MARMARA UNIVERSITY

INSTITUTE FOR GRADUATE STUDIES
IN PURE AND APPLIED SCIENCES

SYNTHESIS OF NEW COMPOUNDS WITH O···C AND O···H INTERACTIONS

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MASTER of SCIENCE THESIS
Chemistry Department
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DOCUMENT OF ACCEPTANCE AND APPROVAL

Gizem SARITEMUR, a Master of Science in Chemistry student of Marmara University Institute for Graduate Studies in Pure and Applied Sciences, defended her thesis entitled "Synthesis of New Compounds with O···C and O··· H Interactions", on January 23, 2015 and has been found to be satisfactory by the jury members.

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APPROVAL

Marmara University Institute for Graduate Studies in Pure and Applied Sciences Executive Committee approves that Gizem SARITEMUR has been granted the degree of Master of Science in Department of Chemistry, Organic Chemistry Program on 26.01.2015
(Resolution no: 2015/03-02).

Director of the Institute

Prof. Dr. Uğur YAHŞİ

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ABSTRACT

SYNTHESIS OF NEW COMPOUNDS WITH O···C AND O···H INTERACTIONS

This thesis work purposes the synthesis of a range of functionalised derivates of naphthalene and biphenyl compounds and investigating of molecular interactions between nucleophilic and electrophilic functional groups.

Section 1 reports the synthesis of *para* methyl, chloro and nitro potassium dibenzoate compounds from corresponding benzoic acids. The structures of the molecules were solved and their X-ray crystallographic data were obtained. Molecular interactions such as hydrogen bonding were discussed.

Section 2 concerned with synthesis of various metal and organic salts from 1,8-naphthalaldehydic acid. Lithium and potassium salts were prepared as metal salts. The structures of the molecules were examined and molecular interactions were compared with the cesium salt which was reported in previous studies. To provide organic salts, 1,8-naphthalaldehydic acid was reacted with a range of organic bases such as morpholine, 4-dimethylaminopyridine and 1,1,3,3-tetramethylguanidine. Molecular geometries were identified by X-Ray crystallography.

In section 3, Suzuki coupling reaction was carried out. The progress of the reaction was monitored by TLC. The product of the reaction was purified by columm chromatography.

Section 4 is involved with preparation of various salts from product of Suzuki reaction. The structures of the molecules were discussed using NMR data.

The characterization of the compounds was achieved by ^{1}H-NMR, ^{13}C-NMR, FT-IR and X-Ray crystallography.

JANUARY 2015 Gizem SARITEMUR

Keywords: Naphthalene, biphenyl, nucleophilic, electrophilic, molecular interactions, hydrogen bond, Suzuki coupling.

ÖZET

O···C VE O···H ETKİLEŞİMLERİNE SAHİP YENİ BİLEŞİKLERİN SENTEZİ

Bu tez çalışması, çeşitli fonksiyel gruplara sahip naftalen ve bifenil bileşiklerinin sentezini ve nükleofilik-elektrofilik fonsiyonel gruplar arasındaki moleküler etkileşimlerin incelenmesini amaçlamaktadır.

1.Bölüm, *para* metil, kloro ve nitro potasyum dibenzoat bileşiklerinin ilgili benzoik asitlerden sentezlenmesini raporlar. Bu bölümde, moleküllerin yapıları çözümlendi ve X-ray kristalografik verileri elde edildi. Hidrojen bağı gibi moleküler etkileşimler tartışıldı.

2.Bölüm, 1,8-naftaldehit asitten çeşitli metal ve organik tuzlarının sentezlenmesiyle ilgilidir. Metal tuzları olarak lityum ve potasyum tuzları hazırlandı. Molekül yapıları incelendi ve moleküler etkileşimleri önceki çalışmalarda raporlanan sezyum bileşiğiyle karşılaştırıldı. Organik tuzları elde etmek için morfolin, 4-dimetilaminopridin ve 1,1,3,3-tetrametilguanidin gibi bazlarla 1,8-naftaldehit asit reaksiyona sokuldu. Moleküler geometriler X-ray kristalografisiyle aydınlatıldı.

3.Bölümde Suzuki coupling reaksiyonu gerçekleştirildi. Reaksiyonun ilerleyişi TLC ile izlendi. Ürün kolon kromatografisiyle saflaştırıldı.

4.Bölüm Suzuki reaksiyoundan elde edilen üründen çeşitli tuzların hazırlanmasıyla ilgilidir. Molekül yapıları NMR verileri kullanılarak tartışıldı.

Moleküllerin karekterizyonu ^{1}H-NMR, ^{13}C-NMR, FT-IR ve X-Ray kristalografik ölçümlerle elde edildi.

OCAK 2015 Gizem SARITEMUR

Anahtar kelimeler: Naftalen, bifenil, nükleofilik, elektrofilik, moleküler etkileşimler, hidrojen bağı, Suzuki coupling.

CLAIM FOR ORIGINALITY

Following compounds were synthesized in this thesis work for the first time and they were identified by ^{1}H-NMR, ^{13}C-NMR, FT-IR and X-Ray crystallography.

Potassium hydrogen di(4-chloro) benzoate **(47)**
Potassium di(4-nitro)benzoate **(48)**
Potassium hydrogen di(4-methyl)benzoate **(49)**
Potassium 8-formyl-1-naphthoate hydrate **(50)**
Lithium 8-formyl-1-naphthoate **(51)**
Salt mixture of 3-hydroxybenzo[de]isochromen- 1(3H)-one, 4-(dimethylamino)pyridin-1-ium and 8-formyl-1-naphthoate **(53)**
Salt mixture of bis(dimethylamino)methaniminium and 8-formyl-1-naphthoate **(54)**
Tetraphenylphosphonium 8-formyl-1-naphthoate (**55)**
Lithium 6H-benzo[c]chromen-6-olate **(59)**
Bis(dimethylamino)methaniminium 6H-benzo[c]chromen-6-olate **(60)**

Prof. Dr. John D. WALLIS **Gizem SARITEMUR**
Prof. Dr. Ümit SALAN

SYMBOLS

Å	: Angstrom
a	: Lattice parameter (angle)
α	: Lattice parameter (length)
b	: Lattice parameter (angle)
β	: Lattice parameter (length)
c	: Lattice parameter (angle)
γ	: Lattice parameter (length)
°C	: Centigrade celsius
δ	: Chemical shift
ρ	: Density
K	: Kelvin
μ	: Absorption coefficent
V	: Volume
Z	: Number of formula units in cells

ABBREVIATIONS

Atch	: Attachment
cp.	: Compare
DNA	: Deoxyribonucleic acid
DMAP	: Dimethylaminopyridine
DMF	: N,N-dimetilformamid
DMSO	: Dimetilsülfoksit
Et	: Ethyl group
Et_2O	: Diethyl ether
EtOAc	: Ethyl acetate
EtOH	: Ethanol
FT-IR	: Fourier transform infrared spectroscopy
g	: Gram
HMDS	: Hexamethyldisilazide
M	: Molarity
Me	: Methyl group
MHz	: Mega Hertz
MeOH	: Methanol
mL	: Milliliter
mmol	: Milimol
m.p.	: Melting point
NMR	: Nuclear magnetic resonance
ppm	: Parts per million
ppb	: Parts per billion
Pr_i	: Isopropyl
R	: Alkyl
THF	: Tetrahydrofuran
TLC	: Thin layer chromatography

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CHAPTER 1

1. INTRODUCTION

Through-space interactions between functional groups play significant role in a wide range of chemical and biochemical processes. Thus, van der Waals forces, hydrogen bonding and dipole-dipole interactions show attractive interactions in supramolecular processes such as crystal packing, host-guest chemistry and the mode of binding of a substrate to a biological receptor protein [1].

1.1. Molecular Interactions

1.1.1. Covalent Bonds

Covalent interactions (bonds), which hold the atoms together within molecules, are formed by sharing of electron pairs between the atoms. They are the strongest bonds, bond energies and lengths vary with the bond type [2].

Table 1.1. Bond energies of some covalent bonds [3]

Bond	Energy (kJ/mol)	Bond	Energy (kJ/mol)
C-C	347	C-H	413
C-O	358	N-H	391
C-N	305	O-H	467
C-F	485	C=C	614
C-Cl	339	C=O	745
C-Br	276	C=N	615
C-I	240	C≡C	839

Table 1.2. Bond lengths of some covalent bonds [4]

Bond		Length (Å)	Bond		Length (Å)
Single bonds			**Double bonds**		
C(sp^3)-C(sp^3)		1.53-1.55	C(sp^2)-C(sp^2)	alkenes	1.31-1.34
C(sp^3)-C(sp^2)		1.49-1.52	C(sp^2)-C(sp^2)	arenes	1.38-1.40
C(sp^2)-C(sp^2)	conjugated	1.45-1.46	C(sp^2)-O(sp^2)	aldehydes and ketones	1.19-1.22
	non-conjugated	1.47-1.48	C(sp^2)-O(sp^2)	esters	1.19-1.20
C(sp)-C(sp)		1.37-1.38	C(sp^2)-O(sp^2)	amides	1.225-1.24
C(sp^3)-O(sp^3)	ethers	1.42-1.44	C(sp^2)-N(sp^2)	imines	1.35
C(sp^3)-N(sp^3)	amines	1.46-1.48			
C-F		1.39-1.43	**Triple bonds**		
C-Cl		1.78-1.85	C(sp)-C(sp)	alkynes	1.17-1.20
C-Br		1.95-1.98			
C-I		2.15-2.18			
C(sp^3)-H		1.09-1.10			
C(sp^2)-H		1.075-1.085			
C(sp)-H		1.06			
N-H		1.00-1.02			
O-H		0.96-0.97			

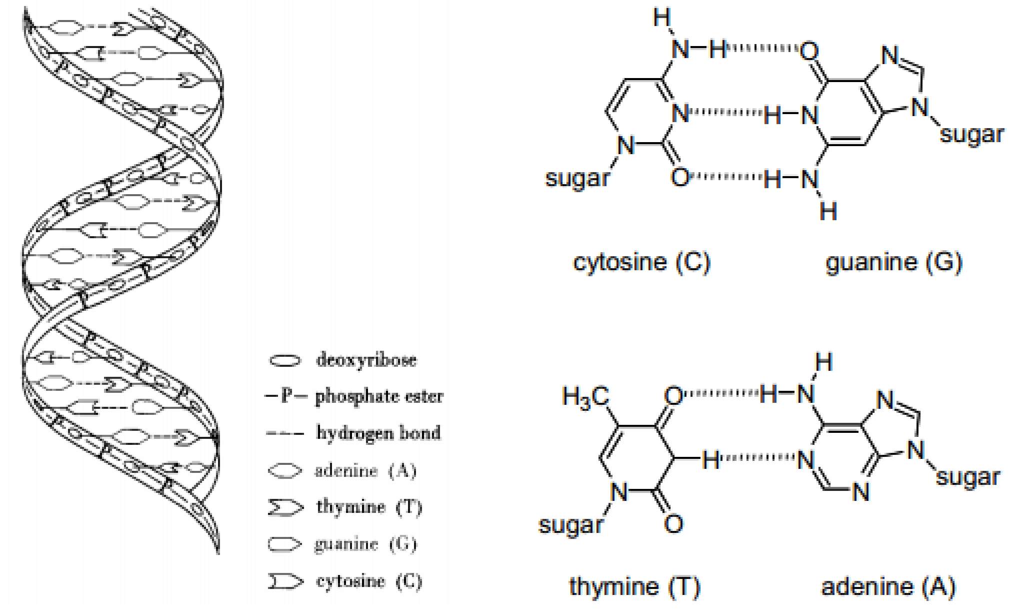
1.1.2. Non-covalent Interactions

Molecules are held together with non-covalent interactions involving dipole-dipole, hydrogen bonding, van der Waals/London dispersion forces. They are considerably weaker than the covalent bonds. Most non-covalent interactions exhibit ~ 40 kJ/mol or less energy [5]. However, non-covalent interactions are very important for biological processes and macromolecules.

Non-covalent interactions such as hydrogen bonding and van der Waals interactions play a fundamental role in formation, structure, stability and function of a wide variety of the molecules [6]. Chemical interactions between a protein and a drug, or a catalyst and its substrate, self-assembly of nanomaterials, and even some chemical reactions are dependent on non-covalent interactions [7].

1.1.3. Hydrogen Bonding

Natural compounds provide extensive examples of non-covalent interactions. For instance, the structure of DNA has two basic models of molecular self-assembly through non-covalent bonds: intermolecular, or "supramolecular chemistry" and intramolecular or "foldamer chemistry". It is well known that DNA exists a double helical structure in solution depending on specific *interstrand* hydrogen bonding between base pairs. These interactions are relevant to supramolecular chemistry, in which molecules are designed with the purpose of specific interaction with other atoms, ions, or molecules to form complexes [8].



(a) (b)

Figure 1.1.a Complementary base pairing in DNA helical structure
Figure 1.1.b Base pairing in DNA (guanine and cytosine form triple hydrogen bonds; adenine and thymine form double hydrogen bonds) [9].

According to the X-ray diffraction studies, the hydrogen bonds holding guanine-cytosine and adenine-thymine complexes are about the same length (2.9±0.1 Å) (Figure 1.1.b) [10].The stability of the DNA double helix is mainly due to *intrastrand* aromatic-aromatic interaction between adjacent bases, relevant to foldamer chemistry, in which molecules are designed to exist in a specific secondary structure via intramolecular interactions (Figure 1.1.a & Figure 1.1.b) [8].

Hydrogen bonding is responsible for the structure of most of the natural compounds. The unusual and complex properties of bulk water, the ability of proteins to fold into stable three-dimensional structures, and the binding of ligands to receptors are based on this non-covalent interaction [11]. An interesting example is spider silk; which has extremely high tensile strength and elasticity because of intermolecular and intramolecular hydogen bonds [8].

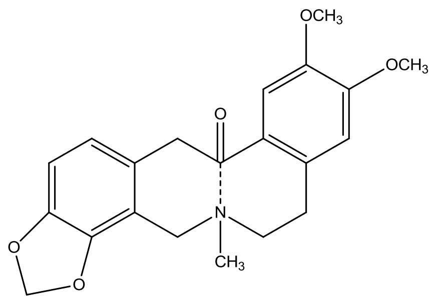
1.1.4. van der Waals Interactions

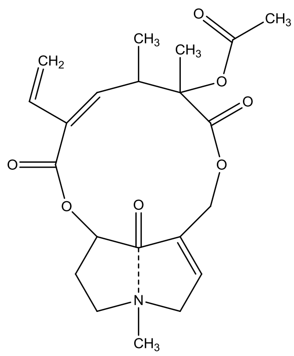
van der Waals interactions between atoms and molecules play key role in many chemical and biological systems. They are delicately balanced with electrostatic and exchange/repulsion interactions which control together the processes such as the structures of proteins, the packing of crystals, the formation of aggregates, host-guest systems, and the orientation of molecules on surfaces [12].

van der Waals radii were assigned from the closest measured intermolecular contacts between *like* atoms in order to estimate of the effective sizes of bonded atoms, and have been modified by Nyburg to explain asymmetric shapes of bonded atoms from the second and later rows of the Periodic Table [1,13,14,15]. Nevertheless, using these parameters to predict the closest interaction distance between *unlike* atoms, by just adding the applicable 'radii' is not likely to be very successful. There may be additional aspects to the interaction which are not present when either atom interacts with one of its own kind [1]. Bent has analysed various types of compounds containing such interactions [1,16]. This is especially relevant for interactions between electron-rich and electron-poor atoms and short contacts has been observed between tertiary amino groups and carbonyl groups [1,17,18].

1.2. Interactions between Electrophilic and Nucleophilic Groups

Interactions between an electron rich and an electron-poor group have been investigated by X-ray crystallography for many years. Accordingly, Bürgi, Dunitz and Schefter examined the interactions between a tertiary amino group and a carbonyl group in a series of alkaloids including molecules **1-2.** They indicated that there is a correlation between a decreasing N···C distance and an increasing C=O bond length, which parallels the process of the corresponding addition reaction (Figure 1.2) [1,18].





1 **2**

Figure 1.2. Chemical structures of compound **1** and **2**

However, it is not enough to decide whether there is an attractive component to an intramolecular interaction from the contact distance alone [1]. Further insight may be obtained by analysis of the experimental charge density, determined from accurate low-temprature X-ray diffraction data, using Bader's 'Theory of Atoms in Molecules' in which bonding interactions are characterised by saddle points in the total electron density [1,19].

Bond forming and bond breaking processes in chemical reactions have been studied by analysing the interaction geometries between pairs of functional groups which have been measured by X-ray diffraction [20,21]. Especially, addition reaction of a nucleophile to a carbonyl group was examined using a range of structures involving a tertiary amino group and a carbonyl group were held in close proximity [17,18,20]. Kirby and Jones studied the structures and spontaneous cleavage of tetrahydropyranyl acetals and glucosides, and a correlation was observed between the length of the exocyclic C-O bond and reactivity [20, 22-24]. Relevant studies have been made on the addition of nucleophiles to triple bonds, nitriles and alkynes. The addition of a nucleophile to an electron-deficient carbon-carbon double bond is a significant reaction in organic synthesis [20].

1.2.1. *Peri* Interactions in Naphthalene Systems

Pairs of groups located at the *peri* positions of a naphthalene ring have provided an important system in order to study the effects of two nearby groups [25]. The *peri*-disubstituted naphthalane framework has been used to analyse nucleophile/electrophile interactions between the common functional groups in organic chemistry [26]. For instance, -NMe_2, -OMe or –SMe groups were investigated as nucleophile and carbonyl based groups or electron deficient alkenes as electrophile *e.g.* **3-9** (Figure 1.3) [26,27]. 1,5-interactions between these functional groups and electrophilic carbon atom on naphthalene systems have been studied extensively.

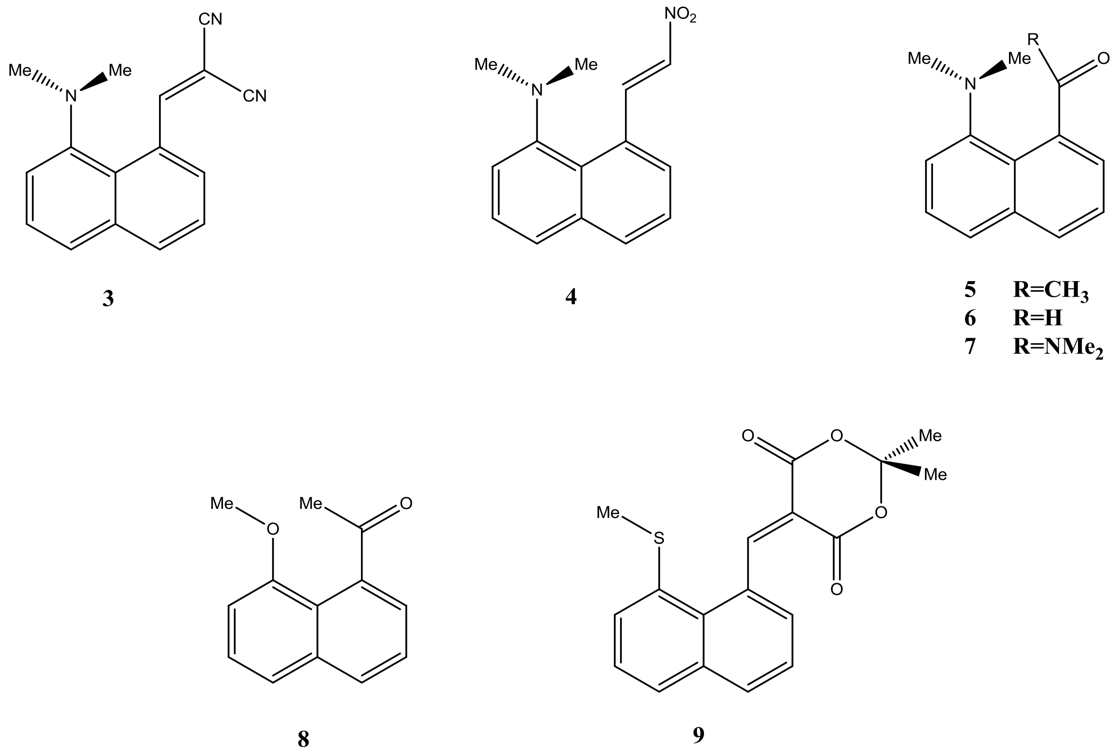
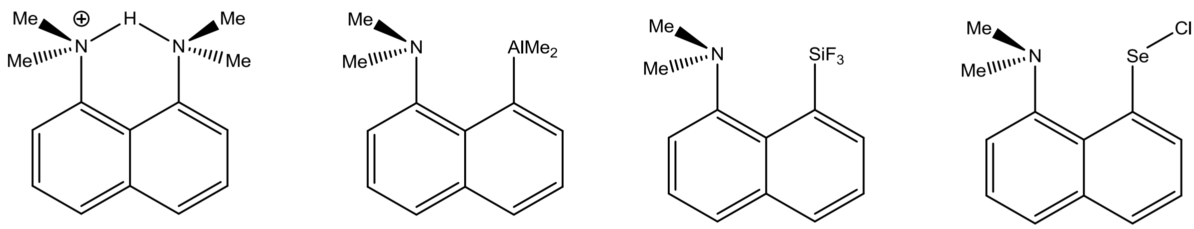


Figure 1.3. Chemical structures of compound **3-9** which exibit 1,5-peri interactions

In addition, *peri*-disubstituted naphthalanes have been examined for various interactions between pairs of substituents, *e.g.* involving hydrogen bonding in the "proton sponge" cations **10** and interactions of - NMe_2 groups with a wide range of functionalities including Al, Si and Se centered groups *e.g.* in **11-13** (Figure 1.4) [26].



10 **11** **12** **13**

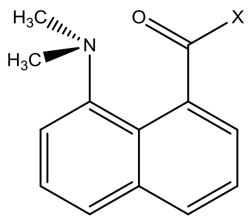
Figure 1.4. Chemical structures of compound **10-13**

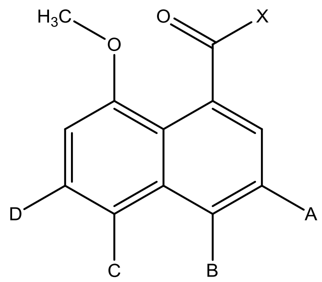
Anthracene systems have also been used similarly for studying functional group interactions. Further insight into these *peri*-interactions is obtained by the studies of the topology of the electron density in the region between the groups [27].

Previous studies have been reported for *peri* interactions of dimethylamino and methoxy groups with carbonyl-containing groups. In spite of the nucleophilic difference between dimethylamino and methoxy groups, the results show that there is not clear systematic difference between the N···C=O and O···C=O distances for interactions with the same carbonyl-containing functional group [1].

Even though dimethylamino and methoxy groups have different nucleophilic characters, N···C=O and O···C=O distances can be shorter or longer depending on the carbonyl containing groups. Thus, in the *peri*-dimethylamino methyl ketone **14** the N···C(=O) distance (2.557(3) Å) is slightly shorter than the O···C=(O) distances in *peri*-methoxy methyl ketones **17** and **18** (2.606(9) and 2.579(3) Å), but for the pairs of *N*,*N*-dimethyl- and *N*,*N*-diisopropylcarboxamides **15,19** and **16,20** the N···C(=O) distances (2.698(3) and 2.764(3) Å) are distinctly longer than the O···C=O distances (2.597(5) and 2.623(2)

Å) (Figure 1.5) [1]. Therefore, this result indicates there is a greater '*peri* bonding' between a methoxy and a carboxamide group than between a dimethylamino and a carboxamide group and is used to explain the slower rate of racemisation of the *peri*-methoxy carboxamide **20** compared to the *peri*-dimethylamino carboxamide **16** which is effected by rotation about the aryl-carbonyl bonds [1,28]. However, the real point is that the N···C distance is much more sensitive to have nucleophilic/electrophilic interactions than the O···C distance.

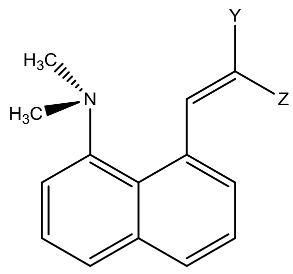
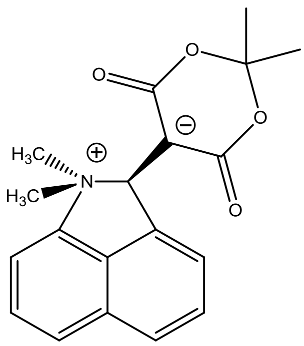
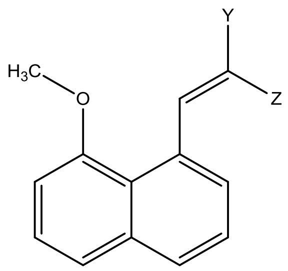




14 X=Me		**17**	X=Me, A=B=C=D=H
15 $X=NMe_2$		**18**	X=Me, A= D=H B=OMe, C=OTs
16 $X= NPr^i_2$		**19**	$X=NMe_2$, A=B=C=D=H
		20	$X= NPr^i_2$, A=B=C=D=H

Figure 1.5. Chemical structures of compound **14-20**

Kirby has worked on naphthalenes containing *peri*-interactions between a dimethylamino group and an electron deficient alkene, *eg.* **21** to **25** [1,29]. Wallis, Bell, O'Leary have investigated naphthalenes containing *peri*-interactions between methoxy groups and electron deficient alkenes, *eg.* **27** and **28**. Along the series **21** to **25,** N···C=C distances increases progressively. Structure of **21** is better represented as the zwitterion **26** with a N-C bond length of 1.651 Å**,** and has the shortest N···C=C distance among the series. Thus, the nucleophilic addition of the Me_2N group to alkene is almost complete (Figure 1.6) [1]. Along the series from **21** to **25**, the greatest degree of *peri* N···C interaction occurs when the alkene's terminal substituents are two lactone carbonyl groups both of which are coplanar with the alkene in **21**. The second largest degree of interaction is in **22** where the alkene substituents are both nitriles [1].

21 Y=Z= -(C(=O)O)$_2$CMe$_2$

22 Y=Z=CN

23 Y=CN, Z=CO_2Et

24 Y=Z=COPh

25 Y=Br, Z=H

26

27 Y=Z= -(C(=O)O)$_2$CMe$_2$

28 Y=Z=CN

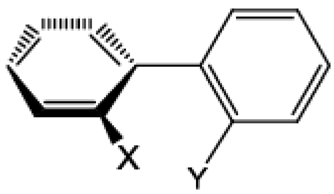
Figure 1.6. Chemical structures of compound **21-28**

O'Leary, Bell, Wallis and Schweizer measured the structures of **27** and **28**, the *peri*-methoxy analogues of compounds **21** and **22** (Figure 1.6). They investigated the degree of interaction between electron-deficient alkenes and methoxy groups. The results showed that in **27** and **28** MeO···C=C separations are longer than the corresponding Me$_2$N···C=C distances (**27**: 2.550(2) Å *cp.* **21**: 1.651(3) Å and **28**: 2.611(1) Å *cp.* **22**: 2.413(2) Å). Due to the fact that an aryl methoxy group has lower nucleophilicity than an aryl dimethylamino group, the aryl methoxy group shows a reduced interaction with the electrophilic alkene [1].

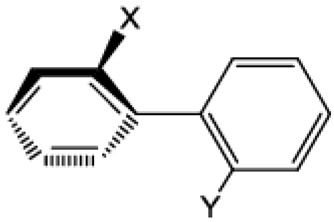
Consequently, the character of nucleophile-electrophile interactions in *peri*-substituted naphthalenes can be concluded by observing the relative sizes of the contact distances between the electrophile and two groups which have different nucleophilicity, and this approach should be transferrable to other systems. Further details of the interactions can be obtained experimentally by examining the topography of the total electron density measured by X-ray diffractometer [1].

1.2.2. Interactions in Substituted Biphenyls

Substituted biphenyls have a crucial role in organic chemistry, because they provide the resolvable enantiomers with axial chirality and broad variety of ligands used in metal catalysed reactions including asymmetric synthesis [30-33]. Moreover, biphenyls can be synthesized efficiently using coupling reactions (*e.g.* Suzuki reaction), and have been used as building blocks in supramolecular chemistry, *e.g.* in catenanes and crystalline biphenyl-peptide hybrids [30,34].



29a



29b

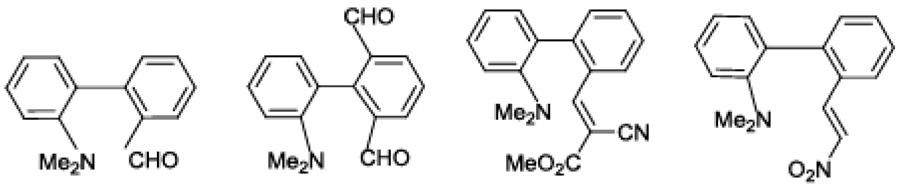
Figure 1.7. *Ortho* substitution in biphenyl framework

Ortho substitution of a biphenyl framework permits the groups to form 1,6 interactions. The inter-ring bond of the biphenyl system is free to rotate. Thus, the functional groups are able to access each other without any force and what is more they are free to rotate well out of the interaction range, too. The functional groups can keep close or they can completely avoid each other, as in conformers **29a** and **29b** (Figure 1.7) [30].

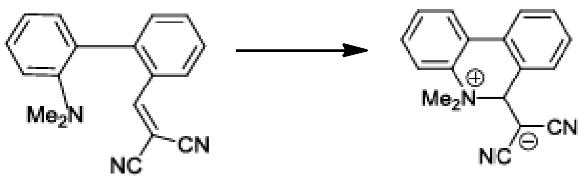
O'Leary and Wallis investigated the interactions between an electrophilic and a nucleophilic functional group located at the *ortho* position of the two rings of the biphenyl framework. They synthesized the following molecules **(30-37)** and measured the bond lengths in the structures by X-ray diffraction (Figure 1.8). According to the results, molecules were divided into two groups compared to the 1,5-N···C=O interaction in methadone **38** (2.912(3) Å). Molecules **31-33** have longer $Me_2N\cdots sp^2C$ interactions in the range 2.929(3)-3.029(3) Å. Molecules **34** and **35** which have noticeable bond formation between the groups to give zwitterionic structures **36** and **37.** Molecules **36** and **37** have remarkably shorter $Me_2N\cdots C$ interactions in the range

1.5857(14)-1.604(3) Å due to the bond formation. The functional groups in these cases do not react or have not any intramolecular interactions [30].

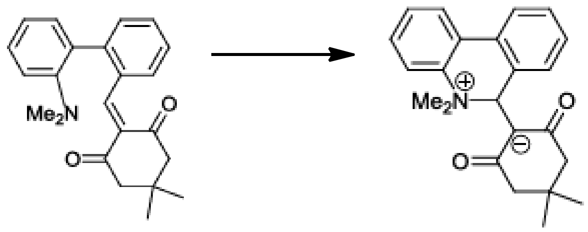
The interactions in the series of biphenyls **30-33** are much more similar to intermolecular interactions between the pairs of functional groups than the start of bonding interactions which are only observed if the groups are forced to be close together. Methadone **38**, with a long 1,5-$Me_2N\cdots C=O$ interaction, also have these unforced interactions [30].



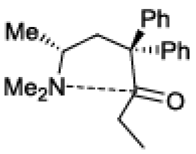
30 **31** **32** **33**



34 **36**



35 **37**



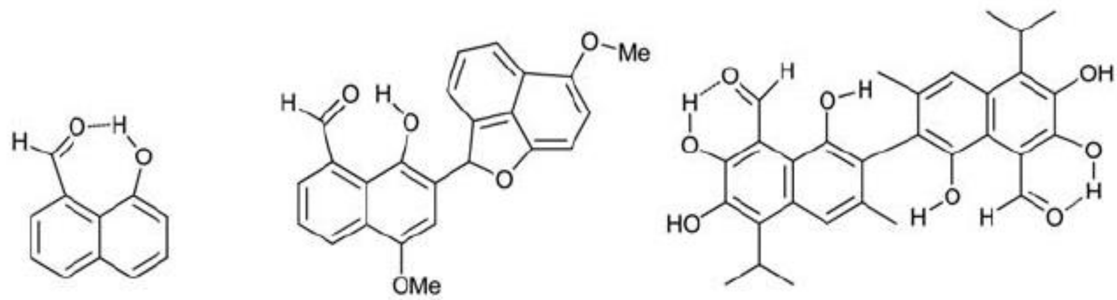
38

Figure 1.8. Chemical structures of compound **30-38**

The previous studies on substituted biphenyls explained the intermolecular interactions between a particular pair of functional groups. The substituted biphenyls are relatively simple to synthesize and crystallize. Therefore, these studies can be extended to different pairs of functional groups and researched separations or bond lengths between the two groups [30].

1.2.3. Hydrogen bond formation in *peri* naphthalene systems

The *peri*-naphthalene systems have been widely used as a model for observing nucleophile/electrophile interactions involving hydrogen groups. Accordingly, crystal structures of **39** and **40** can show hydrogen bond formation between *peri*-related hydroxyl and aldehyde group (Figure 1.9). The hydroxyl and the aldehyde groups are splayed apart on the naphthalene ring, so that the groups are able to form a bond. Even though the hydroxyl hydrogen atom is not unambiguously located in either case, the *peri*-groups are distinctly splayed apart. The structures of **39** and **40** have 2.51-2.54 Å (H)O···O(=C) contact distances with an internal hydrogen bond which causes formation a seven membered ring [26].



39 **40** **41**

Figure 1.9. Chemical structures of compound **39-41**

Molecule **41** gossypol contains a *peri* aldehyde group with both *peri* and *ortho* hydroxyl groups. According to many observations, gossypol clathrates prefer to have an internal hydrogen bond between the aldehyde and the *ortho* hydroxyl group with formation of a six-membered ring. HO···H (C=O) distance is 2.04 Å, so that it is suggestive of an attractive interaction [26].

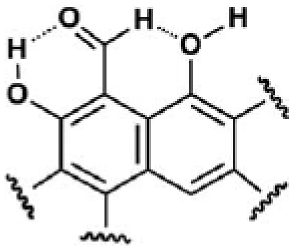
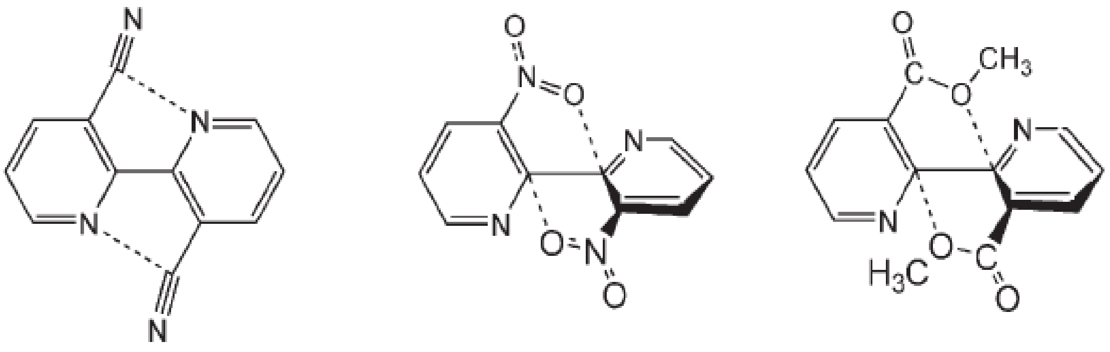


Figure 1.10. Relative locations of the aldehyde and flanking hydoxyl groups in gossypol clathrates

1.2.4. Interactions in 3,3 Disubstituted Bipyridine Structures

The nitrogen atom on the pyridine ring provides a nucleophilic centre. Thus, disubstituted bipyridine structures have been studied and a pair of interactions was observed in some cases. Compound **42** showed N···C≡N interactions between pyridine nitrogen and nitrile carbon (2.695(2) and 2.740(2) Å). However, compounds **43** and **44** did not reveal such interactions between pyridine nitrogen and other electron deficient groups such as nitro or ester (Figure 1.11). The oxygen atom from each nitro or carboxylic ester groups interacted with the 2-carbon atom of the opposite ring (**43**: 2.916(2) and 2.980(2) Å; **44**: 2.849(3) Å). These bipyridine frameworks showed 1,5-interactions between the functional groups [27].

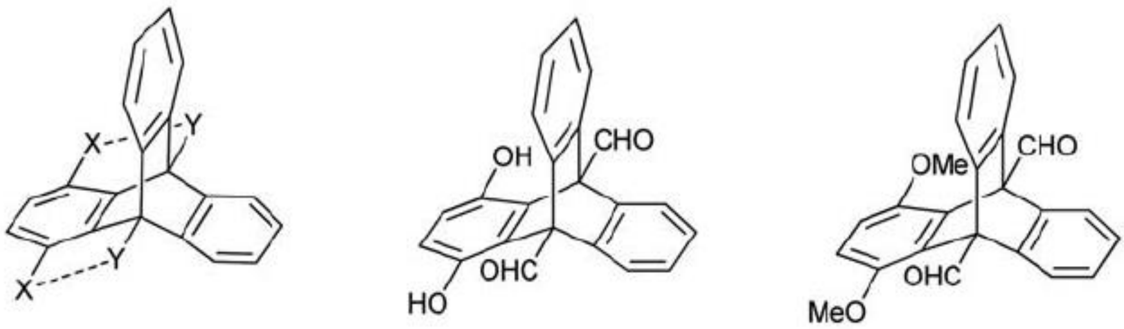


42 **43** **44**

Figure 1.11. Chemical structures of **42-44** which show 1,5-interactions between the functional groups

1.2.5. Interactions in Triptycene Structures

Ortho-substituted triptycene systems show 1,5-nucleophile/electrophile interactions similar to *peri*-naphthalene systems. Accordingly, Wallis, Bresco and Lari used the triptycene skeleton as **44** to investigate 1,5-interactions between a nucleophilic centre and an electrophilic centre. They measured the interactions between hydroxyl or methoxy groups with aldehyde groups in compounds **45** and **46** (Figure 1.12) [26].



44 **45** **46**

X= nucleophilic centre

Y= electrophilic centre

Figure 1.12. Chemical structures of compound **44-46**

X-ray crystallographic measurements show that molecule **45** has remarkable HO···C=O interactions between the functional groups on the both edges of the triptycene system. The O···C separations are 2.621(2) and 2.679(2) Å for the molecule **45**. Molecule **46**, which crystallises with two unique molecules, has four O···C separations in the range 2.528(9)-2.584(9) Å with an average value of 2.547 Å [26].

Thus, the triptycene system has been illustrated to be a useful scaffold for investigating particular interactions between functional groups. Even though triptycene and *peri*-naphthalane systems have been used both to investigate 1,5-interactions, the triptycene systems have more advantages. The group located on the central sp^3 carbon atom can not conjugate with the framework as happens in some *peri*-naphthalene systems [26].

The use of triptycene systems can be extended to future systems which will have partial bond formation depending on the reactivities of the functional groups and *ortho* substituents [26]. In this respect, we are expecting to see more results in the near future.

1.3. Suzuki Coupling Reaction

C-C bond formation reactions are important for synthetic organic chemistry. These reactions have been widely used for various organic processes ranging from supramolecular chemistry to natural product synthesis [35]. In this regard, Pd-catalysed Suzuki coupling reaction is one of the most efficient methods for C-C bond construction [36].

Suzuki coupling reaction (also known as Suzuki reaction, Suzuki-Miyaura cross coupling) is palladium-catalyzed cross-coupling reaction between organoboron compounds and organic halides or triflates [37]. It is possible to perform Suzuki reactions with boranes ($R–BR'_2$), boronic acids [$R–B(OH)_2$], boronates [$R–B(OR')_2$] or organotrifluoroborates [$(R–BF_3)^+$] as the organoboron compound [38]. It provides a convenient and powerful method for the synthesis of biaryl and alkene derivates that are structural components of numerous natural products, agrochemicals, pharmaceuticals and polymers [39,40]. The method was first reported in 1981 by Akira Suzuki and coworkers using the conditions shown in Figure 1.13 [40]. They developed useful methodology for the synthesis of sp^2-sp^2 carbon-carbon bonds between two aromatic rings.

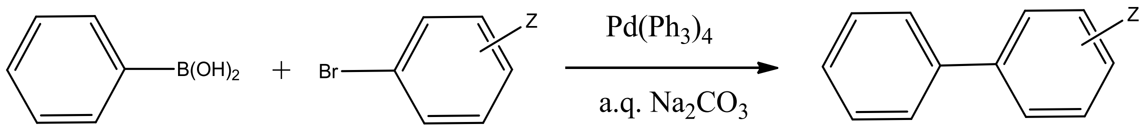


Figure 1.13. Palladium-catalysed cross-coupling reaction of phenylboronic acid with haloarenes proceeds smoothly in the presence of bases to give corresponding biaryls in good yields [40].

Akira Suzuki (Hokkaido University, Japan) shared 2010 Nobel Prize in Chemistry with Richard F. Heck (University of Delaware, USA) and Ei-ichi Negishi (Purdue

University, USA). They were awarded for palladium-catalyzed cross couplings in organic synthesis by the Swedish Academy of Sciences. The prize recognises the work of three chemists, who have developed efficient reactions of linking carbon atoms together to build the complex molecules which are improving our everyday lives. The painkiller naproxen, a generic sold in the US under the brand name Aleve®, Merck & Co.'s allergy treatment Singulair®, and Boscalid®, a fungicide made by BASF SE, are among the chemicals made possible by their work [41].

Today, chemists are researching new applications for improving Suzuki reaction. Many new possibilities were reported during the past decade. Research groups around the world are investigating modifications of the reaction that work in aqueous media or with trace amounts of catalysts. For example, Leadbeater and his team have carried out Suzuki reaction using ultralow (ppb) palladium concentration in water. Kabalka and colleagues have combined a slovent-free, solid state approach with the application of microwave radiation to accomplish coupling reaction in just a few minutes. And also, ionic liquids which are excellent solvents for transition-metal catalysts are being researched [38]. We are expecting to see more investigations and developments for Suzuki reaction in the near future.

1.3.1. Catalytic Cycle of Suzuki Coupling Reaction

As in other cross-coupling reactions, the catalytic cycle of the Suzuki-Miyaura reaction requires a sequence consisting of an oxidative addition, a transmetalation, and a reductive elimination [42].

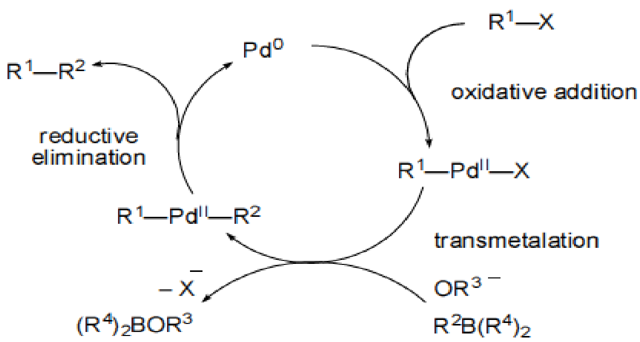


Figure 1.14. General catalytic cycle of Suzuki coupling reaction [42]

The oxidative addition is often the rate-limiting step in the cross-coupling catalytic cycle (Figure 1.14). In this step, Pd(0) catalyst inserts into the C-X bond of the organic halide and is oxidized in the process. The next step is transmetallation, in which an organic group is transferred from the organometallic precursor (e.g. boron species) to the Pd(II) complex. The mechanism then proceeds to last step (reductive elimination) to produce the new C-C bond of the product and regenerate the catalyst [41].

1.3.2. Advantages of Suzuki Coupling Reaction

Among the other coupling reactions (e.g. Kharash coupling, Negishi coupling, Stille coupling, Himaya coupling, Liebeskind–Srogl coupling and Kumuda coupling), Suzuki Reaction has recently become the most popular one [39]. Suzuki Reaction offers many advantages are as follows:

1) Reaction conditions are mild,
2) Boronic acid derivates are commercially available and stable to heat, oxygen and water,
3) Boronic acid derivates are environmentally safer than the other organometallic reagents,
4) The handling and removal of boron-containing by-products are easy as compared to other organometallic reagents, especially for large-scale synthesis of a product [36,39,43-44].

Due to these desirable features, Suzuki Reaction is very important for medicinal chemistry as well as large-scale synthesis of pharmaceuticals and fine chemicals [43]. In recent years, this reaction has been successfully applied for the synthesis of natural products, pharmaceuticals and conducting polymers [39].

CHAPTER 2

2. MATERIAL AND METHOD

This thesis work was studied in Synthetic Chemistry Laboratory, School of Science and Technology, Nottingham Trent University, Nottingham, United Kingdom.

Synthesized compounds in experimental chapter were divided into 4 sections as follows;

2.1. Preparation of Potassium Dibenzoates

2.2. Preparation of Salts of Naphthalaldehydic acid

2.3. Preparation of 6H-benzo[c]chromen-6-ol via Suzuki Coupling Reaction

2.4. Preparation of Salts from 6H-benzo[c]chromen-6-ol

Solution NMR spectra were measured either on a Jeol ECLIPSE 400 spectrometer at 400 MHz for ^{1}H and at 100.6 MHz for ^{13}C or Bruker Topspin spectrometer at 300 MHz for ^{1}H and at 75.5 MHz for ^{13}C, and measured in p.p.m. downfield from TMS with coupling constants reported in Hz. FT-IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR Spectrometer using Attenuated Total Reflection sampling and are reported in cm^{-1}. Chemical analysis data were obtained from Mr. Stephen Boyer, London Metropolitan University. X-ray diffraction datasets were measured either on an Oxford Diffraction Xcalibur diffractometer equipped with a Sapphire detector and an Oxford Cryosystems 700 series Cryostream low temperature system at Nottingham Trent University, or at the UK National Crystallography Service (NCS) at Southampton University.

Melting points of the compounds were determinated using a Stuart SMP30 melting point apparatus.

2.1. Preparation of Potassium Dibenzoates

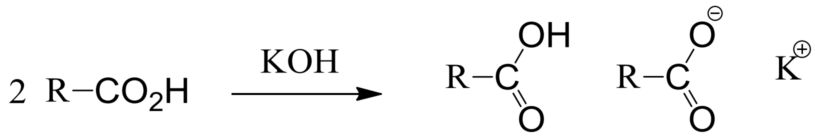
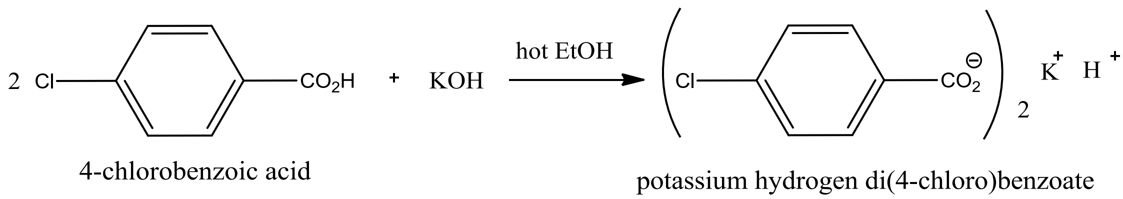


Figure 2.1. General synthesis of potassium dibenzoate compounds

2.1.1. Preparation of Potassium hydrogen di(4-chloro)benzoate



(47)

Figure 2.2. Synthesis of potassium hydrogen di(4-chloro) benzoate **(47)**

To a solution of 4-chlorobenzoic acid (2.00 g, 12.8 mmol) in hot ethanol (20 mL) was added 0.5 equivalent KOH solution (0.36 g, 6.4 mmol KOH in 4 mL water). The mixture was heated while it was stirring. The white crystals were rapidly formed on cooling, they were filtered, washed with ethanol and ether to give potassium hydrogen di(4-chloro)benzoate, as white crystals (1.78 g, 79%).

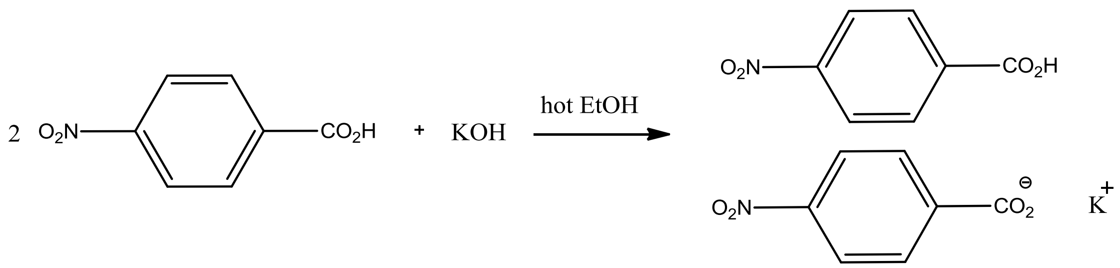
Table 2.1. Experimental results of potassium hydrogen di(4-chloro)benzoate **(47)**

Molecular Formula :	$C_{14}H_9Cl_2KO_4$
Molecular Weight	**:** 351.22 g/mol
Product Weight	**:** 1.78 g
Yield	**:** 79%
Melting Point	**:** >390 ºC
Solubility	**:** MeOH, DMF, DMSO
FT-IR γ_{max}(cm^{-1})	**:** 3060, 1694, 1588, 1570, 1489, 1401, 1286, 1216, 1134, 1112, 1093, 852, 810, 767, 686.
^{1}H NMR δ_H (400 MHz, CD_3OD, 24 ºC):	7.95 (2H, d, *J* = 8.75 Hz, Ar-H_2), 7.41 (2H, d, *J*=8.75 Hz, Ar-H_2).

^{13}C NMR δC (75.5 MHz, CD_3OD, 24 ºC): 171.5 (CO_2^-), 138.7, 134.4, 132.1, 129.3.

Recrystallization: The crystals were dissolved in water with heating. Drops of EtOH were added to the cooled solution (0 ºC) until it went cloudy. Then, it was heated and left to cool again. It started to be cloudy and it was left to crystallize.

2.1.2. Preparation of Potassium di(4-nitro)benzoate



4-nitrobenzoic acid

potassium di(4-nitro)benzoate

(48)

Figure 2.3. Synthesis of potassium di(4-nitro)benzoate **(48)**

To a solution of 4-nitrobenzoic acid (2.00 g, 12 mmol) in hot ethanol (20 mL) was added 0.5 equivalent KOH solution (0.33 g, 6 mmol KOH in 4 mL water). The mixture was stirred and crystals were rapidly formed on cooling, the crystals were filtered and washed with ethanol and ether to give potassium di(4-nitro)benzoate as white crystals (1.38 g, 62%).

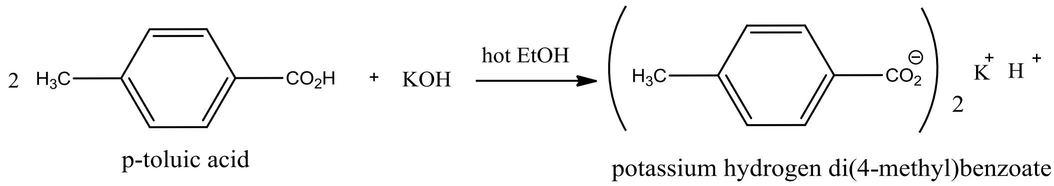
Table 2.2. Experimental results of potassium di(4-nitro)benzoate **(48)**

Molecular Formula :	$C_{14}H_{10}KN_2O_8$
Molecular Weight	**:** 373.34 g/mol
Product Weight	**:** 1.38 g
Yield	**:** 62 %
Melting Point	**:** 271-273ºC
Solubility	**:** DMF, DMSO
FT-IR γ_{max}(cm^{-1})	**:** 3111, 3094, 2445, 1912, 1686, 1629, 1579, 1519, 1382, 1342,

1303, 1287, 1274, 1165, 1134, 1103, 1014, 875, 858, 836, 791, 716, 693.
^{1}H NMR δ_H (400 MHz, CD_3OD, 24 ºC): 8.27 (2H, d, J = 9 Hz, Ar-H_2), 8.17 (2H, d, J = 9 Hz, Ar-H_2).
^{13}C NMR δ_C (75.5 MHz, CD_3OD, 24 ºC): 170.3 (CO_2^-), 151.1, 141.7, 131.6, 124.2.

Recrystallization Process: EtOH was added to the crystals and heated until they dissolve. Then solution was left cooling to crystallize. The crystals were filtered, washed with EtOH and Et_2O.

2.1.3. Preparation of Potassium hydrogen di(4-methyl)benzoate



(49)

Figure 2.4. Synthesis of potassium hydrogen di(4-methyl)benzoate **(49)**

To a solution of *p*-toluic acid (2.00 g, 14.7 mmol) in ethanol (20 mL) was added 0.5 equivalent KOH solution (0.41 g, 7.3 mmol KOH in 4 mL water). The mixture was heated, stirred and left to cool. White crystals were formed. They were filtered and washed with ethanol and ether to give potassium di(4-methyl)benzoate (1.10 g, 49 %).

Recrystallization Process: The crystals were dissolved in water with heating. The solution was cooled to 0 ºC until it went cloudy and it was left to crystallize.

Table 2.3. Experimental results of potassium hydrogen di(4-methyl)benzoate **(49)**

Molecular Formula	**:**	$C_{16}H_{15}KO_4$
Molecular Weight	**:**	310.39 g/mol
Product Weight	**:**	1.10 g
Yield	**:**	49 %
Melting Point	**:**	>390 ºC

Solubility	**:** DMF, DMSO, MeOH, CH_3COOH
FT-IR γ_{max}(cm^{-1})	**:** 3064, 3034, 3012, 2865, 1693, 1608, 1572, 1371, 1293, 1183, 1136, 1116, 1097, 961, 852, 756, 688.

^{1}H NMR δ_H (400 MHz, CD_3OD, 24 °C): 7.87 (2H, d, J = 8.3 Hz, Ar-H_2), 7.23 (2H, d, J = 8.3 Hz, Ar-H_2), 2.38 (3H, s, CH_3).
^{13}C NMR δ_C (75.5 MHz, CD_3OD, 24 °C): 173.0 (CO_2^-), 143.2, 132.8, 130.6, 130.0, 21.5 (CH_3).

2.1.4. Attempted Preparation of *m*-Toluic acid Salt

To a solution of *m*-toluic acid (1.00 g, 7.3 mmol) in hot ethanol (3 mL) was added 0.5 equivalent KOH solution (0.21 g, 3.7 mmol KOH in 2 mL water). The mixture was heated, stirred and left to cool. White crystals of *m*-toluic acid (0.37 g, 74 % yield) were filtered with water and ether. m.p. 109-112 ºC

Although we aimed to obtain potassium hydrogen di(3-methyl)benzoate via the first reaction below (Figure 2.5.), the second reaction below (Figure 2.6.) occured which resulted to obtain *m*-toluic acid as a starting material.

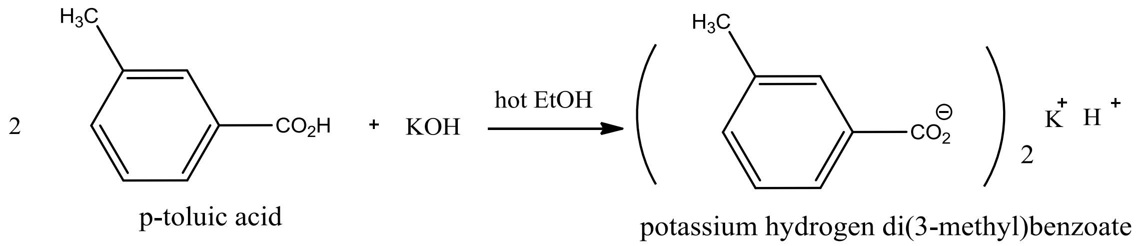


Figure 2.5. Attempted synthesis of potassium hydrogen di(3-methyl)benzoate

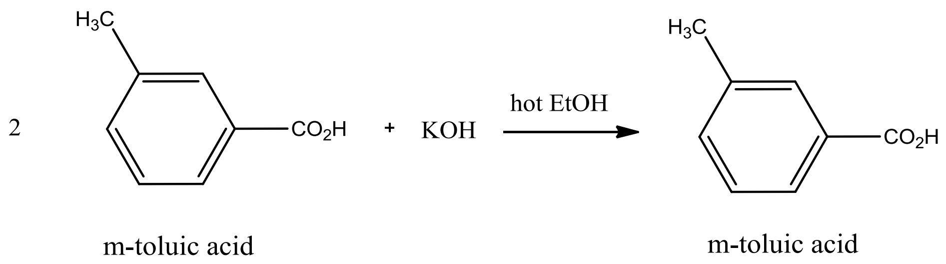
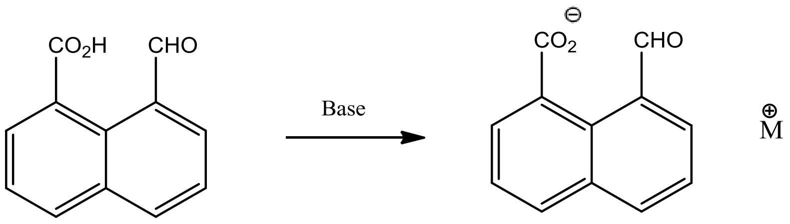


Figure 2.6. The reaction of *m*-toluic acid and KOH gave the starting material as a final product

2.2. Preparation of Salts of Naphthalaldehydic acid



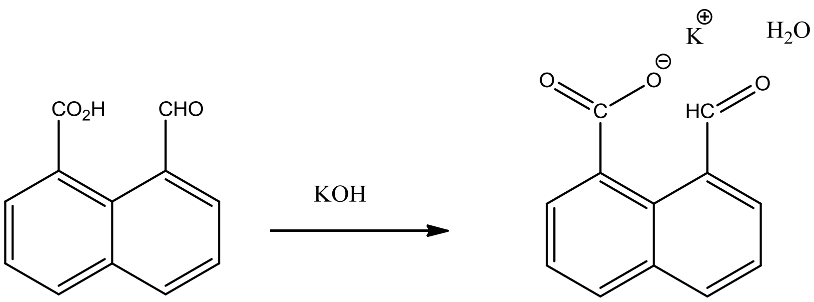
1,8-naphthalaldehydic acid metal salt of naphthalaldehydic acid

Base= KOH

Base= $LiOH.H_2O$

Figure 2.7. General synthesis of salts of naphthalaldehydic acid

2.2.1. Preparation of Potassium Salt of Naphthalaldehydic acid



1,8-naphthalaldehydic acid potassium 8-formyl-1-naphthoate hydrate

(50)

Figure 2.8. Synthesis of potassium 8-formyl-1-naphthoate hydrate **(50)**

To a solution of KOH (0.14 g, 2.5 mmol KOH in 2 mL water) was added 1 equivalent 1,8-naphthalaldehydic acid (0.5 g, 2.5 mmol). The mixture was stirred and left for crystallization. However, the crystals did not form, it was just a solution. The solvent was evaporated, but there were no crystals. Isopropanol was added to the solution until a precipitate formed. The white crystals were filtered under vacuum and washed with isopropanol and diethyl ether to give potassium salt of naphthalaldehydic acid (0.15 g, 23 %).

Table 2.4. Experimental results of potassium 8-formyl-1-naphthoate hydrate **(50)**

Molecular Formula : $C_{12}H_7O_3K.H_2O$

Molecular Weight : 256.29 g/mol

Product Weight : 0.15 g

Yield : 23 %

Melting Point : The molecule decomposes at 290ºC

Solubility : DMF, DMSO, MeOH, CH_3COOH

FT-IR γ_{max}(cm^{-1}) : 3389 br, 3053, 2896, 1677, 1619, 1596, 1578, 1559, 1426, 1407, 1375, 1340, 1240, 1217, 1203, 1167, 1102, 1081, 1015, 972, 956, 931, 845, 828, 794, 783, 759, 687.

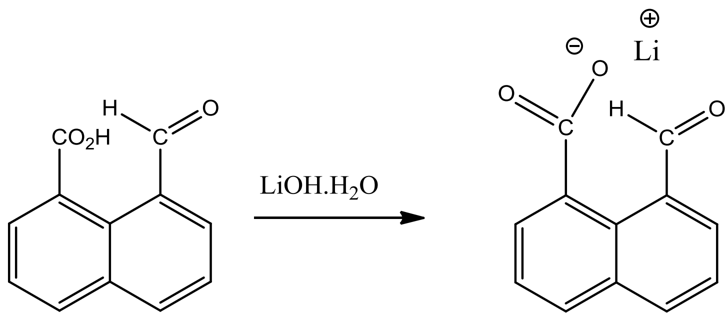
^{1}H NMR δ_H (300 MHz, CH_3OD, 24 ºC): 10.47 (1H, s, C*H*O), 8.13 (1H, dd, *J* = 8.28 and 1.30 Hz, Ar-H_1), 8.00 (1H, dd, *J* = 7.05 and 1.37 Ar-H_1), 7.98 (1H, dd, *J* = 7.96 and 1.23 Hz, Ar-H_1), 7.89 (1H, dd, *J* = 8.45 and 1.33 Hz, Ar-H_1), 7.60 (1H, t, *J* = 8.97 Hz, Ar-H_1), 7.57 (1H, t, *J* = 8.25 Hz, Ar-H_1).

^{13}C NMR δ_C (75.5 MHz, CH_3OD, 24 ºC): 192.7 (*C*HO), 178.9 (*C*O_2^-), 138.6, 135.9, 135.7, 135.2, 130.7, 129.4, 129.2, 128.6, 127.0, 126.1.

Elemental Analysis Found C: 56.34%, H: 3.64%

$C_{12}H_7O_3K.H_2O$ requires C: 56.24%, H: 3.54%.

2.2.2. Preparation of Lithium Salt of Naphthalaldehydic acid



1,8-naphthalaldehydic acid

lithium 8-formyl-1-naphthoate

(51)

Figure 2.9. Synthesis of lithium 8-formyl-1-naphthoate **(51)**

To a solution of 1,8-naphthalaldehydic acid (2.5 mmol 0.5 g) in methanol (6 mL) was added 1 equivalent $LiOH.H_2O$ solution (2.5 mmol, 0.11 g $LiOH.H_2O$ in 2 mL water). The mixture was heated, stirred and left to cool for crystallization. Pale fawn crystals (0.39 g, 76%) were obtained. The reaction was also carried out using ethanol instead of methanol.

Table 2.5. Experimental results of lithium 8-formyl-1-naphthoate **(51)**

Molecular Formula : $C_{12}H_7LiO_3$

Molecular Weight : 206.12 g/mol

Product Weight : 0.39 g

Yield : 76 %

Melting Point : The molecule decomposes at 328 ºC

Solubility : DMF, DMSO, MeOH

FT-IR γ_{max}(cm^{-1}) : 3050, 2875, 1674, 1617, 1582, 1564, 1503, 1426, 1415, 1390, 1352, 1342, 1244, 1205, 1172, 1150, 1105, 1088, 1012, 963, 926, 851, 830, 794, 782, 755, 692.

^{1}H NMR δ_H (300 MHz, CH_3OD, 24 ºC): 10.26 (1H, s, C*H*O), 8.23 (1H, dd, *J* = 8.23 and 1.24 Hz, Ar-H_1), 7.97-8.01 (2H, m, Ar-H_2), 7.91 (1H, dd, *J* = 7.11 and 1.29 Hz, Ar-H_1), 7.60 (1H, t, *J* = 8.18 Hz, Ar-H_1), 7.57 (1H, t, *J* = 8.18 Hz, Ar-H_1).

^{13}C NMR δ_C (75.5 MHz, CH_3OD, 24 ºC): 192.4 (*C*HO), 178.9 (*C*O_2^-), 138.5, 135.9, 135.6, 135.2, 130.7, 129.3, 129.2, 128.6, 127.0, 126.1.

Elemental Analysis: Found C: 70.03%, H: 3.34%.

$C_{12}H_7O_3Li$ requires C: 69.92%, H: 3.42%.

2.2.3. Reaction with Morpholine

Preparation of 3-(N-morpholinyl)-1H,3H-benzo[de]isochromen-1-one

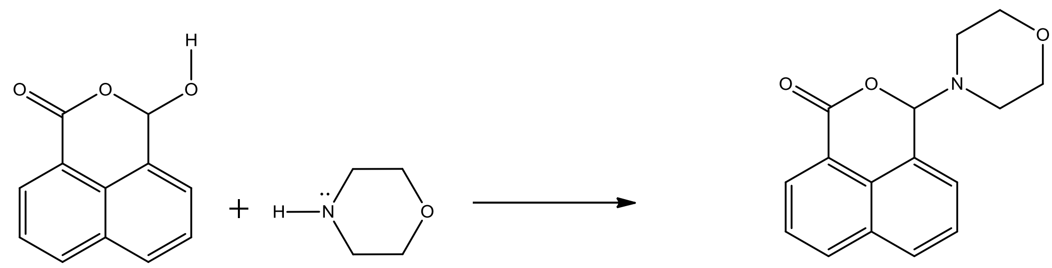


Figure 2.10. Synthesis of 3-(N-morpholinyl)-1H,3H-benzo[de]isochromen-1-one **(52)**

To a solution of 1,8-naphthalaldehydic acid (2.5 mmol, 0.50 g) in hot methanol (6 mL) was added 1 equivalent morpholine (2.5 mmol, 0.22 mL). The reaction mixture was stirred and left to cool for crystallization. The white crystals of **(52)** (0.41 g, 61 %) were filtered and washed with diethyl ether.

Table 2.6. Experimental results of 3-(N-morpholinyl)-1H,3H-benzo[de]isochromen-1-one **(52)**

Molecular Formula :	$C_{16}H_{15}NO_3$
Molecular Weight	**:** 269.29 g/mol
Product Weight	**:** 0.41 g
Yield	**:** 61 %
Melting Point	**:** 158-160 ºC
Solubility	**:** $CHCl_3$, CH_2Cl_2, THF, DMF, DMSO, CH_3COOH
FT-IR γ_{max}(cm^{-1})	**:** 2847, 1698, 1585, 1510, 1390, 1356, 1337, 1317, 1300, 1254, 1234, 1192, 1181, 1135, 1117, 1090, 1069, 1036, 973, 934, 879, 860, 848, 820, 809, 792, 772, 738.
^{1}H NMR δ_H (400 MHz, $CDCl_3$, 24 ºC) :	8.44 (1H, d, J = 7.3 Hz, Ar-H_1), 8.11 (1H, d, J = 8.2 Hz, Ar-H_1), 7.91 (1H, d, J = 8.2 Hz, Ar-H_1), 7.70 (1H, d, J = 6.8 Hz, Ar-H_1), 7.64-7.59 (2H, m, Ar-H_2), 6.50 (1H, s, CH(N)O), 3.69 (4H, t, J = 4.8 Hz,

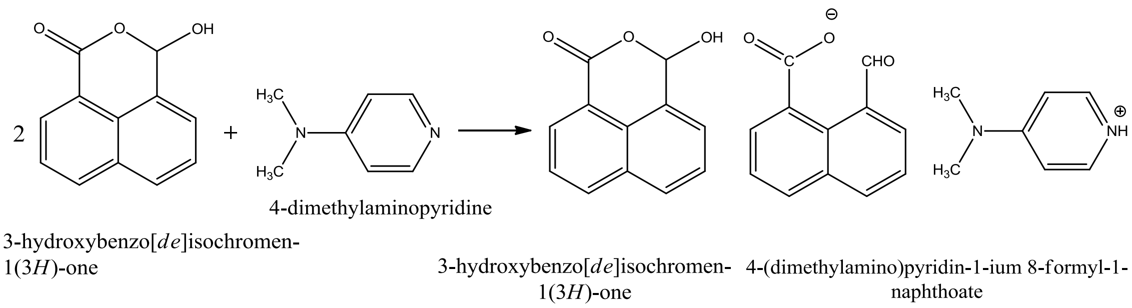
J = 4.8 Hz, 2 x CH_2O), 2.94 -2.77 (4H, m, 2 x CH_2N)

^{13}C NMR δ_C (100.5 MHz, CDCl$_3$, 24 ºC): 164.7 (C=O), 133.6, 132.0, 129.6, 128.9, 128.2, 127.5, 126.7, 126.3, 125.5, 120.1, 97.3 (C(N)O), 66.9 (2 x CH$_2$O), 47.2 (2xCH$_2$N).

2.2.4. Reaction with Pyrrolidine

To a solution of 1,8-Naphthalaldehydic acid (0.5 g) in hot methanol (6 mL) was added 1 equivalent pyrrolidine (0.0025 mol, 0.21 mL). The reaction mixture was stirred and left to cool for crystallization, but only a powder was obtained. m.p. 144-145 ºC

2.2.5. Preparation of Salt mixture of 3-hydroxybenzo[de]isochromen- 1(3H)-one, 4-(dimethylamino)pyridin-1-ium and 8-formyl-1-naphthoate



(53)

Figure 2.11. Synthesis of salt mixture of 3-hydroxybenzo[de]isochromen- 1(3H)-one, 4-(dimethylamino)pyridin-1-ium and 8-formyl-1-naphthoate **(53)**

To a solution of 1,8-naphthalaldehydic acid (2.5 mmol, 0.5 g) in hot methanol (6 mL) was added 1 equivalent 4-dimethylaminopyridine (2.5 mmol, 0.31 g). The reaction mixture was stirred and left to cool for crystallization. After 1 hour, some crystals grew up. However, the crystals were very small. More methanol was added, the solution was heated and left to cool. The following day, no crystals were appeared. Methanol was evaporated, then drops of ether and methanol were added and left for crystallization. Then more ether was added the flask and scratched with a glass rod. The pale fawn crystals of **(53)** were appeared (0.30 g, 23 %). They were filtered and washed with ether.

Table 2.7. Experimental results of salt mixture of 3-hydroxybenzo[de]isochromen-1(3H)-one, 4-(dimethylamino)pyridin-1-ium and 8-formyl-1-naphthoate **(53)**

Molecular Formula : $C_{31}H_{26}N_2O_6$

Molecular Weight : 522.55 g/mol

Product Weight : 0.30 g

Yield : 23 %

Melting Point : 131-133 ºC

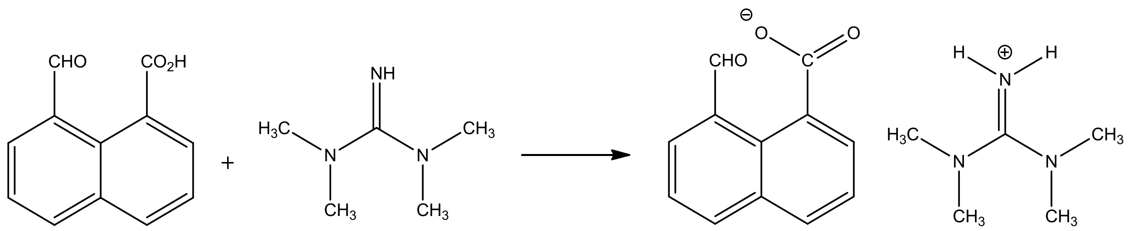
Solubility : $CHCl_3$, CH_2Cl_2, DMF, DMSO, EtOH, MeOH, CH_3CN

FT-IR γ_{max}(cm^{-1}) : 1713, 1681, 1646, 1559, 1516, 1506, 1484, 1443, 1431, 1394, 1374, 1347, 1336, 1316, 1214, 1175, 1092, 1077, 1067, 989, 955, 928, 841, 826, 810, 774, 758, 743, 732, 682, 654.

^{1}H NMR δ_H (300 MHz, $CDCl_3$, 24 ºC) : 8.41 (1H, dd, J = 7.22 and 1.13 Hz, Ar-H_1), 8.11 – 8.14 (3H, m, 2-,6-*H*(DMAP) + Ar-H_1), 7.94 (1H, br d, J = 8.15, Ar-H_1), 7.73 (1H, br d, J = 7.04 Hz, Ar-H_1), 7.60 -7.67 (2H, m, Ar-H_2), 7.10 (1H, s, CH(O)(OH)), 6.47 (2H, dd, J = 5.24 and 1.30 Hz, 3-,5-*H*(DMAP), 4.90 (1H, br s, OH), 3.01 (6H, s, $N(CH_3)_2$).

^{13}C NMR δ_C (75.5 MHz, $CDCl_3$, 24 ºC): 164.6 (*C*=O), 154.7, 148.1, 133.5, 132.0, 130.1, 129.8, 128.6, 127.5, 126.6, 126.3, 125.4, 120.7, 106.5, 100.7 (*C*(O)(OH), 39.1 (DMAP).

2.2.6. Preparation of Salt mixture of bis(dimethylamino)methaniminium and 8-formyl-1-naphthoate



1,8-naphthalaldehydic acid 1,1,3,3-tetramethylguanidine bis(dimethylamino)methaniminium 8-formyl-1-naphthoate

(54)

Figure 2.12. Synthesis of salt mixture of bis(dimethylamino)methaniminium and 8-formyl-1-naphthoate **(54)**

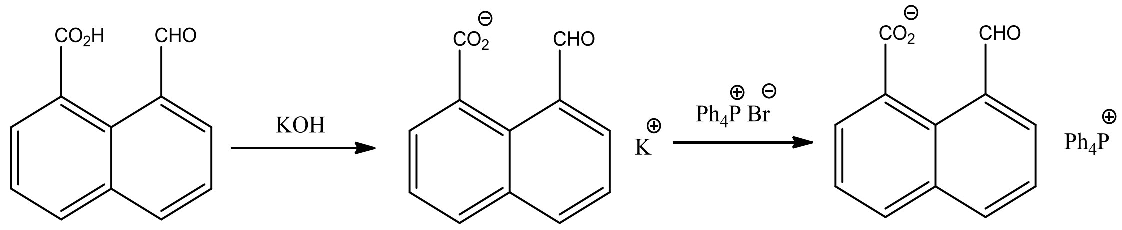
To a solution of 1,8-naphthalaldehydic acid (2.5 mmol, 0.5 g) in THF (5 mL) was added 1 equivalent 1,1,3,3-tetramethylguanidine (2.5 mmol, 0.32 mL). The reaction mixture was stirred and left for crystallization. It was slowly crystalised at room temperature. 0.19 g caramel colour crystals of **(54)** were obtained (0.19 g, 24 %).

Table 2.8. Experimental results of salt mixture of bis(dimethylamino)methaniminium and 8-formyl-1-naphthoate **(54)**

Molecular Formula :	$C_{17}H_{21}N_3O_3$
Molecular Weight :	315. 37 g/mol
Product Weight :	0.19 g
Yield :	24 %
Melting Point :	116-118 ºC
Solubility :	$CHCl_3$, CH_2Cl_2, THF, DMF,DMSO, EtOH,MeOH,CH_3CN
FT-IR γ_{max}(cm^{-1}) :	2934 br, 1683, 1596, 1559, 1502, 1469, 1453, 1428, 1405, 1374, 1359, 1348, 1334, 1260, 1240, 1210, 1099, 1061, 1034, 955, 881, 844, 778, 755, 717, 682.
^{1}H NMR δ_H (300 MHz, $(CD_3)_2CO$, 24 ºC) :	8.08 (1H, dd, J = 7.10 and 1.32 Hz, Ar-H_1), 7.94 (1H, dd, J = 8.22 and 1.25 Ar-H_1), 7.88 (2H, br d, J = 8.28, Ar-H_2), 7.51 (1H, dd, J = 7.13 and 7.13 Hz, Ar-H_1).

^{13}C NMR δ_C (75.5 MHz, $(CD_3)_2CO$, 24 ºC): 172.0 (CO_2^-), 164.3 (N_2C=N), 164.0, 135.2, 134.9, 134.6, 132.4, 130.8, 129.3, 128.9, 127.0, 126.7, 126.0, 39.8 (2 x N-$(CH_3)_2$).

2.2.7. Preparation of Tetraphenylphosphonium 8-formyl-1-naphthoate



1,8-naphthalaldehydic acid | potassium 8-formyl-1-naphthoate | tetraphenylphosphonium 8-formyl-1-naphthoate

(55)

Figure 2.13. Synthesis of tetraphenylphosphonium 8-formyl-1-naphthoate (**55)**

To a solution of KOH (2.5 mmol, 0.14 g) in water (20 mL) was added 1 equivalent 1,8-naphthalaldehydic acid (2.5 mmol, 0.5 g). Then, 1 equivalent tetraphenylphosphonium bromide (0.0025 mmol, 1.05 g) was added to the reaction mixture. It was stirred for 1 hour at room temperature. After 1 hour, the mixture was extracted with CH_2Cl_2 (35 mL x 2 times). The organic layer was collected, then dried (Na_2SO_4) and evaporated to yield a fawn soft solid of **(55)** (0.80 g, 59 %).

Table 2.9. Experimental results of tetraphenylphosphonium 8-formyl-1-naphthoate **(55)**

Molecular Formula :	$C_{36}H_{27}O_3P$
Molecular Weight :	538.57 g/mol
Product Weight :	0.80 g
Yield :	59 %
Melting Point :	75-80ºC
Solubility :	$CHCl_3$, CH_2Cl_2, DMF, DMSO, EtOH, MeOH, CH_3CN,

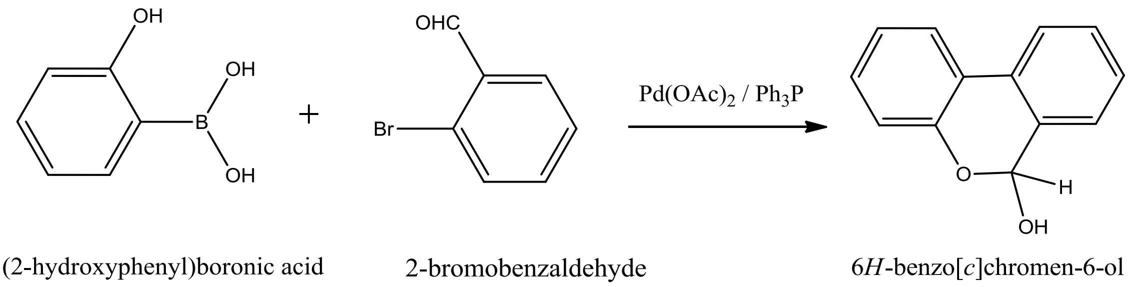
isopropanol, CH_3COOH

FT-IR γ_{max}(cm^{-1}) : 3417, 3062, 1710, 1683, 1615, 1586, 1576, 1563, 1515, 1484, 1436, 1410, 1375, 1337, 1259, 1241, 1105, 1081, 1068, 1027, 995, 957, 926, 846, 816, 784, 758, 719, 687.

^{1}H NMR δ_H (300 MHz, $CDCl_3$, 24 ºC): 8.53 (1H, s, CHO), 8.16 (1H, dd, J = 7.15 and 1.25 Hz, Ar-H_1), 7.92 (1H, dd, J = 8.3, 1.2 Hz, Ar-H_1), 7.88 (6H, m, 4 x *para*-Ph-*H*, Ar-H_2), 7.77 (8H, m, 4 x *meta*-Ph-*H*), 7.61 (8H, m, 4 x *ortho*-Ph-*H*), 7.49 (2H, m, Ar-H_2), 2.89 (4H, br, 2 x H_2O).

^{13}C NMR δ_C (100.5 MHz, $CDCl_3$, 24 ºC): 170.2 (CO_2^-), 135.8 (d, $J_{C,P}$ = 3.0 Hz, para-C), 134.3 (d, $J_{C,P}$ = 10.2 Hz, *meta*-*C*), 130.8 (d, $J_{C,P}$ = 12.8 Hz, *ortho*-*C*), 117.4 (d, $J_{C,P}$ = 88.5 Hz, *ipso*-*C*).

2.3. Preparation of 6H-benzo[c]chromen-6-ol via Suzuki Coupling Reaction

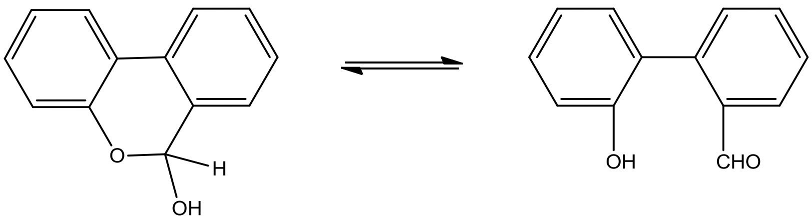


(56)

Figure 2.14. Synthesis of 6H-benzo[c]chromen-6-ol **(56)**

To a 250 mL round bottomed flask (equipped with a magnetic stir bar and condenser) was added 2-hydroxyphenylboronic acid (7.2 mmol, 1.00 g), 2-bromobenzaldehyde (7.2 mmol, 0.85 mL), palladium acetate (0.06 mmol,14 mg), triphenylphosphine (0.19 mmol, 50 mg), n-propanol (20 mL), 2 M Na_2CO_3 (6.5 mL) mixed with distilled water (4 mL). The reaction was heated to reflux under nitrogen environment. It was left to stir for 5 hours at 120 ºC. The reaction was followed by TLC. After 5 hours, the reaction's colour was yellow. The reaction was cooled to room temperature and diluted with ethyl acetate (100 mL). It was transferred to a separating funnel and an organic layer (cloudy-beige colour) and aqueous layer (dark green emulsion) were separated with ethyl acetate (50 mL). Organic extracts were collected and dried with Na_2SO_4, and evaporated under reduced pressure to give a dark orange oil (1.53 g). This was purified by columm chromatography (SiO_2, 5:1 cyclohexane/EtOAc) to yield **(56)** as a white solid (1.10 g, 77 %).

There is an equilibrium between 6H-benzo[c]chromen-6-ol and 2'-hydroxy-[1,1'-biphenyl]-2-carbaldehyde at room temperature (Figure 2.15).



6*H*-benzo[*c*]chromen-6-ol　　　　2'-hydroxy-[1,1'-biphenyl]-2-carbaldehyde

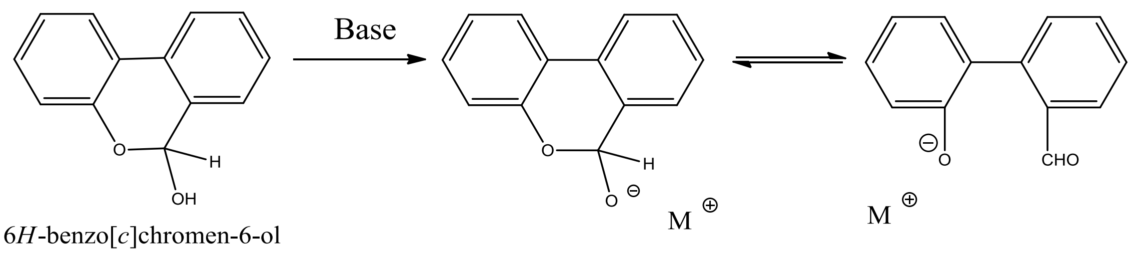
(56)　　　　**(57)**

Figure 2.15. Equilibrium between compound **(56)** and **(57)**

Table 2.10. Experimental results of 6H-benzo[c]chromen-6-ol **(56)**

Molecular Formula :	$C_{13}H_{10}O_2$
Molecular Weight	**:** 198.22 g/mol
Product Weight	**:** 1.10 g
Yield	**:** 77 %
Melting Point	**:** 87-89 ºC
Solubility	**:** $CHCl_3$, CH_2Cl_2, THF, DMF, DMSO, CH_3OH, CH_3COOH
FT-IR γ_{max}(cm^{-1})	**:** 3443 br, 1609, 1598, 1458, 1598, 1446, 1489, 1427,1301,1247,1195, 1159,1030,1131,1100, 1050,1010, 983, 940, 880, 858, 848, 811, 756, 748,730, 716, 704.
^{1}H NMR δ_H (300 MHz, $(CD_3)_2CO$):	7.92-7.96 (2H, d x d, Ar-H_2), 7.36-7.52 (3H, m, Ar-H_3), 7.29 (1H, t, Ar-H_1), 7.09 (1H, t, Ar-H_1), 7.02 (1H, d, Ar-H_1), 6.41 ((1H, d, Ar-H_1), 6.21 (1H, s, CHO_2).
^{13}C NMR δ_C 100 MHz, $(CD_3)_2CO$):	152.5, 133.5, 130.1, 129.9, 129.6, 128.5, 127.1, 123.9, 122.7, 122.6, 122.5, 119.2, 93.5 (CHO_2).

2.4. Preparation of the Salts from 6H-benzo[c]chromen-6-ol



Base= Li HMDS, M^+= Base cation= Li^+

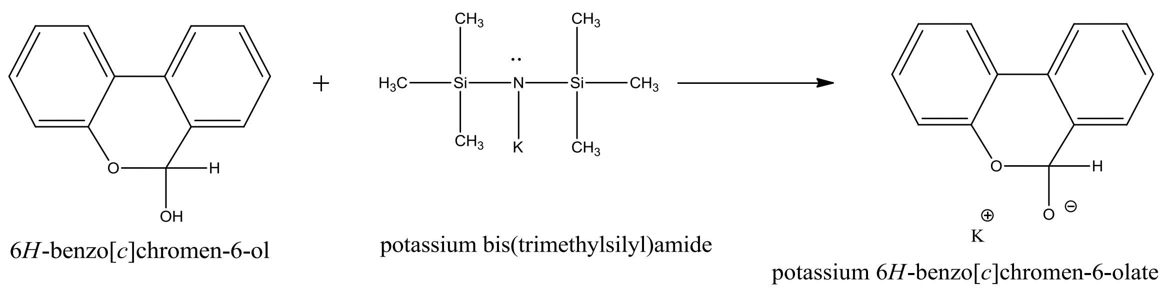
Base= K HMDS, M^+= Base cation= K^+

Base= 1,1,3,3-Tetramethylguanidine, M^+= Base cation= $C_5H_{14}N_3^+$

Figure 2.16. General synthesis of the salts from 6H-benzo[c]chromen-6-ol

2.4.1. Preparation of Potassium 6H-benzo[c]chromen-6-olate

To a solution of 6H-benzo[c]chromen-6-ol (0.25 mmol, 50 mg) in THF (2 mL) was added 1 equivalent potassium hexamethyldisilazane solution (0.25 mmol, 0.5 mL). The mixture was stirred at room temperature under nitrogen environment for 1 hour. After 1 hour, the solvent was removed on vacuum. Removal of the solvent under reduced pressure gave a yellow solid.

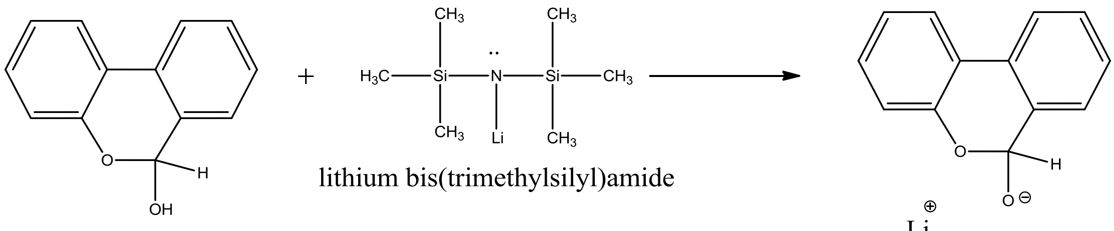


(58)

Figure 2.17. Synthesis of potassium 6H-benzo[c]chromen-6-olate **(58)**

2.4.2. Preparation of Lithium 6H-benzo[c]chromen-6-olate

To a solution of 6H-benzo[c]chromen-6-ol (0.25 mmol, 50 mg) in THF (2 mL) was added 1 equivalent lithium hexamethyldisilazane (0.25 mmol, 43 mg) in THF (2 mL). The reaction mixture was stirred at room temperature under nitrogen environment for 1 hour. After 1 hour, the solvent was removed under high vacuum and on hot water. A fawn waxy solid as **(59)** (30 mg, 33 %) was obtained.



6*H*-benzo[*c*]chromen-6-ol

lithium bis(trimethylsilyl)amide

lithium 6*H*-benzo[*c*]chromen-6-olate

(59)

Figure 2.18. Synthesis of lithium 6H-benzo[c]chromen-6-olate **(59)**

Table 2.11. Experimental results of lithium 6H-benzo[c]chromen-6-olate **(59)**

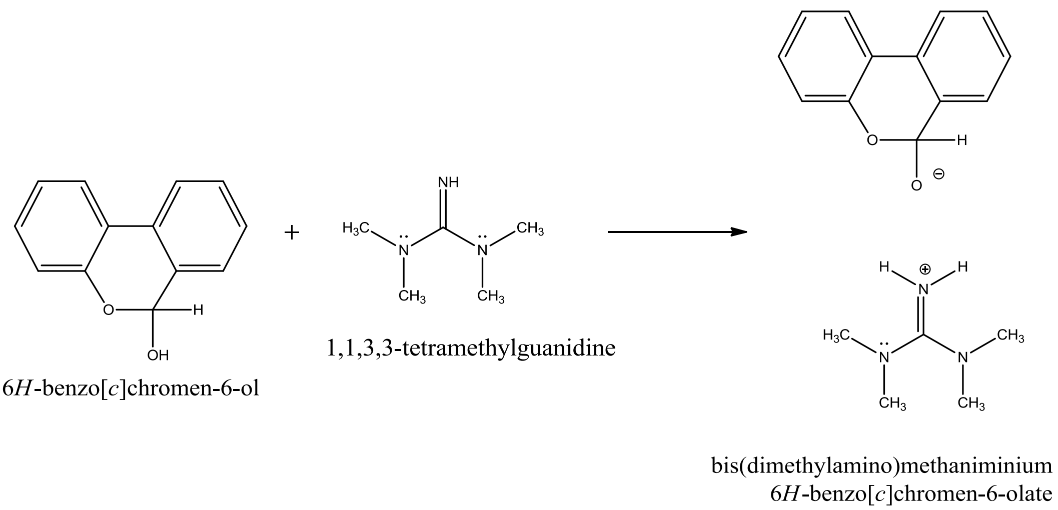
Molecular Formula	: $C_{19}H_{28}LiNO_2Si_2$
Molecular Weight	: 365.54 g/mol
Product Weight	: 0.03g
Yield	: 33 %
Melting point	: 219-222 ºC

^{1}H NMR δ_H (400 MHz, $(CD_3)_2CO$): 7.81 (1H, dd, J = 7.78, 1.50 Hz, Ar-H_1), 7.78 (1H, d, J = 7.51 Hz, Ar-H_1), 7.36 (1H, dt, J = 7.50, 1.40 Hz, Ar-H_1), 7.28 (1H, dt, J = 7.50 and 1.27 Hz, Ar-H_1), 7.18-7.23 (2H, m, Ar-H_2), 7.03 (1H, dt, J = 7.71 and 1.26 Hz, Ar-H_1), 6.87 (1H, dd, J = 8.10 and 0.90 Hz, Ar-H_1), 5.66 (1H, s, CHO_2).

^{13}C NMR δ_C (100 MHz, $(CD_3)_2CO$): 151.8, 133.2, 129.0, 128.3, 127.8, 127.3, 127.0, 124.1, 122.6, 121.6 (doubly degenerate), 117.2, 72.7 (CHO_2).

FT-IR γ_{max}(cm^{-1}) : 1589, 1479, 1456, 1439, 1378, 1295, 1249, 1215, 1171, 1041, 1004, 884, 837, 750, 728, 667.

2.4.3. Preparation of Bis(dimethylamino)methaniminium 6H-benzo[c]chromen-6-olate



(60)

Figure 2.19. Synthesis of bis(dimethylamino)methaniminium 6H-benzo[c]chromen-6-olate **(60)**

To a solution of 2-Hydroxy-biphenyl-2’carbaldehyde (0.25 mmol, 50 mg) in THF (2 mL) was added 1 equivalent 1,1,3,3-Tetramethylguanidine (0.25 mmol, 29 mg, 0.032 mL). The reaction mixture was stirred under nitrogen environment for 48 hours. After 48 hours, a yellow oil was obtained. Ether was added to the flask and scratched with a glass rod. A yellow oil (0.04 g, 51 %) was obtained as a product.

Table 2.12. Experimental results of bis(dimethylamino)methaniminium 6H-benzo[c]chromen-6-olate **(60)**

Molecular Formula :	$C_{18}H_{23}N_3O_2$
Molecular Weight	**:** 313.39 g/mol
Product Weight	**:** 0.04 g
Yield	**:** 51 %
^{13}C NMR δ_C (75 MHz, $(CD_3)_2CO$):	152.5, 133.5, 130.1, 129.9, 129.7, 128.5, 127.1, 123.9, 122.7, 122.6, 122.5, 119.2, 93.7, 39.6.

CHAPTER 3

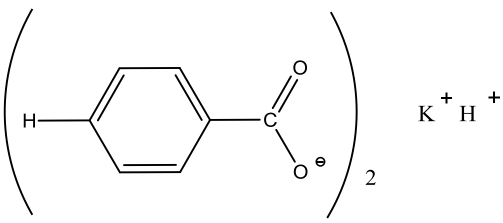
3. RESULTS AND DISCUSSION

We interested in preparing novel compounds which have naphthalene and biphenyl frameworks. We investigated bond formation between the functional groups by X-ray crystallographic measurements. Structures were solved and refined with the SHELXS and SHELXL suites using XSEED interface. Molecular illustrations were made with Mercury.

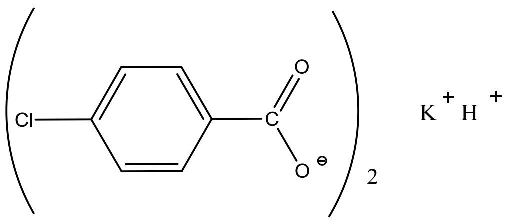
3.1. Potassium Dibenzoates

In earlier studies, the crystal structures and NMR spectra of a series of Group 1A dibenzoates were reported [46]. The potassium hydrogen dibenzoate showed six-coordinate potassium (potassiums were linked by bridging benzoate O atoms), and the labile (O)H atom is involved in a short hydrogen bond. In contrast the corresponding cesium salt showed eight coordinate metal ion, but the labile H atoms is involved in a short hydrogen bond, as well [45].

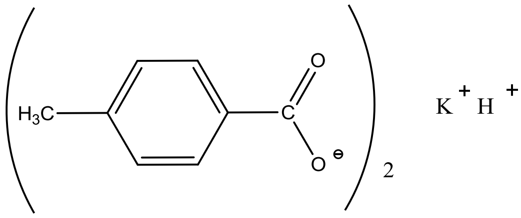
In this thesis work, we investigated 4-methyl, 4-chloro and 4-nitro potassium dibenzoate salts in which the aromatic ring was substituted to provide further examples of tight hydrogen bonding. Thus, we chose the location of the substituents as far from the carboxylic acid group as possible. In this respect, the 4-methyl, 4-chloro and 4-nitrobenzoic acids reacted with 0.5 equivalents of potassium hydroxide in order to obtain their corresponding potassium hydrogen dibenzoates. It was also noted that preparation of potassium hydrogen dibenzoate salt from m-toluic acid was an unsuccessful attempt. NMR data and melting point indicated m-toluic acid as a product. The salt of *m*-toluic acid could not be formed because of the steric effect. The crystal structures of the potassium hydrogen 4-methyl, 4-chloro and 4-nitro-dibenzoates were determined at low temperatures.



(61)



(47)



(49)

Figure 3.1. Molecular structures of potassium hydrogen dibenzoate **(61)**, 4-methyl **(49)** and 4-chloro **(47)** potassium hydrogen dibenzoates

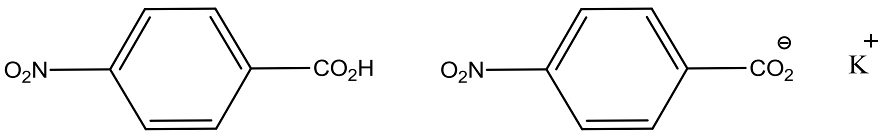


Figure 3.2. Molecular structure of potassium di(4-nitro)benzoate **(49)**

Table 3.1. Selected molecular geometry including hydrogen bonding [45]

Compound	**Potassium hydrogen dibenzoate (61)**	**Potassium hydrogen di(4-methyl)benzoate (49)**	**Potassium hydrogen di(4-chloro)benzoate (47)**	**Potassium hydrogen di(4nitro)benzoate (48)**
O---O /Å	2.456	2.455	2.450	2.521
O-H /Å	0.84(3)	0.80(7)	0.82(4)	0.91(3)
OH---O /Å	1.62	1.66	1.63	1.61
O-H---O /^{o}	173.96	166.1	166.0	177.4
C=O / Å	1.244(2)	1.241(5)	1.239(2)	1.218(3)
C-OH	1.293(2)	1.293(5)	1.289(3)	1.314(2)
C-C(O_2H)	1.495(3)	1.494(6)	1.498(3)	1.493(3)

All of the compounds show hydrogen bonding. There are similar hydrogen bonding situations in unsubstituted, *para* methyl and chloro dibenzoates, with a proton lying between two centrosymmetrically related O atoms which are 2.450 to 2.456 Å apart. The 4-nitro case is quite different. There is a hydrogen bond between the 4-nitrobenzoic acid and 4-nitrobenzoate anion, with O---O separation of 2.521 Å which is longer than the other three structures. The structure of the 4-methyl and chloro compounds allow hydrogen bonding easier than 4-nitro compound.

Table 3.2. Crystal data for potassium hydrogen 4-methyl **(49)**, 4-chloro **(47)** and 4-nitro **(48)** dibenzoates [45,46]

Compound	Unsubstituted **(61)**	4-methyl **(49)**	4-chloro **(47)**	4-nitro **(48)**
Formula	$C_7H_5O_2.C_7H_6O_2.K$	$C_8H_7O_2.C_8H_8O_2.K$	$C_7H_4O_2Cl.C_7H_5O_2Cl.$ K	$C_7H_4NO_4.C_7H_5NO_4.K$
M_r	282.33	310.38	351.23	374.35
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
a /Å	29.586(2)	34.015(19)	32.974(9)	39.963(3)
b /Å	3.7964(3)	3.824(2)	3.7735(10)	11.2909(5)
c /Å	11.1214(8)	11.102(6)	11.129(3)	17.1301(11)
α /º	90	90	90	103.990(5)
β /º	97.096(9)	90.849(8)	90.469(4)	90.125(5)
γ /º	90	90	90	92.653(4)
V /Å^3	1239.59(16)	1443.9(14)	1384.7(7)	749.14(8)
ρ /gcm^{-3}	1.513	1.428	1.685	1.660
μ /mm^{-1}	0.435	0.380	0.781	0.405
Space group	*C2/c*	*C2/c*	*C2/c*	*P-1*
Z	4	4	4	2
T (K)	120	100	100	150(2)
No of reflections, no of reflections with I>2σ(I)	1428, 1203	1279, 943	1594, 1426	3392, 2952
Final R (I>2σ(I)), wR (all)	0.0432, 0.1114	0.0773, 0.2050	0.0519, 0.1193	0.0461, 0.1159

The crystal structures of the potassium hydrogen dibenzoates with *para* methyl and chloro groups are similar to the unsubstituted potassium hydrogen dibenzoate. They are all monoclinic in space group C2/c and have similar unit cells. However, the crystal structure of of the *para* nitro potassium dibenzoate is quite different from the others. It is triclinic in space group *P-1* and has a different unit cell. The nitro group of *para* nitro potassium dibenzoate coordinates with potassium. The other dibenzoates do not have that interaction [45].

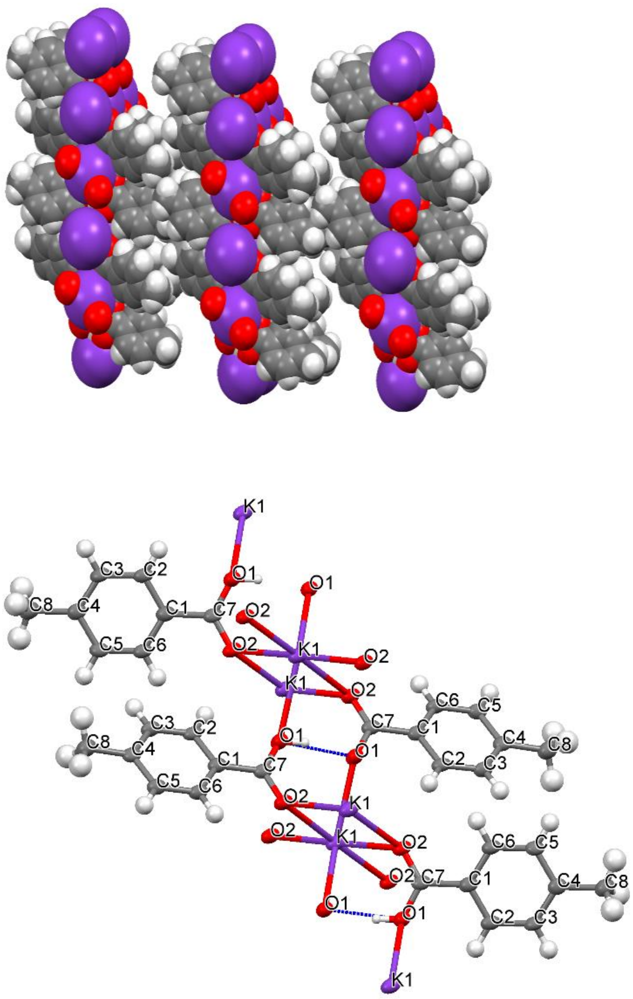


Figure 3.3. Two views of the crystal structure of potassium hydrogen di(4-methyl)benzoate **(49)** [45]

The second picture shows hydrogen bond formation. The benzene rings are so close to each other that there is no place for other groups to substitute in the *ortho* or *meta* position.

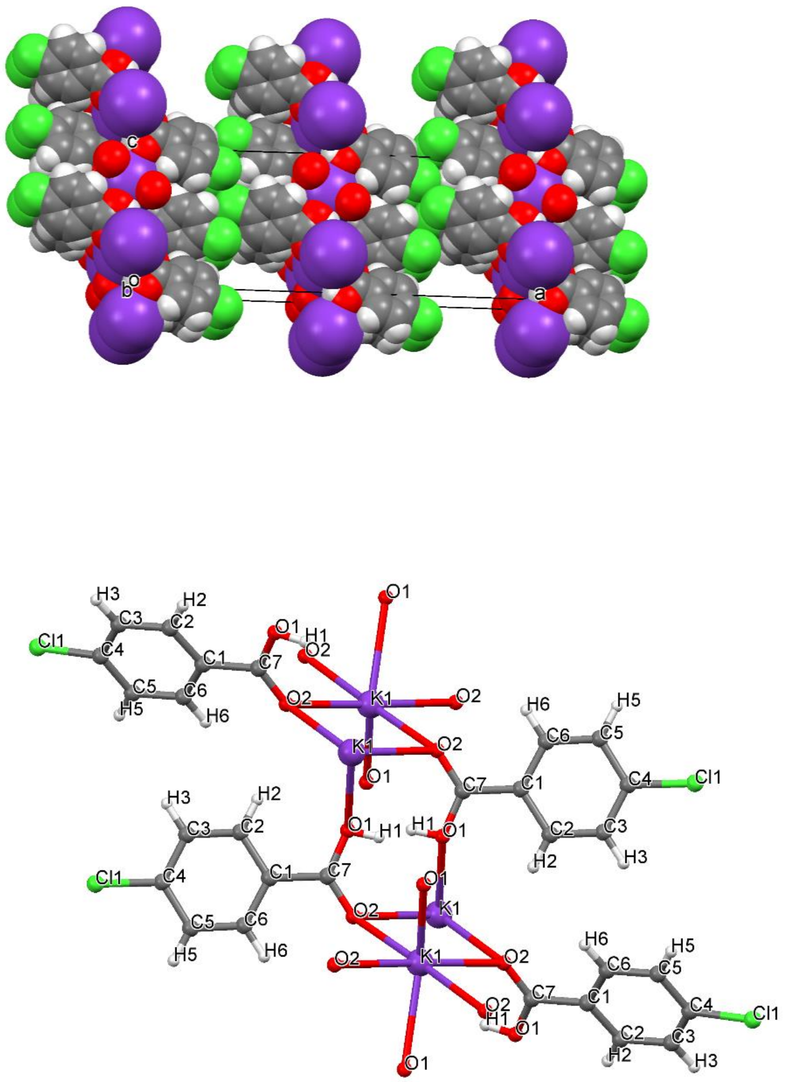


Figure 3.4. Two views of the crystal structure of potassium hydrogen di(4-chloro)benzoate **(47)** [45]

The second picture shows hydrogen bond formation. The benzene rings are so close to each other that there is no place for other groups to substitute in the *ortho* or *meta* position.

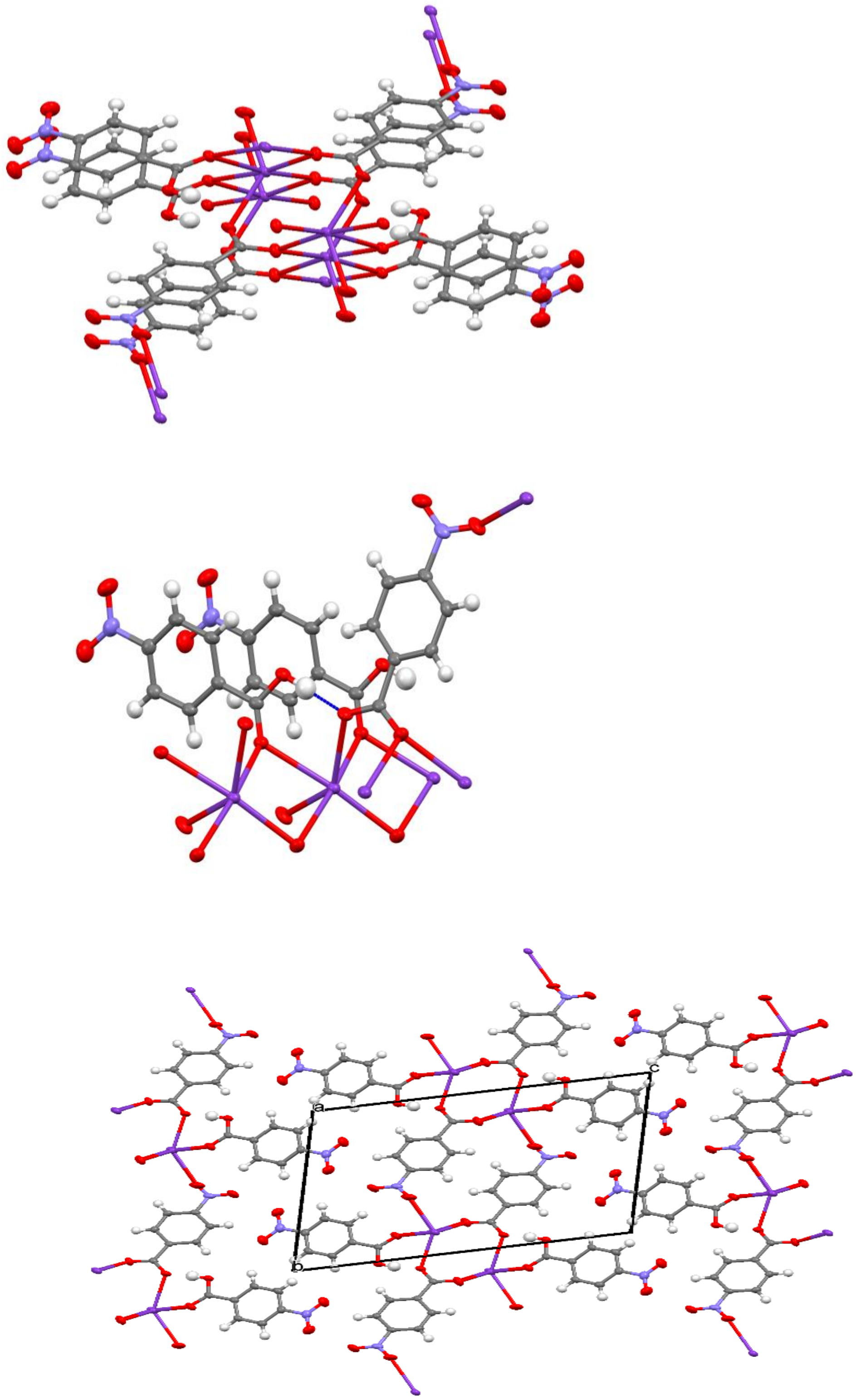


Figure 3.5. Three views of the crystal structure of potassium di(4-nitro)benzoate **(49)** [47]

There is a hydrogen bond between the 4-nitrobenzoic acid and 4-nitrobenzoate anion.

3.2. Metal Salts of 1,8-Naphthalaldehydic acid

We used the anion of naphthalaldehydic acid to look for interactions between the carboxylate anion and the aldehyde group to parallel earlier studies on interactions of amines with carbonyl groups. The acid itself exists in a cyclised form, in which the OH group has added to the carbonyl group. The previous studies on cesium salt showed that the anion existed in a uncyclised form with both a carboxylate and an aldehyde group [47].

In this thesis work, we extended the studies to the potassium salt and the lithium salt. The potassium salt was synthesized from the reaction of 1,8-Naphthalaldehydic acid and KOH solution. The lithium salt was synthesized from the reaction of 1,8-Naphthalaldehydic acid and $LiOH.H_2O$ solution. Both of the crystals were grown from methanol and their crystal structures measured at low temperature [47].

According to the X-ray crystallographic measurements, the potassium salt is very similar to the cesium salt which was studied previously, and surprisingly the potassium ion is eight coordinate, which is quite rare, with six coordinate being more common. The potassium salt is a hydrate with a water molecule included in the crystal structure, as observed for the cesium salt [47].

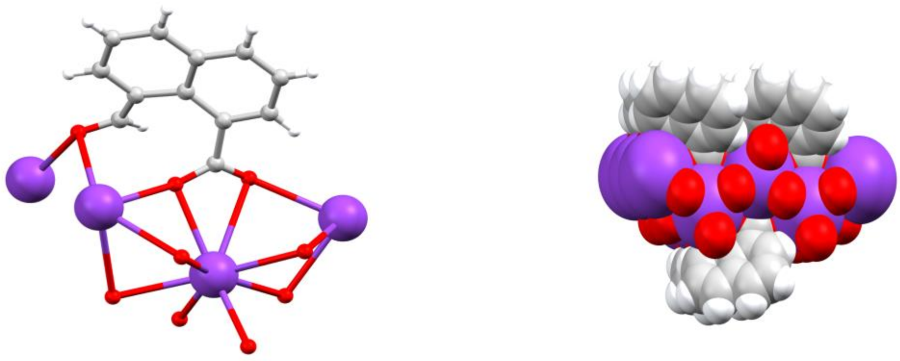


Figure 3.6. Crystal structure of potassium 8-formyl-1-naphthoate hydrate **(50)** [47]

In the potassium salt, an oxygen atom of the carboxylate group makes a close contact with the aldehyde group of 2.522 Å, and the angle of approach to the aldehyde group is 111.8°. In the carboxylate group, the longer C-O bond (1.280 Å) is attacking the aldehyde. Details of the interactions are given in the Table 3.3.

Table 3.3. Selected molecular geometry for Li **(51)**, K **(50)** and Cs salts [47]

	O---CHO /Å	O---C=O / °	C(H)=O /Å	(O)C-O(---CHO) /Å	O-C(-O---CHO) /Å
Li salt **(51)**	2.429	108.5	1.224	1.256	1.259
K salt **(50)**	2.522	111.8	1.212	1.280	1.240
Cs salt	2.502	110.9	1.217	1.270	1.246

The lithium salt is four coordinate at lithium and does not contain any water. The structure is reasonably well determined but could not be refined to a low Rfactor yet. This is probably due to twinning in the crystal, and a suitable model has not been found. However, the lithium salt also contains an interaction between a carboxylate O atom and an aldehyde group. The interaction distance is shorter than in the other salts (2.429 Å), but the two carboxylate C-O bonds are of similar length [47].

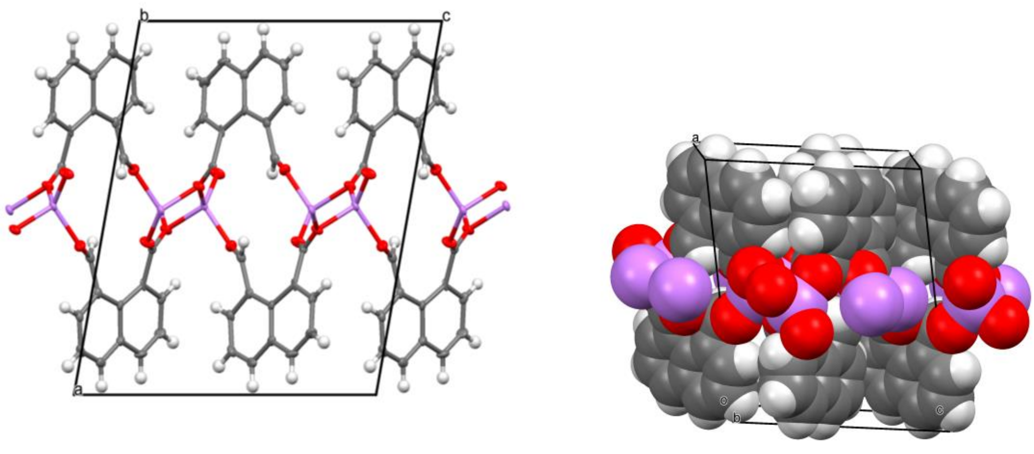


Figure 3.7. Crystal structure of lithium 8-formyl-1-naphthoate **(51)** [47]

3.3. Organic Salts of 1,8-Naphthalaldehydic acid

To provide more salts, 1,8-naphthalaldehydic acid was reacted with a range of organic bases such as morpholine, 4-dimethylaminopyridine and tetramethylguanidine. More bases were tried **(**for instance; tetraphenylphosphonium and pyrrolidine), but only these three gave nice crystalline materials.

The secondary amine morpholine reacted with 1,8-naphthaldehydic acid to give 3-(N-morpholinyl)-1H,3H-benzo[de]isochromen-1-one **(52)** is an amino lactone compound not a salt. This product was confirmed by a measurement of its crystal structure.

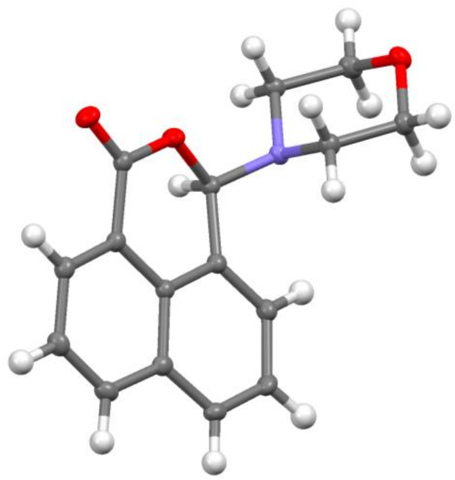


Figure 3.8. Crystal structure of 3-(N-morpholinyl)-1H,3H-benzo[de]isochromen-1-one **(52)**

X-ray crystallographic data of the molecule **(52)** was figured out as follows:
O-C 1.497 Å and 1.345 Å and C=O 1.212 Å.

There is no similar compound which has been Xrayed. The next nearest is the compound with code MXNAPO in the Cambridge Crystallographic Database which has a -OMe group instead of morpholine [48]. However, the morpholine adduct has been reported once. They quote a m.p. of 161-162 ºC, but do not give any spectral data [49]. There are some similar compounds which have been prepared, but with $-NEt_2$ or $-N(isopropyl)_2$ instead of morpholine. [50].

Reaction with 4-dimethylaminopyridine gave a solid which X-ray crystallography showed contained the protonated base, an anion of naphthalaldehydic acid and also a further molecule of naphthaladehydic acid in its cyclised form.

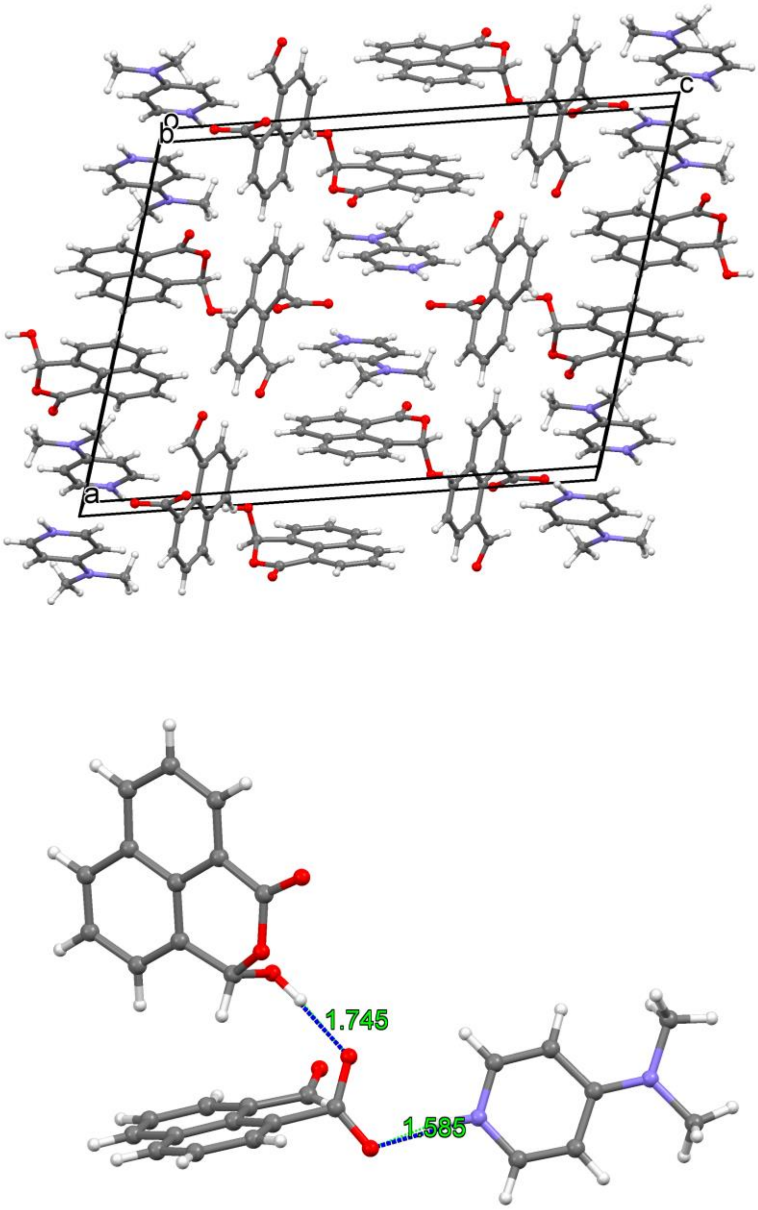


Figure 3.9. Crystal structure of salt mixture of 3-hydroxybenzo[de]isochromen- 1(3H)-one, 4-(dimethylamino)pyridin-1-ium and 8-formyl-1-naphthoate **(53)**

Reaction with 1,1,3,3-tetramethylguanidine gave a simple salt of naphthaldehydic acid. The crystal structure showed clearly a protonated guanidine and a naphthaldehydic acid anion.

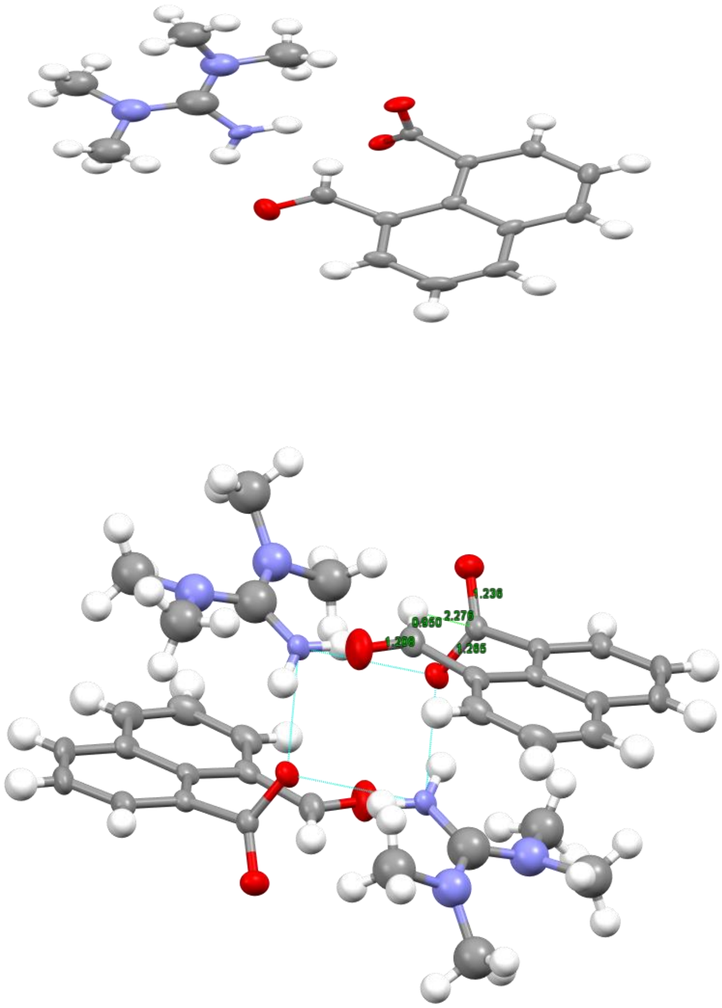


Figure 3.10. Crystal Structures of salt mixture of bis(dimethylamino)methaniminium and 8-formyl-1-naphthoate **(54)**

It is most interesting to note that in the crystal structures of the DMAP and guanidine salts the conformation of the anion are similar, but quite different to those seen in the lithium, potassium and cesium salts. Instead of showing an interaction between the carboxylate O atom and the aldehyde group, the aldehyde group now lies nearer to the plane of the naphthalene with its hydrogen atom directed towards the carboxylate group whose plane lies well out of the naphthalene ring's plane. So in this case the aldehyde group has directed its more positive end towards the electron rich carboxylate group. The distance between the aldehyde hydrogen and the carboxylate carbon atom is in the range 2.263-2.276 Å, which is very short compared to the sum of the van der Waals radii for these two atoms of 2.8 Å. The details of the molecular geometries are given in Table 3.4.

Table 3.4. Selected molecular geometries of DMAP salt **(53)** and Guanidine salt **(54)**

	H---CO_2	Angle of aldehyde to the naphthalene ring	Angle of carboxylate to the naphthalene ring	Carboxylate C-O bonds.
DMAP salt **(53)**	2.263	23.0	68.9	1.232, 1.240
Guanidine salt **(54)**	2.276	15.2	68.9	1.236, 1.265

The structures of these two series of salts have shown two different modes of interaction between a carboxylate and an aldehyde group. Either a carboxylate O atom is directed towards the aldehyde carbonyl group with an interaction distance in the range 2.429-2.522 Å or the aldehyde directs its hydrogen atom at the carboxylate with an interaction distance in the range 2.263-2.276 Å, which is very short compared to the sum of the van der Waals radii for these two atoms of 2.8 Å.

The tetraphenylphosphonium salt was prepared by extracting an aqueous solution of the potassium salt and tetraphenylphosphonium chloride.

3.4. Attempted Salt Formation

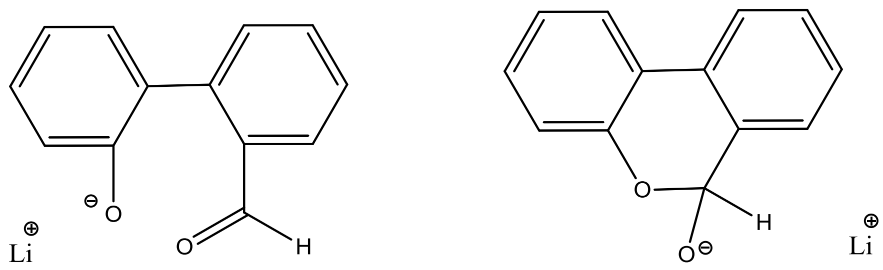
Salt formation was attempted using lithium or potassium hexamethyldisilazide (HMDS). The biphenyl was dissolved in THF under nitrogen at room temperature and the solution treated with the HMDS base and later the solvents were removed under high vacuum so that hexamethyldisilazine was also removed. The NMR spectra of the residues were recorded. Some variation of conditions was also tried, for example refluxing the reaction mixture, but this made things worse.

3.4.1. Potassium Salt of Suzuki Product (58)

The NMR spectra observed from the preparation of the potassium salt are more complex, and do not correspond to a simple compound. Some much milder conditions will have to be used in the future to prepare HMDS potassium salt. Addition of further ligands for the potassium may stabilise a suitable product.

3.4.2. Lithium Salt of Suzuki Product (59)

For the lithium salt a sample was obtained which gave reasonably simple NMR spectra, with one main component. In the ^{1}H NMR there are four doublets and four triplets in the aromatic region, which do not correspond to starting material. There is no obvious aldehyde hydrogen resonance, but there is a signal at 5.66 ppm. This suggests that the structure is still cyclised as structure B, rather than A which has a free aldehyde group. The ^{13}C NMR shows a signal at 72.7 ppm which may be the carbon between the two O atoms, with the negative charge on one O atom causing a upfield shift from the position observed in starting material (93.5 ppm).



A **B**

Figure 3.11. A and **B**: Two possible structures of lithium 2'-formyl-[1,1'-biphenyl]-2-olate **(59)**

3.4.3. 1,1,3,3-Tetramethylguanidine Salt of Suzuki Product (60)

^{13}C data look like starting material with a small amount of tetramethyl guanidine in it.
1,1,3,3-Tetramethylguanidine has not been as strong enough base to deprotonate the Suzuki product. Therefore, future work should concentrate on stronger bases.

CHAPTER 4

4. CONCLUSIONS

In this thesis work, new compounds which have naphthalene and biphenyl framework were synthesized. Molecular interactions between electron-rich and electron-poor groups were researched.

The compounds were identified by ^{1}H-NMR, ^{13}C-NMR, FT-IR and X-Ray crystallography. As a consequence of the thesis, following papers are being prepared for publication:

1. Wallis, J.D. ; Saritemur, G. ; Pitak, B.M. ; Coles, S.J., “Para-Substituted Potassium Hydrogen Dibenzoates” “***in preparation for CrystEngComm***”

2. Wallis, J.D. ; Saritemur, G. ; Nomes, L.; Pitak, B.M. ; Coles, S.J., “O···C Interactions in the Salts of Naphthaldehydic Acid” “***in preparation for CrystEngComm***”

4.1. Potassium Dibenzoates

4-methyl, 4-chloro and 4-nitrobenzoic acids reacted with KOH to get their corresponding potassium hydrogen dibenzoates. Consequently, 4-methyl and 4-chloro benzoates have similar crystal data and structure, 4-nitro-dibenzoate was unlike. Nevertheless, it can be noted that all of the molecules contain hydrogen bonding.

4.2. Salts of Naphthalaldehydic acid

Metal salts and organic salts of 1,8-Naphthalaldehydic acid were prepared to examine the interactions between the carboxylate anion and the aldehyde group.

Potassium salt and lithium salt were synthesized as metal salts. X-ray crystal data of the crystals show that the potassium salt is very similar to the cesium salt which was studied previously. Both potassium salt and cesium salt contain a water molecule in the crystal structure. However, lithium salt does not contain any water molecule in the crystal structure. Eventually, both potassium salt and lithium salt have an interaction between a carboxylate O atom and an aldehyde group.

1,8-Naphthalaldehydic acid reacted with morpholine, 4-dimethylaminopyridine and 1,1,3,3-tetramethylguanidine to synthesize organic salts. However, the reaction with morpholine gave an amino lactone compound not a salt. Reaction with 1,1,3,3-tetramethylguanidine gave a salt mixture of a protonated guanidine and a naphthaldehydic acid anion.

X-ray data show that in the crystal structures of the DMAP and guanidine salts, the conformation of the anion are similar, but quite different to those seen in the lithium, potassium and cesium salts. The aldehyde group now lies nearer to the plane of the naphthalene, instead of showing an interaction between the carboxylate O atom and the aldehyde group.

4.3. Suzuki Coupling Reaction

6H-benzo[c]chromen-6-ol was synthesized as a biphenyl compound via Suzuki Coupling Reaction. It was purified by columm chromatography. The structure of the molecule was proven by ^{1}H and ^{13}C NMR data. And also, the equilibrium reaction between 6H-benzo[c]chromen-6-ol and 2'-hydroxy-[1,1'-biphenyl]-2-carbaldehyde was observed.

4.4. Salts from Product of Suzuki Coupling Reaction

6H-benzo[c]chromen-6-ol reacted with Li HMDS, K HMDS and 1,1,3,3-tetramethylguanidine in order to prepare corresponding salts. However, K HMDS and 1,1,3,3-tetramethylguanidine bases were not enough to deprotonate the Suzuki product. Li HMDS was the only base to get the salt of Suzuki product. Therefore, future work should concentrate on stronger bases.

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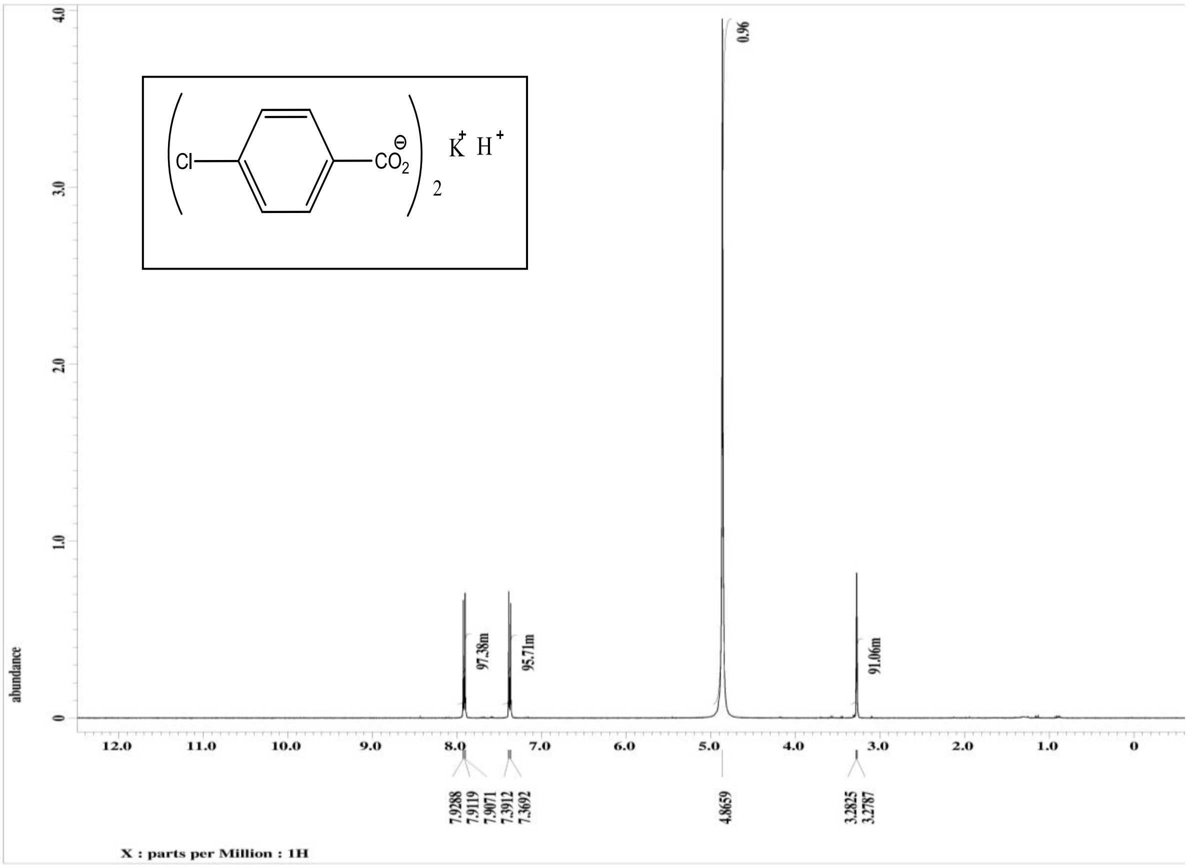
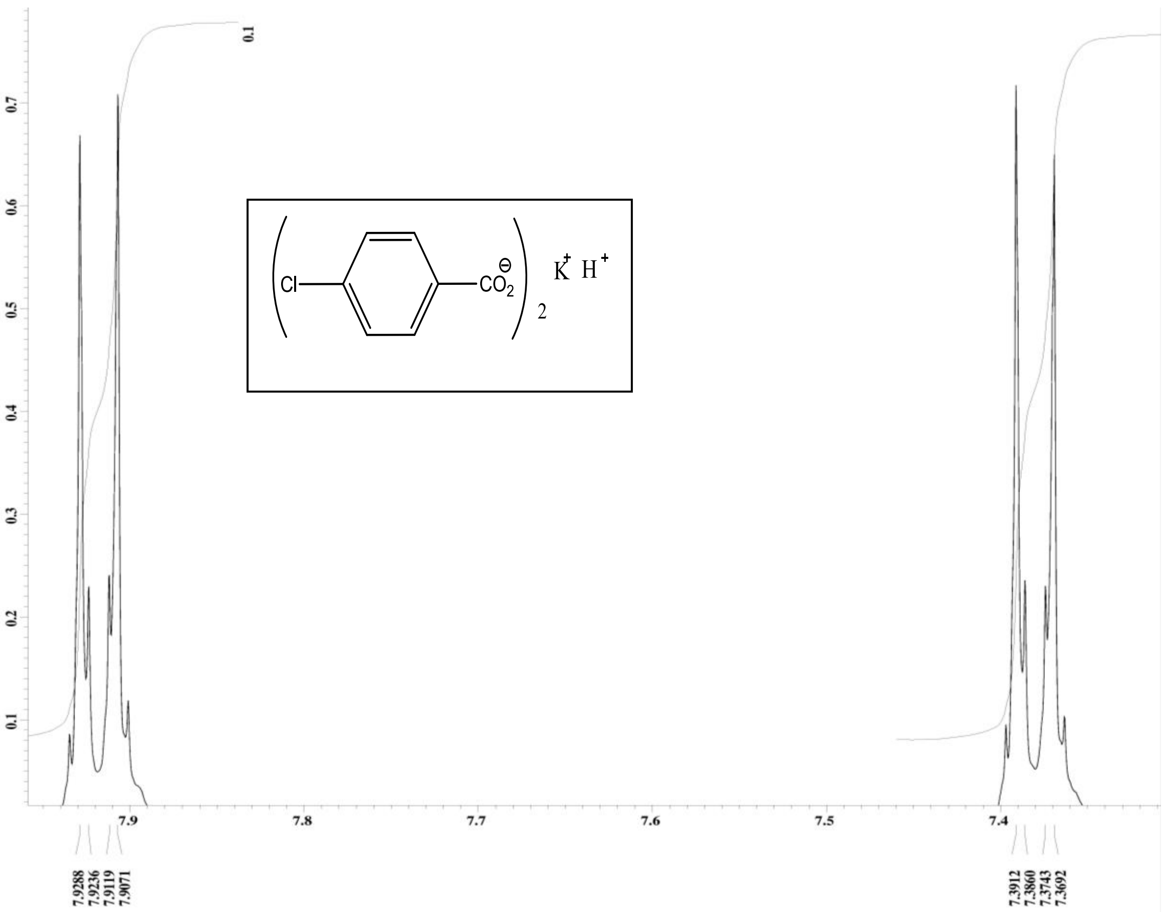
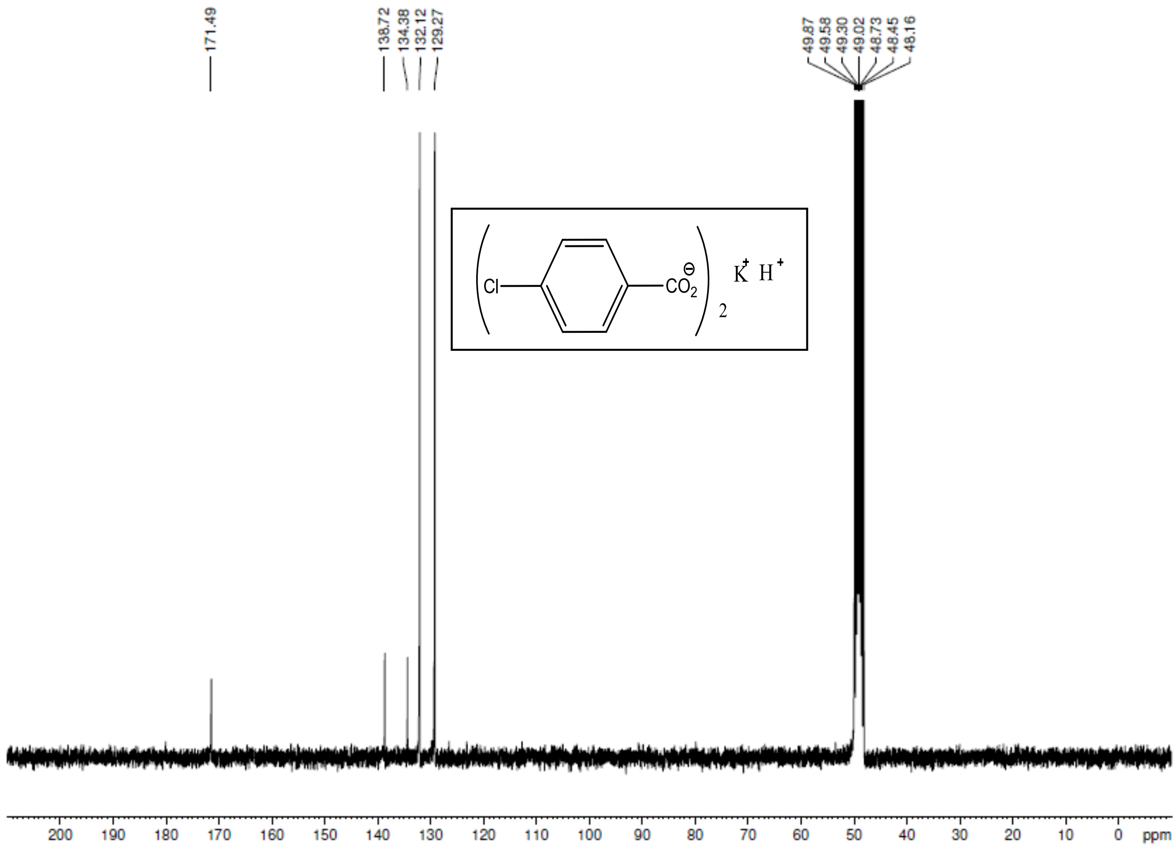
ATTACHMENTS



Atch 1.a. ^{1}H NMR spectrum of potassium hydrogen di(4-chloro) benzoate **(47)**



Atch 1.b. Expanded ^{1}H NMR spectrum of potassium hydrogen di(4-chloro) benzoate **(47)-**Aromatic region



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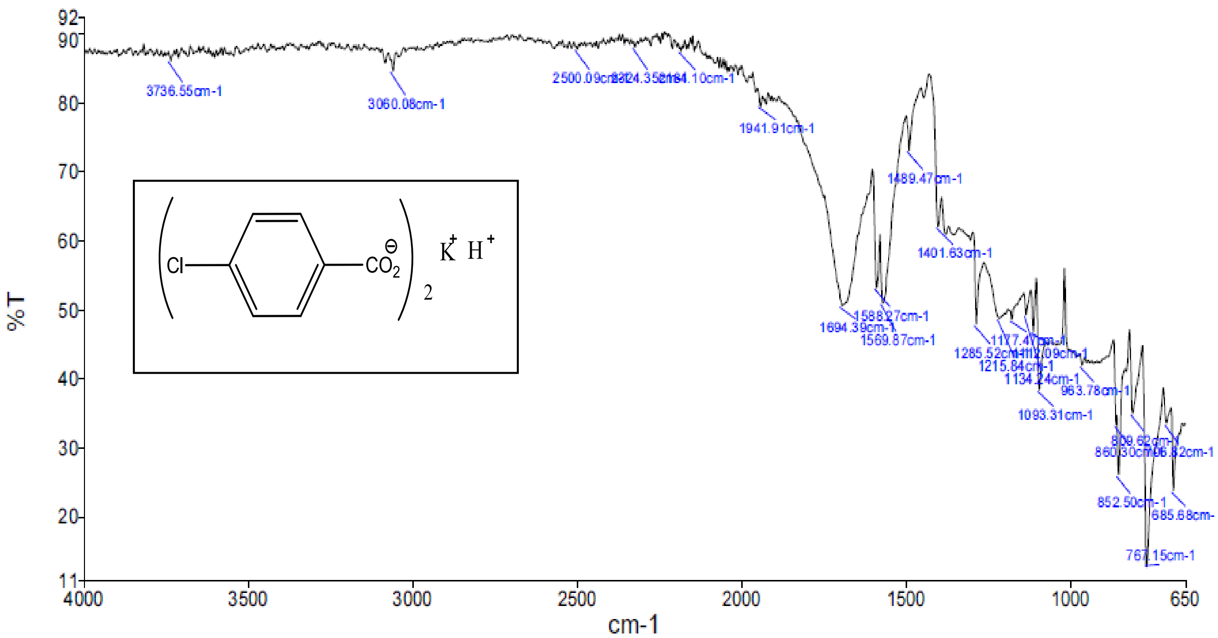

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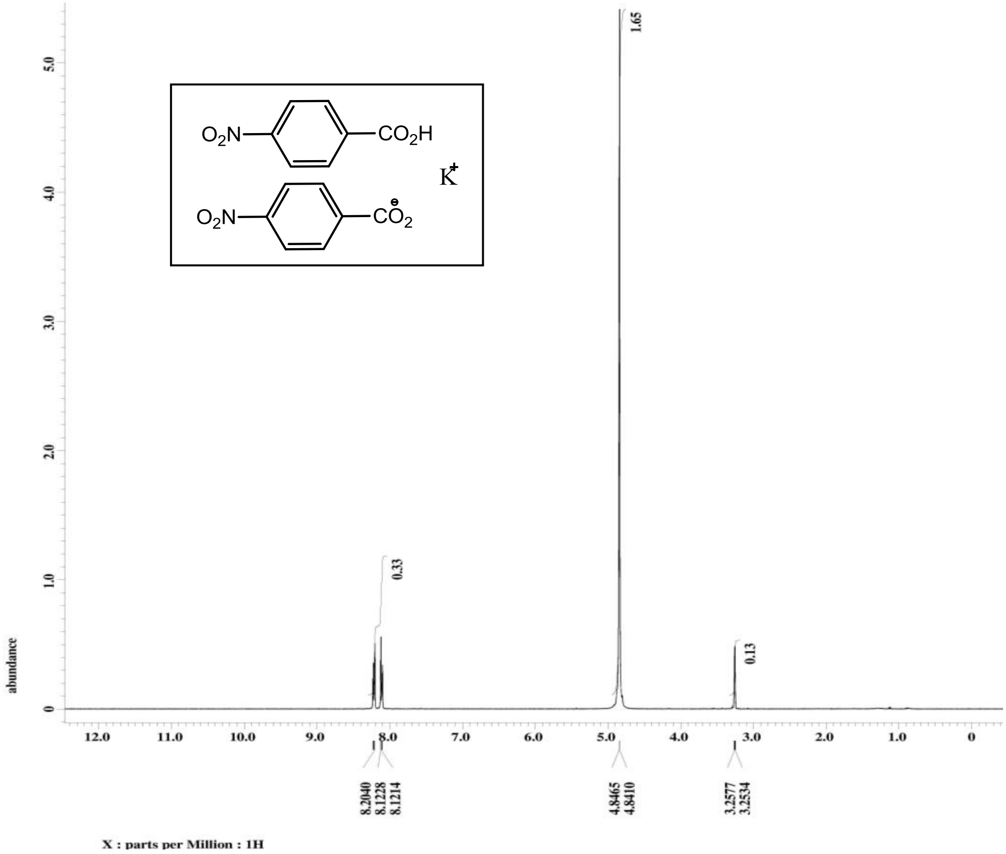

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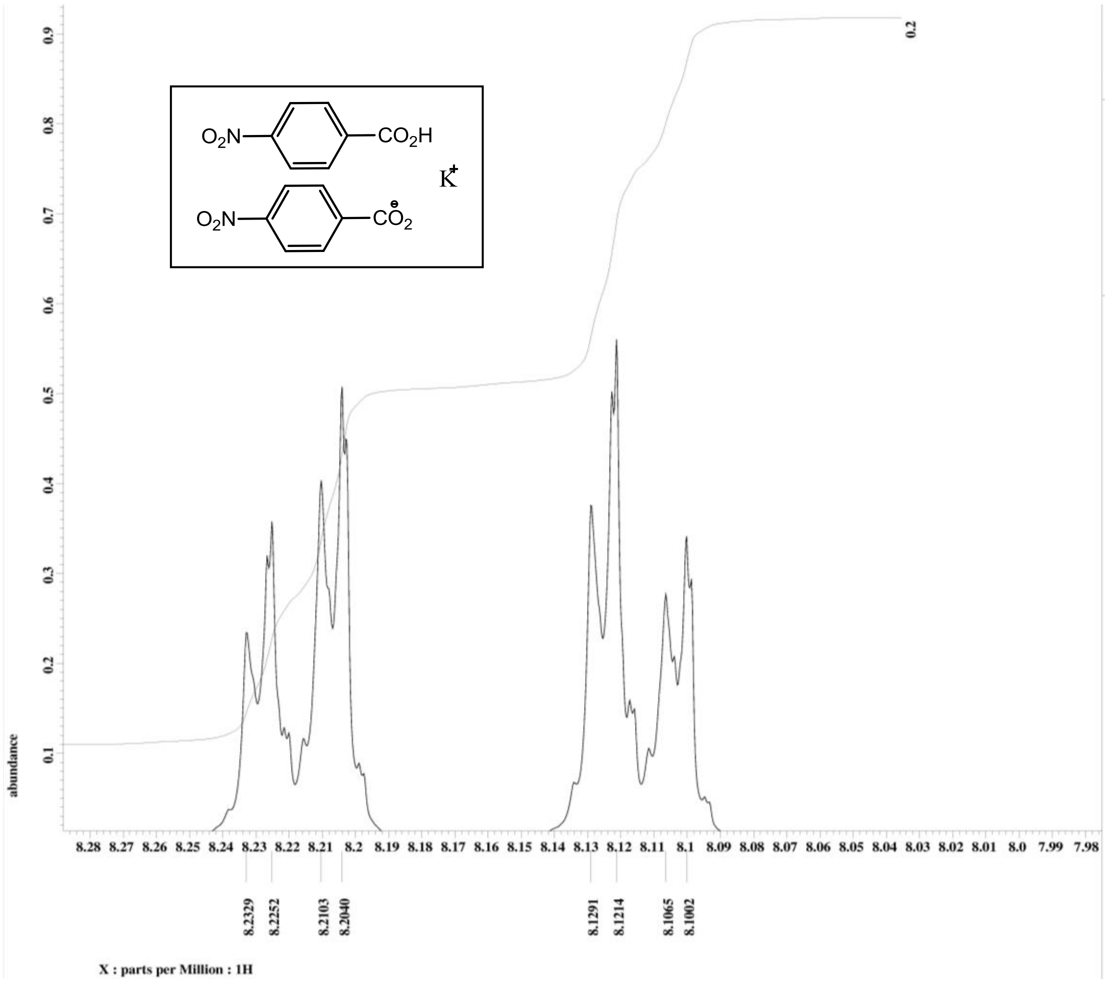
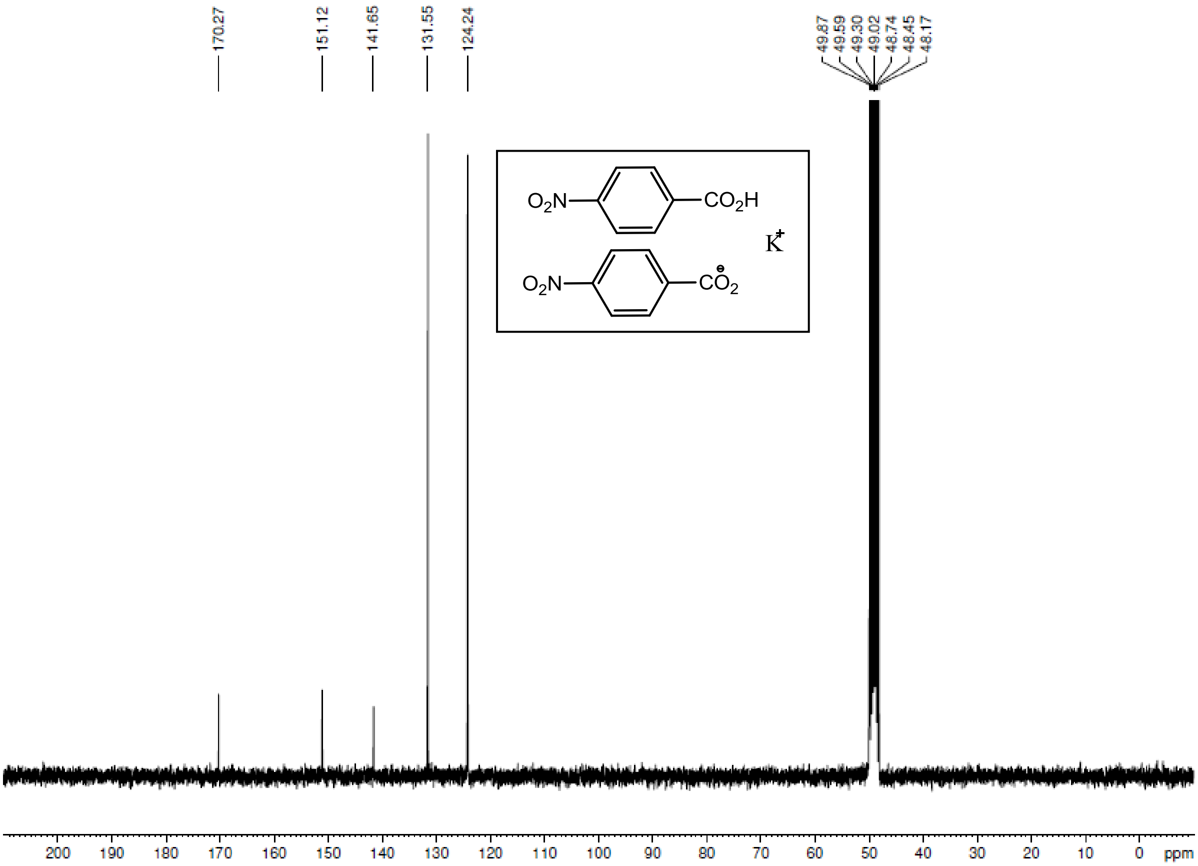


Atch 2.b. Expanded ^{1}H NMR spectrum of potassium di(4-nitro) benzoate **(48)-** Aromatic region



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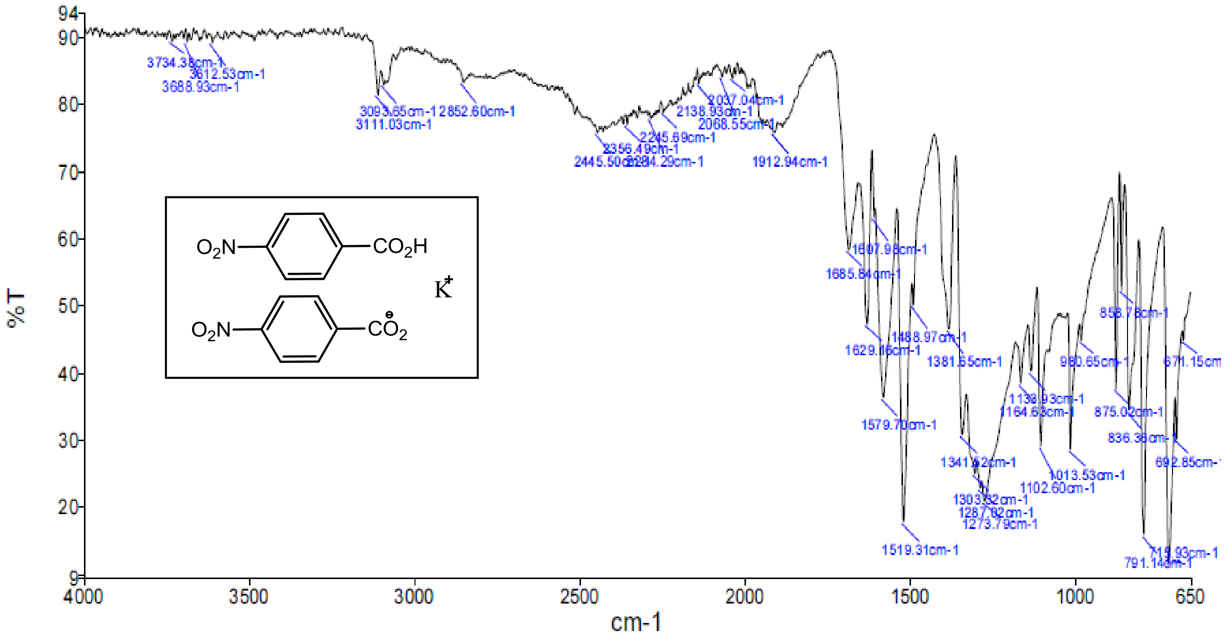

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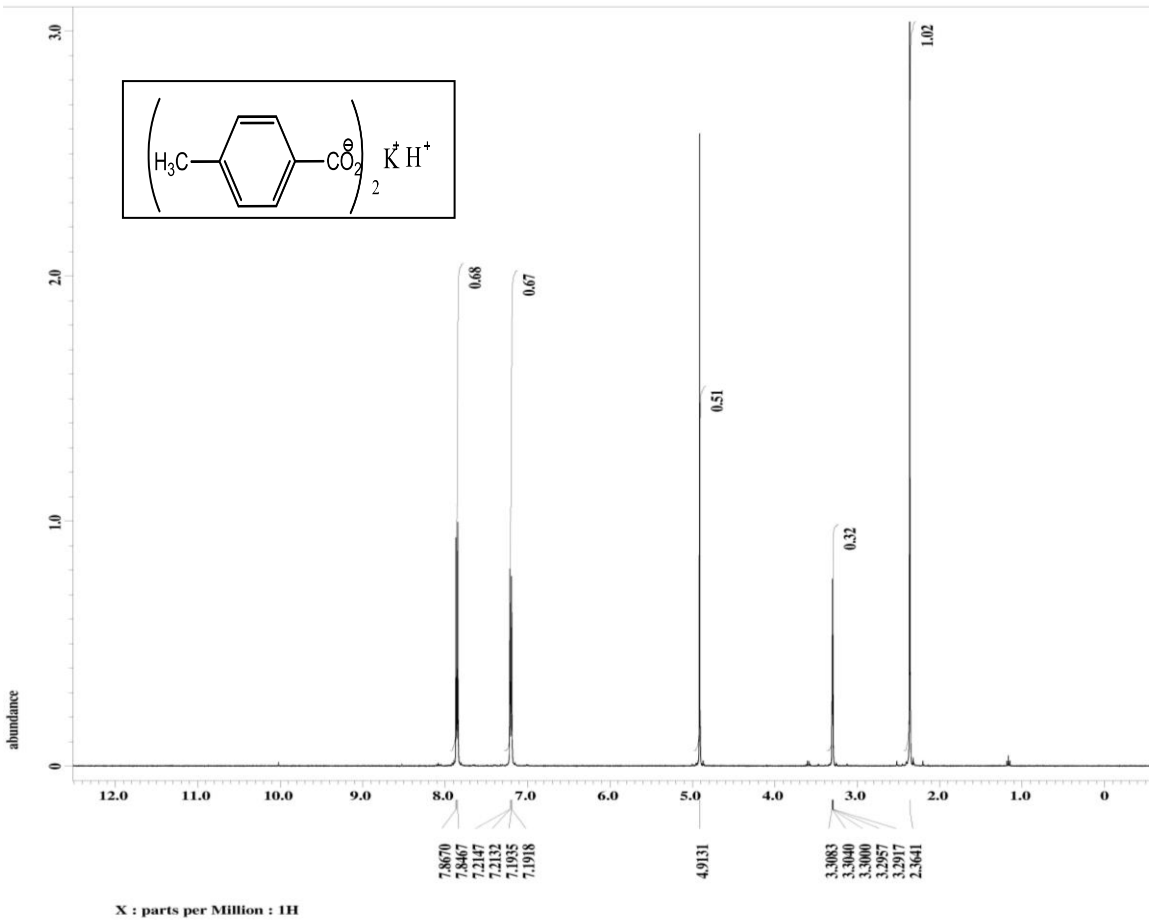

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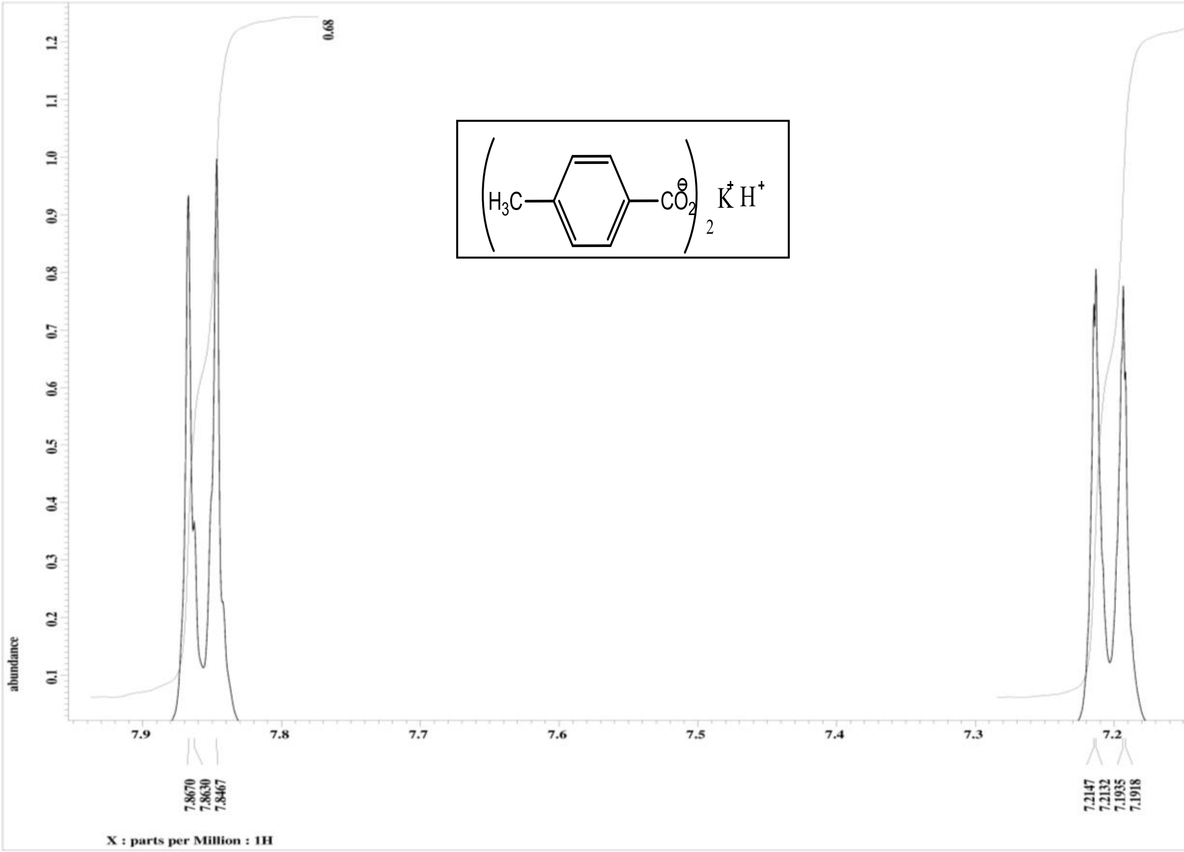
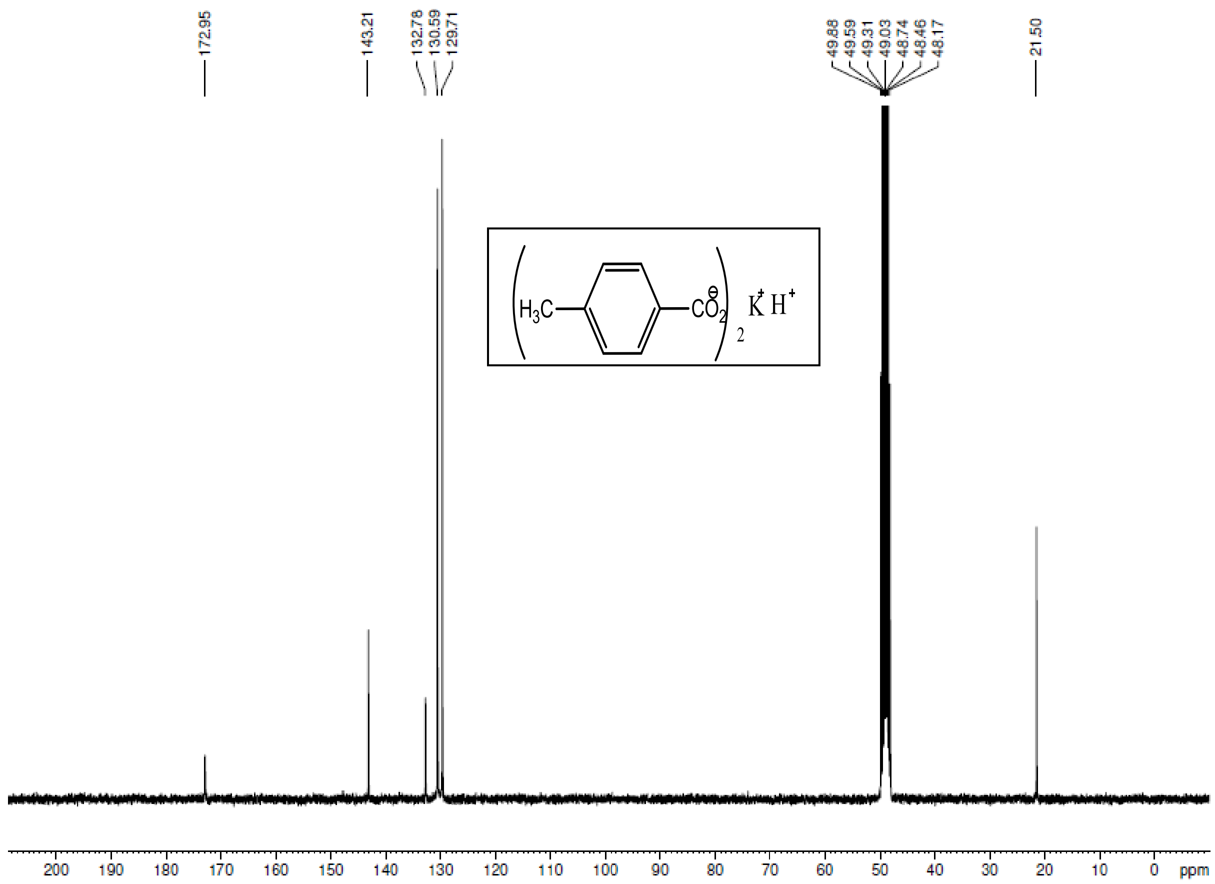
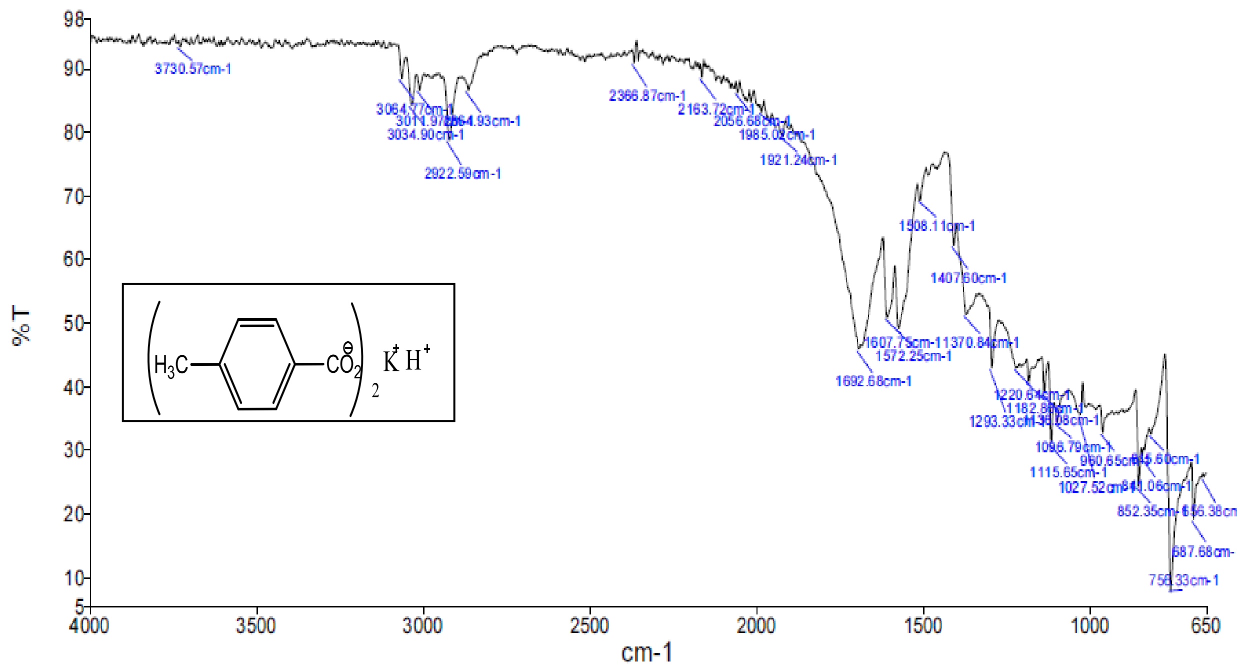


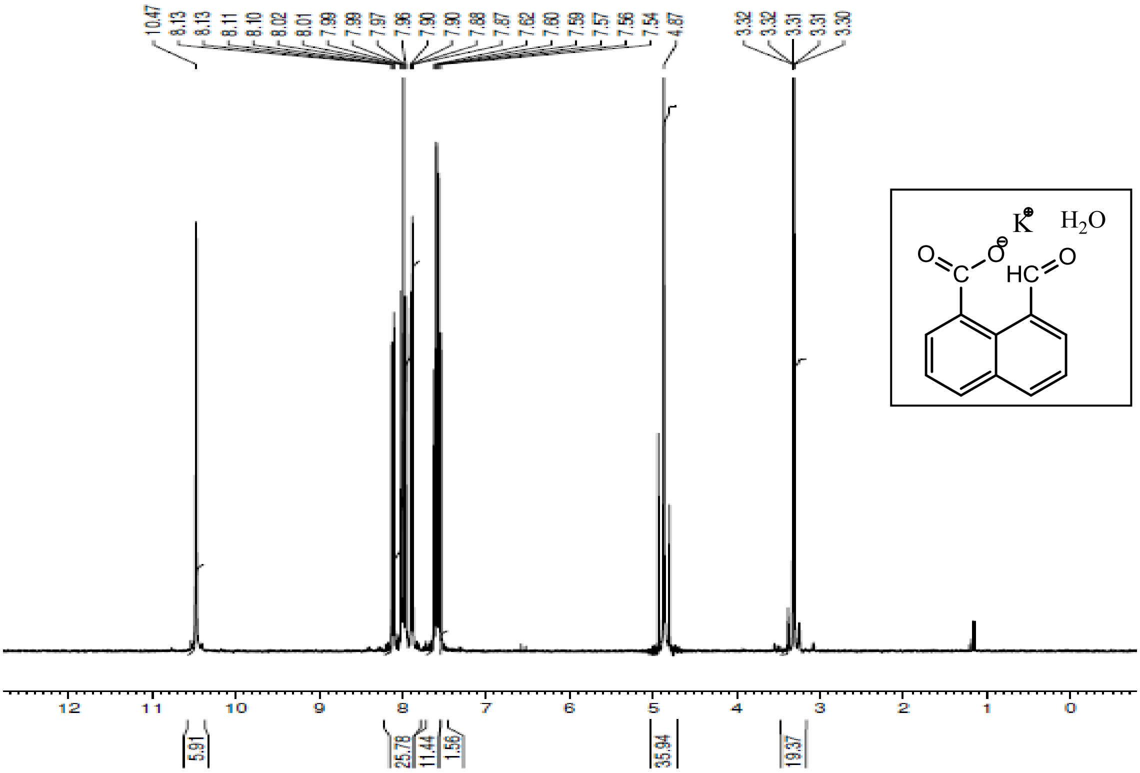
Atch 3.b. Expanded ^{1}H NMR spectrum of potassium hydrogen di(4-methyl) benzoate **(49)**-Aromatic region



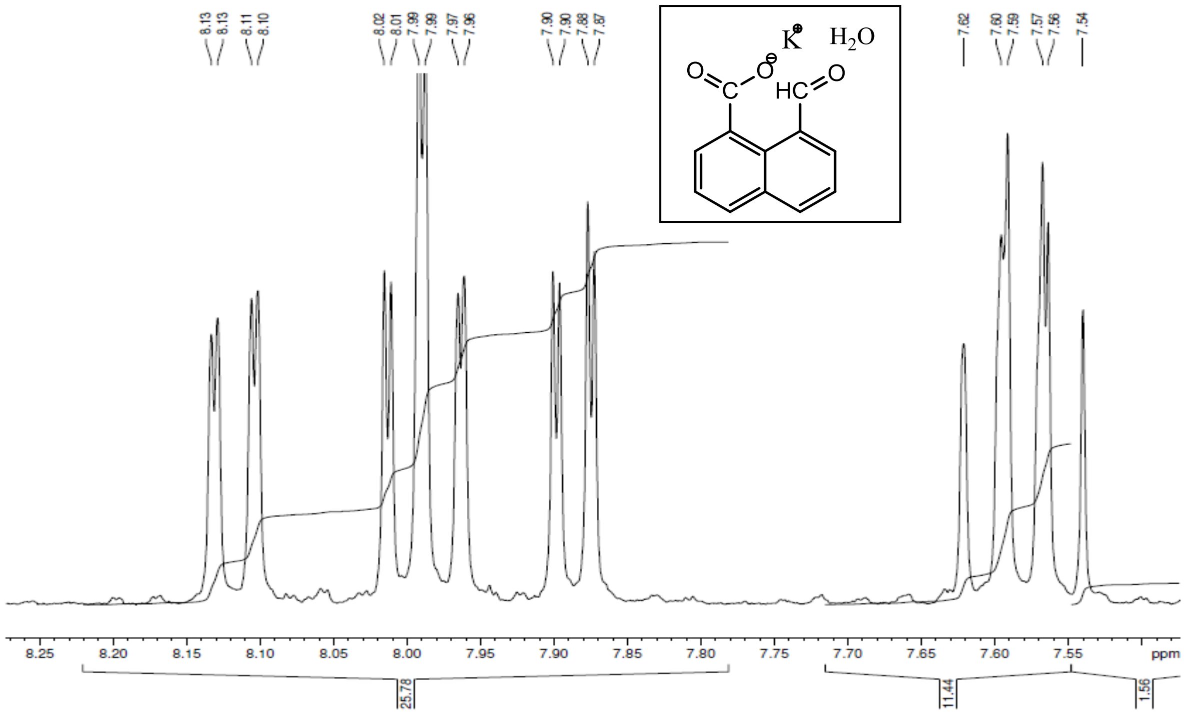
Atch 3.c. ^{13}C NMR spectrum of potassium hydrogen di(4-methyl) benzoate **(49)**



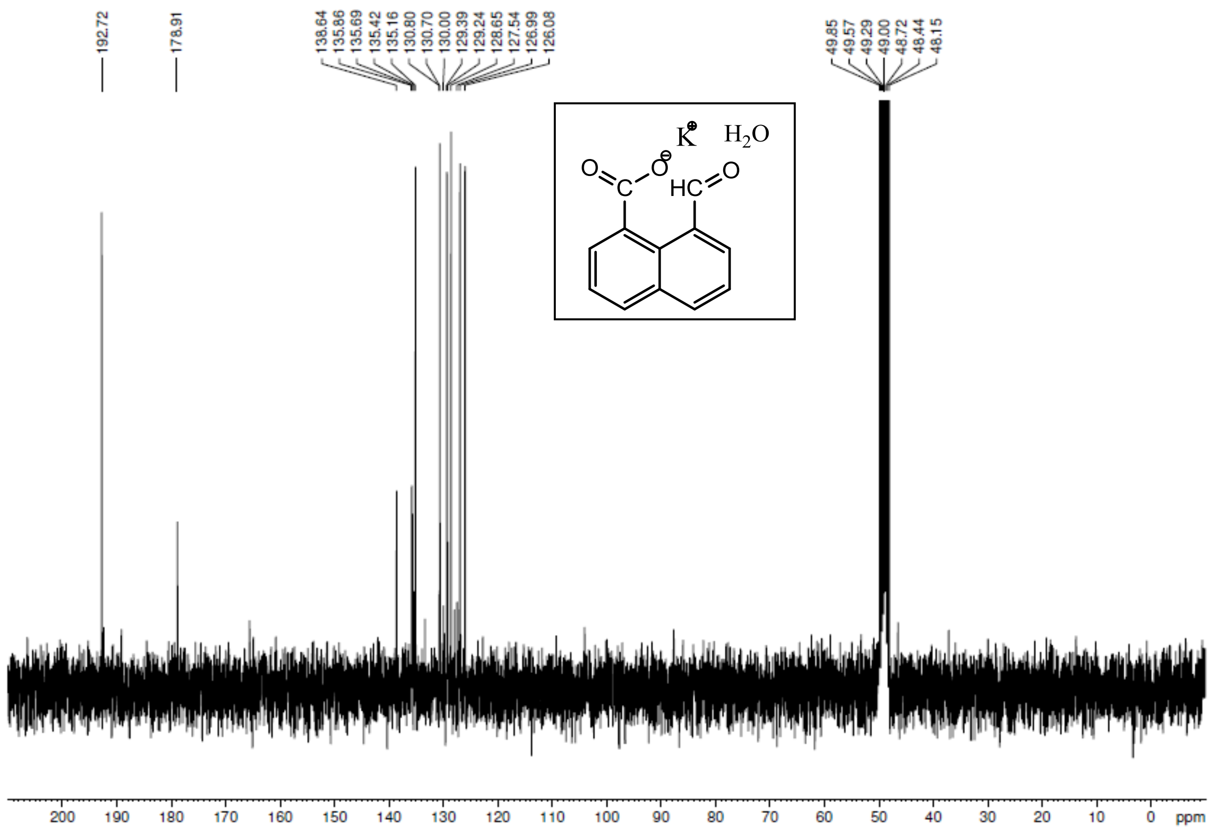
Atch 3.d. FT-IR spectrum of potassium hydrogen di(4-methyl) benzoate **(49)**



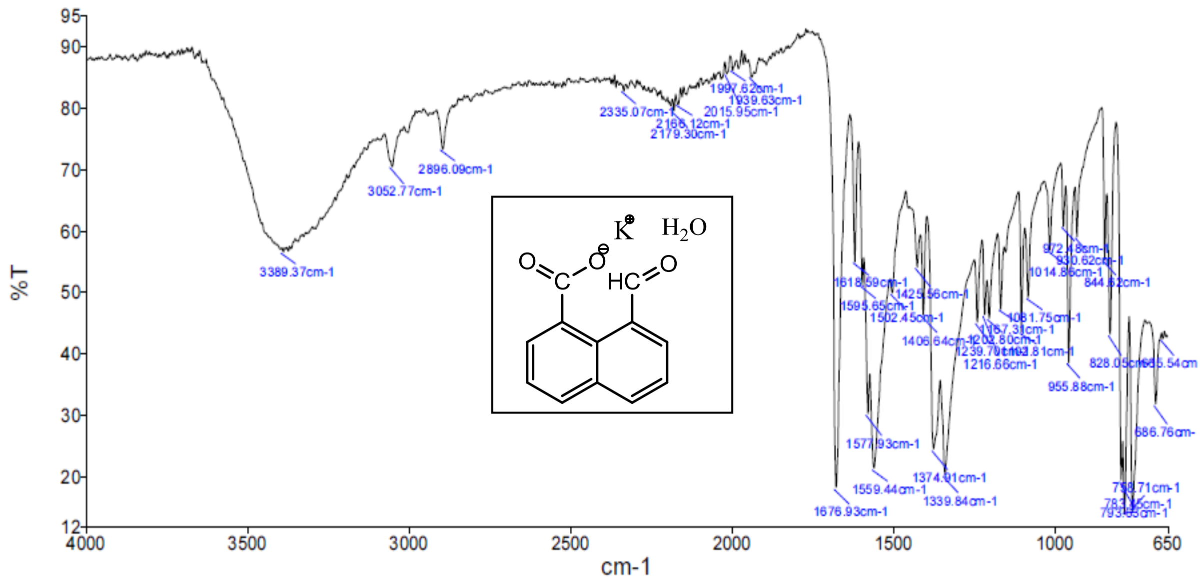
Atch 4.a. [1]H NMR spectrum of potassium 8-formyl-1-naphthoate hydrate **(50)**



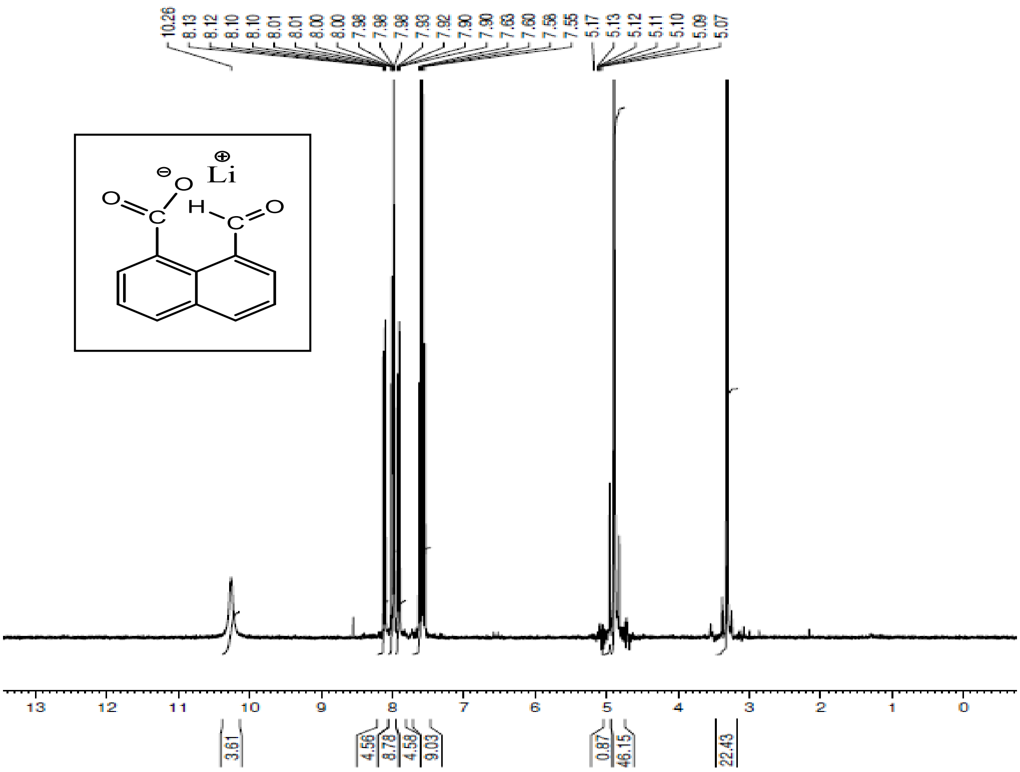
Atch 4.b. Expanded [1]H NMR spectrum of potassium 8-formyl-1-naphthoate hydrate **(50)**



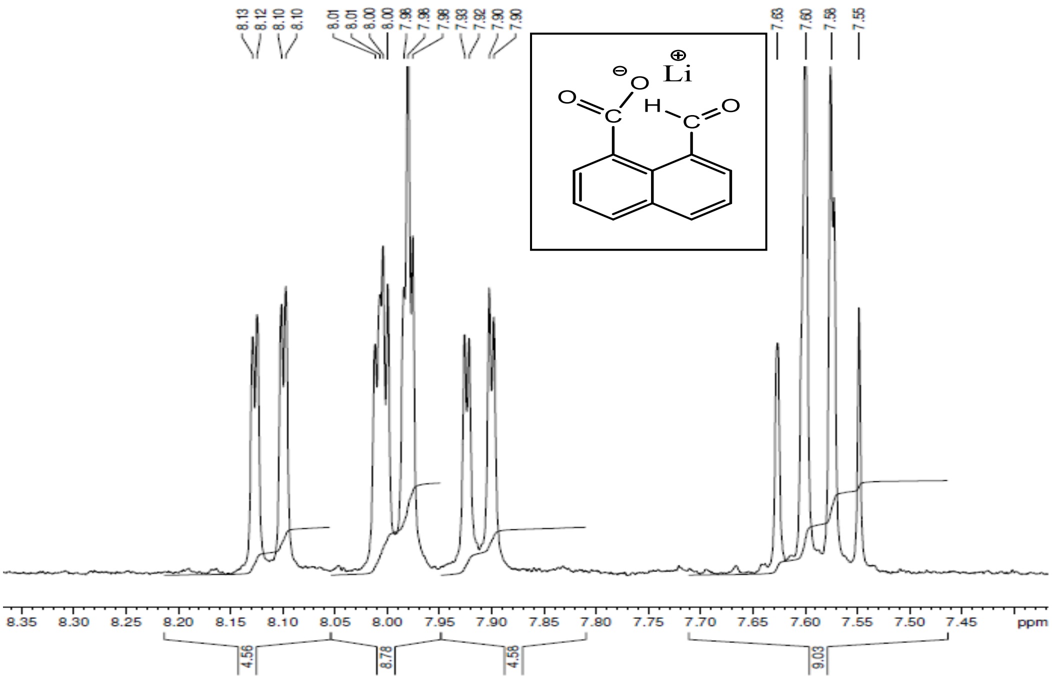
Atch 4.c. ^{13}C NMR spectrum of potassium 8-formyl-1-naphthoate hydrate **(50)**



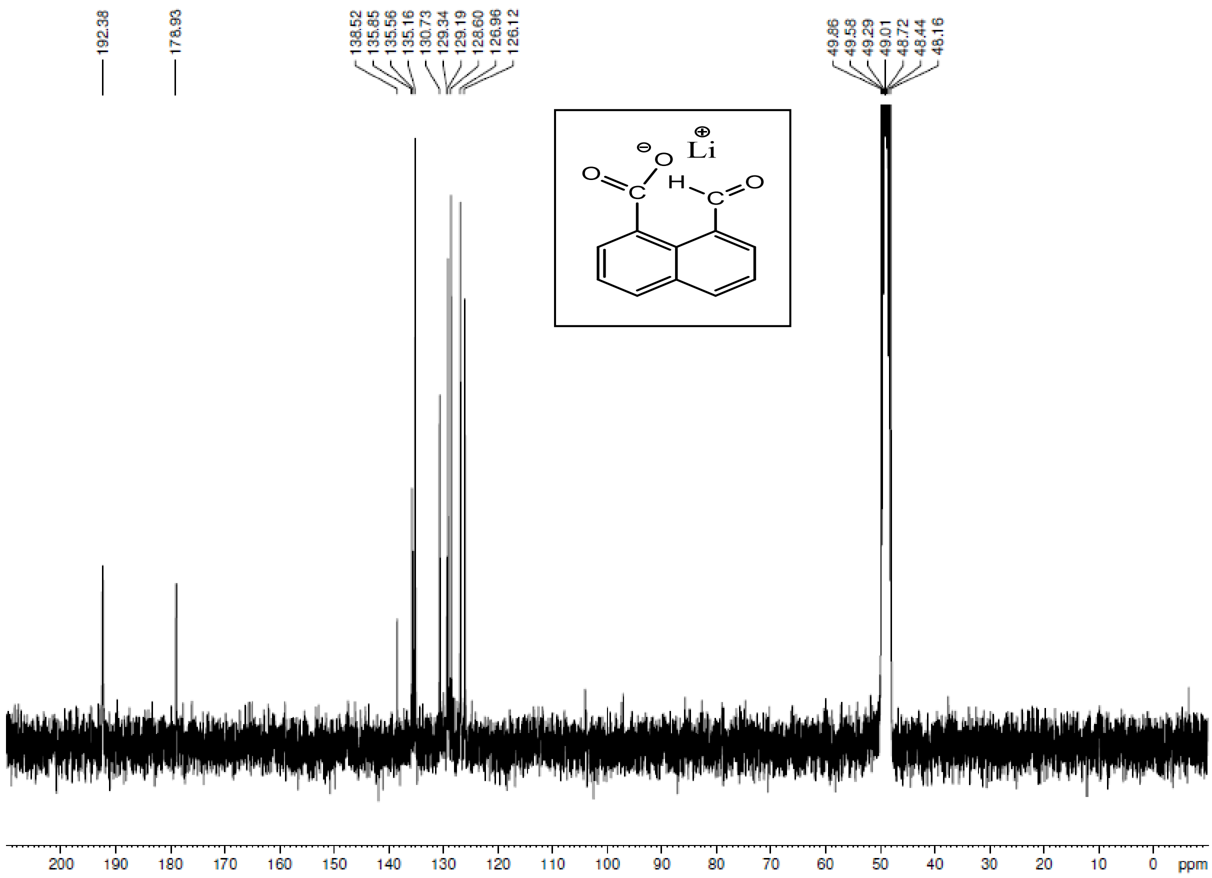
Atch 4.d. FT-IR spectrum of potassium 8-formyl-1-naphthoate hydrate **(50)**



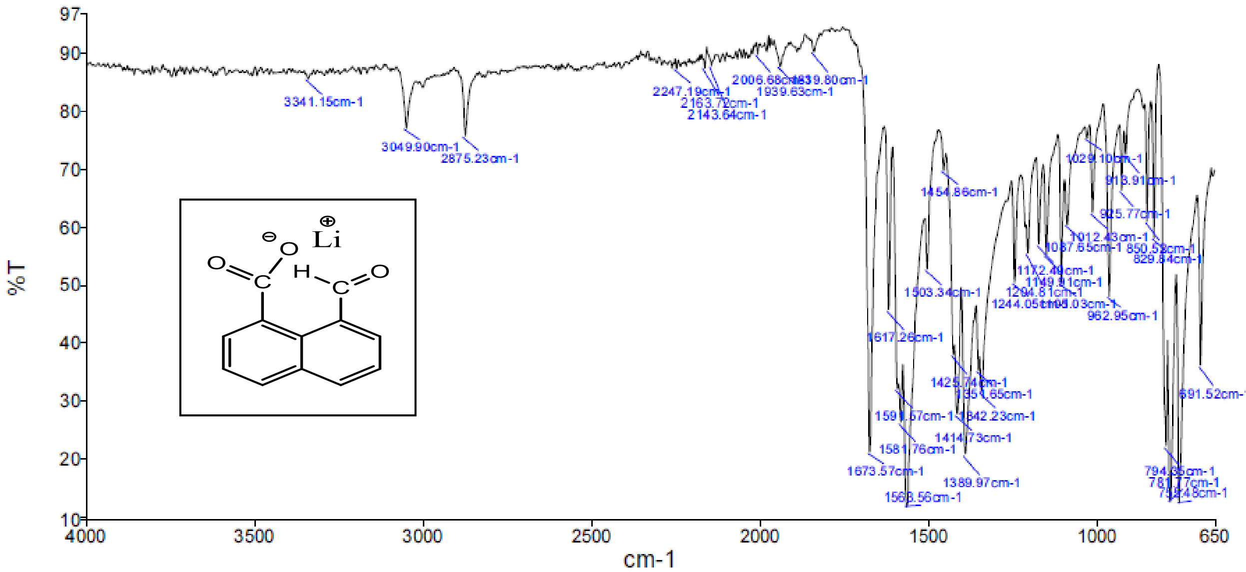
Atch 5.a. ^{1}H NMR spectrum of lithium 8-formyl-1-naphthoate **(51)**



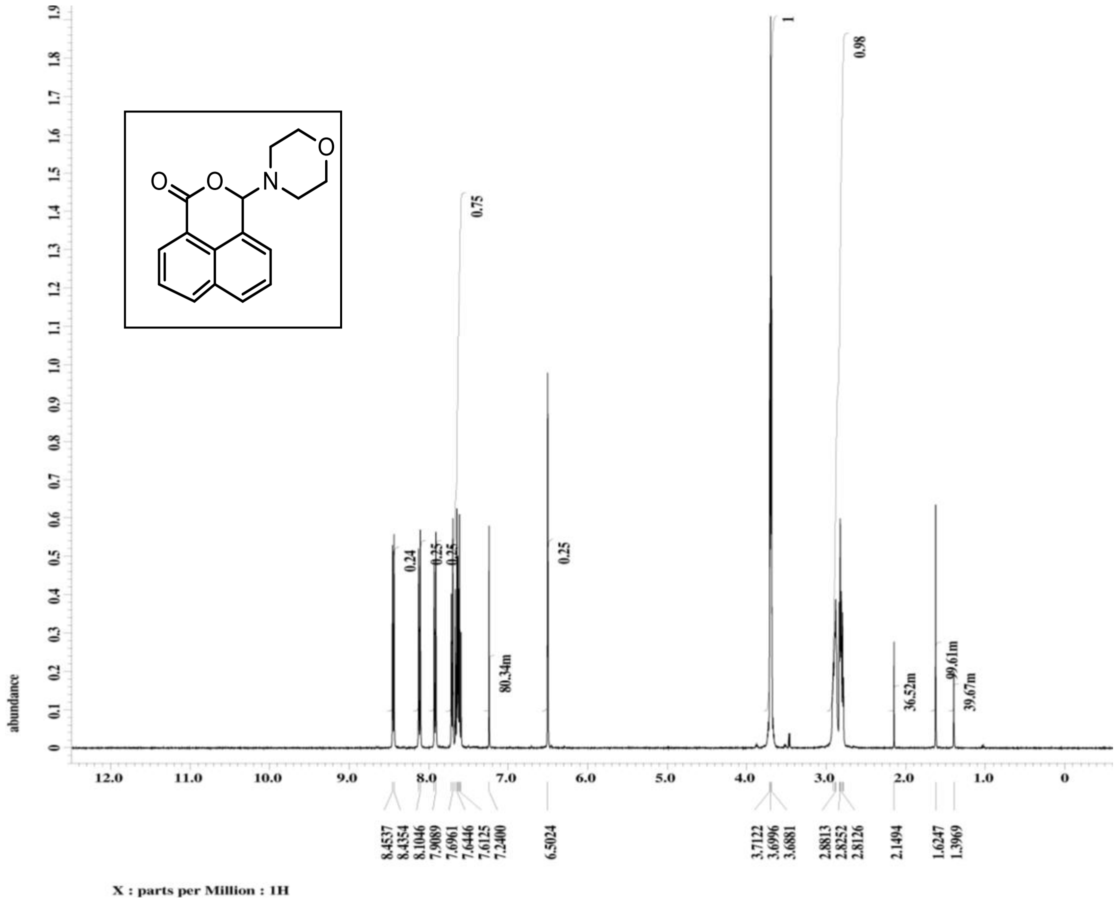
Atch 5.b. Expanded ^{1}H NMR spectrum of lithium 8-formyl-1-naphthoate **(51)**



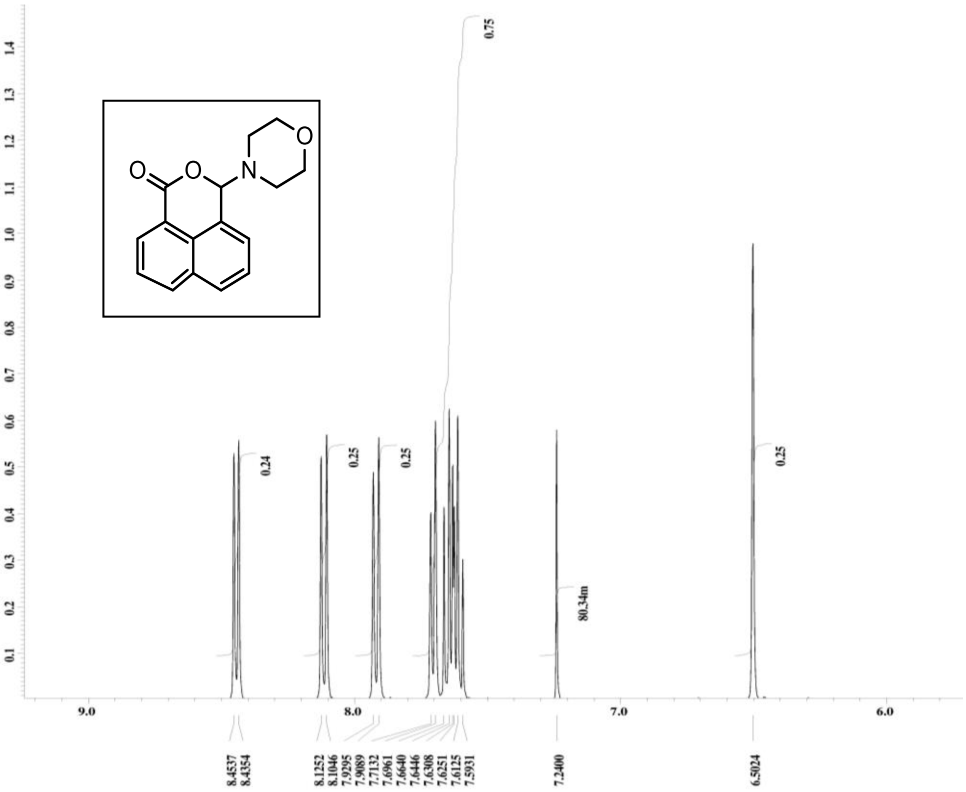
Atch 5.c. ^{13}C NMR spectrum of lithium 8-formyl-1-naphthoate **(51)**



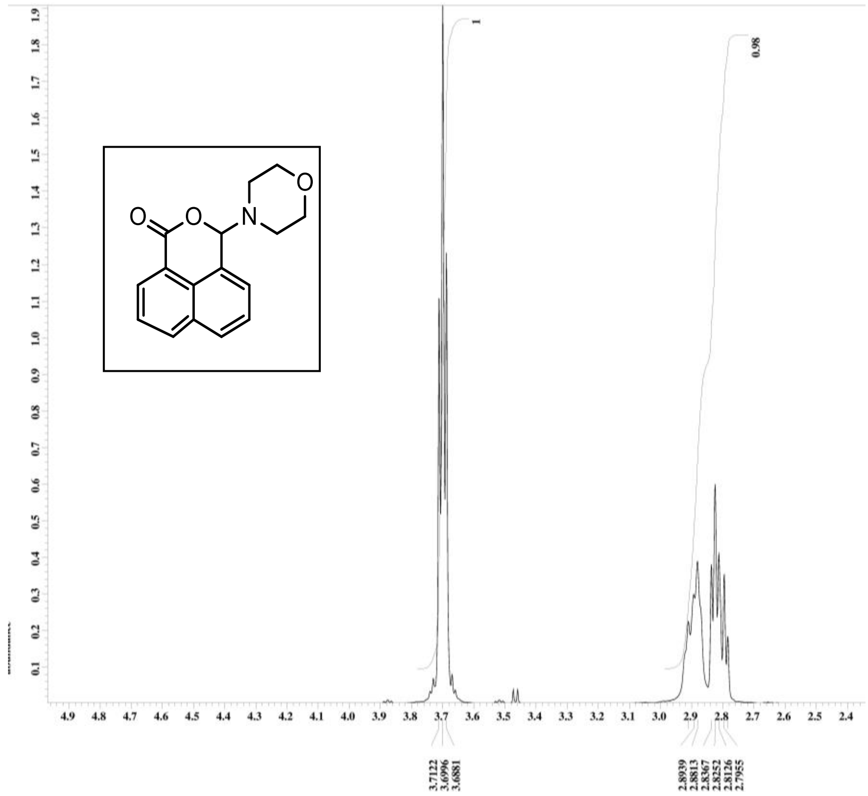
Atch 5.d. FT-IR spectrum of lithium 8-formyl-1-naphthoate **(51)**



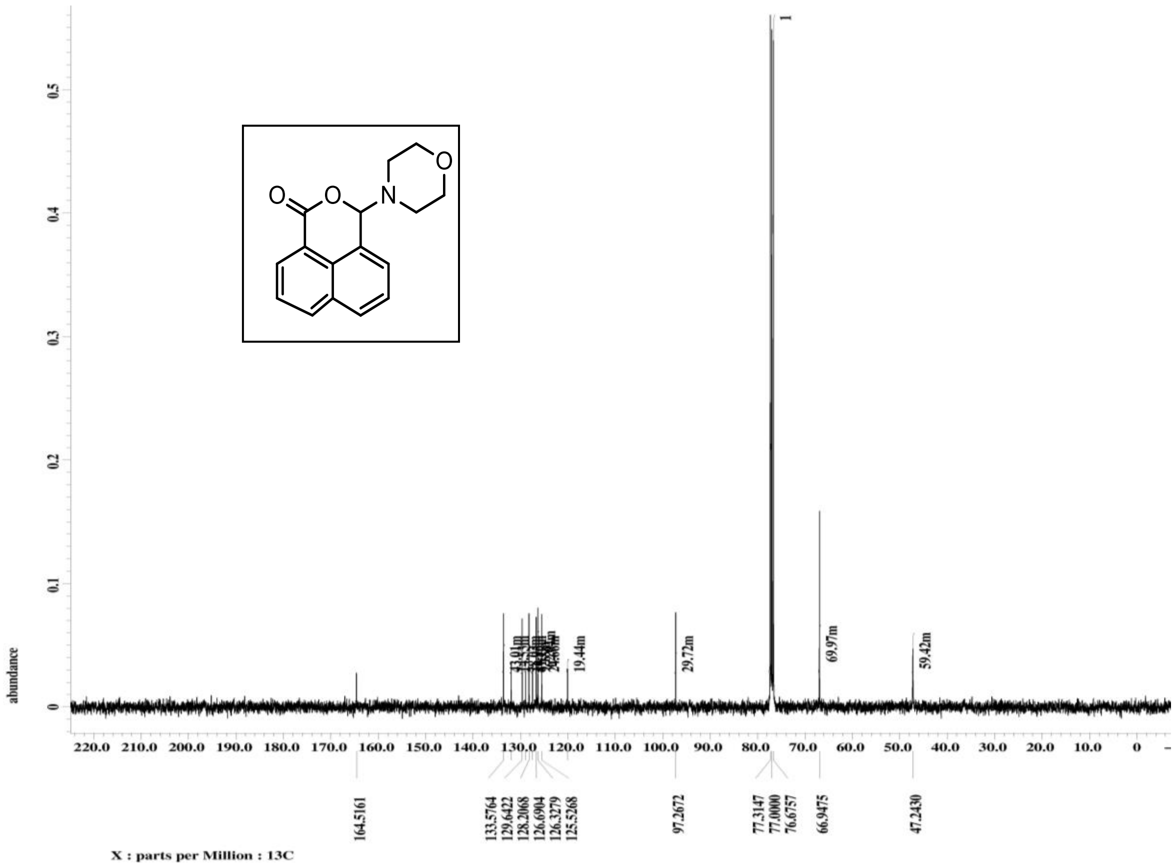
Atch 6.a. ^{1}H NMR spectrum of 3-(N-morpholinyl)-1H,3H-benzo[de]isochromen-1-one **(52)**



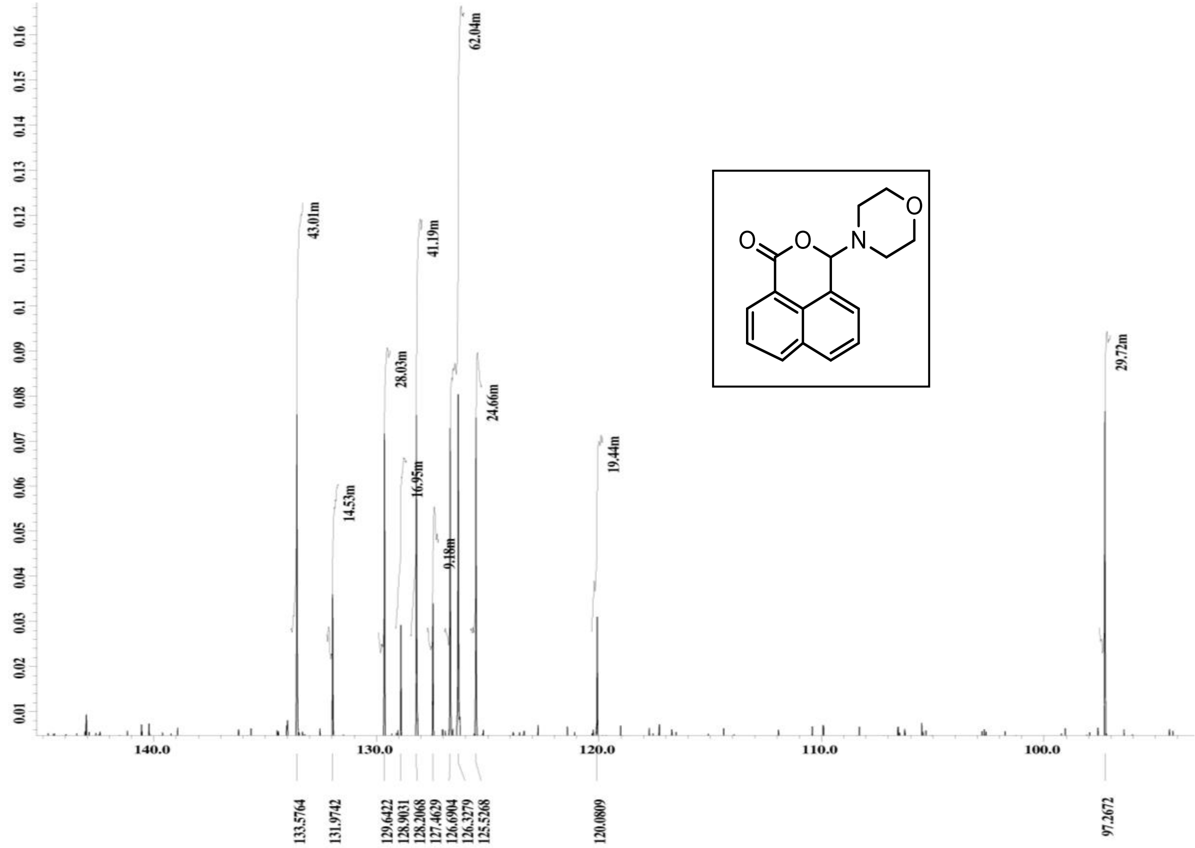
Atch 6.b. Expanded ^{1}H NMR spectrum of 3-(N-morpholinyl)-1H,3H-benzo[de]isochromen-1-one **(52)**-Aromatic region



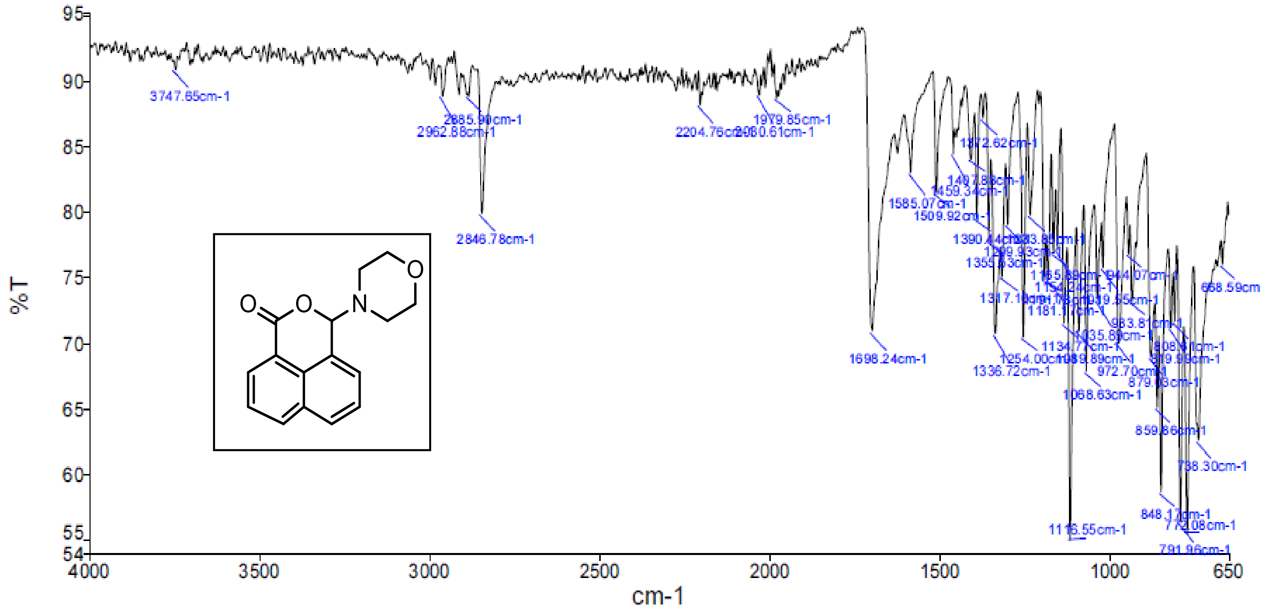
Atch 6.c. Expanded [1]H NMR spectrum of 3-(N-morpholinyl)-1H,3H-benzo[de]isochromen-1-one **(52)**-Aliphatic region



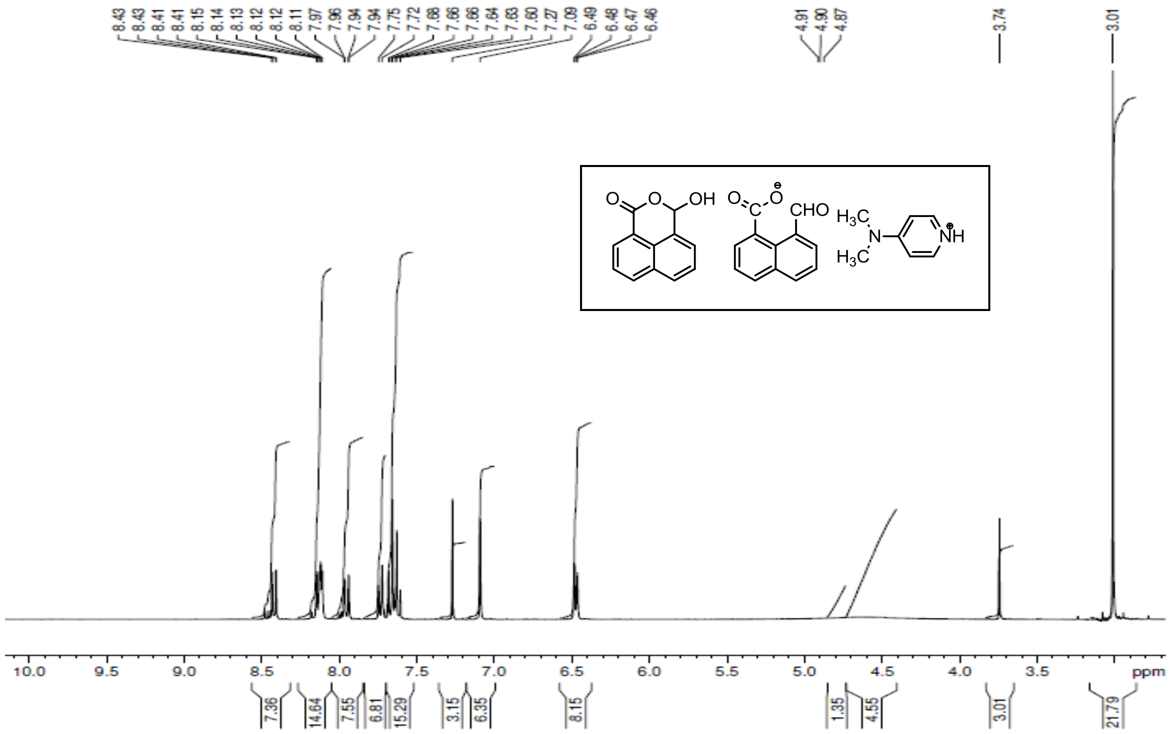
Atch 6.d. ^{13}C NMR spectrum of 3-(N-morpholinyl)-1H,3H-benzo[de]isochromen-1-one **(52)**



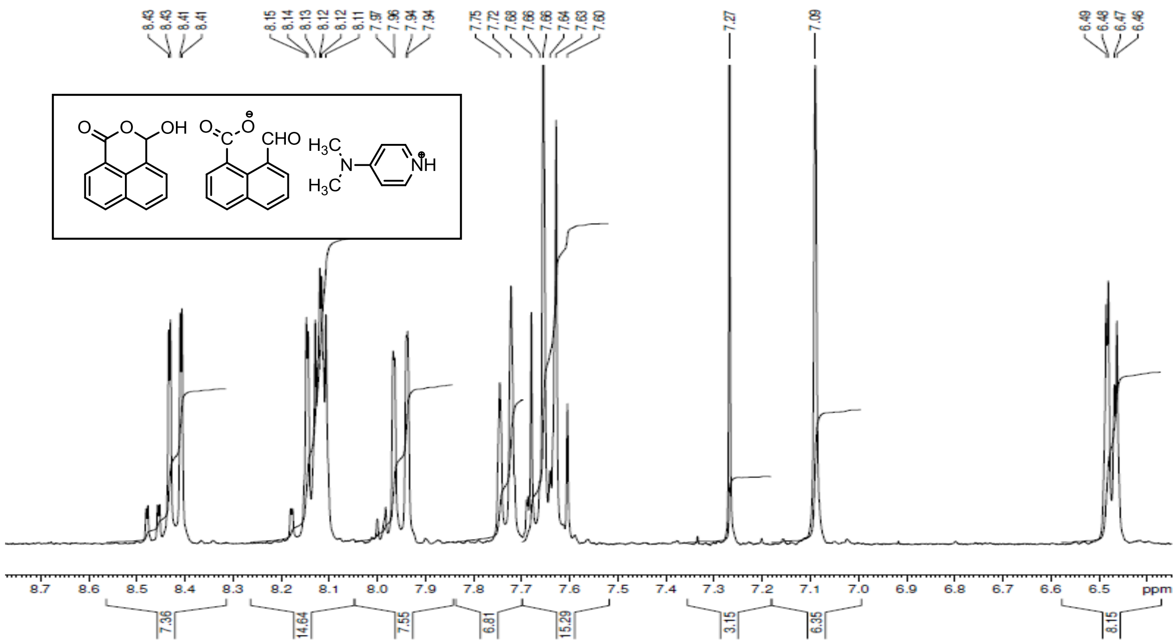
Atch 6.e. Expanded ^{13}C NMR spectrum of 3-(N-morpholinyl)-1H,3H-benzo[de]isochromen-1-one **(52)**



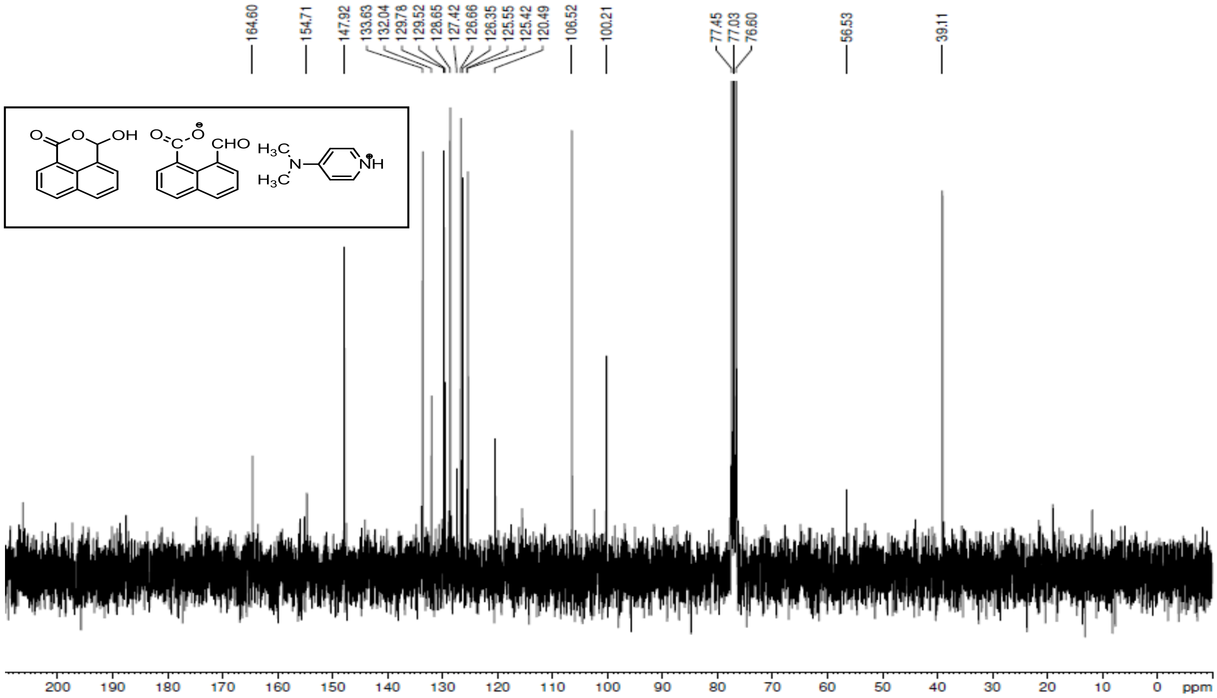
Atch 6.f. FT-IR spectrum of 3-(N-morpholinyl)-1H,3H-benzo[de]isochromen-1-one **(52)**



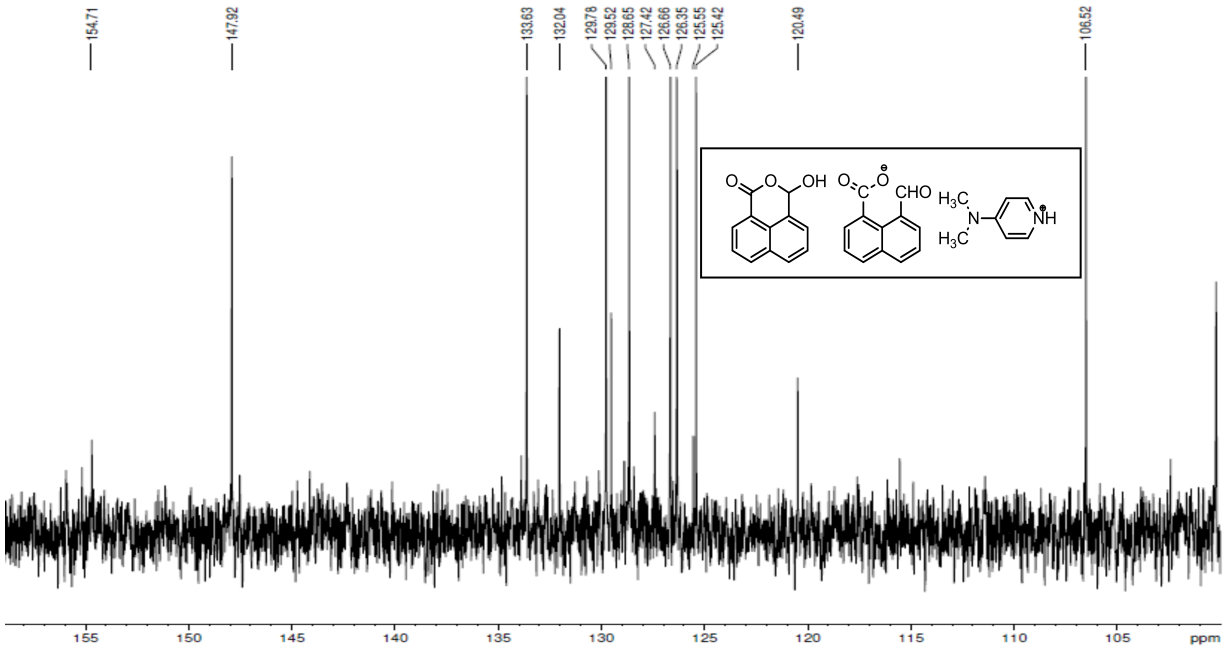
Atch 7.a. ^{1}H NMR spectrum of salt mixture of 3-hydroxybenzo[de]isochromen- 1(3H)-one, 4-(dimethylamino)pyridin-1-ium and 8-formyl-1-naphthoate **(53)**



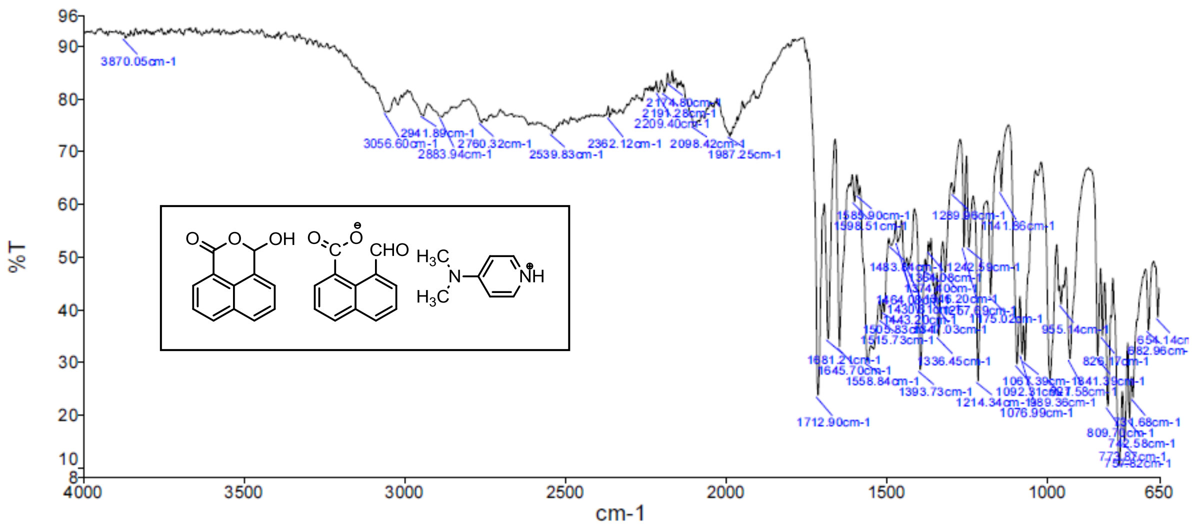
Atch 7.b. Expanded ^{1}H NMR spectrum of salt mixture of 3-hydroxybenzo[de]isochromen- 1(3H)-one, 4-(dimethylamino)pyridin-1-ium and 8-formyl-1-naphthoate **(53)**-Aromatic region



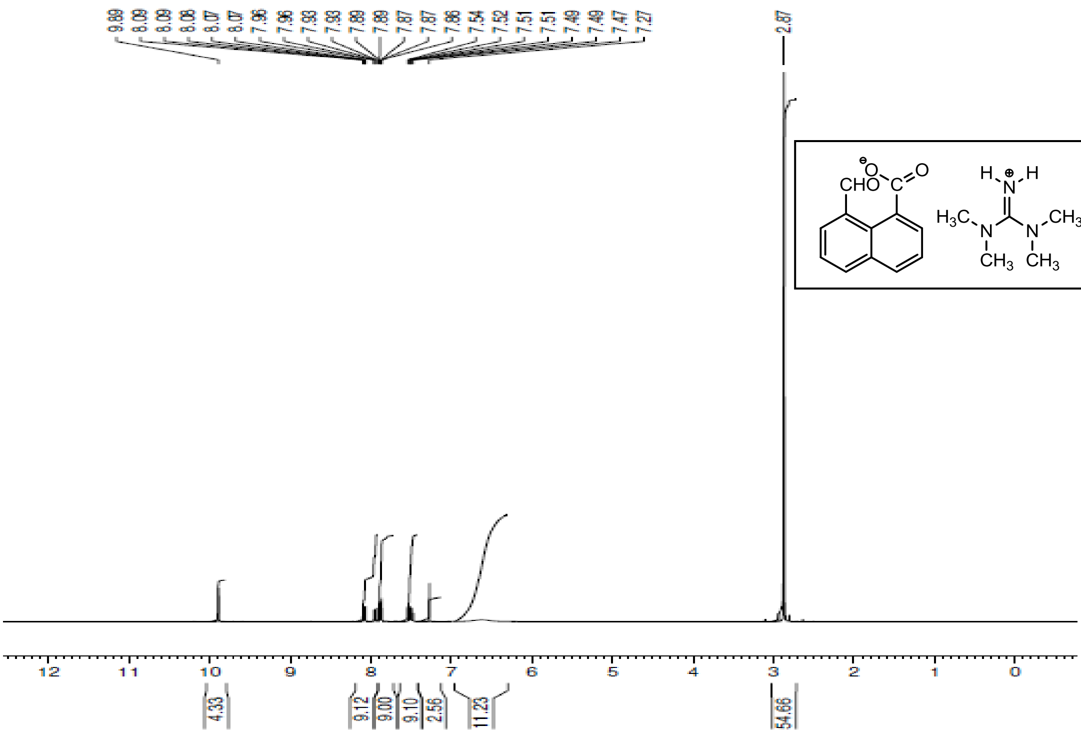
Atch 7.c. ^{13}C NMR spectrum of salt mixture of 3-hydroxybenzo[de]isochromen- 1(3H)-one, 4-(dimethylamino)pyridin-1-ium and 8-formyl-1-naphthoate **(53)**



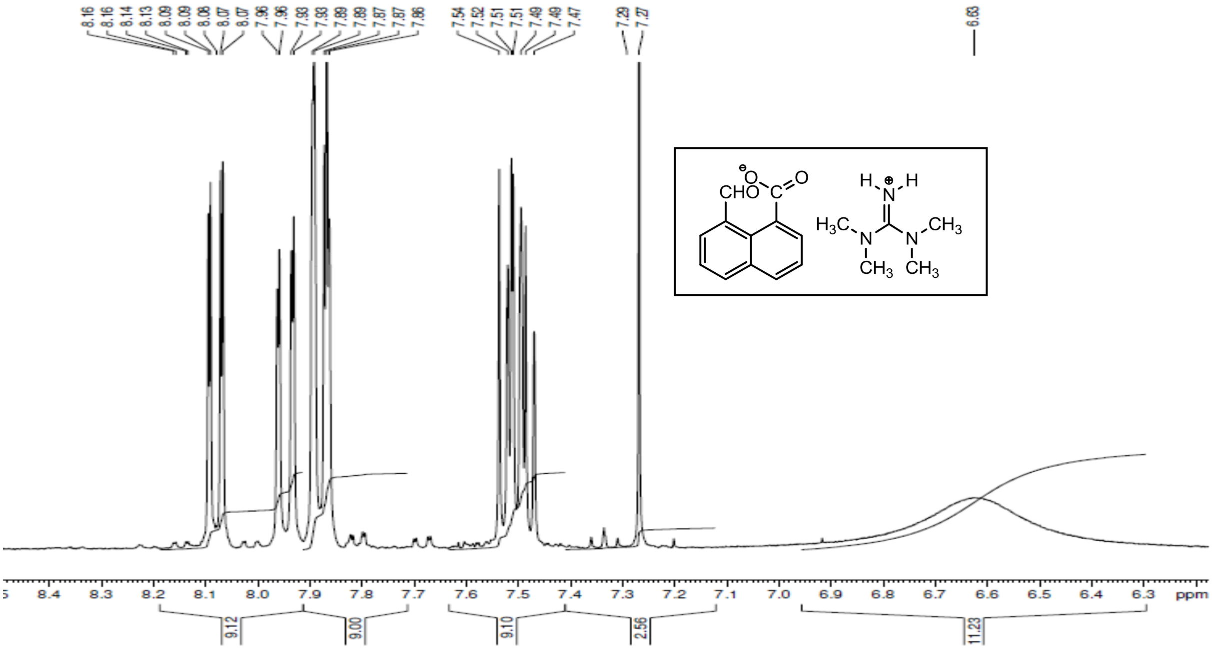
Atch 7.d. Expanded ^{13}C NMR spectrum of salt mixture of 3-hydroxybenzo[de]isochromen- 1(3H)-one, 4-(dimethylamino)pyridin-1-ium and 8-formyl-1-naphthoate **(53)**



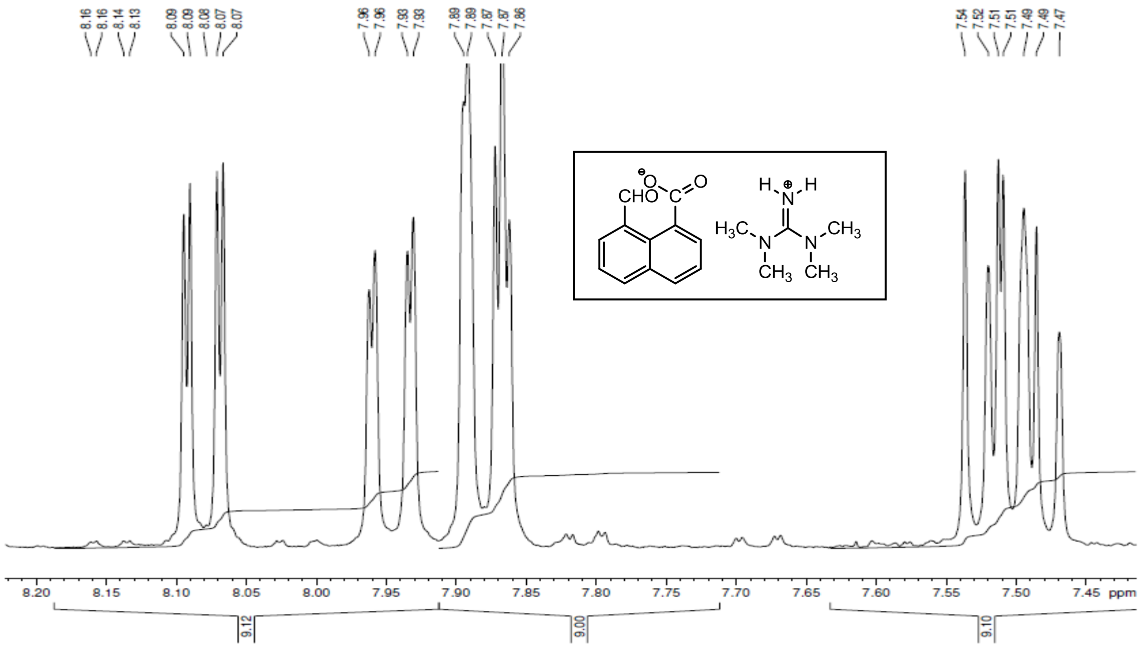
Atch 7.e. FT-IR spectrum of salt mixture of 3-hydroxybenzo[de]isochromen- 1(3H)-one, 4-(dimethylamino)pyridin-1-ium and 8-formyl-1-naphthoate **(53)**



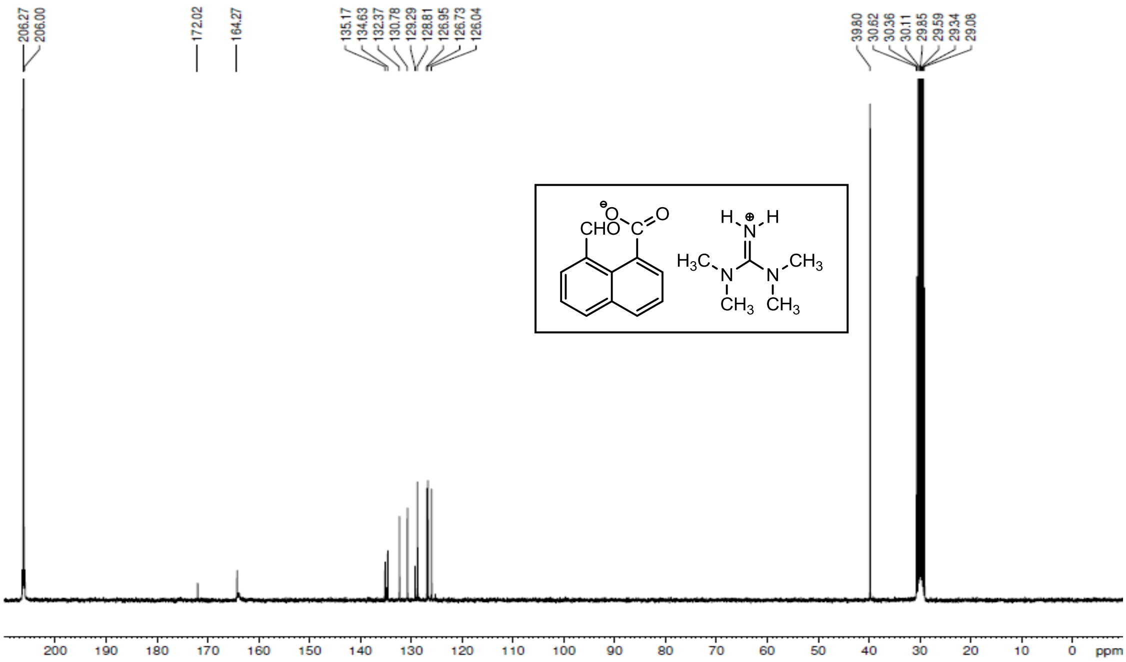
Atch 8.a. ^{1}H NMR spectrum of salt mixture of bis(dimethylamino)methaniminium and 8-formyl-1-naphthoate **(54)**



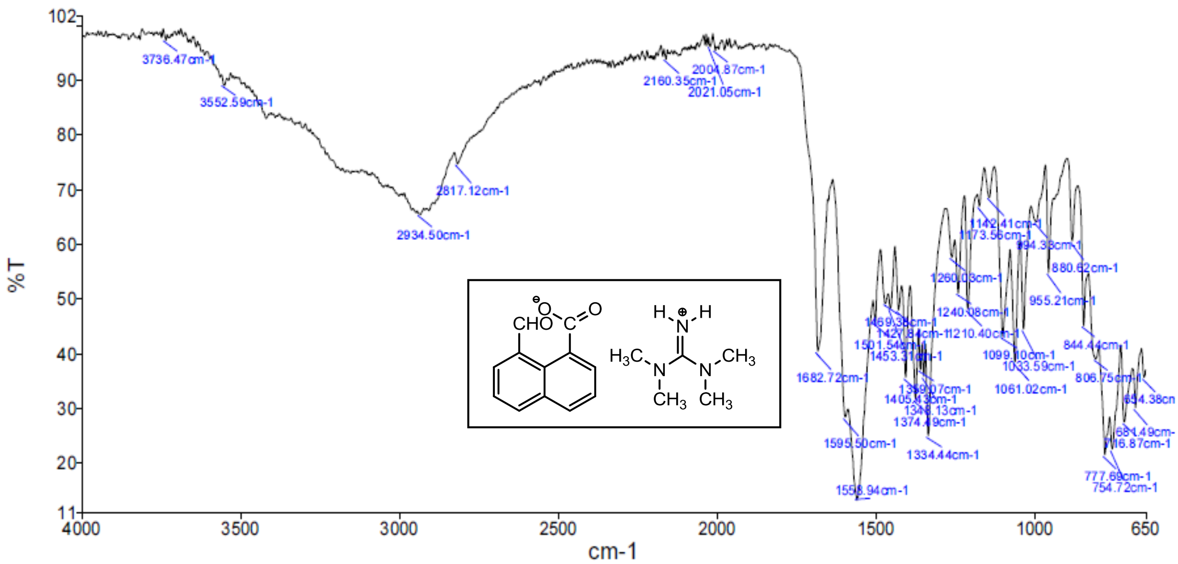
Atch 8.b. Expanded [1]H NMR spectrum of salt mixture of bis(dimethylamino)methaniminium and 8-formyl-1-naphthoate **(54)**



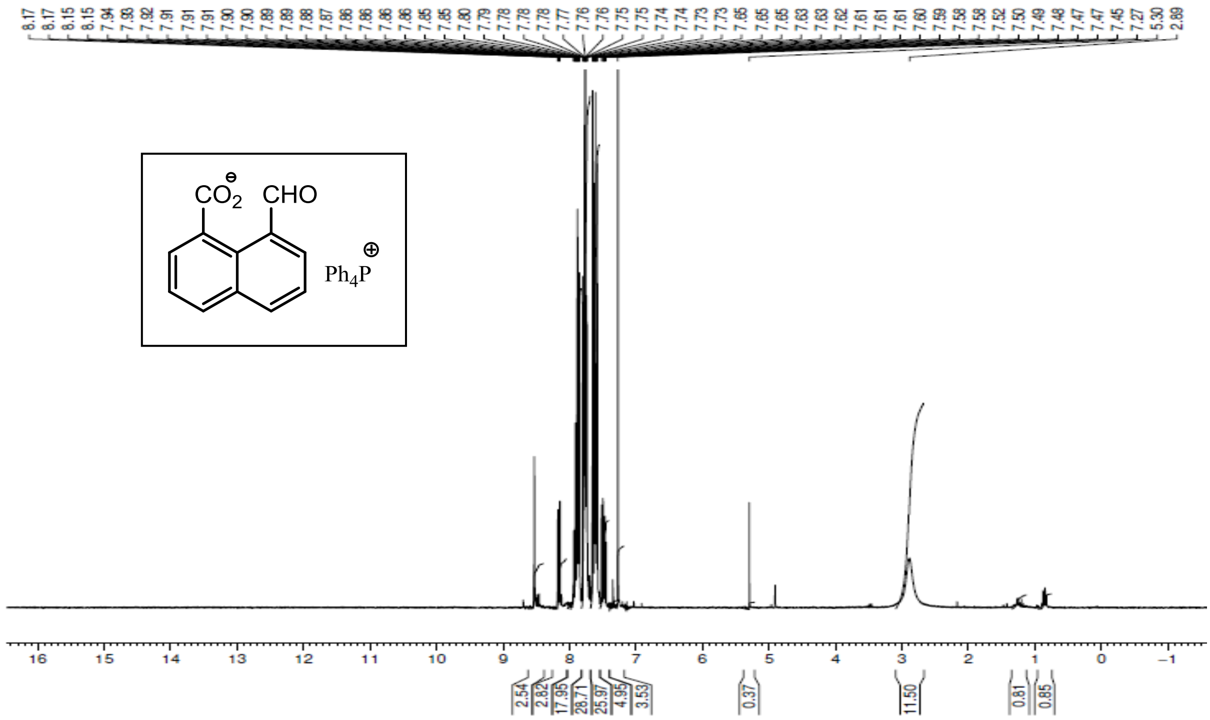
Atch 8.c. Expanded [1]H NMR spectrum of salt mixture of bis(dimethylamino)methaniminium and 8-formyl-1-naphthoate **(54)**



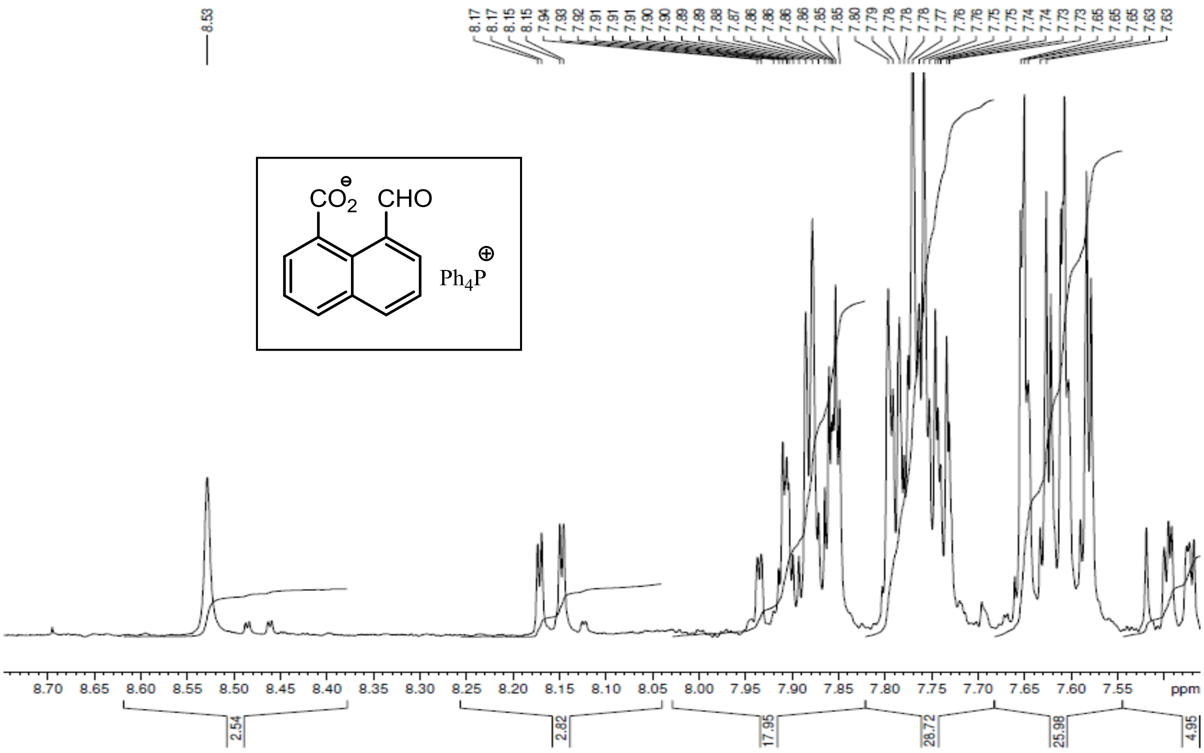
Atch 8.d. ^{13}C NMR spectrum of salt mixture of bis(dimethylamino)methaniminium and 8-formyl-1-naphthoate **(54)**



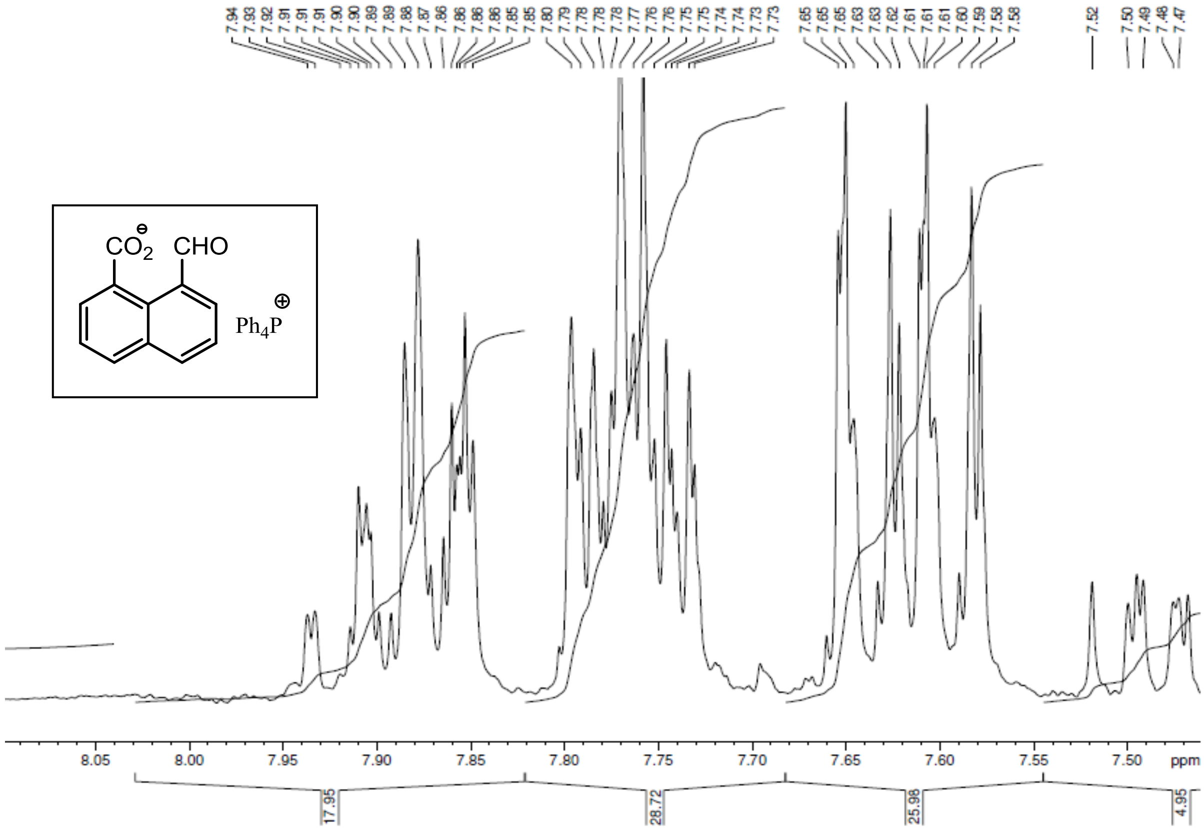
Atch 8.e. FT-IR spectrum of salt mixture of bis(dimethylamino)methaniminium and 8-formyl-1-naphthoate **(54)**



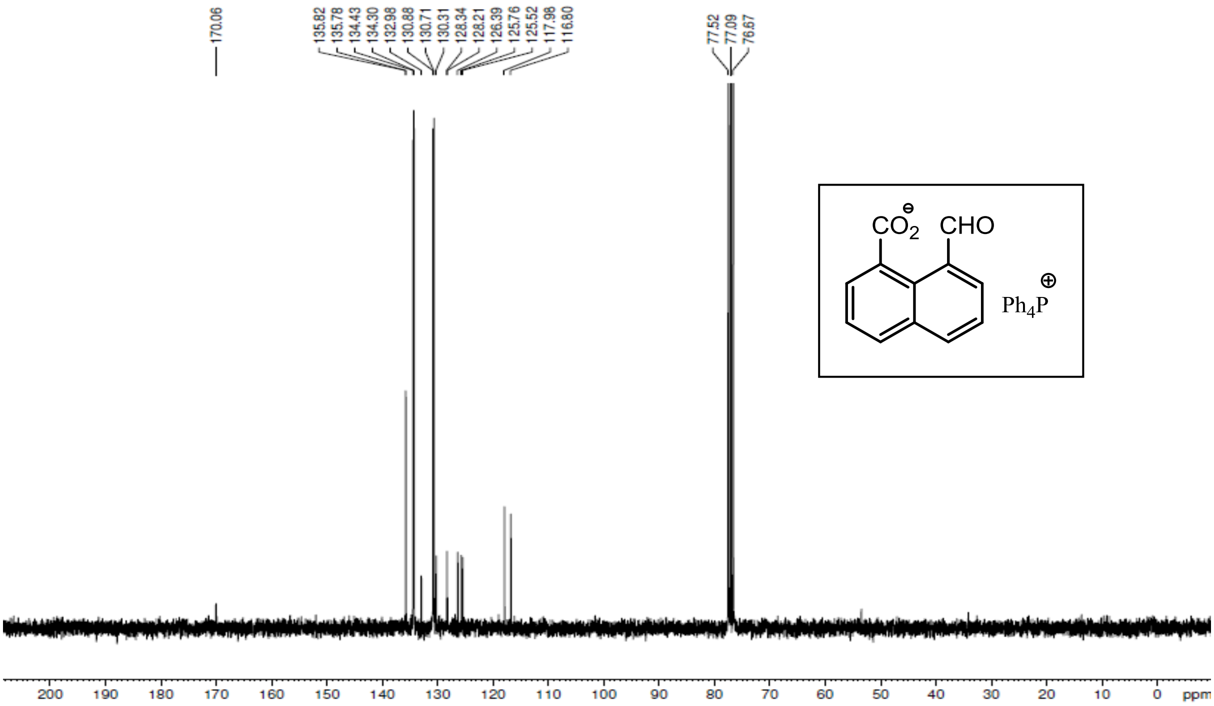
Atch 9.a. ^{1}H NMR spectrum of tetraphenylphosphonium 8-formyl-1-naphthoate **(55)**



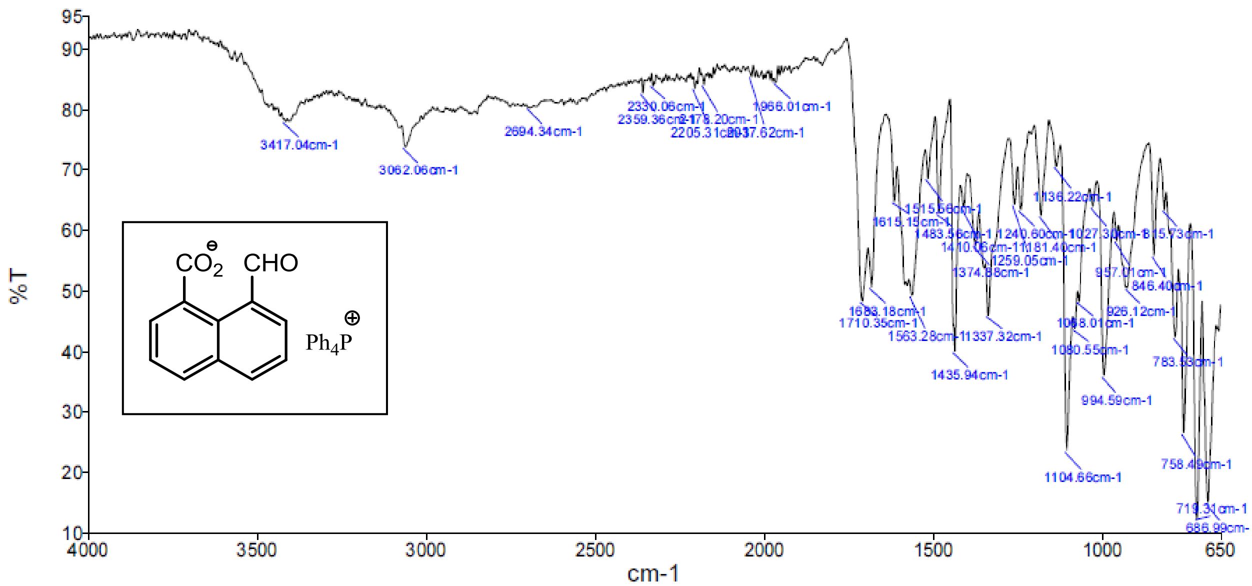
Atch 9.b. Expanded ^{1}H NMR spectrum of tetraphenylphosphonium 8-formyl-1-naphthoate **(55)**-Aromatic region



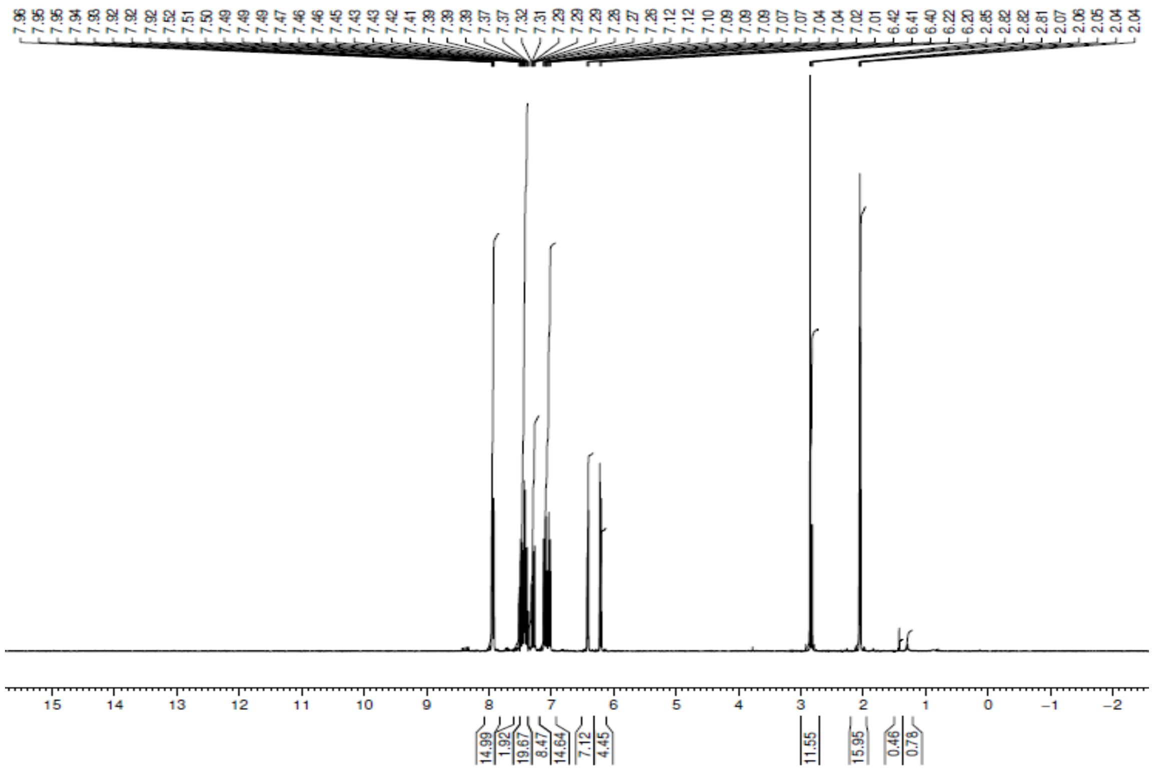
Atch 9.c. Expanded [1]H NMR spectrum of tetraphenylphosphonium 8-formyl-1-naphthoate **(55)**-Aromatic region



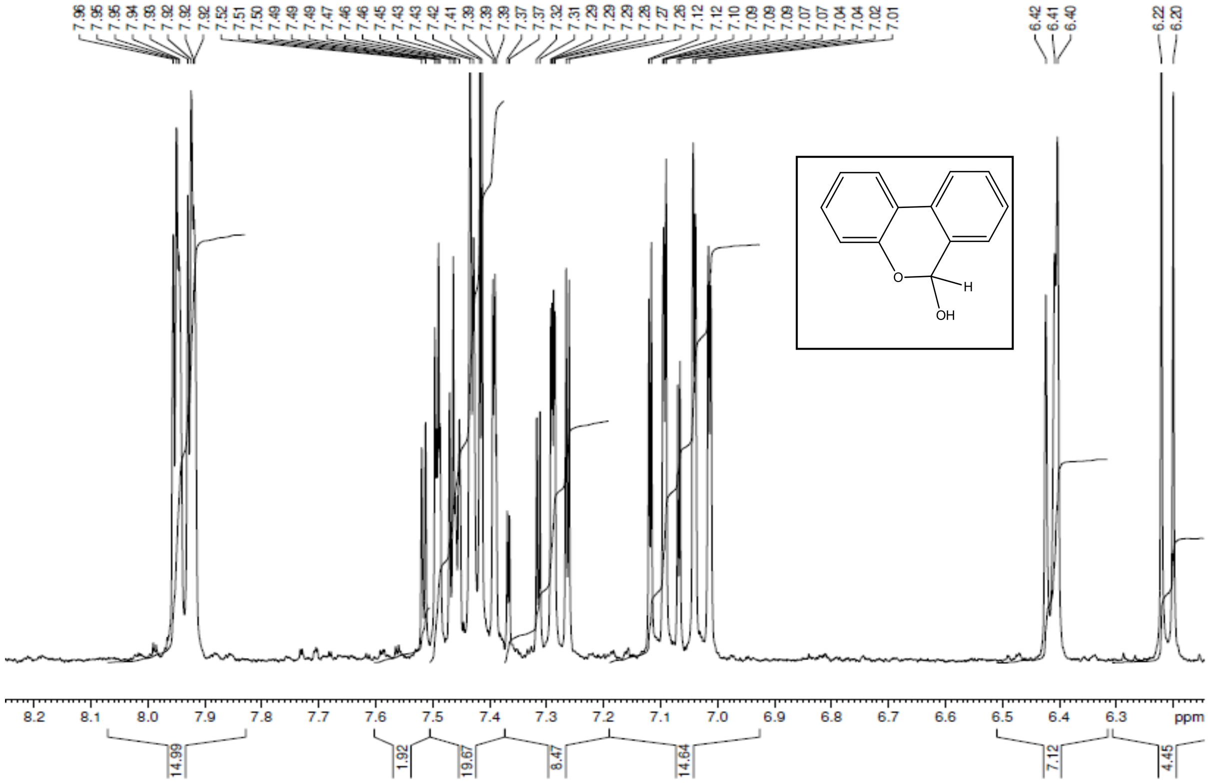
Atch 9.d. ^{13}C NMR spectrum of tetraphenylphosphonium 8-formyl-1-naphthoate **(55)**



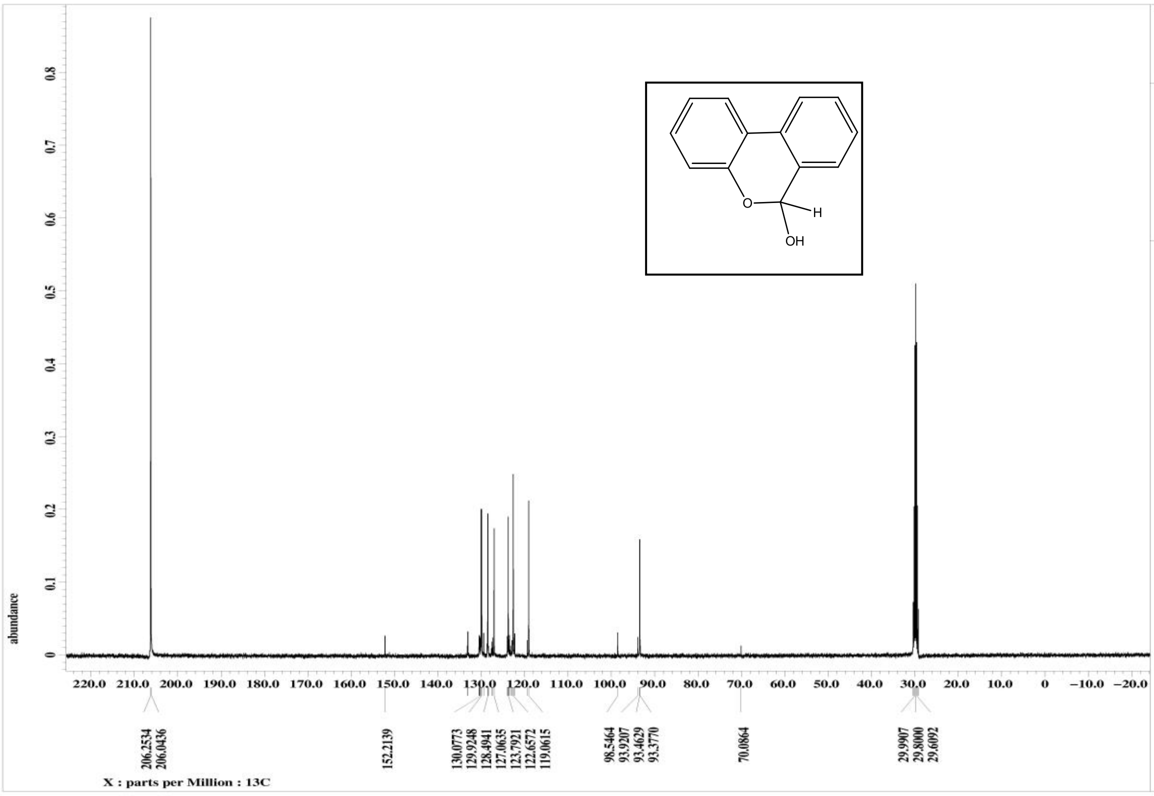
Atch 9.e. FT-IR spectrum of tetraphenylphosphonium 8-formyl-1-naphthoate **(55)**



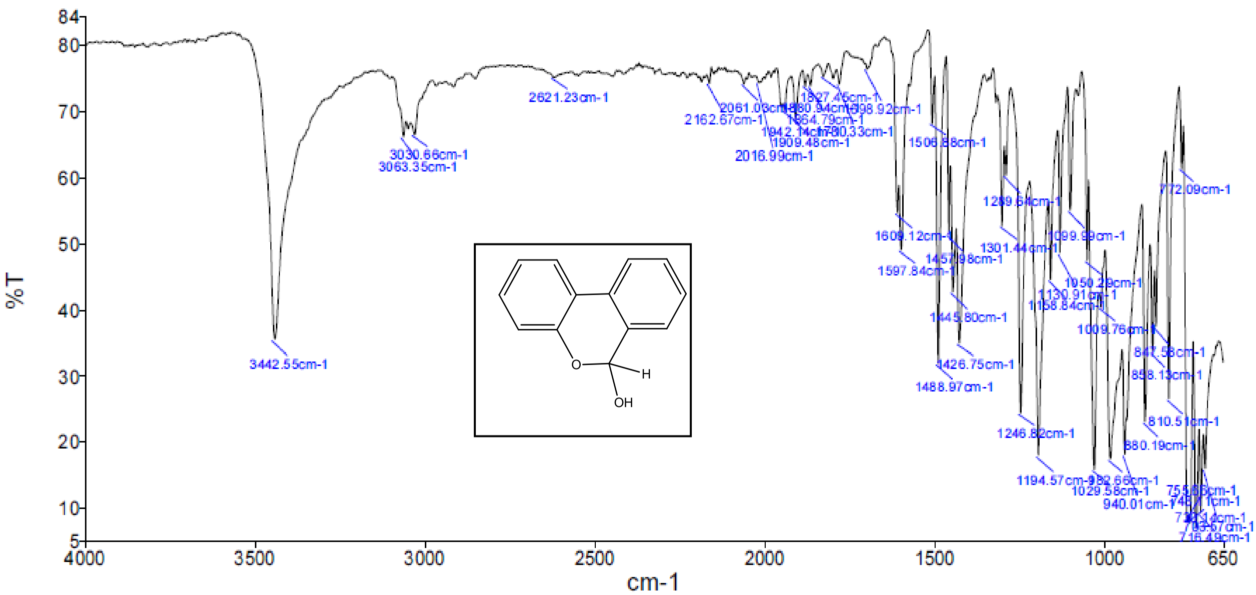
Attch 10.a. ^{1}H NMR spectrum of 6H-benzo[c]chromen-6-ol **(56)**



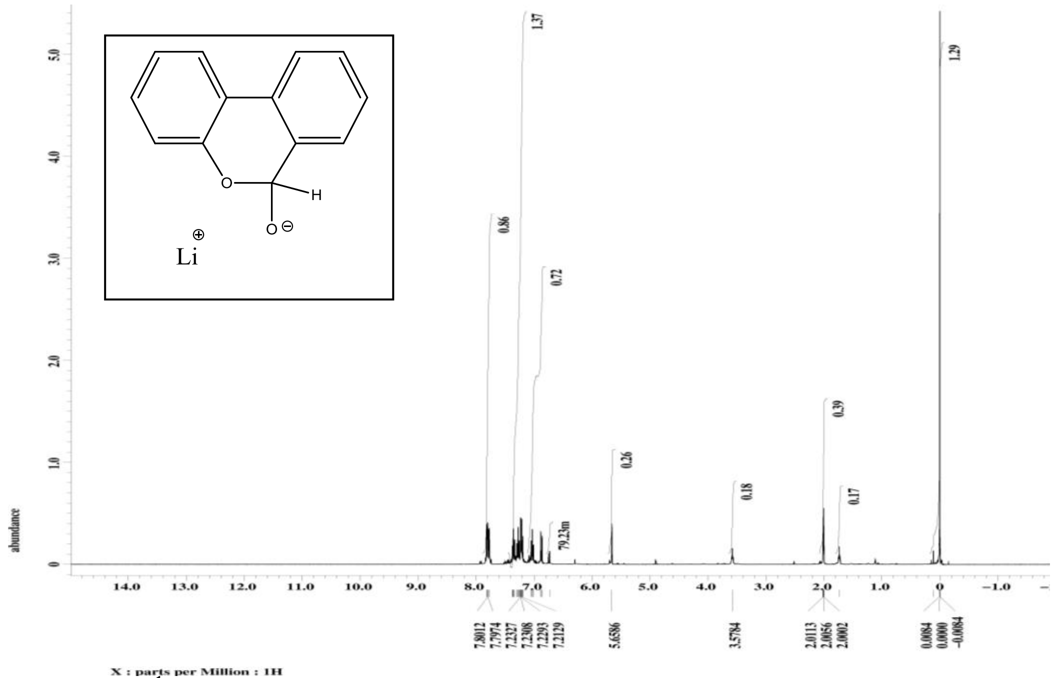
Attch 10.b. Expanded ^{1}H NMR spectrum of 6H-benzo[c]chromen-6-ol **(56)**



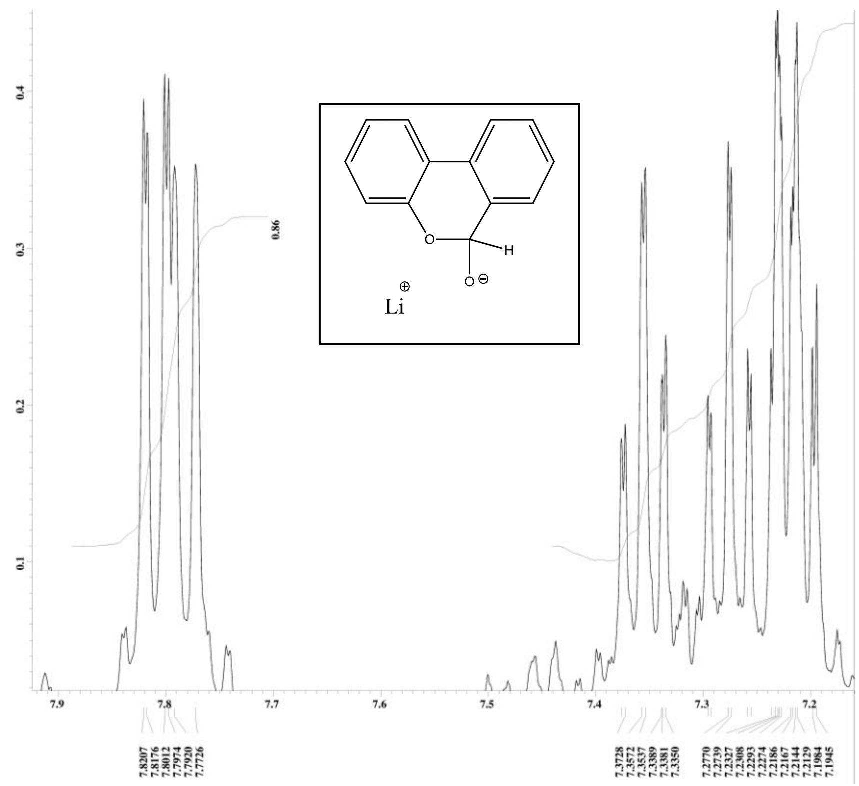
Atch 10.c. ^{13}C NMR spectrum of 6H-benzo[c]chromen-6-ol **(56)**



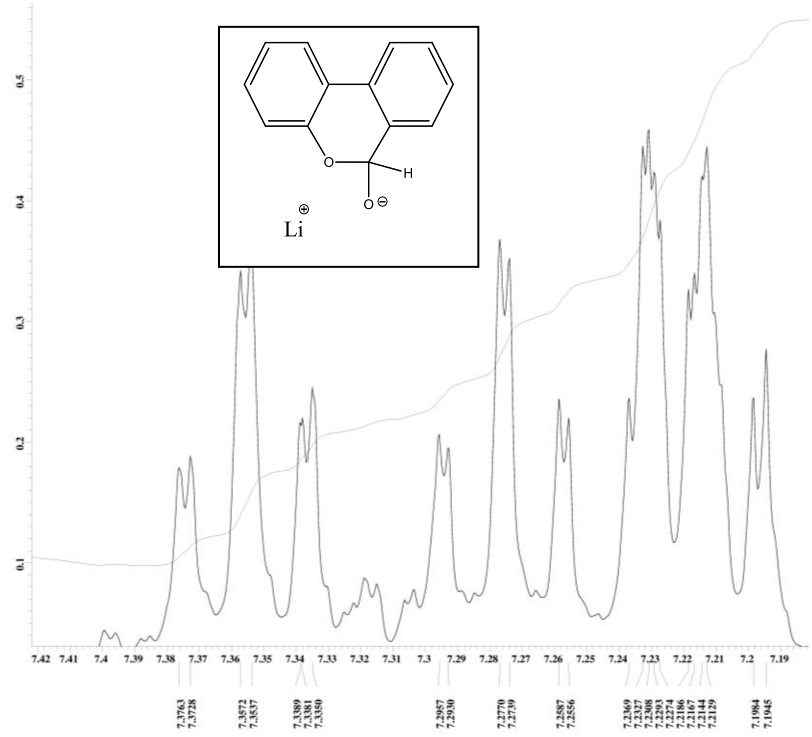
Atch 10.d. FT-IR spectrum of 6H-benzo[c]chromen-6-ol **(56)**



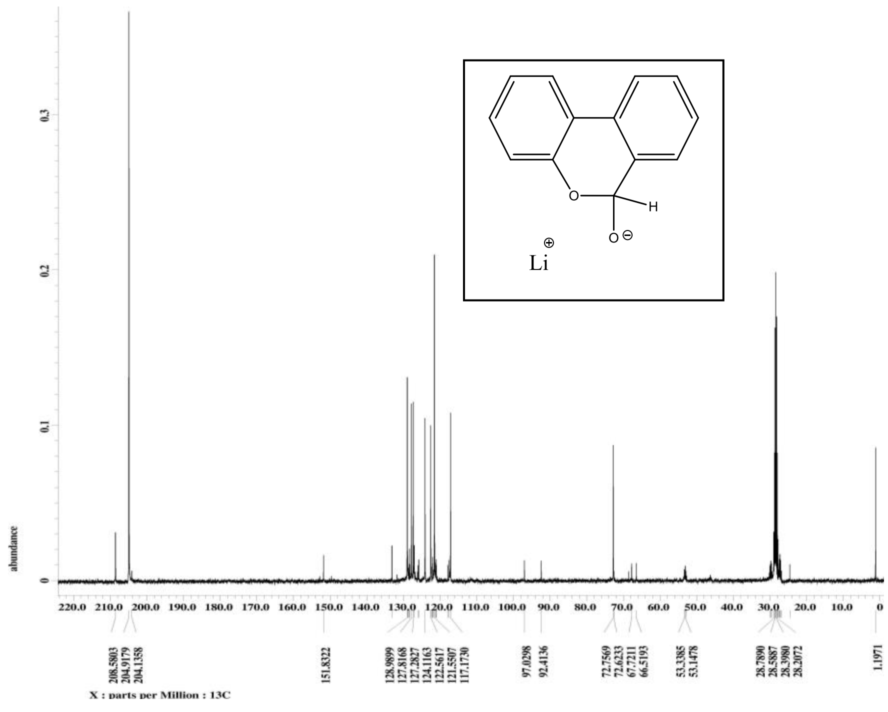
Atch 11.a. ^{1}H NMR spectrum of lithium 6H-benzo[c]chromen-6-olate **(59)**



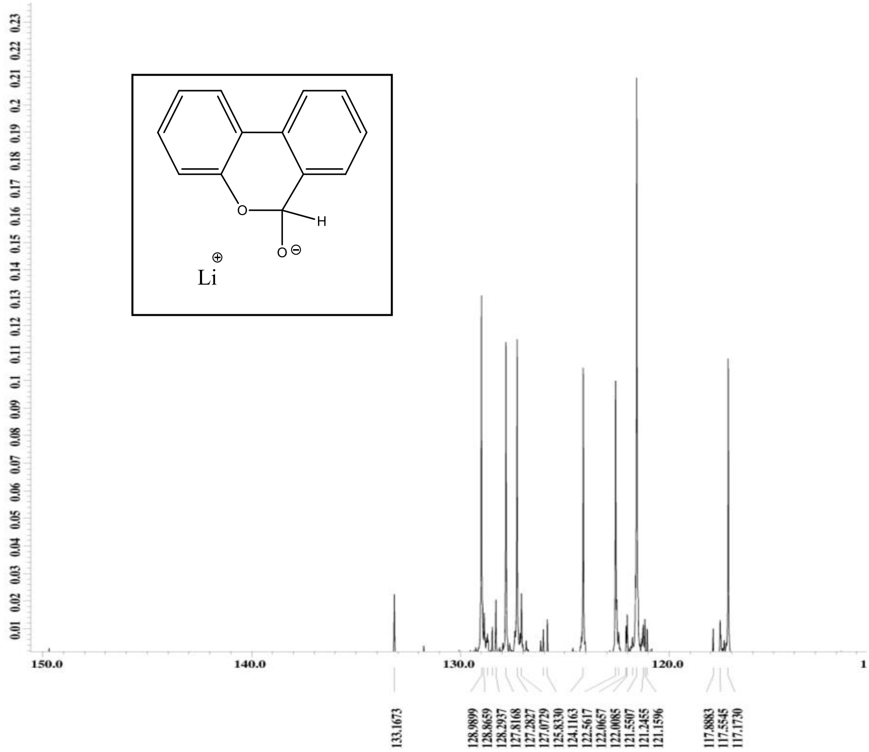
Atch 11.b. Expanded ^{1}H NMR spectrum of lithium 6H-benzo[c]chromen-6-olate **(59)**



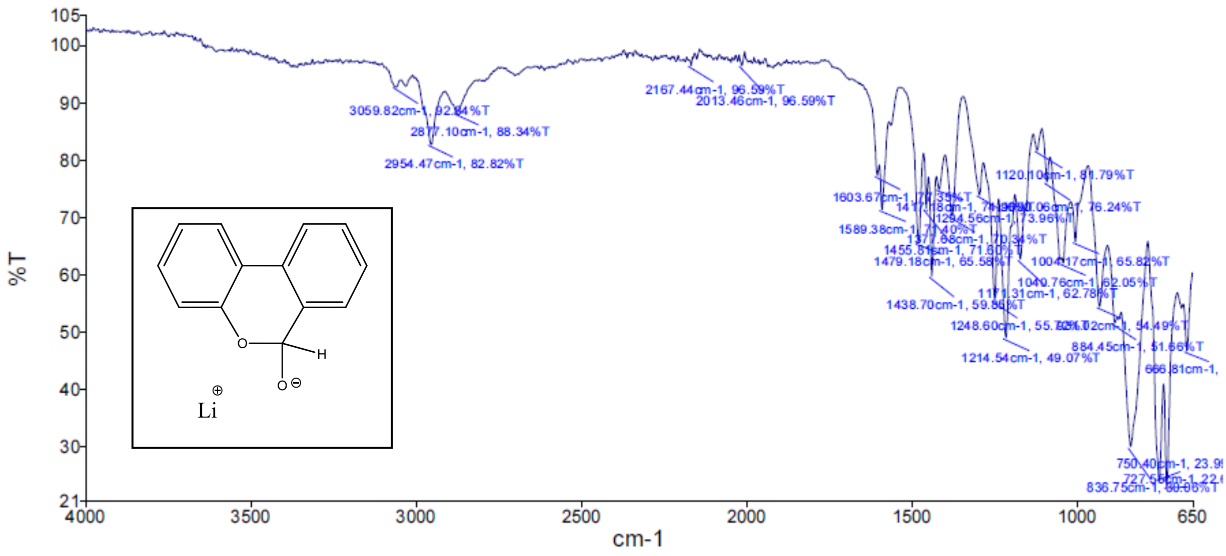
Atch 11.c. Expanded ^{1}H NMR spectrum of lithium 6H-benzo[c]chromen-6-olate **(59)**



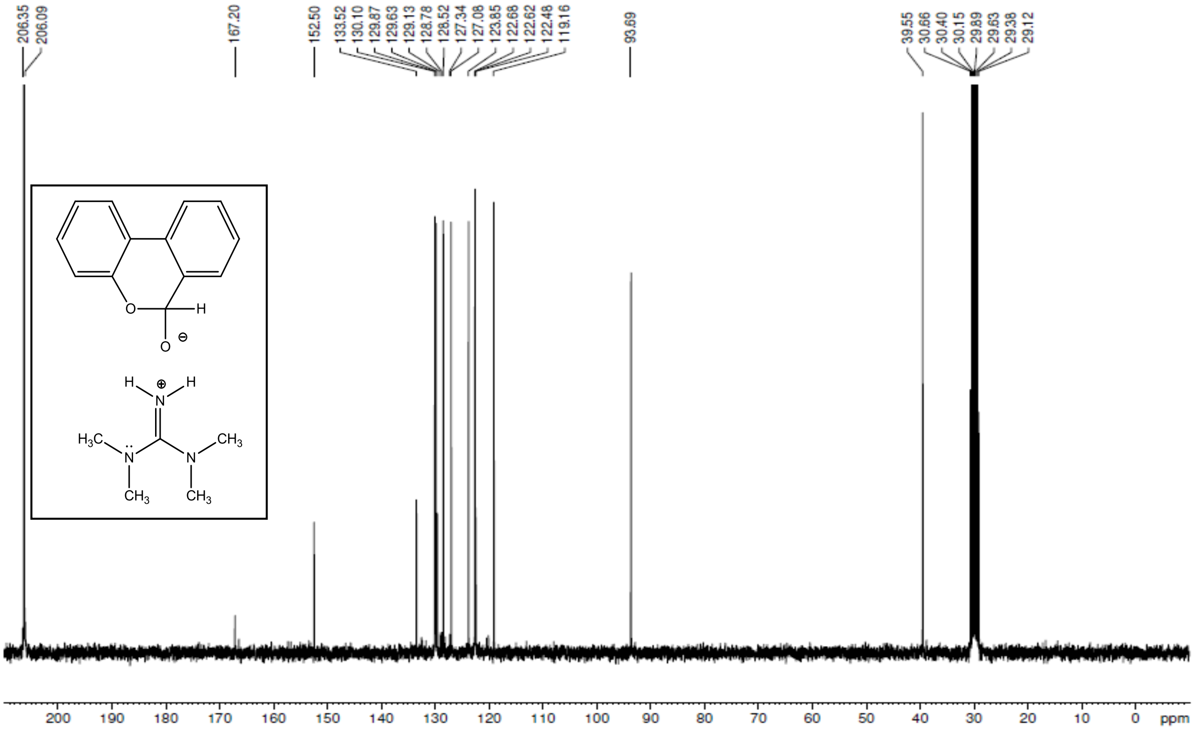
Atch 11.d. ^{13}C NMR spectrum of lithium 6H-benzo[c]chromen-6-olate **(59)**



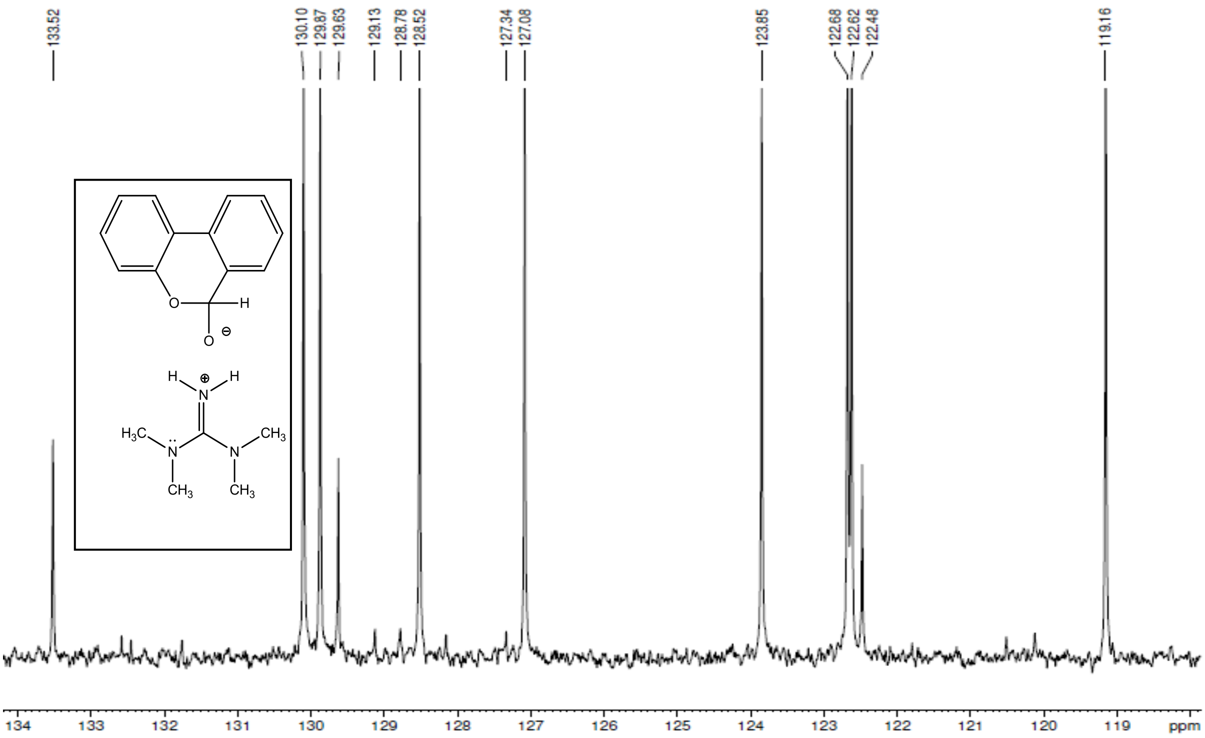
Atch 11.e. Expanded ^{13}C NMR spectrum of lithium 6H-benzo[c]chromen-6-olate **(59)**



Atch 11.f. FT-IR spectrum of lithium 6H-benzo[c]chromen-6-olate **(59)**



Atch 12.a. ^{13}C NMR spectrum of bis(dimethylamino)methaniminium 6H-benzo[c]chromen-6-olate **(60)**



Atch 12.b. Expanded ^{13}C NMR spectrum of bis(dimethylamino)methaniminium 6H-benzo[c]chromen-6-olate **(60)**

RESUME

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Nottingham Trent University	M.Sc. Chemistry Erasmus Exchange Student	2013-2014
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PUBLICATIONS

1) Wallis, J.D. ; Saritemur, G. ; Pitak, B.M. ; Coles, S.J., "Para-Substituted Potassium Hydrogen Dibenzoates", ***"in preparation for CrystEngComm"***

2) Wallis, J.D. ; Saritemur, G. ; Nomes, L.; Pitak, B.M. ; Coles, S.J., "O⋯C Interactions in the Salts of Naphthaldehydic Acid", ***"in preparation for CrystEngComm"***