CHAPTER IV

SYNTHESIS OF NOVEL WATER SOLUBLE PHOTOSTABILIZERS

IV.1 ABSTRACT

Synthesis, spectral characterization and photostabilization study of novel compounds having the dual characteristics of the surfactant as well as the photostabilizer is reported in this chapter. The effect of photostabilization on Disulfoton, an organophosphorous insecticide, was examined in methanol, when exposed to UV radiation in the presence of these photostabilizers in 1:1 mole ratio and based on the percentage recovery of Disulfoton from the solution after 12 h exposure to UV radiation in the presence and absence of photostabilizers.

IV.2 INTRODUCTION AND OBJECTIVE

The sunlight have wavelength from the x-ray region to the infrared region but due to the presence of effective ozone gas layer in the stratosphere, light only with the wavelength greater than 290 nm reaches to the earth surface.[1] Light having the wavelength in the region 290-400 nm known as the active 'UV region' and is responsible to induce photochemical reaction/degradation of many organic molecules.[1] Following **Figure IV.1** represents the average solar-energy distribution.[2]

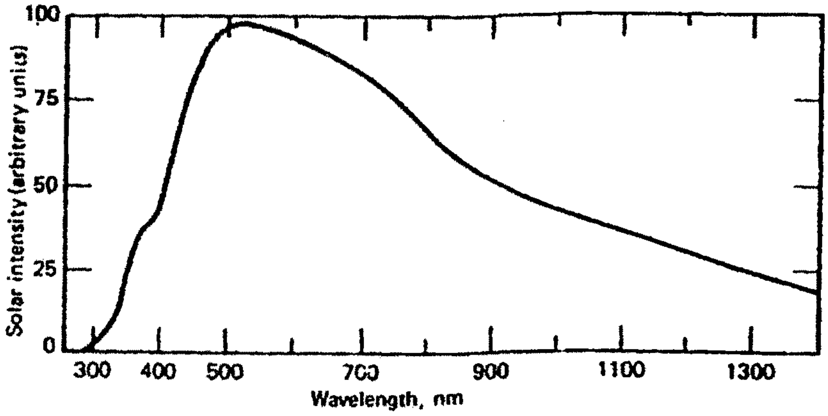


Figure IV.1

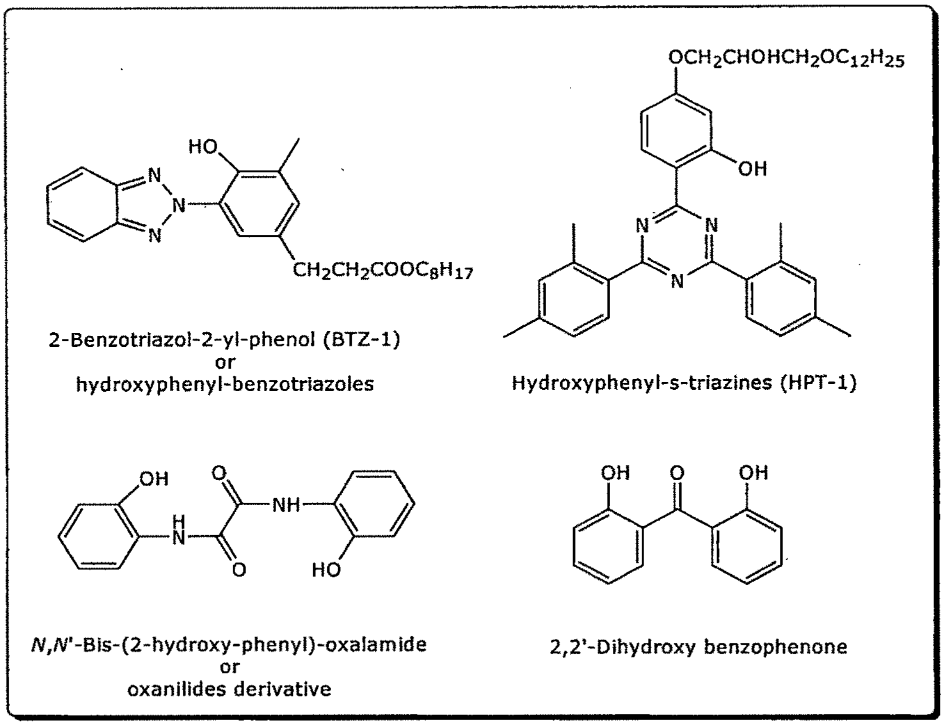
Many organic compounds when exposed to sunlight are prone to undergo chemical reactions subsequent to electronic excitations.[3] Therefore, need of protecting material against solar radiation in outdoor applications has motivated numerous activity in the area of photodegradation and its mechanisms.[4-6] The damaging UV radiation in the sunlight is responsible for the discoloration of dyes and pigments, weathering and yellowing of plastics, loss of gloss and mechanical properties (cracking), sunburnt skin, degradation of pesticides/bio-pesticides and other problems associated to UV light. Paints, plastics, pesticides, wood and cosmetic manufacturers therefore have a great deal of interest in offering products that remain unaltered for long periods of time under the worst light exposure conditions.[7-12, 34]

Sensitivity to sunlight/UV light, limits the use of some synthetic or natural pesticides in agriculture. Classical approaches to overcome this problem generally involve chemically modified molecular structures of the pesticides or use of the UV absorbing molecules in the formulations. However, in the former method any chemical modification in structure may seriously affect the pesticidal activity of that compound and may cause ecological problems.[11] Therefore, the latter method, which is free from the above-mentioned disadvantages, is more suitable to extend the environmental life of the pesticides.[12-15] In order to offer an effective protection against UV irradiation, the prime requirement for the UV absorber molecules is the ability to transform the absorbed radiation energy into less damaging thermal energy *via* photophysical process.[4,16-21] The mechanism of photostabilization mainly due to any of the following processes.[22]

(1) Preferential absorption of light by photostabilizer, thereby preventing photo-excitation of the organic molecules.

(2) Transfer of the excess energy from the excited organic molecules to the photostabilizers through various energy transfer mechanisms.[23]

It is known that different photostabilizers function by different mechanisms. It is advisable to prevent the excess use of the photostabilizers and other additives like emulsifiers/surfactants to avoid the environmental problems. The four most important UV absorber classes are the hydroxyphenyl-benzotriazoles (BTZ), hydroxyphenyl-s-triazines (HPT), hydroxybenzophenones and oxanilides. [24, 25]



2-Benzotriazol-2-yl-phenol (BTZ-1)
or
hydroxyphenyl-benzotriazoles

Hydroxyphenyl-s-triazines (HPT-1)

N,*N*'-Bis-(2-hydroxy-phenyl)-oxalamide
or
oxanilides derivative

2,2'-Dihydroxy benzophenone

Figure IV.2

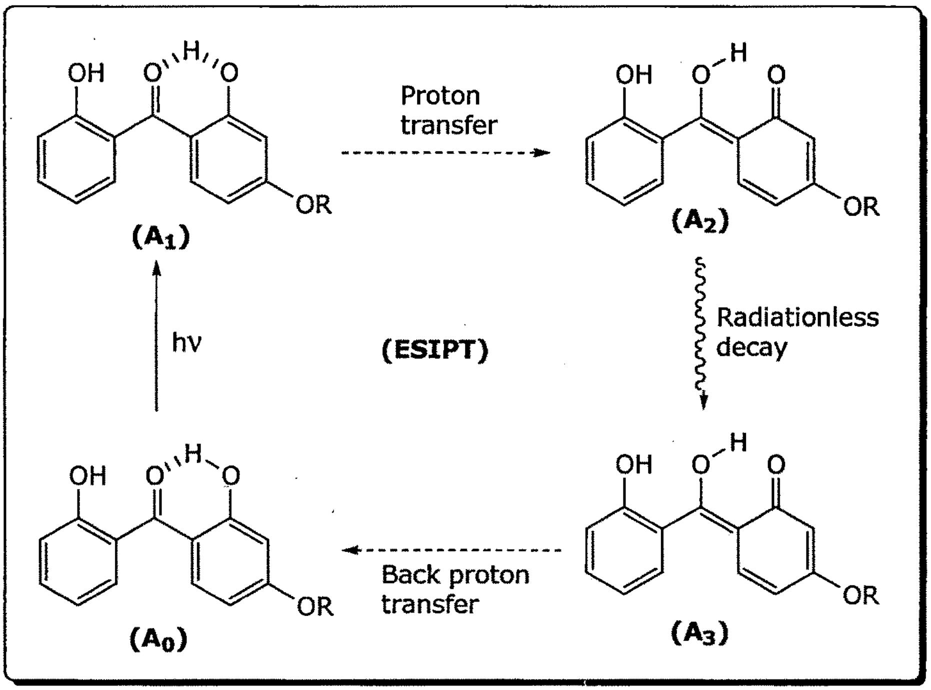


Figure IV.3

Intramolecularly hydrogen bonded UV absorbers such as o-hydroxybenzophenones, 2-(2-hydroxyaryl)-benzotriazoles and 2-(2-hydroxyaryl)-1, 3, 5-triazines (**Figure IV.2**) are widely used for protection against photodegradation owing to their exceptional photostabilizing properties and small quantum yields of photodecomposition (10^{-7} to 10^{-6}).[24,25] These compounds possess an efficient radiationless mechanism (keto-enol tautomerism) of energy dissipation. The molecule in the first excited state (**A_1**) undergoes an excited state intramolecular proton transfer (**ESIPT**) to create another species in its first excited singlet state (**A_2**). This excited proton-transferred species loses its energy by a non radiation decay process as thermal energy (**A_3**). It should be noted that the contribution of this energy to the thermal degradation of the compound is negligible compared to the much stronger thermal energy reaching the compound from the solar radiation.[26] The original form of the photostabilizer (**A_0**) is regenerated by a reverse proton transfer mechanism, [27-31] as shown in **Figure IV.3**.

Klopffer [18] reported that certain derivatives of benzophenones might undergo a variety of mechanistic pathways of energy dissipation, following the excitation to (**A_1**), including the formation of triplet states. This mechanism is responsible for the exceptionally high photostabilities of these molecules.[32] This type of mechanism (ESIPT/keto-enol tautomerism) is not possible in the case of 4,4'-dihydroxy benzophenones.[33] The interruption of the intramolecular hydrogen bond inhibits the progress of the mechanism and resulting the loss of the photostability of the molecule. Also the environment around the stabilizer is a critical factor for the efficiency of the mechanism of energy dissipation.[4] Proton acceptor moieties are capable of disrupting the internal hydrogen bond of these compounds increasing their photoreactivity and increase the rate of photodegradation. Absorbed energy in these systems is released by the radiation processes.

Phenyl salicylate is another important compound in the class of intramolecularly hydrogen bonded photostabilizers. This compound do not dissipate absorbed energy by direct absorption of UV light but instead undergo photo-fries type rearrangement on prolonged exposure to light, convert into strongly absorbing 2,4'- and 2,2'-dihydroxy benzophenones (**Figure IV.4**). These two molecules then dissipate absorbed energy through above described mechanism. The mechanism by which 2-(2'-hydroxyphenyl) benzotriazoles dissipate the energy of absorbed radiant energy involves tautomeric structures as shown in the following figure. Thus, 2-hydroxybenzophenones and 2-(2'-hydroxyphenyl) benzotriazoles contribute to stability by absorbing UV radiation and quenching photoexcited chromophores.

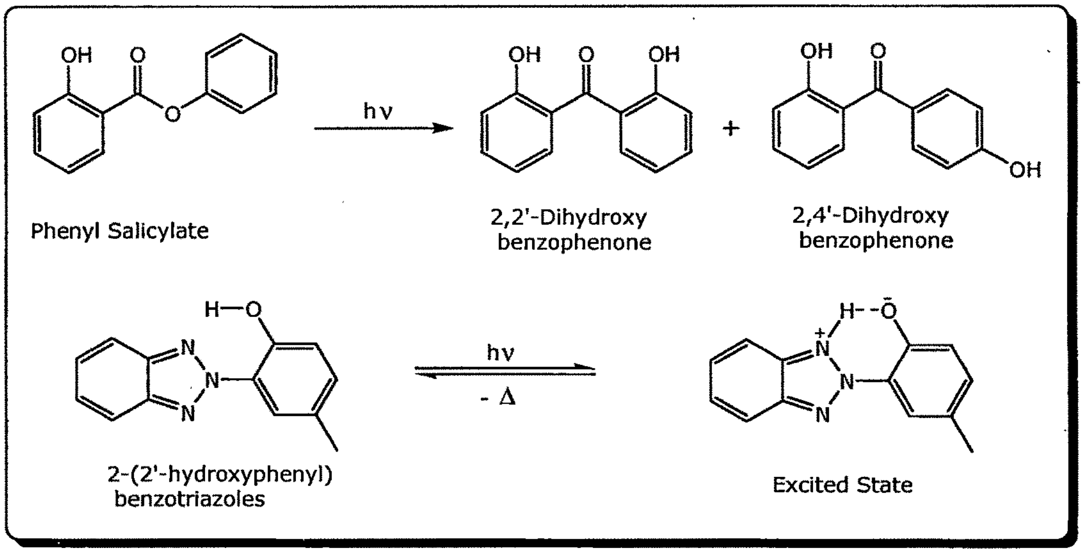
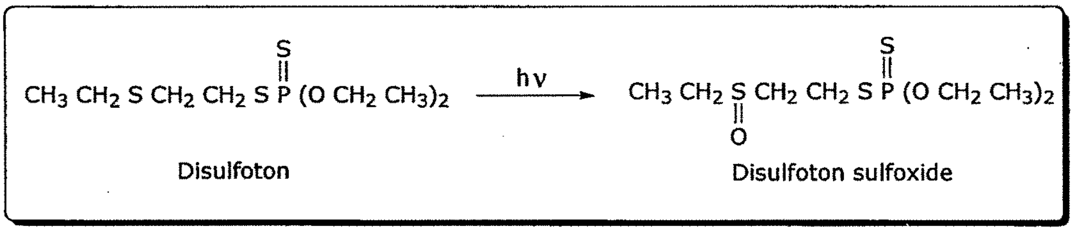


Figure IV.4

Besides increasing life span of pesticide[34], these materials have wide range of applications to reduce the destructive effects of UV radiation.[35-42]

Aim of this work is to design and prepare novel compounds having water-solubility and effective photostabilization property by structural modification in 2,4-dihydroxy benzophenone. The resultant final structure possesses properties of both surfactant as well as the photostabilizers, preventing the loss of intramolecular hydrogen bonding of the original structural unit.

Disulfoton is a selective, systemic organophosphate insecticide and acaricide that is especially effective against sucking insects. It is used to control aphids, leafhoppers, thrips, beet flies, spider mites, and coffee leaf miners. Disulfoton products are used on cotton, tobacco, sugar beets, cole crops, corn, peanuts, wheat, ornamentals, cereal grains, and potatoes.[43] Approximately 1.7 million pounds are used annually in US alone, on cotton (61 %), wheat (16 %), a variety of vegetable crops, plantation-grown Christmas trees, and home gardens. It is formulated as a granular product that is incorporated in the soil, an emulsifiable liquid that can be applied as a foliar treatment and in irrigation water, and as a 95 % active ingredient liquid for seed treatment of cotton. It is a systemic insecticide and is absorbed rapidly into plant tissues, conferring toxicity to many or all plant parts.



$$CH_3\,CH_2\,S\,CH_2\,CH_2\,S\,\overset{\overset{S}{\|}}{P}\,(O\,CH_2\,CH_3)_2 \xrightarrow{h\nu} CH_3\,CH_2\,\underset{\underset{O}{\|}}{S}\,CH_2\,CH_2\,S\,\overset{\overset{S}{\|}}{P}\,(O\,CH_2\,CH_3)_2$$

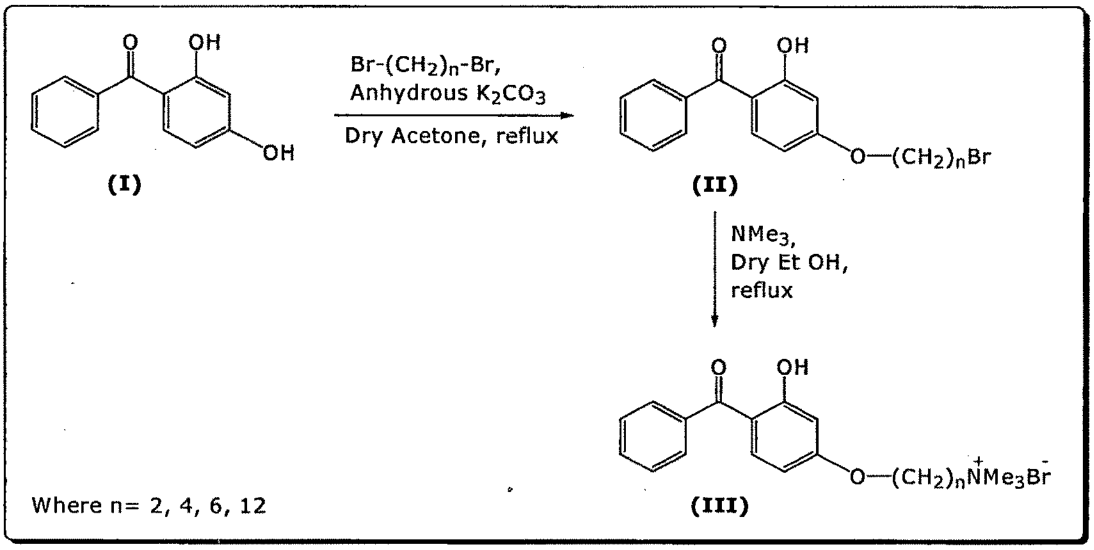
Figure IV.5

Disulfoton is very sensitive to photolysis amongst several other pesticides including organophosphorus, organonitrogens, organochlorines and pyrethroids by exposure to UV-radiation (320-400 nm).[44] Disulfoton sulfoxide has been recognized to be the product of Disulfoton under the irradiation of natural sunlight or UV radiation and it is very toxic to mammals and humans.[43,45,46]

Effective photostabilization study of Disulfoton was carried out using the water-soluble quaternary ammonium salts **(III, Scheme 1)** under irradiation from on HPMV-lamp for 12 h and analysis of percentage recovery of Disulfoton in methanol by HPLC.

IV.3 RESULTS AND DISCUSSION

Structural modification of 2,4-dihydroxy benzophenone **(I)** led to the formation of water-soluble quaternary ammonium salt **(III)** via monoalkylation of **(I)**, as shown in the **Scheme 1**. Monoalkylation of **(I)** was achieved by refluxing mixture of **(I)**, alkyl dibromide and anhydrous potassium carbonate in dry acetone. The alkylation occured at 4th position in benzophenone was evident from the IR absorptions at 2961 cm^{-1} in **1**, 3016 cm^{-1} in **2**, 3077 cm^{-1} in **3**, 2960 cm^{-1} in **4**, 3050 cm^{-1} in **5**, 2945 cm^{-1} in **6**, 3049 cm^{-1} in **7**, 3013 cm^{-1} in **8** for intramolecularly hydrogen bonded –OH groups and characteristic absorption bands at 1628 cm^{-1} in **1**, 1624 cm^{-1} in **2**, 1630 cm^{-1}in **3** and **8**, 1634 cm^{-1} in **4**, 1629 cm^{-1} in **5** and **7**, 1638 cm^{-1} in **6** for the carbonyl group respectively. This is also in agreement with the earlier observation that 2,4-dihydroxy benzophenone when reacted with epichlorohydrin gave the corresponding glycidyl ether, 2-hydroxy-4(2,3-epoxypropoxy)benzophenone (HEPBP).[47] The monoalkylated compounds were then subjected for quaternization by refluxing them with excess of trimethyl amine in dry methanol. After completion of the reaction (TLC) solvent was removed under reduced pressure from the reaction mixture and the solid thus obtained was recrystalized several times from the mixture of dry acetone and few drops of methanol. Structures of all the compounds **(II and III)** were deduced from their UV, FTIR, PMR, ^{13}C NMR and elemental analysis.



Scheme 1

Structures of (**II** and **III**) were readily established through their spectral and analytical data. Its IR spectrum showed a characteristic absorption bands at 1628 in **1**, 1624 in **2**, 1630 in **3** and **8**, 1634 in **4**, 1629 in **5** and **7**, 1638 in **6** and 1275 in **1**, 1261 in **2** and **5**, 1259 in **3**, 1264 in **4** and **6**, 1265 in **8**, 1262 in **7** cm^{-1} for the carbonyl and ether linkage respectively. Monoalkylated compounds (**1, 3, 5, 7**) show the characteristic absorption bands between 533-580 cm^{-1} for terminal methylene bromide. The intramolecularly hydrogen bonded –OH groups were found to exhibit absorption at 2961 in **1**, 3016 in **2**, 3077 in **3**, 2960 in **4**, 3050 in **5**, 2945 in **6**, 3049 in **7** and 3013 in **8**. ^1H NMR spectra exhibited a sharp singlet at δ_H 12.5 for the hydroxy group proton on C_2 (**1, 3, 5, 7**) or C_3 (**2, 4, 6, 8**) carbon. Two separate triplets at 4.33-3.99 and 3.64-3.38 for two protons of $-O-C\underline{H}_2-$ and terminal methylene bromide respectively were seen along with the other characteristics signals for the aromatic ring protons. The proton on C_3 gave a double doublet (J= ~1 Hz) with a small meta coupling to the proton on C_5. Similar kind of meta coupling also observed in the case of the quaternary salts. The ^{13}C NMR of (**II**) displayed diagnostic signals at δ_C 28.42-34.01 and 164.51-165.86 for the methylene bromide and intramolecularly bonded hydroxy group bearing C_2, carbons respectively. The characteristics signal at δ_C 200 obtained for the ketonic carbon, among other additional signals for the aromatic ring carbons.

The characteristic medium absorption bands on 3016 and 1490 cm^{-1} in **2**, 2960 and 1490 cm^{-1} in **4**, 3000 and 1502 cm^{-1} in **6** and 3013 & 1507 cm^{-1} in **8**, confirm the presence of quaternary ammonium salt. Triplets at δ_H 4.63-4.03 and 4.13-3.47 for two protons of $-O-C\underline{H}_2-$ and terminal methylene ($-C\underline{H}_2N$) respectively. Sharp singlet appeared at δ_H 3.45 in **2**, 3.34 in **4**, 3.31 in **6** and 3.27 in **8** for methyl proton confirm the presence of trimethyl ammonium salt along with the other characteristics signals for the aromatic ring protons. The ^{13}C NMR of (**III**) displayed diagnostic signals at δ_C 53.66 in **2**, 52.53 in **4**, 52.57 in **6**, 52.47 in **8** for the three methyl carbons of quaternary ammonium salt and δ_C 164.09 in **2**, 164.77 in **4**, 165.10 in **6**, 165.25 in **8**, for the intramolecularly bonded hydroxy group bearing C_3 carbons. The elemental analyses of all the compounds were in good agreement.

Above results prompted us to study the effective photostabilization of Disulfoton using the water-soluble quaternary ammonium salt **(III)** under irradiation from on HPMV-lamp for 12 h based on the percentage recovery of Disulfoton in methanolic solution by HPLC analysis. The percentages remaining of Disulfoton recovered from the solutions after 12 h of exposure to UV radiation are shown in **Table I**. After completion of the irradiation experiments (12 h), the residual amount of Disulfoton in the presence of different photostabilizers **(2, 4, 6, 8)** were found to be ~ 85 % in methanol. In case of pure Disulfoton (no photostabilizer) only 61.80 % recovered. From the above data it is observed that all the four water-soluble quaternary salts **(III)** were effective towards the UV radiation at a distance of 3.8 cm from the UV source. There was no remarkable effect of spacer (n) on the photostabilization but it affects the solubility of that compound in water at room temperature. As the chain length of spacer increases, solubility decreases at room temperature in water. Comparison of percentage recovery of Disulfoton from the solution after 12 h exposing to UV radiation in the presence and absence of different photostabilizers indicated that the addition of **(2)** in Disulfoton (in 1:1 mole ratio) provides best photostabilization (87.44 %) in methanolic solution among the four photostabilizers **(2, 4, 6, 8)**. From the HPLC data, Disulfoton without any photostabilizers decomposed up to 38.20 %, where as use of the suitable photostabilizers prevented the decomposition up to 25.62 %. From the economical point of view, it might be a very good achievement to stabilize such type of expensive and toxic pesticide. It is worthwhile to mention that the use of such water-soluble photostabilizers in the formulation of pesticides might eliminate the cost of the emulsifiers during actual field applications on larger scale.

Table I : Percentage recovery of Disulfoton in presence and absence of UV absorber on exposure to UV radiation; (Disulfoton: UV absorber, 1:1 mole ratio)

Sr. No.	Samples	% Recovery
1	Disulfoton (without photostabilizer)	61.80
2	**2** ($C_{18}H_{22}O_3NBr$)	87.44
3	**4** ($C_{20}H_{26}O_3NBr$)	84.07
4	**6** ($C_{22}H_{30}O_3NBr$)	85.86
5	**8** ($C_{28}H_{42}O_3NBr$)	86.45

IV.4 EXPERIMENTAL

Melting points were recorded in open capillary tubes and are uncorrected. Ultraviolet spectra were recorded on a Perkin-Elmer Lambda-19 Spectrometer. Infrared spectra were recorded on a Perkin-Elmer PC-16 FTIR Spectrophotometer. NMR spectra were recorded either on a Bruker-300-FT-NMR or on a Bruker-AC-400-FT-NMR using $CDCl_3$ or ($CDCl_3$ + DMSO) as solvent containing tetramethylsilane as an internal standard. Microanalyses were performed on a Perkin-Elmer 2400 series-II Laser instrument. Column chromatography was performed using Acme's silica gel (60–120 mesh size) and the elution was done using mixture of light petroleum and ethyl acetate. The percent yields are reported based on the isolated material after column chromatography. Thin layer chromatography was performed using Acme's silica gel for TLC and spots were visualized in iodine vapor.

Identification and quantitative analysis of the starting material and their photoproducts in the sample-solution was done using a UV-1000, P-200 spectra-physics, high performance liquid chromatography (HPLC) equipped with a UV-100 variable wavelength UV-Vis detector. The HPLC column was fitted with a 4.6 mm I.D. (250 mm length, Hypersil ODS and 5 micron particle size. The mobile phase was a mixture of acetonitrile and water (60:40 v/v).

General procedure for the Monoalkylation of 2,4-dihydroxy benzophenone (II):

2,4-Dihydroxy benzophenone (I, 1.0 mole), anhydrous potassium carbonate (1.5 mole) and alkyl dibromide (1.5 mole) were added in dry acetone (60 mL). The mixture was refluxed in water bath for 8 to 10 h. In the case of higher member (n = 12) the refluxing period was extended up to 16 h. After completion of the reaction (TLC), solvent was removed under reduced pressure and the reaction mixture was poured into ice-cold water (65 mL). The aqueous layer was extracted with ethyl acetate (3 x 25 mL) and combined organic extracts were washed with dilute sodium hydroxide solution (3 %) to remove any unreacted 2,4-dihydroxy benzophenone (I) followed by water (25 mL). Drying over anhydrous sodium sulphate and removal of solvent under reduced pressure furnished dark yellow residue, which was chromatographed using mixture of light petroleum and ethyl acetate (96:4) to furnish the monoalkylated product of 2,4-dihydroxy benzophenone **(II, Scheme 1)** as light yellow coloured crystalline solid **(Table I)**.

General procedure for the Synthesis of Quaternary ammonium compounds (III):

All the quaternary ammonium salts **(III, Scheme 1)** were prepared by refluxing the corresponding monoalkylated compounds (**II**, 1 mole) with trimethyl amine (1.8 mole, excess) in dry ethanol (85 mL) at 80-85 °C for 96 to 102 h. At the end of this period (TLC), solvent was removed under reduced pressure from the reaction mixture and the solid thus obtained was recrystalized several times from the mixture of dry acetone and few drops of methanol to obtain water-soluble white solid **(Table II)**.

Table II: Melting points and % yields of monoalkylated 2,4-dihydroxy benzopheneone **(II)** and Quaternary ammonium salt **(III)**

Compound	n	Molecular formula	mp (°C)	% Yield
1	2	$C_{15}H_{13}O_3Br$	93	63.82
2	2	$C_{18}H_{22}O_3$ NBr	111	53.71
3	4	$C_{17}H_{17}O_3Br$	84	61.32
4	4	$C_{20}H_{26}O_3$ NBr	168	54.93
5	6	$C_{19}H_{21}O_3Br$	64	65.86
6	6	$C_{22}H_{30}O_3$ NBr	162	57.28
7	12	$C_{25}H_{33}O_3Br$	62	48.29
8 *	12	$C_{28}H_{42}O_3$ NBr *	144	43.52

* Sparingly soluble in water at room temperature

Chemicals

Disulfoton (99 %) was purchased from Fluka while the rest of the chemicals and HPLC solvents were purchased from Glaxo (Qualigens) India Ltd. All the chemicals and solvents were used without any purification.

Standard Solutions

Standard solutions of pure Disulfoton (0.5 mg/mL) were prepared along with four different UV absorbers (**2, 4, 6, 8**) in the mole ratio of 1:1 (Disulfoton:UV absorber) and 1:0 (no UV absorber) in dry methanol. The solutions were stored in amber colored bottles between 0-4 °C and the Disulfoton content in each was determined by analytical HPLC.

Irradiation Experiments

The standard solutions of pure Disulfoton prepared as above with and without individual UV absorbers in methanol (20 ml), placed in a Pyrex immersion–well type of a photochemical reactor were irradiated individually using a high-pressure mercury vapor lamp (HPMV, 250 W-Bajaj India) for 12 h at a distance 3.8 cm from the source. The irradiated solutions were withdrawn (5 ml) after 12 h and diluted with the solvent and analyzed for the remaining Disulfoton content by analytical HPLC. Control samples were irradiated and analyzed similarly.

(1) [4-(2-Bromo ethoxy)-2-hydroxy phenyl] phenyl methanone:

Light yellow crystalline solid (63.82 %), mp 93°C. ν_{max}: 2961, 1628, 1598, 1275, 1228, 1191, 1077, 1024, 751 and 580 cm^{-1}. UV (λ_{max}): 320 nm. δ_H (400 MHz, $CDCl_3$): 12.64 (sharp S, 1H of –OH at C_2), 7.61 (d, 2H at $C_{2'}$ & $C_{6'}$), 7.56 (t, merged, 1H at $C_{4'}$), 7.50 (d, 1H at C_6), 7.45 (t, 2H at $C_{3'}$& $C_{5'}$), 6.49 (d, 1H at C_5), 6.42 (dd, J = 1 Hz 1H at C_3), 4.33 (t, 2H at –O-C$\underline{H}_2$-), 3.64 (t, 2H at -C$\underline{H}_2$-Br), δ_c (75.5 MHz, $CDCl_3$): 28.42 (-$\underline{C}H_2$-Br), 67.91 (-O-$\underline{C}H_2$-), 101.83 (C_3 carbon), 107.53 (C_5 carbon), 113.60 (C_1 carbon), 128.35 (two carbon at $C_{3'}$ & $C_{5'}$), 128.89 (two carbon at $C_{2'}$ & $C_{6'}$), 131.61 (C_6 carbon), 135.44 ($C_{4'}$ carbon), 138.15 ($C_{1'}$ carbon), 164.51 (C_2 carbon), 166.20 (C_4 carbon), 200.07 (keton carbon). Elemental analysis: Found C; 56.23 %, H; 3.97 % requires C; 56.07 %, H; 4.07 % for $C_{15}H_{13}O_3Br$.

(2) [2-(4-Benzoyl-3-hydroxy phenoxy) ethyl] trimethyl ammonium bromide:

White crystalline solid (53.71 %), mp 111°C. ν_{max}: 3016, 2925, 1624, 1593, 1490, 1475, 1198, 1179, 1049, 1036, and 747 cm^{-1}. UV (λ_{max}): 320 nm. δ_H (400 MHz, $CDCl_3$ + DMSO): 12.49 (sharp S, 1H of –O$\underline{H}$ at C_3), 7.60 (d, merged with t, 2H at $C_{2'}$ & $C_{6'}$), 7.59

(t, merged, 1H at C$_{4'}$), 7.53 (d, merged with t, 1H at C$_5$), 7.51 (t, 2H at C$_{3'}$ & C$_{5'}$), 6.64 (d, 1H at C$_6$), 6.52 (dd, J = 1 Hz 1H at C$_2$), 4.63 (t, 2H at –O-C$\underline{H}_2$-), 4.13 (t, 2H at -C$\underline{H}_2$-N), 3.45 (sharp S, 9H of –C$\underline{H}_3$ × 3). δ_c (75.5 MHz, CDCl$_3$): 53.66 (three carbons at -CH$_3$ × 3), 62.13 (-$\underline{C}$H$_2$-N), 64.10 (-O-$\underline{C}$H$_2$-), 101.84 (C$_2$ carbon), 106.88 (C$_6$ carbon), 113.42 (C$_4$ carbon), 127.91 (two carbons at C$_{3'}$ & C$_{5'}$), 128.30 (two carbons at C$_{2'}$ & C$_{6'}$), 131.33 (C$_5$ carbon), 134.85 (C$_{4'}$ carbon), 137.32 (C$_{1'}$ carbon), 164.09 (C$_3$ carbon), 164.99 (C$_1$ carbon), 199.31 (keton carbon). Elemental analysis: Found C; 56.23 %, H; 5.97 %, N; 3.24 requires C; 56.84 %, H; 5.78 %, N; 3.68 for $C_{18}H_{22}O_3NBr$.

(3) [4-(4-Bromo butoxy)-2-hydrtoxy pheny] phenyl methanone:

Light yellow crystalline solid (61.32 %), mp 84°C. ν_{max} : 3077, 2941, 1630, 1259, 1231, 1197, 1075,1042, 745, 602 and 533 cm^{-1}. UV (λ_{max}): 320 nm. δ_H (400 MHz, CDCl$_3$): 12.64 (sharp S, 1H of –OH at C$_2$), 7.60 (d, 2H at C$_{2'}$ & C$_{6'}$), 7.54 (t, merged, 1H at C$_{4'}$), 7.53 (d, 1H at C$_6$), 7.47(t, 2H at C$_{3'}$& C$_{5'}$), 6.48 (d, 1H at C$_5$), 6.38 (dd, J = 1 Hz 1H at C$_3$), 4.05 (t, 2H at –O-C$\underline{H}_2$-), 3.47 (t, 2H at -C$\underline{H}_2$-Br), 2.04 (q, 4H at –CH$_2$- × 2). δ_c (75.5 MHz, CDCl$_3$): 27.69, 29.35 (2 × –$\underline{C}$H$_2$-), 33.23 (-$\underline{C}$H$_2$-Br), 67.36 (-O-$\underline{C}$H$_2$-), 101.65 (C$_3$ carbon), 107.64 (C$_5$ carbon), 113.20 (C$_1$ carbon), 128.34 (two carbon at C$_{3'}$ & C$_{5'}$), 128.89 (two carbon at C$_{2'}$ & C$_{6'}$), 131.51 (C$_6$ carbon), 135.33 (C$_{4'}$ carbon), 138.30 (C$_{1'}$ carbon), 165.51 (C$_2$ carbon), 166.35 (C$_4$ carbon), 200.03 (keton carbon). Elemental analysis: Found C; 58.80 %, H; 4.50 % requires C; 58.75 %, H; 4.87 % for $C_{17}H_{17}O_3Br$.

(4) [4-(4-Benzoyl-3-hydroxy phenoxy) butyl] trimethyl ammonium bromide:

White crystalline solid (54.93 %), mp 168 °C. ν_{max} : 3651, 2960, 1636, 1592, 1490, 1264, 1197, 1054, 1016 and 754 cm^{-1}. UV (λ_{max}): 320 nm. δ_H (400 MHz, CDCl$_3$ + DMSO): 12.54 (sharp S, 1H of –O$\underline{H}$ at C$_3$), 7.62 (d, merged with t, 2H at C$_{2'}$ & C$_{6'}$), 7.57 (t, merged, 1H at C$_{4'}$), 7.54 (d, merged with t, 1H at C$_5$), 7.49 (t, 2H at C$_{3'}$ & C$_{5'}$), 6.52 (d, 1H at C$_6$), 6.46 (dd, J = 1 Hz 1H at C$_2$), 4.15 (t, 2H at –O-C$\underline{H}_2$-), 3.66 (t, 2H at -C$\underline{H}_2$-N), 3.34 (sharp S, 9H at –C$\underline{H}_3$ × 3), 1.93 (q, 4H at central –CH$_2$- × 2). δ_c (75.5 MHz, CDCl$_3$): 19.28 & 25.13 (two carbons at –$\underline{C}$H$_2$- × 2), 52.53 (three carbons at -$\underline{C}$H$_3$ × 3), 65.22 (-$\underline{C}$H$_2$-N), 66.87 (-O-$\underline{C}$H$_2$-), 101.36 (C$_2$ carbon), 107.02 (C$_6$ carbon), 112.66 (C$_4$ carbon), 127.88 (two carbon at C$_{3'}$ & C$_{5'}$), 128.24 (two carbon at C$_{2'}$ & C$_{6'}$), 131.17 (C$_5$ carbon), 134.78 ($C_{4'}$ carbon), 137.50 ($C_{1'}$ carbon), 164.77 (C_3 carbon), 165.26 (C_1 carbon), 199.26 (keton carbon). Elemental analysis: Found C; 58.60 %, H; 6.52 %, N; 3.30 % requires C; 58.82 %, H; 6.37 %, N; 3.43 % for $C_{20}H_{26}O_3NBr$.

(5) [4-(6-Bromo hexyloxy)-2-hydroxy phenyl] phenyl methanone:

Light yellow crystalline solid (65.86 %), mp 64°C. ν_{max} : 3050, 2936, 1629, 1597, 1261, 1226, 1197, 1073, 1041, 742, 603 and 568 cm^{-1}. UV (λ_{max}): 320 nm. δ_H (400 MHz, $CDCl_3$): 12.69 (sharp S, 1H of $-O\underline{H}$ at C_2), 7.60 (d, 2H at $C_{2'}$ & $C_{6'}$), 7.53 (t, merged, 1H at $C_{4'}$), 7.51 (d, 1H at C_6), 7.48 (t, 2H at $C_{3'}$& $C_{5'}$), 6.47 (d, 1H at C_5), 6.38 (dd, J = 1 Hz 1H at C_3), 3.99 (t, 2H at $-O-C\underline{H}_2-$), 3.40 (t, 2H at $-C\underline{H}_2-Br$), 1.81 (q, 8H at central $-C\underline{H}_2- \times 4$). δ_c (75.5 MHz, $CDCl_3$): 25.11, 27.76, 28.69, 32.53 (four carbons at $-\underline{C}H_2- \times$ 4), 33.67 ($-\underline{C}H_2-Br$), 68.09 ($-O-\underline{C}H_2-$), 101.48 (C_3 carbon), 107.57 (C_5 carbon), 112.90 (C_1 carbon), 128.19 (two carbons at $C_{3'}$ & $C_{5'}$), 128.75 (two carbons at $C_{2'}$ & $C_{6'}$), 131.35 (C_6 carbon), 135.14 ($C_{4'}$ carbon), 138.18 ($C_{1'}$ carbon), 165.62 (C_2 carbon), 166.24 (C_4 carbon), 199.77 (keton carbon). Elemental analysis: Found C; 60.38 %, H; 5.35 % requires C; 60.77 %, H; 5.57 % for $C_{19}H_{21}O_3Br$.

(6) [6-(4-Benzoyl-3-hydroxy phenoxy) hexyl] trimethyl ammoniun bromide:

White crystalline solid (57.28 %), mp 162 °C. ν_{max} : 3000, 2945, 1686, 1638, 1574, 1502, 1471, 1264, 1197, 1165, 1076, 1040 and 744 cm^{-1}. UV (λ_{max}): 320 nm. δ_H (400 MHz, $CDCl_3$ + DMSO): 12.54 (sharp S, 1H of $-O\underline{H}$ at C_3), 7.60 (d, merged with t, 2H at $C_{2'}$ & $C_{6'}$), 7.56 (t, merged, 1H at $C_{4'}$), 7.53 (d, merged with t, 1H at C_5), 7.48 (t, 2H at $C_{3'}$ & $C_{5'}$), 6.47 (d, 1H at C_6), 6.44 (dd, J = 1 Hz 1H at C_2), 4.04 (t, 2H at $-O-C\underline{H}_2-$), 3.56 (t, 2H at $-C\underline{H}_2-N$), 3.31 (sharp S, 9H at $-C\underline{H}_3 \times 3$), 1.78 (q, 8H at central $-CH_2- \times 4$). δ_c (75.5 MHz, $CDCl_3$): 22.29, 24.90, 25.23, 28.03 (four carbons at $-\underline{C}H_2- \times$ 4), 52.57 (three carbons at $-\underline{C}H_3 \times$ 3), 65.72 ($-\underline{C}H_2-N$), 67.53 ($-O-\underline{C}H_2-$), 101.14 (C_2 carbon), 107.02 (C_6 carbon), 112.42 (C_4 carbon), 127.83 (two carbons at $C_{3'}$ & $C_{5'}$), 128.20 (two carbons at $C_{2'}$ & $C_{6'}$), 131.07 (C_5 carbon), 134.75 ($C_{4'}$ carbon), 137.53 ($C_{1'}$ carbon), 165.10 (C_3 carbon), 165.39 (C_1 carbon), 199.28 (keton carbon). Elemental analysis:

Found C; 60.92 %, H; 6.95 %, N; 2.97 % requires C; 60.55 %, H; 6.88 %, N; 3.21 % for $C_{22}H_{30}O_3NBr$.

(7) [4-(12-Bromo dodecyloxy)-2-hydroxy phenyl] phenyl methanone:

Light yellow crystalline solid (48.29 %), mp 62°C. ν_{max} : 3049, 2948, 1629, 1595, 1262, 1046, 748 and 542 cm^{-1}. UV (λ_{max}): 320 nm. δ_H (300 MHz, $CDCl_3$): 12.68 (sharp S, 1H of $-O\underline{H}$ at C_2), 7.60 (d, 2H at $C_{2'}$ & $C_{6'}$), 7.55 (t, merged, 1H at $C_{4'}$), 7.53 (d, 1H at C_6), 7.49 (t, 2H at $C_{3'}$& $C_{5'}$), 6.48 (d, 1H at C_5), 6.38 (dd, J = 1 Hz 1H at C_3), 3.99 (t, 2H at $-O-C\underline{H}_2-$), 3.38 (t, 2H at $-C\underline{H}_2-Br$), 1.43 (q, 20H at central $-C\underline{H}_2- \times 10$). δ_c (75.5 MHz, $CDCl_3$): 25.94, 28.17, 28.76, 28.97, 29.31, 29.43, 29.51, 32.84 (ten carbons at $-\underline{C}H_2- \times 10$), 34.01 ($-\underline{C}H_2-Br$), 68.48 ($-O-\underline{C}H_2-$), 101.53 ($C_3$ carbon), 107.74 (C_5 carbon), 112.97 (C_1 carbon), 128.27 (two carbons at $C_{3'}$ & $C_{5'}$), 128.85 (two carbons at $C_{2'}$ & $C_{6'}$), 131.39 (C_6 carbon), 135.19 ($C_{4'}$ carbon), 138.34 ($C_{1'}$ carbon), 165.86 (C_2 carbon), 166.37 (C_4 carbon), 199.88 (keton carbon). Elemental analysis: Found C; 65.53 %, H; 6.89 % requires C; 65.07 %, H; 7.15 % for $C_{25}H_{33}O_3Br$.

(8) [12-(4-Benzoyl-3-hydroxy phenoxy) dodecyl] trimethyl ammonium bromide:

White crystalline solid (43.52 %), mp 144 °C. ν_{max} : 3013, 2923, 1630, 1507,1468, 1284, 1265, 1194, 1165, 1035 and 745 cm^{-1}. UV (λ_{max}): 320 nm. δ_H (400 MHz, $CDCl_3$ + DMSO): 12.59 (sharp S, 1H of $-O\underline{H}$ at C_3), 7.61 (d, merged with t, 2H at $C_{2'}$ & $C_{6'}$), 7.57 (t, merged, 1H at $C_{4'}$), 7.53 (d, merged with t, 1H at C_5), 7.50 (t, 2H at $C_{3'}$ & $C_{5'}$), 6.47 (d, 1H at C_6), 6.43 (dd, J = 1 Hz 1H at C_2), 4.03 (t, 2H at $-O-C\underline{H}_2-$), 3.47 (t, 2H at $-C\underline{H}_2-N$), 3.27 (sharp S, 9H at $-C\underline{H}_3 \times 3$), 1.55 (q, 20H at central $-C\underline{H}_2- \times 10$). δ_c (75.5 MHz, $CDCl_3$): 22.35, 25.23, 25.56, 28.26, 28.47, 28.58, 28.76 (ten carbons at $-\underline{C}H_2- \times 10$), 52.47 (three carbons at $-\underline{C}H_3 \times 3$), 65.89 ($-\underline{C}H_2-N$), 67.87 ($-O-\underline{C}H_2-$), 101.10 ($C_2$ carbon), 107.03 (C_6 carbon), 112.32 (C_4 carbon), 127.80 (two carbons at $C_{3'}$ & $C_{5'}$), 128.16 (two carbons at $C_{2'}$ & $C_{6'}$), 131.01 (C_5 carbon), 134.69 ($C_{4'}$ carbon), 137.55 ($C_{1'}$ carbon), 165.25 (C_3 carbon), 165.40 (C_1 carbon), 199.22 (keton carbon). Elemental analysis: Found C; 64.55 %, H; 8.10 %, N; 2.51 % requires C; 64.61 %, H; 8.07 %, N; 2.69 % for $C_{28}H_{42}O_3NBr$.

IV.5 CONCLUSION

There are four most important UV absorber classes as mentioned earlier, which include the hydroxyphenyl-benzotriazoles (BTZ), hydroxyphenyl-s-triazines (HPT), hydroxybenzophenones and oxanilides. We chose 2,4- hydroxybenzophenone, which functions as a photostabilizer through an excited state intramolecular proton transfer (ESIPT) mechanism. It was thought that monoalkylation at fourth position followed by quaternization would render it water soluble while still retaining its photostabilizer property. With this aim in mind compounds **(2, 4, 6, 8)** were prepared having varied length of methylene spacers and their photostabilizing activity was examined, which showed satisfactory results. We have presented herein the idea of designing and synthesizing the novel water soluble compounds having properties of photostabilizers. Further research in this direction can lead to development of more useful and general compounds of interest in this class.

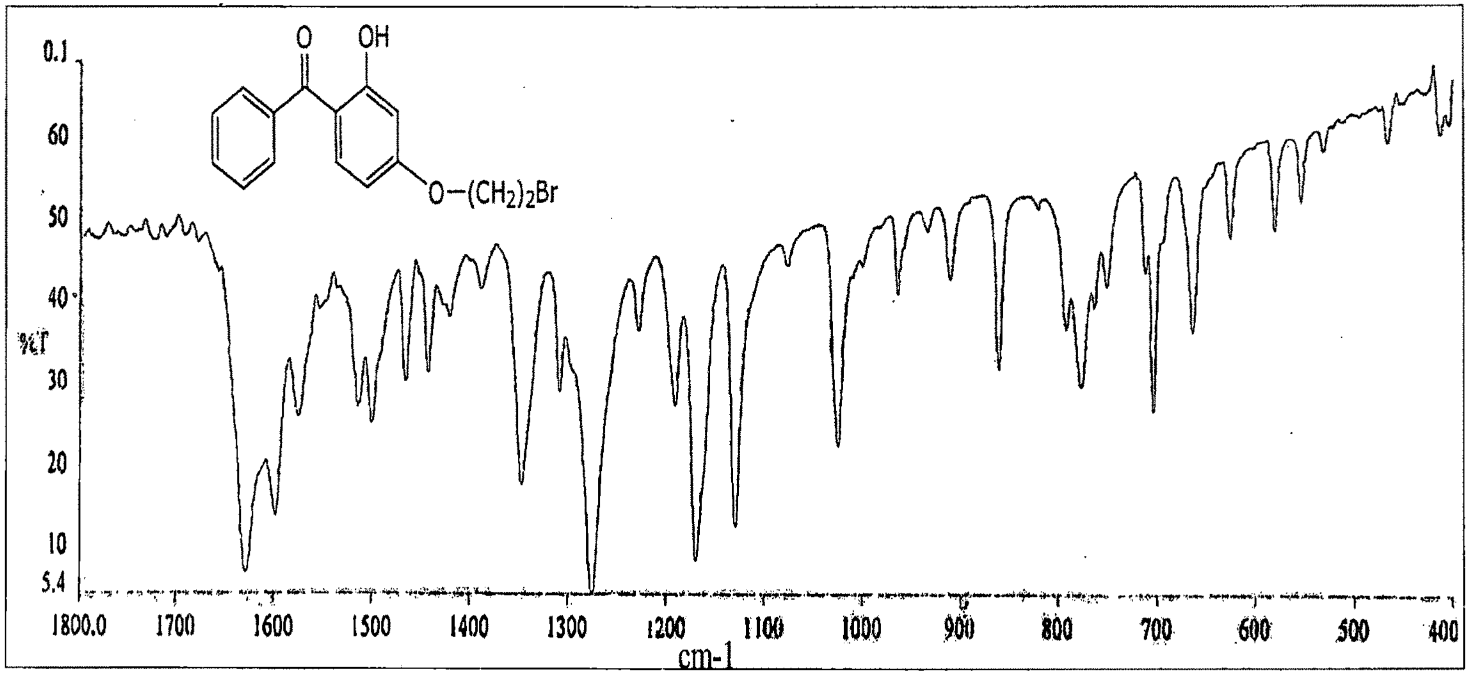


Figure IV.6: FTIR Spectrum of the compound 1

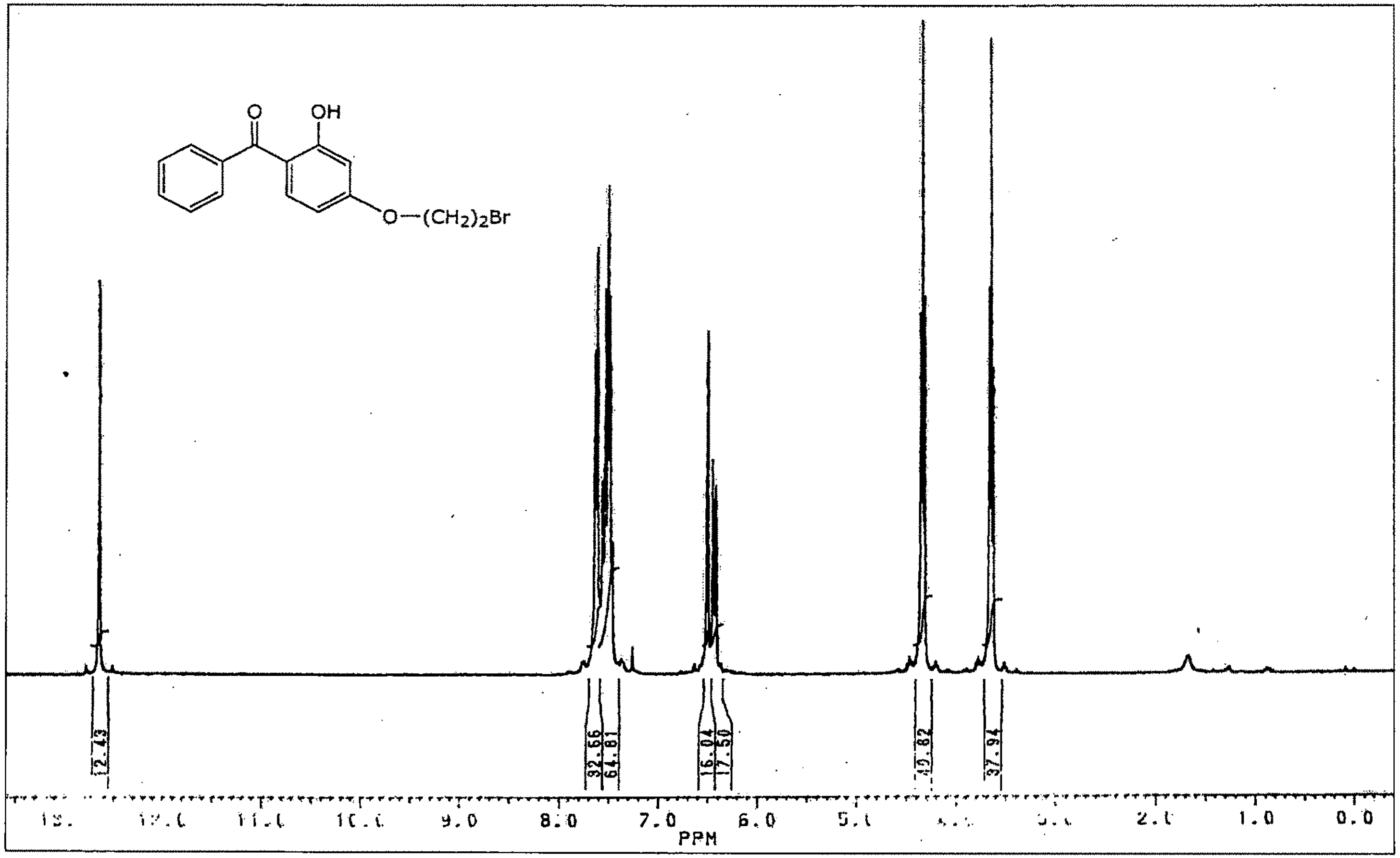


Figure IV.7: PMR Spectrum of the compound 1

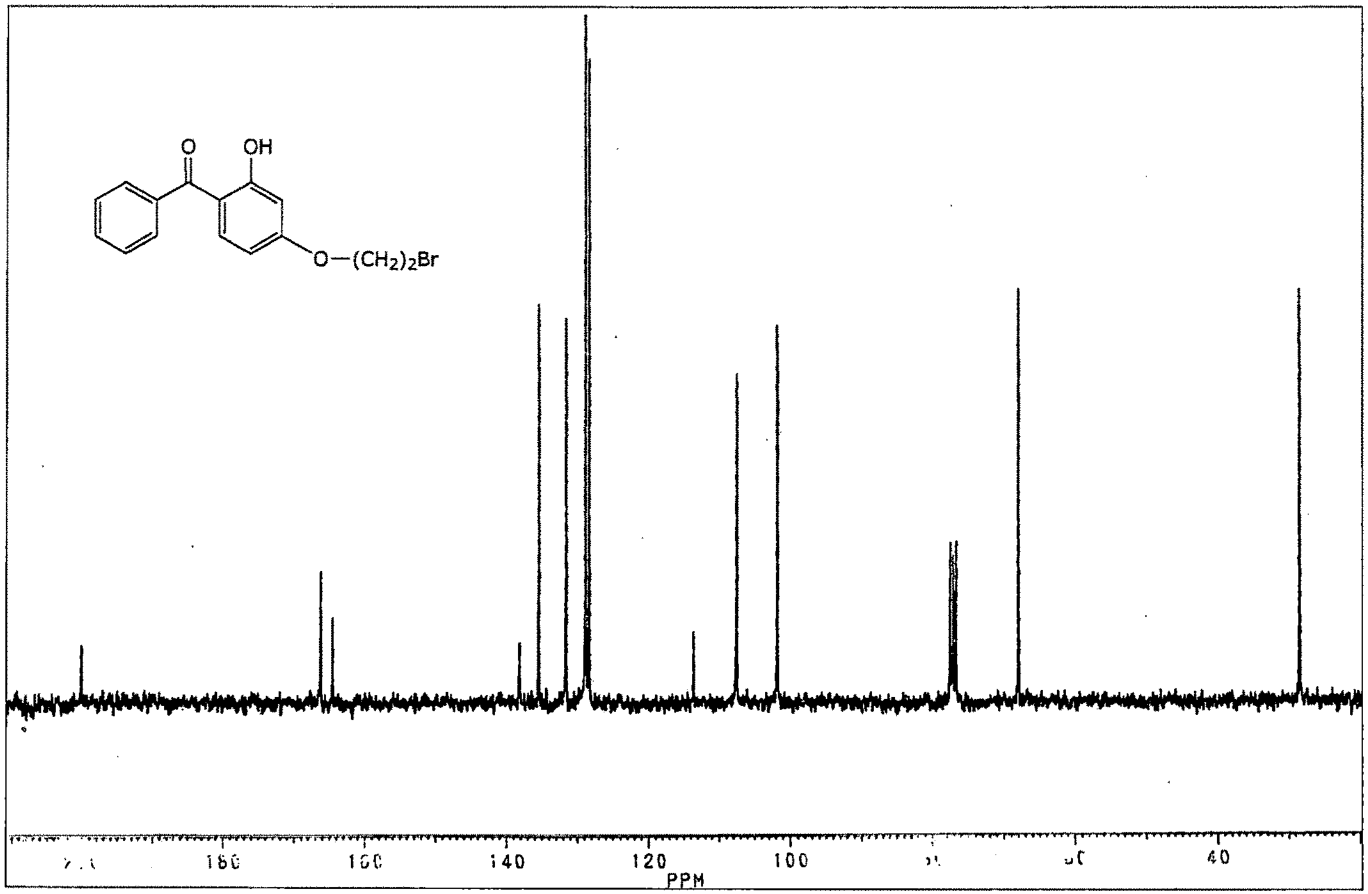


Figure IV.8: ^{13}C NMR of the compound 1

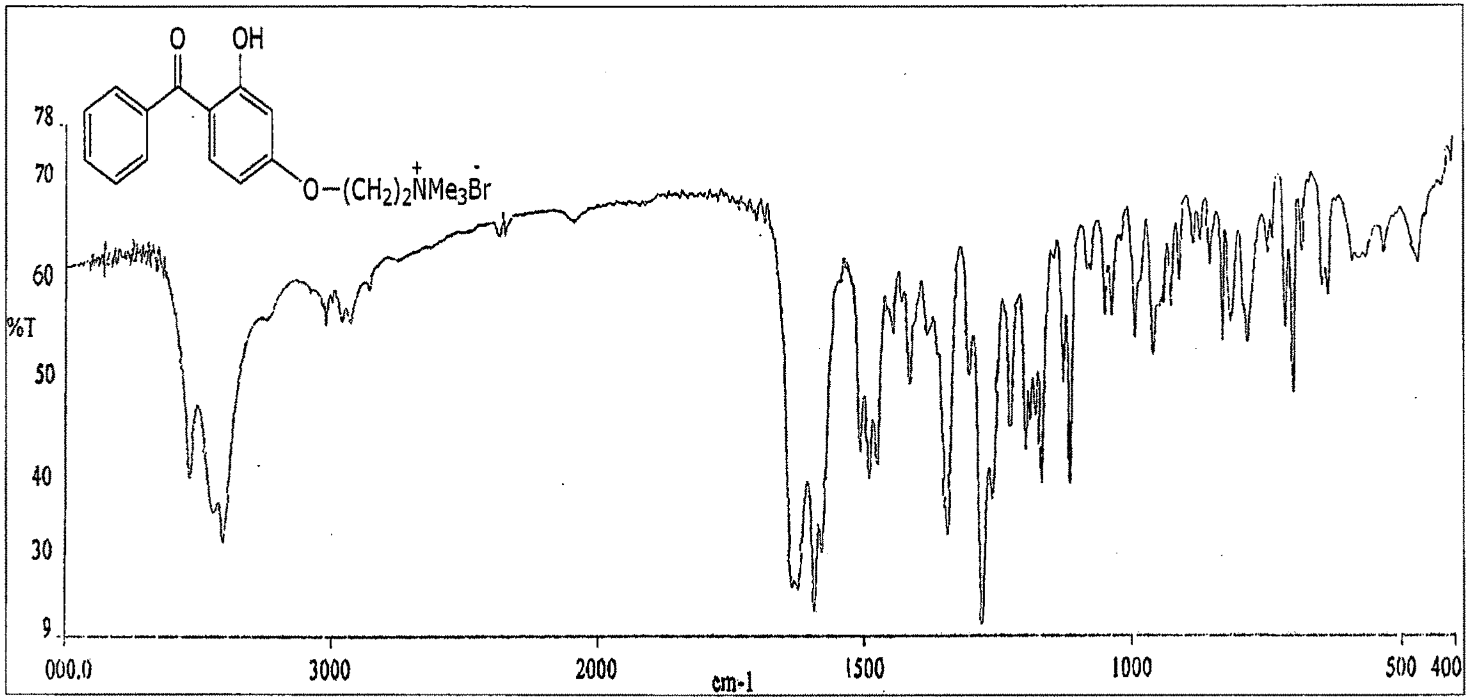


Figure IV.9: FTIR Spectrum of the compound 2

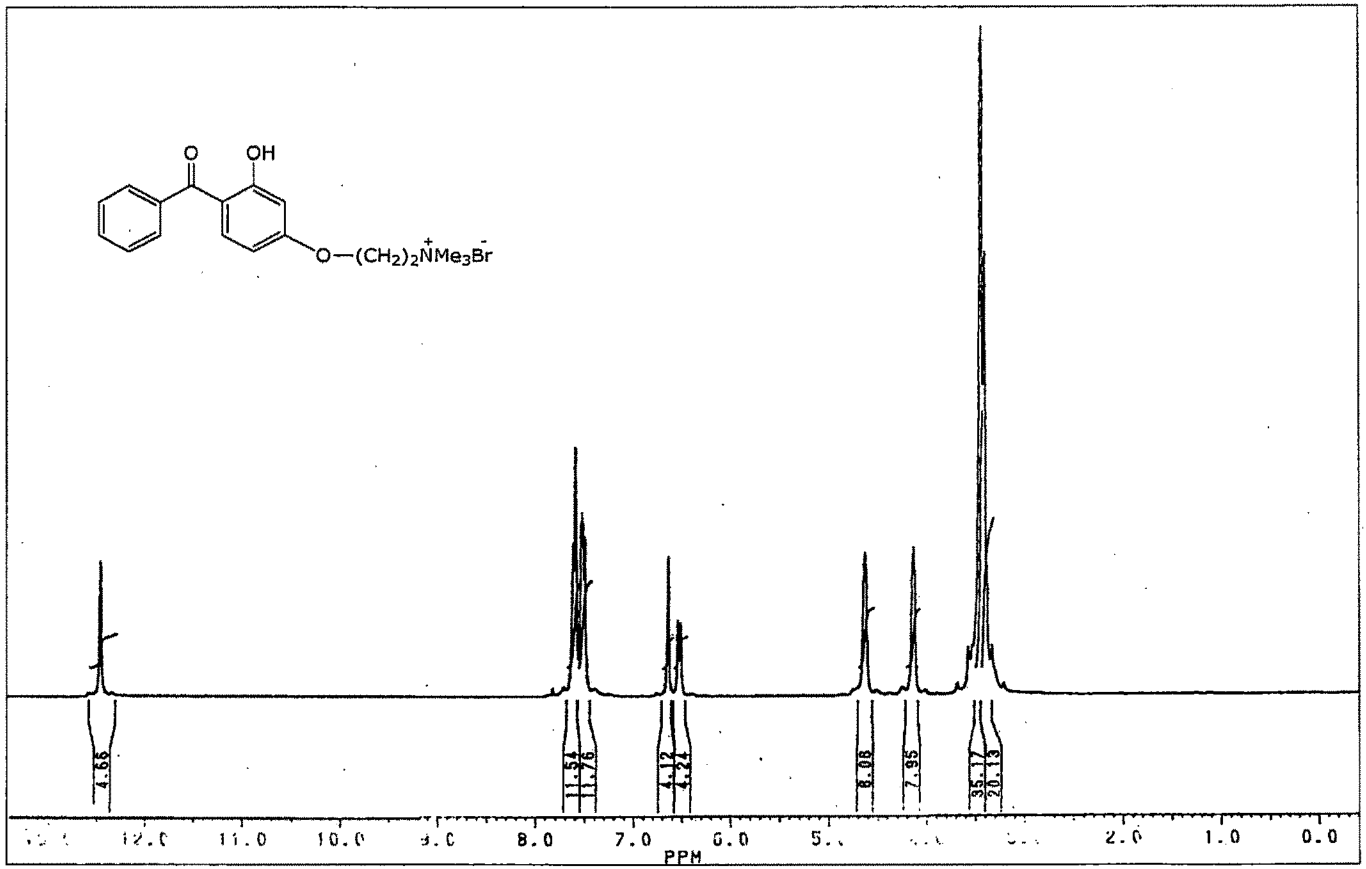


Figure IV.10: PMR Spectrum of the compound 2

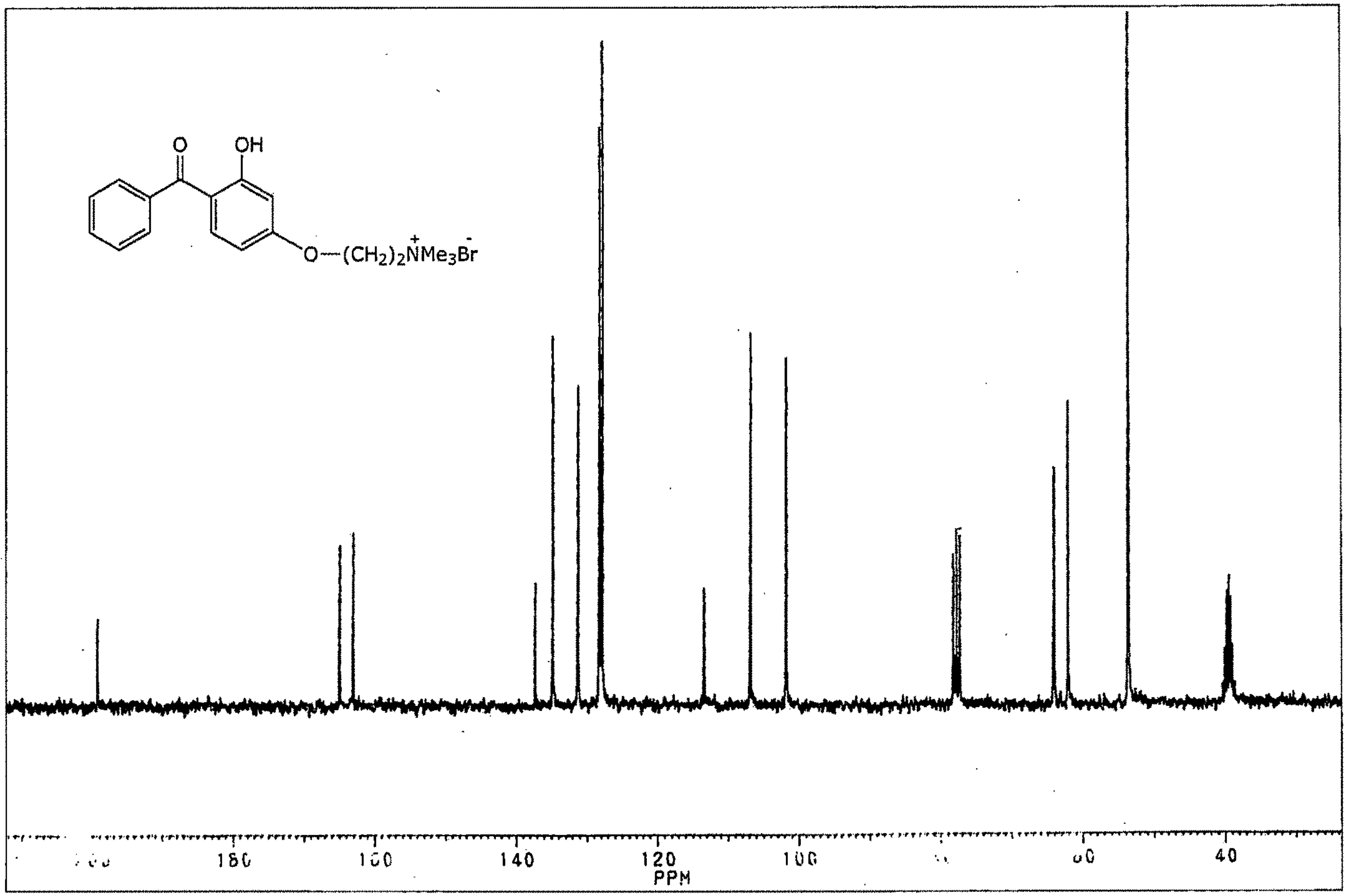


Figure IV.11: ^{13}C NMR of the compound 2

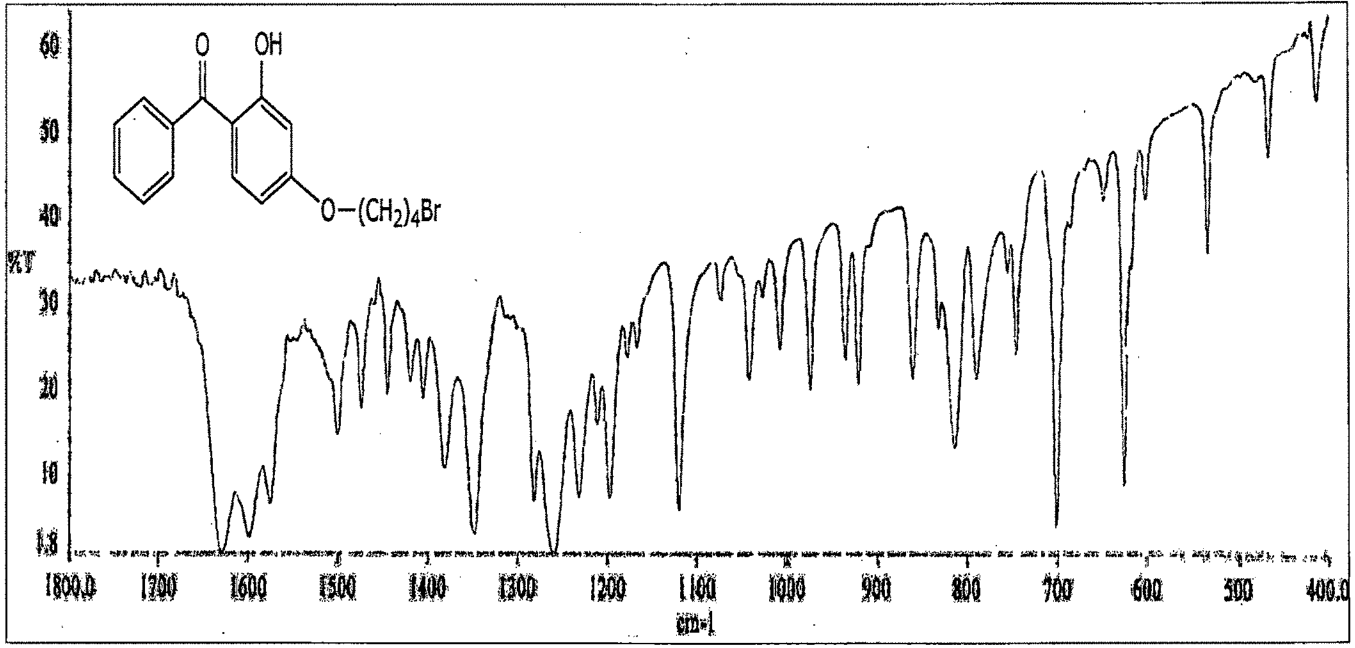


Figure IV.12: FTIR Spectrum of the compound 3

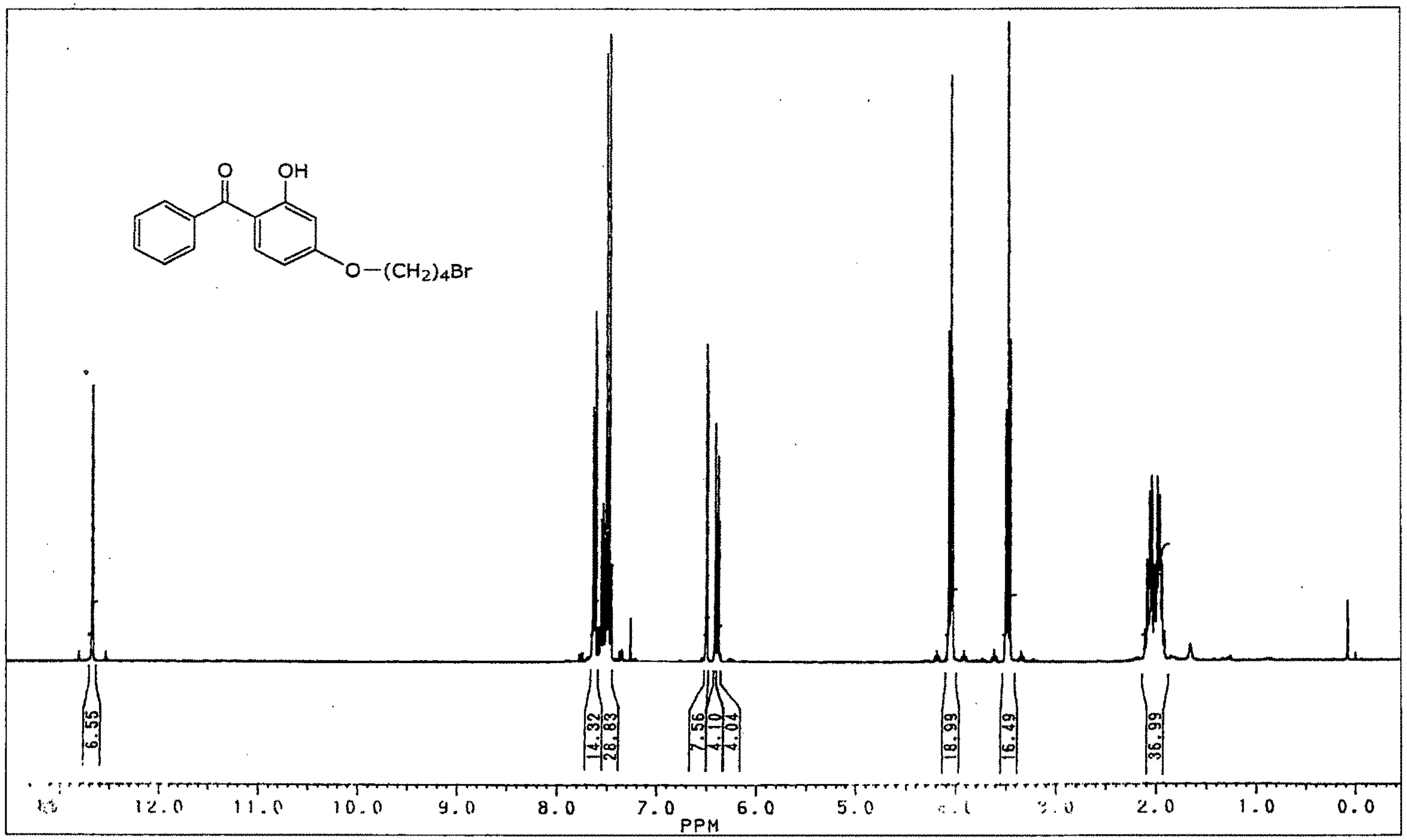


Figure IV.13: PMR Spectrum of the compound 3

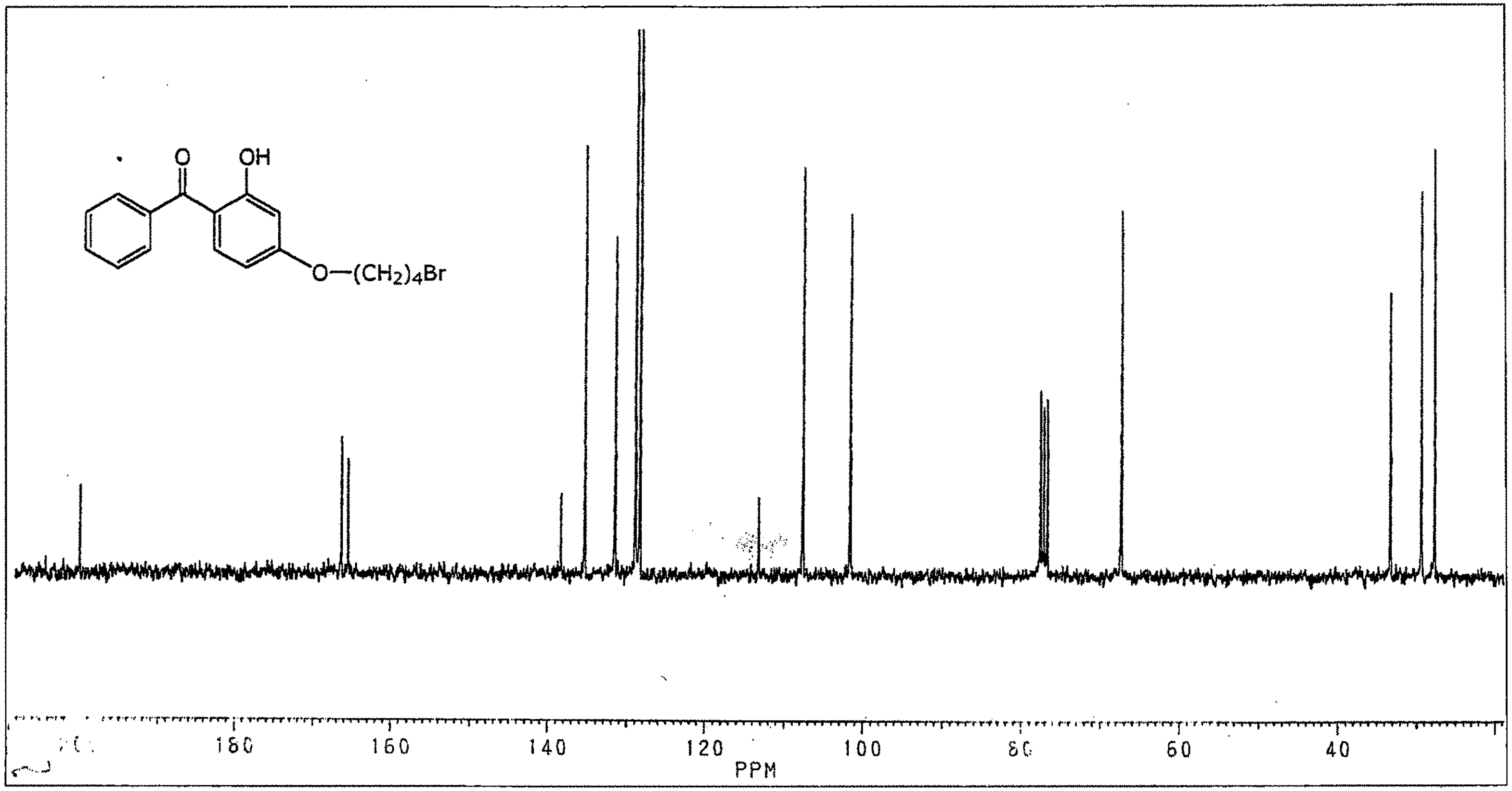


Figure IV.14: ^{13}C NMR of the compound 3

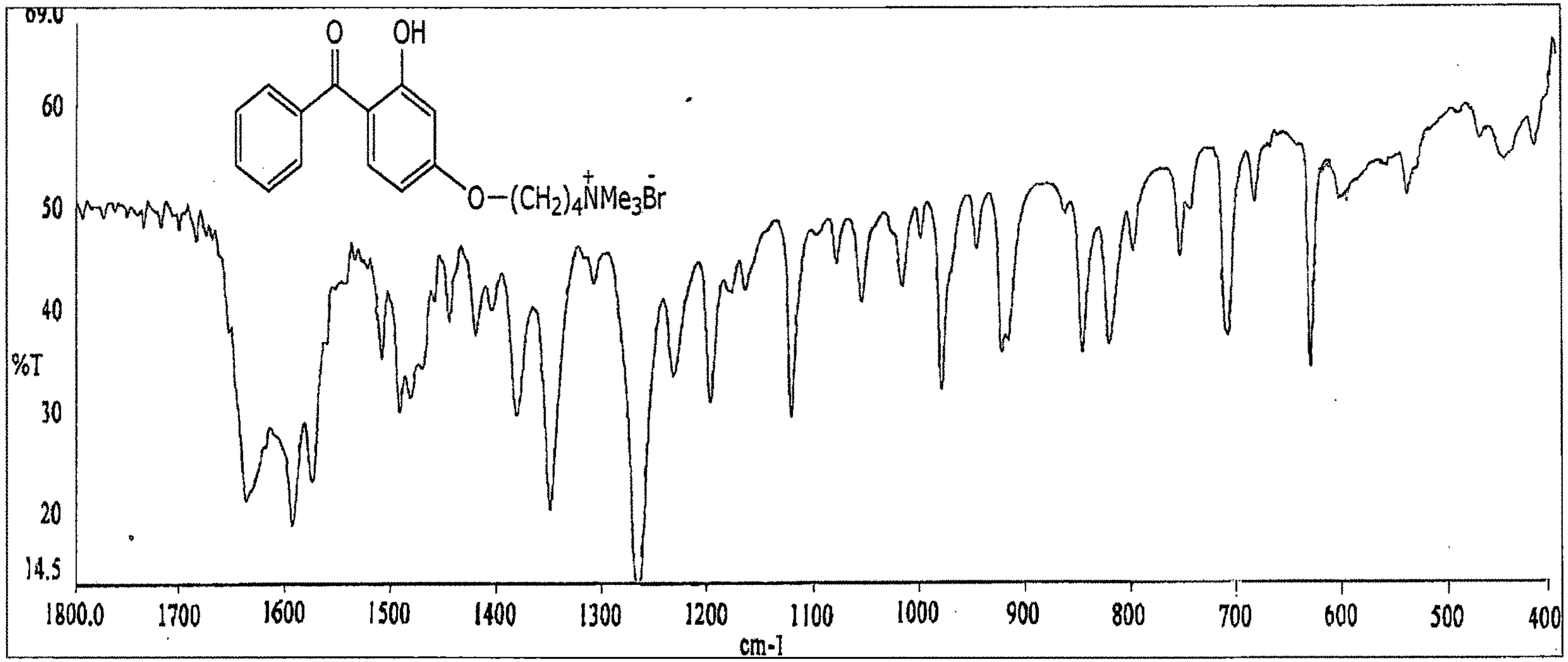


Figure IV.15: FTIR Spectrum of the compound 4

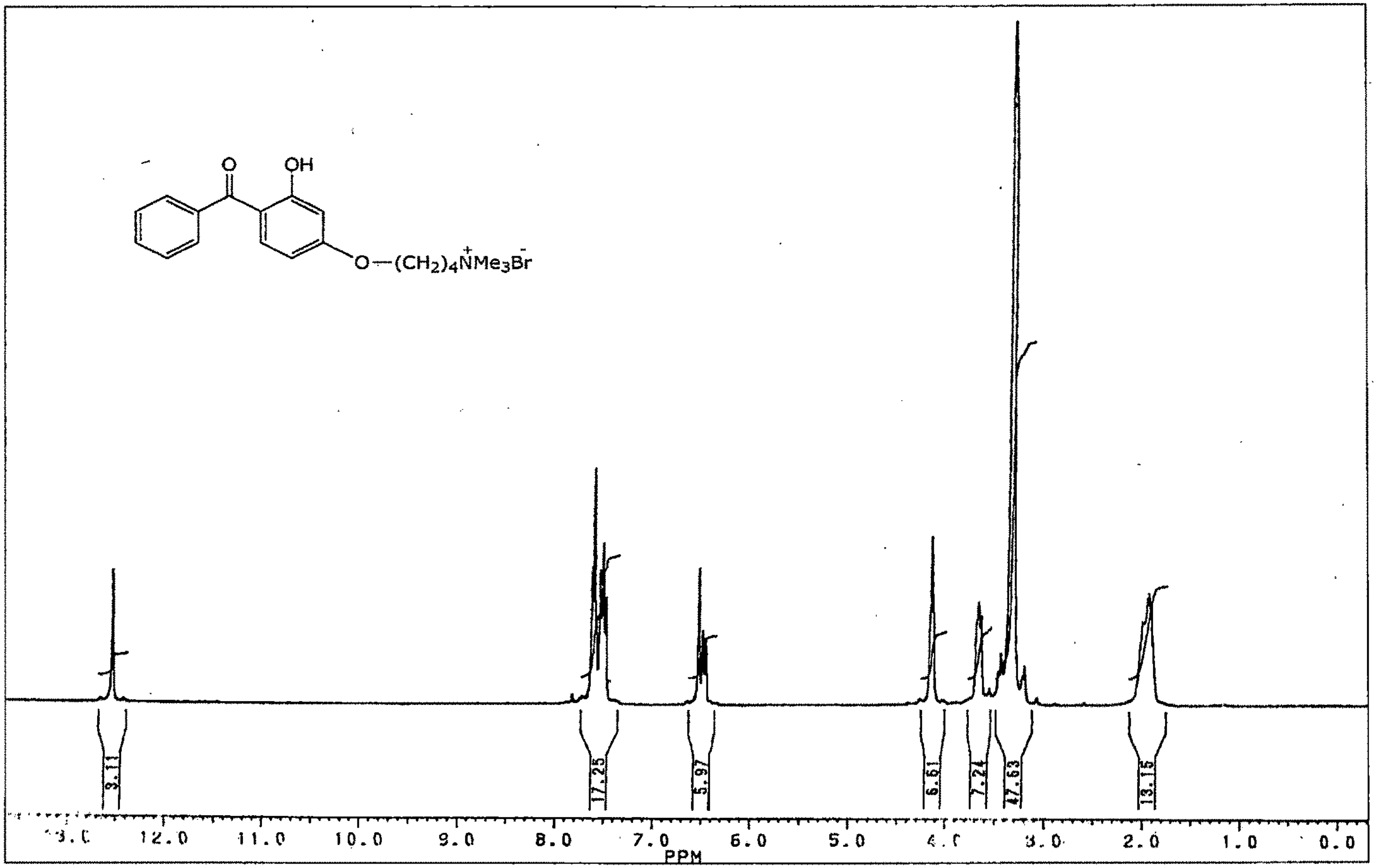


Figure IV.16: PMR Spectrum of the compound 4

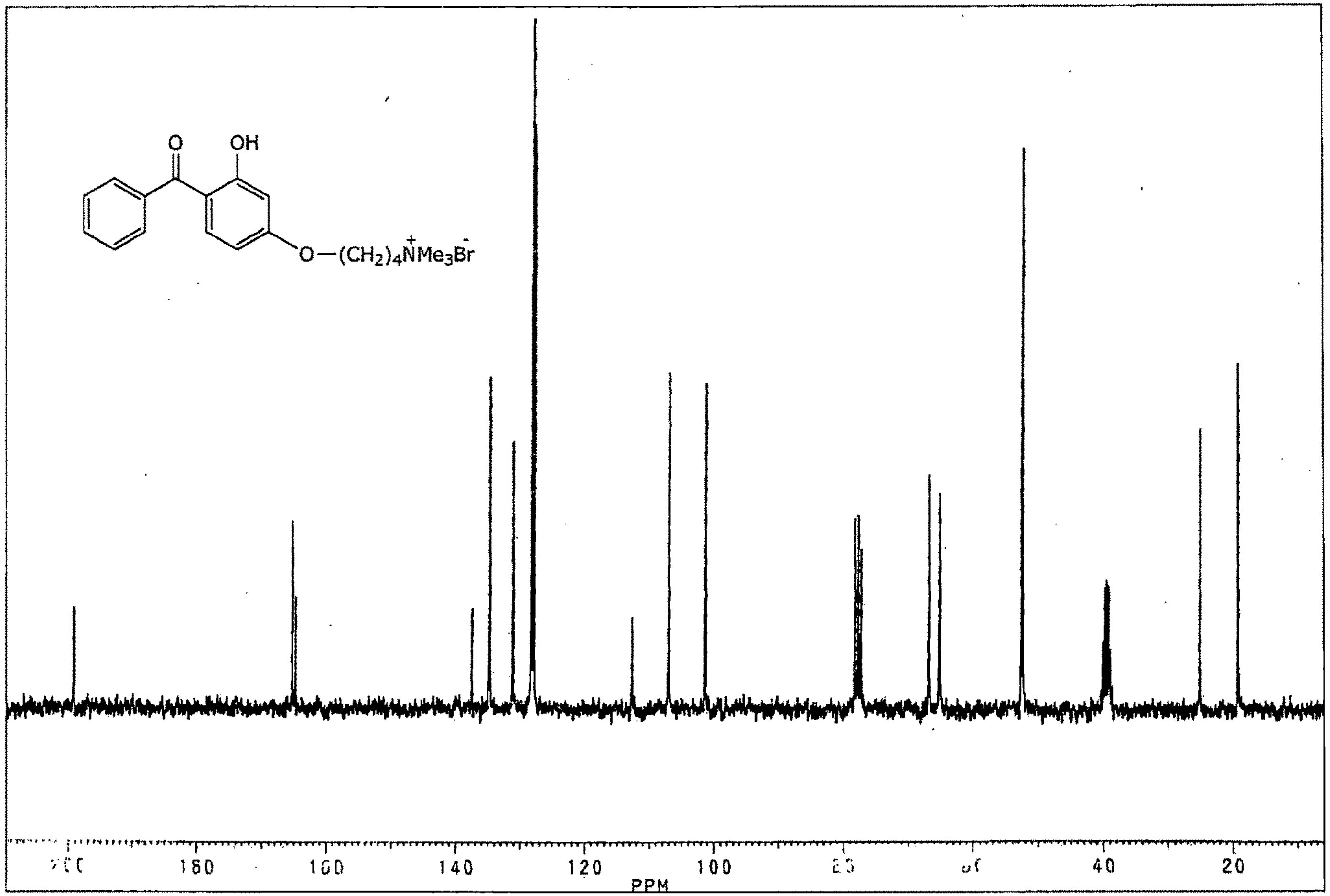


Figure IV.17: ^{13}C NMR of the compound 4

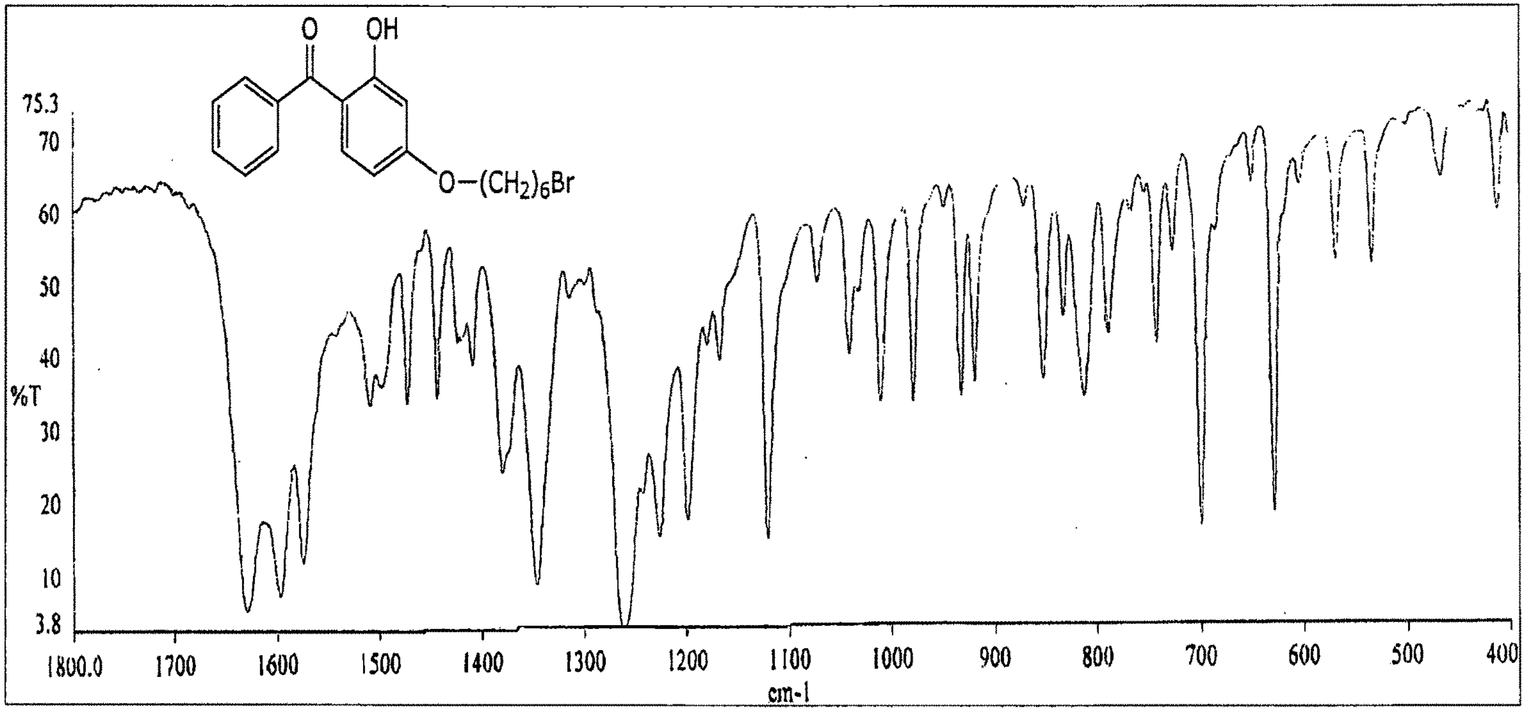


Figure IV.18: FTIR Spectrum of the compound 5

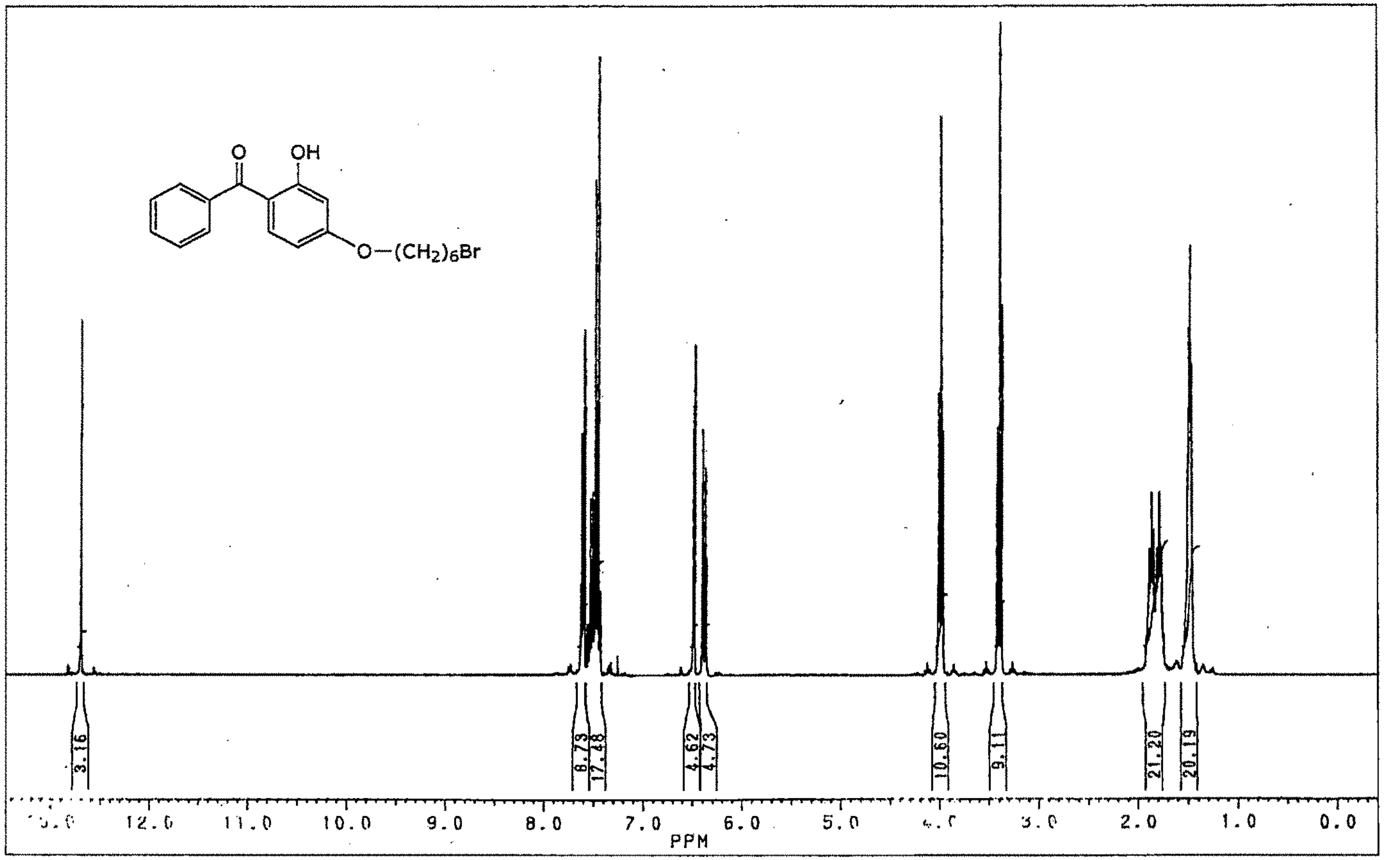


Figure IV.19: PMR Spectrum of the compound 5

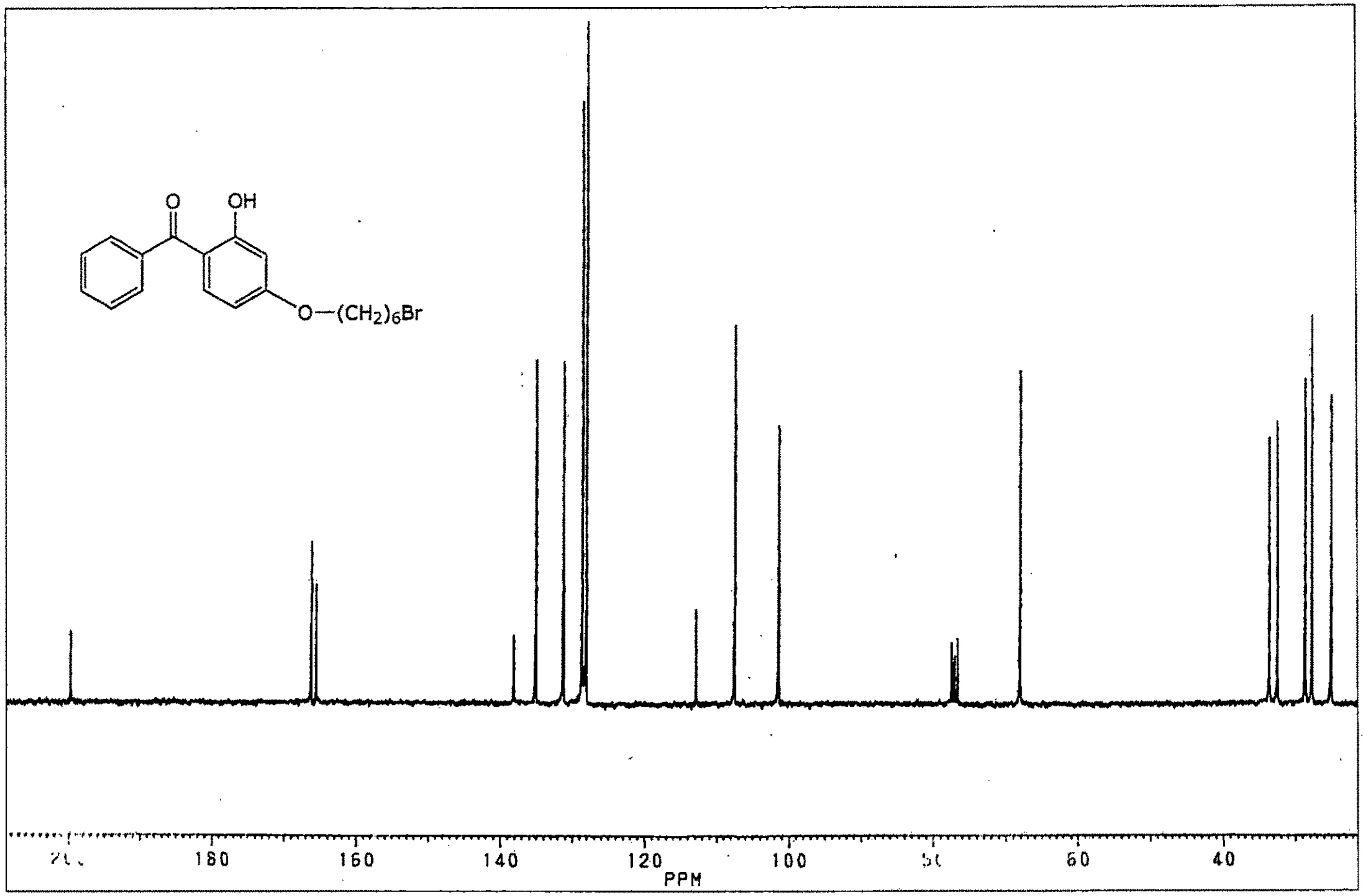


Figure IV.20: ^{13}C NMR of the compound 5

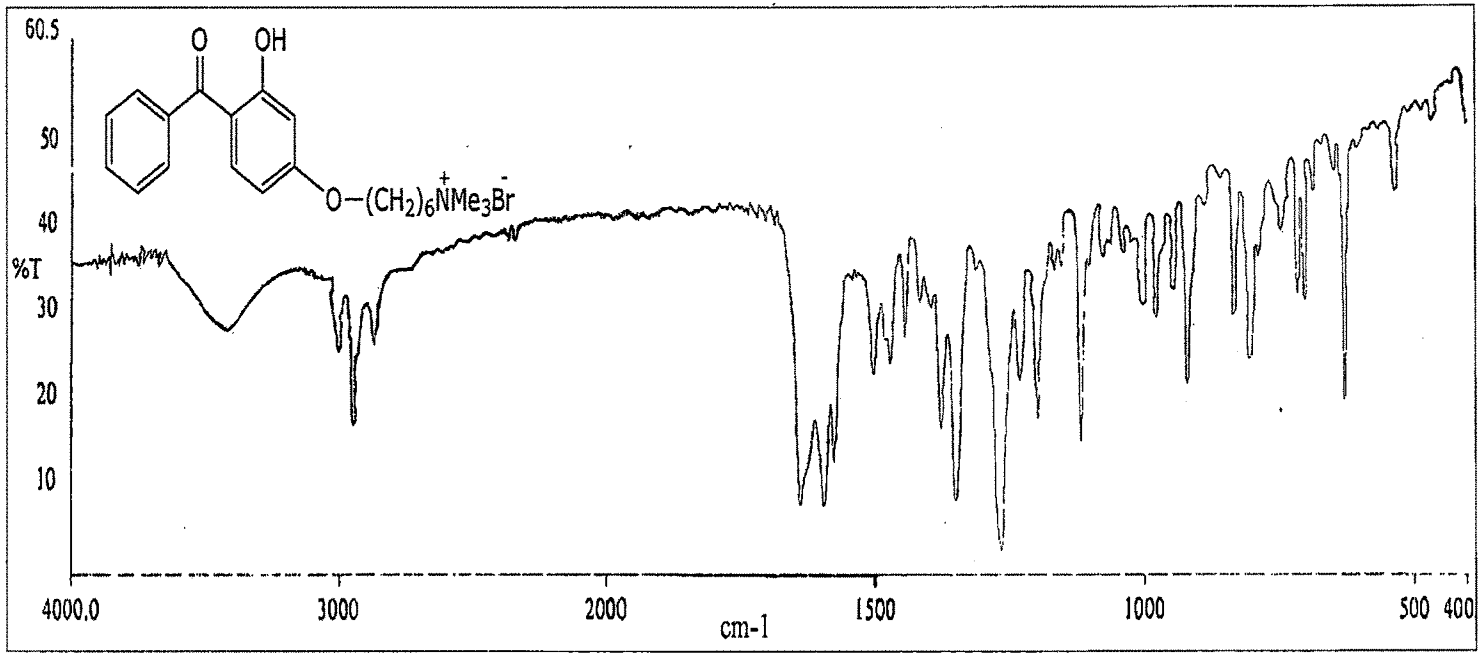


Figure IV.21: FTIR Spectrum of the compound 6

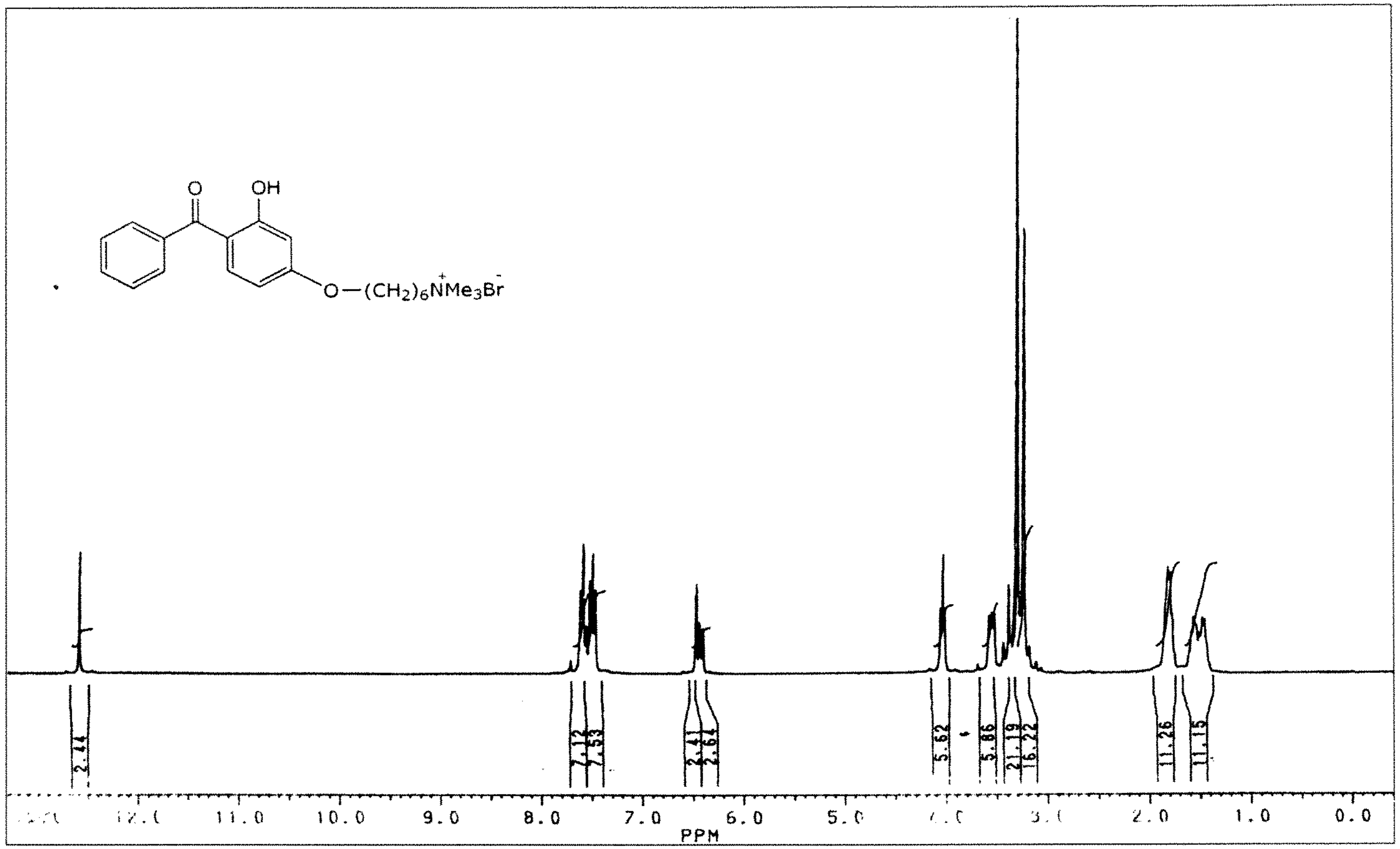


Figure IV.22: PMR Spectrum of the compound 6

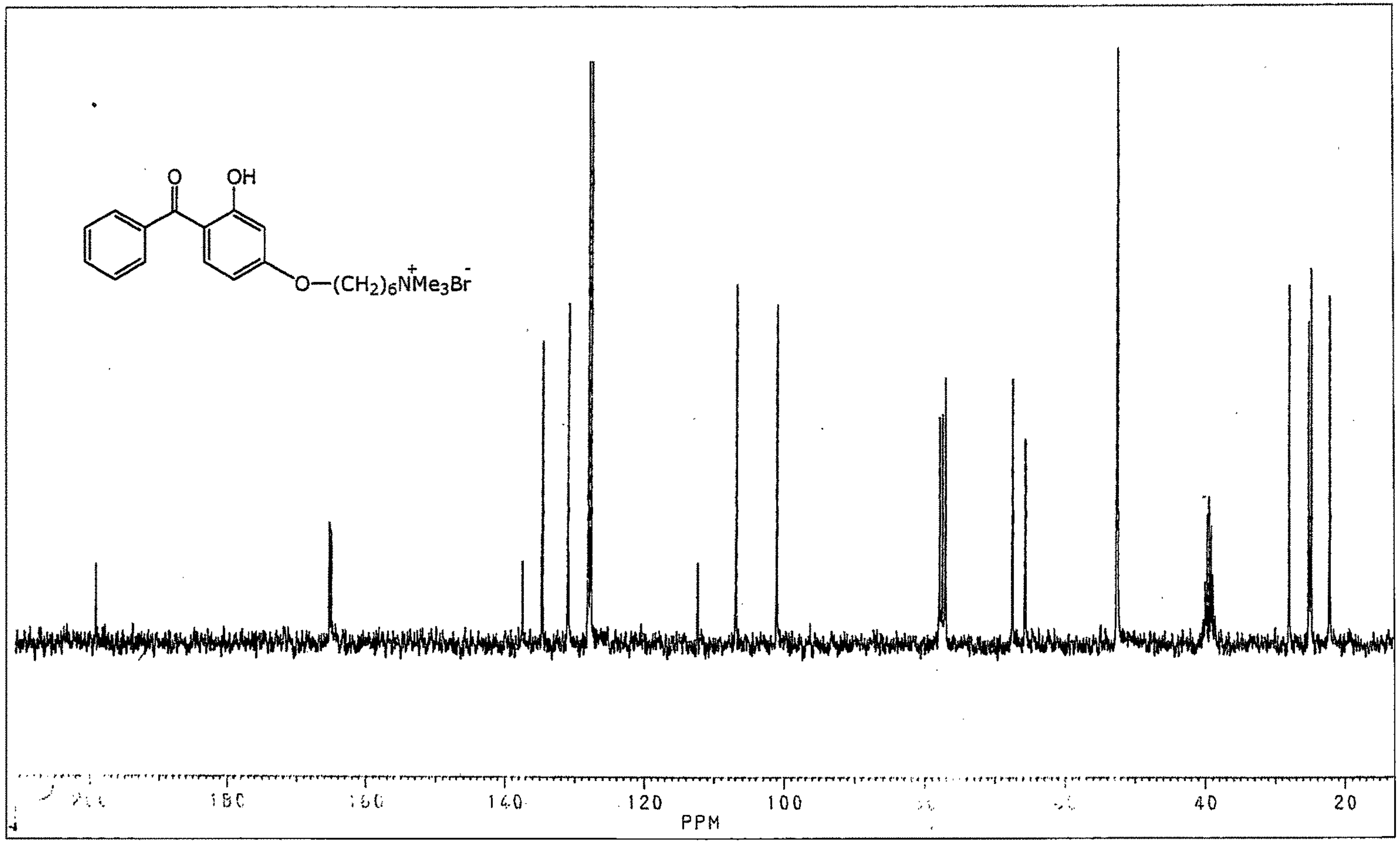


Figure IV.23: ^{13}C NMR of the compound 6

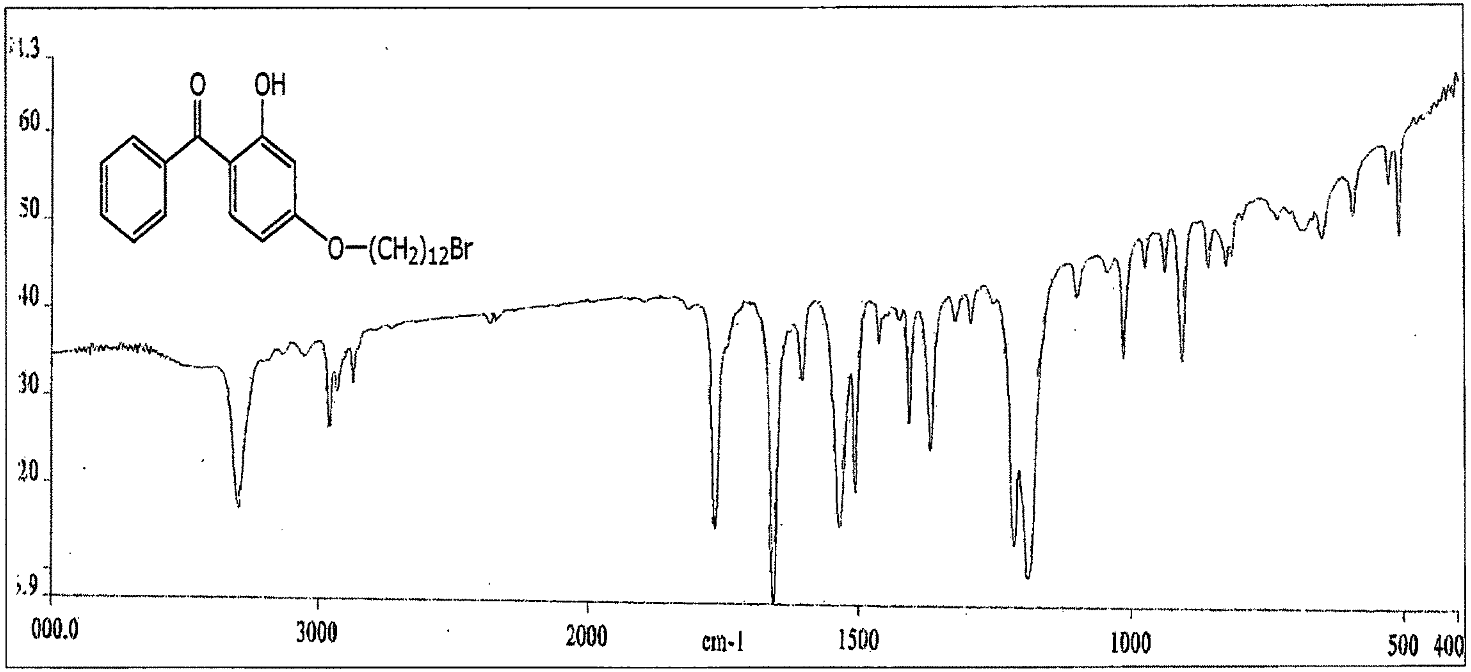


Figure IV.24: FTIR Spectrum of the compound 7

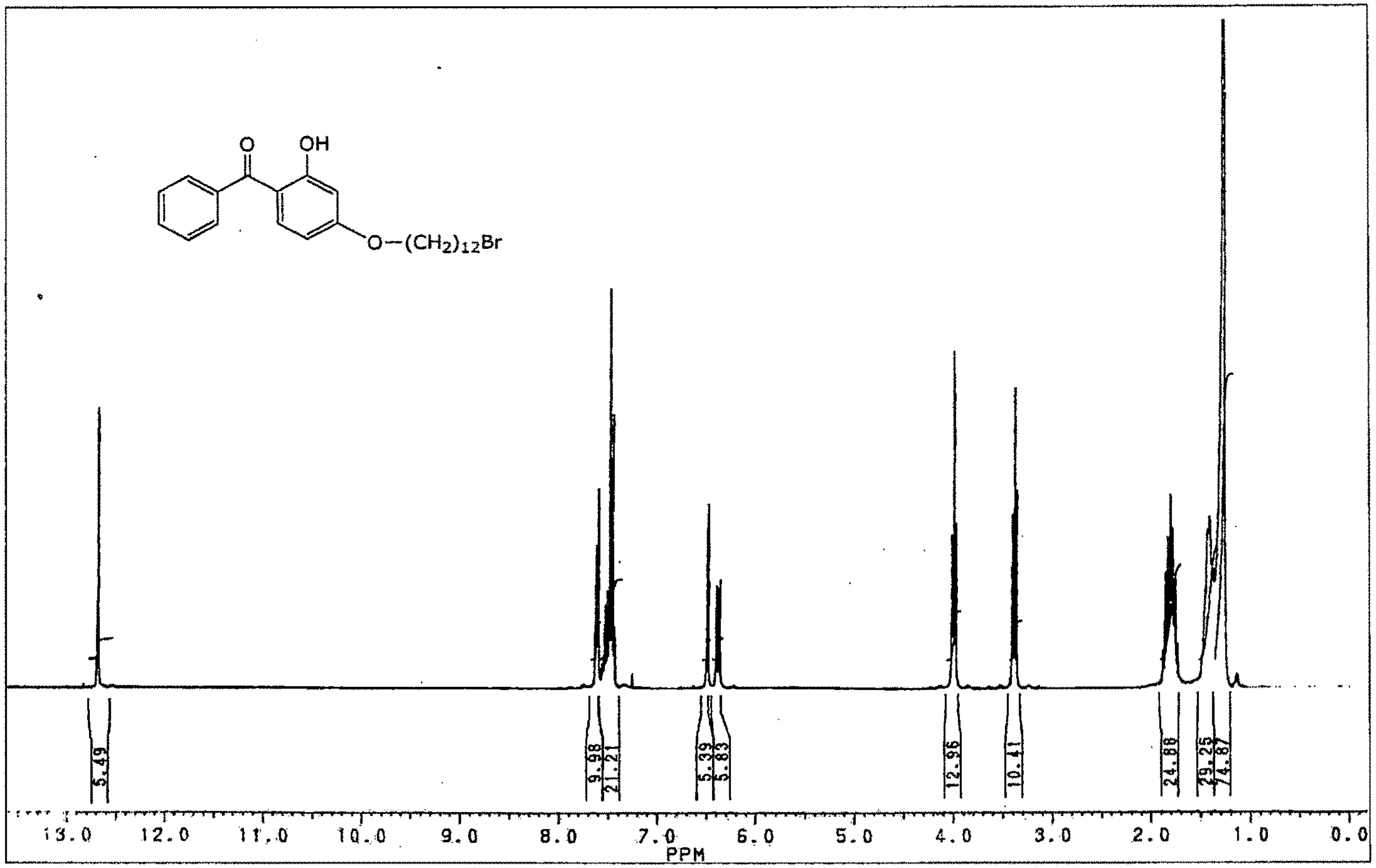


Figure IV.25: PMR Spectrum of the compound 7

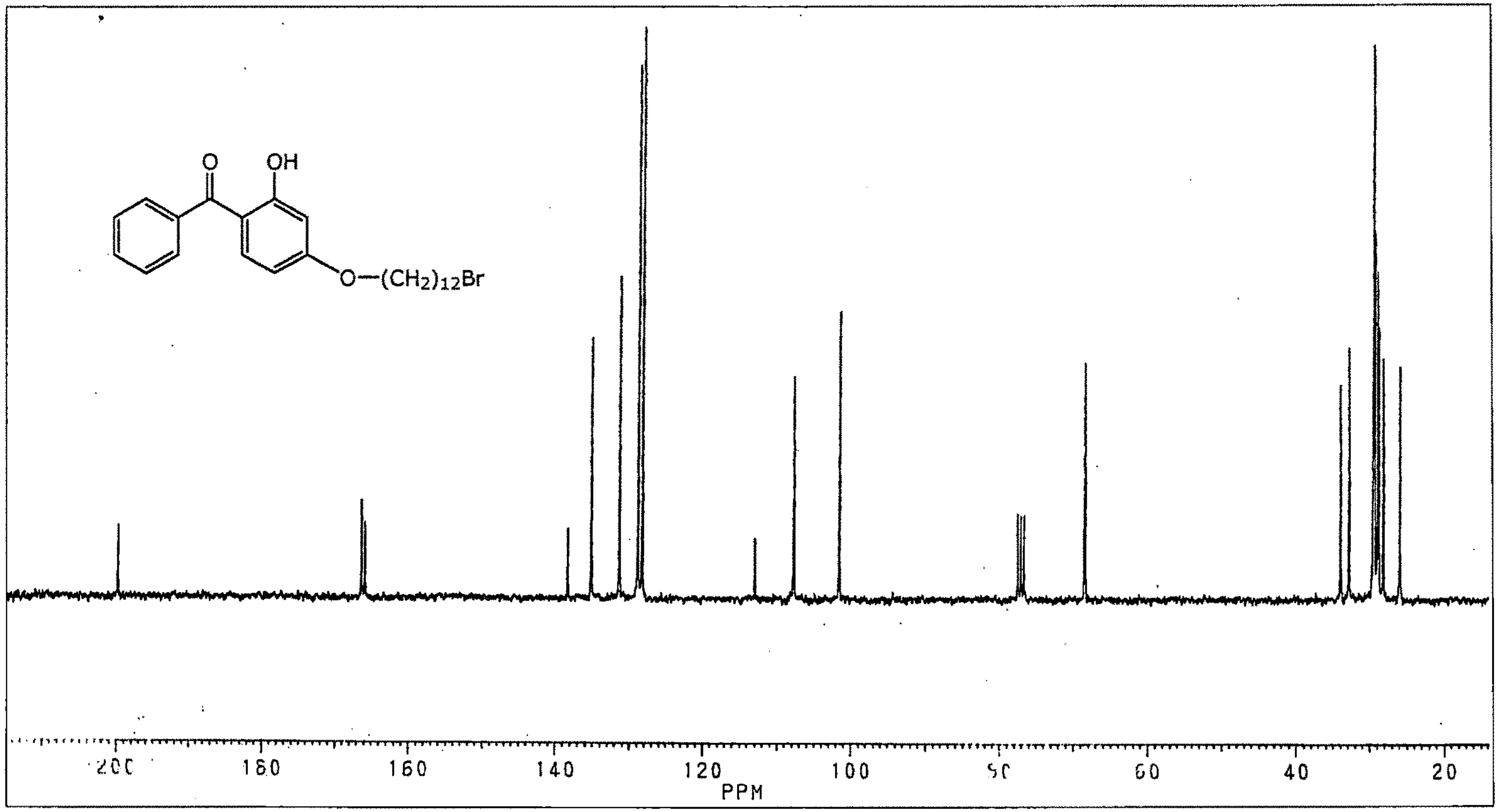


Figure IV.26: ^{13}C NMR of the compound 7

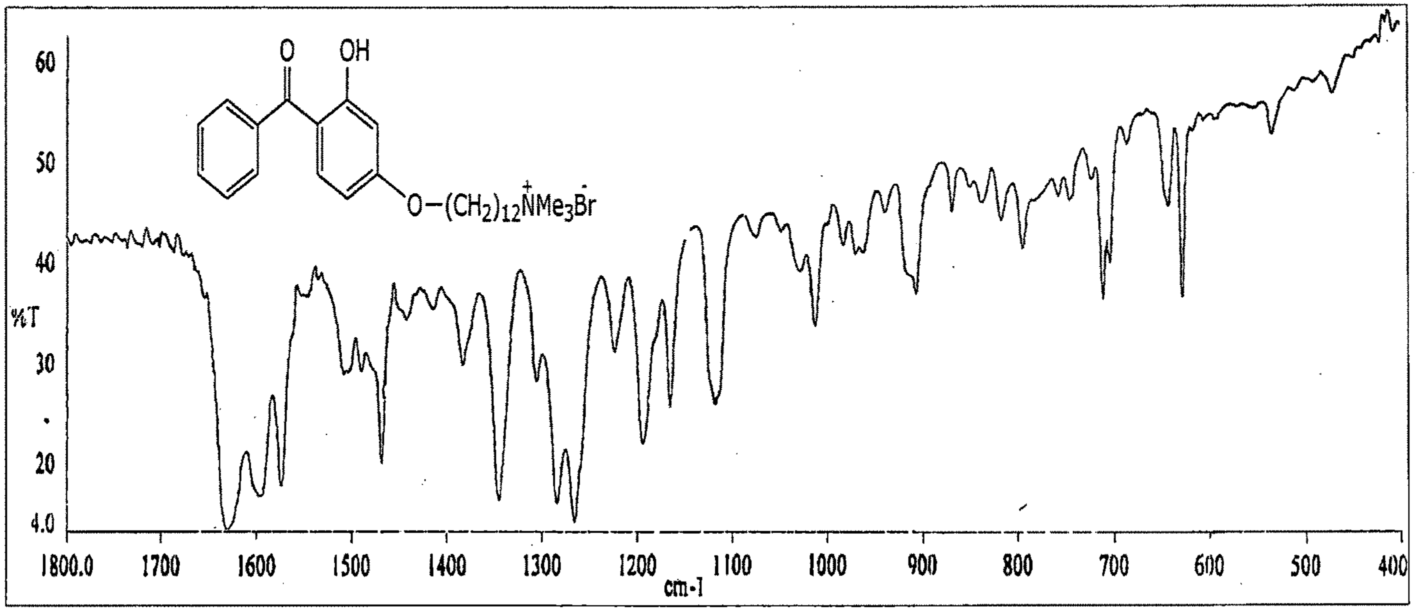


Figure IV.27: FTIR Spectrum of the compound 8

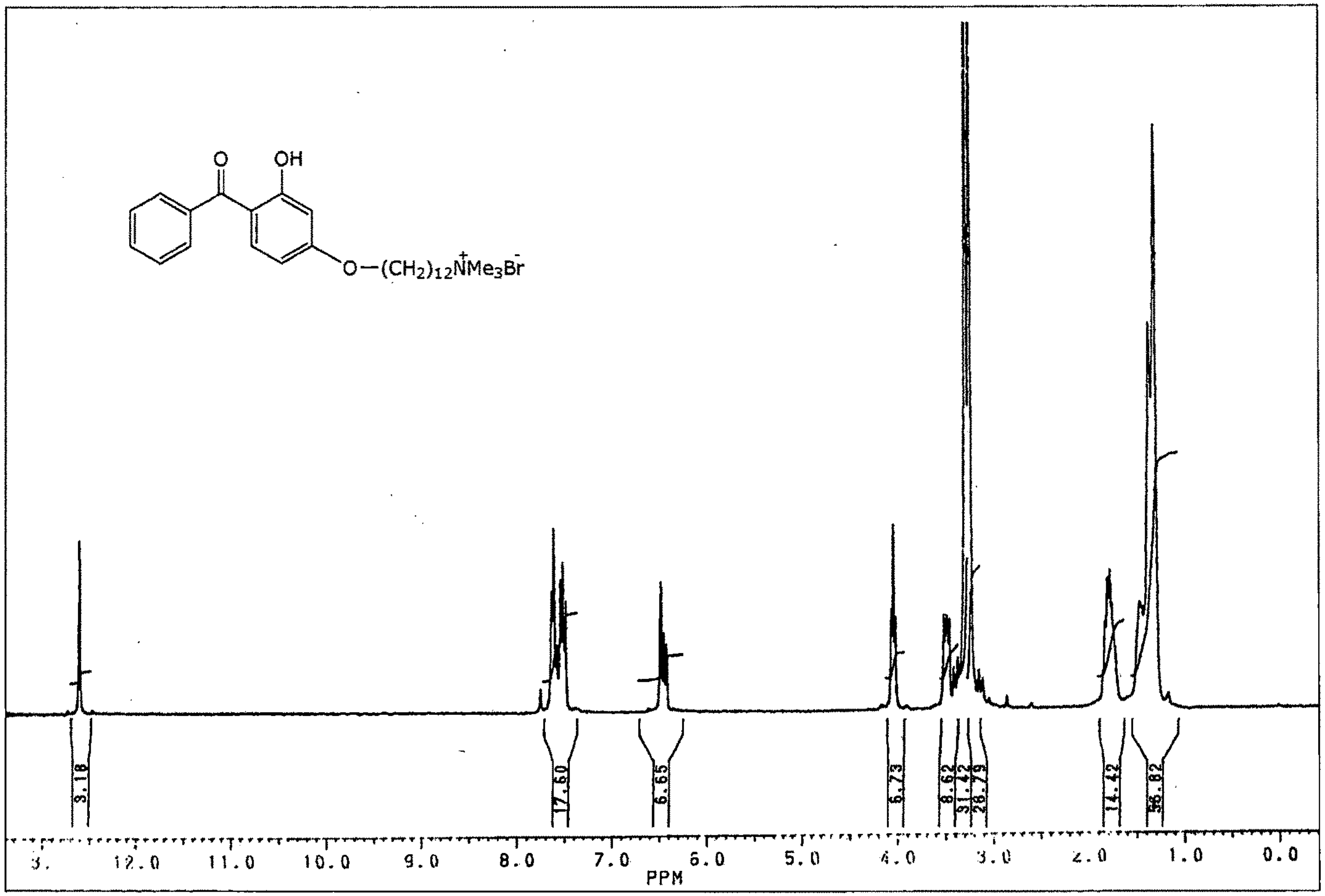


Figure IV.28: PMR Spectrum of the compound 8

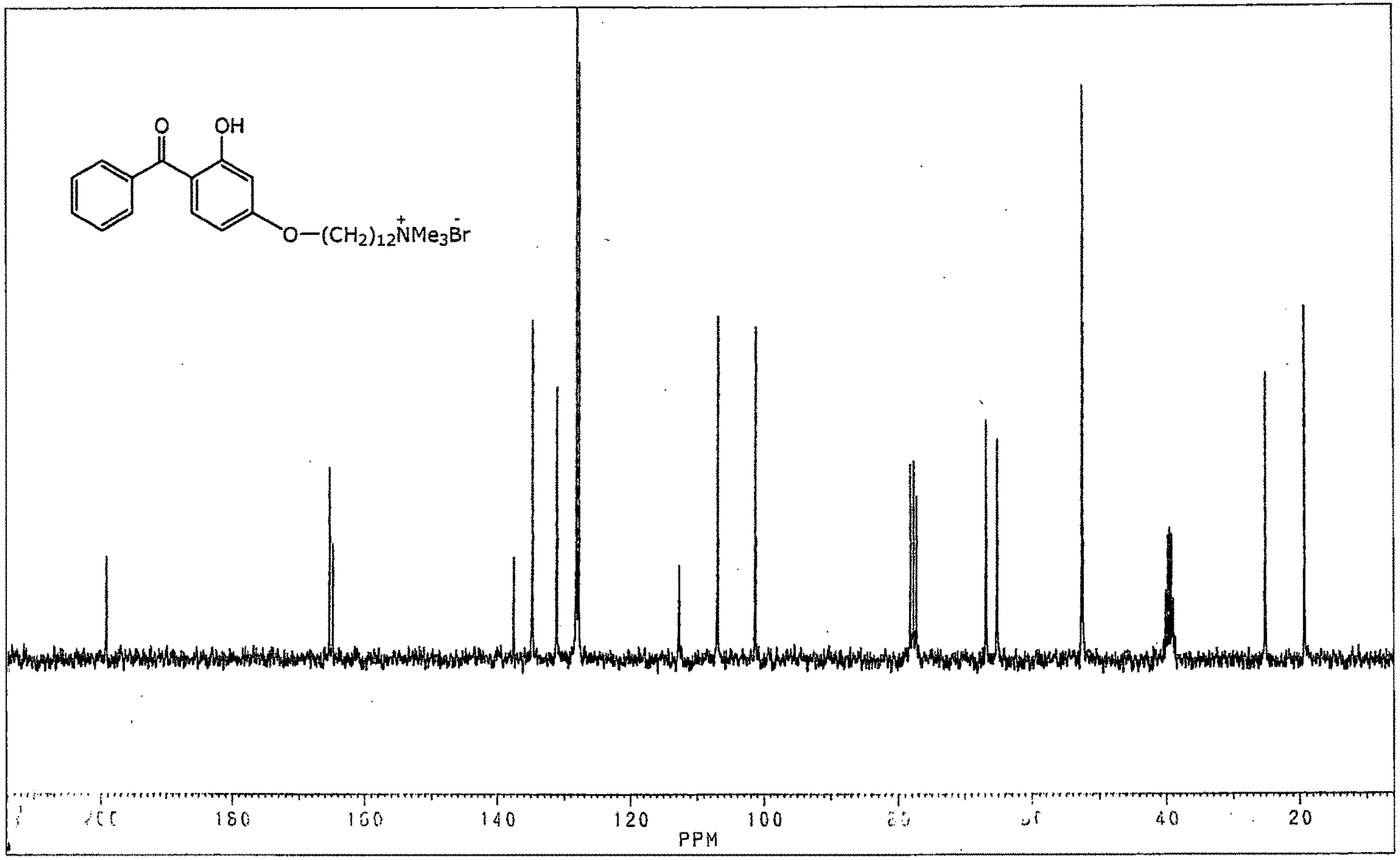


Figure IV.29: ^{13}C NMR of the compound 8

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