

SUPPORTING INFORMATION

SYNTHESIS, CHARACTERIZATION AND INSECTICIDAL EVALUATION OF SOME p-TERT-BUTYLTHIACALIX[4]ARENE DERIVATIVES AGAINST COWPEA APHID, APHIS CRACCIVORA (KOCH)

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1. General Information:

All commercially available reagents were purchased from Merck, Aldrich and Fluka and were used without further purification. All reactions were monitored by thin layer chromatography (TLC) using precoated plates of silica gel G/UV-254 of 0.25 mm thickness (Merck 60F254) using UV light (254 nm/365 nm) for visualization. Melting points were detected with a Kofler melting points apparatus and uncorrected. Infrared spectra were recorded with a FT-IR-ALPHABROKER-Platinum-ATR spectrometer and are given as cm^{-1} using the attenuated total reflection (ATR) method. ^1H NMR and ^{13}C NMR spectra for all compounds were recorded in $\text{DMSO}-d_6$ on a Bruker Bio Spin AG spectrometer at 400 MHz and 100 MHz, respectively. For ^1H NMR, chemical shifts (δ) were given in parts per million (ppm) with reference to tetramethylsilane (TMS) as an internal standard ($\delta=0$); coupling constants (J) were given in hertz (Hz) and data are reported as follows: chemical shift, integration, multiplicity (s=singlet, d=doublet, t= triplet, q=quartet, m=multiplet, dd=doublet of doublets). For ^{13}C NMR, TMS ($\delta=0$) or DMSO ($\delta=39.51$) was used as internal standard and spectra were obtained with complete proton decoupling. Elemental analyses were obtained on a Perkin-Elmer CHN-analyzer model. For microwave irradiations were carried out in a Kenstar OM9925E MW oven (2450 MHz, 800 W).

2. General procedure for the Synthesis of compounds 2a-c:

A mixture of *p-tert*-butylthiacalix[4]arene tetrahydrazides **1a**, **1b** or **1c** and dimethylformamide dimethyl acetal (DMF DMA) in 30 mL dioxane as a solvent. The reaction mixture was refluxed for 4 h concentrated to 15 mL and left to cool for one hour. The white precipitate was filtered, dried then weighted and the yield calculated ranged from 85-95%.

Synthesis of 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis[N,N-dimethyl-N'-(2-oxyethanethioyl)formohydrazonamide]-2,8,14,20-tetrathiacalix[4]arene 3a-c (general methods).

A mixture of 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis [N,N-dimethyl-N'-(2-oxyacetyl)-formohydrazonamide]-2,8,14,20-tetrathiacalix[4]arene **2a** (0.5g, 0.41mmol) with Lawesson's reagent (0.58 g, 4.95 mmol) in 40 ml chloroform, has been refluxed for 24 h. The mixture was concentrated almost to dryness, 50 ml of water was added and was stirred for 2h. The white solid product was separated and filtered. The product was purified by chromatography using CH₂Cl₂ / CH₃CH₂OH mixture (100:1) volume percent. The yield calculated ranged from 90%.

3a, *cone*, yield 80%; white powder; Mp 270 °C, IR (KBr, v/cm⁻¹): 3420 (NH), 3090.5, 2962 (C-H aliph.). ¹H NMR (400 MHz, DMSO) δ: 1.33 (s, 36H, Bu^t), 3.81(s, 24H, N(CH₃), 5.75 (s, 8H, OCH₂CS), 7.01 (s, 8H, ArH), 7.74 (s, 4H, N=CH), 9.65(s, 4H, CSNH). ¹³C NMR (100 MHz, CDCl₃) δ: 30.75, 31.32, 34.13, 55.37, 113.49, 113.65, 132.72, 133.21, 162.26, 163.11.

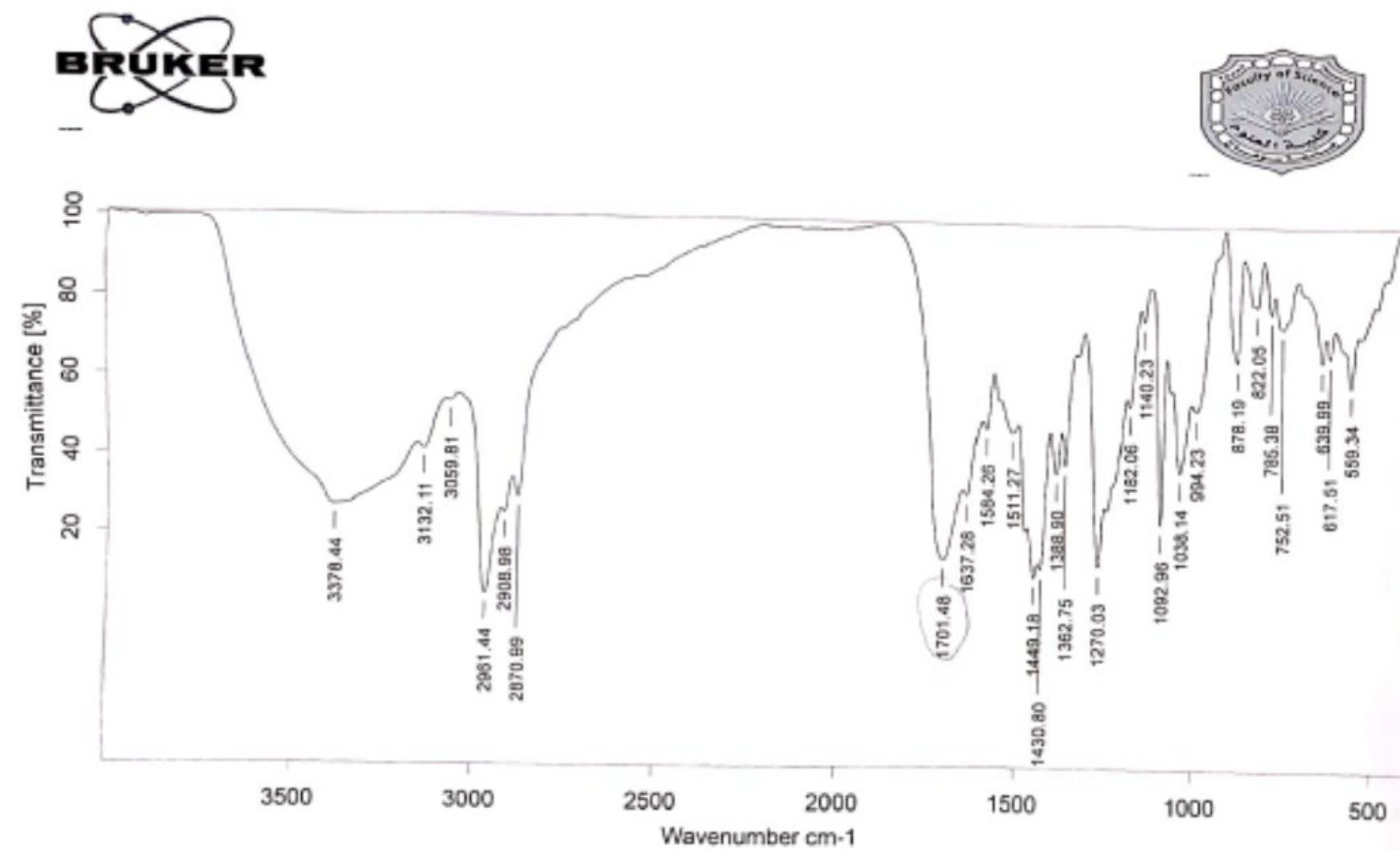
Synthesis of 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis[N,N-dimethyl-N'-(2-oxyethanethioyl)formohydrazonamide]-2,8,14,20-tetrathiacalix[4]arene 3a and b (general methods).

A mixture of 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis [N,N-dimethyl-N'-(2-oxyacetyl)-formohydrazonamide]-2,8,14,20-tetrathiacalix[4]arene **2b** or **2c** (0.5g, 0.41mmol) with Lawesson's reagent (0.58 g, 4.95 mmol) in 40 ml chloroform, has been refluxed for 24 h. The mixture was concentrated approximately to dryness then 50 ml of methanol was added. The white solid product was separated, filtrated and washed with methanol. The product was left to dry overnight then weighted and the yield calculated ranged from 80-90%.

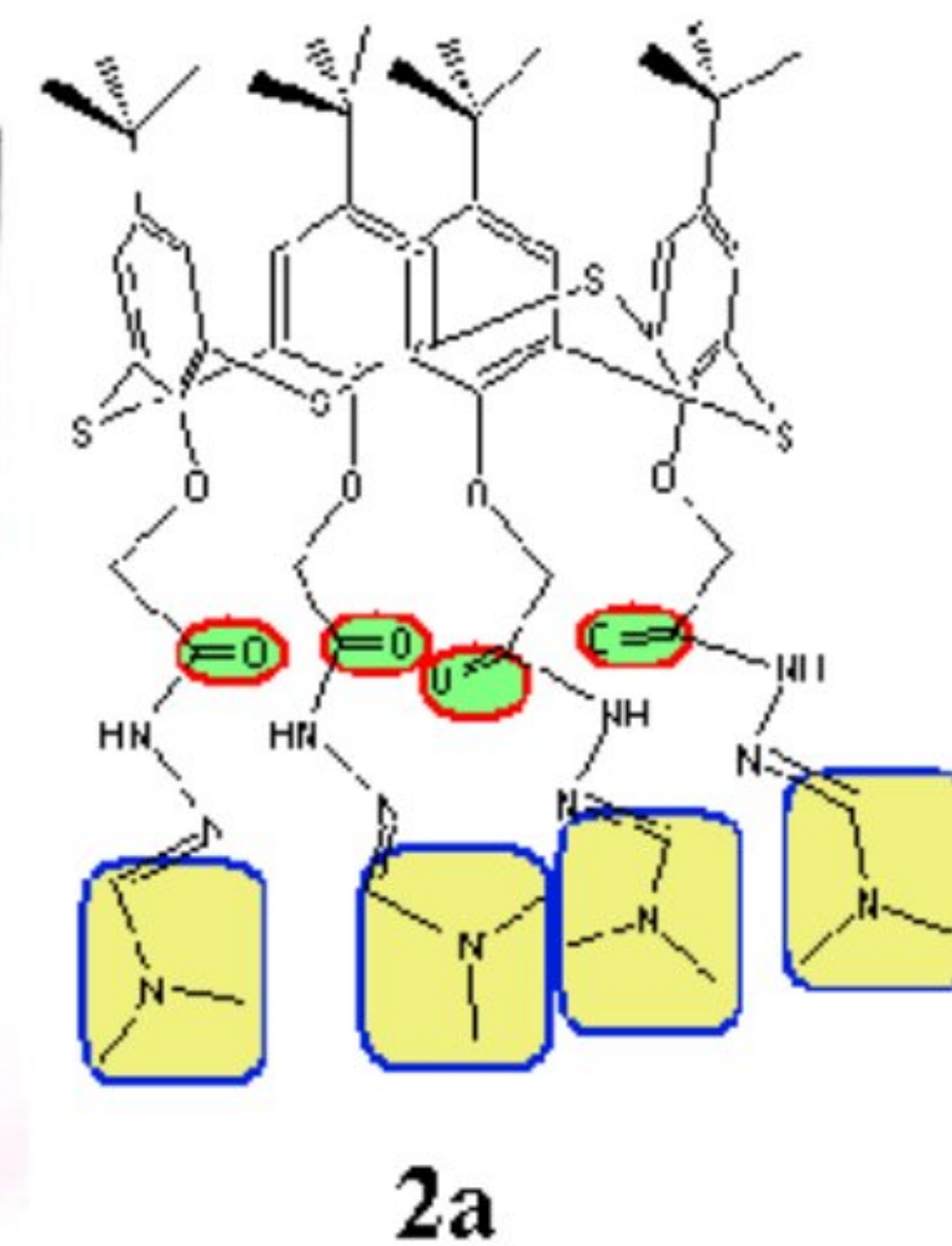
3b, *partial-cone*, white powder; Mp: 130 °C. IR (KBr, ν/cm^{-1}): 3426 (NH), 3067.47, 2962 (CO), 1262 (COC). ^1H NMR (400 MHz, CDCl_3) δ : 0.97 (s, 18H, Bu^t), 1.15 (s, 9H, Bu^t), 1.37 (s, 9H, Bu^t), 2.75-2.89(m, 18, $3\text{N}(\text{CH}_3)_2$), 3.73-3.85(m, 6H, $\text{N}(\text{CH}_3)_2$), 5.43(s, 4H, $2\text{OCH}_2\text{CS}$), 5.56-5.60(d, 2H, OCH_2CS), 5.63-5.67(d, 2H, OCH_2CS), 6.92-7.97 (m, 8H, ArH + 4H, N=CH), 8.59(s, 1H, CSNH), 9.00(s, 1H, CSNH), 9.24(s, 1H, CSNH). ^{13}C NMR (100 MHz, CDCl_3) δ : 30.94, 31.16, 31.49, 34.17, 34.45, 34.57, 55.32, 64.31, 68.96, 113.62, 127.15, 128.43, 129.14, 129.29, 130.12, 131.03, 132.72, 135.33, 135.69, 148.31, 148.47, 152.02, 153.83, 154.16, 154.93, 157.27, 157.85, 164.63, 165.96, 167.00.

3c, *1,3-alternate*, white powder; Mp: 265 °C. IR (KBr, ν/cm^{-1}): 3421 (NH), 3090.5, 1233 (COC). ^1H NMR (400 MHz, DMSO) δ : 0.94 (s, 36H, Bu^t), 2.09(s, 24H, $4\text{N}(\text{CH}_3)_2$), 5.42 (s, 8H, OCH_2CS), 7.17 (s, 8H, ArH), 8.30 (s, 4H, N=CH), 9.46 (s, 4H, CSNH). ^{13}C NMR (100 MHz, CDCl_3) δ : 29.65, 30.97, 34.25, 65.06, 127.98, 128.53, 148.33, 153.70, 155.55, 166.00.

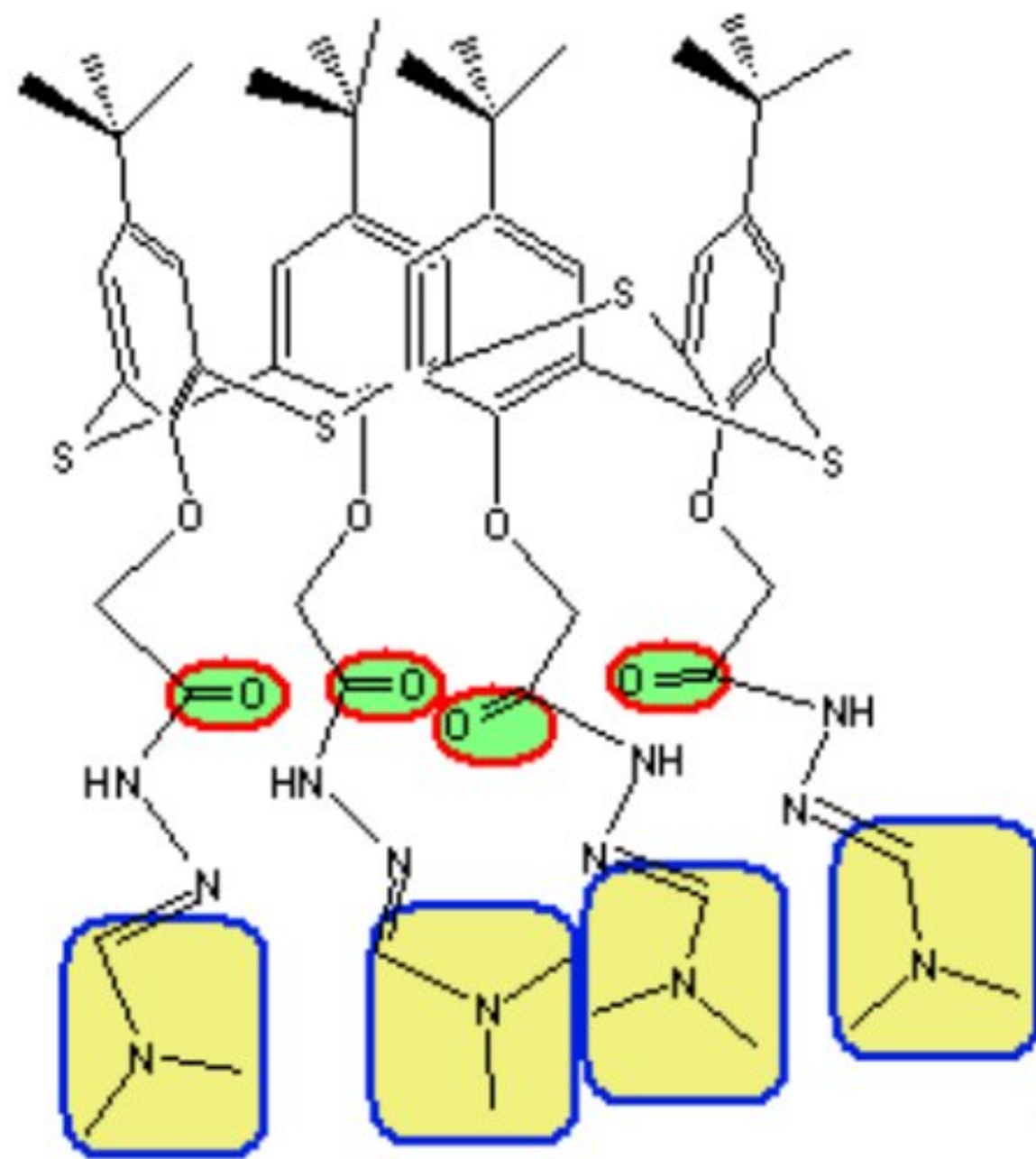
3.1- IR, ¹H and ¹³C-NMR Spectra of Compound 2a:-



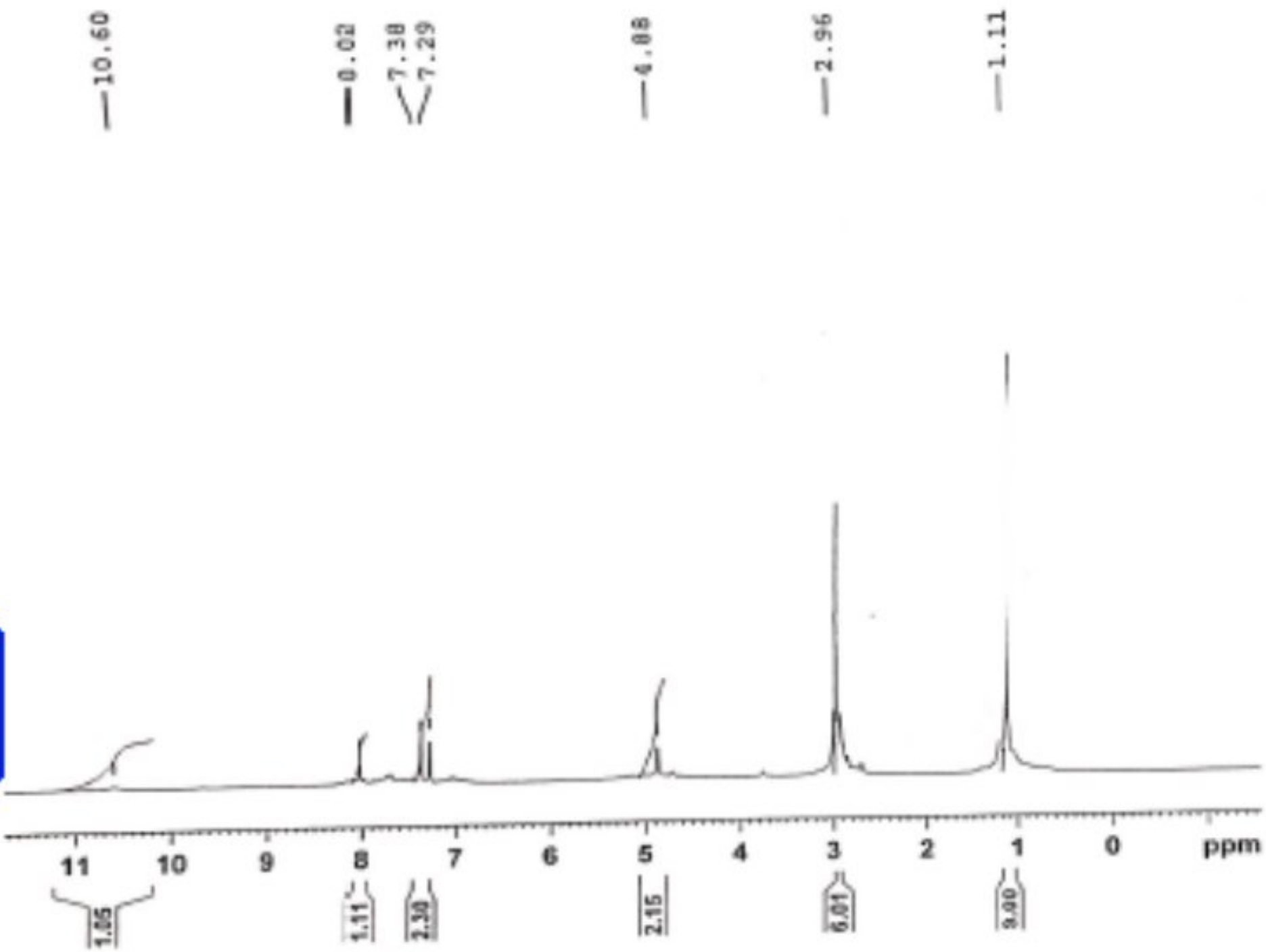
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OM-39
proton_su CDCl3 (C:\nmr-data) Student 21



2a



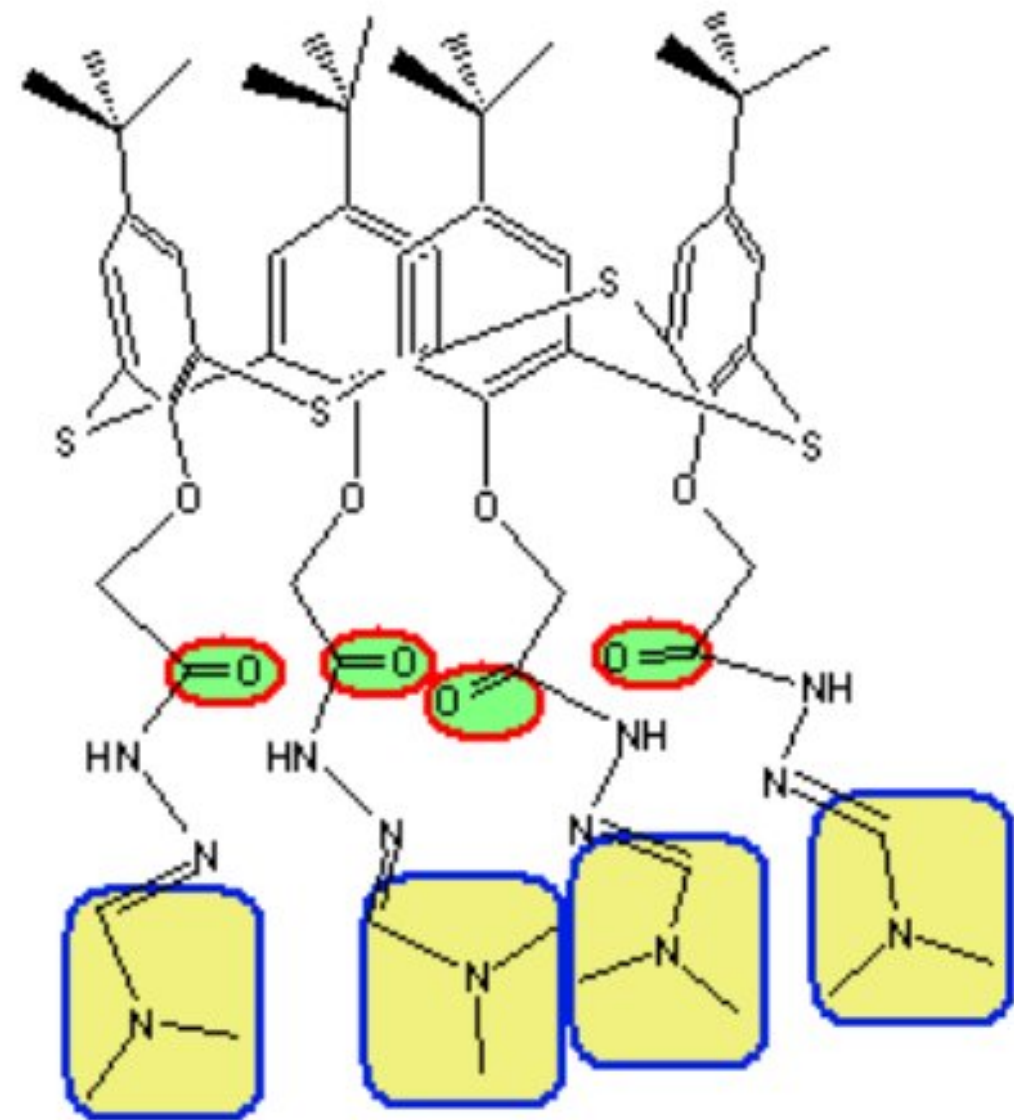
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PROCNO 1

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SOLVENT CDCl3
NS 20
DS 2
SWH 8012.820 Hz
FIDRES 0.122166 Hz
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D1 1.00000000 sec
TDR 1

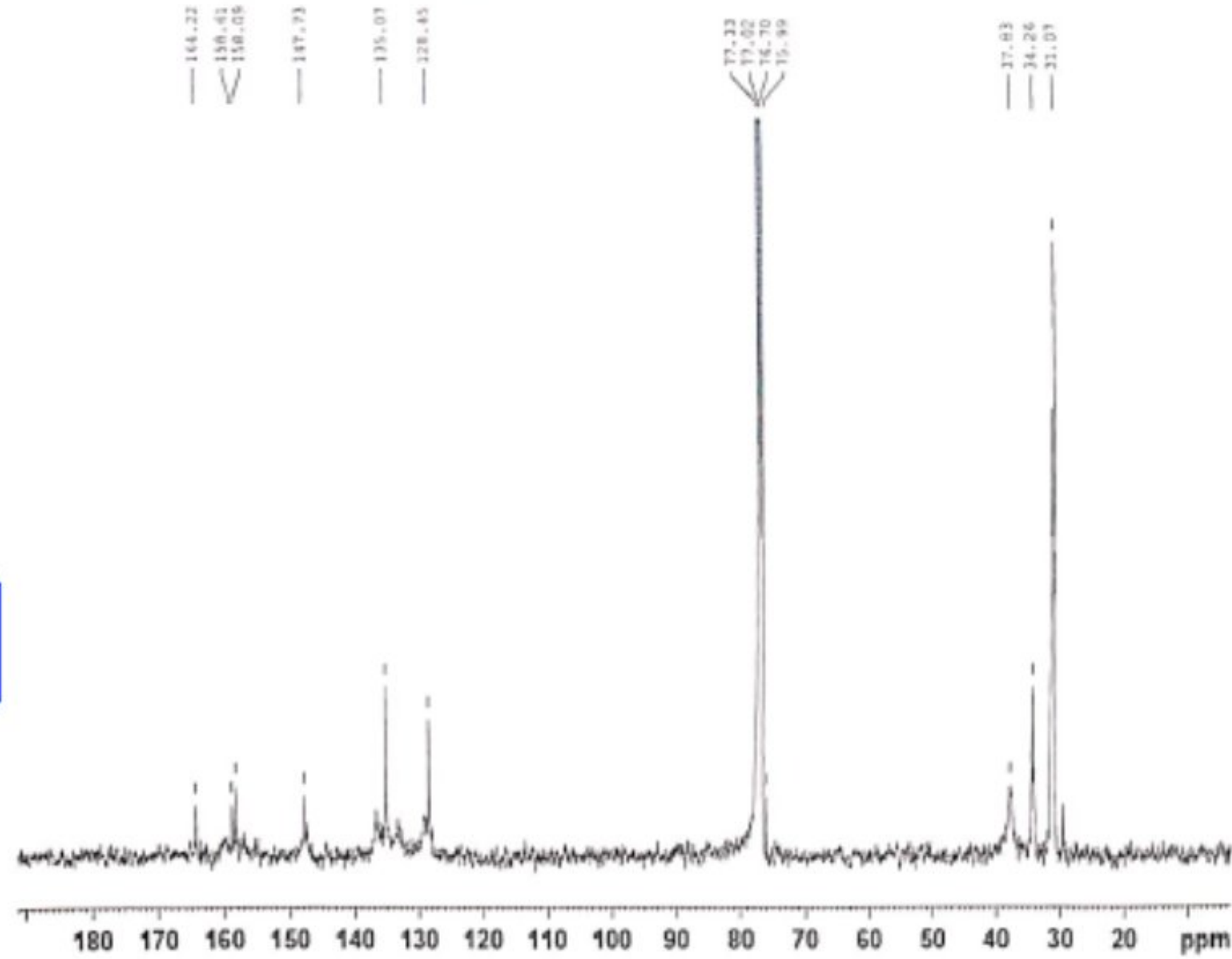
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PL1 12.00 dB
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F2 - Processing parameters
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OK-64
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2a



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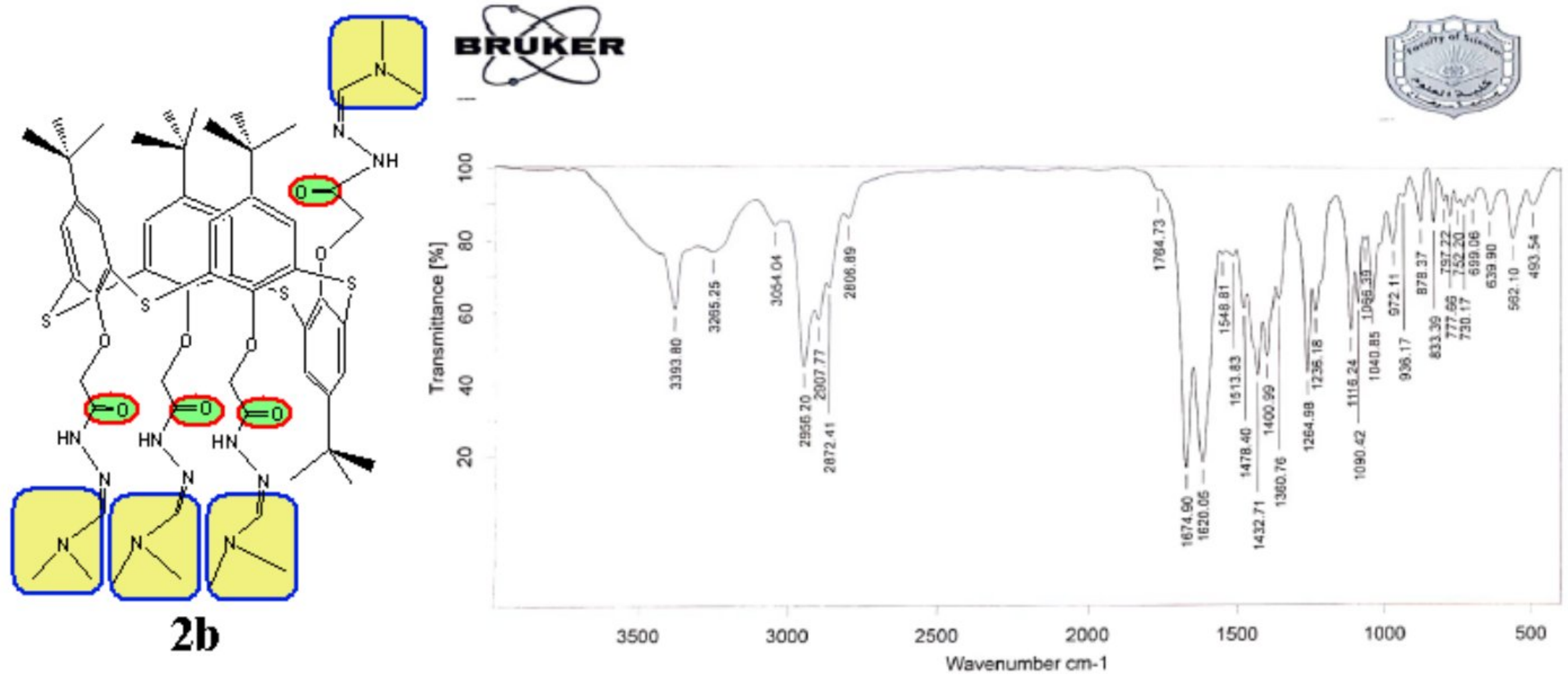
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 FIDRES 0.366798 Hz
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 DE 6.50 usec
 TE 308.1 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TDD 1

----- CHANNEL f1 -----
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 P1 9.50 usec
 PLW1 56.0000000 W

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 PLW13 0.33284000 W

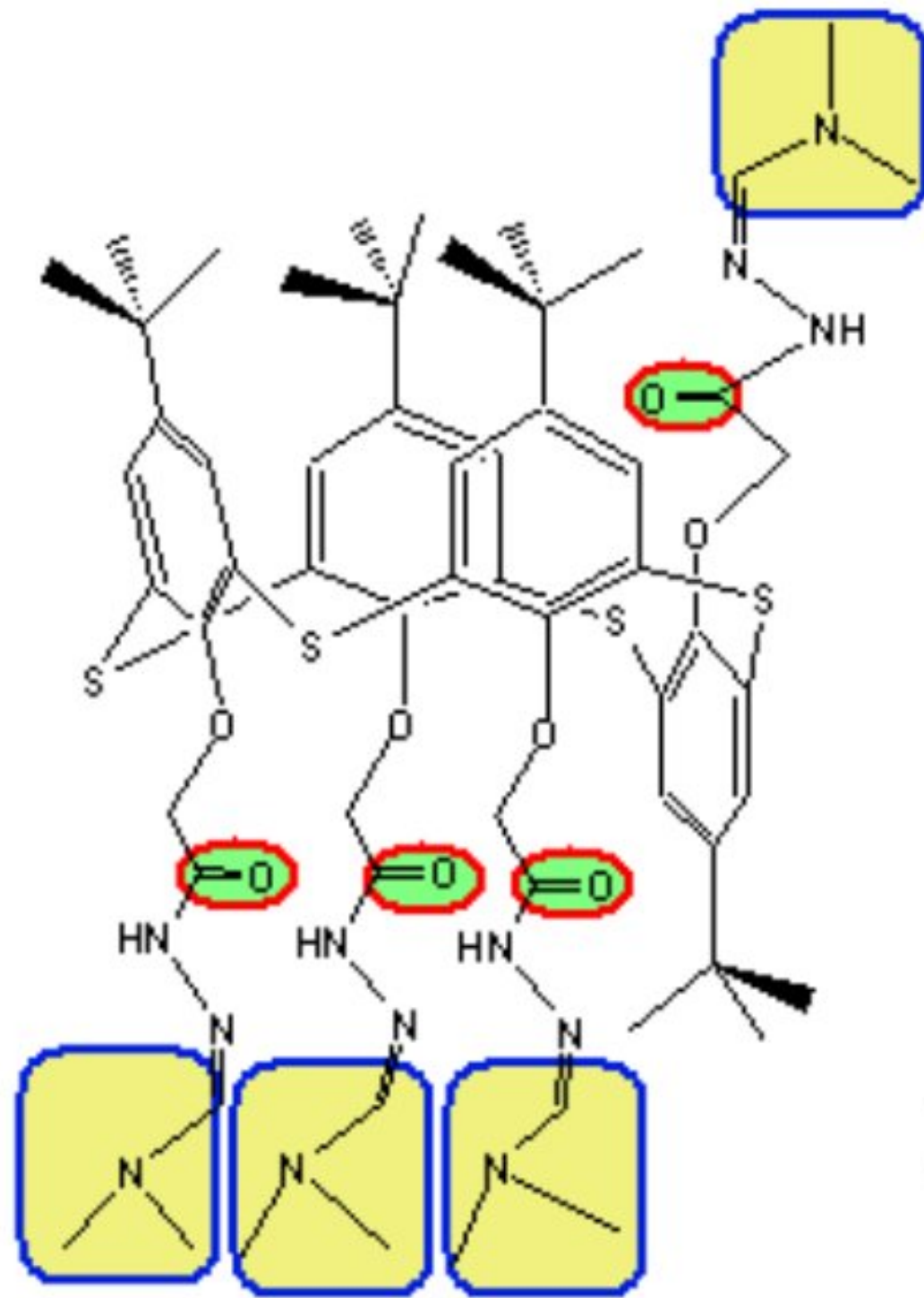
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3.2. IR, ¹H and ¹³C-NMR Spectra of Compound 2b:-

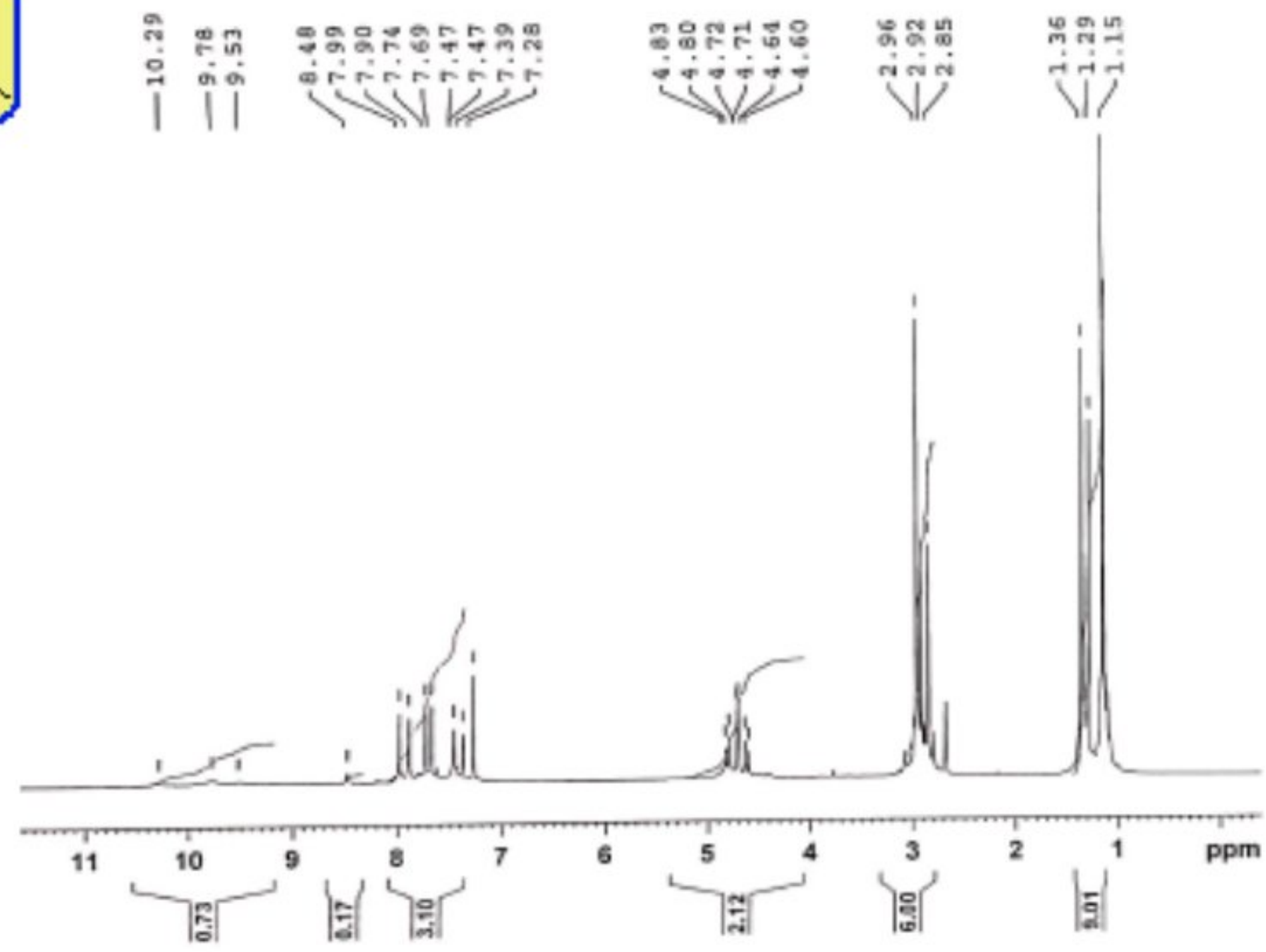


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OM-40
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2b



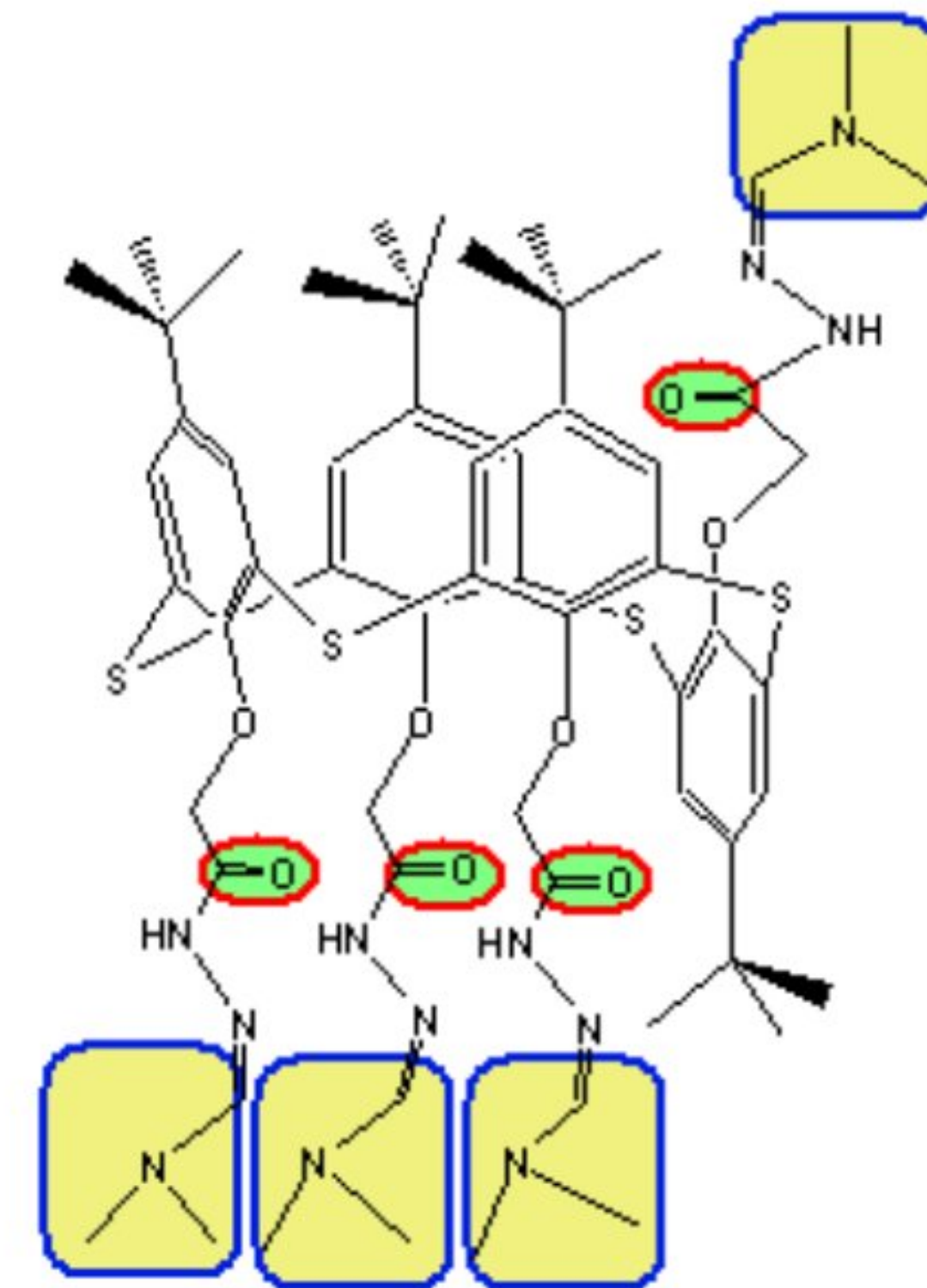
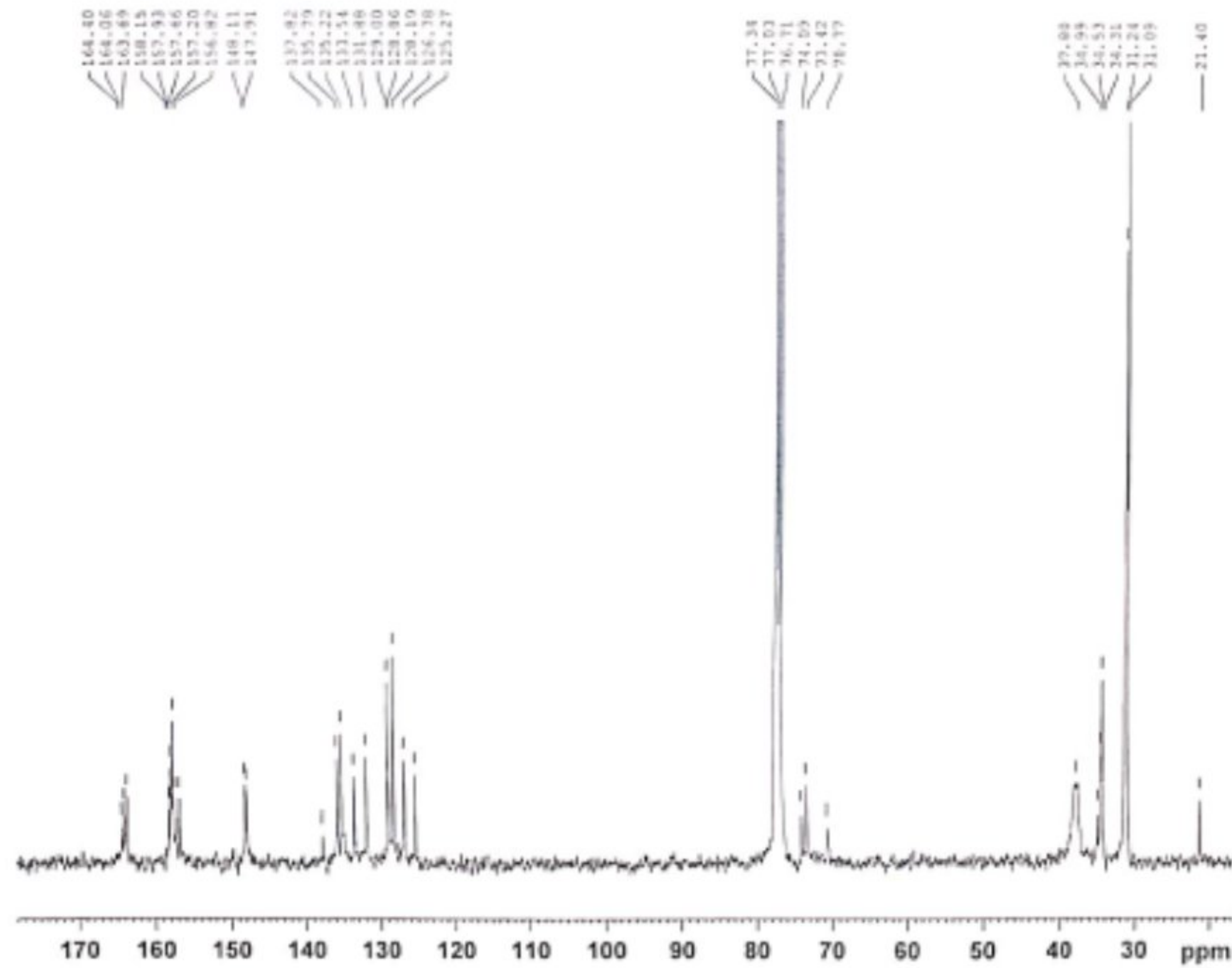
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 DS 2
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 FIDRES 0.122264 Hz
 AQ 4.029445 sec
 RG 335
 INW 62.480 usec
 DE 6.50 usec
 VE 388.2 K
 DO 1.0000000 sec
 CDE 1

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 NUC1 1H
 P1 12.00 usec
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 VC 1.88

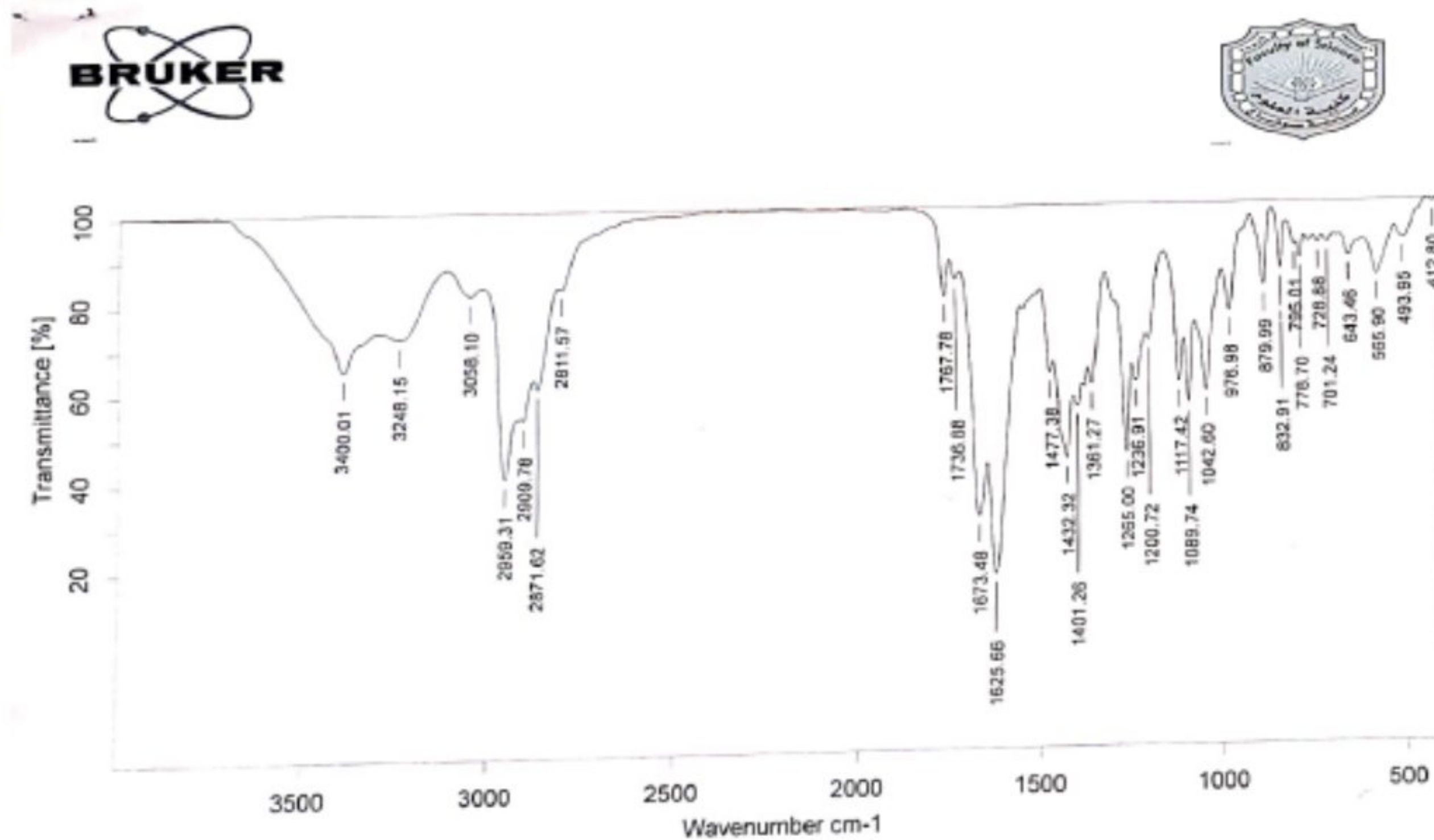
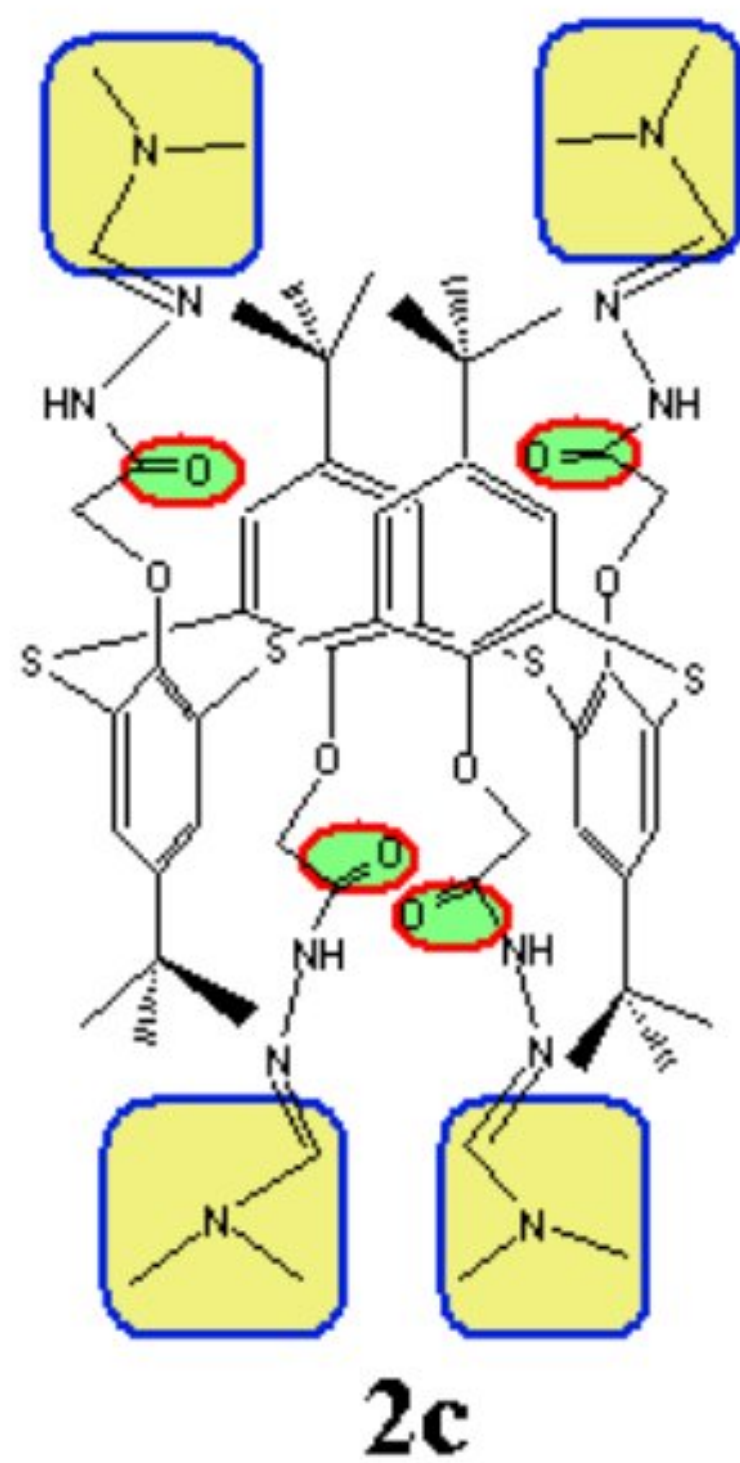
OM-33
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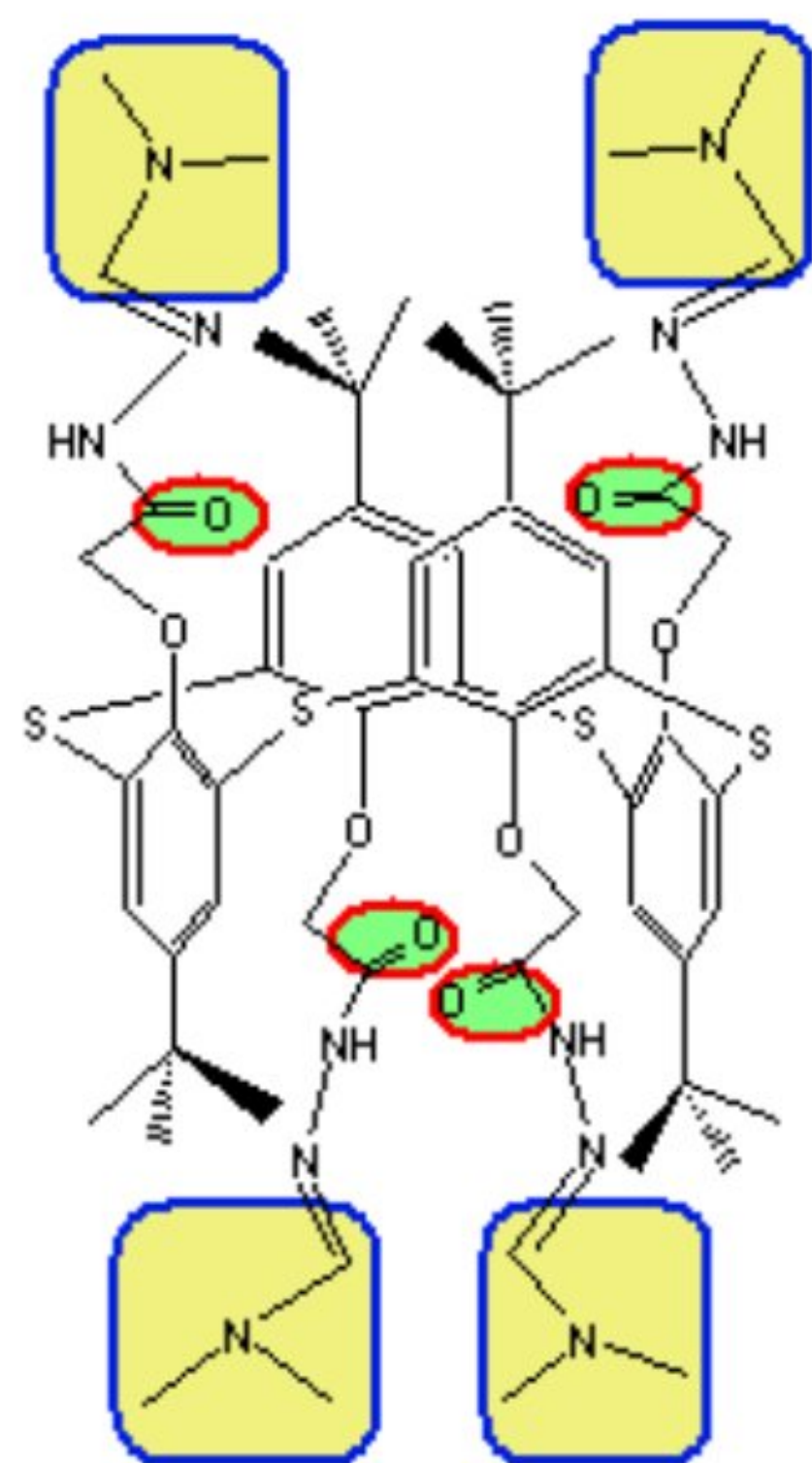
2b

F2 - Processing parameters
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 GB 0
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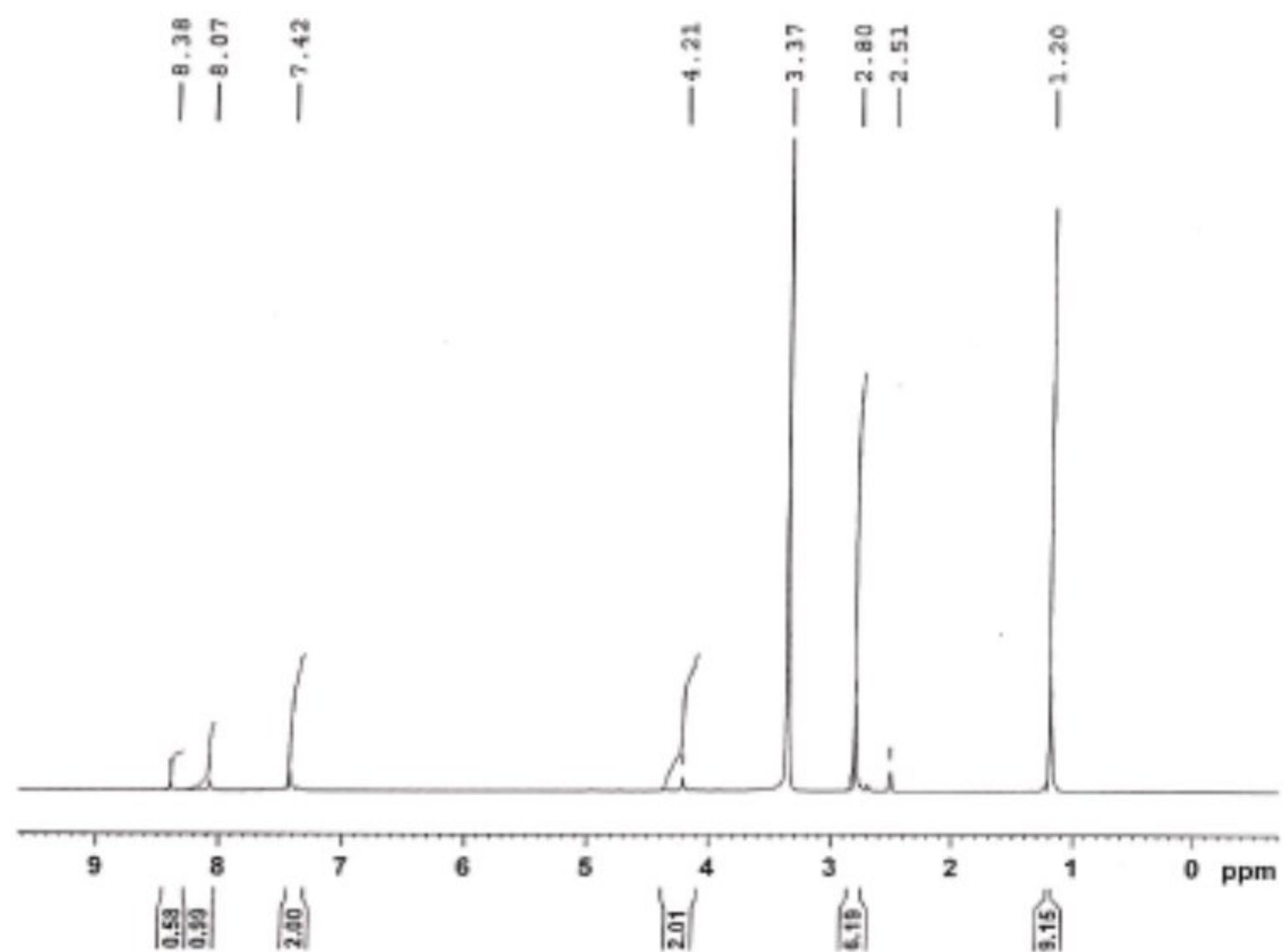


Sample Name: OM-30



2c

on-47
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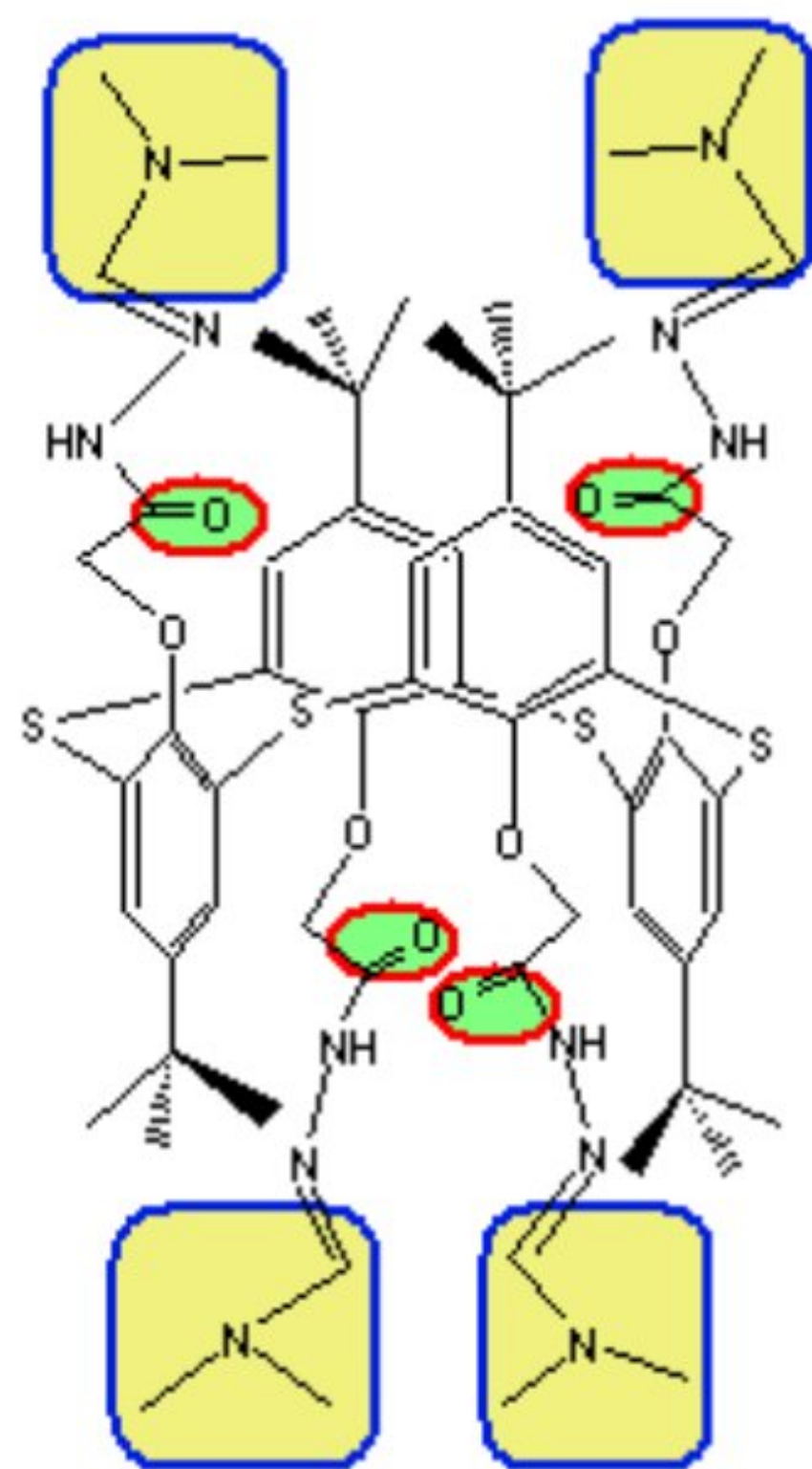
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PROCNO   1

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PULPROG  zgpg
TD        65536
SOLVENT  DMSO
NS        20
DS        2
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FIDRES    0.122266 Hz
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RG         69.22
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TD0       1

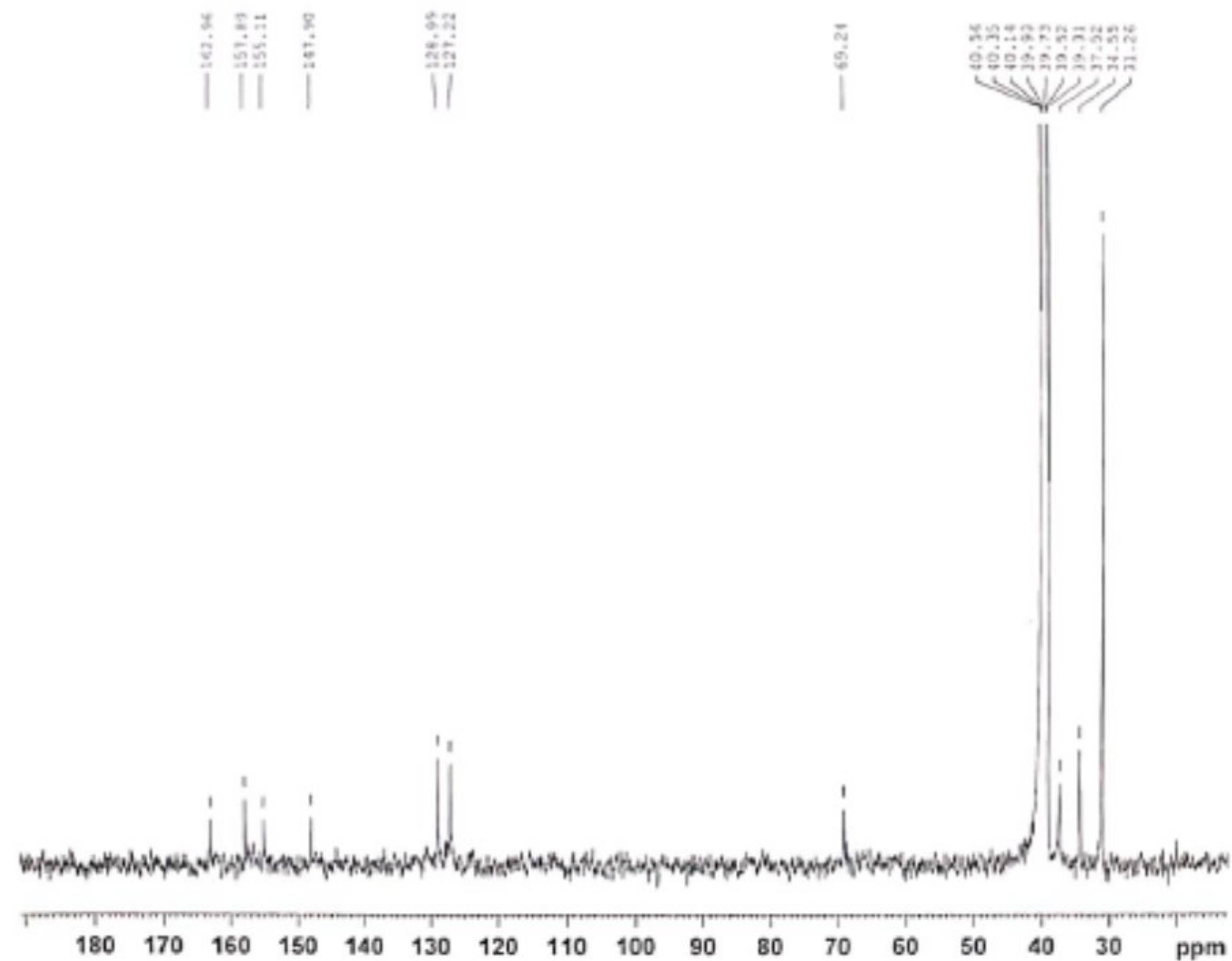
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PL1       0.00000000 W

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PC        1.00
  
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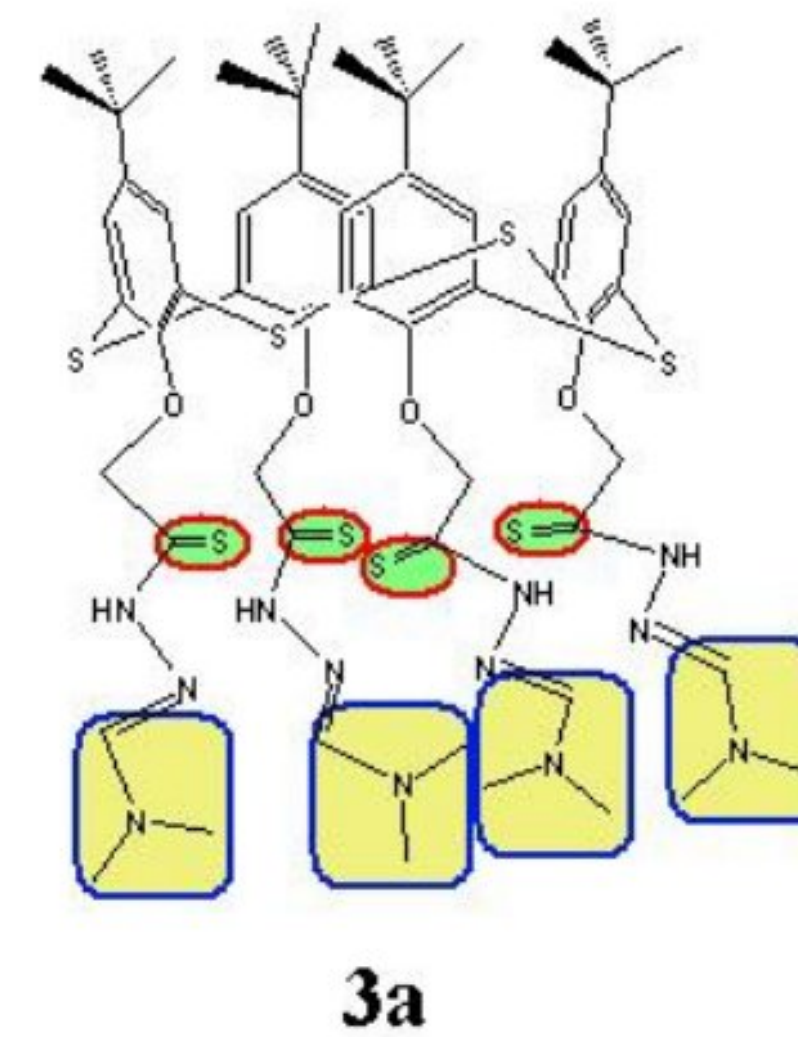
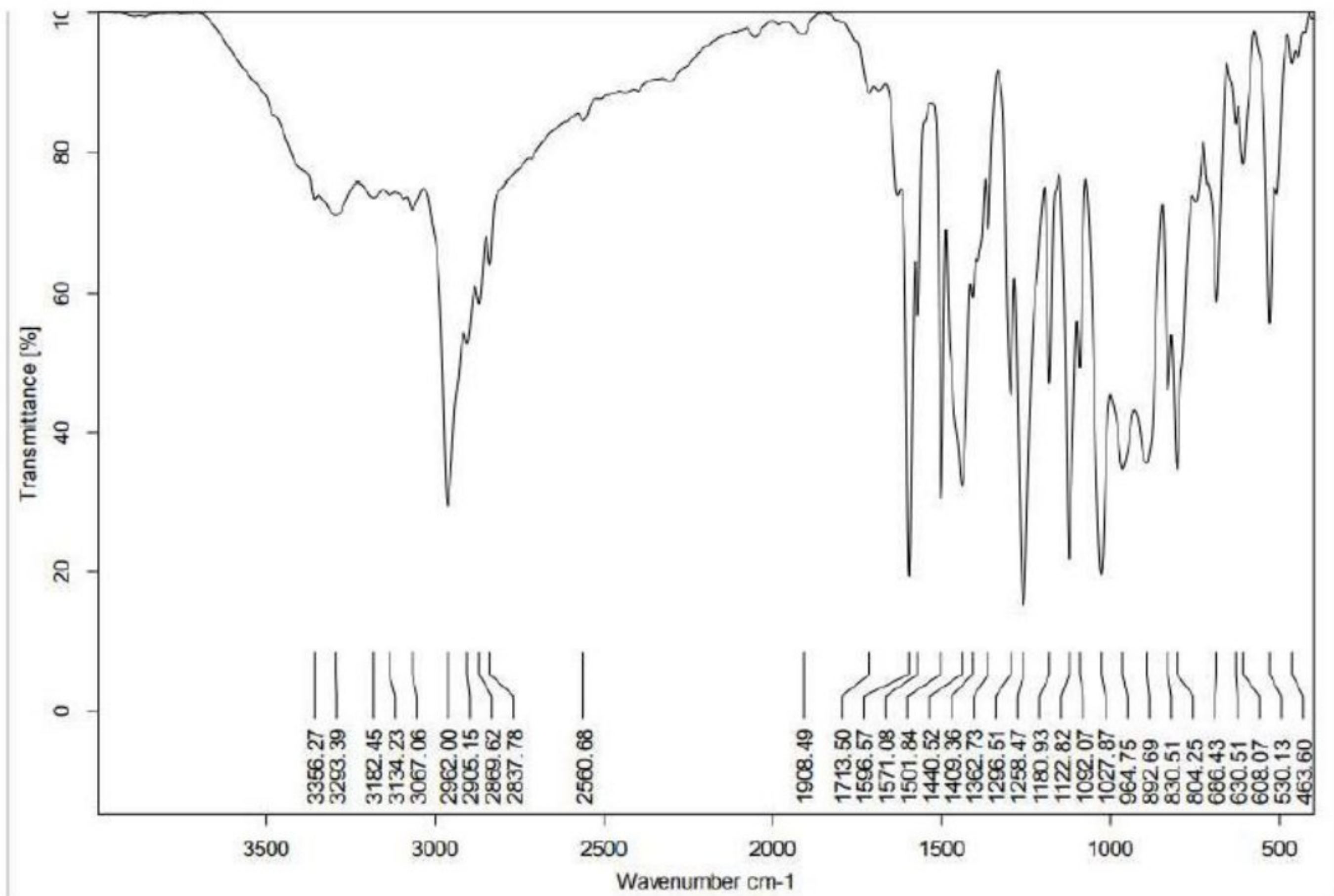


2c

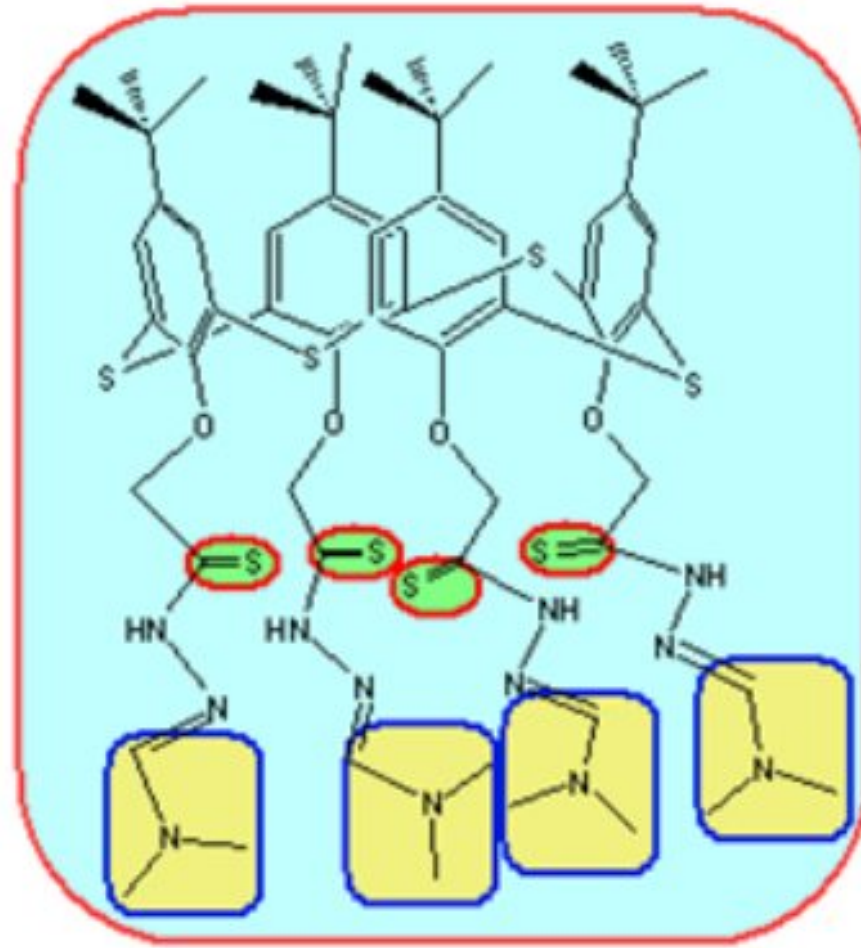
OM-47
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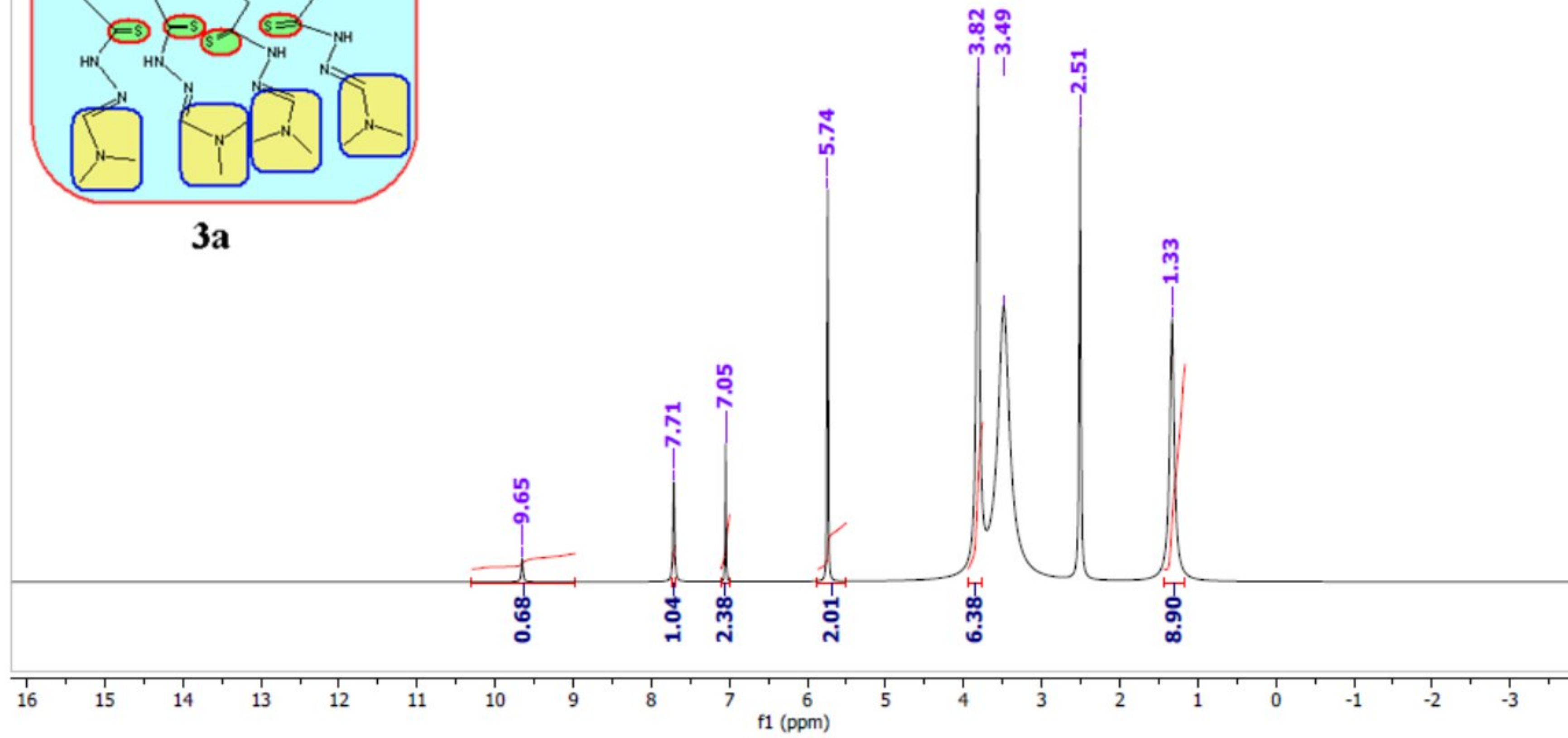
3.4. IR, ¹H and ¹³C-NMR Spectra of Compound 3a:-



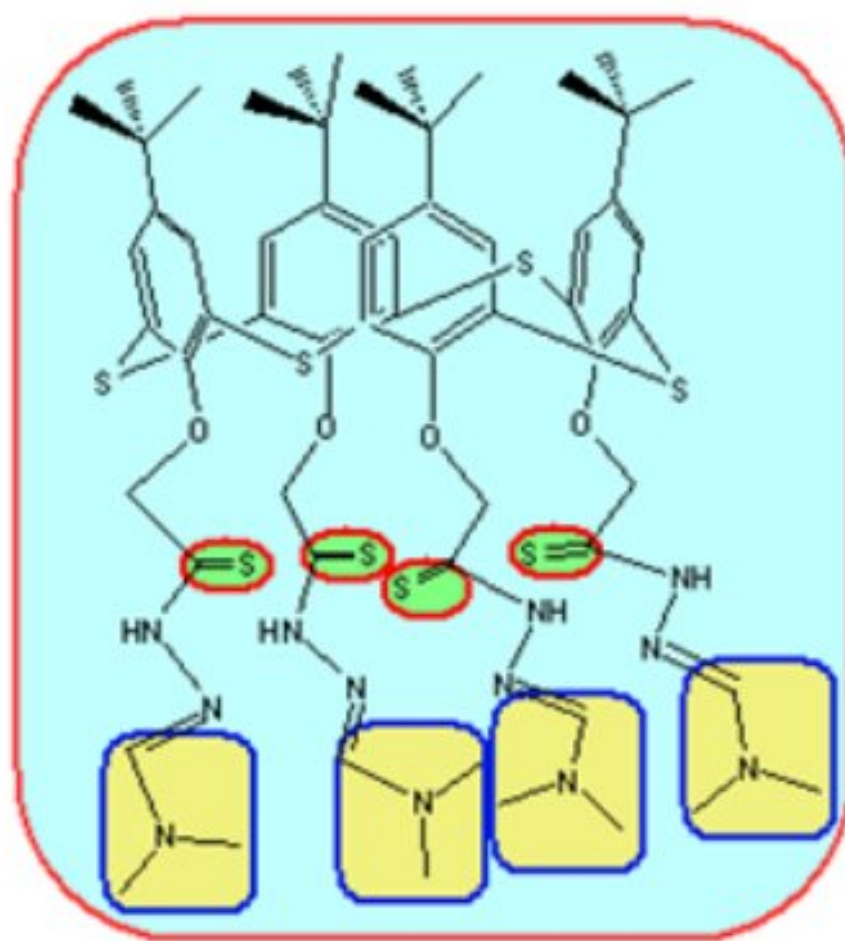
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P-21
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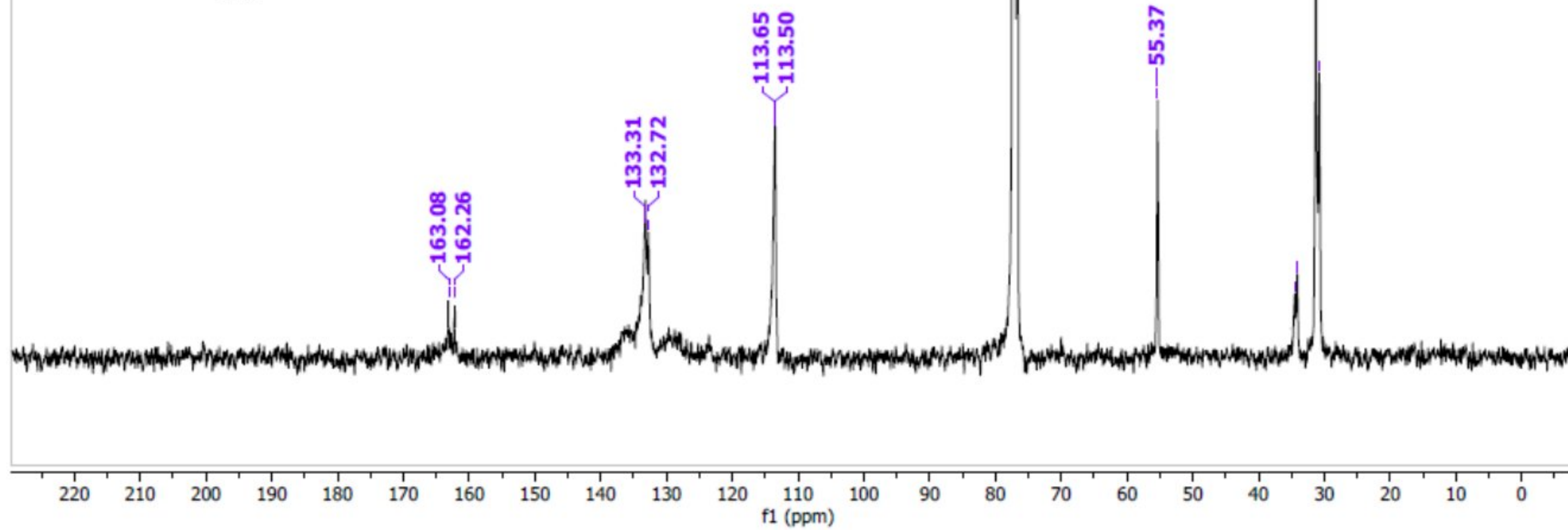
3a



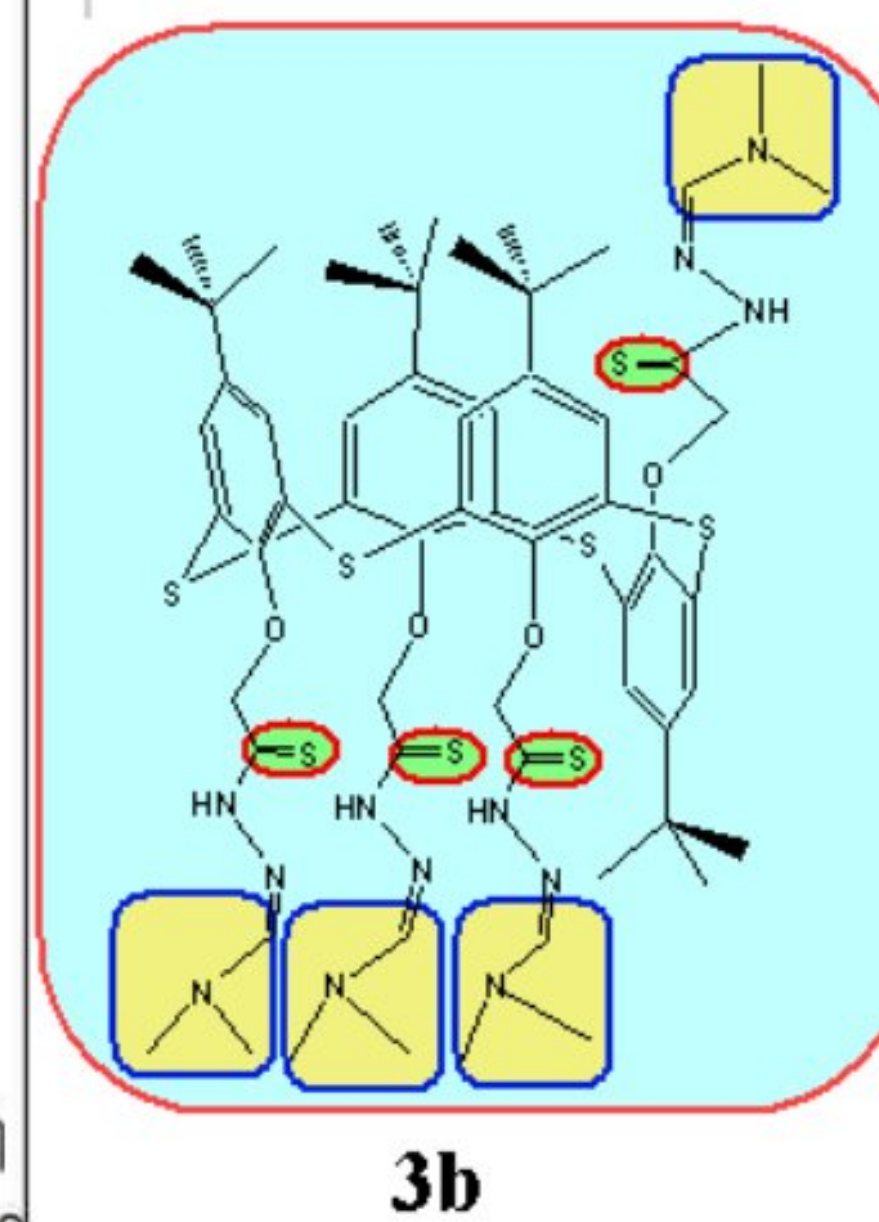
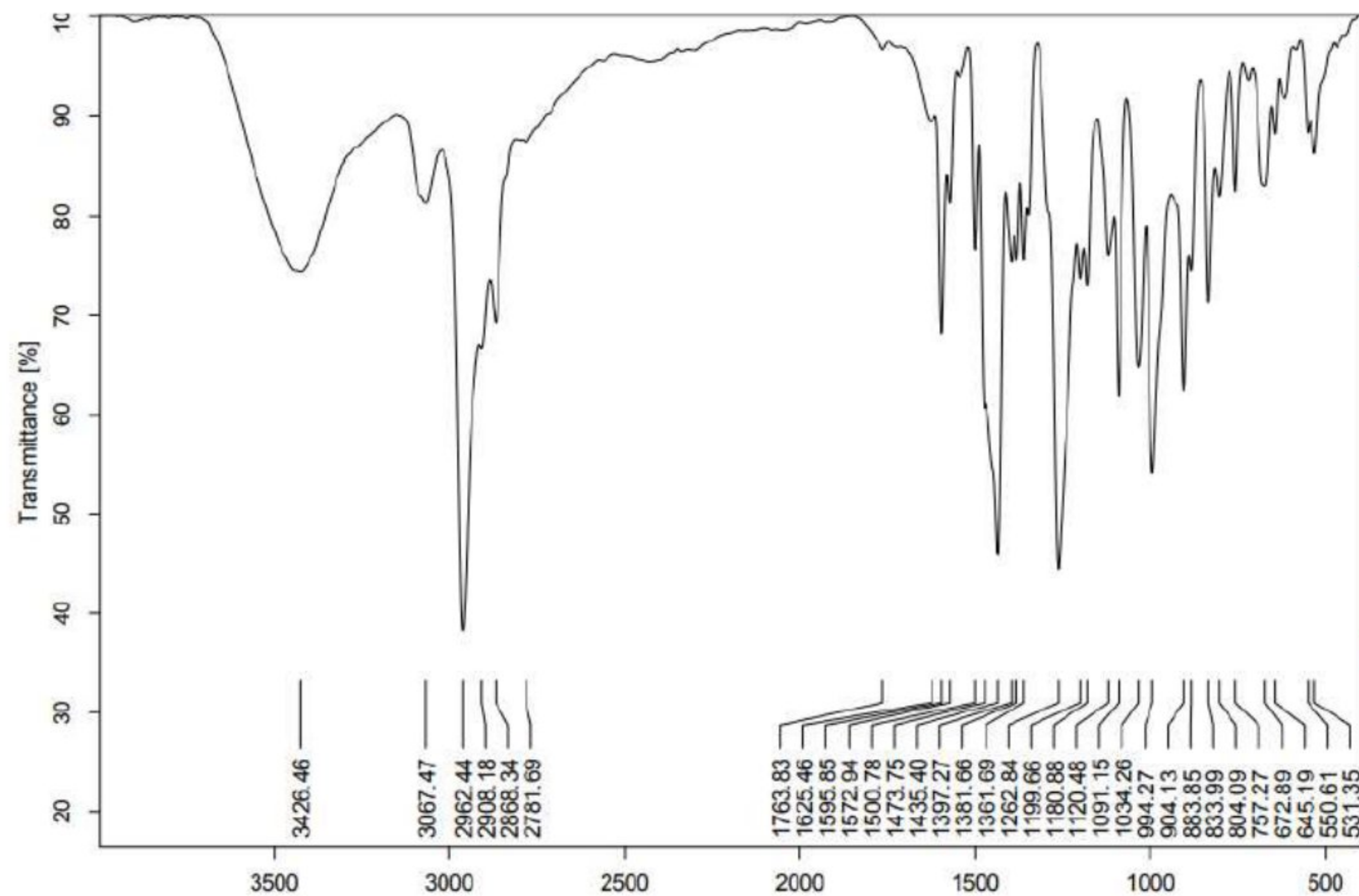
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3a

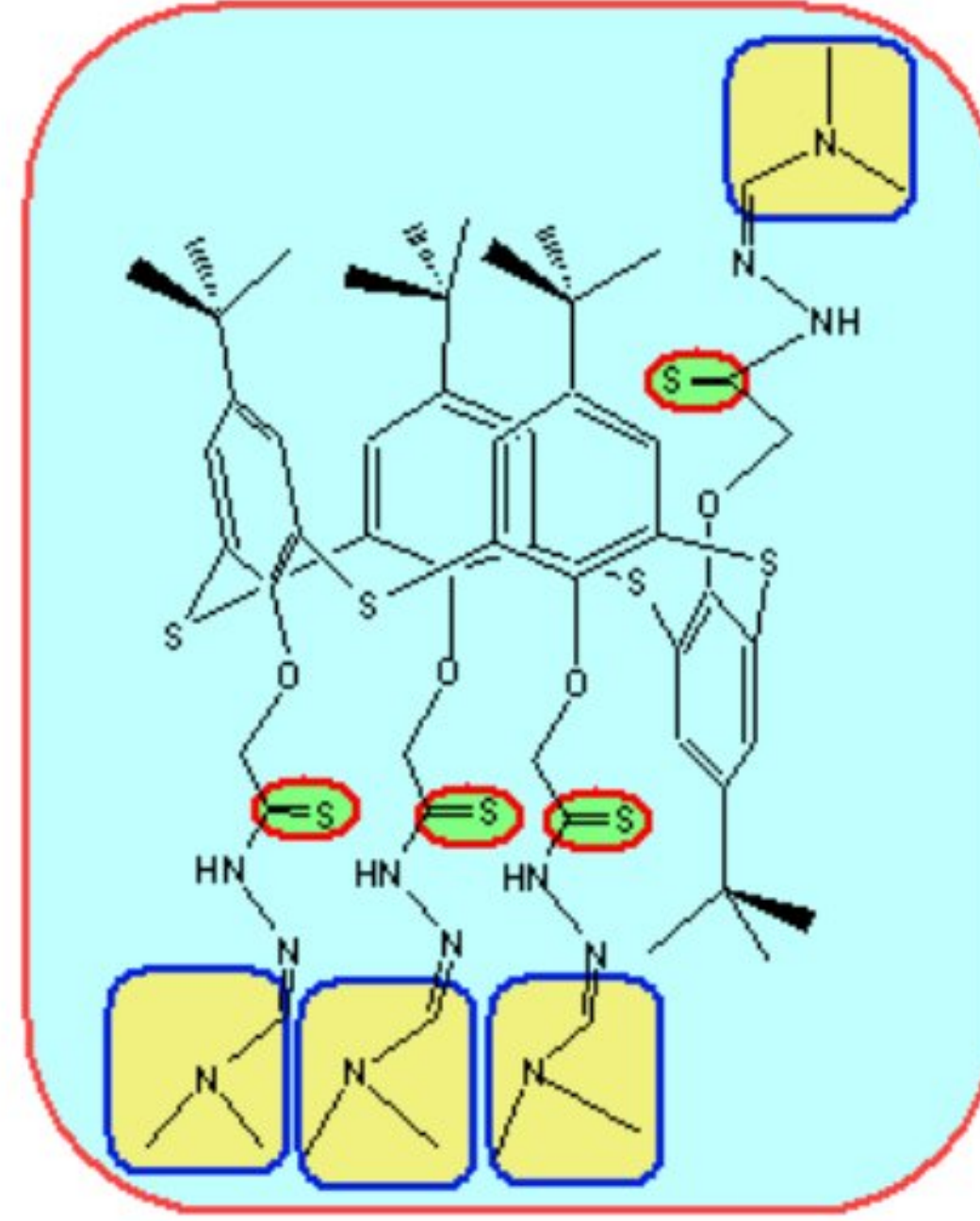
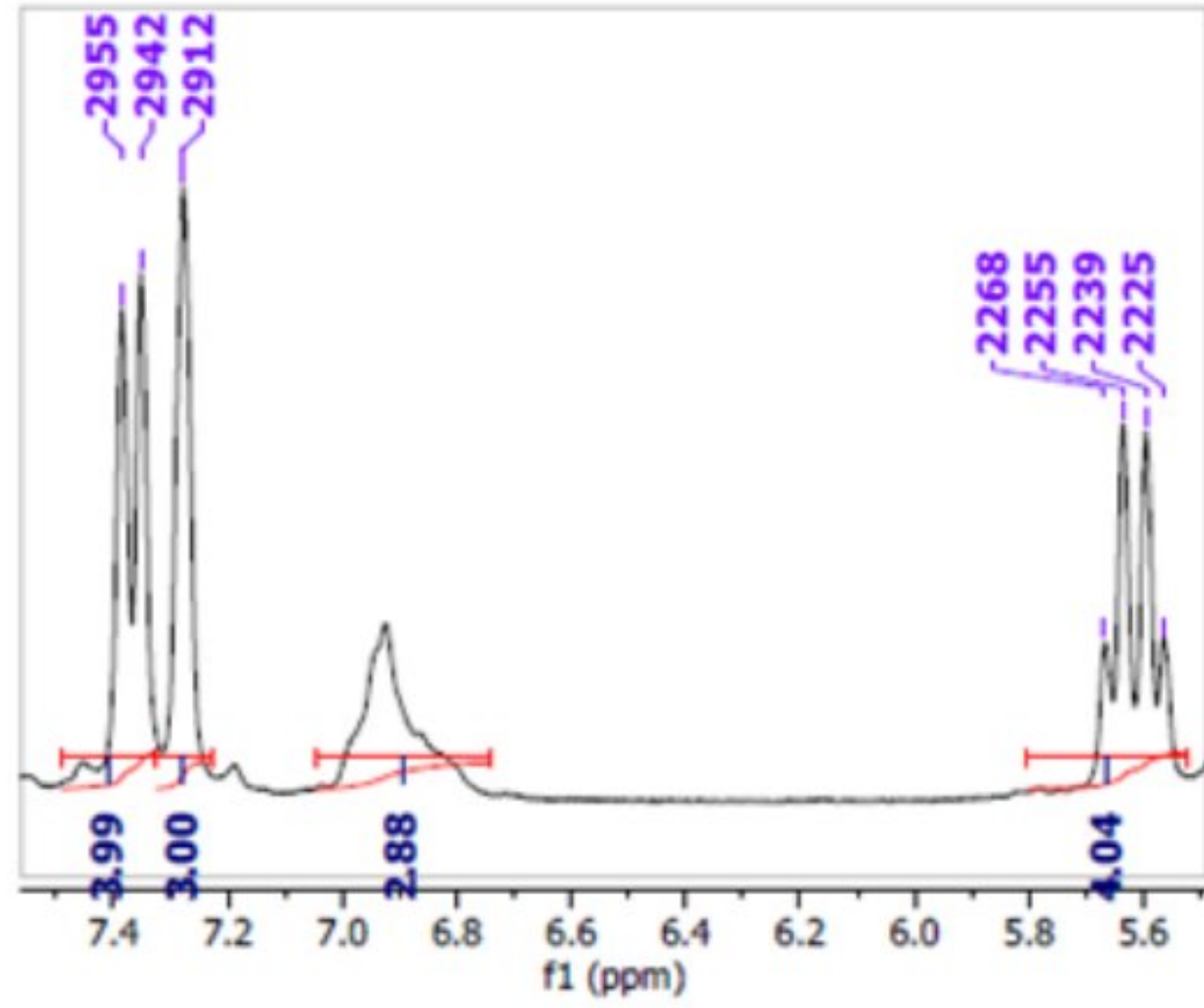


3.5. IR, ¹H and ¹³C-NMR Spectra of Compound 3b:-

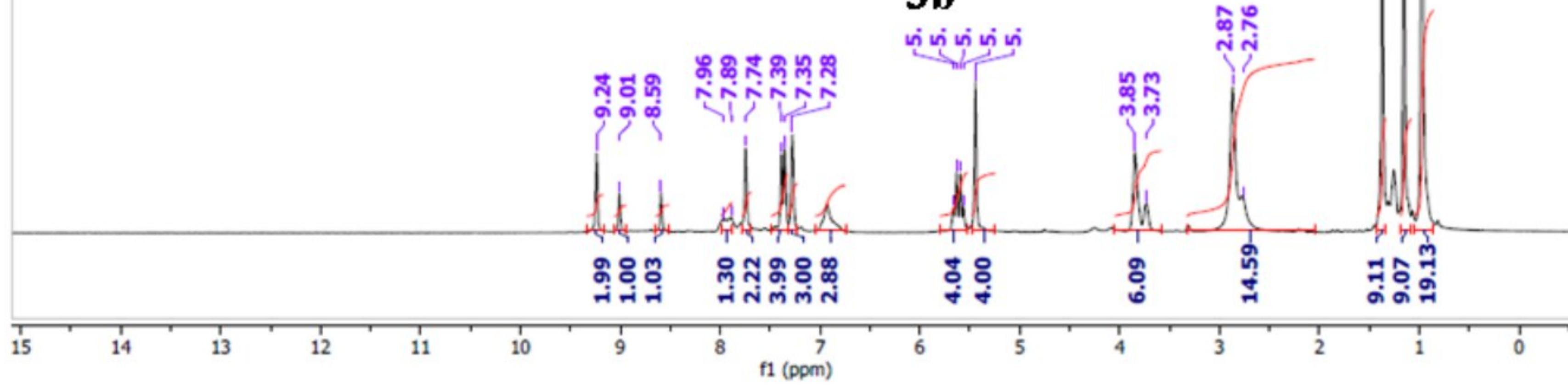


3b

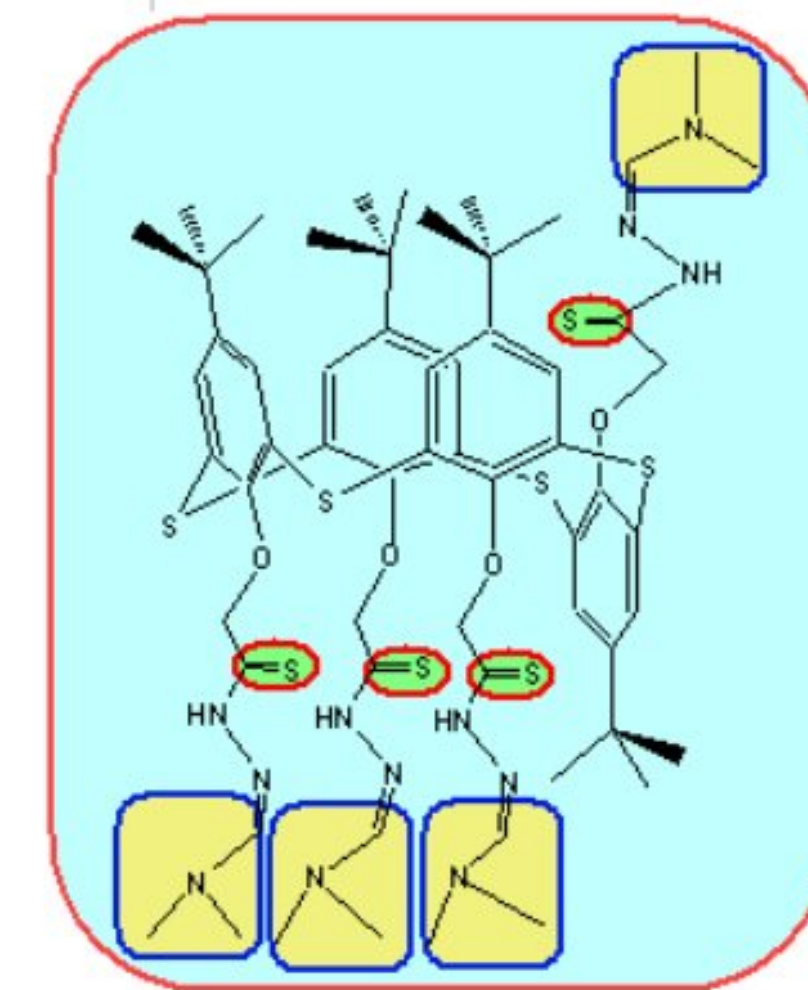
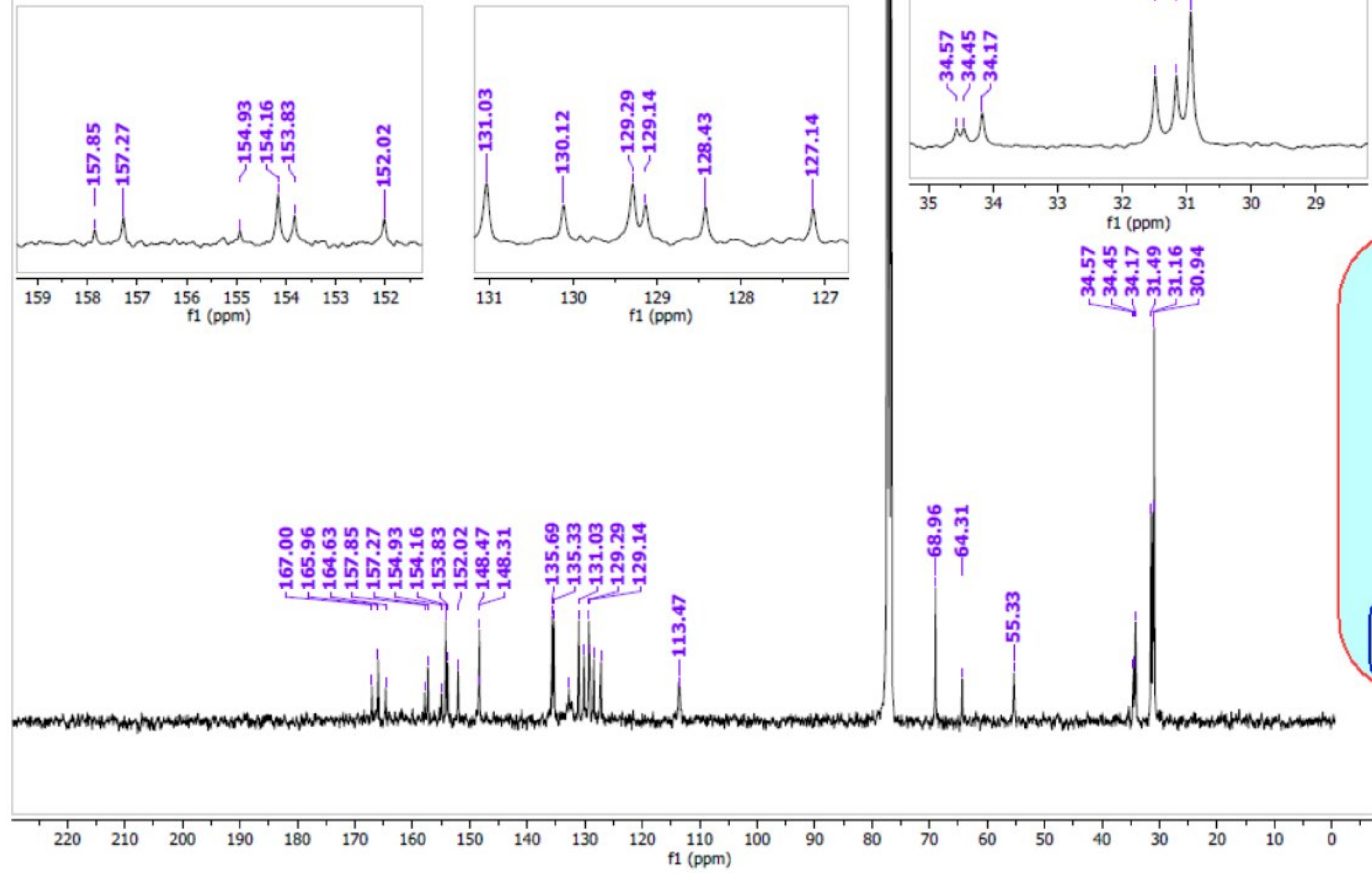
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P-2
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3b

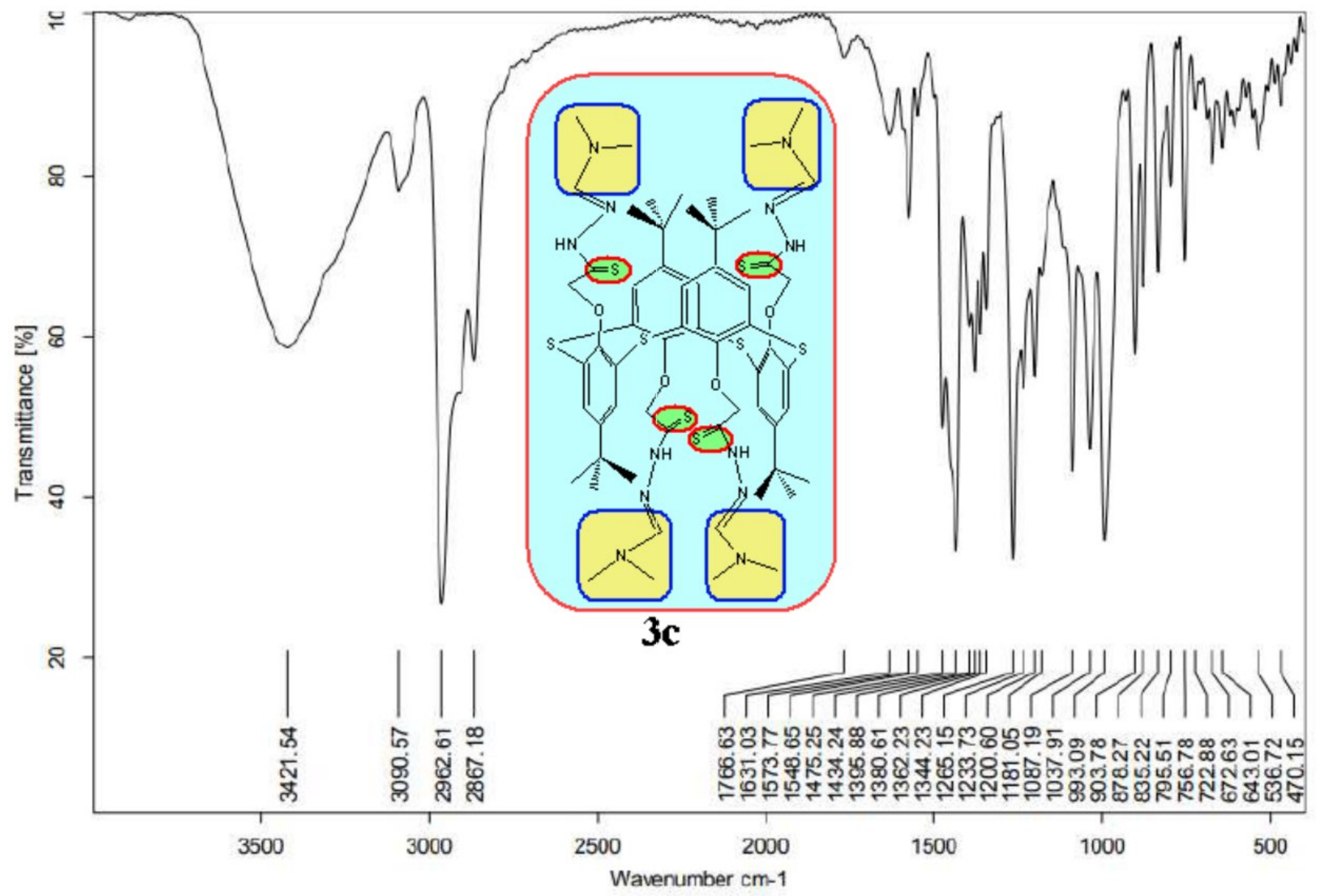


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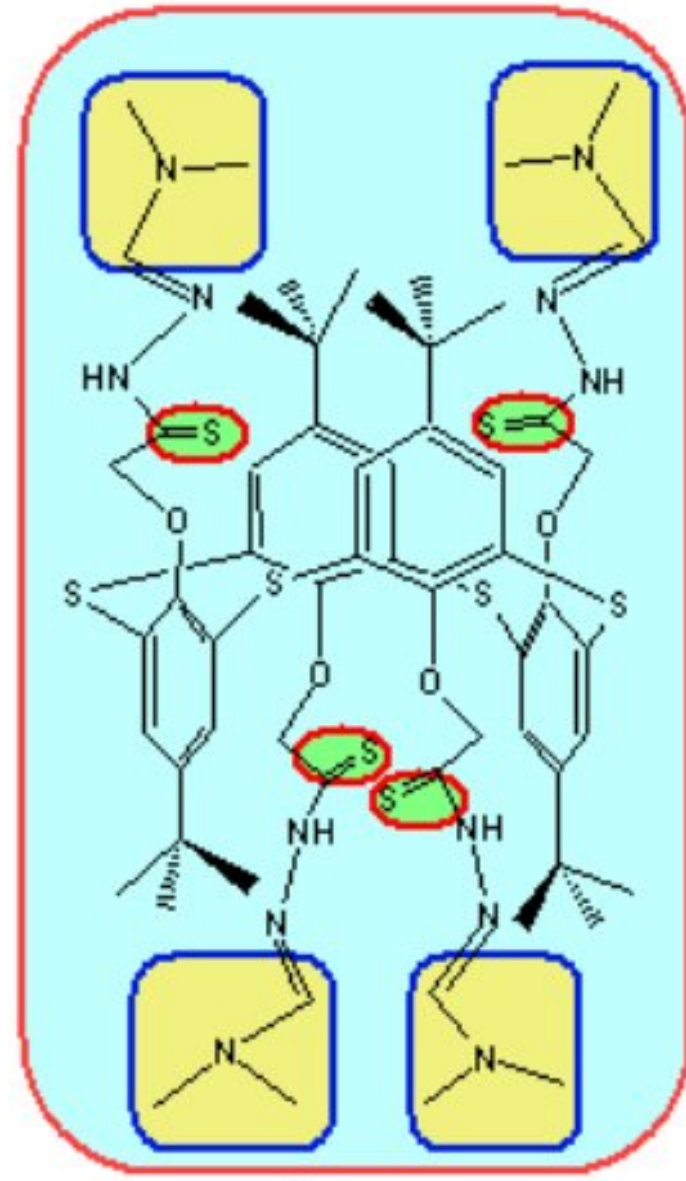


3b

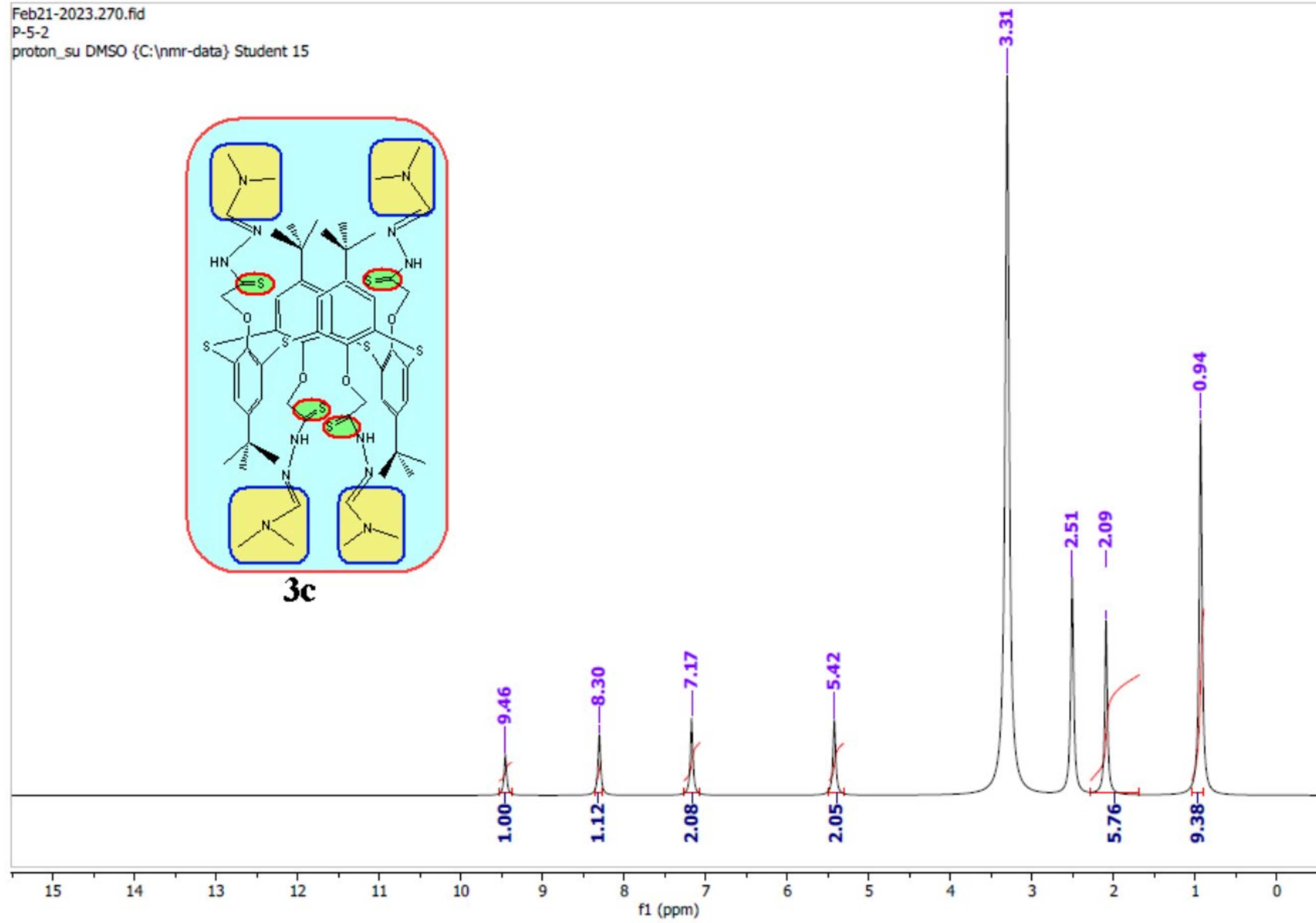
3.6. IR, ^1H and ^{13}C -NMR Spectra of Compound 3c:-



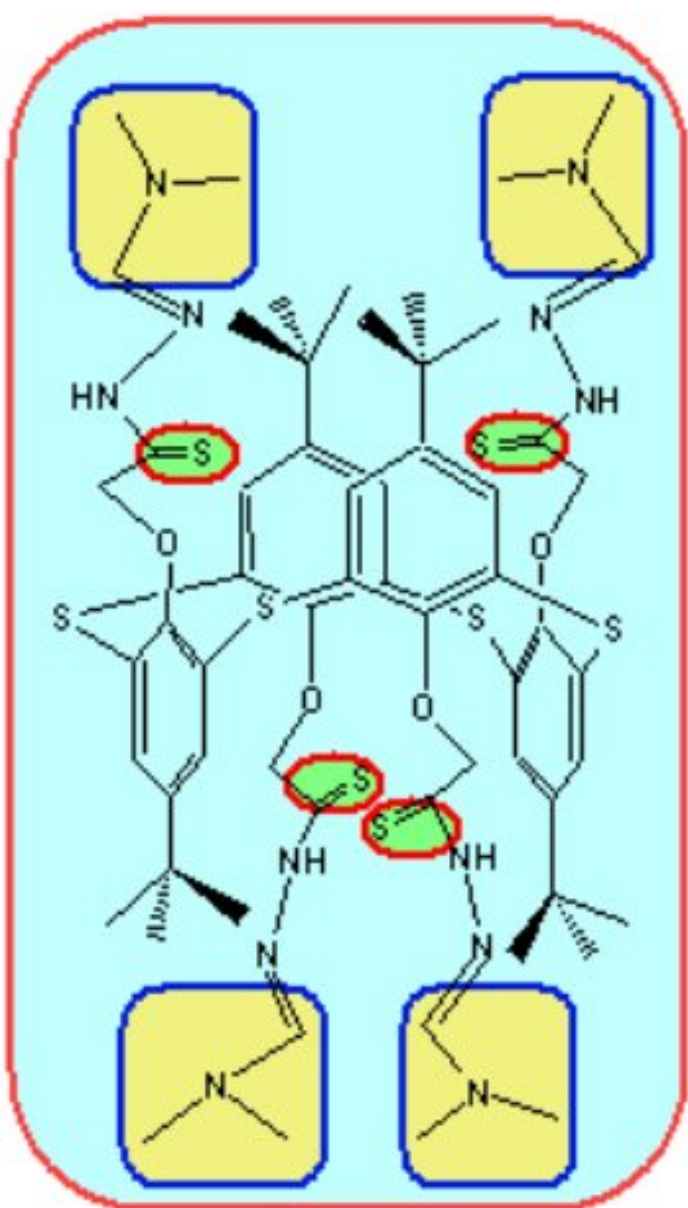
Feb21-2023.270.fid
P-5-2
proton_su DMSO (C:\nmr-data) Student 15



3c



Jan19-2023.20.fid
P-8-2
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3c

