This direct method of C-C coupling opens up an inexpensive and environmentally friendly alternative to existing multistage synthesis routes conventional in organic synthesis.

The problem addressed by the present invention was that of providing an electrochemical process in which anilines can be coupled to one another, and multistage syntheses using metallic reagents can be dispensed with. In addition, access to new products is to be enabled in this way.

Summary

In one aspect, there is provided an electrochemical process for preparing biaryldiamines, comprising the process steps of:
a) introducing a solvent or solvent mixture and a conductive salt into a reaction vessel,
b) adding an aniline to the reaction vessel,
c) introducing two electrodes into the reaction solution,
d) applying a voltage to the electrodes,
e) coupling the aniline to itself to give a biaryldiamine, wherein the two aryl rings are joined directly to one another via a C-C bond and wherein the reaction solution is free of organic oxidizing agents.

In another aspect, there is provided an electrochemical process for preparing biaryldiamines, comprising the process steps of:
a') introducing a solvent or solvent mixture and a conductive salt into a reaction vessel,
b') adding a first aniline having an oxidation potential $|E_{Ox}1|$ to the reaction vessel,
c') adding a second aniline having an oxidation potential $|E_{Ox}2|$ to the reaction vessel, where: $|E_{Ox}2| > |E_{Ox}1|$ and $|E_{Ox}2| - |E_{Ox}1| = |\Delta E|$,
the second aniline being added in excess relative to the first aniline,
and the solvent or solvent mixture being selected such that $|\Delta E|$ is in the range from 10 mV to 450 mV,
d') introducing two electrodes into the reaction solution,
e') applying a voltage to the electrodes,
f') coupling the first aniline to the second aniline to give a biaryldiamine, wherein the two aryl rings are joined directly to one another via a C-C bond.

In an embodiment, the present disclosure is an~~There is provided an~~ electrochemical process for preparing biaryldiamines, comprising the process steps of:
a) introducing a solvent or solvent mixture and the conductive salt into a reaction vessel,

b) adding the anilines, which may be two different anilines or just one aniline, to the reaction vessel,

c) introducing two electrodes into the reaction solution,

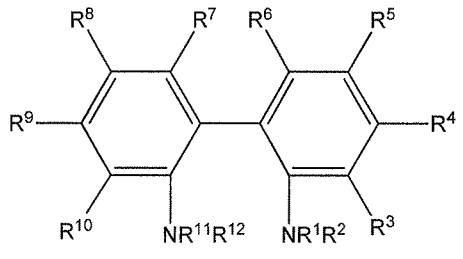
d) applying a voltage to the electrodes,

e) coupling the first aniline to itself or to the second aniline to give a biaryldiamine.

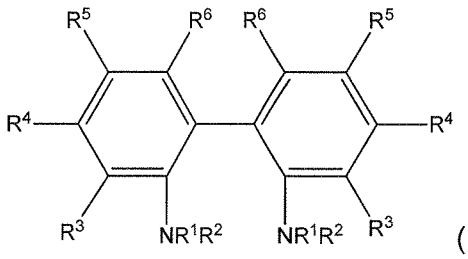
Detailed Description

The problem is solved by a process according to Claim 1 or 2.

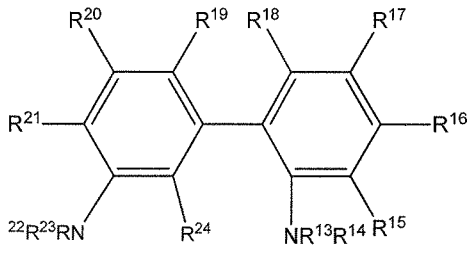
Compounds of one of the general formulae (**I**) to (**IV**) can be prepared by the process described:



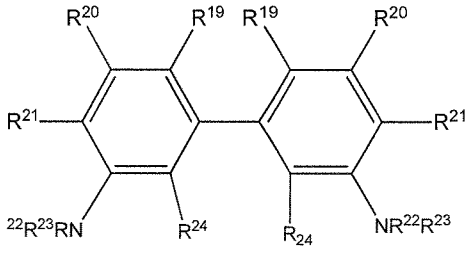
(**I**)



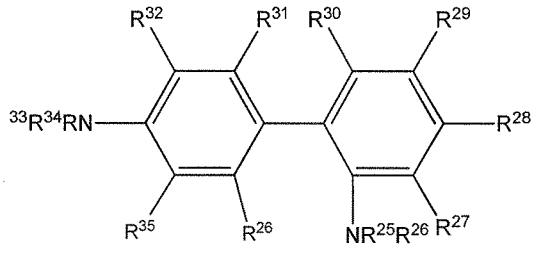
(**I'**)



(**II**)



(**II'**)



(**III**)

Claims

1. Electrochemical process for preparing biaryldiamines, comprising the process steps of:
a) introducing a solvent or solvent mixture and the conductive salt into a reaction vessel,
b) adding the anilines, which may be two different anilines or just one aniline, to the reaction vessel,
c) introducing two electrodes into the reaction solution,
d) applying a voltage to the electrodes,
e) coupling the first aniline to itself or to the second aniline to give a biaryldiamine.

2. Electrochemical process for preparing biaryldiamines, comprising the process steps of:
a') introducing a solvent or solvent mixture and a conductive salt into a reaction vessel,
b') adding a first aniline having an oxidation potential $|E_{Ox}1|$ to the reaction vessel,
c') adding a second aniline having an oxidation potential $|E_{Ox}2|$ to the reaction vessel, where: $|E_{Ox}2| > |E_{Ox}1|$ and $|E_{Ox}2| - |E_{Ox}1| = |\Delta E|$,
the second aniline being added in excess relative to the first aniline,
and the solvent or solvent mixture being selected such that $|\Delta E|$ is in the range from 10 mV to 450 mV,
d') introducing two electrodes into the reaction solution,
e') applying a voltage to the electrodes,
f') coupling the first aniline to the second aniline to give a biaryldiamine.

3. Process according to Claim 2,
wherein the second aniline is used in at least twice the amount relative to the first aniline.

4. Process according to either of Claims 2 and 3,
wherein the ratio of first aniline to second aniline is in the range from 1:2 to 1:4.

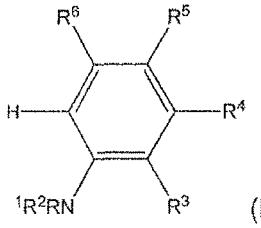
5. Process according to any of Claims 2 to 4,
wherein the solvent or solvent mixture is selected such that $|\Delta E|$ is in the range from 20 mV to 400 mV.

6. Process according to any of Claims 1 to 5,

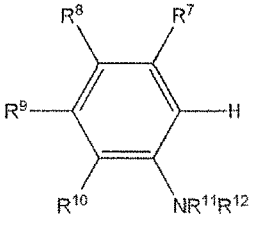
wherein the reaction solution is free of organic oxidizing agents.

7. Process according to any of Claims 2 to 6,

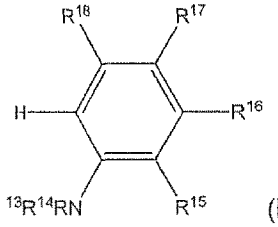
wherein the first aniline and the second aniline are selected from: **Ia, Ib, IIa, IIb, IIIa, IIIb, IVa, IVb**:



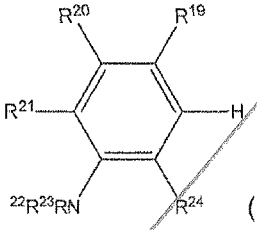
(Ia)



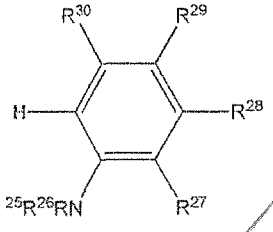
(Ib)



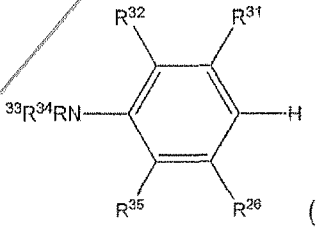
(IIa)



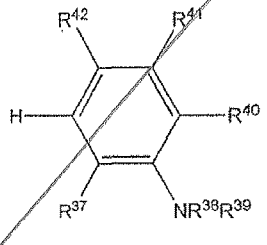
(IIb)



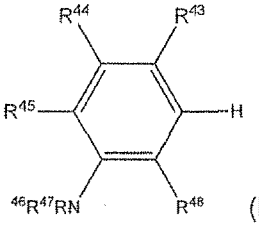
(IIIa)



(IIIb)



(IVa)



(IVb)

where the substituents R^1 to R^{48} are each independently selected from the group of hydrogen, hydroxyl, (C_1-C_{12})-alkyl, (C_1-C_{12})-heteroalkyl, (C_4-C_{14})-aryl, (C_4-C_{14})-aryl-(C_1-C_{12})-alkyl, (C_4-C_{14})-aryl-O-(C_1-C_{12})-alkyl, (C_3-C_{14})-heteroaryl, (C_3-C_{14})-heteroaryl-(C_1-C_{12})-alkyl, (C_3-C_{12})-cycloalkyl,

$(C_3\text{-}C_{12})$-cycloalkyl-$(C_1\text{-}C_{12})$-alkyl, $(C_3\text{-}C_{12})$-heterocycloalkyl, $(C_3\text{-}C_{12})$-heterocycloalkyl-$(C_1\text{-}C_{12})$-alkyl, O-$(C_1\text{-}C_{12})$-alkyl, O-$(C_1\text{-}C_{12})$-heteroalkyl, O-$(C_4\text{-}C_{14})$-aryl, O-$(C_4\text{-}C_{14})$-aryl-$(C_1\text{-}C_{14})$-alkyl, O-$(C_3\text{-}C_{14})$-heteroaryl, O-$(C_3\text{-}C_{14})$-heteroaryl-$(C_1\text{-}C_{14})$-alkyl, O-$(C_3\text{-}C_{12})$-cycloalkyl, O-$(C_3\text{-}C_{12})$-cycloalkyl-$(C_1\text{-}C_{12})$-alkyl, O-$(C_3\text{-}C_{12})$-heterocycloalkyl, O-$(C_3\text{-}C_{12})$-heterocycloalkyl-$(C_1\text{-}C_{12})$-alkyl, halogens, S-$(C_1\text{-}C_{12})$-alkyl, S-$(C_1\text{-}C_{12})$-heteroalkyl, S-$(C_4\text{-}C_{14})$-aryl, S-$(C_4\text{-}C_{14})$-aryl-$(C_1\text{-}C_{14})$-alkyl, S-$(C_3\text{-}C_{14})$-heteroaryl, S-$(C_3\text{-}C_{14})$-heteroaryl-$(C_1\text{-}C_{14})$-alkyl, S-$(C_3\text{-}C_{12})$-cycloalkyl, S-$(C_3\text{-}C_{12})$-cycloalkyl-$(C_1\text{-}C_{12})$-alkyl, S-$(C_3\text{-}C_{12})$-heterocycloalkyl, $(C_1\text{-}C_{12})$-acyl, $(C_4\text{-}C_{14})$-aroyl, $(C_4\text{-}C_{14})$-aroyl-$(C_1\text{-}C_{14})$-alkyl, $(C_3\text{-}C_{14})$-heteroaroyl, $(C_1\text{-}C_{14})$-dialkylphosphoryl, $(C_4\text{-}C_{14})$-diarylphosphoryl, $(C_3\text{-}C_{12})$-alkylsulphonyl, $(C_3\text{-}C_{12})$-cycloalkylsulphonyl, $(C_4\text{-}C_{12})$-arylsulphonyl, $(C_1\text{-}C_{12})$-alkyl-$(C_4\text{-}C_{12})$-arylsulphonyl, $(C_3\text{-}C_{12})$-heteroarylsulphonyl, (C=O)O-$(C_1\text{-}C_{12})$-alkyl, (C=O)O-$(C_1\text{-}C_{12})$-heteroalkyl, (C=O)O-$(C_4\text{-}C_{14})$-aryl,

where the alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, aryl and heteroaryl groups mentioned are optionally mono- or polysubstituted, and

the following combinations are possible here:

first aniline	**Ia**	**Ib**	**IIa**	**IIb**	**IIIa**	**IIIb**	**IVa**	**IVb**
second aniline	**Ib**	**Ia**	**IIb**	**IIa**	**IIIb**	**IIIa**	**IVb**	**IVa**

~~AMENDED~~ CLAIMS

~~received at the International Office on June 2, 2014 (06.02.2014)~~

1. Electrochemical process for preparing biaryldiamines, comprising the process steps of:
a) introducing a solvent or solvent mixture and ~~the~~ a conductive salt into a reaction vessel,
b) adding an aniline to the reaction vessel,
c) introducing two electrodes into the reaction solution,
d) applying a voltage to the electrodes,
e) coupling the aniline to itself to give a biaryldiamine, wherein the two aryl rings are joined directly to one another via a C-C bond and wherein the reaction solution is free of organic oxidizing agents.

2. Electrochemical process for preparing biaryldiamines, comprising the process steps of:
a') introducing a solvent or solvent mixture and a conductive salt into a reaction vessel,
b') adding a first aniline having an oxidation potential $|E_{Ox}1|$ to the reaction vessel,
c') adding a second aniline having an oxidation potential $|E_{Ox}2|$ to the reaction vessel, where: $|E_{Ox}2| > |E_{Ox}1|$ and $|E_{Ox}2| - |E_{Ox}1| = |\Delta E|$,
the second aniline being added in excess relative to the first aniline,
and the solvent or solvent mixture being selected such that $|\Delta E|$ is in the range from 10 mV to 450 mV,
d') introducing two electrodes into the reaction solution,
e') applying a voltage to the electrodes,
f') coupling the first aniline to the second aniline to give a biaryldiamine, wherein the two aryl rings are joined directly to one another via a C-C bond.

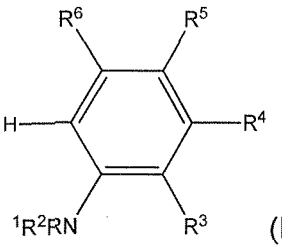
3. Process according to Claim 2,
wherein the second aniline is used in at least twice the amount relative to the first aniline.

4. Process according to either of Claims 2 and 3,
wherein the ratio of first aniline to second aniline is in the range from 1:2 to 1:4.

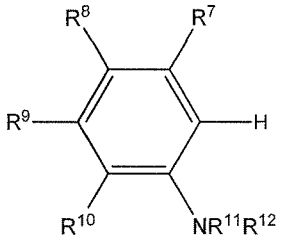
5. Process according to any of Claims 2 to 4,
wherein the solvent or solvent mixture is selected such that $|\Delta E|$ is in the range from 20 mV to 400 mV.

6. Process according to any of Claims ~~1~~2 to 5,
wherein the reaction solution is free of organic oxidizing agents.

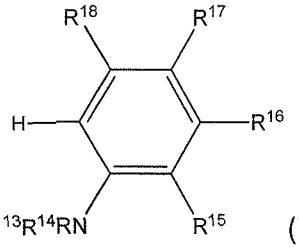
7. Process according to any of Claims 2 to 6,
wherein the first aniline and the second aniline are selected from: **Ia**, **Ib**, **IIa**, **IIb**, **IIIa**, **IIIb**, **IVa**, **IVb**:



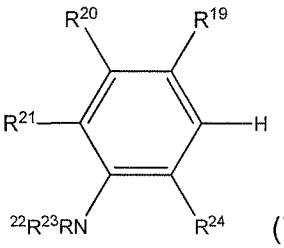
(**Ia**)



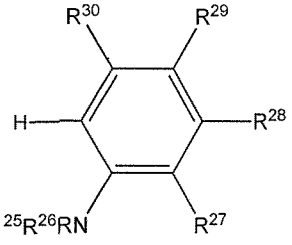
(**Ib**)



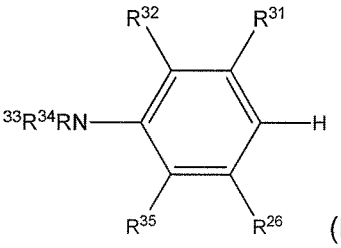
(**IIa**)



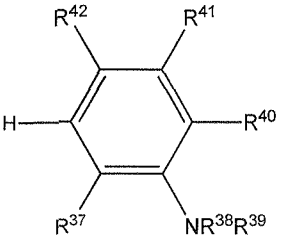
(**IIb**)



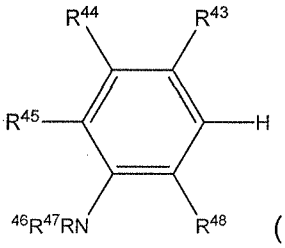
(**IIIa**)



(**IIIb**)



(**IVa**)



(**IVb**)

where the substituents R^1 to R^{48} are each independently selected from the group of hydrogen, hydroxyl, (C_1-C_{12})-alkyl, (C_1-C_{12})-heteroalkyl, (C_4-C_{14})-aryl, (C_4-C_{14})-aryl-(C_1-C_{12})-alkyl, (C_4-C_{14})-aryl-O-(C_1-C_{12})-alkyl, (C_3-C_{14})-heteroaryl, (C_3-C_{14})-heteroaryl-(C_1-C_{12})-alkyl, (C_3-C_{12})-cycloalkyl,

$(C_3\text{-}C_{12})$-cycloalkyl-$(C_1\text{-}C_{12})$-alkyl, $(C_3\text{-}C_{12})$-heterocycloalkyl, $(C_3\text{-}C_{12})$-heterocycloalkyl-$(C_1\text{-}C_{12})$-alkyl, O-$(C_1\text{-}C_{12})$-alkyl, O-$(C_1\text{-}C_{12})$-heteroalkyl, O-$(C_4\text{-}C_{14})$-aryl, O-$(C_4\text{-}C_{14})$-aryl-$(C_1\text{-}C_{14})$-alkyl, O-$(C_3\text{-}C_{14})$-heteroaryl, O-$(C_3\text{-}C_{14})$-heteroaryl-$(C_1\text{-}C_{14})$-alkyl, O-$(C_3\text{-}C_{12})$-cycloalkyl, O-$(C_3\text{-}C_{12})$-cycloalkyl-$(C_1\text{-}C_{12})$-alkyl, O-$(C_3\text{-}C_{12})$-heterocycloalkyl, O-$(C_3\text{-}C_{12})$-heterocycloalkyl-$(C_1\text{-}C_{12})$-alkyl, halogens, S-$(C_1\text{-}C_{12})$-alkyl, S-$(C_1\text{-}C_{12})$-heteroalkyl, S-$(C_4\text{-}C_{14})$-aryl, S-$(C_4\text{-}C_{14})$-aryl-$(C_1\text{-}C_{14})$-alkyl, S-$(C_3\text{-}C_{14})$-heteroaryl, S-$(C_3\text{-}C_{14})$-heteroaryl-$(C_1\text{-}C_{14})$-alkyl, S-$(C_3\text{-}C_{12})$-cycloalkyl, S-$(C_3\text{-}C_{12})$-cycloalkyl-$(C_1\text{-}C_{12})$-alkyl, S-$(C_3\text{-}C_{12})$-heterocycloalkyl, $(C_1\text{-}C_{12})$-acyl, $(C_4\text{-}C_{14})$-aroyl, $(C_4\text{-}C_{14})$-aroyl-$(C_1\text{-}C_{14})$-alkyl, $(C_3\text{-}C_{14})$-heteroaroyl, $(C_1\text{-}C_{14})$-dialkylphosphoryl, $(C_4\text{-}C_{14})$-diarylphosphoryl, $(C_3\text{-}C_{12})$-alkylsulphonyl, $(C_3\text{-}C_{12})$-cycloalkylsulphonyl, $(C_4\text{-}C_{12})$-arylsulphonyl, $(C_1\text{-}C_{12})$-alkyl-$(C_4\text{-}C_{12})$-arylsulphonyl, $(C_3\text{-}C_{12})$-heteroarylsulphonyl, (C=O)O-$(C_1\text{-}C_{12})$-alkyl, (C=O)O-$(C_1\text{-}C_{12})$-heteroalkyl, (C=O)O-$(C_4\text{-}C_{14})$-aryl,

where the alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, aryl and heteroaryl groups mentioned are optionally mono- or polysubstituted, and

the following combinations are possible here:

first aniline	**Ia**	**Ib**	**IIa**	**IIb**	**IIIa**	**IIIb**	**IVa**	**IVb**
second aniline	**Ib**	**Ia**	**IIb**	**IIa**	**IIIb**	**IIIa**	**IVb**	**IVa**