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(54) Title: ALDEHYDE PHENOL CONDENSATES

(57) Abstract: A solvent-soluble oligomer or polymer comprising an open-chain condensate of an aldehyde of formula R - CHO (I). Wherein R is a substituted or unsubstituted hydrocarbon group, for example, an alkyl group, or a fluorinated alkyl group, having from 5 to 20 carbon atoms, an alkenyl group, or a fluorinated alkenyl group, having from 5 to 20 carbon atoms, an aralkyl group, or a fluorinated aralkyl group, having from 5 to 20 carbon atoms, or a substituted or non-substituted aryl or fluorinated aryl group, or a precursor or derivative thereof, with a mono- or polyhydric phenol, or a precursor or derivative thereof. The oligomers and polymers find use, for example, in the surface modification of a wide range of materials.

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ALDEHYDE PHENOL CONDENSATES

This invention relates to aldehyde phenol condensates, and more particularly to certain novel oligomers and polymers, and mixtures thereof, prepared by the condensation of aldehydes and phenols and precursors or derivatives thereof, and optional introduction of surface reactive groups.

Phenol-aldehyde resins manufactured by polycondensation processes are widely used in industry. An example of such a manufacturing process is described in GB 1089936. Aldehyde-resorcinol condensations have also been described by Niederl and Vogel, J. Am. Chem. Soc. (1940), 62, 2512-14 and Sen and Sinha, J. Am. Chem. Soc. (1923), 45, 2984-96.

Aldehyde phenol cyclic condensates are also known, and, for example, certain cyclic tetrameric structures known variously as calixarenes and cone-type calix [4] resorcinarenes have been described in WO97/39077 and EP0671220, together with their use as surface modifying agents. Calixarenes can be prepared, for example, from polyhydric phenols and aldehydes by acid-catalysed condensation in an organic solvent under reflux or elevated temperature conditions. A detailed review of the different types of calixarenes and their methods of manufacture is given in Bohmer, Angew. Chem. Int. Ed. Engl. 1995, 34, 713-715.

Calixarenes can be difficult to purify, and separation from coloured impurities can also be difficult, which somewhat reduces their useful applications. The development of new aldehyde phenol condensates, which are simpler to manufacture and have improved properties,

would therefore be highly desirable.

Certain new open-chain oligomers and polymers, and mixtures of such oligomers and polymers have now been
5 discovered, which are prepared by the acid catalysed condensation of an aldehyde and a mono- or polyhydric phenol, or their precursors or derivatives.

In a first aspect, the invention provides a solvent-
10 soluble oligomer or polymer comprising an open-chain condensate of an aldehyde of formula:



15

wherein R is a substituted or unsubstituted hydrocarbon group, for example, an alkyl group, or a fluorinated alkyl group, having from 5 to 20 carbon atoms, an alkenyl group, or a fluorinated alkenyl group, having from 5 to
20 20 carbon atoms, an aralkyl group, or a fluorinated aralkyl group, having from 5 to 20 carbon atoms, or a substituted or non-substituted aryl or fluorinated aryl group, which alkyl, alkenyl, aralkyl or aryl groups may contain substituent hetero-atoms, or a precursor or
25 derivative thereof, with a mono- or polyhydric phenol, or a precursor or derivative thereof.

In a second aspect, the invention provides a method of manufacturing a solvent-soluble oligomer or polymer
30 comprising an open-chain condensate of an aldehyde of formula (I), or a precursor or derivative thereof, and a mono- or polyhydric phenol, or a precursor or derivative thereof, which comprises condensing the aldehyde and the phenol, or their precursors or derivatives, in the
35 presence of an acid catalyst.

In a third aspect, the invention provides a solvent-soluble open-chain oligomer or polymer, or a mixture of oligomers or polymers, or both, prepared by the acid catalysed condensation of an aldehyde of formula (I), or
5 a precursor or derivative thereof, and a mono- or polyhydric phenol, or a precursor or derivative thereof.

In a fourth aspect, the invention provides a method of
10 changing the surface properties of a material, which comprises contacting the material with a solution or dispersion of an oligomer or polymer comprising an open-chain condensate of an aldehyde of formula (I), or a precursor or derivative thereof, and a mono- or
15 polyhydric phenol, or a precursor or derivative thereof, in a liquid medium.

It has been found to be unnecessary to isolate or purify individual oligomers and polymers from the condensation
20 reaction mixture, and for many applications it is preferred to use a mixture of oligomers and/or polymers for changing the surface properties of a material in the fourth aspect of the invention.

25 It is frequently found that the reaction products of the method of the second aspect of the invention are colourless mixtures, and for many purposes these are preferred for use in the fourth aspect of the invention.

30 In formula (I) the group R can be a substituted or unsubstituted hydrocarbon group, preferably an alkyl group, an alkenyl group, an aralkyl group, or similar, and may contain hetero-atoms, for example, oxygen, nitrogen or sulphur atoms in the alkyl or alkenyl chain,
35 or in substituent side groups of the alkyl, alkenyl or

aralkyl groups.

The group R is preferably an alkyl group having from 6 to 18 carbon atoms, more preferably from 7 to 15 carbon atoms, and most preferably from 9 to 12 carbon atoms. R may be a straight chain or branched chain alkyl group, and may have other substituents having hydrophobic properties, for example, fluorine atoms. Preferably the group R is a perfluoroalkyl group, preferably comprising from 10 to 30 fluorine atoms, more preferably from 15 to 25 fluorine atoms, or an alkyl chain terminated with a perfluoroalkyl segment having, for example, 6, 8 or 10 carbon atoms.

In other embodiments the group R can comprise a plurality of repeating units such as $(-\text{CH}_2-\text{CH}_2-\text{O}-)$, one or more end groups such as $-(\text{OCH}_2\text{CH}_2)_m\text{OMe}$, and/or nitrogen heterocyclic groups, for example, pyridyl and/or N-alkyl and S-alkyl groups. The terminal segment can comprise, for example, perfluoroalkenyl or hydroxyperfluoroalkyl.

Examples of suitable aldehydes include hexanal, octanal, decanal, undec-10-al, dodecanal, perfluoro-1-H-2,2-H-hexanal, perfluoro-1-H-2,2-H-octanal and perfluoro-1-H-2,2-H-decanal.

Where R is an alkenyl group (which term in this specification includes both alkene and alkyne groups), the oligomers and polymers of the invention can be further chain extended or cross-linked, and this is a further aspect of the invention. Chain extension or cross-linking can be accomplished, for example, by the use of ultraviolet light, irradiation, or by other free-radical initiators. Chain extension or cross-linking may, for example, improve the binding of the aldehyde

where m is an integer, preferably from 1 to 16, more preferably from 1 to 4, phenol condensate to a substrate surface, improve the strength of any mono- or multilayer film present on the surface, or provide sites for binding
5 other reactive groups.

Precursors and derivatives of the aldehyde of formula (I) include the corresponding acetals, for example O-1, 3-dioxanylethyl-O-methyltriethyleneglycol, and the
10 corresponding imines.

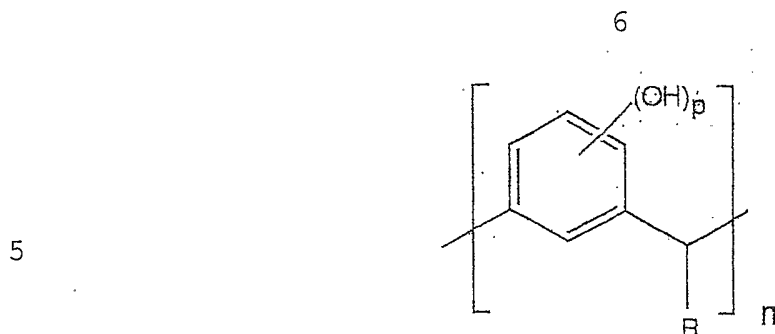
The mono- or polyhydric phenol preferably comprises a hydroxyl-substituted benzene ring, for example resorcinol or pyrogallol. Other polyhydric phenols which can be
15 used include, for example, orcinol (5-methylbenzene-1,3-diol), 2- and 5-alkylresorcinols, and 5-methoxyresorcinol. Mono- or polyhydric phenols comprising more than one aryl group, or fused aryl groups are, however, not excluded. Examples of such more complex
20 phenols include, for example, dihydroxynaphthalenes.

Precursors and derivatives of mono- and polyhydric phenols that may be used in the invention include, for
25 example, phenyl ethers.

In a preferred embodiment of the invention, the oligomer or polymer is an open-chain condensate comprising the
unit:

30

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where n is an integer greater than or equal to 1, p is 2 or 3, and R is as previously defined, the condensate
 10 having at least one terminal group selected from H atoms, alkenyl groups, hydroxyalkyl groups, dihydroxyaryl groups, trihydroxyaryl groups, perfluoroalkyl groups and perfluoroalkenyl groups.

15 Preferably n is an integer of from 2 to 6.

In addition to the terminal groups recited above, the new oligomers and polymers in accordance with the invention can also be terminated by other chain terminating atoms
 20 or groups, as desired.

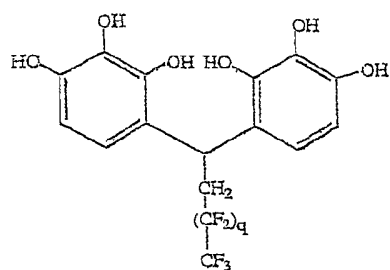
The oligomers and polymers of the present invention preferably have molecular masses of less than around 2500 Daltons, more preferably less than 2000, most preferably
 25 less than 1500 Daltons.

Specific examples of oligomers and polymers according to

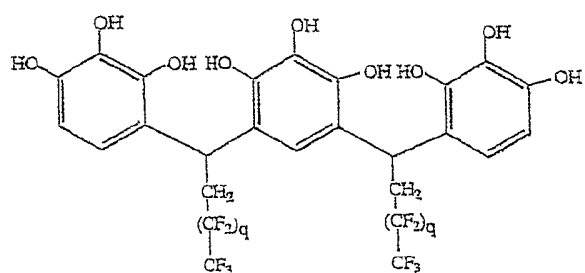
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the invention include:

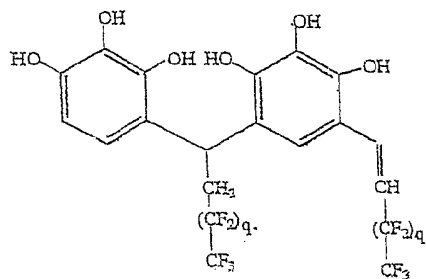
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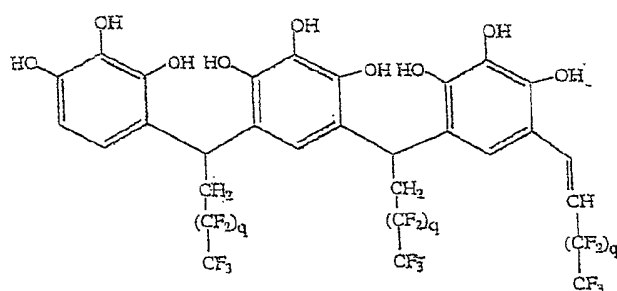
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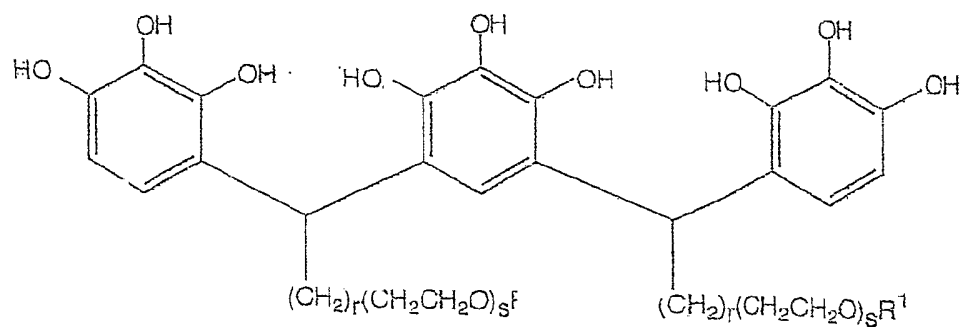
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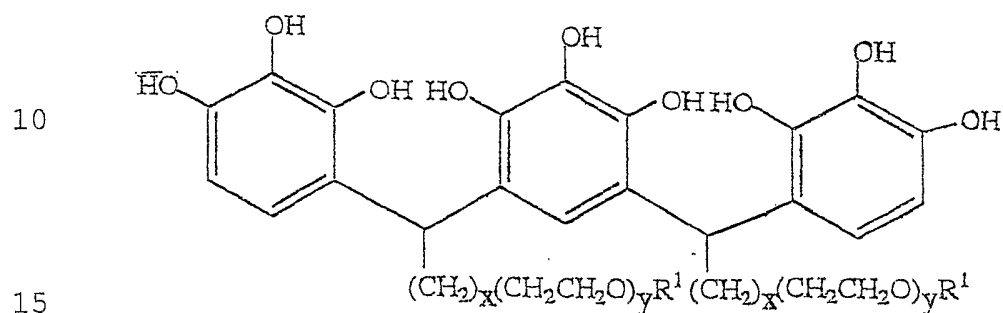
Where q is an integer of from 6 to 18,

30

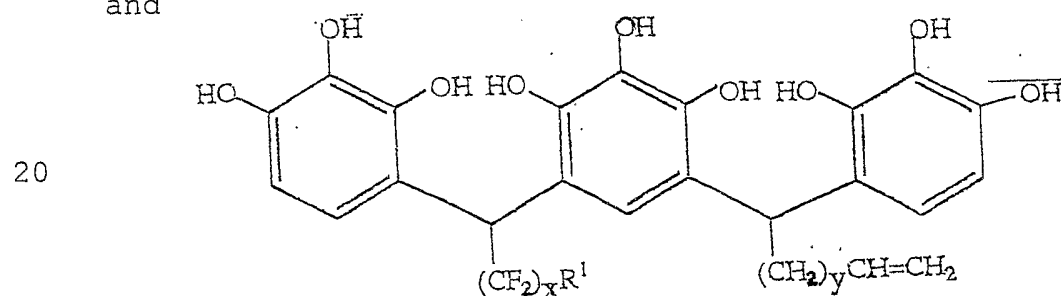


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Where r is an integer of from 1 to 3, s is an integer of from 2 to 4, and R^1 is $-\text{CF}_3$, an alkyl group, or a branched perfluoroalkyl group,



and



Where x is an integer of from 6 to 18, preferably 1 to 3, y is an integer of from 4 to 16, preferably 2 to 4, and R_1 is as before.

30 The condensation reaction can be performed at ambient temperatures, although the use of elevated temperatures is not excluded, provided that the principal products of the reaction are open-chain condensates. Preferably the condensation reaction is carried out at a temperature of

35 from 15 to 30°C.

It has been found that the products of the condensation

reaction also depend upon the reaction time. A reaction time of from 1 to 48 hours, preferably from 10 to 20 hours, for example, about 16 hours, is usually appropriate, but shorter or longer times can be used to produce different product mixtures as desired.

The condensation reaction is preferably carried out without the presence of a solvent, and for example, the reactants, together with the acid catalyst, can be ground together in a suitable vessel. It has been found that such solventless procedures usually give rise to colourless products, usually in a period of minutes. Where a solvent is present, it has been found that the nature of the organic solvent influences the chain length of the oligomers and polymers. Suitable solvents that may be used are aprotic organic solvents such as, for example, tetrahydrofuran (THF), ethyl acetate, and ether.

The nature of the catalyst influences the reaction yield, and strong acids such as hydrochloric acid, trifluoroacetic acid and sulphuric acid are preferred. Other acids that can be used include toluene-p-sulfonic acid and oxalic acid.

The ratio of the reactants influences the complexity of the product mixture obtained, and preferred equivalent ratios include, for example, 1:1, 1:1.5, and 2:1 phenol:aldehyde.

The method of the fourth aspect of the invention can be used to change the surface properties of a wide range of materials. In many instances, the method can be used to change the contact angle of a surface to water or oil droplets, or to render a surface hydrophobic or water repellent and/or oleophobic or oil repellent. In this

aspect, the method can be applied to a wide range of substrates, and especially hydrophilic substrates including, for example, paper, cotton, wood, leather, hair, teeth; metals, for example, steel, zinc, copper, nickel, and aluminium; stone, glass; fabrics (especially hydrophilic synthetic fabrics), and hydrophilic polymeric materials. Other substrates, such as plastics materials and metals can be rendered oleophobic by the method of the invention. Oleophobic properties are particularly improved by the use of fluoro-substituted aldehyde phenol condensates according to the invention. For example, application of the fluoro-substituted condensates in aqueous emulsions, after drying, can render surfaces painted with emulsion paint both hydrophobic and oleophobic. An important potential application of aldehyde phenol condensates of the invention comprising polyethylene glycol pendant chains and their terminal alkyl ethers, is in the inhibition of protein adhesion, notably but not exclusively when applied to biomedical inserts and related devices. Other surface properties, for example, conductivity, may also be changed by the method of the invention.

In the method of the fourth aspect of the invention, the aldehyde phenol condensate solution or dispersion can simply be sprayed on to the substrate, or the substrate can be dipped into the solution or dispersion as appropriate. The aldehyde phenol condensate can be applied dissolved or dispersed in an organic solvent, such as, for example, tetrahydrofuran or acetone. Alternatively, the aldehyde phenol condensate can be applied as a dilute aqueous emulsion, comprising a small quantity of a volatile organic solvent. The concentration of the aldehyde phenol condensate in the solvent or emulsion is preferably from 0.001 to 10% by weight, more

preferably from 0.01 to 5% by weight, most preferably from 0.05 to 1.5% by weight. The method is preferably carried out at ambient temperatures up to about 30°C.

5 In another important fifth aspect of the invention, the phenol aldehyde condensates of the first aspect of the invention can be further reacted to introduce surface reactive groups into the oligomer or polymer chain. By "surface reactive groups" in this specification is meant
10 groups which are capable of reacting with surfaces in order to bind the oligomer or polymer thereto. Such groups include, for example, aromatic ring substituents such as amino groups, especially when flanked by hydroxyl groups, and unsaturated ether groups.

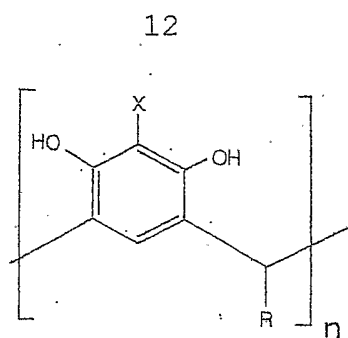
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In the method of the fifth aspect of the invention, the aldehyde phenol condensates of the first aspect of the invention can, for example, be reacted with primary or secondary amines together with formaldehyde to give
20 Mannich products in which a hydrogen atom flanked by hydroxyl groups on a aromatic ring is replaced by a monoalkylaminomethyl or dialkylaminomethyl group. Such new oligomers and polymers can give improved binding to metals and are also included in the invention. Such
25 compounds can, for example, have the formula:

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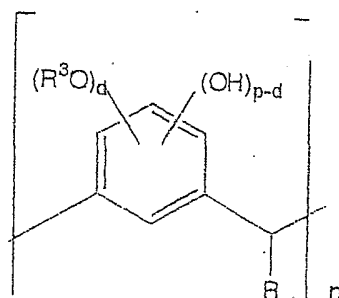
Where X is $-\text{CH}_2\text{NR}^2_2$ or $-\text{OR}^2$, R^2 is a substituted or unsubstituted alkyl or alkenyl group, preferably having from 1 to 6 carbon atoms, and R and n are as previously defined.

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20

In another example of the method of the fifth aspect of the invention, the aldehyde phenol condensates of the first aspect of the invention can be partially or completely etherified by treatment with a base and an appropriate alkenyl halide, for example, an allyl or propargyl halide, to insert one or more polymerisable groupings into the aromatic ring which are important for film durability in certain applications of the method of the fourth aspect of the invention. Such new oligomers and polymers are also included in the invention and can, for example, have the formula:

13



5
10 Where R^3 is a polymerisable group, for example, an alkenyl, alkynyl, or alkoxycarbonyl group, p is 2 or 3, is 1 or 2, and n is as previously defined.

15 Various embodiments of oligomers and polymers and methods of manufacturing and using them in accordance with the invention are illustrated by the following Examples.

20 Evaluation of the surface modifications obtained is by dip and dry treatment of standard kitchen paper with known concentrations of oligomers and polymers followed by drying under standard conditions in air either at ambient temperature or at 140°C. Oil refers to standard reagent grade liquid paraffin. NMR refers to proton NMR in acetone. MALDI refers to matrix assisted desorption ionisation spectrometry which is a non-fragmenting method for obtaining molecular masses in the region 500 to 25,000 daltons. THF refers to tetrahydrofuran and TFA refers to trifluoroacetic acid.

Example 1

Perfluoro-1-H-2,2-H-decanal (0.57 g) (derived from
5 perfluorooctyl iodide and ethyl vinyl ether) together
with resorcinol (136 mg, 1 equiv.) in tetrahydrofuran
(THF) (4.5 ml.) were treated with conc. hydrochloric acid
(1ml.). The mixture was stirred at 20°C for 24h. The
slightly turbid mixture was evaporated *in vacuo* at 25mm
10 and 50°C to give a residue (660 mg.) MALDI (Figure 1)
spectrometry showed molecular weight (663) consistent
with a 2:1 phenol:aldehyde condensate as the main
product. NMR was consistent with this structure. This
material gave high and persistent contact angles with
15 water and with oil on kitchen paper treated by dipping in
a 0.2% solution of the material in THF at ambient
temperature and drying at 140°. These effects persisted
for at least 5 days. When the kitchen paper was treated
with a 0.1% solution of the material in THF, water beads
20 disappeared after 5 min. but oil beads persisted for at
least 24h.

Example 2

25 Perfluoro-1-H-2,2-H-decanal (513 mg.) and resorcinol (122
mg, 1 equiv.) in ether (5 ml.) were treated with
trifluoroacetic acid (1ml.) and the mixture was stirred
at 20°C for 19h. Evaporation as above gave a residue (513
mg), (MALDI Figure 2). Kitchen paper, treated with this
30 material as a 0.2% solution in THF at ambient
temperature, floated on water for at least 17 h and oil
drops gave high contact angles. Water drops had lower
contact angles than for the pyrogallol derived material
of Example 3 below.

When ethyl acetate was used as the reaction solvent, MALDI spectrometry showed the main product to be the 2:3 phenol:aldehyde condensate.

5 When conc. HCl (1ml.) was used in place of trifluoroacetic acid and with a reaction time of 24 h, the slightly turbid reaction mixture was evaporated to give a product (660 mg) whose MALDI spectrum showed 2:1
10 phenol condensate as well as other products with slightly larger molecular weights. At 0.2% in THF, this material gave oil and water protection over 4 days to kitchen paper floating on the surface of water.

Example 3

15 Perfluoro-1-H-2,2-H-decanal (621 mg) and pyrogallol (169mg, 1 equiv.) in ether (5 ml.) were treated with trifluoroacetic acid (1ml.) and the mixture was stirred at 20° C for 60 h. The mixture was evaporated *in vacuo* at
20 50° to give a residue (657mg.). This material gave high and persistent contact angles with oil on kitchen paper treated by dipping in a 0.2% THF solution of the material at ambient temperature, and drying at 140°. Paper floated for 5 days and there was no oil soak in. The same
25 results were obtained with tetrahydrofuran (THF) as reaction solvent.

When conc. HCl (1ml.) was used in place of trifluoroacetic acid and with a reaction time of 24 h,
30 the slightly turbid reaction mixture was evaporated to give a product (660 mg) whose MALDI (Figure 3) spectrum showed 2:1 phenol condensate as well as other products with slightly larger molecular weights.

At 0.2% in THF, this material gave oil and water
35 protection over 4 days to kitchen paper floating on the

surface of water.

Example 4

5 Perfluoro-1-H-2,2-H-decanal (570 mg) and pyrogallol (233mg, 1.5 equiv.) in THF (5.5 ml.) were treated with conc. hydrochloric (1ml.) and the mixture was stirred at 20°C for 24 h. The mixture was evaporated *in vacuo* at 50° to give a residue (710 mg.) MALDI (Figure 4) spectrometry
10 showed a complex mixture of materials in the molecular weight range 565 to 887.

This material gave high and persistent contact angles with oil on kitchen paper treated with a 0.2% solution in THF, dipped at ambient temperature and dried at 140°.

15 Contact angles with water were low but paper floated on water 5 days and there was no oil soak in.

When, in the method of Example 4, THF was replaced by ethyl acetate as solvent and the reaction was carried out
20 at 20°C for 60 hours, the product was shown by MALDI (Figure 5) spectrometry to contain two sets of oligomers with molecular weights centred at 663 and 1303 respectively. The surface effects were similar to those of Example 4.

25

Example 4a

Perfluoro-1-H-2,2-H-octanal (3.4 g.), pyrogallol (1.18 g. 1 equivalent) and toluene-p-sulfonic acid (5 mg.) were ground together for 10 minutes and then set aside
30 at 20°. After 18 h. the mixture was a viscous gum and after 42 h was an amorphous solid. The product at 0.2% in THF gave excellent long term (<1 week) water and oil resistance to kitchen paper. MALDI showed mass peaks at 1016 and 1032 consistent with a 2:1 aldehyde-pyrogallol condensate (Figure 6).
35

Example 4b

Perfluoro-1-H-2, 2-H-octanal (1.0 g. 2.76 mMol), undec-10-enal (232 mg. 1.38 mMol.) pyrogallol (0.52 g. 4.14 mMol) and toluene-p-sulfonic acid (2.6 mg.) were ground together for 15 minutes and then set aside at 20°. After 60 h., the mixture was ground with light petroleum bp 40-60° to remove any unreacted undecenal and the mixture was filtered to give the product (836 mg). NMR showed incorporation of both aldehydes (terminal vinyl group and perfluoroalkyl chains) in this product and MALDI showed a mixture of many components (Figure 7). A strong peak at 978 was consistent with combination of two pyrogallol residues with one each of the aldehydes. Kitchen paper test at 0.2 % in THF showed 5 minute resistance to oil and water drops.

Example 5

- (i) Decanal (1.1 g.) and pyrogallol (888 mg., 1 equiv.) in tetrahydrofuran (5 ml.) were treated with conc. sulfuric acid (1 drop, 33 mg.) and the mixture was stirred for 65 hr at 20°C. Sodium bicarbonate (60 mg.) was added and after being thoroughly stirred the mixture was poured into ice-water (200 ml.). The gummy insoluble product was removed and dissolved in methanol. Evaporation gave the product (1.45 g.). NMR was consistent with aldehyde-phenol oligomers. Tests of kitchen paper dipped at ambient temperature in a 0.5% tetrahydrofuran solution of the product showed that it conferred the ability to float on water.
- (ii) Decanal (1.2g.) and pyrogallol (969 mg., 1 equiv.)

in tetrahydrofuran (5 ml.) were treated with trifluoroacetic acid (2ml.) and the mixture was stirred for 19 hr at 20°C. A portion (2.5 ml.) of the solution was removed and evaporated to give the product (740 mg.) The NMR showed an aldehyde-phenol condensate and MALDI (Figure 8) was consistent with a 4:4 non cyclic oligomer.

In the kitchen paper drip and dry test using a 0.5% solution in acetone the paper floated for 12h. and gave high contact angles with water. At 0.25%, paper gives a high (ca. 80°) water contact angle but water drops soaked in after 2 min.

After 5 days, the remainder of the solution was evaporated to give a residue (1.29 g.), which was much less soluble in chloroform than the shorter term material. NMR was closely similar to the previous (short reaction time material). MALDI (Figure 9) showed a main product with a slightly higher (1077) molecular weight.

The kitchen paper dip and dry test with a 0.5% solution in acetone showed improved water resistance but lower than in the preceding Examples.

Formation of the aldehyde phenol condensates can also be achieved by grinding the reagents together in the absence of a solvent. Typically, pyrogallol (0.9 g.) and decanal (1.1 g., 1 equiv.) were ground in a pestle and mortar for 15 minutes with toluene-p-sulfonic acid hydrate (15 mg.). The mixture gradually became more and more viscous and at the end of the grinding period gave a free flowing solid. The same results were achieved with the use of 1.2 mg. of toluene-p-sulfonic acid but with a reaction time of 60 hours. The NMR spectrum of the product obtained was essentially identical with that obtained as above. The

paper test gave very high contact angles and excellent persistence using 1% by weight solutions of the product in THF. The product has an advantage over the solution-based procedure of giving essentially colourless test solutions and samples.

Example 6

Decanal (1.418g.) and resorcinol (1g.) in tetrahydrofuran (5 ml.) were treated with trifluoroacetic acid (1 ml.) and the mixture was stirred for 28 hr. Evaporation gave a residue (2.3g.) whose NMR showed phenol-aldehyde condensate. At 0.5% at 20°C in acetone the kitchen paper dip and dry test showed water beading but 2 min soak-in time. At 1% in THF kitchen paper floated on water for many hours and water drops persisted for many hours also.

When the acid catalyst was conc. HCl (1ml.) and THF (7 ml.) was the solvent, NMR again showed the product to be aldehyde-phenol condensate and in the kitchen paper dip and dry test at 0.5% in THF the water soak-in time was again ca 2 min. At 1% in THF there was good persistence of floating and drops but somewhat less well than with TFA catalysis.

Example 6a

Pyrogallol (1 g.), decanal (1.24 g. 1 equivalent) and toluene-p-sulfonic acid (1.2 mg.) were ground together with a pestle and mortar. After 5 min. there was thickening of the mixture and after 2 days it had set to a hard white solid. MALDI showed the main component to be a tetrameric phenol-aldehyde condensate (Figure 10).

Example 6b

Decanal (2.83g.) resorcinol (2g. 1 equivalent) and toluene-p-sulfonic acid (6 mg) were ground together for 10 minutes and then set aside at 20° for 15 h. The hard solid which resulted (was dissolved in acetone (60 ml.) and anhydrous potassium carbonate (15 g.) was added. The mixture was stirred under reflux for 15 minutes and then a solution of propargyl bromide (80% w/w in toluene, 1.2 g. 50% hydroxyl equivalent) in acetone (5 ml.) was added to the refluxing solution in three equal portions at 20 minute intervals. The mixture was then boiled under reflux for 2 days and poured into water (150 ml.). The mixture was extracted with ether (3 x 60 ml.) and the extracts were washed successively with 1M HCL and water. The extracts were dried (and evaporated to give the product (4.5 g.)). The IR spectrum (Figure 11a) showed bands at 3312 cm^{-1} (triple bond C-H) and at 2123 cm^{-1} (C-C triple bond). MALDI showed a mixture of compounds (figure 11). Kitchen paper test for water at 1% in THF showed excellent water resistance

Example 6c

Decanal (7.09 g.) resorcinol (5 g. 1 equivalent) and toluene-p-sulfonic acid (5mg) were ground together for 10 minutes and then set aside at 20° for 15 h. A portion (1 g.) of the hard solid which resulted after 60h. was further ground with dibutylamine (484 mg. 1 equivalent for a Mannich reaction), paraformaldehyde (350 mg., 3 moles excess) and toluene-p-sulfonic acid (5 mg.). After 16 h., the mixture was taken up in acetone (50 ml.) and filtered to remove excess of paraformaldehyde. The filtrates were evaporated in *vacuo* to constant weight to remove any unreacted

dibutylamine, giving the product whose NMR showed a peak for methylene groups adjacent to nitrogen absent from the starting material and an intensified terminal methyl group signal. MALDI showed a mixture of compounds (Figure 12). Reaction schemes for Examples 6b and 6c are illustrated in Figure 14.

Example 7

O-1,3 -Dioxanylethyl -O-methyltriethyleneglycol

Triethyleneglycol monomethyl ether (2.24 g) and 1,3-dioxanylethyl bromide (4g.) (50% excess) were dissolved in 60-80 petrol (20ml). Tetrabutylammonium bromide (0.324g) was added together with sodium hydroxide (14 g.) in water (14 ml.). The mixture was stirred vigorously under reflux for 21 h cooled, and brought close to neutrality by dropwise addition of conc. HCL. After complete neutralisation with acetic acid, the top layer (petrol) was removed and evaporated to give a residue (2.02g) which was kugelled. Fr. 1 bath 125°/25 mm (0.20 g.) Fr 2 bath 240°/9mm (1.15 g) NMR consistent with the coupled structure.

Aldehyde-pyrogallol Condensate

The above dioxanyl PEG ether (910 mg) and pyrogallol (413 mg., 1 mole) were dissolved in ethanol under argon and conc. hydrochloric acid (0.6 ml) was added. The mixture was allowed to stand at 20° for 18h. Water (40 ml) was added, the mixture was warmed and decanted. The

decantate was evaporated (1.3g) (no IR carbonyl group) and was extracted with cold acetone leaving a dark residue A. Evaporation of the acetone solution gave a residue (709 mg) whose NMR spectrum was consistent with
5 an aldehyde phenol condensate. The reaction scheme is illustrated in Figure 15.

The insoluble material A was extracted with boiling THF. Evaporation of the THF solution gave a dark residue which was extracted with cold acetone (15ml) to
10 give a clear extract giving, on evaporation, a residue (190 mg) as a dark powder softening at 97-100° and melting at 157-9°. MALDI was consistent with that of the PEG pyrogallol tetramer together with some lower molecular weight condensates (Figure 13). This
15 material applied on a dip and dry basis at 0.6% in methanol to steel gives a change in contact angle from 70° to 10°.

The reader's attention is directed to all papers and
20 documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.
25

All of the features disclosed in this specification (including any accompanying claims, abstract and

drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

5

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

10

The invention is not restricted to the details of any foregoing embodiments. The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

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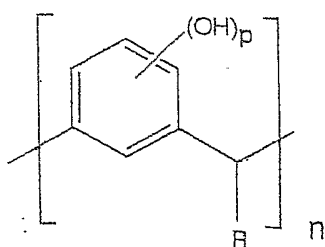
CLAIMS

1. A solvent-soluble oligomer or polymer comprising an
5 open-chain condensate of an aldehyde of formula:
$$R - CHO \quad (I)$$

wherein R is a substituted or unsubstituted hydrocarbon
group, or a precursor or derivative thereof, with a mono-
or polyhydric phenol, or a precursor or derivative
10 thereof.
2. An oligomer or polymer according to claim 1, wherein
R is an alkyl group, or a fluorinated alkyl group,
having from 5 to 20 carbon atoms, an alkenyl group,
15 or a fluorinated alkenyl group, having from 5 to 20
carbon atoms, an aralkyl group, or a fluorinated
aralkyl group, having from 5 to 20 carbon atoms, or
a substituted or non-substituted aryl or fluorinated
aryl group, which alkyl, alkenyl, aralkyl or aryl
20 groups may contain substituent hetero-atoms.
3. An oligomer or polymer according to claim 2, in
which R is an alkyl group, an alkenyl group, a
hydroxyalkyl group or a perfluoroalkyl group.
25
4. An oligomer or polymer according to any one of
claims 1 to 3, that is present in a mixture of such
oligomers or polymers.
- 30 5. An oligomer or polymer according to any one of the
preceding claims, that is colourless.
6. An oligomer or polymer according to any one of the
preceding claims, in which the group R is an alkyl
35 group having from 7 to 15 carbon atoms.

25

7. An oligomer or polymer according to claim 6, in which the group R is a fluorinated alkyl group.
- 5 8. An oligomer or polymer according to any one of claims 1 to 5, in which the group R is an alkenyl group having from 7 to 15 carbon atoms.
- 10 9. An oligomer or polymer according to claim 8, that is capable of chain extension or cross-linking in the presence of a free-radical initiator.
- 15 10. An oligomer or polymer according to any one of the preceding claims, wherein the mono- or polyhydric phenol comprises a hydroxyl-substituted benzene ring.
- 20 11. An oligomer or polymer according to any one of the preceding claims, which is an open-chain condensate comprising the units:



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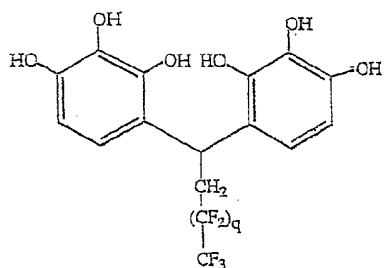
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where n is an integer greater than or equal to 1, p is 2 or 3, and R is as previously defined, the condensate having at least one terminal group selected from H atoms, alkenyl groups, hydroxyalkyl groups, dihydroxyaryl groups and trihydroxyaryl groups.

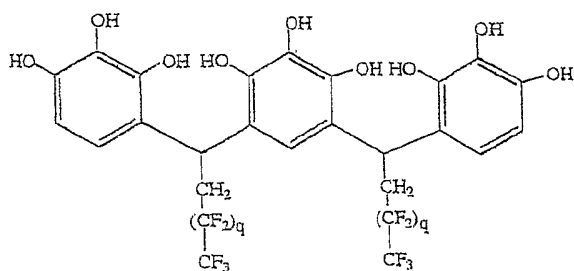
12. An oligomer or polymer according to claim 11, wherein n is an integer of from 2 to 4.
13. An oligomer or polymer according to any one of the preceding claims, having a molecular mass of less than 2000 Daltons.
14. An oligomer or polymer according to one of the following formulae:

27

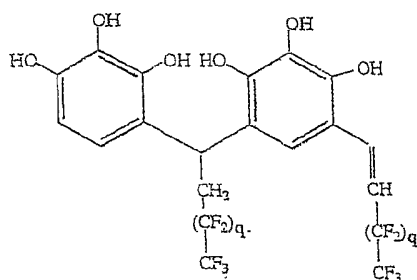
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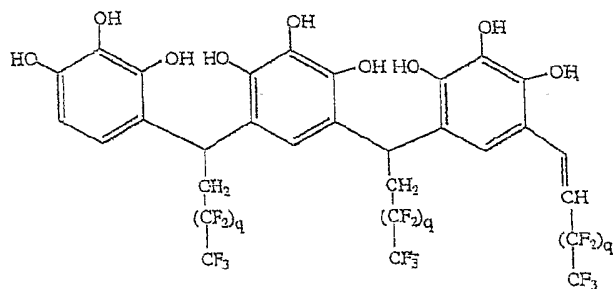
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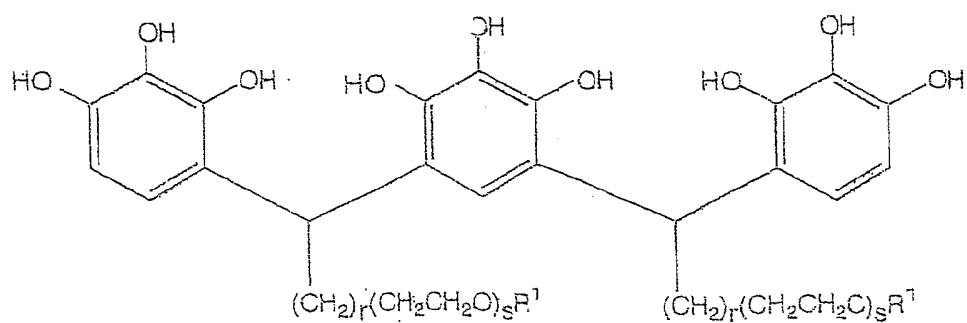


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Where q is an integer of from 6 to 18.

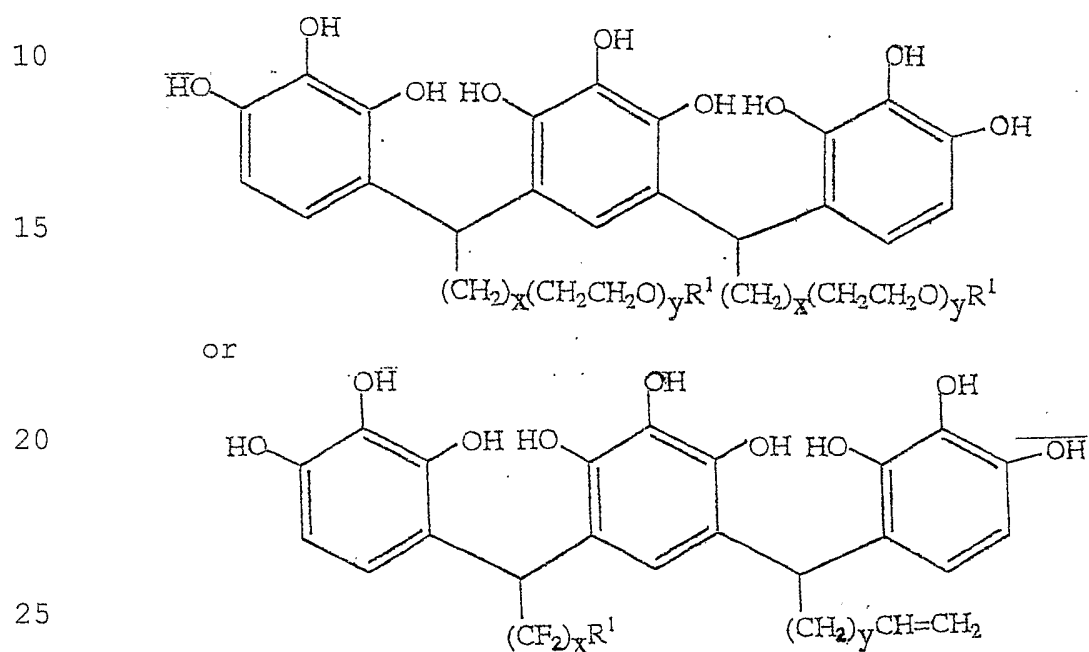
30 15. An oligomer or polymer according to the formula:

35



where r is an integer of from 1 to 3, s is an integer of from 2 to 4 and R^1 is $-\text{CF}_3$ or a branched perfluoroalkyl group.

16. An oligomer or polymer according to the formula:



Where x is an integer of from 6 to 18, y is an integer of from 4 to 16 and R^1 is $-\text{CF}_3$, an alkyl group, or a branched perfluoroalkyl group.

17. An oligomer or polymer substantially as hereinbefore described.

18. A method of manufacturing a solvent-soluble oligomer or polymer comprising an open-chain condensate of an aldehyde of formula (I), or a precursor or derivative thereof, and a mono- or polyhydric phenol, or a precursor or derivative thereof, which comprises condensing the aldehyde and the phenol, or their precursors or derivatives, in the presence of an acid catalyst.
19. A method according to claim 18, wherein the group R in formula (I) is an alkyl group having from 7 to 15 carbon atoms.
20. A method according to claim 18 or 19, wherein the group R is a fluorinated alkyl group.
21. A method according to any one of claims 18 to 20, wherein the group R is a perfluorinated alkyl group comprising from 15 to 25 fluorine atoms.
22. A method according to any one of claims 18 to 21, wherein the aldehyde is hexanal, octanal, decanal, undec-10-al, dodecanal, perfluoro-1-H-2,2-H-hexanal, perfluoro-1-H-2,2-H-octanal and perfluoro-1-H-2,2-H-decanal.
23. A method according to any one of claims 18 to 22, wherein the group R is an alkenyl group.
24. A method according to claim 23, which further comprises polymerising the condensate in the presence of a free-radical initiator.
25. A method according to any one of claims 18 to 24, in which the mono- or polyhydric phenol comprises a

hydroxyl-substituted benzene ring.

26. A method according to any one of claims 18 to 25, in
which the mono- or polyhydric phenol is resorcinol
5 or pyrogallol.
27. A method according to any one of claims 18 to 26, in
which the precursor or derivative of the aldehyde of
formula (I) is an acetal or an imine.
10
28. A method according to any one of claims 18 to 27, in
which the precursor or derivative of the mono- or
polyhydric phenol is a phenyl ether.
- 15 29. A method according to any one of claims 18 to 28,
that is carried out at a temperature of from
15 to 30°C.
- 20 30. A method according to any one of claims 18 to 29,
that is carried out in the presence of an aprotic
organic solvent.
31. A method according to any one of claims 18 to 30,
that is carried out in the presence of a strong acid
25 catalyst.
32. A method according to any one of claims 18 to 31,
wherein the phenol to aldehyde equivalent ratio is
from 1:1 to 2:1.
30
33. A method according to any one of claims 18 to 32,
which further comprises reacting the phenol aldehyde
condensate to introduce surface reactive groups into
the oligomer or polymer chain.
35

34. A method according to claim 33, which comprises the step of reacting the aldehyde phenol condensate with a primary or secondary amine together with formaldehyde to give a Mannich product in which a hydrogen atom flanked by hydroxyl groups on an aromatic ring is replaced by a monoalkylaminomethyl or dialkylaminomethyl group.
35. A method according to claim 34, in which the amine is dibutylamine.
36. A method according to claim 33, which comprises the step of partially or completely etherifying the aldehyde phenol condensate with a base and an alkenyl halide to insert polymerisable groups therein.
37. A method according to claim 36, in which the alkenyl halide is an allyl or propargyl halide.
38. A method for the manufacture of an oligomer or polymer substantially as described in the Examples.
39. A method for the manufacture of an oligomer or polymer substantially as hereinbefore described.
40. A solvent-soluble open-chain oligomer or polymer, or a mixture of oligomers or polymers, or both, prepared by the acid catalysed condensation of an aldehyde of formula (I), or a precursor or derivative thereof, and a mono- or polyhydric phenol, or a precursor or derivative thereof.
41. An oligomer or polymer prepared by a method

according to any one of claims 18 to 39.

42. An oligomer or polymer, or mixture of oligomers or polymers, or both, according to any one of claims 1 to 17 when prepared by a method according to any one of claims 18 to 39.

43. A method of changing the surface properties of a material, which comprises contacting the material with a solution or dispersion of an oligomer or polymer comprising an open-chain condensate of an aldehyde of formula (I), or a precursor or derivative thereof, and a mono- or polyhydric phenol, or a precursor or derivative thereof, in a liquid medium.

44. A method according to claim 43, wherein there is used a mixture of oligomers and/or polymers.

45. A method according to claim 44 or 45, wherein there is used an oligomer or polymer according to any one of claims 1 to 17.

46. A method according to any one of claims 43 to 45 wherein there is used an oligomer or polymer prepared by a method according to any one of claims 18 to 39.

47. A method according to any one of claims 43 to 46, in which the aldehyde phenol condensate is applied dissolved or dispersed in an organic solvent.

48. A method according to claim 47, wherein the concentration of the aldehyde phenol condensate in the solvent is from 0.01 to 5% by weight.

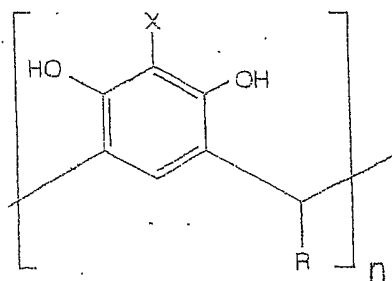
49. A method of changing the surface properties of a substrate substantially as described in the Examples.

5

50. A method of changing the surface properties of a substrate substantially as hereinbefore described.

51. An oligomer or polymer having the formula:

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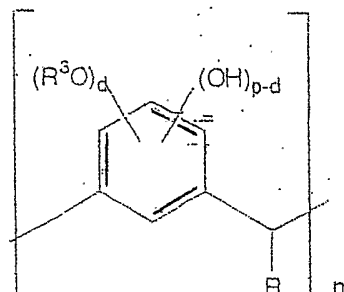
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Where X is $-\text{CH}_2\text{NR}^2_2$ or $-\text{OR}^2$, R^2 is a substituted or unsubstituted alkyl or alkenyl group, preferably having from 1 to 6 carbon atoms, R is a substituted or unsubstituted hydrocarbon group and n is an integer greater than or equal to 1.

20

52. An oligomer or polymer having the formula:

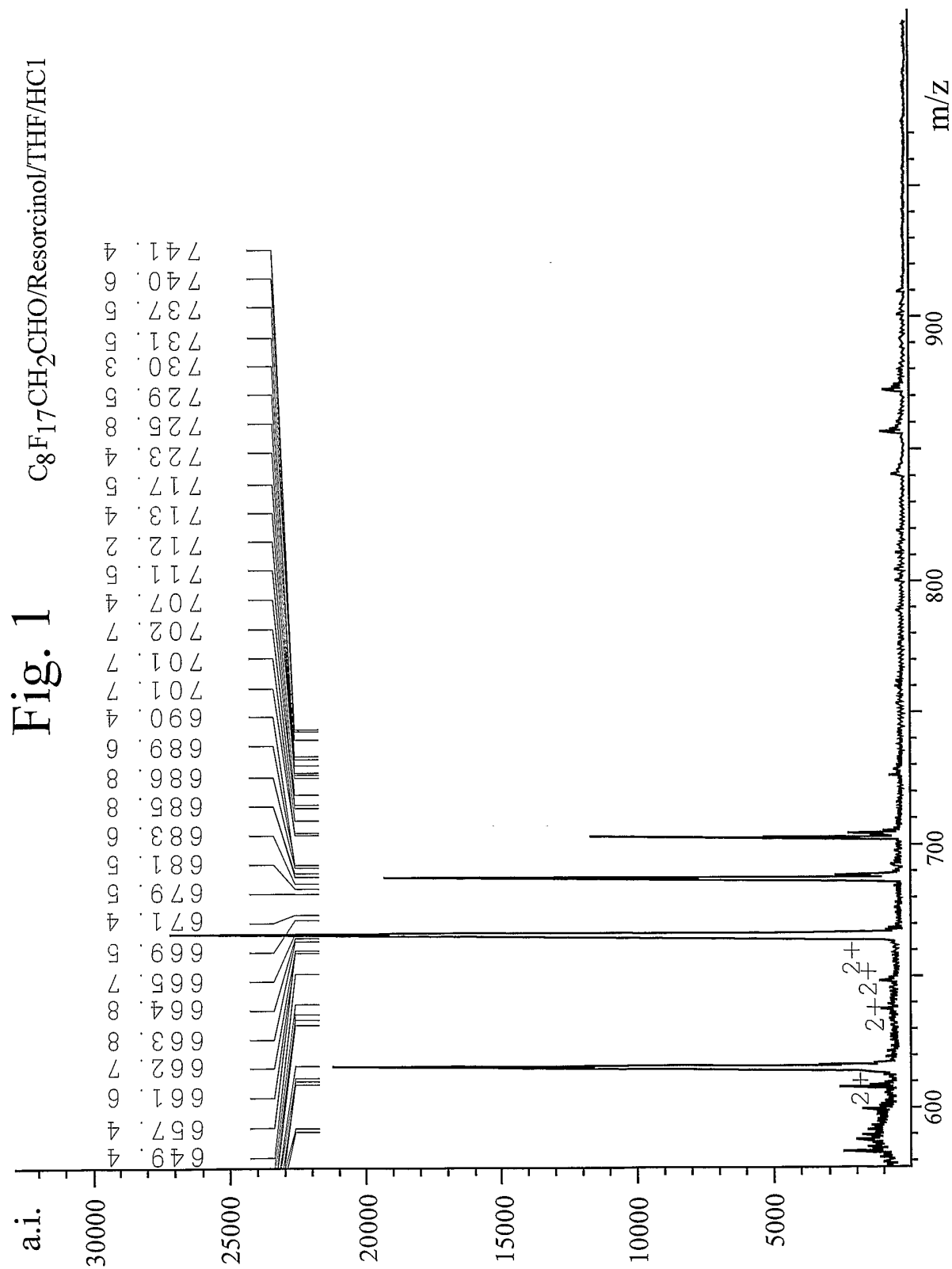
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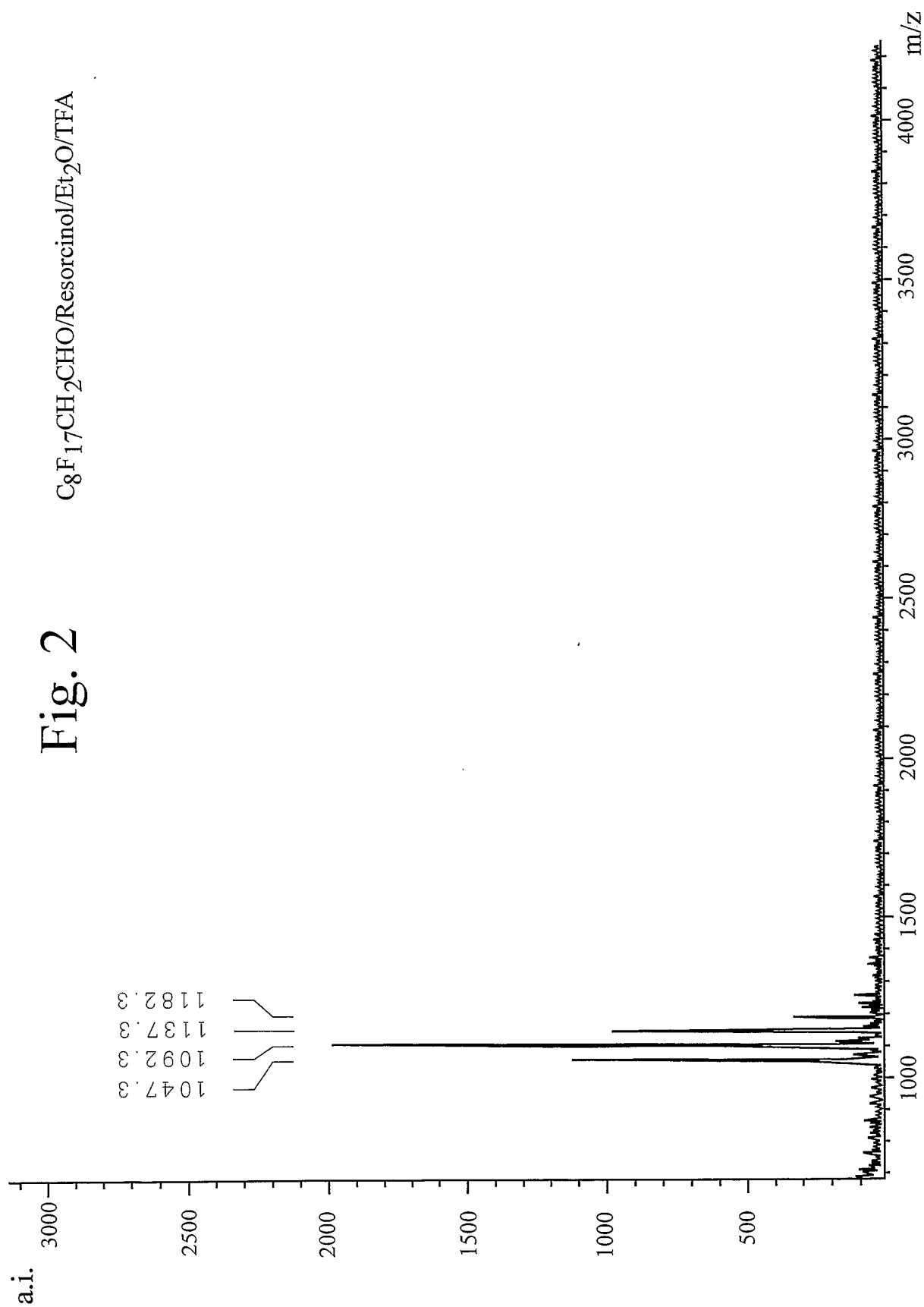
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Where R^3 is a polymerisable group, for example, an alkenyl, alkynyl, or alkoxycarbonyl group, p is 2 or 3, d is 1 or 2, and n is an integer greater than or equal to 1.

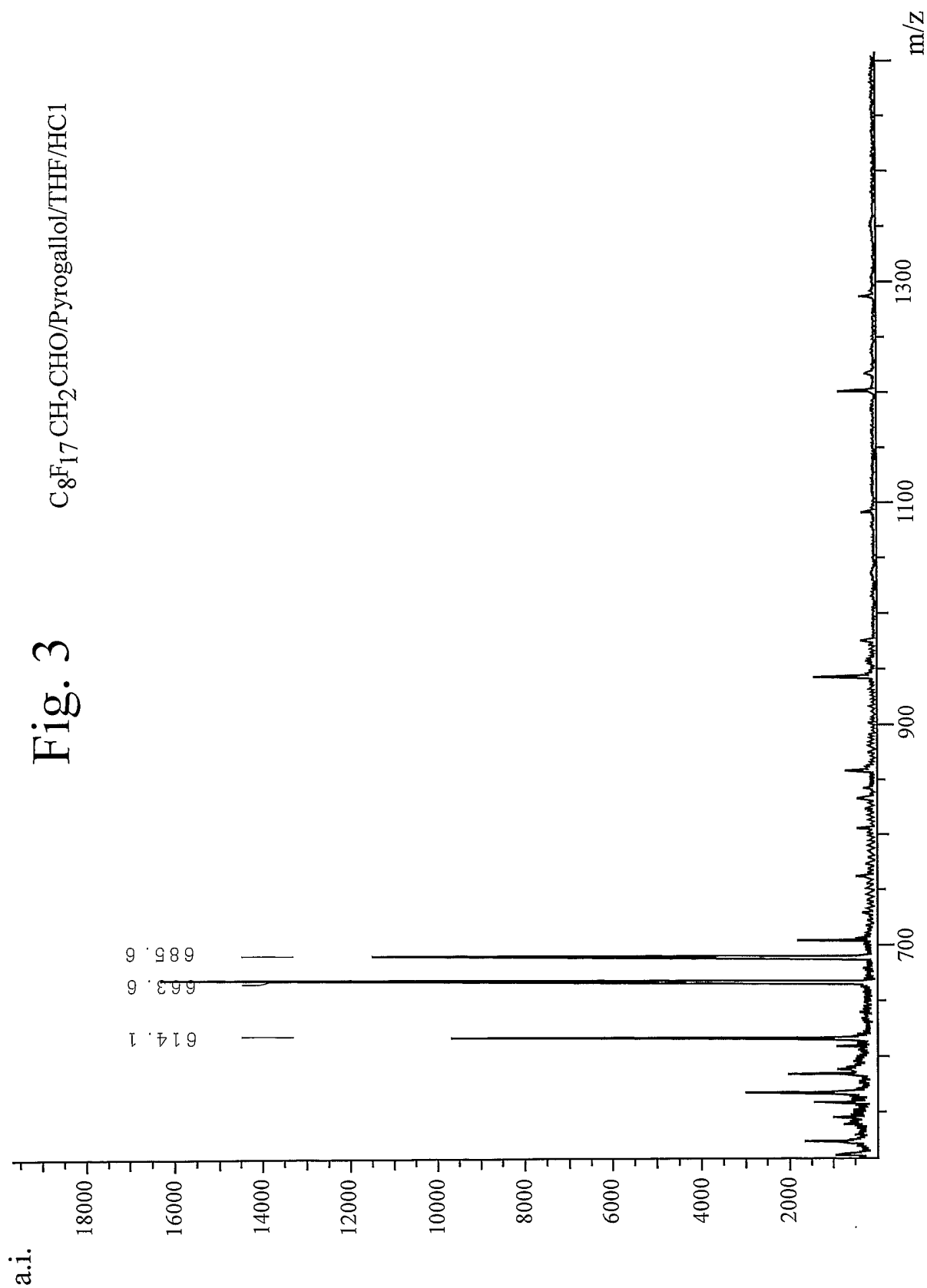
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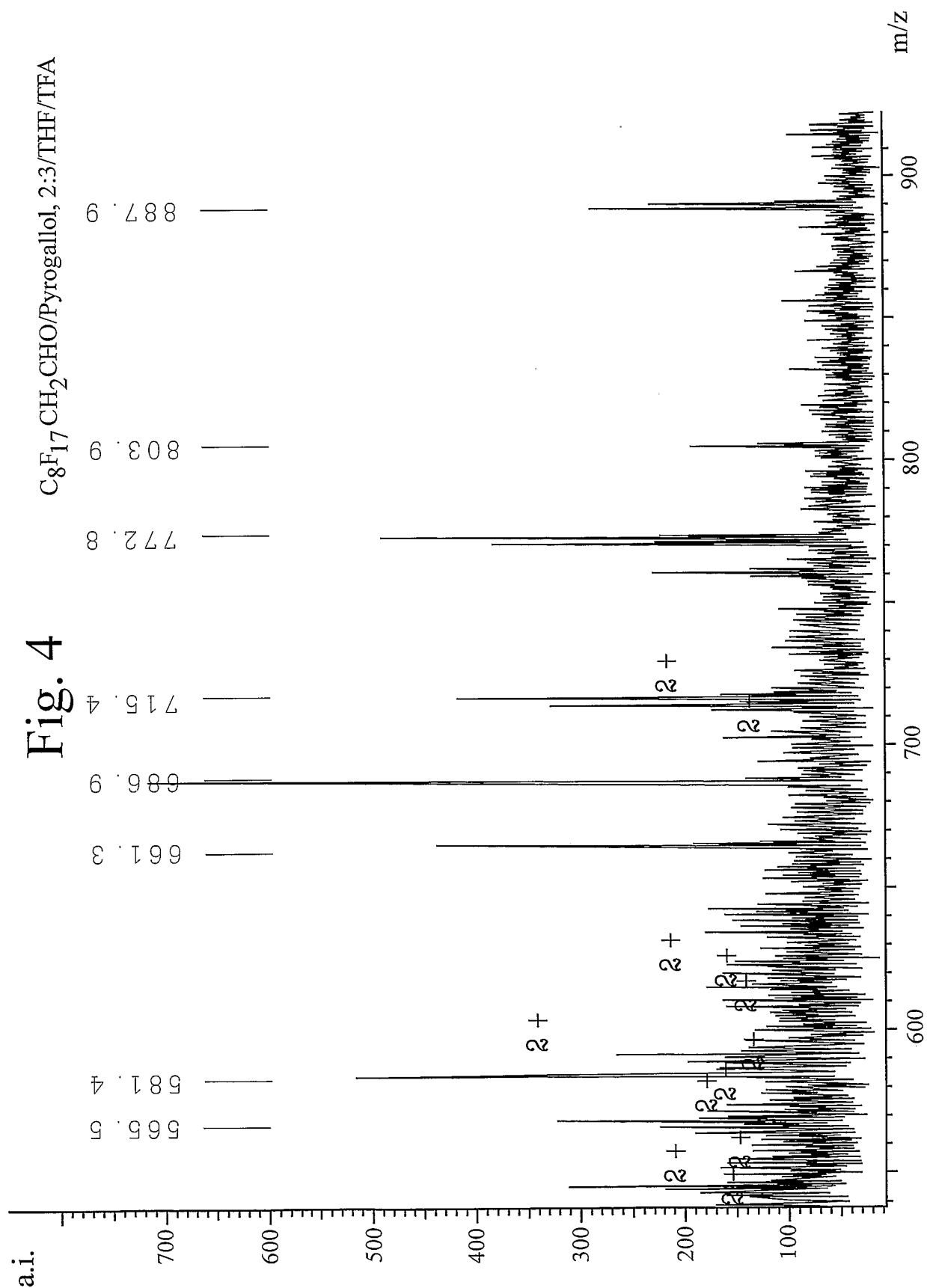
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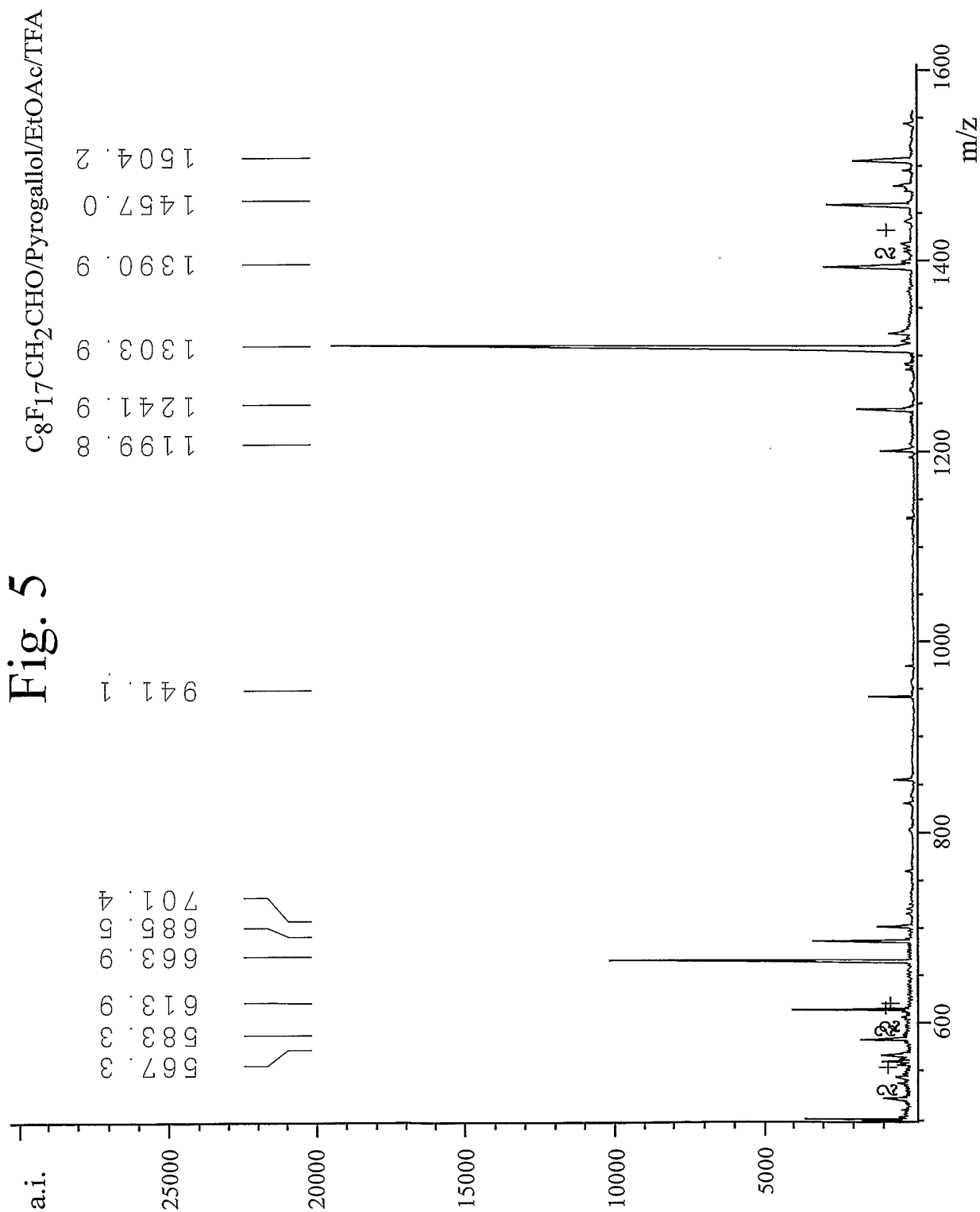
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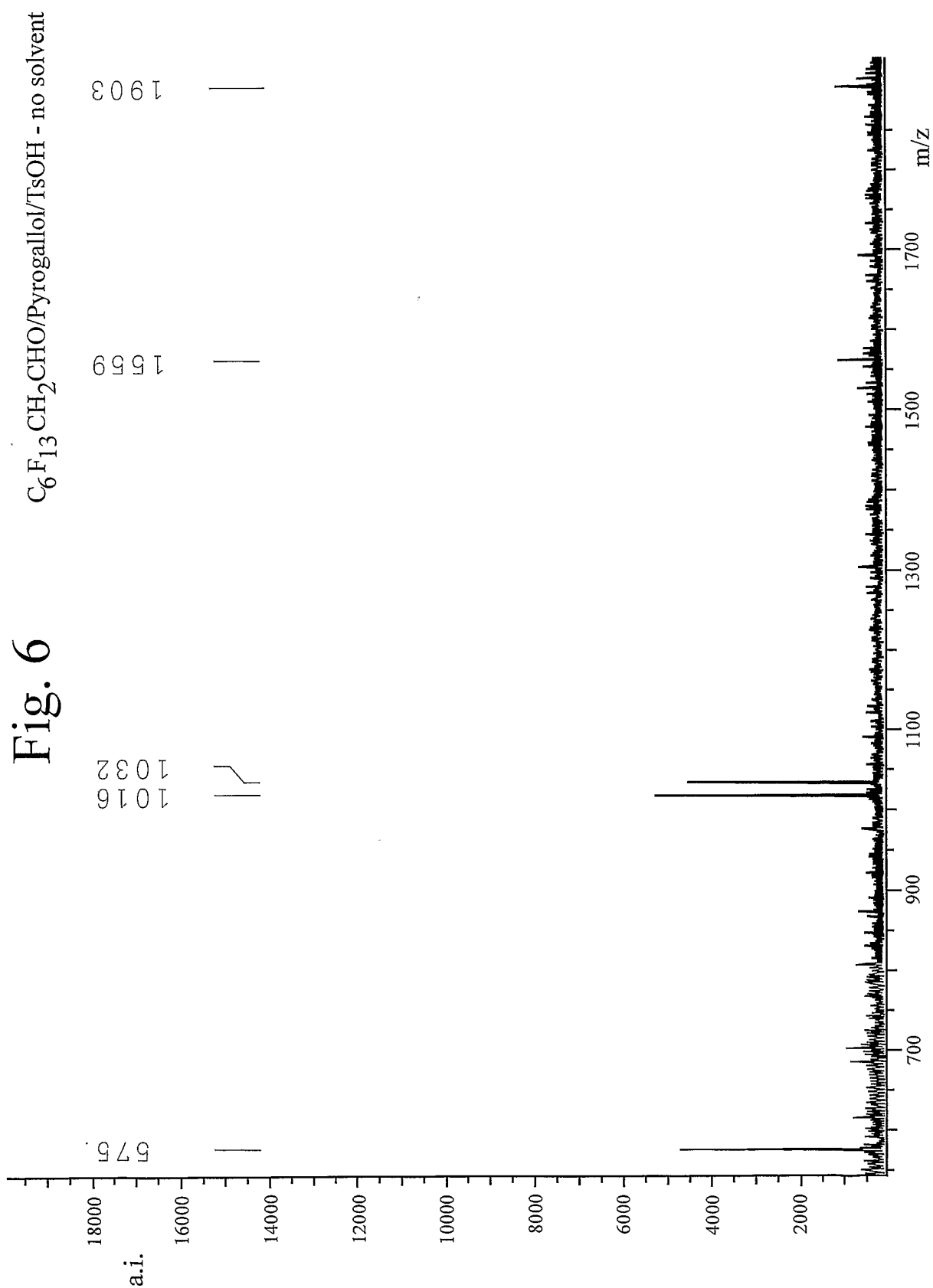
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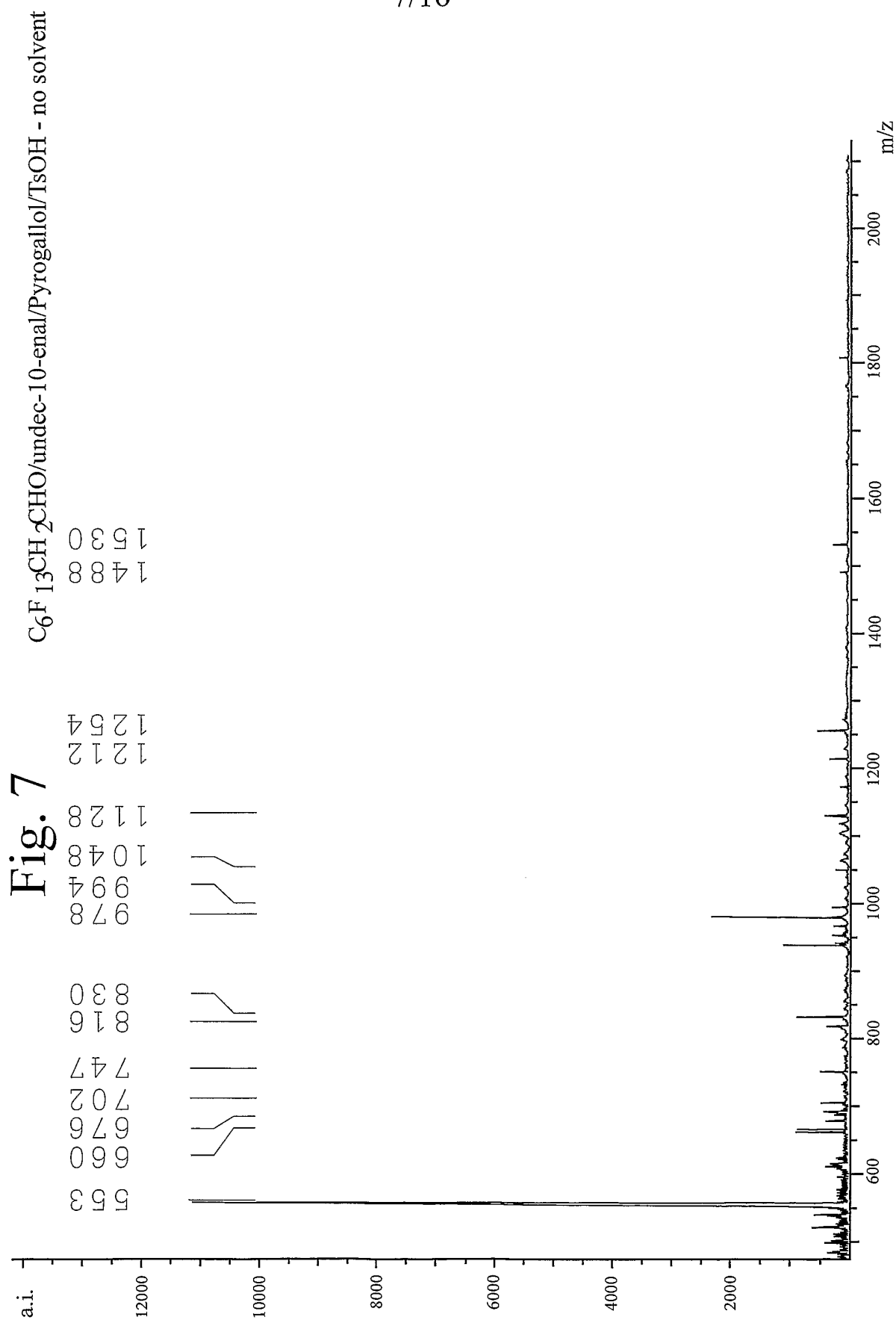
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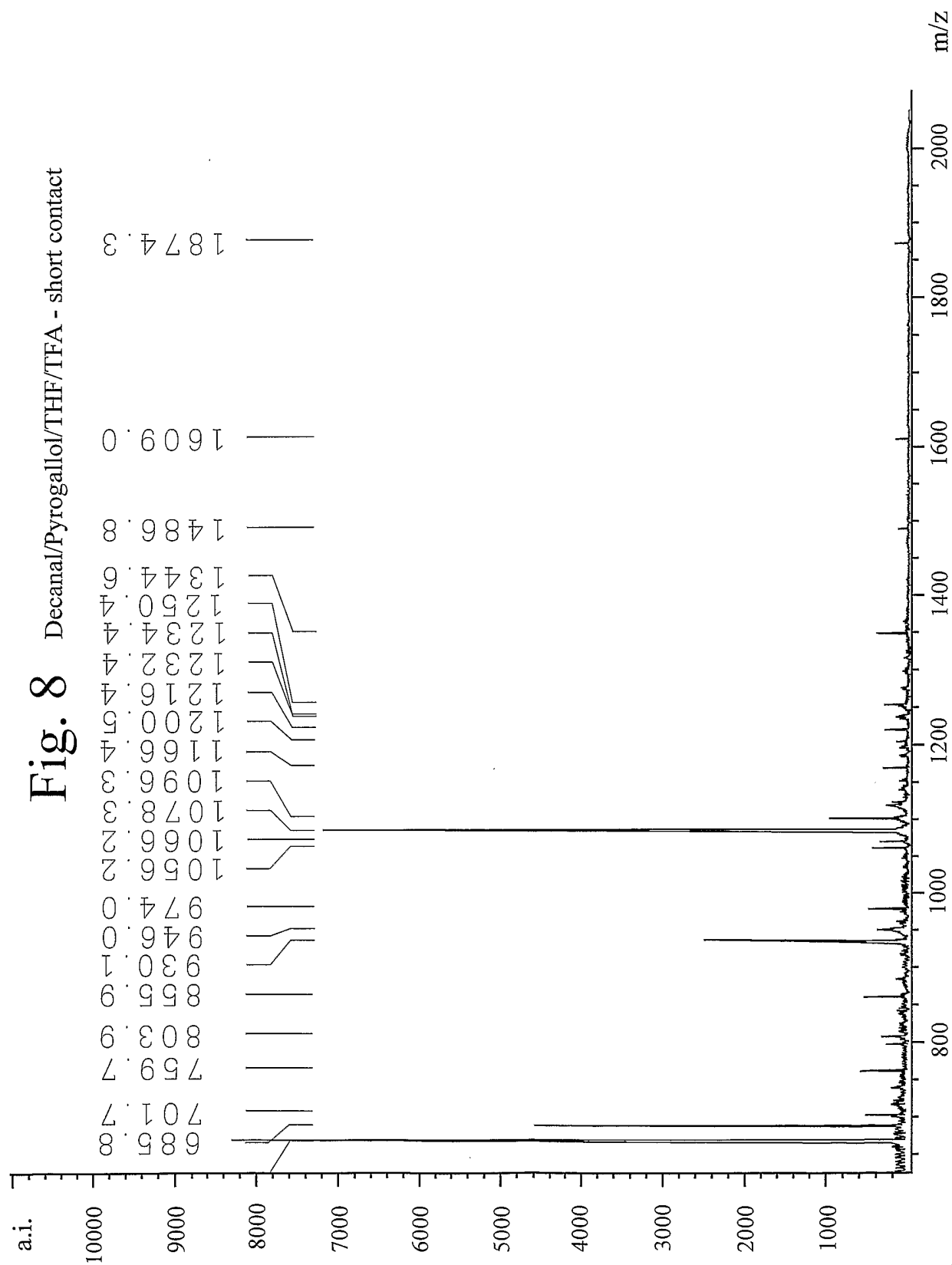
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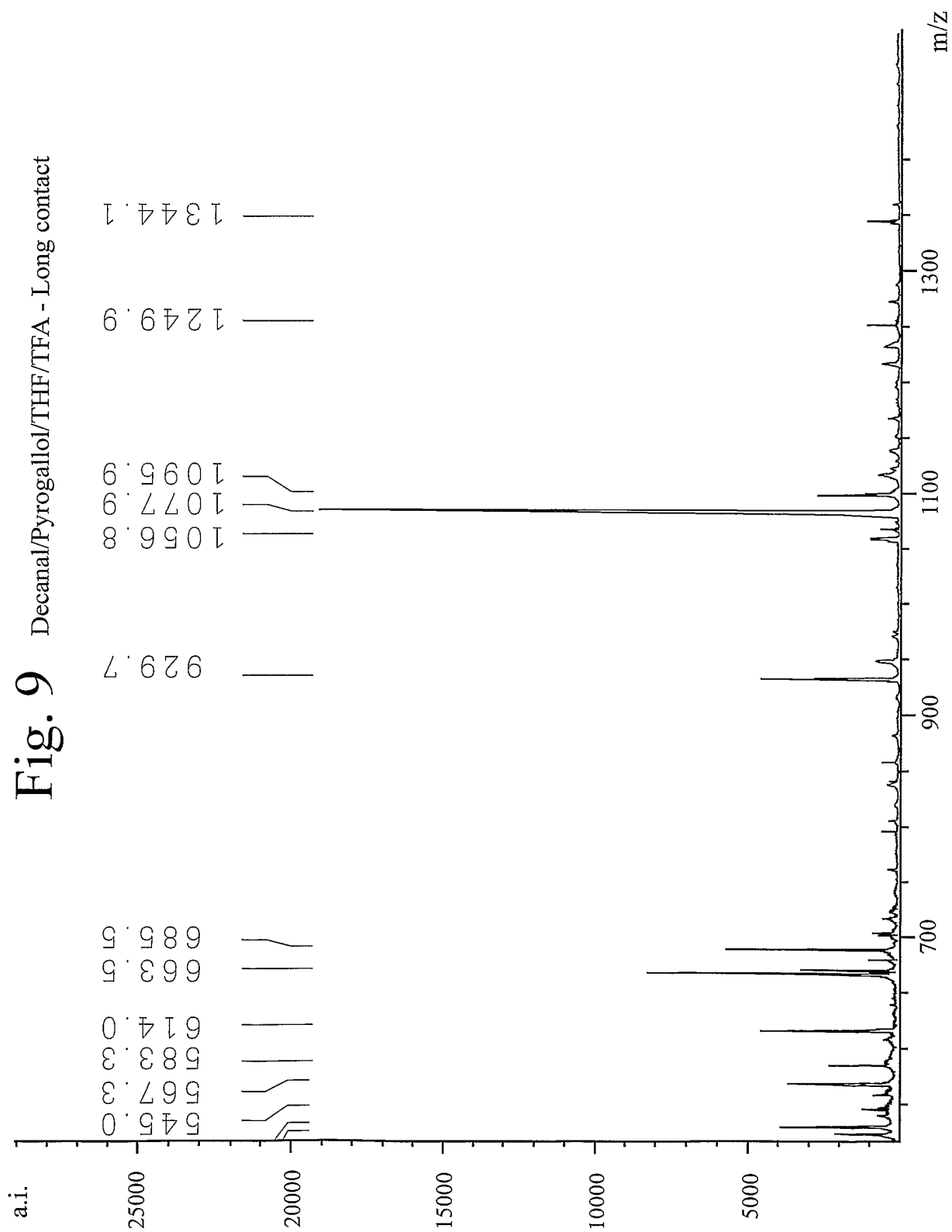
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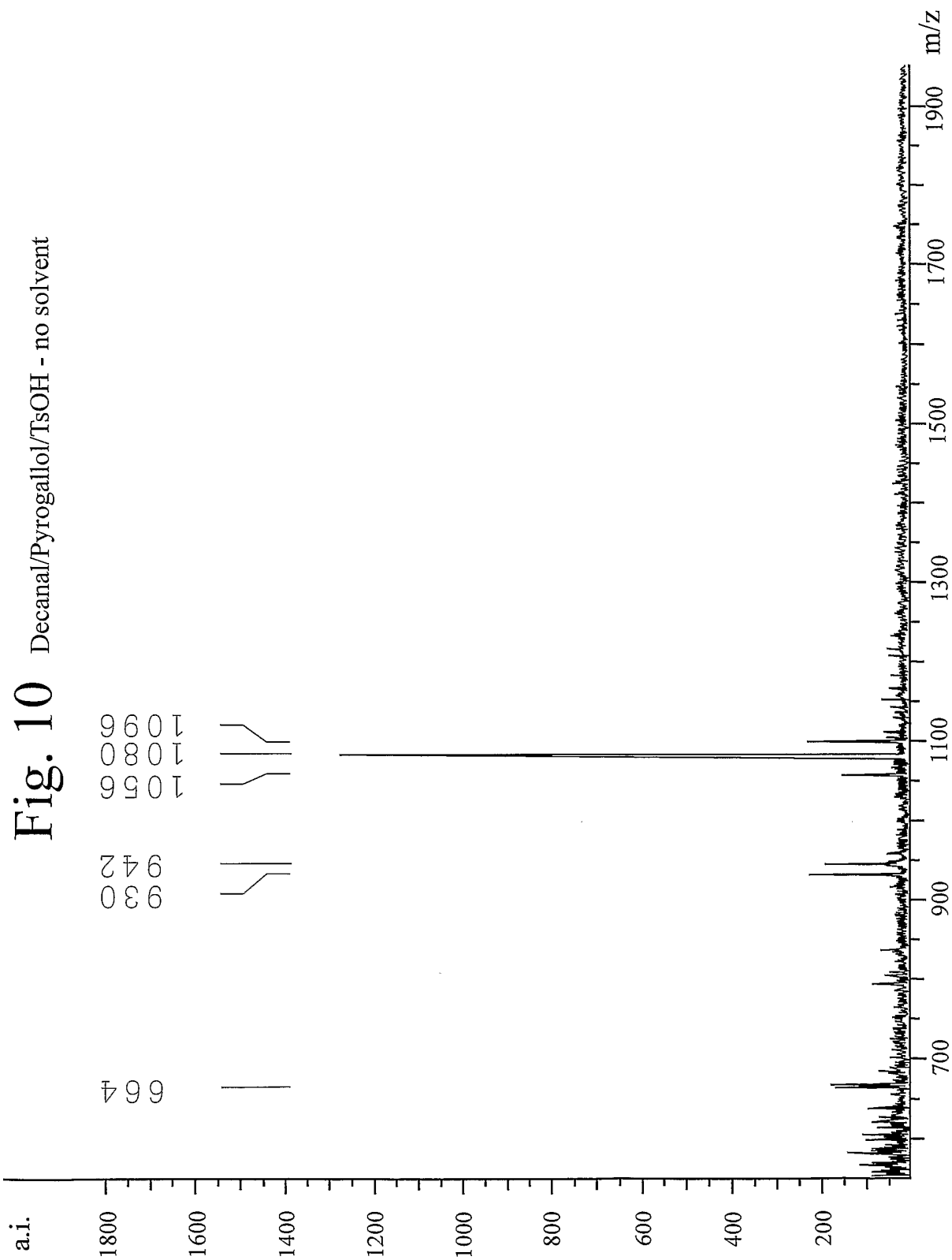
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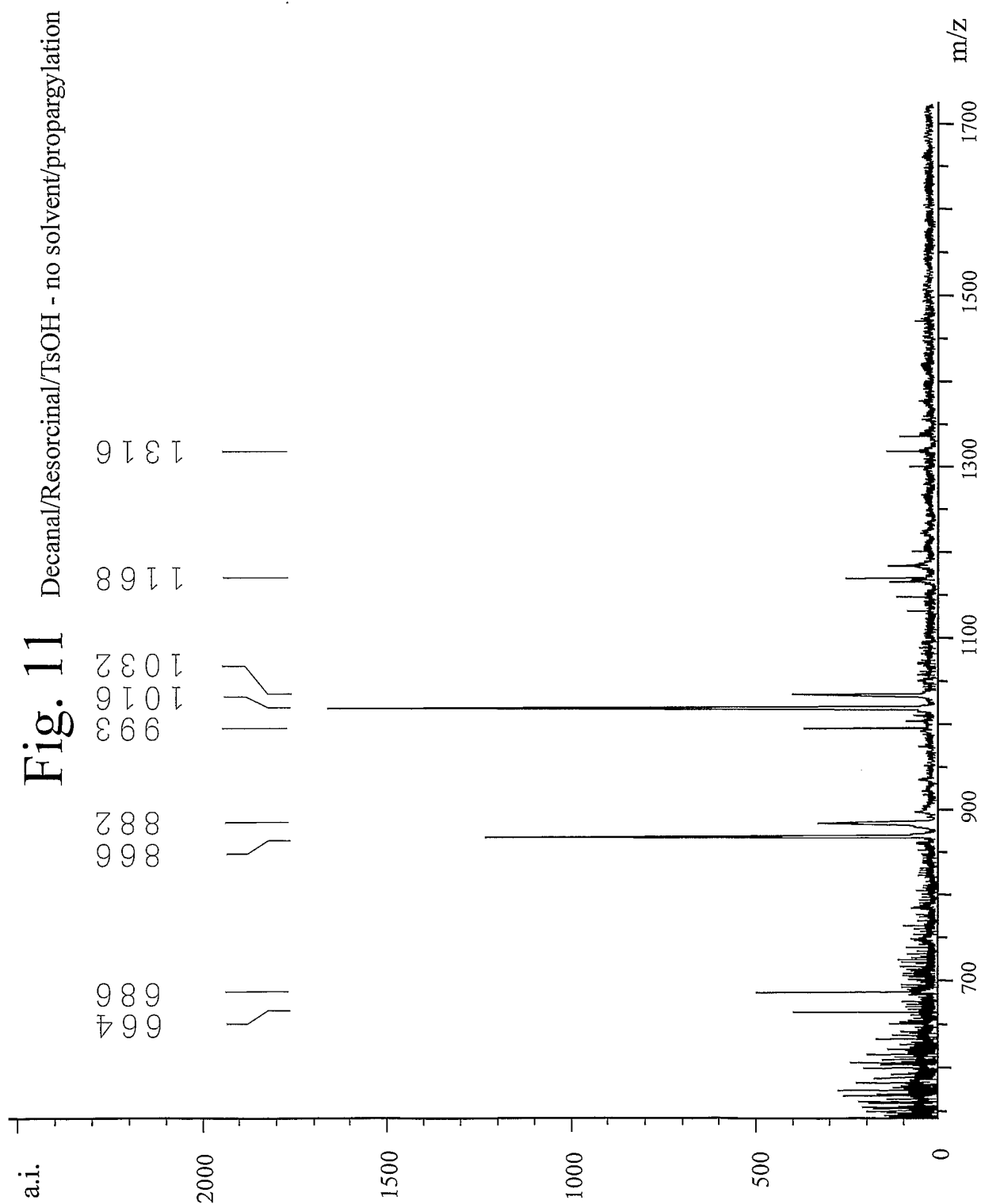
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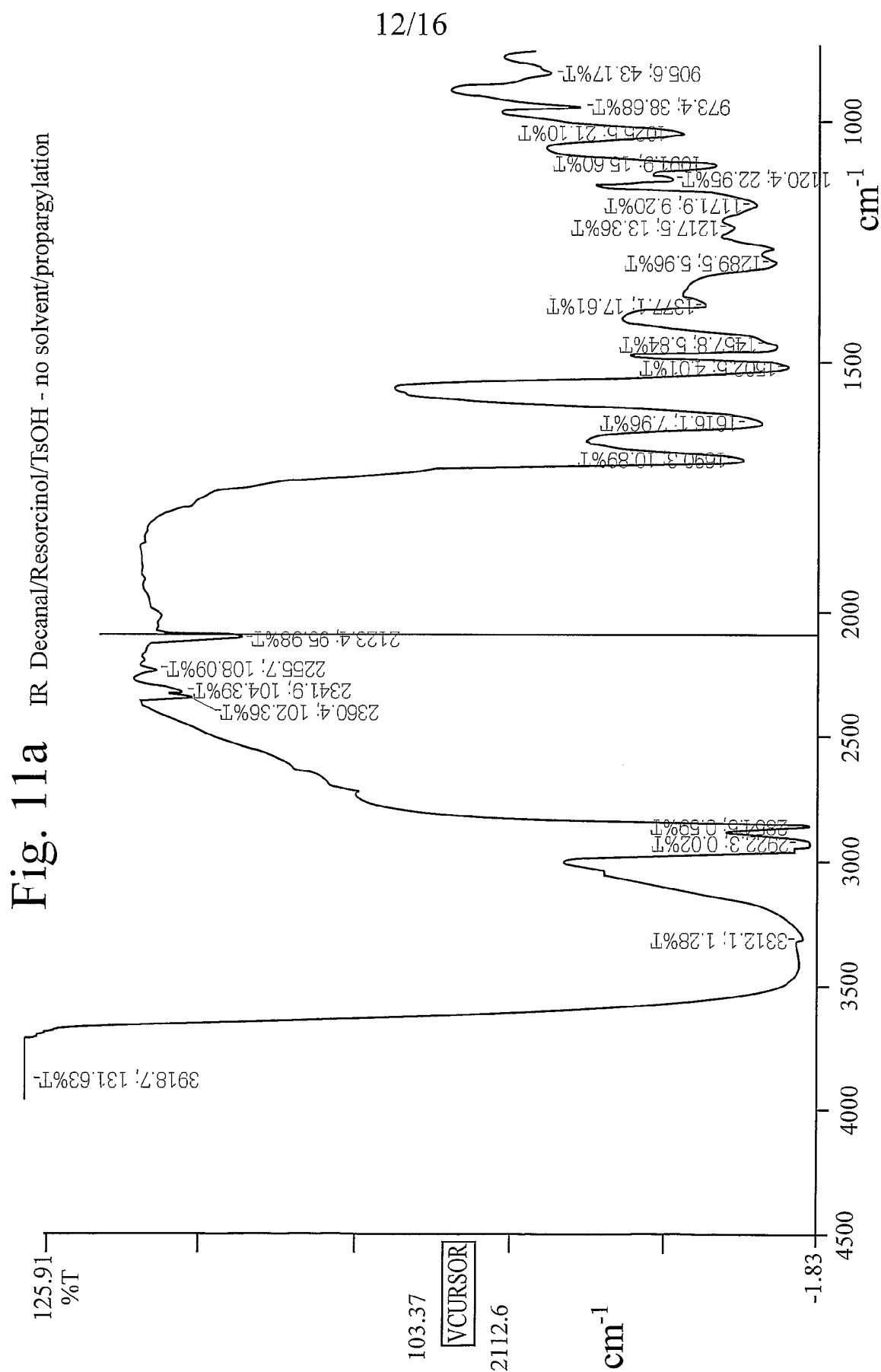


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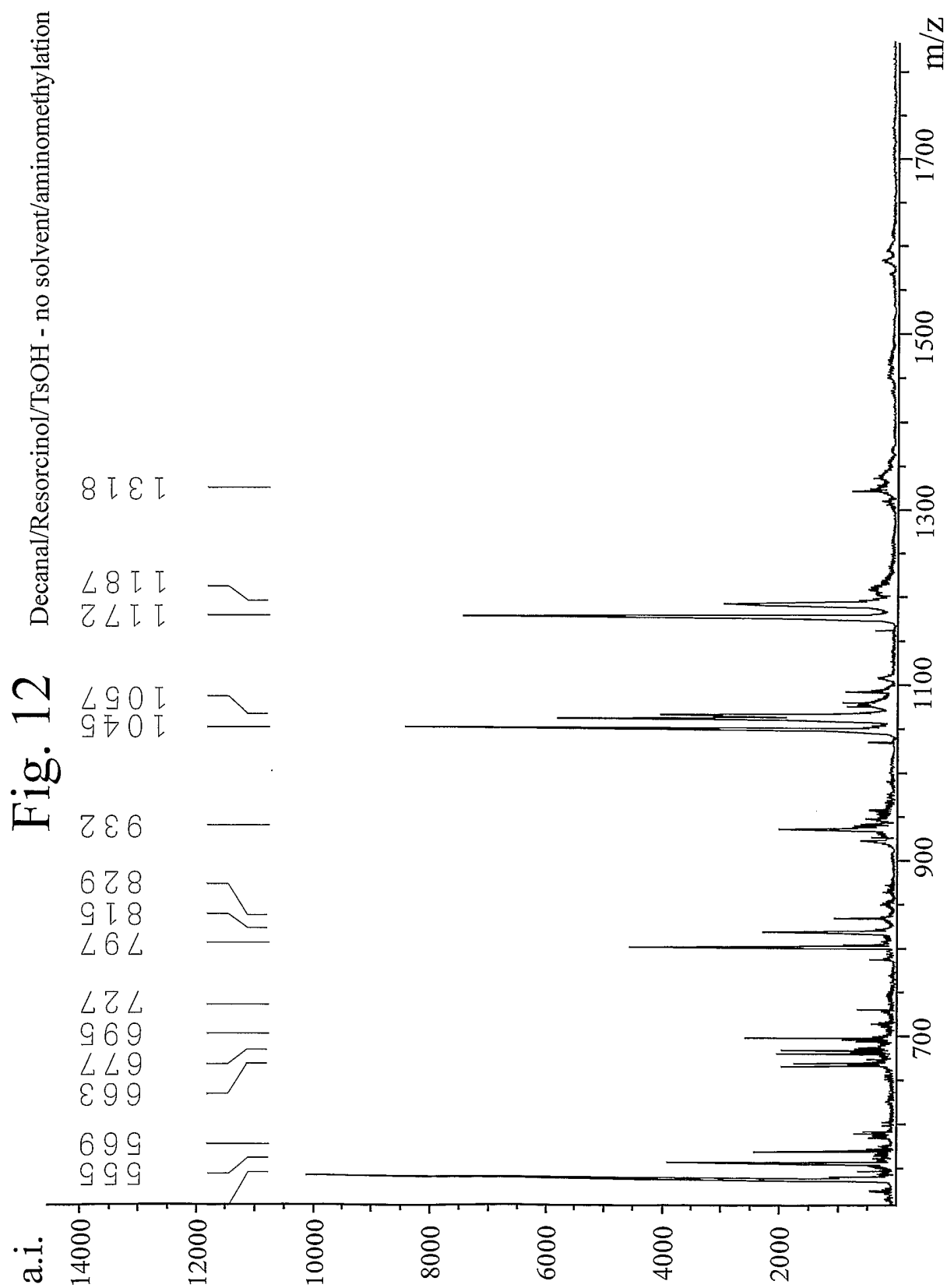


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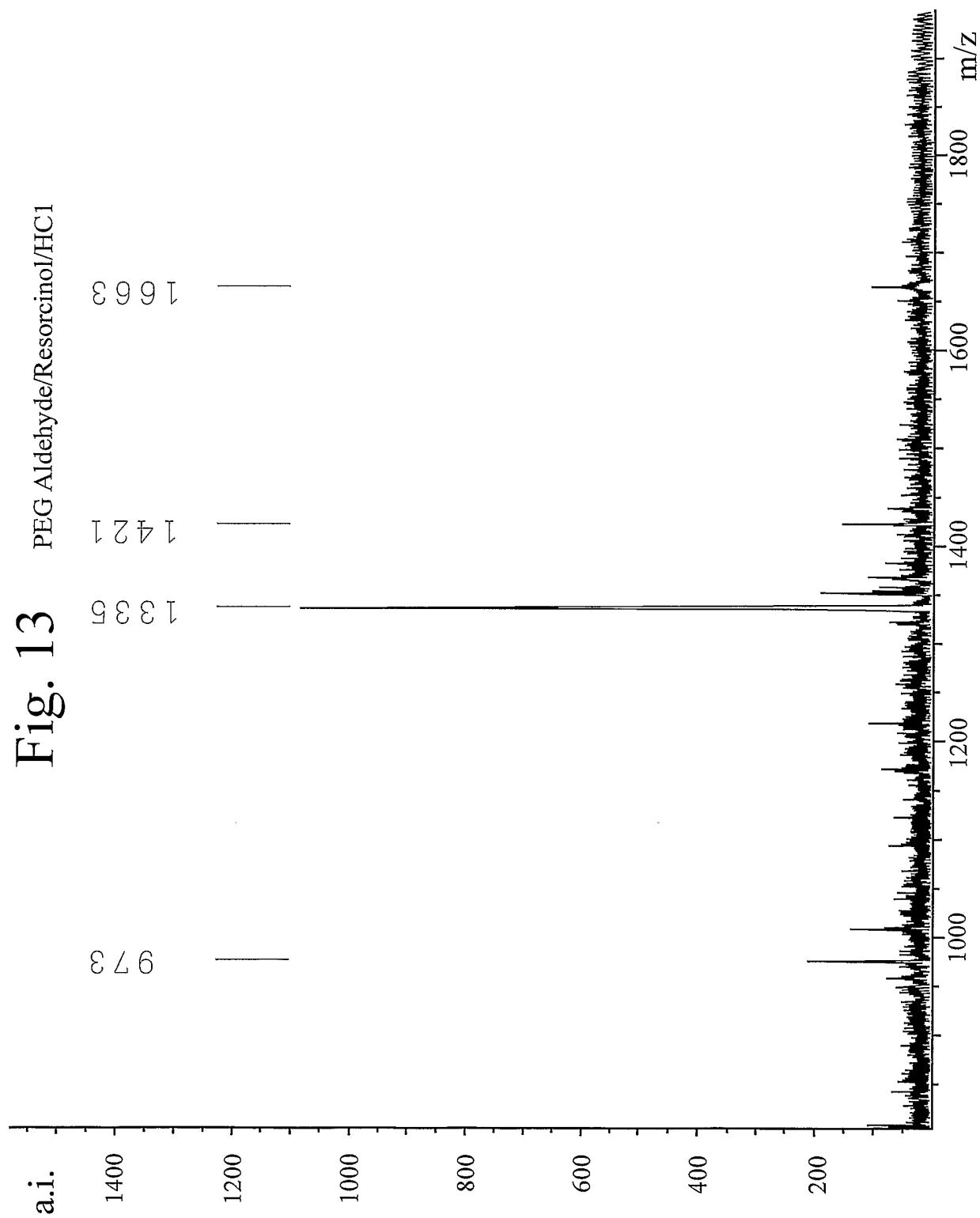




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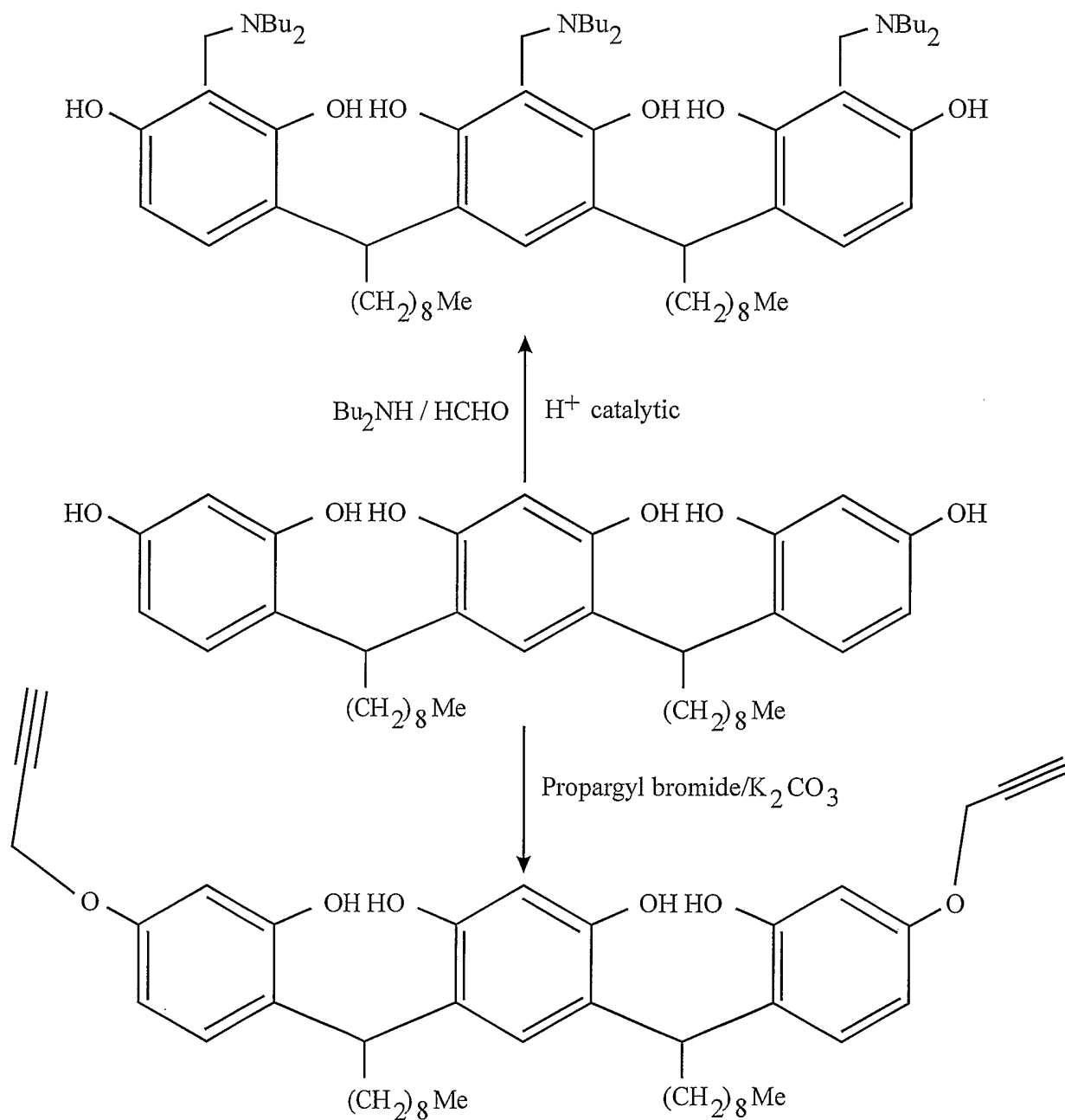
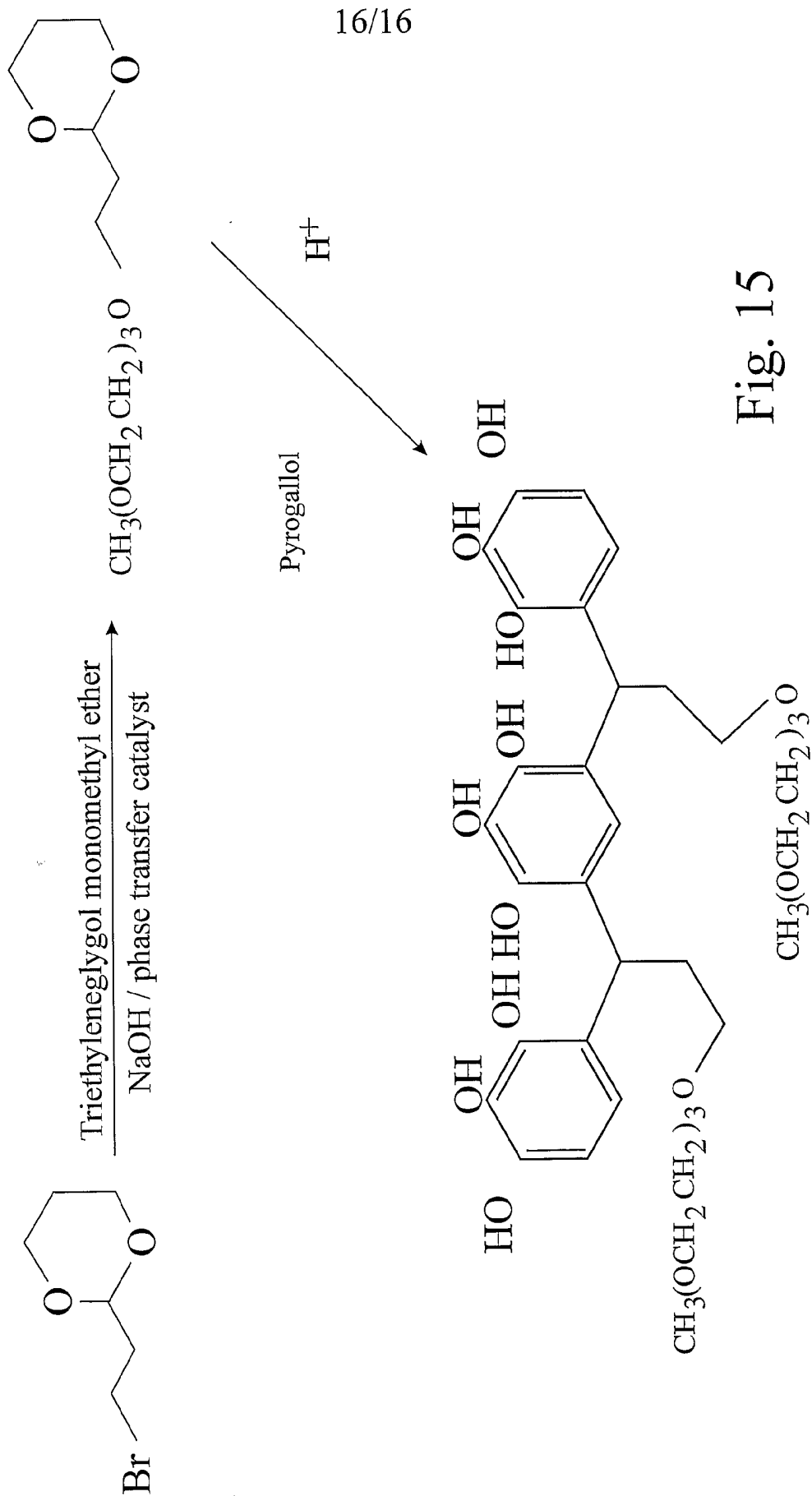


Fig. 14



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Fig. 15

INTERNATIONAL SEARCH REPORT

Int nal Application No

PCT/GB 03/03621

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C39/367 C07C39/373 C07C43/11 C08G8/24 C08G8/20
D21H19/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

BEILSTEIN Data, CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 358 624 A (MARK ET AL) 9 November 1982 (1982-11-09) column 7 -column 8; claims ----	1-8, 17-23, 25, 29-32, 38-42
X	US 4 365 098 A (MARK ET AL) 21 December 1982 (1982-12-21) column 3 -column 6; claims ----	1-8, 17-23, 25, 29-32, 38-42
X	GB 1 001 351 A (ETHYL CORPORATION) 18 August 1965 (1965-08-18) claims; examples 48-51 ----- -/--	1,11,12, 18,25, 40-42



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

8 October 2003

Date of mailing of the international search report

17/10/2003

Name and mailing address of the ISA

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Authorized officer

Van Geyt, J

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 03/03621

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 323 494 A (TENNECO CHEMICALS) 18 July 1973 (1973-07-18) claims -----	1, 18, 25, 40-42

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 03/03621

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1-13,17-52 (all in part)
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-13,17-52 (all in part)

1. Present claims 1, 11, 18, 33, 36, 40, 43, 51 and 52 relate to an extremely large number of possible compounds, their preparation and/or their use. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compounds, their preparation and/or their use claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the compounds, their use and/or their preparation explicitly claimed or described in the examples.

2. Present claims 1, 5, 9, 13, 18 and 40 relate to a product defined by reference to a desirable characteristic or property, namely the product should be solvent-soluble (claims 1, 18 and 40), the product should be colourless (claim 5), the product should be capable of chain extension or cross-linking (claim 9), or the molecular mass should be less than 2000 Daltons (claim 13). The claims cover all products having this characteristic or property, whereas the application provides support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT for only a very limited number of such products. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claims also lack clarity (Article 6 PCT). An attempt is made to define the product/compound/method/apparatus by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible. Consequently, the search has been carried out for those parts of the claims which appear to be clear, supported and disclosed, namely those parts relating to the products explicitly claimed or described in the examples.

3. The formula of claim 15 can be seen as misleading: the moiety $(CH_2)_r$ attached to the side-chain should be $-CH_2-(CH_2)_{r-1}$ in order to satisfy the structure of the compound. The same has to be said *mutatis mutandis* for the formulae in claim 16.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 03/03621

Patent document cited in search report		Publication date	Patent-family member(s)	Publication date
US 4358624	A	09-11-1982	EP 0067851 A1 JP 57502056 T WO 8202380 A1	29-12-1982 18-11-1982 22-07-1982
US 4365098	A	21-12-1982	EP 0067856 A1 JP 57502055 T WO 8202381 A1 US 4467121 A	29-12-1982 18-11-1982 22-07-1982 21-08-1984
GB 1001351	A	18-08-1965	NONE	
GB 1323494	A	18-07-1973	BE 765323 A1 DE 2121446 A1 FR 2091048 A5 IT 1019010 B NL 7105692 A	30-08-1971 13-01-1972 14-01-1972 10-11-1977 03-11-1971