Pd(II) AND Pt(II) COORDINATION COMPOUNDS OF NOVEL SCHIFF BASE LIGANDS INCORPORATING AROMATIC RING

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MASTER THESIS
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Prepared as
Master Thesis

KARABÜK
July 2023

I certify that in my opinion the thesis submitted by Mustafa Mundher Khalaf AL-AZZAWI titled “Pd(II) AND Pt(II) COORDINATION COMPOUNDS OF NOVEL SCHIFF BASE LIGANDS INCORPORATING AROMATIC RING” is fully adequate in scope and in quality as a thesis for the degree of Master of Science.

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This thesis is accepted by the examining committee with a unanimous vote in the Department of Chemistry as a Master of Science thesis. 05/07/2023

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Mustafa Mundher Khalaf AL-AZZAWI

ABSTRACT

M. Sc. Thesis

Pd(II) AND Pt(II) COORDINATION COMPOUNDS OF NOVEL SCHIFF BASE LIGANDS INCORPORATING AROMATIC RING

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In this study, three tridentate Schiff base ligands obtained from the reactions of 2-aminomethyl thiophene, 2-aminomethyl pyridine, 2-aminomethyl piperidine amines with 2-hydroxybenzaldehyde were synthesized, and their corresponding metal complexes with platinum(II) and palladium(II) salts were prepared. The ligands act as a monoanionic manner and coordinate to the metal center through the O atom of the hydroxide and N atom of the imine bond to form neutral bis-chelating square-planar complex [ML_2]. The ligands and the corresponding Pd(II) and Pt(II) complexes were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, mass spectrometry, and the structure of C1 complex was determined by single-crystal X-Ray analysis.

Key Words : Schiff base, Ligand synthesis, Metal complex, Platinum, Palladium.
Science Code : 20103

ÖZET

Yüksek Lisans Tezi

AROMATİK HALKA İÇEREN YENİ SCHİFF BAZI LİGANDLARININ Pd(II) VE Pt(II) KOORDİNASYON BİLEŞİKLERİ

Mustafa Mundher Khalaf AL-AZZAWI

Karabük Üniversitesi
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Temmuz 2023, 80 sayfa

Bu çalışmada, 2-aminometiltiyofen, 2-aminometilpiridin, 2-aminometilpiperidin amin bileşiklerinin , 2-hidroksibenzaldehit ile kondenzasyon reaksiyonlarından elde edilen, üç adet üç-dişli Schiff baz ligandları sentezlendi. Bu ligandların platin(II) ve paladyum(II) tuzları ile kompleksleri hazırlandı. Ligandların mono-anyonik olarak hidroksi oksijen atomu ve imin N atomu üzrinden metal merkezine bağlandığı ve homoleptik nötral bis-şelat kompleks kare-düzlem [ML_2] kompleks oluşturdukları kütle, ^{1}H ve ^{13}C NMR ile desteklenmiştir. Tüm ligandların ve oluşturdukları Pd(II) ve Pt(II) komplekslerinin yapıları FT-IR, ^{1}H NMR. ^{13}C NMR, kütle analizi ile aydınlatılmıştır. Ayrıca, C1 kompleksinin tek-kristal X-Ray analizi yapılmıştır.

Anahtar Sözcükler : Schiff baz, Ligand sentezi, Metal kompleksi, Platin, Paladyum
Bilim Kodu : 20103

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LIST OF ABBREVIATIONS

°C **:** degrees Celsius

g : gram

ml : milliliter

mmol : millimole

DMF : N, N-dimethylformamide

DMSO : dimethyl sulfoxide

FT-IR : Fourier Transform Infrared Spectroscopy

M.W : Molecular Weight

DCM : dichloromethane

NMR : Nuclear magnetic resonance spectroscopy

MS : Mass spectrometry

ppm : parts per million

al. : aliphatic

ar. : aromatic

PART 1

THE AIM AND IMPORTANCE OF THE STUDY

Due to their many applications and ability to produce potent coordination compounds with transition metals, Schiff bases and derivatives are a crucial area of study in coordination chemistry. Derivatives of Schiff bases with aromatic heterocyclic rings containing nitrogen and sulfur in their structure yield stable coordination complexes of great biological interest. On the other hand, heterocyclic Schiff bases complexes with platinum or palladium exhibit cytotoxicity akin to that of cisplatinum complex. Therefore, the present complexes prepared will be of great importance to explore their cytotoxicity against certain tumor lines. The search for such complexes has increased in the past decade to produce anti-cancer therapies with few or no side effects.

PART 2

INTRODUCTION

Coordination compounds have existed in nature since the beginning of the earth and are formed in ways still unknown to geologists [1, 2]. They are also found in the bodies of living organisms and play crucial roles in life processes such as hemoglobin, chlorophyll and vitamin B_{12} [3]–[5]. Such as those that catalyze the conversion of methanol to ethane or that convert water to oxygen, vice versa oxygen to water and from nitrogen to ammonia [5]. The history of coordination complexes goes back to the significant progress that took place in the field of inorganic chemistry at the beginning of the nineteenth century when a new type of organic synthesis appeared, through which metals are introduced into the structural structure of organic compounds, and that was by the chemist William Christopher Zeise (1831) who reported the preparation of the compound $K[PtCl_3(\eta^2\text{-}C_2H_4)]$, which has been named Zeise's salt Figure 0.1, and also the first bond of type eta (η)-bonding was reported, which arises from the sharing of a common electron pair between the empty orbital of metal atom and adjacent atoms [6].

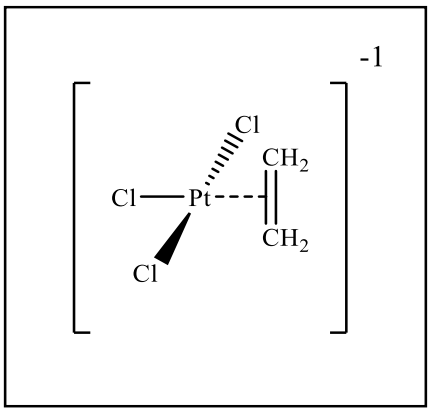

Figure 2.1. Zeise's salt [6].

Also, the complex Prussia blue $Fe_4[Fe(CN)_6]_3$ (Figure 2.2) is considered one of the first complexes that were prepared and produced and used to obtain the blue color[7], [8].

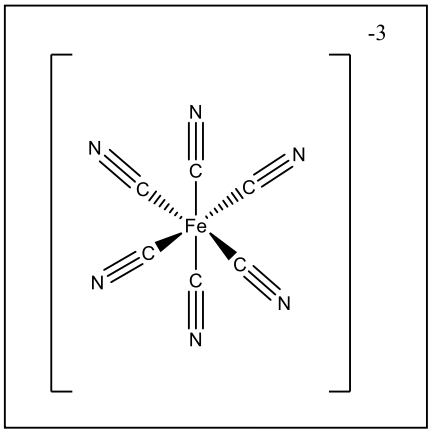

Figure 2.2. Prussian blue complex [7,8].

However, from the date of preparation of the first compound until the end of the eighteenth century, prior to the discovery of Fernier and the publication of his theory of coordination compounds in 1893, coordination compounds suffered from a lack of understanding of their composition. They began to focus on the study and preparation of many coordination compounds [9], [10].

1.1. SCHIFF'S BASES

These compounds and other imines were discovered by the German chemist Hugo Schiff in 1864 during his research on aldehydes, where the Schiff base ligand known at the time was of the salt type used in industrial dyes, as in Figure 2.3 [11][12].

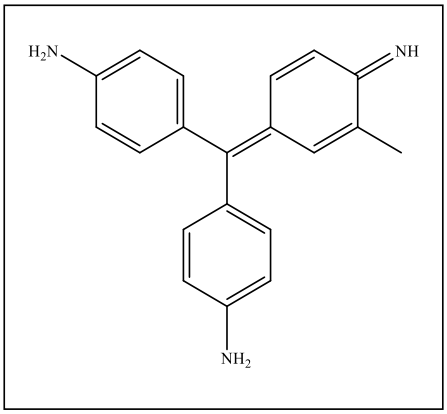

Figure 2.3. Fuchsine's structure [11].

Schiff's bases are chemical compounds containing a (-HC = N-) bond obtained by acid catalysis or thermal condensation of a ketone or aldehyde with an amine [13] though the reaction of Schiff's base preparation is reversible, because of the hydrolysis the imine gets, it stays straightforward until the reaction is complete. Some Schiff base variants remain stable for unknown reasons. In the presence of water or even if the medium is an acidic solution, others quickly decompose by water and turn into an aldehyde. To get rid of the problem of hydrolysis, the reaction conditions are controlled, and the use of dry solvents and other procedures that withdraw the water produced from the reaction as recommended by the IUPAC. Schiff bases are defined as (imines) containing an $R_2C = NR'$ (R' H) hydrocarbyl group on the nitrogen atom [12], as shown in the general reaction of preparing Schiff bases Figure 2.4 .

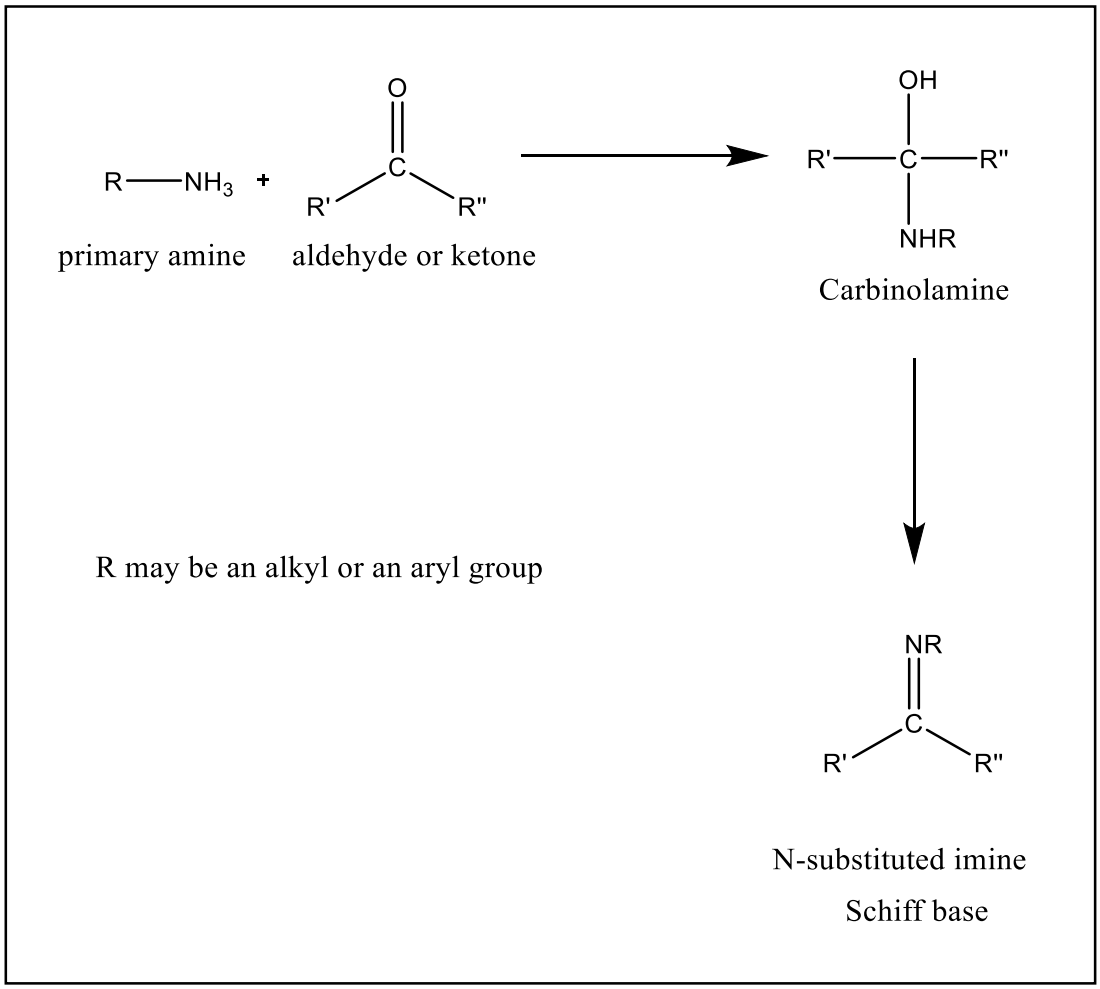

Figure 2.4. General method of preparing Schiff bases [13].

Schiff bases and their derivatives are valuable compounds in the synthesis of organic compounds based on biologically active minerals, a large section of which are used as anti-inflammatory, malaria treatments, antipyretics, antifungals [14]–[17] of antioxidant drugs [18]–[20]. These compounds are also included in the field of manufacturing sensors [21] and the field of medical imaging [22] and the chemistry of catalysts [23] and antimicrobial treatments [24] Most of the organic compounds used today as treatments for diseases and antitumors are not biologically effective unless minerals are included in their composition[25]. The only electron pair present on the imine nitrogen atom acts as a source of electrons that enable the formation of a suitable donor bond for a metal ion to form a coordination complex [26]. Schiff bases are among the ligands that can form double, triple, or tetragonal chelated bonds and, therefore, form very stable metal complexes [27]. Figure 2.5 shows some Schiff bases that contain more than one donor atom.

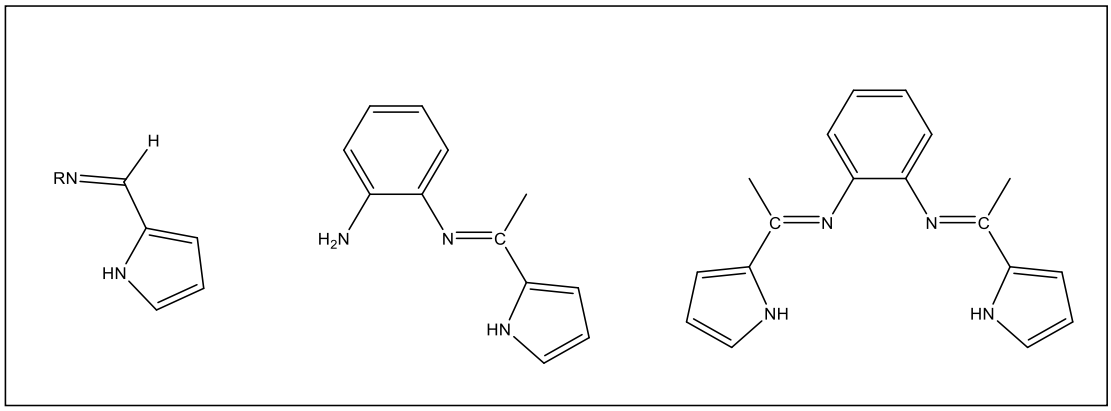

Figure 2.5. Some Schiff Bases [28].

Schiff bases produce stable ligands if aromatic aldehydes are used in their structure, and they are more stable than ligands in which aldehydes are used [29] In addition to the ligands formed by Schiff bases, these ligands are easy to coordinate with most transition metals [30], [31]. Schiff bases may not be consistent with metal through a nitrogen atom only because many Schiff bases have a second functional group, naturally OH and SH groups, or another N atom, which is close to the imine group. These clusters can allow five or six chelating rings to form when coordinated with different metal ions [32], [33]. The presence of more than one donor atom, in addition to the presence of organic aromatic rings, all these elements unite to form strong, stable complex structures consistent with metals [34], [35]. Therefore, Schiff bases are key to the formation of coordination compounds containing large organic rings [30] .

1.2. COORDINATION CHEMISTRY IN PLATINUM AND PALLADIUM COMPLEXES

Ground state electronic configuration of palladium [Kr] $4d^8\ 5s^2$ while that for platinum is [Xe] $5d^8\ 6s^2$, the common oxidation state of both metals is (+2) with the possibility of their presence in other oxidation states (0, +1, +3, +4). The atoms of platinum and palladium metals with oxidation state (+4) form complexes with six bonding axes with octahedral geometry. The atoms of platinum and palladium metals with an oxidation state (+2) form complexes with four bonding axes with square-planar geometry.

1.3. HISTORY OF CISPLATINUM COORDINATION COMPOUNDS DISCOVERY

The discovery of platinum dates back to 1844 [36] and one of the first discovered platinum salts is the green Magnus salt with the formula $[Pt(NH_3)_4][PtCl_4]$, in 1828 the Italian scientist Peroni tried to prepare the green Magnus salt. During the preparation, he produced two compounds. The first is salt Green Magnus salt, and the second salt with a yellow color was distinguished between the two salts through their solubility in hydrochloric acid, where the green Magnus salt is insoluble in hydrochloric acid, while the resulting yellow salt is soluble in hydrochloric acid, so Peroni was able to separate the two salts from each other and knew at the time. The salt that Beruni prepared was called Beruni salt [37], [38].

1.4. METALLIC COMPOUNDS ARE ANTI-CANCER THERAPIES

In 1965, Barnett Rosenberg, a biophysicist at the University of Michigan, and his group conducted experiments on the effect of electric current on bacteria (E. coli). Electrophoresis, it was observed that the bacteria showed filamentous growth. At first, Rosenberg and his group hoped that the passage of electric current caused the growth of bacteria. However, several studies found that the reason was the formation of one of the platinum compounds at one of the electrodes [39], [40]. After researching the nature and quality of these compounds, it was found that the compound formed is $[PtCl_6](NH_4)_2$, which was the cause of stopping the division and elongation of bacteria, as well as the compound $[PtCl_4(NH_3)_2]$ [41]. While the compounds in the form of trans did not have any effect after this discovery, many experiments were conducted on these compounds. The effect of these compounds was studied on white Swiss mice with cancer. The results were satisfactory because these compounds worked effectively on killing cancer cells. Despite the side effects of the treatment, the experiments on cisplatinum continued [42]. There currently exist no better drugs than these for treating malignant tumors. After completing clinical trials, the drug was approved as a therapeutic protocol in the United States in 1979 [42]. Studies continued to improve the drug's performance and reduce its side effects, and several cisplatin derivatives were produced. Studies have been conducted to use this structure in the

formation of other complexes based on other metals, such as palladium, and compounds based on these metals have achieved great success in treating cancer and other diseases and one of the most famous of these compounds cisplatin, miboplatin, oxaliplatin, enloplatin, picoplatin, carboplatin nedaplatin and lobaplatin[43]–[45]. Figure 2.6 shows some of the most important mineral complexes used to treat cancerous tumors.

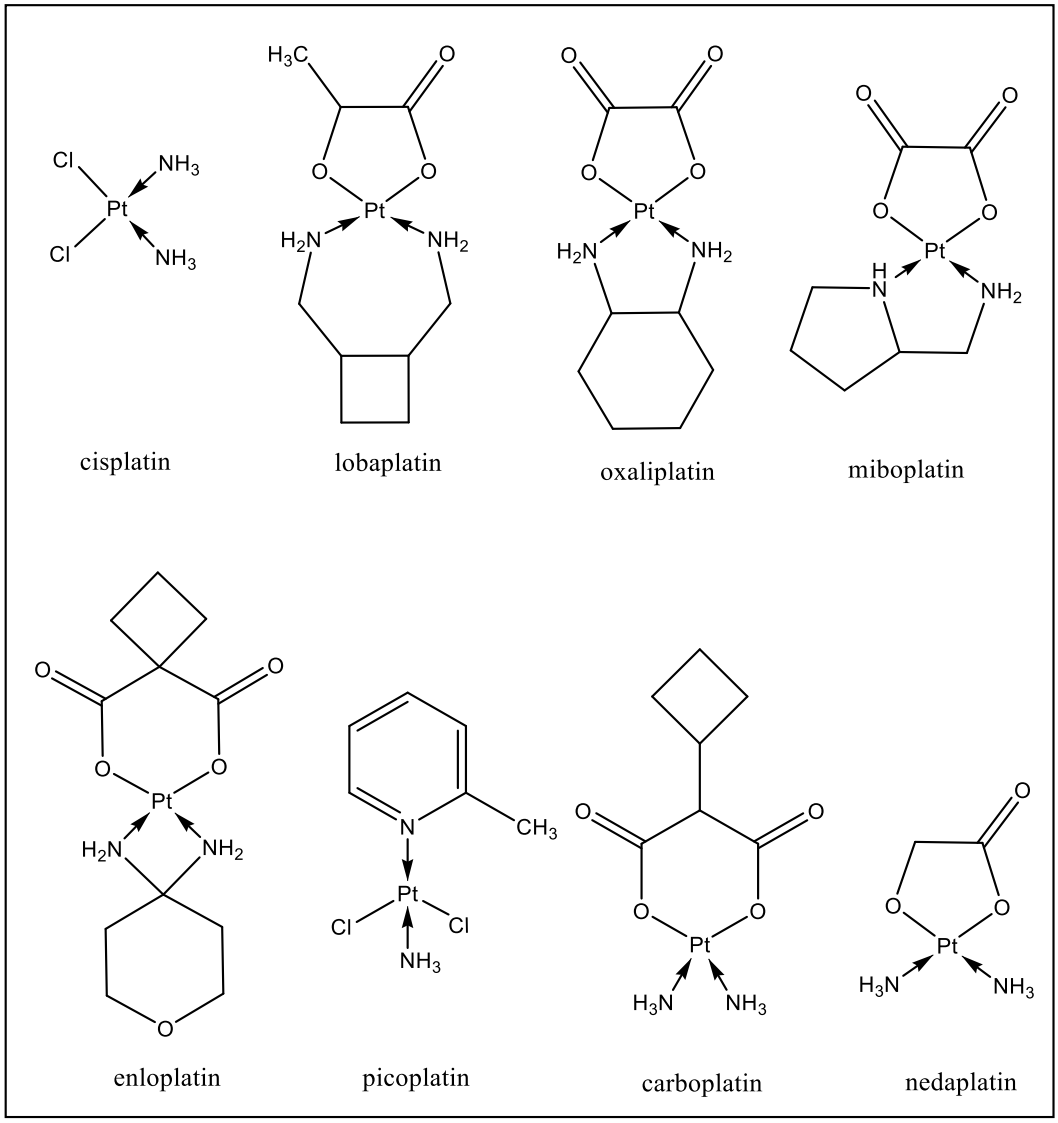

Figure 2.6. The commonly used drugs for cancer treatment [42].

Carboplatin and cisplatin are among the most important compounds that have made a breakthrough and fundamental change in reducing tumors. Because these two compounds have a significant effect in fighting cancer cells in the lung, ovaries, testes,

and pancreas. When carboplatin was used instead of cisplatin, the side effects on patients were much less than when cisplatin was used. Despite the great success of these compounds, there are still negative side effects that cannot be ignored. Inhibition of bone marrow activity, low platelets, kidney poisoning, neurotoxicity, nausea and vomiting, and many other side effects [46], [47]. Despite these side effects, no stronger alternative than these compounds has been found so far for treating cancerous diseases and tumors. When examining pathological cases where this drug is used as a treatment, we will find that more than half of the cases are treated with these compounds [48]–[54]. Due to the great success in clinical treatment with platinum-containing drugs, medicinal inorganic chemistry has received much attention [54], [55]. Other metal compounds also showed good antitumor activity, prompting researchers to search for complexes other than platinum complexes [56]. So that the side effects are few and therefore antitumor drug research is moving towards the development of new compounds such as palladium-containing organometallic compounds [52], [55], [57], [58]. Palladium(II) complexes have emerged as an alternative candidate for platinum complexes, researchers have considered the many anti-cancer drug due to their similar structure to platinum(II) complexes [58]. Several palladium complexes have been studied as potential candidates to replace well-known platinum complexes [59]–[62]. In addition, trans (platinum-palladium) complexes have a toxic effect against cancer cells, and in recent years their ability to kill cells has been extensively investigated, as some trans-platinum complexes showed high cytotoxicity against cancer, using lower concentrations than their counterparts, *cis* complexe where complexities appear trans-[$PtCl_2$(4-pic)(pt)] (1) and trans-[$PtCl_2$(4-pic)(pz),HCl] (2) high cytotoxic activity an ovarian and colon cancer [72]. The trans-[$Pt(PPh_2allyl)_2(\kappa1\text{-}S\text{-}Spy)_2$] (3) complex was also shown to Toxin activity through apoptosis in cancer cells [73]. In addition, some trans-palladium complexes showed selective toxic activity against cancer cells, such astrans-chloridobis [(pyrrolymethylidene) (Benz-2-yl-methyl)amine-κN]methyl palladium(II) (4) and trans-dichloridobis[(pyrrolymethylidene) (furan-2-ylmethyl) amine-κN] methyl palladium (II) (5) [74]. Figure 2.7 shows some of the transient platinum and palladium complexes with toxic activity against cancer cells.

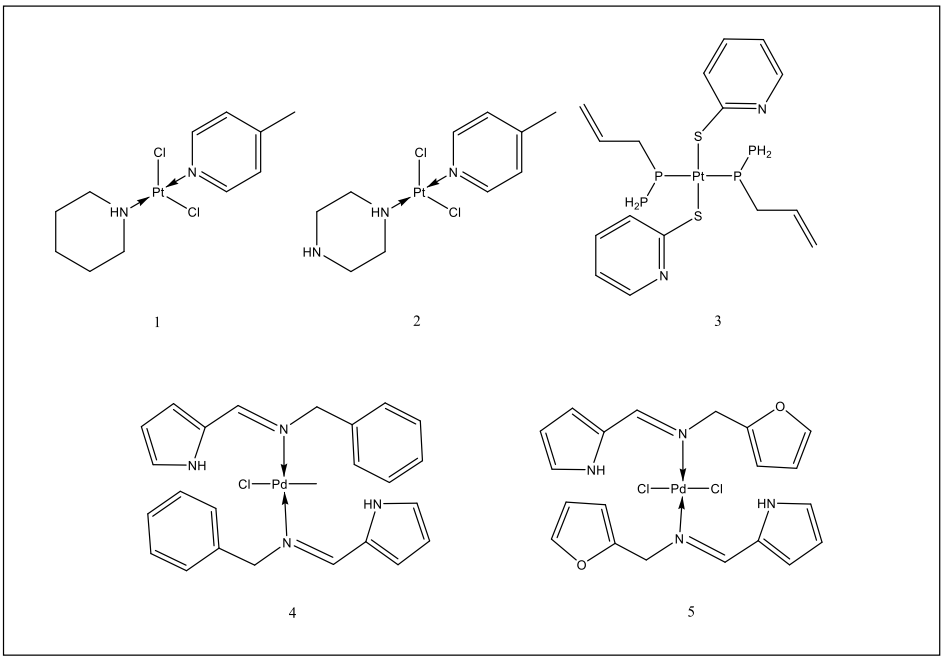

Figure 2.7. *Trans*-platinum and palladium complexes [73] [74].

PART 3

PREVIOUS STUDIES

New Palladium(II) and Platinum(II) Complexes with the Model Nucleobase 1-Methylcytosine: DNA interactions and antitumor activity of organometallic palladium and platinum complexes, which are derived from 2-(dimethylaminomethyl) phenyl (dmba) and pentafluorphenyl groups were prepared using the model nucleobase 1-methylcytosine. Crystal structures of [Pd(bpzm*)(C_6F_5)(1-Mecyt)]ClO_4, [Pt(dmba)(DMSO)(1-Mecyt)]-ClO_4, *cis*-[Pd(C_6F_5)$_2$(1-Mecyt))$_2$], and cis-[Pd(t-BuNC)(C_6F_5)-(1-Mecyt)$_2$]ClO_4 was generated by X-ray diffraction. There are extensive hydrogen bonds (NH···O, C-H···F or C-H···O) in all compounds. The prepared complexes were more active against cancer cells than cisplatin. It was shown that most cancer cells experienced a planned death [59].

Three Pd(II) and Pt(II) complexes' antiproliferative qualities and biomolecular connections, three complexes of the metals platinum and palladium with single (imidazoline-2-imine) and double (imidazoline-2-imine) chelating linkages were prepared as anti-cancer agents. (1) [Pd(DMEAImiPr)Cl_2], (2) [Pd(DACH(ImiPr)$_2$)Cl_2] (3) [Pt(DMEAImiPr)Cl_2]. These metal complexes against certain cancer cell lines show moderate to strong cytotoxic effects. The spectrophotometric analysis examined to study how these complexes interacted with the model DNA oligos, protein molecules. The readings from the ESI-MS clearly show how approximations occur. UV-Vis absorption and emission spectroscopy experiments were used to investigate the binding of these metal complexes to calf thymus DNA (CT-DNA). The observed cytotoxic effects may be attributed to the exceptional capacity of the investigated complexes 1-3 to bind DNA. Intriguingly, our findings showed that DNA binding and 1 to 3 anti-cancer activities occur in the following order: 2 > 3 > 1 [75]. The Figure 3.1 shows the prepared complexes.

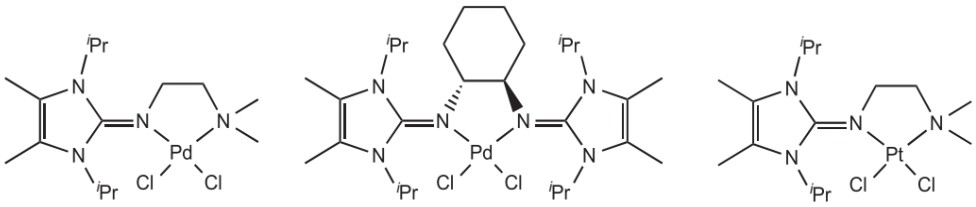

Figure 3.1. Pd(DMEAImiPr)Cl_2] (1), [Pd(DACH(ImiPr)$_2$)Cl_2] (2), [Pt(DMEAImiPr)Cl_2] (3) [75].

Palladium(II) and Platinum(II) Complexes: Synthesis, Characterization, Crystal Structures, and in Vitro Antitumor Activity with 2-Acetyl-4-Methylthiazole Thiosemicarbazone and 2-Acetylpyrazine Thiosemicarbazone. New Schiff bases were prepared: I HAMTTSC (2-Acetyl-4-methylthiazole thiosemi- carbazone), II HAPTSC (2-Acetylpyrazine thiosemicarbazone), and their complexes with Pt(II) and Pd(II):
1. [Pt (AMTTSC)Cl], 2. [Pt (AMTTSC)$_2$], 3. [Pd (AMTTSC)Cl], 4. [Pd (AMTTSC)$_2$], 5. [Pt (APTSC)Cl], 6. [Pt (APTSC)$_2$], 7. [Pd (APTSC)Cl], and 8. [Pd (APTSC)$_2$] produced synthetically. Showed in vitro antitumor activity of Schiff bases and 1, 2, 4, 5, and 6 against two human cancer cell lines (HT-29 and HuTu-80); therefore, these compounds have been considered agents with potential antitumor activity [76].

Palladium(II) and platinum(II) complexes with phenylalanine ester: synthesis, crystal structures, and cytotoxicities. Synthesized palladium(II) and platinum(II) phenylalanine ester complexes with a pyridine moiety coordinated to a metal core. From each complex, single crystals may be effectively harvested. When compared to other Pt(II) compounds, the produced Pd(II) complex demonstrated substantial cytotoxicity [77].

Four new palladium(II) and platinum(II) complexes with 1-(2-aminoethyl) pyrrolidine, diclofenac, and mefenamic acid were synthesized and characterized: Four single-core palladium (II) and platinum (II) complexes were synthesized in vitro to test the effects of these complexes on human serum paraoxonase 1 activity. Donor ligand 1-(2-aminoethyl) pyrrolidine and nonsteroidal were used to create palladium(II) and platinum(II) complexes. Complexes were [Pd(2-amepyr)$_2$](dicl)$_2$, [Pt(2-amepyr)2](dicl)$_2$, [Pd(2-amepyr)$_2$](mef)$_2$, [Pt(2-amepyr)2](mef)$_2$·2H_2O. These

complexes underwent spectroscopic, thermal, and elemental investigations to be identified [78].

Characterization, theoretical calculations, antibacterial and anti-cancer tests, and investigations of interaction with CT-DNA of Pt(II) and Pd(II) complexes with ibuprofen hydrazide with palladium(II) [$Pd(C1_3H_2ON_2O)_2Cl_2$] and platinum(II) [$Pt(Cl_3H_2ON_2O)_2Cl_2$] complexes were prepared using an ibuprofen hydrazide derivative (Labeled HIB) and are identified using chemical and spectroscopic techniques. In the complexes, the [$PdCl_2(HIB)_2$] compound is active against an ovarian cancer cell line, according to in vitro antiproliferative tests OVCAR-03 [79].

New Pt(II) and Pd(II) complexes with 2,2'-dithiobis(benzothiazole) ligand: synthesis, characteristics, antitumor, and antibacterial activity mono- and dinuclear Pt(II) and Pd(II) complexes with 2,2'-dithiobis(benzothiazole) (DTBTA) were prepared [Pt (DTBTA)(DMSO)Cl]Cl $CHCl_3$(1) and [$Pd_2(\mu\text{-}Cl)_2(DTBTA)_2]Cl_2$(2) The structural characteristics of them were determined by elemental analysis, IR, ^{1}H NMR, and ^{13}C NMR research. Against two human cancer cell lines, antitumor activity human breast cancer (MCF-7) and hepatocellular carcinoma (HepG2), and only the first compound's antimicrobial activity has shown cytotoxic efficacy [80].

New Complexes of Platinum and Palladium Based on Pyrrole Schiff Bases: Anti-cancer activity, characterization, synthesis, and X-ray structure Complexes of platinum Pt(II) (C1–C5) and palladium Pd(II) were created. From the Schiff base ligands, R-(phenyl) methanamine(L1), R-(pyridin-2-yl)methanamine(L2), and R-(furan-2-yl)methanamine (L3) (R-(E)-N-((1H-pyrrol-2-yl) methylene)) are herein reported. FTIR, $_1$H NMR, UV-Vis, and ^{13}C NMR characterized the complexes. Human non-cancerous (MCF-12A) and cancerous (Caco-2, HeLa, HepG2, and PC-3) cell lines were used to test the anti-cancer activity and mechanism of the complexes. For CT-DNA, the complex had a high affinity for DNA binding. All six cell strains, including five malignant ones, had their cell viability lowered by C3 by more than 80%. The selectivity of the C5 complex was likewise extremely high[74].

PART 4

CHEMICALS AND MATERIALS

4.1. USED DEVICES

- Nuclear Magnetic Resonance (NMR) Spectroscopy: AGILENT 400/54 model spectroscopy instrument (400 MHZ), Chemistry Department, Faculty of Basic Sciences, Recep Tayyip Erdogan University
- FT-IR spectroscopy :(Nicolet™ iS™ 5, Thermo Scientific) coupled with the attenuated total reflection (ATR) technique (iD7 Thermo Scientific), Karabuk University Department of Chemistry
- Mass: Thermo Scientific TSQ Quantum Access MAX, Central Research Laboratory of Recep Tayyip Erdogan University (MERLAB)
- Mass 2: MALDI-MS (Bruker Micro flex LT MALDI-TOF MS), Gebze Technical University, Faculty of Basic Sciences, Department of Chemistry
- X-ray diffractometer: Model: Bruker / D8 QUEST, Application, and research center for scientific and technology research at Sinop University

4.2. CHEMICALS USED

Table 4.1. Chemicals used.

	Chemical	Source
1	ethanol	Merck
2	methanol	Merck
3	acetone	Merck
4	thiophene-2-ylmethanamine	Aldrich
5	pyridine-2-ylmethanamine	Across
6	piperidine-2-ylmethanamine	Aldrich
7	2-hydroxybenzaldehyde	Fluka
8	Pd (DMSO)Cl_2	Synthesized from $PdCl_2$(Aldrich)
9	K_2PtCl_4	Aldrich
10	DMF	Merck
11	DCM	Erba
12	Silica gel	Merck
13	DMSO	Merck

PART 5

EXPERIMENTAL

5.1. SYNTHESIS OF THE LIGANDS

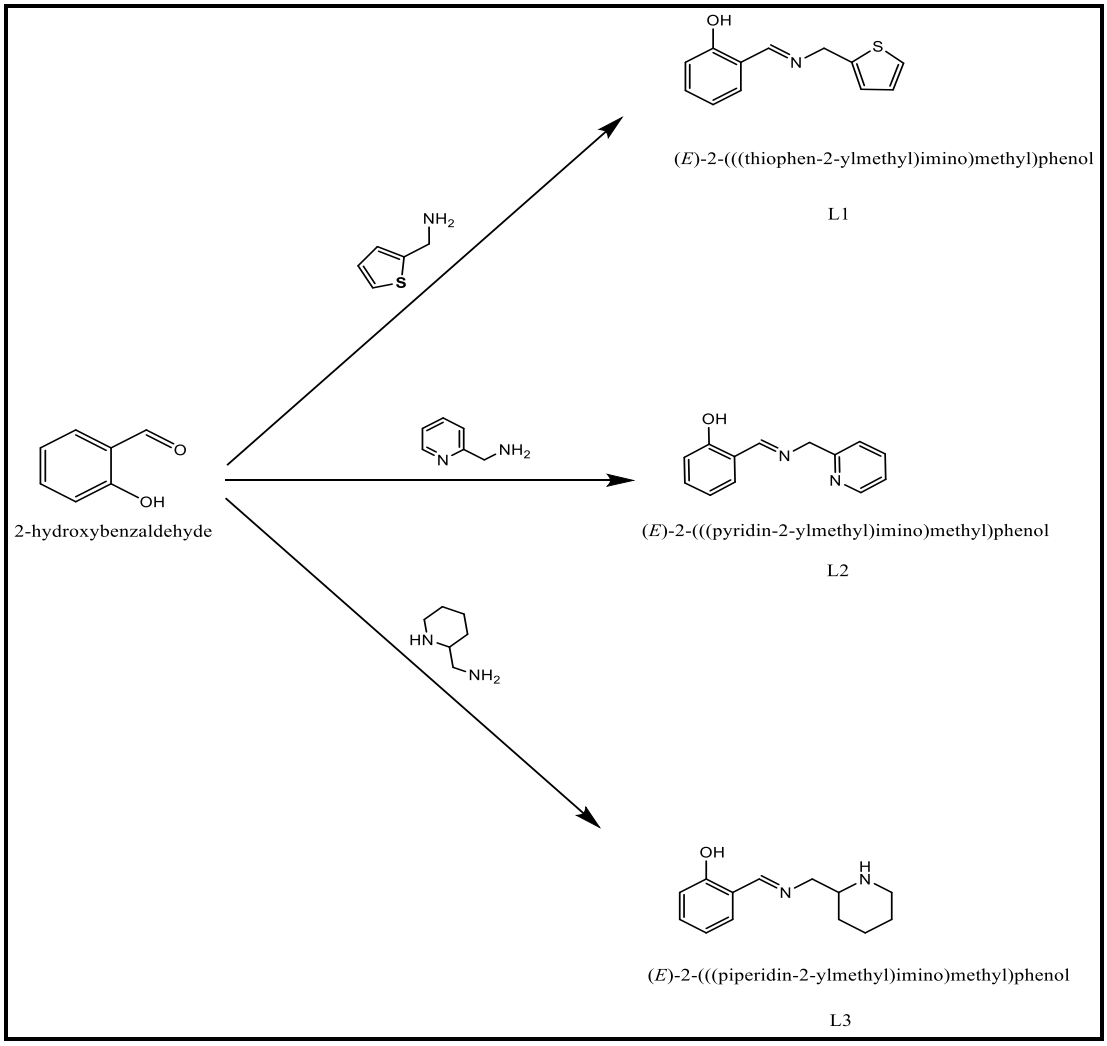

Figure 5.1. General Synthesis Scheme of Ligands.

The ligands were synthesized by the traditional process for making Schiff bases, which involves heat condensation of an amine and an aldehyde [74], [83]. 2-hydroxybenzaldehyde (0.009 mol) was dissolved in (10 ml) DCM, and (0.009 mol) of

primer amine was dissolved in (10 ml) of DCM. Then, two solutions were gradually mixed by adding dropwise with continuous stirring at room temperature. After the addition is complete, a clear yellow solution was formed. The mixture was refluxed at 65°C for three hours continuously. The resulting solution was dark yellow. The solvent was evaporated by a rotary evaporator. In order to ensure that the solvent evaporated, the product was kept at room temperature for 24 hours. The approximate yield of the product was L1 90%, L2 88%, and L3 76%.

5.1.1. (E)-2-(((thiophen-2-ylmethyl)imino)methyl)phenol (L1)

FT-IR (ATR, cm^{-1}) : 3064, 2835, 1627, 1579, 1493, 1459, 1434, 1408, 1376, 1360, 1312, 1276, 1209, 1150, 1115, 1077, 1036, 1022, 993, 969, 851, 783, 752, 652, 549, 502, 464, 424, 418.

^{1}H NMR (400 MHz, dmso) δ 13.20 (s, 1H), 8.62 (t, J = 1.5 Hz, 1H), 7.49 – 7.38 (m, 2H), 7.32 (ddd, J = 8.7, 7.2, 1.8 Hz, 1H), 7.03 (dd, J = 3.5, 1.1 Hz, 1H), 6.99 (dd, J = 5.1, 3.4 Hz, 1H), 6.94 – 6.84 (m, 2H), 4.95 (d, J = 1.2 Hz, 2H).

^{13}C NMR (101 MHz, dmso) δ 166.98, 160.81, 141.78, 133.01, 132.27, 127.54, 125.83, 125.81, 119.22, 119.08, 116.93, 57.04.

ESI Mass (*m/z*): 217.78 (L), 274.83 (L+3H_2O)

5.1.2. (E)-2-(((pyridin-2-ylmethyl) imino)methyl)phenol (L2)

FT-IR (ATR cm^{-1}) :3050, 3008, 2858, 1627, 1587, 1570,1487, 1472, 1458,1433, 1277, 1253,1149, 1117,1047, 994, 893, 841, 747, 653, 610, 561, 539, 496, 463, 423.

^{1}H NMR (400 MHz, dmso) δ 13.39 (s, 1H), 8.72 (s, 1H), 8.53 (d, J = 5.2 Hz, 1H), 7.81 – 7.68 (m, 2H), 7.47 (d, J = 7.6 Hz, 1H), 7.39 – 7.22 (m, 3H), 6.89 (d, J = 4.6 Hz, 1H), 4.89 (s, 2H).

^{13}C NMR (101 MHz, dmso) δ 167.86, 161.01, 158.21, 149.71, 137.43, 132.96, 132.26, 122.94, 122.54, 119.09, 116.94, 97.82, 64.33.

ESI Mass (*m/z*): 213.09 (L), 222.96 (L+H_2O)

5.1.3. (E)-2-(((piperidin-2-ylmethyl) imino)methyl)phenol (L3)

FT-IR (ATR cm^{-1}) : 3049, 2930, 2850, 2802, 1663, 1629, 1582, 1485, 1458, 1411, 1323, 1277, 1260, 1229, 1149, 1116, 1103, 1078, 1044, 1030, 982, 929, 883, 853, 809, 779, 751,736, 654, 587, 551, 514, 489, 458, 443.

^{1}H NMR (400 MHz, dmso) δ 13.26 (s, 1H), 8.47 (s, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 7.3 Hz, 1H), 3.50 (h, *J* = 6.3 Hz, 2H), 3.09 (dd, *J* = 9.5, 6.5 Hz, 2H), 2.94 (s, 1H), 2.72 (s, 1H), 1.78 (d, *J* = 10.1 Hz, 1H), 1.74 – 1.66 (m, 2H), 1.59 (t, *J* = 14.8 Hz, 2H), 1.48 (d, *J* = 9.3 Hz, 1H).

^{13}C NMR (101 MHz, dmso) δ 167.10, 158.85, 132.07, 130.15, 129.37, 118.11, 116.70, 56.99, 48.91, 48.55, 28.89, 25.02, 23.77.

Mass (*m/z*): 218.97 (L).

5.2. SYNTHESIS OF COMPLEXES

5.2.1. Synthesis of palladium(II) complexes (C1, C3 and C5)

A solution of L (0.001 mol) in DCM (20 ml) was added dropwise to a stirred solution of Pd(DMSO)Cl_2 (0.001 mol) in DCM (20 ml). Upon addition, the color of the solution turns to brown, and when the addition was complete, the solution turned into a light orange color. The solution was refluxed for 24 hours at 60 °C. During this time, the color of the solution became light orange. Yellow crystals were formed in the solution, collected by filtration, washed with DCM, and air-dried. The complexes were further purified by column chromatography over Silica gel using DMF solvent. Figure 5.2 shows the possible structures of the prepared complexes.

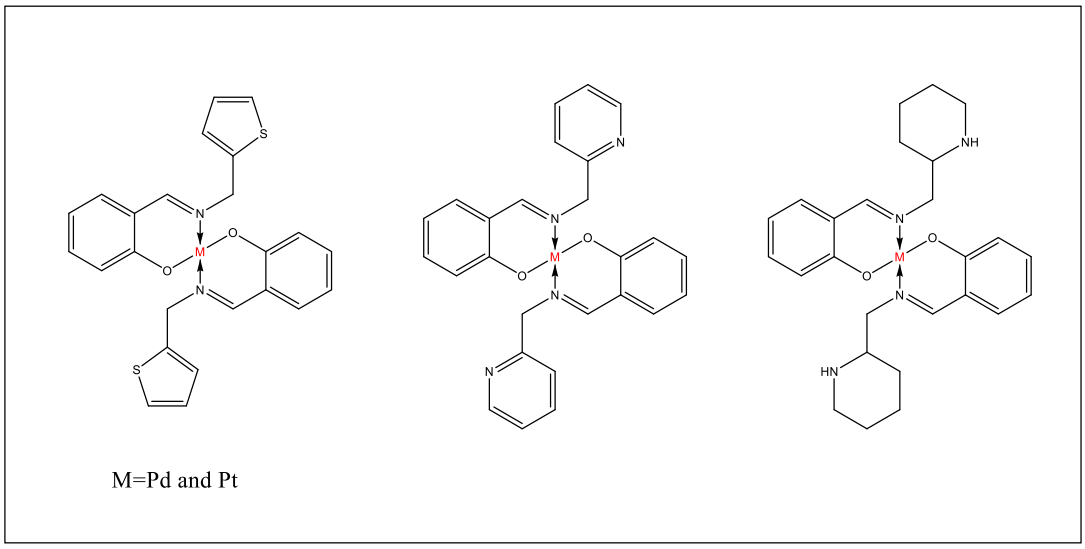

Figure 5.2. The possible structures of the prepared complexes.

5.2.1.1. Pd-L1 Complex (C1)

FT-IR (ATR cm^{-1}) 3102, 2999, 2915, 1609, 1597, 1534, 1463, 1446, 1432, 1395, 1350, 1336, 1316, 1263, 1251, 1207, 1195, 1146, 1127, 1077, 1034, 1013, 970, 953, 936, 854, 848, 837, 827, 808, 755, 736, 703, 616, 596, 508 ,469, 442.

^{1}H NMR (400 MHz, dmso) δ 8.32 (s, 1H), 7.42 – 7.36 (m, 2H), 7.32 – 7.24 (m, 2H), 7.13 (d, J = 3.6 Hz, 1H), 6.98 – 6.91 (m, 1H), 6.86 (d, J = 8.2 Hz, 1H), 5.08 (s, 2H).

MALDI-TOF MS: 539.1 (PdL_2), 561.5 (PdL_2+Na).

5.2.1.2. Pd-L2 Complex (C3)

FT-IR (ATR cm^{-1}) 3193, 3047, 2775, 1716, 1658, 1599, 1525, 1467, 1436, 1386, 1316, 1283, 1260, 1196, 1151, 1092, 1021, 897, 853, 752, 713, 681, 661, 513, 493, 462.

^{1}H NMR (400 MHz, dmso) δ 8.72 (d, J = 6.1 Hz, 1H), 8.58 (d, J = 4.9 Hz, 1H), 7.33 (t, J = 7.6 Hz, 3H), 7.05 – 6.80 (m, 4H), 4.61 (d, J = 6.8 Hz, 2H).

MALDI-TOF MS: 527.9 (PdL_2), 555.952 (PdL_2+1.5 H_2O).

5.2.1.3. Pd-L3 Complex (C5)

FT-IR (ATR γ cm^{-1}) 3088, 3047, 2989, 2928, 2863, 1623, 1599, 1527, 1444, 1394, 1369, 1349, 1312, 1226, 1205, 1190, 1145, 1126, 1089, 1072, 1043, 1025, 975, 937, 922, 902, 873, 862, 853, 783, 744, 738, 656, 624, 611, 549, 510, 477, 464, 437.

^{1}H NMR (400 MHz, dmso) δ 7.90 (s, 1H), 7.85 (s, 1H), 7.32 – 7.17 (m, 2H), 6.70 (d, J = 2.3 Hz, 1H), 3.80 – 3.39 (m, 4H), 2.96 – 2.87 (m, 1H), 1.90 – 1.16 (m, 6H).

MALDI-MS: 324.0 (PdL).

5.2.2. Synthesis of Platinum complexes (C2 ,C4 and C6)

A solution of L (0.001 mol) in DCM (10 ml) was added dropwise with stirring to the solution of K_2PtCl_4 (0.001 mol) in water (30 ml). After the addition was completed, The solution was changed to orange. At 60 °C, the solution was refluxed for 24 hours. The solution's color changed to a light brown throughout this process, and the crystalline precipitate was then collected, dried, and recrystallized from DMF. The collected crystals were light brown. The complexes were further purified by column chromatography over Silica gel using DMF solvent.

5.2.2.1. Pt-L1 Complex (C2)

FT-IR (ATR cm^{-1}) 3078, 2920, 2851, 2161, 2084, 1722, 1647, 1600, 1433, 1381, 1247, 1149, 1101, 1016, 951, 825, 755, 702, 660, 448.

^{1}H NMR (400 MHz, dmso) δ 9.02 – 6.33 (m, 7H), 4.61 (d, J = 6.6 Hz, 2H).

MALDI-MS: 628.6 (PtL_2), 662.9 (PtL_2+$2H_2O$)

5.2.2.2. Pt-L2 Complex (C_4)

FT-IR (ATR γ cm^{-1}) 3076, 2923, 2160, 1718, 1647, 1605, 1567, 1439, 1385, 1323, 1287, 1228, 1153, 1098, 1058, 901, 861, 756, 681, 518, 468, 448.

^{1}H NMR (400 MHz, dmso) δ 8.90 (d, J = 5.9 Hz, 1H), 7.82 (d, J = 7.8 Hz, 2H), 7.60 (s, 2H), 7.45 (s, 2H), 6.94 (d, J = 6.2 Hz, 2H), 4.61 (d, J = 5.7 Hz, 2H).

MALDI-MS: 617.6 (PtL_2).

5.2.2.3. Pt-L3 Complex (C_6)

FT-IR (ATR cm^{-1}) 3458, 3266, 3189, 3099, 2985, 2943, 2923, 2860, 2160, 1725, 1648, 1576, 1454, 1446, 1427, 1364, 1343, 1300, 1286, 1269, 1218, 1181, 1172, 1096, 1074, 1056, 1033, 1001, 967, 959, 937 , 876, 858, 790, 733, 660, 575, 526, 473, 459.

^{1}H NMR (400 MHz, dmso) δ 7.49 – 6.30 (m, 5H), 3.55 (s, 2H), 3.27 – 3.19 (m, 1H), 3.05 (d, J = 12.0 Hz, 1H), 2.78 (s, 2H), 2.00 – 1.24 (m, 6H).

MALDI-MS: 422.318 ($PtL+0.5\ H_2O$)

PART 6

RESULTS AND DISCUSSIONS

The ligands (L1−L3) were synthesized by the standard Schiff bases condensation reaction of 2-hydroxybenzaldehyde either with thiophene-2-methenamine (L1), pyridine-2-methenamine (L2), or piperidine-2-methenamine (L3) as shown in Figure 6.1. The corresponding complexes were examined using ^{1}H NMR, ^{13}C NMR, single crystal X-ray, mass, and FT-IR. The traditional method of preparing Schiff base ligands, which is the reaction of aliphatic or aromatic aldehydes or ketones with aliphatic or aromatic primary amines, was used to prepare Schiff bases. As shown in Figure 6.1, the mechanism of forming a Schiff base is a nucleophilic addition to the carbonyl group, where the amine group plays the role of a nucleophile in the first step of the mechanism. The electrons on the amine nitrogen attack the aldehyde or ketone to give a worried intermediate compound, carbinolamine, which is followed by water loss by acid or base catalysis. The rate-limiting step for forming a Schiff base is the dehydration of carbinolamine [84]–[86].

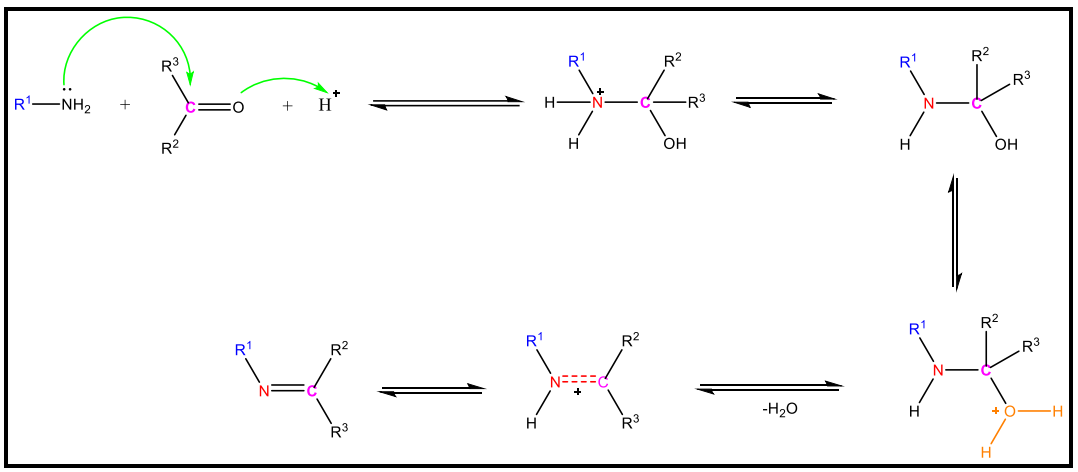

Figure 6.1. Schiff bases preparation mechanism [84]–[86].

Metal complexes (C1-C6) were obtained through the reaction of $Pd(DMSO)Cl_2$ and K_2PtCl_4 salts with ligand (L) in DCM solution. The complexes (C1, C2, C3, C4, C5, and C6) were produced utilizing the L1, L2, and L3 ligands in a reaction of 1:1 (metal/ligand) molar ratios. The complexes (C1, C2, C3, C4, C5, and C6) were *trans*-geometric and bound in a metal/ligand ratio of 1:2.

6.1. FT-IR SPECTRUM

The characteristic bonding of the ($-NH_2$) group was determined in the stretching vibration range (3367, 3361, and 3285) cm^{-1} for compounds (thiophene-2-methenamine, pyridine-2-methenamine, and piperidine-2-methenamine) respectively, and the characteristic bonding of the carbonyl group (C=O) for compound (2-hydroxybenzaldehyde) was determined at 1660 cm^{-1}. However, the characteristic values of these groups did not appear in the prepared ligands, and this indicates the formation of a double bond (C=N), as shown in Figure 6.2 for the L3 ligand.

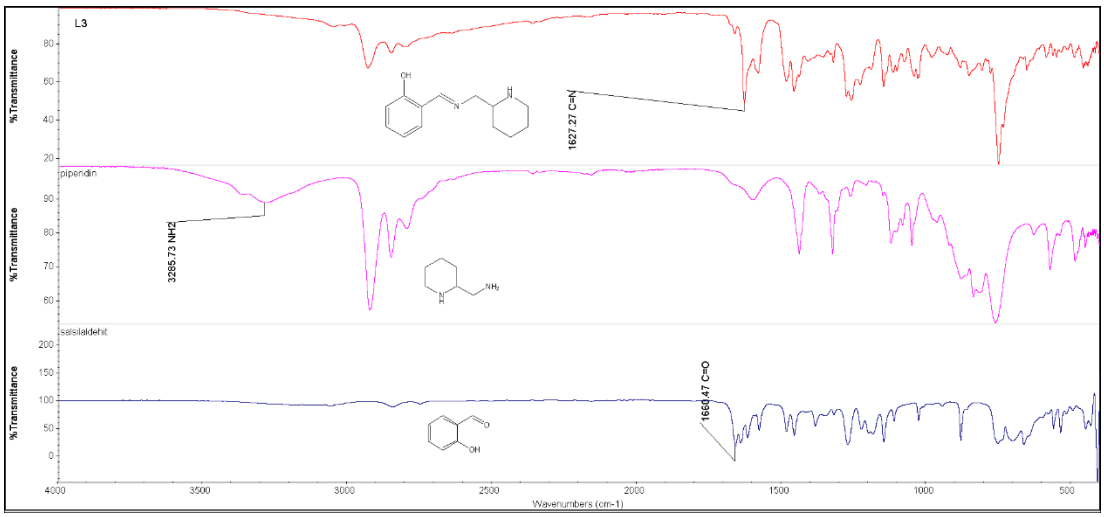

Figure 6.2. FT-IR for L3 , 2-hydroxybenzaldehyde and piperidin-2-ylmethanamine.

The characteristic of the carrier ligands of the azomethine(C=N) functional group was identified in the stretching vibration range of 1629 –1626 cm^{-1}. At the same time, the expansion vibration range of the C-H_{ar} group is observed in the range of 3048-3064 cm^{-1}. As for the complexes vibration range of the C-H_{al} group was observed in the range of 2930-2834 cm^{-1}. In complexes, the C-H_{ar} tensile vibration ranges in the range

of 3047-3102 cm^{-1}. The azomethine (C=N) functional group was identified in the stretching vibration range in the range of 1609-1657 cm^{-1}, The C-H_{al} vibration ranges in the range of 2998-2775 cm^{-1}, Pt-N vibration ranges in the range of 755-702 cm^{-1}, Pd-N vibration ranges in the range of 660-595 cm^{-1} [87]. The shifts in the azomethine vibration bands in the complexes, as shown in Figure 6.3, indicate that the electron pair located on the nitrogen atom in the azomethine group has created a coordination bond with the central metal atom.

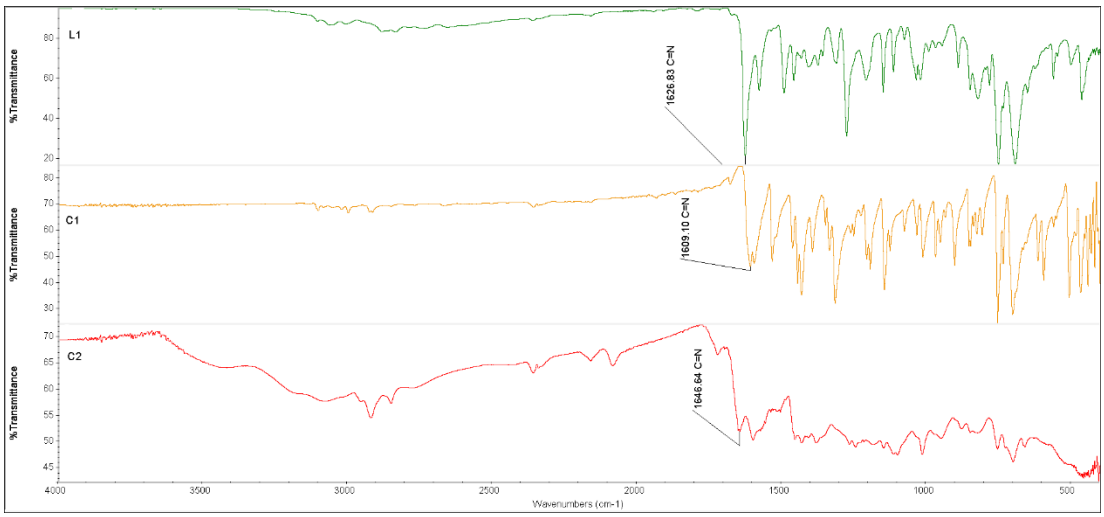

Figure 6.3. FT-IR for L1 , C1 and C2.

This change is due to the electronic transition from azomethine's empty pi-antibonding orbitals to metal d-orbitals [88]. In the C6 complex, the NH peak of piperidine observed at 3266 cm^{-1} did not change much compared to the ligand (3244cm^{-1}), that is, it did not participate in coordination. In the C2 complex, the peak at 3418 cm^{-1} belongs to the hydrogen-bonded crystalline water and is also observed in the Maldi-Tof peaks.The frequencies for the azomethine functional groups were compared. The other functional groups are shown in Table 6.1.

Table 6.1. FT-IR frequency values of ligands and complexes.

	υ (CH) $_{Ar}$	**υ(CH) $_{Al}$**	**υ (C=N)**	**υ (C=C)**	**υ (Pd-N**	**υ (Pt-N)**
L1	3064	2834	1626	1578 1492 1458		
C1	3102	2998	1609	1432 1446 1463	595	
C2	3077	2850	1646	1432 1600		702
L2	3050	2857	1627	1587 1570 1487		
C3	3047	2775	1657	1599 1525 1466	660	
C4	3076	2923	1647	1605 1567 1439		755
L3	3048	2930	1629	1581 1485 1458		
C5	3088	2988	1623	1598 1525 1444	610	
C6	3098	2943	1648	1576 1454 1445		733

6.2. ^{1}H NMR SPECTRA

The selected ^{1}H NMR peaks of the ligands are shown in Figure 6.4. L1 ligand; at 8.62 ppm as the -CH- peak, at 4.95 ppm the peak for the -CH_2- group, and at 13.2 ppm the peak for the -OH group. L2 ligand; at 8.72 ppm as the -CH- peak, at 4.89 ppm the peak for the -CH_2- group, and at 13.39 ppm the peak for the -OH group. L3 ligand; at 8,47 ppm -CH- peak, at 3.50, 3.09 ppm the peak for the -CH_2- group, and at 13.26 ppm the peak for the -OH group.

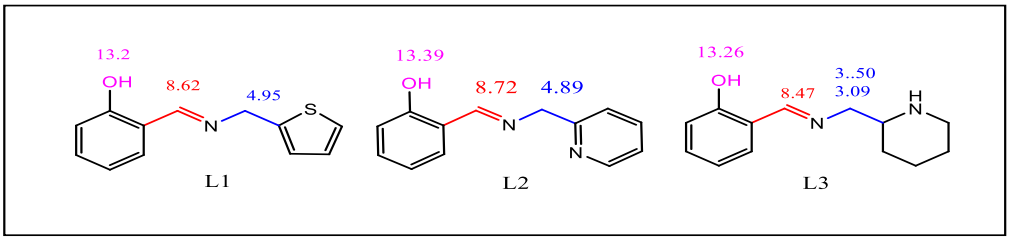

Figure 6.4. Selected ^{1}H NMR peaks of the ligands.

The (-CH=N-) peaks: C1 complex; at 8.32 ppm, C2 complex; at 9.02 ppm, C3 complex; at 8.72 ppm, C4 complex; at 8.90 ppm, C5 complex; at 7.90 ppm, C6 complex; at 7.49 ppm. The comparison between the peaks that belong to the ligands and the complexes about the azomethine group, it is clear that the coordination bond established between the *d*-orbitals of metal and the pi-electrons of the azomethine group, as revealed by the diffrenecs in the chemical shift of the azomethine group upon coordination to the metal center [89] as shown in Figure 0.5. In addition, the hydroxyl proton peaks in the spectrum of the ligands disappear in the metal complexes as shown in Figure 6.6,. This confirms the coordination of the ligand as a monoanionic manner through the O atom, and in turn is consistent with the proposed structure of the complexes as depicted in Fig. 6.5.

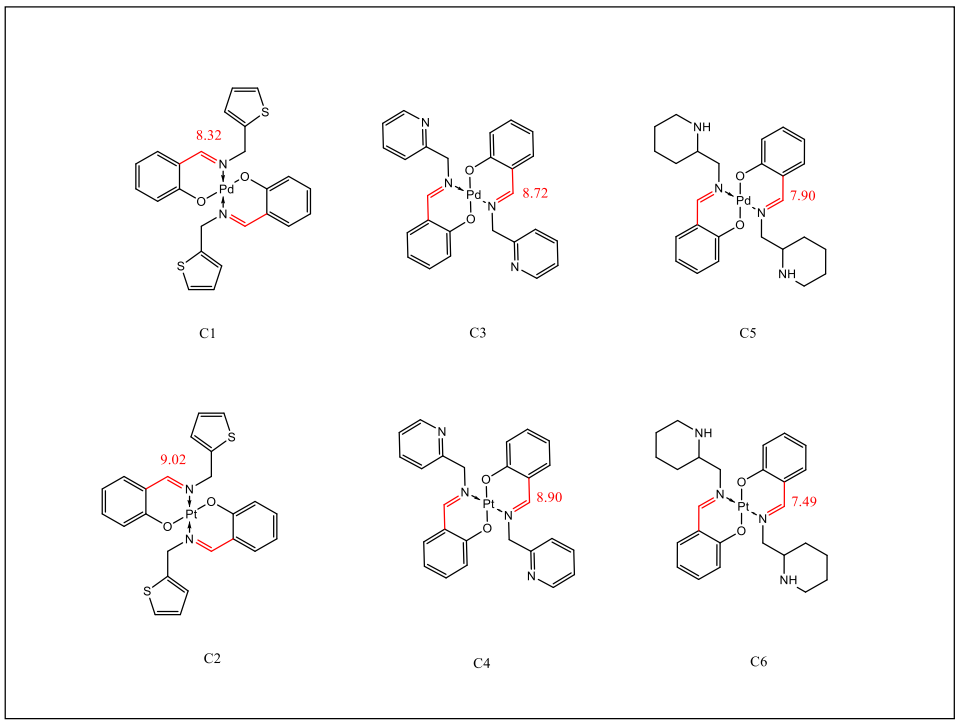

Figure 6.5. ^{1}H NMR peaks of the coordination complexes.

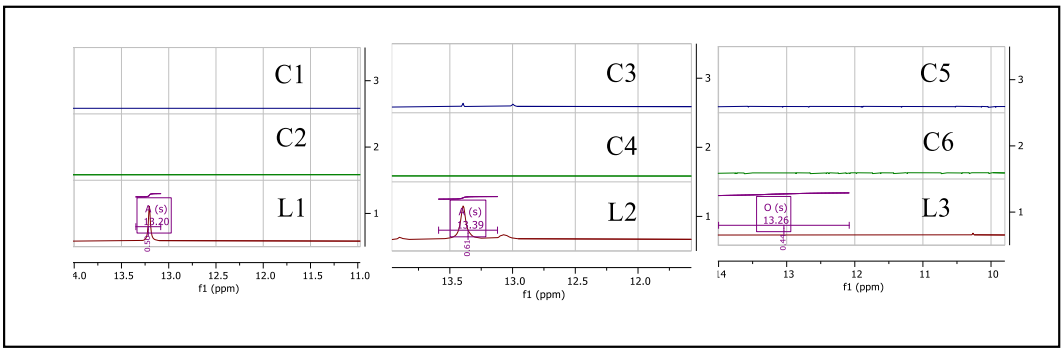

Figure 6.6. The ligand spectrum of the hydroxyl group.

6.3. ^{13}C NMR SPECTRA

The ^{13}C NMR peaks for the ligands are shown in Figure 6.7. L1 ligands; there were 12 carbon peaks. As expected, the azomethine peak was observed at 166.98 ppm, and the (-CH_2-) group peak was identified at 57.04 ppm. L2 ligands; there were 13 carbon peaks, as expected. Azomethine peak is observed at 167.86 ppm. The (-CH_2-) group peak was determined to be 64.33 ppm. L3 ligands; there were 13 carbon peaks, as expected. Azomethine peak was observed at 167.10 ppm. The (-CH_2-) group peak was determined to be 63.40 ppm. Figure 6.7 ^{13}C NMR peaks of L1, L2 and L3 ligands.

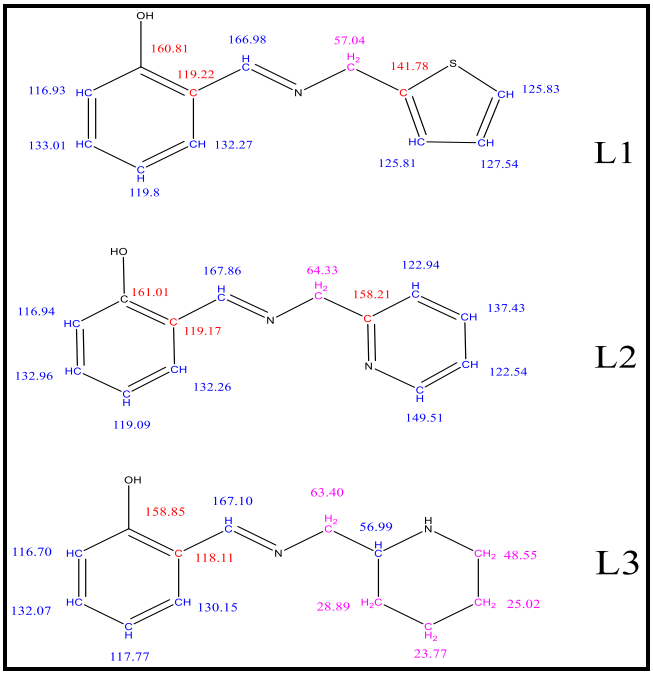

Figure 6.7. ^{13}C-NMR peaks of L1, L2 and L3 ligands.

6.4. ^{13}C NMR-DEPT SPECTRA

L1: C peaks: 160.81, 119.22, 141.78; CH peaks: 125.83, 127.54, 125.81, 166.98, 132.27; CH_2 peak: 57.04. L2: C peaks: 161.01, 119.17, 158.21, CH peaks: 122.94, 137.43, 122.54, 149.51, 167.86, 132.26, 119.09, 132.96, 116.94, CH_2 peaks: 64.33. L3: C peaks: 158.85, 118.11; CH peaks: 56.99, 167.10, 130.15, 117.77, 132.07, 116.70; CH_2 peaks: 63.40, 48.55, 25.02, 23.77, 28.89. The ^{13}C NMR-DEPT SPECTRA confirm the structures of the synthesized compounds.

6.5. MASS SPECTRUMS

The outcomes of theoretical estimates of the ligands' molecular weights for L1, L2, and L3 were: 217.3, 212.3, and 218.3 $gmol^{-1}$, respectively. The ligands L1, L2, and L3 are shown in Table 6.2 and are identical to that of calculated theoretically.

Table 6.2. ESI-Mass Peaks of The Ligands.

	ligand	Molecular weight	ESI-Mass Peaks
1	L1	217.3	217.8
2	L2	212.3	213.1
3	L3	218.3	219.0

6.6. MALDI-TOF MASS ANALYSIS OF THE COMPLEXES

Theoretical and experimental MALDI-TOF MS results for complexes (C1-C6) are shown in Table 6.3.

Table 6.3. MALDI-TOF Mass results of the complexes.

	Complex	Theoretical molecular weight	MALDI-TOF Peaks
1	C1 : $[Pd(L1)_2]$	538.9	539.1
2	C1 :$[Pd(L1)_2]$ +Na	561.9	561.5
3	C2 :$[Pt(L1)_2]$	627.6	628.6
4	C2 :$[Pt(L1)_2]$ +$2H_2O$	663.7	663.0
5	C3 :$[Pd(L2)_2]$	528.9	527.9
6	C3 :$[Pd(L2)_2]$ + $1.5H_2O$	555.9	556.0
7	C4 :$[Pt(L2)_2]$	617.6	617.6
8	C5 :[Pd(L3)]	323.7	324.0
9	C6 :[Pt(L3)] +0,5 H_2O	422.4	422.3

6.7. X-RAY CRYSTALLOGRAPHY

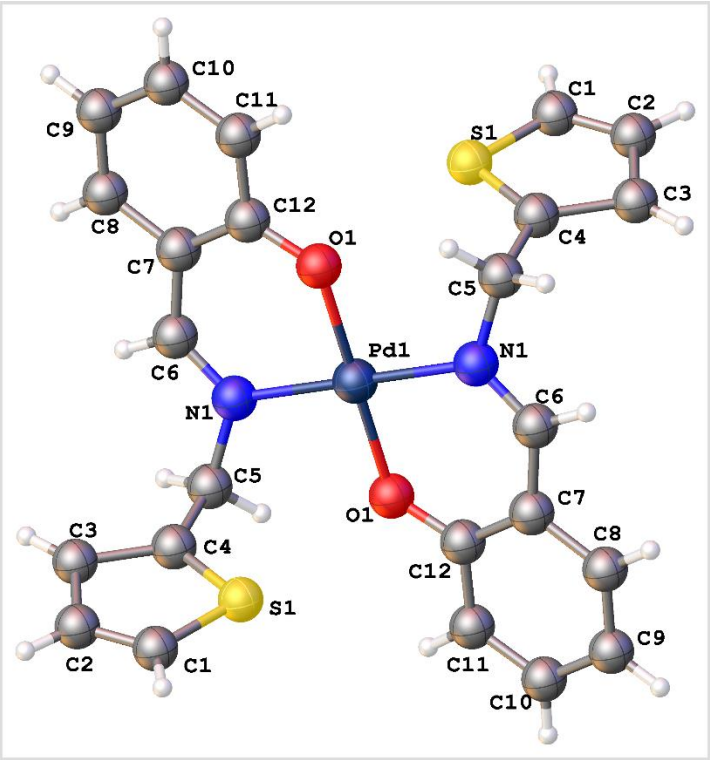

Figure 6.8. X-ray Crystal Structure for C1 Complex.

$[Pd(L1)_2]$ crystals were obtained by slow evaporation of the DMSO solution of C1 (Figure 6.8). The compound crystallizes in the monoclinic *C2/c* with two complex molecules in the unit cell. The Pd atom is coordinated by the O, N atoms of the (E)-2-(((thiophen-2-ylmethyl)imino)methyl)phenol ligand. The coordination bond lengths Pd–N and Pd–O lie in the expected ranges. The two molecules of L1 have very similar bond lengths. The bond lengths and bond angles in the thiophene ring and benzene ring are usual and close to those found in similar systems, and the angles between (O11-Pd1-O1) (180°) and (N11-Pd1-N1) (180°) refer to the complex geometry as an ideal square-planar. The results were identical and complementary to the rest of the analyses. Tables of single crystal data, bond angles and bond lengths for C1 (6.4, 6.5 and 6.6) are as follows.

Table 6.4. Structure and data refinement Parameters for C1.

compound	**Pd(L1)$_2$**
formula	$C_{24}H_{20}N_2O_2PdS_2$
space group	C2/c
cell lengths	a/Å 21.000(4)
	b/Å 5.9928(10)
	c/Å 17.163(3)
cell angles	α/° 90
	β/° 94.297(11)
	γ/° 90
cell volume	2153.9(7)
Z	4
temperature	273.15 K

Table 6.5. Selected Bond Angles for C1.

Atom Bond	**Angle/°**
O1-Pd1-O1^1	180.0
O1-Pd1-N1	92.0
O1^1-Pd1-N1	88.0

Table 6.6. Selected Bond Lengths for C1.

	Atom	**Atom**	**Length/Å**
1	Pd	O1	1.983
2	Pd	O1^1	1.983
3	Pd	N1^1	2.030
4	Pd	N1	2.030

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APPENDIX A.

SPECTRUMS

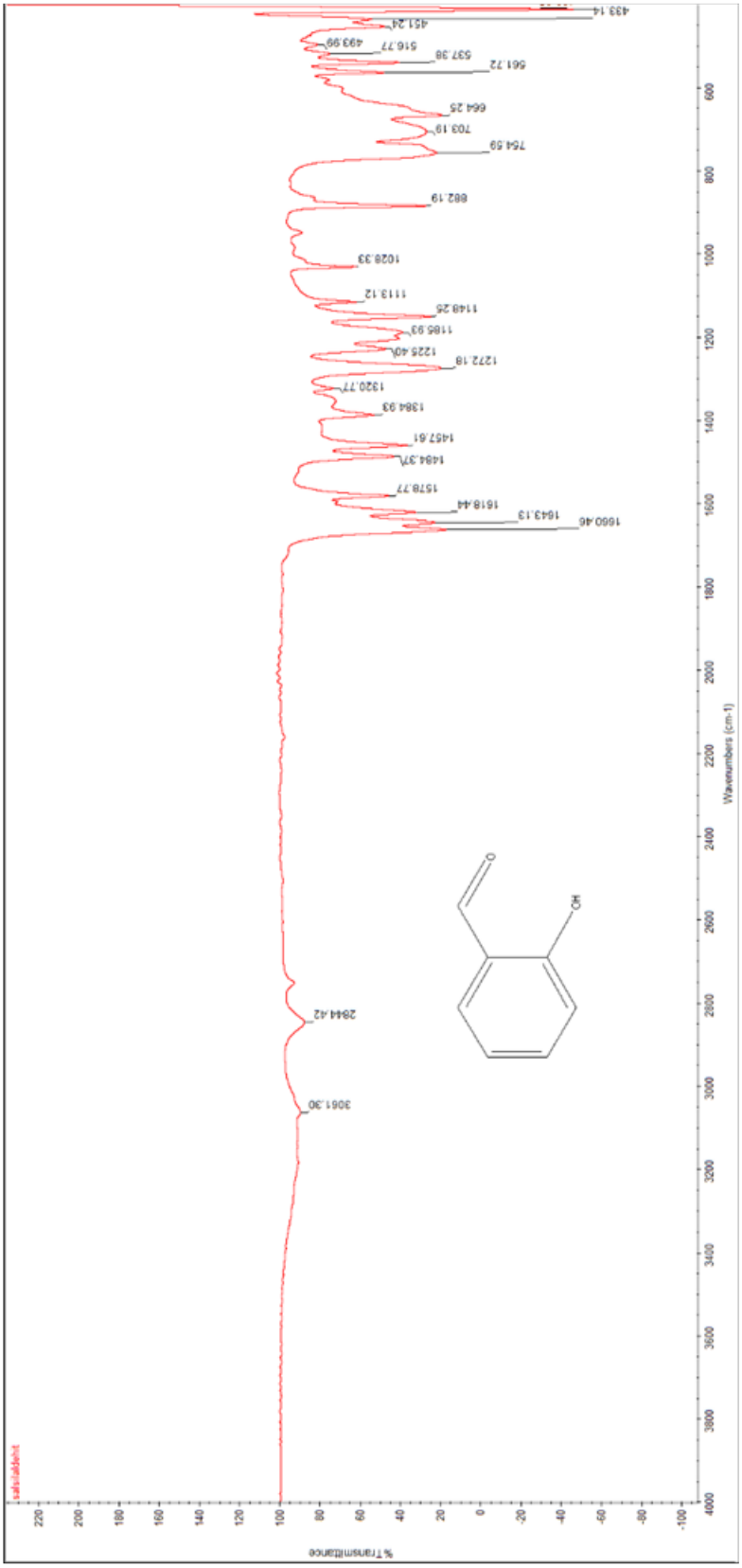

Figure Appendix A.1. AD.E. 2-hydroxybenzaldehyde FTIR spectrum

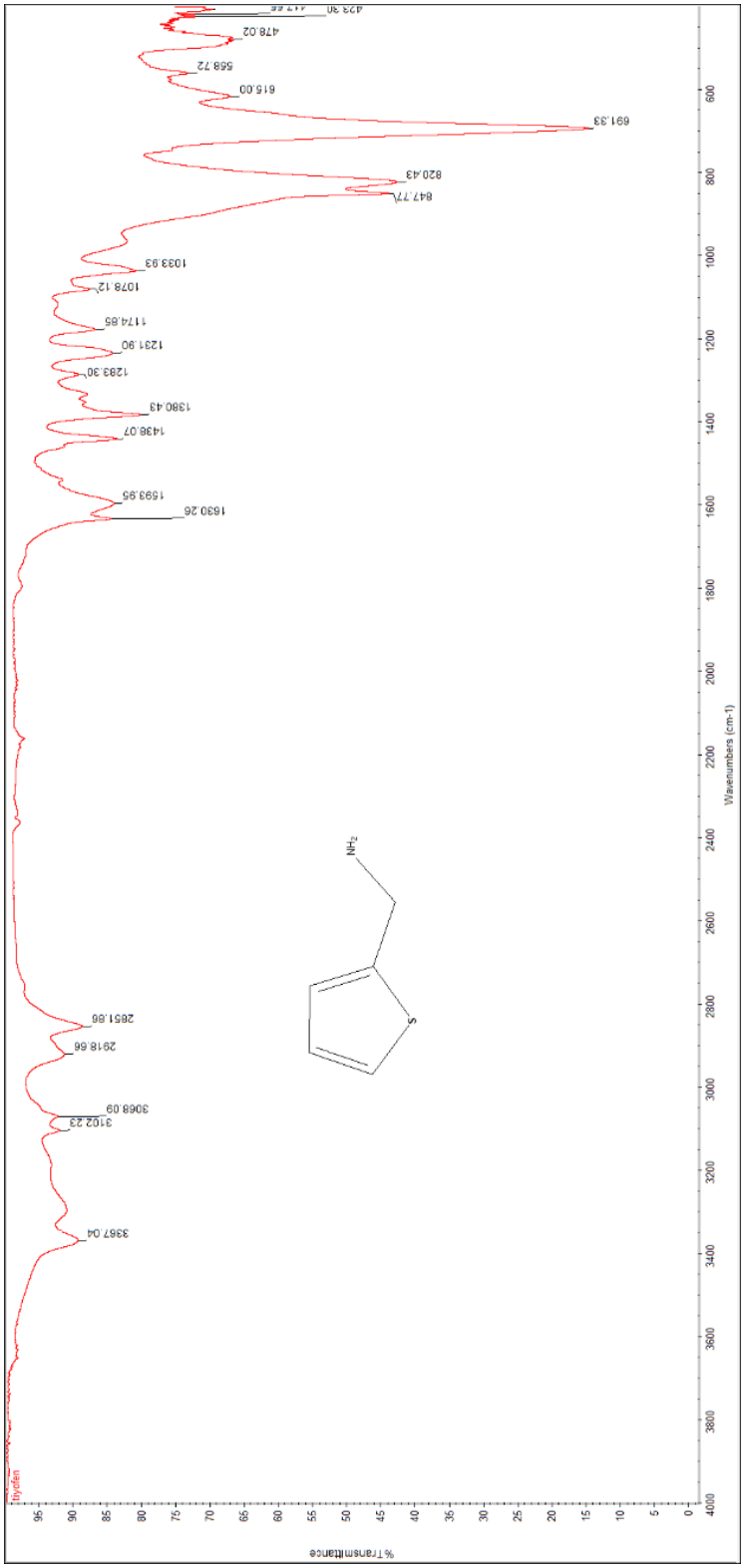

Figure Appendix A.2. AD.E. FTIR spectrum of thiophen-2-yl methanamine

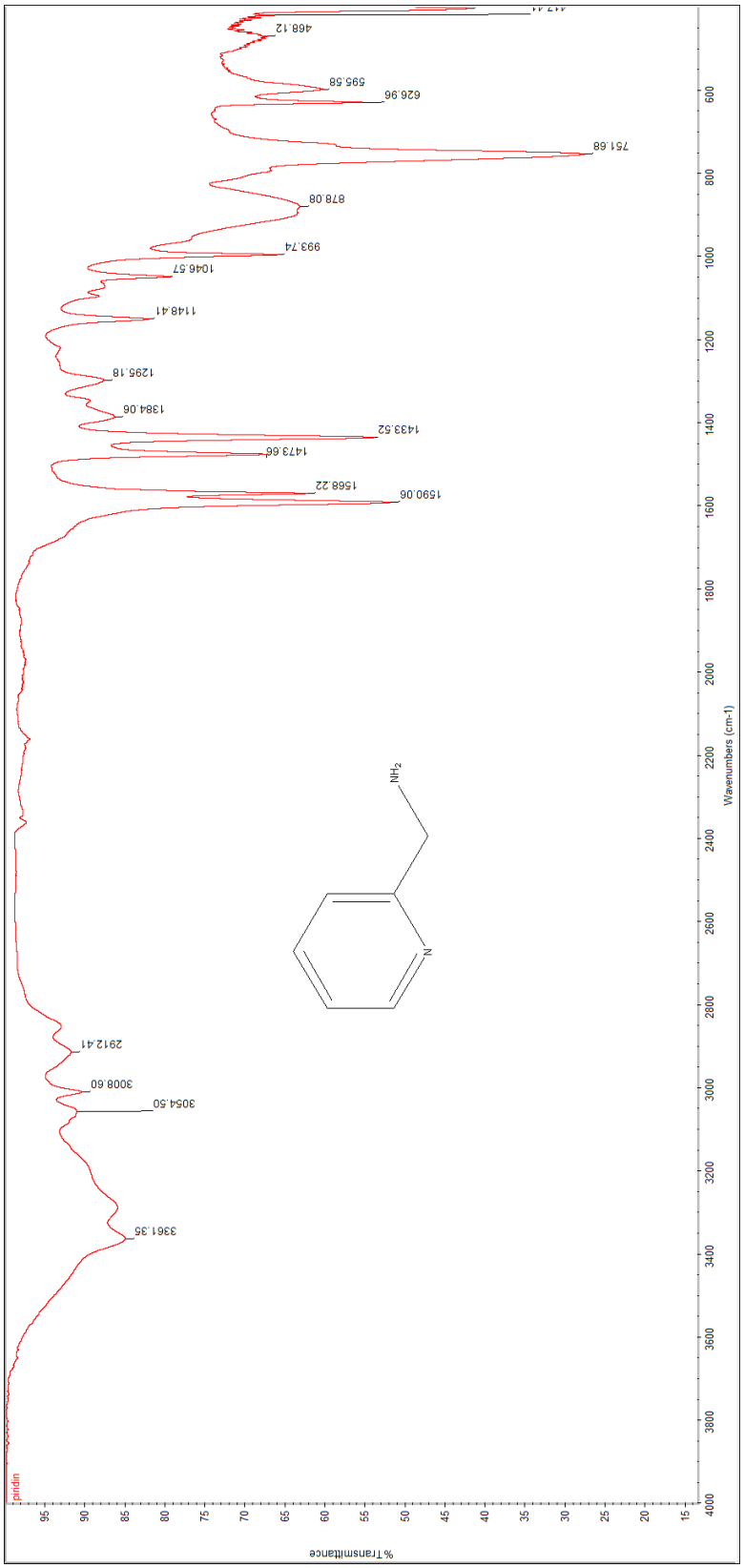

Figure Appendix A.3. AD.E. FTIR spectrum of pyridin-2-ylmethanamine

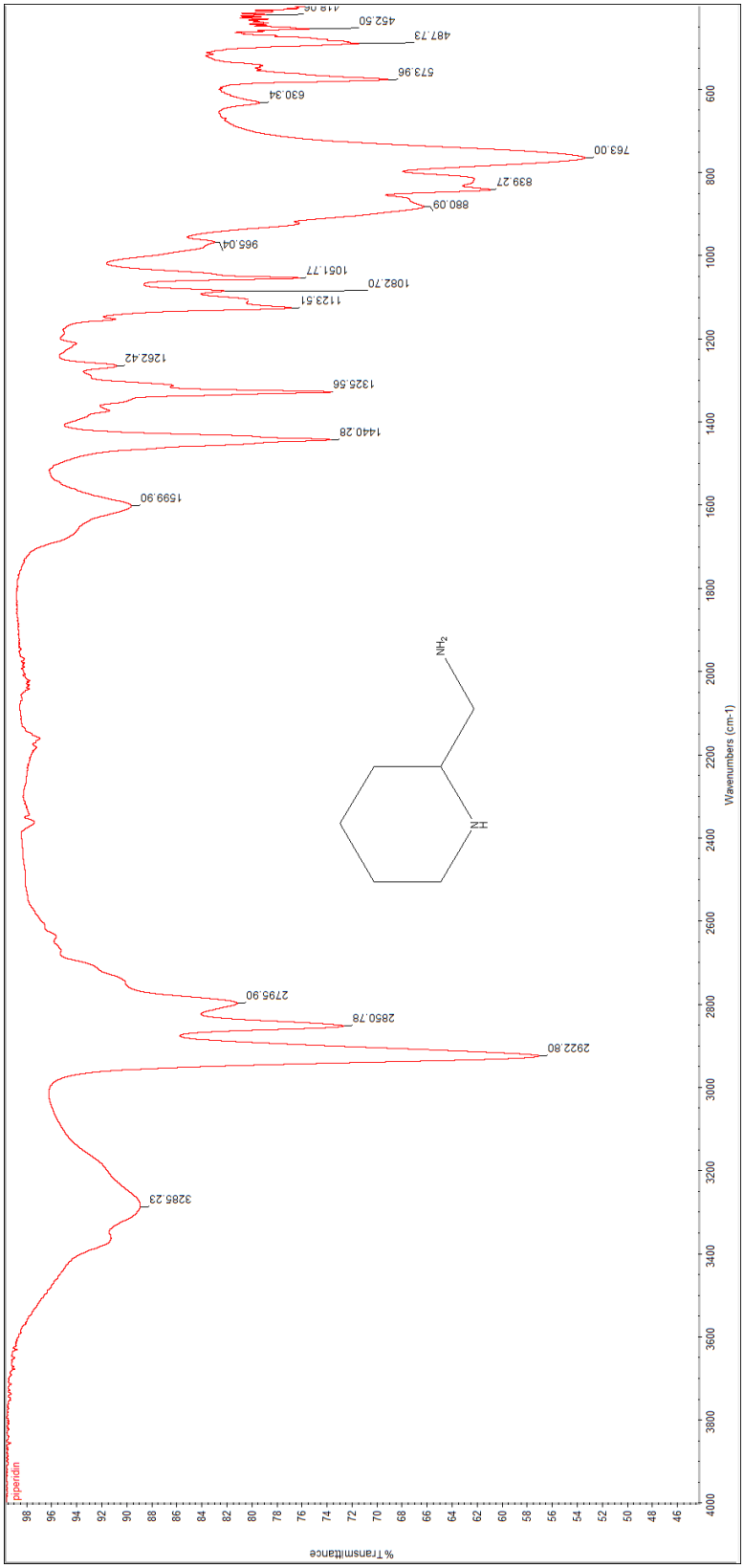

Figure Appendix A.4. AD.E. FTIR spectrum of piperidin-2-ylmethanamine.

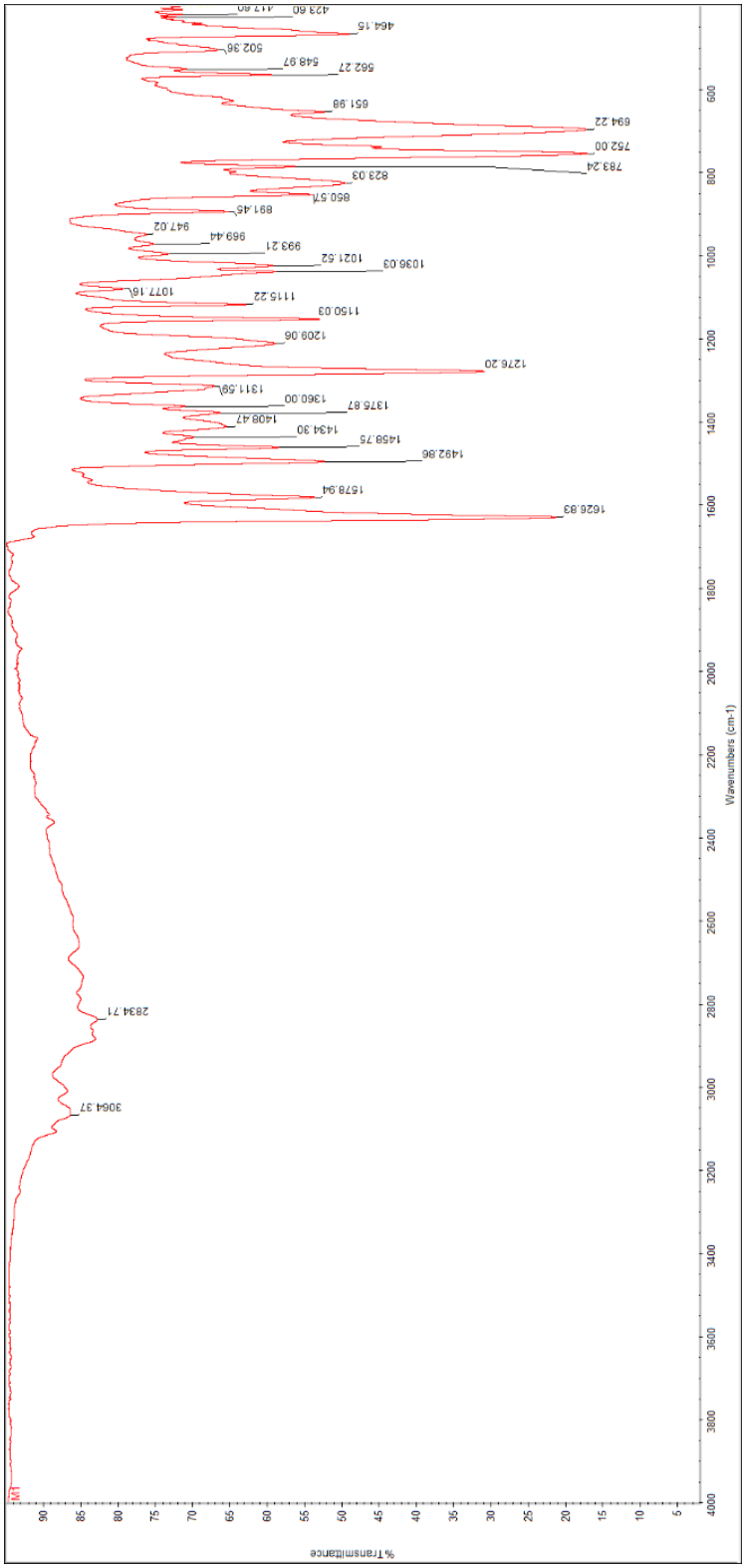

Figure Appendix A.5. AD.E. FTIR spectrum of (E)-2-(((thiophen-2-ylmethyl)imino)methyl)phenol

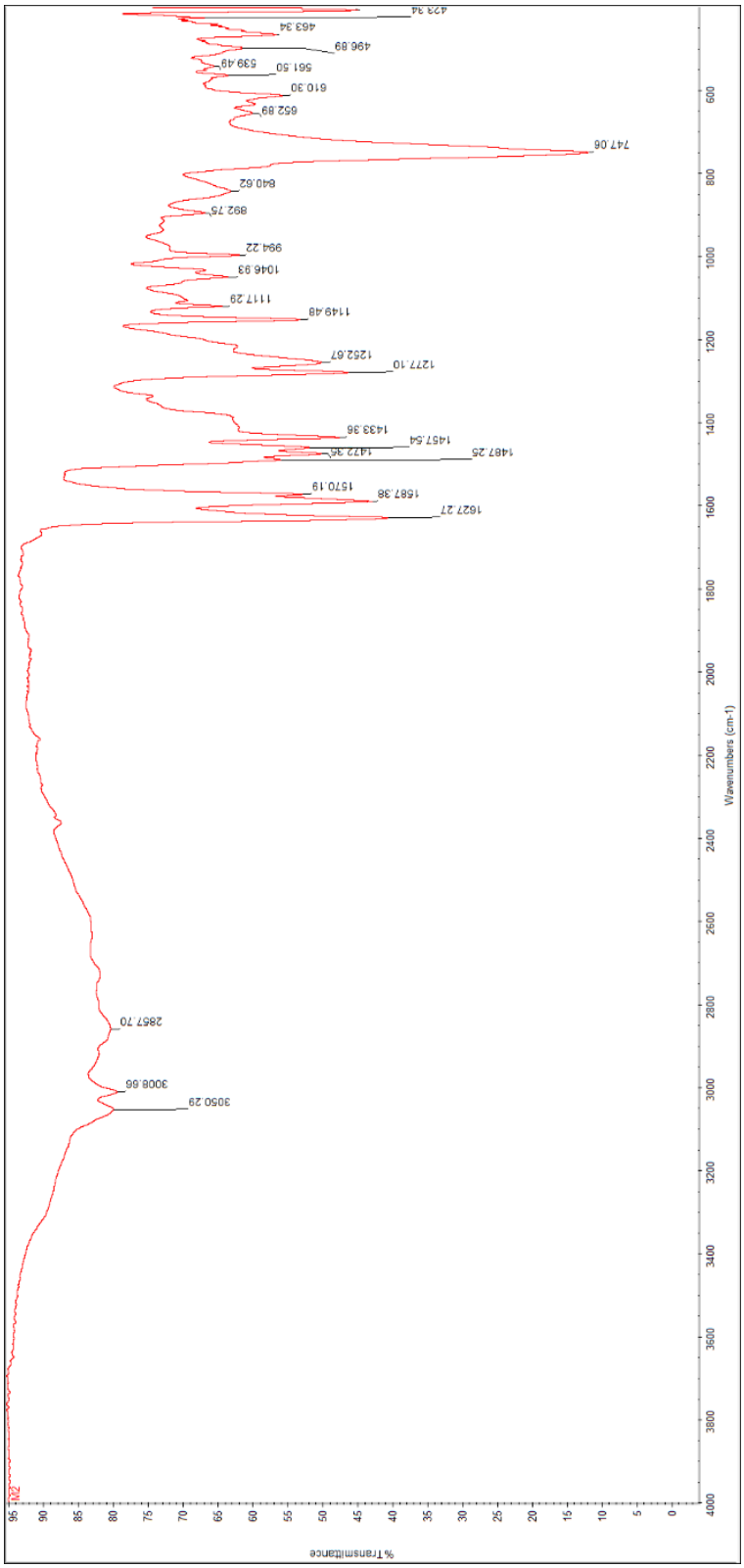

Figure Appendix A.6. (E)-2-(((pyridin-2-ylmethyl) imino)methyl)phenol

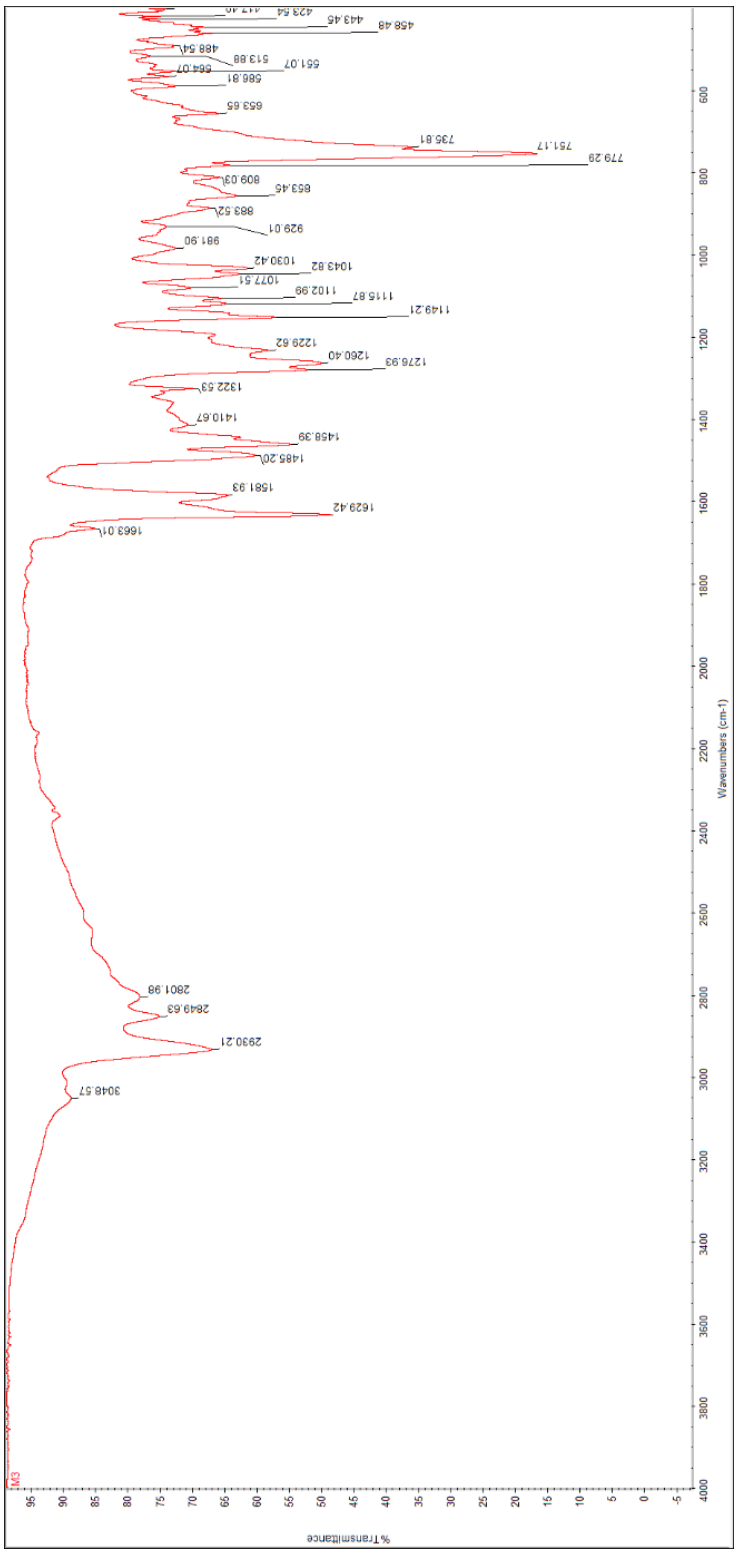

Figure Appendix A.7. AD.E. FTIR spectrum of (E)-2-(((piperidin-2-ylmethyl)imino)methyl)phenol

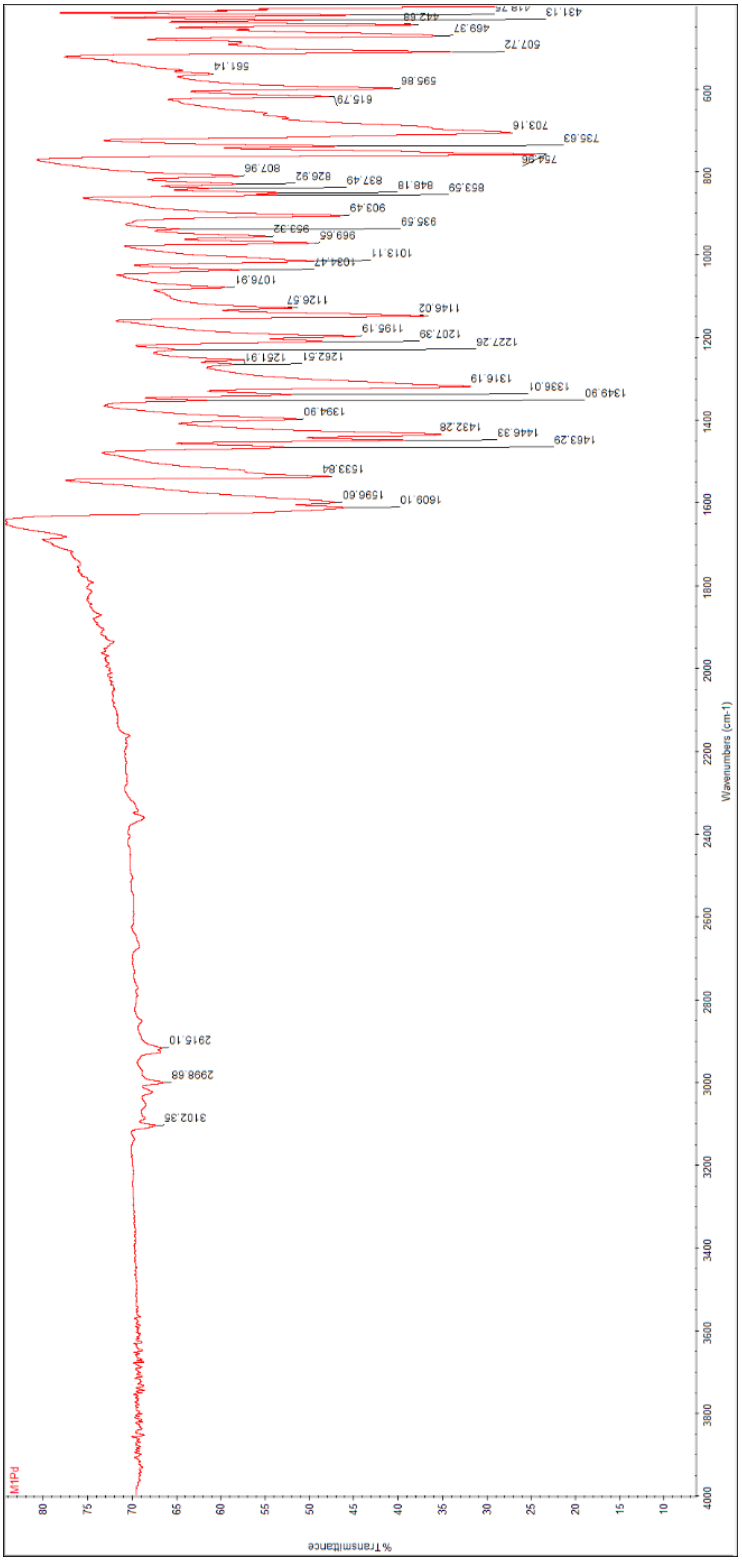

Figure Appendix A.8. AD.E. FTIR spectrum of C1

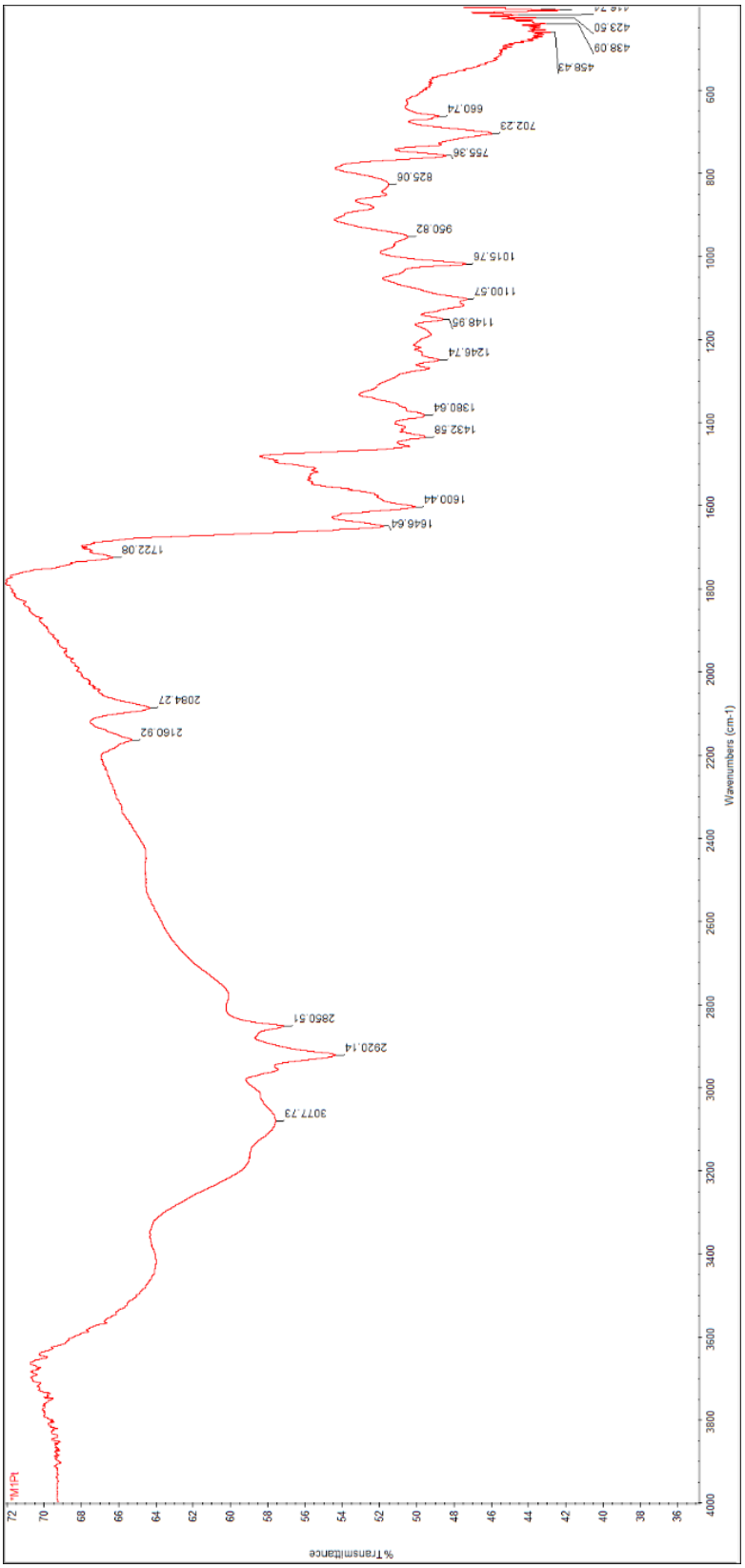

Figure Appendix A.9. AD.E. FTIR spectrum of C2

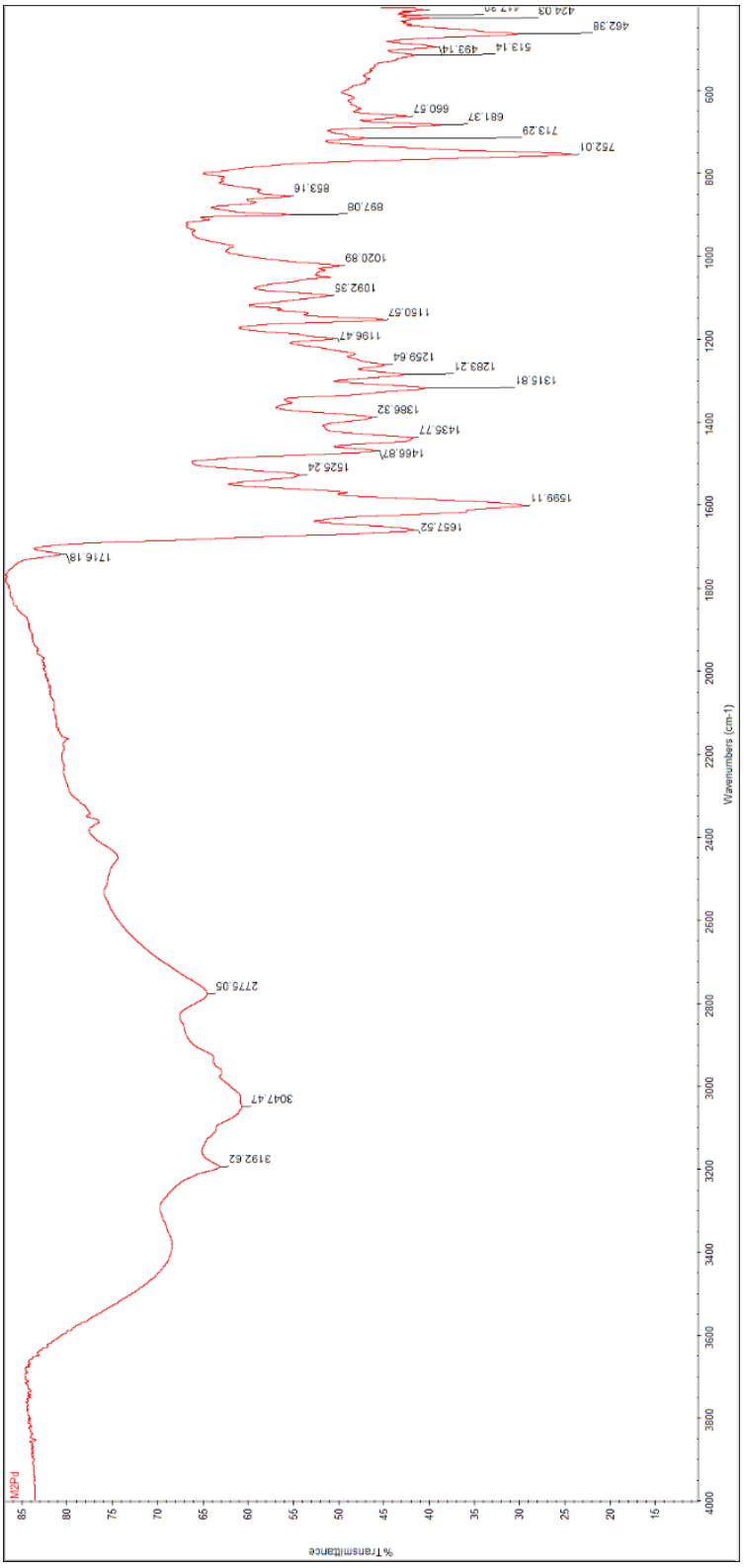

Figure Appendix A.10. AD.E. FTIR spectrum of C3

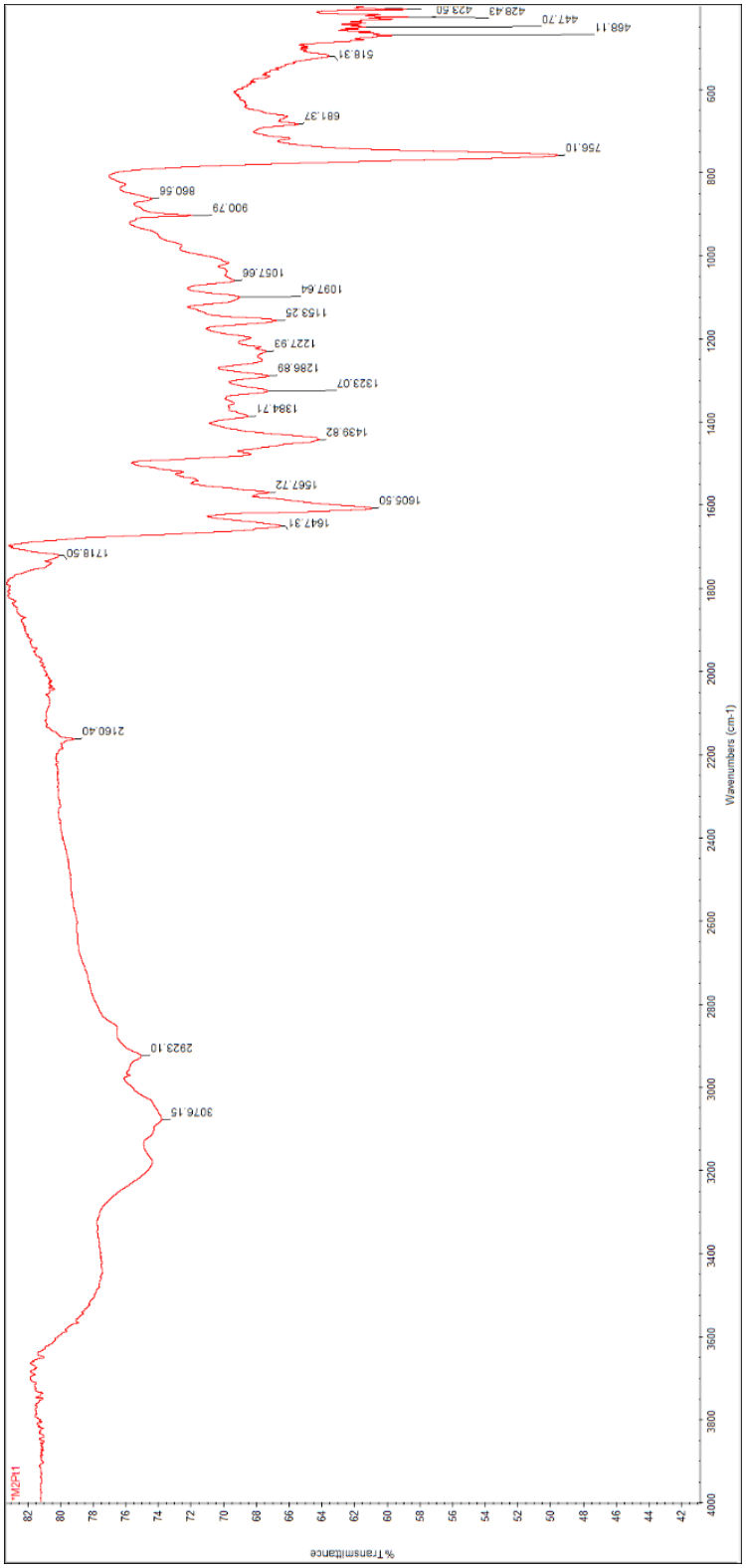

Figure Appendix A.11. AD.E. FTIR spectrum of C4

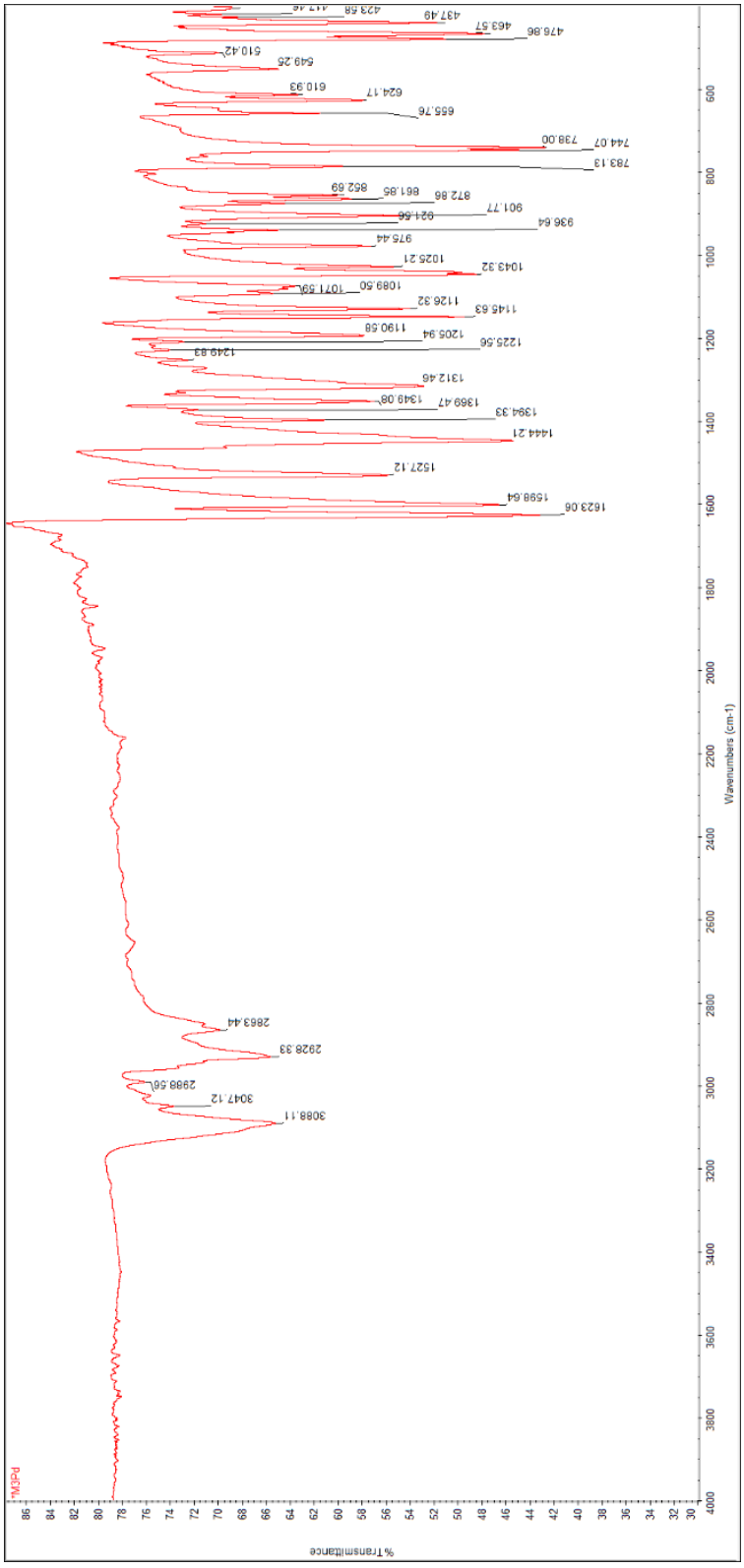

Figure Appendix A.12. AD.E. FTIR spectrum of C5

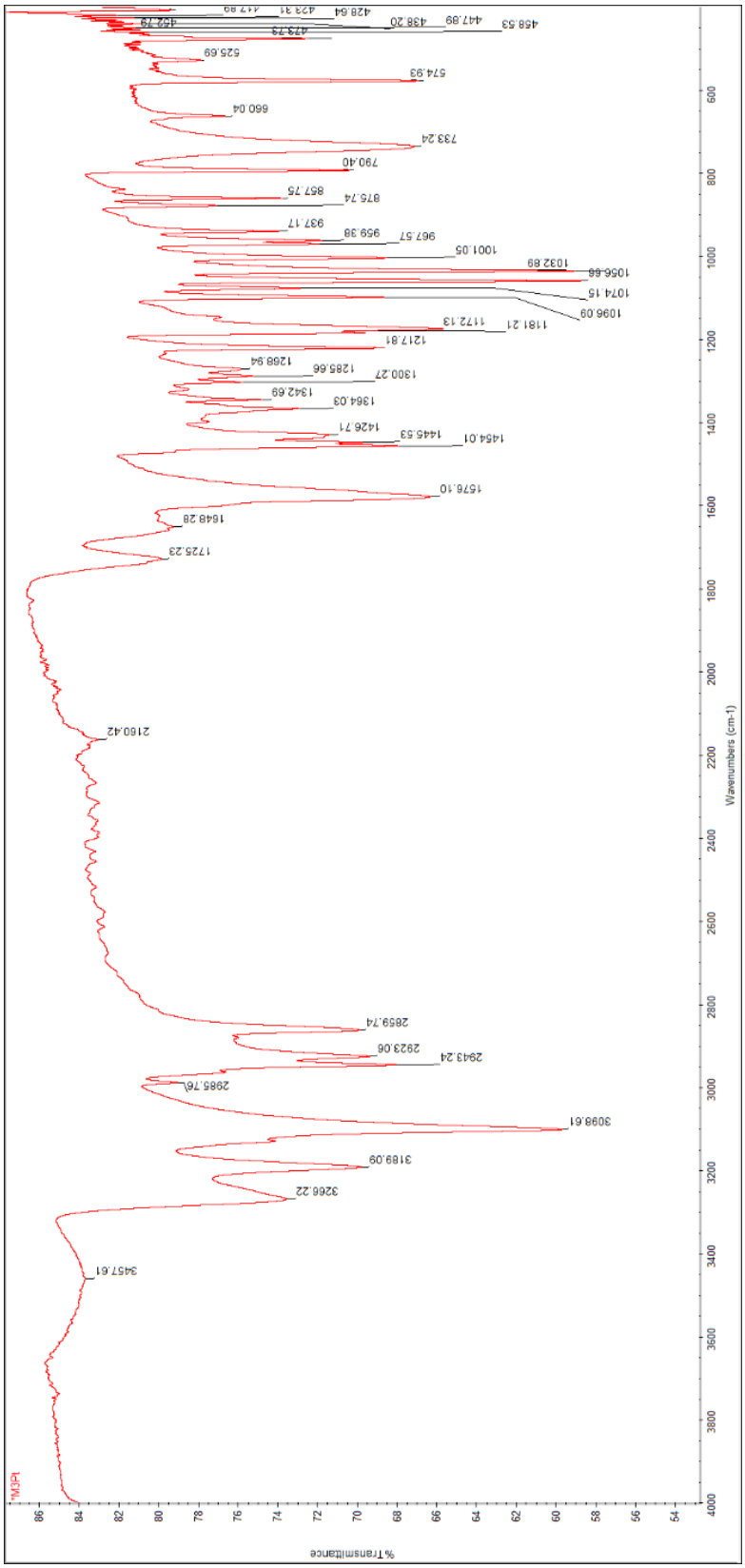

Figure Appendix A.13. AD.E. FTIR spectrum of C6

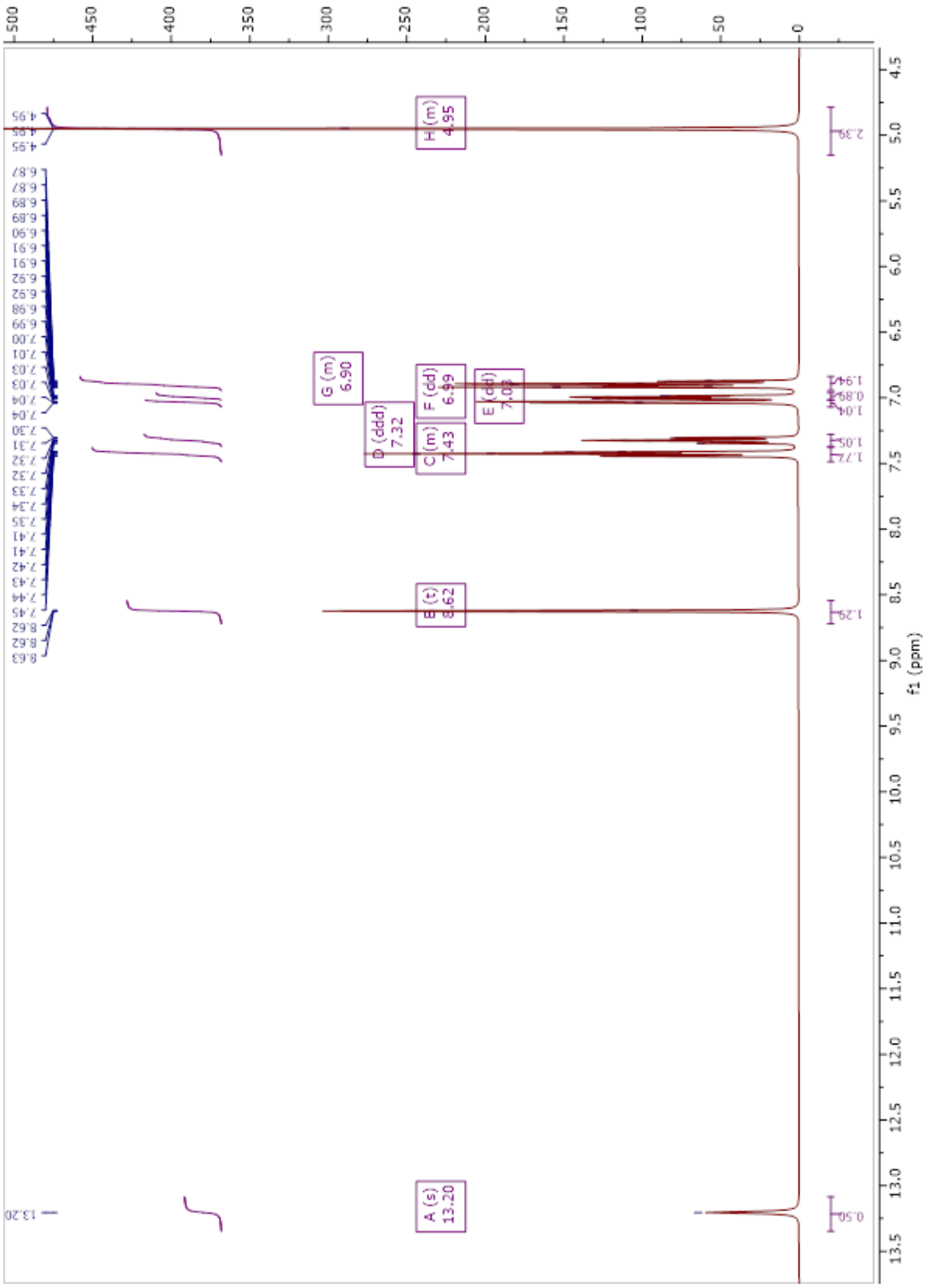

Figure Appendix A.14. The 1H NMR spectrum of ligand L1

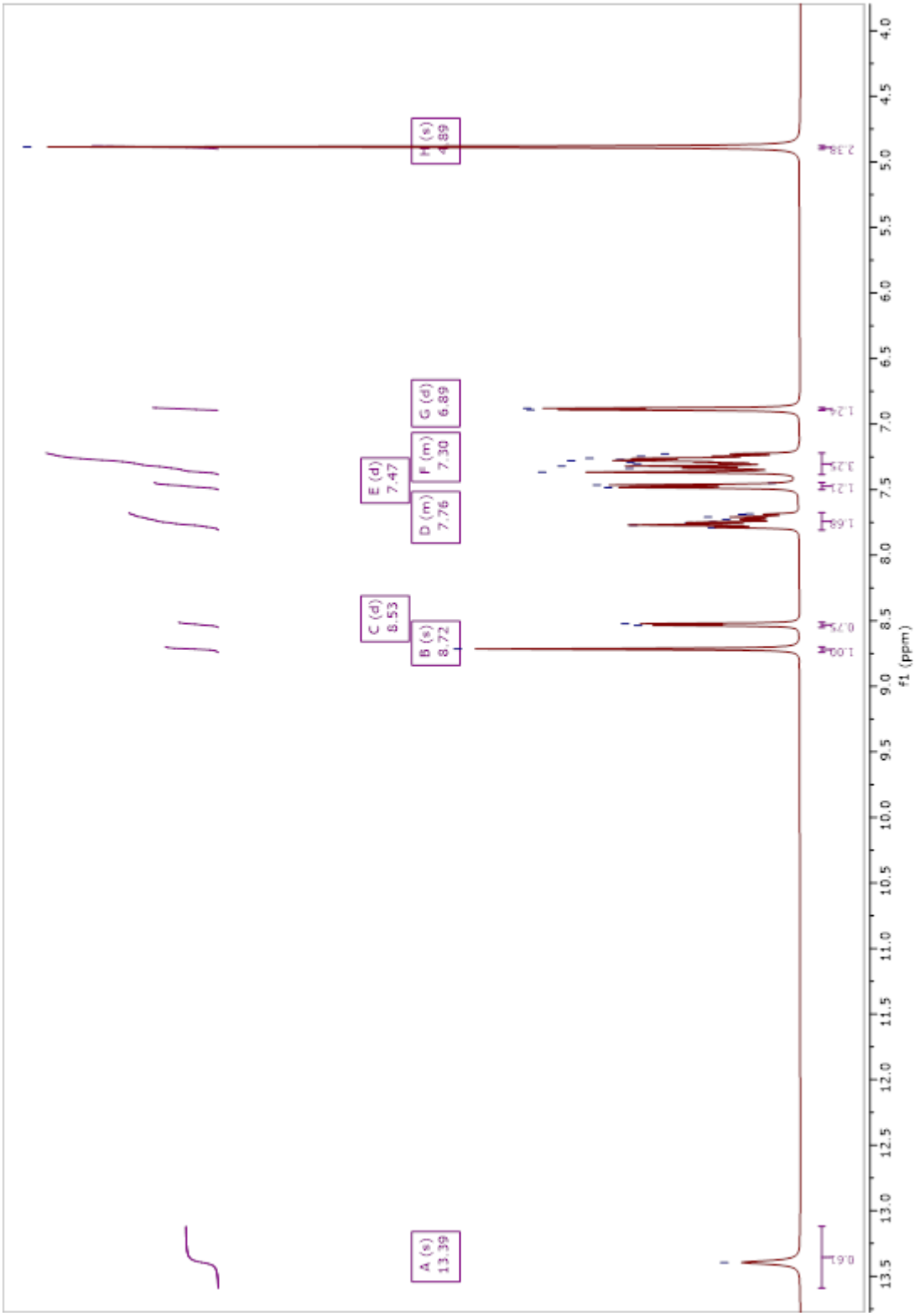

Figure Appendix A.15. AD.E. The 1H NMR spectrum of ligand L2

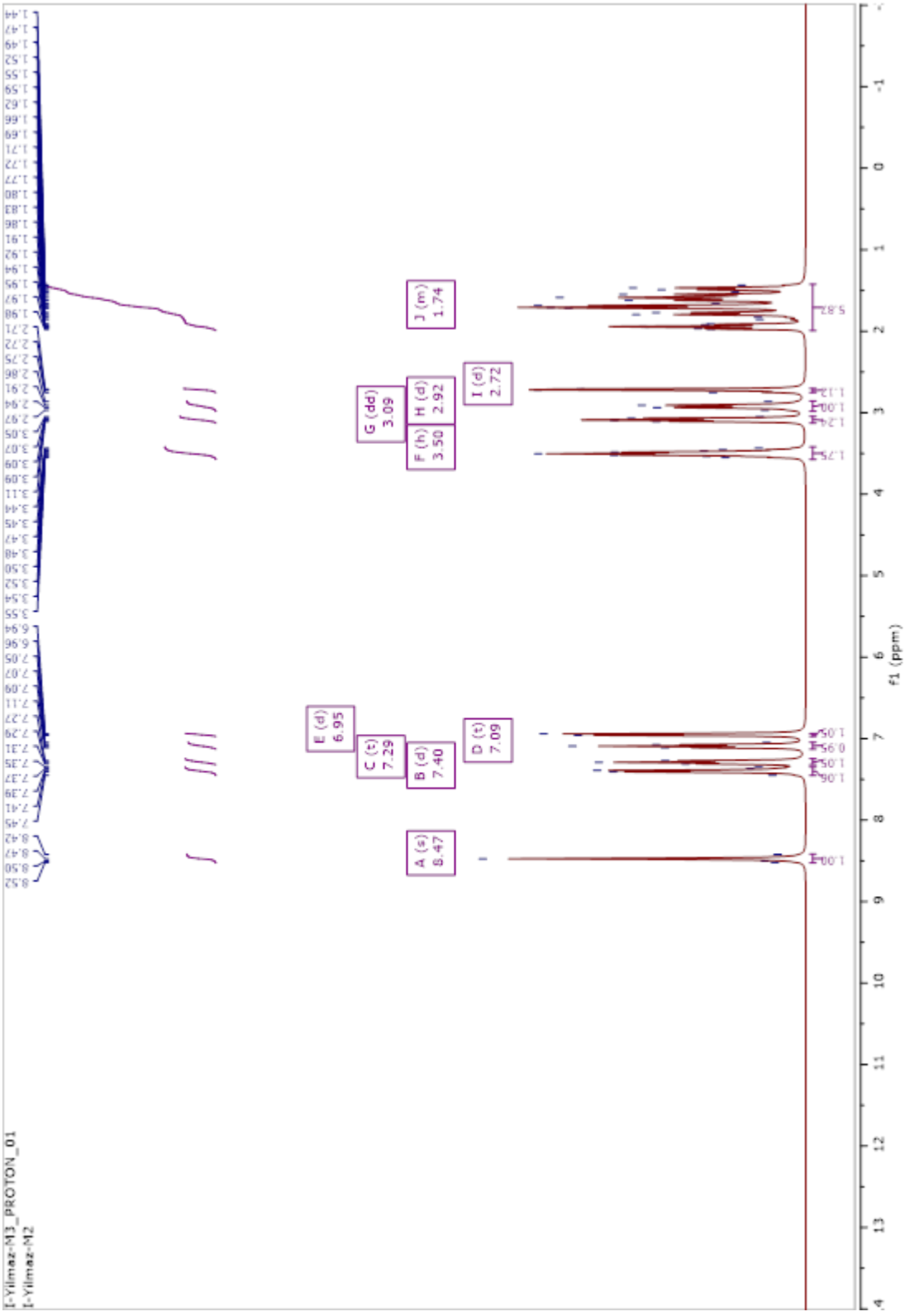

Figure Appendix A.16. AD.E. The 1H NMR spectrum of ligand L3

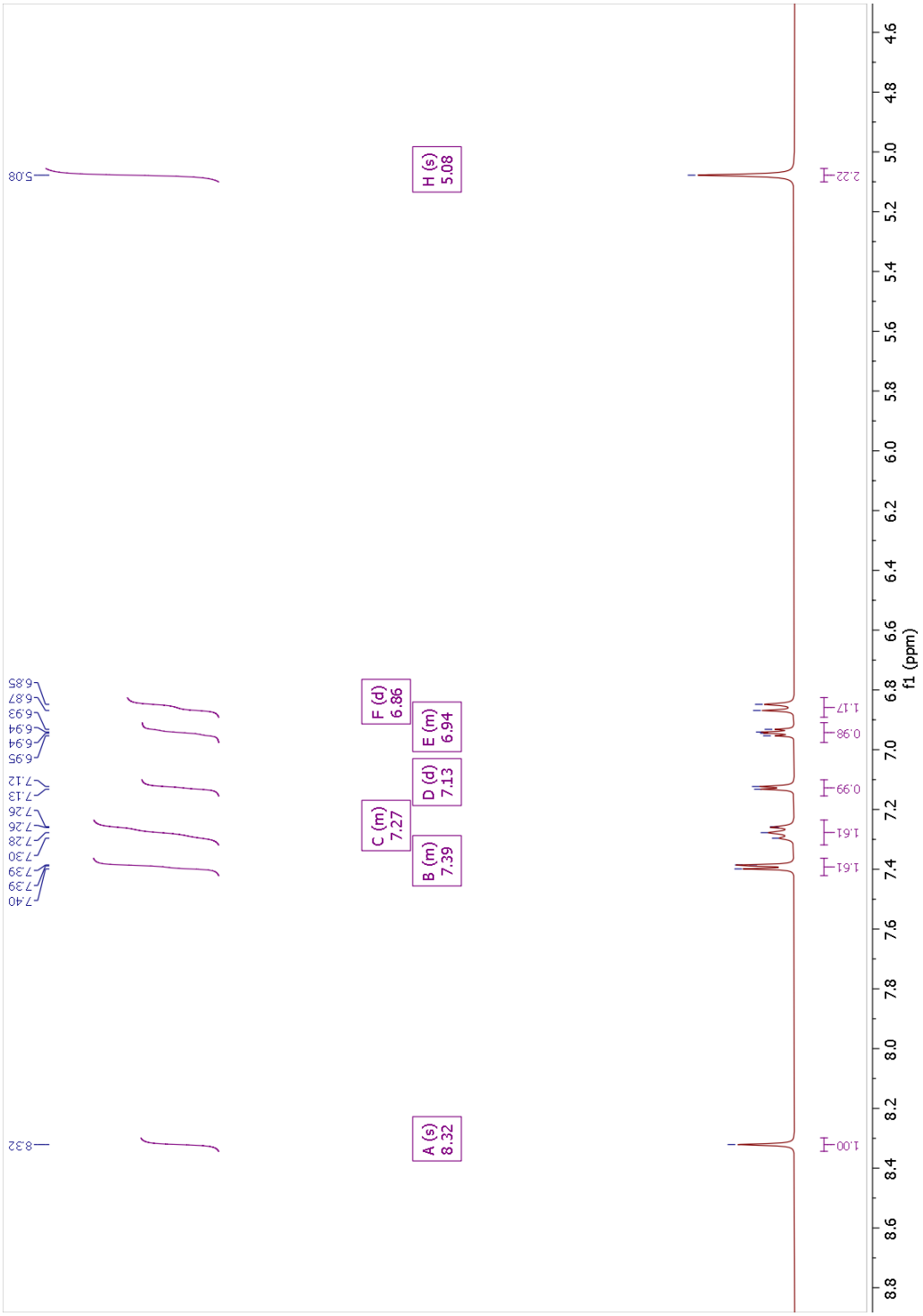

Figure Appendix A.17. AD.E. The 1H NMR spectrum of complex C1

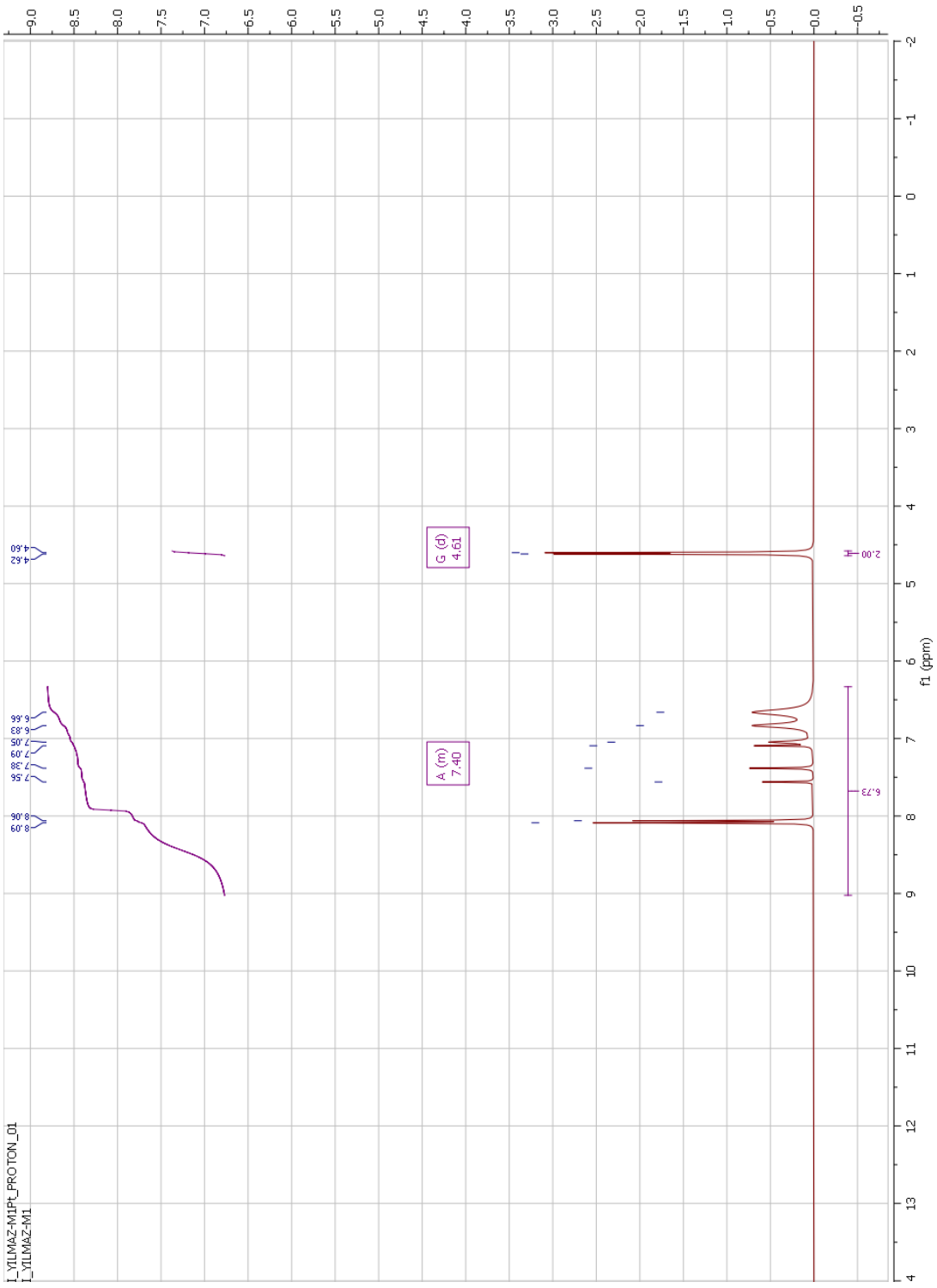

Figure Appendix A.18. AD.E. The 1H NMR spectrum of complex C2

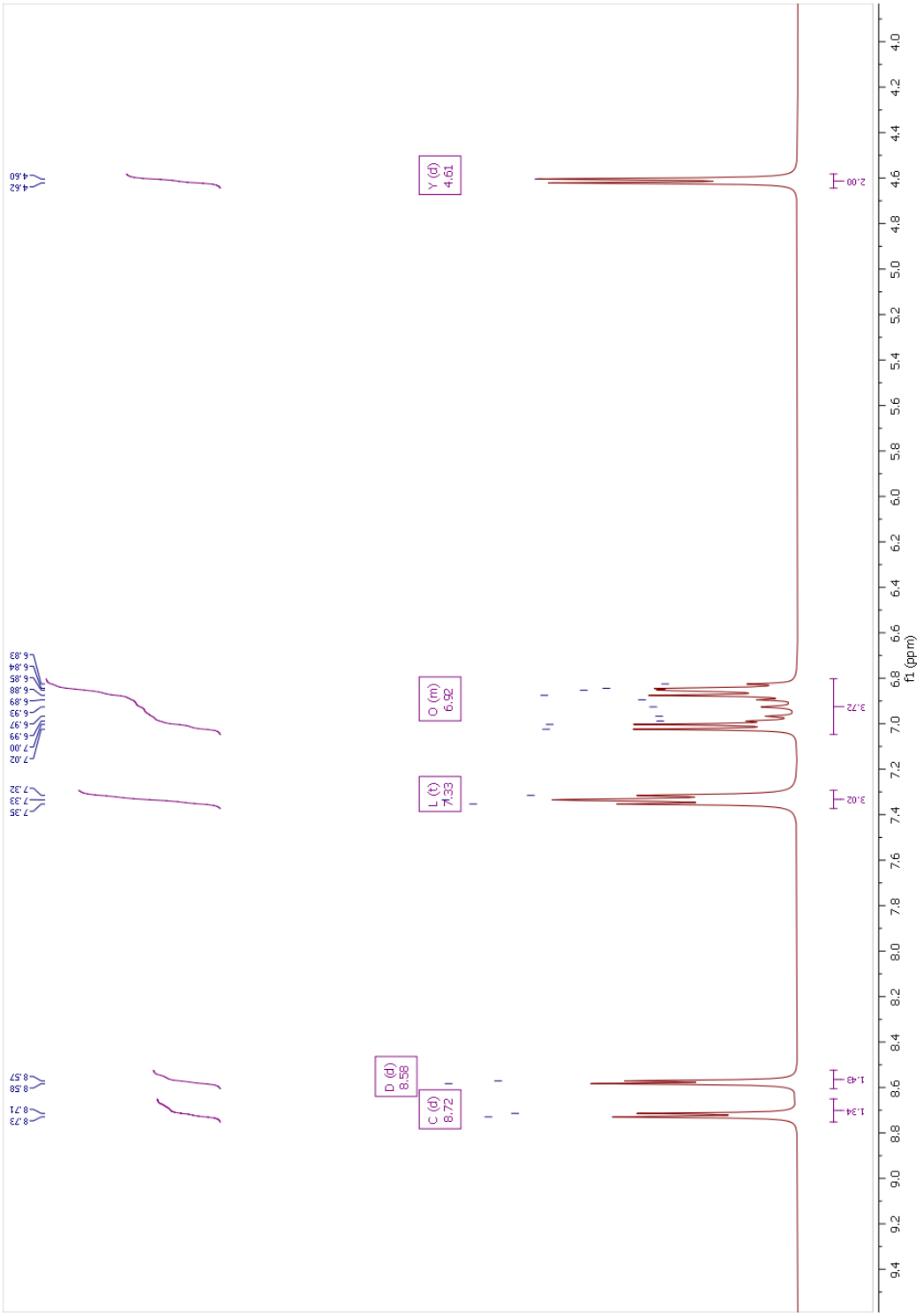

Figure Appendix A.19. AD.E. The 1H NMR spectrum of complex C3

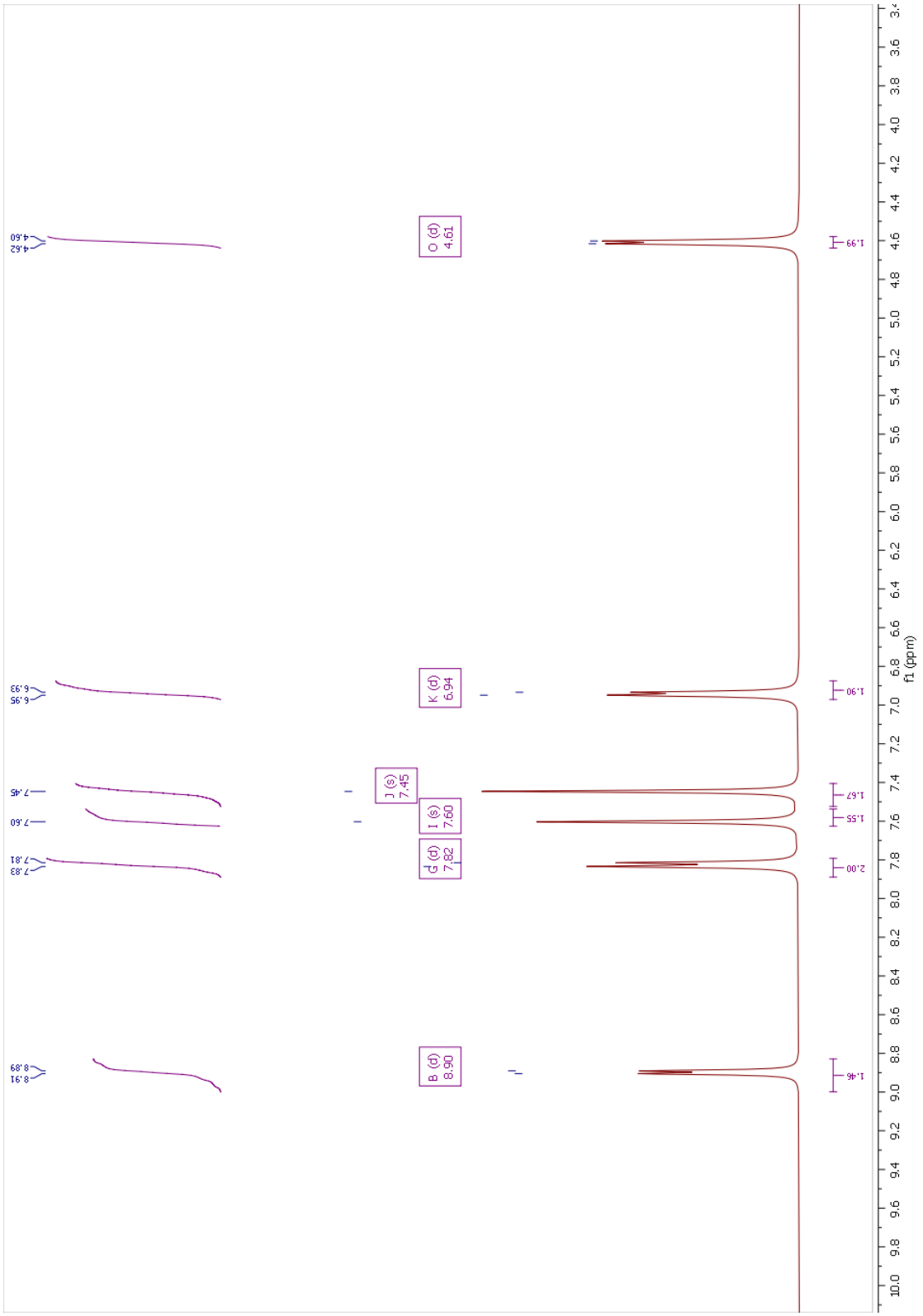

Figure Appendix A.20. AD.E. The 1H NMR spectrum of complex C4.

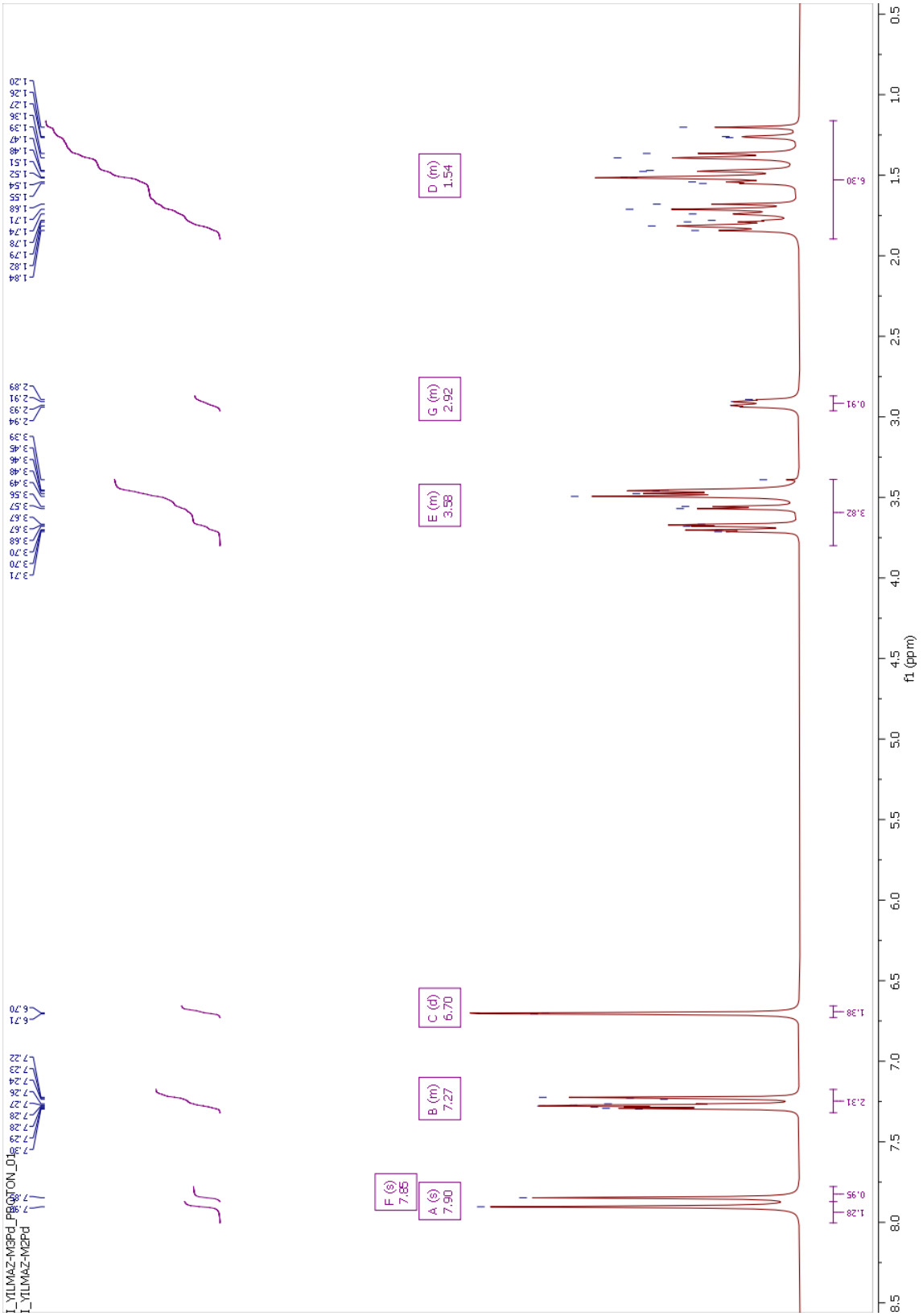

Figure Appendix A.21. AD.E. The 1H NMR spectrum of complex C5

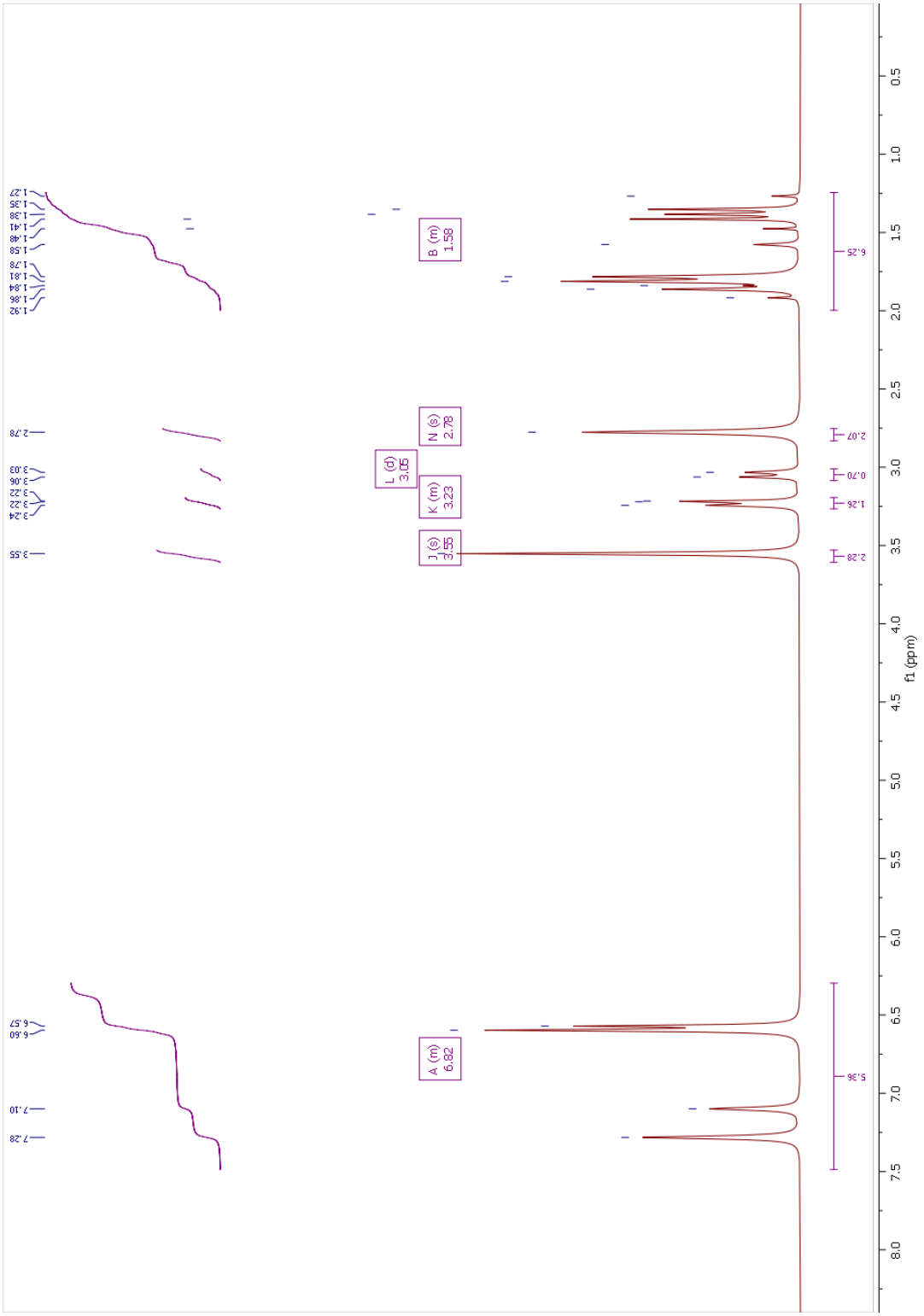

Figure Appendix A.22. AD.E. The 1H NMR spectrum of complex C6

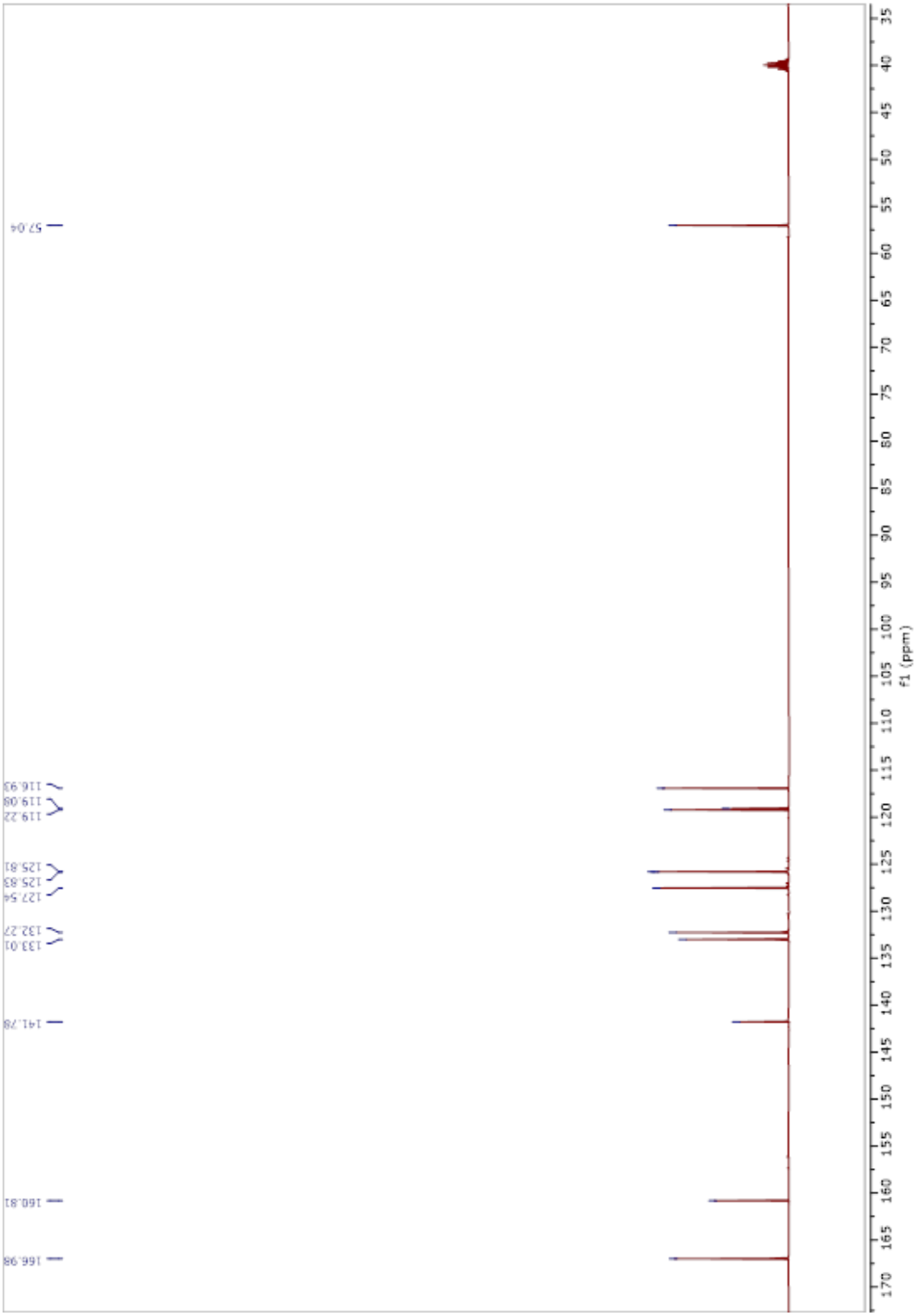

Figure Appendix A.23. AD.E. The 13C NMR spectrum of ligand L1

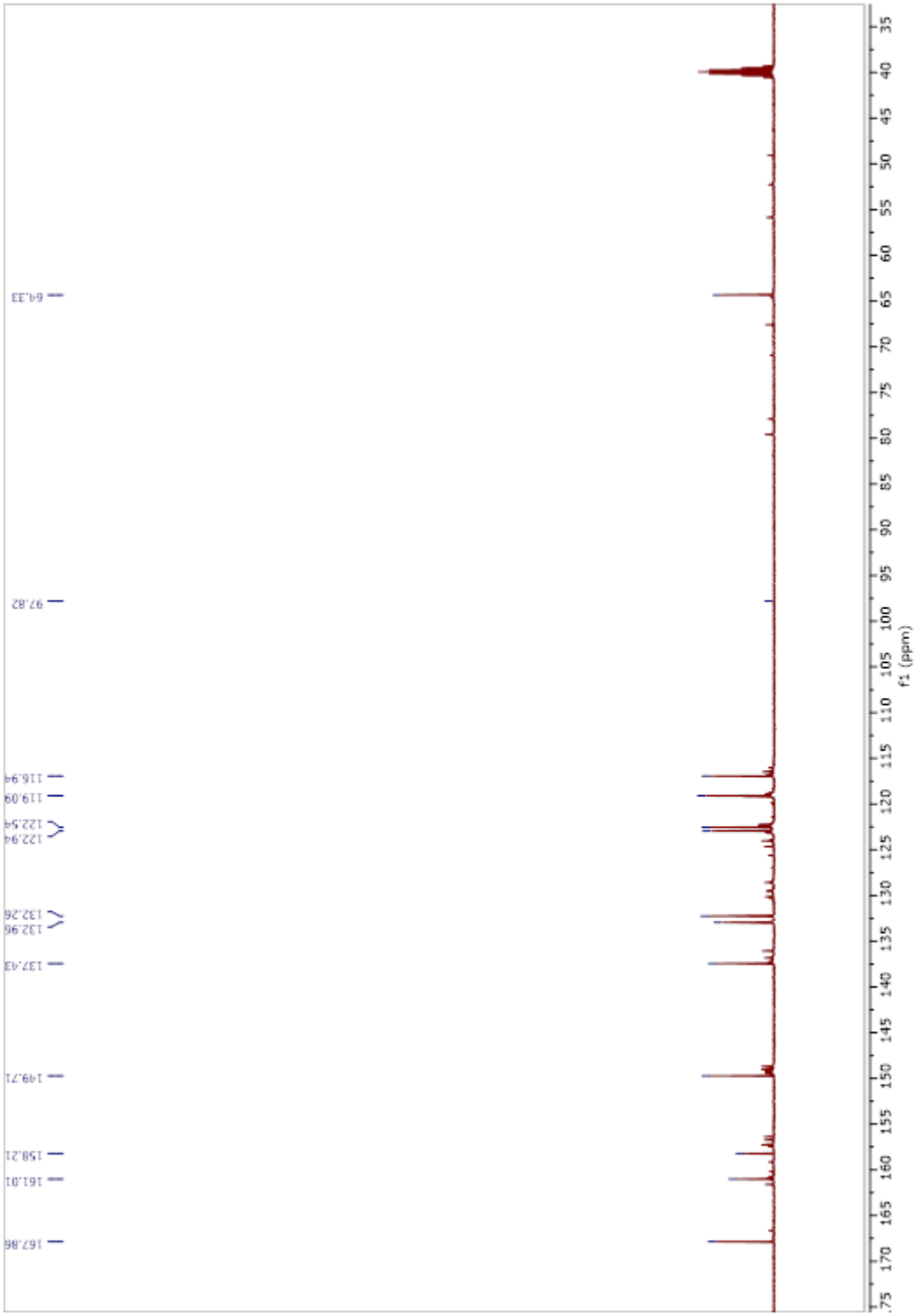

Figure Appendix A.24. AD.E. The 13C NMR spectrum of ligand L2

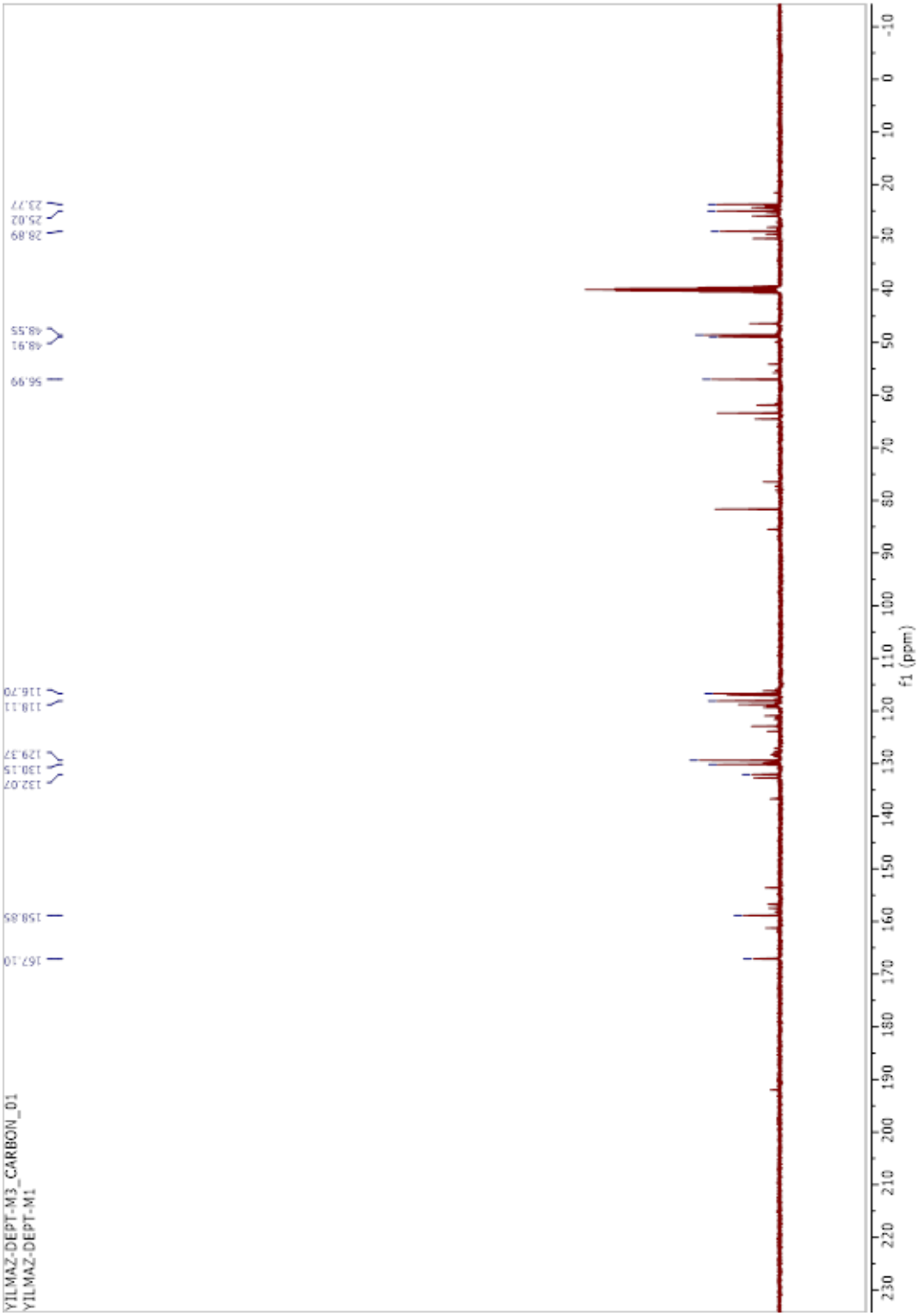

Figure Appendix A.25. AD.E. The 13C NMR spectrum of ligand L3

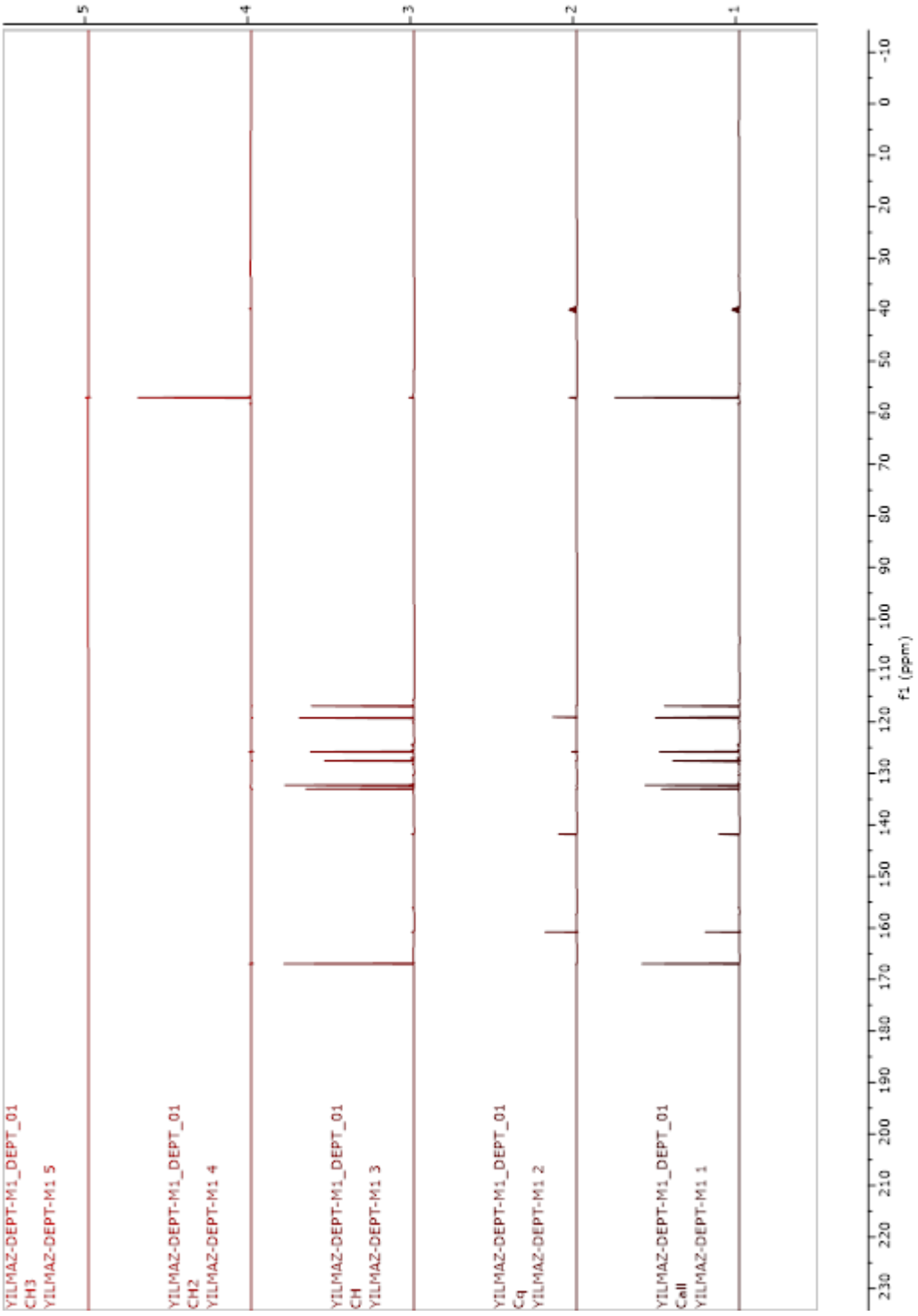

Figure Appendix A.26. AD.E. The 13C NMR DEPT spectrum of ligand L1

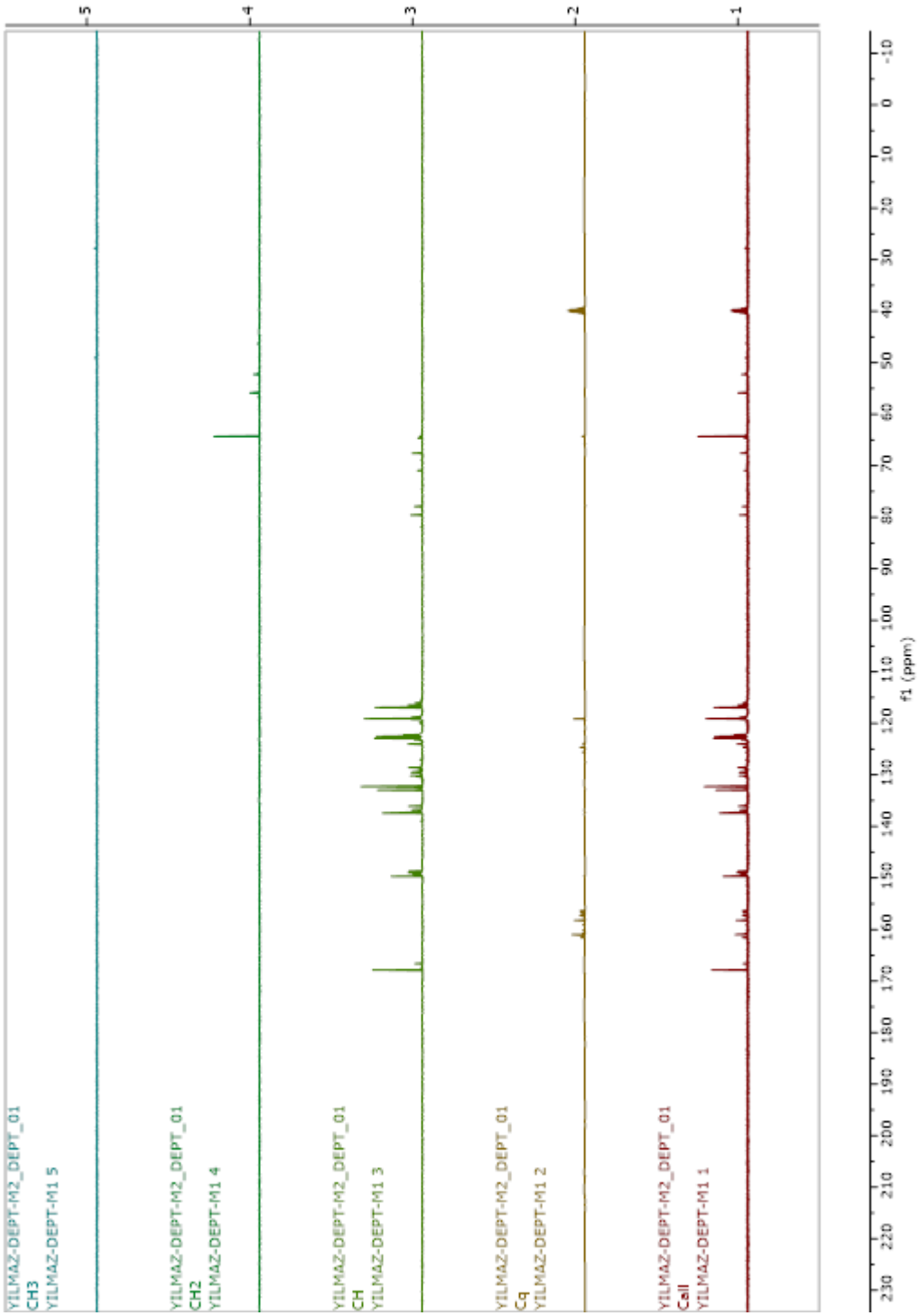

Figure Appendix A.27. AD.E. The 13C NMR DEPT spectrum of ligand L2

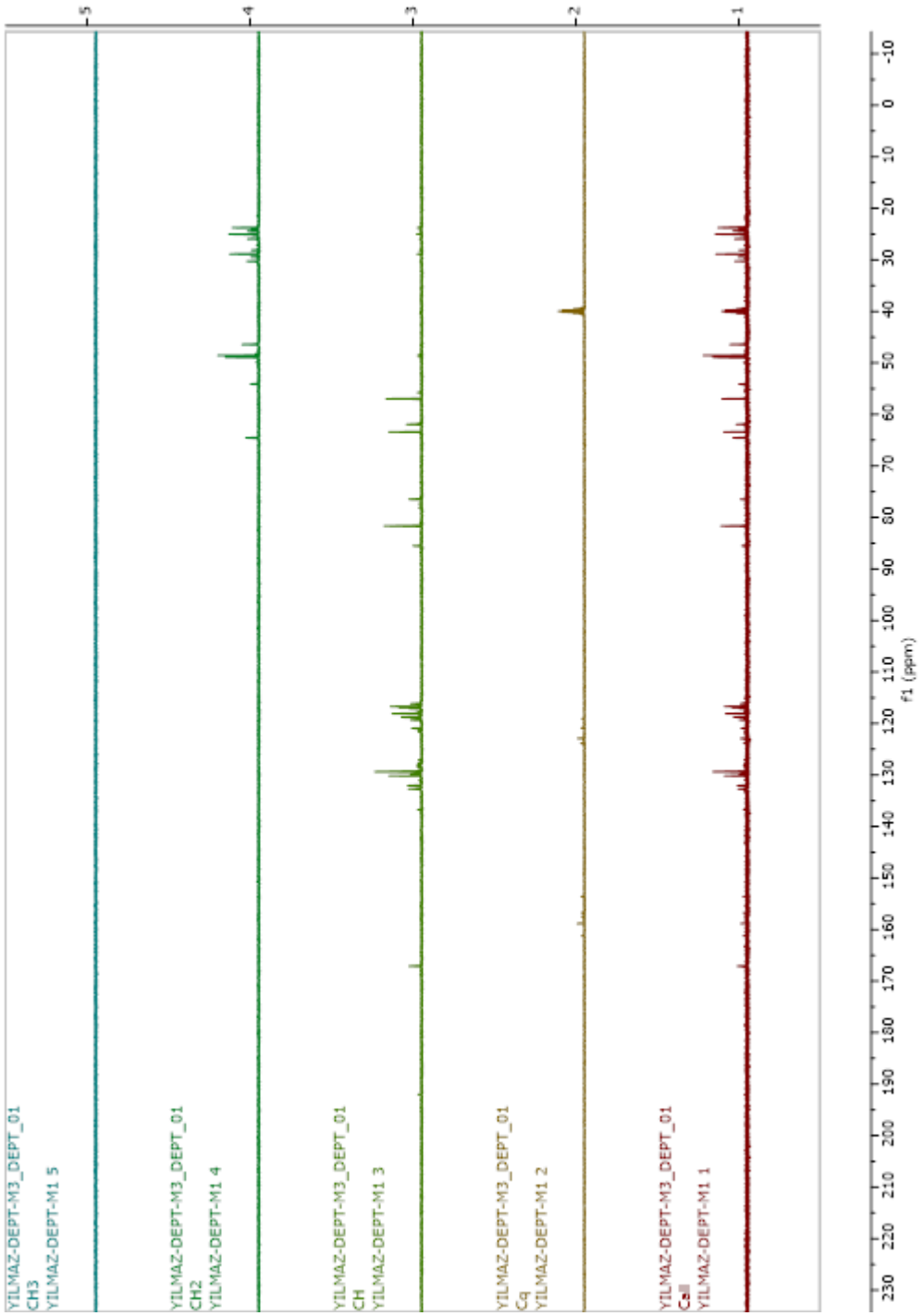

Figure Appendix A.28. AD.E. The 13C NMR DEPT spectrum of ligand L3

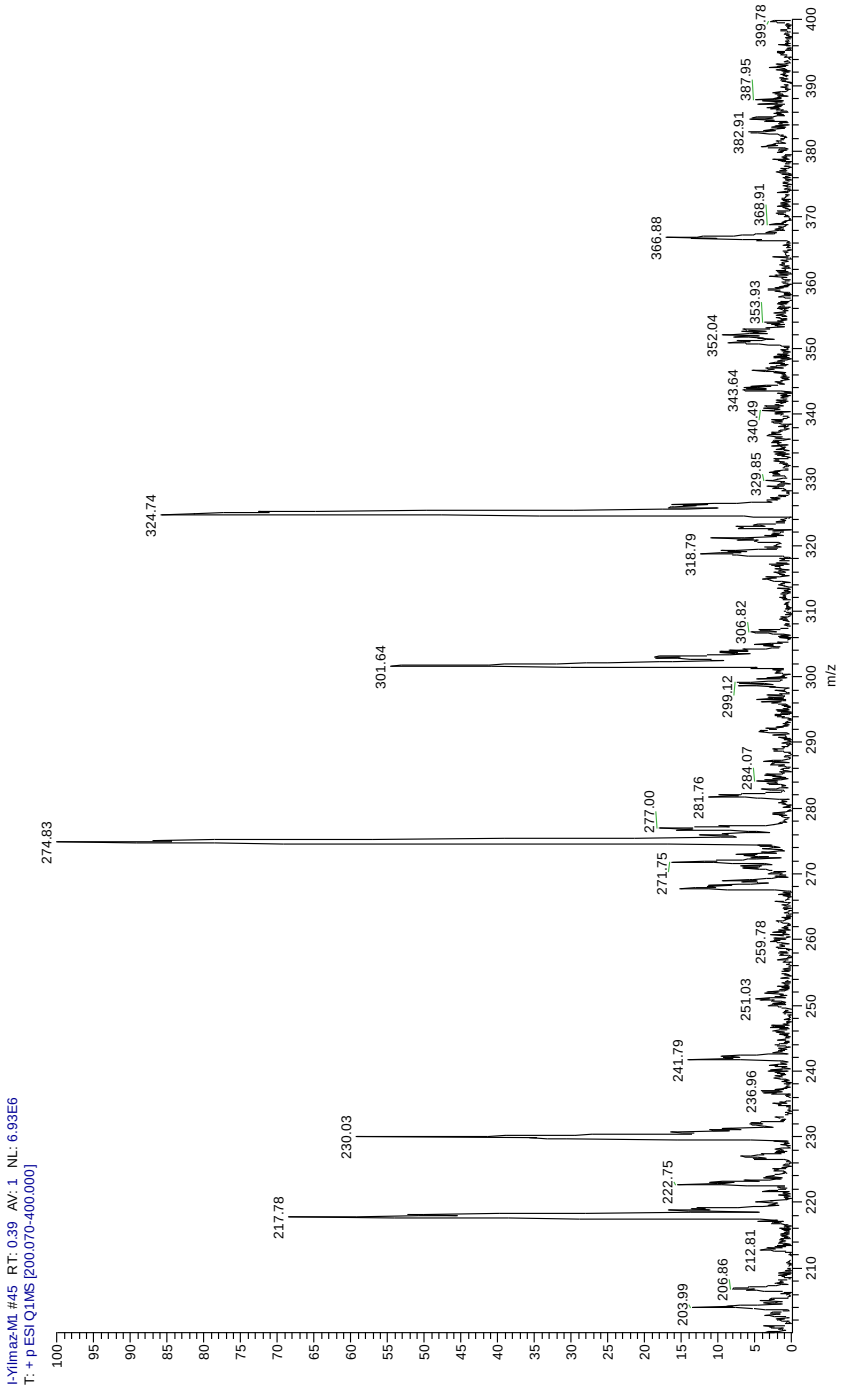

Figure Appendix A.29. AD.E. Mass spectrum of ligand L1

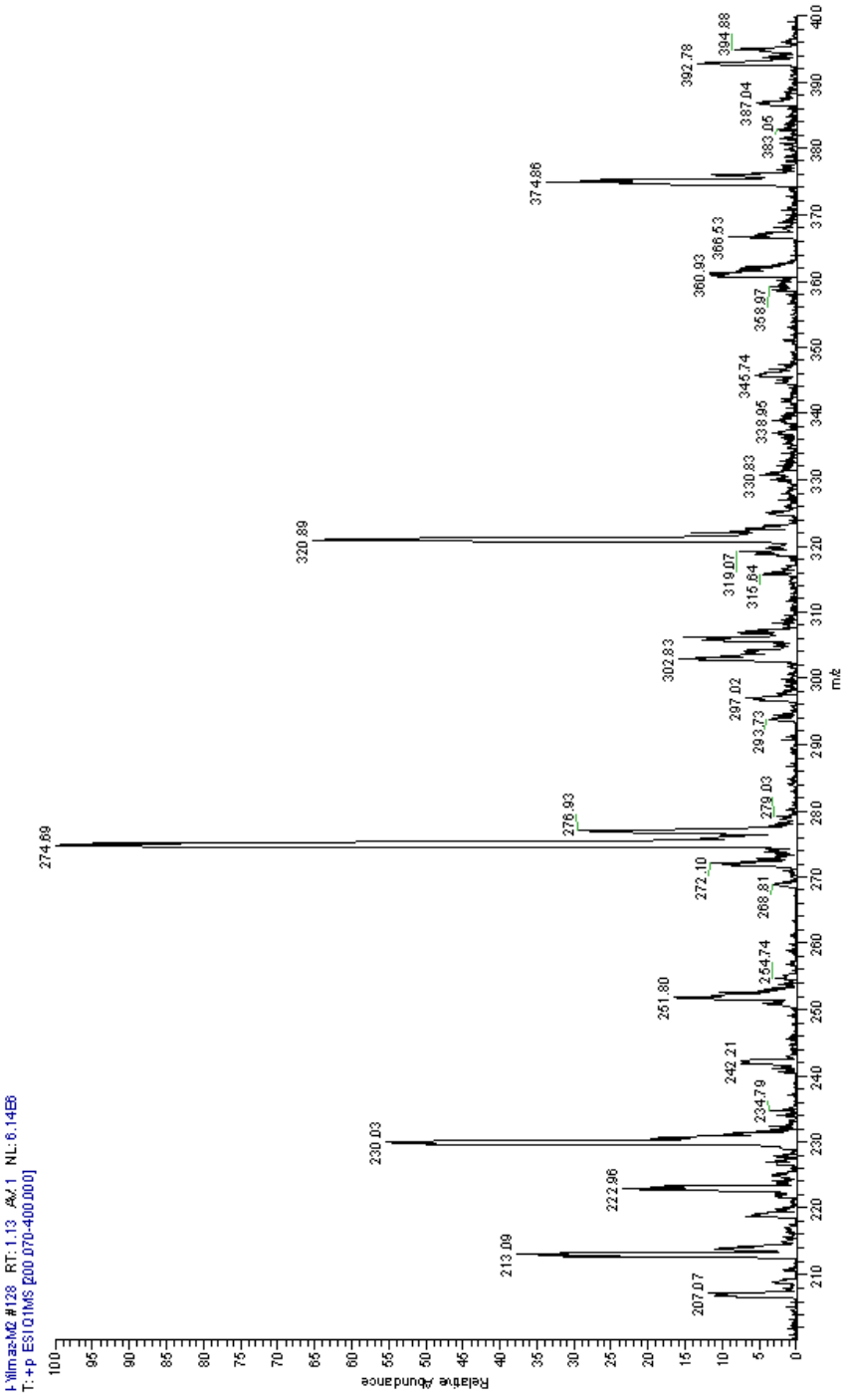

Figure Appendix A.30. AD.E. Mass spectrum of ligand L2

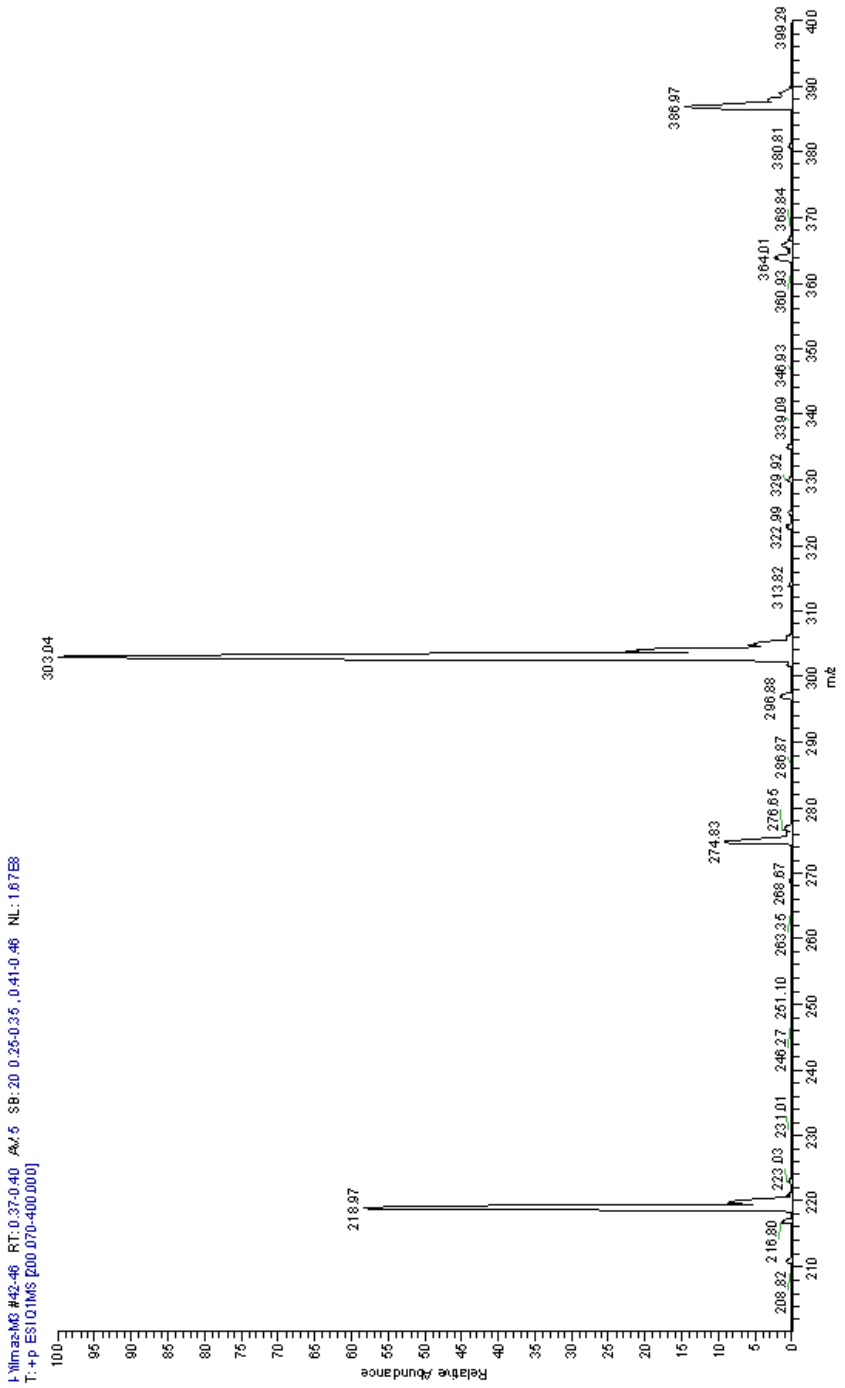

Figure Appendix A.31. AD.E. Mass spectrum of ligand L3

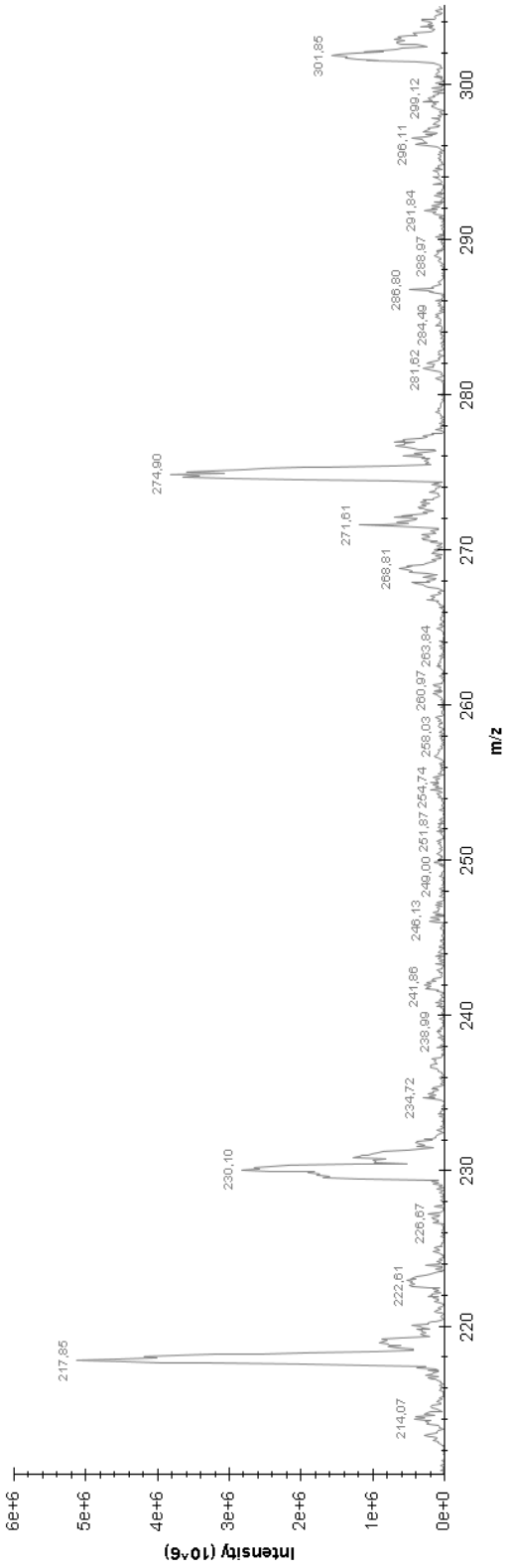

Figure Appendix A.32. AD.E. MALDI-TOF MS spectrum of ligand L1

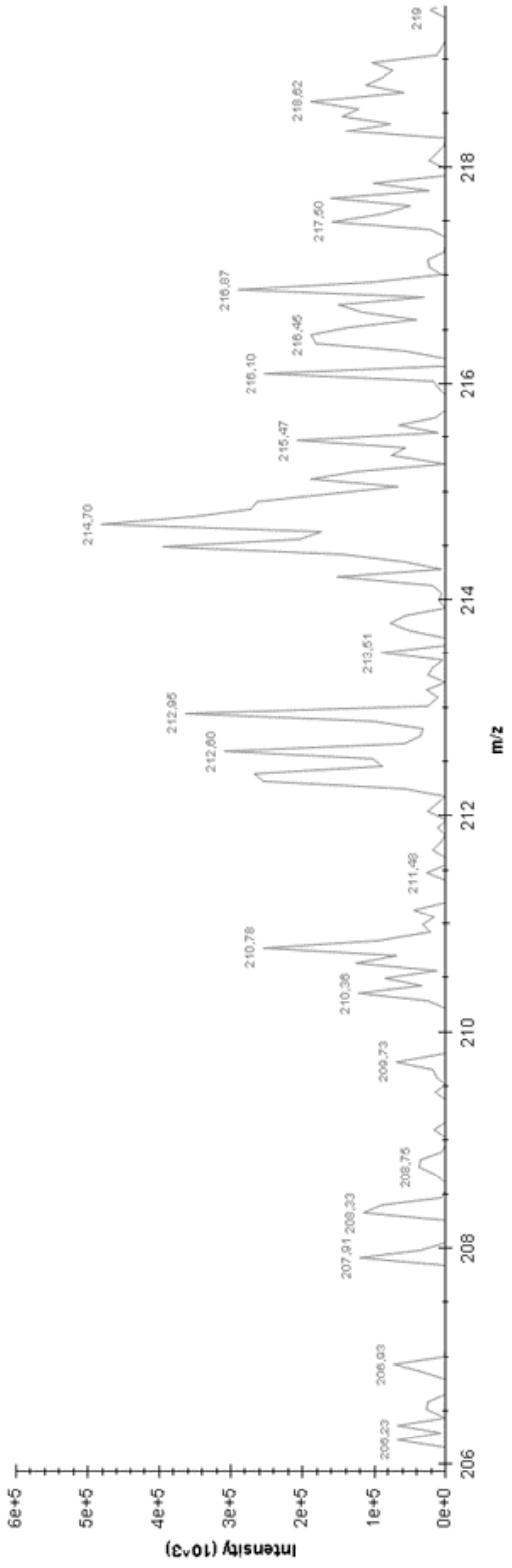

Figure Appendix A.33. AD.E. MALDI-TOF MS spectrum of ligand L2

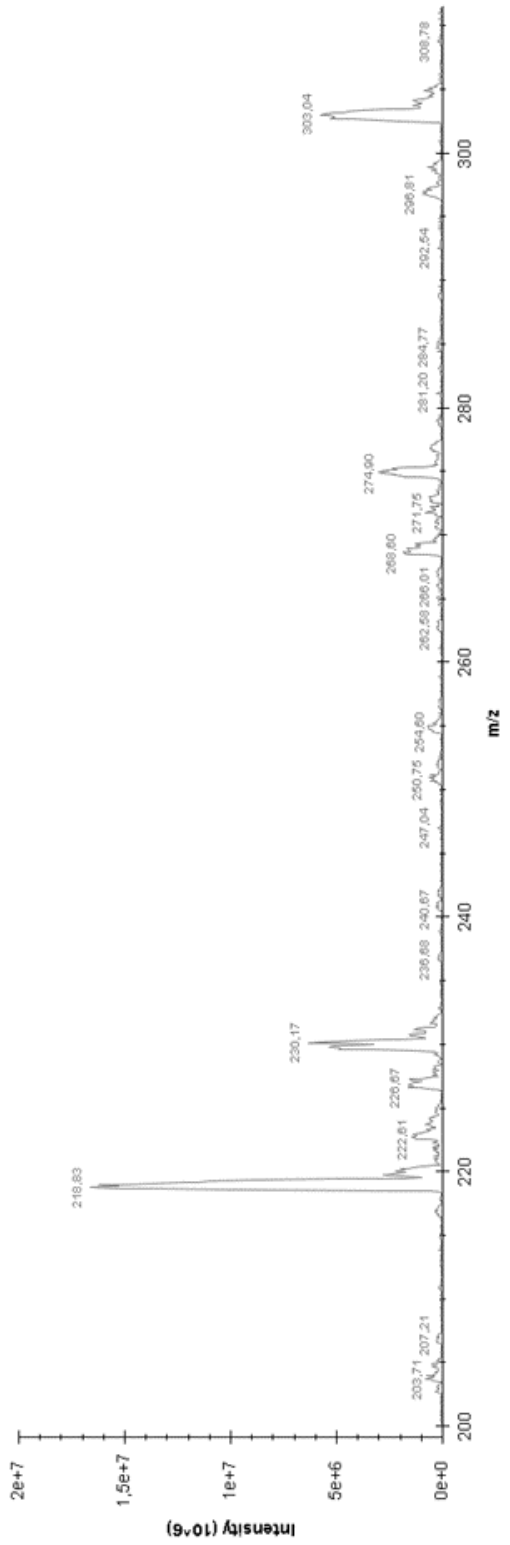

Figure Appendix A.34. AD.E. MALDI-TOF MS spectrum of ligand L3

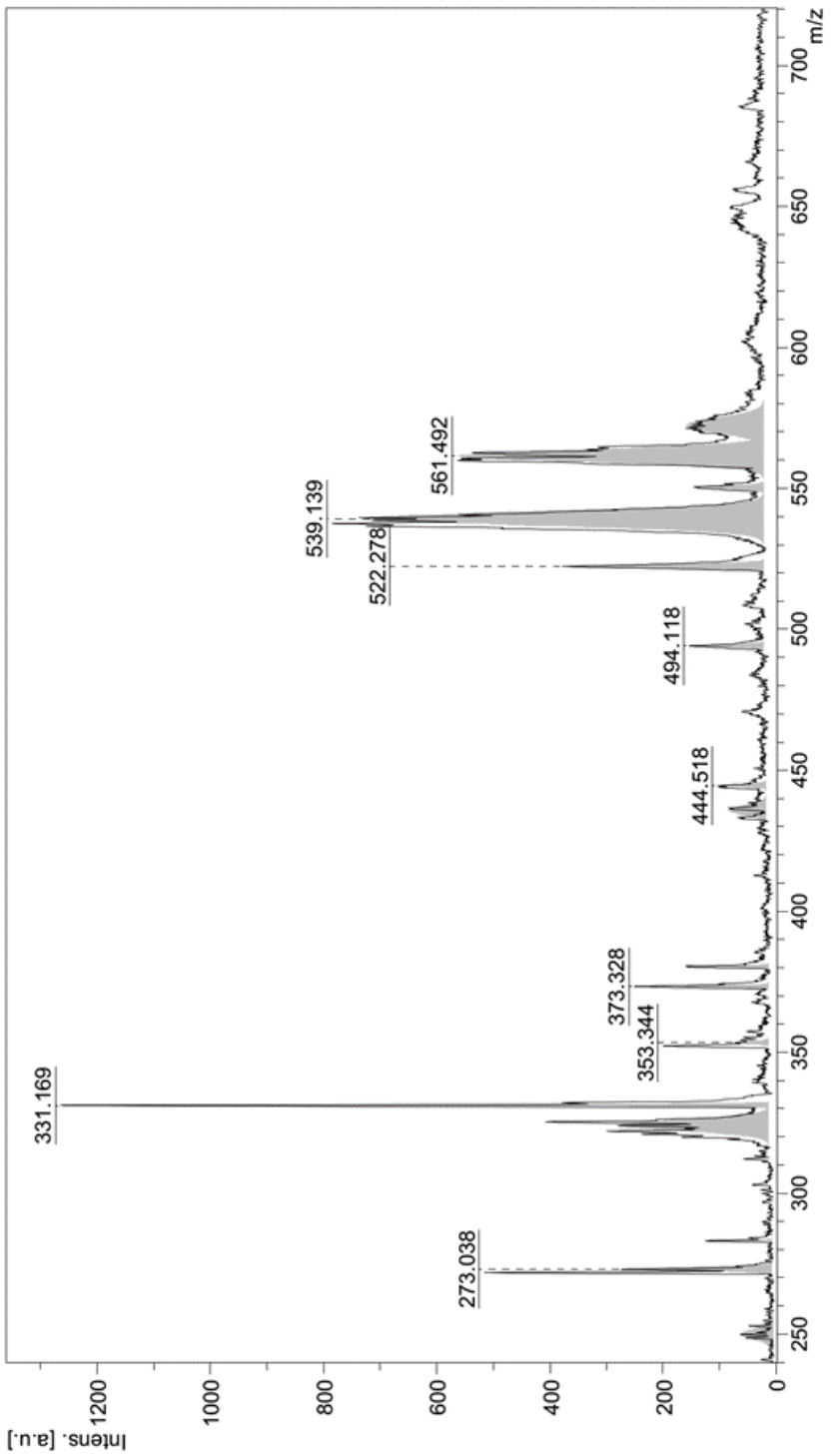

Figure Appendix A.35. AD.E. MALDI-TOF MS spectrum of complex C1

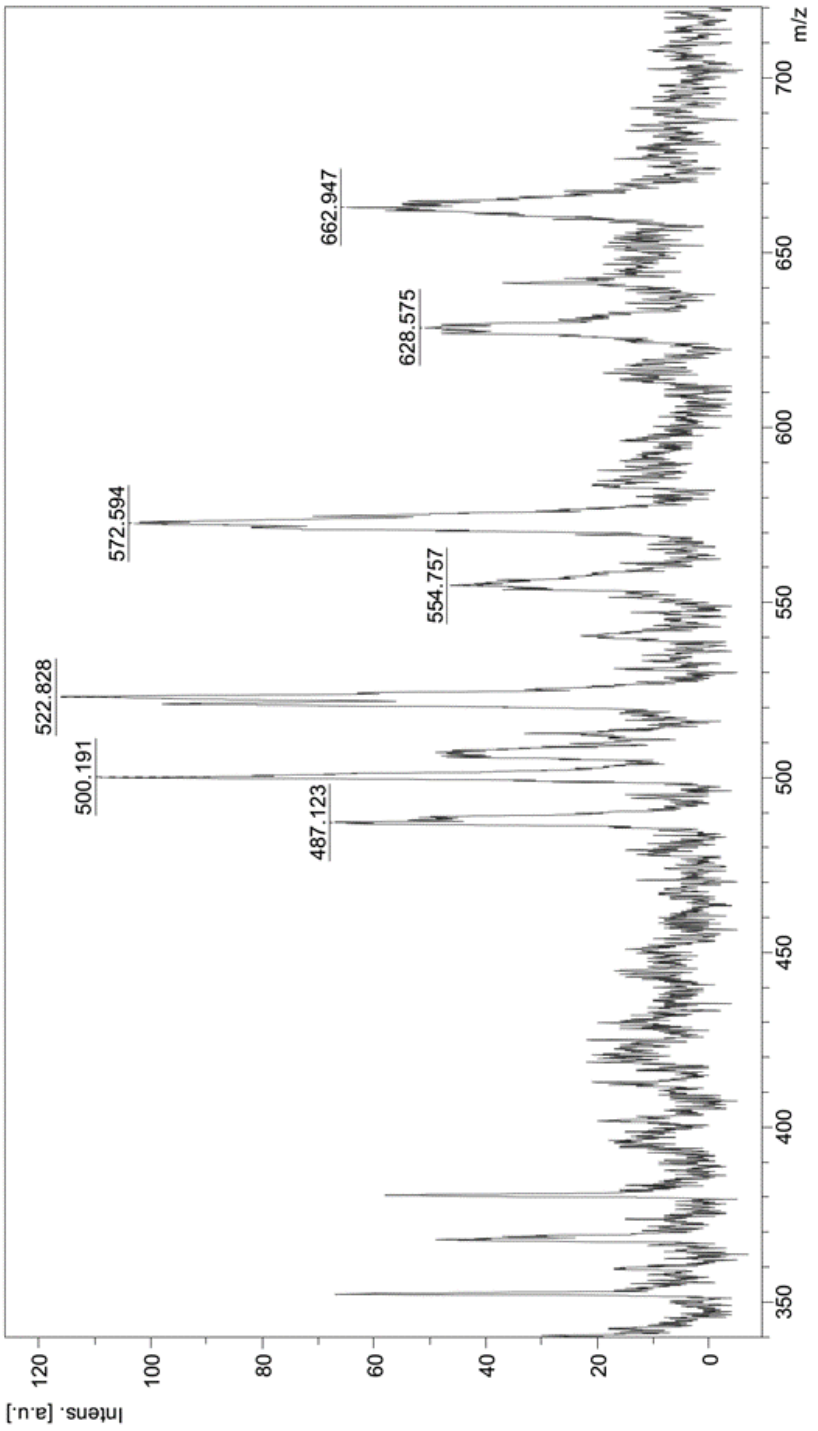

Figure Appendix A.36. AD.E. MALDI-TOF MS spectrum of complex C2

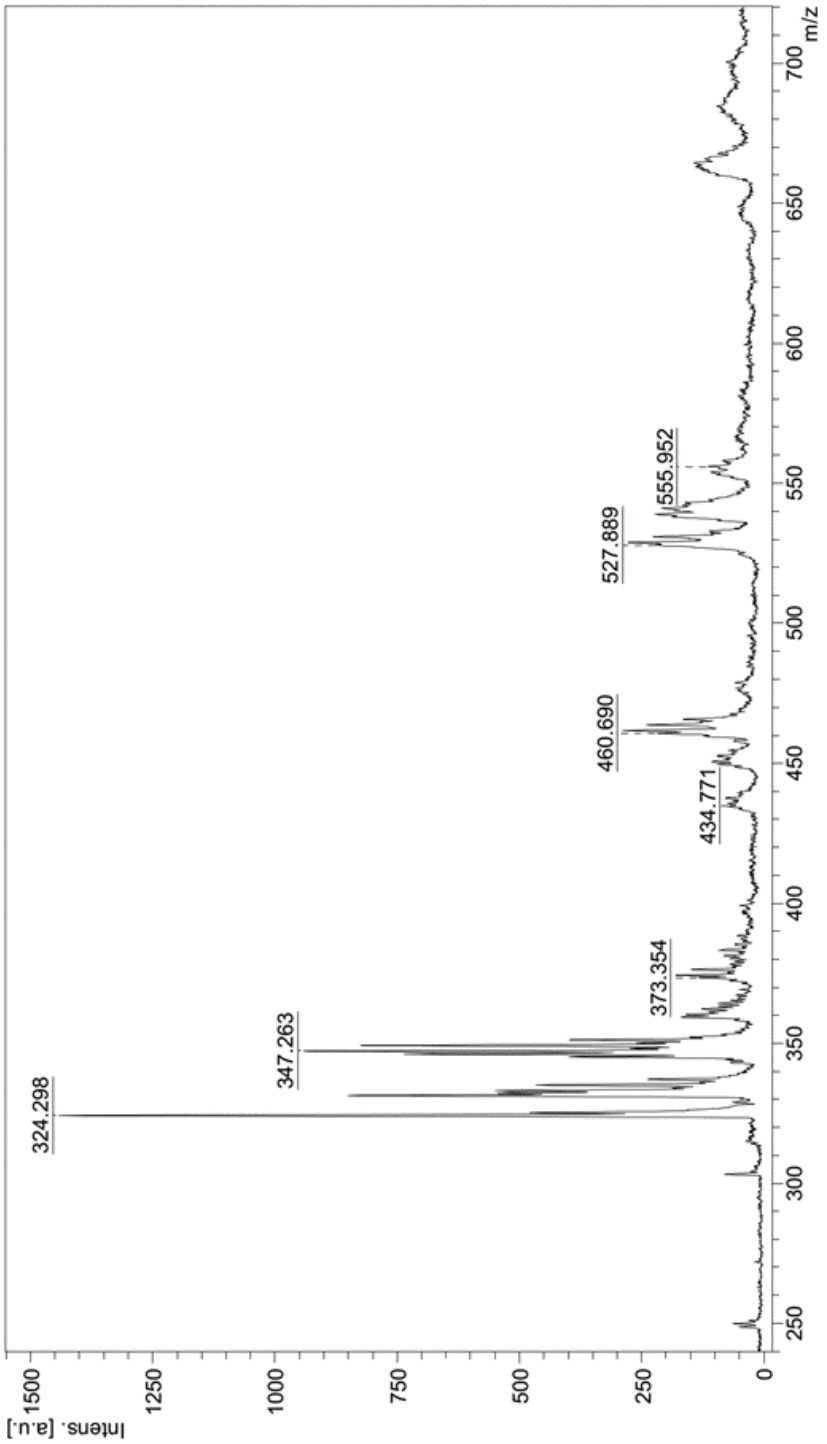

Figure Appendix A.37. AD.E. MALDI-TOF MS spectrum of complex C3

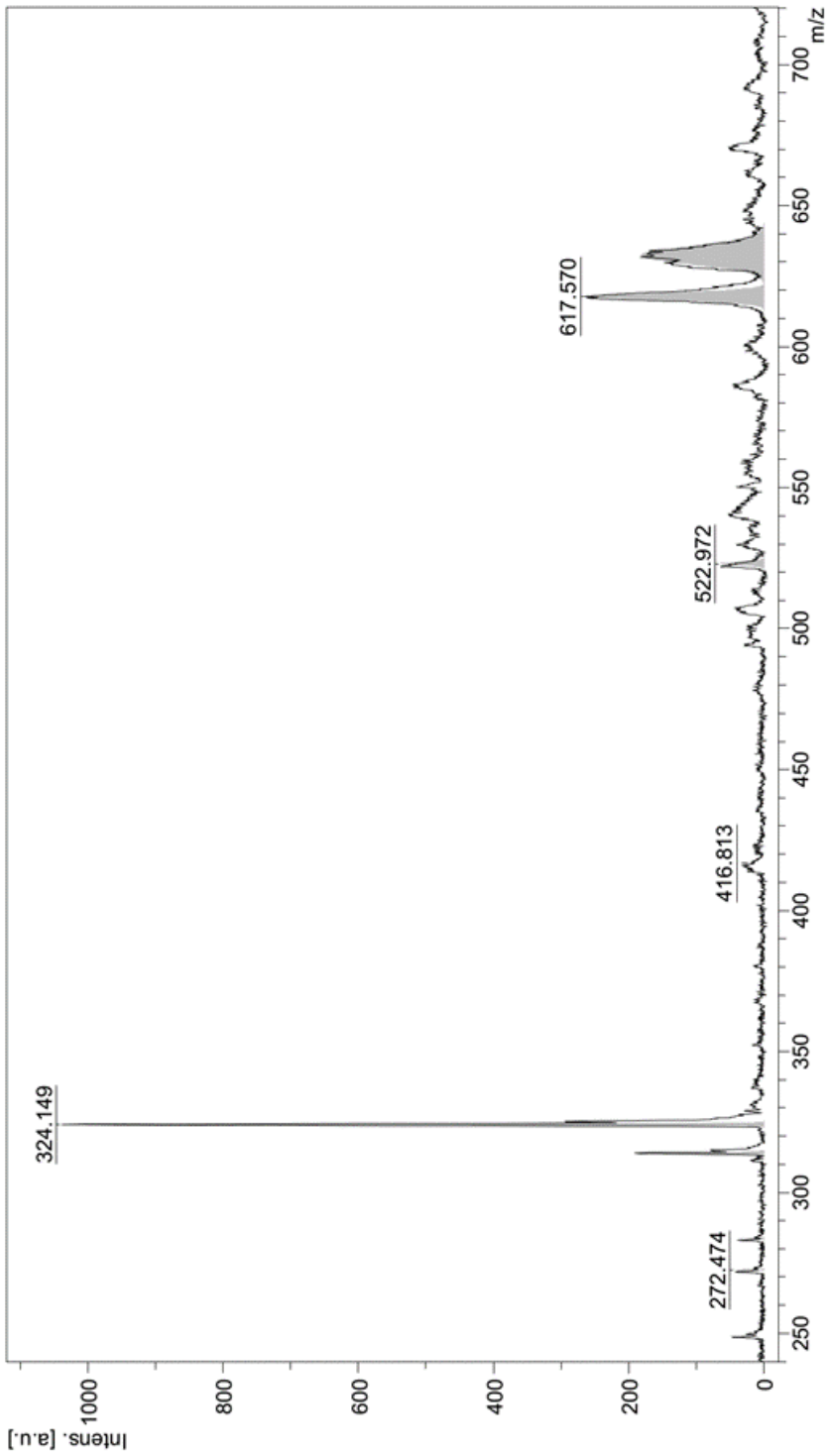

Figure Appendix A.38. AD.E. MALDI-TOF MS spectrum of complex C4

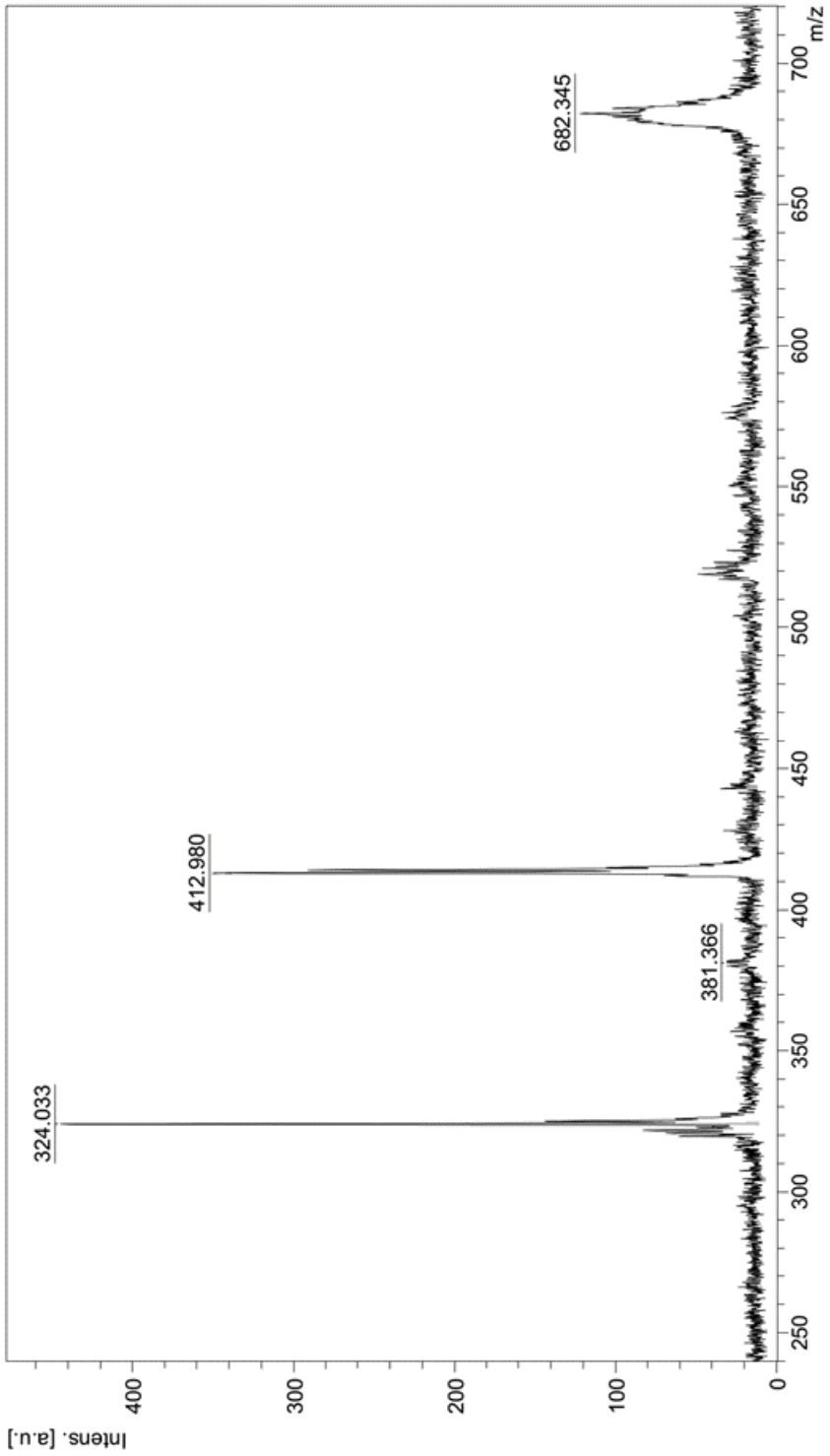

Figure Appendix A.39. AD.E. MALDI-TOF MS spectrum of complex C5

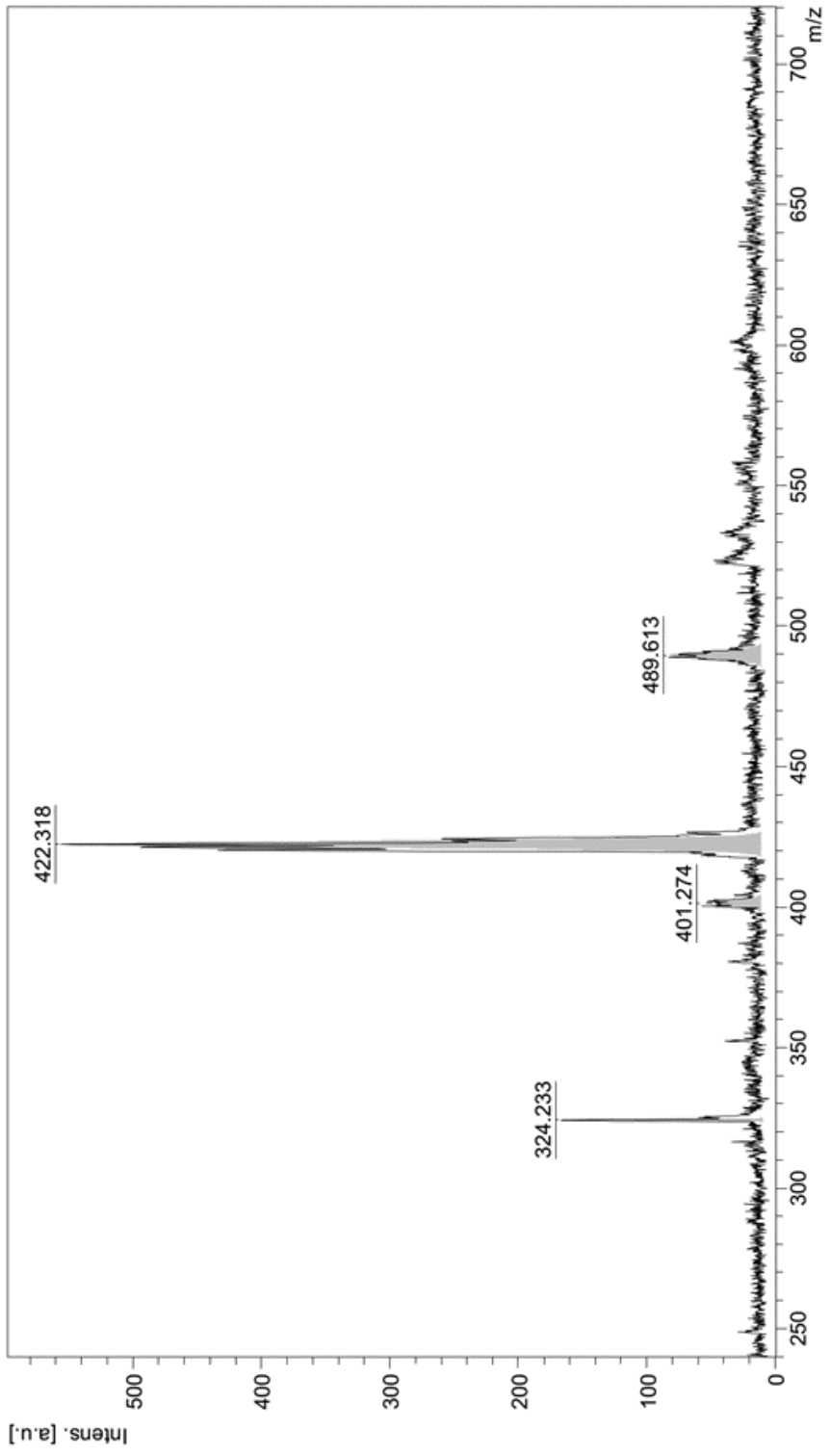

Figure Appendix A.40. AD.E. MALDI-TOF MS spectrum of complex C6

RESUME

Mustafa Mundher Kahlaf AL-AZZAWI he graduated from Sadaa Al Iraq Boys' High School in 2009. He graduated from Tikrit University, Faculty of Science, Department of Chemistry, which he started in 2009. He graduated in 2013. In 2021, he started his graduate studies at Karabuk University, Institute of Science, Department of Chemistry.