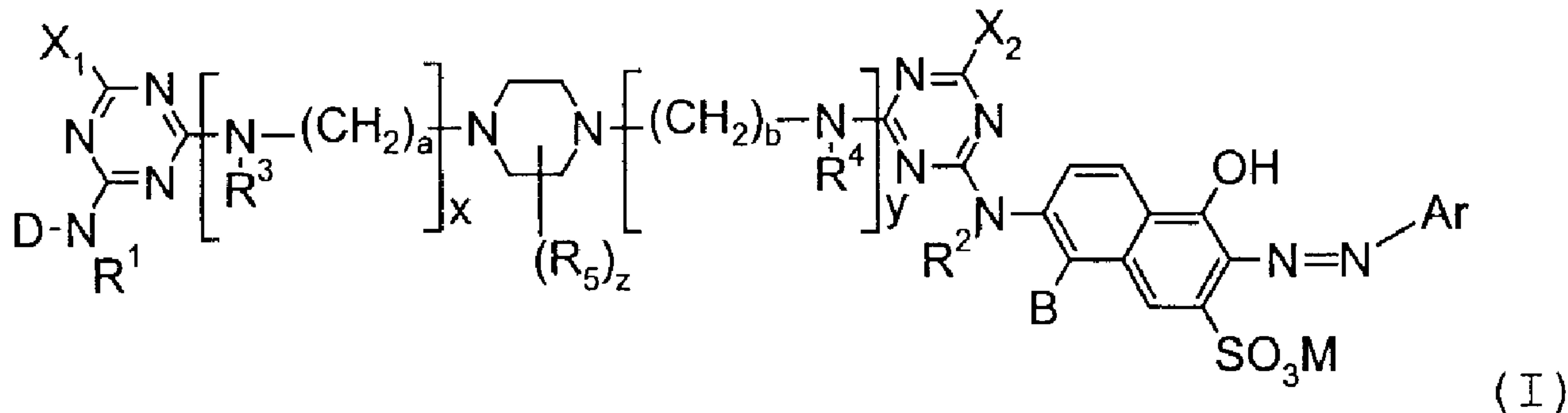




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 (54) Title: FIBRE REACTIVE SCARLET AZO DYES



(57) Abrégé/Abstract:

The present invention refers to dyestuffs of the formula I wherein Ar is a group of the formula II or of the formula III, D is a group of the formula IV, or of the formula V wherein the variables are defined as given in claim 1, processes for their preparation and their use for dyeing and printing hydroxy- and/or carboxamido-containing fibre materials.

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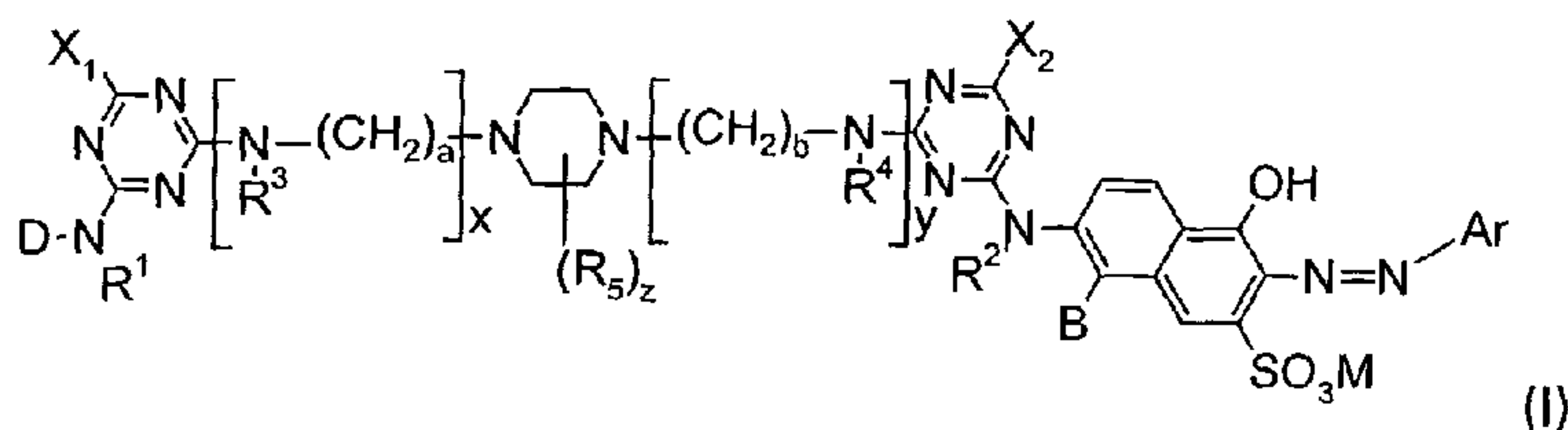
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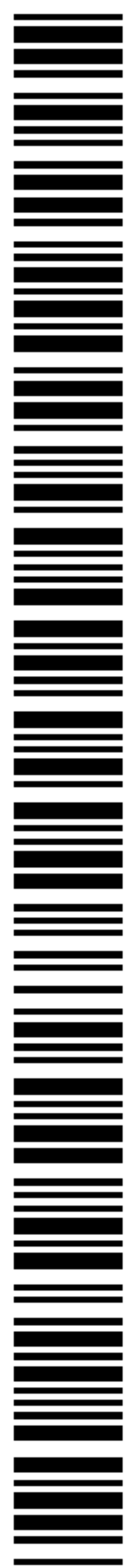
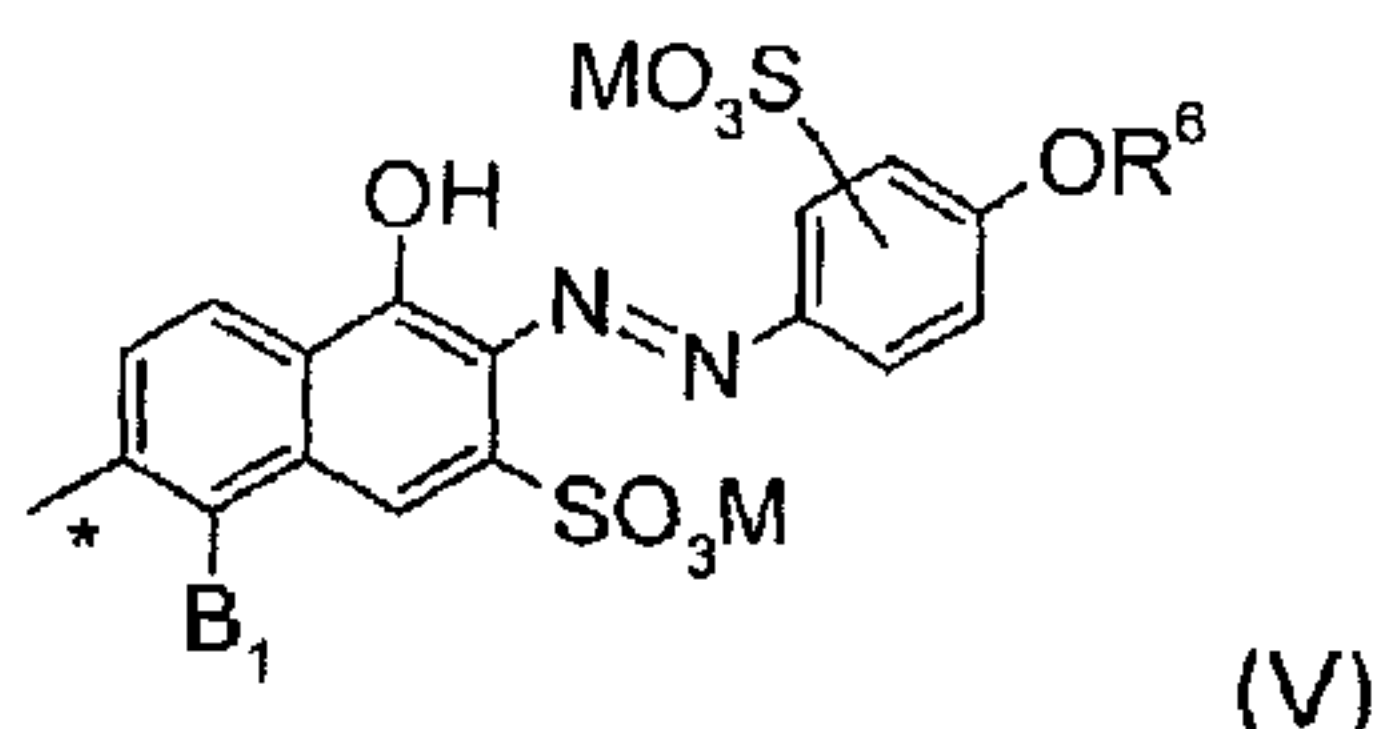
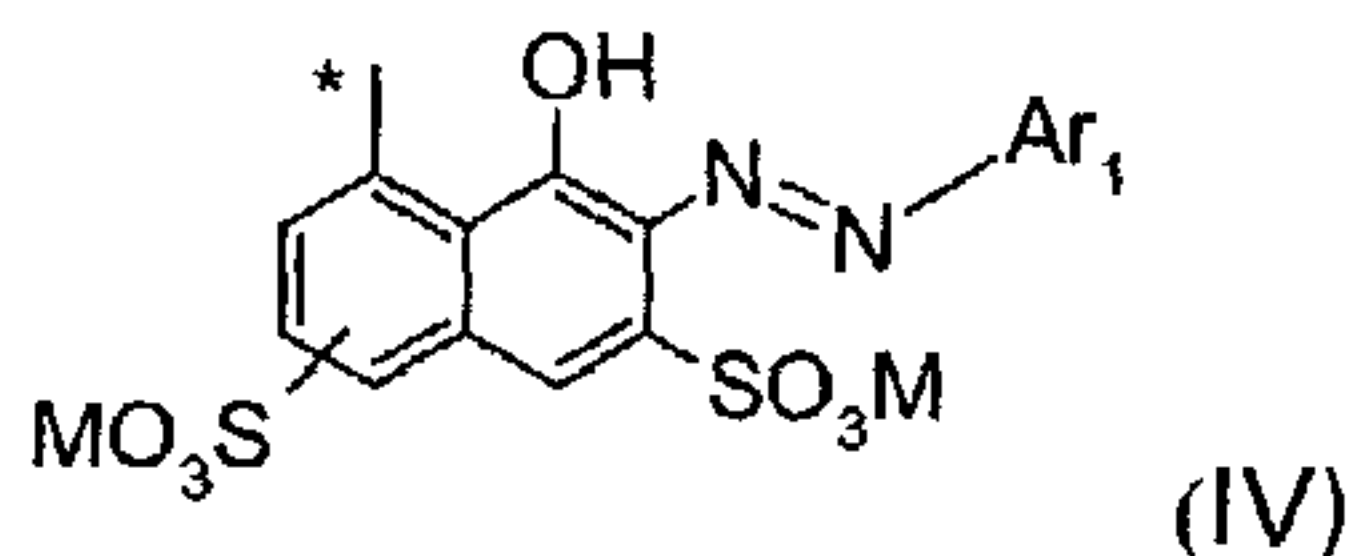
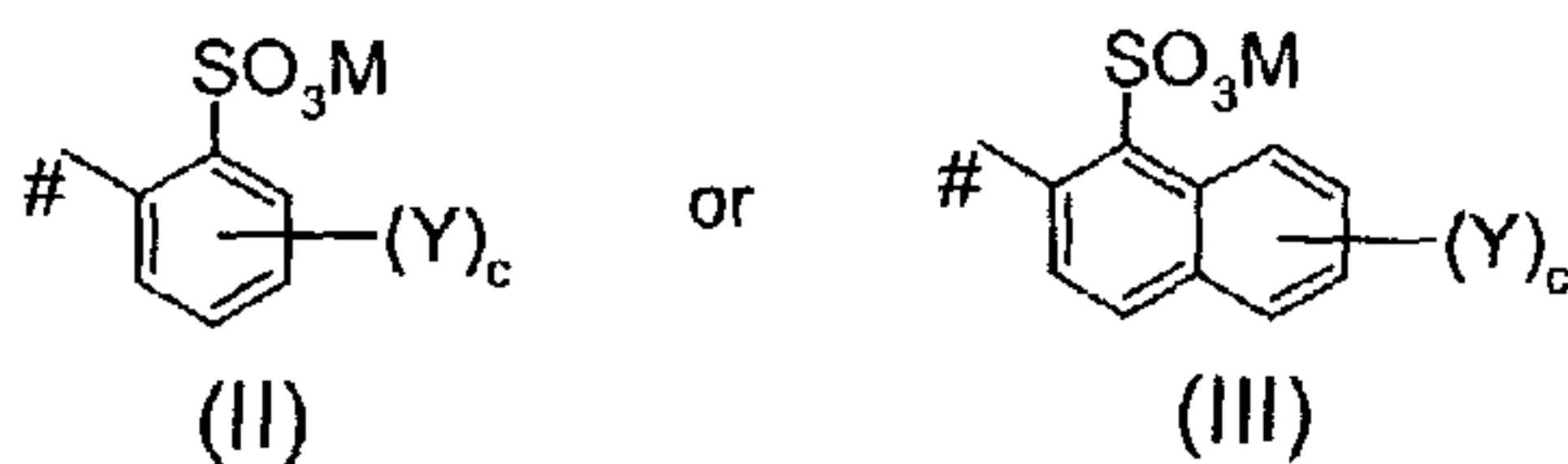
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(54) Title: FIBRE REACTIVE SCARLET AZO DYES



(57) Abstract: The present invention refers to dyestuffs of the formula I wherein Ar is a group of the formula II or of the formula III, D is a group of the formula IV, or of the formula V wherein the variables are defined as given in claim 1, processes for their preparation and their use for dyeing and printing hydroxy- and/or carboxamido-containing fibre materials.



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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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Description

5 Fibre Reactive Scarlet Azo Dyes

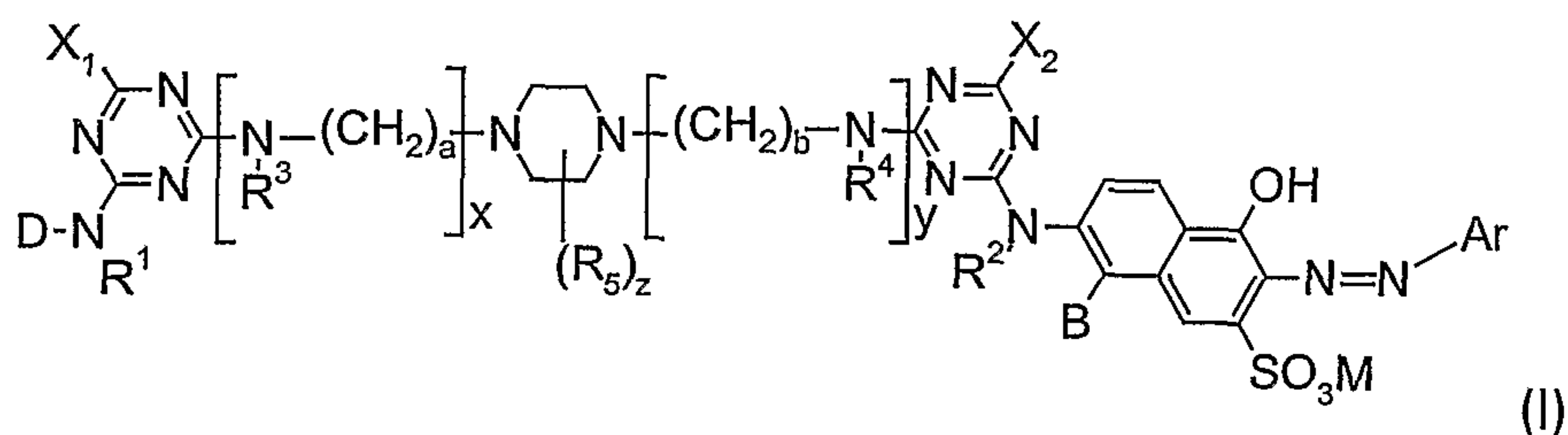
The present invention relates to the field of fibre-reactive dyes.

10 Dyestuffs containing chromophores linked via a piperazine type linking unit are known from literature and are described for example in EP-A-0126265, EP-A-0693538 and WO99/05224.

The inventor of the present invention has surprisingly found that dyestuffs with a very strong and economic scarlet shade exhibiting excellent fastness properties
 15 can be obtained if piperazine type linking units are used to link two different chromophores each selected from a specific range of chromophores as defined below.

The present invention claims dyestuffs of the formula I

20



wherein

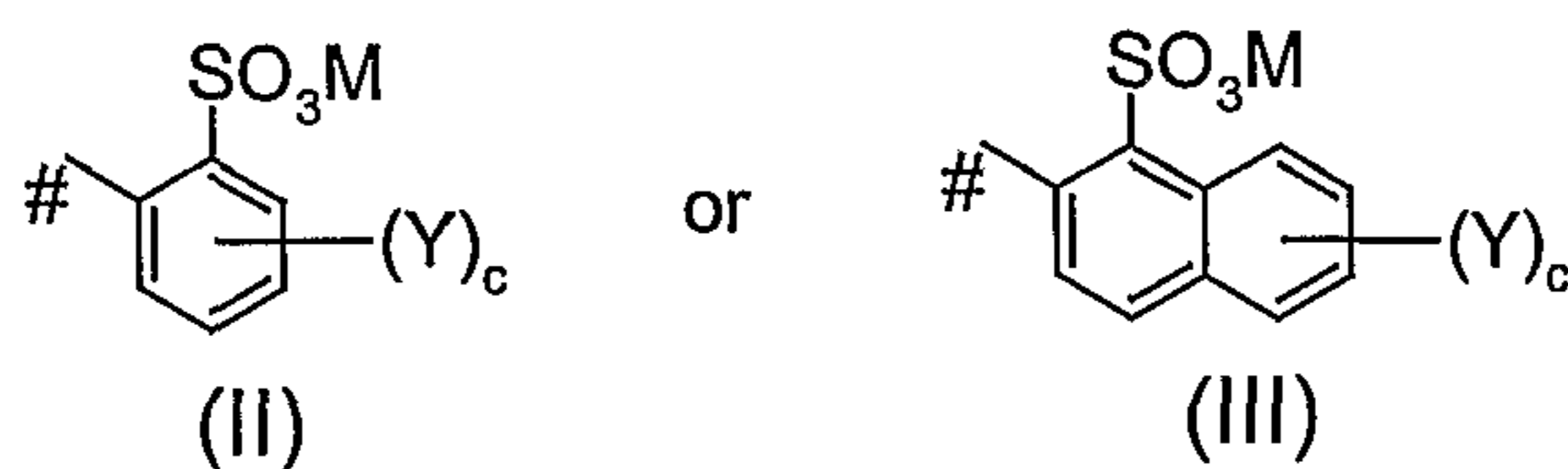
25 each of R^1 , R^2 , R^3 , R^4 and R^5 , independently, is H or an optionally substituted alkyl group;

each of X_1 and X_2 , independently, is a labile atom or group;

B is H or SO_3M ;

M is H, an alkali metal, an ammonium ion or the equivalent of an alkaline earth metal;

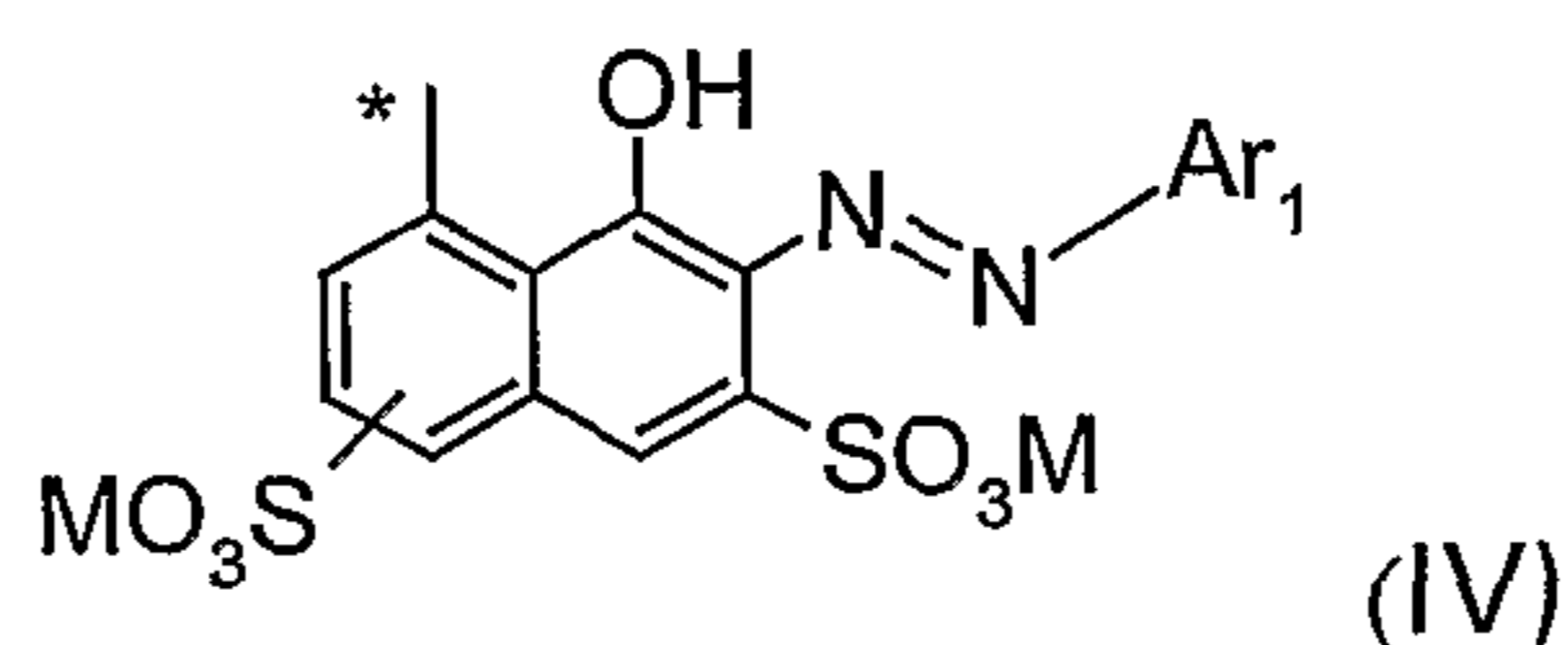
Ar is a group of the formula II or of the formula III



wherein

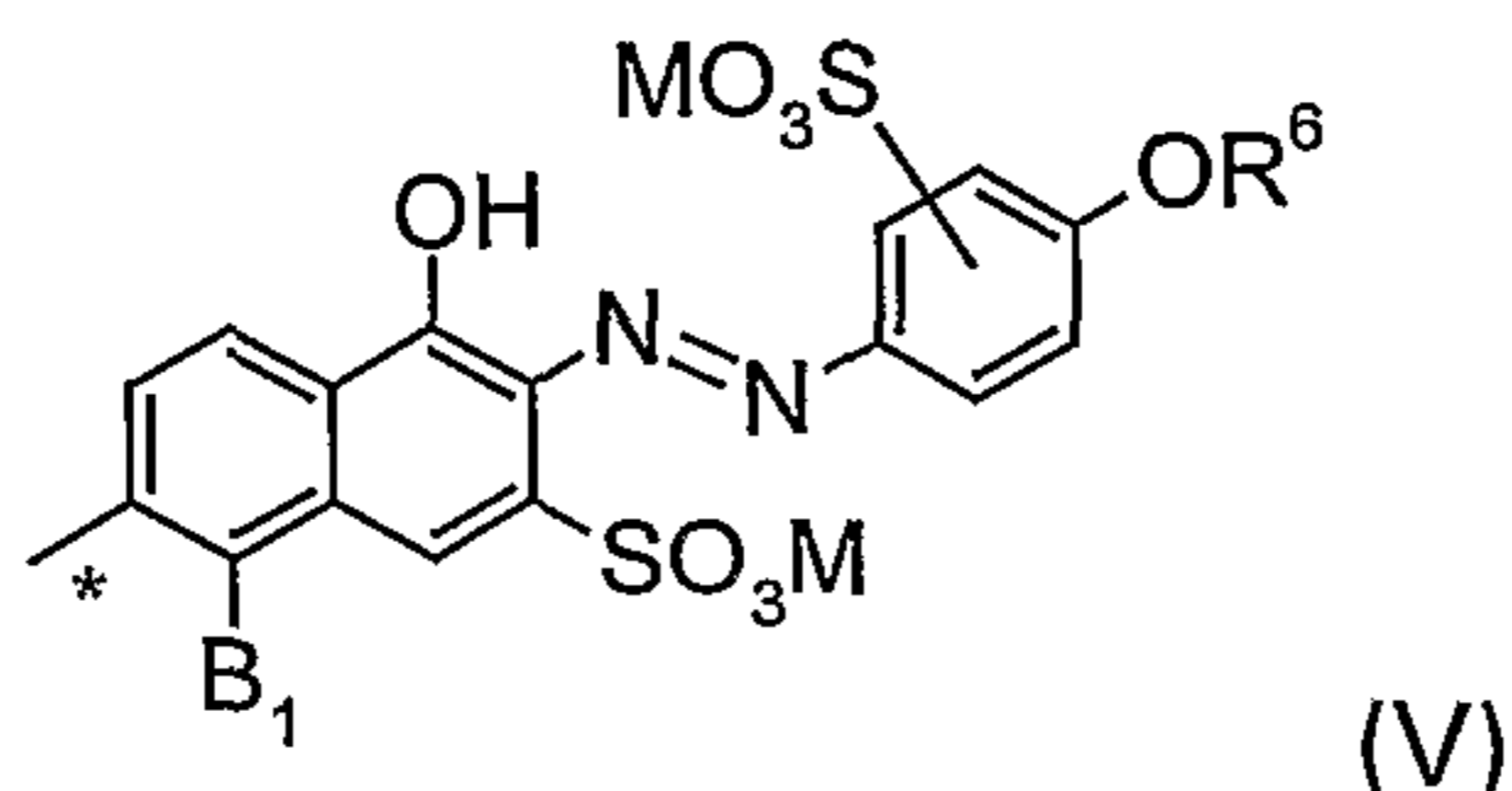
- 5 Y is SO_3M or an alkyl group, c is 0, 1 or 2, M is defined as given above and # indicates the bond to the azo group in formula I;

D is a group of the formula IV



- 10 wherein Ar_1 is defined as Ar, M is defined as given above and * indicates the bond to the NR^1 group of formula I; or

D is a group of the formula V



wherein R^6 is an alkyl group, B_1 is defined as B and M and * are defined as given above;

- 15 each of x and y, independently, is 0 or 1 and at least one of x and y is 1;
each of a and b is 2 to 5 and when each of x and y is 1, $a > b$; and
z is 0, 1, 2, 3 or 4.

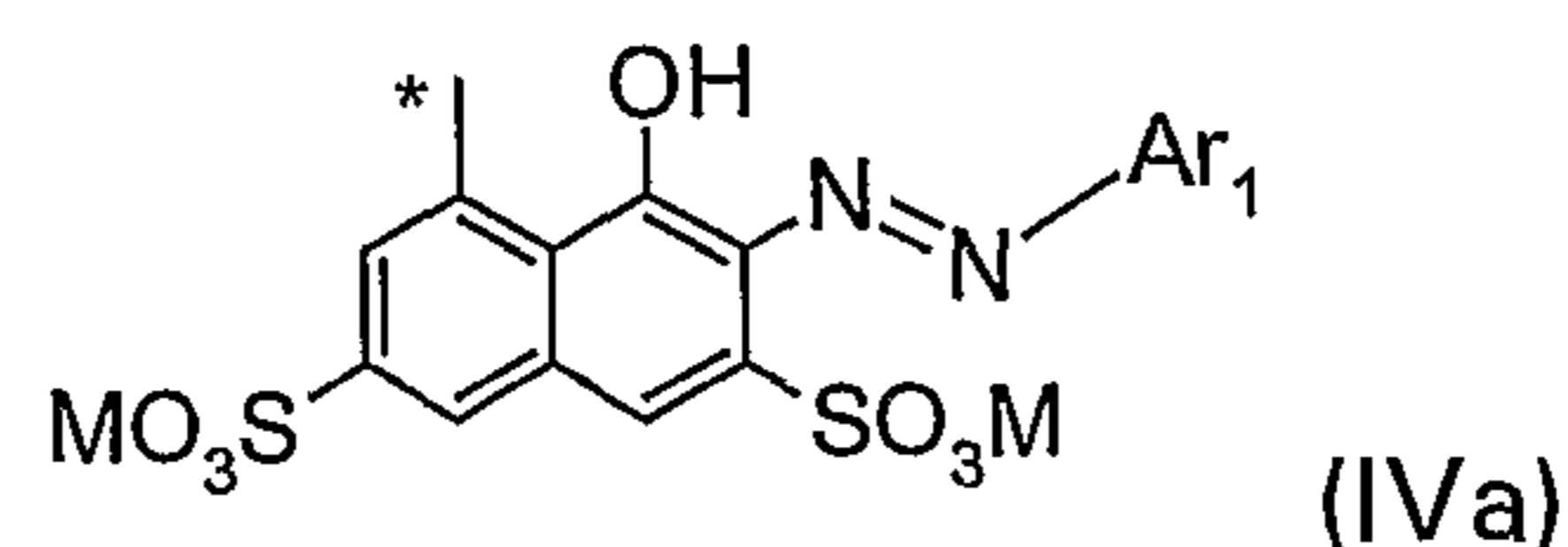
- 20 Alkyl groups may be straight-chain or branched and are preferably $(\text{C}_1\text{-C}_4)$ -alkyl groups, for example methyl, ethyl, n-propyl, i-propyl or n-butyl. Substituted alkyl groups are preferably substituted by hydroxyl, $(\text{C}_1\text{-C}_4)$ -alkoxy, halogen or carboxyl groups.

R^1 to R^6 are preferably H or methyl. R^3 , R^4 and R^5 are especially preferably H.

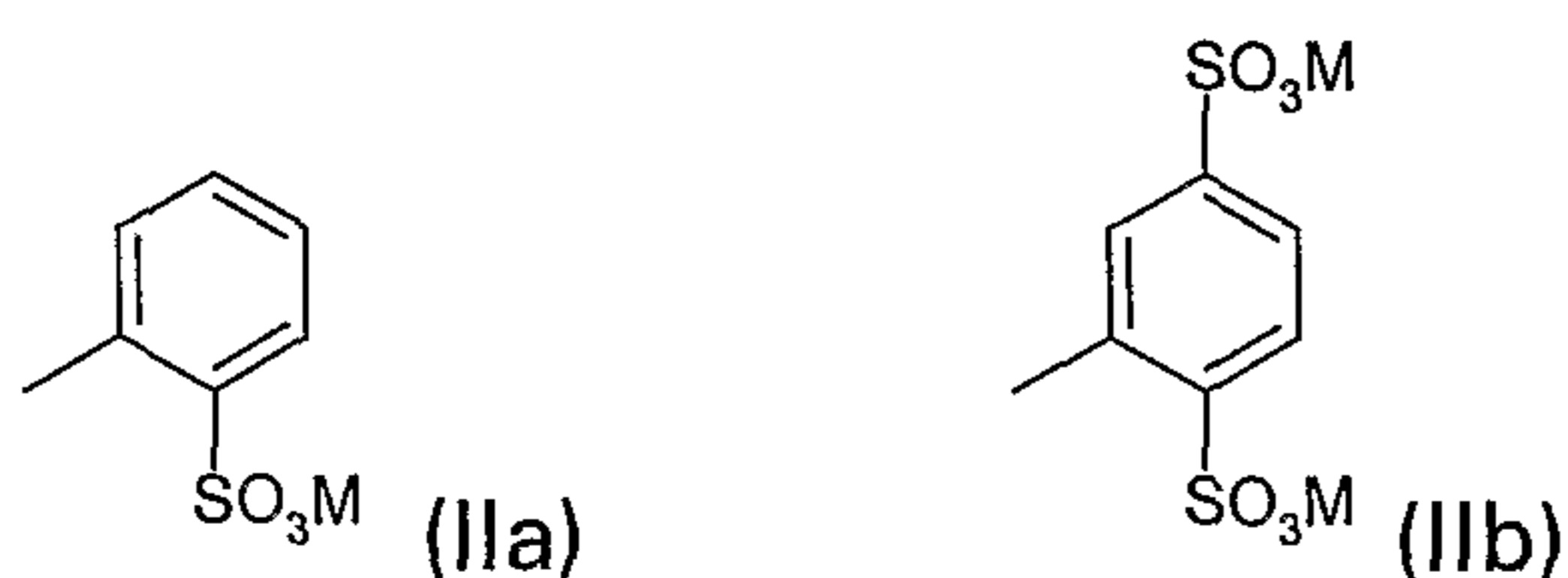
- 25 X_1 and X_2 are preferably halogen like fluorine and chlorine and are especially preferably chlorine.

M is preferably H, an alkaline metal, like sodium, potassium and lithium and is especially preferably sodium.

D is preferably a group of the formula IVa



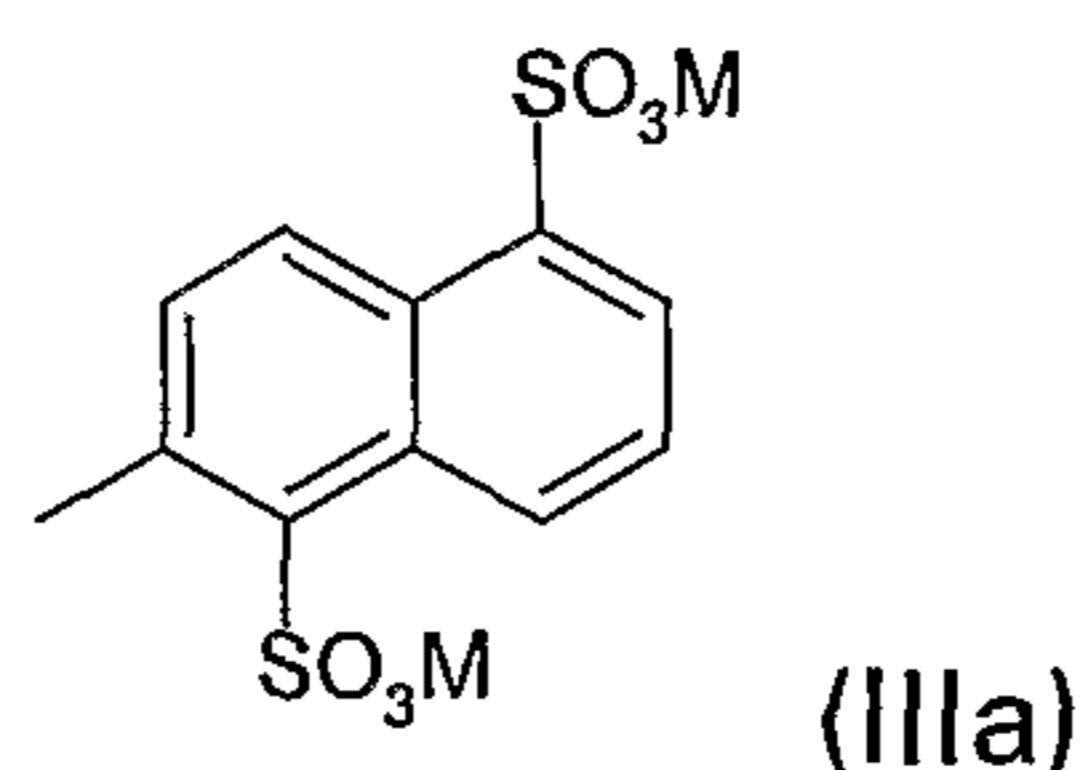
5 wherein M, Ar₁ and * are defined as given above. D is especially preferably a group of the formula IVa wherein Ar₁ is a group of the formula IIa or IIb



wherein M is defined as given above.

10 If D is a group of the formula IVa with Ar₁ = a group of the formula IIa or IIb, R¹ is preferably H.

Ar is preferably a group of the formula IIIa

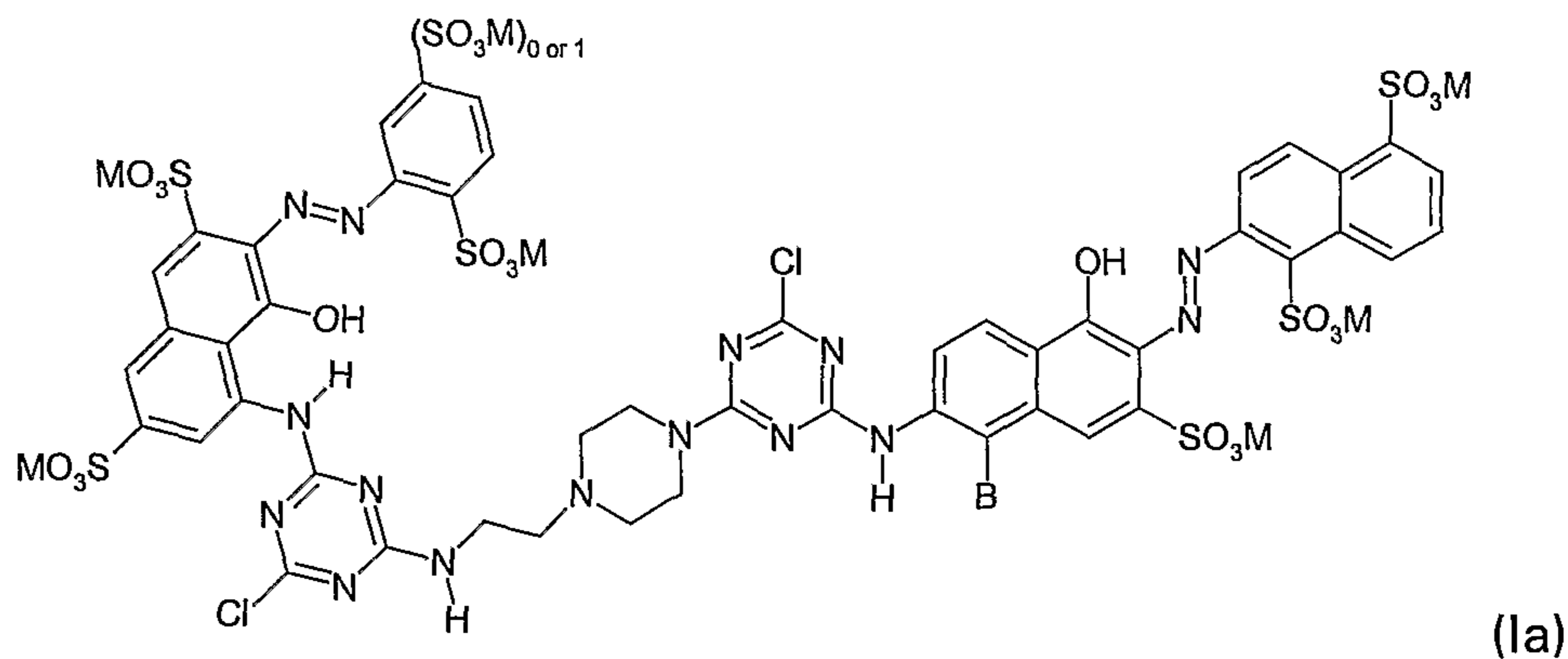


wherein M is defined as given above.

15 If Ar is a group of the formula IIIa, R² is preferably H or methyl. If Ar is a group of the formula IIIa, R² and B are especially preferably H.

In preferred dyestuffs of the formula I x = 1 and y = 0 and a = 2 or x = 0 and y = 1 and b = 2.

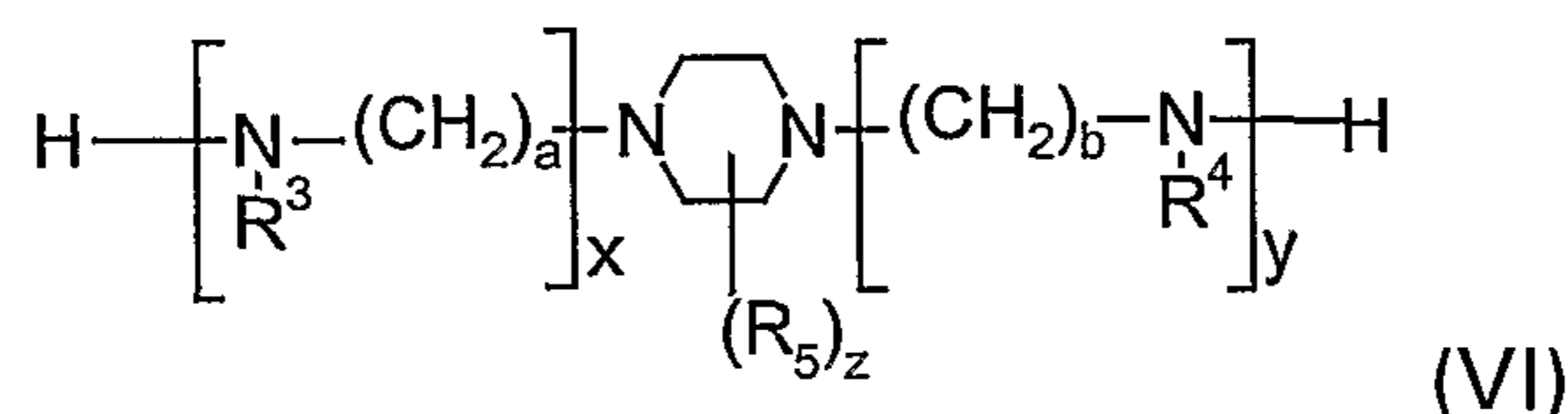
Especially preferred dyestuffs of the formula I are the dyestuffs of the formula Ia



aqueous solutions. The aqueous solutions (liquid preparations) may include the
 aforementioned buffer substances in an amount which is generally up to 10% by
 weight, for example 0.1 to 10% by weight, preference being given to up to 4%
 by weight, especially 2 to 4% by weight.

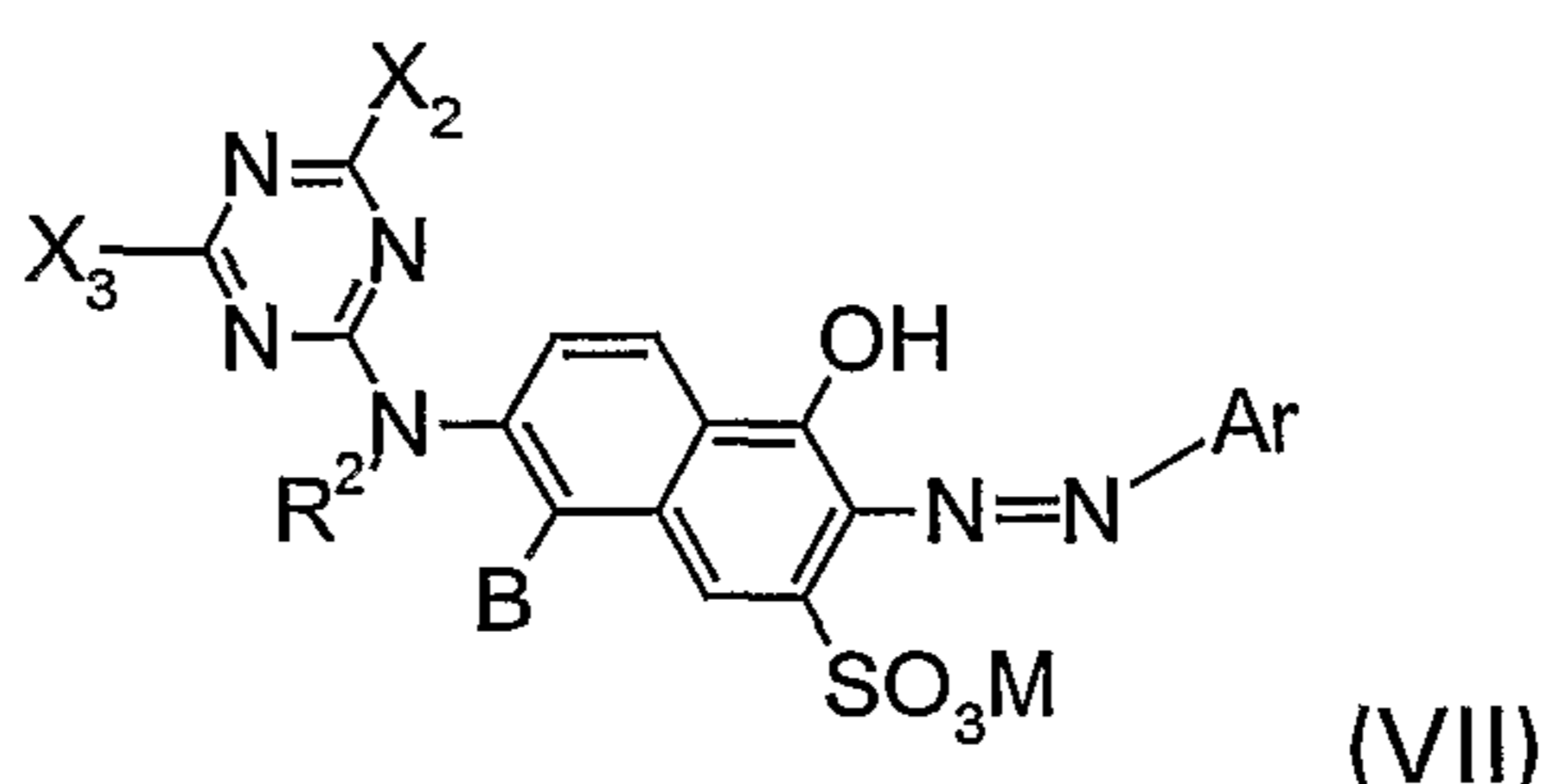
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A dyestuff of the formula I may for example be prepared by reacting a piperazine
 compound of the formula VI

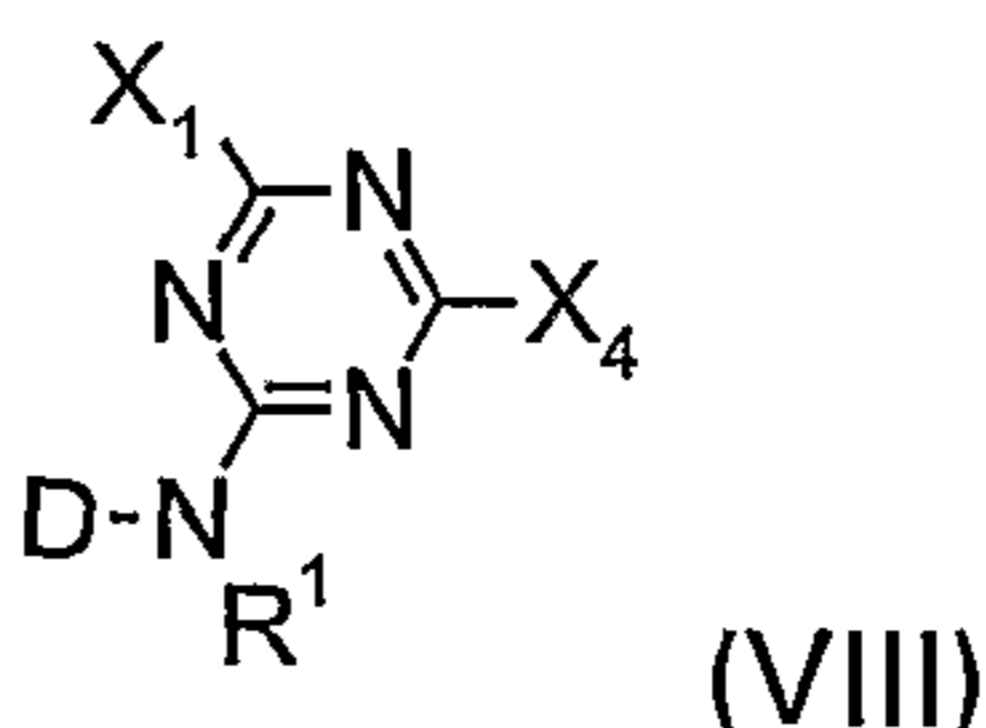


wherin R^3 , R^4 , R^5 , a , b , x , y , and z are defined as given above, with a compound
 of the formula VII

10



wherein B , M , R^2 , X_2 and Ar are defined as given above and X_3 is a labile atom
 or a group capable of reaction with an amine, preferably chlorine,
 and with a compound of the formula VIII

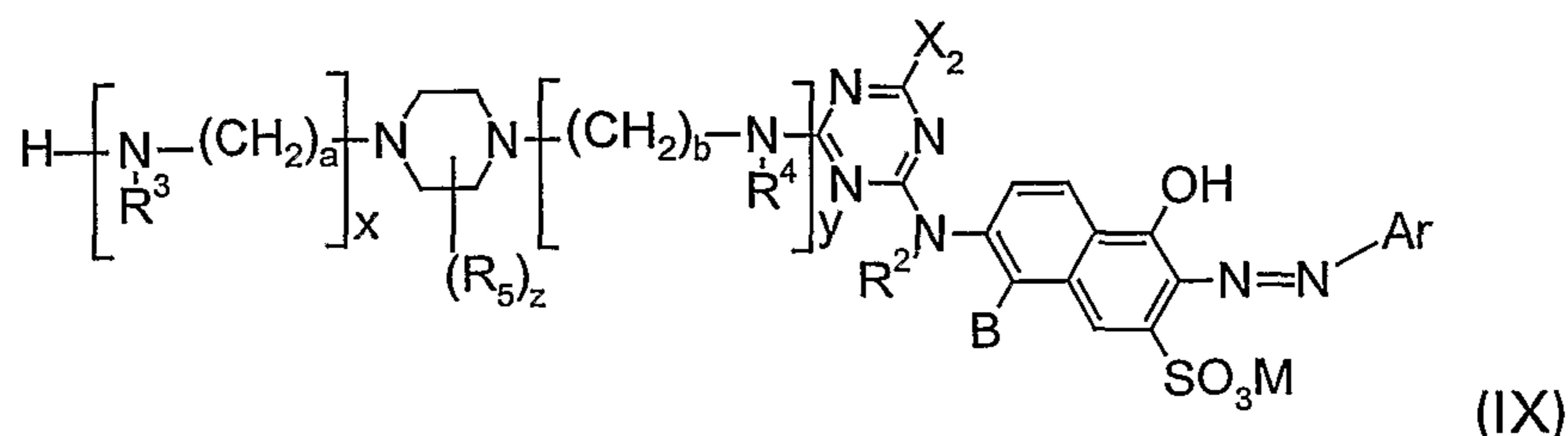


15

wherein D , R^1 and X_1 defined as given above and X_4 has one of the meanings of
 X_3 .

It is possible to react a compound of formula VI first with a compound of the
 formula VII to form a compound of the formula IX

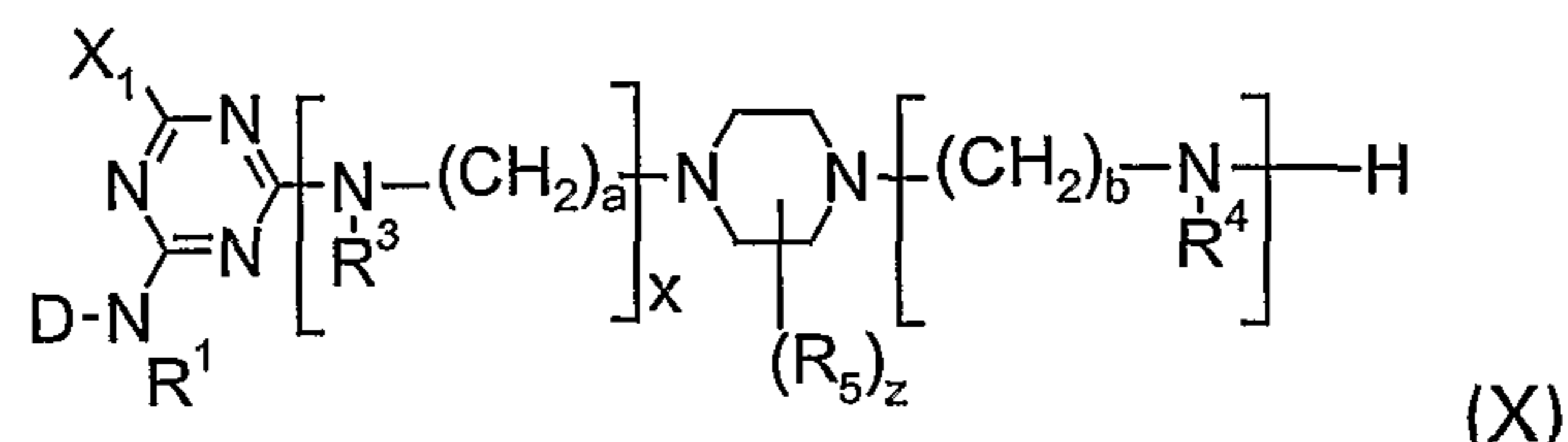
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wherein all variables are defined as given above,

which is then reacted with a compound of the formula VIII to a dyestuff of the formula I.

As an alternative is it also possible to react a compound of the formula VI first
5 with a compound of the formula VIII to form the compound of the formula X



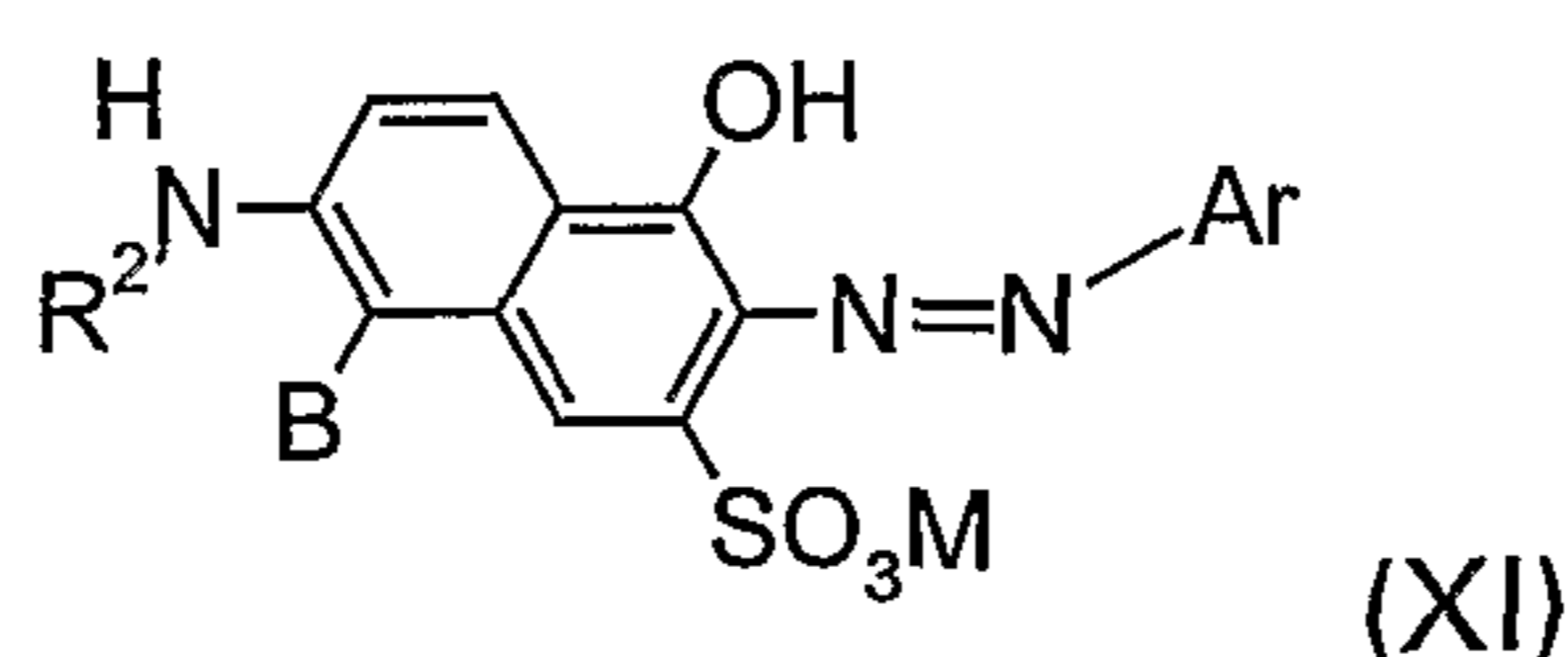
wherein all variables are defined as given above,

which is then reacted with a compound of the formula VII to a dyestuff of the formula I.

10 In general, one mole of a compound of the formula VI is reacted with 1 mole of a compound of the formula VII and 1 mole of a compound of the formula VIII in a manner known per se to a skilled person.

The compounds of the formulae VI, VII and VIII are known or can easily be
15 prepared by a skilled person using methods which are known per se.

As an example, a compound of the formula VII, wherein X₂ is chlorine can be obtained by reacting cyanuric chloride with a compound of the formula XI



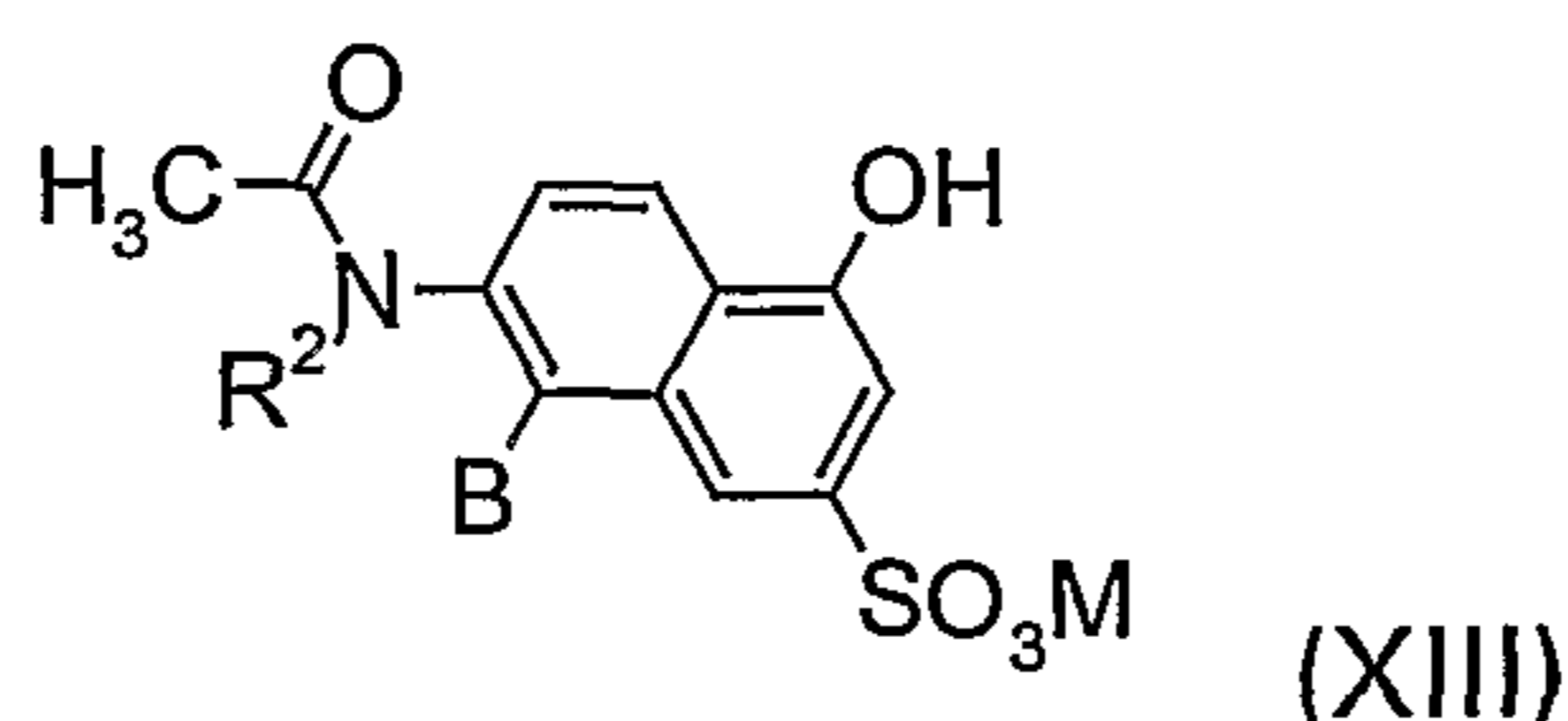
20 wherein B, M, R² and Ar are defined as given above.

The compound of the formula XI can be prepared by means of customary diazotization and coupling reactions in a manner familiar to those skilled in the art using a diazotized amine of the formula XII

25



and a coupling component of the formula XIII



wherein Ar, B, M and R² are defined as given above and subsequently removing the acetyl group (-COCH₃) by saponification.

- 5 The dyestuffs of the instant invention are suitable for dyeing and printing hydroxy- and/or carboxamido-containing fibre materials by the application and fixing methods numerous described in the art for fibre-reactive dyes, in scarlet to mid-red shades with good aqueous solubility, color build-up, wash off and robustness to process variables. Moreover, the dyeings obtained surprisingly
10 show very good lightfastness properties.

The present invention therefore also provides for use of the inventive dyestuffs for dyeing and printing hydroxy- and/or carboxamido-containing fibre materials and processes for dyeing and printing such materials using a dyestuff according
15 to the invention. Usually the dyestuff is applied to the substrate in dissolved form and fixed on the fibre by the action of an alkali or by heating or both.

Hydroxy-containing materials are natural or synthetic hydroxy-containing materials, for example cellulose fibre materials, including in the form of paper, or
20 their regenerated products and polyvinyl alcohols. Cellulose fibre materials are preferably cotton but also other natural vegetable fibres, such as linen, hemp, jute and ramie fibres. Regenerated cellulose fibres are for example staple viscose and filament viscose.

25 Carboxamido-containing materials are for example synthetic and natural polyamides and polyurethanes, in particular in the form of fibres, for example wool and other animal hairs, silk, leather, nylon-6,6, nylon-6, nylon-11, and nylon-4.

Application of the inventive dyestuffs is by generally known processes for dyeing and printing fiber materials by the known application techniques for fibre-reactive dyes. The dyestuffs according to the invention are highly compatible with similar dyes designed for high temperature (80-100°C) applications and are
5 advantageously useful in exhaust dyeing processes.

Similarly, the conventional printing processes for cellulose fibres, which can either be carried out in single-phase, for example by printing with a print paste containing sodium bicarbonate or some other acid-binding agent and the colorant, and subsequent steaming at appropriate temperatures, or in two
10 phases, for example by printing with a neutral or weakly acid print paste containing the colorant and subsequent fixation either by passing the printed material through a hot electrolyte-containing alkaline bath or by overpadding with an alkaline electrolyte-containing padding liquor and subsequent batching of this treated material or subsequent steaming or subsequent treatment with
15 dry heat, produce strong prints with well defined contours and a clear white ground. Changing fixing conditions has only little effect on the outcome of the prints. Not only in dyeing but also in printing the degrees of fixation obtained with dye mixtures of the invention are very high. The hot air used in dry heat fixing by the customary thermofix processes has a temperature of from 120 to
20 200°C. In addition to the customary steam at from 101 to 103°C, it is also possible to use superheated steam and high pressure steam at up to 160°C.

The inventive dyestuffs can in addition be used to produce inks useful for printing the substrates described above, for example textiles, especially cellulosic
25 textiles, and paper. Such inks can be used in all technologies, for example conventional printing, ink-jet printing or bubble-jet printing (for information on such printing technologies see for example Text. Chem. Color, Volume 19(8), pages 23 ff and Volume 21, pages 27 ff).

30 Acid-binding agents responsible for fixing the dyes to cellulose fibres are for example water-soluble basic salts of alkali metals and of alkaline earth metals of inorganic or organic acids, and compounds which release alkali when hot. Of

particular suitability are the alkali metal hydroxides and alkali metal salts of weak to medium inorganic or organic acids, the preferred alkali metal compounds being the sodium and potassium compounds. These acid-binding agents are for example sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate, potassium carbonate, sodium formate, sodium dihydrogenphosphate and disodium hydrogenphosphate.

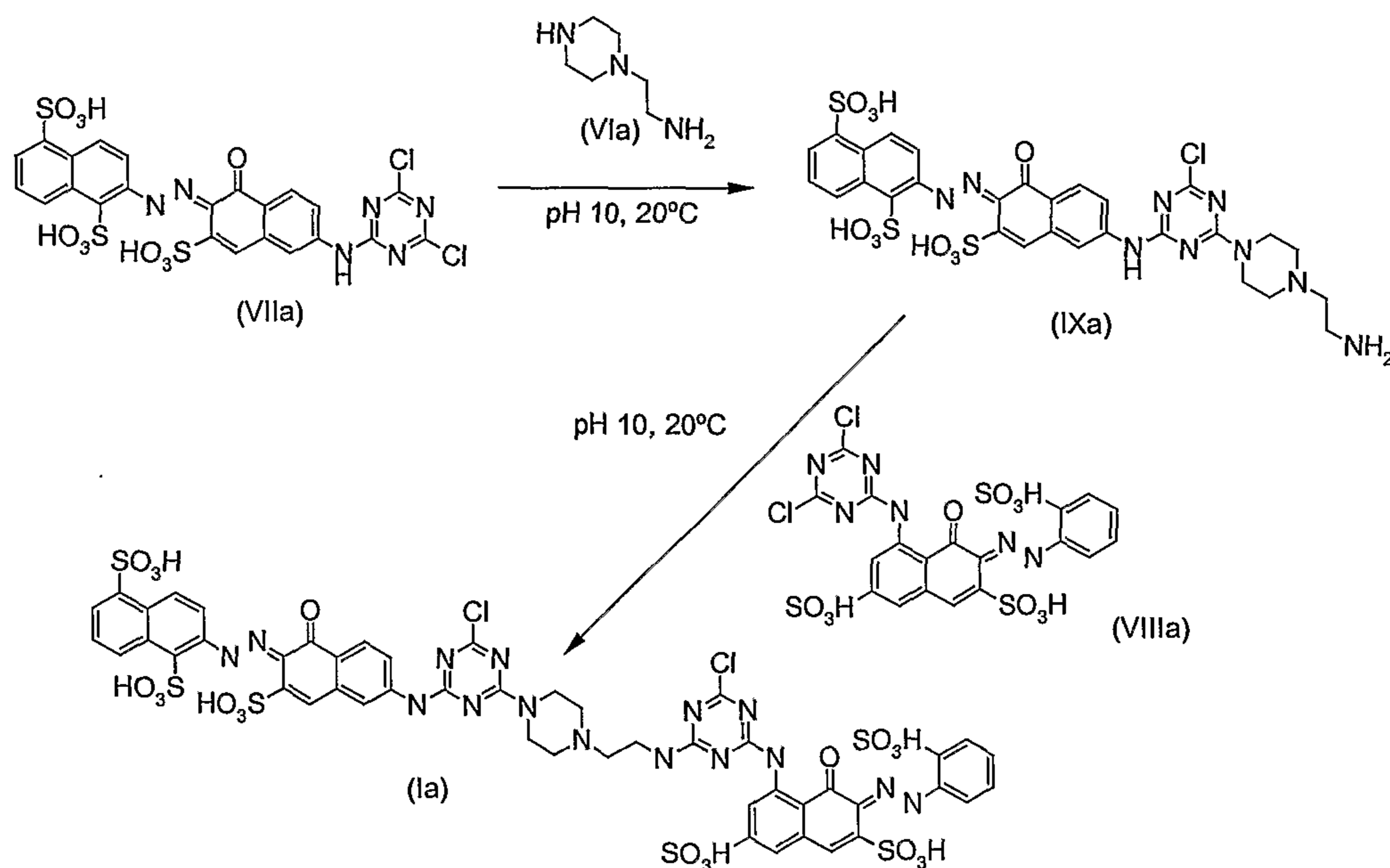
Treating the dyestuffs according to the invention with the acid-binding agents with or without heating bonds the dyes chemically to the cellulose fibre. Especially the dyeings on cellulose, after they have been given the usual aftertreatment of rinsing to remove unfixed dye portions, show excellent properties.

The dyeings of polyurethane and polyamide fibres are customarily carried out from an acid medium. The dyebath may contain for example acetic acid and/or ammonium sulfate and/or acetic acid and ammonium acetate or sodium acetate to bring it to the desired pH. To obtain a dyeing of acceptable levelness it is advisable to add customary leveling auxiliaries, for example based on a reaction product of cyanuric chloride with three times the molar amount of an aminobenzenesulfonic acid or aminonaphthalenesulfonic acid or based on a reaction product of for example stearylamine with ethylene oxide. In general the material to be dyed is introduced into the bath at a temperature of about 40°C and agitated therein for some time, the dyebath is then adjusted to the desired weakly acid, preferably weakly acetic acid, pH, and the actual dyeing is carried out at temperature between 60 and 98°C. However, the dyeings can also be carried out at the boil or at temperatures up to 120°C (under superatmospheric pressure).

Example 1

1-(2-aminoethyl) piperazine (IVa) (1.3g, 0.01 mol) was added dropwise to a stirred suspension of the orange dichlorotriazinyl dye (VIIa) (0.01 mol) in water (400 mls) at ambient temperature and pH6. The pH was then adjusted to 10 with sodium hydroxide solution and maintained at this pH for 30 minutes, yielding a slurry of the orange dye (IXa). To this suspension was added the red dichlorotriazinyl dye (VIIIa) (13.56g, 0.01 mol) and the solution was maintained at pH 10 and ambient temperature overnight. The pH was adjusted to 6 with 2N HCl and the dye precipitated by the addition of methylated spirit. The precipitated dye was filtered off and dried to give the expected dye (Ia) (12.5g). ($\lambda_{\text{max}} = 510\text{nm}$, $\epsilon = 76000$, $\nu_{1/2} = 102\text{nm}$). Other analytical data were in full agreement with the expected structure.

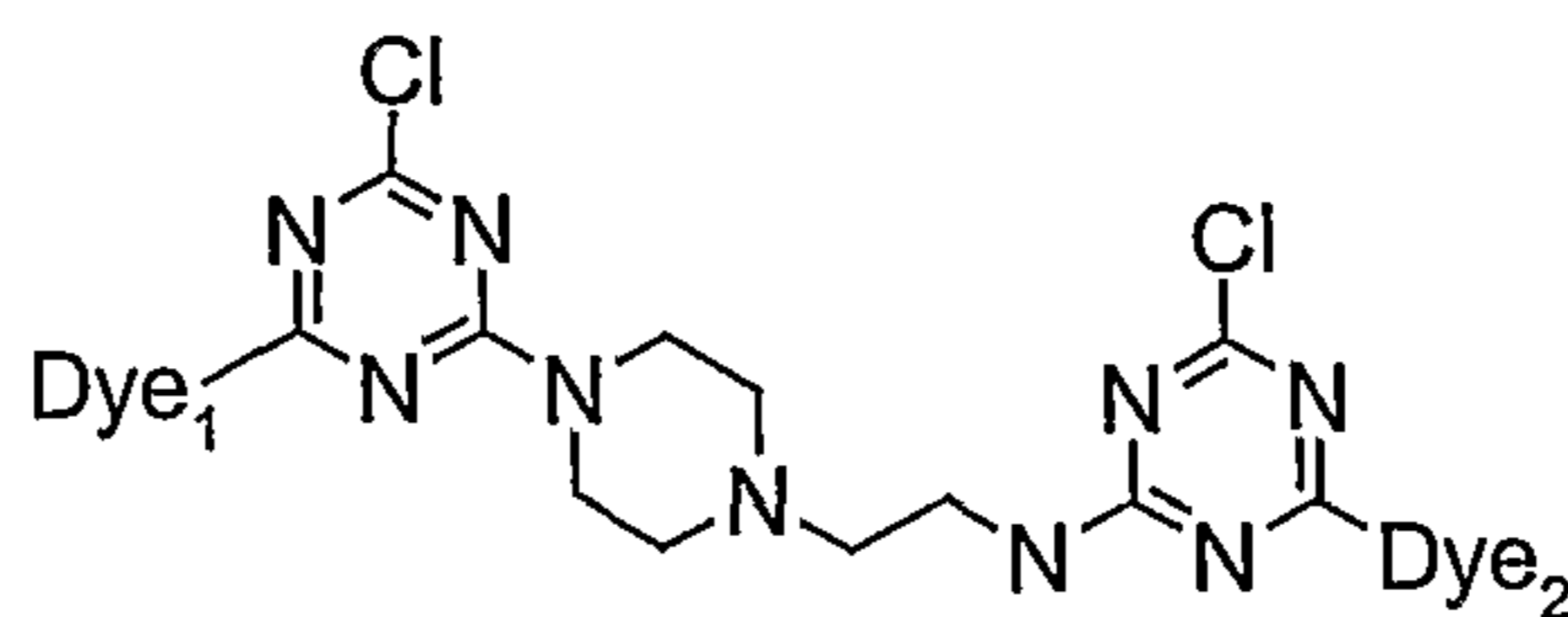
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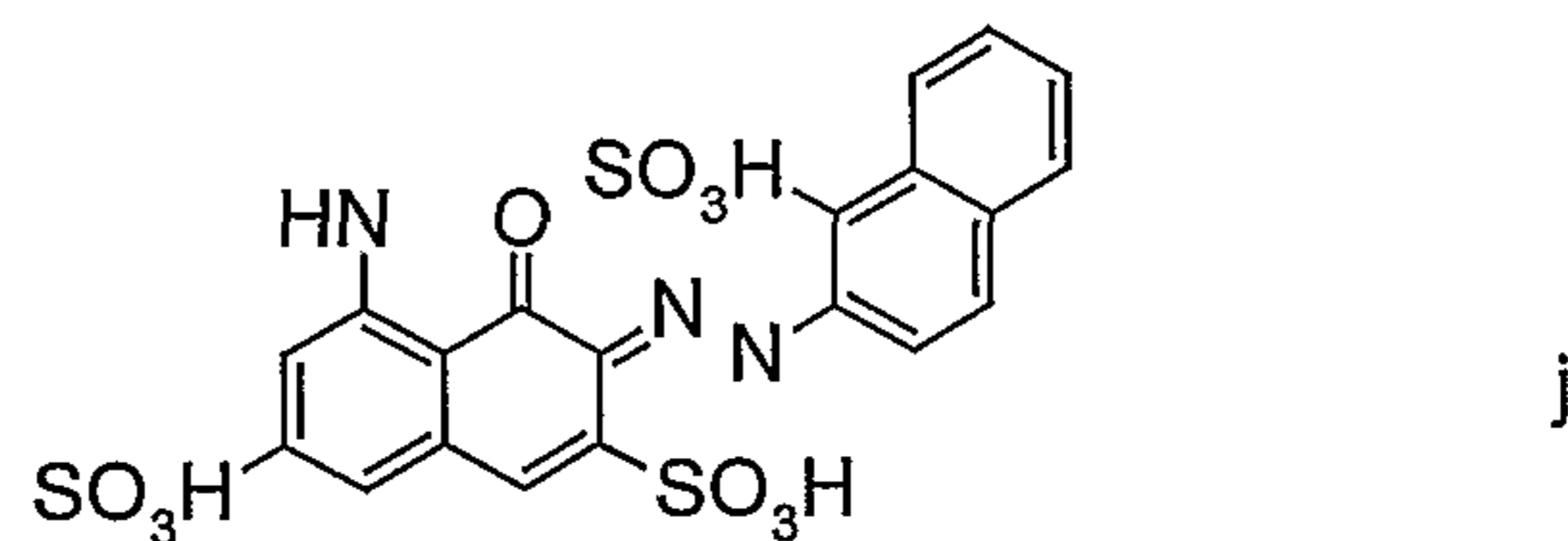
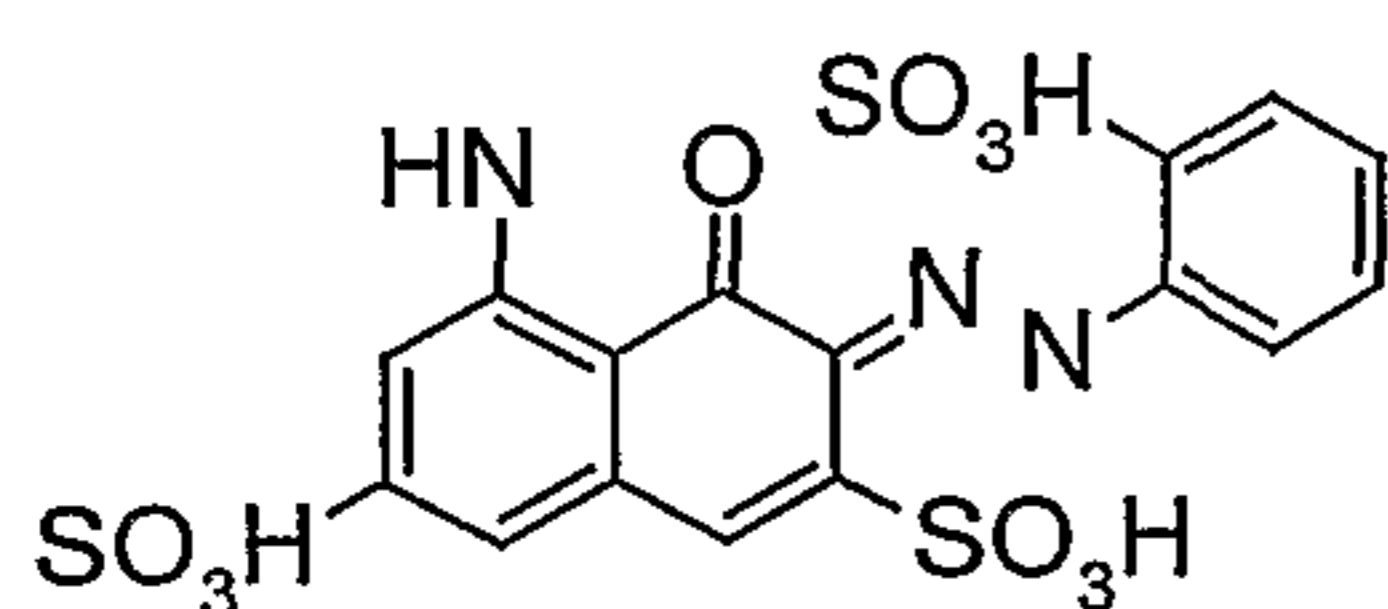
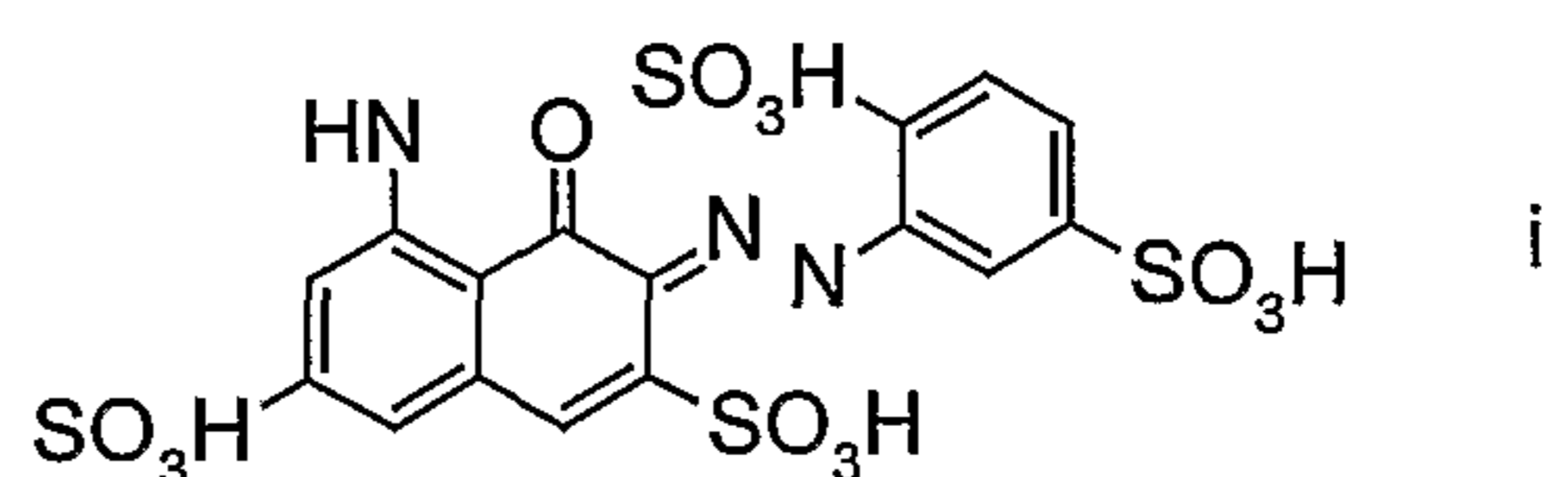
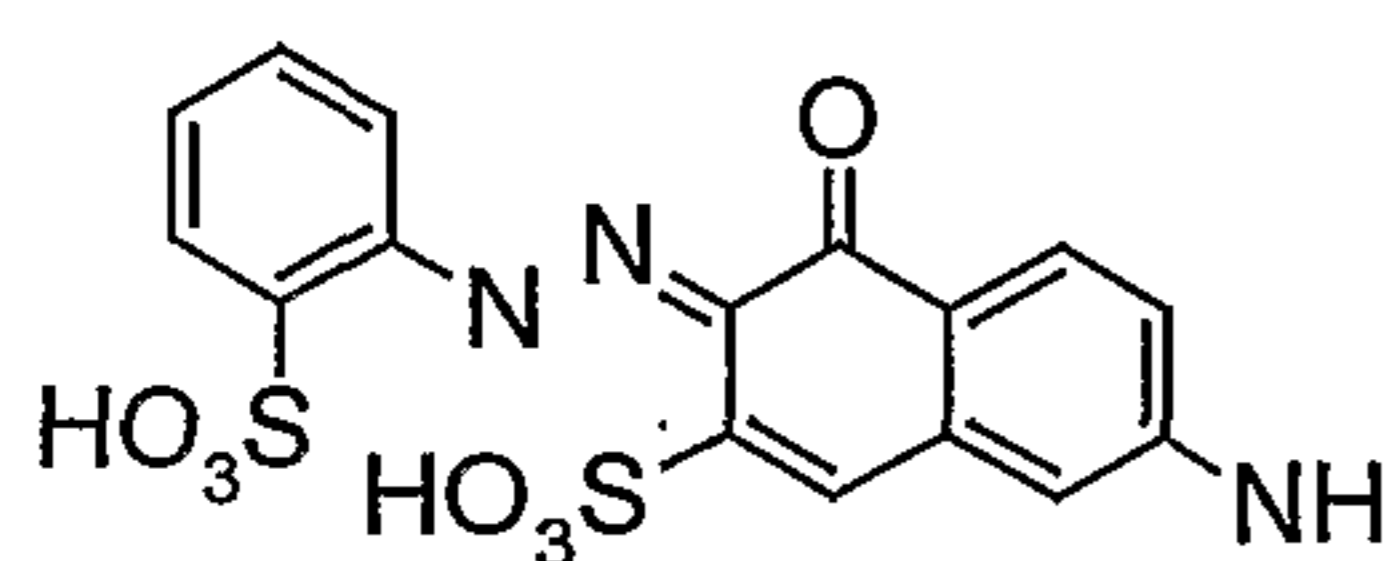
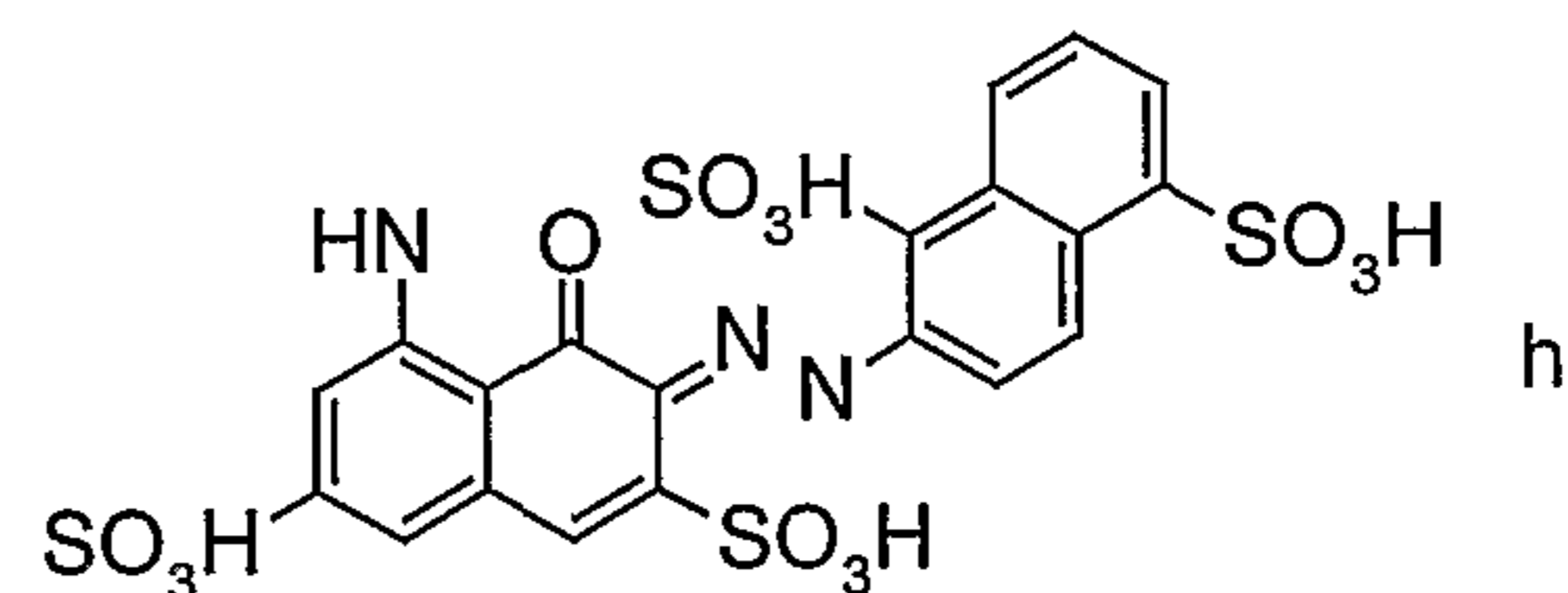
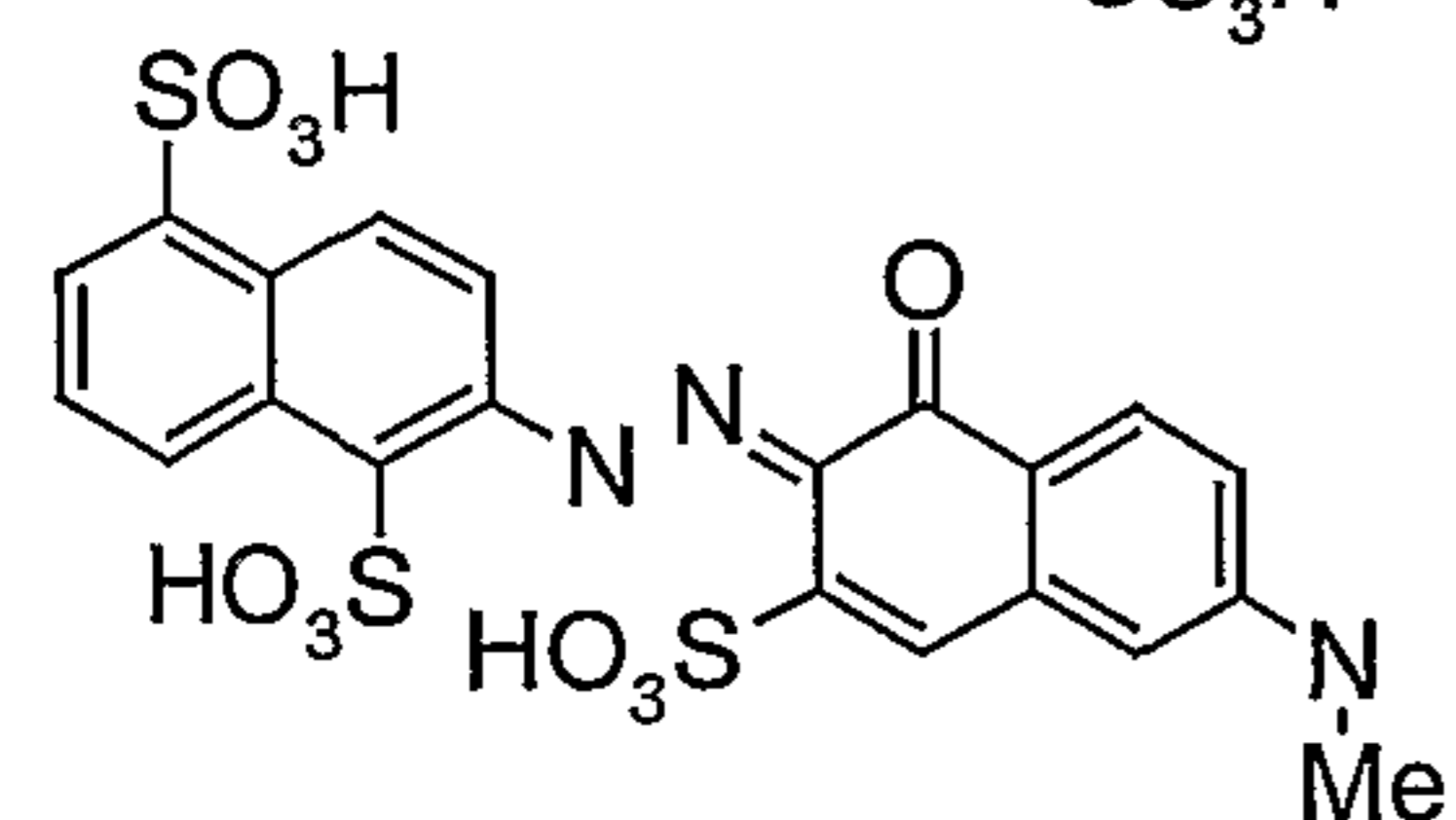
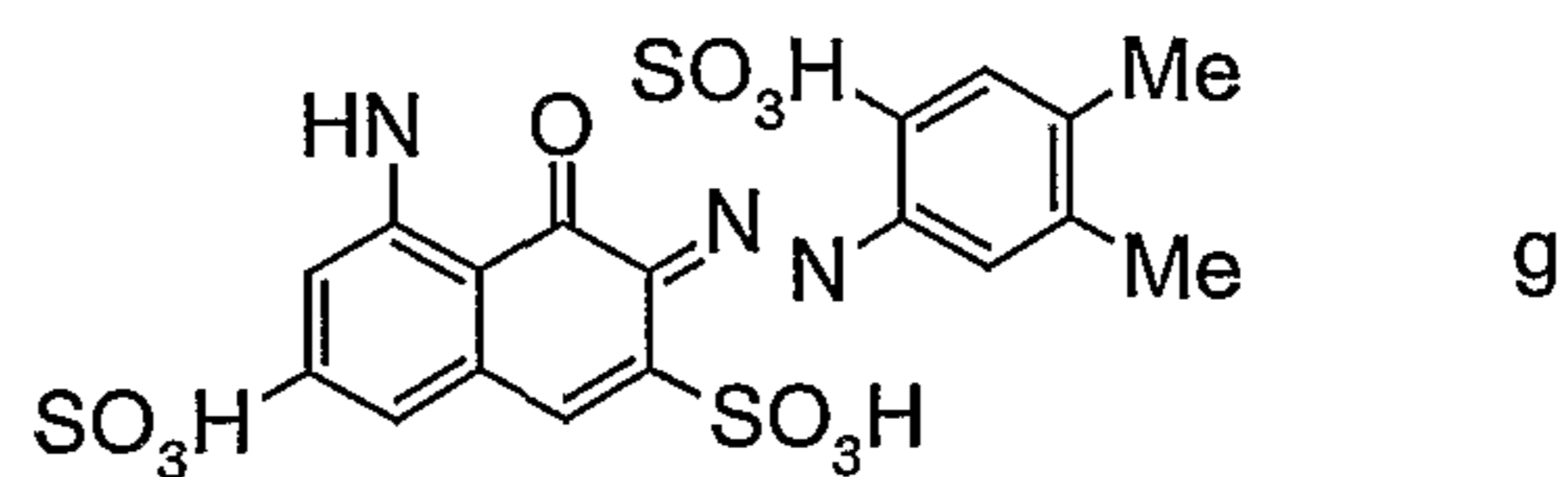
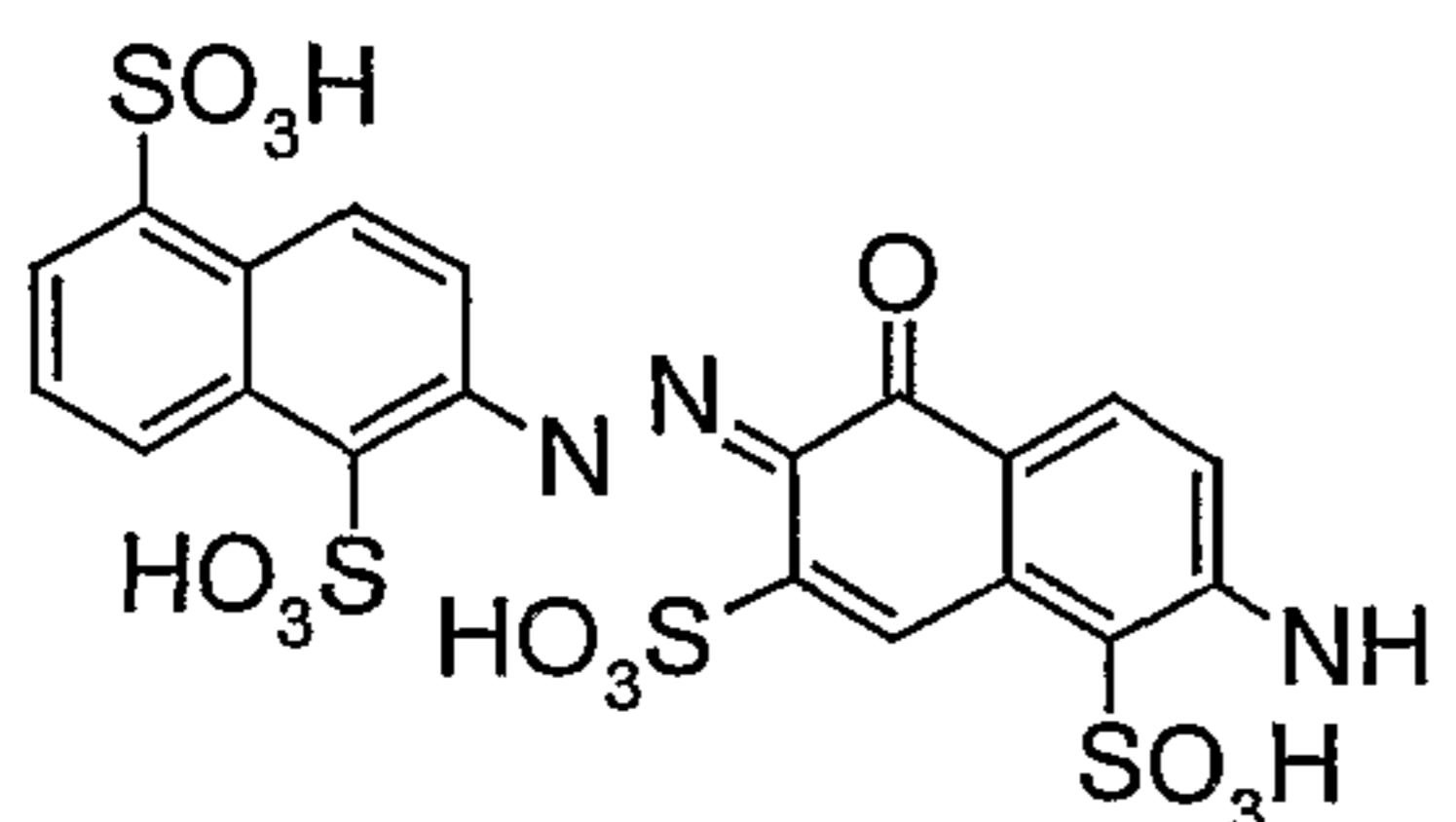
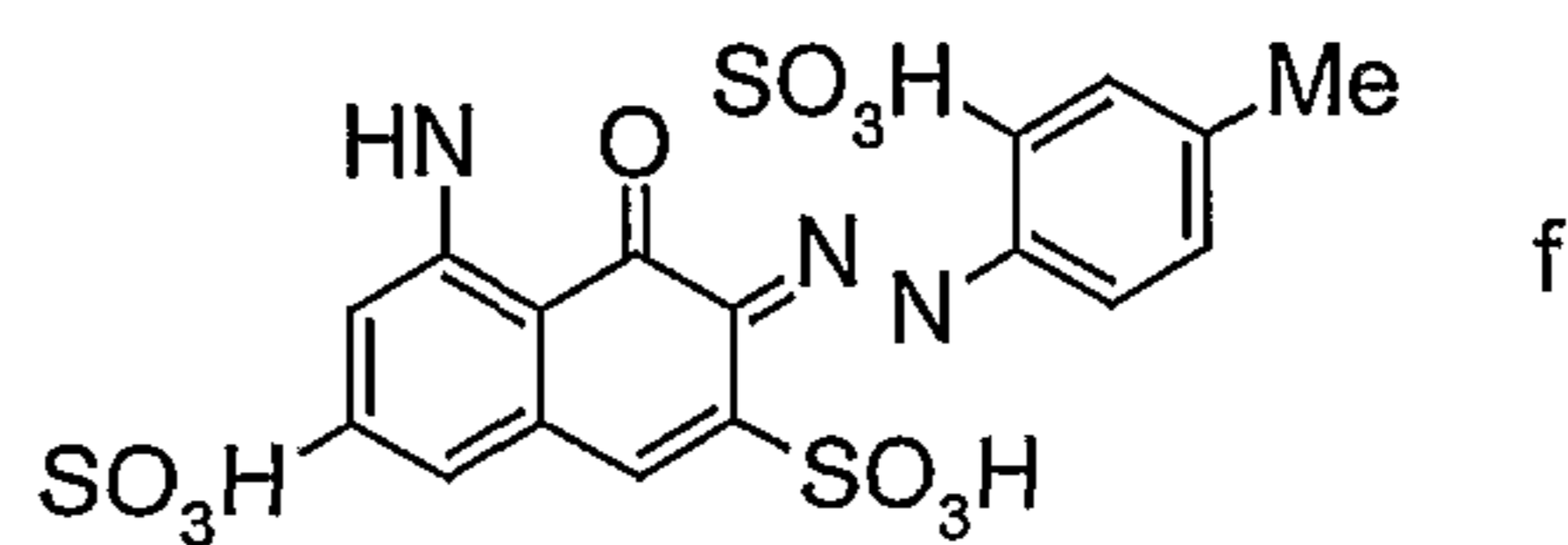
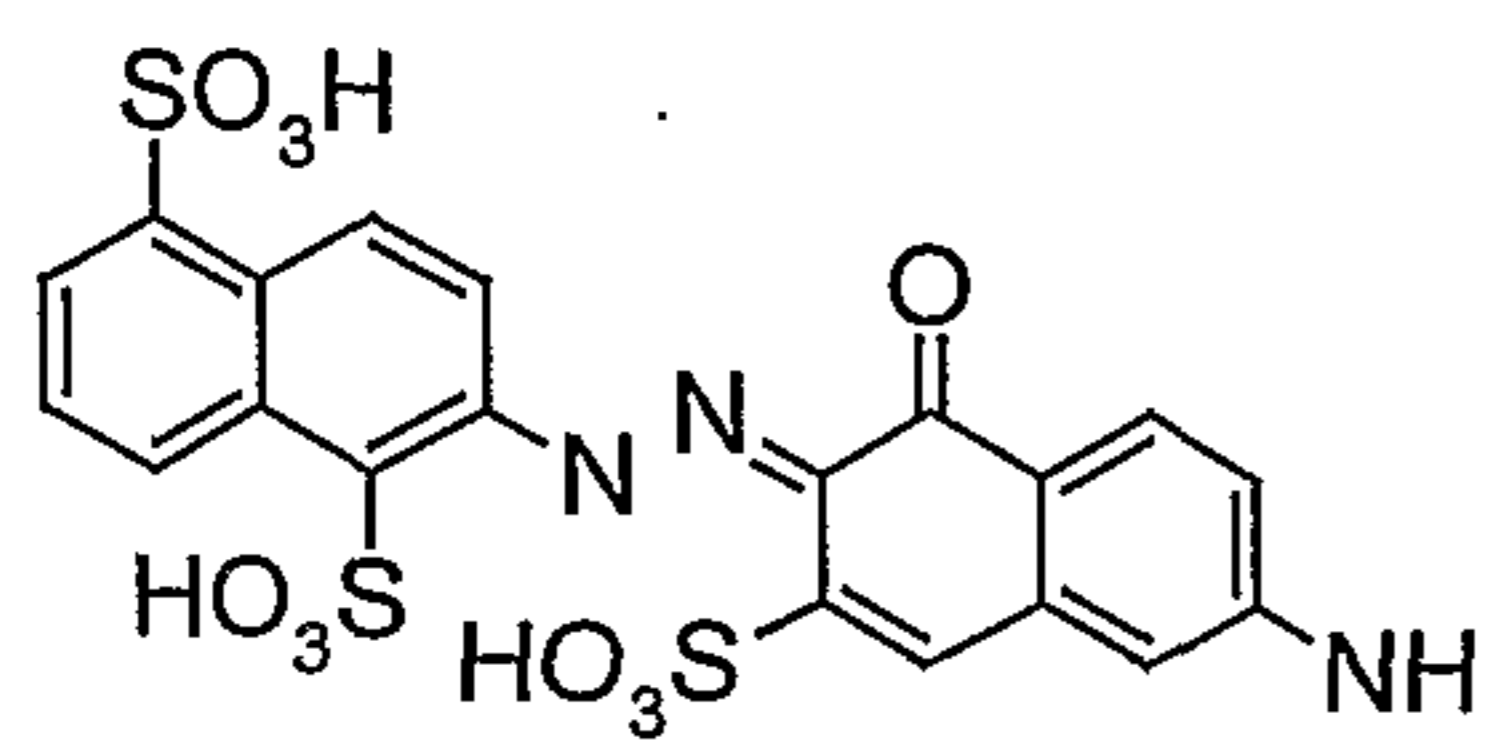
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Following exactly analogous procedures the following dyes (examples 2 – 17) were synthesised.



5

Example	Dye 1	Dye 2	λ max/nm
2	e	d	506
3	h	d	511
4	e	a	508
5	c	e	510
6	a	f	513
7	c	f	514
8	a	g	514
9	e	b	508
10	b	f	513
11	a	h	513
12	c	h	514
13	b	h	513
14	h	b	512
15	b	e	509
16	i	a	506
17	a	i	508
18	c	j	511



5

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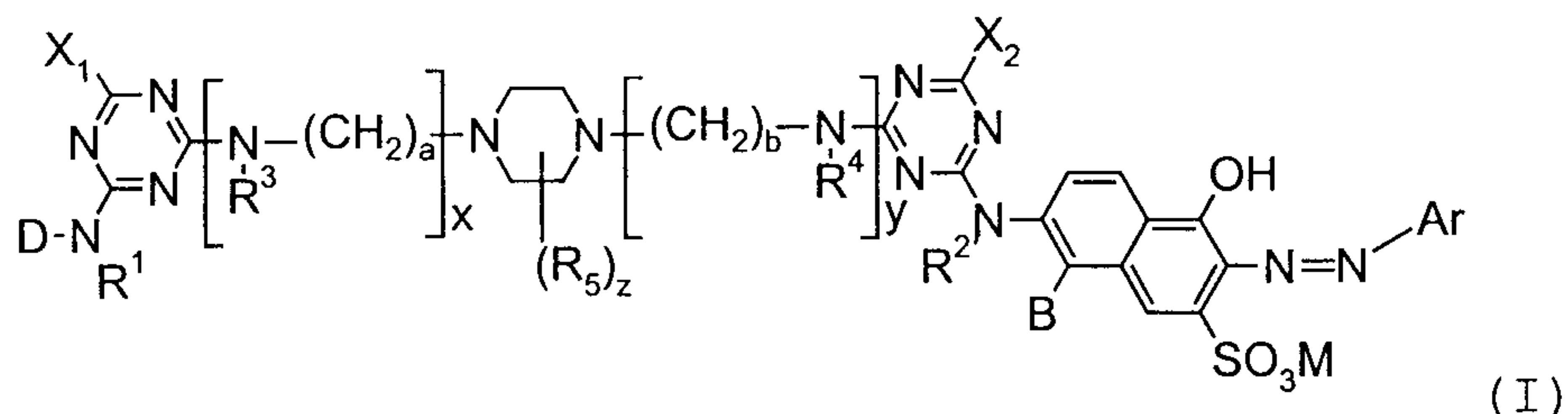
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CLAIMS:

1. A dyestuff of the formula I



wherein

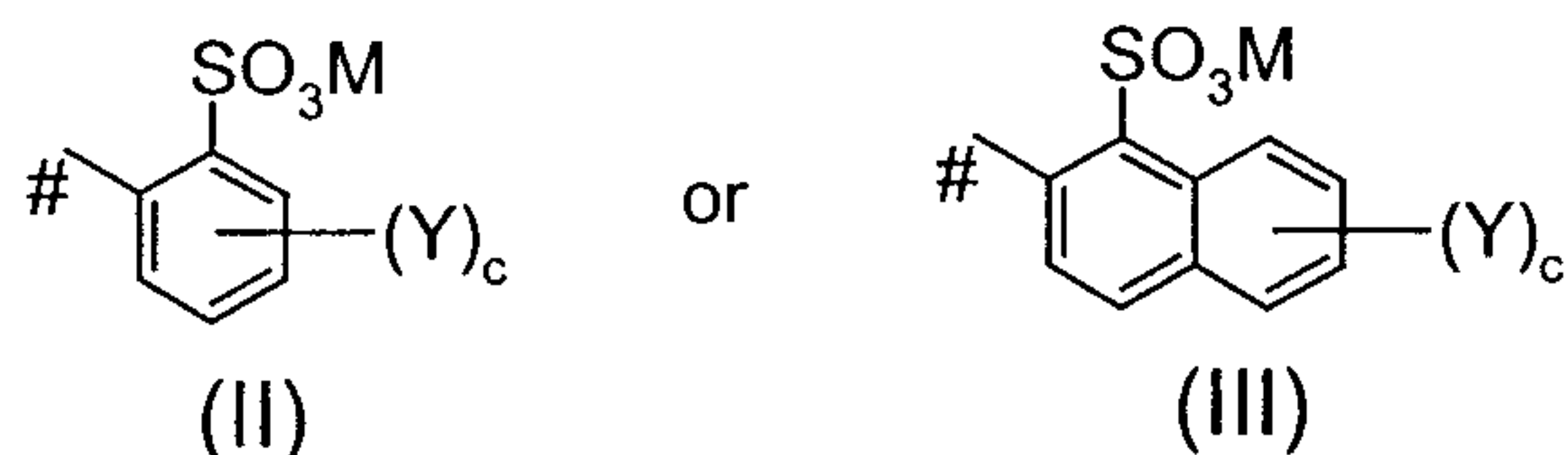
5 each of R^1 , R^2 , R^3 , R^4 and R^5 , independently, is H or an optionally substituted alkyl group;

each of X_1 and X_2 , independently, is a labile atom or group;

B is H or SO_3M ;

10 M is H, an alkali metal, an ammonium ion or the equivalent of an alkaline earth metal;

Ar is a group of the formula II or of the formula III

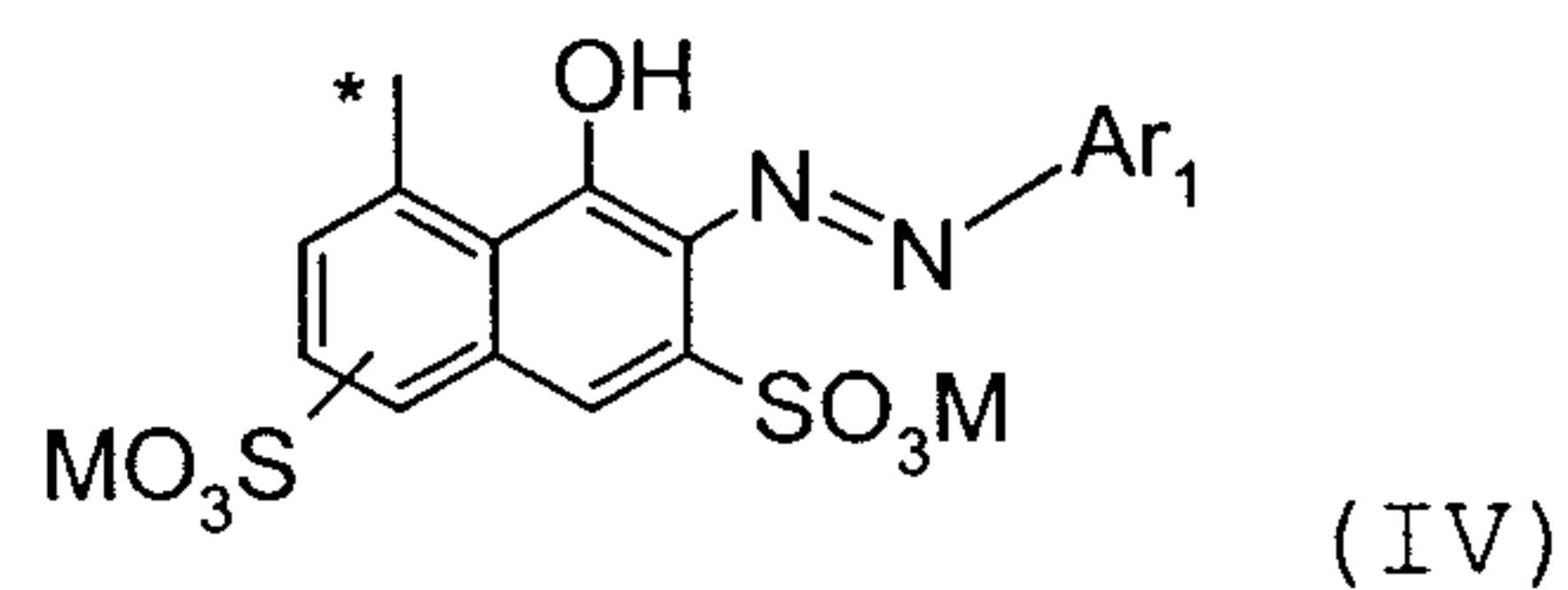


wherein

15 Y is SO_3M or an alkyl group, c is 0, 1 or 2, M is defined as given above and # indicates the bond to the azo group in formula I;

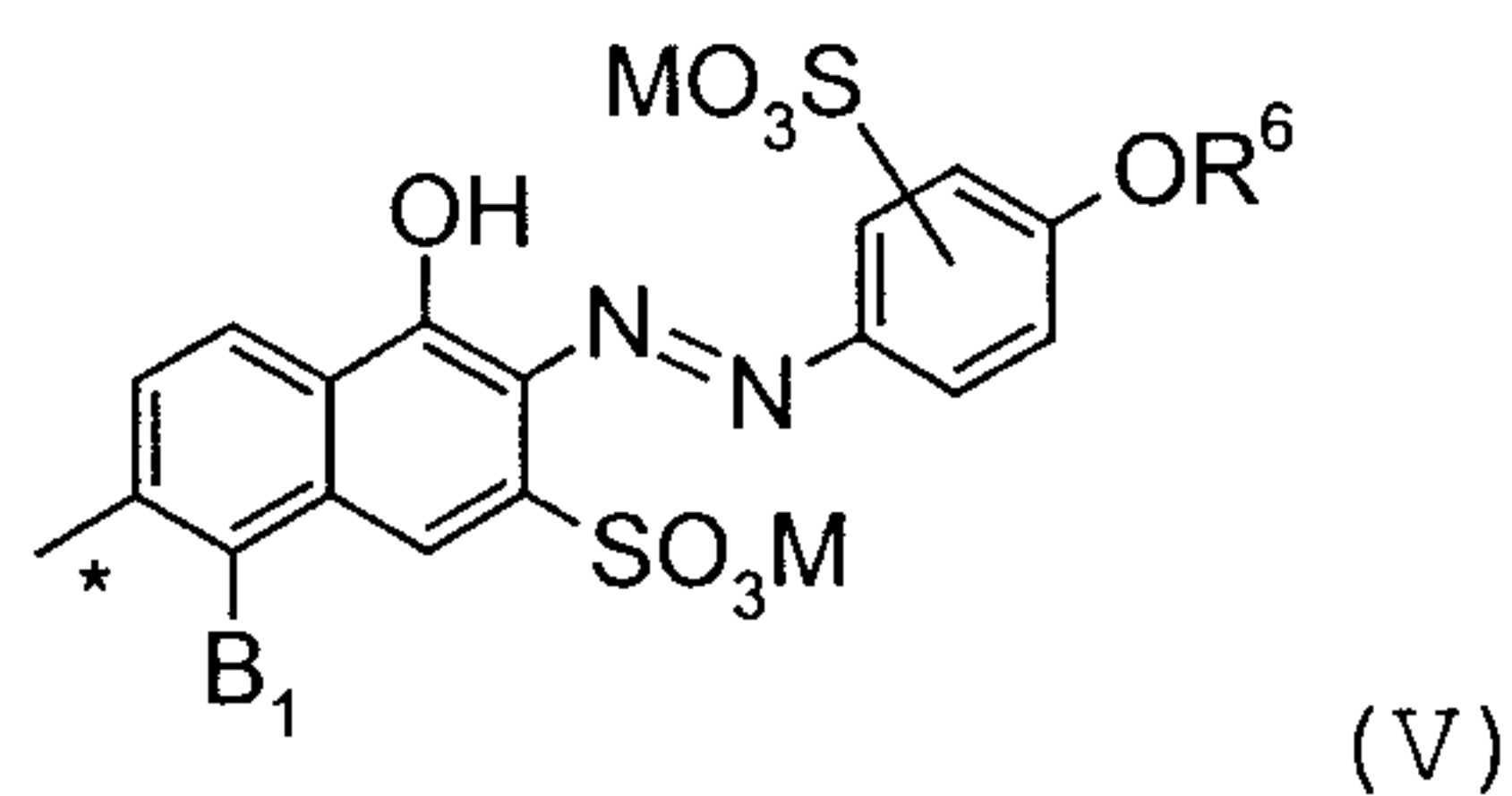
D is a group of the formula IV

29357-32



wherein Ar₁ is defined as Ar, M is defined as given above and * indicates the bond to the NR¹ group of formula I; or

D is a group of the formula V



wherein R⁶ is an alkyl group, B₁ is defined as B and M and * are defined as given above;

each of x and y, independently, is 0 or 1 and at least one of x and y is 1;

each of a and b is 2 to 5 and when each of x and y is 1, a > b; and

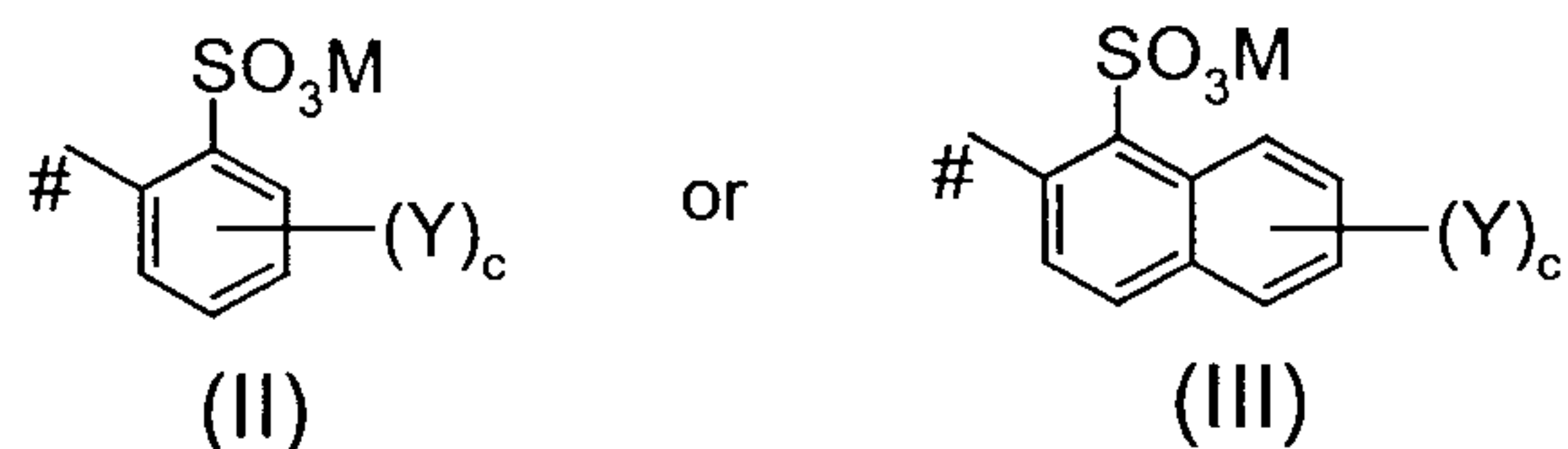
z is 0, 1, 2, 3 or 4.

2. A dyestuff as claimed in claim 1, wherein X₁ and X₂ are halogen.

3. A dyestuff as claimed in claim 1 or 2, wherein M is H or an alkaline metal.

4. A dyestuff as claimed in any one of claims 1 to 3, wherein Ar is a group of the formula II or of the formula III

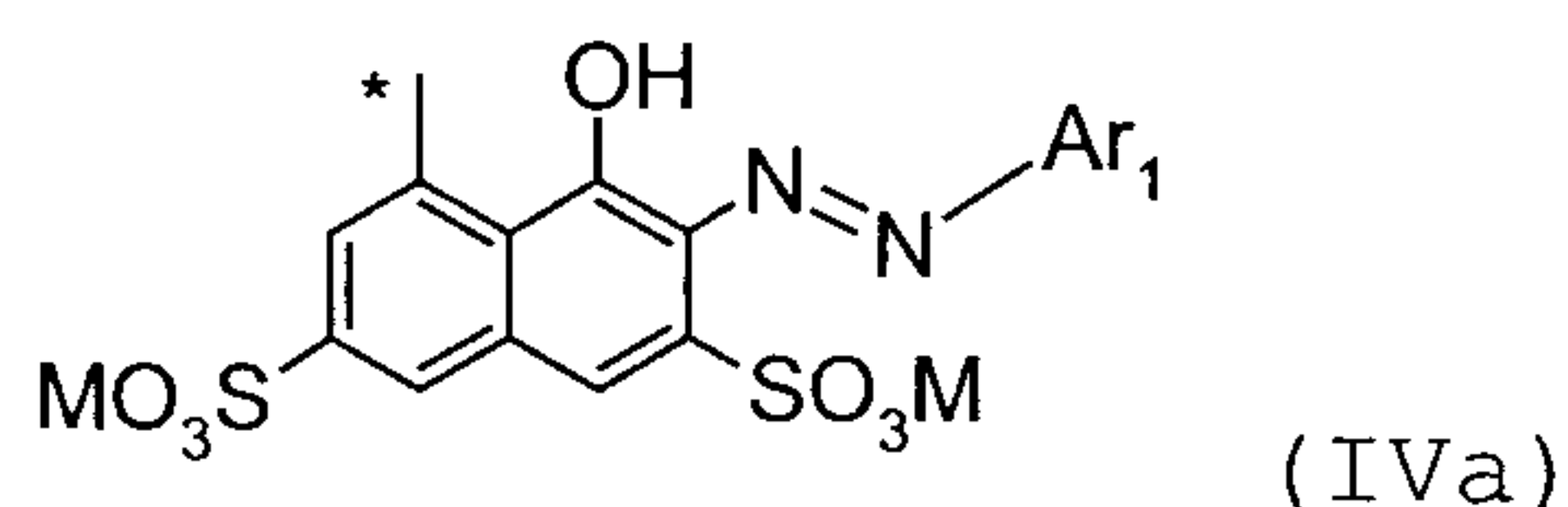
29357-32



wherein

Y is SO₃M or an alkyl group, c is 0, 1 or 2, M is defined as given in claim 1 and # indicates the bond to the azo group
5 in formula I.

5. A dyestuff as claimed in any one of claims 1 to 4, wherein D is a group of the formula IVa



wherein M, Ar₁ and * are defined as given in claim 1.

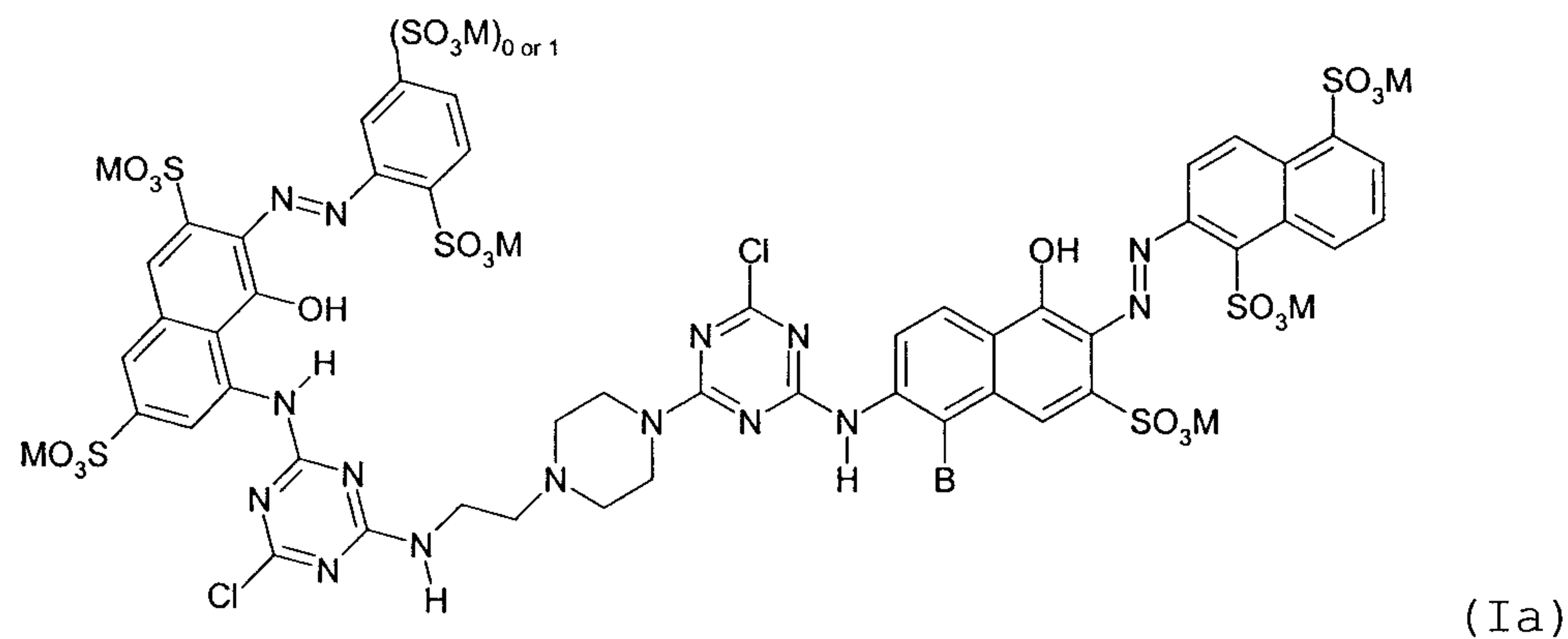
10 6. A dyestuff as claimed in claim 5, wherein Ar₁ is a group of the formula IIa or IIb



wherein M is defined as given in claim 1.

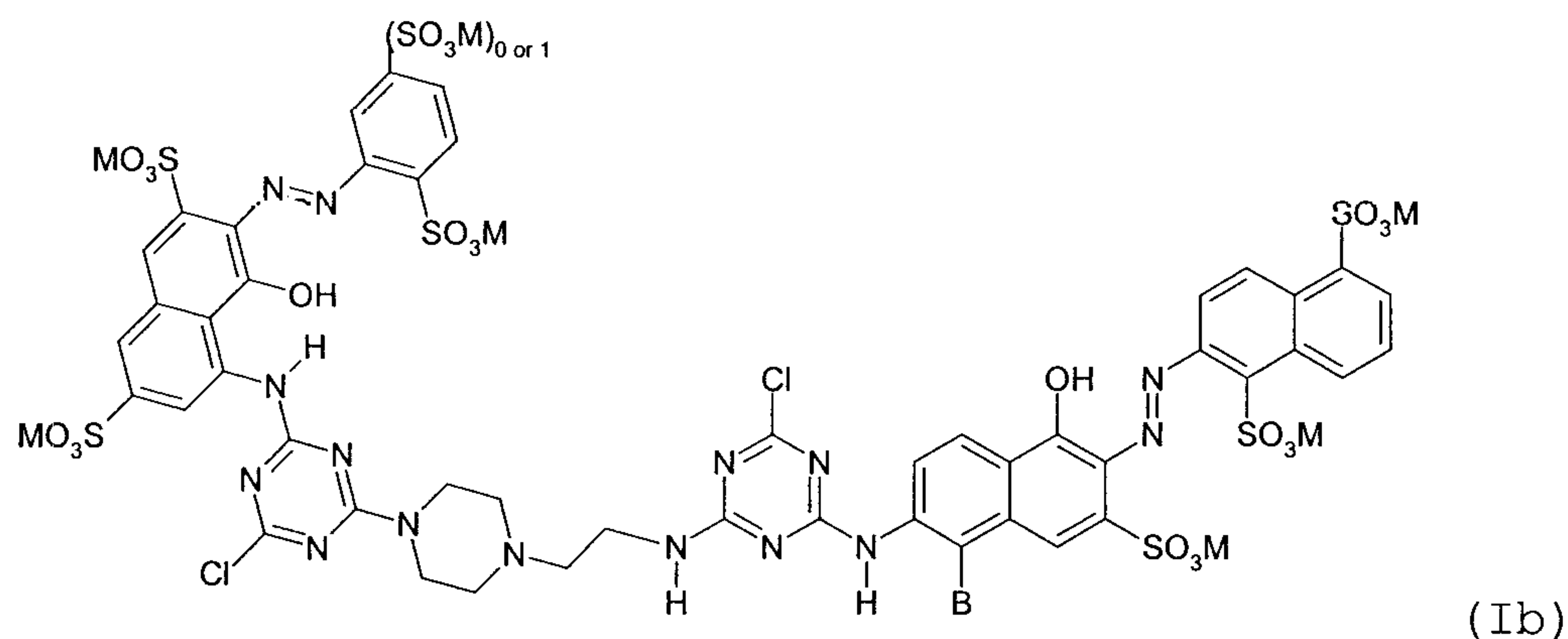
7. A dyestuff as claimed in any one of claims 1 to 6
15 of the formula Ia

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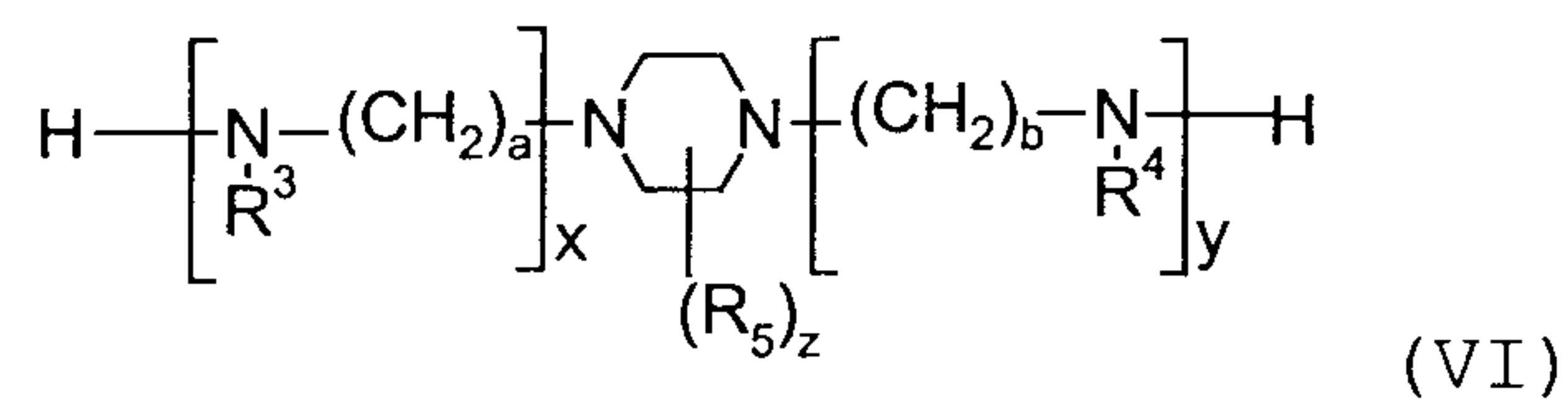
wherein B and M are defined as given in claim 1.

8. A dyestuff as claimed in any one of claims 1 to 6 of the formula Ib



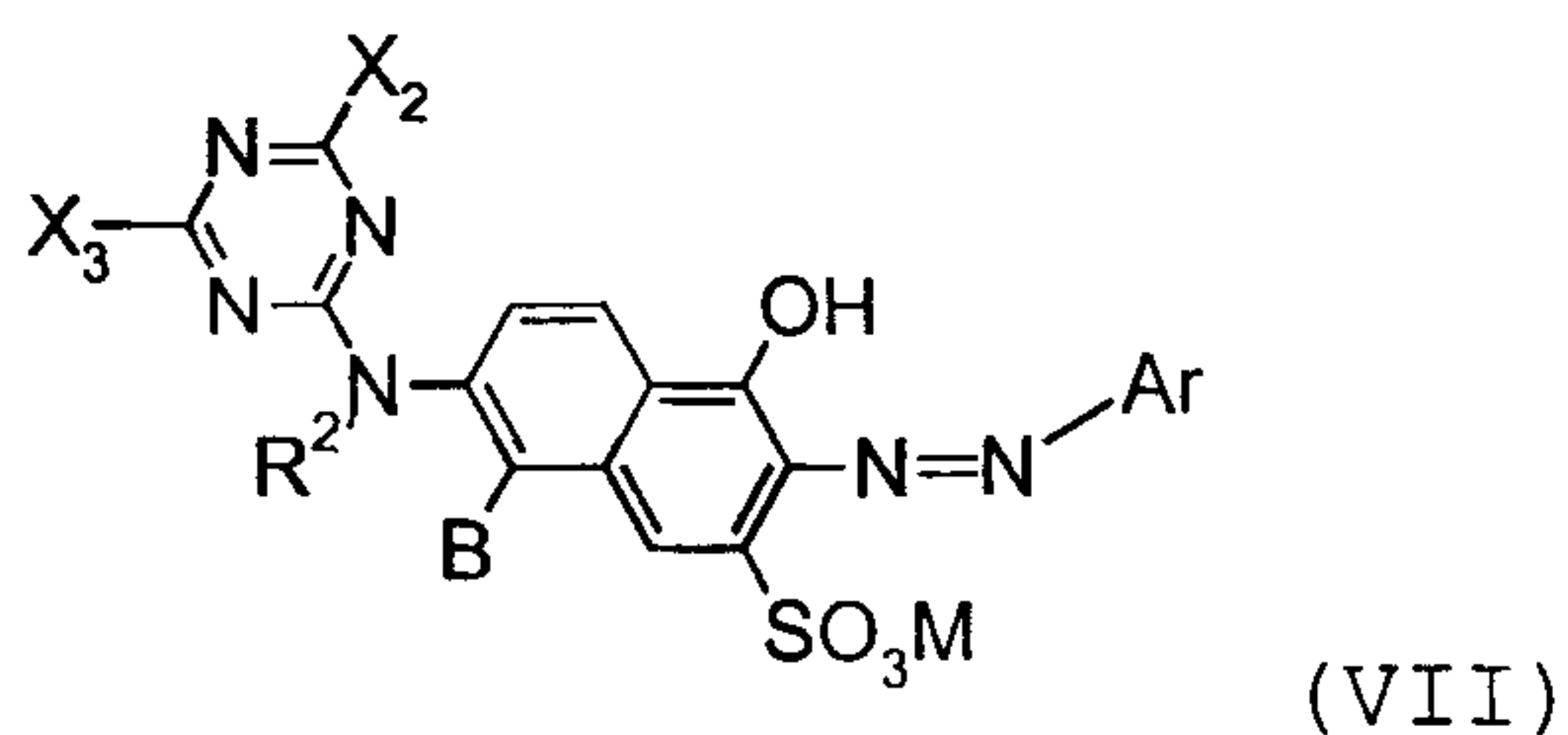
wherein B and M are defined as given in claim 1.

9. A process for preparing a dyestuff of formula I as claimed in any one of claims 1 to 8 by reacting a piperazine compound of the formula VI

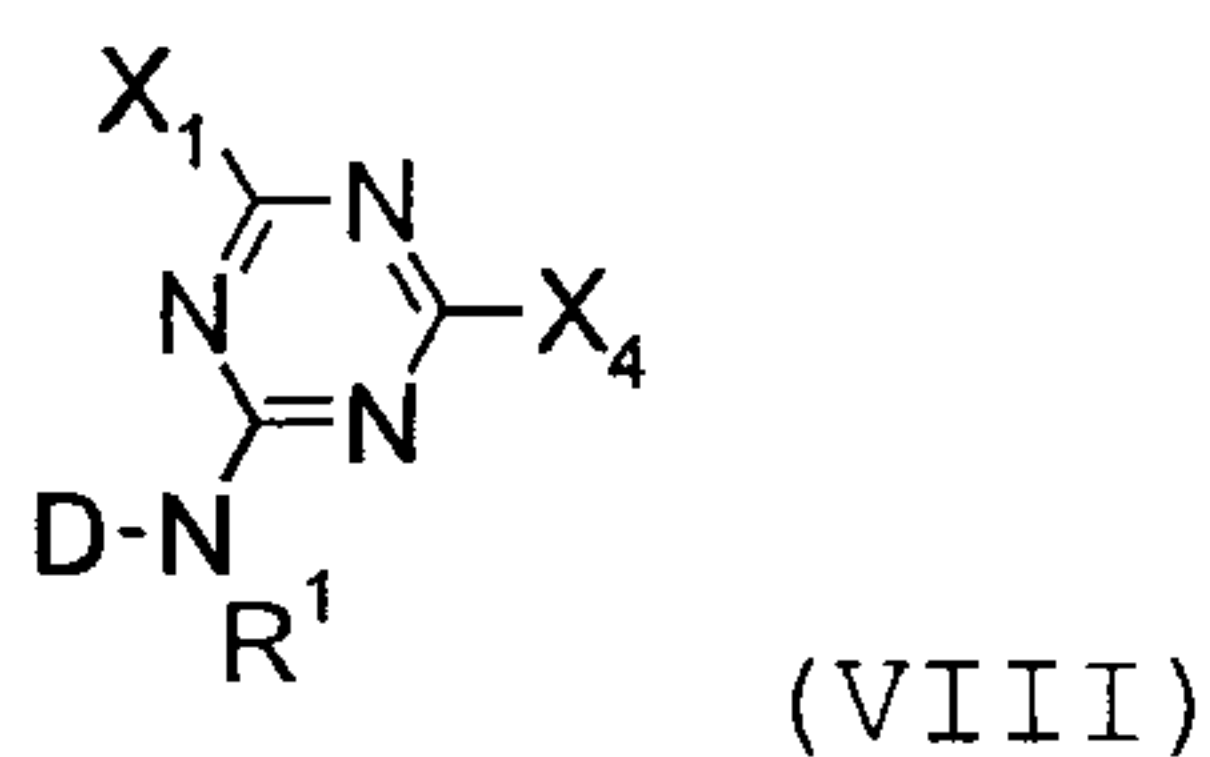


wherein R^3 , R^4 , R^5 , a , b , x , y , and z are defined as given in claim 1, with a compound of the formula VII

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wherein B, M, R², X₂ and Ar are defined as given in claim 1 and X₃ is a labile atom or a group capable of reaction with an amine and with a compound of the formula VIII



5

wherein D, R¹ and X₁ defined as given in claim 1 and X₄ has one of the meanings of X₃.

10. Use of a dyestuff of the formula I as claimed in any one of claims 1 to 8 for dyeing and printing hydroxy-
10 and/or carboxamido-containing fibre materials.

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PATENT AGENTS

