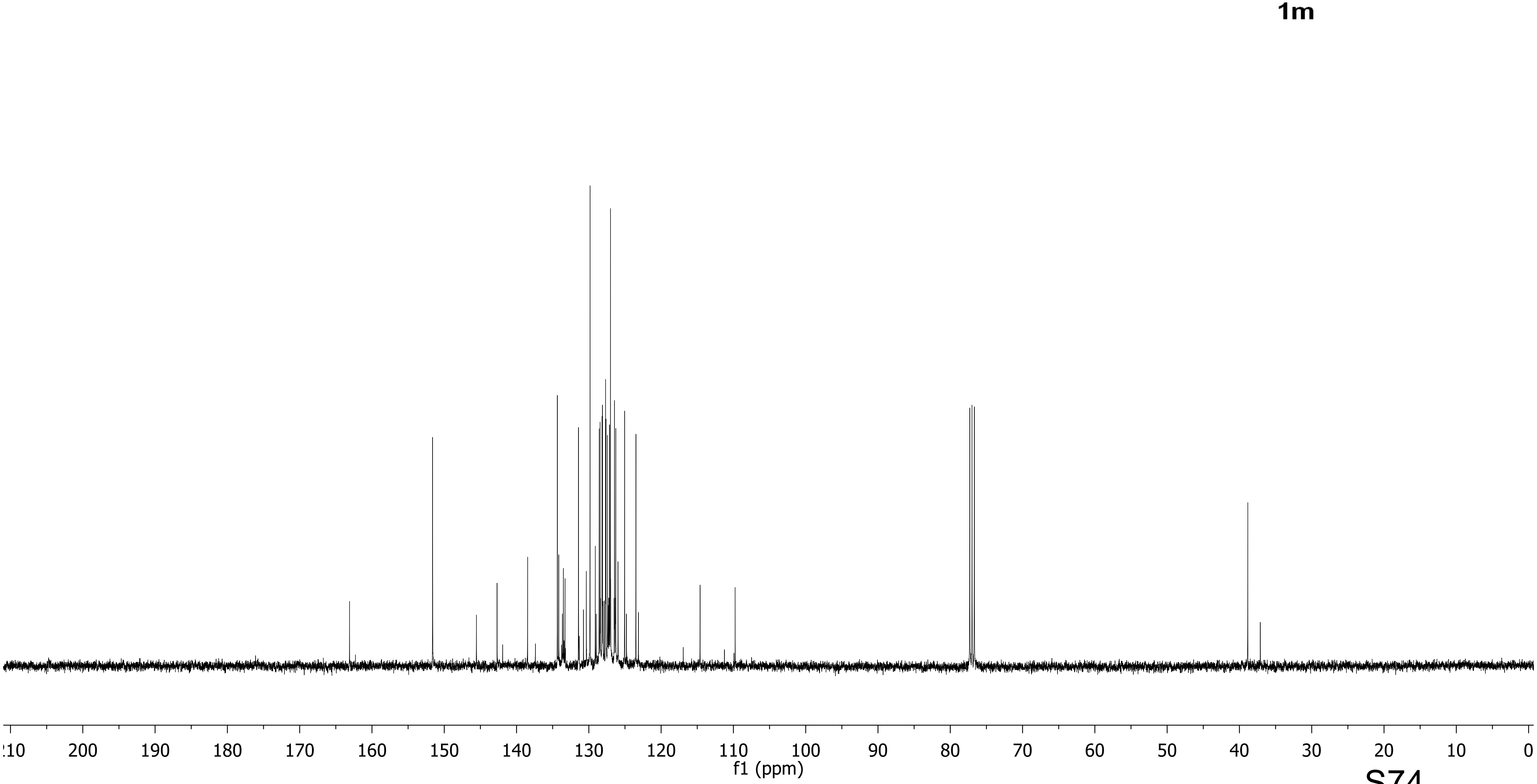
142.57
138.42
137.36
132.55
132.23
131.87
131.50
131.00
130.85
130.62
129.87
129.72
129.64
129.20
129.05
128.69
128.41
128.30
128.13
128.07
127.88
127.85
127.55
127.33
127.03
126.03
122.73
122.67
121.40
121.16
77.31
76.99
76.67
38.88
37.14
Solvent CDCl3
Spectrometer Frequency 100
CN
N
NO2
O
1l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

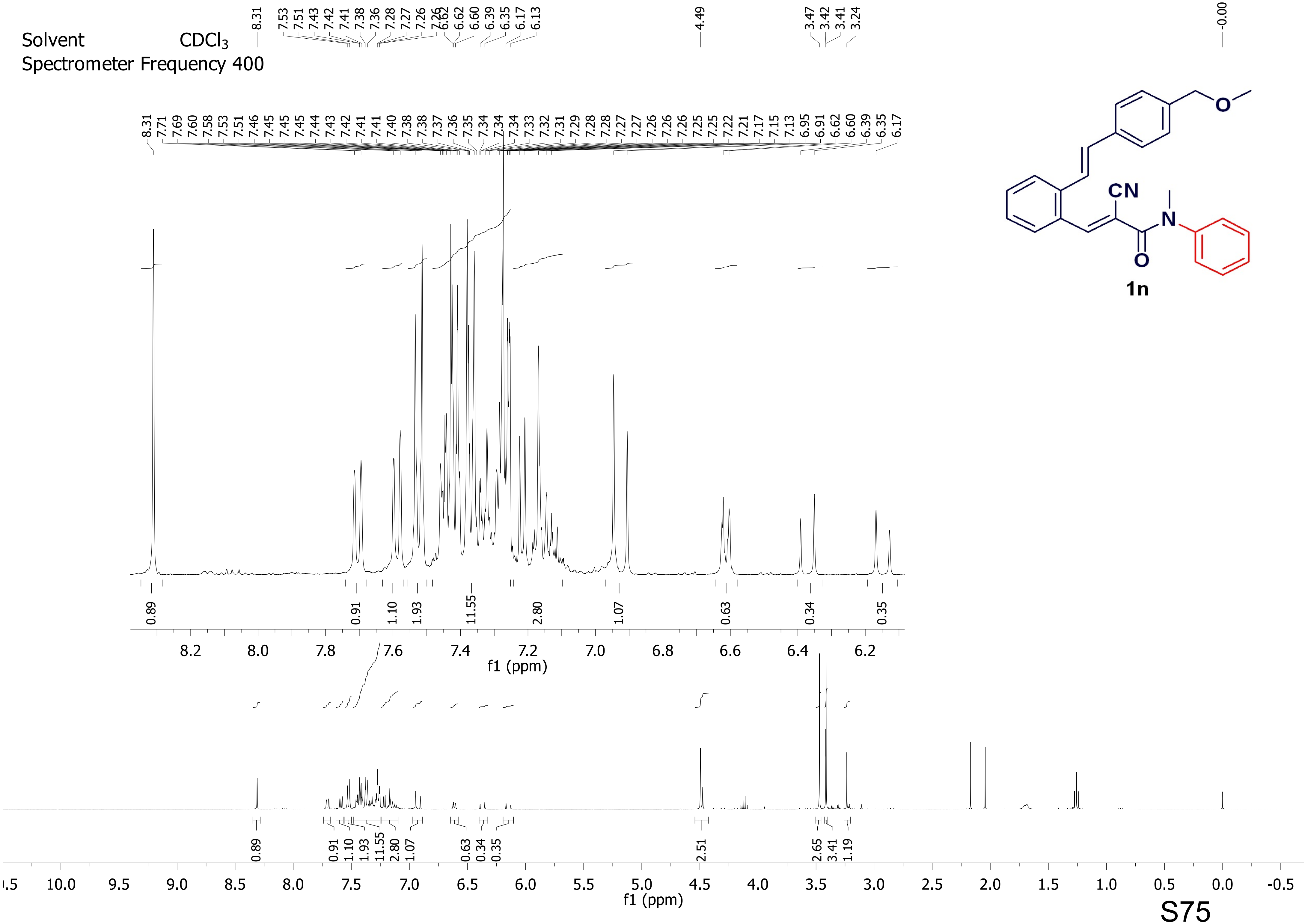

8.35
7.87
7.87
7.85
7.83
7.82
7.75
7.75
7.73
7.71
7.62
7.50
7.49
7.49
7.47
7.47
7.45
7.43
7.42
7.42
7.40
7.34
7.32
7.28
7.28
7.28
7.27
7.26
7.11
7.07
6.65
6.63
6.49
6.45
6.39
6.35
5.99
5.98
5.98
5.98
5.98
3.47
3.24
1.65
Solvent CDCl3
Spectrometer Frequency 400
CN
N
O
1m
1.00
4.81
2.05
1.34
6.56
5.79
0.57
1.35
0.47
0.55
3.04
0.69
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

Solvent CDCl$_3$
Spectrometer Frequency 100

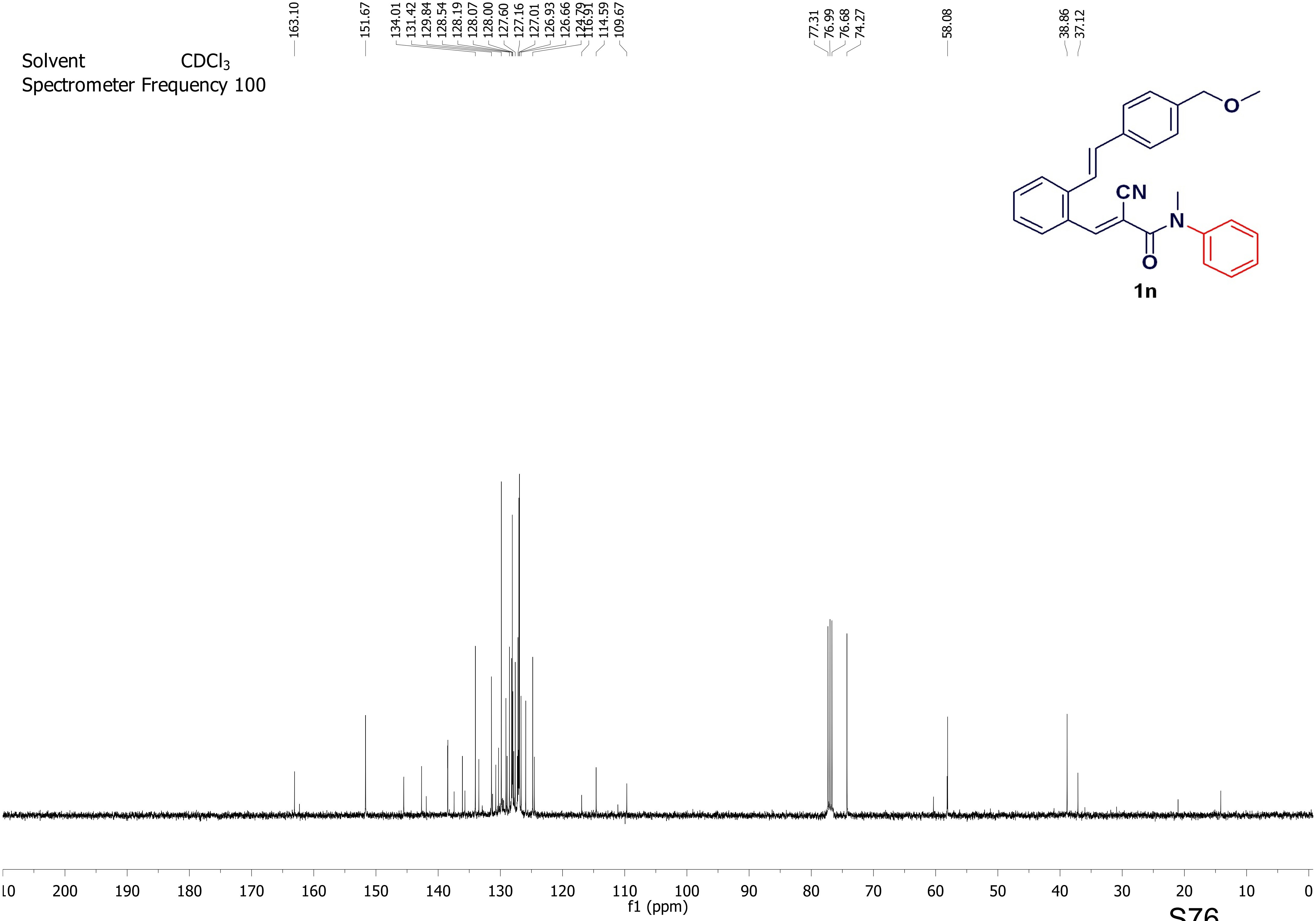


1m

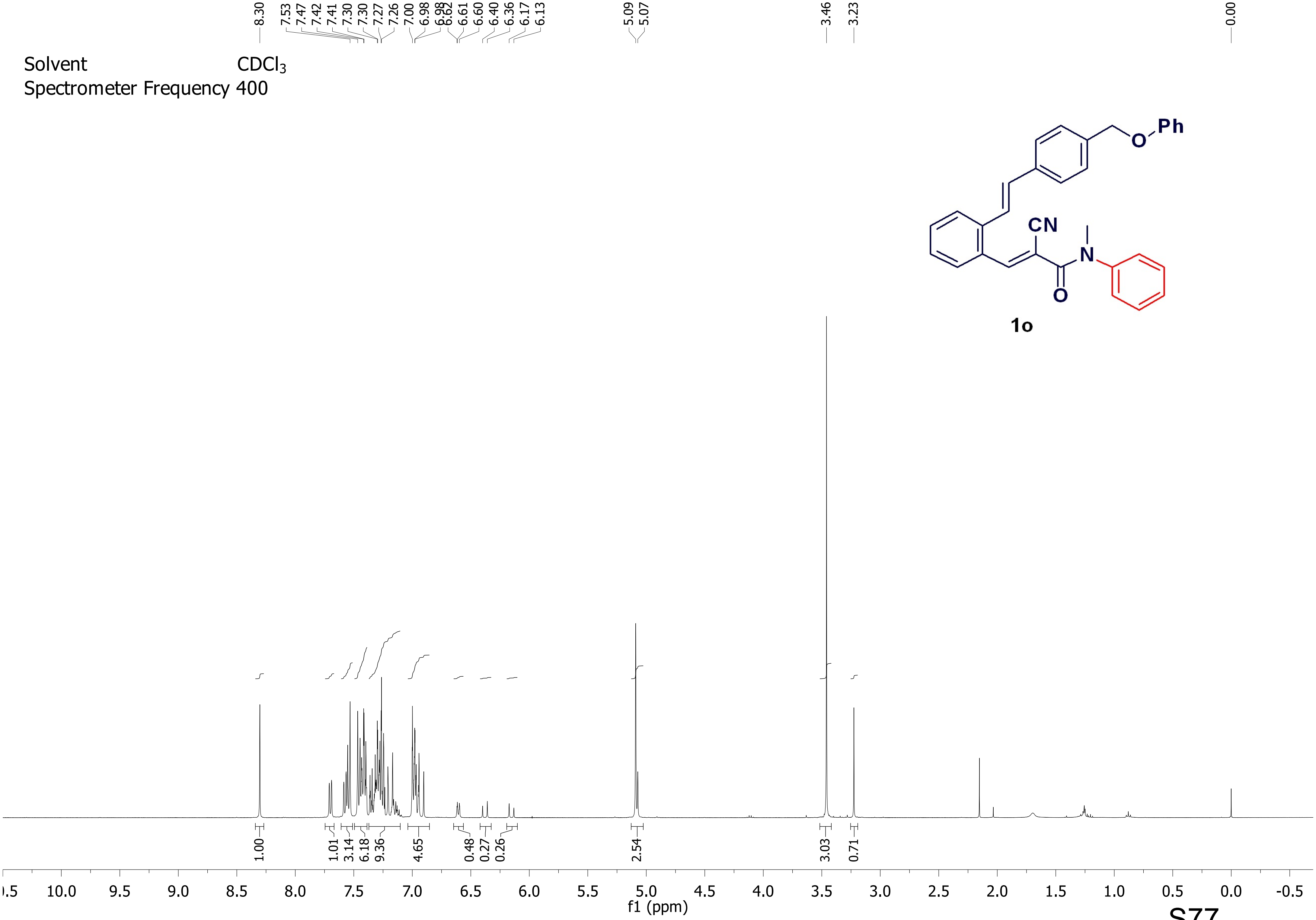



Solvent CDCl3
Spectrometer Frequency 400
8.31
7.53
7.51
7.43
7.42
7.41
7.38
7.36
7.28
7.27
7.26
7.26
6.62
6.62
6.60
6.39
6.35
6.17
6.13
4.49
3.47
3.42
3.41
3.24
-0.00
8.31
7.71
7.69
7.60
7.58
7.53
7.51
7.46
7.45
7.45
7.45
7.44
7.43
7.42
7.41
7.41
7.40
7.38
7.38
7.37
7.36
7.35
7.34
7.34
7.34
7.33
7.32
7.31
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.26
7.25
7.25
7.22
7.21
7.17
7.15
7.13
6.95
6.91
6.62
6.60
6.39
6.35
6.17
0.89
0.91
1.10
1.93
11.55
2.80
1.07
0.63
0.34
0.35
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
f1 (ppm)
CN
N
O
O
0.89
0.91
1.10
1.93
11.55
2.80
1.07
0.63
0.34
0.35
2.51
2.65
3.41
1.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

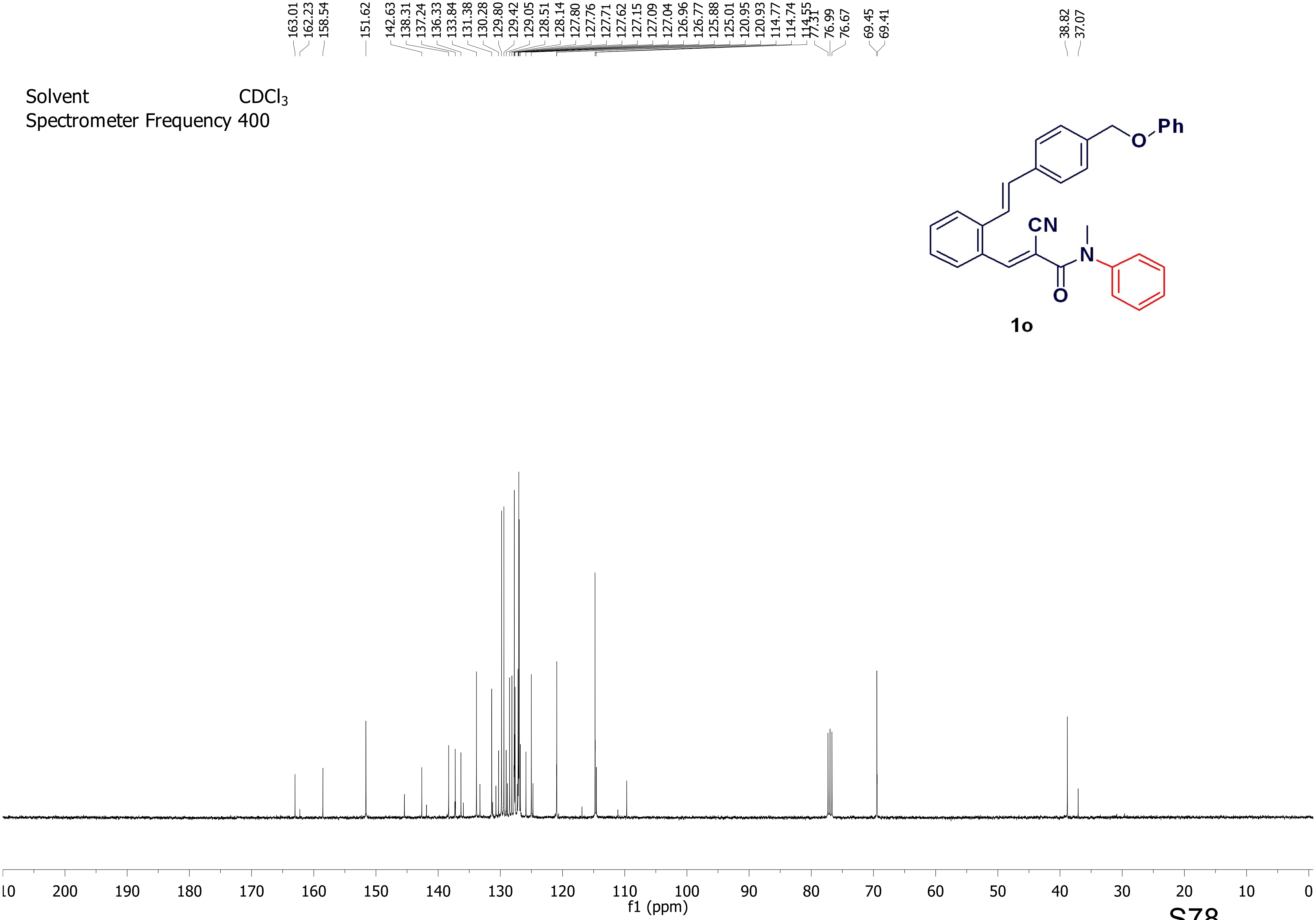
1n


Solvent CDCl$_3$
Spectrometer Frequency 100
163.10
151.67
134.01
131.42
129.84
128.54
128.19
128.07
128.00
127.60
127.16
127.01
126.93
126.66
124.79
116.91
114.59
109.67
77.31
76.99
76.68
74.27
58.08
38.86
37.12
CN
N
O
1n
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Solvent CDCl$_3$
Spectrometer Frequency 400

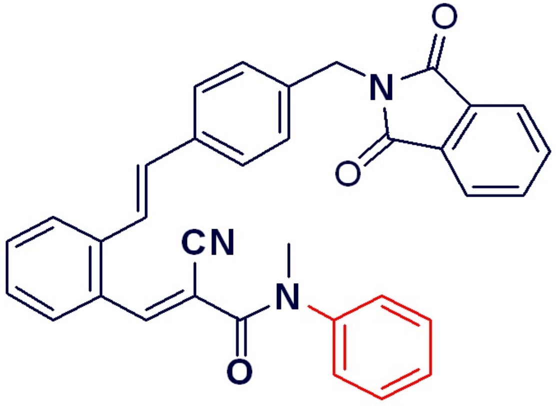


1o

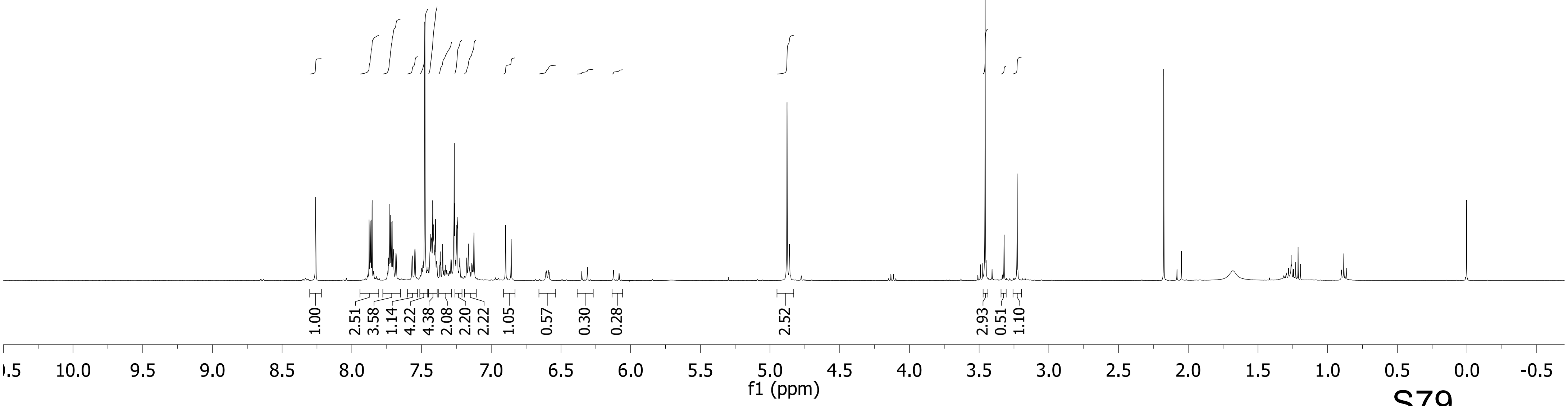

163.01
162.23
158.54
151.62
142.63
138.31
137.24
136.33
133.84
131.38
130.28
129.80
129.42
129.05
128.51
128.14
127.80
127.76
127.71
127.62
127.15
127.09
127.04
126.96
126.77
125.88
125.01
120.95
120.93
114.77
114.74
114.55
77.31
76.99
76.67
69.45
69.41
38.82
37.07
Solvent CDCl$_3$
Spectrometer Frequency 400
CN
N
O
O
Ph
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

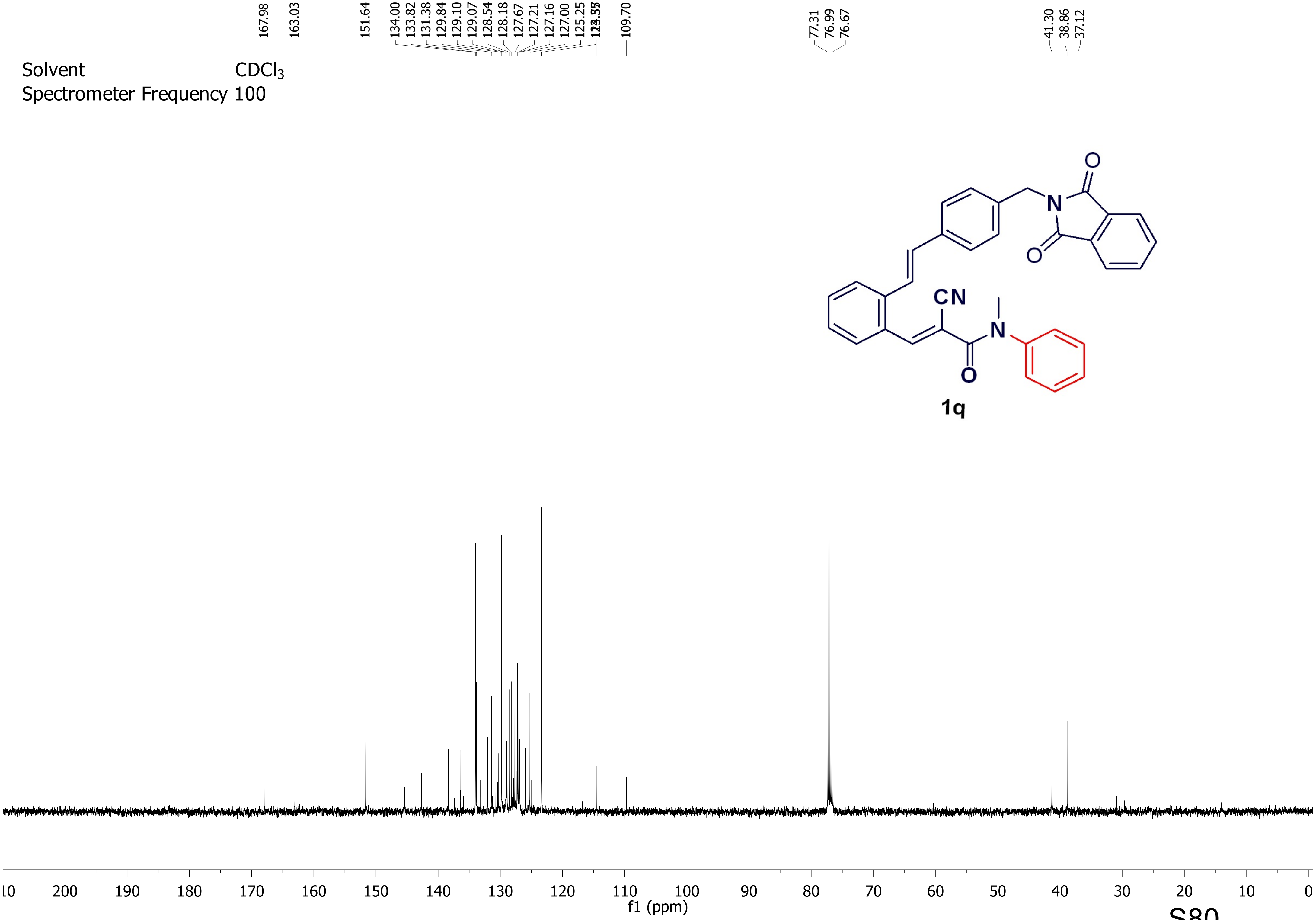
1o

Solvent CDCl$_3$
Spectrometer Frequency 400



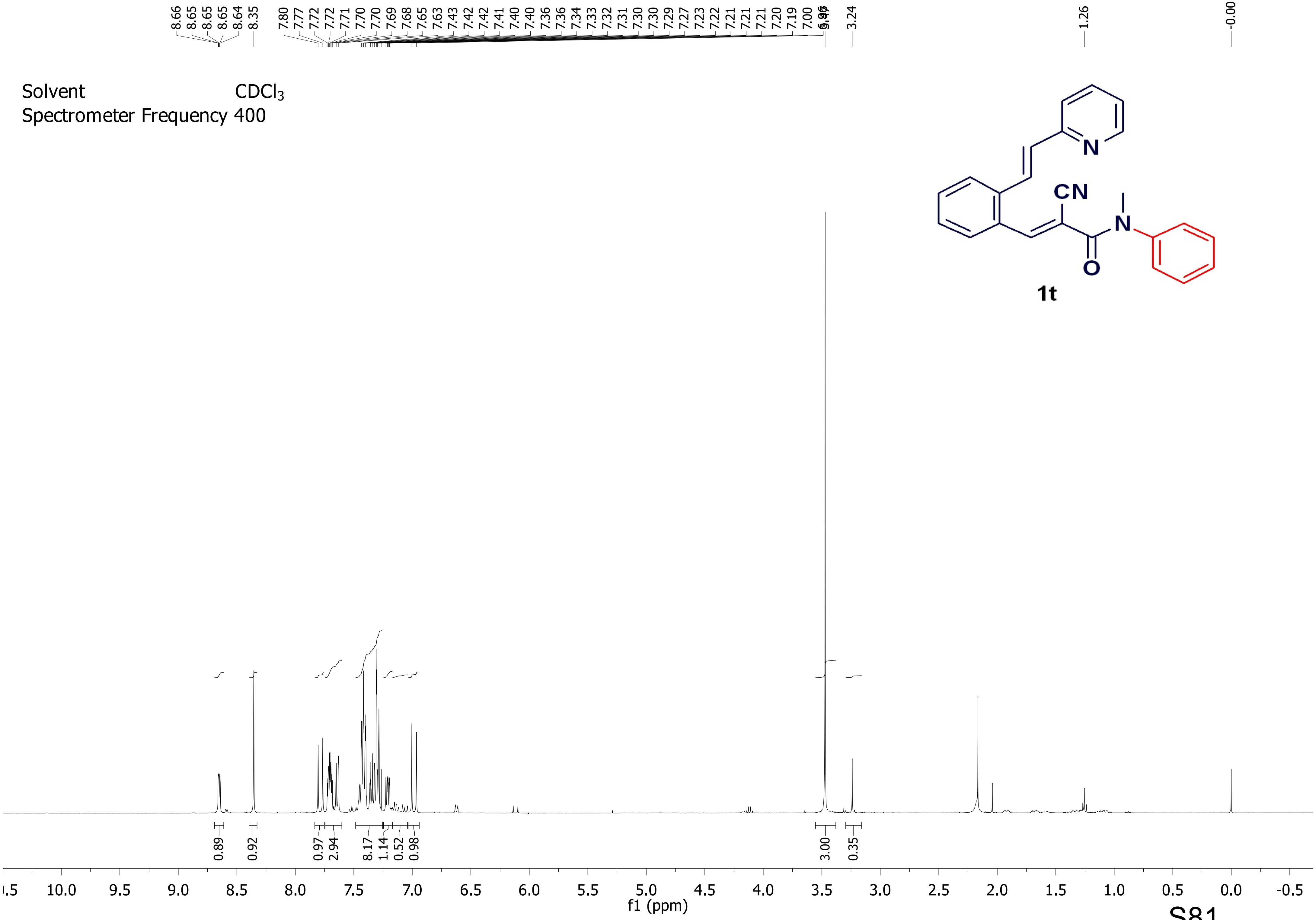
1q

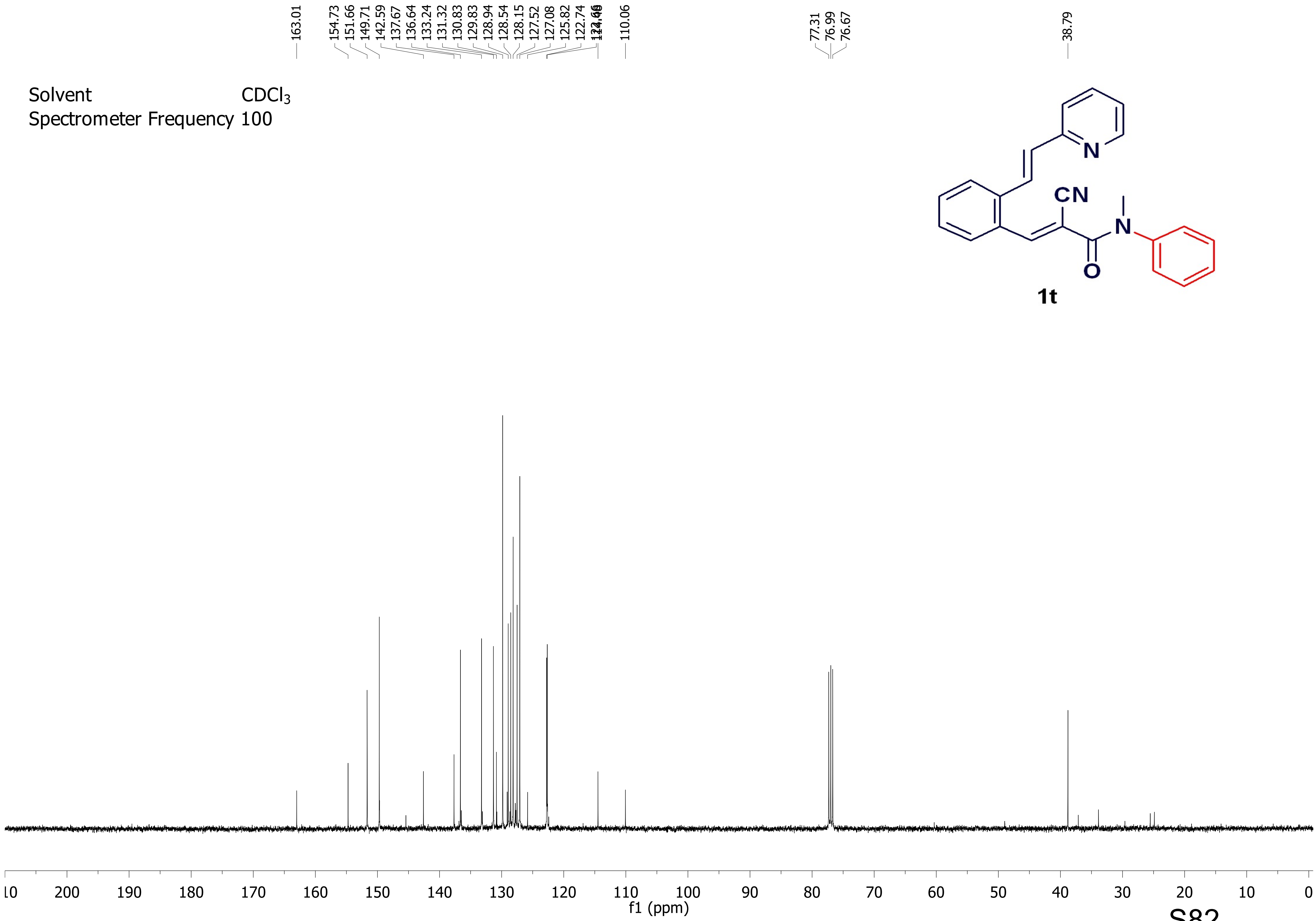




Solvent CDCl$_3$
Spectrometer Frequency 100

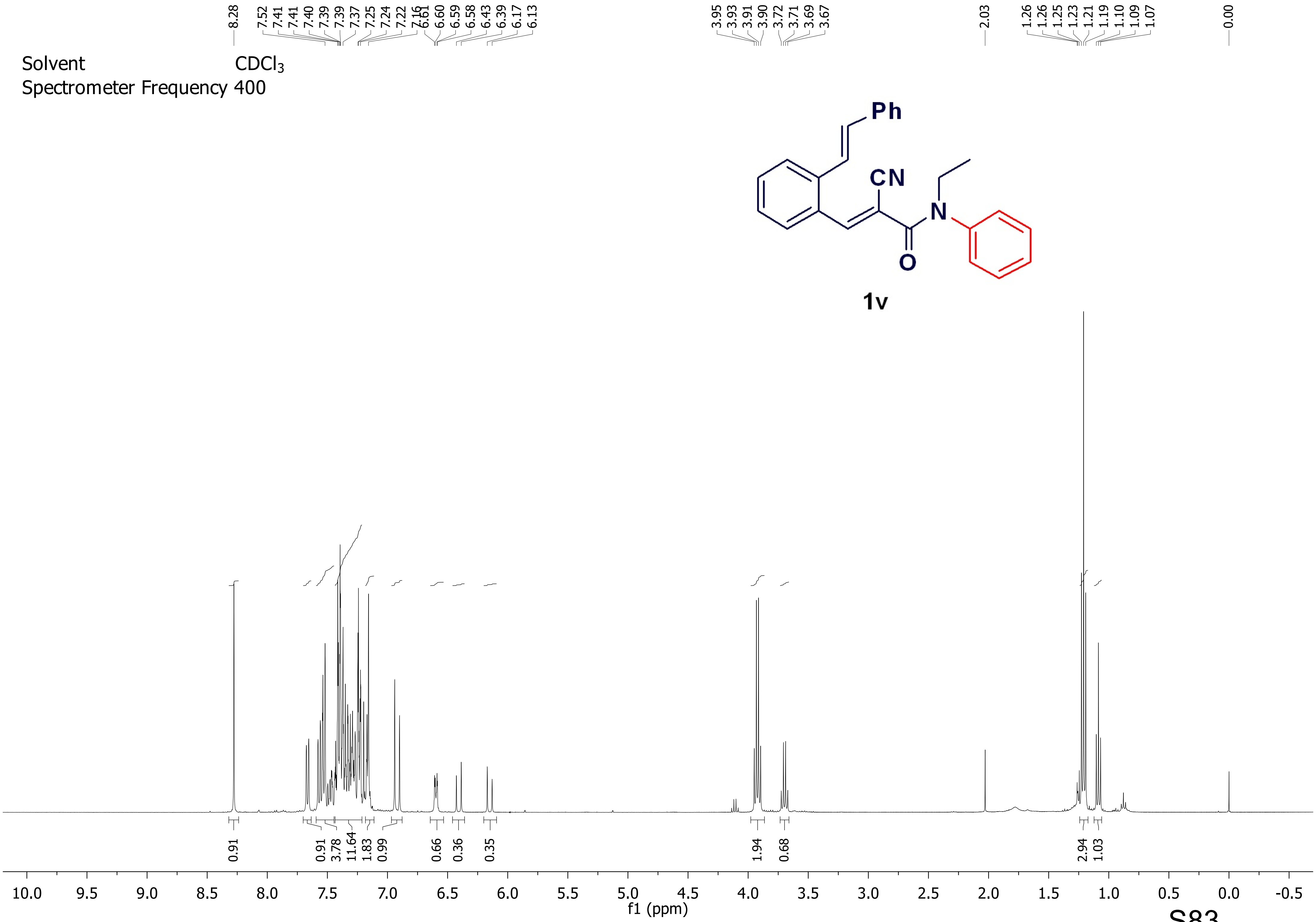
1q


8.66
8.65
8.65
8.65
8.64
8.35
7.80
7.77
7.72
7.72
7.71
7.70
7.70
7.69
7.68
7.65
7.63
7.43
7.42
7.42
7.41
7.40
7.40
7.36
7.36
7.34
7.33
7.32
7.31
7.30
7.30
7.29
7.27
7.23
7.22
7.21
7.21
7.21
7.20
7.19
7.00
6.96
3.47
3.24
1.26
-0.00
Solvent CDCl$_3$
Spectrometer Frequency 400
CN
N
N
O
1t
0.89
0.92
0.97
2.94
8.17
1.14
0.52
0.98
3.00
0.35
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

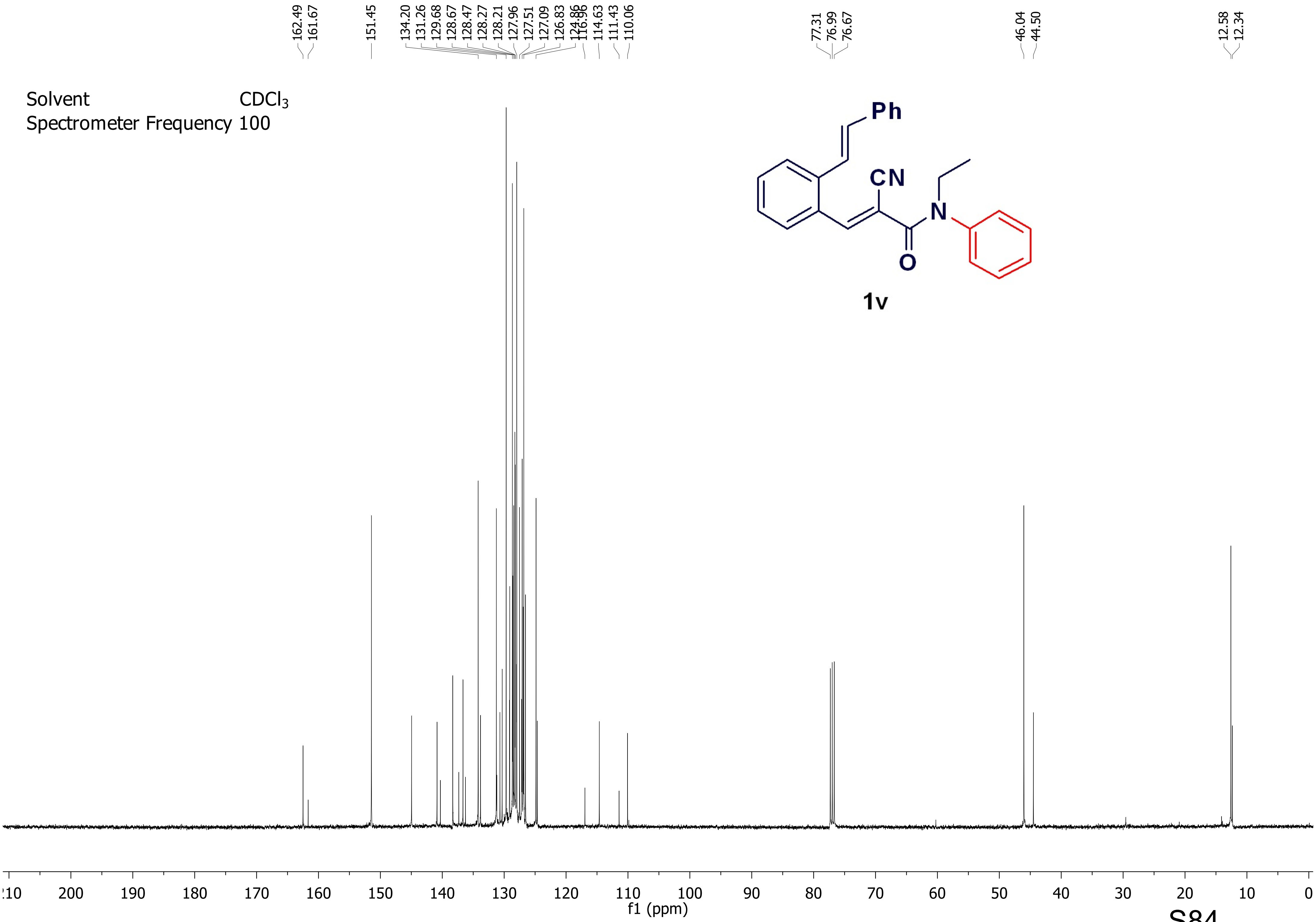

163.01
154.73
151.66
149.71
142.59
137.67
136.64
133.24
131.32
130.83
129.83
128.94
128.54
128.15
127.52
127.08
125.82
122.74
122.66
114.40
110.06
77.31
76.99
76.67
38.79
Solvent CDCl₃
Spectrometer Frequency 100
CN
N
N
O
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

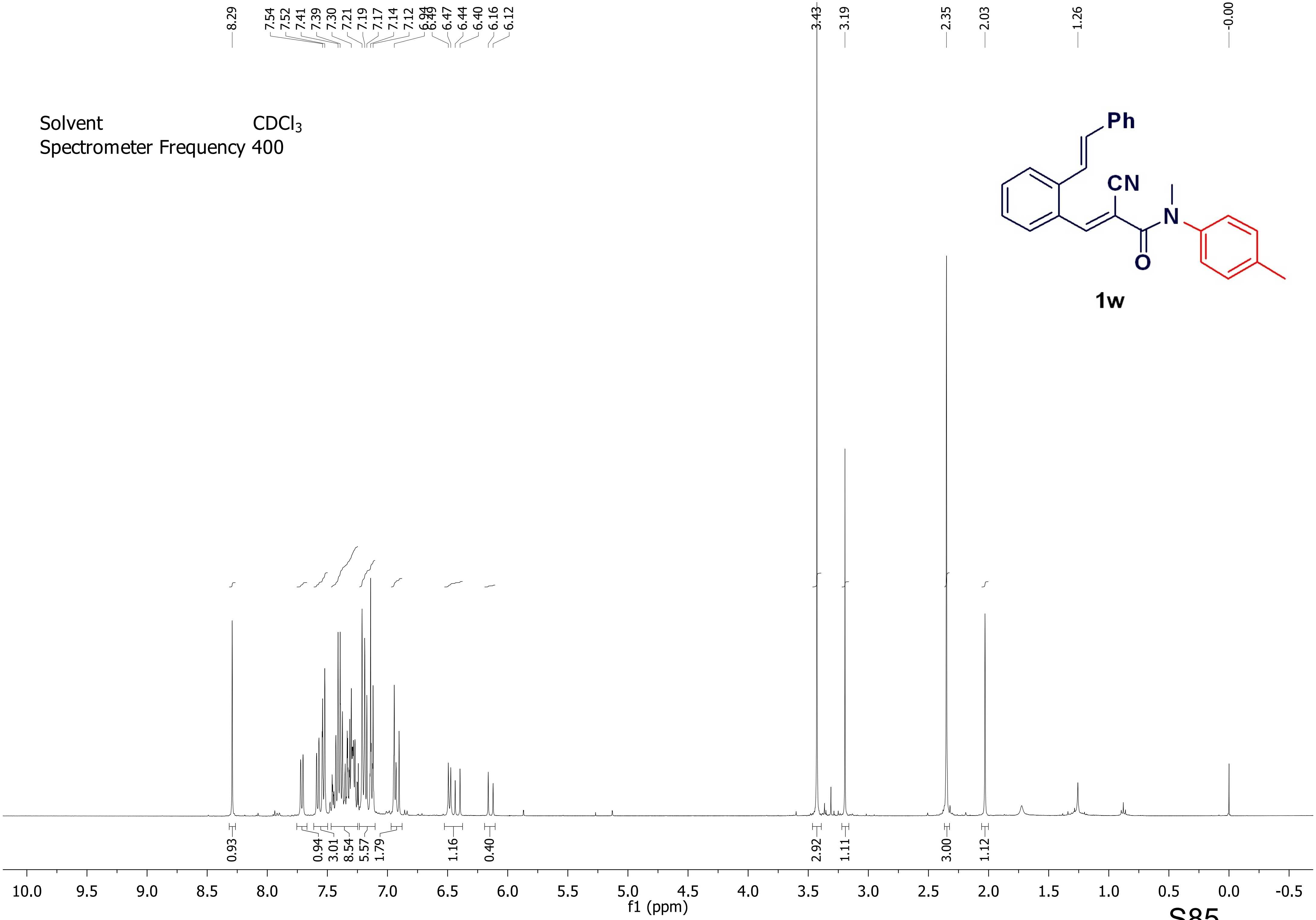
1t

Solvent CDCl$_3$
Spectrometer Frequency 400



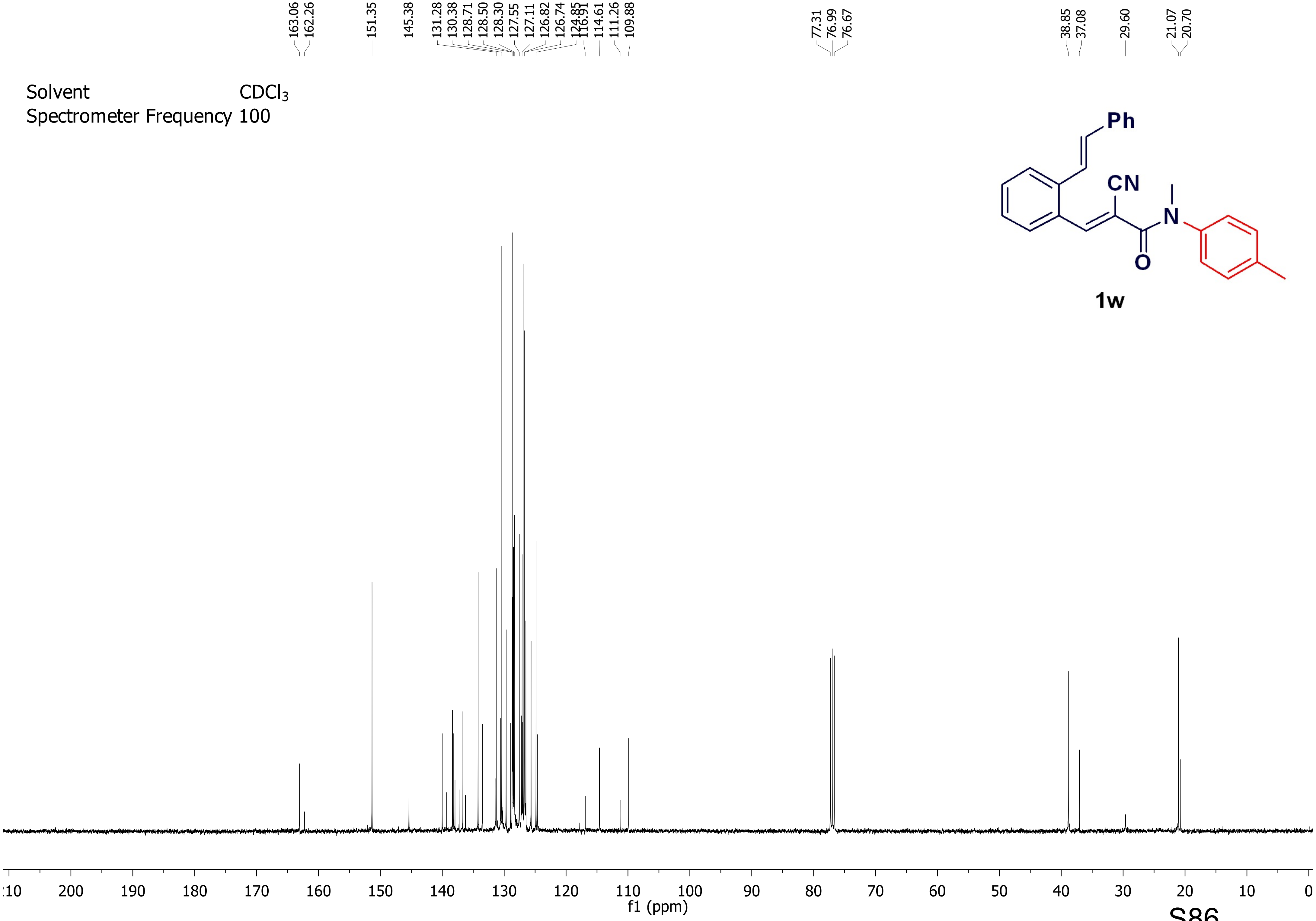
1v


162.49
161.67
151.45
134.20
131.26
129.68
128.67
128.47
128.27
128.21
127.96
127.51
127.09
126.83
124.86
116.96
114.63
111.43
110.06
77.31
76.99
76.67
46.04
44.50
12.58
12.34
Solvent CDCl$_3$
Spectrometer Frequency 100
Ph
CN
N
O
1v
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

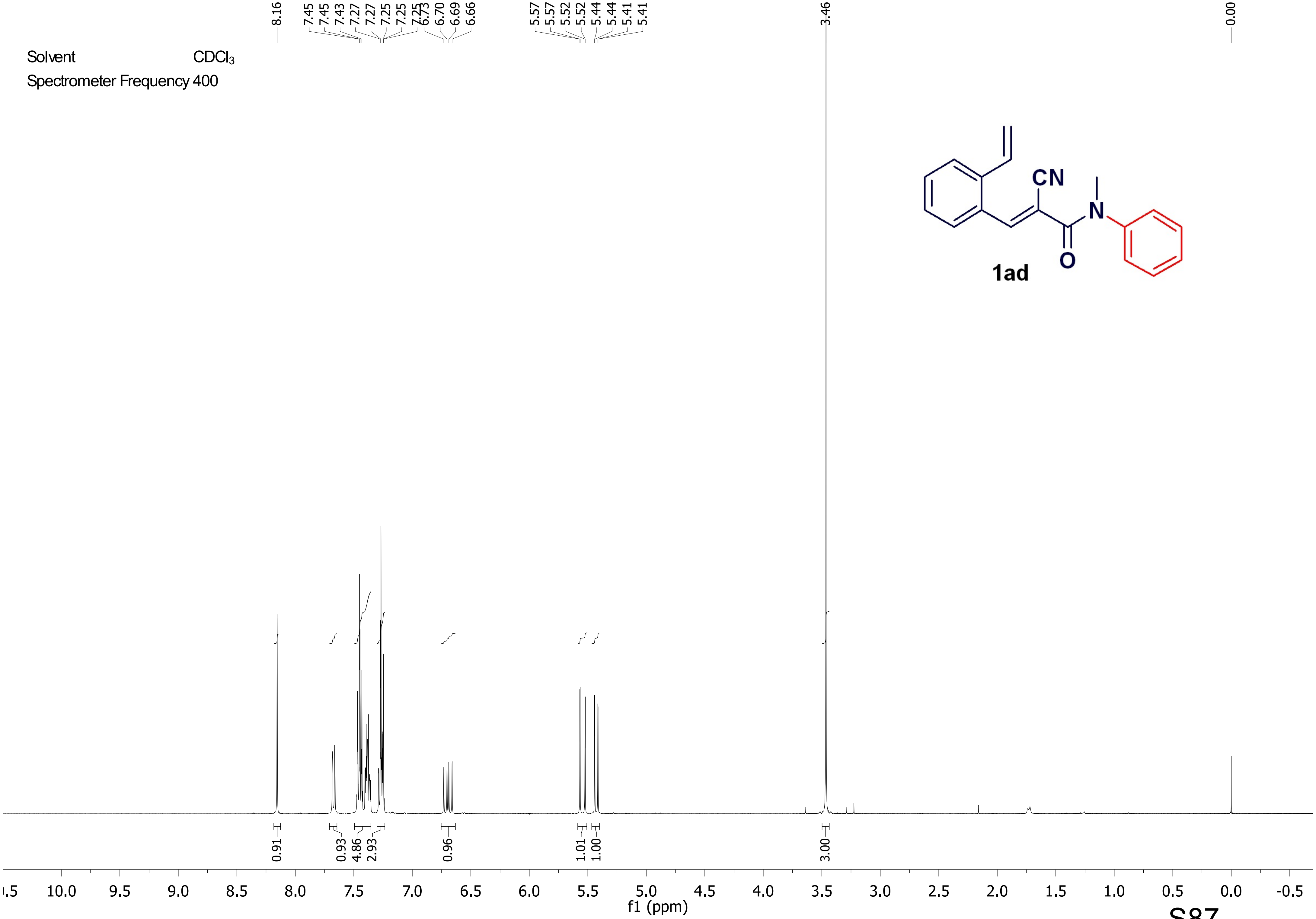

8.29
7.54
7.52
7.41
7.39
7.30
7.21
7.19
7.17
7.14
7.12
6.94
6.49
6.47
6.44
6.40
6.16
6.12
3.43
3.19
2.35
2.03
1.26
-0.00
Solvent CDCl$_3$
Spectrometer Frequency 400
Ph
CN
N
O
0.93
0.94
3.01
8.54
5.57
1.79
1.16
0.40
2.92
1.11
3.00
1.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

1w

Solvent CDCl$_3$
Spectrometer Frequency 100

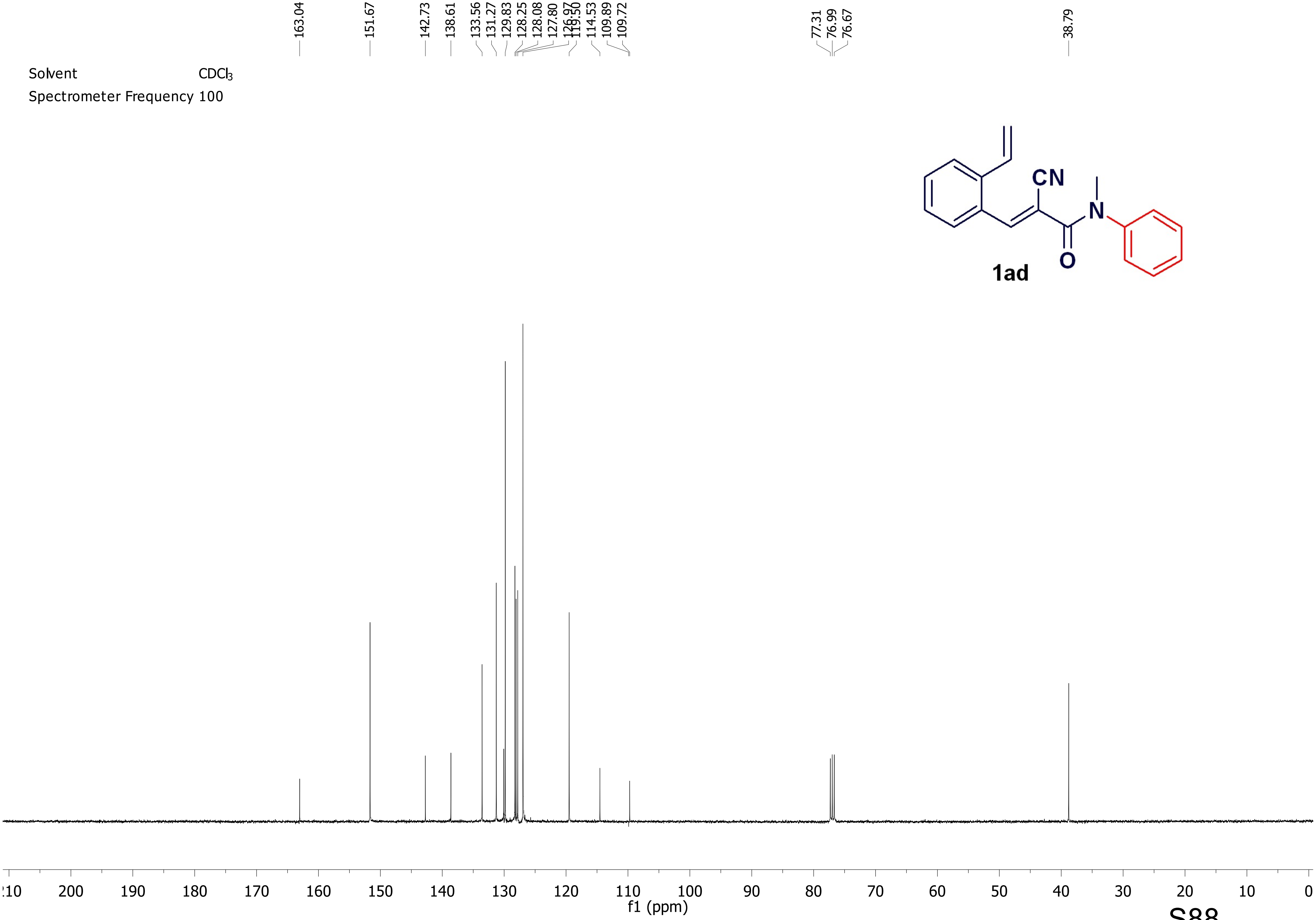


1w

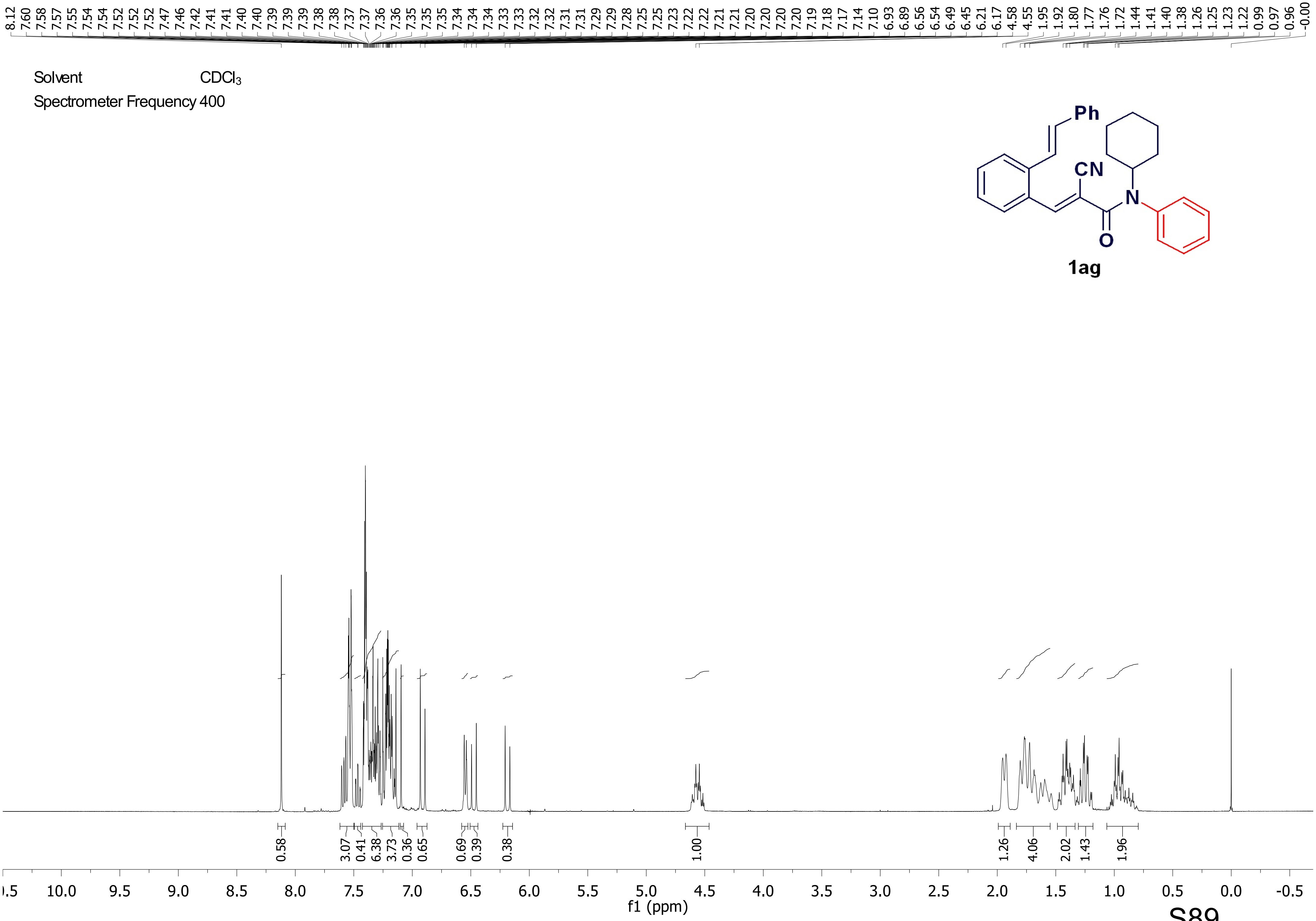

Solvent CDCl$_3$
Spectrometer Frequency 400
8.16
7.45
7.45
7.43
7.27
7.27
7.25
7.25
7.25
6.73
6.70
6.69
6.66
5.57
5.57
5.52
5.52
5.44
5.44
5.41
5.41
3.46
0.00
CN
N
O
1ad
0.91
0.93
4.86
2.93
0.96
1.01
1.00
3.00
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

Solvent CDCl$_3$

Spectrometer Frequency 100



1ad


8.12
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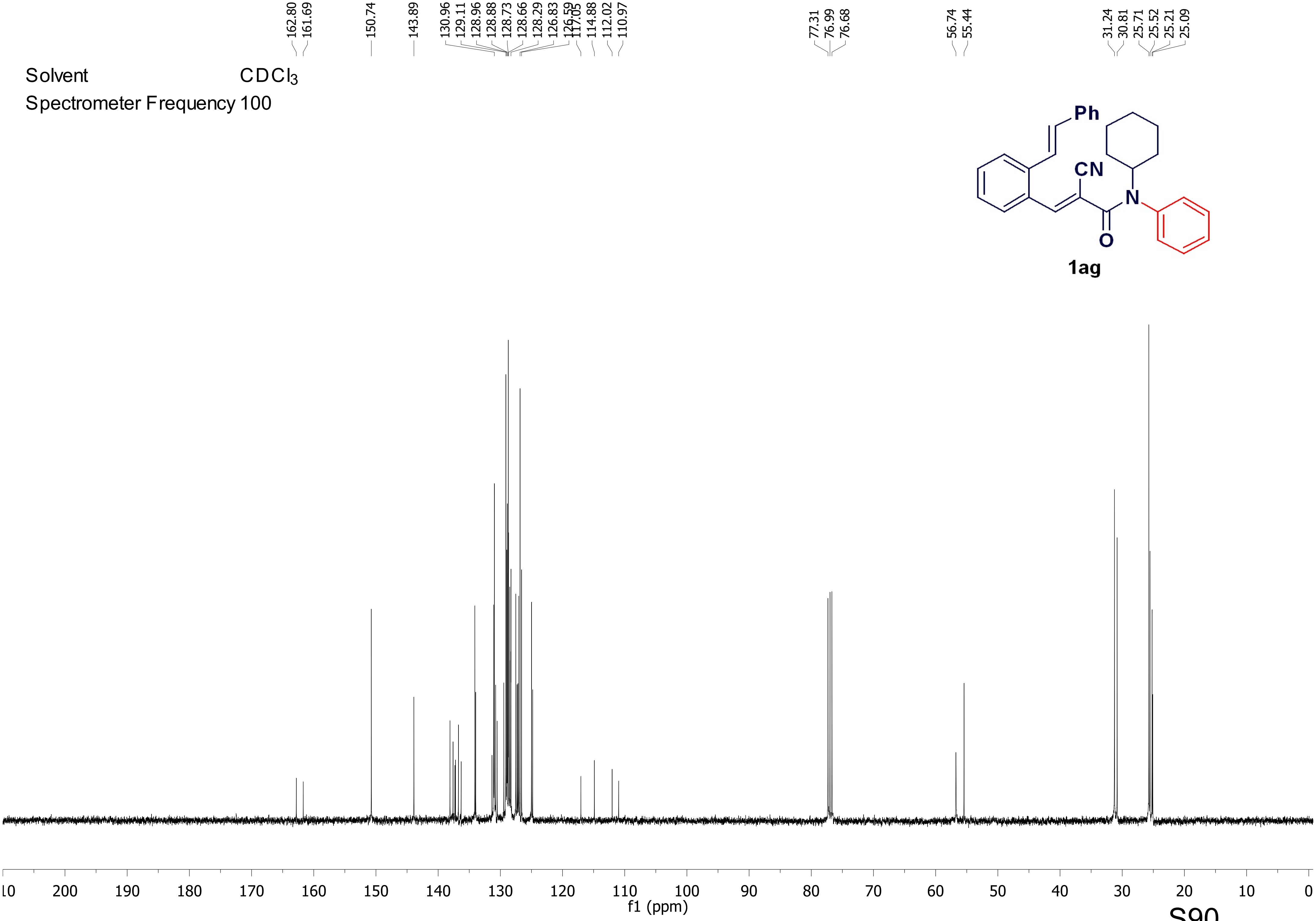
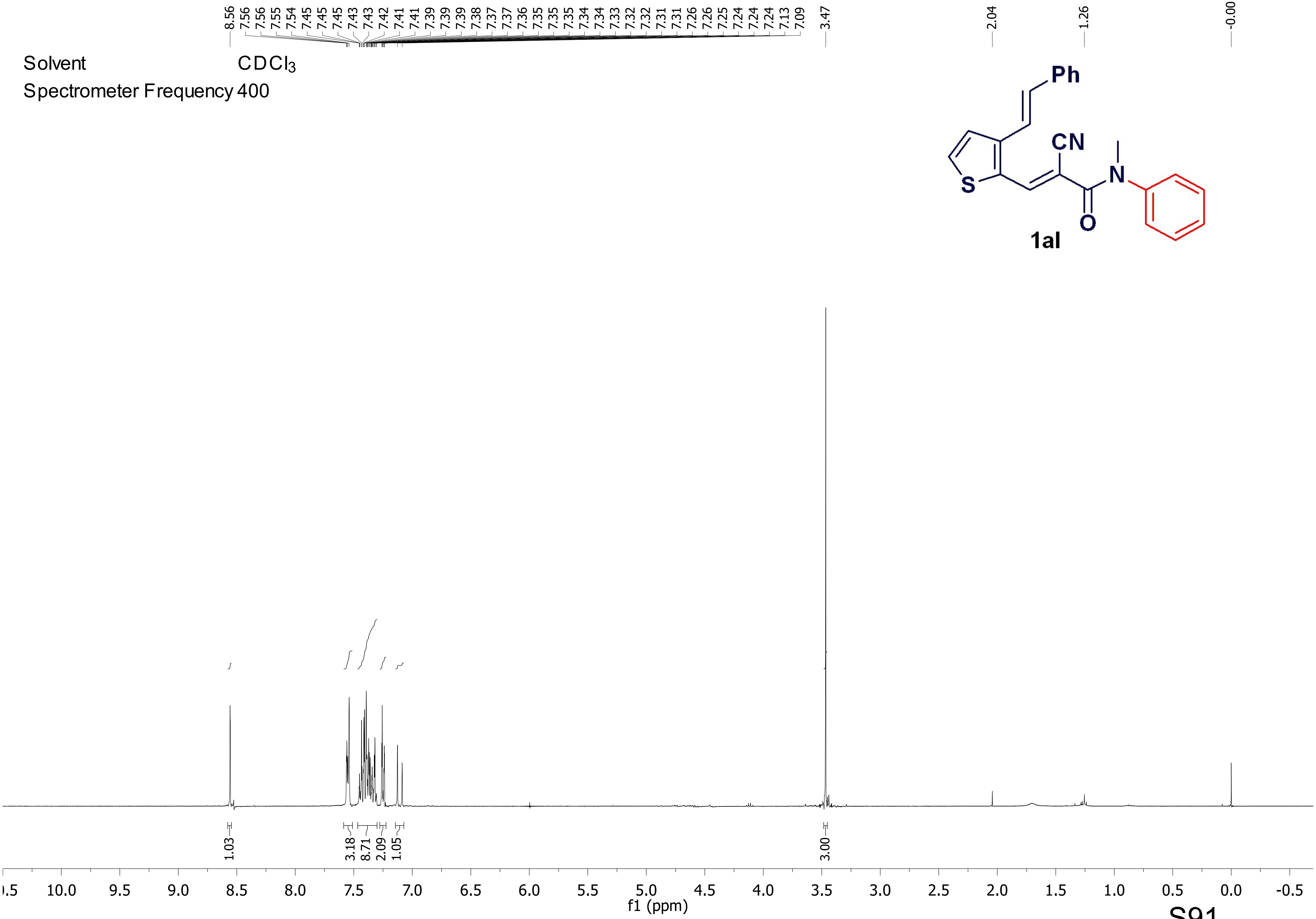
7.58
7.57
7.55
7.54
7.54
7.52
7.52
7.52
7.47
7.46
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.29
7.29
7.28
7.25
7.25
7.23
7.22
7.22
7.21
7.21
7.20
7.20
7.20
7.20
7.19
7.18
7.17
7.14
7.10
6.93
6.89
6.56
6.54
6.49
6.45
6.21
6.17
4.58
4.55
1.95
1.92
1.80
1.77
1.76
1.72
1.44
1.41
1.40
1.38
1.26
1.25
1.23
1.22
0.99
0.97
0.96
-0.00
Solvent CDCl$_3$
Spectrometer Frequency 400
Ph
CN
N
O
1ag
0.58
3.07
0.41
6.38
3.73
0.36
0.65
0.69
0.39
0.38
1.00
1.26
4.06
2.02
1.43
1.96
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

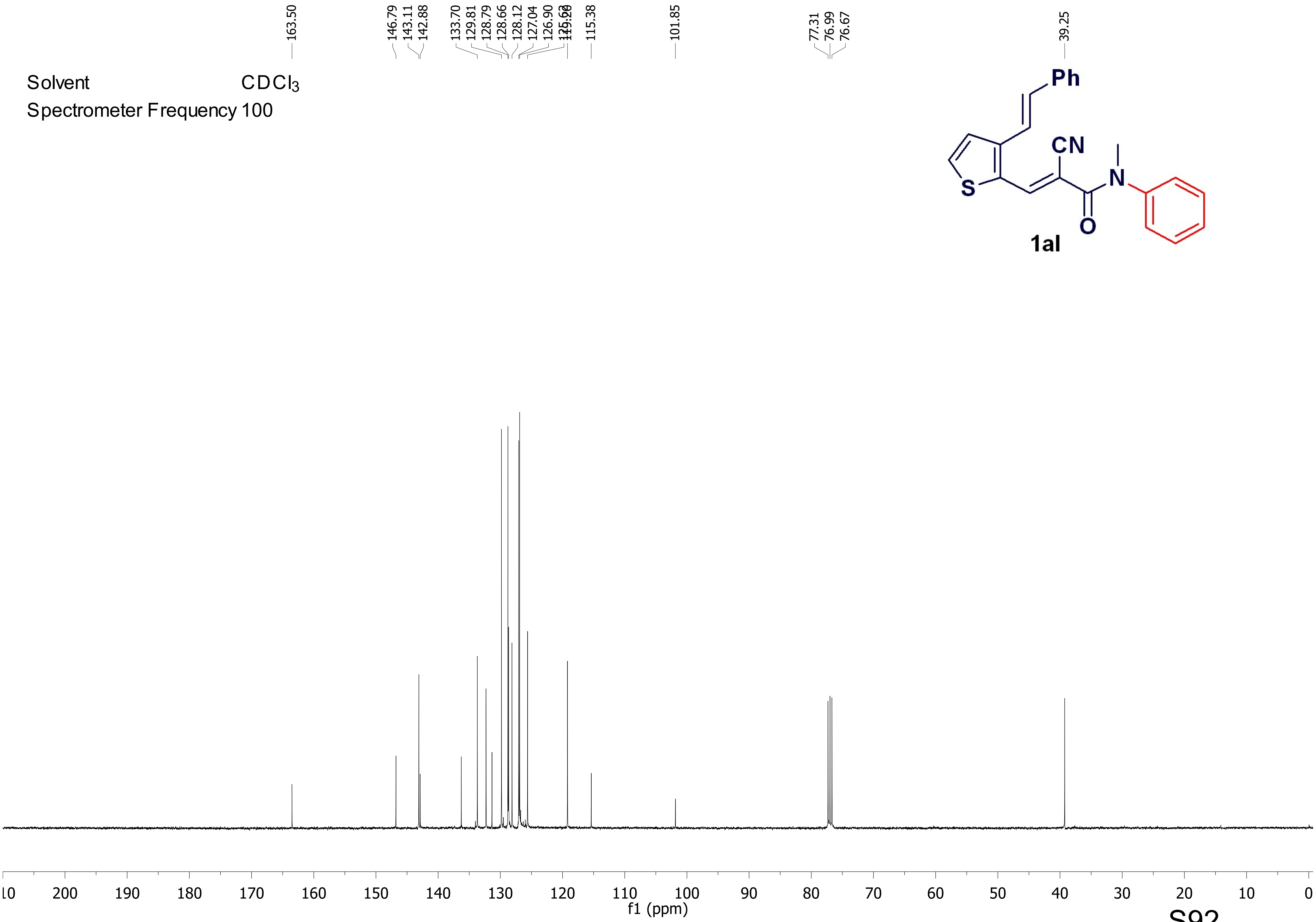
Solvent CDCl$_3$
Spectrometer Frequency 100

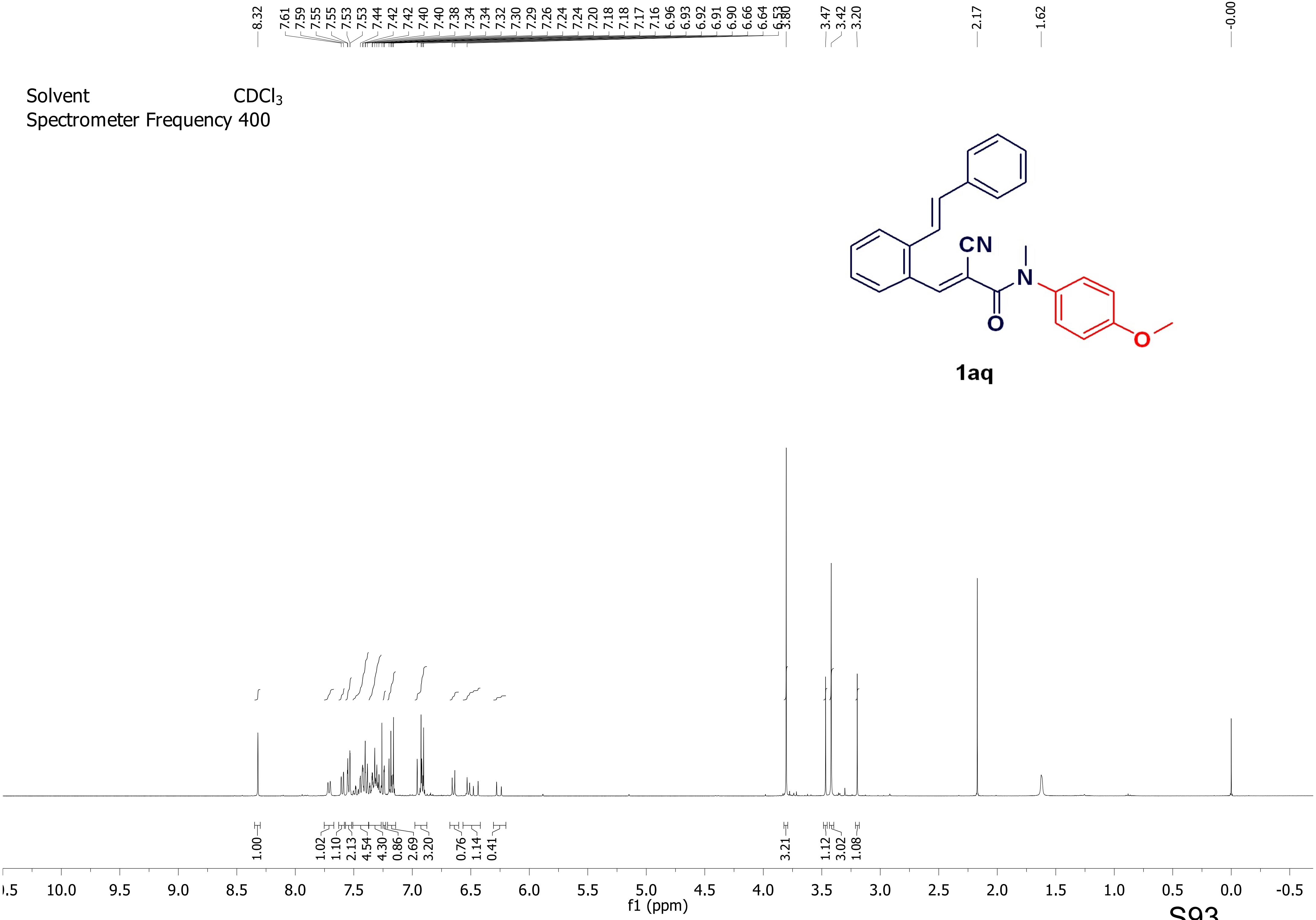


Solvent CDCl$_3$
Spectrometer Frequency 400



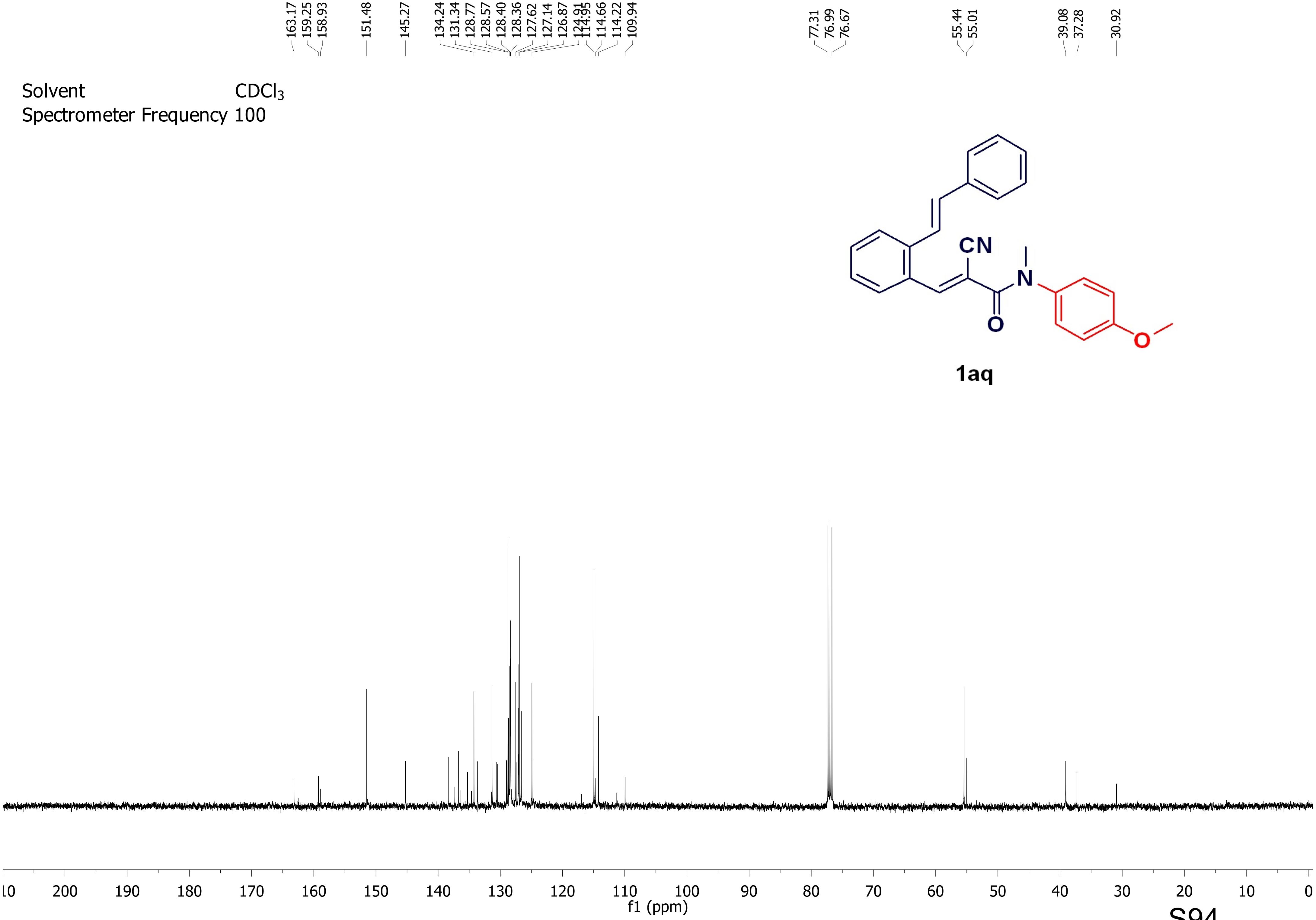
Solvent CDCl$_3$
Spectrometer Frequency 100



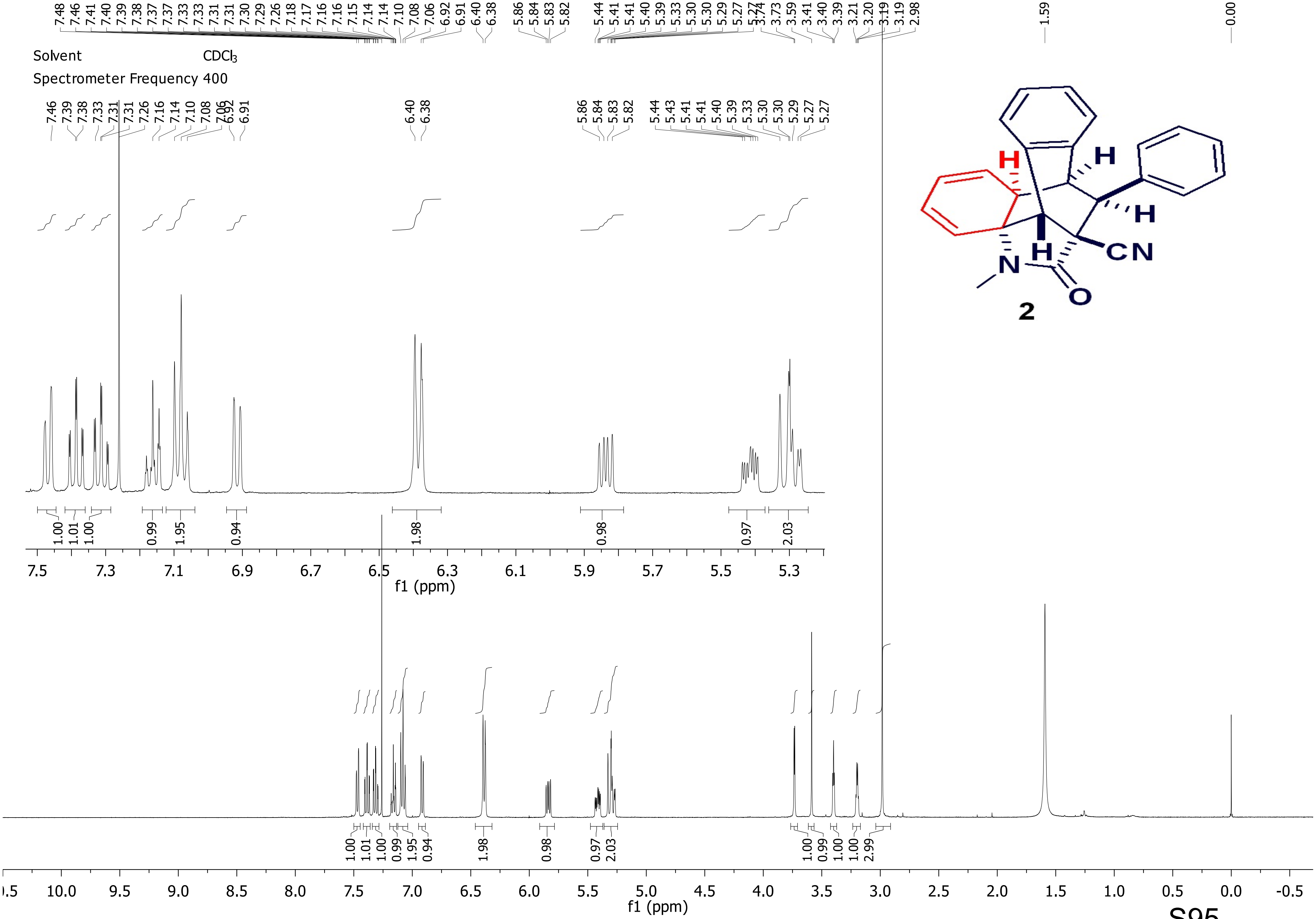


Solvent CDCl$_3$
Spectrometer Frequency 400

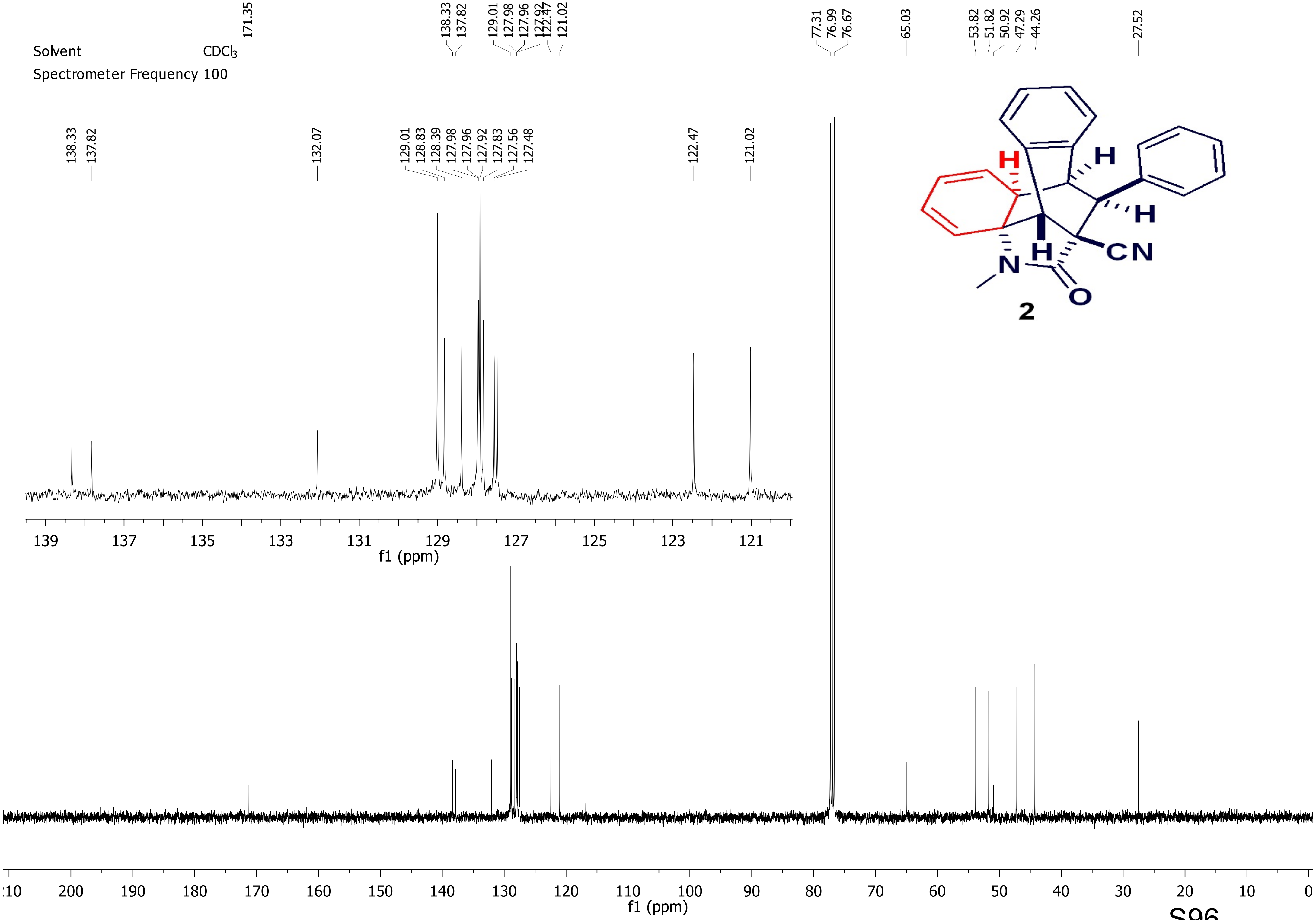
1aq

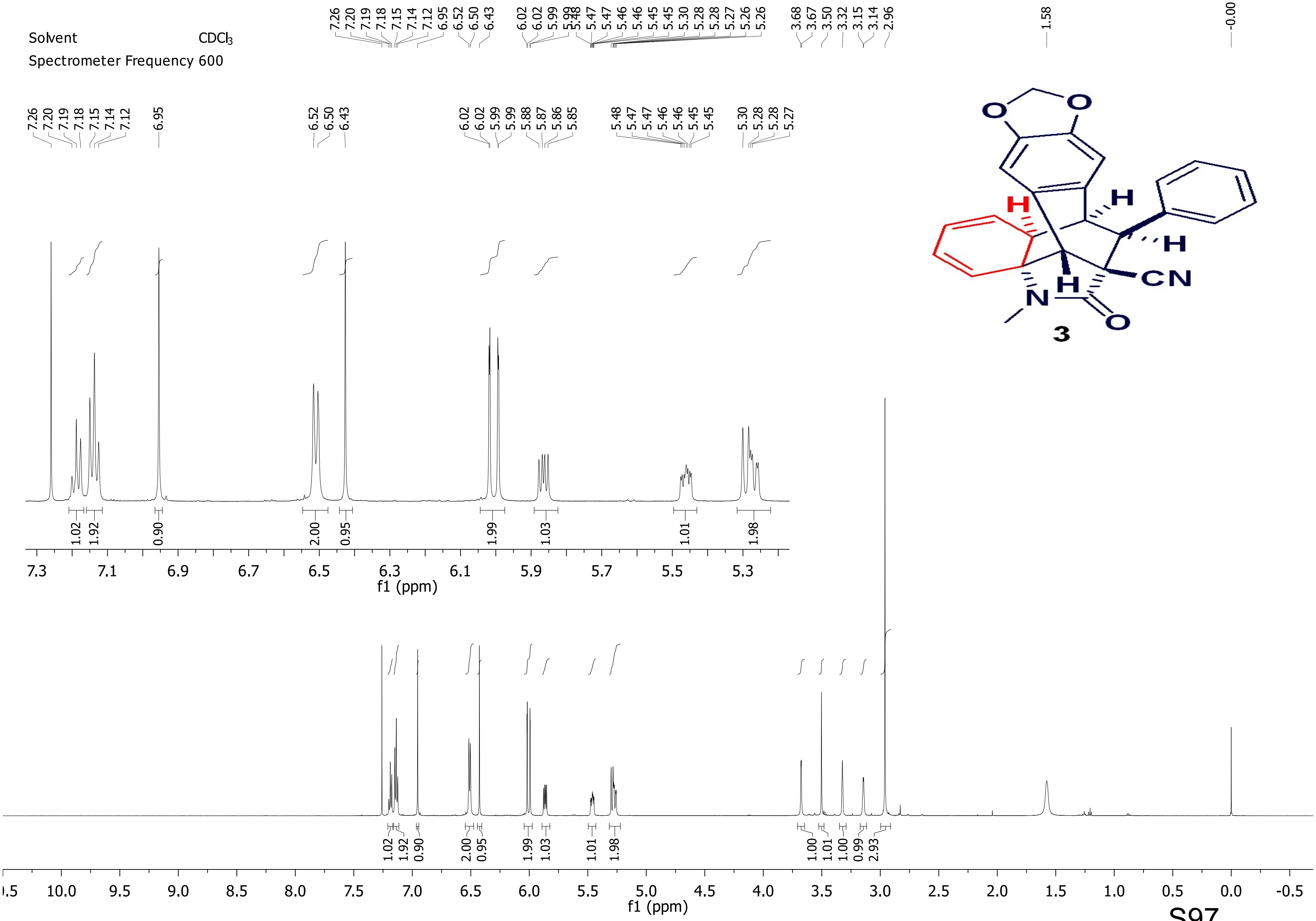


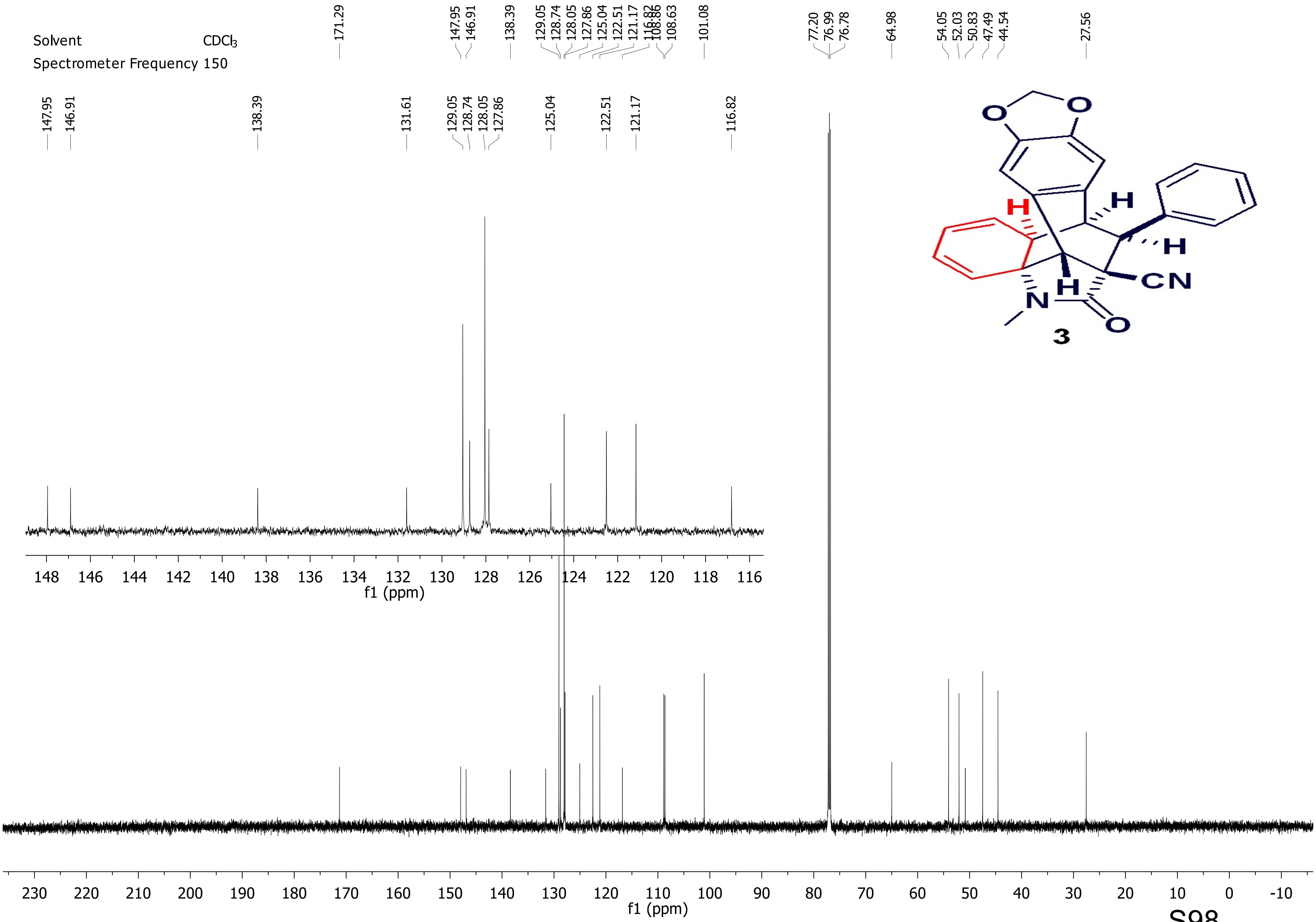
Solvent CDCl$_3$
Spectrometer Frequency 100

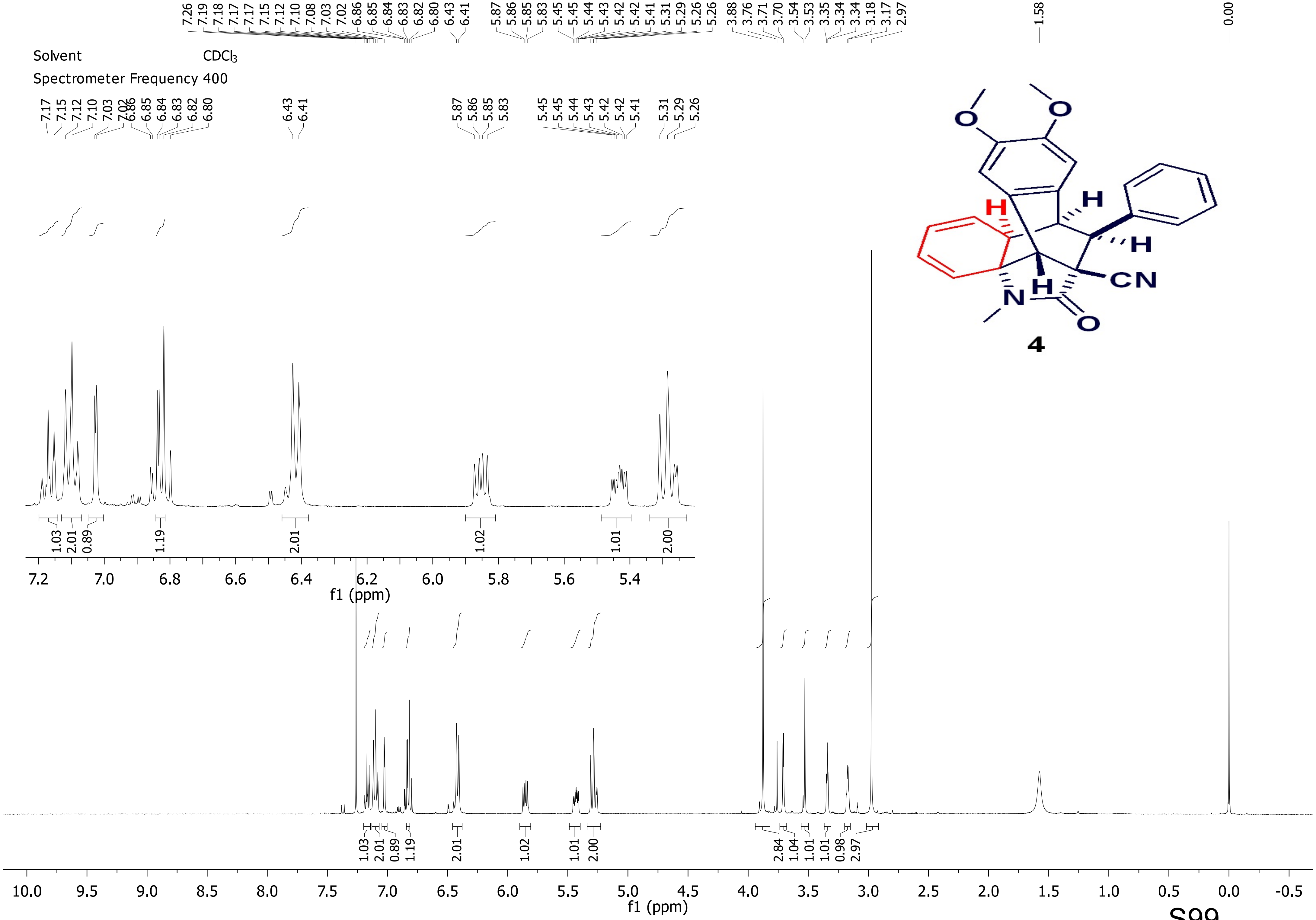

7.48 7.46 7.41 7.40 7.39 7.38 7.37 7.37 7.33 7.33 7.31 7.31 7.30 7.29 7.26 7.18 7.17 7.16 7.16 7.15 7.14 7.14 7.10 7.08 7.06 6.92 6.91 6.40 6.38 5.86 5.84 5.83 5.82 5.44 5.41 5.41 5.40 5.39 5.33 5.30 5.30 5.29 5.27 5.27 3.74 3.73 3.59 3.41 3.40 3.39 3.21 3.20 3.19 3.19 2.98 1.59 0.00
Solvent CDCl$_3$
Spectrometer Frequency 400
7.46 7.39 7.38 7.33 7.31 7.31 7.26 7.16 7.14 7.10 7.08 7.06 6.92 6.91 6.40 6.38 5.86 5.84 5.83 5.82 5.44 5.43 5.41 5.41 5.40 5.39 5.33 5.30 5.30 5.29 5.27 5.27
1.00 1.01 1.00 0.99 1.95 0.94 1.98 0.98 0.97 2.03
7.5 7.3 7.1 6.9 6.7 6.5 6.3 6.1 5.9 5.7 5.5 5.3
f1 (ppm)
H
H
H
H
CN
N
O
1.00 1.01 1.00 0.99 1.95 0.94 1.98 0.98 0.97 2.03 1.00 0.99 1.00 1.00 2.99
.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

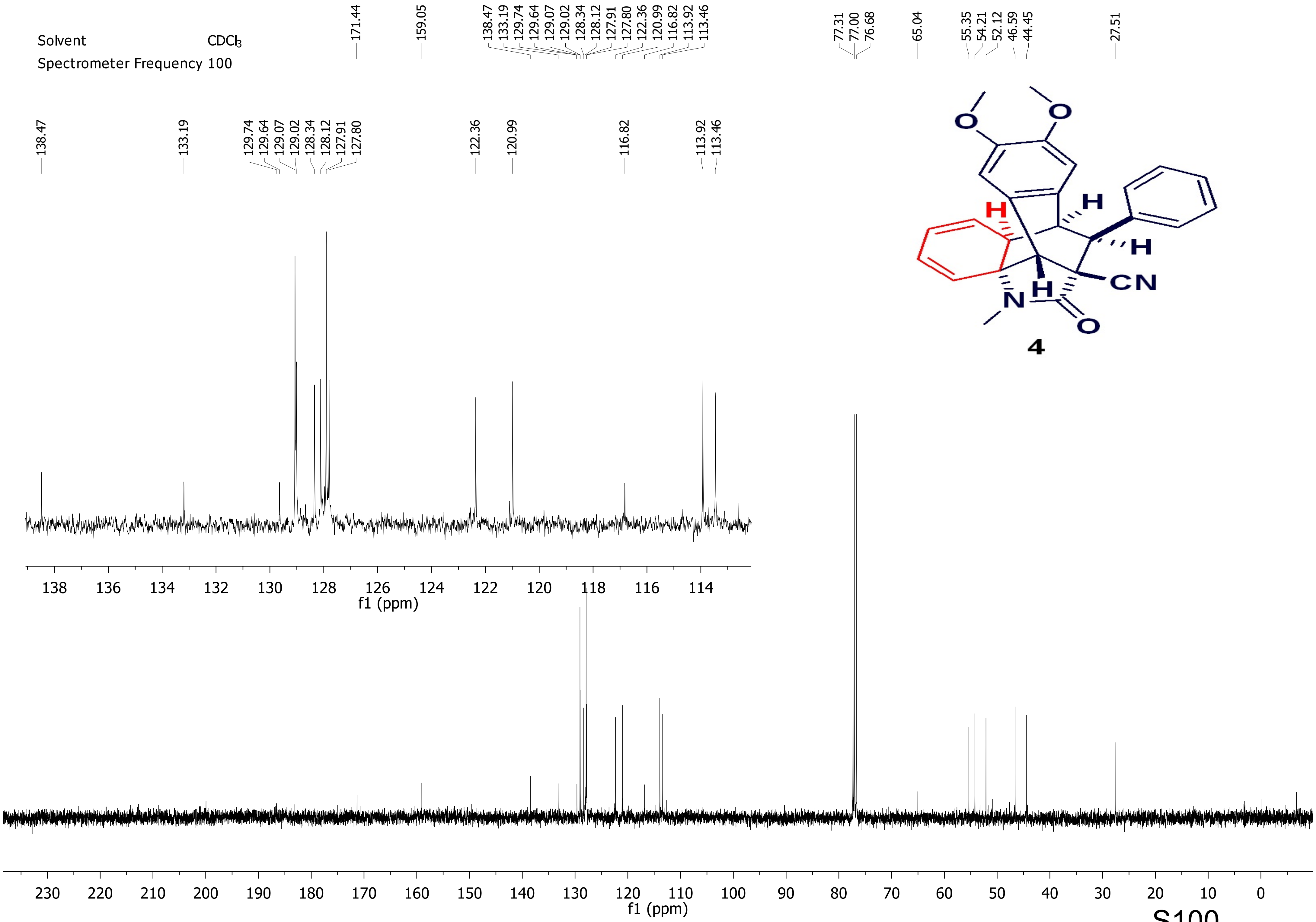
2

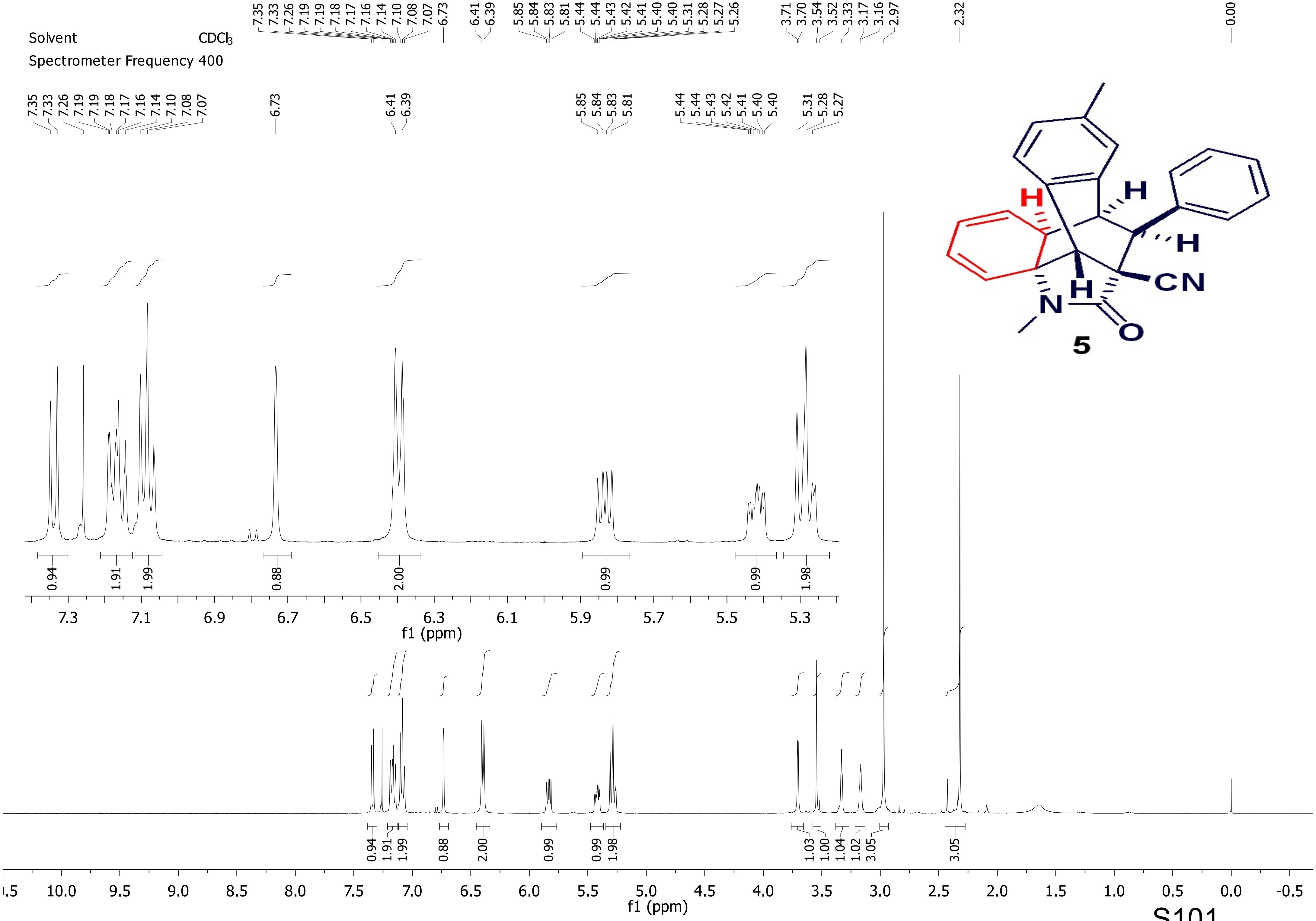

Solvent CDCl3
Spectrometer Frequency 100
171.35
138.33
137.82
129.01
127.98
127.96
127.92
122.47
121.02
77.31
76.99
76.67
65.03
53.82
51.82
50.92
47.29
44.26
27.52
138.33
137.82
132.07
129.01
128.83
128.39
127.98
127.96
127.92
127.83
127.56
127.48
122.47
121.02
139
137
135
133
131
129
127
125
123
121
f1 (ppm)
H
H
H
H
N
CN
O
2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

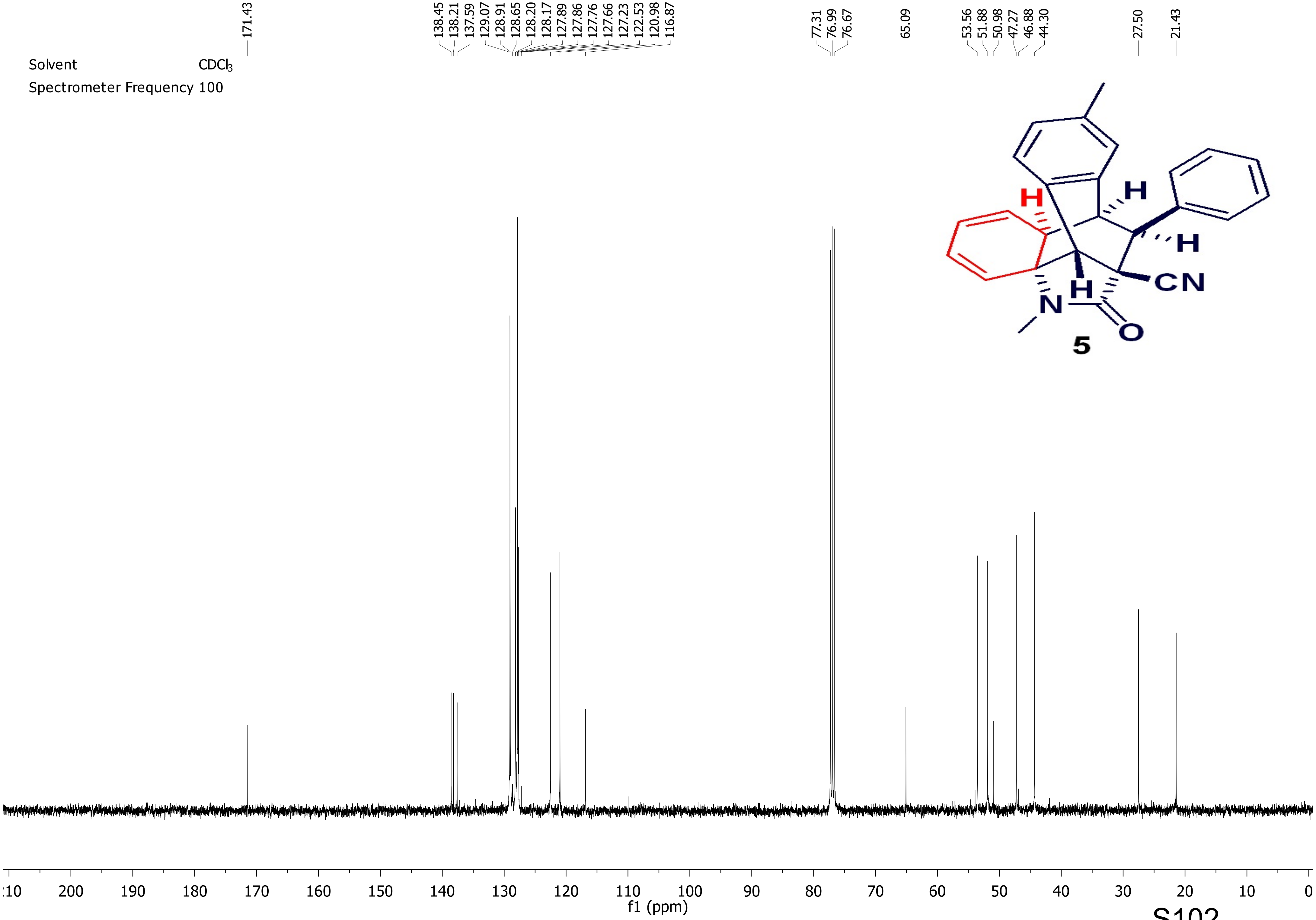

Solvent CDCl3
Spectrometer Frequency 600
7.26 7.20 7.19 7.18 7.15 7.14 7.12 6.95 6.52 6.50 6.43 6.02 6.02 5.99 5.99 5.48 5.47 5.47 5.46 5.46 5.45 5.45 5.30 5.28 5.28 5.27 5.26 5.26 3.68 3.67 3.50 3.32 3.15 3.14 2.96 1.58 -0.00
7.26 7.20 7.19 7.18 7.15 7.14 7.12 6.95 6.52 6.50 6.43 6.02 6.02 5.99 5.99 5.88 5.87 5.86 5.85 5.48 5.47 5.47 5.46 5.46 5.45 5.45 5.30 5.28 5.28 5.27
1.02 1.92 0.90 2.00 0.95 1.99 1.03 1.01 1.98
7.3 7.1 6.9 6.7 6.5 6.3 6.1 5.9 5.7 5.5 5.3
f1 (ppm)
O O H H H N H CN O
3
1.02 1.92 0.90 2.00 0.95 1.99 1.03 1.01 1.98 1.00 1.01 1.00 0.99 2.93
.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

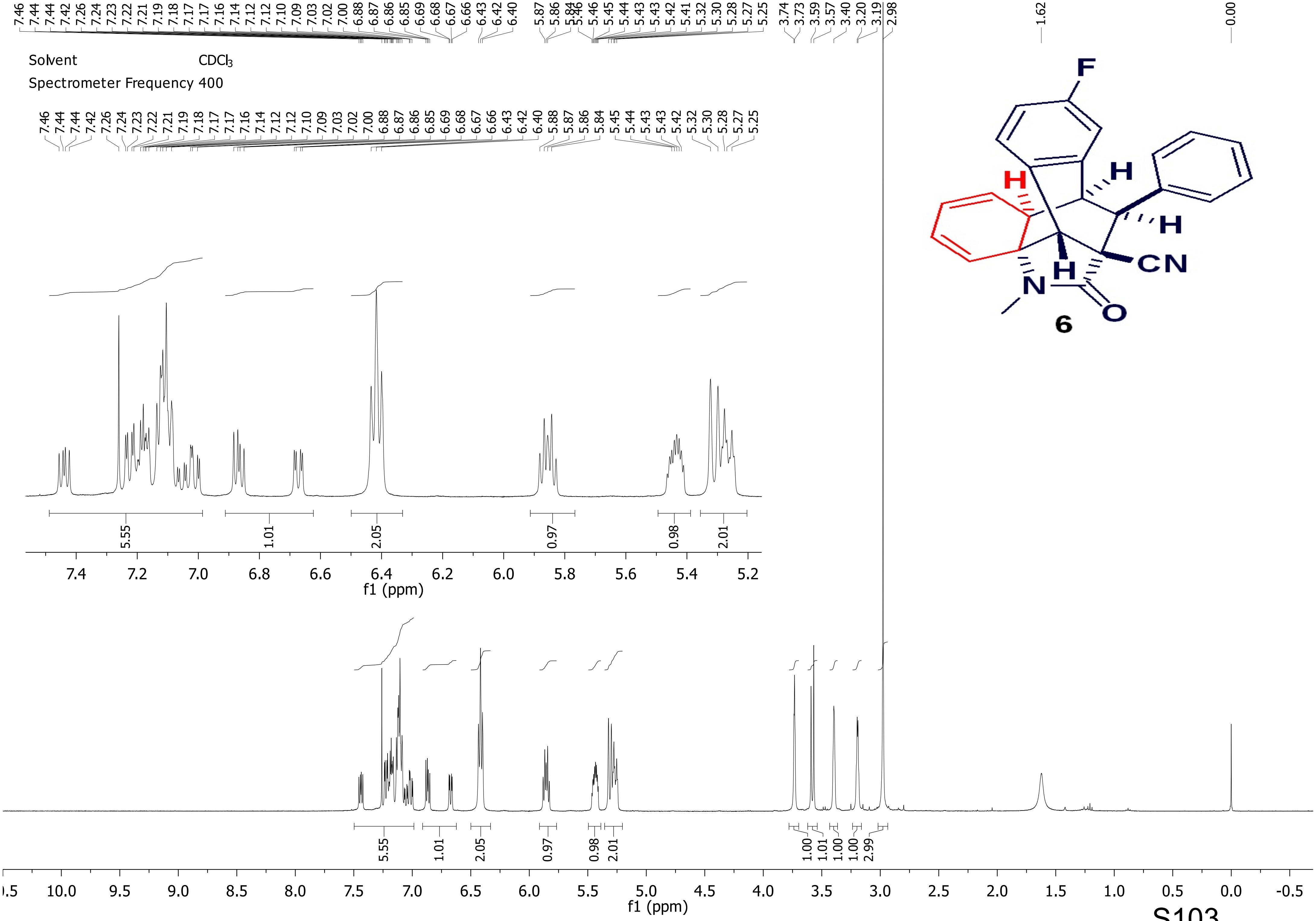

Solvent $CDCl_3$
Spectrometer Frequency 150
171.29
147.95
146.91
138.39
129.05
128.74
128.05
127.86
125.04
122.51
121.17
116.82
108.86
108.63
101.08
77.20
76.99
76.78
64.98
54.05
52.03
50.83
47.49
44.54
27.56
147.95
146.91
138.39
131.61
129.05
128.74
128.05
127.86
125.04
122.51
121.17
116.82
148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116
f1 (ppm)
O
O
H
H
H
H
CN
N
O
3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.26 7.19 7.18 7.17 7.17 7.15 7.12 7.10 7.08 7.03 7.02 6.86 6.85 6.84 6.83 6.82 6.80 6.43 6.41 5.87 5.86 5.85 5.83 5.45 5.45 5.44 5.43 5.42 5.42 5.41 5.31 5.29 5.26 5.26 3.88 3.76 3.71 3.70 3.54 3.53 3.35 3.34 3.34 3.18 3.17 2.97
1.58
0.00
Solvent CDCl₃
Spectrometer Frequency 400
7.17 7.15 7.12 7.10 7.03 7.02 6.86 6.85 6.84 6.83 6.82 6.80
6.43 6.41
5.87 5.86 5.85 5.83
5.45 5.45 5.44 5.43 5.42 5.42 5.41
5.31 5.29 5.26
1.03 2.01 0.89 1.19 2.01 1.02 1.01 2.00
7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4
f1 (ppm)
O
O
H
H
H
CN
H
N
O
4
1.03 2.01 0.89 1.19 2.01 1.02 1.01 2.00 2.84 1.04 1.01 1.01 0.98 2.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


Solvent CDCl₃
Spectrometer Frequency 100
171.44
159.05
138.47
133.19
129.74
129.64
129.07
129.02
128.34
128.12
127.91
127.80
122.36
120.99
116.82
113.92
113.46
77.31
77.00
76.68
65.04
55.35
54.21
52.12
46.59
44.45
27.51
O
O
H
H
H
H
CN
N
O
4
138 136 134 132 130 128 126 124 122 120 118 116 114
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

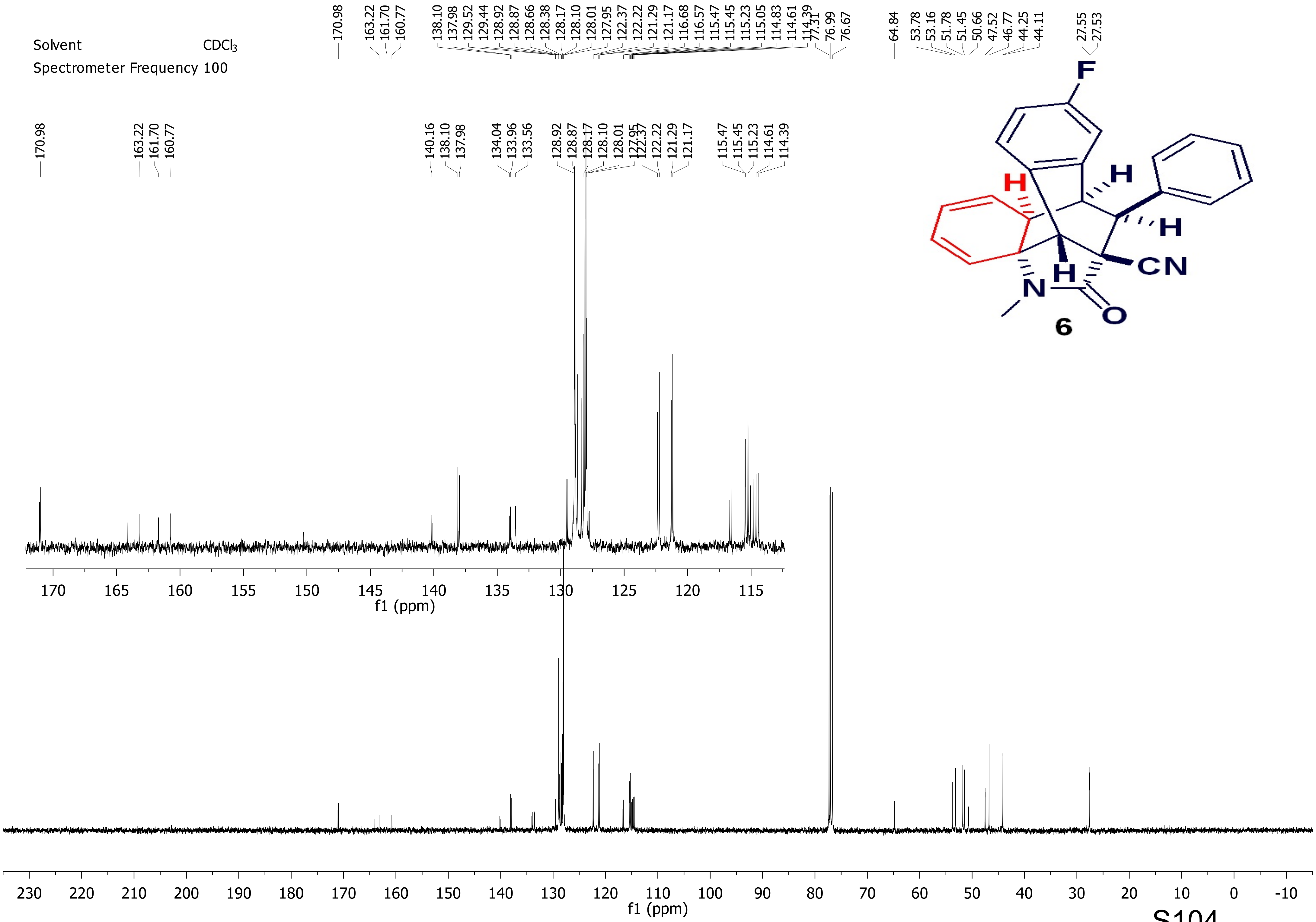

Solvent CDCl3
Spectrometer Frequency 400
7.35 7.33 7.26 7.19 7.19 7.18 7.17 7.16 7.14 7.10 7.08 7.07 6.73 6.41 6.39 5.85 5.84 5.83 5.81 5.44 5.44 5.43 5.42 5.41 5.40 5.40 5.31 5.27 5.26 3.71 3.70 3.54 3.52 3.33 3.17 3.16 2.97 2.32 0.00
7.35 7.33 7.26 7.19 7.19 7.18 7.17 7.16 7.14 7.10 7.08 7.07 6.73 6.41 6.39 5.85 5.84 5.83 5.81 5.44 5.44 5.43 5.42 5.41 5.40 5.40 5.31 5.28 5.27
0.94 1.91 1.99 0.88 2.00 0.99 0.99 1.98
7.3 7.1 6.9 6.7 6.5 6.3 6.1 5.9 5.7 5.5 5.3
f1 (ppm)
H
H
H
H
CN
N
O
5
0.94 1.91 1.99 0.88 2.00 0.99 0.99 1.98 1.03 1.00 1.04 1.02 3.05 3.05
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

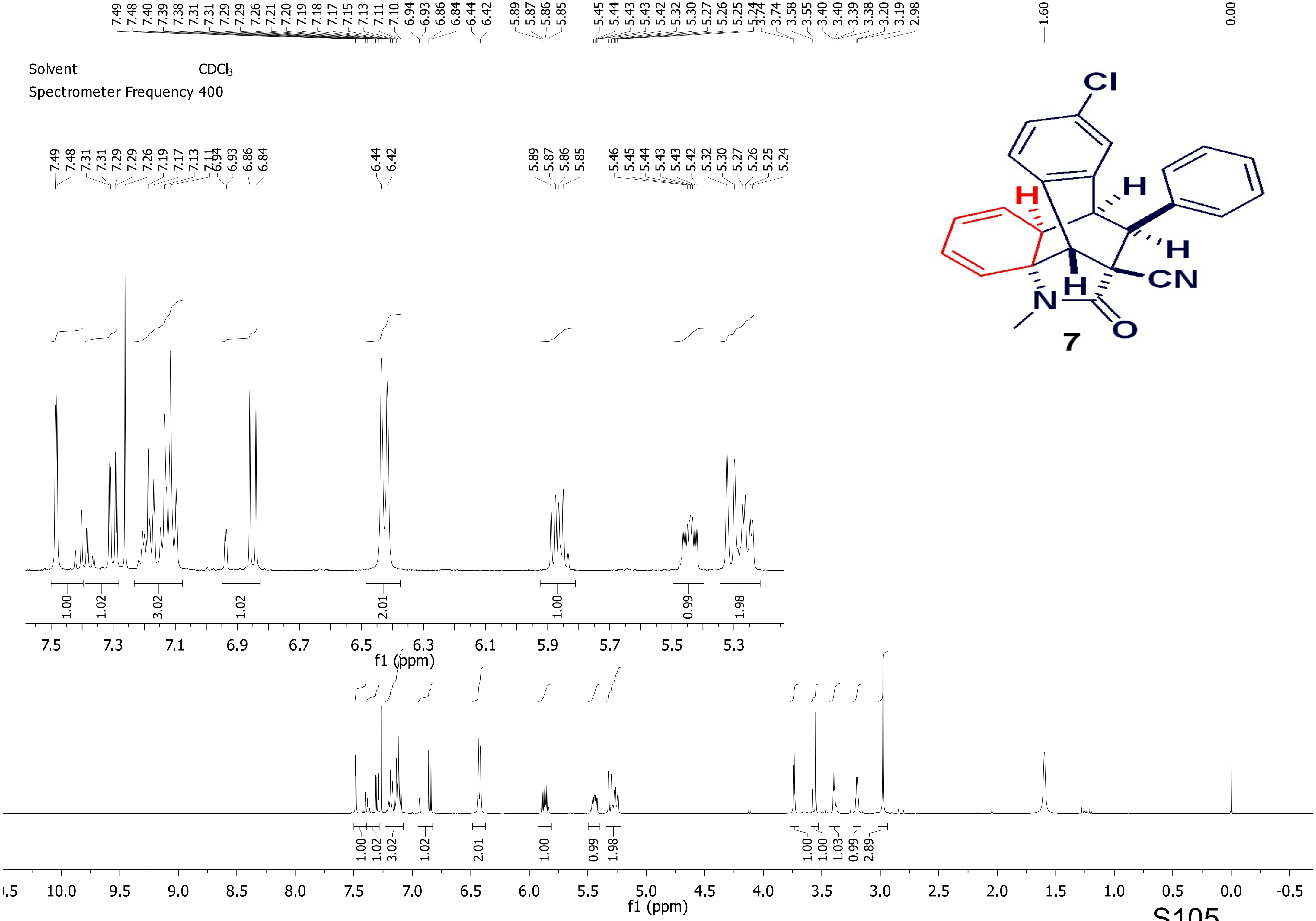

Solvent CDCl$_3$
Spectrometer Frequency 100
171.43
138.45
138.21
137.59
129.07
128.91
128.65
128.20
128.17
127.89
127.86
127.76
127.66
127.23
122.53
120.98
116.87
77.31
76.99
76.67
65.09
53.56
51.88
50.98
47.27
46.88
44.30
27.50
21.43
H
H
H
H
N
CN
O
5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



Solvent CDCl$_3$

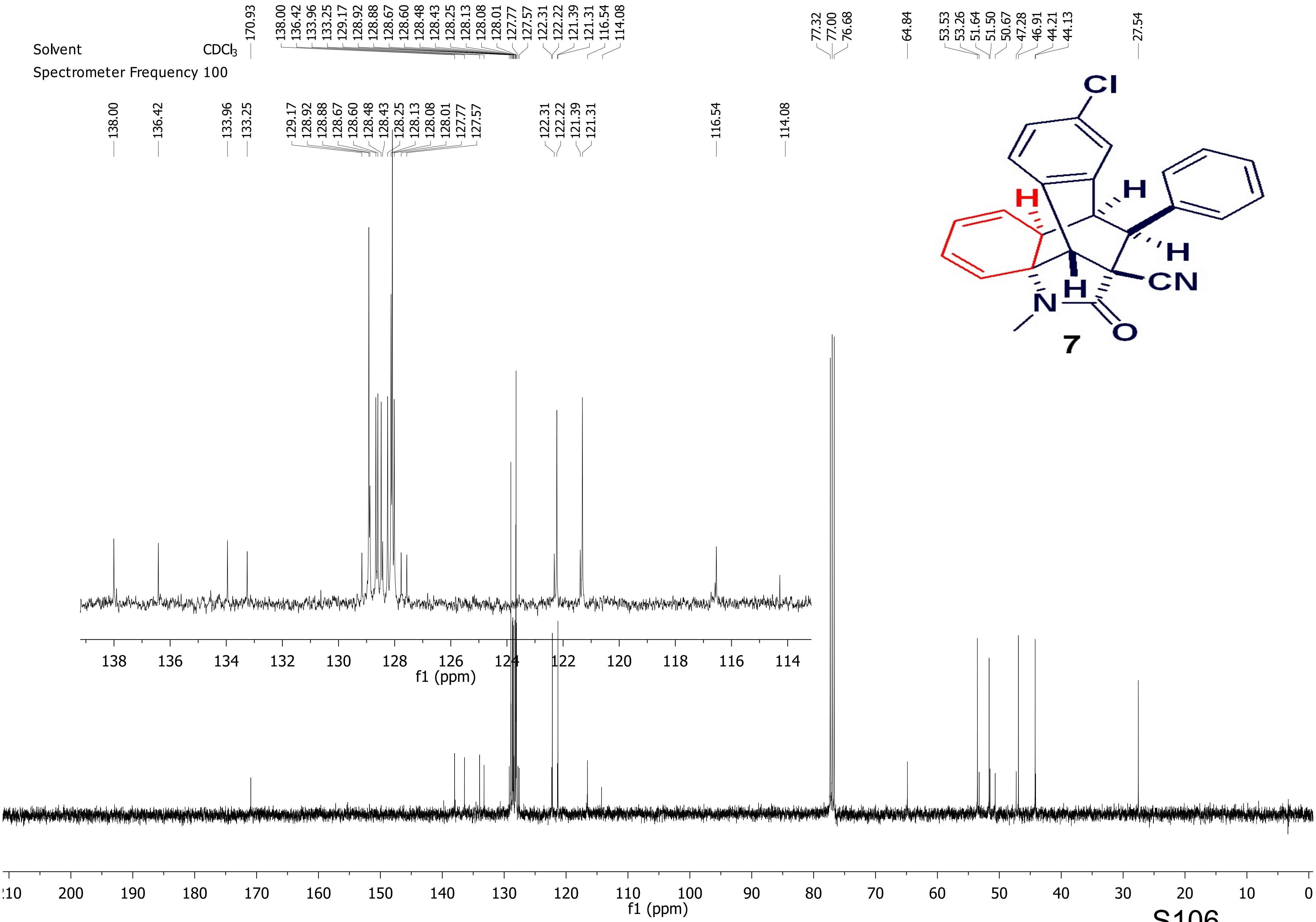
Spectrometer Frequency 400


Solvent CDCl3
Spectrometer Frequency 100
170.98
163.22
161.70
160.77
138.10
137.98
129.52
129.44
128.92
128.87
128.66
128.38
128.17
128.10
128.01
127.95
122.37
122.22
121.29
121.17
116.68
116.57
115.47
115.45
115.23
115.05
114.83
114.61
114.39
77.31
76.99
76.67
64.84
53.78
53.16
51.78
51.45
50.66
47.52
46.77
44.25
44.11
27.55
27.53
170.98
163.22
161.70
160.77
140.16
138.10
137.98
134.04
133.96
133.56
128.92
128.87
128.17
128.10
128.01
127.95
122.37
122.22
121.29
121.17
115.47
115.45
115.23
114.61
114.39
F
H
H
H
H
CN
N
O
6
170
165
160
155
150
145
140
135
130
125
120
115
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.49 7.48 7.40 7.39 7.38 7.31 7.31 7.29 7.29 7.26 7.21 7.20 7.19 7.18 7.17 7.15 7.13 7.11 7.10 6.94 6.93 6.86 6.84 6.44 6.42 5.89 5.87 5.86 5.85 5.45 5.44 5.43 5.43 5.42 5.32 5.30 5.27 5.26 5.25 5.24 3.74 3.74 3.58 3.55 3.40 3.40 3.39 3.38 3.20 3.19 2.98 1.60 0.00
Solvent CDCl3
Spectrometer Frequency 400
7.49 7.48 7.31 7.31 7.29 7.29 7.26 7.19 7.17 7.13 7.11 6.94 6.93 6.86 6.84 6.44 6.42 5.89 5.87 5.86 5.85 5.46 5.45 5.44 5.43 5.43 5.42 5.32 5.30 5.27 5.26 5.25 5.24
1.00 1.02 3.02 1.02 2.01 1.00 0.99 1.98
7.5 7.3 7.1 6.9 6.7 6.5 6.3 6.1 5.9 5.7 5.5 5.3
f1 (ppm)
Cl
H
H
H
CN
H
N
O
1.00 1.02 3.02 1.02 2.01 1.00 0.99 1.98 1.00 1.00 1.03 0.99 2.89
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

7

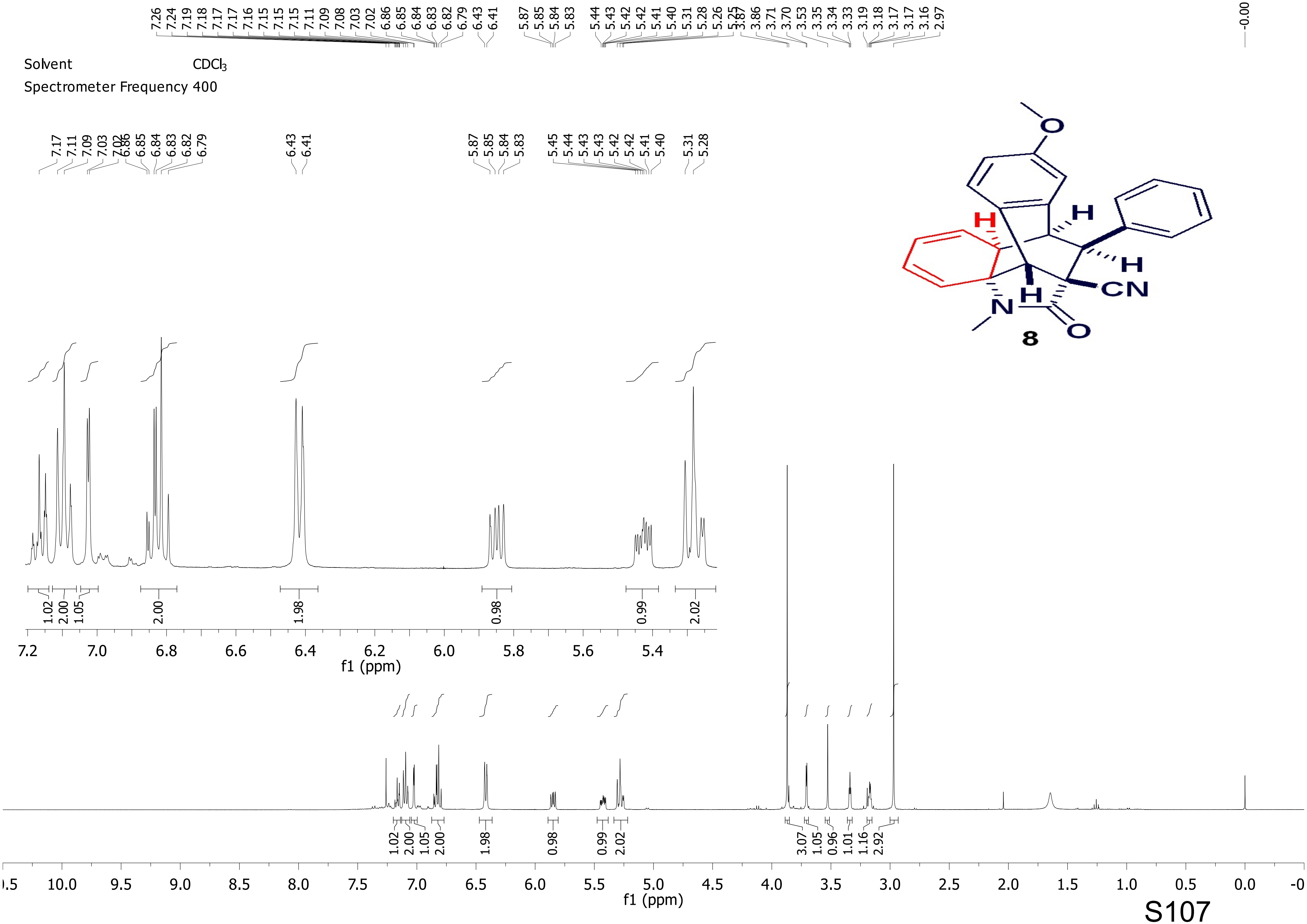
Solvent CDCl$_3$
Spectrometer Frequency 100

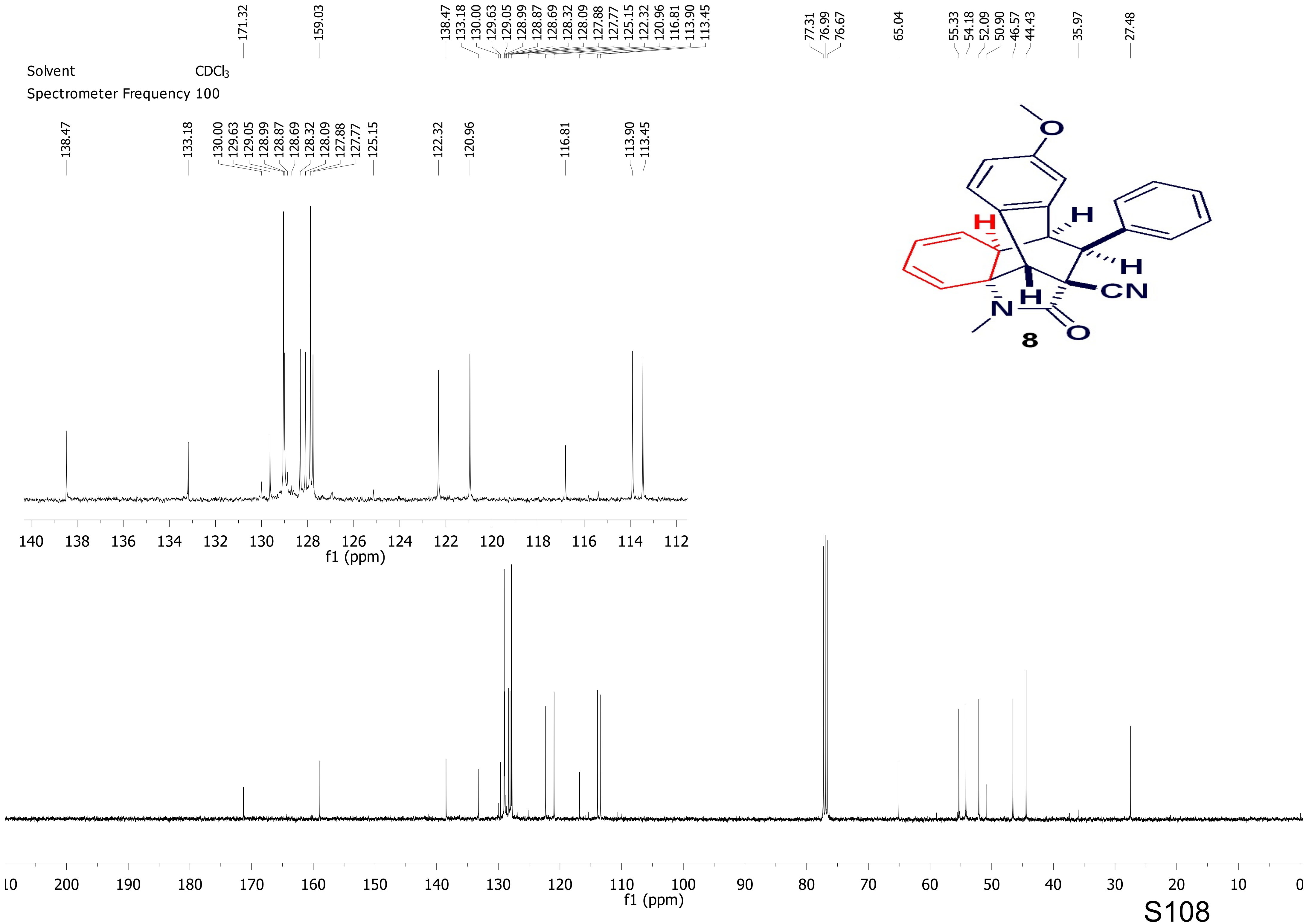


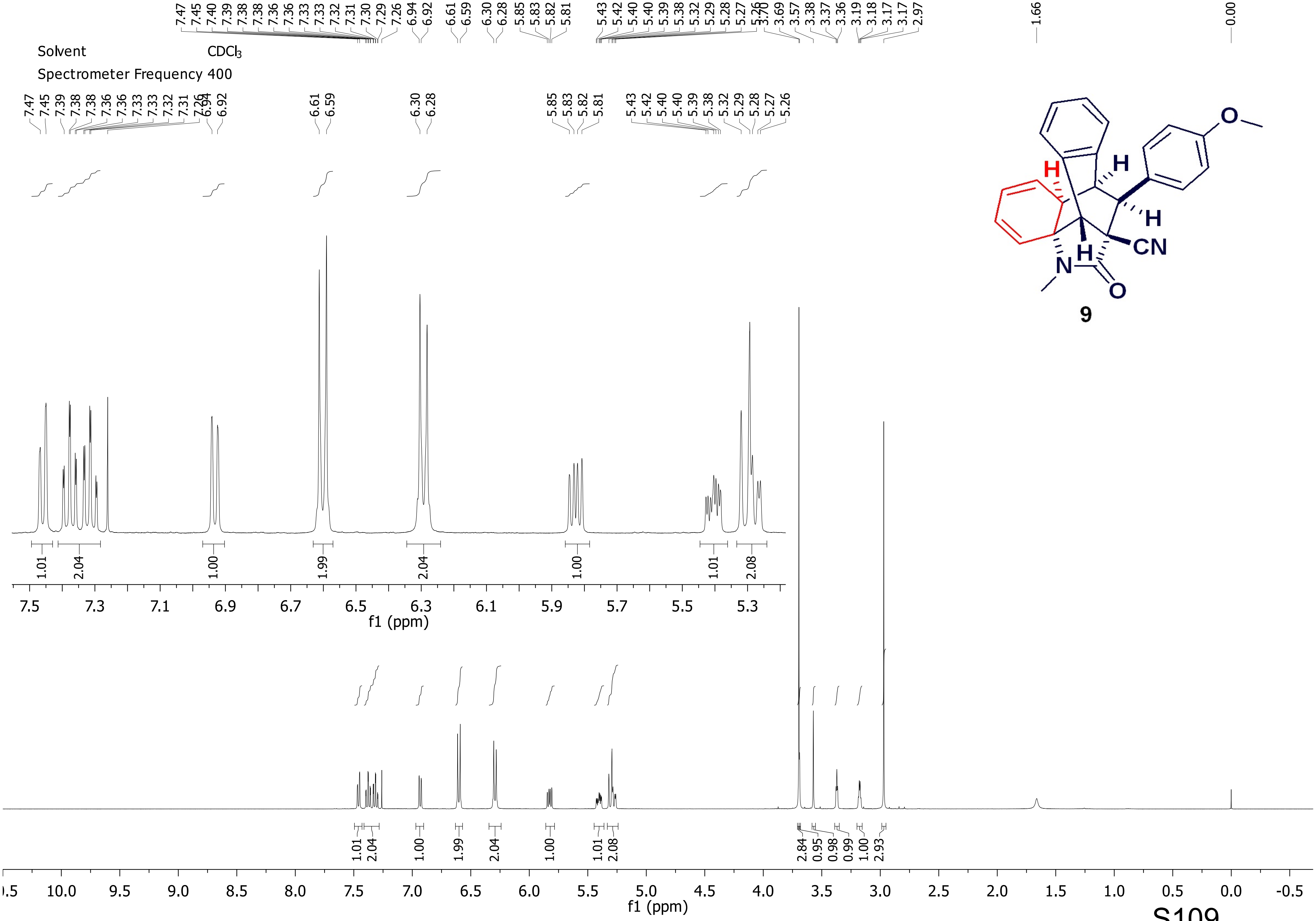
7

Solvent CDCl$_3$

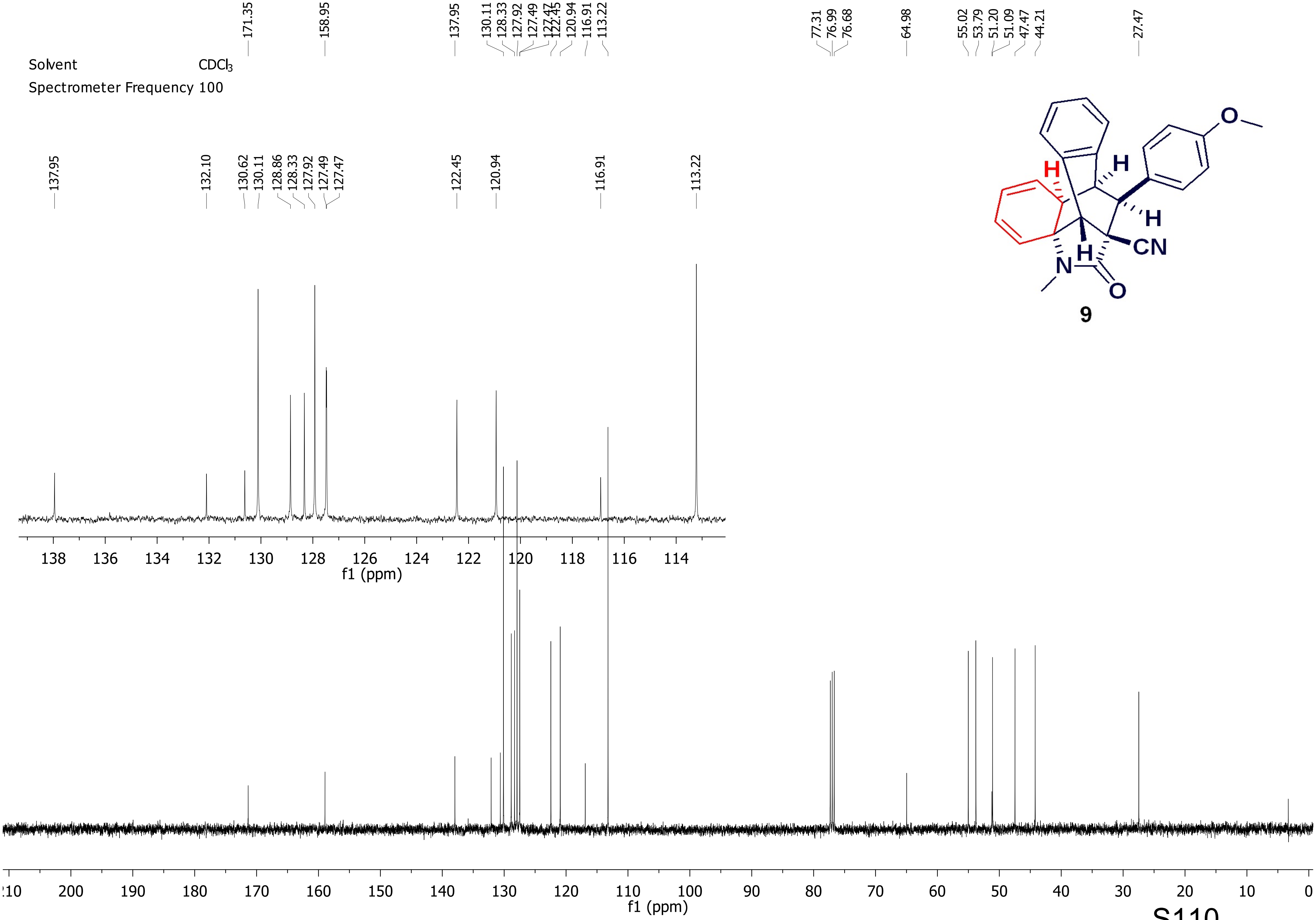
Spectrometer Frequency 400

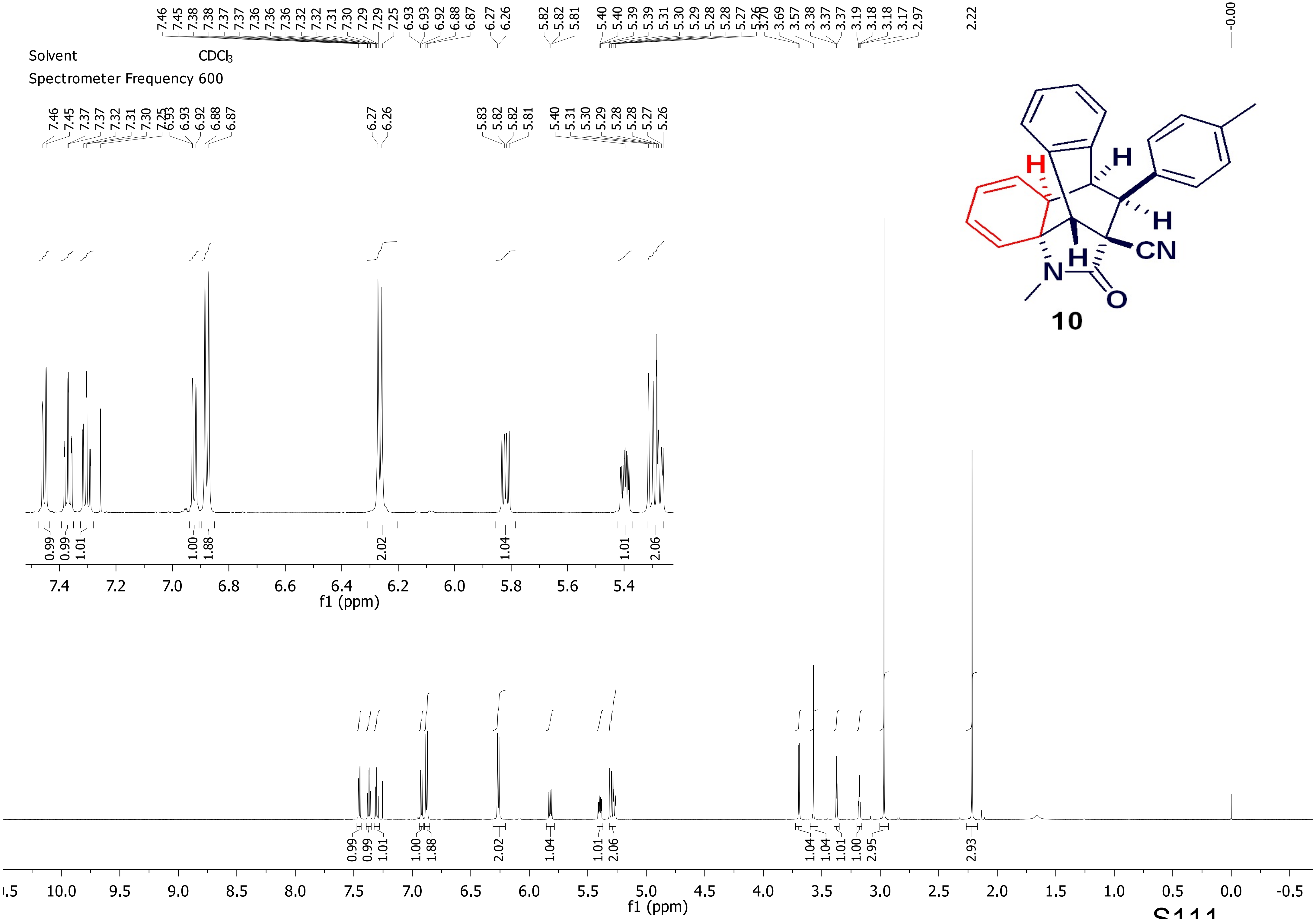



171.32
159.03
138.47
133.18
130.00
129.63
129.05
128.99
128.87
128.69
128.32
128.09
127.88
127.77
125.15
122.32
120.96
116.81
113.90
113.45
77.31
76.99
76.67
65.04
55.33
54.18
52.09
50.90
46.57
44.43
35.97
27.48
Solvent CDCl$_3$
Spectrometer Frequency 100
138.47
133.18
130.00
129.63
129.05
128.99
128.87
128.69
128.32
128.09
127.88
127.77
125.15
122.32
120.96
116.81
113.90
113.45
140
138
136
134
132
130
128
126
124
122
120
118
116
114
112
f1 (ppm)
O
H
H
H
N
H
CN
O
8
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.47 7.45 7.40 7.39 7.38 7.38 7.36 7.36 7.33 7.33 7.32 7.31 7.30 7.29 7.26 6.94 6.92 6.61 6.59 6.30 6.28 5.85 5.83 5.82 5.81 5.43 5.42 5.40 5.40 5.39 5.38 5.32 5.29 5.28 5.27 5.26 3.70 3.69 3.57 3.38 3.37 3.36 3.19 3.18 3.17 3.17 2.97 1.66 0.00
Solvent CDCl3
Spectrometer Frequency 400
7.47 7.45 7.39 7.38 7.38 7.36 7.36 7.33 7.33 7.32 7.31 7.26 6.94 6.92 6.61 6.59 6.30 6.28 5.85 5.83 5.82 5.81 5.43 5.42 5.40 5.40 5.39 5.38 5.32 5.29 5.28 5.27 5.26
1.01 2.04 1.00 1.99 2.04 1.00 1.01 2.08
7.5 7.3 7.1 6.9 6.7 6.5 6.3 6.1 5.9 5.7 5.5 5.3
f1 (ppm)
1.01 2.04 1.00 1.99 2.04 1.00 1.01 2.08 2.84 0.95 0.98 0.99 1.00 2.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
O
H
H
H
H
CN
N
O

9

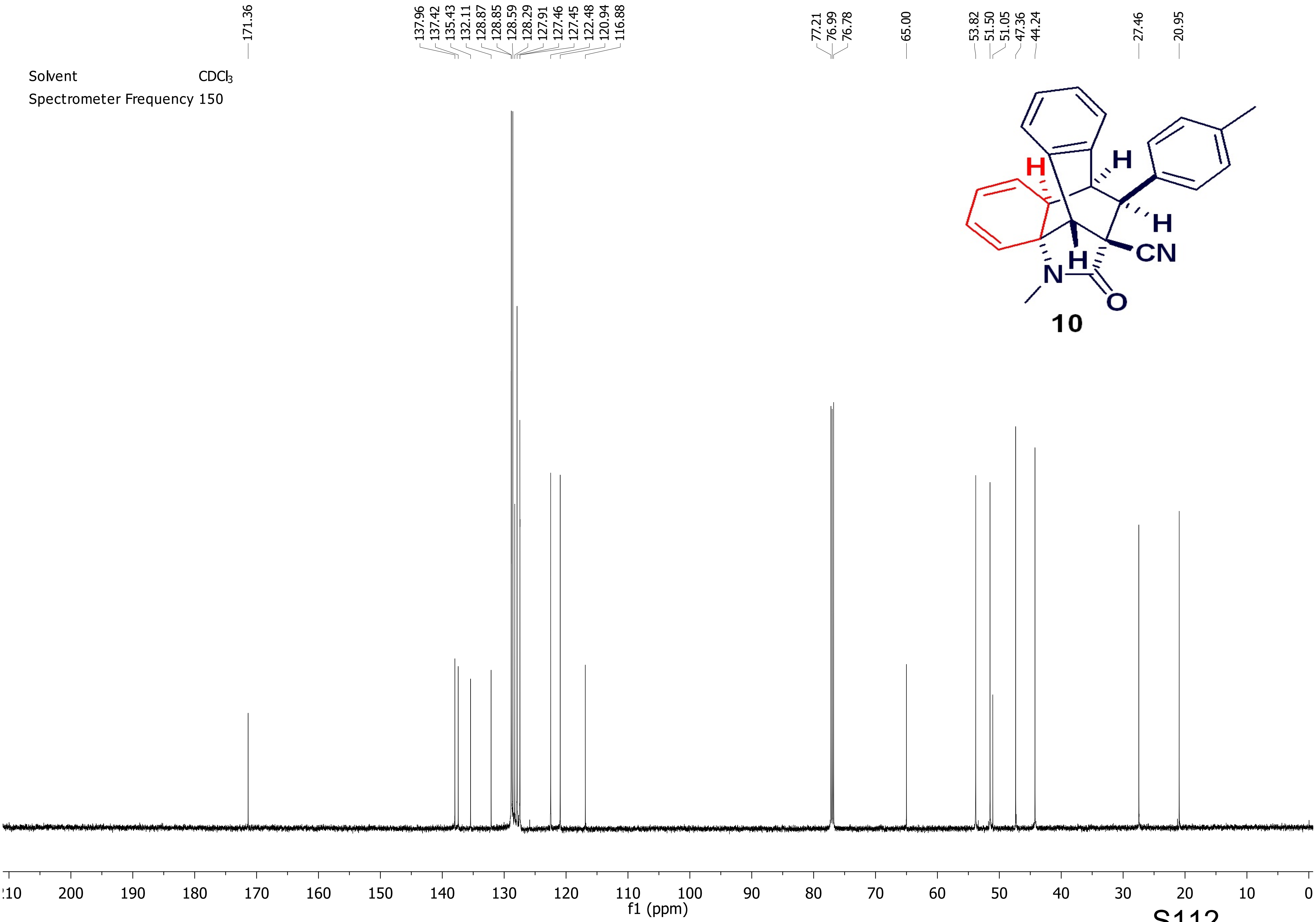

Solvent CDCl$_3$
Spectrometer Frequency 100
171.35
158.95
137.95
130.11
128.33
127.92
127.49
127.47
122.45
120.94
116.91
113.22
77.31
76.99
76.68
64.98
55.02
53.79
51.20
51.09
47.47
44.21
27.47
137.95
132.10
130.62
130.11
128.86
128.33
127.92
127.49
127.47
122.45
120.94
116.91
113.22
138 136 134 132 130 128 126 124 122 120 118 116 114
f1 (ppm)
O
H
H
H
H
CN
N
O
9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

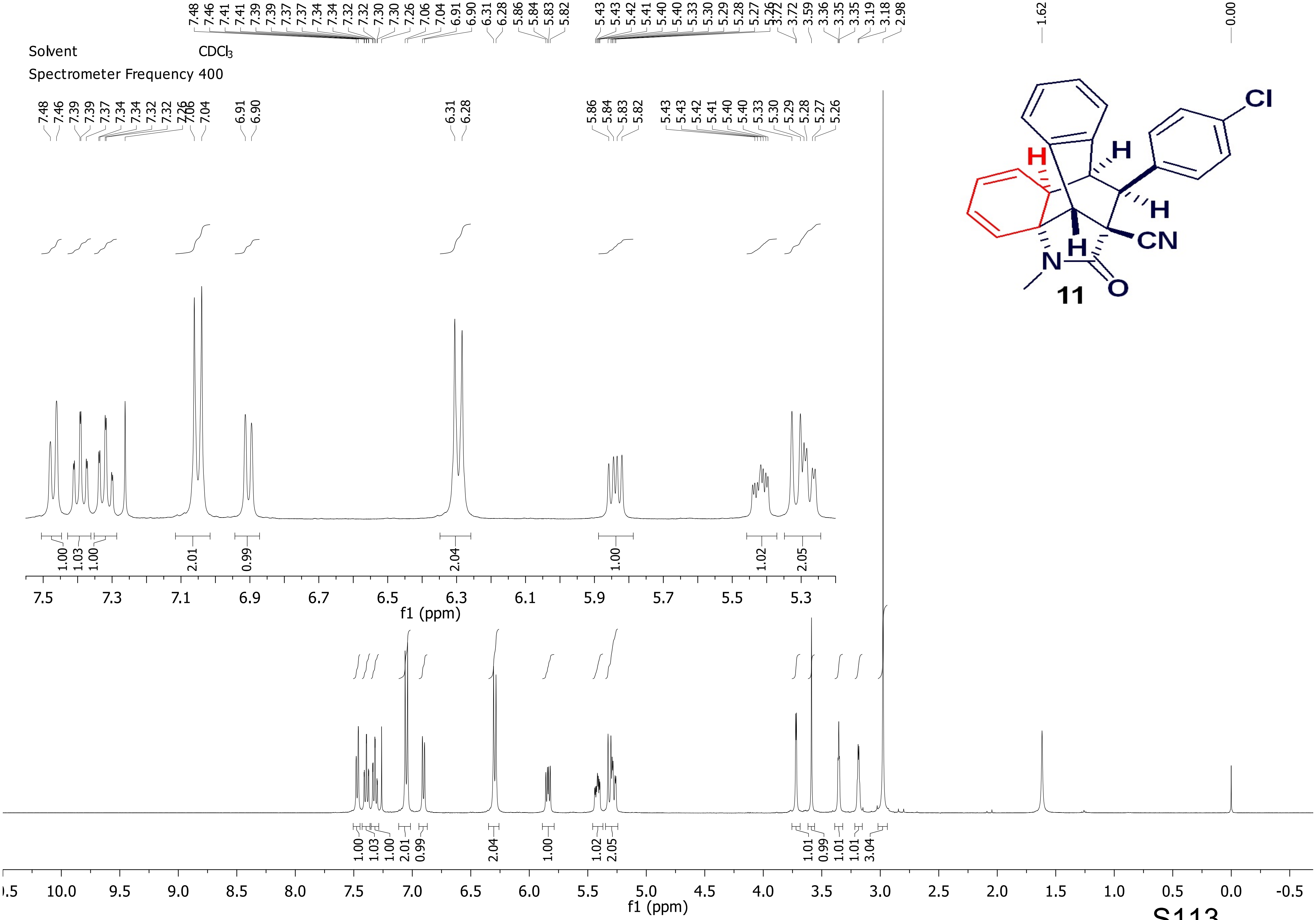

7.46 7.45 7.38 7.38 7.37 7.37 7.36 7.36 7.36 7.32 7.32 7.31 7.30 7.29 7.29 7.25 6.93 6.93 6.92 6.88 6.87 6.27 6.26 5.82 5.82 5.81 5.40 5.40 5.39 5.39 5.31 5.30 5.29 5.28 5.28 5.27 5.26 3.70 3.69 3.57 3.38 3.37 3.37 3.19 3.18 3.18 3.17 2.97 2.22 -0.00
Solvent CDCl3
Spectrometer Frequency 600
7.46 7.45 7.37 7.37 7.32 7.31 7.30 7.25 6.93 6.93 6.92 6.88 6.87 6.27 6.26 5.83 5.82 5.82 5.81 5.40 5.31 5.30 5.29 5.28 5.28 5.27 5.26
0.99 0.99 1.01 1.00 1.88 2.02 1.04 1.01 2.06
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4
f1 (ppm)
H H H H CN N O
0.99 0.99 1.01 1.00 1.88 2.02 1.04 1.01 2.06 1.04 1.04 1.01 1.00 2.95 2.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

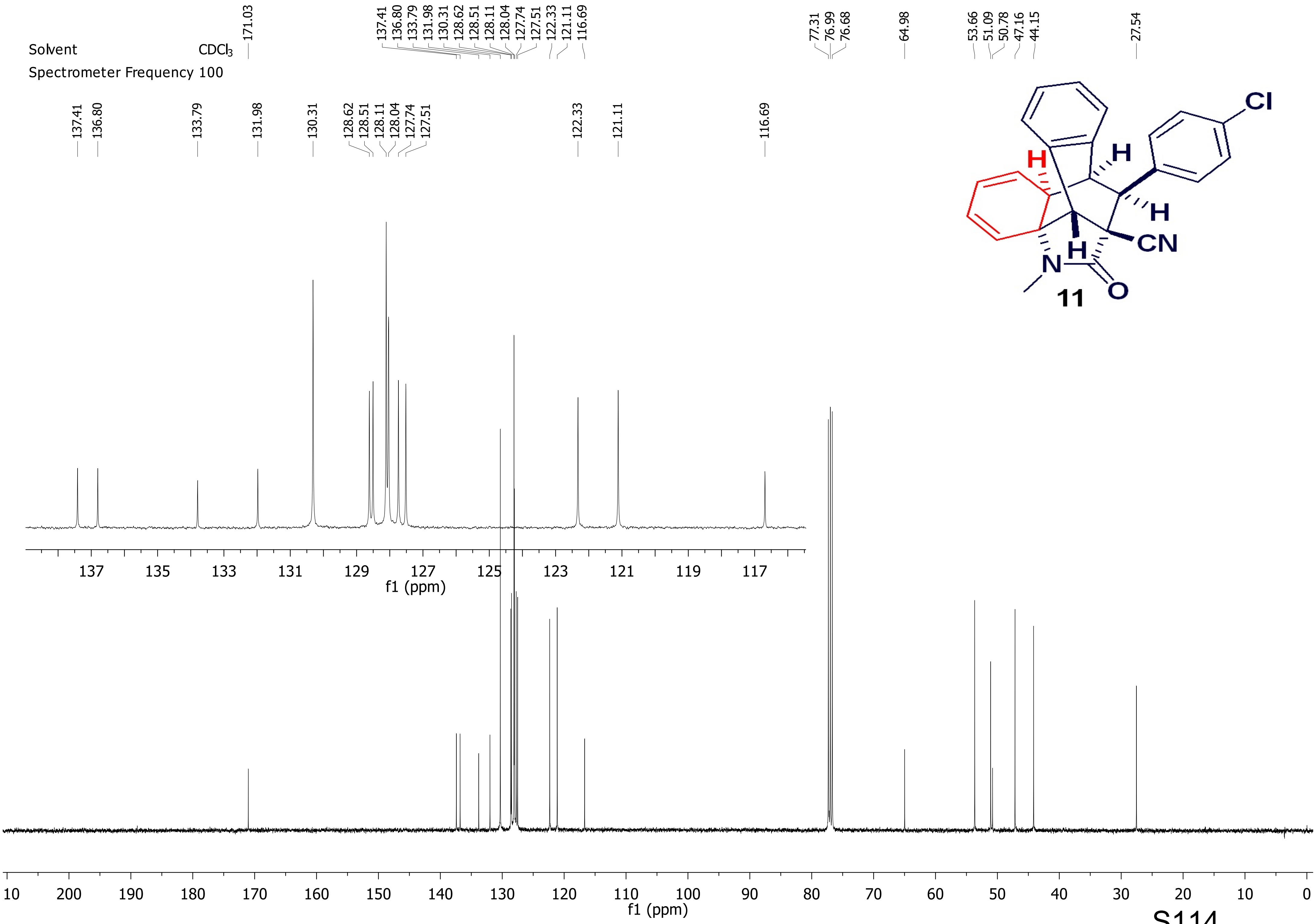
10

Solvent CDCl3

Spectrometer Frequency 150

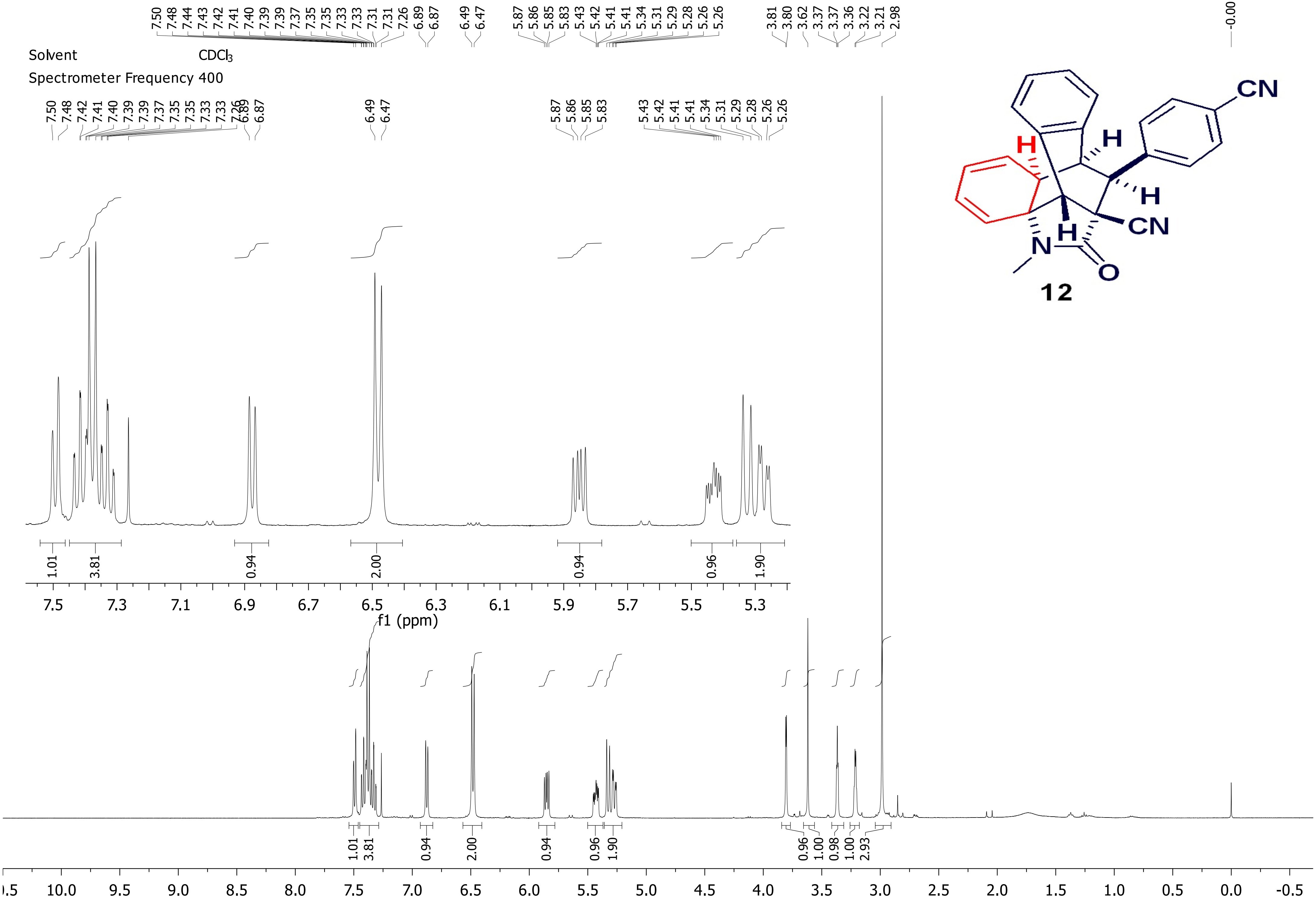



Solvent CDCl$_3$
Spectrometer Frequency 400
7.48 7.46 7.41 7.41 7.39 7.39 7.37 7.37 7.34 7.34 7.32 7.32 7.30 7.30 7.26 7.06 7.04 6.91 6.90 6.31 6.28 5.86 5.84 5.83 5.82 5.43 5.43 5.42 5.41 5.40 5.40 5.33 5.30 5.29 5.28 5.27 5.26 3.72 3.72 3.59 3.36 3.35 3.35 3.19 3.18 2.98 1.62 0.00
7.48 7.46 7.39 7.39 7.37 7.34 7.34 7.32 7.32 7.26 7.06 7.04 6.91 6.90 6.31 6.28 5.86 5.84 5.83 5.82 5.43 5.43 5.42 5.41 5.40 5.40 5.33 5.30 5.29 5.28 5.27 5.26
1.00 1.03 1.00 2.01 0.99 2.04 1.00 1.02 2.05
7.5 7.3 7.1 6.9 6.7 6.5 6.3 6.1 5.9 5.7 5.5 5.3
f1 (ppm)
1.00 1.03 1.00 2.01 0.99 2.04 1.00 1.02 2.05 1.01 0.99 1.01 1.01 3.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
Cl
H
H
H
H
CN
N
O
11

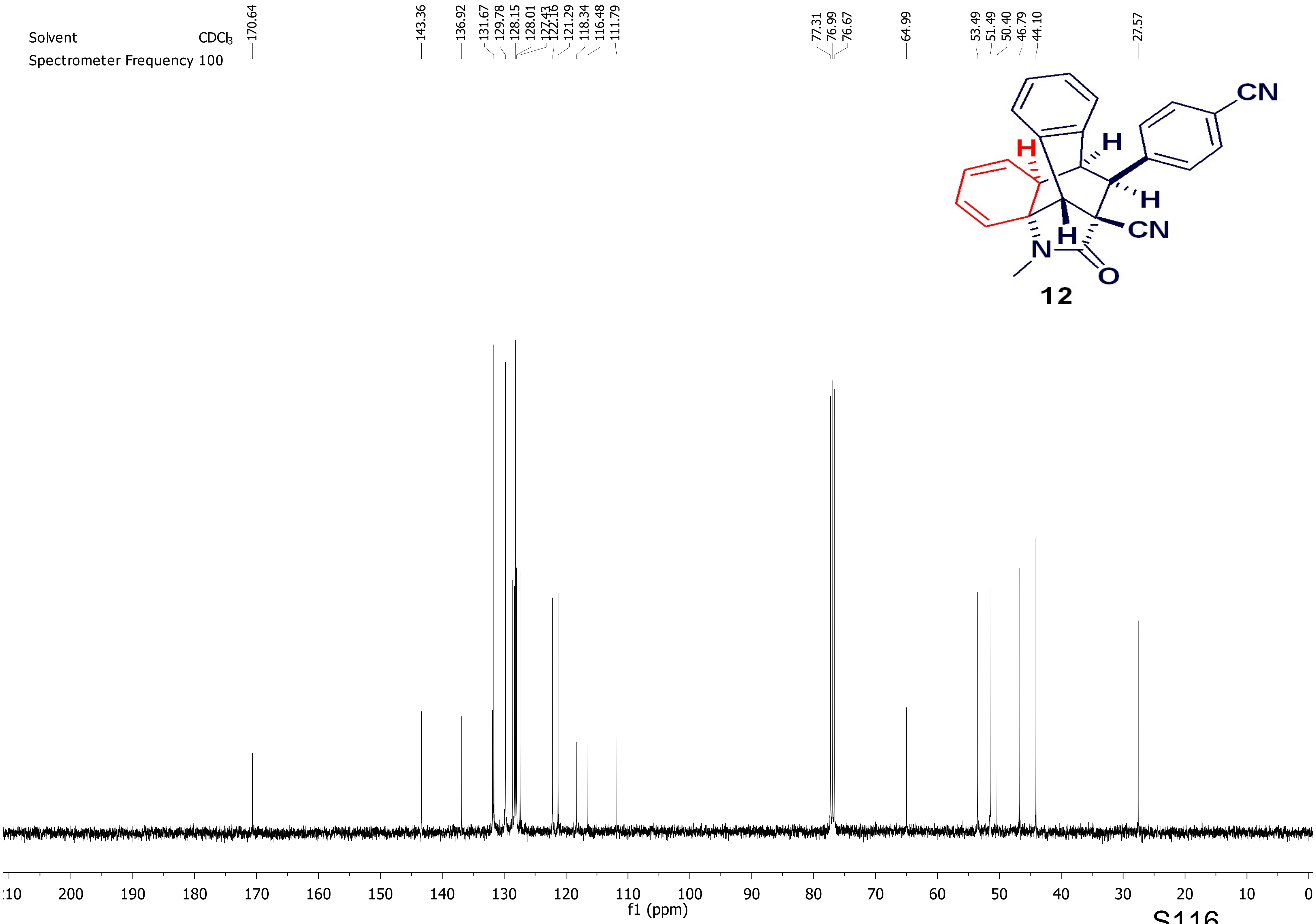

Solvent CDCl$_3$
Spectrometer Frequency 100
171.03
137.41
136.80
133.79
131.98
130.31
128.62
128.51
128.11
128.04
127.74
127.51
122.33
121.11
116.69
77.31
76.99
76.68
64.98
53.66
51.09
50.78
47.16
44.15
27.54
137 135 133 131 129 127 125 123 121 119 117
f1 (ppm)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
Cl
H
H
H
H
CN
N
O
11

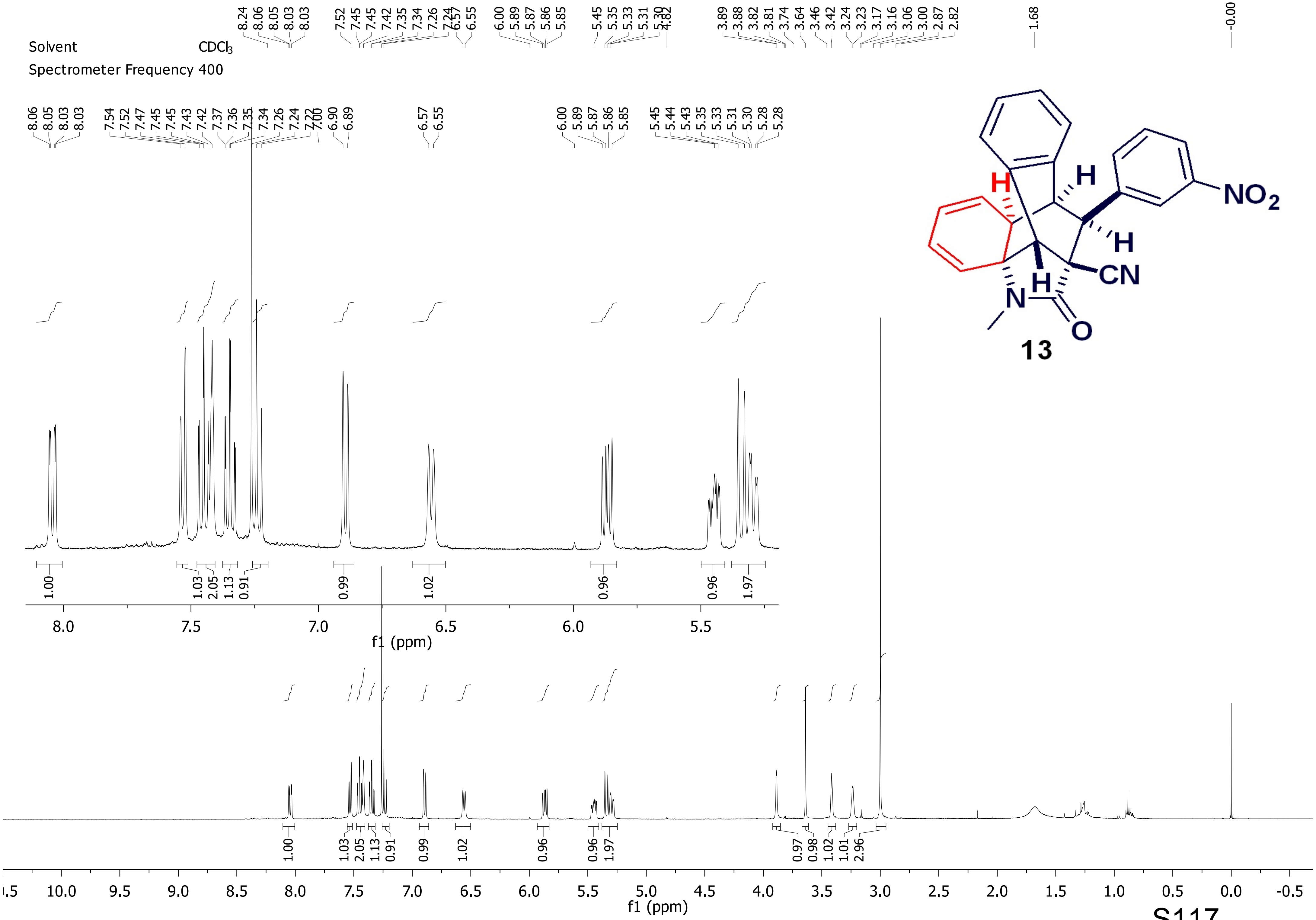
Solvent CDCl3

Spectrometer Frequency 400



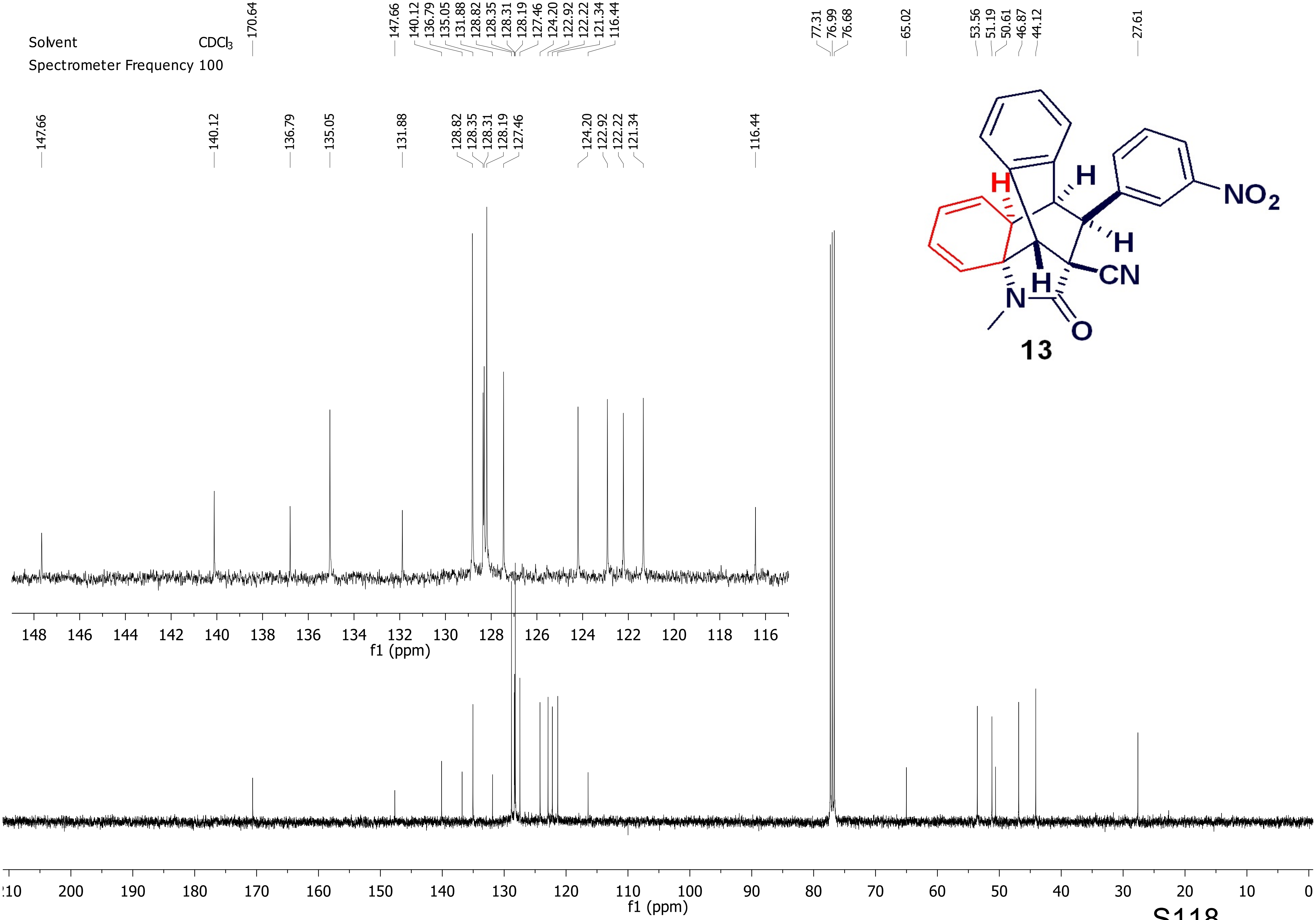
12


Solvent CDCl3
Spectrometer Frequency 100
170.64
143.36
136.92
131.67
129.78
128.15
128.01
127.43
122.16
121.29
118.34
116.48
111.79
77.31
76.99
76.67
64.99
53.49
51.49
50.40
46.79
44.10
27.57
CN
H
H
H
H
CN
N
O
12
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

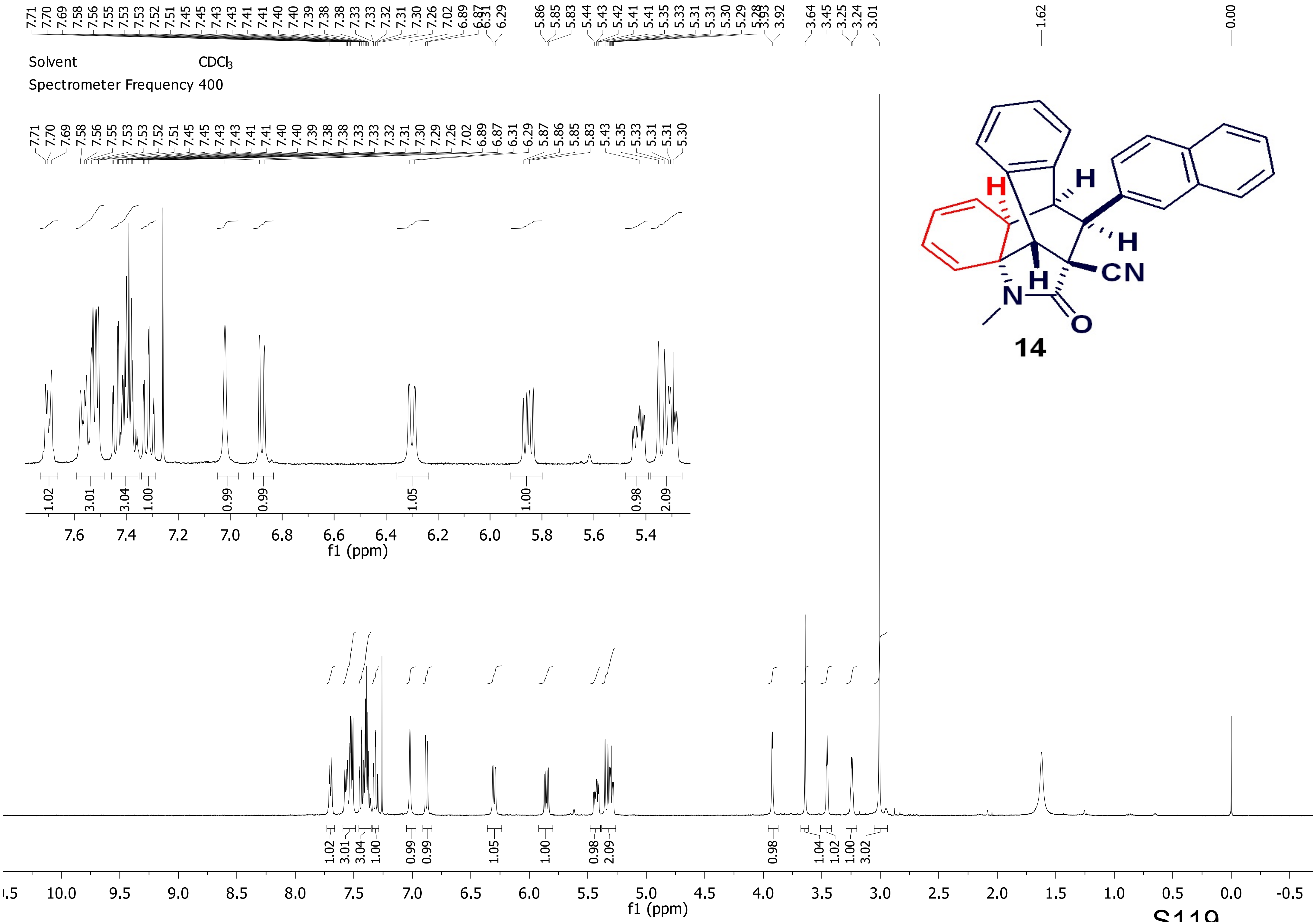

Solvent CDCl3
Spectrometer Frequency 400
8.24 8.06 8.05 8.03 8.03 7.52 7.45 7.45 7.42 7.35 7.34 7.26 7.24 6.57 6.55 6.00 5.89 5.87 5.86 5.85 5.45 5.35 5.33 5.31 5.30 4.82 3.89 3.88 3.82 3.81 3.74 3.64 3.46 3.42 3.24 3.23 3.17 3.16 3.06 3.00 2.87 2.82 1.68 -0.00
8.06 8.05 8.03 8.03 7.54 7.52 7.47 7.45 7.45 7.43 7.42 7.37 7.36 7.35 7.34 7.26 7.24 7.22 7.00 6.90 6.89 6.57 6.55 6.00 5.89 5.87 5.86 5.85 5.45 5.44 5.43 5.35 5.33 5.31 5.30 5.28 5.28
1.00 1.03 2.05 1.13 0.91 0.99 1.02 0.96 0.96 1.97
8.0 7.5 7.0 6.5 6.0 5.5
f1 (ppm)
1.00 1.03 2.05 1.13 0.91 0.99 1.02 0.96 0.96 1.97 0.97 0.98 1.02 1.01 2.96
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
H
H
H
H
NO2
CN
N
O

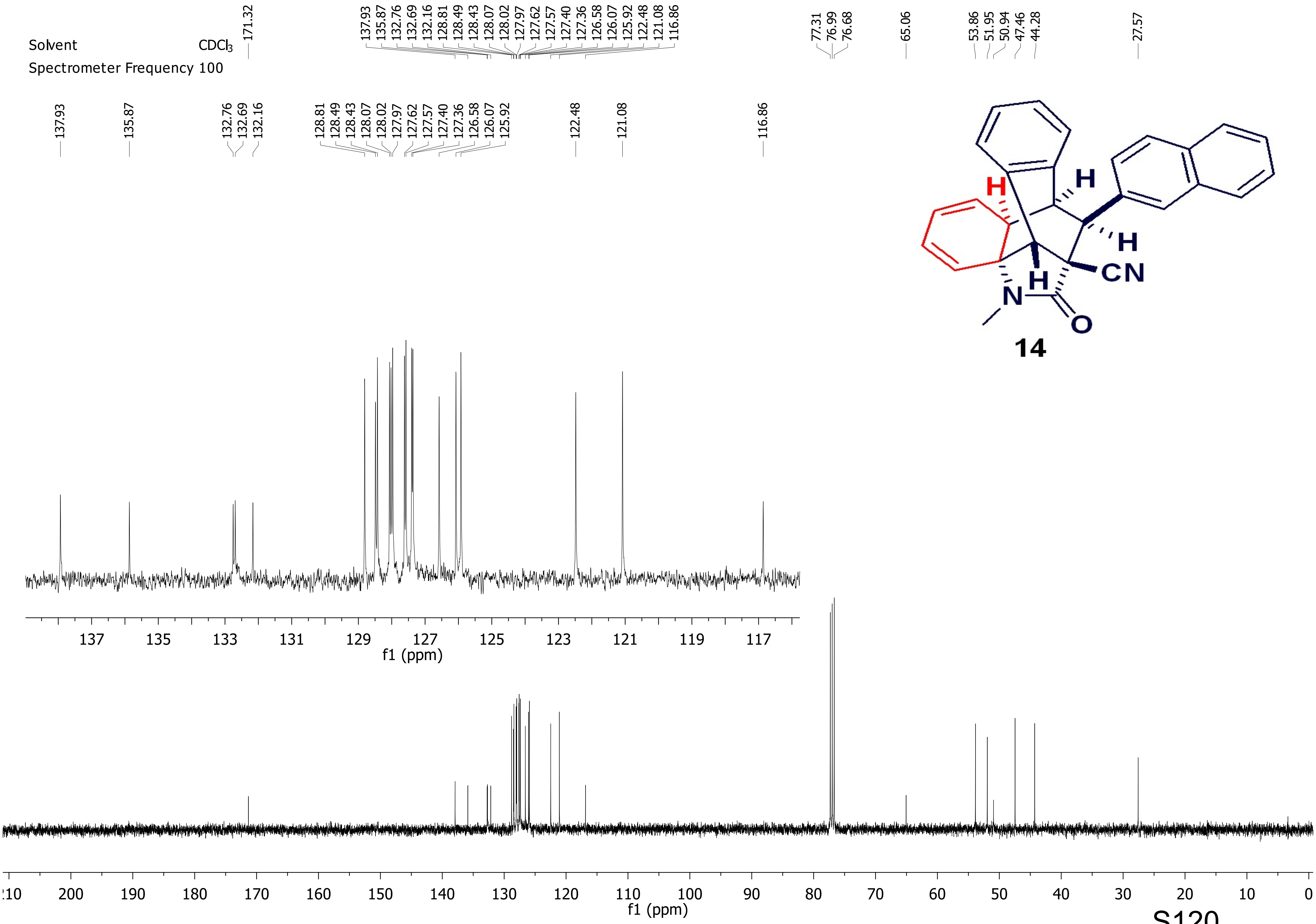
13

Solvent CDCl$_3$
Spectrometer Frequency 100

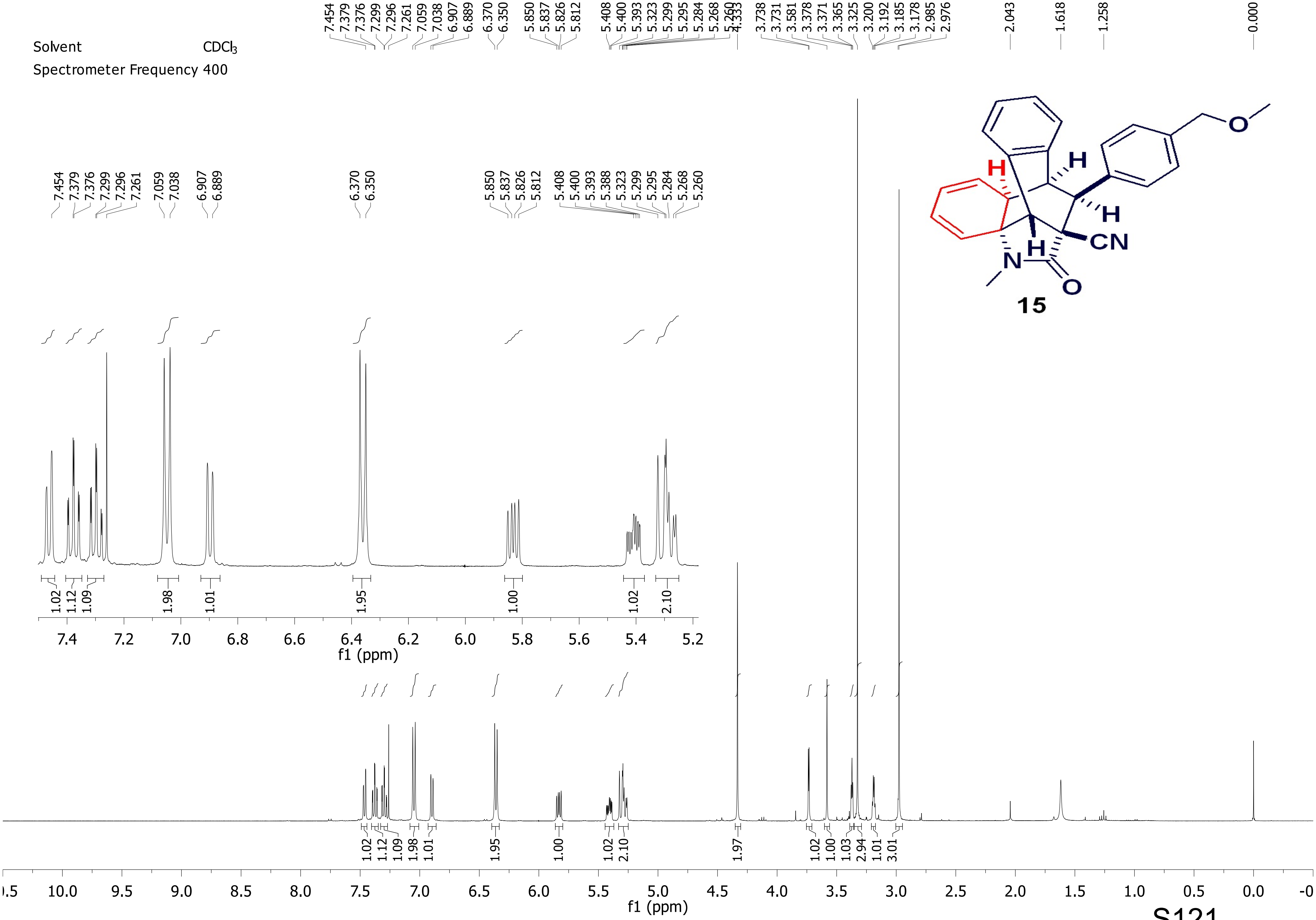


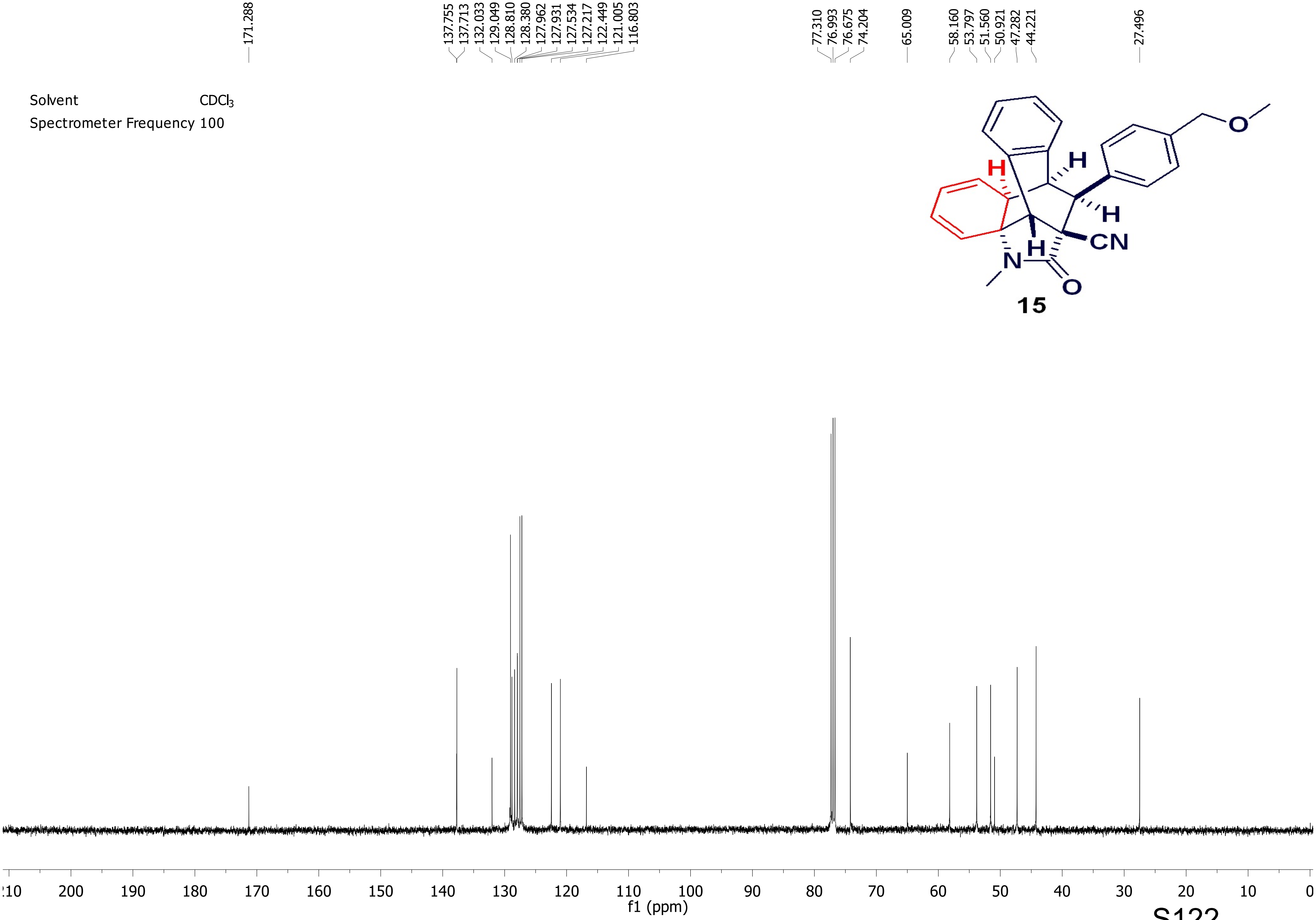
13


7.71 7.70 7.69 7.58 7.56 7.55 7.53 7.53 7.52 7.51 7.45 7.45 7.43 7.43 7.41 7.41 7.40 7.40 7.39 7.38 7.38 7.33 7.33 7.32 7.31 7.30 7.26 7.02 6.89 6.87 6.31 6.29 5.86 5.85 5.83 5.44 5.43 5.42 5.41 5.41 5.35 5.33 5.31 5.31 5.30 5.29 5.28 3.93 3.92 3.64 3.45 3.25 3.24 3.01 1.62 0.00
Solvent CDCl3
Spectrometer Frequency 400
7.71 7.70 7.69 7.58 7.56 7.55 7.53 7.53 7.52 7.51 7.45 7.45 7.43 7.43 7.41 7.41 7.40 7.40 7.39 7.38 7.38 7.33 7.33 7.32 7.31 7.30 7.29 7.26 7.02 6.89 6.87 6.31 6.29 5.87 5.86 5.85 5.83 5.43 5.35 5.33 5.31 5.31 5.30
1.02 3.01 3.04 1.00 0.99 0.99 1.05 1.00 0.98 2.09
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4
f1 (ppm)
H
H
H
H
N
CN
O
14
1.02 3.01 3.04 1.00 0.99 0.99 1.05 1.00 0.98 2.09 0.98 1.04 1.02 1.00 3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


Solvent CDCl$_3$
Spectrometer Frequency 100
171.32
137.93
135.87
132.76
132.69
132.16
128.81
128.49
128.43
128.07
128.02
127.97
127.62
127.57
127.40
127.36
126.58
126.07
125.92
122.48
121.08
116.86
77.31
76.99
76.68
65.06
53.86
51.95
50.94
47.46
44.28
27.57
137.93
135.87
132.76
132.69
132.16
128.81
128.49
128.43
128.07
128.02
127.97
127.62
127.57
127.40
127.36
126.58
126.07
125.92
122.48
121.08
116.86
137
135
133
131
129
127
125
123
121
119
117
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
H
H
H
H
CN
N
O

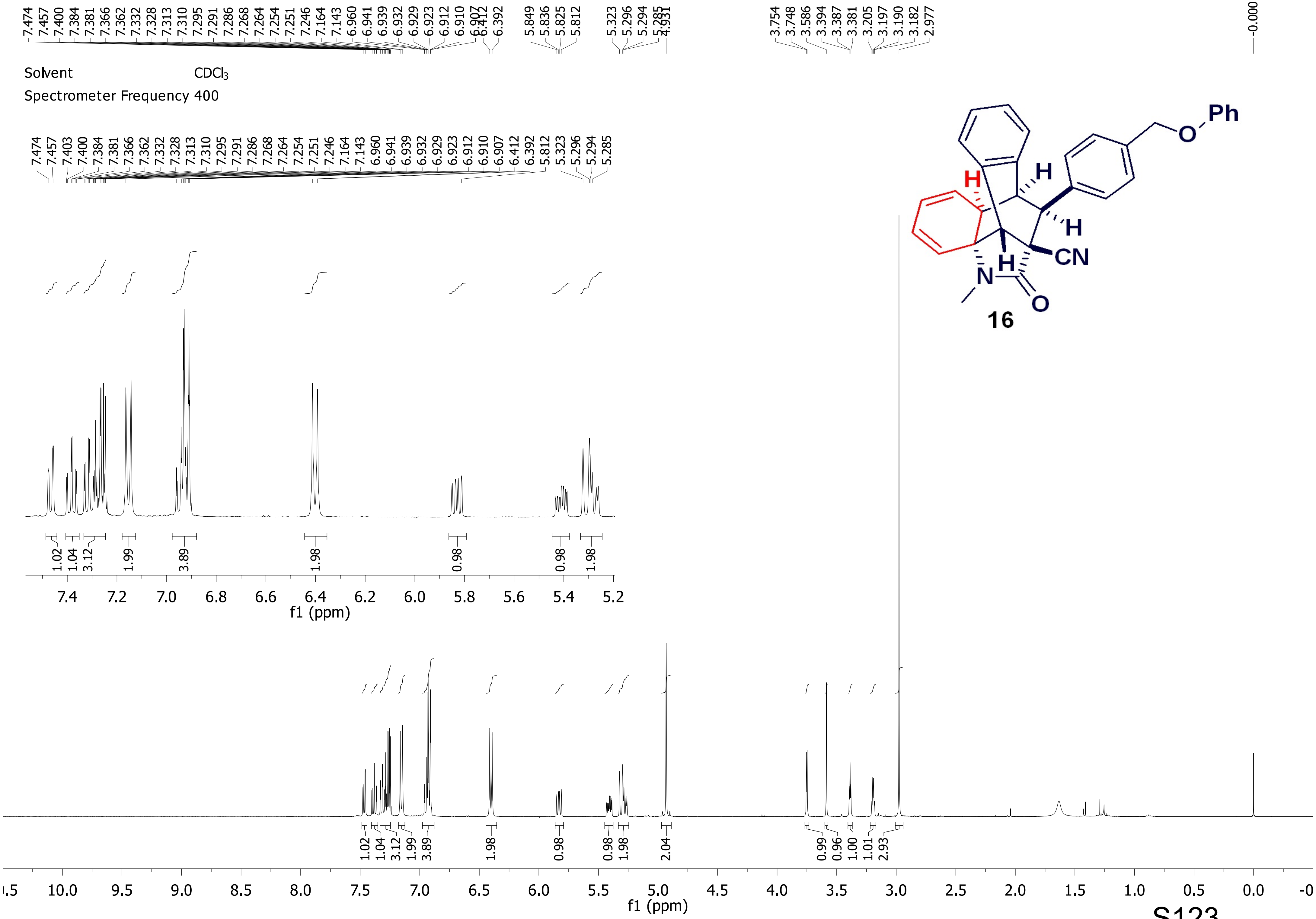
14


Solvent CDCl3
Spectrometer Frequency 400
7.454
7.379
7.376
7.299
7.296
7.261
7.059
7.038
6.907
6.889
6.370
6.350
5.850
5.837
5.826
5.812
5.408
5.400
5.393
5.388
5.323
5.299
5.295
5.284
5.268
5.260
4.333
3.738
3.731
3.581
3.378
3.371
3.365
3.325
3.200
3.192
3.185
3.178
2.985
2.976
2.043
1.618
1.258
0.000
1.02
1.12
1.09
1.98
1.01
1.95
1.00
1.02
2.10
1.97
1.02
1.00
1.03
2.94
1.01
3.01
f1 (ppm)
H
H
H
CN
H
N
O
O
15

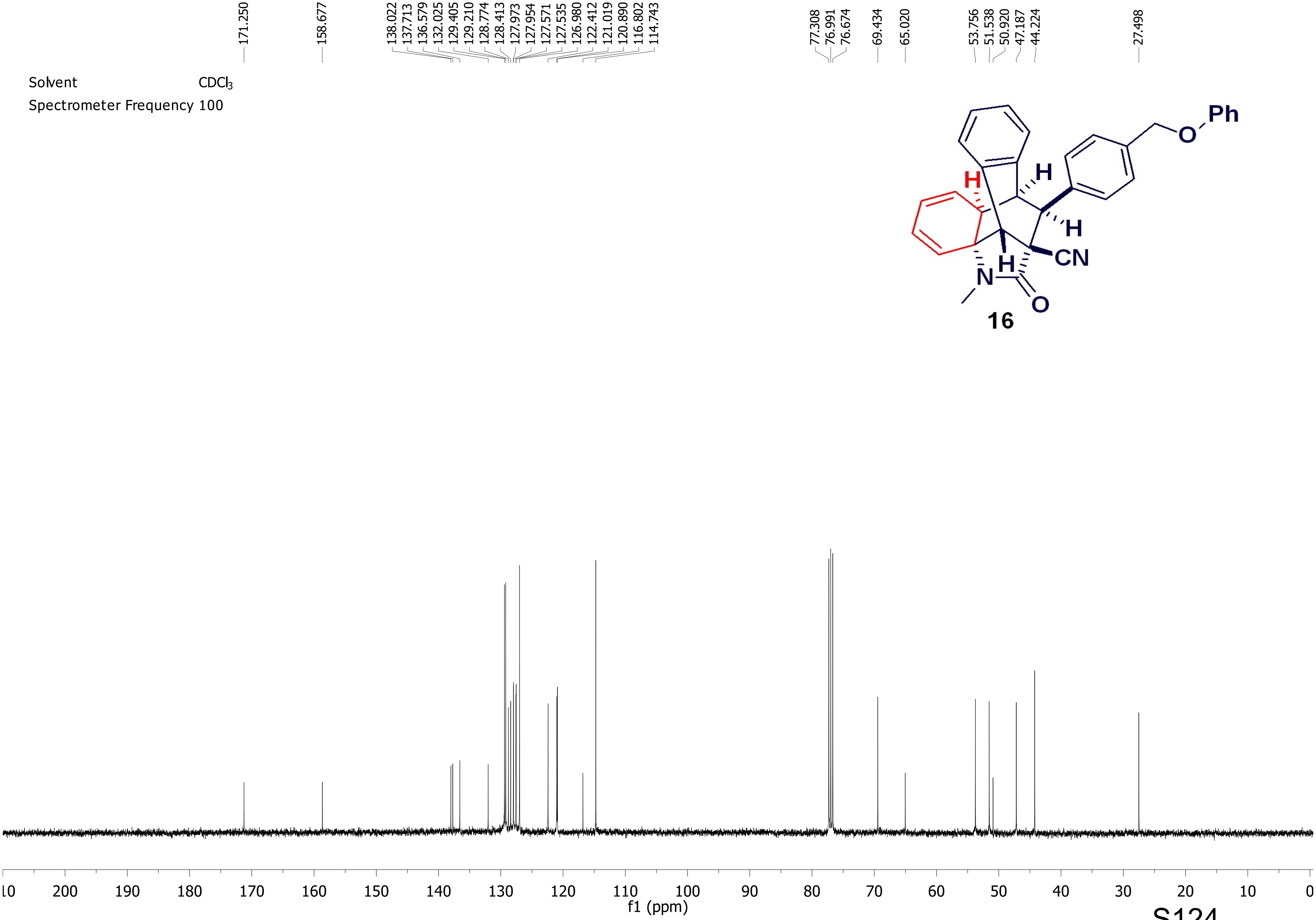


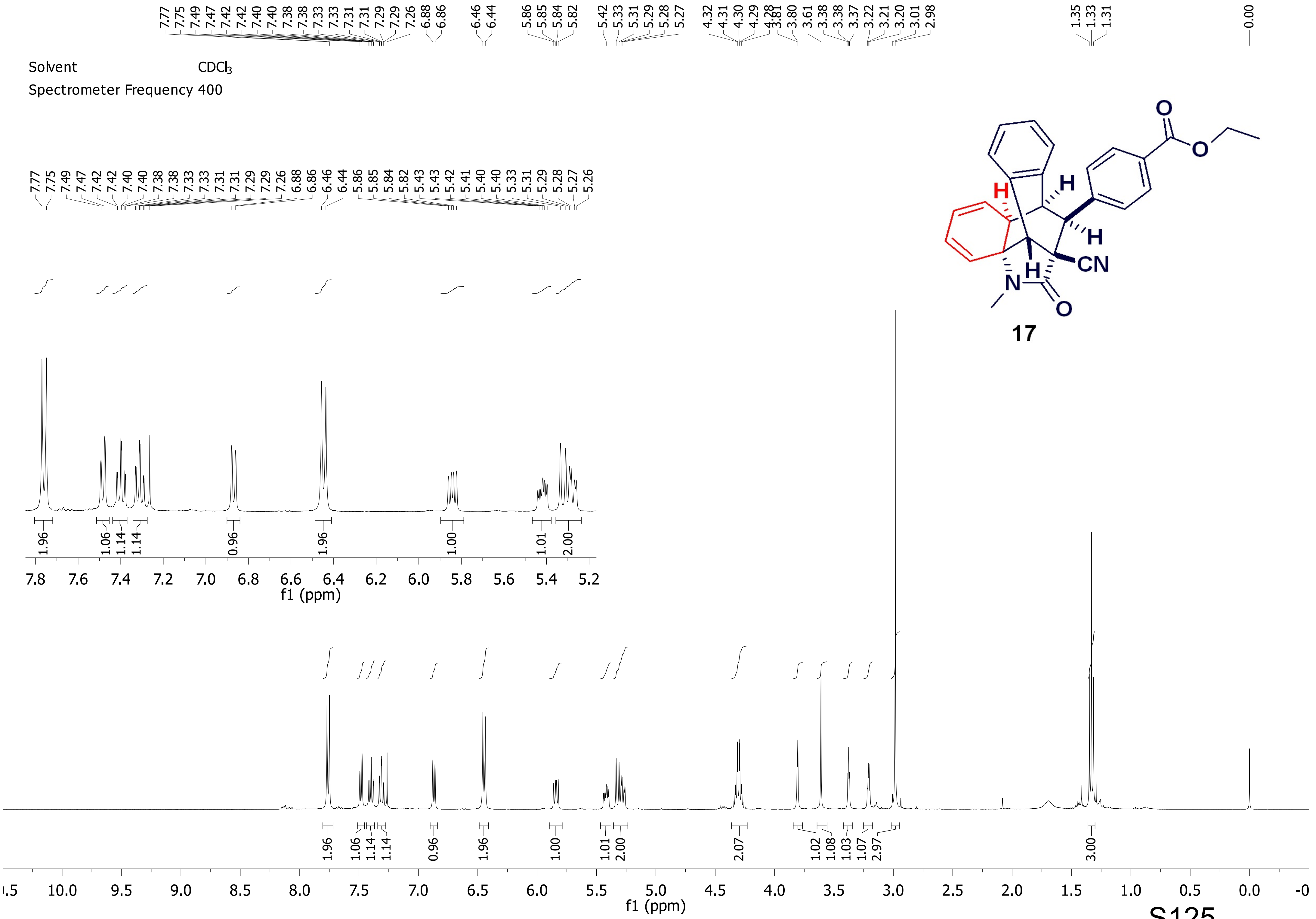
Solvent CDCl$_3$
Spectrometer Frequency 100

15


7.474
7.457
7.400
7.384
7.381
7.366
7.362
7.332
7.328
7.313
7.310
7.295
7.291
7.286
7.268
7.264
7.254
7.251
7.246
7.164
7.143
6.960
6.941
6.939
6.932
6.929
6.923
6.912
6.910
6.907
6.412
6.392
5.849
5.836
5.825
5.812
5.323
5.296
5.294
5.285
4.931
3.754
3.748
3.586
3.394
3.387
3.381
3.205
3.197
3.190
3.182
2.977
-0.000
Solvent CDCl3
Spectrometer Frequency 400
7.474
7.457
7.403
7.400
7.384
7.381
7.366
7.362
7.332
7.328
7.313
7.310
7.295
7.291
7.286
7.268
7.264
7.254
7.251
7.246
7.164
7.143
6.960
6.941
6.939
6.932
6.929
6.923
6.912
6.910
6.907
6.412
6.392
5.812
5.323
5.296
5.294
5.285
1.02
1.04
3.12
1.99
3.89
1.98
0.98
0.98
1.98
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
f1 (ppm)
Ph
O
H
H
H
CN
H
N
O
1.02
1.04
3.12
1.99
3.89
1.98
0.98
0.98
1.98
2.04
0.99
0.96
1.00
1.01
2.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

16

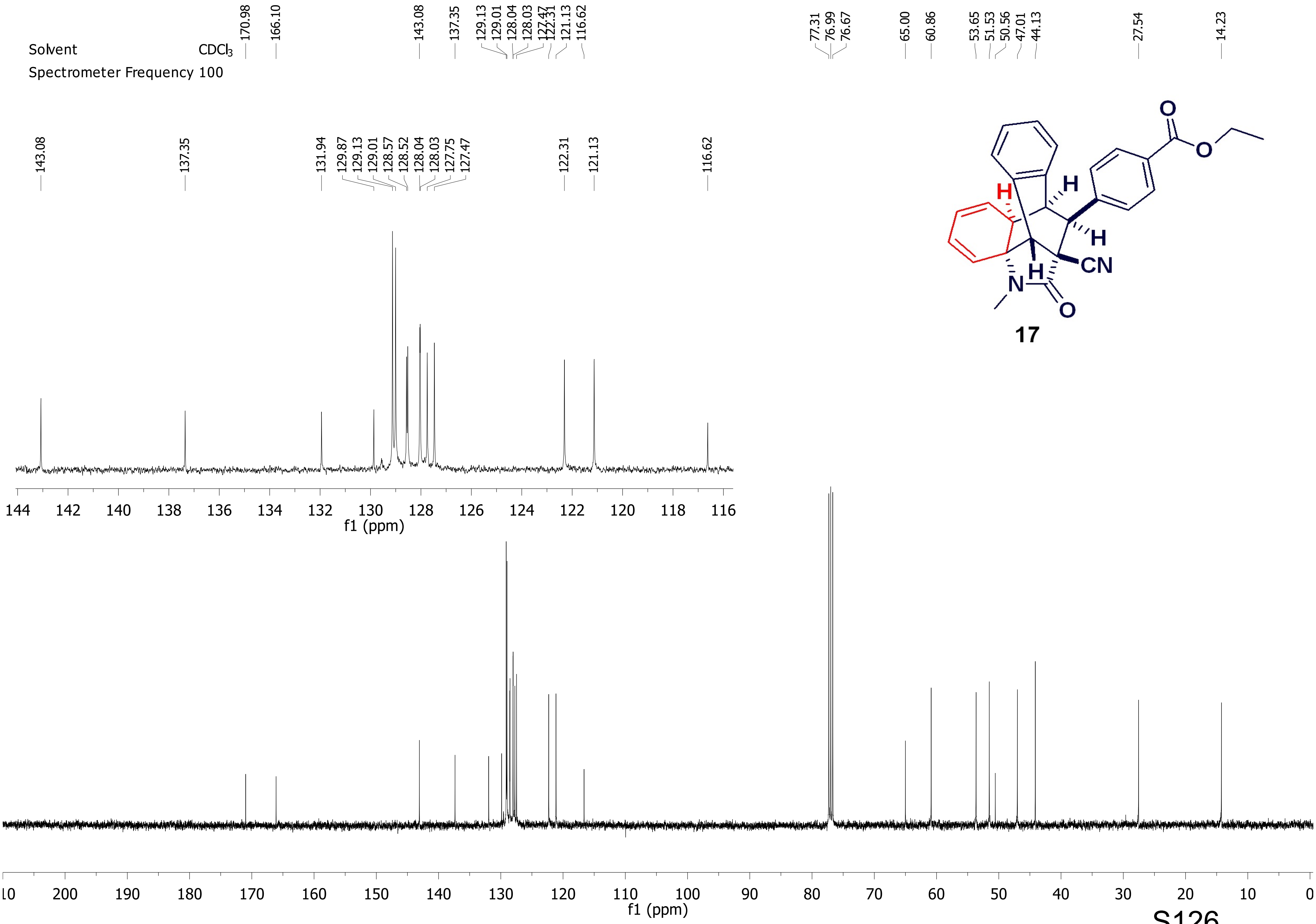

171.250
158.677
138.022
137.713
136.579
132.025
129.405
129.210
128.774
128.413
127.973
127.954
127.571
127.535
126.980
122.412
121.019
120.890
116.802
114.743
77.308
76.991
76.674
69.434
65.020
53.756
51.538
50.920
47.187
44.224
27.498
Solvent CDCl$_3$
Spectrometer Frequency 100
H
H
H
H
N
CN
O
O
Ph
16
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



Solvent CDCl$_3$

Spectrometer Frequency 400

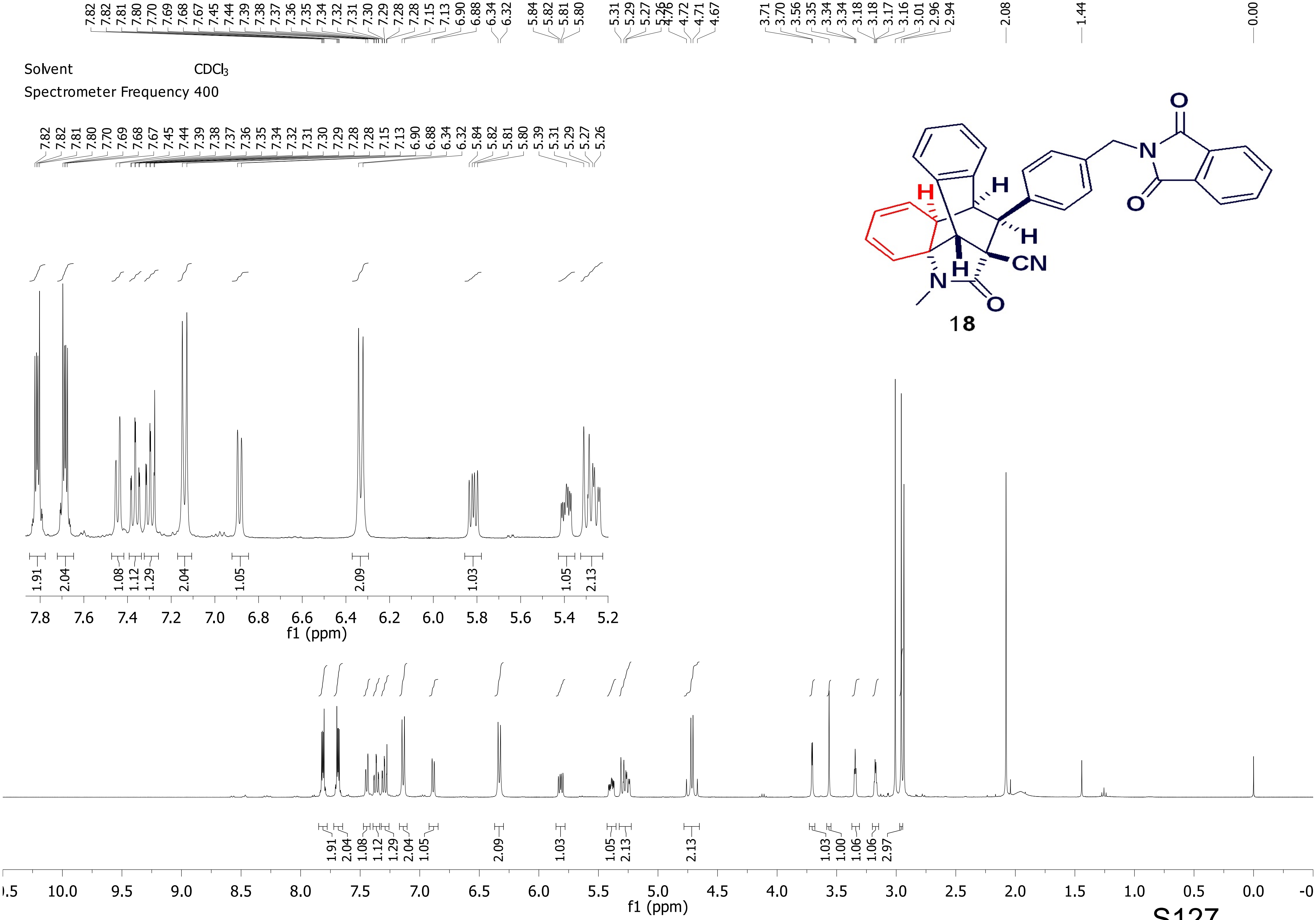
17

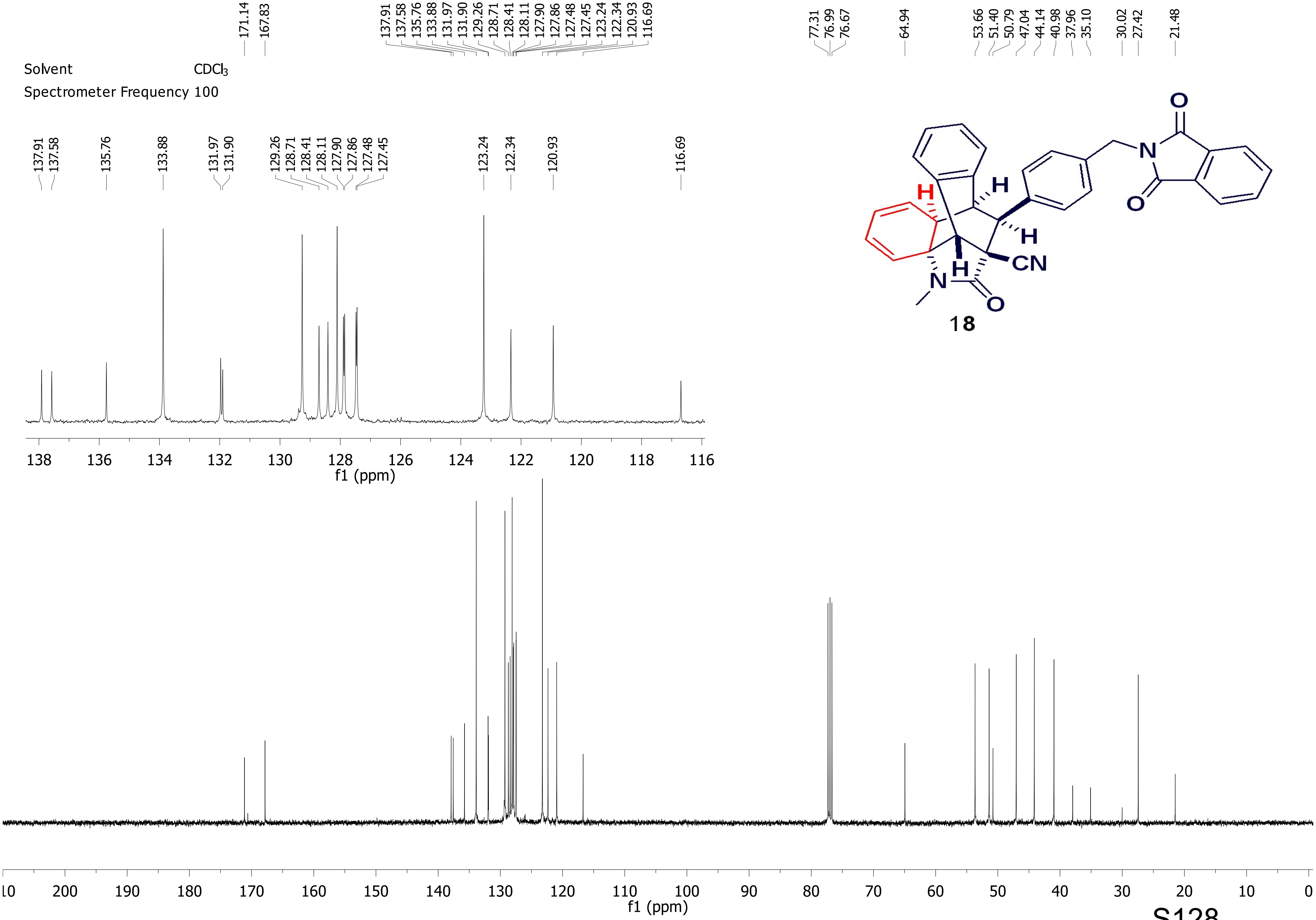

Solvent CDCl$_3$
Spectrometer Frequency 100
170.98
166.10
143.08
137.35
129.13
129.01
128.04
128.03
127.47
122.31
121.13
116.62
77.31
76.99
76.67
65.00
60.86
53.65
51.53
50.56
47.01
44.13
27.54
14.23
143.08
137.35
131.94
129.87
129.13
129.01
128.57
128.52
128.04
128.03
127.75
127.47
122.31
121.13
116.62
144 142 140 138 136 134 132 130 128 126 124 122 120 118 116
f1 (ppm)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
O
H
H
H
H
CN
N
O

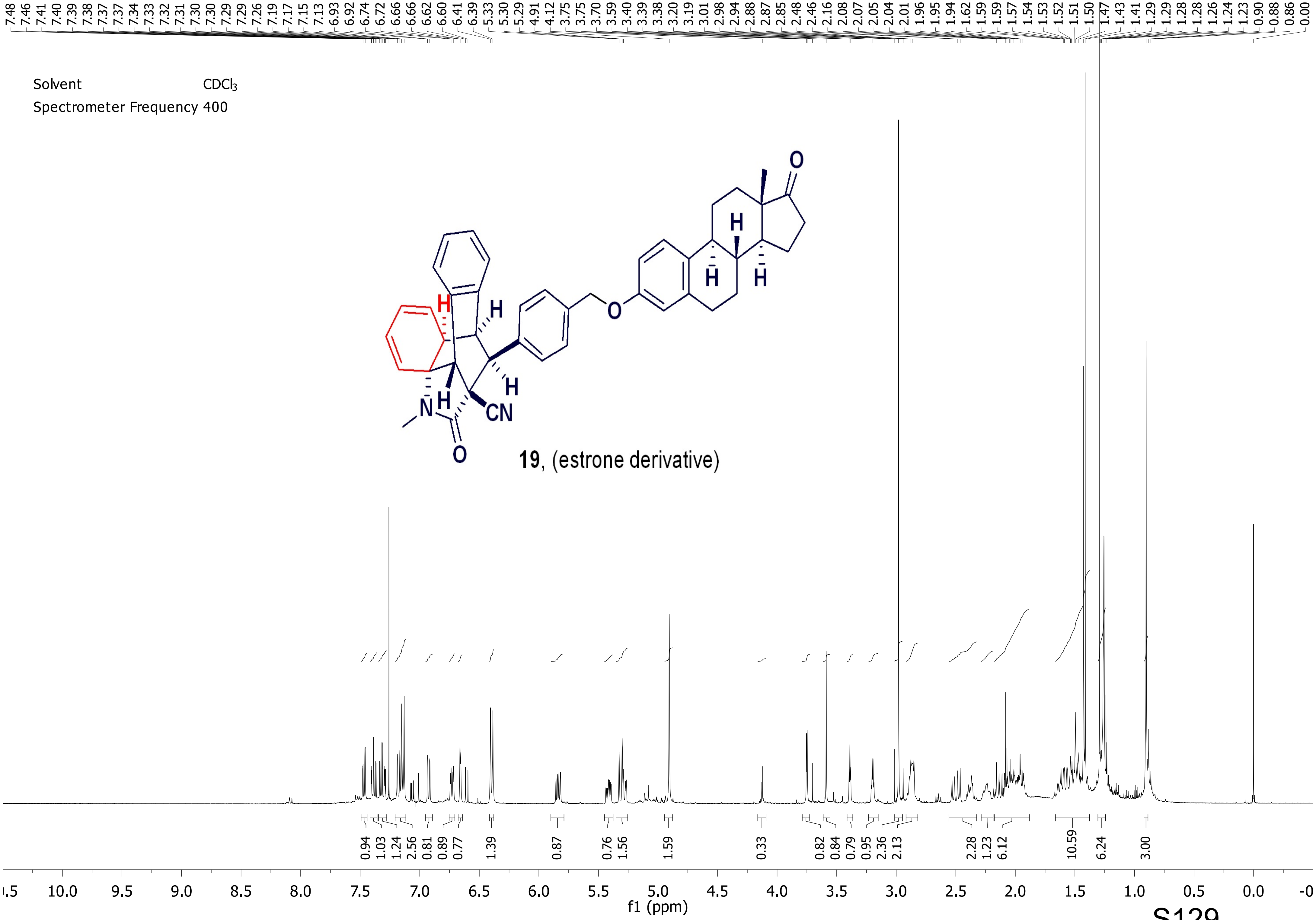
17

Solvent CDCl$_3$

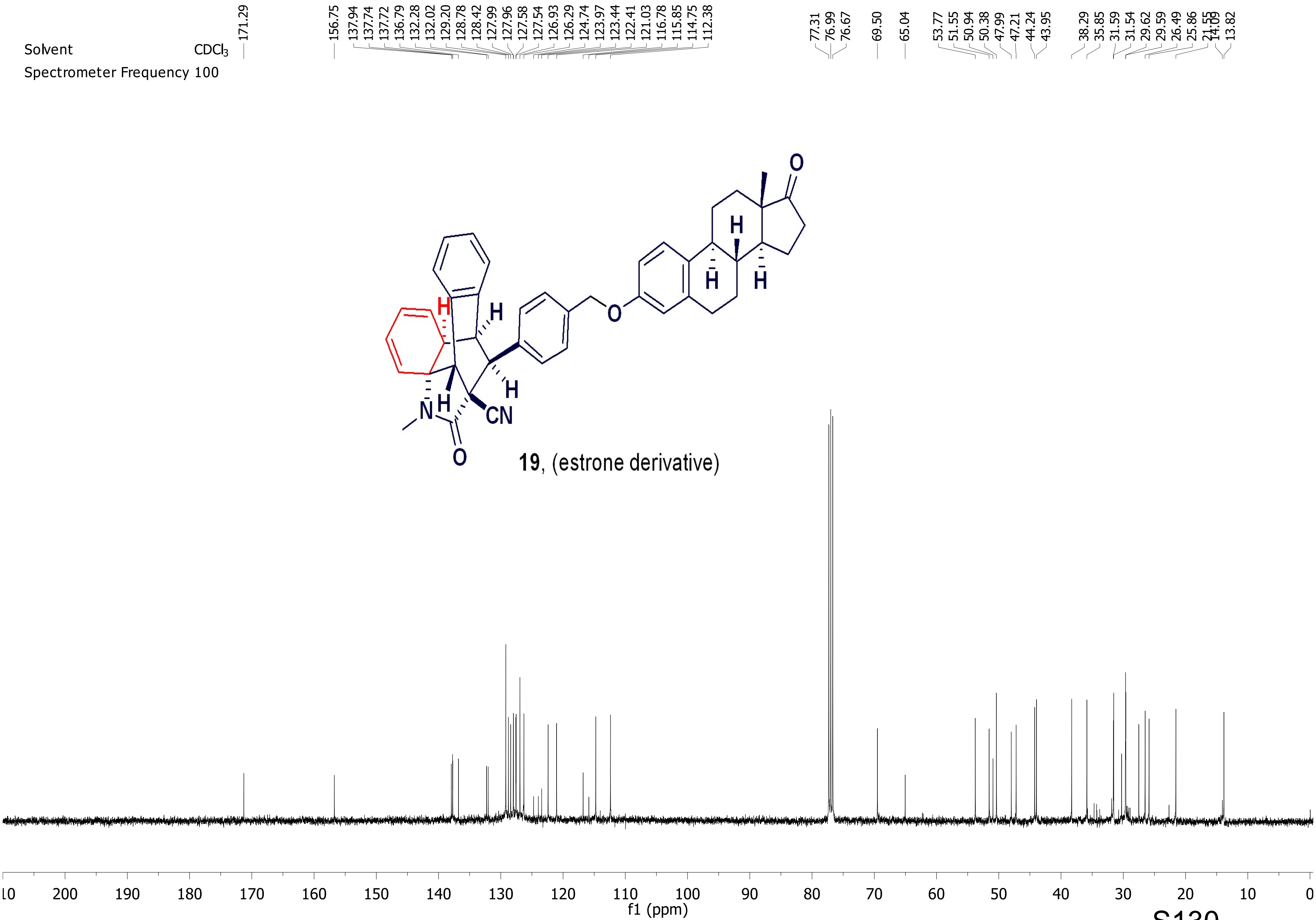
Spectrometer Frequency 400



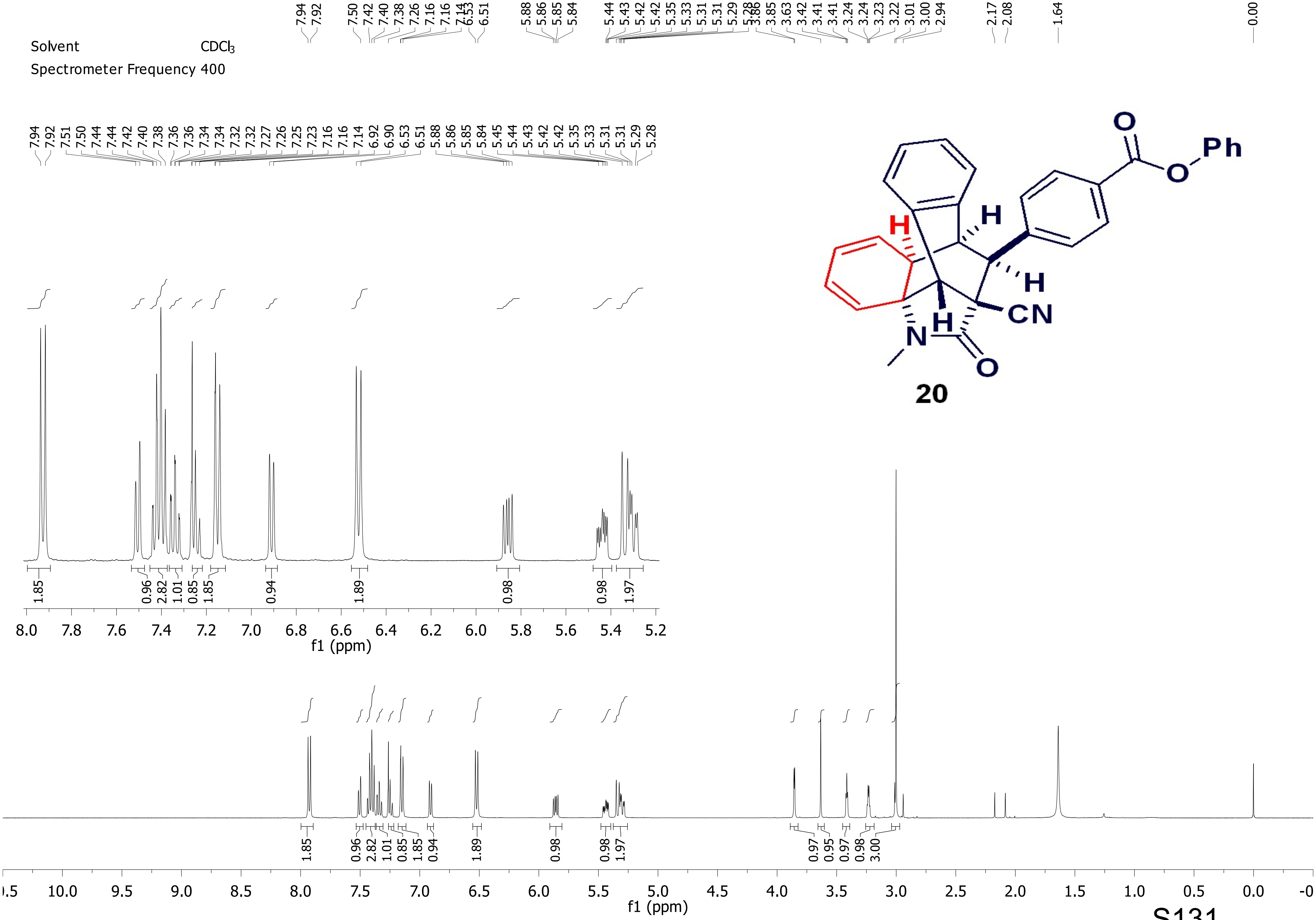

171.14
167.83
137.91
137.58
135.76
133.88
131.97
131.90
129.26
128.71
128.41
128.11
127.90
127.86
127.48
127.45
123.24
122.34
120.93
116.69
77.31
76.99
76.67
64.94
53.66
51.40
50.79
47.04
44.14
40.98
37.96
35.10
30.02
27.42
21.48
Solvent CDCl3
Spectrometer Frequency 100
138
136
134
132
130
128
126
124
122
120
118
116
f1 (ppm)
H
H
H
H
CN
N
N
O
O
O
18
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

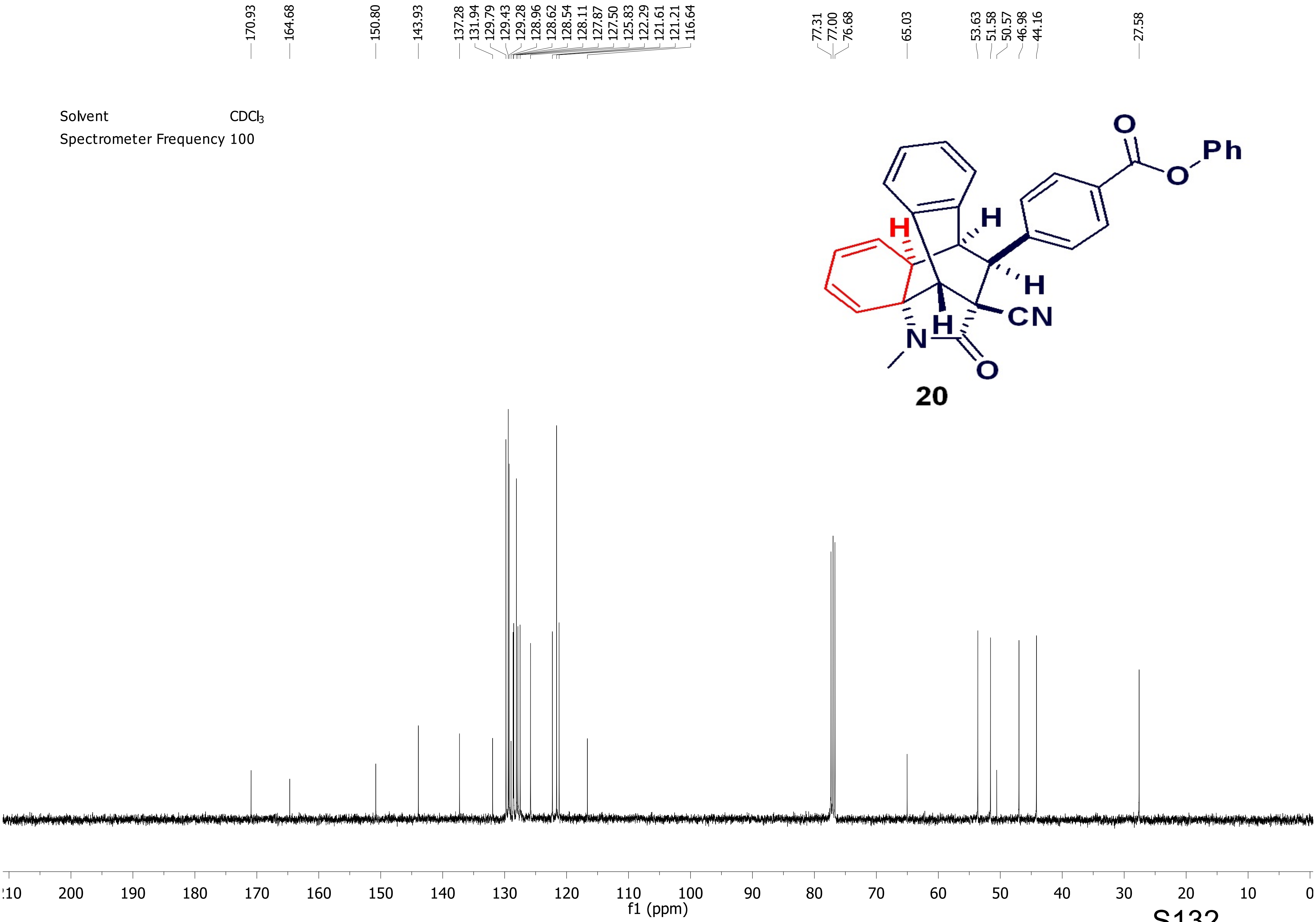


19, (estrone derivative)

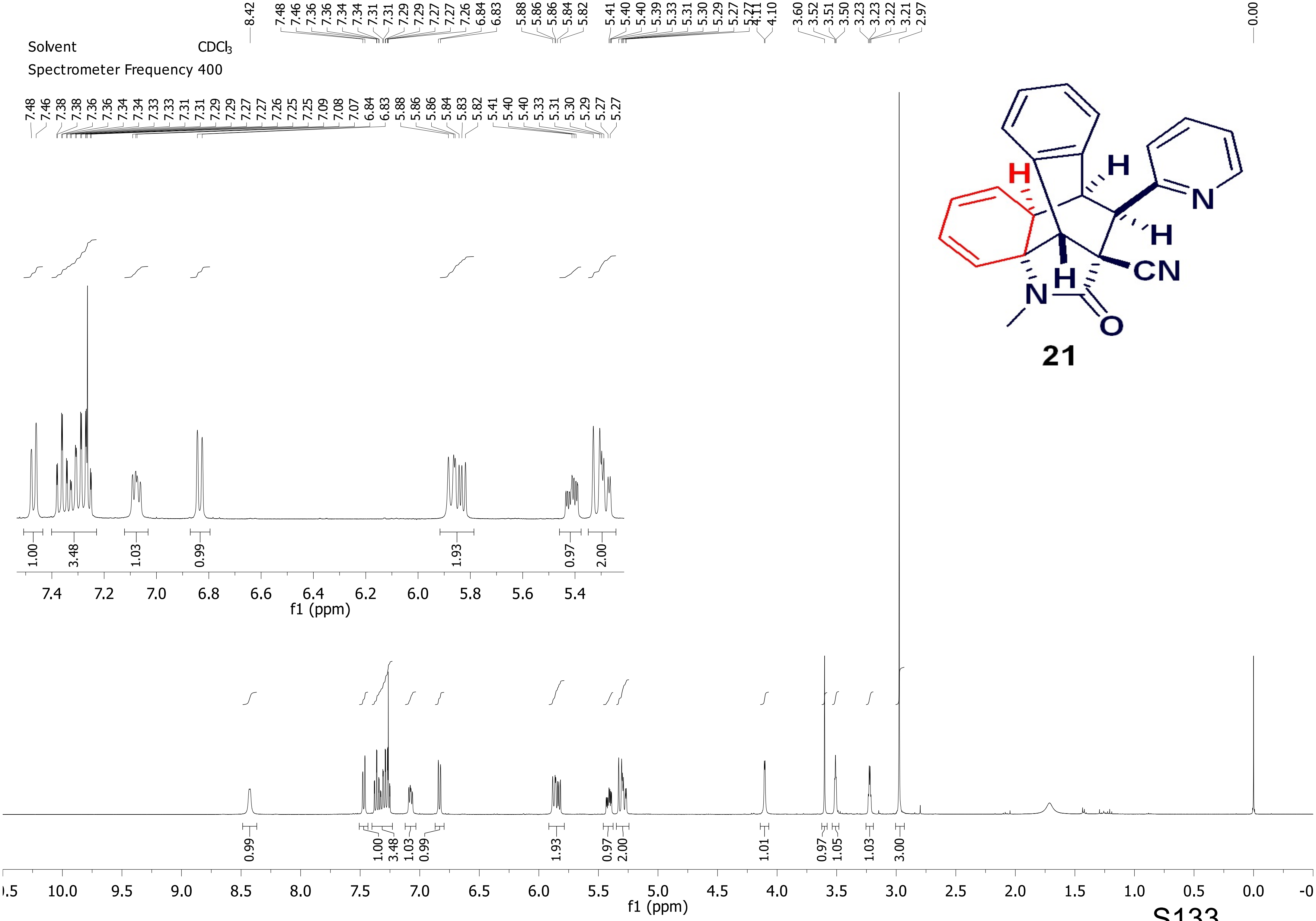


19, (estrone derivative)

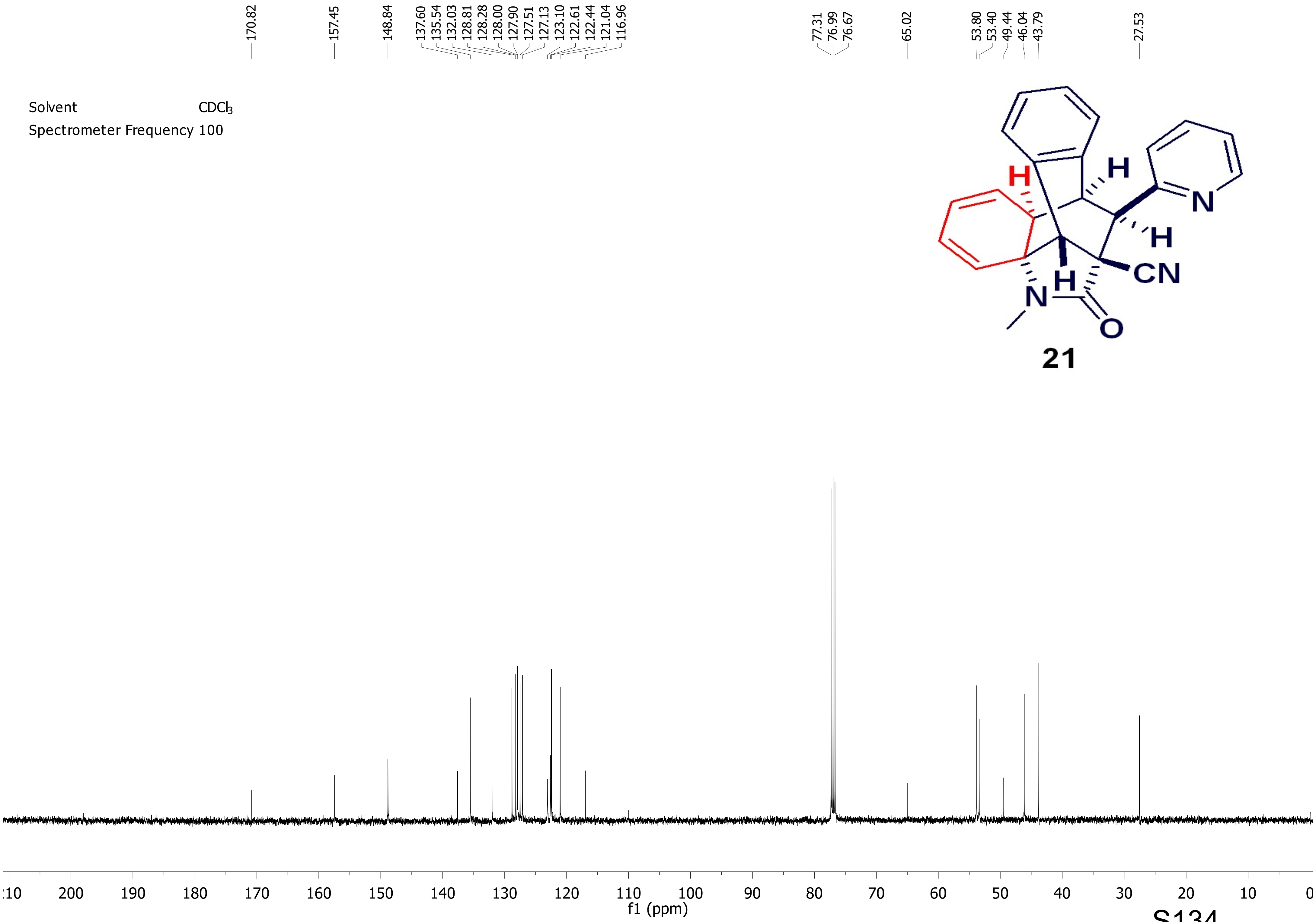

Solvent CDCl3
Spectrometer Frequency 400
7.94 7.92 7.50 7.42 7.40 7.38 7.26 7.16 7.16 7.14 6.53 6.51 5.88 5.86 5.85 5.84 5.44 5.43 5.42 5.35 5.33 5.31 5.31 5.29 5.28 3.86 3.85 3.63 3.42 3.41 3.41 3.24 3.24 3.23 3.22 3.01 3.00 2.94 2.17 2.08 1.64 0.00
7.94 7.92 7.51 7.50 7.44 7.44 7.42 7.40 7.38 7.36 7.36 7.34 7.34 7.32 7.32 7.27 7.26 7.25 7.23 7.16 7.16 7.14 6.92 6.90 6.53 6.51 5.88 5.86 5.85 5.84 5.45 5.44 5.43 5.42 5.42 5.35 5.33 5.31 5.31 5.29 5.28
O
Ph
O
H
H
H
CN
H
N
O
20
1.85 0.96 2.82 1.01 0.85 1.85 0.94 1.89 0.98 0.98 1.97
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2
f1 (ppm)
1.85 0.96 2.82 1.01 0.85 1.85 0.94 1.89 0.98 0.98 1.97 0.97 0.95 0.97 0.98 3.00
.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


170.93
164.68
150.80
143.93
137.28
131.94
129.79
129.43
129.28
128.96
128.62
128.54
128.11
127.87
127.50
125.83
122.29
121.61
121.21
116.64
77.31
77.00
76.68
65.03
53.63
51.58
50.57
46.98
44.16
27.58
Solvent CDCl$_3$
Spectrometer Frequency 100
O
O
Ph
H
H
H
CN
H
N
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

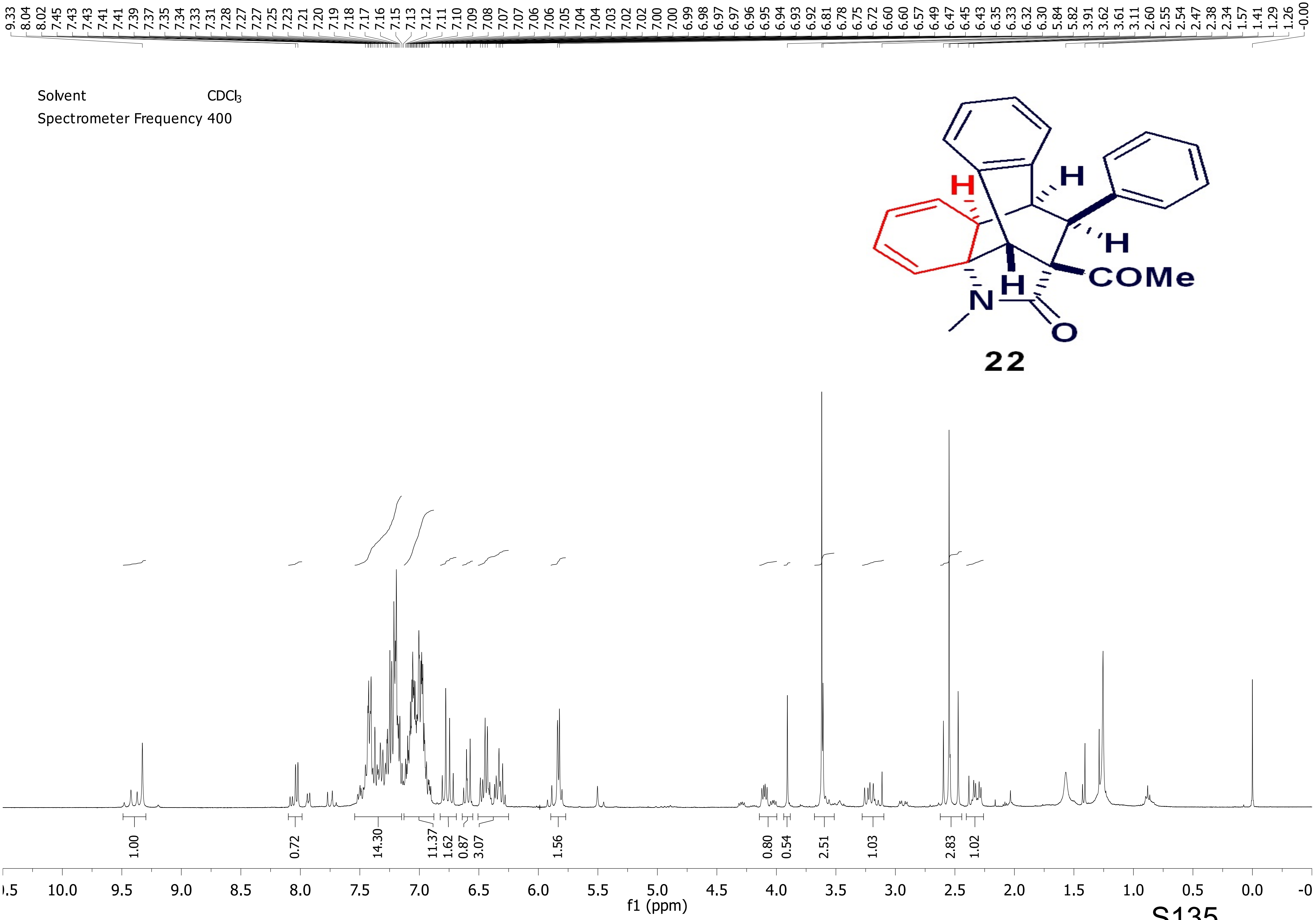
20

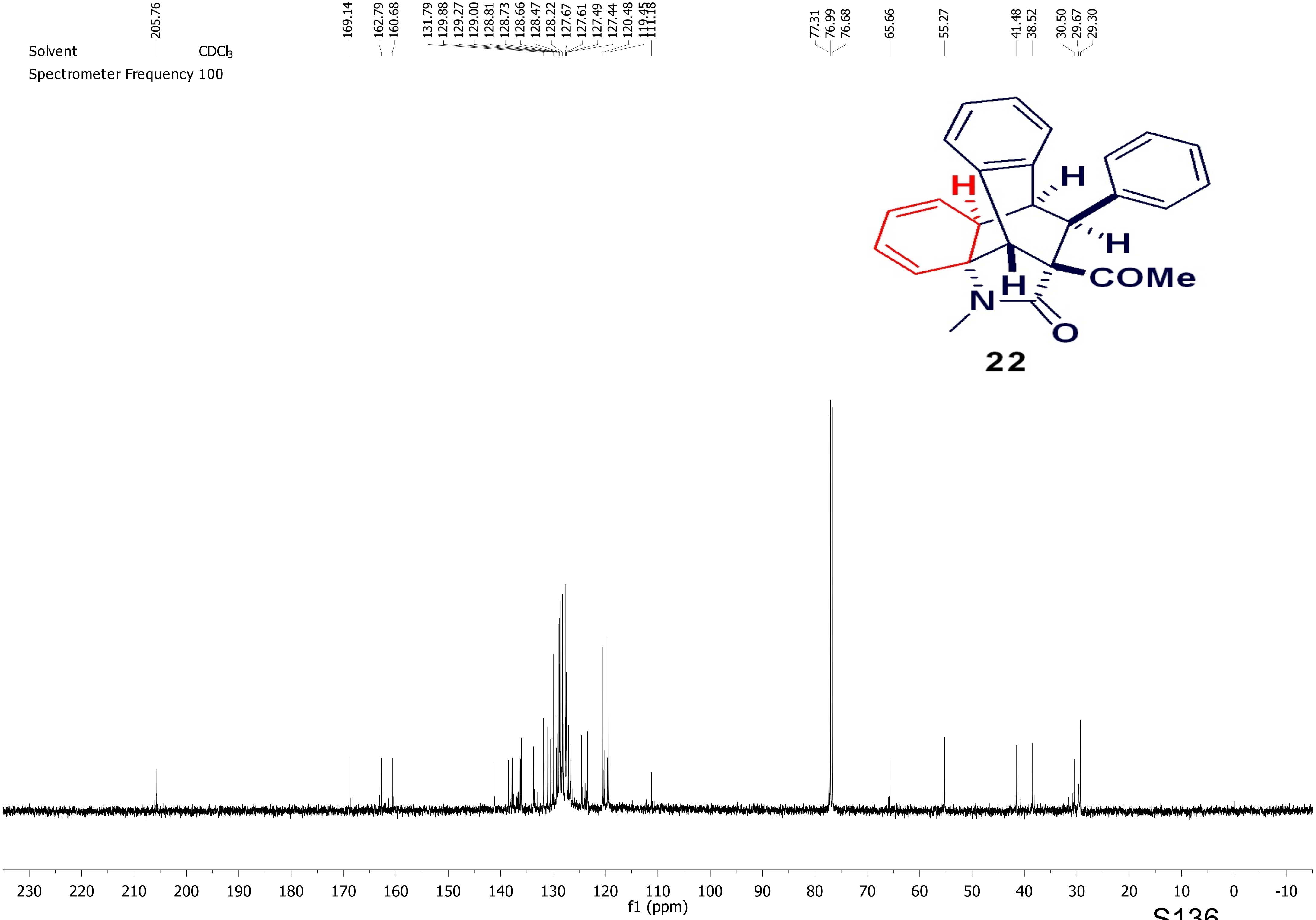

Solvent CDCl3
Spectrometer Frequency 400
8.42
7.48 7.46 7.36 7.36 7.34 7.34 7.31 7.31 7.29 7.29 7.27 7.27 7.26 6.84 6.83
5.88 5.86 5.86 5.84 5.82
5.41 5.40 5.40 5.39 5.33 5.31 5.30 5.29 5.27 5.27 4.11 4.10
3.60 3.52 3.51 3.50 3.23 3.23 3.22 3.21 2.97
0.00
7.48 7.46 7.38 7.38 7.36 7.36 7.34 7.34 7.33 7.33 7.31 7.31 7.29 7.29 7.27 7.27 7.26 7.25 7.25 7.09 7.08 7.07 6.84 6.83 5.88 5.86 5.86 5.84 5.83 5.82 5.41 5.40 5.40 5.33 5.31 5.30 5.29 5.27 5.27
1.00
3.48
1.03
0.99
1.93
0.97
2.00
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4
f1 (ppm)
H
H
N
H
CN
H
N
O
0.99
1.00
3.48
1.03
0.99
1.93
0.97
2.00
1.01
0.97
1.05
1.03
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

21

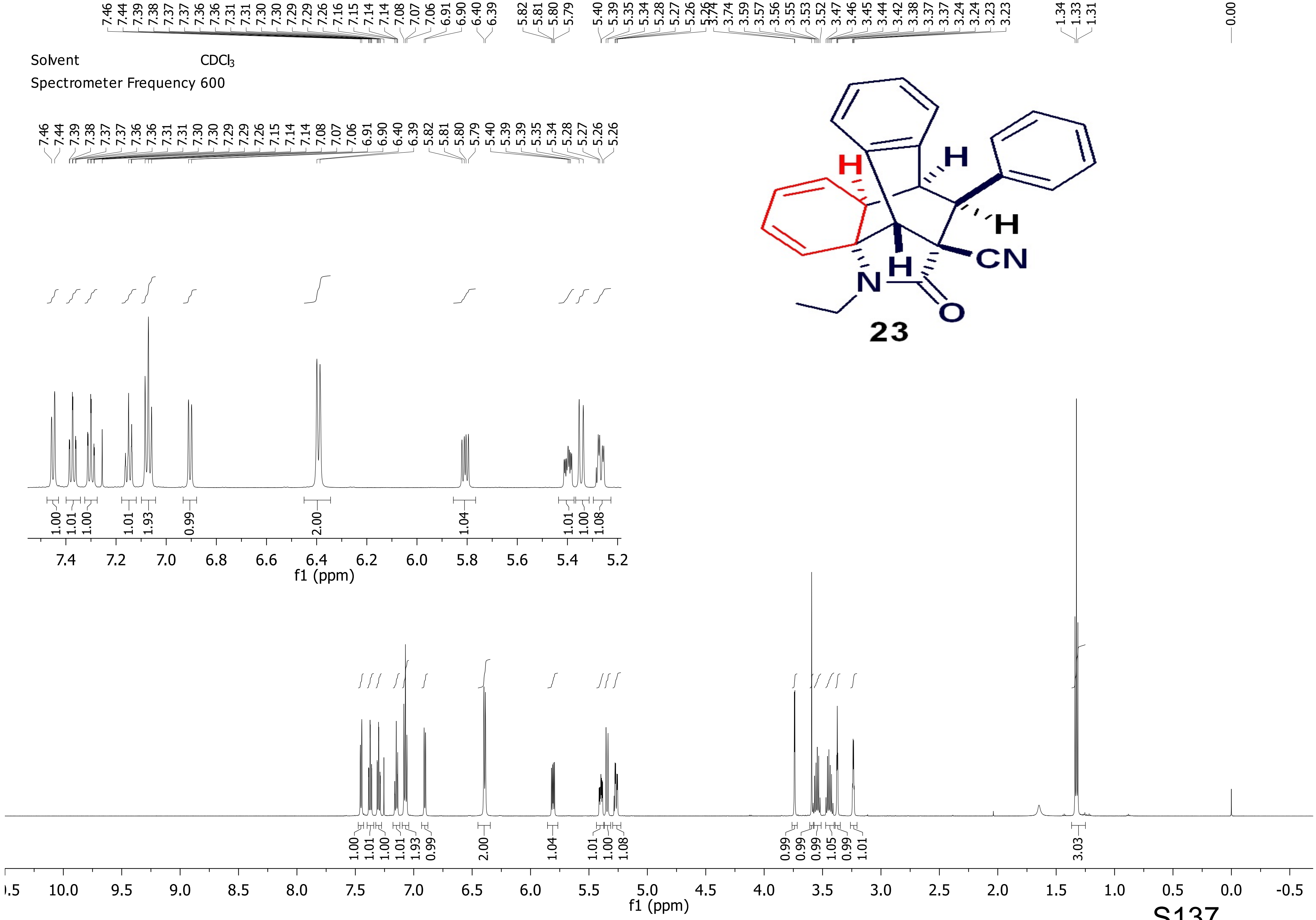

170.82
157.45
148.84
137.60
135.54
132.03
128.81
128.28
128.00
127.90
127.51
127.13
123.10
122.61
122.44
121.04
116.96
77.31
76.99
76.67
65.02
53.80
53.40
49.44
46.04
43.79
27.53
Solvent CDCl3
Spectrometer Frequency 100
H
H
N
H
CN
N
H
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

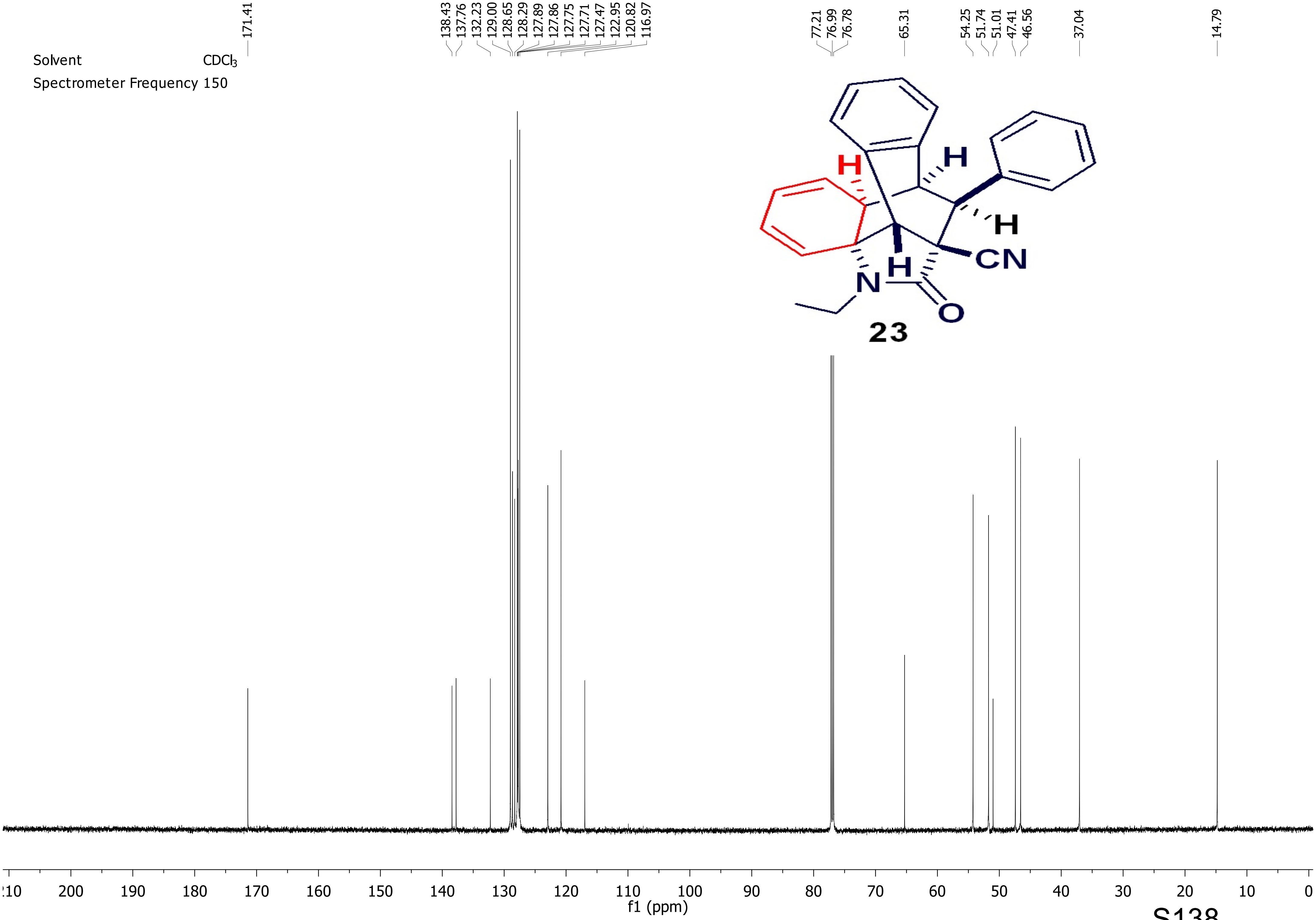
21


9.33
8.04
8.02
7.45
7.43
7.43
7.41
7.41
7.39
7.37
7.35
7.34
7.33
7.31
7.28
7.27
7.27
7.25
7.23
7.21
7.20
7.19
7.18
7.17
7.16
7.15
7.13
7.12
7.11
7.10
7.09
7.08
7.07
7.07
7.06
7.06
7.05
7.04
7.04
7.03
7.02
7.02
7.00
7.00
6.99
6.98
6.97
6.97
6.96
6.95
6.94
6.93
6.92
6.81
6.78
6.75
6.72
6.60
6.60
6.57
6.49
6.47
6.45
6.43
6.35
6.33
6.32
6.30
5.84
5.82
3.91
3.62
3.61
3.11
2.60
2.55
2.54
2.47
2.38
2.34
1.57
1.41
1.29
1.26
-0.00
Solvent CDCl3
Spectrometer Frequency 400
H
H
H
COMe
H
N
O
22
1.00
0.72
14.30
11.37
1.62
0.87
3.07
1.56
0.80
0.54
2.51
1.03
2.83
1.02
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

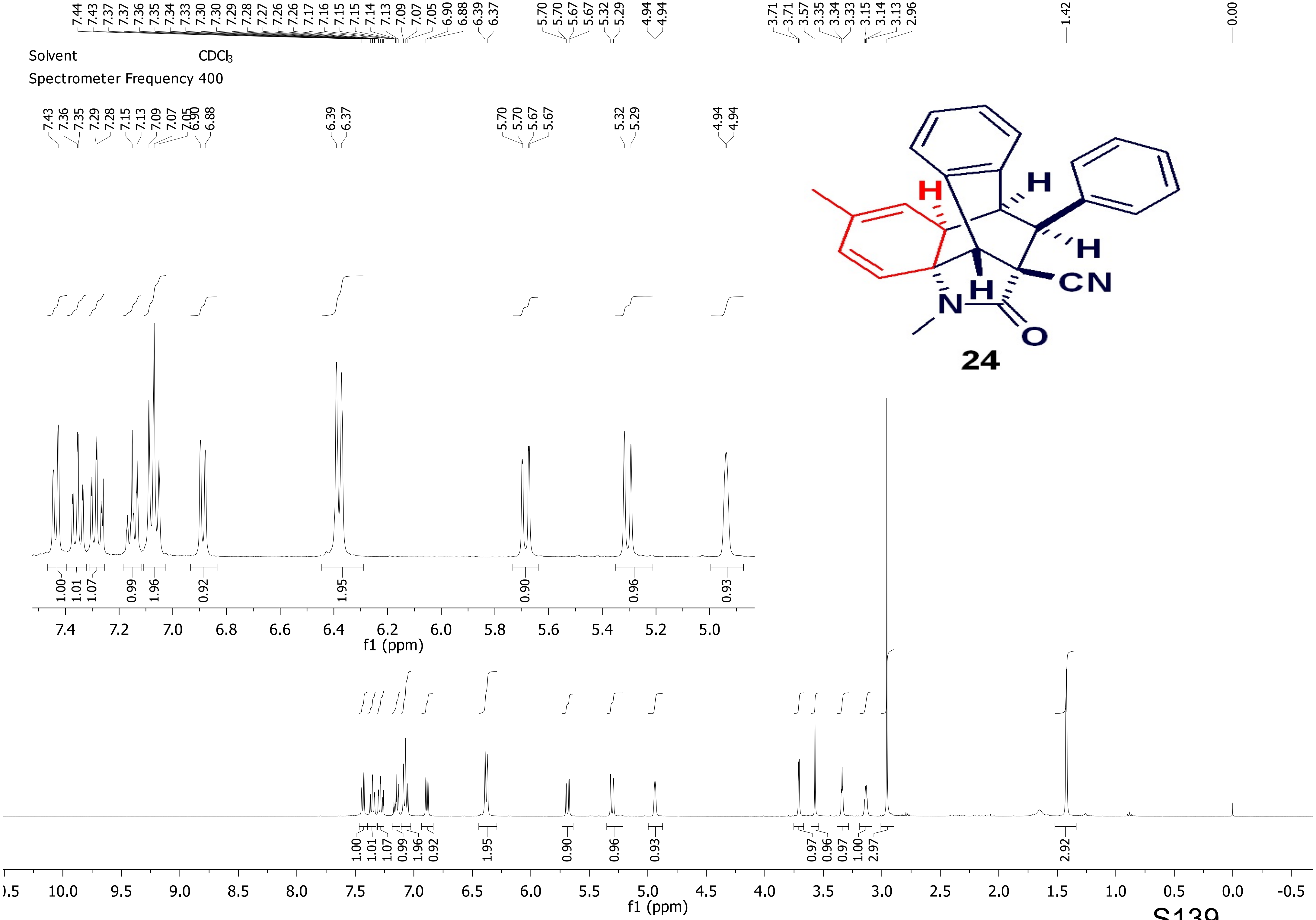

205.76
169.14
162.79
160.68
131.79
129.88
129.27
129.00
128.81
128.73
128.66
128.47
128.22
127.67
127.61
127.49
127.44
120.48
119.45
111.18
77.31
76.99
76.68
65.66
55.27
41.48
38.52
30.50
29.67
29.30
Solvent CDCl3
Spectrometer Frequency 100
H
H
H
H
N
COMe
O
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

22

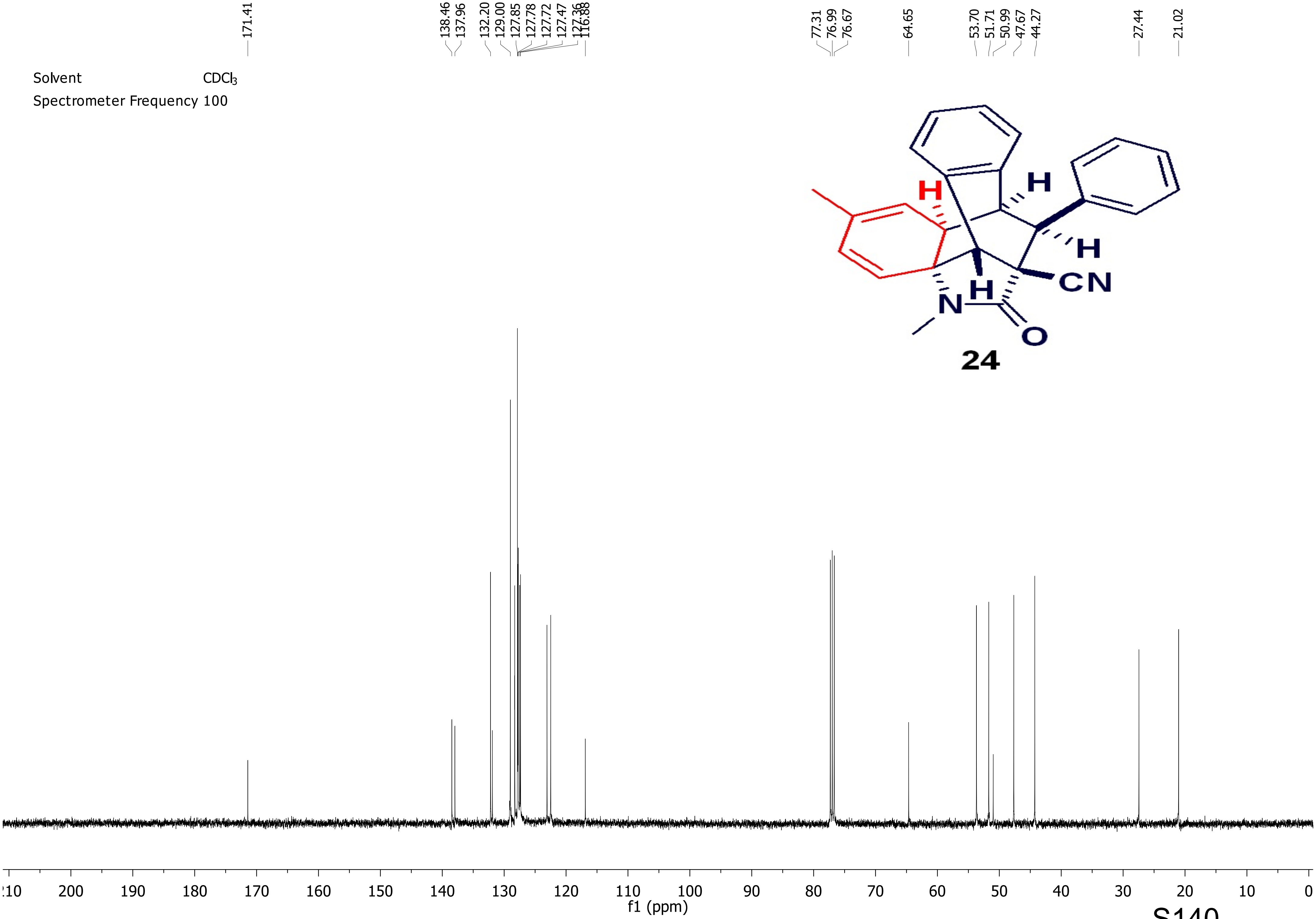

7.46 7.44 7.39 7.38 7.37 7.37 7.36 7.36 7.31 7.31 7.30 7.30 7.29 7.29 7.26 7.16 7.15 7.14 7.14 7.08 7.07 7.06 6.91 6.90 6.40 6.39 5.82 5.81 5.80 5.79 5.40 5.39 5.35 5.34 5.28 5.27 5.26 5.26 3.74 3.74 3.59 3.57 3.56 3.55 3.53 3.52 3.47 3.46 3.45 3.44 3.42 3.38 3.37 3.37 3.24 3.24 3.23 3.23 1.34 1.33 1.31 0.00
Solvent CDCl3
Spectrometer Frequency 600
7.46 7.44 7.39 7.38 7.37 7.37 7.36 7.36 7.31 7.31 7.30 7.30 7.29 7.29 7.26 7.15 7.14 7.14 7.08 7.07 7.06 6.91 6.90 6.40 6.39 5.82 5.81 5.80 5.79 5.40 5.39 5.35 5.34 5.28 5.27 5.26 5.26
H
H
H
H
N
CN
O
23
1.00 1.01 1.00 1.01 1.93 0.99 2.00 1.04 1.01 1.00 1.08
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2
f1 (ppm)
1.00 1.01 1.00 1.01 1.93 0.99 2.00 1.04 1.01 1.00 1.08 0.99 0.99 0.99 1.05 0.99 1.01 3.03
.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

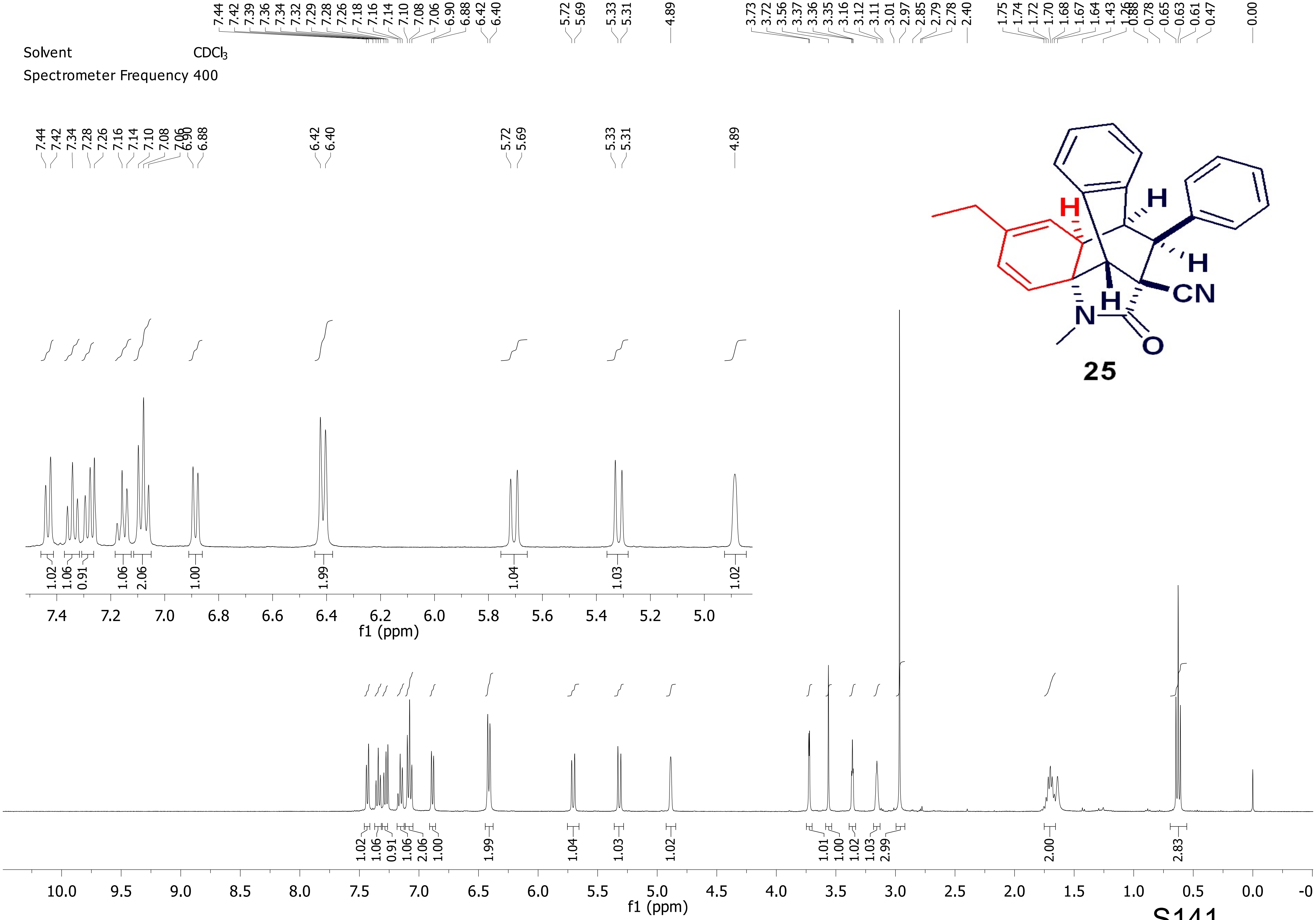

Solvent CDCl3
Spectrometer Frequency 150
171.41
138.43
137.76
132.23
129.00
128.65
128.29
127.89
127.86
127.75
127.71
127.47
122.95
120.82
116.97
77.21
76.99
76.78
65.31
54.25
51.74
51.01
47.41
46.56
37.04
14.79
H
H
H
H
N
CN
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

23

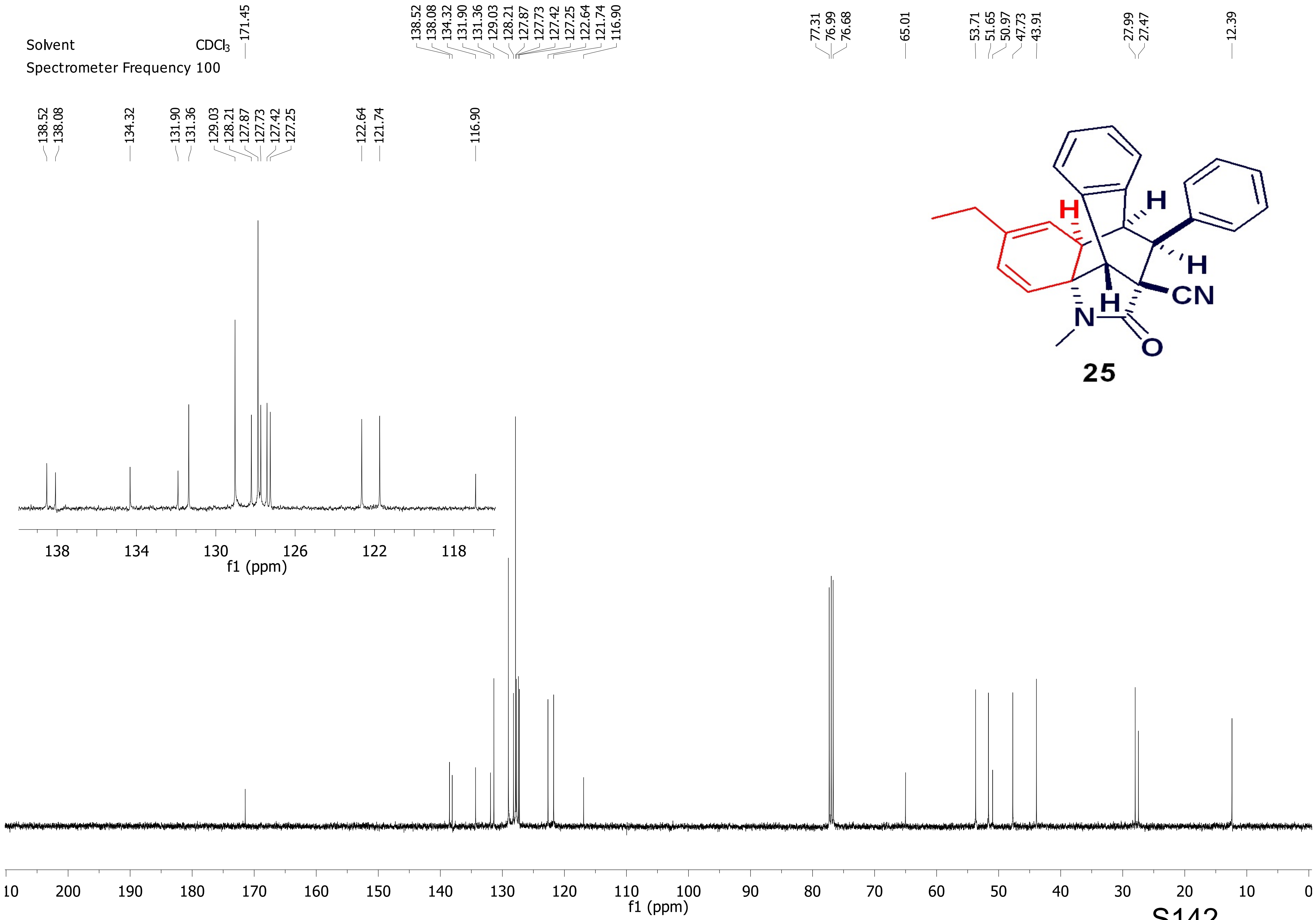

7.44 7.43 7.37 7.37 7.36 7.35 7.34 7.33 7.30 7.30 7.29 7.28 7.27 7.26 7.26 7.17 7.16 7.15 7.15 7.14 7.13 7.09 7.07 7.05 6.90 6.88 6.39 6.37
5.70 5.70 5.67 5.67 5.32 5.29 4.94 4.94
3.71 3.71 3.57 3.35 3.34 3.33 3.15 3.14 3.13 2.96
1.42
0.00
Solvent CDCl3
Spectrometer Frequency 400
7.43 7.36 7.35 7.29 7.28 7.15 7.13 7.09 7.07 7.05 6.90 6.88
6.39 6.37
5.70 5.70 5.67 5.67
5.32 5.29
4.94 4.94
1.00 1.01 1.07 0.99 1.96 0.92 1.95 0.90 0.96 0.93
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0
f1 (ppm)
H
H
H
CN
H
N
O
1.00 1.01 1.07 0.99 1.96 0.92 1.95 0.90 0.96 0.93 0.97 0.96 0.97 1.00 2.97 2.92
.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

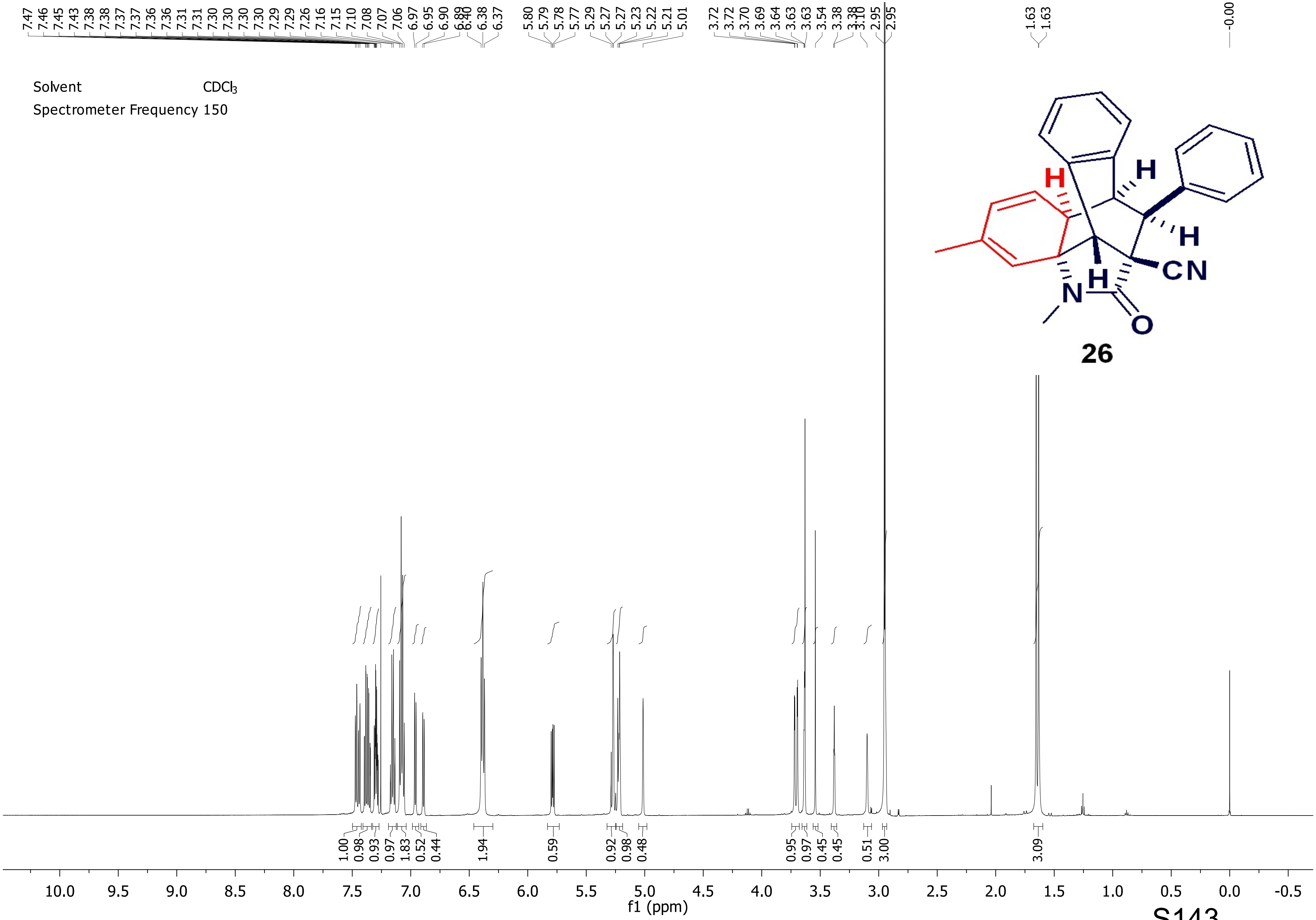
24

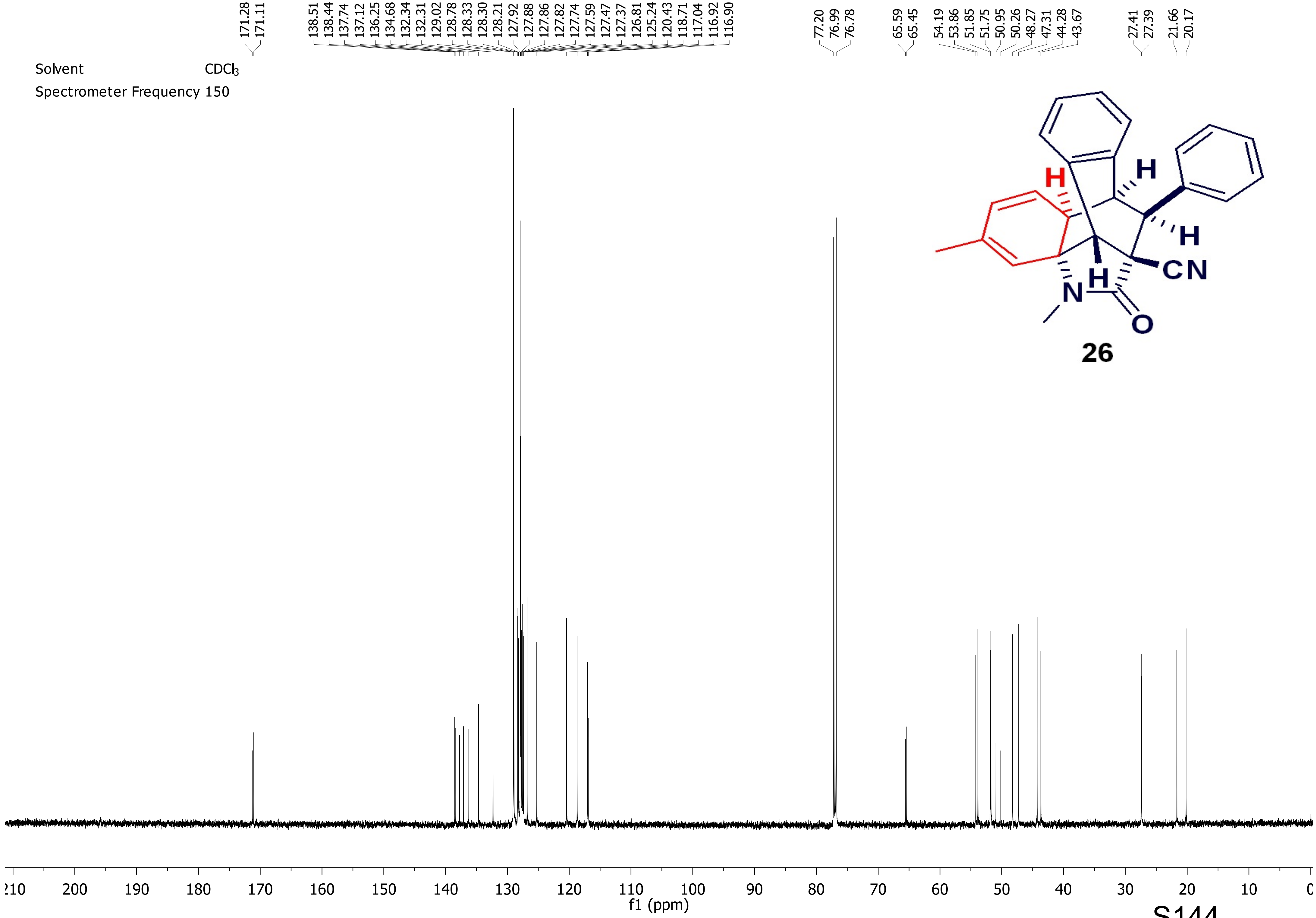

171.41
138.46
137.96
132.20
129.00
127.85
127.78
127.72
127.47
127.36
116.88
77.31
76.99
76.67
64.65
53.70
51.71
50.99
47.67
44.27
27.44
21.02
Solvent CDCl$_3$
Spectrometer Frequency 100
H
H
H
H
CN
N
O
24
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



7.44 7.42 7.39 7.36 7.34 7.32 7.29 7.28 7.26 7.18 7.16 7.14 7.10 7.08 7.06 6.90 6.88 6.42 6.40 5.72 5.69 5.33 5.31 4.89 3.73 3.72 3.56 3.37 3.36 3.35 3.16 3.12 3.11 3.01 2.97 2.85 2.79 2.78 2.40 1.75 1.74 1.72 1.70 1.68 1.67 1.64 1.43 1.26 0.88 0.78 0.65 0.63 0.61 0.47 0.00
Solvent CDCl3
Spectrometer Frequency 400
7.44 7.42 7.34 7.28 7.26 7.16 7.14 7.10 7.08 7.06 6.90 6.88 6.42 6.40 5.72 5.69 5.33 5.31 4.89
1.02 1.06 0.91 1.06 2.06 1.00 1.99 1.04 1.03 1.02
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0
f1 (ppm)
H
H
H
H
CN
N
O
25
1.02 1.06 0.91 1.06 2.06 1.00 1.99 1.04 1.03 1.02 1.01 1.00 1.02 1.03 2.99 2.00 2.83
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

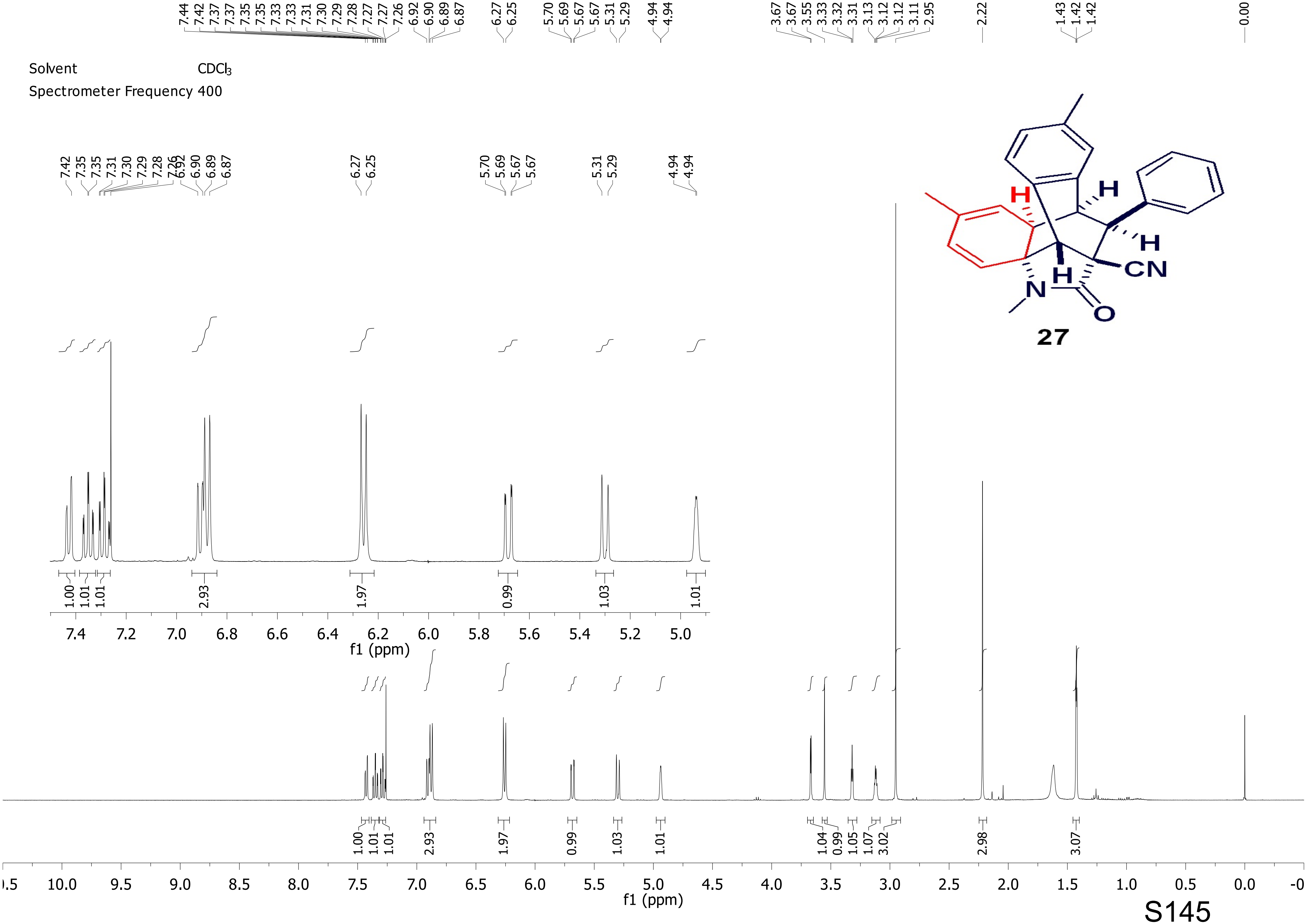

Solvent CDCl3
Spectrometer Frequency 100
171.45
138.52
138.08
134.32
131.90
131.36
129.03
128.21
127.87
127.73
127.42
127.25
122.64
121.74
116.90
77.31
76.99
76.68
65.01
53.71
51.65
50.97
47.73
43.91
27.99
27.47
12.39
138
134
130
126
122
118
f1 (ppm)
H
H
H
H
CN
N
O
25
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.47
7.46
7.45
7.43
7.38
7.38
7.37
7.37
7.36
7.36
7.31
7.31
7.30
7.30
7.30
7.30
7.29
7.29
7.26
7.16
7.15
7.10
7.08
7.07
7.06
6.97
6.95
6.90
6.89
6.40
6.38
6.37
5.80
5.79
5.78
5.77
5.29
5.27
5.27
5.23
5.22
5.21
5.01
3.72
3.72
3.70
3.69
3.64
3.63
3.63
3.54
3.38
3.38
3.10
2.95
2.95
1.63
1.63
-0.00
Solvent CDCl3
Spectrometer Frequency 150
H
H
H
CN
H
N
O
26
1.00
0.98
0.93
0.97
1.83
0.52
0.44
1.94
0.59
0.92
0.98
0.48
0.95
0.97
0.45
0.45
0.51
3.00
3.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

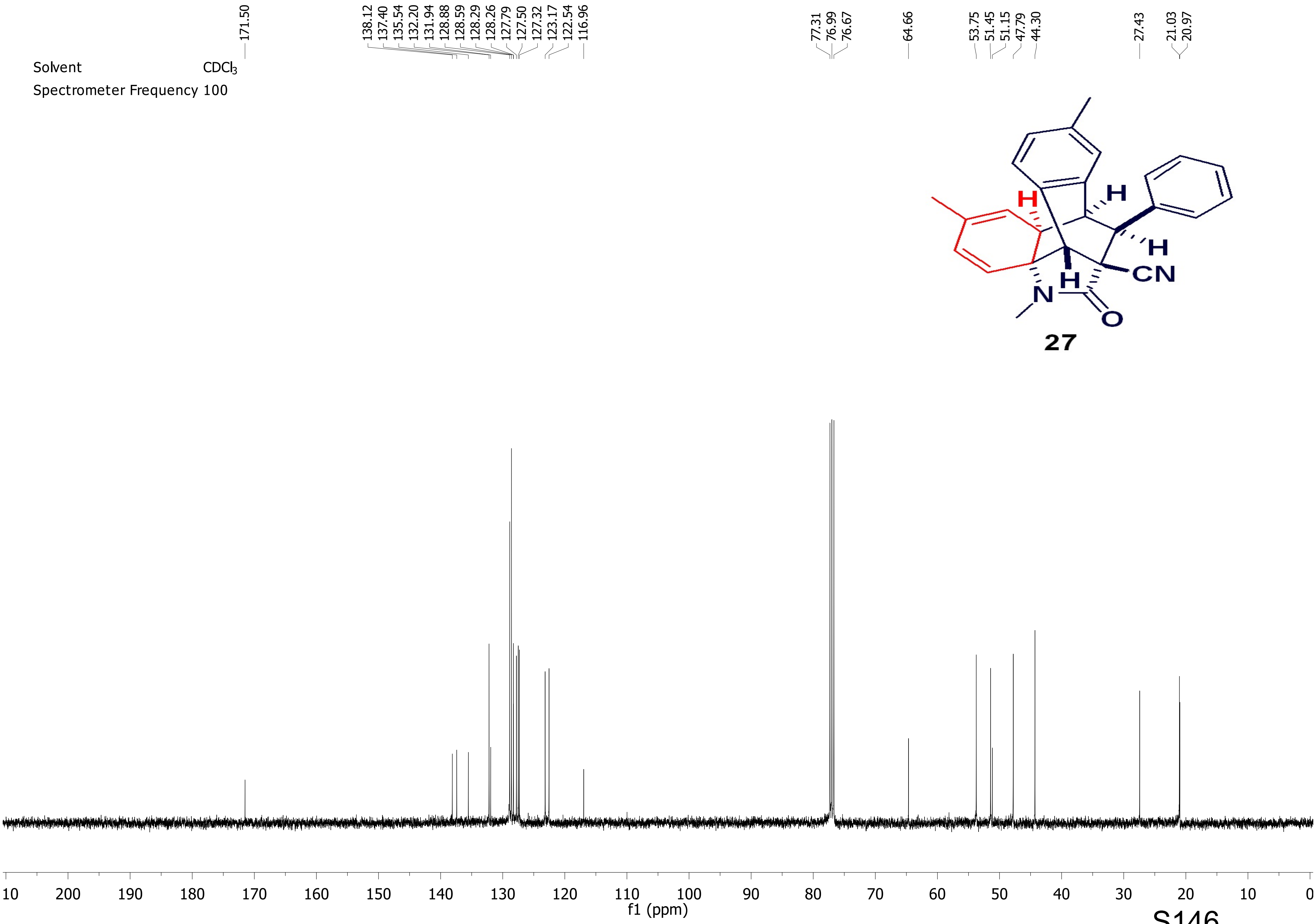

171.28
171.11
138.51
138.44
137.74
137.12
136.25
134.68
132.34
132.31
129.02
128.78
128.33
128.30
128.21
127.92
127.88
127.86
127.82
127.74
127.59
127.47
127.37
126.81
125.24
120.43
118.71
117.04
116.92
116.90
77.20
76.99
76.78
65.59
65.45
54.19
53.86
51.85
51.75
50.95
50.26
48.27
47.31
44.28
43.67
27.41
27.39
21.66
20.17
Solvent CDCl$_3$
Spectrometer Frequency 150
H
H
H
H
CN
N
O
26
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

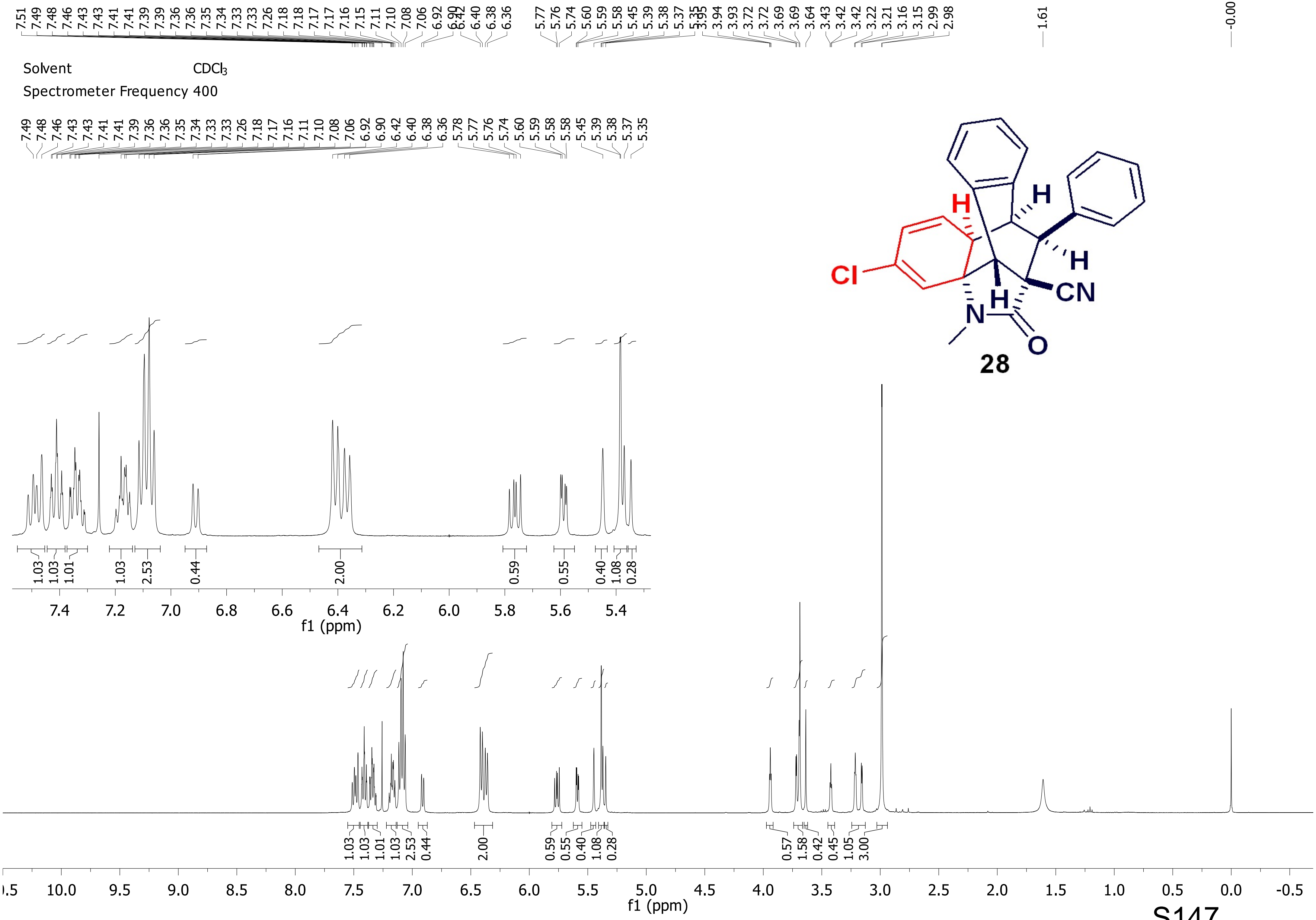
Solvent CDCl3

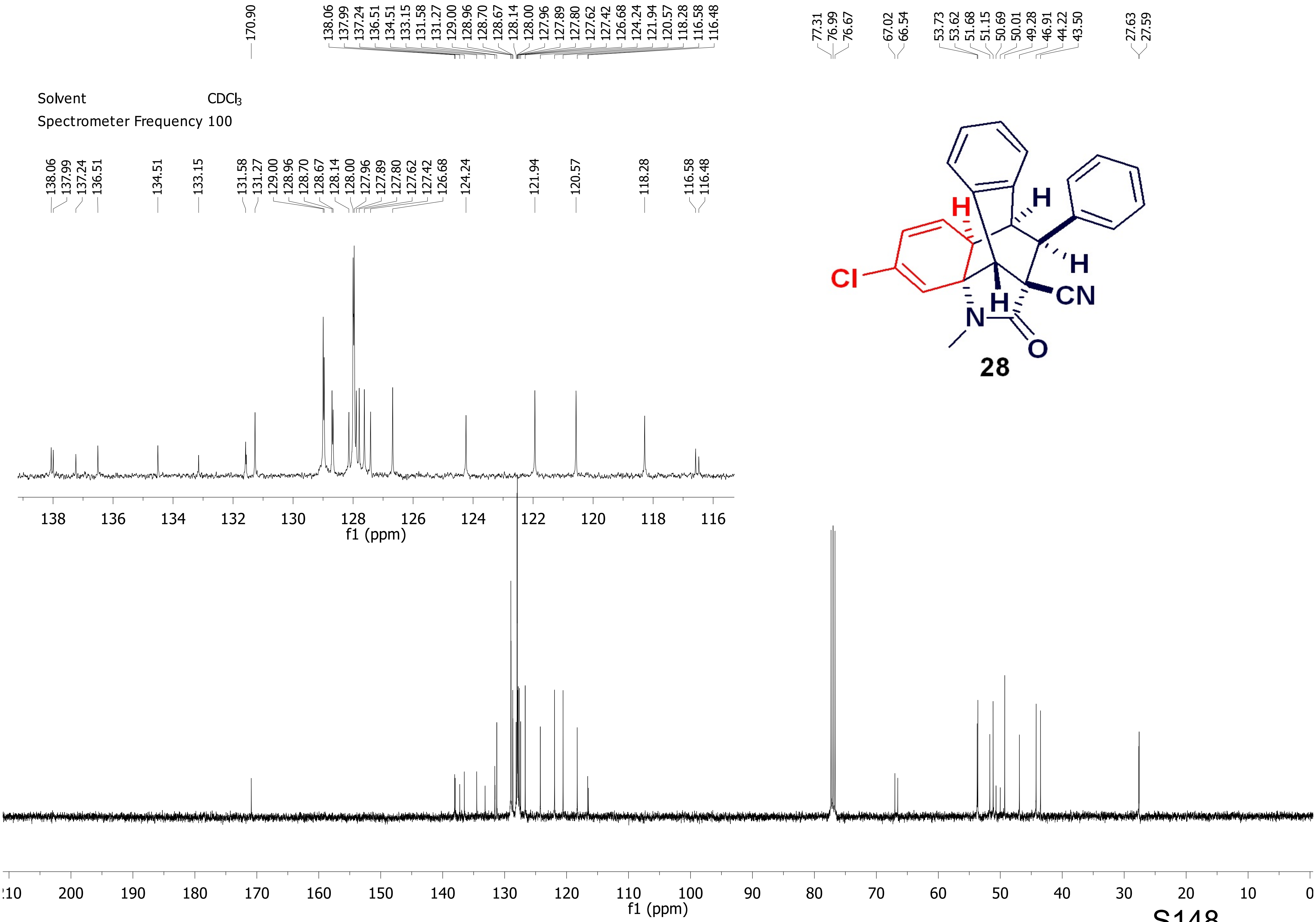
Spectrometer Frequency 400



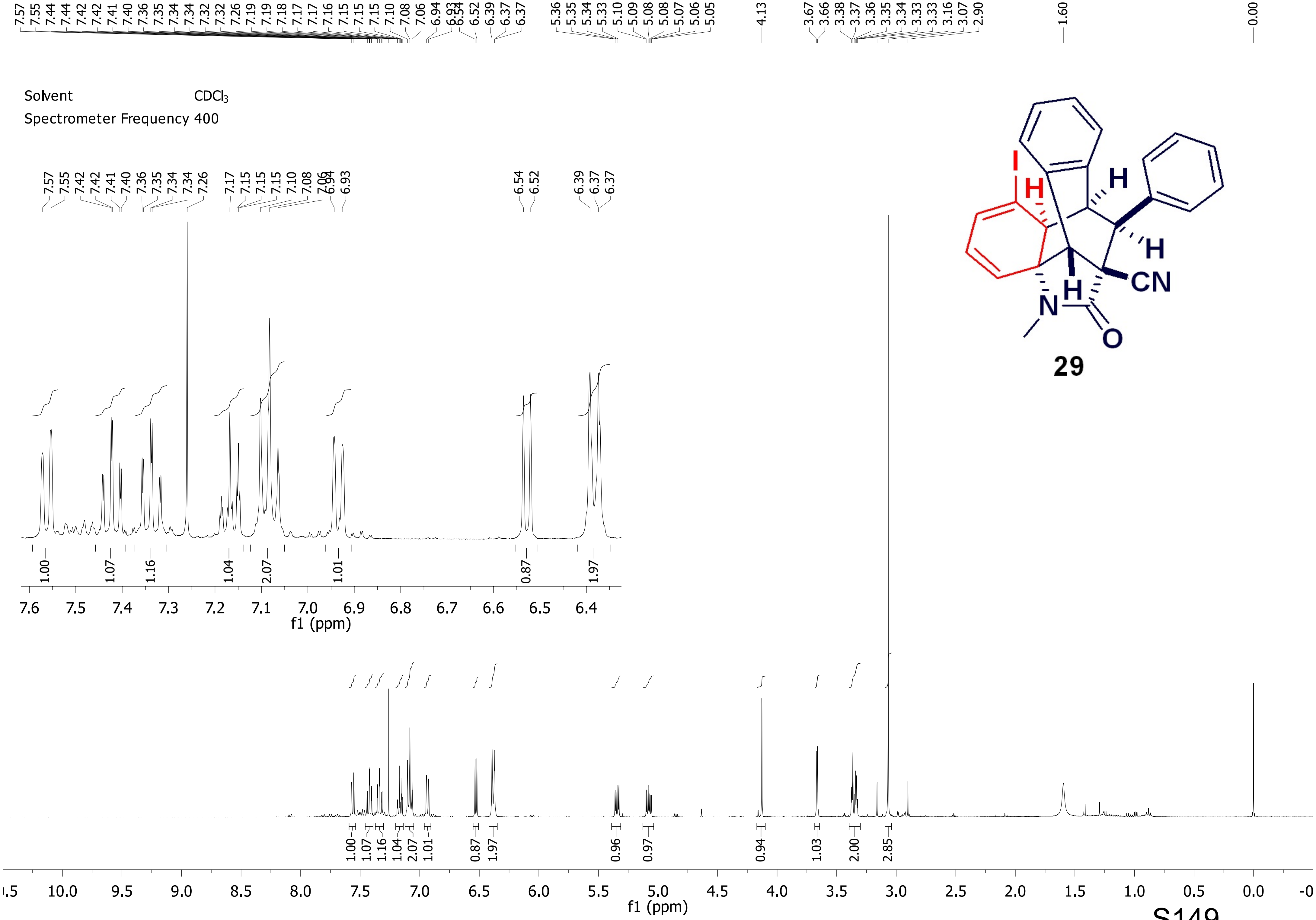
27


171.50
138.12
137.40
135.54
132.20
131.94
128.88
128.59
128.29
128.26
127.79
127.50
127.32
123.17
122.54
116.96
77.31
76.99
76.67
64.66
53.75
51.45
51.15
47.79
44.30
27.43
21.03
20.97
Solvent CDCl3
Spectrometer Frequency 100
H
H
H
H
CN
N
O
27
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

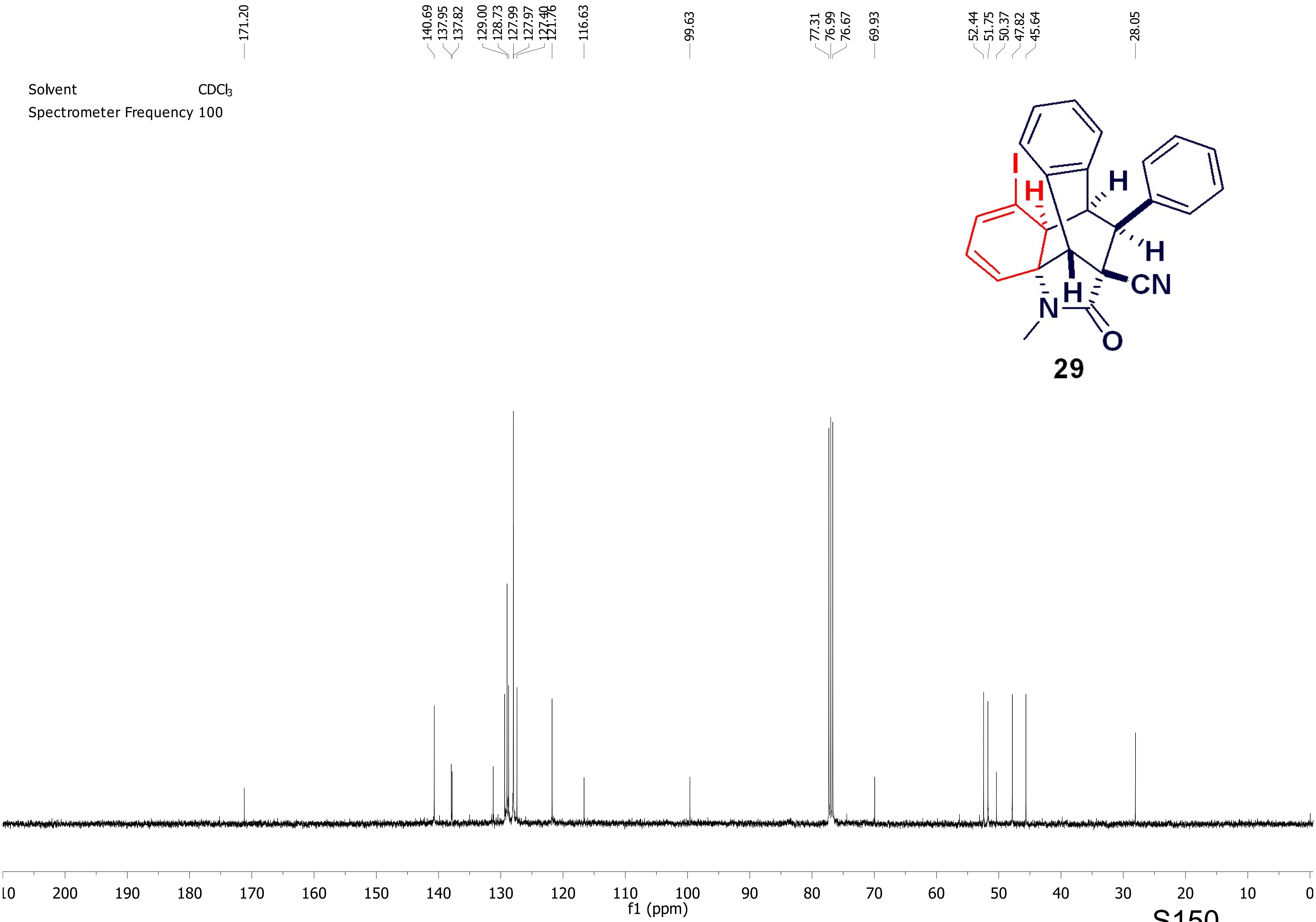

7.51 7.49 7.48 7.46 7.43 7.43 7.41 7.41 7.39 7.39 7.36 7.36 7.35 7.34 7.33 7.33 7.26 7.18 7.18 7.17 7.17 7.16 7.15 7.11 7.10 7.08 7.06 6.92 6.90 6.42 6.40 6.38 6.36 5.77 5.76 5.74 5.60 5.59 5.58 5.45 5.39 5.38 5.37 5.35 3.95 3.94 3.93 3.72 3.72 3.69 3.69 3.64 3.43 3.42 3.42 3.22 3.21 3.16 3.15 2.99 2.98 1.61 -0.00
Solvent CDCl$_3$
Spectrometer Frequency 400
7.49 7.48 7.46 7.43 7.43 7.41 7.41 7.39 7.36 7.36 7.35 7.34 7.33 7.33 7.26 7.18 7.17 7.16 7.11 7.10 7.08 7.06 6.92 6.90 6.42 6.40 6.38 6.36 5.78 5.77 5.76 5.74 5.60 5.59 5.58 5.58 5.45 5.39 5.38 5.37 5.35
1.03 1.03 1.01 1.03 2.53 0.44 2.00 0.59 0.55 0.40 1.08 0.28
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4
f1 (ppm)
H
H
H
H
Cl
CN
N
O
28
1.03 1.03 1.01 1.03 2.53 0.44 2.00 0.59 0.55 0.40 1.08 0.28 0.57 1.58 0.42 0.45 1.05 3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


170.90
138.06
137.99
137.24
136.51
134.51
133.15
131.58
131.27
129.00
128.96
128.70
128.67
128.14
128.00
127.96
127.89
127.80
127.62
127.42
126.68
124.24
121.94
120.57
118.28
116.58
116.48
77.31
76.99
76.67
67.02
66.54
53.73
53.62
51.68
51.15
50.69
50.01
49.28
46.91
44.22
43.50
27.63
27.59
Solvent CDCl$_3$
Spectrometer Frequency 100
138 136 134 132 130 128 126 124 122 120 118 116
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
H
H
H
H
Cl
CN
N
O

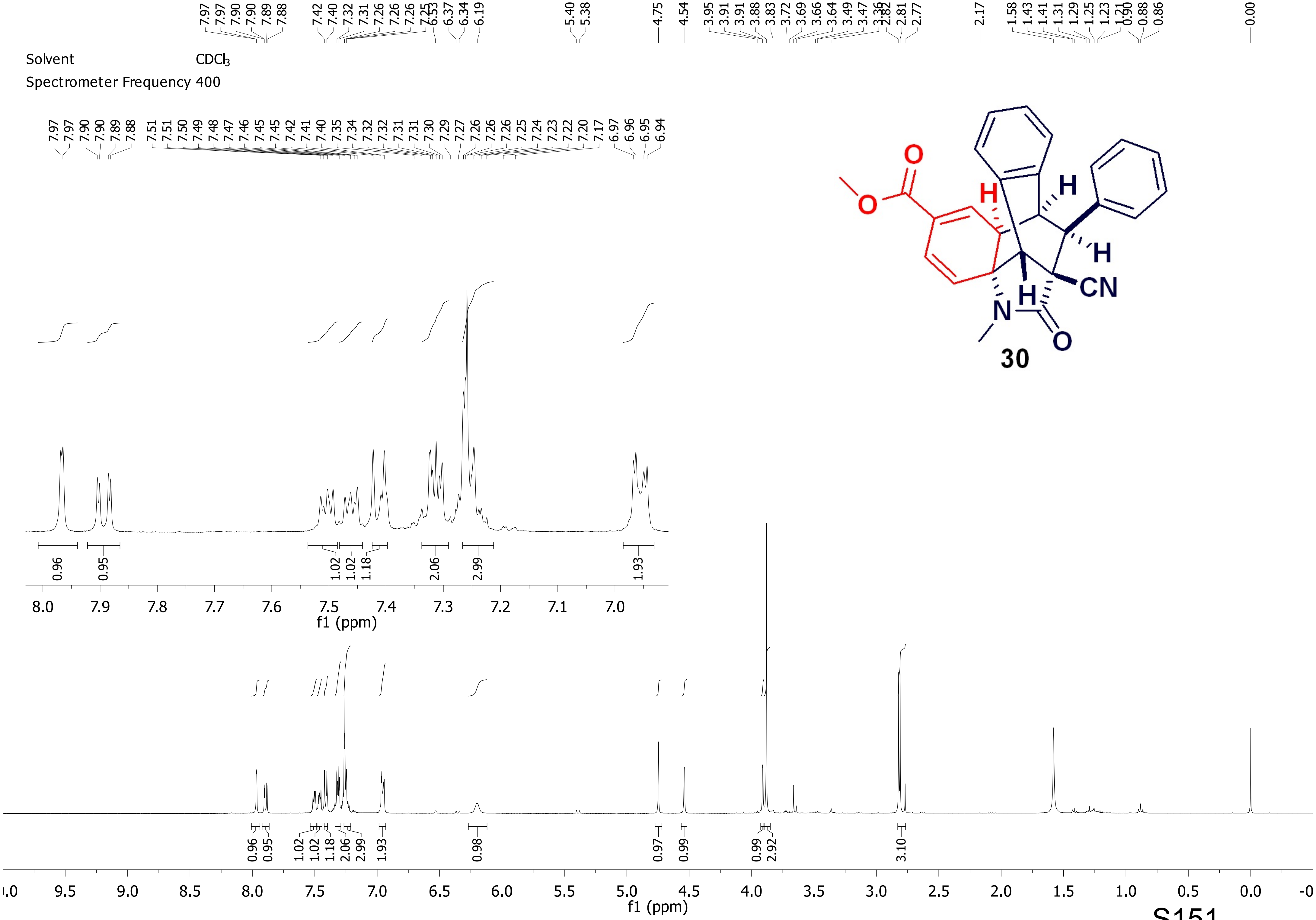
28


7.57 7.55 7.44 7.44 7.42 7.42 7.41 7.40 7.36 7.35 7.34 7.34 7.32 7.32 7.26 7.19 7.19 7.18 7.17 7.17 7.16 7.15 7.15 7.15 7.10 7.08 7.06 6.94 6.93 6.54 6.52 6.39 6.37 6.37 5.36 5.35 5.34 5.33 5.10 5.09 5.08 5.08 5.07 5.06 5.05 4.13 3.67 3.66 3.38 3.37 3.36 3.35 3.34 3.33 3.33 3.16 3.07 2.90 1.60 0.00
Solvent CDCl3
Spectrometer Frequency 400
7.57 7.55 7.42 7.42 7.41 7.40 7.36 7.35 7.34 7.34 7.26 7.17 7.15 7.15 7.15 7.10 7.08 7.06 6.94 6.93 6.54 6.52 6.39 6.37 6.37
1.00 1.07 1.16 1.04 2.07 1.01 0.87 1.97
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4
f1 (ppm)
I
H
H
H
CN
H
N
O
1.00 1.07 1.16 1.04 2.07 1.01 0.87 1.97 0.96 0.97 0.94 1.03 2.00 2.85
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

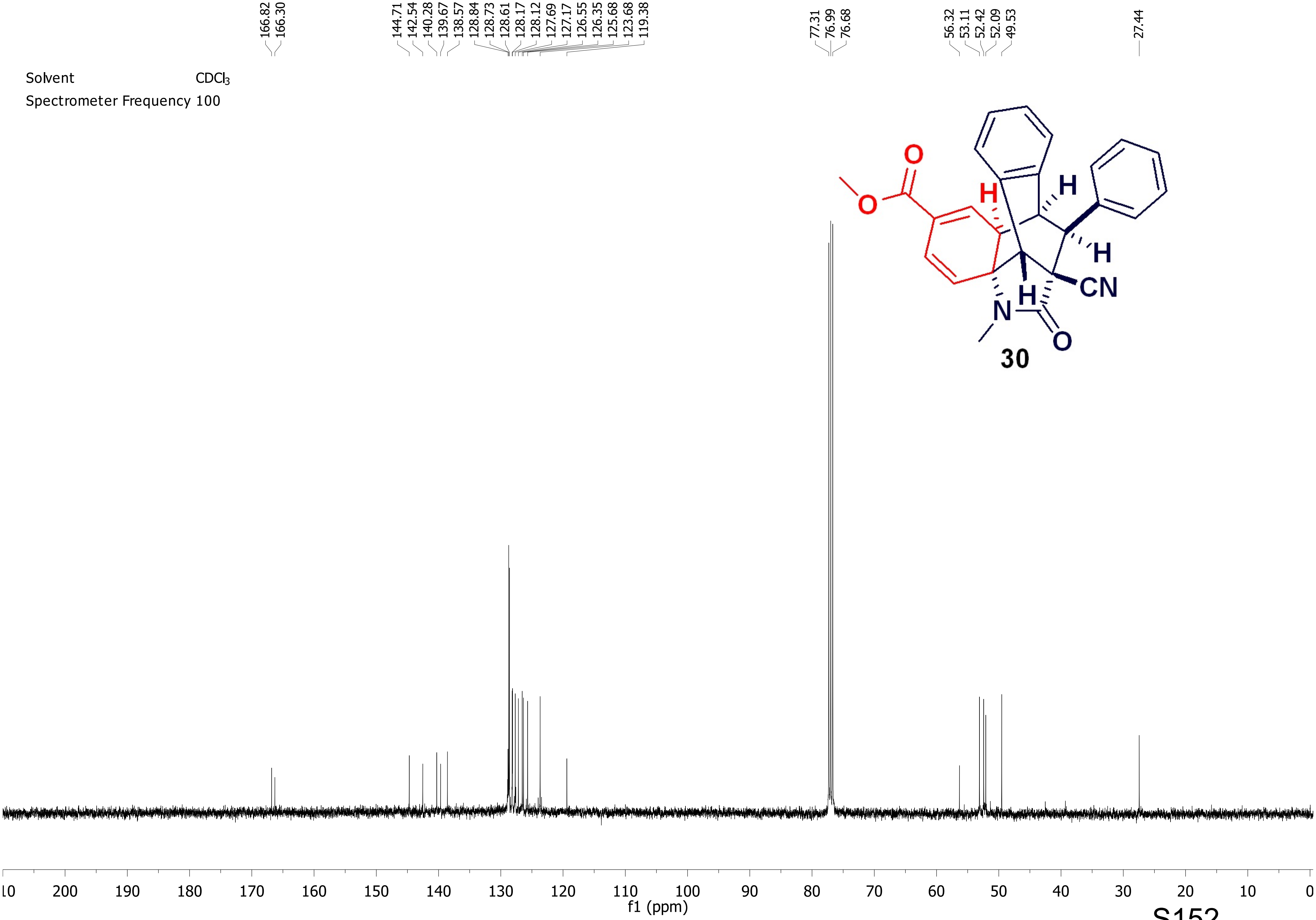
29


171.20
140.69
137.95
137.82
129.00
128.73
127.99
127.97
127.40
121.76
116.63
99.63
77.31
76.99
76.67
69.93
52.44
51.75
50.37
47.82
45.64
28.05
Solvent CDCl3
Spectrometer Frequency 100
I
H
H
H
H
CN
N
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

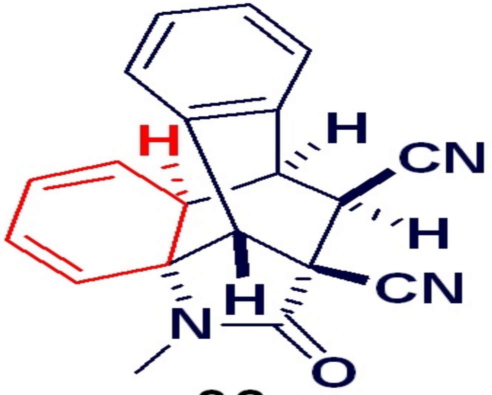
29


Solvent CDCl3
Spectrometer Frequency 400
7.97 7.97 7.90 7.90 7.89 7.88 7.42 7.40 7.32 7.31 7.26 7.26 7.26 7.25 6.53 6.37 6.34 6.19 5.40 5.38 4.75 4.54 3.95 3.91 3.91 3.88 3.83 3.72 3.69 3.66 3.64 3.49 3.47 3.36 2.82 2.81 2.77 2.17 1.58 1.43 1.41 1.31 1.29 1.25 1.23 1.21 0.90 0.88 0.86 0.00
7.97 7.97 7.90 7.90 7.89 7.88 7.51 7.51 7.50 7.49 7.48 7.47 7.46 7.45 7.45 7.42 7.41 7.40 7.35 7.34 7.32 7.32 7.31 7.31 7.30 7.29 7.27 7.26 7.26 7.26 7.25 7.24 7.23 7.22 7.20 7.17 6.97 6.96 6.95 6.94
0.96 0.95 1.02 1.02 1.18 2.06 2.99 1.93
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
O
O
H
H
H
CN
H
N
O
0.96 0.95 1.02 1.02 1.18 2.06 2.99 1.93 0.98 0.97 0.99 0.99 2.92 3.10
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

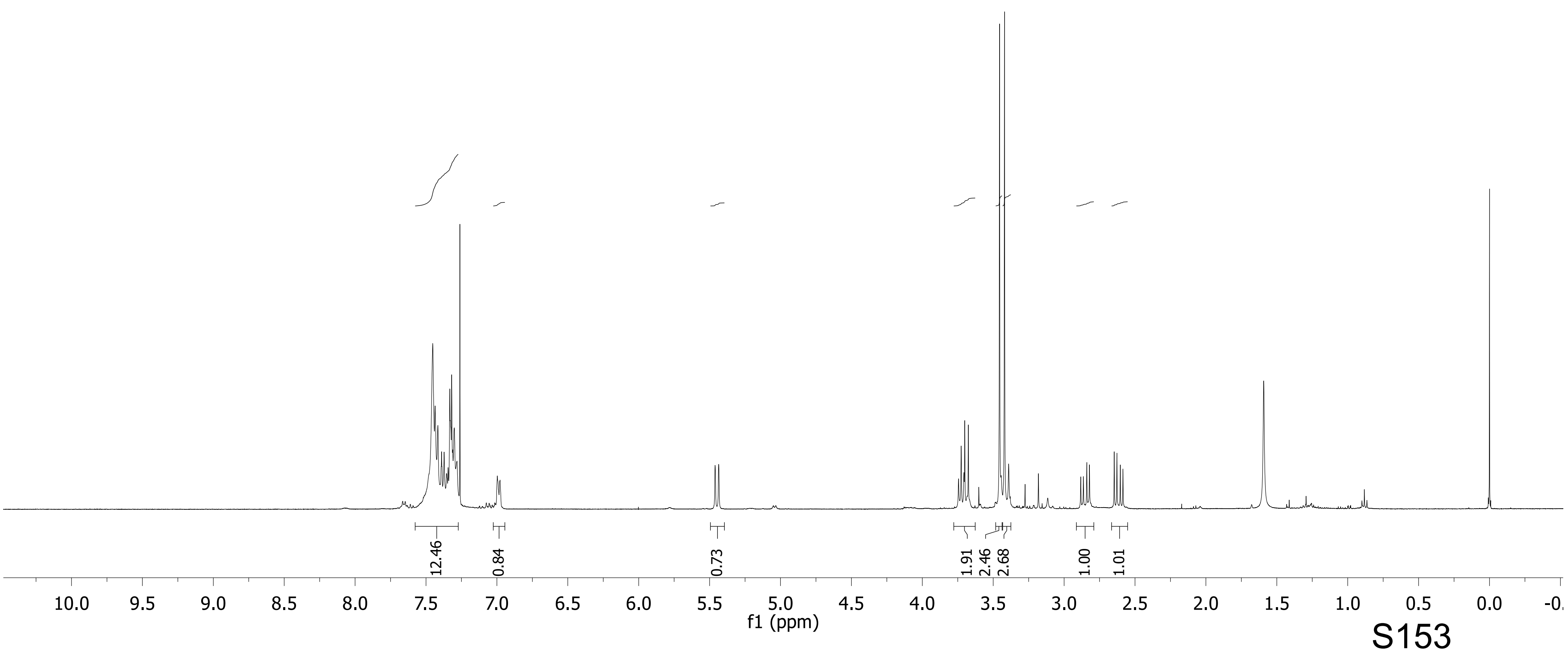
30

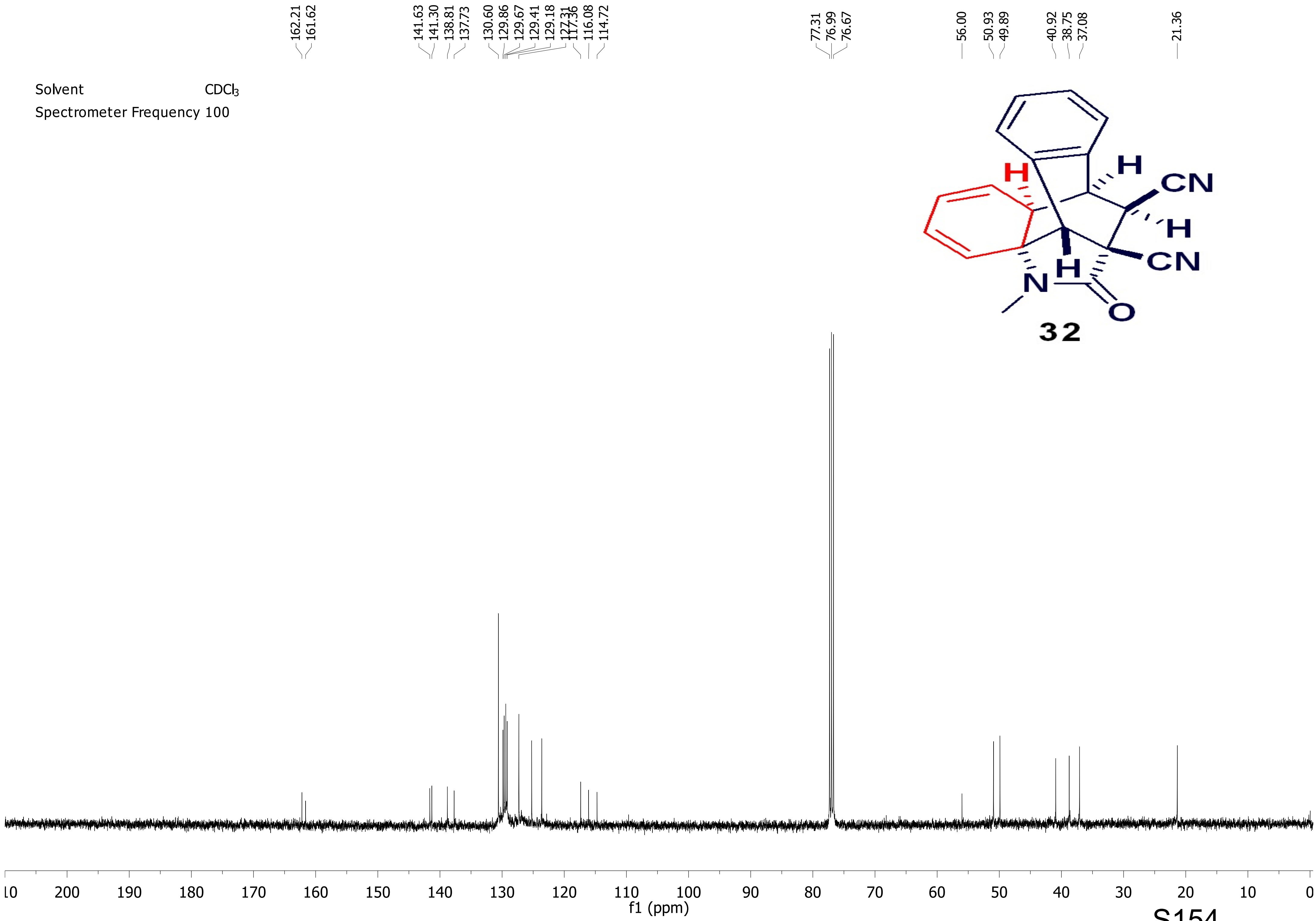

166.82
166.30
144.71
142.54
140.28
139.67
138.57
128.84
128.73
128.61
128.17
128.12
127.69
127.17
126.55
126.35
125.68
123.68
119.38
77.31
76.99
76.68
56.32
53.11
52.42
52.09
49.53
27.44
Solvent CDCl$_3$
Spectrometer Frequency 100
O
O
H
H
H
CN
H
N
O
30
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Solvent CDCl$_3$
Spectrometer Frequency 400

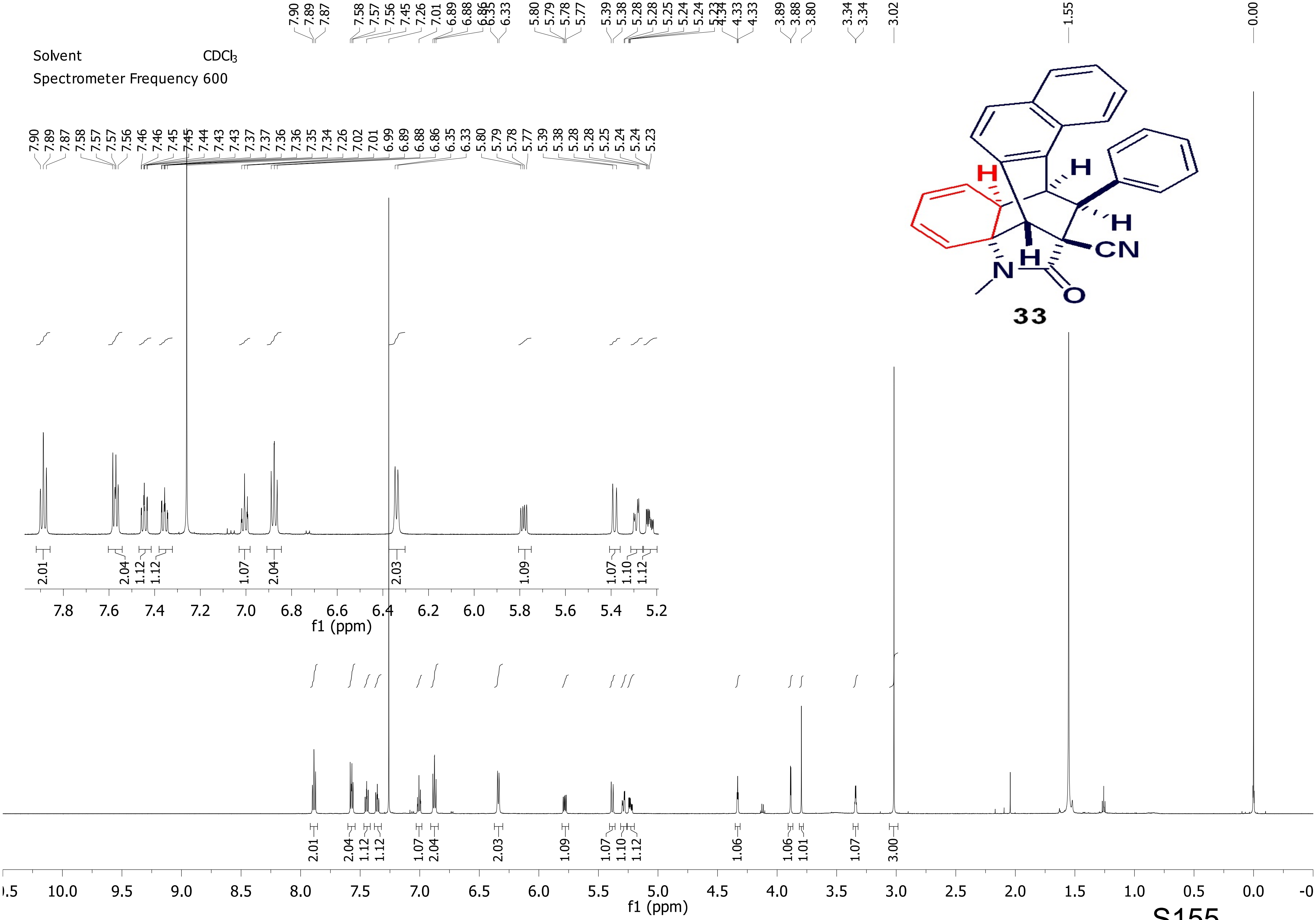


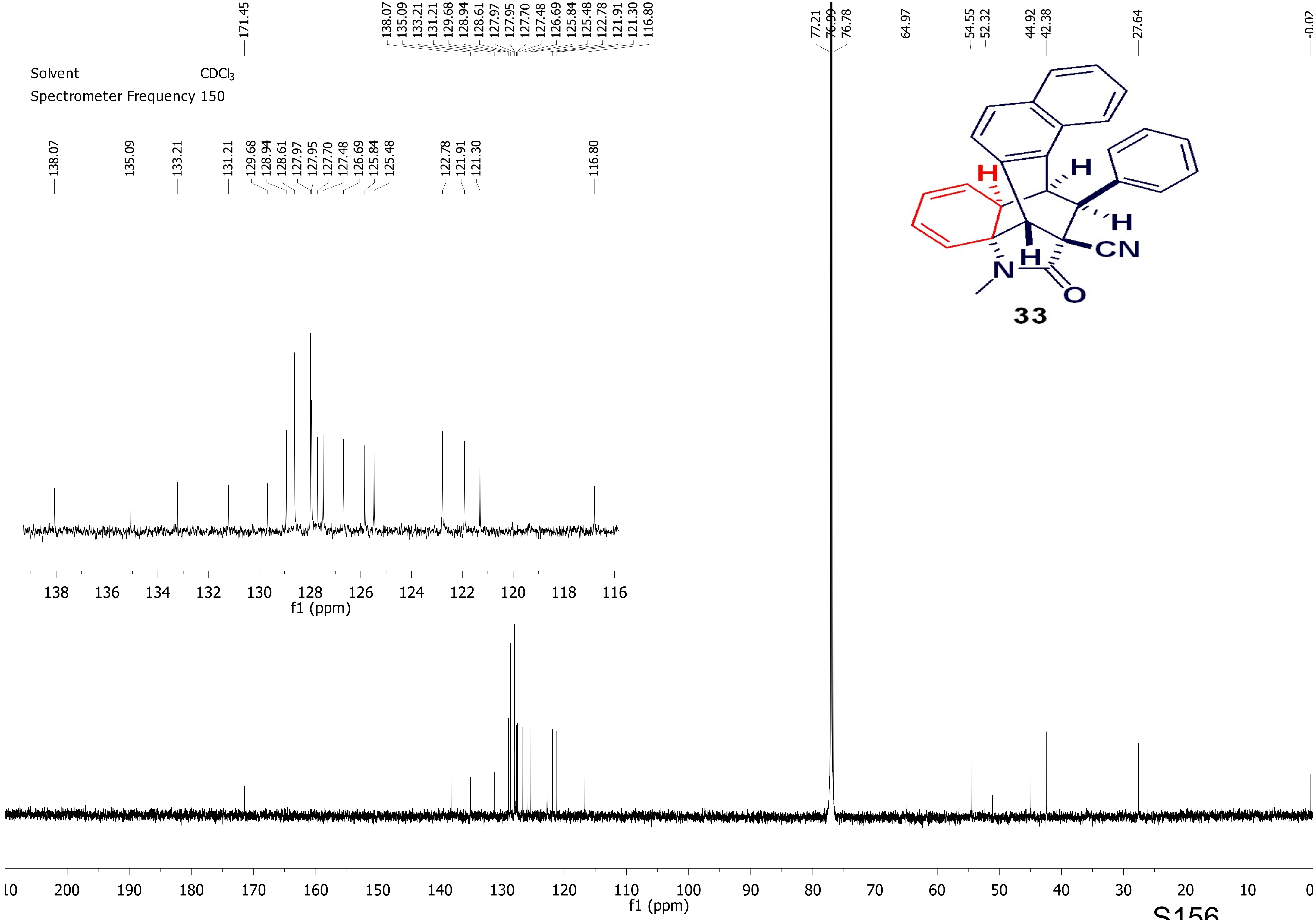
32




162.21
161.62
141.63
141.30
138.81
137.73
130.60
129.86
129.67
129.41
129.18
127.31
117.36
116.08
114.72
77.31
76.99
76.67
56.00
50.93
49.89
40.92
38.75
37.08
21.36
Solvent CDCl3
Spectrometer Frequency 100
H
H
CN
H
CN
H
N
O
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

32

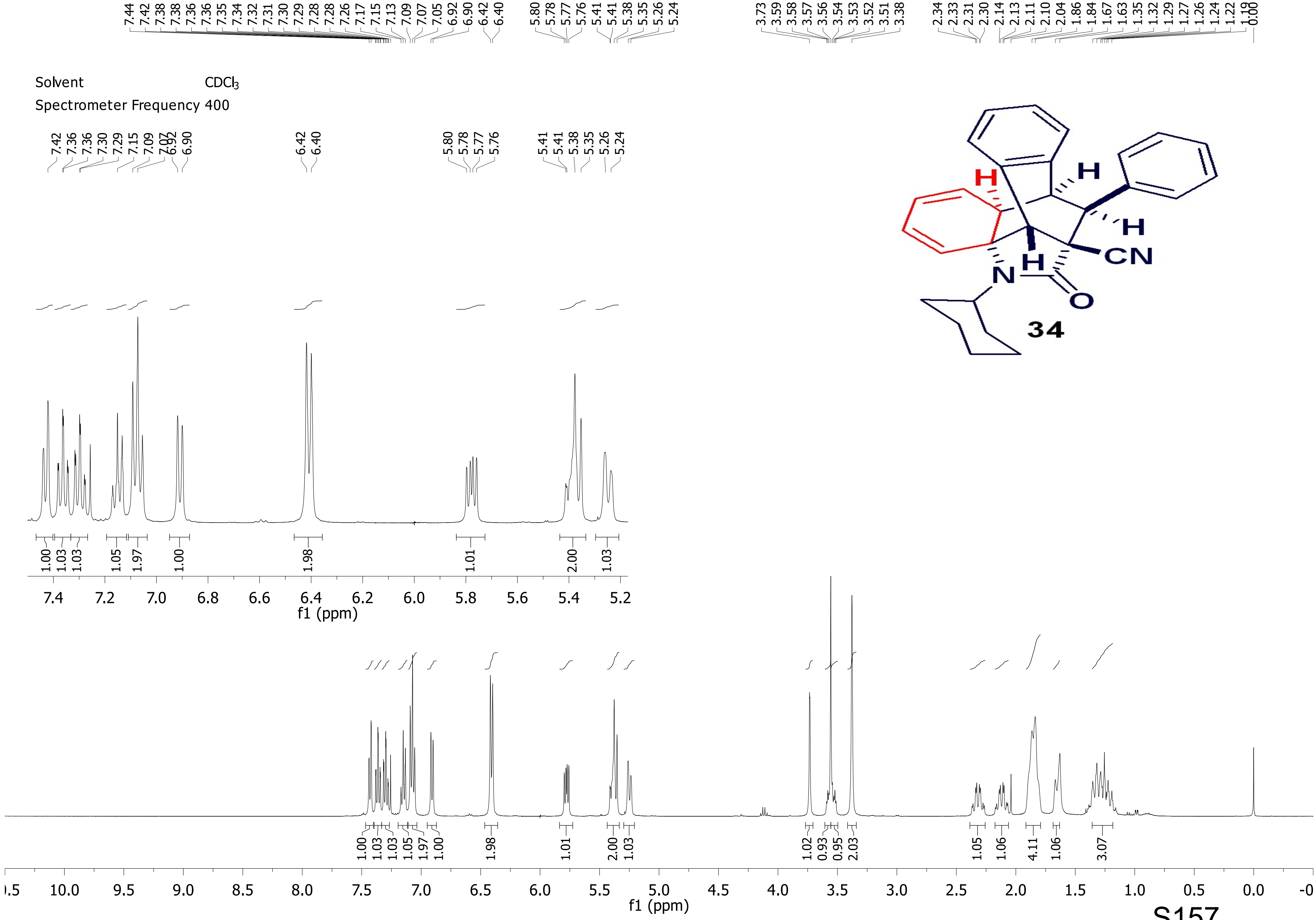

Solvent CDCl$_3$
Spectrometer Frequency 600
7.90 7.89 7.87 7.58 7.57 7.56 7.45 7.26 7.01 6.89 6.88 6.86 6.35 6.33 5.80 5.79 5.78 5.77 5.39 5.38 5.28 5.28 5.25 5.24 5.24 5.23 4.34 4.33 4.33 3.89 3.88 3.80 3.34 3.34 3.02 1.55 0.00
7.90 7.89 7.87 7.58 7.57 7.57 7.56 7.46 7.46 7.45 7.45 7.44 7.43 7.43 7.37 7.37 7.36 7.36 7.35 7.34 7.26 7.02 7.01 6.99 6.89 6.88 6.86 6.35 6.33 5.80 5.79 5.78 5.77 5.39 5.38 5.28 5.28 5.25 5.24 5.24 5.23
H
H
H
CN
N
H
O
33
2.01 2.04 1.12 1.12 1.07 2.04 2.03 1.09 1.07 1.10 1.12
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2
f1 (ppm)
2.01 2.04 1.12 1.12 1.07 2.04 2.03 1.09 1.07 1.10 1.12 1.06 1.06 1.01 1.07 3.00
).5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


Solvent CDCl$_3$
Spectrometer Frequency 150
171.45
138.07
135.09
133.21
131.21
129.68
128.94
128.61
127.97
127.95
127.70
127.48
126.69
125.84
125.48
122.78
121.91
121.30
116.80
77.21
76.99
76.78
64.97
54.55
52.32
44.92
42.38
27.64
-0.02
138 136 134 132 130 128 126 124 122 120 118 116
f1 (ppm)
H
H
H
H
CN
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

33

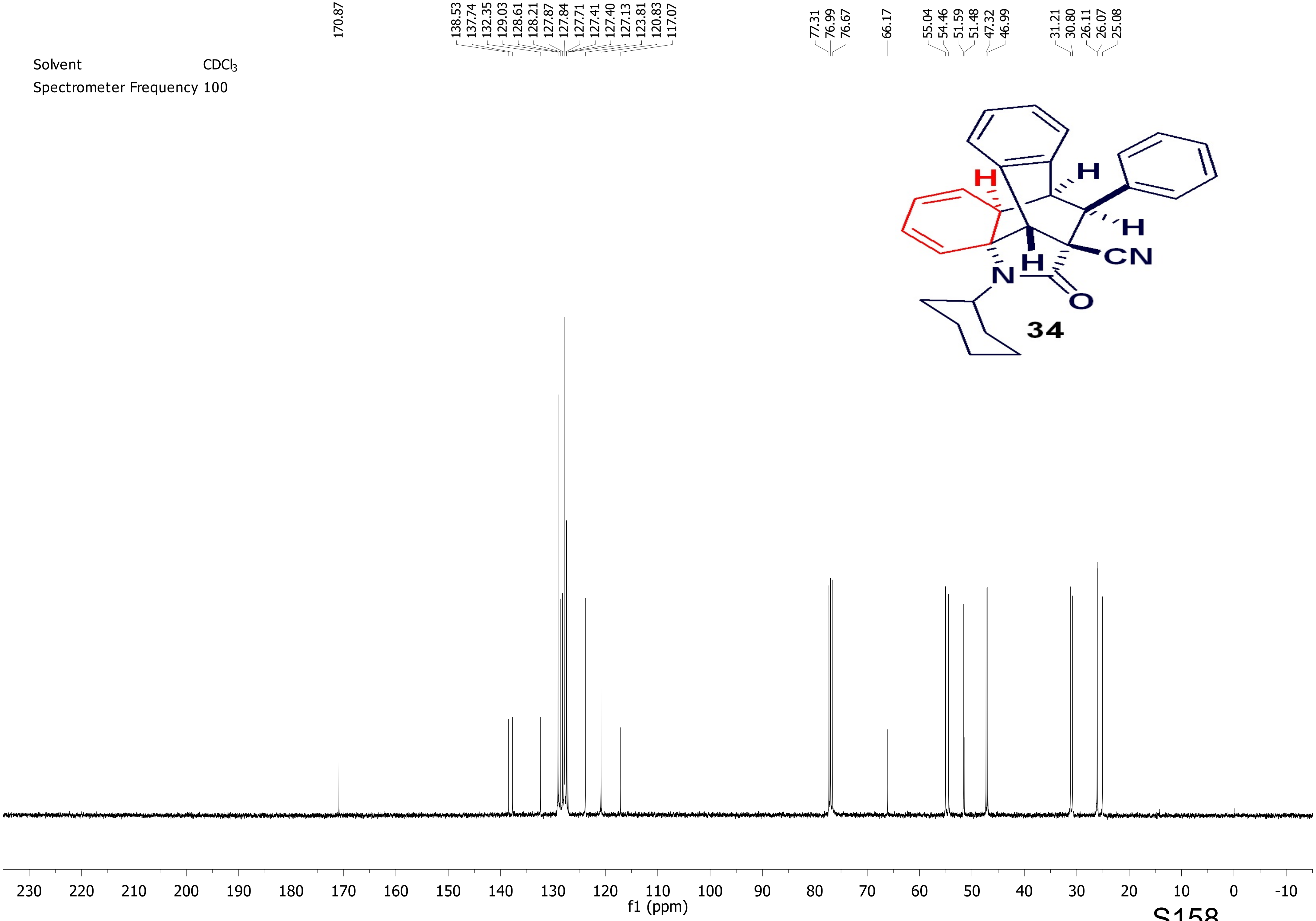
Solvent CDCl$_3$

Spectrometer Frequency 400



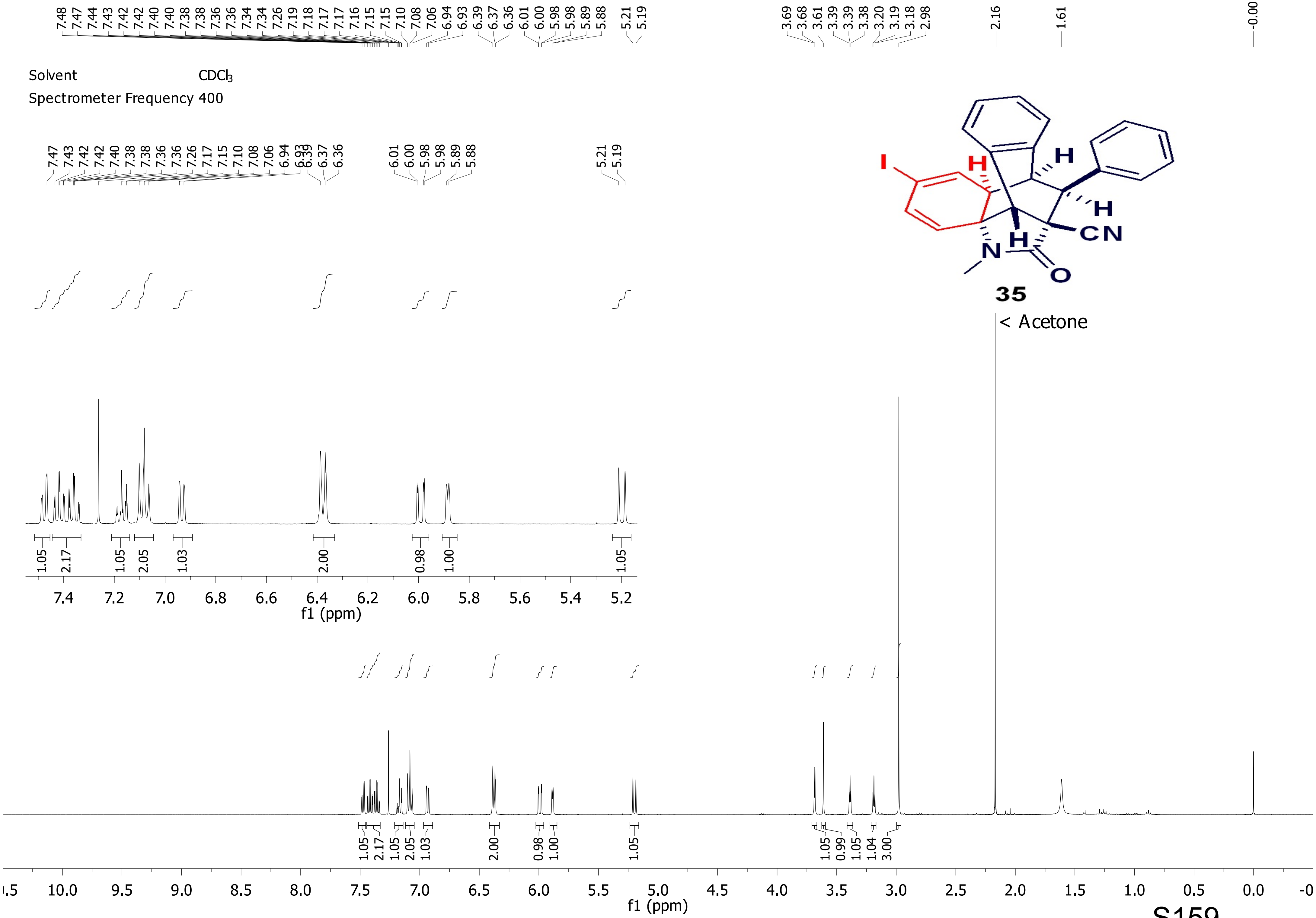
34

Solvent CDCl$_3$
Spectrometer Frequency 100



Solvent CDCl$_3$

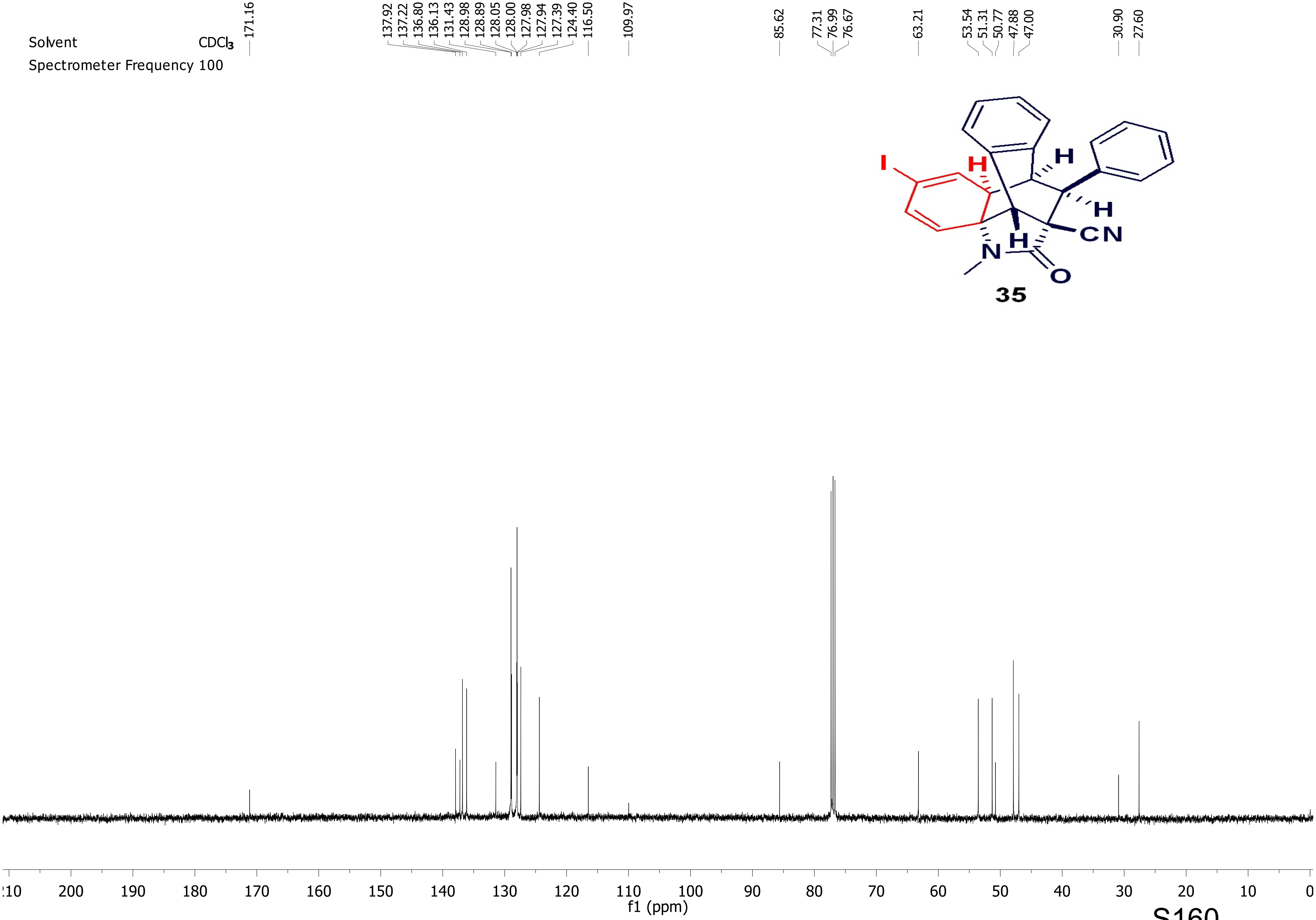
Spectrometer Frequency 400



35

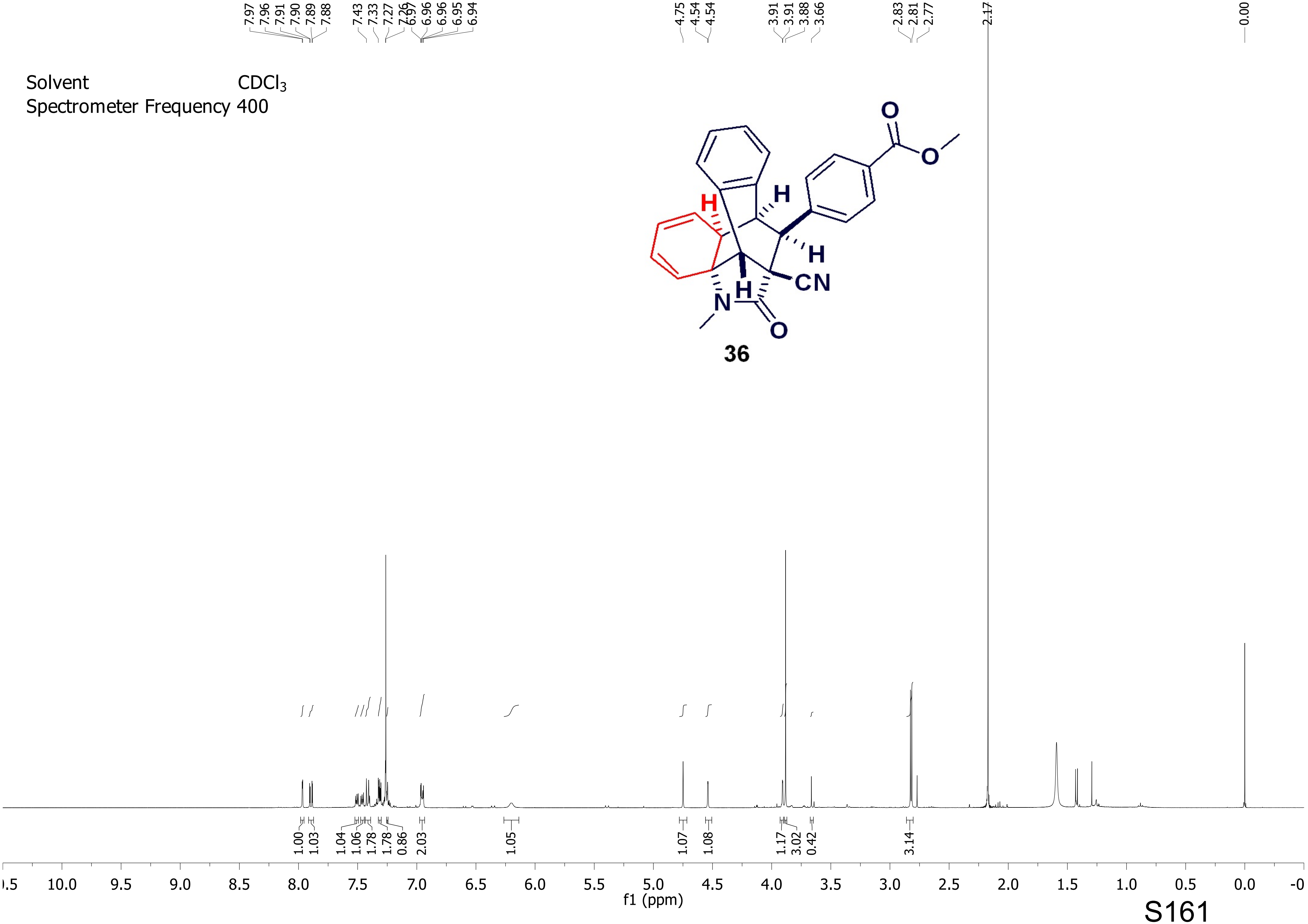
Solvent CDCl$_3$

Spectrometer Frequency 100

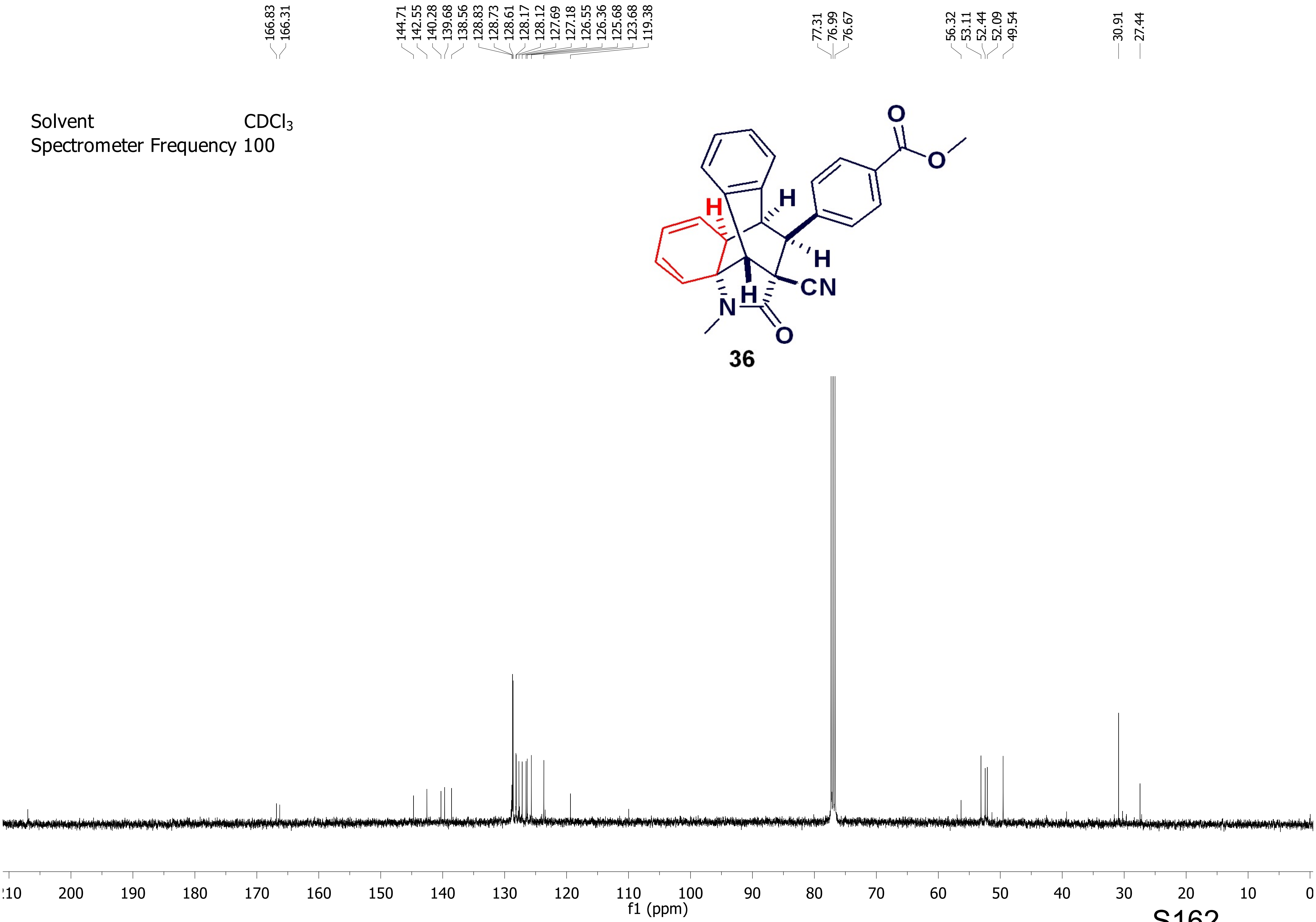


Solvent CDCl$_3$

Spectrometer Frequency 400

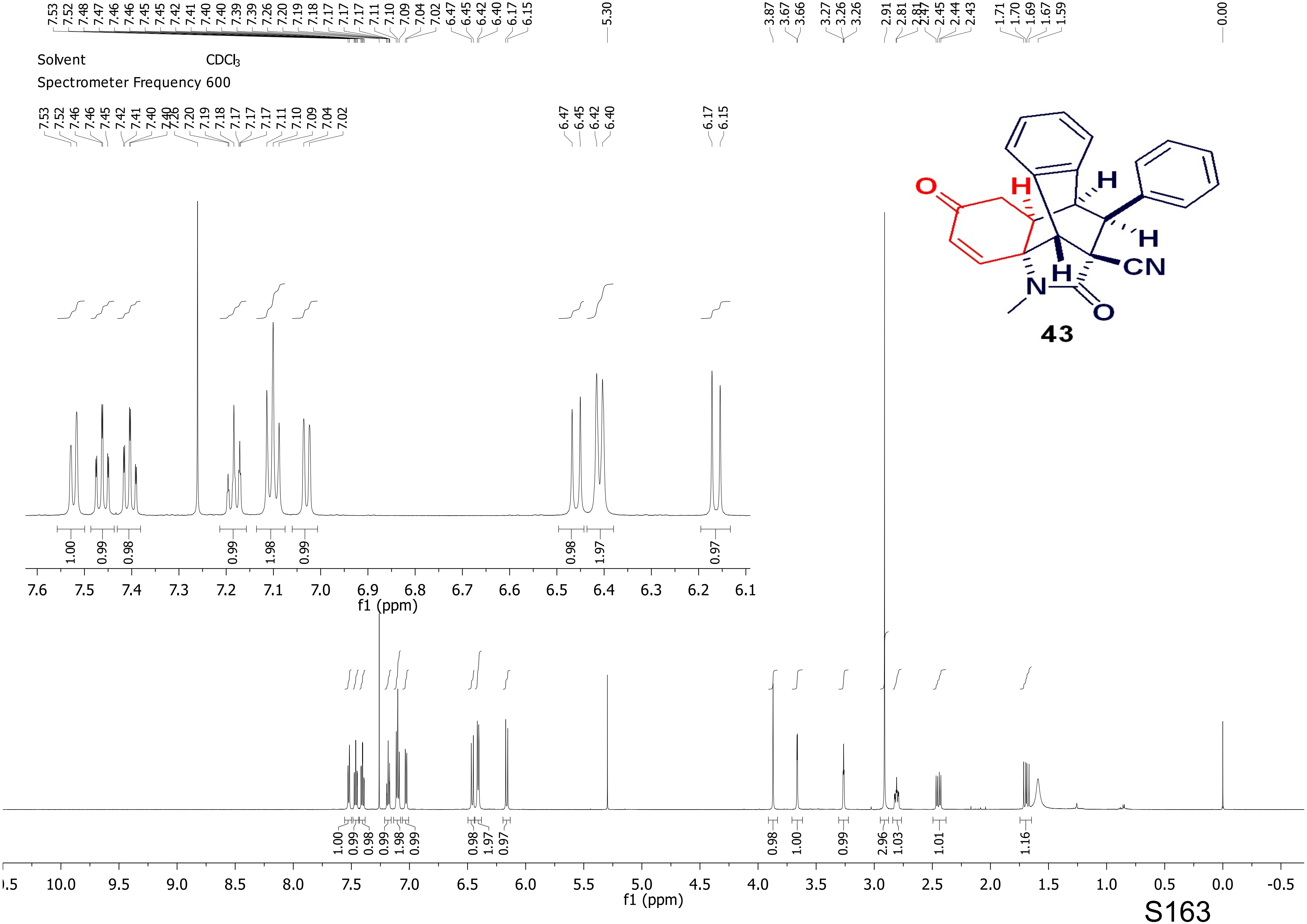


36

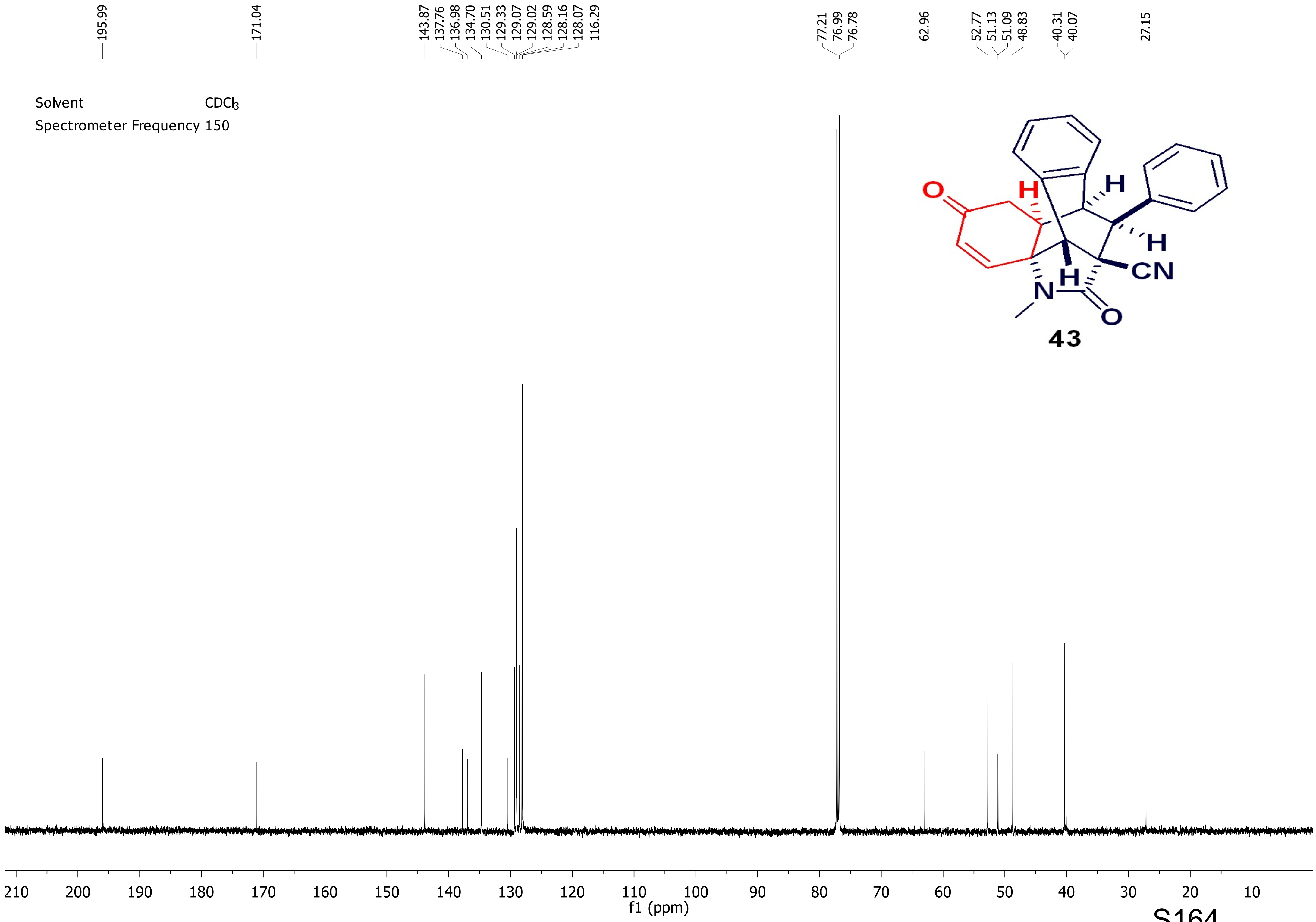


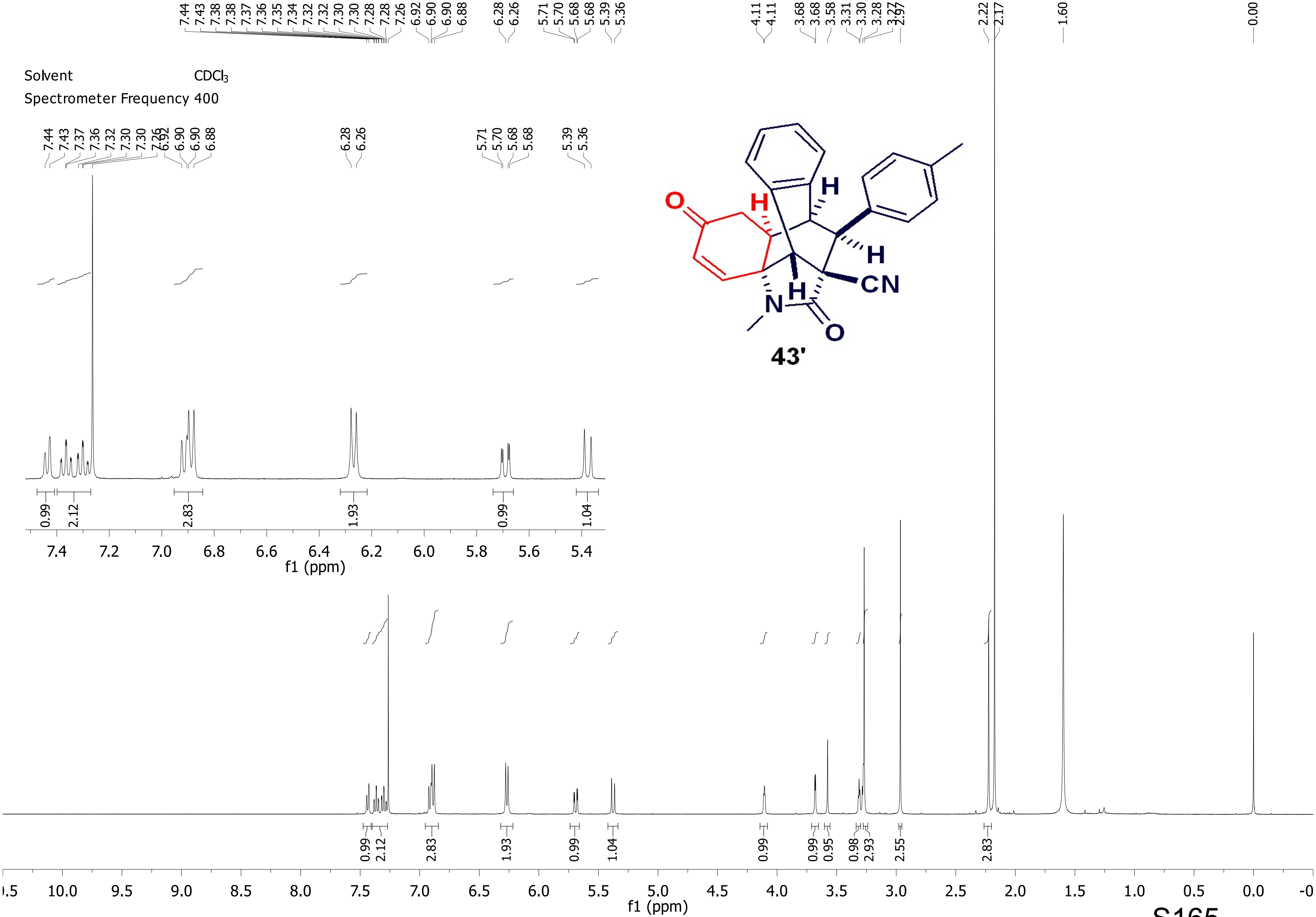
Solvent CDCl$_3$
Spectrometer Frequency 100

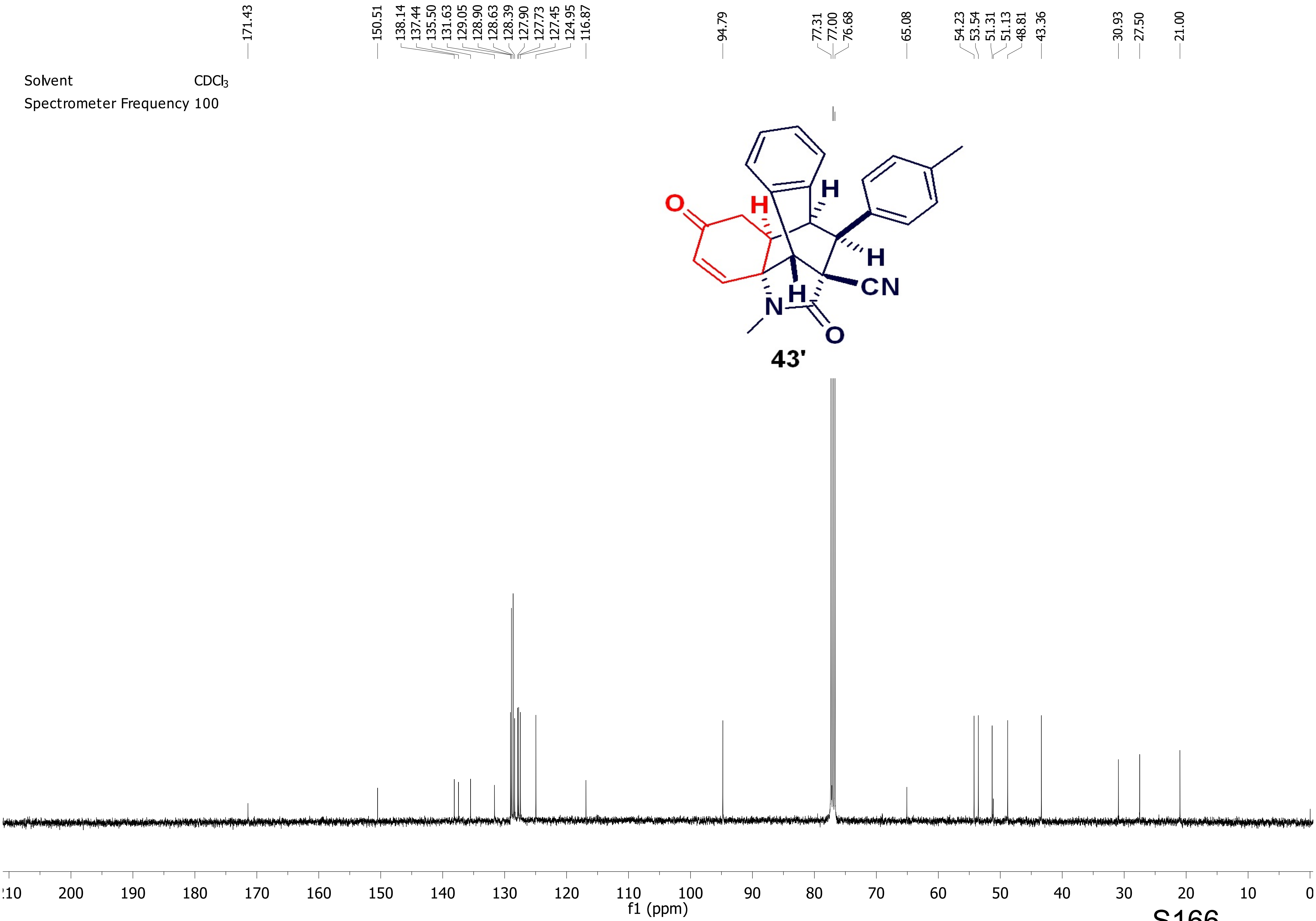
36

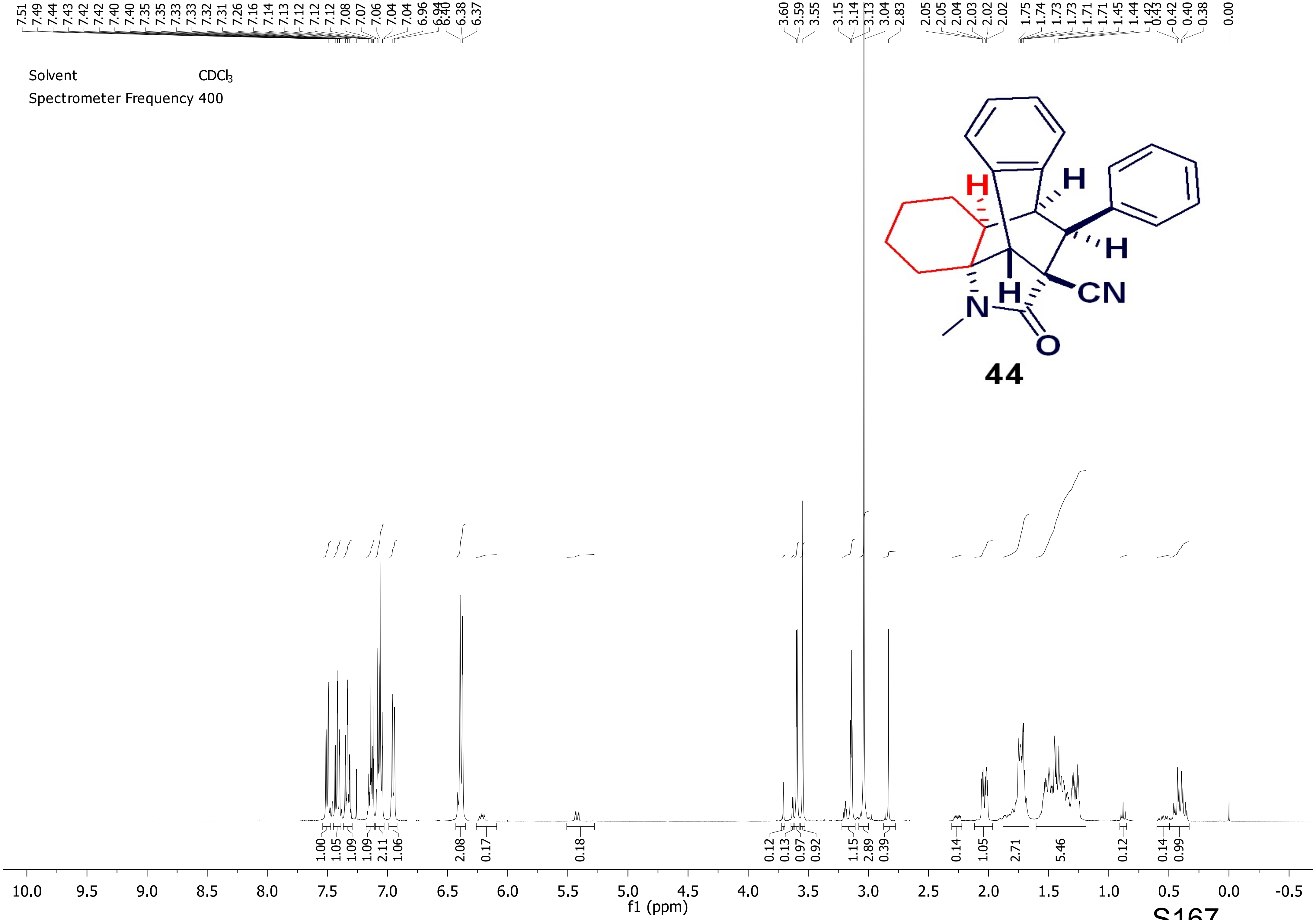


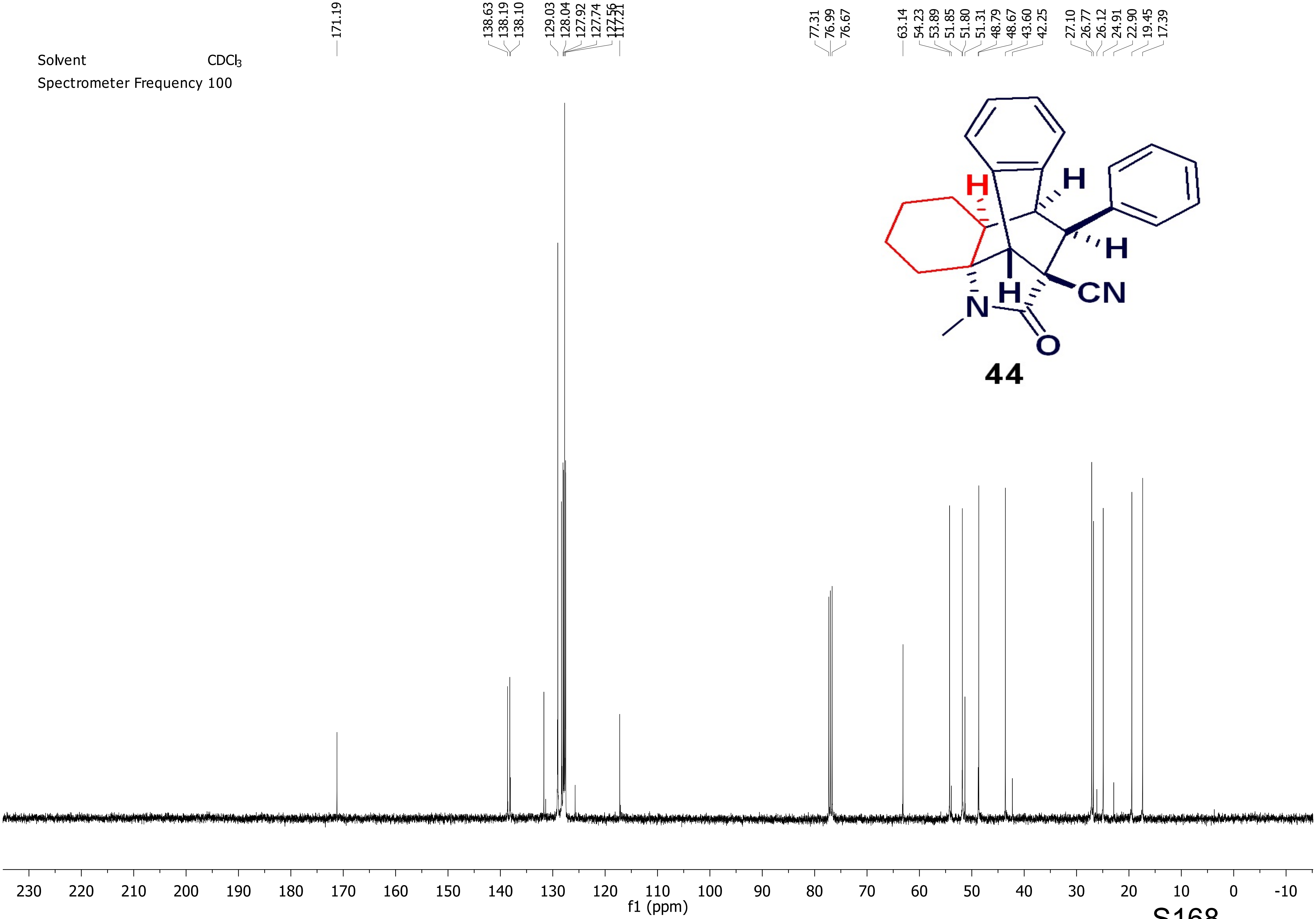
7.53
7.52
7.48
7.47
7.46
7.46
7.45
7.45
7.42
7.41
7.40
7.40
7.39
7.39
7.26
7.20
7.19
7.18
7.17
7.17
7.17
7.11
7.10
7.09
7.04
7.02
6.47
6.45
6.42
6.40
6.17
6.15
5.30
3.87
3.67
3.66
3.27
3.26
3.26
2.91
2.81
2.81
2.47
2.45
2.44
2.43
1.71
1.70
1.69
1.67
1.59
0.00
Solvent CDCl$_3$
Spectrometer Frequency 600
7.53
7.52
7.46
7.46
7.45
7.42
7.41
7.40
7.40
7.26
7.20
7.19
7.18
7.17
7.17
7.17
7.11
7.10
7.09
7.04
7.02
6.47
6.45
6.42
6.40
6.17
6.15
1.00
0.99
0.98
0.99
1.98
0.99
0.98
1.97
0.97
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
f1 (ppm)
O
H
H
H
H
CN
N
O
43
1.00
0.99
0.98
0.99
1.98
0.99
0.98
1.97
0.97
0.98
1.00
0.99
2.96
1.03
1.01
1.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


195.99
171.04
143.87
137.76
136.98
134.70
130.51
129.33
129.07
129.02
128.59
128.16
128.07
116.29
77.21
76.99
76.78
62.96
52.77
51.13
51.09
48.83
40.31
40.07
27.15
Solvent CDCl3
Spectrometer Frequency 150
O
H
H
H
H
N
CN
O
43
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

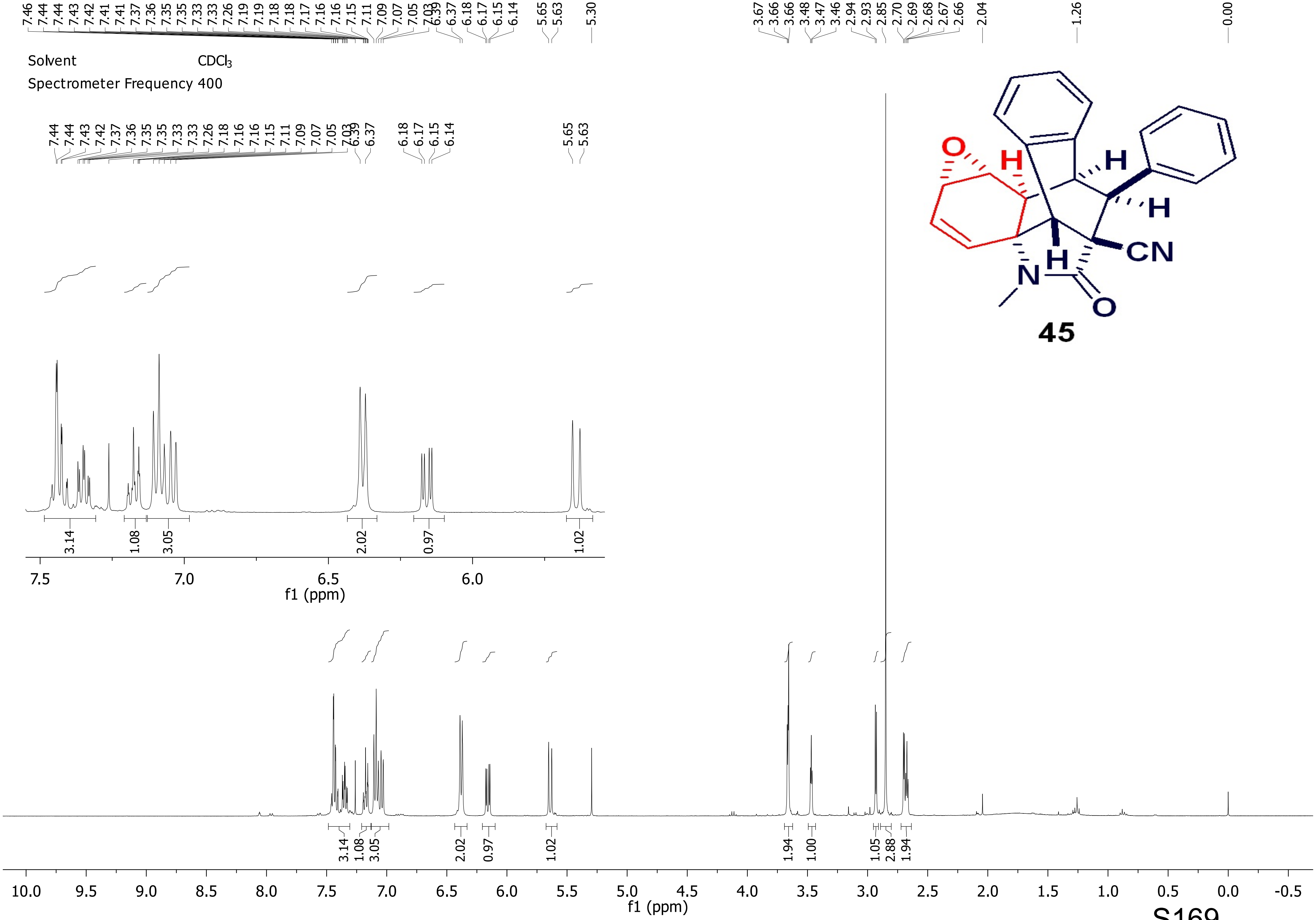

7.44
7.43
7.38
7.38
7.37
7.36
7.35
7.34
7.32
7.32
7.30
7.30
7.28
7.28
7.26
6.92
6.90
6.90
6.88
6.28
6.26
5.71
5.70
5.68
5.68
5.39
5.36
4.11
4.11
3.68
3.68
3.58
3.31
3.30
3.28
3.27
2.97
2.22
2.17
1.60
0.00
Solvent CDCl3
Spectrometer Frequency 400
7.44
7.43
7.37
7.36
7.32
7.30
7.30
7.26
6.92
6.90
6.90
6.88
6.28
6.26
5.71
5.70
5.68
5.68
5.39
5.36
0.99
2.12
2.83
1.93
0.99
1.04
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
f1 (ppm)
O
H
H
H
H
CN
N
O
43'
0.99
2.12
2.83
1.93
0.99
1.04
0.99
0.99
0.95
0.98
2.93
2.55
2.83
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

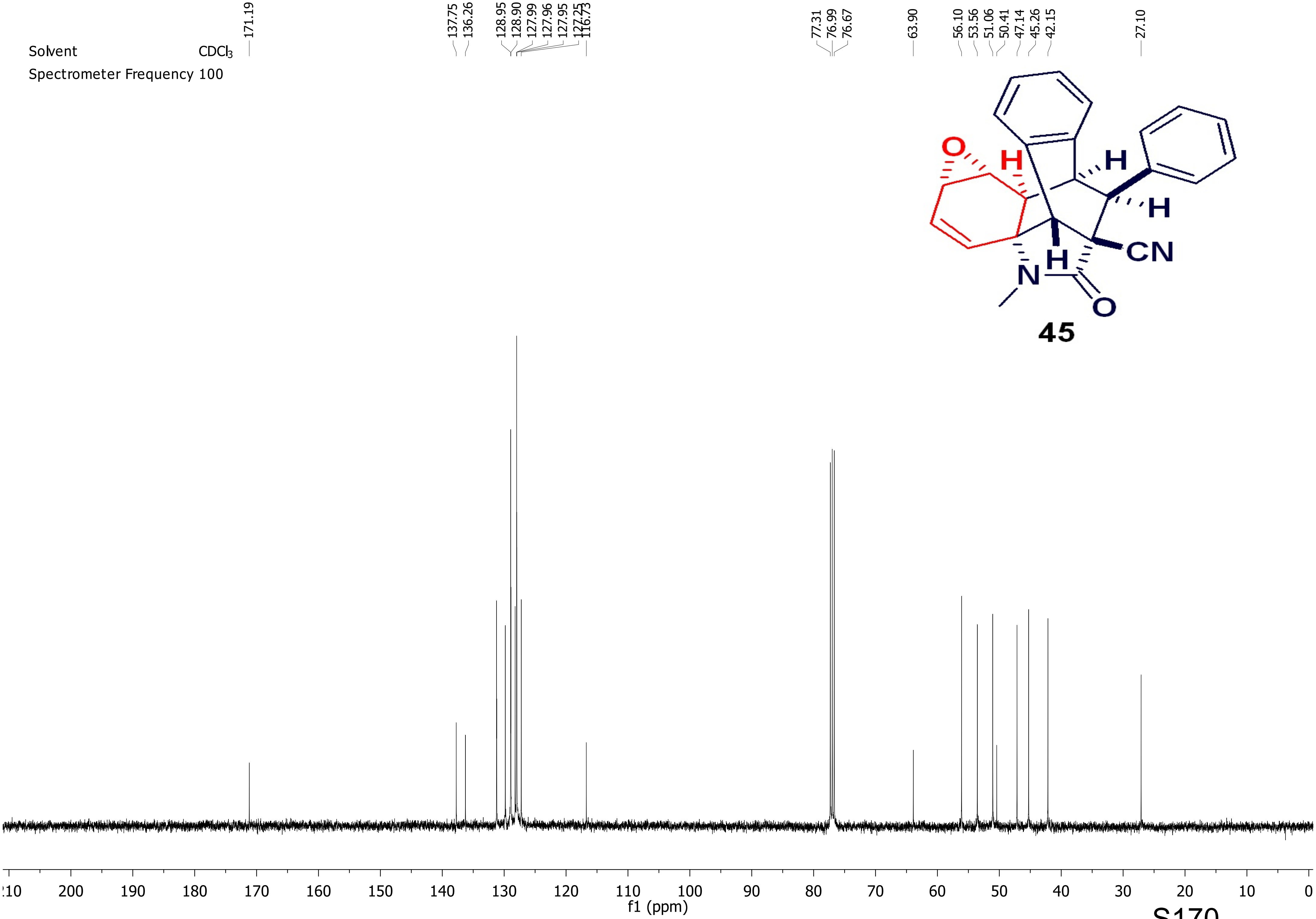

171.43
150.51
138.14
137.44
135.50
131.63
129.05
128.90
128.63
128.39
127.90
127.73
127.45
124.95
116.87
94.79
77.31
77.00
76.68
65.08
54.23
53.54
51.31
51.13
48.81
43.36
30.93
27.50
21.00
Solvent CDCl3
Spectrometer Frequency 100
O
H
H
H
H
CN
N
O
43'
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.51
7.49
7.44
7.43
7.42
7.42
7.40
7.40
7.35
7.35
7.33
7.33
7.32
7.31
7.26
7.16
7.14
7.13
7.12
7.12
7.12
7.08
7.07
7.06
7.04
7.04
6.96
6.94
6.40
6.38
6.37
3.60
3.59
3.55
3.15
3.14
3.13
3.04
2.83
2.05
2.05
2.04
2.03
2.02
2.02
1.75
1.74
1.73
1.73
1.71
1.71
1.45
1.44
1.42
0.43
0.42
0.40
0.38
0.00
Solvent CDCl3
Spectrometer Frequency 400
H
H
H
H
N
CN
O
44
1.00
1.05
1.09
1.09
2.11
1.06
2.08
0.17
0.18
0.12
0.13
0.97
0.92
1.15
2.89
0.39
0.14
1.05
2.71
5.46
0.12
0.14
0.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


Solvent CDCl$_3$
Spectrometer Frequency 100
171.19
138.63
138.19
138.10
129.03
128.04
127.92
127.74
127.56
117.21
77.31
76.99
76.67
63.14
54.23
53.89
51.85
51.80
51.31
48.79
48.67
43.60
42.25
27.10
26.77
26.12
24.91
22.90
19.45
17.39
H
H
H
H
N
CN
O
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

44


7.46 7.44 7.44 7.43 7.42 7.41 7.41 7.37 7.36 7.35 7.35 7.33 7.33 7.26 7.19 7.19 7.18 7.18 7.17 7.16 7.16 7.15 7.11 7.09 7.07 7.05 7.03 6.39 6.37 6.18 6.17 6.15 6.14 5.65 5.63 5.30
3.67 3.66 3.66 3.48 3.47 3.46 2.94 2.93 2.85 2.70 2.69 2.68 2.67 2.66 2.04 1.26 0.00
Solvent CDCl$_3$
Spectrometer Frequency 400
7.44 7.44 7.43 7.42 7.37 7.36 7.35 7.35 7.33 7.33 7.26 7.18 7.16 7.16 7.15 7.11 7.09 7.07 7.05 7.03 6.39 6.37 6.18 6.17 6.15 6.14 5.65 5.63
3.14 1.08 3.05 2.02 0.97 1.02
7.5 7.0 6.5 6.0
f1 (ppm)
O
H
H
H
CN
H
N
O
45
3.14 1.08 3.05 2.02 0.97 1.02 1.94 1.00 1.05 2.88 1.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 100
171.19
137.75
136.26
128.95
128.90
127.99
127.96
127.95
127.25
116.73
77.31
76.99
76.67
63.90
56.10
53.56
51.06
50.41
47.14
45.26
42.15
27.10
O
H
H
H
H
CN
N
O
45
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: I

```
Bond precision:   C-C = 0.0017 A           Wavelength=0.71073

Cell:             a=10.5120(2)     b=11.1768(2)       c=15.6769(2)
                  alpha=90         beta=92.894(2)     gamma=90
Temperature:      113 K

                 Calculated                   Reported
Volume           1839.54(5)                   1839.54(5)
Space group      P 21/c                       P 1 21/c 1
Hall group       -P 2ybc                      -P 2ybc
Moiety formula   C25 H20 N2 O                 C25 H20 N2 O
Sum formula      C25 H20 N2 O                 C25 H20 N2 O
Mr               364.43                       364.43
Dx,g cm-3        1.316                        1.316
Z                4                            4
Mu (mm-1)        0.081                        0.081
F000             768.0                        768.0
F000'            768.29
h,k,lmax         12,13,18                     12,13,18
Nref             3243                         3243
Tmin,Tmax        0.981,0.984                  0.495,1.000
Tmin'            0.980

Correction method= # Reported T Limits: Tmin=0.495 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.000           Theta(max)= 25.000

                                                        wR2(reflections)=
R(reflections)= 0.0335( 2900)                           0.0827( 3243)

S = 1.066                   Npar= 254
```

```
The following ALERTS were generated. Each ALERT has the format
       test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         28 Report
PLAT005_ALERT_5_G No Embedded Refinement Details Found  in the CIF     Please Do !
PLAT230_ALERT_2_G Hirshfeld Test Diff for    C2       --C24      .        7.6 s.u.
PLAT793_ALERT_4_G Model has Chirality at C2          (Centro SPGR)          S Verify
PLAT793_ALERT_4_G Model has Chirality at C3          (Centro SPGR)          R Verify
PLAT793_ALERT_4_G Model has Chirality at C4          (Centro SPGR)          R Verify
PLAT793_ALERT_4_G Model has Chirality at C9          (Centro SPGR)          S Verify
PLAT793_ALERT_4_G Model has Chirality at C10         (Centro SPGR)          S Verify
PLAT793_ALERT_4_G Model has Chirality at C17         (Centro SPGR)          S Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............        960 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   0 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  10 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   6 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

---

checkCIF publication errors

Alert level A

```
PUBL004_ALERT_1_A  The contact author’s name and address are missing,
             _publ_contact_author_name and _publ_contact_author_address.
PUBL005_ALERT_1_A  _publ_contact_author_email, _publ_contact_author_fax and
             _publ_contact_author_phone are all missing.
            At least one of these should be present.
PUBL006_ALERT_1_A  _publ_requested_journal is missing
            e.g. ’Acta Crystallographica Section C’
PUBL008_ALERT_1_A  _publ_section_title is missing. Title of paper.
PUBL009_ALERT_1_A  _publ_author_name is missing. List of author(s) name(s).
PUBL010_ALERT_1_A  _publ_author_address is missing. Author(s) address(es).
PUBL012_ALERT_1_A  _publ_section_abstract is missing.
            Abstract of paper in English.
```

```
   7 ALERT level A = Data missing that is essential or data in wrong format
   0 ALERT level G = General alerts. Data that may be required is missing
```

Publication of your CIF

You should attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the nature of your study may justify the reported deviations from journal submission requirements and the more serious of these should be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. *checkCIF* was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

If level A alerts remain, which you believe to be justified deviations, and you intend to submit this CIF for publication in a journal, you should additionally insert an explanation in your CIF using the Validation Reply Form (VRF) below. This will allow your explanation to be considered as part of the review process.

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

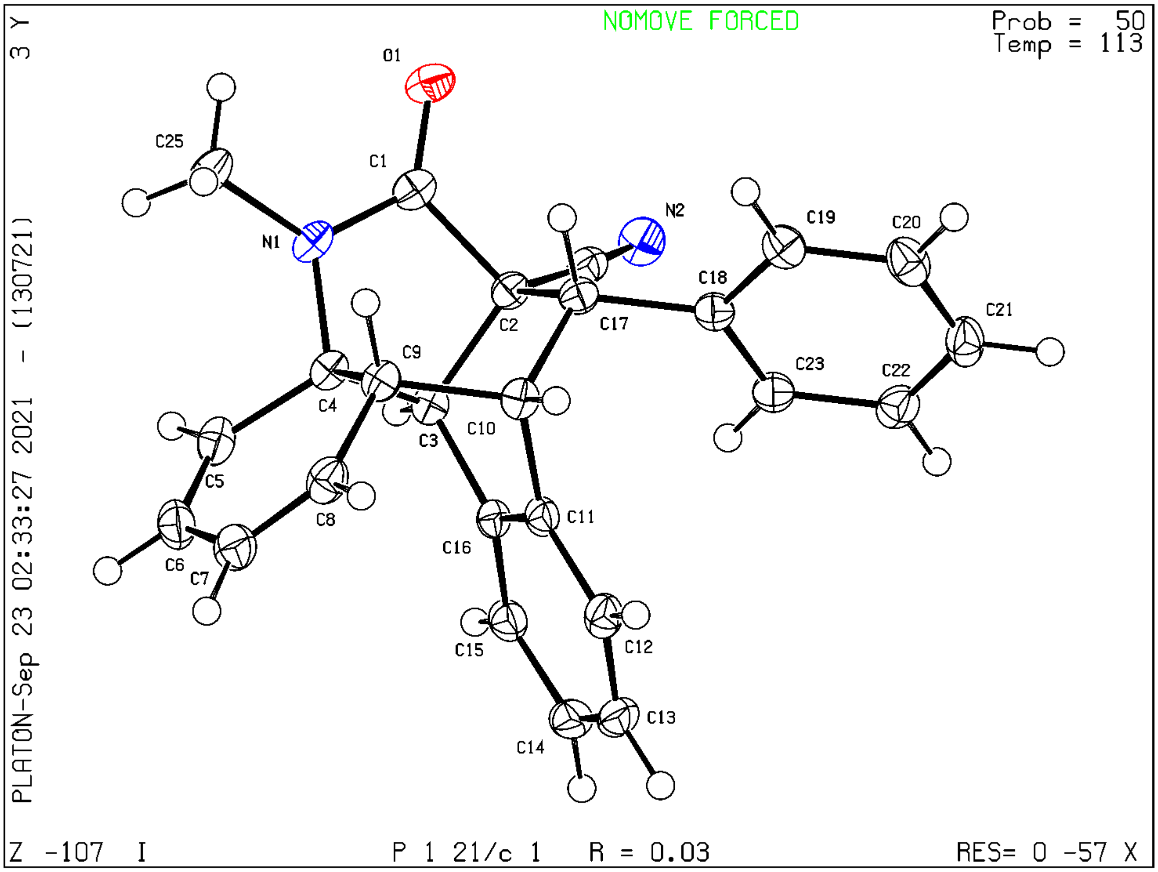
```
# start Validation Reply Form
_vrf_PUBL004_GLOBAL
;
PROBLEM: The contact author's name and address are missing,
RESPONSE: ...
;
_vrf_PUBL005_GLOBAL
;
PROBLEM: _publ_contact_author_email, _publ_contact_author_fax and
RESPONSE: ...
;
_vrf_PUBL006_GLOBAL
;
PROBLEM: _publ_requested_journal is missing
RESPONSE: ...
;
_vrf_PUBL008_GLOBAL
;
PROBLEM: _publ_section_title is missing. Title of paper.
RESPONSE: ...
;
_vrf_PUBL009_GLOBAL
;
PROBLEM: _publ_author_name is missing. List of author(s) name(s).
RESPONSE: ...
;
_vrf_PUBL010_GLOBAL
;
PROBLEM: _publ_author_address is missing. Author(s) address(es).
```

```
RESPONSE: ...
;
_vrf_PUBL012_GLOBAL
;
PROBLEM: _publ_section_abstract is missing.
RESPONSE: ...
;
# end Validation Reply Form
```

If you wish to submit your CIF for publication in Acta Crystallographica Section C or E, you should upload your CIF via the web. If you wish to submit your CIF for publication in IUCrData you should upload your CIF via the web. If your CIF is to form part of a submission to another IUCr journal, you will be asked, either during electronic submission or by the Co-editor handling your paper, to upload your CIF via our web site.

PLATON version of 13/07/2021; check.def file version of 13/07/2021

Datablock I - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) k11107-jjw-dtpg82_auto

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: k11107-jjw-dtpg82_auto

```
Bond precision:   C-C = 0.0021 A          Wavelength=0.71073

Cell:             a=10.3638(3)     b=11.3229(3)       c=16.6651(5)
                  alpha=90         beta=93.655(3)     gamma=90
Temperature:      113 K

                 Calculated                  Reported
Volume           1951.64(10)                 1951.64(10)
Space group      P 21/c                      P 1 21/c 1
Hall group       -P 2ybc                     -P 2ybc
Moiety formula   C26 H22 N2 O                C26 H22 N2 O
Sum formula      C26 H22 N2 O                C26 H22 N2 O
Mr               378.46                      378.45
Dx,g cm-3        1.288                       1.288
Z                4                           4
Mu (mm-1)        0.079                       0.079
F000             800.0                       800.0
F000'            800.30
h,k,lmax         12,13,19                    12,13,19
Nref             3441                        3383
Tmin,Tmax        0.984,0.988                 0.746,1.000
Tmin'            0.984

Correction method= # Reported T Limits: Tmin=0.746 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.983           Theta(max)= 24.999

                                                      wR2(reflections)=
R(reflections)= 0.0437( 2759)                         0.1206( 3383)

S = 1.097                  Npar= 265
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      2.195 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.595         58 Report
```

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         29 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          1 Report
PLAT793_ALERT_4_G Model has Chirality at C2          (Centro SPGR)          R Verify
PLAT793_ALERT_4_G Model has Chirality at C3          (Centro SPGR)          S Verify
PLAT793_ALERT_4_G Model has Chirality at C4          (Centro SPGR)          S Verify
PLAT793_ALERT_4_G Model has Chirality at C5          (Centro SPGR)          R Verify
PLAT793_ALERT_4_G Model has Chirality at C13         (Centro SPGR)          R Verify
PLAT793_ALERT_4_G Model has Chirality at C20         (Centro SPGR)          R Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints ............         984 Note
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        62% Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File          1 Note
PLAT967_ALERT_5_G Note: Two-Theta Cutoff Value in Embedded .res ..       50.0 Degree
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          6 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  13 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   3 ALERT type 2 Indicator that the structure model may be wrong or deficient
   4 ALERT type 3 Indicator that the structure quality may be low
   7 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

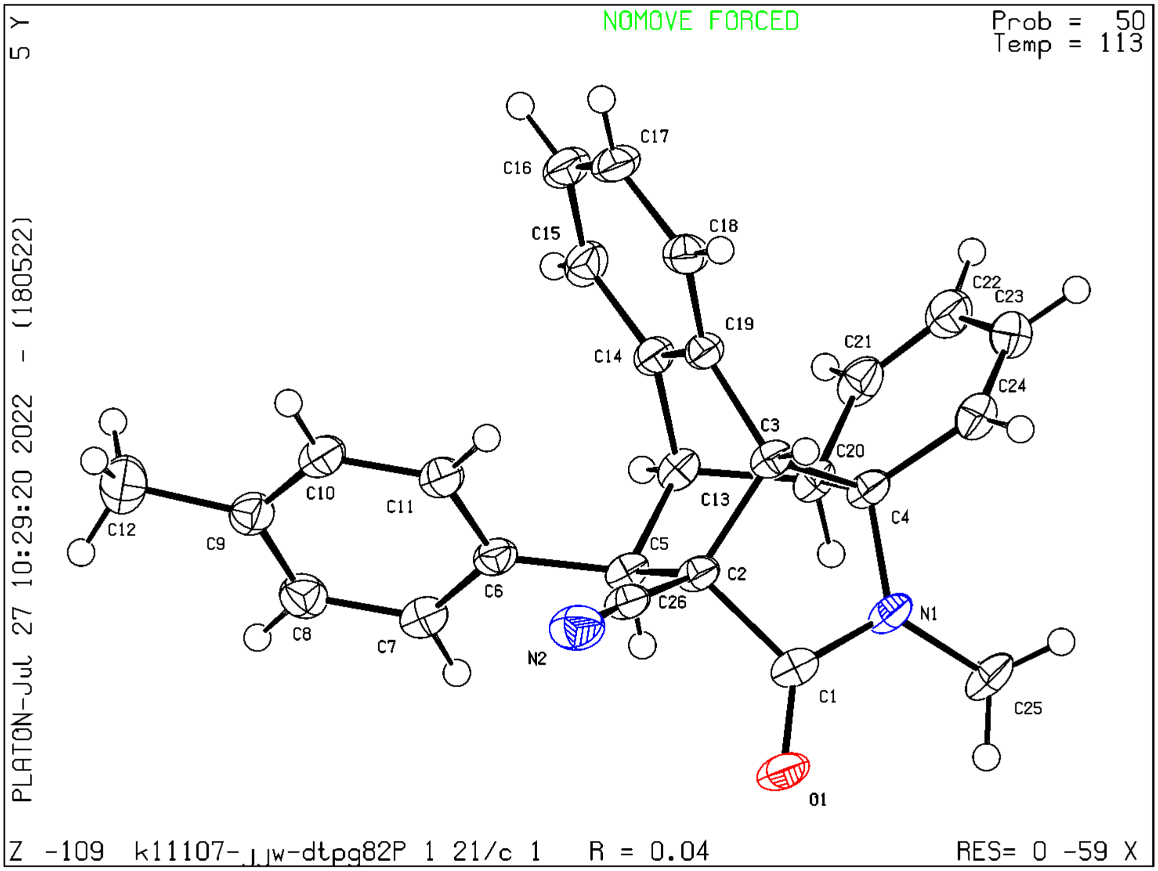
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 18/05/2022; check.def file version of 17/05/2022

Datablock k11107-jjw-dtpg82_auto - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) shelx

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: shelx

```
Bond precision:   C-C = 0.0030 A           Wavelength=0.71073

Cell:             a=10.5513(6)     b=10.5230(6)       c=22.0654(12)
                  alpha=90         beta=99.639(2)     gamma=90
Temperature:      200 K

                 Calculated                  Reported
Volume           2415.4(2)                   2415.4(2)
Space group      P 21/n                      P 21/n
Hall group       -P 2yn                      -P 2yn
Moiety formula   C27 H24 N2 O [+ solvent]    C27 H24 N2 O
Sum formula      C27 H24 N2 O [+ solvent]    C27 H24 N2 O
Mr               392.48                      392.48
Dx,g cm-3        1.079                       1.079
Z                4                           4
Mu (mm-1)        0.066                       0.066
F000             832.0                       832.0
F000'            832.31
h,k,lmax         12,12,26                    12,12,26
Nref             4292                        4280
Tmin,Tmax        0.984,0.998                 0.983,0.998
Tmin'            0.983

Correction method= # Reported T Limits: Tmin=0.983 Tmax=0.998
AbsCorr = MULTI-SCAN

Data completeness= 0.997           Theta(max)= 25.070

                                                        wR2(reflections)=
R(reflections)= 0.0557( 3779)                           0.1635( 4280)

S = 1.091                  Npar= 273
```

The following ALERTS were generated. Each ALERT has the format
      test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
ABSTY02_ALERT_1_C  An _exptl_absorpt_correction_type has been given without
            a literature citation. This should be contained in the
            _exptl_absorpt_process_details field.
            Absorption correction given as multi-scan
SHFSU01_ALERT_2_C  The absolute value of parameter shift to su ratio > 0.05
            Absolute value of the parameter shift to su ratio given   0.071
            Additional refinement cycles may be required.
PLAT080_ALERT_2_C Maximum Shift/Error ............................       0.07 Why ?
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      2.518 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.596         10 Report
               1  2  0,  -1  1  1,  -2  1  2,  -1  1  2,  -1  0  3,   0  1  3,
               0  1  4,   0  2  5,  -3  3  8,   7  1 19,
PLAT913_ALERT_3_C Missing # of Very Strong Reflections in FCF ....          4 Note
              -1  1  1,   0  0  2,  -2  1  2,   0  1  4,
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) .          2 Check
```

Alert level G

```
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical          ? Check
PLAT230_ALERT_2_G Hirshfeld Test Diff for    C19      --C20      .        5.3 s.u.
PLAT605_ALERT_4_G Largest Solvent Accessible VOID in the Structure        205 A**3
PLAT793_ALERT_4_G Model has Chirality at C3          (Centro SpGr)          R Verify
PLAT793_ALERT_4_G Model has Chirality at C10         (Centro SpGr)          S Verify
PLAT793_ALERT_4_G Model has Chirality at C11         (Centro SpGr)          S Verify
PLAT793_ALERT_4_G Model has Chirality at C18         (Centro SpGr)          R Verify
PLAT793_ALERT_4_G Model has Chirality at C19         (Centro SpGr)          S Verify
PLAT793_ALERT_4_G Model has Chirality at C21         (Centro SpGr)          S Verify
PLAT869_ALERT_4_G ALERTS Related to the Use of SQUEEZE  Suppressed          ! Info
PLAT883_ALERT_1_G Absent Datum for _atom_sites_solution_primary ..     Please Do !
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        74% Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          2 Note
              -1  0  1,   0  0  2,
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File          5 Note
               0  0  2,  -1  0  1,   0  1  3,  -1  1  2,   1  2  0,
PLAT969_ALERT_5_G The ’Henn et al.’ R-Factor-gap value ...........      4.520 Note
              Predicted wR2: Based on SigI**2  3.62 or SHELX Weight 15.06
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          9 Info
```

---

   0 **ALERT level A** = Most likely a serious problem - resolve or explain
   0 **ALERT level B** = A potentially serious problem, consider carefully
   7 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
  16 **ALERT level G** = General information/check it is not something unexpected

   3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   5 ALERT type 2 Indicator that the structure model may be wrong or deficient
   6 ALERT type 3 Indicator that the structure quality may be low
   8 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

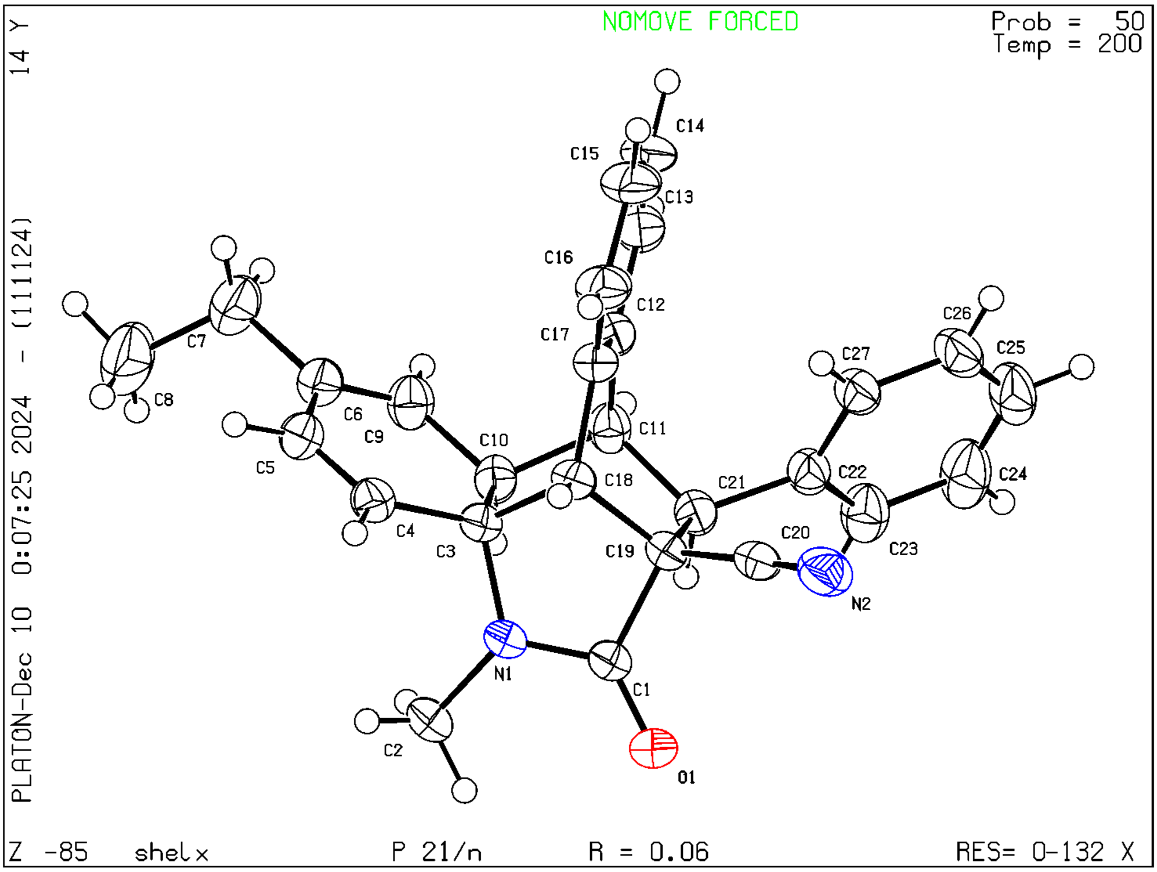
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 11/11/2024; check.def file version of 11/11/2024

Datablock shelx - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) k11111-jjw-btpb-83_auto

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: k11111-jjw-btpb-83_auto

```
Bond precision:   C-C = 0.0020 A          Wavelength=0.71073

Cell:             a=10.3481(3)     b=11.4470(3)       c=15.7580(4)
                  alpha=90         beta=92.878(2)     gamma=90
Temperature:      130 K

                 Calculated                    Reported
Volume           1864.26(9)                    1864.25(9)
Space group      P 21/c                        P 1 21/c 1
Hall group       -P 2ybc                       -P 2ybc
Moiety formula   C25 H20 N2 O2                 C25 H20 N2 O2
Sum formula      C25 H20 N2 O2                 C25 H20 N2 O2
Mr               380.43                        380.43
Dx,g cm-3        1.355                         1.355
Z                4                             4
Mu (mm-1)        0.087                         0.087
F000             800.0                         800.0
F000'            800.33
h,k,lmax         12,13,18                      12,13,18
Nref             3283                          3284
Tmin,Tmax        0.990,0.991                   0.785,1.000
Tmin'            0.974

Correction method= # Reported T Limits: Tmin=0.785 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.000           Theta(max)= 24.997

                                                 wR2(reflections)=
R(reflections)= 0.0392( 2857)                    0.1036( 3284)

S = 1.090                  Npar= 263
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

● Alert level G

```
PLAT230_ALERT_2_G Hirshfeld Test Diff for    C2       --C24      .        6.4 s.u.
PLAT398_ALERT_2_G Deviating  C-O-C   Angle From 120 for O2       .       60.3 Degree
PLAT793_ALERT_4_G Model has Chirality at C2          (Centro SPGR)          S Verify
PLAT793_ALERT_4_G Model has Chirality at C3          (Centro SPGR)          R Verify
PLAT793_ALERT_4_G Model has Chirality at C4          (Centro SPGR)          S Verify
PLAT793_ALERT_4_G Model has Chirality at C7          (Centro SPGR)          S Verify
PLAT793_ALERT_4_G Model has Chirality at C8          (Centro SPGR)          R Verify
PLAT793_ALERT_4_G Model has Chirality at C9          (Centro SPGR)          S Verify
PLAT793_ALERT_4_G Model has Chirality at C10         (Centro SPGR)          S Verify
PLAT793_ALERT_4_G Model has Chirality at C11         (Centro SPGR)          S Verify
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        72% Note
PLAT967_ALERT_5_G Note: Two-Theta Cutoff Value in Embedded .res ..       50.0 Degree
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         12 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   0 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  13 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   3 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   8 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

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Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 12/09/2022; check.def file version of 09/08/2022

Datablock k11111-jjw-btpb-83_auto - ellipsoid plot