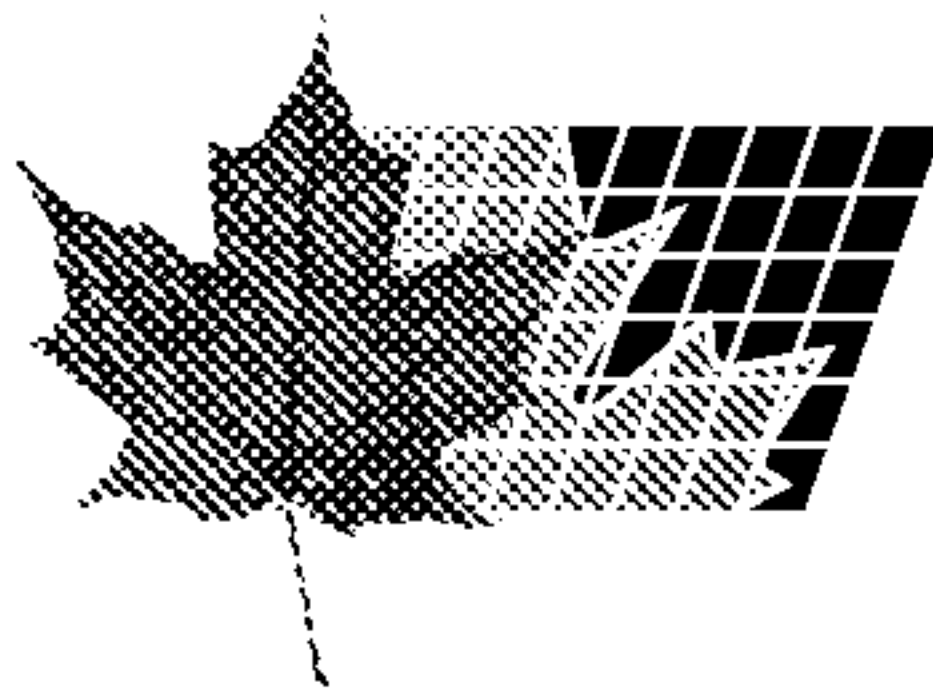




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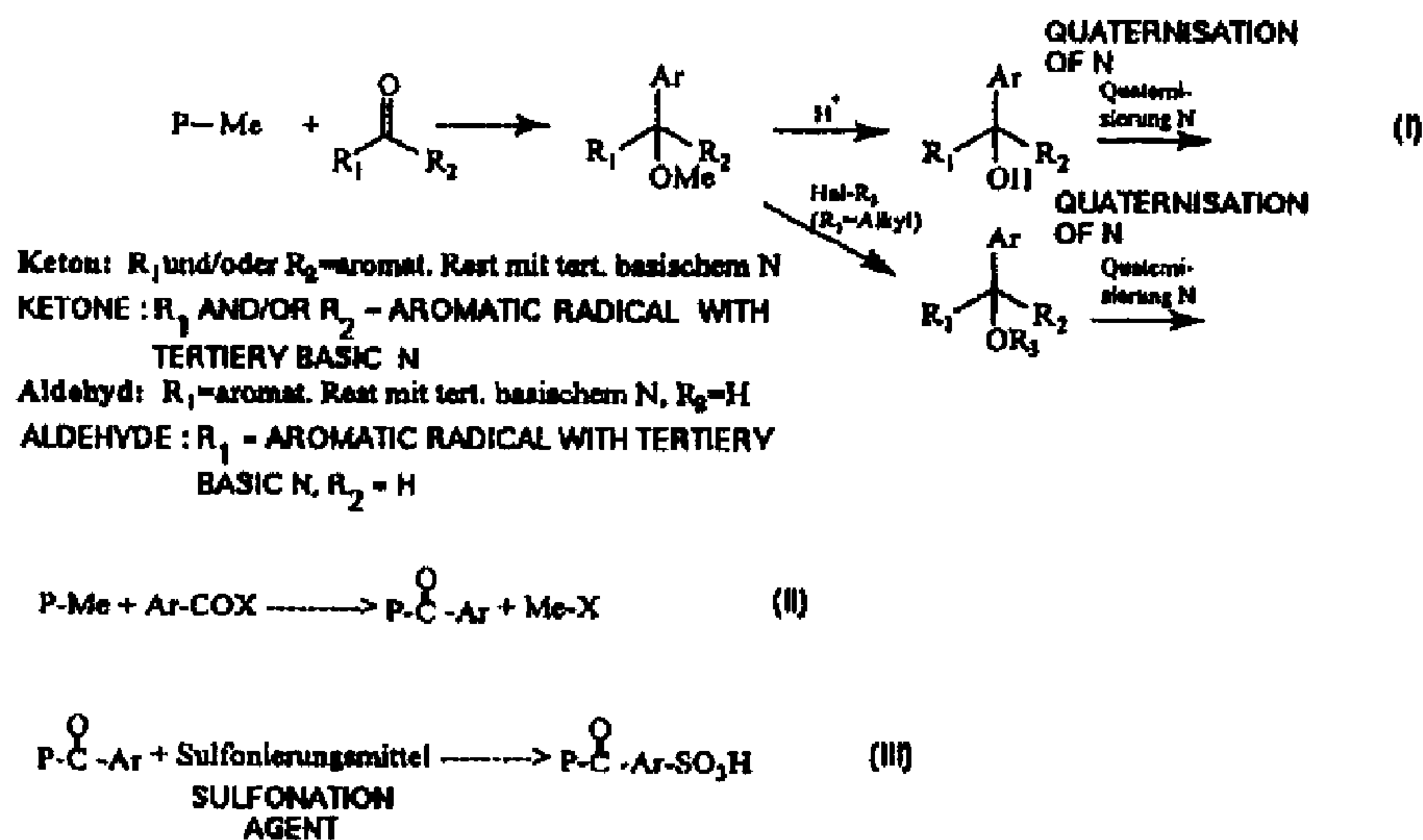
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(54) MODIFICATION DE TECHNOLYMERES AVEC DES
GROUPES N BASIQUES ET DES GROUPES ECHANGEURS
D'IONS DANS LA CHAÎNE LATÉRALE

(54) MODIFICATION OF ENGINEERING-POLYMERS WITH BASIC
N GROUPS AND ION-EXCHANGE GROUPS IN THE SIDE
CHAIN



(57) The present invention relates to the reaction and to the reaction products of organo-metallic compounds, preferably Li organic compounds, deprotonised engineering-polymers with an aryl main chain and with various aromatic carbonyl compounds containing tertiary basic N. This invention essentially relates to: a) the reaction of a metallised polymer P-Me with aromatic aldehydes and ketones and the potentially resulting reactions (I) (in the case of ketone: R_1 and/or R_2 represent an aromatic residue with tertiary basic N, while in the case of aldehyde: R_1 represents an aromatic residue with tertiary basic N and R_2 represents H); b) the reaction of a metallised polymer P-Me with aromatic carboxylic acid esters ($X=OR$) or with carboxylic acid halides ($X=Hal$) and the potentially resulting reactions (II), wherein if Ar is an aromatic radical with tertiary basic N, the quaternisation of tertiary N with alkane halides is possible (when using dialkane halides: simultaneous covalent cross-linking), and if Ar is an aromatic radical that can be sulfonated: (III); c) acid-base polymer mixtures and membranes made of acid-base polymer mixtures obtained by: mixing the acidic and basic reaction products mentioned in the reaction equations a) and b); mixing basic polymers of the present invention with arbitrary acidic polymers.



PCT
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(21) Internationales Aktenzeichen: PCT/EP99/05862 (22) Internationales Anmeldedatum: 12. August 1999 (12.08.99) (30) Prioritätsdaten: 198 36 514.4 12. August 1998 (12.08.98) DE (71) Anmelder (für alle Bestimmungsstaaten ausser US): UNI-VERSITÄT STUTTGART [DE/DE]; Lehrstuhl und Institut für Chemische Verfahrenstechnik, Böblinger Strasse 72, D-70199 Stuttgart (DE). (72) Erfinder; und (75) Erfinder/Anmelder (nur für US): KERRES, Jochen [DE/DE]; Astenweg 11, D-73760 Ostfildern (DE). ULLRICH, Andreas [DE/DE]; Braungartweg 6, D-73734 Esslingen (DE). HÄRING, Thomas [DE/DE]; Aixheimer Strasse 21, D-70619 Stuttgart (DE). (74) Anwälte: JÖNSSON, Hans-Peter usw.; von Kreisler Selting Werner, Deichmannhaus am Dom, D-50667 Köln (DE). (81) Bestimmungsstaaten: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO Patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), eurasisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI Patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Veröffentlicht Mit internationalem Recherchenbericht. Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist; Veröffentlichung wird wiederholt falls Änderungen eintreffen.		
(54) Title: MODIFICATION OF ENGINEERING-POLYMERS WITH BASIC N GROUPS AND ION-EXCHANGE GROUPS IN THE SIDE CHAIN (54) Bezeichnung: MODIFIKATION VON ENGINEERINGPOLYMEREN MIT N-BASISCHEN GRUPPEN UND MIT IONENAUSTAUSCHERGRUPPEN IN DER SEITENKETTE (57) Abstract The present invention relates to the reaction and to the reaction products of organo-metallic compounds, preferably Li organic compounds, deprotonised engineering-polymers with an aryl main chain and with various aromatic carbonyl compounds containing tertiary basic N. This invention essentially relates to: a) the reaction of a metallised polymer P-Me with aromatic aldehydes and ketones and the potentially resulting reactions (I) (in the case of ketone: R₁ and/or R₂ represent an aromatic residue with tertiary basic N, while in the case of aldehyde: R₁ represents an aromatic residue with tertiary basic N and R₂ represents H); b) the reaction of a metallised polymer P-Me with aromatic carboxylic acid esters (X=OR) or with carboxylic acid halides (X=Hal) and the potentially resulting reactions (II), wherein if Ar is an aromatic radical with tertiary basic N, the quaternisation of tertiary N with alkane halides is possible (when using dialkane halides: simultaneous covalent cross-linking), and if Ar is an aromatic radical that can be sulfonated: (III); c) acid-base polymer mixtures and membranes made of acid-base polymer mixtures obtained by: mixing the acidic and basic reaction products mentioned in the reaction equations a) and b); mixing basic polymers of the present invention with arbitrary acidic polymers. Ketone: R₁ und/oder R₂=aromat. Rest mit tert. basischem N KETONE: R₁ AND/OR R₂ - AROMATIC RADICAL WITH TERTIERY BASIC N Aldehyd: R₁=aromat. Rest mit tert. basischem N, R₂=H ALDEHYDE: R₁ - AROMATIC RADICAL WITH TERTIERY BASIC N, R₂ = H P-Me + Ar-COX → P-C(=O)-Ar + Me-X (II) P-C(=O)-Ar + Sulfonierungsmittel → P-C(=O)-Ar-SO₃H (III) Sulfonation AGENT		

TITLE

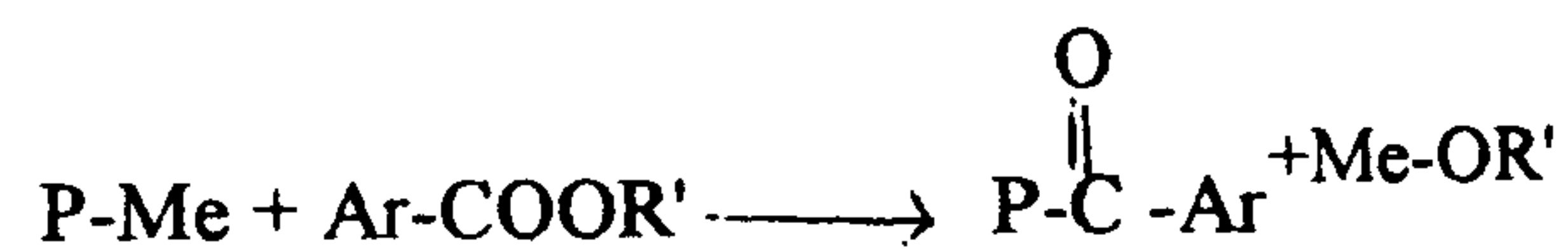
Modification of Engineering Polymers with Basic N-groups and Ion Exchange Groups in the Lateral Chain

DESCRIPTION OF THE INVENTION

1. Object of the invention

Objects of the invention are:

- (1) A method for the lateral chain modification of engineering aryl main chain polymers with arylene-containing basic N-groups by the addition of aromatic ketones and aldehydes containing tertiary basic N-groups (such as for example tertiary amine, pyridine, pyrimidine, triazine...) to the metallised polymer.
- (2) Lateral chain modified polymers obtained by the method (1), whereby the lateral chain contains at least one aromatic group which carries a tertiary basic N.
- (3) A method for the quaternising of tertiary N of the modified polymers (2) with halogen alkanes in order thus to incorporate anion exchanger groups into the lateral chain modified polymer.
- (4) Engineering aryl main chain polymers carrying in the lateral chain anion exchanger functions and obtainable by the method (3).
5. A method for the lateral chain modification of engineering main chain polymers with arylene-containing basic N groups by the following reaction of aromatic carboxylic acid Ar-COOR' containing tertiary basic N groups (such as for example tertiary amine, pyridine, pyrimidine, triazine...) with the metallised polymer P-Me :

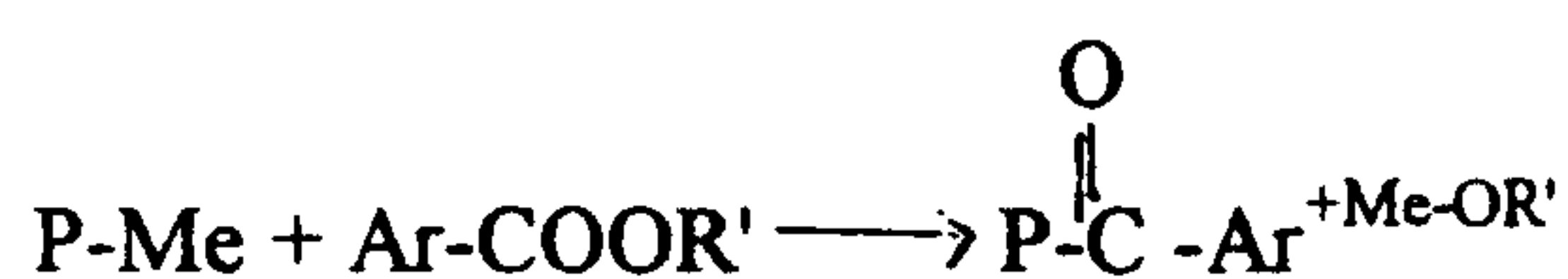


- (6) Lateral chain modified polymers obtained by the method (5) in which the side chain contains at least one aromatic group which carries a tertiary basic N.
- (7) A method of quaternising the tertiary N in the modified polymers (6) with halogen alkanes in order thus to incorporate anion exchanger groups into the lateral chain modified polymer.

(8) Engineering aryl main chain polymers carrying in the lateral chain anion exchanger functions obtainable by the method (7).

(9) A method for the lateral chain modification of engineering aryl main chain polymers with aromatic groups containing sulphonic acid radicals by the following sequence of reactions:

(9a) Reaction of the aromatic carboxylic acid ester Ar-COOR' or carboxylic acid halide Ar-COHal with the metallised polymer P-me:



(9b) Controlled electrophilic sulphonation of the lateral group with sulphuric acid $\text{SO}_3/\text{P}(\text{O})(\text{OR})_3$, ClSO_3H , etc. The lateral group is in this case so selected that its reactivity for sulphonation is substantially higher than the reactivity of the polymer main chain for sulphonation.

(10) Engineering aryl main chain polymers which only carry sulphonic acid functions in the lateral chain, obtainable by the method (9).

(11) Membranes of the polymers (2), (4), (6), (8) or (10) in which the membranes may be unvulcanised or covalently cross-linked.

(12) A method of producing acid-based blends/acid-based blend membranes from the basic polymers (2), (4), (6), (8) with polymers containing sulphonic acid, phosphonic acid or carboxyl groups.

(13) A method of producing acid-based blends/acid-based blend membranes from the basic polymers (2), (4), (6), (8) with the polymer (10) containing sulphonic acid groups.

(14) Acid-based blends/acid-based blend membranes obtainable by methods (12) and (13), whereby the blends/blend membranes may in addition be covalently cross-linked.

(15) Use of ion exchange polymers (4), (8), (10), (14) as membranes in membrane processes such as in polymer electrolyte membrane fuel cells (PEFC), direct methanol fuel cells (DMFC) and electrodialysis.

(16) Use of hydrophilic polymers (2), (6) containing the basic N in the lateral group as membranes in dialysis and in reversal osmosis, nanofiltration, diffusion dialysis, gas permeation, pervaporation and perstraction.

2. Technical problem to be resolved by this invention

For many application in membrane technology (reversal osmosis, nanofiltration, micro- and ultrafiltration, electrodialysis, diffusion dialysis, membrane electrolysis, membrane fuel cells), hydrophilised or chemically stable polymers containing ion exchange groups are needed but these however are only commercially available in limited amounts - even today, in some cases vinyl polymers the chemical stability of which is limited are still being employed in the above-mentioned applications. Furthermore, the band width of the properties of these commercial polymers is not very great.

3. State of the art and its disadvantages

a) Polymers modified with basic N

There are still relatively few basic N-modified polymers on the market, the most important being mentioned below:

- poly(4-vinyl pyridine), poly-2-vinyl pyridine) and copolymers.

These two polymers are commercially available, also as block copolymers with polystyrene. They are used for example as pre-stages for anion exchange membranes (Reiner, Ledjeff¹, Gudernatsch, Krumbholz²) or complexed with Schiff's bases containing cobalt for selective oxygen permeation³. The drawback with this class of polymer is the tertiary C-H-bond in the polymer main chain, which is susceptible to oxidation.

- polybenzimidazols

Polybenzimidazols are a class of polymers which have considerable chemical and mechanical stability. Many types of polybenzimidazols (fully and partly aromatic) have already been synthesised and examined⁴. However, only a few types are produced commercially, of which the most important is the polymer PBI (poly[(2,2-m-phenylene)-

5,5'-bibenzimidazol) produced by Celanese under the commercial name CELAZOLE. Inter alia, this polymer is used in the form of low-flammability textiles⁵ for the Fire Brigade. The drawbacks with this polymer are that it is difficult to dissolve in organic solvents and so has poor working properties; furthermore, it is very expensive.

- polyethylene imine

Polyethylene imine is used in organic chemistry and biochemistry as a precipitating agent for proteins⁶. The advantage of this polymer is that by virtue of its highly hydrophilic nature (1 N on 2 C), it is water soluble and therefore, in its pure form, there will not form any resistant membranes and furthermore, by virtue of its purely aliphatic structure, it is not very chemically stable.

b) Anion exchange polymers and membranes

The commercial anion exchange polymers and membranes can be divided into two main categories:

- anion exchange polymers which are produced by reaction of chlorinated⁷ or bromomethylated⁸ polymers with tertiary amines. The drawback with this reaction is the cancerogenic nature of the halomethylation reaction and the lack of chemical stability of the aromatic-CH₂-NR₃⁺ grouping.
- anion exchange polymers produced by the alkylation of tertiary N, for example of poly(vinyl pyridine)^{1,2,9} with halogen alkanes^{1,2}. The disadvantage with this reaction is that only very few commercial polymers with tertiary N are available (see above) and thus the band width of the membrane properties to be achieved is limited. The drawback with poly(vinyl pyridine)s is the limited chemical stability (see above).

c) Cation exchange polymers sulphonated in the lateral group

There are very few commercial polymers and membranes of this type. The most important of both representatives shall be mentioned here:

- nafion¹⁰

This polymer has a perfluoralkyl main chain and a perfluorether lateral chain at the end of

which hangs a sulphonic acid group. This polymer is used in all applications which require great chemical membrane stability, for example membrane fuel cells¹¹. The disadvantage with this polymer is its high price (\$800 US/sq.m) and the complicated production process¹⁰.

- poly-X 2000¹²

This polymer consists of a poly(phenylene) main chain and an aryl lateral chain, the precise name is poly(oxy-1,4-phenylene-carbonyl-1,4-phenylene). This polymer is sulphonated¹² only at the end of the lateral chain. According to statement¹², this polymer in the sulphonated form has good proton conductivity levels even at temperatures in excess of 100°C at which the proton conductivity of sulphonated poly(ether ether ketone) (PEEK) already drops markedly. This property could be brought out by a better association of the sulphonic acid groups in the poly-X 2000, since the sulphonic acid groups are in the lateral chain in the case of the poly-X 2000 - in the sulphonated PEEK, the sulphonic acid groups are in the main chain and consequently, on account of the rigidity of the PEEK main chain, they associate less readily. A drawback with this polymer is its poorer thermal stability compared with sulphonated PEEK¹² and the fact that it is not commercially available.

4. Object of the invention

As a result of this invention, aryl main chain polymers and membranes which are modified with basic nitrogen in the lateral group and which are therefore hydrophilised become accessible which have very good thermal and mechanical stability. Furthermore, this invention opens a way to chemically stable cation and anion exchange membranes which additionally, by reason of the presence of the ion exchange groups in the lateral chain, display a greater degree of freedom for forming ion exchange group associates than if the ion exchange groups were present in the polymer main chain.

5. Problemn resolved by the invention (description of the invention)

The description of the invention is sub-divided into five parts for reasons of clarity:

- a basic N-modified polymers by an addition reaction to lithiated polymers
- b basic N-modified polymers by substitution reaction with lithiated polymers

- c anion exchange polymers and membranes
- d cation exchange polymers sulphonated in the lateral group
- e acid-based blends and acid-based blend membranes from polymers a or b with any desired sulphonated polymers or with the cation exchange polymers d.

a) Basic N-modified polymers by addition reaction to lithiated polymers

Guiver tells of PSU hydrophilically modified in the lateral chain via a metallising reaction and subsequent addition of selected aldehydes or ketones, forming PSU¹³ modified with OH groups in the lateral chain (Fig. 1). The following degrees of substitution were achieved: benzaldehyde 1.9, benzophenone 1.0, acetone 0.5.

Surprisingly, now, it has been found that according to the reaction in Fig. 1, aromatic ketones and aldehydes which contain tertiary N can be added to lithiated PSU. Examples of such basic aromatic ketones which can be added are (Fig. 2):

- 2,2'-bipyridyl ketone
- 4,4'-bis(dimethyl amino)-benzophenone (Michler's ketone)
- 4,4'-bis(diethyl amino)-benzophenone.

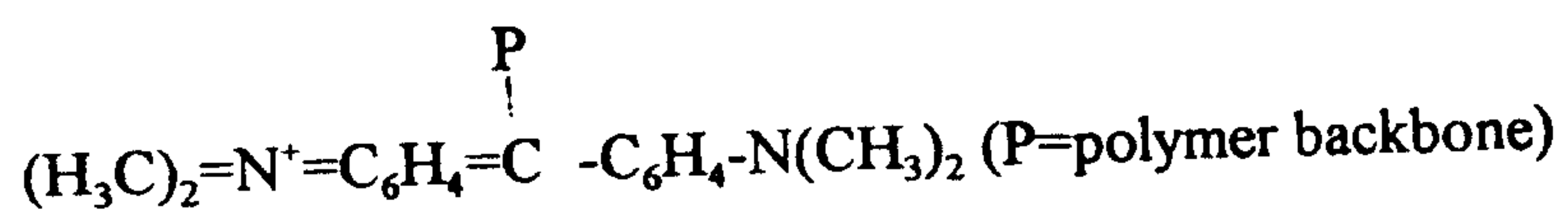
Examples of addable basic aromatic aldehydes are (Fig. 2):

- 4-dimethyl amino benzaldehyde
- 4-diethyl amino benzaldehyde
- pyridine-2-aldehyde, pyridine-3-aldehyde, pyridine-4-aldehyde.

Where this reaction is concerned, the degrees of substitution are dependent upon the size of the basic aromatic compound. Thus, with the sterically hindered ketons 2,2-bipyridyl ketone, 4,4'-bis(dimethyl amino)-benzophenone (Michler's ketone) and 4,4'-bis(diethyl amino)-benzophenone, degrees of substitution of about 1 are reached while degrees of substitution of up to 2 can be achieved with the above-mentioned less sterically hindered aldehydes.

Upon synthesis of the product of addition of 4,4'-bis(diethyl amino)-benzophenone to lithiated PSU, it was surprisingly found that the substituted polymer was coloured, the colour deepening from pale green to very dark green in time, by exposure to the air. This

is probably attributable to oxidation of the PSU addition product by atmospheric oxygen according to the reaction shown in Fig. 3. Presumably, a triphenyl methane dye¹⁴ is produced. This reaction points away to chromophoric groups which can be bonded on lithiable polymers. These chromophoric groups are positively charged which means they constitute anion exchanger groupings since the compensating ions, e.g. Cl⁻, are interchangeable. Since the compensating ions are interchangeable, the oxidised basic polymer displays ion conductivity which it was possible to prove experimentally. Since the positive charge is distributed mesomerically over the system:



these anion exchange groups are very stable in comparison with normal anion exchange groups.

If it is intended to prevent oxidation of the PSU addition product, the Li-alcoholate intermediate compound which forms during the addition reaction can be captured with alkyl halides Alk-Hal, forming the ether PSU-C(C₁R₂)-OAlk. Thus, the addition compound becomes more oxidation stable than the addition compound with the free OH-group.

b) Polymers modified by basic N by substitution reaction with lithiated polymers

If low molecular aromatic carboxylic acid esters are caused to react with Li-organic compounds, then in most cases the lithium salts of tertiary alcohols are obtained (Fig. 4)¹⁶. Surprisingly, it has been found that the reaction of basic compounds such as for example isonicotinic acid ethyl ester and N, N-dimethyl amino benzoic acid ethyl ester with lithiated PSU can, under the selected conditions (low temperature, low polymer concentration in the solution of the lithiated PSU, excess of a basic compound) can be arrested at the ketone stage (Fig. 5).

In this way, it is possible from lithiated polymers to produce such polymers as are modified with basic N-groups (tertiary N such as pyridile or dialkyl amino group) in the aromatic lateral chain. By virtue of its aromatic nature and by reason of the bonding on

the polymer main chain via a carbonyl function, the lateral chain becomes very oxidation stable. The synthesised polymers which contain tertiary N can, in a further step, be converted by N-quaternisation into oxidation stable anion exchange polymers (see c)).

c) Anion exchange polymers and membranes

The above-mentioned polymers which are modified with basic tertiary N in the aromatic lateral chain can, now, be reacted by means of conventional processes¹⁵ to produce anion exchange polymers and membranes, whereby even anion exchange membranes are accessible by the following method: a solution of the lithiable polymer modified with tertiary-N in the lateral group is produced in a dipolar-aprotic solvent (NMP, DMAc, DMF, DMSO, sulpholane, etc.), halogen alkanes and halogen dialkanes in the desired molar ratio are added to the solution in order to generate the desired density of cross-linking and the solvent is evaporated off at elevated temperature. During membrane formation, the tertiary-N are quaternised to anion exchange groups, the dihalogen alkanes at the same time forming a covalent network in the membrane.

d) Cation exchange polymers which are sulphonated in the lateral group

On a basis of the reaction presented in b) (reaction of an aromatic carboxylic acid ester with lithiated aryl polymer with the bonding of an aromatic lateral group to the aryl main chain polymer via a carbonyl group), aryl main chain polymers which are sulphonated in the lateral group become accessible, subject to the aromatic lateral group being more easily electrophilically sulphonatable than the polymer main chain. In order to achieve this, the aromatic hydrocarbon present in the lateral group must have the greatest electron density of all the aromatic rings of the polymer. A reaction to obtain an aryl main chain polymer sulphonated in the aromatic lateral chain is shown in Fig. 6. In the case of the PSU Udel® sulphonated in the aromatic lateral chain, the aromatic hydrocarbon at the end of the aromatic lateral chain has the greatest electron density of the entire molecule. For this reason, this aromatic hydrocarbon is sulphonated and in fact in the p-position in relation to the ether bridge since the electronically also possible o-position is sterically hindered in relation to the ether bridge.

- e) *Acid-based blends and acid-based blend membranes from the polymers a or b polymers sulphonated as desired or with the cation exchange polymers d*

The newly obtained polymers listed in sub-paragraphs a, b and d as well as any sulphonated polymers can be combined to produce new acid-based blends and acid-based blend membranes. The location of the acid and basic groups at the end of the aromatic lateral chain opens a way to better association of the ion exchange groups in the blends since the position of the acid and basic groups at the end of the lateral group is less sterically impeded than if these groups were in the polymer main chain. A better possibility of association of acid and basic groups can result in an increase in local concentration of ion exchange groups in the polymer matrix and thus to a higher level of proton conductivity even at relatively low concentrations of ion exchange groups than in the case of rigid aryl main chain polymers modified with acid and basic groups in the main chain. The morphology of the perfluorinated ion exchange polymer Nafion in which the sulphonic acid groups are strongly associated (clustered)¹⁰ on account of the extremely hydrophobic perfluorinated backbone, can consequently be "copied" with such new acid-based blends. In addition to the ionic cross-linking by the polysalt formation:



in that to the mixture of acid with basic polymers in the solvent, dihalogen alkanes are added which, during membrane formation,



with quaternisation of the tertiary N.

6. Examples of embodiment

6.1 Reaction of N,N-dimethyl amino benzaldehyde with lithiated PSU

Batch:

11.05 g PSF Udel P 1800 (0.025 mol) dried

500 ml THF anhydrous

5 ml n-BuLi 10 N (0.05 mol)

10 g 4-dimethyl amino benzaldehyde (0.13 mol), dissolved in 20 ml THF

Procedure

Under barrier gas, fill the THF into the reaction vessel. Afterwards, the dried polymer is introduced with argon into the reaction vessel accompanied by stirring and thorough rinsing. Once the polymer has been dissolved, it is cooled to -65°C in a strong argon flow. The polymer solution is then titrated with n-BuLi until a slight yellow/orange colouring indicates that the reaction mixture is now anhydrous. Afterwards, the 10 N n-BuLi is injected within 10 mins. Stirring follows for 30 mins. Afterwards, the solution of 4-dimethyl amino benzaldehyde in THF is injected. Stir until such time as the reaction mixture has lost its colour. Maximum waiting time at -65°C is 1 hour. Afterwards, the acetone cold bath is taken away and replaced by an ice bath. Allow to warm to 0°C and stir for 1 hour at 0°C . Afterwards, the reaction mixture is precipitated in 2 litres isopropanol. Dry at 50°C firstly in a diaphragm pump vacuum then in an oil pump vacuum. Afterwards, the polymer is ground, suspended in 500 ml methanol and dried once again in a vacuum at 50°C . The chemical structural formula of the modified PSU formed is shown in Fig. 7.

Elementary analysis and the ^1H -NMR spectrum of the polymer reveal a substitution degree of approximately 2 groups per PSU repetition unit.

6.2 Reaction of bis(N,N-diethyl amino)benzophenone with lithiated PSU

Batch:

11.05 g PSU Udel P 1800 (0.025 mol), dried

600 ml THF anhydrous

3 ml n-BuLi 10 N (0.03 mol)

25 g 4,4'-bis-diethyl amino benzophenone dissolved in 50 ml THF (0.077 mol)

Procedure:

Under barrier gas, fill the THF into the reaction vessel. Afterwards, the dried polymer is introduced with argon into the reaction vessel accompanied by stirring and thorough rinsing. Once the polymer has been dissolved, it is cooled to -30°C in a strong argon flow. The polymer solution is then titrated with n-BuLi until a slight yellow/orange colouring indicates that the reaction mixture is now anhydrous. Afterwards, the 10 N n-BuLi is injected within 10 mins. Stirring follows for 50 mins. Afterwards, the solution of 4,4'-diethyl amino benzophenone is injected. Stir until such time as the reaction mixture has lost its colour, not more than 24 hours. Afterwards, a mixture of 20 ml isopropanol with 2 ml of water is injected into the reaction solution and afterwards warmed to room temperature. The polymer is precipitated in 2 litres of isopropanol, filtered off and washed with isopropanol. Afterwards, the polymer is stirred into 300 ml i-PrOH. Afterwards, it is filtered off again, suspended again in i-PrOH, stirred and filtered off. Afterwards, the polymer is added to 5 litres of water and stirred. After filtration, it is once again added to 5 litres of water and stirred again. Subsequently, a further filtration process follows and then washing to pH7 and afterwards dried at 80°C. The chemical structural formula of the modified PSU formed is shown in Fig. 8.

Elementary analysis and the ¹H-NMR spectrum of the polymer disclose a substitution degree of approximately 1 group per PSU repetition unit. The polymer is coloured green, a situation which can be attributed to partial formation of triphenyl methyl chromophores by oxidation accompanied by cleavage of the OH group (see Fig. 3). If the polymer is allowed to stand at elevated temperature in dilute acid, the colour deepens to a black-green. With ¹H- and ¹³C-NMR, it was possible to show that the reaction of the reaction

product 6.2 shown in Fig. 3 actually takes place: the ^1H and the ^{13}C signal of the OH proton, of which the position could be identified by H/D exchange as being recumbent with a chemical shift of 5.8 ppm (^1H -NMR) or a chemical shift of 85 ppm (^{13}C -NMR), had almost completely disappeared after the reaction products 6.2 had been stored in dilute acid at 60°C with air having access.

Formation of the chromophoric group can be prevented by etherifying the OH group by a reaction of the PSU-Li-alkoxide with methyl iodide for example (Fig. 9). The oxidised reaction product 6.2 displays ion conductivity which can be attributed to the causes outlined in para. 5 a). To this end, films of the oxidised polymer were assessed by impedance spectroscopy in 0.5 N HCl with and without secondary HCl treatment.

Results:

Polymer film	Film thickness [μm]	R_s [$\Omega \cdot \text{sq.cm}$]	R_{sp} [$\Omega \cdot \text{cm}$]
6.2 + secondary treatment	55	7.6	500
6.2 without secondary treatment	155	4.6	840

6.3 Reaction of 2,2'-dipyridyl ketone with lithiated PSU

Batch:

6.88 g PSU Udel P 1800 (0.01556 mol) dried

400 ml THF anhydrous

1.7 ml n-BuLi 10 N (0.017 mol)

3.89 g di(2-pyridyl)-ketone (0.021 mol), dissolved in 20 ml THF

Procedure:

Under barrier gas, fill the THF into the reaction vessel. Afterwards, the dried polymer is introduced with argon into the reaction vessel accompanied by stirring and thorough

rinsing. Once the polymer has been dissolved, it is cooled to -30°C in a strong argon flow. The polymer solution is then titrated with n-BuLi until a slight yellow/orange colouring indicates that the reaction mixture is now anhydrous. Afterwards, the 10 N n-BuLi is injected within 10 mins. Stirring follows for 30 mins. Afterwards, the solution of di(2-pyridyl)-ketone is injected into THF.

Stir until the reaction mixture has lost its colour, at most 48 hours at -30°C .

Subsequently, inject a mixture of 10 ml isopropanol with 1 ml water into the reaction solution and allow to warm up to room temperature. Precipitate the polymer in 2 litres isopropanol, filter off and wash with isopropanol and methanol.

The precipitated polymer is filtered off again, dried and stirred in 100 ml MeOH. Afterwards, it is filtered off again, suspended once again in MeOH, stirred, filtered off and dried at 80°C . The structural formula of the reaction product is shown in Fig. 10.

The degree of substitution of the modified PSU in terms of dipyridyl groups, determined by elementary analysis, amounts to about 0.85 per PSU repetition unit.

6.4 Reaction of isonicotinic acid ethyl ester with lithiated PSU

Batch:

8.84 g PSU Udel P 1800 (0.02 mol), dried

300 ml THF anhydrous

4 ml n-BuLi 10 N (0.04 mol)

10.5 ml isonicotinic acid ethyl ester (0.07 mol)

Procedure

Under barrier gas, fill the THF into the reaction vessel. Afterwards, the dried polymer is introduced with argon into the reaction vessel accompanied by stirring and thorough rinsing. Once the polymer has been dissolved, it is cooled to -30°C in a strong argon flow. The polymer solution is then titrated with n-BuLi until a slight yellow/orange colouring indicates that the reaction mixture is now anhydrous. Afterwards, the 10 N n-BuLi is injected. Stirring follows for 50 mins. Afterwards, inject the isonicotinic acid ethyl ester

and stir until the reaction mixture has lost its colour, at most 24 hours at -30°C . Afterwards, inject the mixture of 20 ml isopropanol with 2 ml water into the reaction solution and allow to warm to room temperature. Precipitate the polymer in 2 ml isopropanol, filter off and wash with isopropanol. Afterwards, stir the polymer in 300 ml i-PrOH. Subsequently, filter off again, suspend once more in i-PrOH, stir and filter off. After filtration, add to 5 litres water again and stir afresh. Afterwards, filter off once more and afterwards dry at 80°C . The reaction product is shown in Fig. 11.

The degree of substitution of the modified PSU with 4-pyridyl carbonyl groups amounts to 1.65, determined by $^1\text{H-NMR}$ and elementary analysis.

6.5 Reaction of N,N-dimethyl amino benzoic acid ethyl ester with lithiated PSU

Batch:

11.05 g PSU Udel P 1800 (0.025 mol), dried

600 ml THF anhydrous

5 ml n-BuLi 10 N (0.05 mol)

48.32 g N,N-dimethyl amino benzoic acid ethyl ester, dissolved in 100 ml THF (0.25 mol)

Procedure:

Under barrier gas, fill the THF into the reaction vessel. Afterwards, the dried polymer is introduced with argon into the reaction vessel accompanied by stirring and thorough rinsing. Once the polymer has been dissolved, it is cooled to -60°C in a strong argon flow. The polymer solution is then titrated with n-BuLi until a slight yellow/orange colouring indicates that the reaction mixture is now anhydrous. Afterwards, the 10 N n-BuLi is injected within 10 mins. Stirring follows for 50 mins. Afterwards, the solution of N,N-dimethyl amino benzoic acid ethyl ester is injected in THF. Stir for 10 mins. Then inject the mixture of 20 ml isopropanol with 2 ml water into the reaction solution and warm up to room temperature. Precipitate the polymer in 2 litres isopropanol, filter off and wash with isopropanol and methanol. The precipitated polymer is filtered off again, dried and stirred in 100 ml MeOH. Afterwards, it is filtered off again, suspended again in MeOH,

stirred, filtered off and dried at 80°C. The result of elementary analysis shows a substitution degree of 0.75 p-N,N-dimethyl amino phenyl carbonyl groups per PSU repetition unit. As further tests have shown, the degree of substitution can be increased by a longer reaction time of the lithiated PSU with N,N-dimethyl amino benzoic acid ethyl ester. The reaction product of this reaction (with a p-N,N-dimethyl amino phenyl carbonyl group per PSU repetition unit) is shown in Fig. 12.

6.6 Acid-base blend membrane of reaction product 6.2 with sulphonated PSU

4 g sulphonated PSU Udel® in the SO₃Li form are dissolved in 25 g N-methyl pyrrolidinone. Afterwards, 1 g of the reaction product from reaction 6.2 (1.1 groups per PSU repetition unit) is added to the solution and stirred until dissolved. Afterwards, the very dark green solution is filtered off, de-gassed and applied as a thin film into a glass plate. The solution is then evaporated off at 120°C. Afterwards, the glass plate is placed in a bath with full desalinated water whereupon the polymer membrane becomes detached from the glass plate. Afterwards, the membrane is first treated in 10% sulphuric acid at 70°C and then given a secondary treatment in completely desalinated water. Afterwards, the membrane is characterised.

Characterisation results:

Ion exchange capacity:	1.35 meq SO ₃ H/g
Swelling (H ⁻ -form, RT):	33.14%
Specific resistance (H ⁺ -form, RT)	27.6 Ω cm

6.7 Acid-base blend membrane consisting of reaction product 6.4 with sulphonated PSU

4 g sulphonated PSU Udel® in the SO₃Li form are dissolved in 25 g N-methyl pyrrolidinone. Afterwards, 1 g of the reaction product of reaction 6.2 (1.65 groups per PSU repetition unit) is added to the solution and stirred until dissolved. Afterwards, the solution is filtered, de-gassed and applied as a thin film to a glass plate. The solvent is

then evaporated off at 120°C. The glass plate is then laid in a bath with fully desalinated water, whereupon the polymer membrane forme becomes detached from the glass plate. The membrane is then given a secondary treatment at 70°C firstly in 10% sulphuric acid and then in fully desalinated water. The membrane is then characterised.

Characterisation results:

Ion exchange capacity:	1.09 meq SO ₃ H/g
Swelling (H ⁺ -form, RT):	24.6%
Specific resistance (H ⁺ -form, RT):	21.2 Ωcm

6.8 Acid-base blend membrane consisting of reaction product 6.5 with sulphonated PSU

4 g sulphonated PSU Udel® in the SO₃Li form are dissolved in 25 g N-methyl pyrrolidinone. Afterwards, 1 g of the reaction product from reaction 6.2 (0.75 groups per PSU repetition unit) is added to the solution and stirred until dissolved. Afterwards, the solution is filtered, de-gassed and applied as a thin film to a glass plate. Afterwards, the solvent is evaporated off at 120°C. The glass plate is then placed in a bath with fully desalinated water, whereupon the polymer membrane formed becomes detached from the glass plate. The membrane is then given a secondary treatment at 70°C firstly in 10% sulphuric acid and then in fully desalinated water. Afterwards, the membrane is characterised.

Characterisation results:

Ion exchange capacity:	1.11 met SO ₃ H/g
Swelling (H ⁺ -form, RT):	23.5%
Specific resistance (H ⁺ -form, RT):	17.6 Ωcm

7. Novelty of the invention

The aforementioned novel polymers and membranes and the method of producing them have not been described hitherto in the literature.

8. Advantages of the invention

The invention covers new polymers and membranes which are chemically stable on account of the aromatic lateral chain and which can be further modified under control:

- By quaternising the basic N with alkyl halides, new anion exchange polymers and membranes can be produced which, by reason of the direct bonding of the basic N on the aromatic lateral chain become chemically more stable than commercial anion exchange polymers and membranes. Due to the possibility of using dihalogen alkanes, the anion exchange polymer membranes can furthermore be covalently cross-linked at the same time.
- The synthesis of polymers with aromatic lateral groups which are sulphonated in the aromatic lateral group can improve the association of the sulphonic acid groups in the polymer matrix and thus lead to higher levels of proton conductivity even at relatively low ion exchange group concentrations.
- The acid-base blends and acid-base blend membranes according to the invention may display a better ion exchange group association than acid-base blends and acid-base blend membranes, in which the acid and basic groups are present in the polymer main chain, since the lateral groups are more movable than the polymer main chain. In addition to the ionic cross-linking due to the polysalt formation, these blends and blend membranes can, by covalent cross-linking, be further stabilised in terms of swelling and thus mechanical stability.

9. Key words

Aryl main chain polymers

Modification with side groups containing basic tertiary N

Anion exchange polymers

Anion exchange polymer membranes

Cation exchange polymers

Cation exchange polymer membranes

Aromatic carboxyl acid esters containing basic tertiary N

Carboxylic acid halides

Aromatic ketones and aldehydes containing basic tertiary N

Acid-base polymer blends

Acid-base polymer blend membranes

Metallised aryl main chain polymer

Membrane fuel cells

Membranes

Membrane methods

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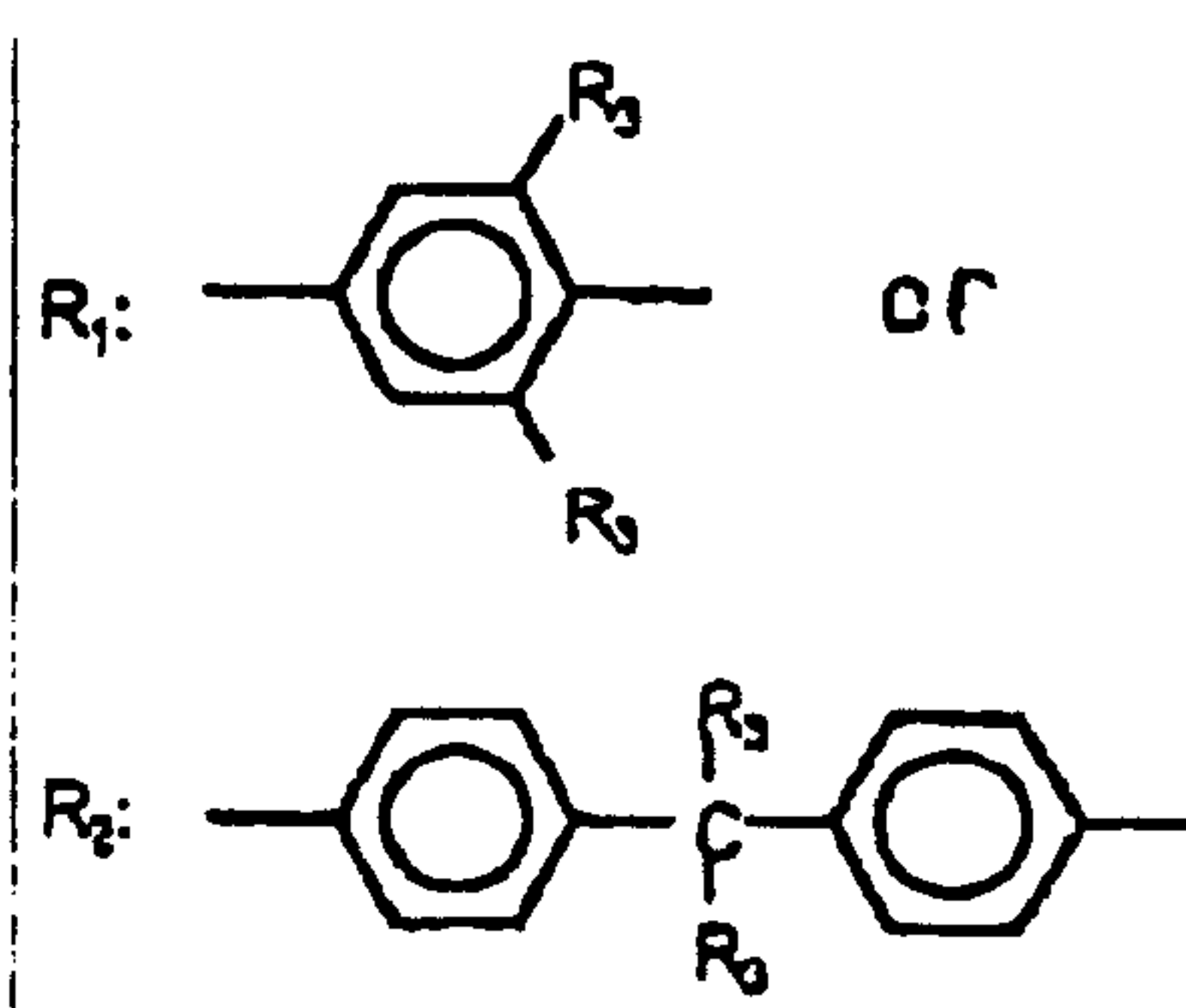
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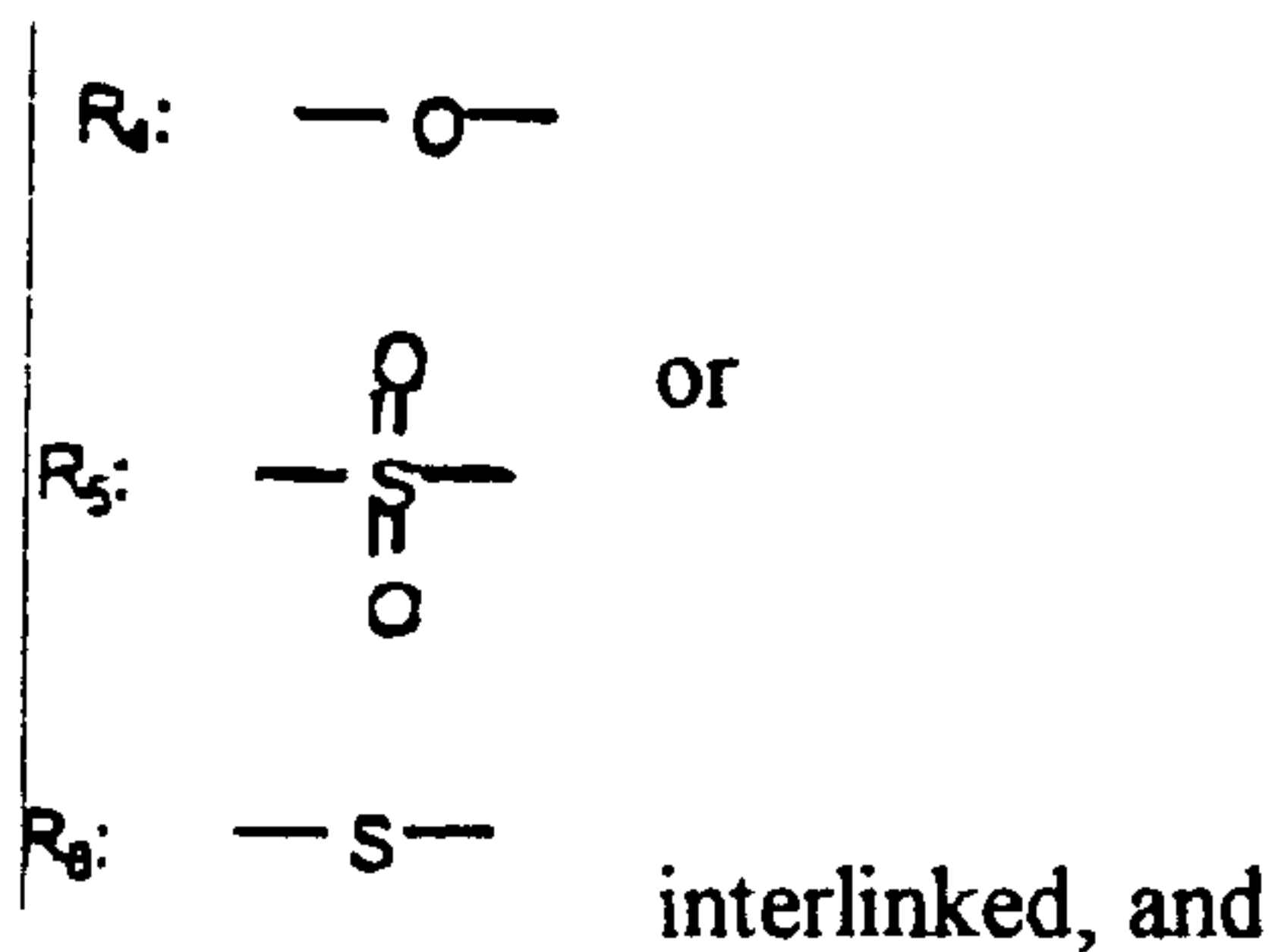
PATENT CLAIMS

1. A method for the lateral chain modification of engineering aryl main chain polymers with aryl-containing N-basic groups and which can be deprotonised with metalorganic compounds, in which

a) metallised polymers P-Me are reacted with the basic constituents of polymer P with

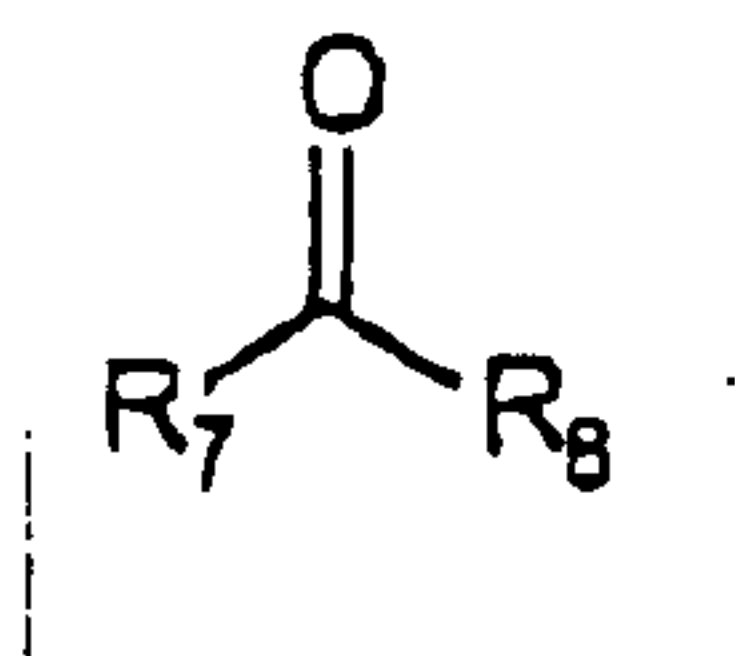


in which $R_3 = \text{H}$, alkyl or aryl, which are linked via



Me stands for an alkali metal cation,

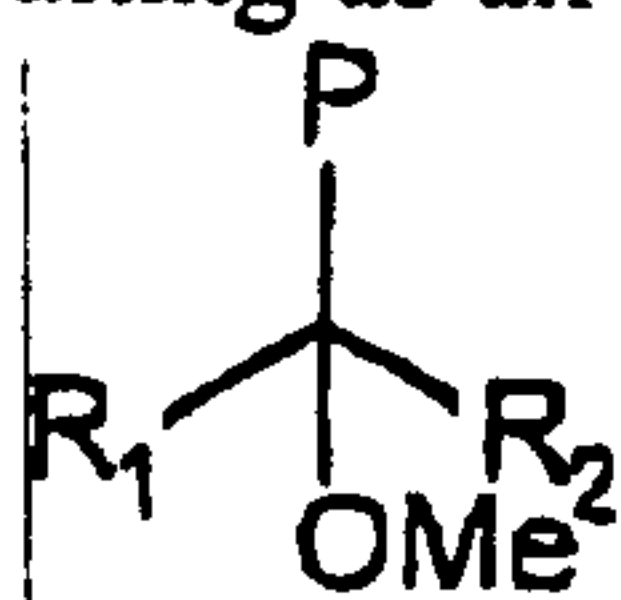
with aromatic ketones or aldehydes containing tertiary basic N-groups to the general formula



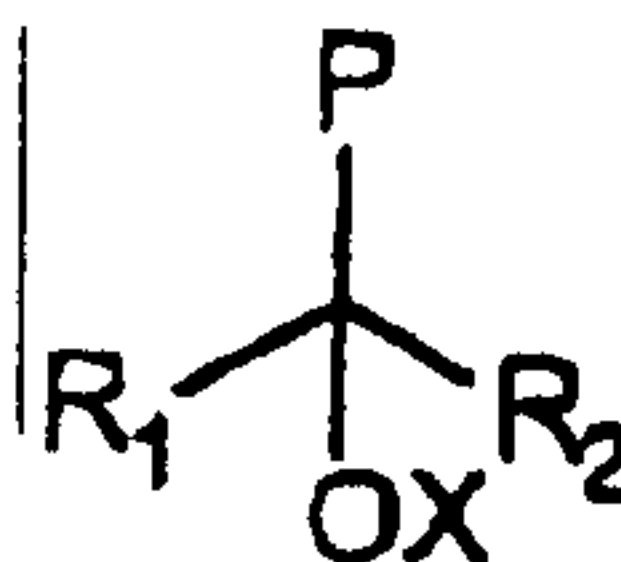
in which R_7 and R_8 stand respectively for a pyridine, pyrimidine, triazine, imidazole, pyrazole, triazole, thiazole or oxazole radical and in the case of aldehydes R_8 for a hydrogen radical

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b) the Me alcoholate resulting as an intermediate product of step a)



is protonised with water or etherified with halogen alkanes Hal-R₃



in which X = H or R₃.

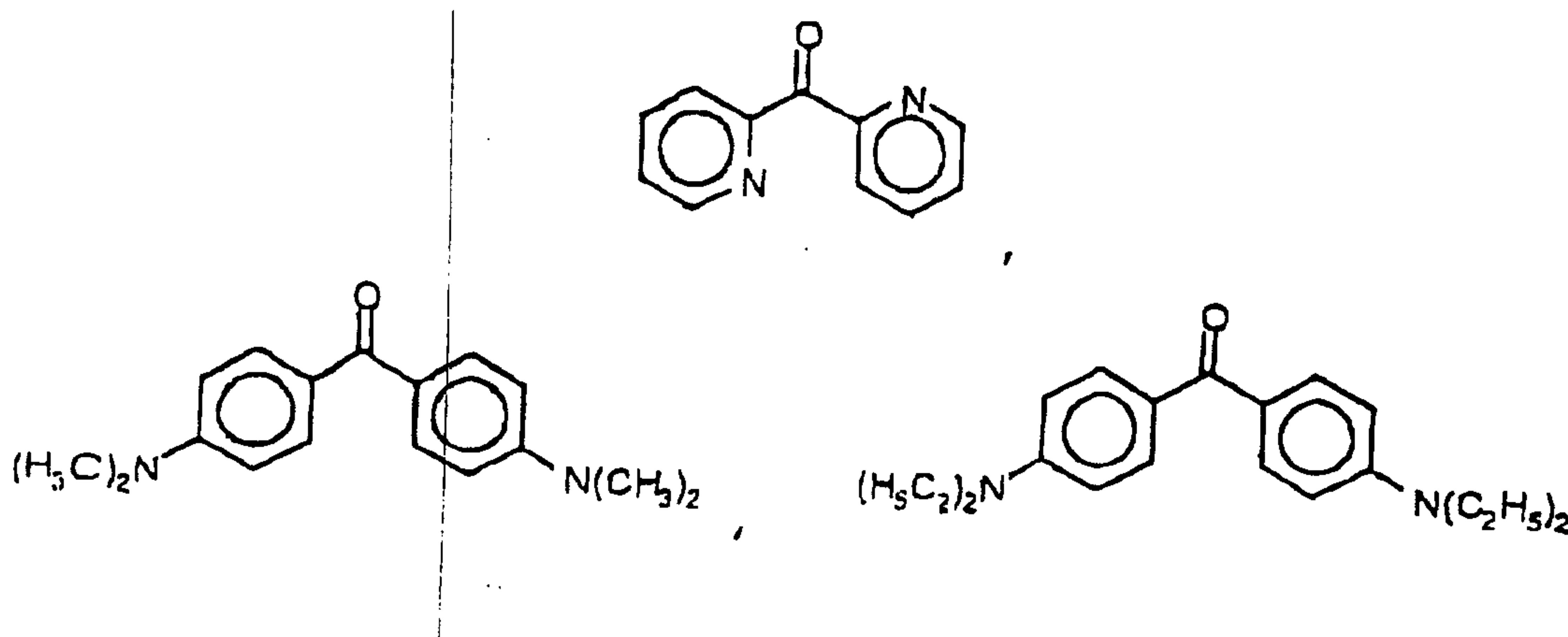
2. A method according to claim 1, characterised in that a polyether sulphone is used as the polymer P.

3. A method according to claim 2, characterised in that the polyether sulphones are selected from

- polyether sulphone (PSU Udel®): R₂(R₃=CH₃)-R₄-R₁(R₃=H)-R₅R₁-R₄
- polyether sulphone (PES Victrex®): R₁-R₅-R₁-R₄
- polyphenyl sulphone (PPhSU Radel R®): R₁(R₃=H)-R₁(R₃=H)-R₄-R₁(R₃=H)-R₅-R₁-R₄
- polyether ether sulphone (PEES Radel A®): [R₄-R₁(R₃=H)-R₄-R₁(R₃=H)-R₅-R₁(R₃=H)]_n-[R₄-R₁(R₃=H)-R₅-R₁(R₃=H)]_m, $\frac{n}{m} = 0.18$

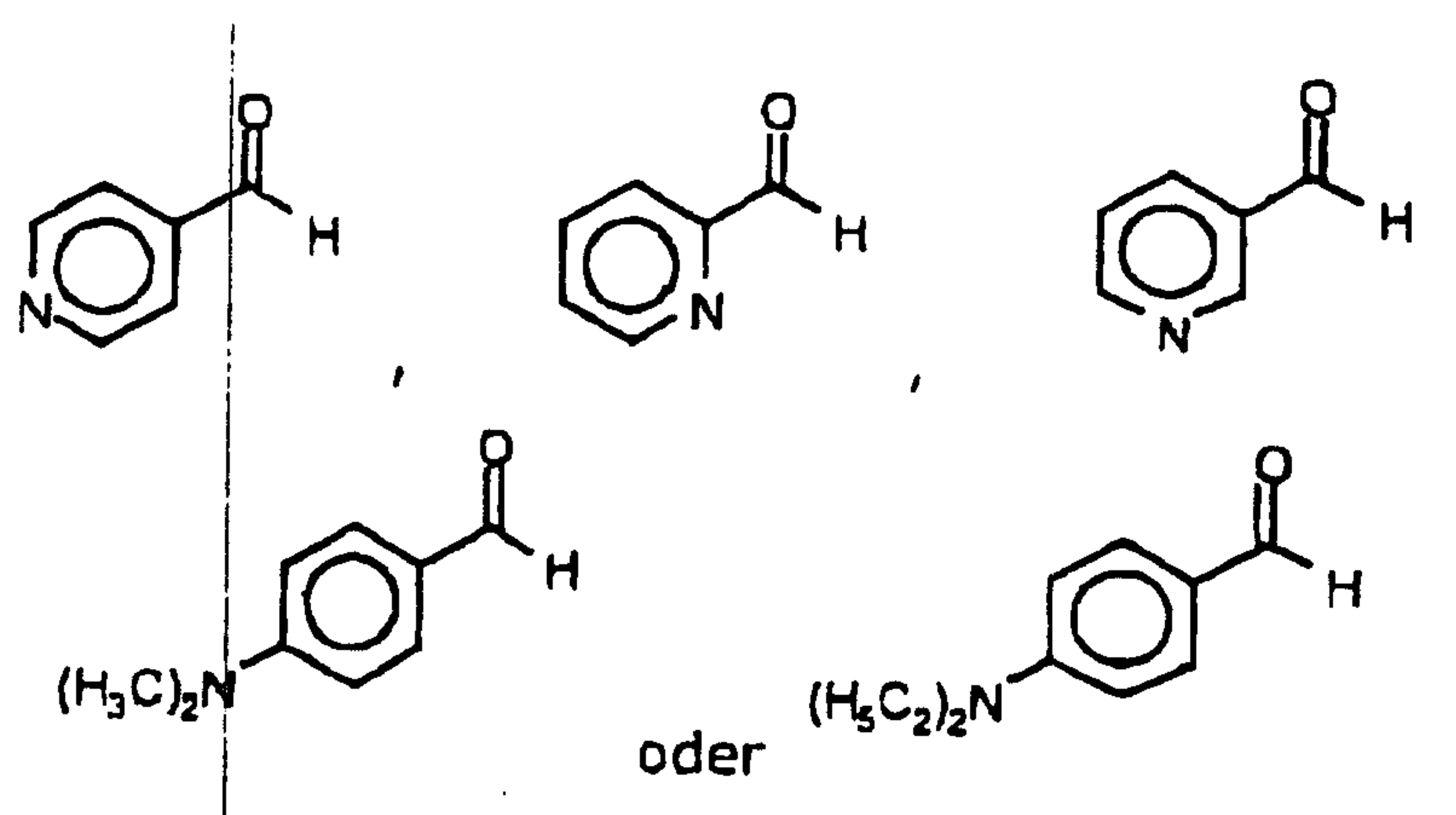
4. A method according to claim 1, characterised in that the alkali metal cations are selected from Li or Na.

5. A method according to one of claims 1 to 4, characterised in that the aromatic ketones or aldehydes are selected from



2,2'-bipyridine-5,5'-dicarbonyl

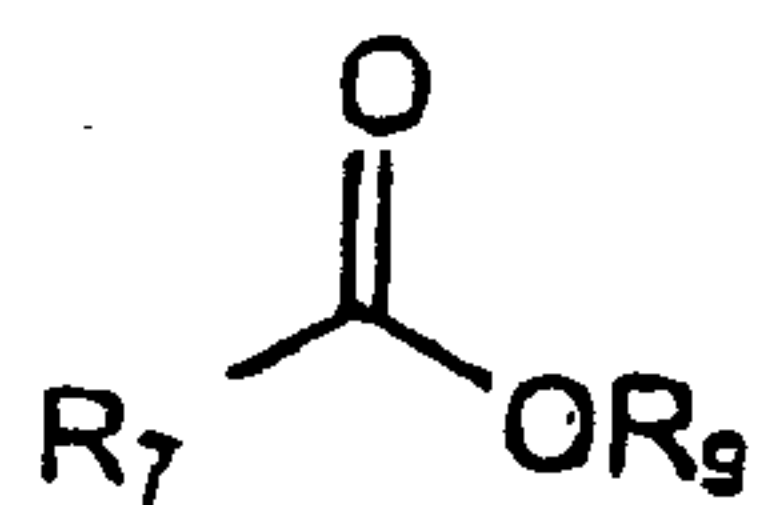
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6. A method according to one of claims 1 to 5, characterised in that halogen monoalkanes are used as the halogen alkanes.

7. A method according to one of claims 1 to 5, characterised in that halogen alkanes for quaternising and covalent cross-linking mixtures of halogen mono- and halogen dialkanes are used.

8. A method for the lateral chain modification of engineering aryl main chain polymers in which metallised polymers P-Me according to the definition in claim 1 are reacted with aromatic carboxylic acid derivatives to the general formula which contain tertiary basic N-groups,



in which R_7 has the above-mentioned meaning and R_9 stands for an alkyl radical, aryl radical or halogen radical.

9. A method according to claim 8, characterised in that in a further step, a solution of the engineering aryl main chain polymer is reacted with halogen alkanes.

10. a method according to claim 9, characterised in that mixtures of halogen monomer- and halogen dialkanes is used for quaternising and covalent cross-linking.

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11. A method of sulphonating lateral chain-modified engineering aryl main chain polymers obtainable according to claim 8, characterised in that these are reacted with a sulphonating agent.
12. A method according to claim 9, characterised in that the sulphonating agent is selected from sulphuric acid, $\text{SO}_3/\text{P}(\text{O})(\text{OR})_3$ or ClSO_3H .
13. Engineering aryl main chain polymers obtaining according to one of claims 1 to 12.
14. A method producing anion exchange polymers, characterised in that metallised polymers P-Me according to claim 1 are first reacted with diaromatic ketones containing tertiary groups, oxidising them in dilute mineral acid in solution or dispersion and exposing them to the action of an oxidation agent particularly in acid phase and in the presence of air.
15. Anion exchange polymer obtainable according to claim 14.
16. A method of producing polymer membranes characterised in that polymers according to claims 13 or 15 are dissolved in a dipolar aprotic solvent, the polymer solution being applied to a carrier in the form of a thin film, after which the solvent is evaporated off.
17. A method of producing acid-base polymer blend membranes characterised in that polymers obtainable according to one of claims 1 to 8 are mixed with further polymers and with polymers in acid or salt form containing sulphonate, phosphonate or carboxylate groups in a dipolar aprotic solvent, the solution of the polymers being applied to a carrier in the form of a thin film after which the solvent is evaporated off.
18. A method according to claim 17, characterised in that the further polymers are selected from polymers obtainable according to one of claims 11 or 12.

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19. A method of producing anion exchange polymer blend membranes characterised, in that polymers according to claim 13 are mixed with further polymers with polymers in acid or salt form containing sulphonate, phosphonate or carboxylate groups in a dipolar aprotic solvent and in that the solution of the polymers is applied to a carrier in the form of a thin film after which the solvent is evaporated off.
20. A method according to one of claims 14 to 19, characterised in that a glass plate, a woven material or a fleece is used as the carrier.
21. Possibly covalently cross-linked polymer blend membrane obtainable according to one of claims 16 to 19.
22. Use of possibly covalently cross-linked polymer blend membranes according to claim 21 as a membrane in membrane processes, particularly in polymer electrolyte membrane fuel cells (PEDC), direct methanol fuel cells (DMFC), diffusion dialysis and electrodialysis.
23. Use of hydrophilic possibly covalently cross-linked polymer blend membranes according to claim 21 as a membrane in dialysis, reversal osmosis, nanofiltration, gas permeation, pervaporation or perstraction.

AMENDED PAGE

DRAWINGS

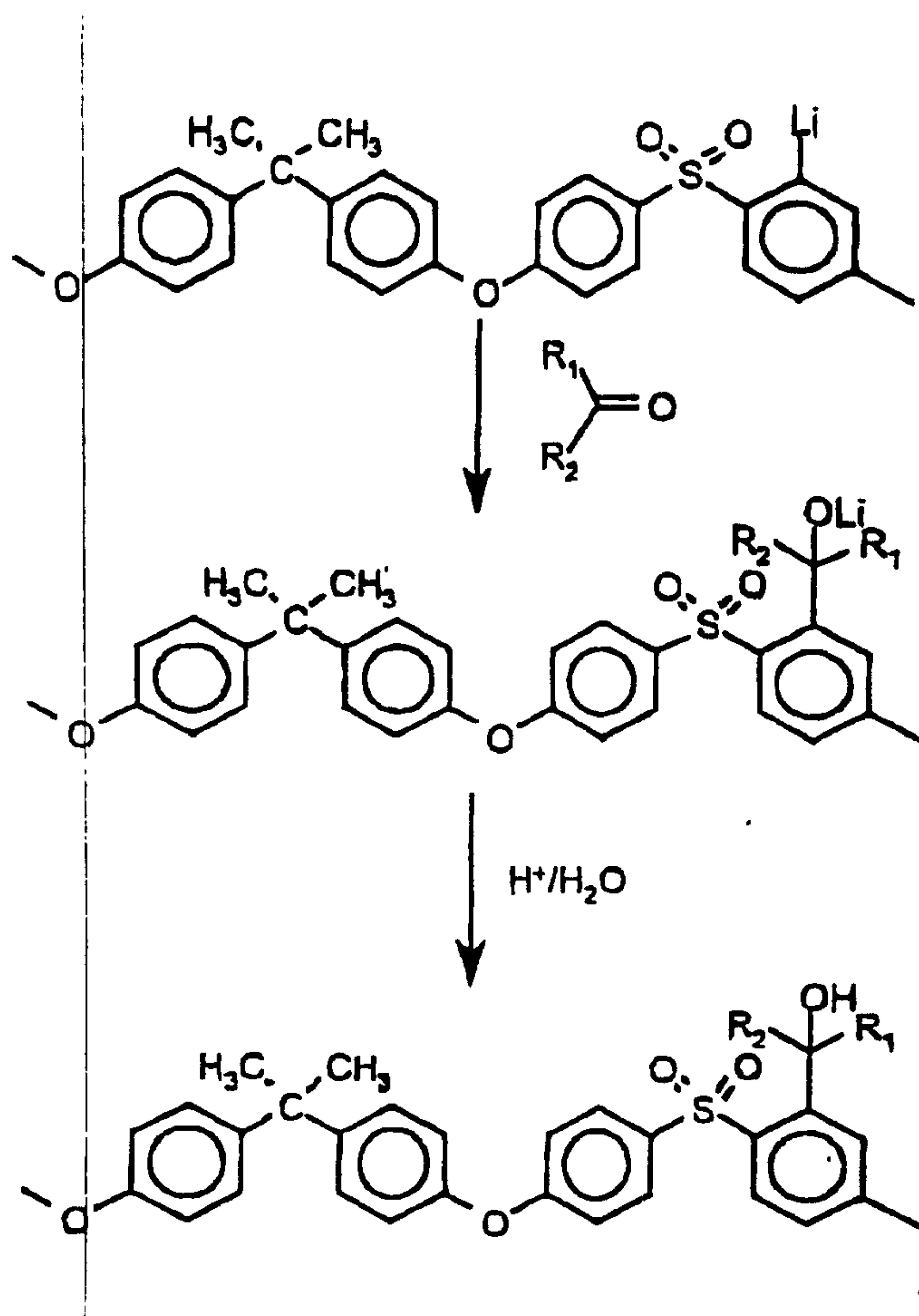
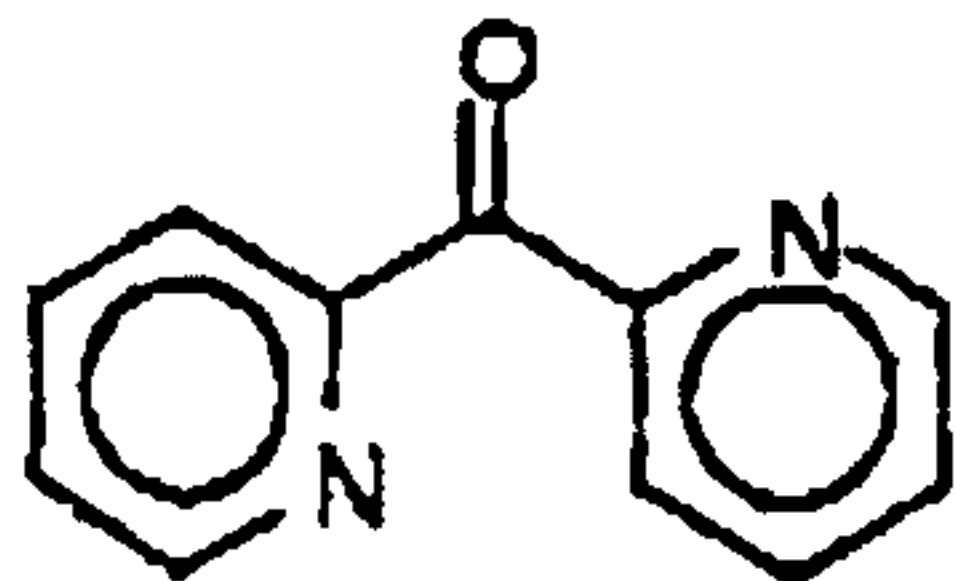


Fig. 1 Reaction of lithiated PSU with benzaldehyde, benzophenone and acetone¹³

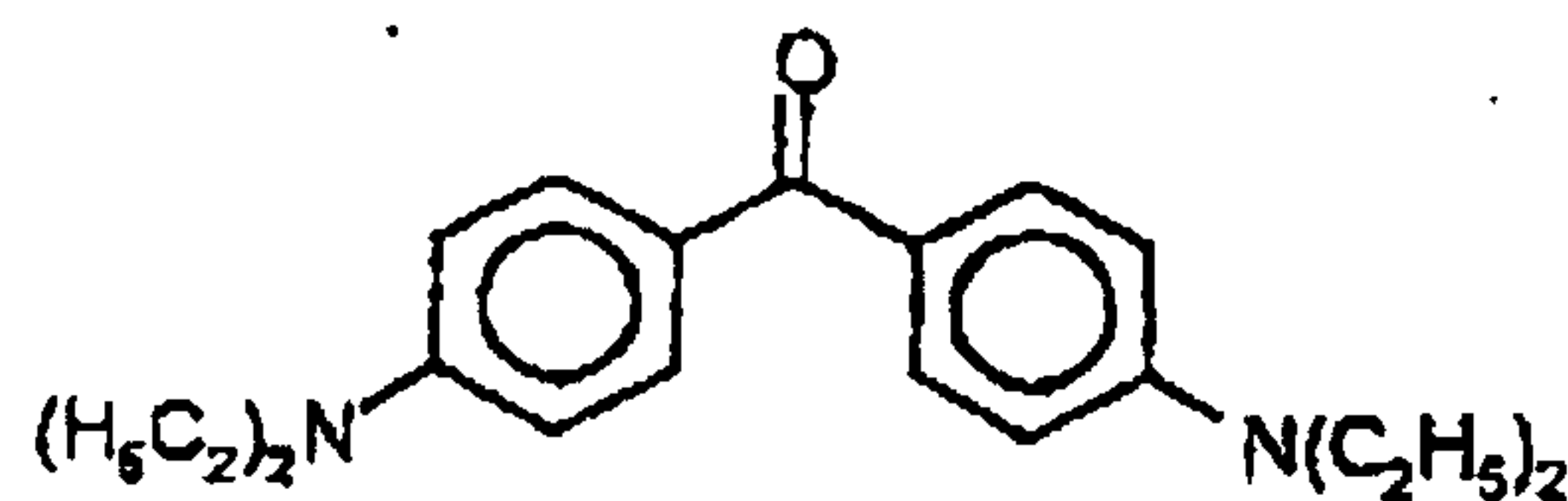
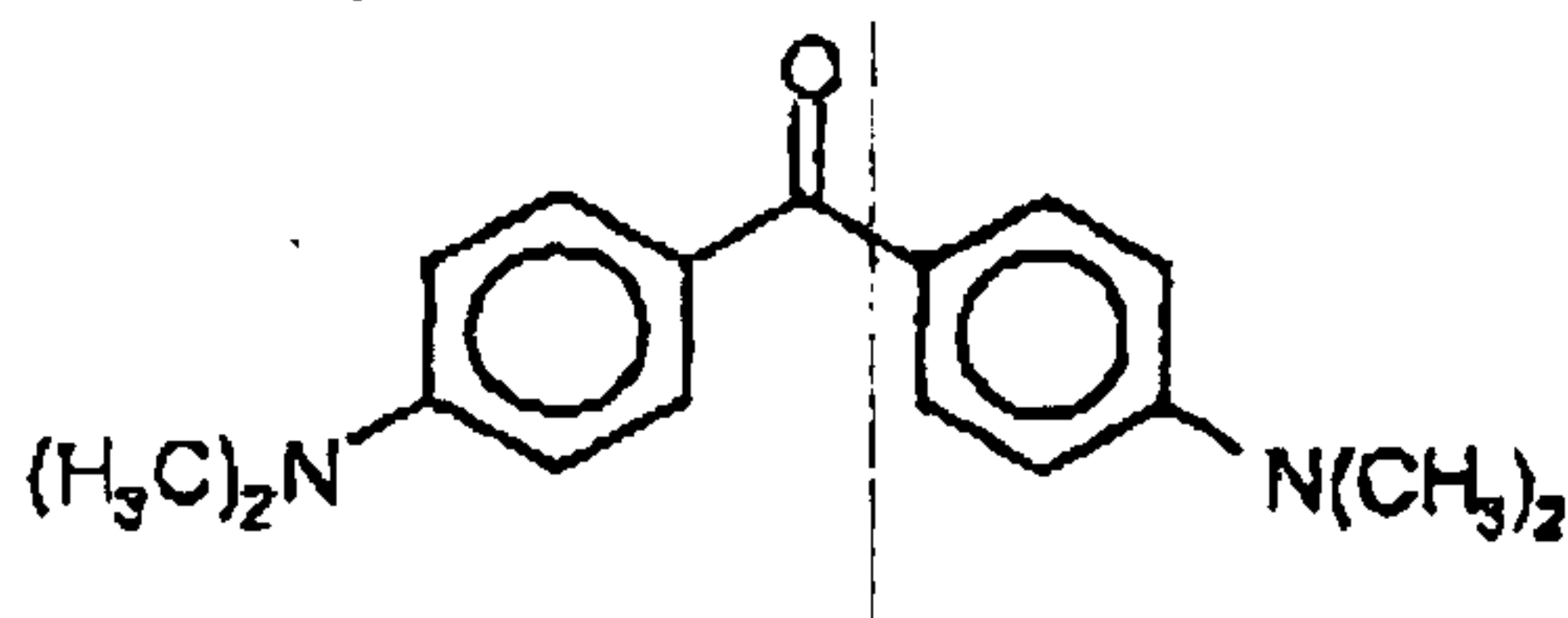
$R_1=H$, $R_2=phenyl$; benzaldehyde; $R_1=R_2=phenyl$: benzophenone;

$R_1-R_2=CH_3$: acetone

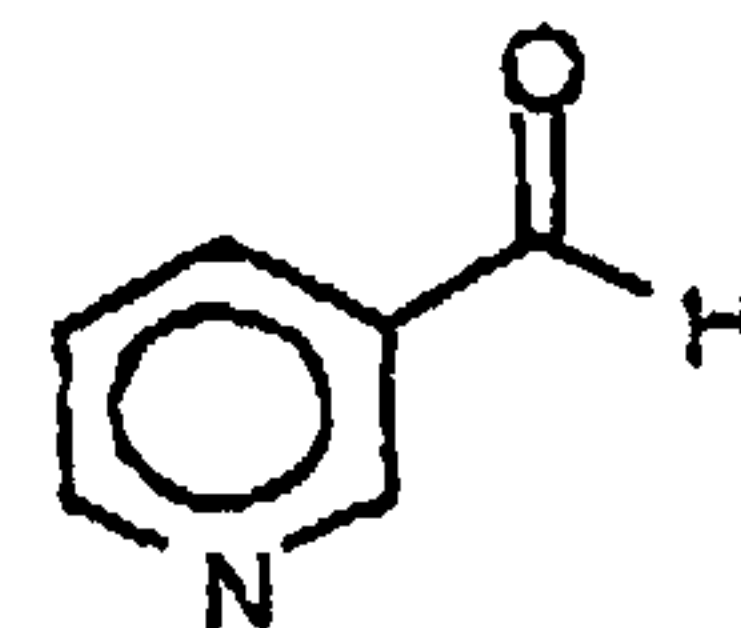
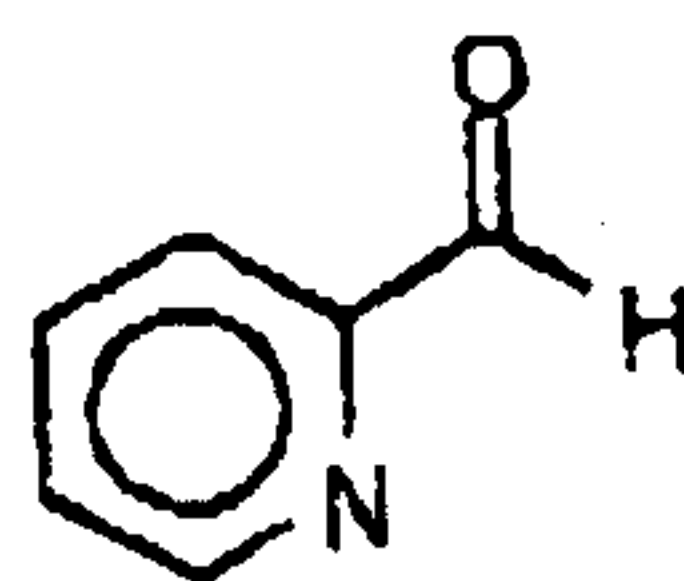
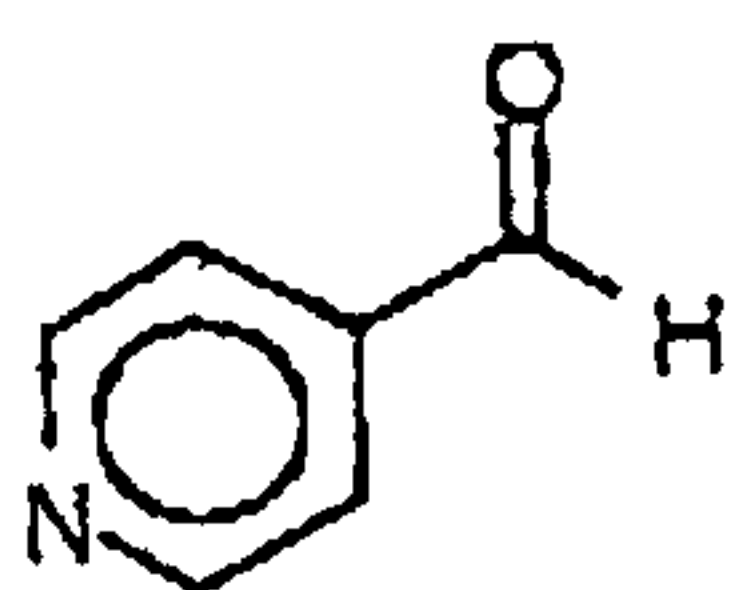
di-2-pyridyl ketone



4,4'-bis-dimethyl amino)-benzophenone (Michler's ketone), 4,4'-bis(diethyl amino)-benzophenone:



pyridine-2-aldehyde, pyridine-3-aldehyde, pyridine-4-aldehyde



4-dimethyl amino benzaldehyde, 4-diethyl amino benzaldehyde

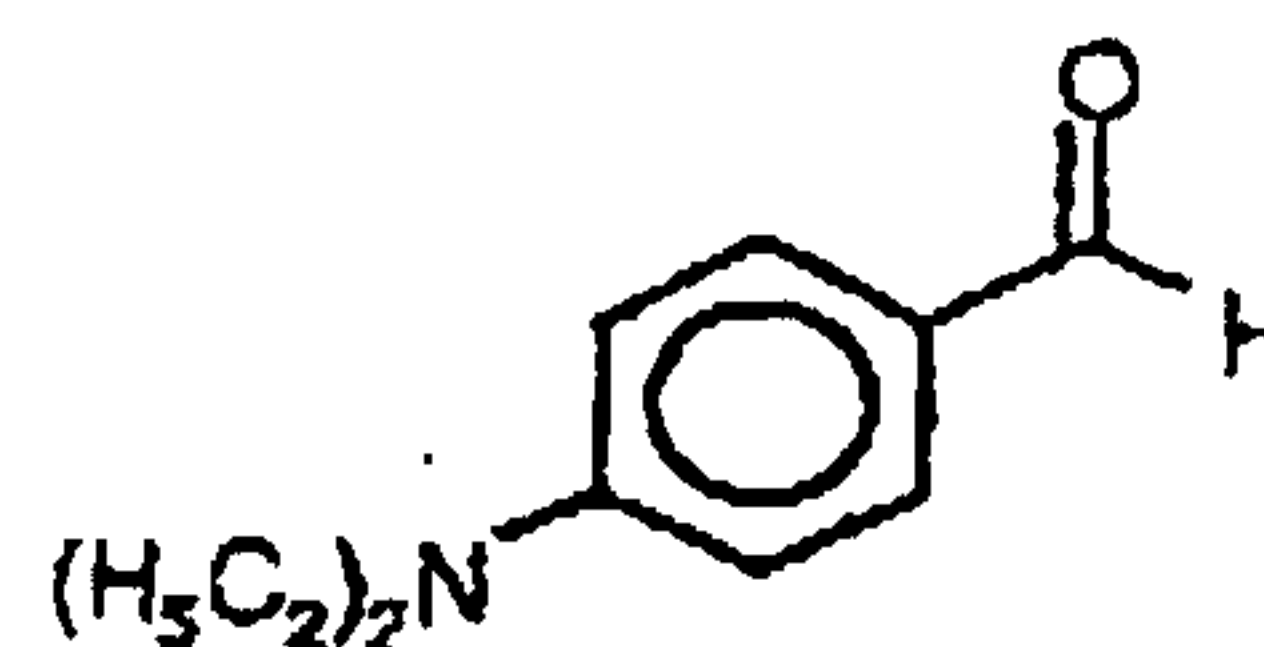
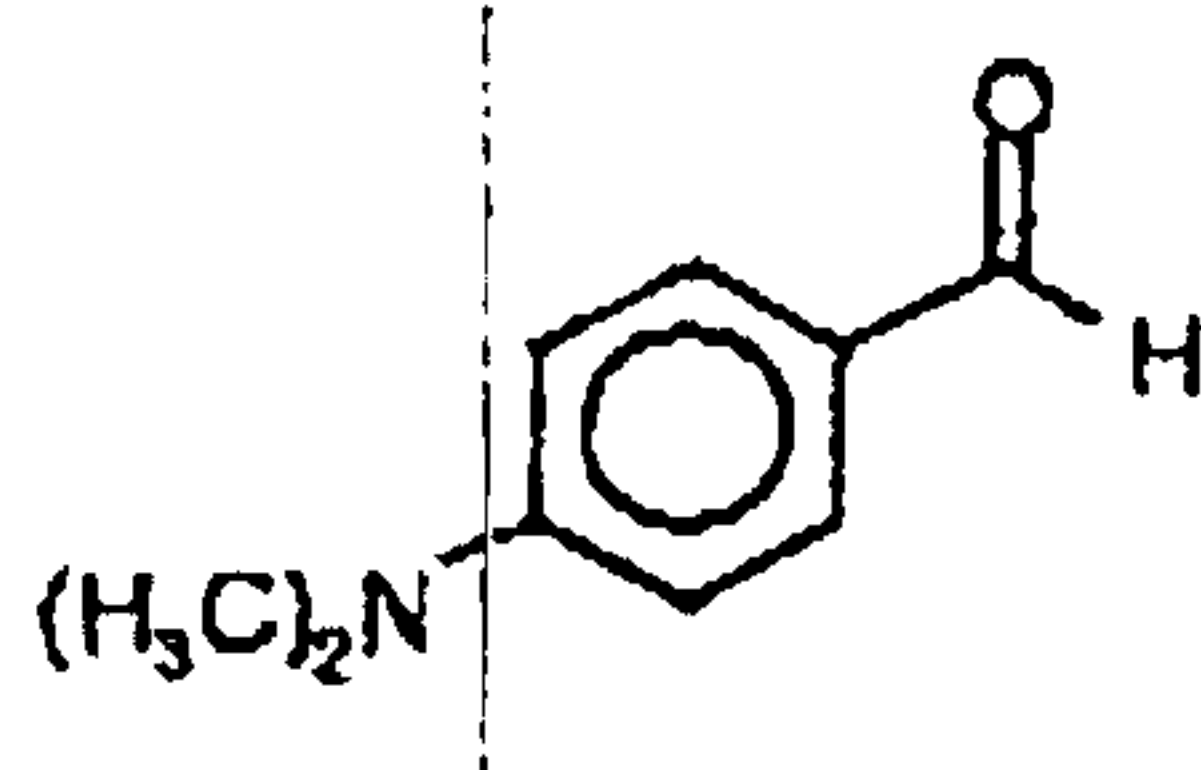


Fig.2: After reaction in Fig. 1, aldehydes and ketones which can be added to lithiated PSU

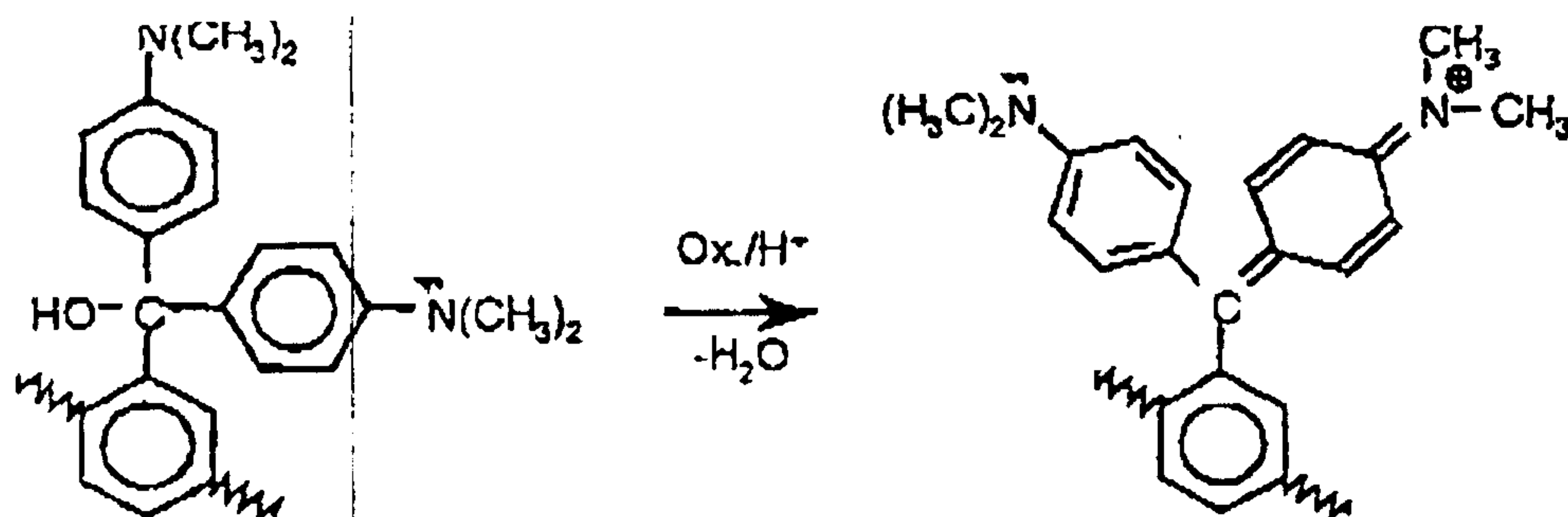


Fig.3: Presumed oxidation reaction of the adduct of 4,4'-bis-diethyl amino)-benzophenone to lithiated PSU forming a chromophoric group on the PSU

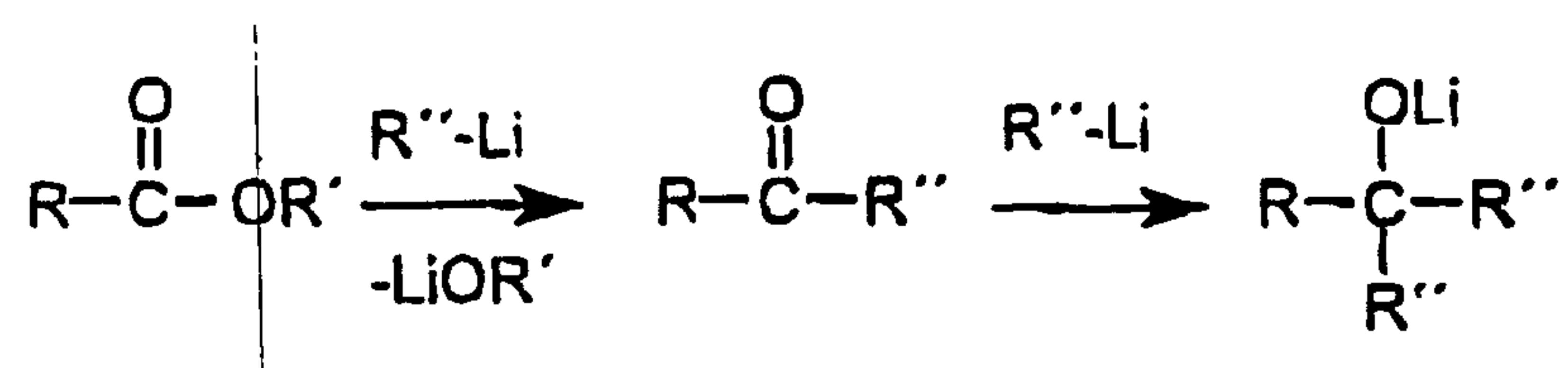


Fig.4: Normal reaction of Li organic compounds with carboxylic acid esters¹⁶

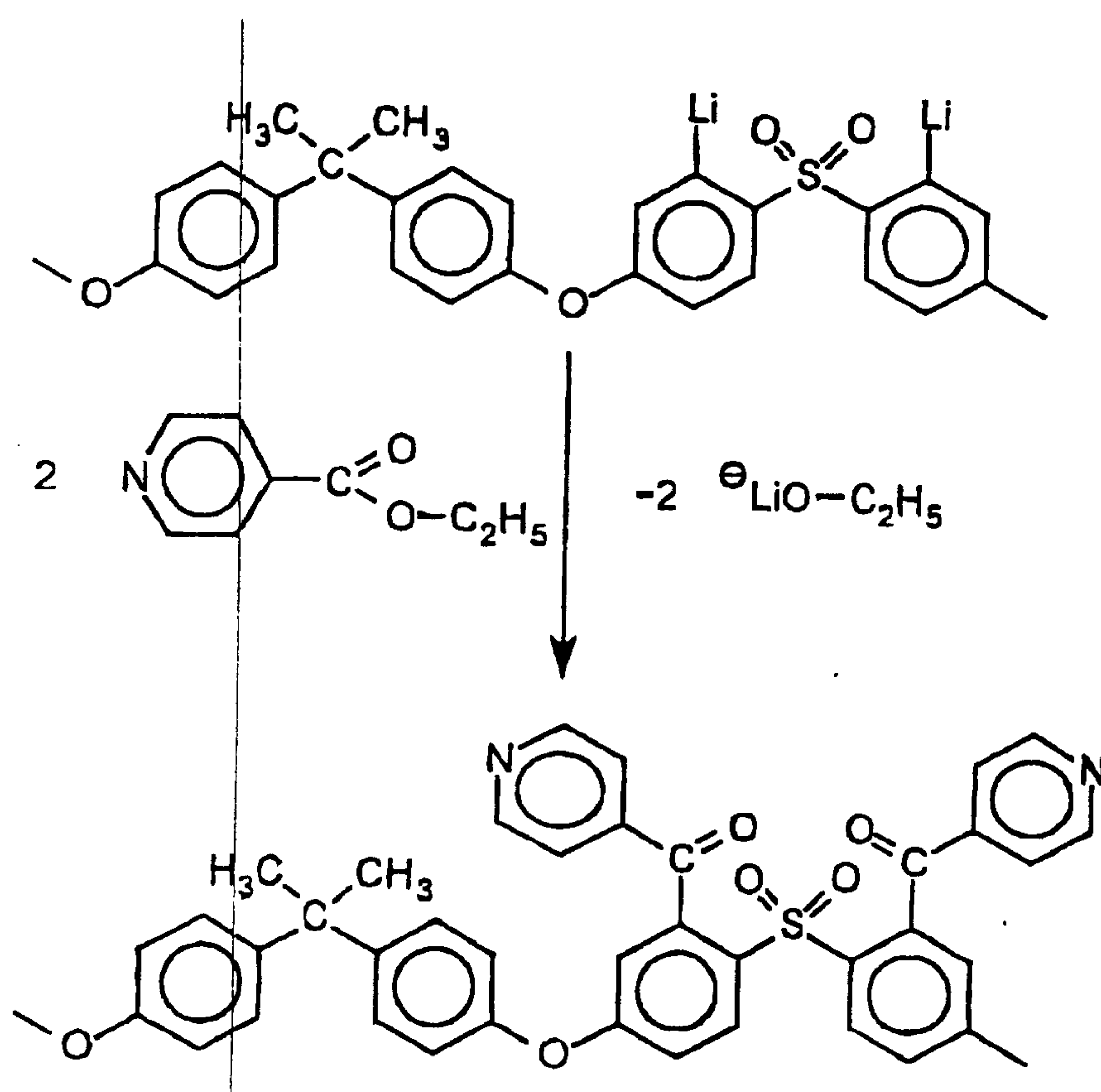


Fig.5: Reaction of lithiated PSU with isonicotinic acid ethyl ester

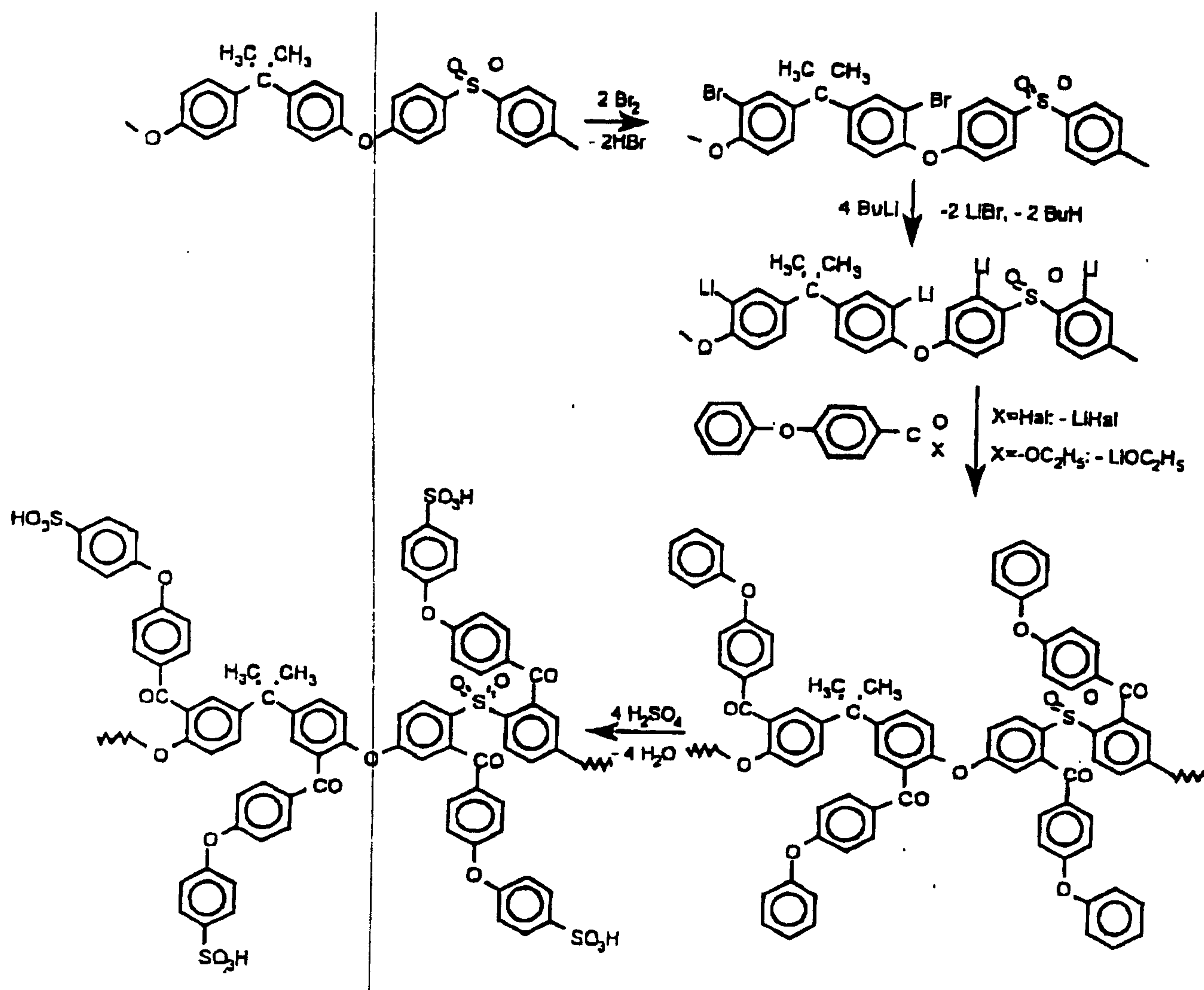


Fig. 6: Sequence of reactions for obtaining polysulphone PSU Udel® sulphonated in the aromatic lateral chain

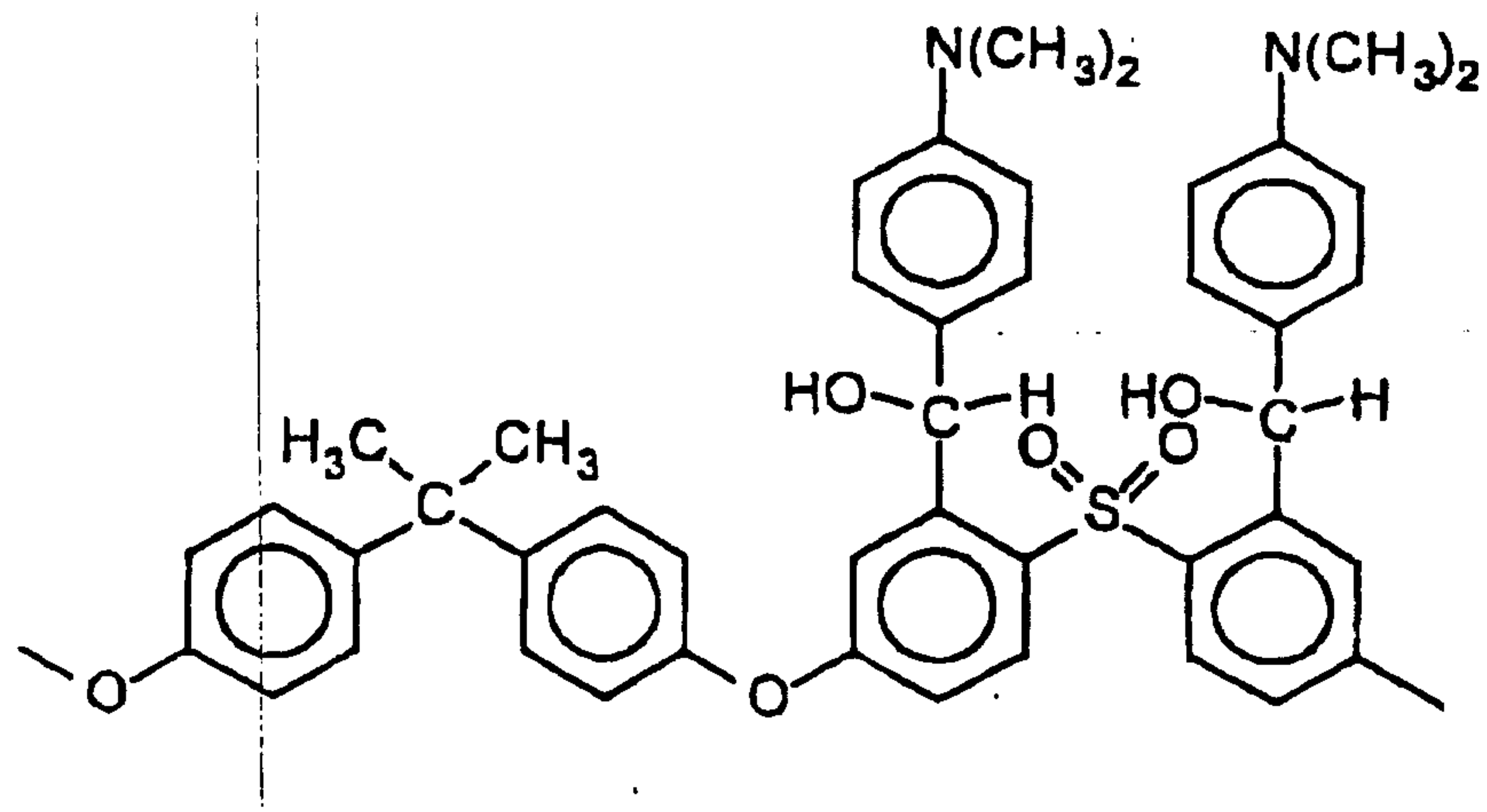


Fig.7: Reaction product of lithiated PSU with N,N-dimethyl amino benzaldehyde

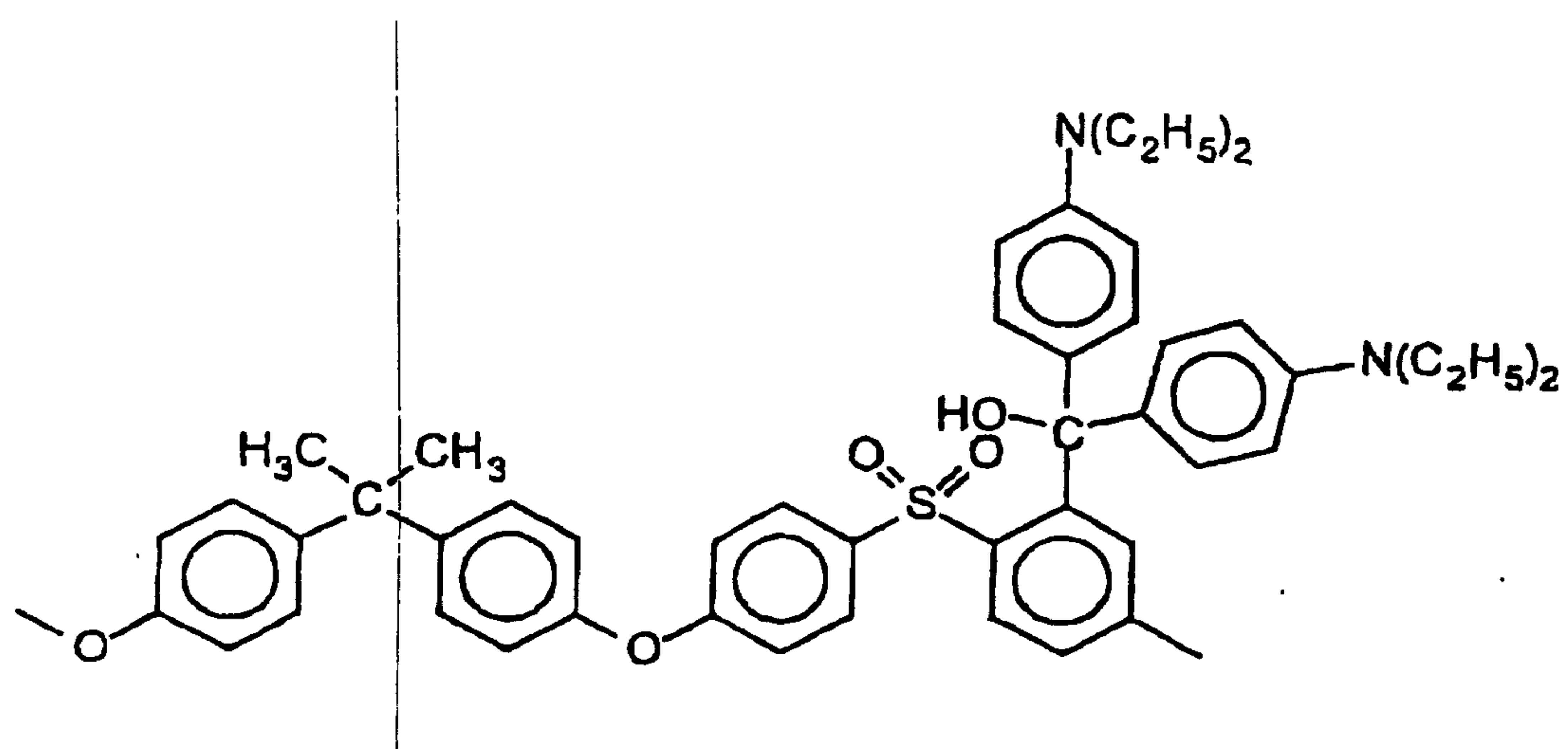


Fig.8: Reaction product of lithiated PSU with bis-(N,N-diethyl amino)benzophenone

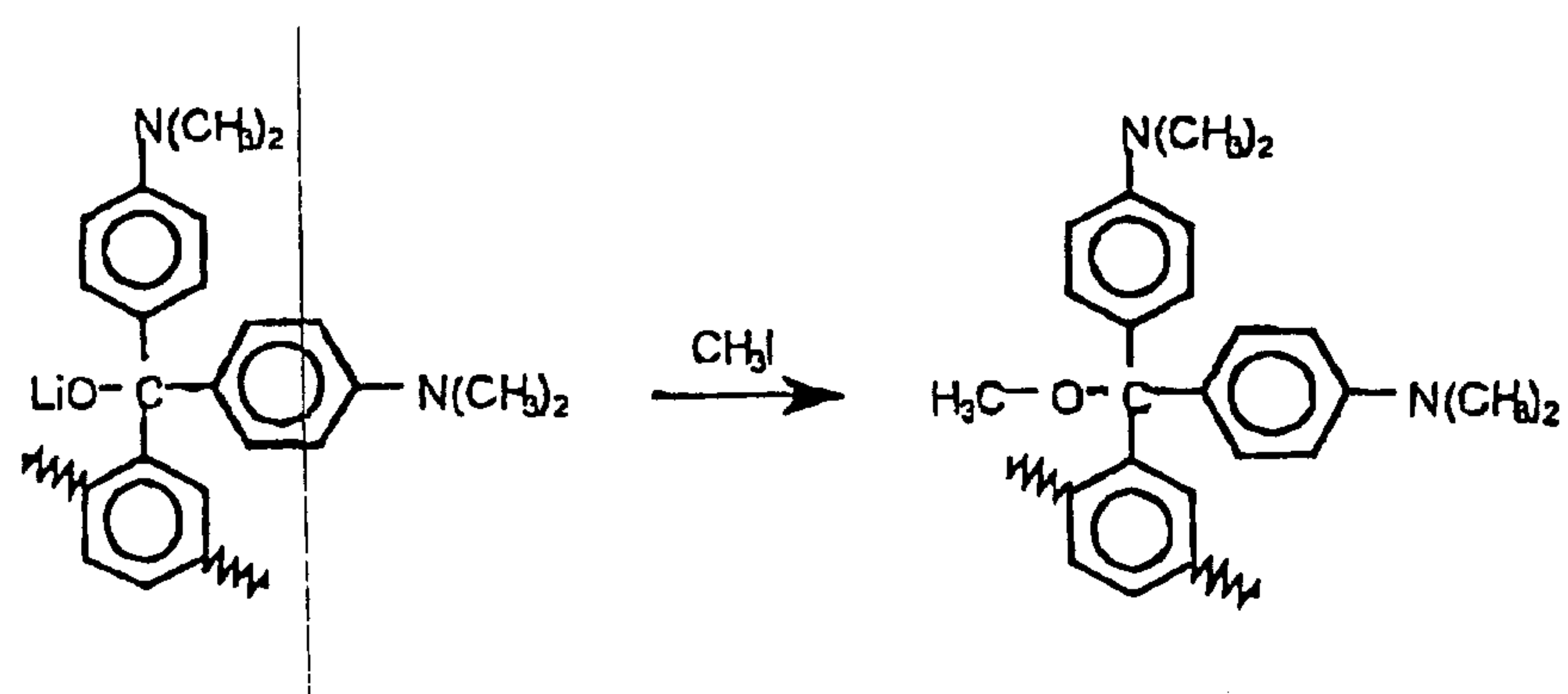


Fig.9: Etherification of the PSU Li alcoholate

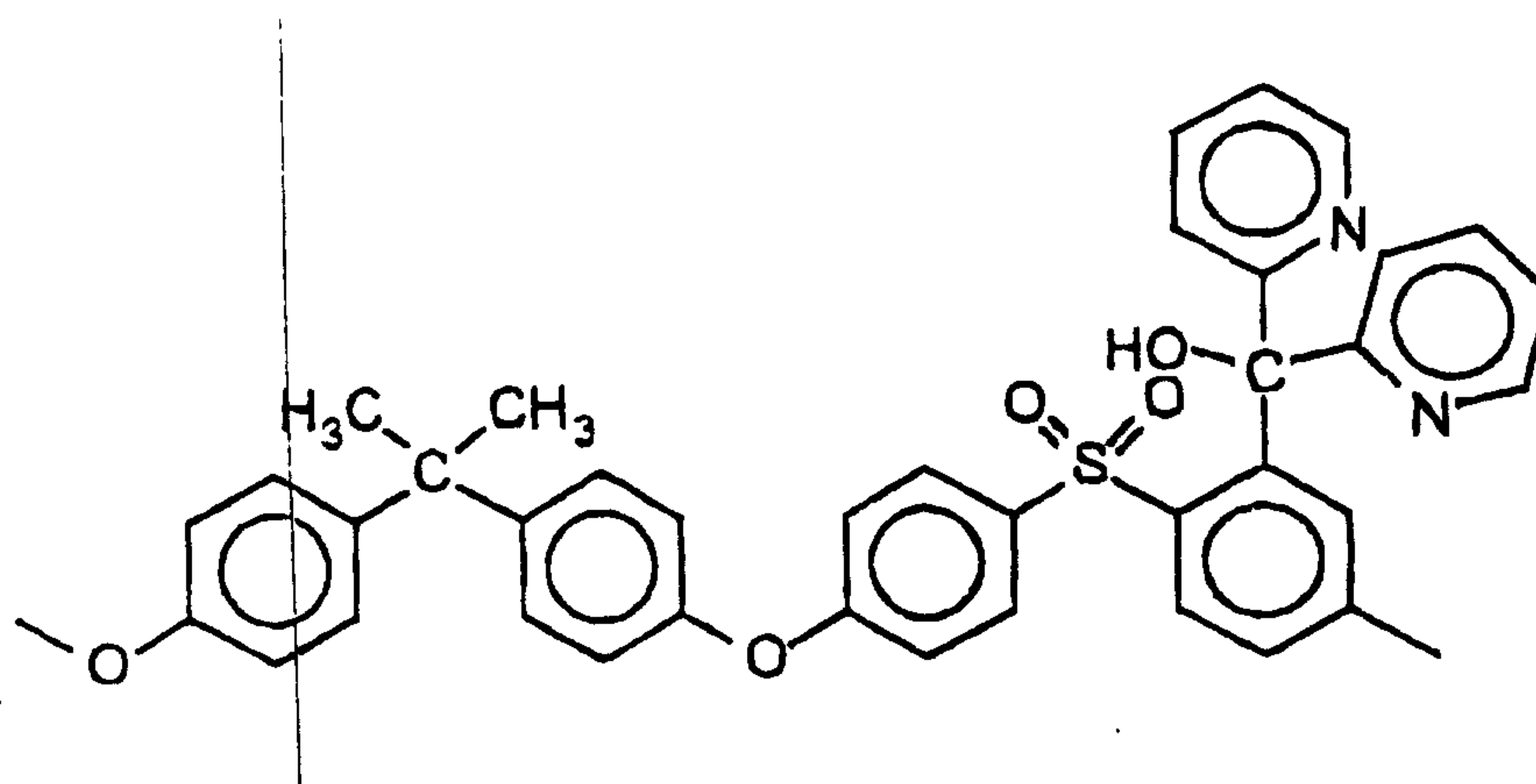


Fig. 10: Structural formula of the reaction product of lithiated PSU with Di(2-pyridyl)ketone

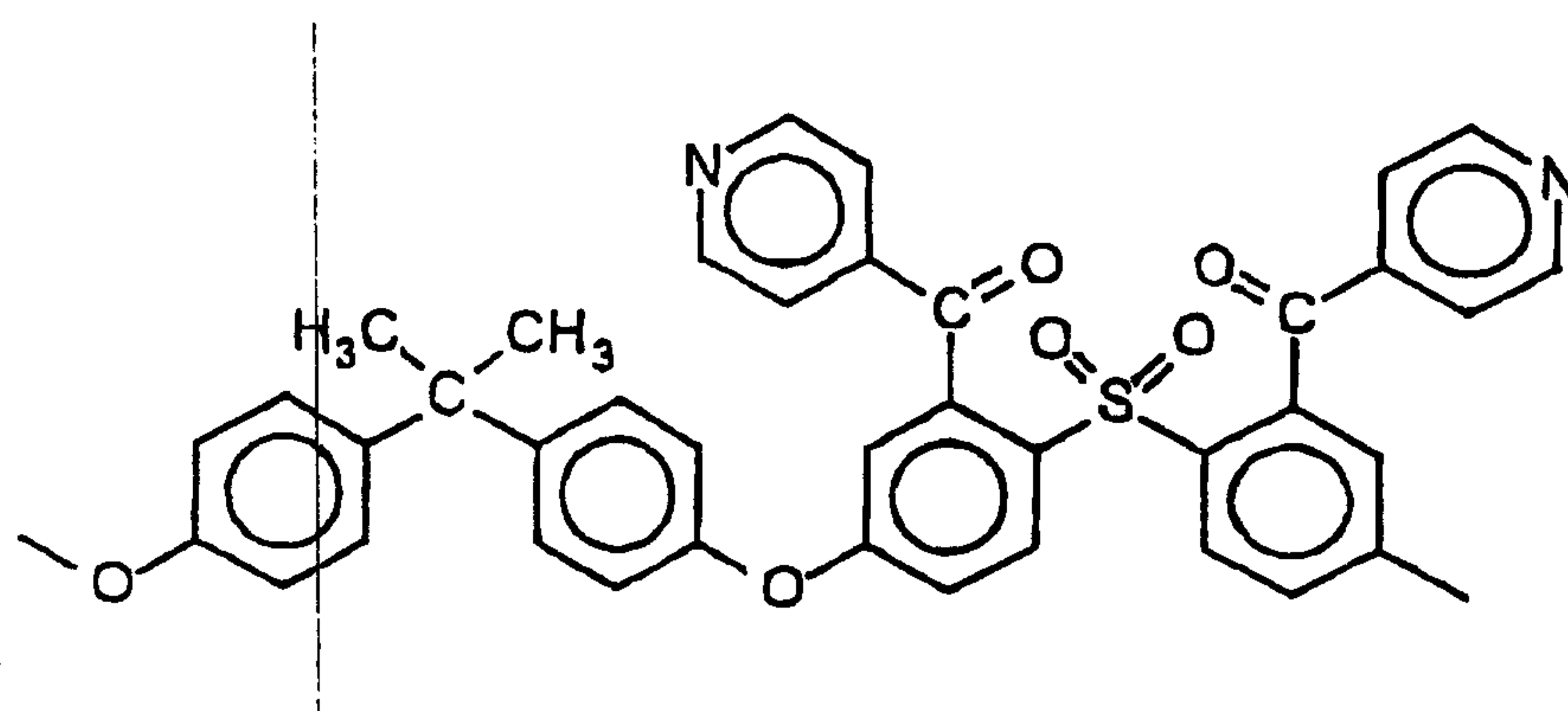


Fig. 11: Product of reaction of lithiated PSU with isonicotinic acid ethyl ester

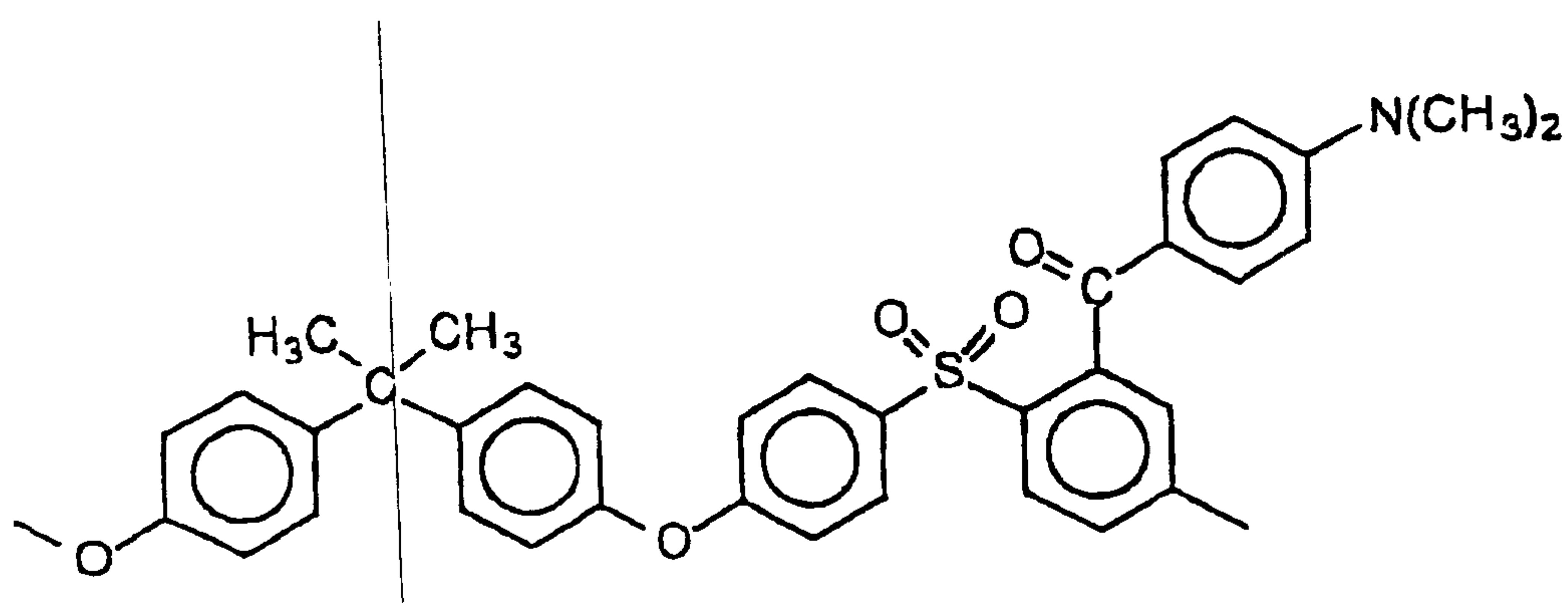


Fig. 12: Product of reaction of lithiated PSU with N,N-dimethyl amino benzoic acid ethyl ester

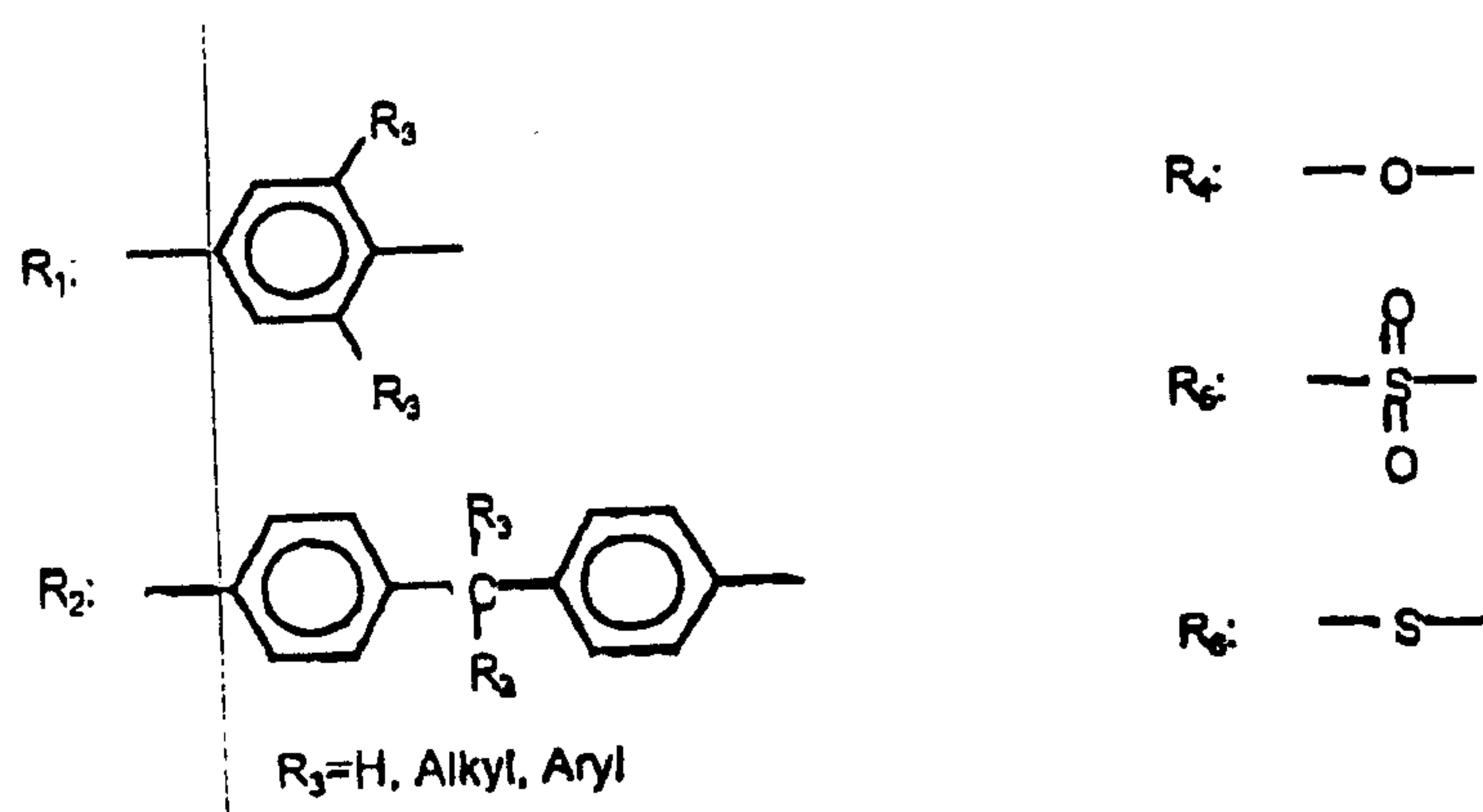


Fig. 13: Groups of aryl main chain polymers usable for the method according to the invention

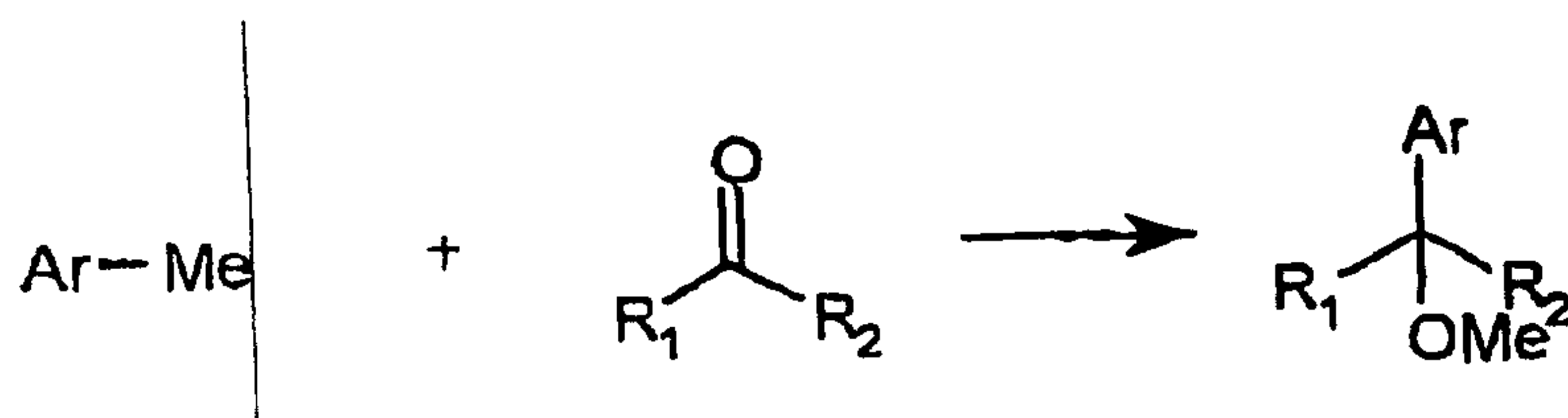
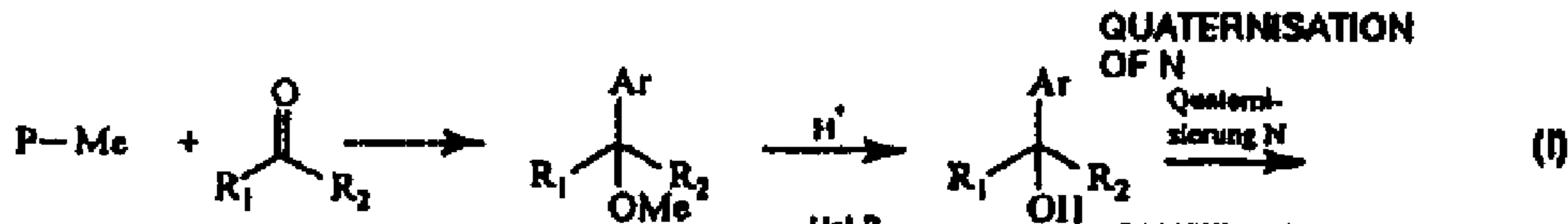


Fig. 14: Reaction according to the invention and involving metallised polymers with ketones or aldehydes containing aromatic tertiary basic nitrogen (Ar=aryl main chain polymer, see Fig. 13; Me=Li, Na; R_1 =aromatic group containing basic tertiary N; R_2 =H or alkyl or aryl group, which may additionally contain tertiary basic N).



Keton: R₁ und/oder R₂ = arom. Rest mit tert. basischem N

KETONE: R₁ AND/OR R₂ - AROMATIC RADICAL WITH TERTIERY BASIC N

Aldehyd: R₁ = arom. Rest mit tert. basischem N, R₂ = H

ALDEHYDE: R₁ - AROMATIC RADICAL WITH TERTIERY BASIC N, R₂ = H

