CHAPTER 3

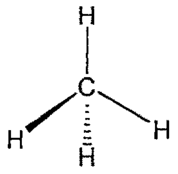
Designing Functionalised Polyaromatic Systems for Well-controlled Macromolecular Synthesis

3. Designing Functionalised Polyaromatic Systems for Well-controlled Macromolecular Synthesis

3.1 Introduction

Symmetry is one of the most fundamental properties of matter. Symmetry is present in the fundamental particles to the shape of the universe. Symmetry makes things beautiful. Flowers are attractive due to the symmetrical shape in addition to the fragrance and colour gifted by nature. Almost all animals have a symmetrically looking body, which can be divided into two parts looking similar to each other and are mirror images of each other. Symmetry is also present in some famous man made structures such as the pyramids in Egypt and the Taj Mahal in Agra. Their magnificent symmetrical structures built years ago attract tourists around the world.

Symmetrical objects are always aesthetically appealing. As far as chemistry is concerned molecules and crystals have different types of symmetry present in them. Compounds having symmetry can be classified according to the symmetry element they possess. Methane **1**, the simplest organic molecule, has C_3 symmetry while dodecahedron **2** or [60]fullerene **3** with round shape has I_h element of symmetry. The compounds with



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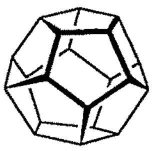

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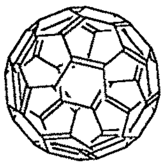

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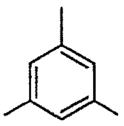
three-fold symmetry belong to the point group C_3 or D_3. In recent years, a number of papers appeared dealing with the synthesis, properties and application of the compounds with C_3 symmetry.[1]

C_3 Symmetric compounds have been built up by carrying out triple substitution on either nitrogen, benzene or triazine.[2] Benzene ring provides a flat and rigid platform as a nucleus to grow C_3 symmetric compounds. Mesitylene or 1,3,5-trimethyl benzene **4** is a



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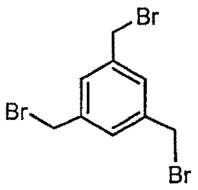

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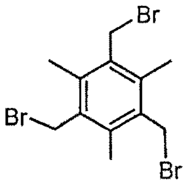

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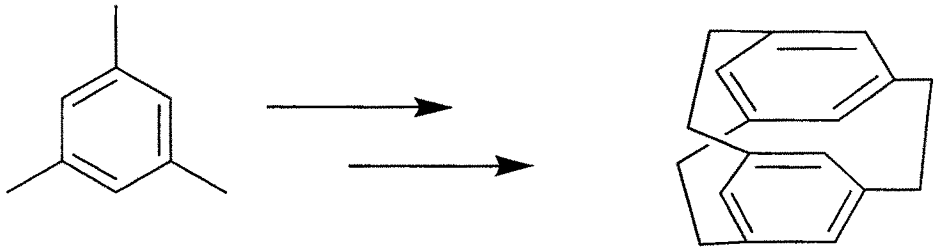
versatile, easily available, cheap starting material provided with three handles in the form of three methyl groups. It has been widely used in preparation of a variety of compounds[3,4,5,6] and materials.[7,8] Mesitylene has been used for preparation of

(2_3)[1,3,5] cyclophane[9] **7** and in an attempted synthesis of sumanene **8** resulting in the synthesis of sico-sumanene.[10]



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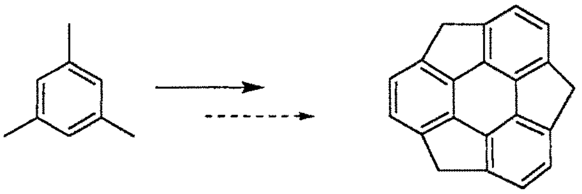

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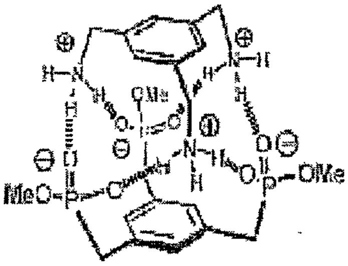
1,3,5- and 2,4,6- differently alkynyl benzenes have been reported starting from mesitylene **4** via 1,3,5-triformyl-2,4,6-tribromobenzene.[11] Mesitylene has been converted to 2,4,6 tris- (bromomethyl) mesitylene **6** in a good yield by bromomethylation using paraformaldehyde and hydrobromic acid[12] which can be replaced by the mixture of potassium bromide and concentrated sulphuric acid.[4] The bromomethylated mesitylene has also been employed in synthesis of C_3 symmetric tripodal molecules.[13,14,15,16] Interestingly, 2,4,6-tris(bromomethyl)mesitylene **6** has been employed for preparation of the triphoshonate, which gave ball-shaped molecular complex **9** with its tris- ammonium counter part.[17]



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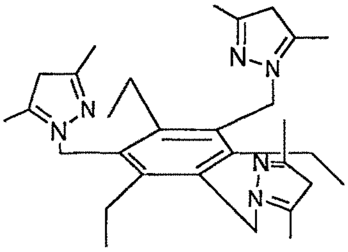
1,3,5-Tris(bromomethyl)benzene **5** and its derivatives have been coupled with various five membered heterocyclic compounds such as imidazole, oxazole, and pyrazole. The resulting C_3 symmetric compounds have been employed as the synthetic receptors, binding with the different types of cationic or anionic guests.[18] The heterocyclic tripodal host molecules form enforced cavity with locking of one of the conformer having all the three arms at the same side of the aromatic ring while binding with the guest molecules. The receptors have been shown to have selectivity for one guest over the other. For example, the host with pyrazoles (e.g. **10)** or oxazoles attached acting as binding sites selectively recognize NH_4^+ ion over K^+ ion.[18(c, d)] The receptor



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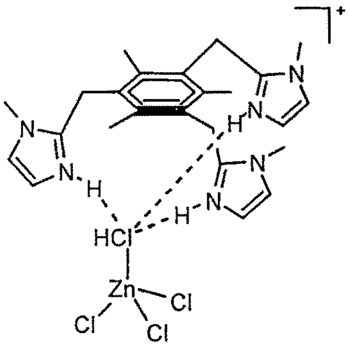
with the tris(imidazolylaminomethyl) group is selective for citrate ions over succinate, acetate, and glutanate ions. It has been employed as a sensor for colorimetric chemosensing for tartarate or maleate in beverages.[18(f)]

The compounds with tris(imidazolylmethyl) groups attached to benzene or mesitylene act as ligands forming complexes with transition metals giving different types of networks or assemblies.[19] The ligands have also been used for complexing with zinc or ruthenium salts (**11** and **12**). It was found to be hydrogen bonded complex with $ZnCl_4$ and was compared with a parachute by the authors.[20]



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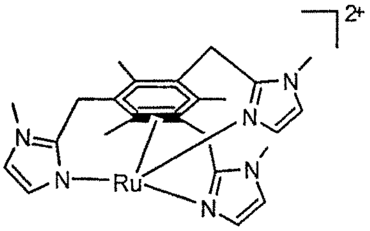

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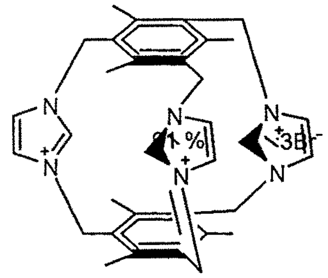
1-Hydroxybenzodifuran derivative prepared during the study of the reaction of citronellal with electron rich phenols was triply coupled with 1,3,5 tris-bromomethyl mesitylene giving a corresponding C_3-symmetric trisubstituted product.[21] Tris(imidazolylmethyl) mesitylene and its corresponding benzimidazolyl analogue have been conveniently coupled with 1,3,5 tris-bromomethyl mesitylene using high dilution technique giving tri-cationic azolophane structures **13, 14** in high yield.[22]



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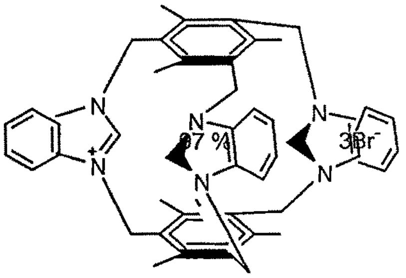

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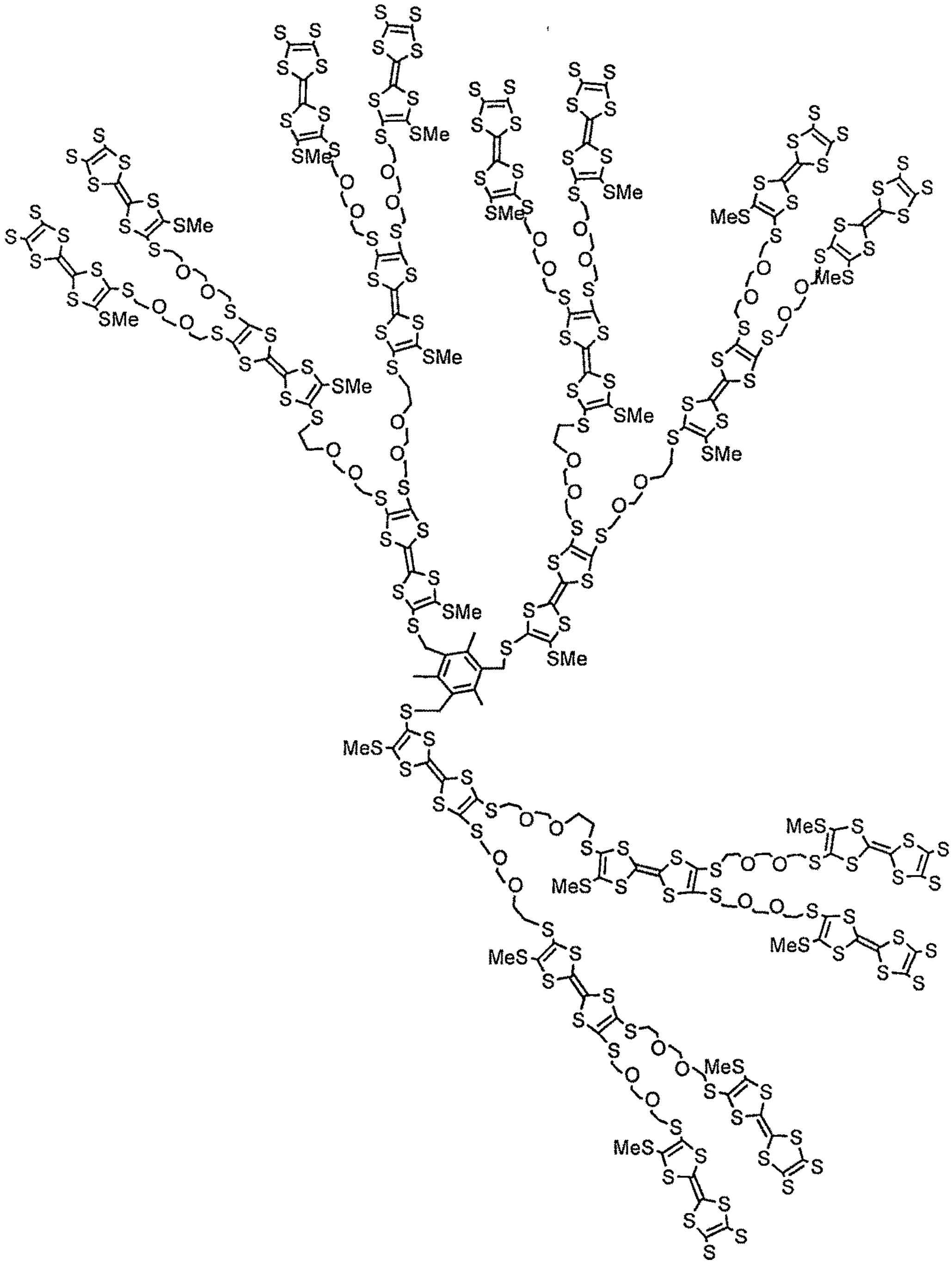
A dendritic macromolecule **15** has been synthesized by coupling 1,3,5-tris(bromomethyl)mesitylene with preformed tetra(thiafulvelene) connected via ethylene glycol units in a convergent synthesis using cesium hydroxide in aqueous alcoholic DMF.[23] Palladium containing metallodendrimers with hydrophobic dendrons at the



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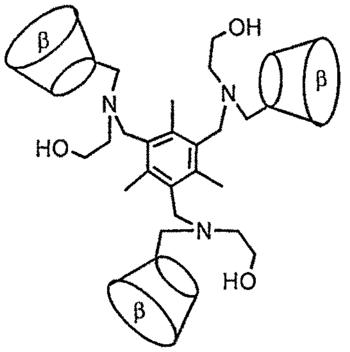
periphery have been reported by Reinhoudt *et al* using the convergent approach. These dendrimers show increased solubility in apolar organic solvents.

A tripodal structure having 2 to 3 ruthenium nuclei in a chain separated by oxygens termed as metallodendrimers have been prepared and characterised.[24] Interesting host molecules have been prepared by coupling 1,3,5-tris(bromomethyl)mesitylene with the preformed molecules having cavity in their structure. Thus 6-deoxy-6-hydroxy ethyl amino-β–cyclodextrin was reacted with 1,3,5-tris(bromomethyl)mesitylene in presence of a base to give a molecule with three cyclodextrins **16**.[25] Similarly it was also coupled with hydroxy calix[4]arenes resulting in a novel molecular receptor.[26]



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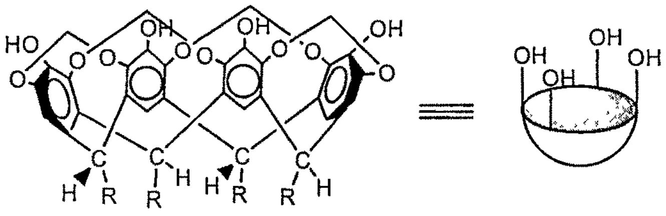
In an equally interesting but more challenging synthesis three hemicarceplexes **17** connected giving cyclic trimer with a rigid barrel-shaped molecule **18** which was closed from both the sides using 1,3,5-(trisbromomethyl)mesitylene entrapping three DMF molecules permanently inside the cavity.[27]



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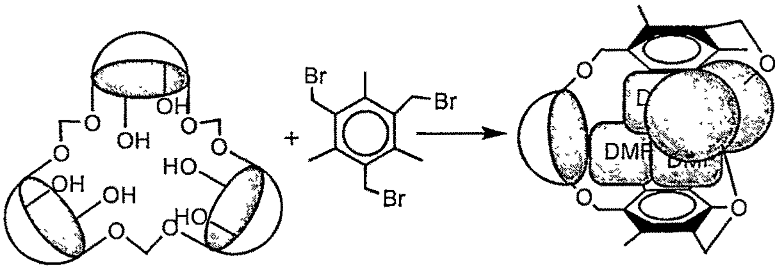

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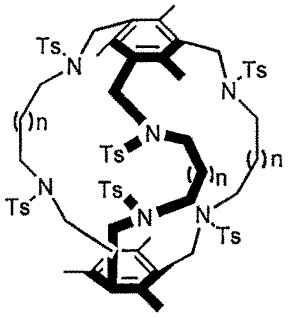
A macrobicyclic cryptand **19** with two tosyl amino groups present in the linking chains was prepared by coupling two units of 1,3,5-tris(bromomethyl)mesitylene via N-tosyl-ω-bisaminoethane or propane in a one-step or in a divergent process giving a closed structure which could act as a host for a variety of guests.[28]



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3.2 Aim and Objectives

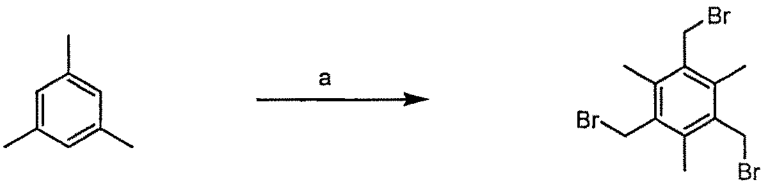
Looking at the diversity, applications and possibilities lying in the C_3 symmetric compounds, we decided to prepare and study some functionalised C_3 symmetric molecules beginning with mesitylene and its derivatives. The functionalities present in the resulting compounds should be further applicable in introducing the required moiety or in expanding the molecule. Thus with a view to present novel advanced building blocks with the aromatic ring providing central rigid platform synthesis of C_3 symmetric functionalised molecules has been undertaken. The resulting tripodal compounds constructed here should have greater flexibility which may allow them to attain the conformation and geometry according to the demand or need of guest molecules or for constructing larger host molecules. These systems are expected to be useful in preparation of dendrimeric structures. The molecules have been designed with the possibility of introducing chiral sensors or chelating sites with greater secondary interactions. 1,3,5-trimethylbenzene or mesitylene **4** can be converted to 1,3,5- tris(bromomethyl)benzene **5** by triple free radical substitution using NBS in the presence of AIBN or UV light or both normally in a low yield because of competitive further substitutions. On the other hand, bromomethylation of mesitylene gives a good yield of 1,3,5-tris(bromomethyl)mesitylene **6**. Bromomethylation was carried out by reacting mesitylene, paraformaldehyde and HBr in acetic acid (31%) giving a good yield of **6** for its use as the starting material for the preparation of C_3 symmetric compounds. While looking for a suitable counterpart for carrying out triple substitution reactions, we considered different functional aromatic compounds including aromatic amines, phenols, halides, phosphorus compounds, thiols etc. We decided to employ various phenolic aldehydes for this purpose. Phenolic aldehydes would not require protection of any functional group and most of them are readily available or can easily be prepared. In general, the coupling of a benzyl halide and a phenol does not pose any difficulty. A formyl group is not affected under the reaction conditions. Thus the coupling reactions of tris(bromomethyl)mesitylene with phenolic aldehydes would result in the compounds having formyl groups ortho or para to the newly formed linkage. Any additional substituent on the ring might also be useful in case it is required.

This chapter reports the synthesis and characterisation of five new C_3 symmetric tripodal compounds having three formyl groups useful for further manoeuvring of the designed molecules for different applications.

3.3 Results and discussion

As mentioned, this chapter involves the preparation of C_3 symmetric tripodal aromatic compounds having a central aromatic ring. The central aromatic ring was provided by 1,3,5-tris(bromomethyl)mesitylene. The later compound was conveniently prepared by bromomethylation of mesitylene using paraformaldehyde and HBr in acetic acid (31%). There are several methods reported [4,12,13] for bromomethylation of aromatic compounds. In other methods, alkali bromides have been used instead of HBr giving lower yield with no apparent advantage except HBr is avoided and is replaced by alkali halide and concentrated sulphuric acid.

Scheme-1



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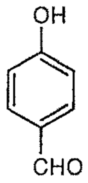
Reagent and conditions: a) Paraformaldehyde, HBr/HOAc, 12h, 95^{0}C, 91 %

The phenolic aldehydes included in our synthesis are 4-hydroxybenzaldehyde **20**, 2-hydroxybenzaldehyde (salicaldehyde) **21**, 3-methoxysalicyldehyde (*o*-vaniline) **22**, 4-hydroxy-3-methoxybenzaldehyde (vanillin) **23**, and 2-hydroxynaphthaldehyde **24**. Except 2-hydroxynaphthaldehyde the other phenolic aldehydes are readily available and are inexpensive. 2-Hydroxynaphthaldehyde **24** was found to be costly and so was prepared in laboratory from β-naphthol using the Riemer-Tiemann reaction.[29] Other phenolic aldehydes were used without further purification. The tri-substitution on tris(bromomethyl)mesitylene **6** with the phenolic aldehydes was carried out in dry acetone using K_2CO_3 or Cs_2CO_3 in an inert atmosphere under nitrogen. K_2CO_3 was satisfactory for the reaction with phenols other than salicaldehyde and 2-hydroxy naphthaldehyde. The reaction of 2-hydroxynaphthaldehyde with **6** failed to give the desired product with K_2CO_3 at different temperatures and was getting degraded without giving the coupling reaction. Salicaldehyde **21** was stable under the reaction conditions but also did not couple when K_2CO_3 was used. There was a drastic change in the results for both these reactions when the base was changed to Cs_2CO_3 at room temperature, and the desired product was isolated. Careful comparison of the reaction indicated that the presence of Cs^+ ion must be providing template effect and holding the reactants using secondary effects in the required orientation, facilitating the reaction and simultaneously acting as a base (**Figure 1**).



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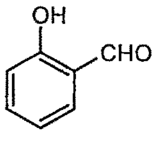

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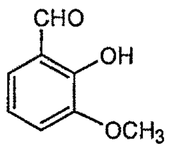

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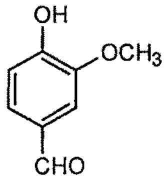

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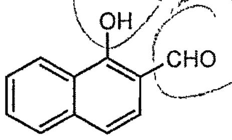

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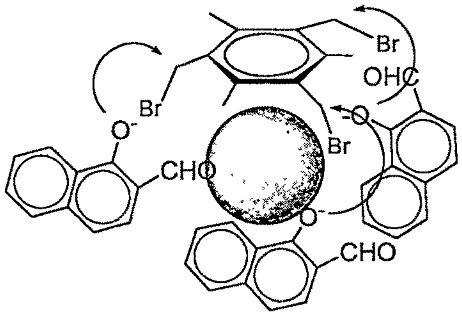
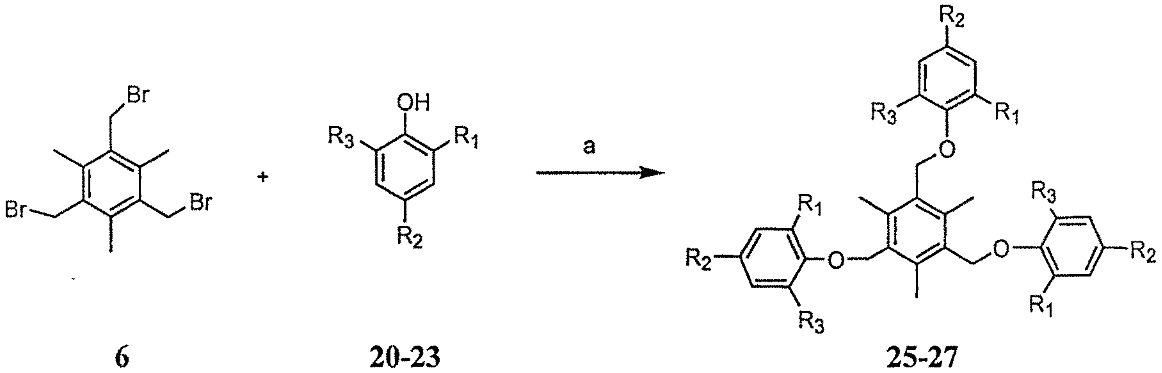


Figure-1

The bases used in these reactions were weak and safe enough not to give any side reactions except mono- or di- substitution taking place during the course of the reaction.

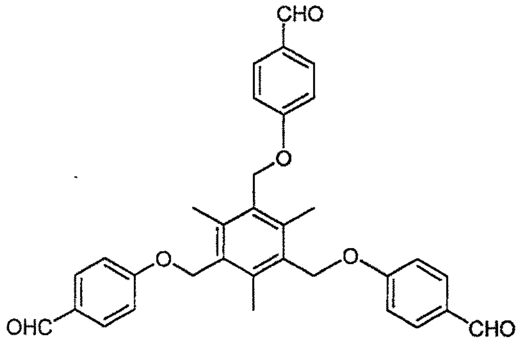
Scheme-2



6 **20-23** **25-27**

R_1, R_2, R_3 = H/CHO/OCH_3

Reagents and Conditions: K_2CO_3, acetone, Δ, 3h, 75-85%



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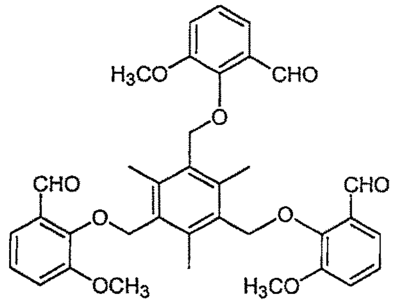

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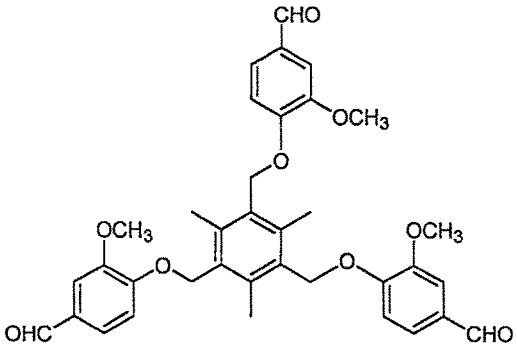

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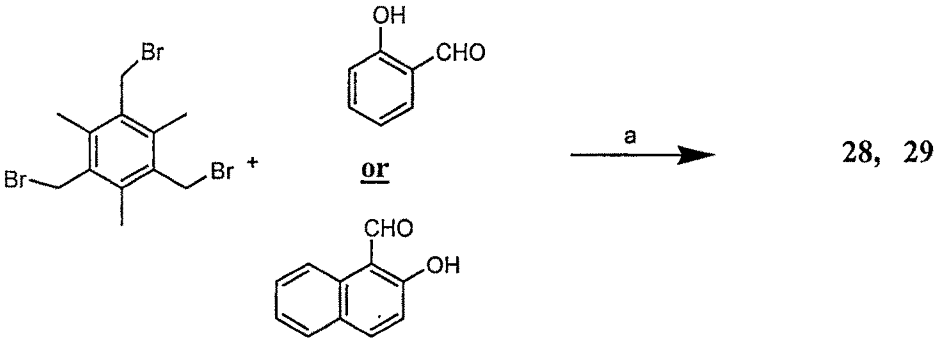
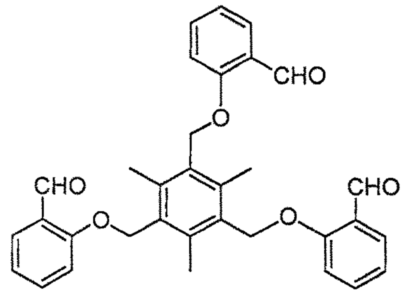
Scheme-3



Reagents and Conditions: a) Cs_2CO_3, acetone, Δ, 2–3h, 60-65%



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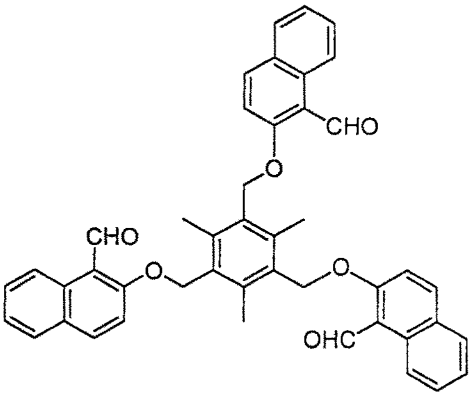

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The three-fold sustitutution reactions have resulted in satisfactory to good yield changing from 65 to 85%. 2-Hydroxybenzaldehyde and 4-hydroxybenzaldehyde gave the product with no further substitution on the aromatic podands except the formyl groups. On the other hand, the vanillin isomers provided extra binding sites in the form of a methoxty group an ortho position to the ether linkage. It helps in binding or in coordination near the centre of the C_3-symmetric molecule. The methoxy groups brought in by the reaction of *p*-vanillin would not be helpful to the functionality introduced by the reaction with the formyl group as it is present away from both the ether linkages. The product obtained from the reaction of *o*-vanillin has all the three functionalities placed together and so the methoxy and the benzyloxy ether would be supportive to any chelating site generated from the reaction with the formyl group. This situation seems to be advantageous compared to the tripodal structures obtained from the reactions with salicyldehyde where there is only the benzyloxy group ortho to the formyl group. The substitution product from 2-hydroxynaphthaldehyde is different from all the other C_3 symmetric structures prepared over here. It provides an extended aromatic structure on all the three sides of the molecule. Due to this, an extended π stacking interaction can take place with the guest molecules or even cation-π cloud secondary interactions may also take place in a reversible fashion, which can be used to an advantage in a host-guest interaction or in the preparation of closed cage-like structure.

The three-fold substitution reactions were confirmed by characterisation using various available analytical methods. The presence of formyl group was clearly apparent from IR specra. The C=O stretching frequency was observed around 1682 to 1693 cm^{-1} and C-H stretching absorption 2830 to 2855 cm^{-1}.

In PMR the symmetrical structure of the products were reflected with the number of signals. The formyl group proton was observed in the range of 9.89 to 10.4ppm. The methyl groups attached to the central ring give singlet near 2.5ppm. The benzyloxy methylene group was also observed as singlet at between 5.2 to 5.4ppm. The methoxy group in the vanilline products was obtained at about 3.9ppm. The signals in the aromatic region were observed between 7 to 8 ppm with the pattern according to substituent present on them.

The product with naphthaldehyde substitution has characteristic PMR spectrum with a methyl group on an aromatic ring as a singlet at 2.6 ppm and a singlet at 5.4 ppm for the $-CH_2$ group attached to the oxygen. All the aromatic protons distinctly separated between 7.4-8.2ppm and most downfield signals at 9.28ppm for the proton at the positon 8 of the naphthyl ring. This signal is absent in the PMR of the product obtained with the salicyldehyde where all the other features are present. In total, there are 4 doublets and 2 triplets. The proton of the formyl group is observed at lower value of 10.8ppm as a singlet. The spectrum supports C_3 symmetric structure of the molecule.

3.4Experimental

Mesitylene and Cs_2CO_3 were purchased from Sigma-Aldrich chemicals. Paraformaldehyde, HBr in HAc (33%), o-vanillin, vanillin, salicaldehyde, p-hydroxy benzaldehyde were purchased from S-d-fine Chemical. All the solvents and other chemicals were obtained from Suvidhinath Chemicals. Solvents were purified by standard methods and reagents were used without purification.

Melting points were taken on a Gallenkamp 350 micro melting apparatus by open capillary method and are uncorrected. Infrared spectra were recorded using Perkin-Elmer 16PC as KBr discs between 4000-600 cm^{-1}. ^{1}H-NMR spectra were recoreded on Bruker-AVX 200MHz and 400 MHz and ^{13}C-NMR spectra on Bruker-AVX 50.13 MHz. ^{1}H- and ^{13}C-NMR spectra were recorded in DMSO-d_6 or $CDCl_3$ with TMS as the internal standard. Elemental analysis were recorded on Perkin-Elmer 240 C, H, N analyser.

1,3,5-Tris(bromomethyl)-2,4,6-trimeth benzene[1] (6) or Tris-(bromomethyl)mesitylene)

To a mixture of mesitylene(12.0 gm.;0.1 mol) paraformaldehyde (10.0gm.;0.33mol) and 50 mL of glacial acetic acid was added 70 mL of 31% HBr in HAc rapidly. The mixture was stirred for 12 hrs. at 95^0C and then poured into 100mL of water. The solid product was filtered off with suction and dried in vacuum.

Tris-(bromomethyl)mesitylene was obtained as a white solid after recrystallization from dichloromethane.

Yield:	36.3 g (91%)
M.P.:	185^0 C Lit ?

Preparation of aryloxy tri-aldehydes 1-

General Procedure:

A phenolic aldehyde (3 mmol) was refluxed with K_2CO_3 (14.49 mmol) in dry acetone (50 mL) for 30 min. after which 1,3,5-tris (bromomethyl)-2,4,6-trimethyl benzene was added and the mixture was further stirred under reflux for 3 hrs. The solvent was removed and water (100mL) was added. The solid product thus obtained was filtered and recrystallised.

1,3,5 –Tris((4-formylphenyloxy)methyl)-2,4,6-trimethyl benzene (25)

4-Hydroxy benzaldehyde (0.366 gm., 3mmol) and K_2CO_3 (2gm.,14.49 mmol) in dry acetone 50 mL were refluxed with stirring for 30 min. followed by the addition of 1,3,5-tris (bromomethyl)-2,4,6-trimethyl benzene (0.399 gm.,1mmol) and further refluxed for 3 hrs. After work-up the crude product was recrystallized from ethanol giving a light yellow crystalline solid.

Yield:	0.4 gm. (76.62%)

M.P.:	194^0 C
IR (KBr, cm^{-1}):	1681, 2831, 1582, 1374,2931, 1506, 752.
^{1}H-NMR (CDCl$_3$, δppm):	2.45 (s, 9H,-CH$_3$) 3.1 (s, 6H, Ar-CH$_2$-O-Ar) 9.8 (s, 3H, -CHO) 7.0 (d, aromatic) 7.3 (d,aromatic).
^{13}C-NMR (CDCl$_3$, δppm):	16.03 (Ar-$\underline{C}H_3$) 65.2 (Ar-$\underline{C}H_2$-O-Ar) 190.7(-$\underline{C}$HO) 114.8-167.9 (aromatic carbons).
Anal. Calcd. for $C_{33}H_{30}O_6$:	% **C** 75.86, **H** 5.7
Found:	% **C** 76.2, **H** 5.75

1,3,5-Tris ((2-formyl-6-methoxy phenyloxy)methyl)-2,4,6-trimethylbenzene (26)

3-Methoxy 2-hydroxy benzaldehyde (*o*-vanillin) (0.459 gm.,3mmol) was refluxed with K_2CO_3 (2 gm.,14.49 mmol) in dry acetone (50 mL) with stirring for 30 min. when 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (0.399 gm.,1mmol) was added and the mixture was further refluxed for 3 hrs. The product was crystallised from acetonitrile.

Yield:	0.510 gm. (82.5%).
M.P.:	208 ^{0} C.
IR (KBr, cm^{-1}):	1693, 2839, 1594, 1388, 2940, 751.
^{1}H-NMR (CDCl$_3$,δppm):	2.45 (s, 9H,-C$\underline{H}_3$) 3.96 (s,9H,-OC$\underline{H}_3$) 5.45 (s, 6H, Ar-C$\underline{H}_2$-O-Ar) 10.15 (s, 3H, -C$\underline{H}$O) 7.2 (m, aromatic), 7.4 (dd,aromatic)
^{13}C-NMR (CDCl$_3$,δppm):	16.0 (Ar-$\underline{C}H_3$), 56.09 (Ar-O-$\underline{C}H_3$), 77.03 (Ar-$\underline{C}H_2$-O-Ar), 190.9(-$\underline{C}$HO), 114-154.1 (aromatic carbons).

Anal. Calcd. for $C_{36}H_{42}O_9$: % **C** 69.9, **H** 6.79

Found: % **C** 70.3, **H** 6.31

1,3,5 Tris-((4-formyl-2-methoxy phenyloxy)methyl) 2,4,6 trimethyl benzene (27)

2,4,6 trimethyl benzene and 4-hydroxy 3-methoxy benzaldehyde (vanillin) (0.459 gm., 3mmol) were stirred under reflux with K_2CO_3 (2gm., 14.49 mmol) in dry acetone (50 mL) for 30 min. followed by addition of 1,3,5-tris (bromomethyl)-2,4,6-trimethyl benzene (0.399 gm.,1mmol) and further refluxed for 3 hrs. The product was crystallised from dioxan.

Yield: 0.525 gm. (84.95%)

M.P.: 212^0 C.

IR (KBr, cm^{-1}): 2922, 2829, 1691, 1600, 1508, 1372

^{1}H-NMR ($CDCl_3$, δppm): 2.46 (s, 9H, $-CH_3$), 3.87 (s, 9H,$-OCH_3$), 5.2 (s, 6H, Ar-CH_2-O-Ar), 9.9(s, 3H, -CHO), 7.5(dd, aromatic), 7.2(d) and 7.4 (d, aromatic).

^{13}C-NMR ($CDCl_3$,δppm): 16.1 (Ar-$\underline{C}H_3$), 55.9 (Ar-O-$\underline{C}H_3$), 63.7 (Ar-$\underline{C}H_2$-O-Ar), 190.9(-$\underline{C}$HO), 106.4-154.1 (aromatic carbons).

Anal. Calcd. For $C_{36}H_{42}O_9$: % C 69.9, H 6.79

Found: % C 69.8, H 5.72.

1,3,5-Tris((2-formylphenyloxy) methyl)-2,4,6-trimethyl benzene (28)

A mixture of 1,3,5-tris(bromomethyl)-2,4,6-trimethyl benzene (2.0gm., 5mmol), salicylaldehyde 2.198 gm., 1.91 ml, 17.5 mmol) and Cs_2CO_3 (1.955 gm., 6mmol) was stirred for 3h in 100 ml of acetone at room temperature. The reaction mixture was poured into crushed ice and the white solid separated was filtered under suction. The solid was purified by column chromatography (Silica gel, Pet.ether: EtOAc: 70:30) to yield a white crystalline solid.

Yield: 63.07% (1.65 gm.)

M.P.: 184°C

IR (KBr, cm^{-1})**:** 2921, 1596, 1508, 2744, 2862, 1684, 1371, 756.

^{1}HNMR: 2.48 (s, 9H,Ar-CH_3), 5.25 (s, 6H, Ar-CH_2-O-Ar), 10.4 (s, 3H, -CHO), 7.9, 7.59, 7.2 (aromatic protons).

Anal. Calcd. For $C_{33}H_{30}O_6$: % **C** 75.86, **H** 5.7

Found: % **C** 75.71, **H** 5.38

1,3,5-Tris ((2-formylnaphthyloxy) methyl) 2,4,6 trimethyl benzene (29)

A mixture of 1,3,5-tris (bromomethyl)-2,4,6-trimethyl benzene (2.0gm., 5mmol), 2-hydroxy 1-naphthaldehyde (3.44gm., 20 mmol) and Cs_2CO_3 (1.955 gm., 6mmol)was stirred for 2h in 100 ml of acetone at room temperature under N_2 atmosphere. The reaction mixture was transferred into crushed ice to yield a white solid, which was filtered by suction. The solid was recrystallized from ethyl acetate to obtain a shiny white solid.

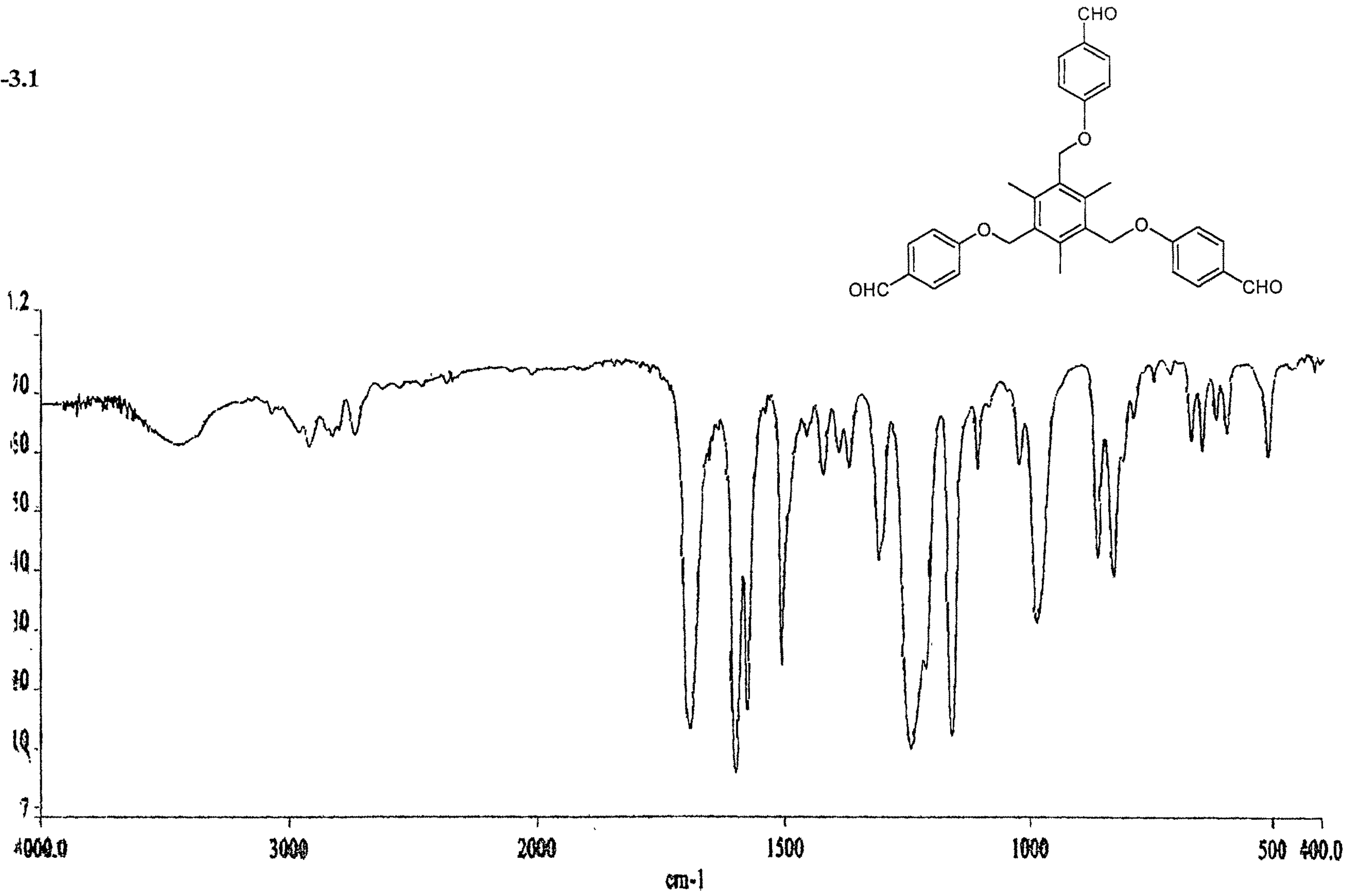
Yield: 65%(2.05 gm.)

M.P.: 124°C

IR (KBr, cm^{-1}): 3053, 1589,1509,1670, 2870,2794, 1618, 1369,751.7

^{1}HNMR($CDCl_3$, δppm): 2.5 (s, 9H,Ar-CH_3), 5.4 (s, 6H, Ar-CH_2-O-Ar), 10.8 (s, 3H, -CHO), 9.3, 8.15, 7.8, 7.6, 7.5, 7.4 (aromatic protons)

Spectrum-3.1



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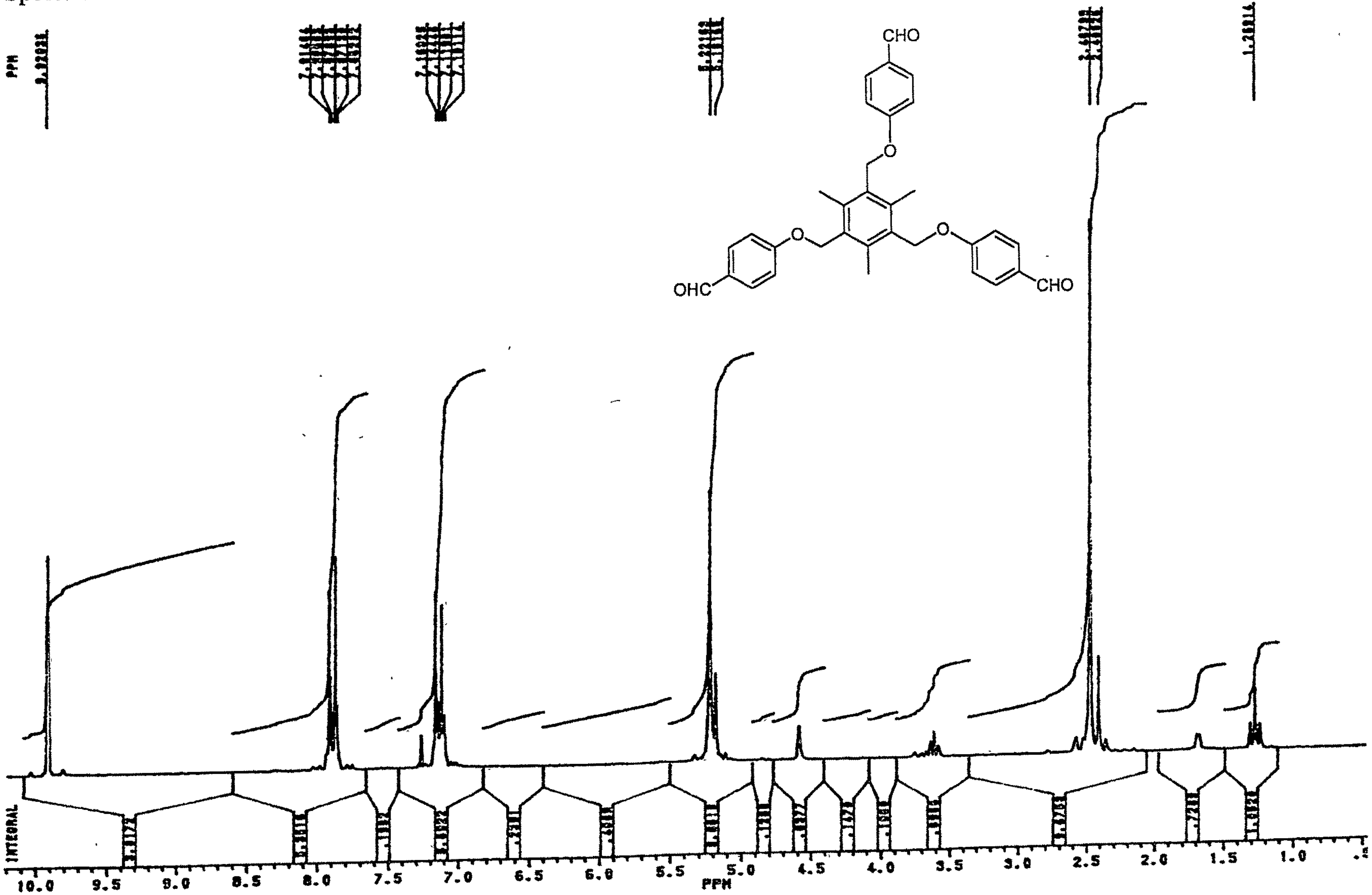
Spectrum-3.2



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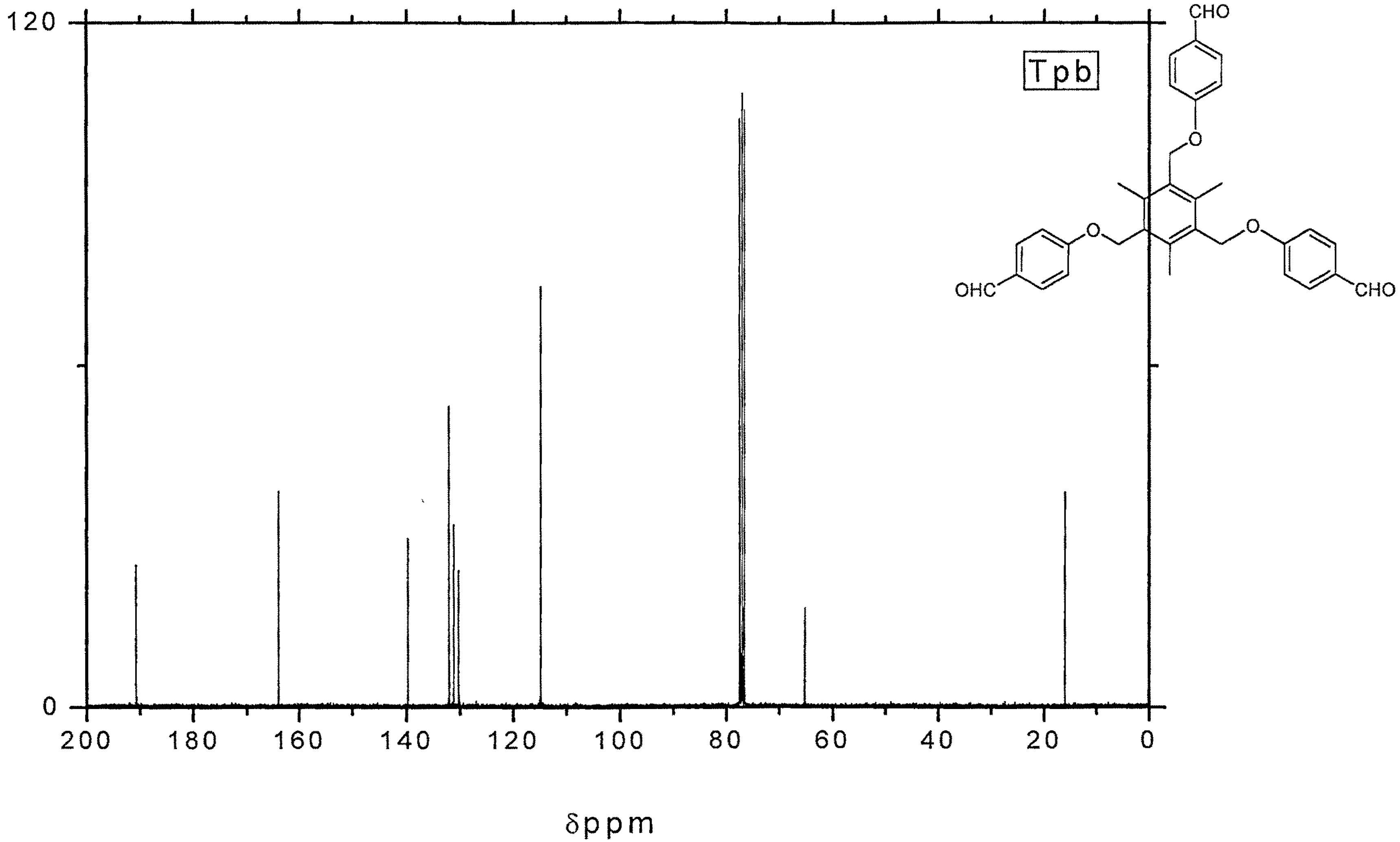
Spectrum-3.3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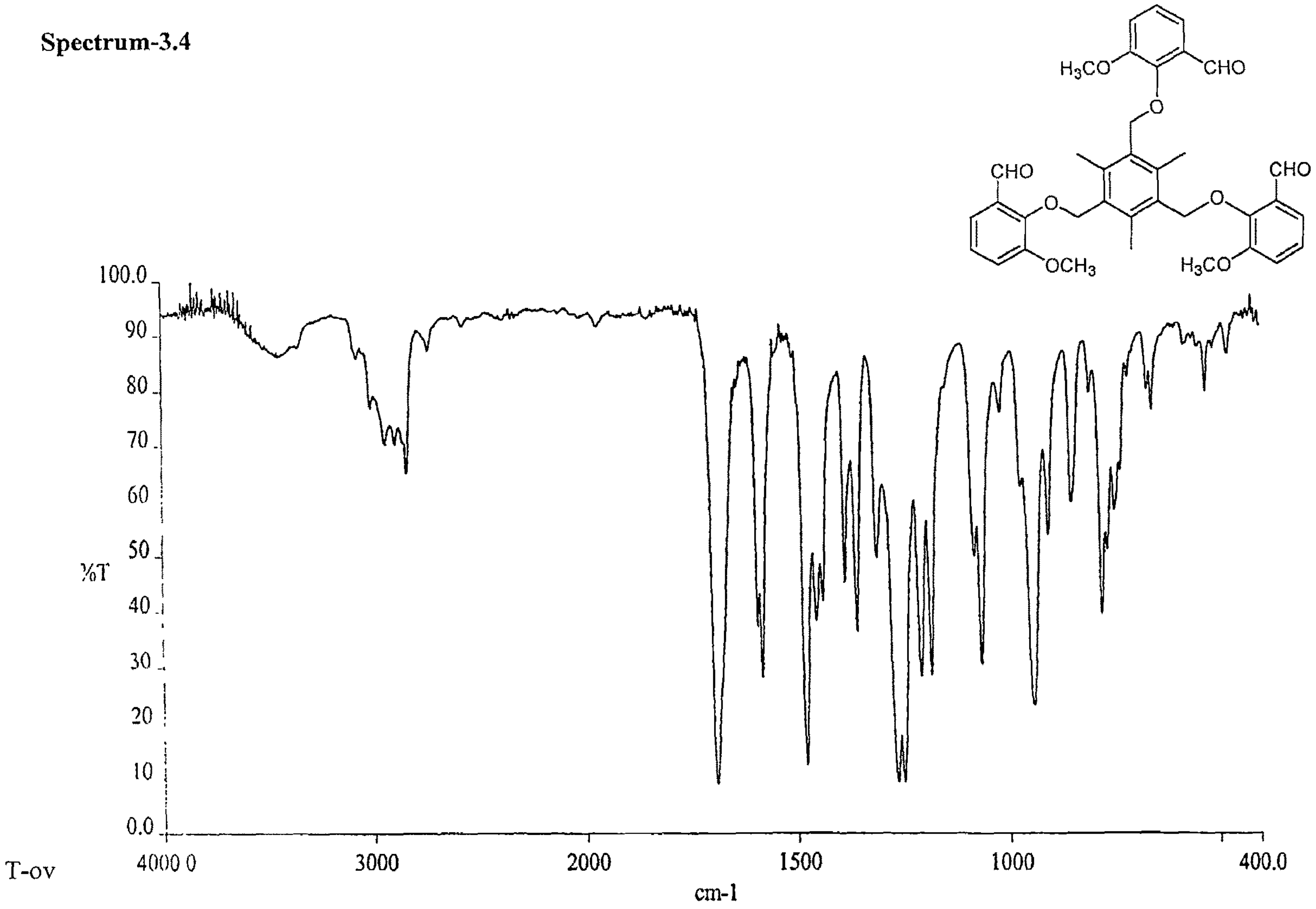
δppm

Spectrum-3.4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20
10
0.0
T-ov
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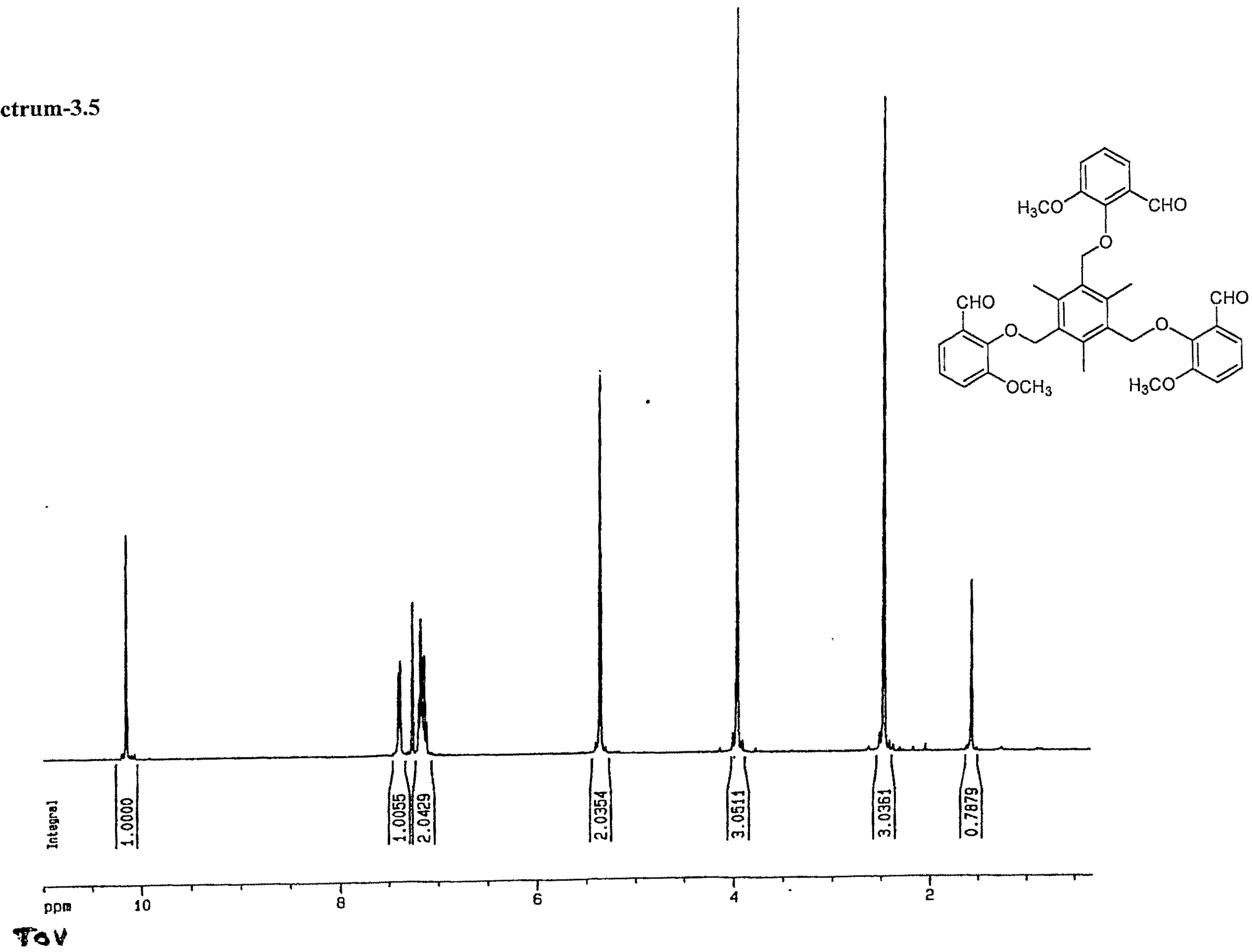
2000
1500
1000
400.0
cm-1

Spectrum-3.5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ppm
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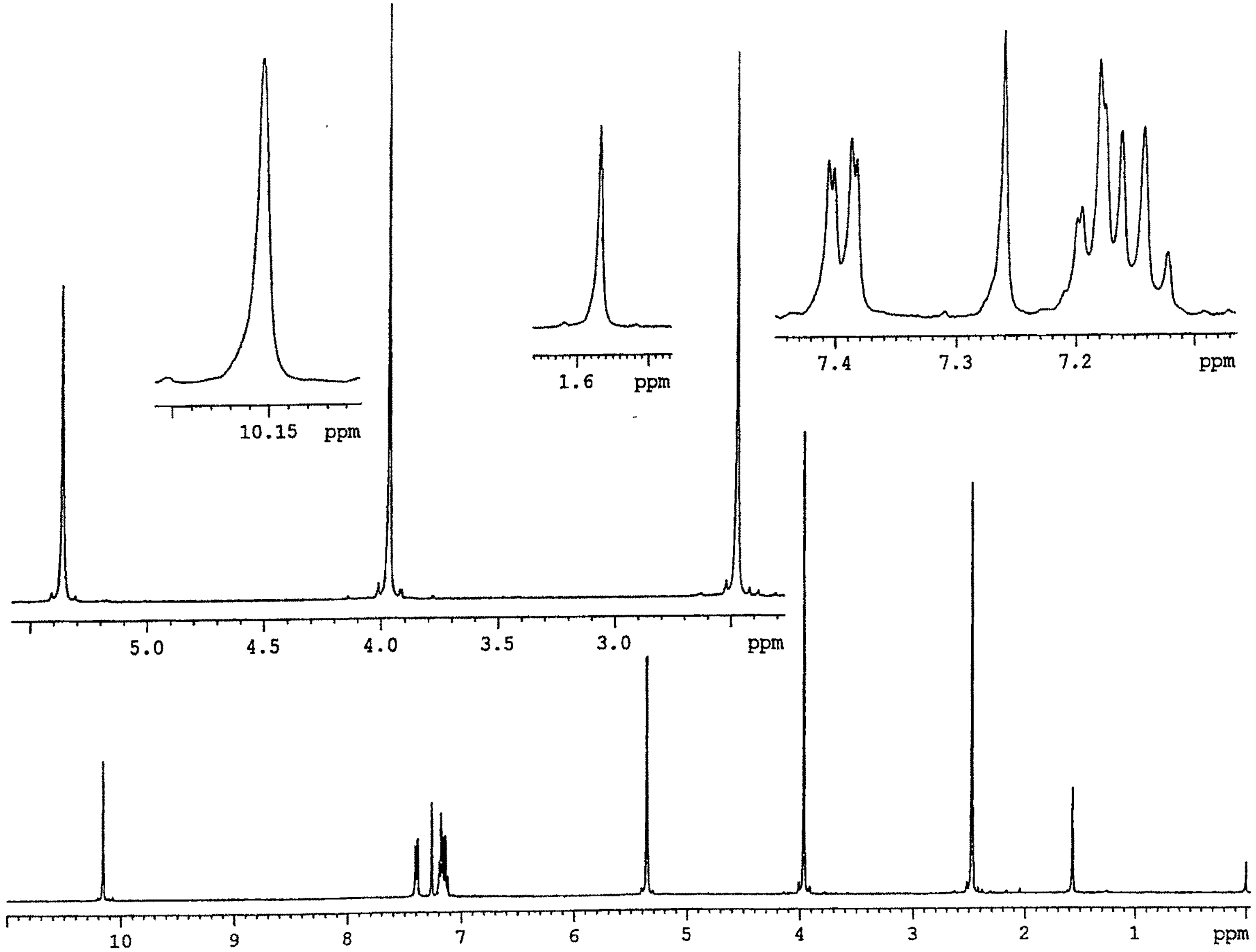
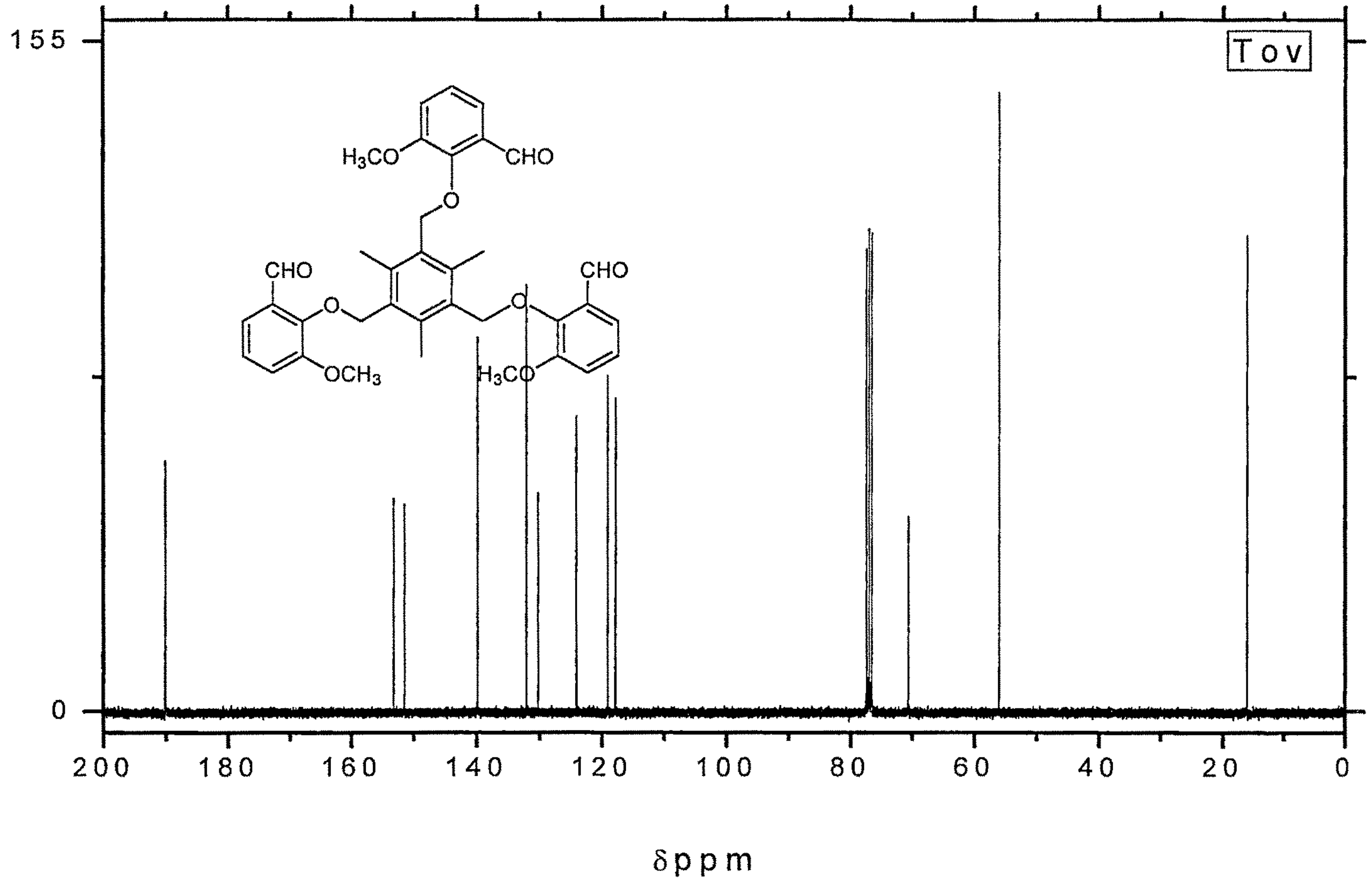
8
6
4
2
ToV



Tov-exp

Spectrum-3.6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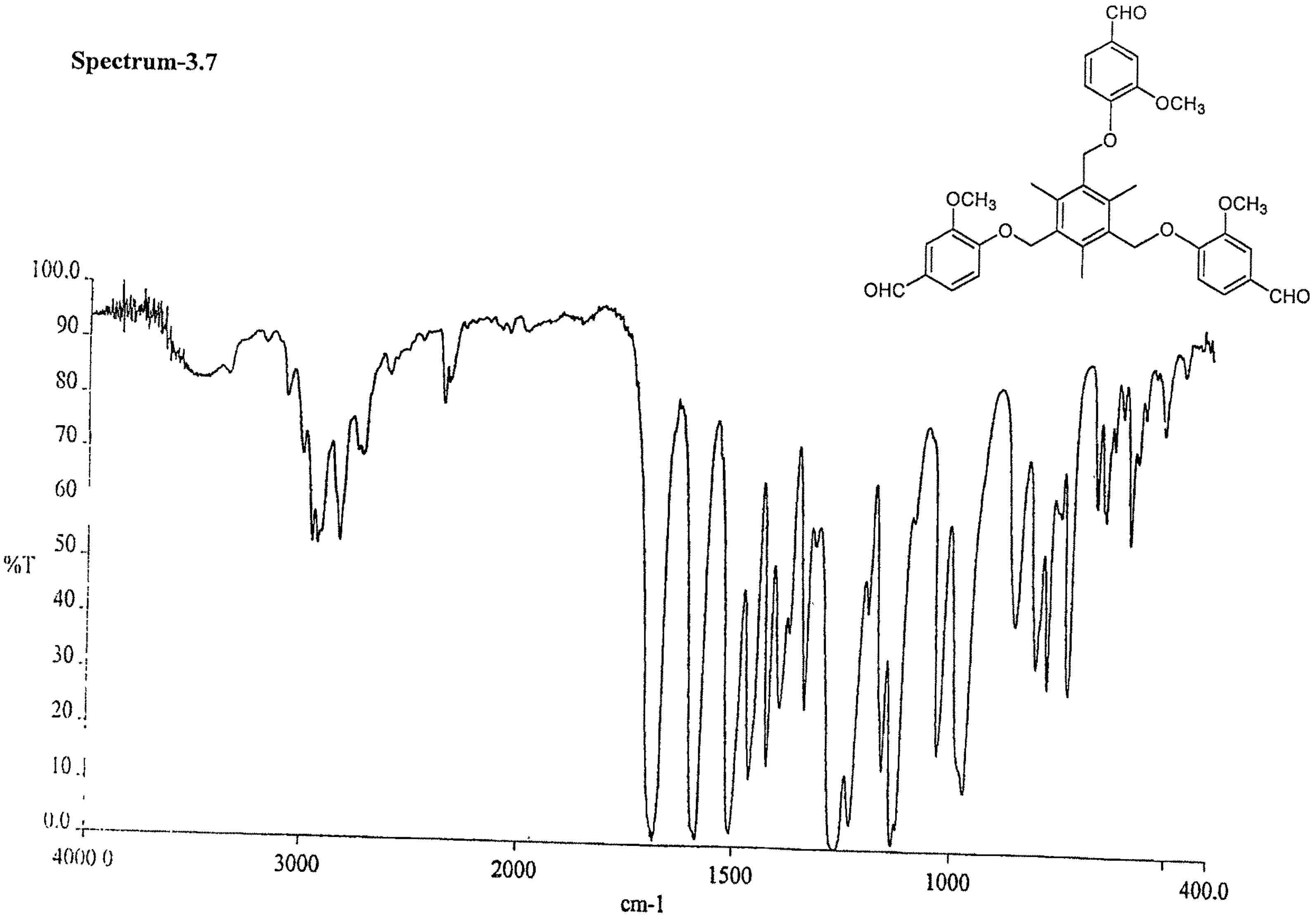
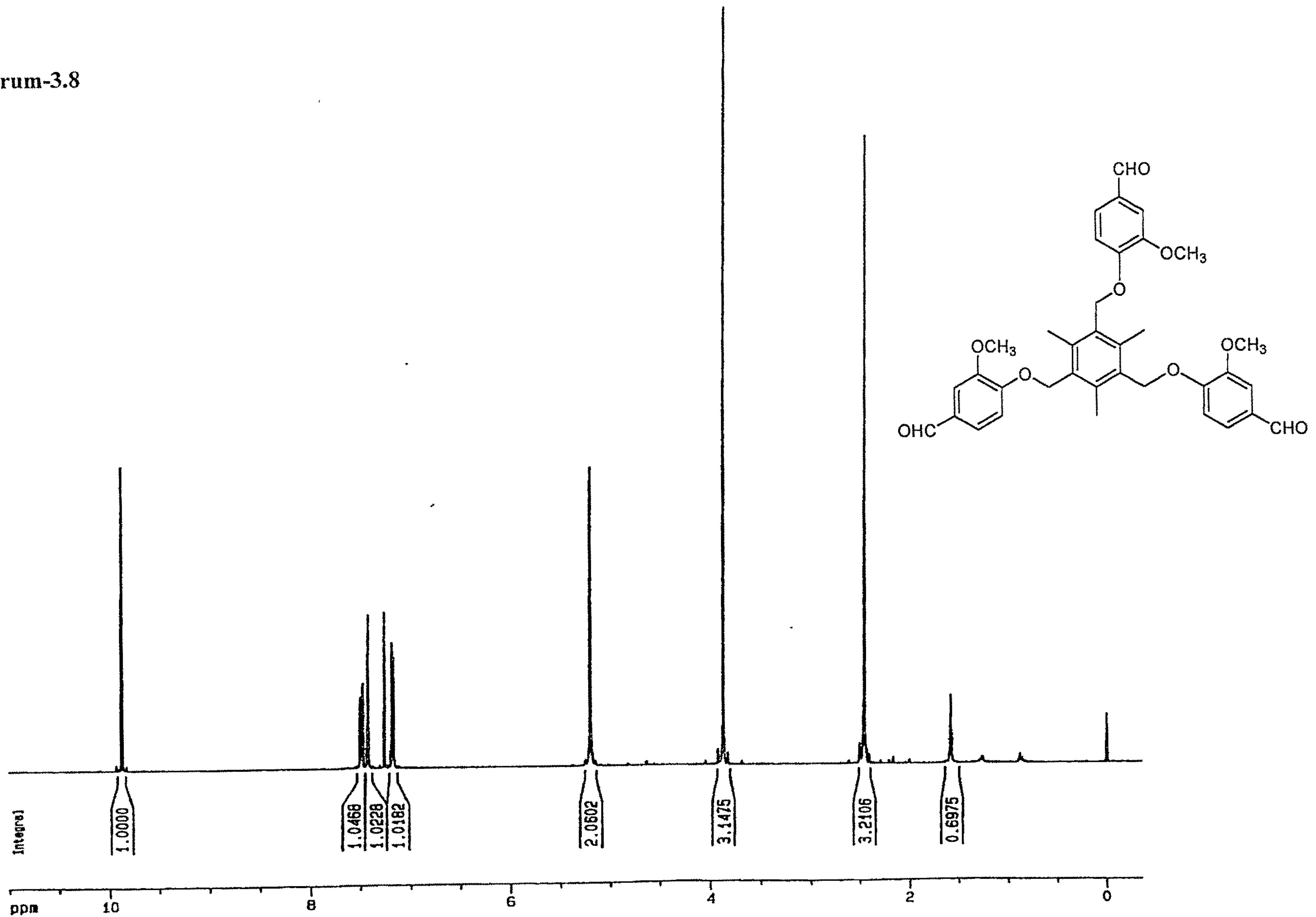
δ p p m

Spectrum-3.7



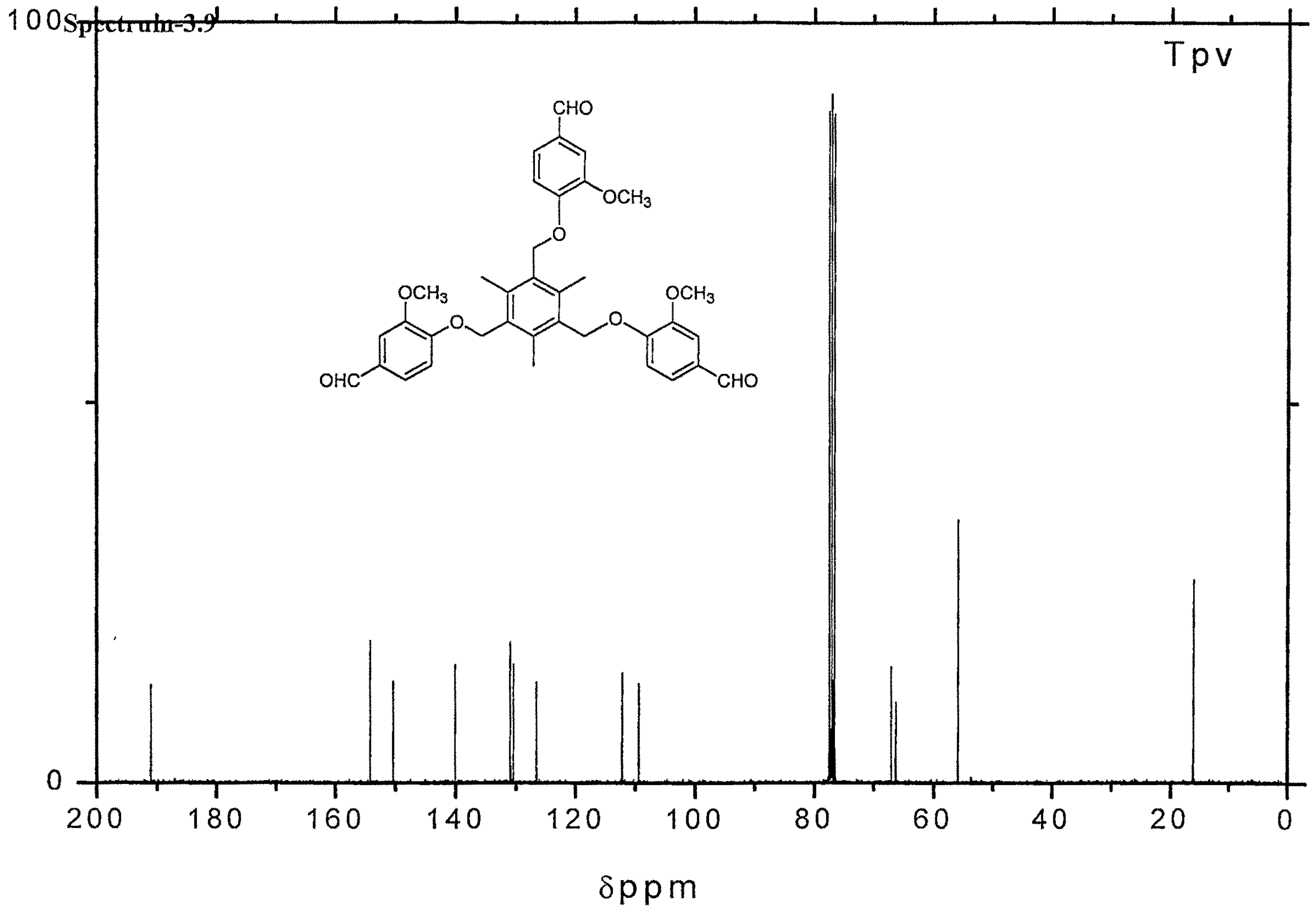
Tpv

Spectrum-3.8



TP✓

Spectrum-3.9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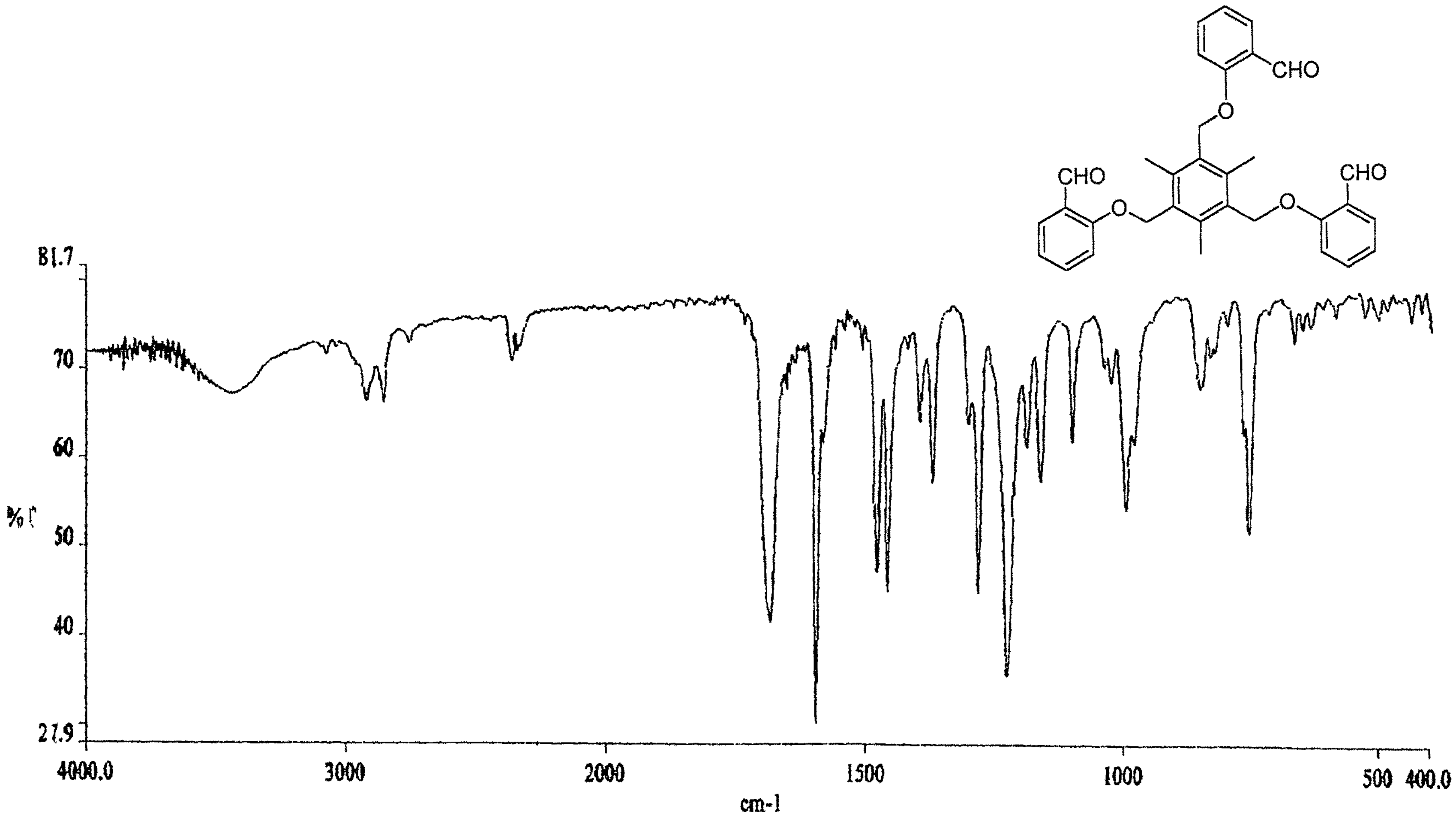
δppm

Spectrum-3.10



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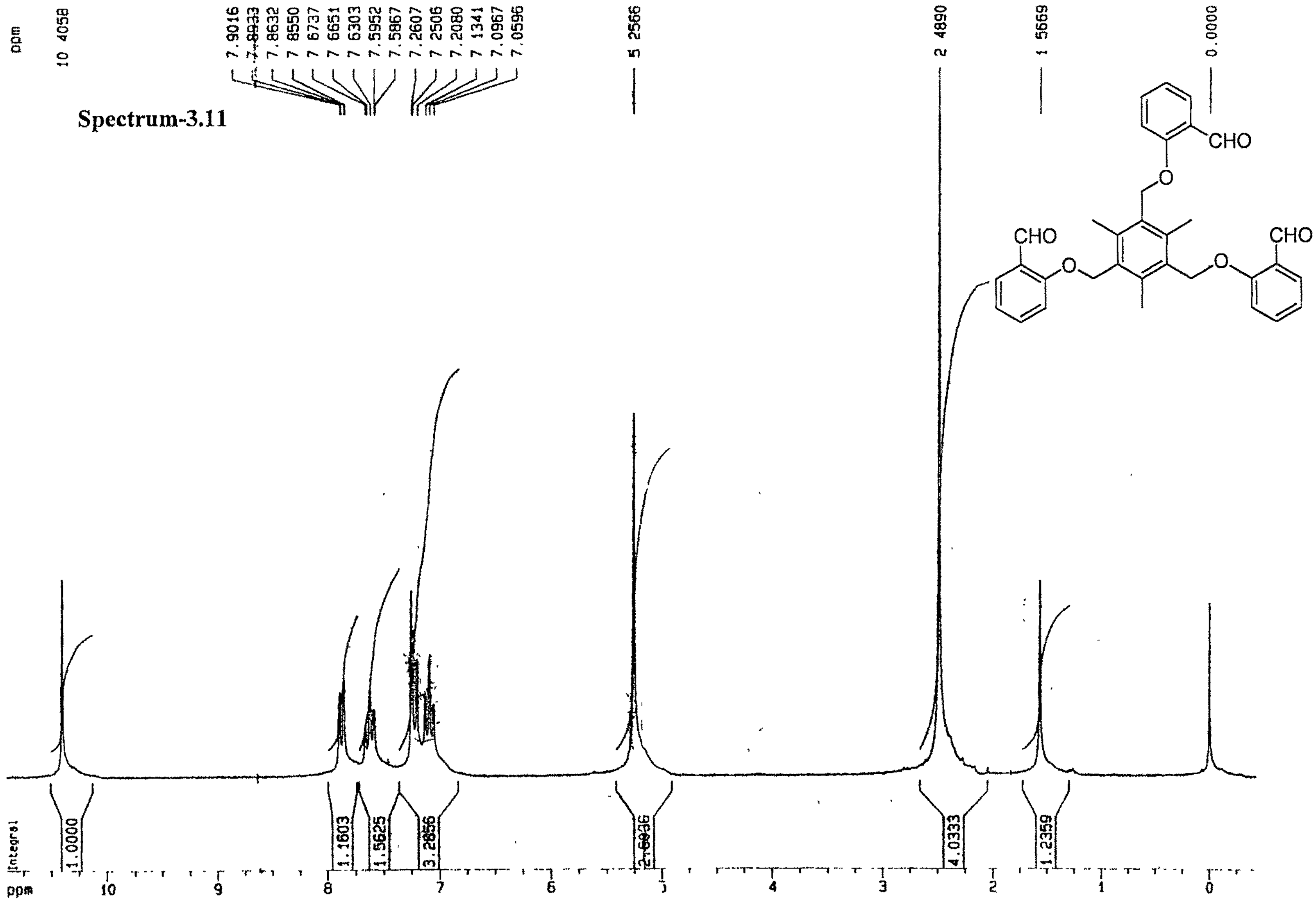

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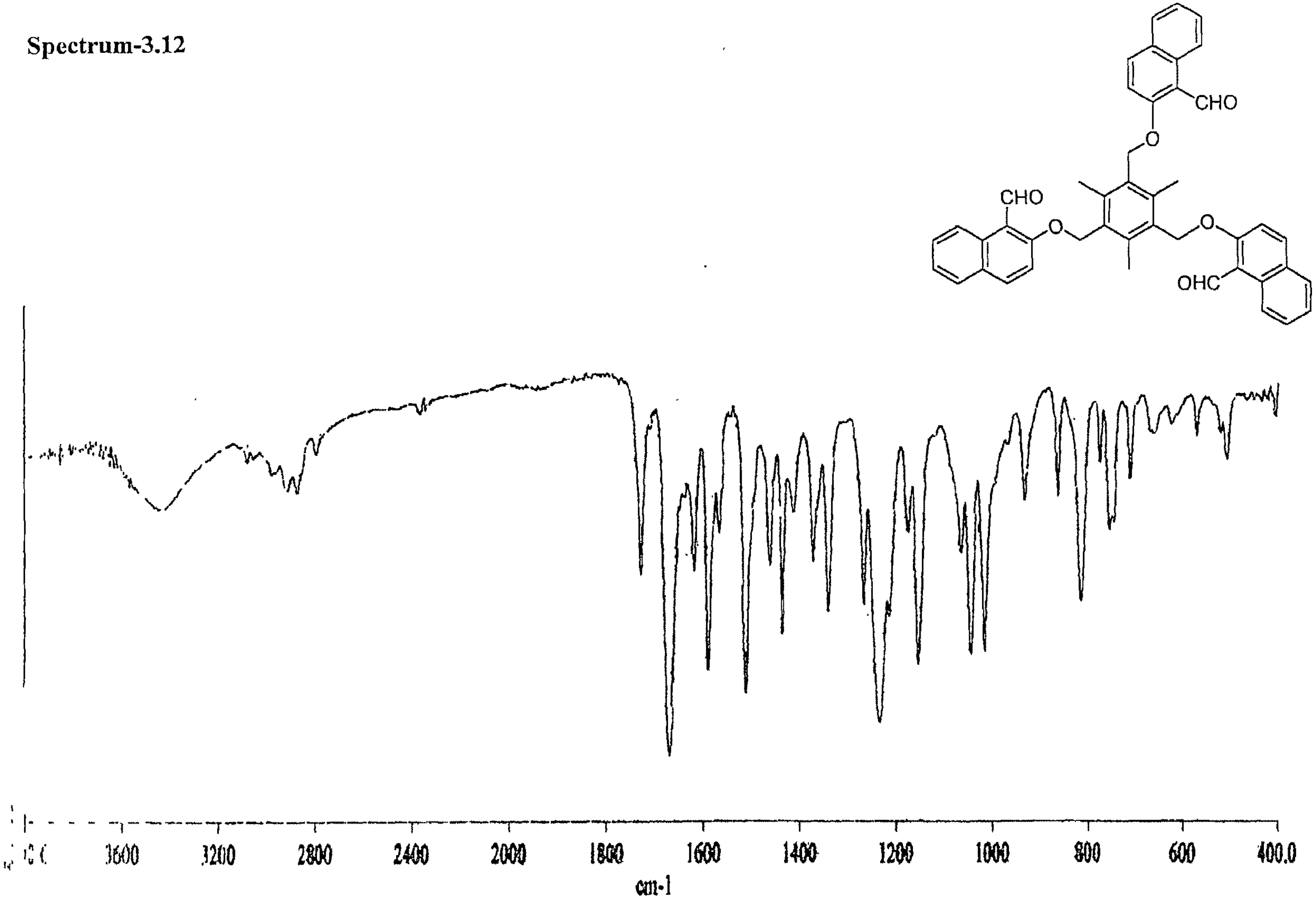

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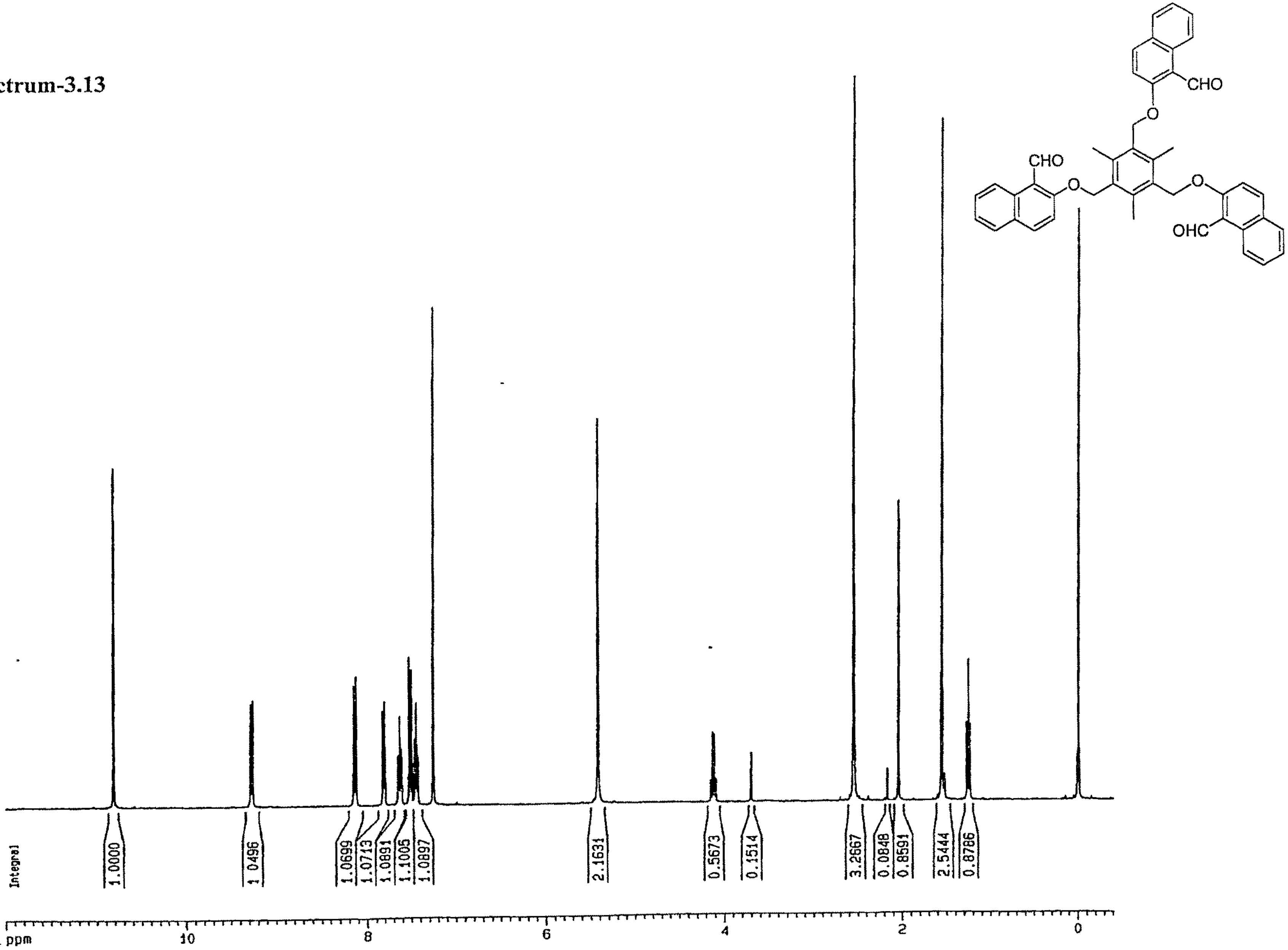
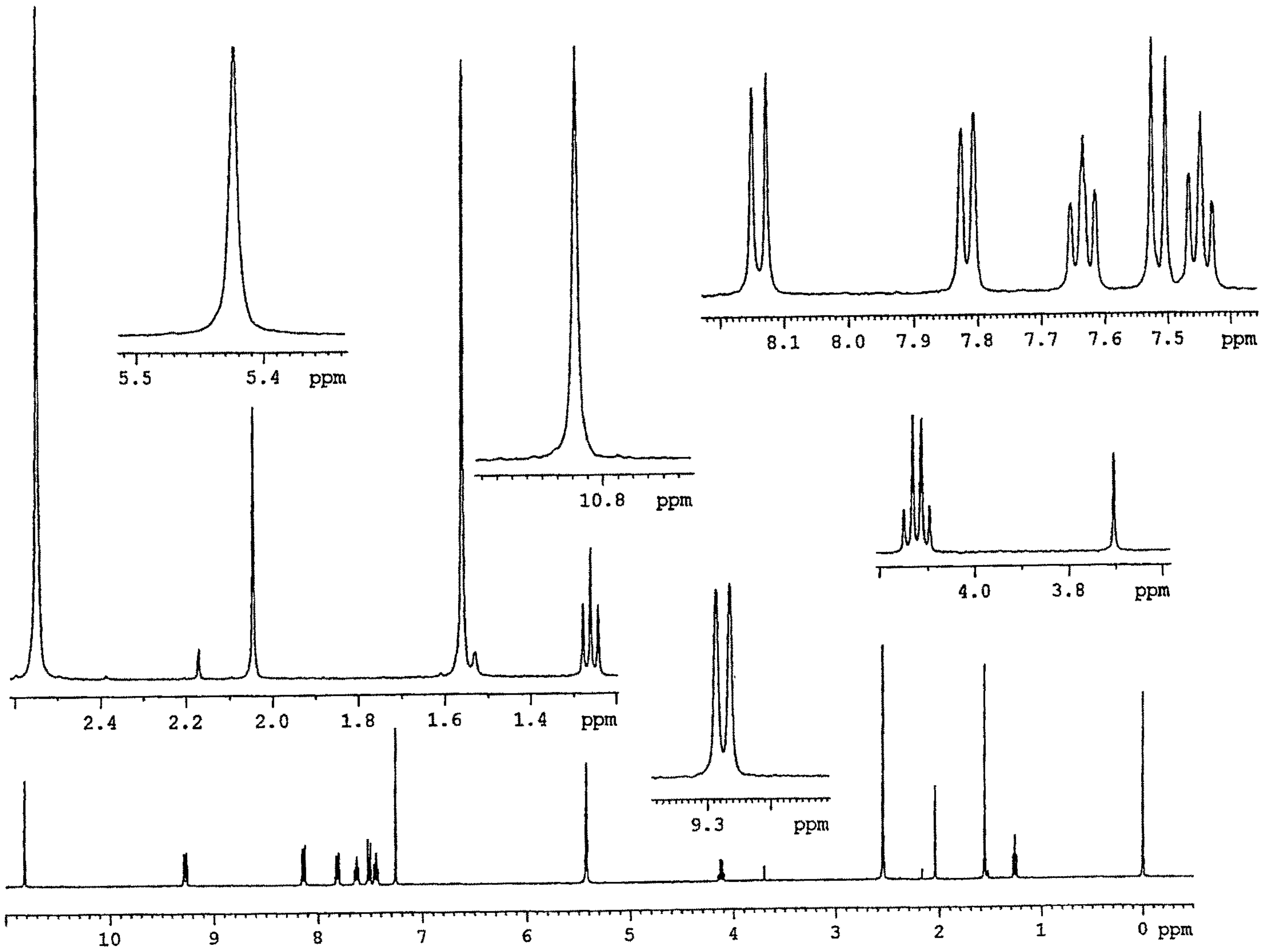
Spectrum-3.13

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1.8
1.6
1.4
ppm
9.3
ppm
10
9
8
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6
5
4
3
2
1
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ppm

Tbn

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