Electronic Supporting Information

Unconventional sulfur transfer behaviour of 4-hydroxy-dithiocoumarin: An easy access to biologically potent 1,2-dithiolane scaffolds

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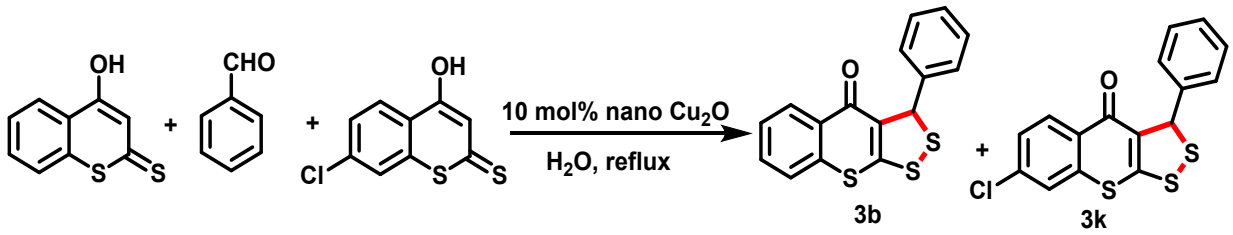
Content

l. General Information and Methods

^{1}H and ^{13}C NMR spectra were recorded on 400 MHz, 600 MHz and 100 MHz, 150 MHz spectrometer TMS as internal reference; chemical shifts (δ scale) are reported in parts per million (ppm). ^{1}H NMR Spectra are reported in the order: multiplicity, coupling constant (*J*value) in hertz (Hz) and no of protons; signals were characterized as s (singlet), d (doublet), t (triplet), m (multiplet) and b s (broad singlet). IR spectra were recorded in KBr. HRMS spectra were recorded using ESI and APCI (TOF) mode. The X-ray crystal structures were determined with a diffractometer. Complete crystallographic data of **3c** (CCDC no.1454211), for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, Copies of this information may be obtained free of charge from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk or via: www.ccdc.cam.ac.uk).

2. Control experiments

To examine the sulfur transfer behaviour between two different 4-hydroxydithiocoumarins, we have examined a reaction with 4-hydroxydithiocoumarin, 7-chloro-4-hydroxydithiocoumarin and 4-methylbenzaldehyde using 10 mol% Cu_2O nanoparticles in water under reflux conditions. We have isolated both the cyclic product as expected. It shows that sulfur transfer is taking place among themselves.



Scheme S1. Control Experiments

3. Crystal Data and Structure Refinement for Compound 3d

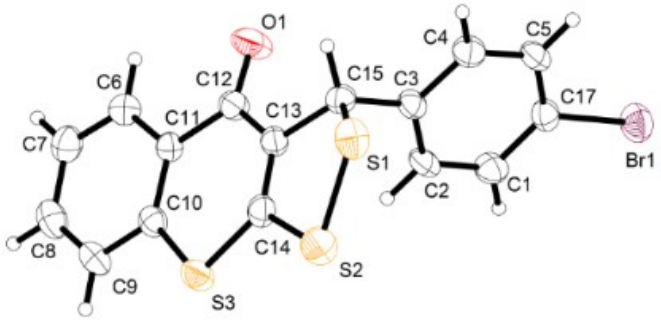


Figure S1. ORTEP view of the compound **3d**

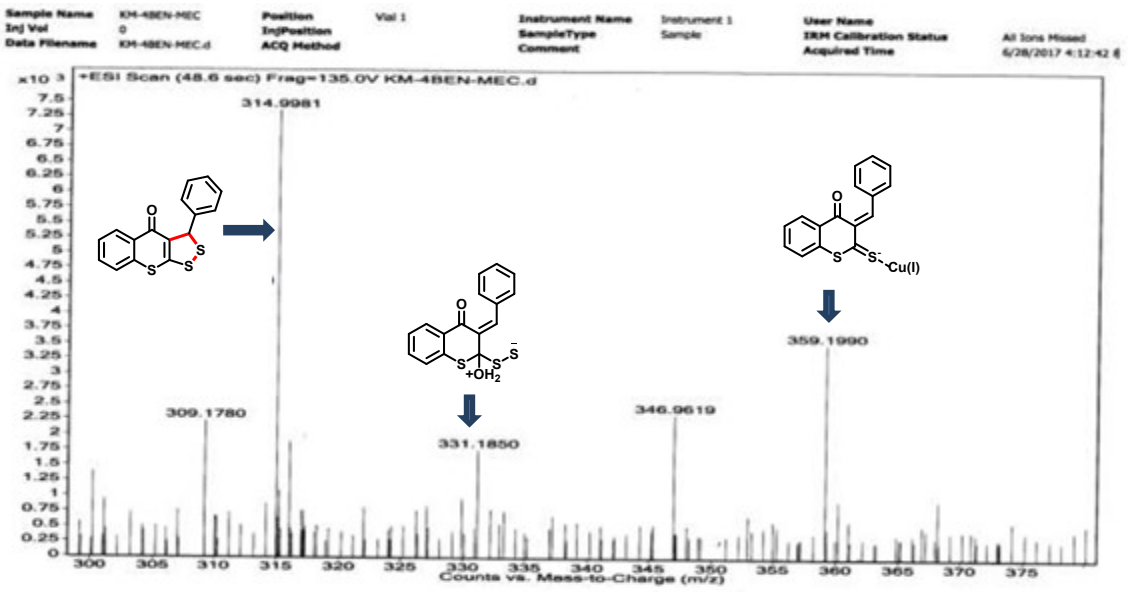
Table S1 Data collection and refinement statistics for the compounds **3d**

Entry	Identification code	Compound **3d**
01	Empirical formula	C16 H9 Br O S3
02	Formula weight	393.32
03	Temperature	296(2) K
04	Wavelength	0.71073
05	Radiation type	Mo K\a
06	Radiation source	Fine-focus sealed tube
07	Crystal system	Orthorhombic
08	Space group	P 21 21 21
09	Cell length	a = 5.5072(2) b = 12.8308(4) c = 21.2270(7)
10	Cell Angle	α 90 β 90 γ 90
11	Cell Volume	1499.94(9)
12	Density	1.742

13	Completeness to theta	25°/ 97% 25.04
14	Absorption correction	multi-scan
15	Refinement method	Full-matrix least-squares on F2
16	Index ranges	-6<=h<=6, -15<=k<=15, -25<=l<=25
17	Reflection number	0.0415 (2162)
18	Theta range	3.29-20.20
19	Cell formula units Z	4
20	CCDC no	1572813

4. Mass of intermediate

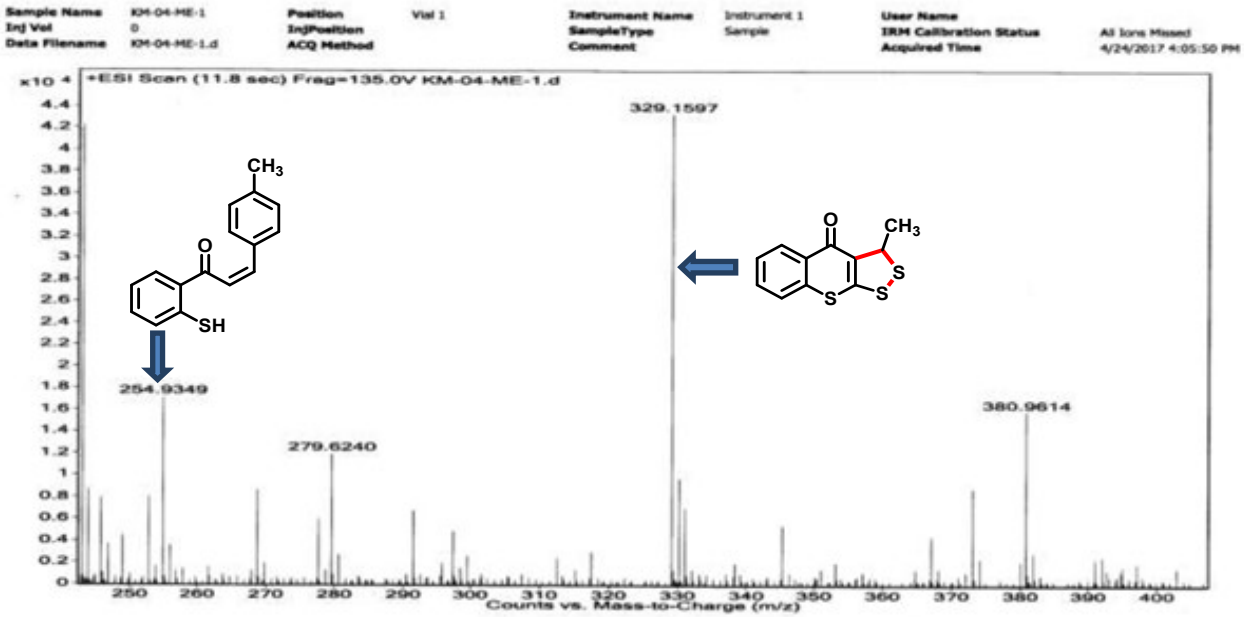
This mechanism was supported by the HRMS of compounds **3a** and **4** while carrying out the reaction of 4-hydroxydithiocoumarin and 4-methylbenzaldehyde. When the reaction was performed with 4-hydroxydithiocoumarin and benzaldehyde, we got the intermediate **B** and **E** in



the crude reaction mixture along with **3b**.

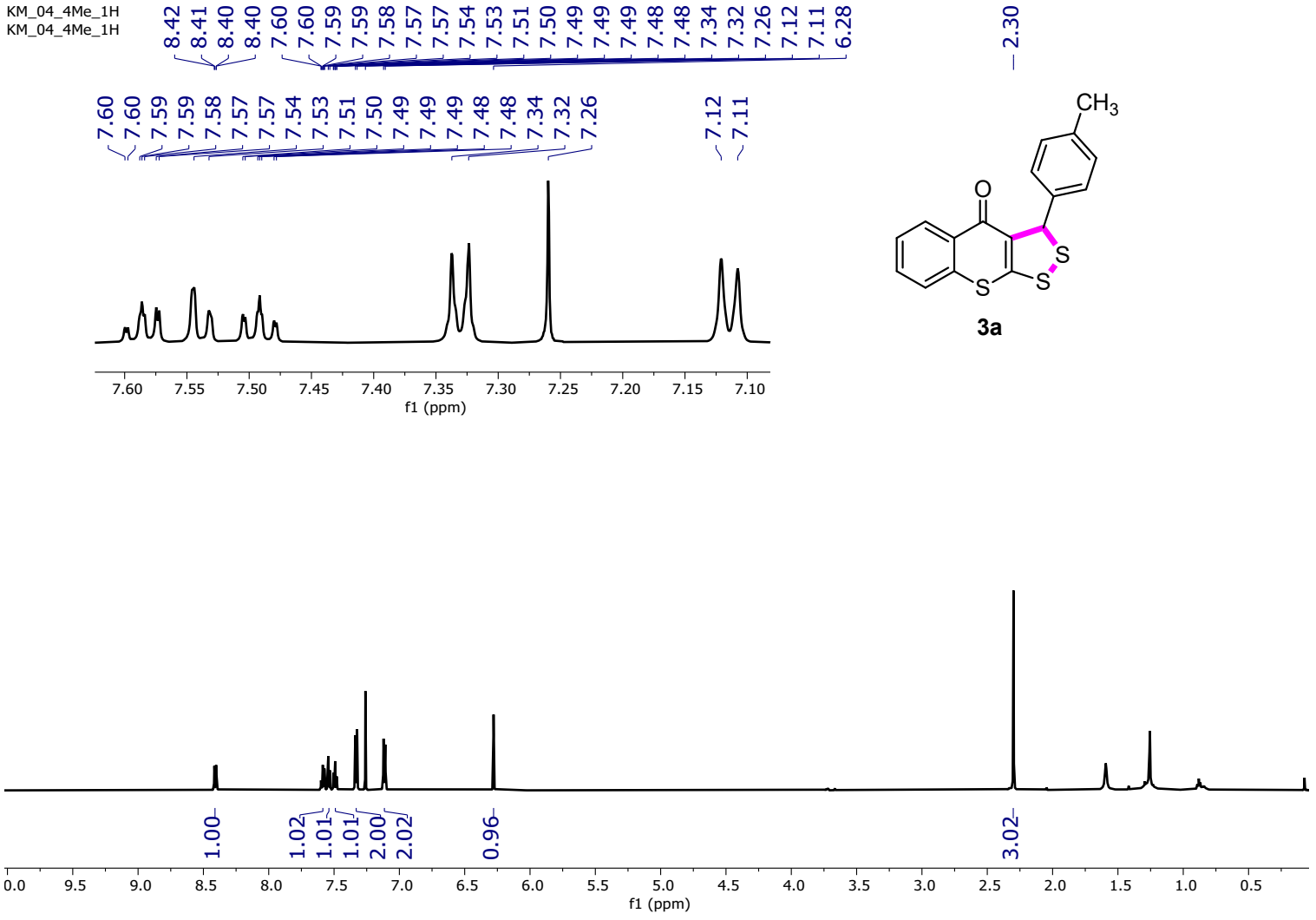
Figure S2. Mass analysis of crude mixture of the compound **3a**

Figure S3. Mass analysis of crude mixture of the compound **3b**

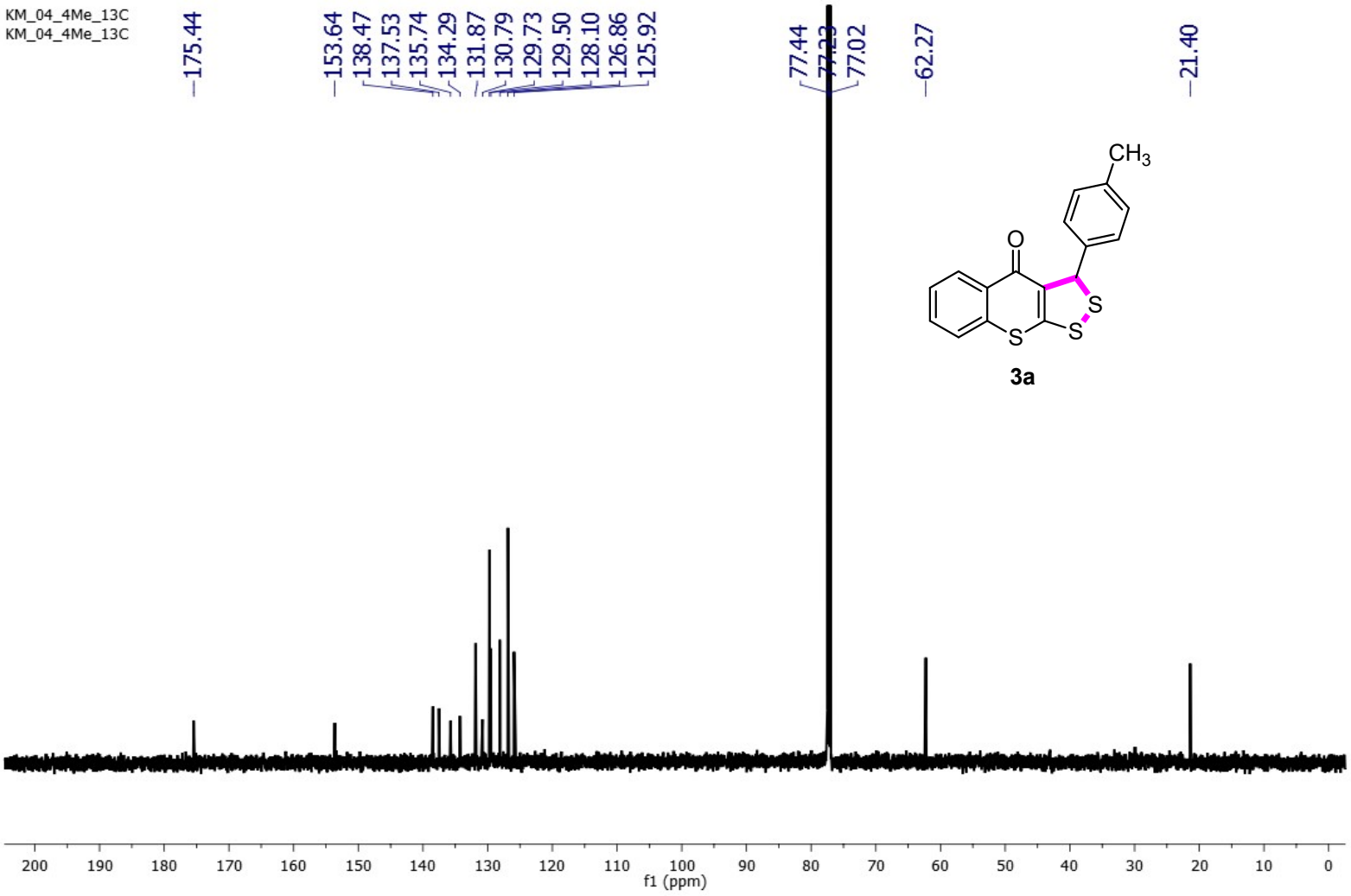


5. Copies of ^{1}H NMR, ^{13}C NMR, and HRMS spectra of all Compounds

^{1}HNMR spectra of compound: 3a



^{13}CNMR spectra of compound: 3a



HRMS spectra of compound: 3a

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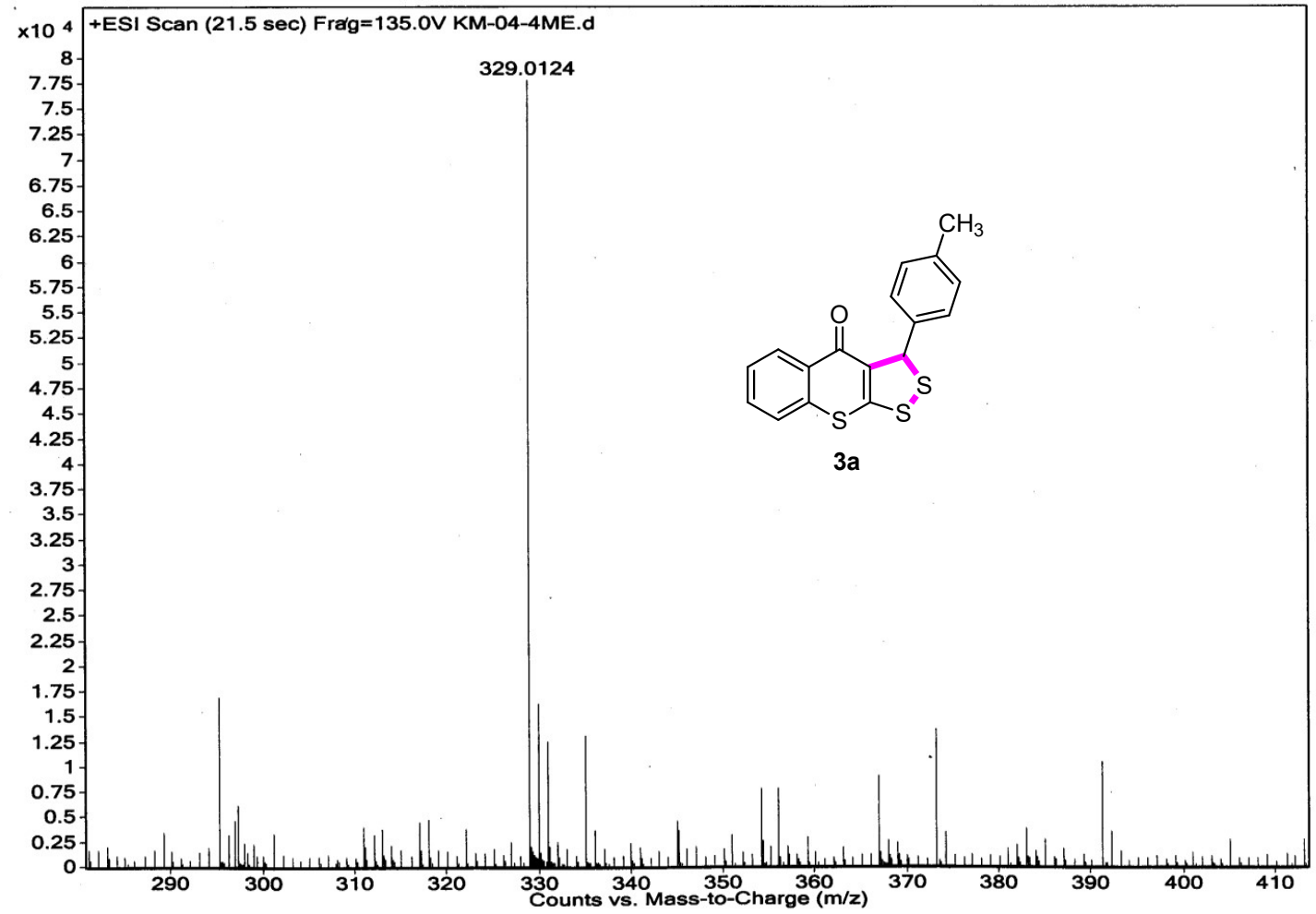
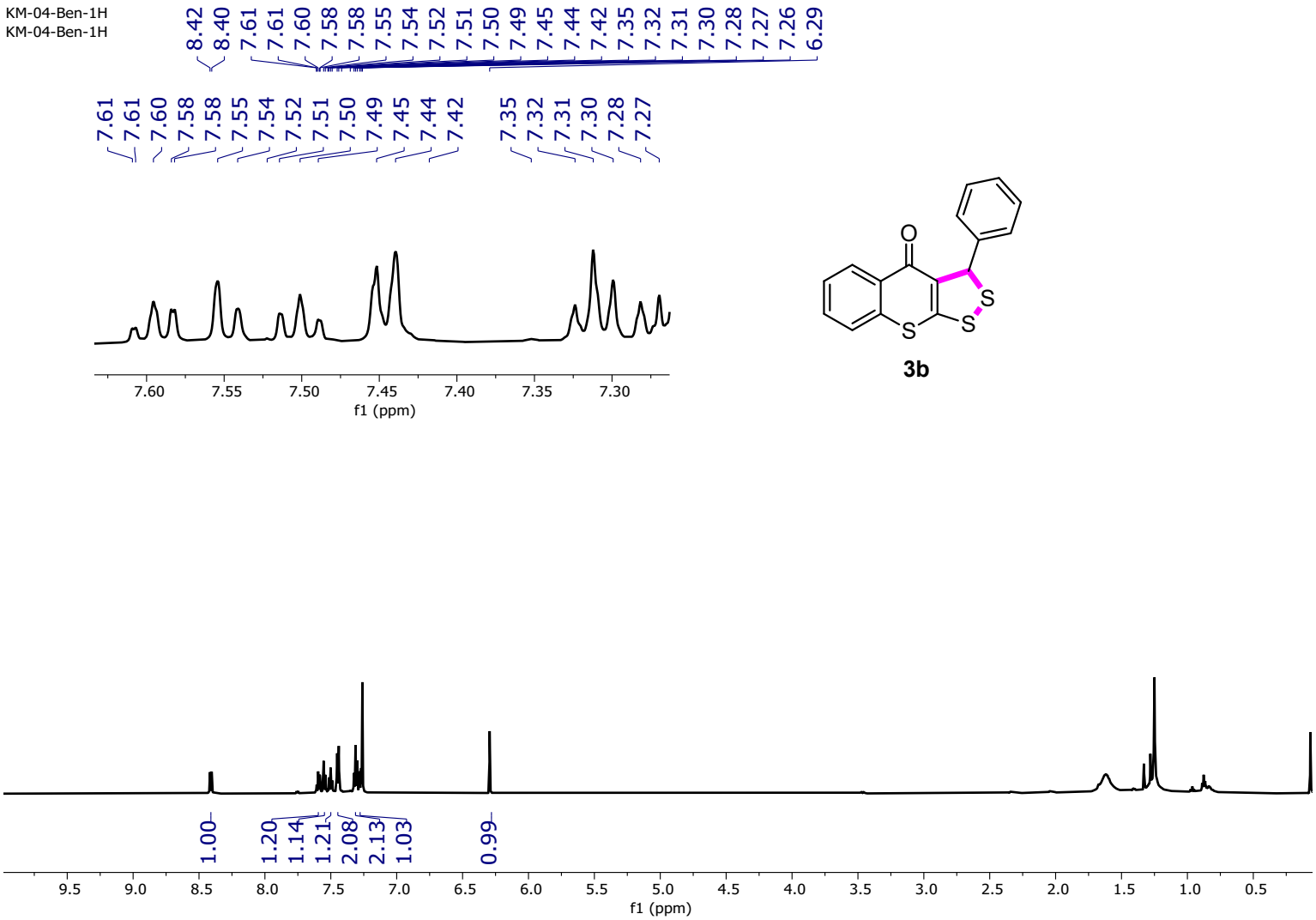
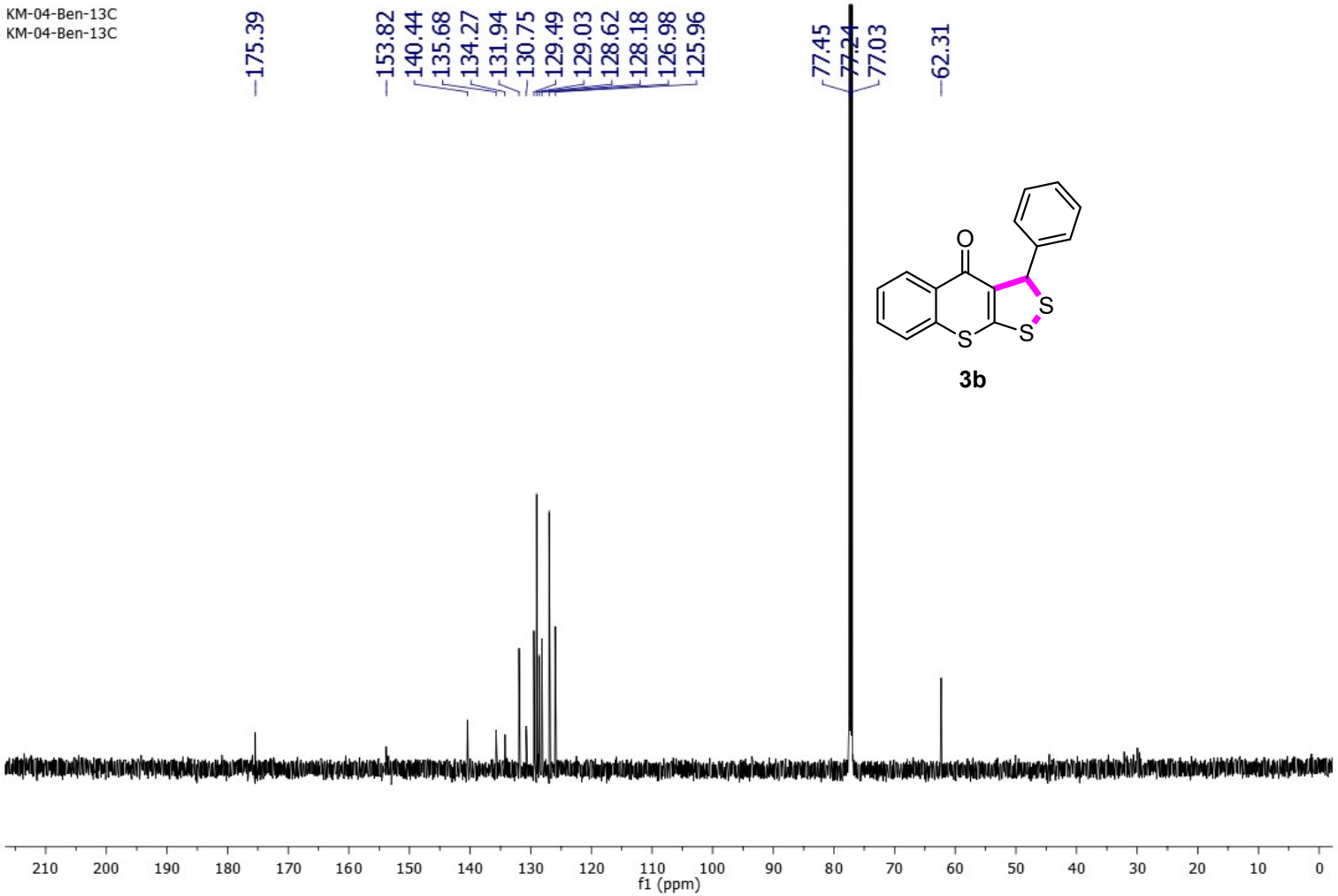
Inj Vol	InjPosition	SampleType	IRM Calibration Status
Data Filename	ACQ Method	Comment	Acquired Time



^{1}HNMR spectra of compound: 3b



^{13}CNMR spectra of compound: 3b



HRMS spectra of compound: 3b

Sample Name	KM-04-BEN	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
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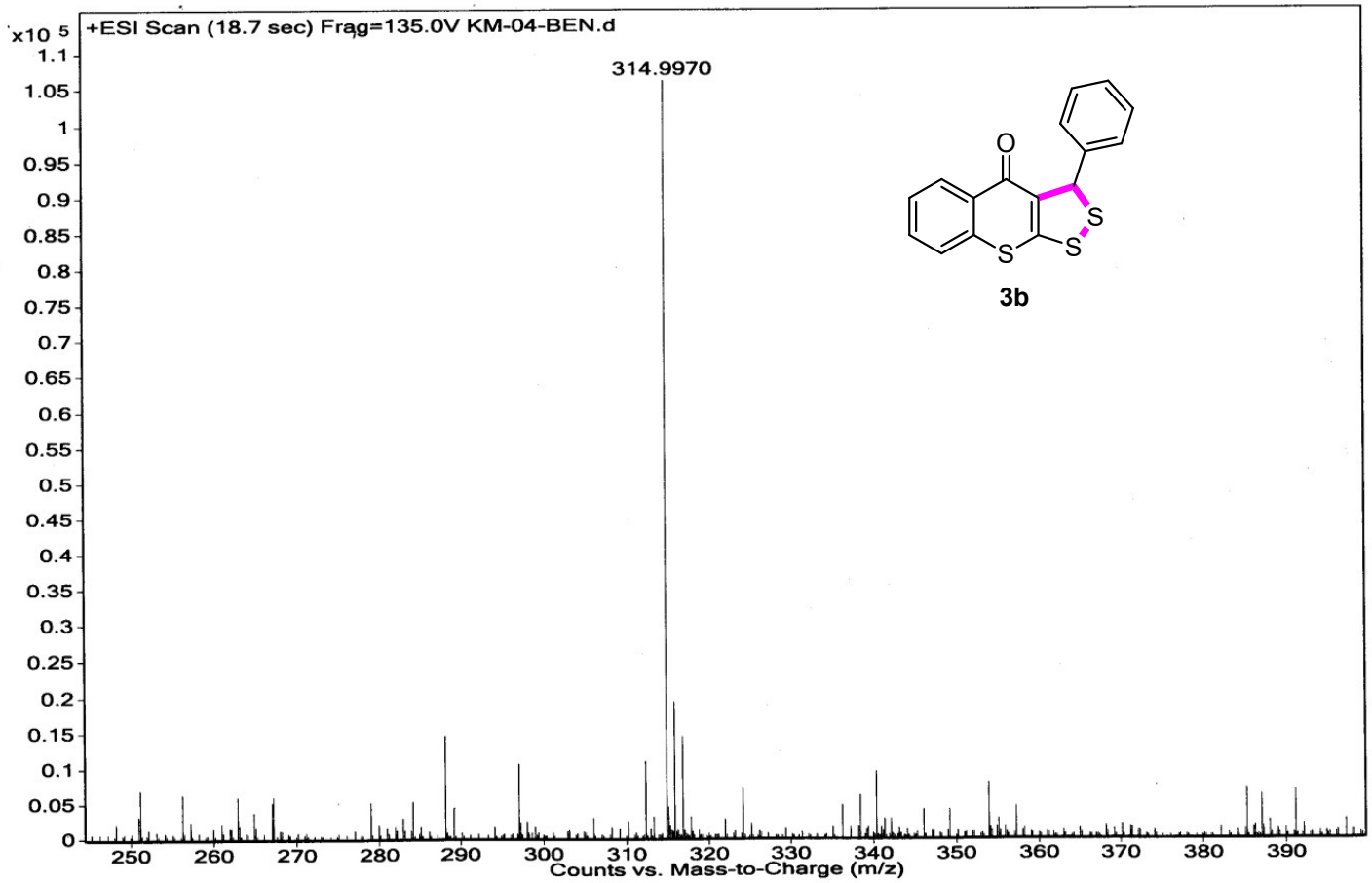
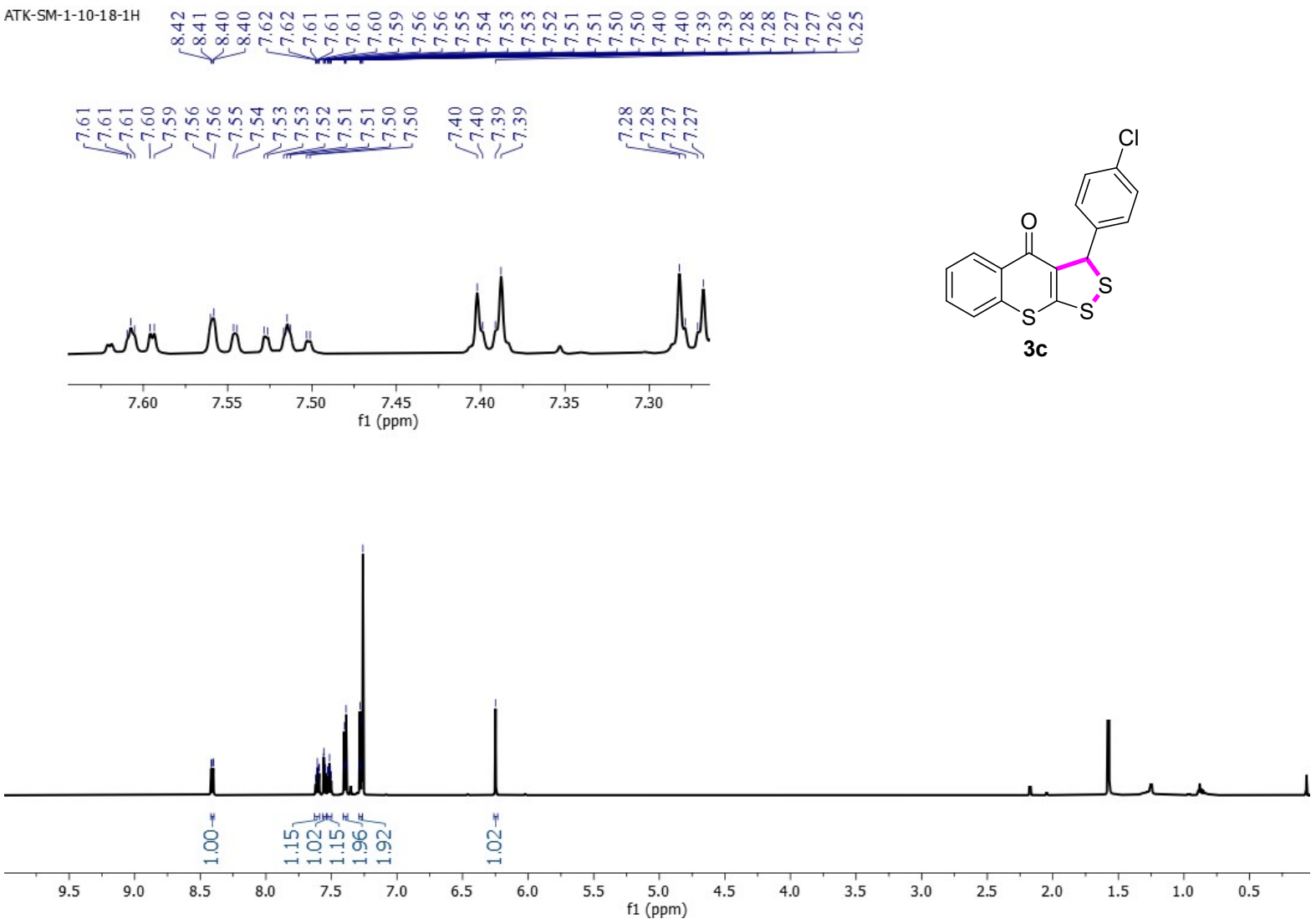
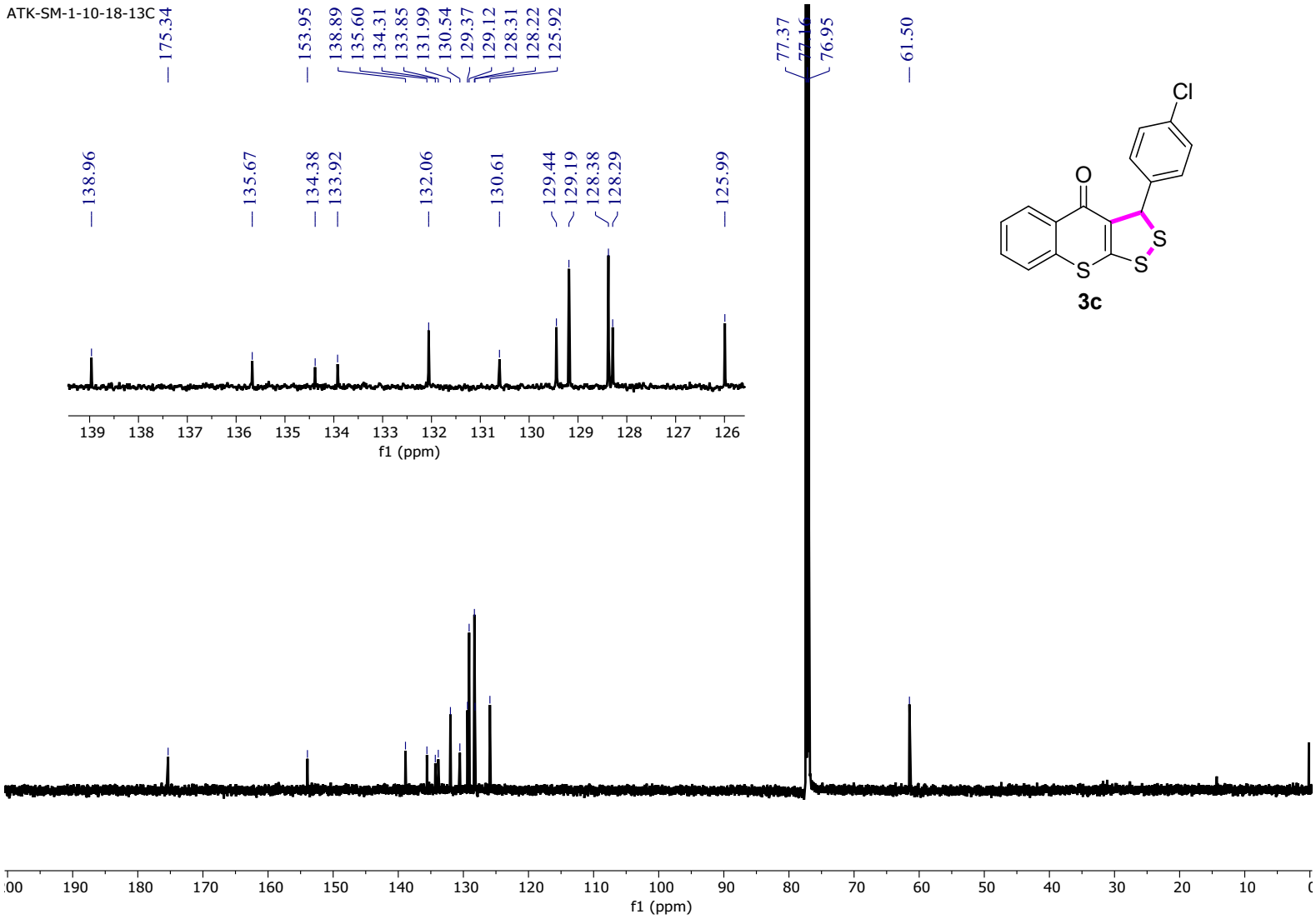


[1]HNMR spectra of compound: 3c



^{13}CNMR spectra of compound: 3c



HRMS spectra of compound: 3c

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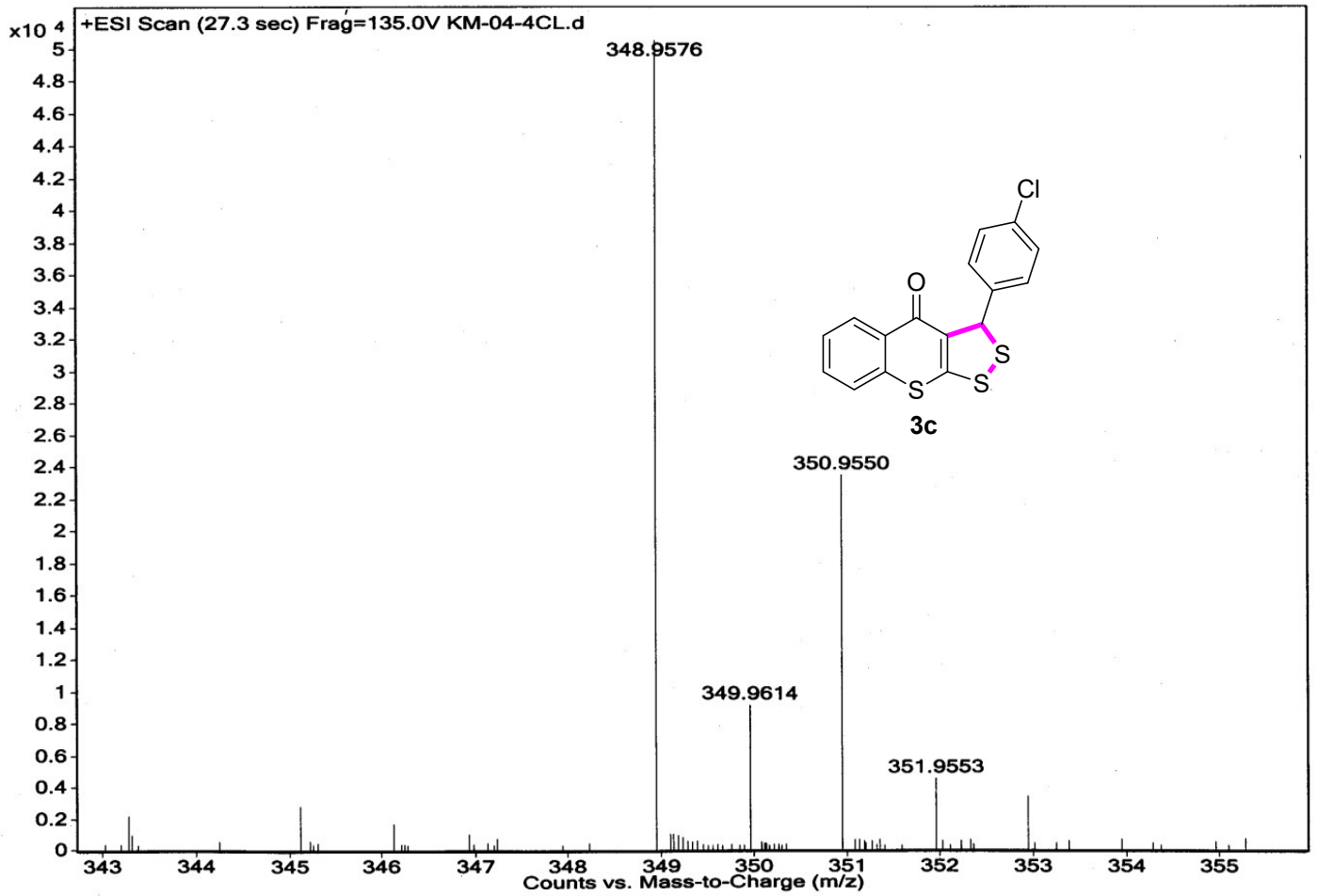
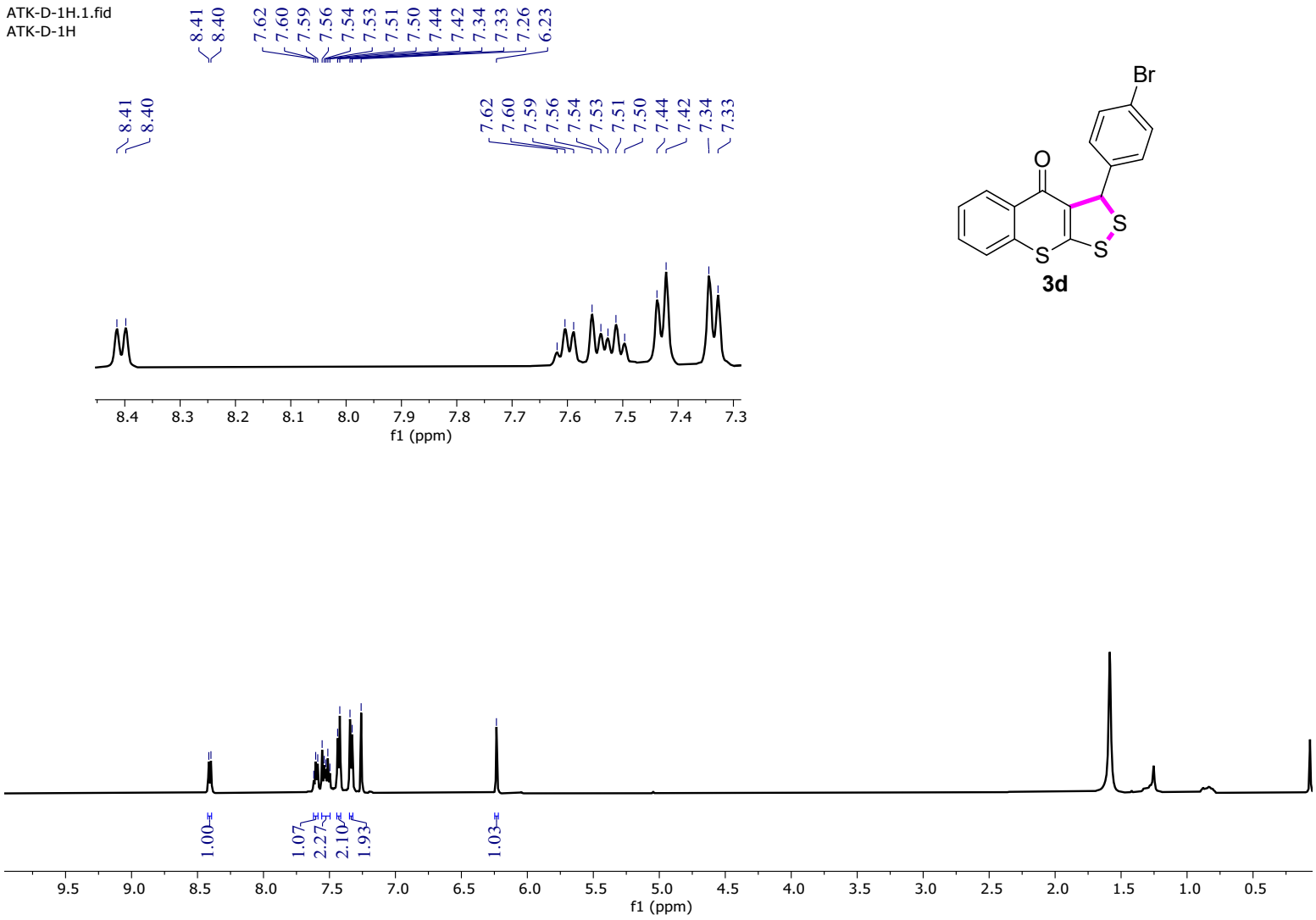
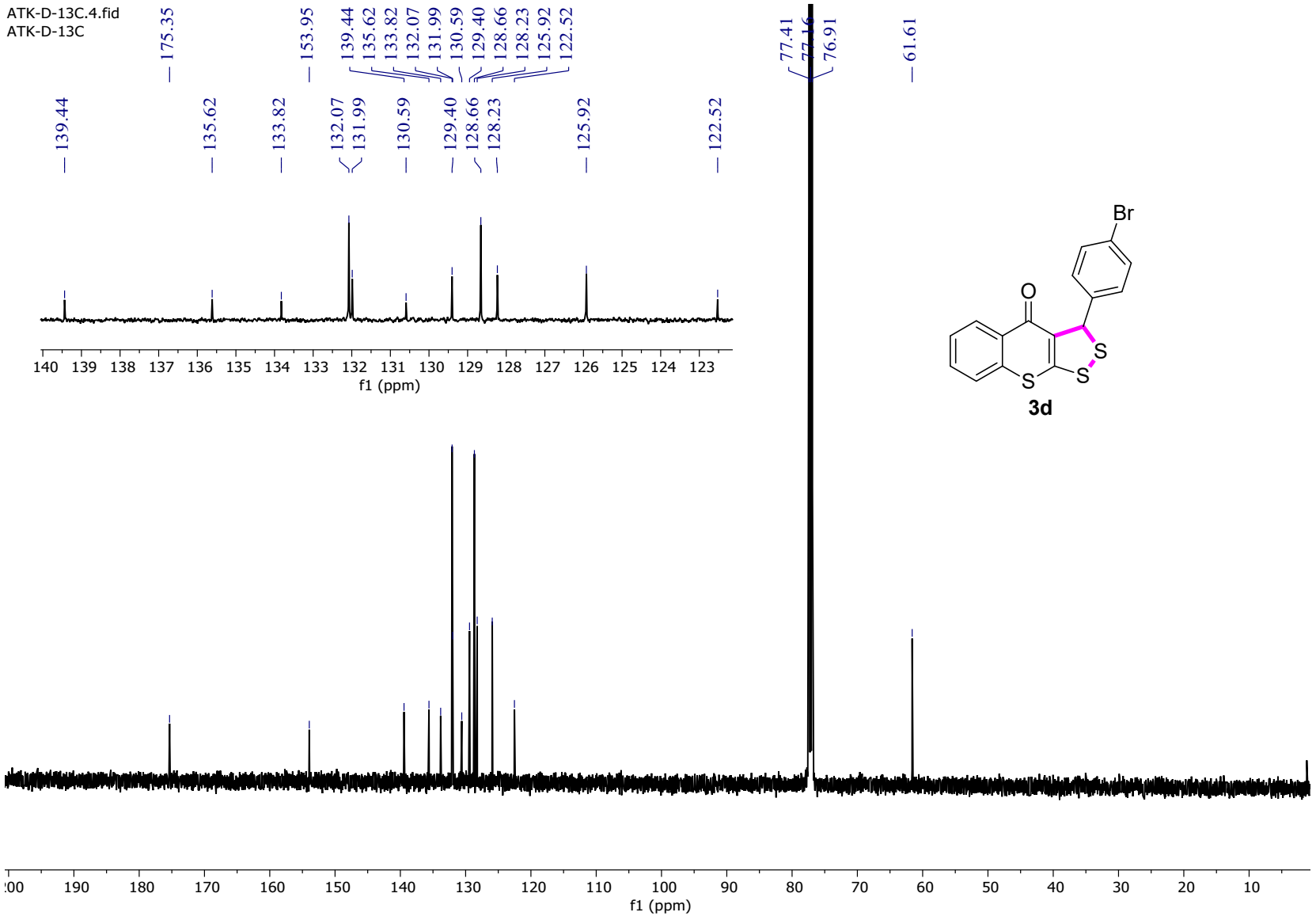


^{1}HNMR spectra of compound: 3d



^{13}CNMR spectra of compound: 3d



HRMS spectra of compound: 3d

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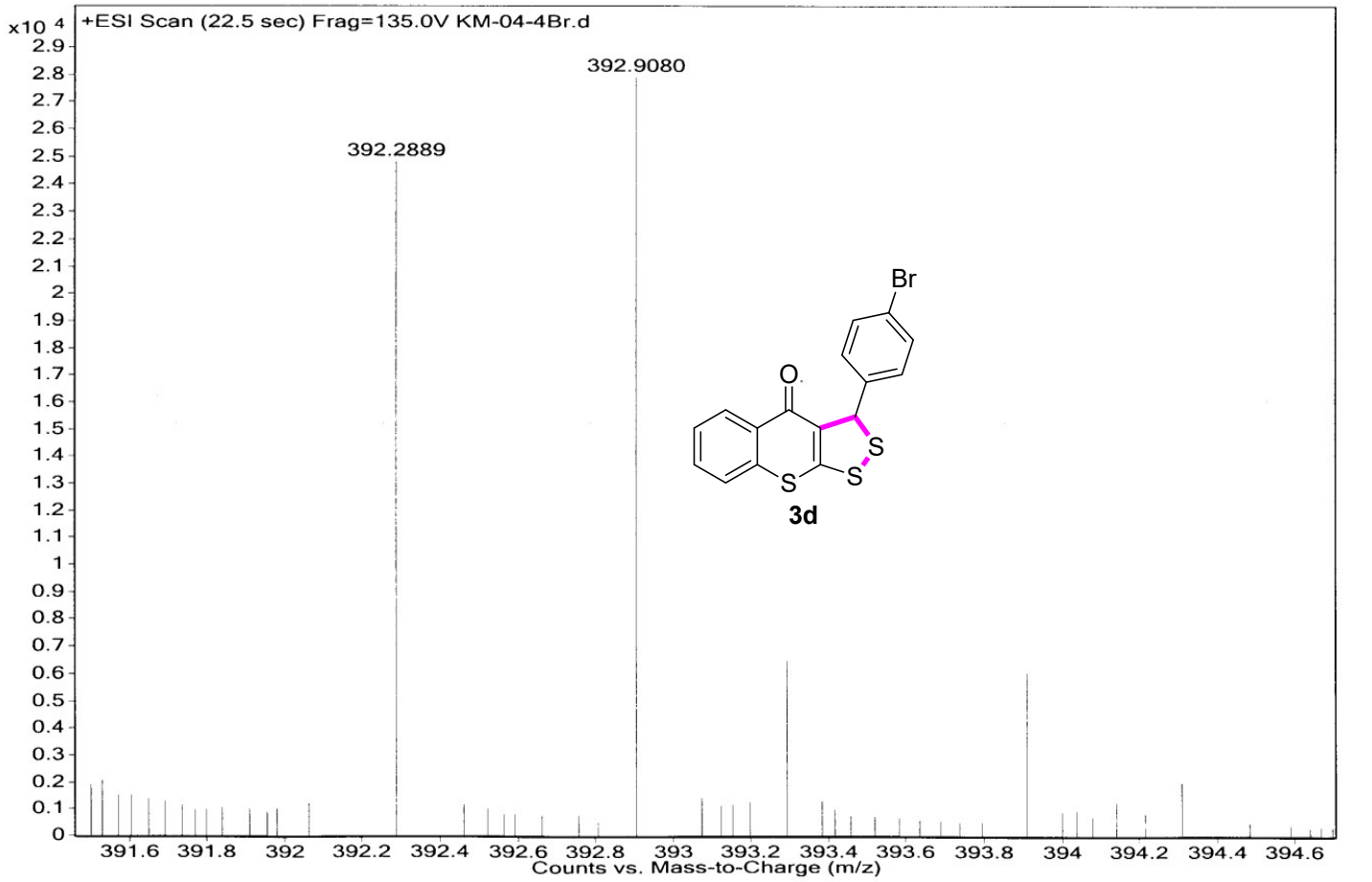
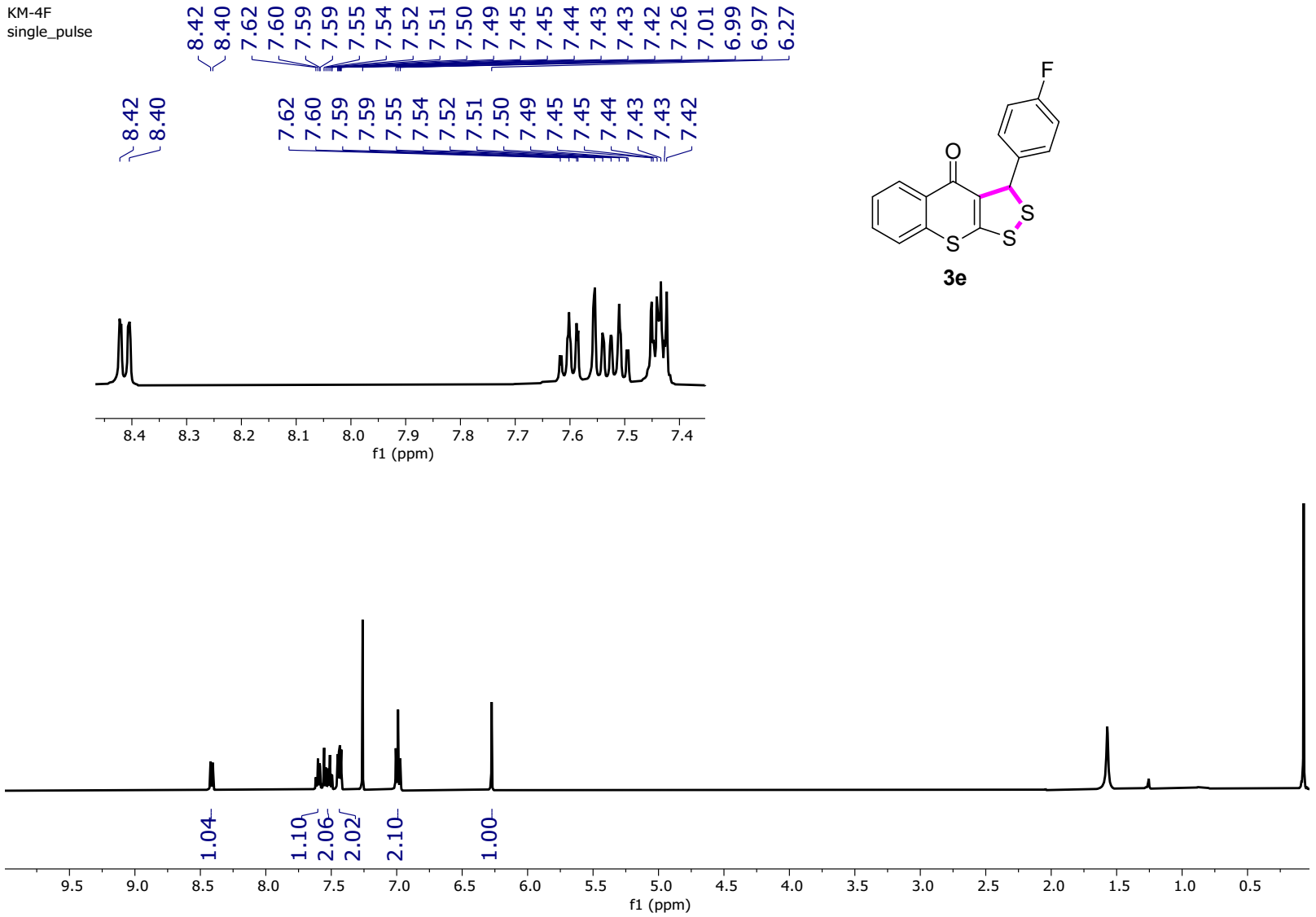


^{1}HNMR spectra of compound: 3e



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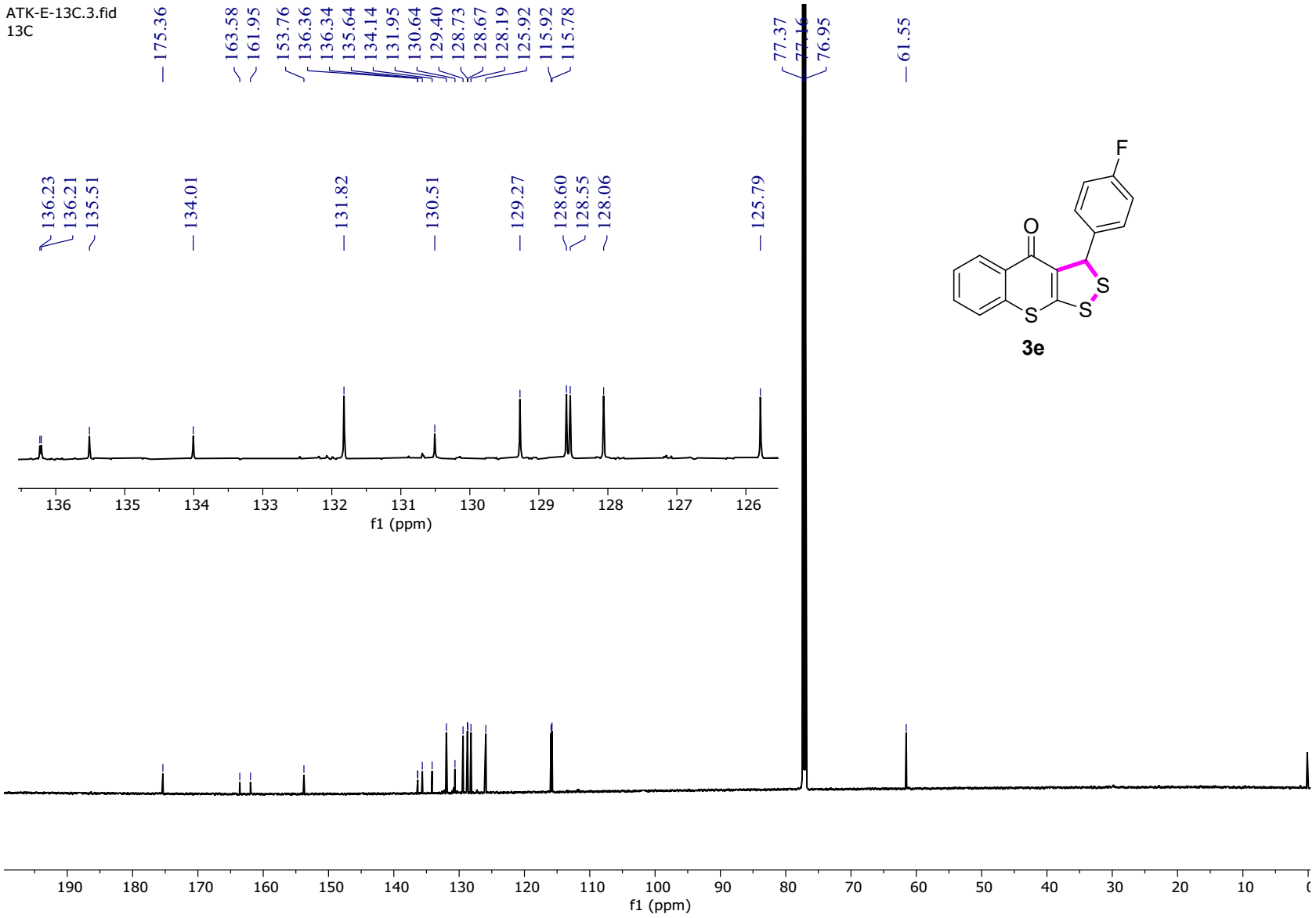

HRMS spectra of compound: 3e

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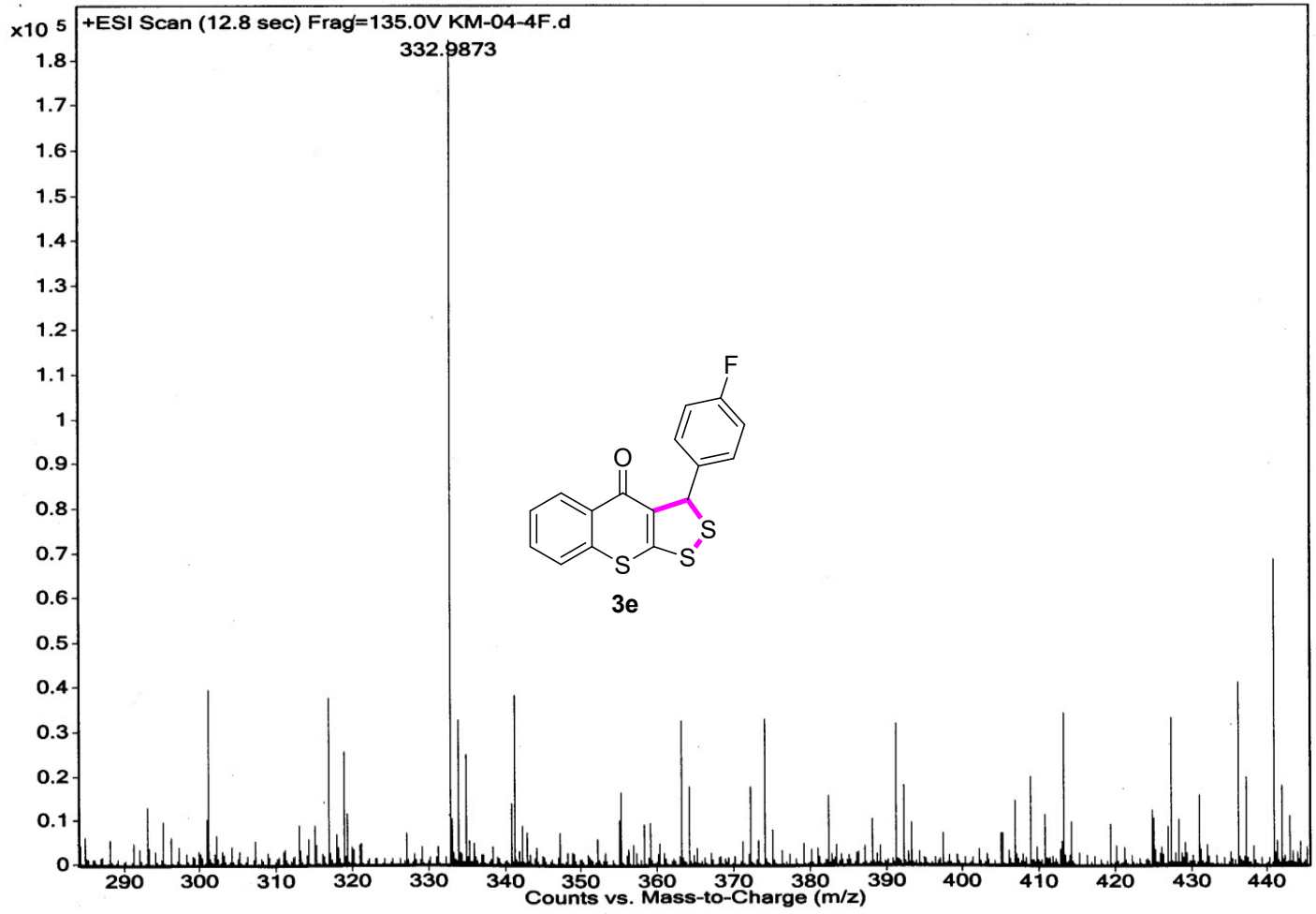
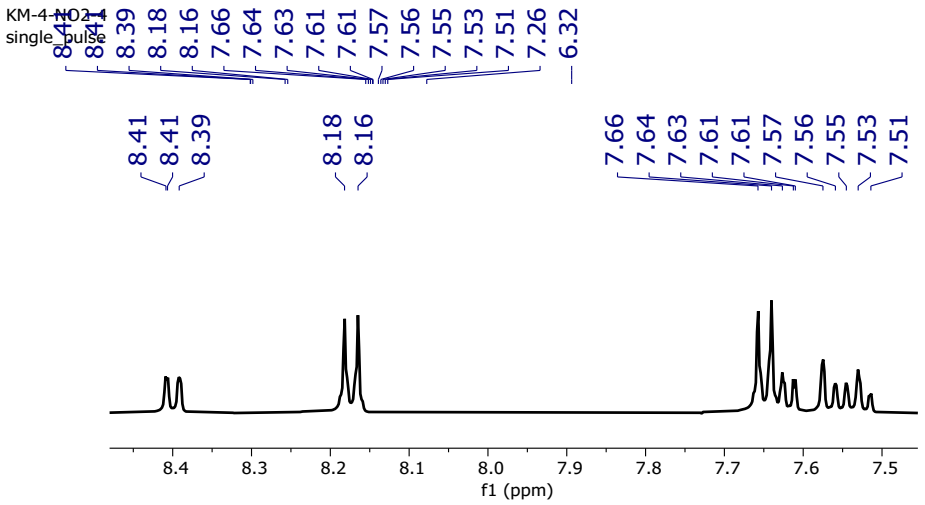
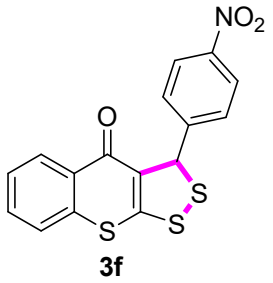


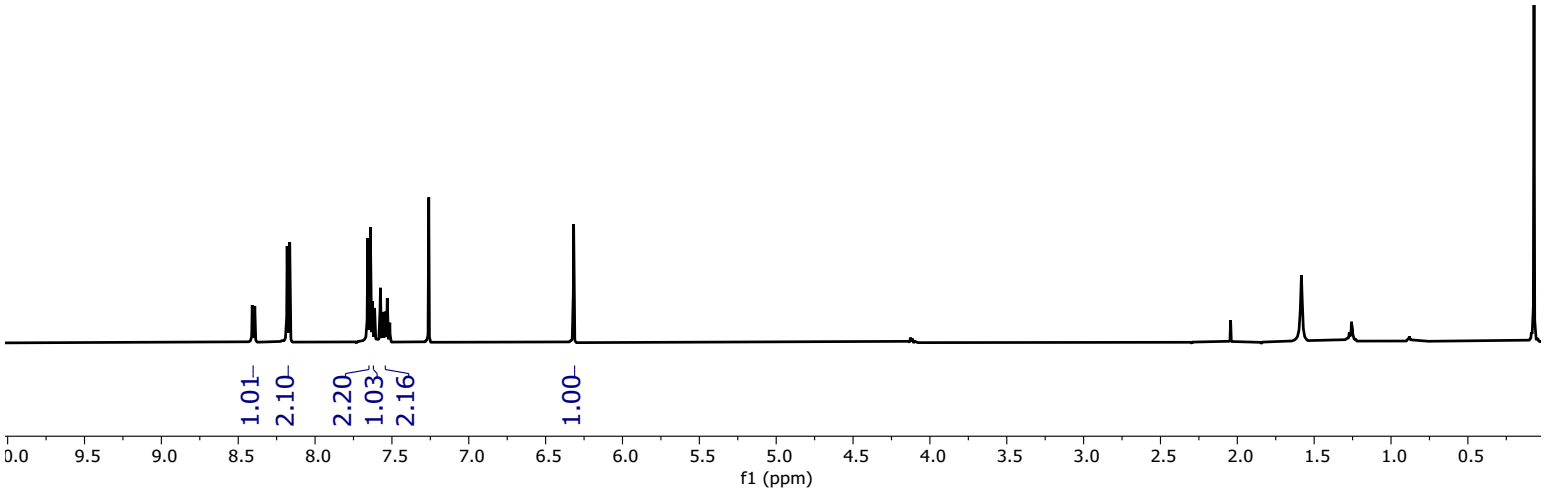
3e

[1]HNMR spectra of compound: 3f

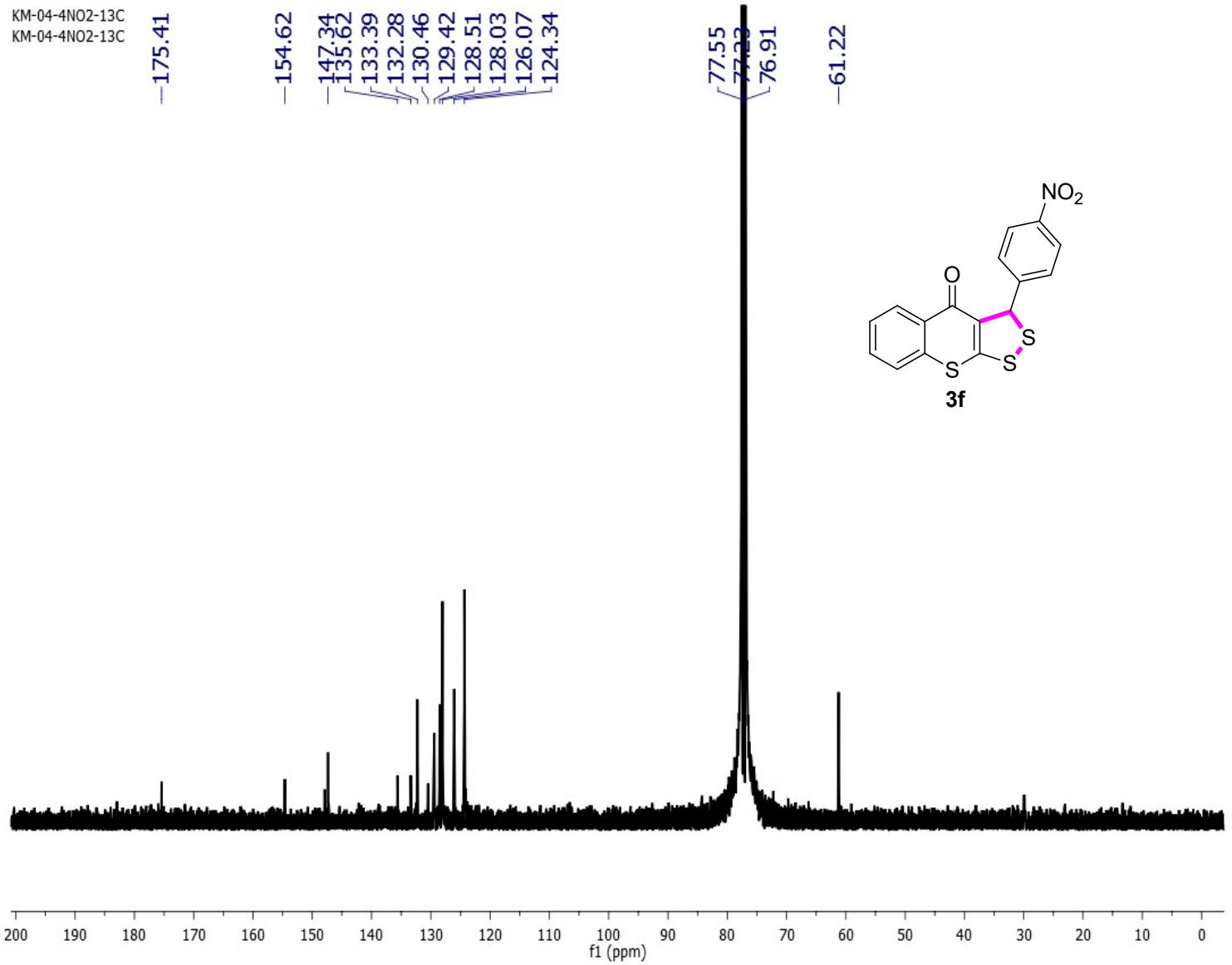




3f



^{13}CNMR spectra of compound: 3f



HRMS spectra of compound: 3f

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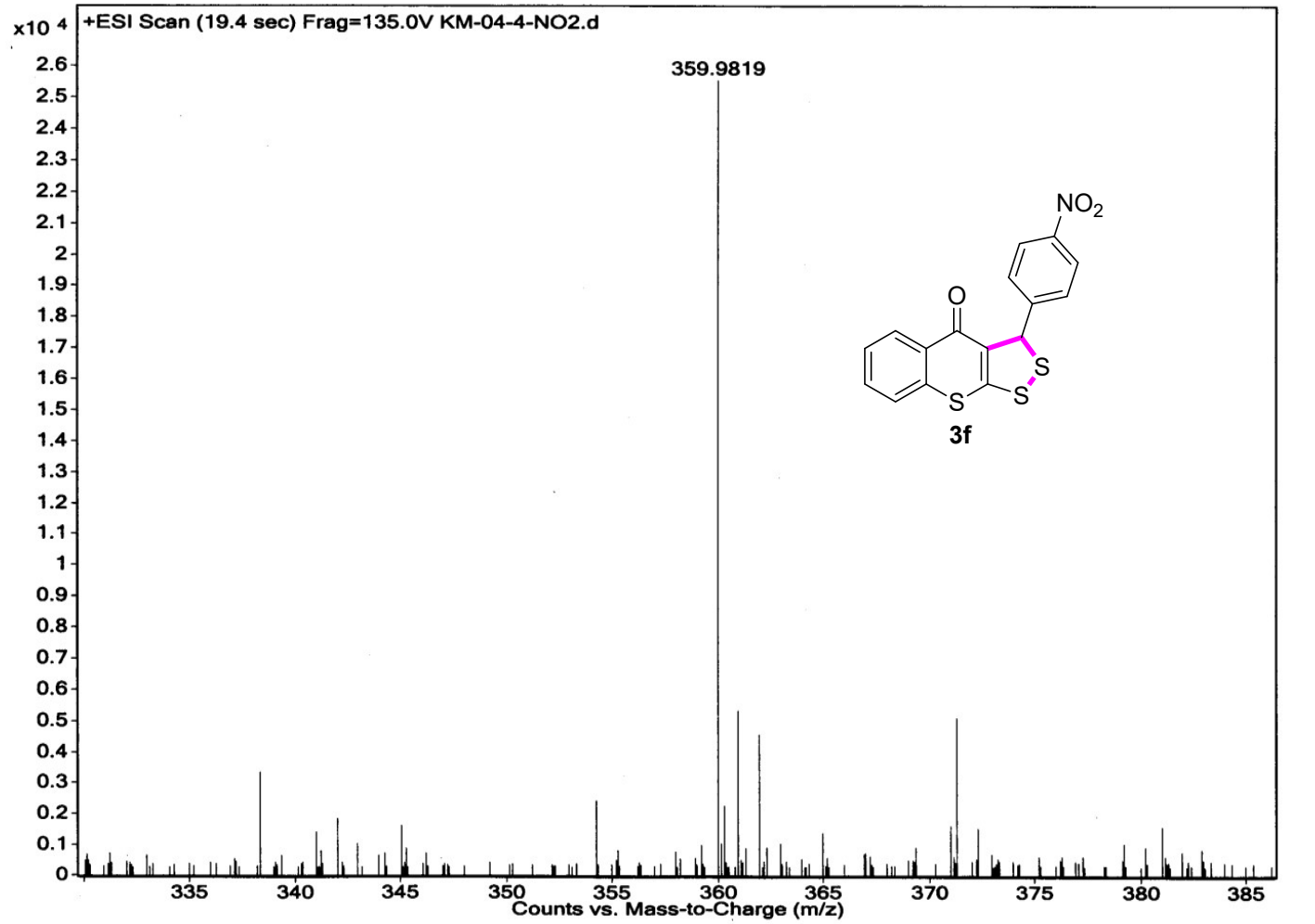
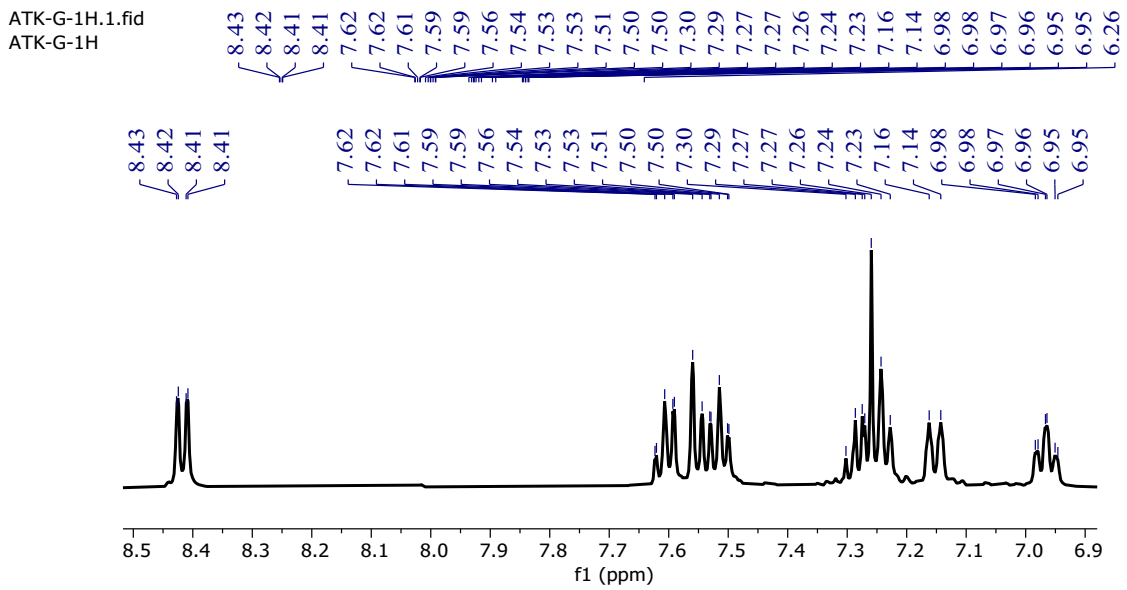
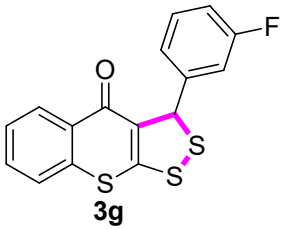
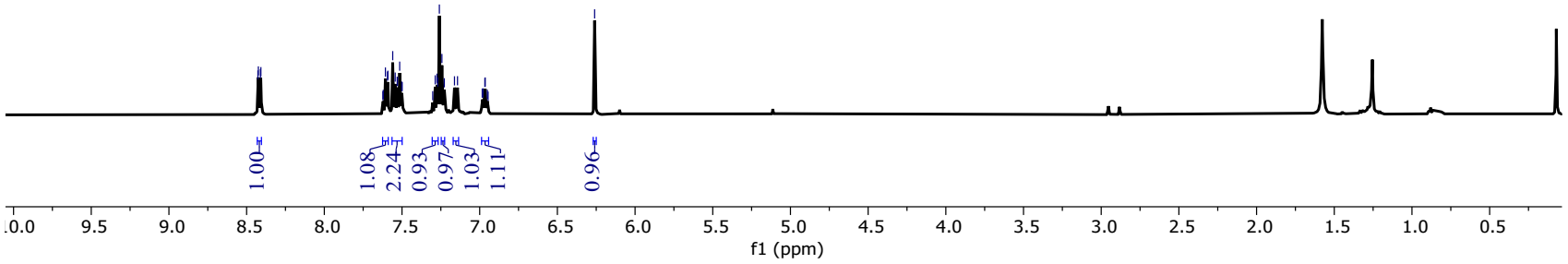


^{1}HNMR spectra of compound: 3g

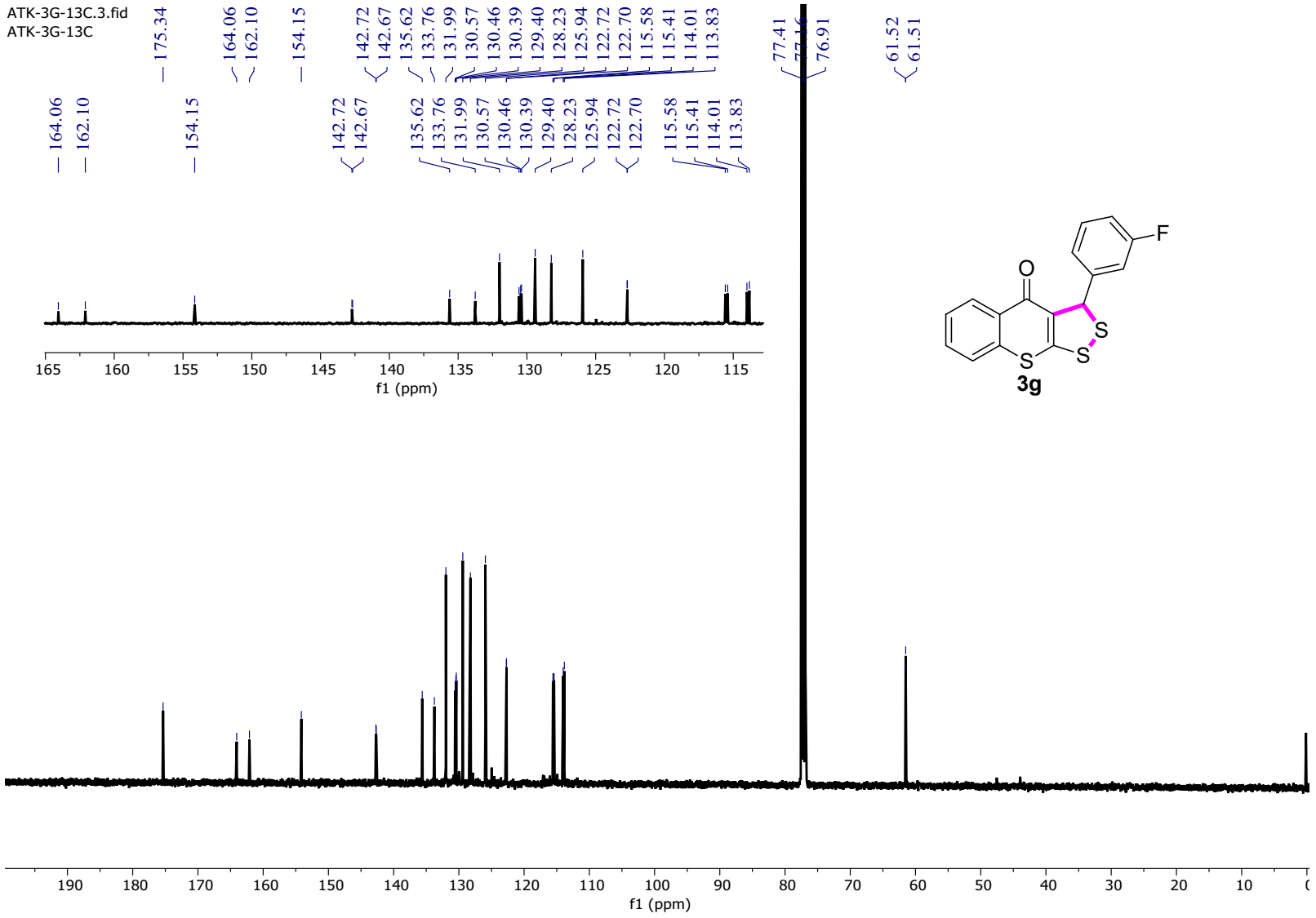




3g



^{13}C NMR spectra of compound: 3g



HRMS spectra of compound: 3g

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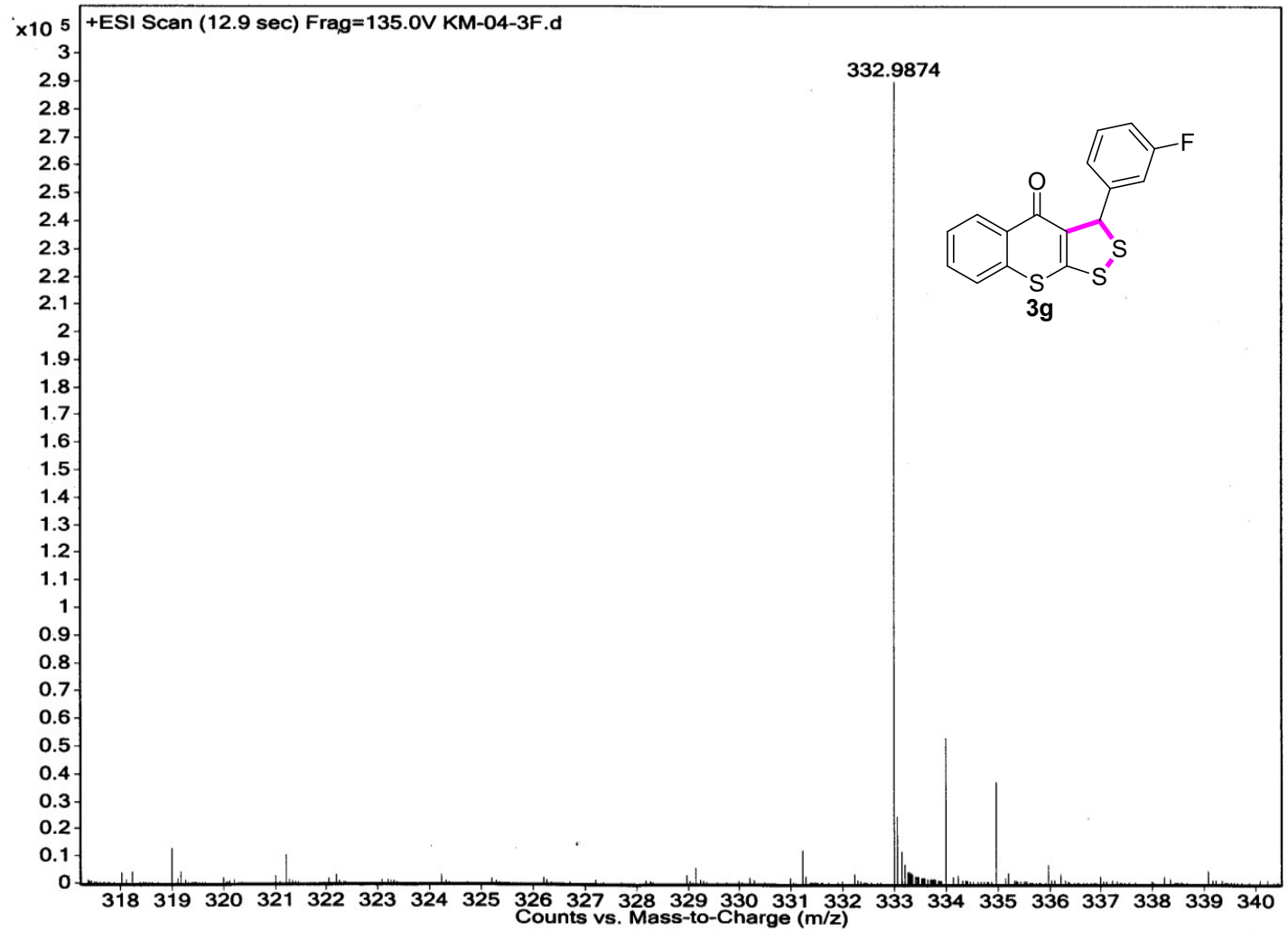
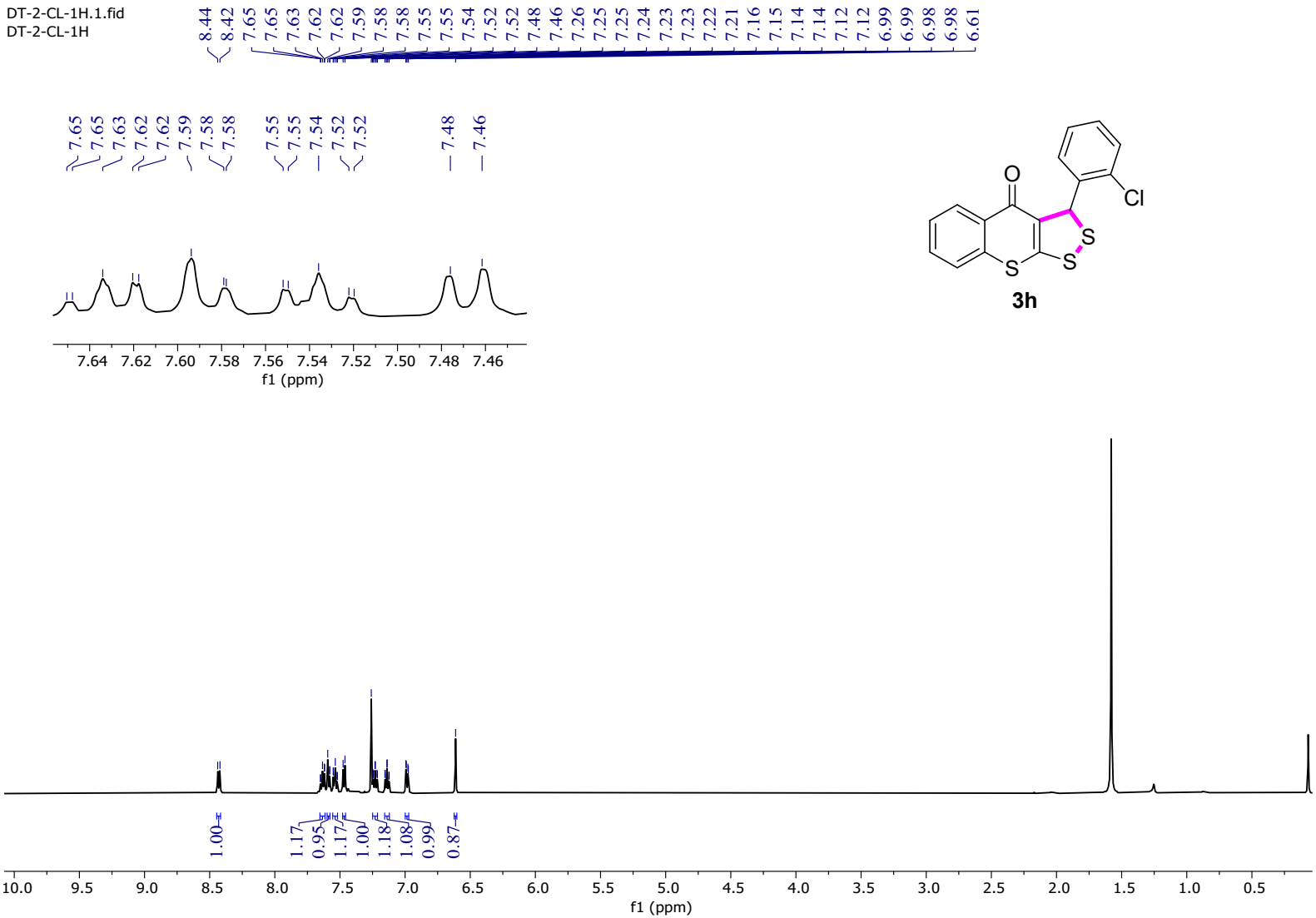
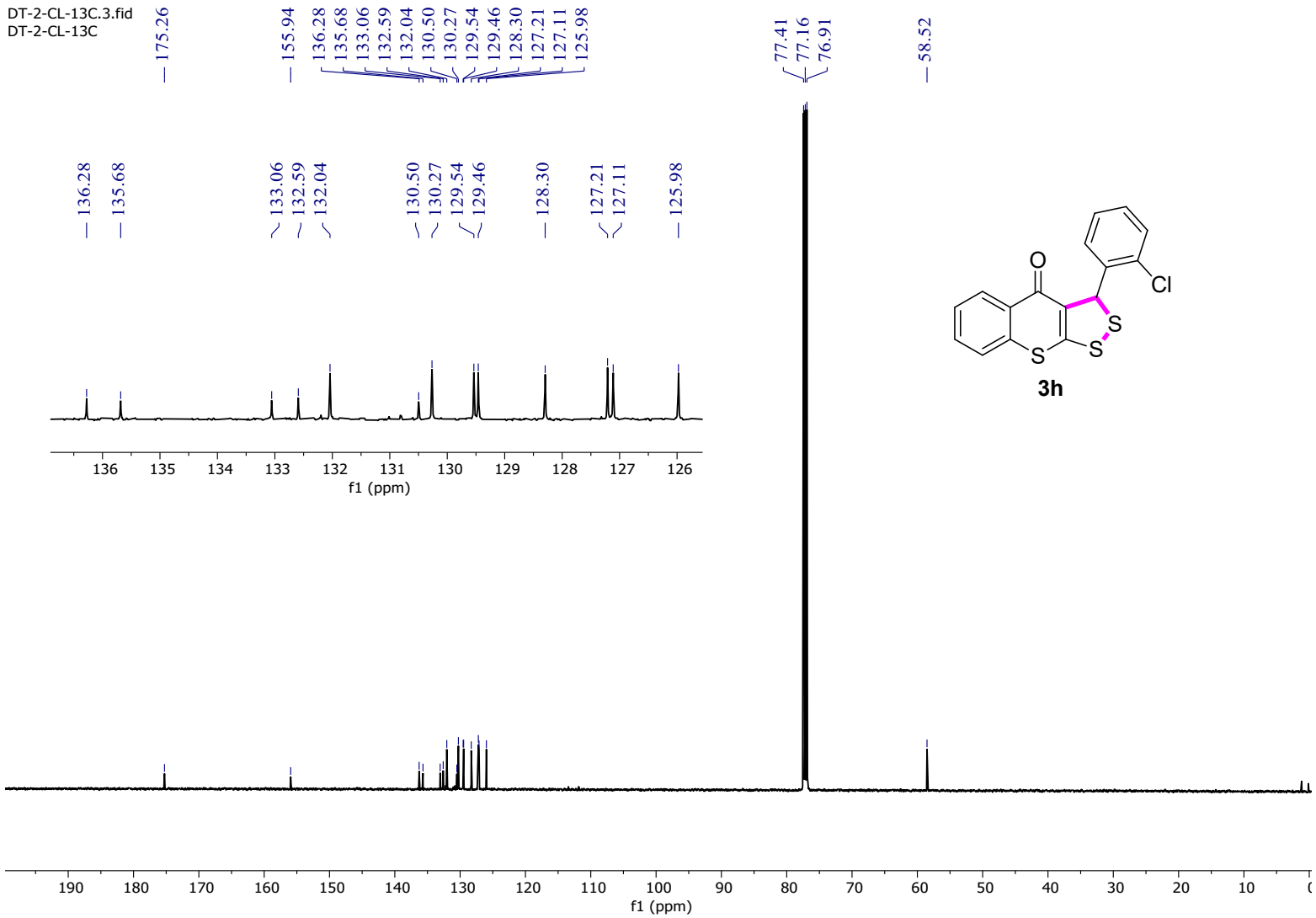


^{1}HNMR spectra of compound: 3h



^{13}CNMR spectra of compound: 3h



HRMS spectra of compound: 3h

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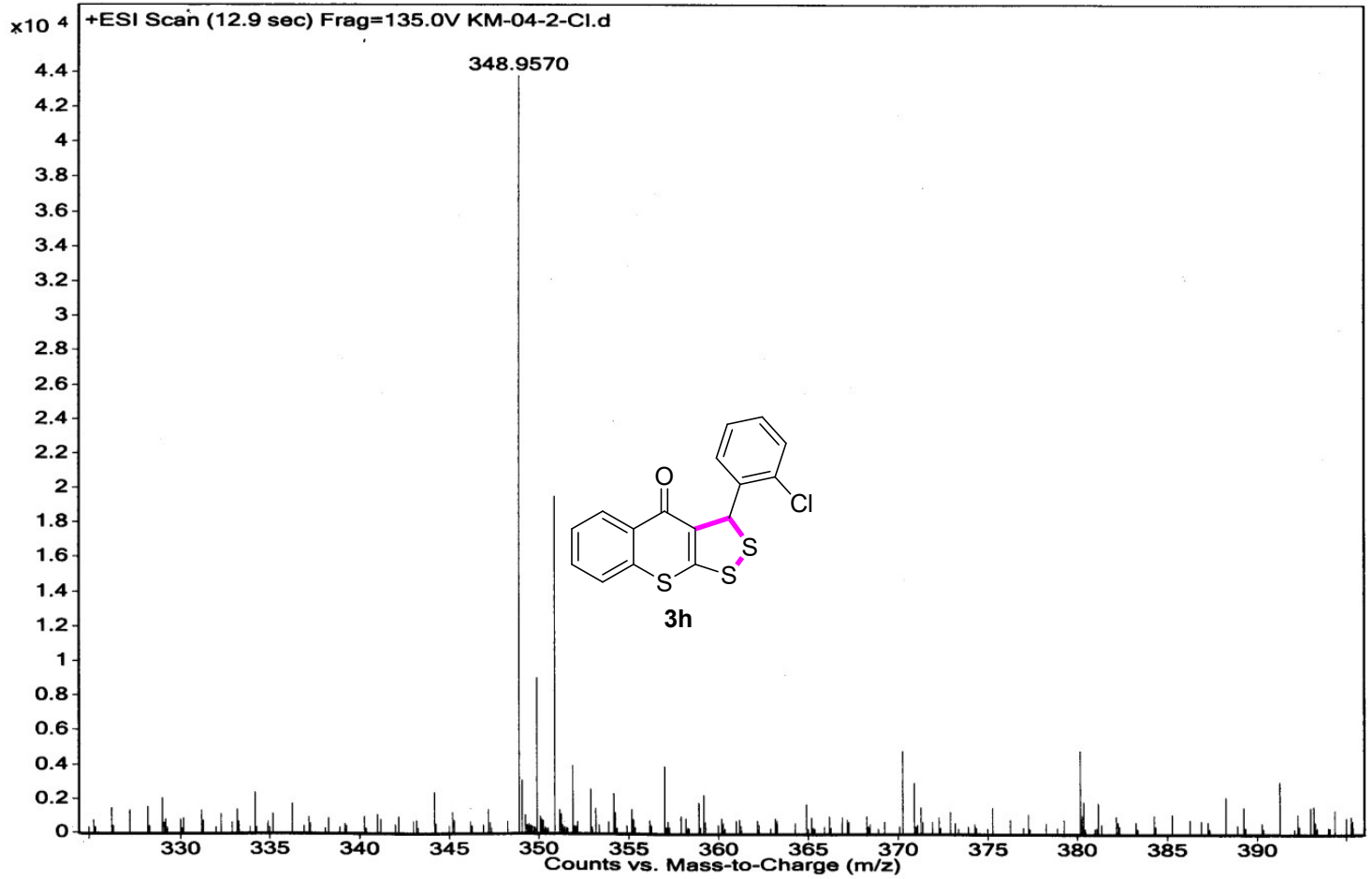
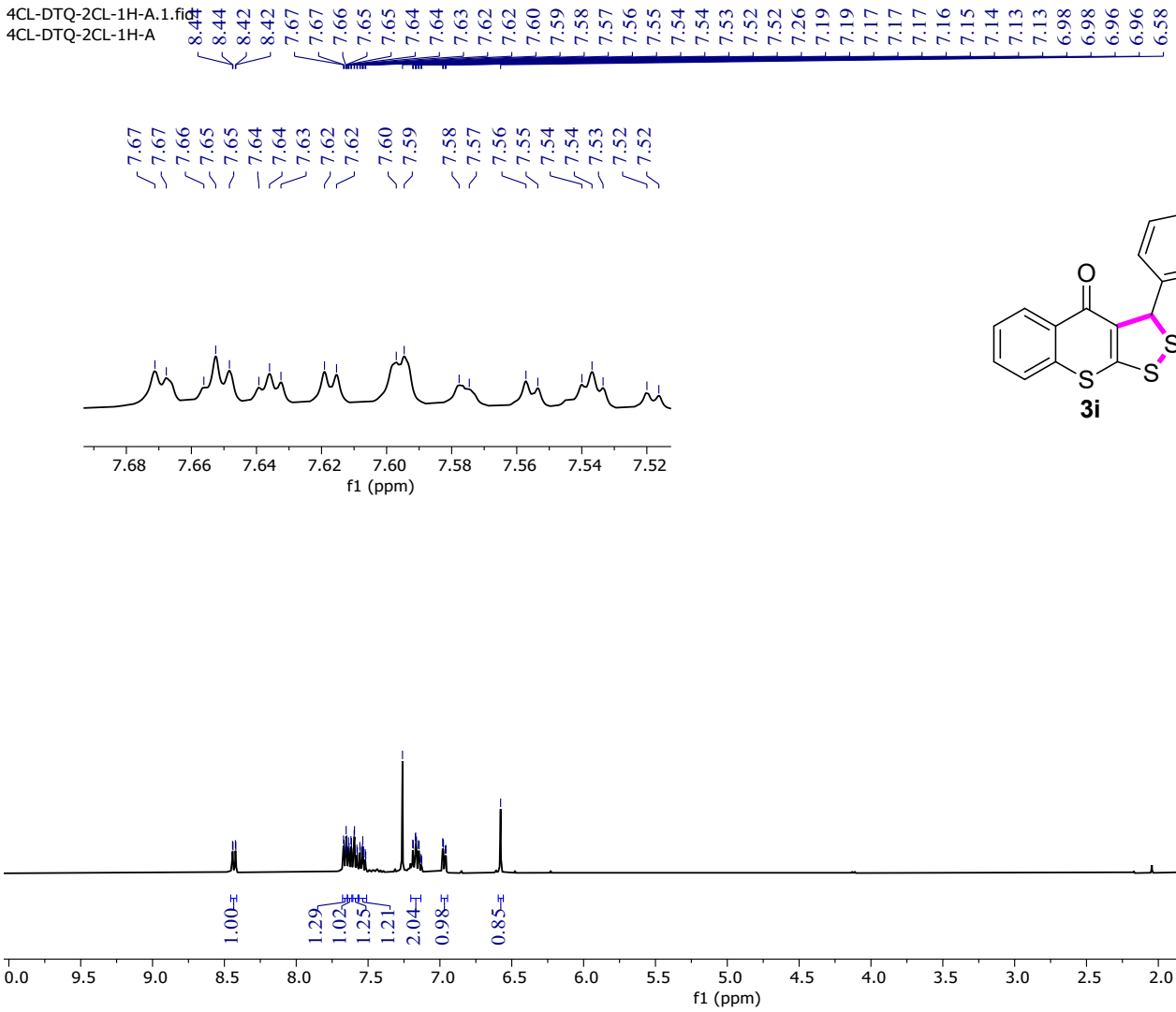
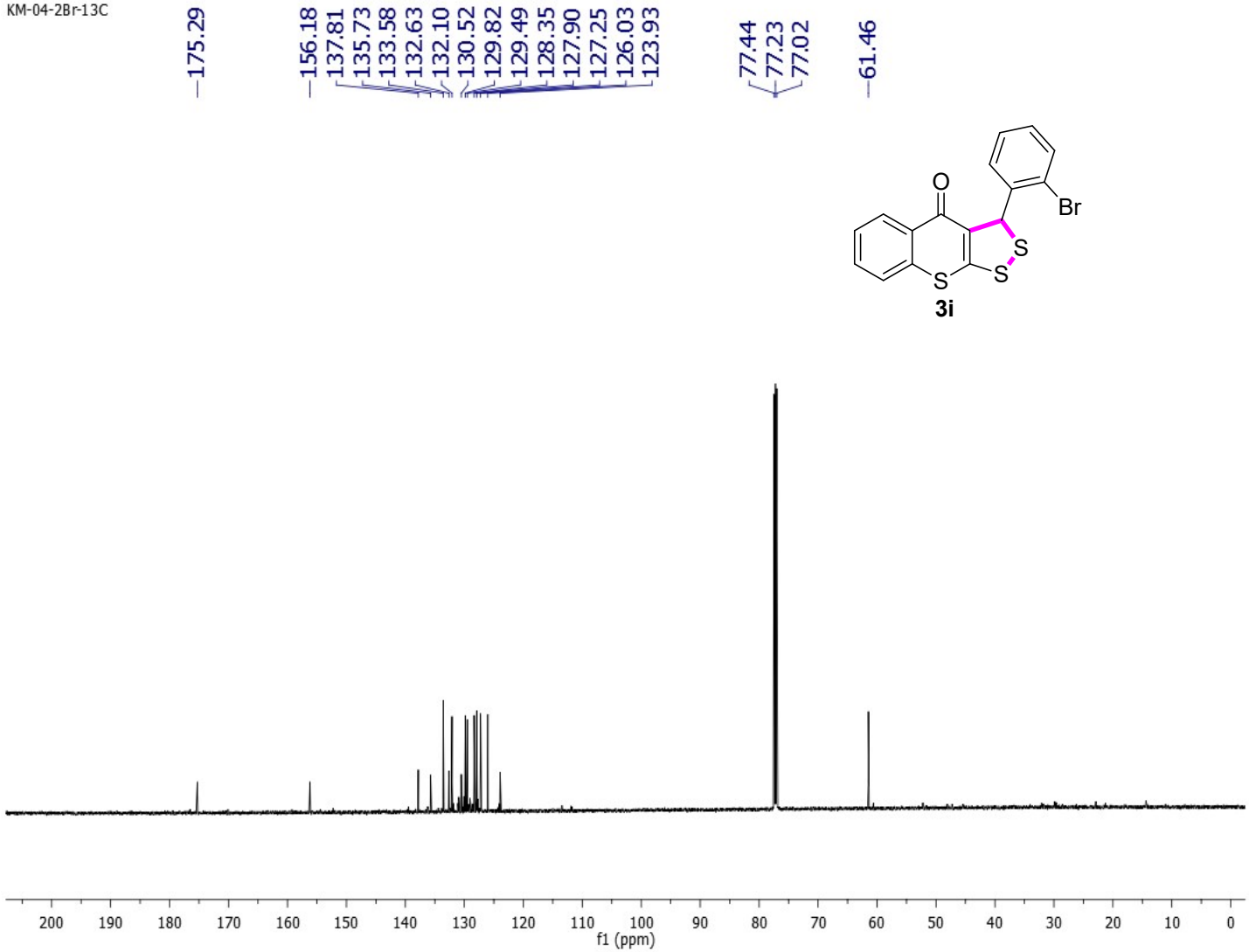


^{1}HNMR spectra of compound: 3i



^{13}CNMR spectra of compound: 3i



HRMS spectra of compound: 3i

Sample Name	Unavailable	**Position**	Unavailable	**Instrument Name**	Unavailable	**User Name**	Unavailable
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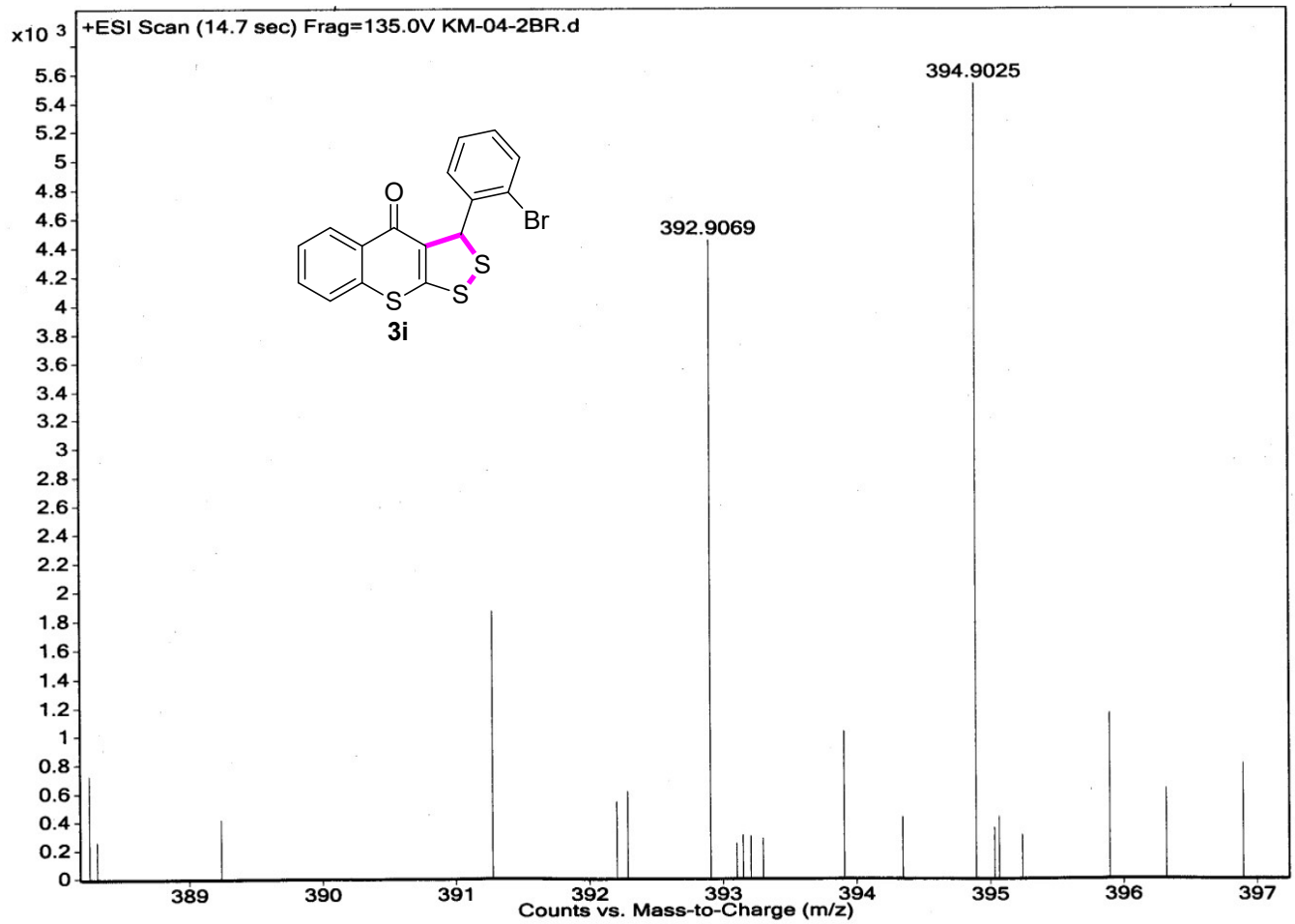
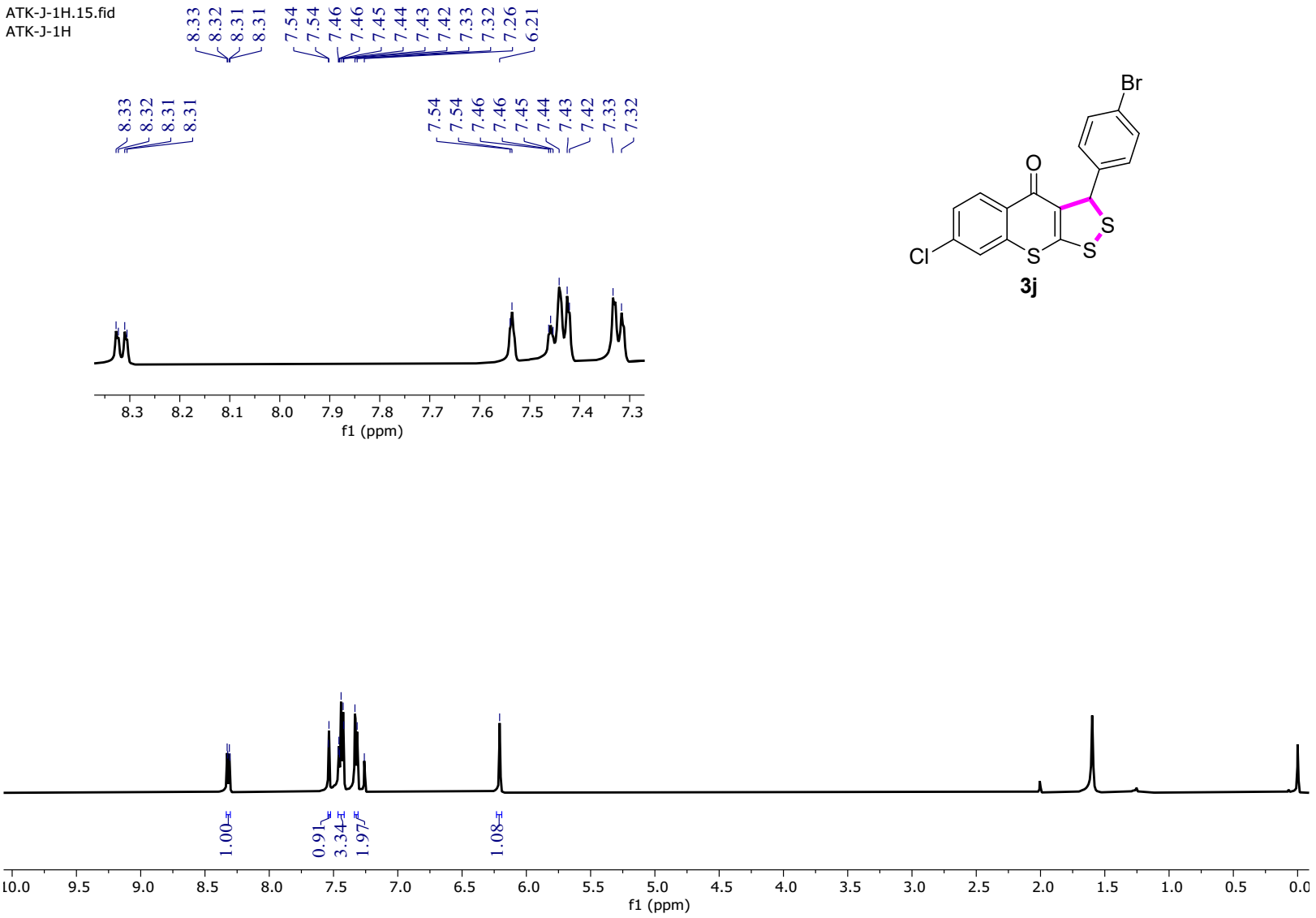
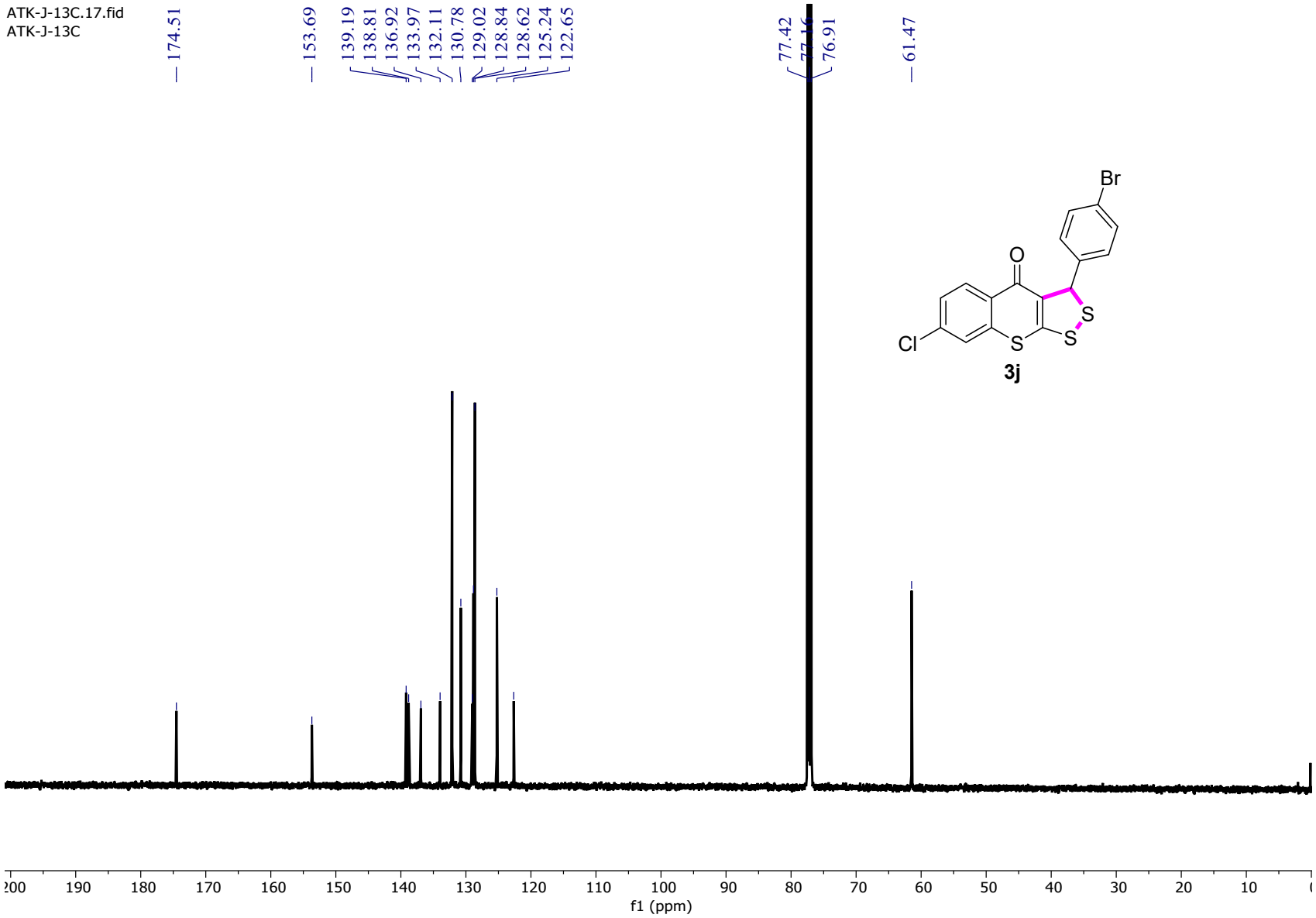


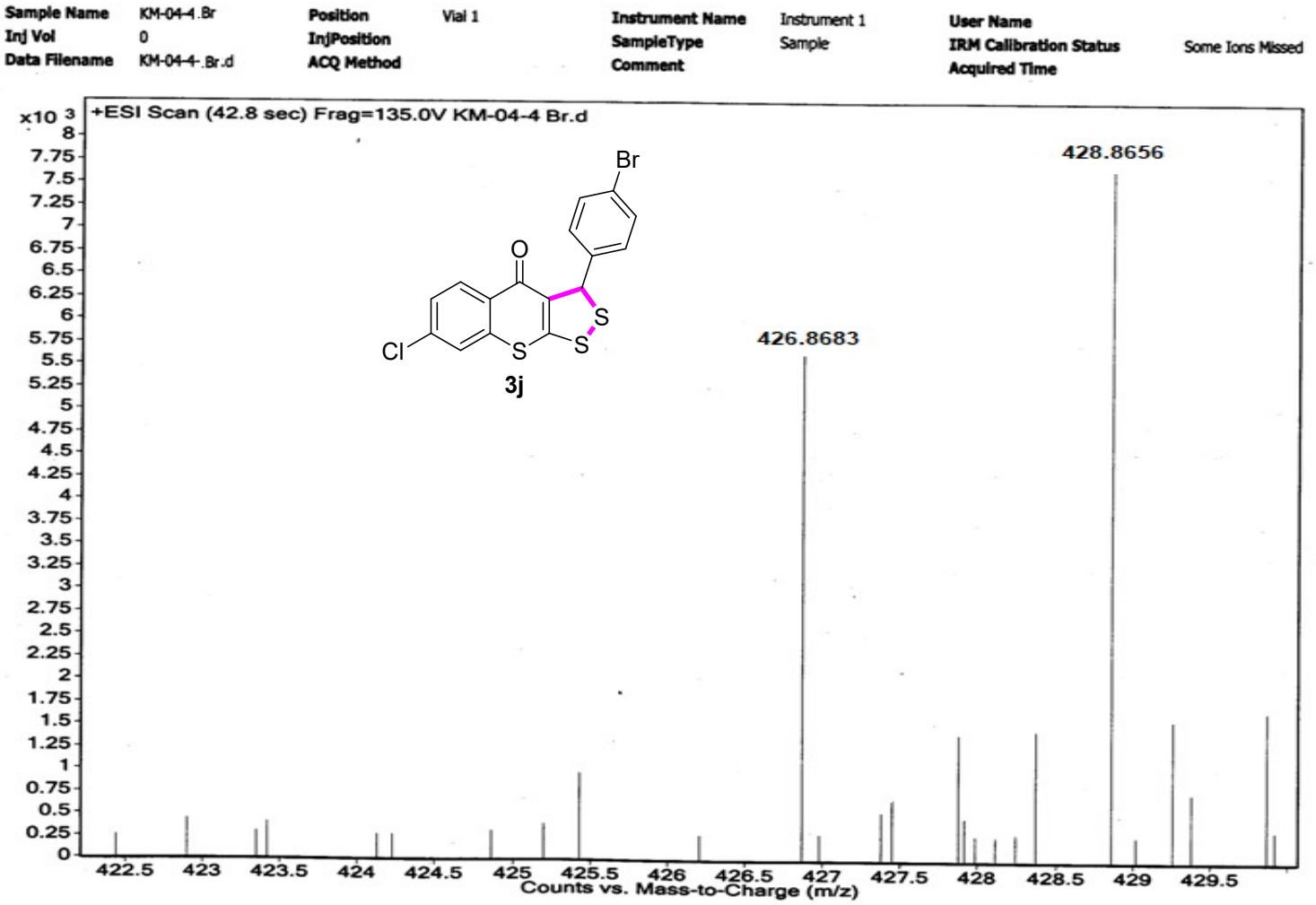
^{1}HNMR spectra of compound: 3j



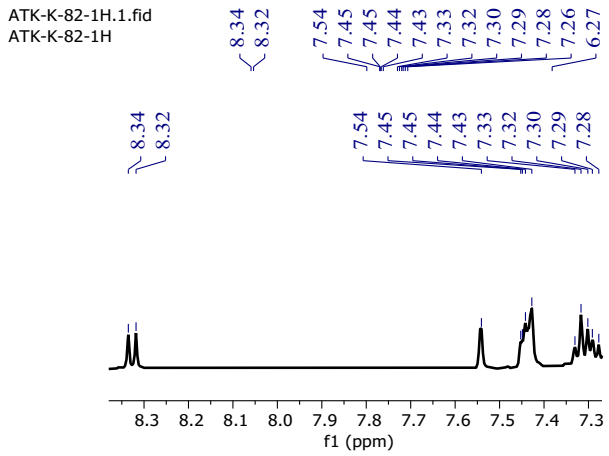
^{13}C NMR spectra of compound: 3j

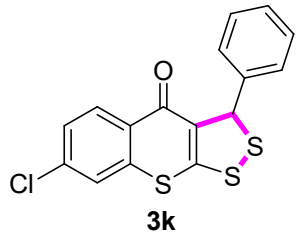


HRMS spectra of compound: 3j

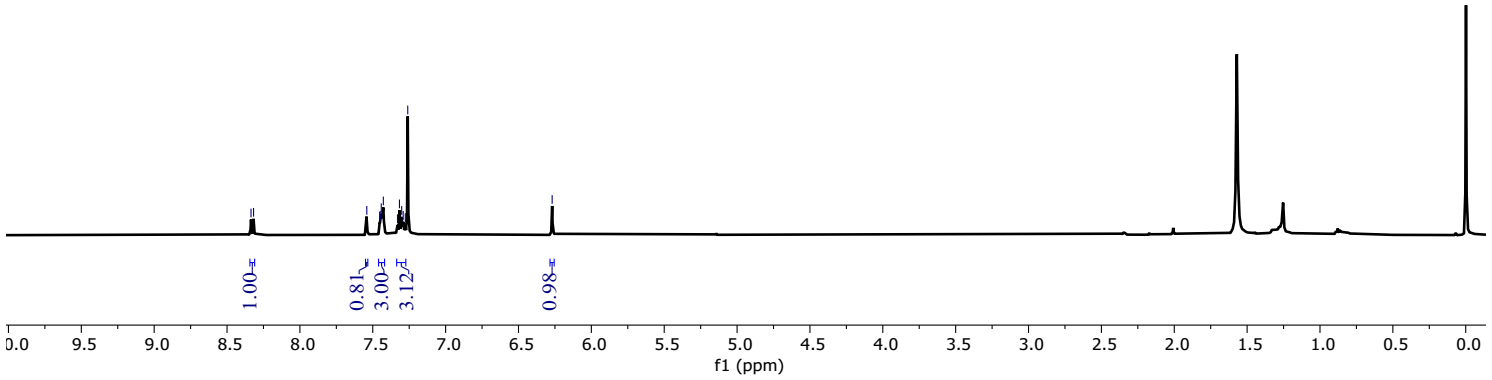


^{1}HNMR spectra of compound: 3k

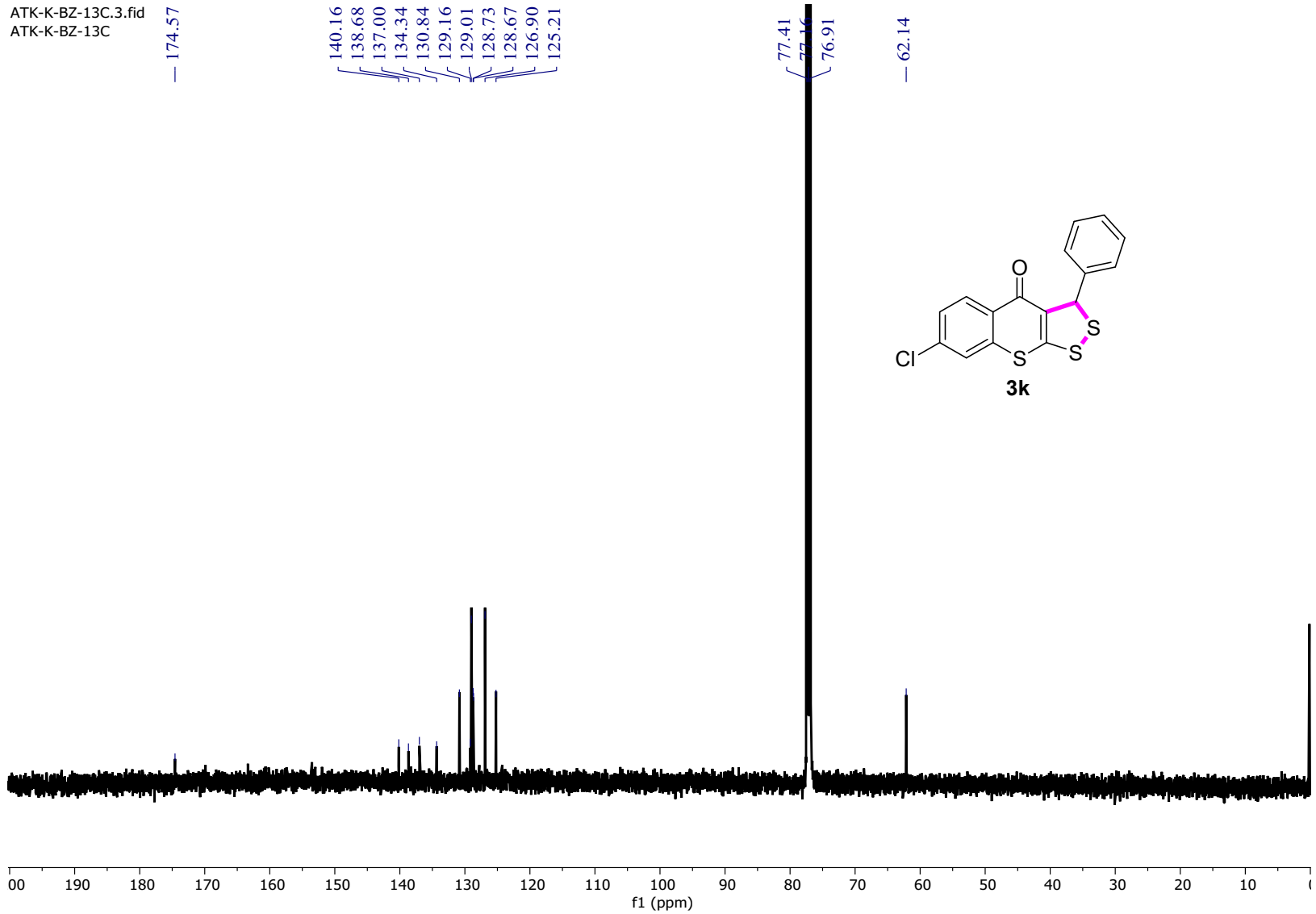




3k



^{13}CNMR spectra of compound: 3k



HRMS spectra of compound: 3k

Sample Name	KM-04-4-BEN	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
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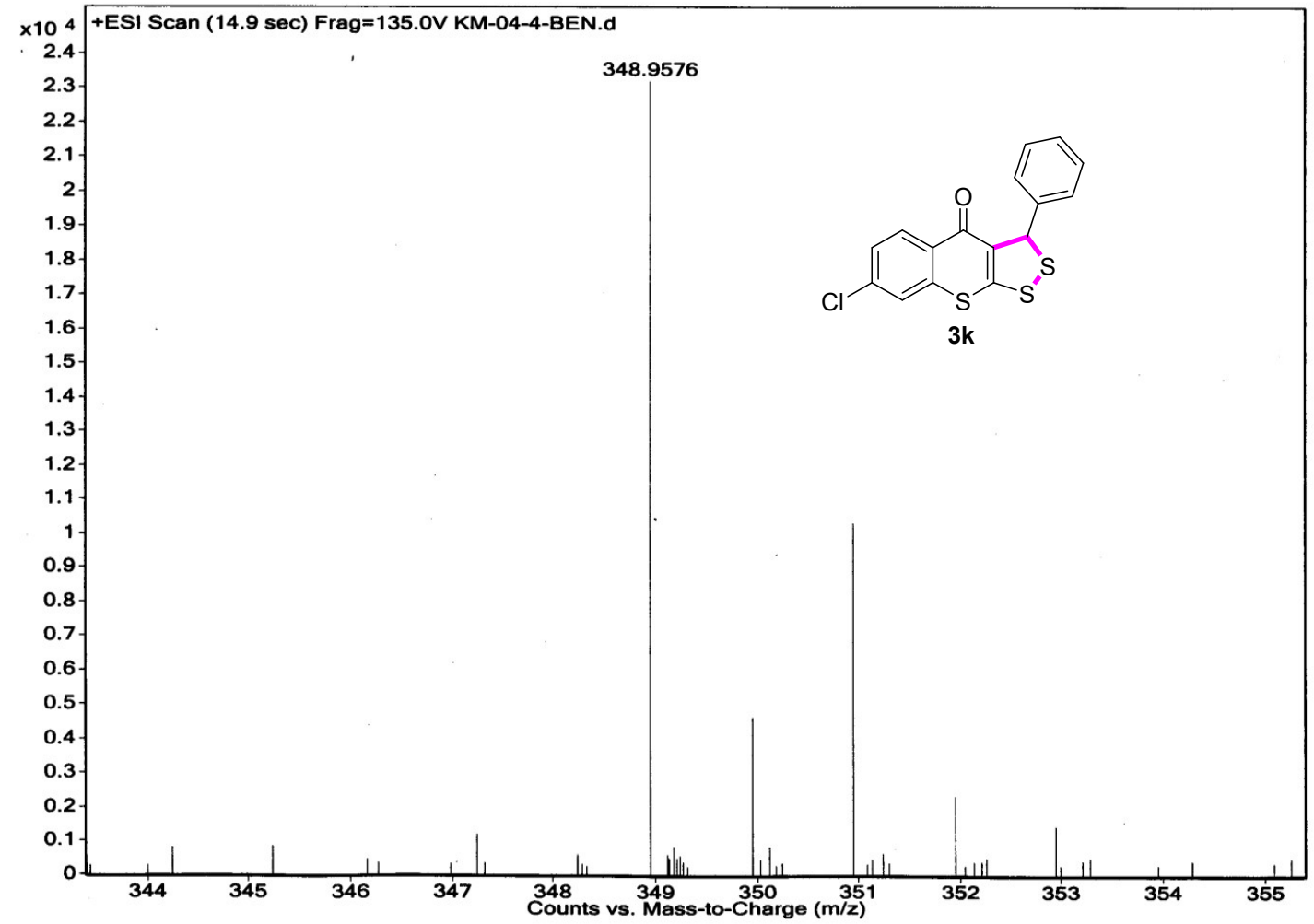
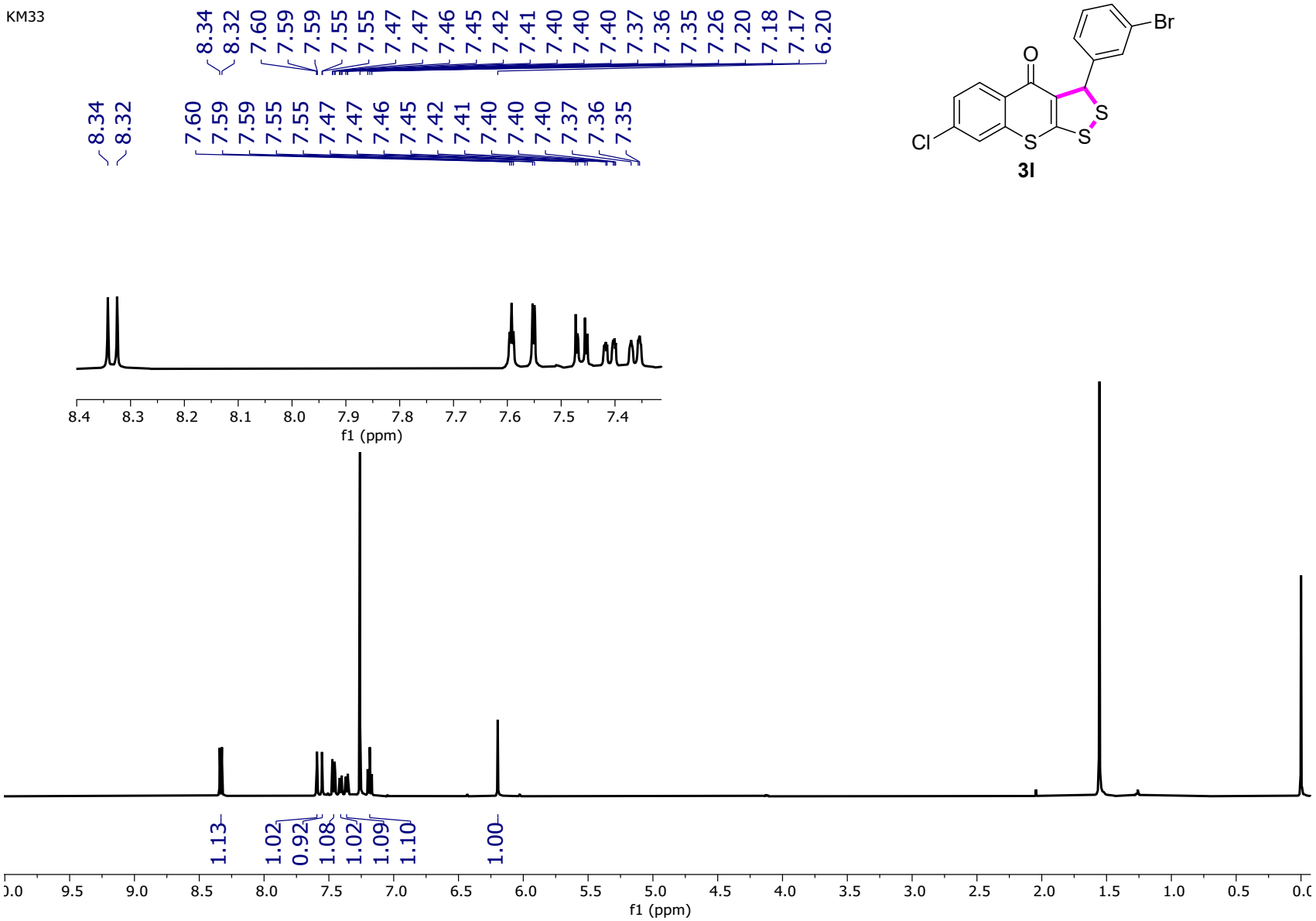
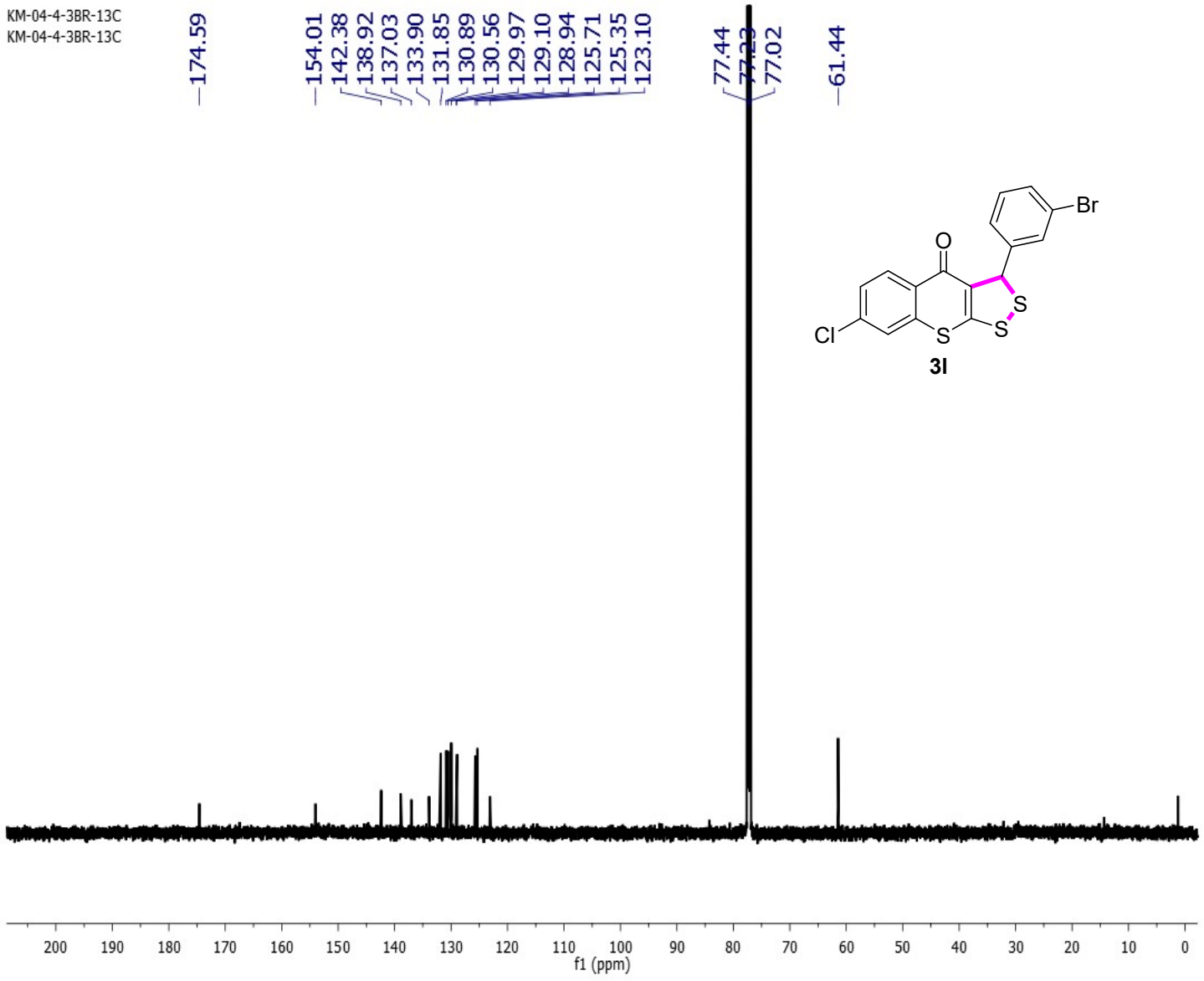


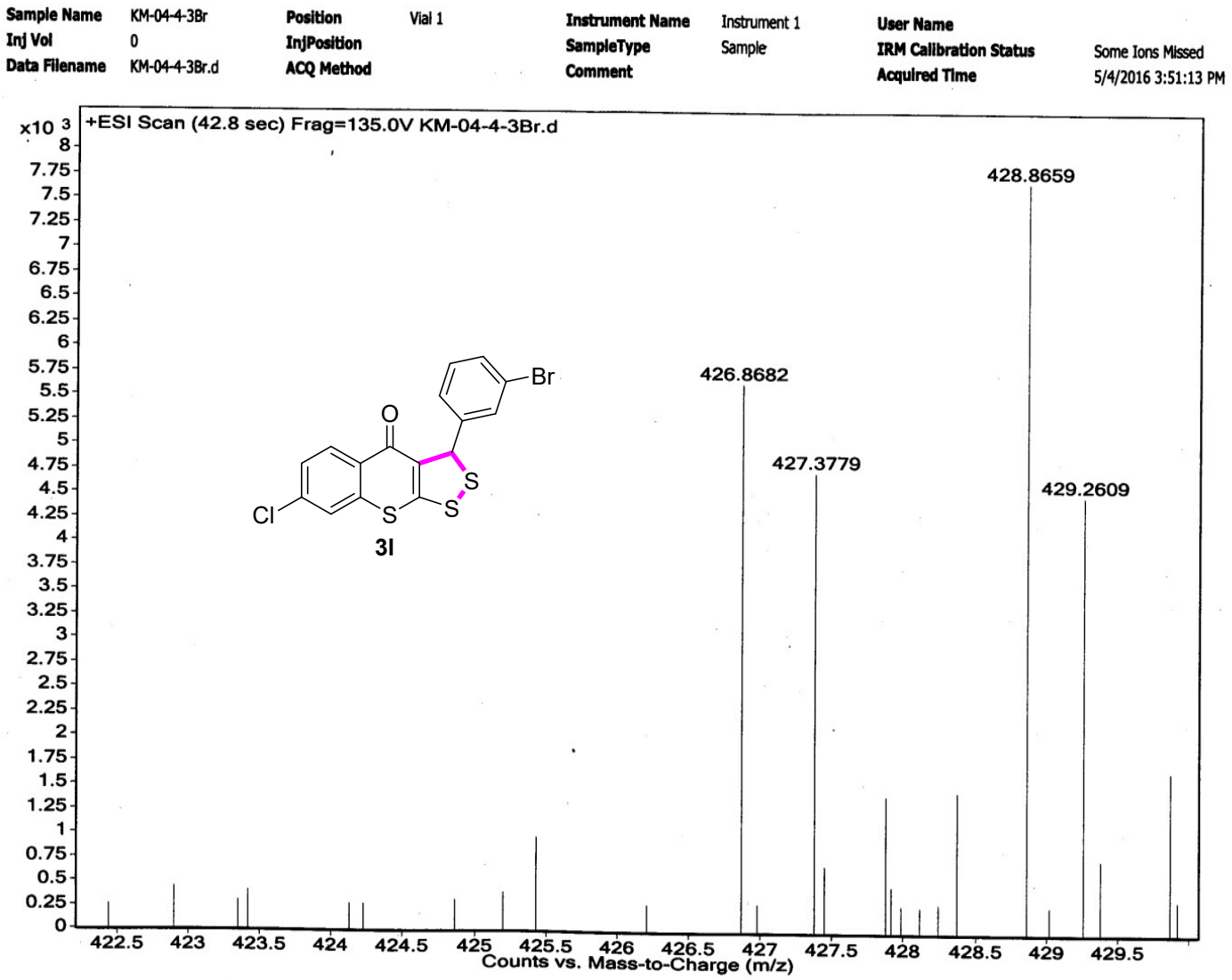
^{1}H NMR spectra of compound: 3l



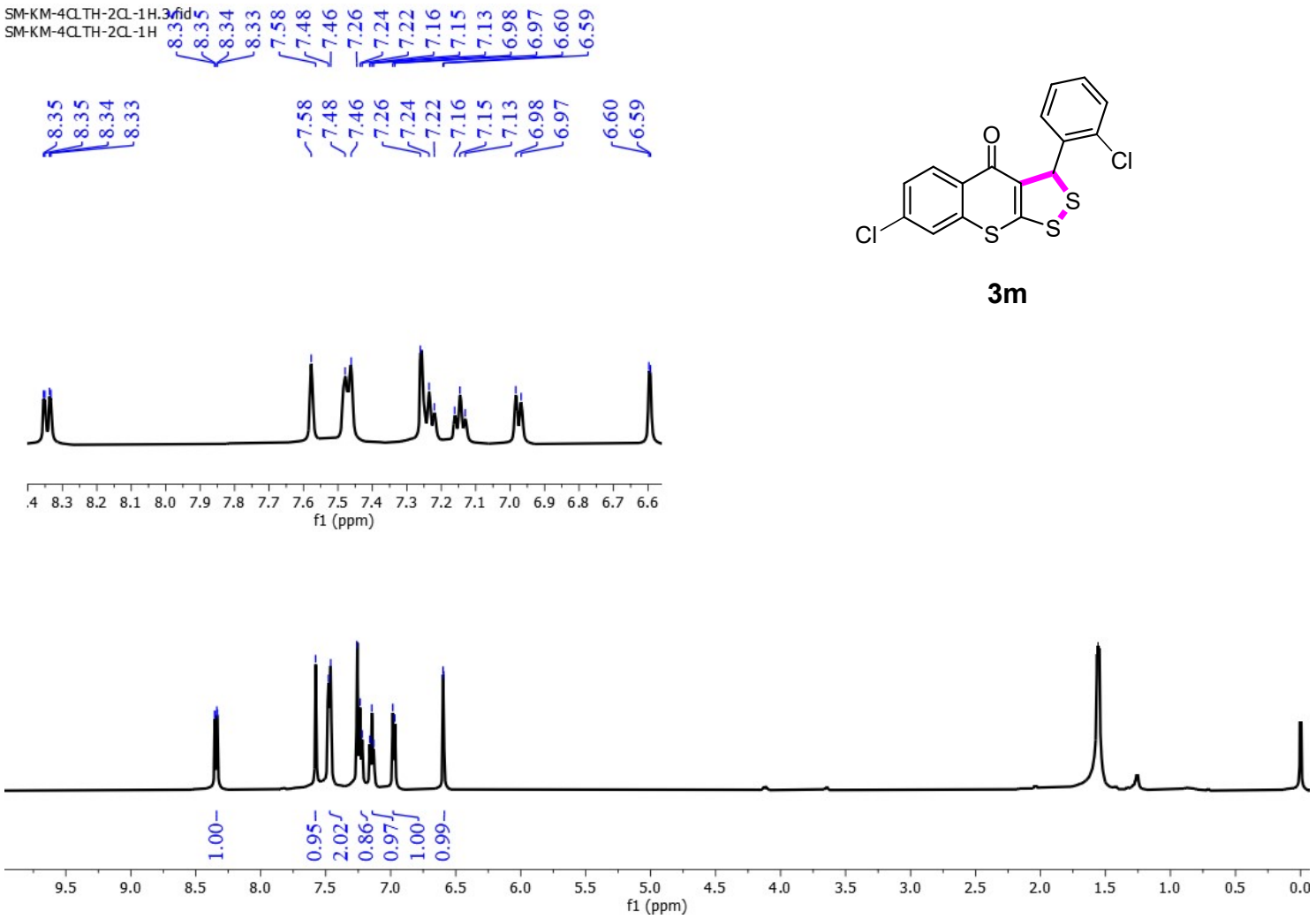
^{13}CNMR spectra of compound: 3l



HRMS spectra of compound: 3l

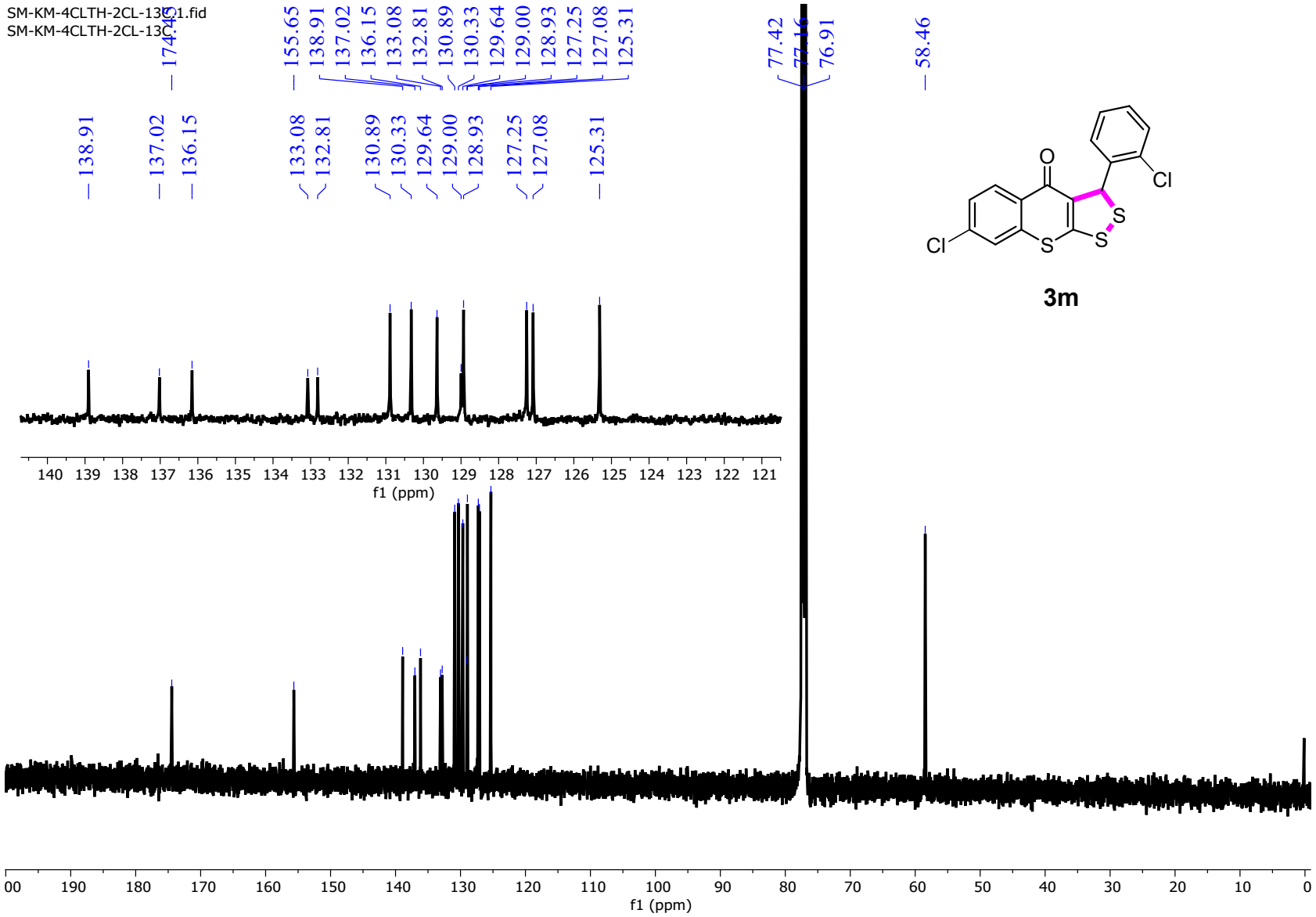


[1]HNMR spectra of compound: 3m



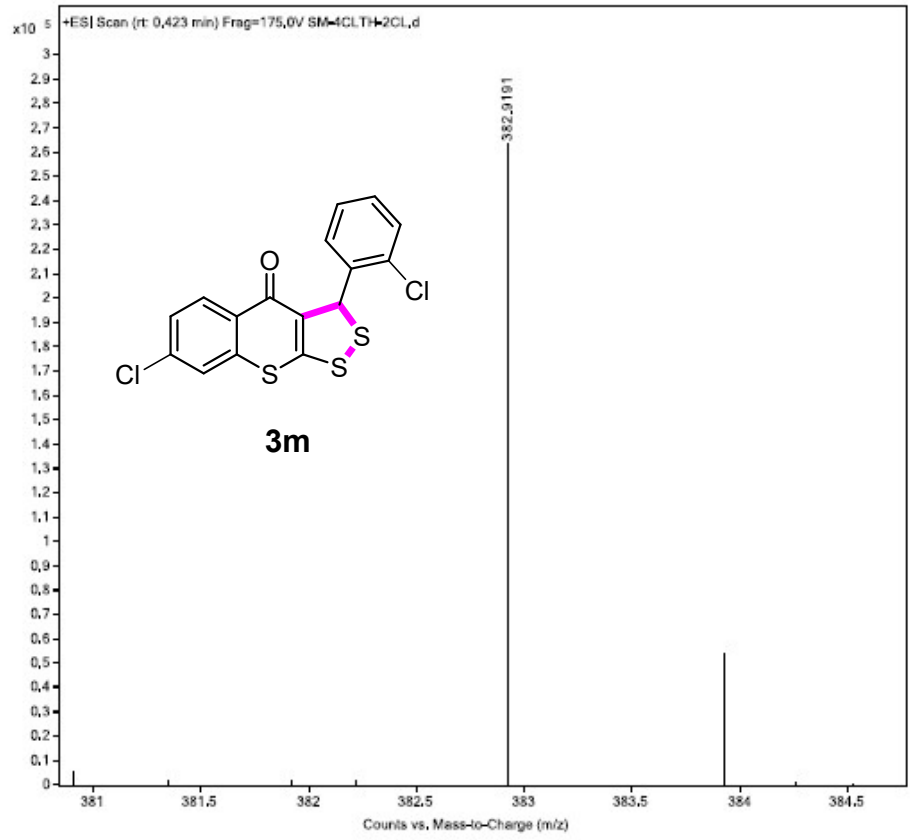
3m

^{13}CNMR spectra of compound: 3m

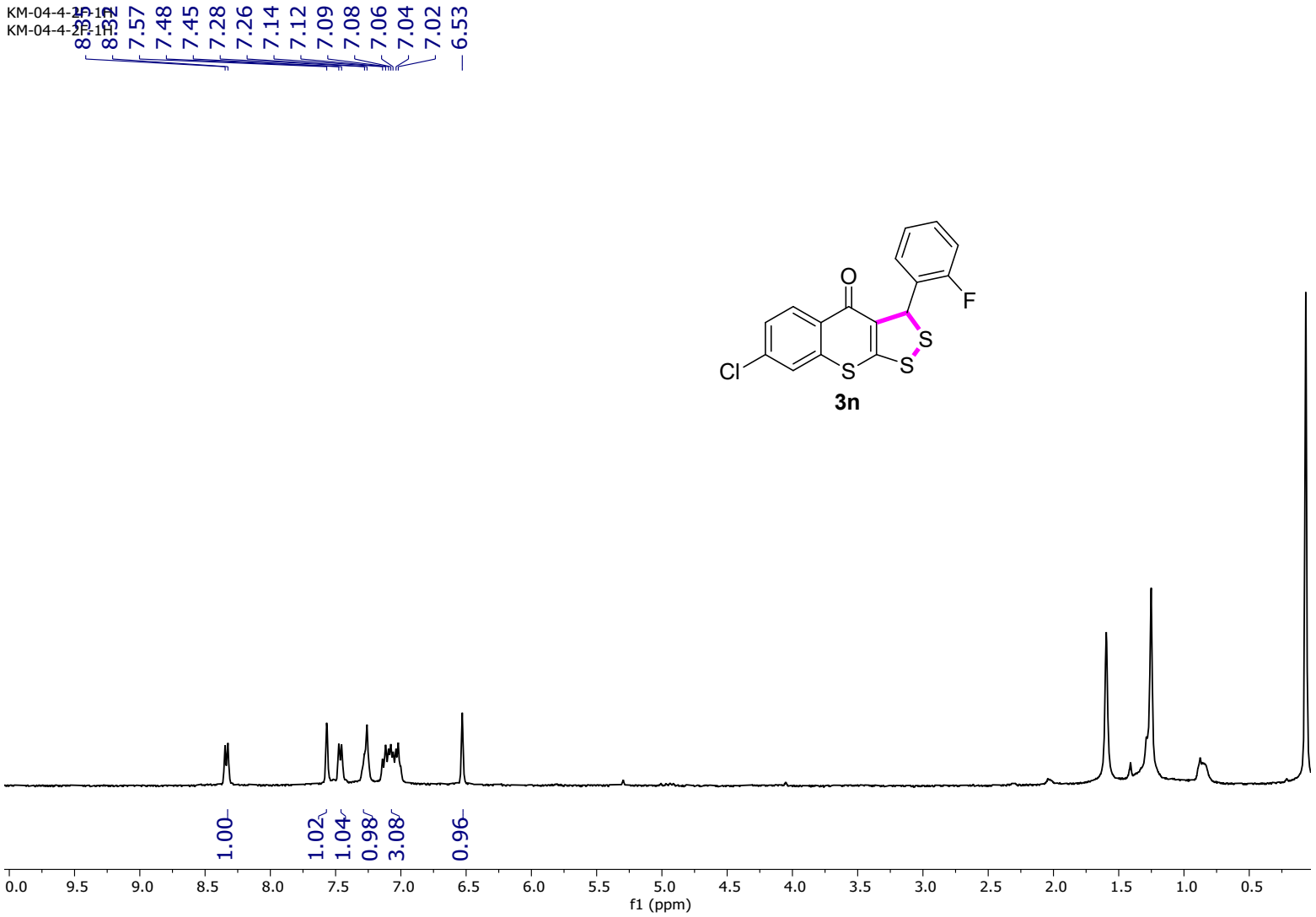


HRMS spectra of compound: 3m

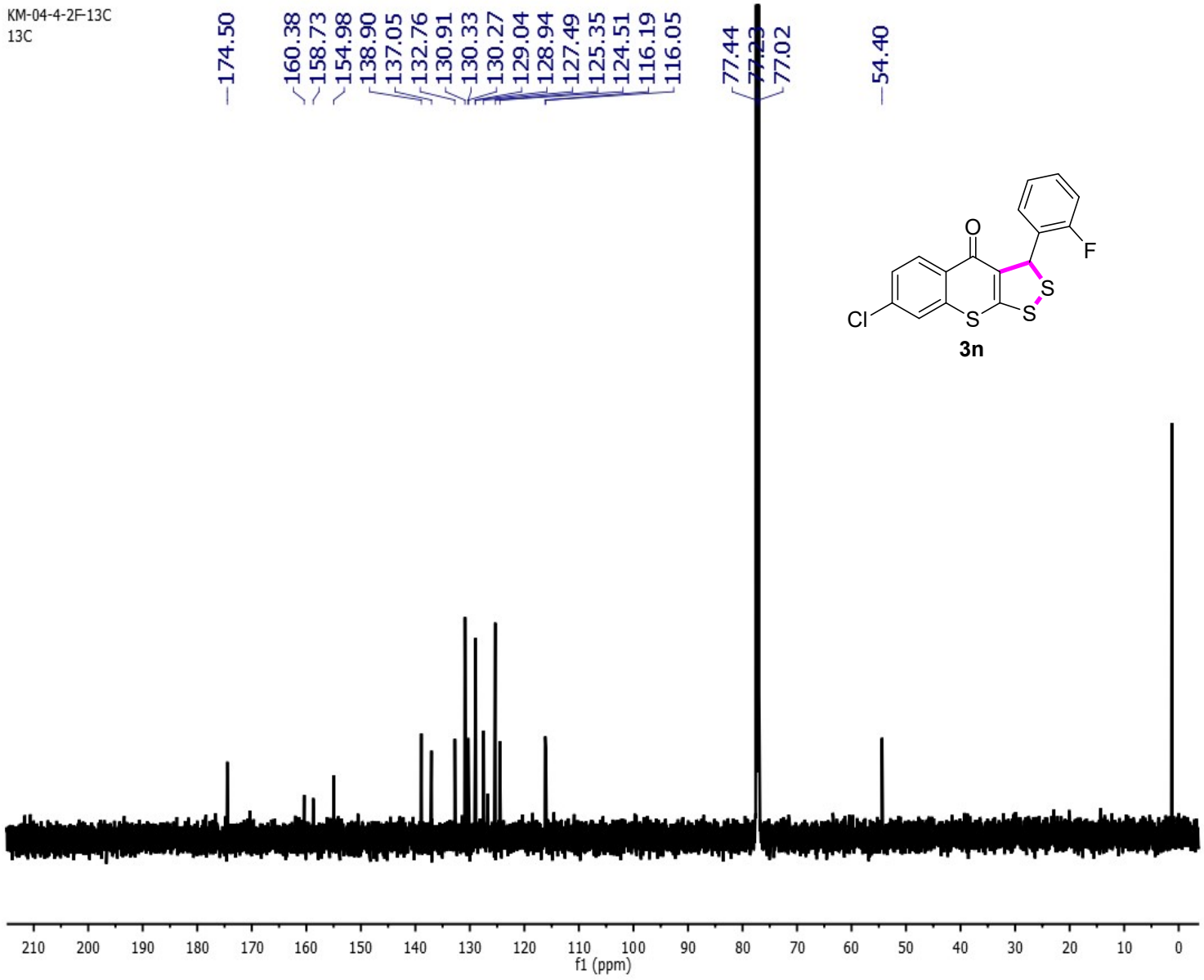
Sample Name	SAMPLE	**Position**	P1-C2	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	20	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	SM-4CLTH-2CL.d
ACQ Method	ESI ALS 100-1000.m	**Comment**		**Acquired Time**	06-08-2021 12:01:41 (UTC+05:30)



[1]HNMR spectra of compound: 3n

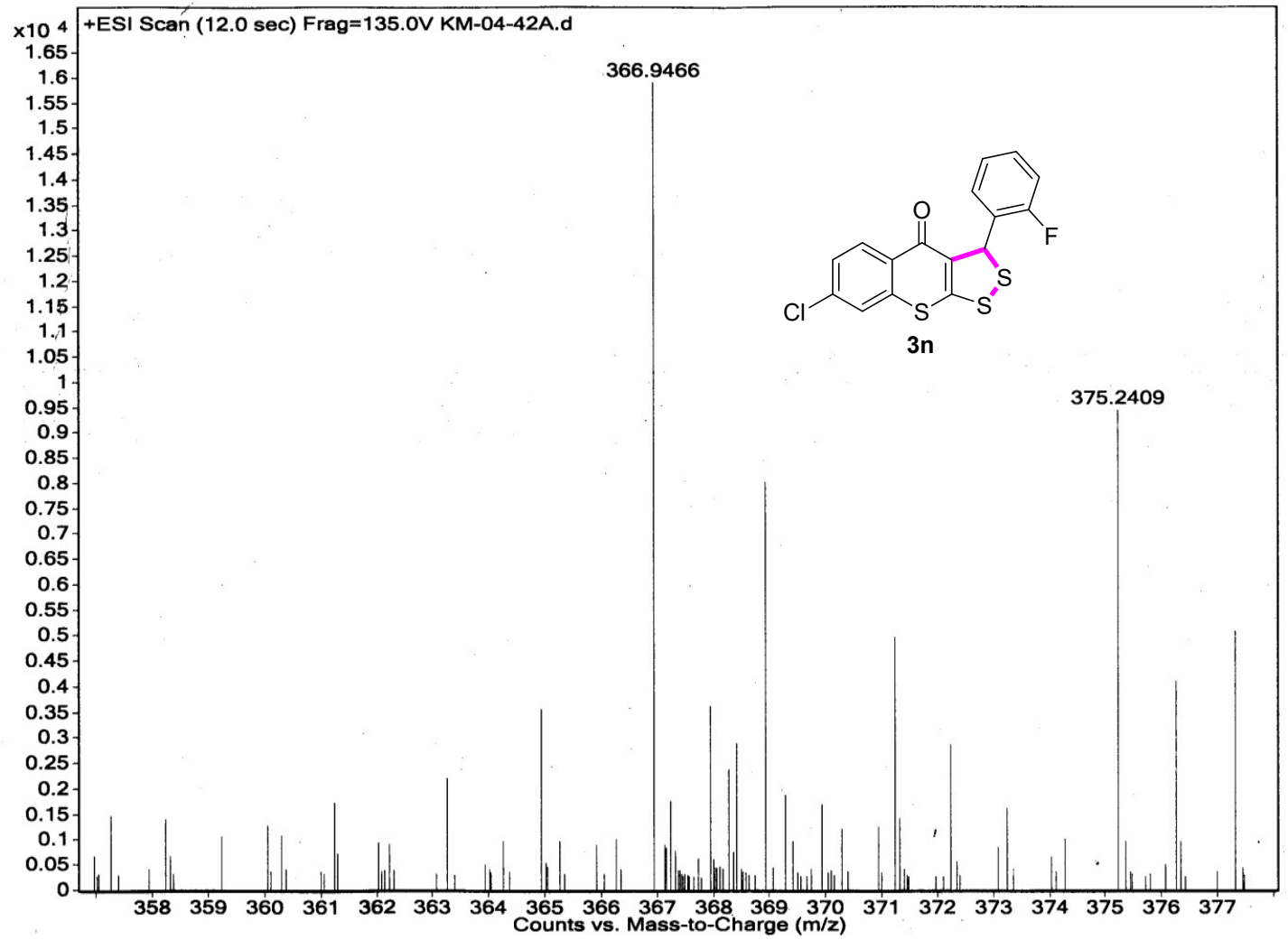


^{13}CNMR spectra of compound: 3n

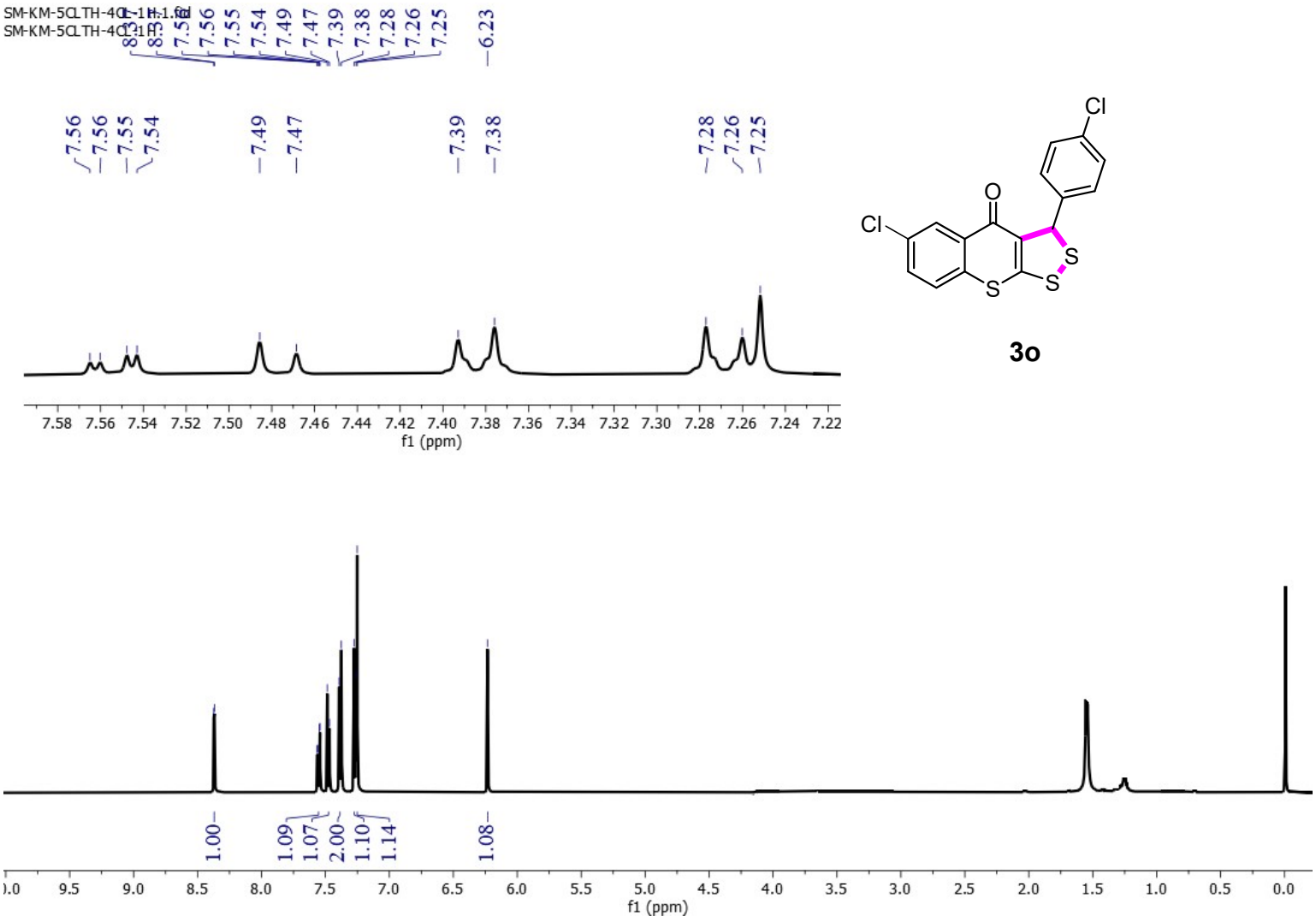


HRMS spectra of compound: 3n

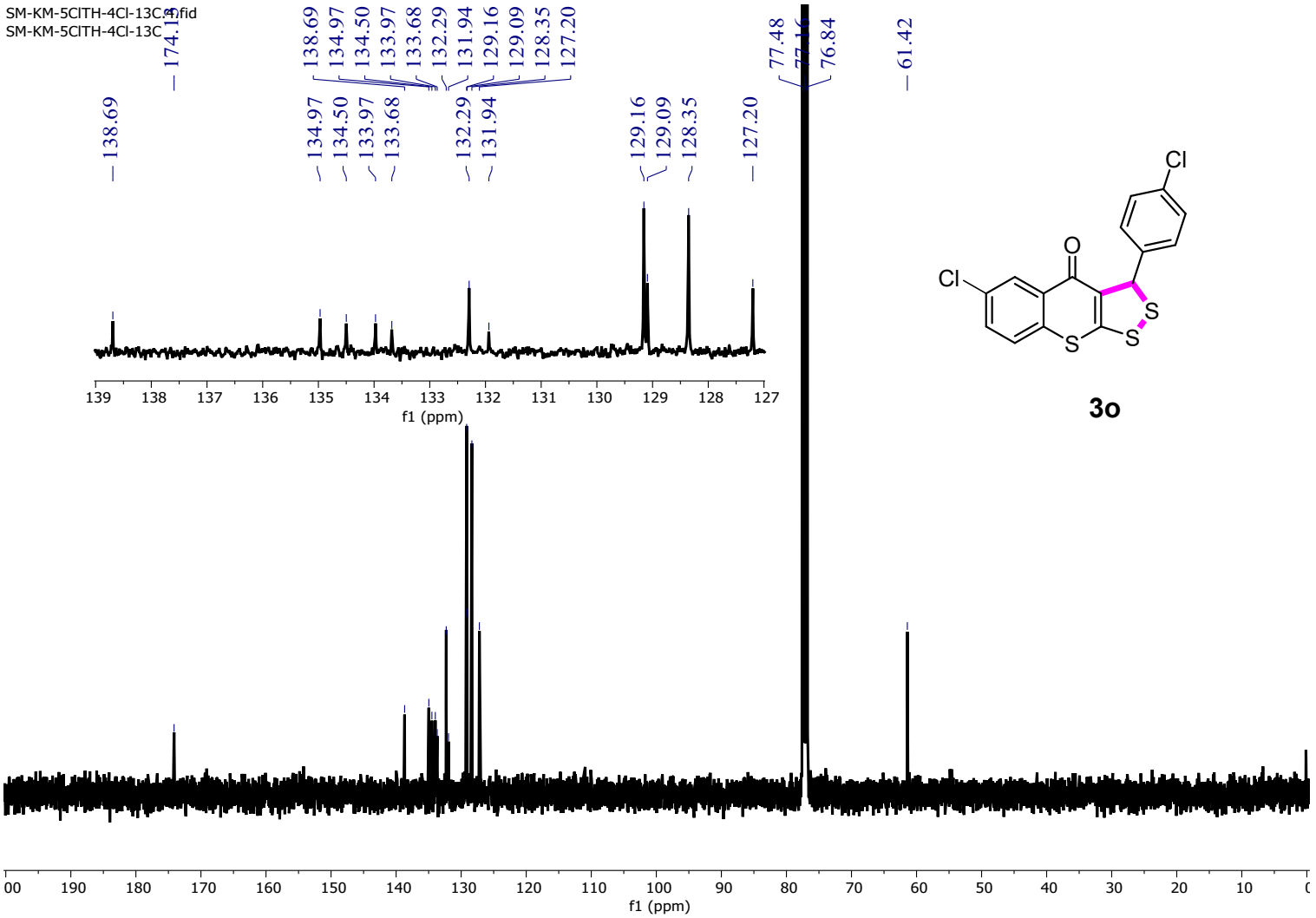
Sample Name	Unavailable	**Position**	Unavailable	**Instrument Name**	Unavailable	**User Name**	Unavailable
Inj Vol	Unavailable	**InjPosition**	Unavailable	**SampleType**	Unavailable	**IRM Calibration Status**	All Ions Missed
Data Filename	KM-04-42A.d	**ACQ Method**		**Comment**	Sample information is unavailable	**Acquired Time**	Unavailable



^{1}H NMR spectra of compound: 3o



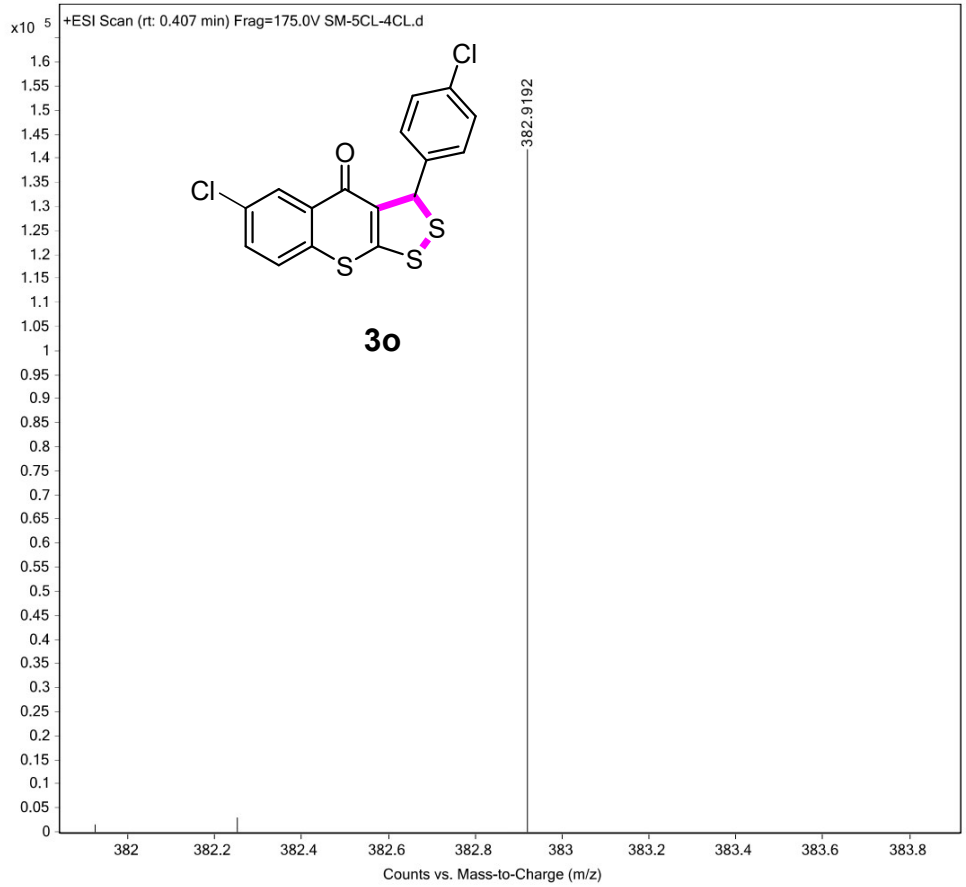
^{13}C NMR spectra of compound: 3o



3o

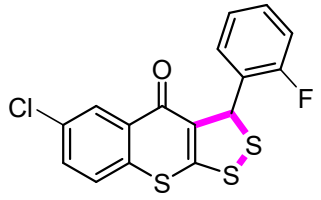
HRMS of compound: 3o

Sample Name	SAMPLE	**Position**	P1-A10	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	20	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	SM-5CL-4CL.d
ACQ Method	ESI ALS 100-1000.m	**Comment**		**Acquired Time**	13-08-2021 13:42:32 (UTC+05:30)

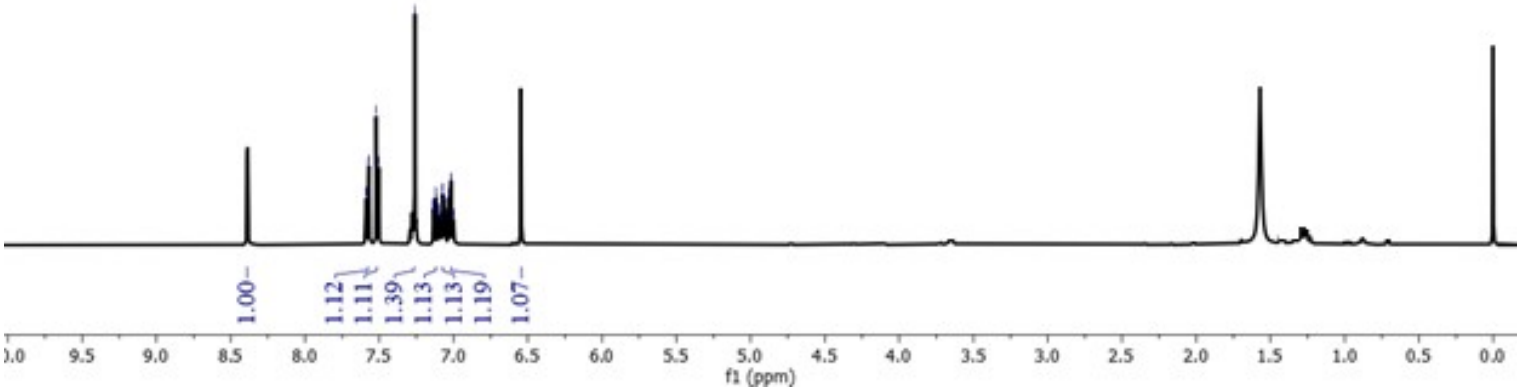


3o

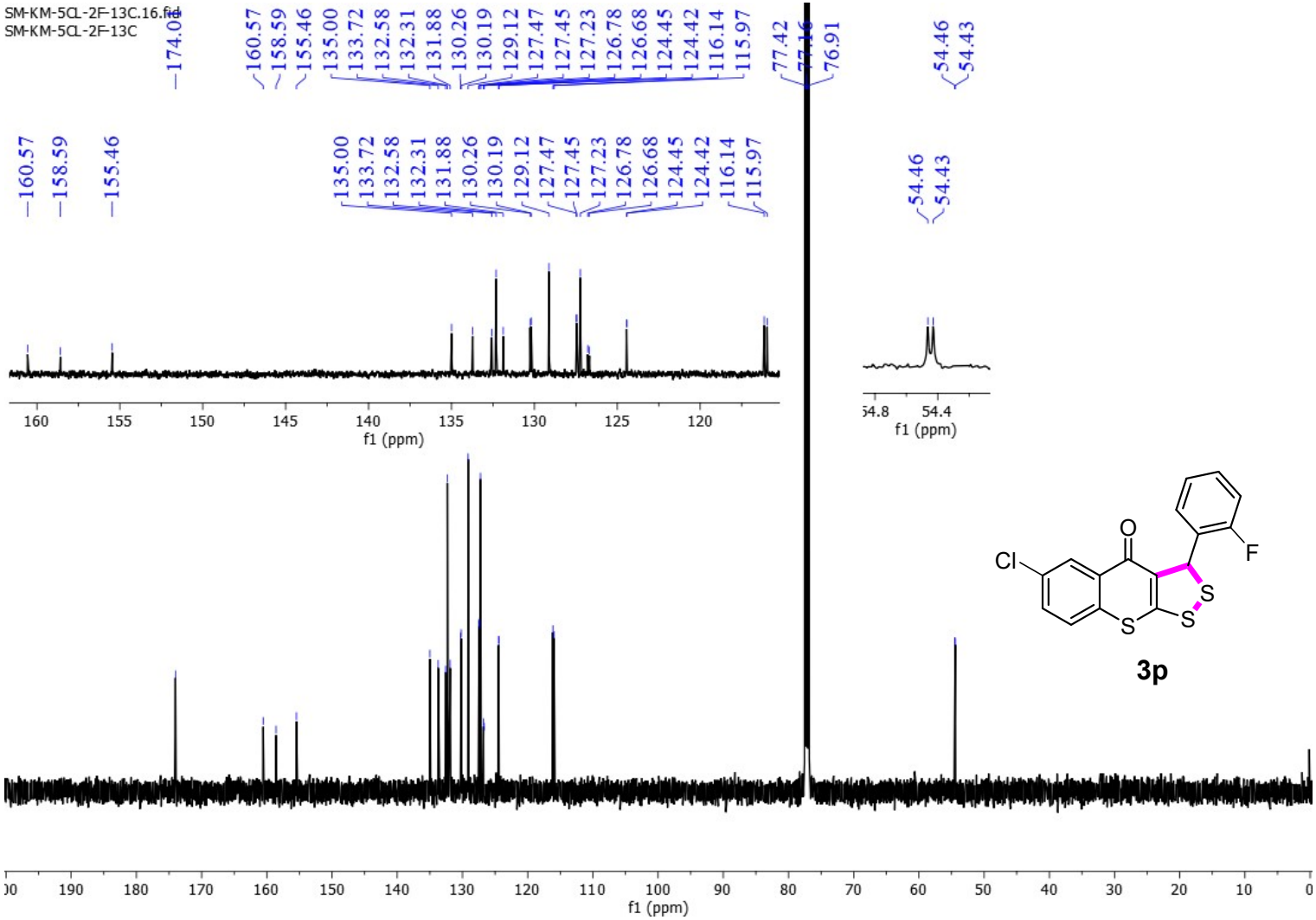
[1]HNMR spectra of compound: 3p



3p



^{13}C NMR spectra of compound: 3p



HRMS of compound: 3p

Sample Name	SAMPLE	**Position**	P1-A9	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	20	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	SM-5CL-2F.d
ACQ Method	ESI ALS 100-1000.m	**Comment**		**Acquired Time**	13-08-2021 13:31:02 (UTC+05:30