AN ABSTRACT OF THE THESIS OF

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Title: Synthesis of Substituted Planar Triarylmethane.

Abstract approved: Eric L. Trump

Two protective groups, benzyl and butyl, were utilized to protect the central carbon of sesquixanthene in electrophilic substitution reactions. Attempts were also made to perform substitution on unprotected sesquixanthene.

Nitration was carried out on sesquixanthene where the central carbon was protected and where the central carbon was unprotected. After bromination and nitration, cleavage of the protective group by oxidation was successful. Reduction of the nitro groups to amino groups by tin metal and stannous chloride was also attempted, but because of inavailability of necessary analytical methods, the results were inconclusive.

SYNTHESIS OF SUBSTITUTED
PLANAR TRIARYLMETHANES

A Thesis
Presented to
the Department of Chemistry
EMPORIA STATE UNIVERSITY

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
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LIST OF IR SPECTRA

LIST OF NMR SPECTRA

INTRODUCTION

Triarylmethane dyes have been used in many areas of chemistry. They are useful reagents for indicators,[1] dichromatic titration and redox indicators, determining the presence of traces of halide irons,[2] and the spectrophotometric determination of Sb(III),[3] Ta(V),[4] Ga(III),[5] In,[6] to list just a few. They are used in ball point pen inks[7] and as corrosion inhibitors.[8] Several triarylmethane dyes are good indicators of the titration for Fe(II), Ti(III), Cr(II), Cu(I) with Ce(IV), and for the titration of Fe(II), $Fe(CN)_6^{4-}$, U(IV), Mo(V) and hydroquinone with dichromate.

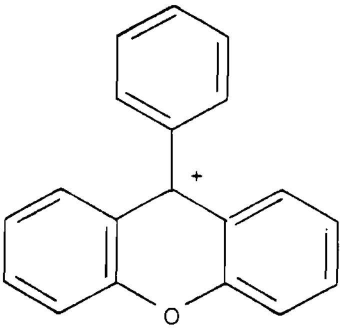
Except for the azodyes, triphenylmethane and xanthene dyes are the most commonly used reagents in the spectrophotometric determination of metals. Reports on the most common and well known substances--aluminon, phenylfluorone, malachite green, brilliant green, crystal violet, and rhodamine--were published over a half century ago. In the phenol red group, for example, phenolsulfonphthalein has been used for the kinetic determination of copper,[9] the decomposition of the dye being recorded spectrophotometrically.

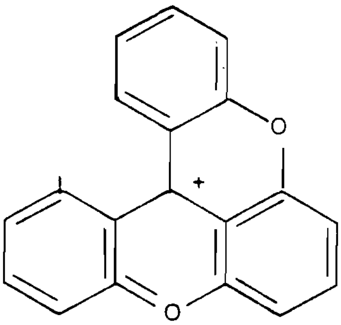
Two problems with these indicators are that their reactions are not all reversible and they are often not stable in oxidizing solutions. In spite of these disadvantages, they have been commonly used.[10,11]

The unique properties of the central carbon atom have aroused much chemical interest in triarylmethane dyes. A free radical, a cation, or an anion can occupy the central position, with resonance delocalization on the aromatic rings. The stabilization of triarylmethane dyes is dependent on the degree of twist of three phenyl rings. The dye has maximum stability when the rings are coplanar, but this is normally impossible, so a propeller-shaped molecule results.[12,13]

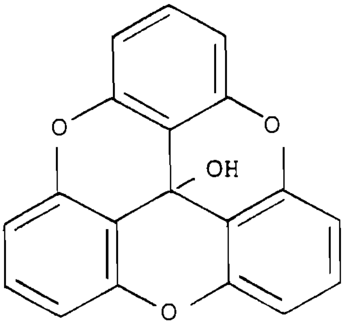
The stability of triarylmethanes is also dependent on the ring substituents. Ortho-substitution decreases the stabilization because of large steric effect. The cation of this para-methyl substituted triarylmethane is five times as stable as the cation of tris ortho-methyl substituted triarylmethane.[14] It may be seen that the effect of ortho substitution is large and the effect is most readily attributed to steric factors. Increasing the degree of ring twist will decrease the degree of ring resonance and thus decrease stabilization.

The use of oxygen bridges to force planarity of triarylmethane or triaryl radicals has been investigated and numerous 9-substituted xanthyl (I) free radicals have been reported by Conant.[15] Stability increased because of the oxygen bridges. The two oxygen bridged molecule (II) in the xanthyl series has also been reported.[16] This radical was reported to be 100% dissociated in benzene at room temperature since dilute solutions of the radical were found to obey Beer's law and no darkening of the solution occurred on warming. The authors have interpreted this high degree of dissociation as being due to high resonance stabilization in the free radical due to planarity of the system. When compound (II) is compared with compound (I), it is observed that compound (II) shows greater stabilization due to second oxygen bridge.

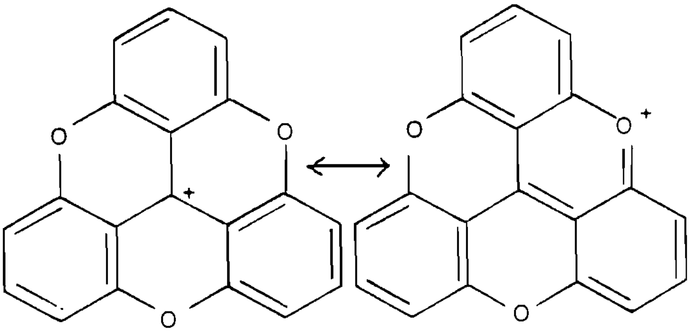

(I)


(II)

Sesquixanthydrol (III) was of considerable synthetic and chemical interest to us. It has an unusually high basicity caused by resonance distribution of the positive charge to the oxygen bridge as shown in structure (IV).



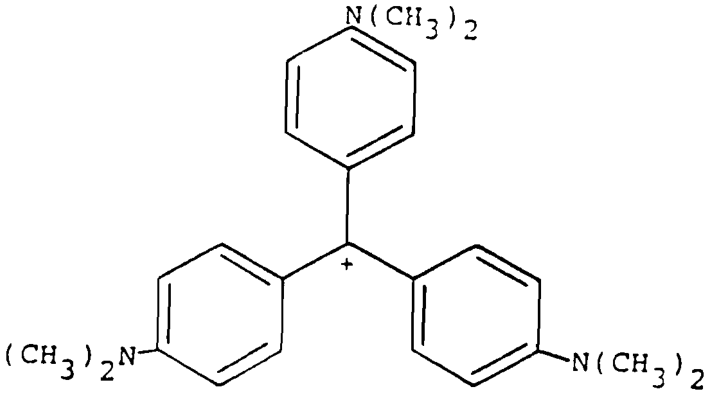
(III)


(IV)

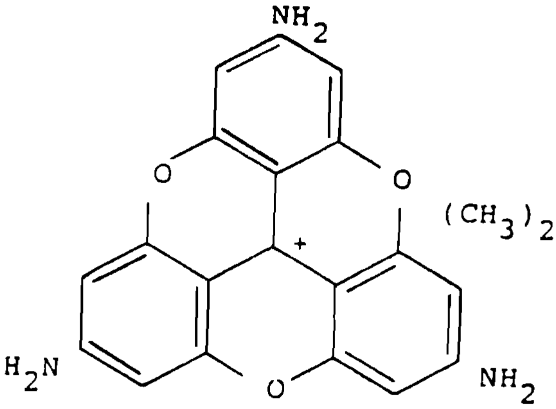
In a sufficiently acidic solution, sesquixanthydryl is protonated and loses water. This type of compound is called a "secondary base" and the equilibrium constant is expressed in terms of K_{R+}.[18] Triphenylcarbinol, has a pK_{R+} of -6.63.[19] Based on the differences between the resonance structure of triarylmethane and sesquixanthene, the pK_{R+} for sesquixanthene is expected to be much larger than -6.63. Generally, electron donating groups should stabilize the carbonium ion and increase pK_{R+}. Three para dimethylamino groups increase the pK_{R+} to 9.63 and three para methoxy groups change the pK_{R+} to 0.82.

The planar sesquixanthydryl cation (IV) is noted for its exceptional stability. Propeller-shaped crystal violet (V), which contains electron-donating dialkylamino groups, is noted for its intense color, but it is not fluorescent. In fluorescent Rhodamine B(VI),[20] which contains dialkylamino groups, two of the three rings are locked into the same plane by an oxygen bridge. Combining the planarity of the sesquixanthydryl cation with electron donating group such as crystal violet (V) produces compound such as triamino-sesquixanthene (VII) is the objective of our research. Such a series of compounds would be expected to be intensely colored and strongly fluorescent.

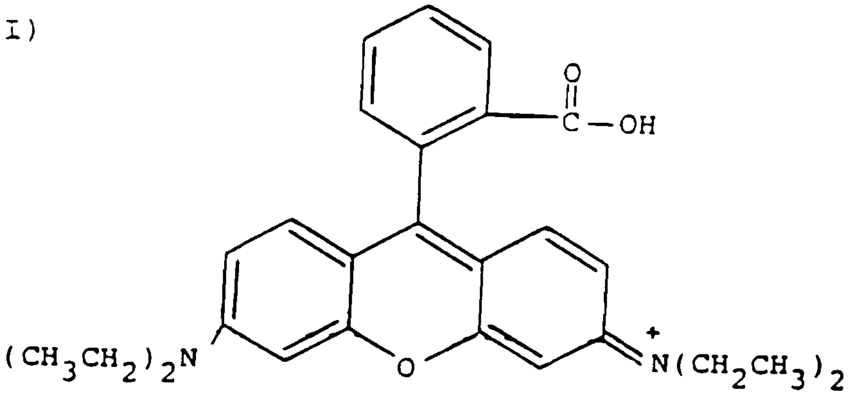
A known synthetic route[21] for the preparation of amino substituted sesquixanthene dyes is to start with a substituted benzene which has a good leaving group, such as 3,5-dimethoxy fluorobenzene. This route avoids protecting the central carbonium ion. Our primary purpose was to create a different synthetic route which would allow us to synthesize the sesquixanthene base first and then add protecting group to form a sesquixanthene dye as an intermediate, then to replace a hydrogen on the aromatic ring with an amino group, forming a basic amino dye. When this synthesis was carried out, we had the opportunity to investigate the activity of the central carbon, the protective ability of different substituted groups, and the relationship between fluorescence and color.



(V)



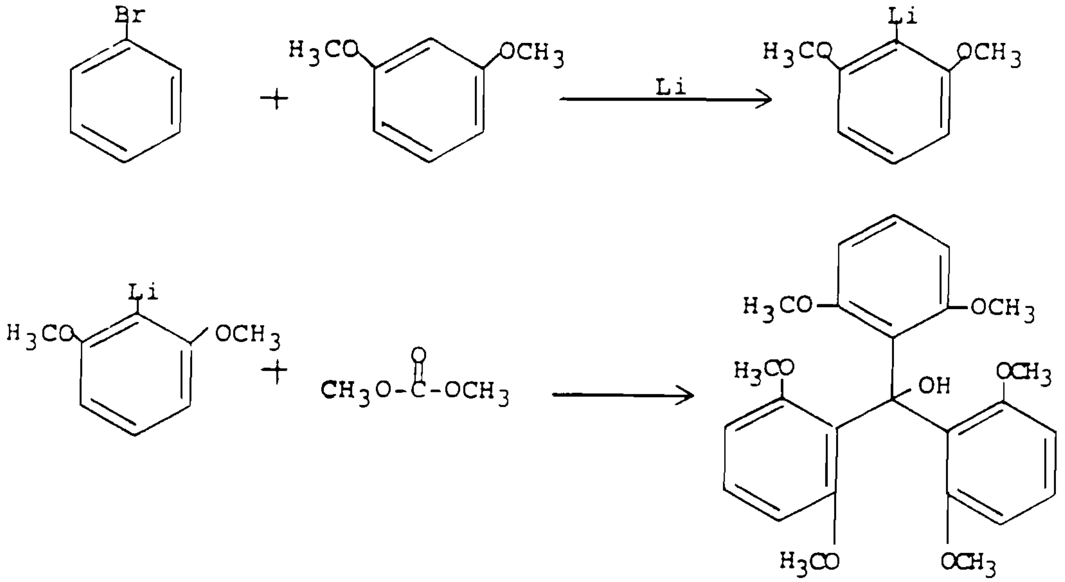
(VII)



(VI)

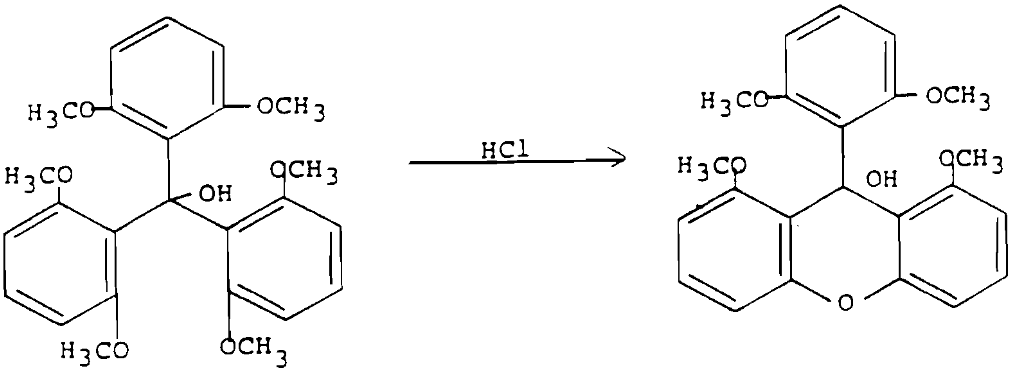
EXPERIMENT SECTION

Synthesis of 2,6,2′,6′,2",6"-hexamethoxytriphenylcarbinol



A solution of phenyl lithium was prepared by the addition of bromobenzene (19.5 g,0.125 mole) to 65 mL of ether with lithium wire (2.0 g 0.290 mole) and 30 mL of diethyl ether. 1,3-dimethyl benzene (15.0 g, 0.109 mole) was added and the reaction mixture was allowed to stand at room temperature under an atmosphere of nitrogen for sixty hours. 2,6-dimethoxy phenyl lithium was formed as white crystals.[29] Dimethyl carbonate (3.24 g, 0.036 mole) in 200 mL of benzene was added and the reaction mixture was refluxed for three days under a protective nitrogen atmosphere. A white solid formed in the reaction mixture during this time. After cooling, the reaction mixture was poured into 300 mL of water to produce an aqueous layer and an organic layer. The organic layer was separated from the aqueous layer, washed twice with water, dried over sodium sulfate and concentrated to yield a grey residue. The residue was recrystallized once from ether to yield 14.98 g (47%) of 2,6,2′,6′,2",6"-hexamethoxytriphenyl carbinol with melting point 163-164°C. The product was verified by IR spectrum Figure 1.

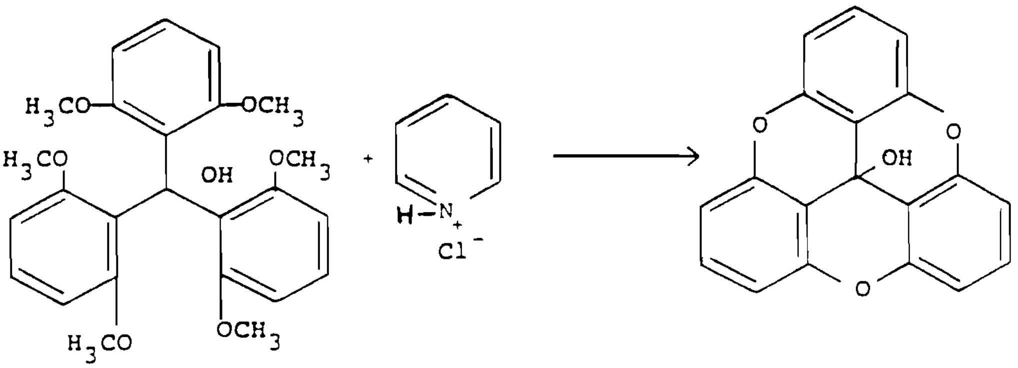
Synthesis of 9-(2,6-dimethoxyphenyl)-1,8-dimethoxyxanthydrol



A solution of 2,6,2′,6′,2",6"-hexamethoxytriphenylcarbinol (4.0 g, 0.0508 mole) in 1,000 mL of water and 10 mL of concentrated hydrochloric acid was heated for two hours on a sand bath. The initial deep purple solution became deep red during the reaction and a white precipitate formed. The precipitate was collected by suction filtration and dried under vacuum to yield 3.48 g (96%) of 9-(2,6-dimethoxyphenyl)-1,8-dimethoxyxanthydrol. The product was purified by one recrystallization from benzene-acetone to give 2.58g of material with melting point 295-298°C. This was identified by infrared spectrum Figure 2. and NMR spectrum Figure 18.

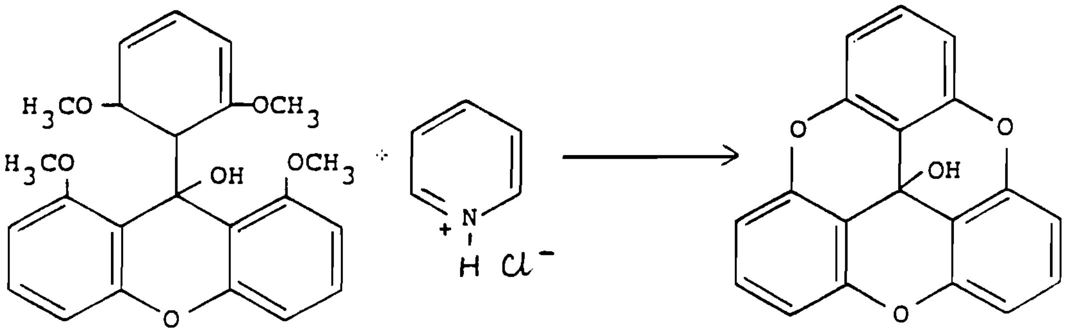
Synthesis of sesquixanthydrol:

A. from 2,6,2′,6′,2",6"-hexamethoxytriphenylcarbinol



Pyridine hydrochloride (50.0 g, 0.435 mole) and 2,6,2′,6′,2",6"-hexamethoxytriphenylcarbinol (10.0 g, 0.023 mole) were mixed and heated with stirring at 195^{0}C for one hour. The initial purple mass gradually became liquid under these conditions and took on a red color. The reaction mixture was washed into one litter of water to produce a red solid and a yellow aqueous solution. The solution was filtered to remove the red solid and was then basified with potassium hydroxide to produce a white solid. This product was purified by recrystallization from a solution of diethyl ether, benzene, and ethanol to yield 0.9 g of pure material which was identified as sesquixanthydrol.

B. from 9-(2,6-dimethoxyphenyl)-1,8-dimethoxyxanthydrol

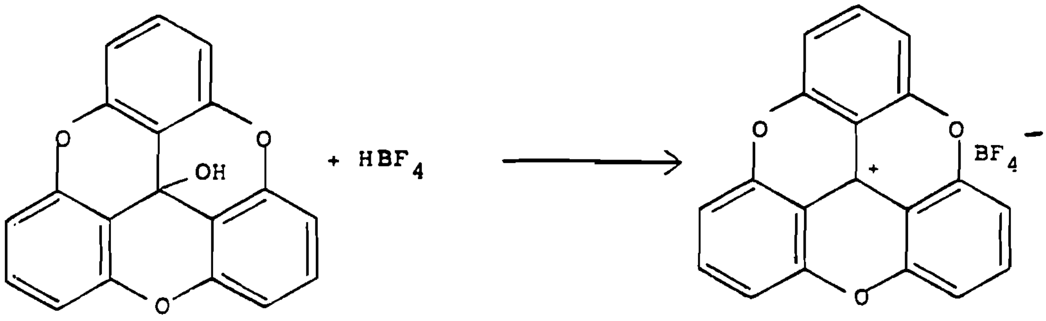


9-(2,6-dimethoxyphenyl)-1,8-dimethoxyxanthydrol (2.5 g, 0.006 mole) and pyridine hydrochloride (7.0 g, 0.061 mole) were mixed and heated at maximum reflux on a sand bath for one hour. The initial solid became a deep red liquid. At the end of this time, the red liquid reaction product was poured into water and the solids remaining in the reaction flask were washed out with water. A red solid remained undissolved in the water while the solution was a reddish yellow color. The solution was filtered to remove the red material and was then basified with potassium hydroxide which discharged the yellow color of the solution and produced a light brown precipitate. The precipitate was collected and dried under vacuum to yield 1.75 g (89%) of sesquixanthydrol. The product was recrystallized once from ether, purified by passing it through aluminum absorption column to yield 1.17 g (65%) of white pure sesquixanthydrol with melting point 303°C. The product was verified by Infrared spectrum Figure 3, and NMR spectrum

Figure 19.

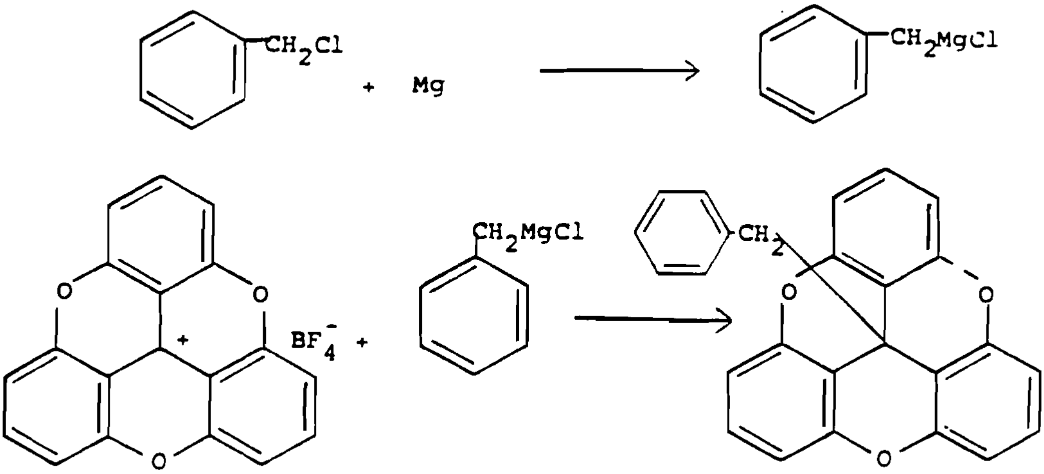
Synthesis of benzyl sesquixanthene and butyl sesquixanthene.

a. Reaction with fluoroboric acid.



Sesquixanthydrol (2.0 g, 0.007 mole) was dissolved in 200 ml ether and fluoroboric acid (1.75 ml, 0.014 mole) was added in the presence of acetic anhydride. The reaction mixture was stirred at room temperature for one hour. A yellow colored solid gradually formed. The solution was separated by suction filtration, and the solid was washed with 20 Ml benzene to yield 2.3 g (94%) of fluoboric sesquixanthydrol with melting point above 350°C. verified by infrared spectrum Figure 4.

b. Reaction with benzyl magnesium chloride.

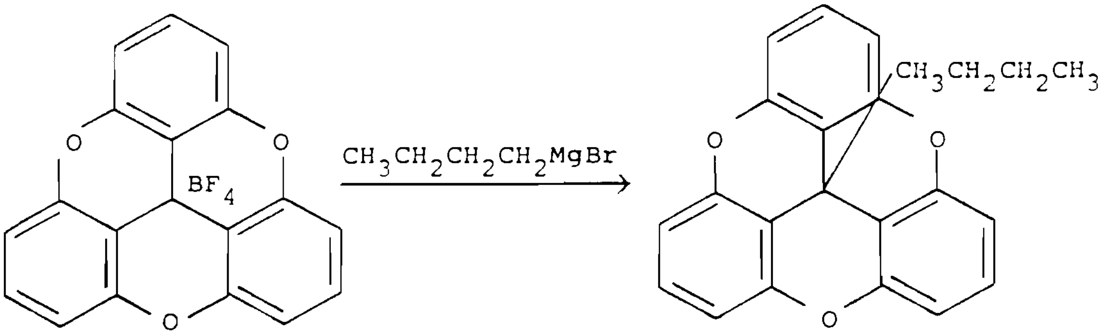


Fluroboric sesquixanthene (1.7 g, 0.0046 mole) was added to 100 mL of diethyl ether. Freshly prepared benzyl magnesium chloride was added dropwise under nitrogen while stirring. The yellow solid disappeared gradually. The solution was allowed to stand for 30 minutes after all solid had disappeared. The solution was washed using 40% concentrated HCl. The organic layer was separated from the aqueous layer, washed once with water, dried over sodium sulfate and concentrated to yield a light brown solid. The brown solid was recrystallized once from hexane to yield 1.45 g (84%) of pure benzyl sesquixanthydrol with melting point 173-175°C. The product was analyzed spectroscopically using IR and NMR, giving the infrared spectrum Figure 5, and NMR spectrum Figure 20.

c. Reaction with butyl magnesium bromide.

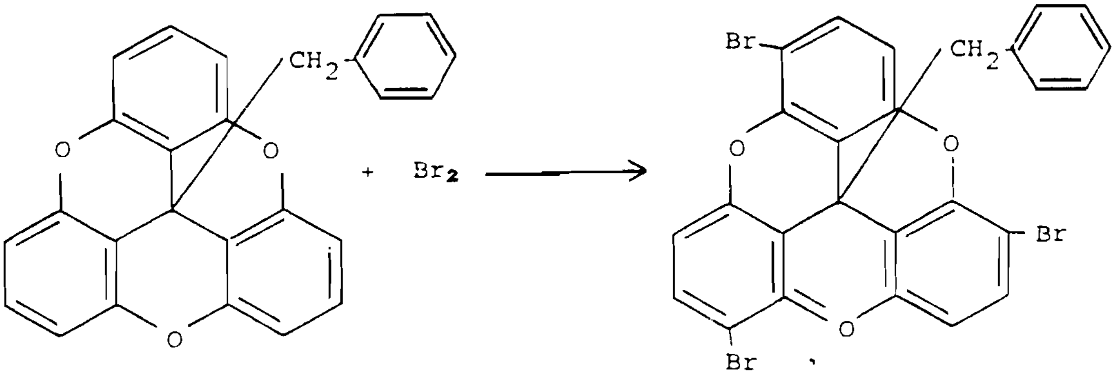
$$CH_3CH_2CH_2CH_2OH \quad + \quad Br \longrightarrow CH_3CH_2CH_2CH_2Br$$

$$CH_3CH_2CH_2CH_2Br \quad + \quad Mg \longrightarrow CH_3CH_2CH_2CH_2MgBr$$



Fluoboric sesquixanthene (0.8 g, 0.002 mole) was added in 70 mL of ethyl ether. Freshly prepared butyl magnesium bromide was added dropwise under nitrogen with stirring. The yellow solid disappeared gradually. The solution was allowed to stand for 30 minutes after all the solid disappeared. The solution was washed with 10% hydrochloric acid. The organic layer was separated from aqueous layer, washed once with water, dried over sodium sulfate and concentrated to yield a light brown solid. The brown solid was recrystallized once from hexane to yield 0.7 g (95%) of white, pure butyl sesquixanthene with melting point 161-161.5°C. The product was analyzed spectroscopically using IR and NMR, giving the infrared spectrum Figure 6 and NMR spectrum Figure 21.

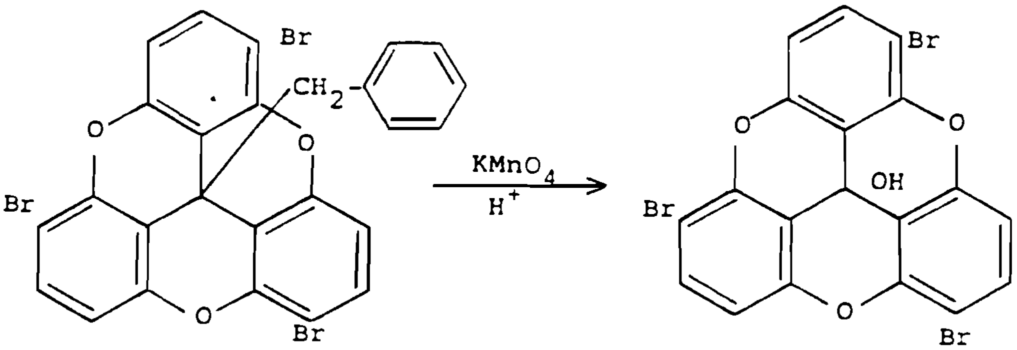
<u>Synthesis of 1,1′,1″-tribromo-benzyl sesquixanthene / 1,1′,1″-tribromo butyl sesquixanthene:</u>



Finely powdered benzyl sesquixanthene or butyl sesquixanthene was placed in a weighing bottle cover, and then the bottle cover was placed in a large neck Erlenmeyer flask (the ideal vessel is a desiccator). Another weighing bottle cover containing chemical quantitative bromine liquid (neat) was set side by side with weighing bottle cover in the

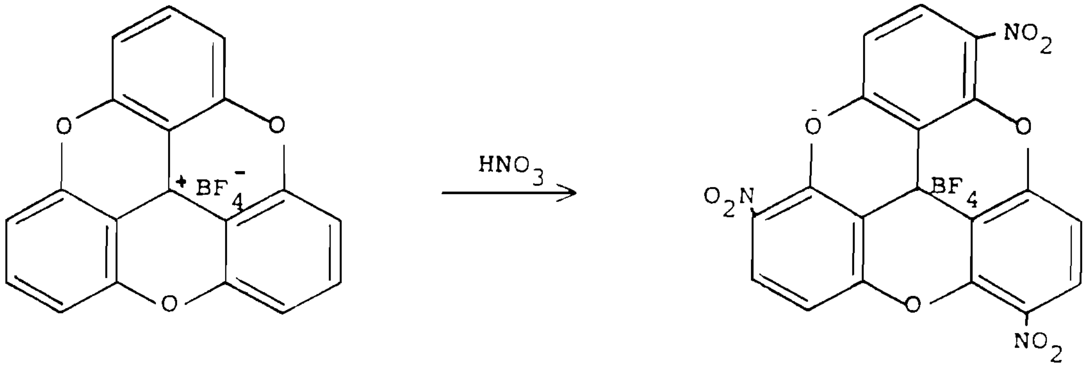
Erlenmeyer flask. A rubber stopper sealed the erlenmeyer flask. In the flask, benzyl sesquixanthene / butyl sesquixanthene was in contact with bromine vapor. The Erlenmeyer flask and its contents was allowed to stand 8 hours or overnight. During this period, a needle was inserted, at two hour intervals, to provide a means of escape for the hydrogen bromide. The orange solid was then removed from the Erlenmeyer flask and allowed to stand in the air under the hood for four hours to allow the evaporation of bromine. The crude 2,2′,2″-tribromo benzyl sesquixanthene was dissolved in 30 mL of benzene, filtered and cooled in an ice-bath. The resulting crystals were filtered and air dried. Both of the products were light pink color. For tribromo benzyl sesquixanthene, the melting point was 261°C and for butyl tribromosesquixanthene, the melting point was 220°C. The products were analyzed by IR spectrum, Figures 7 and 8, and NMR spectrum Figure 22.

Cleavage of protective group.



A solution was prepared by adding 1,1′,1″-tribromo benzyl sesquixanthene (0.18 g, 0.0003 mole) in 80 mL of diethyl ether, potassium permanganate (0.14 g, 0.0009 mole) in 20 mL of water, and 2 mL of sulfuric acid. The mixture was allowed to reflux overnight. At the end of the reaction, a white solid product was formed between the ether and aqueous layers. The solid mixture was collected by suction filtration and then poured into ethyl ether with stirring for ten minutes. The ether insoluble portion was separated by suction filtration. The ether layer was dried over sodium sulfate and concentrated to yield a white solid with melting point at 308°C. This product was analyzed by IR spectrum and this spectrum is shown in Figure 9.

<u>Synthesis of Fluroboric trinitrosesquixanthene.</u>



Fluroboric sesquixanthene 0.6 g, 0.0016 mole) was placed in an Erlenmeyer flask, and 30 mL of concentrated nitric acid was added. The Erlenmeyer flask was heated and maintained in a 50°C water bath for two hours. After cooling, a small portion was dried in air. A needle-shaped product was formed. The rest was poured into 100 mL of crushed ice. At this time, a golden orange colored solid was formed. The product was collected by suction filtration, dried in 80°C oven to yield 0.39 g, 0.0009 mole (59%) of the product, which was platelet shaped with a melting point above 350°C. The product was analyzed by IR in Figure 10 and NMR in Figure 23. A test by iron (II) hydroxide was positive.

Reduction reaction of fluoroboric trinitrosesquixanthene.

The procedure of reducing the fluoroboric trinitrosesquixanthene was the same as the procedure for the reduction reaction of butyl trinitrosesquixanthene, but the color of the product was different. The melting point was above 360°C. The IR spectrum is presented in Figure 11.

Synthesis of Butyl trinitrosesquixanthene.

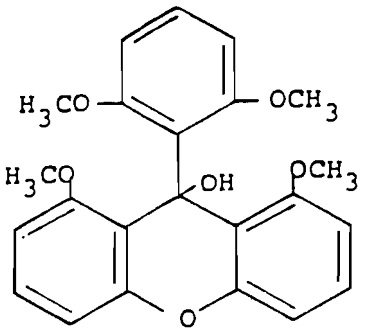
The nitration procedure with butyl sesquixanthene was almost the same as the procedure for the nitration reaction of fluoroboric sesquixanthene. The only difference was that a little sulfuric acid was added. The melting point was 292-296°C. The product was analyzed by IR spectrum, Figure 12.

Reduction of butyl trinitrosesquixanthene.

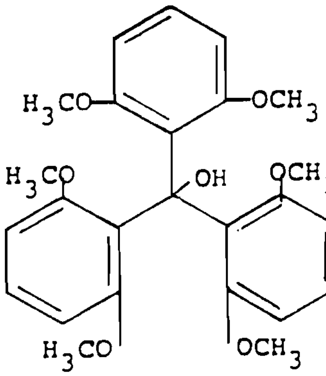
Butyl trinitrosesquixanthene (1.32 g 0.003 mole) was placed in round-bottomed flask which was fitted with a reflux condenser. 100 mL of concentrated hydrochloric acid was added. The mixture was heated with vigorous stirring in order to dissolve the fluoroboric trinitrosesquixanthene. After the solid dissolved (it was difficult to dissolve all of the solid), granulated tin metal (2.5 g, 0.02 mole) was added in very small portions during a 6 hours period. After adding tin metal, the color of the solution changed from yellow to orange. When the reaction was complete, an orange solid precipitated. As the reaction mixture cooled, the product was separated by suction filtration. The solid portion was washed with 20 mL of water and dried in the air at 110°C to yield (0.56 g, 50%) a reddish orange colored powder with a melting point of 219-222°C. This product did not dissolve in ether, or benzene, but was slightly soluble in water. The IR spectrum of the product shown in Figure 13.

DISCUSSION

There are two possible precursors to sesquixanthydrol. Both are alcohols, the structures are shown as (I) and (II).



(I)



(II)

Of these two precursors, (I) is much more viable, as (II) is formed only with great difficulty.

In considering synthetic routes to sesquixanthydrol the most promising method utilized a ring closure reaction.[22] Pyridine hydrochloride appears to be the most effective ring closure agent for this reaction. Since the alcohol (II) exhibits large steric hindrance due to the methoxy groups, the conditions for ring closure of compound (II) were extremely difficult to optimize. The synthetic route from alcohol (II) was abandoned at this point and attempts were directed toward a synthesis of alcohol(I), for which steric factors are less extreme.

2,2′,6′,2",6"-dimethoxytriphenylcarbinol is very acid sensitive. It formed appreciable amounts of the deep purple cation even in distilled water. In ethyl ether, its initial colorless solution rapidly changed to purple while evaporating the ether in the atmosphere. It is water soluble, but also slightly soluble in ether and benzene. Not only is it a deep purple color but also a high adhesive ability as well. At low pH, it will lose two of its methoxy groups and form one oxygen bridge.

It is important to protect the central carbonium ion in ring substitution reactions. Since the central carboxyl group is extremely active and easy to oxidize, it must be protected by a group such as benzyl or n-butyl. Two Grignard reagents, benzyl magnesium chloride and butyl magnesium bromide, were successfully made and successfully reacted with sesquixanthyl fluoroborate forming benzyl sesquixanthene and butyl sesquixanthene. The protection of the central carbon seemed perfect.

Two routes were designed to synthesize tris-4,4′4″-amino sesquixanthene. One involved the synthesis of tris-4,4′4″-nitro sesquixanthene intermediate, and then, the subsequent reduction of the nitro groups to amino groups. The other involved halogenation of the phenyl rings first, then utilized the benzyne mechanism to replace the halogens by amino groups. The halogenation followed by benzyne elimination-addition was expected to give a higher yield of the desired product, 4,4′,4″-triamino sesquixanthene.

Nitration or halogenation were expected to be easy to carry out. Theoretically, the ether groups should be strongly activating. On the other hand, when the central carbon carries a positive change, the rings should be deactivated with respect to electrophilic substitution.

Bromination of benzyl sesquixanthene in ethyl ether was unsuccessful. When benzyl sesquixanthene was allowed to stand with bromine for three days, the reactants retained their yellow color and looked the same as the starting material even in the presence of ferric chloride. We believe that 1,1′,1″-bromo benzyl sesquixanthene should be white.

Bromination of benzyl sesquixanthene and butyl sesquixanthene by bromine vapor was successful. The product of the bromination reaction was analyzed by IR. From the IR spectrum, Figures 7 and 8, it was impossible to determine which isomer was produced.

Normally, the substitution pattern is identified by two bands in IR spectrum, the stronger absorption bands are below 900 cm^{-1}. These out-of-plane bending and ring puckering bands are very intense. The overtone and combination bands at 2000-1600 cm^{-1} are also useful. Unfortunately, this type of band analysis is suitable only for simple aromatic ring systems. For complicated aromatic compounds, these two areas cannot offer reliable identification.[23] Using a high resolution instrument and relatively pure samples, the C-Br stretch will appear at 690-515 cm^{-1}, but cannot be observed with most instruments.[24]

The product obtained from bromination of benzyl sesquixanthene could not be identified by its IR spectrum, but could be identified by the Bielstein test.[25] The green flame indicated that bromination had occurred. When the same method was applied to the bromination of sesquixanthyl fluoroborate, the Bielstein test was negative, even though the reactant changed color. Neither the IR (IR Figure 15) nor chemical tests could prove that a reaction had occurred.

Since a better synthesis method to brominate benzyl sesquixanthene could not be find, we tried to nitrate benzyl and butyl sesquixanthenes. We utilized a mixture of three parts nitric acid and one part sulfuric acid. At room temperature, benzyl sesquixanthene dissolved instantly, but the product became pitch like at about 80°C. What substitute was formed is unknown. After this procedure failed to give the desired product, we tried concentrated nitric acid. It seems that nitration in cold nitric acid was very slow, even after twenty hours. In hot nitric acid benzyl sesquixanthene dissolved faster and a reaction occurred. The product obtained from nitration was also green. After neutralization and filtration, the cotton-like product was analyzed by IR. From the IR spectrum shown in Figure 14, there was no stretching peak at 1600-1500 cm^{-1} and 1300-1250 cm^{-1}. Around 3447 cm^{-1}, there is a large peak, which represents the O-H stretch. Since these peaks are all located within the area of aromatic absorption, we cannot be sure whether nitration was successful or not.

Nitration of benzyl sesquixanthene was not successful. From the IR spectrum, Figure 10, we can see that two peaks appear at 3406 and 3476 cm^{-1}, and it doesn't show Csp^2-H stretch in the range 3000-2900 cm^{-1}. Obviously, the protecting group was too weak to withstand oxidation by nitric acid.

Oxidation of benzyl sesquixanthene with potassium permanganate was difficult. Basic, neutral, and acidic reaction conditions were attempted, and different ratios of potassium permanganate to benzyl sesquixanthene were tried. Generally, oxidation by potassium permanganate occurs rapidly in basic solution. Treatment with potassium permanganate in basic solution failed. Boiling for twenty-four hours in neutral solution also failed. Although potassium permanganate will slowly decompose in acidic conditions, its high oxidation ability was critical in this reaction. Oxidation occurred after sulfuric acid was added and the reaction occurred very rapidly. According to IR Figure 19, the wide peak at 3500 cm^{-1} may be due to moisture. The peak at 3081 cm^{-1} was aromatic C-H stretch. The aromatic absorption peak at 1600.8 cm^{-1} was smaller. Since the IR spectrum shows methylene Csp^3-H stretch, there are two possibilities. One is that the sample was not pure enough, the other was that it was not cleaved by oxidation. In the IR spectrum, the aromatic major characteristic peak 1600 cm^{-1} was less intense. Other peaks, such as 1464 and 1047 cm^{-1} were unchanged. C-O-C absorption at

1267 cm^{-1} was also present.

The oxidation product was barely soluble in non-polar organic solvents, however these product did dissolved in common NMR solvent after several days. Although several solutions were prepared for NMR analysis, none of these gave satisfactory results because they were too dilute.

Sesquixanthyl fluoroborate seemed easier to nitrate. Although neither IR and NMR spectrums can distinctly indicate that the $-NO_2$ function group was present, we can say that nitration was successful. This conclusion is based upon both the iron (II) hydroxide test[26] and the sodium fusion test[27], both showing positive results. Further, the product after nitration showed more intense fluorescence than the un-nitrated material.

The reaction to reduce $-NO_2$ to $-NH_2$ was unsuccessful, although the color of the product after reduction changed from yellow to orange and to reddish orange. Neither the IR, NMR spectrum, nor chemical tests indicated success. There was no evidence of a color change caused by the substituting amino group. If $-NH_2$ was successfully attached on the aromatic ring, it would be expected to be mostly meta substitution because of -O- group attached at both ortho position. If an amino group occupies the meta position, the compound would not show a color change.[28]

CONCLUSION

Synthesis of a bromine-substituted sesquixanthene was successful. In the bromination reaction, the sesquixanthene whose central carbon was protected showed better results in terms of higher yield and fluorescence than those whose central carbon was not protected. But in cleavage of the protective group, an improved oxidation method needs to be developed.

Synthesizing nitro-substituted sesquixanthene was also successful. This succeeded whether or not the molecule's central carbon was well-protected. Nitro-sesquixanthene has high fluorescence and high solubility in both polar and nonpolar solvents.

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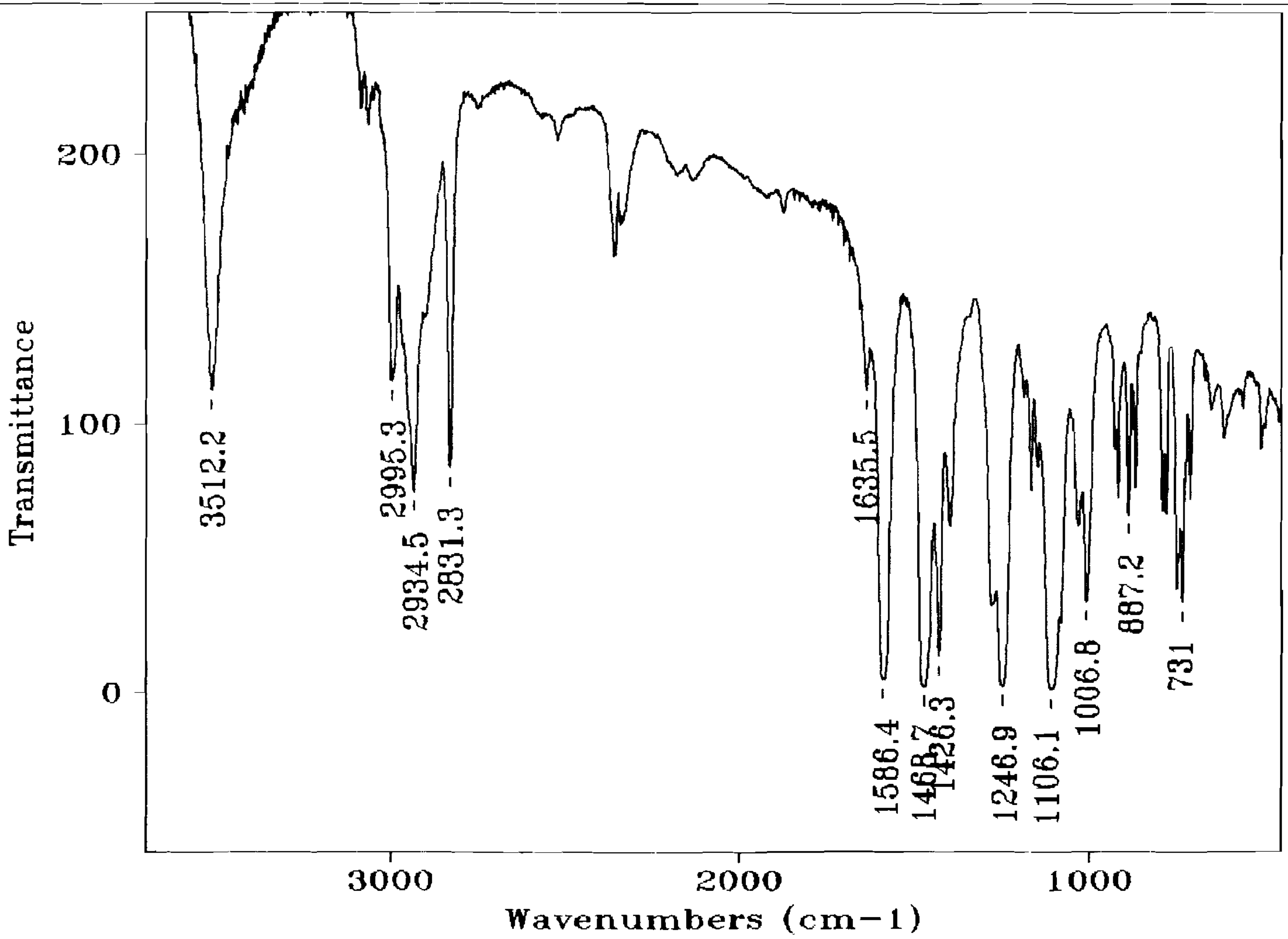
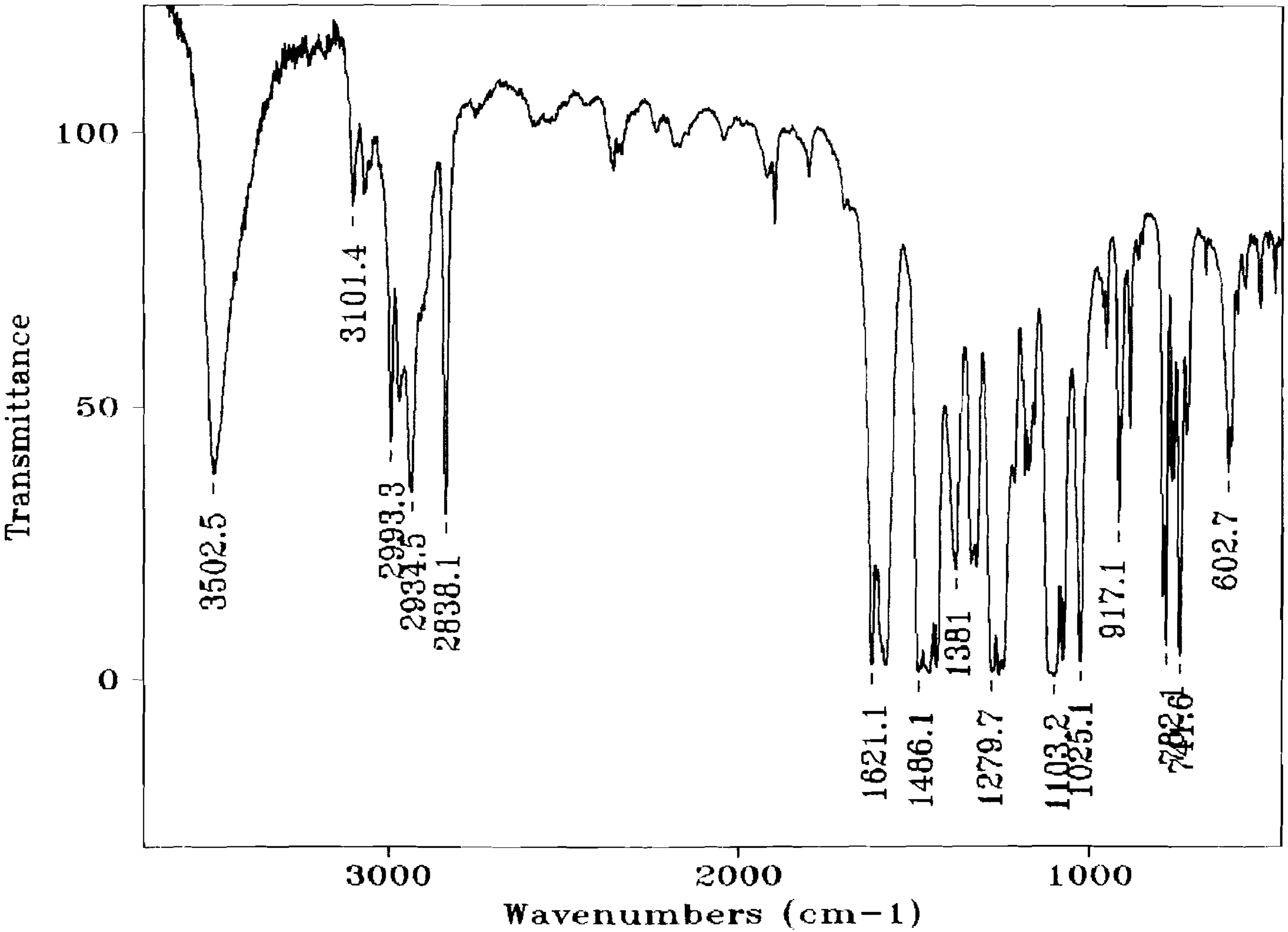
Figure 1: IR spectrum of 2,6,2′,6′,2″,6″-hexamethoxytriphenylcarbinol (KBr pellet)



IR spectrum No.1 Res= 2 cm−1

2,6,2',6',2'',6''−hexamethoxytriphenylcarbinol

Figure 2: IR spectrum of 9-(2,6-dimethoxyphenyl)-1,8-dimethoxyxanthydrol
(KBr pellet)

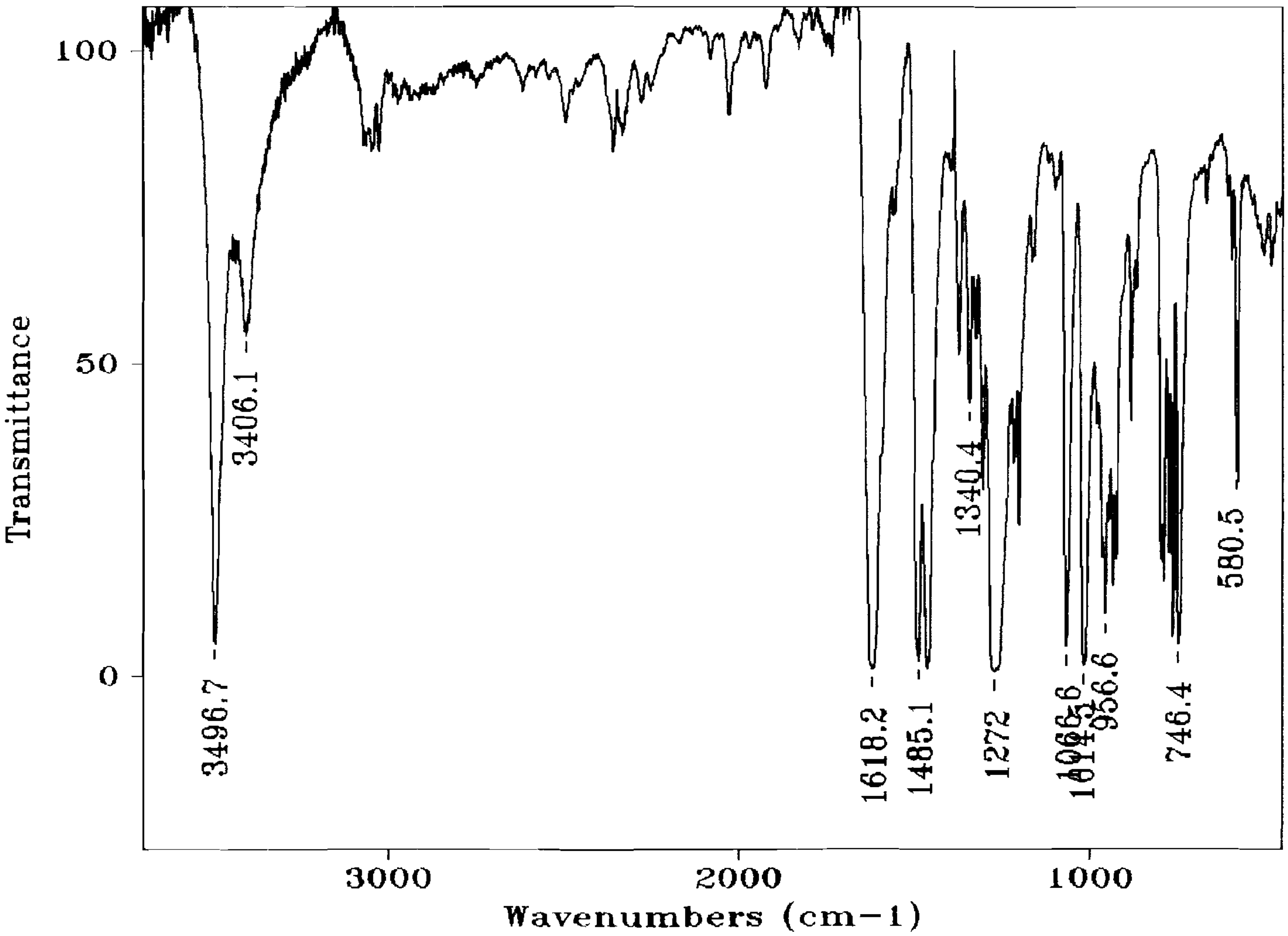


Ir spectrum No.2 Res= 2 cm−1

9−(2,6−dimethoxyphenyl)−1,8−dimethoxyxanthydrol

Figure 3: IR spectrum of sesquixanthydrol

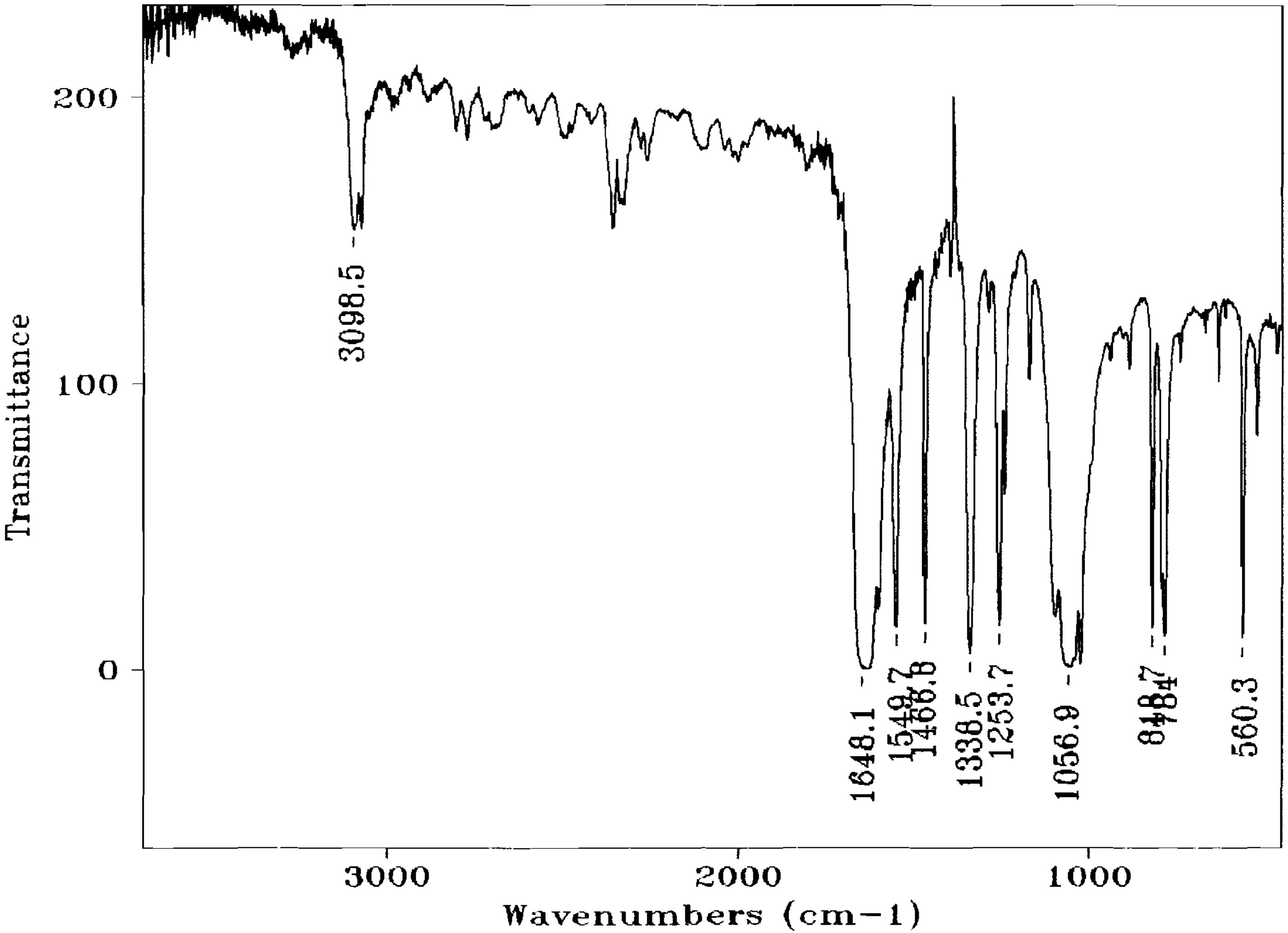
(KBr pellet)



IR spectrum No.3 Res= 2 cm−1

Sesquixanthydrol

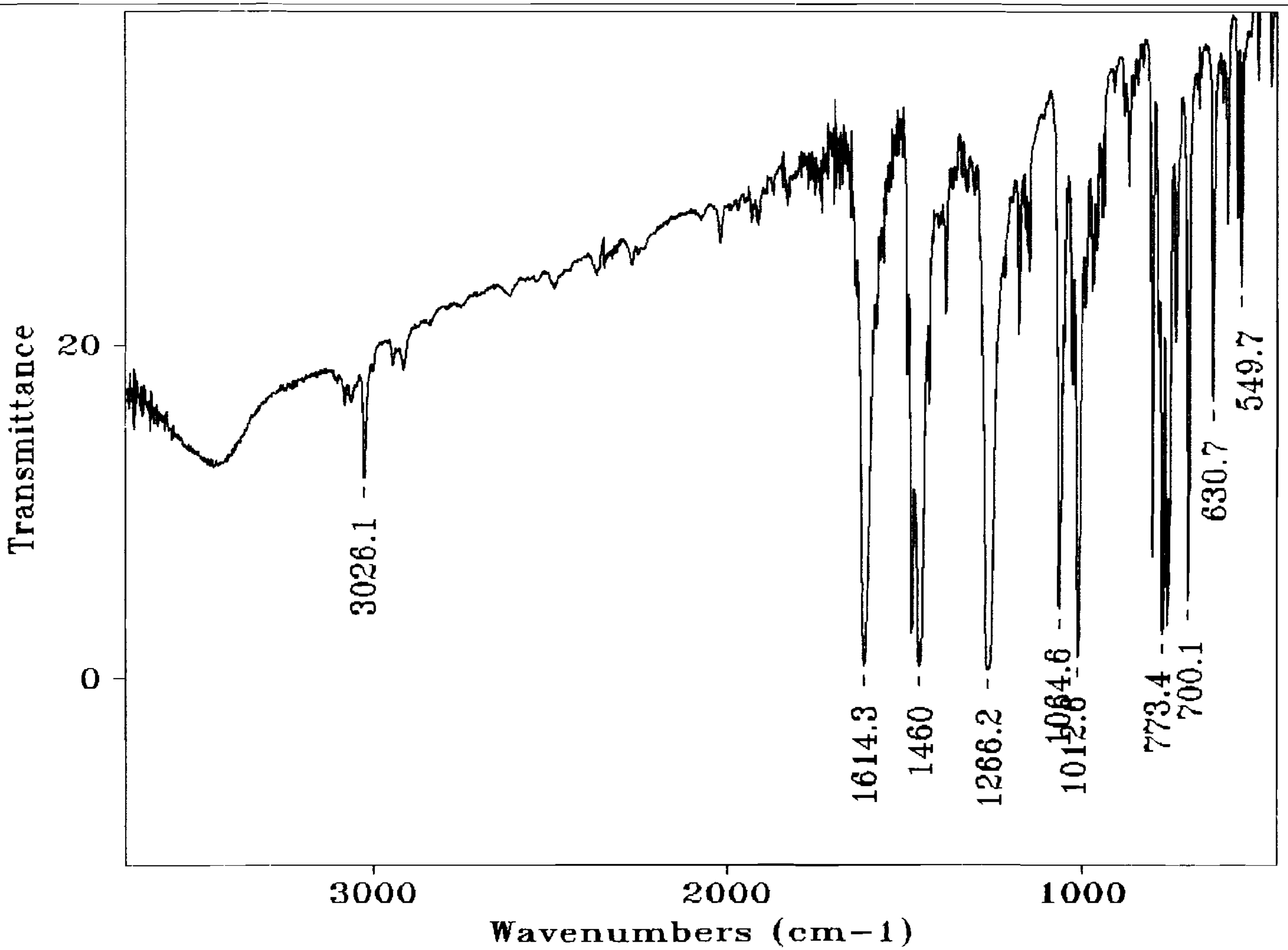
Figure 4: IR spectrum of fluroboric sesquixanthene (KBr pellet)



IR spectrum No.4 Res= 2 cm−1

Fluroboric Sesquixanthene

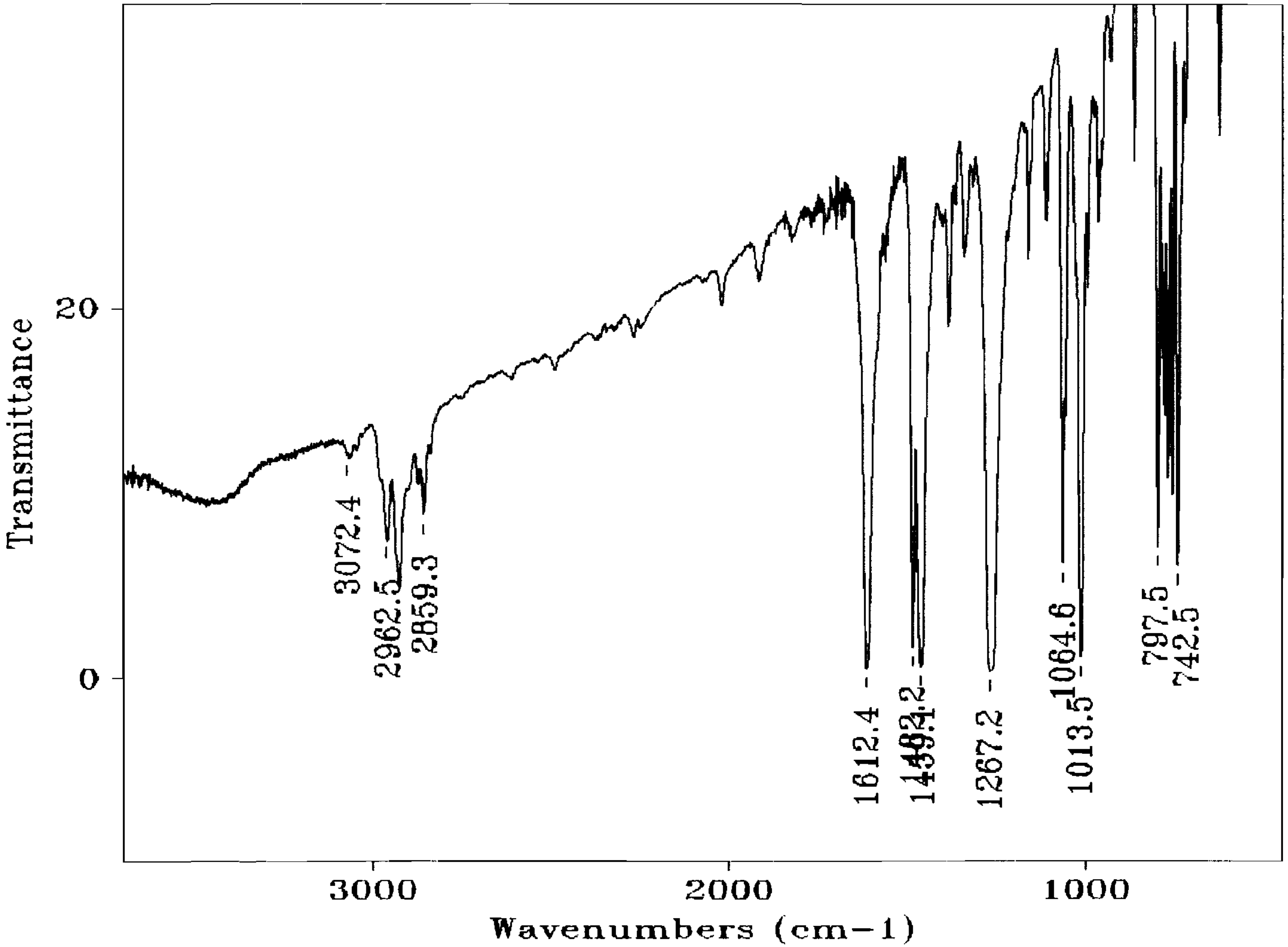
Figure 5: IR spectrum of Benzyl Sesquixanthene (KBr pellet)



IR spectrum No.5 Res= 2 cm−1

Benzyl Sesquixanthene

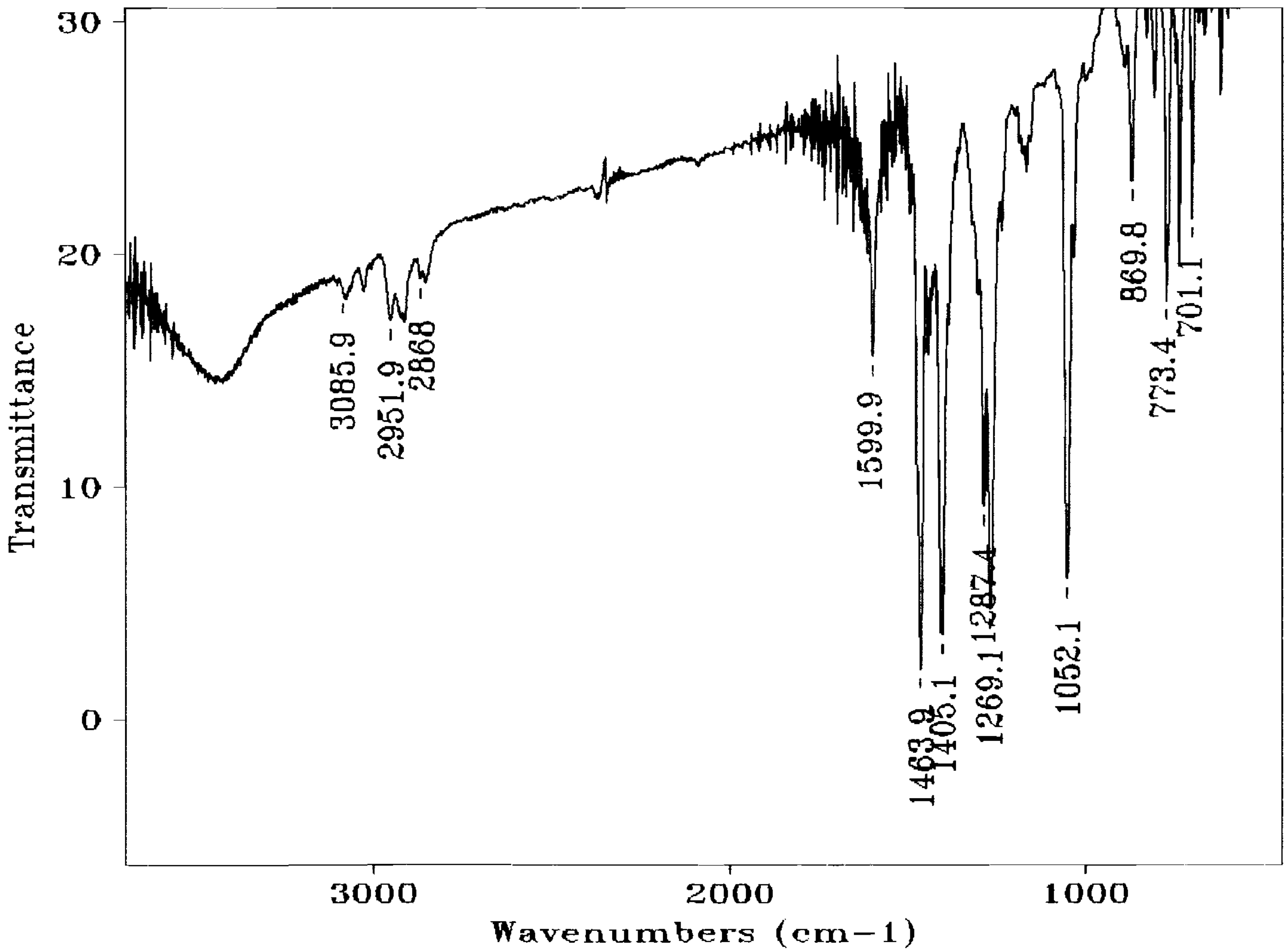
Figure 6: IR spectrum of Butyl Sesquixanthene (KBr pellet)



IR spectrum No.6 Res= 2 cm−1

Butyl Sesquixanthene

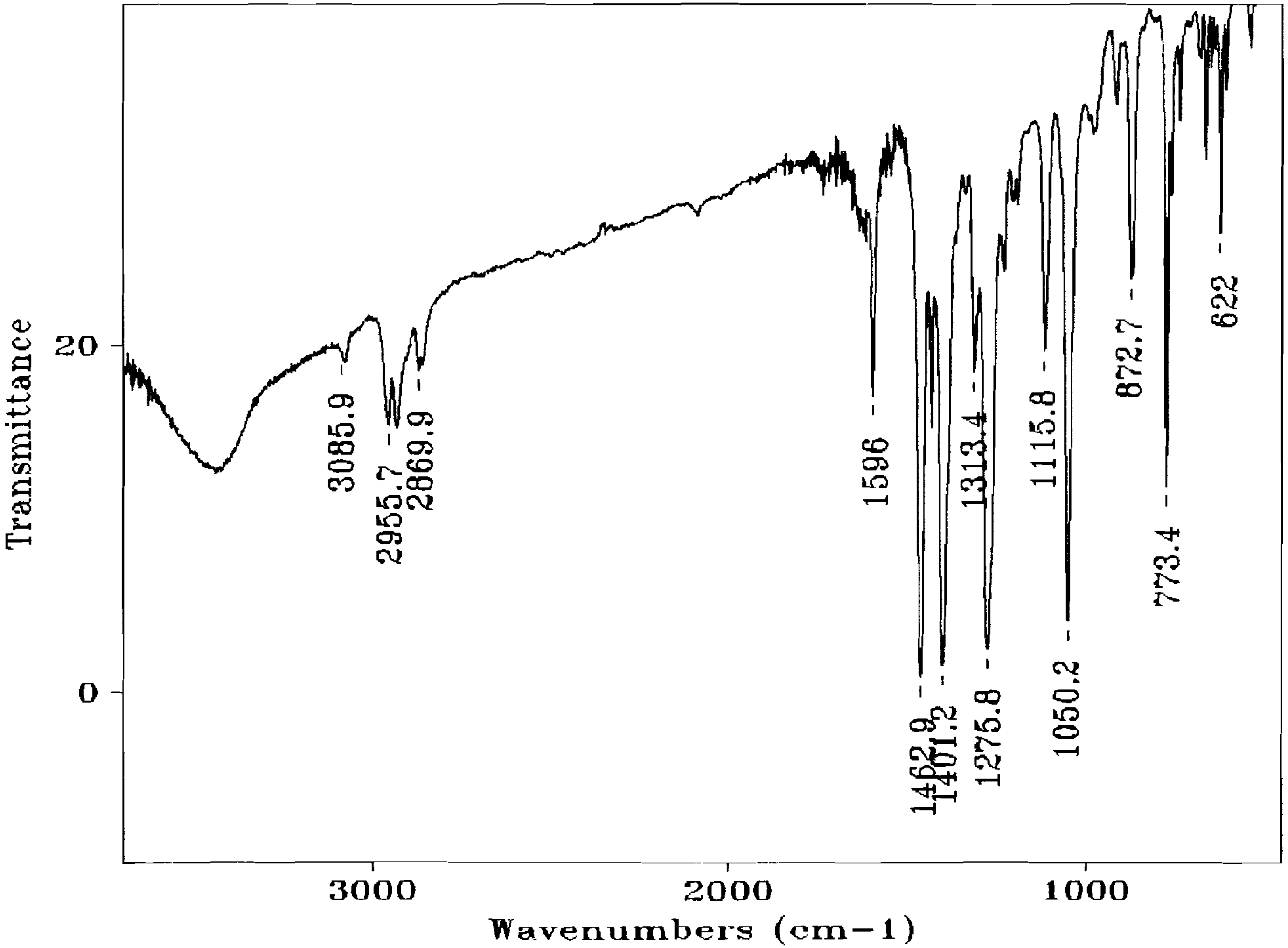
Figure 7: IR spectrum of the product obtained from the bromination of benzyl Sesquixanthene (KBr pellet)



IR spectrum No.7 Res= 2 cm−1

Benzyl tribromosesquixanthene

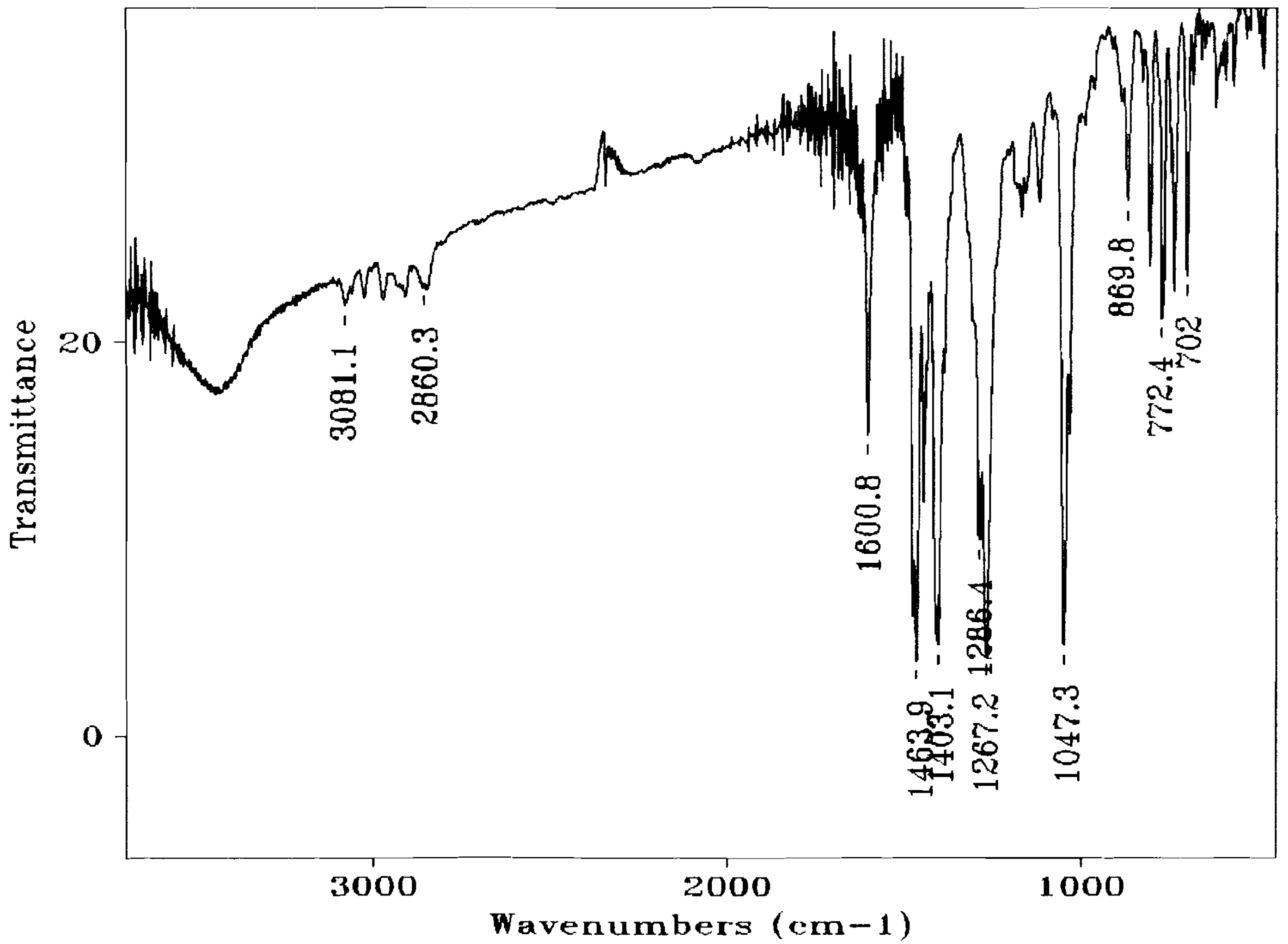
Figure 8: IR spectrum of product obtained from the bromination of butyl sesquixanthene (KBr pellet)



IR spectrum No.8 Res= 2 cm−1

Butyl tribromosesquixanthene

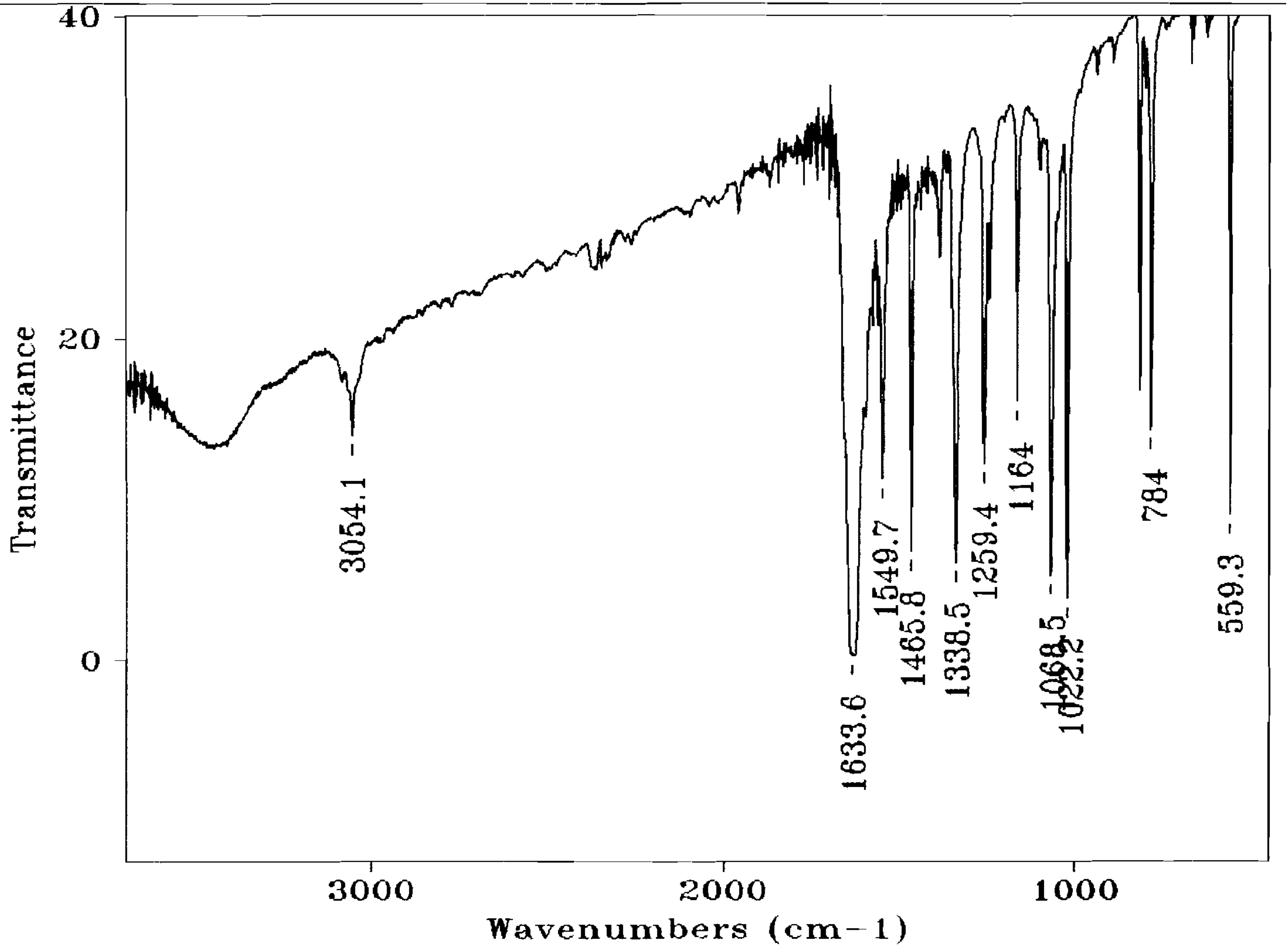
Figure 9: IR spectrum of the product obtained from the oxidation of benzyl trinitrosesquixanthene (KBr pellet)



IR spectrum No.9 Res= 2 cm-1

3,3',3''-Tribromosesquixanthene

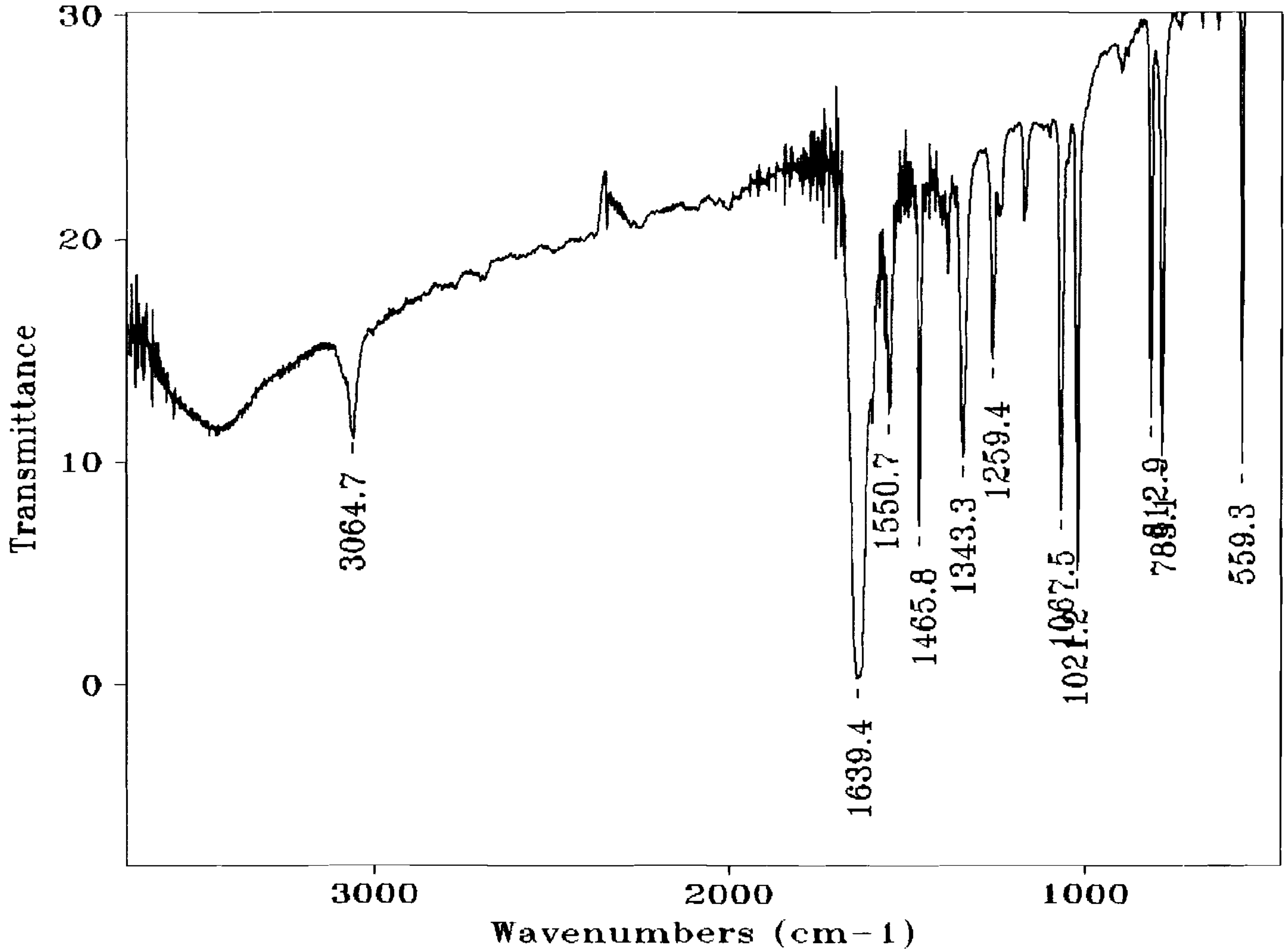
Figure 10: IR spectrum of the product obtained from the nitration of fluoroboric sesquixanthene (KBr pellet)



IR spectrum No.10 Res= 2 cm−1

Fluoroboric Trinitrosesquixanthene

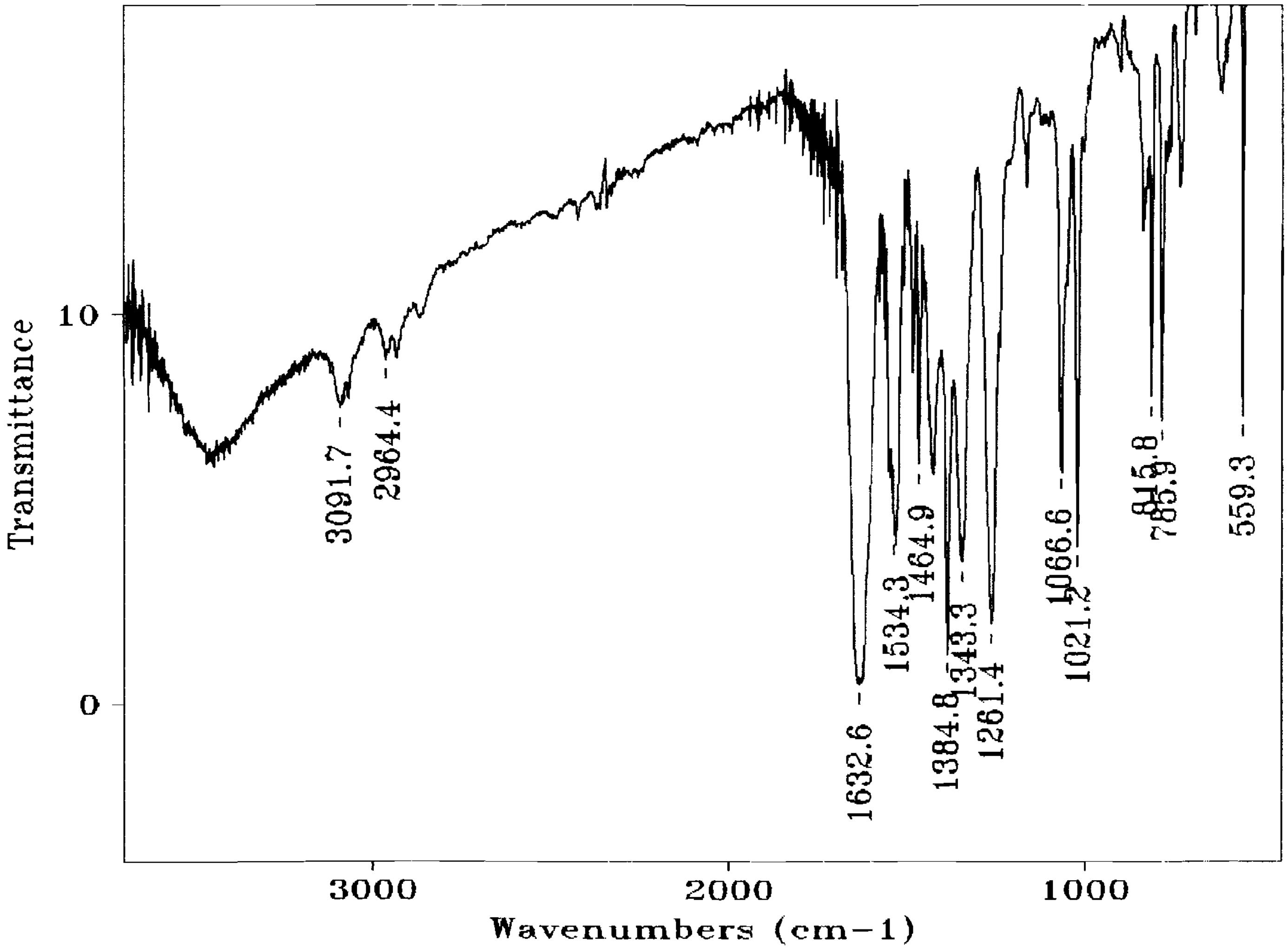
Figure 11: IR spectrum of the product obtained from the reduction of fluoroboric tribromosesquixanthene (KBr pellet)



IR spectrum No.11 Res= 2 cm−1

Reduction of fluoroboric trinitrosesquixanthene

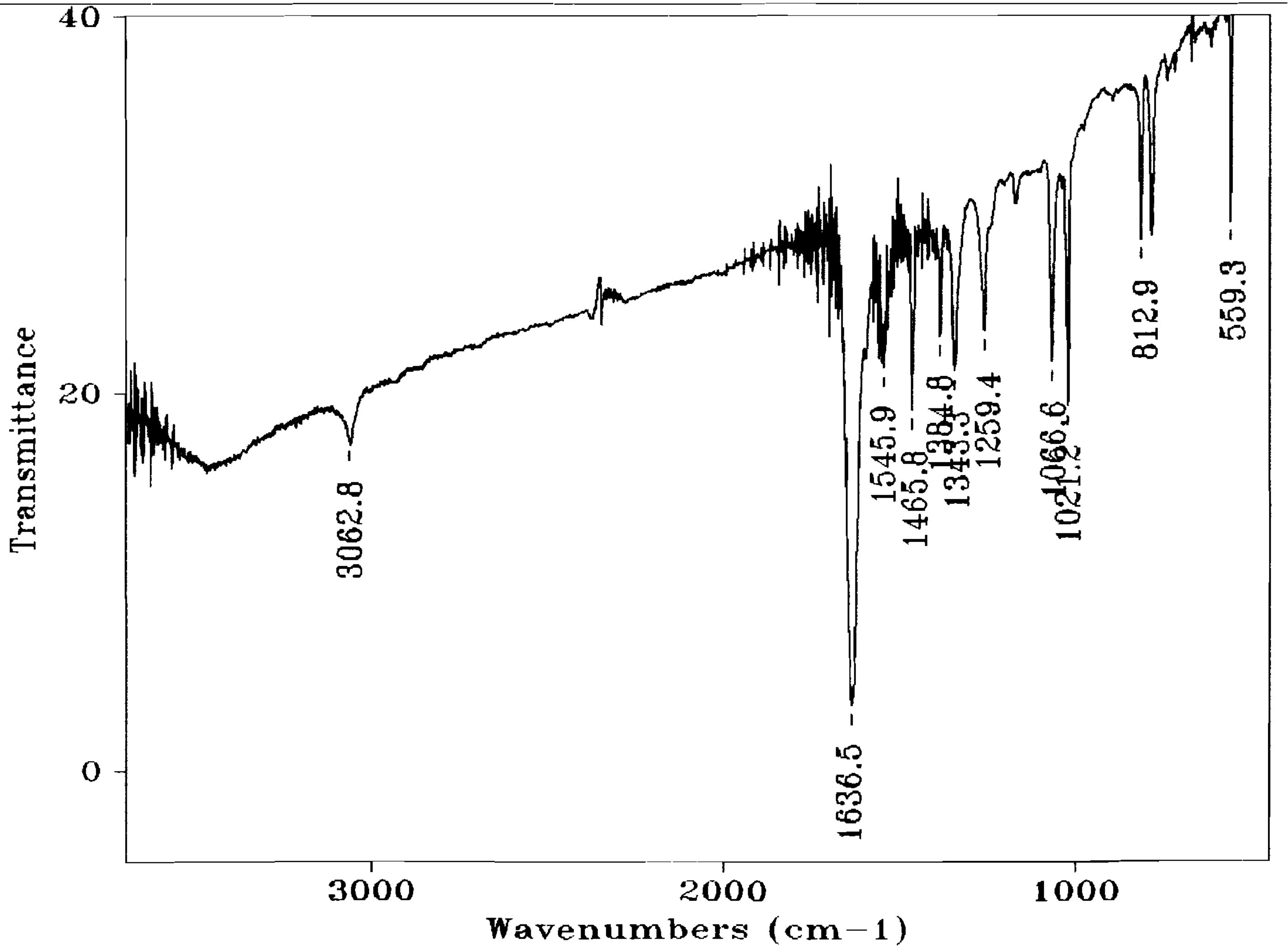
Figure 12: IR spectrum of the product obtained from the nitration of butyl sesquixanthene
(KBr pellet)



IR spectrum No.12 Res= 2 cm-1

Butyl trinitrosesquixanthene

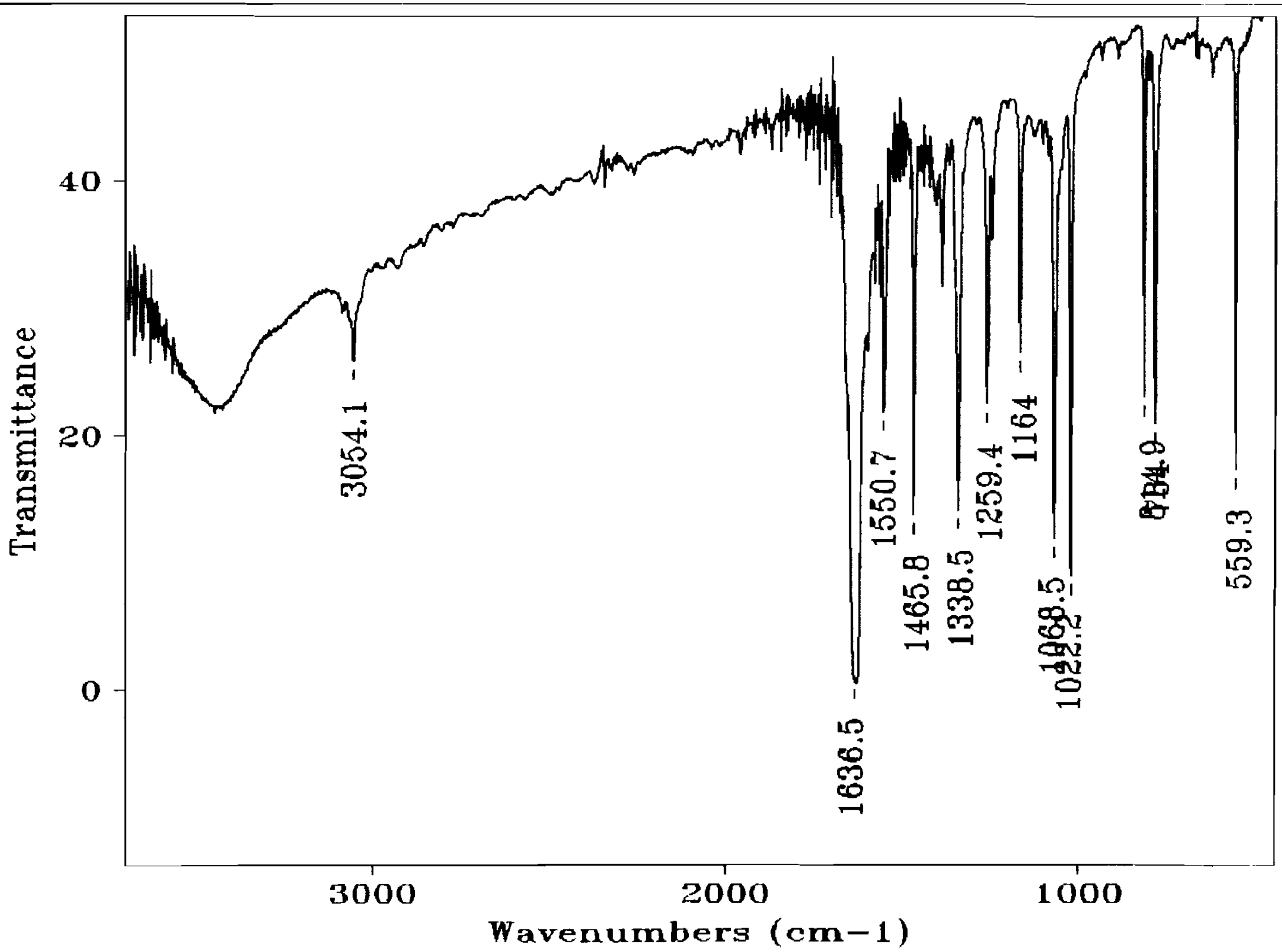
Figure 13: IR spectrum of the product obtained from the reduction of butyl sesquixanthene (KBr pellet)



IR spectrum No.13 Res= 2 cm−1

The product of butyl sesquixanthene nitration reduction

Figure 15: IR spectrum of the product obtained from the bromination of fluoroboric sesquixanthene
(KBr pellet)

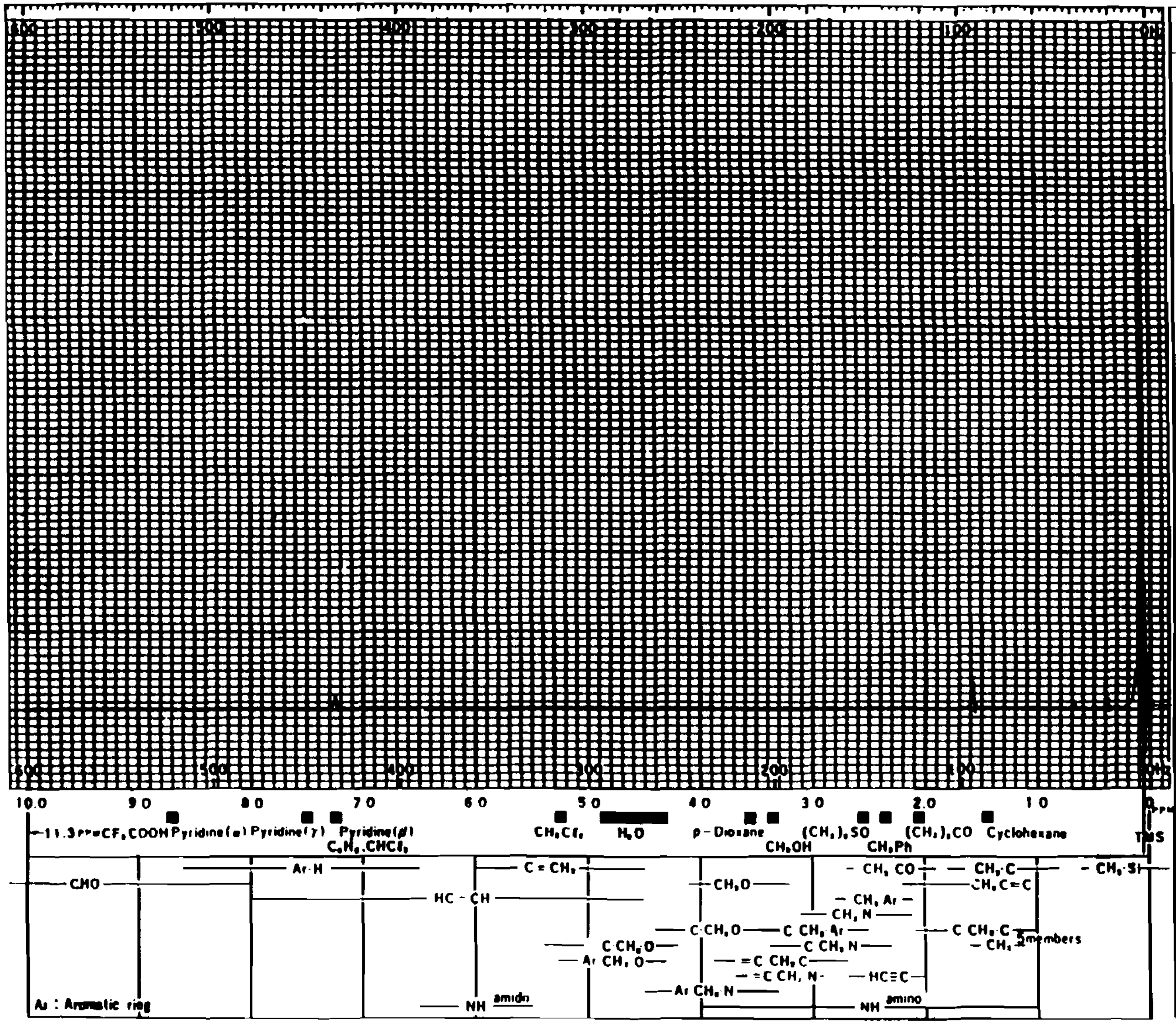


IR spectrum No.15 Res= 2 cm−1

Fluoroboric tribromosesquixanthene

Figure 16. NMR spectrum of the solvent $CDCl_3$

Reference: TMS



HITACHI PERKIN ELMER

¹H SPECTRUM NO.: 1

SAMPLE: D-chloroform

REFERENCE: TMS

SOLVENT: No

CONC:

AMPLITUDE:

SPECTRUM: 7

INTEGRAL:

H₁ LEVEL: X

H₀ LEVEL:

GAIN:

SWEEP WIDTH:

FILTER Hz: X

SWEEP TIME:

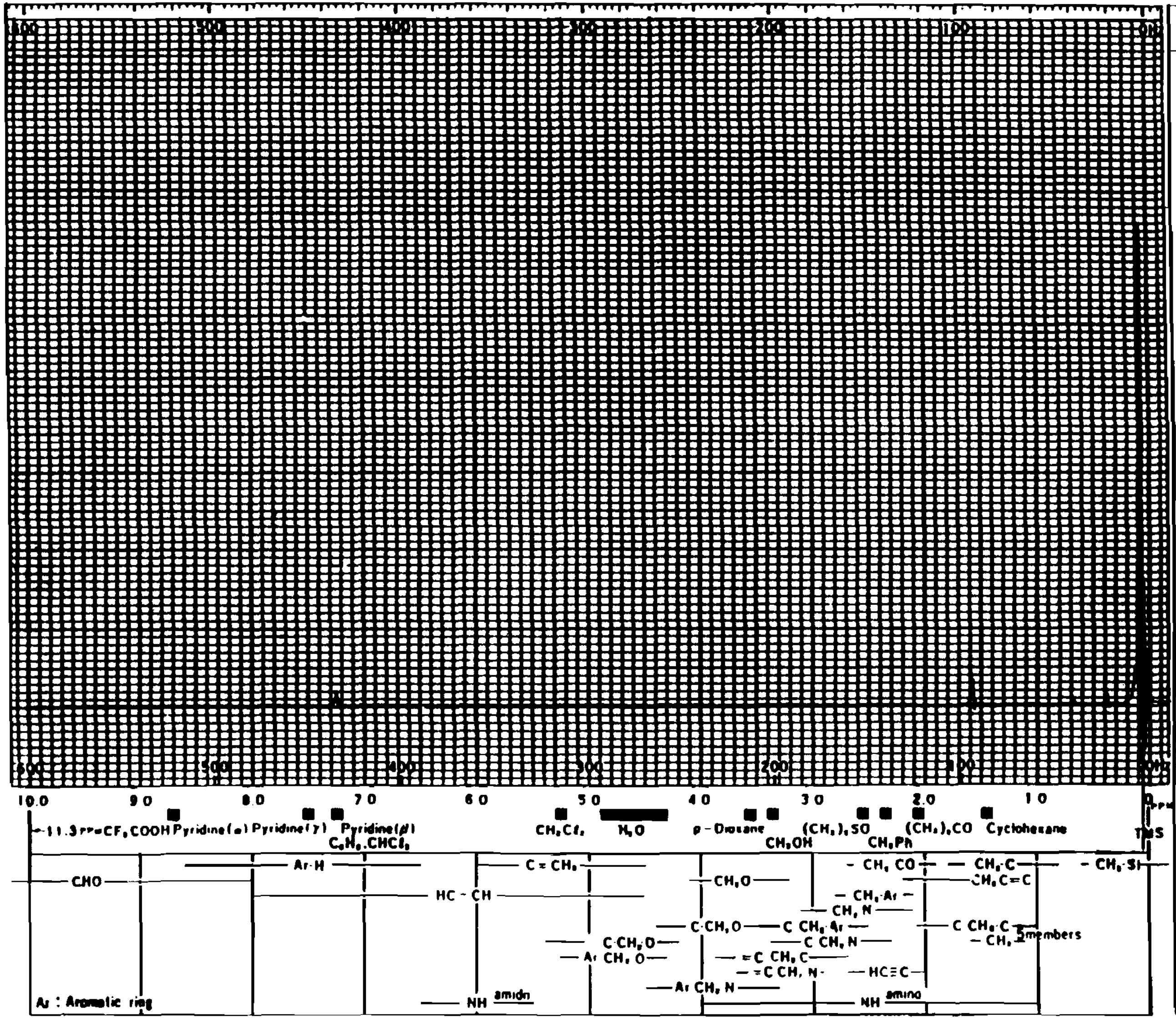
☒300/150SEC ☐ / SEC

DATE: 04/15/93

OPERATOR:

REMARKS:

CHART NO. 438-7808 570/38018



HITACHI PERKIN ELMER

¹H SPECTRUM NO.: 1

SAMPLE: D-chloroform

REFERENCE: TMS

SOLVENT: No

CONC:

AMPLITUDE:

SPECTRUM: 7

INTEGRAL:

H₁ LEVEL: X

H₀ LEVEL:

GAIN:

SWEEP WIDTH: X

FILTER Hz: X

SWEEP TIME:

☒300/150SEC ☐ / SEC

DATE: 04/15/93

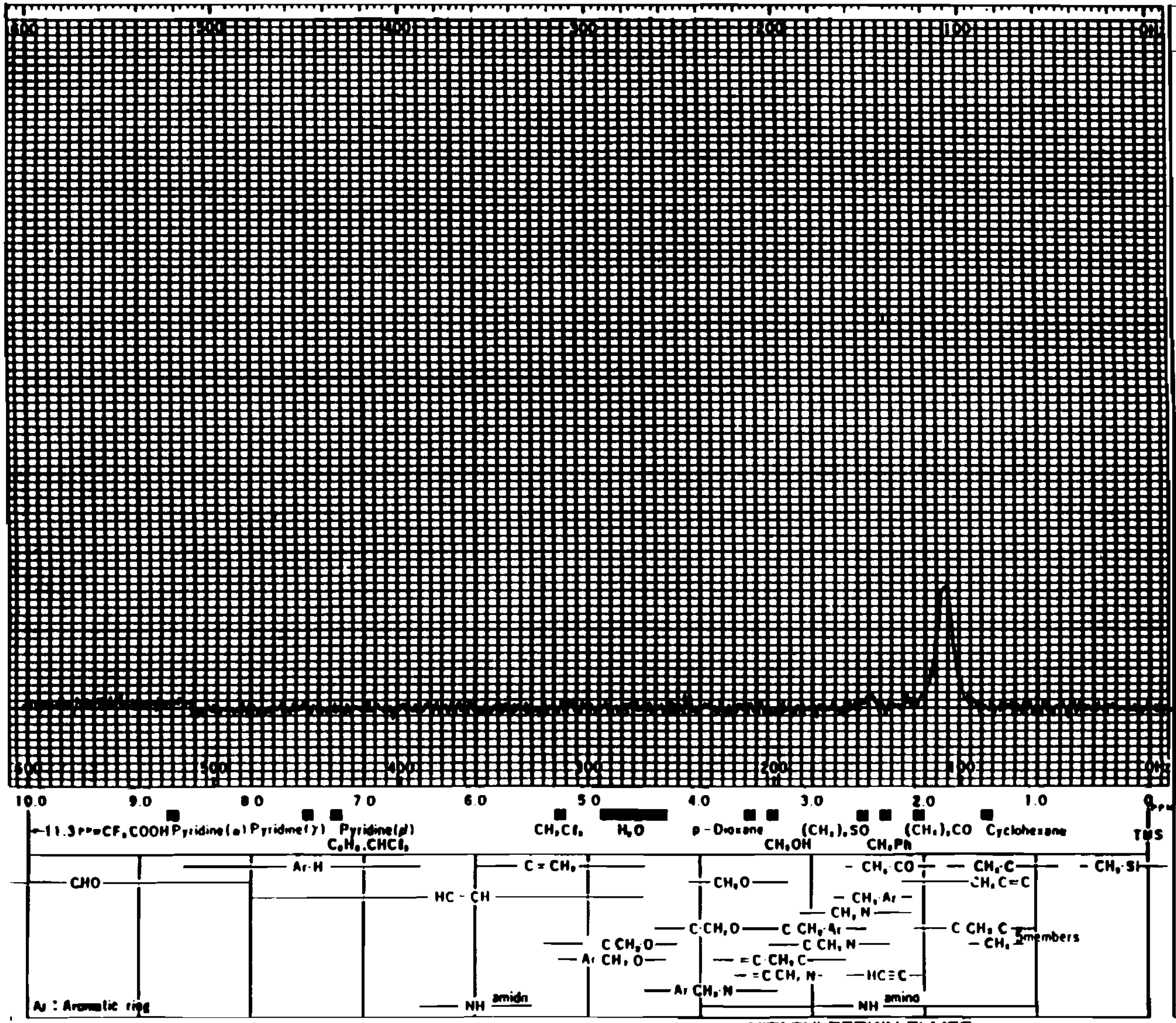
OPERATOR:

REMARKS:

CHART NO. [illegible] 570/58018

Figure 17: NMR spectrum of deuterated acetone

Reference: TMS



HITACHI PERKIN ELMER

¹H SPECTRUM NO. : 2

SAMPLE : D-acetone

REFERENCE : TMS

SOLVENT : No

CONC :

AMPLITUDE :

SPECTRUM : 13

INTEGRAL :

H₁ LEVEL :

H₂ LEVEL :

GAIN :

SWEEP WIDTH :

FILTER Hz :

SWEEP TIME : ☒300/150SEC ☐ / SEC

DATE : 04/15/93

OPERATOR :

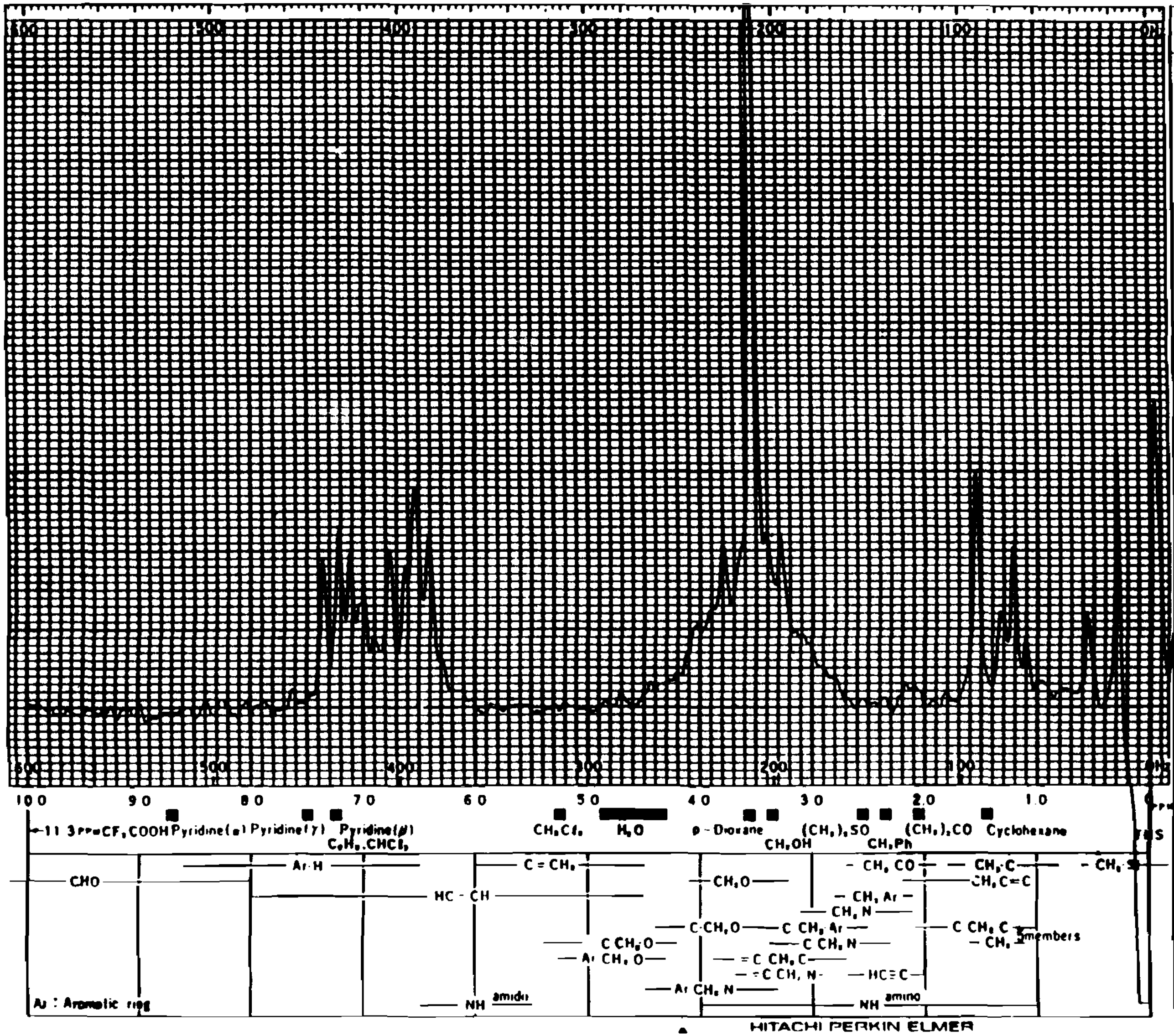
REMARKS :

CHART NO. [illegible]

Figure 18: NMR spectrum of 9-(2,6-dimethoxyphenyl)-1,8-dimethoxyxanthydrol

Solvent: $CDCl_3$

Reference: TMS



¹H SPECTRUM NO. : 3

SAMPLE :

9-(2,6-dimethoxyhpenyl)

1,8-dimethoxyxanthydrol

REFERENCE : TMS

SOLVENT : $DCCl_3$

CONC :

AMPLITUDE :

SPECTRUM : 11

INTEGRAL :

H₁ LEVEL : X

H₂ LEVEL :

GAIN :

SWEEP WIDTH :

FILTER Hz : X

SWEEP TIME :

☒300/150SEC ☐ / SEC

DATE : 04/15/93

OPERATOR :

REMARKS :

CHART NO. [illegible]

Figure 19: NMR spectrum of sesquixanthydrol

Solvent: $CDCl_3$

Reference: TMS

HITACHI PERKIN ELMER

¹H SPECTRUM NO.: 4

SAMPLE: Sesquixanthene

REFERENCE: TMS

SOLVENT: DCCl₃

CONC:

AMPLITUDE:

SPECTRUM: 13

INTEGRAL: 12

H₁ LEVEL:

H₂ LEVEL:

GAIN:

SWEEP WIDTH:

FILTER Hz: X

SWEEP TIME:

☒ 300/150SEC ☐ / SEC

DATE: 05/08/93

OPERATOR:

REMARKS:

CHART NO. 438-7[illegible]

Figure 20: NMR spectrum of benzyl sesquixanthene

Solvent: $CDCl_3$

Reference: TMS

¹H SPECTRUM NO. : 5

SAMPLE :

Benzyl Sesquixanthene

REFERENCE : TMS
SOLVENT : $DCCl_3$
CONC :

AMPLITUDE :
SPECTRUM : 12
INTEGRAL : 9

H_1 LEVEL : X

H_2 LEVEL :

GAIN :

SWEEP WIDTH : X

FILTER Hz : X

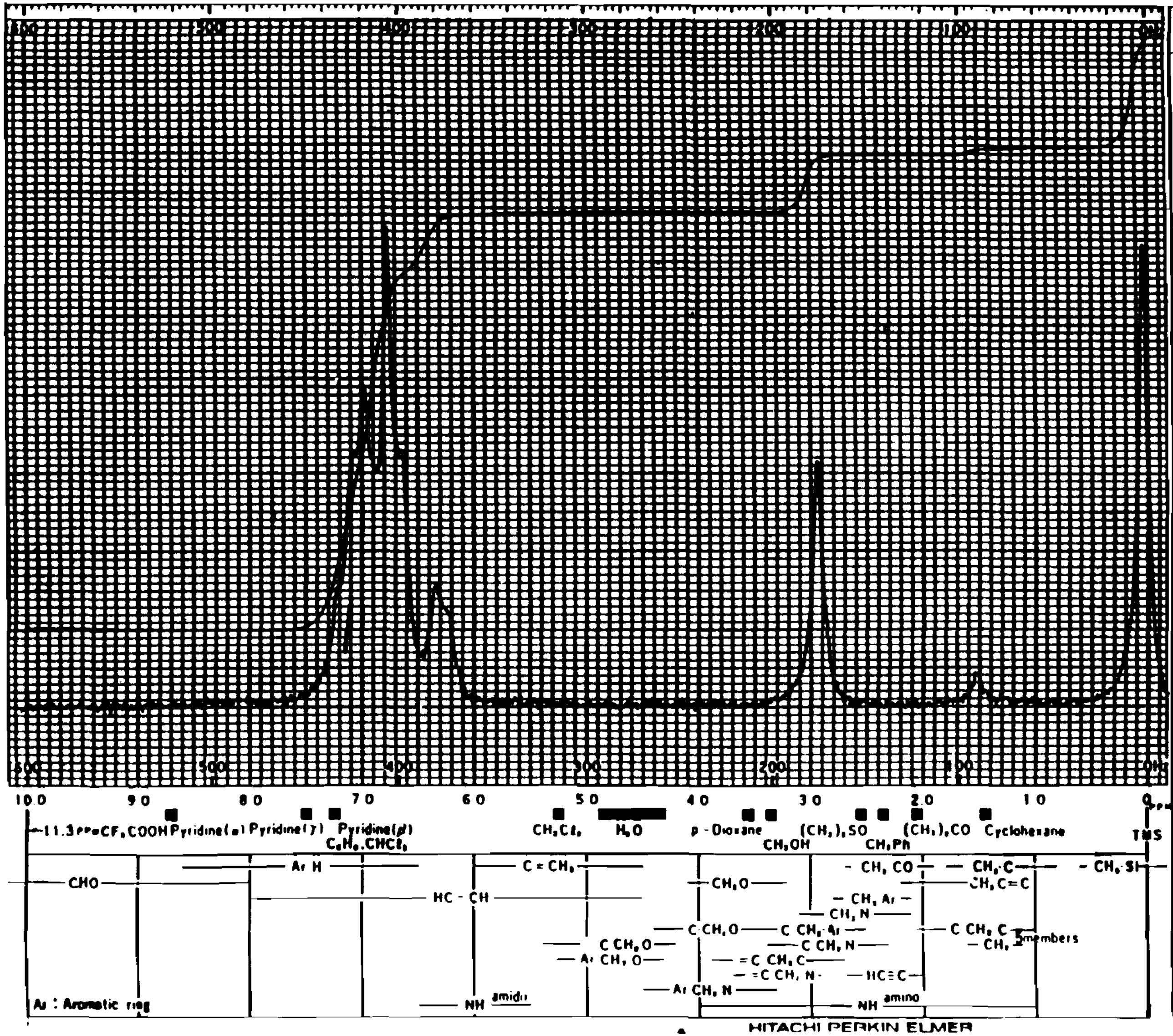
SWEEP TIME :
☒ 300/150SEC ☐ / SEC

DATE : 05/04/93

OPERATOR :

REMARKS :

CHART NO. 43[illegible]



HITACHI PERKIN ELMER

¹H SPECTRUM NO. : 5

SAMPLE :

Benzyl Sesquixanthene

REFERENCE : TMS
SOLVENT : DCCl$_3$
CONC :

AMPLITUDE :
SPECTRUM : 12
INTEGRAL : 9

H$_1$ LEVEL : X

H$_2$ LEVEL :

GAIN :

SWEEP WIDTH :

FILTER Hz : X

SWEEP TIME :
☒ 300/150SEC ☐ / SEC

DATE : 05/04/93

OPERATOR :

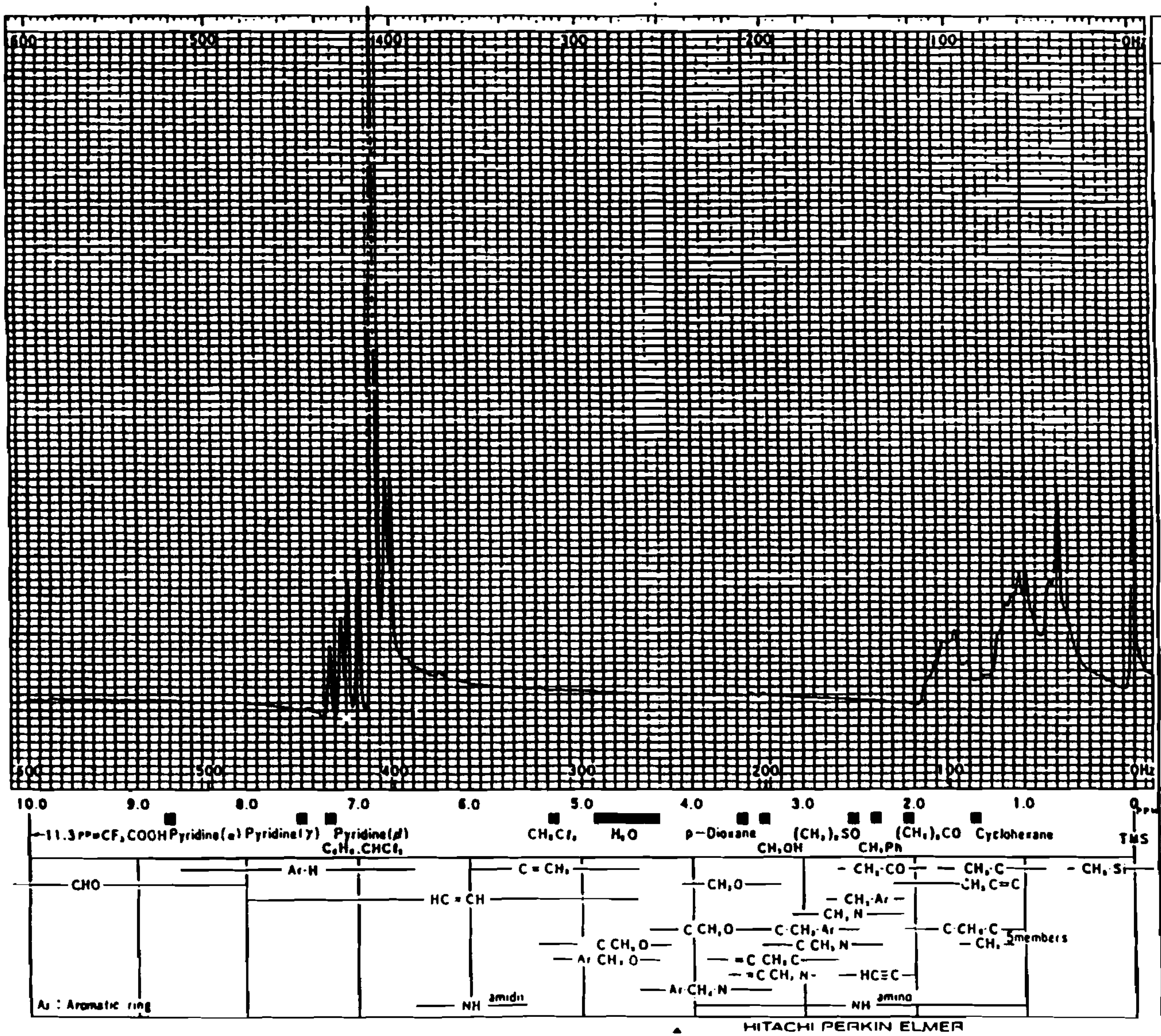
REMARKS :

CHART NO. 4[illegible]-7[illegible] 570/30018

Figure 21: NMR spectrum of butyl sesquixanthene

Solvent: $CDCl_3$

Reference: TMS



^{1}H SPECTRUM NO.: 6

SAMPLE: Butyl sesquixanthene

REFERENCE: TMS

SOLVENT: $DCCl_3$

CONC:

AMPLITUDE:

SPECTRUM: 9

INTEGRAL:

H_1 LEVEL: X

H_0 LEVEL:

GAIN:

SWEEP WIDTH:

FILTER Hz: X

SWEEP TIME: ☐300/150SEC ☐ / SEC

DATE: 05/04/93

OPERATOR:

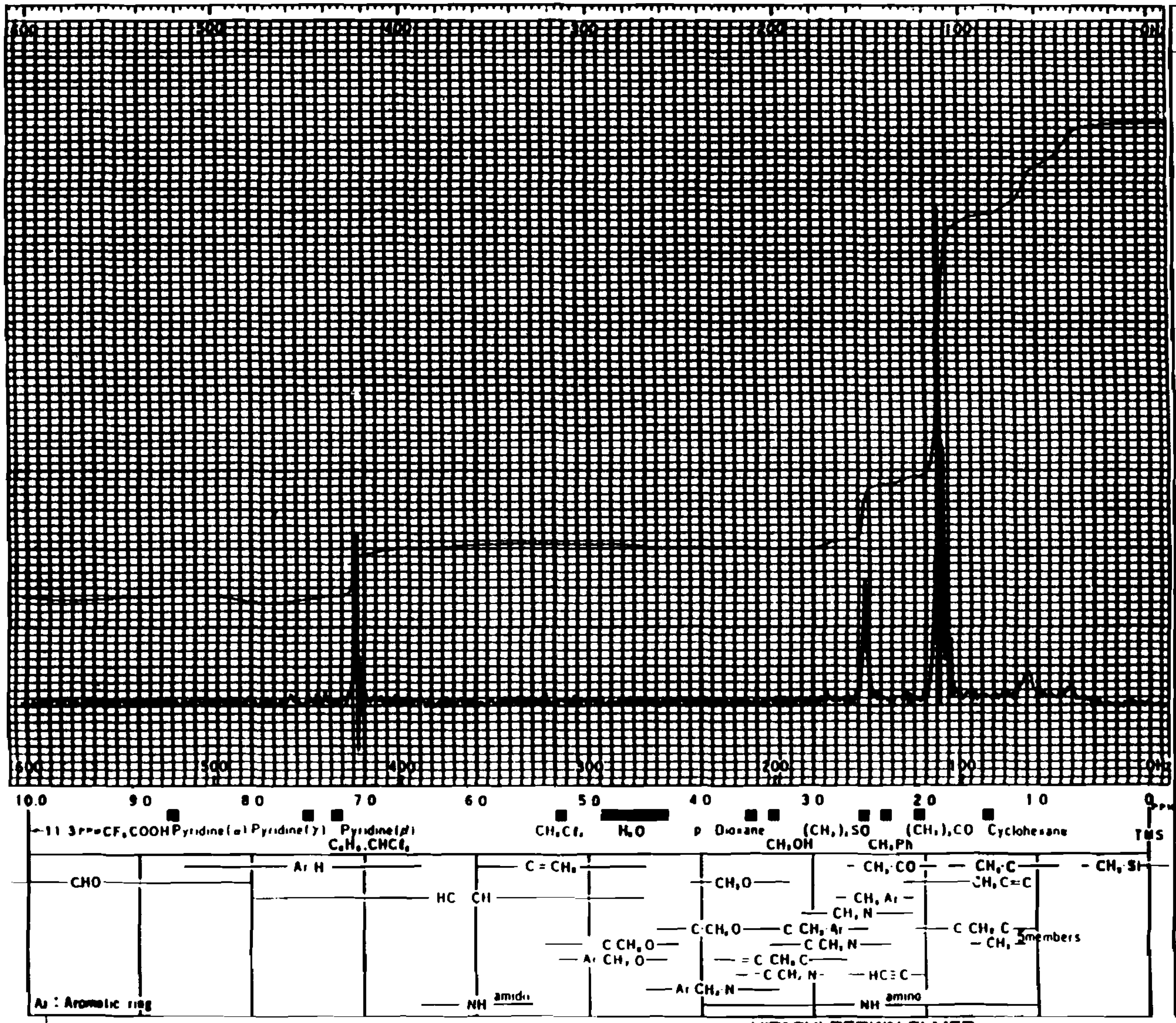
REMARKS:

CHART NO. 430-7808

Figure 22: NMR spectrum of the product obtained from the bromination of benzyl sesquixanthene

Solvent: Deuterated acetone

Reference: TMS



HITACHI PERKIN ELMER

¹H SPECTRUM NO. : 7

SAMPLE :

Benzyl tribromo sesquixanthene

REFERENCE : TMS
SOLVENT : DCCl₃
CONC :

AMPLITUDE :
SPECTRUM : 12
INTEGRAL : 7

H₁ LEVEL :

H₀ LEVEL :

GAIN :

SWEEP WIDTH :

FILTER Hz :

SWEEP TIME :
■ 300/150SEC ☐ / SEC

DATE : 04/15/[illegible]

OPERATOR :

REMARKS :

CHART NO. 430-7000

Figure 23: NMR spectrum of the product obtained from the nitration of fluoroboric sesquixanthene

Solvent: Deuterated acetone

Reference: TMS

HITACHI PERKIN ELMER

¹H SPECTRUM NO.: 8

SAMPLE:
Fluoroboric Trinitro-sesquixanthene

REFERENCE: TMS
SOLVENT: D-acetone
CONC:

AMPLITUDE:
SPECTRUM: 13
INTEGRAL: 12

H₁ LEVEL:
H₀ LEVEL:
GAIN:
SWEEP WIDTH:
FILTER Hz:
SWEEP TIME:
■300/150SEC ☐ / SEC
DATE: 05/08/93
OPERATOR:

REMARKS:

CHART NO. 430-7808

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Yilin Qiao
Signature of Author

September 1st, 1994
Date

Synthesis of Substituted Planar Triarylmethanes
Title of Thesis

Signature of Graduate Office Staff Member

August 31, 1994
Date Received