Synthesis of Cyclic (Alkyl)(Amino) Carbene (CAAC) – Mercury(II) Complexes

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A dissertation submitted for the partial fulfilment of
BS-MS dual degree in Science

Department of Chemical Sciences,
Indian Institute of Science Education and Research Mohali
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Dedicated to my best friends,

who have been my inspiration to lead a successful life.

Certificate of Examination

This is to certify that the dissertation titled "Synthesis of Cyclic (Alkyl)(Amino) Carbene–Mercury(II) Complexes" submitted by Mr. Sabari V R (Reg. No. MS11054) for the partial fulfilment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

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Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Sanjay Singh at the Department of Chemical Sciences, Indian Institute of Science Education and Research Mohali. This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

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In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

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Acknowledgement

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Notations and Abbreviations

°	degree (angle)
δ	chemical shift in ppm
Å	angstrom
°C	degree celsius
$\tilde{\nu}$	wave number
Ac	acetyl group (CH_3CO)
AP	atomic probe
Ar	aryl
calcd	calculated
d	doublet
decomp.	decomposition
DMSO	dimethylsulfoxide
DMSO-d_6	duetrated dimethylsulfoxide
ES	electron spray ionization
HRMS	high resolution mass spectrometry
Hz	hertz

IR	infrared spectroscopy
J	coupling constant
m	multiplet
m/z	mass/charge
Me	methyl group (CH_3)
MHz	mega hertz
Mp	melting point
MS	mass spectrometry
NMR	nuclear magnetic resonance
ppm	parts per million
s	singlet
t	triplet
THF	tetrahydrofuran
V	volume
Z	no. of molecules in the unit cell

Abstract

The thesis presents about the recently discovered family of carbene called Cyclic Alkyl(Amino) Carbene. The chapter 1 of this thesis starts with a brief introduction about the two unshared valence electron containing divalent species known as carbenes with their stability and electronic structures. The most commonly used carbenes in chemistry are diaminocarbenes also, known as classical NHCs. A concise information about their electronic properties, transition metal complexes, catalytic activities have been mentioned. Other family of carbenes like cyclic (alkyl)(amino) carbenes (CAACs), bis(amino)cyclopropenylidenes (BACs), acyclic di(amino)carbenes (ADACs), acyclic (alkyl)(amino)carbene (AAACs) have been delineated with due comparison of classical NHCs and CAACs. The CAACs are more nucleophilic as well as more electrophilic than diaminocarbenes due to their unique steric and electronic properties. The CAACs electronic properties and structures, their uses to stabilize unusual diamagnetic/paramagnetic main group metals and transition metal species, activation of small molecules, catalytic activities have been specified in this chapter.

During the course of the thesis, the mercury complexes of CAAC have been synthesized. The synthetic and characterization of these CAAC-mercury(II) complexes are mentioned here.

CHAPTER 1

1. Introduction

Lewis bases are substances having a lone pair of electrons that can be used to stabilize electron deficient transition metal atoms by filling their vacant orbitals to provide them a stable electronic configuration. Therefore, Lewis base acts as a ligand that donates electron pair and the transition metal acts as an electron acceptor to form coordinate bond with them.

Carbenes propounds an interesting and important class of divalent carbon containing neutral compounds having a divalent carbon atom with six-electrons in the valence shell. Carbene carbon atom can either acquire bent or linear geometry. Linear geometry signifies *sp* hybridization and bent geometry signifies sp^2 hybridization. In *sp* hybridization carbon atom acquires two degenerate orbitals p_x and p_y whereas in sp^2 hybridization $p_{y(p_\pi)}$ orbital remains unchanged and the orbital p_x gets stabilized as it gains some s character (σ orbital) by lowering the energy. Therefore the two non-bonded electrons of carbon can be either in two different orbitals having parallel spin (called triplet state) or can be paired in the σ or p_π orbitals (singlet state). Therefore, singlet carbenes can be considered as having a filled and vacant orbital making them ambiphilic in nature (Lewis base and Lewis acid) whereas triplet carbenes contain singly occupied orbitals and are regarded as biradicals.[1]

Fig 1.1: Possible electronic configurations of carbenes

Despite many approaches since 1835[2] the isolation of free uncoordinated carbene remained unambiguous, until in 1988, Bertand and co-workers isolated the first phosphorus and silicon substituents stable carbene.[3] In 1991, Arduengo reported for the first time the isolation of free carbene, named as the nucleophilic heterocyclic carbenes (NHCs).[4] N-heterocyclic

carbenes (NHC) are termed to be heterocyclic species containing one carbene carbon and at least one nitrogen atom within the ring structure. Till the time to hitherto these NHCs have been used widely in laboratory to industries for many fields including catalytic transformation, as organocatalysts and their coordination to transition metals. Chart 1.1 shows a brief picture about the classical NHCs and their application.[5] The first examples of NHC-metal complexes were isolated in 1968 by Wanzlick[6] and Ofele[7] by synthesizing imidazol-2-ylidene bearing Hg(II) and Cr(0) species, respectively. The inherent σ-donor ability of the sp^2-hybridized lone pair that can be accommodated into a σ-accepting orbital makes NHCs as one of the robust candidate to be a ligand for transition metals. There are many classes of carbene compounds with different substitution patterns, ring sizes which fall under the category of NHCs. The σ donation being the basic component in metal ligand binding, the NHC having sp^2 hybridized lone pairs donates electrons to σ-accepting orbital of the transition metal. The π-back-bonding of metal towards the carbene p orbital accounts for about 20% of the overall bond energy. NHC carry similarity with the coordination characteristics of phosphines, due to its strong σ-donating nature and weak π-accepting nature. But the NHC being higher in electron donating tendency than phosphines makes them stronger metal-ligand bonding. The higher catalytic stability and lesser rate of decomposition of NHCs make it a good catalyst. The application of NHC-transition metal complexes in Mizoroki-Heck reaction as a catalyst proved its first homogenous catalysis in organic transformation. The NHCs steric and electronic factors help to stabilize Pd catalyst in cross coupling reactions.

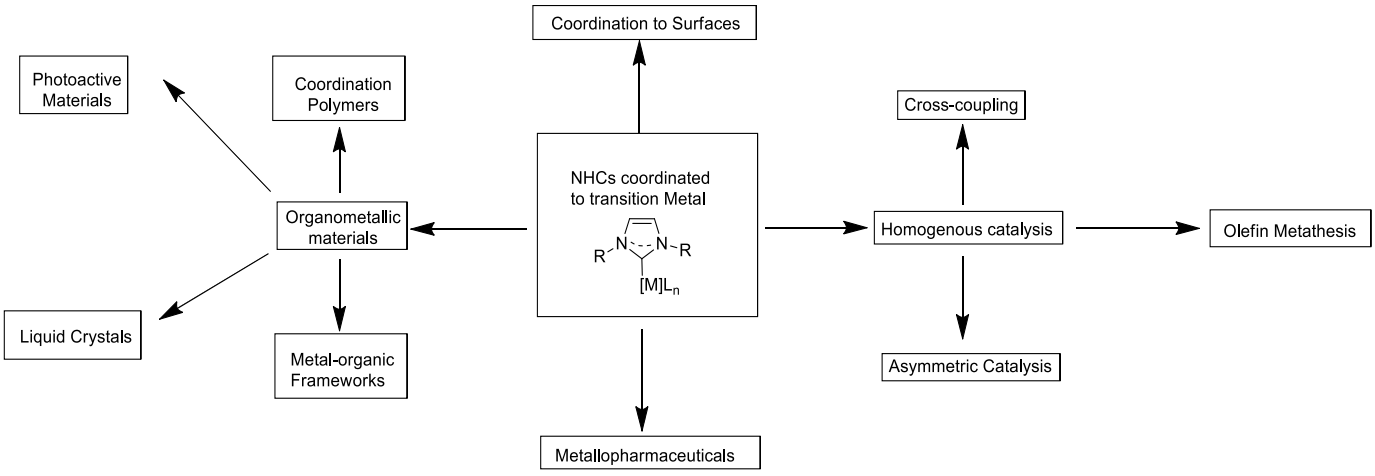
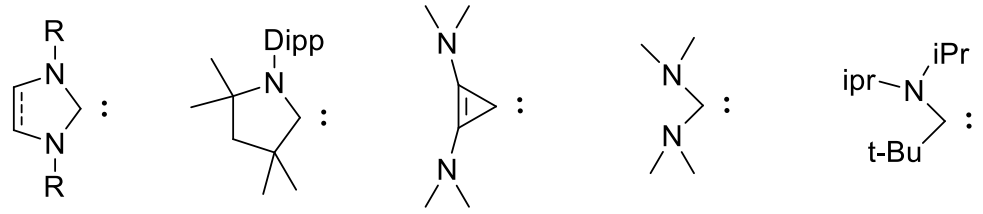


Chart 1.1. Application of NHCs (Chart adapted from *Nature*, **2014**, *510*, 485–496)

The late transition metal chemistry of NHCs has been well characterized and studied which has been further explored for its catalytic application. NHC Complexes with Ru, Rd, Ni, Pd, Ir, Pt, Cu and Au are well developed with its catalytic applications. Important catalytic applications for reduction, polymerization, hydrogenation, hydrosililation, isomerization, C-H bond activation, cyclization reactions and many other reactions are known with above metal complexes of NHCs.[8]

Other carbenes similar to NHCs like cyclic (alkyl)(amino)carbene (CAACs), bis(amino)cyclopropenylidene (BACs), acyclic di(amino)carbenes (ADACs), acyclic (alkyl)(amino)carbene (AAACs) (Fig 1.2) are being explored recently.[9] Among these carbenes the cyclic carbenes are less nucleophilic than acyclic carbenes and the BACs are the most nucleophilic carbene. The reason for being more nucleophilic nature of acyclic carbenes is their wider bond angles that reduce the s character of the lone pair. Similarly, also the acyclic carbenes are more electrophilic than their cyclic counterparts due to the free rotation of the amino group. The presence of σ-electron donating and non-π-donating alkyl groups on CAAC make its more electrophilic as well as more nucleophilic than the σ-electron withdrawing and π donating nature of amino substituent of imidazol-2-ylidene (NHCs). While the BAC being more nucleophilic (but not electrophilic) than NHCs and CAAC due to the stability it attained by aromaticity.



NHC CAAC BAC ADAC AAAC

Fig 1.2: Schematic representation of NHCs, CAACs, BACs, ADACs and AAACs

The work in this thesis presents about the cyclic (alkyl)(amino)carbenes (CAACs) (Fig 1.3) which has surpassed the notion of routine carbene chemistry and lead tremendous development in modern carbene chemistry, due to its unique steric and electronic properties.

The presence of a quaternary carbon at the α position to the carbene center, with strong σ-donors and weak π-acceptors features provides CAACs a wide range of structural features to be possible and makes it unique among all other ligands.

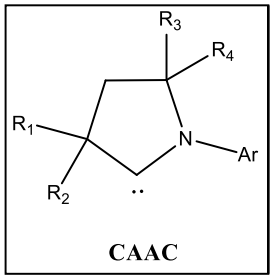


Fig 1.3: Cyclic alkyl(amino) carbene (CAAC)

Due to its unique steric and electronic properties CAAC based carbenes are known to stabilize electron rich main group element based species like nucleophilic boron **(C)**,[10] zero valent phosphorus **(G)**[11] and triatomic silicon(0) **(F)**[12] molecule and the isolation of different oxidation states of antimony compounds (0,+1)[13] (Fig 1.4). The CAAC's ability to delocalize electron density from adjacent centers helped to isolate radical species of boron **(D)** and **(E)**[10] and phosphorous **(H)**[11] (Fig 1.4).

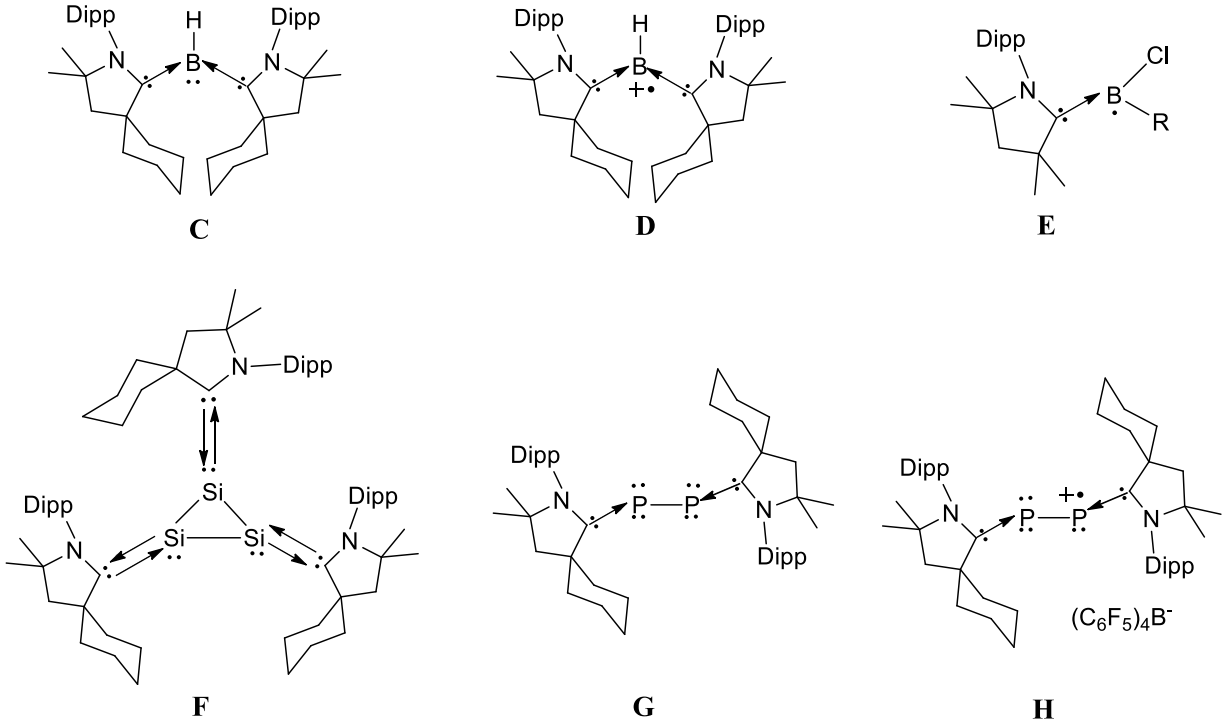


Fig 1.4: Some examples of CAACs stabilized unusual main group species.

The CAACs can also activate small molecules such as CO,[14] H_2,[15] P_4[16] as well as enthalpically strong bonds like B-H, Si-H, N-H and P-H,[17] however the classical NHCs showed inertness toward these substrates.

Complexes of various transition metals are known with CAACs. Transition metals with zero oxidation states are known to be isolated using CAACs for example, *bis*(CAAC)M complexes of Au,[18] Cu,[19] Co & Fe,[20] Ni,[21] Mn,[22] and Zn[23] have been isolated where the metal M is in zero oxidation state. Other low coordinate metal complexes with 14-electron species of rhodium and palladium[24] have been isolated which were otherwise unable to be stabilized by classical NHCs and phosphines.

In contrast to the classical NHCs, the higher basicity of CAACs make them poor leaving group, which make them poor candidates for organocatalysts.

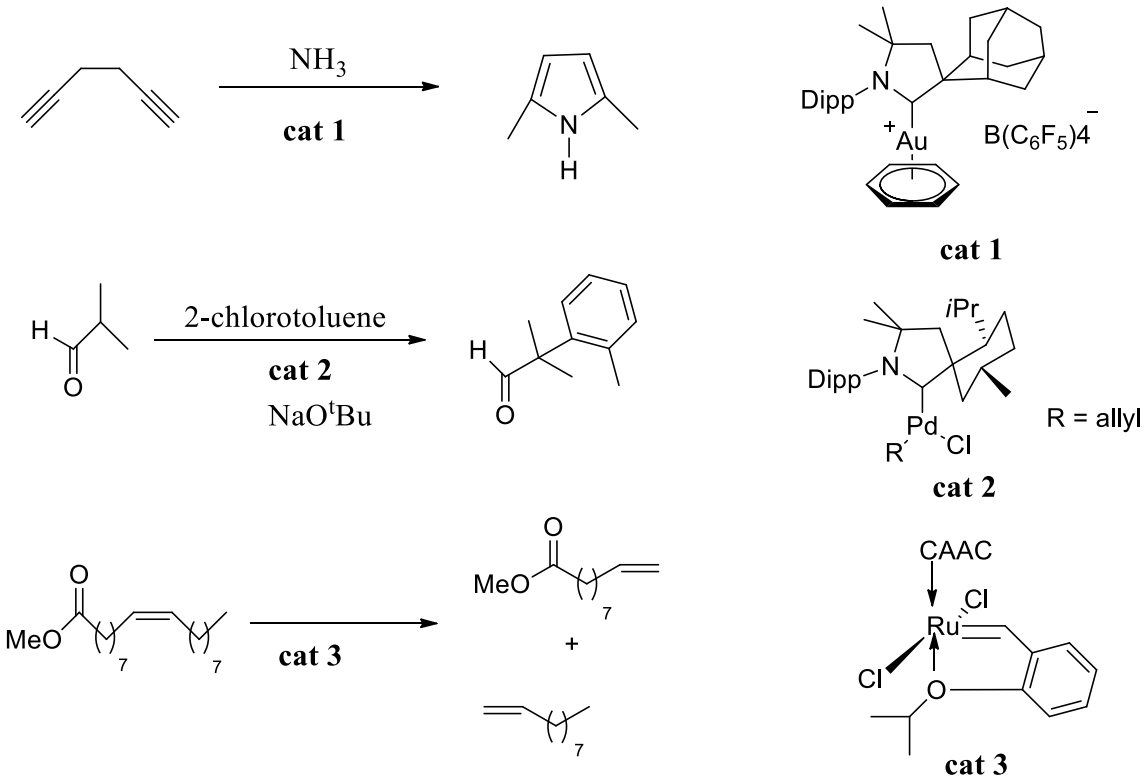
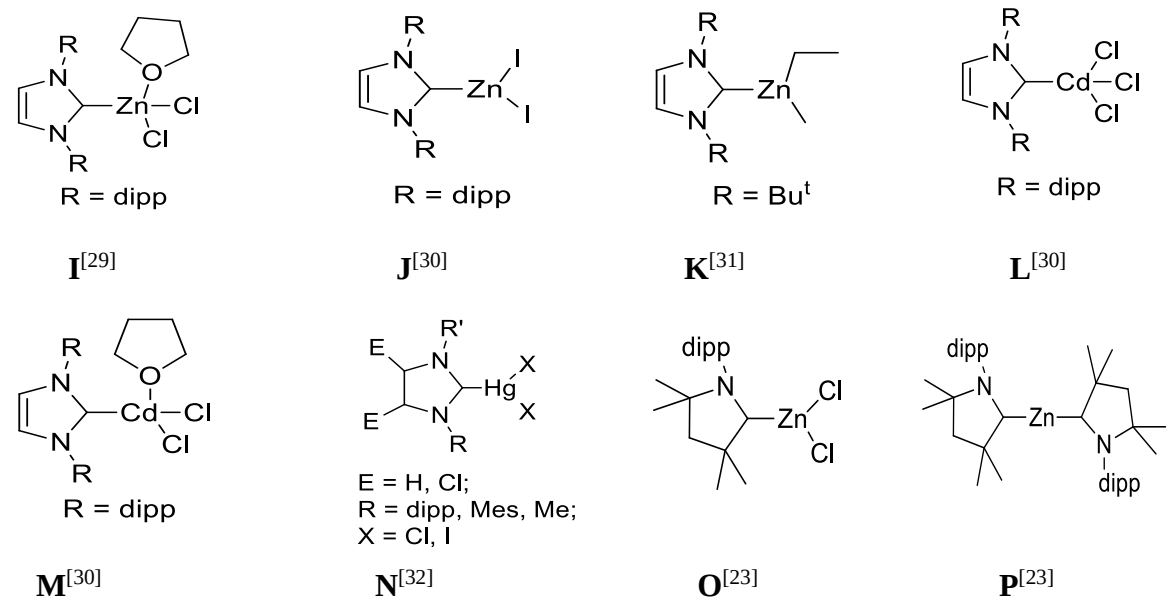


Fig 1.5: CAACs act as ancillary ligands in catalysts for the reactions of hydroamination **(I)**, alpha arylation of ketone **(I)** and ethanolysis **(J)**.

But in contrast to the catalytic properties shown by phosphines and cyclic diaminocarbenes in reactions such as oxidative addition, transmetallation and reductive elimination, the excessive steric hindrance present in their skeleton poses drawback in the coupling of bulky reactants which can be overcome by using CAACs due their conformational flexibility of alkyl substituent on quaternary carbon atom. Fisher type carbenes are less stable in normal conditions of organometallic catalysis due to the cleavage of metal-carbon bonds, but the CAAC-metal complexes can survive and show high catalytic activities. The CAAC-Au complexes proved more resistant to the oxidation and less prone to halogen cleavage of Au-C bonds than Au(I) complexes of imidazole-based ligands due to the strong carbon-metal bonds in CAAC-metal complexes.[25]



I[29] **J**[30] **K**[31] **L**[30] **M**[30] **N**[32] **O**[23] **P**[23]

Fig 1.6: Some of the group 12 metal complexes with NHCs and CAACs. **I–K** are examples of Zn-NHC metal complexes, **L–M** are examples of Cd–NHCs metal complexes, **N** is an example of Hg-NHC metal complexes and **O-P** represents the Zn-CAAC metal complexes.

The low coordinate unsaturated metal complexes play an important role in catalytic processes. As the CAAC ligands have been able to stabilize low coordinate transition metal complexes, the cationic CAAC-gold complex **cat 1** (Fig 1.5) has been used as an efficient catalyst for hydroamination reactions of ammonia and secondary amines with internal or terminal alkynes.[26] The CAAC-palladium complexes **cat 2** (Fig 1.5) have been able to show catalytic properties like α-arylation of aldehydes.[27] The CAAC-ruthenium complex **cat 3** (figure 1.5) is an excellent catalyst for ethanolysis of methyl oleate,[28] when the NHC was replaced with the CAAC backbone in the Grubbs catalyst.

Due to the novel properties of CAAC we focused on syntheses and isolation of group 12 metal complexes of CAACs with Zn, Cd, and Hg halides. With the chemistry of Zn and Cd remains homologous, the Hg diverges from it. The Hg is noble due to its neutral character however the Zn and Cd are very electropositive. For example the dichloride species of Zn and Cd have typical ionic structures however the $HgCl_2$ forms linear molecules in their crystal structure. Therefore it was suspected that carbene chemistry of these metal complexes will not be homologous along the group.

In comparison to other transition metals the ability to serve as d_π donors is very low in group 12 metals. Hence the isolation of group 12 metal complexes with CAACs remain difficult than NHCs because of the high π accepting nature of CAACs. Even though the metal known with the first reported NHC-metal complex was mercury, isolation of CAAC-mercury complex is not reported till date. Only CAAC-metal complexes with Zn have been reported belonging to the group 12 family of the periodic table. We therefore focused on isolating CAAC-metal complexes of mercury and cadmium, with exploring their catalytic activity and isolating low valent and cationic states of mercury and cadmium. Some known NHC and CAAC with group 12 metal complexes have been shown in Fig 1.6.

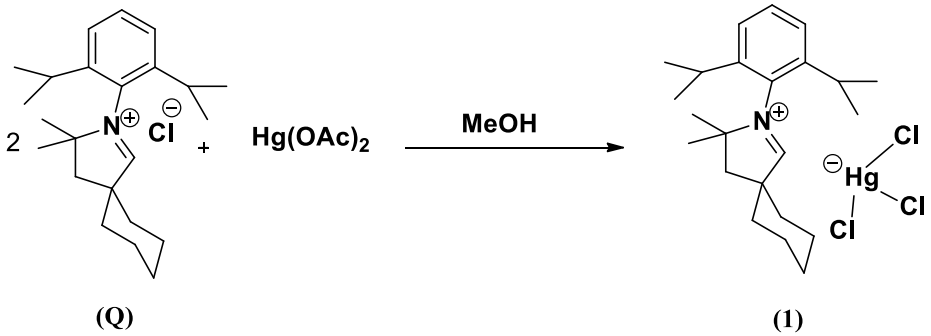
Following these directions we were able to synthesis the first CAAC-mercury(II) complexes, while the synthesis of CAAC-cadmium complex was of failure. Here we have discussed the preparation and isolation of $[CAACH]^+[HgCl_3]^-$ **(1)**, $[CAAC{\cdot}HgCl(\mu\text{-}Cl)]_2$ **(2)**, $[CAAC{\cdot}HgBr(\mu\text{-}Br)]_2$ **(3)**, $[CAAC{\cdot}HgI(\mu\text{-}I)]_2$ **(4)** and $[CAAC]_2O$ **(5).** Molecular structures of

these compounds have been studied thoroughly using NMR, HRMS, IR and single crystal X-ray diffraction technique.

2. Results and Discussion

2.1. Synthesis of $[CAACH]^+[HgCl_3]^-$ (1):

A 2:1 stoichiometric reaction between $[CAACH]^+Cl^-$ **(Q)** and mercury(II) acetate was performed in methanol that afforded colorless crystalline salt of $[CAACH]^+[HgCl_3]^-$ **(1)** (Scheme 2.1). The resulting compound **1** is stable in air and moisture and this colorless crystalline solid decomposed at 247 °C. Compound **1** is soluble in methanol and DMSO and partially soluble in chlorinated solvents like chloroform and was insoluble in other hydrocarbon solvents.



(Q) **(1)**

Scheme 2.1: Synthesis of $[CAACH]^+[HgCl_3]^-$ **(1)**.

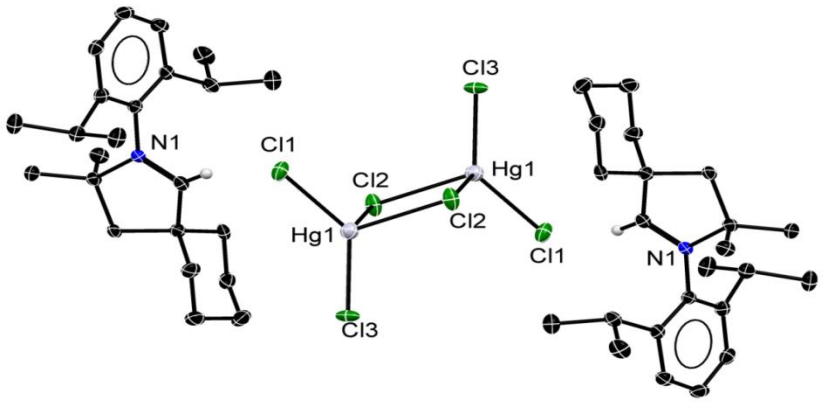


Fig 2.1(a): Single crystal X−ray structure of $[CAACH]^+[HgCl_3]^-$ **(1)**. All hydrogen atoms except on the carbenoid carbon have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Hg(1)-Cl(1) 2.402(9), Hg(1)-Cl(3) 2.407(8), Hg(1)-Cl(2) 2.608(9), 2.683(8), C(1)-H(1) 0.924(4); Hg(1)-Cl(2)-Hg(1) 90.84(4), Cl(2)-Hg(1)-Cl(1) 101.17(3), Cl(2)-Hg(1)-Cl(3) 106.85(3), Cl(1)-Hg(1)-Cl(3) 133.03(3), C(2)-C(1)-N 114.66(3).

In principle, the reaction of $Hg(OAc)_2$ with two equivalents of $[CAACH]^+Cl^-$ should give the $CAAC{\cdot}HgCl_2$ complex. Reaction of $[CAACH]^+Cl^-$ with $Hg(OAc)_2$ in a 2:1 molar ratio in MeOH gave a product that showed a change in the chemical shift of the carbenium proton to 9.47 ppm as compared to 10.32 ppm for the carbenium proton in $[CAACH]^+Cl^-$. Also the ^{13}C NMR of carbenoid carbon showed chemical shift from 193.0 of $[CAACH]^+Cl^-$ to 192.9. Therefore, it was clear that the product of this reaction was an ionic compound and not the expected adduct ($CAAC{\cdot}HgCl_2$). Identity of this counter anion as $[HgCl_3]^-$ was confirmed by HRMS signal at *m/z* = 306.8734 and single crystal X-ray diffraction studies. The molecular structure of $[CAACH]^+[HgCl_3]^-$ **(1)** is depicted in Fig 2.1(a) and the crystal data of compound **1** are given in Table 4.1. X-ray quality crystals of **1** were obtained by keeping its methanol solution at 4 °C. The solid state structure of **1** shows $P2_1/n$ space group and consists of discrete ion-pairs with weak interaction between the ion pairs. The counter anion $[HgCl_3]^-$ exists in dimeric form with distorted tetrahedral geometry and the two $[CAACH]^+$ cations have weak ionic interaction with the dimeric anion, $[HgCl_3]^-$. The crystal structure of $[CAACH]^+[HgCl_3]^-$ **(1)** showed several C···H···Cl interactions (2.725 Å, 2.520 Å) between the hydrogen atoms on imine carbon and chlorine atoms of $HgCl_3^-$ unit, leading to the formation of one dimensional network (Fig 2.1(b)).

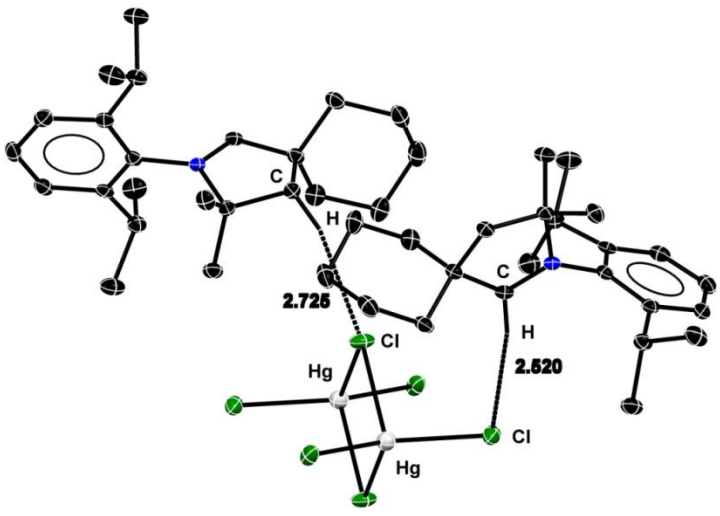
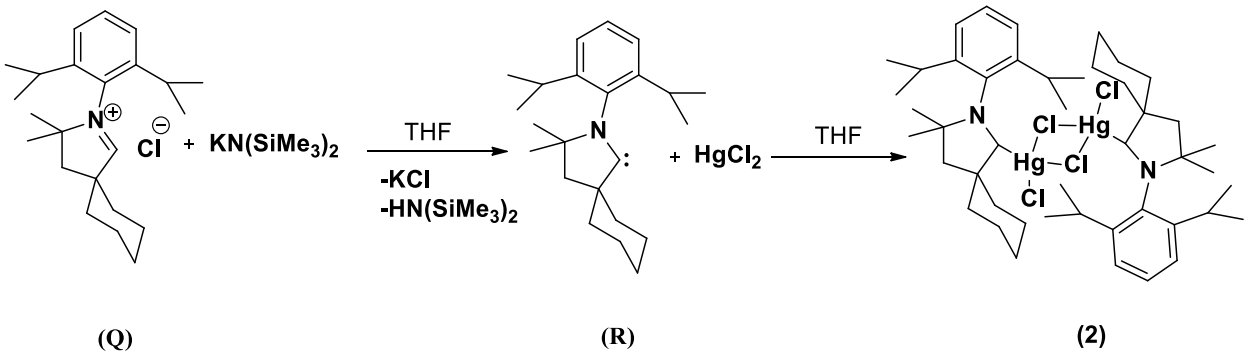


Fig 2.1(b): Perspective view of $[CAACH]^+[HgCl_3]^-$ **(1)** to show the C-H···Cl interactions. All hydrogen atoms except those participating in the C-H···Cl contacts have been omitted for clarity.

2.2. Synthesis of *[CAAC·HgCl(μ-Cl)]$_2$ (2):*

The reaction of $[CAACH]^+Cl^-$ with $K[N(SiMe_3)_2]$ in equal amounts in THF afforded free carbene **(R)**. This *insitu* generated free carbene was reacted with equimolar amount of $HgCl_2$ to afford the complex $[CAAC{\cdot}HgCl(\mu\text{-}Cl)]_2$ **(2)** which gave colorless crystals on storing its original solution at room temperature. Complex **2** is stable to air and moisture, this colorless crystalline solid decomposed at 269 °C. Compound **2** is partially soluble in DMSO and is insoluble in most of the chlorinated and hydrocarbon solvents.



(Q) **(R)** **(2)**

***Scheme 2.2*:** Synthesis of the adduct $[CAAC{\cdot}HgCl(\mu\text{-}Cl)]_2$ **(2)**.

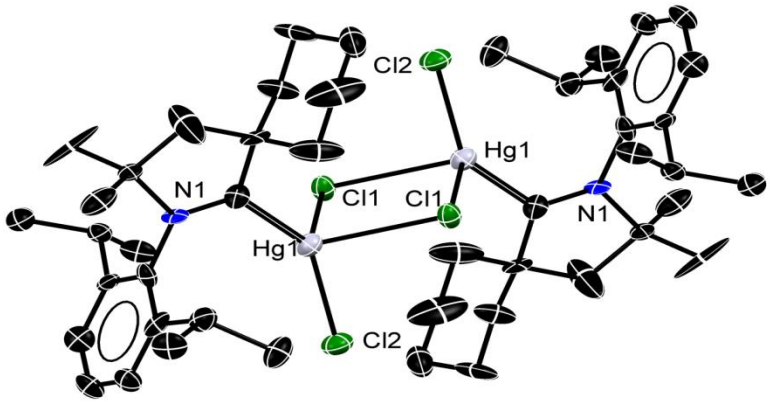


Fig 2.2(a): Single crystal X-ray structure of $[CAAC{\cdot}HgCl(\mu\text{-}Cl)]_2$ **(2)**. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Hg(1)-Cl(2) 2.391(4), Hg(1)-Cl(1) 2.716(4), Hg(1)-C(1) 2.153(1); Hg(1)-Cl(1)-Hg(1) 94.76(1), Cl(1)-Hg(1)-Cl(1) 85.24(1), Cl(2)-Hg(1)-Cl(1) 93.04(1), 96.61(1), C(1)-Hg(1)-Cl(1) 103.84(5), 111.08(4), C(1)-Hg(1)-Cl(2) 142.17(4).

Formation of complex **2** could be confirmed by the disappearance of the singlet at 10.32 ppm in ^{1}H NMR for the carbenium proton, that was observed for the precursor $[CAACH]^{+}Cl^{-}$. Also the ^{13}C NMR of carbenoid carbon showed chemical shift from 193.0 of $[CAACH]^{+}Cl^{-}$ to 245.0. The HRMS data of **2** revealed the presence of $[M–2Cl]^{2+}$, that corresponds to the loss of Cl from the monomer at 562.2180. The X-ray quality crystals of **2** were obtained from THF at room temperature. The molecular structure of **2** consists of CAAC unit coordinated to mercury atom of $HgCl_2$. Unlike the case of NHC-mercury Chloride complexes[32] which were monomeric, complex **2** with mercury atoms have distorted tetrahedral geometry are dimeric with bridging Hg-Cl-Hg interactions. The C-Hg bond distance of 2.15 Å in **2** is similar to that observed for NHC-mercury complexes. The molecular structure of the dimer $[CAAC{\cdot}HgCl(\mu\text{-}Cl)]_2$ **(2)** and the selected bond angles and distances are given in Fig 2.2(a). The crystal data of the compound **2** are given in Table 4.2. The crystal structure of dimer, $[CAAC{\cdot}HgCl(\mu\text{-}Cl)]_2$ **(2)** shows the C···H···Cl interactions (2.803 Å, 2.741 Å) between hydrogens of the diisopropyl substituents and phenyl ring with non-bridged chlorine atoms, leading to the formation of one dimensional network (Fig 2.1(b)).

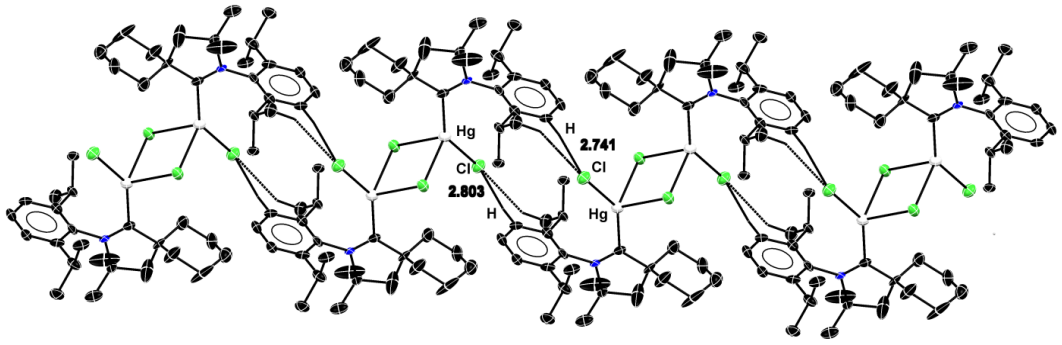
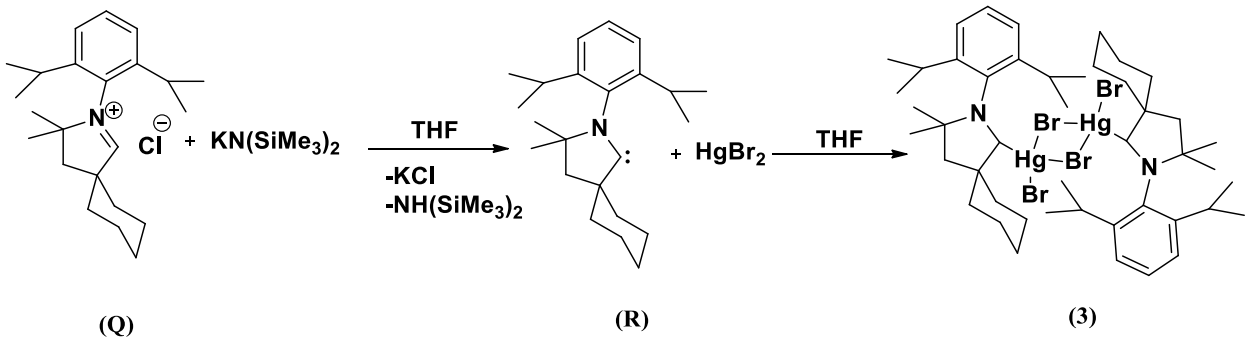


Fig 2.2(b): 1D network of $[CAAC{\cdot}HgCl(\mu\text{-}Cl)]_2$ **(2)** formed by the C-H···Cl interactions. All hydrogen atoms except those participating in the C-H···Cl contacts have been omitted for clarity.

2.4. Synthesis of *[CAAC·HgBr(μ-Br)]₂ (3):*

The reaction of $[CAACH]^{+}Cl^{-}$ with $K[N(SiMe_3)_2]$ in equal amounts in THF afforded free carbene **(R)**. This *insitu* generated free carbene was reacted with equimolar amount of $HgBr_2$ to afford the complex $[CAAC{\cdot}HgBr(\mu\text{-}Br)]_2$ **(3)** which gave colorless crystals on

storing its original solution at room temperature. The resulting complex **3** is stable in air and moisture, this colorless crystalline solid decomposes at 256 °C.



(Q) **(R)** **(3)**

***Scheme 2.3*:** Synthesis of the adduct [CAAC·HgBr(μ-Br)]$_2$ **(3)**.

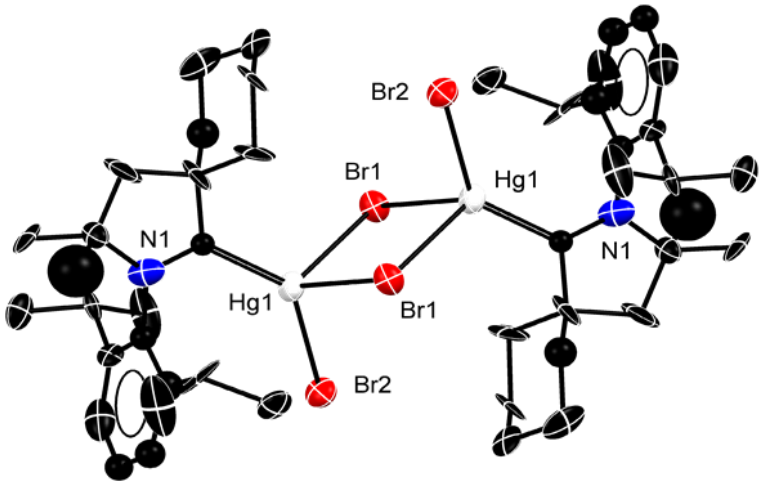


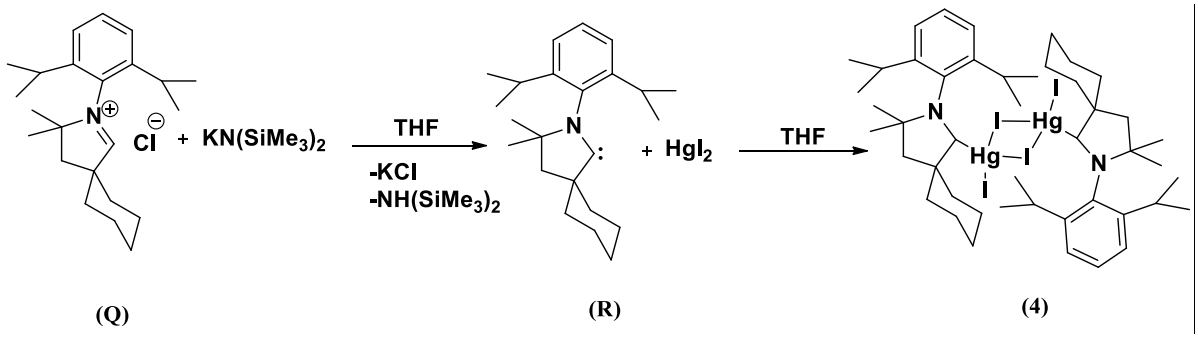
Fig 2.3: Single crystal X-ray structure of [CAAC·HgBr(μ-Br)] $_2$ **(3)**. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Hg(1)-Br(2) 2.733(3), Hg(1)-Br(1) 2.536(3), Hg(1)-C(1) 2.12(2); Hg(1)-Br(1)-Hg(1) 93.01(8), Br(1)-Hg(1)-Br(1) 86.99(8), Br(2)-Hg(1)-Br(1) 100.67(9), 102.05(10), C(1)-Hg(1)-Br(1) 115.6(6), 103.70(6), C(1)-Hg(1)-Br(2) 136.01(6).

Compound **3** is partially soluble in DMSO and is insoluble in most of the chlorinated and hydrocarbon solvents. The formation of this complex was confirmed by the disappearance of singlet peak at 10.32 ppm in ^{1}H NMR for the carbenium proton, that was observed for the precursor [CAACH]$^{+}$Cl^{-}. Also the ^{13}C NMR of carbenoid carbon showed chemical shift from 193.0 of [CAACH]$^{+}$Cl^{-} to 244.6.

Further the HRMS data revealed the presence of $[M–Br]^+$, corresponding to the loss of Br from the dimer CAAC·$HgBr_2$ and $[M– 2Br]^{2+}$ corresponding to the loss of Br from the monomer CAAC·$HgBr_2$ at 1291.2565 and 606.1647, respectively, where M is complex **3**. The X-ray quality crystals of **3** were obtained from its THF solution at room temperature. Single crystal X-ray data of complex **3** shows dimer formation in the solid state as $[CAAC·HgBr(\mu\text{-}Br)]_2$ **(3)** (Fig 2.3) with C-Hg distance of 2.12 Å. The NHC-$HgBr_2$ also showed the same dimeric form like **3**. The crystal data of **3** is given in Table 4.3. The structural features of complex **3**, including the dimer formation was identical to the adduct $[CAAC·HgCl(\mu\text{-}Cl)]_2$ **(2)**.

2.4. Synthesis of *$[CAAC·HgI(\mu\text{-}I)]_2$(4):*

The reaction of $[CAACH]^+Cl^-$ with $K[N(SiMe_3)_2]$ in equal amounts in THF afforded free carbene CAAC **(R)**. This *insitu* generated free carbene was reacted with equimolar amount of HgI_2.



***Scheme 2.4*:** Synthesis of the adduct $[CAAC·HgI(\mu\text{-}I)]_2$ **(4)**.

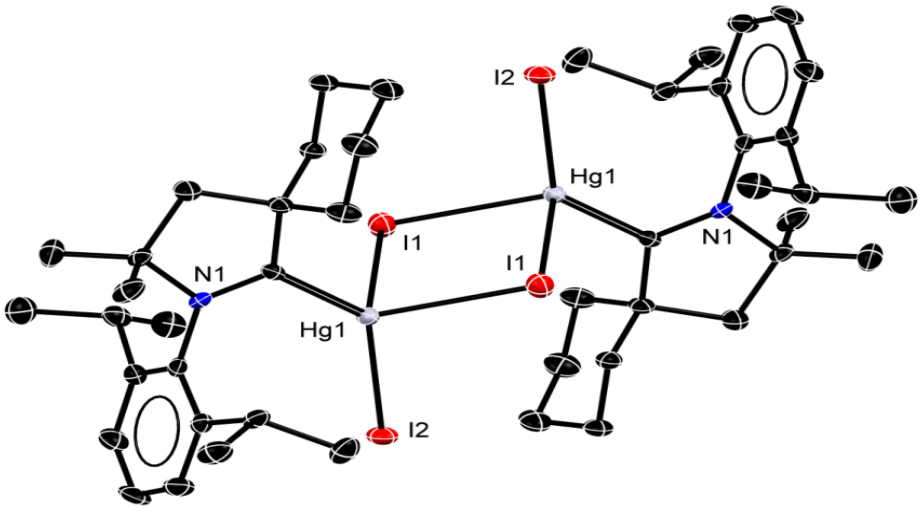


Fig 2.4(a): Single crystal X−ray structure of [CAAC·HgI(μ-I)]$_2$ **(4)**. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Hg(1)-I(2) 2.704(3), Hg(1)-I(1) 2.889(5), Hg(1)-C(1) 2.167(3); Hg(1)-I(1)-Hg(1) 88.58(2), I(1)-Hg(1)-I(1) 91.42(2), I(2)-Hg(1)-I(1) 103.83(2), 98.35(2), C(1)-Hg(1)-I(1) 106.56(1), 112.87(1), C(1)-Hg(1)-I(2) 134.42(1).

Colorless crystals of CAAC·HgI$_2$ **(4)** complex were obtained at room temperature which was stable in air and moisture and this crystalline solid decomposed at 263 °C. Complex **4** is partially soluble in DMSO and is insoluble in most of the other chlorinated and hydrocarbon solvents. The formation of the complex **4** was confirmed by the disappearance of the singlet at 10.32 in ^{1}H NMR for the carbenium proton of precursor [CAACH]$^{+}$Cl^{-}. Also the ^{13}C NMR of carbenoid carbon showed chemical shift from 193.0 of [CAACH]$^{+}$Cl^{-} to 245.18. The HRMS data revealed the presence of [M+2H**]**$^{2+}$ and [M–2I]$^{2+}$ and at 782.0620 and 654.1520, respectively. Single crystal X-ray data of complex **4** showed dimer formation in the solid state as [CAAC·HgI(μ-I)]$_2$ **(4)** (Fig 2.4(a)) with C-Hg distance of 2.17 Å. The crystal data of **4** are given in Table 4.4. The structural features of complex **4**, including the dimer formation and the formation of one dimensional network was identical to the adduct [CAAC·HgCl(μ-Cl)]$_2$ **(2)**. The NHC-HgBr$_2$ also showed the same dimeric form like **4**. The crystal structure of dimer, [CAAC·HgI(μ-I)]$_2$ **(4)** shows the C···H···I interactions (2.891 Å) between hydrogens of

aromatic ring with non-bridged iodine atoms, leading to the formation of one dimensional network (Fig 2.4(b)).

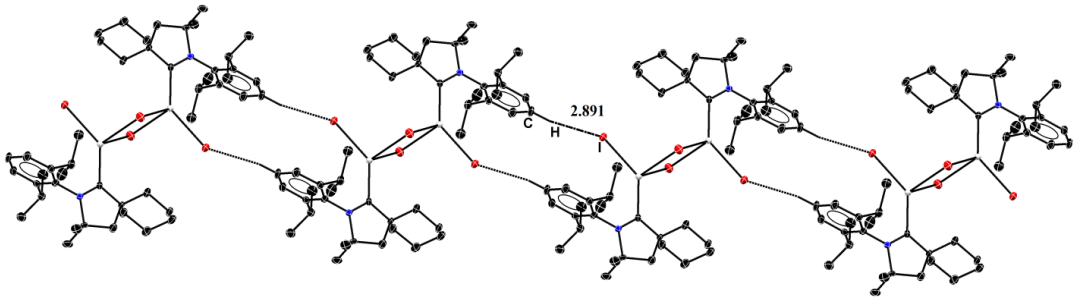
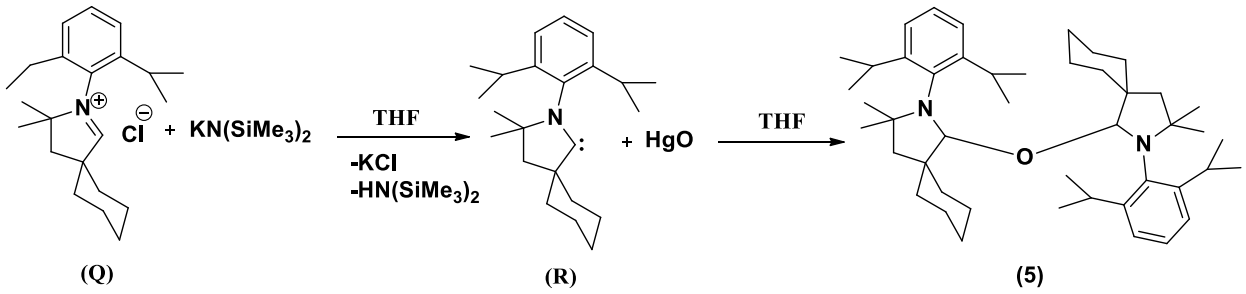


Fig 2.4(b): 1D network of $[CAAC{\cdot}HgI(\mu\text{-}I)]_2$ **(4)** formed by the C-H···I interactions. All hydrogen atoms except those participating in the C-H···I contacts have been omitted for clarity.

2.5. Synthesis of *[CAACH]$_2$O (5):*

The reaction of $[CAACH]^+Cl^-$ with $K[N(SiMe_3)_2]$ in equal amounts in THF afforded free carbene CAAC **(R)**. Subsequently reaction of this *insitu* generated free carbene with equimolar amount of HgO was expected to produce CAAC·HgO adduct. However, colorless crystals of $[CAACH]_2O$ **(5)** were obtained at room temperature which was stable to air and moisture. This thermally stable colorless crystalline solid melts around 195 ^oC. The compound **5** was soluble in most of the solvents like methanol, chloroform and hydrocarbon solvents.



***Scheme 2.5*:** Synthesis of $[CAACH]_2O$ **(5)**.

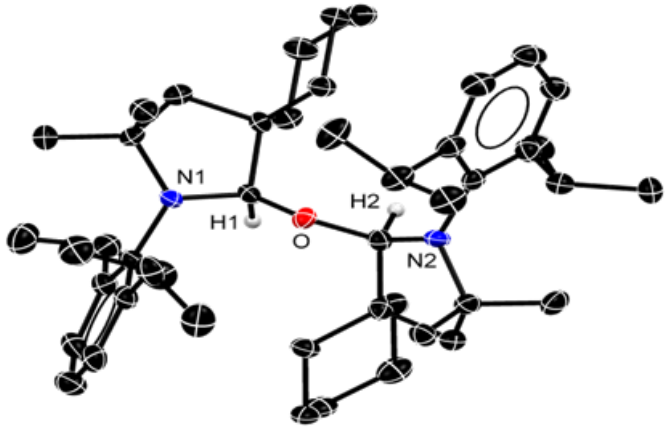


Fig 2.5: Single crystal X−ray structure of $[CAACH]_2O$ **(5)**. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: C-O 1.467(3); C-O-C115.03(2).

In principle the reaction of equivalent amount of **R** and HgO should give CAAC·HgO complex. The compound **5** might have formed either due the deposition of mercury from CAAC·HgO in the reaction mixture or H_2O have reacted with **U** which might have come from THF. The formation of the compound **5** was confirmed from X-ray crystal structure analysis which was comparable to $(Me_2\text{-}CAACH)_2O$ molecule.[33] The X-ray quality crystals where obtained from crystallisation in THF at room temperature. The molecular structure of **5** consists of a oxygen bridged between two [CAACH] units with C-O distance of 1.46 Å (Fig 2.5). The crystal data of **5** are given in Table 4.5. The formation **5** was further confirmed by the carbenium protons around 4.69 ppm and two septets at 3.92 and 3.09 ppm. However the HRMS data revealed the presence of fragmented species of **5** like $[CAACO + H]^+$ and $[CAACH]^+$ at 342.2785 and 326.2837, respectively.

3. Experimental Section:

3.1. General

All manipulations were performed under nitrogen/argon atmosphere using Schlenk or glove box techniques. All chemicals were purchased from Sigma-Aldrich and used without further purification. The starting material cyclic (alkyl)(amino) carbene salt, $[CAACH]^{+}Cl^{-}$ was prepared by following the reported procedures.[34] IR spectra of the complexes were recorded in the range 4500–400 cm^{-1} with a Perkin–Elmer Lambda 35-spectrophotometer. The ^{1}H and ^{13}C spectra were recorded with a Bruker 400 MHz spectrometer with TMS as external reference; chemical shift values are reported in ppm. High-resolution mass spectrometry was performed with Waters SYNAPT G2-S instrument.

3.2. Single Crystal X-ray structural determination

Single crystal X-ray diffraction data of **1**, **2**, **3**, **5** were collected using a Rigaku XtaLAB mini diffractometer equipped with Mercury375M CCD detector. The data were collected with graphite monochromatic MoKα radiation (λ = 0.71073 Å) at 100.0(2) K using scans. During the data collection the detector distance was 50 mm (constant) and the detector was placed at 2θ = 29.85° (fixed) for all the data sets. The data collection and data reduction were done using Crystal Clear suite.[35] Single crystal X-ray diffraction data for compounds **4** was collected on a Bruker *AXS KAPPA APEX-II* CCD diffractometer (Monochromatic MoKα radiation) equipped with Oxford Cryosystem 700 plus at 100 K. Data collection and unit cell refinement for the data sets were done using the Bruker APPEX-II suite, data reduction and integration were performed using SAINTV 7.685A (Bruker AXS, 2009)[36] and absorption corrections and scaling were done using SADABSV2008/1 (Bruker AXS, 2009)[36]. The crystal structures were solved by using either OLEX2[36] or WINGX package using SHELXS-97[37] and the structure were refined using SHELXL-97 2008.47. All non-hydrogen atoms were refined anisotropically. All the figures were generated using Mercury 3.2.

3.3. *Preparation of [CAACH]$^+$[HgCl$_3$]$^-$ (1)*

A mixture of [CAACH]$^+$Cl$^-$ (0.72 g, 2.0 mmol) and Hg(OAc)$_2$ (0.32 g, 1.0 mmol) was taken in 50 mL methanol. The resulting suspension was stirred at room temperature for overnight. The solution was filtered, concentrated and subsequently kept for crystallization. Colorless crystals were obtained at room temperature in overnight. Yield: 0.399 g, 63%. Mp: 237-245^{o}C (decomp). **IR** (KBr, cm^{-1}) $\tilde{\nu}$: 2967, 2927, 2861(C-H alkane stretch), 1715, 1671, 1640 (C=N stretch), 1579, 1465, 1443 (C=C aromatic stretch, CH_2 bend, CH_3 bend), 1272, 1191, 1138, 1088, 1050 (C-N stretch). **^{1}H NMR** (400 MHz, CD_3OD): δ = 9.47 (s, 1H, C*H*=N), 7.61 (t, 1H, *Ar*, $^3J_{H\text{-}H}$ = 8 Hz), 7.50 (d, 2H, *Ar*, $^3J_{H\text{-}H}$ = 8 Hz), 2.81 (sept, 2H, C*H*Me$_2$, $^3J_{H\text{-}H}$ = 6.8 Hz), 2.56 (s, 2H, C*H$_2$*), 2.06-1.63 (m, 10H, *H$_2$*Cy), 1.60 (s, 6H, *Me*), 1.40 (d, 6H, CH*Me$_2$*, $^3J_{H\text{-}H}$ = 6.8 Hz), 1.16 (d, 6H, CH*Me$_2$*, $^3J_{H\text{-}H}$ = 6.8 Hz). **^{13}C NMR**(100 MHz, CD_3OD): δ = 192.9 (N=*C*H), 145.8, 133.2, 126.6, 85.1, 54.0, 39.8, 35.1, 30.7, 29.1, 26.4, 25.8, 22.5, 22.34. **MS** (ES,-ve): *m/z* calcd for [M-CAACH]$^-$ 306.8745; found 306.8734, **MS** (ES, +ve): *m/*z calcd for [M-HgCl$_3$]$^+$ 326.2847; found 326.2842.

3.4. *Preparation of [CAAC·HgCl(μ-Cl)]$_2$ (2)*

A mixture of [CAACH]$^+$Cl$^-$ (0.36 g, 1.0 mmol) and K[N(SiMe$_3$)$_2$] (0.2 g, 1.0 mmol) was taken in 20 mL THF. The resulting suspension was stirred at room temperature for 2 h. The solution was filtered to remove KCl and subsequently added to $HgCl_2$ (0.27 g, 1.0 mmol). The resulting suspension was stirred at room temperature for overnight. The solution was filtered, concentrated and subsequently kept for crystallization. Yield: 0.462 g, 77% Mp: 269-275^{o}C (decomp). **IR** (KBr, cm^{-1}) $\tilde{\nu}$: 2972, 2931, 2863 (C-H stretch), 1595, 1462, 1445 (C=C aromatic stretch, CH_2 bend, CH_3 bend), 1387 (CH_3 bend), 1264, 1137, 1110, 1049 (C-N stretch), 932, 809, 775. **^{1}H NMR** (400 MHz, DMSO-d$_6$): δ = 7.53-7.39 (m, 3H, *Ar*), 2.69 (sept, 2H, C*H*Me$_2$, $^3J_{H\text{-}H}$ = 6.4 Hz), 2.33 (s, 2H, C*H$_2$*), 2.46-2.33, 1.75-1.30 (m, 10H, *H$_2$*C$_{Cy}$), 1.42 (s, 6H, *Me*), 1.25 (d, 6H, CH*Me$_2$*, $^3J_{H\text{-}H}$ = 6.4 Hz), 1.20 (d, 6H, CH*Me$_2$*, $^3J_{H\text{-}H}$ = 6.4 Hz). **^{13}C NMR** (100 MHz, DMSO-*d$_6$*): δ = 245.0 (C-Hg), 145.2, 132.6, 131.1, 126.4, 86.5, 67.1, 58.9, 43.7, 35.7, 29.0, 28.4,

28.3, 26.9, 25.2, 24.9, 21.0. **MS** (AP,+ve): *m/z* calcd for $[M\text{-}2Cl]^{2+}$ 562.2158; found 562.2180.

3.5. *Preparation of [CAAC·HgBr(μ-Br)]₂ (3)*

A mixture of $[CAACH]^{+}Cl^{-}$ (0.36 g, 1.0 mmol) and $K[N(SiMe_3)_2]$ (0.2 g, 1.0 mmol) was taken in 20 mL THF. The resulting suspension was stirred at room temperature for 2 h. The solution was filtered to remove KCl and subsequently added to $HgBr_2$ (0.36 g, 1.0 mmol). The resulting suspension was stirred at room temperature for overnight. The solution was filtered, concentrated and subsequently kept for crystallization. Colorless crystals were obtained at room temperature in overnight. Yield: 0.535 g, 78%. Mp: 256-258ºC (decomp). **IR** (KBr, cm^{-1}) $\tilde{\nu}$: 2972, 2934, 2859 (C-H stretch), 1595, 1554, 1455, 1448 (C=C aromatic stretch, CH_2 bend, CH_3 bend), 1387, 1370 (CH_3 bend), 1264, 1141, 1110, 1049 (C-N stretch), 929, 906, 775. **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 7.54-7.40 (m, 3H, *Ar*), 2.69 (sept, 2H, C*H*Me$_2$, $^3J_{H\text{-}H}$ = 6.8 Hz), 2.34 (s, 2H, CH_2), 2.46-2.39, 1.76-1.28 (m, 10H, H_2C_{Cy}), 1.43 (s, 6H, *Me*), 1.25 (d, 6H, CH*Me*$_2$, $^3J_{H\text{-}H}$ = 6.8 Hz), 1.21 (d, 6H, CH*Me*$_2$, $^3J_{H\text{-}H}$ = 6.8 Hz). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 244.6 (C-Hg), 145.1, 144.4, 132.8, 132.6, 131.2, 130.9, 126.5, 125.9, 86.6, 84.4, 67.0, 59.3, 59.0, 43.7, 36.2, 33.0, 29.1, 28.9, 28.6, 28.3, 28.2, 26.5, 24.9, 24.5, 23.5, 21.0. **MS** (AP+ve): *m/z* calcd for $[M–2Br]^{2+}$ 606.1644; found 606.1647; calcd for $[M–Br]^{+}$ 1291.2458; found 1291.2565.

3.6. Preparation of [CAAC·HgI(μ-I)]₂ (4)

A mixture of $[CAACH]^{+}Cl^{-}$ (0.36 g, 1.0 mmol) and $K[N(SiMe_3)_2]$ (0.2 g, 1.0 mmol) was taken in 20 mL THF. The resulting suspension was stirred at room temperature for 2 h. The solution was filtered to remove KCl and subsequently added to HgI_2 (0.45 g, 1.0 mmol). The resulting suspension was stirred at room temperature for overnight. The solution was filtered, concentrated and subsequently kept for crystallization. Colorless crystals were obtained at room temperature in overnight. Yield: 0.613 g, 81%. Mp: 263-265ºC (decomp). **IR** (KBr, cm^{-1}) $\tilde{\nu}$: 2972, 2931, 2859 (C-H stretch), 1547, 1462, 1445

(C=C aromatic stretch, CH_2 bend, CH_3 bend), 1390, 1370 (CH_3 bend), 1264, 1141, 1107, 1052 (C-N stretch), 933, 806, 772. **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 7.51-7.39 (m, 3H, *Ar*), 2.69 (sept, 2H, C*H*Me$_2$, $^3J_{H\text{-}H}$ = 8 Hz), 2.32 (s, 2H, CH_2), 2.55-2.46, 1.78-1.28 (m, 10H, H_2C_{Cy}), 1.45 (s, 6H, *Me*), 1.25-1.22 (d, 12H, CH*Me*$_2$, $^3J_{H\text{-}H}$ = 8 Hz). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 245.18 (C-Hg), 145.1, 144.3, 144.2, 132.9, 132.6, 131.7, 131.0, 130.7, 126.3, 125.7, 125.3, 86.4, 83.9, 83.4, 60.2, 59.9, 58.9, 52.3, 29.1, 29.0, 28.9, 28.4, 28.3, 26.9, 25.7, 25.0, 23.8, 21.8, 21.2, 21.0. **MS** (AP,+ve): *m/z* calcd for $[M+2H]^{2+}$ 782.0648; found 782.0620; calcd for $[M-2I]^{2+}$ 654.1525; found 654.1520; calcd for $[M-I]^+$ 1433.2078; obs: 1433.2157.

3.7. Preparation of [CAACH]$_2$O (5)

A mixture of $[CAACH]^+Cl^-$ (0.72 g, 2.0 mmol) and K[N(SiMe$_3$)$_2$] (0.4 g, 2.0 mmol) was taken in 30 mL THF. The resulting suspension was stirred at room temperature for 2 h. The solution was filtered to remove KCl and subsequently added to HgO (0.22 g, 1.0 mmol).The resulting suspension was stirred at room temperature for overnight. The solution was filtered, concentrated and subsequently kept for crystallization. Colorless crystals were obtained at room temperature in overnight. Yield: 0.254 g, 38%. Mp: 191-195^{o}C; **IR** (KBr, cm^{-1}) $\tilde{\nu}$: 2970, 2926, 2861 (C-H stretch), 1442 (C=C aromatic stretch, CH_2 bend, CH_3 bend), 1381(CH_3 bend), 1324, 1255, 11781130, 1061 (C-N stretch, C-O-C stretch), 935, 886, 842, 809, 769, 700, 615, 534, 465.**^{1}H NMR** ($CDCl_3$, 400 MHz): δ= 7.18-7.09 (m, 6H, Ar*H*), 4.69 (s, 2H, $C_{carbene}H$), 3.90 (sept, 2H, C*H*Me$_2$, $^3J_{H\text{-}H}$ = 6.5 Hz), 3.09 (sept, 2H, C*H*Me$_2$, $^3J_{H\text{-}H}$ = 6.8 Hz), 2.09, 2.06 (s, 2H, CH_2), 1.65-0.22 (m, 20H, H_2C_{Cy}), 1.39-1.37 (m, 12H, CH*Me*$_2$), 1.38 (s, 6H, *Me*), 1.18(s, 6H, CH*Me*$_2$, $^3J_{H\text{-}H}$ = 6.8 Hz), 1.11(s, 6H, CH*Me*$_2$, $^3J_{H\text{-}H}$ = 6.8 Hz), 0.85 (s, 6H, *Me*). **^{13}C NMR** ($CDCl_3$, 400 MHz): 152.8, 148.8, 141.7, 126.5, 124.4, 123.6, 103.1, 68.1, 61.4, 53.2, 46.8, 42.3, 32.5, 29.9, 28.4, 28.1, 27.5, 27.3, 25.8, 24.9, 24.8, 23.9, 23.7. **MS** (AP,+ve): calcd for $[CAACO + H]^+$ 342.2797; obs: 342.2785; calcd for $[CAACH]^+$ 326.2848; obs: 326.2837.

4. Crystal Data and Refinement Details:

Table 4.1. Crystal data and structure refinement details for [CAACH$^+$][HgCl$_3^-$] (1)

Empirical formula	$C_{23}H_{36}Cl_3HgN$	
Formula weight	633.51	
Temperature	100.0(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 14.528(10) Å	α= 90°
	b = 11.547(8) Å	β= 105.65(3)°
	c = 15.732(10)Å	γ = 90°
Volume	2541.2(3)Å^3	
Z	4	
Density (calculated)	1.656 Mg/m^3	
Absorption coefficient	6.382 (MoKα)/ mm^{-1}	
F(000)	1241	
Crystal size	0.2 x 0.2 x 0.2 mm^3	
θ range for data collection	4.64to 25.35°	
Index ranges	$-17 \le h \le 16$, $-13 \le k \le 11$, $-18 \le l \le 18$	
Reflections collected	15123	
Independent reflections	4618 (R_{int} = 0.0218)	
Completeness to θ = 50.00°	99.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restrains / parameters	4618 / 0 / 262	
Goodness-of-fit on F^2	1.024	
Final R indices (I>2 σ(I))	R1 = 0.0224, wR2 = 0.0585	
R indices (all data)	R1 = 0.0255, wR2 = 0.0601	
Largest diff. Peak and hole	1.320 and –0.9945 e.Å^{-3}	
Diffractometer / detector	Rigaku XtaLAB mini diffractometer / Mercury375M CCD	
Detector distance / tube power	49.85 mm / 50KV, 12mA	

Table 4.2. Crystal data and structure refinement details for [CAAC·HgCl(μ-Cl)]$_2$ (2).

Empirical formula	$C_{23}H_{35}Cl_2HgN$
Formula weight	597.01
Temperature	100.0(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 10.963(4) Å α = 90°
	b = 17.283(6) Å β = 100.239(14)°
	c = 12.479(4)Å γ = 90°
Volume	2326.8(14) Å^3
Z	4
Density (calculated)	1.704 Mg/m^3
Absorption coefficient	6.853 (MoKα)/ mm^{-1}
F(000)	1176
Crystal size	0.2 x 0.2 x 0.2 mm^3
θ range for data collection	3.0to 27.5°
Index ranges	$-13 \le h \le 13$, $-20 \le k \le 20$, $-15 \le l \le 15$
Reflections collected	20597
Independent reflections	4250 (R_{int} = 0.2636)
Completeness to θ = 50°	99 %
Refinement method	Full-matrix least-squares on F^2
Data / restrains / parameters	4250/ 0/ 250
Goodness-of-fit on F^2	1.084
Final R indices (I>2 σ(I))	R1 = 0.0829, wR2 = 0.1848
R indices (all data)	R1 = 0.1109, wR2 = 0.2098
Largest diff. Peak and hole	4.396 and –2.515 e.Å^{-3}
Diffractometer / detector	Rigaku XtaLAB mini diffractometer / Mercury375M CCD
Detector distance / tube power	49.85 mm / 50KV, 12mA

Table 4.3. Crystal data and structure refinement details for [CAAC·HgBr(μ-Br)]$_2$ (3).

Empirical formula	$C_{23}H_{35}Br_2HgN$	
Formula weight	685.93	
Temperature	100.0(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 14.007(5) Å	α = 90°
	b = 9.482(4) Å	β = 98.19(3)°
	c = 18.167(6)Å	γ = 90°
Volume	2388.1(15) Å^3	
Z	4	
Density (calculated)	1.908 Mg/m^3	
Absorption coefficient	9.800 (MoKα)/ mm^{-1}	
F(000)	1320	
Crystal size	0.2 x 0.2 x 0.2 mm^3	
Index ranges	$-16 \le h \le 12$, $-11 \le k \le 11$, $-21 \le l \le 15$	
Reflections collected	6894	
Independent reflections	4182 (R_{int} = 0.1779)	
Completeness to θ = 50°	99 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restrains / parameters	4182/ 0/ 215	
Goodness-of-fit on F^2	1.181	
Final R indices (I>2 σ(I))	R1 = 0.1249, wR2 = 0.3123	
R indices (all data)	R1 = 0.1677, wR2 = 0.3821	
Largest diff. Peak and hole	8.590 and –4.700 e.Å^{-3}	
Diffractometer / detector	Rigaku XtaLAB mini diffractometer / Mercury375M CCD	
Detector distance / tube power	49.85 mm / 50KV, 12mA	

Table 4.4. Crystal data and structure refinement details for [CAAC·HgI(μ-I)]$_2$ (4).

Empirical formula	$C_{23}H_{35}HgI_2N$
Formula weight	779.91
Temperature	100.0(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 14.186(4) Å α = 90°
	b = 9.686(2) Å β = 99.539(3)°
	c = 18.558(5)Å γ = 90°
Volume	2514.6(11) Å^3
Z	4
Density (calculated)	2.060 Mg/m^3
Absorption coefficient	8.585 (MoKα)/ mm^{-1}
F(000)	1464
Crystal size	0.2 x 0.2 x 0.2 mm^3
θ range for data collection	4.565to 25.349°
Index ranges	$-17 \leq h \leq 17$, $-11 \leq k \leq 11$, $-22 \leq l \leq 22$
Reflections collected	27994
Independent reflections	4582 (R_{int} = 0.0414)
Completeness to θ = 50°	99 %
Refinement method	Full-matrix least-squares on F^2
Data / restrains / parameters	4582 / 0 / 250
Goodness-of-fit on F^2	1.057
Final R indices (I>2 σ(I))	R1 = 0.0250, wR2 = 0.0667
R indices (all data)	R1 = 0.0261, wR2 = 0.0673
Largest diff. Peak and hole	1.912 and –2.095 e.Å^{-3}
Diffractometer / detector	Bruker AXS KAPPA APEX-II CCD diffractometer
Detector distance / tube power	50 mm / 50KV, 30mA

Table 4.5. Crystal data and structure refinement details for $[CAACH]_2O$ (5).

Empirical formula	$C_{46}H_{72}N_2O$	
Formula weight	669.08	
Temperature	100.0(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 23.842(4) Å	α = 90°
	b = 15.089(2) Å	β = 105.612(9)°
	c = 26.250(5)Å	γ = 90°
Volume	9095(3) $Å^3$	
Z	21	
Density (calculated)	1.079 Mg/m^3	
Absorption coefficient	0.064 (MoKα)/ mm^{-1}	
F(000)	3265.23	
Crystal size	0.2 x 0.2 x 0.2 mm^3	
θ range for data collection	3.0 to 27.5°	
Index ranges	$-25 \le h \le 28$, $-18 \le k \le 18$, $-26 \le l \le 31$	
Reflections collected	54621	
Independent reflections	16655 (R_{int} = 0.1598)	
Completeness to θ = 50°	99 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restrains / parameters	16655/ 0/ 1041	
Goodness-of-fit on F^2	1.453	
Final R indices (I>2 σ(I))	R1 = 0.1457, wR2 = 0.3855	
R indices (all data)	R1 = 0.1961, wR2 = 0.4474	
Largest diff. Peak and hole	3.8211 and –0.7958 e.$Å^{-3}$	
Diffractometer / detector	Rigaku XtaLAB mini diffractometer / Mercury375M CCD	
Detector distance / tube power	49.85 mm / 50KV, 12mA	

5. Conclusions

Chapter 1 describes the synthesis of first mercury based CAAC-metal complexes. The most conventional and economical hydroiminiumation route has been followed in the preparation of the CAAC salt.[34] This CAAC salt is used to generate *insitu* CAAC carbene which is further reacted to mercury(II) halides (halides = Cl, Br, I) at room temperature to isolate their corresponding CAAC-mercury adducts $[CAAC{\cdot}HgCl(\mu\text{-}Cl)]_2$ **(2)**, $[CAAC{\cdot}HgBr(\mu\text{-}Br)]_2$ **(3)**, $[CAAC{\cdot}HgI(\mu\text{-}I)]_2$ **(4)**, respectively. The direct method to synthesize the $CAAC.HgCl_2$ adduct *via* oxidative route following the $NHC.HgCl_2$ preparation by reacting $[CAACH]^+Cl^-$ with mercuric acetate, produced [CAACH]+[HgCl3]$^-$ **(1)** salt only. The reaction of free CAAC carbene with HgO could not afford CAAC·HgO complex but rather resulted in the formation of a new ether molecule $[CAACH]_2O$ **(5).** The molecules reported in present work have been characterized thoroughly using NMR, HRMS, IR spectroscopy and single crystal X-ray technique.

6. Future Directions

The continuation of the current work will focus on:

(i) Isolating *bis*(CAAC)Hg complex by reduction of CAAC·Hg(II) halides with suitable reducing agents like KC_8.

(ii) Isolating CAAC-Hg cation using suitable oxidising agents with the CAAC·Hg(II) halides.

(iii) To study catalytic activities of the low valent CAAC·Hg(II) halides.

7. References:

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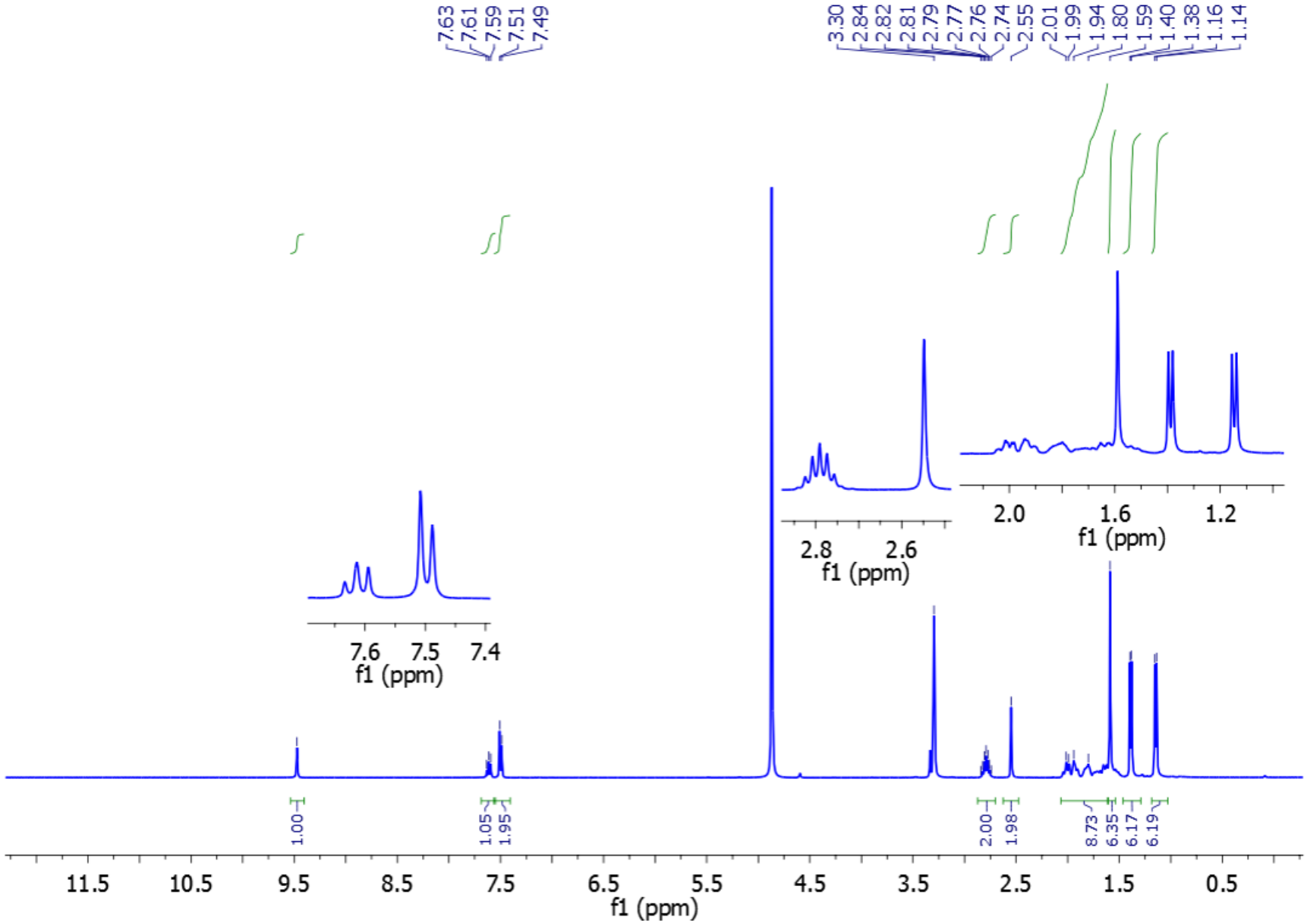
Supporting Information

Heteronuclear NMR spectra (^{1}H, ^{13}C), HRMS spectra and IR-spectra of new compounds reported in this dissertation

Contents

^{1}H NMR of **1** in MeOD



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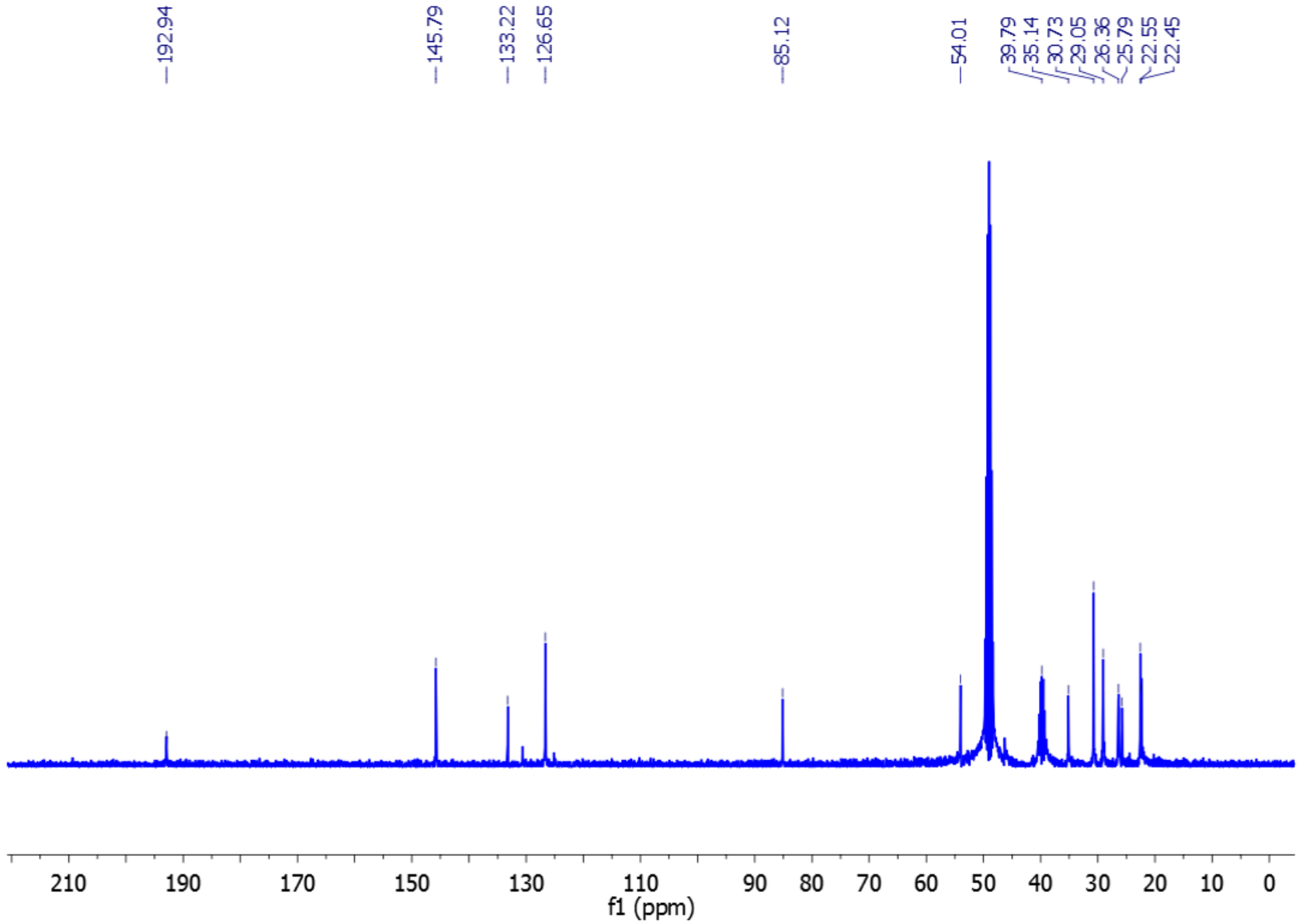

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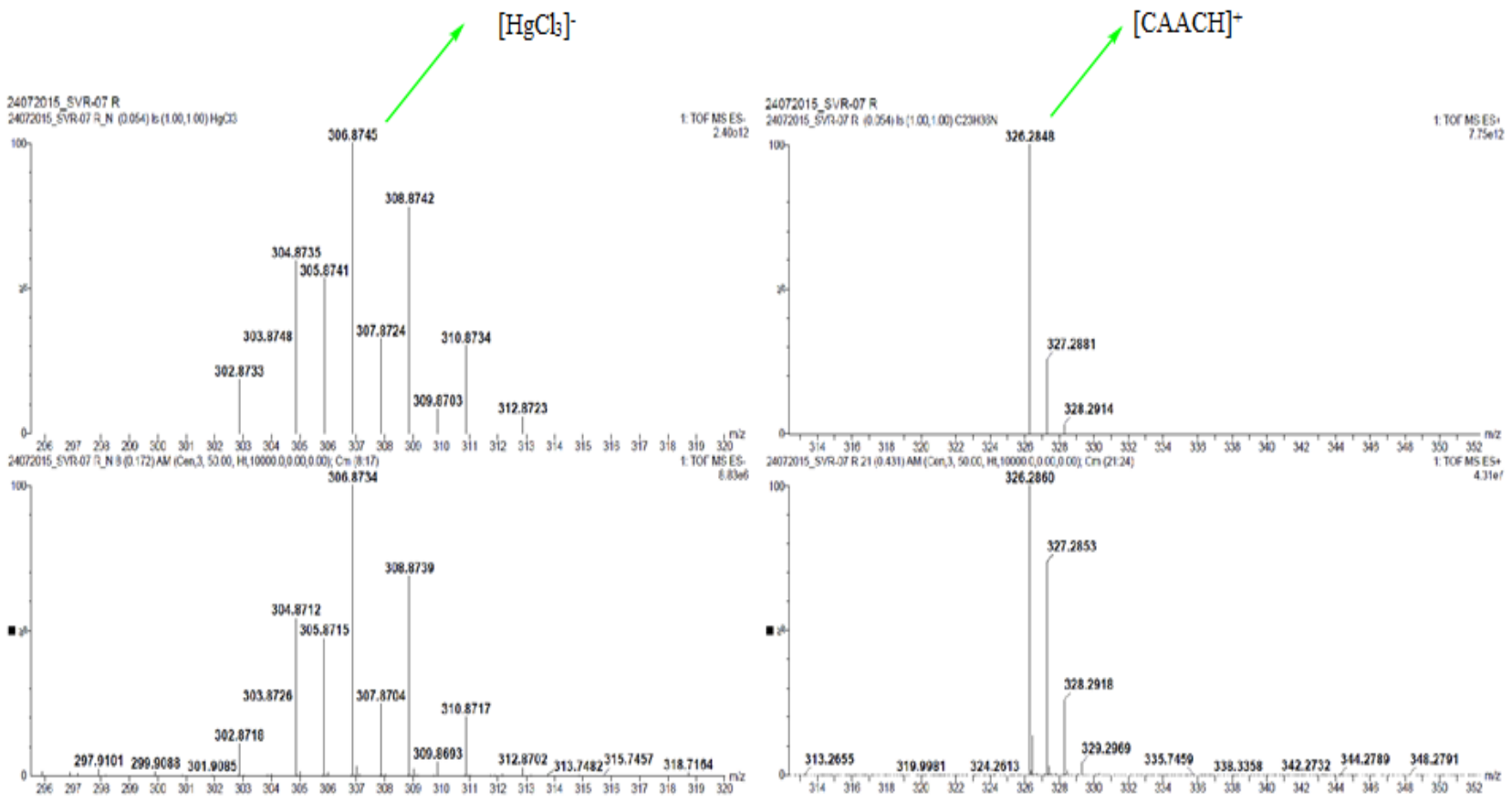
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312.8723
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309.8693
312.8702
313.7482
315.7457
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[CAACH]+
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m/z

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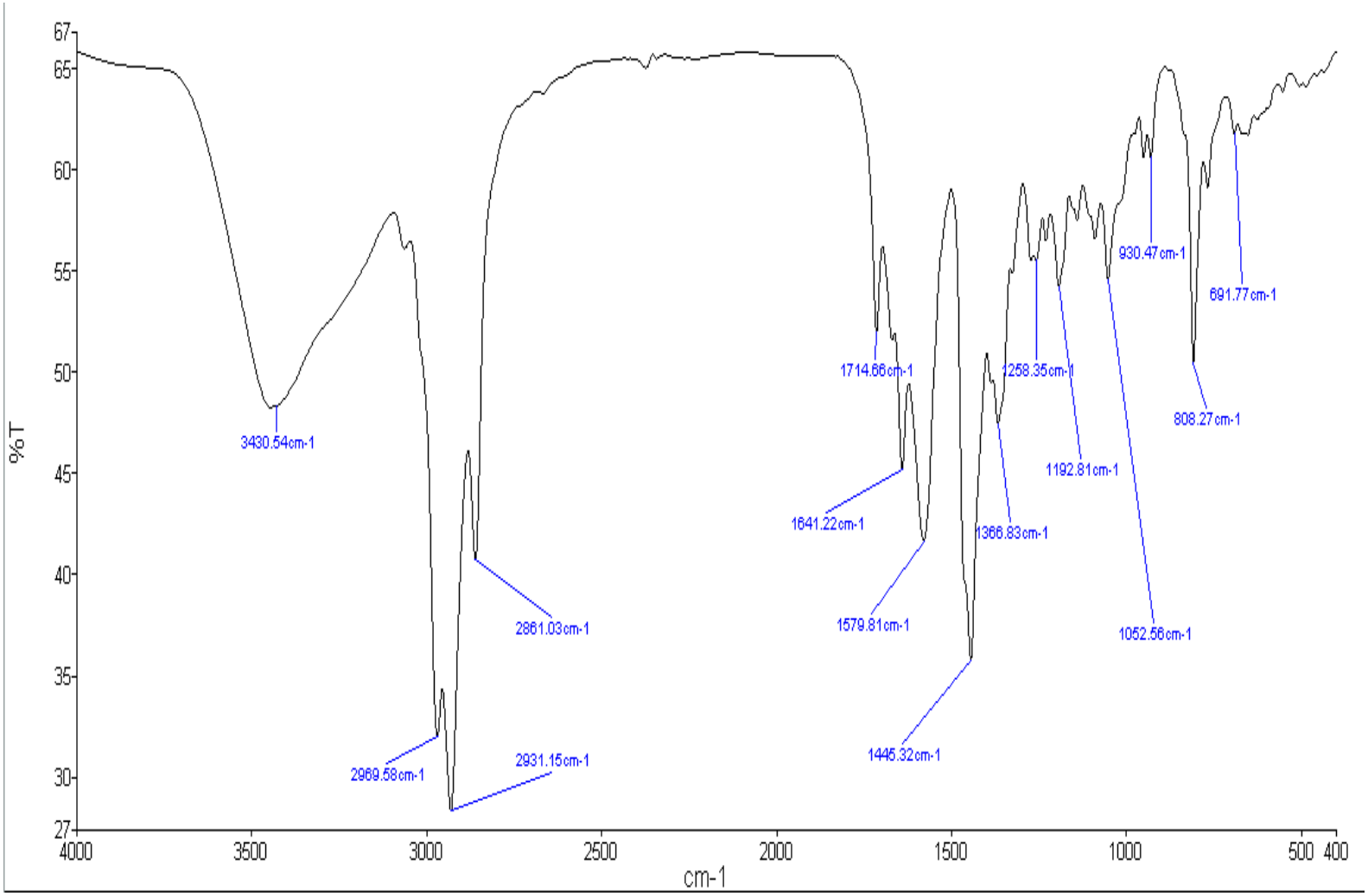
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1579.81cm-1
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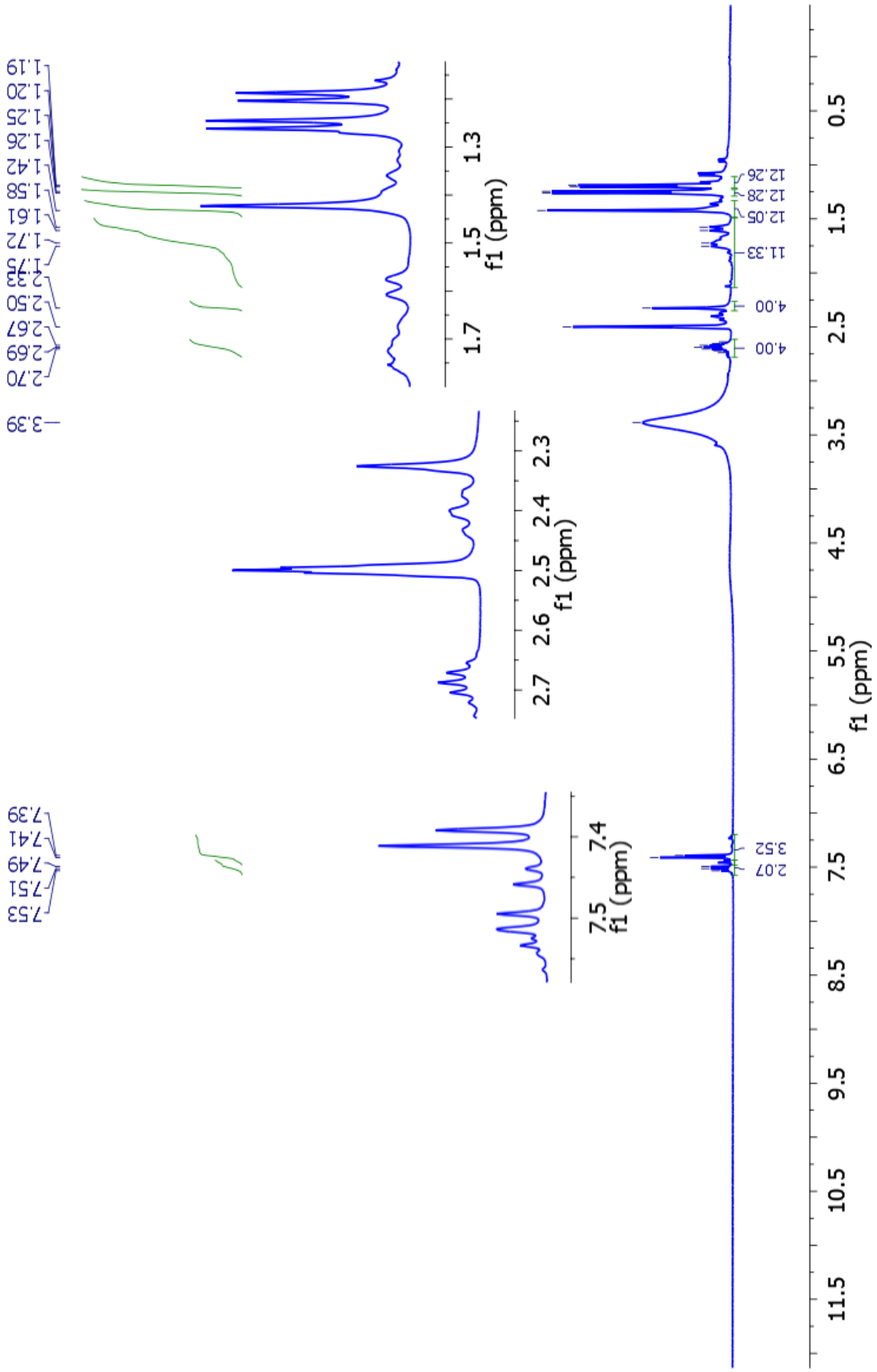
^{1}H NMR of **2** in DMSO-d_6.



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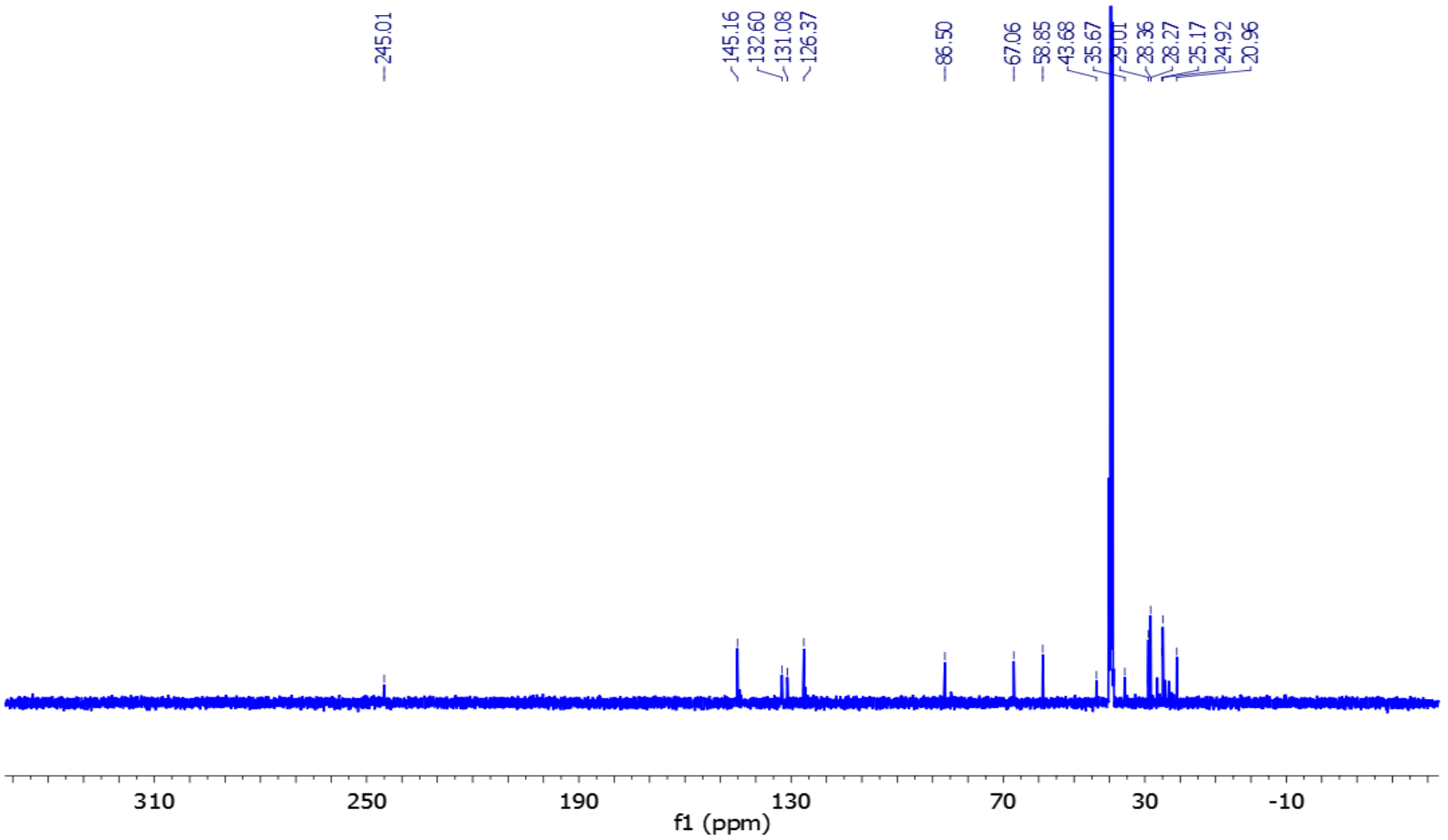

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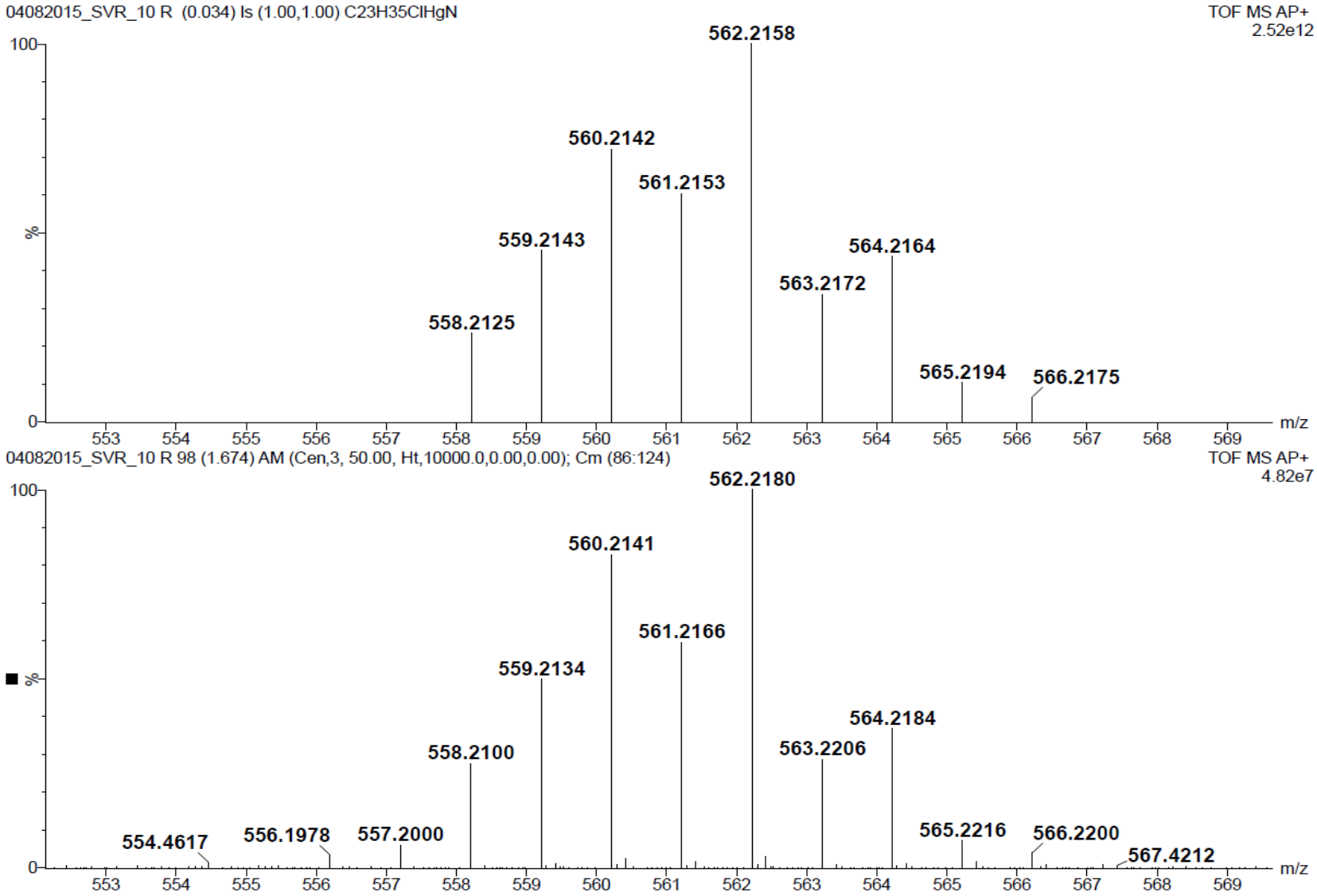

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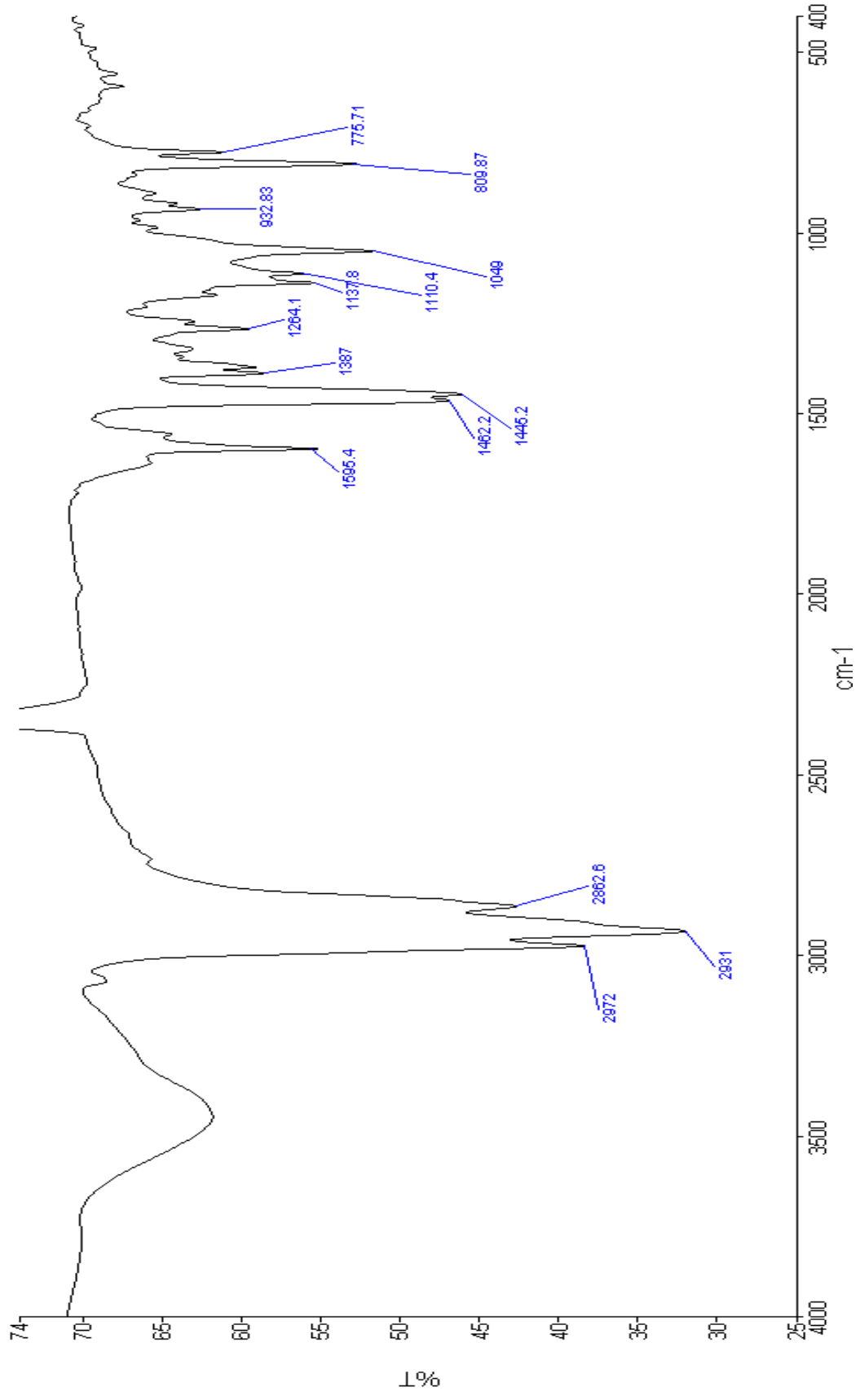
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1000
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60
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40
35
30
25
2931
2972
2862.6
1595.4
1462.2
1446.2
1387
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1137.8
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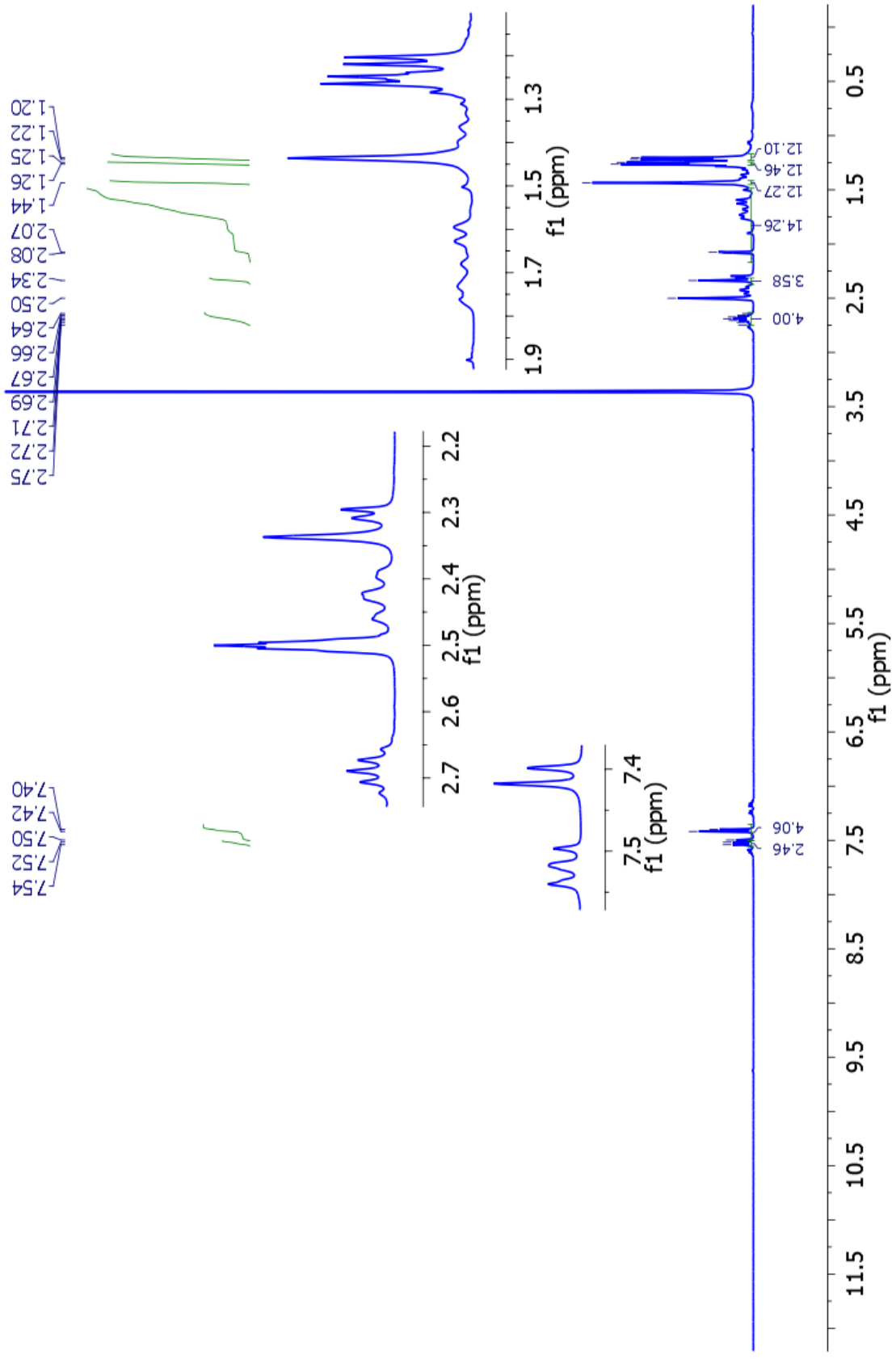
809.87
775.71

^{1}H NMR of **3** in DMSO-d_6



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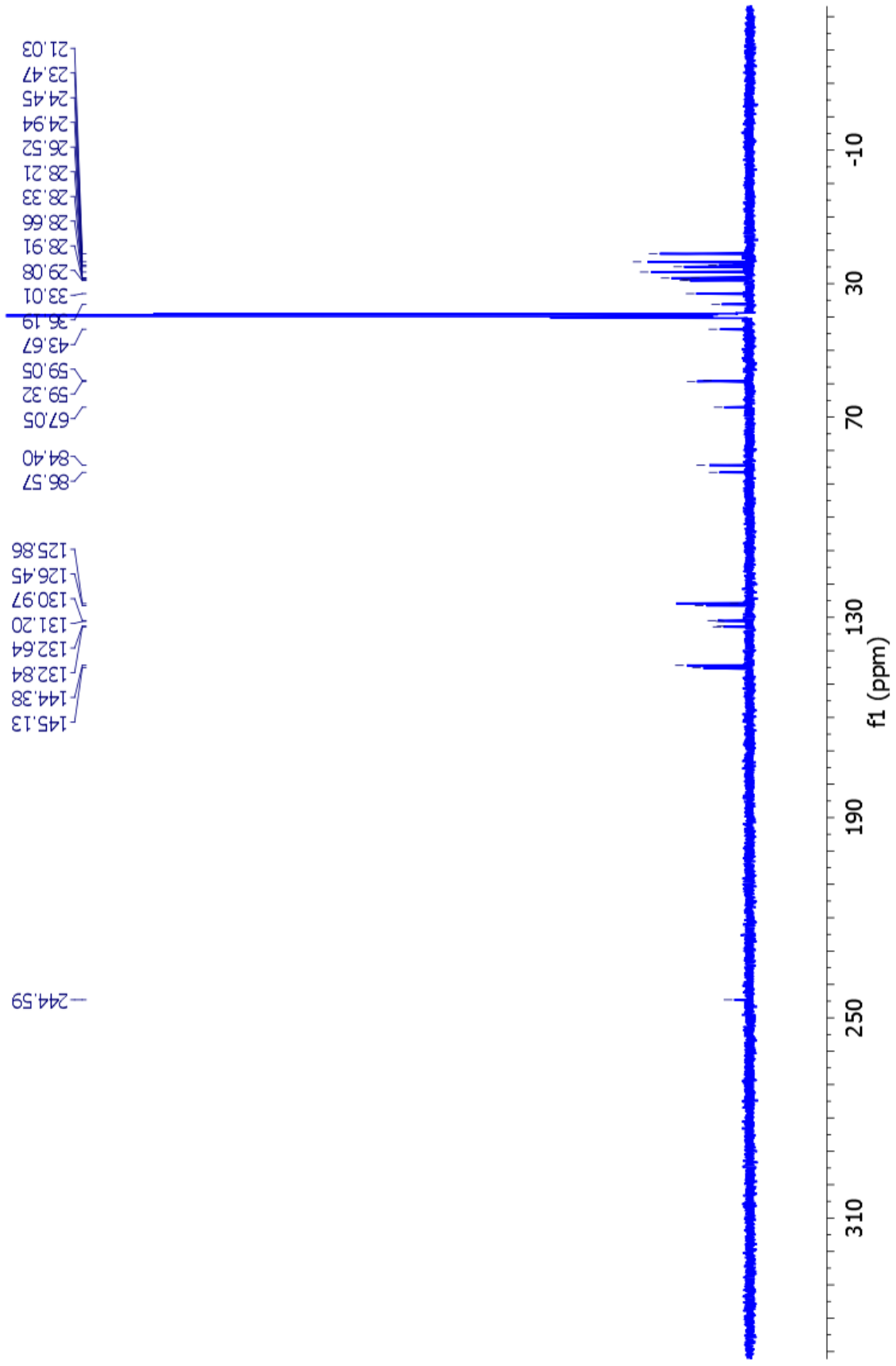
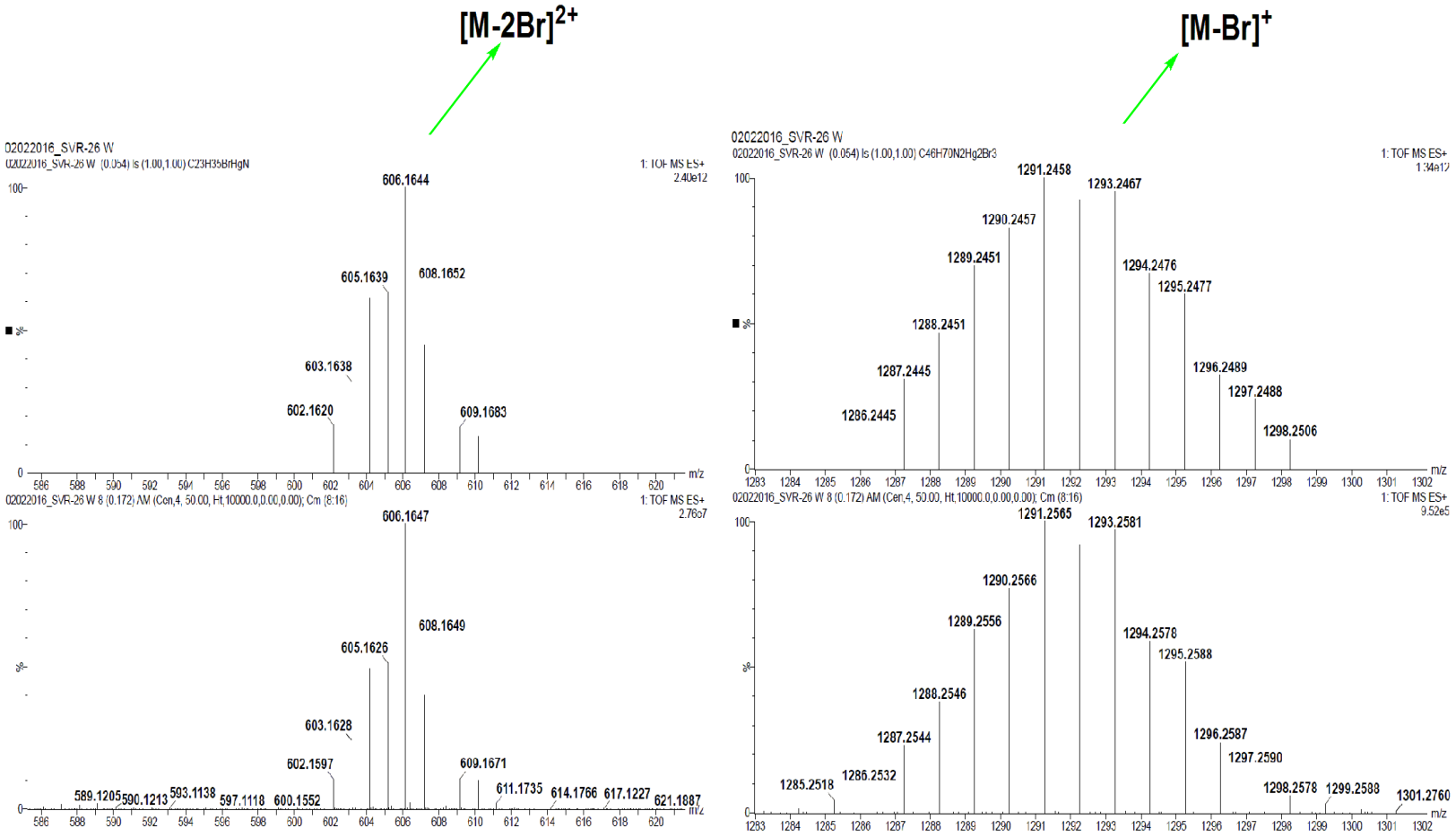


MS (AP, +ve) of **3**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597.1118
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611.1735
614.1766
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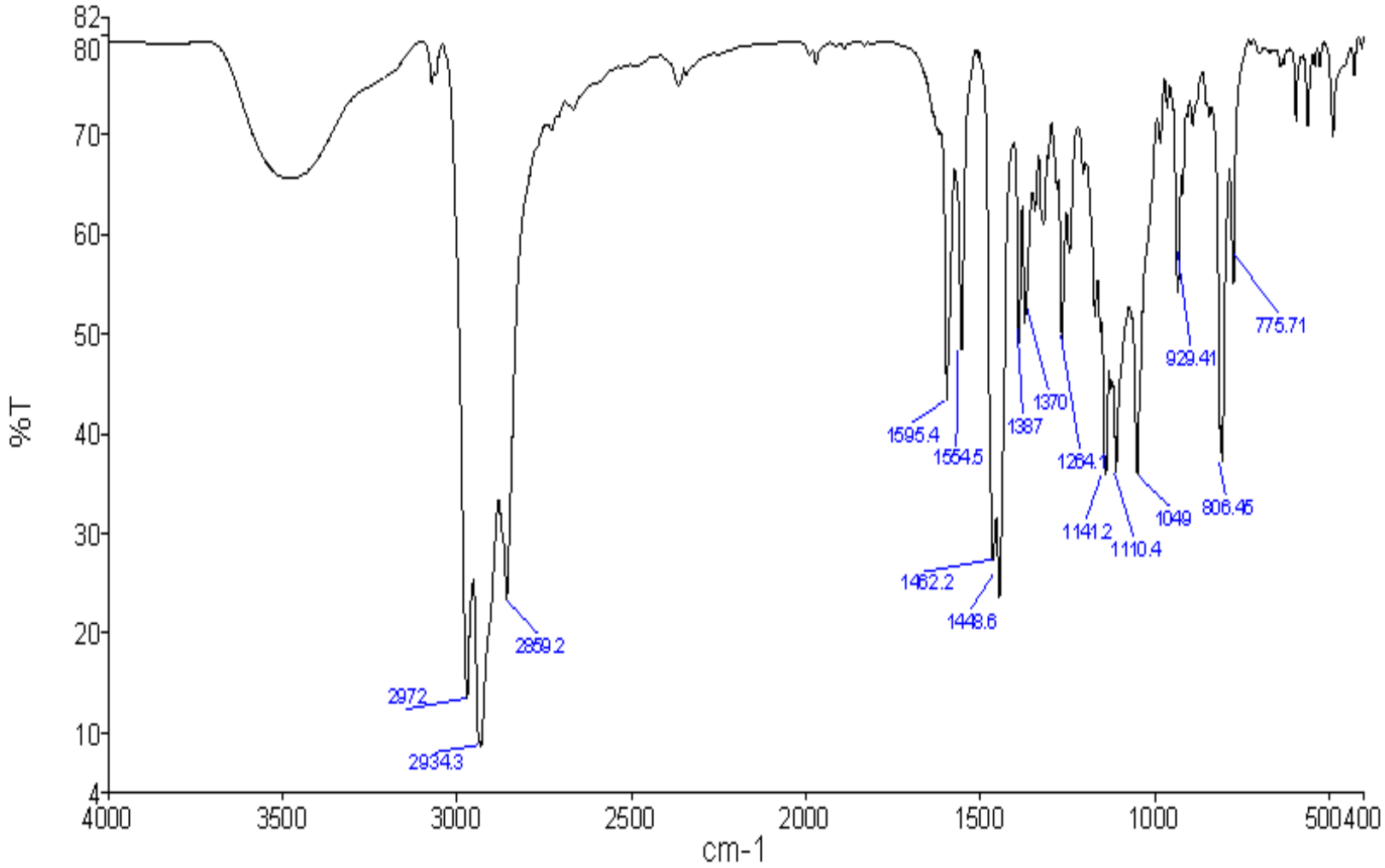
IR (KBr) of **3**.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500400
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2859.2
1595.4
1554.5
1462.2
1448.6
1387
1370
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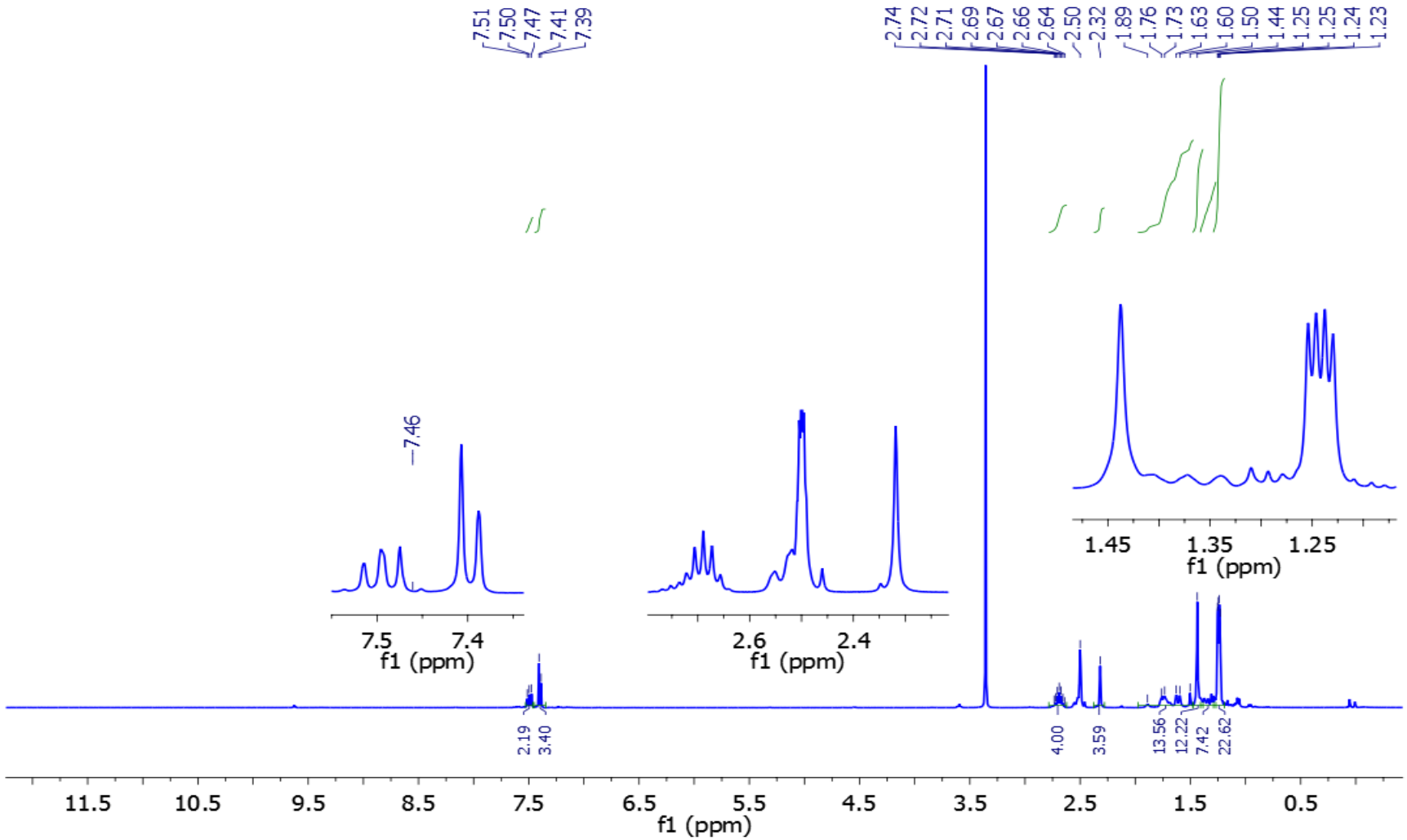
1141.2
1110.4
1049
929.41
806.46
775.71

^{1}H NMR of **4** in DMSO-d_6



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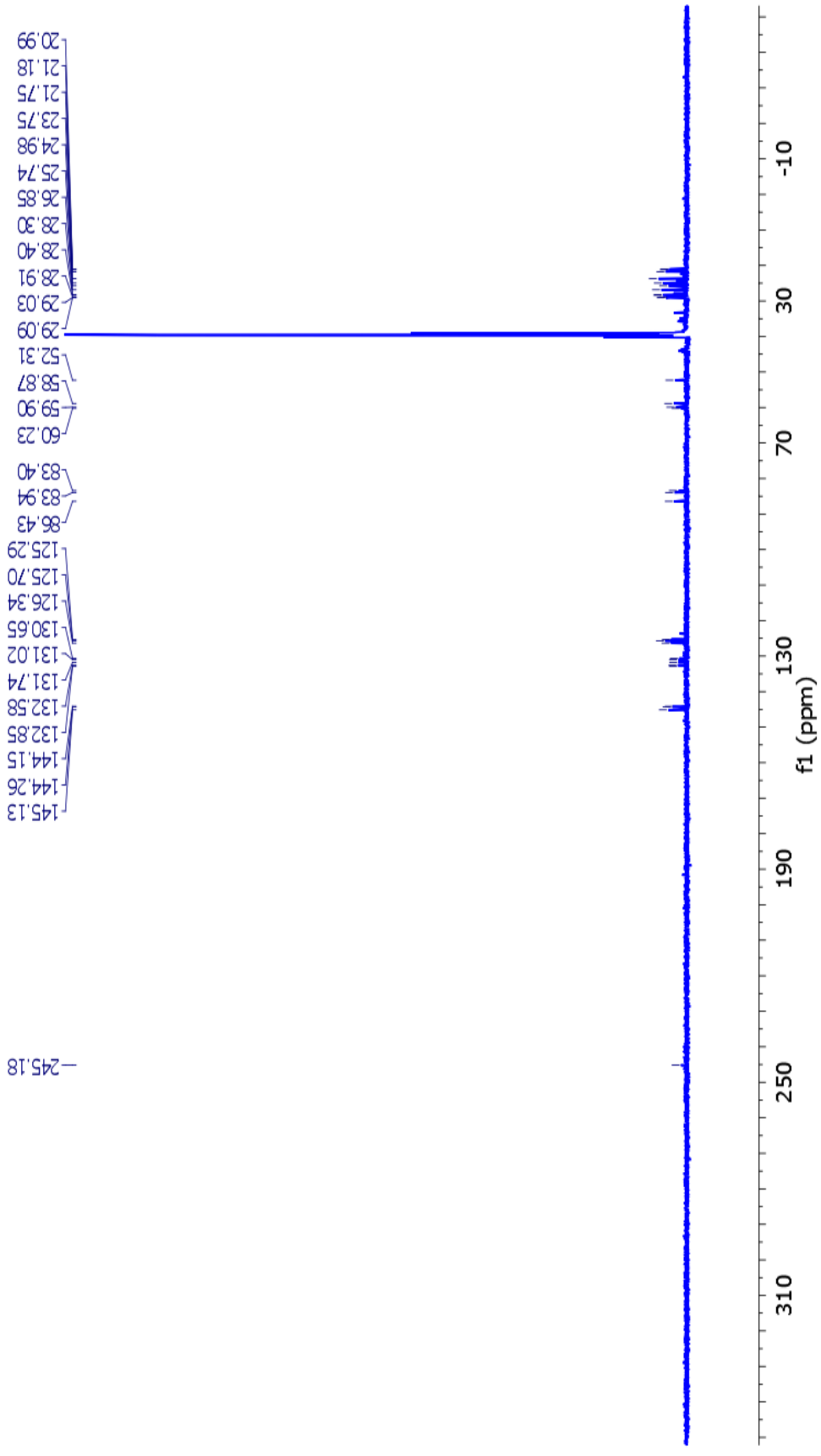

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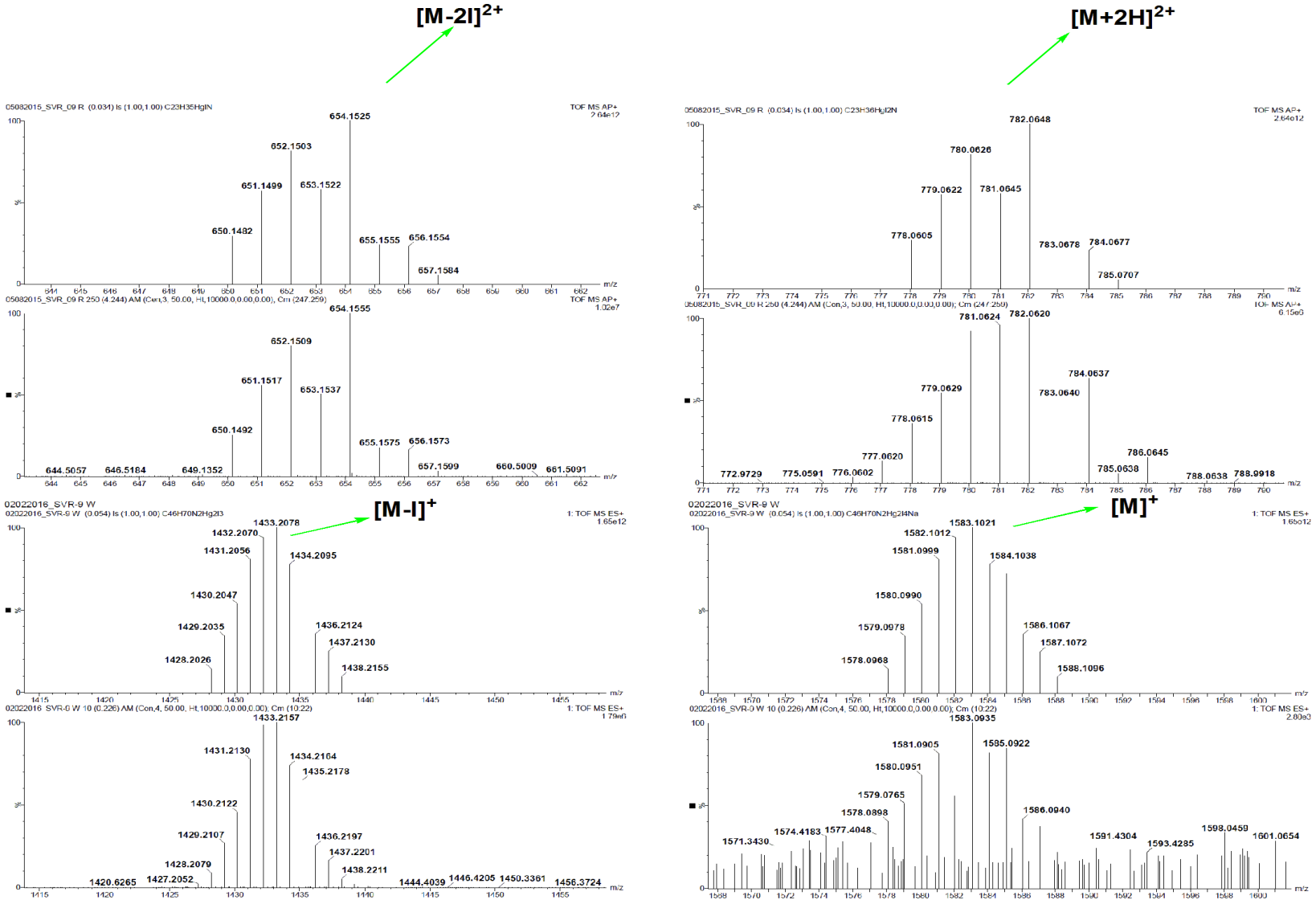
[M-2I]2+
[M+2H]2+
[M-I]+
[M]+
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TOF MS AP+
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654.1525
652.1503
651.1499
653.1522
650.1482
655.1555
656.1554
657.1584
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TOF MS AP+
1.02e7
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652.1509
651.1517
653.1537
650.1492
655.1575
656.1573
644.5057
646.5184
649.1352
657.1599
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661.5091
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1432.2070
1431.2056
1434.2095
1430.2047
1429.2035
1436.2124
1437.2130
1428.2026
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1431.2130
1434.2164
1435.2178
1430.2122
1429.2107
1436.2197
1437.2201
1428.2079
1438.2211
1420.6265
1427.2052
1444.4039
1446.4205
1450.3361
1456.3724
05082015_SVR_09 R (0.034) Is (1.00,1.00) C23H36HgI2N
TOF MS AP+
2.64e12
782.0648
780.0626
779.0622
781.0645
778.0605
783.0678
784.0677
785.0707
05082015_SVR_09 R 250 (4.244) AM (Cen,3, 50.00, Ht,10000.0,0.00,0.00), Cm (247:259)
TOF MS AP+
6.15e6
781.0624
782.0620
784.0637
779.0629
783.0640
778.0615
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785.0638
772.9729
775.0591
776.0602
788.0638
788.0918
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1581.0999
1584.1038
1580.0990
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1586.1067
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1578.0968
1588.1096
02022016_SVR-9 W 10 (0.226) AM (Cen,4, 50.00, Ht,10000.0,0.00,0.00), Cm (10:22)
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1586.0940
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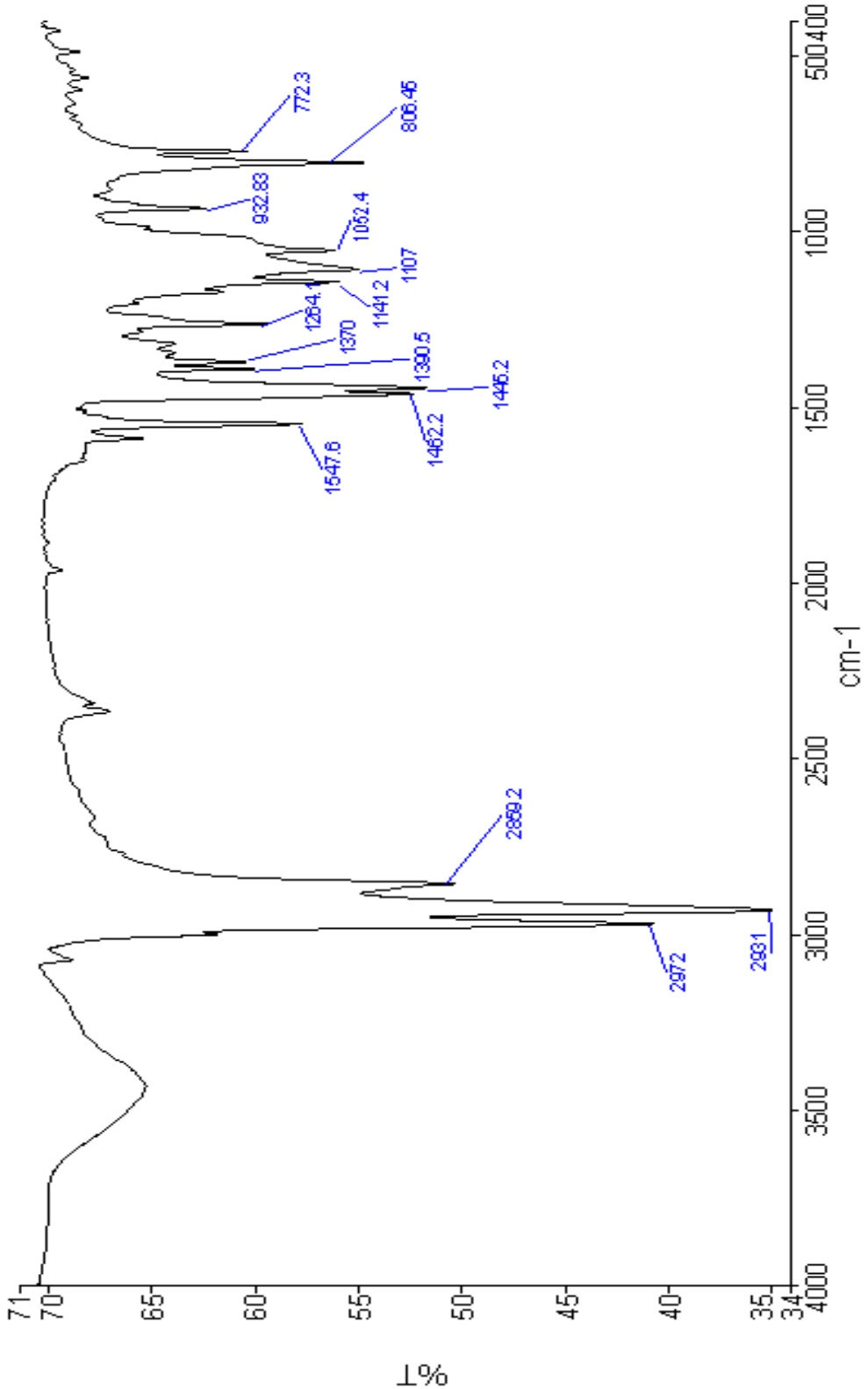
1574.4183
1577.4048
1591.4304
1593.4285
1598.0459
1601.0654

IR (KBr) of **4**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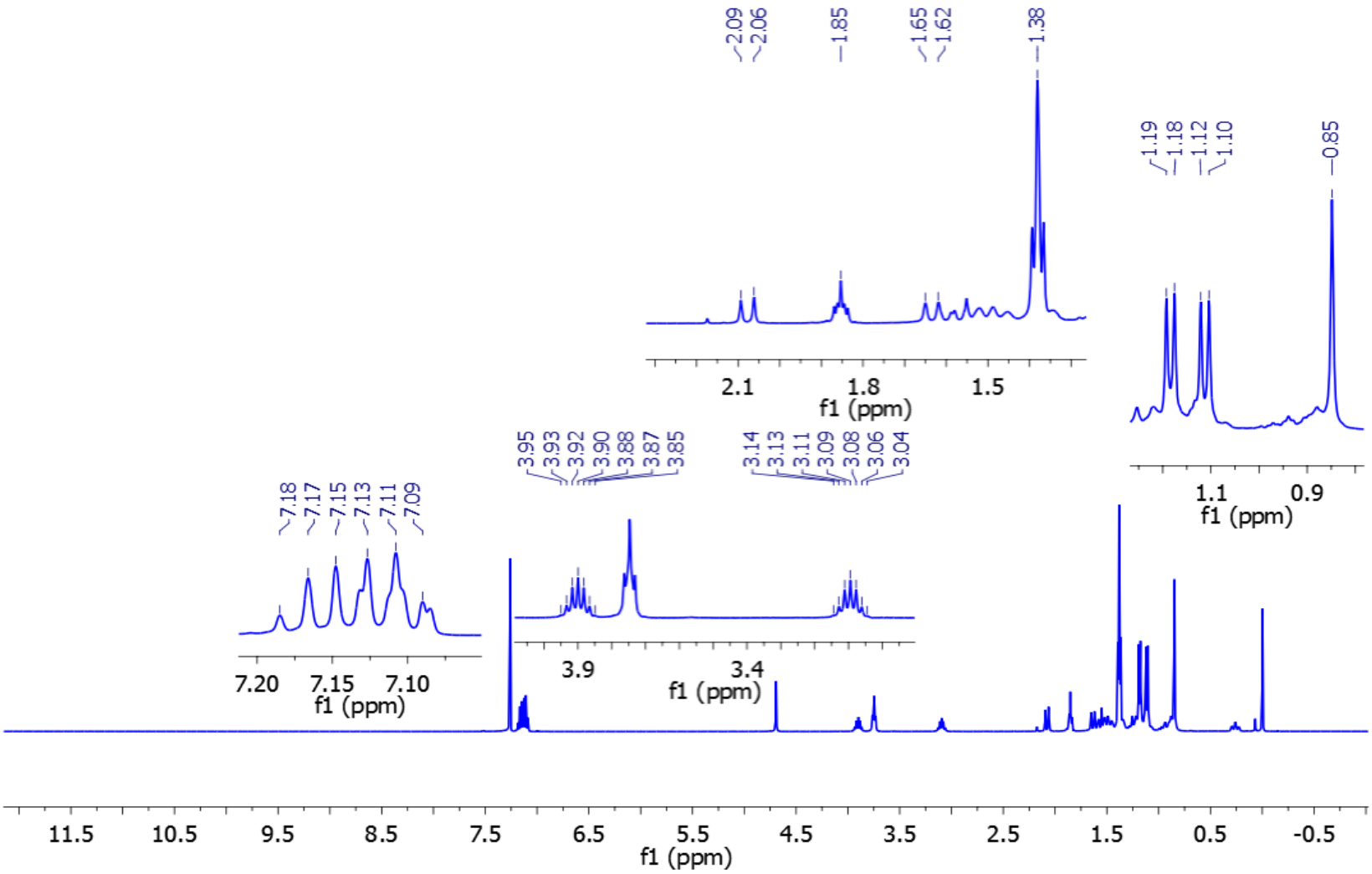
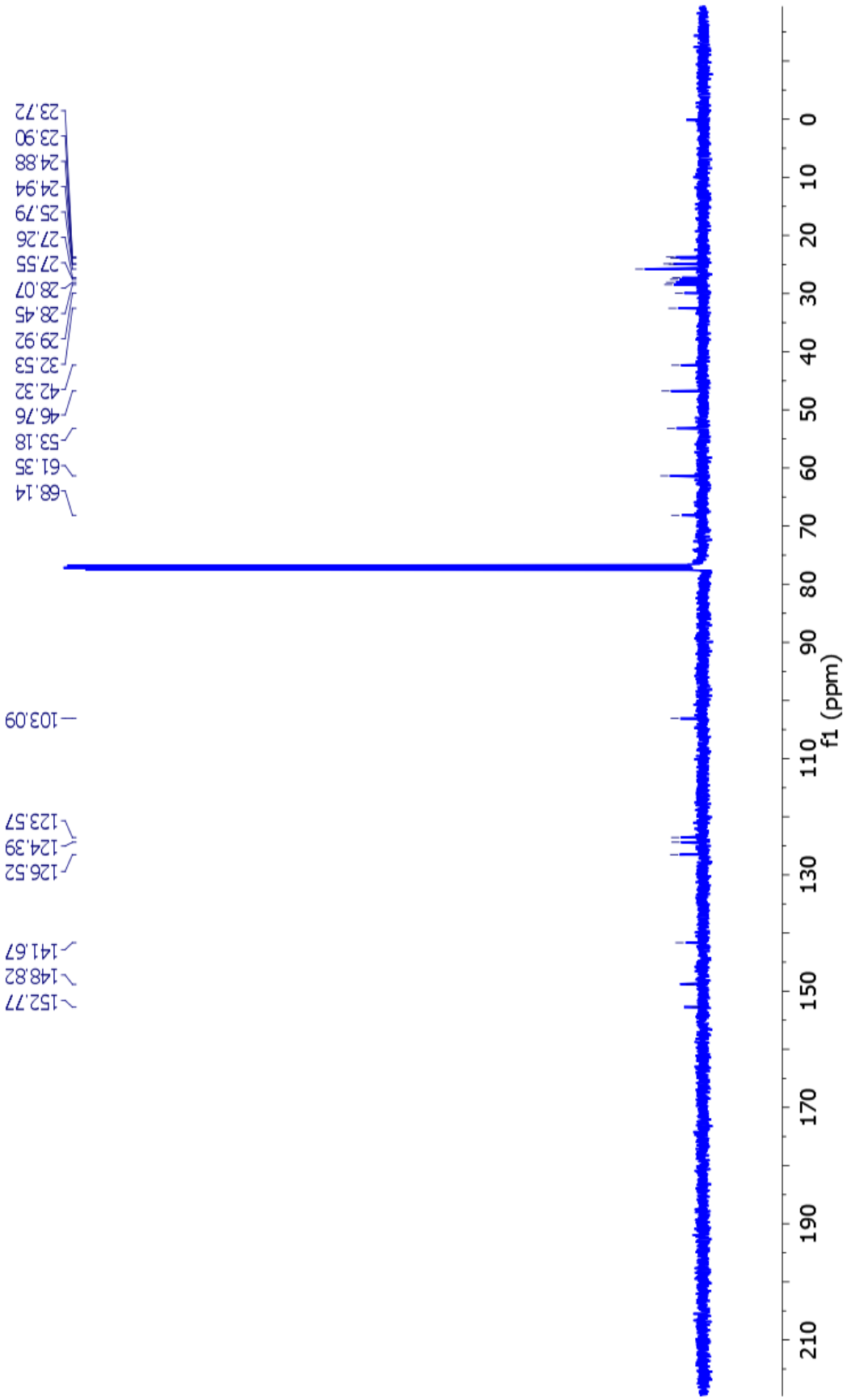
cm-1
4000
3500
3000
2500
2000
1500
1000
500
400
772.3
806.46
932.88
1052.4
1107
1141.2
1264.4
1370
1390.5
1446.2
1462.2
1547.6
2869.2
2931
2972

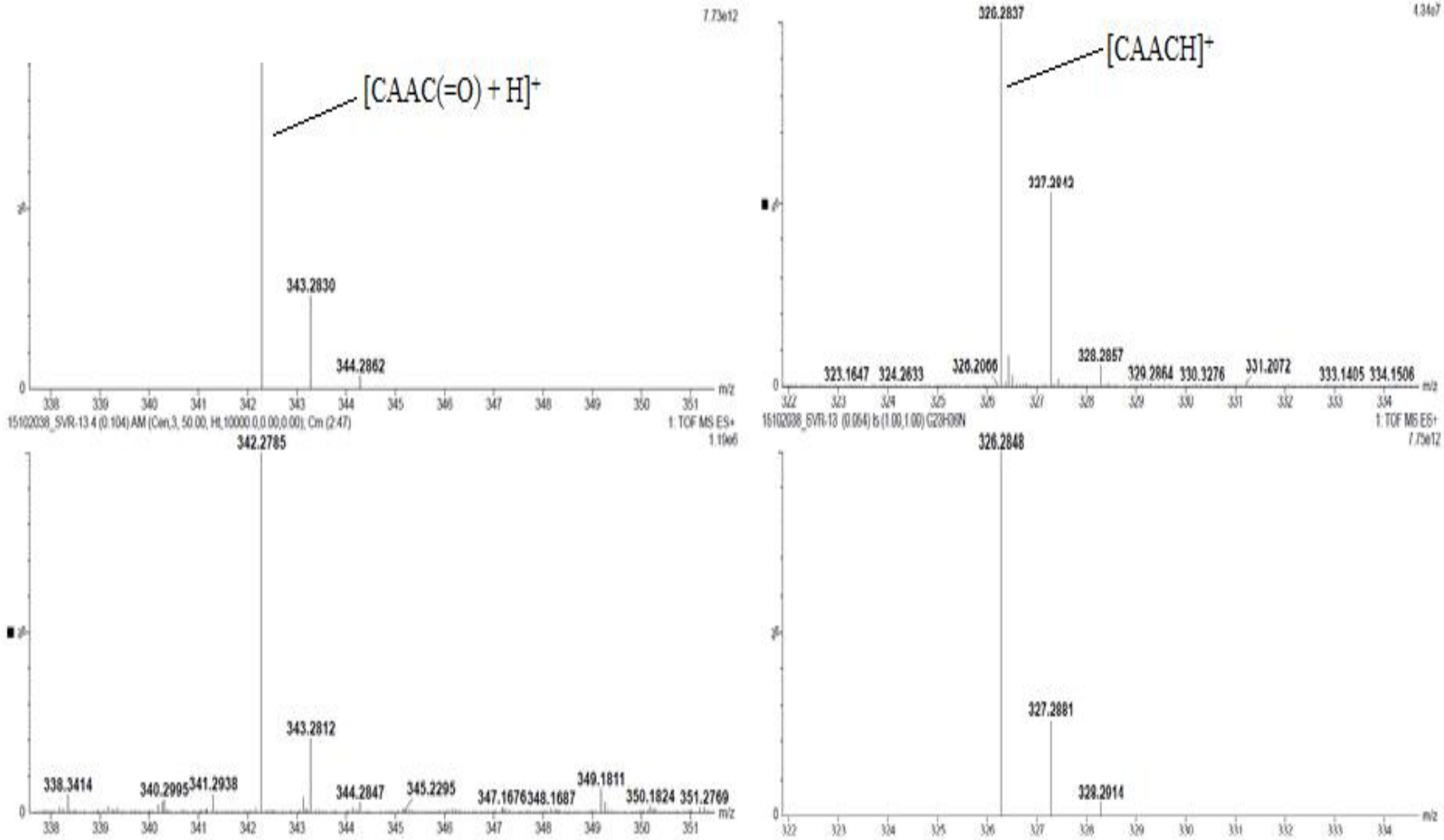
^{1}H NMR of **5** in $CDCl_3$



^{13}C NMR of **5** in $CDCl_3$



MS (AP, +ve) of **5**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347.1676
348.1687
349.1811
350.1824
351.2769
[CAACH]+
326.2837
327.2842
323.1647
324.2633
326.2066
328.2857
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331.2072
333.1405
334.1506
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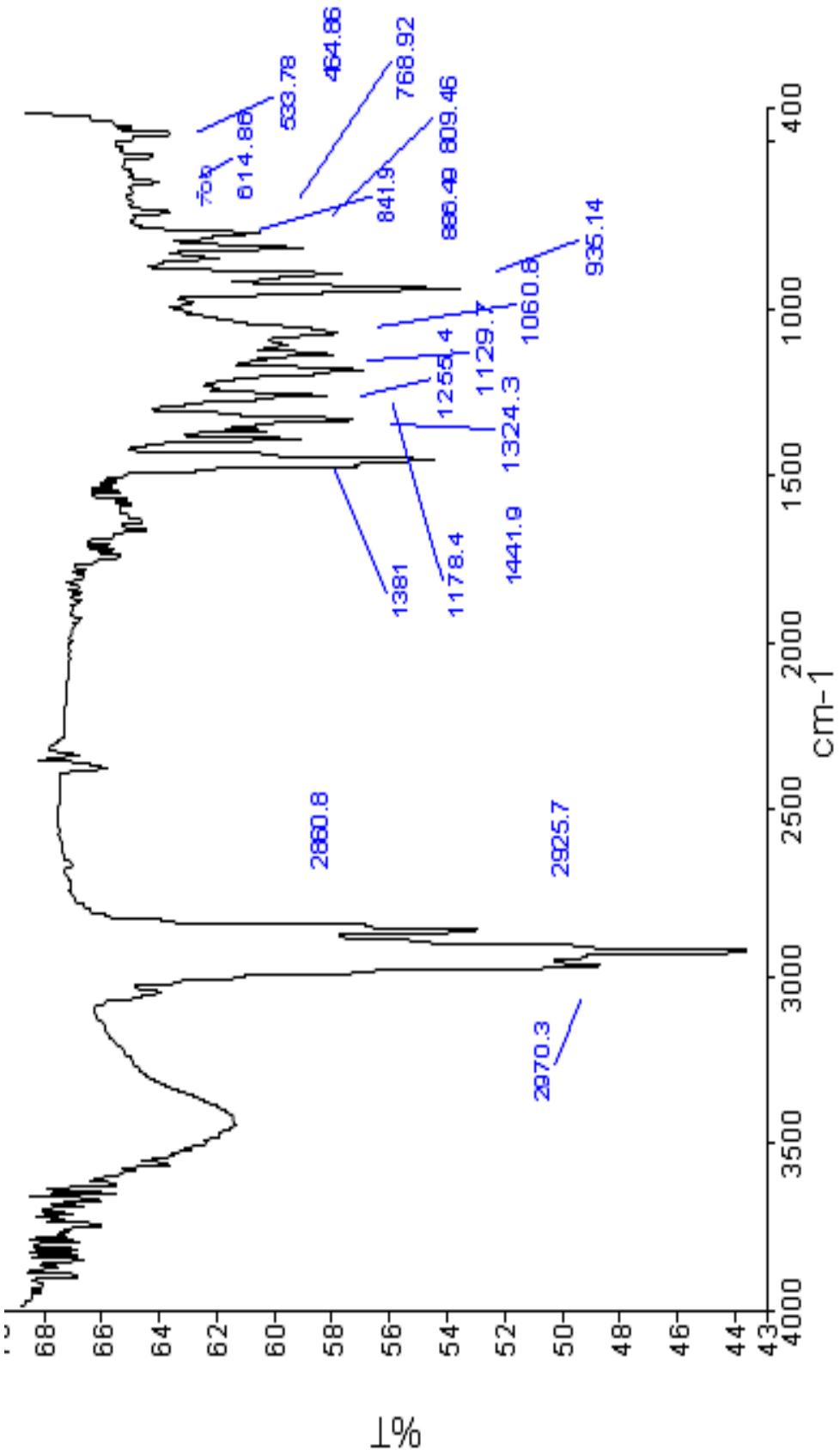
327.2881
328.2914

IR (KBr) of **5.**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1129.7
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841.9
768.92
614.86
533.78
464.86