# Supporting Information

## C-H Functionalization of Imidazo[1,5-*a*]pyridines:A Metal-free Approach for Methylene Insertion to Access C($sp^2$)-C($sp^3$)-H-C($sp^2$) Bond Formation

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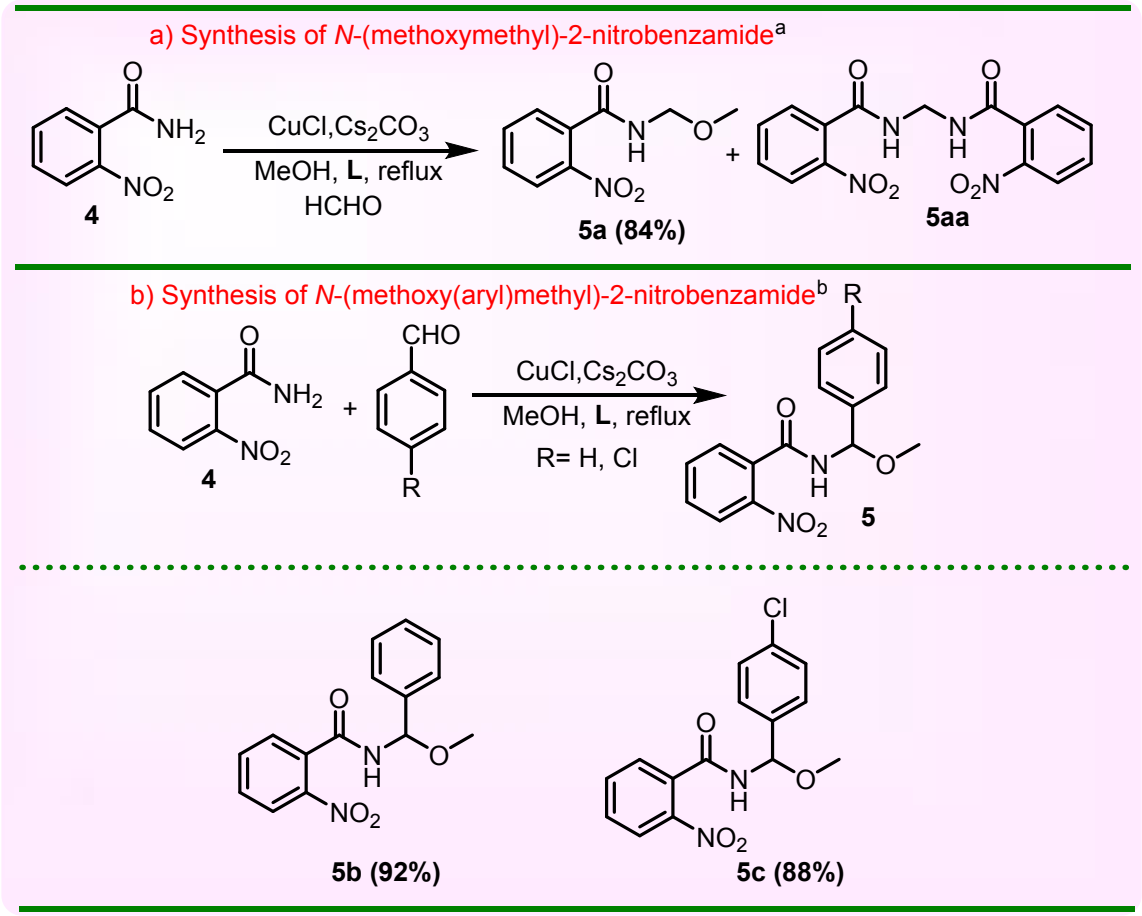
## 1. Optimization studies forN-(methoxy(aryl)methyl)-2-nitrobenzamide (5a-5c):

In accordance with the findings from literature report 1c, our experimentation initiated with the utilization of a commercial formaldehyde solution and 2-nitrobenzamide in the presence of copper sulfate and potassium carbonate, along with the ligand TMEDA in methanol solvent, to assess the viability of the reaction[1]. Over a period of time, the anticipated product 5aa was successfully observed. Subsequently, we sought to investigate the reaction outcome by substituting the ligand TMEDA with our compound 3a (**L**). Gratifyingly, the use of ligand **L** resulted in the formation of another major product, **5a(Table S1)**.

Encouraged by this outcome, we systematically optimized the reaction conditions**(Table S2)**.

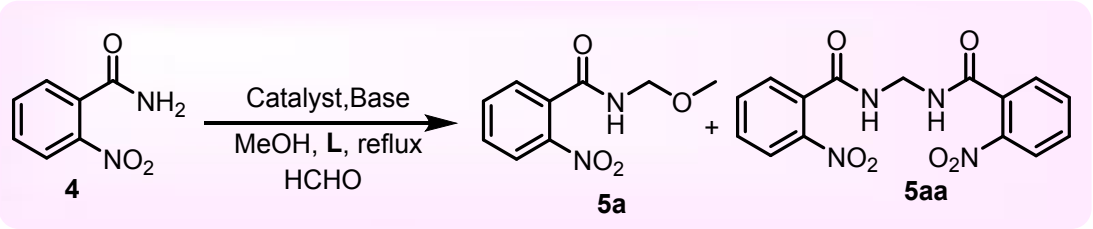
Initially, we identified copper(I) chloride as the most effective catalyst when paired with potassium carbonate as the base under reflux conditions, surpassing other copper catalysts. Further optimization led us to discover that caesium carbonate outperformed other bases.Subsequent optimization efforts focused on reaction time, revealing that a 10hour duration yielded the best results whereas stirring the reaction for less or more hours yielded comparatively less yield. Temperature variations were explored, with room temperature showing no product formation and 50°C resulting in a lower yield of the desired product **5a**. Additionally, conducting the reaction in other solvent Ethanol (Table S2,entry 13) and without ligand L(entry 14) failed to produce the desired product**5a** in both cases.After careful consideration of all the results, entry 10 in table S2 was determined as the optimal conditionfor the reaction. Applying the same optimized conditions to benzaldehyde and 4-chloro benzaldehyde, we successfully obtained the desired corresponding products, **5b** and **5c**, in 8 hours.

**Table S1: Synthesis of *N*-(methoxy(aryl)methyl)-2-nitrobenzamide**




[a]Reaction Conditions: **4** (0.30 mmol), **HCHO** (1.0 mL), CuCl (10 mol%), $Cs_2CO_3$ (0.45 mmol), L (5 mol%), MeOH (1.0 mL),
[b]Reaction Conditions: **4** (0.30 mmol), **ArCHO** (0.30 mmol), CuCl (10 mol%), $Cs_2CO_3$ (0.45 mmol), L (5 mol%), MeOH (1.0 mL)

**Table S2: Optimization Studies for *N*-(methoxymethyl)-2-nitrobenzamide[a]**



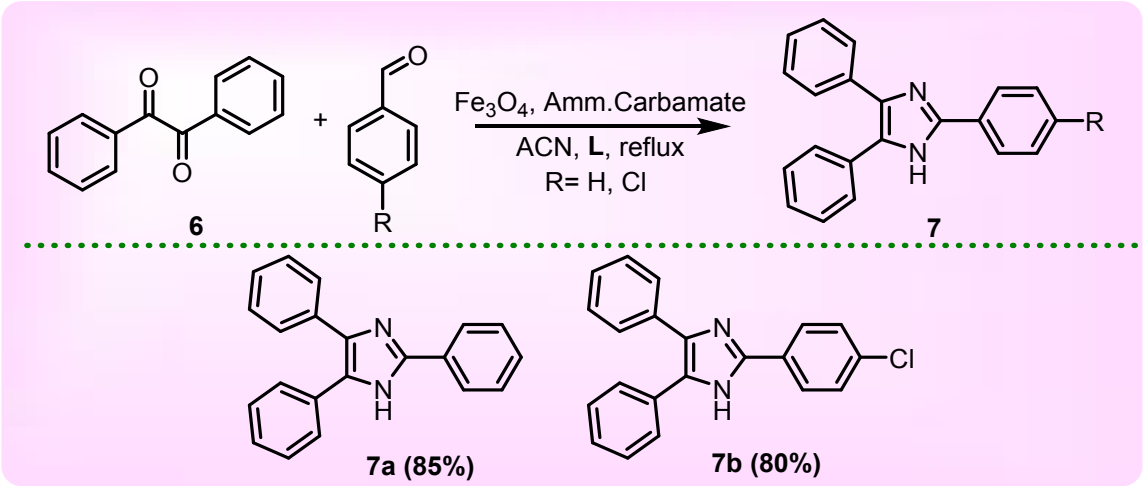

| S.No. | Catalyst | Base | Reaction temp (°C) | Reaction time (h) | Product 5a (% Yield)[b] | Product 5aa (% Yield)[b] |
|---|---|---|---|---|---|---|
| **1** | $CuSO_4.5H_2O$ | $K_2CO_3$ | reflux | 6 | 52 | 31 |
| **2** | CuI | $K_2CO_3$ | reflux | 6 | 47 | 32 |
| **3** | CuCl | $K_2CO_3$ | reflux | 6 | 56 | 34 |
| **4** | $CuCl_2$ | $K_2CO_3$ | reflux | 6 | 52 | 30 |
| **5** | $Cu(OAc)_2.H_2O$ | $K_2CO_3$ | reflux | 6 | 50 | 33 |
| **6** | CuCl | KOH | reflux | 6 | 42 | 45 |
| **7** | CuCl | NaOH | reflux | 6 | 41 | 46 |
| **8** | CuCl | $Cs_2CO_3$ | reflux | 6 | 69 | 21 |
| **9** | CuCl | $Cs_2CO_3$ | reflux | 8 | 78 | 14 |
| **10** | CuCl | $Cs_2CO_3$ | reflux | 10 | 84 | 10 |
| **11** | CuCl | $Cs_2CO_3$ | reflux | 12 | 80 | 12 |
| **12**[c] | CuCl | $Cs_2CO_3$ | reflux | 10 | 0 | 78 |
| **13**[d] | CuCl | $Cs_2CO_3$ | reflux | 10 | 0 | 37 |
| **14** | CuCl | $Cs_2CO_3$ | rt | 10 | NR | 27 |
| **15** | CuCl | $Cs_2CO_3$ | 50 | 10 | 57 | 31 |

[a]Reaction Conditions: **4** (0.30 mmol), **HCHO** (1.0 mL), catalyst (10 mol%), base (0.45 mmol), L (5 mol%), MeOH (1.0 mL), [b]Isolated Yield, [c]EtOH (1.0 mL), [d]Without ligand L

## 2. Optimization studies for 2-(aryl)-4,5-diphenyl-1*H*-imidazole (7a-7b):

Similarly, to broaden the scope of the ligand's influence, we conducted the synthesis of 2-(aryl)-4,5-diphenyl-1*H*-imidazole[2] based on literature report 2b.

**Table S3: Synthesis of 2-(aryl)-4,5-diphenyl-1*H*-imidazole[a]**




[a]Reaction Conditions: **6** (0.24 mmol), **ArCHO** (0.24 mmol), $Fe_3O_4$(10 mol%), Ammonium Carbamate (0.48 mmol), L (10 mol%), ACN (1.0 mL)

The initial reaction involving benzil and benzaldehyde, with $Fe_3O_4$ as the catalyst and ammonium carbamate as the ammonium source in MeOH under reflux without ligand L, yielded minimal product **7a**. Despite extending the reaction time to over 20 hours, the desired product was obtained in meager quantities. Consequently, optimization efforts were undertaken to improve the yield (**Table S4**).Among various iron catalysts explored, $Fe_3O_4$ emerged as the most effective. The introduction of ligand **L** significantly enhanced the yield, highlighting the positive influence of the ligand on the reaction. Subsequent screening of solvents revealed that acetonitrile (ACN) outperformed others, and stirring the reaction without solvent also confirmed its efficacy. Room temperature conditions resulted in no product formation, while at 60°C, a lower yield was observed compared to reflux conditions.Further optimization included determining the optimal reaction time, with 4 hours identified as yielding the maximum product. Additionally, alternative ammonium sources were explored, ultimately selecting ammonium carbamate as the most effective. With the optimized conditions in hand (entry 12, Table S4), the 4-chlorobenzaldehyde yielded the corresponding desired product **7b** in good yield.

**Table S4: Optimization Studies for 2-phenyl-4,5-diphenyl-1*H*-imidazole[a]**


| S.No. | Catalyst | Solvent | Ammonium Source | Reaction temp (°C) | Reaction time (h) | Product 7a (% Yield)[b] |
|---|---|---|---|---|---|---|
| **1**[c] | $Fe_3O_4$ | MeOH | Amm.carbamate | reflux | 3 | 13 |
| **2**[c] | $Fe_2O_3$ | MeOH | Amm.carbamate | reflux | 3 | 7 |
| **3**[c] | FeO | MeOH | Amm.carbamate | reflux | 3 | 9 |
| **4**[c] | $FeCl_3.6H_2O$ | MeOH | Amm.carbamate | reflux | 3 | Traces |
| **5** | $Fe_3O_4$ | MeOH | Amm.carbamate | reflux | 3 | 61 |
| **6** | $Fe_3O_4$ | ACN | Amm.carbamate | reflux | 3 | 74 |
| **7** | $Fe_3O_4$ | Toluene | Amm.carbamate | reflux | 3 | 70 |
| **8** | $Fe_3O_4$ | Dioxane | Amm.carbamate | reflux | 3 | 68 |
| **9** | $Fe_3O_4$ | - | Amm.carbamate | 100 | 3 | 60 |
| **10** | $Fe_3O_4$ | ACN | Amm.carbamate | rt | 3 | - |
| **11** | $Fe_3O_4$ | ACN | Amm.carbamate | 60 | 3 | 67 |
| **12** | $Fe_3O_4$ | ACN | Amm.carbamate | reflux | 4 | 85 |
| **13** | $Fe_3O_4$ | ACN | Amm.carbamate | reflux | 5 | 79 |
| **14** | $Fe_3O_4$ | ACN | Amm.carbonate | reflux | 4 | 78 |
| **15** | $Fe_3O_4$ | ACN | Liq Ammonia | reflux | 4 | 69 |

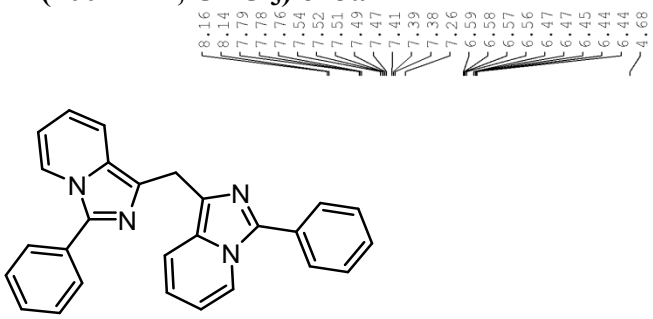
[a]Reaction Conditions: **6** (0.24 mmol), **PhCHO** (0.24 mmol), catalyst (10 mol%), Ammonium Source (0.48 mmol), L (10 mol%), Solvent (1.0 mL), [b]Isolated Yield,
[c]Without ligand L

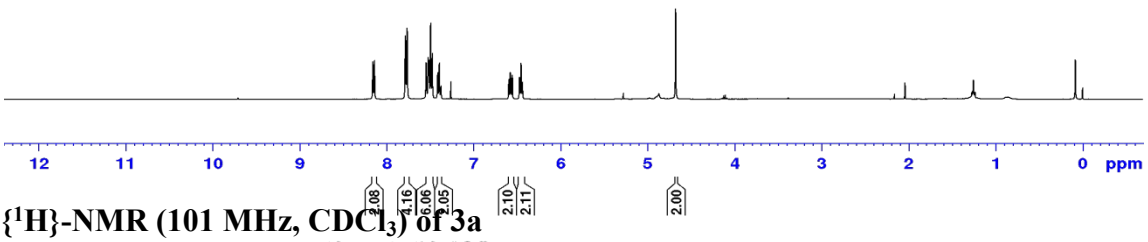
## 3. Refernces:


1. (a) Halli, J.; Hofman, K.; Beisel, T.;Manolikakes, G.Synthesis of N-Acyl-N, O-acetals from Aldehydes, Amides and Alcohols. *Eur. J. Org. Chem.* **2015**, *2015,* 4624-4627. (b) Tan, B.Y.H.; Teo, Y.C. Efficient cobalt-catalyzed C–N cross-coupling reaction between benzamide and aryl iodide in water. *Org.Biomol. Chem.* **2014**, *12*, 7478-7481. (c) Panda, N.;Mothkuri, R.; Nayak, D.K. Copper-Catalyzed Regioselective Synthesis of N-Aryl Amides from Aldoximes and Aryl Halides. *Eur. J. Org. Chem.* **2014**, *2014*,1602-1605.
2. (a) Sohail, M.; Bilal, M.; Maqbool, T.; Rasool, N.; Ammar, M.; Mahmood, S.; Malik, A.; Zubair, M.; Ashraf, G.A. Iron-catalyzed synthesis of N-heterocycles via intermolecular and intramolecular cyclization reactions: A review. *Arab. J. Chem.* **2022**, *15*, 104095. (b) Hosseini, S.; Kiasat, A. R.; Farhadi, A.$Fe_3O_4$@ $SiO_2$/Bipyridinium Nanocomposite as a Magnetic and Recyclable Heterogeneous Catalyst for the Synthesis of Highly Substituted Imidazoles Via Multi-Component Condensation Strategy.*PolycyclAromat Compd.***2021**, *41*, 762-771.

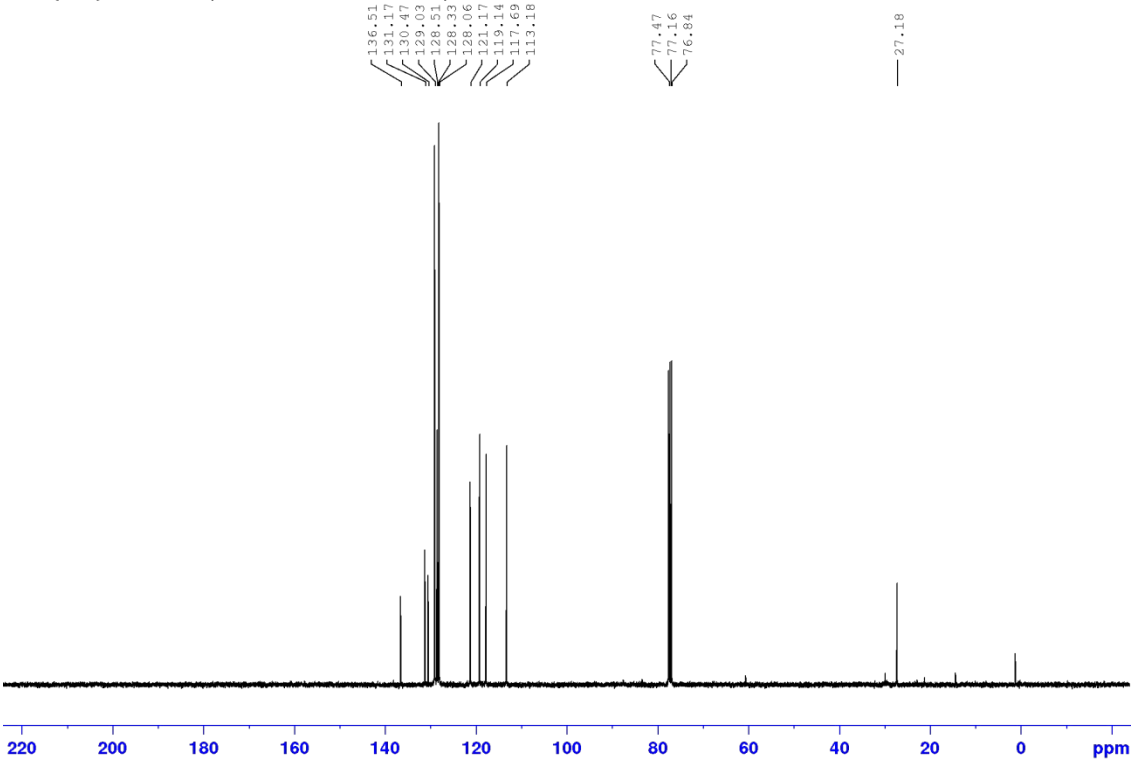
## 4. NMR and HRMS Spectra

**$^{1}$H-NMR (400 MHz, $CDCl_3$) of 3a**

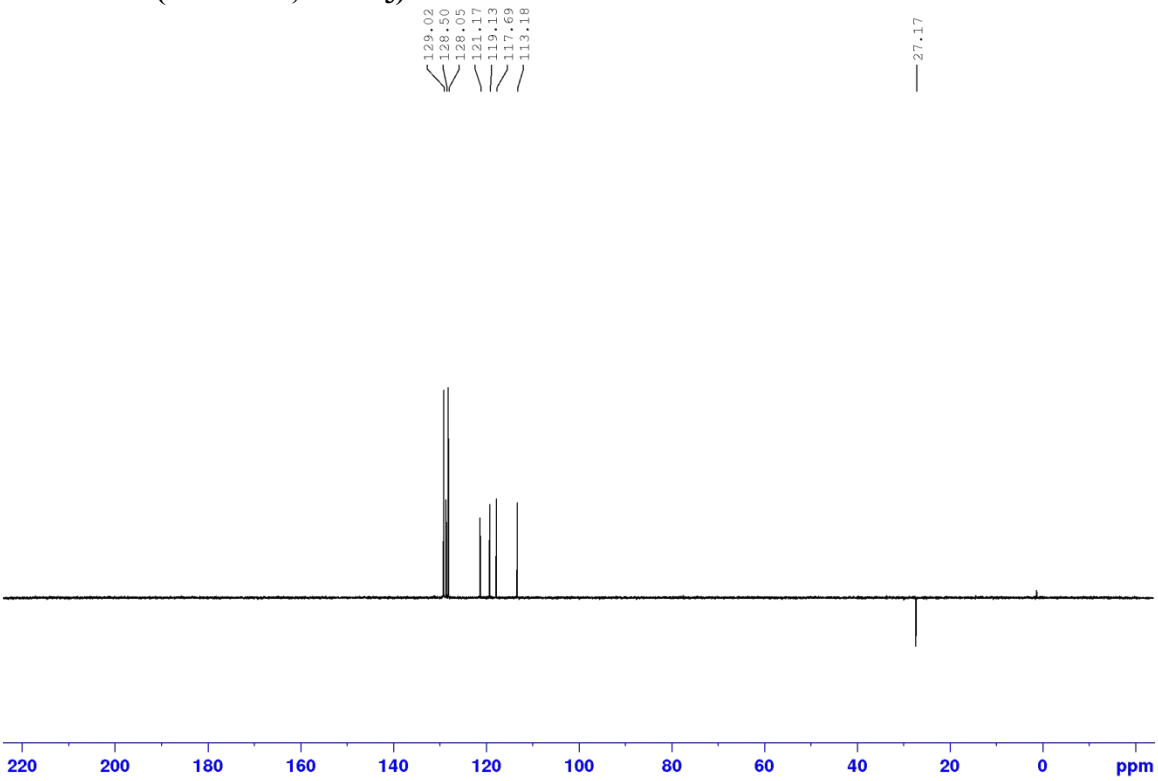


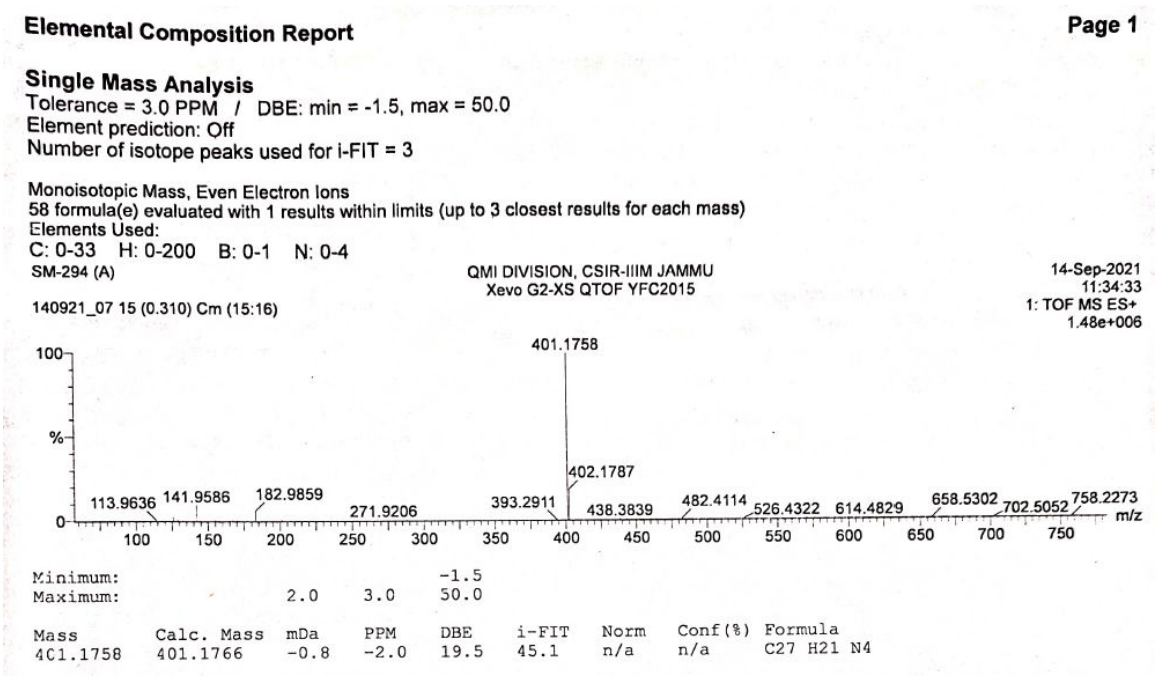

**$^{13}$C{$^{1}$H}-NMR (101 MHz, $CDCl_3$) of 3a**



**DEPT-135 (101 MHz, $CDCl_3$) of 3a**




**HRMS of 3a**



**Elemental Composition Report** Page 1

**Single Mass Analysis**
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Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
58 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
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QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

14-Sep-2021
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| Maximum: | | 2.0 | 3.0 | 50.0 | | | | |
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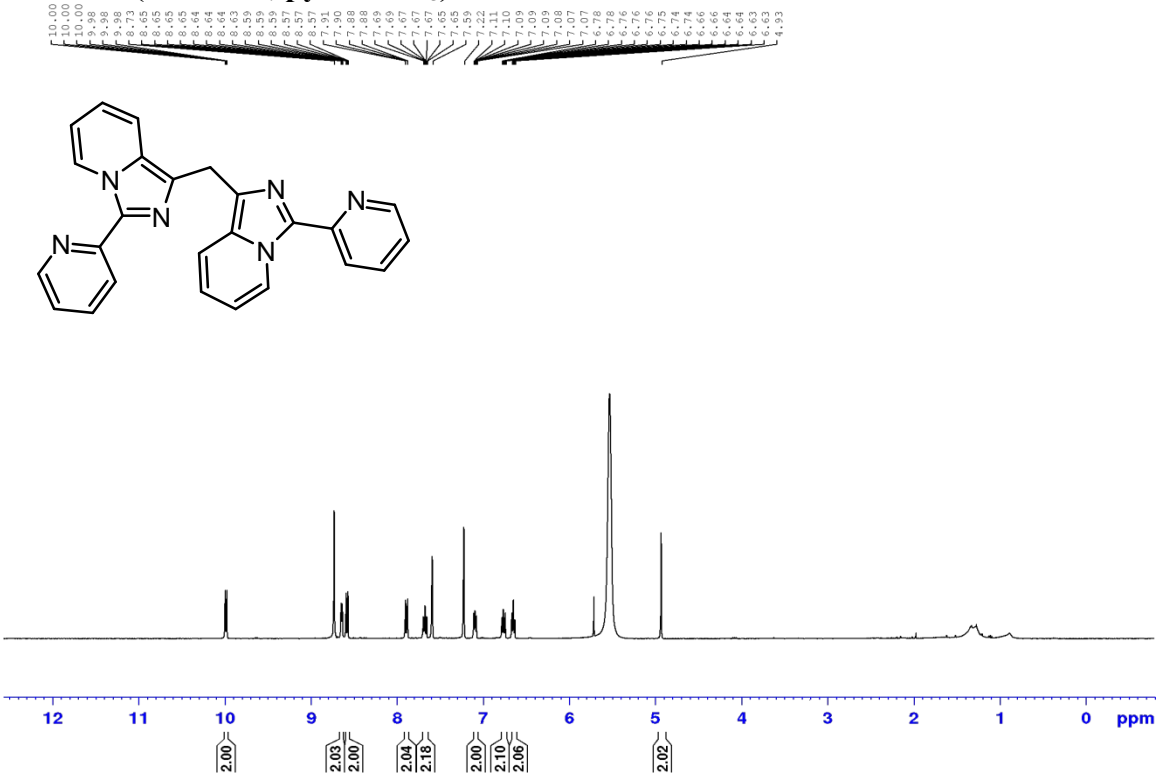
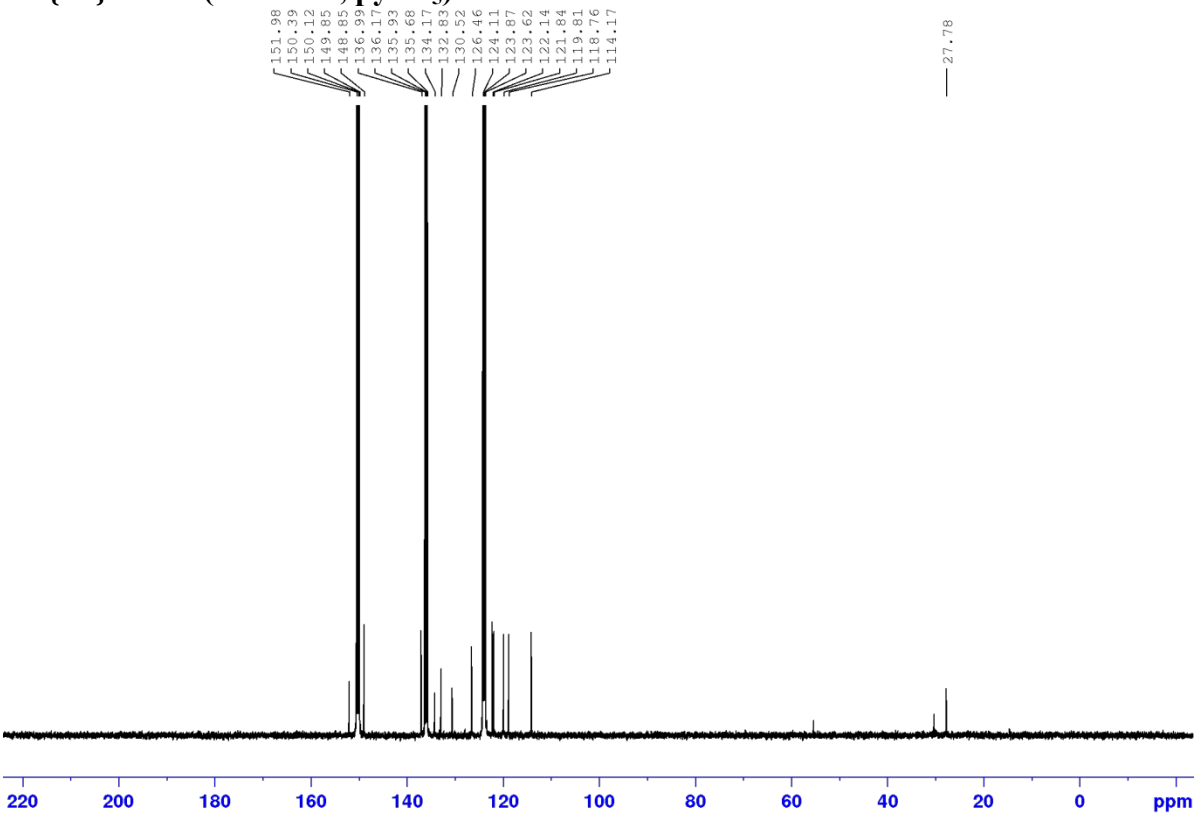



**$^{13}$C{$^{1}$H}-NMR (101 MHz, pyr-$d_5$) of 3b**



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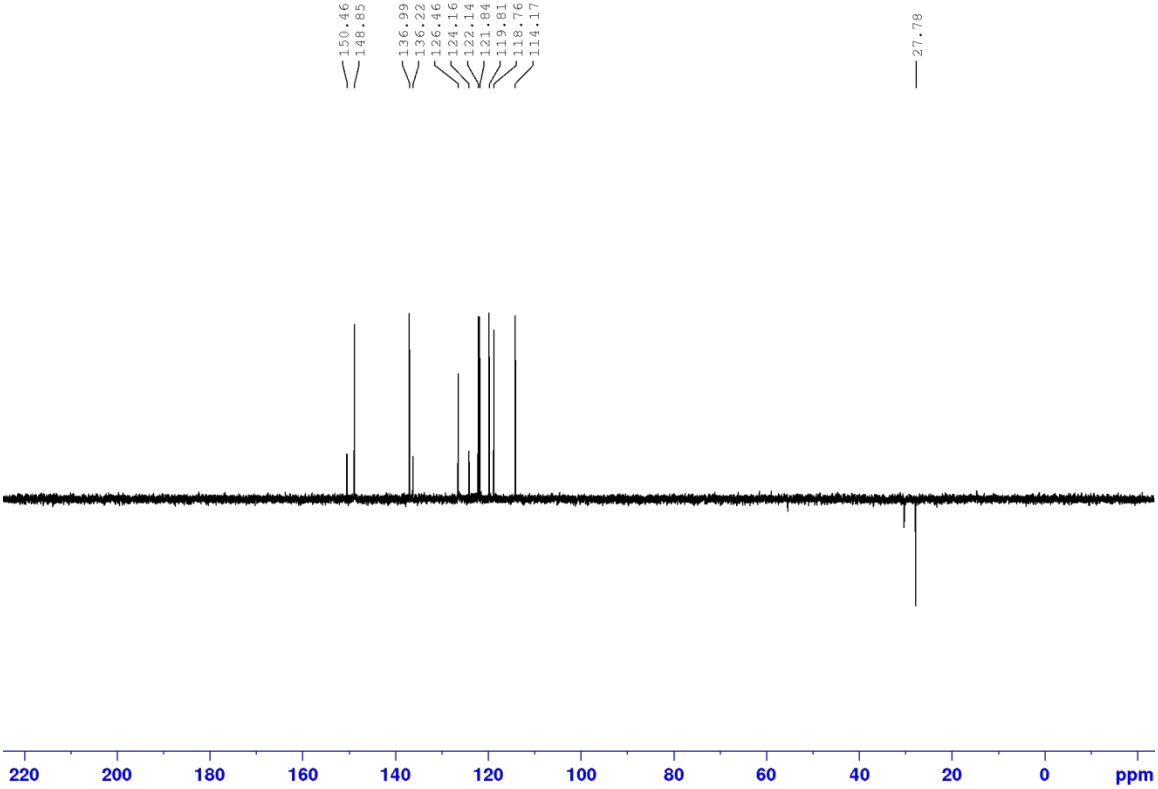


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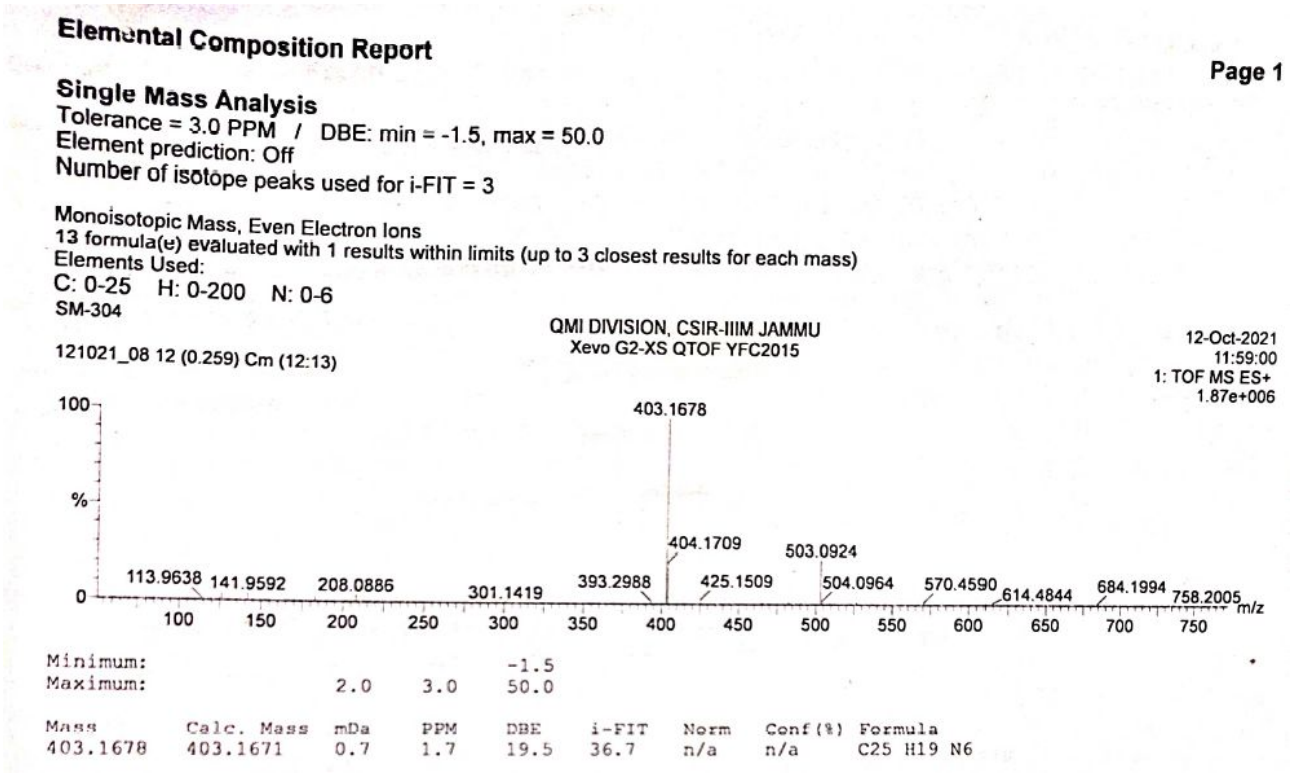
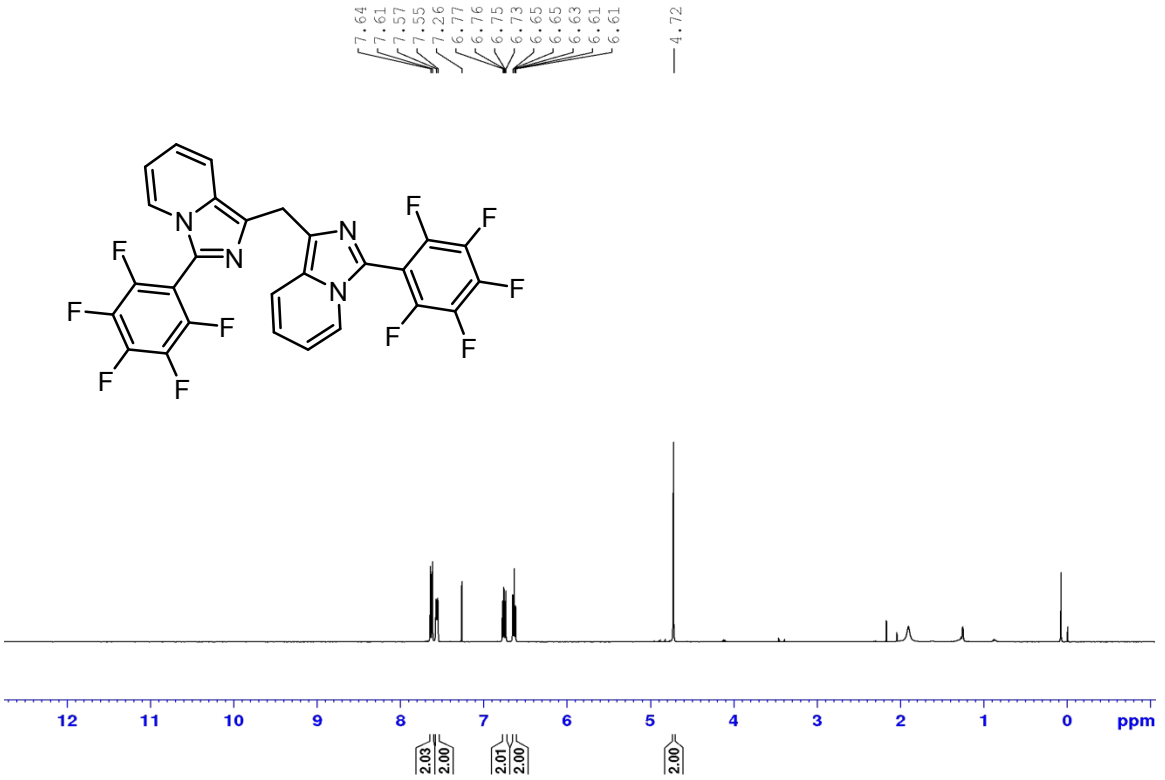


**$^{1}$H-NMR (400 MHz, $CDCl_3$) of 3c**

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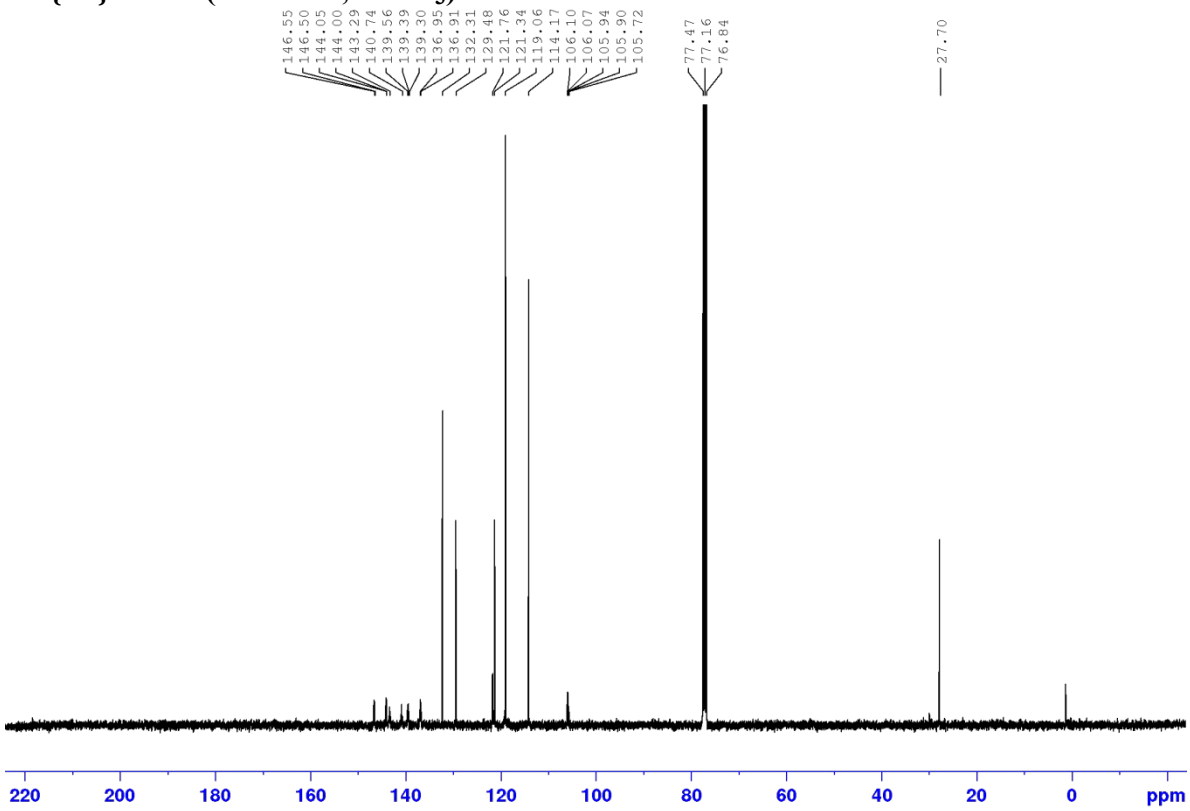

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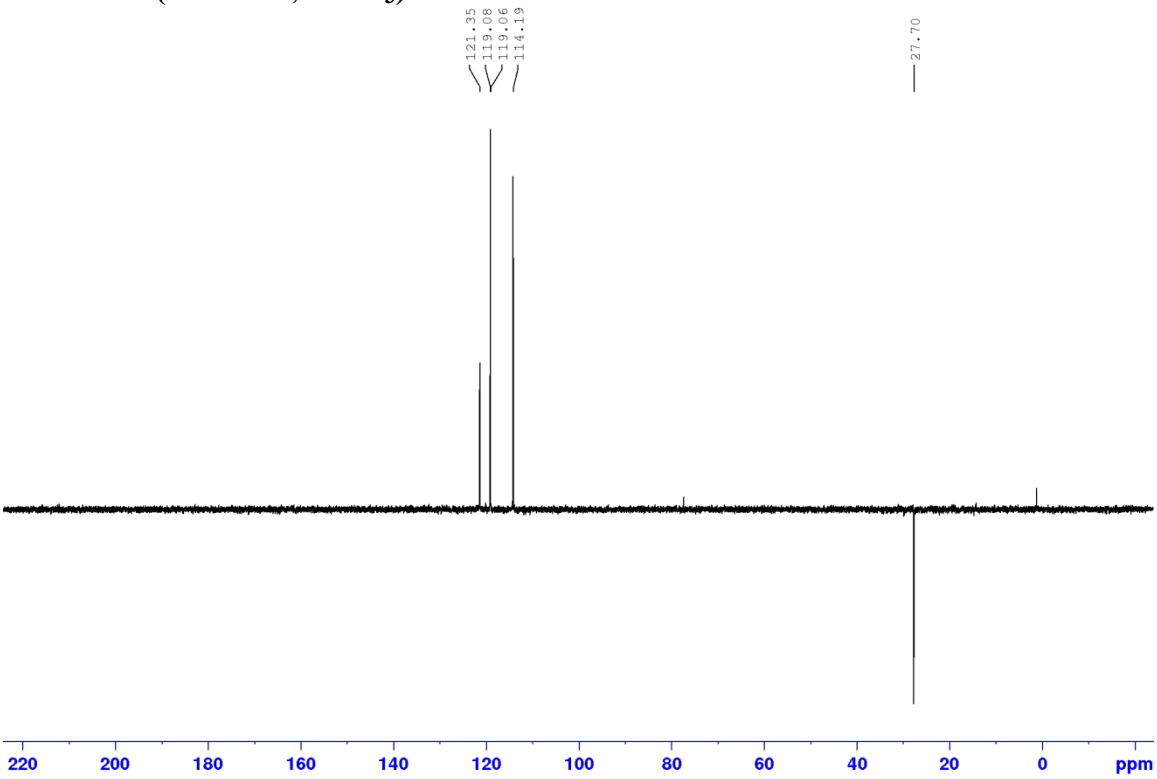
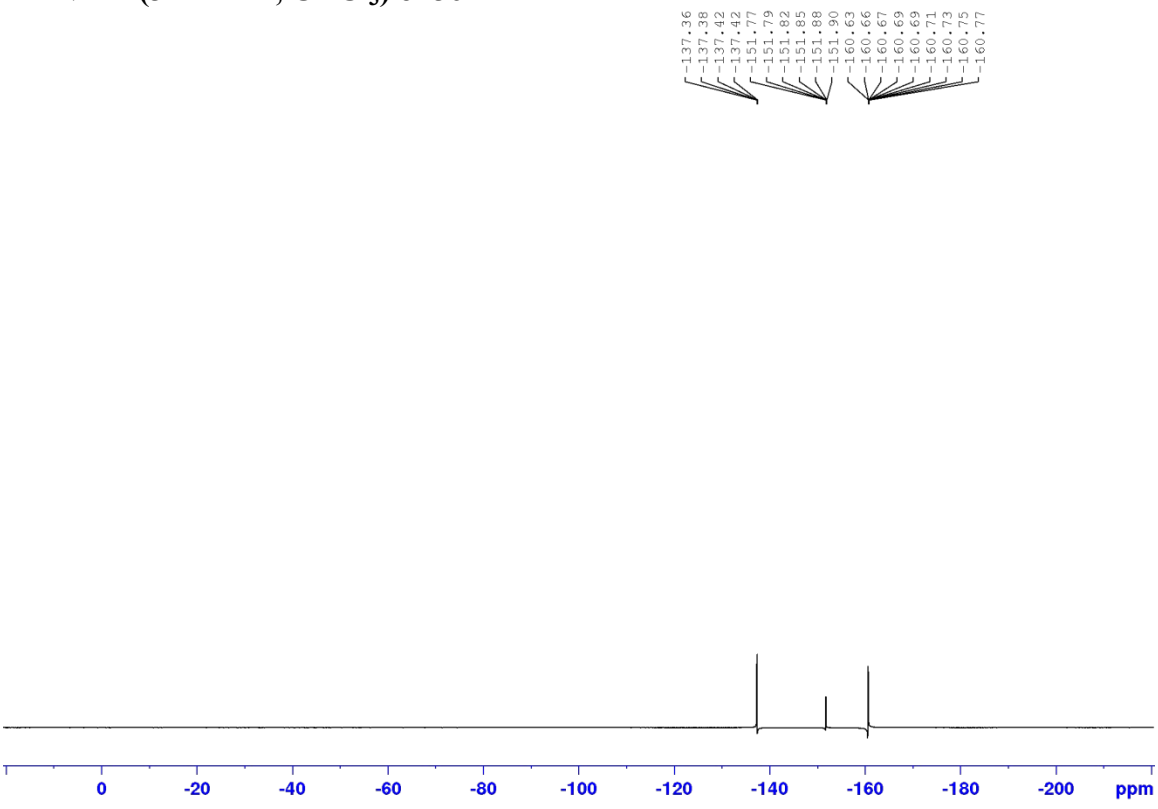



**$^{19}$F-NMR (377 MHz, $CDCl_3$) of 3c**



## HRMS of 3c

**Elemental Composition Report** Page 1

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Monoisotopic Mass, Even Electron Ions
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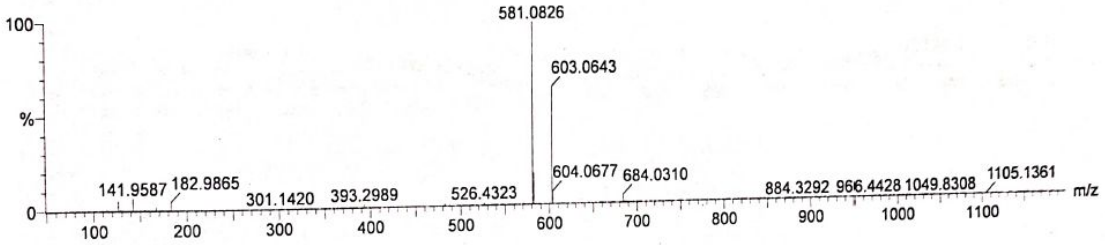


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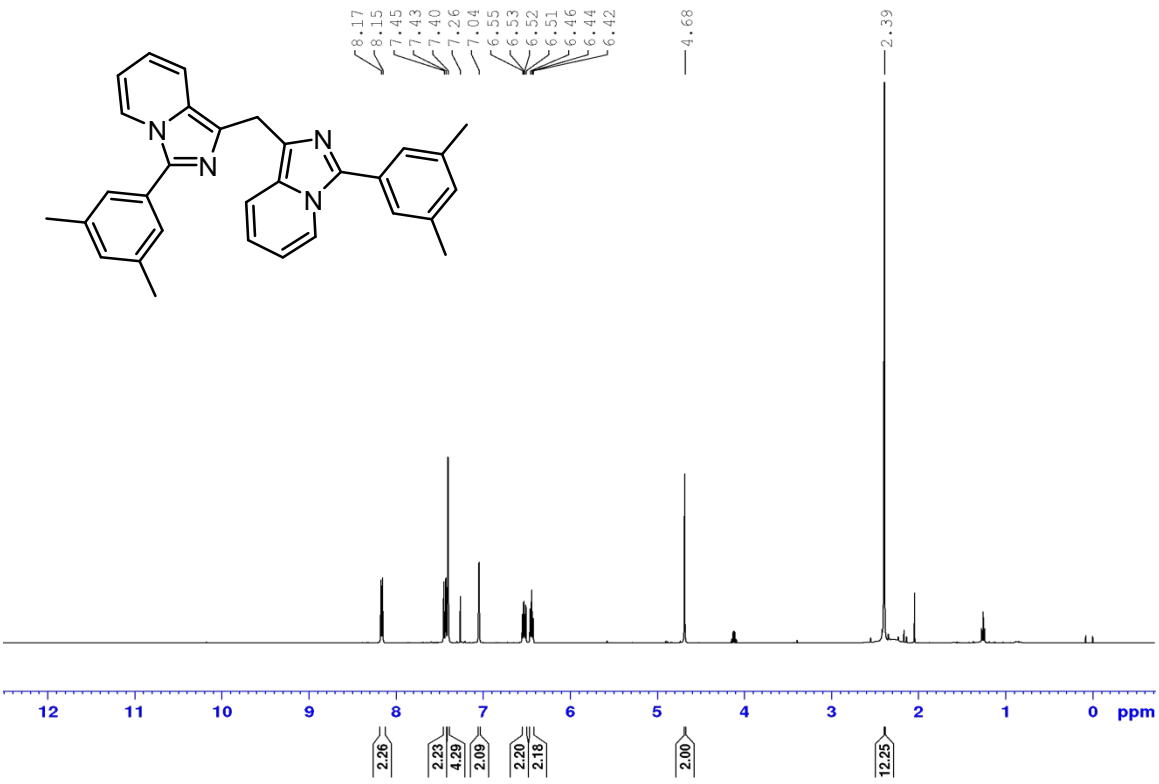
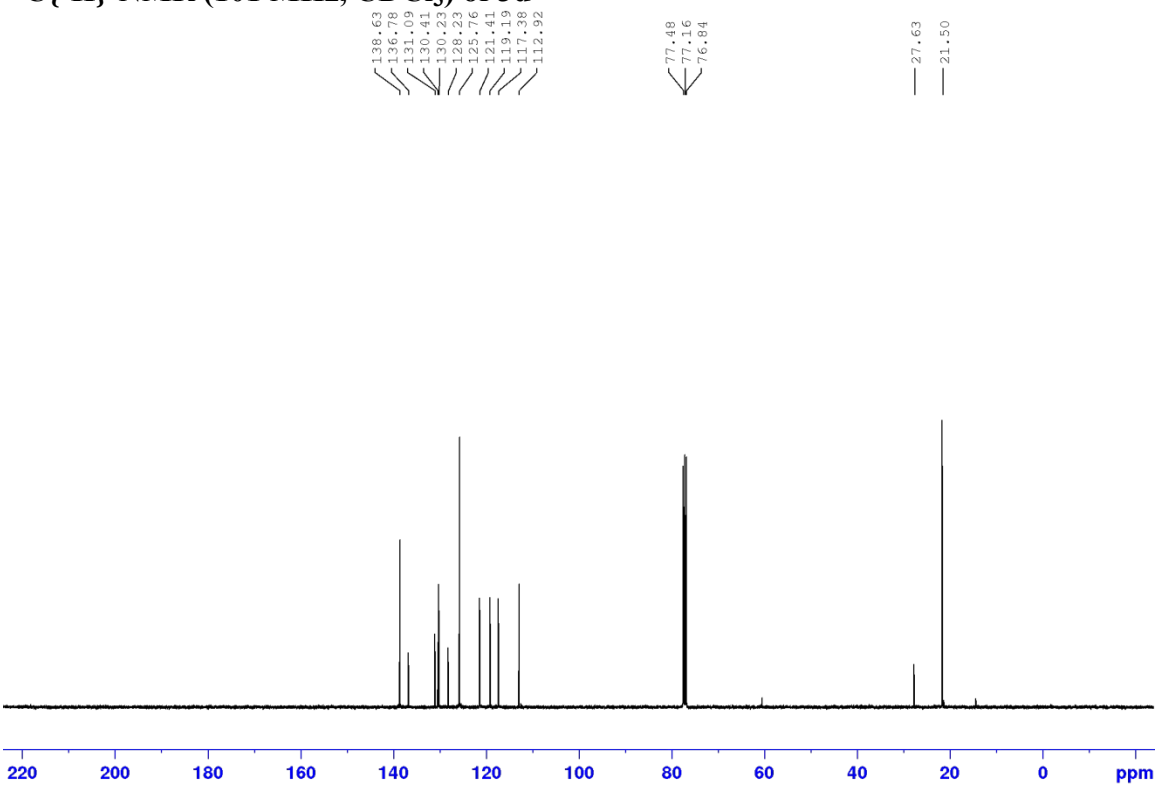
| 581.0826 | 581.0824 | 0.2 | 0.3 | 19.5 | 35.6 | n/a | n/a | C27 H11 N4 F10 |

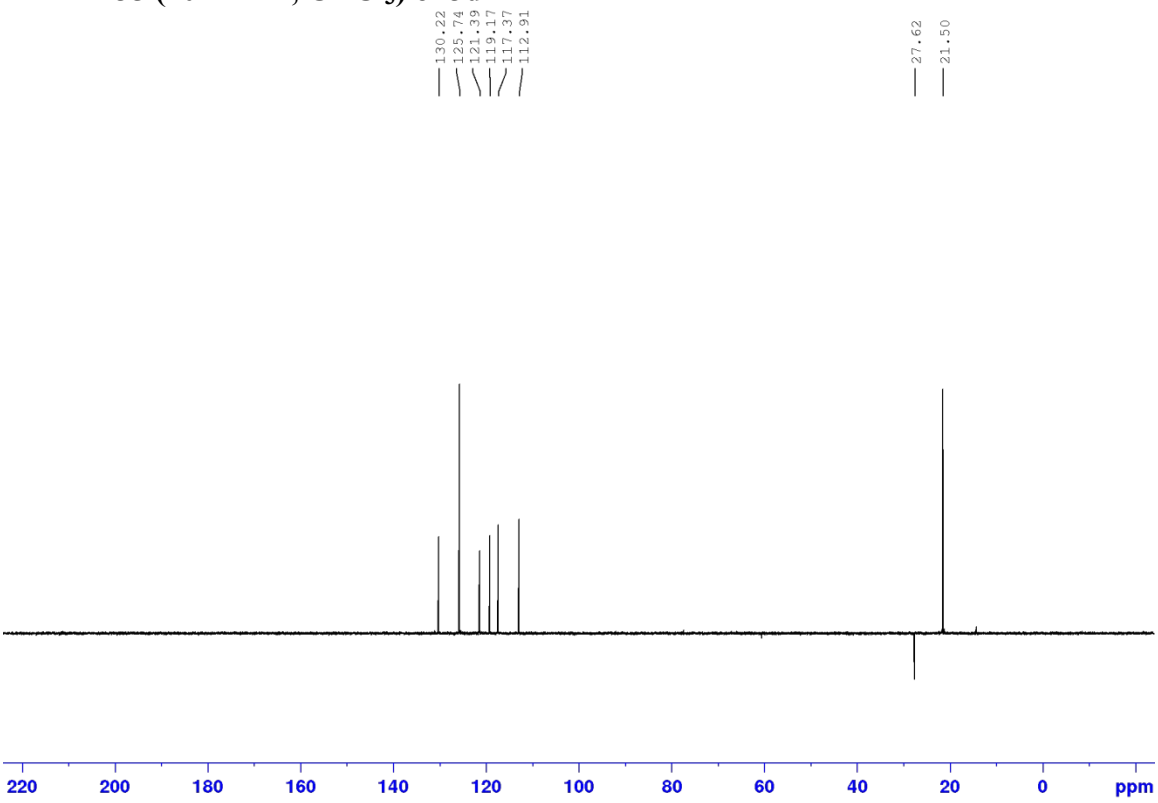
## $^1$H-NMR (400 MHz, $CDCl_3$) of 3d



**$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$) of 3d**




**DEPT-135 (101 MHz, $CDCl_3$) of 3d**



## HRMS of 3d

**Elemental Composition Report** **Page 1**

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Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
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SM-314

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

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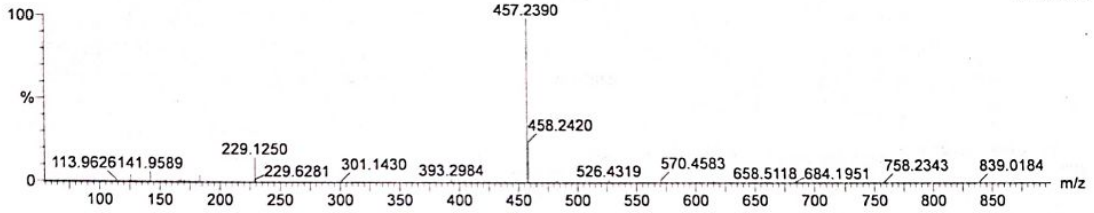


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|---|---|---|---|---|---|---|---|---|
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| Maximum: | | 2.0 | 3.0 | 50.0 | | | | |
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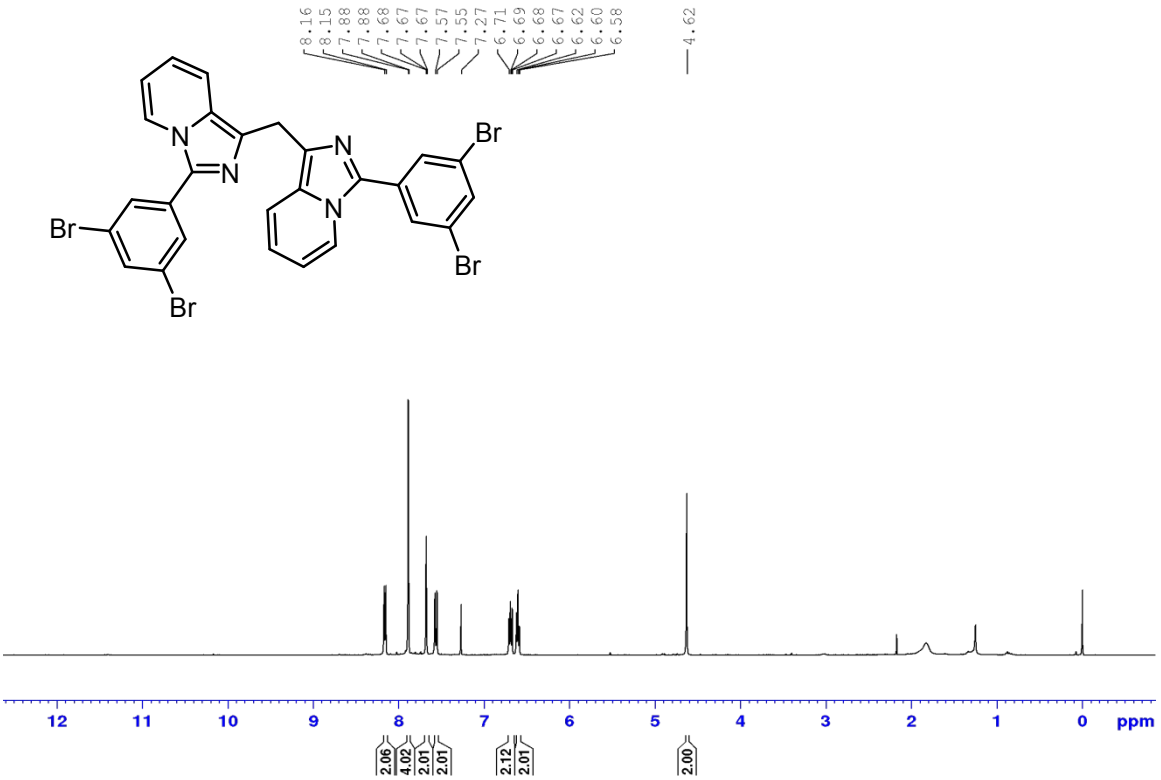
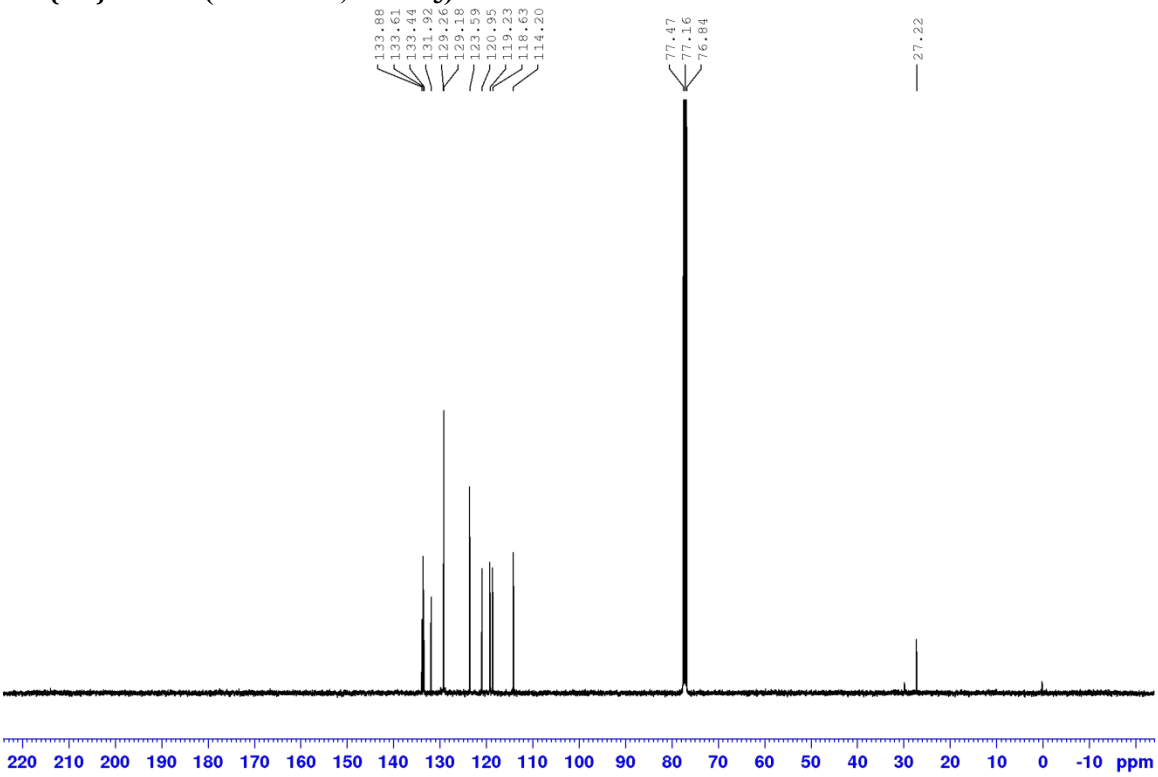
## $^1$H-NMR (400 MHz, $CDCl_3$) of 3e



**$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$) of 3e**

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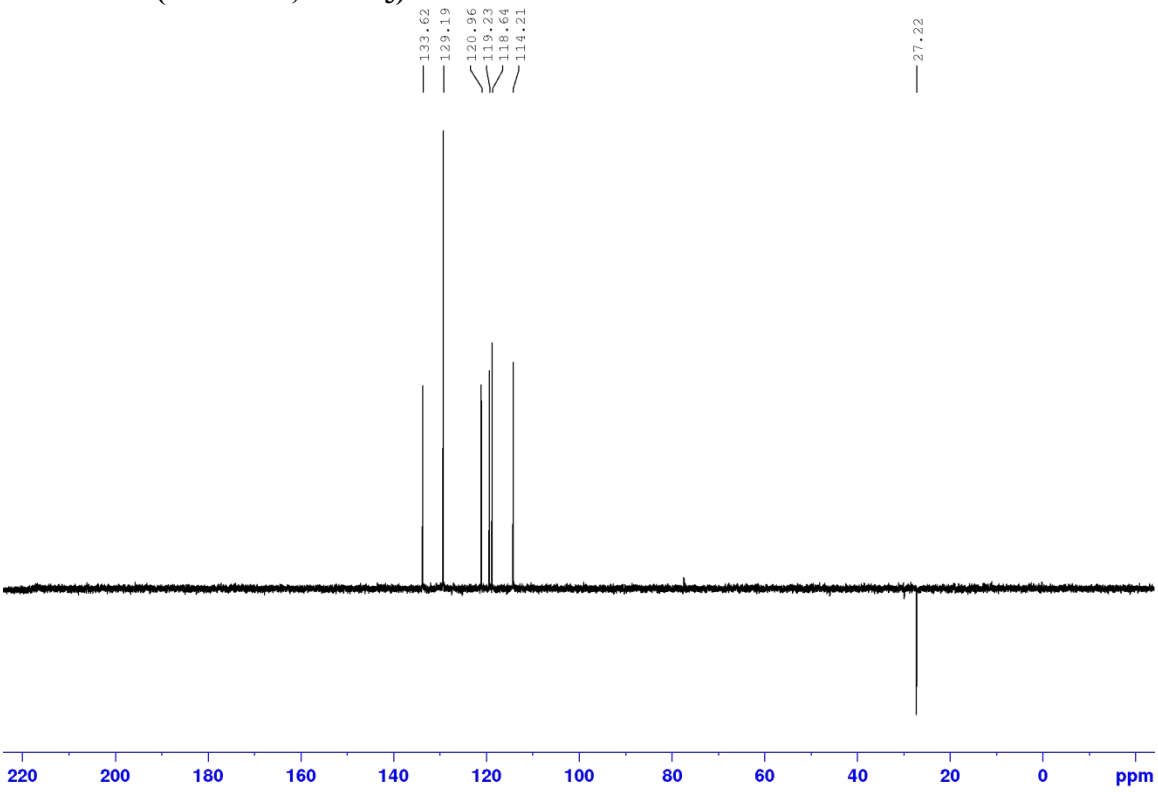

## HRMS of 3e

Elemental Composition Report

Page 1

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Monoisotopic Mass, Even Electron Ions
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SM-369

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QMI DIVISION, CSIR-IIIM JAMMU
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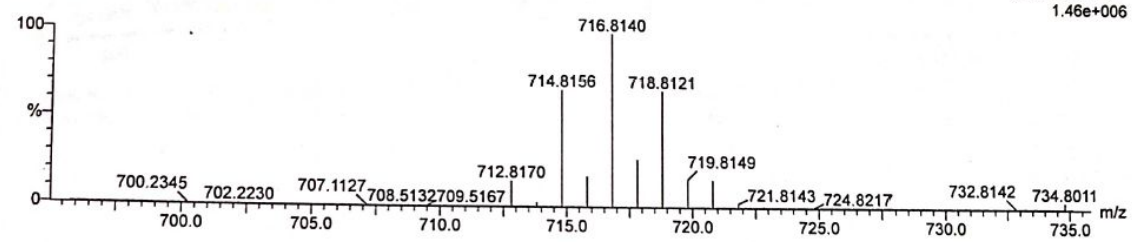


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|---|---|---|---|---|---|---|---|---|
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| Maximum: | | 2.0 | 50.0 | 50.0 | | | | |
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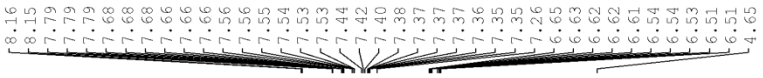
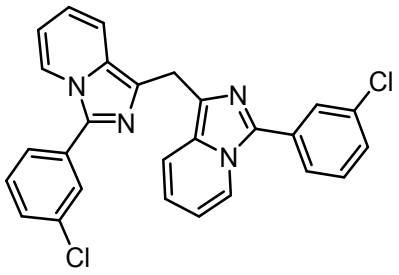
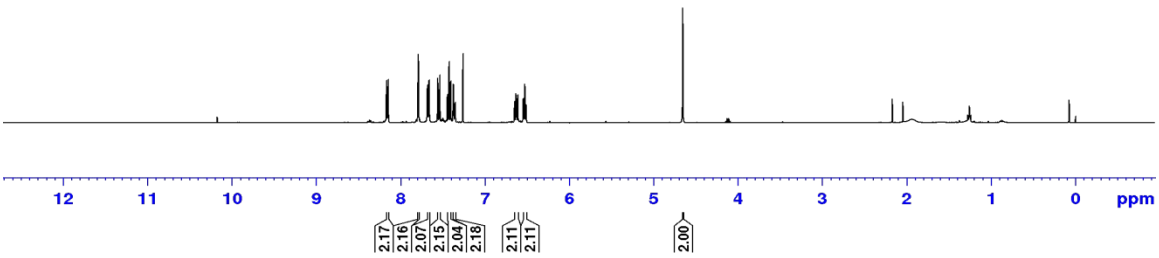
| 712.8170 | 712.8187 | -1.7 | -2.4 | 19.5 | 596.3 | n/a | n/a | C27 H17 N4 Br4 |

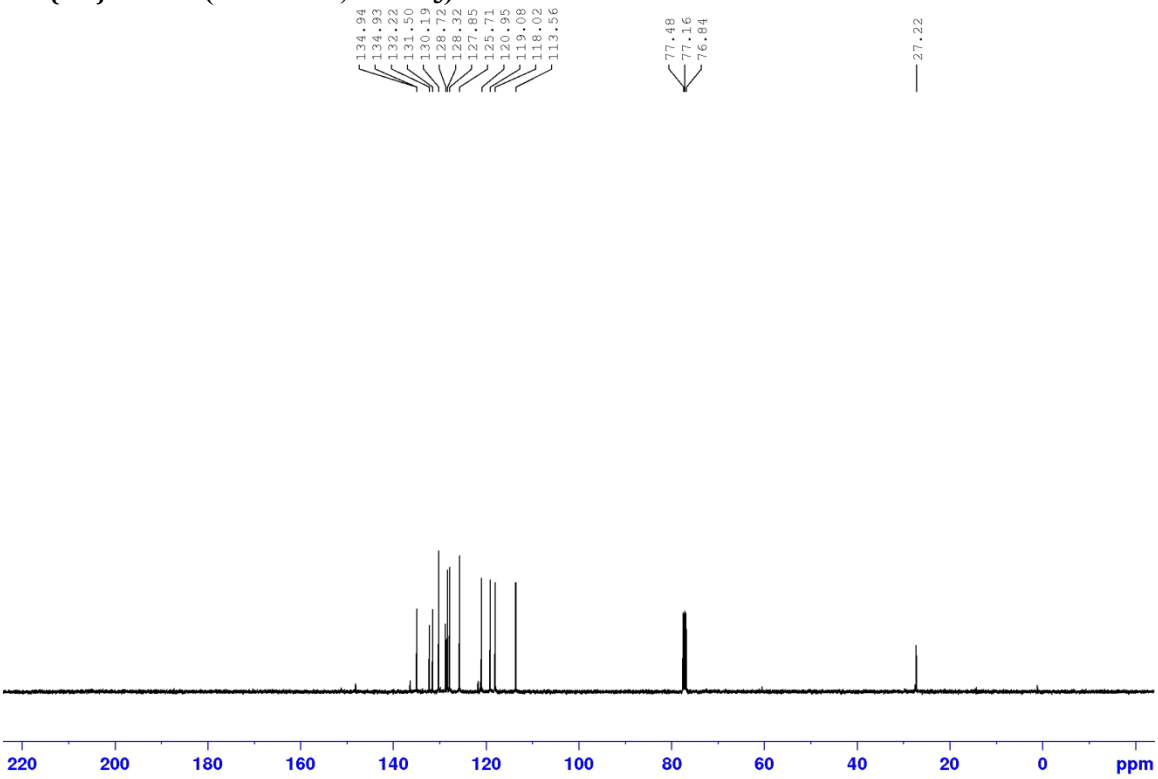
## $^1$H-NMR (400 MHz, $CDCl_3$) of 3f



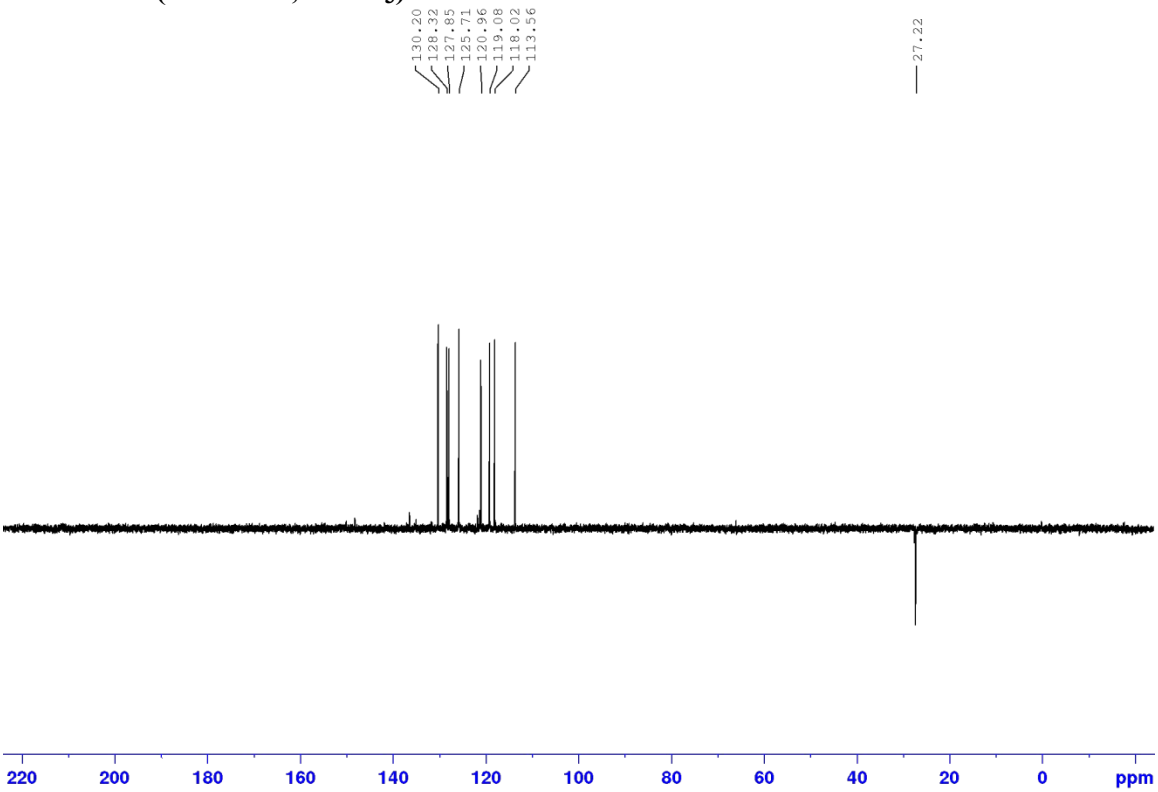



**$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$) of 3f**




**DEPT-135 (101 MHz, $CDCl_3$) of 3f**



## HRMS of 3f

**Elemental Composition Report** Page 1

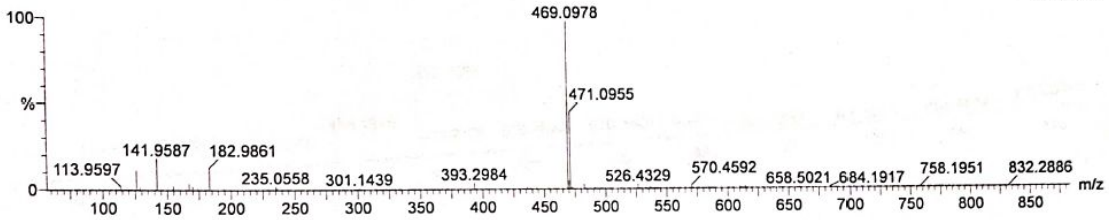
**Single Mass Analysis**
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
22 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-27 H: 0-200 N: 0-4 Cl: 0-2
SM-316

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

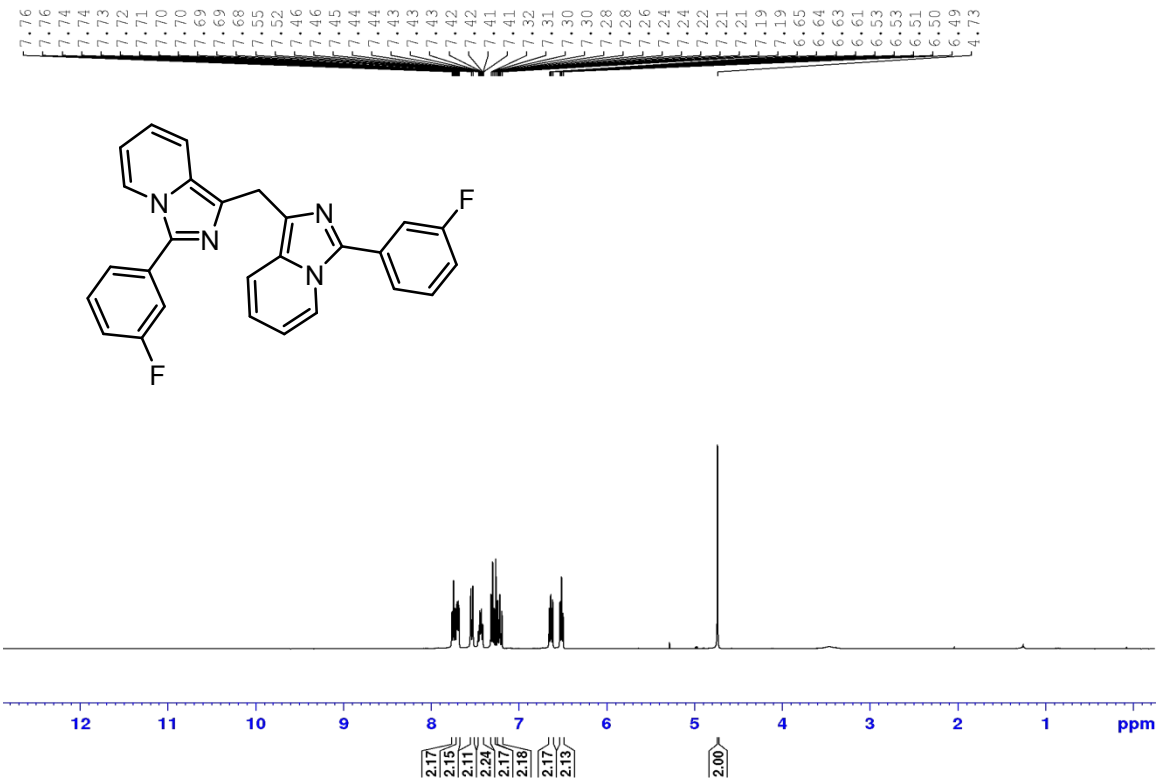
12-Oct-2021
12:06:59
1: TOF MS ES+
2.62e+005

121021_11 14 (0.293) Cm (14)

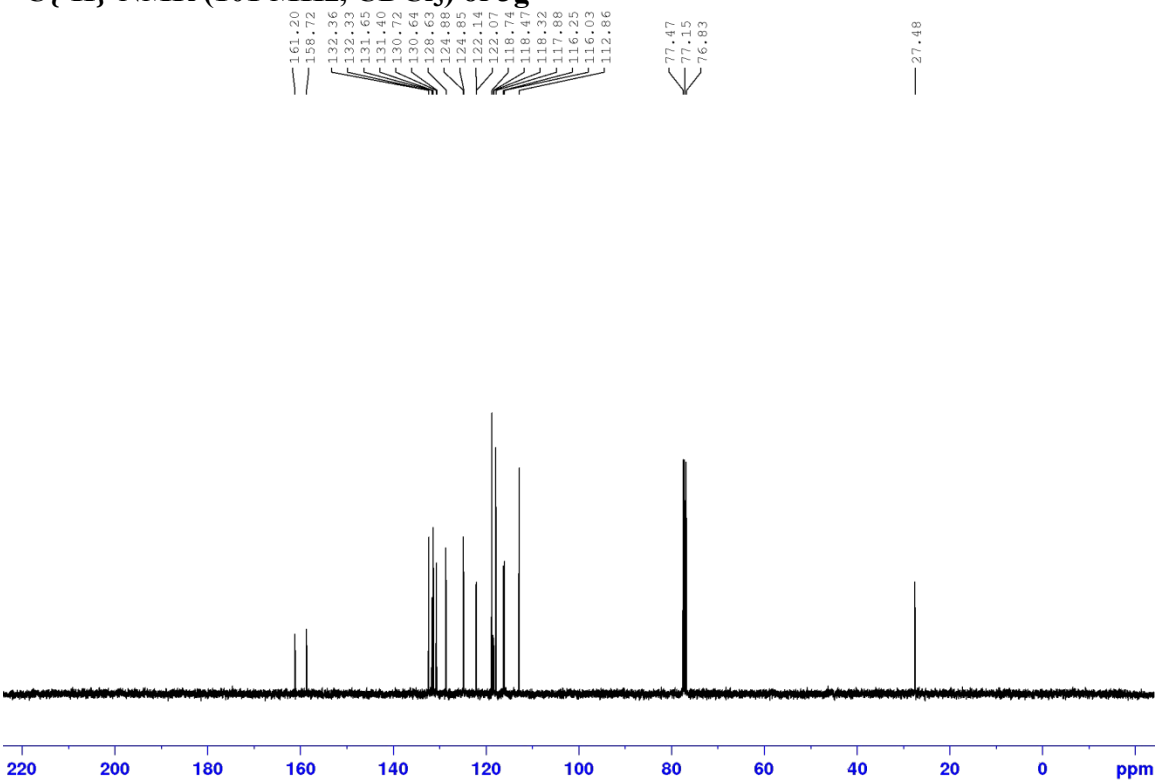



| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 2.0 | 3.0 | 50.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 469.0978 | 469.0987 | -0.9 | -1.9 | 19.5 | 32.0 | n/a | n/a | C27 H19 N4 Cl2 |

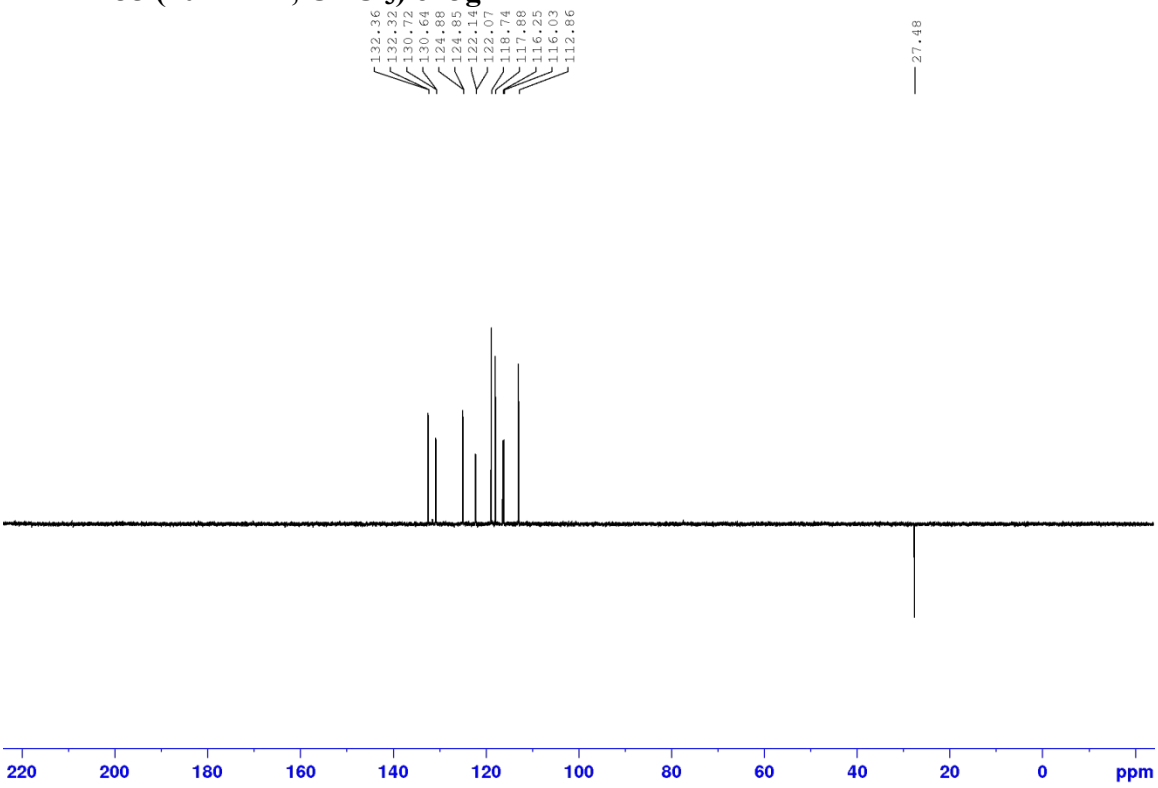
## $^1$H-NMR (400 MHz, $CDCl_3$) of 3g



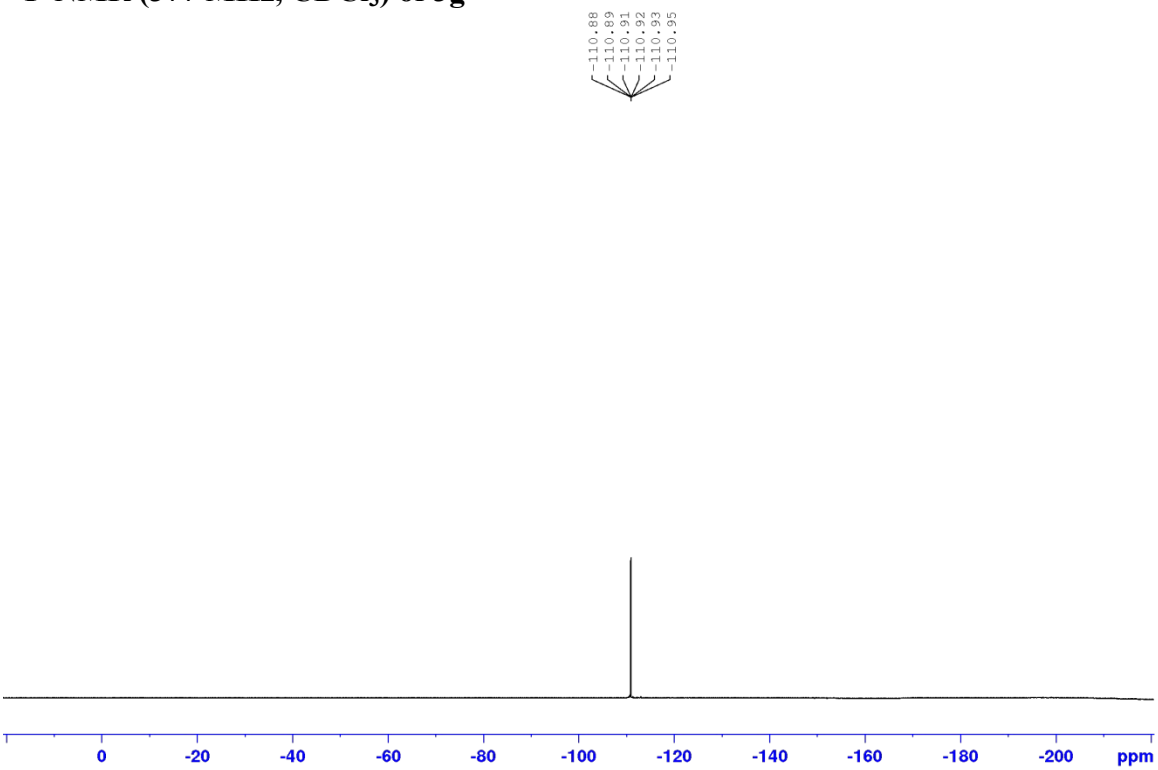
**$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$) of 3g**




**DEPT-135 (101 MHz, $CDCl_3$) of 3g**



## $^{19}$F-NMR (377 MHz, $CDCl_3$) of 3g



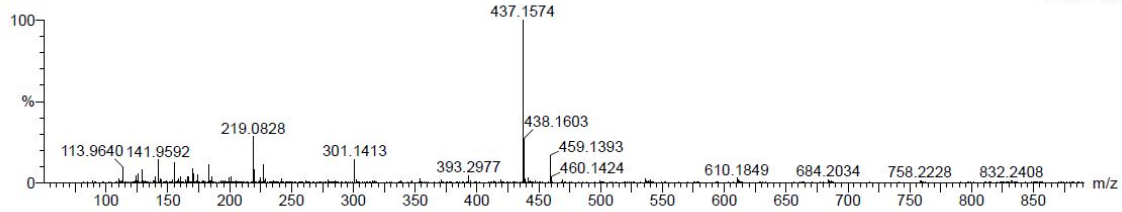

## HRMS of 3g

**Elemental Composition Report** **Page 1**

**Single Mass Analysis**
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

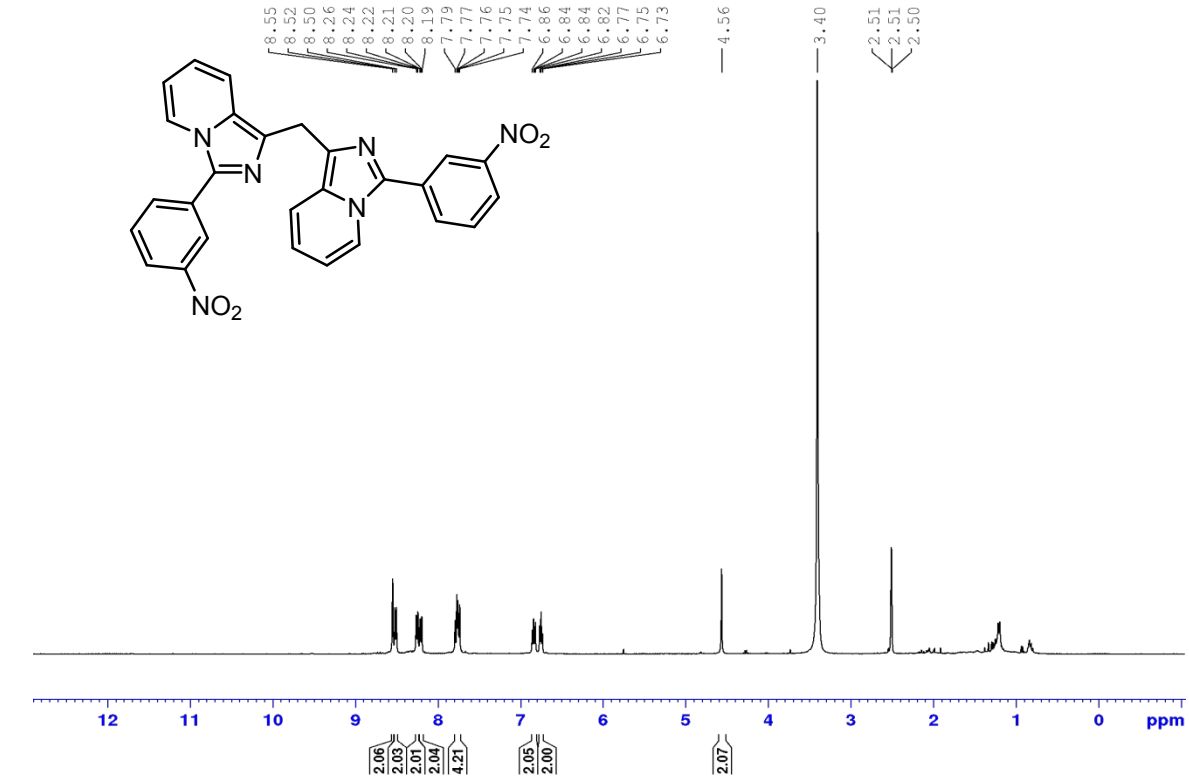
Monoisotopic Mass, Even Electron Ions
24 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-27 H: 0-100 N: 0-4 F: 0-2

SM-380 QMI DIVISION, CSIR-IIIM JAMMU 12-Jul-2023
Xevo G2-XS QTOF YFC2015 11:46:56
120723_02 14 (0.293) 1: TOF MS ES+
9.46e+005

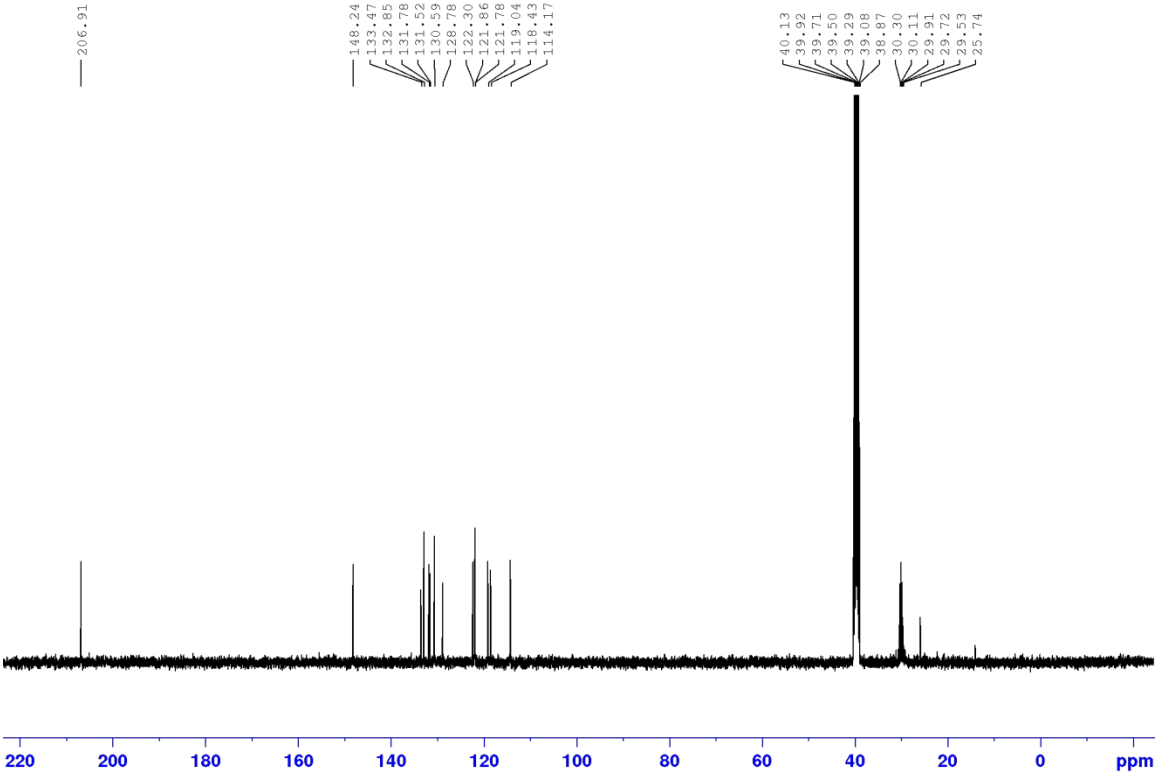



| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 2.0 | 50.0 | 50.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 437.1574 | 437.1578 | -0.4 | -0.9 | 19.5 | 733.9 | n/a | n/a | C27 H19 N4 F2 |

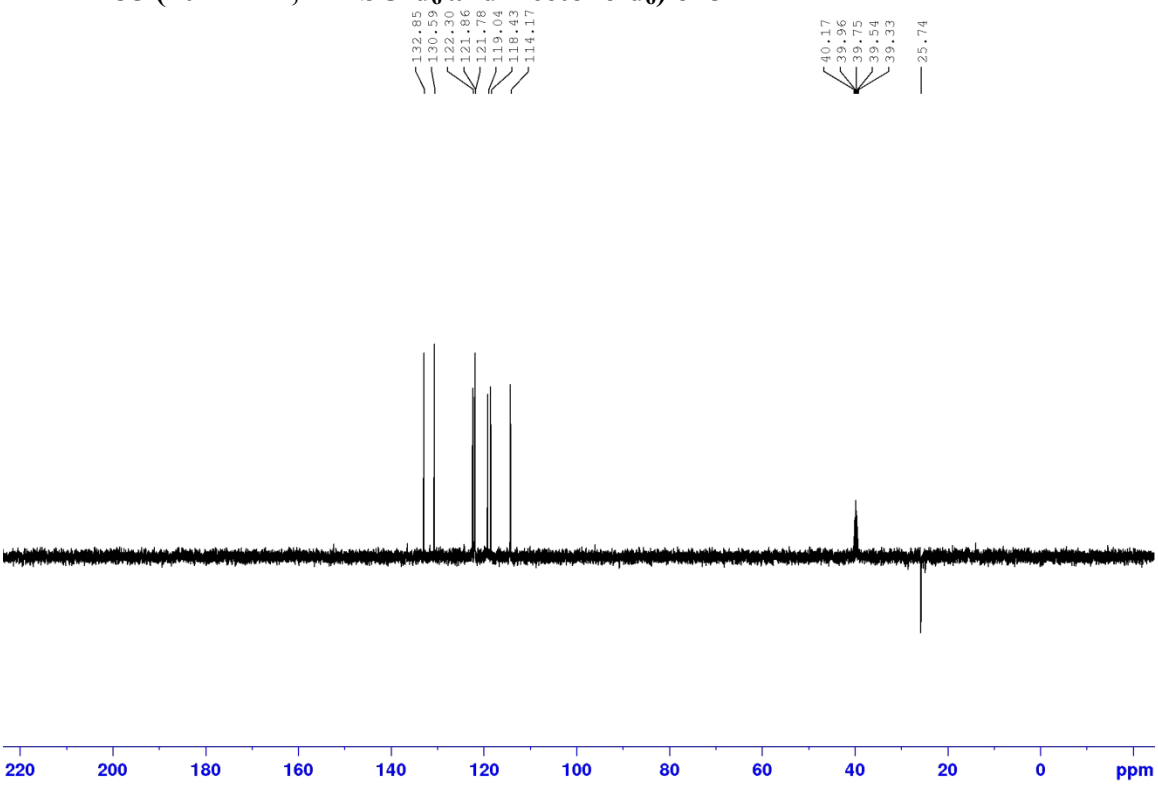
**$^{1}$H-NMR (400 MHz, DMSO-d$_6$ and Acetone-d$_6$) of 3h**



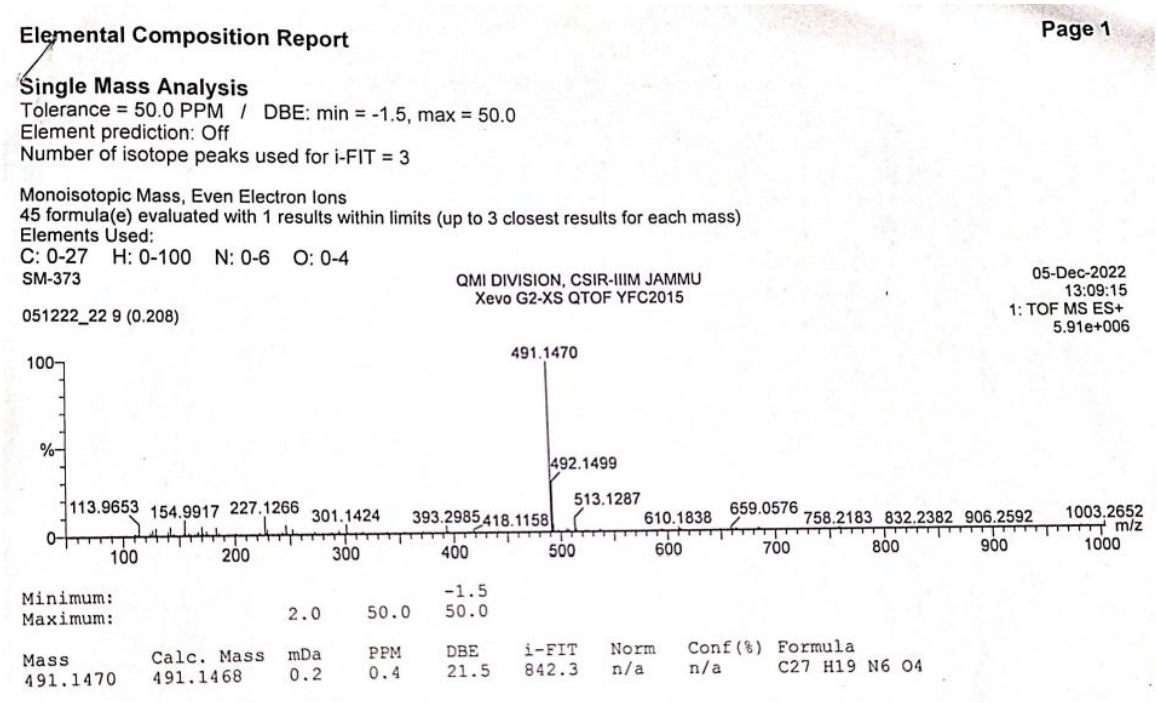

**$^{13}$C{$^{1}$H}-NMR (101 MHz, DMSO-d$_6$ and Acetone-d$_6$) of 3h**



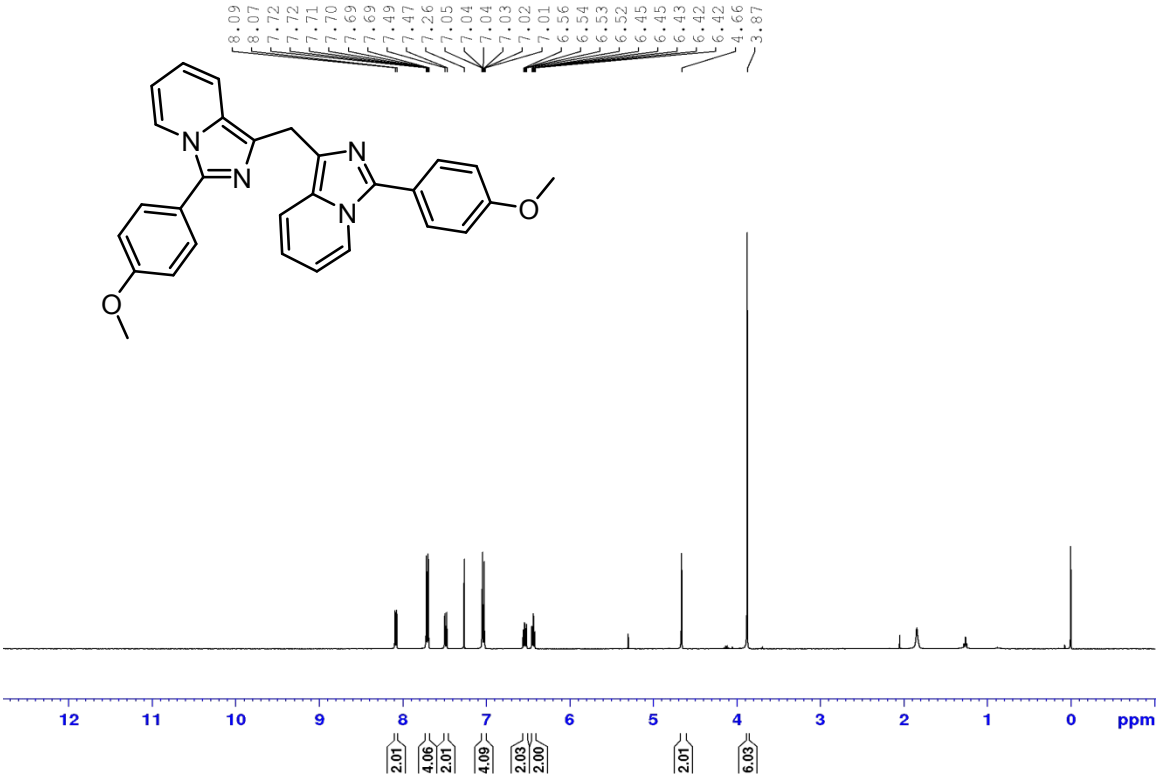
**DEPT-135 (101 MHz, DMSO-$d_6$ and Acetone-$d_6$) of 3h**



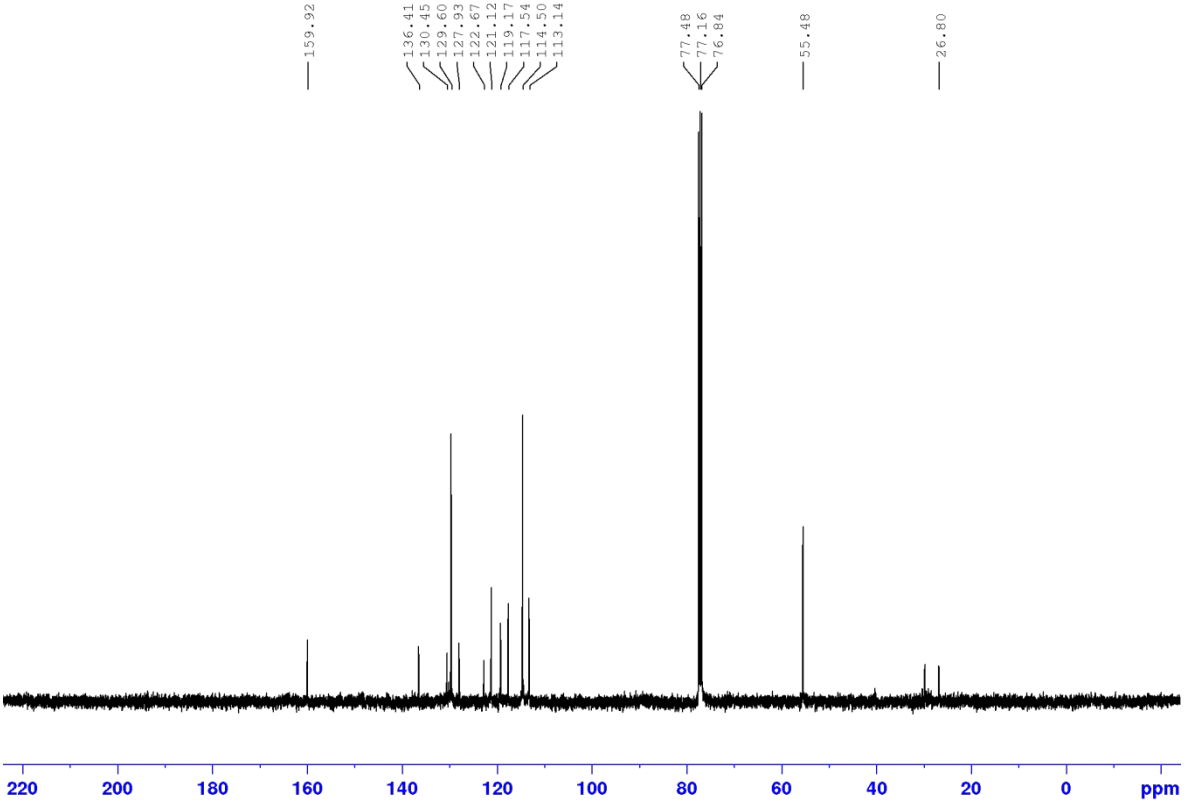

**HRMS of 3h**



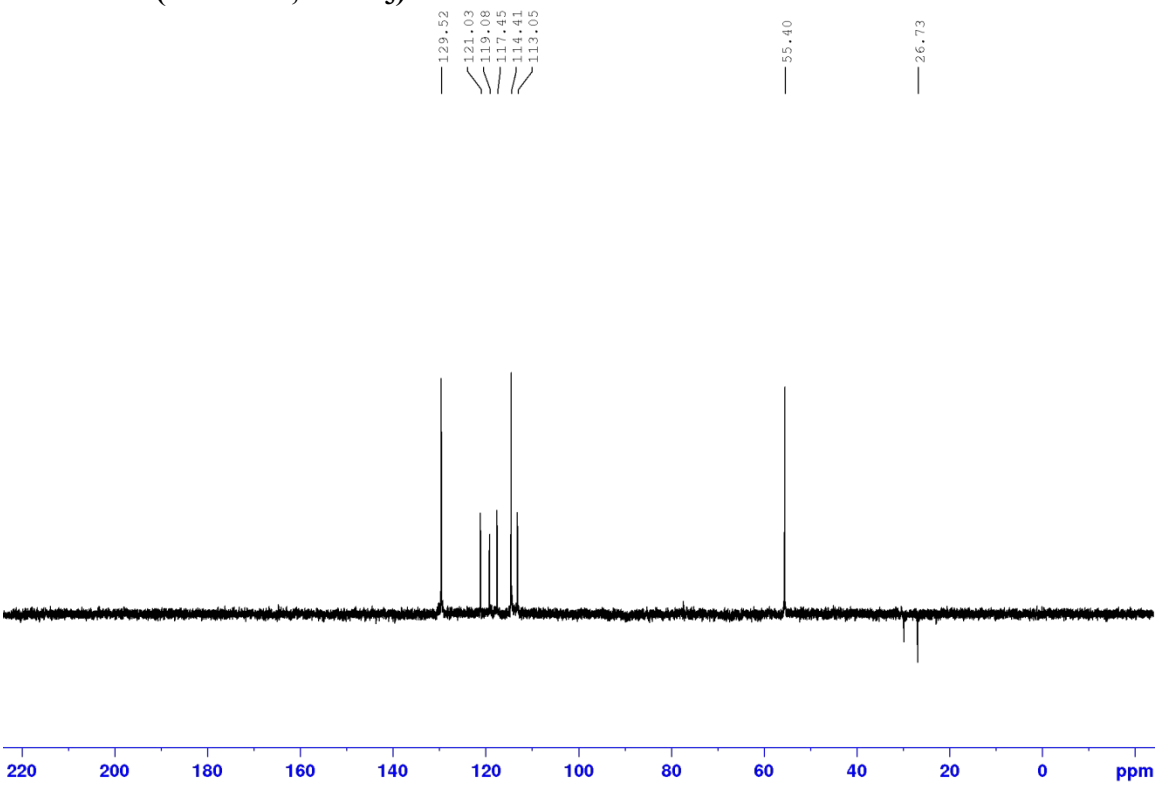
**$^{1}$H-NMR (400 MHz, $CDCl_3$) of 3i**



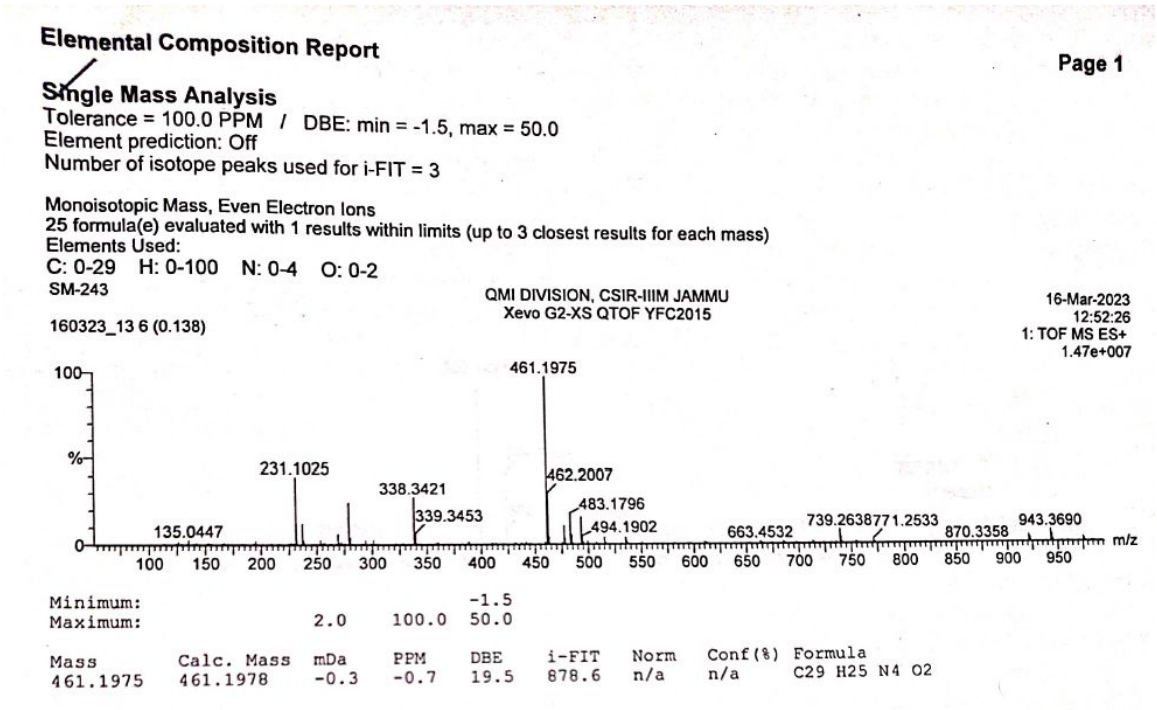

**$^{13}$C{$^{1}$H}-NMR (101 MHz, $CDCl_3$) of 3i**



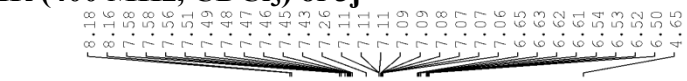
**DEPT-135 (101 MHz, $CDCl_3$) of 3i**

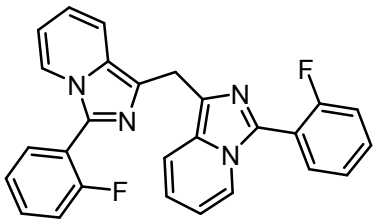


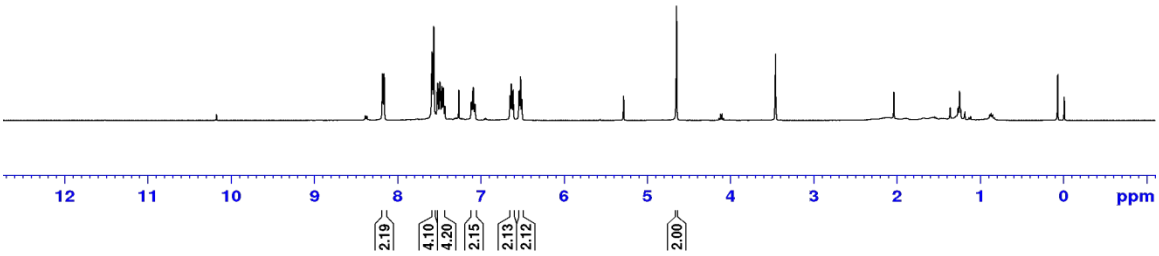

**HRMS of 3i**



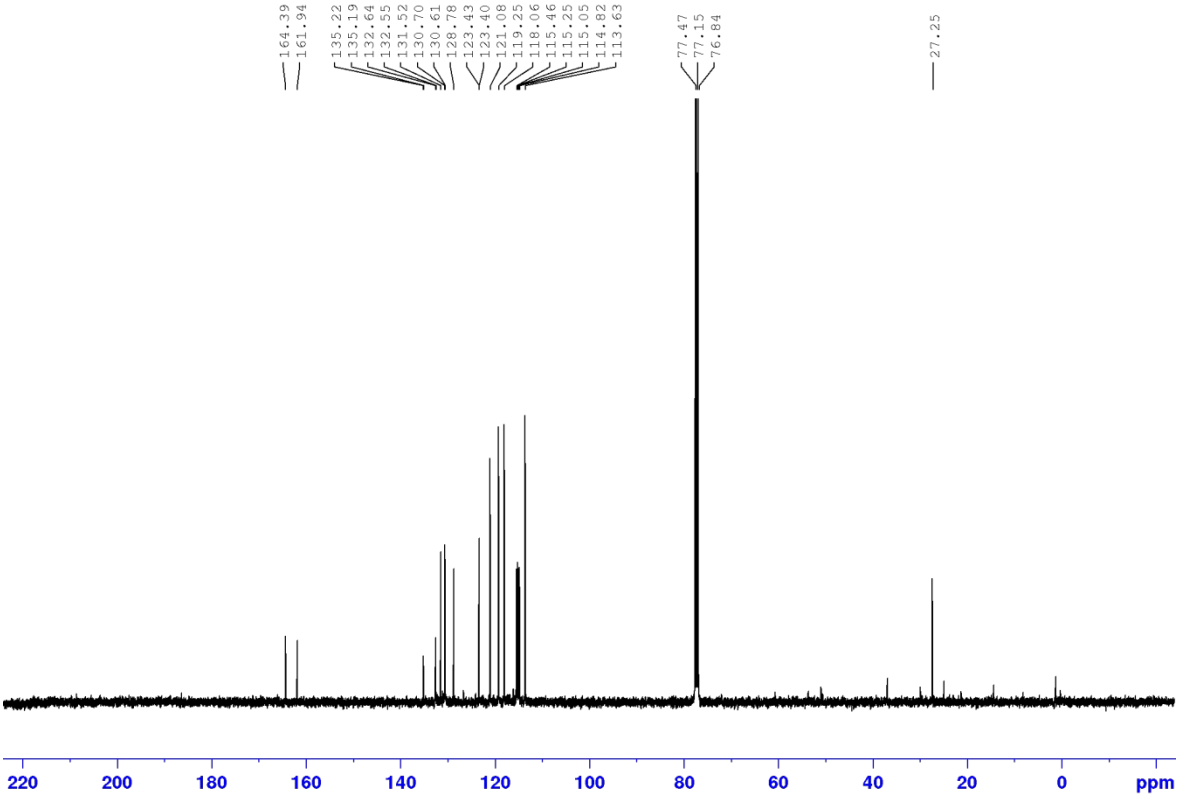
**$^{1}$H-NMR (400 MHz, $CDCl_3$) of 3j**



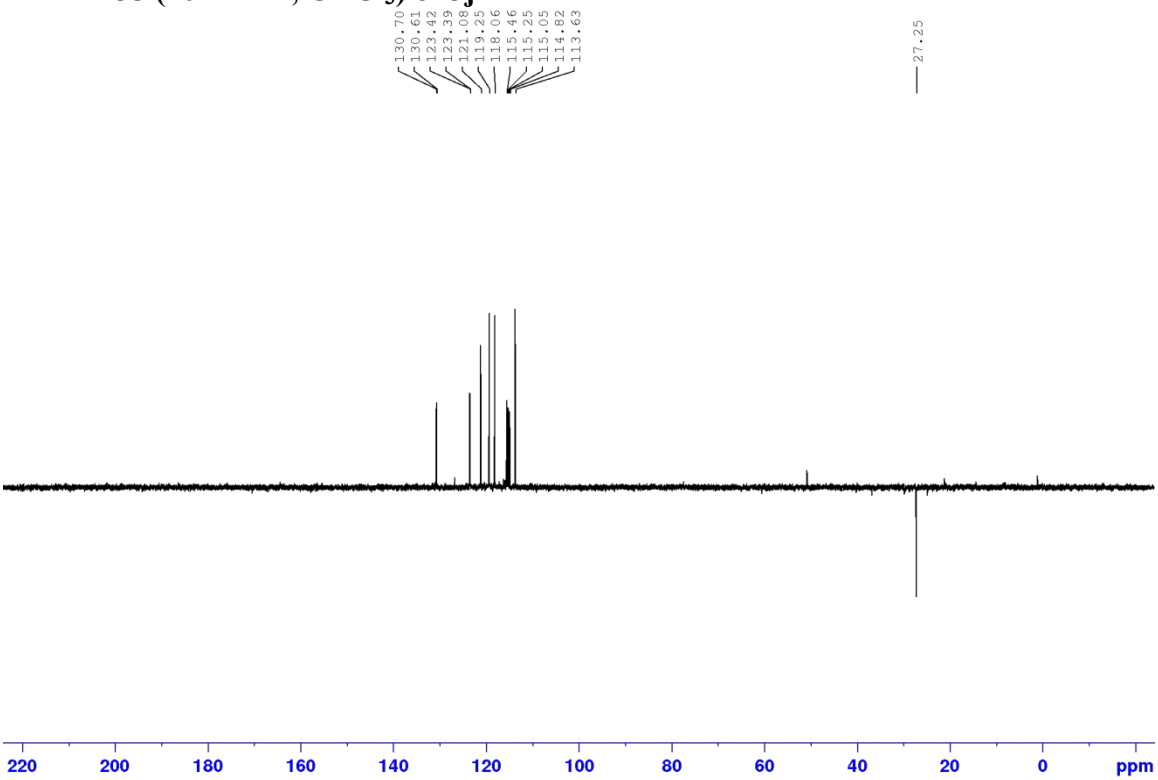



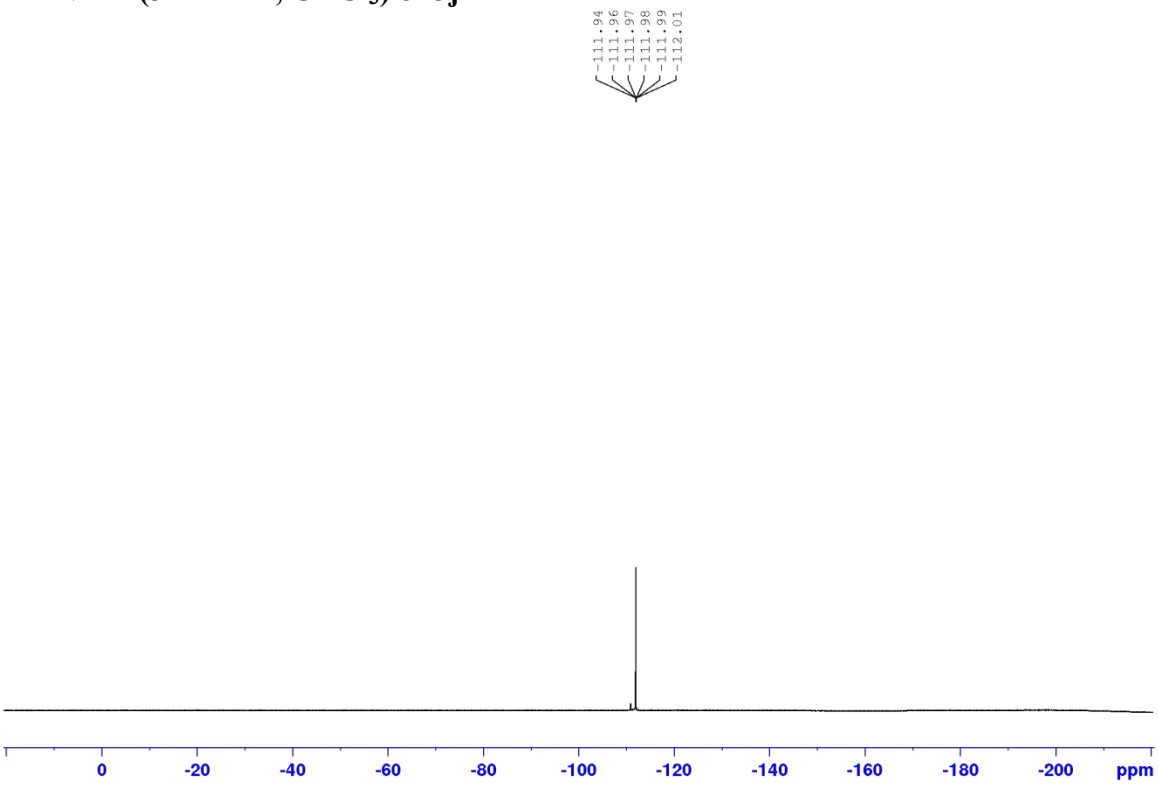

**$^{13}$C{$^{1}$H}-NMR (101 MHz, $CDCl_3$) of 3j**



**DEPT-135 (101 MHz, $CDCl_3$) of 3j**




**$^{19}$F-NMR (377 MHz, $CDCl_3$) of 3j**



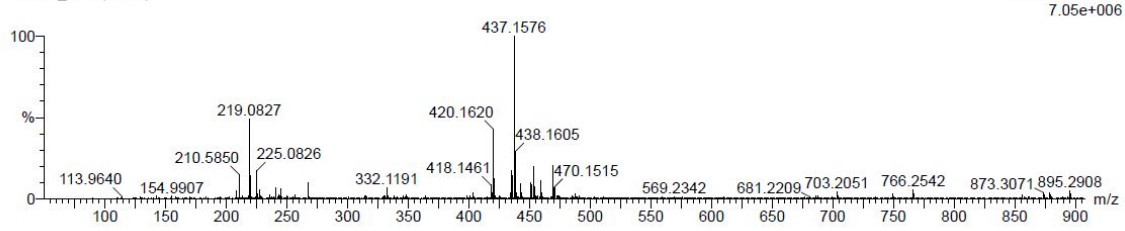
## HRMS of 3j

**Elemental Composition Report** **Page 1**

**Single Mass Analysis**
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

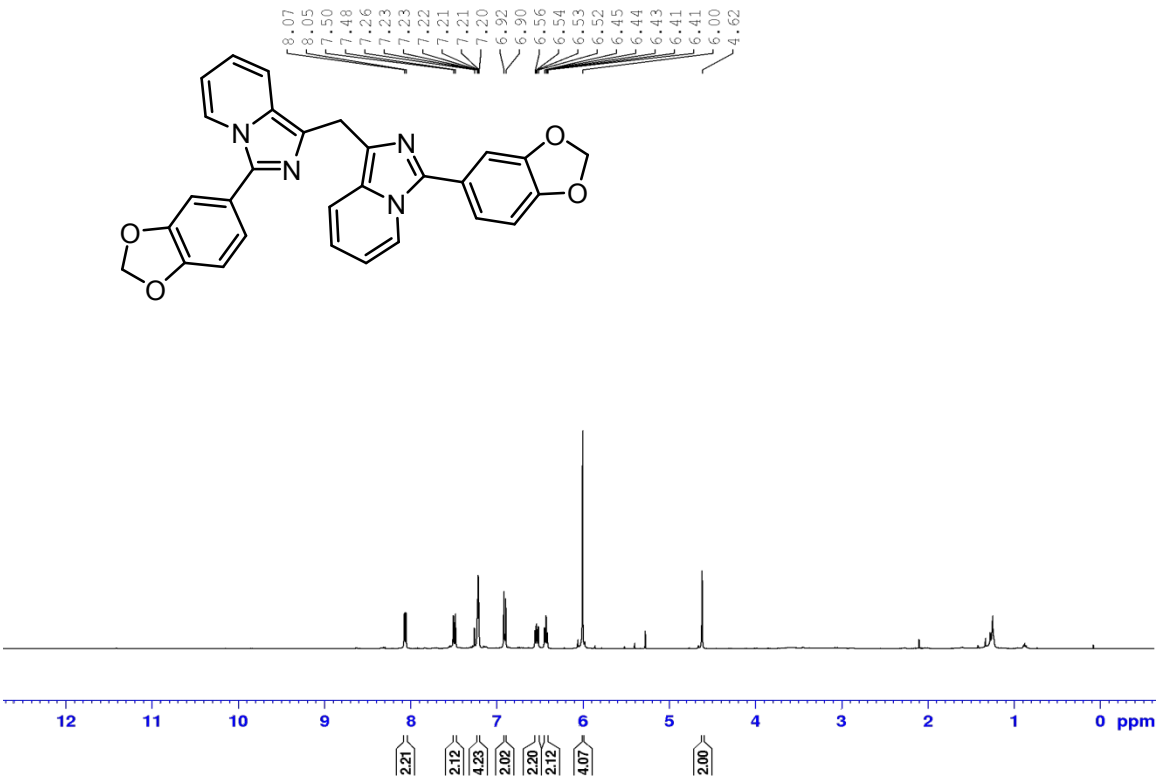
Monoisotopic Mass, Even Electron Ions
24 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-27 H: 0-100 N: 0-4 F: 0-2

SM-377 QMI DIVISION, CSIR-IIIM JAMMU 12-Jul-2023
Xevo G2-XS QTOF YFC2015 11:49:31
120723_03 5 (0.121) 1: TOF MS ES+
7.05e+006

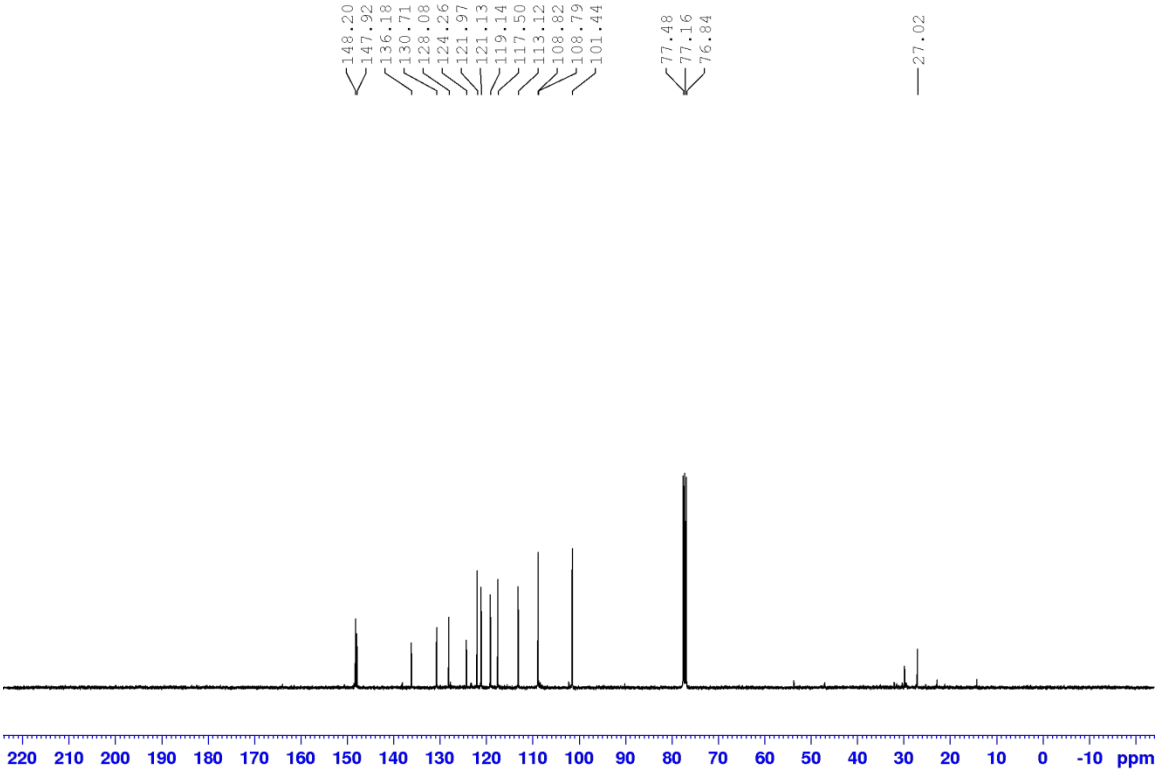



| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 2.0 | 50.0 | 50.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 437.1576 | 437.1578 | -0.2 | -0.5 | 19.5 | 854.9 | n/a | n/a | C27 H19 N4 F2 |

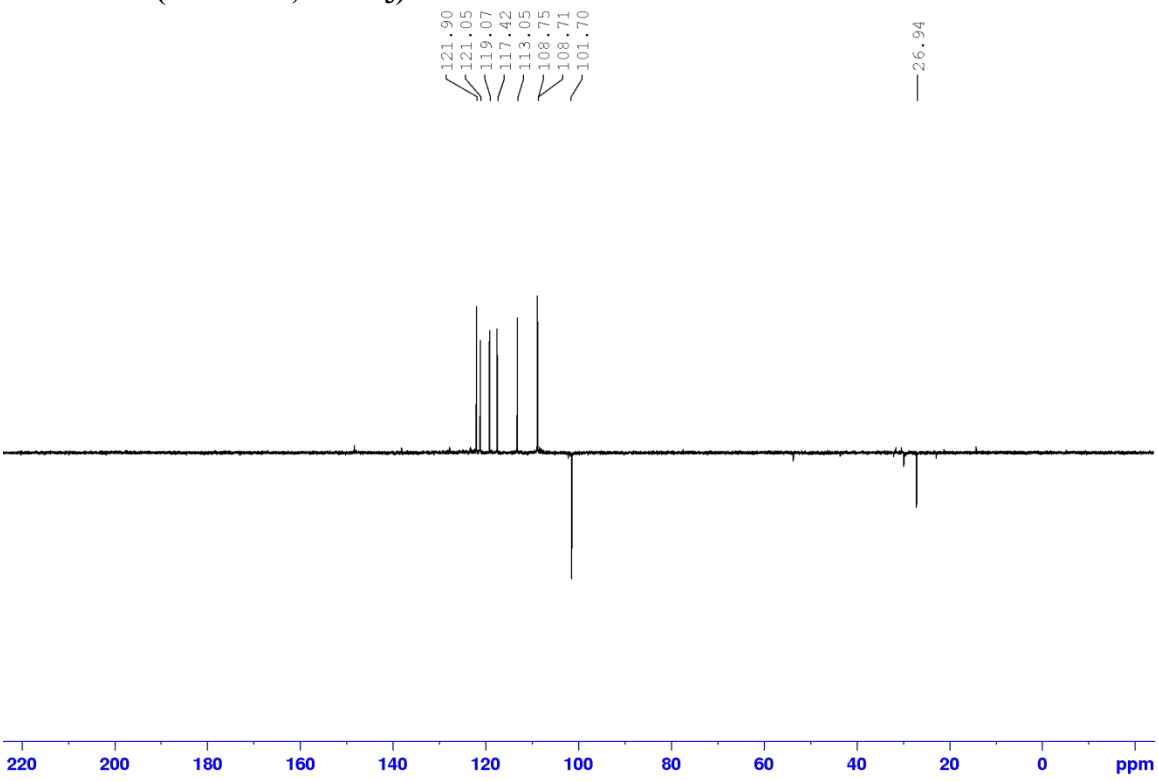
## $^1$H-NMR (400 MHz, $CDCl_3$) of 3k



**$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$) of 3k**




**DEPT-135 (101 MHz, $CDCl_3$) of 3k**



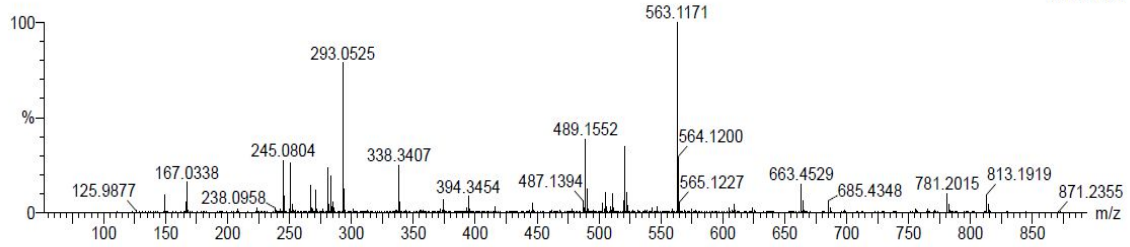
## HRMS of 3k

**Elemental Composition Report** **Page 1**

**Single Mass Analysis**
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

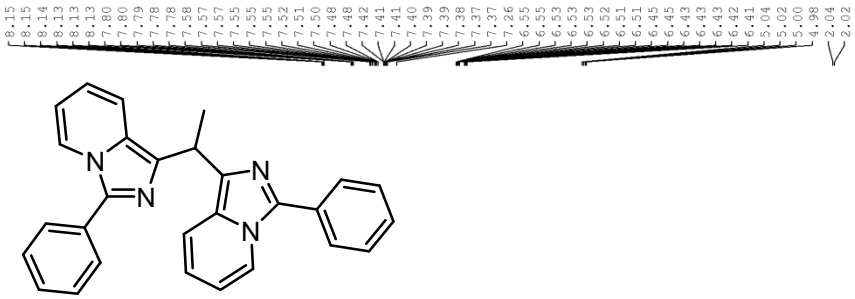
Monoisotopic Mass, Even Electron Ions
35 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-29 H: 0-100 N: 0-4 O: 0-4

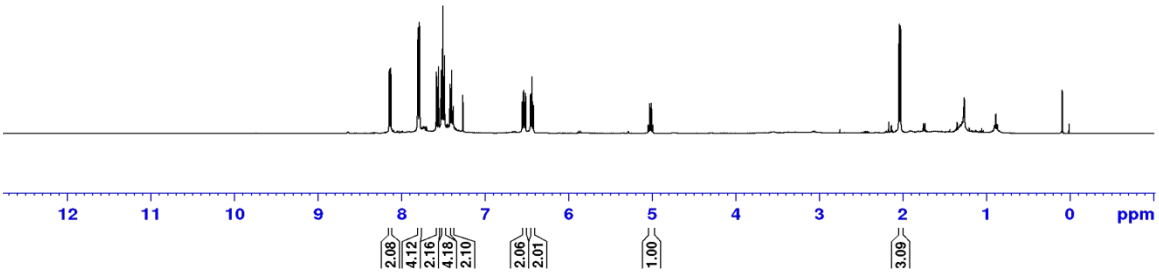
SM-IMBIS — QMI DIVISION, CSIR-IIIM JAMMU — 06-Oct-2023 14:46:06
061023_31 5 (0.121) — Xevo G2-XS QTOF YFC2015 — 1: TOF MS ES+ 5.80e+006



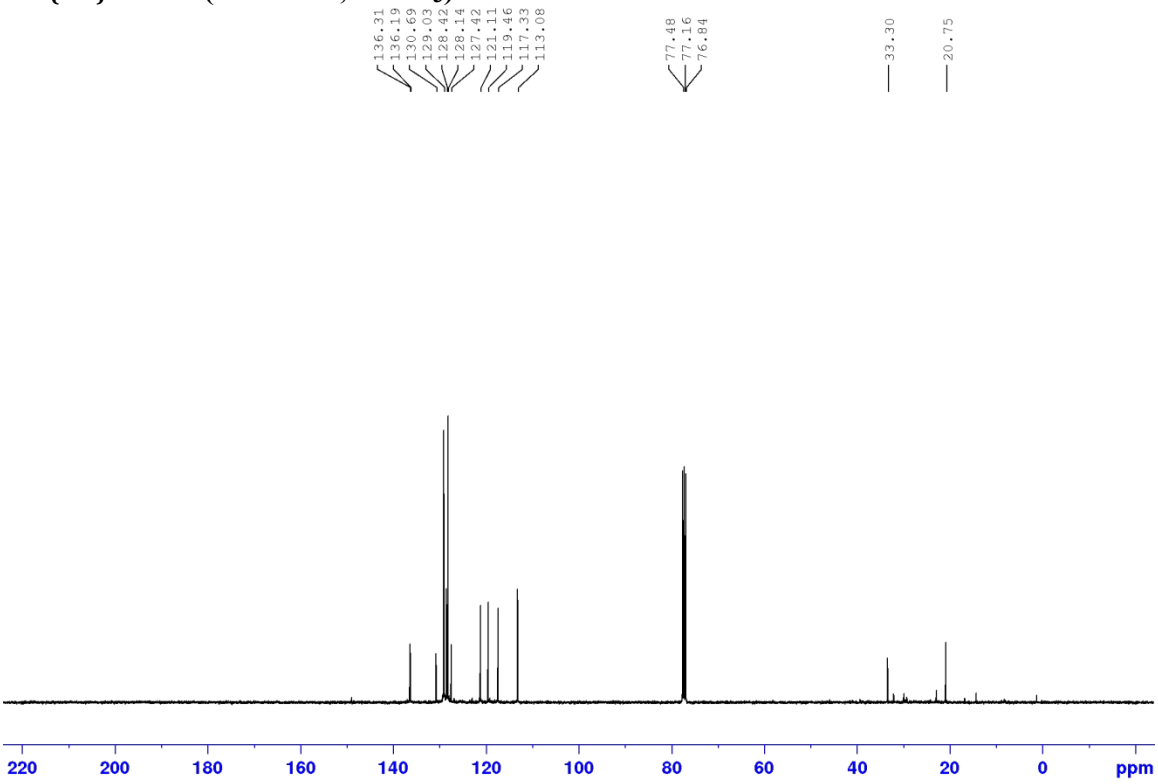

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 2.0 | 100.0 | 50.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 489.1552 | 489.1563 | -1.1 | -2.2 | 21.5 | 803.8 | n/a | n/a | C29 H21 N4 O4 |

## $^1$H-NMR (400 MHz, $CDCl_3$) of 3l

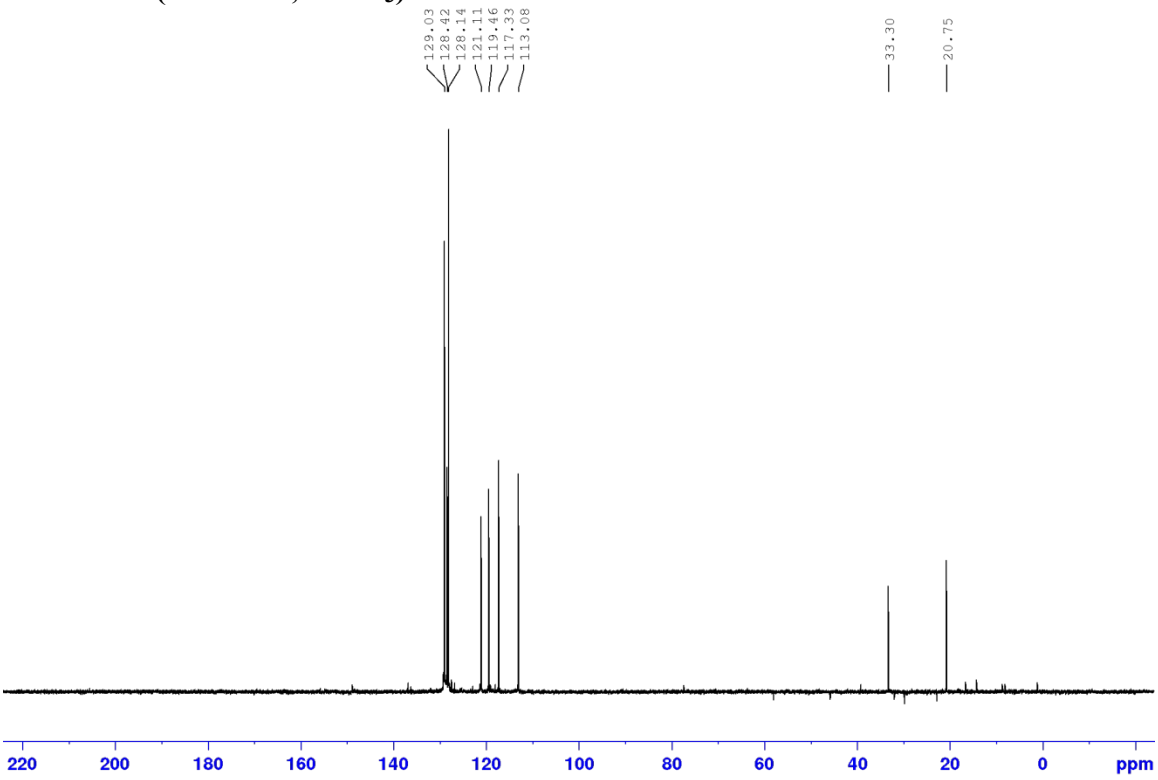


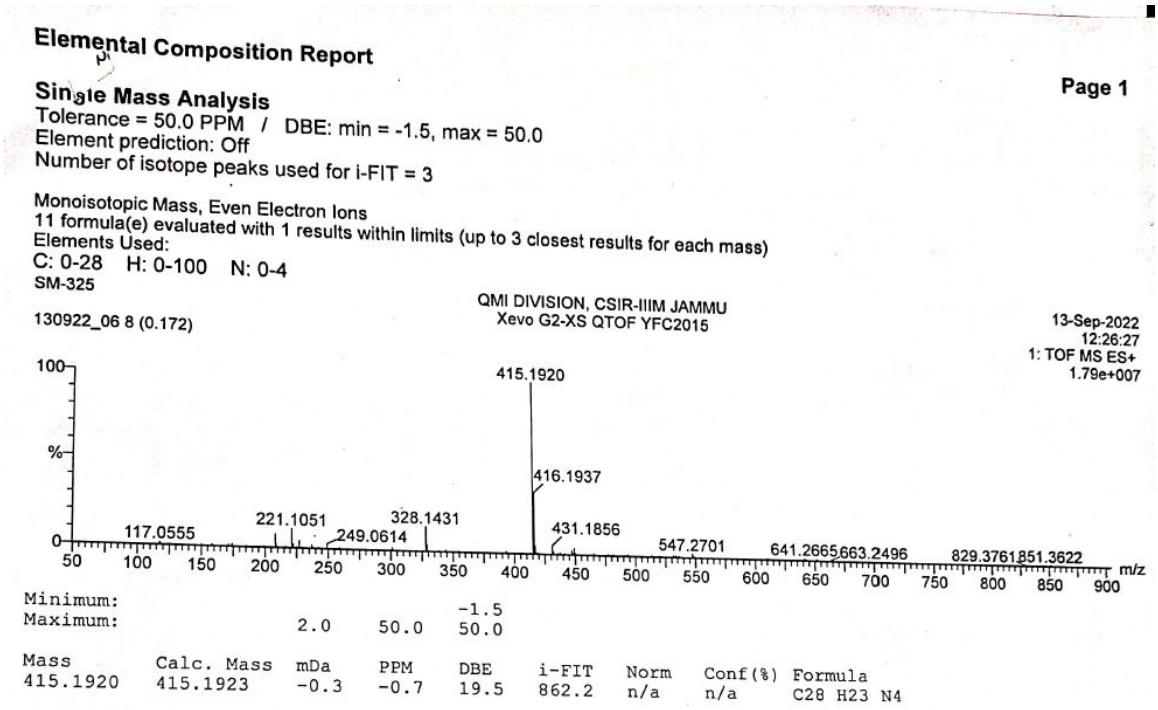
**$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$) of 3l**




**DEPT-135 (101 MHz, $CDCl_3$) of 3l**



**HRMS of 3l**



Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
11 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-28 H: 0-100 N: 0-4
SM-325

130922_06 8 (0.172)

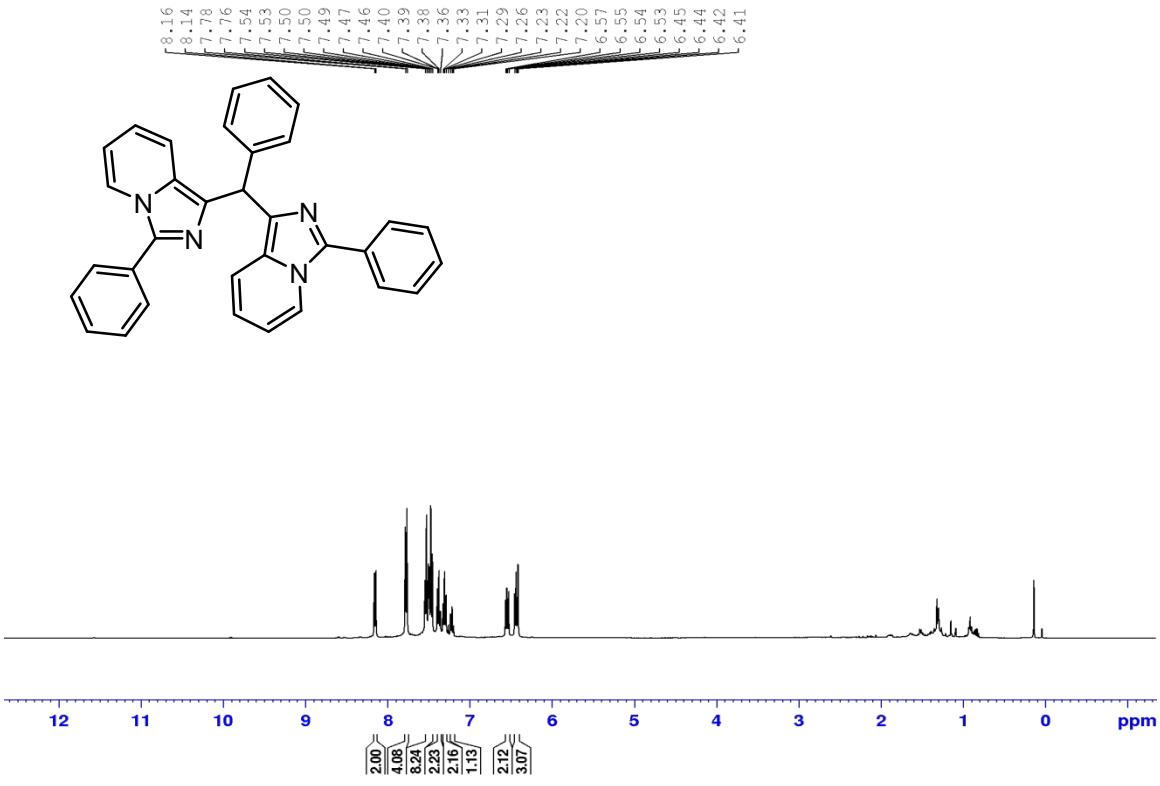
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

13-Sep-2022
12:26:27
1: TOF MS ES+
1.79e+007

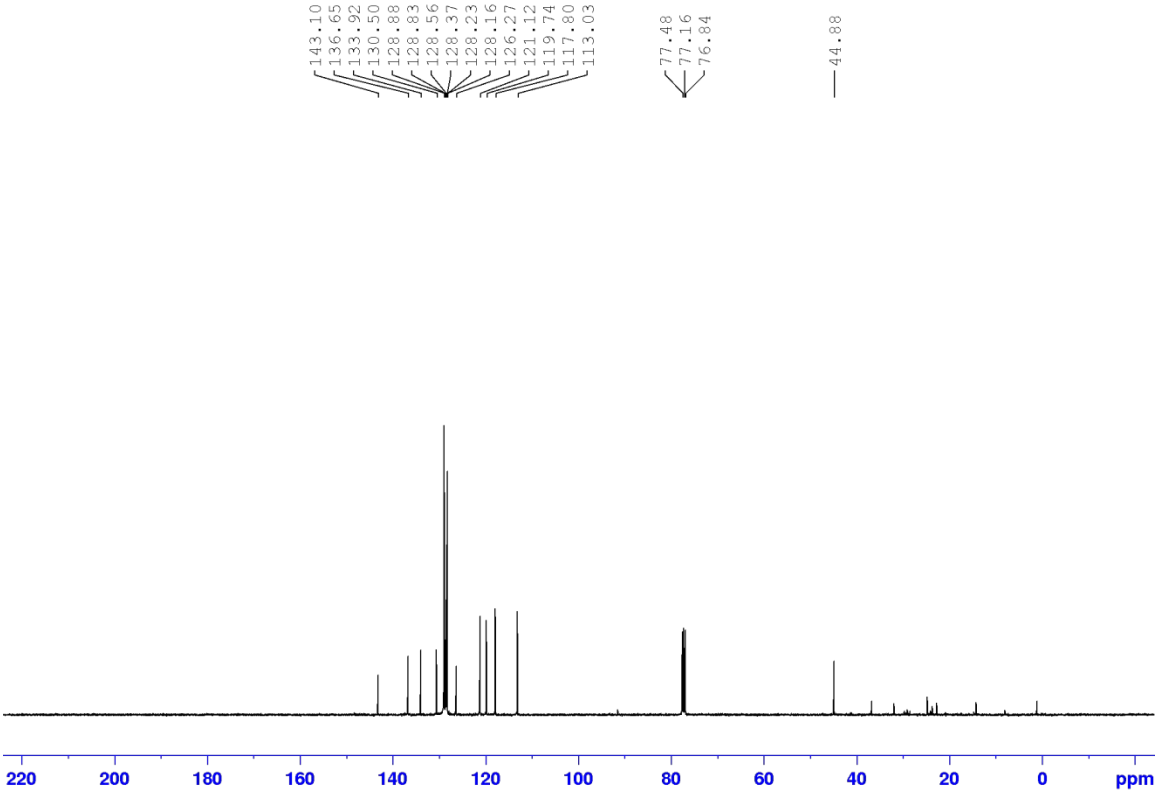


| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 2.0 | 50.0 | 50.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 415.1920 | 415.1923 | -0.3 | -0.7 | 19.5 | 862.2 | n/a | n/a | C28 H23 N4 |

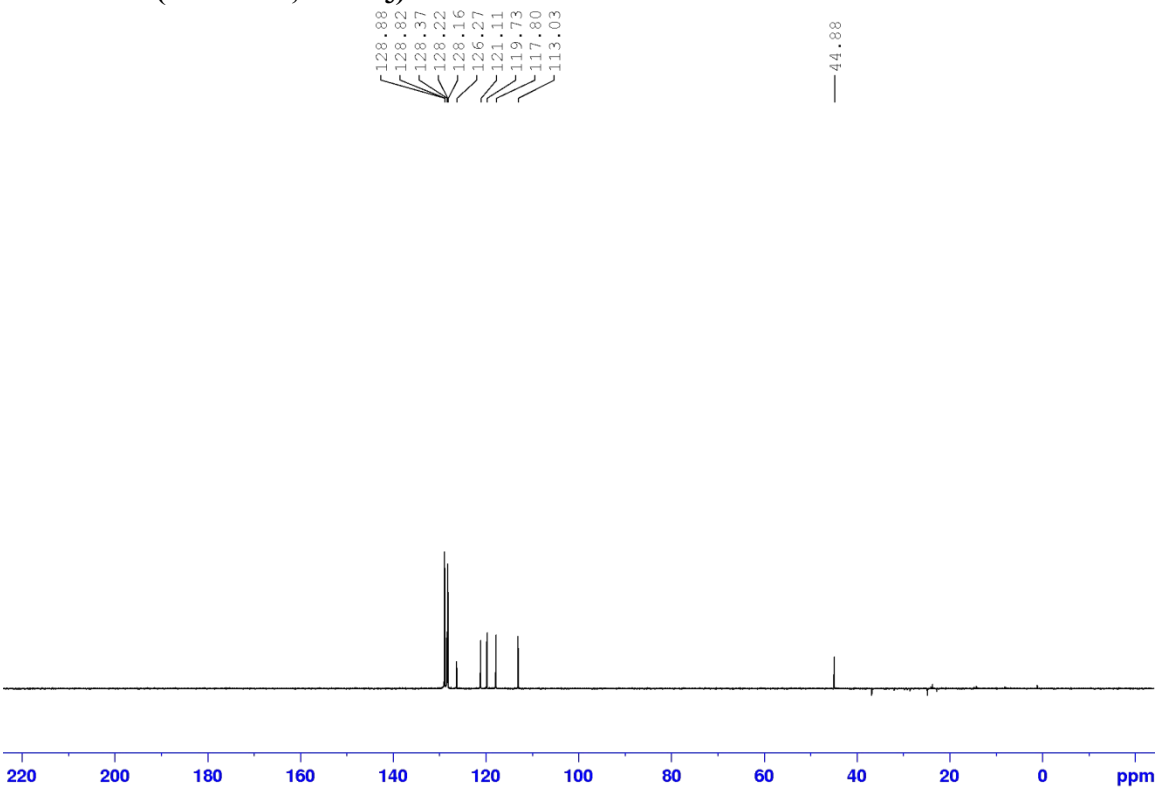
**$^1$H-NMR (400 MHz, $CDCl_3$) of 3m**



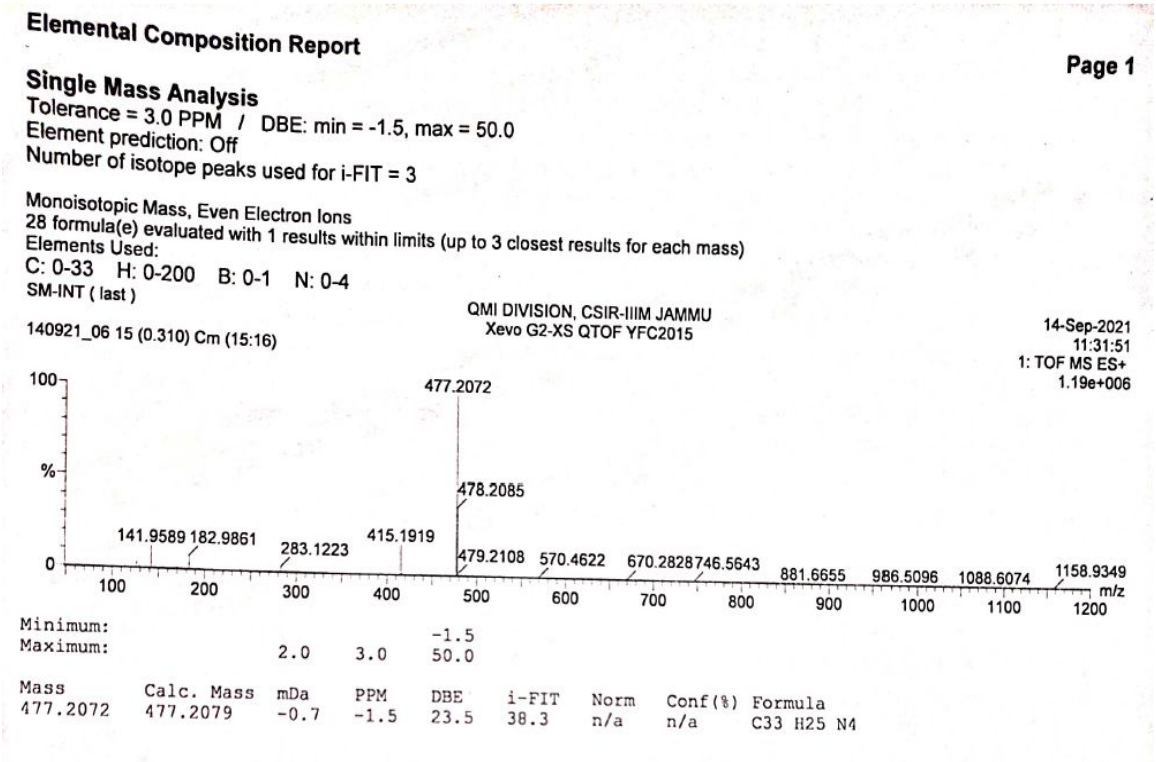
**$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$) of 3m**



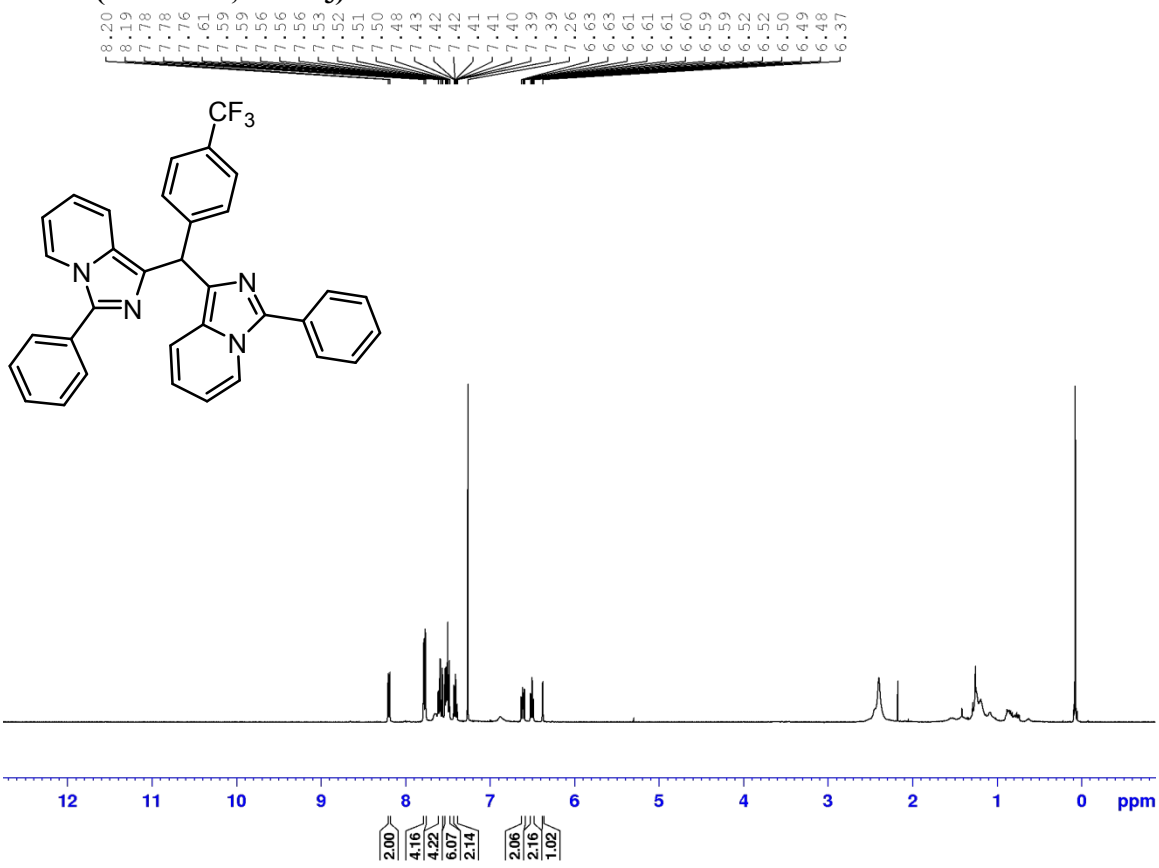

**DEPT-135 (101 MHz, $CDCl_3$) of 3m**



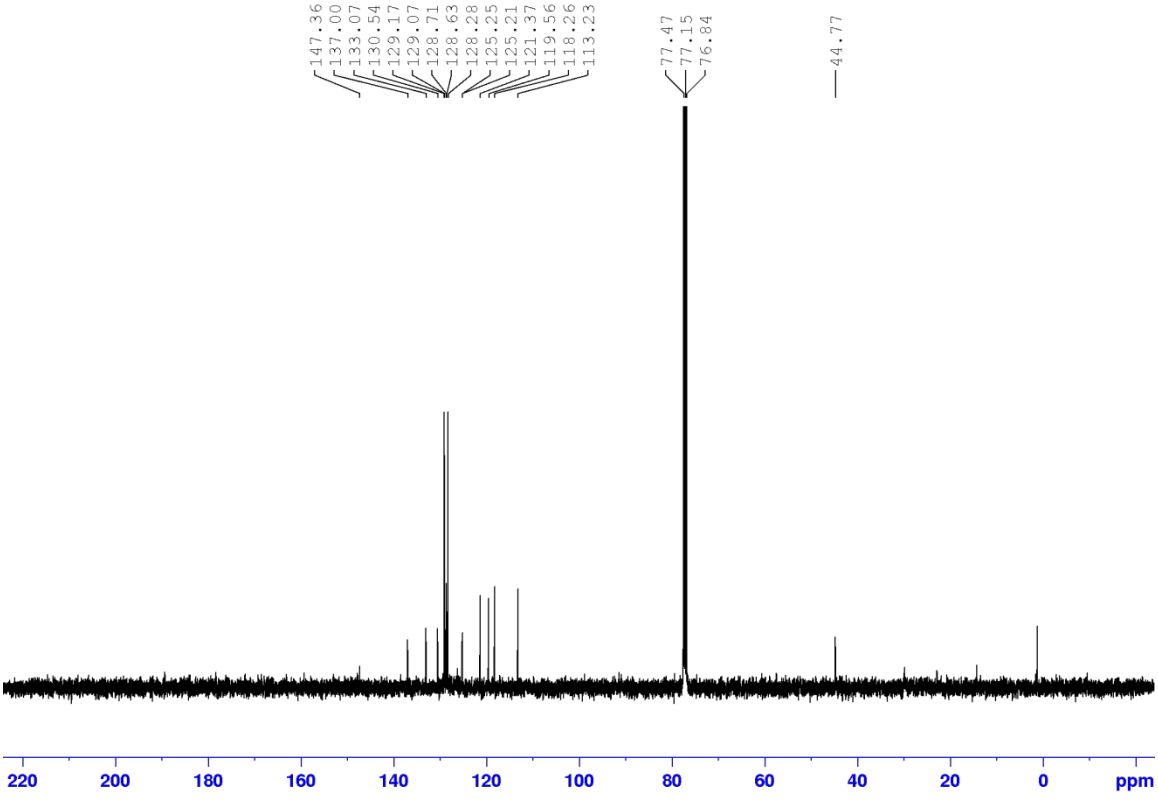
**HRMS of 3m**



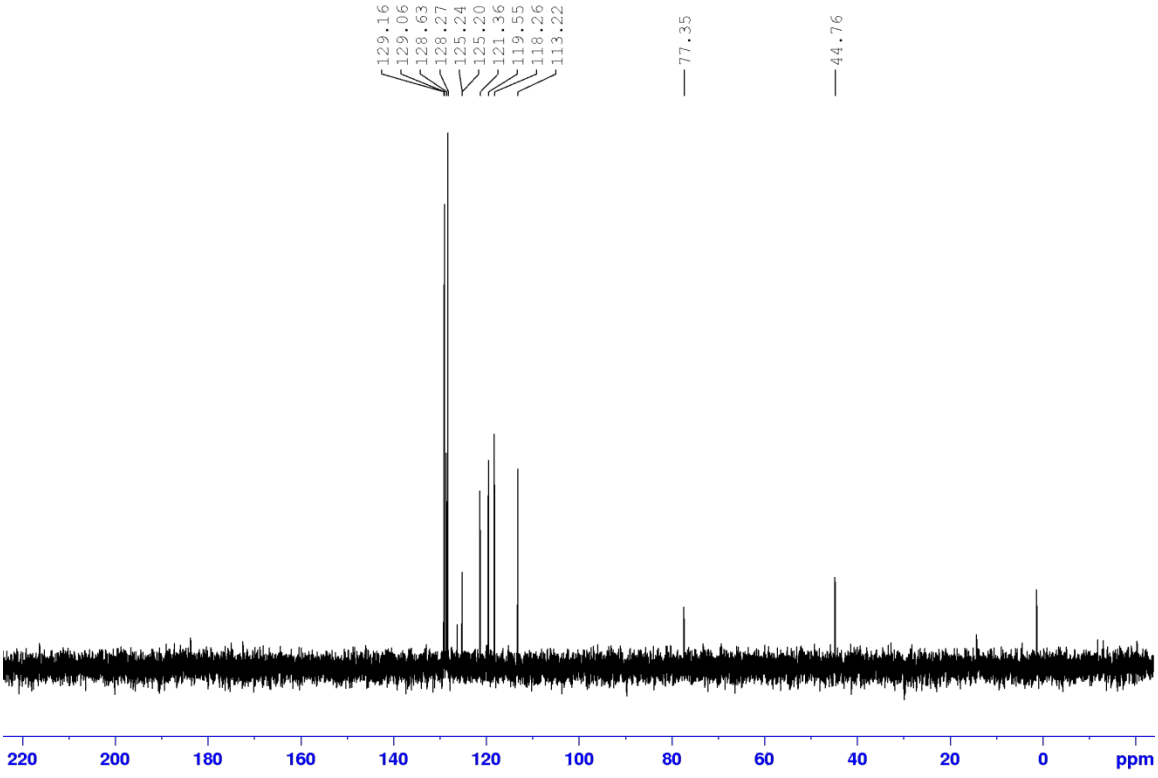

**$^1$H-NMR (400 MHz, $CDCl_3$) of 3n**



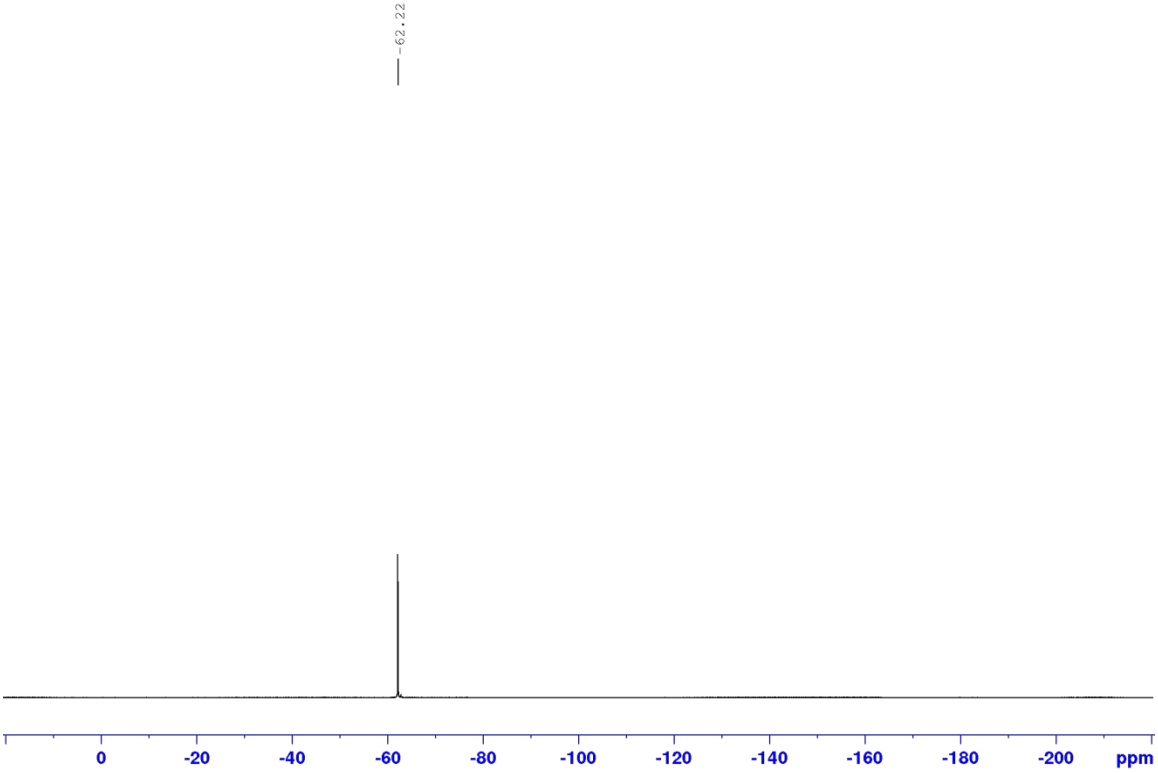
**$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$) of 3n**




**DEPT-135 (101 MHz, $CDCl_3$) of 3n**



**$^{19}$F-NMR (377 MHz, $CDCl_3$) of 3n**




**HRMS of 3n**

**Elemental Composition Report** **Page 1**

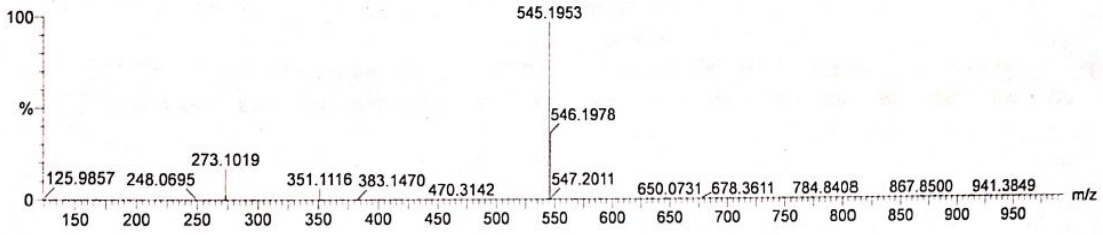
**Single Mass Analysis**
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
32 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-34 H: 0-200 N: 0-4 F: 0-3

SM-328
071221_23 46 (0.913) Cm (46:47)

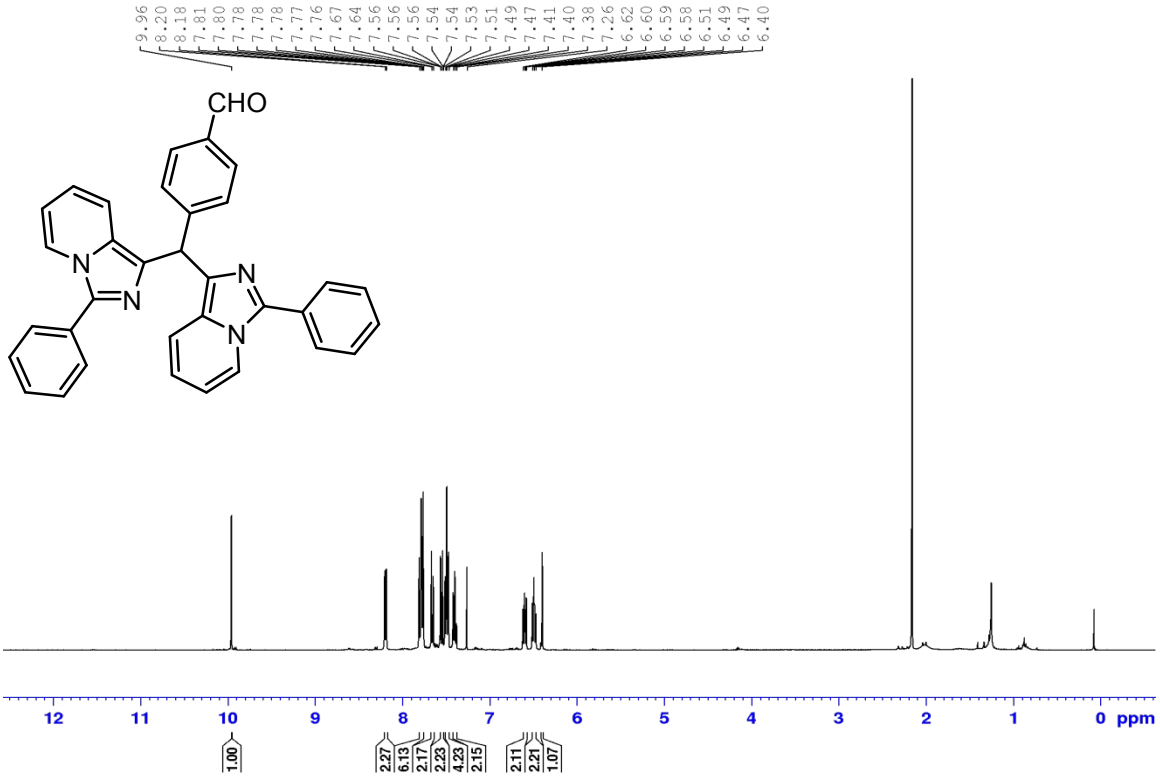
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

07-Dec-2021
15:50:30
1: TOF MS ES+
2.63e+006

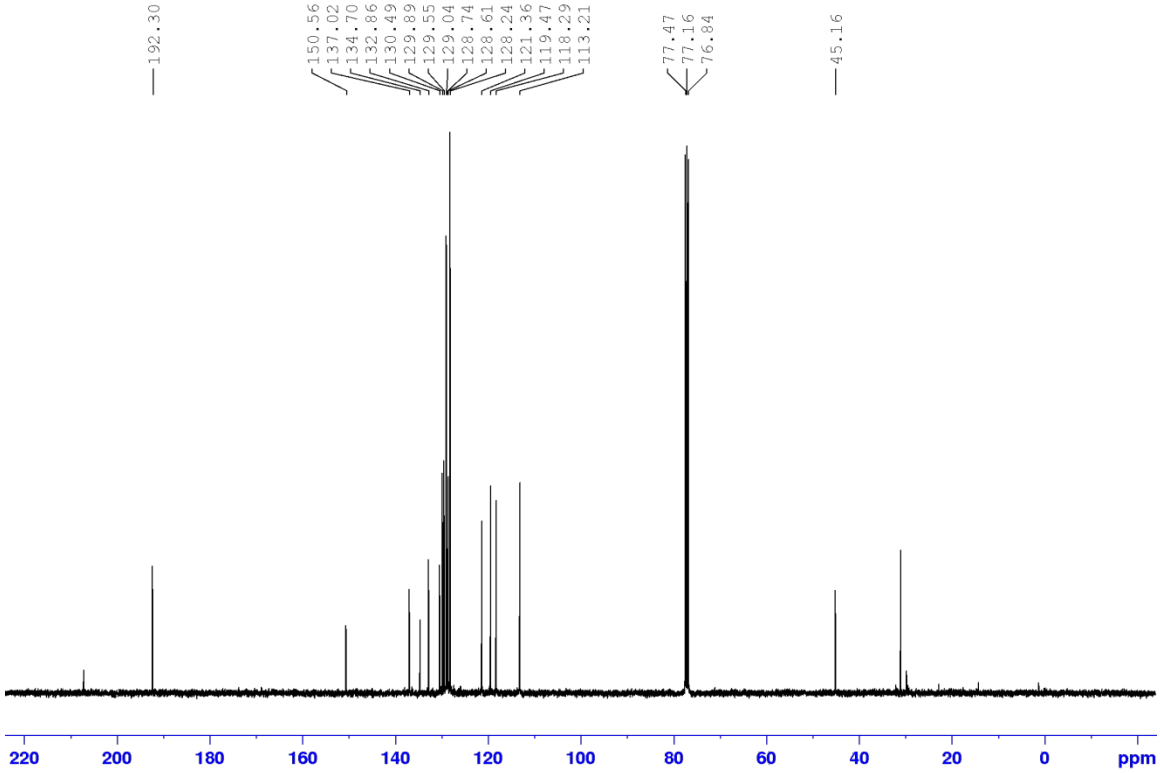



| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 2.0 | 50.0 | 50.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 545.1953 | 545.1953 | 0.0 | 0.0 | 23.5 | 36.2 | n/a | n/a | C34 H24 N4 F3 |

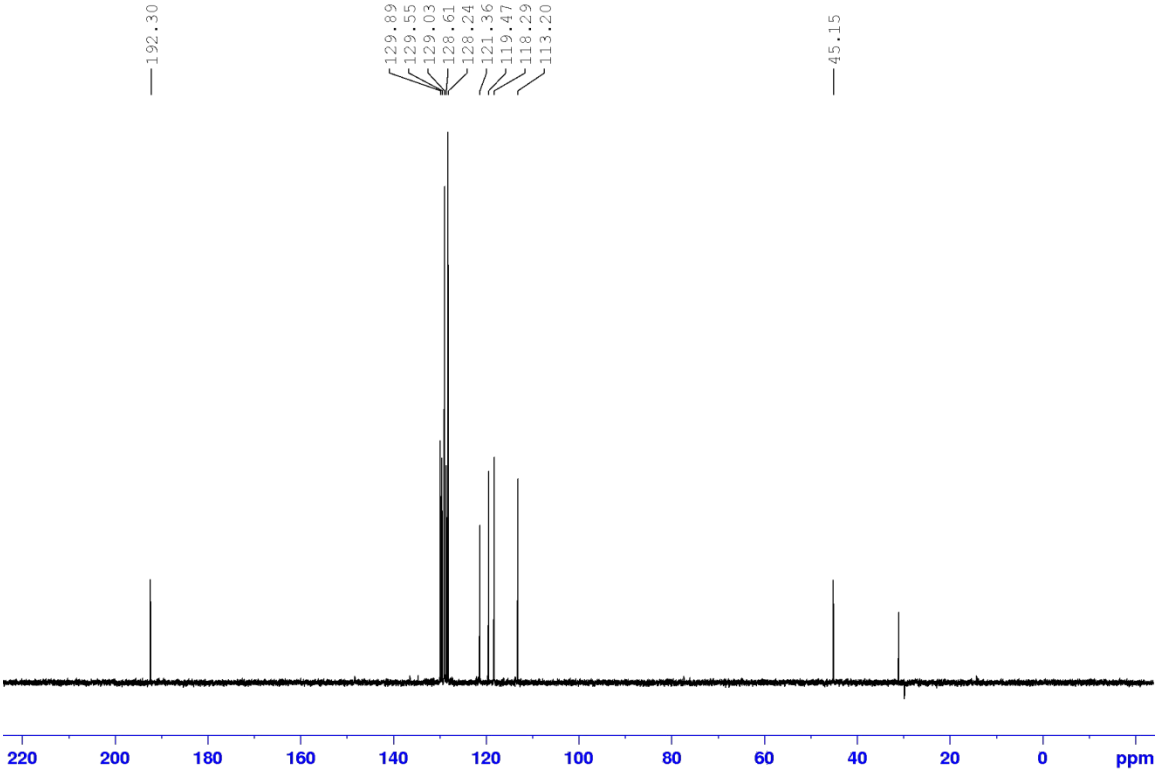
**$^{1}$H-NMR (400 MHz, $CDCl_3$) of 3o**




**$^{13}$C{$^{1}$H}-NMR (101 MHz, $CDCl_3$) of 3o**



## DEPT-135 (101 MHz, $CDCl_3$) of 3o



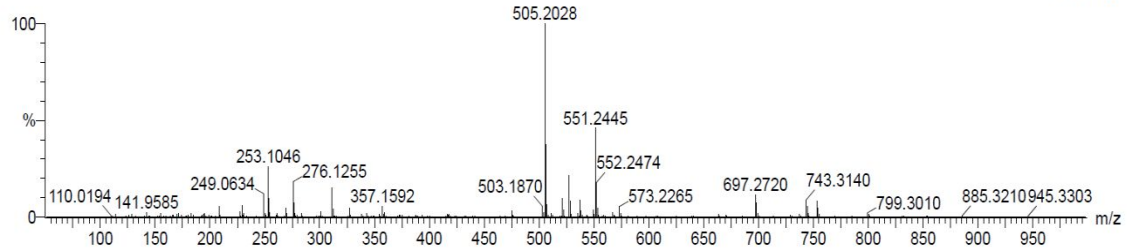

## HRMS of 3o

**Elemental Composition Report** **Page 1**

**Single Mass Analysis**
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

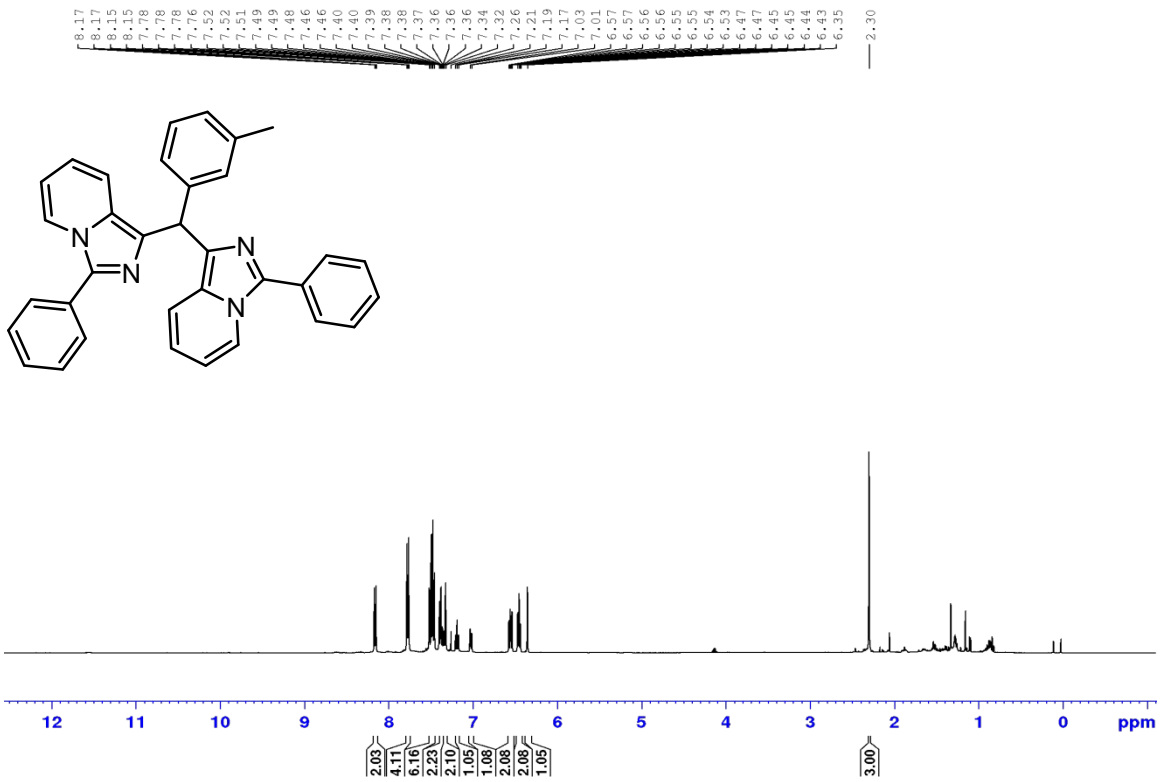
Monoisotopic Mass, Even Electron Ions
25 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-34 H: 0-100 N: 0-4 O: 0-1

SM-423 — QMI DIVISION, CSIR-IIIM JAMMU — 30-Jun-2023 12:36:36
300623_06 4 (0.104) — Xevo G2-XS QTOF YFC2015 — 1: TOF MS ES+ 4.77e+006

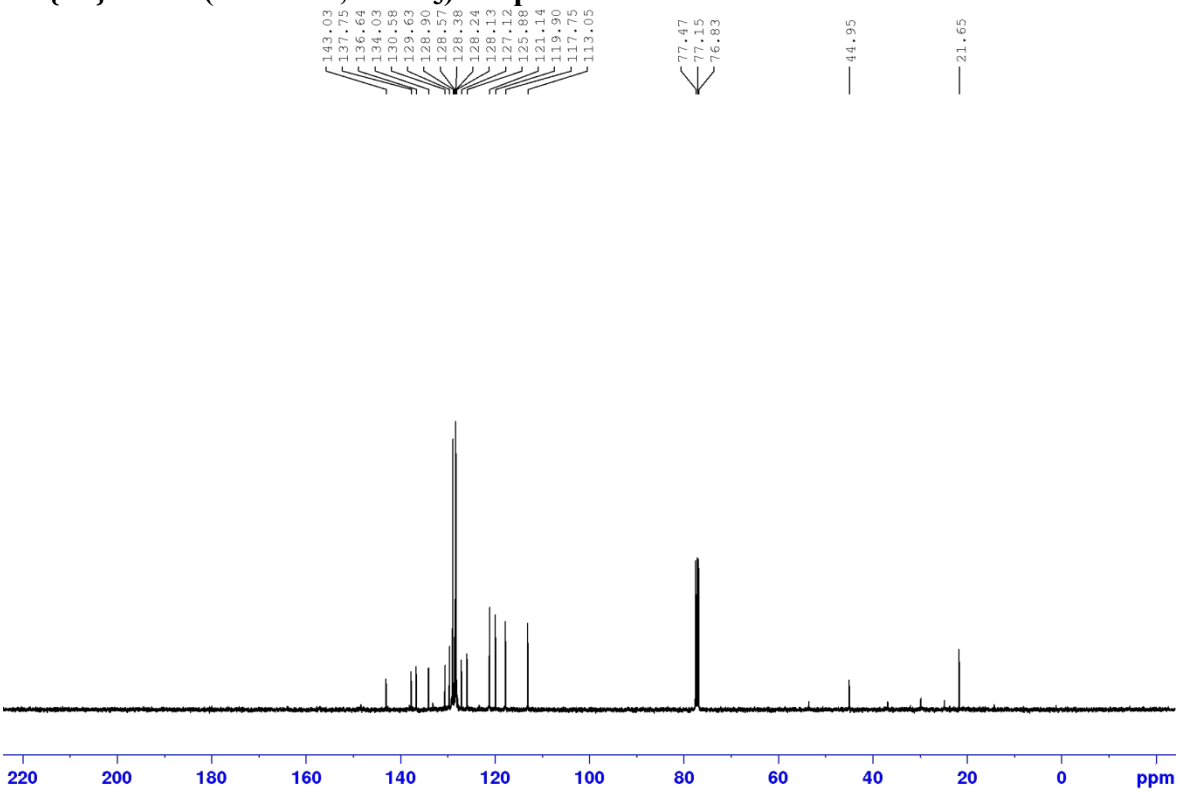



| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 2.0 | 100.0 | 50.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 505.2028 | 505.2028 | 0.0 | 0.0 | 24.5 | 798.7 | n/a | n/a | C34 H25 N4 O |

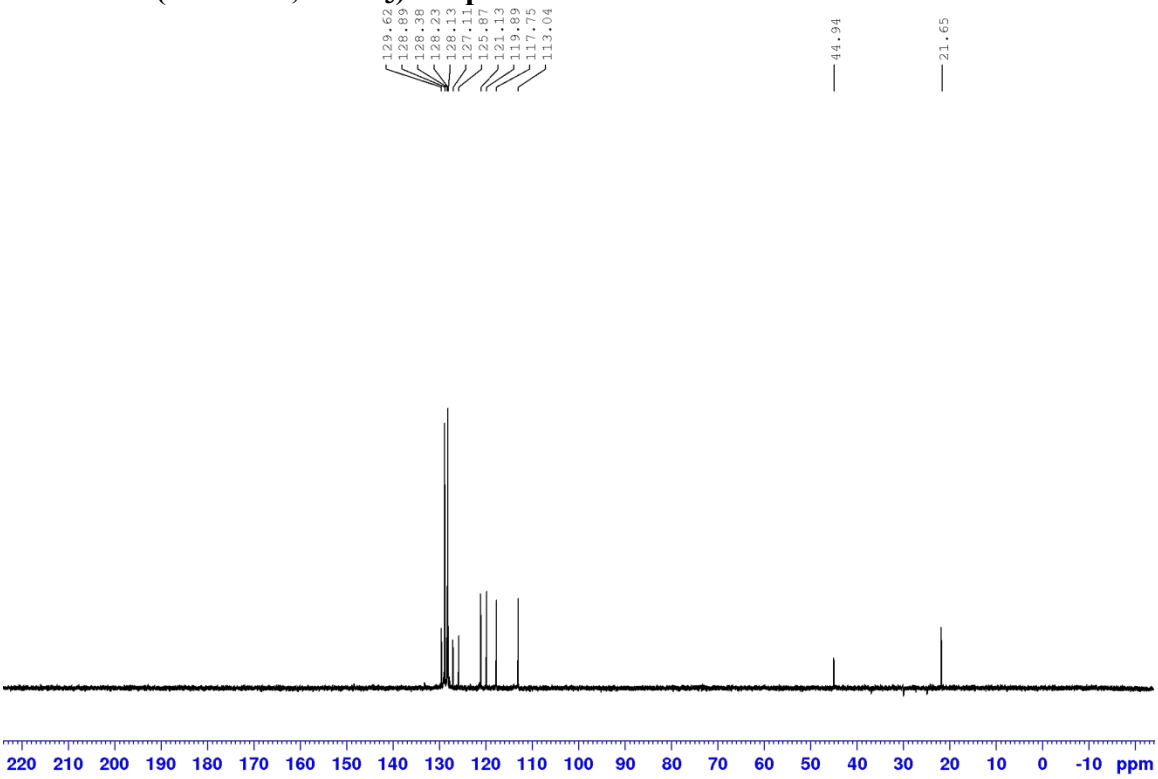
**$^{1}$H-NMR (400 MHz, $CDCl_3$) of 3p**



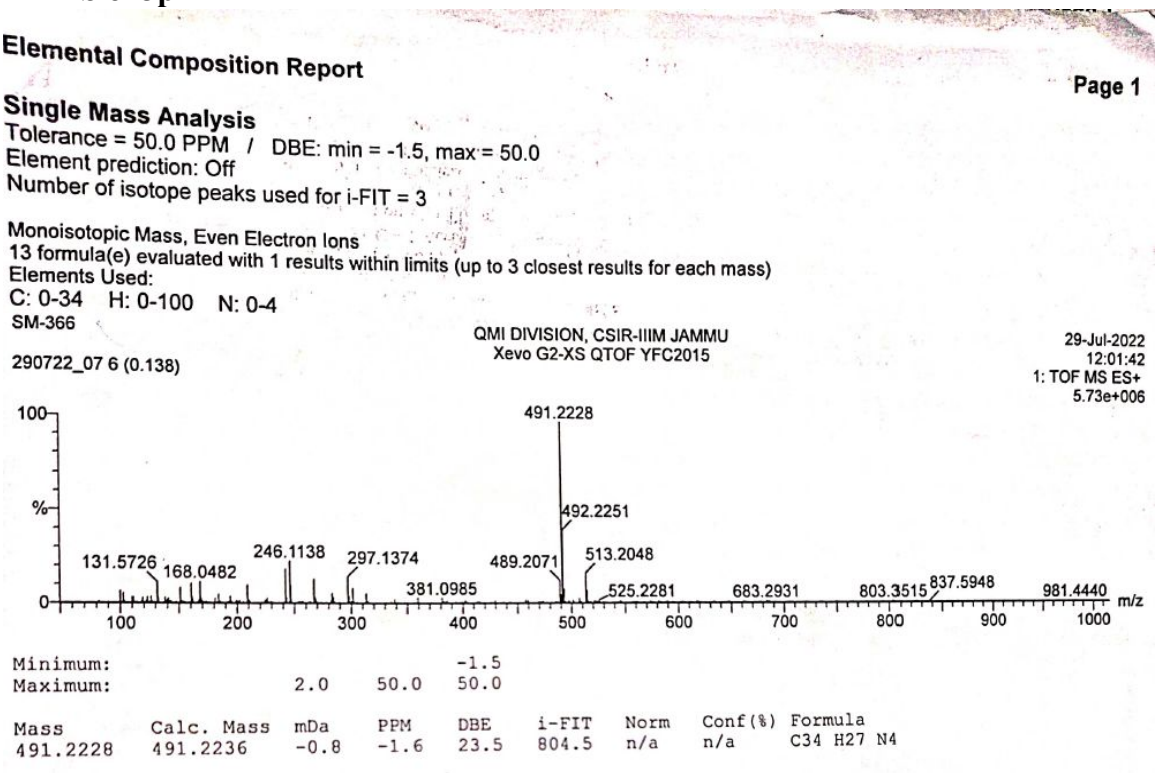

**$^{13}$C{$^{1}$H}-NMR (101 MHz, $CDCl_3$) of 3p**



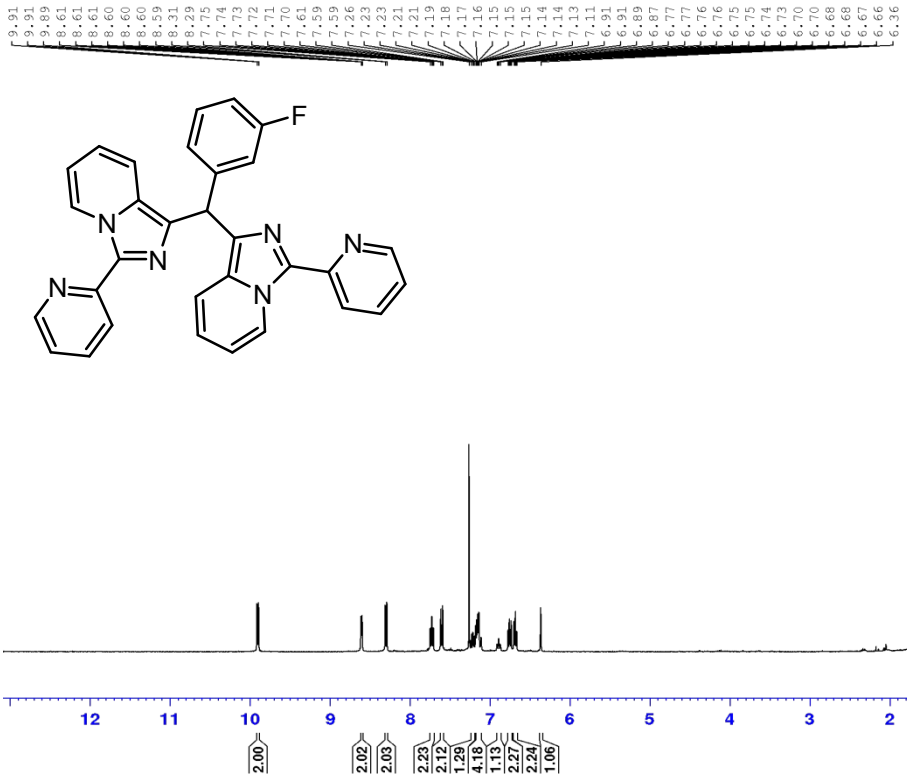
**DEPT-135 (101 MHz, $CDCl_3$) of 3p**



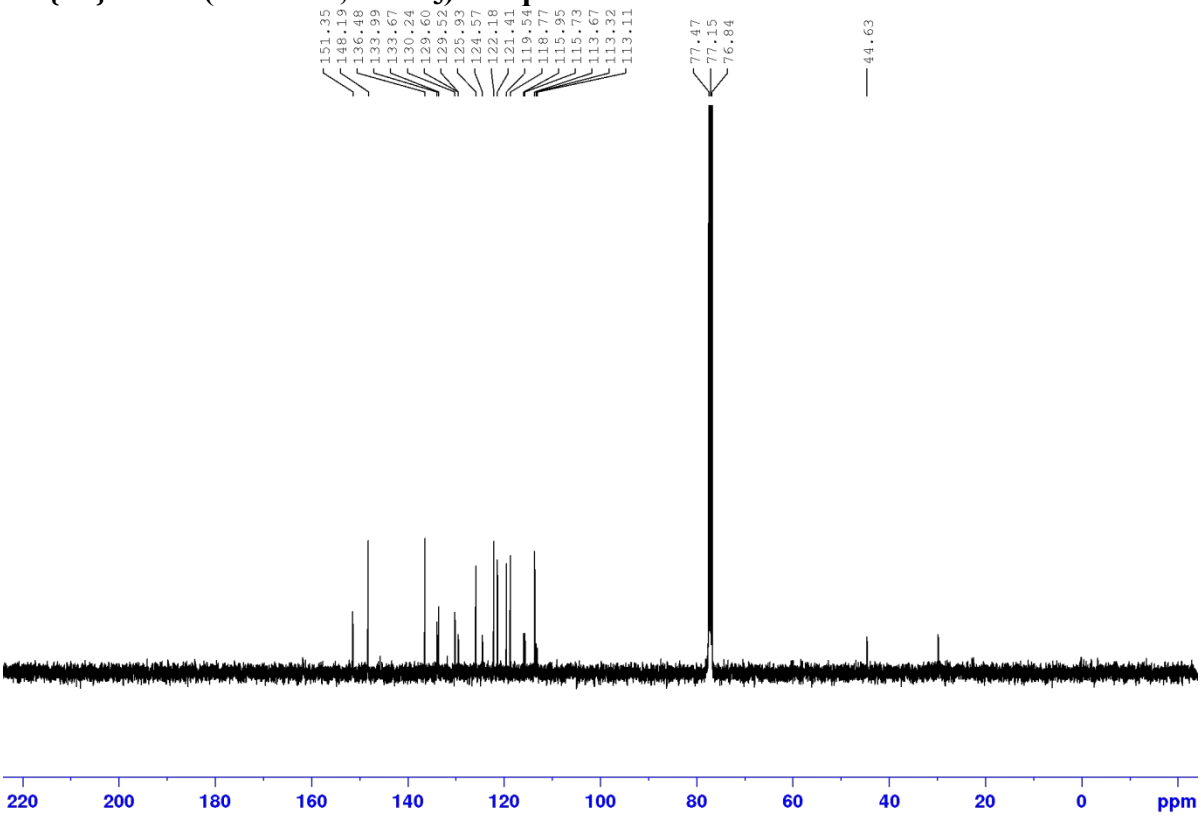

**HRMS of 3p**



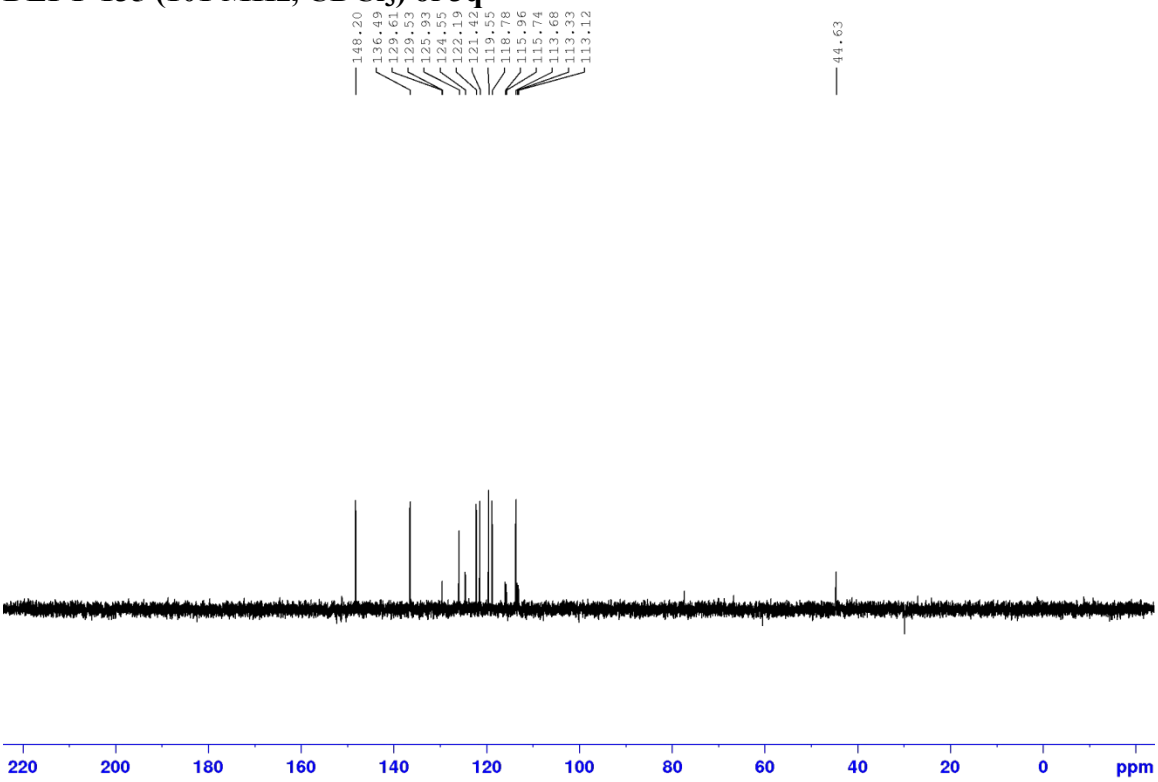
**$^{1}$H-NMR (400 MHz, $CDCl_3$) of 3q**



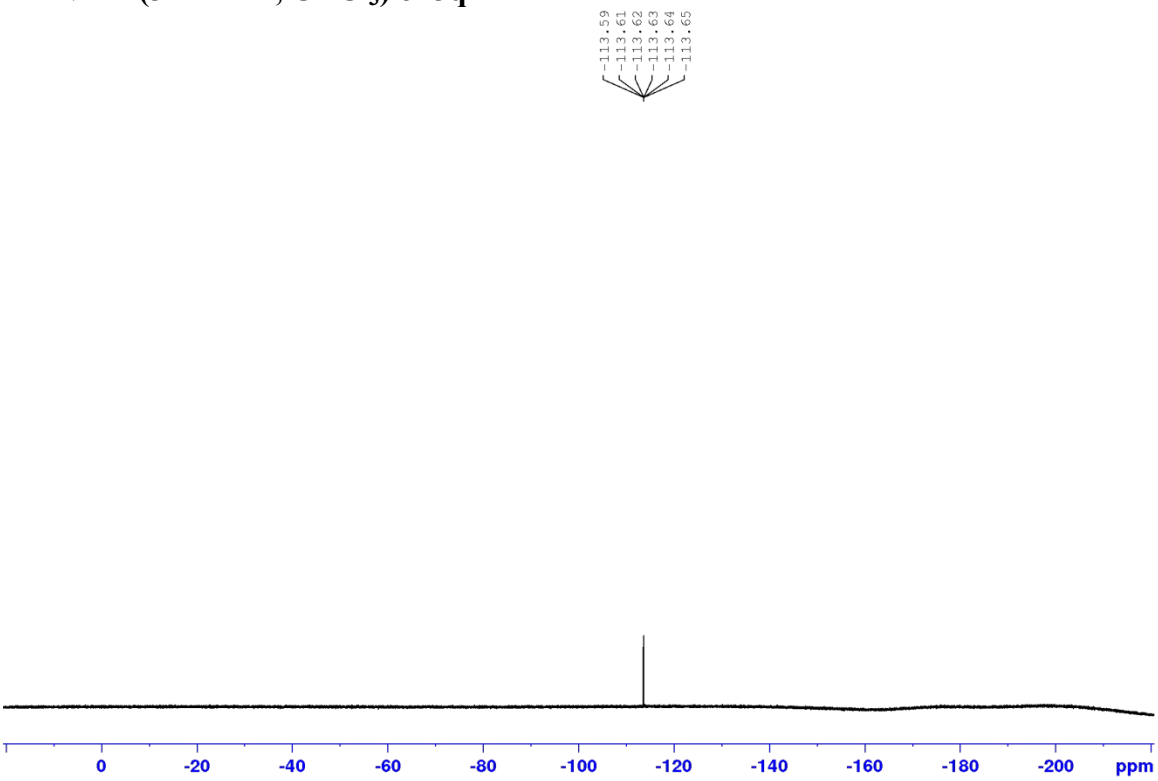

**$^{13}$C{$^{1}$H}-NMR (101 MHz, $CDCl_3$) of 3q**



**DEPT-135 (101 MHz, $CDCl_3$) of 3q**




**$^{19}$F-NMR (377 MHz, $CDCl_3$) of 3q**



## HRMS of 3q

ental Composition Report

Page 1

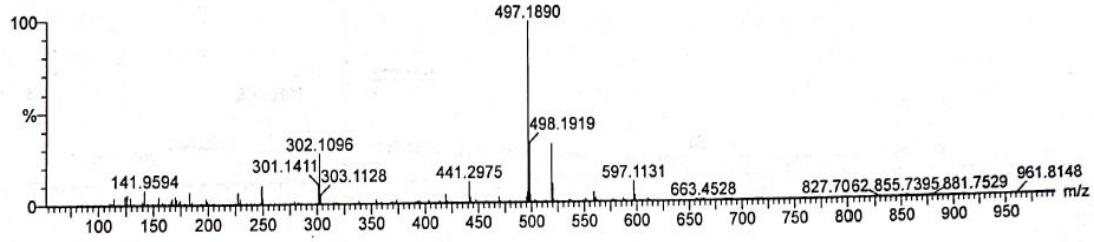
ingle Mass Analysis
olerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
25 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-31 H: 0-100 N: 0-6 F: 0-1

SM-415
160323_16 9 (0.208)

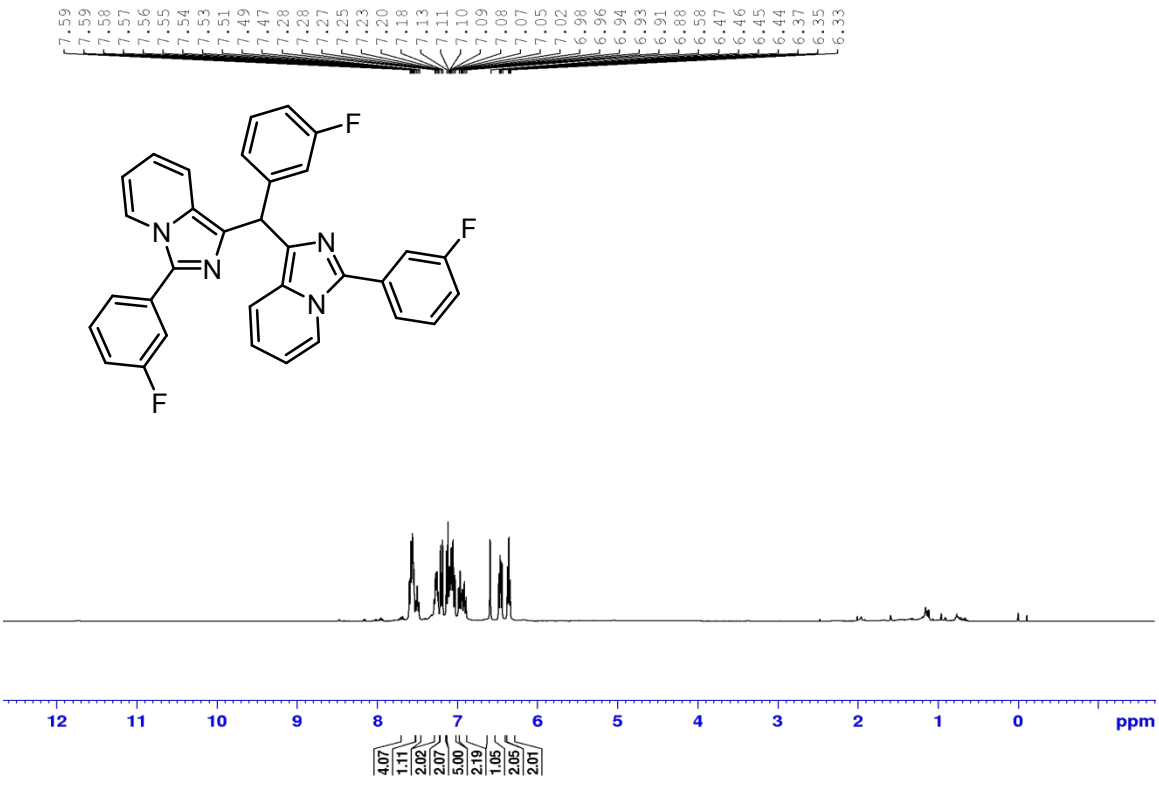
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

16-Mar-2023
13:00:16
1: TOF MS ES+
2.36e+006

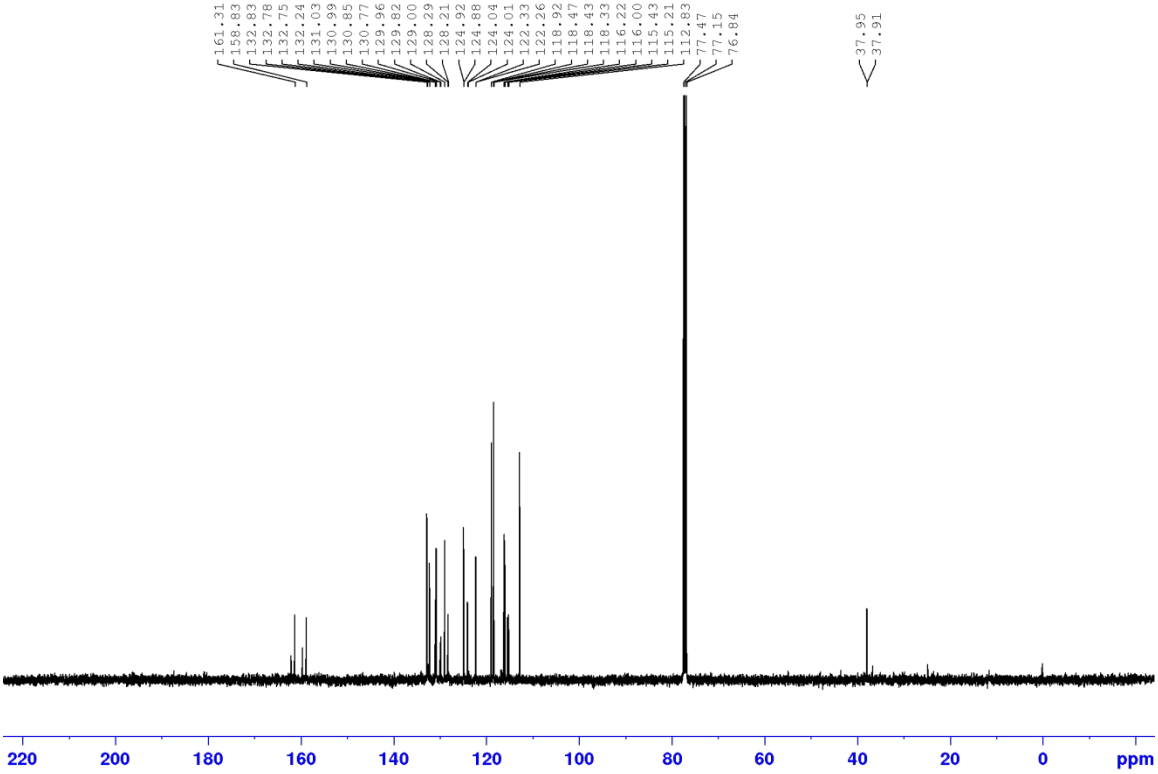



| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 2.0 | 100.0 | 50.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 497.1890 | 497.1890 | 0.0 | 0.0 | 23.5 | 773.3 | n/a | n/a | C31 H22 N6 F |

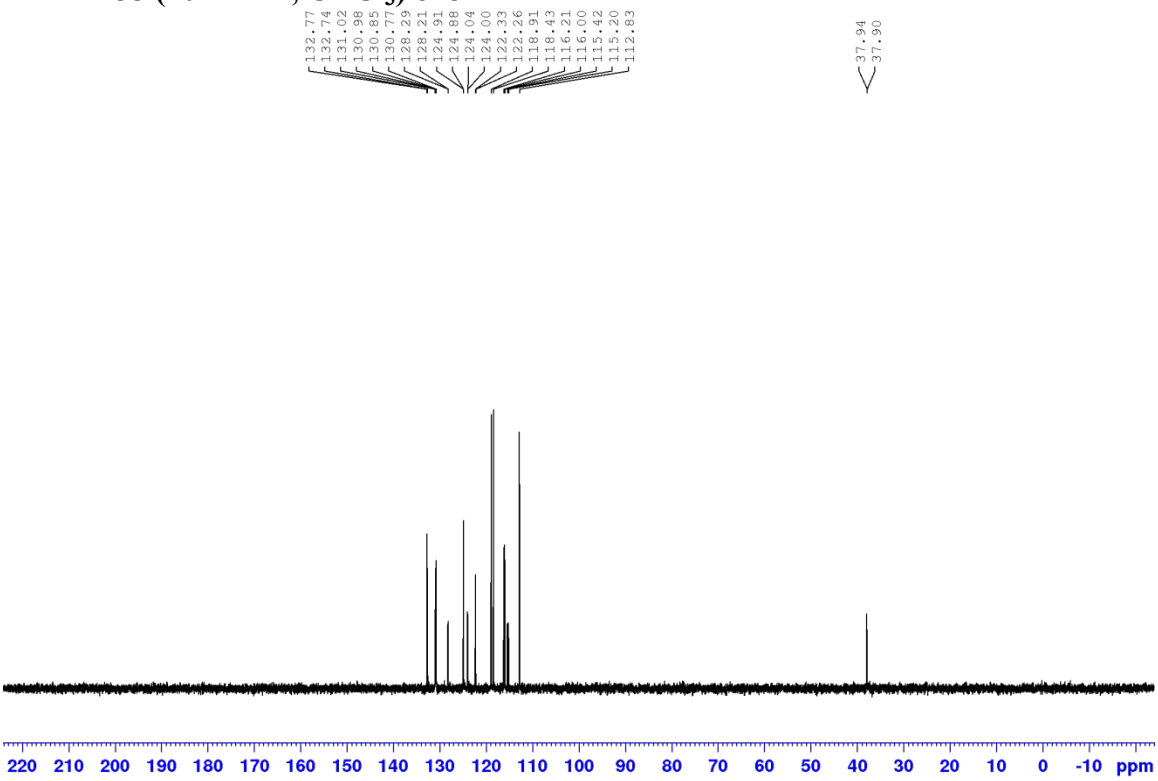
## $^1$H-NMR (400 MHz, $CDCl_3$) of 3r



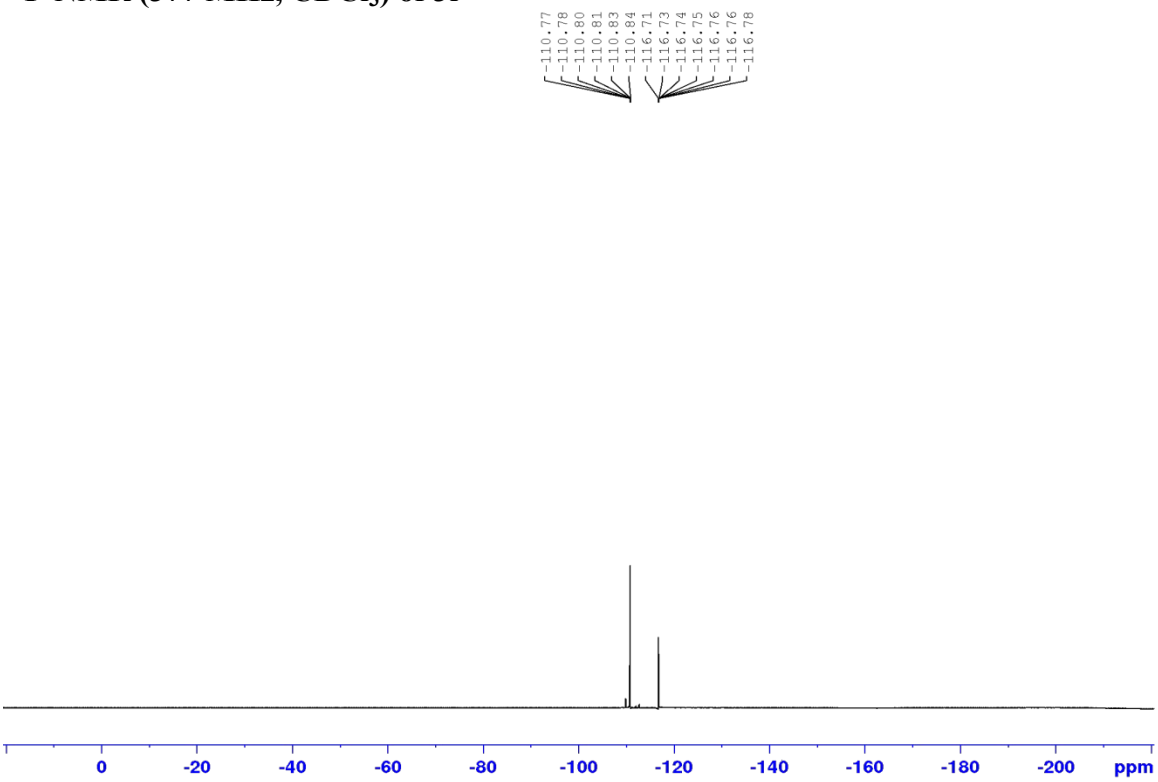
**$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$) of 3r**



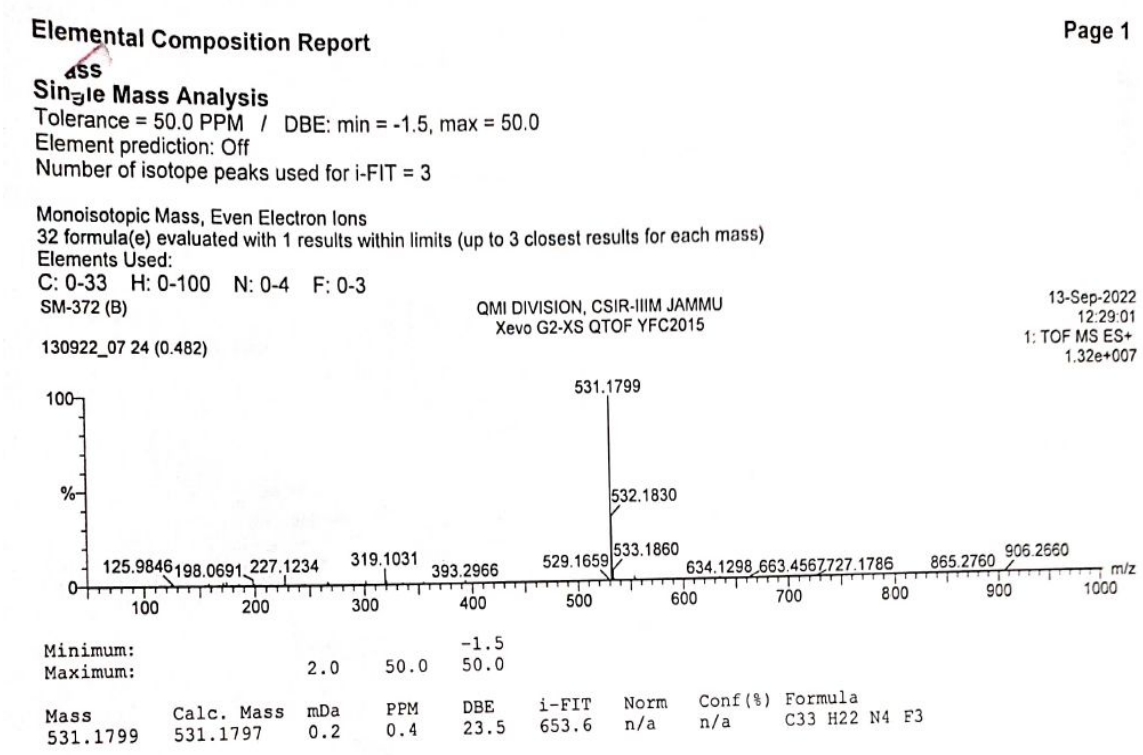

**DEPT-135 (101 MHz, $CDCl_3$) of 3r**



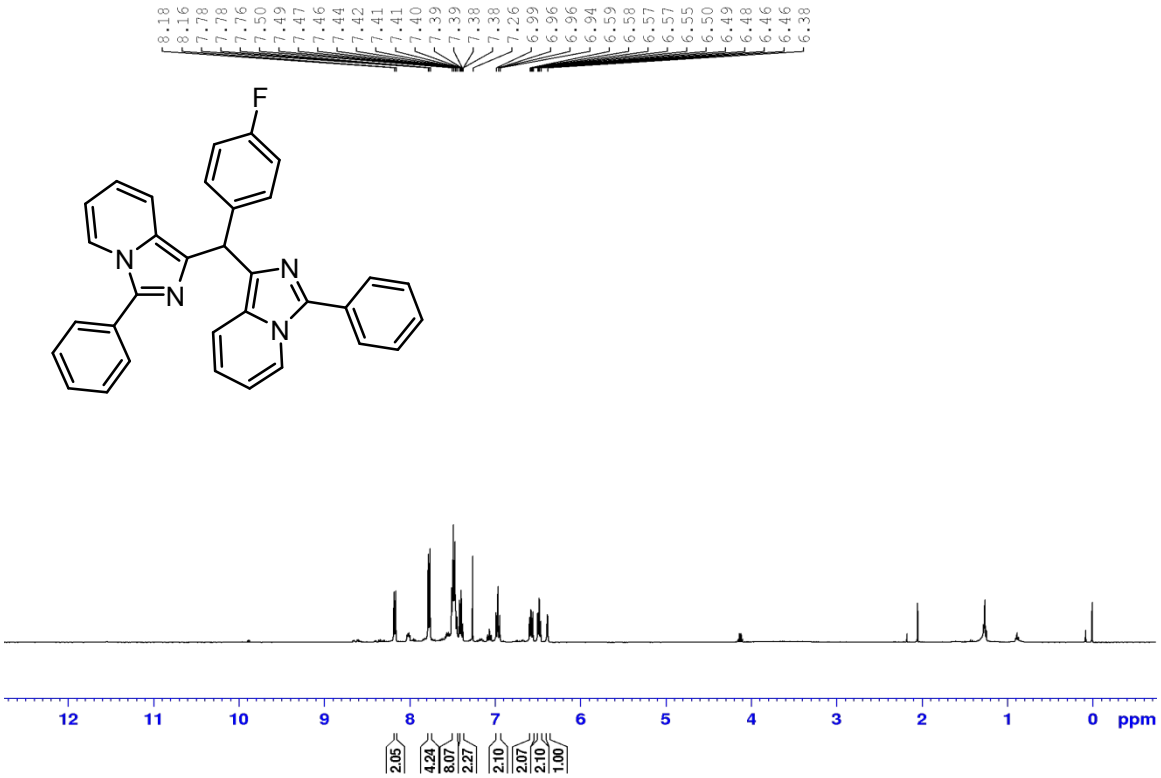
**$^{19}$F-NMR (377 MHz, $CDCl_3$) of 3r**



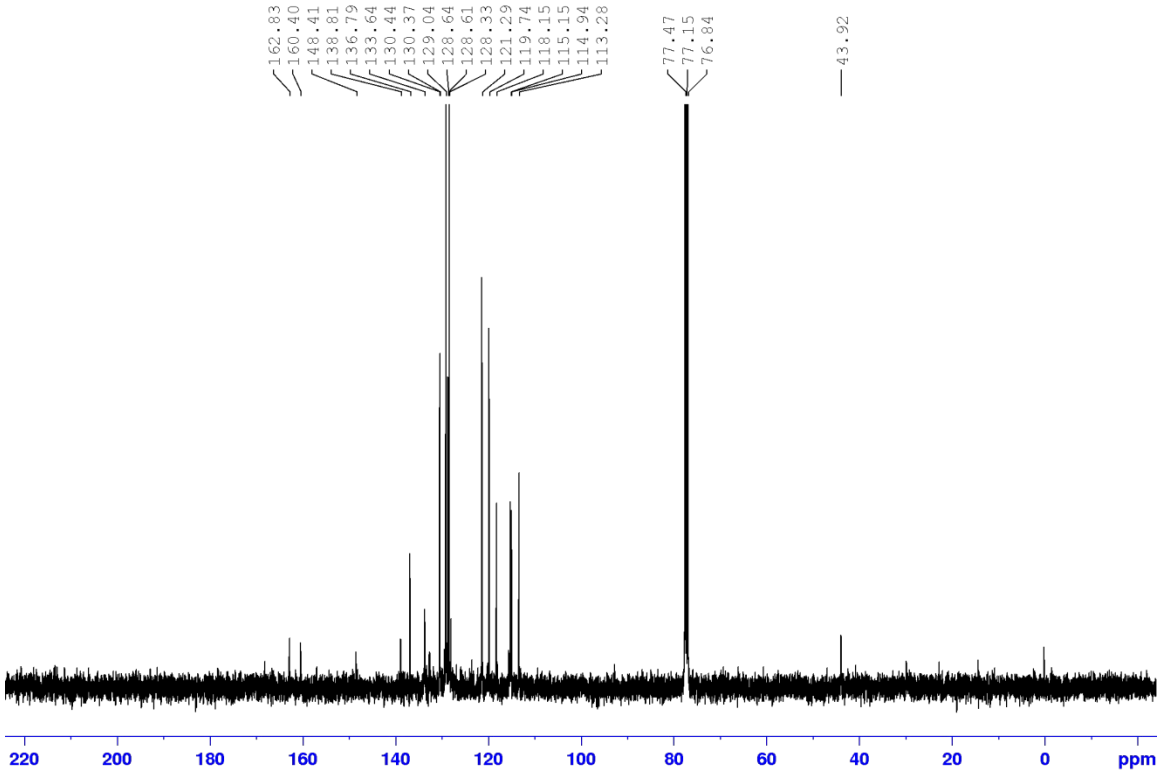

**HRMS of 3r**



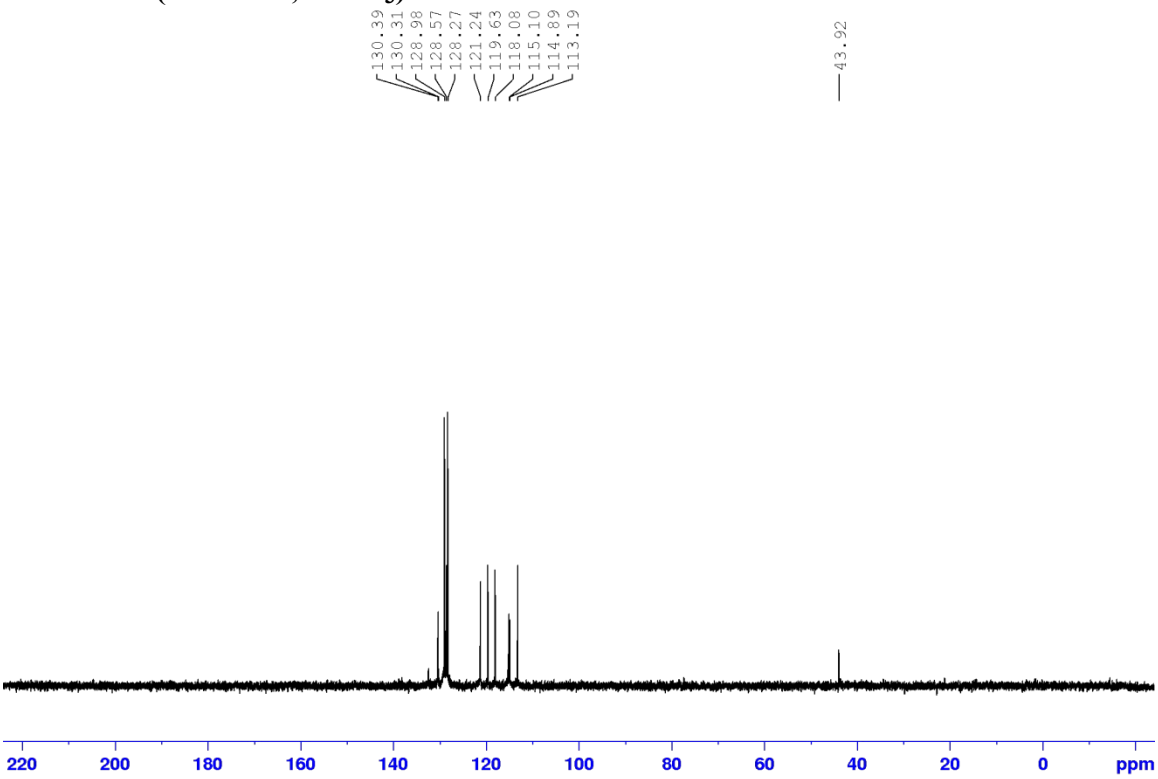
**$^{1}$H-NMR (400 MHz, $CDCl_3$) of 3s**



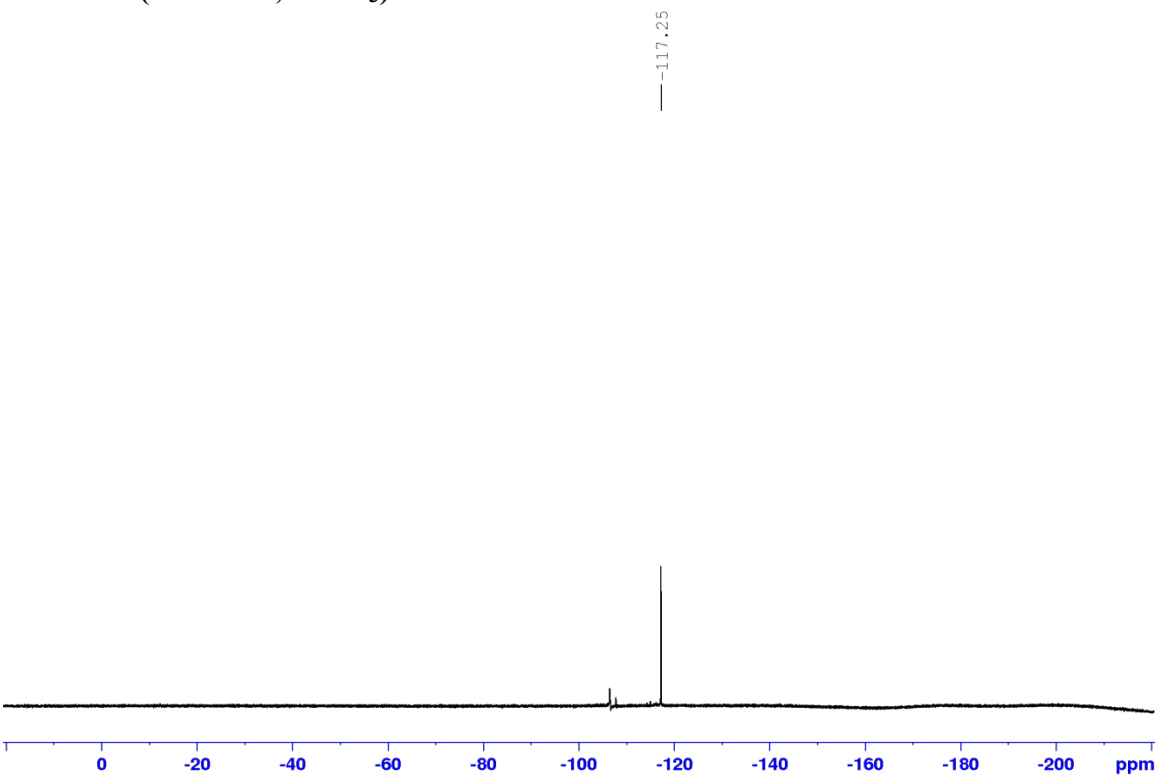

**$^{13}$C{$^{1}$H}-NMR (101 MHz, $CDCl_3$) of 3s**



**DEPT-135 (101 MHz, $CDCl_3$) of 3s**




**$^{19}$F-NMR (377 MHz, $CDCl_3$) of 3s**



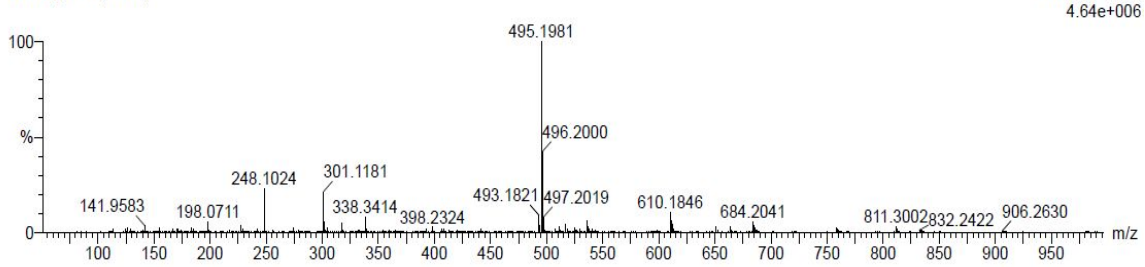
## HRMS of 3s

**Elemental Composition Report** **Page 1**

**Single Mass Analysis**
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

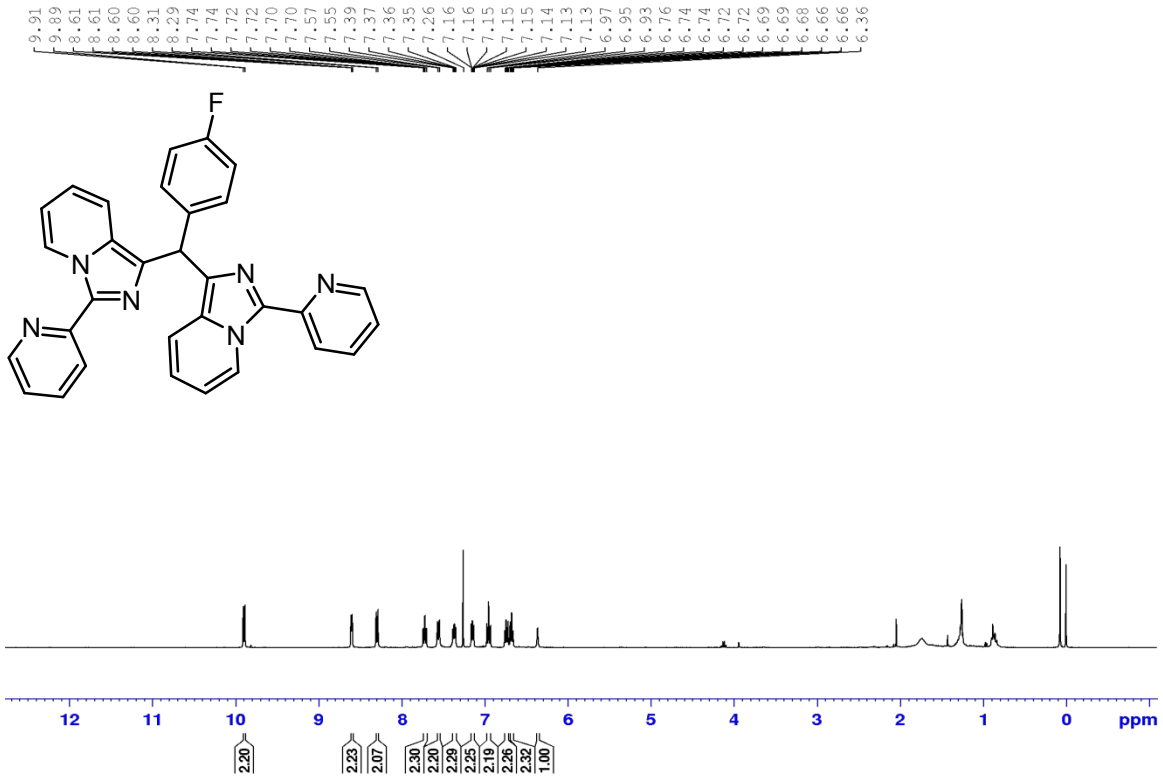
Monoisotopic Mass, Even Electron Ions
21 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-33 H: 0-100 N: 0-4 F: 0-1

SM-420 | QMI DIVISION, CSIR-IIIM JAMMU | 30-Jun-2023
Xevo G2-XS QTOF YFC2015 | 12:28:53
300623_03 7 (0.155) | 1: TOF MS ES+
4.64e+006

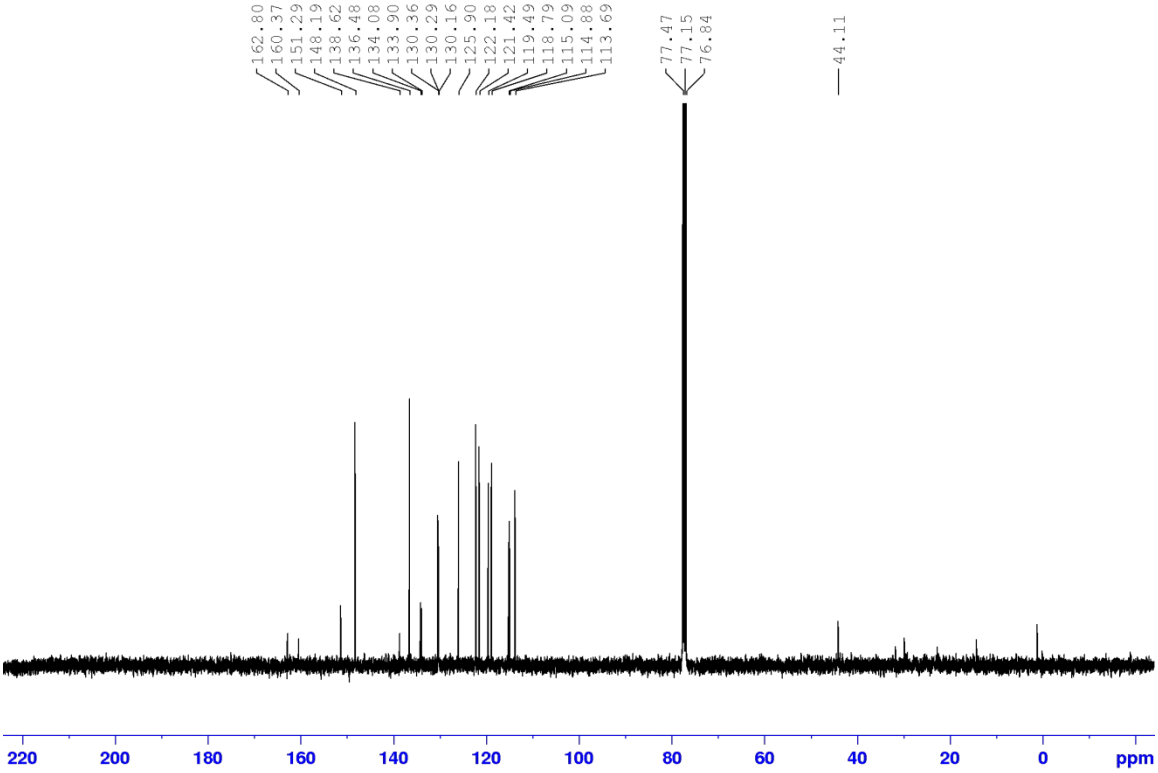



| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 2.0 | 100.0 | 50.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 495.1981 | 495.1985 | -0.4 | -0.8 | 23.5 | 860.5 | n/a | n/a | C33 H24 N4 F |

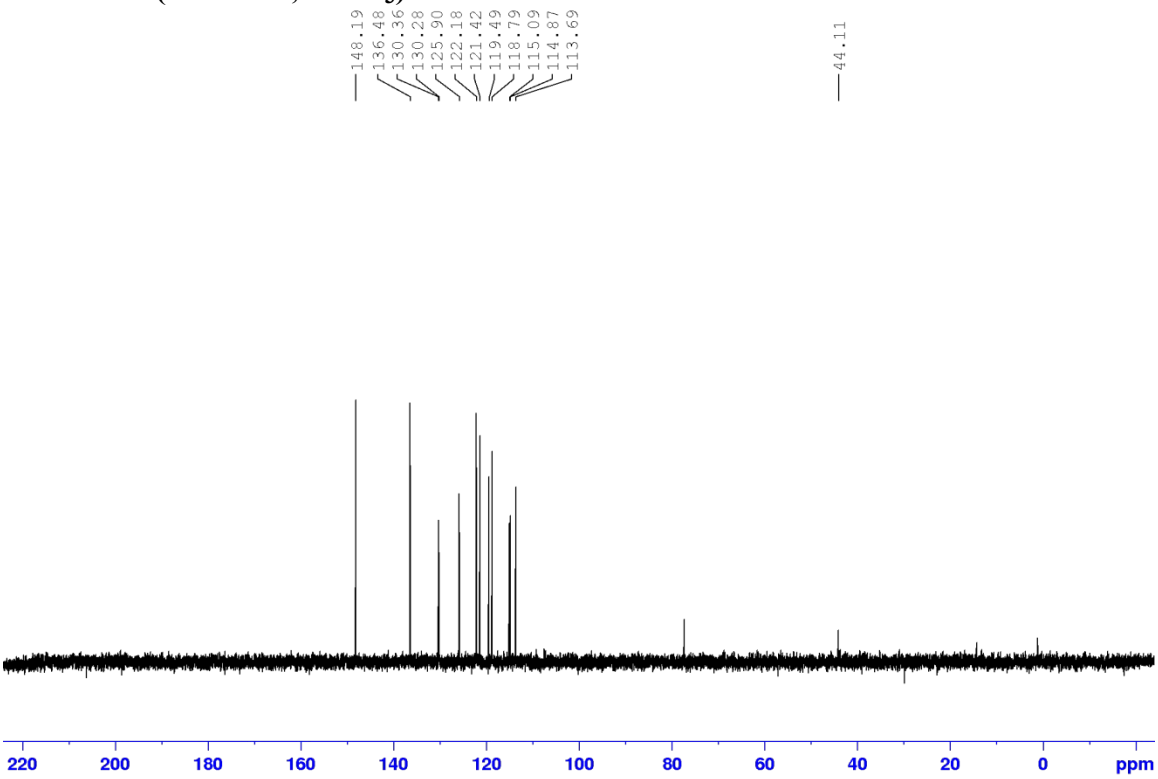
## $^1$H-NMR (400 MHz, $CDCl_3$) of 3t



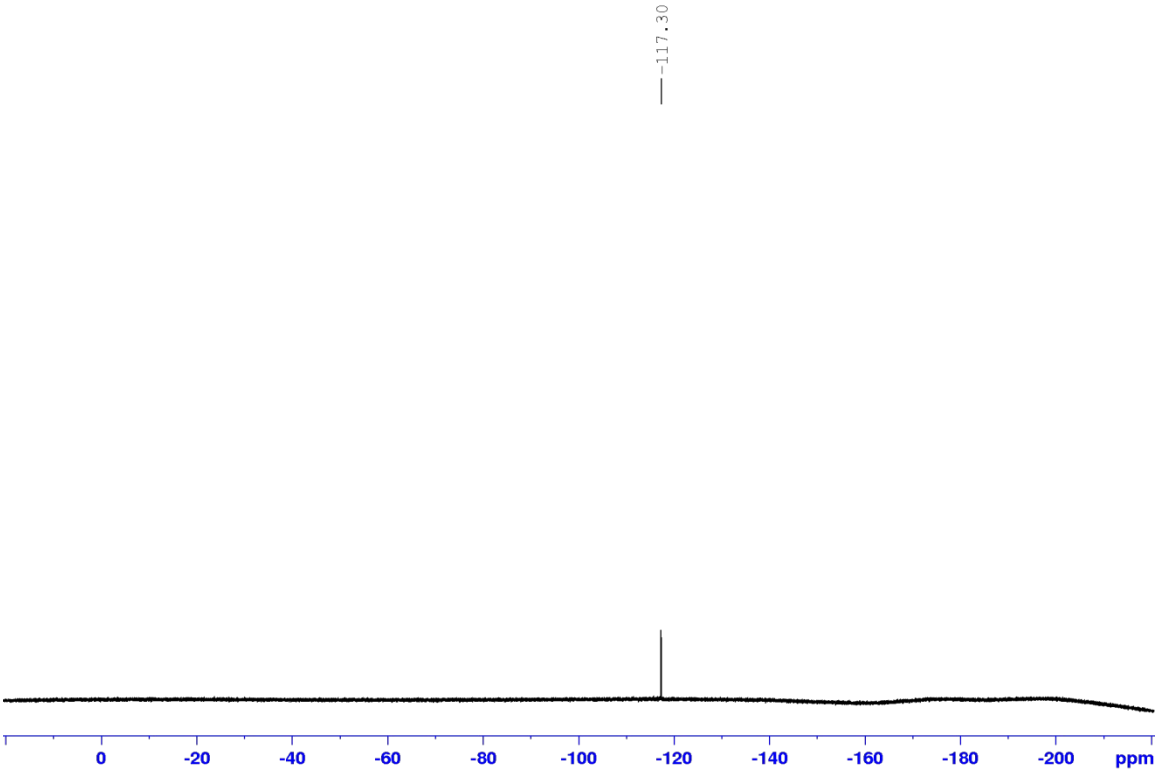
**$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$) of 3t**




**DEPT-135 (101 MHz, $CDCl_3$) of 3t**



## $^{19}$F-NMR (377 MHz, $CDCl_3$) of 3t




## HRMS of 3t

**Elemental Composition Report** **Page 1**

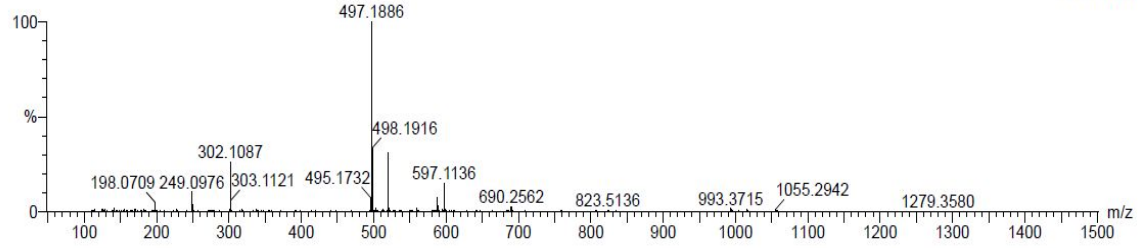
**Single Mass Analysis**
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
25 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-31 H: 0-100 N: 0-6 F: 0-1

SM-421
300623_04 9 (0.208)

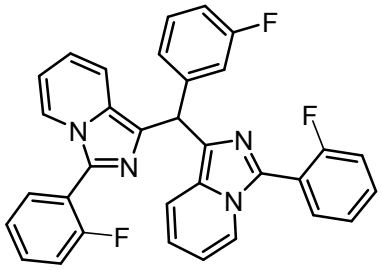
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

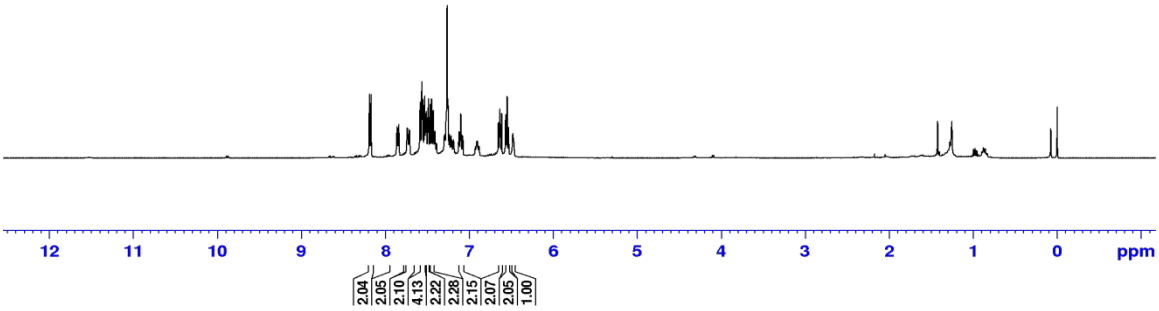
30-Jun-2023
12:31:27
1: TOF MS ES+
9.81e+006



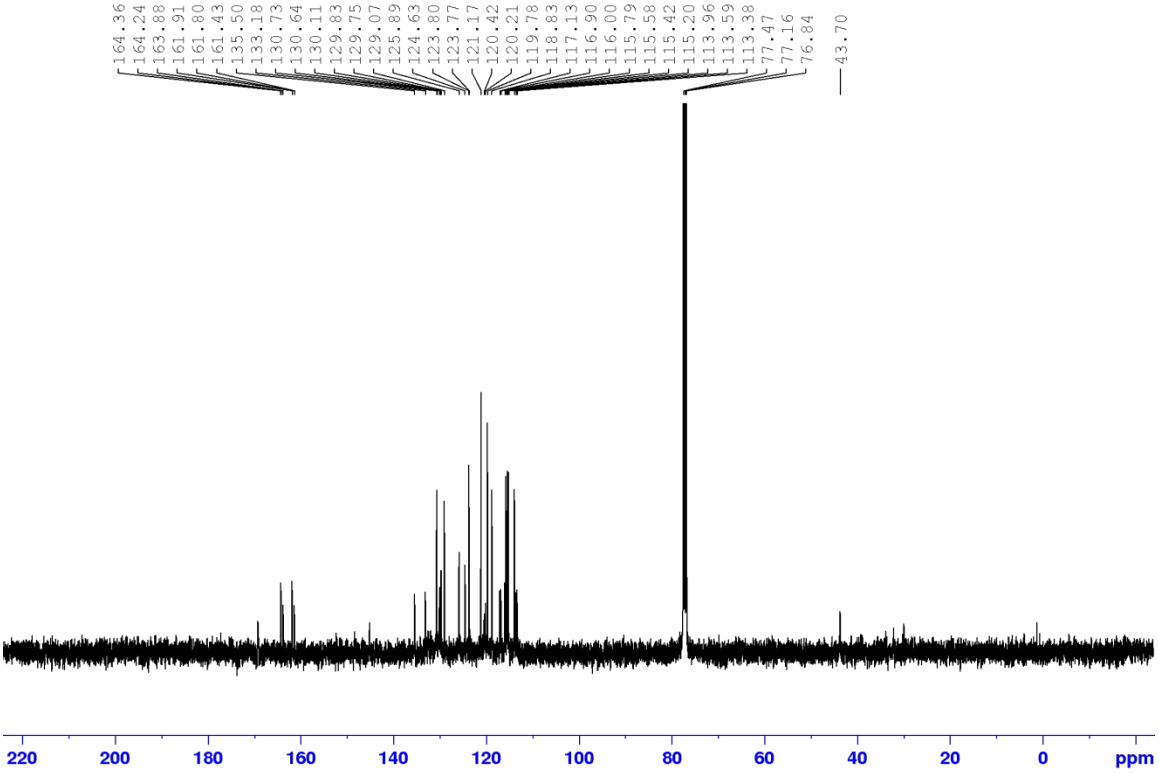

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 2.0 | 100.0 | 50.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 497.1886 | 497.1890 | -0.4 | -0.8 | 23.5 | 803.9 | n/a | n/a | C31 H22 N6 F |

**$^{1}$H-NMR (400 MHz, $CDCl_3$) of 3u**

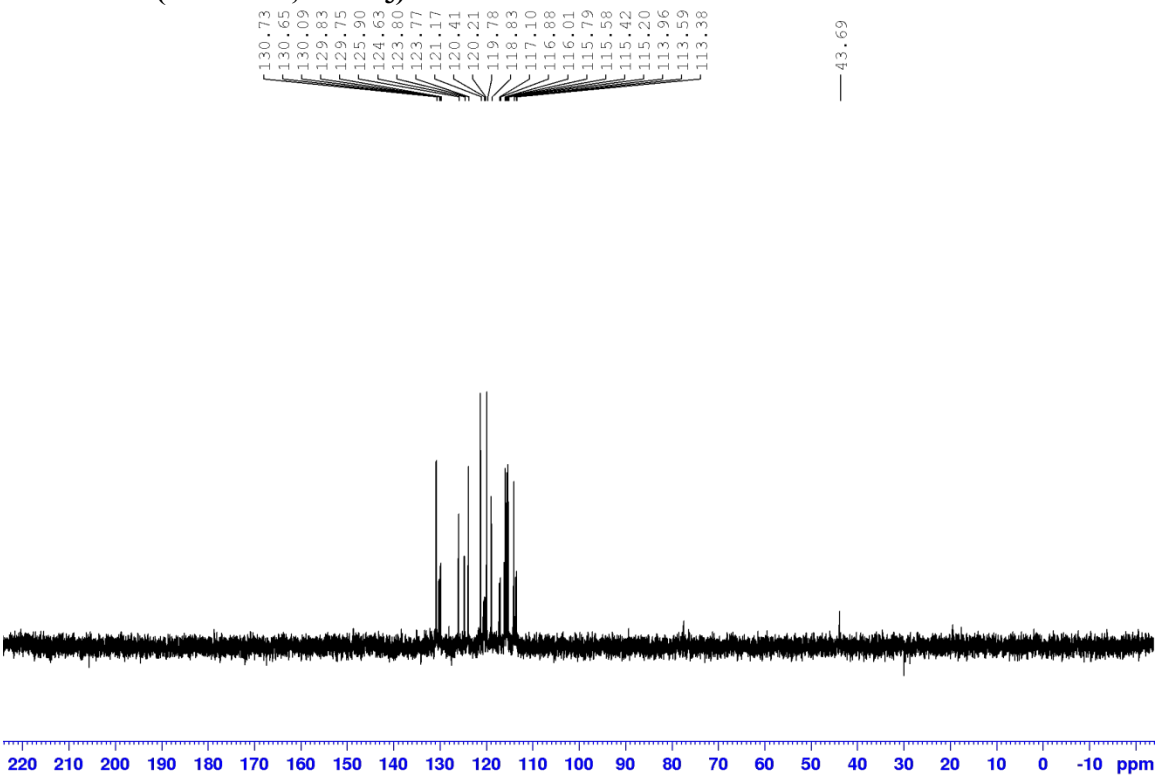



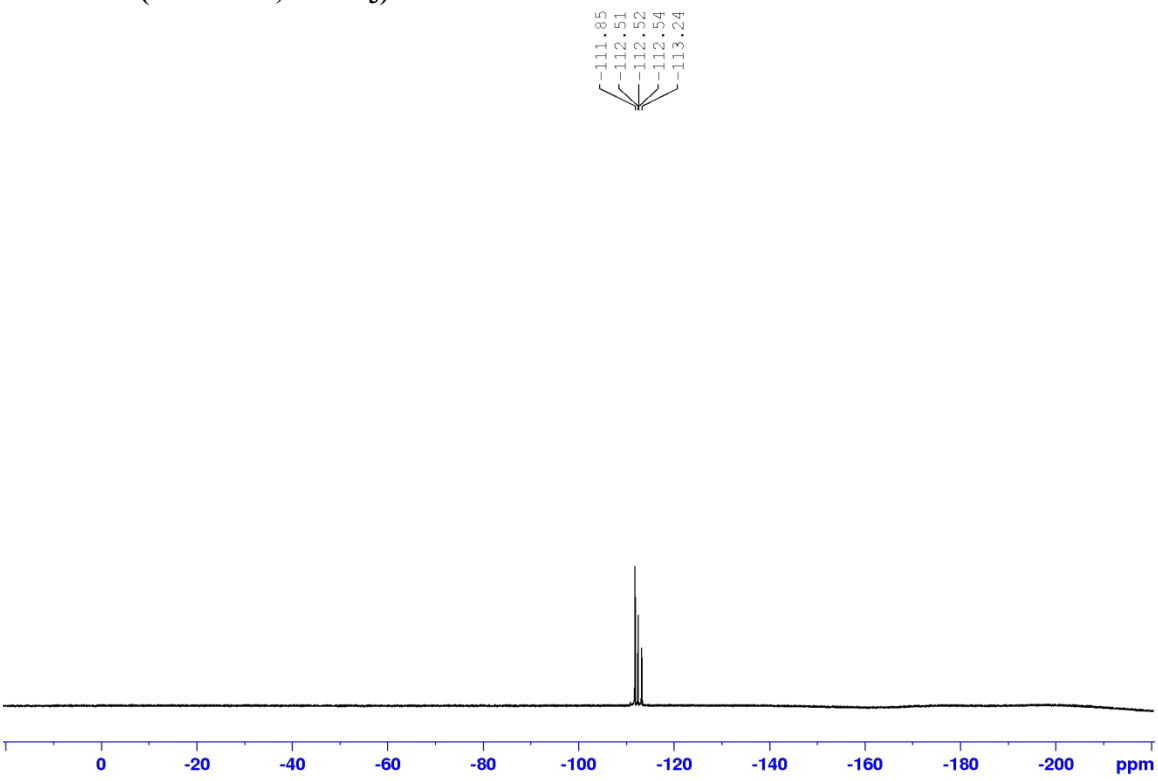

**$^{13}$C{$^{1}$H}-NMR (101 MHz, $CDCl_3$) of 3u**



**DEPT-135 (101 MHz, $CDCl_3$) of 3u**




**$^{19}$F-NMR (377 MHz, $CDCl_3$) of 3u**



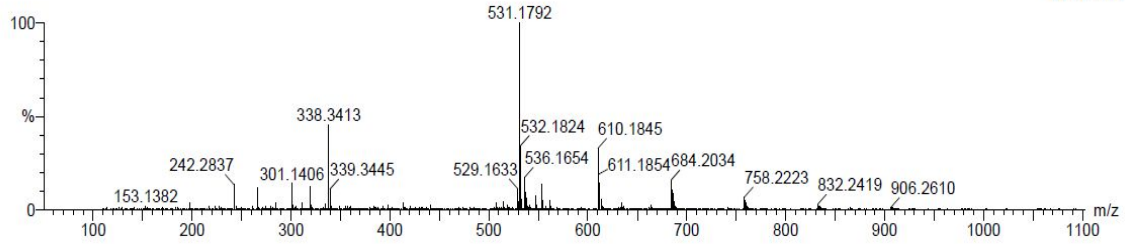
## HRMS of 3u

**Elemental Composition Report** **Page 1**

**Single Mass Analysis**
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

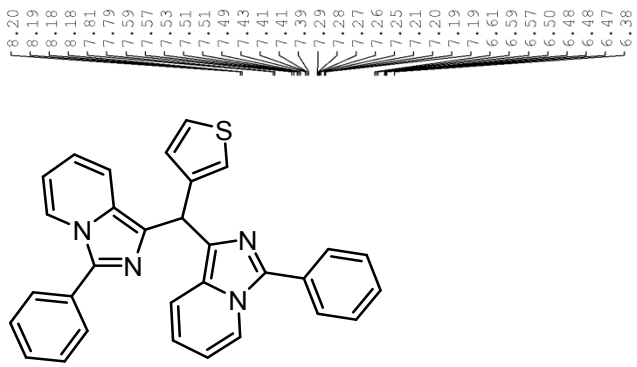
Monoisotopic Mass, Even Electron Ions
32 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-33 H: 0-100 N: 0-4 F: 0-3

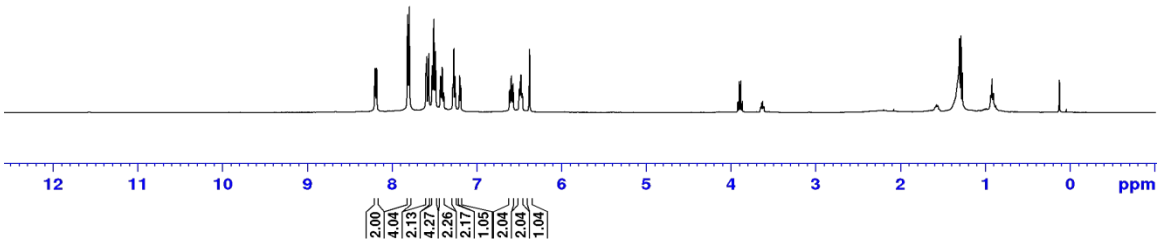
SM-422 QMI DIVISION, CSIR-IIIM JAMMU 30-Jun-2023
Xevo G2-XS QTOF YFC2015 12:26:12
300623_02 6 (0.138) 1: TOF MS ES+
7.77e+006



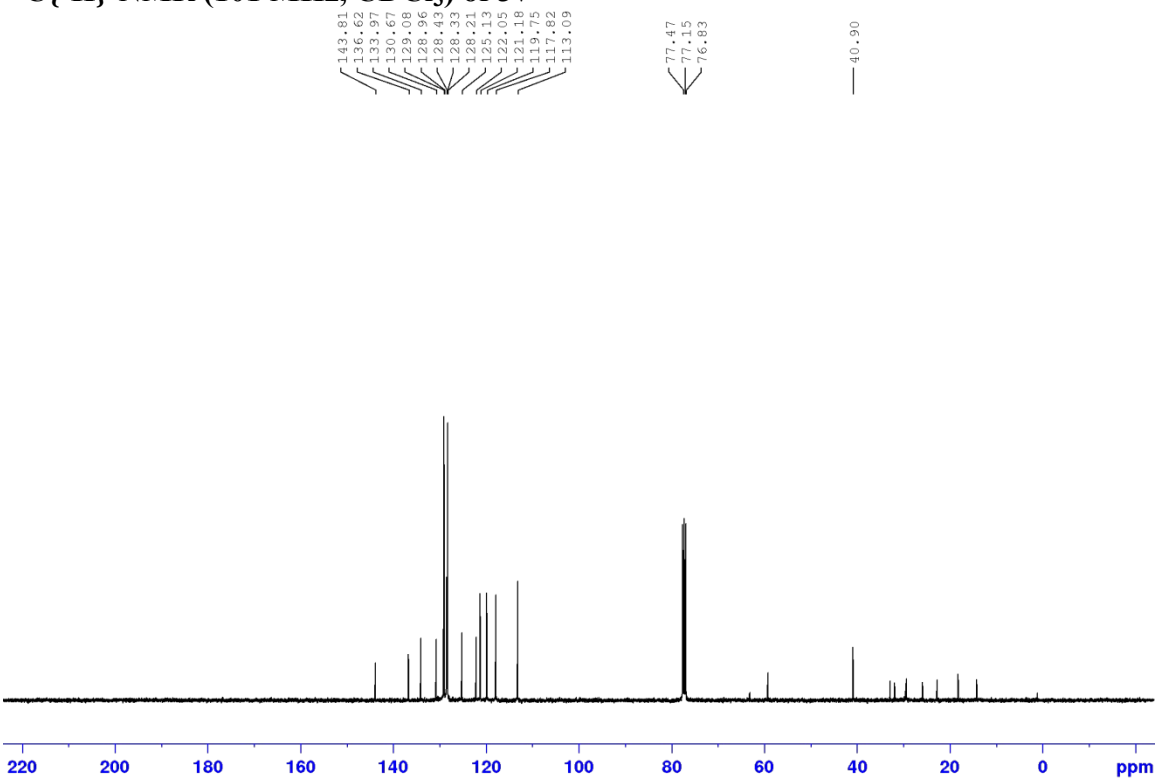

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 2.0 | 100.0 | 50.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 531.1792 | 531.1797 | -0.5 | -0.9 | 23.5 | 945.7 | n/a | n/a | C33 H22 N4 F3 |

## $^1$H-NMR (400 MHz, $CDCl_3$) of 3v

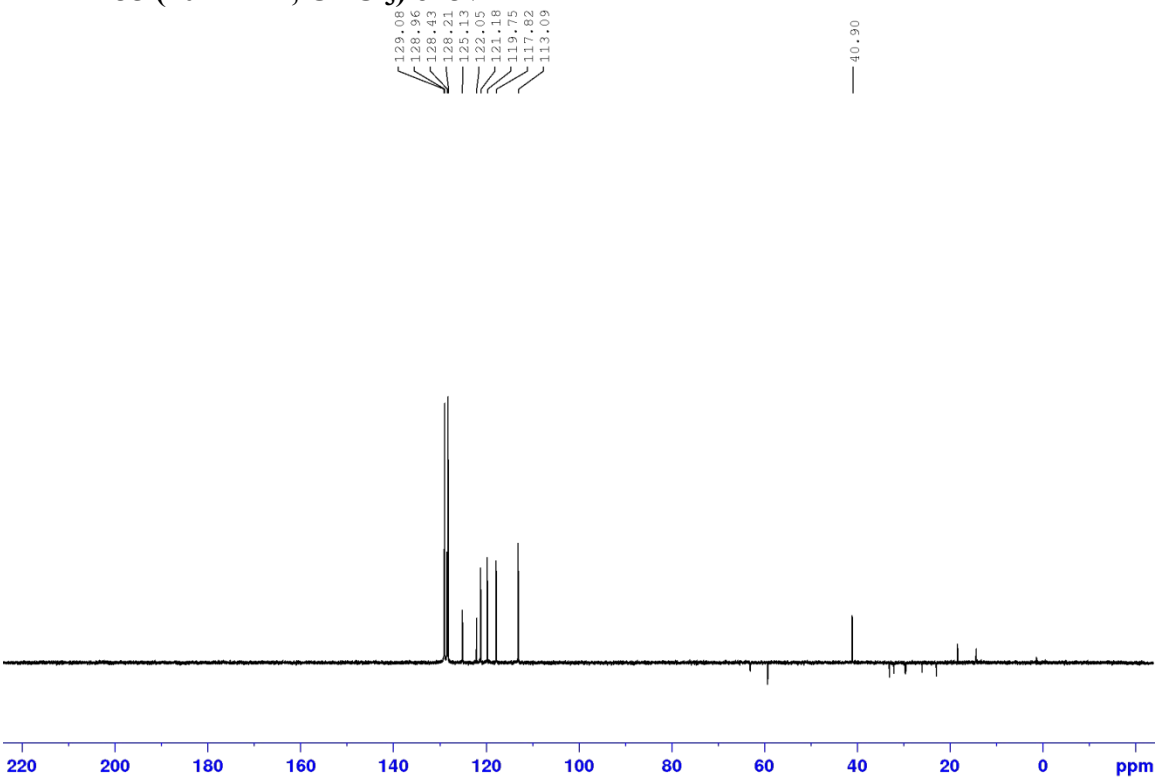


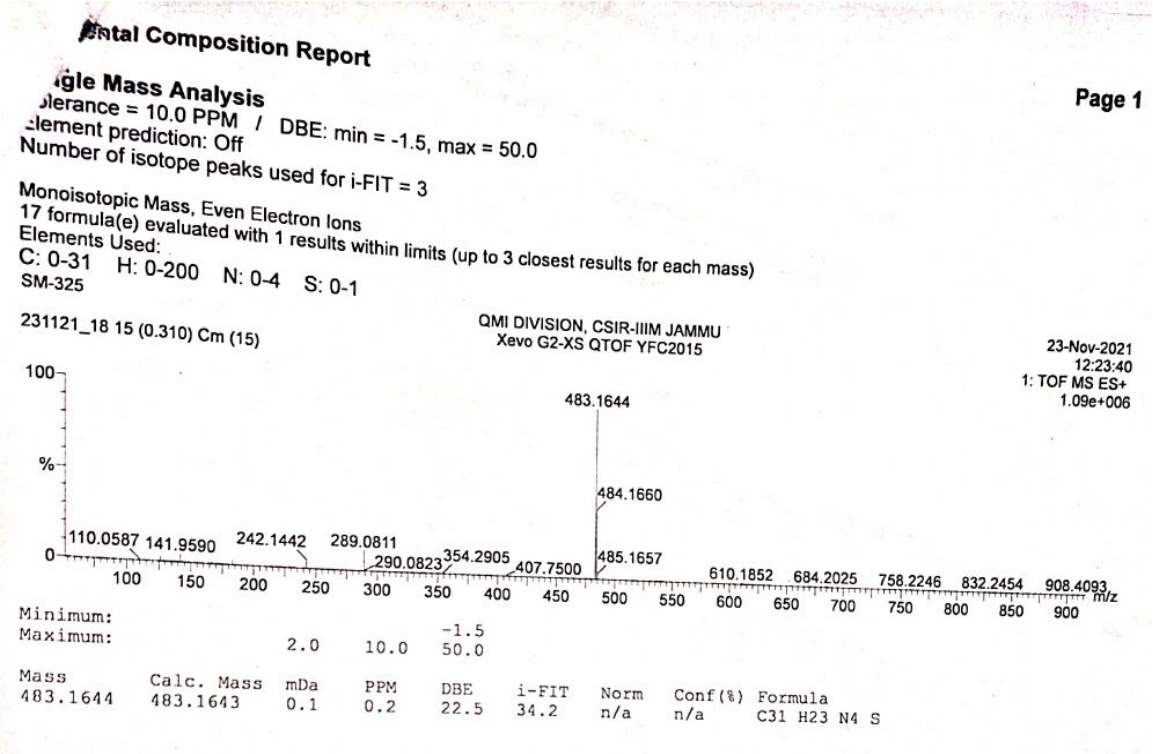
**$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$) of 3v**



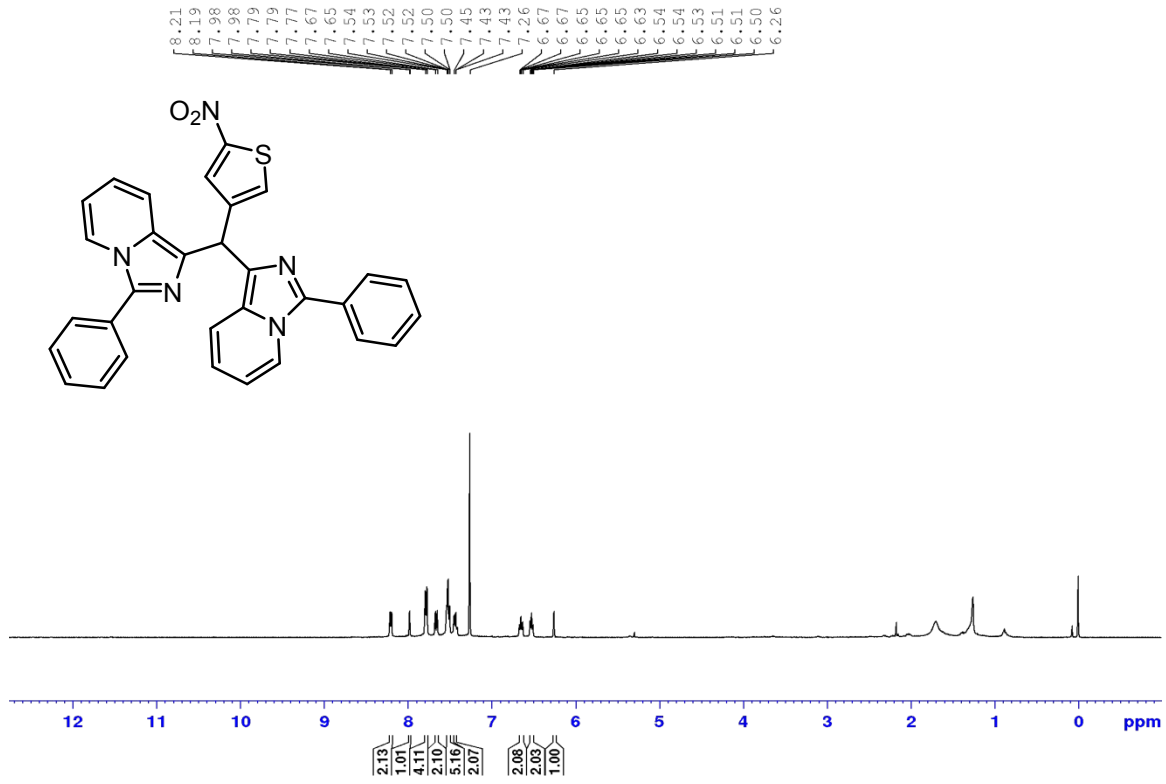

**DEPT-135 (101 MHz, $CDCl_3$) of 3v**



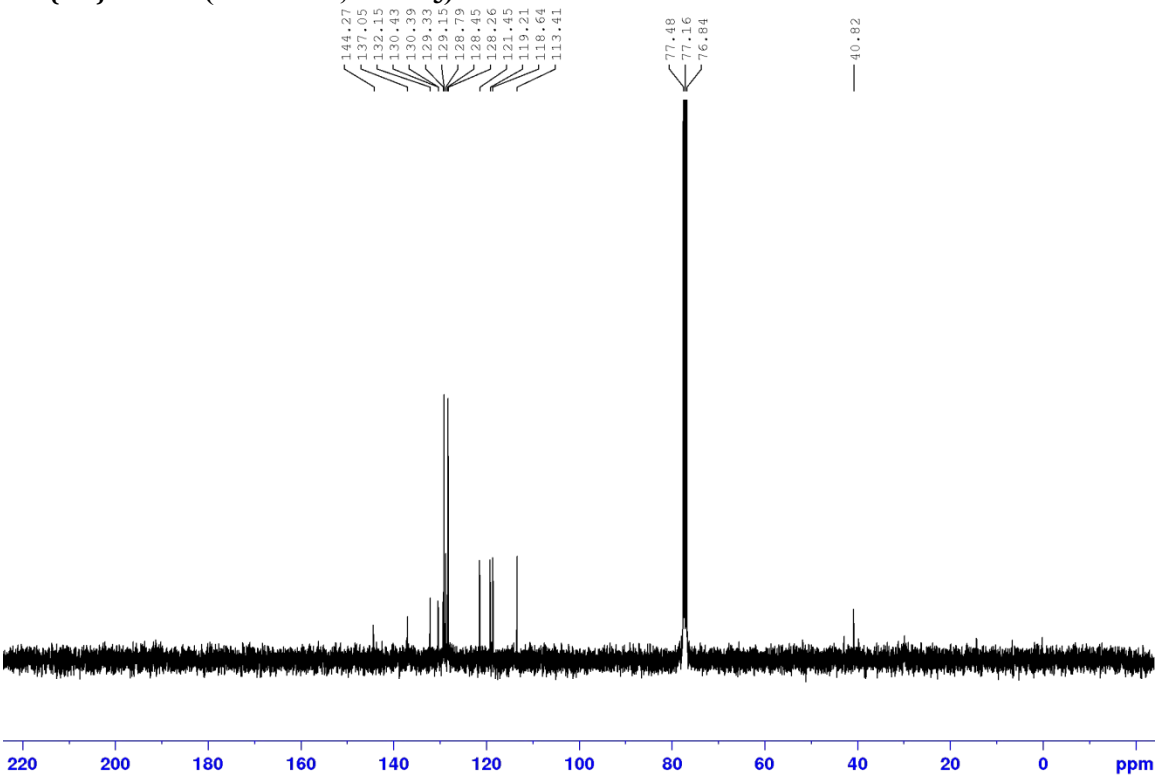
**HRMS of 3v**



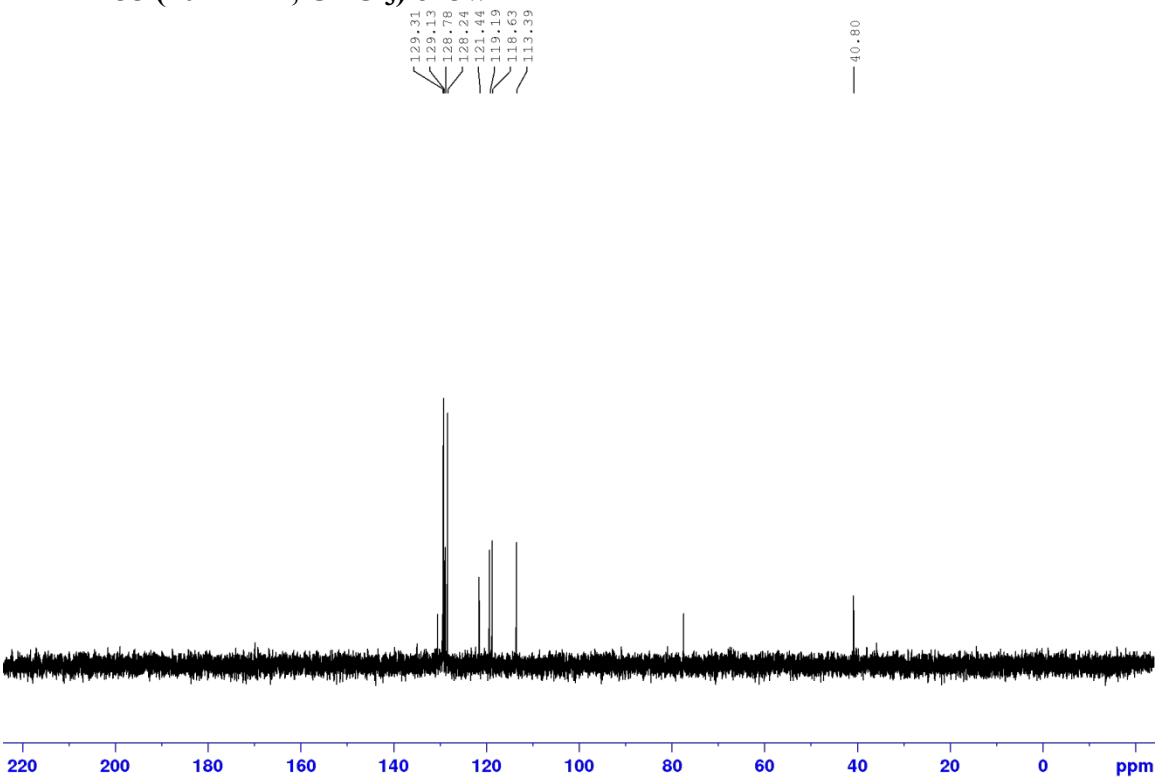

**$^1$H-NMR (400 MHz, $CDCl_3$) of 3w**



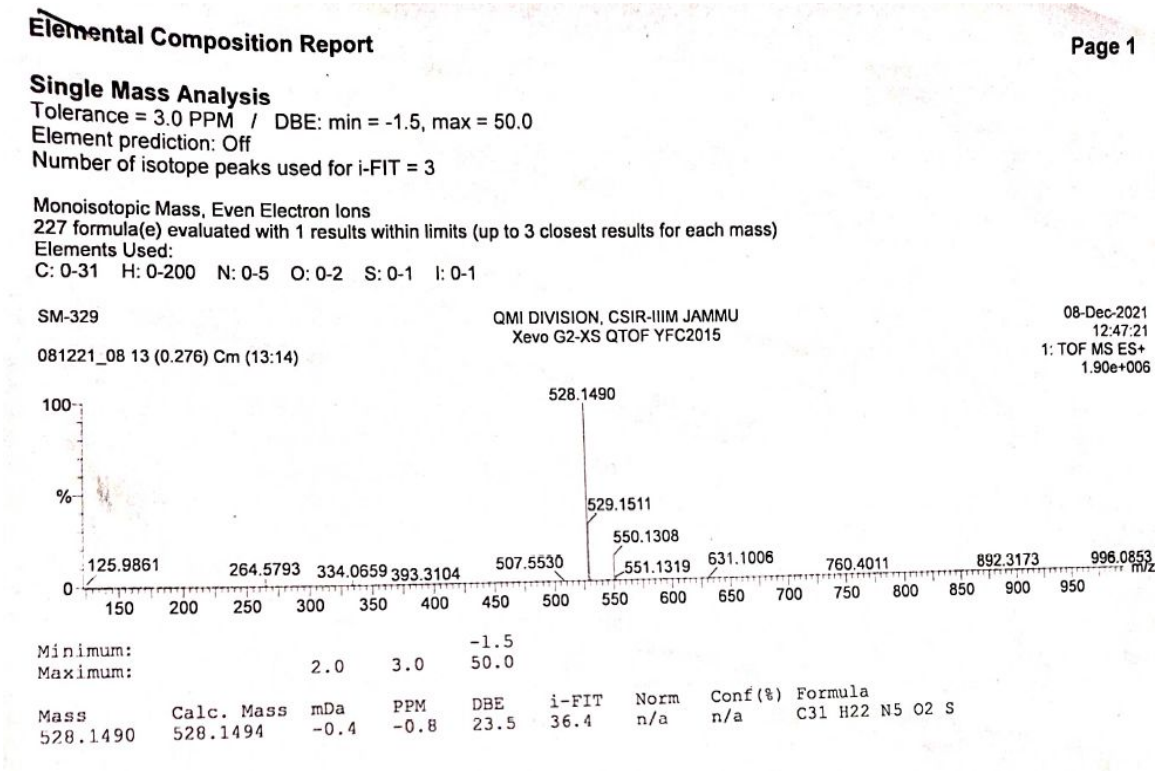
**$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$) of 3w**



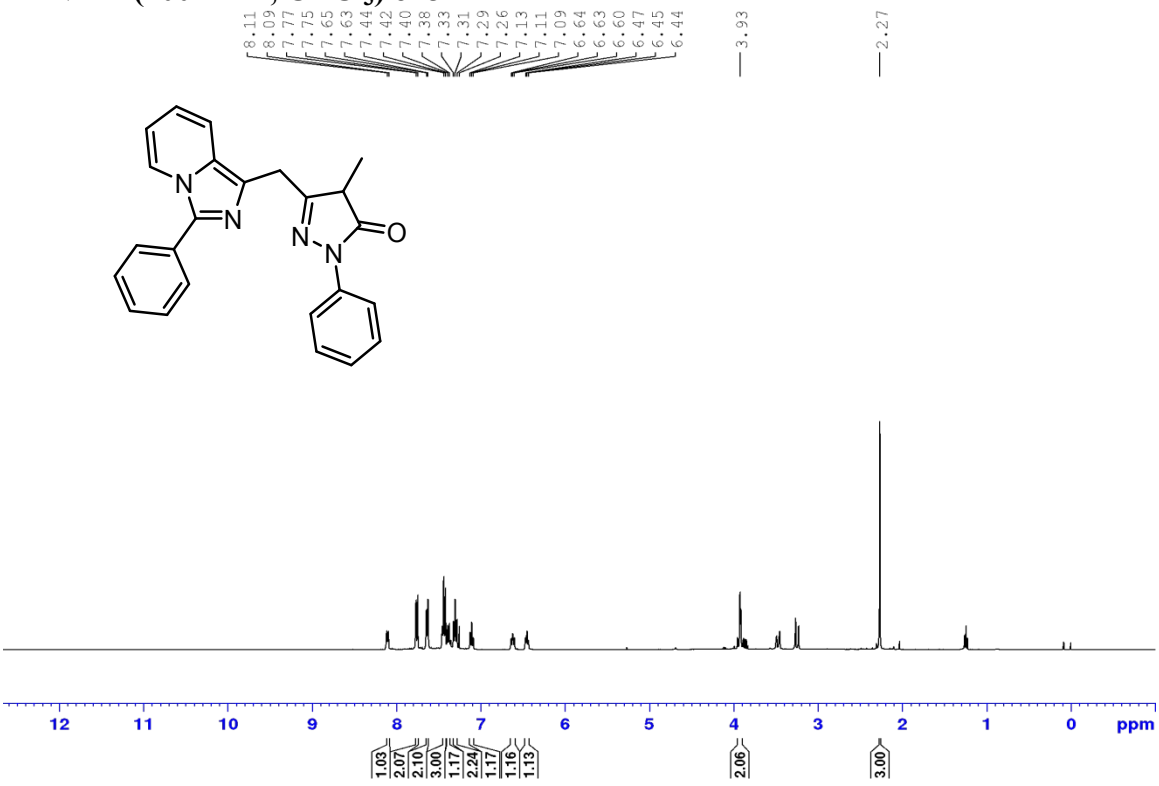

**DEPT-135 (101 MHz, $CDCl_3$) of 3w**



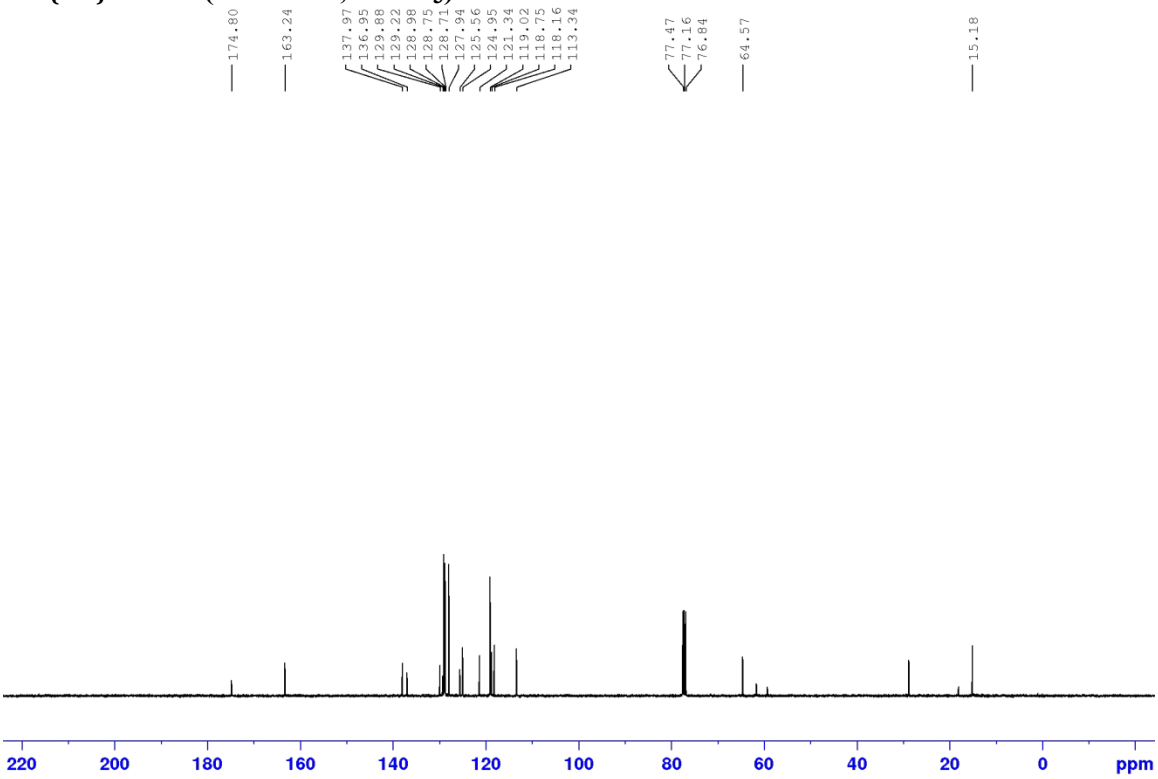
## HRMS of 3w



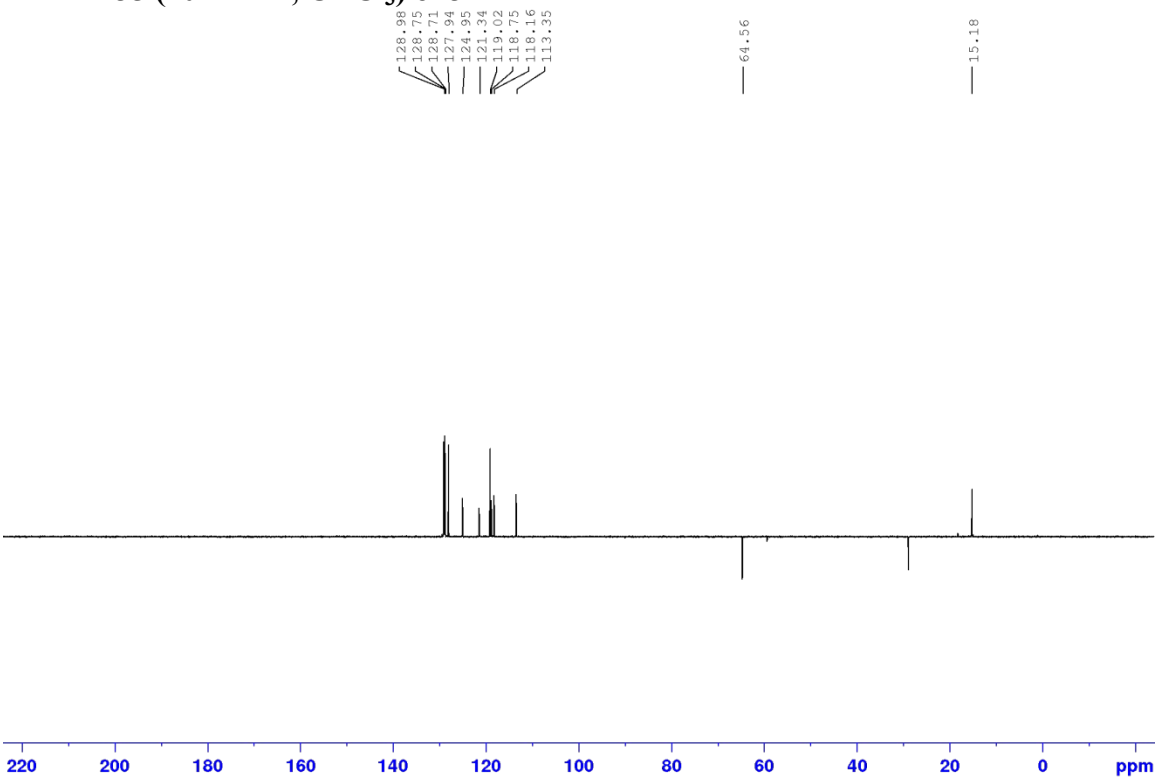

## $^1$H-NMR (400 MHz, $CDCl_3$) of 3x



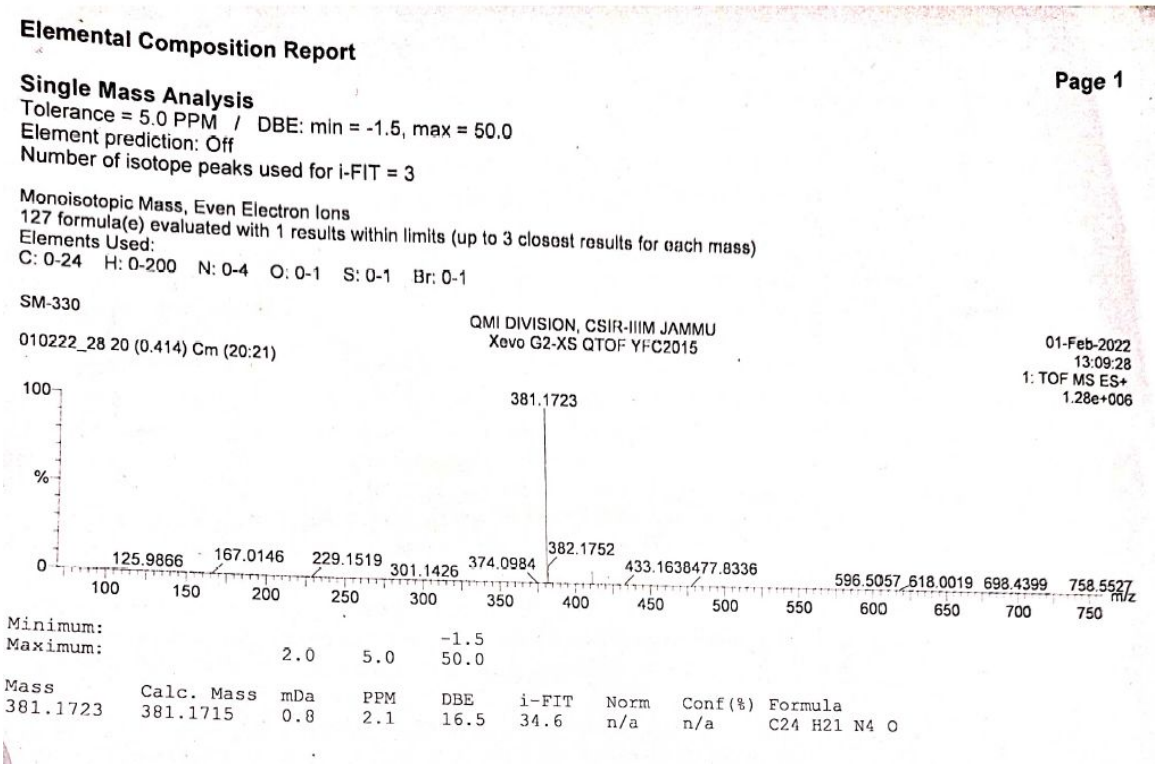
**$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$) of 3x**



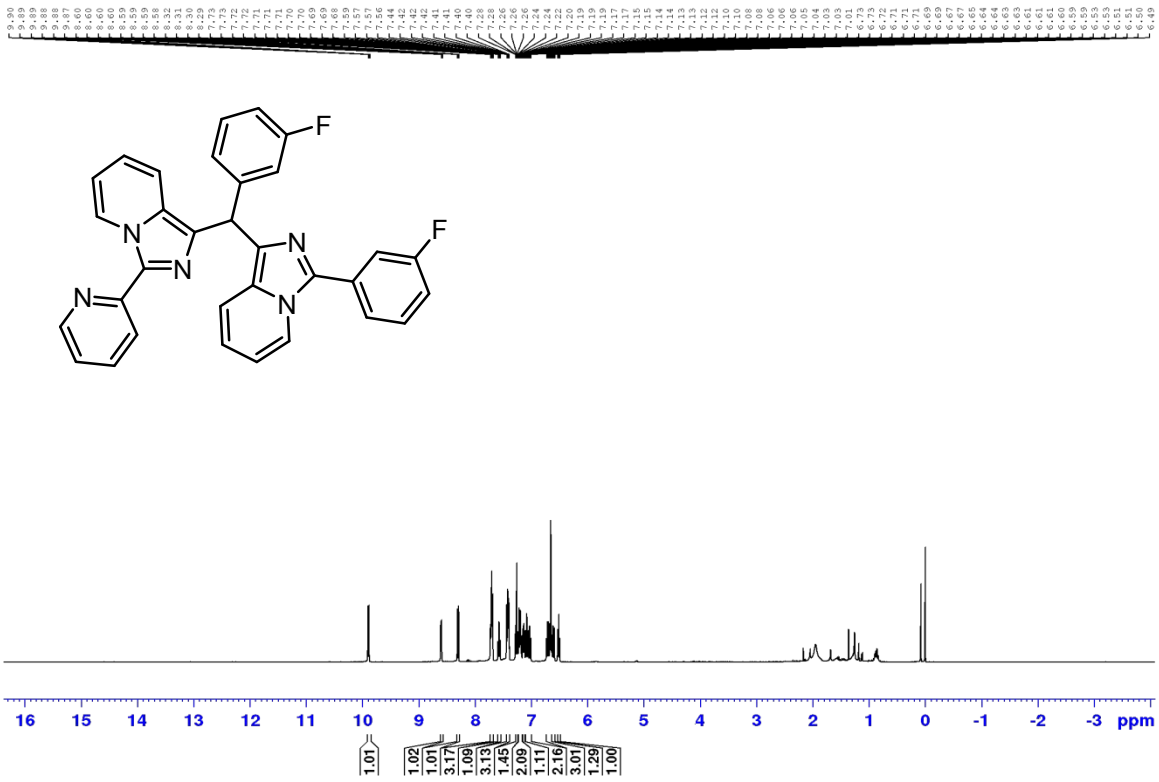

**DEPT-135 (101 MHz, $CDCl_3$) of 3x**



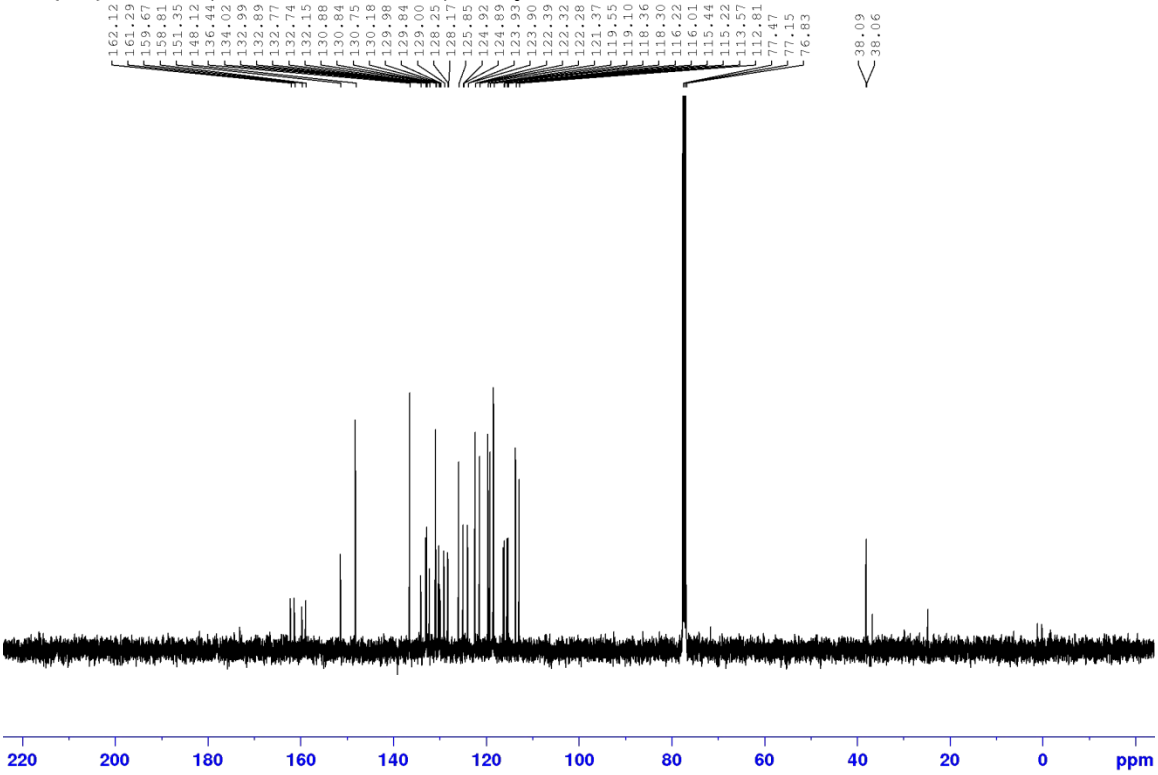
## HRMS of 3x



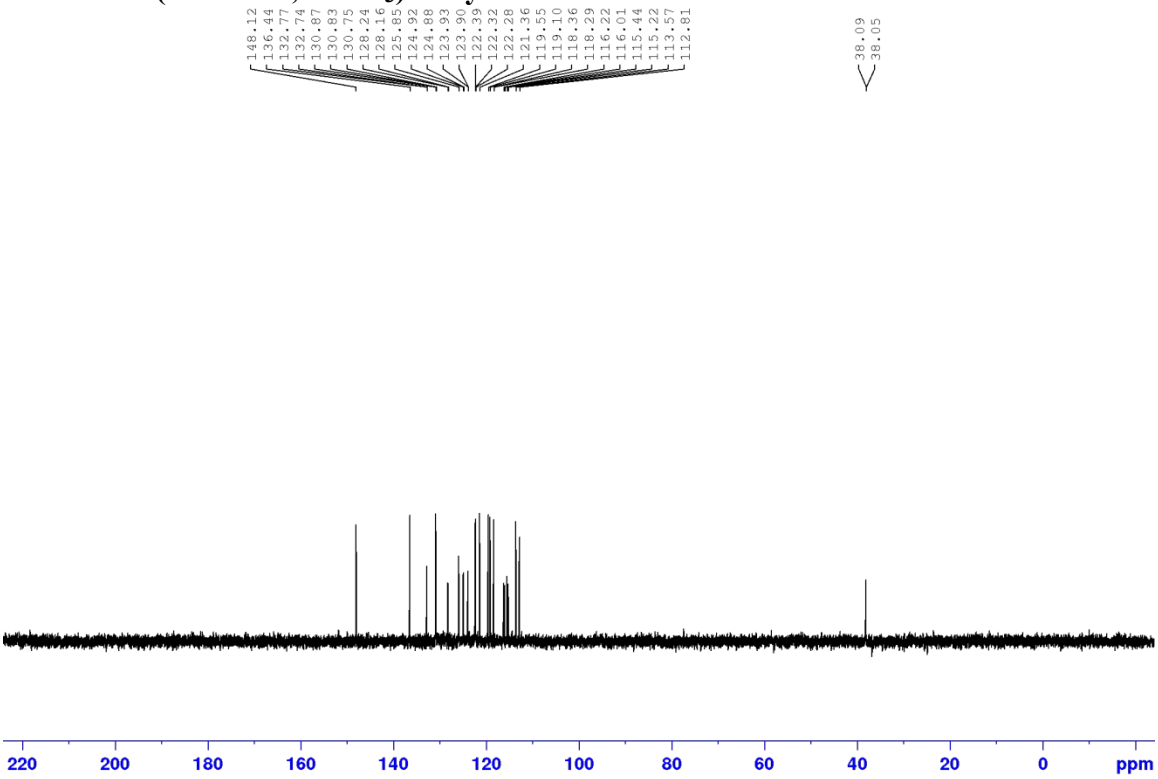

## $^1$H-NMR (400 MHz, $CDCl_3$) of 3y



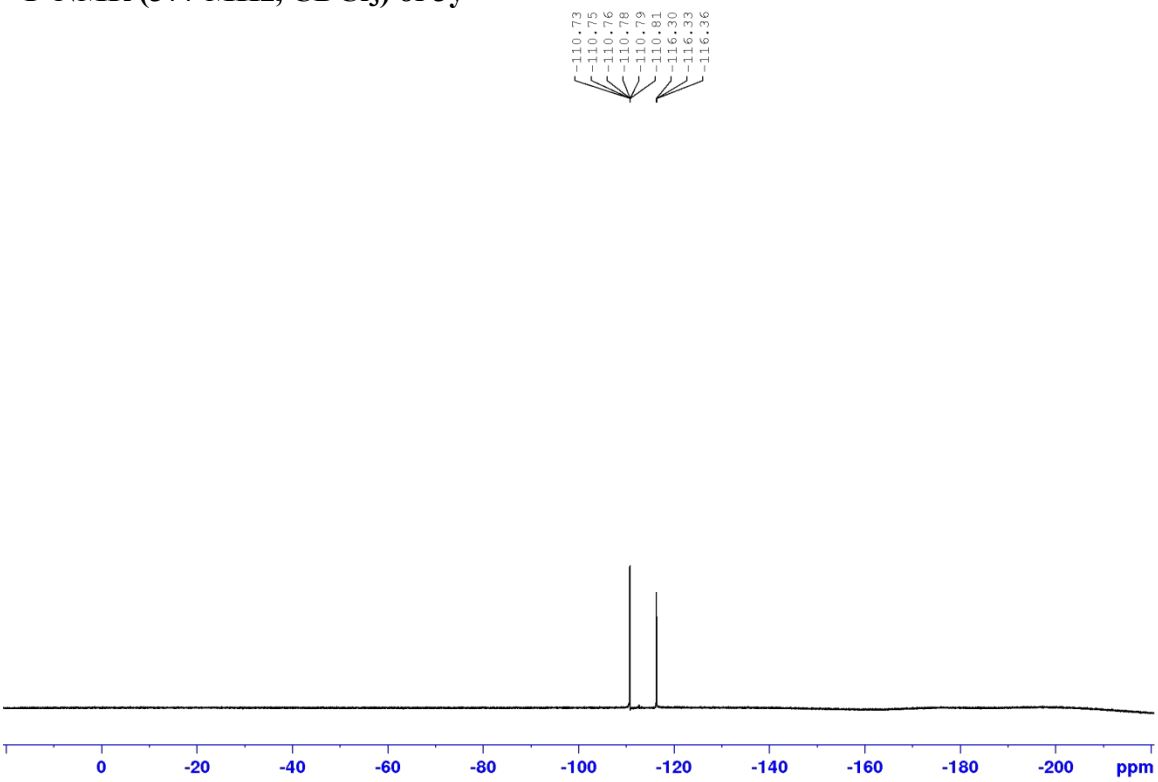
**$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$) of 3y**



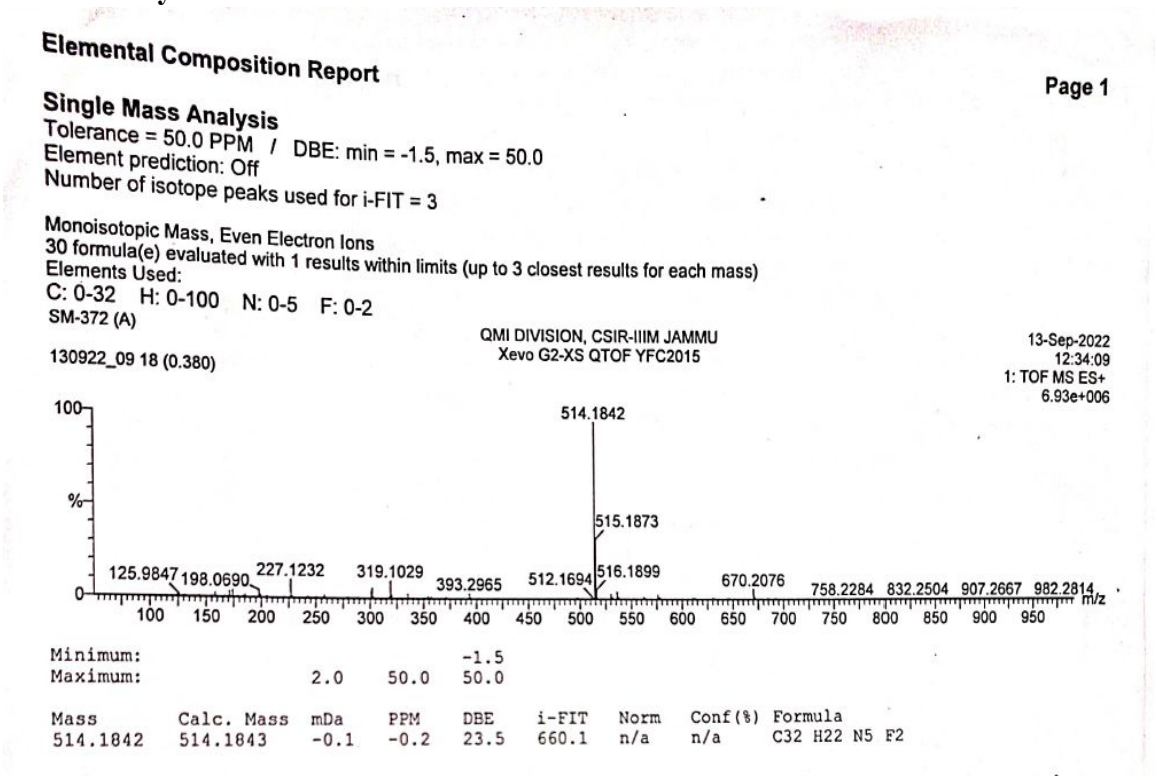

**DEPT-135 (101 MHz, $CDCl_3$) of 3y**



**$^{19}$F-NMR (377 MHz, $CDCl_3$) of 3y**




**HRMS of 3y**



**Elemental Composition Report**

Page 1

**Single Mass Analysis**
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
30 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-32 H: 0-100 N: 0-5 F: 0-2
SM-372 (A)

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

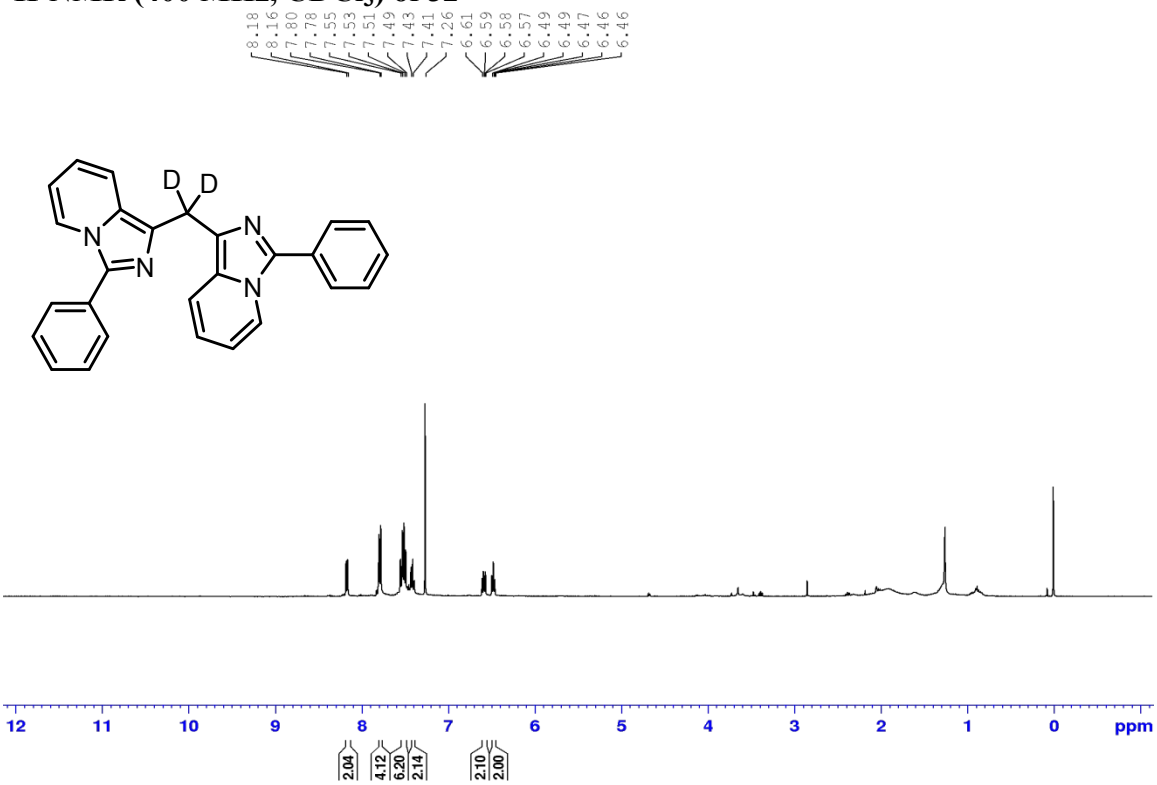
130922_09 18 (0.380)

13-Sep-2022
12:34:09
1: TOF MS ES+
6.93e+006

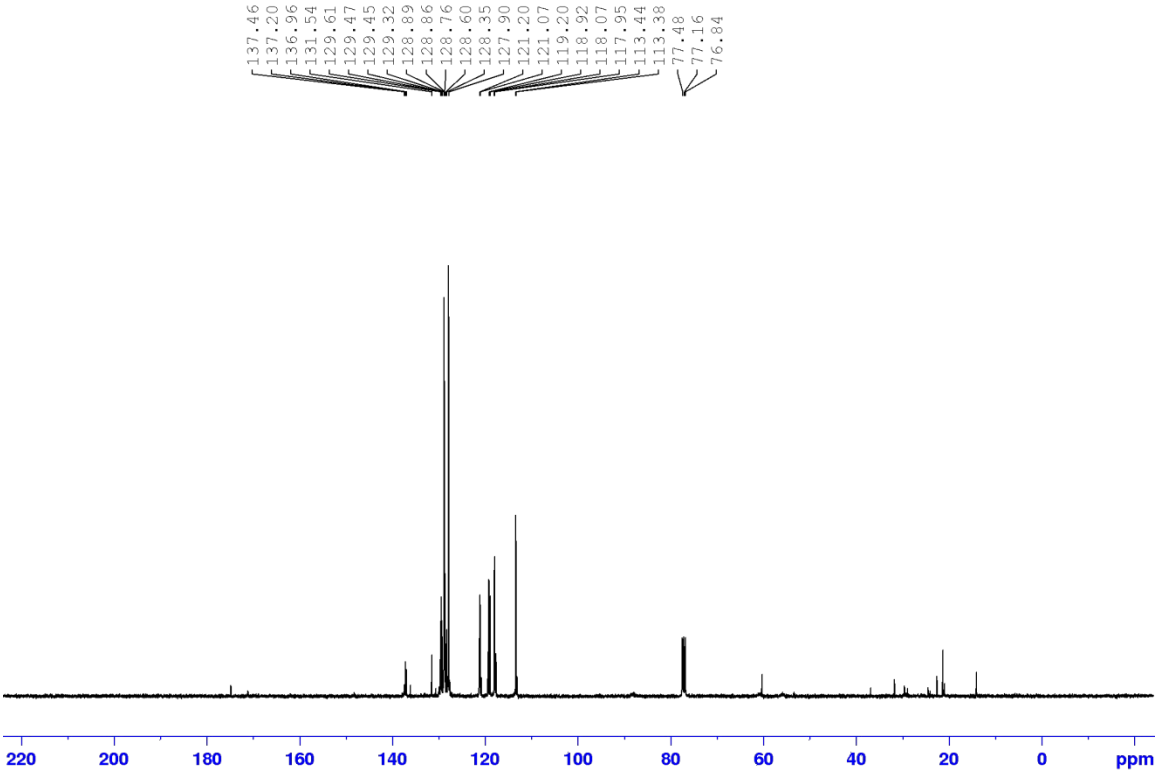


| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 2.0 | 50.0 | 50.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 514.1842 | 514.1843 | -0.1 | -0.2 | 23.5 | 660.1 | n/a | n/a | C32 H22 N5 F2 |

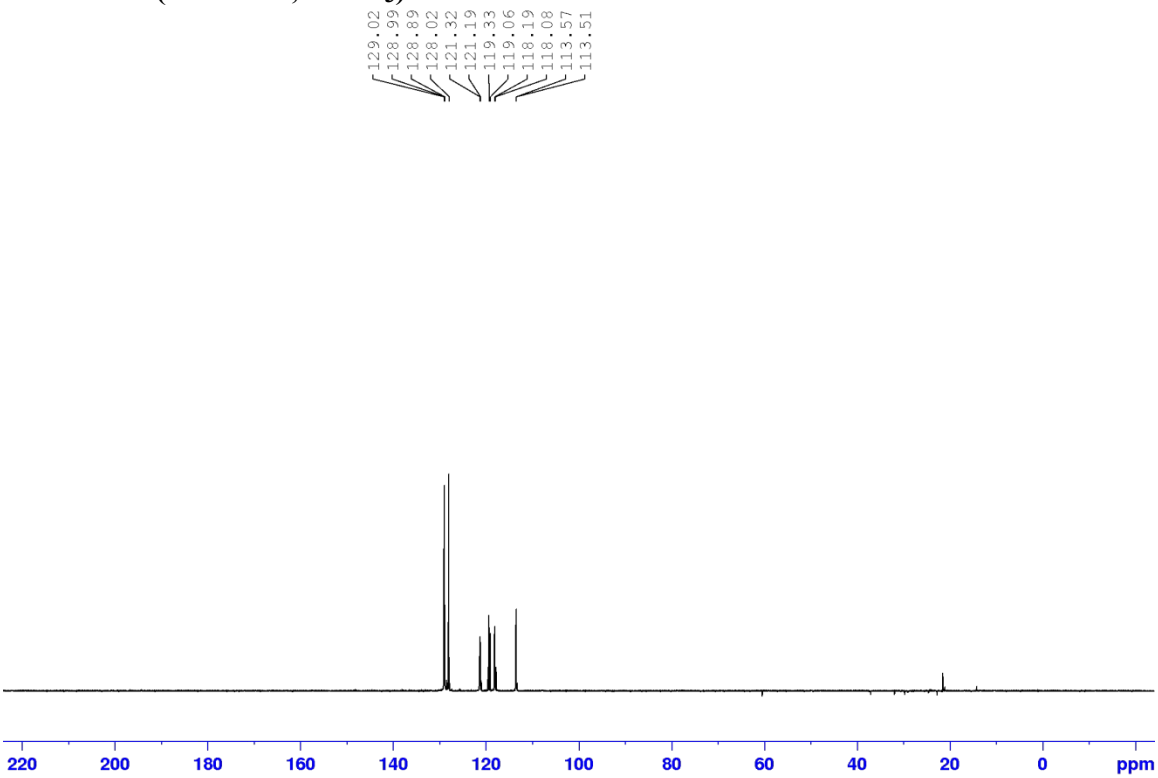
**$^{1}$H-NMR (400 MHz, $CDCl_3$) of 3z**



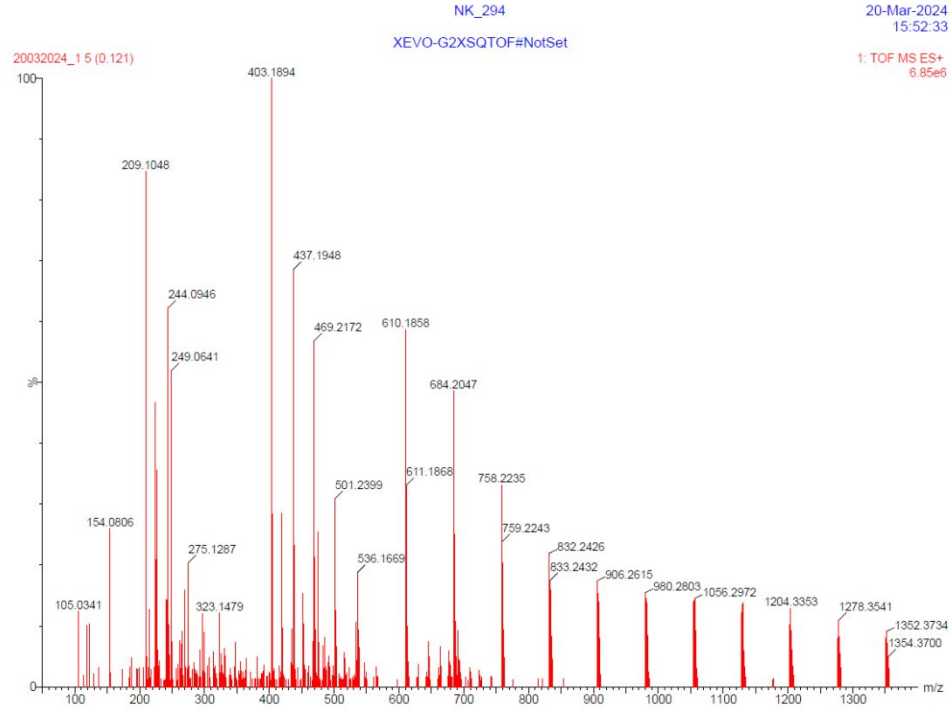

**$^{13}$C{$^{1}$H}-NMR (101 MHz, $CDCl_3$) of 3z**

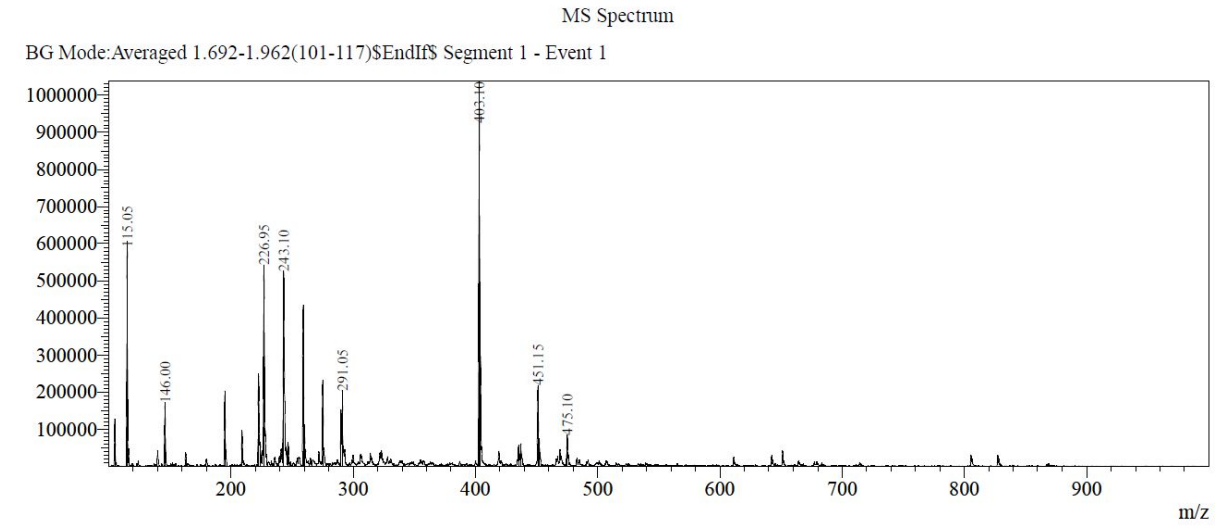


**DEPT-135 (101 MHz, $CDCl_3$) of 3z**

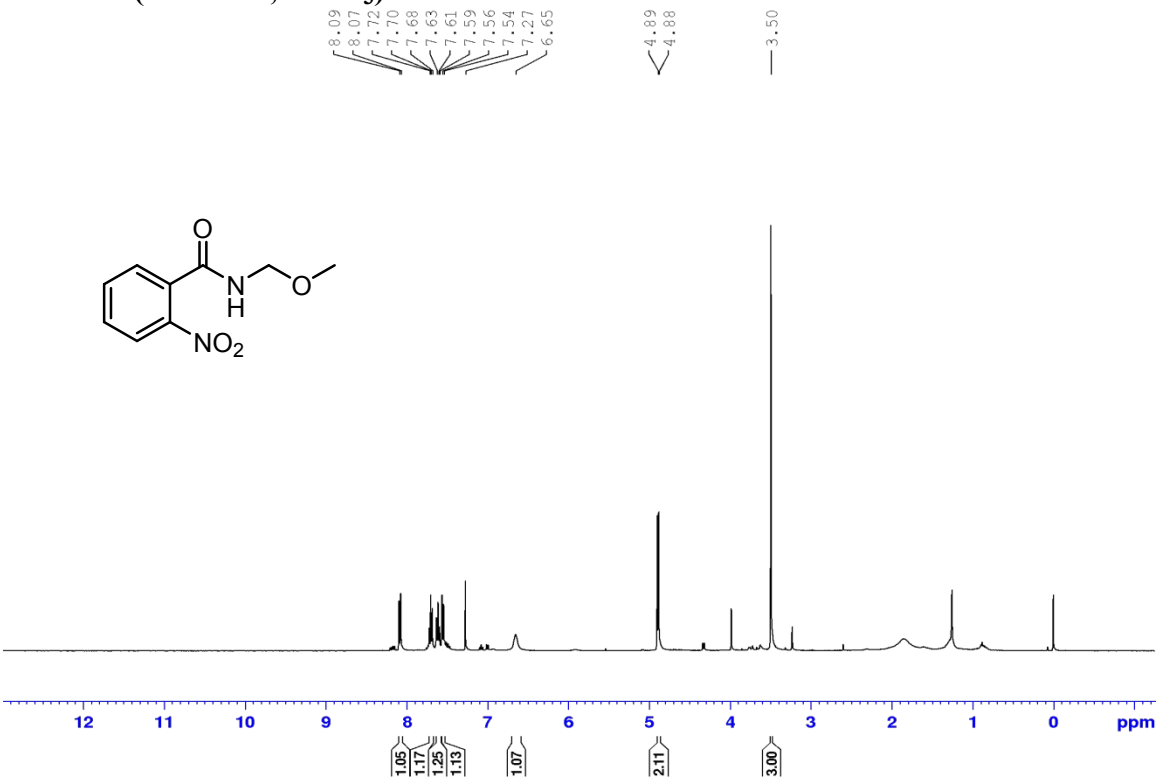



**HRMS of 3z**

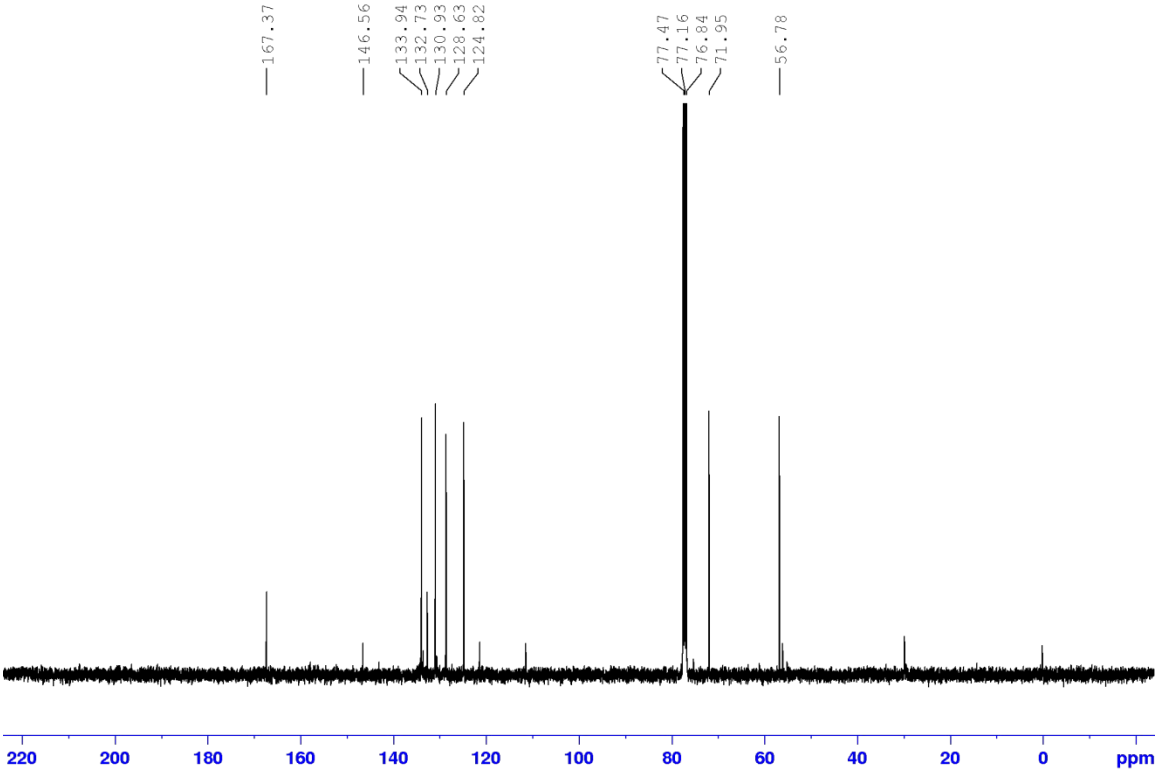




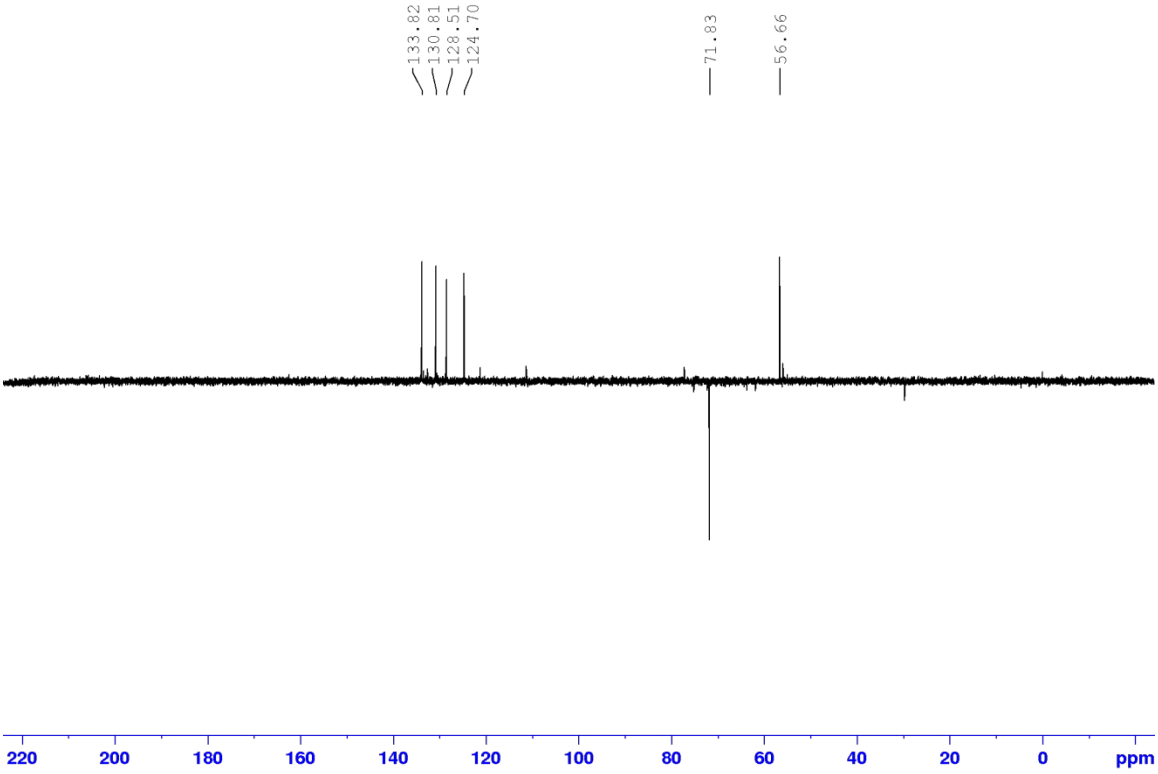

**$^1$H-NMR (400 MHz, $CDCl_3$) of 5a**



**$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$) of5a**




**DEPT-135 (101 MHz, $CDCl_3$) of 5a**



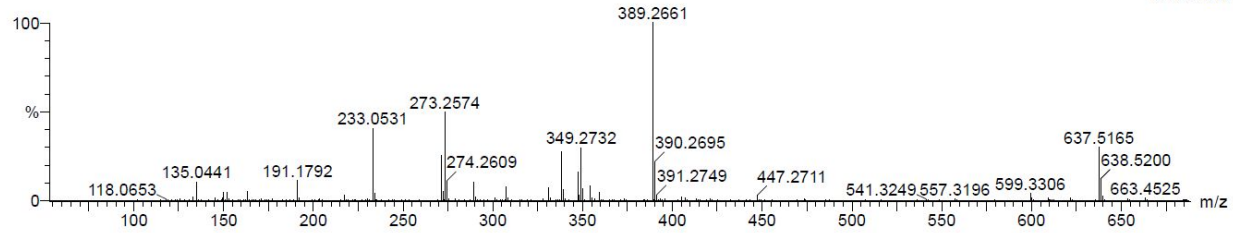
## HRMS of 5a

**Elemental Composition Report** **Page 1**

**Single Mass Analysis**
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

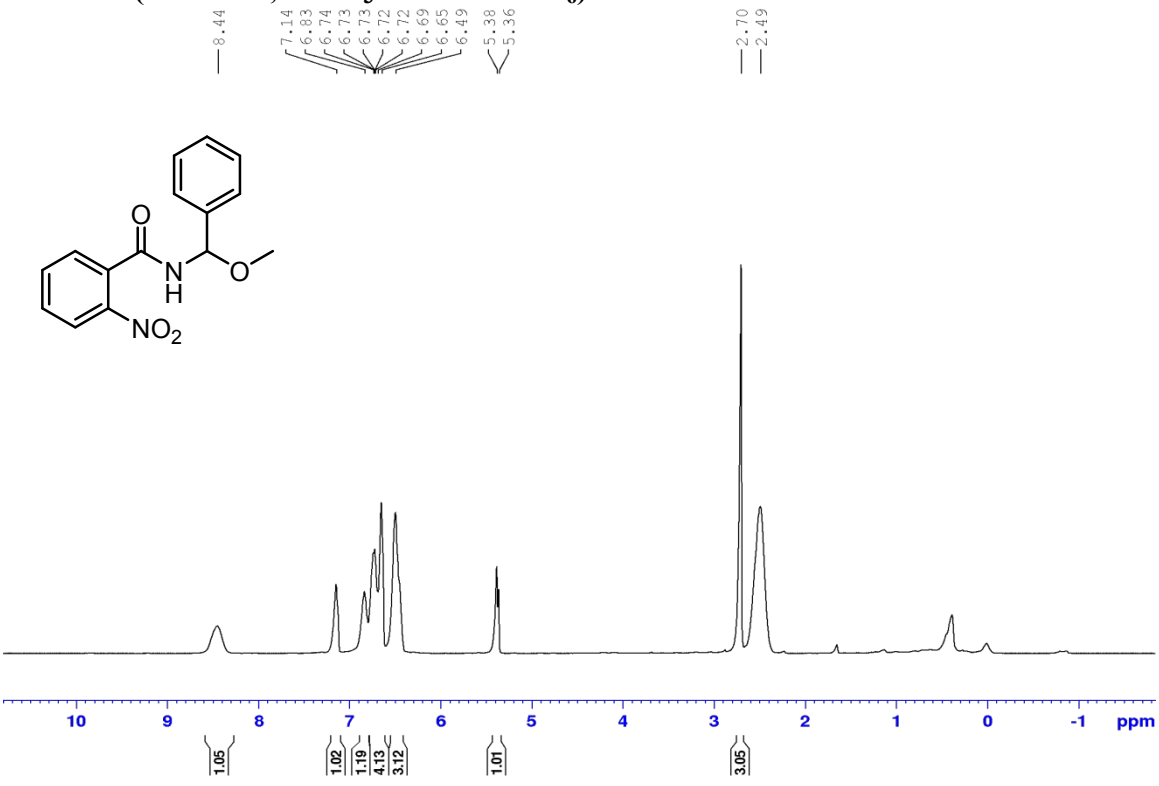
Monoisotopic Mass, Even Electron Ions
31 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-9 H: 0-100 N: 0-2 O: 0-4 Na: 0-1

SM-NITRO Desired
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015
26-Dec-2023
14:24:55
261223_04 5 (0.121)
1: TOF MS ES+
6.12e+006

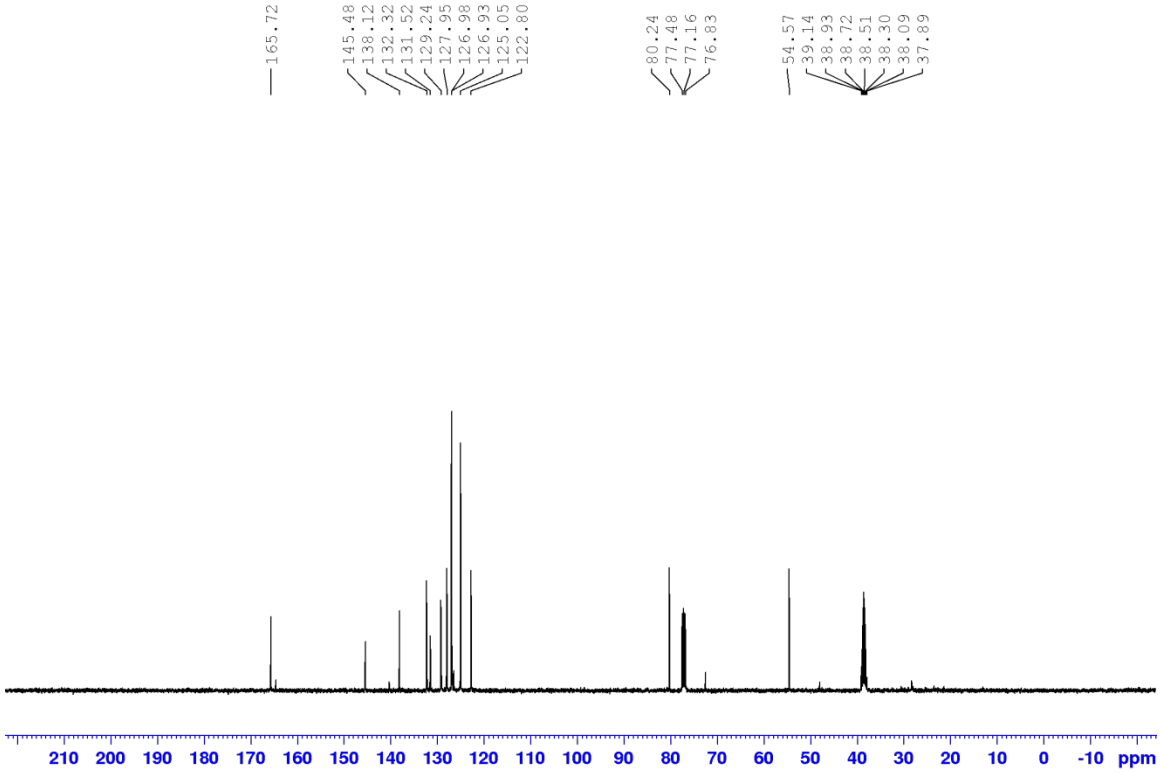



| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 2.0 | 50.0 | 50.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 233.0531 | 233.0538 | -0.7 | -3.0 | 5.5 | 1284.3 | n/a | n/a | C9 H10 N2 O4 Na |

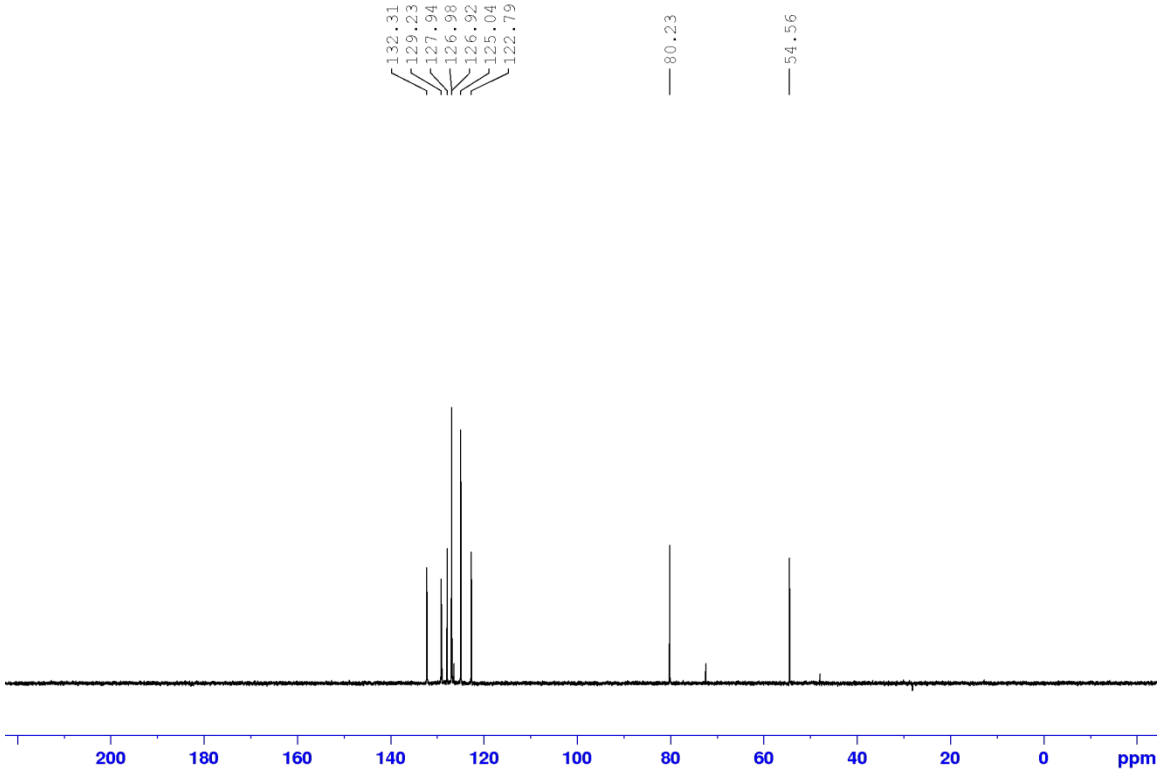
## $^1$H-NMR (400 MHz, $CDCl_3$ and DMSO-$d_6$) of 5b



**$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$ and DMSO-$d_6$) of5b**




**DEPT-135 (101 MHz, $CDCl_3$ and DMSO-$d_6$) of 5b**



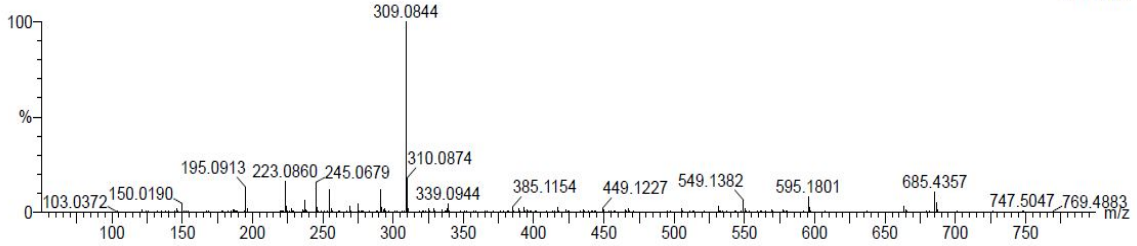
## HRMS of 5b

**Elemental Composition Report** **Page 1**

**Single Mass Analysis**
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

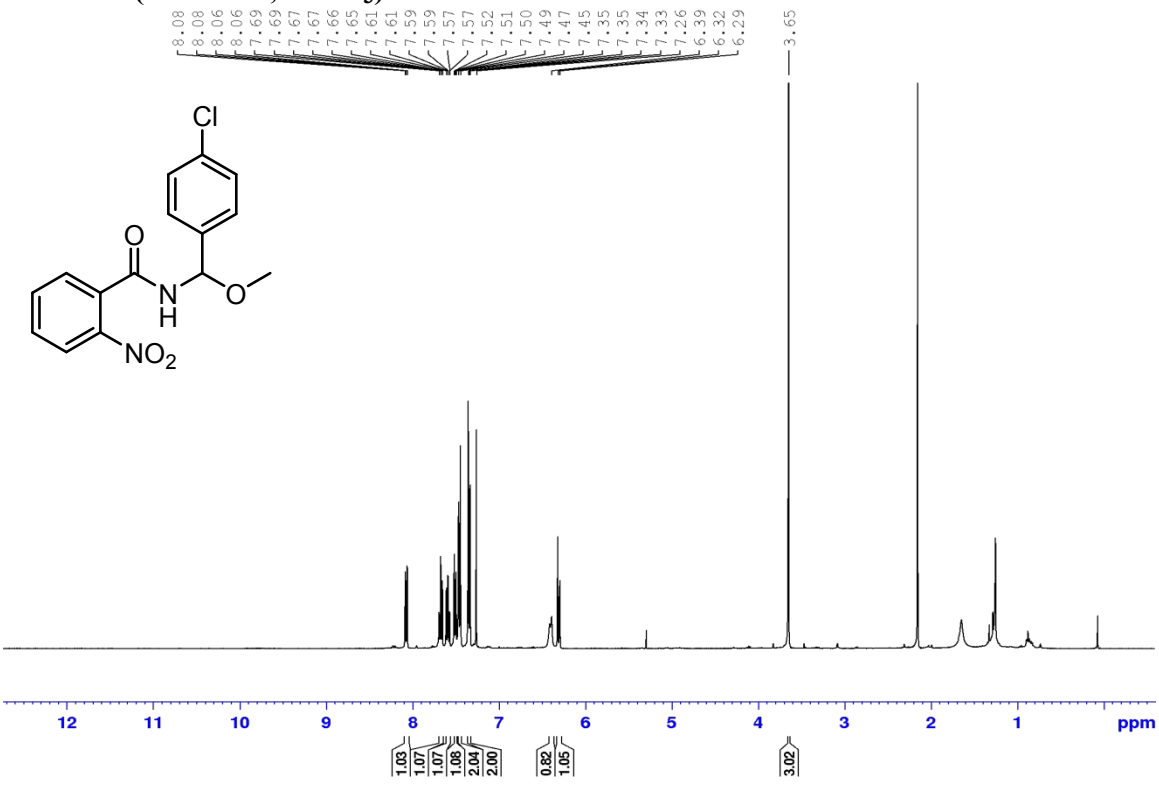
Monoisotopic Mass, Even Electron Ions
33 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-15 H: 0-100 N: 0-2 O: 0-4 Na: 0-1

SM-NITRO PH
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015
06-Oct-2023
14:32:57
061023_26 6 (0.138)
1: TOF MS ES+
1.38e+007

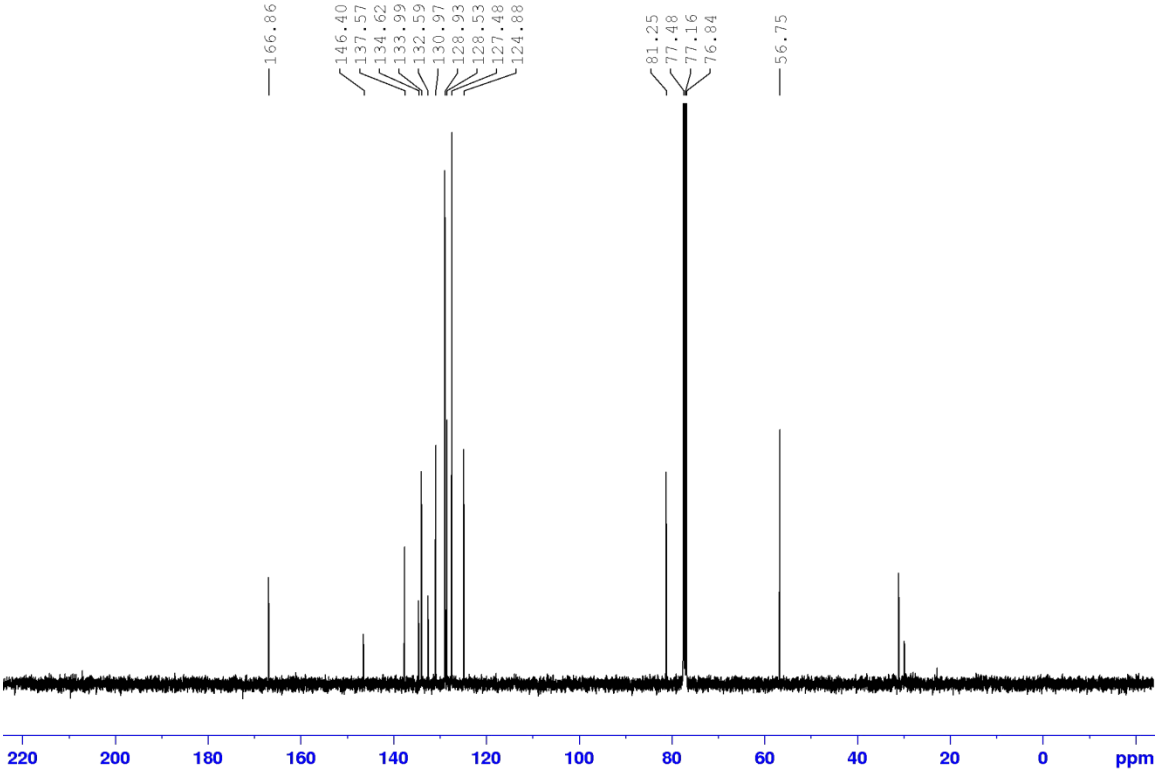



| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 2.0 | 100.0 | 50.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 309.0844 | 309.0851 | -0.7 | -2.3 | 9.5 | 979.2 | n/a | n/a | C15 H14 N2 O4 Na |

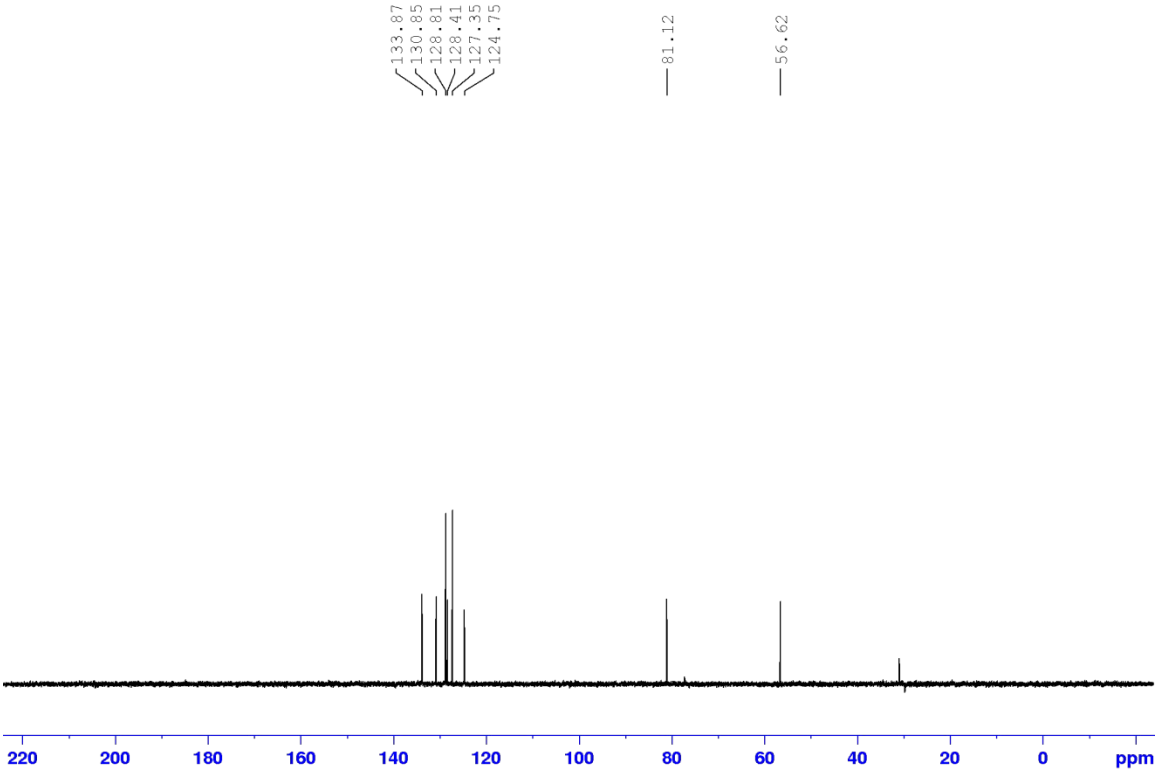
## $^1$H-NMR (400 MHz, $CDCl_3$) of 5c



**$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$) of5c**




**DEPT-135 (101 MHz, $CDCl_3$) of 5c**



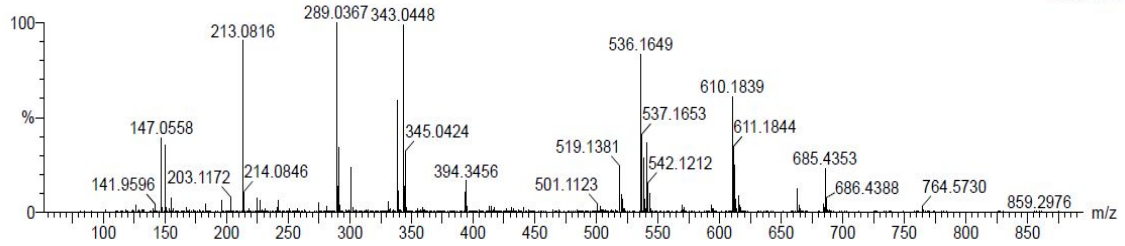
## HRMS of 5c

**Elemental Composition Report** **Page 1**

**Single Mass Analysis**
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
63 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-15 H: 0-100 N: 0-2 O: 0-4 Na: 0-1 Cl: 0-1

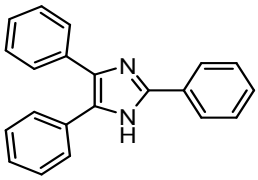
SM-4Cl NO
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015
06-Oct-2023
14:38:06
061023_28 6 (0.138)
1: TOF MS ES+
1.34e+006

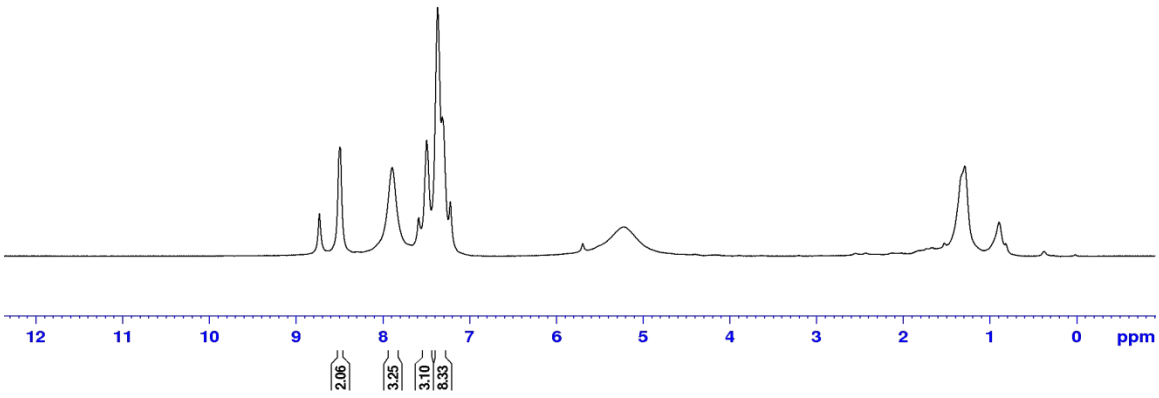



| | | | | |
|---|---|---|---|---|
| Minimum: | | | -1.5 | |
| Maximum: | | 2.0 | 100.0 | 50.0 |

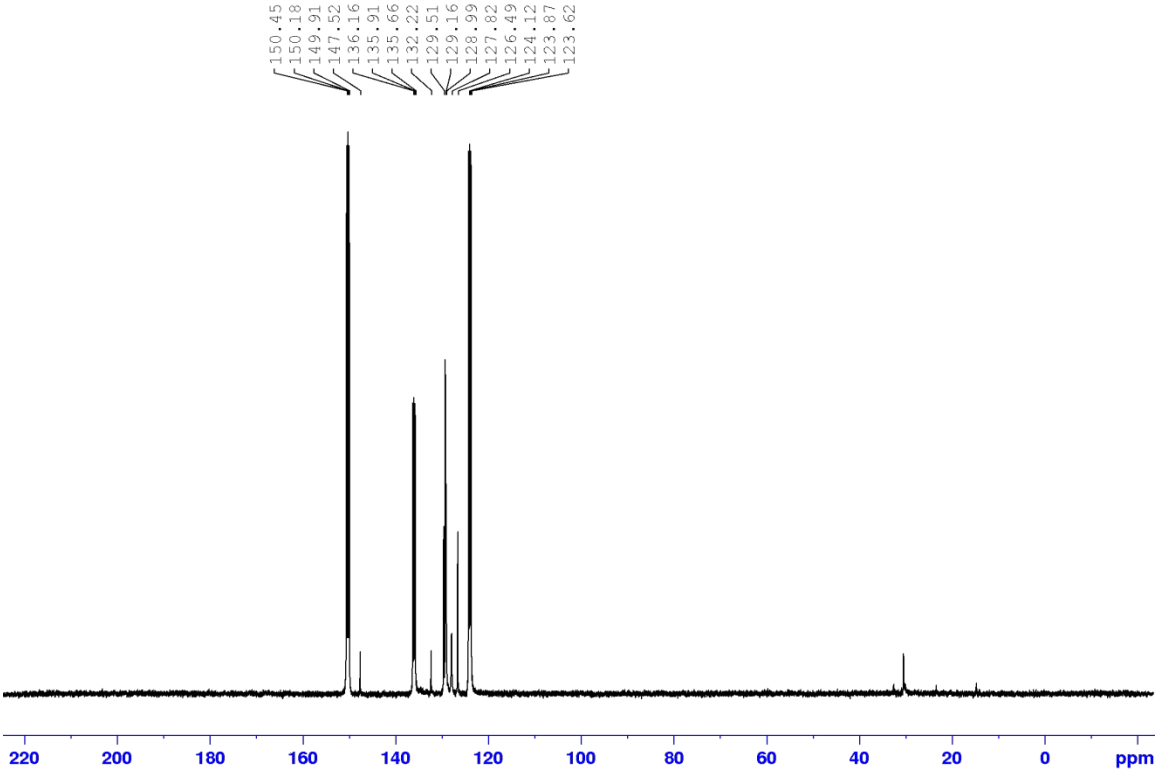
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
|---|---|---|---|---|---|---|---|---|
| 343.0448 | 343.0462 | -1.4 | -4.1 | 9.5 | 913.7 | n/a | n/a | C15 H13 N2 O4 Na Cl |

## $^1$H-NMR (400 MHz, pyridine-$d_5$) of 7a

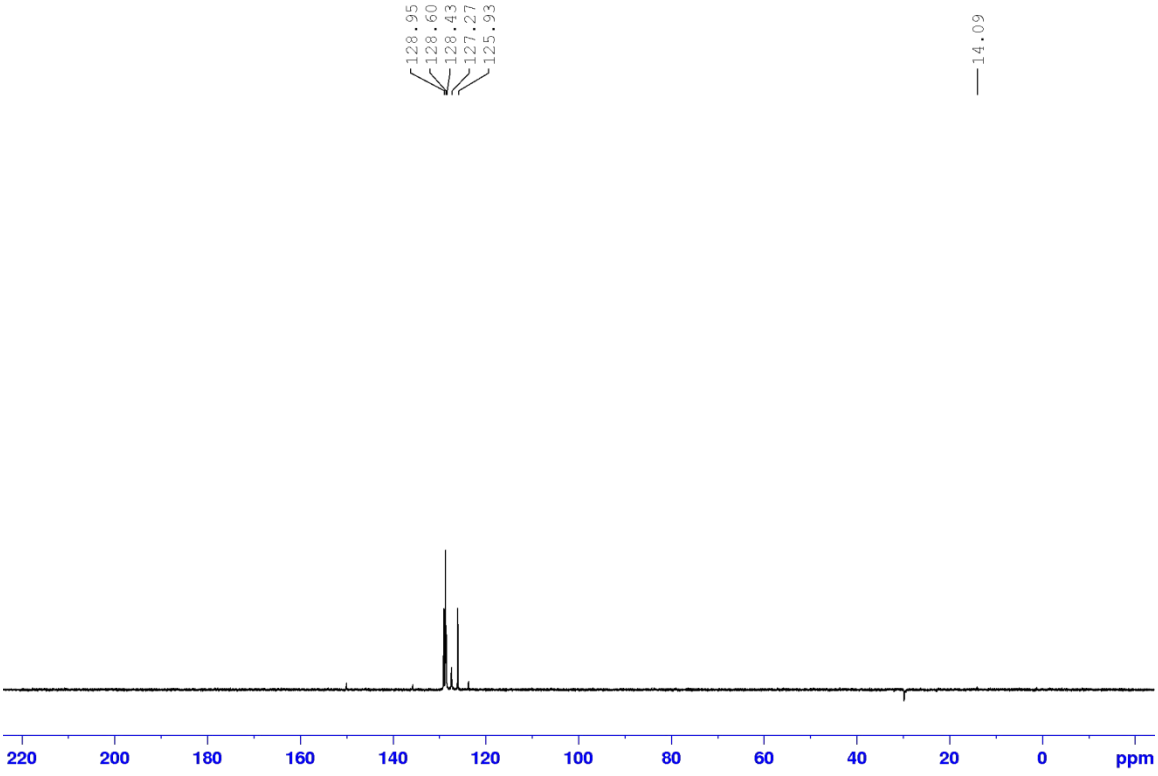



**$^{13}C\{^{1}H\}$-NMR (101 MHz, pyridine-$d_5$) of 7a**




**DEPT-135 (101 MHz, pyridine-$d_5$) of 7a**



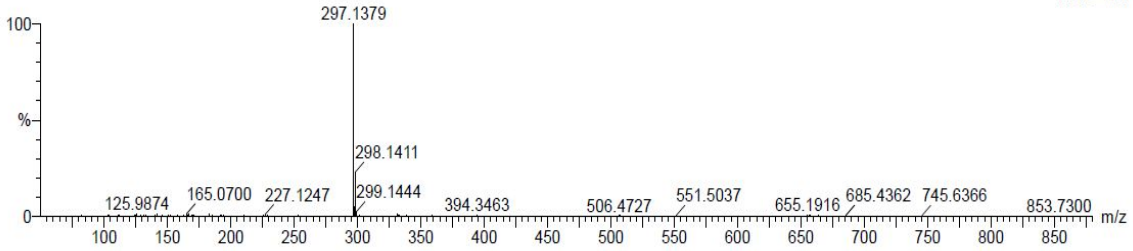
## HRMS of 7a

**Elemental Composition Report** **Page 1**

**Single Mass Analysis**
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

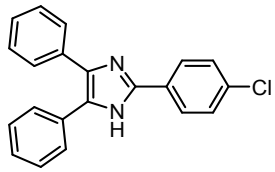
Monoisotopic Mass, Even Electron Ions
6 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-21 H: 0-100 N: 0-2

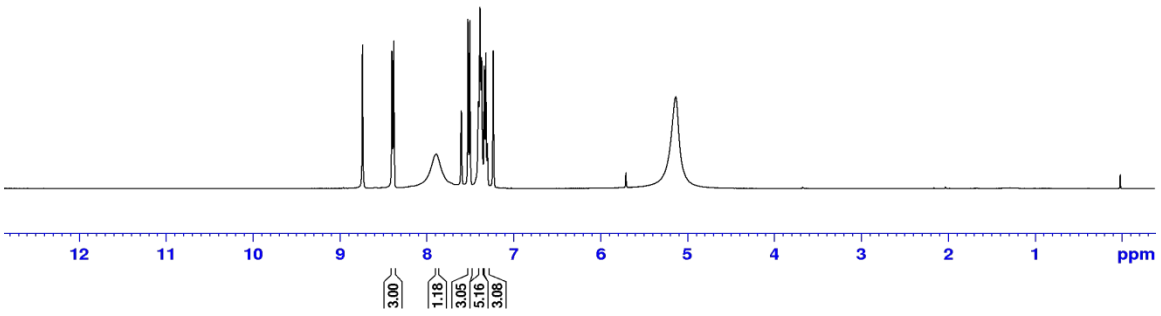
SM-BENZ
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015
06-Oct-2023
14:51:15
061023_33 9 (0.208)
1: TOF MS ES+
1.01e+007



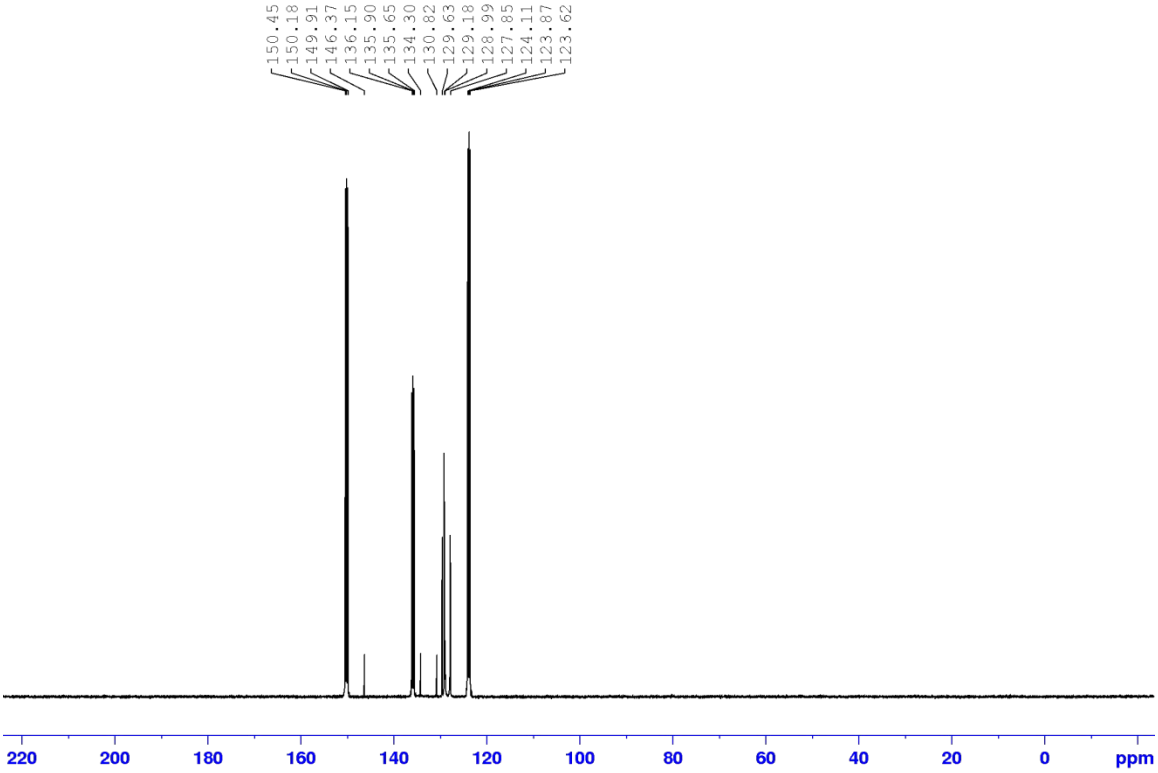

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 2.0 | 100.0 | 50.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 297.1379 | 297.1392 | -1.3 | -4.4 | 14.5 | 948.0 | n/a | n/a | C21 H17 N2 |

## $^{1}$H-NMR (400 MHz, pyridine-$d_5$) of 7b

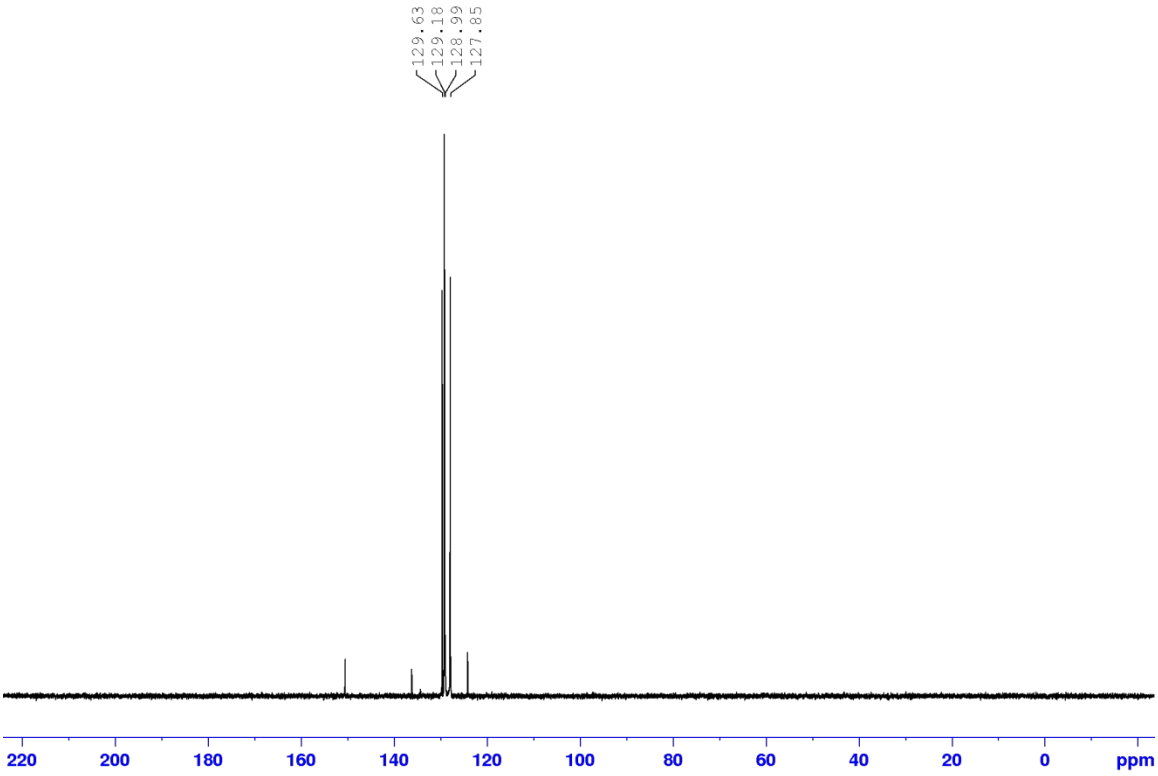



**$^{13}C\{^{1}H\}$-NMR (101 MHz, pyridine-$d_5$) of7b**




**DEPT-135 (101 MHz, pyridine-$d_5$) of 7b**



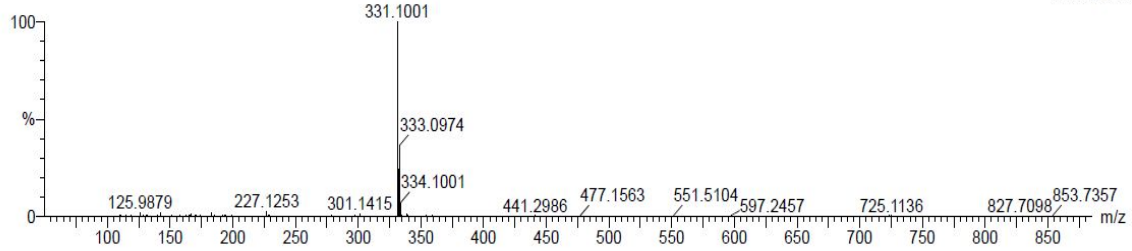
## HRMS of 7b

**Elemental Composition Report** **Page 1**

**Single Mass Analysis**
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-21 H: 0-100 N: 0-2 Cl: 0-1

SM-4Cl BEN
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015
06-Oct-2023
14:35:32
061023_27 4 (0.104)
1: TOF MS ES+
6.25e+006




| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | |
| Maximum: | | 2.0 | 100.0 | 50.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 331.1001 | 331.1002 | -0.1 | -0.3 | 14.5 | 916.3 | n/a | n/a | C21 H16 N2 Cl |