TRIBENZOAZAACEPENTALENIDE ANION: DISCOVERY OF AN UNUSUALLY PLANAR AROMATIC COMPOUND

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TRIBENZOAZAACEPENTALENIDE ANION: DISCOVERY OF AN UNUSUALLY PLANAR AROMATIC COMPOUND

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ABSTRACT

TRIBENZOAZAACEPENTALENIDE ANION: DISCOVERY OF AN UNUSUALLY PLANAR AROMATIC COMPOUND

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With the discovery of fullerenes, the interest in synthesis of non-planar aromatic compounds increased significantly and these types of materials became important targets among the synthetic chemistry community. The dihydroacepentalenediide, the dianion of acepentalene was one of the widely sought targets which was synthesized in 1986 starting from triquinacene. Triquinacene itself also attracted significant attention due being potential precursor of dodecahedrane and possible homoaromaticity it might possess. Although many derivatives of triquinacene structure has been synthesized, hetero-analogues of the compound did not get attention until much later. The Mascal group was the first to realize the synthesis of nitrogen and oxygen containing derivatives where both showed remarkable structural properties and reactivities. The tribenzotriquinacene was also widely examined similar to triquinacene and many derivatives were realized over the years. Yet its heteroanalogues have never been studied. This study describes our efforts for nitrogen analogue, tribenzoazatriquinacene and its aromatic anion tribenzoazaacepentalenide. Tribenzoazatriquinacene was successfully synthesized starting from commercially available 5-dibenzosuberenone in 8 steps, including a remarkable cascade of cyclization/hydrogenation reaction. The existence of the corresponding 22π aromatic anion, tribenzoazaacepentalenide, was also successfully shown via a low-temperature NMR experiment.

Keywords: Convex Polycycles, Aromaticity, Fragments of Fullerenes

ÖZ

TRİBENZOAZAASEPENTALENİT ANYONU: OLAĞANDIŞI DÜZLEMSEL AROMATİK BİLEŞİĞİN KEŞFİ

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Ağustos 2020, 72 sayfa

Fullerenlerin keşfini takiben, düzlemsel olmayan aromatik yapıların sentezi kimya alanında büyük ilgi topladı ve bu materyaller sentetik kimyacılar arasında önemli bir hedef haline geldi. Dihidroasepentalenediide, asepentalene'in dianyonu geniş çapta aranan hedeflerden biri olup 1986 yılında trikuinasenden başlanarak sentezlenmiştir. Trikuinasenin kendisi dodekahedranın teorik öncüsü olması ve muhtemel homoaromatikliği nedeniyle önemli miktarda ilgi çekmiştir. Trikuinasen yapısının pek çok türevi sentezlenmesine karşın hetero-analogları uzun zaman sonraya kadar ilgi çekmemiştir. Mascal grubu oksijen ve azot içeren türevlerinin sentezini ilk fark edenler oldular. Bu moleküller dikkat çekici yapısal özellikler ve reaktivite göstermektedir. Tribenzotrikuinasen yapısı da geniş çapta incelenmiş, trikuinasen gibi pek çok türevi yıllar içinde keşfedilmiştir. Buna rağmen hetero-analoglarının şu güne kadar üzerinde çalışılmamıştır. Bu çalışma azot analoğu, tribenzoazatrikuinasenin ve aromatik anyonu tribenzoazaasepentalenitin gerçekleştirilmesi üzerine olan çabamızı tanımlamaktadır. Tribenzoazatrikuinasenin sentezi başarılı olarak ticari olarak satılan 5-dibenzosuberenone molekülünden, dikkate değer halkalaşma/hidrojenlendirme reaksiyonu içeren 8 basamakta tamamlanmıştır. 22π Aromatik anyon tribenzoazaasepentalenit, varlığı başarılı bir şekilde düşük dereceli NMR deneyleriyle gösterilmiştir.

Anahtar Kelimeler: Dışbükey Polisiklik Yapılar, Aromatiklik, Fulleren Parçaları.

To all people who sacrifice in the name of science…

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TABLE OF CONTENTS

LIST OF SCHEMES

SCHEMES

LIST OF FIGURES

FIGURES

LIST OF ABBREVIATIONS

ABBREVIATIONS

ACN:	Acetonitrile
AcOH:	Acetic Acid
DCM:	Dichloromethane
DMF:	Dimethylformamide
DMSO:	Dimethyl sulfoxide
EtOAc:	Ethyl Acetate
HRMS:	High Resolution Mass Spectroscopy
mCPBA:	*meta*-Chloroperoxybenzoic Acid
MeOH:	Methanol
NICS:	Nucleus Independent Chemical Shifts
NMR:	Nuclear Magnetic Resonance
p-TSA:	*para*-Toluenesulfonic acid
RT:	Room Temperature
TFA:	Trifloroacetic Acid
THF:	Tetrahydrofuran
TLC:	Thin Layer Chromatography

CHAPTER 1

INTRODUCTION

1.1 Fullerenes

Buckminsterfullerene or short fullerene (**1**) is a closed cage molecule that consist solely of carbons bounded to each other via double and single bonds (Figure 1.1). These carbon cages exist with the rule of having 20+2n atoms. (Kroto et al., 1991). Fullerenes were discovered by Harold Kroto, Robert Curl, and Richard Smalley while vaporizing carbon in the helium atmosphere (Kroto et al., 1985) and they were awarded Nobel Prize in Chemistry in 1996 (*Nobel Prize 1996*, n.d.) for their work. The discovery of fullerene was significant in the sense that it showed us carbon still manages to surprise us with new allotropes. After the discovery of fullerenes, attention to the convex polycyclic structures has increased. The studies on C_{60} revealed that fullerene-based materials show extraordinary charge conducting properties and high ionic mobility compared to usual conductors (Shaheen et al., 2001). Fullerenes are now being used in a variety of fields ranging from renewable energy to medical sciences (Bühl & Hirsch, 2001; Zhang et al., 2014).

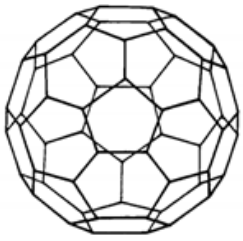

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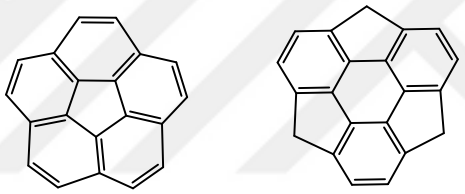
Figure 1.1 The structure of fullerene

1.2 Fragments of Fullerenes

Just like fullerene derivatives, their fragments have also become essential targets among scientists. One of the reasons for this interest arises from the fact that while most of these fragments are aromatic, they are non-planar. By having this textbook changing property -having aromatic properties yet being non-planar- they draw significant attention from the scientific community and are widely examined. Among the fragments of fullerenes, corannulene (**2**) and sumanene (**3**) are the most known and studied examples (Figure 1.2). Corannulene (**2**) consists of benzene rings fused with cyclopentane ring. The compound obeys the rule of having a $4n+2\pi$ electron both in inner cyclopentadienyl anion and outer cyclopentadecaheptaenyl cation (Barth & Lawton, 1971), an "aromatic-in-aromatic" compound.



2 **3**

Figure 1.2 Structure of corannulene (**2**) and sumanene (**3**)

Sumanene (**3**) has four benzene rings fused with three cyclopentane rings. The structure's edges resemble the petals in the sunflower. Therefore, the name sumanene has chosen for the compound, which means sunflower in both Hindi and Sanskrit (Mehta et al., 1993). Due to its three benzylic positions, the structure was easily functionalized to yield theoretically interesting structures (Sakane et al., 2009; Szumna, 2010; Tanikawa et al., 2011).

1.3 Smallest Fullerene C_{20} and Its Fragments

The smallest possible fullerene is C_{20}, composed of only five membered rings. Because of the large angle strain the molecule possess its synthesis was not deemed possible. However in 2000, its existence was proven in the seminal study by Prinzbach through gas-phase debromination of brominated dodecahedrane (Prinzbach et al., 2000).

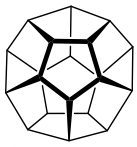


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Figure 1.3 Structure of dodecahedrane

The synthesis of dodecahedrane (**4**) itself gathered a lot of attention, not only being the precursor of to the smallest possible fullerene but also being one of the Platonic hydrocarbons. Platonic hydrocarbons share the same geometric structure as Platonic solids (Daintith, 2008). Platon associated the elements with these solids; the earth was a cube, the fire was tetrahedron, the air was octahedron, water was icosahedron, and dodecahedron was the heavenly material (L. A. Paquette, 1982). This idea largely accepted as earliest atom theory as it suggested that the materials composed of smaller particles. Represented as the "heavenly material", the synthesis of dodecahedrane (**4**) became a significant target among synthetic organic chemists. The group of Leo Paquette was first to synthesize dodecahedrane (**4**) in 1982 and results were published in the seminal paper where they describe their motivation for synthesis due to dodecahedrane's symmetric, aesthetically pleasing, and complex structure. The synthesis of this structure that possesses perfect icosahedral symmetry, was achieved in 23 steps starting from cyclopentadienide anion (Ternansky et al., 1982).

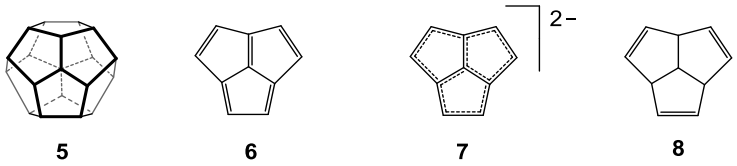
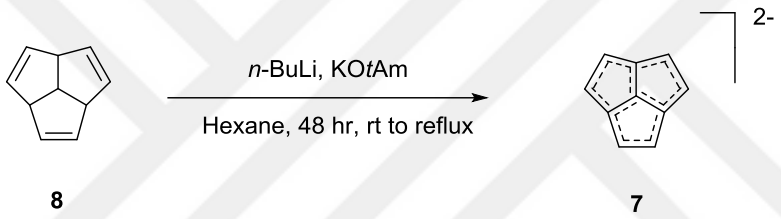


Figure 1.4 Structures of C_{20} (**5**), acepentalene(**6**), acepentalenide (**7**), triquinacene (**8**).

Half-clipping of C_{20} (**5**), is acepentalene (**6**) which is an antiaromatic compound. However, its dianion acepentalenide (**7**) is a non-planar aromatic structure. The successful synthesis of acepentalenide (**7**) was achieved directly from triquinacene (**8**), by de Meijere and co-workers in a remarkable superbase induced dehydrogenation (scheme 1.1).



Scheme 1.1 Synthesis of acepentalenide dianion. Reagents and conditions: *a.* *n*-BuLi, potassium *tert*-amyl alkoxide, *n*-hexane, 24-hour rt, then 24-hour reflux.

The reaction was performed by using *n*-BuLi and potassium *tert*-amyl alkoxide (KO*t*Am) and hexane as solvent. The mixture further refluxed for the completion of the reaction (scheme 1.1). The ^{1}H-NMR spectrum showed only one singlet, however spectrum became more complicated as the product slowly decomposed in THF at -40 °C (Lendvai et al., 1986).

1.4 Triquinane and Triquinacene Chemistry

The triquinanes (**9**) are a general tricyclo undecane ring systems and they can be found in form of both in angular and linear form. They can be found in nature hence triquinane derivatives has been important targets among number of research groups (Hudlicky et al., 1980; Paquette & Han, 1979).

The triquinacene (**8**) has been investigated in detail due to the possibility of possessing homoaromaticity. It also plays an essential role in being the possible precursor of dodecahedrane (**4**) through a dimerization reaction (Woodward et al., 1964). After the successful synthesis of the triquinacene, a number of work has been published about the compound ranging from metal complexes (Codding et al., 1982) to thermochemical and theoretical studies (Verevkin et al., 1998).

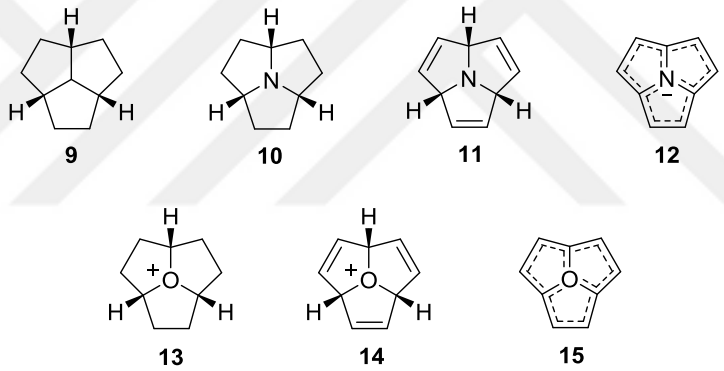
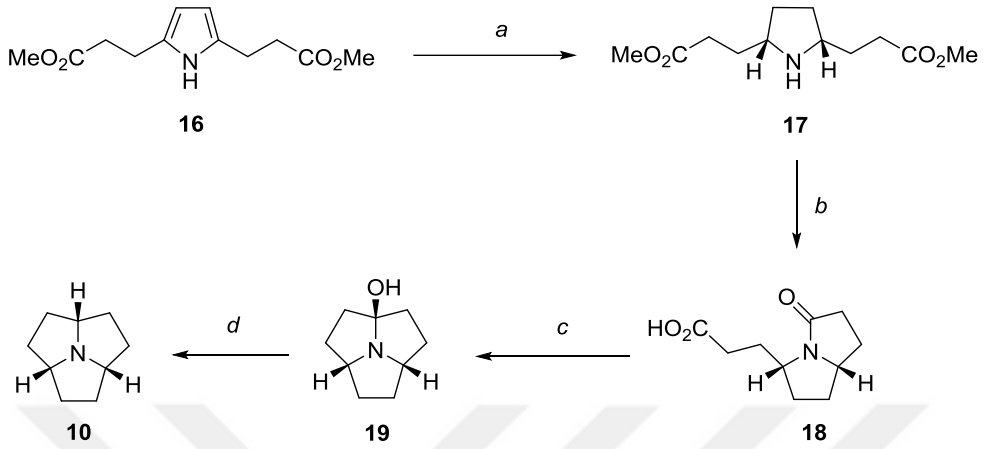


Figure 1.5 Triquinane (**9**), azatriquinane (**10**)azatriquinacene (**11**), azaacepentalenide (**12**), oxatriquinane (**13**), oxatriquinacene (**14**), oxaacepentalene (**15**)

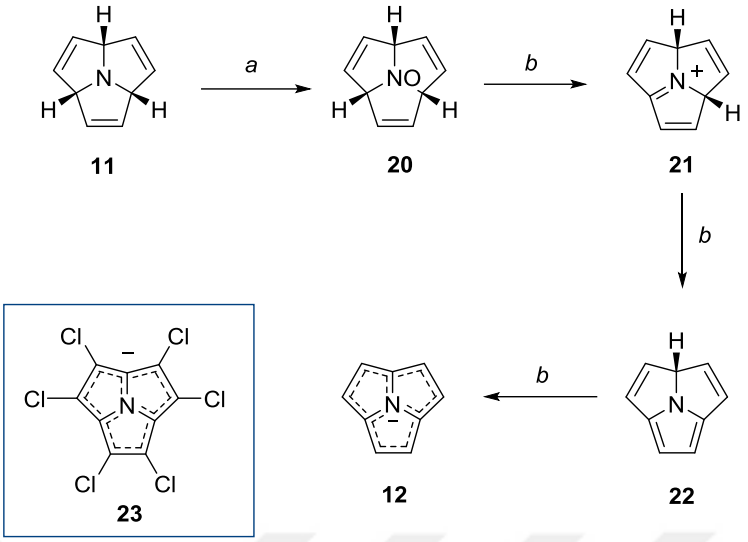
Although the triquinane (**9**) and triquinacene (**8**) chemistry attracted that much attention, the heteroatom-containing analogue of these compounds were not studied until the mid-90s. The Mascal group successfully synthesized the nitrogen (**10, 11)** and oxygen-containing (**13, 14**) analogues and a number of fundamentally interesting observations have been made with these heteroatom containing triquinanes. (Hext et al., 1998; Mascal et al., 2008).

(Mark Mascal et al., 1996)(Mark Mascal et al., 1996)



Scheme 1.2 Synthetic pathway of azatriquinane. Reagents and conditions: a. H_2, Rh/Al_2O_3; b. heat, xylenes; c. heat, soda-lime; d. $LiAlH_4$, THF, heat.

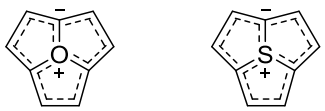
The synthesis of the aza-analogue, azatriquinane (**10**) began with diastereoselectively reduction of **16** via hydrogenation over rhodium on alumina to give the target pyrrolidine product **17**. Refluxing **17** in xylene gave the first cyclization product **18**, and the final cyclization was performed with dry distillation over soda lime to give the core structure of azatriquinane. The dehydration of the alcohol group on compound **19** was performed with strong reducing agent $LiAlH_4$ to give azatriquinane (**10**) (scheme 1.2). The compound **10** possesses a convex shape, and according to the NMR data, the compound is the most basic trialkyl amine ever known. This compound is even more basic than quinuclidine (Mascal et al., 1996).



Scheme 1.3 Synthesis of azaacepentalenide anion. Reagents and conditions: *a*. *m*-CPBA; *b*. n-BuLi

The synthesis of a nitrogen analogue of non-planar aromatic compound acepentalenide (**7**), the azaacepentalenide anion (**12**), was performed successfully by the Mascal group. The first step of the synthesis was the oxidation of the **11** with *m*-CPBA to yield stable N-oxide (**20)**. Then, in d_8-THF, **20** treated with excess *n*-BuLi to give aromatic azaacepentalenide anion (**12**) (scheme 1.3). NMR data and NICS calculations showed that azaacepentalenide anion (**12**) is aromatic yet have a convex structure, similar to acepentalenide (**7**) (Mascal & Bertran, 2005). Likewise, hexachloroazatriquinane was oxidized and treated with LiHMDS to yield perchloroazaacepentalene (**23**). This aromatic anion is highly stable, and its tetrabutylammonium salt could be even chromatographed on alumina. (Mascal & Bertran, 2005).

After the synthesis of azatriquinane (**10**) and the corresponding aromatic anion **12**, new members this family of compounds were pursued. According to the theoretical calculations, oxygen (**15**) and sulfur (**24**) analogues of the aromatic system in the triquinane framework would have higher aromaticity compared to benzene (Mascal, 2007).



15 **24**

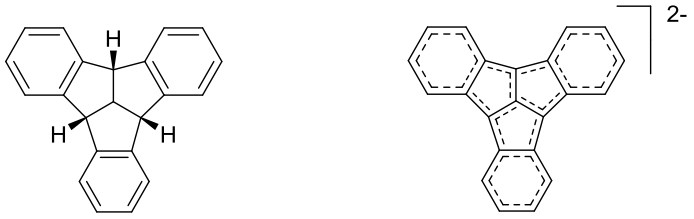
Figure 1.6 Structures of oxygen and sulfur analogues of acepentalenide.

The parent oxygen containing triquinane, oxatriquinane (**13**) was synthesized successfully and the system reveled a number of literature altering and exciting properties. First of all, although it is an oxonium ion, oxatriquinane showed remarkable stability. Compound **13** was refluxed in water for three days, and no decomposition was observed (Mascal et al., 2008). Also, its PF_6^- and SbF_6^- salts can be chromatographed on silica. Furthermore, the trimethyloxatriquinane derivative (**26**) gives S_N2 reaction on a tertiary center on the contrary to the common belief of the S_N2 reaction does not happen on tertiary centers (Mascal et al., 2010).

13 **26**

Figure 1.7 Structures of oxatriquinacene (**13**) and trimethyloxatriquinane (**26**)

1.5 Tribenzotriquinacene

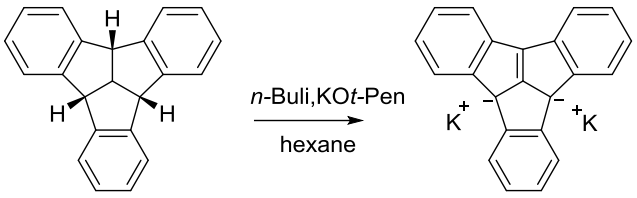


27 28

Figure 1.8 Structure of tribenzotriquinacene (**27**) and tribenzoacepentalendiide (**28**)

The tribenzotriquinacene (**27**) compound has an interesting structure where three benzene rings isolated from each other with nearly orthogonal geometry in 3D space due to concave shape of the **27** The compound **27** is a challenging synthetic target and its non-planar aromatic anion (**28**) has also been an important synthetic target. The first synthesis of tribenzotriquinacene was achieved in 1984 by the group of Dietmar Kuck (Kuck, 1984).

The aromatic tribenzacepentalenediide (**28**) was synthesized in one-pot reaction from **27** by using Lochmann-Schlosser base. (Haag et al., 1995).



27 28

Scheme 1.4 Synthesis of tribenzacepentalenediide (**28**)

The tribenzotriquinacene molecule is widely examined as it can be a precursor to a wide variety of compounds with symmetric bowl-shape geometry.

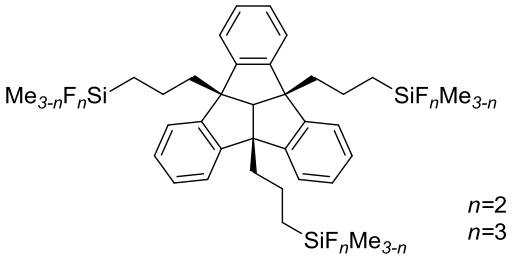


Figure 1.9 Structure of tribenzotriquinacene based poly-Lewis-acid

In the last 40 years, Lewis-acidic groups carried by different hosts became synthetic targets and several derivatives of **28** with Lewis-acidic groups like $SnMe_3$, SiF_3, $SiMeF_2$ are reported. Tribenzotriquinacene (**28**) can carry six $SiMe_3$ or $SnMe_3$ groups which makes **28** good candidate for poly-Lewis-acid based structures. By attachment of SiF_3 groups to the structure by flexible arms, triple Lewis-acid of tribenzotriquinacene was synthesized (Tomaschautzky et al., 2017).

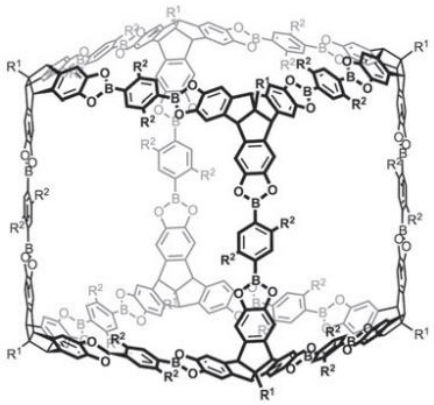


Figure 1.10 Structure of molecular cube made with triquinacene

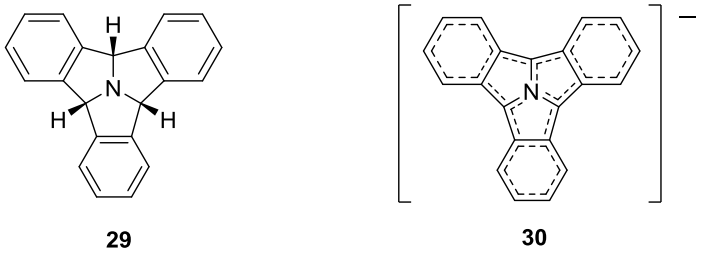
In a recent seminal study, the dynamic assembly of triquinacene compounds to molecular cubes has been demonstrated (figure 1.10). The synthesis of these metal-free novel nano-cubes was achieved in a one-pot reaction using substituted tribenzotriquinacene and a diboronic ester (Klotzbach et al., 2014).

1.6 Aim of the Study

Hundreds of triquinacene derivatives were synthesized, and many studies were performed addressing their properties: from rearrangement chemistry to metal complexations. Even though many interesting studies were performed on the triquinacene framework, the hetero-analogues of this system were not investigated for years as mentioned. These investigations of heterosystems resulted in many firsts in the literature such as non-planar aromatic anions, oxonium ions that can survive boiling water and SN_2 reaction on a tertiary center as detailed above.

Like triquinacene**,** there are various important studies on different areas of research about tribenzotriquinane, such as the synthesis of non-planar aromatic derivatives and self-assemble molecular cubes. **Surprisingly, syntheses of the hetero-analogues of tribenzotriquinacene, which also represents the tribenzo derivatives of heterotriquinacenes have not been pursued in the literature.**

The main aim of this thesis is the synthesis of tribenzoazatriquinacene and its derivatives to unravel any unusual reactivity and/or structural property that these structures might reveal. Synthesis of novel, aromatic derivative of tribenzoazatriquinacene, azaacepentalinide was also a major target (Figure 1.8).



29 **30**

Figure 1.11 The structures of tribenzoazatriquinacene (**29**) and tribenzoazaacepentalenide anion (**30**)

CHAPTER 2

RESULTS and DISCUSSION

2.1 Theoretical Studies of Tribenzoazatriquinacene and Tribenzoazaacepentalenide

2.1.1 Gaussian Calculations

By using theoretical calculations using Gaussian with the method of B3LYP/ 6-31+g(d,p), structural properties of tribenzoazatriquinacene (**29**), and tribenzoazaacepentalenide ion (**30**) were examined. According to these calculations, the tribenzoazatriquinacene (**29**) has the following energy minimum structure, as shown in figure 2.1.

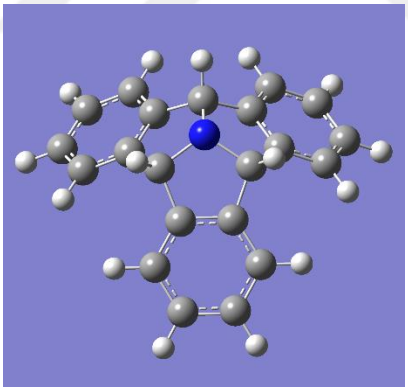


Figure 2.1 The Energy minimum structure of Tribenzoazatriquinacene (**29**)

It can be clearly seen that, just like azatriquinane (**10**) (Mascal et al., 2000), tribenzoazatriquinacene (**29**) compound possesses a convex structure. Similar to this result, tribenzooxatriquinacene (**31**) is also possess bowl shape (Kepil, 2020). The detailed examination of the compound shows that the C-N bond has a length of 1.49 Å. The results were consistent with similar systems.

Tribenzoazaacepentalenide was also examined theoretically. The figure 2.2 shows the resulting structures of these calculations.

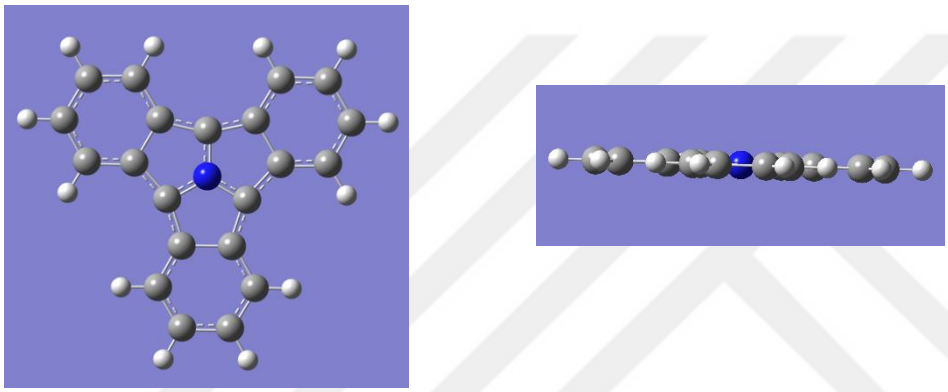
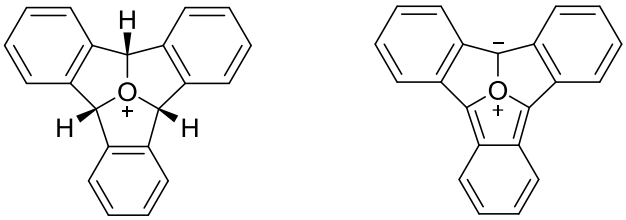


Figure 2.2 Minimum energy structure of tribenzoazaacepentalenide and its side view

Although calculations clearly showed that **30** is perfectly planar, the aromatic benzene free analogue of this molecule, azaacepentalenide (**12**) possessed a convex structure. This unexpected result was investigated making correlations to a similar system, tribenzooxaacepentalene (**32**).



31 32

Figure 2.3 Structures of tribenzooxatriquinacene (**31**) and tribenzooxaacepentalene (**32**)

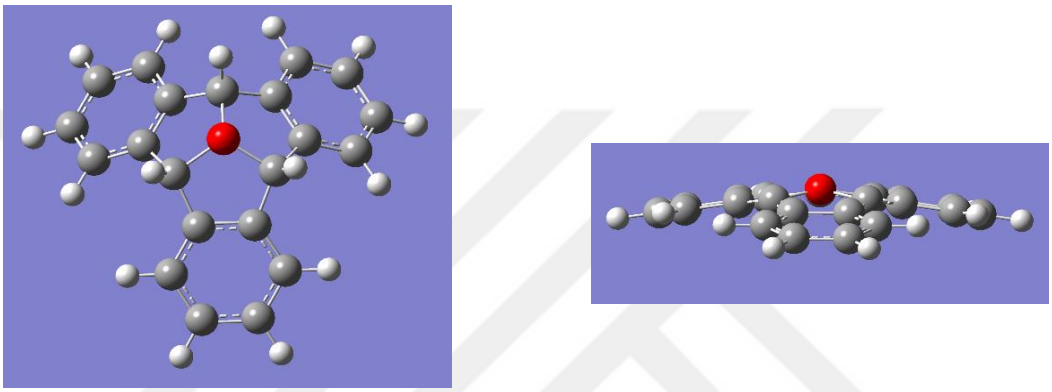


Figure 2.4 Front and side view of minimum energy structure of tribenzooxaacepentalene (**32**)

Previously published calculations clearly showed that **24**, benzene free aromatic derivative of tribenzooxaacepentalene (**32**), possess a bowl-shaped structure (Kepil, 2020). Our calculations showed that **32** is also clearly bowl-shaped (figure 2.4). However, as mentioned above tribenzoazaacepentalenide (**30**) structure is planar. Our initial idea was that this observation could be explained by an increased delocalization of electrons on the aza-system. For the oxo-analogue we envisioned that the extend of conjugation with just benzene rings was not enough for planarization of the system. Hence, derivatives with extended conjugation were designed and calculated. Benzene units on the tribenzooxaacepentalene (**32**) replaced with naphthalene, anthracene, and final pyrene units. All these new structures were carefully optimized. Results clearly showed that the system stayed bowl-shaped even

in the case of pyrenes. Actually, the system was even more puckered compared to the parent compound (figure 2.5).

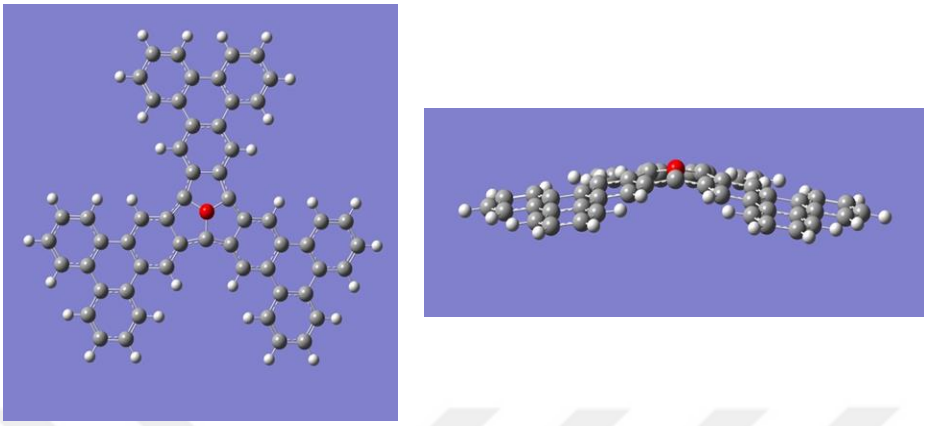


Figure 2.5 Energy minimum structure of compound pyrene substituted derivative of **30**

One major difference between the oxa and aza cases is the fact that complete planarization of oxo case requires oxygen to have 4 covalent bonds. Although existence of these type of species were recently uncovered (Stoyanov et al., 2012), the energy cost is apparently substantial.

Although our investigation still ongoing we believe there are two competing energies in the system: **1.** The energy cost of the ring strain from having an sp^2 like nitrogen in the fused center of three 5-membered rings, **2.** The energy gain from aromaticity with better overlap from planarization. While energy **1** dominates the azaacepentalenide (**12**) system, we believe energy **2** dominates the Tribenzoazaacepentalenide (**30**) system.

2.1.2 NICS Calculations

Aromaticity of the systems were evaluated by the nucleus independent chemical shift (NICS) criterion described by Schleyer and co-workers (Chen et al., 2005).

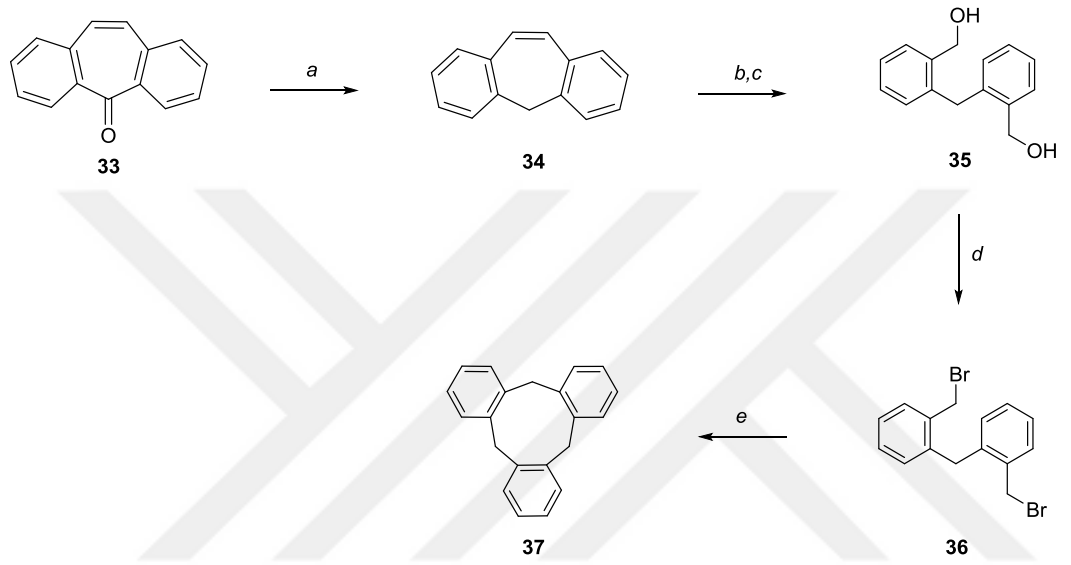
According to the NICS calculations, tribenzoazaacepentalenide shows significant aromatic character, with isotropic NICS value calculated as -10.58 (NICS1 values were calculated over 5-membered rings using B3LYP density functional level of theory using the 6-311++G(d,p) basis set.). For the benzene, this value is -10.22, which shows tribenzoazaacepentalenide possesses even higher aromatic stabilization energy. This value is also comparable to one calculated for azaacepentalinide (**12**) system ($NICS_{exo}$ = -9.64 for the energy minimum structure and $NICS_{planar}$ = -11.45 for the planar transition state)(Mascal, 2007).

2.2 Synthesis of Tribenzoazatriquinacene and Tribenzoazaacepentalenide

Retrosynthetic analyses for the synthesis of the targeted tribenzoazatriquinacene and tribenzoazaacepentalenide was envisioned to start from known literature compound 10,15-dihydro-5*H*-tribenzo[a,d,g][9]annulene, which will be further referred to as the core unit.

2.2.1 Synthesis of Core Unit (37)

The synthesis of the core unit was performed according to the pathway shown in Figure 2.3 with modifications to published literature (Yamato et al., 2001). It is important to note here though that in most cases literature reports did not include any experimental details.

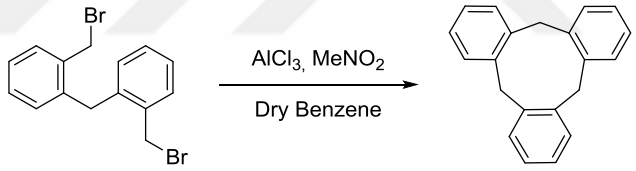


Scheme 2.1 Synthetic pathway of the core unit. Reagents and conditions: *a*. $LiAlH_4$, $AlCl_3$, Et_2O, reflux, 3.5 hr., 97%; *b*. O_3, MeOH, 0°C, 6 hr.; c. $LiAlH_4$, THF, reflux, 3 hr., 76%; *d. 33 wt.* % HBr in AcOH, rt, 3 hr., 88%; *e*. dry benzene, $AlCl_3$, CH_3NO_2, rt, 5 hr., 56%.

The synthesis started with reduction of the commercially available compound dibenzosuberenone **33** with $LiAlH_4$-$AlCl_3$ mixture in good yield. Ozonolysis followed by reduction gave the diol **35**. For ozonolysis, dibenzosuberene (**34**) compound stirred in cold methanol while O_2/O_3 gas purging through the solution for 6 hours which gave the corresponding meta-stable ozonide. The solvent was carefully evaporated under reduced pressure and temperature below 25°C. The next part of the synthesis was the reduction of the ozonolysis product which was performed with $LiAlH_4$ to get the diol **35**.

The diol was dibrominated using the nucleophilic substitution reaction with HBr in AcOH. Due to issues in obtaining the HBr in AcOH commercially other alternatives were pursued. Appel reaction was one of the reactions that was pursued to get the desired dibrominated product (Shi et al., 2016). Although modifications were done on the addition rate of Br_2 and temperature, the yield of the reaction was lower compared to HBr in AcOH. In another approach HBr in water was utilized. The starting material was not soluble at room temperature hence the temperature was increased to 85°C. The dibrominated product **36** was obtained in comparable yields and after work-up without any purification.

For the synthesis of the core unit **37**, a double Friedel-Crafts reaction was performed. Dry benzene served as both reagent and solvent. In benzene, $AlCl_3$ was added followed by the addition of nitromethane. To $AlCl_3$-benzene solution, dilute solution of compound **36** was added by using dropping funnel to eliminate the formation of side products, mainly addition of benzene unit to compound **36** by Friedels-Crafts (scheme 2.2).

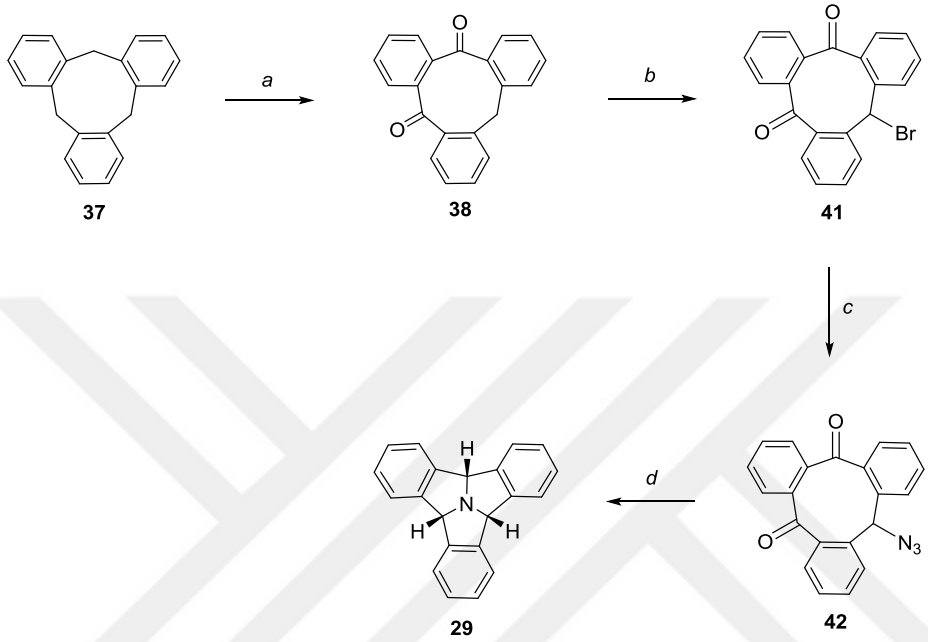


36 **37**

Scheme 2.2 Synthetic scheme of compound **37**

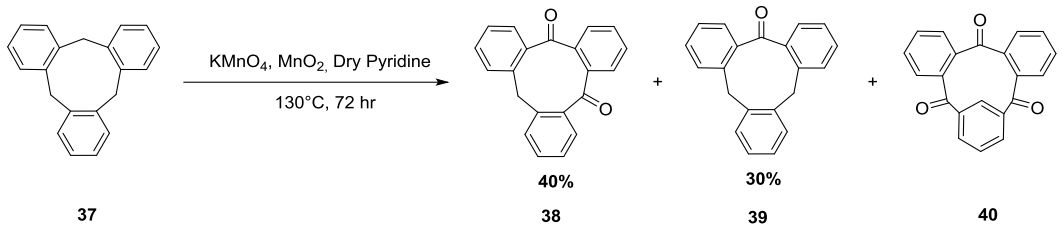
2.2.2 Towards the Synthesis of Tribenzoazatriquinacene Structure

The synthesis of the tribenzoazatriquinacene (**29**) molecule was performed according to the pathway shown in Scheme 2.3.



Scheme 2.3 Synthetic pathway of Tribenzoazatriquinacene. Reagents and conditions: *a*. $KMnO_4$, MnO_2, dry pyridine, reflux,18 hr., 40%; *b.* Br_2, dry CCl_4, 500 W, reflux, 28%; *c.* NaN_3, DMF, 80°C, 48 hr. 97%; *d.* Pd-C, H_2, MeOH, $CHCl_3$, 25°C, 64%.

Oxidation of the core unit was one of the most important steps to achieve the synthesis of both tribenzoazatriquinacene (**29**) and tribenzoazaacepentalenide (**30**). The oxidation was performed with $KMnO_4$ and MnO_2 in dry pyridine at 130°C (scheme 2.4).



Scheme 2.4 Reaction scheme of core unit oxidation

The core unit **37** possesses three positions for oxidation. The expectation was to get mono, di, and tri oxidations on the core unit. TLC of the reaction showed three different products as expected and these compounds were isolated successfully. Although the two products identified as mono (**39**) and di (**38**) oxidation products, the NMR of the third product did not match with the expected triketone. After the examination of the NMR data, the product was predicted to be **40**, as shown in the figure 2.6 (İğci, 2017). Another issue regarding this oxidation reaction was the low yields. To increase efficiency in this step, modifications were pursued. The procedure could not be performed with larger quantities (over 500 mg) as the yield decreased with an increasing amount of starting material. When the $KMnO_4$ that was used in the form of grains that were pulverized to powder, the yield of the reaction was improved, and reaction could be performed in almost a gram scale.

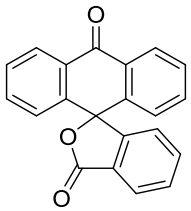


Figure 2.6 Side product structure of bromination reaction

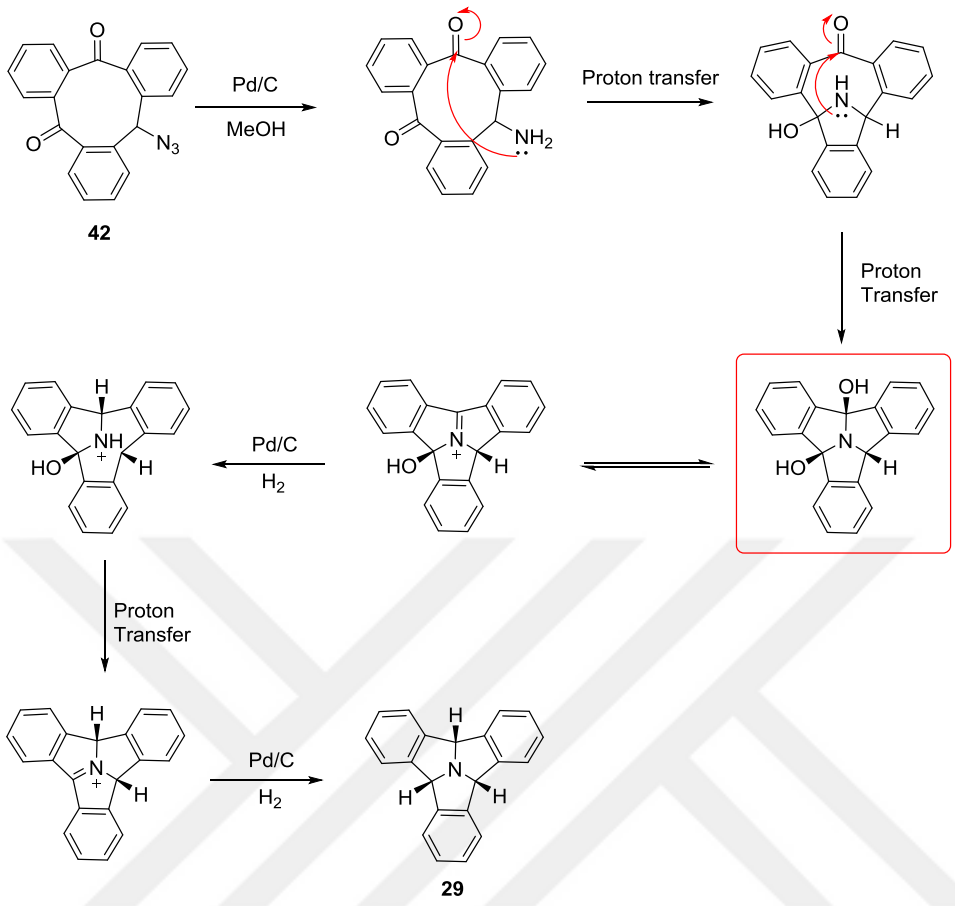
The next step of the synthesis was the bromination of the diketone **38**. The unit has a dibenzylic position open for radicalic bromination. As the bromine source, firstly, NBS was used with radicalic initiators like benzoyl peroxide and AIBN, yet there was no formation of the target product observed. In these attempts, the equivalency of the NBS were changed as well as the light source. After a series of unsuccessful attempts, the bromine source was changed to molecular bromine. On our initial attempts, with dry CCl_4 and 500W light, the product was obtained albeit in low yields. When we pushed the reaction longer formation of a side product was observed. According to the NMR analysis, the compound predicted as the compound in Figure 2.6 (Wright et al., 2014).

During the reaction HBr is produced therefore, the addition of mild basic compound into the reaction was envisioned to prevent side product formation. Although side product formation was not completely eliminated, slight improvement in yields were achieved.

The most well-known solvent for the radicalic bromination is CCl_4. However, CCl_4 is highly carcinogenic, and cannot be imported. Hence a need of a solvent which is commercially available and less hazardous arise. For this purpose, dry DCM, chloroform, and dichloroethane were utilized; nevertheless, the reaction did not proceed in these solvents, and the starting material was recovered. During the literature search for an alternative solvent, α,α,α-trifluorotoluene was promoted as a better alternative for CCl_4 in bromination reactions (Daley & Landolt, 2005) This solvent in dry form is commercially available.

Although the formation of the desired brominated diketone **41** was observed the formation of the side product was faster. We realized that the polarity of the solvent has a direct effect for the ratio between **41** and the side product. When we analyzed solvent polarities, the solvent that was closest to CCl_4 that was commercially available was benzene. When benzene was utilized in the reaction product formation was clearly observed with similar yield to CCl_4. Our optimization of this step is currently underway to improve reaction time and high quantity experiments.

The synthesis of the compound **41** was a crucial point for the successful synthesis of targets as the modifications can be easily done on the molecule by substitution reactions. Towards the synthesis of tribenzoazatriquinacene, the azide unit was introduced by an S_N2 reaction. The reaction was done with NaN_3 at 80°C, 48 hours in DMF. The reaction adjusted not to exceed 100°C due to the explosive nature of the azide containing compounds. When we checked the reaction with TLC no progress was observed. Although it is a medium size ring system, having no reaction was peculiar. Hence, we checked the crude NMR of the reaction. The proton, on the carbon with bromine, resonates at 6.71 ppm. The crude NMR showed that in addition to peak at 6.71 ppm, a proton at 6.26 ppm was also observed. It was attributed to the proton on the carbon with azide as this proton expected to resonate at high field due to azide's less electronegative nature than bromine. It was concluded that the reaction was happening yet changes could not be observed with TLC. This change in the spectrum was monitored until all the starting material was consumed and the title product was then isolated by column chromatography.

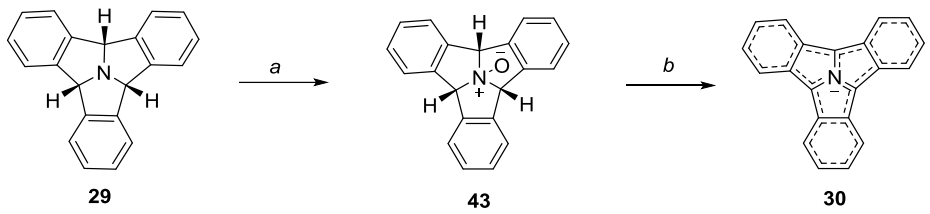


Scheme 2.5 Reaction mechanism of production of tribenzoazatriquinacene

For the tribenzoazatriquinacene structure, the synthetic approach was to get compound **42** and by hydrogenation convert azido group to amino group which would then cyclize two times to give the aminal highlighted red in scheme 2.3. The hydrogenation reaction was done in 10:1.5 MeOH/Chloroform solution. NMR and HRMS data clearly showed our elusive target, tribenzoazatriquinacene was synthesized in pot. The proposed mechanism for the production of the tribenzoazatriquinacene (**29**) is shown in Scheme 2.5.

2.2.3 Towards the Synthesis of Tribenzoazaacepentalenide Structure

The synthetic pathway that was utilized for tribenzoazaacepentalenide (**30**) starting from the tribenzoazatriquinacene (**29**) shown in scheme 2.6.

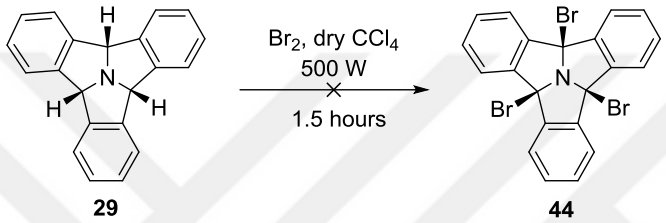


Scheme 2.6 Synthetic pathway of tribenzoazaacepentalenide anion. Reagents and conditions: *a.* *m*-CPBA, dry DCM, 0°C to 25°C, 20 hr., 57%; *b.* *n*-BuLi, d_8-THF, -78°C, 2 hr.

The first step of the synthesis was the oxidation of nitrogen in the **29** by using *m*-CPBA under an inert atmosphere. For the aromatization reaction, compound (**43**) was treated with *n*-BuLi in d_8-THF under inert atmosphere at -78°C then warmed to room temperature. In the beginning, the solution was colorless, and after the addition of *n*-BuLi, the color changed from red brown to fluorescent yellow. The solution was transferred to the NMR tube for analysis. When the ^{1}H NMR spectrum examined, two sets of downfield shifted aromatic peaks could be observed. No peak was observed that belonged to the α-hydrogens of the starting material was observed. According to this information, it was concluded that the targeted new novel aromatic compound **30** was synthesized successfully. For further characterization, ^{13}C NMR analysis was attempted however compound **30** decomposed during acquisition of the data. As the product decomposition could not be examined during the reaction, there was no certain information about how long the product remain stable. In the first NMR spectra, the peaks belong to the decomposition product can be seen hence the decomposition might be happening concurrently to the production of compound **30.**

2.2.4 Modifications on the Tribenzoazatriquinacene

For the functionalization of the tribenzoazatriquinacene structure, some modifications were attempted. After successful modifications, the synthesis of tripodal metal ligand complexes will be performed. By halogenating α-positions followed by heteroatom assisted substitutions, functional derivatives of tribenzoazatriquinacene were pursued.



Scheme 2.7 Bromination reaction scheme of Tribenzoazatriquinacene

For the bromination, the synthesis was done based on the radicalic bromination performed on the carbon-analogue of **29** compound **27**. As there are three positions open for bromination, the production of mono, di, and tribromide compounds was expected. After the reaction, the crude NMR data could not be assigned; therefore, HRMS analysis was performed.

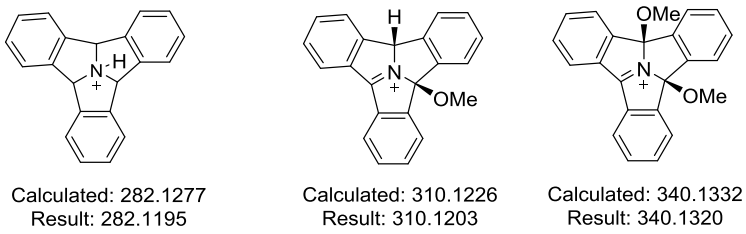
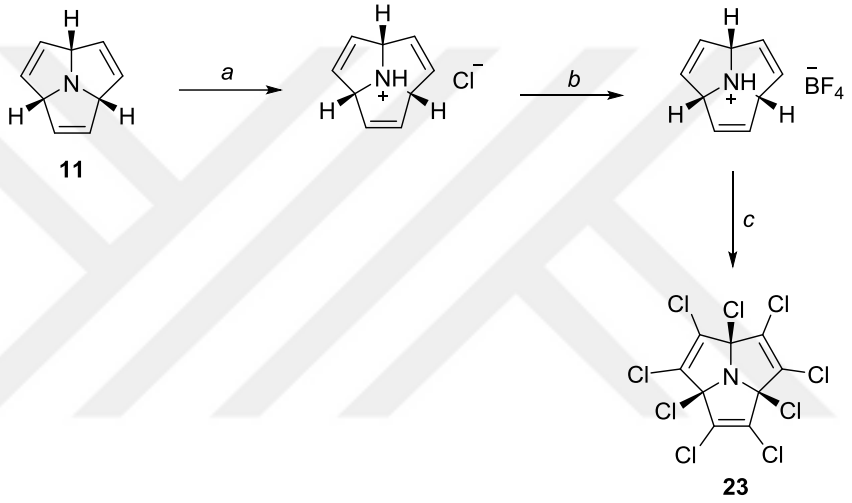


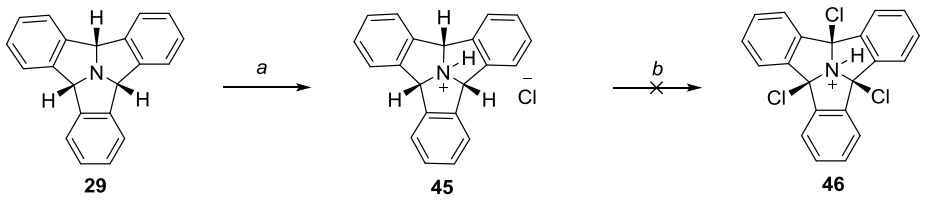
Figure 2.7 Structures proposed according to the HRMS results of compound **44**

As the sent sample was crude, there were different peaks of the different molecular weights, yet there was no sign of bromine in the molecule. When the data was examined, it was concluded that attachment of the methoxy group on the compound occurred. The reason behind this might be the use of methanol as a solvent for the HRMS analysis and the high reactivity of the compound under the analysis conditions. The proposed structures according to the HRMS results shown in figure 2.7.



Scheme 2.8 Synthetic pathway of chlorination of azatriquinane. Reagents and conditions: *a*. 0.5M aqueous HCl; *b*. sat. aqueous $NaBF_4$; *c*. SO_2Cl_2, hν. (Mascal et al., 1996)

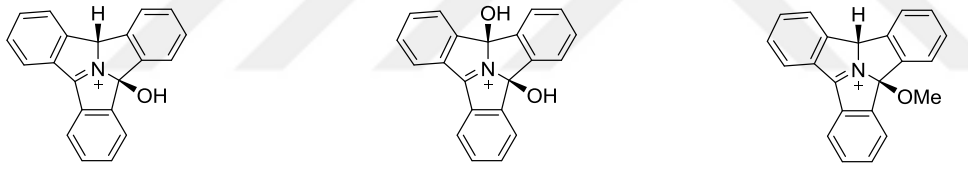
Another modification was the chlorination of the tribenzoazatriquinacene compound. For this synthesis same pathway of synthesizing chlorinated azatriquinane (scheme 2.8) was followed. To reach the targeted compound **23**, the chlorine salt of azatriquinacene was produced then by using saturated $NaBF_4$ solution, BF_4^- salt was made. This salt was chlorinated by using radicalic chlorination conditions to give compound **23** (Mascal et al., 1996)



29 45 46

Scheme 2.9 Chlorination reaction scheme of Tribenzoazatriquinacene. Reagents and conditions: a. HCl, chloroform, MeOH, 94%; b. SO_2Cl_2, 500W, 8.5 hr.

Similar to the literature (Mascal et al., 1996), the **29** treated with a 0.5M HCl solution to yield the chloride, which would then be converted to BF_4^- salt by using $NaBF_4$. All the solvent from the reaction evaporated under low pressure to produce chlorine salt of the **29**. The molecule **45** treated with $NaBF_4$ solution in water and extracted with DCM. The NMR spectrum of the expected salt showed that molecule was deprotonated to tribenzoazatriquinacene (**29**) then its BF_4 salt. Hence, we decided to proceed with the synthesis by using the chloride salt (scheme 2.9).



Calculated: 296.1070, 297.1137
Result: 296.1073, 297.1112

Calculated: 310.1226, 313.1053
Result: 310.1218, 313.1068

Calculated: 310.1226
Result:310.1218

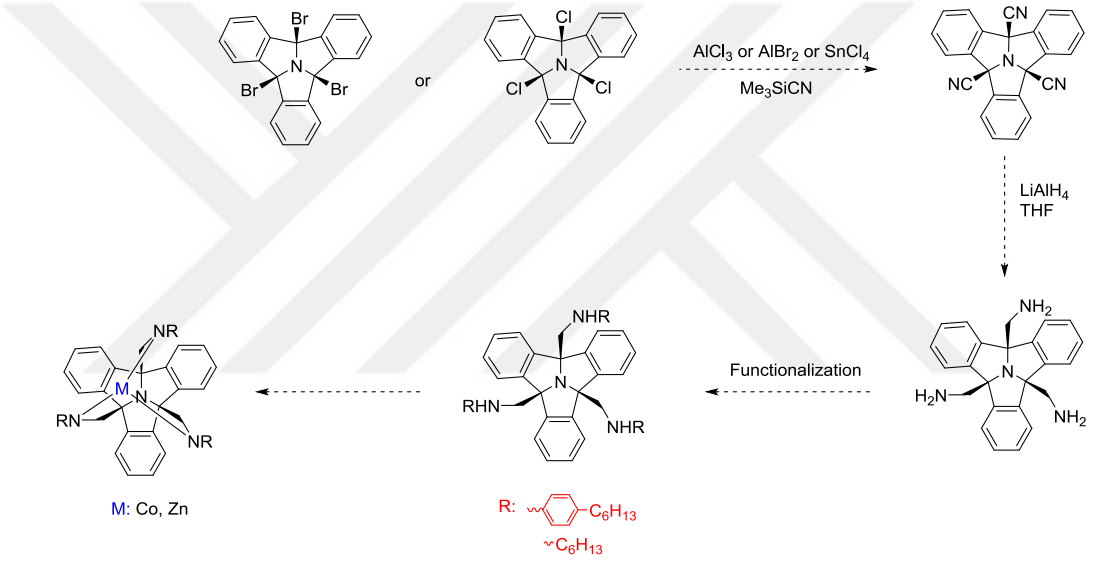
Figure 2.8 Structures formed according to the HRMS results of compound **46**

The starting material was chlorinated by light-induced halogenation. The crude mixture was attempted to be purified by column chromatography, yet the non-chlorinated starting compound was retrieved from the column. Therefore, the reaction repeated, and the crude mixture sent for the HRMS analysis. Just like the brominated tribenzoazatriquinacene, there was no peak that belonged to the product, and it was concluded that the same phenomenon happened again, and the mixture reacted with HRMS solvent and water. So, the formation of products predicted in figure 2.8 were occurred.

2.3 Future Work

Primarily the reactivity of tribenzoazatriquinacene (**29**) and Tribenzoazaacepentalenide anion (**30**) would be investigated. The instability and planar structure of tribenzoazaacepentalenide anion would be studied to understand the nature of this interesting molecular system.

The synthesis of tripodal ligands are popular in coordination and catalysis chemistry. As a future work, tripodal metal ligand complexes based on novel tribenzoazatriquinacene will be synthesized according to the scheme 2.10.



Scheme 2.10 Synthetic route for tripodal complexes of Tribenzoazatriquinacene

CHAPTER 3

CONCLUSION

This thesis focused on the synthesis of novel tribenzoazatriquinacene structure and aromatic tribenzoazaacepentalenide anion. These compounds were successfully synthesized and characterized by NMR and/or HRMS analysis. For their syntheses, the core unit **37** was synthesized successfully with good yield and oxidation was performed on the structure to yield dione **38.** The bromination of compound **38** was one of the significant obstacles in the synthetic pathway due to solvent unavailability and low yield of the reaction. The steps up to and including bromination has been repeated many times to get reasonable amounts of material for further reactions. The substitution of the azide group and reduction of this group was the main route for the synthesis of the tribenzoazatriquinacene (**29**). The hydrogenation of the azido unit resulted in a cascade of reactions which gave the final target compound tribenzoazatriquinacene (**29**) elegantly. The novel aromatic anion, tribenzoazaacepentalenide was also successfully synthesized by oxidation of **29**, followed by n-BuLi induced eliminations and deprotonation.

CHAPTER 4

EXPERIMENTAL

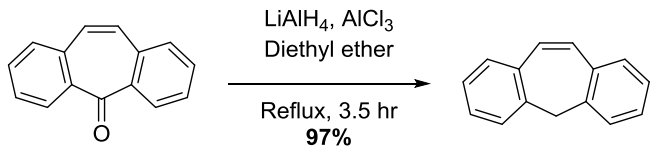
4.1 Methods and Materials

For the ^{1}H and ^{13}C spectra Bruker Avance III Ultrashield (400 MHz) NMR spectrometer was used. The chemical shifts were reported in ppm (parts per million) downfield from an internal TMS (trimethylsilane) reference. The spin multiplicities reported as following symbols: s for singlet, d for doublet, t for triplet, q for quartet, dd for doublet of doublet, td for triplet of doublet and m for multiplet. The coupling constants (J) were reported in hertz (Hz). NMR spectra were processed with MestReNova software. Column chromatography was performed in thick walled glass columns using silica Gel 60 (Merck 230-400 mesh) and aluminium oxide 90 active basic (Merck 0.063-0.200 mm) treated with 10% water. Thin layer chromatography was performed by using TLC Merck Silica Gel 60 F254 prepared 0.25 mm plates and visualization was done by using UV lamp. The mobile phases of chromatography solvent mixtures refer to the volume: volume ratio. All commercially available starting materials and reagents were provided by Aldrich Chemical and used directly. The dry solvents used in reactions, with the exception of dry benzene and CCl_4, were obtained from Mbraun MBSPS5 solvent drying system. The inert atmosphere was obtained by using Argon gas.

4.2 Equipment

$CDCl_3$, d_6-DMSO and d_8-THF was the solvents used for the ^{1}H and ^{13}C NMR analyses on Bruker Spectrospin Avance DPX-400 Spectrometer and TMS was used as the internal reference. High resolution mass spectroscopy was performed to determine exact masses of the novel compounds using Waters Synapt MS System.

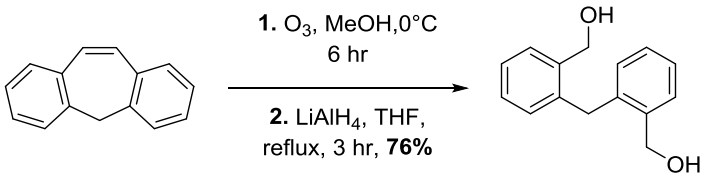
4.3 Synthesis of 5H-dibenzo[a,d][7]annulene (34)



33 **34**

The target compound was synthesized according to literature (Schmuck & Wienand, 2002)., $AlCl_3$ (7.1 g, 54 mmol) was dissolved in Et_2O (25 mL) and $LiAlH_4$ (2.0 g, 52 mmol) was dissolved in dry Et_2O (38 mL) in two separate flasks. $LiAlH_4$ solution was added to $AlCl_3$ solution at room temperature and the mixture was stirred for 30 minutes under argon atmosphere. Later, this mixture added slowly to the 5-dibenzosuberenone (**33**) (10 g, 48 mmol) in dry THF (50 mL) at 0°C. The mixture was refluxed for 3 hours then stirred at room temperature overnight. To quench the reaction, the system was cooled to 0°C and, 15% NaOH solution (2 mL) and distilled water (10 mL) were added in a dropwise fashion. $MgSO_4$ was added and the mixture was filtered through celite. The residues were washed with excess THF (500 mL) and combined filtrates were concentrated under reduced pressure to yield target compound **34** as a white solid (9.0 g, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 4H), 7.30 – 7.28 (m, 2H), 7.26 – 7.17 (m, 2H), 7.04 (s, 2H), 3.75 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.26, 135.31, 131.66, 128.54, 128.23, 128.00, 126.19, 41.77 ppm.

4.4 Synthesis of (methylenebis(2,1-phenylene))dimethanol (35)

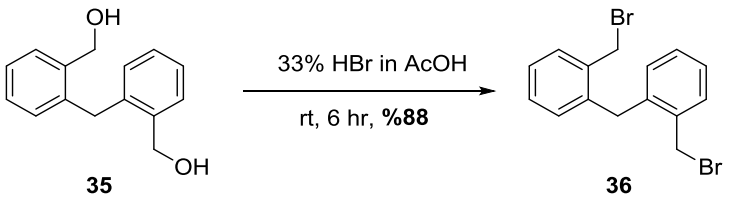


34 35

The synthesis was according to the literature with small modifications (Schmuck & Wienand, 2002). Compound **2** (2.5 g, 13 mmol) was suspended in dry MeOH (100 mL) at 0°C and O_2/O_3 mixture was bubbled through the mixture for 6 hours. To remove excess O_3, the system was further bubbled with argon for 30 minutes. The excess solvent removed under reduced pressure carefully with keeping the bath temperature below 25°C (CAUTION!). The resulting yellow oil was dissolved in dry Et_2O (40 mL) under argon atmosphere and a solution of $LiAlH_4$ (2.5 g, 66 mmol) in dry Et_2O (45 mL) was added dropwise at 0°C. The mixture was refluxed for 3 hours then stirred overnight at room temperature. The reaction mixture was diluted with Et_2O (100 mL) and water (2.5 mL), 15% NaOH solution (2.5 mL) and water (7.5 mL) were added dropwise respectively. $MgSO_4$ was added and the mixture was filtered through celite. The residue was washed with Et_2O and EtOH and the combined filtrates were concentrated. The residue was then recrystallized by using toluene to give compound **3** as a white solid. (2.26 g, 9.9 mmol, 76%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.40 (d, J = 7.4 Hz, 2H), 7.18 (t, J = 7.2 Hz, 2H), 7.11 (t, J = 7.3 Hz, 2H), 6.81 (d, J = 7.4 Hz, 2H), 5.09 (t, J = 5.4 Hz, 2H), 4.44 (d, J = 5.3 Hz, 4H), 3.94 (s, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 140.19, 137.22, 128.80, 126.85, 126.70, 125.92, 60.70, 33.49 ppm.

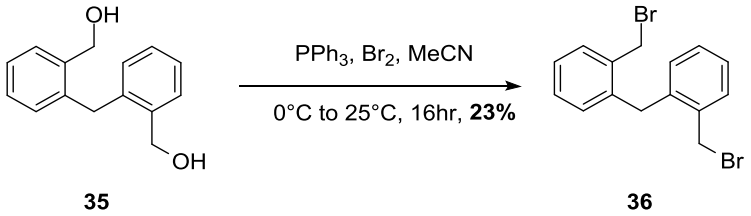
4.5 Synthesis of bis(2-(bromomethyl)phenyl) methane (36)

4.5.1



The compound synthesized was according to the literature with some modifications (W. Y. Lee & Park, 1993). In a reaction flask containing compound **35** (0.773 g, 3.39 mmol) was added 33% HBr in AcOH (12 mL) while the mixture was stirring at room temperature. To avoid loss of HBr the flask was tightly closed, and the mixture was stirred at room temperature for 6 hours. The solution was diluted with DCM (50 mL) and saturated $NaHCO_3$ solution (100 mL) was added. After the gas formation stopped, phases were separated. The aqueous phase was then extracted with DCM (3x60 mL). Combined organic phases were dried with $MgSO_4$ and the solvent was evaporated to yield the title compound as a cream-colored solid. (1.06 g, 2.99 mmol, 88% yield.) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 2H), 7.17 (m, 4H), 6.98 – 6.78 (m, 2H), 4.43 (s, 4H), 4.22 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.72, 136.04, 130.69, 130.35, 129.26, 127.21, 34.64, 31.87 ppm.

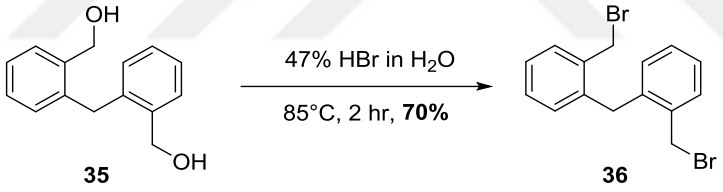
4.5.2



35 **36**

(Shi et al., 2016) Under argon atmosphere at 0°C, triphenylphosphine (0.603 g) was dissolved in MeCN and Br_2 (0.12 mL) was added dropwise. To the resultant mixture, compound **35** (0.250 g, 1.08 mmol) was added in one portion and the mixture was warmed to the room temperature. The mixture was stirred for 16 hours and concentrated under reduced pressure. Purification with silica gel chromatography (2:1 DCM/Hexane) gave compound **36** as a light yellow solid (0.090 g, 23% yield).

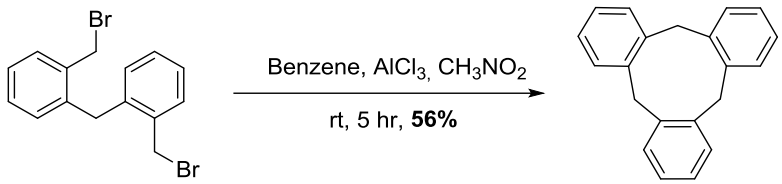
4.5.3



35 **36**

In a reaction flask, compound **35** (1.00 g, 4.3 mmol) and HBr in H_2O solution (25 mL) was added in the room temperature. During the addition of acidic solution gas evolution was observed and **3** did not dissolved in the acidic solution. The reaction mixture was heated to 85°C and stirred for 2 hours. The mixture was allowed to cool room temperature and diluted with DCM then saturated $NaHCO_3$ solution was added. The aqueous phase extracted with DCM (3x50 mL) and organic phases collected were dried with $MgSO_4$. After the filtration excess solvent evaporated under low pressure to give light yellow solid **36** (1.08 g, 70% yield).

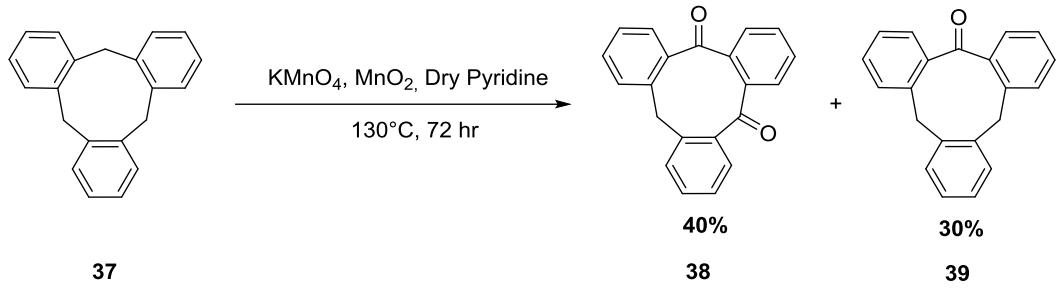
4.6 Synthesis of 10,15-dihydro-5H-tribenzo[a,d,g][9]annulene (Core Unit (37))



36 **37**

The synthesis was done according to a modification of a method used in literature for another compound (Yamato et al., 2001). In two different reaction flasks under argon atmosphere, $AlCl_3$ (1.4 g, 10.2 mmol) and CH_3NO_2 (3.6 mL) were dissolved in dry benzene (70 mL) and compound **36** (1.8 g, 5.0 mmol) dissolved in dry benzene (300 mL). Compound **36** added to the $AlCl_3$ solution dropwise. This reaction was stirred overnight at room temperature then, 1% HCl solution (310 mL) was added. The mixture washed with water (3x50 mL) and extracted with Et_2O (3x150 mL). Organic phase collected, dried with $MgSO_4$ and concentrated under low pressure. Obtained solid purified with silica column chromatography (1:6 DCM/Petroleum ether) to give white solid **5** (0.73 g, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 5.7, 3.5 Hz, 6H), 7.11 (dd, *J* = 5.7, 3.4 Hz, 6H), 4.93 (d, *J* = 13.3 Hz, 3H), 3.78 (d, *J* = 13.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.51, 130.09, 127.00, 37.21 ppm.

4.7 Synthesis of 10,15-dihydro-5H-tribenzo[a,d,g][9]annulen-5-one (39)and 5H-tribenzo[a,d,g][9]annulene-5,10(15H)-dione (38)



(Wright et al., 2014) Starting compound **37** (0.850 g, 3.14 mmol) was dissolved in dry pyridine (15 mL) in a reaction flask under argon atmosphere. To this solution, finely powdered $KMnO_4$ (20.0 g, 127 mmol) and activated MnO_2 (22.0 g, 253 mmol) were added and the mixture refluxed at 130 °C for 72 hours. Then it cooled to room temperature and filtered on Celite with DCM (500 mL) and EtOAc (500 mL). The filtrate was collected and concentrated on low pressure. Obtained solidpurified over silica column chromatography (6 DCM:1 Hexane). (**39**: 270 mg, 30% yield; **38**e: 372 mg, 40% yield.)

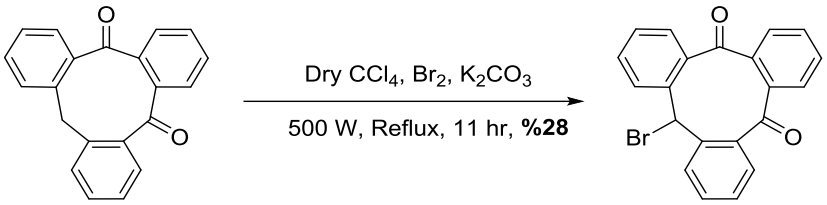
5H-tribenzo[a,d,g][9]annulene-5,10(15H)-dione (**38**)

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.48 (ddd, *J* = 27.4, 5.7, 3.4 Hz, 4H), 7.27 (dt, *J* = 30.8, 7.2 Hz, 4H), 7.02 (d, *J* = 7.5 Hz, 2H), 3.87 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.05, 140.33, 139.89, 139.28, 132.27, 130.85, 130.32, 129.08, 127.96, 127.28, 37.71 ppm.

10,15-dihydro-5H-tribenzo[a,d,g][9]annulen-5-one (**39)**

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.31 (dd, *J* = 7.5, 1.6 Hz, 2H), 7.26 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.13 (s, 4H), 7.04 (dd, *J* = 7.6, 1.1 Hz, 2H), 3.77 (s, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.95, 140.61, 139.84, 137.94, 132.62, 131.43, 130.44, 129.83, 127.21, 126.98, 37.70 ppm.

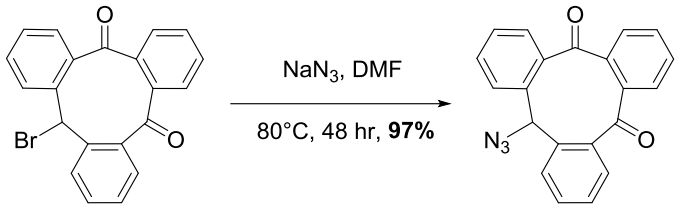
4.8 Synthesis of 15-bromo-5H-tribenzo[a,d,g][9]annulene-5,10(15H)-dione (41)



38 **41**

The compound was synthesized according to the general literature methods. In a reaction flask under argon atmosphere dry CCl_4 (55 mL), K_2CO_3 (0.99 g, 7.16 mmol) and **38** (0.42 g, 1.41 mmol) were added together. To this mixture Br_2 solution (1.0 M, 1.8 mL) was added dropwise. The reaction exposed to 500W light for 11 hours by cooling the solution for 10 min in every 1 hour. Excess bromine and solvent were evaporated under low pressure then dissolved in DCM (20 mL) and extracted with diluted $NaHSO_3$ solution. The aqueous phase extracted with DCM (5x20 mL). collected organic phases dried with $MgSO_4$. After filtration, the filtrates concentrated under low pressure. Obtained solid purified with silica column chromatography (3:1 DCM/Hexane). The product (**41**) obtained as a white solid (0.15 g, 28% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 5.8, 3.4 Hz, 2H), 7.60 – 7.53 (m, 6H), 7.44 (dt, *J* = 44.7, 7.5 Hz, 2H), 6.78 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.81, 140.44, 139.68, 138.25, 132.65, 131.59, 129.91, 128.80, 128.47, 47.93 ppm.

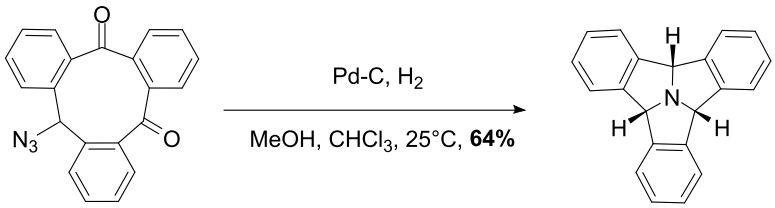
4.9 Synthesis of 15-azido-5H-tribenzo[a,d,g][9]annulene-5,10(15H)-dione (42)



41 **42**

(J. H. Lee et al., 2012)The compound **41** (0.2 g, 0.53 mmol) was dissolved in DMF (75 mL) in a reaction flask and to this mixture, NaN_3 (0.133 g, 2.05 mmol) was added and stirred at 80°C for 48 hours. After the starting compound finished, the reaction cooled to the room temperature and diluted with $CHCl_3$. To get rid of DMF in the reaction medium, distilled water (300 mL) added to the solution and the aqueous phase extracted with $CHCl_3$ (150 mL). Collected organic phase dried over $MgSO_4$ and filtered. Filtrates were concentrated under low pressure to yield light yellow solid (**42**) (0.175g, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.57 (m, 6H), 7.50 (td, *J*=7.6 Hz, *J*=1.5 Hz, 2H), 7.43 – 7.34 (m, 4H), 6.26 (s, 1H) ppm.^{13}C NMR (100 MHz, $CDCl_3$) δ 196.84, 139.81, 139.24, 138.74, 132.60, 131.41, 128.82, 128.63, 128.22, 126.50, 61.12 ppm. IR: 2103.26 (-N_3).

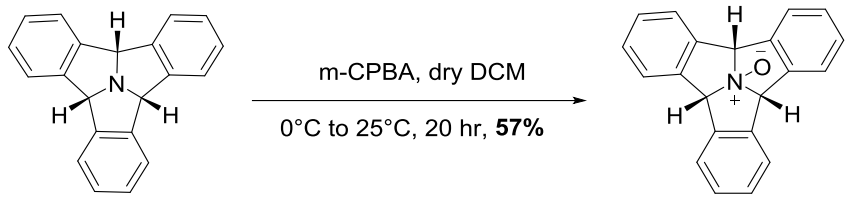
4.10 Synthesis of (4bs,8bs,12bs)-8b,12b-dihydro-4bH-dibenzo[1,2:6,7] pyrrolizino[3,4,5-ab]isoindole (29)



42 **29**

The synthesis of novel molecule was done based on a procedure for another compound in the literature (Roy et al., 2013). The compound **42** (0.077 g, 0.225 mmol) dissolved in a two-neck reaction flask with $CHCl_3$/MeOH solution (1.5/10). To this mixture Pd-C (0.133 mg, 1.13 mmol) was added and stirred for 3 hours in H_2 filled flask. The suspension filtered through celite with methanol and the filtrates were concentrated. Obtained solid purified using basic alumina column chromatography (5% MeOH-DCM). (0.041 g, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 6H), 7.21 – 7.15 (m, 6H), 5.95 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.57, 128.09, 121.87, 74.35 ppm. HRMS calculated for $C_{21}H_{16}N$ 282.1283, found 282.1283.

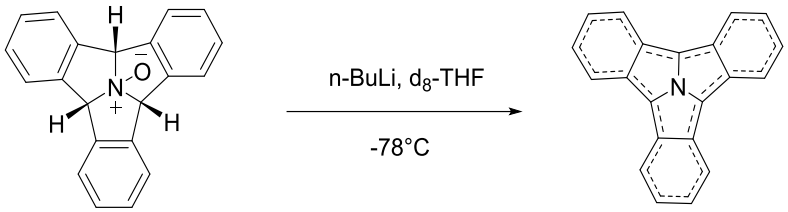
4.11 Synthesis of (4bs,8bs,12bs)-8b,12b-dihydrodibenzo[1,2:6,7]pyrrolizino [3,4,5-ab]isoindole 13(4bH)-oxide (43)



29 **43**

Synthesis was done according to the literature with some modifications (Mascal & Bertran, 2005). Compound **29** (0.08 g, 0.284 mmol) was dissolved in dry DCM (8 mL) in a reaction flask under inert atmosphere. In another flask, m-CPBA (0.108 g) was dissolved in DCM (3.5 mL) and added to the reaction flask in a dropwise fashion at 0°C then warmed to room temperature. The reaction stirred at room temperature for 20 hours. Resultant solution concentrated under low pressure and purified by alumina column chromatography (5% MeOH/ DCM). White solid (**43**) (0.048 g, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 6H), 7.40 – 7.36 (m, 6H), 6.50 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.35, 129.55, 122.09, 94.40 ppm.

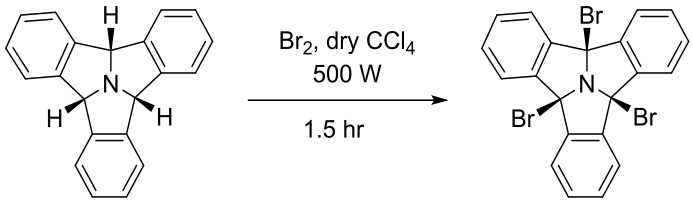
4.12 Synthesis of 8bH-dibenzo[1,2:6,7]pyrrolizino[3,4,5-ab]isoindol-8b-ide (30)



43 **30**

(Mark Mascal & Bertran, 2005) The compound **43** (8.3 mg, 0.028 mmol**)** was dissolved in d_8-THF (0.7 mL) In a reaction flask under inert atmosphere starting. The reaction cooled to the -78°C then, n-BuLi (7.15 mg, 0.112 mmol) added dropwise. Upon this addition clear-colorless solution became red brown. Reaction flask warmed to the room temperature and during this process the color of the solution changed to yellow-green (fluorescence was observed). The crude product was directly used for analyses without purification due to instability of the compound **30**. ^{1}H NMR (400 MHz, THF-d_8) δ 8.22 (dd, J = 5.9, 3.2 Hz, 6H), 7.12 (dd, J = 6.1, 3.1 Hz, 6H) ppm.

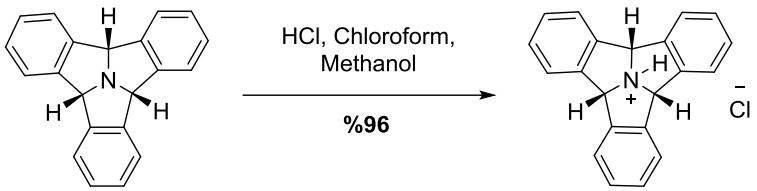
4.13 Synthesis of (4bs,8bs,12bs)-4b,8b,12b-tribromo-8b,12b-dihydro-4bH-dibenzo[1,2:6,7]pyrrolizino[3,4,5-ab]isoindole (44)



30 **44**

The compound **30** (0.02 g, 0.071 mmol) was dissolved in freshly distilled dry CCl_4 (7 mL), then to this solution 1M Br_2 solution (0.5 mL) was added dropwise. The resultant mixture was stirred while exposed to 500 W light for 1.5 hours. To get rid of unreacted bromine, the mixture diluted with DCM (20 mL) and extracted with sodium bisulfide solution. The aqueous phase washed with DCM (3x20 mL) then, collected organic phases dried over $MgSO_4$. The filtrates were concentrated under reduced pressure to yield an orange solid (0.032 mg crude).

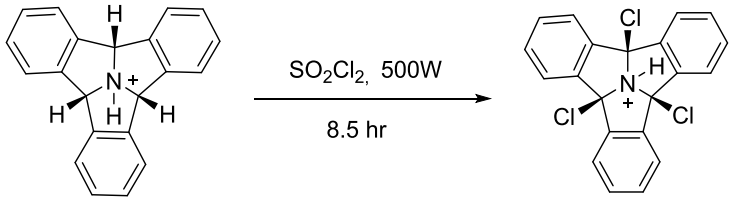
4.14 Synthesis of (4bs,8bs,12bs)-4b,8b,12b,13-tetrahydrodibenzo[1,2:6,7] pyrrolizino[3,4,5-ab]isoindol-13-ium (45)



29 **45**

The synthesis was performed according to the literature (Gerson et al., 1998). **29** (27 mg, 0.096 mmol) was dissolved in $CHCl_3$ (2.0 mL) and MeOH (1.0 mL). To this mixture 0.5 M HCl solution was added and stirred for 15 minutes. The resultant solution concentrated under low pressure to yield a white solid (**45**) (26 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.66 (br, s, 1H), 7.55 – 7.50 (m, 6H), 7.44 – 7.39 (m, 6H), 6.75 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.75, 130.22, 122.31, 75.41 ppm.

4.15 Synthesis of (4bs,8bs,12bs)-4b,8b,12b-trichloro-4b,8b,12b,13-tetrahydrodibenzo[1,2:6,7]pyrrolizino[3,4,5-ab]isoindol-13-ium (46)



45 **46**

(Gerson et al., 1998). The compound **45** (0.023 g, 0.073 mmol) and SO_2Cl_2 (3 mL) were stirred together while exposing 500W for 8.5 hours in inert atmosphere. The excess solvent in the mixture evaporated to yield a yellow solid.

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APPENDICES

A. NMR Spectra

Both ^{1}H and ^{13}C NMR analysis was carried on Bruker Spectrospin Avance DPX-400 Spectrometer and tetramethylsilane was used as internal reference. $CDCl_3$, d_6-DMSO, MeOD and d_8-THF were used as NMR solvents.

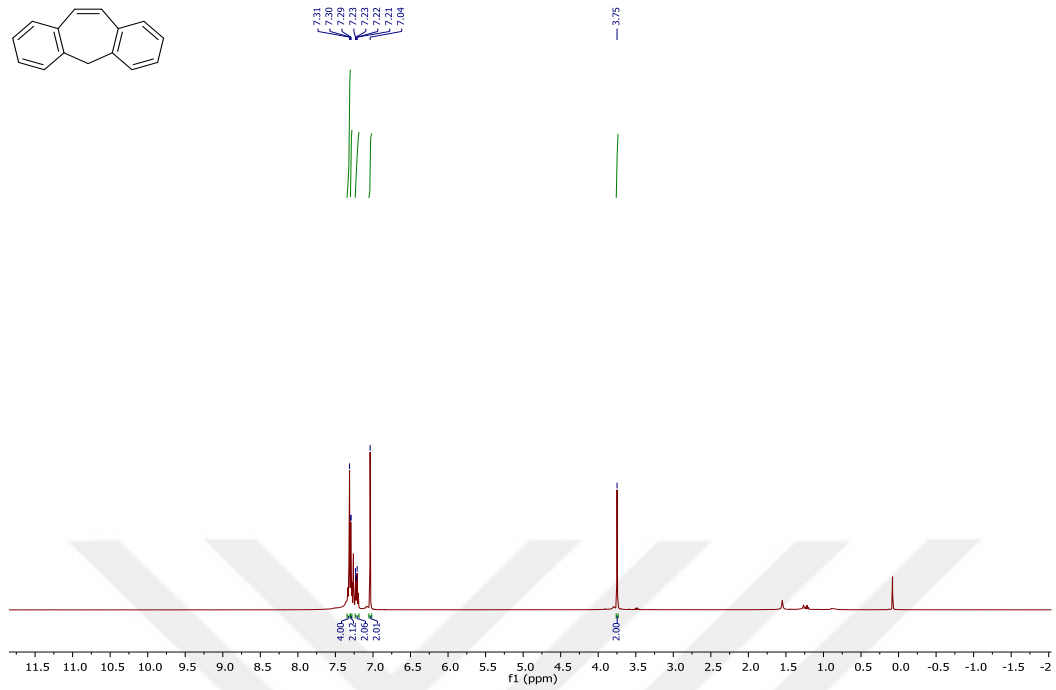


Figure 4.1 ^{1}H-NMR Spectrum of compound 5H-dibenzo[a,d][7]annulene (**34**)

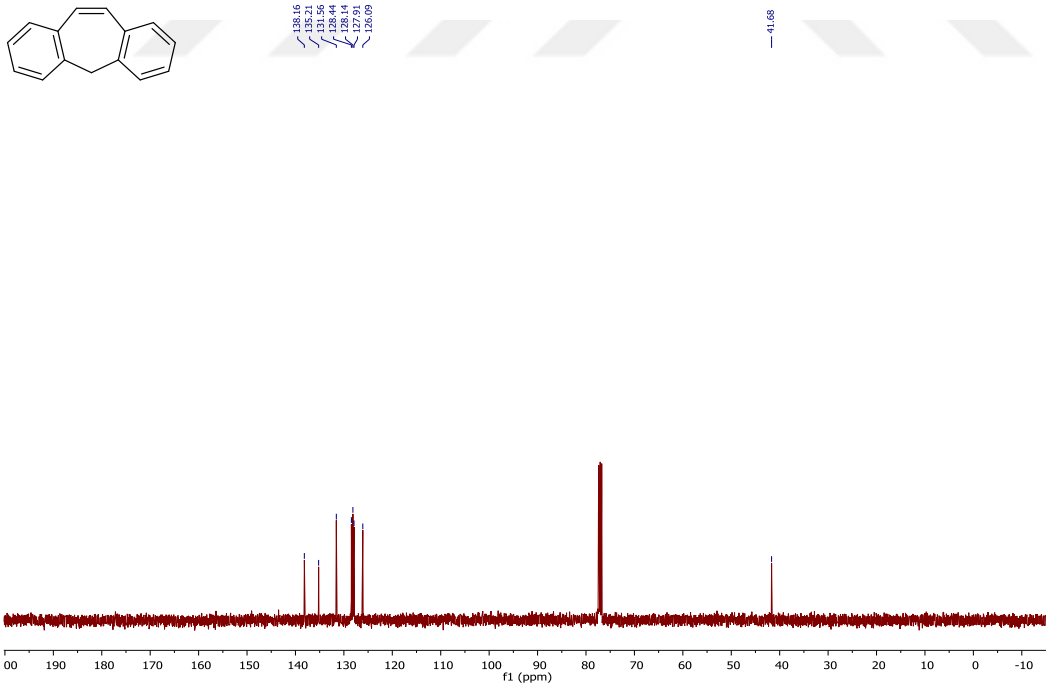


Figure 4.2 ^{13}C-NMR spectrum of the compound 5H-dibenzo[a,d][7]annulene (**34**)

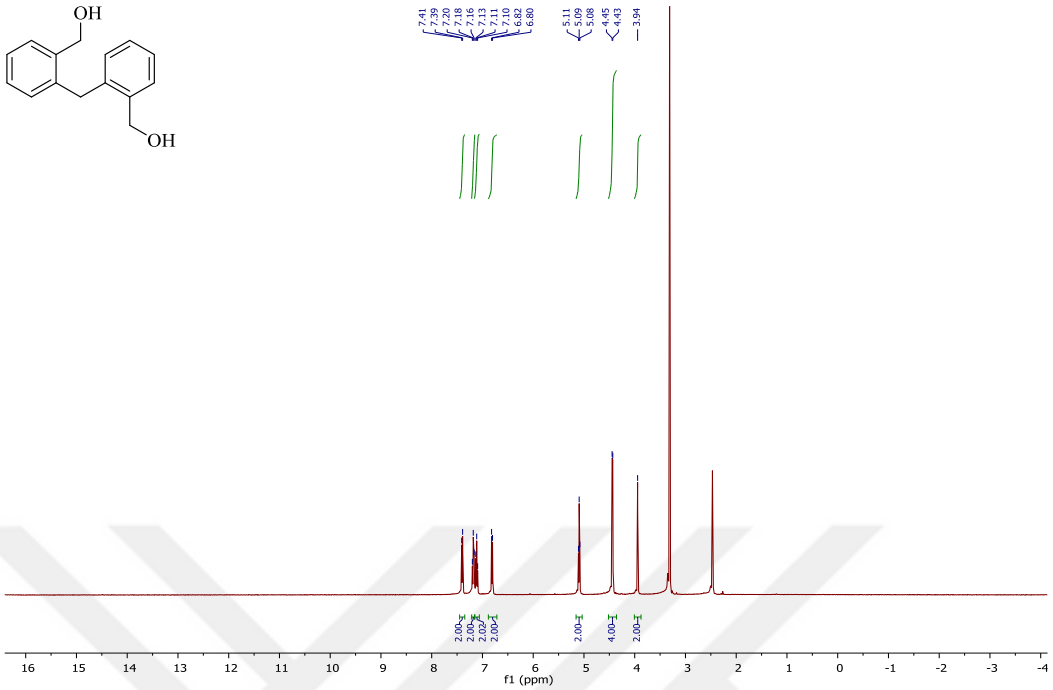


Figure 4.3 ^{1}H-NMR Spectrum of compound (methylenebis(2,1-phenylene)) dimethanol (**35**)

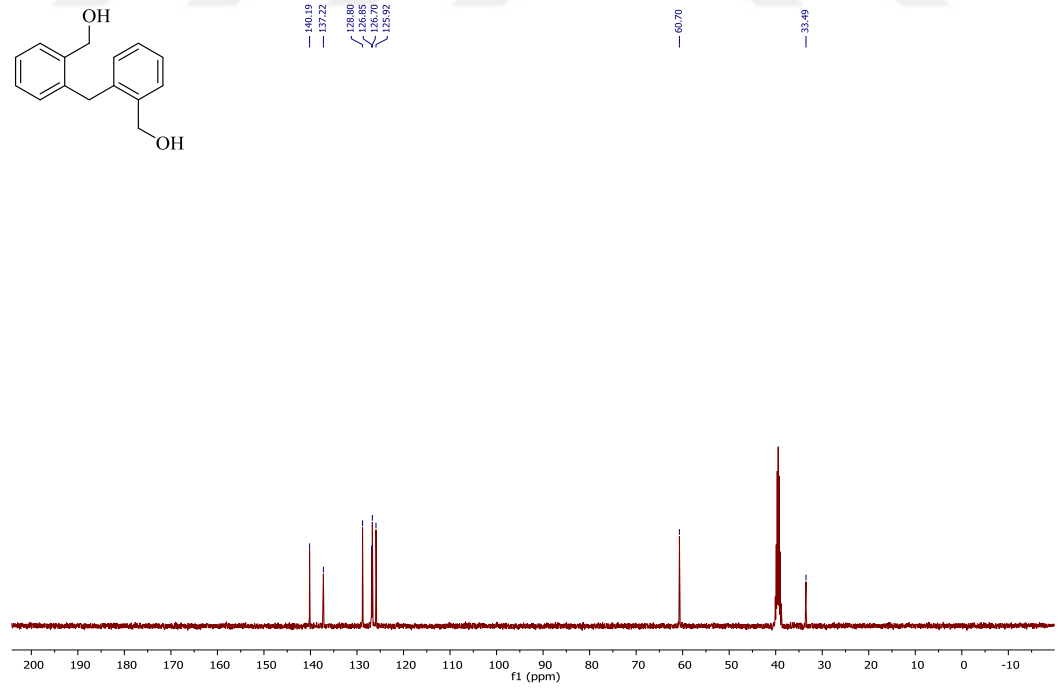


Figure 4.4 ^{13}C-NMR Spectrum of compound (methylenebis(2,1- phenylene)) dimethanol (**35**)

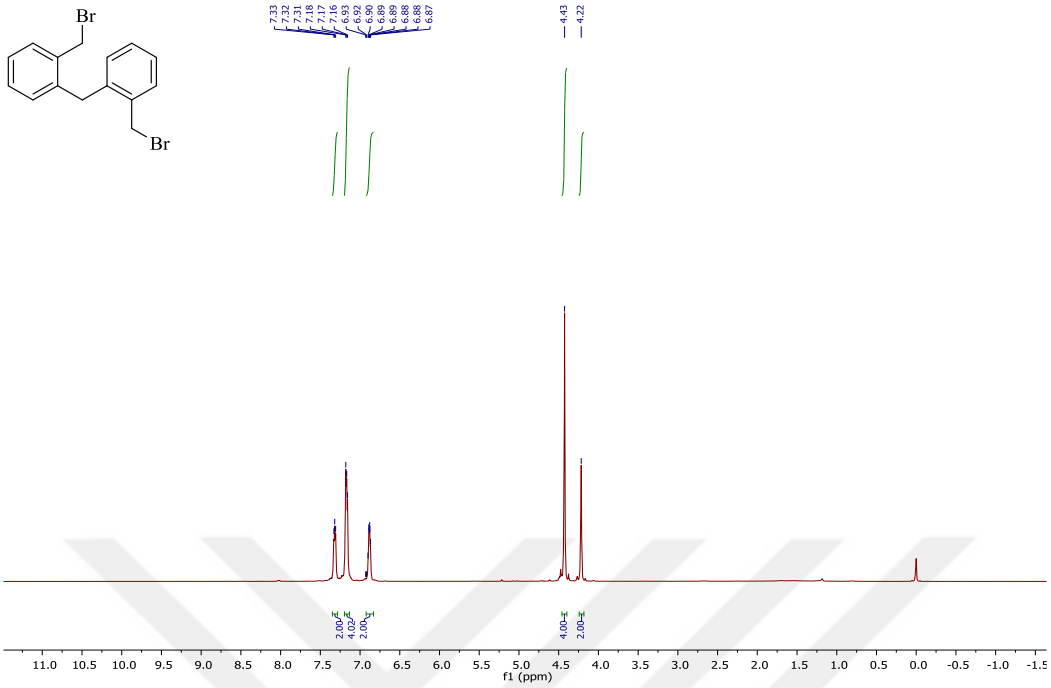


Figure 4.5 ^{1}H-NMR Spectrum of compound bis(2-(bromomethyl)phenyl) methane (**36**)

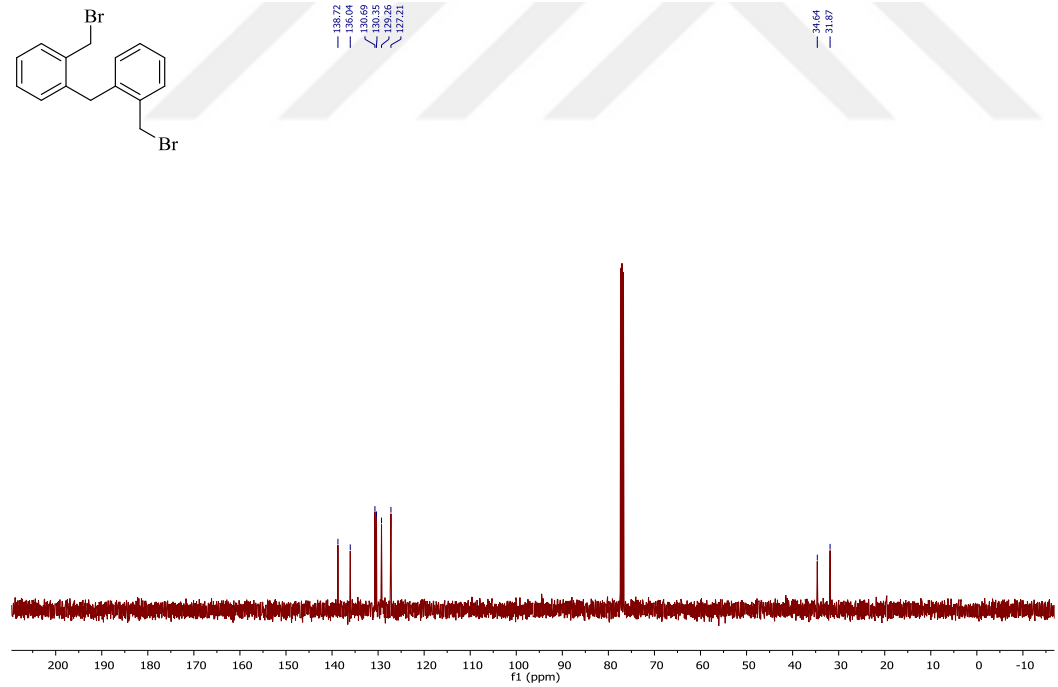


Figure 4.6 ^{13}C-NMR Spectrum of compound bis(2-(bromomethyl)phenyl) methane (**36**)

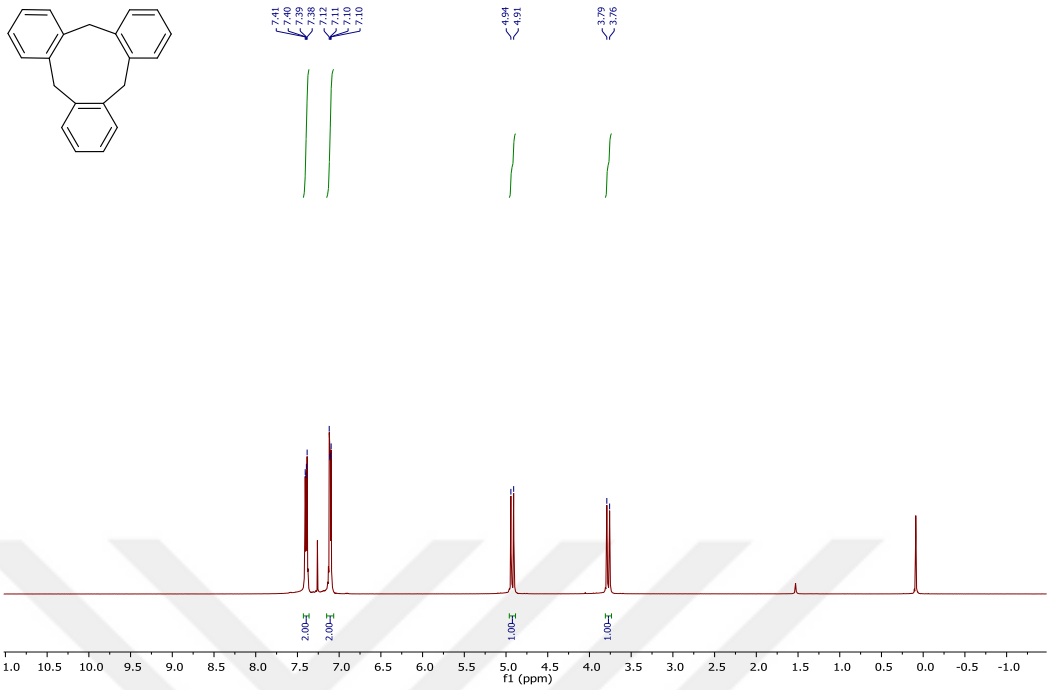


Figure 4.7 ^{1}H-NMR Spectrum of compound 10,15-dihydro-5H-tribenzo[a,d,g] [9]annulene (**37**)

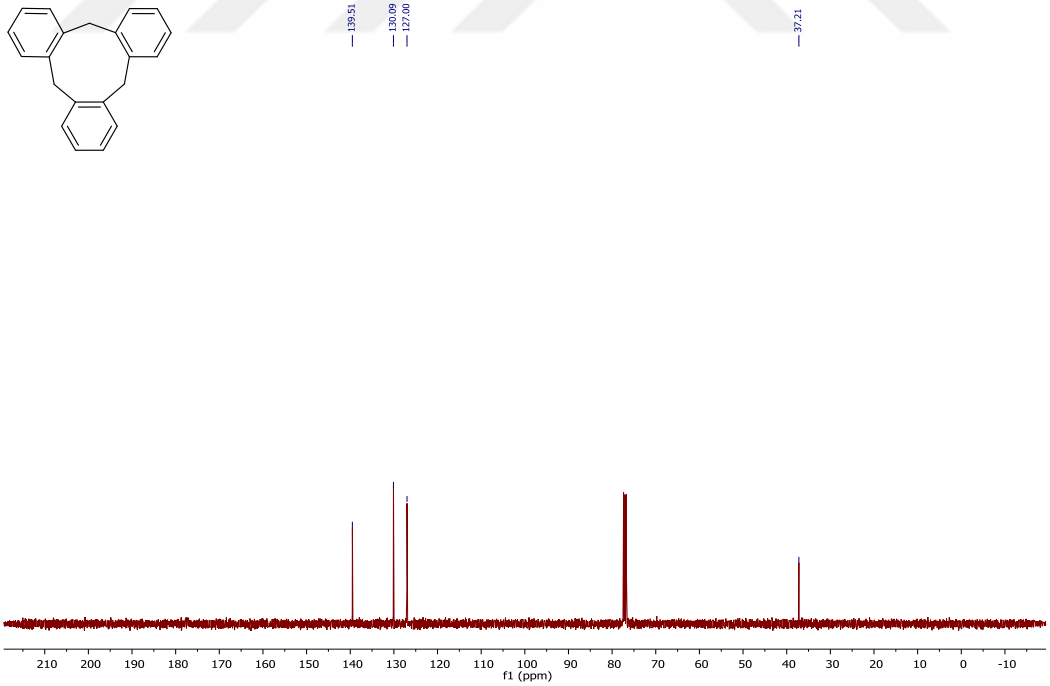


Figure 4.8 ^{13}C-NMR Spectrum of compound 10,15-dihydro-5H-tribenzo[a,d,g] [9]annulene (**37**)

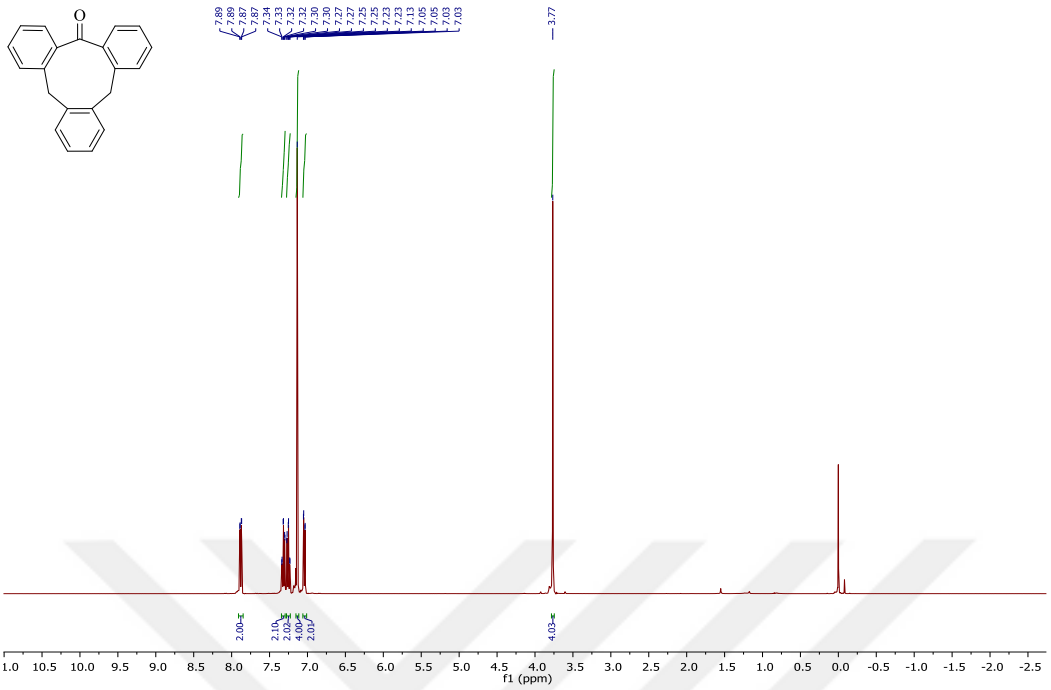


Figure 4.9 ^{1}H-NMR Spectrum of compound 10,15-dihydro-5H-tribenzo[a,d,g][9] annulen-5-one (**39**)

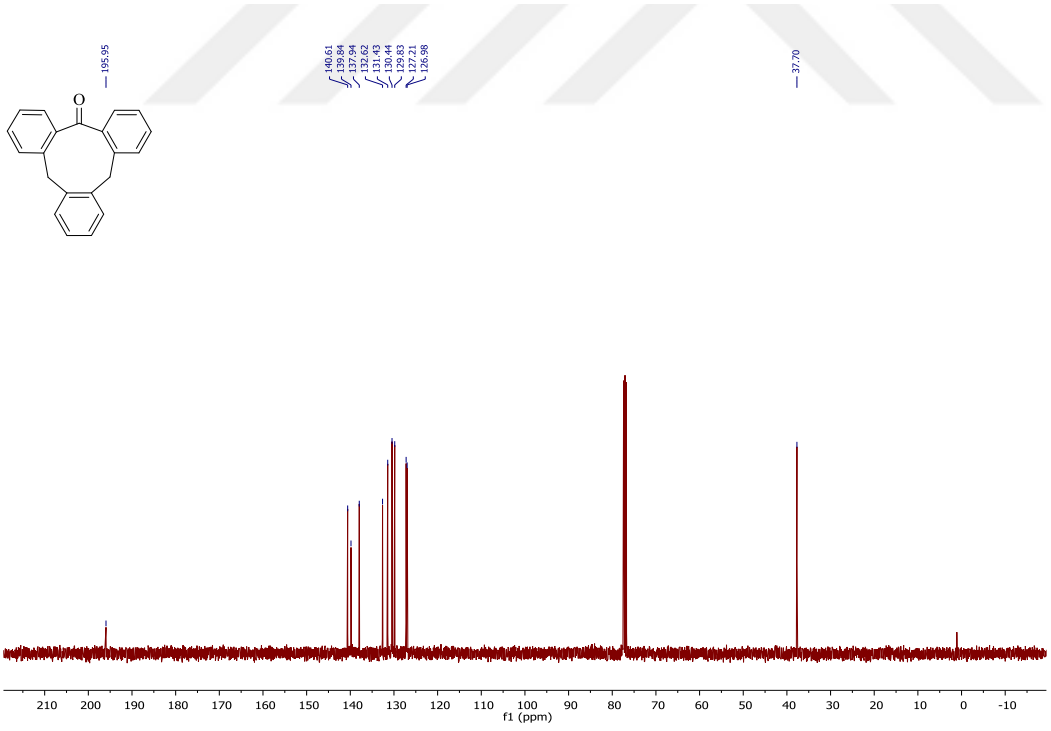


Figure 4.10 ^{13}C-NMR Spectrum of compound 10,15-dihydro-5H-tribenzo[a,d,g] [9]annulen-5-one (**39**)

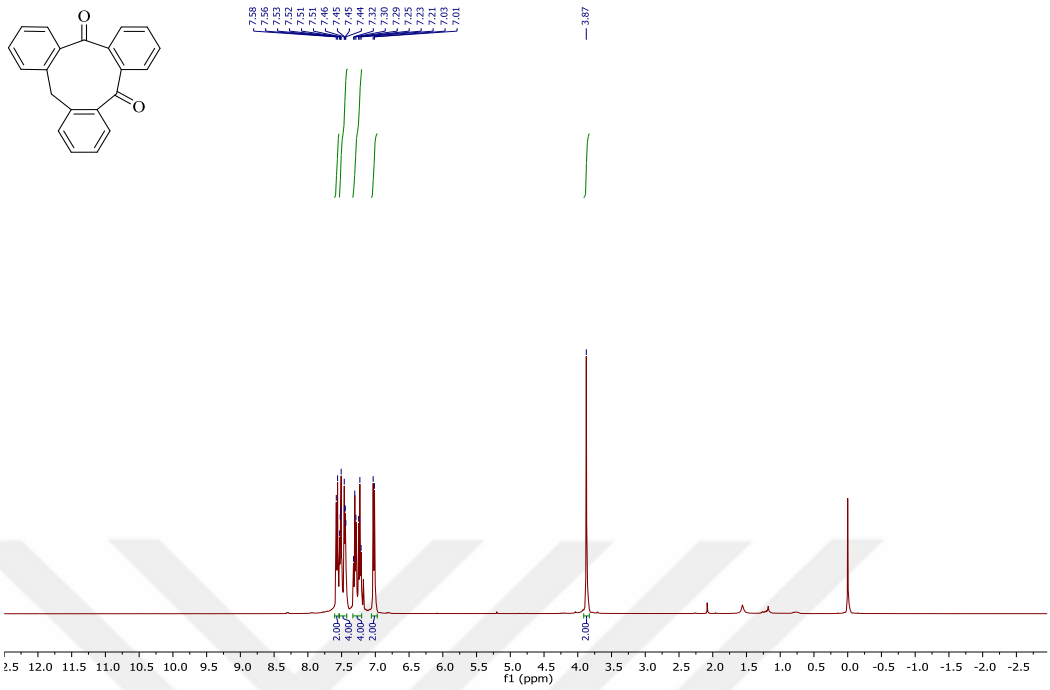


Figure 4.11 ^{1}H-NMR Spectrum of compound 5H-tribenzo[a,d,g][9]annulene-5,10 (15H)-dione (**38**)

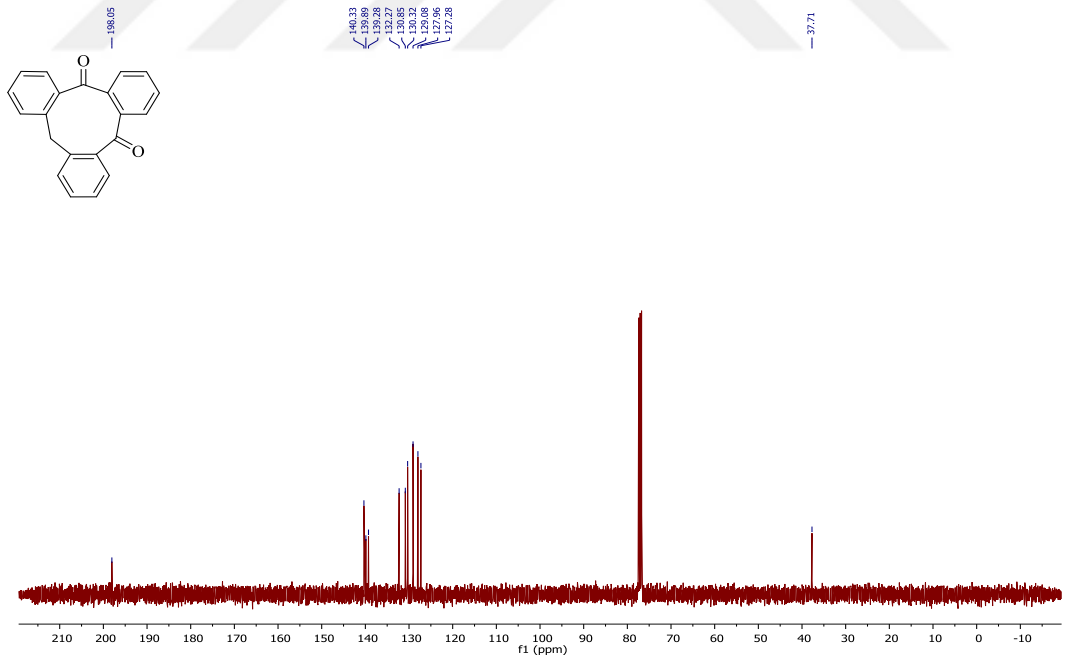


Figure 4.12 ^{13}C-NMR Spectrum of compound 5H-tribenzo[a,d,g][9]annulene-5,10(15H)-dione (**38**)

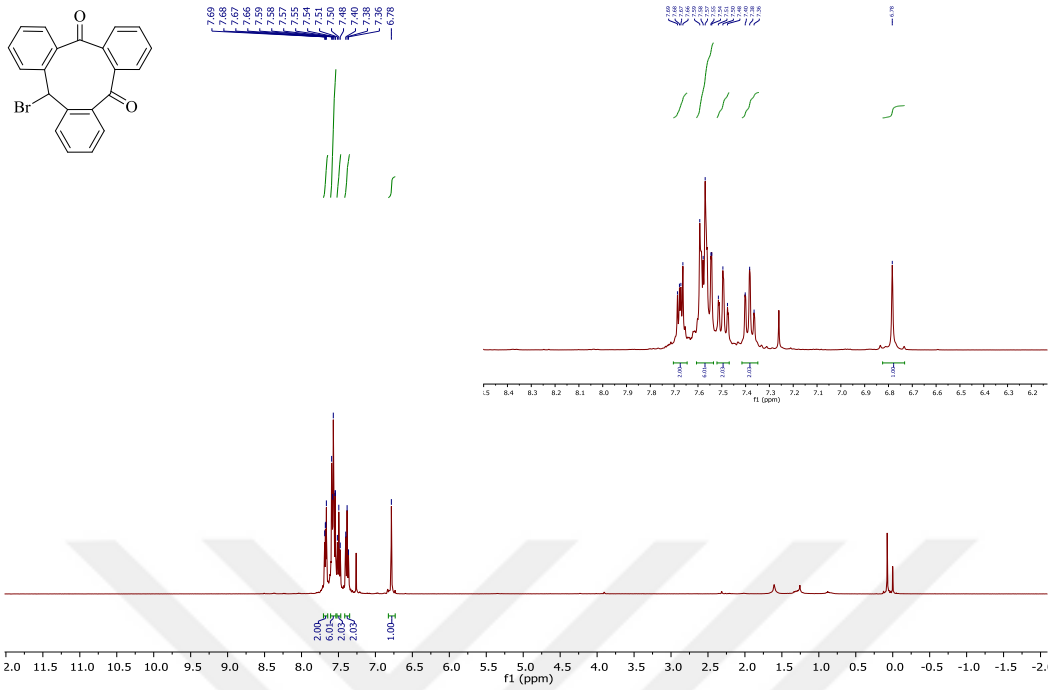


Figure 4.13 ^{1}H-NMR Spectrum of compound 15-bromo-5H-tribenzo[a,d,g] [9]annulene-5,10(15H)-dione (**41**)

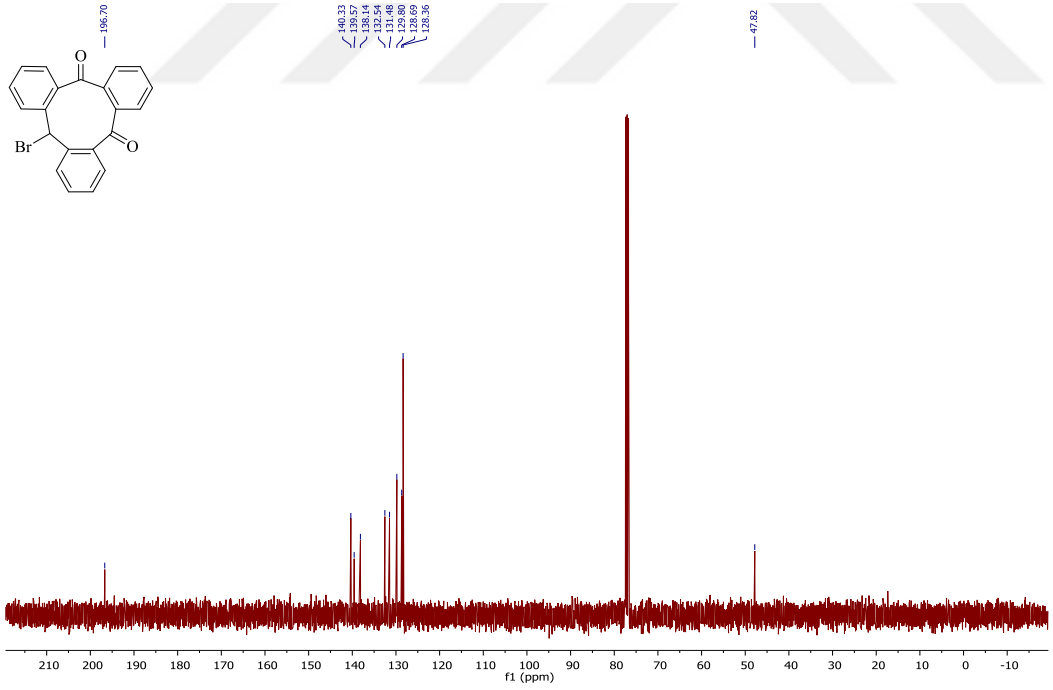


Figure 4.14 ^{13}C-NMR Spectrum of compound 15-bromo-5H-tribenzo[a,d,g][9]annulene-5,10(15H)-dione (**41**)

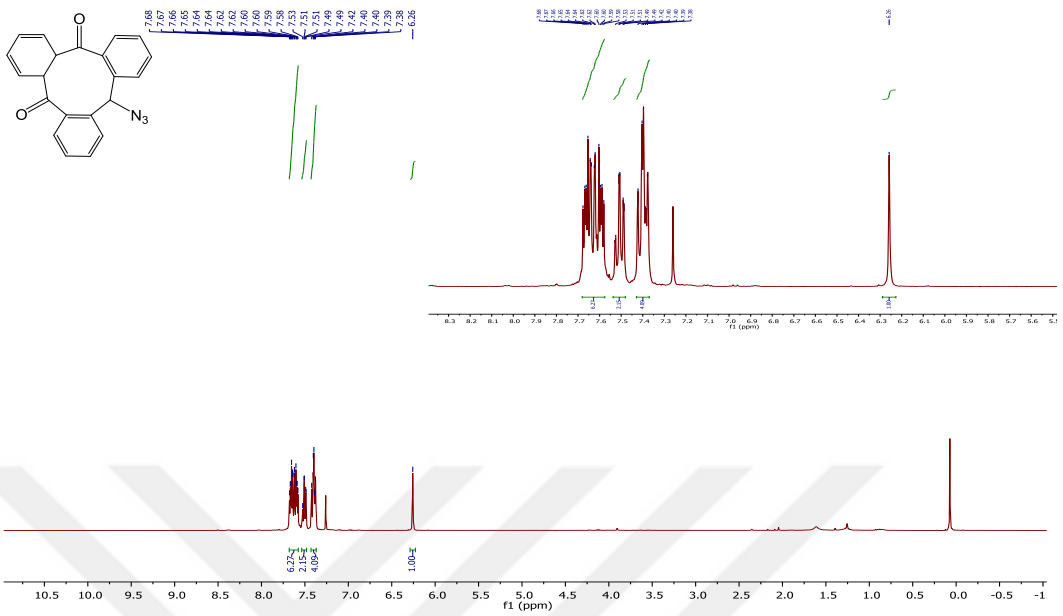


Figure 4.15 ^{1}H-NMR Spectrum of compound 15-azido-5H-tribenzo[a,d,g][9]annulene-5,10(15H)-dione (**42**)

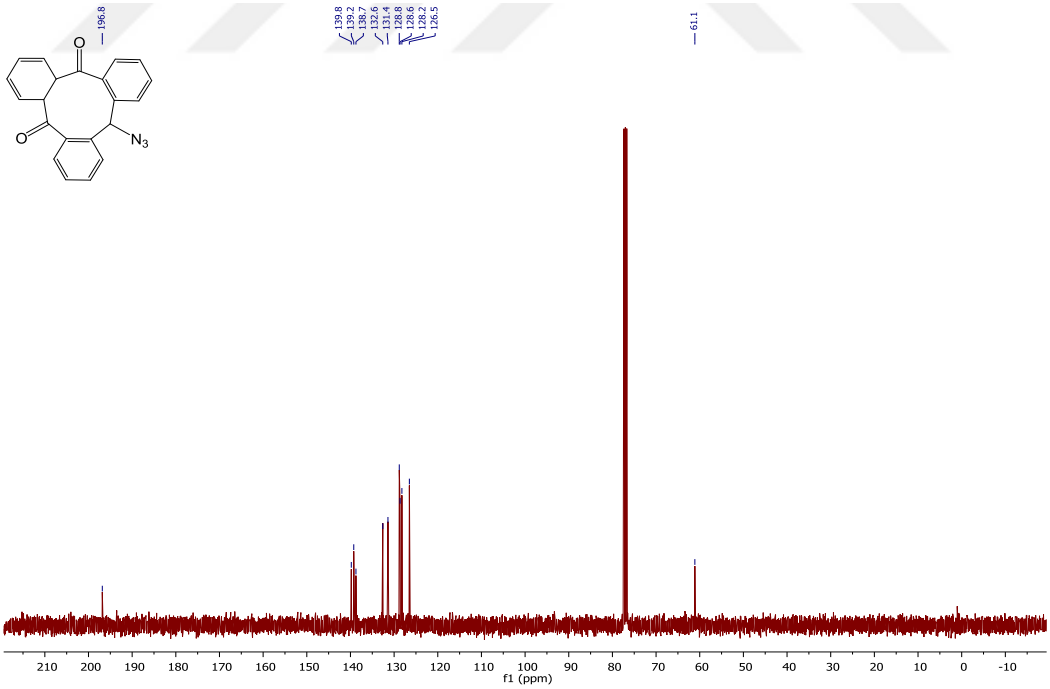


Figure 4.16 ^{13}C-NMR Spectrum of compound 15-azido-5H-tribenzo[a,d,g][9]annulene-5,10(15H)-dione (**42**)

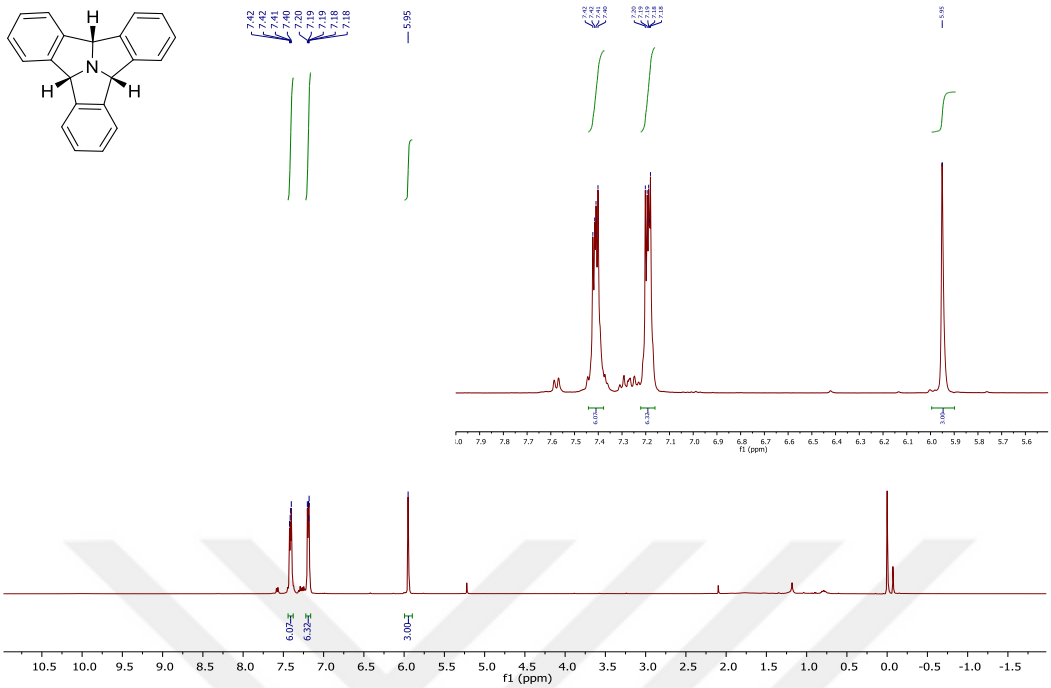


Figure 4.17 ^{1}H-NMR Spectrum of compound (4bs,8bs,12bs)-8b,12b-dihydro-4bH- dibenzo[1,2:6,7]pyrrolizino[3,4,5-ab]isoindole (**29**)

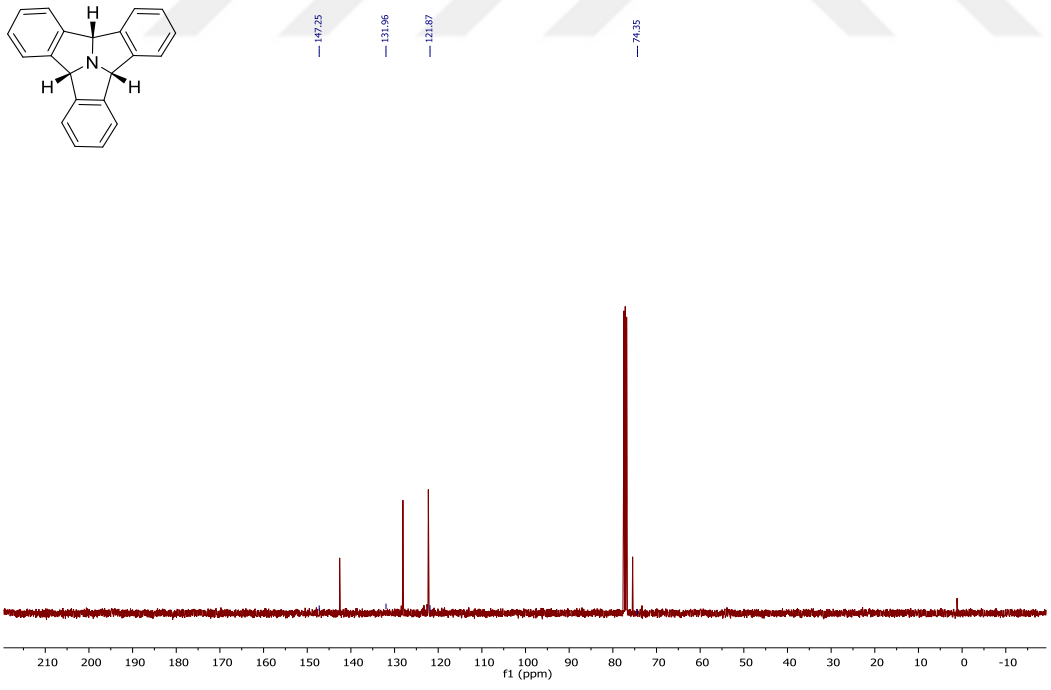


Figure 4.18 ^{13}C-NMR Spectrum of compound (4bs,8bs,12bs)-8b,12b-dihydro-4bH-dibenzo[1,2:6,7]pyrrolizino[3,4,5-ab]isoindole (**29**)

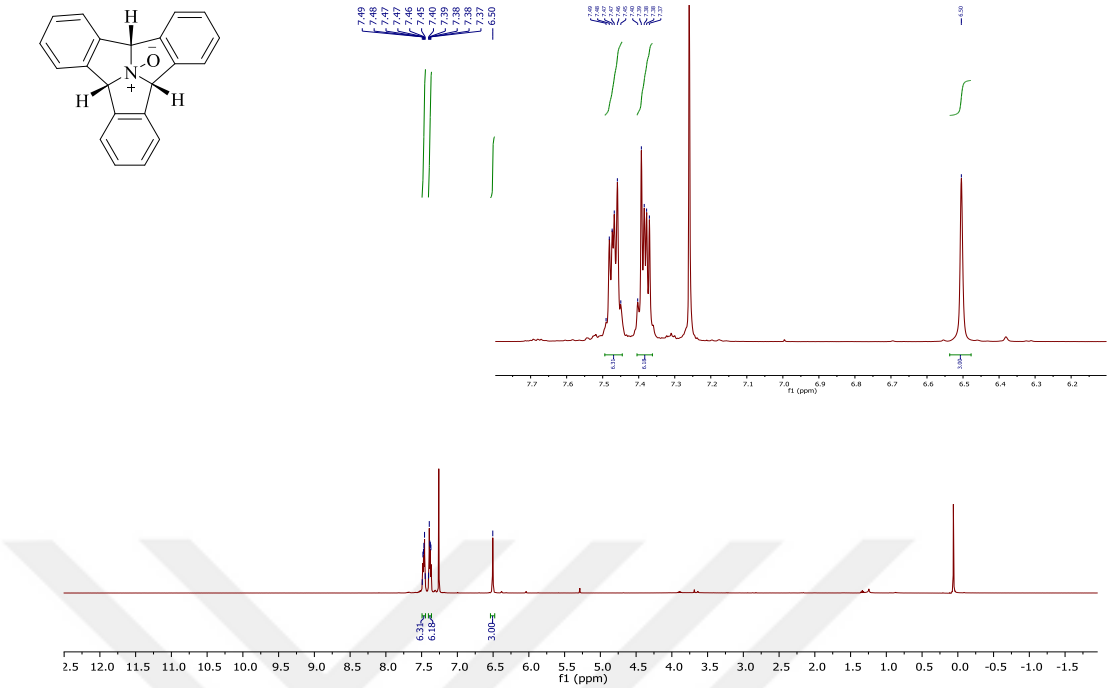


Figure 4.19 ^{1}H-NMR Spectrum of compound (4bs,8bs,12bs)-8b,12b-dihydrodibenzo[1,2:6,7]pyrrolizino[3,4,5-ab]isoindole 13(4bH)-oxide (**43**)

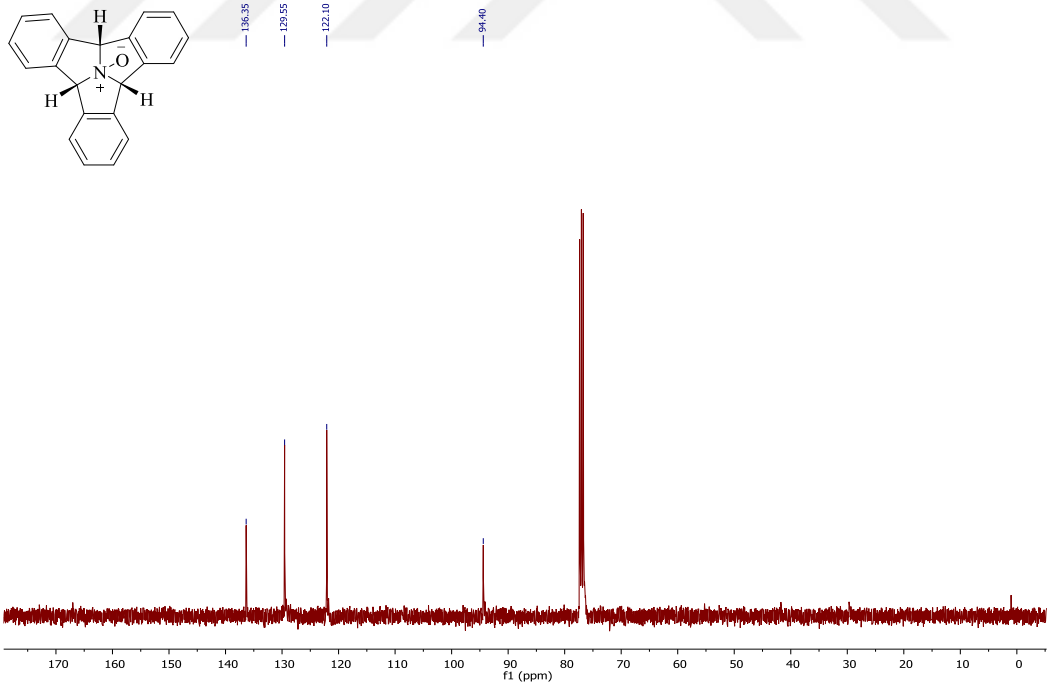


Figure 4.20 ^{13}C NMR Spectrum of compound (4bs,8bs,12bs)-8b,12b-dihydrodibenzo[1,2:6,7]pyrrolizino[3,4,5-ab]isoindole 13(4bH)-oxide (**43**)

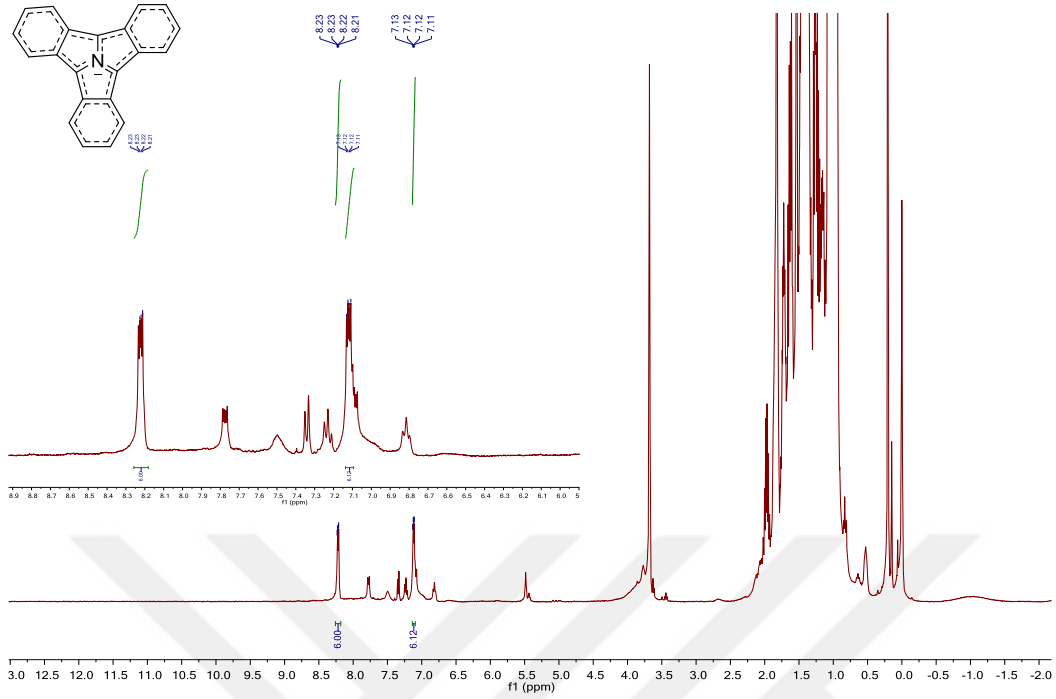


Figure 4.21 ^{1}H-NMR Spectrum of compound 8bH-dibenzo[1,2:6,7]pyrrolizino [3,4,5-ab]isoindol-8b-ide (**30**)

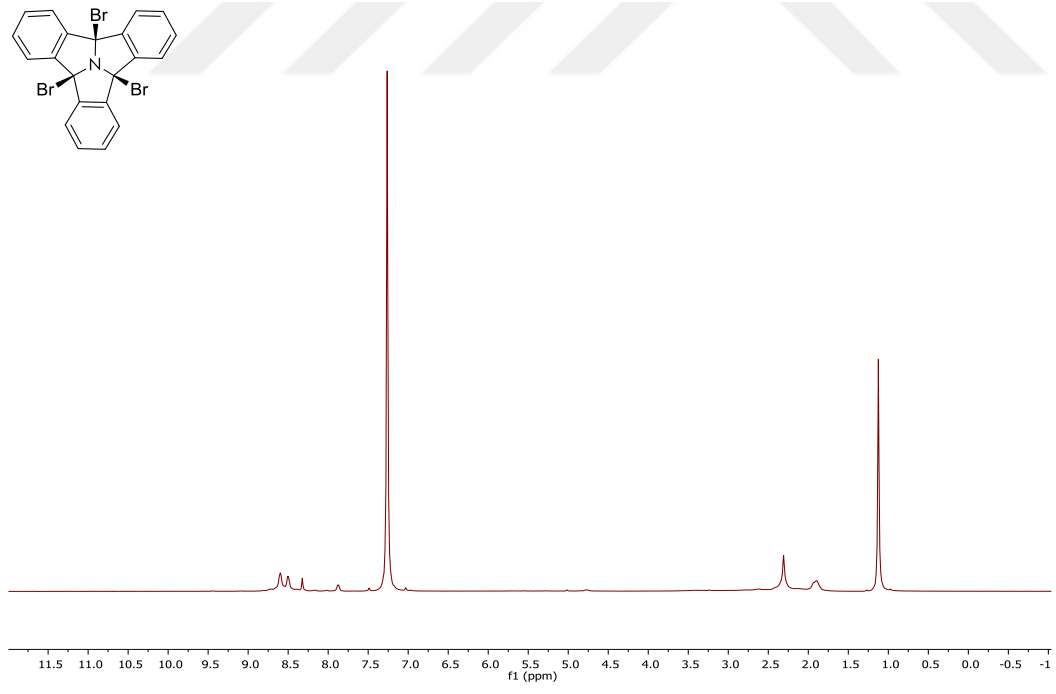


Figure 4.22 ^{1}H-NMR Spectrum of compound (4bs,8bs,12bs)-4b,8b,12b-tribromo-8b,12b-dihydro-4bH-dibenzo[1,2:6,7]pyrrolizino[3,4,5-ab]isoindole (**44**)

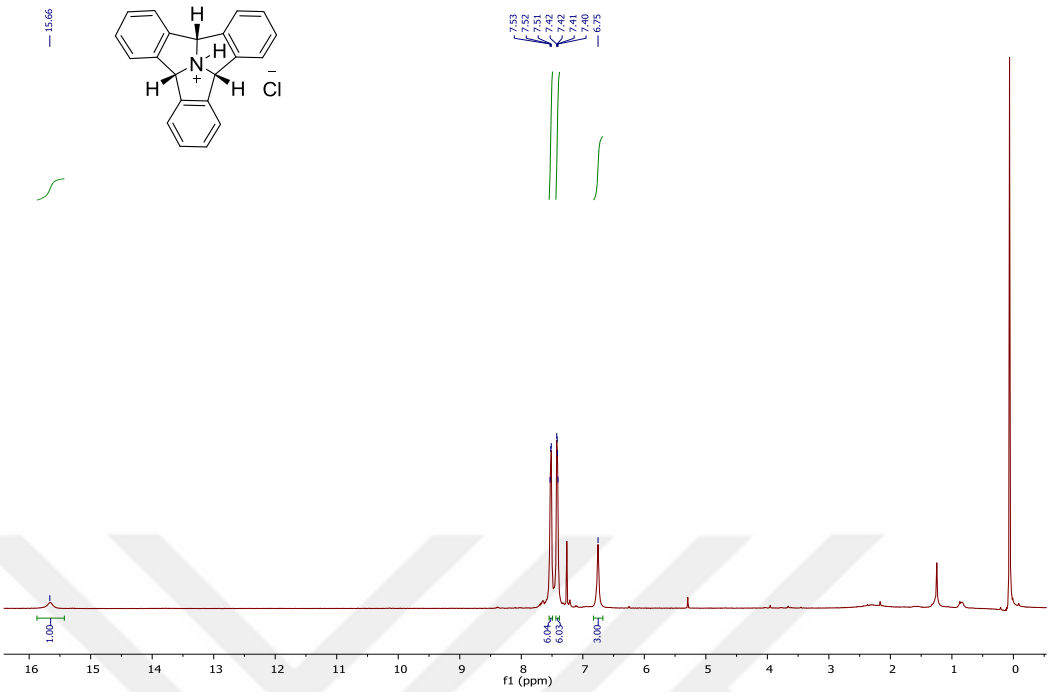


Figure 4.23 ^{1}H-NMR Spectrum of compound (4bs,8bs,12bs)-4b,8b,12b,13-tetrahydrodibenzo[1,2:6,7]pyrrolizino[3,4,5-ab]isoindol-13-ium (**45**)

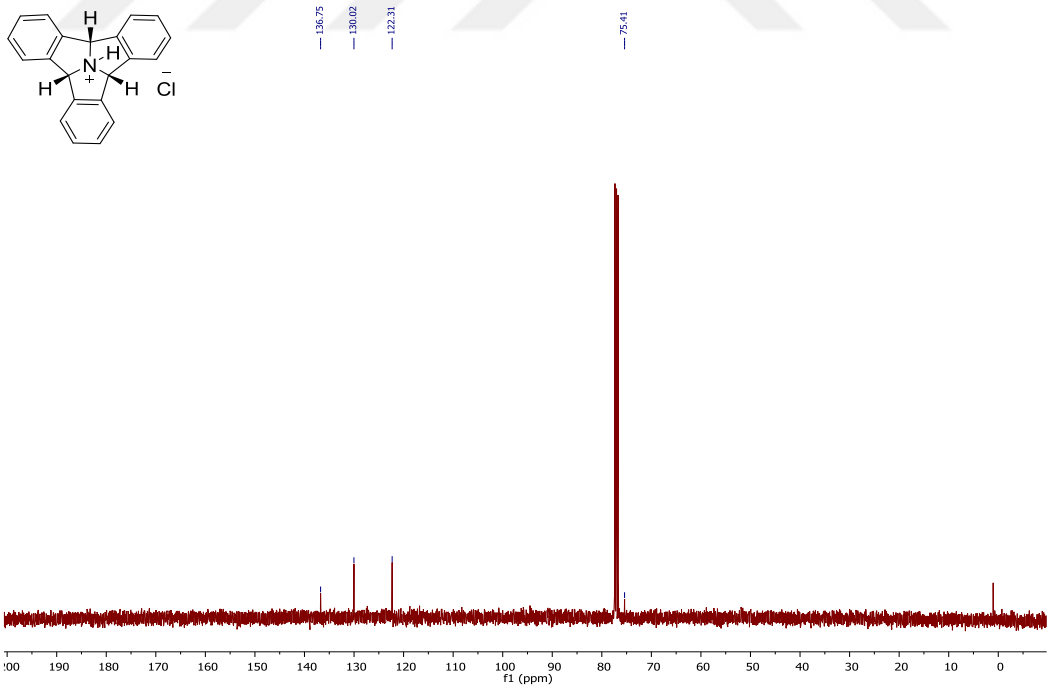


Figure 4.24 ^{13}C NMR Spectrum of compound (4bs,8bs,12bs)-4b,8b,12b,13-tetrahydrodibenzo[1,2:6,7]pyrrolizino[3,4,5-ab]isoindol-13-ium (**45**)

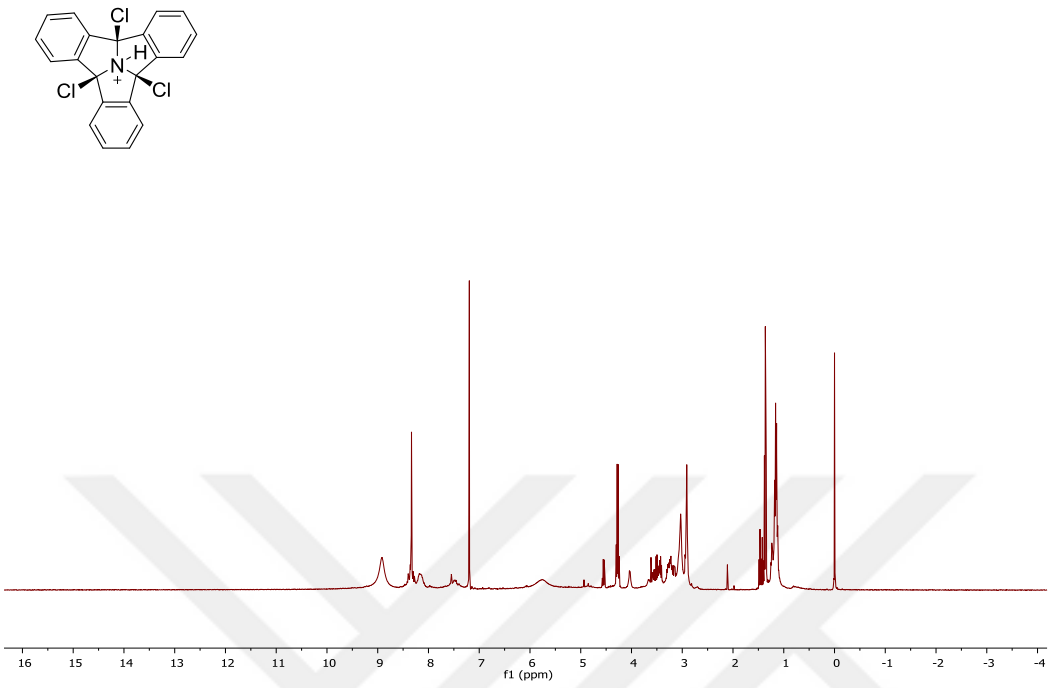


Figure 4.25 ^{1}H-NMR Spectrum of compound (4bs,8bs,12bs)-4b,8b,12b-trichloro-4b,8b,12b,13-tetrahydrodibenzo[1,2:6,7]pyrrolizino[3,4,5-ab]isoindol-13-ium (**46**)

B. HRMS Data

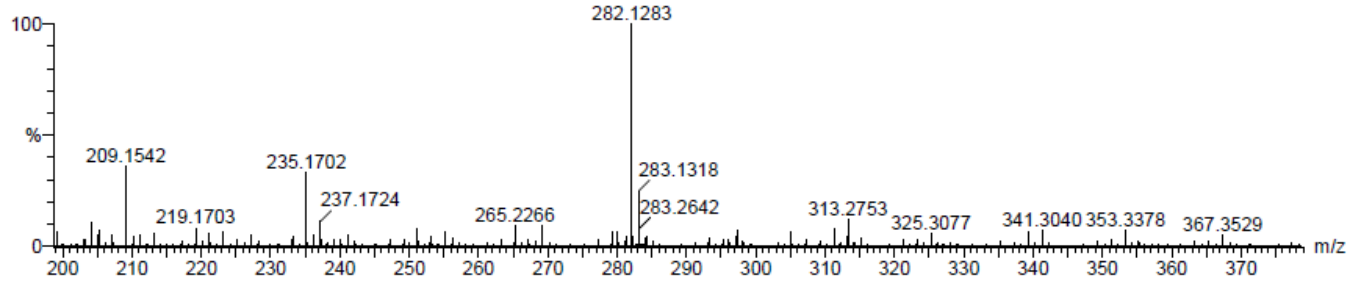
High Resolution Mass Spectroscopy (HRMS) analysis was performed using Waters Synapt MS System at METU Central Laboratory.

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5000.0 PPM / DBE: min = -5.5, max = 1000.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
1 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 21-21 H: 15-16 N: 1-1

24425_20181001_01-03 23 (0.897) Cm (8:23) 1: TOF MS ES+ 7.11e+003



Minimum:				-5.5			
Maximum:		1000.0	5000.0	1000.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
282.1283	282.1283	0.0	0.0	14.5	338.6	0.0	C21 H16 N

Figure 4.26 Mass analysis report of compound (4bs,8bs,12bs)-8b,12b-dihydro-4bH-dibenzo[1,2:6,7] pyrrolizino[3,4,5-ab]isoindole (**29**)

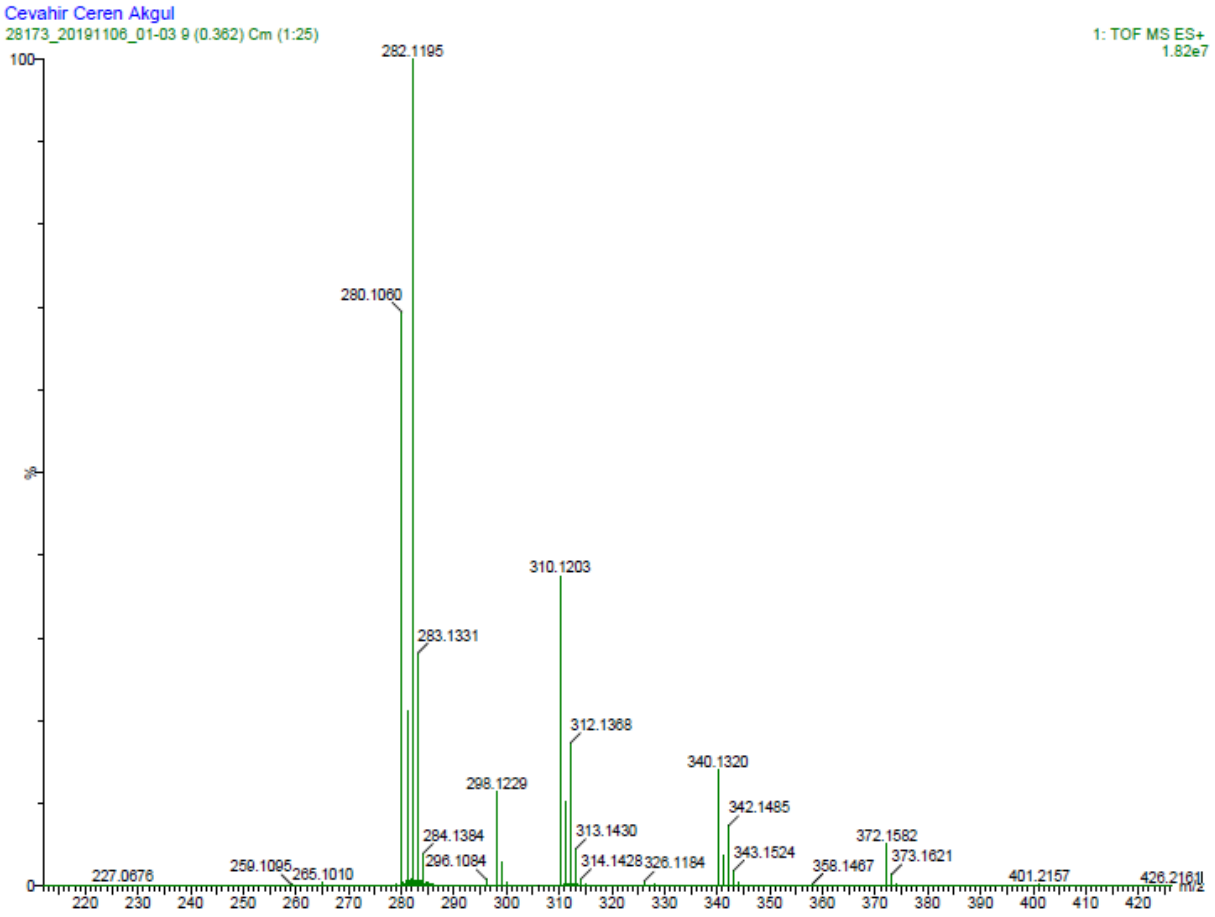


Figure 4.27 Mass analysis report of compound **44**.

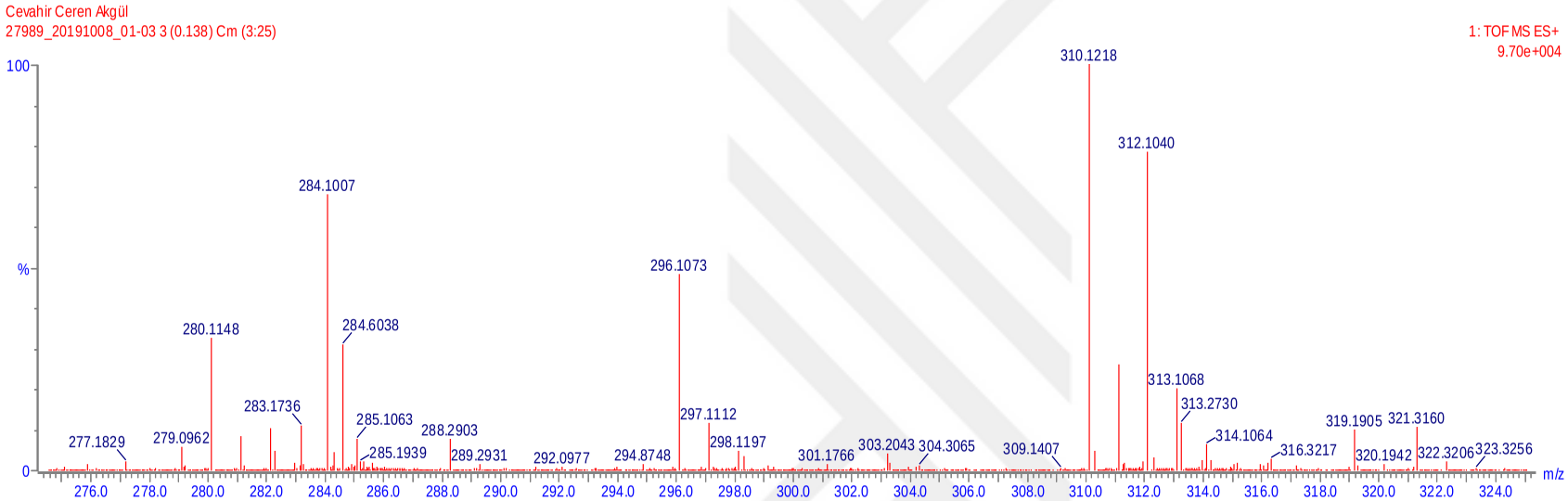


Figure 4.28 Mass analysis report of compound **46**.

C. IR Spectra

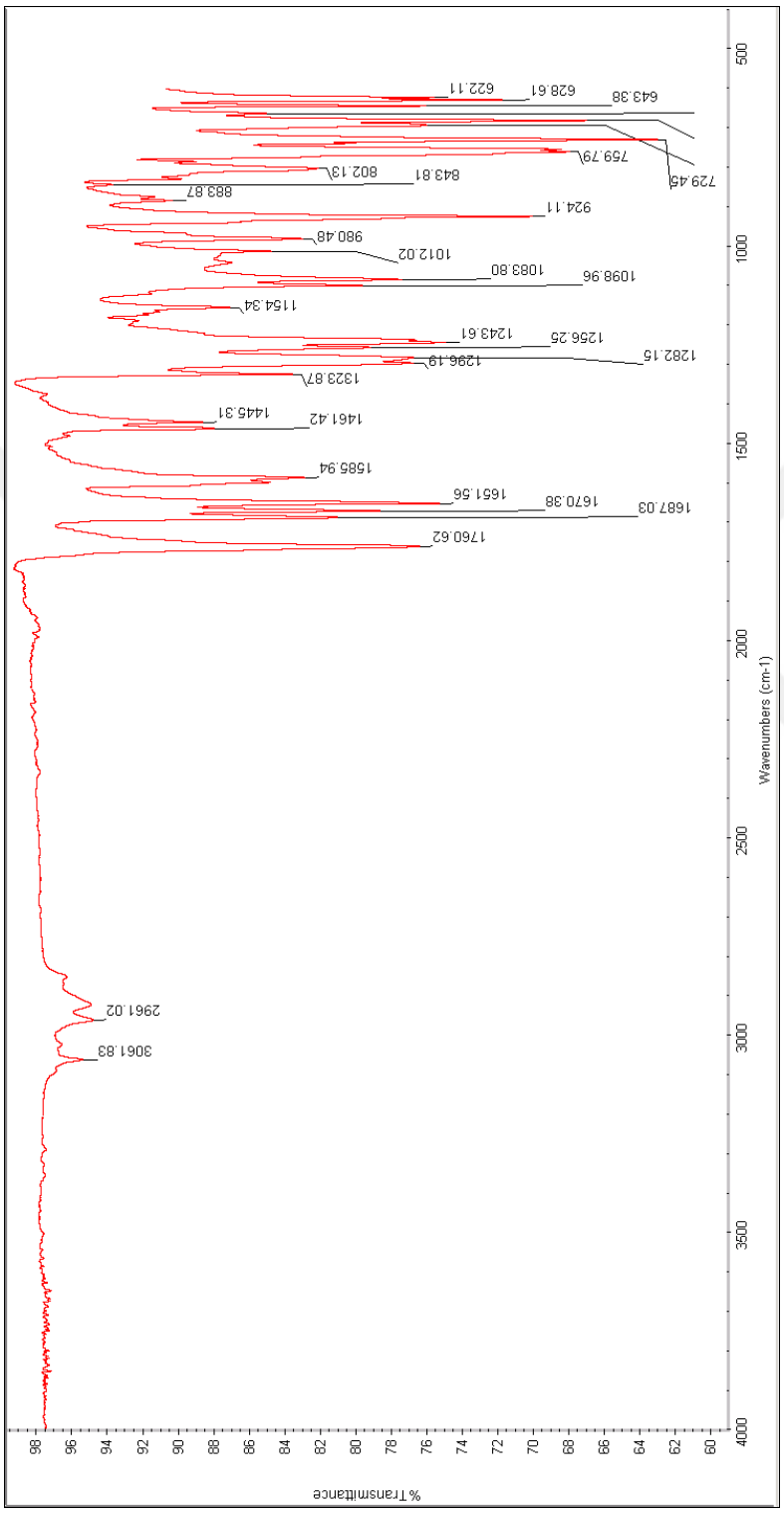


Figure 4.29 IR spectrum of the compound **41**

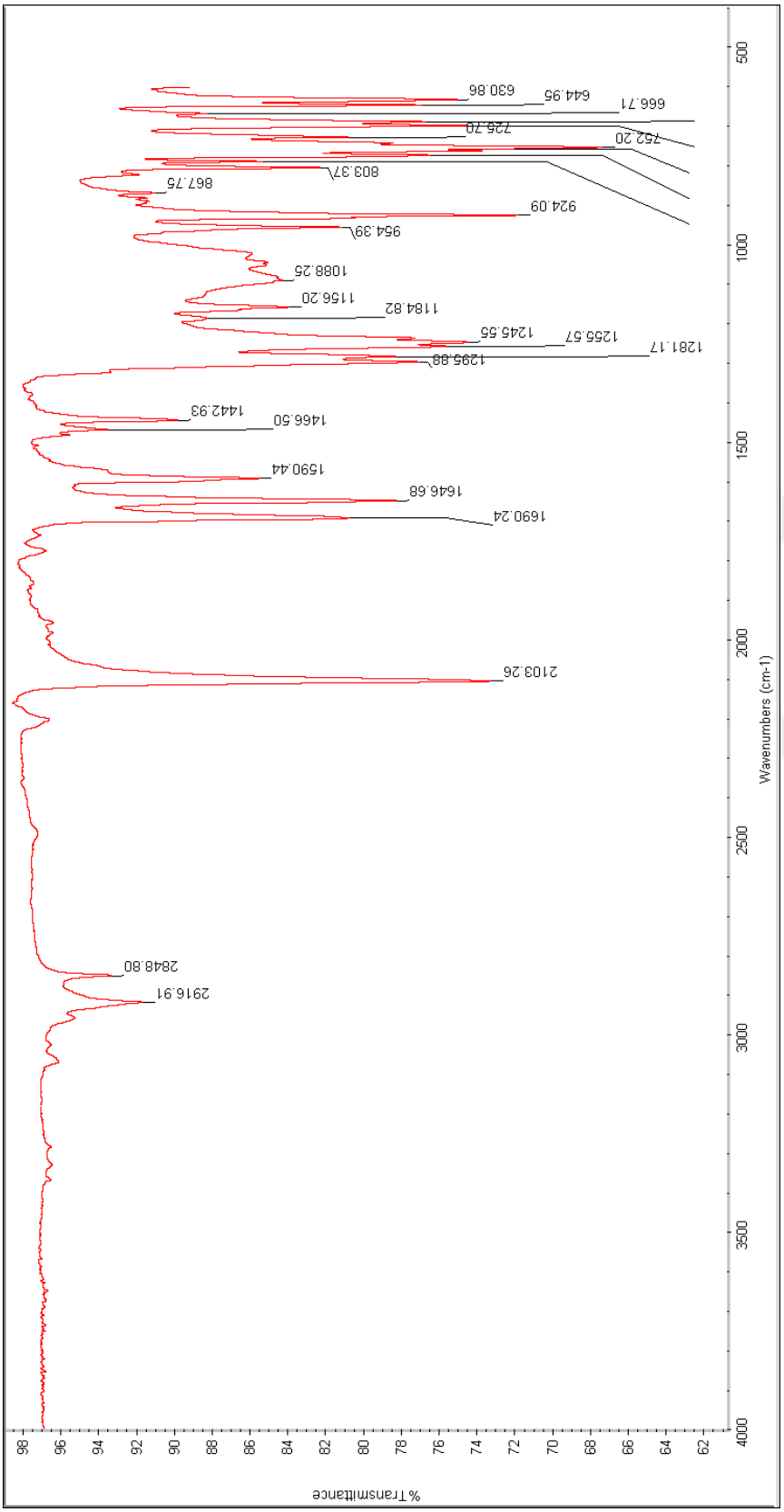


Figure 4.30 IR Spectrum of the compound **42**