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Ministry of Higher Education and Scientific Research
University of Babylon
College of Science for Women
Department of Chemistry

Synthesis of New Polyamides Based on Some Troger's Bases Molecules

A Thesis

Submitted to the Council of the College of Science for Women / University of Babylon as a Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemistry

By

Mohammed Jabber Jassim

Supervised By
Asst. Prof. Dr. Sadiq AbdulHussein Karim

2022 A **1444 H**

بسم الله الرّحمن الرّحيم

فَتَعَالَى اللَّهُ الْمَلِكُ الْحَقُّ وَلَا تَعْجَلْ بِالْقُرْآنِ مِنْ قَبْلِ أَنْ يُقْضَىٰ إِلَيْكَ وَحْيُهُ وَقُلْ رَبِّ زِدْنِي عِلْمًا

صدق الله العلي العظيم

سورة طه الاية ﴿١١٤﴾

dedication

To whom I saw the path of my life... and drew my strength from her... To the unstoppable struggle... To the fountain of selfless giving... To my dear mother, may God grant her long life

To the late who gave his life for us... To my father, may God have mercy on him

To whom who supported me to my wife

For all family and friends

To everyone who taught me a letter

Everyone who supported me and supported even with a smile

I dedicate the fruits of my labor and effort

Mohammed

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Praise be to Allah, Lord of the Worlds. Praise be to God who helped me and helped me to complete this message.

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I also express my thanks and gratitude to the Dean of the College of Science for Girls, the Head of the Chemistry Department, Dr. ***Hazem Al-Jubouri****, and all my professors who helped me and gave their valuable advice.*

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Finally, I would like to express my sincere thanks and appreciation to my family members who have helped and supported me throughout this period until I reached this stage.

Mohammed

Supervisor's Certification

I, certify thesis entitle

" Synthesis of New Polyamides Based on Some Troger's Bases Molecules" was prepared by **" mohammed jabber "** under my supervision at the Department of Chemistry/ College of Science WSCI/University of Babylon as a partial fulfillment of the requirements for the Degree of Master in Science / Chemistry

Signature:

Name: Dr. Sadiq Abdul Hussein Karim

Scientific Degree: Assistant Professor

Address: College of science WSCI /Department of Chemistry

Date: / / 2022

Recommendation of Head of Chemistry Department

According to the available recommendation , I forward this thesis for Discussion

Signature of Chemistry Department

Name: Dr.Hazim Yahya Mohammed

Scientific Degree : Assistant Professor

Address : Head of Chemistry Department

University of Babylon / College of Science for Woman

Date: / / 2022

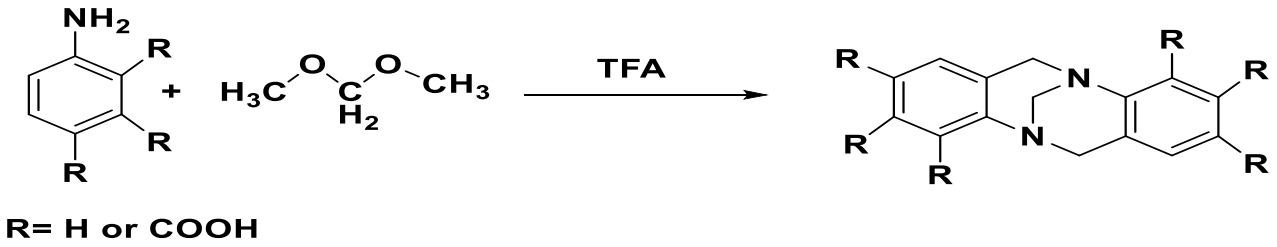
Summary

In general, in this thesis, new polyamides are synthesized and characterized based on the derivatives of Tröger's bases. To achieve this, the four Tröger's bases (TB1, TB2, TB3, TB4) (Scheme I) are synthesized containing carboxyl groups through the interaction of amino benzoic acid derivatives with dimethoxy methane in TFA. The first three Tröger's bases (TB1, TB2, TB3) are used as monomers. Through a condensation reaction, the novel polyamides based on Tröger's bases are created in three pathways based on the type of monomer. The first pathway : includes synthesis of polyamides (TB1O1-TB1O6) by reaction monomer TB1with diamine compounds [(3,3`-Dimethy1-4,4`-diamindipheny1methane), (2,6-Diaminotoluene), (2,4,6-Trimethyl-m-phenylenediamine),(2,3,5,6-Tetramethyl-l,4-pheny1enediami- ne), 9,9-Bi(4-aminophenyl)flourene, (2-Nitro-1,4-phenylenediamine)].

The second pathway : includes synthesis of polyamides (TB2P7–TB2P12) by reaction monomer TB2 with diamine compounds [(3,3`-Dimethy1-4,4`-diamindipheny1methane), (2,6-Diaminotoluene),(2,4,6-Trimethyl-m-phenylenediamine),(2,3,5,6-Tetramethyl-l,4-pheny1enediamine), 9,9-Bi(4-aminophenyl)flourene, (2-Nitro-1,4-phenylenedi- amine)].

The third pathway : includes synthesis of polyamides (TB3M13-TB3M18) by reaction monomer TB3 with diamine compounds [(3,3`-Dimethy1-4,4`-diamindipheny1methane), (2,6-Diaminotoluene), (2,4,6-Trimethyl-m-phenylenediamine), (2,3,5,6-Tetramethyl-l,4-pheny1enediamine), 9,9-Bi(4-amino- phenyl)flourene, (2-Nitro-1,4-phenylenediamine)] (scheme II shows synthesis of polyamides)

Through analyzing physical characteristics such as solubility and melting point, as well as employing IR, mass spectrometry, XRD ^{1}HNMR spectrum, and ^{13}CNMR spectrum, the produced monomers were identified. Polyamides were also characterized by FTIR, TGA, ^{1}H NMR and ^{13}C HNR.



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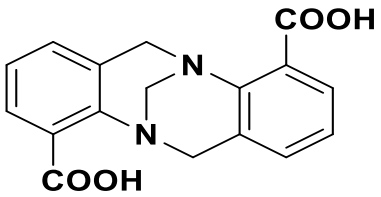

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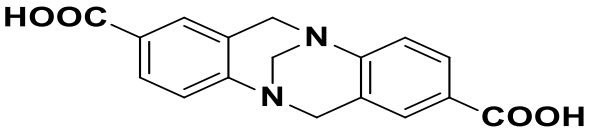

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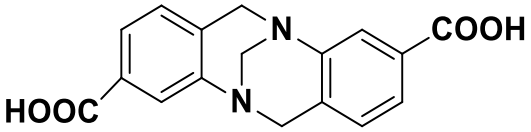

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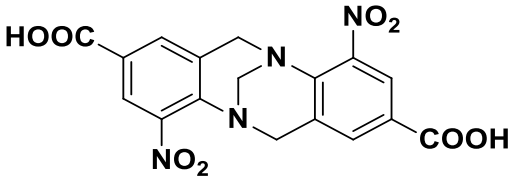
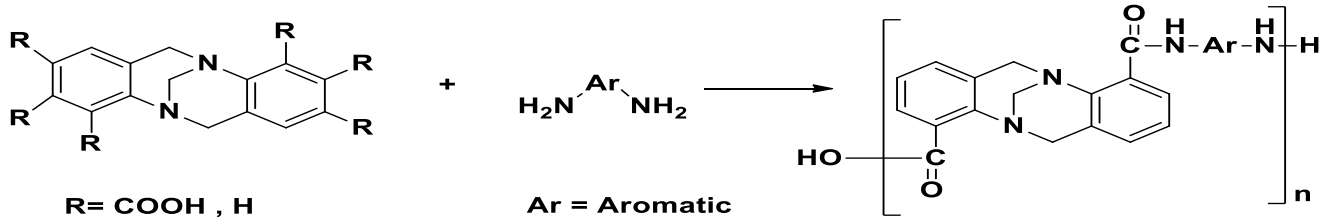
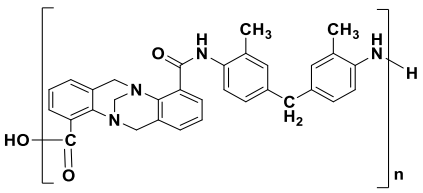


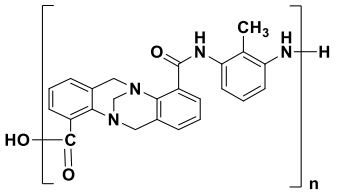
Scheme I show the synthesis of Troger base molecules (TB1-4)



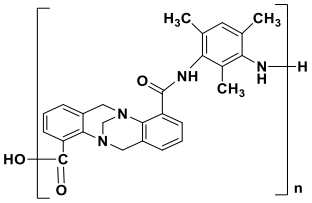
TB1-4



TB1O1



TB1O2



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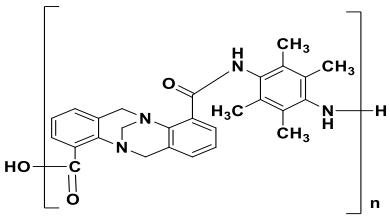

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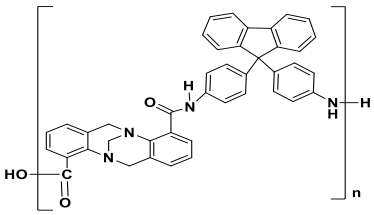

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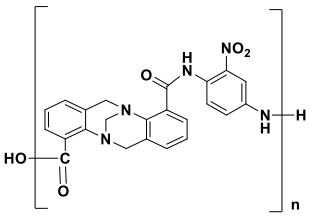

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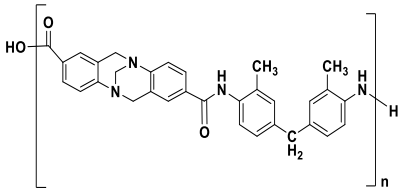
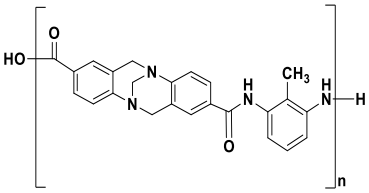


TB2P7



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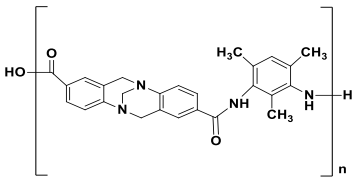

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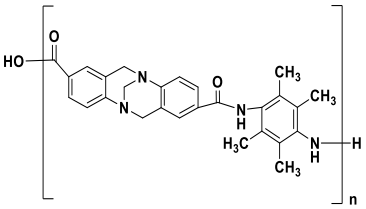

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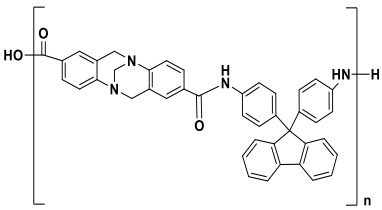

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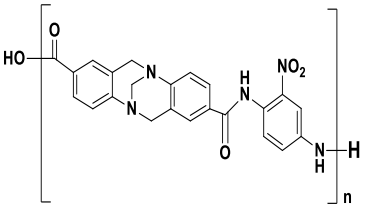

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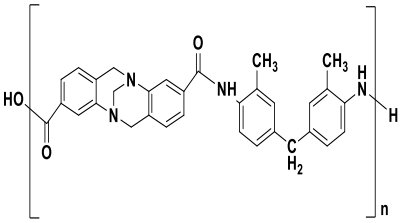
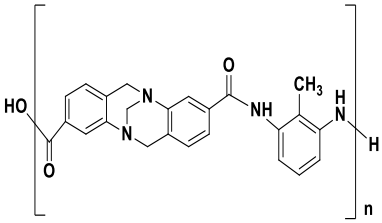
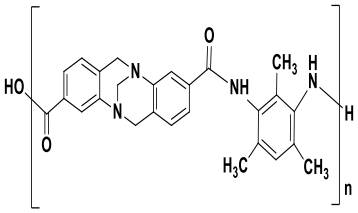


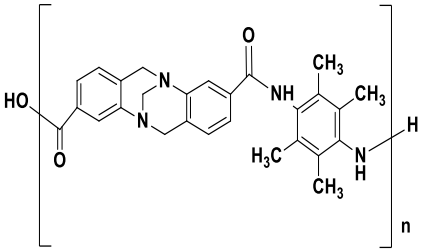
TB3M13



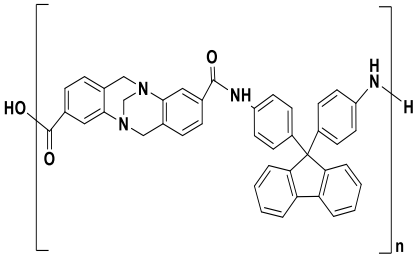
TB3M14



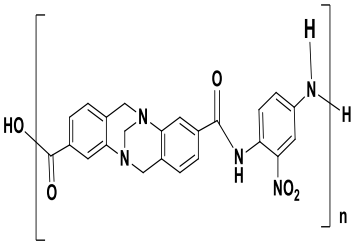
TB3M15



TB3M16



TB3M17



TB3M18

Scheme II shows the synthesis of polyamides

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List of acronyms

Number	Acronym	name
1	TFA	Trifluoroacetic acid
2	NBS	N-bromosuccinimade
3	DMF	N,N-dimethylfomamide
4	Tf	trifluoromethylsulfonyl
5	NCS	N-Chlorosuccinimade
6	HMTA	Hexamethylenetetraamine
7	DMDO	3,3-dimethyldioxirane
8	SSA	Silica sulfuric acid
9	TR	Trogeration reaction
10	MHM	C2H4Br2 and Li2CO3 in DMF , at 110 oC
11	ES	enantioseparation with dibenzoyl tartaric acid in dry CH3CN or (CH3)2CO

Chapter one

Introduction

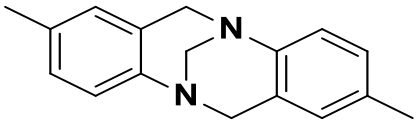
and

Literature Review

1. Introduction

1.1. Tröger base

Juliuse Tröger in 1887 synthesized and separated the first Tröger's base-1 **[**(2,8-dimethy1-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazcine] as shown in **structure (1-1)** from the condensation of *p*-aminotoluene with formalin in present acid catalyst.[1]

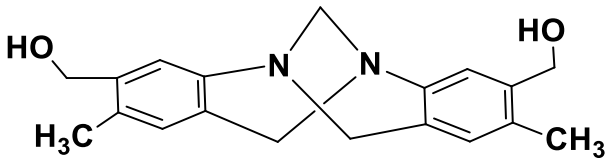


Structure 1-1:Tröger base-1

This reaction can be carried out using any suitable aryl amine with methanal in the acid catalyst,[2] but many materials do not work well with this approach, likely due to solubility issues.[3] Then after that, sources are found for methylene, such as paraformaldehyde, Hexamethylenetetraamine, dimethoxymethane, or dimethylsulfoxide (DMSO), and in an acidic environment, such, as trifluoroacetic acid, hydrochloric acid , or acetic acid.[4]

The structural structure remained unproven until came M.A. Spielm used acytion, nitration, and reduction to prove the structure of the Tröger base in 1935.[5] Then by single-crystal X-ray diffraction, it was used by Larson and Wilcox, and the Tröger base was branded as a wonderful molecule,[6] due to the structure of the base containing two nitrogen atoms stereogenic it forms a twisted rigid V shape.[7] It is not possible to distinguish between chiral nitrogen homologs because of the rapid reflection of the bridge atoms at normal temperatures. However, the stiff bicyclic unit inhibits the reflection of the bridgehead nitrogen atom. There are two types of enantiomers for Tröger's base[1]forms (5S,11S)-(+) and (5R,11R)-(-).[8]

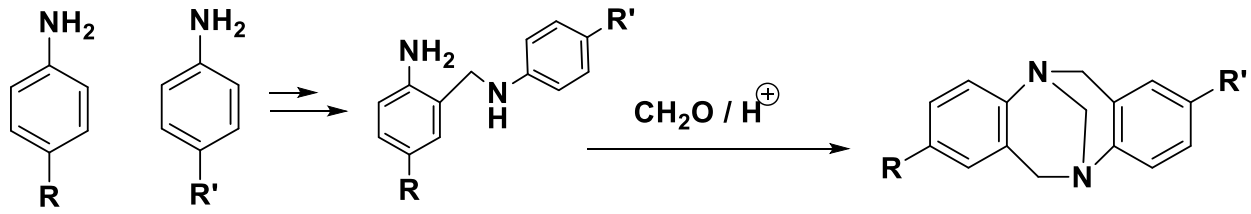
In 1988 Irving Sucholeiki, [9] *et. al* used an aniline-formalin condensation pathway to prepare various types of Tröger's base analogs, the researchers pointed out that the shape of Tröger's base analogs can be easily altered by changing the functional groups neighboring to the diazosin for example Structure (1-2) shows that these molecules can be used in the preparation of samples of enzymes and synthetic receptors.



Structure (1-2): TB contains a methanol group

A method has been found by Thomas H. and Craig s. [10] (in 1990) to produce asymmetric analogs of TB via a reaction of aniline derivatives which contain various substitutes with the presence of CH_2O followed by a loop of methylene R =CH3 **, OCH3 , Cl , H** R′ = **CH3 , NO2 , Cl , H**

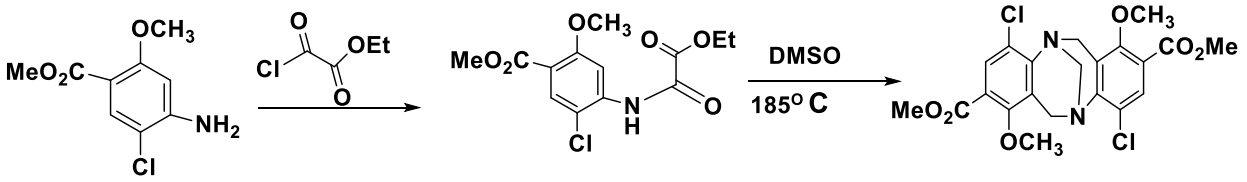
Scheme (1-1) For the first time, it was also possible to synthesis Troger's base analogs with electron-withdrawing groups.



R =CH_3 , OCH_3 , Cl , H **R′** = CH_3 , NO_2 , Cl , H

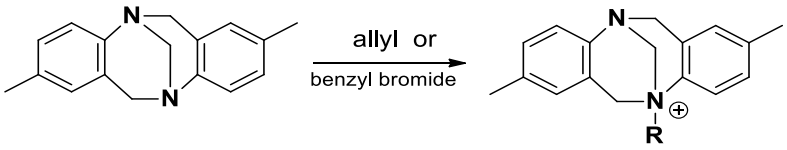
Scheme (1-1):- Synthesis of Troger's base analogues

Danie P. [11] *et al* (in 1993) discovered a novel method for preparing TB-analogues by reacting methyl 4-amino-5-chloro-2-methoxybenzoate with ethyl-2-chloro-2-oxoacetate and then heating the product in DMSO at 186° C Scheme (1-2).



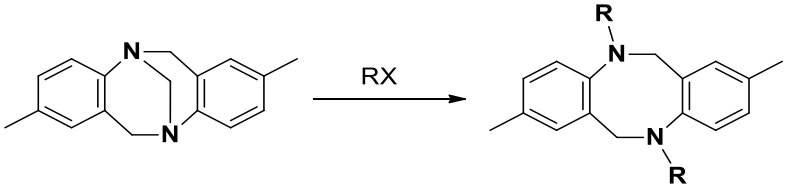
Scheme (1-2):- Preparation TB-analogues from Oxoacetate

The presence of lone pair of electrons that unshared on the nitrogen atom makes it easy to synthesize salt of Tröger's base by interaction with alkyl or benzylbromide as shown in eq.(1-1), but the quaternary overlap of each of the nitrogen atoms is not possible because of the inductive effect. The methylene bridge can be eliminated by interaction with $CO\text{-}CH_3$ or CO-Ar to produce di-acylated as mentioned in the eq.(1-2).[12]



R = CH_3 alkyl , benzyl

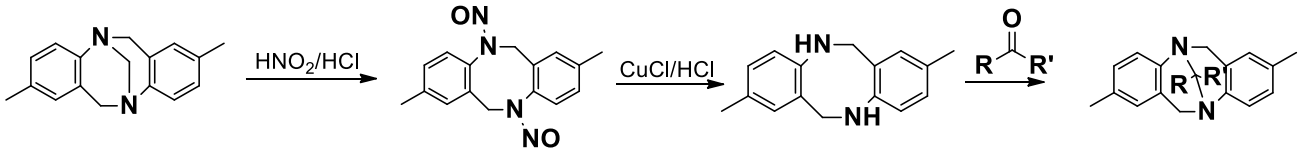
eq.(1-1):- Formation of TB-salt



R = $COCH_3$, COAr

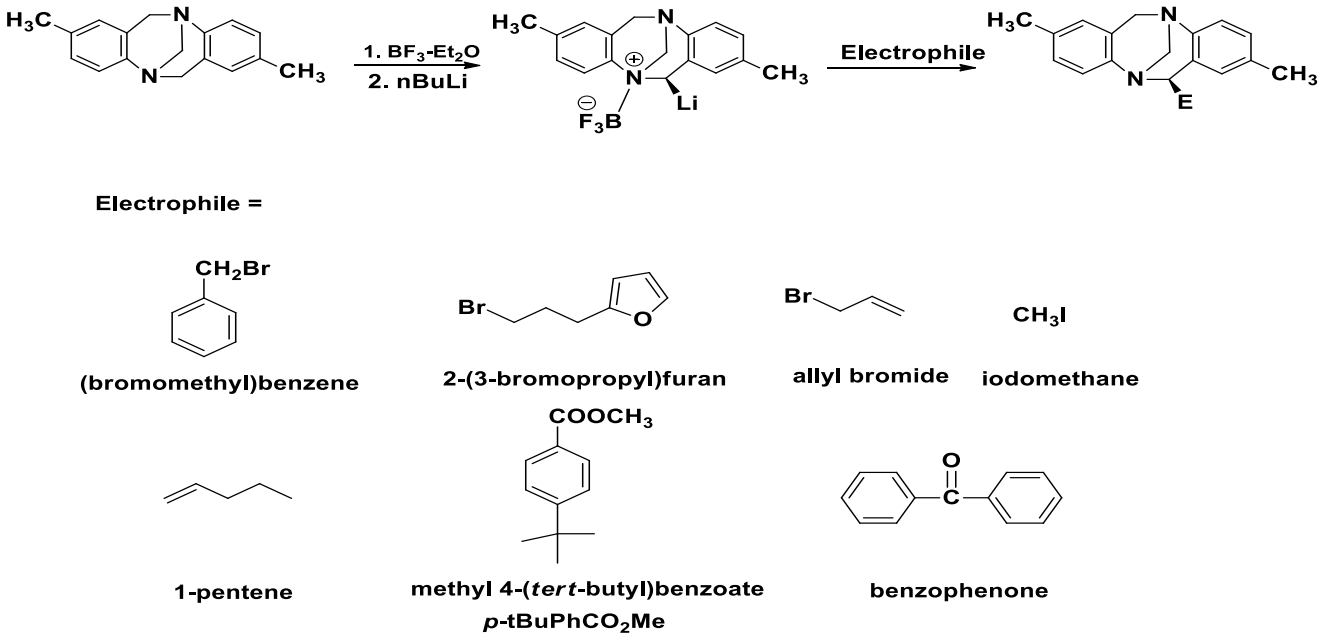
eq.(1-2): - Convert TB to di-acylate

Tröger's base transformation into di-N-nitroso when reaction with HNO_2/HCl produces diversion into diamine by handled with cuprous chloride and hydrogen chloride was then intensified with the types-different aldehydes and ketones to produce of analogues TB as mentioned in Scheme 1-3) .[12]



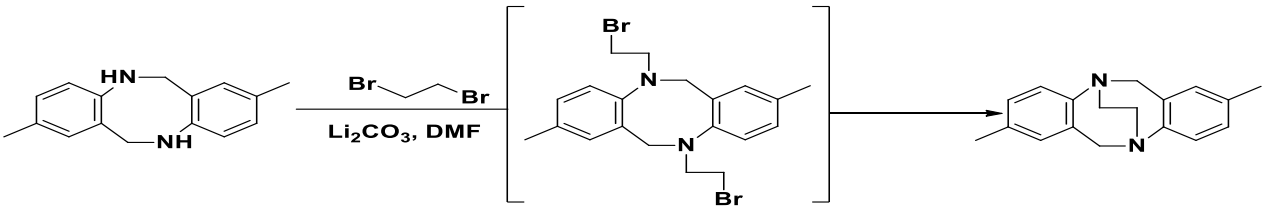
Scheme 1-3):- Produce analogues TB

In 1996 Michael Harmata [13] *et al.* added the electrophile group to the Tröger's base at a benzylmethylene site via a reaction of TB in THF with BF_3-Et_2O and n-BuLi after, then the product is reacted with the electrophilic group as shown in Scheme (1-4).



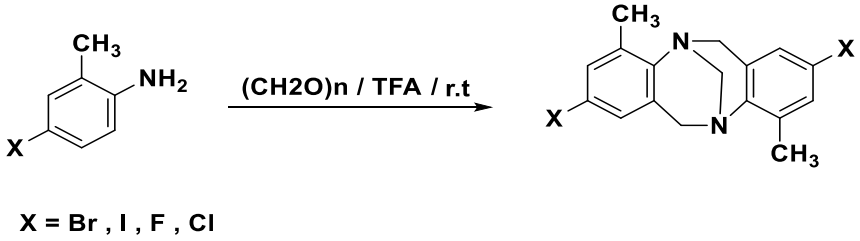
Scheme (1-4):- Formation TB-E

Yasumasa Hamada and Shiho Mukai[14] in 1996 synthesized ethano-TB through a reaction of the 2,8-dimethyl-5,6,11,12-tetrahydrodibenzo[b, f][1,5] diazocine with ethylenedibromide in the existence of Li_2CO_3 in dimethylfumarate (DMF) as in Scheme (1-5) .



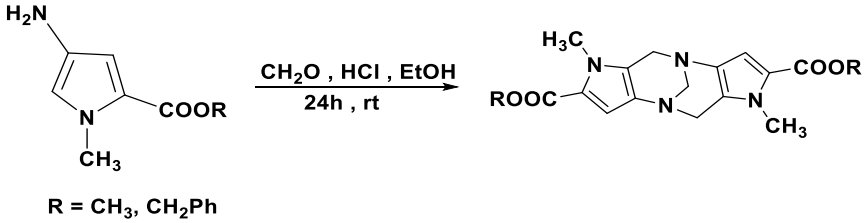
Scheme (1-5):- Synthesis of Ethano-TB

Jacob Jensen and Kenneth Warmmark[15] in 2001 were able to prepare the Tröger's base 2-8-Halogen by condensing the substituted 2-methyl-4-halogenaniline, with the presence of methyl group in site ortho eq.(1-3) which gives a more effective interaction.



eq.(1-3):- Preparation of TB-2,8-X

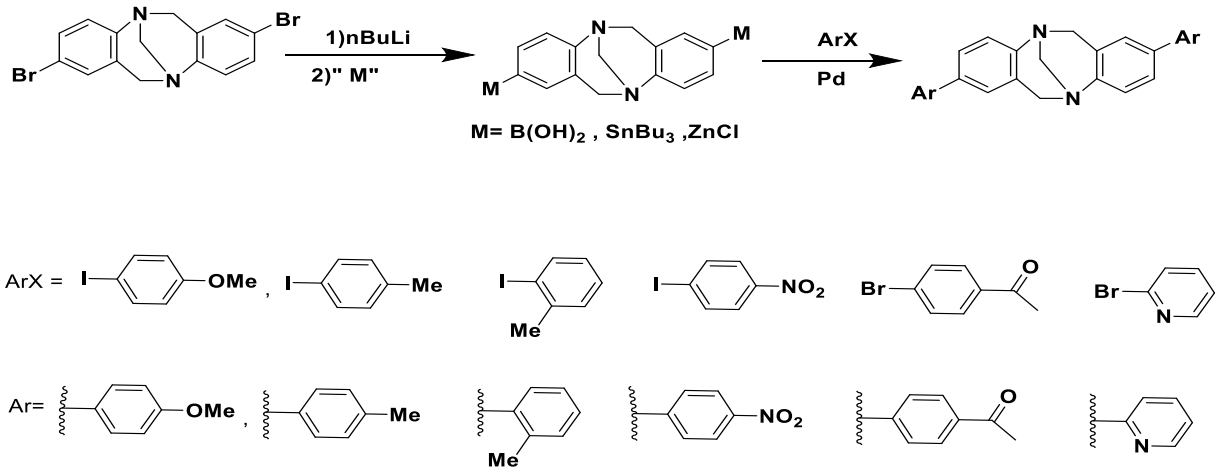
Tröger's base heterocyclic derivatives were synthesized selective receptor systems to be used to extend the synthesis of new substituted by Martin Valik[16] *et al* in 2003, as in eq.(1-4).



eq.(1-4):- Synthesis of Tröger's base heterocyclic derivatives

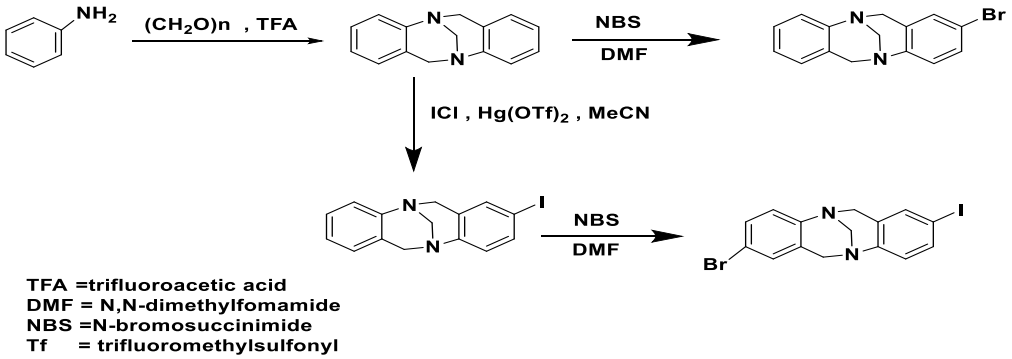
Carlos Solano[17] *et al*.in 2005 were able to create a general method for the metalation reaction. Started with 2,8- dibromo-TB to prepare many derivatives of TB by using the necessary materials and catalysts. Meanwhile, conducted a comparison of three important interactions, Suzuki, Stille, and Negishi.

Finally, they proved that the Suzuki reaction is the most efficient for linking the aromatic and heteroaromatic cracks with the Tröger's base, Scheme (1-6) shows synthesized derivatives-TB.

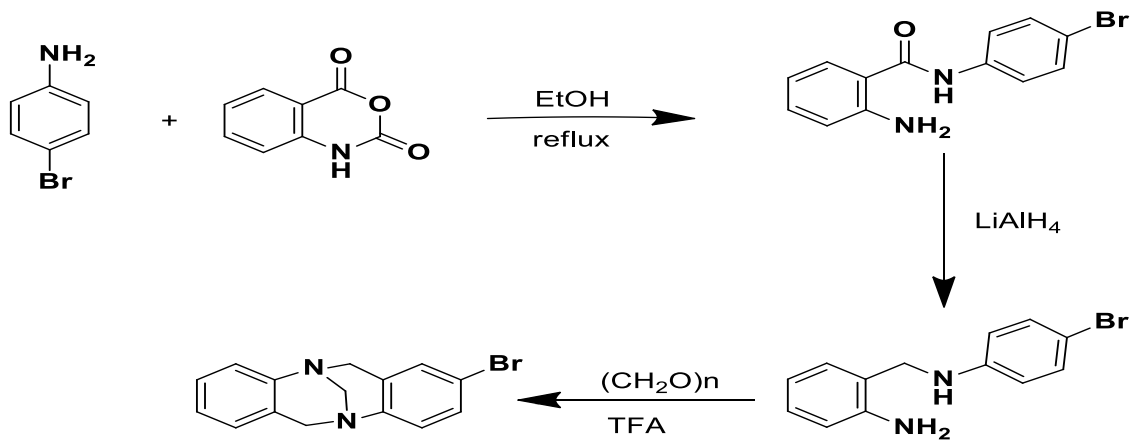


Scheme (1-6): Preparation many derivatives of TB

In 2007 a method was developed by Delphine Didier and Sergey Sergeyev[18] for halogenation of Tröger's base and conversion into unsymmetrical Bromo and iodo (see Scheme (1-7) as well as see Scheme(1-8) the synthesized of mono bromide-TB.

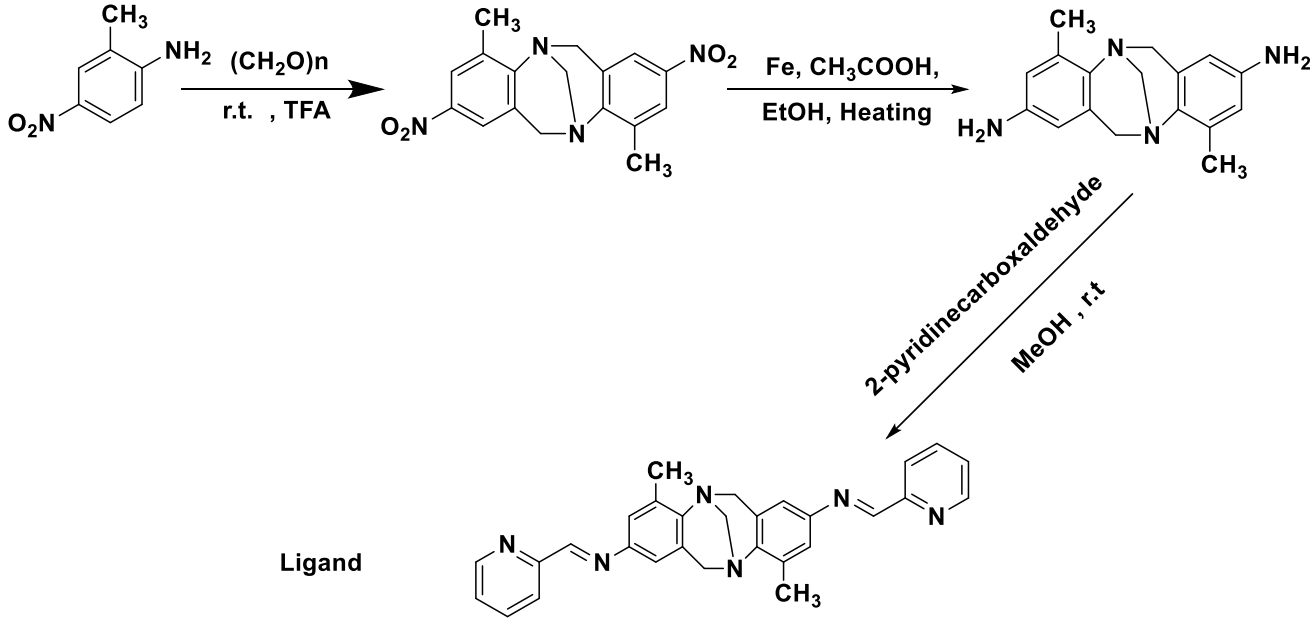


Scheme (1-7):- Synthesized of Unsymmetrical for TB



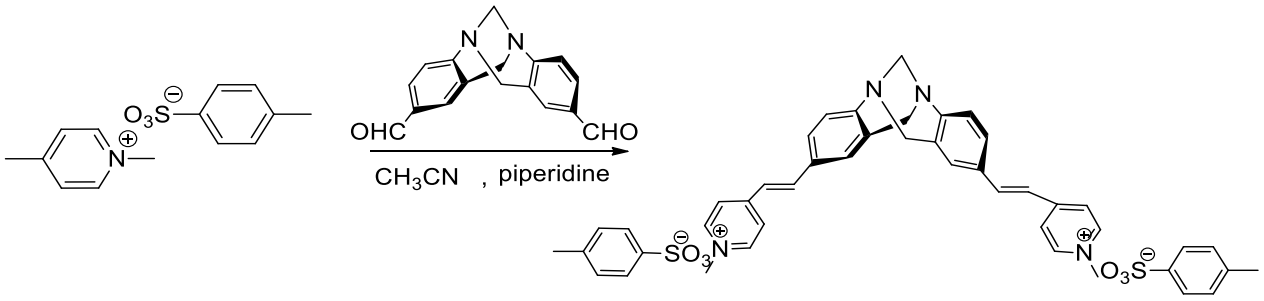
Scheme(1-8): Synthesized Troger's base Mono Bromide

U. Kiehne[19] *et al.* in 2007 used TB- derivative to prepare the Ligand, where the 2,4- dinitro derivative of Troger's base was prepared from condensation of the 2-amino-4-nitro-toluene with $(CH_2O)_n$ in CF_3COOH at room temperature then it's into diamine-TB, this product used form ligand as see in Scheme (1-9) .



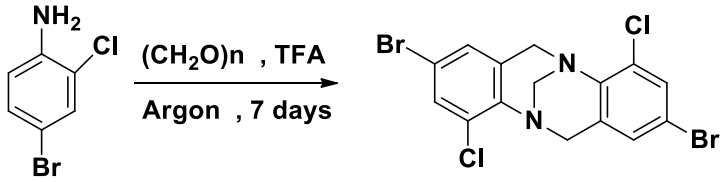
Scheme (1-9):- Preparation of Ligand from TB

The 2,,8-(6H,12H-5,11-meth;anodibenzo[b,f]diazocineylene)-di(p-ethenyl-N-methyl-pyridinium) prepared depended on Troger's base and n-methylpyridiniumtosylate by Chun-Xue Yuan[20] *et al.* in 2007, The salt in solution, the luminescence is nearly undetectable, but in the solid-state very strong emission as shown in eq.(1-5).



eq.(1-5):- Formation of Pyridinium salt from TB

Kai-Xian Zhu[21] *et al.* in 2008 prepared the Troger's base to contain dibromo and dichloro in 2,8 and 4,10 respectively from interaction direct between 2-chloro -4-bromoaniline and paraformaldehyde with the presence of trifluoroacetic acid as in the eq (1-6)

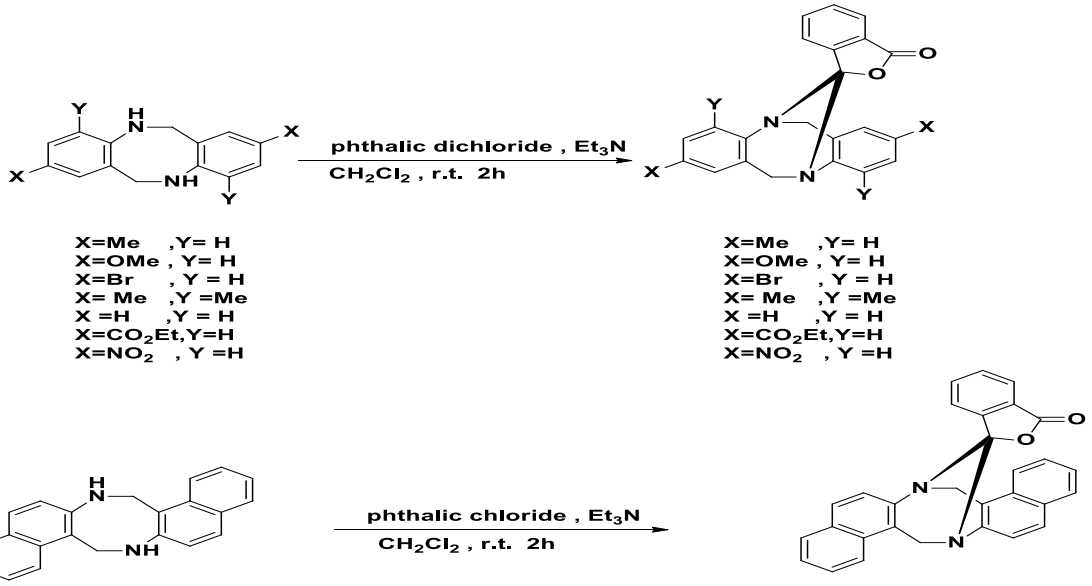


eq.(1-6):- Preparation of TB-dibromo- dichloro

Delphine Didier[22] *et al.* in 2008 studied the field and determined general procedures to prepare TB-analogues by the interaction of aniline and paraformaldehyde, and the presence of trifluoroacetic acid. They showed that this procedure is an optimum method to obtain a good yield, In a few cases, it was useful to impose restrictions on the general procedure represented by

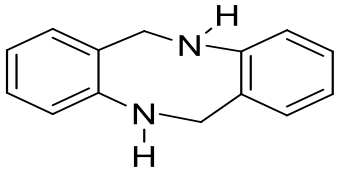
the presence of the very strong electron donating groups, and very strong electron-acceptor groups.

In 2008 Tröger's base derivatives containing lactone were made by Andrew B. Mahon [23] *et al*, from interaction 5,6,11,12-tetrahydrodibenzo [b,f][1,5] diazocine with phthalic chloride in the presence of dicyclohexylmethanediimine, as in eq.(1-7).



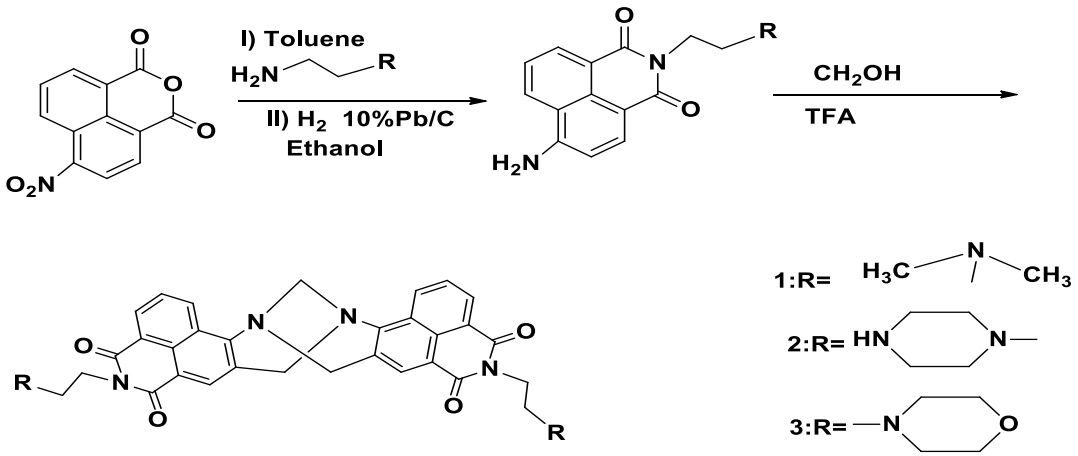
eq.(1-7):- Tröger's base derivatives containing Lactone

Andrew B. Mahon[24] *et al.* proved in 2008 that can produce cyclic disecondary amines by taking off methylene bridge from TB-analogues as in Figure(1-3). Also, they showed that all amines produced can make a reaction with benzaldehyde to produce a methylene bridge.



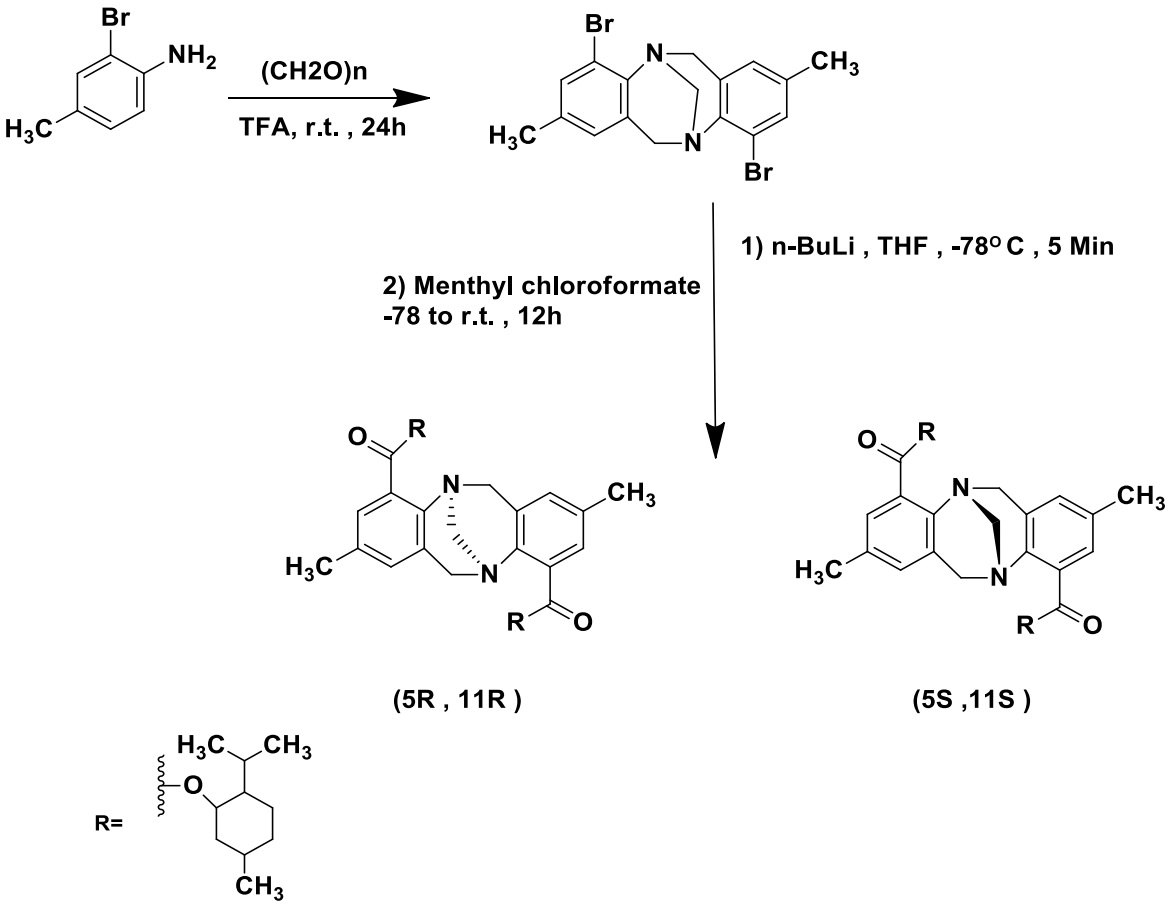
Structure (1-3)*:* 5,6,11,12-tetrahydrodibenzo[b,f][1,5]diazocine

4-amino-1,8-naphthalimide based Tröger's base is prepared by Emma B. Veale *et al.* in 2009 follows two steps, firstly interaction of 4-NO_2-1,8-naphthalic anhydride with 1,2-Bis(methylamino)ethane, 2-(4-methylpiperazin-1-yl)ethanamine, and 2-morpholineethanamine followed by hydrogenolysis in methanol, and secondly the product compound can be converted to Troger's base by the interaction it with HCHO in the CF_3COOH as in the Scheme (1-10).[25]



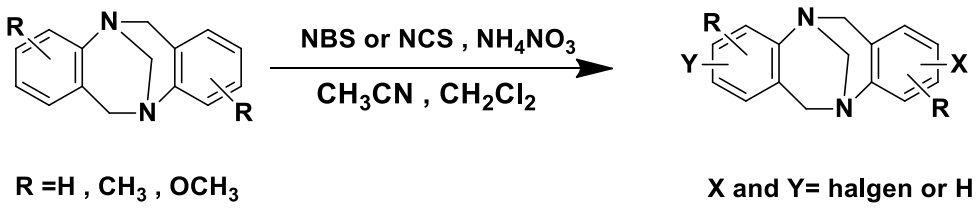
Scheme (1-10): Preparation of 4 -amino -1,8-naphthalimide based Troger's base

Zhong Jin *et al* in 2009 synthesized 4,10-disubstituted Troger's base from interaction 4-amino-3-bromotoluene with $(CH_2O)_n$, and the existence of CF_3COOH at room temperature.The product from this step can react with Menthyl-chloroformat (2-isopropyl-5-methylcyclohexylcarbonchloridate) and n-BuLi in tetrahydrofuran (THF) to grant diastereo'mers (5S,11S) and (5R,11R) as shown in Scheme(1-11).[26]



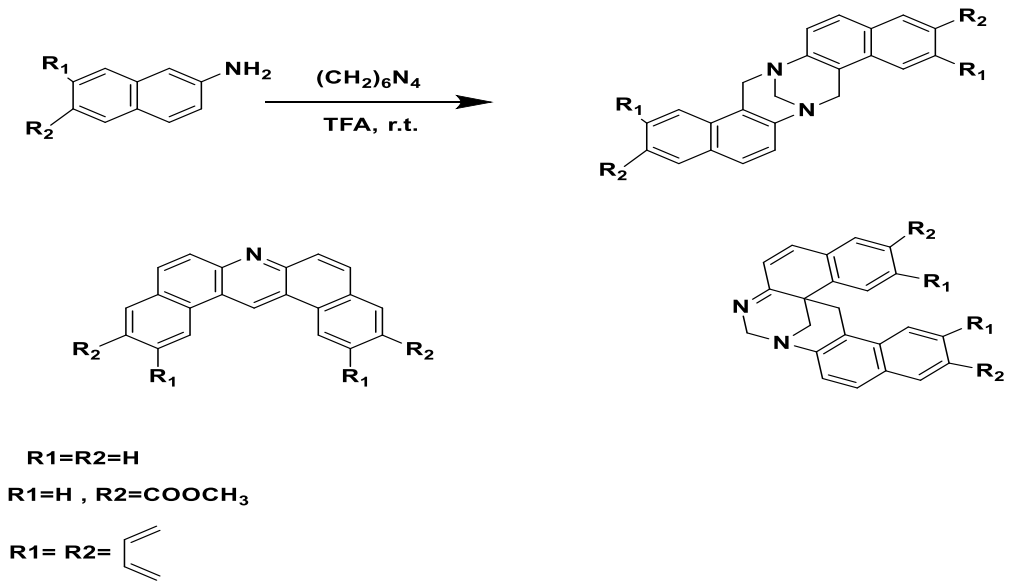
Scheme(1-11):- Synthesized 4,10-disubsituted Troger's base

In 2009, Masoud Faroughi[27] *et al.* showed a new method of preparing mono (and, or di) halo-Tröger's base from interaction of TB-substituted with N-Bromosuccinimide (NBS) or N-chlorosuccinimide (NCS) in the existence of NH_4NO_3 see eq.(1-8).



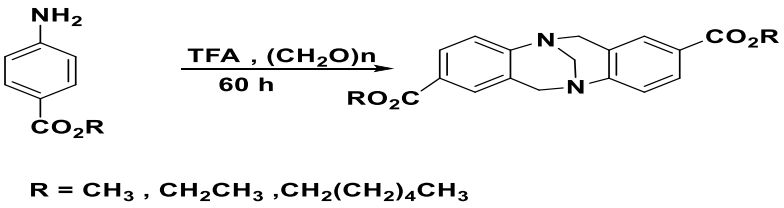
eq.(1-8):- Preparation of mono (and / or di) halo-Tröger's base

Ameneh Tatar [28] *et al.* in 2010 were able to prepare derivatives-TB and side products from 2-Naphthylamine, 6-amino-2-naphthoic acid methylester, and 2-anthrylamine with 1,3,5,7-tetraazaadamantane (HMTA) in CF_3COOH, as shown in eq.(1-9).



eq.(1-9): Prepare derivatives-TB and side product

TB-analogues that contain a 2, 8- diester were prepared by M. Delower H. Bhuiyan[29] *et al.* in 2010, the yield of this reaction was very good, and synthesized the 1,7-, 2,8- , 3,9- and 4,10- diester TB-analogues. Also, They synthesized some compounds for Troger's base analogs from aniline that lack a substitution in the Para sites as shown in eq.(1-10).



eq.(1-10):- Synthesized the 2,8-di ester-TB

The structure below shows forms of compounds that have been synthesized in this reaction

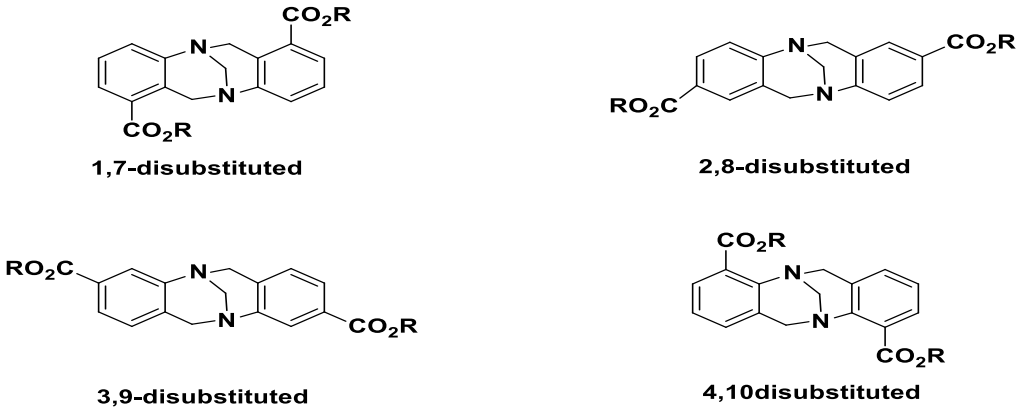
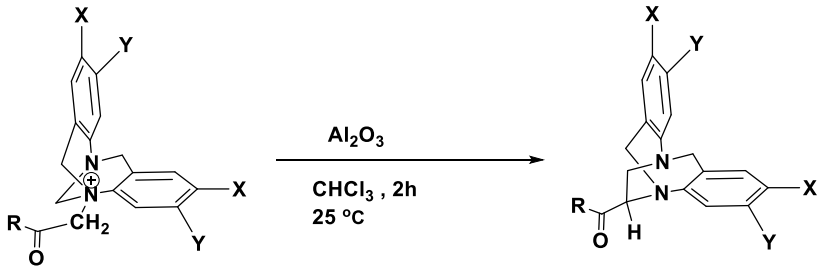


Figure (1-4):- The four potential homologs diester TB-analogues

Selective synthesized the T'B derivative which ethane-bridge substitutes methane-bridge substituted, by Christophe Michon[30] *et al* (in 2010).They used easy method of alkylation and reordered through two-step for produce product high selective as shown in eq.(1-11).

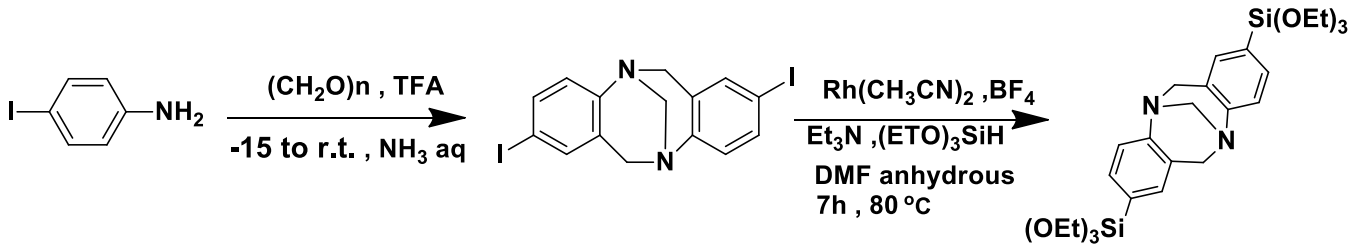


X=Me , Y=H , R =C6H4-*p*-Me
X=Me , Y=H , R =C6H4-*p*-OMe
X=Me , Y=H , R =C6H4-*p*-F
X=Me , Y=H , R =C6H4-*p*-Br
X=OMe , Y=OMe , R =Ph

eq.(1-11) :- Synthesis of ethano-TB

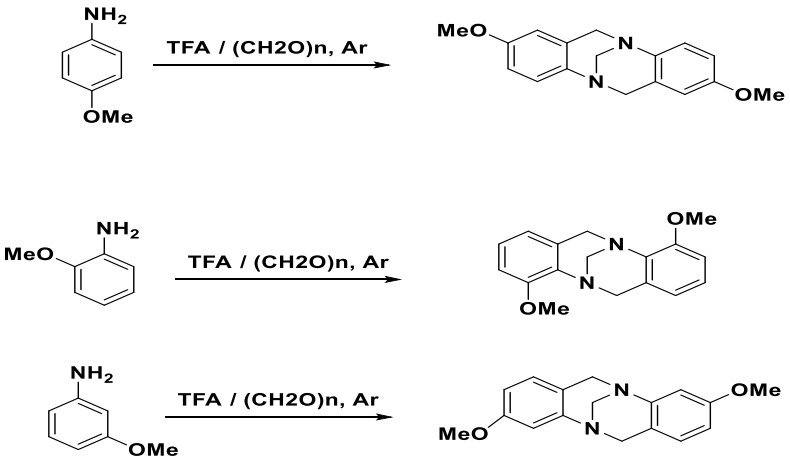
For the first time, Tröger's base units have been covalently integrated into organosilica structure by Evelyne Poli[31] *et al.* (in 2011). The construction was prepared from TB which was prepared earlier. Three substances crossbred have Nano build were prepared by various methods (a) fixation of

the TB on earlier prepared silica by post-synthesized grafting (b)combine the TB pieces into the hard and tidy repeated porosity organosilica with hexagonal structure by se1f assembling method and(c)employ F^- as a catalyst for sol-gel synthesized in the no presence of structural guidance factors as shown in a Scheme(1-12).



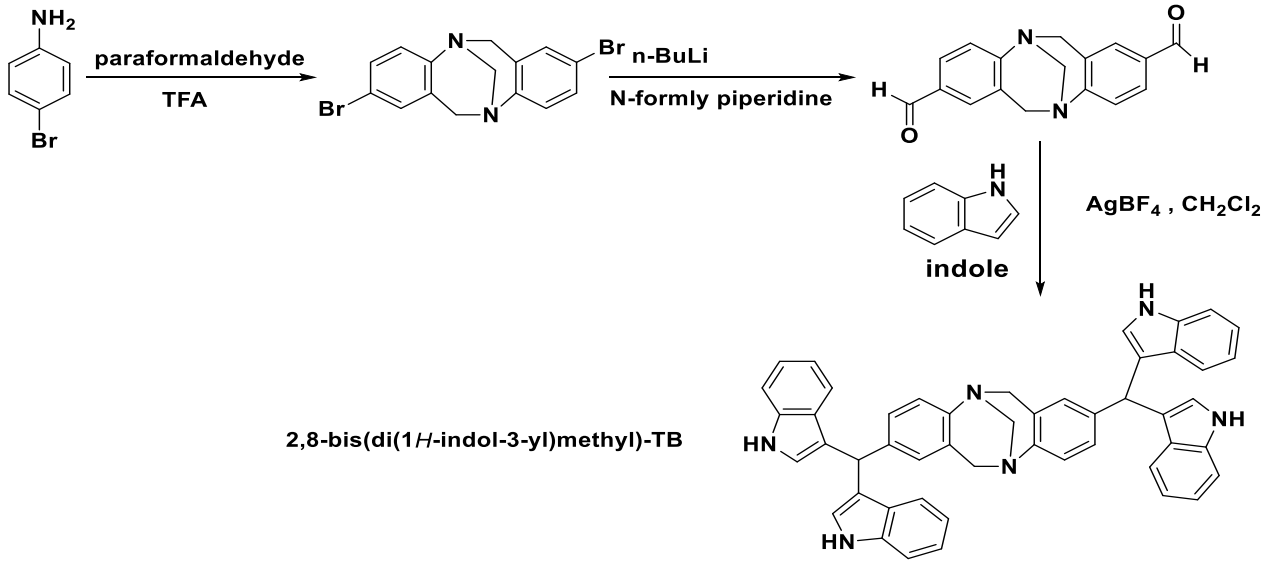
Scheme(1-12):- Synthesis of the di-iodo Troger's base and di-silylated

Proved Qasim M. Malik[32] *et al* in 2011, stated that Troger's base analogues can be synthesis containing -OCH_3 group in the 1,7-, 3,9- or 4,10- site, from reaction para-methoxyaniline with formaldehyde eq.(1-12). These molecules were turned into their dihydroxy analogues when handled with borontribromide. The 4,10-dihydroxy Tröger's base was synthesis direct from para-hydroxyaniline.



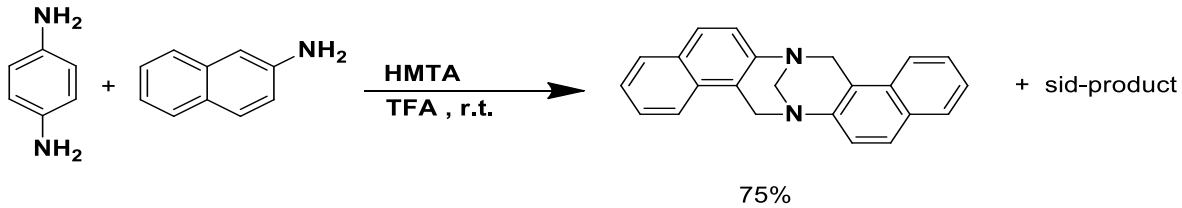
eq.(1-12):- Synthesis of Troger's base analogues containing -OCH_3

A method with high-affinity rates, easy treatment, and clean interaction, making it proffer for synthesized of bis (indoly) methane compounds was founded by Ajam C. Shaikh and Chinpiao Chen (in 2011). It can prepare the 2,8-bis(di(1H-indol-3-yl)methyl)-TB from reaction dialdehyde with indole and $AgBF_4$ in CH_2Cl_2 as shown in Scheme (1-13).[33]



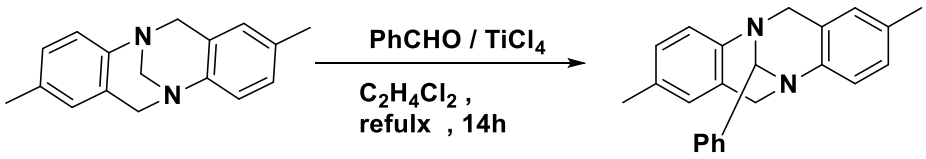
Scheme (1-13):- Prepared the 2,8-bis(di(1*H*-indol-3-yl)methyl)-TB

Bohumil Dolensky *et al.* (in 2012) explained synthesis of naphthalene tris-Tröger's base by reaction of naphthalene with benzene-1,4-diamine and $(CH_2)_6N_4$ (HMTA) in CF_3COOH at 25°C as shown in eq.(1-13). The method can be considered easy and cheap but the interaction produces side products.[34]



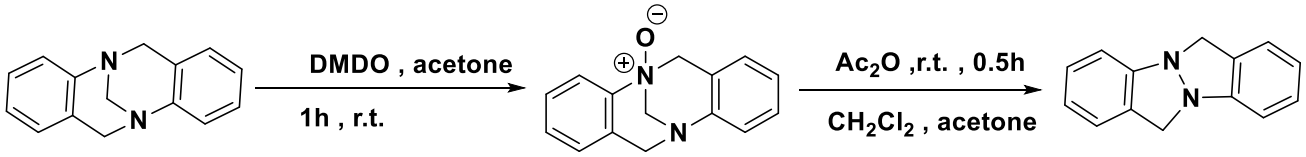
eq.(1-13) : - Synthesis of naphthalene tris-TB

Mariappan Periasamy[35] *et al.* in 2012 improved a method to prepare new Tröger's base derivatives by interchanging interaction bridge-TB with benzenecarbaldehyde in the existence of Titanium tetrachloride ($TiCl_4$) under refluxing ethylene dichloride produce the Tröger's base replaced at the bridge site, as a eq.(1-14).



eq.(1-14):- Interaction bridge-TB

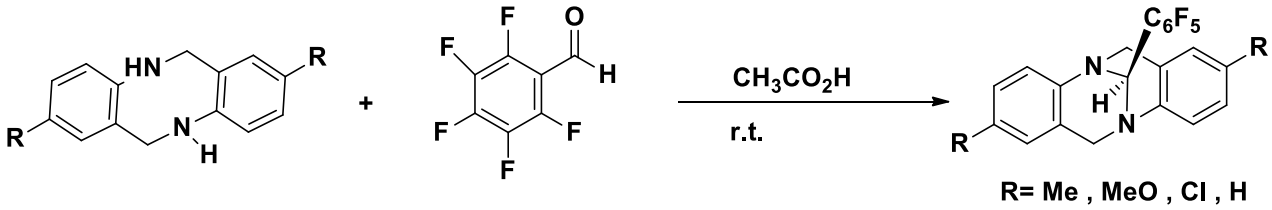
Xuefeng Gao[36] *et al.* (in 2012) developed a method to oxidative some TB compounds and then transformation into hydrazine by the interaction of TB with 3,3-dimethyldioxirane DMDO at 25°C for one hour in propane-2-one. This reaction results in a mono N-oxide, which reacts with acetyl acetate $(CH_3CO)_2O$ in CH_2Cl_2 see Scheme (1-14).



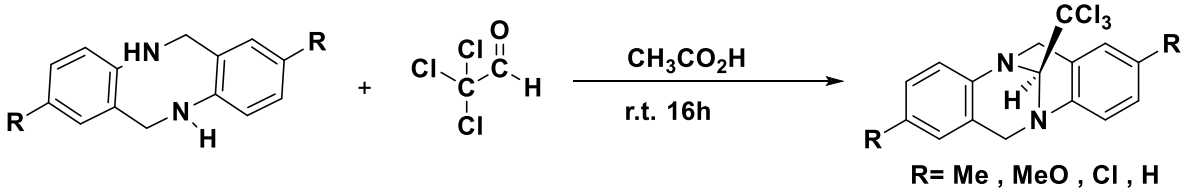
Scheme (1-14):- Oxidative TB compounds and then transformation into hydrazines

Many catalysts have been created from the detection of olefin metathesis processes. However, those dependent on Ruthenium and N-heterocyc1ic carbenes (NHC) 1igands are especially effective. Created of NHC progenitors generated from Tröger's base and its analogues by Eric Musengimana and Claver Fatakanwa[37] in 2013, which can be used to make new metathesis catalysts. Diazocine-TB reacts with pentafluorobenzaldehyde (C_6F_5CHO) in the presence of acetic acid at 25°C as a eq.(1-15), that can be

trichloroacetaldehyde (Cl_3CCHO) and used in place of pentafluorobenzaldehyde as shown in eq.(1-16).

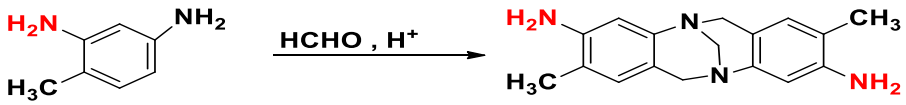


eq.(1-15):- Synthesis of C_6F_5- adduct of TB and its analogues

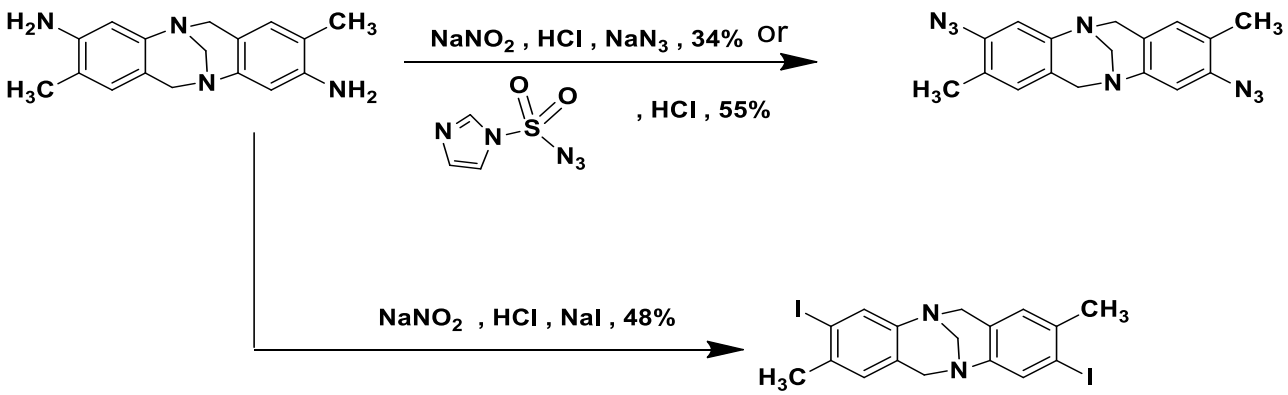


eq.(1-16):- Synthesis of Cl_3C-adduct of TB and its analogues

After nearly 100 years later, Stephan Rigo[38] *et al.* (in 2013) re-prepared (see eq.(1-17) and proved the structure of Hünlich's base which was similar to the Tröger's base, that by NMR and x-ray diffraction, as can conversion the Hünlich's base directly into symmetric di-azido and di-iodo see eq.(1-18).

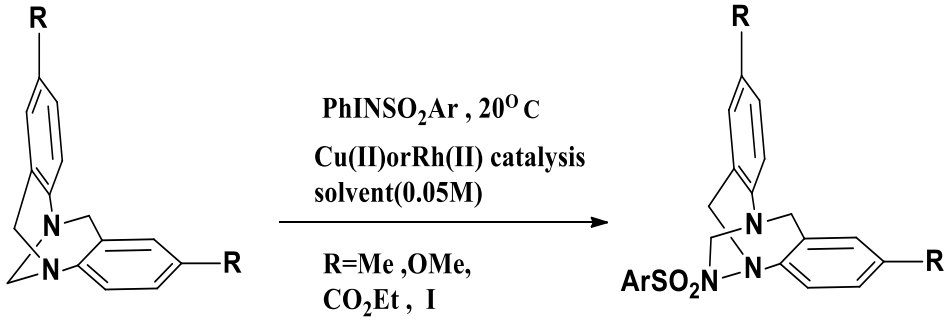


eq.(1-17):- Prepare Hünlich's base



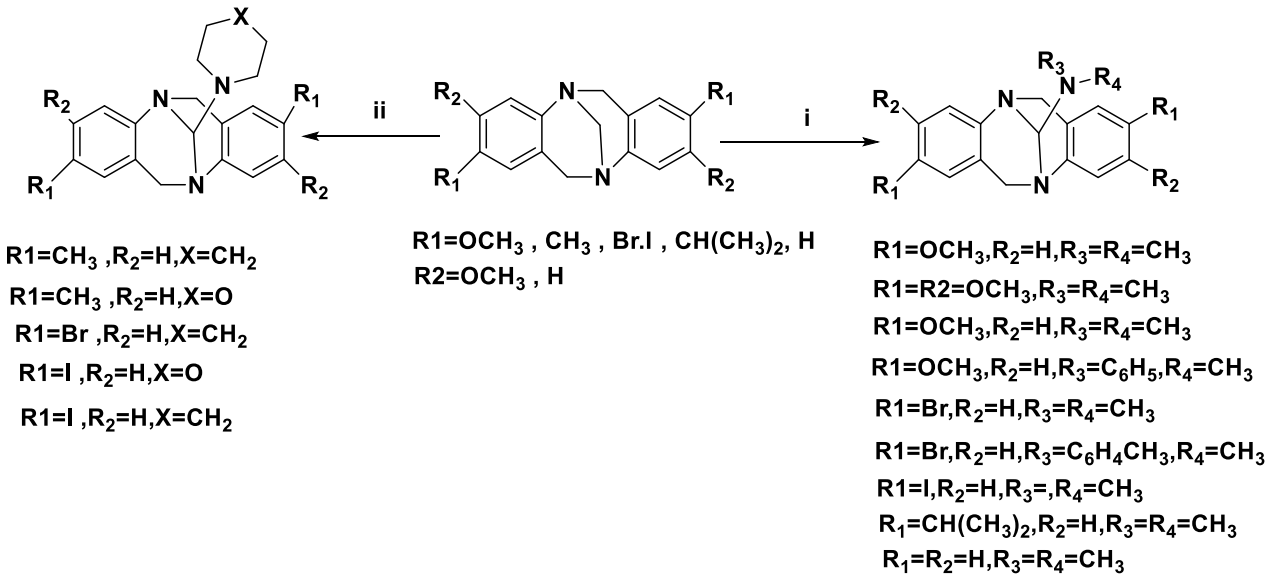
eq.(1-18):- Conversion of the Hünlich's base

The nitrene group was directly entered into carbon-nitrogen bonds by Sandip A. Pujari[39] *et al.* (in 2013) when reaction bridge-TB with $PhINSO_2Ar$ in Cu and diRhodium as catalyst as a eq.(1-19).

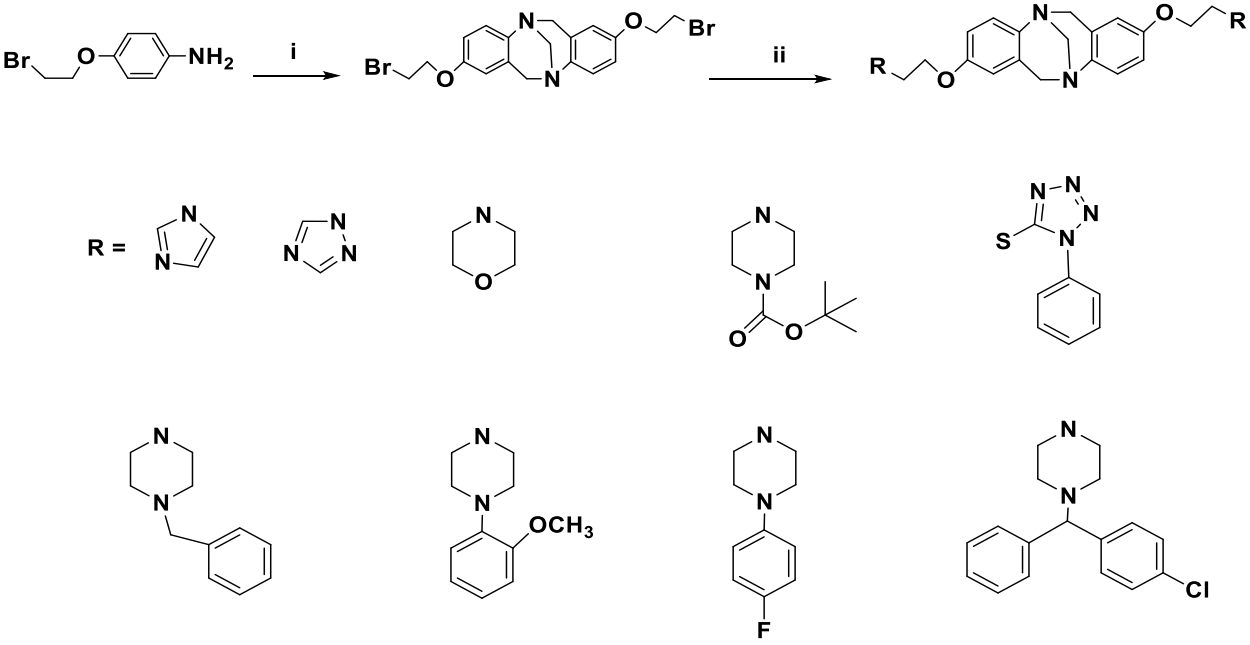


eq.(1-19):- Reaction bridge-TB with $PhINSO_2Ar$

Bhaskar Reddy Manda[40] *et al.* in 2014 synthesized some anti-cancer compounds derived from Tröger's base through the reaction of bridge methylene see Scheme 1-15) as well as a benzene ring see Scheme (1-16).



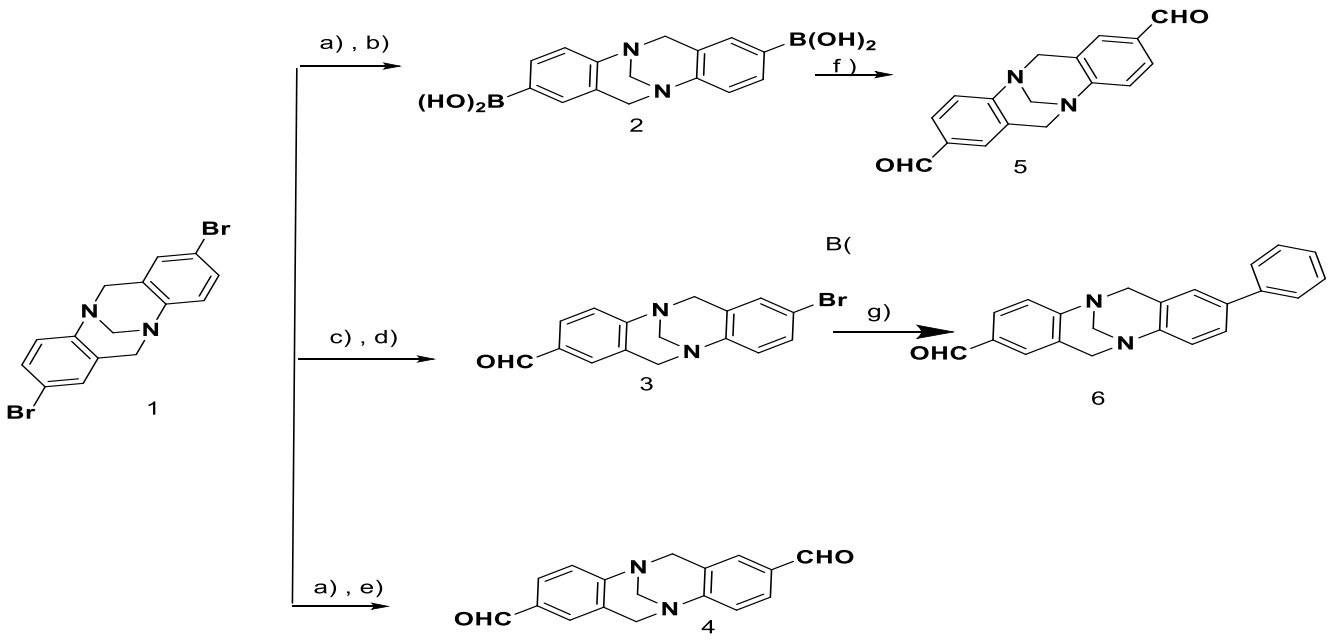
Scheme 1-15):- Reaction methylene bridged TB- analogues. interaction condition : (i) Dimethylformamide ,phosphorus pentachloride , 0° C to room temperature , 2-6 h ; (ii) heterocyclic fomamide , phosphorus trichloride , room temperature , 4-6 h.



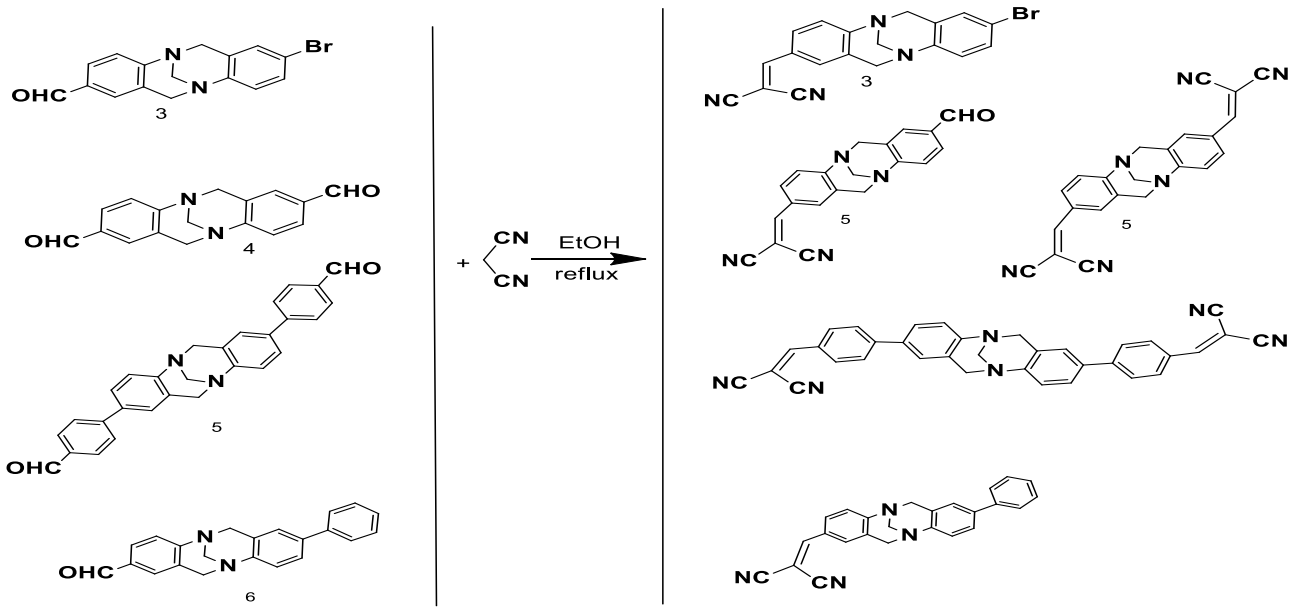
Scheme (1-16):- Reaction of TB-analogues , Terms of reaction :(i) CH_2O solution, HCl , ethanol ,0° C to room temperature , 24 h ; (ii) RH , potassium carbonate , Acetonitrile , reflux , 24h

Yan-Huan Chu [41] *et al.* in 2015 proved that under the supervision of theoretical calculations 2,2-dicyanovinyl was inserted into the Tröger's base

(TB) skeletal to produce numerous new variants with expected good solid-state luminosity. Their optical properties revealed that they showed normal accumulation emissions behavior in the solid state, which is nearly undetectable in solution but extremely luminous (500–550 nm, yellow-green light). Scheme (1-17) and Scheme (1-18) show the method of synthesizing dicyanovinyl-TB.

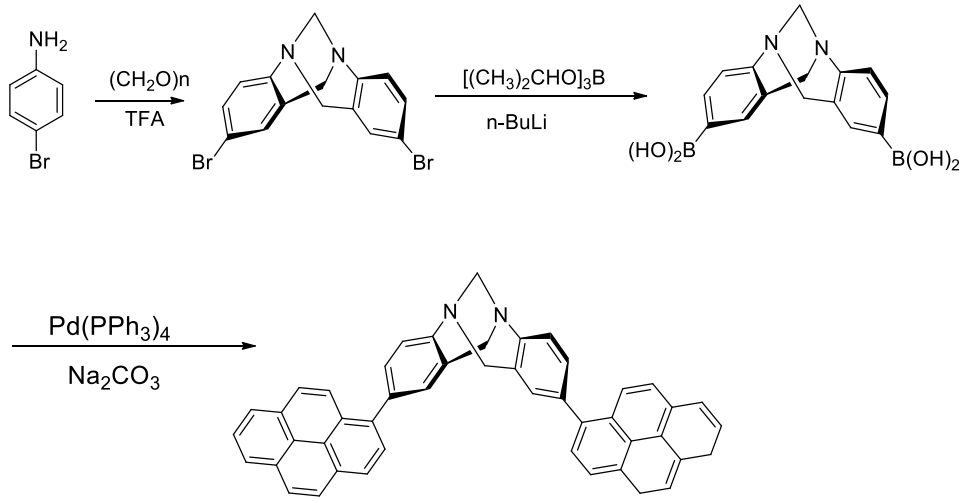


Scheme (1-17) : Synthetic routines for compounds 3–6. Reagents and conditions: (a) n-BuLi, THF, 78 C, 1.5 h; (b) (CH3O)3B, 78°C⟶ rt, 2 min; (c) n-BuLi, THF/Et2O = 1:3, 78 C, 1.5 h; (d) DMF, 78 C–rt, 10 min; (e) DMF, 78 C to rt, 2 min; (f) q-iodobenzaldehyde Pd(PPh3)4,2MK2CO3, toluene, 110 C; (g) PhB(OH)2, Pd(PPh3)4,2MK2CO3, toluene, 110°C



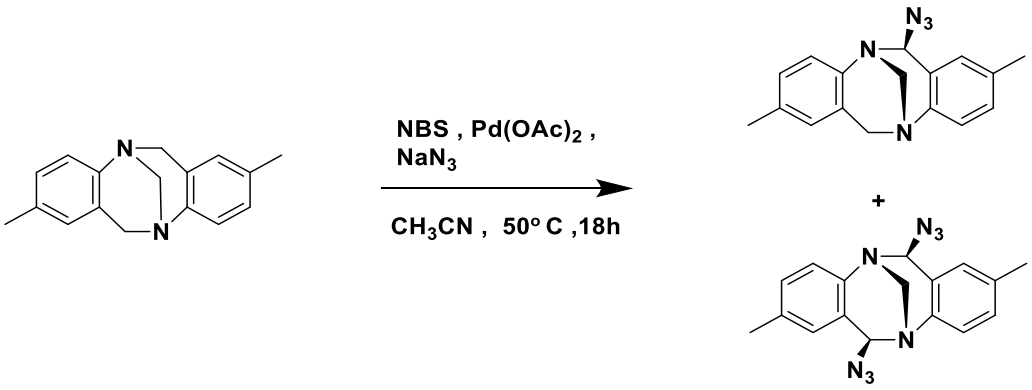
Scheme (1-18):- Inserted 2,2-dicyanovinyl in TB

A new benzo(def)phenanthrene (Pyrene) derivative for Troger's base has been prepared by Zuo-Qin Liang[42] *et al.*(in 2014) by using Zuzuki reaction .First, they prepared TB then they added Boron isopropoxide $[(CH_3)_2CHO]_3B$ and n-BuLi in tetrahydrofuran (THF) to produce TB-borate. This compound, interaction pyrene bromide in the existence of tetrakis(triphenyl phosphine) palladium as a catalyst to afford pyrene-TB as shown in Scheme (1-19).

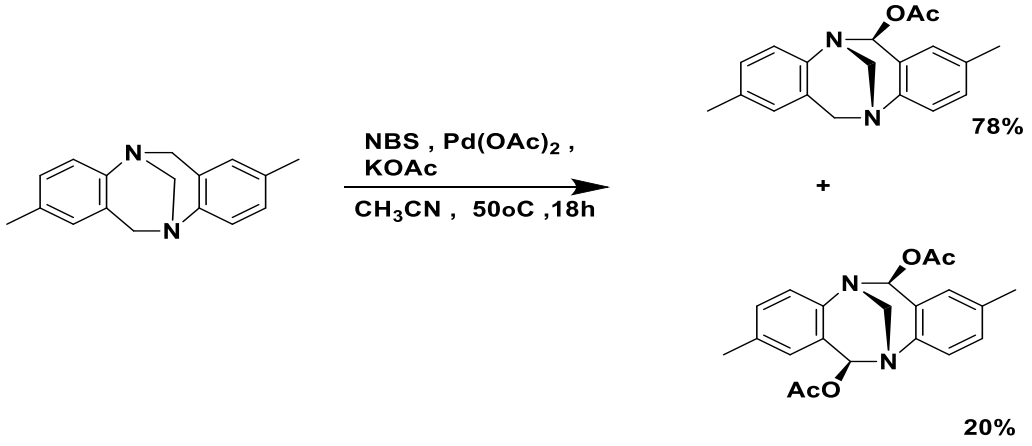


Scheme (1-19):- (Pyrene) derivative for Troger's base

Usually, oxygen or nitrogen is introduced into organic molecules by forming an active intermediate compound, but Raul Pereira[43] *et al.* (in 2016) developed a direct method for introducing these elements on the TB using N-Bromosuccinimide (NBS) and bis(acetate)palladium $Pd(CH_3COO)_2$. This process is axial on NBS to oxidation of the adjacent carbon atom for nitrogen atom in the existence of $Pd(CH_3COO)_2$ then react with nucleophiles like Potassium acetate (KOAc) or Sodium azide (NaN_3) eq.(1-20) and eq.(1-21).



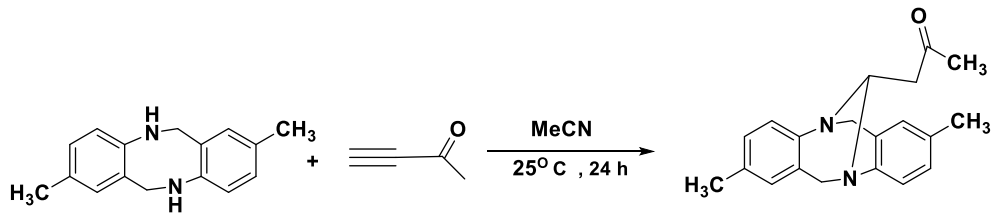
eq.(1-20):- Azidation of adjacent carbon atom for nitrogen atom in TB



eq.(1-21):- Acetoxylation of adjacent carbon atom for nitrogen atom in TB

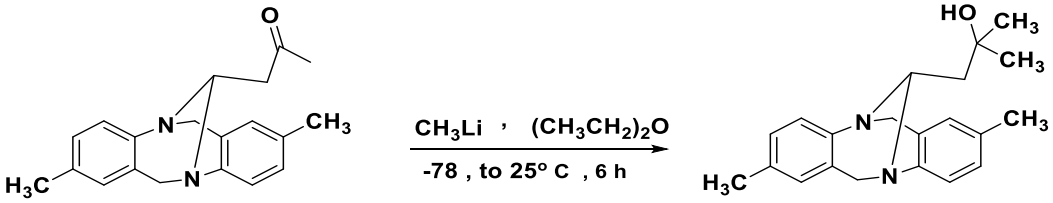
Takuya Kamiyama[44] *et al.* in 2016 prepared TB-analogues from (dibenzo-diazocine) with 3-butyn-2-one in the existence 0f an Acetonitrile at 25° C

and 24h. The product can interact with CH_3Li and ethoxyethane to convert the carbonyl group into a hydroxyl group as shown in eq.(1-22) and eq.(1-23).



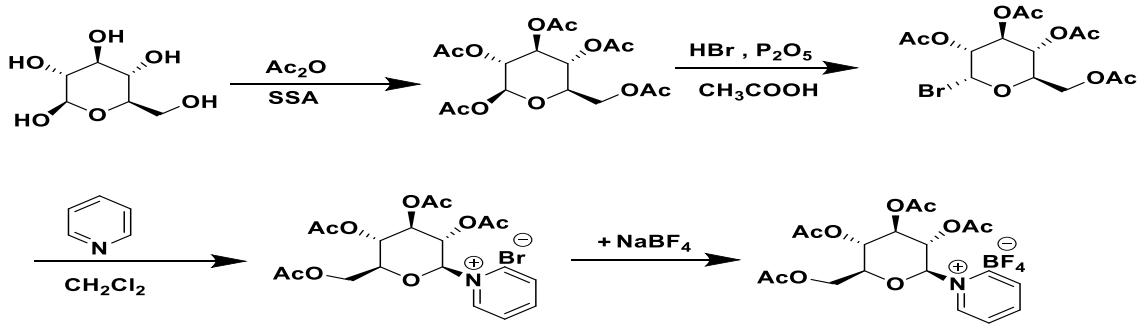
2,8-dimethyl-5,6,11,12-tetrahydrodibenzo[*b*,*f*][1,5]diazocine

eq.(1-22):- Synthesis of 1-(2,8-dimethyl-TB)-propan-2-one

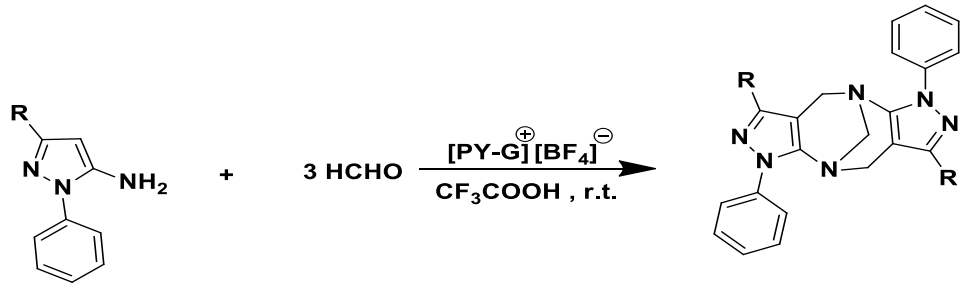


eq.(1-23):- Interaction of 1-(TB)-propan-2-one

Rui Yuan[45] *et al.* (2017) synthesized TB-analogues by a new method to obtain the product in one stride with high selectivity. The first step prepared [pyridinium-G]$^+$[BF_4]$^-$ as shown in the Scheme (1-20), and the second step used the product [pyridinium-G]$^+$[BF_4]$^-$ to make interaction with pyrazole derivatives and HCHO in CF_3COOH as the catalyst for the synthesis of TB-analogues as shown in eq.(1-24).



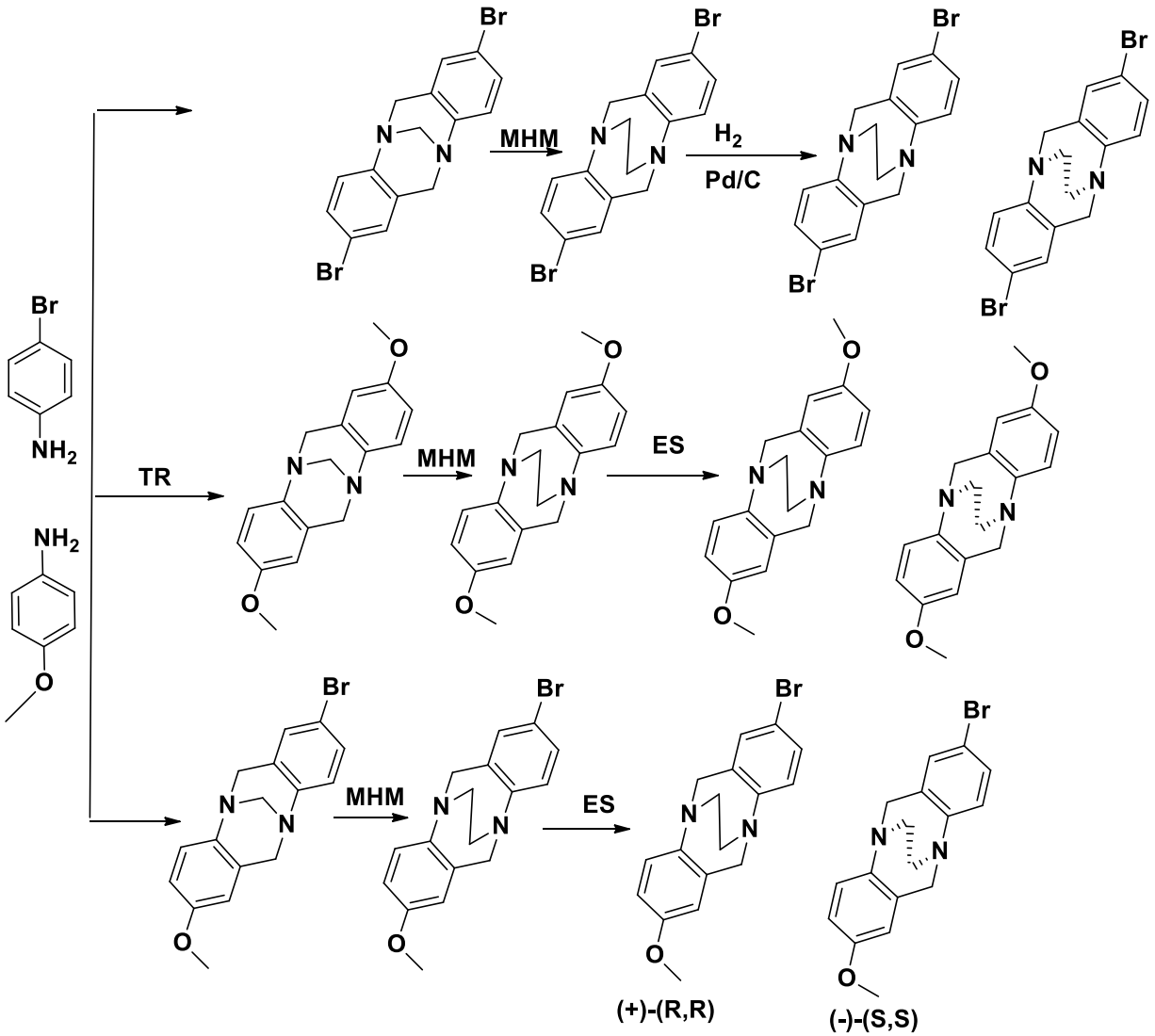
Scheme (1-20):- Synthesized of [pyridinium-G]$^+$[BF_4]$^-$



R = CH_3 , *p*-MePh , *p*-OMePh , Ph , *p*-ClPh

eq.(1-24):- Synthesized of TB-analogues

Masoud Kazem-Rostami[46] in 2020 developed the production method of Troger's base that contains ethylene bridged to increase the rate of yield from the reaction.in addition, produced two useful products, using hybridization method, as the following as shown in Scheme (1-21).



TR= Trogeration reaction
MHM = $C_2H_4Br_2$ and Li_2CO_3 in DMF , at 110 °C
ES = enantioseparation with dibenzoyl tartaric acid in dry CH_3CN or $(CH_3)_2CO$

Scheme (1-21):- Formation of analogues TB

1.2. Diamine

An organic compound with precisely two amino groups is called a diamine. Polyamides, polyimides, and poly urea are all made with diamines as monomers. Due to the fact that primary diamines are the most active, the term diamine is typically used to refer to them.[47] The most significant product is Hexamethylenediamine a precursor to Nylon (6-6), which is followed by ethylenediamine.[48] Many biological substances contain adjacent diamines (1,2-diamines), which are employed as ligands in coordination chemistry.[49]

1.3. Dicarboxylic acid

The organic molecule dicarboxylic acid has two carboxyl functional sites (COOH). HCOORCOOH is the typical molecular formula, where R might be aliphatic or aromatic. In general, dicarboxylic acids and monocarboxylic acids have similar chemical activities and reactivity.[50] Dicarboxylic acids are often employed as a source of active medicinal components and additions, as well as copolymers such as polyamides and polyesters. Adipic acid, which is a predecessor in the manufacturing of nylon, is the most extensively utilized dicarboxylic acid in the industry. Aspartic acid and glutamic acid, two amino acids found in the human body, are examples of dicarboxylic acids.[51] Dicarboxylic acids are major water-soluble components, and their name can be abbreviated to diacid. If succinic, adipic, or glutaric acid is inhaled, eaten, or absorbed via the skin, it can be hazardous. Each of these substances, alone or in conjunction, has no mutagenic properties.[52] Dicarboxylic acids are solids at room temperature and also have greater melting temperatures than monocarboxylic acids with much

the same number of carbon atoms, owing to stronger intermolecular interactions, primarily due to the formation of hydrogen bonds.[53]

1.4. Amides from Dicarboxylic Acids

Monoamides are formed when only one COOH group is exchanged by CONH2, diamides are created when both carboxyl groups are turned into primary amides, and imides are cyclic secondary amides created when two OH groups from the carboxyls are exchanged with one bidentate NH group. When the development of a stable cycle is possible, typical thermal degradation of monoamides of dicarboxylic acids produces either amides or anhydrides, based on the structure of materials.[54] Dicarboxylic acids are significant precursors in the production of various polymers, plasticizers, lubricants, as well as other functional fluids. They are produced by direct carboxylation of unsaturated fatty acids.[55] Long-chain dibasic acids have a high solubility in organic solvents and a moisture content resistance, making them perfect for use in some polymers. Polyamides, polyesters, and alkyd resins have all been produced as condensation polymers.[56]

1.5. Polymers

Two terms make up the polymer. The first term in the word polymer is poly, which means multiple, and the second term is mer, which means part, therefore polymer means multiple parts.[57] The polymerization process transforms monomers into polymers. To form a polymer, the monomers are tightly bound together.[58, 59] Polymers are big molecules with a high molar mass that are created by linking together a large number of tiny molecules known as monomers to form lengthy chains.[60] It can be found in a wide range of items and commodities that are used on a daily basis. The term polymer refers to a large molecule with a high molecular weight that is

made up of numerous structural units that are usually held together by covalent connections.[61] The monomer is a Latin term with two meanings, the first of which is mono, that means one, and the other of which is a portion. Monomers are tiny molecules made up of atoms that join together to form polymers during the polymerization process.[62]

Polymers differ in terms of the type of polymer, the forces of attraction within the chain, the nature of the structure of the chains in the polymer, and the number of monomers.[63] Polymers have characteristics such as easy to create, rusting, acidity, and base resistance, electrically and thermally isolating, inexpensive and it has a low density.[64] Polymers can be classified according to their source: axial normal, natural polymers, and industrial.[65]

1.6. Synthesis of Polymers

1.6.1. Addition Method

A polymer that is generated via simple linkage of monomers without the co-generation of additional products is known as an addition polymer. Condensation polymerization produces products, in general water, whereas addition polymerization does not.[66] Chain polymerization, where the polymer is produced by a chain reaction, where monomer units are consecutively added to an active position, or multi-add, where the polymer is created by addition interaction between kinds of diverse degrees of polymerization, there are two ways to make addition polymers. By frequently adding some simple monomer units, additional polymers are produced. Polymers are unsaturated compounds such as olefins, alkaline, and so on. The free radical pathway is primarily responsible for addition polymerization. The three steps of the free radical mechanism of addition

polymerization are: (1) Initiation of Free Radical (2) Propagation of Free Radical, and (3) Termination of Free Radical.[67]

1.6.2. Condensation method

The polymer is made by polymerizing one or even more kinds of monomers with two or more active groups in each monomer. The polyester polymer which is used in the creation of synthetic yarn for clothes is an example of a polymer generated using the condensation polymerization process.[68] Polymers are established by reaction of condensation in which molecular structures bind to each other, and tiny molecules, such as water or methanol, are lost as by-products, rather than additional polymers containing unsaturated monomer reactions. Condensation polymerization is a type of polymerization.[69] Growth happens step by step, and two molecules are bound together in the process for each other, the end results in the minor loss particles that are always water, the kind of compound formed by condensation polymerization depends on the presence of monomers that do not close the growth chain with a single functional group (functional group) and are therefore of lower molecular weight than the final compounds.By using monomers comprising two-terminal functional groups, linear polymers are built and monomers consisting of in excess of two-terminal three-dimensional polymers are created by combining groups to form a cross-linked structure network, and include condensation polymers on polyamide, polyacetylate, and proteins.[70]

1.7. Polyamides

A polymer with amide bonds (NH-CO) is considered as a repeating unit. Polyamides are found both naturally and synthetically. Polyamides are naturally occurring and are found in proteins such as wool and silk.[71] Artificial polyamides, such as nylons, can be made by step-growth polymerization or solid-phase synthesis, aramids, and sodium polyamides (aspartate) due to their high elasticity and vigor, Synthesized polyamides are usually employed in textiles, the car industry, and other applications. The conveyance industrialization sector is the primary producer of polyamide, accounting for 34% of overall consumption fibers.[72] Aromatic polyamides are known for their high thermal and chemical resistance, as we1l as their high strength and modulus.[71, 73] Polyamides are used in the manufacturing of bedding, carpets, curtains, and upholstery. Truck and aircraft tires, seat belts, parachutes, cables, nets, sleeping bags, tarpaulins, tents, sewing thread, ropes, monofilament fishing string, and dental floss are some of the other specialized uses. Polyamide fibers are often chosen for their high vigor, solidity, and corrosion impedance in a variety of military applications.[74]

1.7.1. Classification

Polypeptides, often known as proteins, are polymers made up of amino acids. Synthetic polyamides are graded based on the structure of their main chain, as shown in (Table 1-1).[75]

Table 1-1:Classification of polyamide and some Examples

type of polyamide	Main chain	Examples of polyamides
Aliphatic polyamides	Aliphatic	Nylon66
polyphthalamides	Semiaromatic	PA6T= hexamethylenediamine + terephthalic acid
Aramids = aromatic polyamides	Aromatic	Paraphenylenediamine + terephthalic acid

In all polyamides, an amide characteristic is produced to bond two monomer molecules jointly. An equivalent combination of a diamine and a diacid, (commonly in the form of a cyclic lactam such as caprolactam)[75] each of these types of predecessors results in a homogeneous polymer. Polyamides copolymerize easily, providing for a diverse variety of monomer combinations and a large number of copolymers. Several nylon polymers are also miscible, enabling the creation of mixtures.[76] Because of their exce1lent resi1ience and hardness, synthesized polyamides are widely utilized in texti1es, the automobile sector, carpets, cooking utensi1s, and sportswear. The transportation processing industry is the largest consumer, accounting for 35% of polyamide sales. [72] Polyamides are wel1-known for their outstanding therma1 stabi1ity, chemical resistance, and tensile qualities. However, these fully aromatic polyamides have some drawbacks and limits, such as extremely high melting points and limited solubility in typical organic solvents. None of them melt before decomposition due to their hardness and firmness. Intermolecular attraction's potency. As a result of the aforementioned properties, processing issues and implementation flaws develop. To solve these challenges and lessen the chain interaction and stiffness nature of the polymer, versatile units such as NHCO, -O-, CH_2, and

SO_2, huge hanging substituents, and non-coplanar moieties are added into the polymer spine.[72, 77-87]

1.7.2. Aliphatic Polyamides

Aliphatic polyamides, a part of polymers created when amide groups are combined into linear alkane chains, are usually referred to as nylons.[88] The dense interchain reaction that produced from hydrogen bonding between amide groups on adjoining chains, in addition to dipole-dipole interactions, is one of the main characteristics of nylons.[89] 1,2 Nylons much like polyethylene have often been used to paradigm a weakly interacting polymer chain, paradigma crystallizable chains with strong exchange reactions can so be done with them. Furthermore, because nylons have a homologous sequence, researchers can dig deeper into the role of hydrogen bonding in mobility, hydration, chain folding, crystallization, and deformation. These experiments are significant not just because they provide new ideas, but also because nylons are one of the most important technical polymers commercially. Finally, because hydrogen bonds are the foundation of peptide bonds in proteins, these findings could be applied to proteins and other biological structures.[90]

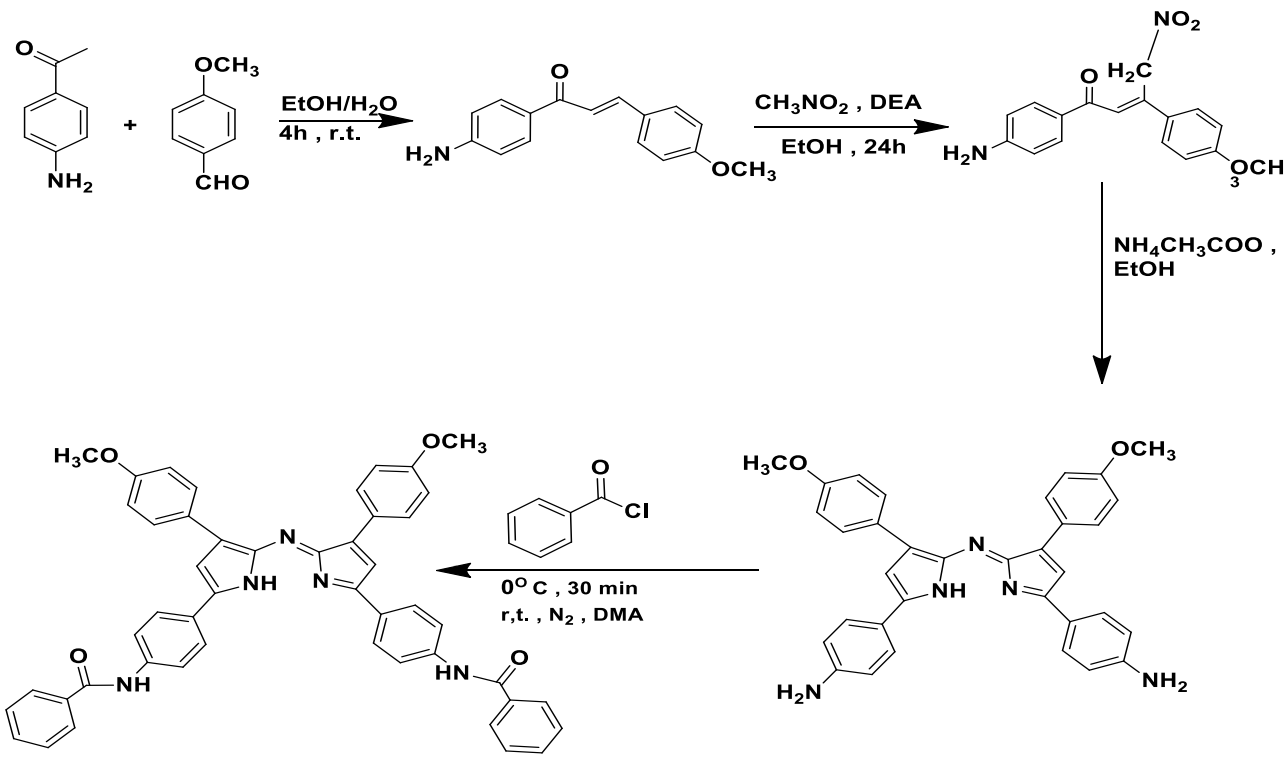
1.7.3. Aromatic Polyamides

Due to their superior thermomechanical stability, wholly aromatic polyamides (aramids) are highly-performance organic matter.[91] Because of their aromatic structure and amide connections, they have distinct features. This results in the formation of stiff rod-like macromolecular chains that interact through strong and highly directional hydrogen bonds.[92] These bonds

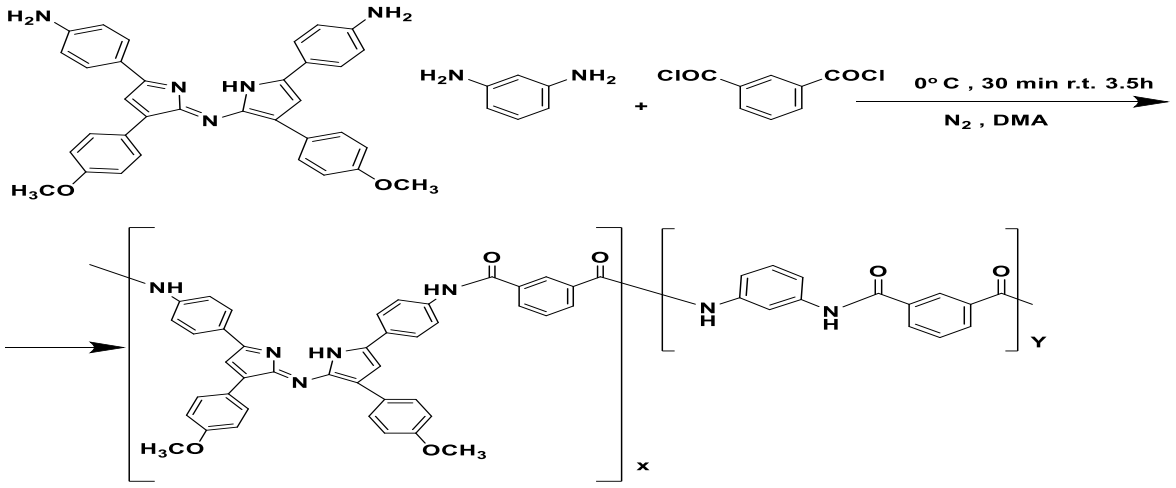
result in successful crystalline microdomains with high intermolecular packing and cohesive capacity. Poly(p-phenylene terephthalamide) and poly(m-phenylene isophthalamide), the two most popular commercial aramids are known commercial aramids, are employed in modern materials and have been converted to generate significant, flame-resistant textiles and varnishes for aviation and weapons applications Body adoration, prophylactic gear, athletic garments, electrical shielding, asbestos replacements, and industrial filters are only a few examples. Because of their chemical nature, they have exceptionally high transformation temperatures that are higher than high degradation temperatures, are only marginally solubility in normal organic solvents, and so must be transformed by solution, improve their treatment and solubility, and bring new chemical functionalities into the polyamide framework or laterally structure, research is ongoing to extend their applicability and keep them at the forefront of scientific research. Aromatic polyamides offer excellent thermomechanical qualities (impact strength tolerance), alkaline opposition, and hydrolyzing stability.[91, 93] Due to their hard spine, particularly the totally p-substituted derivative.[94] They are useful in high-performance applications and will thus satisfy the need for rigid thermo mechanical materials in the polyamides, gas isolation membranes, ion interchange membranes, and chemoresistant sweaters.[92] In reverse, osmosis applications,[95] aramid-based membranes outperform cellulose acetate and can be washed with acid and caustic solutions[94] because of their chemical and pH resistance Aromatic polyamides. On the other hand, they have low solubility and are difficult to handle, which limits their applications.[96] NomexTM and KevlarTM are the two most widely used consumer aramids. NomexTM was invented by Morgan (DuPont) in 1958 and commercialized in 1961. Kwo'lek (Du Pont) discovered KevlarTM in 1965, and in 1971, it

became commercially available. NomexTM is made by polymerizing m-phenylenediamine and isophthaloyl chloride.[94] NomexTM has a sharp melting point (400 degrees Celsius) and is highly thermally stable. Its fiber is made from a strongly polar DMF solution of lithium chloride.[95] Polymerization of various isomers, terephthaloyl chloride, and p-phenylenediamine result in KevlarTM. This purely p-substituted polyamide has a melting point of 500^{o} C, and a Tg of 300^{o} C, which is 100^{o} C higher than NomexTM. Because of its hard rod spine and intermolecular hydrogen bonding, KevlarTM is insoluble in solvent polarity such as NMP, DMAc, and DMF.[94] Including rubber substitutes, commonplace items such as parachutes, vessels, electric engines, thermoplastic tubing, and fan blades as well as cutting-edge materials include optically active materials.

A blue naturally colored fully aromatic polyamide, namely a meta-aramid, was created by copolymerizing a chromophore monomer with isophtaloyl dichloride and m-phenylendiamine by Miriam Trigo-Lopez[97] *et al*. in 2015 (as shown in Scheme (1-22 and Scheme 1-23) This particular monomer has a very high coloring efficiency. It is also designed to keep the reference aramid good mechanical and thermal properties. Surprisingly, not only has the heat resistance been maintained, but it has actually been enhanced.



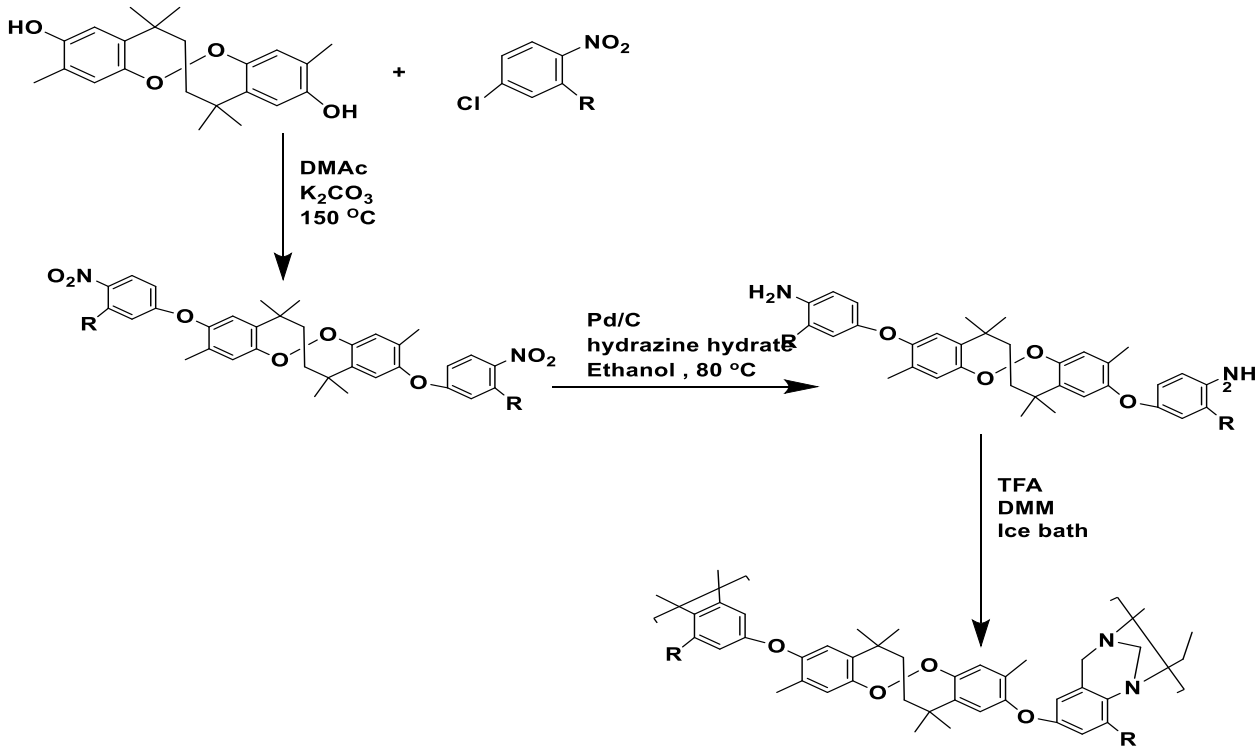
Scheme (1-22):- Synthesis of monomer



Scheme 1-23):- Synthesis of Copolyamide

Glassy polymers gas permeation efficiency can be increased by stiffening the polymer spine to reduce chain packing and increase free volume and gas

permeabilities. Polymerization of two spirobichroman-containing diamine monomers yield two Tröger's Base-based polymers by Caili Zhang[98] *et al.* in 2017 see Scheme(1-24).



Scheme(1-24):- Synthesis of Troger's base based polymers

1.8. The Aim of the Research

1. Synthesis of new Tröger's base and its derivatives
2. Synthesis of new polyamid based on Tröger's base
3. Study of spectroscopy (IR, ^{1}HNMR, ^{13}CNMR) for Tröger's base and polyamides
4. Study of crystal structure through XRD of Tröger's base.
5. Knowledge of the thermal properties of polymers by (TGA)

Chapter Two

Materials and Methods

2. Chemicals and method

2.1. Chemicals

The purity of the materials used ranges between 95% - 99%

Table 2-1: Appear Chemical Materials Manufacture

Number	Chemicals	Company
1	*p*-Aminobenzoic acid	CHD
2	*m*-Aminobenzoic acid	CHD
3	*o*-Aminobenzoic acid	CHD
4	N,N-Dimethylformamide (DMF)	CDH
5	Methanol	CDH
6	4-Amino-2-nitrobenzoic acid	CDH
7	Trifluoroacetic acid	Fluorochem
8	Dimethoxymethane	Fisher chemical
9	Ethanol	Ecochem
10	Diethylether	Riedel-denHaen
11	4,4-Diamino-3,3-dimethyldiphenylmethane	TCI
12	2,6 –Diaminotoluene	TCI
13	9,9-Bi(4-aminophenyl)flourene	TCI
14	2,4,6-Trimethyl-3--phenyldiamine	HIMEDIA
15	2,3,5,6 –Tetramethyl-1,4-phenyl diamine	HIMEDIA
16	2-Nitro-1,4-phenylenediamine	HIMEDIA
17	Anhydrous calciumchloride	Fisher
18	Triphenylphosphite (TPP)	Fisher
19	1-Methyl-2-pyrolidone (NMP)	Fisher
20	Pyridine	Fisher
21	Dimethylsulfoxide (DMSO)	CHEM – SUPPLY
22	Chloroform	Riedel-denHaen

2.2. Instrumental

1. Melting point SMP 30 Stuart [UK] at Department of Chemistry – College of Sciences for Woman –University of Babylon.

2. FTIR Spectrophotometer 8400s Shimadzu "Japan" Department of Chemistry /College of Sciences for Women / University of Babylon.

3. NMR instrument from Bruker, Swit 400 MH_2 for ^{1}HNMR & 100 MH_2 for ^{13}CNMR. With DMSO-d^6 as a solvent.

4. XRD xpert paanaltycal Philips Holland

5. Mass Instrument Specifications; Manufacturer Company: Agilent Technology (HP)

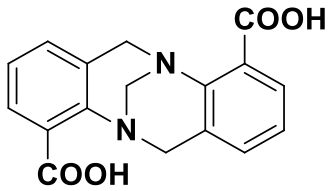
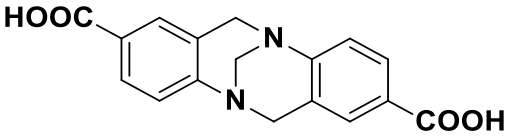
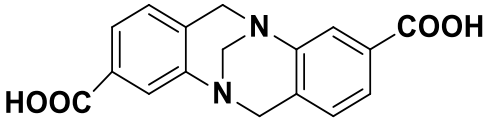
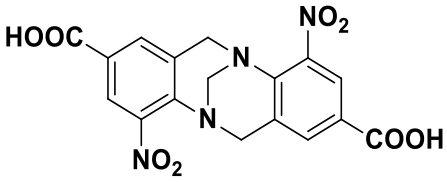
6. Oven Heating materials 2009 Binder (Germany) at Department of Chemistry /College of Sciences for Women / University of Babylon.

7. Magnetic stirrer with hotplate RH B2 IHA (Germany) at Department of Chemistry /College of Sciences for Woman / University of Babylon.

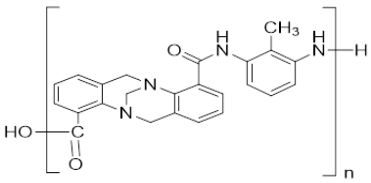
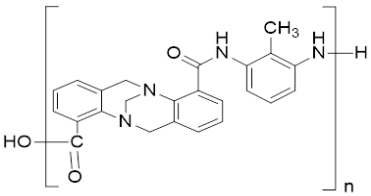
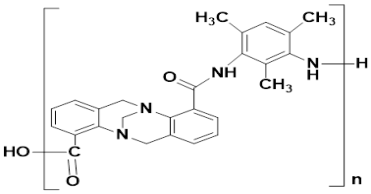
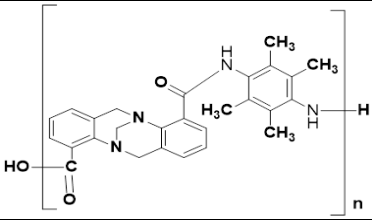
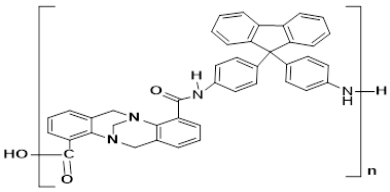
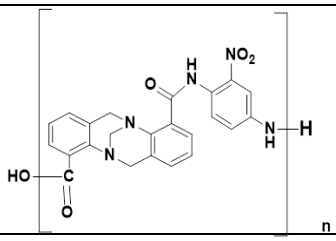
8. Vacuum pump vplls Angyl (Germany) at Department of Chemistry /College of Sciences for Women / University of Babylon.

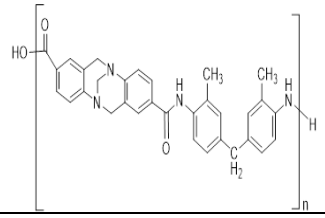
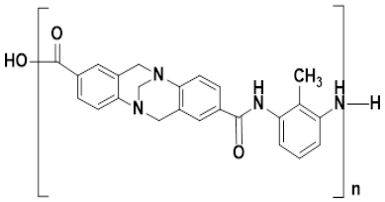
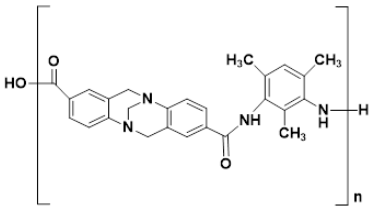
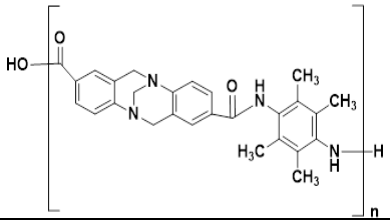
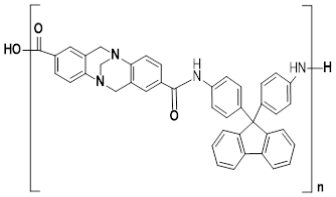
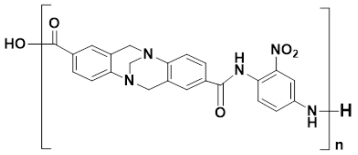
9. Differential Thermal Gravimeter DTG-60 Shimadzu (Japan) at Department of Chemistry /College of Sciences for Women / University of Babylon.

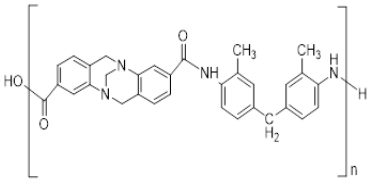
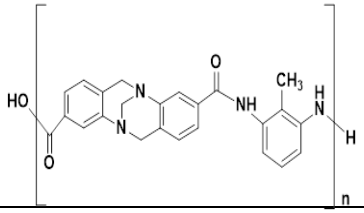
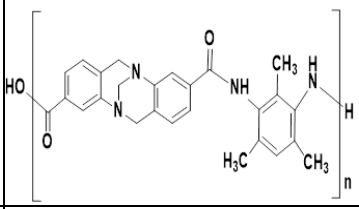
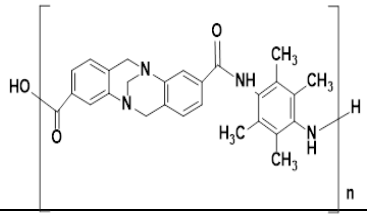
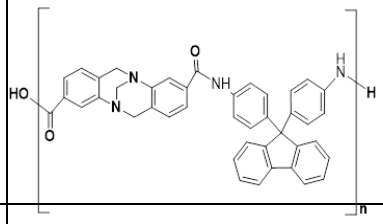
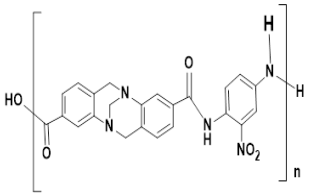
List of synthesized compounds

Number	Structure	Name	Code
1		6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-4,10-dicarboxylic acid	TB1
2		6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-2,8-dicarboxylic acid	TB2
3		6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-dicarboxylic acid	TB3
4		4,10-dinitro-6,12-dihydro 5,11-methanodibenzo [b,f] [1,5] diazocine -2 , 8 -dicarboxylic acid	TB4

List of synthesized polymers

Number	Structure	Name	Code
1		Poly(6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-4,10-dicarboxylic acid – CO- (4,4',Diamino-3,3'dimethyldiphenyl methane)	TB1O1
2		Poly (6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-4,10-dicarboxylic acid-CO- (2,6-diaminotoluene)	TB1O2
3		Poly (6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-4,10-dicarboxylic acid-CO-(2.4,6-trimethyl-m-phenylenediamine)	TB1O3
4		Poly (6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-4,10-dicarboxylic acid-CO-(2,3,5,6- tetra methyl-1,4-phenylenediamine)	TB1O4
5		Poly(6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-4,10-dicarboxylic acid-CO-(9,9- Bi(4-aminophenyl)flourene)	TB1O5
6		poly (6,12-dihydro-5,11-methanodibenzo[b,f][1,5] diazocine-4,10-dicarboxylic acid-CO-(2-Nitro-1,4-phenylenediamine))	TB1O6

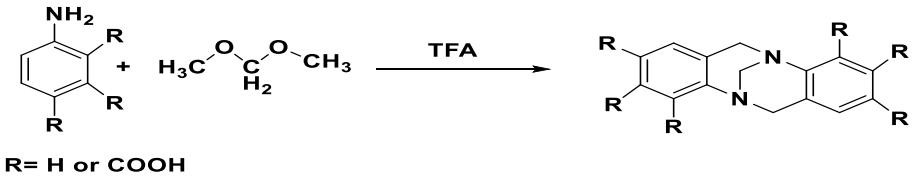
Number	Structure	Name	Code
7		Poly (6,12-dihydro-5,11-methanodibenzo[b,f][1,5] diazocine-2,8-dicarboxylic acid-CO- (4,4',Diamino-3,3'dimethyldiphenyl methane)	TB2P7
8		Poly ((6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-2,8-dicarboxylic acid-CO-(2,6-diaminotoluene))	TB2P8
9		Poly (6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-2,8-dicarboxylic acid-CO-(2.4,6-trimethyl-m-phenylene diamine)	TB2P9
10		Poly (6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-2,8-dicarboxylic acid (TB2))-CO-(2,3,5,6- tetra methyl – 1,4 –phenylene diamine)	TB2P10
11		Poly ((6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-2,8-dicarboxylic acid-CO-(9,9-Bi(4-amino phenyl)flourene))	TB2P11
12		Poly (6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-2,8-dicarboxylic acid-CO-(2-Nitro- 1,4- phenylenediamine)	TB2P12

Number	Structure	Name	Code
13		poly (6,12-dihydro-5,11-methanodibenzo[b,f][1,5] diazocine-3,9-dicarboxylic acid-CO-(4,4'-iamino-3,3'-dimethyldiphenyl methane))	TB3M13
14		poly (6,12-dihydro-5,11-methanodibenzo[b,f][1,5] diazocine-3,9-dicarboxylic acid-CO-(2,6-diaminotoluene)	TB3M14
15		poly (6,12-dihydro-5,11-methanodibenzo[b,f][1,5] diazocine-3,9-dicarboxylic acid-CO-(2.4,6-trimethyl-m-phenylenediamine)	TB3M15
16		poly (6,12-dihydro-5,11-methanodibenzo[b,f][1,5] diazocine-3,9-dicarboxylic acid-CO-(2,3,5,6-tetramethyl-1,4-phenylenediamine)	TB3M16
17		poly (6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-3,9-dicarboxylic acid-CO-(9,9-Bi(4-aminophenyl)flourene)	TB3M17
18		poly (6,12-dihydro-5,11-methanodibenzo[b,f][1,5] diazocine-3,9-dicarboxylic acid-CO-(2-Nitro-1,4-phenylenediamine)	TB3M18

2.3. Method of synthesizing monomers (Tröger's base)[6]

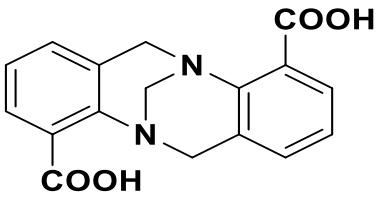
X1: General procedure for Tröger's base derivatives:

A Dimethoxymethane (DMM) (12 ml, 10.30 g, 135.366 mmol) was added to an benzoic acid derivatives (8.00 g, 58.33 mmol), then the mixture was cooled to zero centigrade. TFA was added drop by drop to the mixture, then allow the mixture to be stirred at room temperature for 72 h, then, washed with water, and collected by filter paper. The resulting materials were dried in an electric drying oven. Then was wish by hot ethanol and recrystallized by diethylether.



eq.(2-1): General synthesis of Troger's base

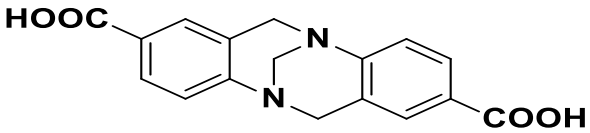
2.3.1. Synthesis of 6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-4,10-dicarboxylic acid (TB1)



Structure 2-1:6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-4,10-dicarboxylic acid

General procedure (X1) followed by ***o*-Aminobenzoic acid** (1eq), DMM(2.5 eq), and trifluoroacetic acid (35 ml) to give (12.00 g, 66.29 %) as a yellow powder. M.p = 186-189° C.

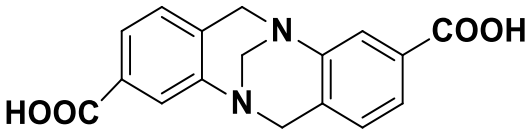
2.3.2. Synthesis of 6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-2,8-dicarboxylic acid (TB2)



Structure 2-2: **6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-2,8-dicarboxylic acid**

General procedure X1 followed by ***p*-Aminobenzoic acid**(1eq) , DMM(2eq) and triflouroacetic acid (35 ml) to give (11.00 g, 60.76 %) as a pink powder. M.p = 230 - 233°C.

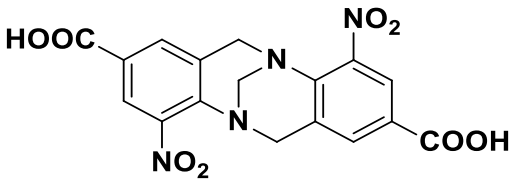
2.3.3. Synthesis of 6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-dicarboxylic acid (TB3)



Structure 2-3: **6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-dicarboxylic acid**

General procedure (X1) followed by **m-Aminobenzoic acid**(1eq) , DMM(2eq) and trifluoroacetic acid (35 ml) to give (10.6 g, 58.56 %) as a red powder. M.p = 91-94^{o} C.

2.3.4. Synthesis of 4,10-dinitro-6,12-dihydro-5,11- methanodibenzo [b,f] [1,5] diazocine-2,8-dicarboxylic acid (TB4)



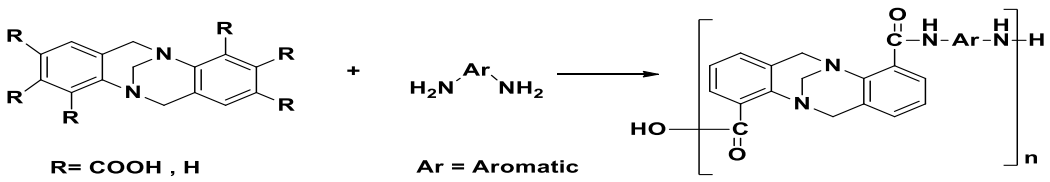
Structure 2-4: 4,10-dinitro-6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-2,8-dicarboxylic acid

General procedure X1 followed by 4-Amino-2-nitrobenzoic acid (2.00 g, 10.98 mmol), DMM (4 ml, 3.43 g, 45.172 mmol), and TFA (40 ml) to afforded (1.5g, 34.15 %) as a yellow powder, M.p = 159-161° C.

2.4. Method of synthesizing for polyamides[5]

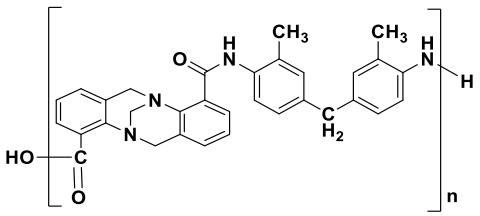
X2: General procedure for polyamides

The polyamides can be prepared by mixing Tröger's base monomer (1 equivalent) with diamine monomer (1equivalent), (2ml) from triphenylphosphite, (1 ml) from pyridine, (3ml) from 1-methyl-2-pyrolidone (NMP) and (0.5 g) from anhydrous calcium chloride, then the mixture is moved by magnetic stirrer and reflexed for 72 h at 110-120^{o} C. After polymerization, the polymer was purified by reflexed with ethanol then the product was thawed in DMSO then precipitate by methanol after that produce powder polymer dry, as in the following general equation eq.(2-2)



eq.(2-2):General synthesis of polyamides polymers

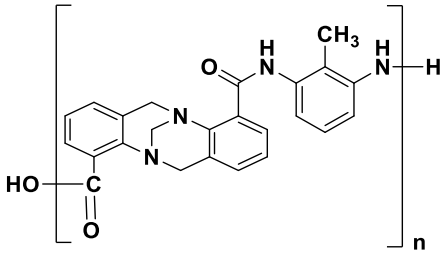
2.4.1. Synthesis of Poly[(6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-4,10-dicarboxylic acid)-CO-(4,4',Diamino-3,3'dimethyldiphenyl methane)] (TB1O1)



Structure 2-5 **: Structure of polyamide TB1O1**

General procedure (X2) thus uses (1 g, 3.2247 mmole) from 6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-4,10-dicarboxylic acid (TB1) with (0.728g 3.2247mmole) from (4,4',Diamino-3,3'dimethyldiphenyl methane) that produces **poly[(6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-4,10-dicarboxylic acid)-CO-(4,4',Diamino-3,3'dimethyldiphenylmethane)]** the product is a greenish yellow powder (0.39 g) , (23.35%).

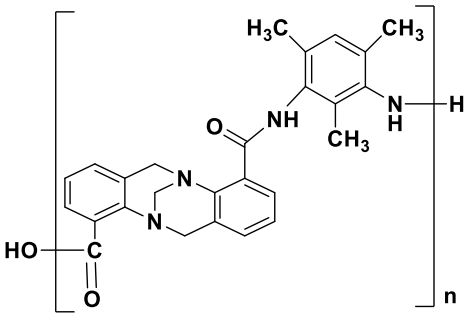
2.4.2. Synthesis of Poly[(6,12-dihydro-5,11-methanodibenzo[b,f][1,5] diazocine-4,10-dicarboxylic acid)-CO-(2,6-diaminotoluene)] (TB1O2)



Structure 2-6: Structure of polyamide TB1O2

General procedure (X2) thus uses (1 g, 3.2247 mmole) 6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-4,10-dicarboxylic acid (TB-1) with (0.394g 3.2247mmole) from (2,6-diamino toluene) that produces **poly**[(**6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-4,10-dicarboxylicacid)-CO-(2,6-diamino- toluene**)] the product is a black powder (0.79 g) , (59.13%).

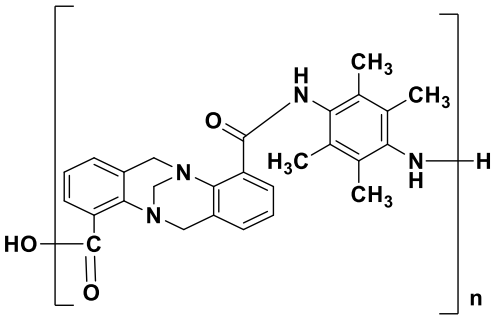
2.4.3. Synthesis of poly[(6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-4,10-dicarboxylic acid)-CO-(2.4,6-trimethyl-m-phenylenediamine)] (TB1O3)



Structure 2-7: Structure of polyamide TB1O3

General procedure (X2) thus uses (1 g, 3.2247 mmole) 6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-4,10-dicarboxylic acid (TB-1) with (0.484g 3.2247mmole) from (2.4,6-trimethyl-m-phenylene diamine) that produces **Poly[(6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-4,10-dicarboxylic acid) -CO- (2.4,6-trimethyl-m-phenylenediamine)]** the product is a mustard color powder (0.25 g), (17.53 %).

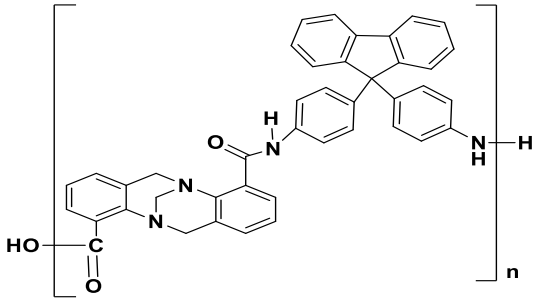
2.4.4. Synthesis of poly [(6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-4,10-dicarboxylic acid)-CO-(2,3,5,6-tetramethyl-1,4-phenylenedia -mine)] (TB1O4)



Structure 2-8: Structure of polyamide TB1O4

General procedure (X2) thus uses (1 g, 3.2247 mmole) 6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-4,10-dicarboxylic acid (TB1) with (0.529 g, 3.2247mmole) from (2,3,5,6-tetramethyl-1,4-phenylenediamine) that produces **poly** [**(6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-4,10-dicarboxylic acid)-CO-(2,3,5,6- tetramethyl-1,4-phenylenediamine)]** the product is a reddish black powder (0.45 g) , (30.59 %).

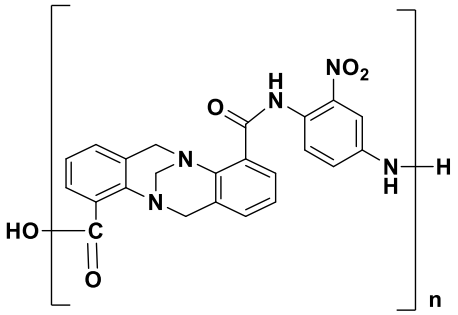
2.4.5. Synthesis of poly [(6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-4,10-dicarboxylic acid)-CO-(9,9- Bi(4-aminophenyl)flourene)] (TB1O5)



Structure 2-9: Structure of polyamide TB1O5

General procedure (X2) thus uses (1 g, 3.2247 mmole) 6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-4,10-dicarboxylic acid (TB1) with (1.123 g, 3.2247mmole) from (9,9-Bi(4-aminophenyl)flourene) that produces **poly[(6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-4,10-dicarboxylic acid)-CO-(9,9-Bi(4-aminophenyl)flourene)]** the product is a yellow powder (0.20 g), (9.67%).

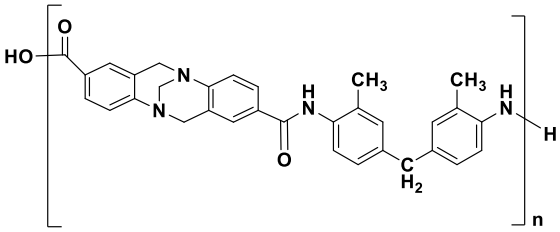
2.4.6. Synthesis of poly(6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-4,10-dicarboxylic acid)-CO-(2-nitro-1,4- phenylenediamine)] (TB1O6)



Structure 2-10: Structure of polyamide TB1O6

General procedure (X2) thus uses (1 g, 3.2247 mmole) 6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-4,10-dicarboxylic acid (TB1) with (0.493 3.2247mmole) from (2-nitro-1,4-phenylenediamine) that produces **poly [(6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-4,10-dicarboxylic acid)-CO- (2-nitro-1,4-phenylenediamine)]** the product is a reddish black powder (0.46 g), (32.06 %).

2.4.7. Synthesis of poly [(6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-2,8-dicarboxylic acid-CO-4,4'-Diamino-3,3'dimethyldiphenylmethane)] (TB2P7)

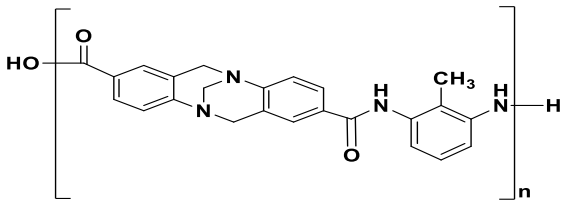


Structure 2-11: Structure of polyamide TB2p7

General procedure (X2) thus uses (1 g, 3.2247 mmole) from (6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-2,8-dicarboxylic acid) (TB2) with (0.728g, 3.2247mmole) from (4,4'-diamino-3,3'-dimethyldiphenylmethane) that produces **poly [(6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-2,8-**

dicarboxylic acid)-CO-(4,4'-diamino-3,3'dimethyldiphenyl methane)] the product is a black powder (0.26 g), (15.57 %).

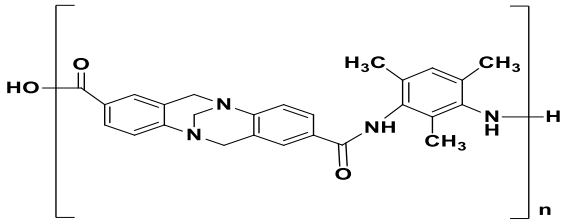
2.4.8. Synthesis of poly [(6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-2,8-dicarboxylic acid)-CO-(2,6-diamino toluene)] (TB2P8)



Structure 2-12: Structure of polyamide TB2p8

General procedure (X2) thus uses (1 g, 3.2247 mmole) from (6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-2,8-dicarboxylic acid (TB2)) with (0.394g 3.2247mmole) from (2,6-diaminotoluene) that produces **poly [(6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-2,8-dicarboxylic acid)-CO-(2,6-diamino toluene)**] the product is a black powder (0.33 g), (24.70 %).

2.4.9. Synthesis of poly [(6,12-dihydro-5,11 methanodibenzo [b,f][1,5] diazocine-2,8-dicarboxylic acid) -CO-(2.4,6-trimethyl-m-phenylenediamine)] (TB2P9)

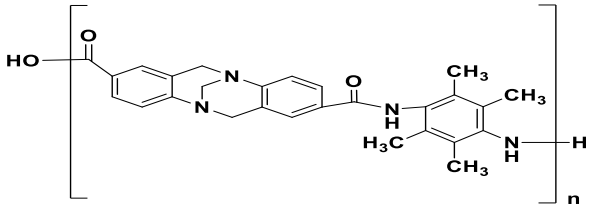


Structure 2-13: Structure of polyamide TB2p9

General procedure (X2) thus uses (1 g , 3.2247 mmole) from (6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-2,8-dicarboxylic acid) (TB2) with (0.484g 3.2247mmole) from (2.4,6-trimethyl-m-phenylenediamine) that

produces **poly[(6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-2,8-dicarboxylic acid)-CO-(2.4,6-trimethyl-m-phenylenediamine)**] the product was a black powder (0.24 g), (16.83 %).

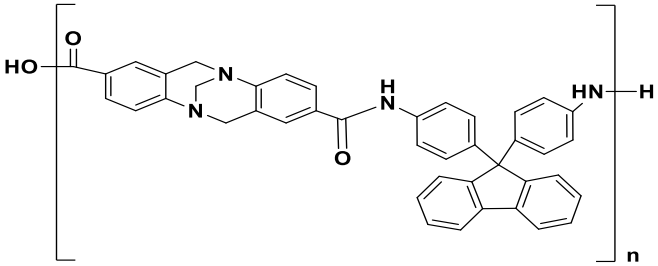
2.4.10. Synthesis of poly [(6,12-dihydro-5, 11-methanodibenzo [b,f] [1,5] diazocine-2,8-dicarboxylic acid)-CO-(2,3,5,6-tetramethyl-1,4-phenylenedi-amine)] (TB2P10)



Structure 2-14: Structure of polyamide TB2p10

General procedure (X2) thus uses (1 g, 3.2247 mmole) from 6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-2,8-dicarboxylic acid (TB2) with (0.529 g, 3.2247mmole) from (2,3,5,6-tetramethyl-1,4-phenylenediamine) that produces **poly [(6,12-dihydro-5, 11-methanodibenzo[b,f] [1,5] diazocine-2,8-dicarboxylic acid)-CO-(2,3,5,6-tetramethyl-1,4-phenylenediamine**)] the product is a reddish black powder (0.29 g), (19.71 %).

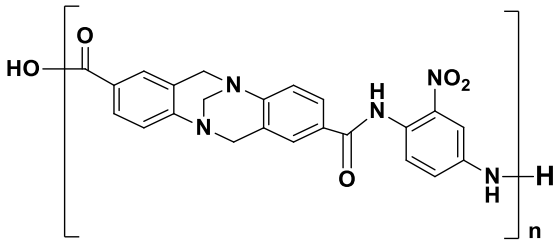
2.4.11. Synthesis of poly [(6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-2,8-dicarboxylic acid)-CO-(9,9-Bi(4-aminophenyl)flourene)] (TB2P11)



Structure 2-15: Structure of polyamide TB2p11

General procedure (X2) thus uses (1 g, 3.2247 mmole) 6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-2,8-dicarboxylic acid (TB2) with (1.123 g, 3.2247mmole) from (9,9–Bi(4-amino phenyl)flourene) that produces **poly [(6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-2,8-dicarboxylic acid)-CO-(9,9- Bi(4-aminophenyl)flourene)**] the product was a yellow powder (0.25 g) , (12.09 %)

2.4.12. Synthesis of poly [(6,12-dihydro-5,11-methanodibenzo[b,f][1,5] diazocine-2,8-dicarboxylic acid)-CO-(2-nitro-1,4-phenylenediamine)] (TB2P12)

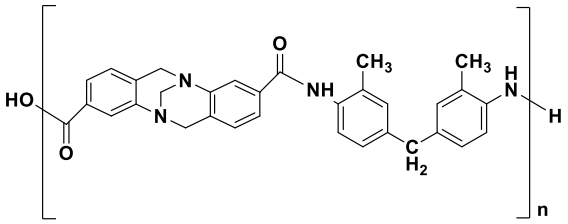


Structure 2-16: Structure of polyamide TB2p12

General procedure (X2) thus uses (1 g, 3.2247 mmole) from 6,12-dihydro-5,11-methanodibenzo[b,f] [1,5] diazocine-2,8-dicarboxylic acid (TB2) with (0.493 g, 3.2247mmole) from (2-nitro-1,4-phenylenediamine) that

produces **poly [(6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-2,8-dicarboxylic acid)-CO-(2-nitro-1,4-phenylenediamine)]** the product is a reddish black powder (0.27 g), (18.82 %).

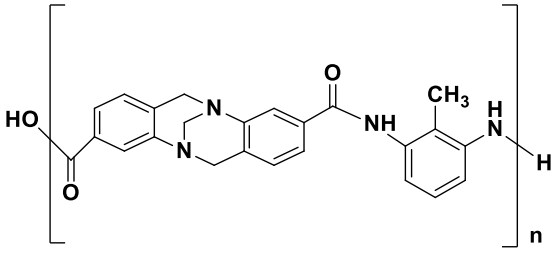
2.4.13. Synthesis of poly[(6,12-dihydro-5,11-methanodibenzo[b,f][1,5] diazocine-3,9-dicarboxylic acid)-CO-(4,4'-diamino-3,3'-dimethyldiphenyl methane)] (TB3M13)



Structure 2-17: Structure of polyamide TB2M13

General procedure (X2) thus uses (1 g, 3.2247 mmole) from (6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-dicarboxylic acid (TB3) with (0.728 g, 3.2247mmole) from (4,4'-diamino-3,3'-dimethyldiphenylmethane) that produces **poly [(6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-dicarboxylic acid)-CO-(4,4'-diamino-3,3'-dimethyldiphenylmethane)]** the product is a black powder (0.24 g), (14.37 %).

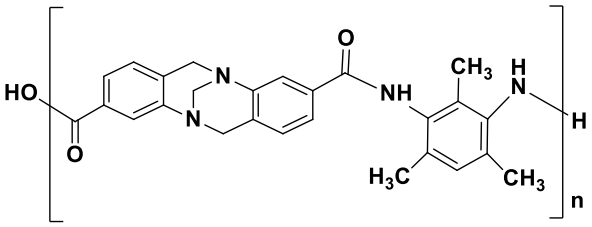
2.4.14. Synthesis of poly [(6,12-dihydro-5,11-methanodibenzo[b,f][1,5] diazocine-3,9-dicarboxylic acid)-CO-(2,6-diaminotoluene)] (TB3M14)



Structure 2-18: Structure of polyamide TB2M14

General procedure (X2) thus uses (1 g, 3.2247 mmole) from (6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-dicarboxylic acid) with (0.394g, 3.2247 mmol) from (2,6-diaminotoluen) that produces **poly [(6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-dicarboxylic acid)-CO-(2,6-diaminotol- uene)]** the product is a reddish black powder (0.21 g), (15.72 %).

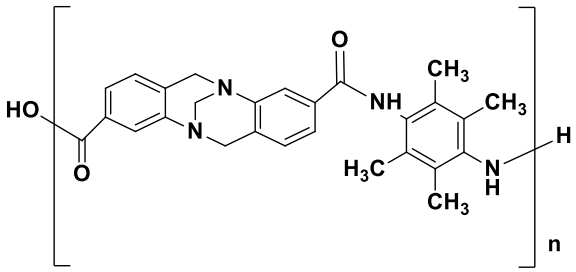
2.4.15. Synthesis of poly [(6,12-dihydro-5,11-methanodibenzo[b,f][1,5] diazocine-3,9-dicarboxylic acid)-CO-(2.4,6-trimethyl-m-phenylenediamin- e)] (TB3M15)



Structure 2-19: Structure of polyamide TB2M15

General procedure (X2) thus uses (1 g, 3.2247 mmole) from (6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-dicarboxylic acid) (TB3) with (0.484g, 3.2247mmole) from (2.4,6-trimethyl-m-phenylenediamine) that produces **poly[(6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-dicarboxylic acid)-CO- (2.4,6-trimethyl-m-phenylenediamine)]** the product is a dark red powder (0.22 g), (15.43 %).

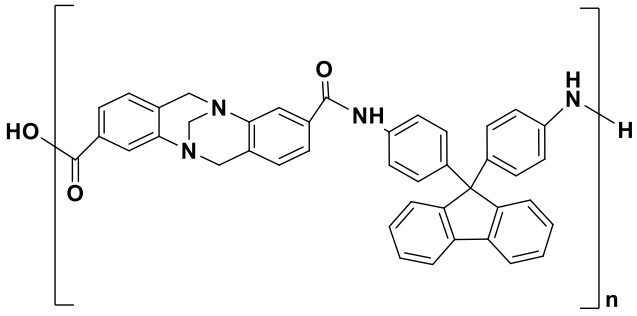
2.4.16. Synthesis of poly [(6,12-dihydro-5,11-methanodibenzo[b,f][1,5] diazocine-3,9-dicarboxylic acid)-CO-(2,3,5,6-tetramethyl-1,4-phenylene diamine)] (TB3M17)



Structure 2-20: Structure of polyamide TB2M116

General procedure (X2) thus uses (1 g, 3.2247 mmole) from 6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-dicarboxylic acid (TB3) with (0.529 g, 3.2247 mmole) from (2,3,5,6- tetramethyl-1,4-phenylenediamine) that produces **poly [(6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-dicarboxylic acid)-CO- (2,3,5,6-tetramethyl-1,4-phenylenediamine)**] the product is a white powder (0.35 g), (23.79 %).

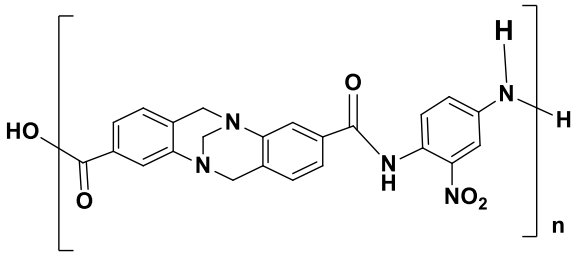
2.4.17. Synthesis of poly (6,12-dihydro-5,11-methanodibenzo[b,f][1,5] diazocine-3,9-dicarboxylic acid)-CO-(9,9-Bi(4-aminophenyl)flourene)] (TB3M17)



Structure 2-21: Structure of polyamide TB2M17

General procedure (X2) thus uses (1 g, 3.2247 mmole) 6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-dicarboxylic acid (TB3) with (1.123 g, 3.2247mmole) from (9,9-Bi(4-aminophenyl)flourene) that produced **poly [(6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-dicarboxylic acid)-CO-(9,9-Bi(4-aminophenyl)flourene)]** the product is a grey powder (0.23 g), (11.12%).

2.4.18. Synthesis of poly [(6,12-dihydro-5,11-methanodibenzo[b,f][1,5] diazocine-3,9-dicarboxylic acid)-CO-(2-nitro-1,4-phenylenediamine)] (TB3M18)



Structure 2-22: Structure of polyamide TB2M18

General procedure (X2) thus uses (1 g, 3.2247 mmole) from 6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine-3,9-dicarboxylic acid (TB3) with (0.493 g, 3.2247mmole) from (2-nitro-1,4-phenylenediamine) that produces **poly [(6,12-dihydro-5,11-methanodibenzo[b,f][1,5] diazocine-3,9-dicarboxylic acid)-CO- (2-nitro-1,4-phenylenediamine)]** the product is a brown powder (0.45 g), (31.36%).

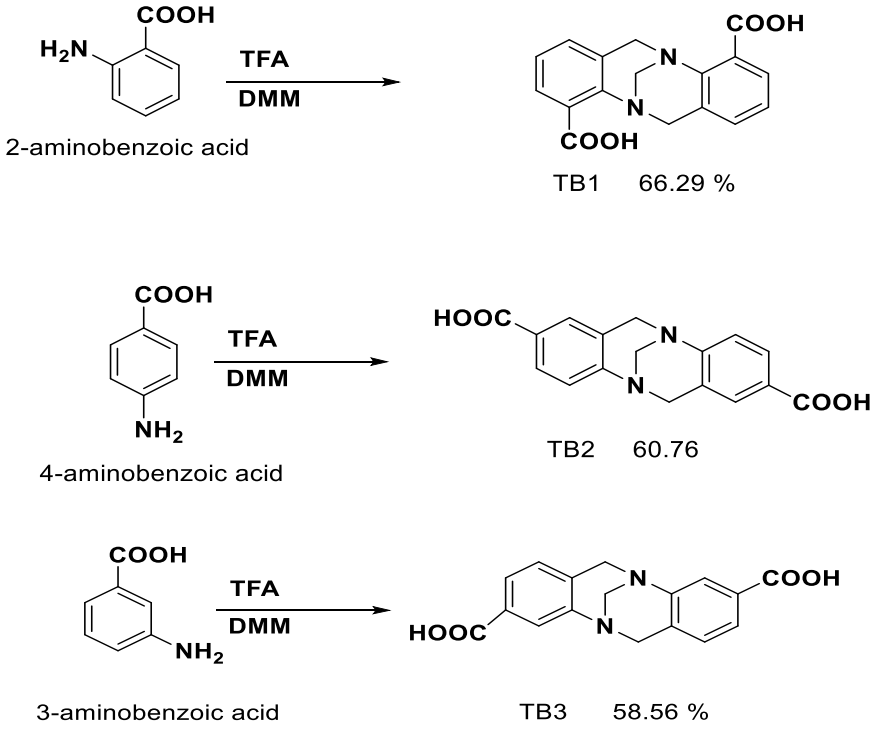
Chapter Three

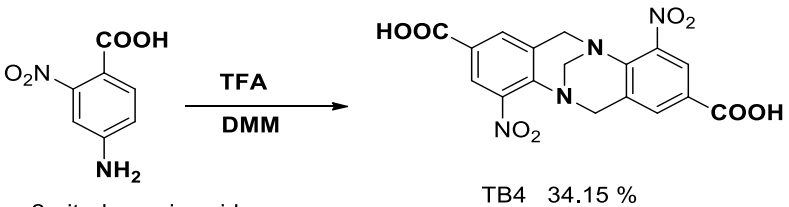
Results and Discussion

3. Results and Discussion

3.1. Synthesize and characterization of monomers (Tröger's base)[6]

Tröger base was synthesized as described in the patent, with the addition of amino benzoic acid dimethoxymethane (DMM), a methylene source, in a super acid (solvent and catalyst) such as trifluoroacetic acid (TFA). One equivalent of pure amino benzoic acid is combined with two and a half equivalents of dimethoxymethane (DMM) and chilled to ice temperature in this synthesis. The TFA (4-5 ml per g of amine) is then gradually added over ten minutes, drop by drop for 72 hours, the reaction mixture is stirred at 25° C temperature in an inert environment. The color of the solution will change from pink to red. Water was used to quench the mixture, then was wished by hot ethanol and recrystallized by diethylether, as shown in eq.(3-1)





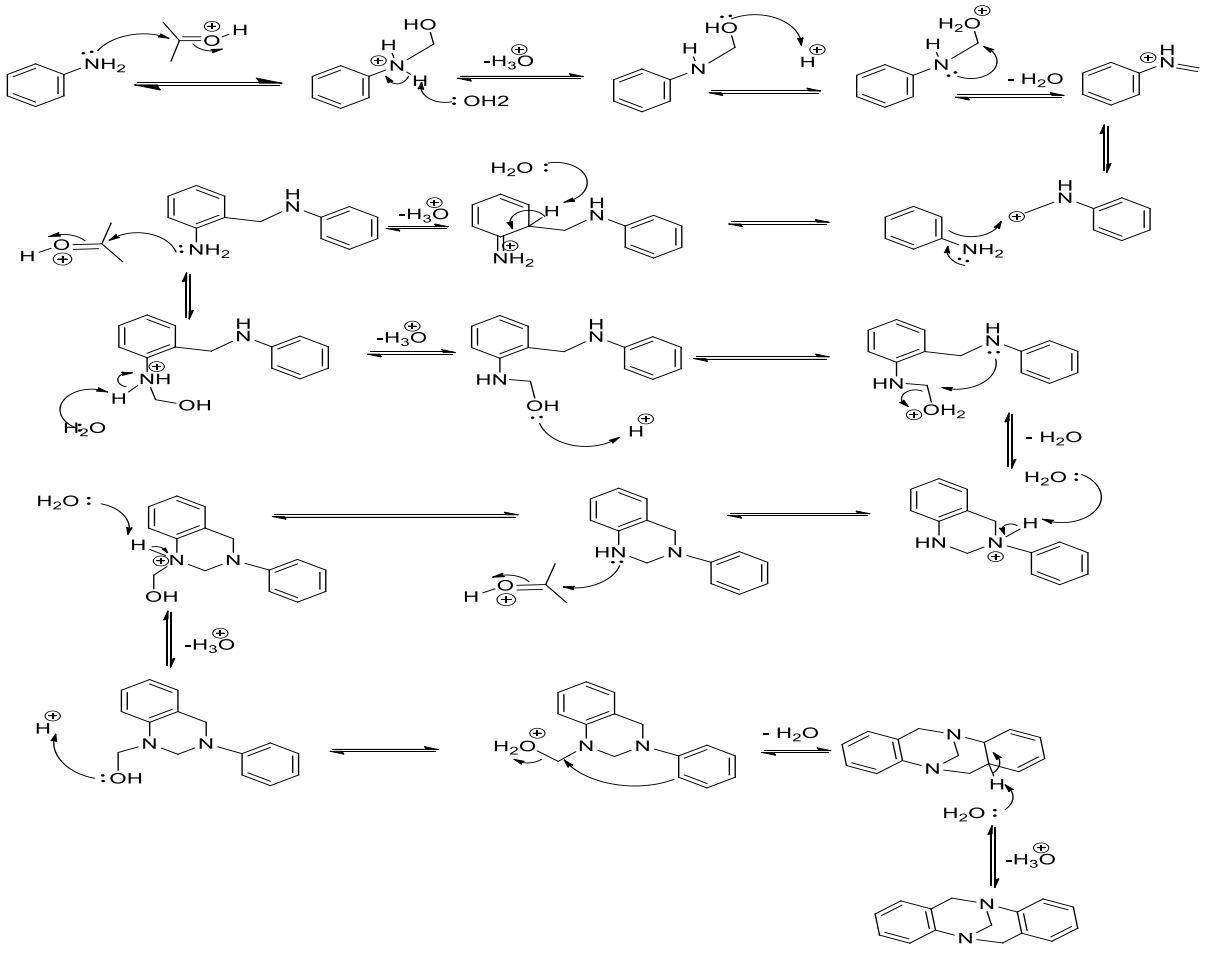
4-amino-2-nitrobenzoic acid

TB4 34.15 %

TFA = CF_3COOH
DMM= $CH_2(OCH_3)_2$

eq.(3-1): Synthesis of (TB1 –TB4)

The above interaction can be illustrated according to the general mechanism shown below in Scheme (3-1)[5]



Scheme (3-1): General Mechanism of synthesis Troger's base

The compounds can be proved by FT-IR, NMR, and XRD. FT-IR It can show the disappearance of the sharp weak peaks of the amine and shows the C_{aliph} –N peak, as well as the carboxyl group as shown in (Table 3-1) and (Figures 3-1 to 3-4).^{1}HNMR which shows the disappearance of the peak amine[N-H] and showing Tröger bases are cyclic from through values peaks for Ar-N-CH_2 and [N-CH_2-N] as shown in (Table 3-2) and (Figure 3-5 to 3-8). ^{13}CNMR of Tröger base is showed to COOH, [$C_{Aromatic}$ –N], [N- C_{aliph} –N], [Ar-CH_2 –N],as shown in (Table 3-3) and (Figure 3-9 to 3-12). Table(3-4) shows some physical properties of (TB1,TB2,TB3,TB4),(Figures 3-13 to 3-16) shows mass spectroscopy for (TB1,TB2,TB3,TB4) and Figure (3-17 to 3-20) shows XRD which explains that TB2 and TB4 are crystalline in which the substitution is in situ para but TB1 and TB3 amorphous .

Table 3-1: FT-IR spectrometer (cm^{-1}) for (TB1, TB2, TB3, TB4)

Model number	O-H For carboxyl group	C-H Aromatic	C-H aliphatic	C=O For carboxyl group	C=C Aromatic	C_{aliph} –N
TB1	3600-2400	3030	2925-2895	1716	1670	1190
TB2	3500-2400	3030	2920-2875	1714	1662	1195
TB3	3600-2400	3082	2952-2850	1707	1670	1193
TB4	3300-2900	3088	2924-2852	1728	1683	1174

Table 3-2: 1HNMR for (TB1, TB2, TB3, TB4)

Model number	Ar-**CH_2**-N	N-**CH_2**-N	-COO**H**	C-H Aliphatic
TB1	4.60	5.16	12.21	2.8
TB2	4.69	5.49	12	2.98
TB3	4.57	5.43	11.30	2.92
TB4	5.29	5.60	13.58	3.44

Table 3-3: ^{13}C NMR for (TB1, TB2, TB3, TB4)

Model	Ar-**CH_2**-N	N-**CH_2**-N	-COO**H**
TB1	60.39	71.74	169
TB2	60.89	71.95	166.80
TB3	60.75	70.46	166.75
TB4	66.88	79.90	162.50

Table 3-4: physical properties of (TB1, TB2, TB3, TB4)

Model	**Melting point ° C**	**color**	**Yield %**
TB1	186 -189	yellow	66.29
TB2	230 – 240	Pink	60.76
TB3	91 – 94	red	58.56
TB4	159 – 161	yellow	34.15

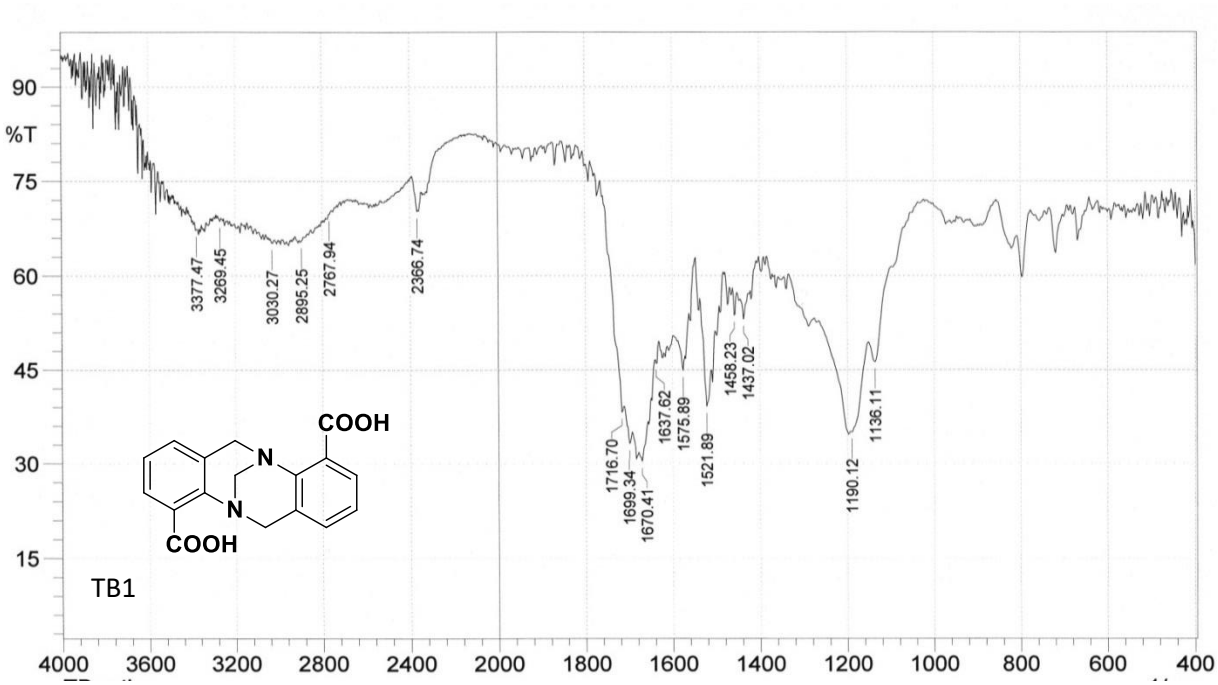


Figure 3-1:Charts FT-IR for (TB1)

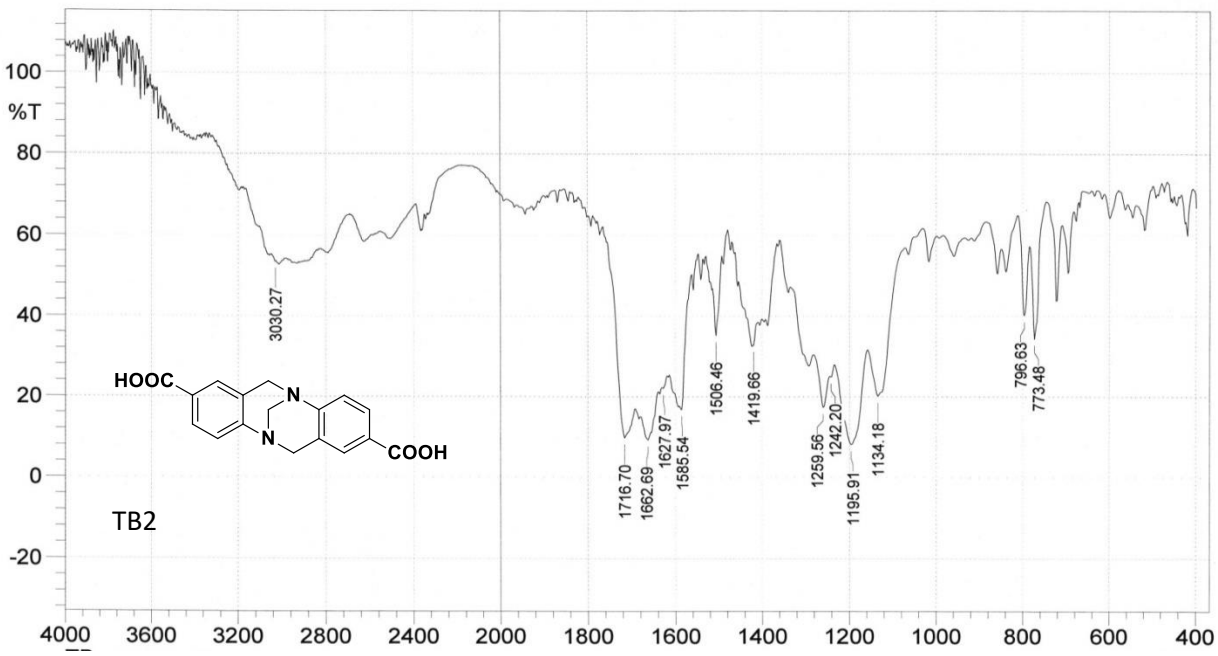


Figure 3-2:Charts FT-IR for (TB2)

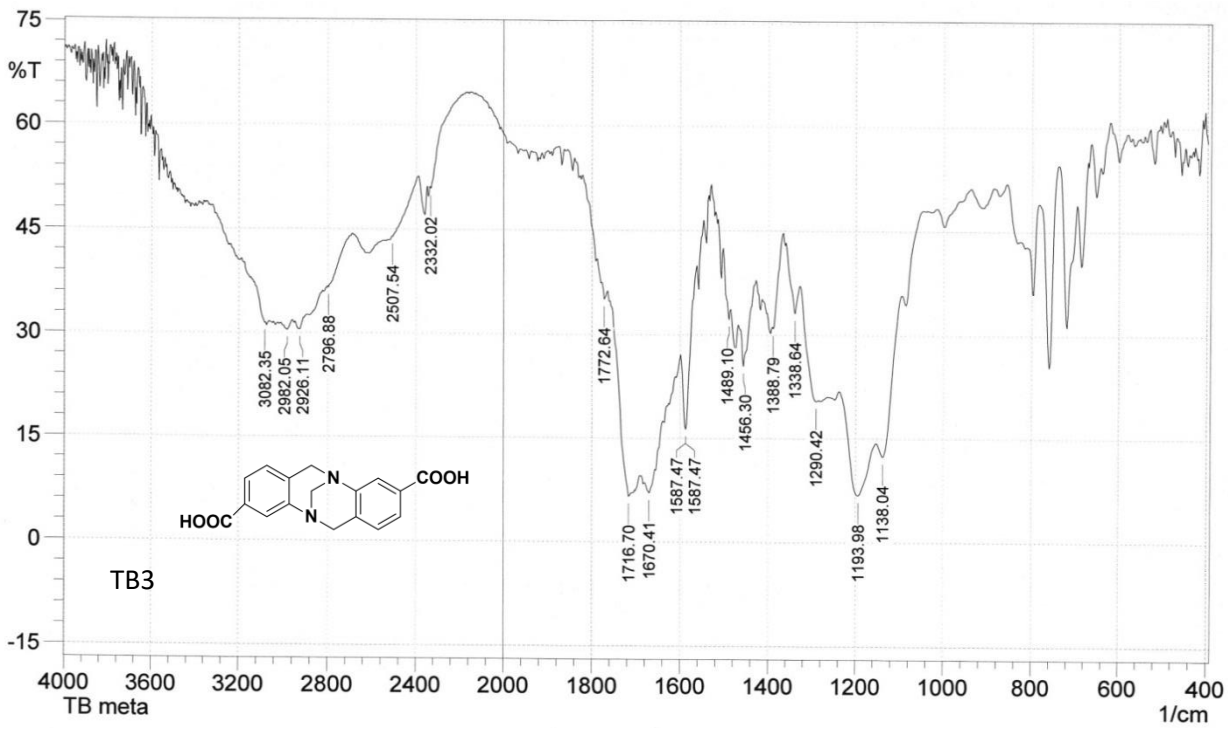


Figure 3-3: Charts FT-IR for (TB1)

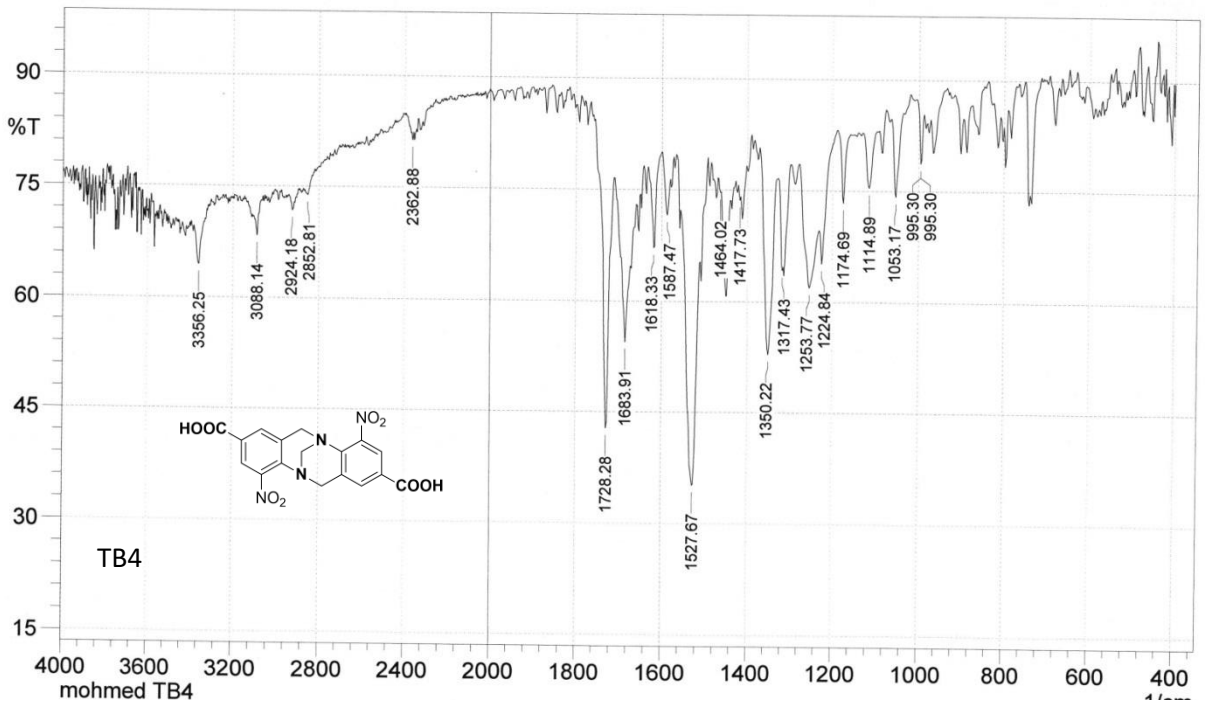


Figure 3-4: Chart FT-IR for (TB4)

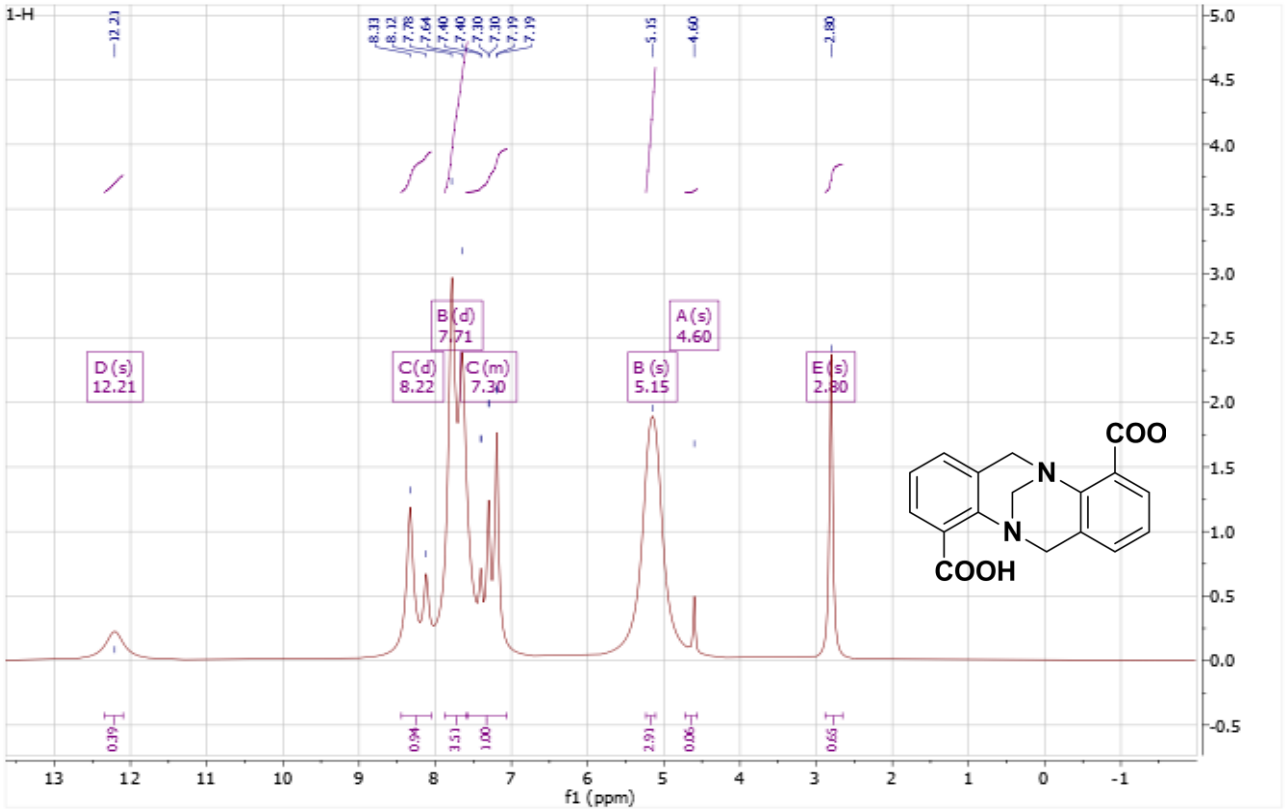


Figure 3-5: Chart 1HNMR for (TB1)

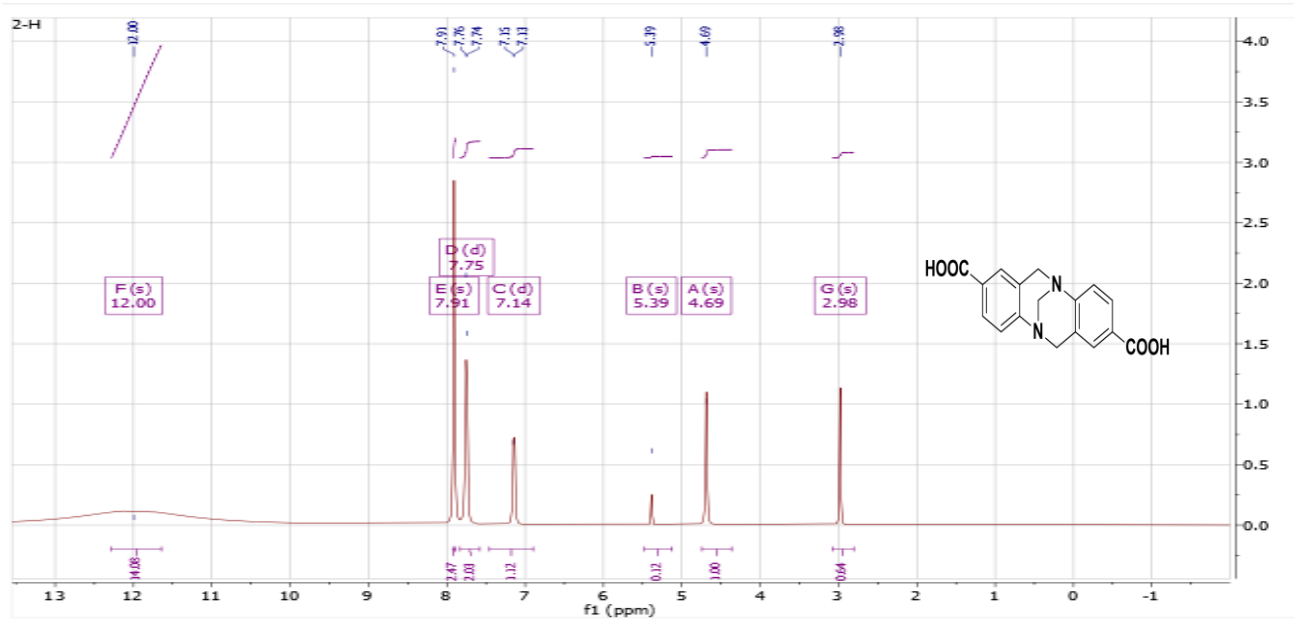


Figure 3-6: Chart 1HNMR for (TB2)

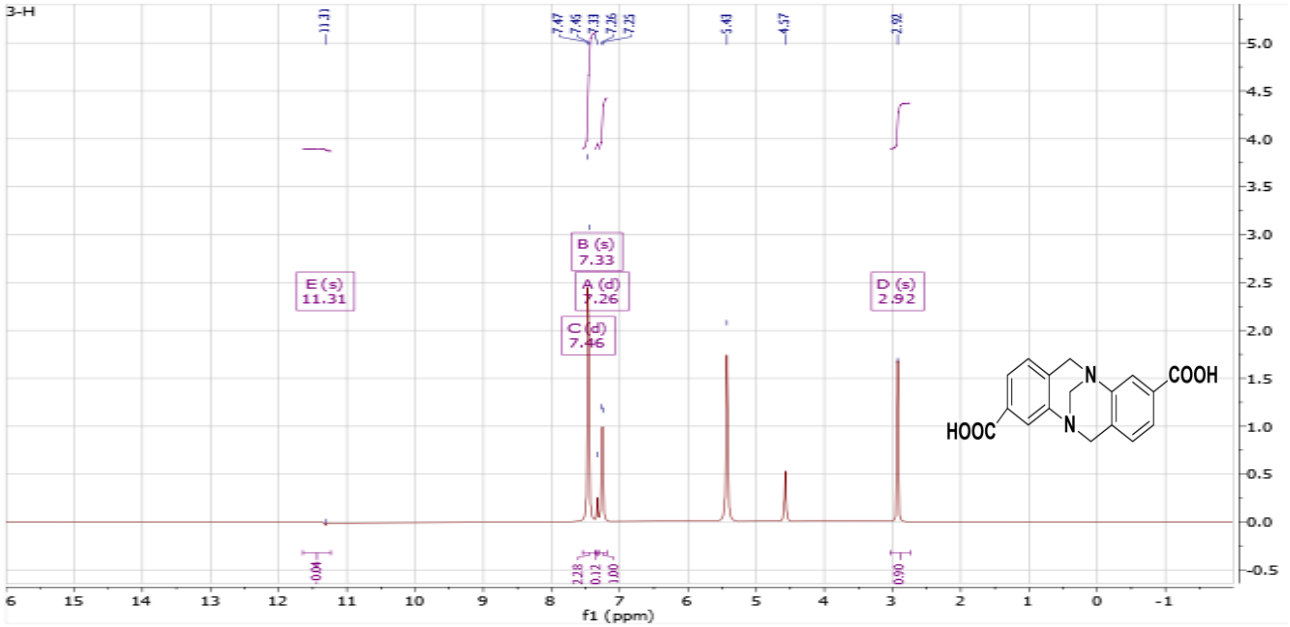


Figure 3-7: Chart 1HNMR for (TB3)

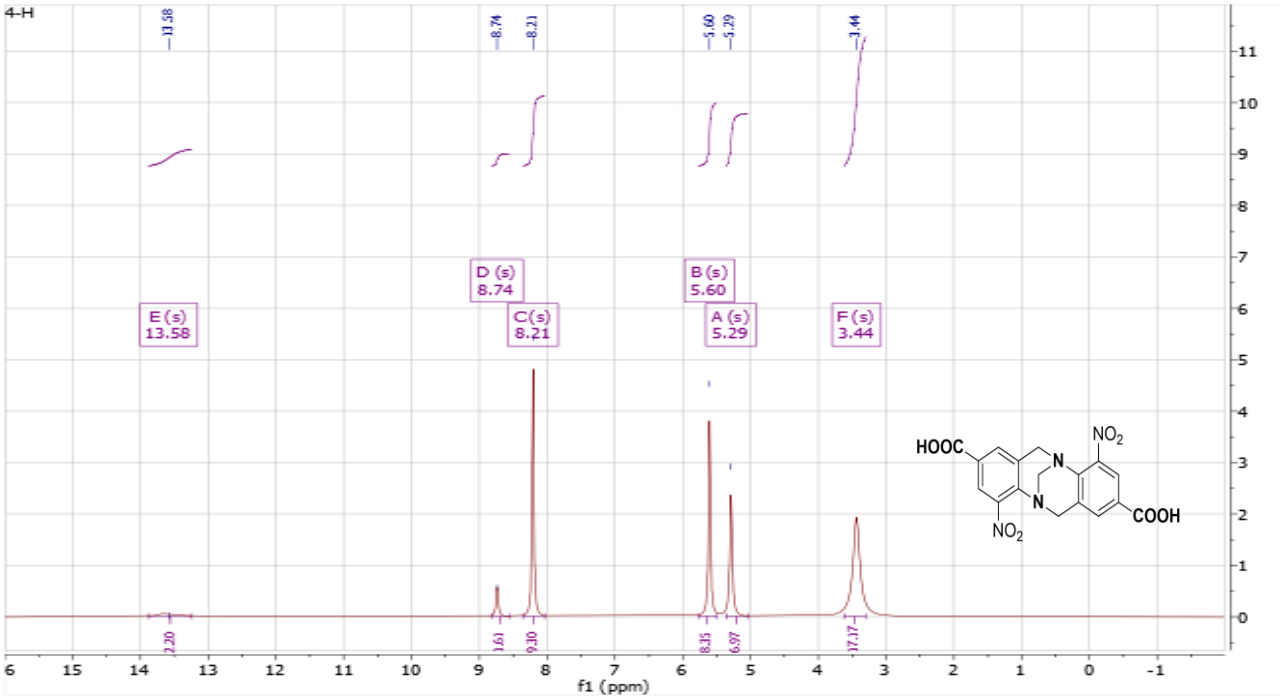


Figure 3-8: Chart 1HNMR for (TB4)

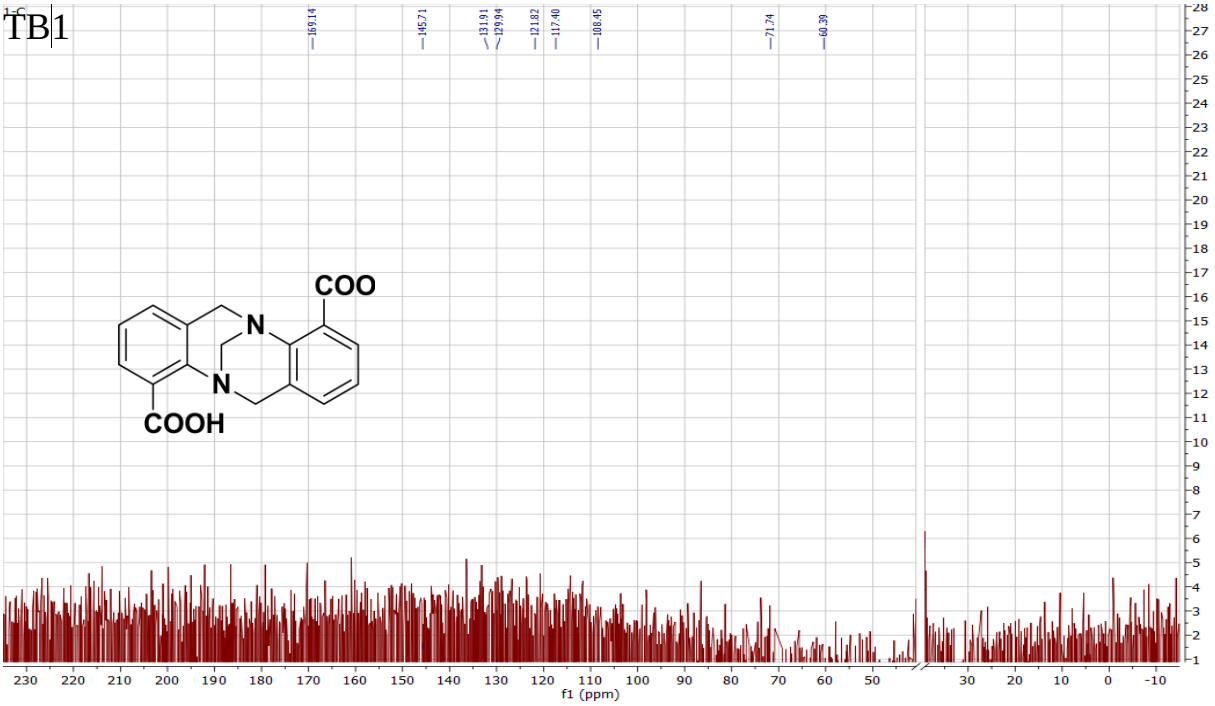


Figure 3-9:Chart ^{13}CNMR for (TB1)

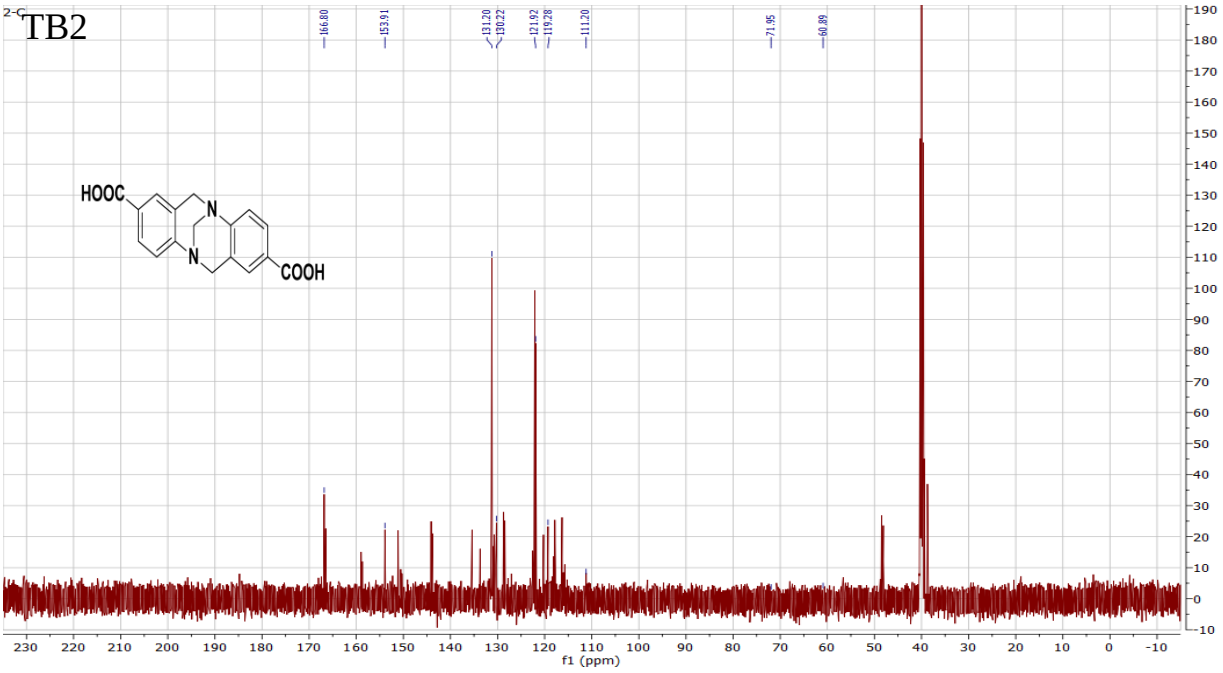


Figure 3-10:Chart ^{13}CNMR for (TB2)

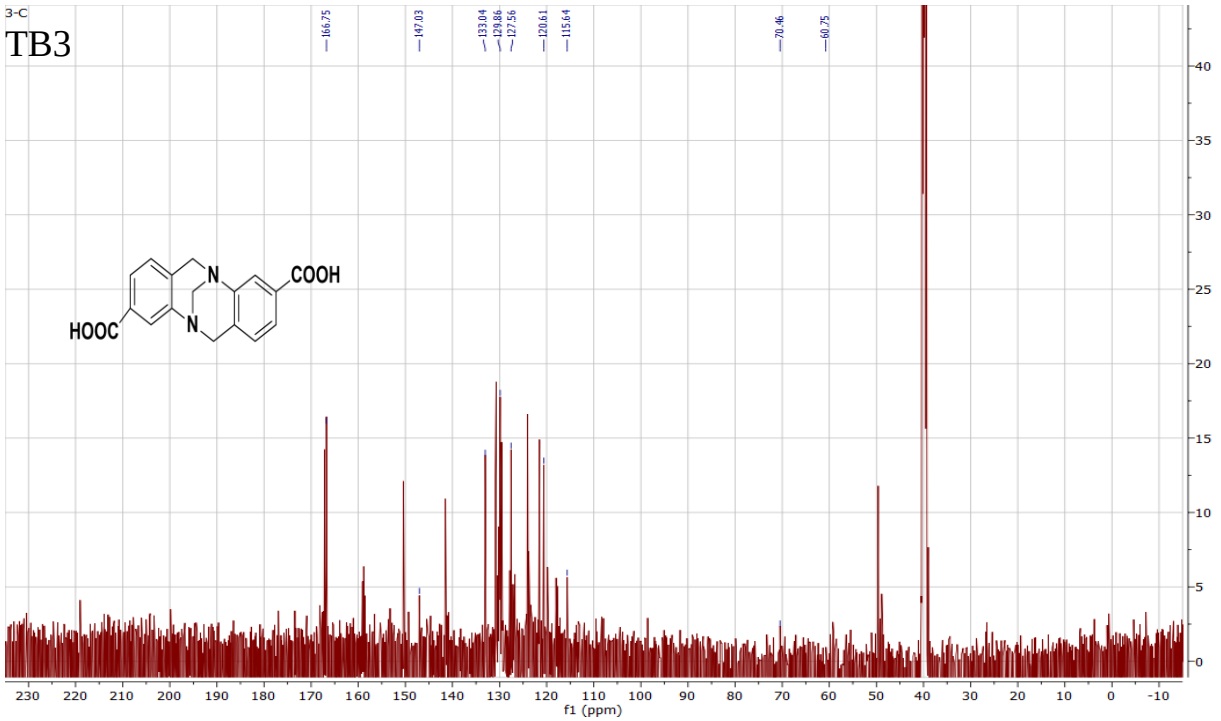


Figure 3-11:Chart ^{13}CNMR for (TB3)

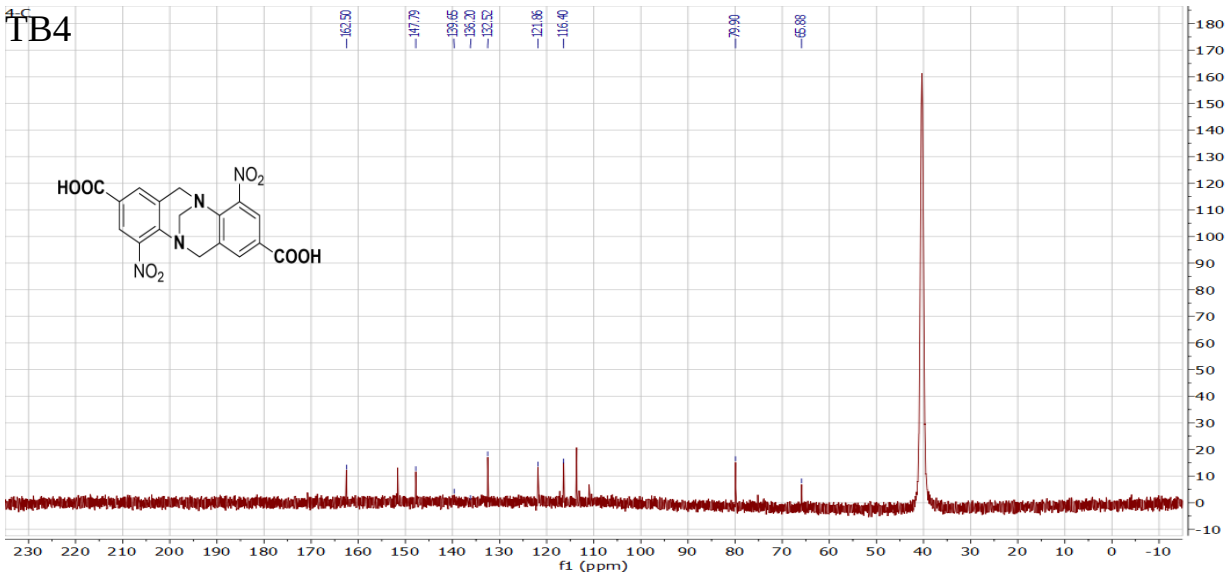


Figure 3-12:Chart ^{13}CNMR for (TB4)

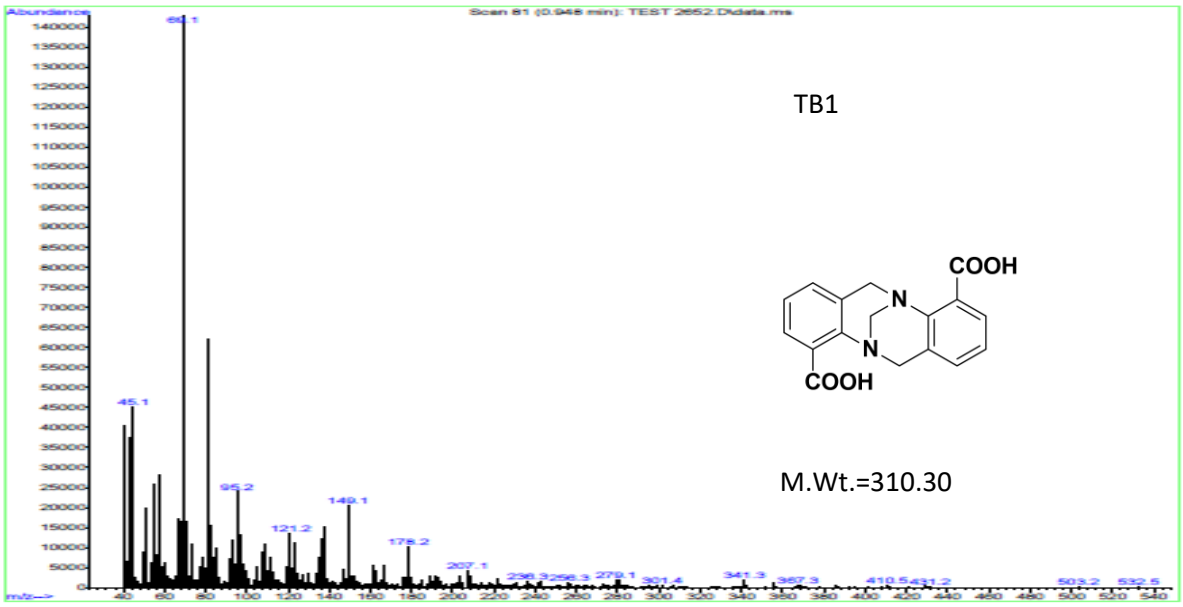


Figure 3-13: Chart mass spectroscopy for (TB1)

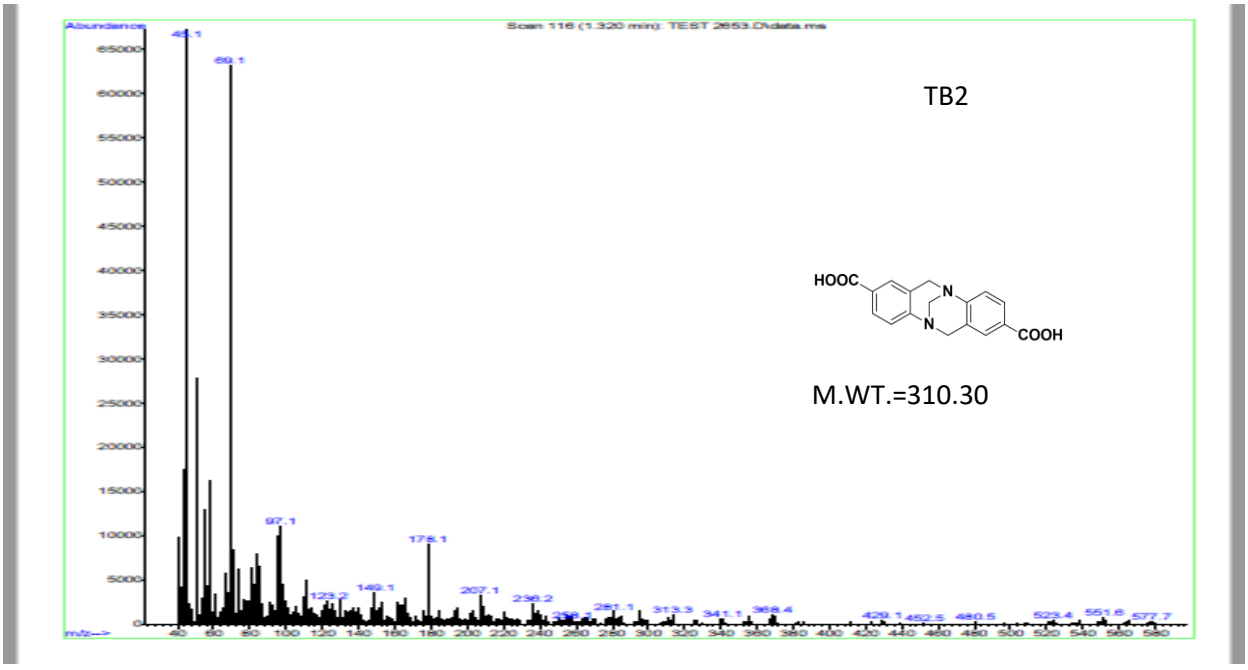


Figure 3-14: Chart mass spectroscopy for (TB2)

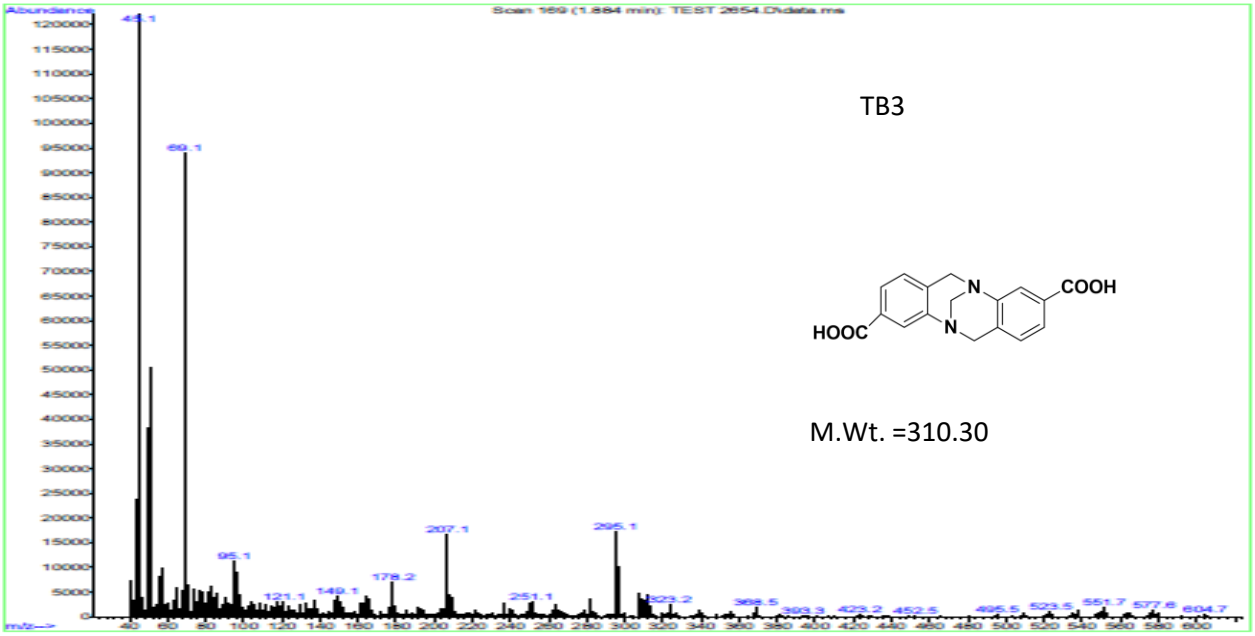


Figure 3-15: Chart mass spectroscopy for (TB3)

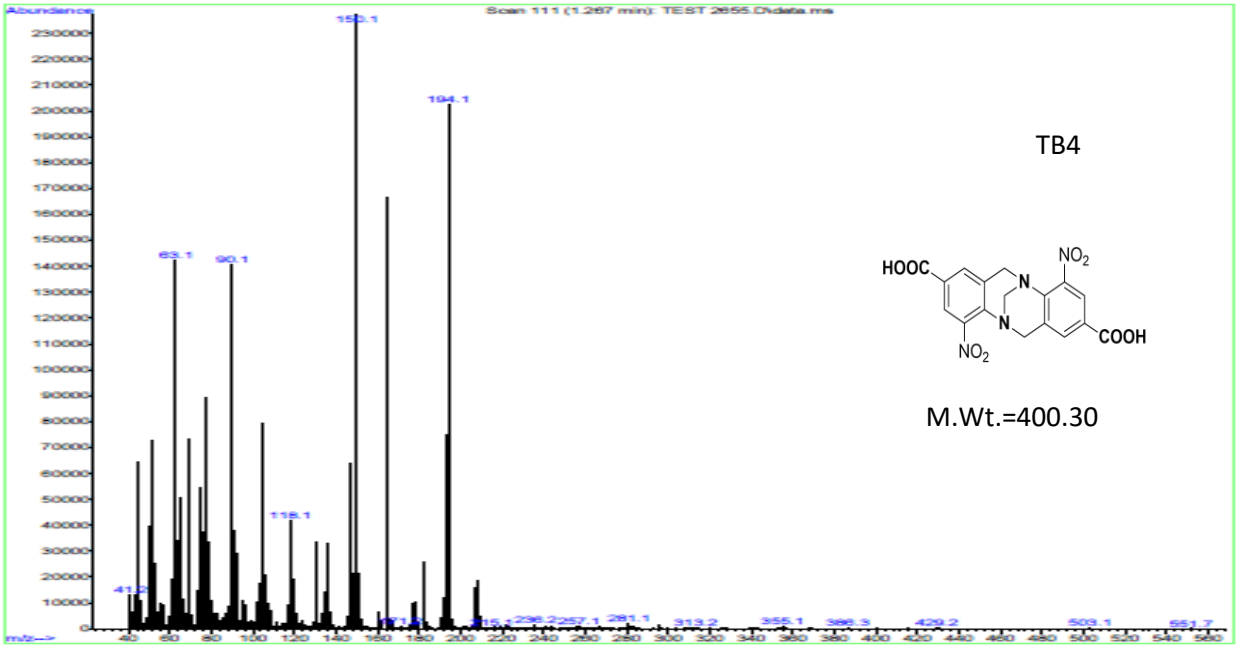


Figure 3-16: Chart mass spectroscopy for (TB4)

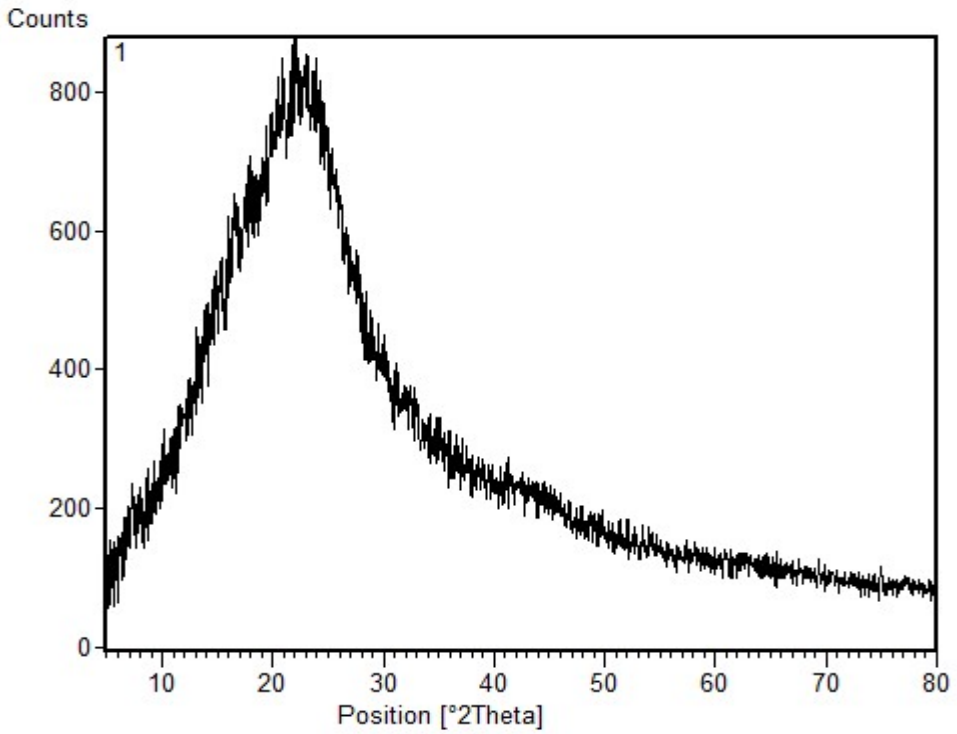


Figure 3-17: Charts XRD for (TB1)

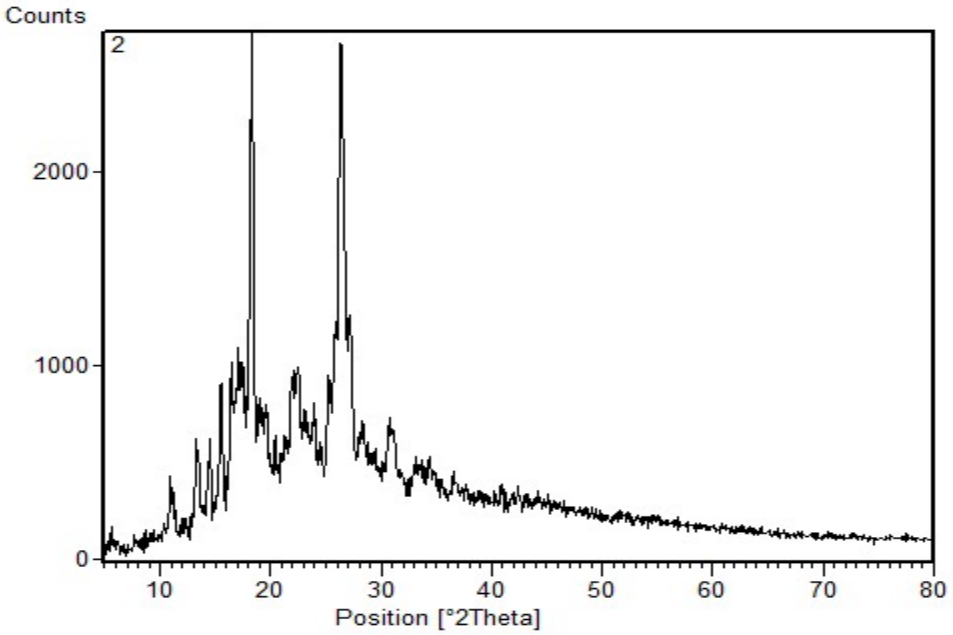


Figure 3-18: Charts XRD for (TB2)

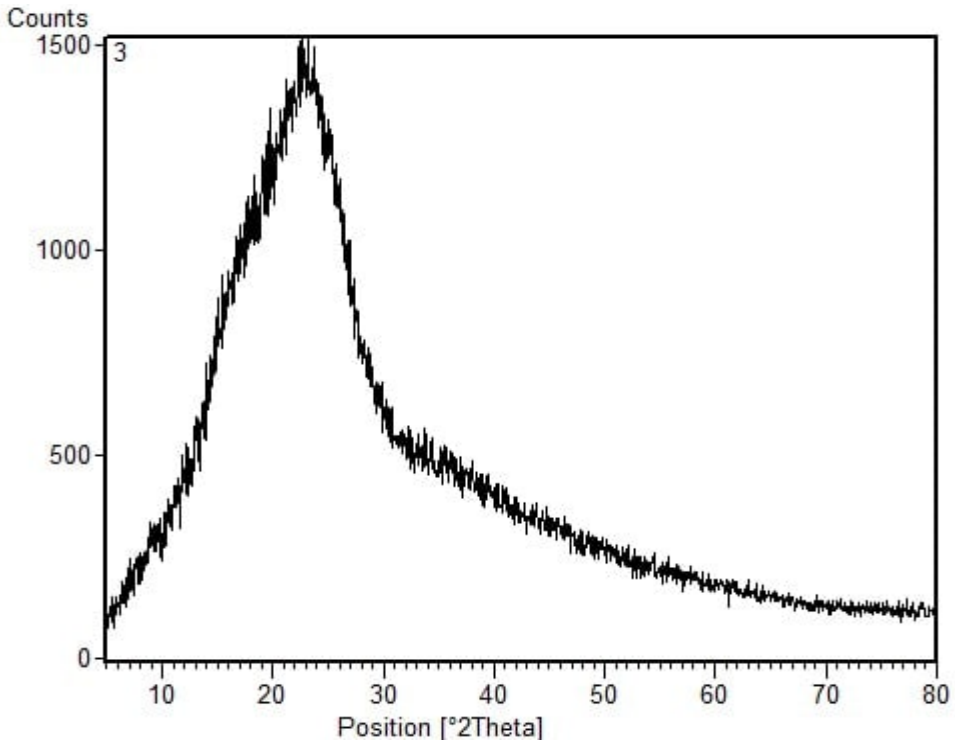


Figure 3-19: Charts XRD for (TB3)

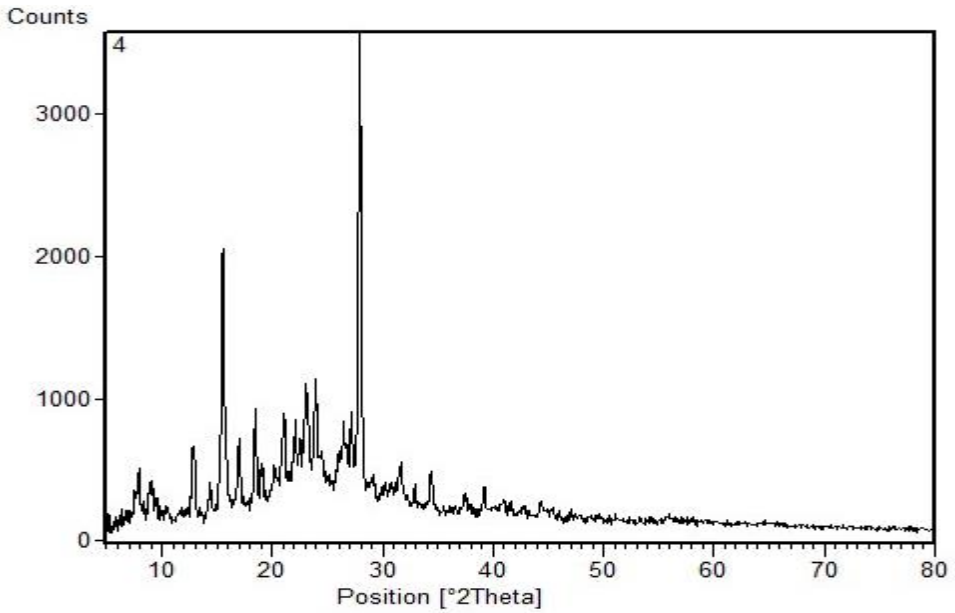


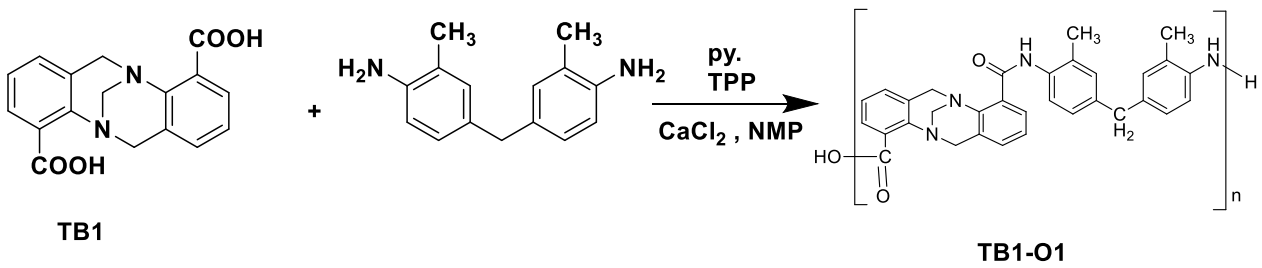
Figure 3-20: Charts XRD for (TB4)

3.2. Synthesize and Characterization of Polyamides [5]

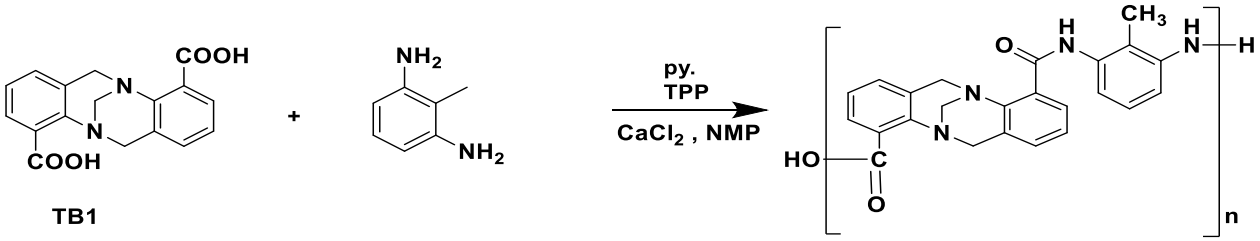
Polyamide can be prepared the s by mixing Tröger's base monomer with diamine monomer. The mixture is dissolved using 1-methyl-2-pyrolidone (NMP), with a TPP as a capacitor agent, and pyridine has also been added as a cata1yst. It has the potency to consolidate with the acid that is released from the reaction medium to produce pyridine salts, preventing the breakdown of the generated amide group. The moisture in the reaction can be removed by adding anhydrous calcium chloride. The unreacted monomers can be removed by ethanol. Also, chloroform is used to remove oligomers. The polyamides can be dissolved in Dimethylsulfoxide and re-deposition by methanol.

3.2.1. Synthesis and characterization of polyamides (TB1O1-TB1O6)

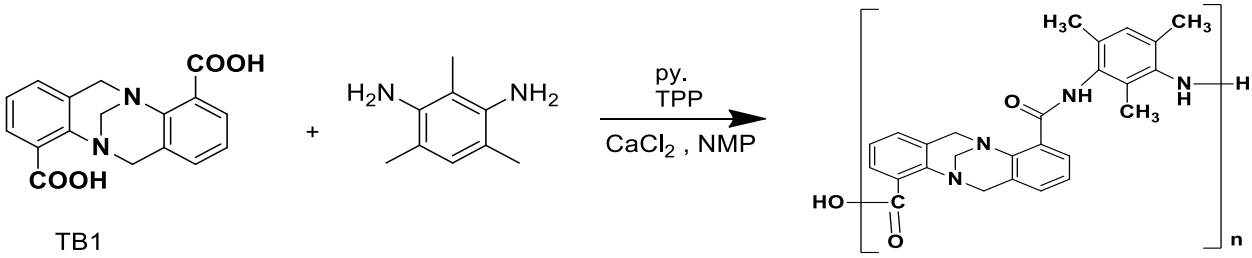
Synthesis of polyamides is produced from interaction (TB1) with diamine aromatic as shown in Equation (3-2).



TB1 TB1-O1

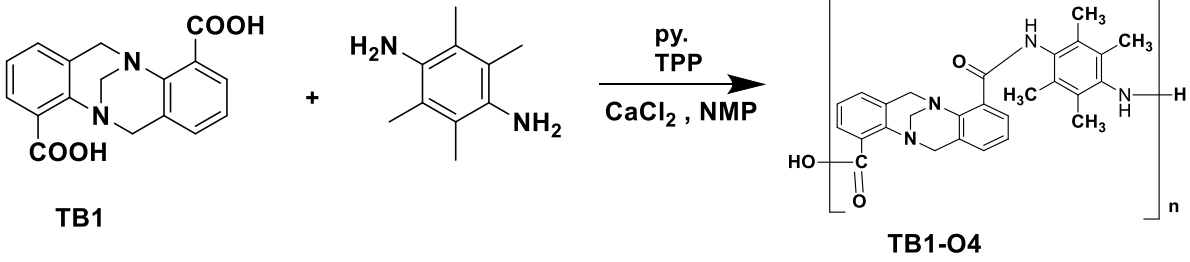


TB1 -O2



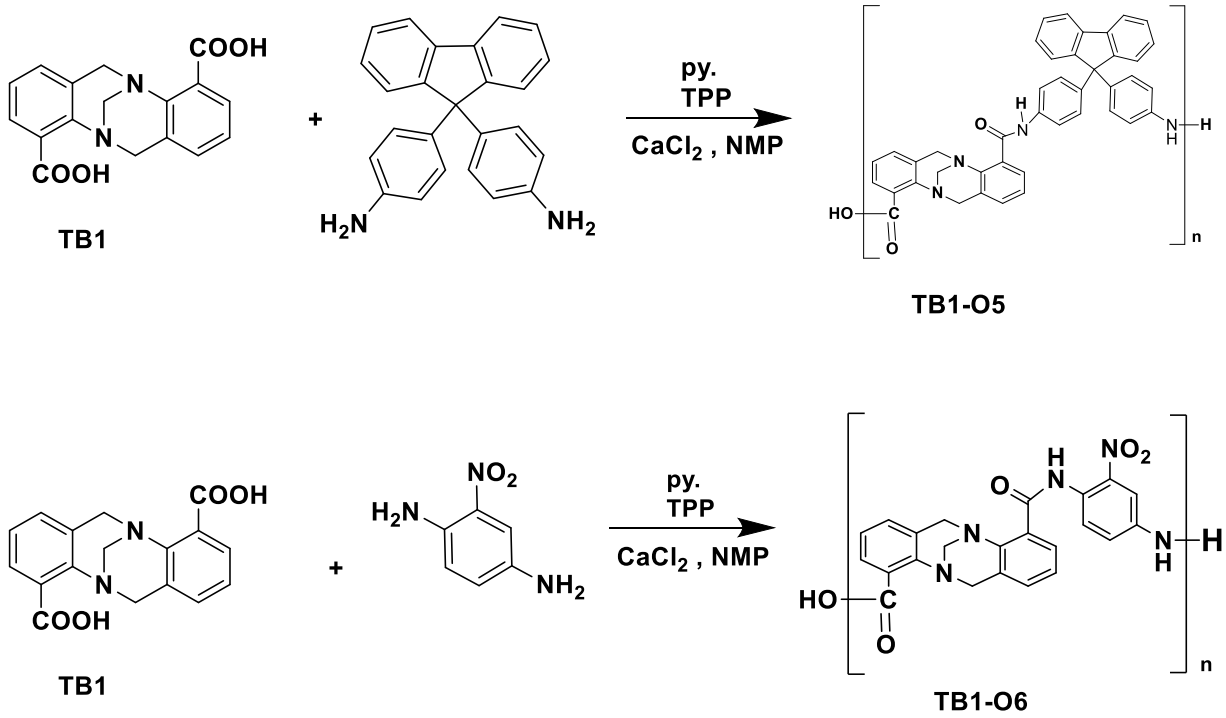
TB1

TB1 -O3



TB1

TB1-O4



eq.(3-2): Synthesis of polyamides (TB1O1 –TB1O6)

eq 3-2 shows the preparation of polyamides (TB1O1-TB1O6), and the determination of the compounds by FT-IR as shown in (Table 3-5) and (Figures 3-21to 3-26). Also, it is identified by ^{1}H NMR (Table3-6) and (Figures 3-27 to 3-32), ^{13}C NMR (Table 3-7) and (Figure 3-33 to 3-3-38), and TGA (Table 3-8) and (Figures 3-39 to 3-44)

Table 3-5:Functional Groups Values in FT-IR for Polymers (TB1O1-TB1O6)

Model number	N-H_2 terminal	COOH terminal	N-H-C=O
TB1O1	3450 , 3360	3200-2450	1670
TB1O2	3547 , 3314	3339-2550	1681
TB1O3	3524 , 3344	3329-2450	1683
TB1O4	3358 ,3200	3200-2450	1670
TB1O5	3423 , 3354	3244-2440	1670
TB1O6	3545 , 3400	3346-2420	1676

Table 3-6: Functional Groups Values in ^{1}HNMR for Polymers (TB1O1-TB1O6)

Model number	N-H_2 terminal	COOH terminal	N-H-C=O
TB1O1	6.28	11.28	9.55
TB1O2	6.56	11.28	9.38
TB1O3	6.28	11.09	9.14
TB1O4	6.27	11.00	9.15
TB1O5	6.10	11.13	9.11
TB1O6	6.40	11.05	9.15

Table 3-7: Functional Groups Values in ^{13}CNMR for Polymers (TB1O1-TB1O6)

Model number	C_{Ar}-N-H_2 terminal	COOH terminal	N-H-C=O
TB1O1	149.00	170.45	164.00
TB1O2	146.04	169.01	163.07
TB1O3	145.15	167.21	169.00
TB1O4	146.14	170.19	168.11
TB1O5	147.71	170.39	162.79
TB1O6	144.99	169.02	167.52

Table 3-8 : TGA study of polymers (TB1O1-TB1O6)

Model number	Initial Degradation	Final Degradation
TB1O1	86.35 -21.67	481.15 -505.74
TB1O2	68.84 -29.17	489.27 – 534.5
TB1O3	161.23– 211.63	444.28-474.86
TB1O4	188.39-239.52	402.73-437.95
TB1O5	147.28-166.15	524.24-583.01
TB1O6	186.79-239.04	445.42-516.19

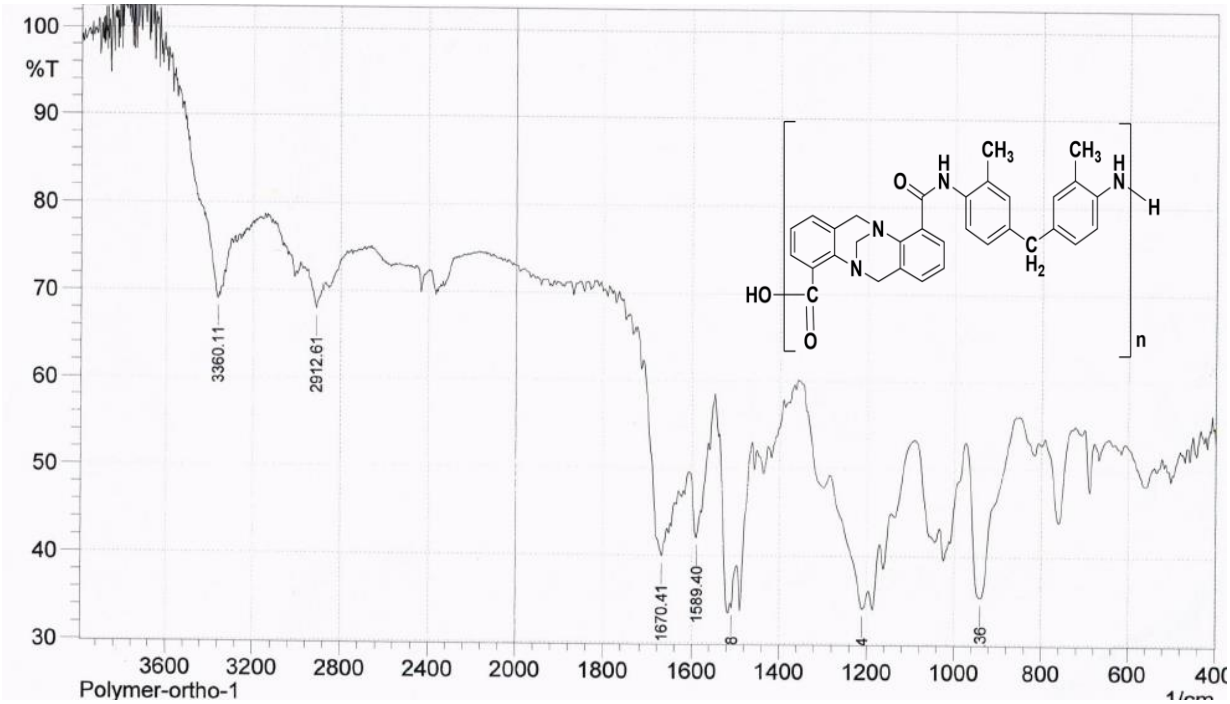


Figure 3-21:Chart of FT-IR for poly(TB1O1)

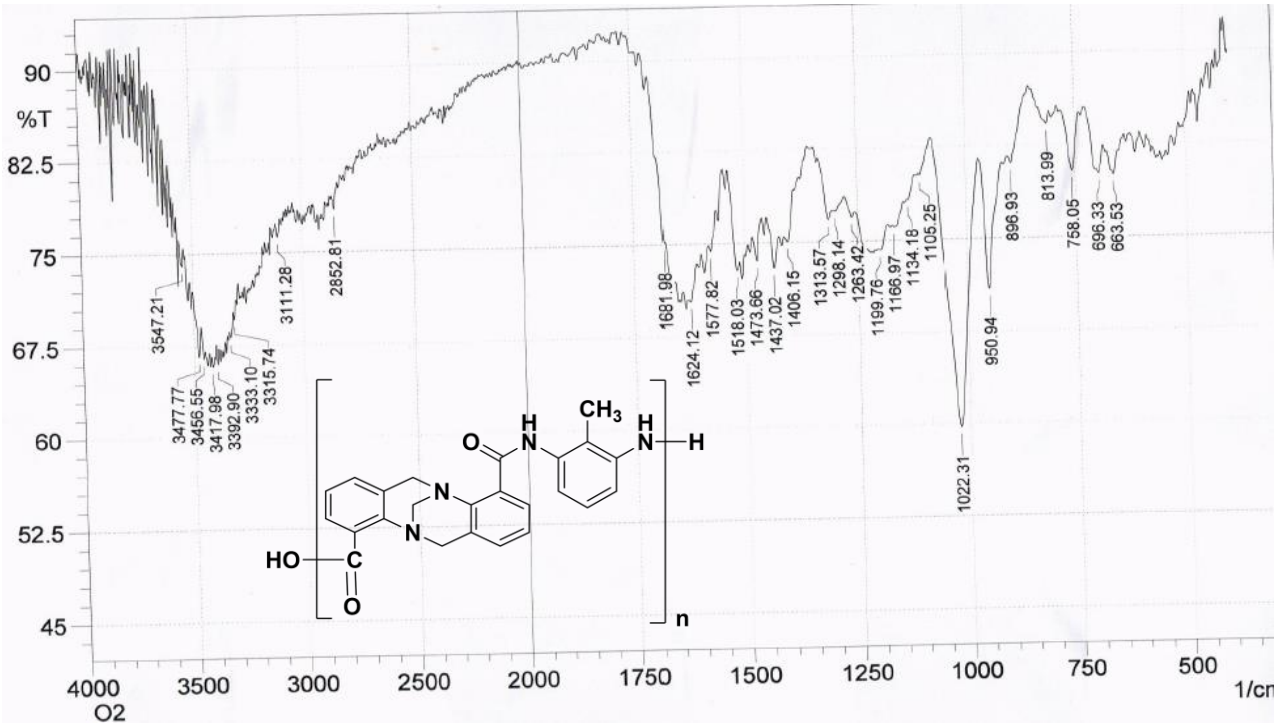


Figure 3-22: Chart of FT-IR for poly(TB1O2)

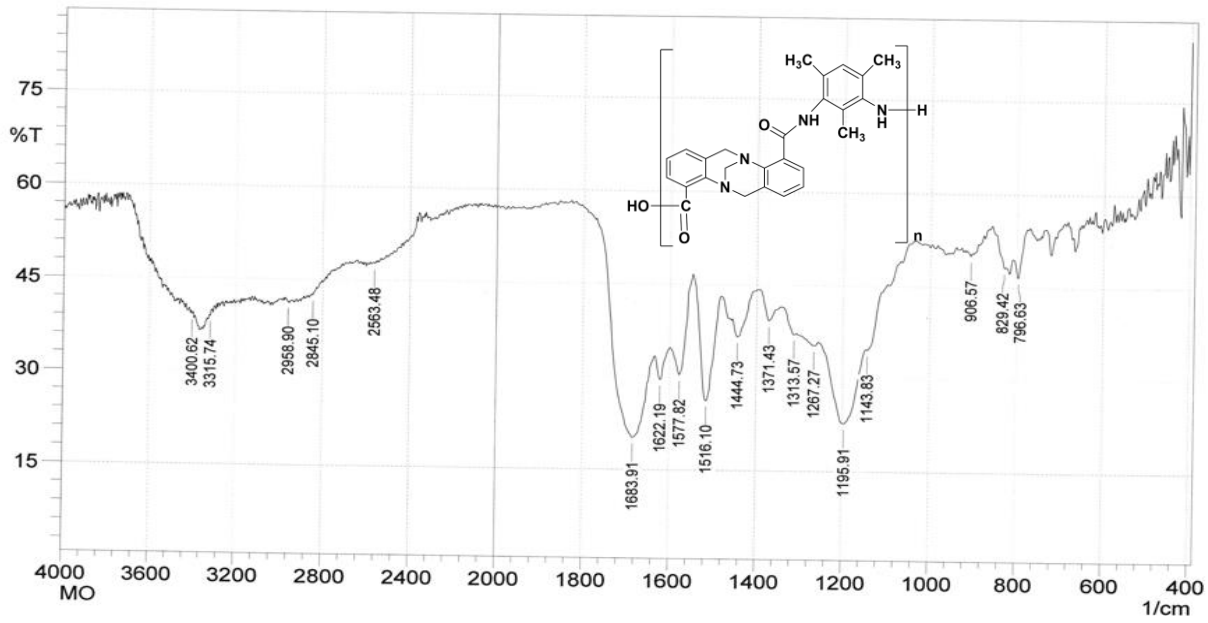


Figure 3-23: Chart of FT-IR for poly(TB1O3)

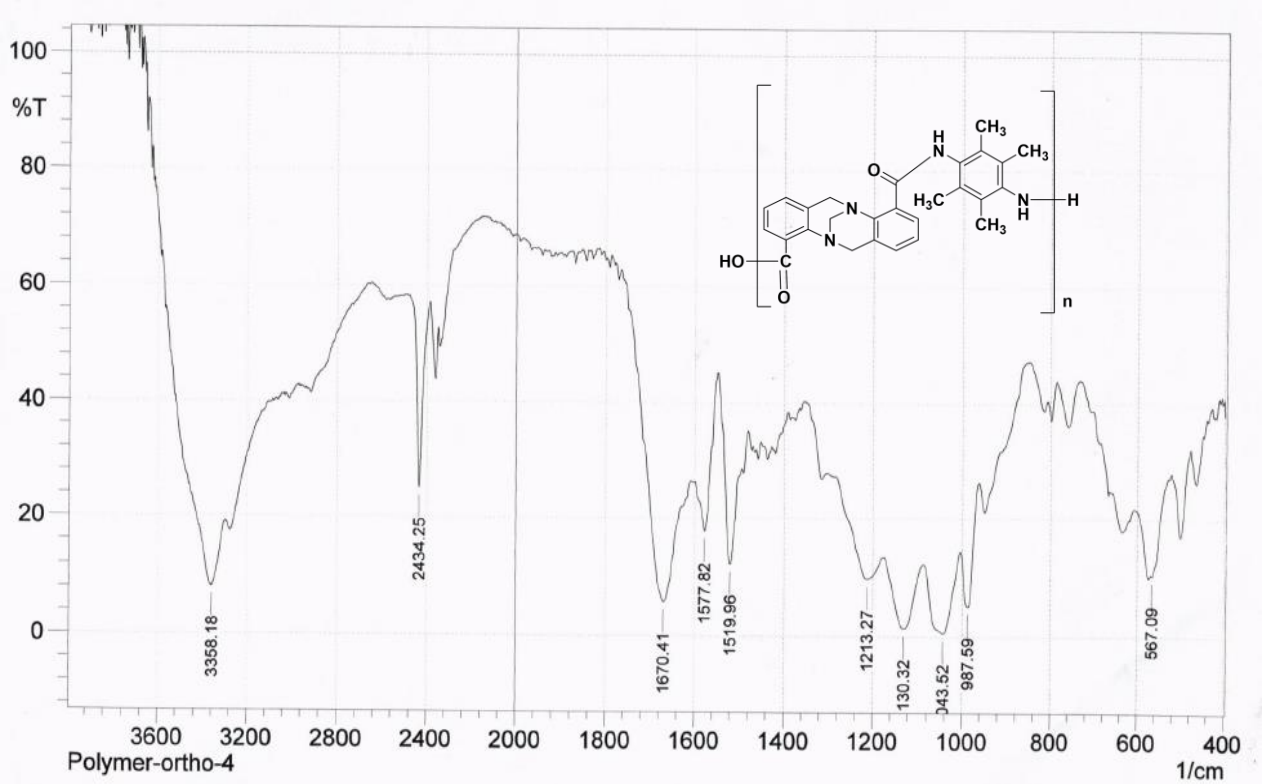


Figure 3-24: Chart of FT-IR for poly(TB1O4)

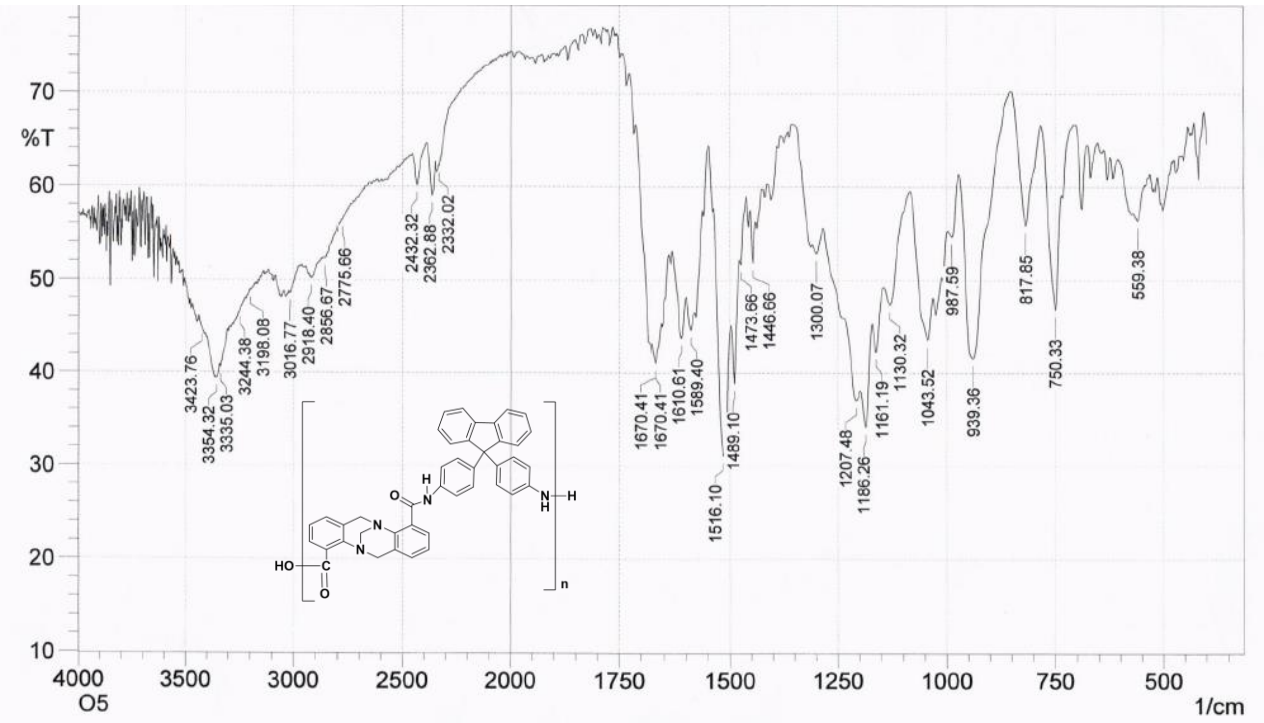


Figure 3-25: Chart of FT-IR for poly(TB1O5)

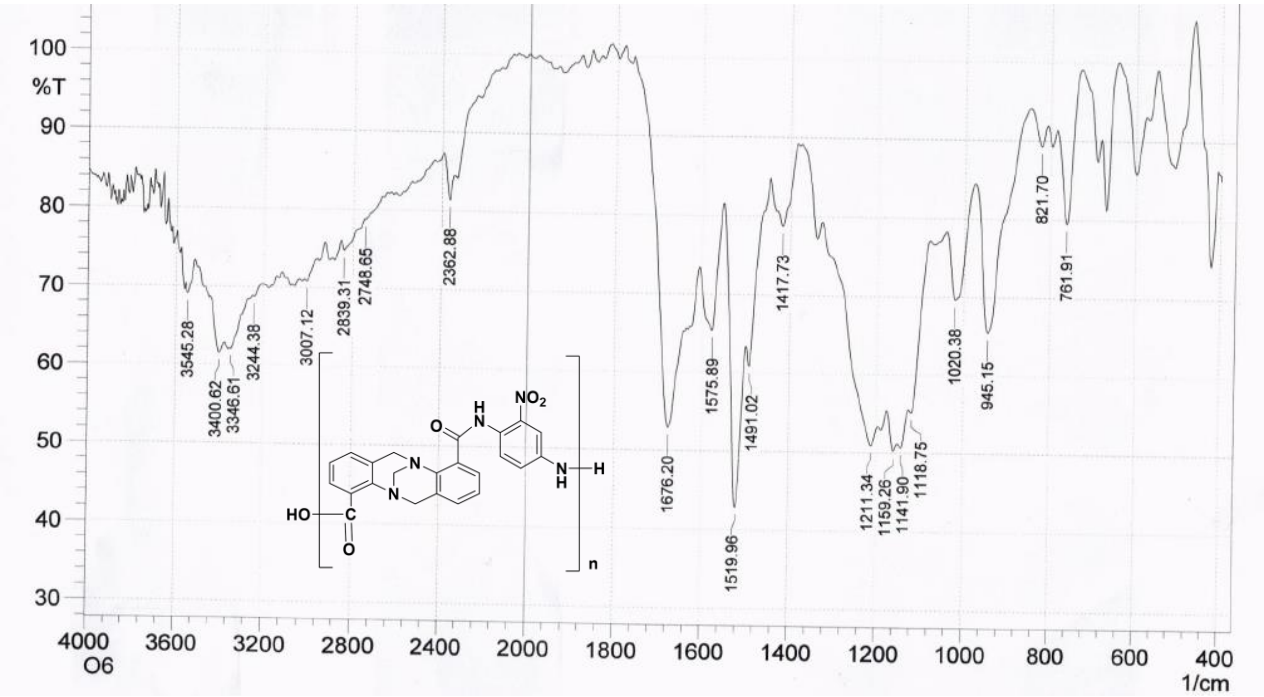


Figure 3-26:Charts of FT-IR for poly(TB1O6)

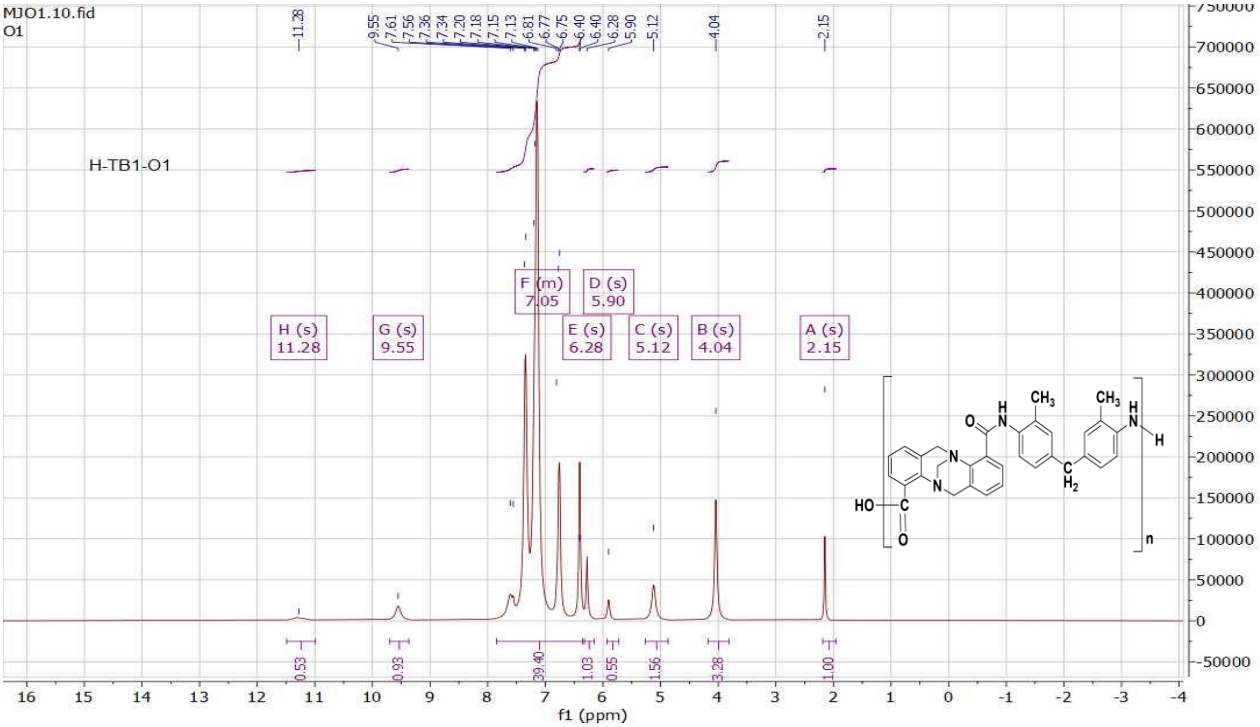


Figure 3-27: Chart of ^{1}HNMR for (TB1O1)

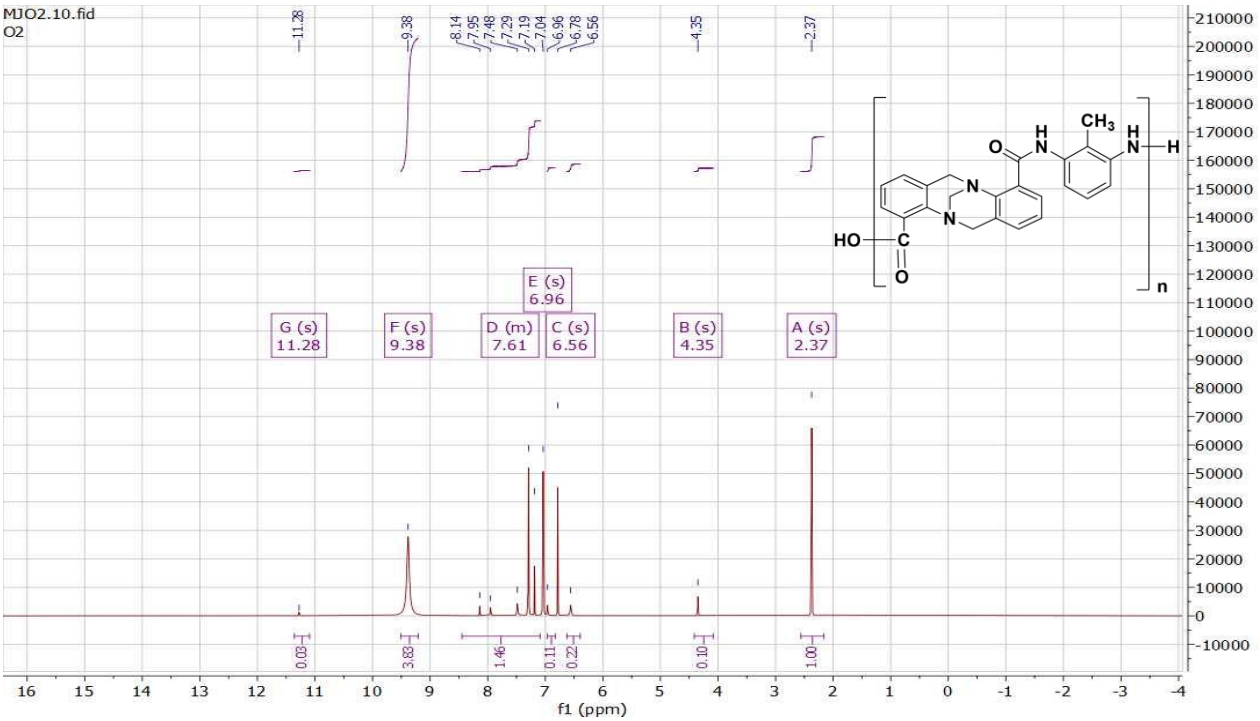


Figure 3-28 :Chart of 1HNMR for (TB1O2)

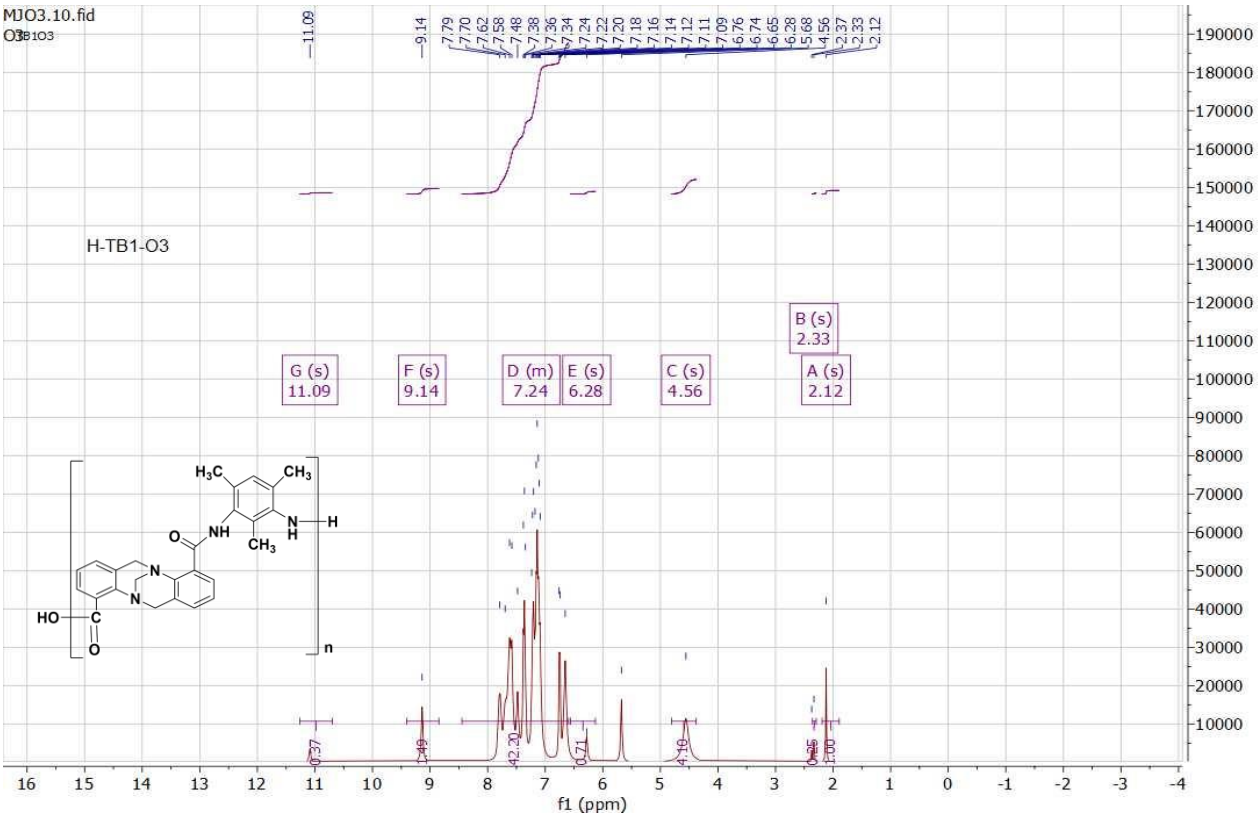


Figure 3-29:Chart of 1HNMR for (TB1O3)

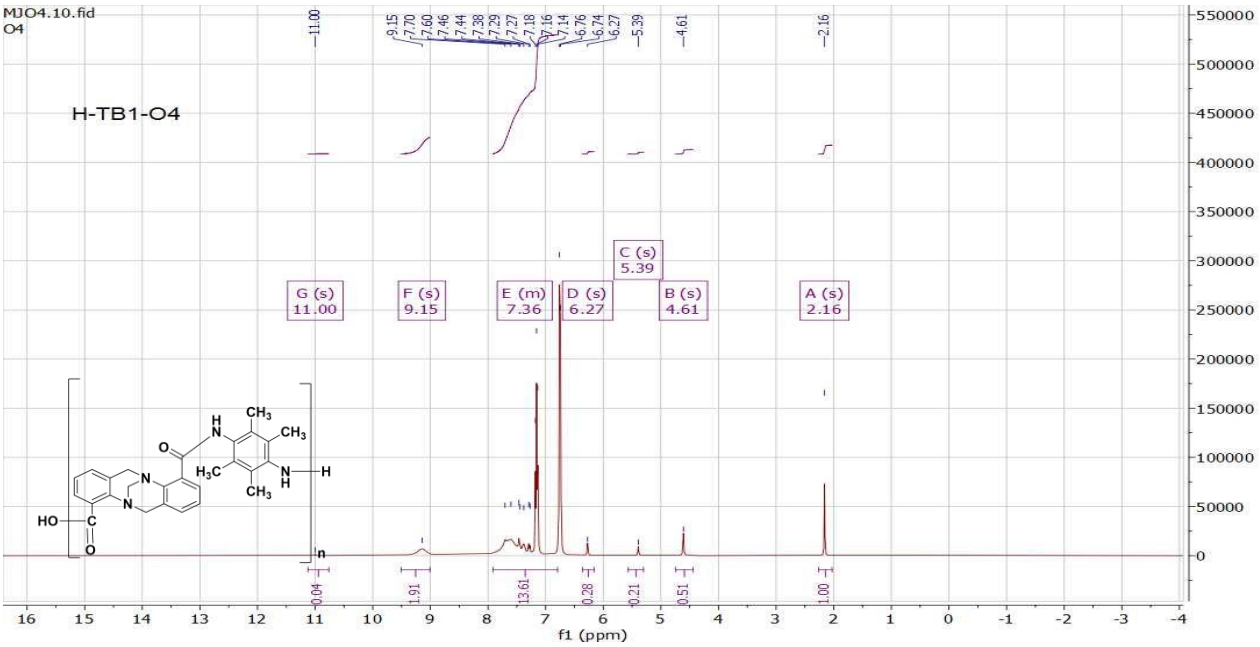


Figure 3-30:Chart of 1HNMR for (TB1O4)

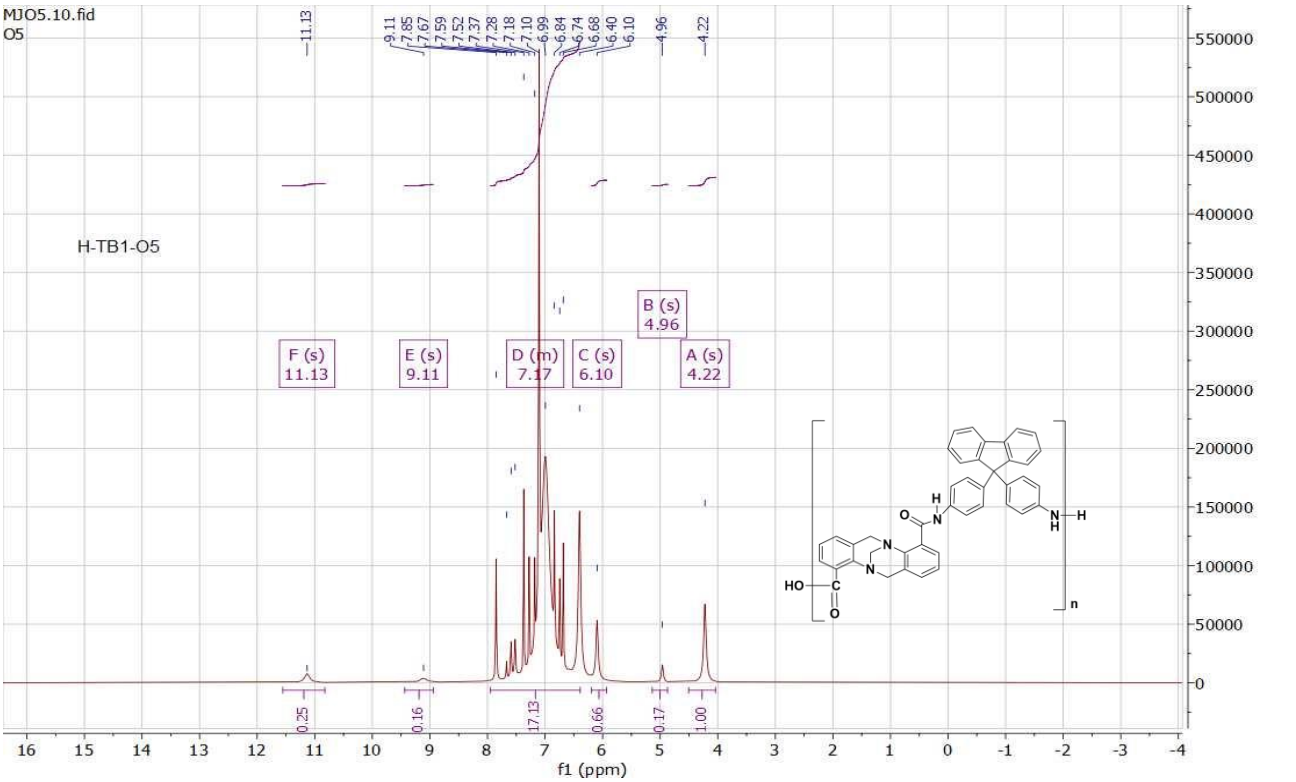


Figure 3-31:Chart of 1HNMR for (TB1O5)

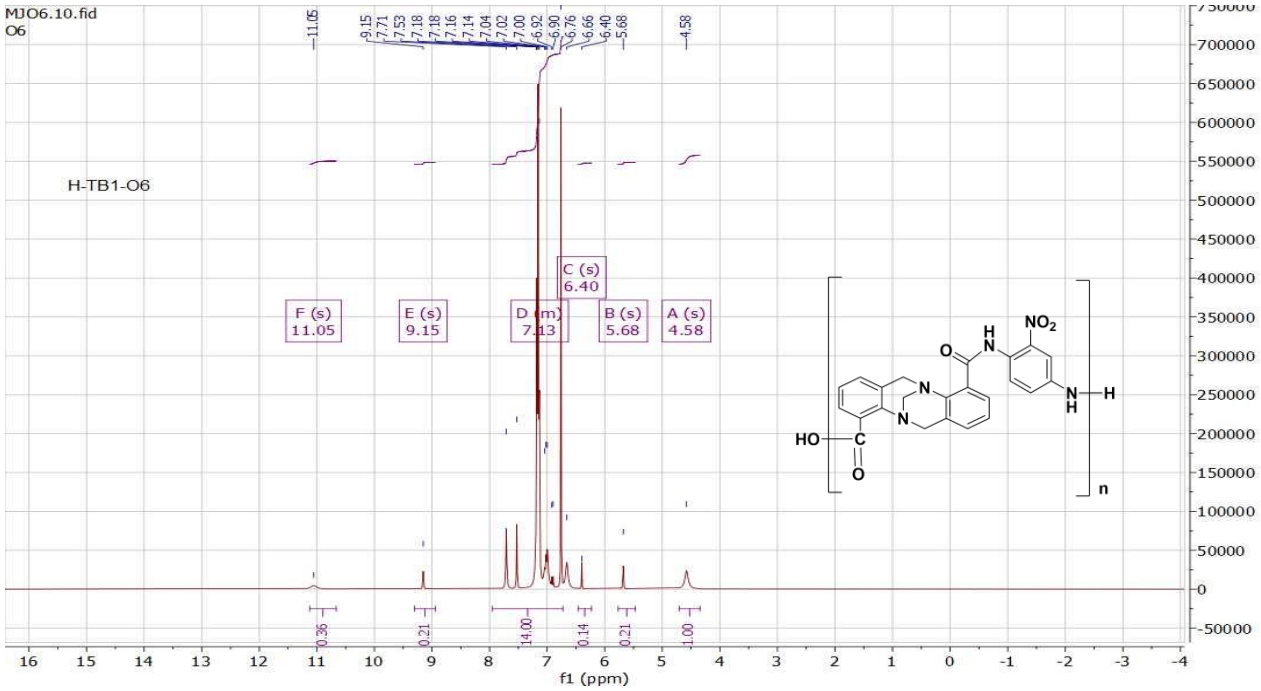


Figure 3-32:Chart of 1HNMR for (TB1O6)

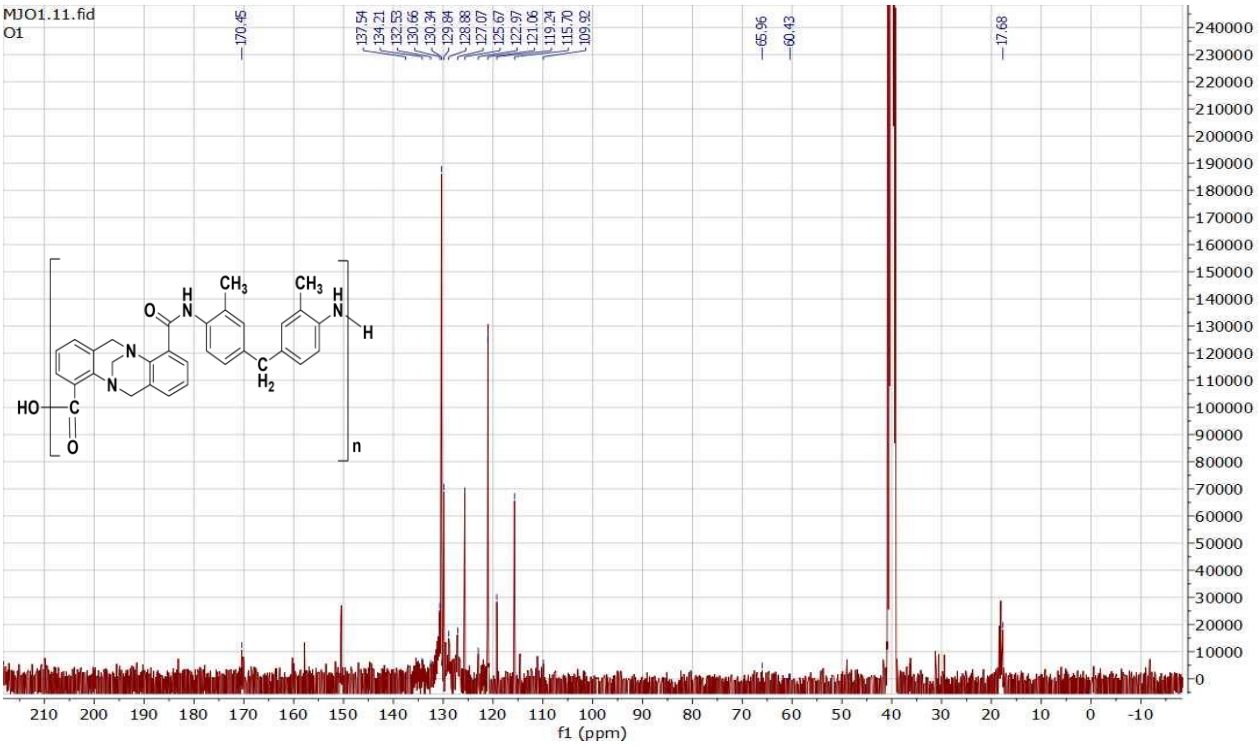


Figure 3-33 :Charts of ^{13}CNMR of (TB1O1)

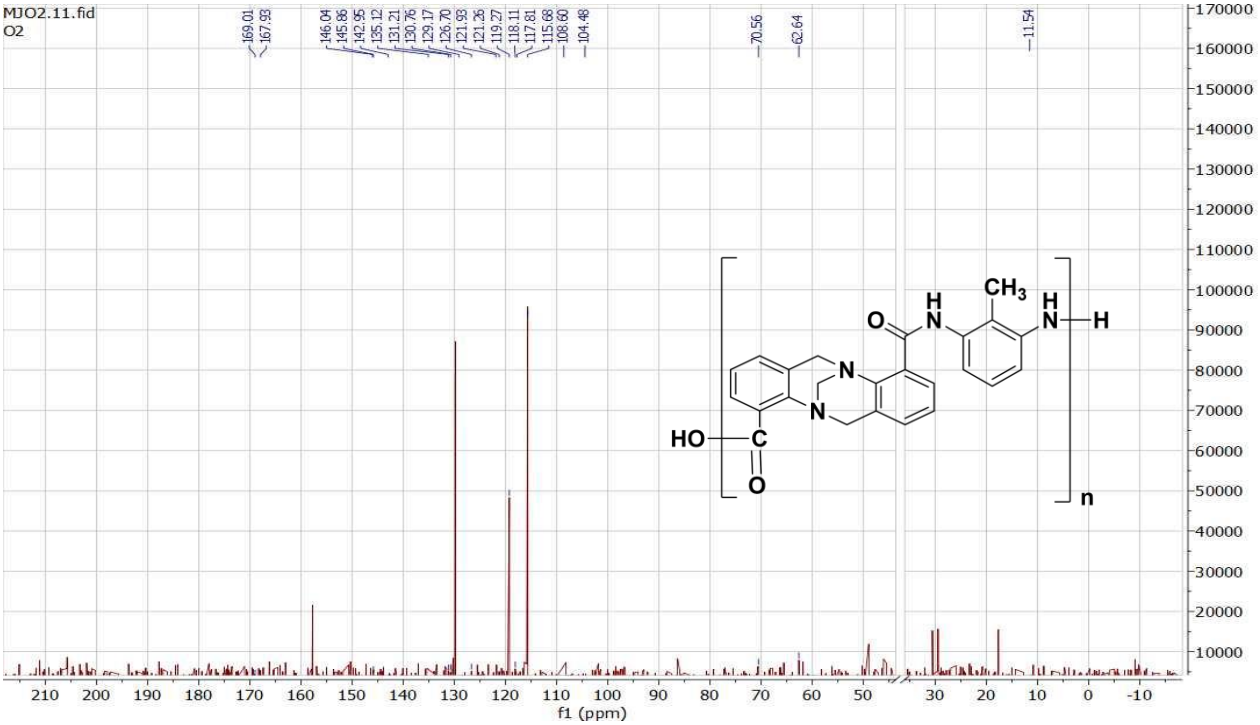


Figure 3-34 :Charts of ^{13}CNMR of (TB1O2)

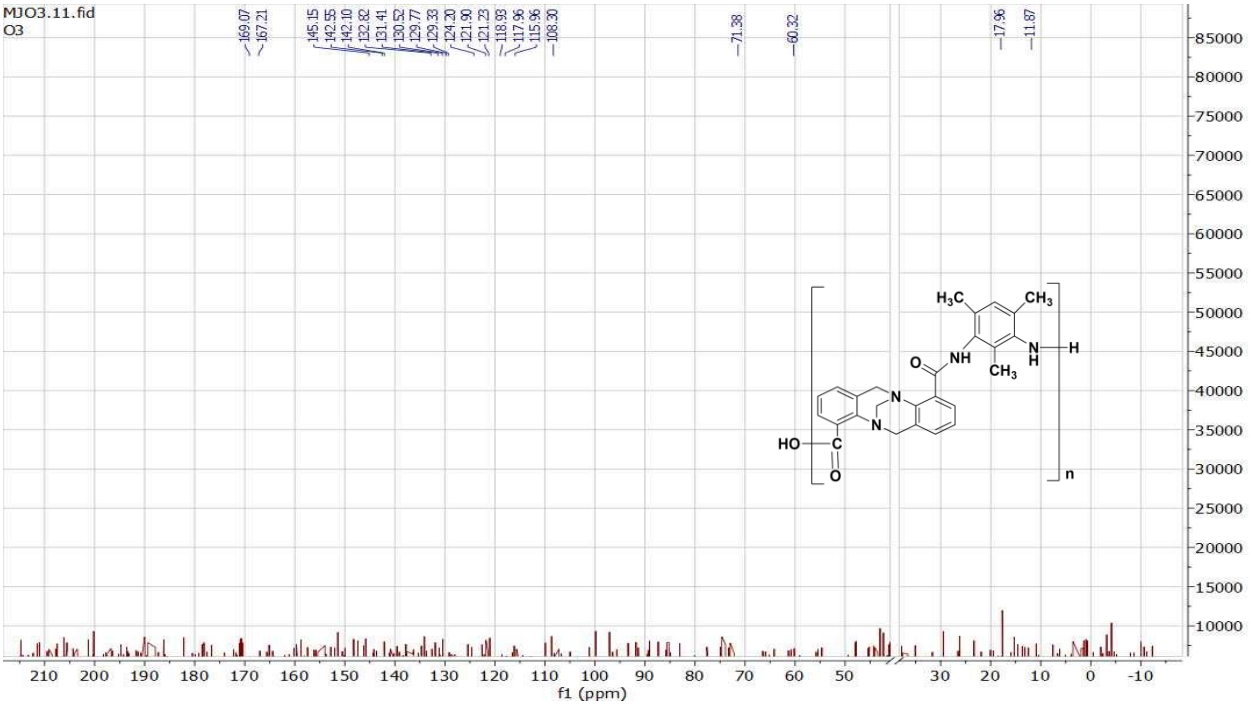


Figure 3-35:Charts of ^{13}CNMR of (TB1O3)

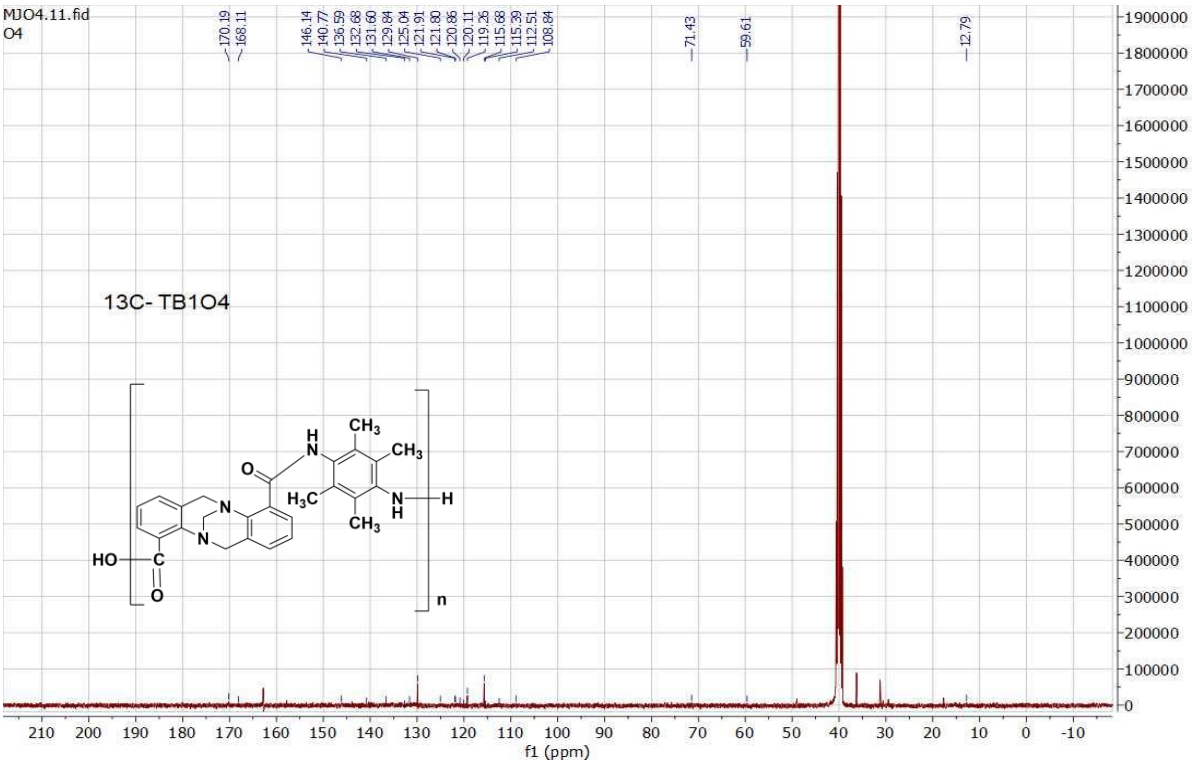


Figure 3-36:Charts of ^{13}CNMR of (TB1O4)

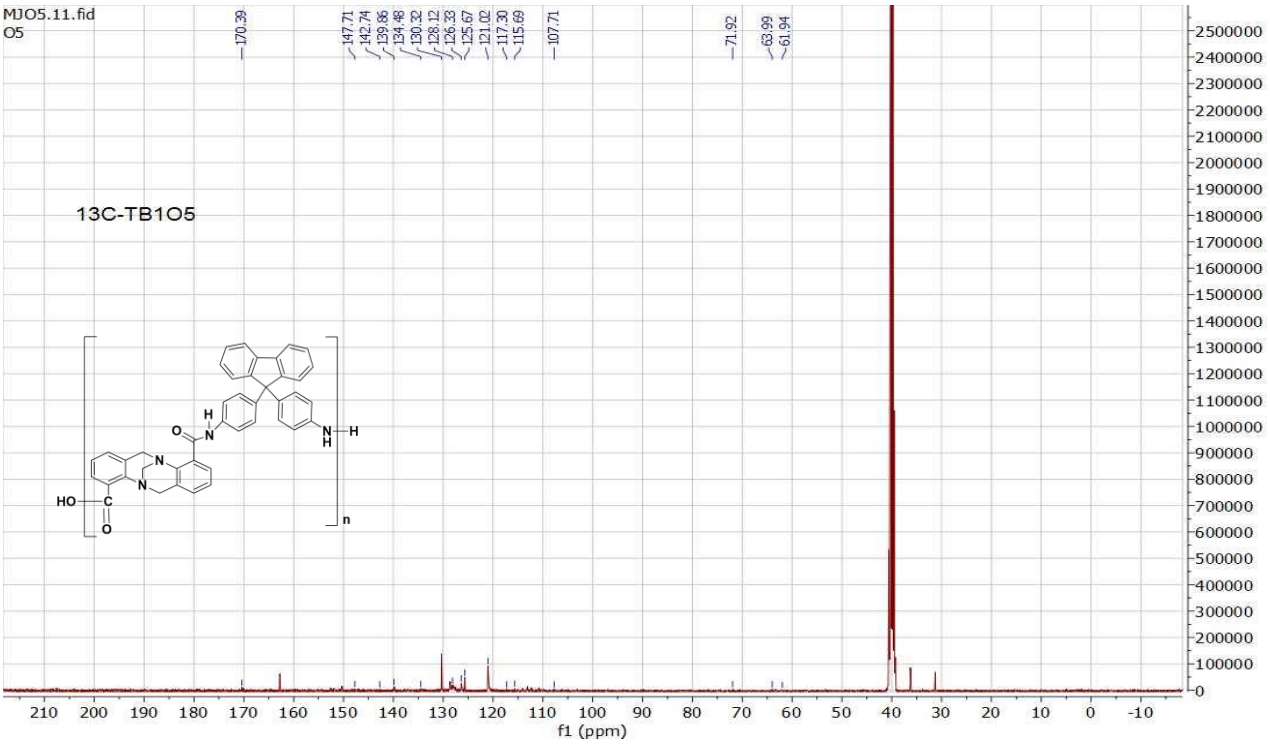


Figure 3-37:Charts of ^{13}CNMR of (TB1O5)

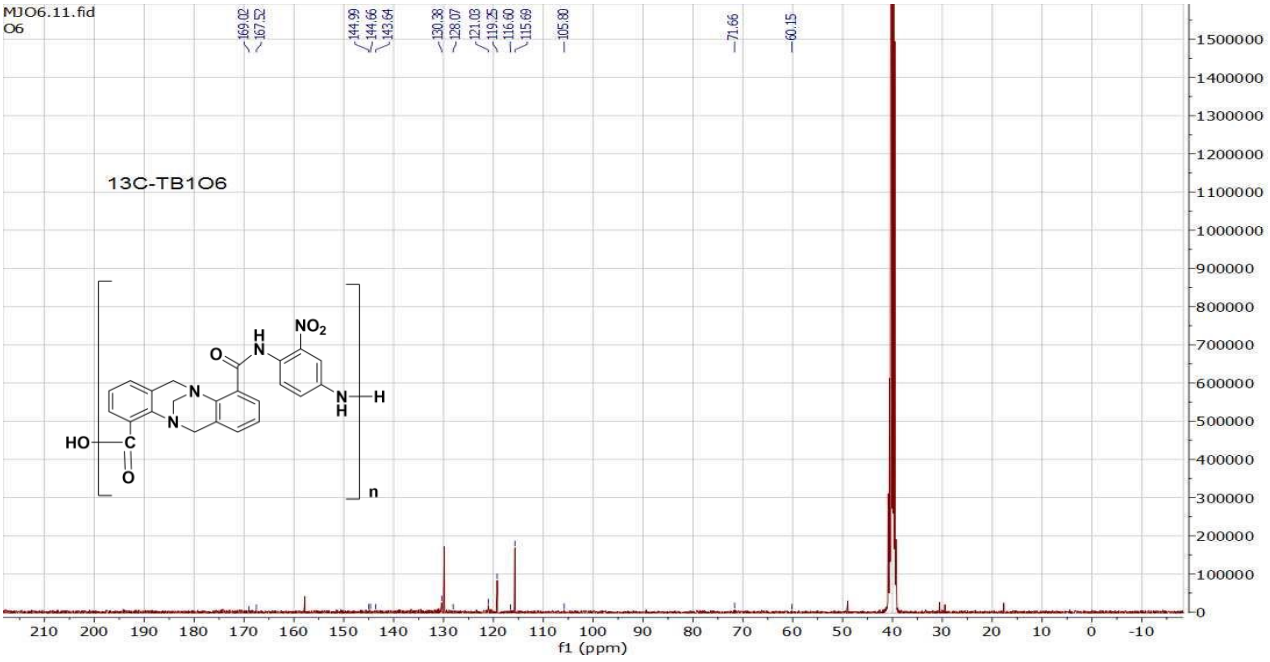


Figure 3-38:Charts of ^{13}CNMR of (TB1O6)

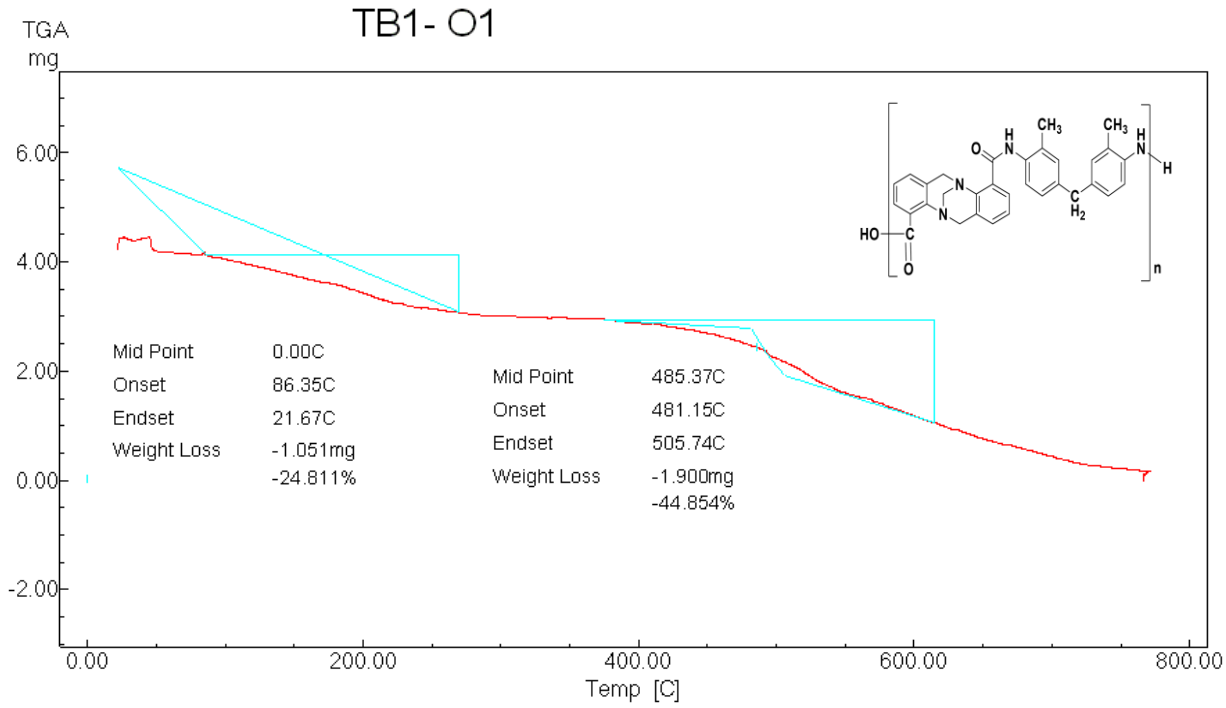


Figure 3-39: Charts of TGA for (TB1O1)

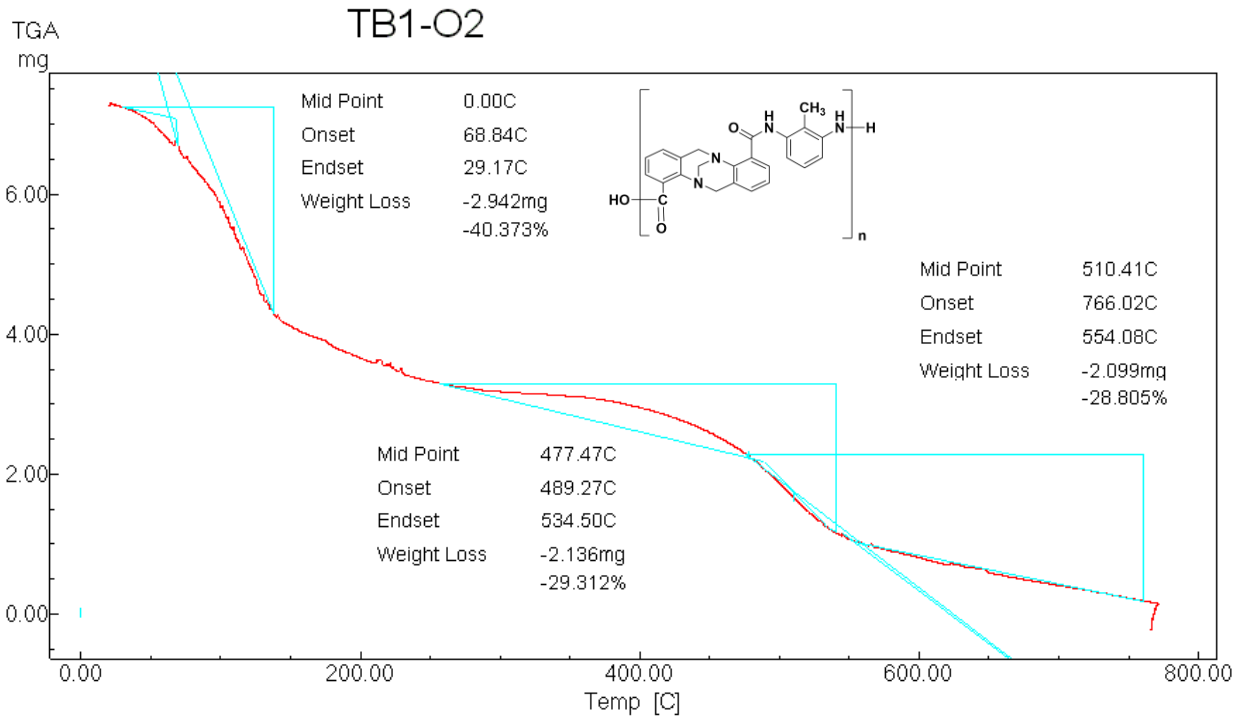


Figure 3-40 :Charts of TGA for (TB1O2)

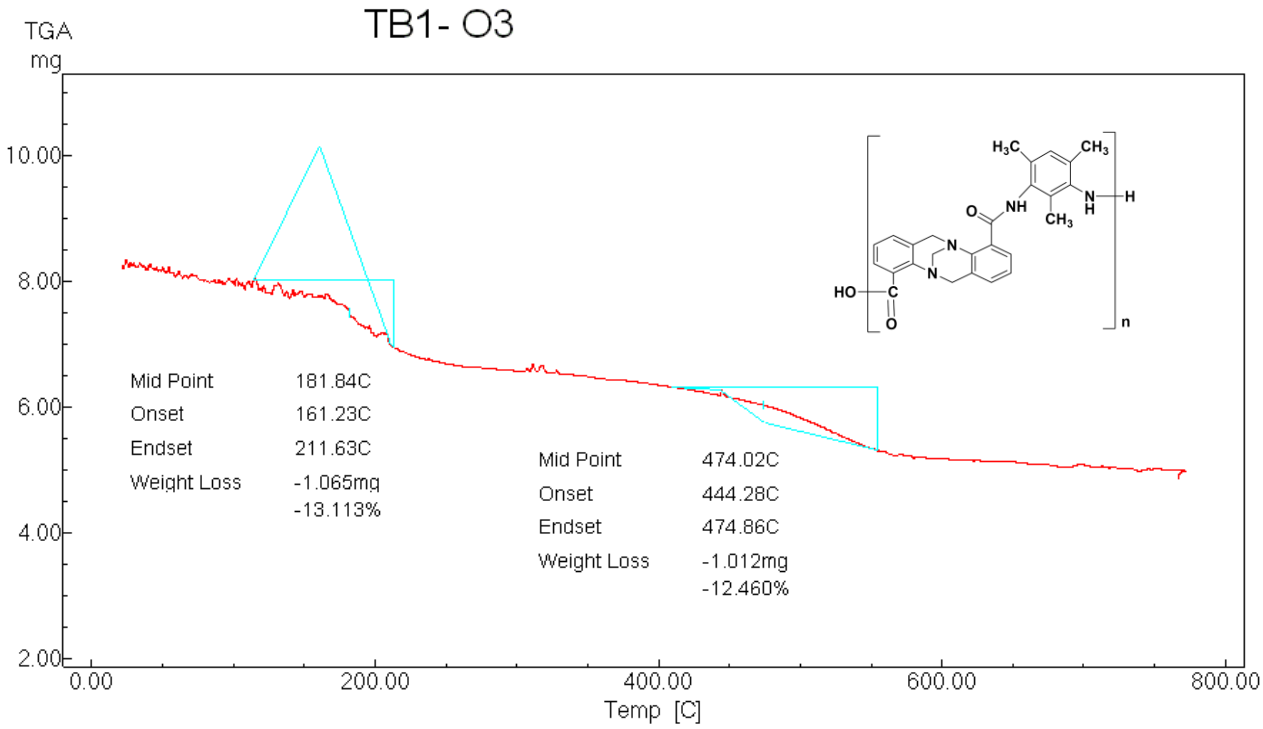


Figure 3-41: :Charts of TGA for (TB1O3)

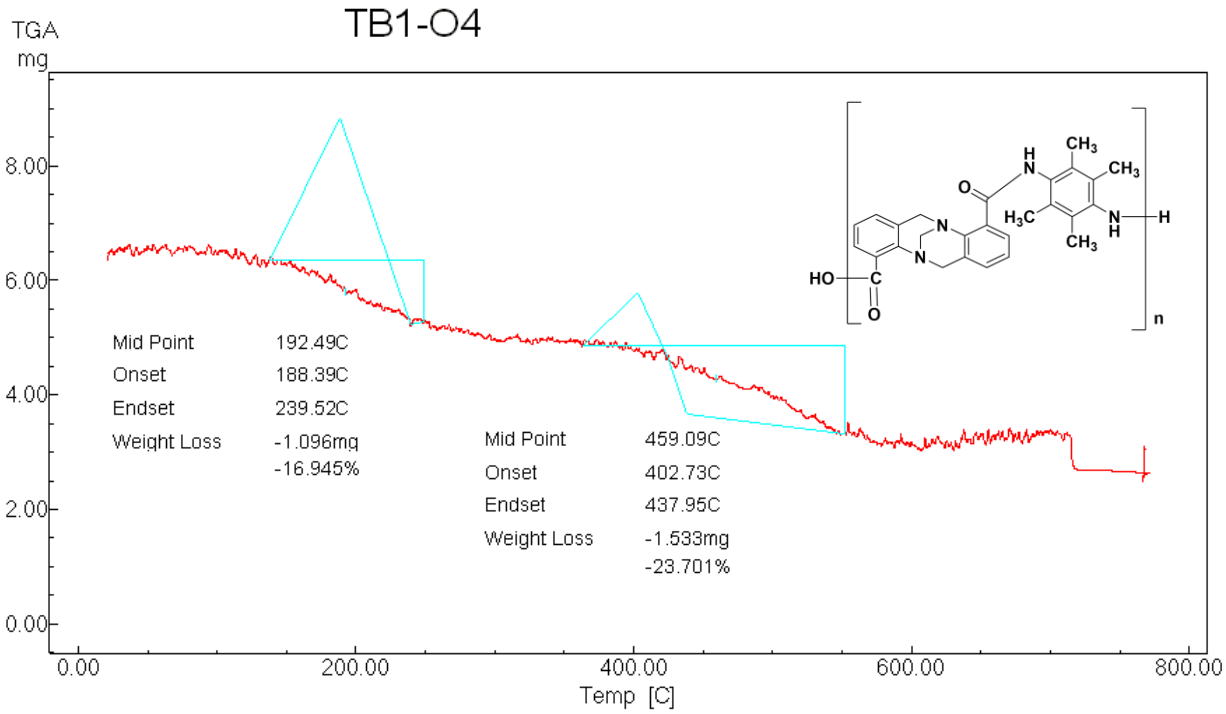


Figure 3-42:Charts of TGA for (TB1O4)

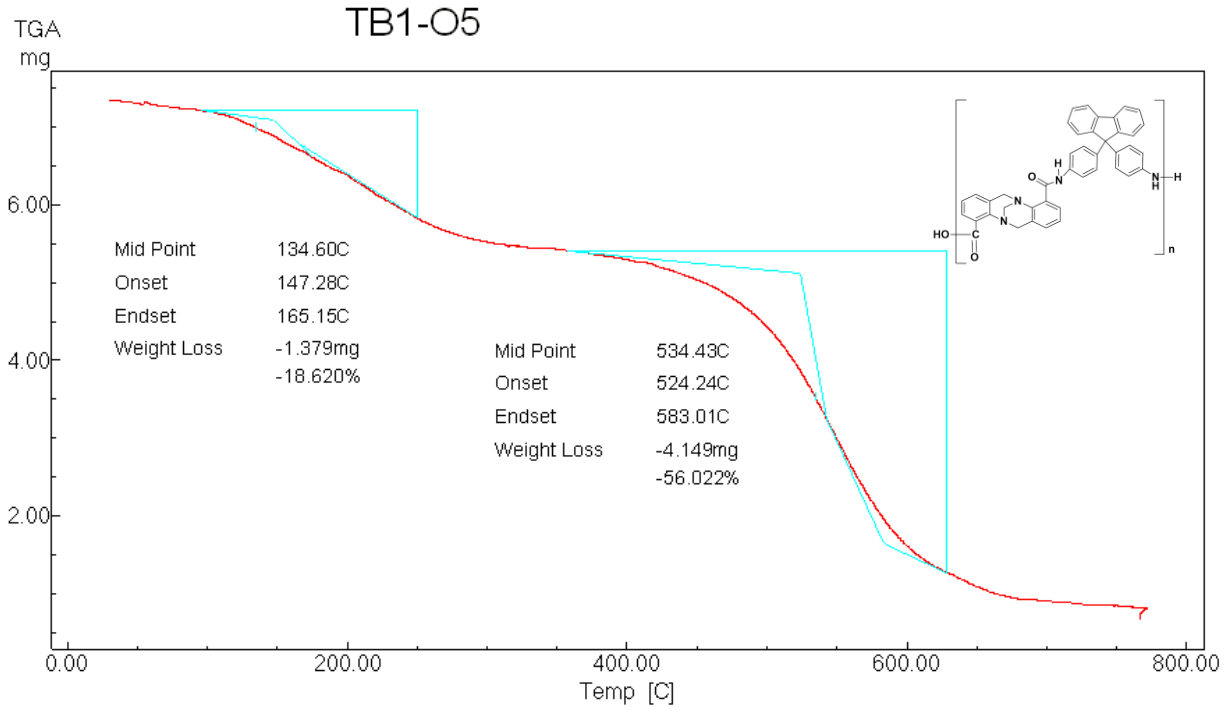


Figure 3-43 Charts of TGA for (TB1O5)

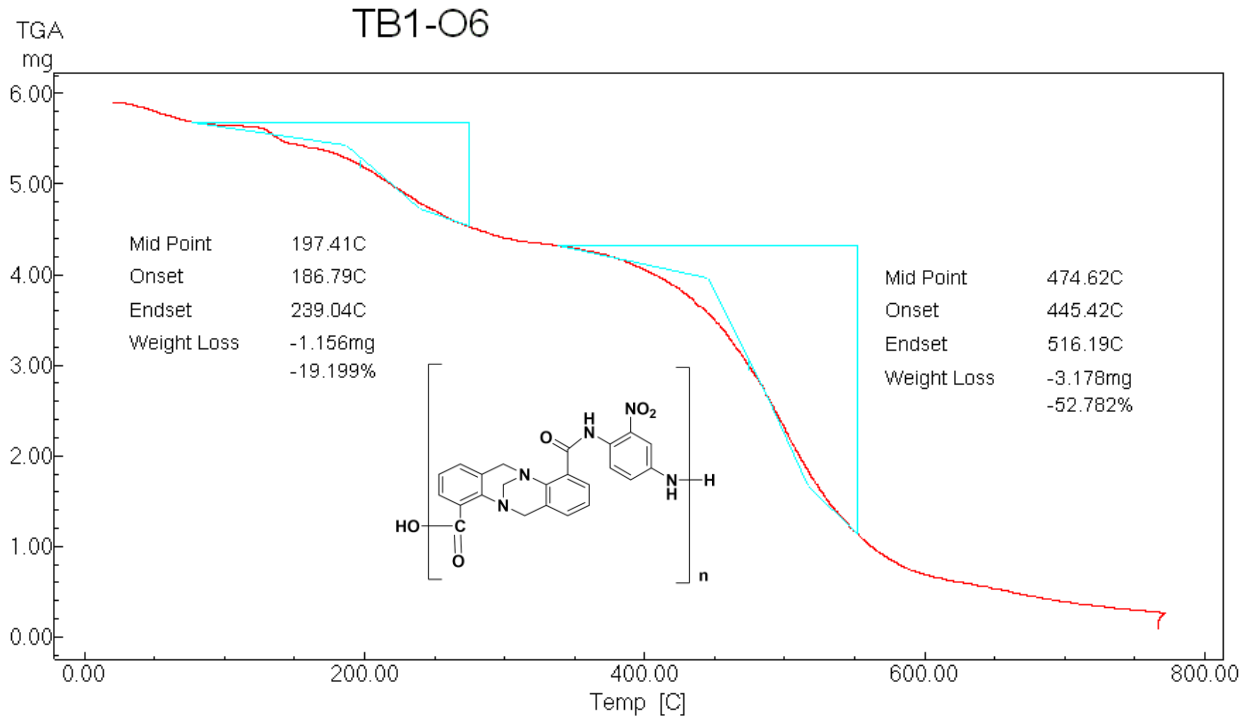
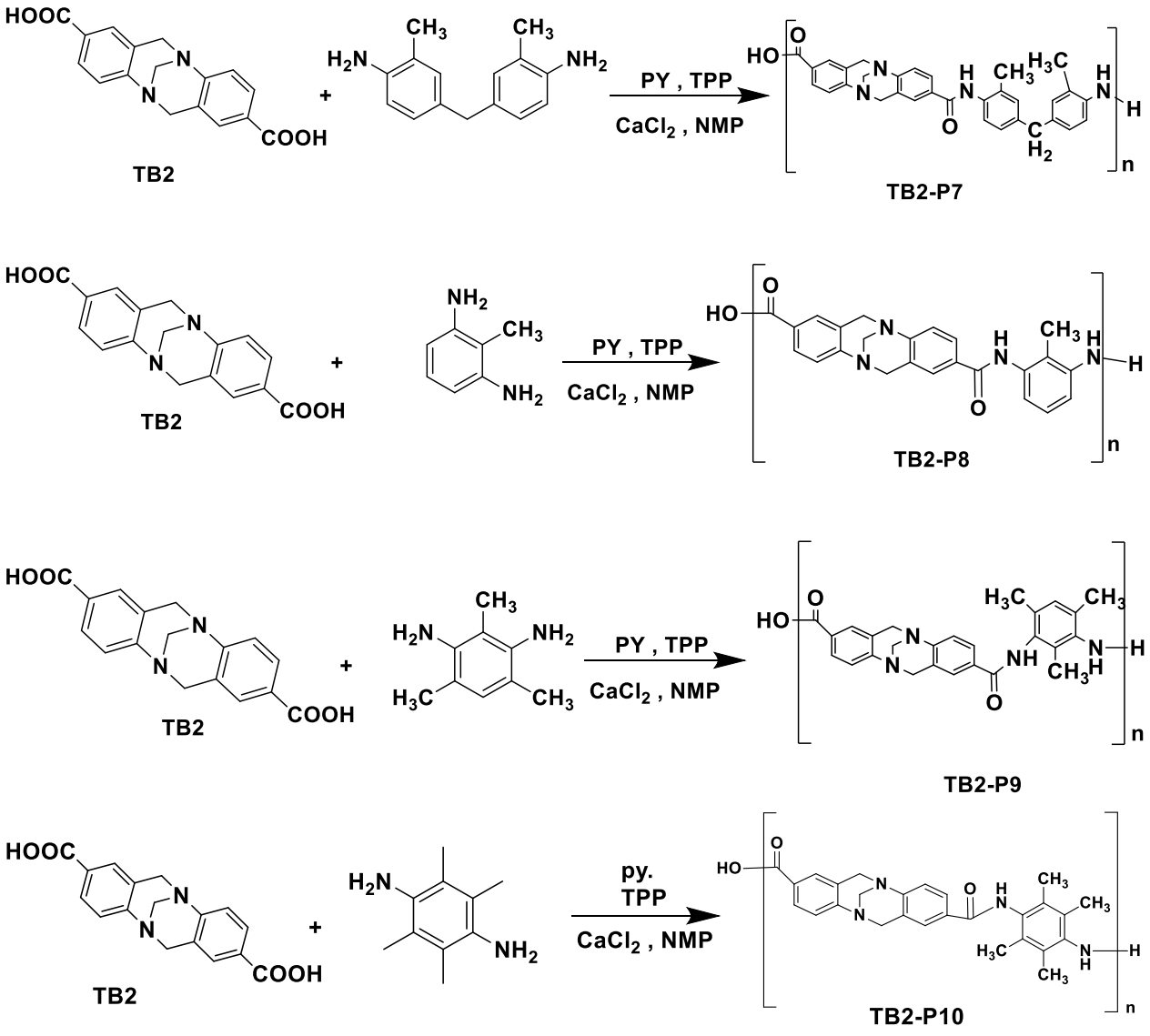
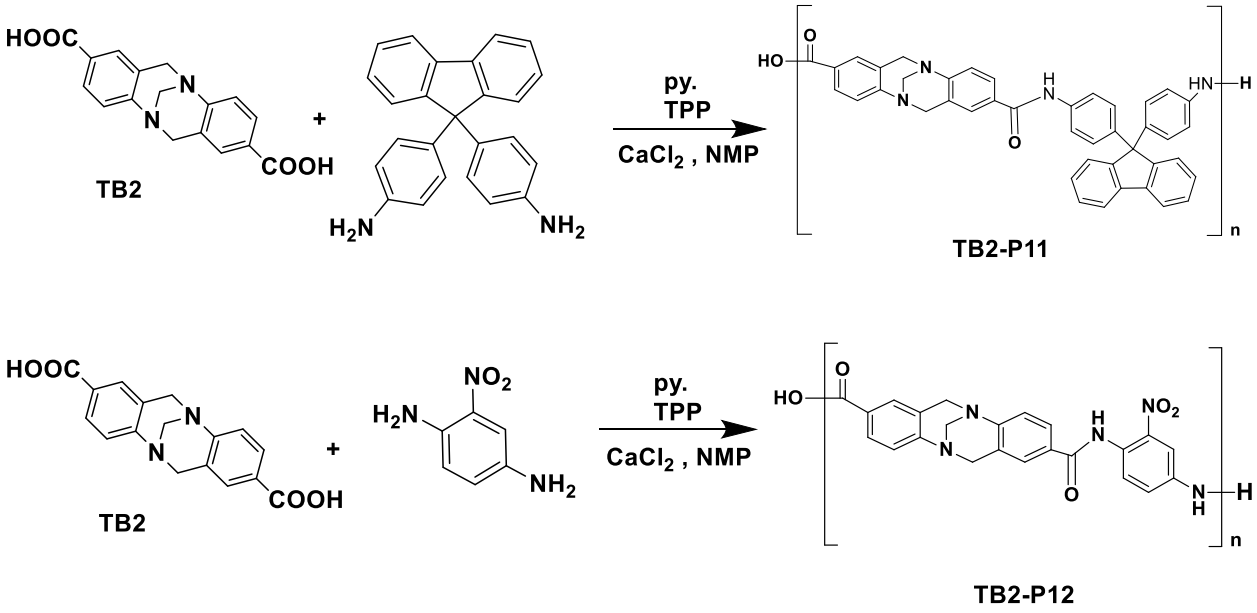


Figure 3-44: Charts of TGA for (TB1O6)

3.2.2. Synthesis and characterization of polyamides (TB2P7-TB2P12)

Synthesis of polyamides is produced from interaction (TB2) with diamine aromatic as shown in eq.(3-3)





eq.(3-3): Synthesis of polyamides (TB1-P7-TB1-P12)

eq (3-3) shows the preparation of polyamides (TB2-P7-TB2-P12), the determination of the compounds by FT-IR as shown in (Table 3-9) and (Figures 3-45 to 3-50) Also, it is identified by ^{1}HNMR (Table 3-10) and (Figures 3-51 to 3-55), ^{13}CNMR (Table 3-11) and (Figure 3-56 to 3-61), and TGA (Table 3-12) and (Figures 3-62 to 3-67)

Table 3-9:Functional Groups Values in FT-IR for Polymers (TB2P7- TB2P12)

Model number	N-H_2 terminal	COOH terminal	N-H-C=O
TB2-P7	3450 , 3358	3273-2450	1668
TB2-P8	3510 , 3377	3219-2440	1664
TB2-P9	3389 , 3335	3330-2580	1660
TB2-P10	3400 , 3329	3209-2400	1668
TB2-P11	3400 , 3338	3234-2500	1666
TB2-P12	3471 , 3371	3200-2400	1660

Table 3-10: Functional Groups Values in ^{1}HNMR for Polymers (TB2-P7- TB2-P12)

Model	N-H_2	COOH	N-H-
TB2-P7	6.28	10.92	9.15
TB2-P8	6.27	11.08	9.15
TB2-P9	6.28	10.94	8.58
TB2-P10	5.88	10.57	8.58
TB2-P11	6.33	11.31	9.15
TB2-P12	6.59	11.28	9.83

Table 3-11:Functional Groups Values in ^{13}CNMR for Polymers (TB2-P7- TB2-P12)

Model	C_{Ar}-N-H_2	COOH	N-H-
TB2-P7	141.87	174.29	165.78
TB2-P8	146.44	169.17	164.63
TB2-P9	142.41	169.04	163.86
TB2-P10	148.11	169.06	167.04
TB2-P11	143.02	168.48	164.51
TB2-P12	144.18	169.34	164.77

Table 3-12 :TGA Study of Polymers (TB2P7-TB2P12)

Model number	Initial Degradation	Final Degradation
TB2-P7	158.75 - 182.77	332.35 - 320.67
TB2-P8	35.30 - 14.97	328.92 - 351.53
TB2-P9	160.79 - 202.19	343.01 - ˉ4860.52
TB2-P10	110.28 - 65.79	465.29 - 473.06
TB2-P11	130.09 - 145.65	392.34 - 394.14
TB2-P12	232.95 - 222.18	572.86 - 577.57

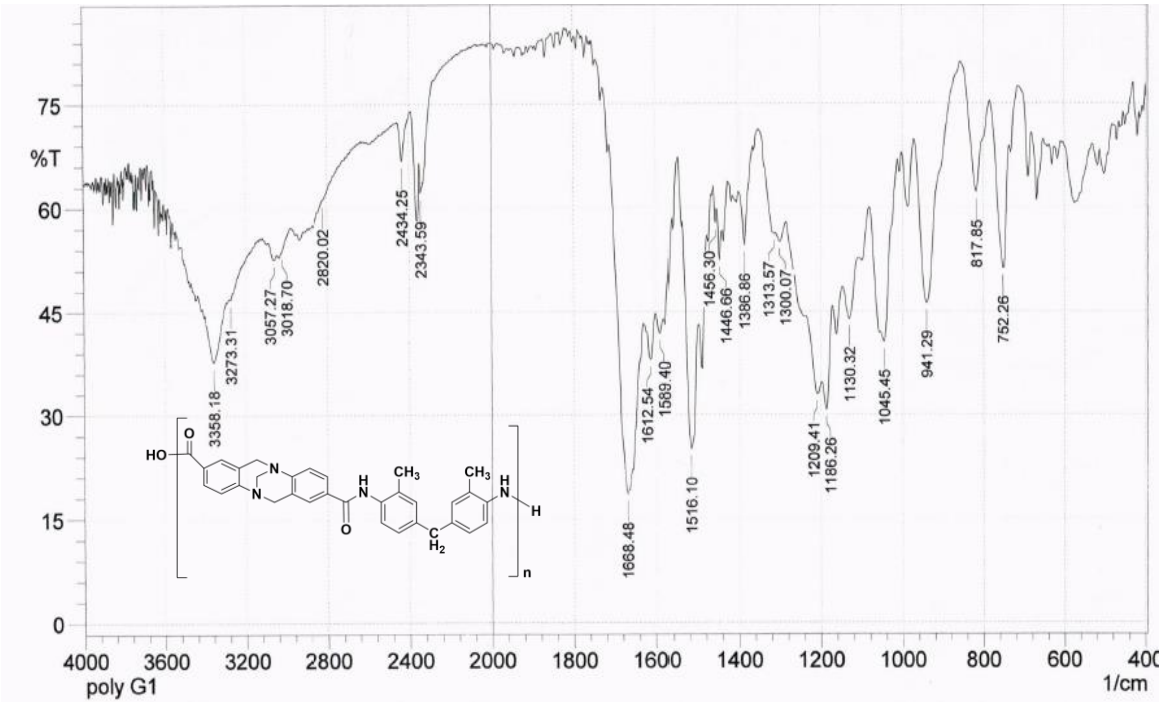


Figure 3-45:Chart of FT-IR for (TB2P7)

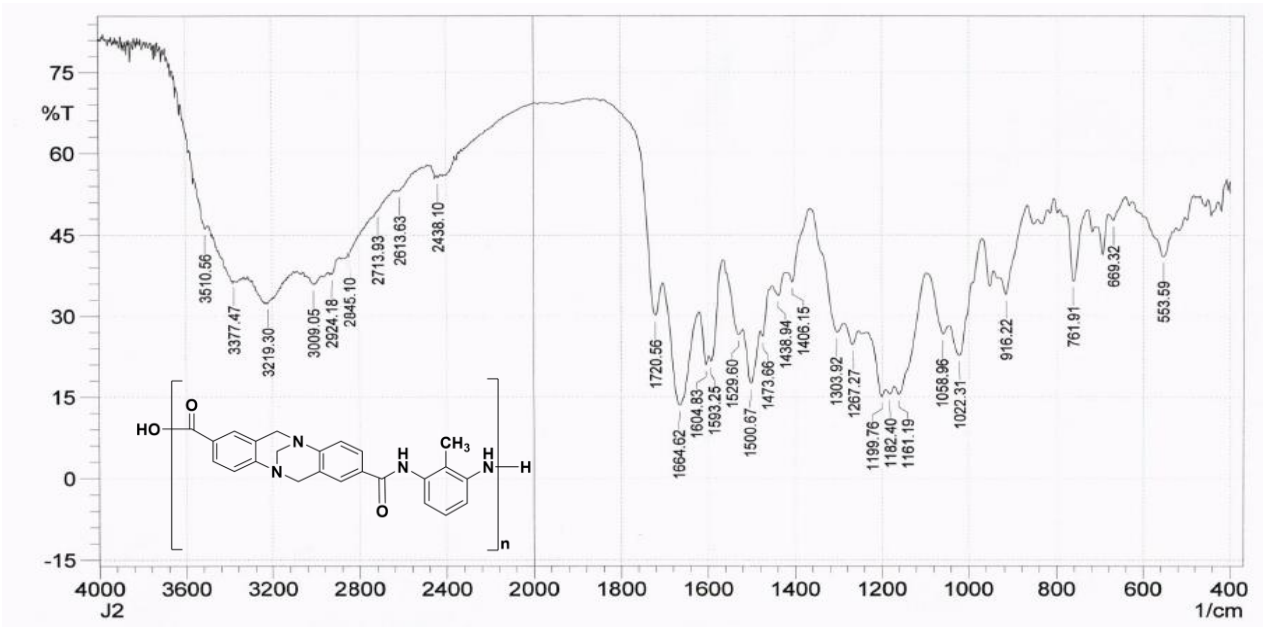


Figure 3-46:Chart of FT-IR for (TB2P8)

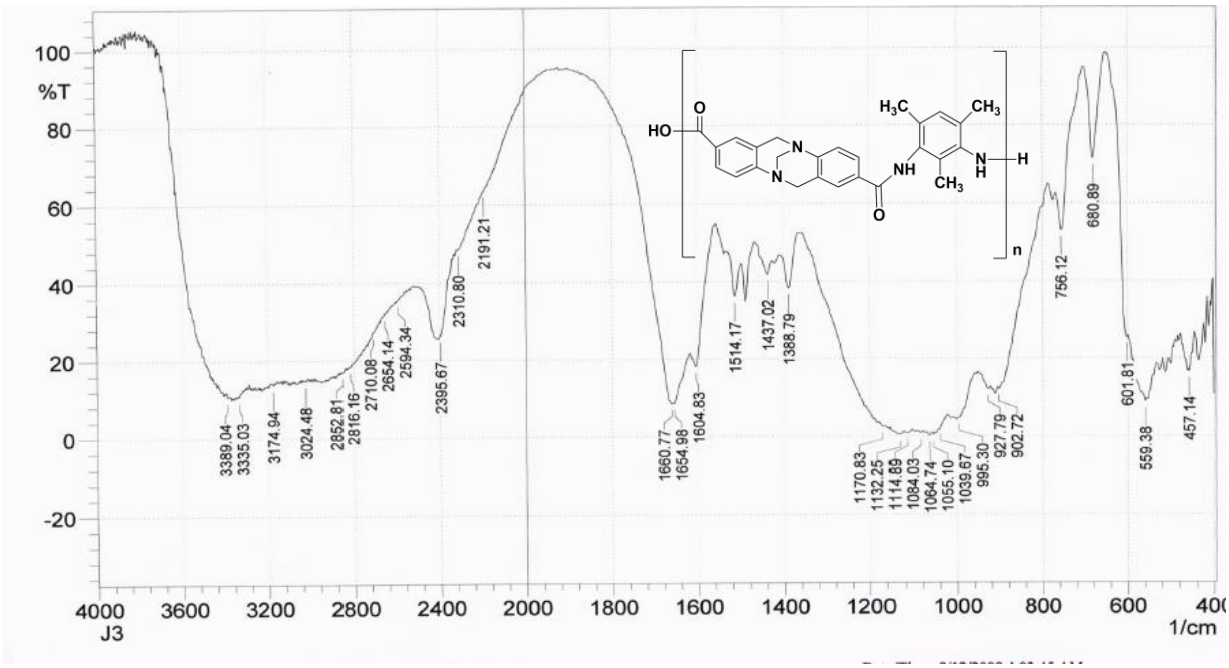


Figure 3-47:Chart of FT-IR for (TB2P9)

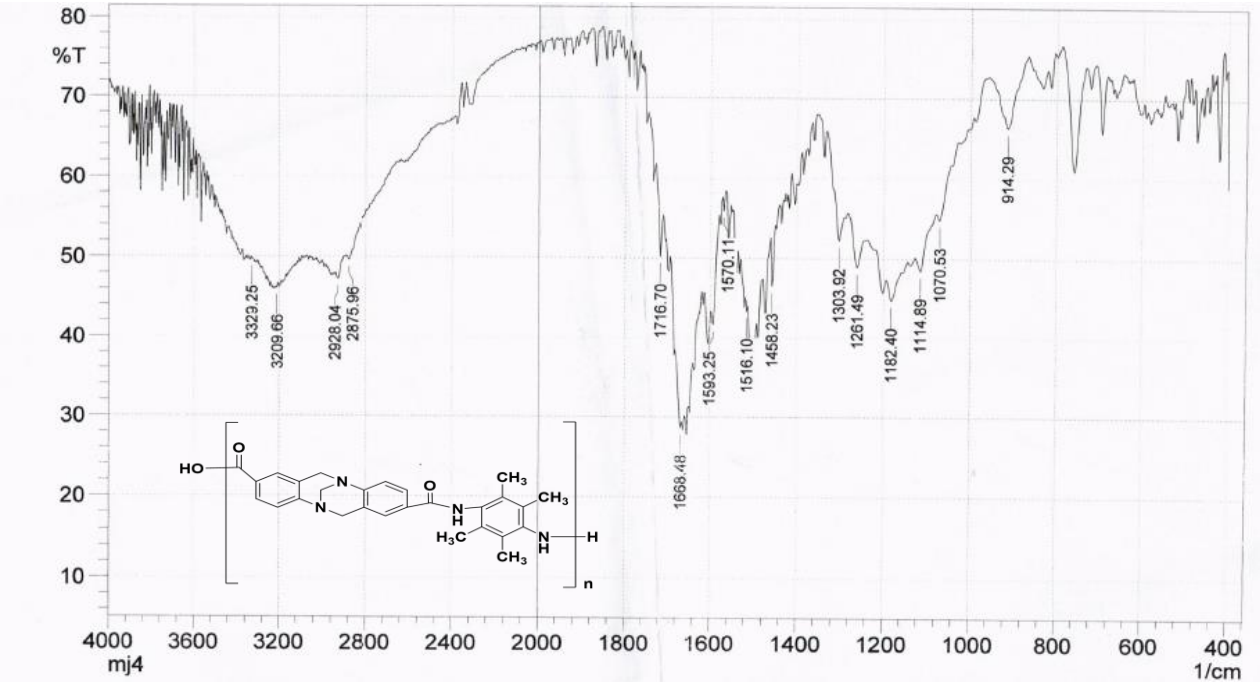


Figure 3-48:Chart of FT-IR for (TB2P10)

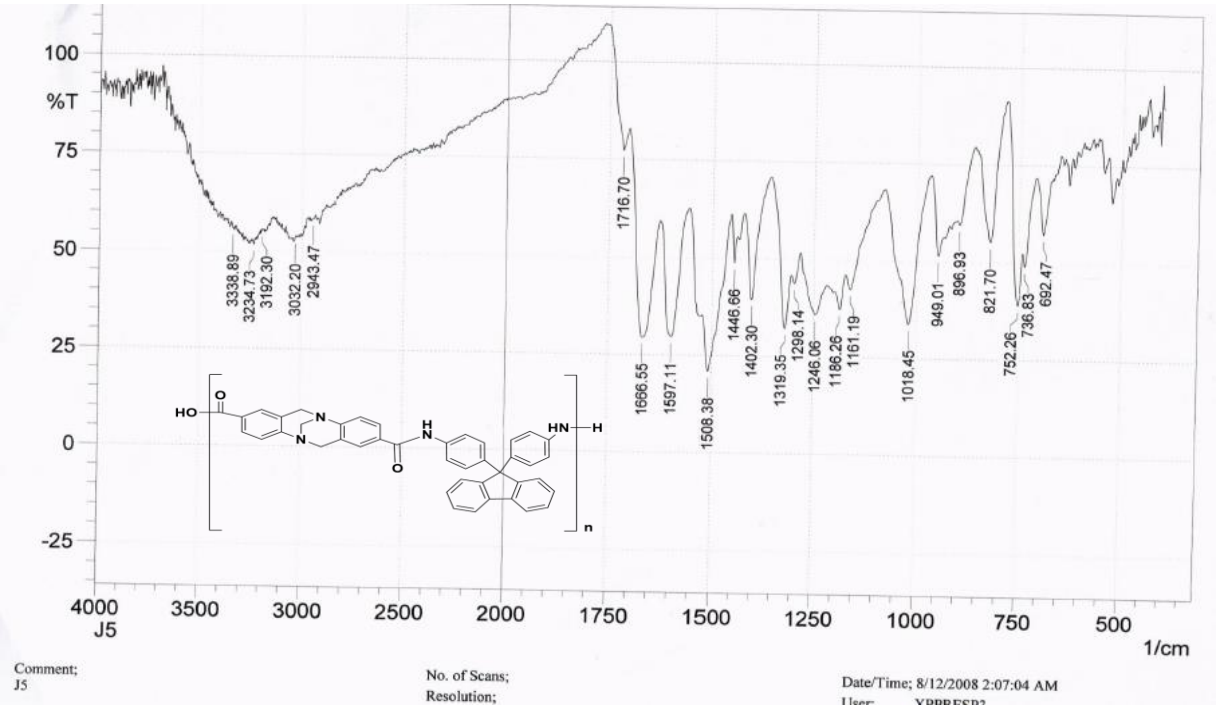


Figure 3-49:Chart of FT-IR for (TB2P11)

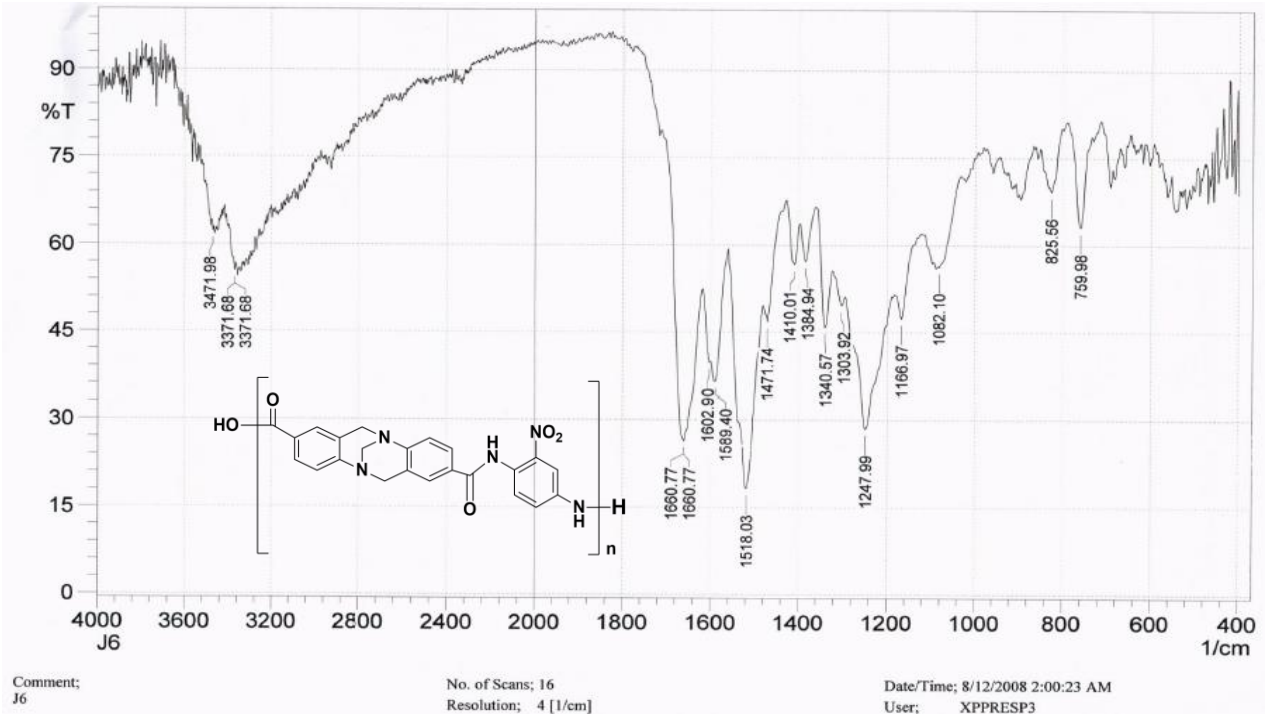


Figure 3-50 :Chart of FT-IR for (TB2P12)

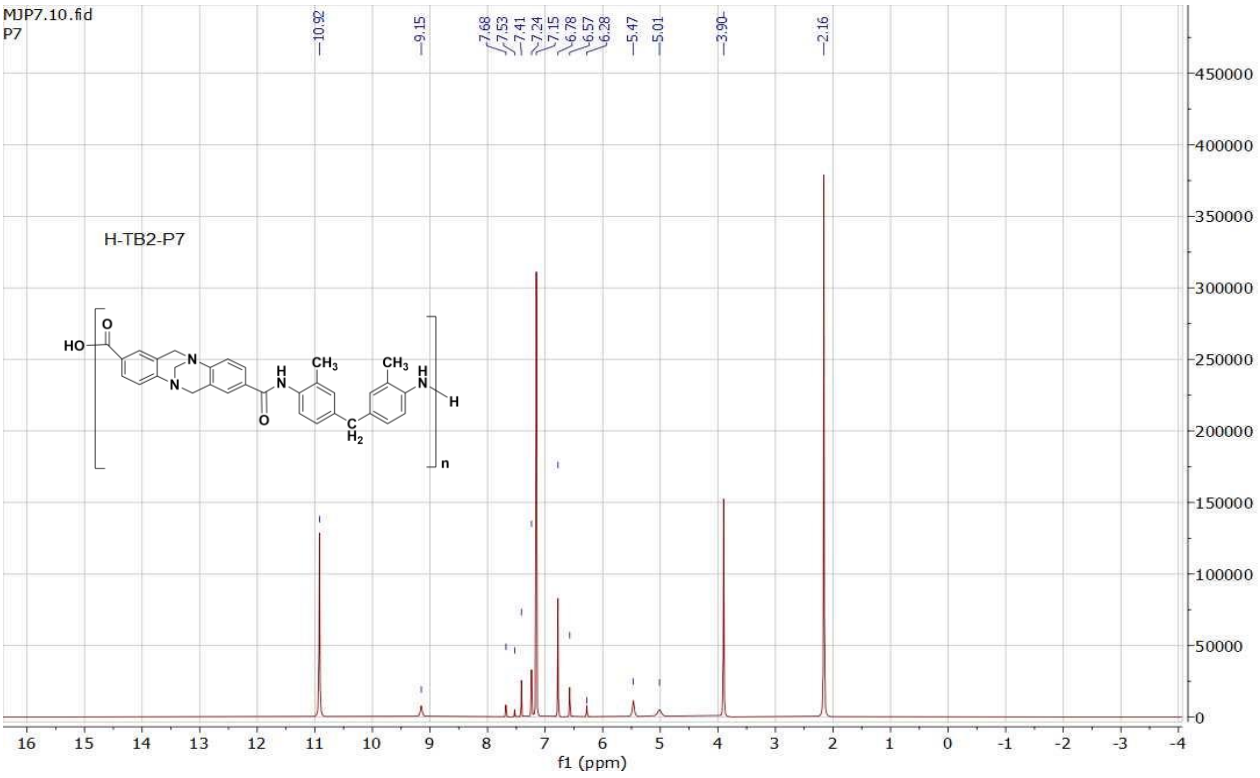


Figure 3-51: Chart of ^{1}HNMR for (TB2P7)

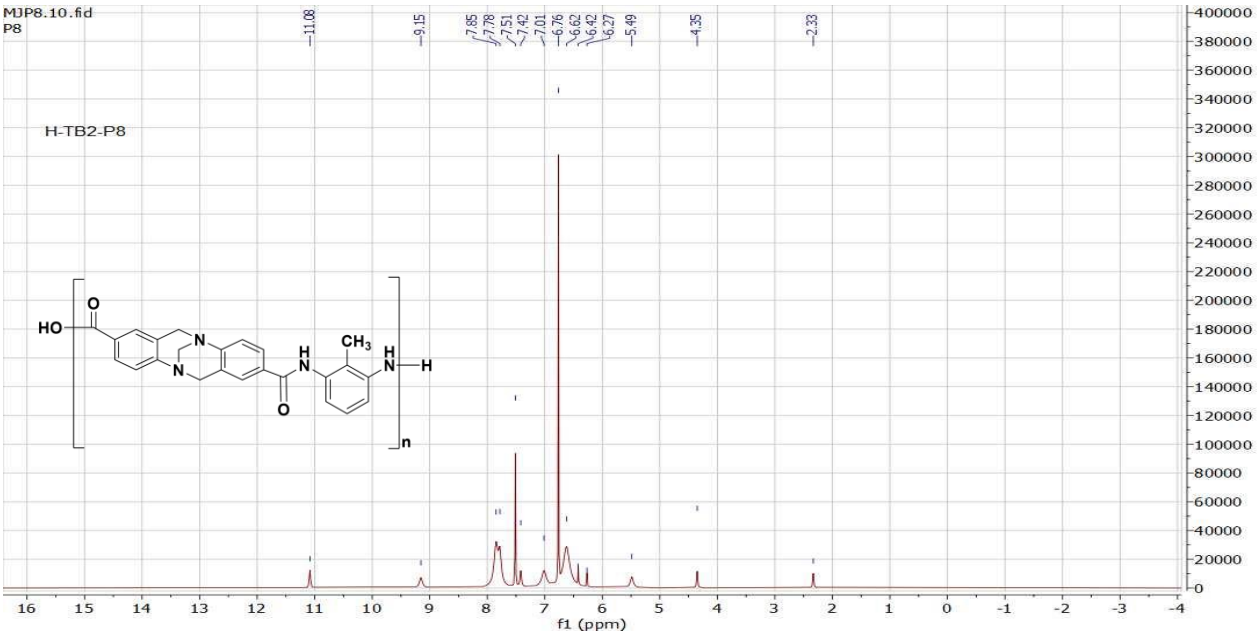


Figure 3-52 : Chart of ^{1}HNMR for (TB2P8)

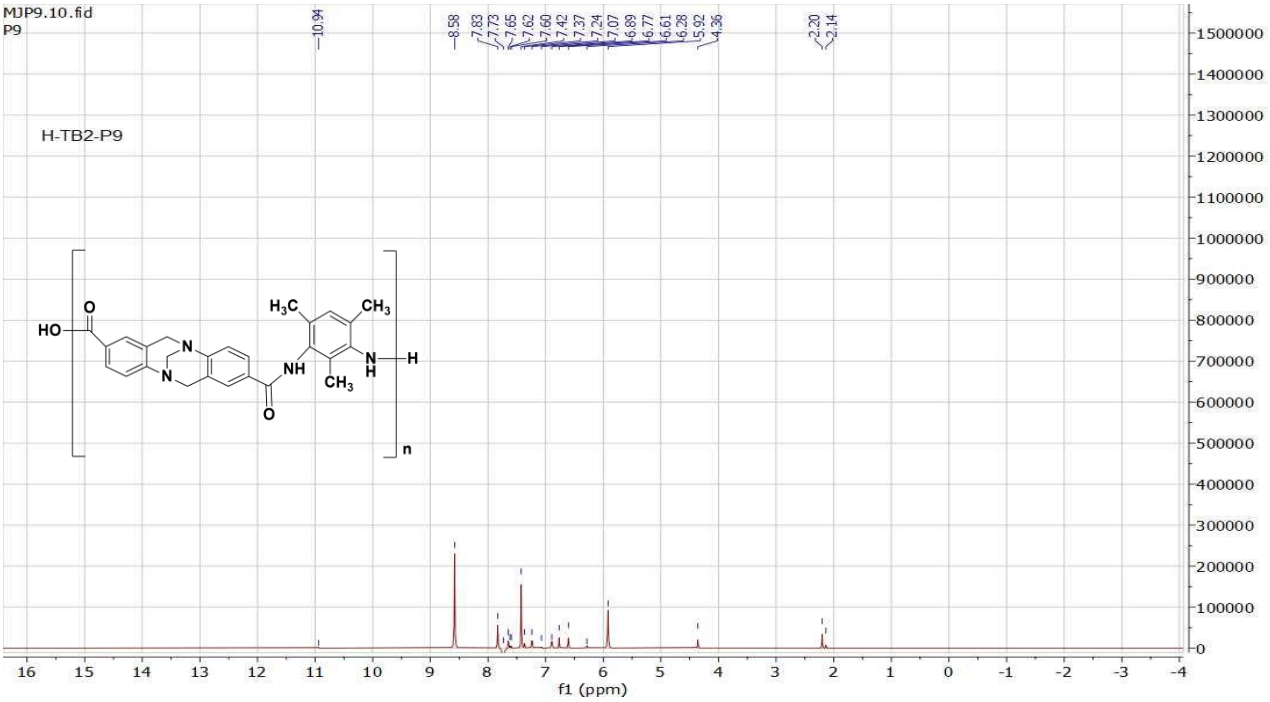


Figure 3-53: Chart of ^{1}HNMR for (TB2P9)

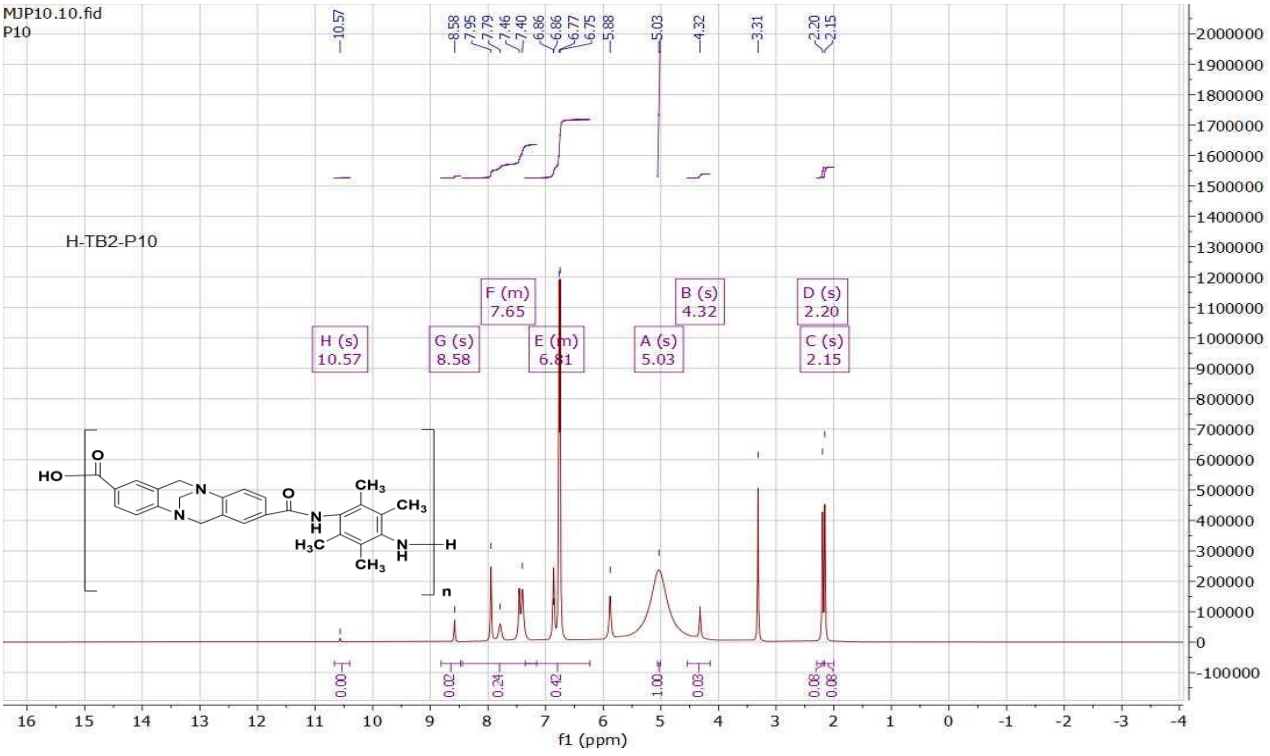


Figure 3-54 : Chart of ^{1}HNMR for (TB2P10)

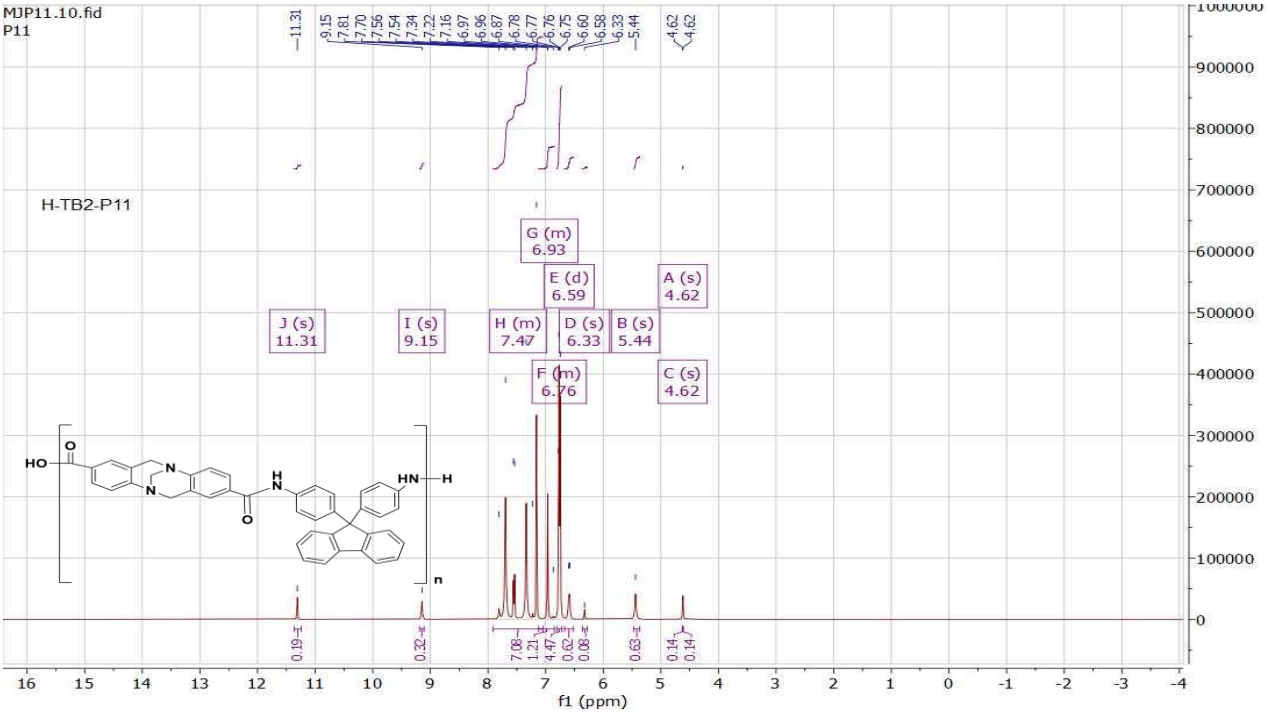


Figure 3-55: Chart of ^{1}HNMR for (TB1P11)

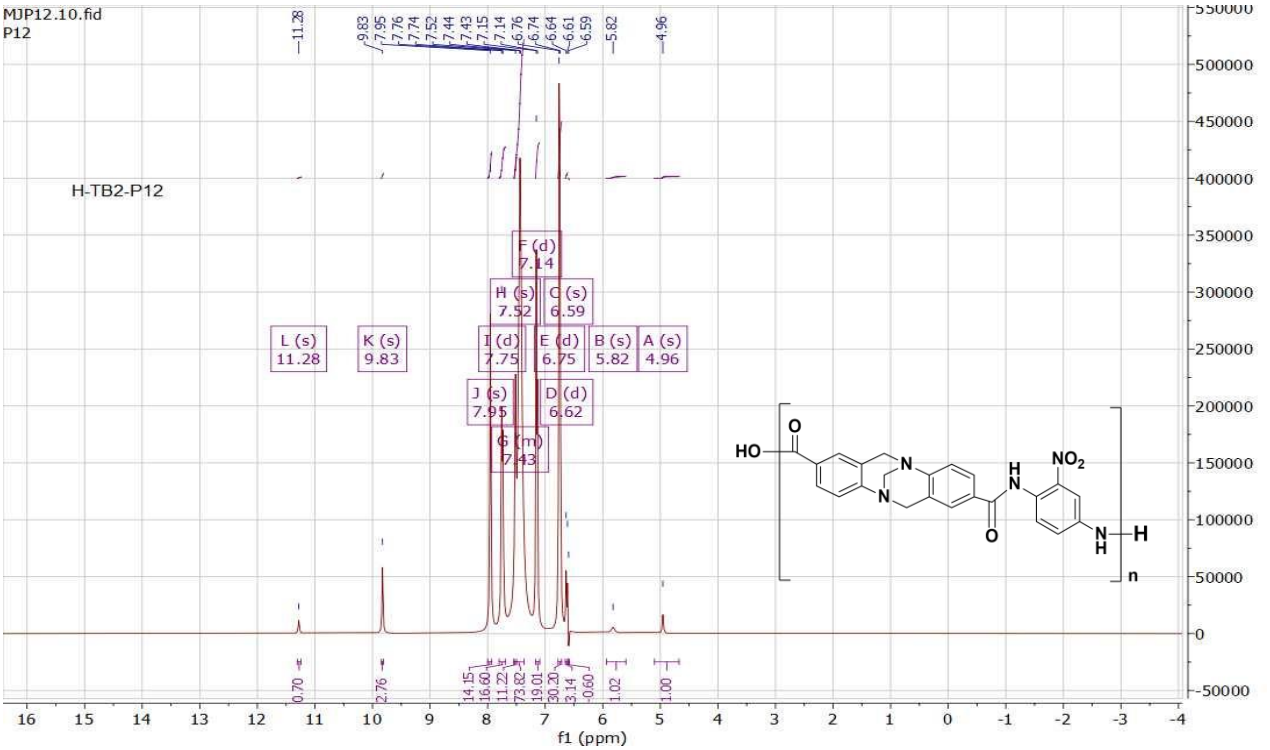


Figure 3-56 :Chart of ^{1}HNMR for (TB1P12)

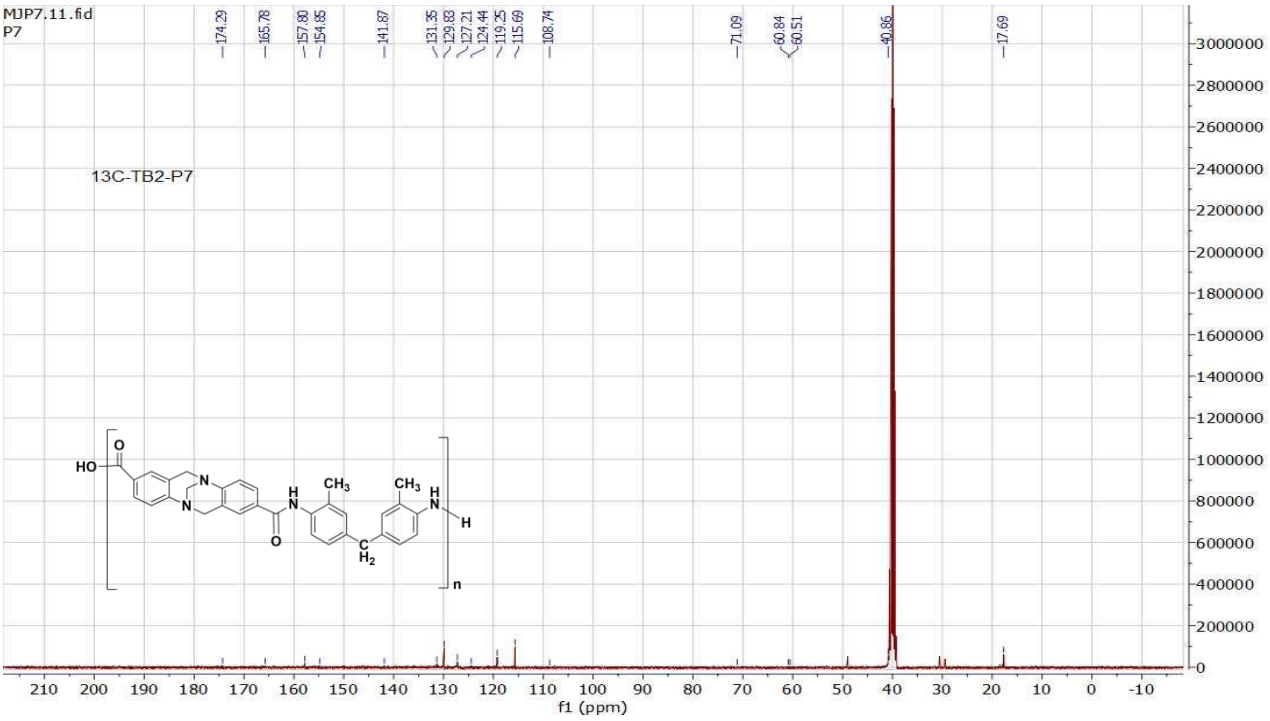


Figure 3-57 :Chart of ^{13}CNMR for (TB2P7)

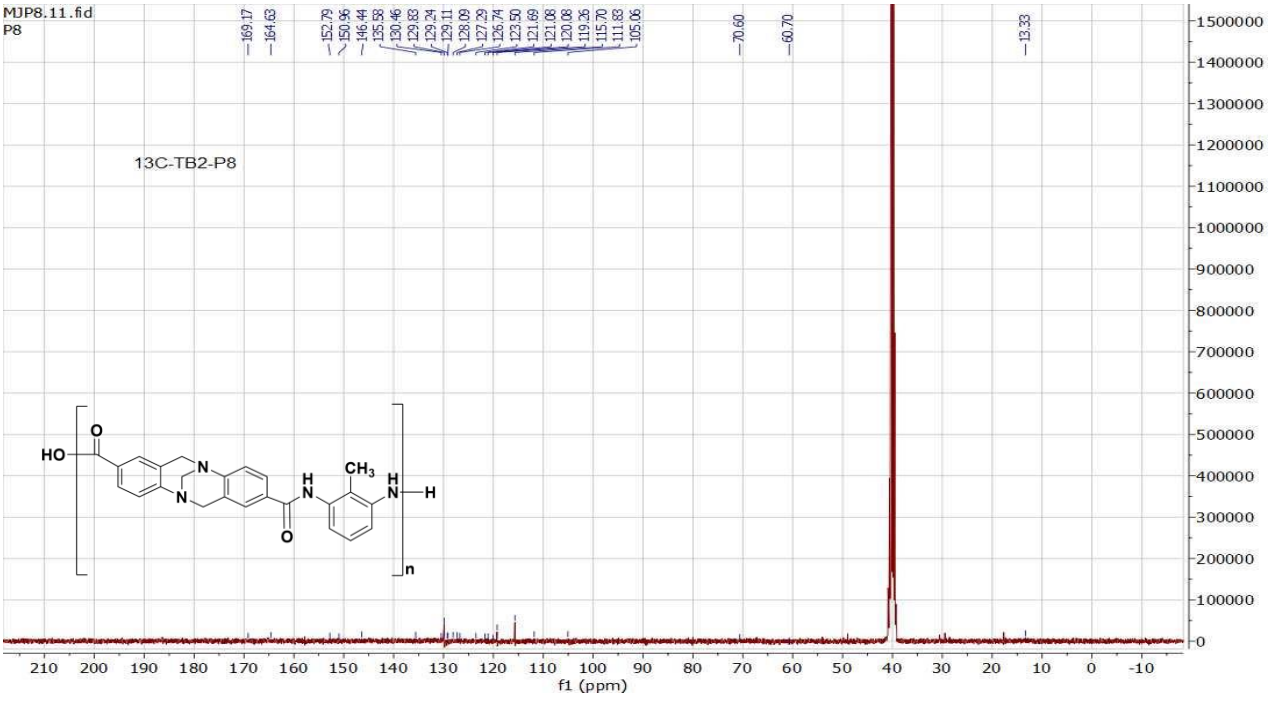


Figure 3-58:Chart of ^{13}CNMR for (TB2P8)

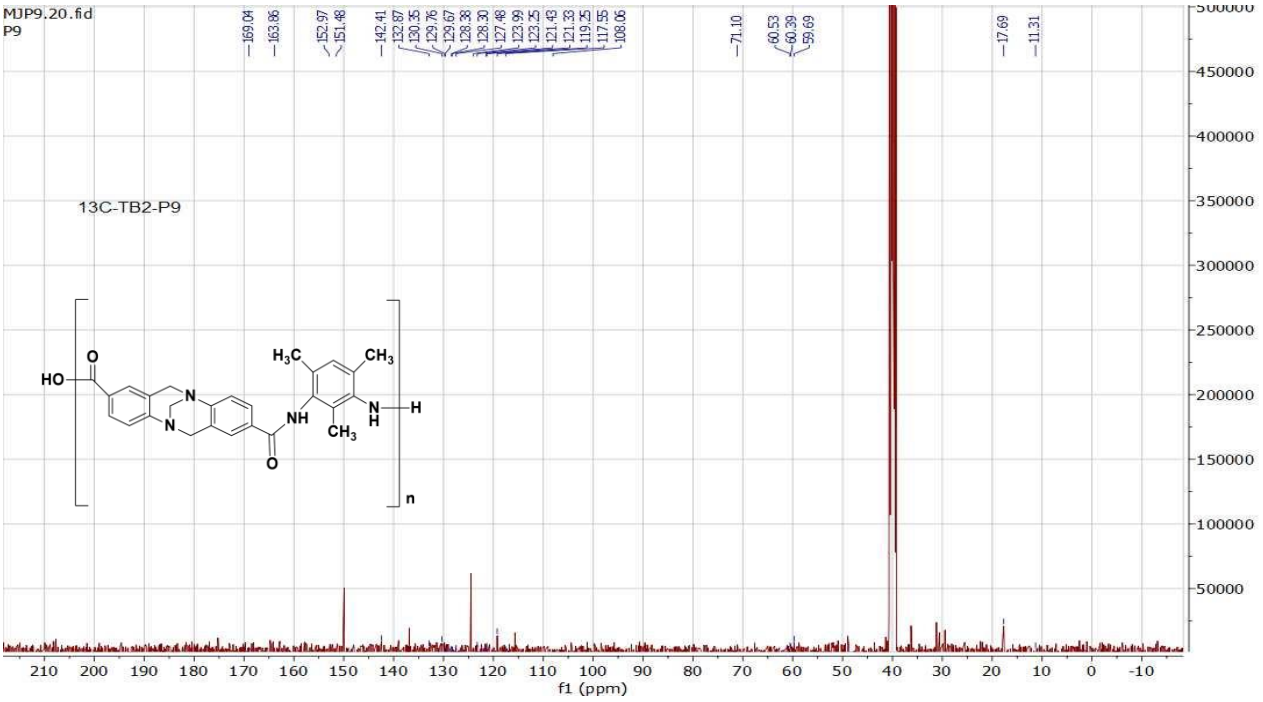


Figure 3-59:Chart of ^{13}CNMR for (TB2P9)

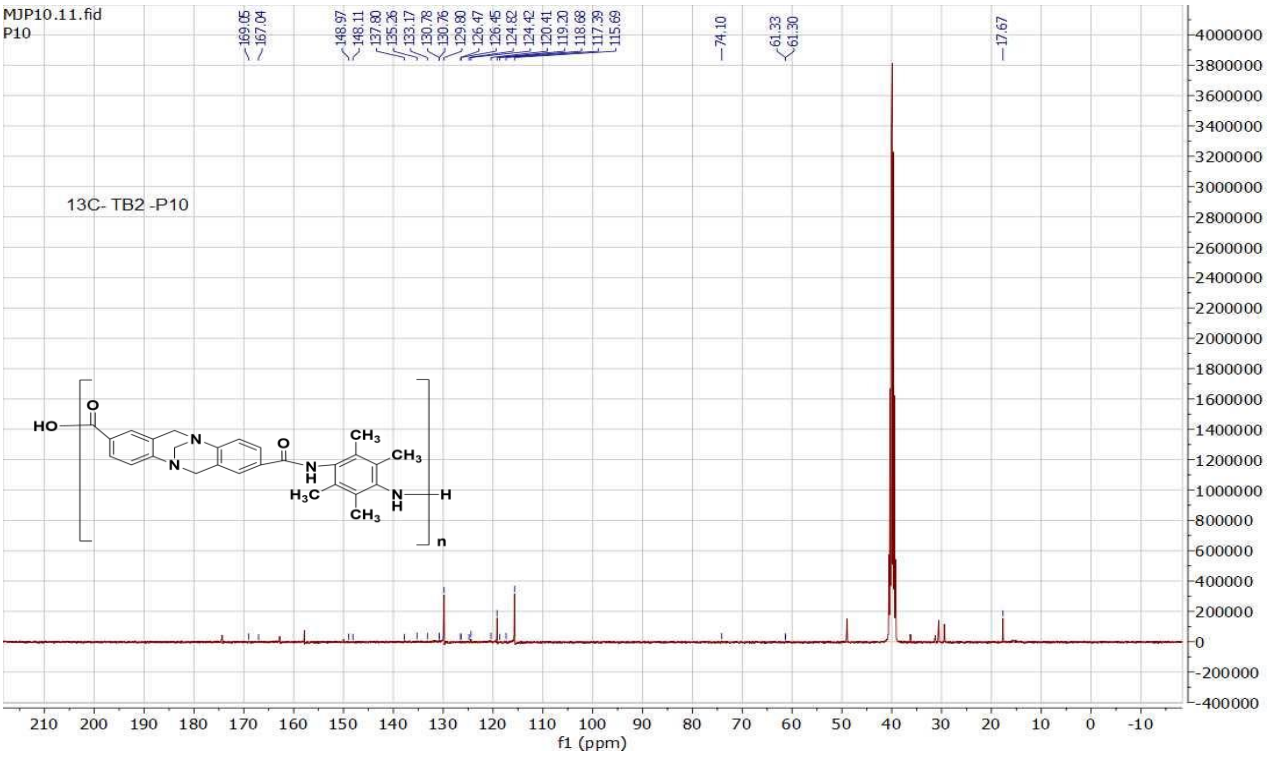


Figure 3-60 :Chart of ^{13}CNMR for (TB2P10)

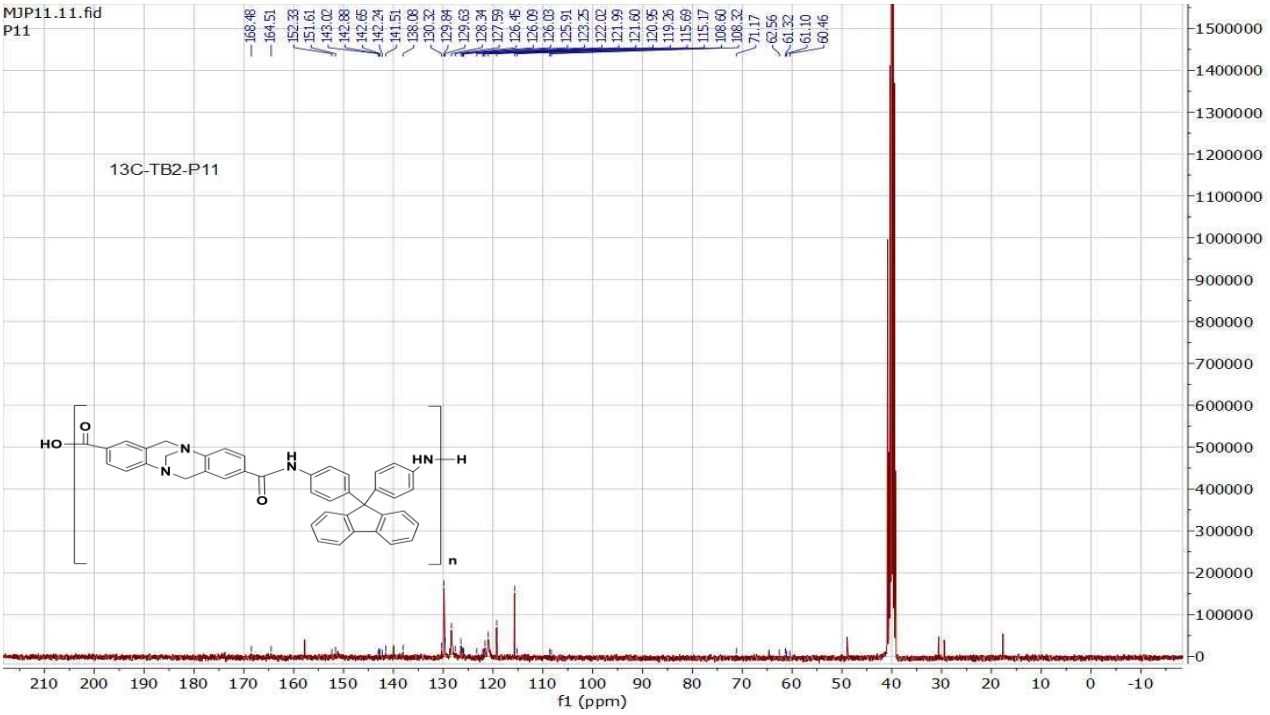


Figure 3-61: :Chart of ^{13}CNMR for (TB2P11)

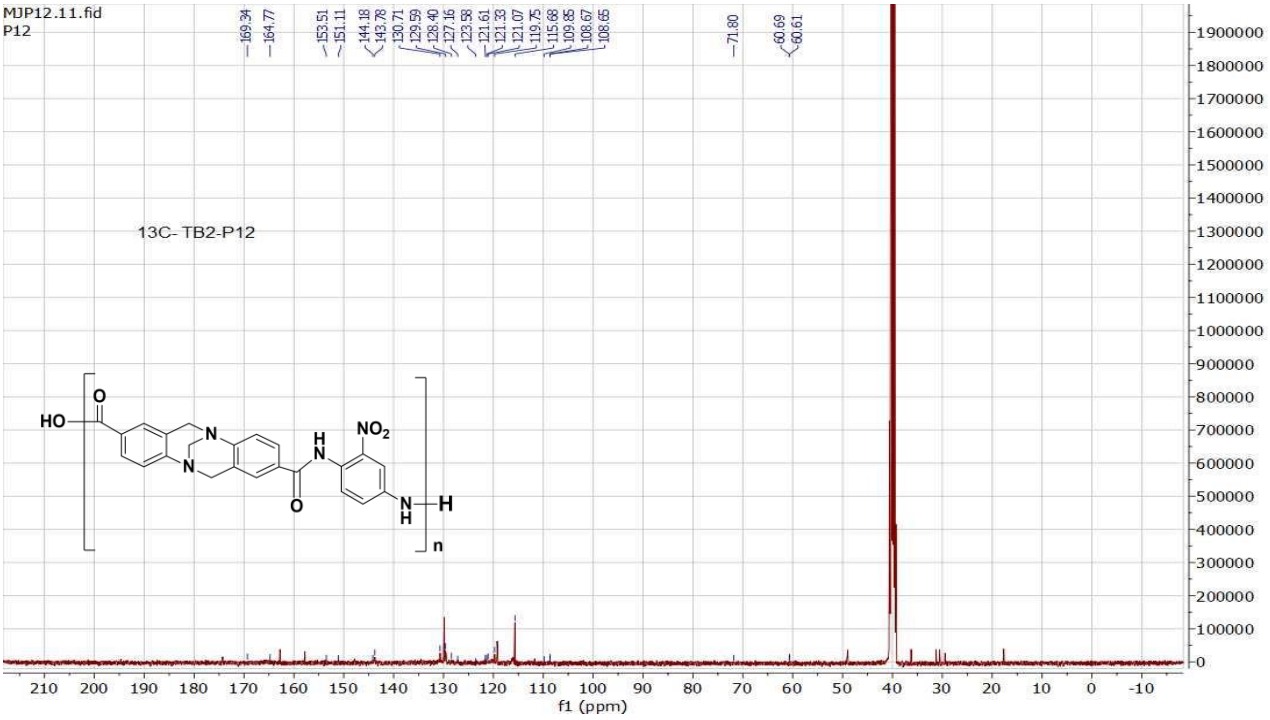


Figure 3-62:Chart of ^{13}CNMR for (TB2P12)

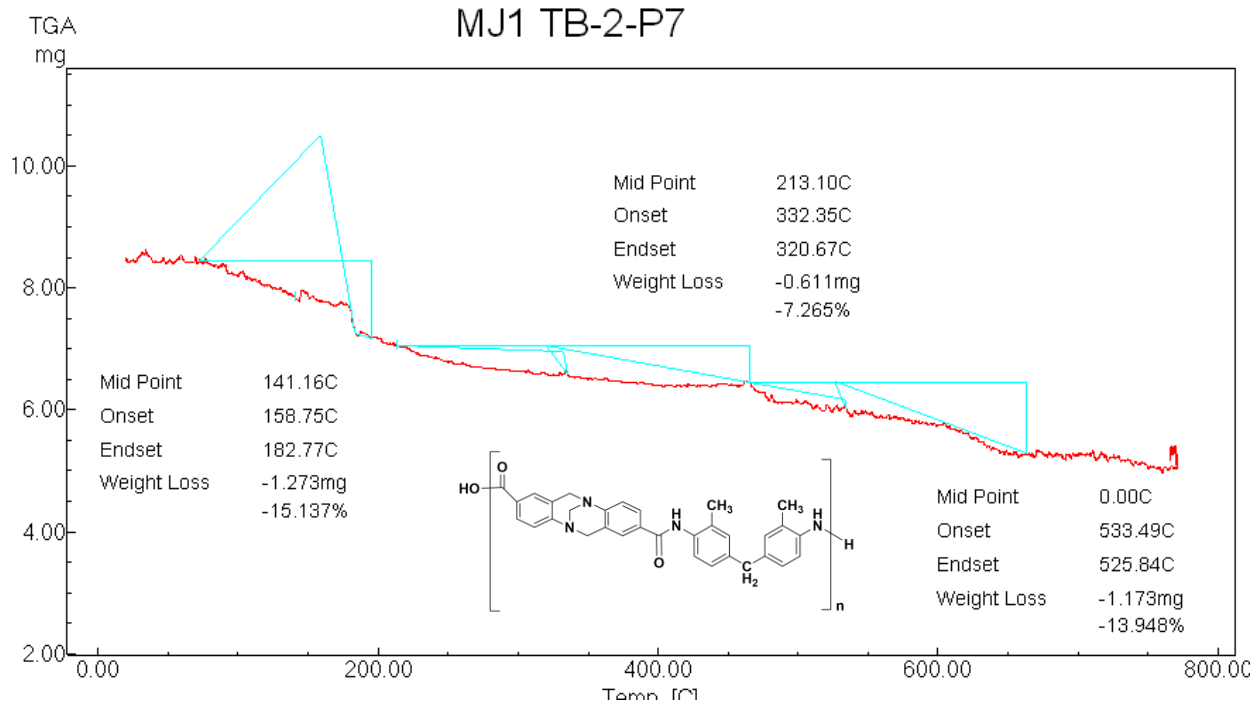


Figure 3-63 : Chart of TGA for (TB2P7)

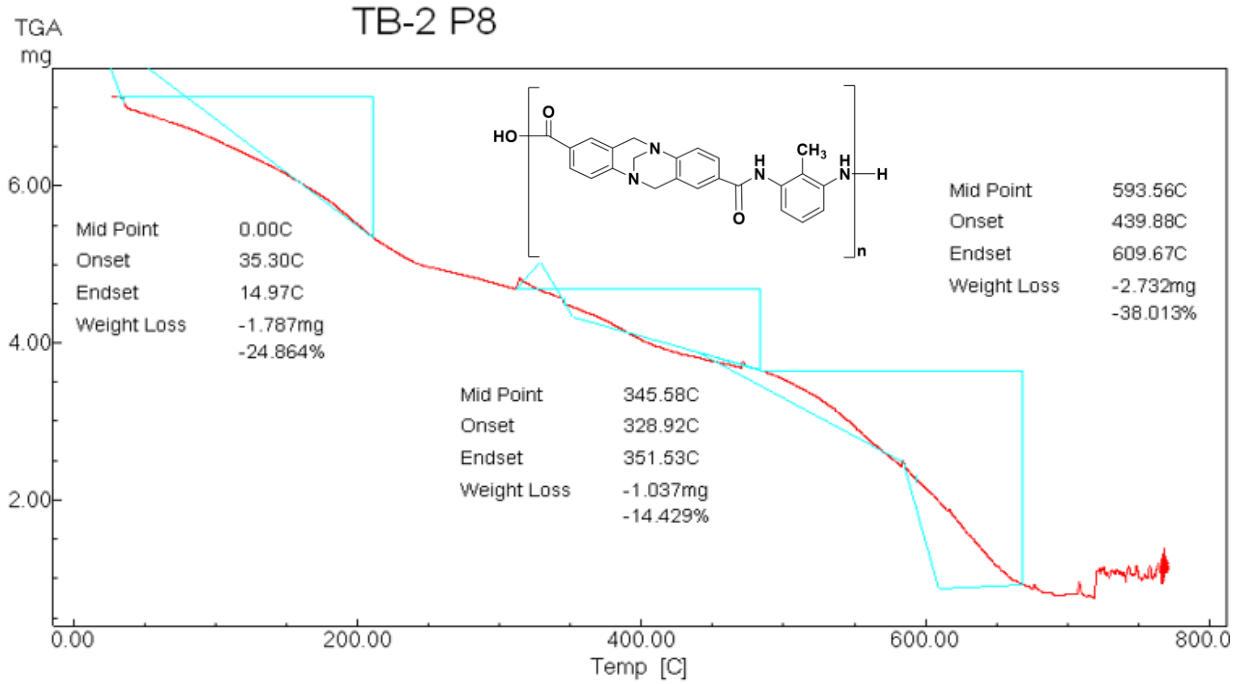


Figure 3-64: Chart of TGA for (TB2P8)

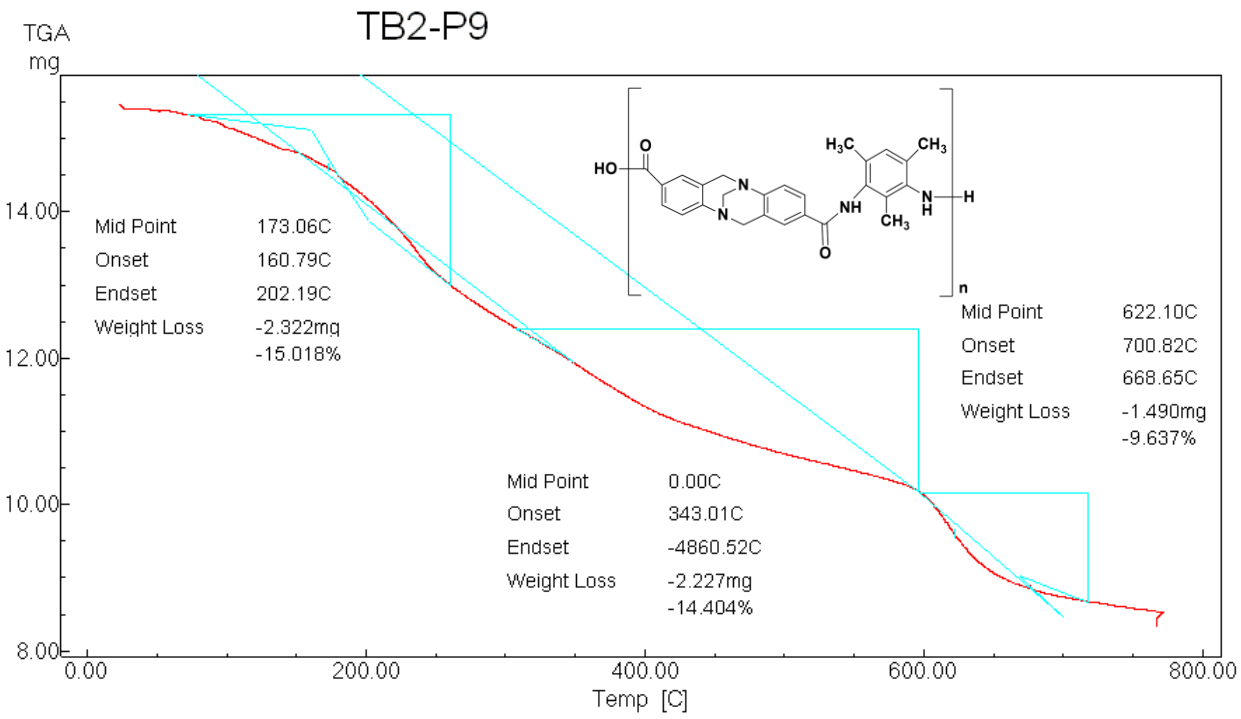


Figure 3-65: : Chart of TGA for (TB2P9)

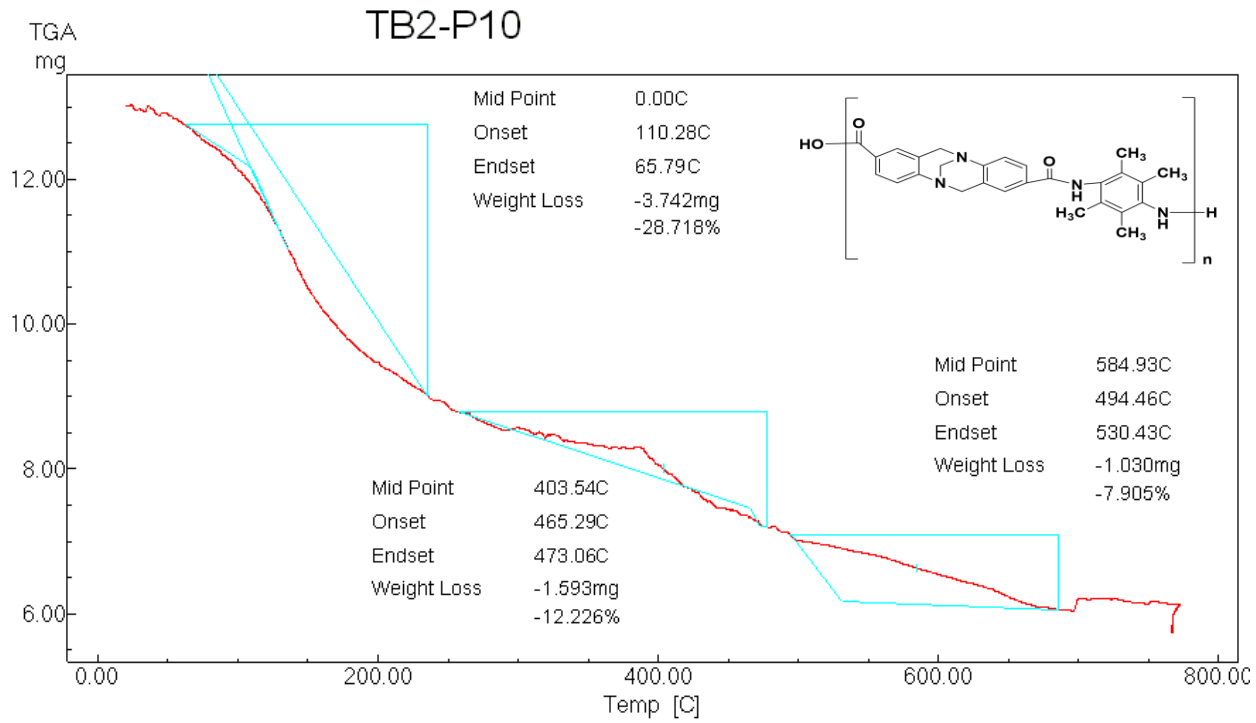


Figure 3-66: Chart of TGA for (TB2P10)

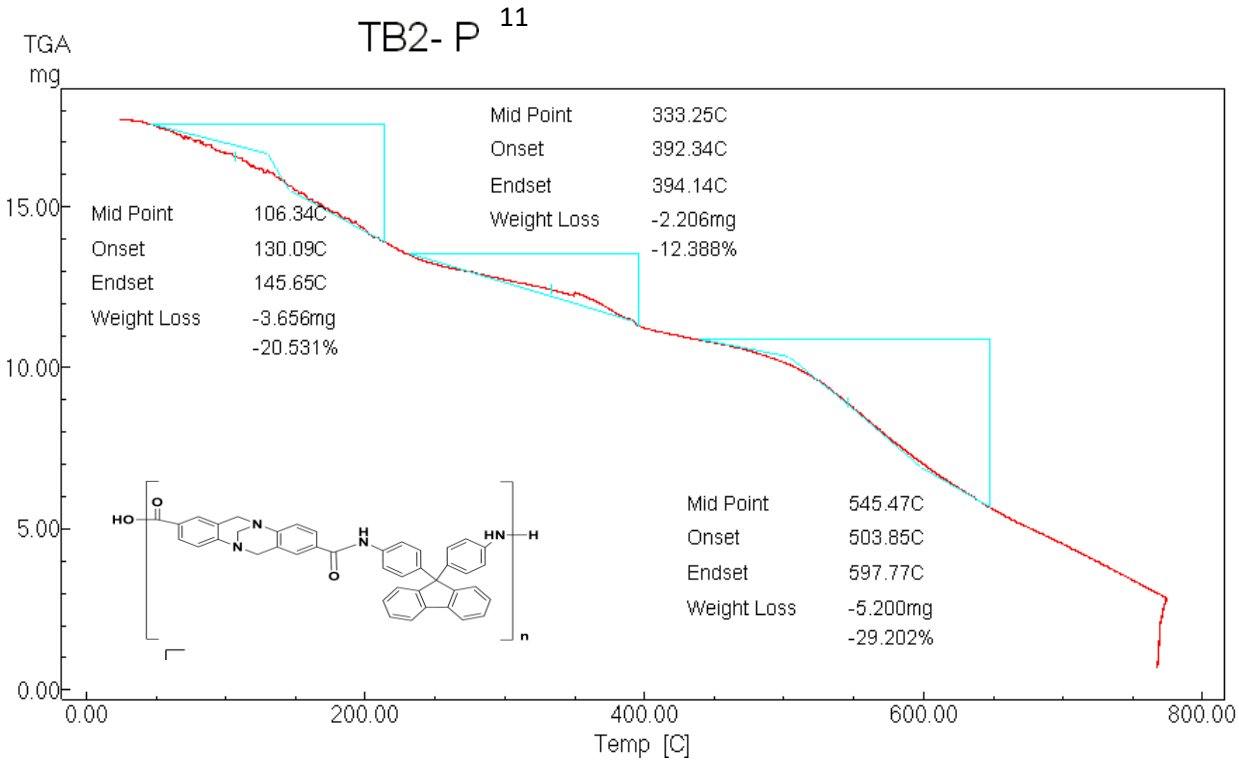


Figure 3-67: Chart of TGA for (TB2P11)

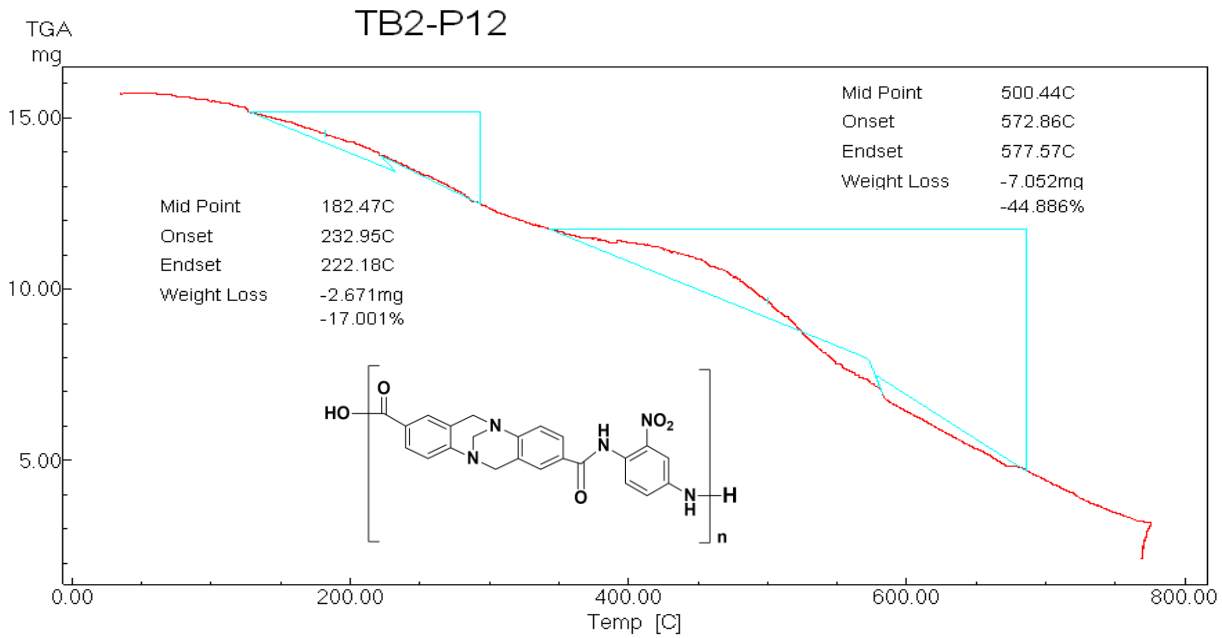
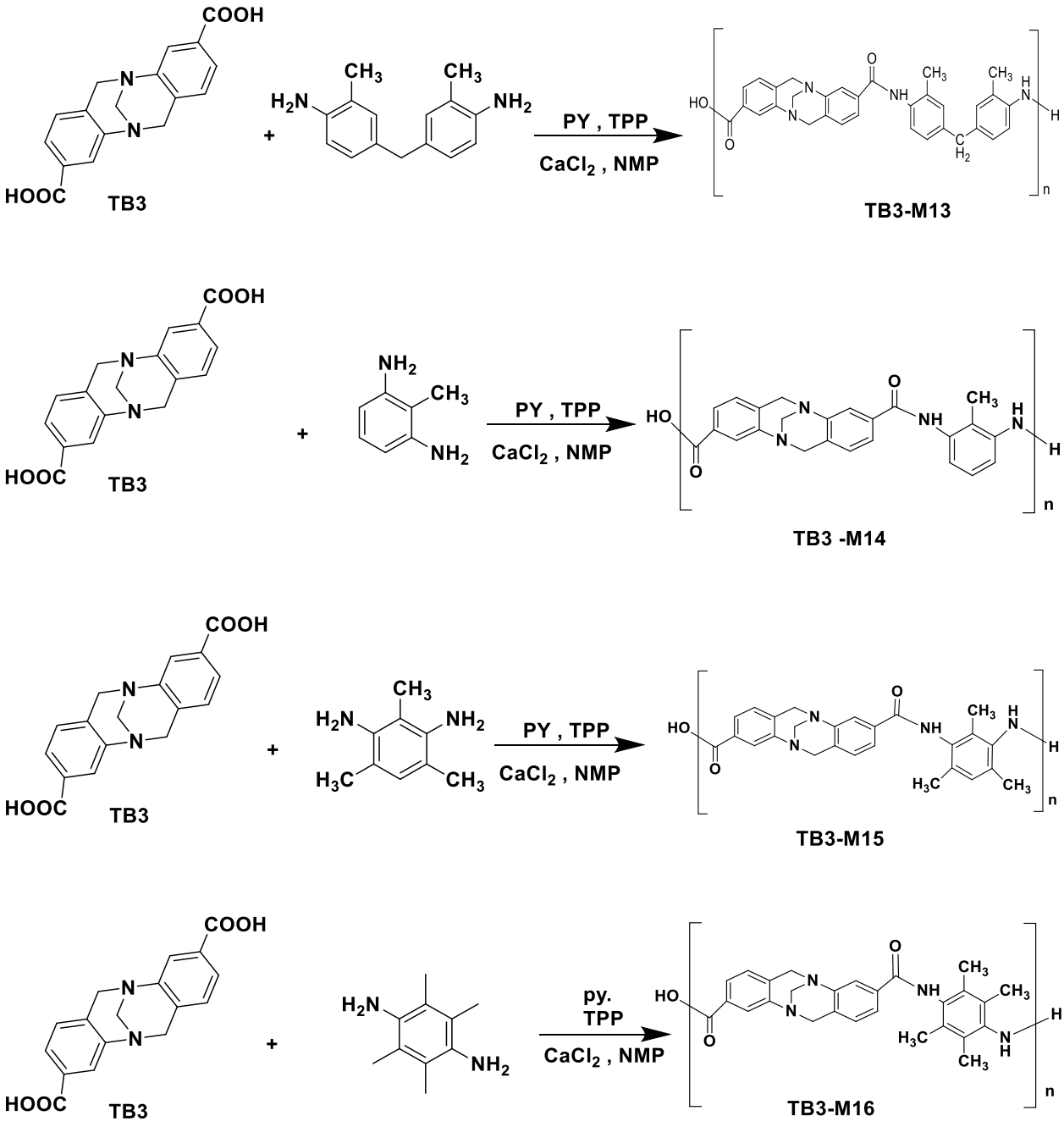
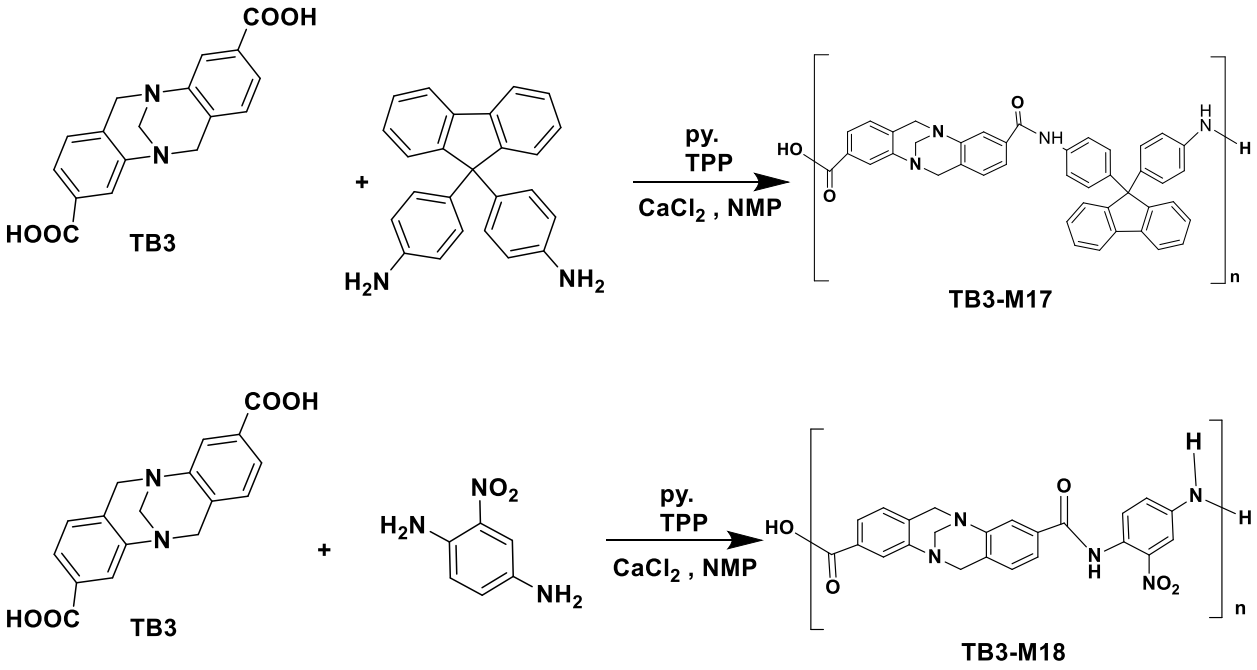


Figure 3-68: Chart of TGA for (TB2P12)

3.2.3. Synthesis and characterization of polyamides (TB3M13-TB3M18)

Synthesis of polyamides is produced from interaction (TB3) with diamine aromatic as shown in eq.(3-4)





eq.(3-4): Synthesis of polyamides (TB3M13-TB3M18)

Equation (3-4) shows the preparation of polyamides (TB3M13-TB3-M18), and the determination of the compounds by FT-IR as shown in (Table 3-13) and (Figures 3-69 to 3-74). Also, it is identified by ^{1}H NMR(Table 3-14) and (Figures 3-75 to 79),^{13}C NMR (Table 3-15) and (Figures 3-80 to 3-85), TGA (Table 3-16) and (Figures 3-86 - 91).

Table 3-13:Functional Groups values in FT-IR for Polymers (TB3-M13- TB3-M18)

Model number	N-H terminal	COOH terminal	N-H-C=O
TB3-M13	3455 , 3356	3256-2557	1662
TB3-M14	3464 , 3342	3234-2474	1668
TB3-M15	3443,3358	3228-2446	1668
TB3-M16	3473 ,3373	3277-2454	1666
TB3-M17	3460 , 3398	3281-2454	1670
TB3-M18	3468 , 3368	3308-2453	1662

Table 3-14:Functional Groups values in ^{1}HNMR for polymers (TB3M13- TB3M18)

Model number	N-H terminal	COOH terminal	N-H-C=O
TB3-M13	6.63	10.94	9.94
TB3-M14	6.65	11.07	9.18
TB3-M15	6.59	10.97	9.79
TB3-M16	6.65	11.02	9.32
TB3-M17	6.39	11.27	9.17
TB3-M18	6.74	11.29	9.15

Table 3-15:Functional Groups values in^{13}CNMR for Polymers (TB3M13- TB3M18)

Model number	C_{Ar}-N-H_2 terminal	COOH terminal	N-H-C=O
TB3-M13	146.53	166.64	162.80
TB3-M14	144.80	166.38	163.62
TB3-M15	146.84	168.04	164.04
TB3-M16	145.68	167.89	162.83
TB3-M17	146.41	167.17	164.21
TB3-M18	144.81	165.78	163.29

Table 3-16: TGA Study of Polymers (TB3M13-TB3M18)

Model number	Initial Degradation	Final Degradation
TB3-M13	48.69 - 99.40	532.53 - 554.48
TB3-M14	228.87 - 230.92	510.74 - 540.21
TB3-M15	178.40 - 200.68	413.43 - 556.84
TB3-M16	188.91 - 215.99	
TB3-M17	208.33 - 257.13	505.00 - 550.68
TB3-M18	261.75 - 248.06	357.64 - 339.89

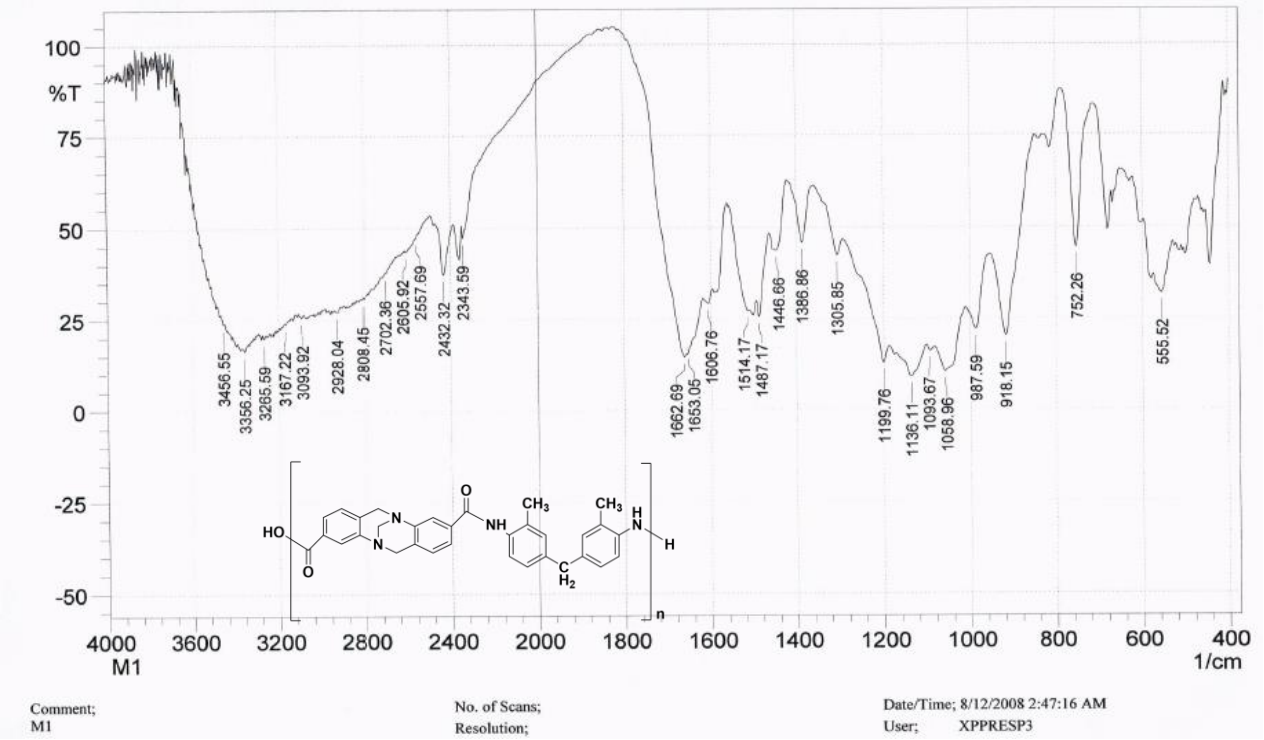


Figure 3-69: Chart of IR for (TB2M13)

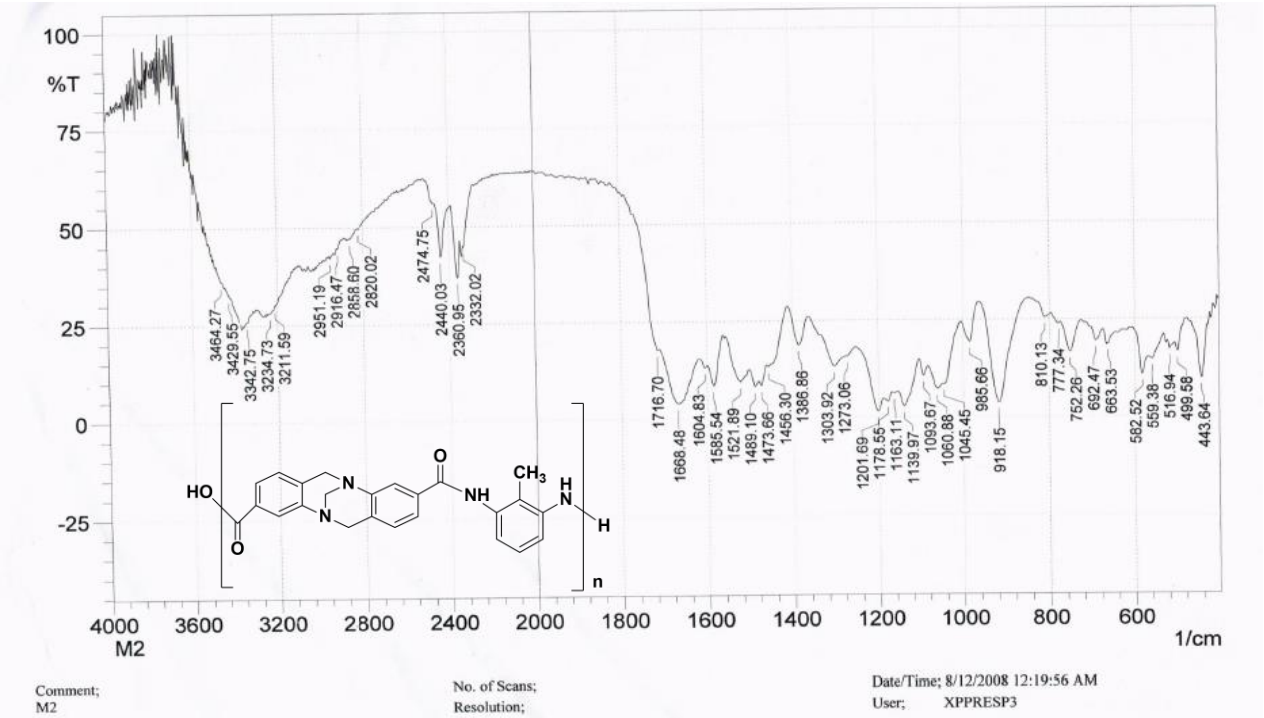


Figure 3-70: Chart of IR for (TB2M14)

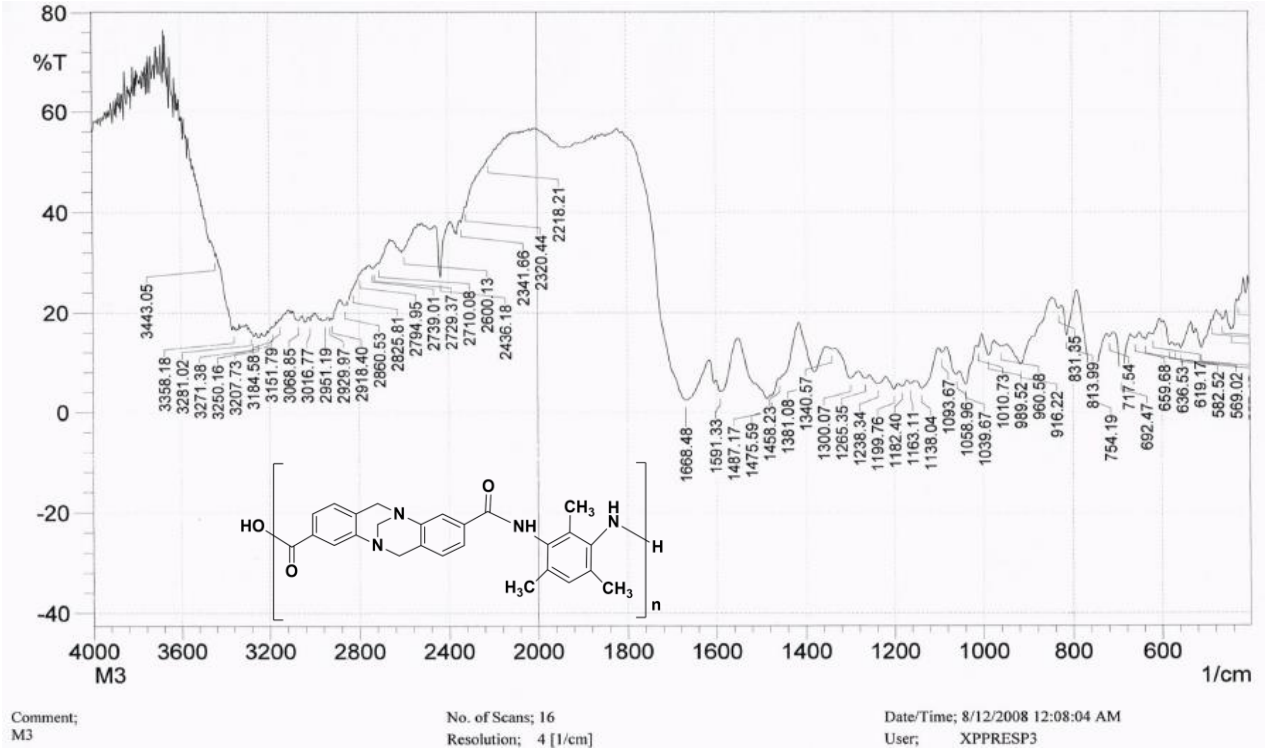


Figure 3-71: : Chart of IR for (TB2M15)

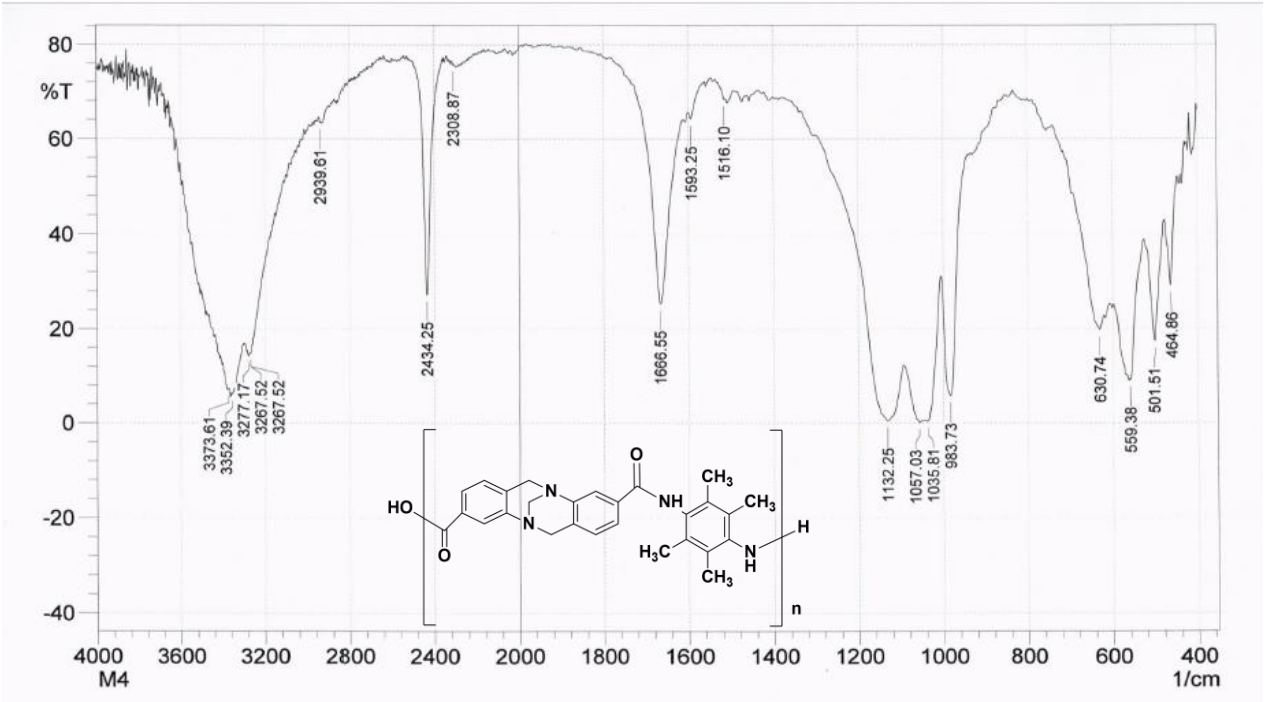


Figure 3-72: Chart of IR for (TB2M16)

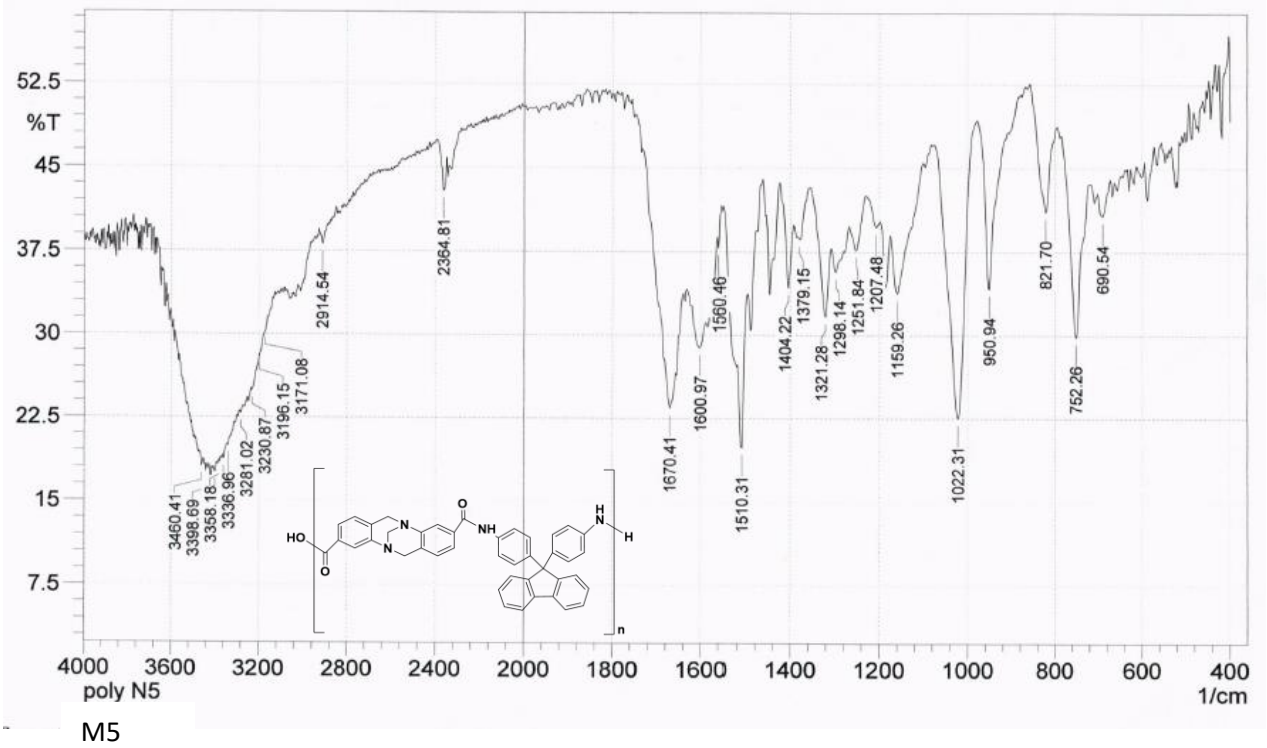


Figure 3-73: Chart of IR for (TB2M17)

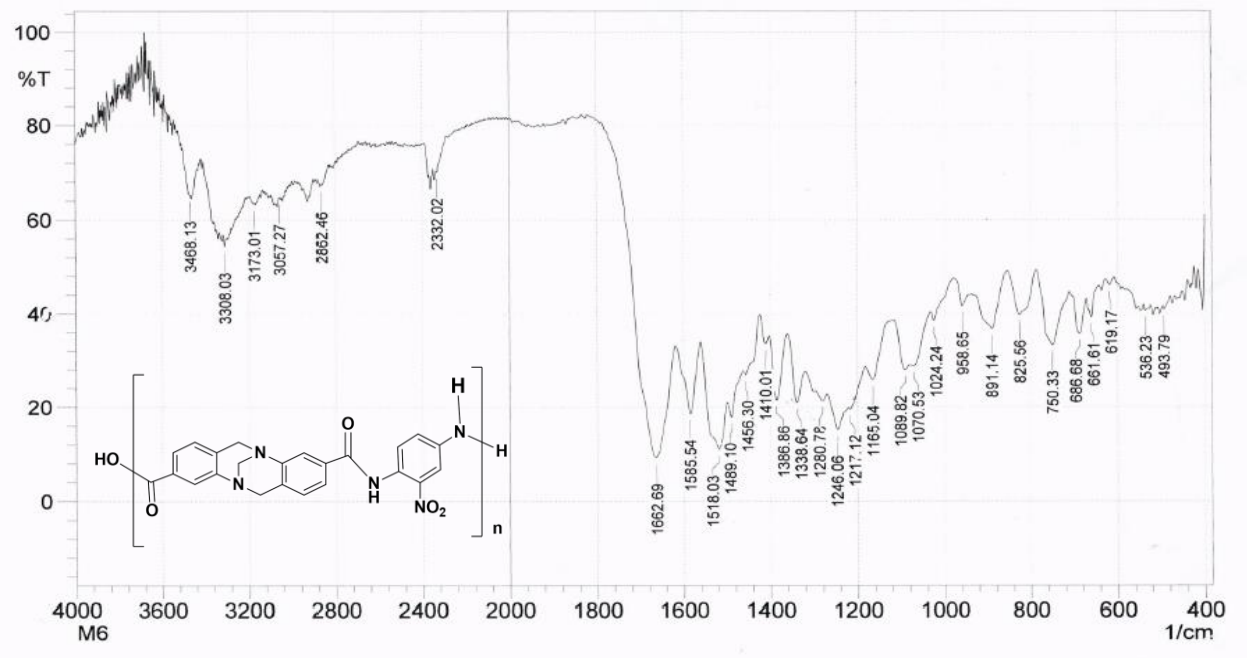


Figure 3-74: Chart of IR for (TB2M18)

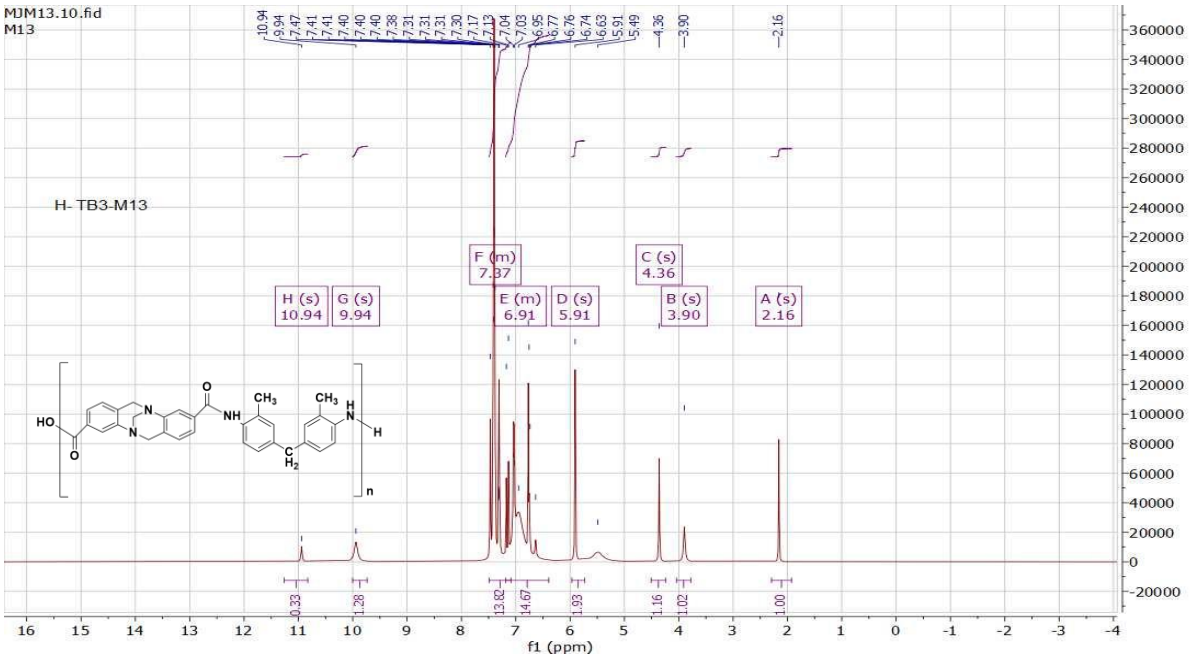


Figure 3-75: Chart of ^{1}HNMR for (TB3M13)

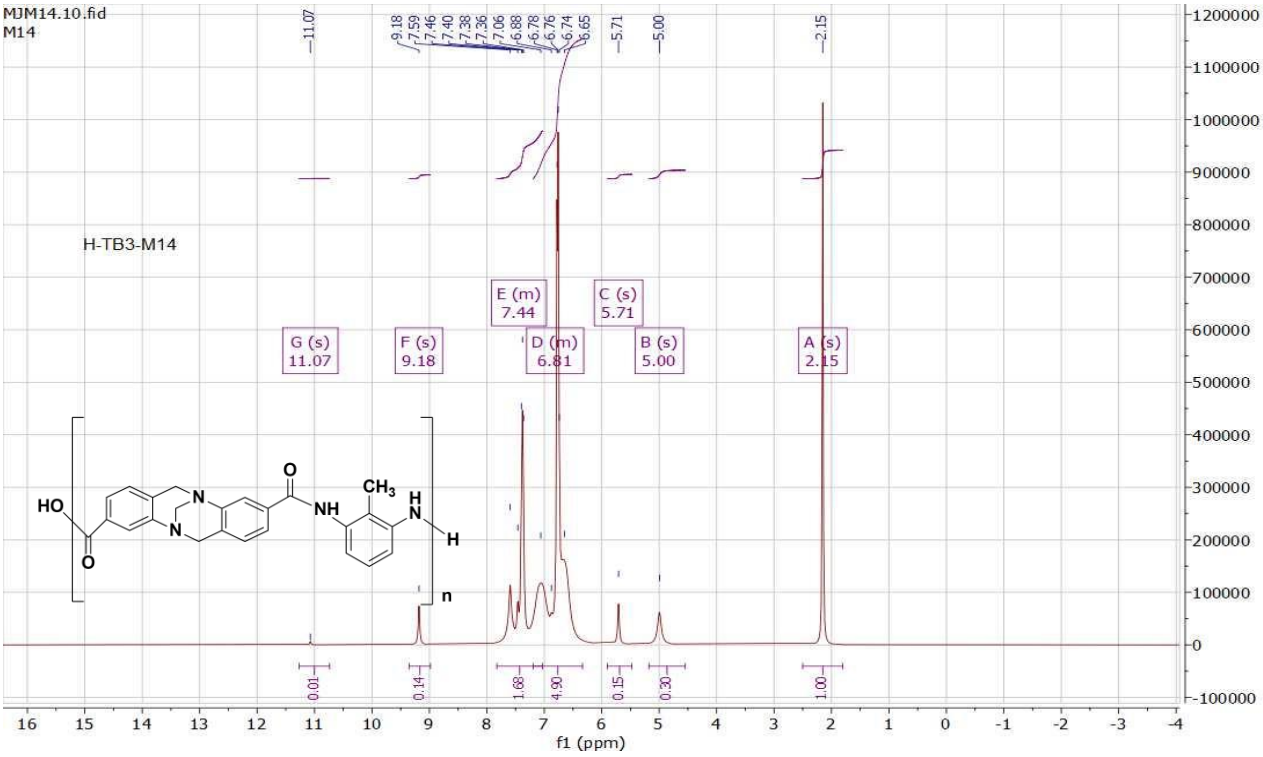


Figure 3-76: Chart of ^{1}HNMR for (TB3M14)

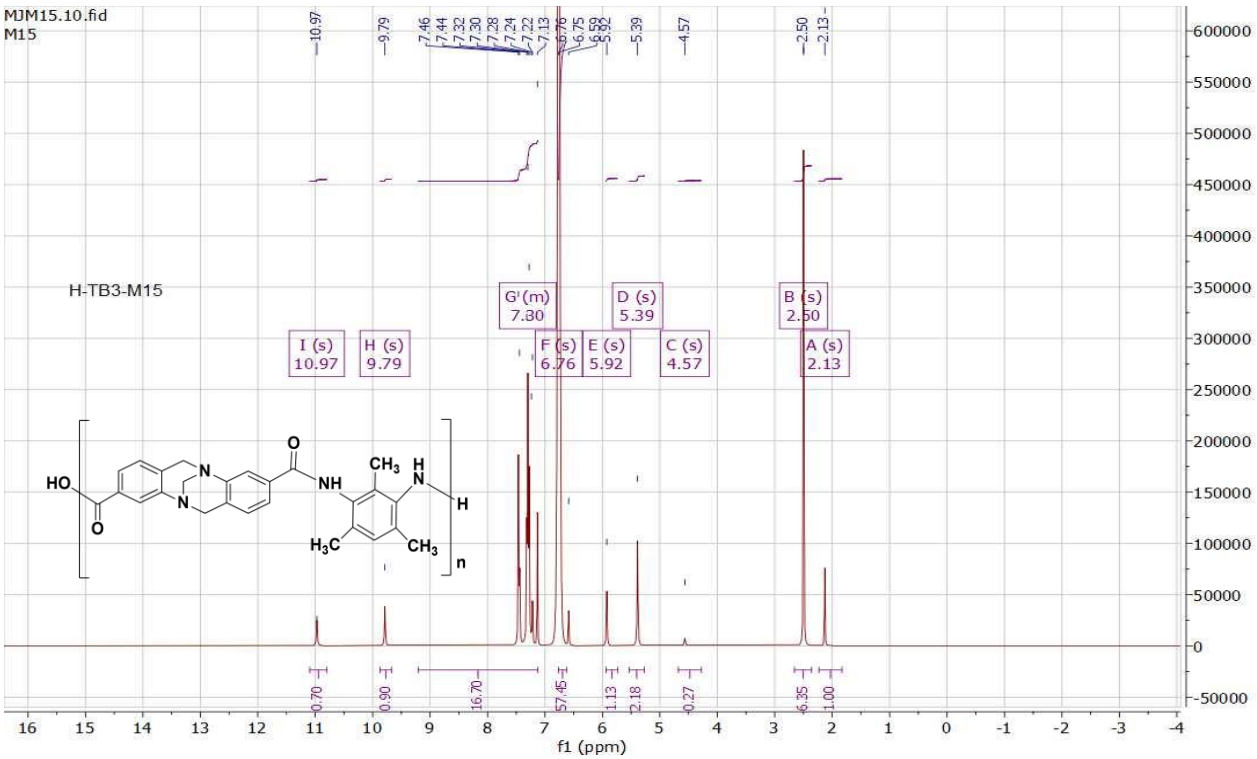


Figure 3-77: Chart of ^{1}HNMR for (TB3M15)

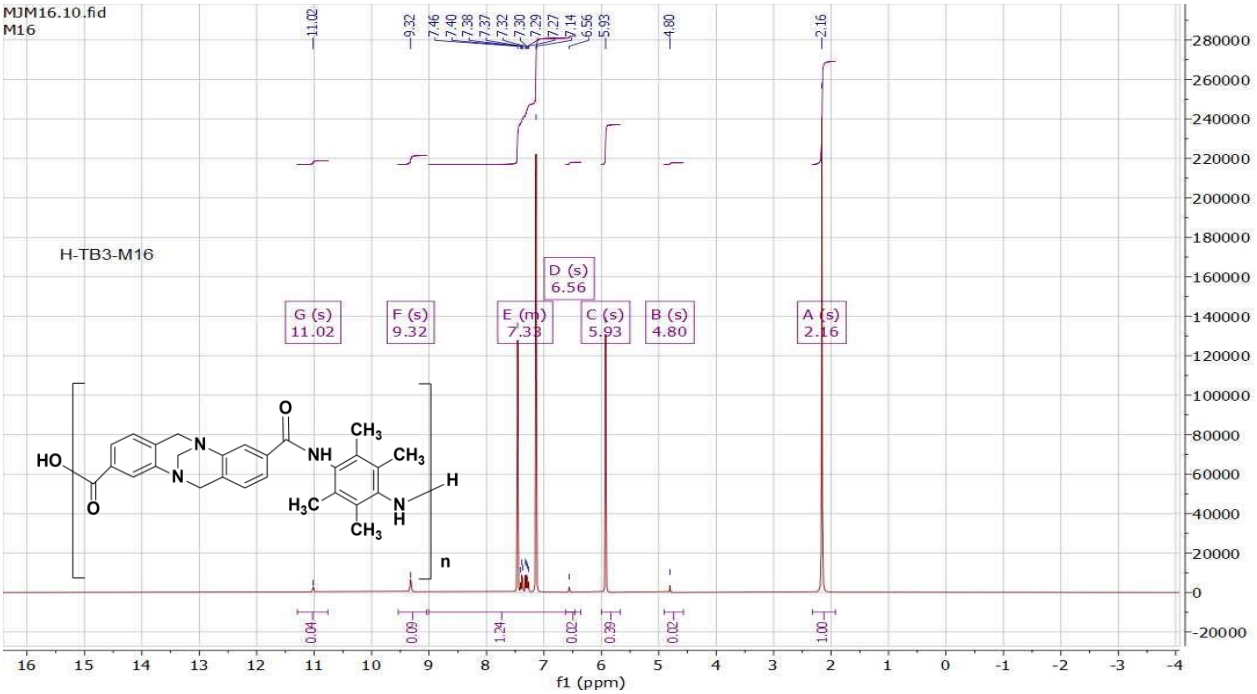


Figure 3-78: Chart of ^{1}HNMR for (TB3M16)

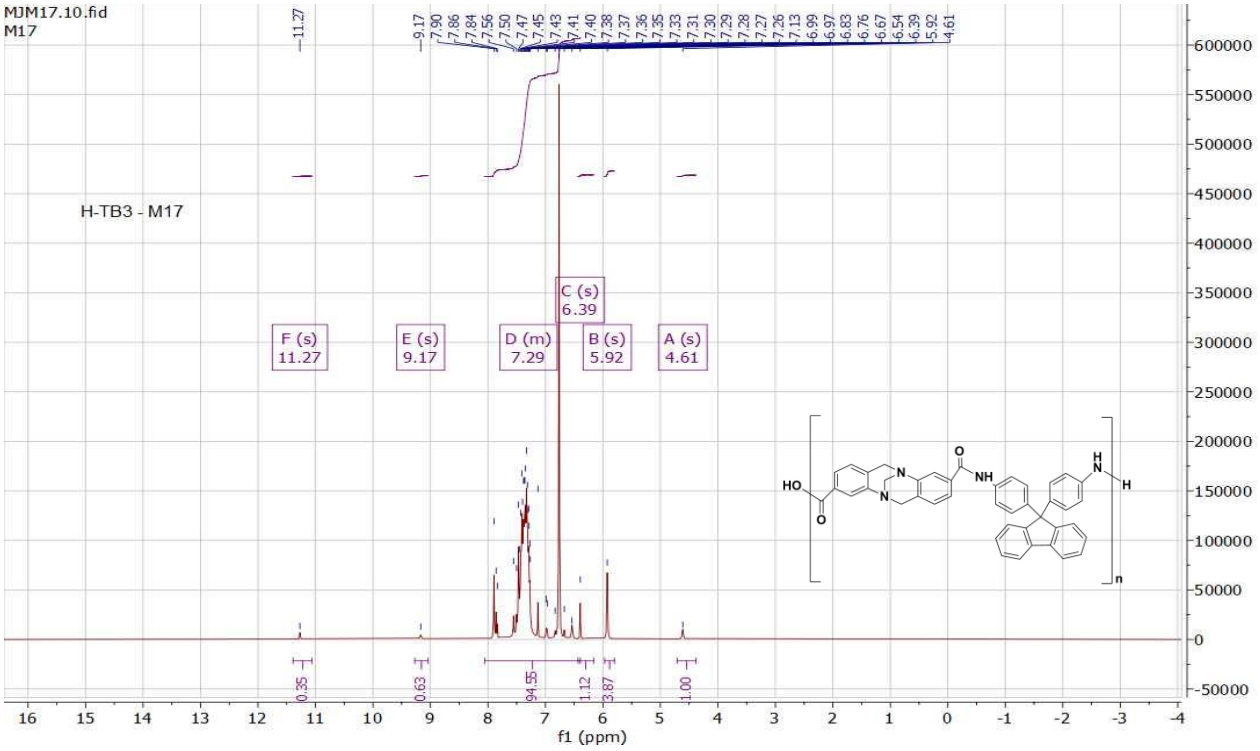


Figure 3-79: Chart of ^{1}HNMR for (TB3M17)

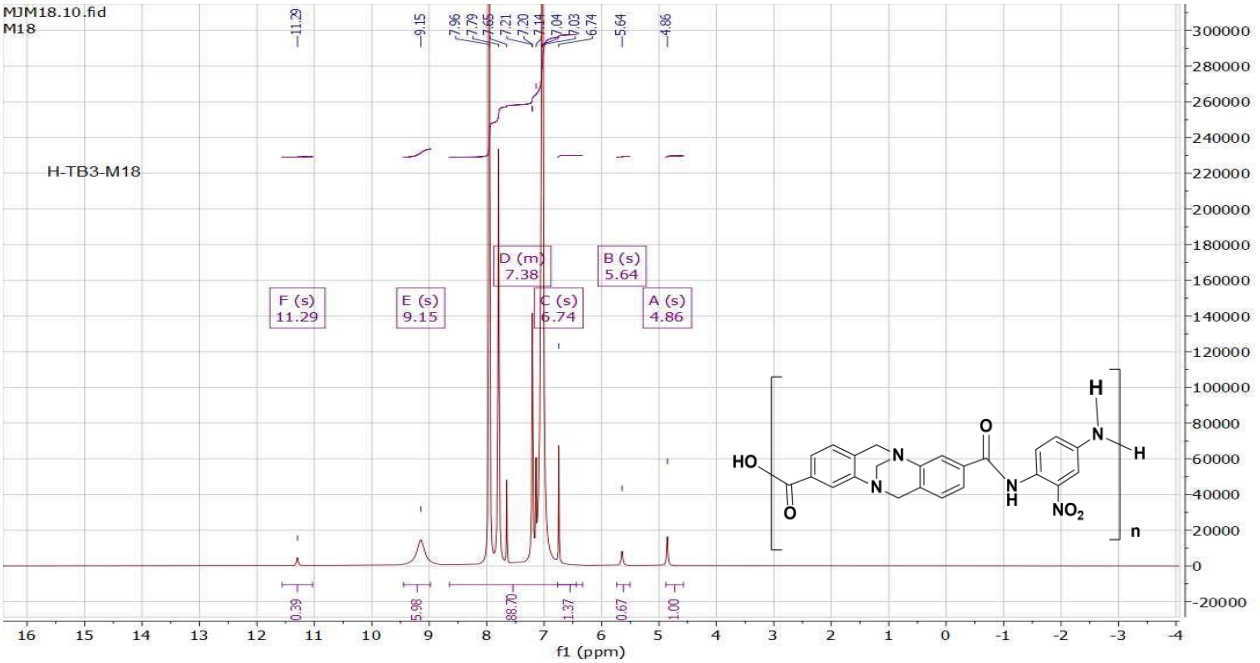


Figure 3-80: Chart of ^{1}HNMR for (TB3M18)

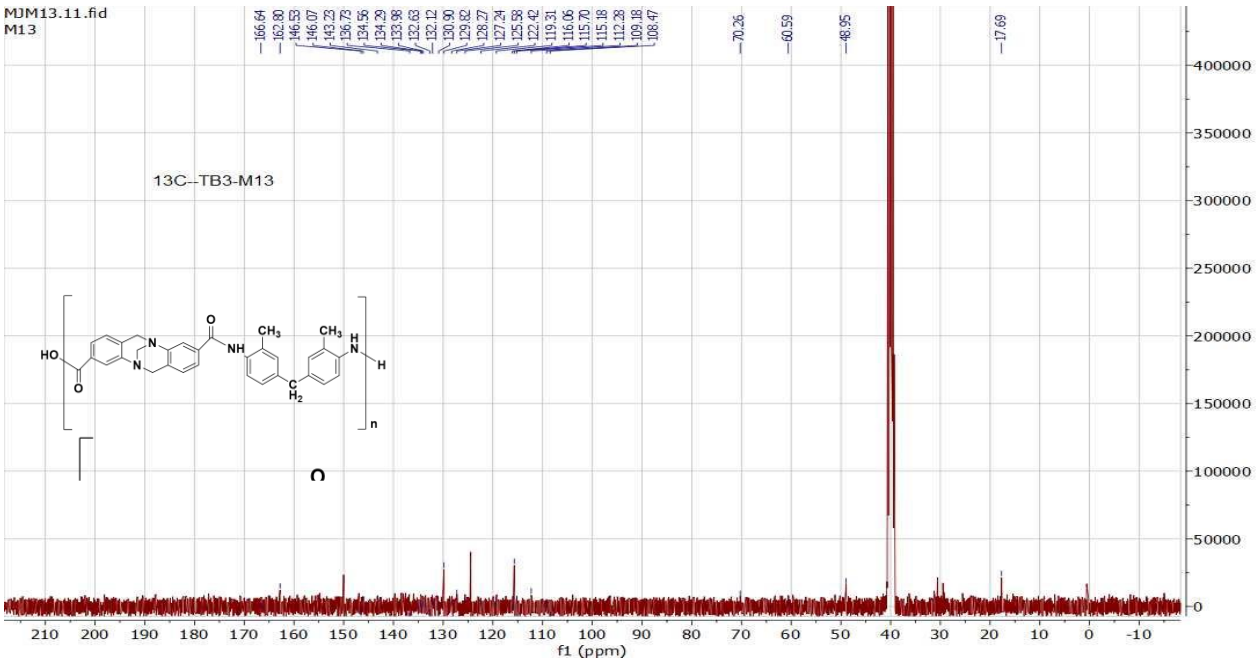


Figure 3-81: Chart of ^{13}CNMR for (TB3M13)

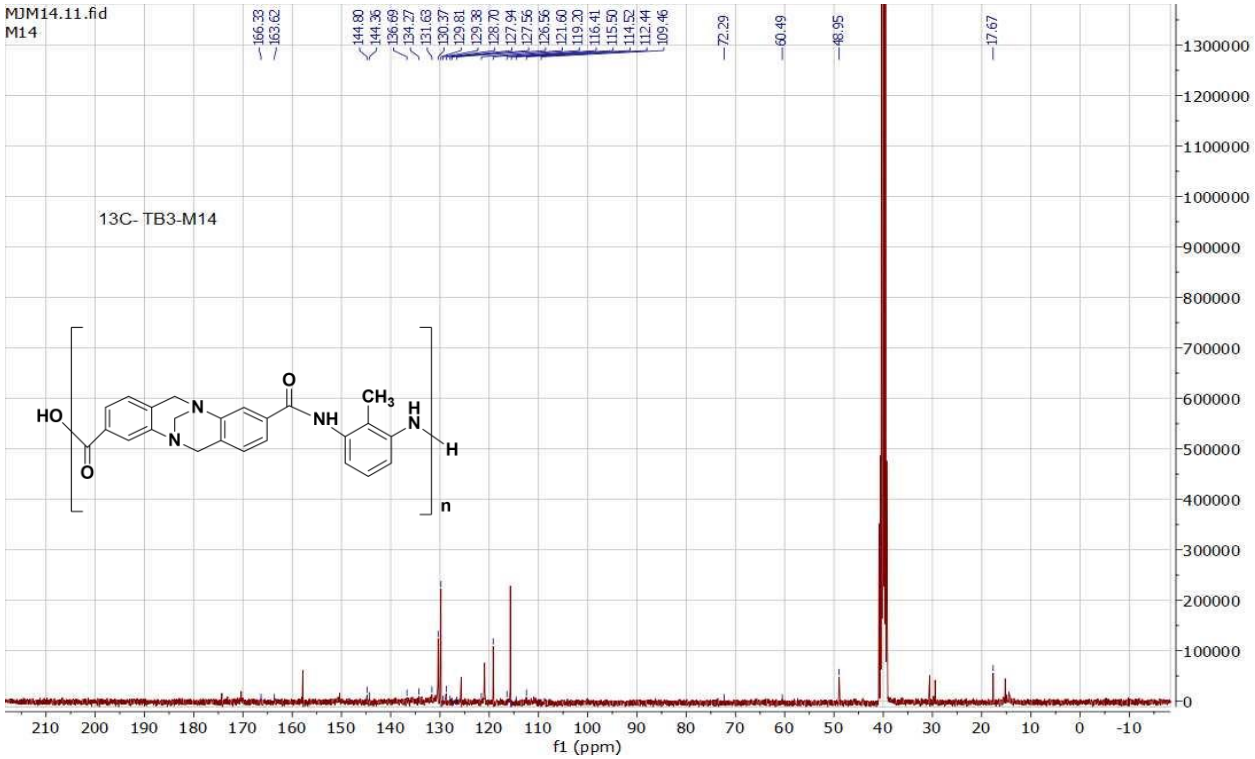


Figure 3-82: Chart of ^{13}CNMR for (TB3M14)

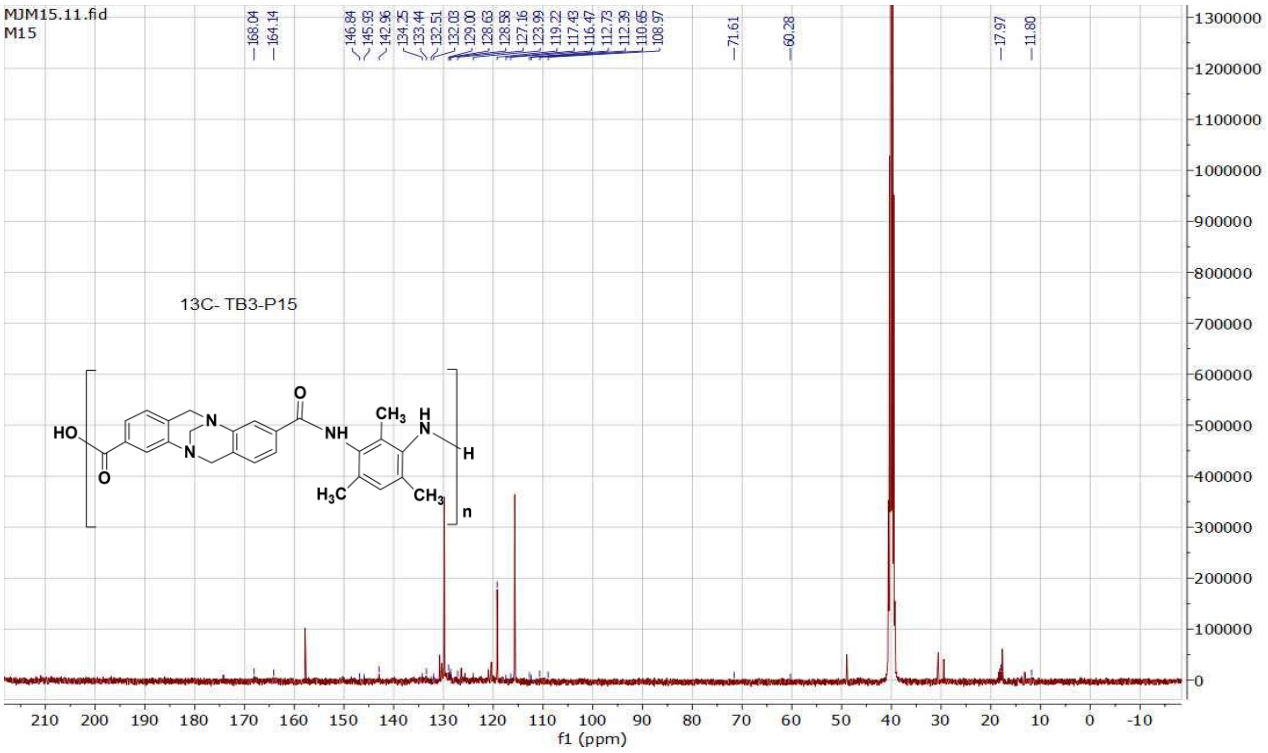


Figure 3-83: Chart of ^{13}CNMR for (TB3M15)

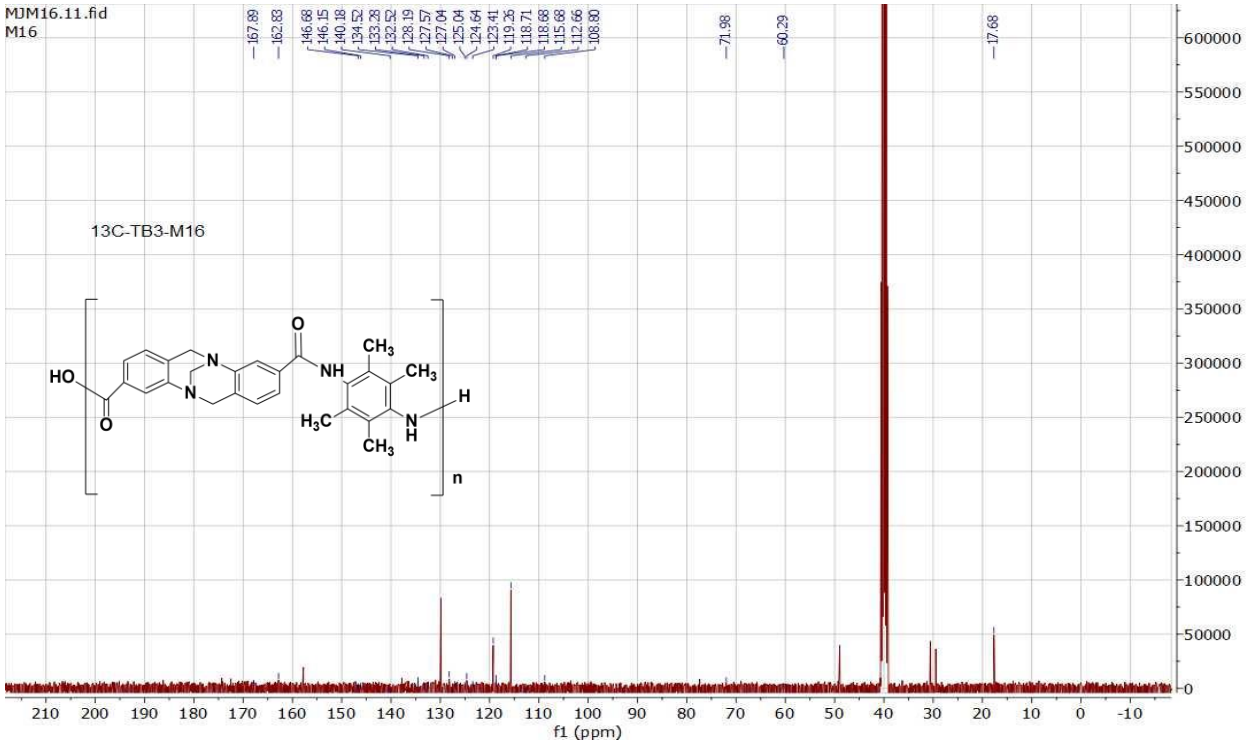


Figure 3-84: Chart of ^{13}CNMR for (TB3M16)

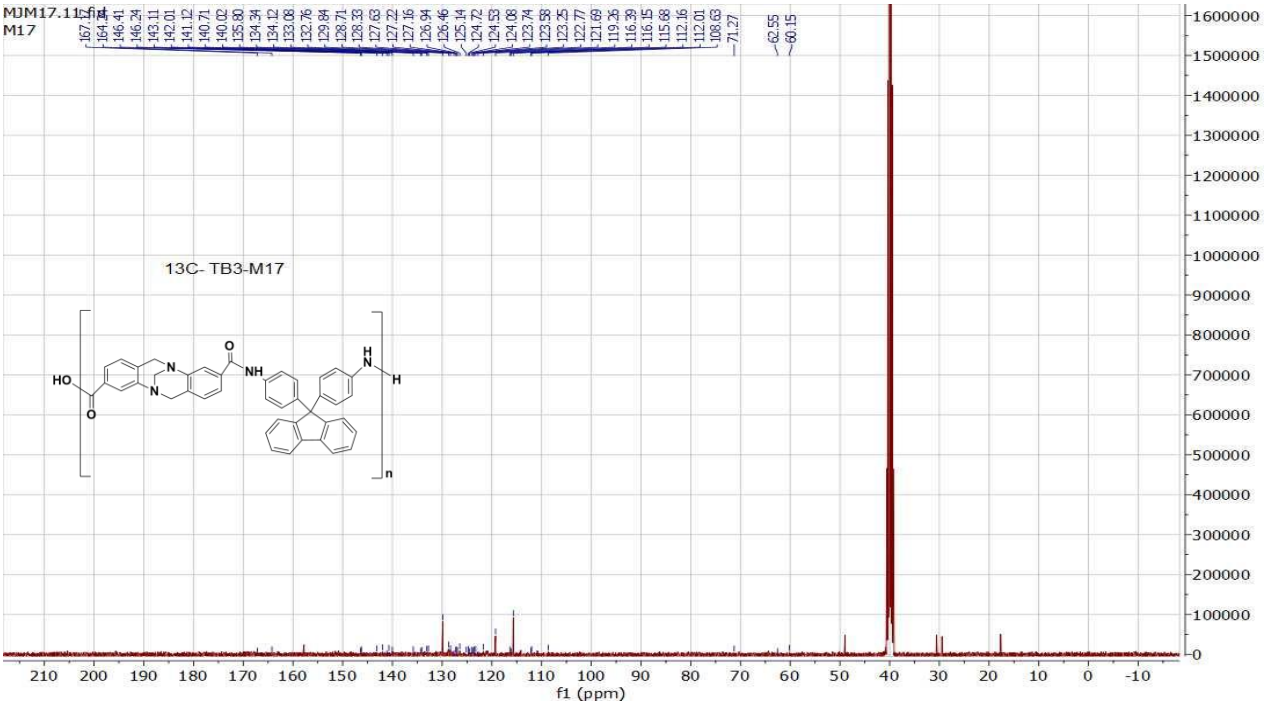


Figure 3-85: Chart of ^{13}CNMR for (TB3M17)

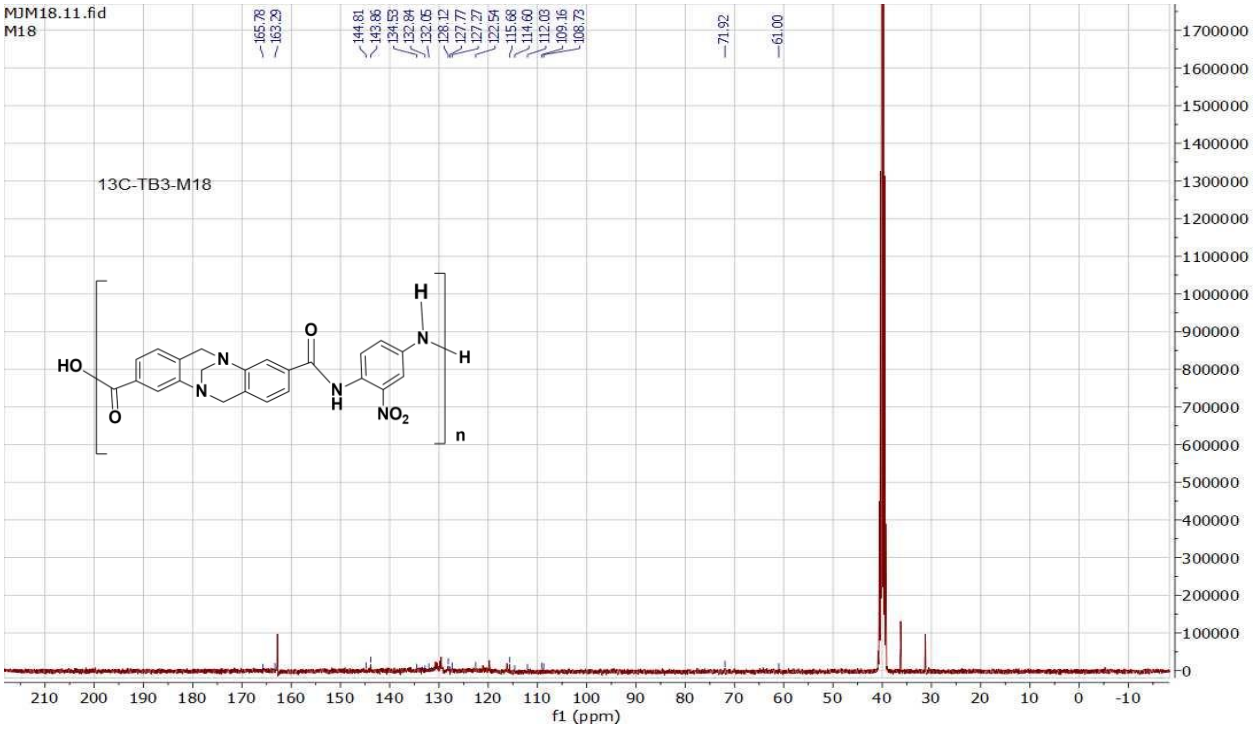


Figure 3-86: Chart of ^{13}CNMR for (TB3M18)

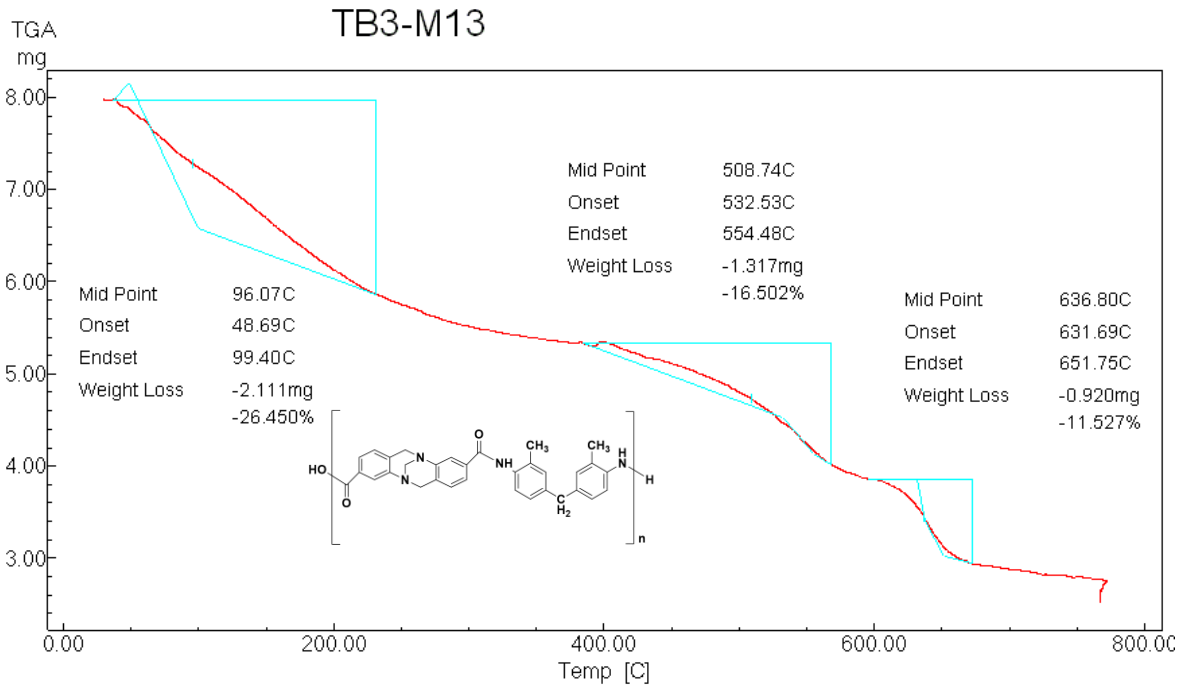


Figure 3-87:Chart of TGA for (TB3M13)

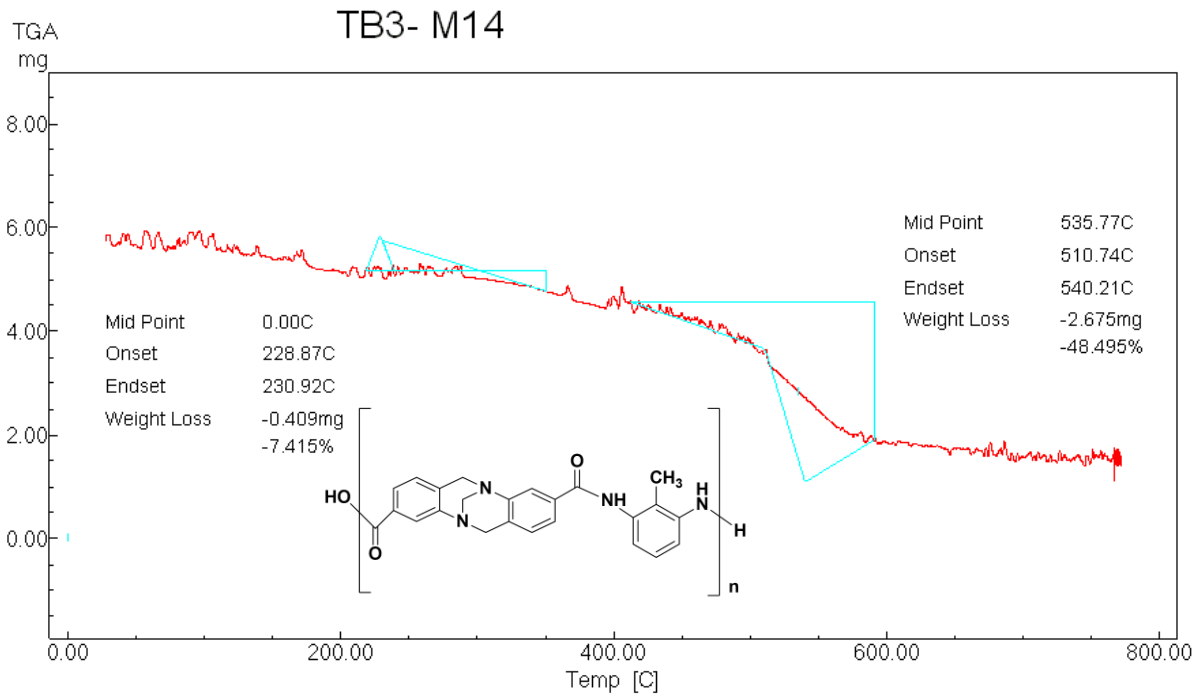


Figure 3-88:Chart of TGA for (TB3M14)

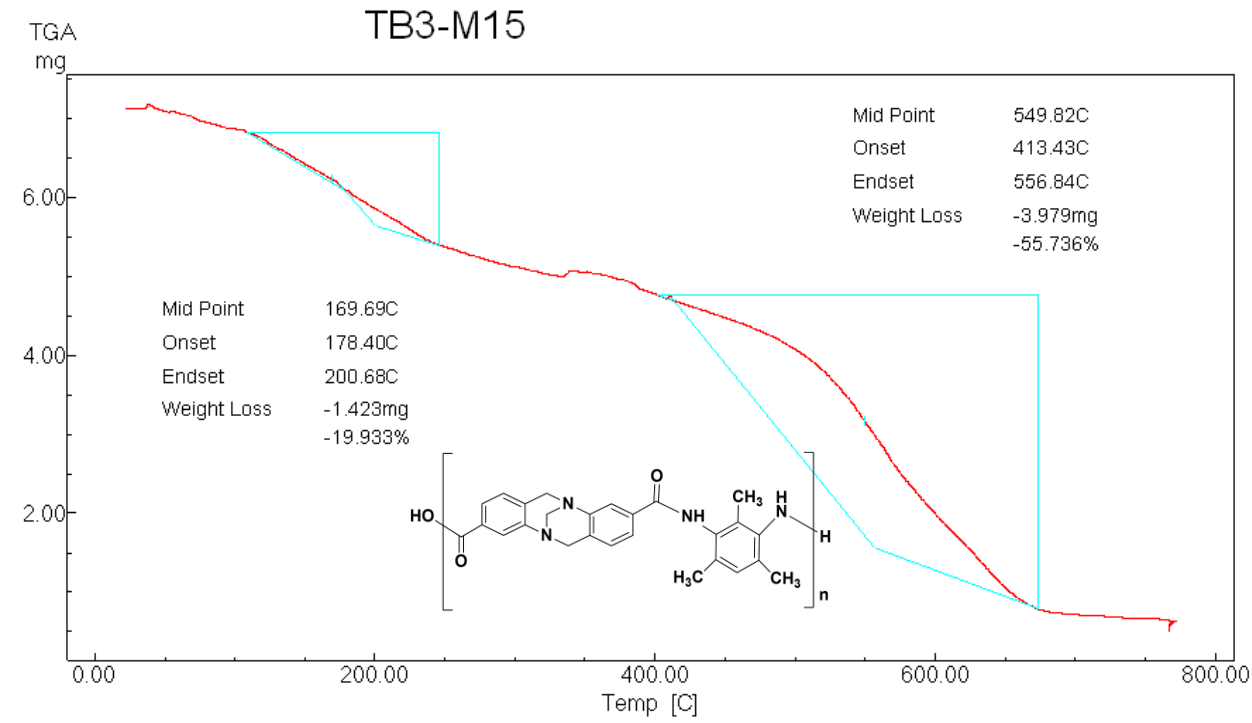


Figure 3-89:Chart of TGA for (TB3M15)

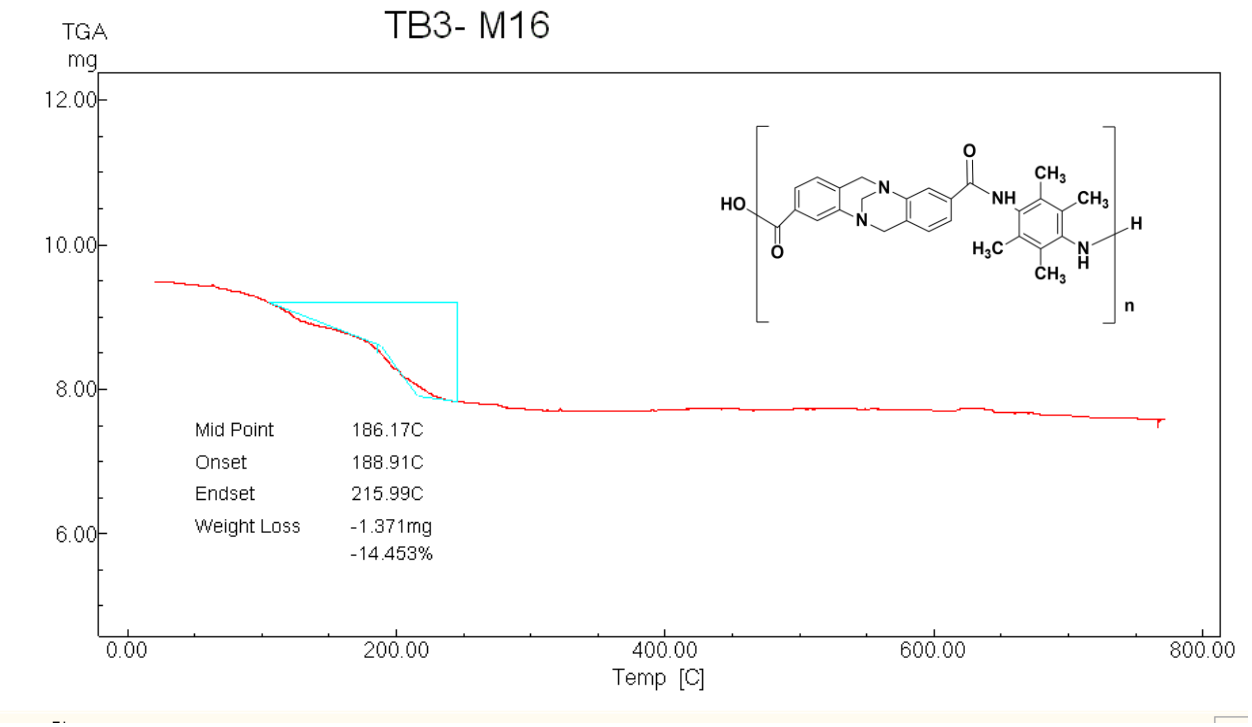


Figure 3-90:Chart of TGA for (TB3M16)

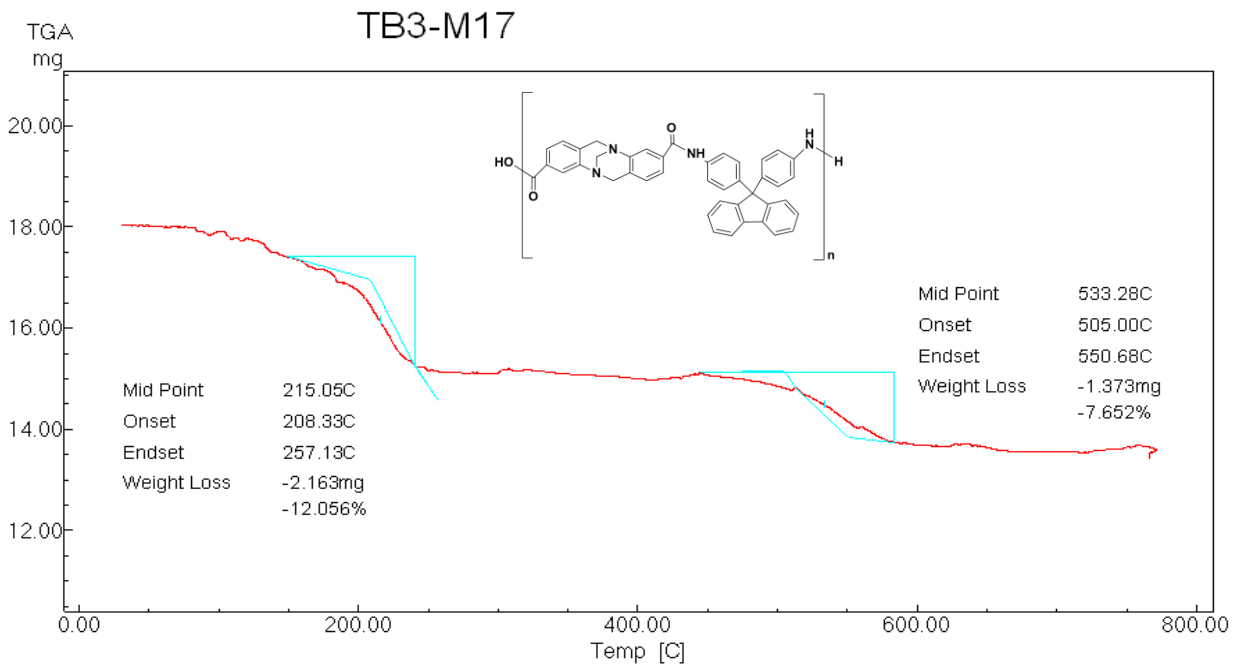


Figure 3-91:Chart of TGA for (TB3M17)

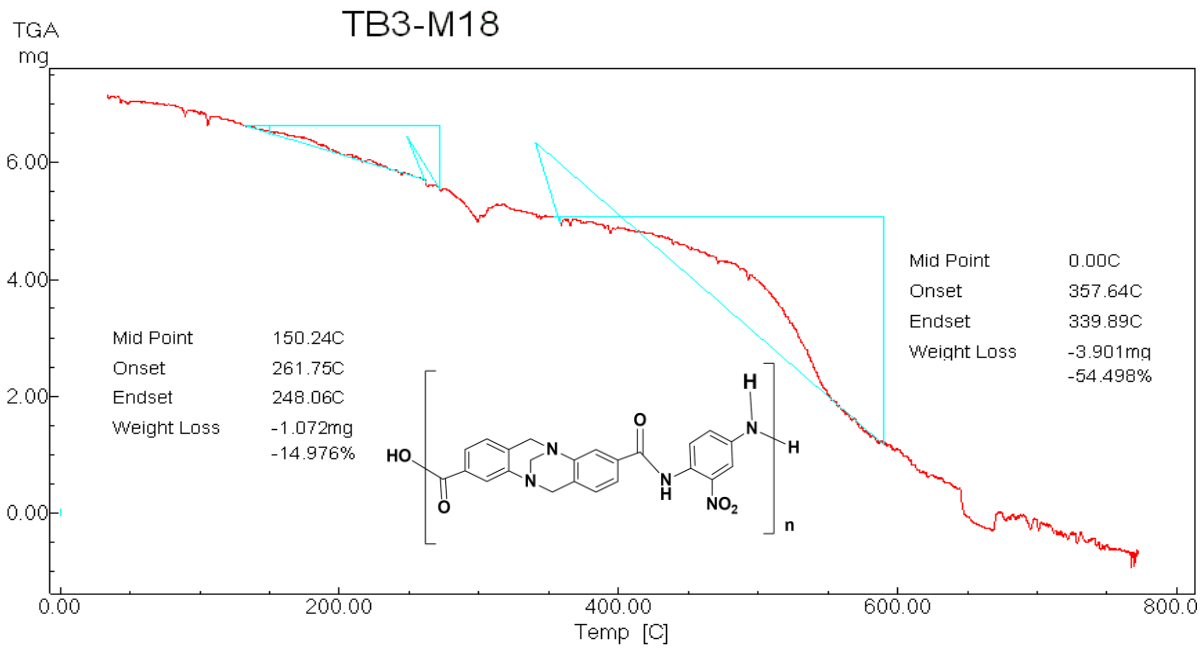


Figure 3-92:Chart of TGA for (TB3M18)

Conclusions

1. The method of preparing Troger bases has pure results and a good product.
2. Prepared Troger's bases were used as a monomer for the first time approximately
3. The polymerization technique is effective and can be applied to aromatic polyamides
4. Troger's bases contain carboxyl groups, which were not converted into acid chlorides but instead employed right away in the polymerization.
5. The thermal stability of several of the prepared polyamides was high.
6. The produced polyamides demonstrated great solubility stability, which is a positive characteristic for polymers

Recommendations

1. Recommend the synthesis of a new Tröger's bases by using other aniline derivatives containing others substituted .
2. Recommend the use of Tröger's bases as monomers with aliphatic. diamines in the synthesis of other types of polymers.
3. Recommend studying the mechanical properties of prepared polymers.
4. Recommend preparing film from these polymers and studying their purification for both liquids and gases permeation after knowing their surface area.
5. I recommend studying the use of these polymers as a surface to conduct oxidation-reduction reactions and others to know their chemical stability.

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الخلاصة

بشكل عام ، في هذه الأطروحة ، تم تحضير و توصيف بولي أميدات جديدة مستندة على مشتقات قواعد تروجر. لتحقيق ذلك ، تم تحضيراربعة مشتقات لقواعد تروجر , TB1 ,TB2 TB3 , TB4 التي تحتوي على مجموعات الكربوكسيل من خلال تفاعل مشتقات حامض البنزويك الأميني مع ثنائي ميثوكسي ميثان في حامض ثلاثي فلورو اسيتيك . تم استخدام قواعد تروجر الثلاثة الأولى(TB1 , TB2 , TB3) كمونومرات ، من خلال تفاعل التكثيف تم إنشاء بولي أميدات جديدة القائمة على قواعد تروجر في ثلاثة مسارات بناءً على نوع المونومر.

المسار الأول: يشمل تحضير البولي أميدات (TB1O1-TB1O6) عن طريق تفاعل مونومر TB1 مع مركبات ثنائي أمين والتي هي:

3,3’-dimethy1-4,4’-diamin0dipheny1methan , 2 ,6-diamino toluene , 2,4,6-trimethyl –m-phenylene diamine, 2,3,5,6- tetramethyl –l,4-pheny1ene di amine , 9,9 – Bi (4-amino phenyl , 2-Nitro- 1,4- phenylene – diamine

المسار الثاني: يشمل التوليف البولي أميدات (TB2P7 –TB2P12) عن طريق تفاعل مونومر TB2 مع مركبات ثنائي الأمين والتي هي :

3,3’-dimethy1-4,4’-diamin0dipheny1methan , 2 ,6-diamino toluene , 2,4,6-trimethyl –m-phenylene diamine, 2,3,5,6- tetra methyl –l,4-pheny1ene di amine , 9,9 – Bi (4-amino phenyl , 2-Nitro- 1,4- phenylene – diamine

والمسار الثالث: يشمل تخليق البولي أميدات (TB3M13- TB3M18) عن طريق تفاعل مونومر TB3 مع مركبات ثنائي أمين والتي هي

3,3’-dimethy1-4,4’-diamin0dipheny1methan , 2 ,6-diamino toluene , 2,4,6-trimethyl –m-phenylene diamine, 2,3,5,6- tetra methyl –l,4-pheny1ene di amine , 9,9 – Bi (4-amino phenyl , 2-Nitro- 1,4- phenylene – diamine

تم تشخيص المونومرات الناتجة من خلال تحليل الخصائص الفيزيائية مثل الذوبان ونقطة الانصهار ، وكذلك استخدام الأشعة تحت الحمراء ، وقياس الطيف الكتلي ، وطيف XRD و ^{1}HNMR ، وطيف ^{13}CNMR . تم تشخيص البولي أميدات أيضًا بواسطة FTIR و TGA و NMR (1H ، 13C).

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تحضير بولي أميدات جديدة مستندة على بعض جزيئات قواعد تروجر

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من متطلبات نيل شهادة الماجستير في العلوم / علوم الكيمياء

من قبل

محمد جابر جاسم

إشراف

أ.م.د. صادق عبد الحسين كريم

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