Supplementary Information (SI) for ChemComm.
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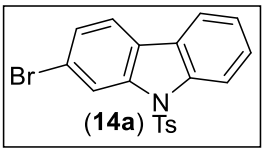
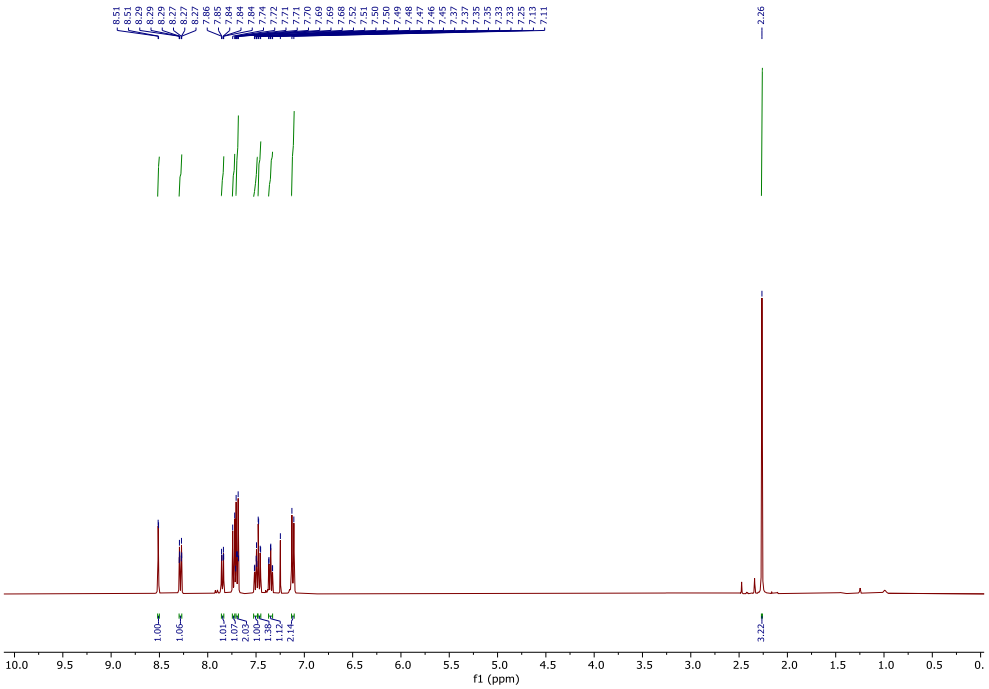
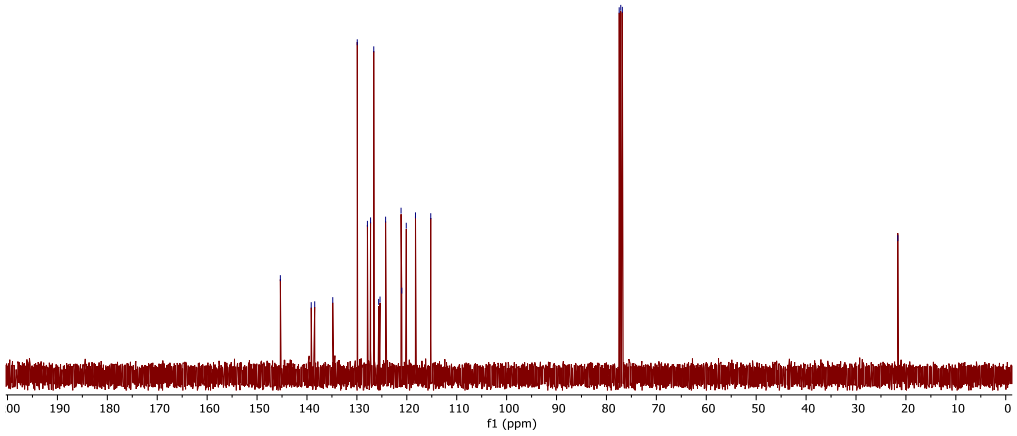
# Spectral Data




$^{1}$H NMR (400 MHz, $CDCl_3$) of **14a**




$^{13}$C NMR (101 MHz, $CDCl_3$) of **14a**

# Display Report

**Analysis Info**

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| Method | Tune_pos_Standard_July2022.m | Operator | IISER Kolkata |
| Sample Name | ab_ram_242 | Instrument | maXis impact 8282001.00127 |
| Comment | | | |

**Acquisition Parameter**

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| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Active | Set Capillary | 4500 V | Set Dry Heater | 200 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 4.0 l/min |
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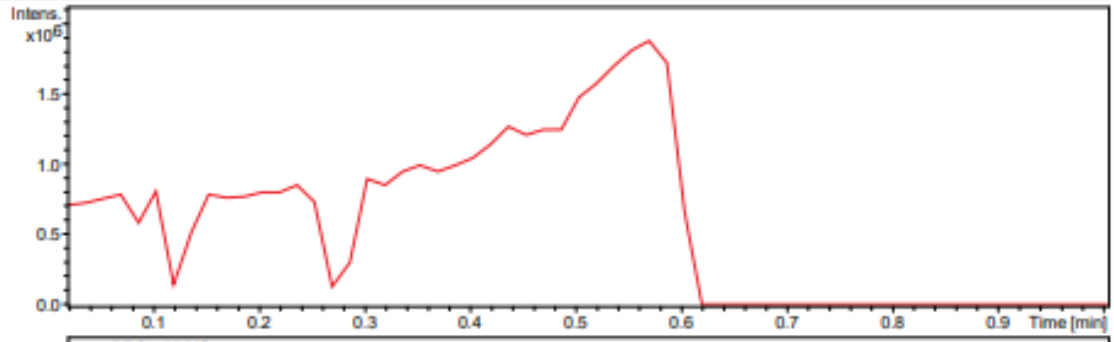
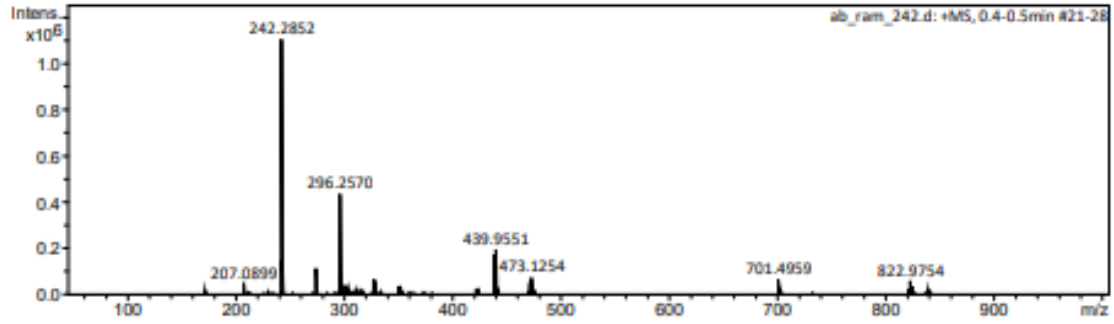
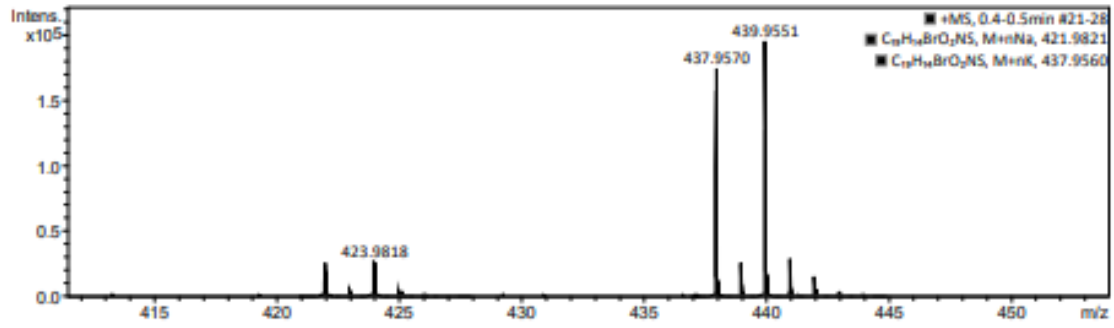
| | | Set Corona | 0 nA | Set APCI Heater | 0 °C |




ab_ram_242.d

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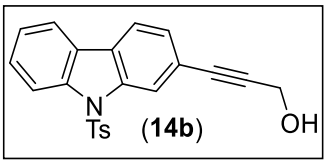
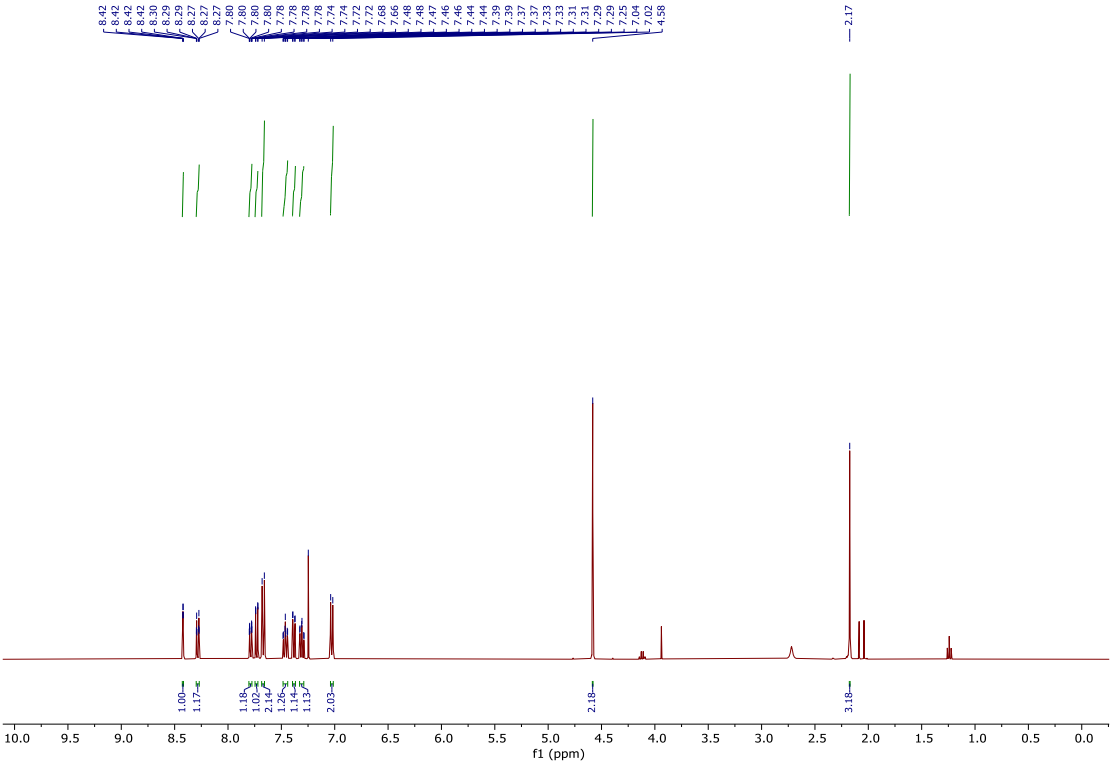
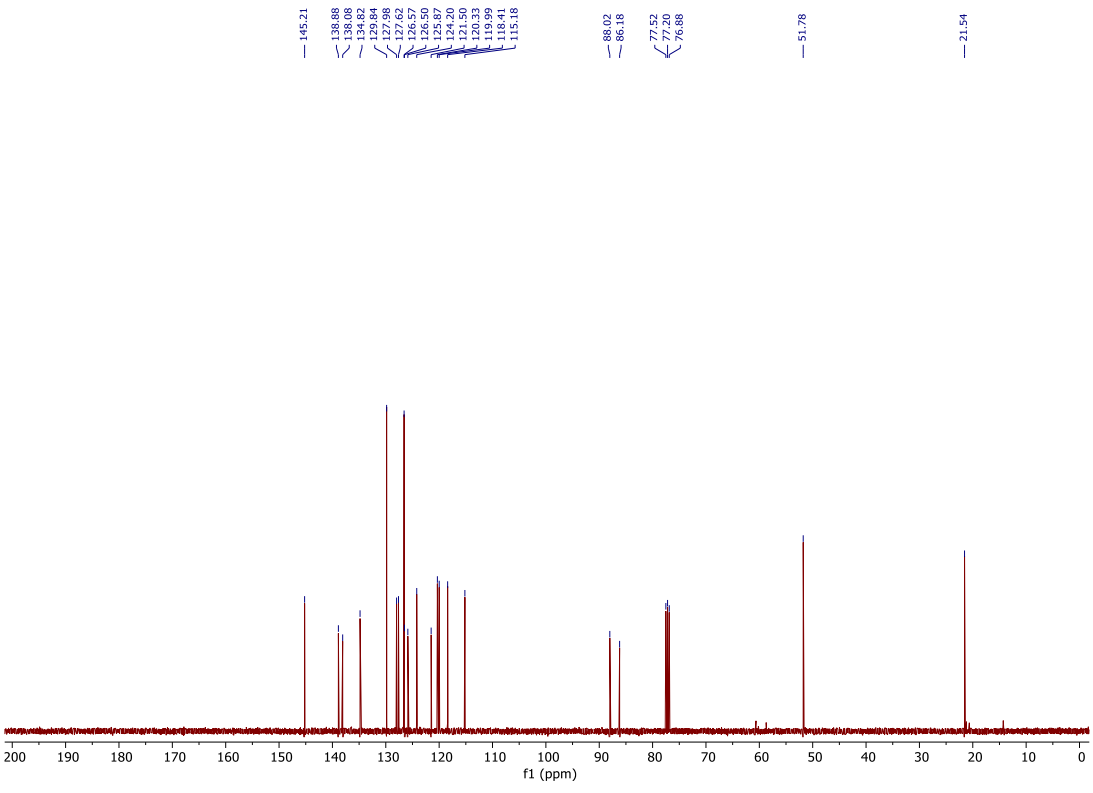
HRMS data of **14a**




$^{1}$H NMR (400 MHz, $CDCl_3$) of **14b**




$^{13}$C NMR (101 MHz, $CDCl_3$) of **14b**

# Display Report

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| Sample Name | ab_ram_184 | Instrument | maXis impact 8282001.00127 |
| Comment | | | |

**Acquisition Parameter**

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| Focus | Active | Set Capillary | 4500 V | Set Dry Heater | 200 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 4.0 l/min |
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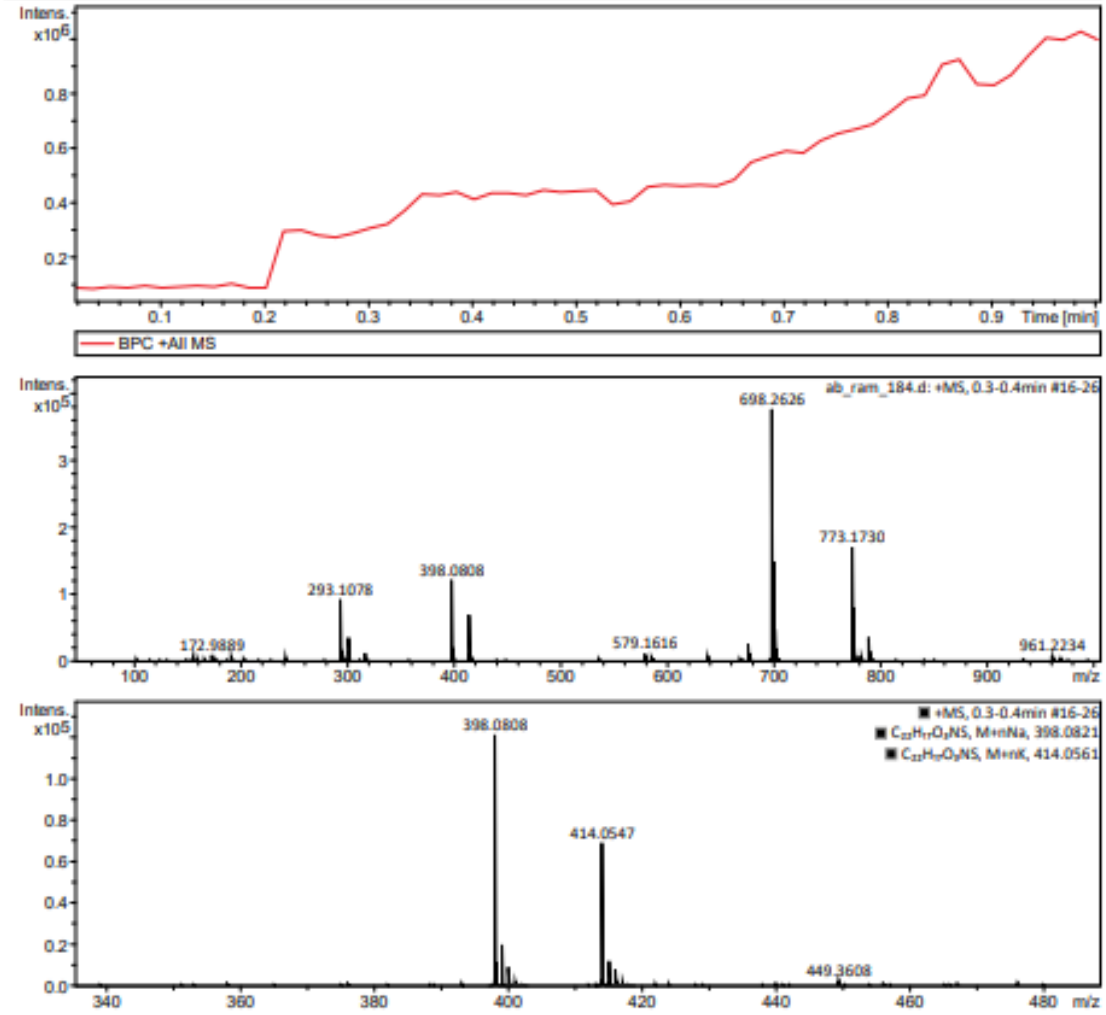
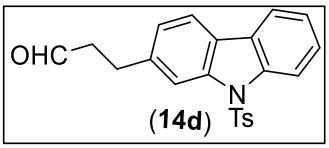
| | | Set Corona | 0 nA | Set APCI Heater | 0 °C |






HRMS data of **14b**



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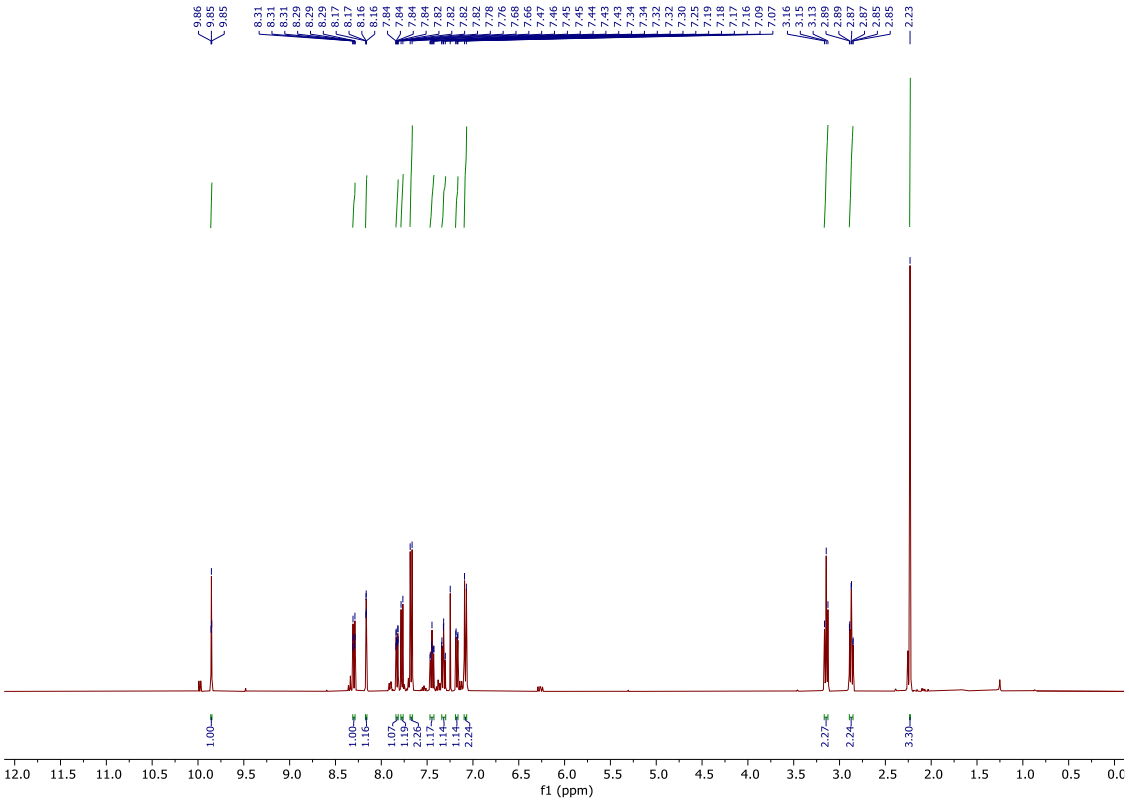
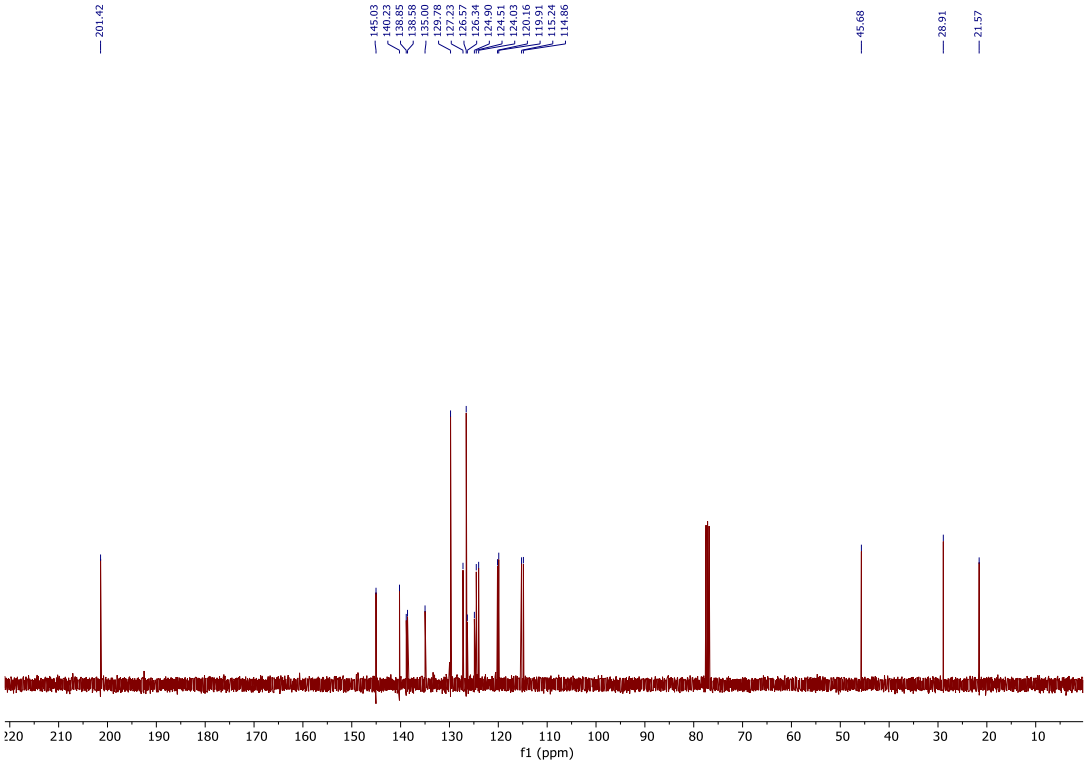



$^{1}$H NMR (400 MHz, $CDCl_3$) of **14d**




$^{13}$C NMR (126 MHz, $CDCl_3$) of **14d**

# Display Report

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| Method | Tune_pos_Standard_July2022.m | Operator | IISER Kolkata |
| Sample Name | ab_ram_188 | Instrument | maXis impact 8282001.00127 |
| Comment | | | |

**Acquisition Parameter**

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| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Active | Set Capillary | 4500 V | Set Dry Heater | 200 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 4.0 l/min |
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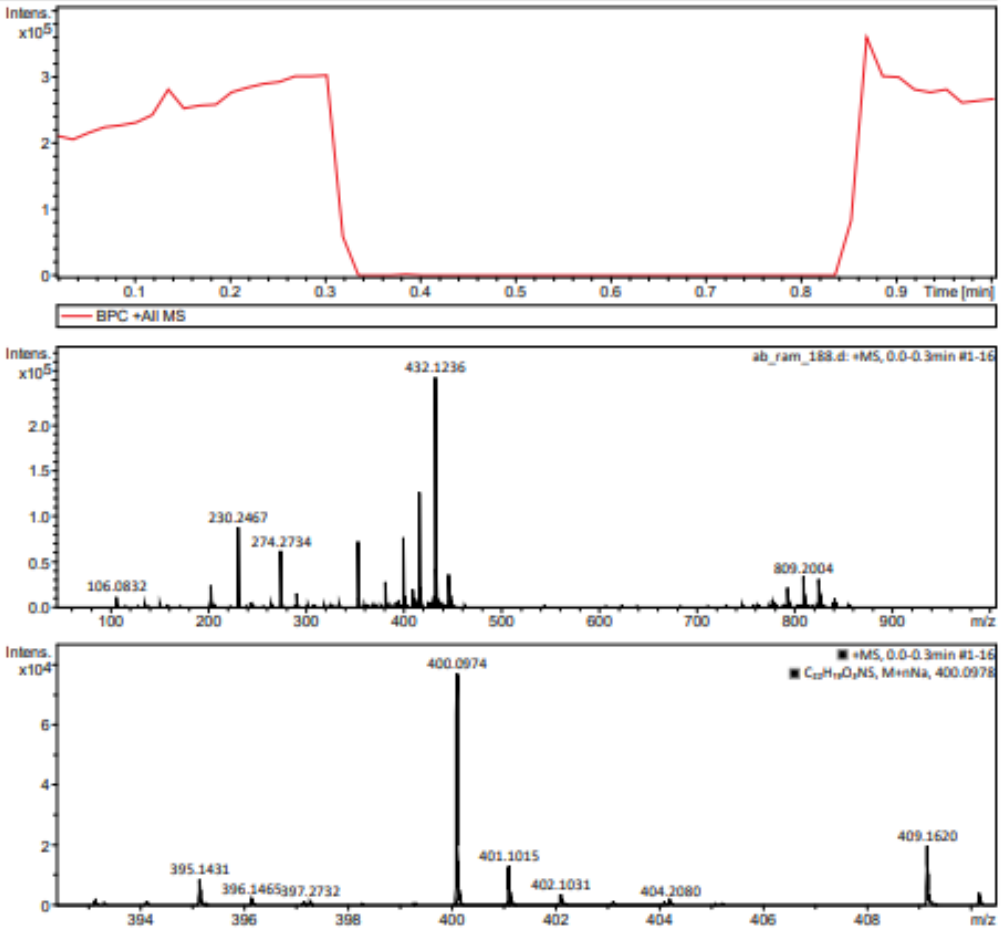
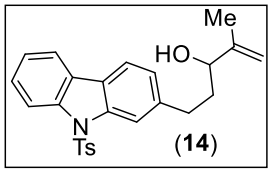
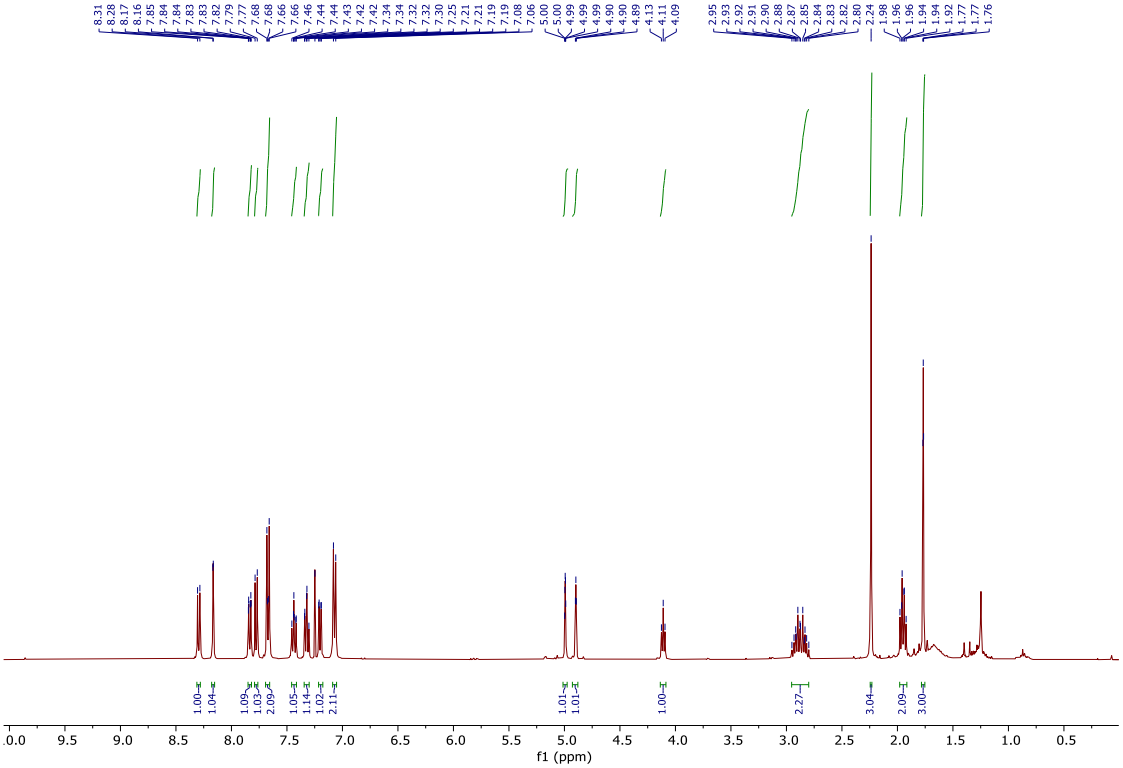
| | | Set Corona | 0 nA | Set APCI Heater | 0 °C |



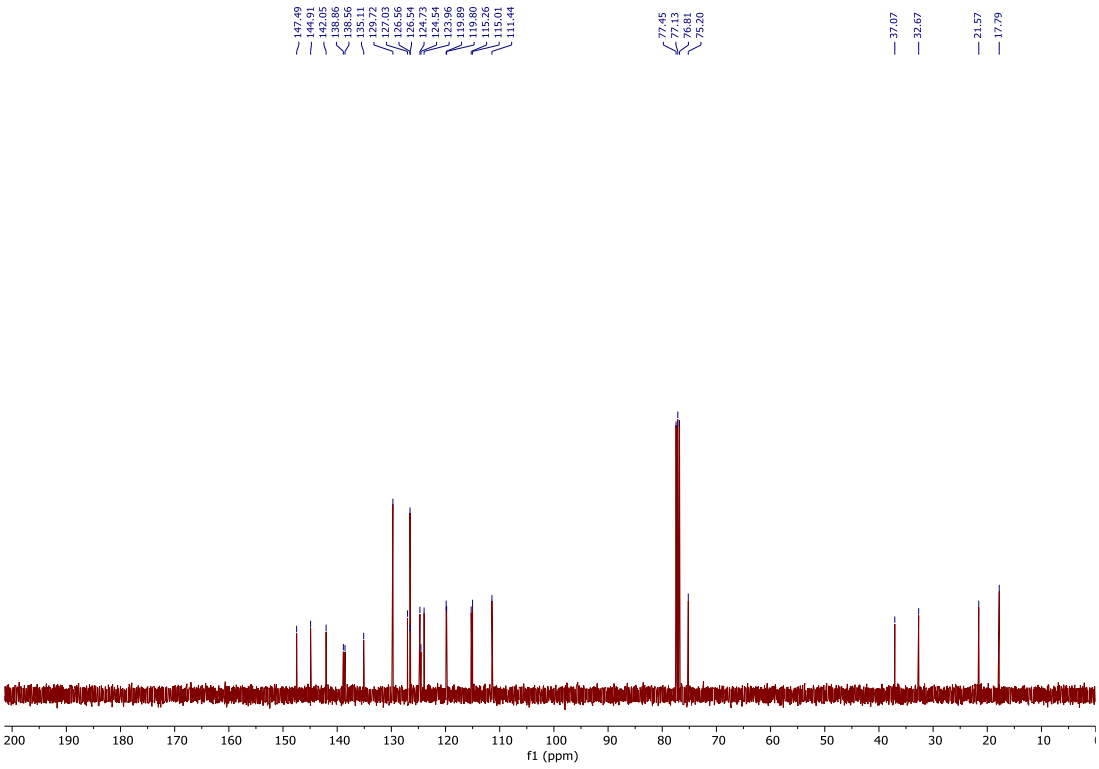



HRMS data of **14d**




$^{1}$H NMR (400MHz, $CDCl_3$) of **14**




$^{13}$C NMR (101 MHz, $CDCl_3$) of **14**

# Display Report

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| Method | Tune_pos_Standard_July2022.m | Operator | IISER Kolkata |
| Sample Name | ab_ram_320_1 | Instrument | maXis impact 8282001.00127 |
| Comment | | | |

**Acquisition Parameter**

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| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Active | Set Capillary | 4500 V | Set Dry Heater | 200 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 4.0 l/min |
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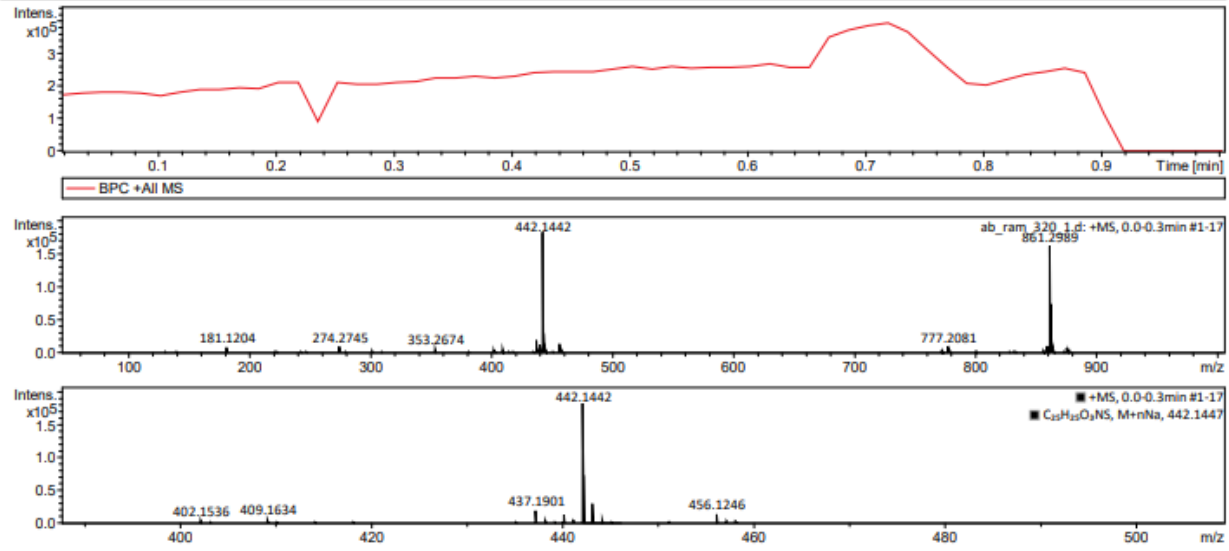


ab_ram_320_1.d

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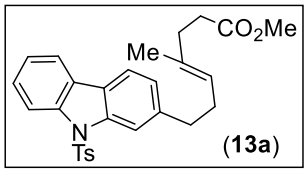
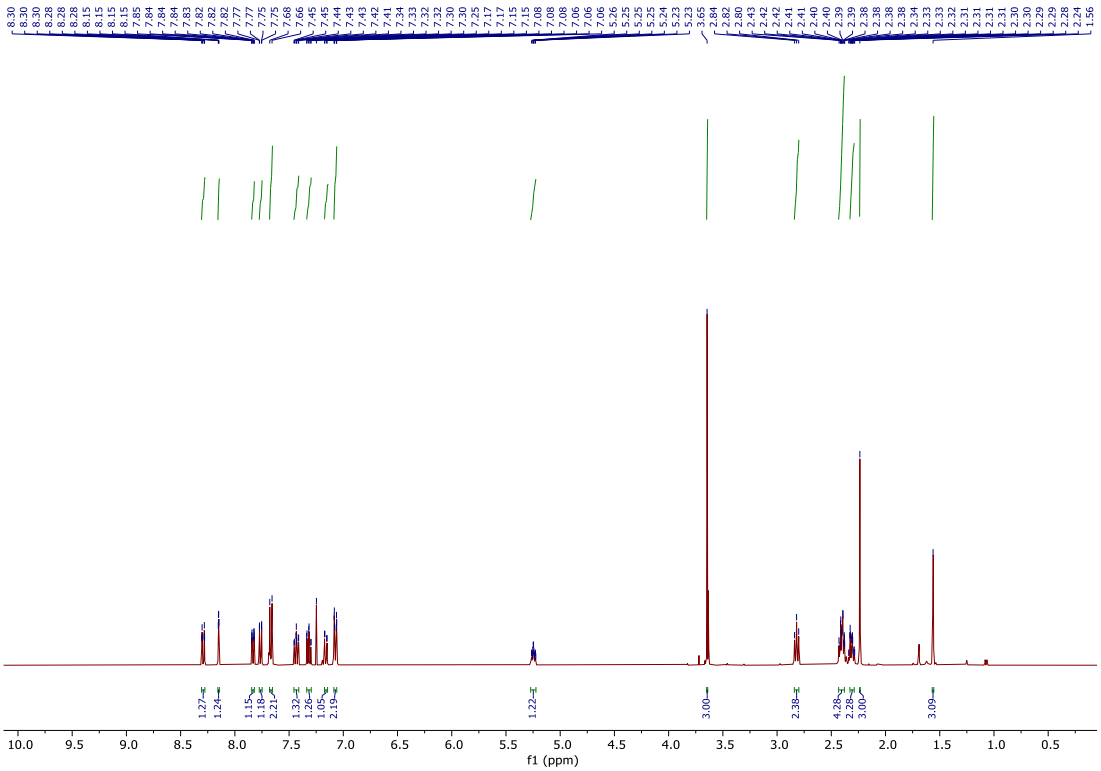
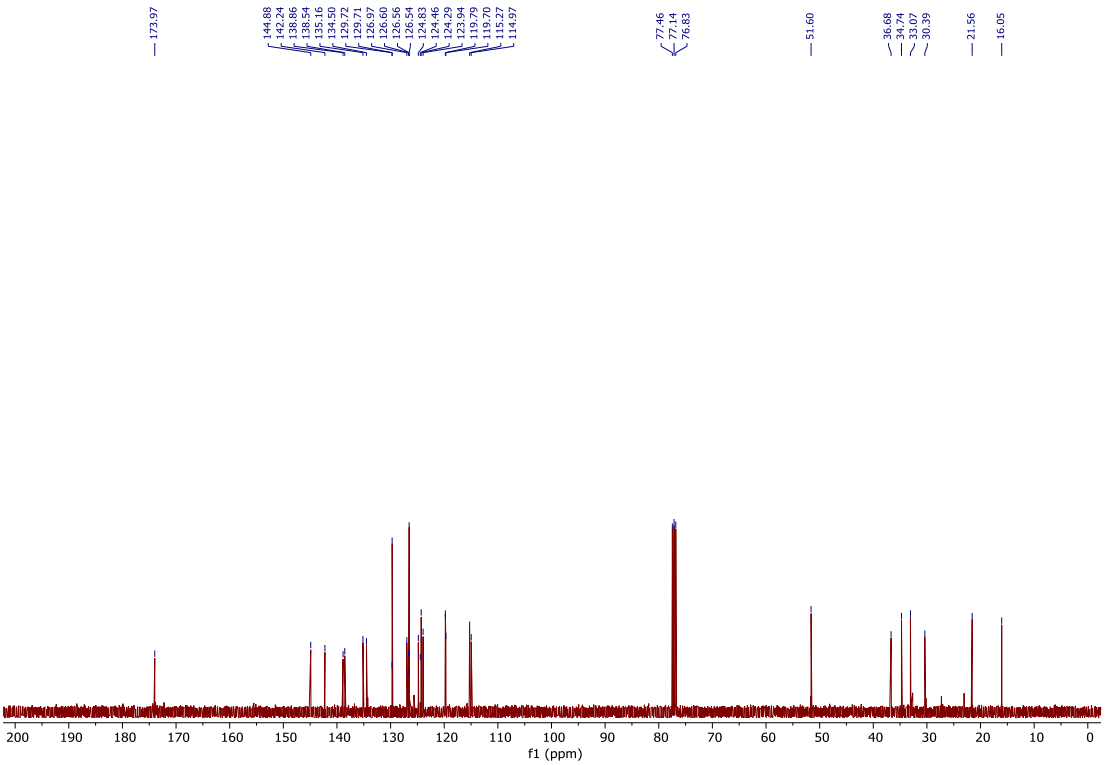
HRMS data of **14**




$^{1}$H NMR (500 MHz, $CDCl_3$) of **13a**




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

# Display Report

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| Method | Tune_pos_Standard_July2022.m | Operator | IISER Kolkata |
| Sample Name | AB_RAM_176 | Instrument | maXis impact 8282001.00127 |
| Comment | | | |

**Acquisition Parameter**

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| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Active | Set Capillary | 4500 V | Set Dry Heater | 200 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 4.0 l/min |
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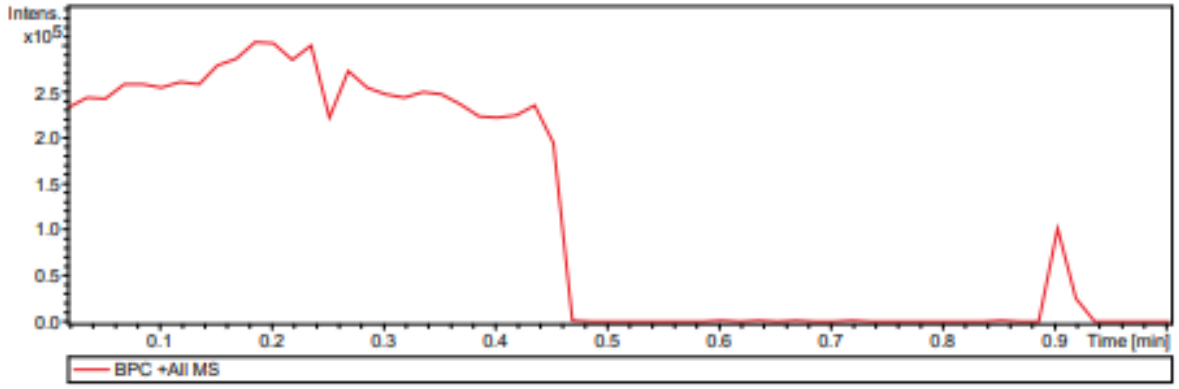
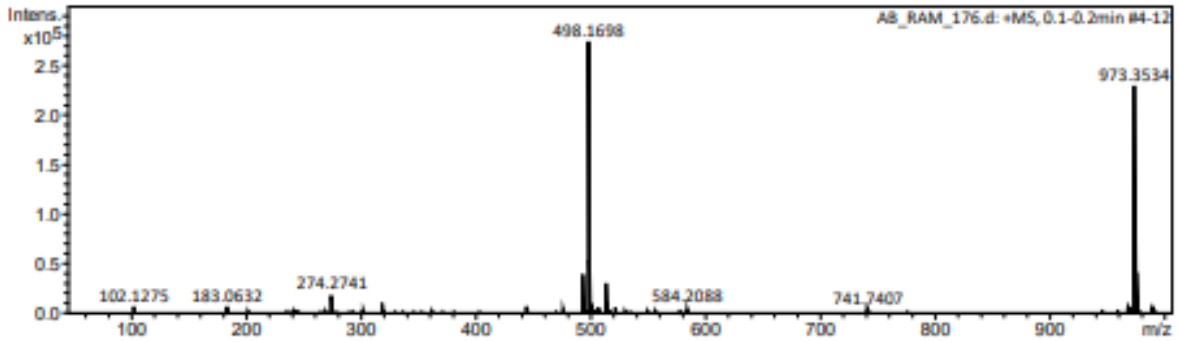
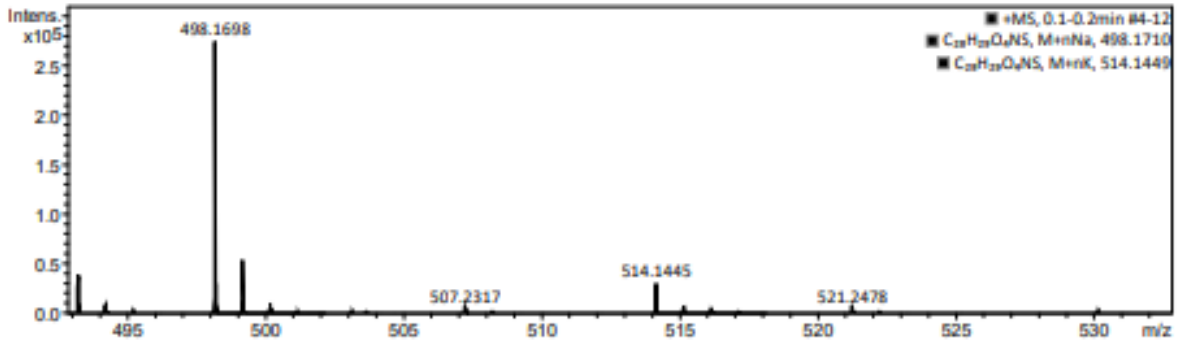
| | | Set Corona | 0 nA | Set APCI Heater | 0 °C |




AB_RAM_176.d

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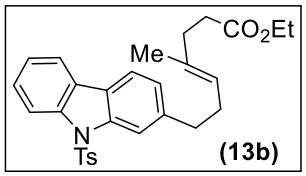
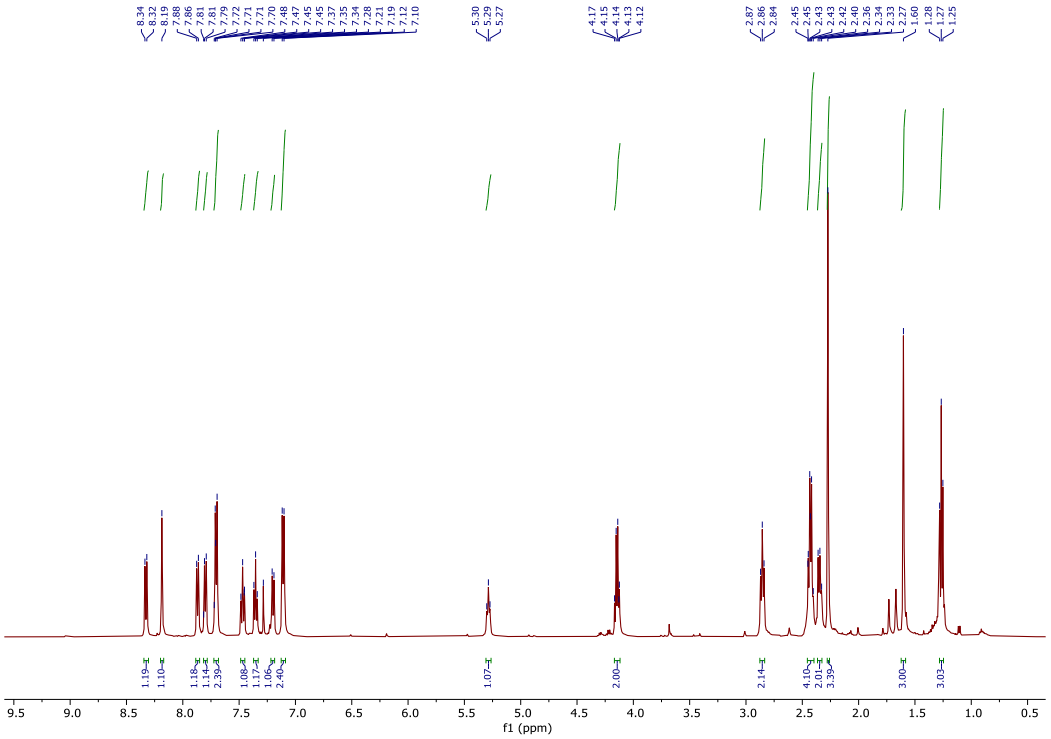
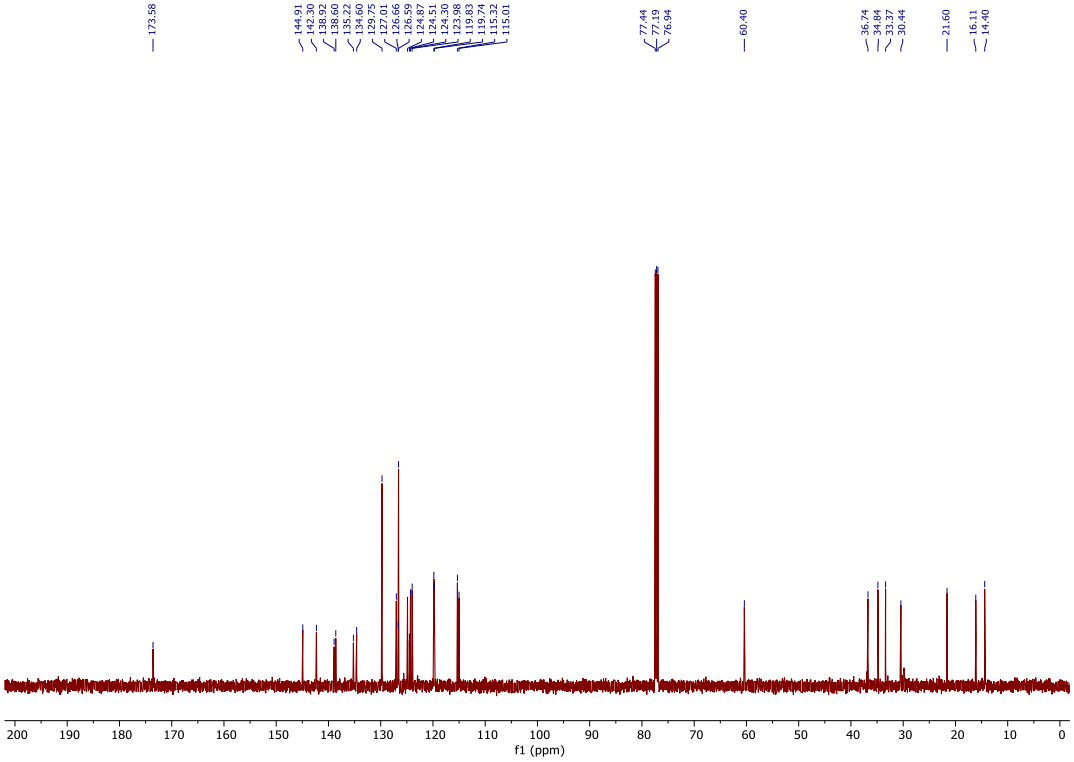
HRMS data of **13a**

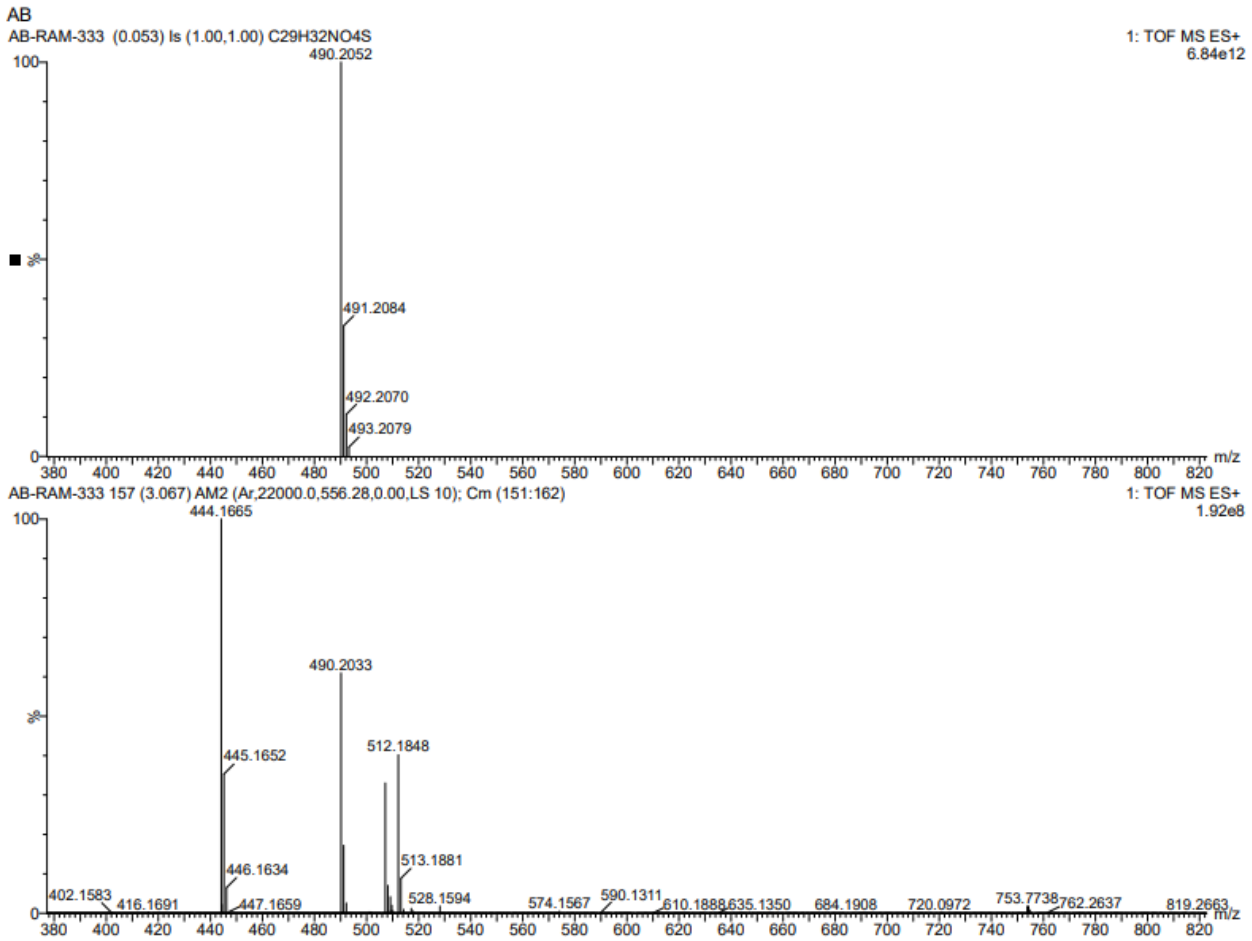


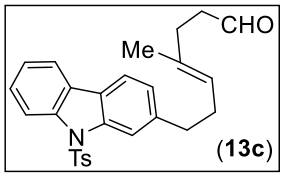

$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **13b**

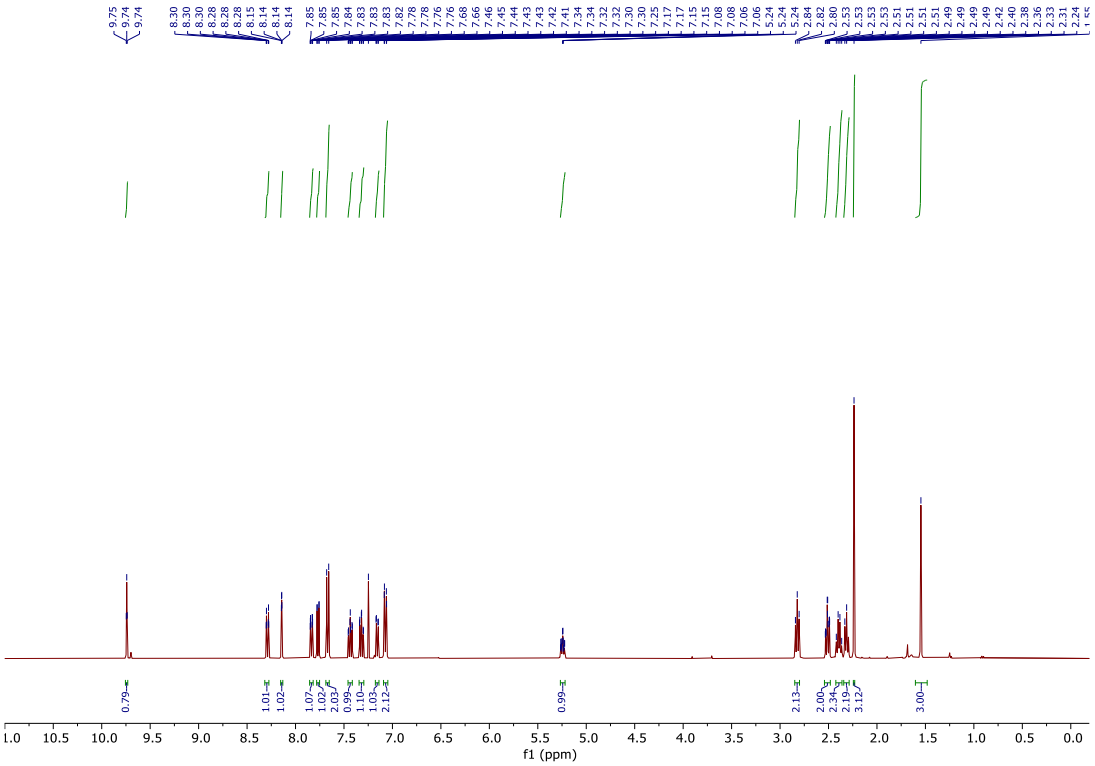



$^{13}$C NMR (125 MHz, $CDCl_3$) of compound **13b**

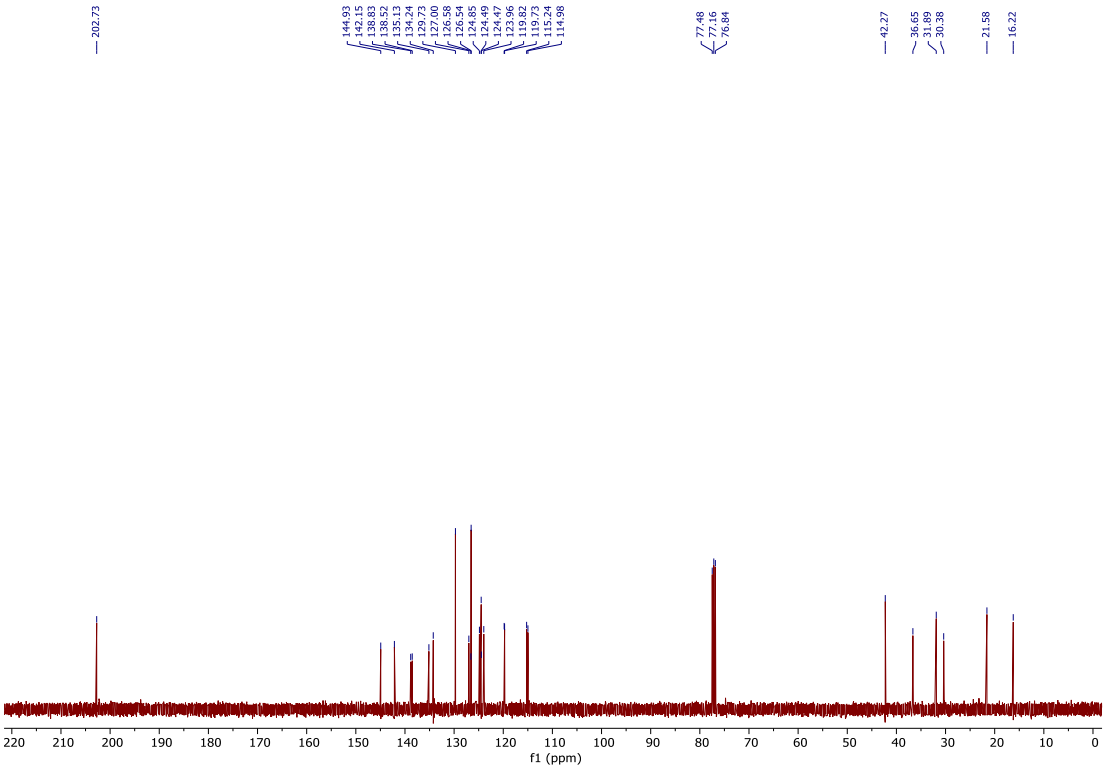



HRMS data of **13b**

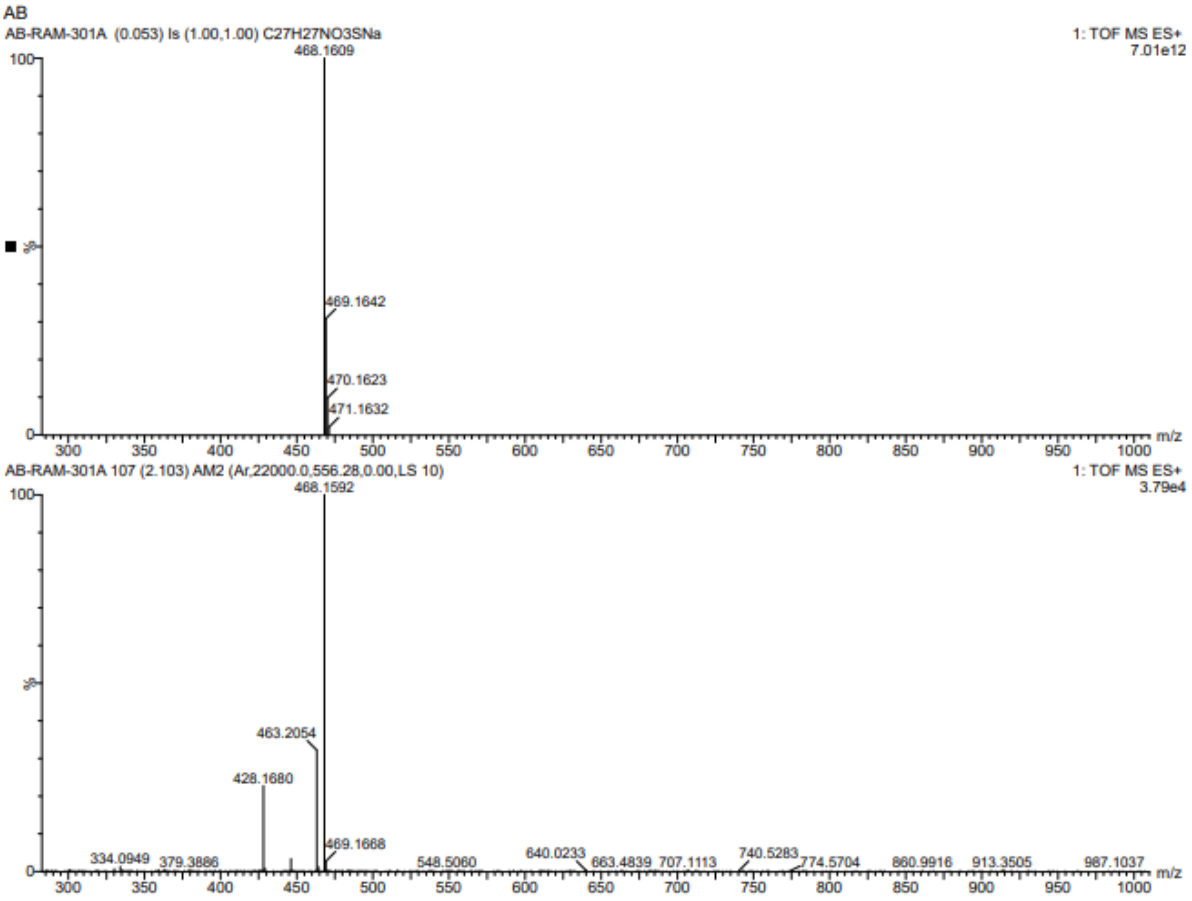


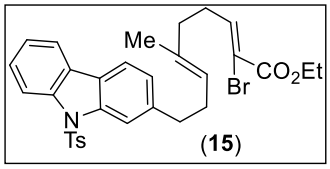

$^{1}$H NMR (400 MHz, $CDCl_3$) of **13c**



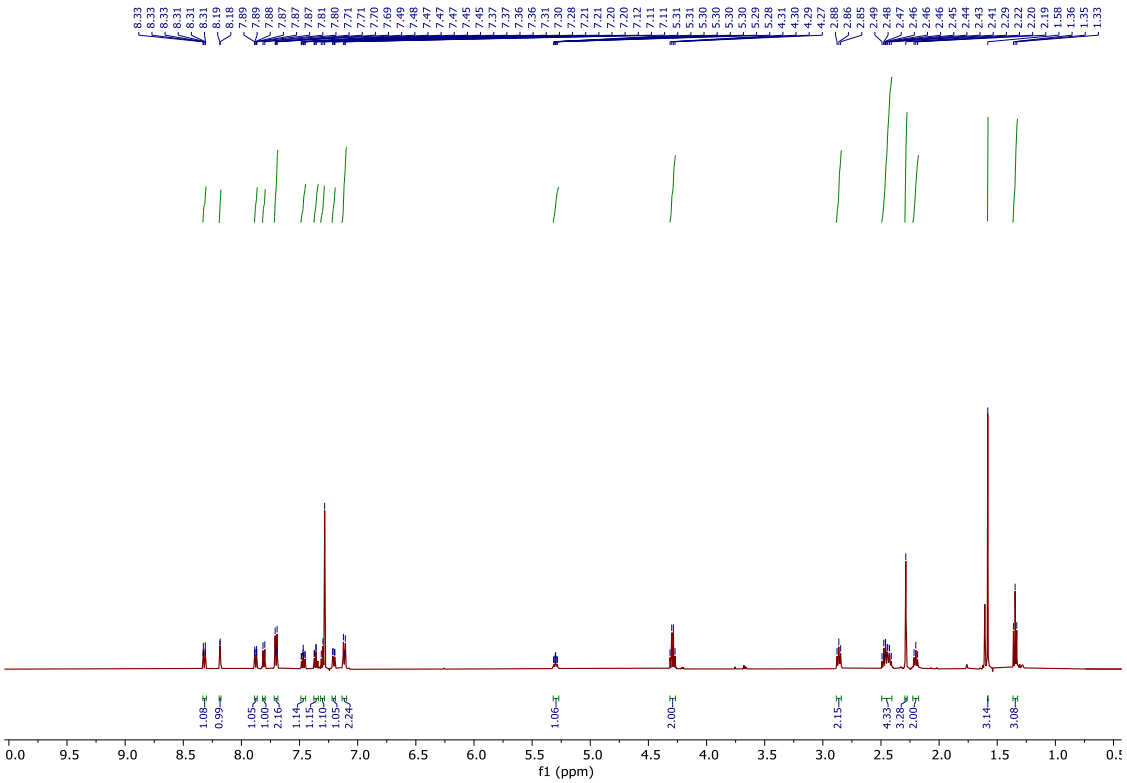

$^{13}$C NMR (126 MHz, $CDCl_3$) of **13c**



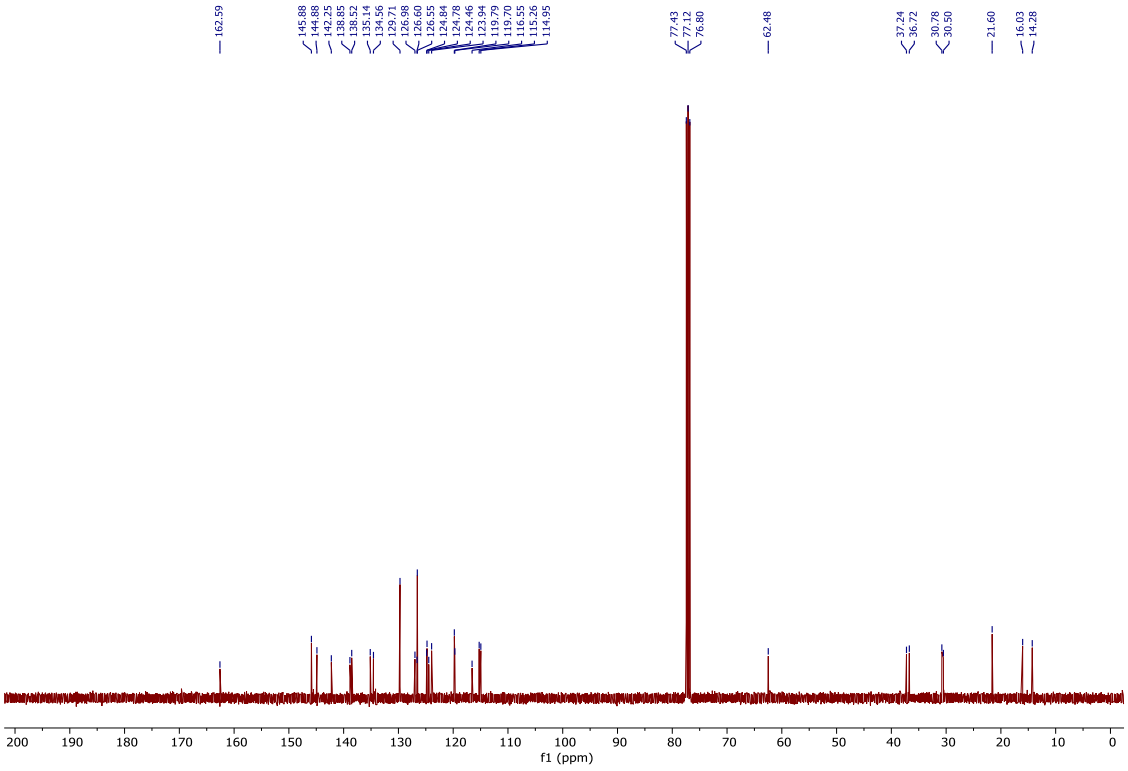

HRMS data of **13c**




(**15**)




$^{1}$H NMR (500 MHz, $CDCl_3$) of **15**




$^{13}$C NMR (101 MHz, $CDCl_3$) of **15**

# Display Report

**Analysis Info**

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| Method | Tune_pos_Standard.m | Operator | IISER Kolkata |
| Sample Name | AB_RAM_303 | Instrument | maXis impact 8282001.00127 |
| Comment | | | |

**Acquisition Parameter**

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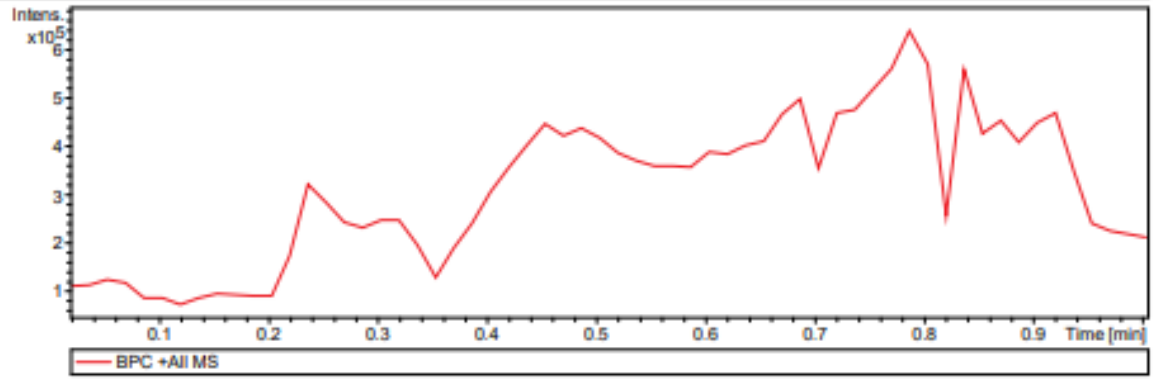
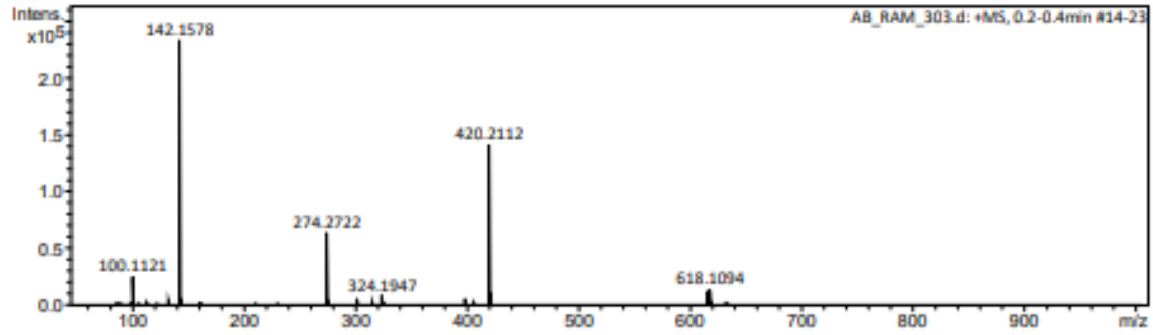
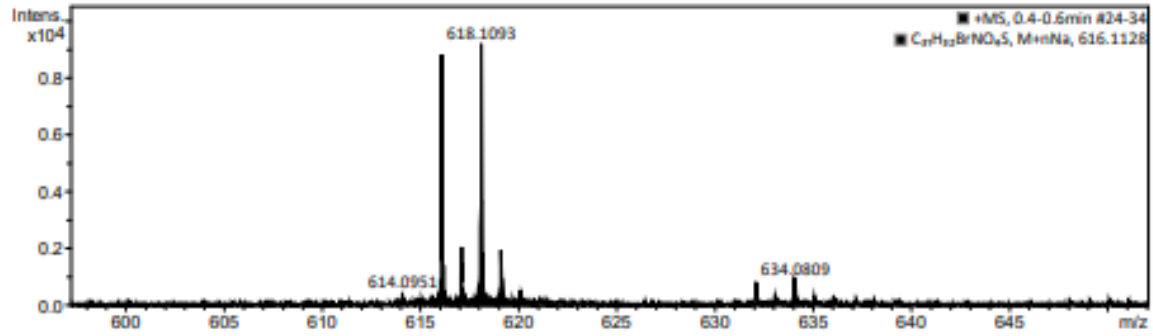
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.5 Bar |
| Focus | Active | Set Capillary | 3400 V | Set Dry Heater | 200 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 1000 m/z | Set Charging Voltage | 2000 V | Set Divert Valve | Source |
| | | Set Corona | 0 nA | Set APCI Heater | 0 °C |




AB_RAM_303.d

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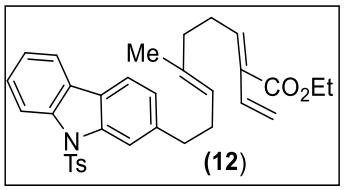
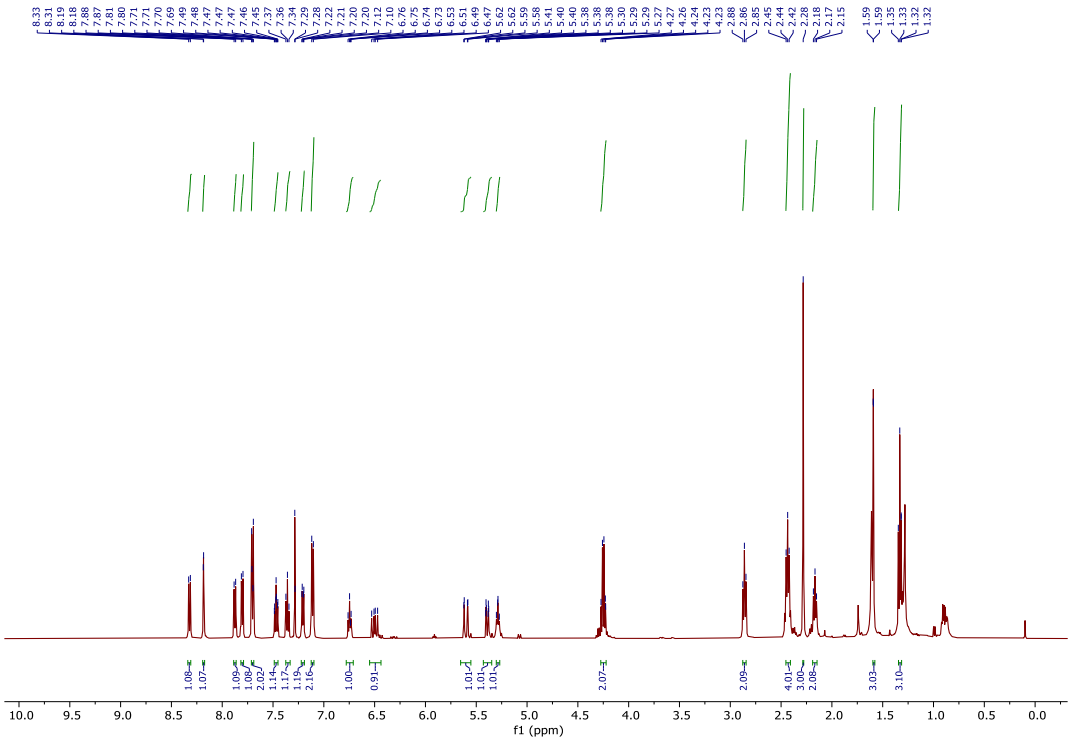
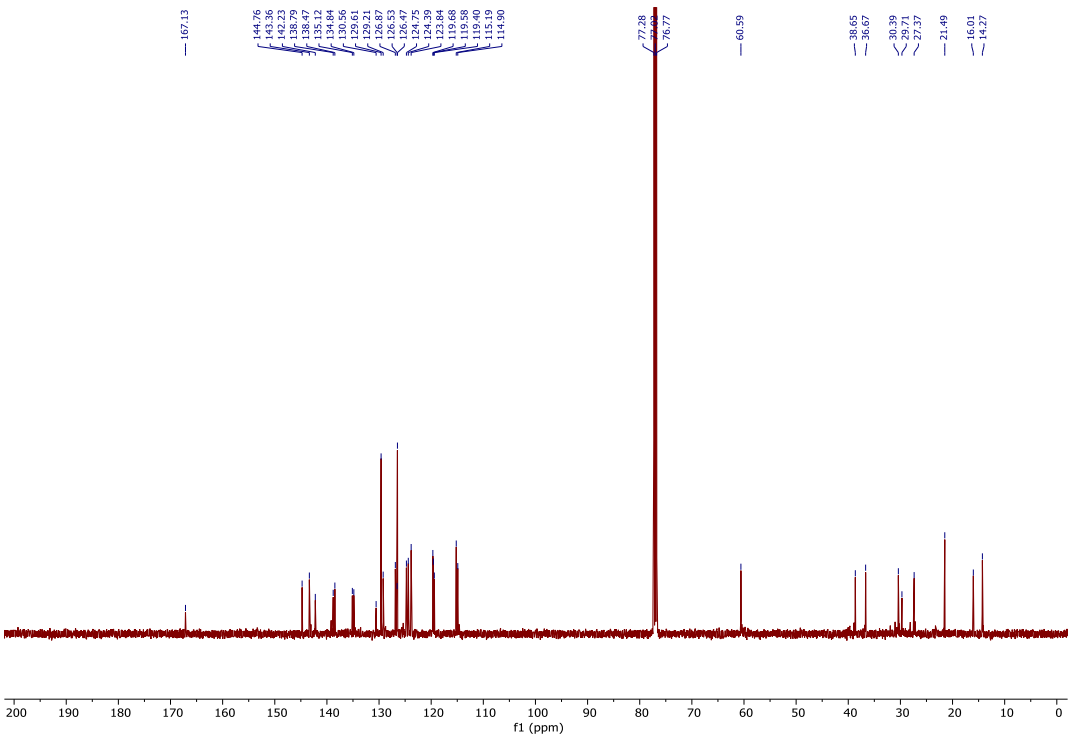



$^{1}$H NMR (500 MHz, $CDCl_3$) of **12**




$^{13}$C NMR (126 MHz, $CDCl_3$) of **12**

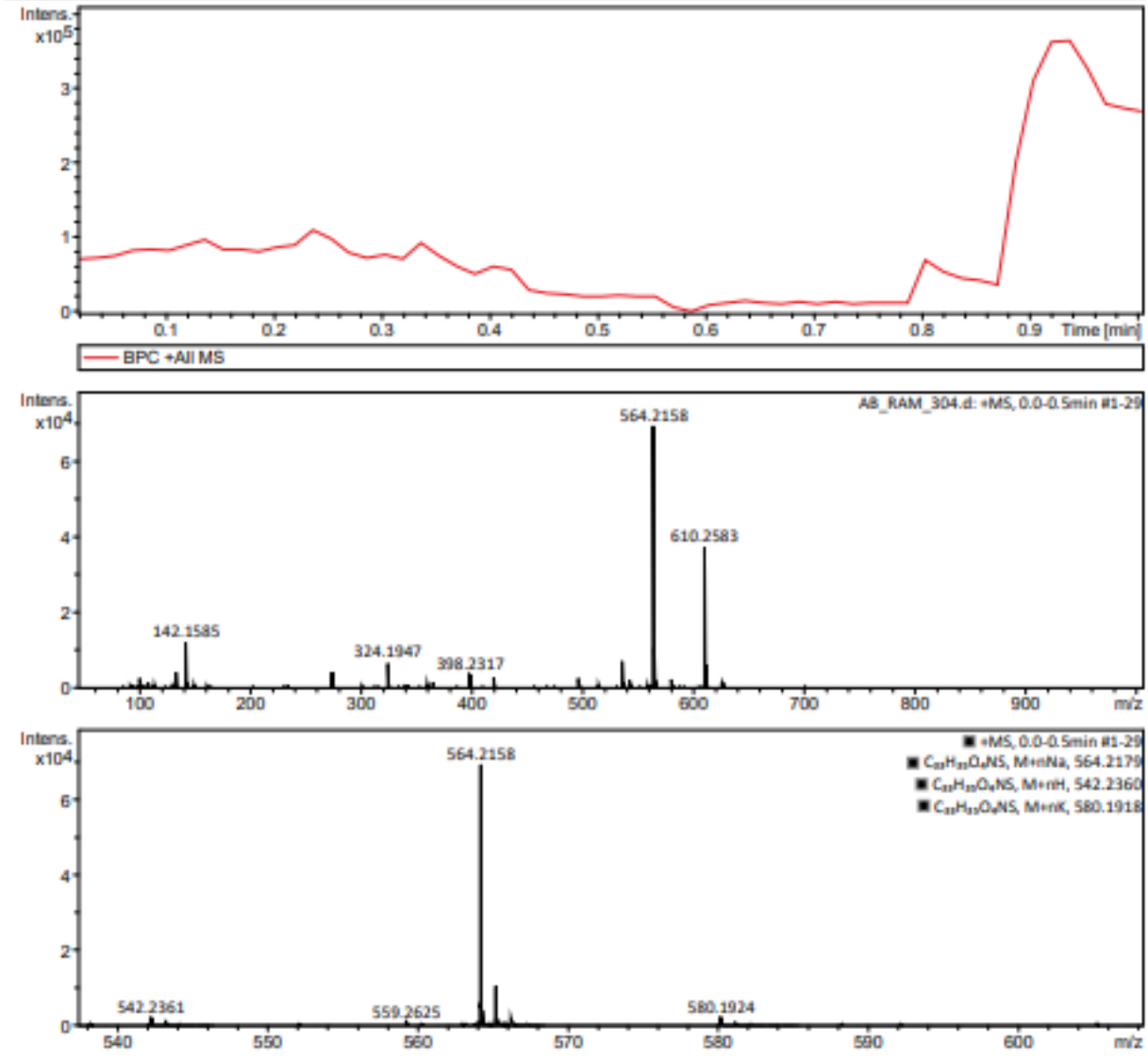
# Display Report

**Analysis Info**

| | | | |
|---|---|---|---|
| Analysis Name | D:\Data\User data\2022\JUNE\AB_RAM_304.d | Acquisition Date | 6/20/2022 1:17:01 PM |
| Method | Tune_pos_Standard.m | Operator | IISER Kolkata |
| Sample Name | AB_RAM_304 | Instrument | maXis impact 8282001.00127 |
| Comment | | | |

**Acquisition Parameter**

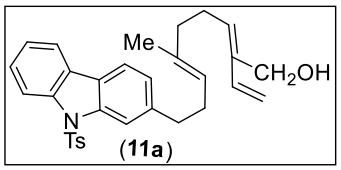
| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.5 Bar |
| Focus | Active | Set Capillary | 3400 V | Set Dry Heater | 200 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 1000 m/z | Set Charging Voltage | 2000 V | Set Divert Valve | Source |
| | | Set Corona | 0 nA | Set APCI Heater | 0 °C |

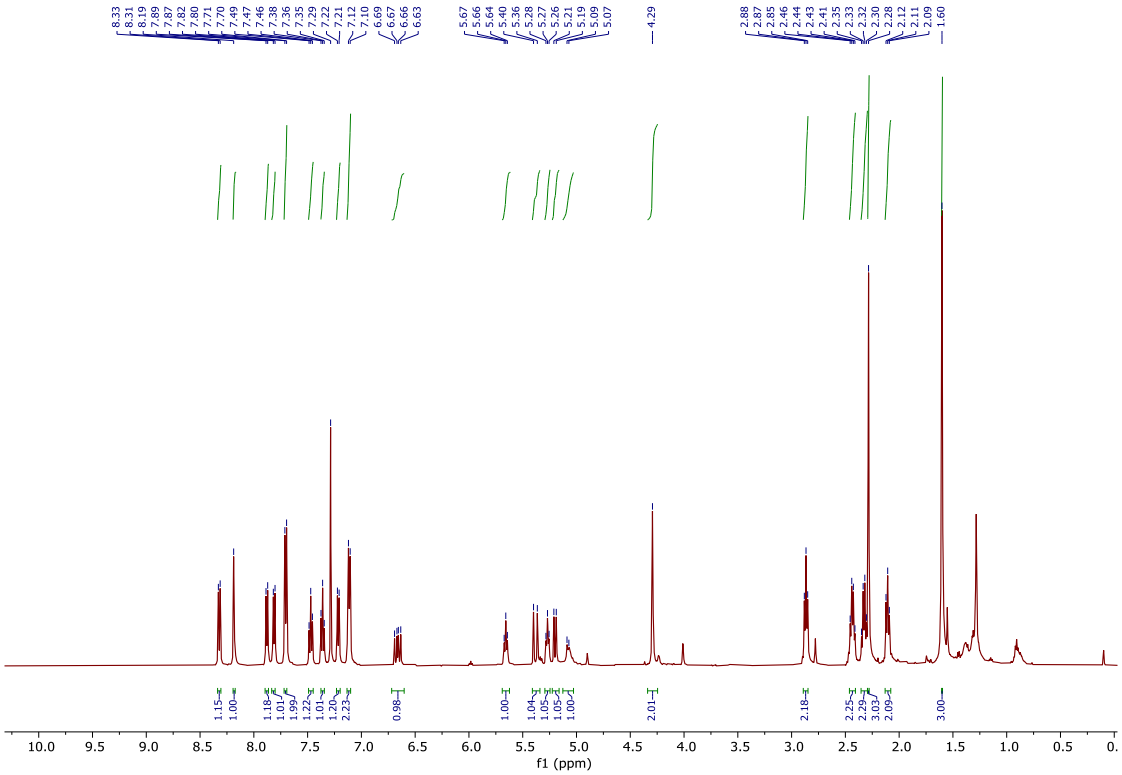



AB_RAM_304.d

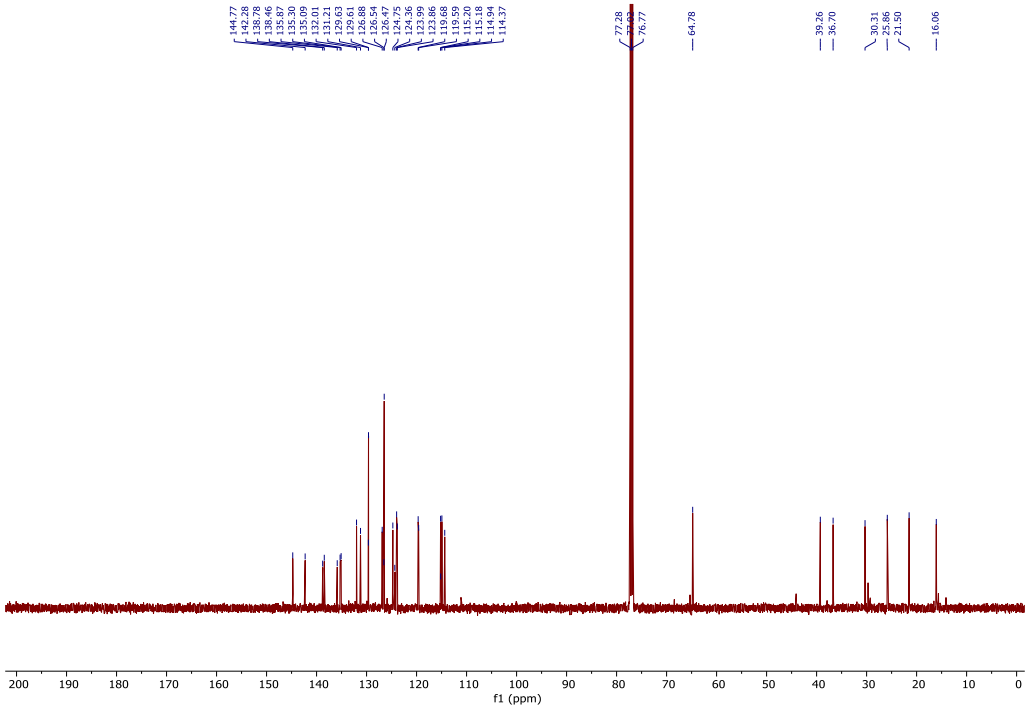
Bruker Compass DataAnalysis 4.1 printed: 6/20/2022 1:25:30 PM by: IISER Kolkata Page 1 of 1

HRMS data of **12**




$^{1}$H NMR (500 MHz, $CDCl_3$) of **11a**




$^{13}$C NMR (126 MHz, $CDCl_3$) of **11a**

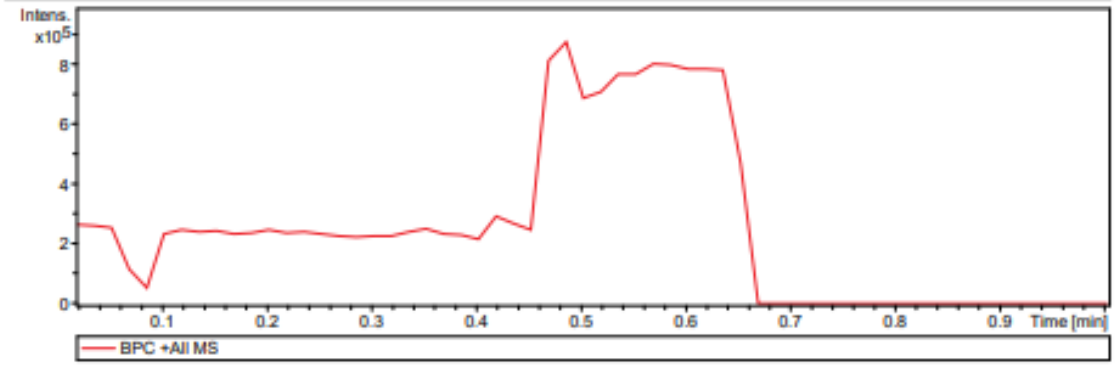
# Display Report

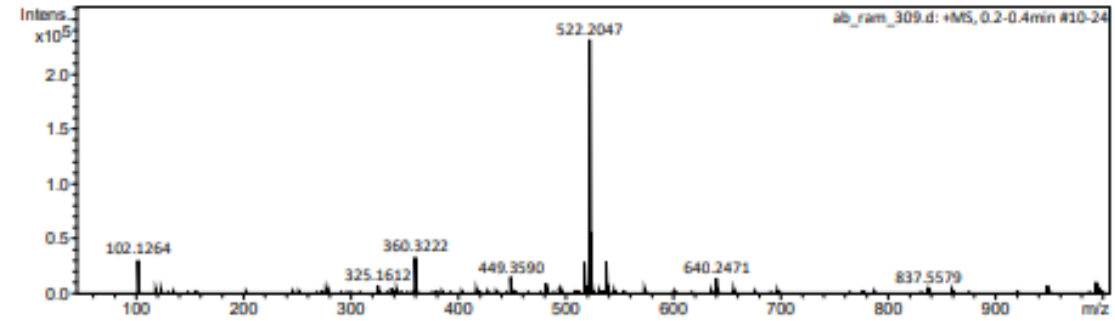
**Analysis Info**

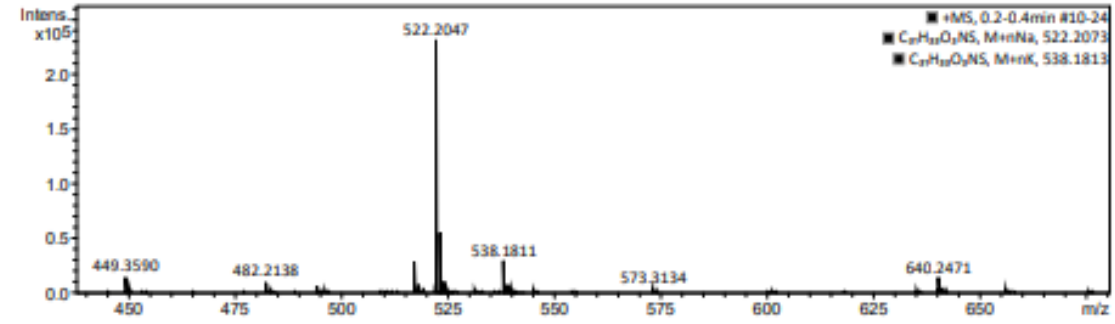
| | | | |
|---|---|---|---|
| Analysis Name | D:\Data\User data\2022\AUGUST\ab_ram_309.d | Acquisition Date | 8/22/2022 11:36:12 AM |
| Method | Tune_pos_Standard_July2022.m | Operator | IISER Kolkata |
| Sample Name | ab_ram_309 | Instrument | maXis impact 8282001.00127 |
| Comment | | | |

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Active | Set Capillary | 4500 V | Set Dry Heater | 200 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 1000 m/z | Set Charging Voltage | 2000 V | Set Divert Valve | Source |
| | | Set Corona | 0 nA | Set APCI Heater | 0 °C |

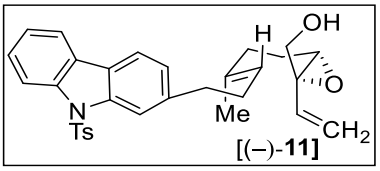


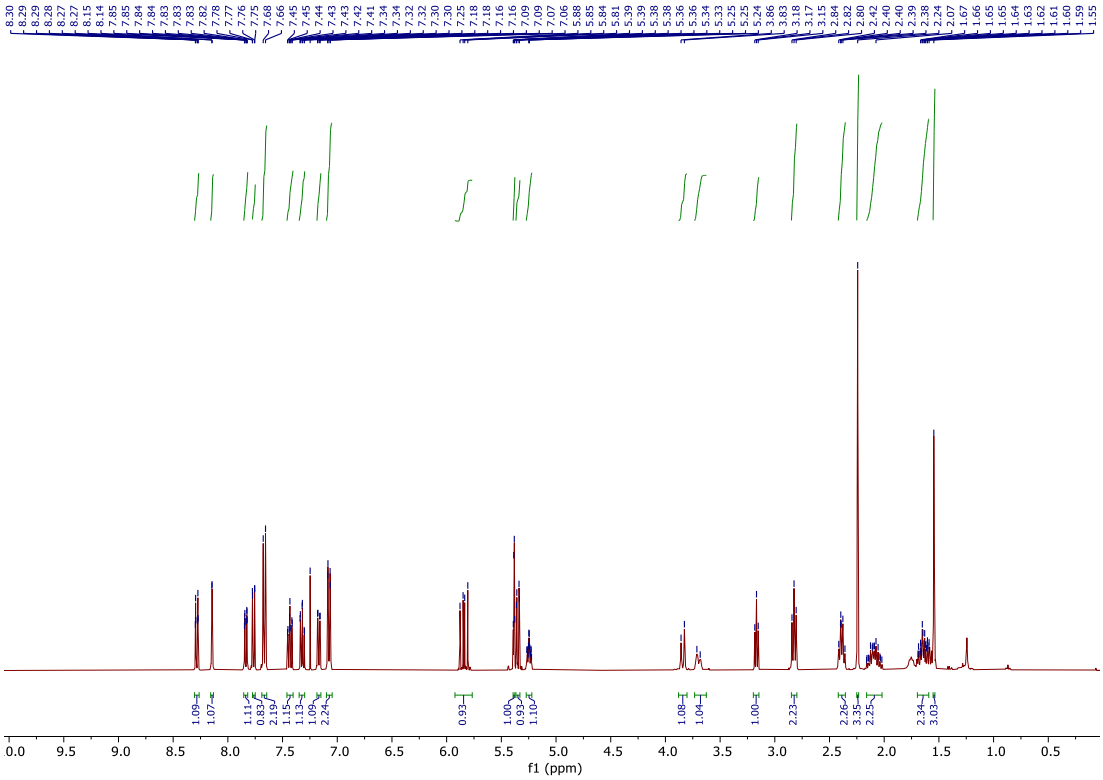



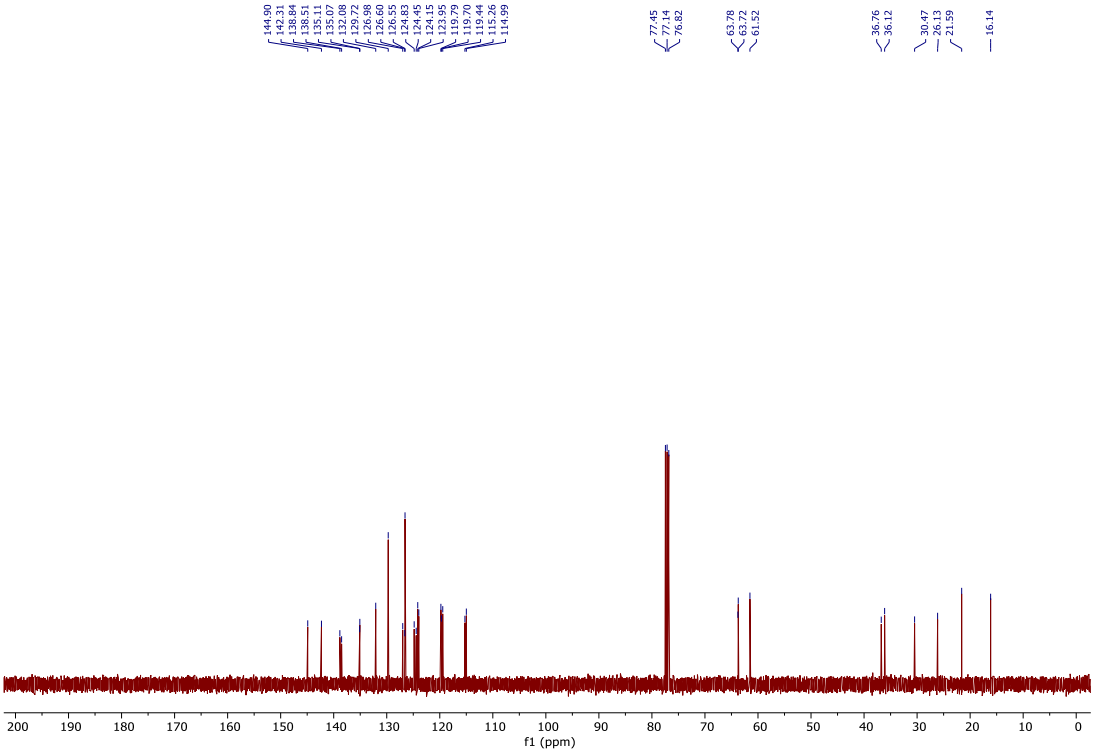



HRMS data of **11a**




$^{1}$H NMR (400 MHz, $CDCl_3$) of compound : [(–)-**11**]




$^{13}$C NMR (101 MHz, $CDCl_3$) of compound : [(–)-**11**]

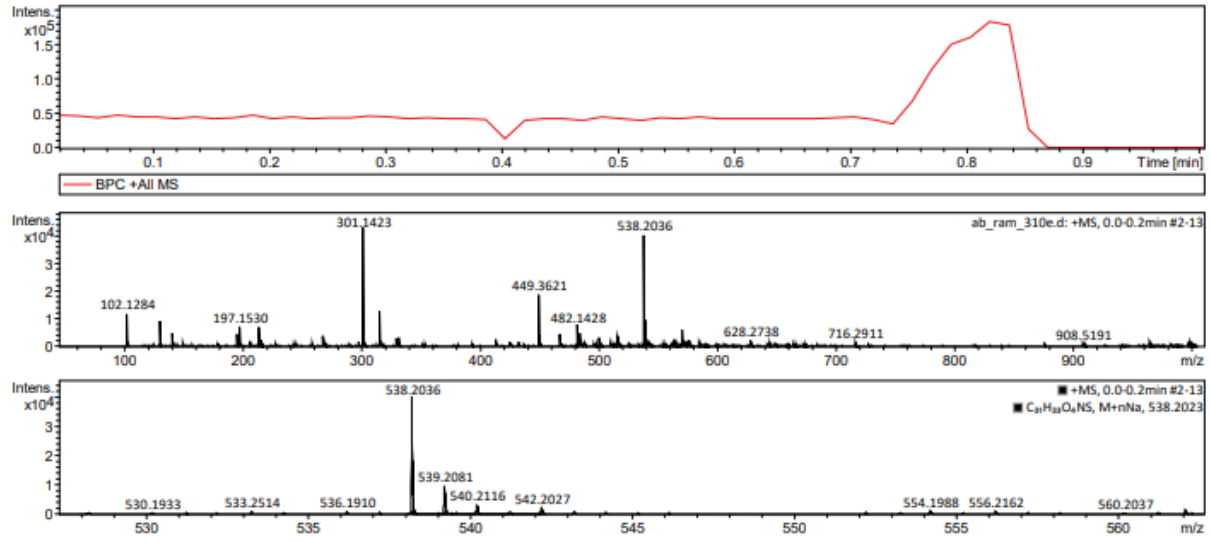
# Display Report

**Analysis Info**

| | | | |
|---|---|---|---|
| Analysis Name | D:\Data\User data\2022\NOV\ab_ram_310e.d | Acquisition Date | 11/7/2022 11:38:22 AM |
| Method | Tune_pos_Standard_July2022.m | Operator | IISER Kolkata |
| Sample Name | ab_ram_310e | Instrument | maXis impact 8282001.00127 |
| Comment | | | |

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Active | Set Capillary | 4500 V | Set Dry Heater | 200 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 1000 m/z | Set Charging Voltage | 2000 V | Set Divert Valve | Source |
| | | Set Corona | 0 nA | Set APCI Heater | 0 °C |












HRMS data of : [(–)-**11**]

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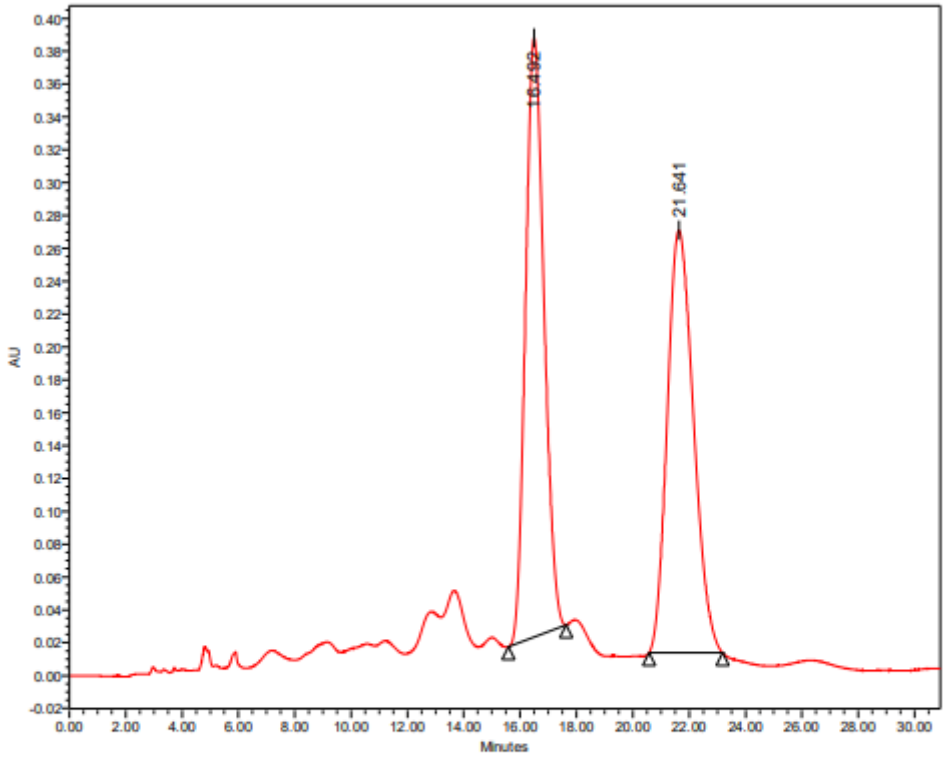
Peak Summary Report




Sample Name: AB_RAM_310_AS-H_15_01_RAC; Date Acquired: 10-03-2023 15:27:22 IST; Vial: 1
Injection: 1

**Peak Summary with Statistics**
**Name:**

| | Sample Name | Vial | Inj | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|---|---|
| 1 | AB_RAM_310_AS-H_15_01_RAC | 1 | 1 | 21.641 | 16603866 | 49.93 | 257196 |
| 2 | AB_RAM_310_AS-H_15_01_RAC | 1 | 1 | 16.492 | 16651571 | 50.07 | 364755 |
| Mean | | | | 19.067 | | | |
| Std. Dev. | | | | 3.641 | | | |

Reported by User: System
Report Method: Peak Summary Report
Report Method ID 1009
Page: 1 of 2

Project Name: AB Research Group
Date Printed:
10-03-2023
16:01:31 Asia/Calcutta

**Peak Summary with Statistics**
**Name:**

| | Sample Name | Vial | Inj | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|---|---|
| % RSD | | | | 19.10 | | | |

**HPLC Data for [(±)-11]-(AS-H Column)**

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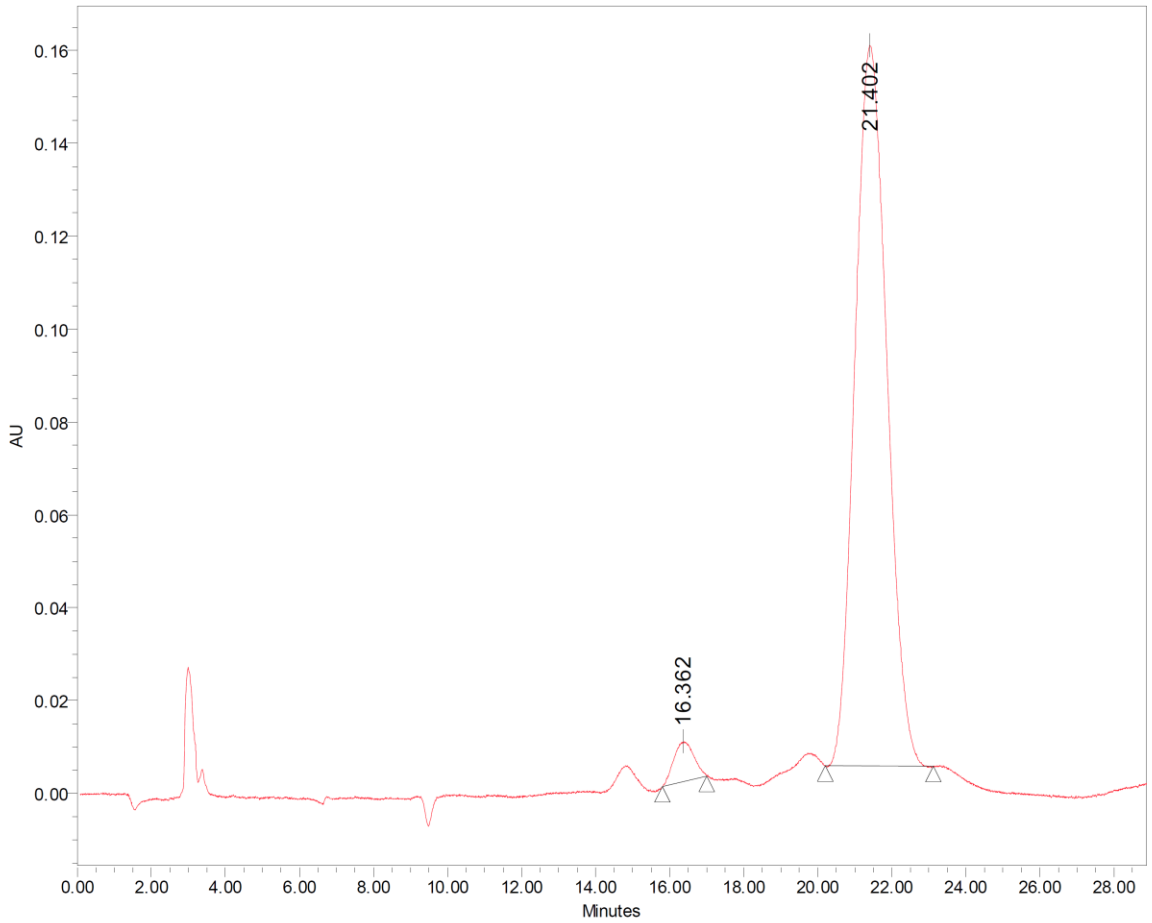
# Peak Summary Report



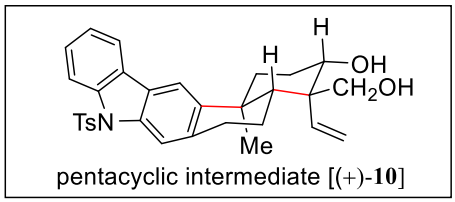

Sample Name: AB_RAM_310_AS-H_15_1_CHI; Date Acquired: 10-03-2023 22:36:48 IST; Vial: 1
Injection: 1

**Peak Summary with Statistics**
**Name:**

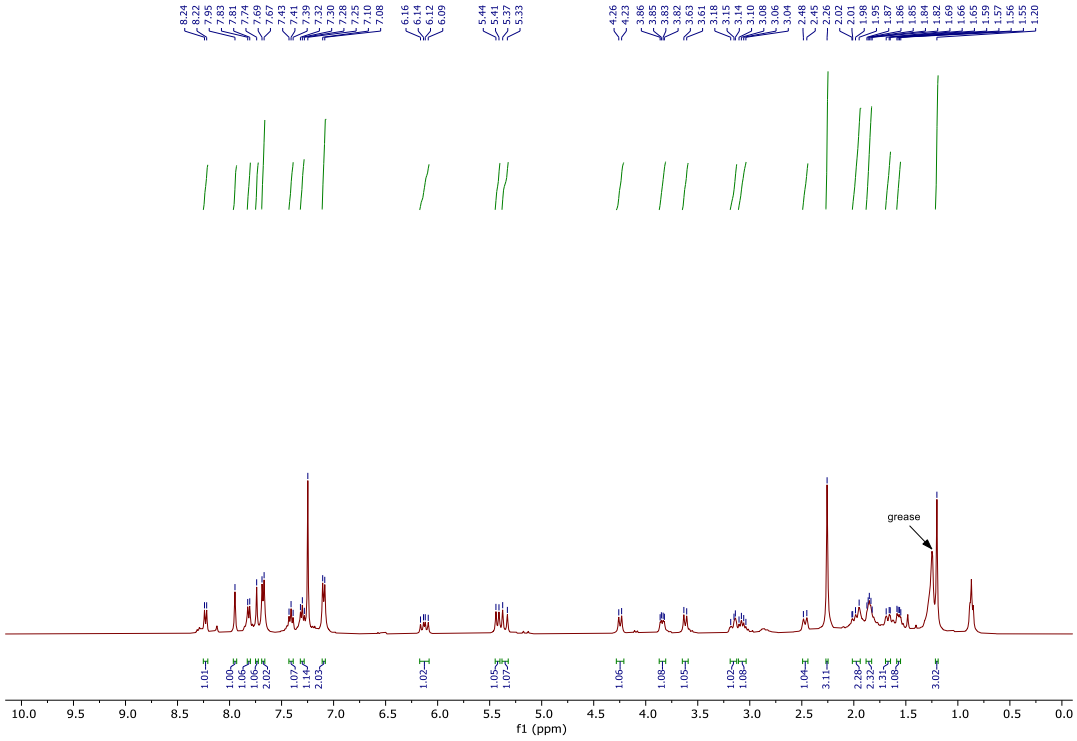
| | Sample Name | Vial | Inj | Retention Time (min) | Area | % Area | Height |
|---|---|---|---|---|---|---|---|
| 1 | AB_RAM_310_AS-H_15_1_CHI | 1 | 1 | 21.402 | 9311757 | 96.61 | 155198 |
| 2 | AB_RAM_310_AS-H_15_1_CHI | 1 | 1 | 16.362 | 326308 | 3.39 | 8643 |
| Mean | | | | 18.882 | | | |
| Std. Dev. | | | | 3.564 | | | |



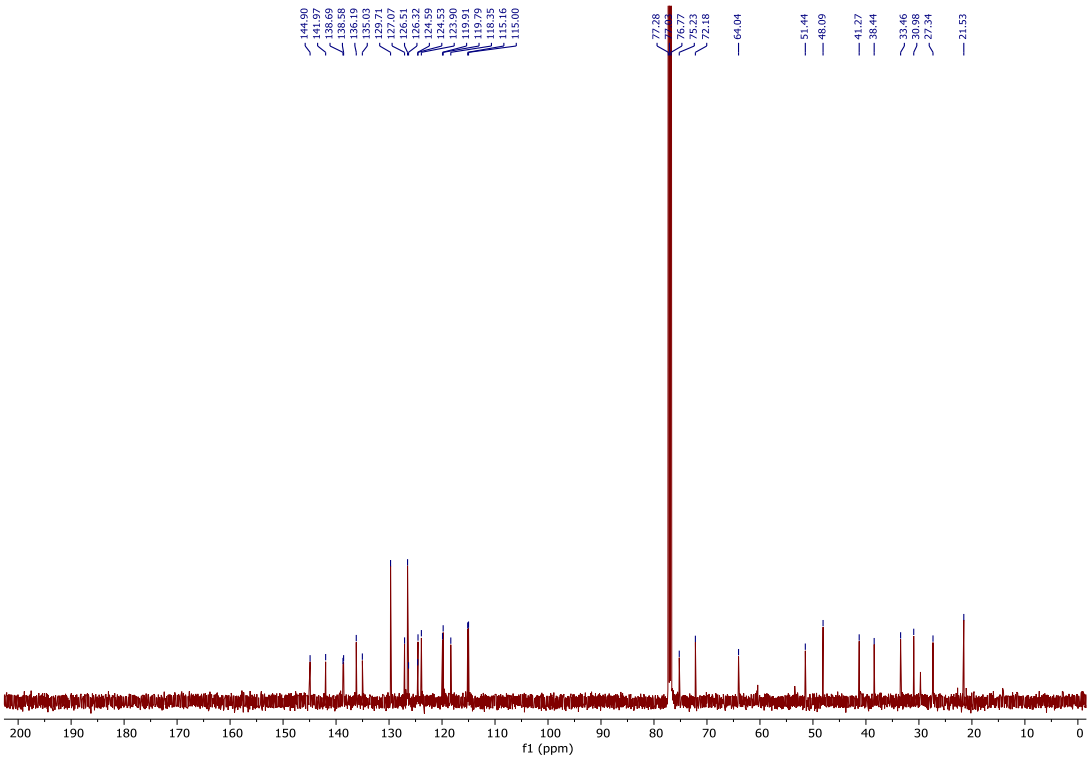
**HPLC Data for [(–)-11]-(AS-H Column)**



pentacyclic intermediate [(+)-**10**]




$^{1}$H NMR (500 MHz, $CDCl_3$) of compound [(+)-**10**]




$^{13}$C NMR (126 MHz, $CDCl_3$) of compound [(+)-**10**]

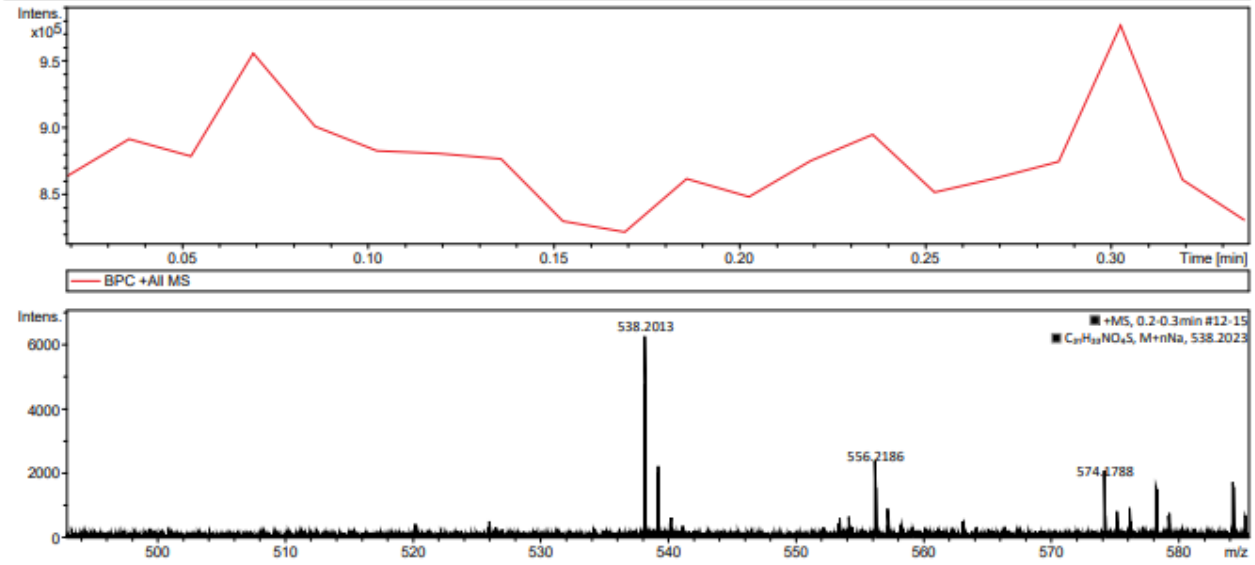
# Display Report

**Analysis Info**

| | | | |
|---|---|---|---|
| Analysis Name | D:\Data\User data\2022\DEC\ab-ram-337.d | Acquisition Date | 12/2/2022 3:49:26 PM |
| Method | Tune_pos_Standard_July2022.m | Operator | IISER Kolkata |
| Sample Name | ab-ram-337 | Instrument | maXis impact 8282001.00127 |
| Comment | | | |

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Active | Set Capillary | 4500 V | Set Dry Heater | 200 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 1000 m/z | Set Charging Voltage | 2000 V | Set Divert Valve | Source |
| | | Set Corona | 0 nA | Set APCI Heater | 0 °C |







ab-ram-337.d

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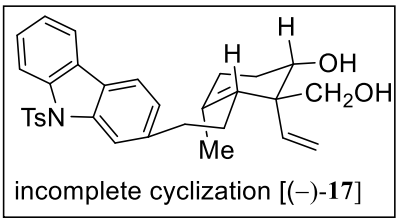
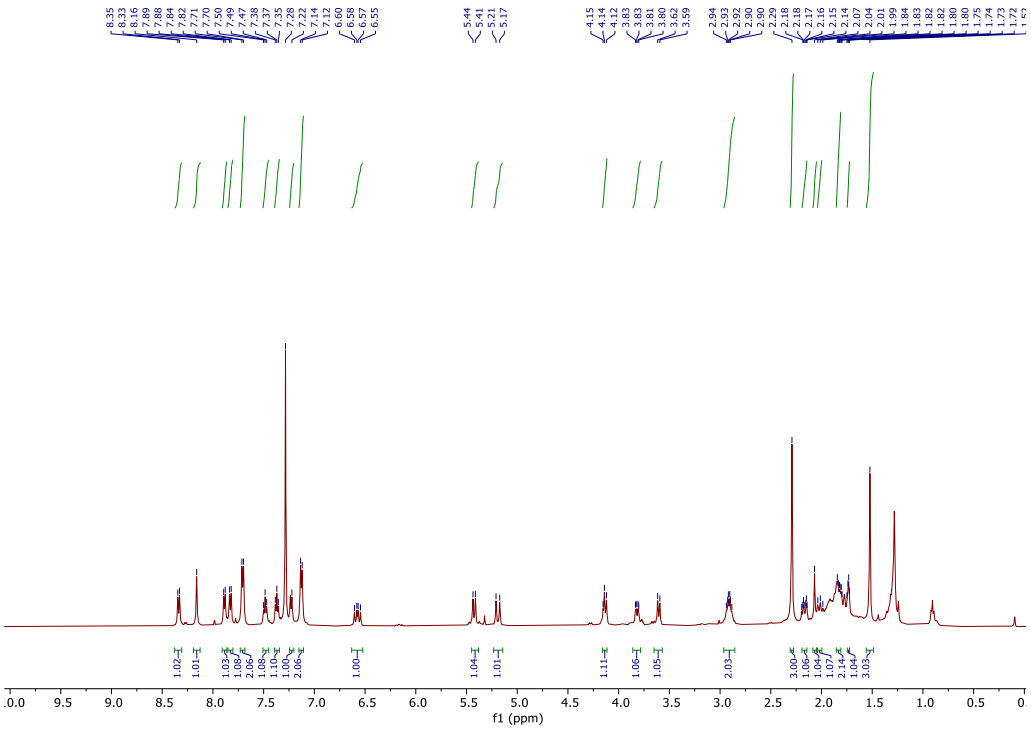
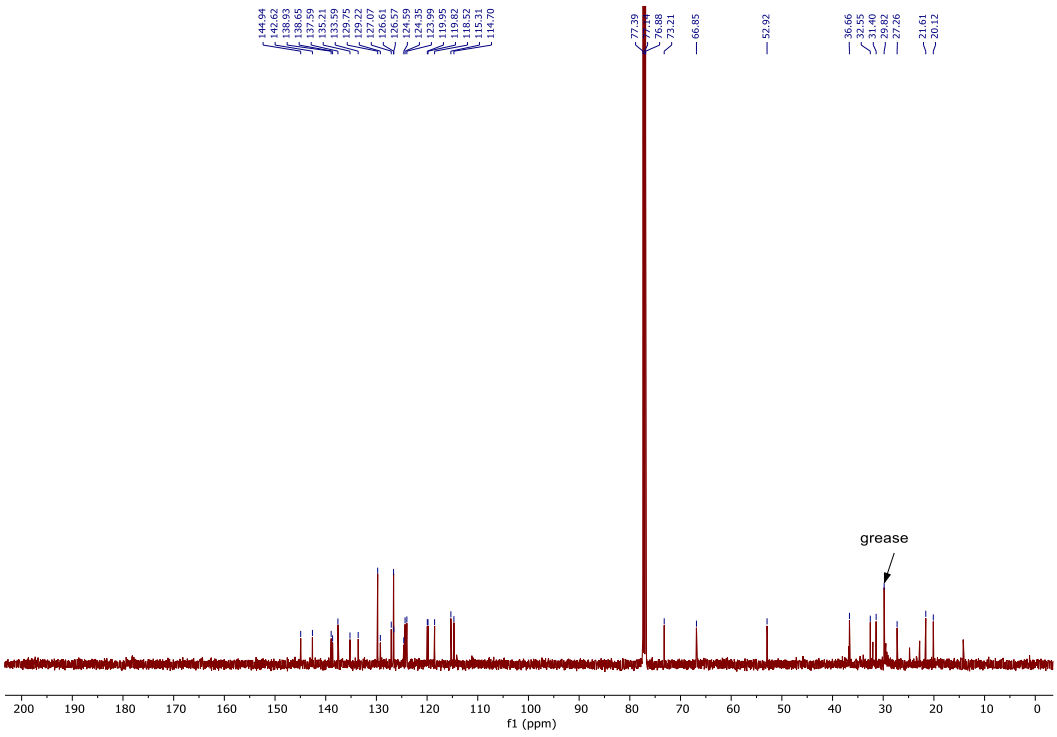
HRMS data of [(+)-**10**]



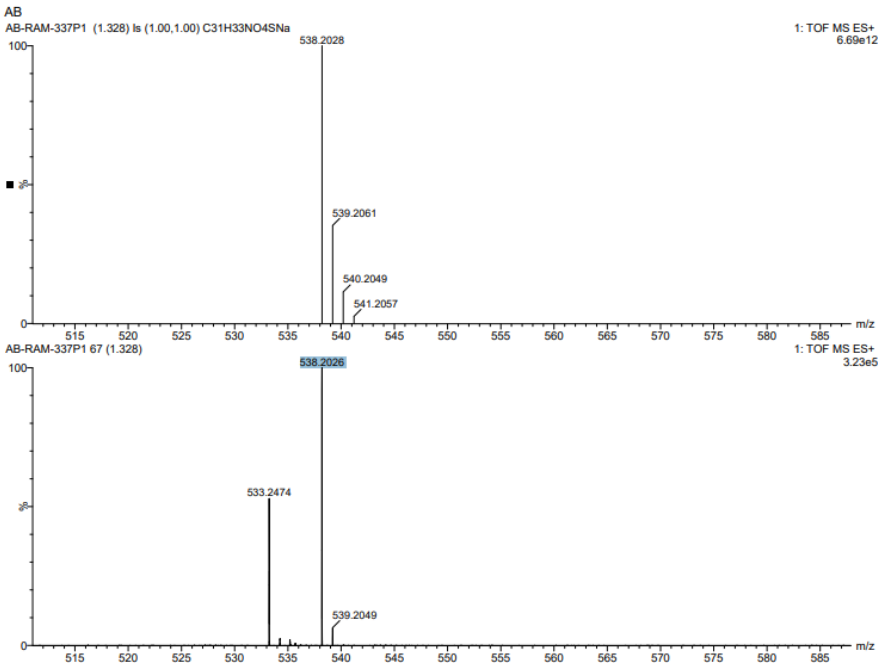

incomplete cyclization [(–)-**17**]



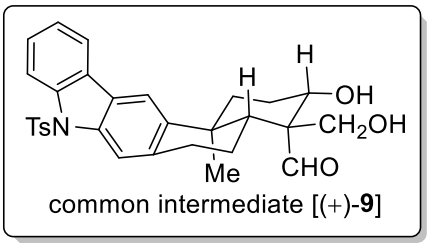

$^{1}$H NMR (500 MHz, $CDCl_3$) of compound [(–)-**17**]



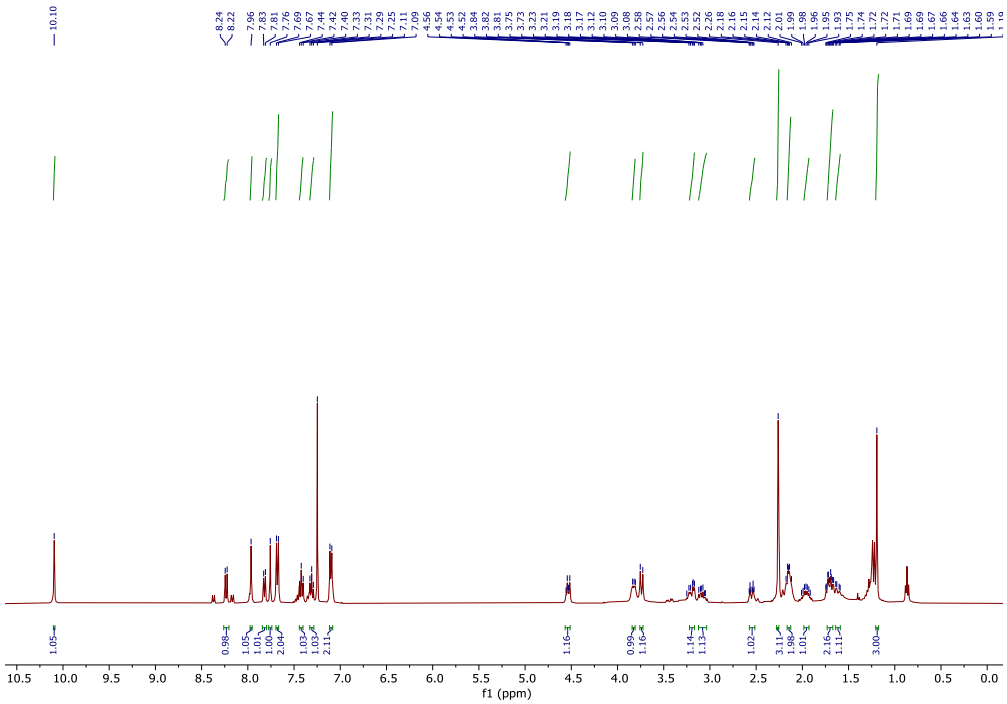

$^{13}$C NMR (126 MHz, $CDCl_3$) of compound [(–)-**17**]



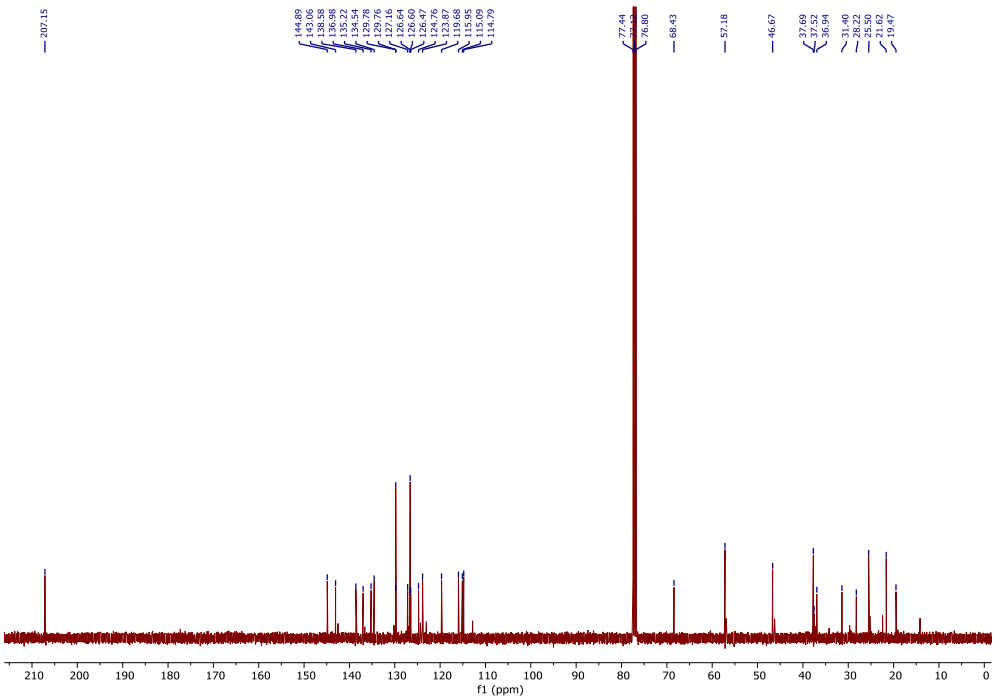

HRMS data of [(−)-**17**]



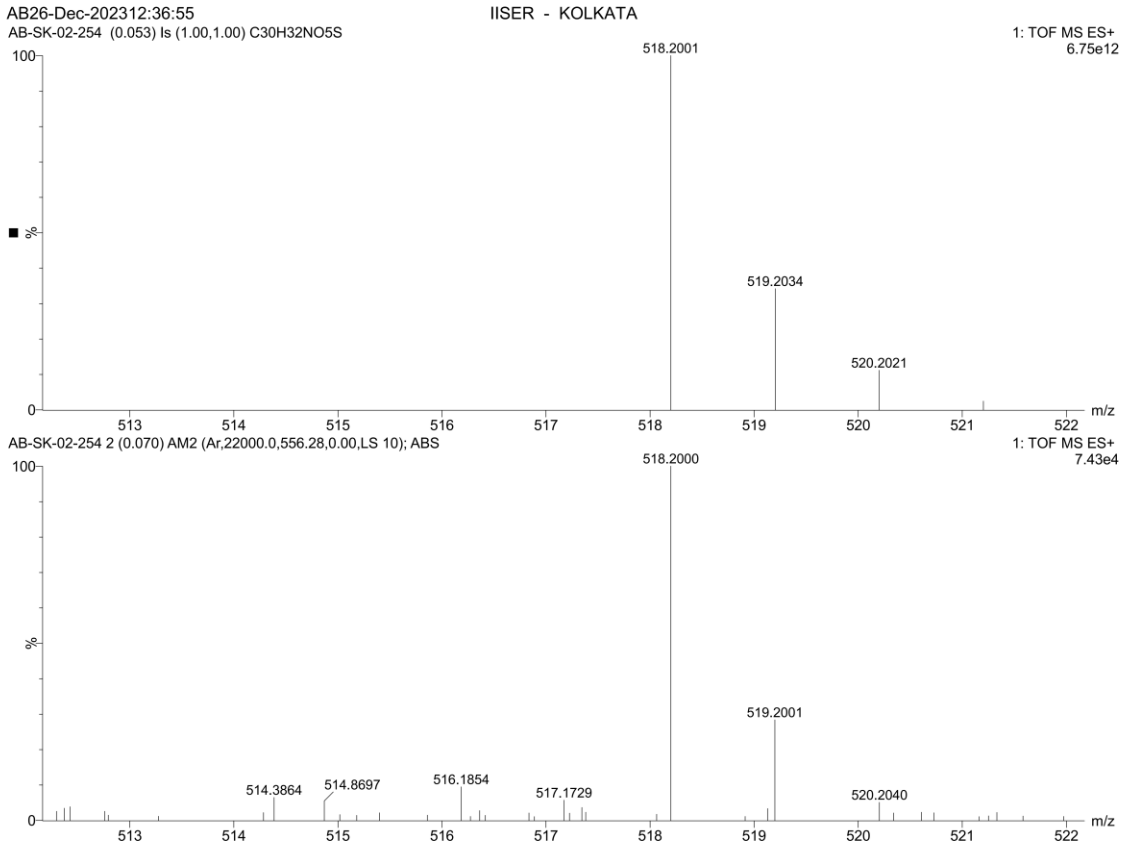
common intermediate [(+)-**9**]



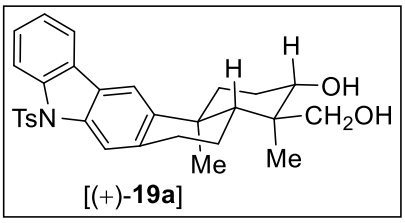

$^{1}$H NMR (400 MHz, $CDCl_3$) of [(+)-**9**]



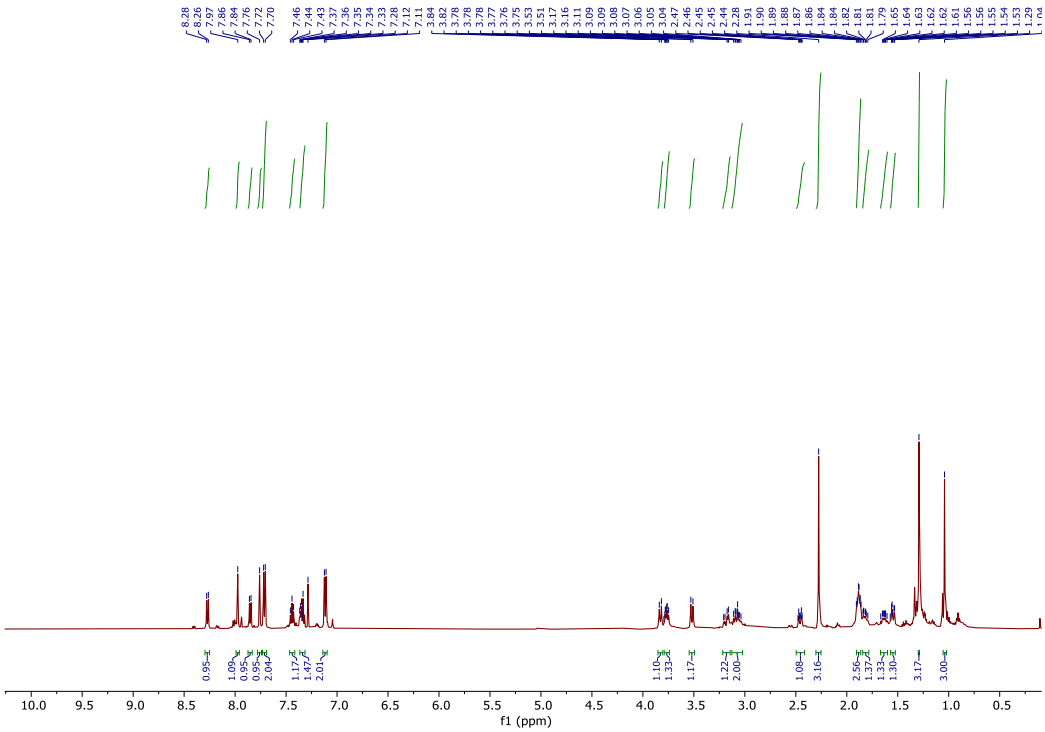

$^{13}$C NMR (101 MHz, $CDCl_3$) of [(+)-**9**]



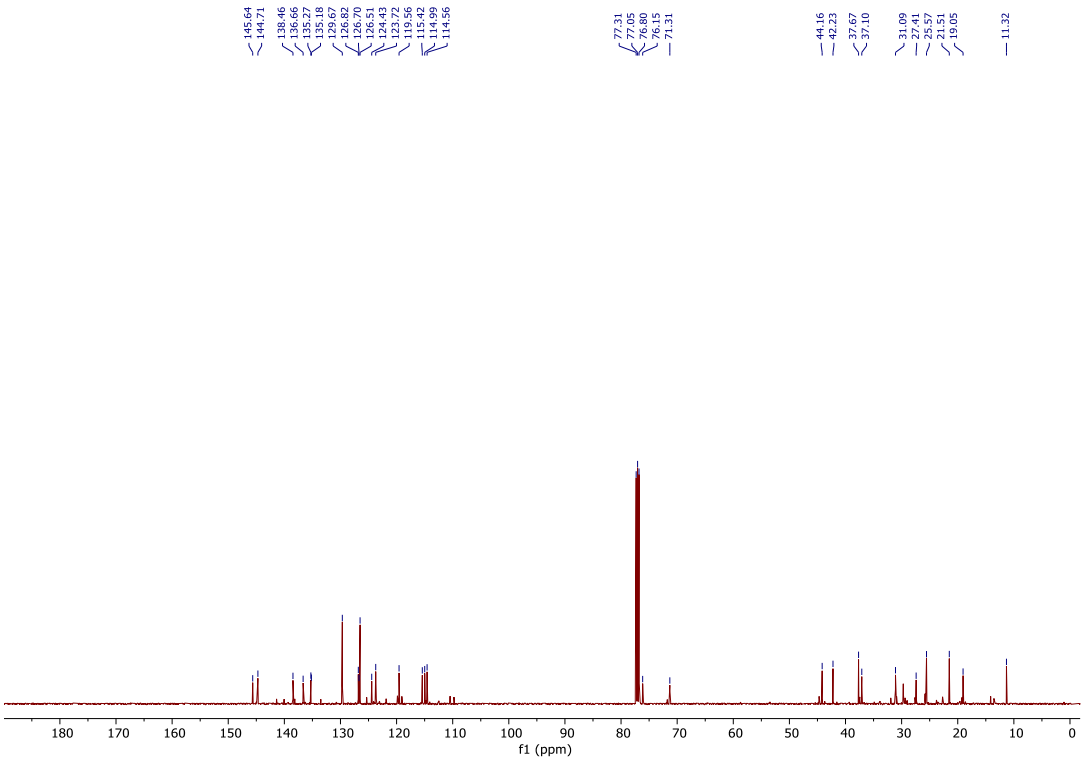

HRMS data of [(+)-**9**]




[(+)-**19a**]




$^{1}$H NMR (500 MHz, $CDCl_3$) of [(+)-**19a**]




$^{13}$C NMR (126 MHz, $CDCl_3$) of [(+)-**19a**]

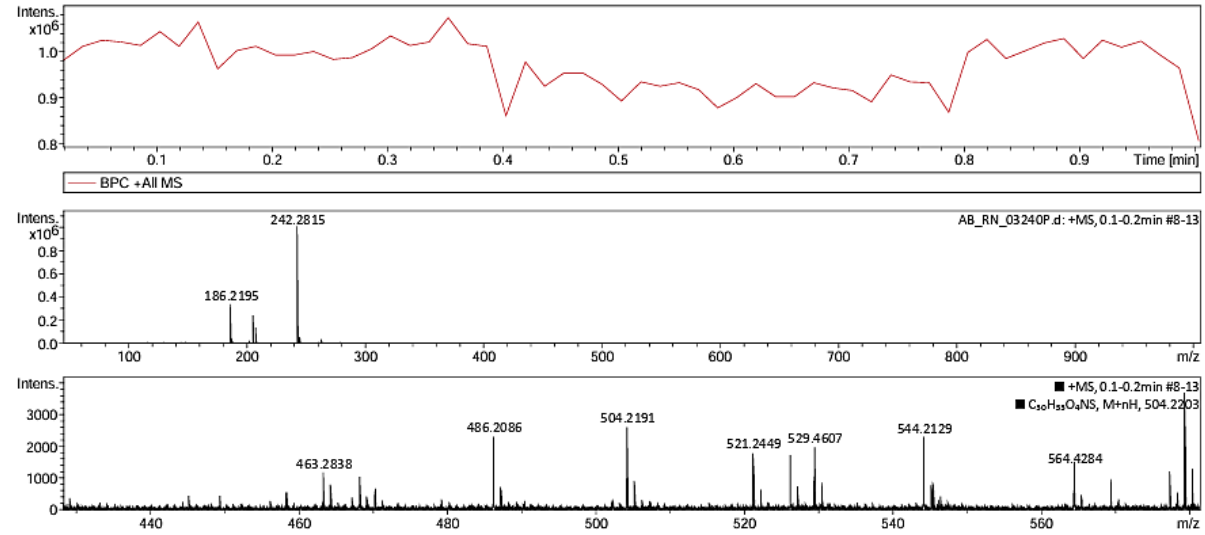
# Display Report

**Analysis Info**

| | | | |
|---|---|---|---|
| Analysis Name | D:\Data\User data\2022\DEC\AB_RN_03240P.d | Acquisition Date | 12/5/2022 11:12:25 AM |
| Method | Tune_pos_Standard_July2022.m | Operator | IISER Kolkata |
| Sample Name | AB_RN_03240P | Instrument | maXis impact 8282001.00127 |
| Comment | | | |

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Active | Set Capillary | 4500 V | Set Dry Heater | 200 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 1000 m/z | Set Charging Voltage | 2000 V | Set Divert Valve | Source |
| | | Set Corona | 0 nA | Set APCI Heater | 0 °C |




AB_RN_03240P.d

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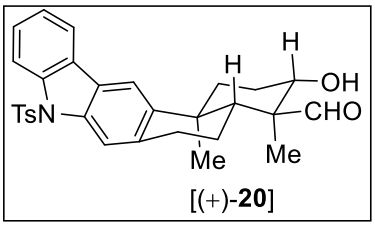
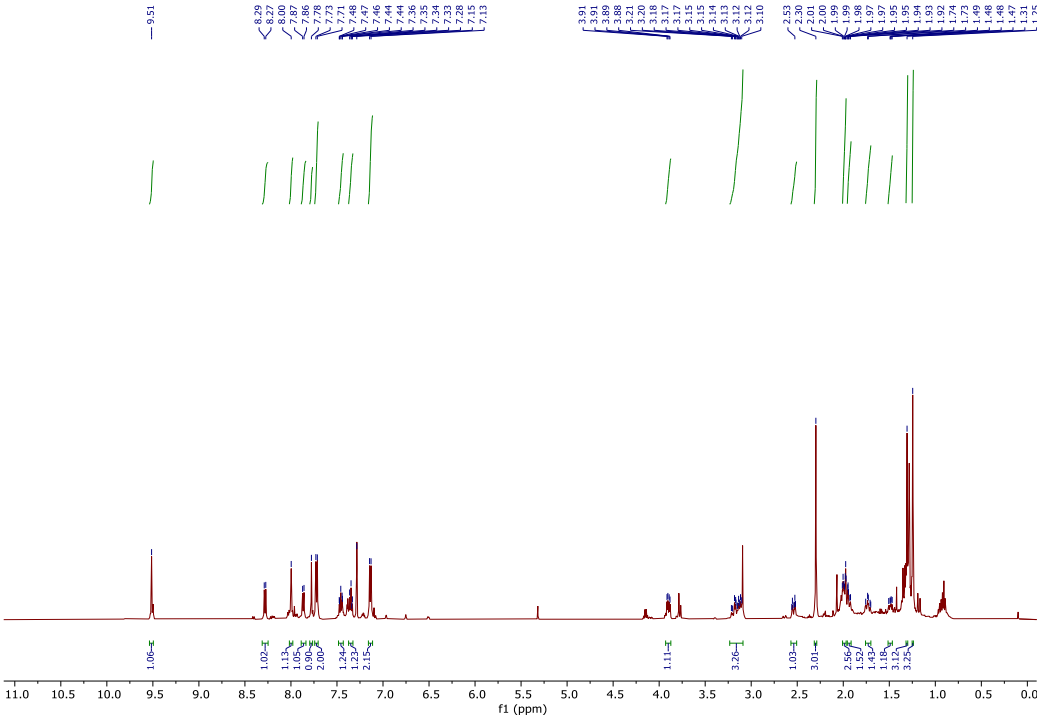
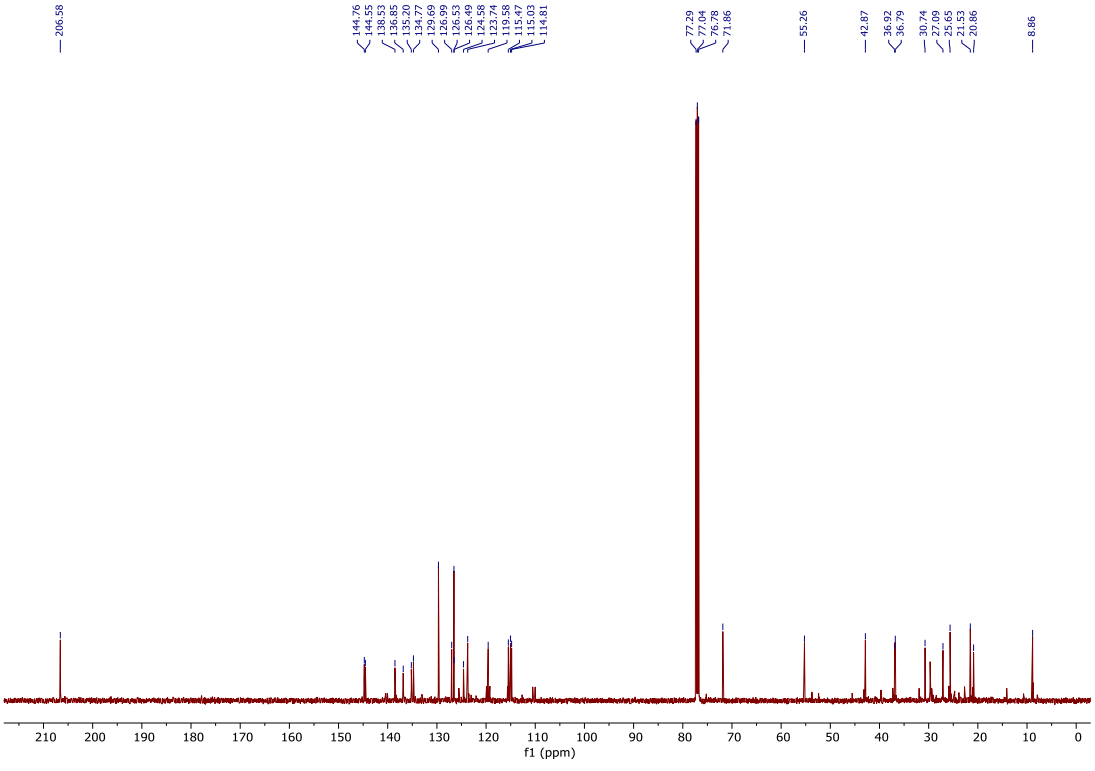
HRMS data of [(+)-**19a**]



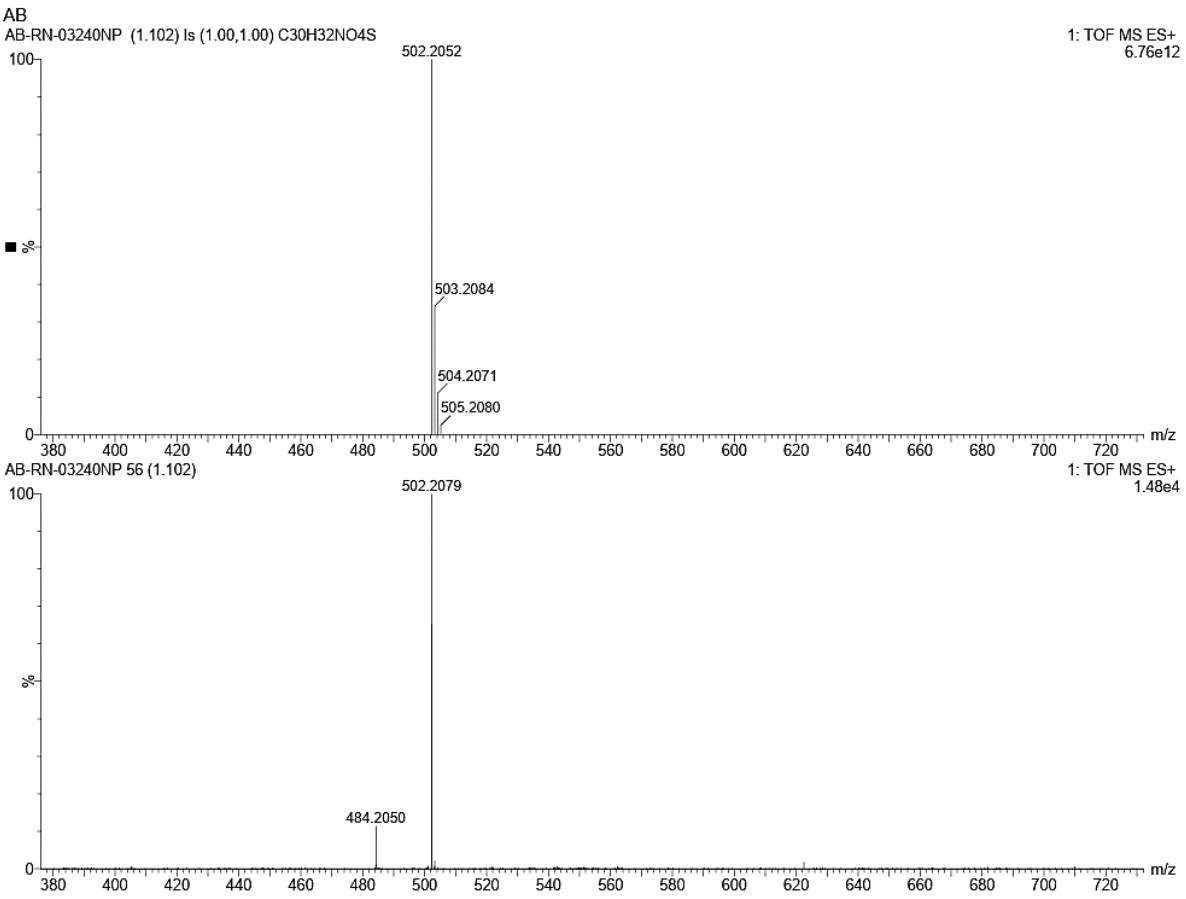

[(+)-**20**]



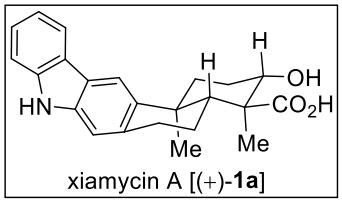

$^{1}$H NMR (500 MHz, $CDCl_3$) of [(+)-**20**]



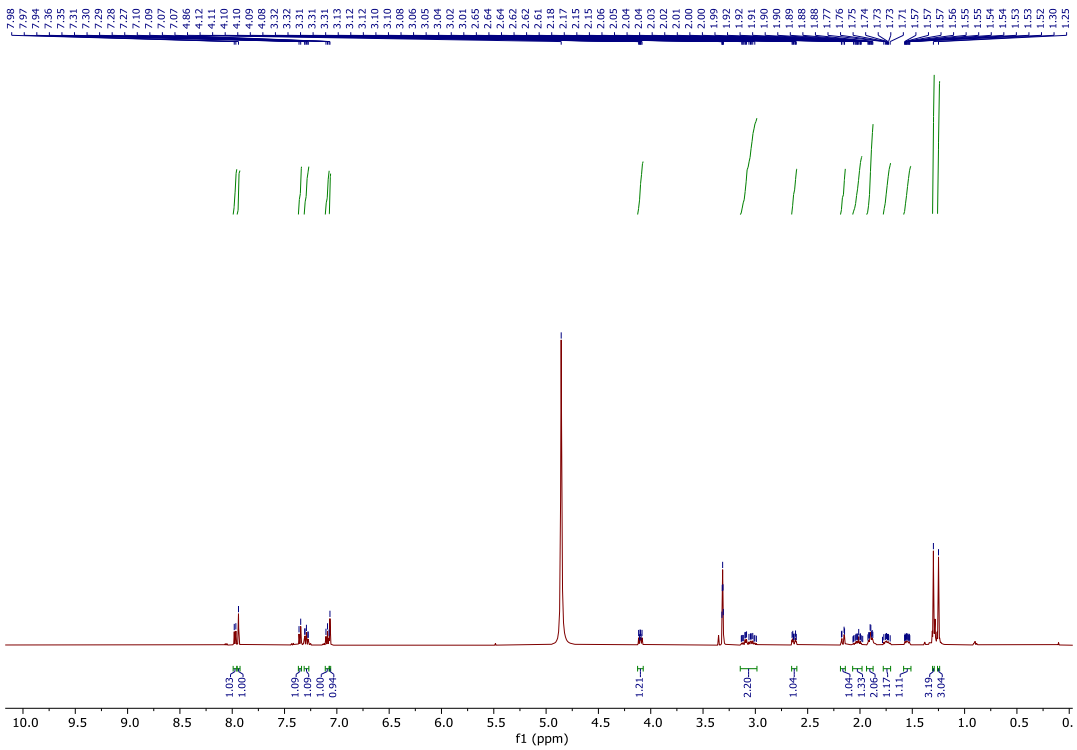

$^{13}$C NMR (126 MHz, $CDCl_3$) of [(+)-**20**]



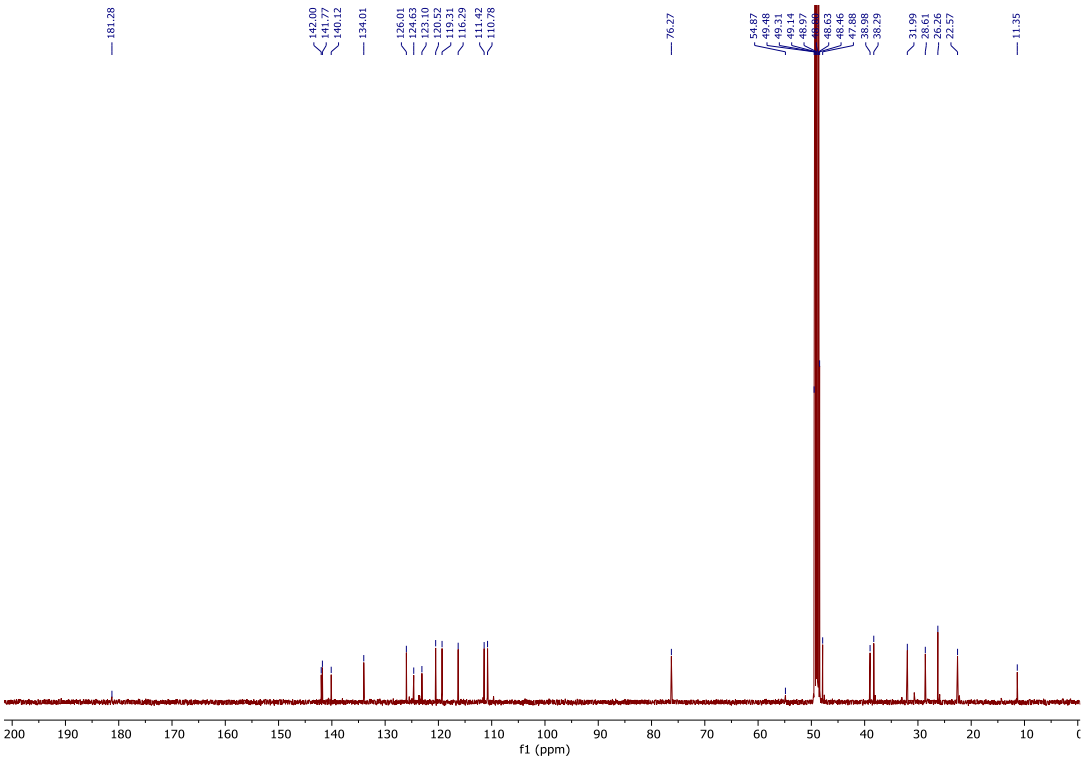

HRMS data of [(+)-**20**]



xiamycin A [(+)-**1a**]




$^{1}$H NMR (500 MHz, $CD_3OD$) of xiamycin A [(+)-**1a**]




$^{13}$C NMR (126 MHz, $CD_3OD$) of xiamycin A [(+)-**1a**]

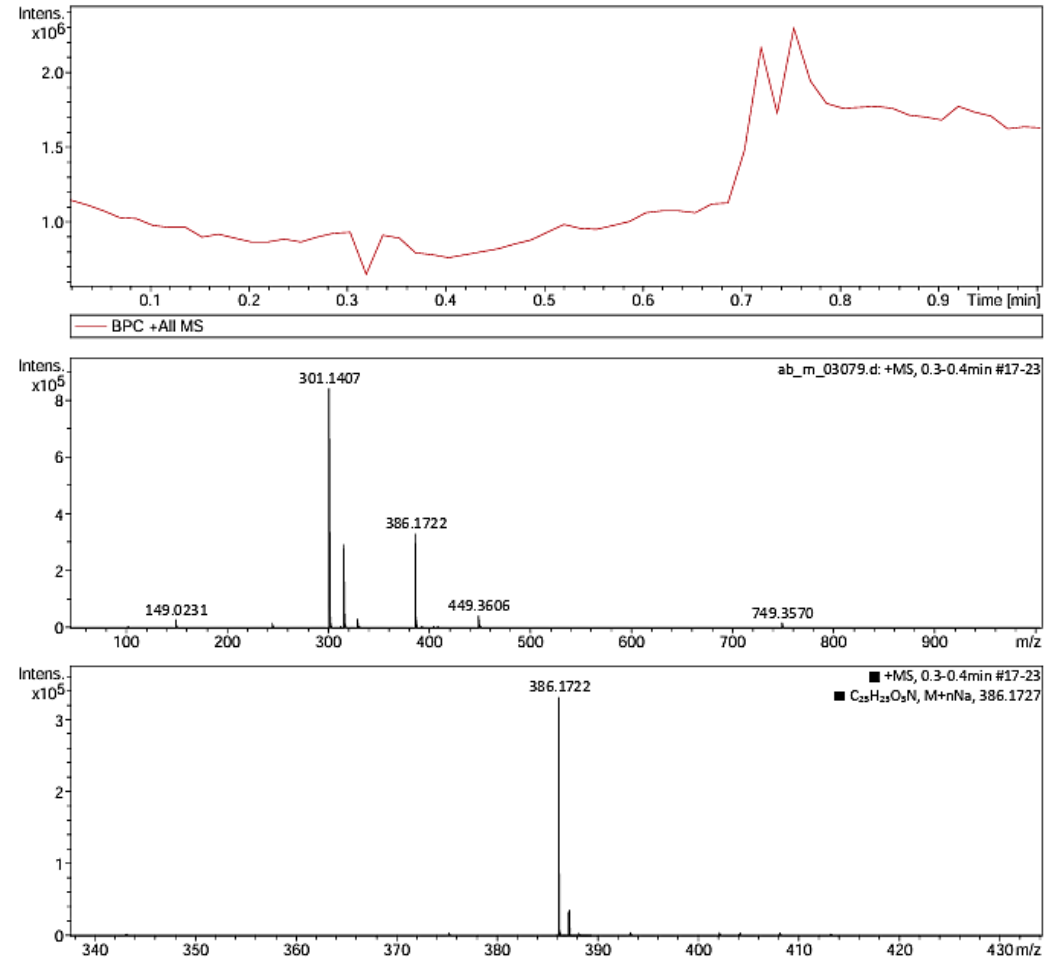
# Display Report

**Analysis Info**

| | | | |
|---|---|---|---|
| Analysis Name | D:\Data\User data\2022\MAY\ab_rn_03079.d | Acquisition Date | 5/12/2022 11:48:58 AM |
| Method | Tune_pos_Standard.m | Operator | IISER Kolkata |
| Sample Name | ab_rn_03079 | Instrument | maXis impact 8282001.00127 |
| Comment | | | |

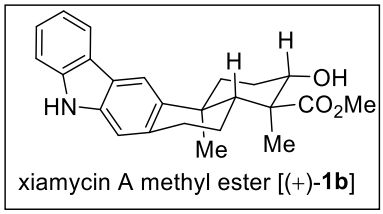
**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.5 Bar |
| Focus | Active | Set Capillary | 3400 V | Set Dry Heater | 200 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 1000 m/z | Set Charging Voltage | 2000 V | Set Divert Valve | Source |
| | | Set Corona | 0 nA | Set APCI Heater | 0 °C |

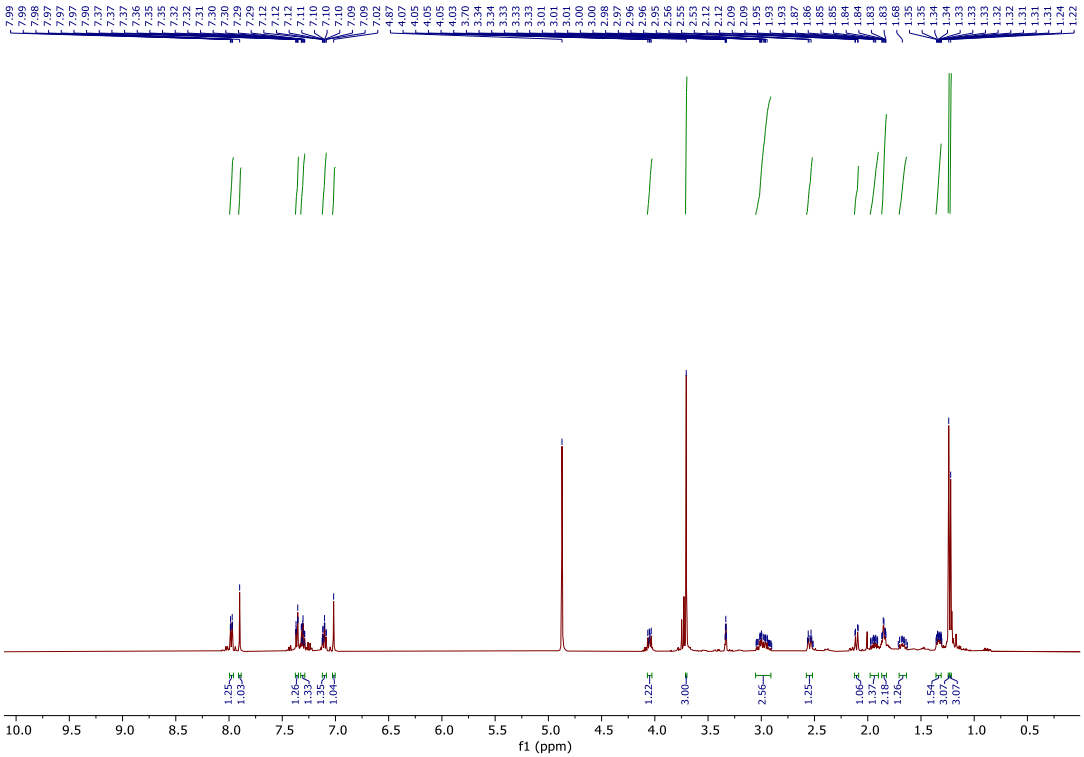




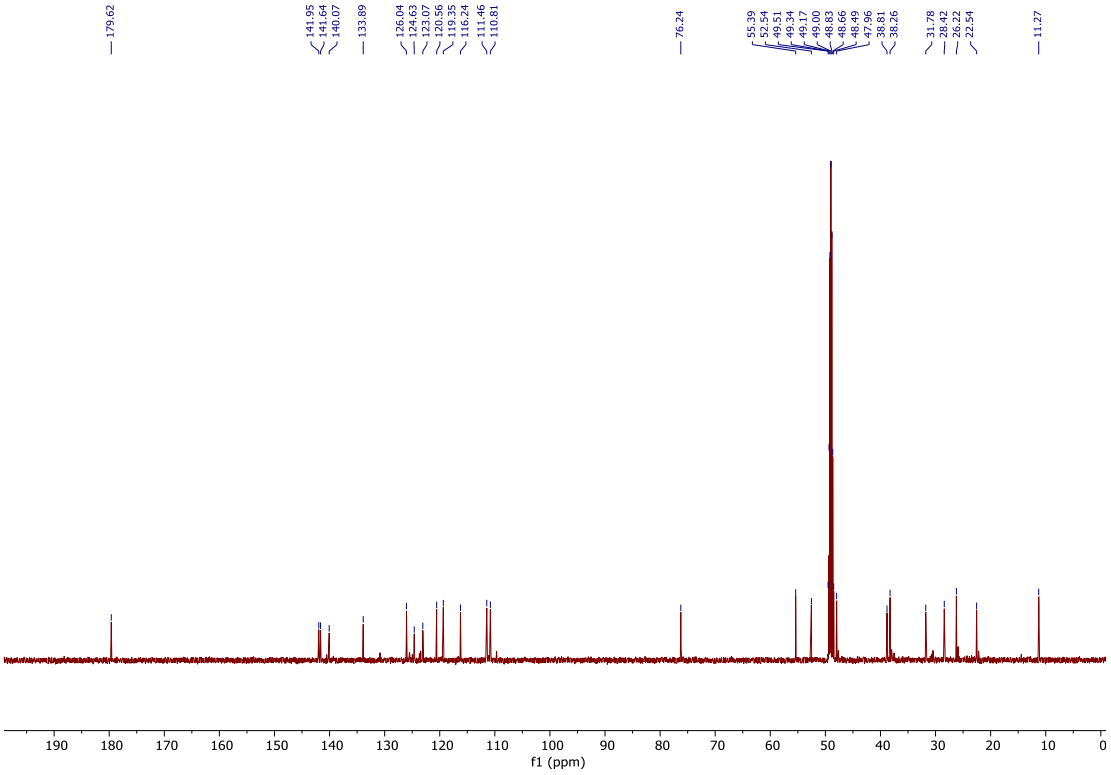

HRMS data of xiamycin A [(+)-**1a**]



xiamycin A methyl ester [(+)-**1b**]




$^{1}$H NMR (500 MHz, $CD_3OD$) of xiamycin A methyl ester [(+)-**1b**]




$^{13}$C NMR (126 MHz, $CD_3OD$) of xiamycin A methyl ester [(+)-**1b**]

# Display Report

**Analysis Info**

| | | | |
|---|---|---|---|
| Analysis Name | D:\Data\User data\2022\NOV\AB-rn_03220.d | Acquisition Date | 11/29/2022 10:38:54 AM |
| Method | Tune_pos_Standard_July2022.m | Operator | IISER Kolkata |
| Sample Name | AB-rn_03220 | Instrument | maXis impact 8282001.00127 |
| Comment | | | |

**Acquisition Parameter**

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|---|---|---|---|---|---|
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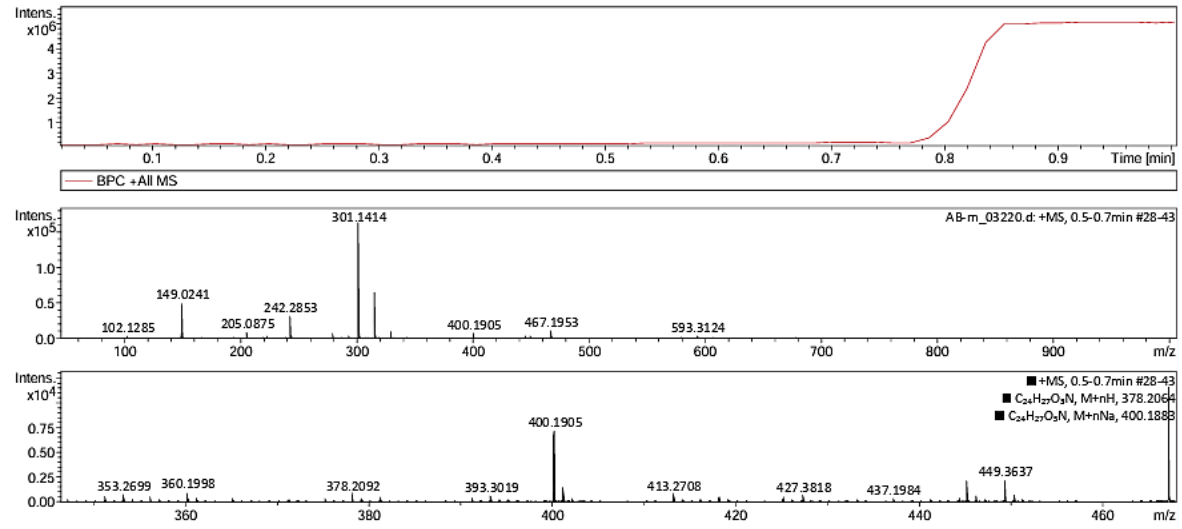
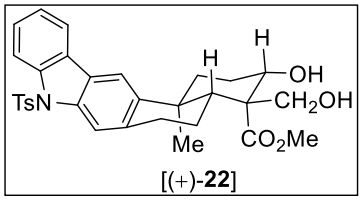
| Focus | Active | Set Capillary | 4500 V | Set Dry Heater | 200 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 1000 m/z | Set Charging Voltage | 2000 V | Set Divert Valve | Source |
| | | Set Corona | 0 nA | Set APCI Heater | 0 °C |



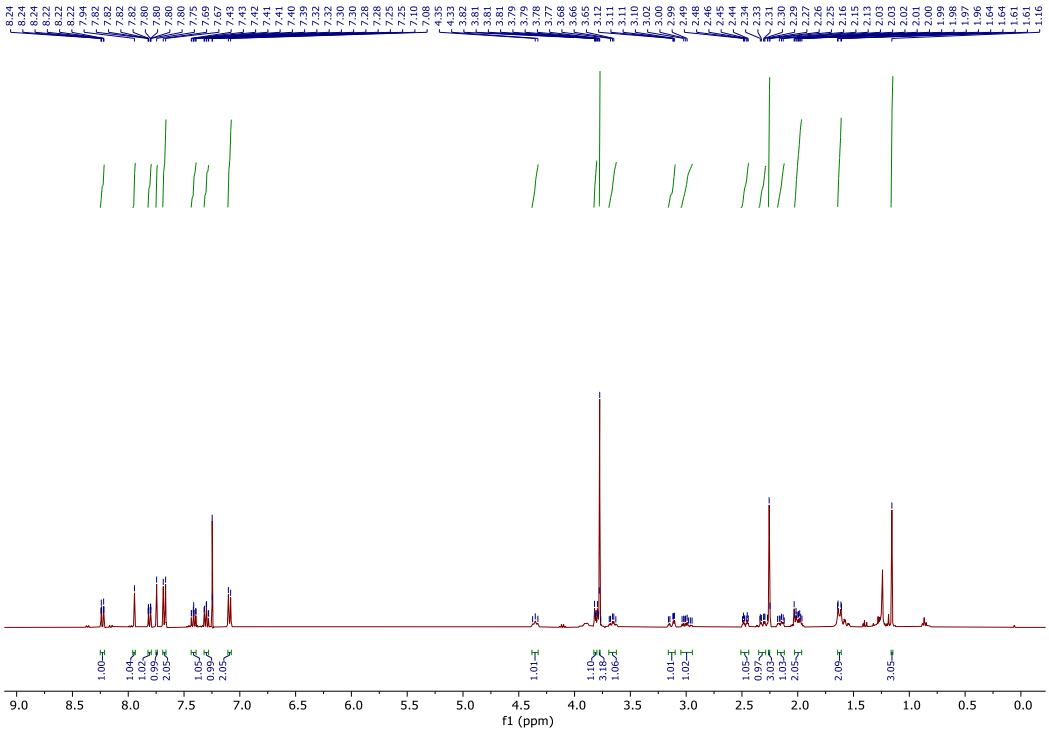

AB-rn_03220.d

Bruker Compass DataAnalysis 4.1 printed: 11/29/2022 10:58:27 AM by: IISER Kolkata Page 1 of 1

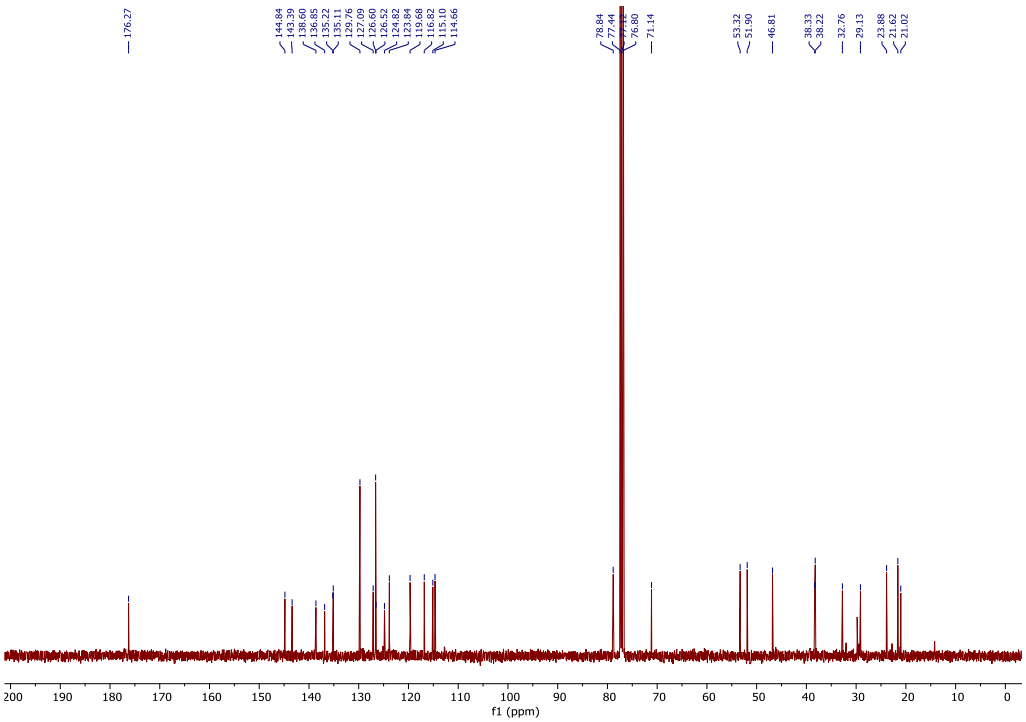
HRMS data of xiamycin A methyl ester [(+)-**1b**]



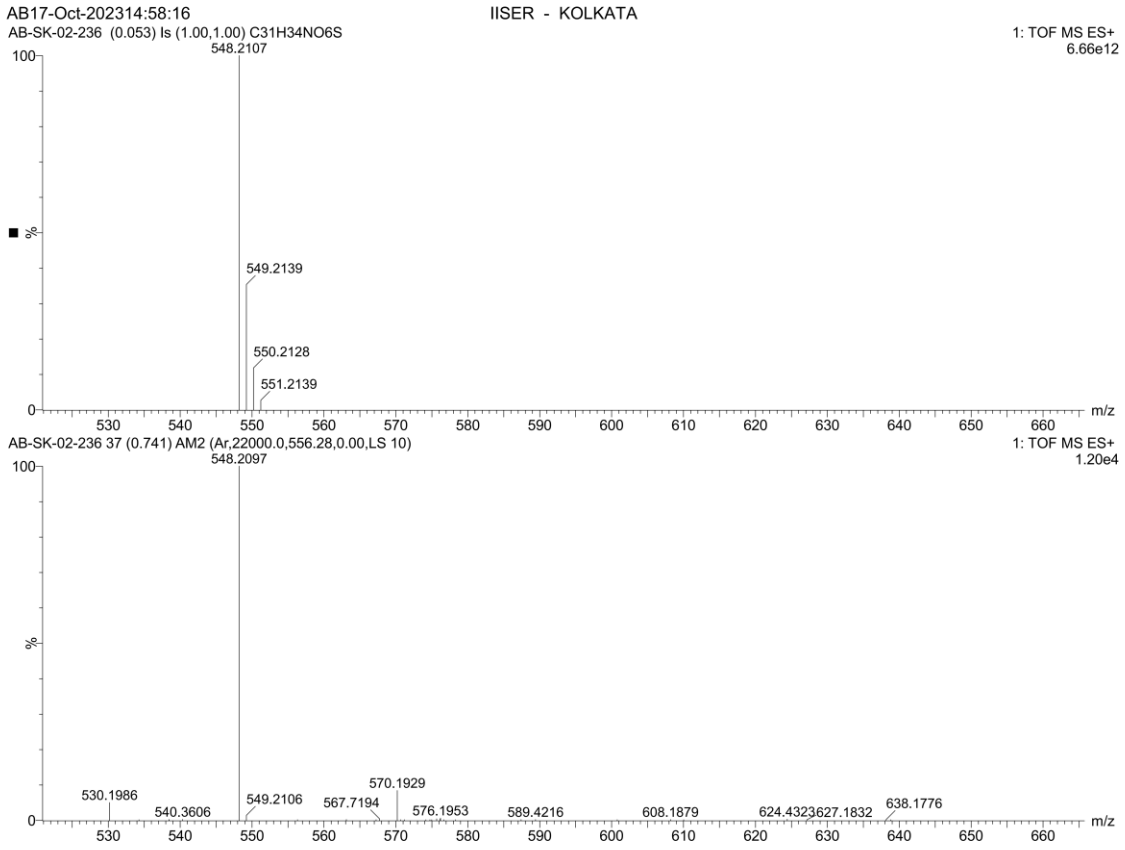

[(+)-**22**]



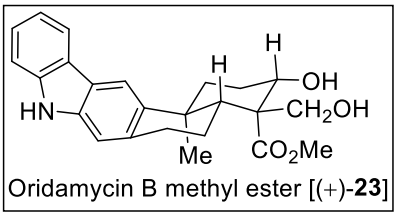

$^{1}$H NMR (400 MHz, $CDCl_3$) of [(+)-**22**]



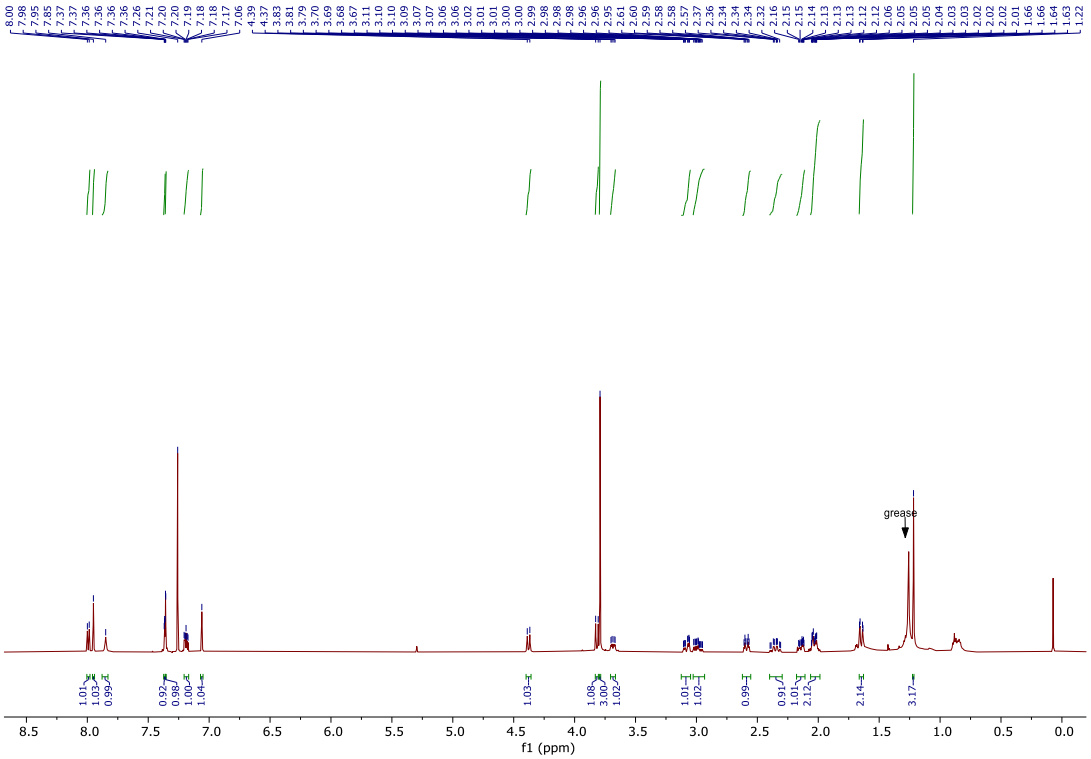

$^{13}$C NMR (101 MHz, $CDCl_3$) of [(+)-**22**]



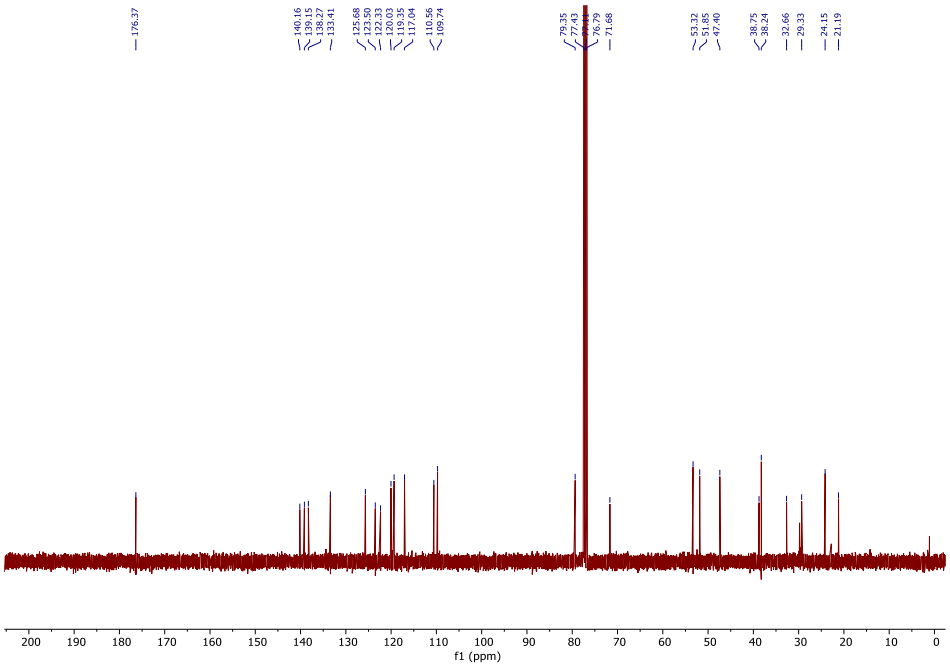

HRMS data of [(+)-**22**]



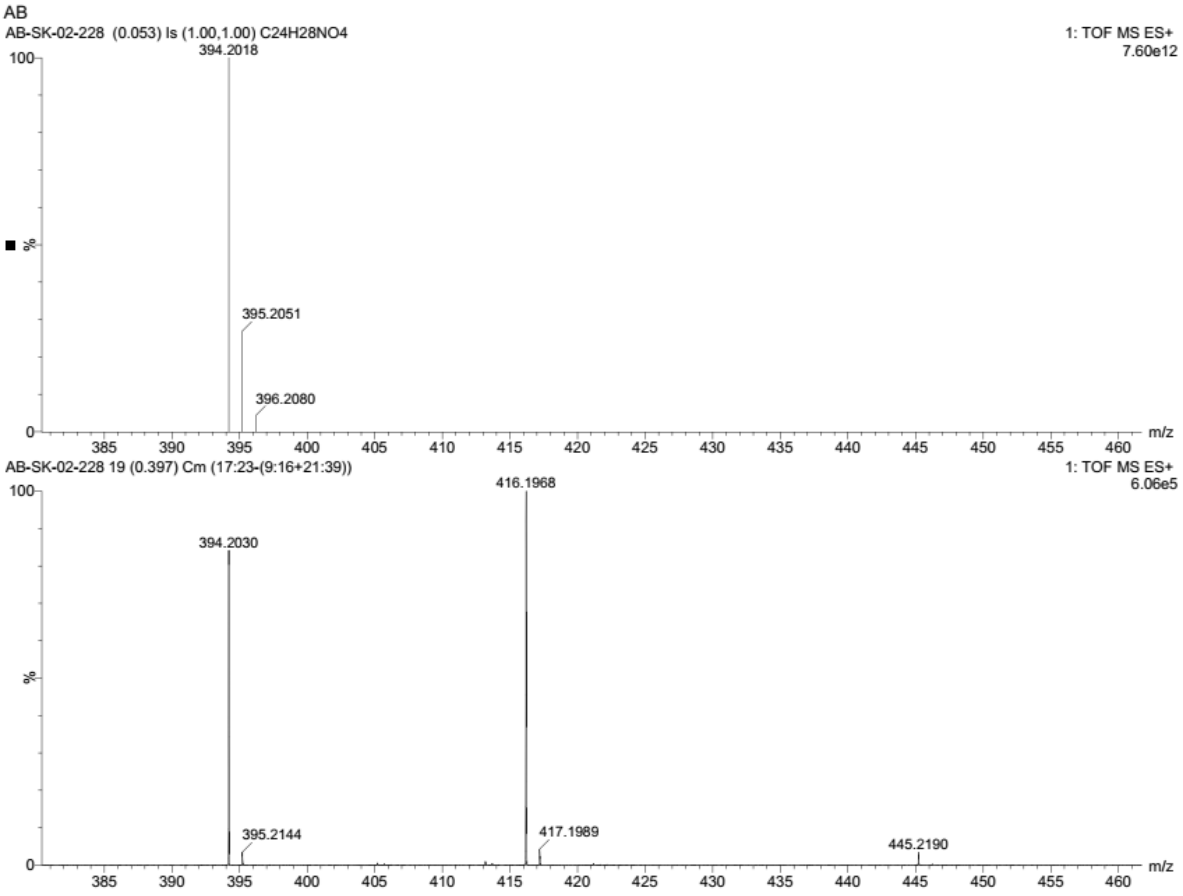
Oridamycin B methyl ester [(+)-**23**]



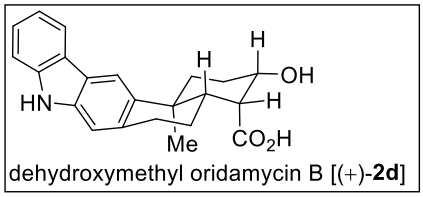

$^{1}$H NMR (500 MHz, $CDCl_3$) of Oridamycin B methyl ester [(+)-**23**]



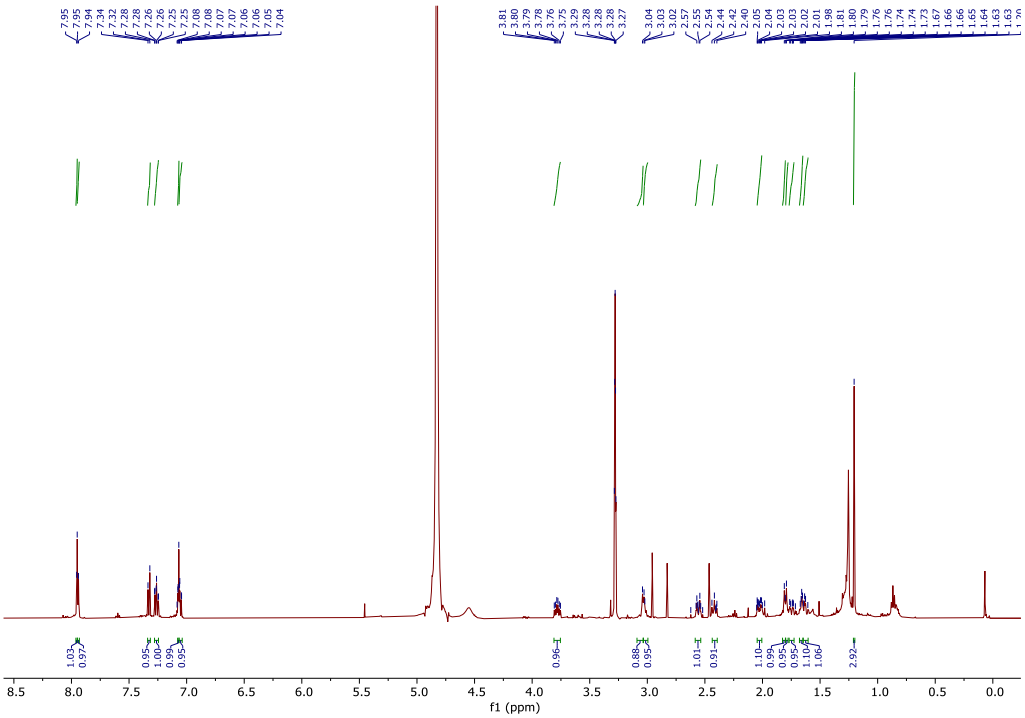

$^{13}$C NMR (101 MHz, $CDCl_3$) of Oridamycin B methyl ester [(+)-**23**]



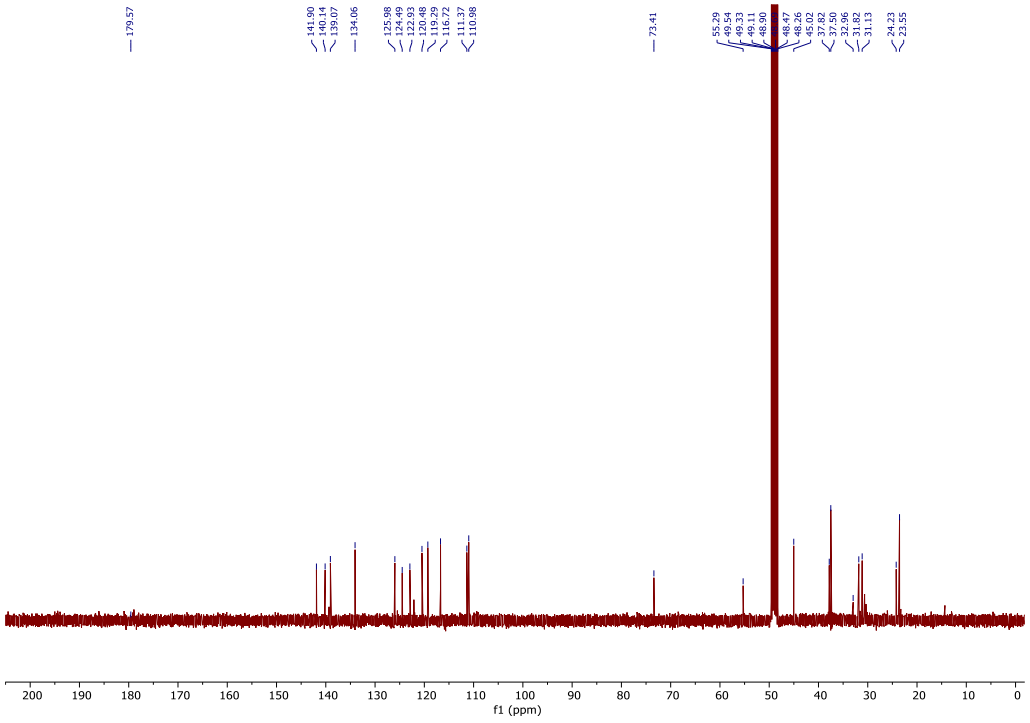

HRMS data of Oridamycin B methyl ester [(+)-**23**]



dehydroxymethyl oridamycin B [(+)-**2d**]




$^{1}$H NMR (500 MHz, $CD_3OD$) of dehydroxymethyl oridamycin B [(+)-**2d**]




$^{13}$C NMR (101 MHz, $CD_3OD$) of dehydroxymethyl oridamycin B [(+)-**2d**]

# Display Report

**Analysis Info**

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|---|---|---|---|
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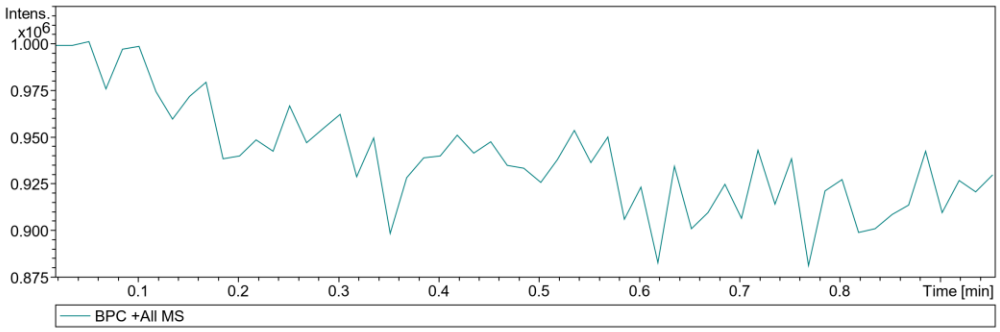
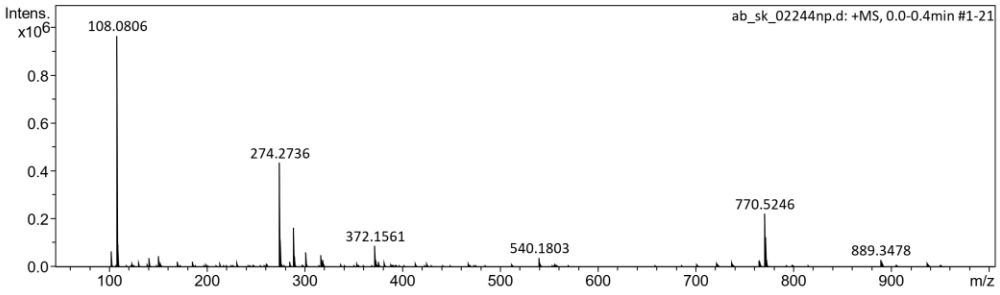
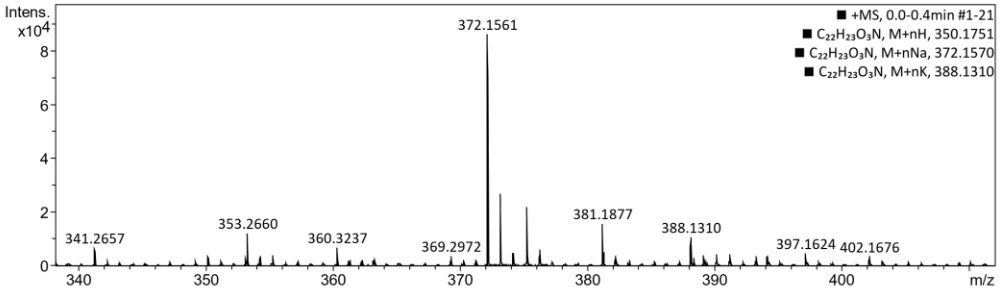
| Method | Tune_pos_Standard_JAN2024.new.m | Operator | IISER Kolkata |
| Sample Name | ab_sk_02244np | Instrument | maXis impact 8282001.00127 |
| Comment | | | |

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Active | Set Capillary | 4500 V | Set Dry Heater | 200 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 1000 m/z | Set Charging Voltage | 2000 V | Set Divert Valve | Source |
| | | Set Corona | 0 nA | Set APCI Heater | 0 °C |

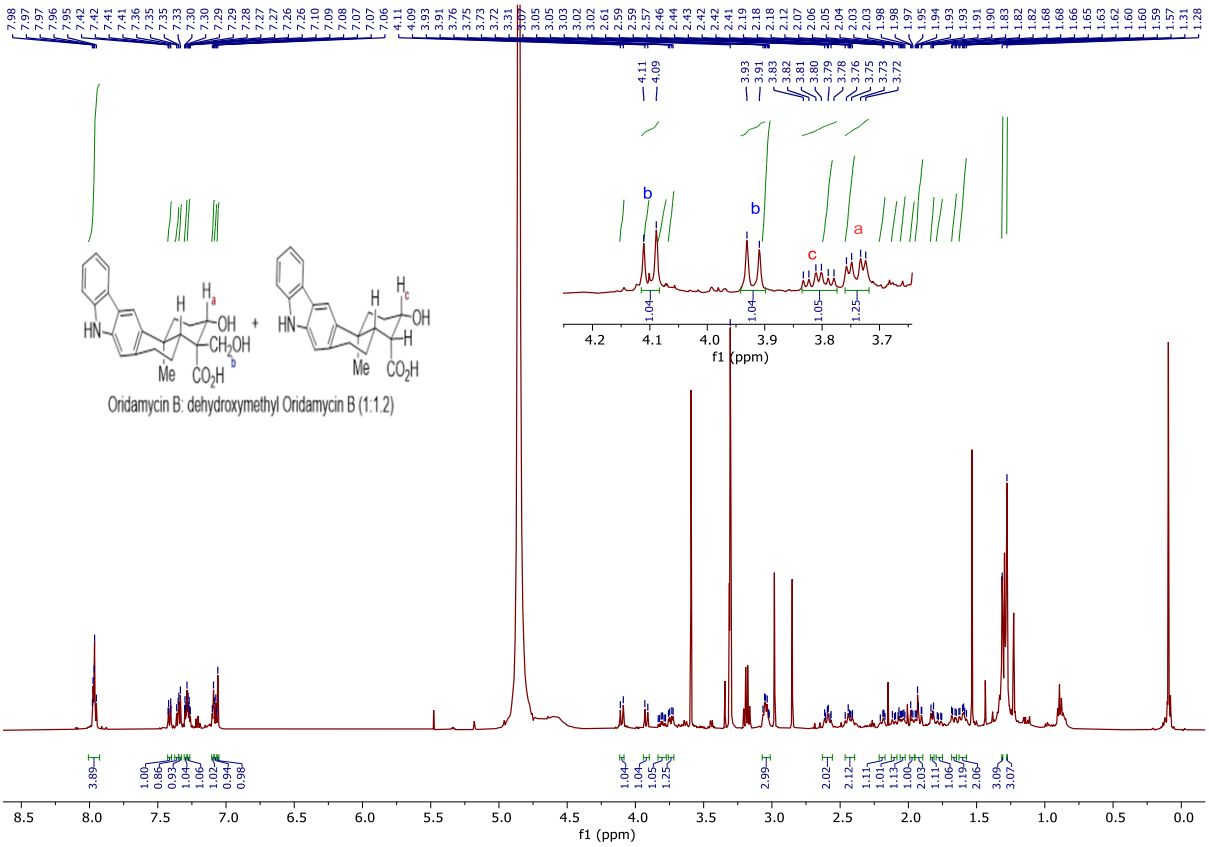


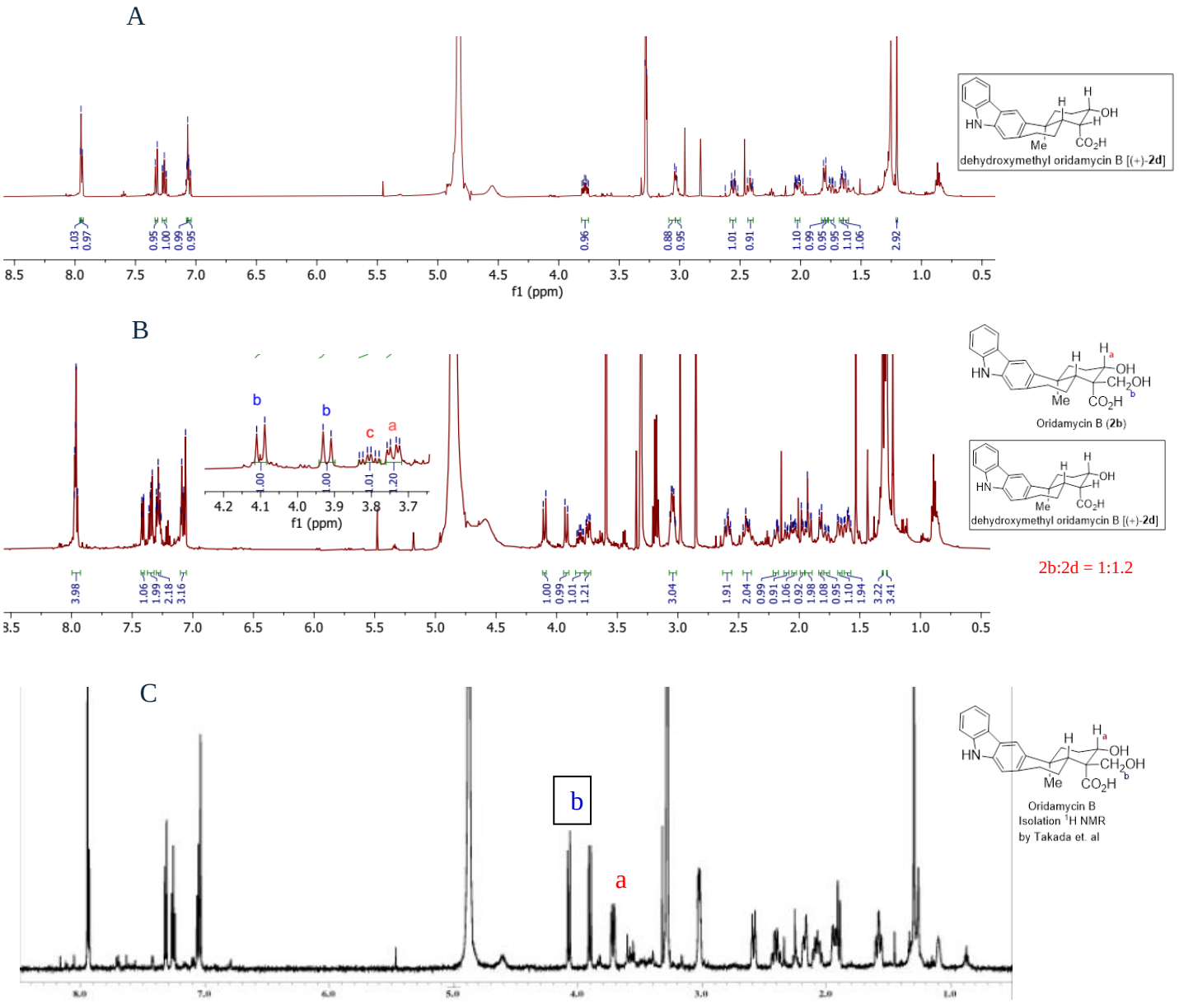






HRMS data of dehydroxymethyl oridamycin B [(+)-**2d**]



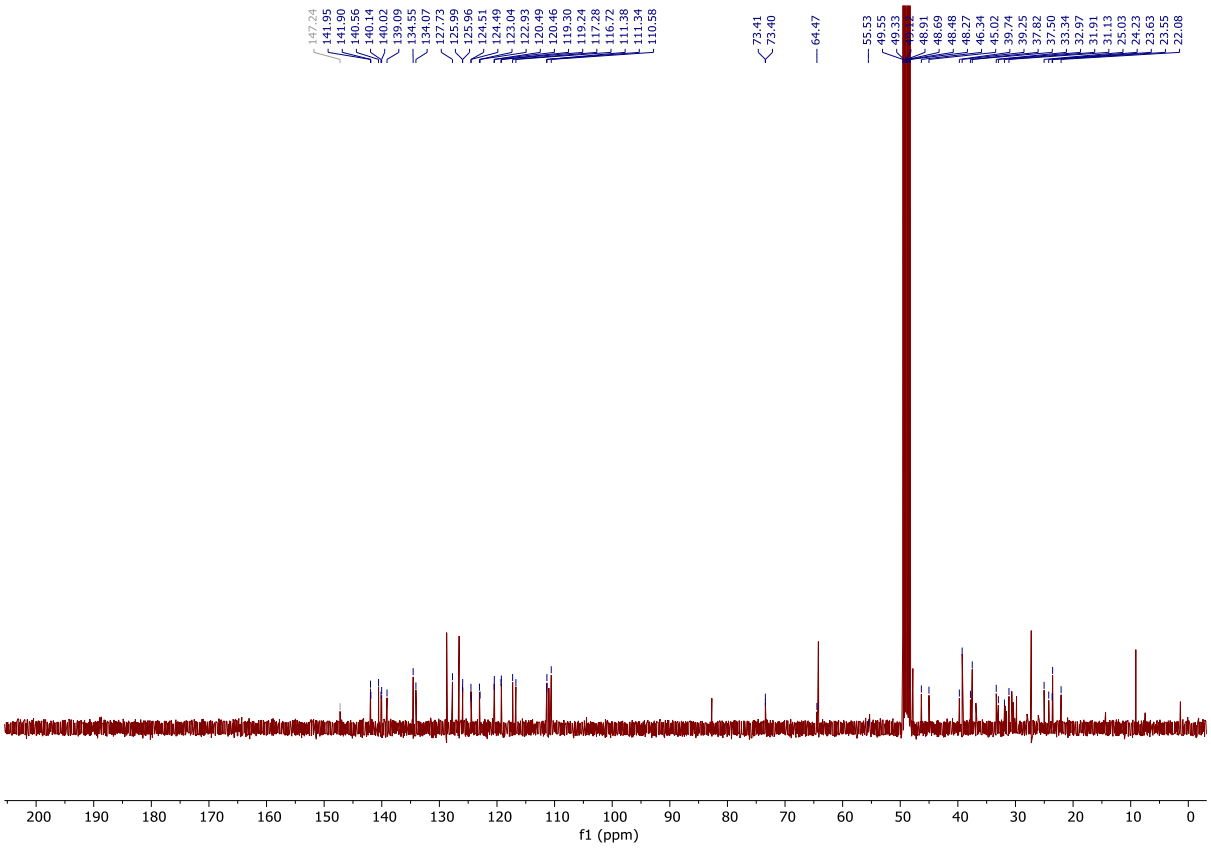

$^{1}$H NMR of Crude reaction mixture on saponification of oridamycin B methyl ester B [(+)-**23**] (Entry No. 8, Table 5) in 500 MHz showing 1:1.2 ratio of oridamycin B [**2b**] and dehydroxymethyl oridamycin B [(+)-**2d**] in $CD_3OD$.



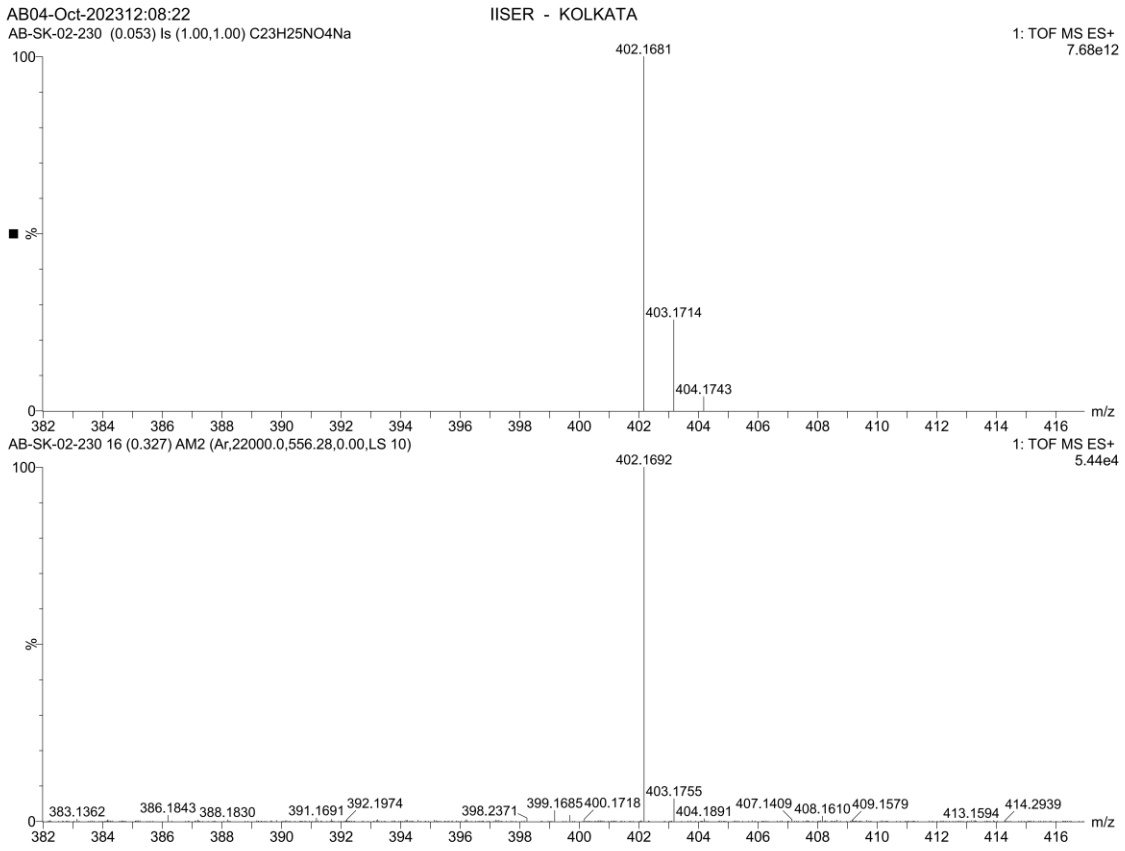

A- $^{1}$H NMR of dehydroxymethyl oridamycin B[(+)-**2d**] in 500 MHz ($CD_3OD$).

B- $^{1}$H NMR of Crude reaction mixture on saponification of Oridamycin B methyl ester B [(+)-**23**] (Entry No. 8, Table 5) in 500 MHz ($CD_3OD$) showing 1:1.2 ratio of Oridamycin B [**2b**] and dehydroxymethyl oridamycin B[(+)-**2d**]

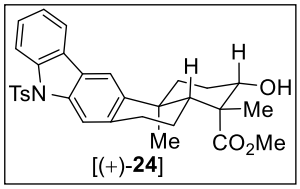
C- $^{1}$H NMR of isolated oridamycin B[**2b**] in 500 MHz ($CD_3OD$) by Takada et al.[6]



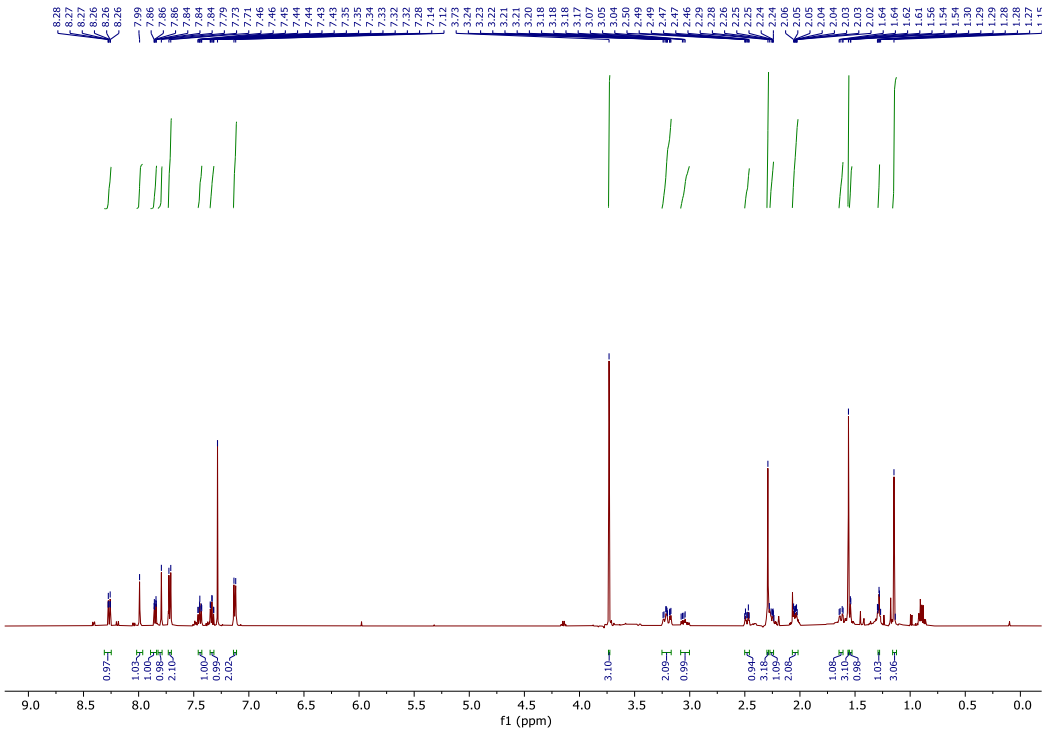

$^{13}$C NMR of Crude reaction mixture on saponification of oridamycin B methyl ester B[(+)-**23**] (Entry No. 8, Table 5) showing 1:1.2 ratio of oridamycin B[**2b**] and dehydroxymethyl oridamycin B[(+)-**2d**] in 101 MHz ($CD_3OD$)



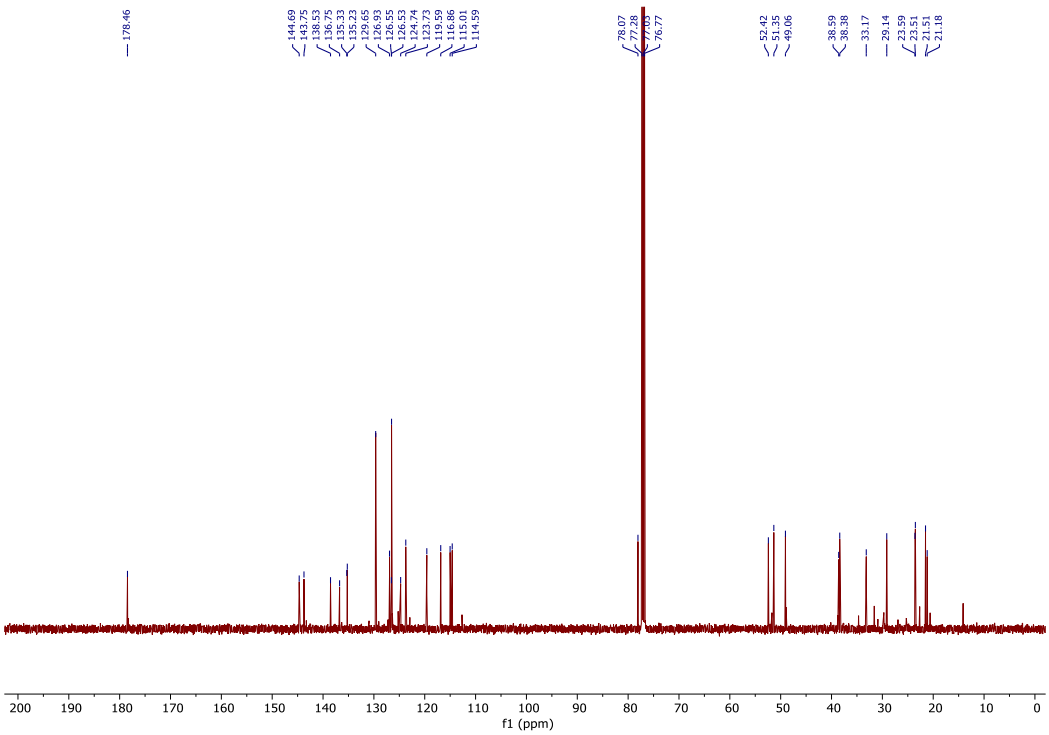

HRMS Data for oridamycin B (**2b**) from Crude Saponification Reaction



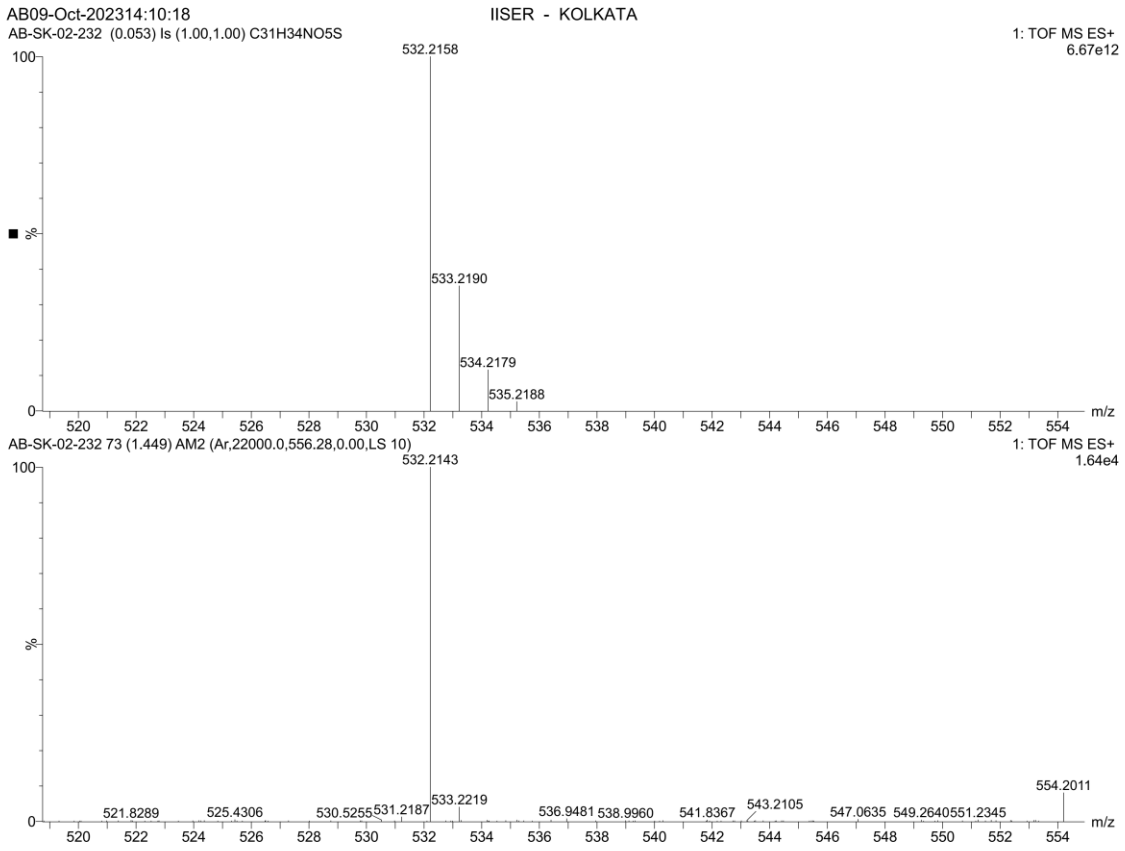
[(+)-**24**]



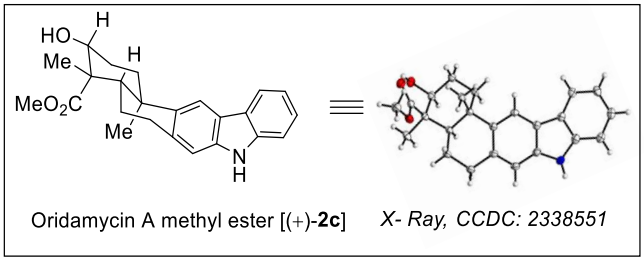

$^{1}$H NMR (500 MHz, $CDCl_3$) of [(+)-**24**]



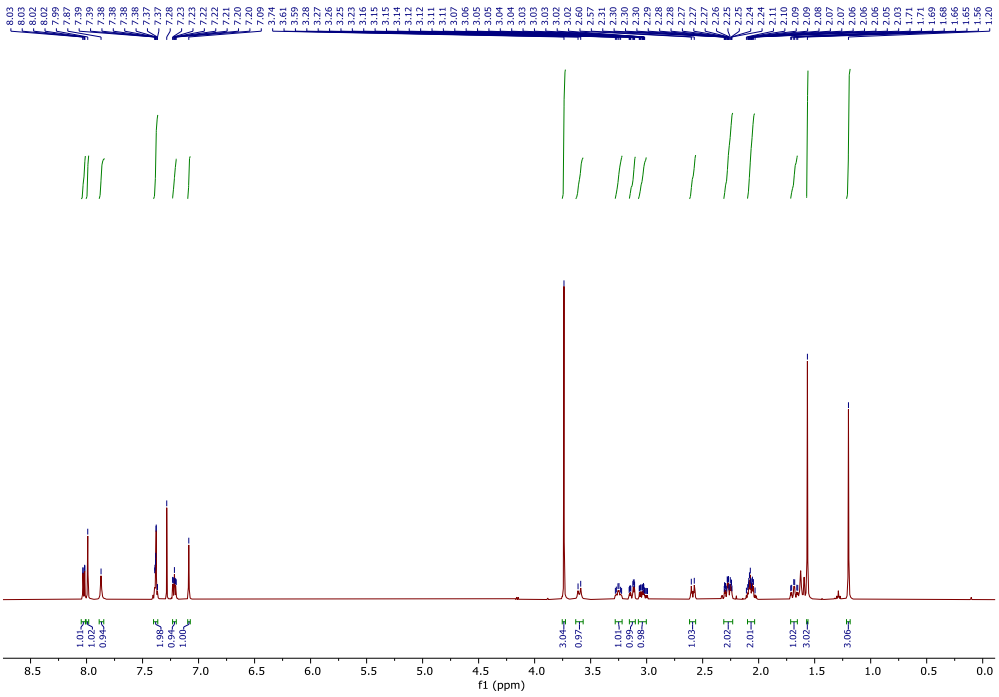

$^{13}$C NMR (126 MHz, $CDCl_3$) of [(+)-**24**]



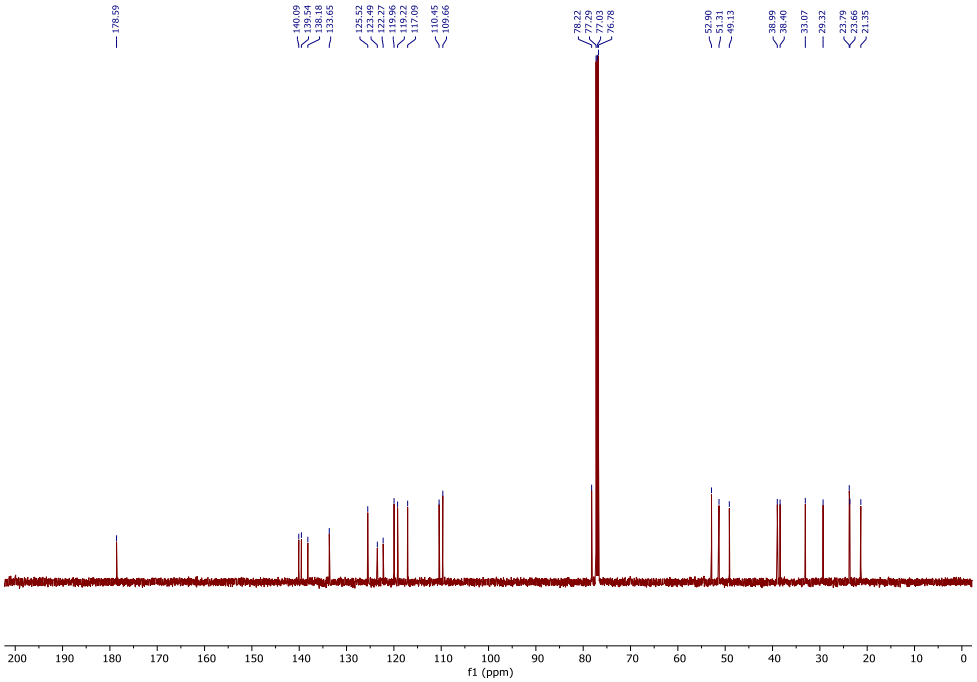

HRMS data of [(+)-**24**]




Oridamycin A methyl ester [(+)-**2c**] *X- Ray, CCDC: 2338551*




$^{1}$H NMR (500 MHz, $CDCl_3$) of oridamycin A methyl ester [(+)-**2c**]




$^{13}$C NMR (126 MHz, $CDCl_3$) of (+)-oridamycin A methyl ester [(+)-**2c**]

# Display Report

**Analysis Info**

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|---|---|---|---|
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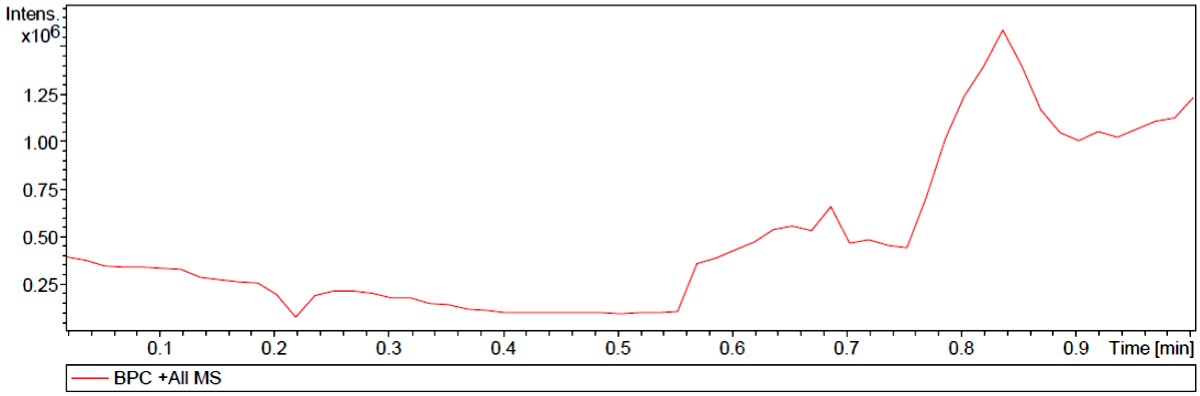
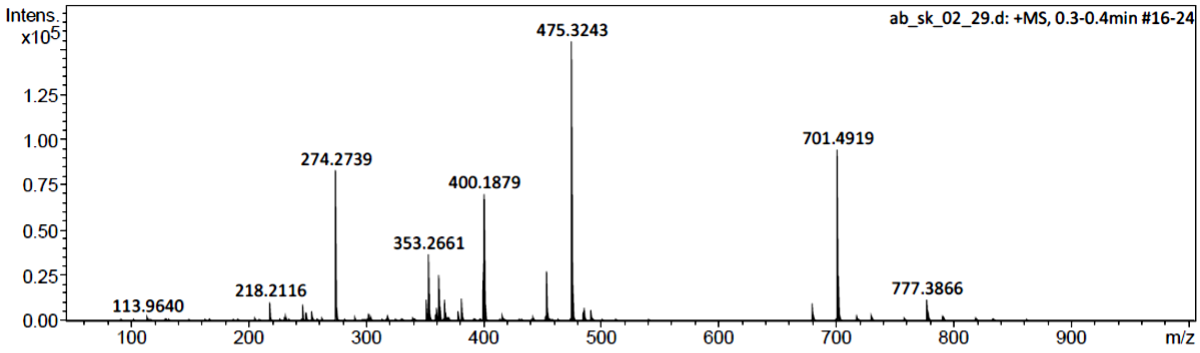
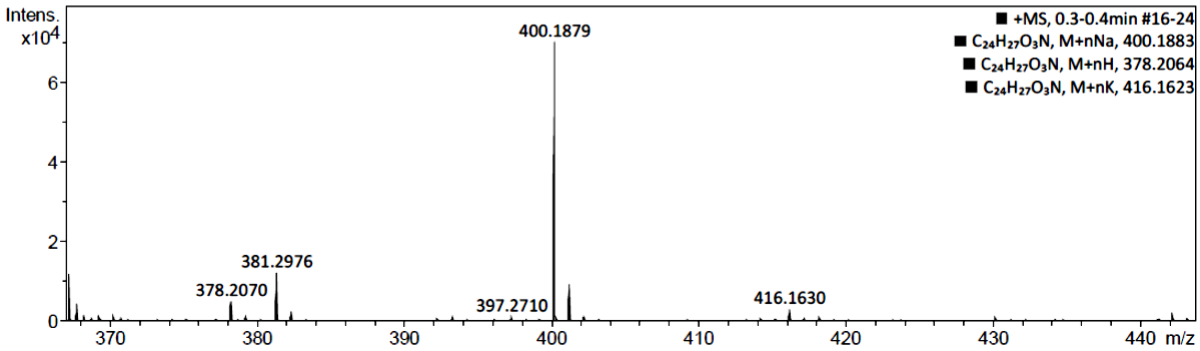
| Method | Tune_pos_Standard.m | Operator | IISER Kolkata |
| Sample Name | ab_sk_02_29 | Instrument | maXis impact 8282001.00127 |
| Comment | | | |

**Acquisition Parameter**

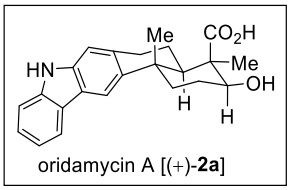
| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.5 Bar |
| Focus | Active | Set Capillary | 3400 V | Set Dry Heater | 200 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 1000 m/z | Set Charging Voltage | 2000 V | Set Divert Valve | Source |
| | | Set Corona | 0 nA | Set APCI Heater | 0 °C |



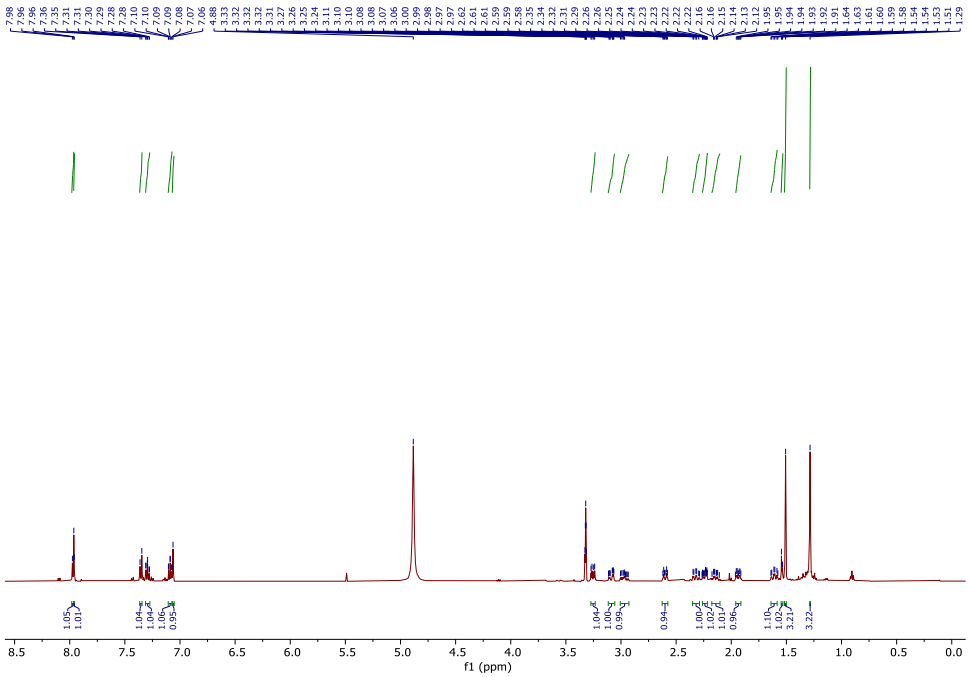



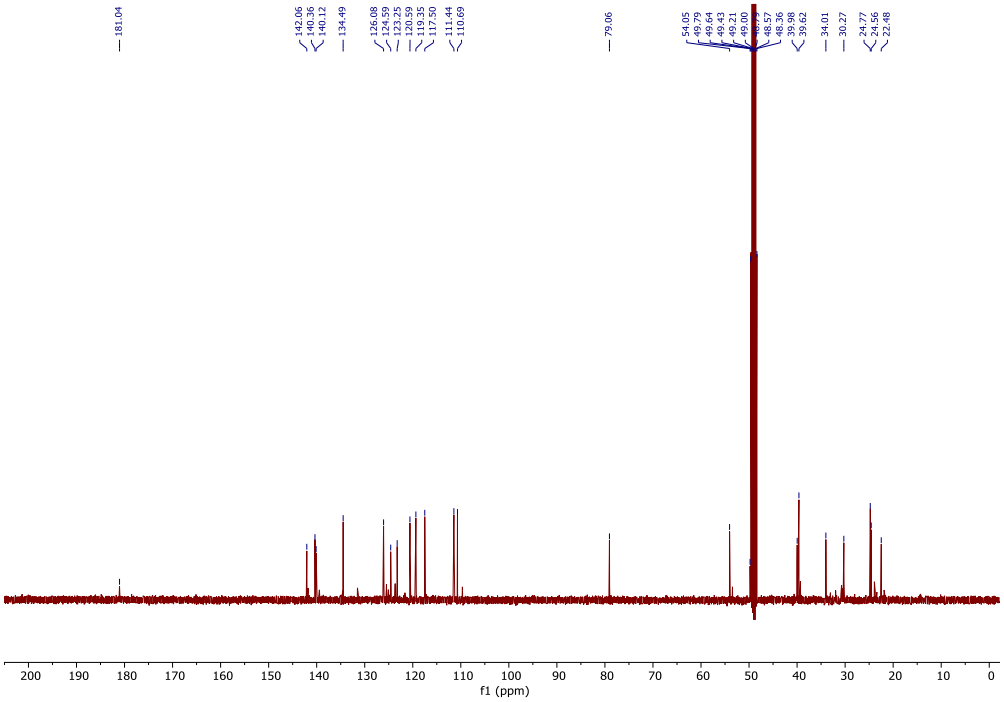

HRMS data of oridamycin A methyl ester [(+)-**2c**]



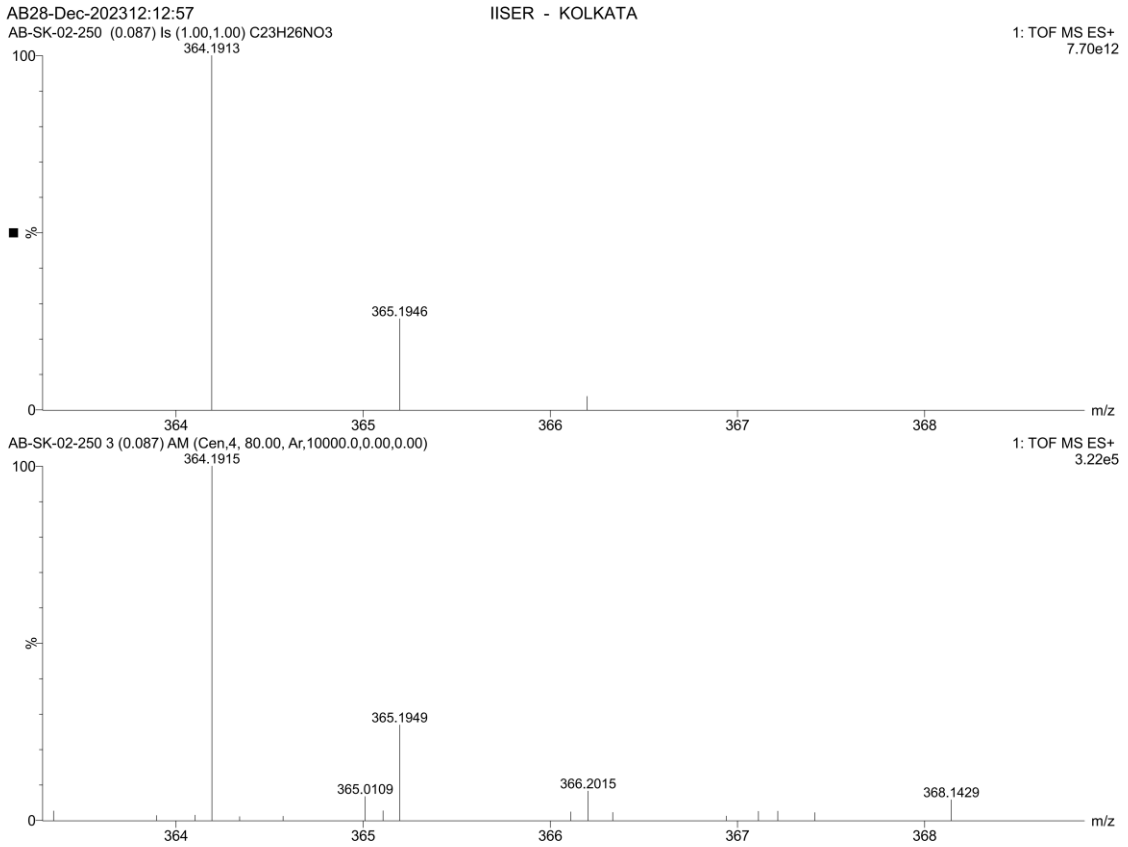
oridamycin A [(+)-**2a**]




$^{1}$H NMR (500 MHz, $CDCl_3$) of oridamycin A [(+)-**2a**]




$^{13}$C NMR (101 MHz, $CDCl_3$) of (+)-oridamycin A [(+)-**2a**]




HRMS data of oridamycin A [(+)-**2a**]