CHAPTER 2

From Colour to Cavity: Application of a Triphenylmethane Dye

2. From Colour to Cavity: Application of a Triphenylmethane Dye

2.1 Introduction

Colour plays an important role in nature. It contributes to make things attractive and distinguishable. There are various factors contributing to the colour of a substance. Some inorganic salts and complexes are coloured due to the presence of transition metal ions. Among organic compounds, aliphatic compounds are generally colourless and deep colour is encountered only in the derivatives of benzene, naphthalene, anthracene and other aromatic compounds.

Chromophores in common sense are the groups responsible for colour and auxochromes are groups which intensify the action of the chromophores and are also responsible for dyeing properties of organic pigments. Dyes are mainly used to give colour to the fibres which are not coloured themselves or to change their natural colour. Originally only natural pigments were used for dyeing fabrics. Later on, a number of synthetic dyes have been prepared and applied. The chemistry of synthetic dyes has evolved and advanced during these years. There are number of dyes being employed by textile and other industries. Dyes are classified according to the structure of chromophore present in them or mode of their applications. Most of them fall into classes

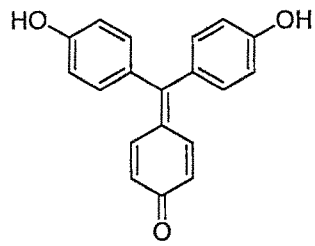
such as nitroso, azo, dipheny methane, triphenyl methane, quinonoid, indigoid, heterocyclic dyes.

2.1.1 Triphenylmethane dyes

Triphenylmethane dyes are coloured because one of the phenyl rings in their structure acquires quinonoid structure producing highly conjugated π-system. The central carbon atom is sp^2 hybridised in this case. All the dyes of this series are prepared by oxidation of benzene derivative or are derived from triphenylmethane or triphenylcarbinol, both of which are colourless. One or more amino groups or hydroxy groups para to the methane carbon atom are necessary for converting them into dyes. There are different kinds of substituents, which may be present in triphenylmethane dyes. Malachite green seems to be more familiar member of this group.

2.1.2 Rosolic acid and supramolecular chemistry

Rosolic acid or aurin **1**, one of the oldest synthetic triphenylmethane dyes was made by oxidation of crude phenol in which p-cresol is also present. It was once used for colouring liquors and varnishes but was later replaced by safer colouring agents due to its toxicity.



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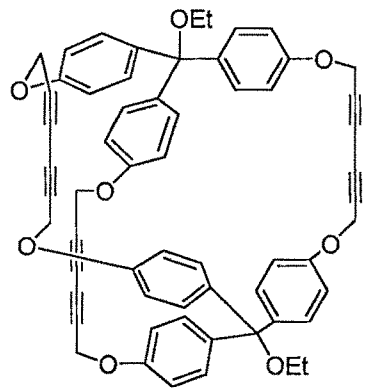
Aurin and its trialkyl or tricarboxylic acid derivatives are found to have neuro-protective activity[1] and anti-HIV activity.[2,3] Unexpectedly these triphenylmethane dyes have also been employed in supramolecular chemistry. Crown rings have been attached with these molecules and they can bind with ions and behave as chromoionophores.[4] The compounds derived from these dyes have also been used as indicators for chirality, solvatochromy and halochromy.[5] They have also been applied in the synthesis of cryptands (e.g. **2**) by connecting two molecules of the dyes via hexa-2,4-diyne linker giving a large rigid cavity bearing molecules.[6] Later on, their absorption and luminescence properties have also been studied. Their complexes with neutral organic guests have been characterised and also hydrogenated to give a spherical shaped cavity.[7]



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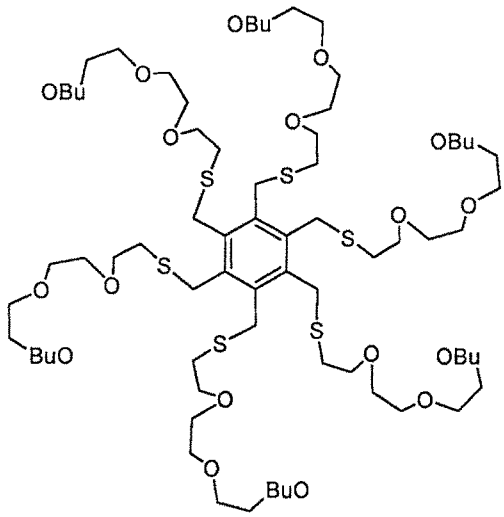
2.1.3 Podand molecules in supramolecular chemistry

Open chain compounds in which two or more chains are attached to a central atom or structure are called podand compounds (**3-6**). Podand molecules are also found in nature for example naturally occurring polyether antibiotics such as monensin and lasolocid selectively bind several metal cations and effectively transport them across biomembranes.[8] When there are more chains involved in formation of this type of compounds (e.g. **3**), they can be compared with octopus[9] who has many hands to hold its pray.



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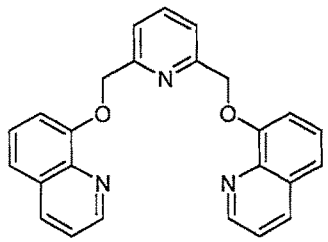
As mentioned in the introduction of this thesis, these flexible podand molecules can bind with ions or molecules if there are donor centres present in the pendant groups of the podand molecules. The capability of podands for complex formation with organic molecules depends on several factors, including the number and nature of the donor atoms, chain size, substituent and topological and conformational properties. In addition a donor atoms or groups in podand the presence of end groups also play an important role by introducing rigidity at the terminals. (See **4**, **5**)[10]



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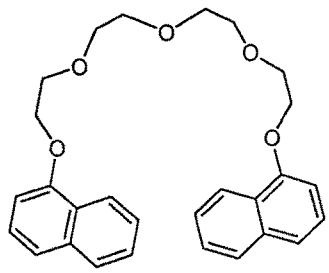

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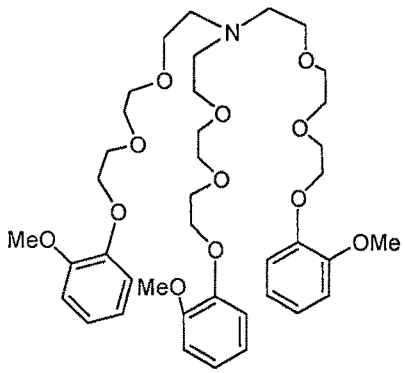
Though the podand compounds have lower binding ability compared to macrocyclic compounds, their flexibility is advantageous as they can adopt the geometry according to the requirements of the guest molecules. This property of course decreases degree of selectivity. The podand molecules can also have multiple bridging and helical binding capabilities, which are absent in other host molecules. For binding ability, a complex structure or the presence of multiple arms is not a mandatory condition. Simple podands such as **6**, **7** also show this ability. Application of trivalent nitrogen atom as a central atom can give C_3 symmetrical tripodal compounds(e.g. **6**).[11]



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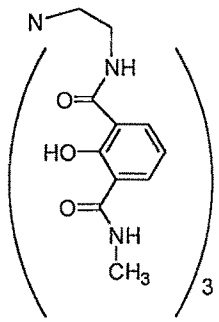

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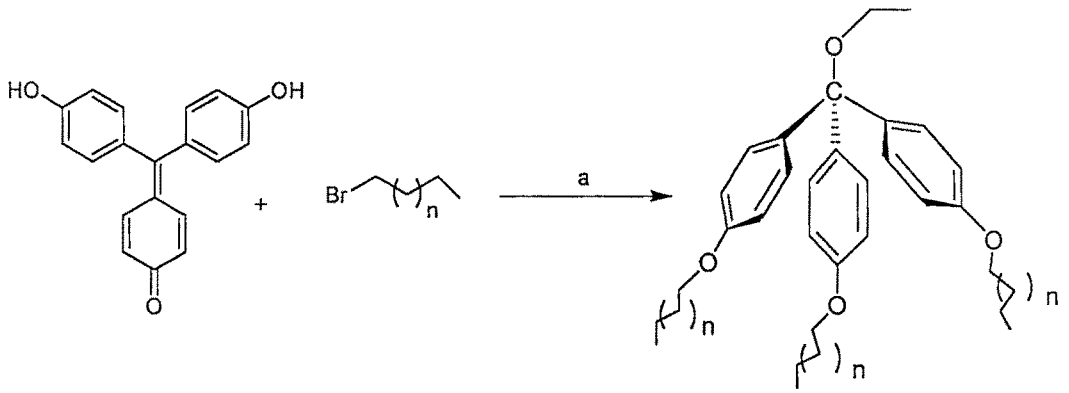
2.2 Aims and Objectives

Impressed by the work of Vögtle in the preparation of closed structured cryptand like host molecules starting from triphenylmethane dyes, we decided to initiate our project on the synthesis and study of aromatic and polyaromatic compounds by applying triphnylmethane pigment aurin for the preparation of tripodal compounds and for the synthesis of the molecules which can have supramolecular interactions. We planned to introduce lipophilic groups in aurin, generating two distinct parts in the molecule giving ar-alkyl podands with carbon as a centre and holding three pendant chains, On the similar line of work, our ultimate goal was to connect the two concave molecules produced from the triphenylmethane compound with the help of alkyl or mainly aryl spacers giving more rigid cavity having the possibility of higher π-stacking interactions.

2.3 Results and Discussion

Aurin was purchased from the market with a reasonable purity (85%) and was directly employed for the synthesis. In a typical reaction (**Scheme 1**), which rosolic acid undergoes, trialkylation of aurin in the presence of base gives pseudo C_3 symmetric compounds, which can be considered as triphenylcarbinol derived compounds.

Scheme 1



1 **8-12** **13-17**

Reagents and conditions: a) K_2CO_3, EtOH, Δ, 12h, 45-50%.

In the presence of a base, the reaction is initiated by nucleophilic attack of the solvent molecule, which is normally alcohol, on the central carbon of triphenylmethane dye. Subsequent O-alkylation results in the final product. During the process, the central sp^2 hybridized carbon is converted into a tetrahedral centre thus destroying the planarity

of the molecule resulting in the loss of dark red colour present due to extended delocalisation. The generation of sp^3 centre pushes the aromatic rings in one plane to one plane to one side and thus gives a cavity formed by three phenyl rings which can provide π stacking binding to appropriate guest molecules. Moreover these cavity compounds can be coupled to give cyclic structure which has been demonstrated by Vogtle et. al.[6, 7] By this reaction (**Scheme 1**), four O–alkyl groups are introduced in the molecule in one shot and the molecule becomes curved from the inherrent planar geometry. We have successfully carried out the preparation of long alkyl chain tripodal compounds by reacting aurin with six different alkyl halides with varying chain length. The minimum chain length is of four carbon chain while the longest alkyl chain used was the eighteen carbon chain. The reactions carried out by refluxing alcoholic solution of rosolic acid and an excess of alkyl halide in presence of K_2CO_3 as a base.

The unreacted coloured impurity was removed by washing with 10% alkali solution and the product extracted with diethyl ether. The product was sensitive to acidic conditions and, a more polar compound was observed while running TLC over silica gel due to the generation of the carbocation at the central carbon atom, again introducing planarity in the molecule. Thus purification of the primary alkylated products was not possible using silica gel column due to acidity of silica gel and neutral alumina was found to be working well for the purification. The reactions gave moderate yield of the product ranging from 40-50% based on the weight of the commercial starting material. The compounds show solvatochromic property as the solution of the product in acidic

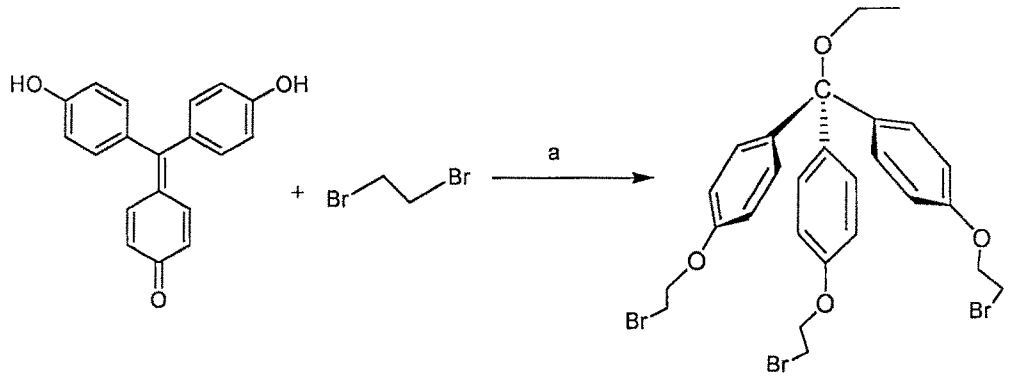
solvents or in presence of acidic catalyst like BF_3.etherate is coloured. With an exception all the products are viscous liquids. The tris-octadecyloxyphenylmethyl product was solid and was observed under a polarizing microscope in case the compound exhibits might be any intermediate mesophase before melting but no such transition phase was observed might be because of the non-planarity of the molecule.

IR spectra of these compounds show strong C-H stretching vibrations for aryl C-H stretching around 2950-2900cm^{-1} and for alkyl stretching between 2850-2870cm^{-1}. C=C stretch of aromatic ring is observed around 1600cm^{-1}while C-H bending absorption is observed around 1245cm^{-1} (see the spectral section).

PMR spectra of these podand compounds show characteristic peaks as expected. p-substituted aromatic rings gave two doublets at 7.3-7.4 and at 6.7-6.9 ppm. Methylene of an alkyl chain attached to oxygen of the aryloxy group gives a signal at 3.9 ppm while methylene of ethyl group attached to carbinol group gives a quartet at 3.1ppm. Methyl group at the end of the chains attached to phenyloxy oxygen are slightly more shielded absorbing at 0.9-1.0 ppm compared to the methyl present in the ethylxoy group giving signal at 1.3 ppm and masked by the signals due to other methylene protons. Methylene group second from the phenyloxy oxygen is deshielded compared to other methylene group and absorps near 1.8 ppm. In case of butyloxyphenylmethyl product each type of the protons are seen separately in PMR (see the spectral section).

With satisfying and encouraging results in the synthesis of tripodal compounds with lipophilic podands, our target was the preparation of cryptand like closed structures. Vögtle group used copper acetate mediated coupling of trispropargyl ether from rosolic acid in the preparation of the closed structure.[6] We decided to employ bi-fucntional alkyl chains and attaching rosolic acid to both ends in a step-wise manner. Thus the reaction of rosolic acid with dibromoethane was carried out in the same manner as with mono-bromoalkanes in ethanol.

\Scheme 2



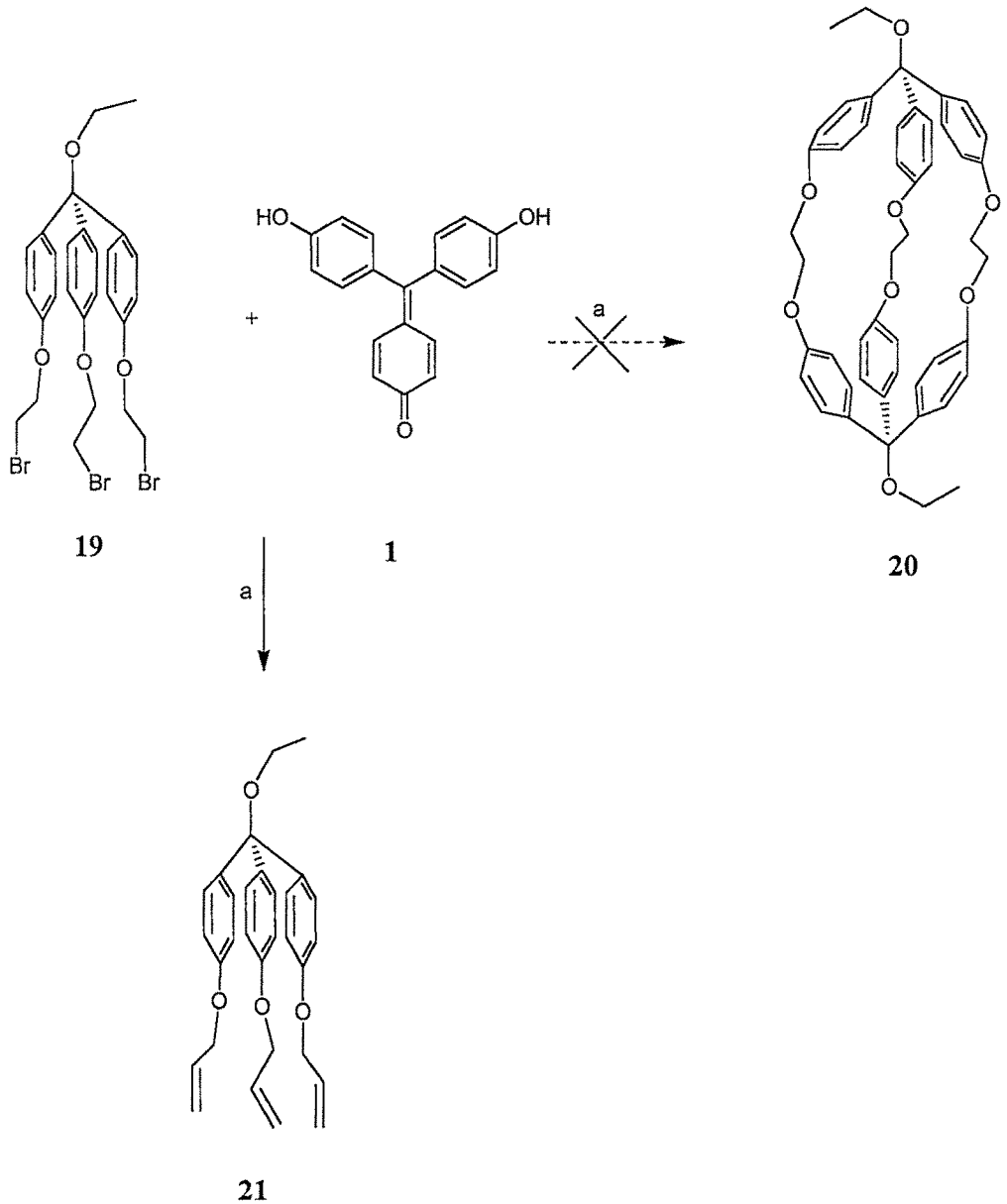
1 **18** **19**

Reagents and conditions: a) K_2CO_3, EtOH, Δ, 12h, 54.6%.

PMR of the product gave two triplets at about 3.6 and 4.2 ppm for the methylenes present in the triply coupled chain. The next step was to cap the resulting product with

another molecule of rosolic acid in an iterative process using high dilution so as to decrease polymerisation. The reaction of the trialkylated product with rosolic acid in the presence of the base resulted in the elimination reaction at the haloalkyl end rather than giving the substitution reaction. The isolated product gives PMR signals for the vinyl group instead of a simplified spectrum. The reaction was carried out by changing various factors. Cs_2CO_3 was employed in place of K_2CO_3 and acetonitrile was employed replacing acetone as a solvent as both of them can have template effect (**Scheme 3**).

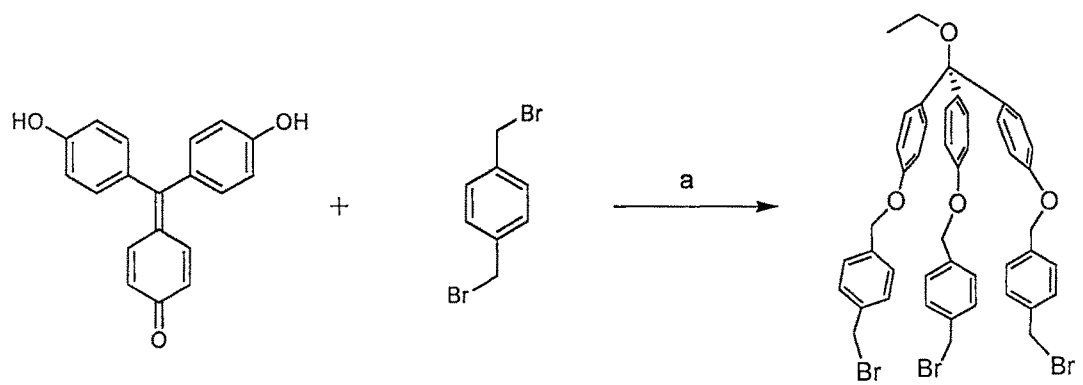
Scheme 3



Reagents and conditions: a) K_2CO_3 / Cs_2CO_3, EtOH, Δ.

Even after repeated attempts, the desired macrocyclic product was not obtained. After facing the difficulty of competing reaction of elimination *vs* substitution, in case of the aliphatic haloalkane attached to rosolic acid, we looked for a better alternative in which not only any competing reaction was prevented but, additional binding features were also embedded. 1,4-Bis(bromomethyl)benzene, which can be easily prepared by bromination of p-xylene was thought to be the right substrate for the application as a spacer in synthesis of targeted cryptands. The aromatic spacer offers π-stacking interactions in addition to binding sites provided by oxygens of the ether linkages. Benzylic sites have higher reactivity for substitution reactions. 1,4-Dibromodimethylbenzene was prepared following the reported procedure.[12]

Scheme 4



1 **22** **23**

Reagents and Conditions: a) K_2CO_3, EtOH, Δ, 12h, 55%.

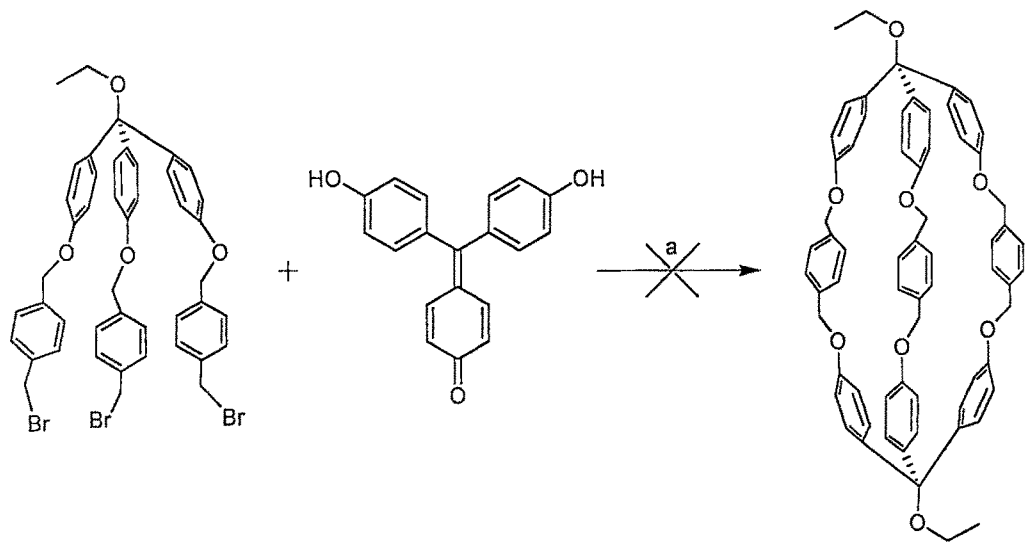
When the coupling reaction was carried out under similar conditions by refluxing the reactants in presence of K_2CO_3, the dibromo xylene was found to be reacting with the ethyl alcohol present as a solvent and also as a substrate. A slight modification in the procedure which included refluxing of rosolic acid with K_2CO_3 in ethanol for 30 minutes before addition of excess of 1,4-dibromomethyl benzene was found to be effective in isolation of the desired product in about 55% yield. Dibromoxylene was used in 25% excess than required for this reaction.

The product has been analysed using IR, PMR and CMR. Two distinct methylene signals are observed at 5.0 and 4.5 ppm for the methylenes of benzyl bromide (-Ar-CH_2-Br) and benzyloxy protons (Ar-CH_2-O-Ar'). Doublets of the aromatic protons are merging for the attached aromatic rings giving signal at 7.37ppm. ^{13}C-NMR shows five distinct signals for sp^3 carbons with the central quaternary carbon appearing at 55ppm. Similarly 8 distinct lines are observed in the aromatic region four of which with higher intensity for the carbons bearing hydrogen. Aromatic carbons attached to oxygen are observed at the most down downfield of all giving the signal at 157ppm.

Coupling of this compound having aromatic tri-podand groups was attempted using high-dilution condition by drop-wise addition of the acetonitrile solution of tris-coupled product to the mixture of one equivalent of rosolic acid, excess of Cs_2CO_3 in excess of acetonitrile having 10% ethanol under reflux with vigorous stirring (**Scheme 5**).

After allowing to react for 24h followed by usual work up and isolation of minor products in small amount however did not show the presence of the highly symmetrical required product. Direct coupling of two molecules of rosolic acid with 3 molecules of 1,4-dibromoxylene was the other alternative for synthesis of the target molecule. The reaction was attempted by simultaneous addition of rosolic acid in ethanol and dibromo xylene in acetonitrile in the suspension of Cs_2CO_3 in excess of acetonitrile providing high-dilution reaction conditions. The only characterisable product isolated after concentration and work-up of the reaction was 1,4-diethyloxymethyl benzene.

Scheme 5



23 **1** **24**

Reagents and Conditions: a) Cs_2CO_3, Acetonitrile, Δ, 24h

Macrocyclic synthesis is obviously more difficult than it appears on paper in a synthetic scheme and so far our attempts to get a closed structure using two units of aurin has not met with the success. There seems to be a number of possible alternative approaches possible which may be tried for achieving success in getting desired macrocyclic compounds with greater binding ability before reaching to any conclusion. Changes in the reaction condition which uses ethanol near the end of the reaction or application of ω-halo alcohols or coupling of two preformed concave molecules are some of the alternatives, which are worth exploring.

2.4 Experimental

Rosolic acid (aurin) was purchased from National Chemicals. Alkyl halides 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 and liquid samples as a thin films between NaCl plates between 4000-500 cm^{-1}. ^{1}H-NMR spectra were recorded on Bruker-AVX 200MHz and 400 MHz. ^{1}H-NMR spectra were recorded in $CDCl_3$ with TMS as the internal standard

Alkylation of rosolic acid in ethanol: compounds 1-5

General procedure:

Rosolic acid (aurin) (1 mmol) was heated together with finely powdered K_2CO_3 (60 mmol) and 1-bromoalkane (5 mmol) in 50 mL of EtOH under reflux for 12 hrs. The mixture was allowed to cool down and water was added followed by addition of 10% aq. NaOH (15 mL) the mixture was extracted with Et_2O (3 x 20 mL). The combined organic extracts were washed with 10% NaOH (3 x 10 mL) and dried over sodium sulphate. The solvent was removed under reduced pressure and the residue was subjected to column chromatography (Alumina :Petroleum ether: EtOAc) to give the product.

Ethyl tris(4-butyloxyphenyl)methyl ether (13)

p-Rosolic acid (Aurin) (0.290gm., 1 mmol) and K_2CO_3 (0.828 gm., 60 mmol) and 1-bromo butane (0.685gm., 0.536 mL, 5 mmol) in EtOH (50 mL) were refluxed for 12 hrs. After work-up and purification by using column chromatography (Alumina: Pet.ether: EtOAc 98:2) to give a colourless liquid.

Yield: 45.63% (0.230gm.)

IR (neat, cm^{-1}): 2958, 2871, 1607, 1505, 1244.

^{1}**HNMR**($CDCl_3$, δ ppm): 1.0 (9H, Ar-$OCH_2(CH_2)_2CH_3$), 1.3 (3H, Ar-$COCH_2CH_3$), 1.6 (6H, Ar-$OCH_2CH_2CH_2CH_3$), 1.8 (6H, Ar-$OCH_2CH_2C_2H_5$), 3.2 (2H, Ar-$COCH_2CH_3$), 4.0 (6H, Ar-$OCH_2(CH_2)_2CH_3$), 6.9 & 7.4 (aromatic protons).

Ethyl tris(4-pentyloxyphenyl) methyl ether(14)

p-Rosolic acid (0.290 g, 1 mmol), K_2CO_3 (0.83g, 6 mmol) and 1-bromo pentane (0.755g, 0.62 ml, 5mmol) was refluxed for 12h in dry ethanol (50 ml). Work-up and purification using column chromatography(Alumina : Pet.ether: EtOAc 98:2) gave a colourless liquid.

Yield: 46% (0.350gm.)

^{1}HNMR($CDCl_3$, δ ppm): 0.9 (9H, Ar-$OCH_2(CH_2)_3CH_3$), 1.2 (3H, t, Ar-$COCH_2CH_3$), 1.28 (12H, m, Ar-$OCH_2CH_2(CH_2)_2CH_3$), 1.76(6H, m, Ar-$OCH_2CH_2(CH_2)_2CH_3$), 3.2 (2H, q, Ar-$COCH_2CH_3$), 3.9 (6H, Ar-OCH_2 $(CH_2)_3CH_3$), 6.8(d) & 7.3 (d, arom. protons).

Ethyl tris(4-octyloxyphenyl) methyl ether(15)

p-Rosolic acid (0.290 g, 1 mmol), K_2CO_3 (0.83g, 6 mmol) and 1-bromo octane (0.965 gm., 0.86 ml, 5 mmol) was refluxed for 12h in dry ethanol (50 ml). Work-up followed by column chromatography(Alumina , Pet.ether: EtOAc 98:2) gave a colorless liquid.

Yield: 46.8% (0.315gm.)

IR (neat, cm^{-1}): 2925, 2855, 1606, 1508, 1247.

^{1}HNMR($CDCl_3$, δ ppm): 0.87 (9H, Ar-$OCH_2(CH_2)_6CH_3$), 1.23 (30H, Ar-OCH_2 $CH_2(CH_2)_5CH_3$), 1.4 (3H, t, Ar-C-O-CH_2CH_3), 1.75 (6H, Ar-OCH_2 $CH_2(CH_2)_5CH_3$), 3.0 (2H, q, $COCH_2CH_3$), 3.9 (6H, Ar-$OCH_2CH_2(CH_2)_5CH_3$), 6.77(d) & 7.26 (d, arom. protons).

Ethyl tris(4-dodecyloxyphenyl) methyl ether(16)

p-Rosolic acid (0.290 g, 1 mmol), K_2CO_3 (0.83g, 6 mmol) and n-bromo dodecane (1.246 gm., 1.22 ml, 5 mmol) was refluxed for 12h in dry ethanol (50 ml). Work-up and column chromatography(Alumina : Pet.ether: EtOAc: 96:4) gave a colorless liquid.

Yield: 46.9% (0.394gm.)

^{1}HNMR($CDCl_3$, δ ppm): 0.9 (9H, Ar-OCH_2 CH_2 $(CH_2)_9$ CH_3), 1.25 (36H, Ar-OCH_2 CH_2 $(CH_2)_9$ CH_3), 1.4 (3H, t, Ar-C-O-CH_2CH_3), 1.7 (6H, Ar-OCH_2 CH_2 $(CH_2)_9$ CH_3), 3.1 (2H, q, Ar-C-O-CH_2CH_3), 3.9 (6H, Ar-$OCH_2CH_2(CH_2)_9CH_3$), 6.8 (d) & 7.3 (d, arom. protons).

Ethyl tris(4-octadecyloxyphenyl)methyl ether(17)

p-Rosolic acid (0.290 gm., 1 mmol), K_2CO_3 (0.83 gm., 6 mmol) and 1-bromo octadecane (1.66gm., 5 mmol) was refluxed for 12h in dry ethanol (50 ml). Work-up followed by column chromatography(Alumina:Pet.ether: EtOAc 96:4) gave a white solid product.

Yield: 49% (0.329gm.)

M.P: 80°C

IR (KBr, cm^{-1}): 2918, 2850, 1607, 1508, 1247.

^{1}HNMR($CDCl_3$, δ ppm): 0.86 (9H, Ar-$OCH_2(CH_2)_{16}CH_3$), 1.2 (90H, Ar-$OCH_2CH_2(CH_2)_{15}CH_3$), 1.4 (3H, t, Ar-C-O-CH_2CH_3), 1.7 (6H, Ar-$OCH_2CH_2(CH_2)_{15}CH_3$), 3.0 (2H, q, Ar-C-O-CH_2CH_3), 3.9 (6H, Ar-$OCH_2(CH_2)_{16}CH_3$), 6.7 & 7.1 (arom. protons),

Ethyl tris(4-(2-bromoethyloxy)phenyl)methyl ether(19)

p-Rosolic acid (0.58g, 2mmol), K_2CO_3 (1.66g, 12 mmol) and 1,2-dibromo ethane (1.88 gm., 0.86 ml, 10 mmol) was refluxed for 12hrs in dry ethanol (100 ml). Work-up (see general procedure) followed by column chromatography (Alumina: Petroleum ether: EtOAc: 90:10) gave a yellow oily product.

Yield: 54.6% (0.350gm.)

IR (KBr, cm^{-1}): 2918, 2850, 1607, 1508, 1247.

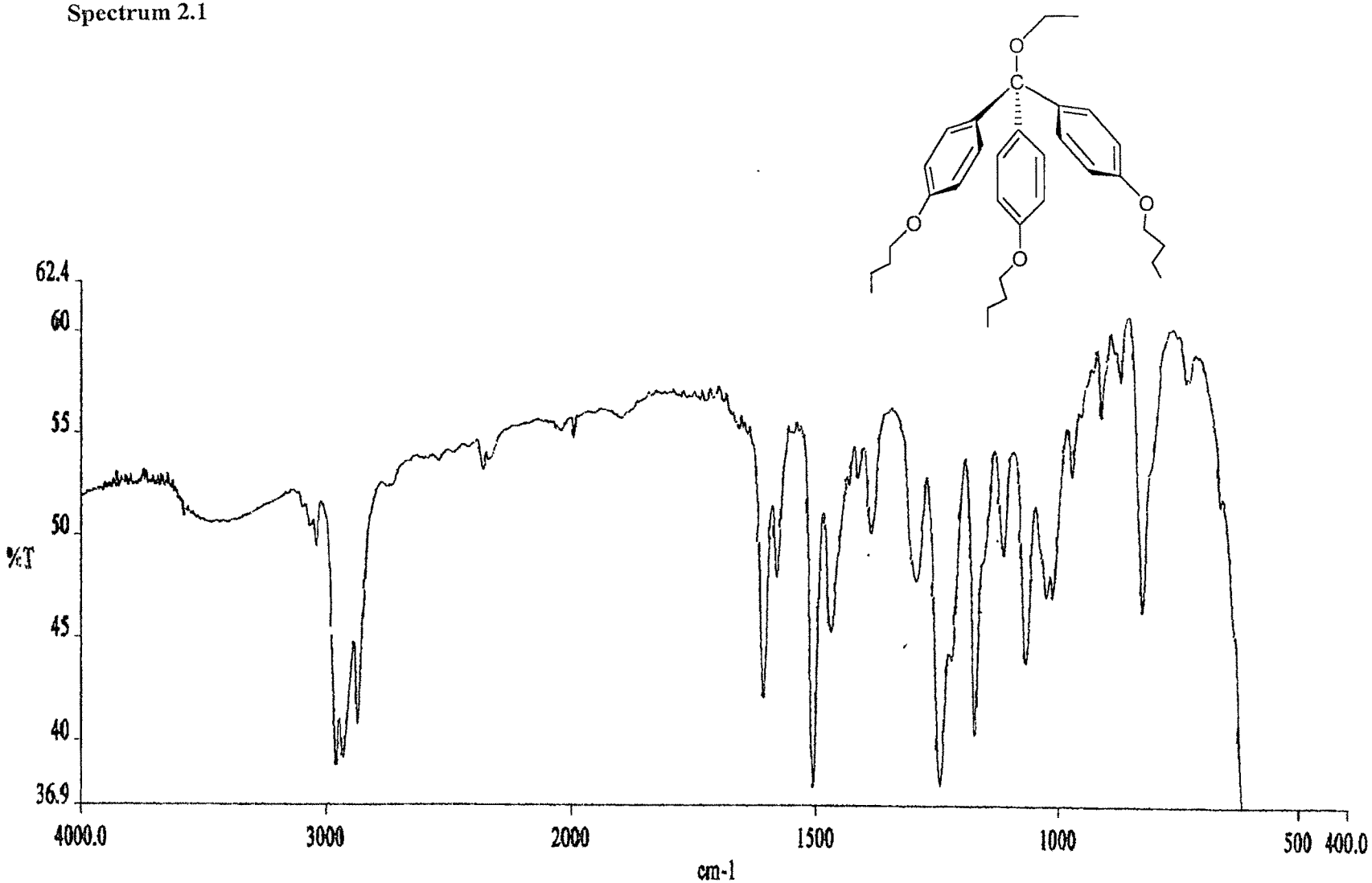
^{1}HNMR ($CDCl_3$, δ ppm): 1.25 (3H, t, Ar-$COCH_2CH_3$), 3.1 (2H, q, Ar-$COCH_2CH_3$), 3.6 (6H, t, Ar-OCH_2CH_2Br), 4.2 (6H, t, Ar-OCH_2CH_2Br), 6.8 (d) & 7.3 (d, arom. protons).

Ethyl tris (4-(4-bromomethylphenylmethyloxy)phenyl)methyl ether(23)

p-Rosolic acid (0.58gm., 2 mmol), K_2CO_3 (1.66gm., 12 mmol) was refluxed in dry ethanol (100ml) for 30 min. after which 1,4-bis(bromomethyl) benzene (2.112gm., 8mmol) was added and the reaction mixture was refluxed for 12h. Work-up and column chromatography (Alumina: Pet.ether: EtOAc 90:10) gave yellow oil.

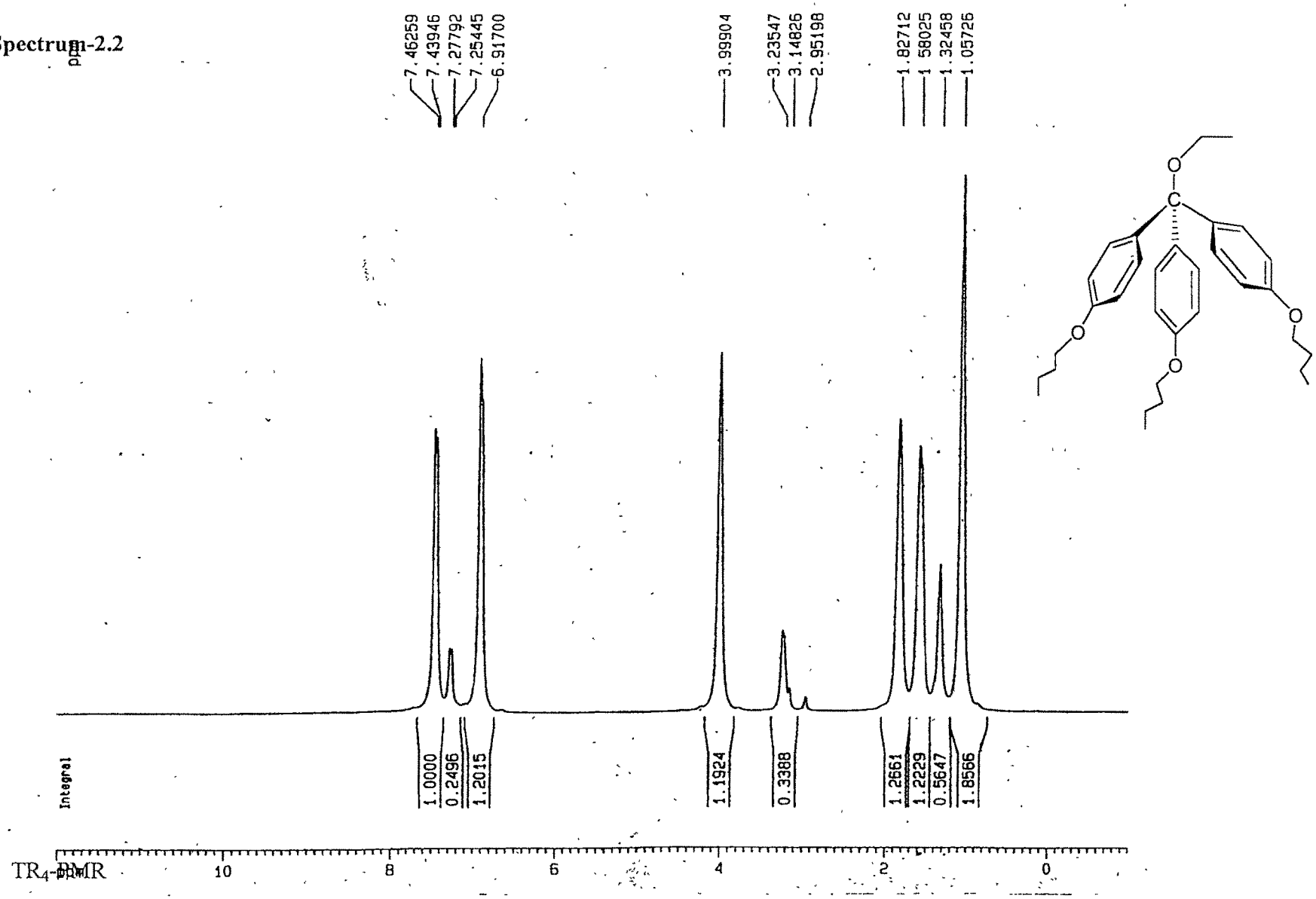
Yield:	55% (0.486gm.)
IR (KBr, cm^{-1}):	2918, 2850, 1608, 1508, 1247
^{1}**HNMR**($CDCl_3$, δ ppm):	1.2 (3H, t, Ar-$COCH_2$**CH_3**), 3.5 (2H, q, Ar-$COCH_2CH_3$), 4.5 (6H, s, Ar-CH_2-Br), 5.0 (6H, s, Ar-CH_2O-Ar), 6.9, 7.0 & 7.4 (arom. protons).
^{13}**C-NMR**($CDCl_3$, δ ppm):	15.1 (Ar-$COCH_2$**CH_3**), 54.4 (Ar-$COCH_2CH_3$), 77.4 (Ar-**C**OCH_2 CH_3), 76.9 (s, Ar-**C**H_2O-Ar), 114.5, 127.5, 130.1, 136.9, 138.3, 157.1 (arom. carbons).

Spectrum 2.1



TR_4

Spectrum-2.2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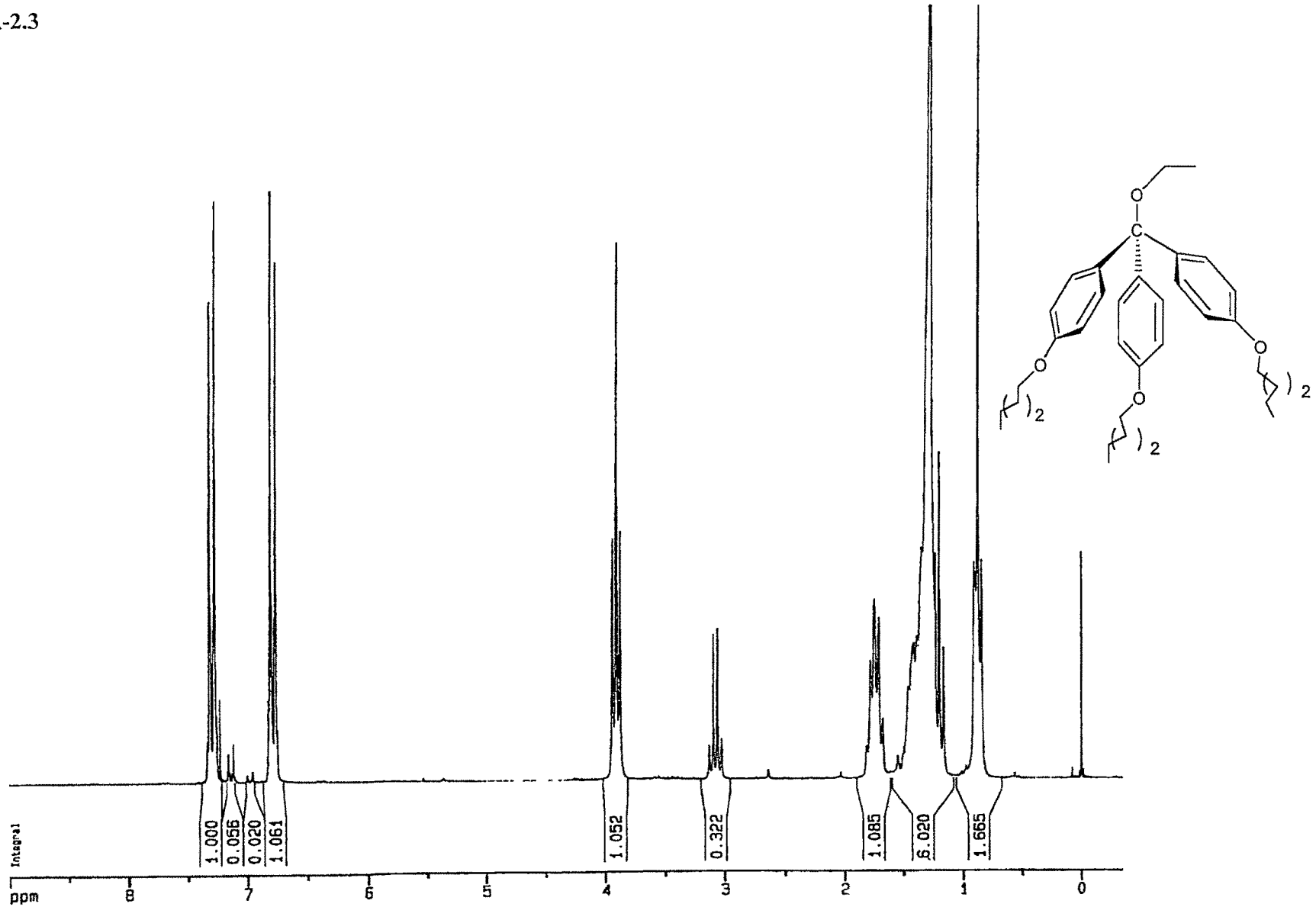
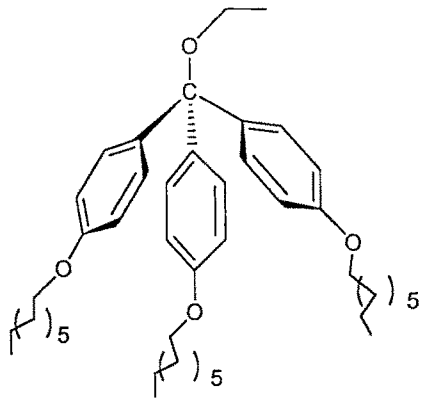
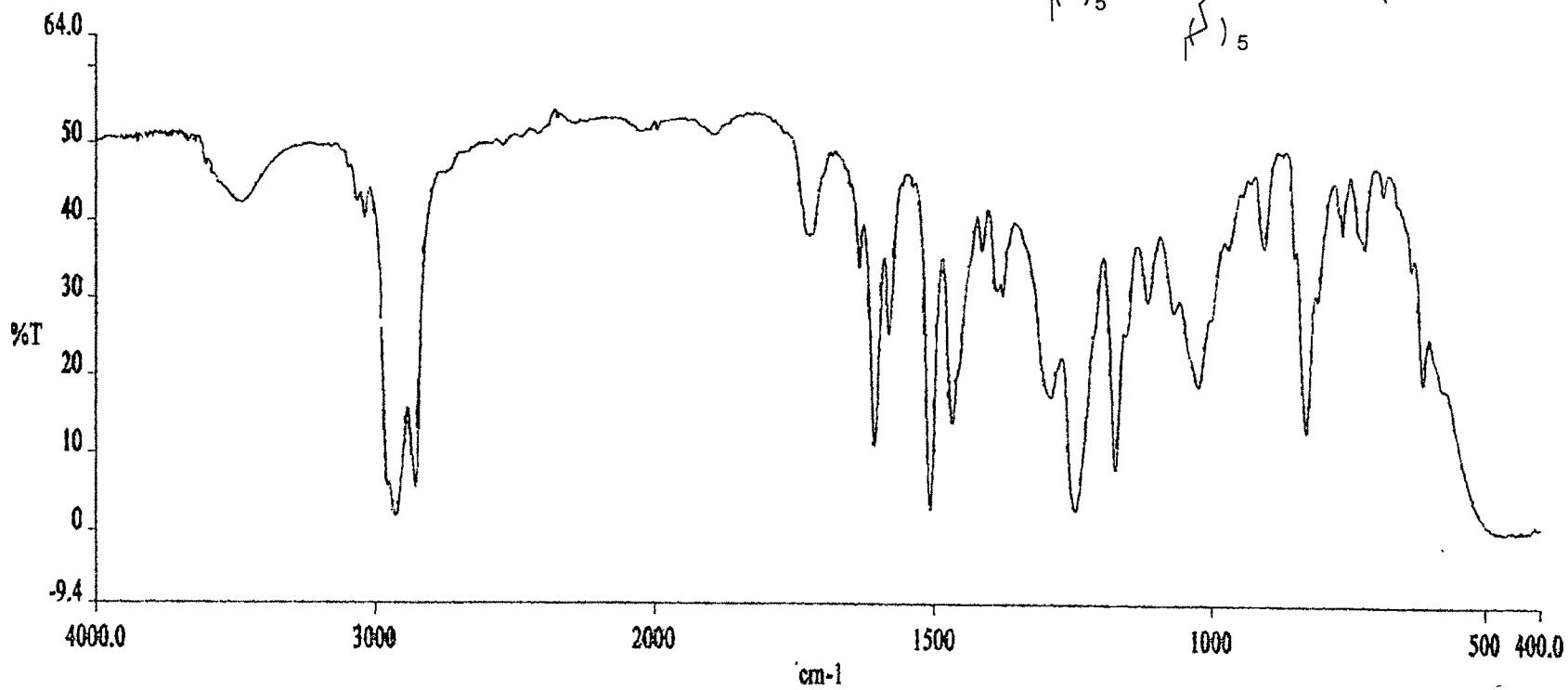
7.43946
7.27792
7.25445
6.91700
3.99904
3.23547
3.14826
2.95198
1.82712
1 58025
1.32458
1.05726
Integral
1.0000
0.2496
1.2015
1.1924
0.3388
1.2661
1.2229
0.5647
1.8566
10
8
6
4
2
0
TR4-PMR

Spectrum-2.3


Integral
1.000
0.056
0.020
1.061
1.052
0.322
1.085
6.020
1.665
ppm
8
7
6
5
4
3
2
1
0

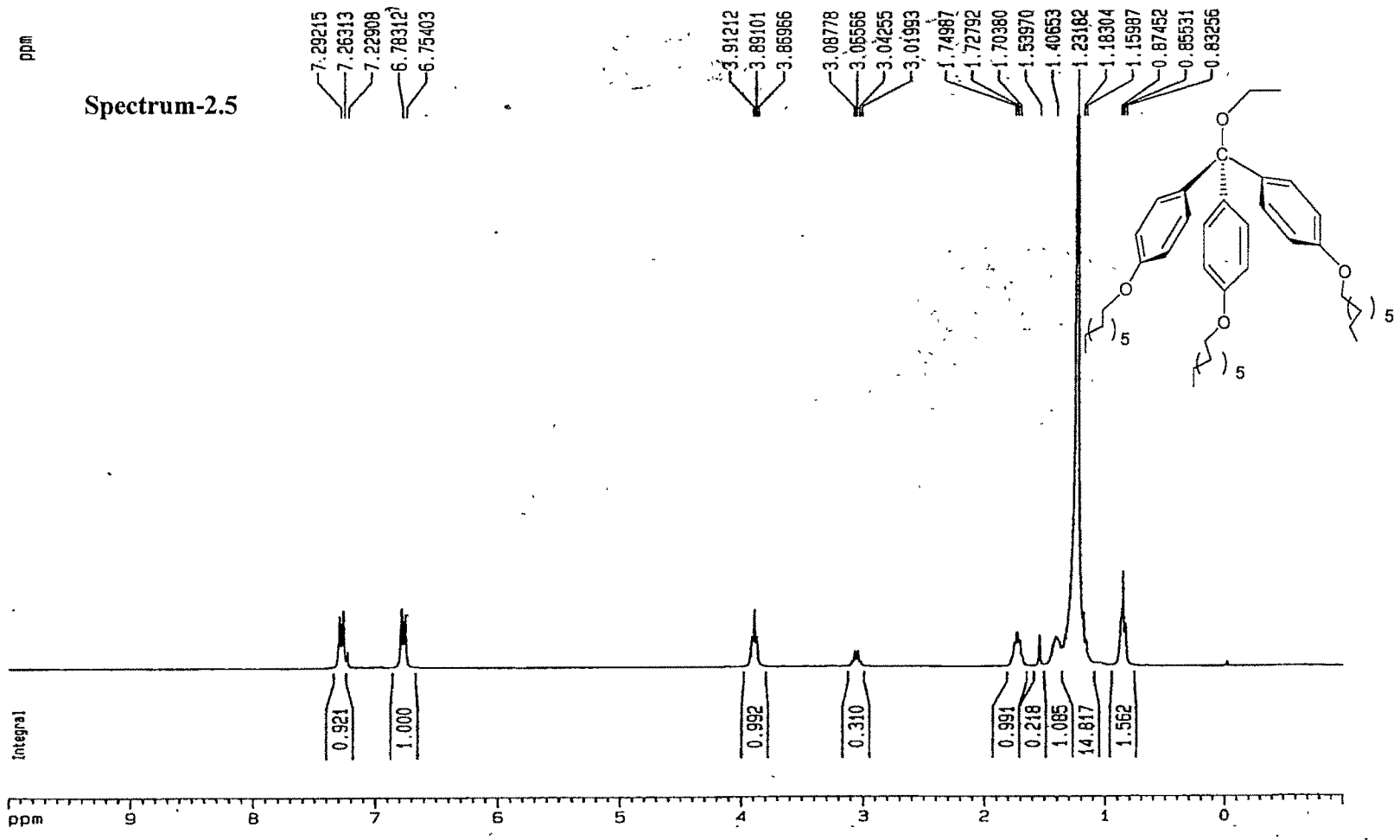
Spectrum-2.4



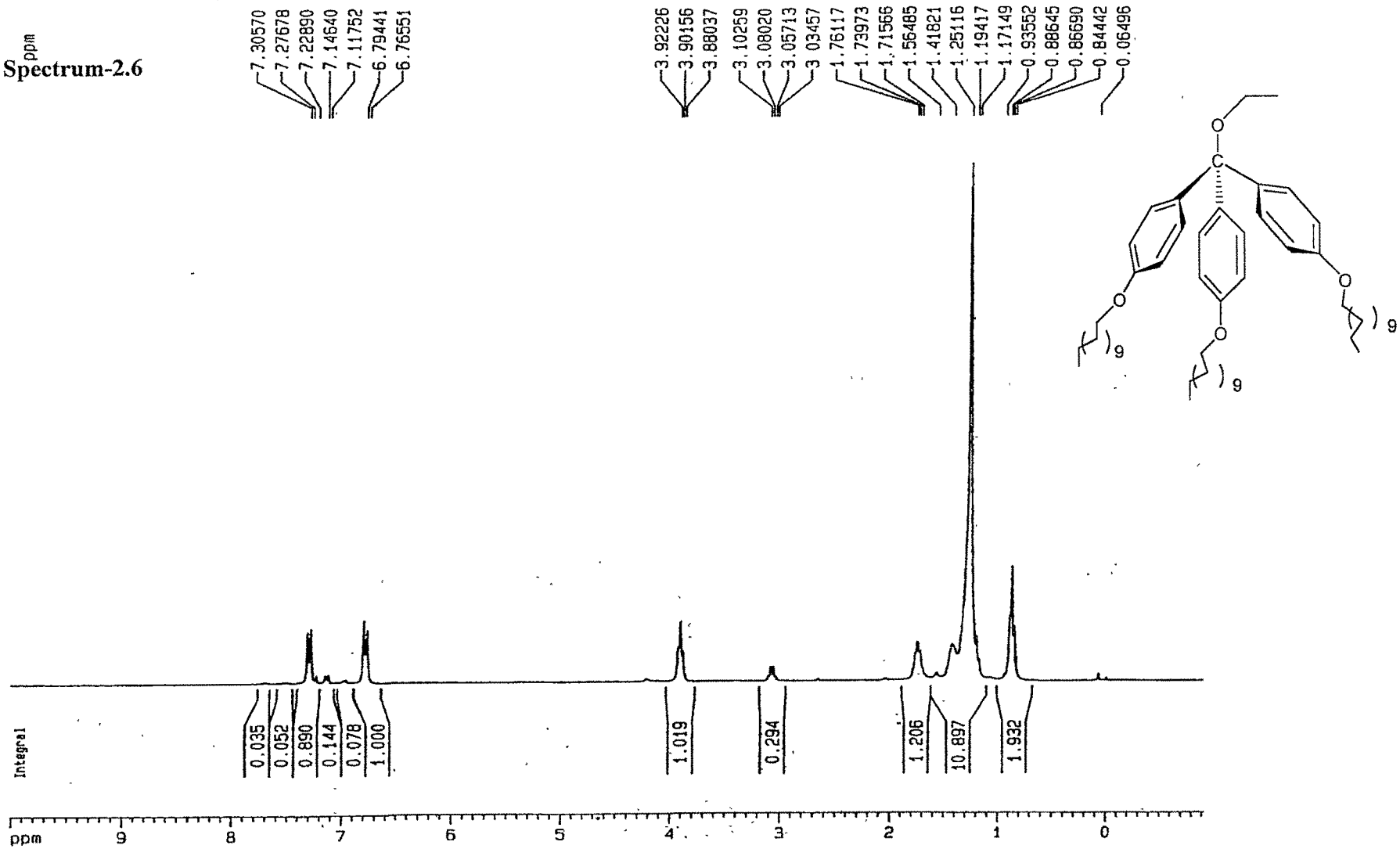


TR8.

Spectrum-2.5

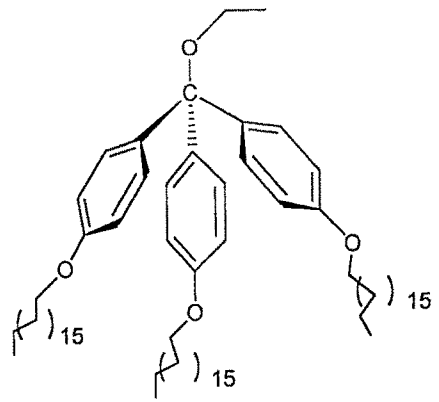

ppm
7.29215
7.26313
7.22908
6.78312
6.75403
3.91212
3.89101
3.86966
3.08778
3.05566
3.04255
3.01993
1.74987
1.72792
1.70380
1.53970
1.40653
1.23182
1.18304
1.15987
0.87452
0.85531
0.83256
Integral
0.921
1.000
0.992
0.310
0.991
0.218
1.085
14.817
1.562
ppm
9
8
7
6
5
4
3
2
1
0

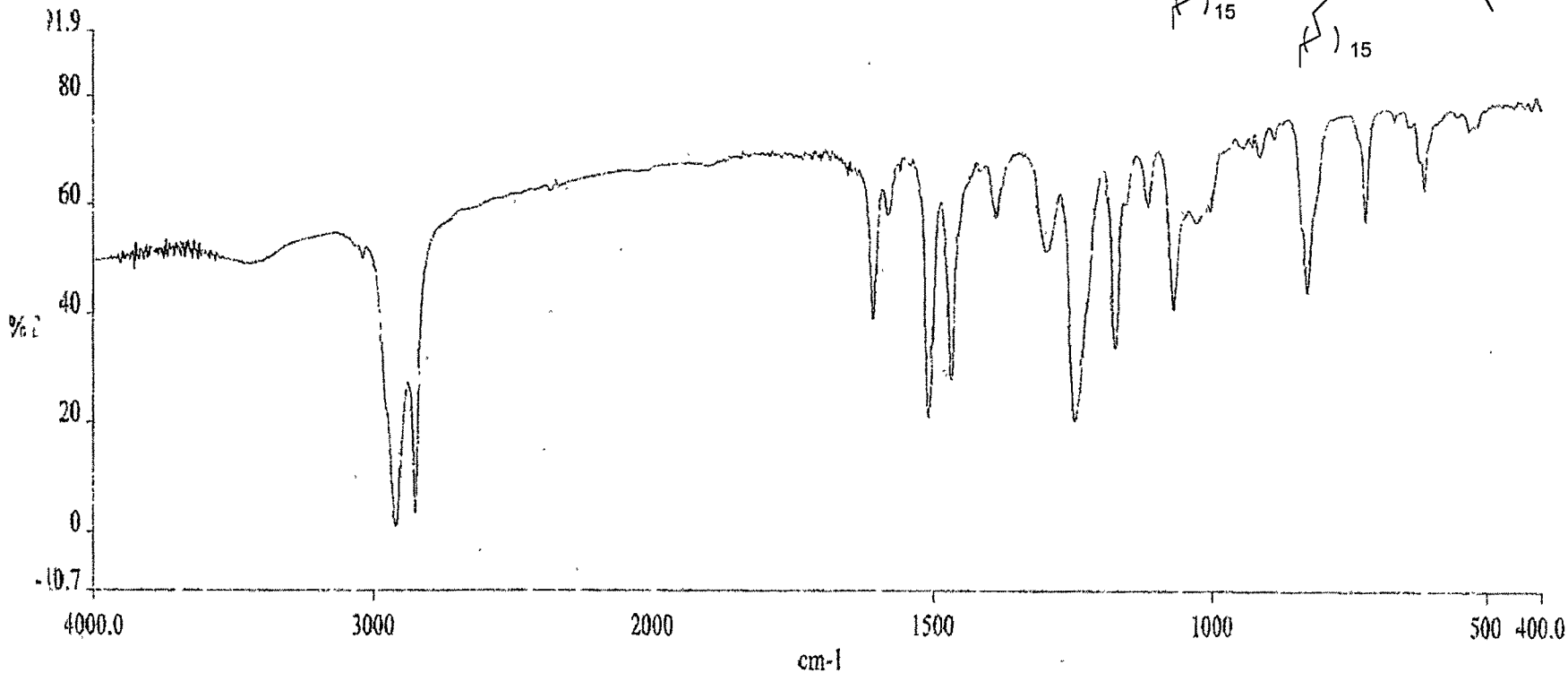
Spectrum-2.6



TR_{12}-PMR

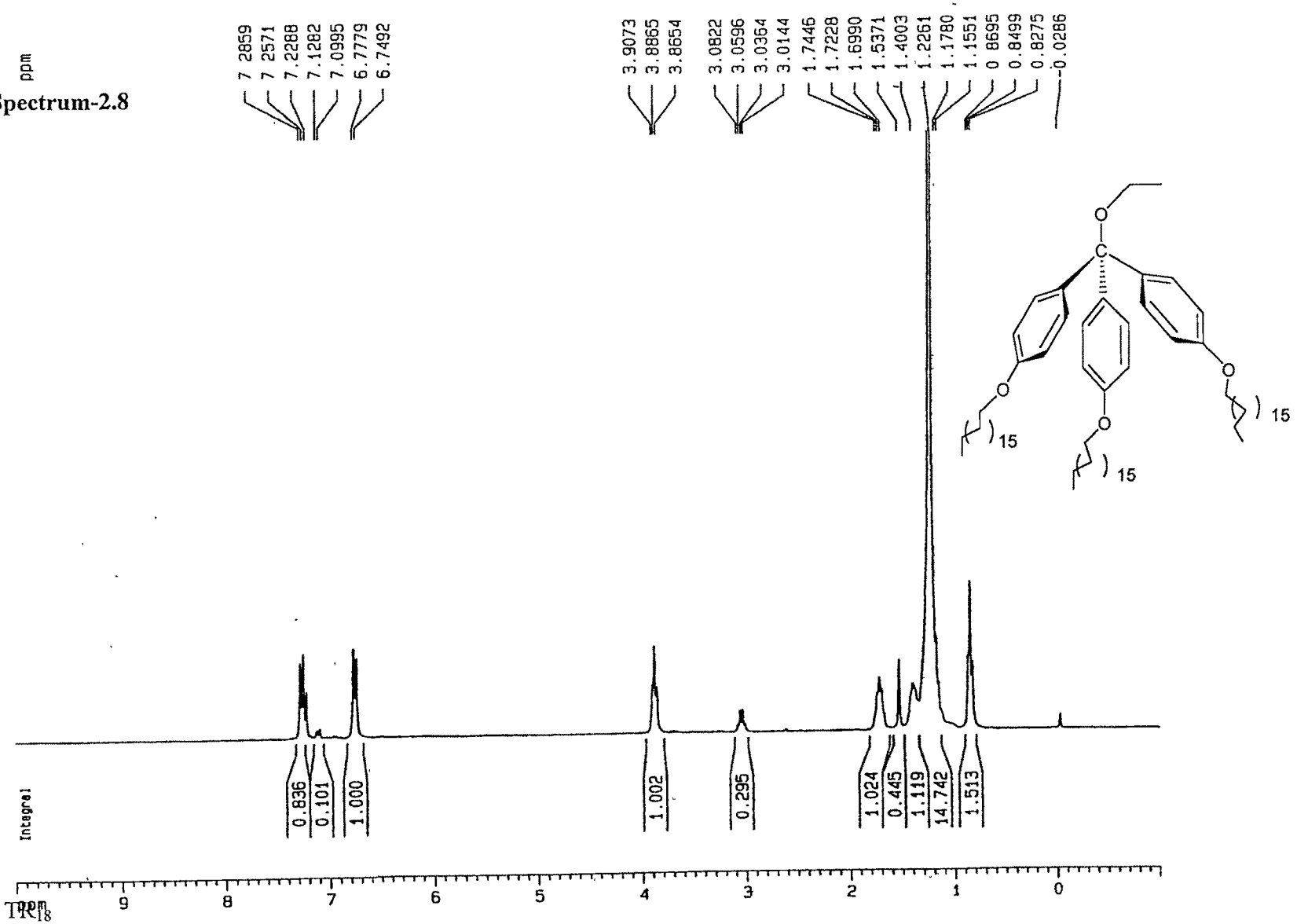
Spectrum-2.7





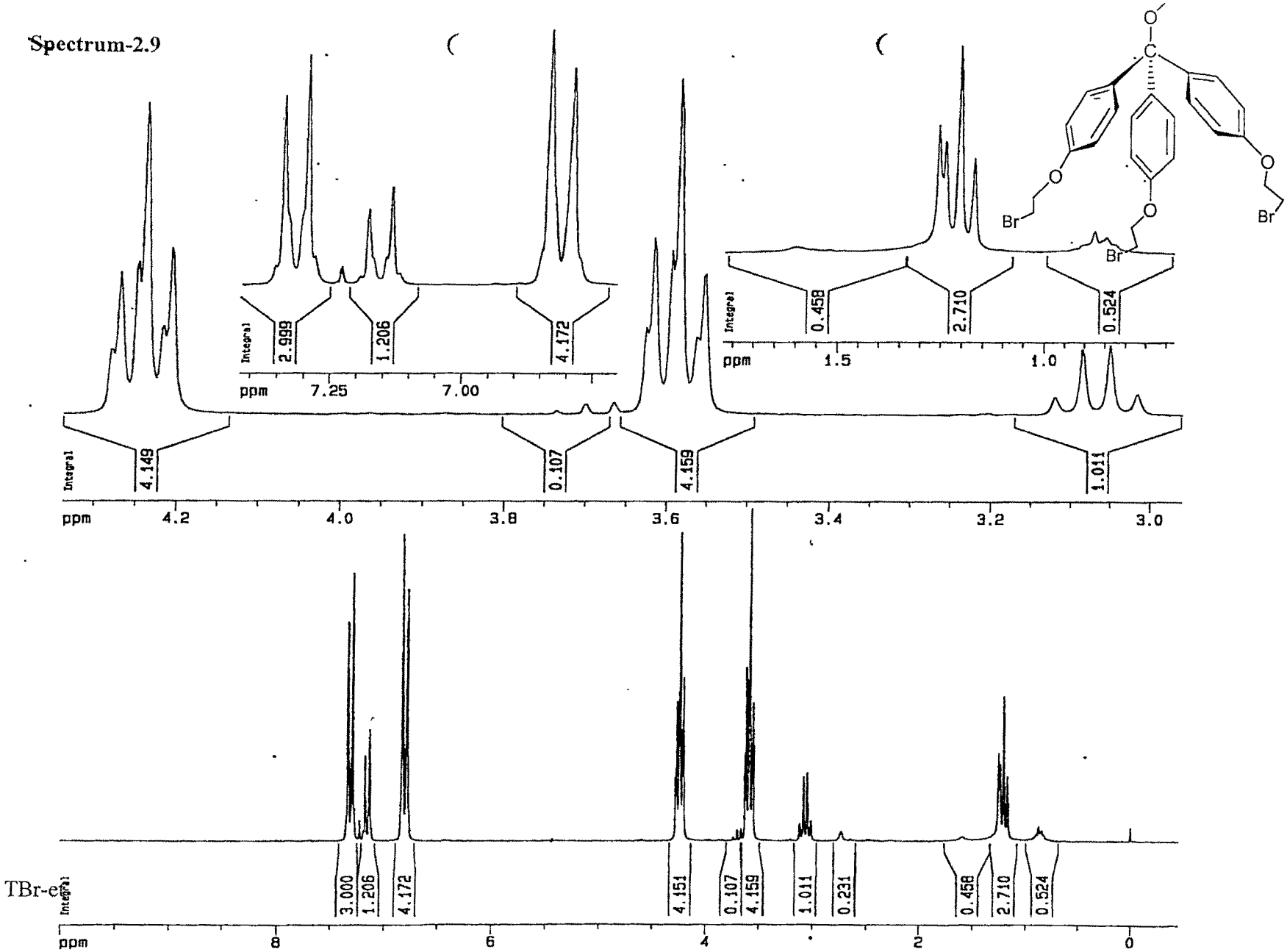
TR18.

Spectrum-2.8



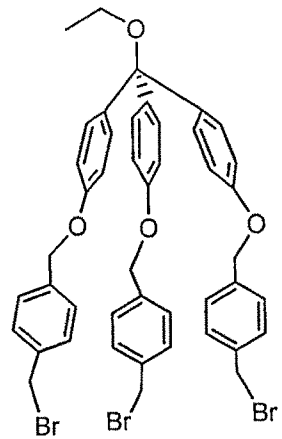
TR18

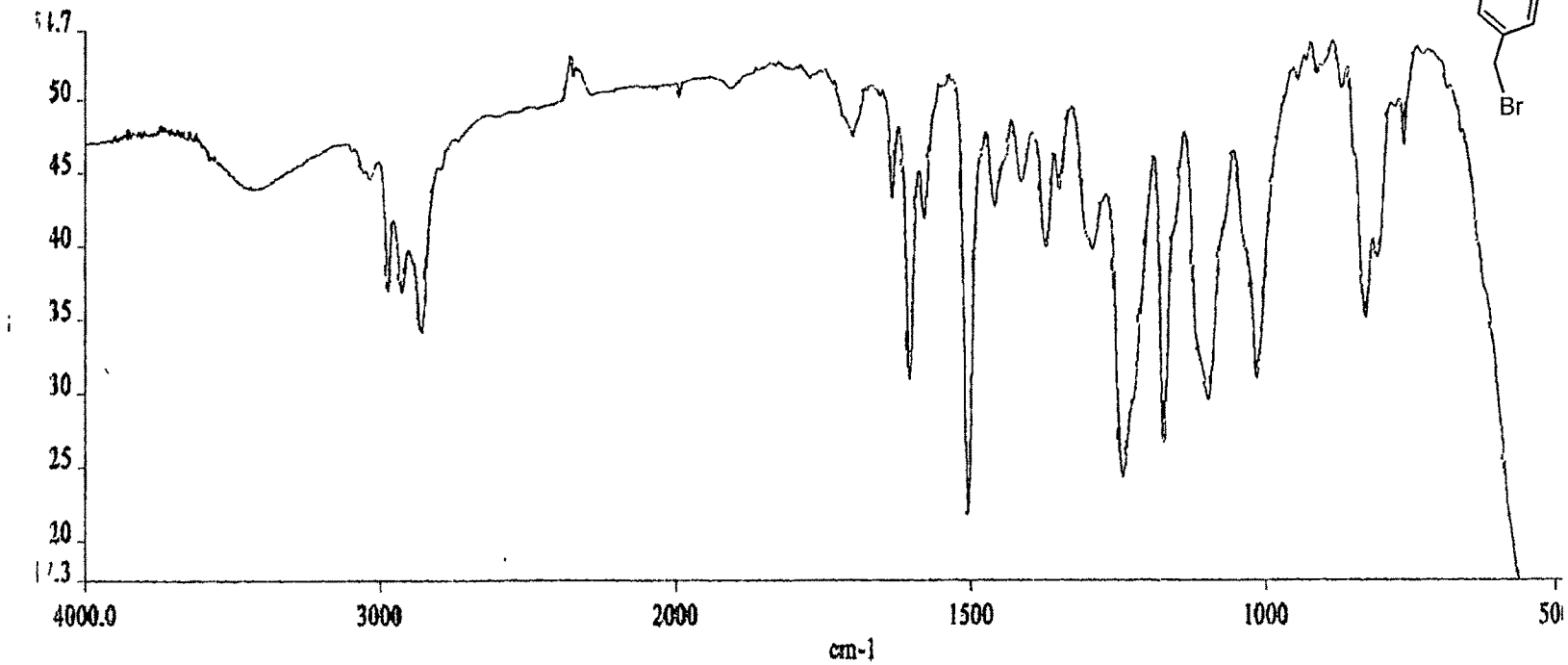
Spectrum-2.9



TBr-e

Spectrum-2.10





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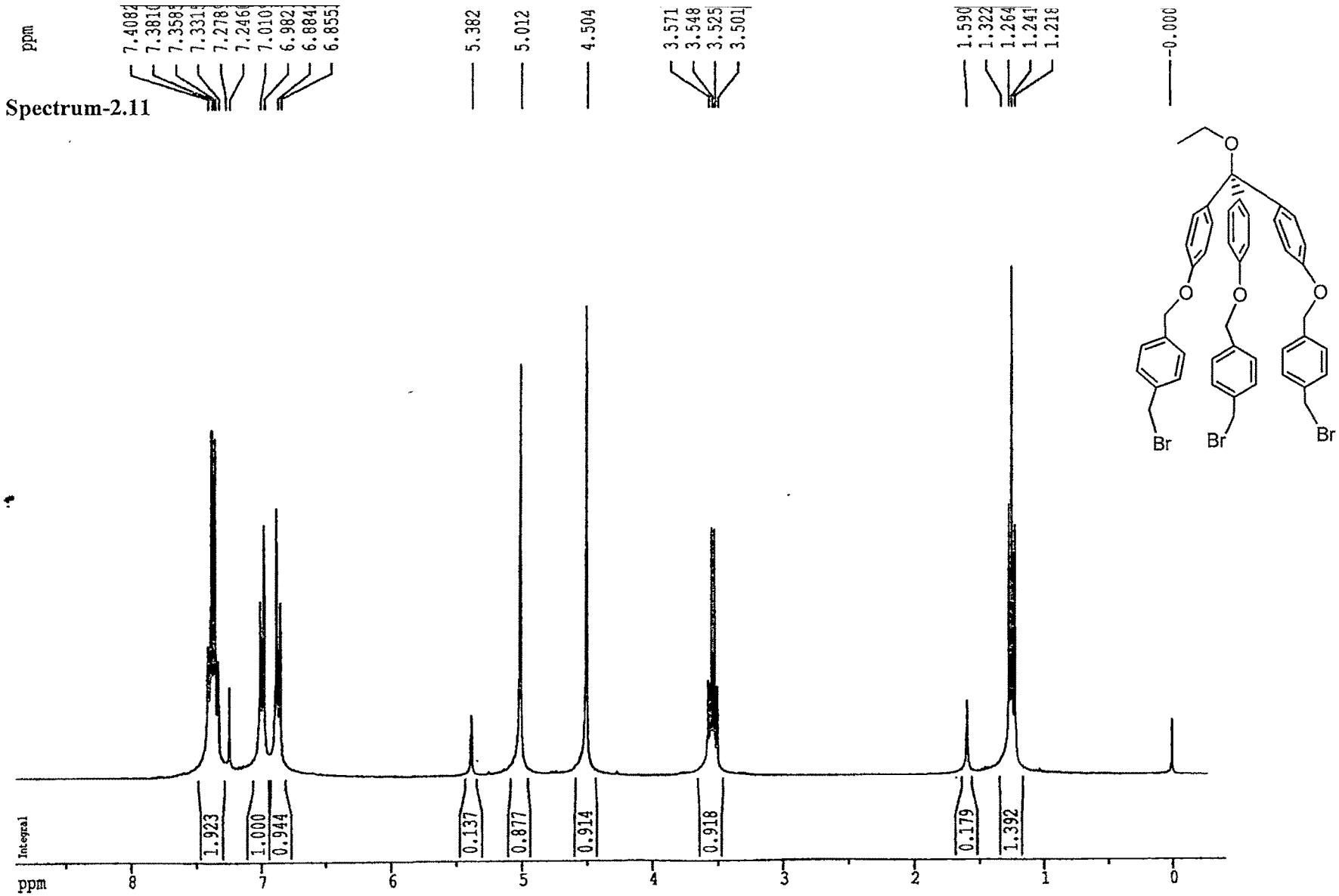
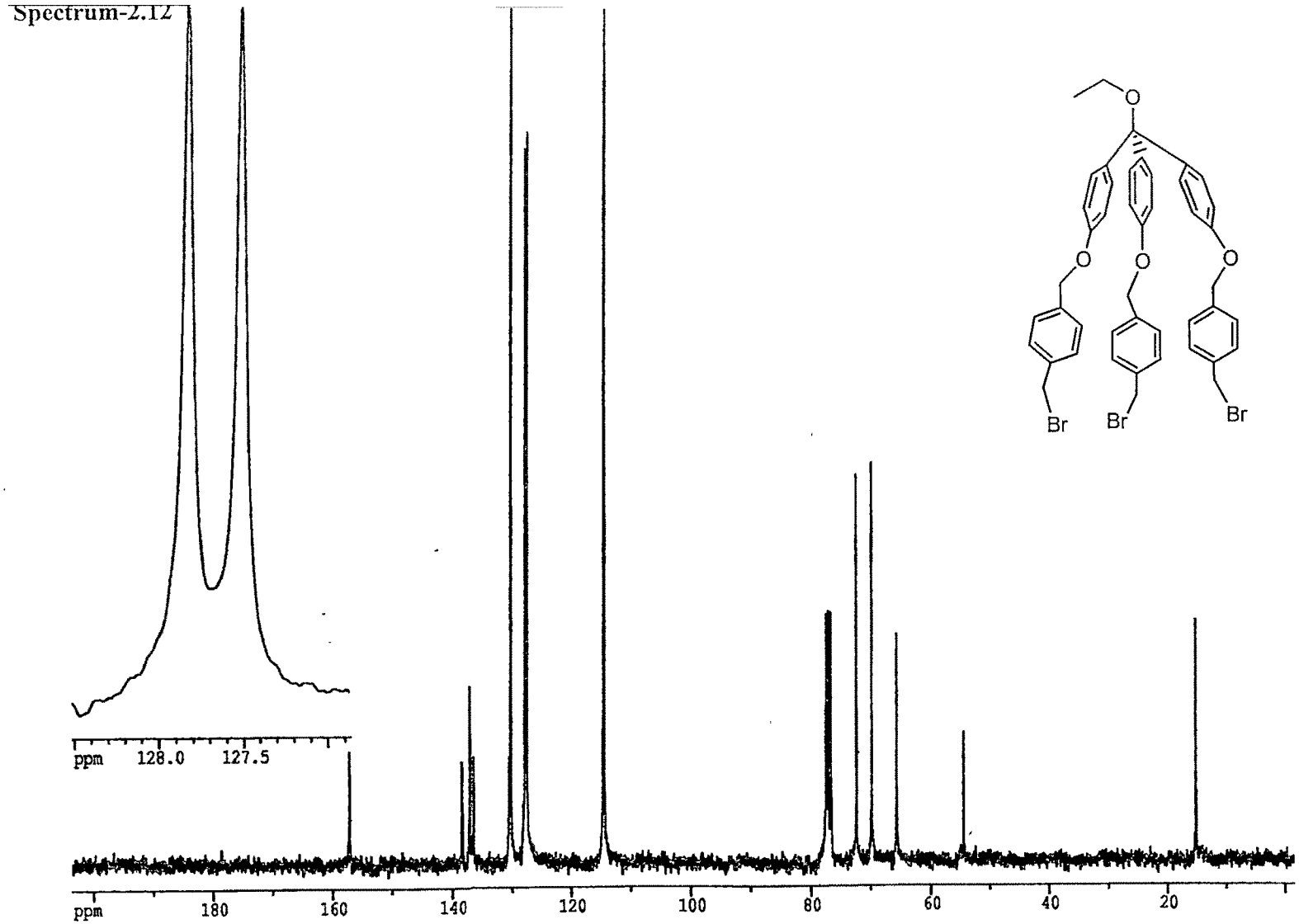
Spectrum-2.11

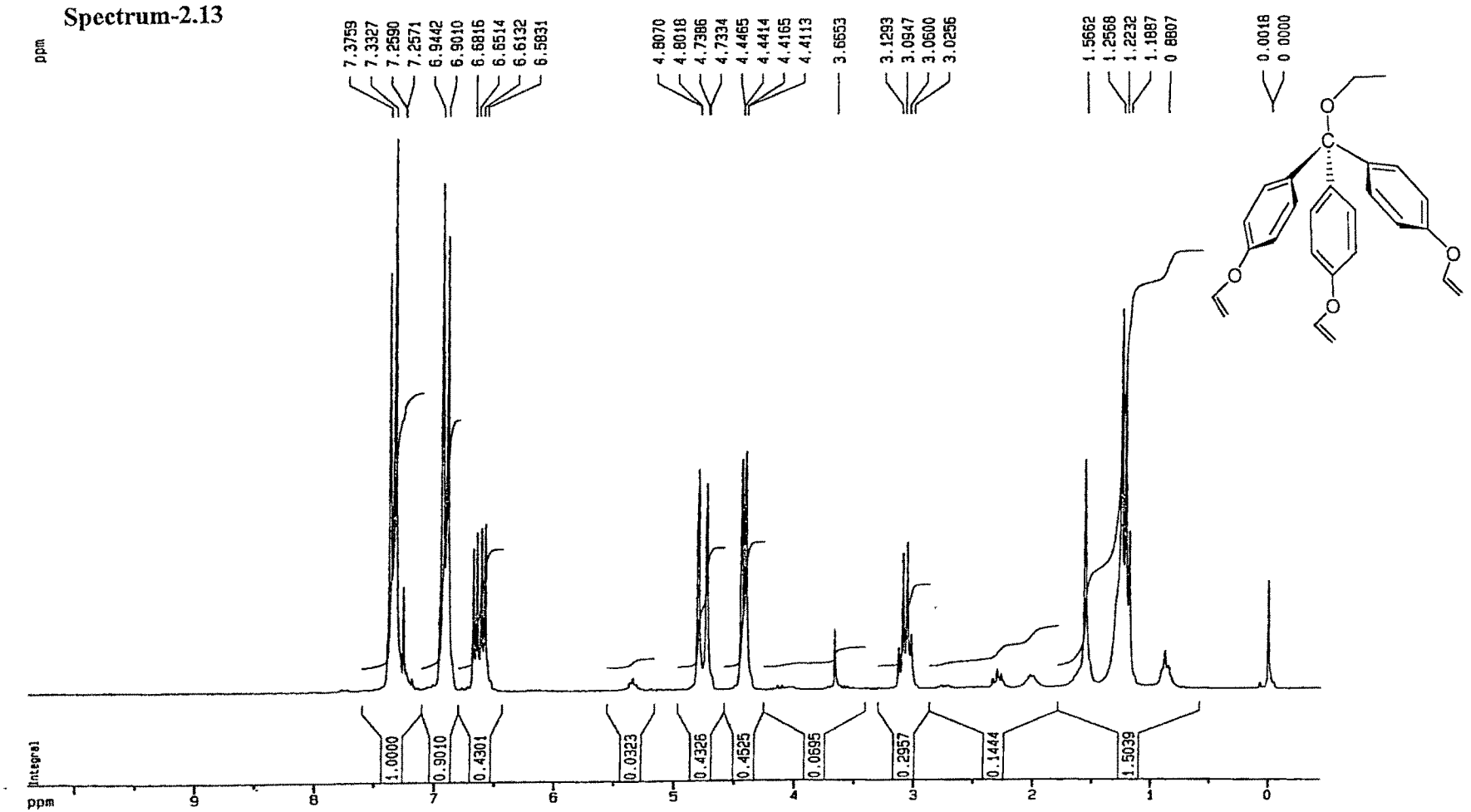


TBrXY


Spectrum-2.12
ppm 128.0 127.5
ppm 180 160 140 120 100 80 60 40 20
O
O
O
O
Br
Br
Br

Tbrxy-13C

Spectrum-2.13



TRelemn.

2.5 References

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