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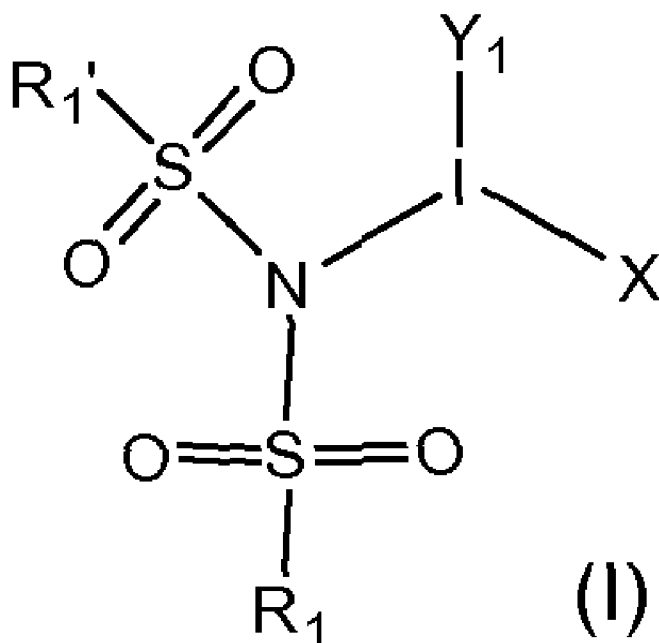
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(54) Title: NOVEL IODINE COMPOUNDS, PROCESSES FOR THEIR PREPARATION AND USE THEREOF AS AMINATION AGENTS



(57) Abstract: The iodine compounds of the present invention corresponds to those of formula (I), wherein R₁, R₁' and X have several meanings. These iodine compounds gives rise to the amination of several substrates without the need of catalysts, especially metal catalysts, and confer to the amination reaction the further advantage of being performed under mild conditions, which is of interest for industrial-scale production of nitrogenated compounds with pharmaceutical, biological or medicinal applications. Therefore, the iodine compounds of the invention are useful as amination agents. The invention also discloses several processes for the preparation of the iodine compounds of formula (I).



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Novel iodine compounds, processes for their preparation and use thereof as amination agents

- 5 The present invention relates to novel iodine compounds of formula (I), processes for their preparation and to the use thereof as amination agents.

BACKGROUND ART

- 10 Nitrogenated compounds are of major pharmaceutical, biological, and medicinal interest. As a consequence, the development of synthetic approaches to the selective incorporation of nitrogen functional groups into organic frameworks is an important endeavor.
- 15 Hypervalent iodine(III) reagents represent powerful reagents for the oxidation of organic molecules and they have been employed as attractive alternative to the more common transition metal promoted oxidations for some cases. In particular, they have been used extensively in oxygenation reactions. Moreover, the emergence of chiral derivatives has allowed for the
- 20 development of a series of efficient asymmetric oxidative transformations, including several oxygenation reactions of alkenes.

- On the contrary, the potential of iodine(III) reagents in oxidative intermolecular carbon-nitrogen bond formation remains widely unexplored. In
- 25 this regard, the aziridination of alkenes mediated by hypervalent iodine compounds for the preparation of aminated compounds has been disclosed in the state of the art (Li J. *et al.*, 2004; Richardson D. R. *et al.*, 2007).

- Generally, C-N bond forming reactions mediated by hypervalent iodine
- 30 reagents as oxidants have relied on the use of transition metal promoters. The range of reactions comprises examples such as aziridination, diamination of alkenes, and allylic amination of alkenes.

- In general, the oxidative direct transfer of nitrogen compounds to alkenes is a
- 35 versatile strategy for the construction of aminated compounds, and the synthesis of such nitrogenated compounds has been mainly developed in the state of the art through a combination of several synthetic steps. Reactions

toward the important class of aziridines have been described using iodine oxidants in combination with metal catalysts. Another process that consists of the transfer of two nitrogen groups onto the alkene is known as 1,2-diamination. This approach allows the preparation of vicinal diamines which are of great synthetic value.

Although the direct diamination of alkenes, i.e. by their direct oxidative transformation, is an especially efficient method for the synthesis of such compounds, said methods are rare and have been carried out in the presence of a metal catalyst. In fact, the direct diamination of alkenes using hypervalent iodine oxidants has been developed in an intramolecular reaction, where the two nitrogen atoms to be transferred are contained within a radical substituent connected to the alkene, in the presence of a palladium, nickel or gold catalyst (Iglesias A. *et al.*, 2009, Muñiz K. *et al.*, 2007).

Alternatively, an intermolecular diamination of unactivated terminal alkenes, which employs a palladium salt as catalyst and saccharin and bissulfonylimide, respectively, as the two different sources of nitrogen has been disclosed (Iglesias A. *et al.*, 2010).

In a different scenario, metal promoters can activate the C-H position next to an alkene giving rise to oxidative allylic amination. Related to this, a mild copper-mediated allylic amination reaction which supports the usability of copper salts as efficient activator/catalyst for amination has been disclosed in the state of the art (Smith K. *et al.*, 2005).

In the last years, there has been an increasing interest in developing mild conditions for the selective amination reactions because processes ranging from fine chemical synthesis to industrial-scale modification of chemical feedstocks would benefit from such conditions.

In spite of the efforts made in the state of the art, there is still the need of further processes which allow the direct amination of given substrates under mild conditions and in the absence of metal promoters or catalysts.

SUMMARY OF THE INVENTION

The present inventors have found novel iodine compounds which, when used in amination reactions, show an appropriate reactivity and selectivity.

5

Regarding the reactivity, the compounds of the present invention allow the direct amination of chemically unrelated substrates such as alkenes, alkynes, aryl substrates or ketones without the requirement of using a catalyst or promotor. As shown below, when an amination is carried out with an iodine
10 compound of the present invention, the reaction is performed under mild conditions and in the absence of a catalyst. This means that the absence of a metal catalyst does not adversely affect the conditions of the amination reaction where the iodine compound of the invention takes part. Therefore, the compounds of the present invention do not only show an appropriate
15 reactivity, giving rise to the amination of several substrates without the need of catalysts, especially metal catalysts, but also confer to the amination reaction the further advantage of being performed under mild conditions, which is of interest for industrial-scale production of nitrogenated compounds with pharmaceutical, biological or medicinal applications.

20

The iodine compounds of the present invention provide the advantage that they allow to achieve several amination reactions. For example, direct intermolecular diamination reactions of non-functionalized substrates, such as alkenes, are still rare and enantioselective versions constitute an unexplored
25 field. The compounds of formula (I) of the present invention solve both quests. This reactivity is, at least, in part conferred by the two N-S bonds included in the structure of the compounds of formula (I).

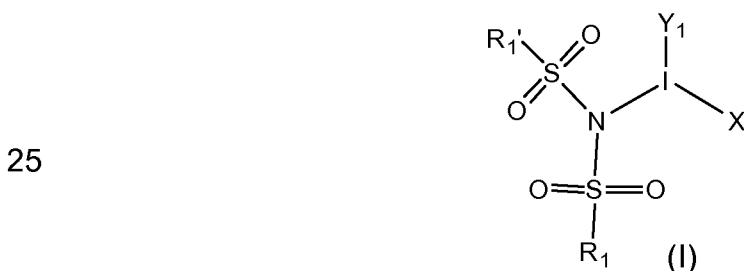
It is known in the state of the art, that the use of metals in industrial processes
30 has to be avoided because they give rise to the generation of contaminating waste and to the possible presence of metal traces in the product of the reaction. The latter is of special relevance in the pharmaceutical field.

The inventors have performed the diamination of terminal and internal
35 alkenes, which all proceed selectively when using a compound of formula (I). For the case of internal alkenes, the reaction leads to single diastereomeric products.

Furthermore, the inventors have performed the diamination of styrene derivatives and oct-1-ene using an enantiopure compound of the present invention, and the reaction occurred with enantioselectivity giving rise to the desired chiral end product. In a similar manner, diamination of (*E*)-1-phenylpropene occurs with diastereoselectivity and enantioselectivity. From these examples, therefore, it can be concluded that the compounds of formula (I) of the present invention allow the enantioselective transfer of two nitrogen atoms onto the prochiral face of an alkene employing a chiral iodine compound of formula (I).

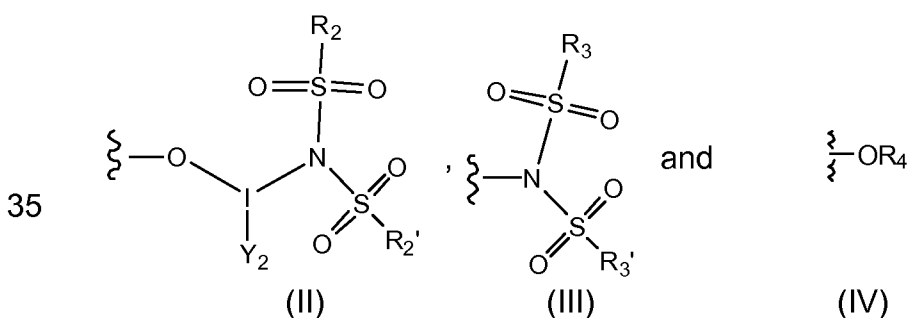
In another set of experiments, iodine compounds of formula (I) were found to convert alkenes into the corresponding allylic amines. Furthermore, they transform alkyl ketones into the corresponding alpha-aminated ketones. Also, terminal acetylenes are converted into acetylenyl amines. All these reactions again rely exclusively on the reactivity that originates from iodine compounds of formula (I), and take place without the need for an additional promotor or catalyst.

20 Thus, in a first aspect the present invention provides a iodine compound of formula (I)



wherein:

30 X is a radical selected from the group consisting of:

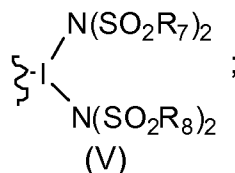


wherein

the wavy line indicates the position through which the X radical binds to the iodine atom of the compound of formula (I);

- 5 Y₁ and Y₂ are C-radicals, same or different, of one of the known ring systems with 1-4 rings, wherein each one of the rings forming said ring system has 3-20 members, each member being independently selected from C, N, O, S, CH, CH₂, and NH, is saturated, partially unsaturated or aromatic, and
- 10 is isolated, partially or totally fused; being each ring forming part of the ring system optionally substituted by at least one radical selected from the group consisting of: halogen, nitro, (C₁-C₁₂)-alkyl, (C₁-C₁₂)-alkoxy, halo(C₁-C₁₂)-alkyl, -OCH(R₅)C(O)Z, and a iodine-radical of formula (V)

15



20 wherein the wavy line indicates the position through which the radical binds to the ring; and

Z is selected from the group consisting of -OR₆ and -NR₉R₁₀; and with the proviso that when one or more of the rings forming part of the ring system is substituted by at least one iodine-radical of formula (V), then X is a radical of formula (III) or (IV);

25

or, alternatively, Y₁ and Y₂ are C-radicals, as defined above, which are bound via a bond between one of the atoms forming part of the ring system of Y₁ and one of the atoms forming part of the ring system of Y₂, thus forming a ring with the moiety -I-O-I- of the compound of formula (I), with the proviso that X is a

30 radical of formula (II);

or, alternatively, Y₁ and Y₂ are C-radicals, as defined above, which are bound via a common atom shared by the ring systems of Y₁ and Y₂, thus forming a ring with the moiety -I-O-I- of the compound of formula (I), with the proviso

35 that X is a radical of formula (II); and

R₁, R₁', R₂, R₂', R₃, R₃', R₇ and R₈ are radicals independently selected from the

group consisting of (C₁-C₁₂)-alkyl; halo(C₁-C₁₂)-alkyl; phenyl; phenyl substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and nitro; (C₁-C₃)-alkyl phenyl; (C₁-C₃)-alkylphenyl being the phenyl moiety substituted by at least a radical selected from the group consisting of (C₁-C₆)-alkyl and (C₁-C₆)-alkoxy; (C₁-C₄)-alkyl-tri-(C₁-C₄)-alkyl silane; and (C₁-C₄)-alkyl-diphenyl-(C₁-C₄)-alkylsilane;

R₄ is a radical selected from the group consisting of (C₁-C₁₂)-alkylcarbonyl; halo(C₁-C₁₂)-alkylcarbonyl; phenylcarbonyl; phenylcarbonyl, the phenyl being substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and nitro; (C₁-C₃)-alkylphenylcarbonyl; (C₁-C₃)-alkylphenylcarbonyl being the phenyl moiety substituted by at least a radical selected from the group consisting of (C₁-C₆)-alkyl and (C₁-C₆)-alkoxy; (C₁-C₁₂)-alkyl; halo(C₁-C₁₂)-alkyl; phenyl; phenyl substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and nitro; (C₁-C₃)-alkylphenyl; (C₁-C₃)-alkylphenyl, being the phenyl moiety substituted by at least a radical selected from the group consisting of (C₁-C₆)-alkyl and (C₁-C₆)-alkoxy; and a radical of formula -CH₂-CH₂-(O-CH₂-CH₂)_n-OH wherein n is an integer from 1 to 30;

R₁, R₁', R₃, R₃', R₇ and R₈ are the same or different;

R₁ and R₁' are the same as R₂ and R₂', respectively;
R₅ is selected from the group consisting of H and (C₁-C₁₂)-alkyl;

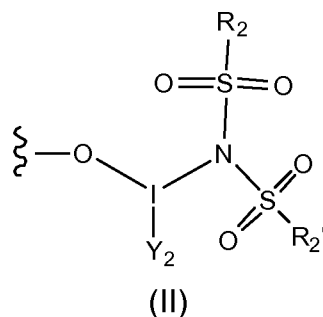
R₆ is selected from the group consisting of (C₁-C₁₂)-alkyl and (C₁-C₃)-alkylphenyl;

R₉ is selected from the group consisting of hydrogen and (C₁-C₁₂)-alkyl; and

R₁₀ is selected from the group consisting of (C₁-C₁₂)-alkyl; phenyl; phenyl substituted by at least a radical selected from the group consisting of halogen, (C₁-C₆)-alkyl, halo(C₁-C₆)-alkyl, nitro and (C₁-C₆)-alkoxy; (C₁-C₃)-alkylphenyl and (C₁-C₃)-alkylphenyl being the phenyl moiety substituted by at least a radical selected from the group consisting of (C₁-C₆)-

alkyl and (C₁-C₆)-alkoxy.

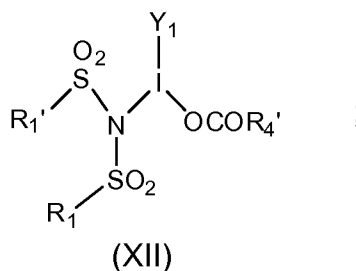
In a second aspect, the present invention provides a process for the preparation of a iodine compound of formula (I) according to the first aspect
 5 of the invention, where X is a radical of formula (II),



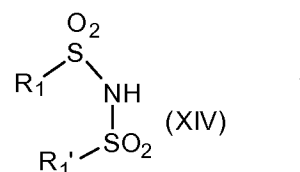
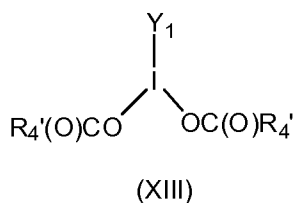
wherein

- 15 (a) when Y₁ is the same as Y₂, then the process comprises any of the steps (a.1) or (a.2):

(a.1) mixing a compound of formula (XII) with a solvent selected from the group consisting of a protic solvent, an aprotic solvent, and a mixture thereof;
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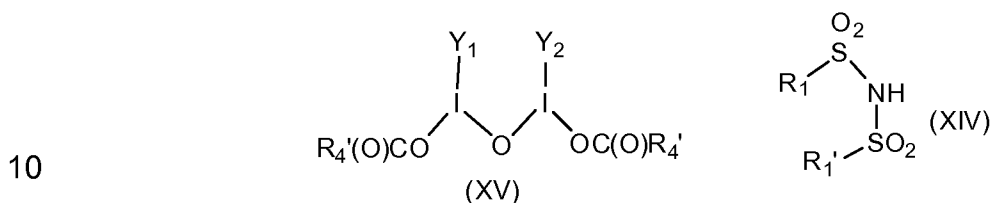


(a.2) mixing a compound of formula (XIII) with a compound of formula (XIV), and a solvent selected from the group consisting of a protic solvent, an aprotic solvent, and a mixture thereof;
 30



or, alternatively,

- b) when Y_1 and Y_2 are the same or different, then the process comprises the step of mixing a compound of formula (XV) with a compound of formula (XIV) and with a solvent selected from the group consisting of: a protic solvent, an aprotic solvent, and a mixture thereof;



wherein

- R_1 , R_1' , Y_1 and Y_2 are as defined above; and
 R_4' is a radical selected from the group consisting of (C₁-C₁₂)-alkyl; halo(C₁-C₁₂)-alkyl; phenyl; phenyl substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and nitro; (C₁-C₃)-alkylphenyl; and (C₁-C₃)-alkylphenyl, being the phenyl moiety substituted by at least a radical selected from the group consisting of (C₁-C₆)-alkyl and (C₁-C₆)-alkoxy.

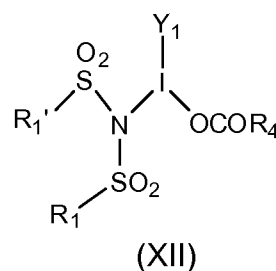
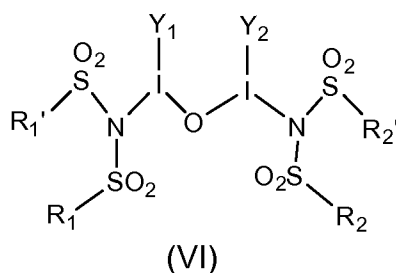
In a third aspect, the present invention provides a process for the preparation of a iodine compound of formula (I) according to the first aspect of the invention, where X is a radical of formula (III),



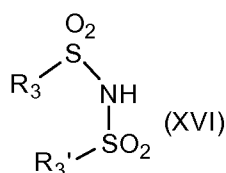
wherein

- (a) when R_1 and R_1' are the same or different than R_3 and R_3' , respectively, then the process comprises the step of mixing a compound of formula (VI) or of formula (XII), as defined below, with a compound of formula (XVI) and a solvent selected from the group consisting of a protic solvent, an aprotic solvent, and a mixture thereof;

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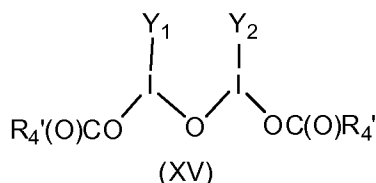
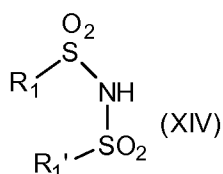
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or, alternatively,

- 15 (b) when R_1 and R_1' are the same as R_3 and R_3' , respectively, then the process comprises the step of mixing a compound of formula (XIV) with a compound of formula (XV) and a solvent selected from the group consisting of a protic solvent, an aprotic solvent, and a mixture thereof;

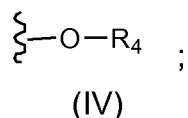
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- 25 wherein R_1 , R_1' , R_2 , R_2' , R_3 , R_3' , R_4' , Y_1 and Y_2 are as defined above.

In a fourth aspect, the present invention provides a process for the preparation of a iodine compound of formula (I) according to the first aspect of the invention, where X is a radical of formula (IV),

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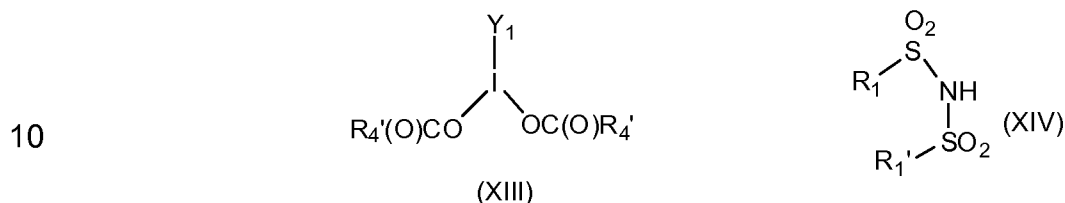
wherein

- when R_4 is a radical selected from the group consisting of (C₁-C₁₂)-alkylcarbonyl; halo(C₁-C₁₂)-alkylcarbonyl; phenylcarbonyl; phenylcarbonyl, the phenyl moiety being substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and
- 35

nitro; (C₁-C₃)-alkylphenylcarbonyl; (C₁-C₃)-alkylphenylcarbonyl being the phenyl moiety substituted by at least a radical selected from the group consisting of (C₁-C₆)-alkyl and (C₁-C₆)-alkoxy;

then, the process comprises the step of mixing a compound of formula (XIII)

- 5 with a compound of formula (XIV), and a solvent selected from the group consisting of a protic solvent, an aprotic solvent, and a mixture thereof,



wherein R₁, R₁', R₄' and Y₁ are as defined above.

- 15 In a fifth aspect, the present invention provides a process for the preparation of a iodine compound of formula (I) according to the first aspect of the invention, where X is a radical of formula (IV),



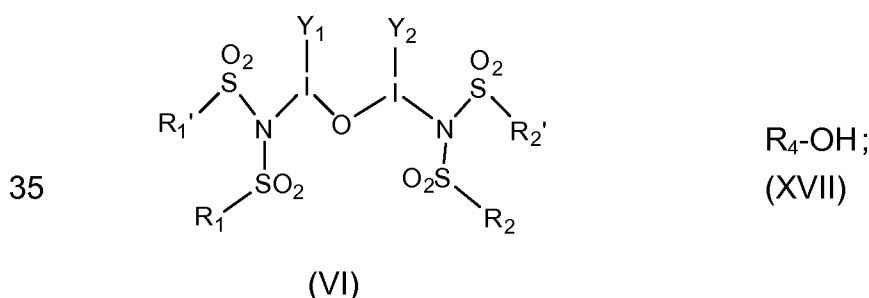
wherein

when R₄ is a radical selected from the group consisting of (C₁-C₁₂)-alkyl; halo(C₁-C₁₂)-alkyl; phenyl; phenyl substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl,

- 25 (C₁-C₆)-alkoxy, and nitro; (C₁-C₃)-alkylphenyl; (C₁-C₃)-alkylphenyl being the phenyl moiety substituted by at least a radical selected from the group consisting of (C₁-C₆)-alkyl and (C₁-C₆)-alkoxy and a radical of formula -CH₂-CH₂-(O-CH₂-CH₂)_n-OH wherein n is an integer from 1 to 30;

then, the process comprises the step of mixing a compound of formula (VI),

- 30 as defined above, with an organic alcohol of formula (XVII)



wherein in the organic alcohol of formula (XVII), said R_4 radical is selected from the group consisting of: (C₁-C₁₂)-alkyl; halo(C₁-C₁₂)-alkyl; phenyl; phenyl substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and nitro;

- 5 (C₁-C₃)-alkylphenyl; (C₁-C₃)-alkylphenyl being the phenyl moiety substituted by at least a radical selected from the group consisting of (C₁-C₆)-alkyl and (C₁-C₆)-alkoxy; and a radical of formula -CH₂-CH₂-(O-CH₂-CH₂)_n-OH wherein n is an integer from 1 to 30; and

- 10 wherein R_1 , R_1' , R_2 , R_2' , Y_1 and Y_2 are as defined above.

In a sixth aspect, the present invention provides the use of a iodine compound of formula (I), as defined in the first aspect of the invention, as amination agent.

15

In a seventh aspect, the present invention provides a process for the amination of a substrate, the process comprising the step of adding the substrate to the mixing step comprised in any of the processes defined in the second, third, fourth and fifth aspects, and wherein the substrate is selected from the group consisting of an alkene, an alkyne, an enolizable ketone compound and an allyl derivative.

20

When the amination reaction is of one-pot type, i.e., mixing the substrate of amination with the reagents responsible for the formation of the iodine compound of formula (I), the compound of formula (I) is firstly formed *in situ* and, then, it gives rise to the amination of the added substrate. Below there are enclosed several examples of one-pot alkene diaminations.

25

In an eighth aspect, the present invention provides a process for the diamination of an alkene, the process comprising the step of mixing the alkene with a iodine compound of formula (I) as defined in the first aspect of the invention, in the presence of a solvent selected from the group consisting of a protic solvent, an aprotic solvent, and a mixture thereof.

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In a ninth aspect, the present invention provides a process for the α -amination of a ketone compound, the process comprising the step of mixing the ketone compound with a iodine compound of formula (I) as defined in the

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first aspect of the invention, and with a bissulfonylimide compound, when X is a radical of formula (IV), in a solvent selected from the group consisting of a protic solvent, an aprotic solvent, and a mixture thereof.

- 5 In a tenth aspect, the present invention provides a process for the amination of an alkyne, the process comprising the step of mixing the alkyne with a iodine compound as defined in the first aspect of the invention which corresponds to a compound of formula VIII:



wherein R₁, R₁', Y₁ and R₄ are as defined above.

- 15 in the presence of a solvent selected from the group consisting of: a protic solvent, an aprotic solvent, and a mixture thereof.

- 20 In an eleventh aspect, the present invention provides a process for the amination of an aryl substrate, the process comprising the step of adding the substrate to the mixing step of any of the processes defined in the second, third, fourth and fifth aspects.

- 25 In a further aspect, the present invention provides a process for the amination of a substrate, the process comprising the step of adding the substrate to the mixing step comprised in any of the processes defined in the second, third, fourth and fifth aspects, and wherein:

- 30 the substrate is selected from the group consisting of an alkene, an alkyne, an enolizable ketone compound and an allyl derivative;
and the amination is carried out in the absence of a catalyst.

DETAILED DESCRIPTION OF THE INVENTION

- 35 As it has been stated above, in a first aspect the present invention provides iodine compounds of formula (I).

The term "known ring system" refers to a ring system which is known in the art and so intends to exclude those ring systems that are not chemically possible.

- 5 According to the present invention, a ring system formed by "isolated" rings means that the ring system is formed by two, three or four rings and said rings are bound via a bond from the atom of one ring to the atom of the other ring.

10 The term "isolated" also embraces the embodiment in which the ring system has only one ring. Illustrative non-limitative examples of known ring systems consisting of one ring are those derived from: cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclopropenyl, cyclobutenyl, cyclopentenyl, phenyl, cycloheptenyl, aziridinyl, oxirenyl, thiiranyl, azetidiny, oxetanyl, pyrrolyl, furanyl, thiophenyl, pyrazolyl, imidazolyl, triazolyl, 15 tetrazolyl, oxazolyl, isoxazolyl, thiazolyl, isothiazolyl, dithiolanyl, pyridinyl, pyranal, pyridazinyl, pyrimidinyl, pyrazinyl, piperazinyl, oxazinyl, thiazinyl, dithianyl, and dioxanyl.

20 According to the present invention, a ring system having rings "totally fused" means that the ring system is formed by two, three or four rings in which two or more atoms are common to two adjoining rings. Illustrative non-limitative examples of known ring systems consisting of two rings totally fused, are those derived from benzofuran, isobenzofuran, indole, indene, dihydroindene, naphthalene, isoindole, indolizine, indoline, isoindoline, purine (e.g., adenine, 25 guanine), benzimidazole, indazole, benzoxazole, benzisoxazole, benzodioxole, benzofurazan, benzotriazole, benzothiofuran, benzothiazole, benzothiadiaazole, heterocyclic chromene, isochromene, chroman, isochroman, benzodioxan, quinoline, isoquinoline, quinolizine, benzoxazine, benzodiazine, pyridopyridine, quinoxaline, quinazoline, cinnoline, 30 phthalazine, naphthyridine, pteridine. Illustrative non-limitative examples of known ring systems consisting of 3 fused rings are carbazole, dibenzofuran, dibenzothiophene, carboline, perimidine, pyridoindole, acridine, xanthene, thioxanthene, oxanthrene, phenoxathiin, phenazine, phenoxazine, phenothiazine, thianthrene, phenanthridine, phenanthroline, phenazine.

35 According to the present invention when the ring system is "partially fused" it means that the ring system is formed by three or four rings, being at least two

of said rings totally fused (i.e. two or more atoms being common to the two adjoining rings) and the remaining ring(s) being bound via a bond from the atom of one ring to the atom of one of the fused rings.

- 5 In one embodiment of the first aspect, the present invention provides a iodine compound wherein:

Y_1 and Y_2 are C-radicals, same or different, of one of the known ring systems with 1-4 rings, wherein each one of the rings forming said ring system

- 10 has 3-7 members, each member being independently selected from C, CH, and CH_2
is saturated, partially unsaturated or aromatic, and
is isolated, partially or totally fused; and

R_1 , R_1' , R_2 , R_2' , R_3 , R_3' , R_7 and R_8 are radicals, same or different,

- 15 independently selected from the group consisting of (C_1-C_{12}) -alkyl; halo (C_1-C_{12}) -alkyl; phenyl; phenyl substituted by at least a radical selected from the group consisting of halo (C_1-C_6) -alkyl, halogen, (C_1-C_6) -alkyl, (C_1-C_6) -alkoxy, and nitro; (C_1-C_3) -alkylphenyl; and (C_1-C_4) -alkyl-tri- (C_1-C_4) -alkyl silane; and
20 R_4 is a radical selected from the group consisting of (C_1-C_{12}) -alkylcarbonyl; halo (C_1-C_{12}) -alkylcarbonyl; phenylcarbonyl; phenylcarbonyl, being the phenyl moiety substituted by at least a radical selected from the group consisting of halo (C_1-C_6) -alkyl, halogen, (C_1-C_6) -alkyl, (C_1-C_6) -alkoxy, and nitro; (C_1-C_3) -alkylphenylcarbonyl; (C_1-C_{12}) -alkyl; halo (C_1-C_{12}) -alkyl; phenyl; phenyl
25 substituted by at least a radical selected from the group consisting of halo (C_1-C_6) -alkyl, halogen, (C_1-C_6) -alkyl, (C_1-C_6) -alkoxy, and nitro; and (C_1-C_3) -alkylphenyl.

In another embodiment of the first aspect, the present invention provides a
30 iodine compound according to the first aspect of the invention, wherein Y_1 and Y_2 are C-radicals, same or different, of one of the known ring systems with 1-2 rings, wherein each one of the rings forming said ring system

- has 5-6 members, each member being independently selected from C, CH, and CH_2 ,
35 is saturated, partially unsaturated or aromatic, and
is isolated, partially or totally fused;
being each ring forming part of the ring system optionally substituted

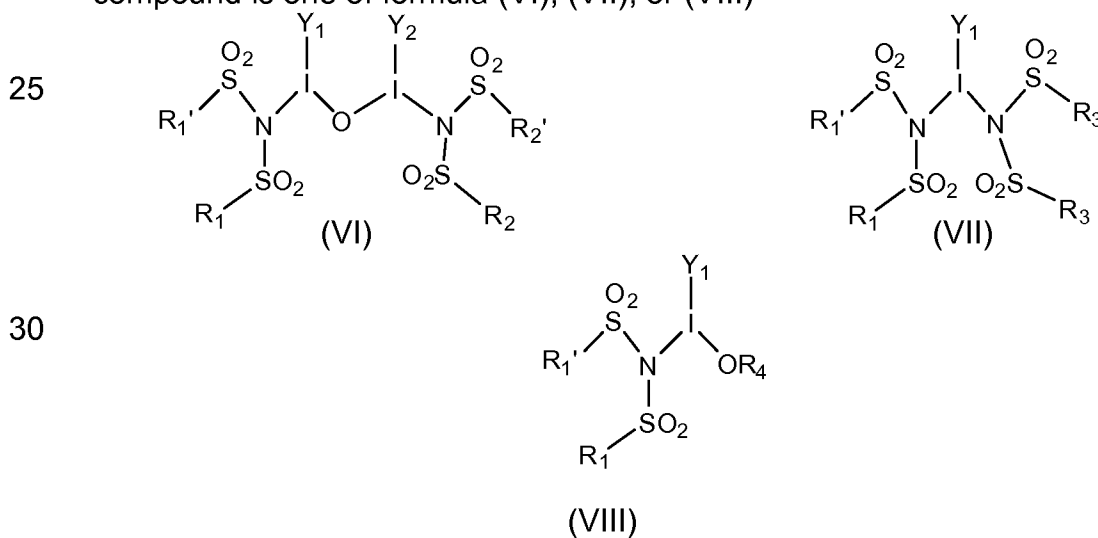
by at least one radical selected from the group consisting of: halogen, nitro, (C₁-C₁₂)-alkyl, halo(C₁-C₁₂)-alkyl, -OCH(R₅)C(O)Z, and a iodine-radical of formula (V)



wherein Z, R₅, R₇ and R₈ are as defined above.

- 10 In still another embodiment of the first aspect of the invention, R₁, R₁', R₂, R₂', R₃, R₃', R₇ and R₈ are radicals, same or different, independently selected from the group consisting of (C₁-C₁₂)-alkyl; halo(C₁-C₁₂)-alkyl; phenyl; phenyl substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and nitro; (C₁-C₃)-alkylphenyl; and (C₁-C₄)-alkyl-tri-(C₁-C₄)-alkyl silane; and
- 15 R₄ is a radical selected from the group consisting of (C₁-C₁₂)-alkylcarbonyl; halo(C₁-C₁₂)-alkylcarbonyl; phenylcarbonyl; phenylcarbonyl being the phenyl moiety substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and nitro; and (C₁-C₃)-alkylphenylcarbonyl; and (C₁-C₁₂)-alkyl.
- 20

In an another embodiment of the first aspect of the invention, the iodine compound is one of formula (VI), (VII), or (VIII)



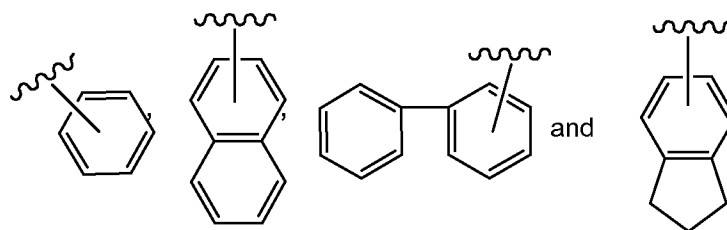
wherein R₁, R₁', R₂, R₂', R₃, R₃', R₄, Y₁ and Y₂ are as defined above.

In an embodiment of the first aspect of the invention, Y_1 and Y_2 are known ring systems comprising at least one aromatic ring.

In another embodiment of the first aspect of the invention, Y_1 and Y_2 are known ring systems consisting of one aromatic ring.

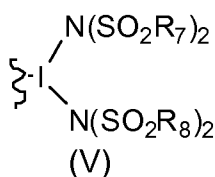
In a further embodiment of the first aspect of the invention, Y_1 and Y_2 are known ring systems selected from the group consisting of:

10



wherein the wavy line indicates the position through which the ring radical binds to the iodine atom of the compound of formula (I), said ring systems being optionally substituted by at least one radical selected from the group consisting of: methyl, $-\text{CF}_3$, nitro, $-\text{OCH}(\text{R}_5)\text{C}(\text{O})\text{Z}$, and a iodine-radical of formula (V)

20



wherein

25

Z is selected from the group consisting of $-\text{OR}_6$ and $-\text{NR}_9\text{R}_{10}$;

R_5 is selected from the group consisting of: hydrogen, methyl, ethyl, i-propyl and t-butyl;

R_6 is selected from the group consisting of: methyl, ethyl, i-propyl and t-butyl; and

30

R_7 and R_8 are methyl;

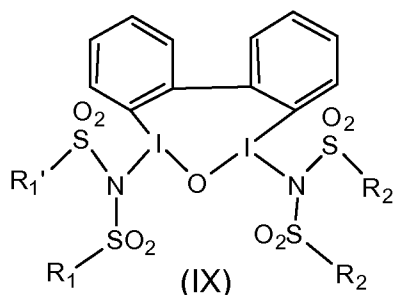
R_9 is hydrogen; and

R_{10} is 2,6-diisopropylphenyl.

In a further embodiment of the first aspect, the present invention provides the iodine compound of formula (VI) as defined above, wherein:

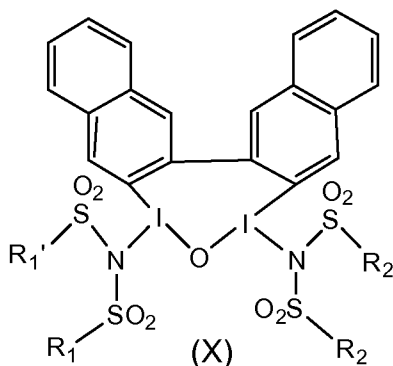
Y_1 and Y_2 are phenyl radicals and are bound via a bond from one of the

atoms forming the phenyl ring of Y_1 to one of the atoms forming the phenyl ring of Y_2 , thus forming a compound of formula (IX)



10 or,

Y_1 and Y_2 are naphthyl radicals and are bound via a bond from one of the atoms forming the naphthyl ring of Y_1 to one of the atoms forming the naphthyl ring of Y_2 , thus forming a compound of formula (X)

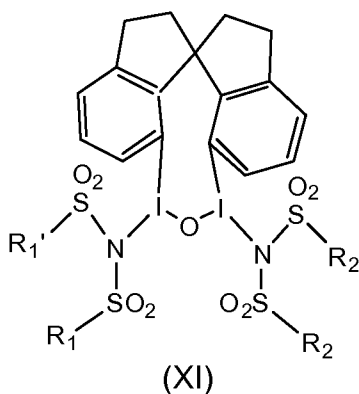


20

or

Y_1 and Y_2 are 2,3-dihydro-1*H*-indenyl radicals and are bound via a common atom shared by both ring systems, thus forming a compound of formula (XI)

25



35

wherein R_1 , R_1' , R_2 and R_2' are as defined above.

In a further embodiment of the first aspect of the invention, R_1 and R_1' are the same as R_3 and R_3' , respectively.

In a further preferred embodiment of the first aspect of the invention, R_1 , R_1' , R_2 , R_2' , R_3 , and R_3' are radicals, independently selected from the group consisting of methyl, 4-nitrophenyl, triethylsilylethyl, and 4-methylphenyl; and

5 R_4 is a radical selected from the group consisting of methylcarbonyl, trifluoromethylcarbonyl, ethylcarbonyl, isopropylcarbonyl, tert-butylcarbonyl, methyl, ethyl, isopropyl and tert-butyl.

In still another embodiment of the first aspect of the invention, the iodine

10 compound is selected from the group consisting of:

- μ -oxo-bis[bis(4-methyl-*N*-tosylbenzenesulfonamide)(phenyl)iodine(III)];
- μ -oxo-bis[bis(4-methyl-*N*-tosylbenzenesulfonamide)(4-nitro-phenyl)iodine(III)];
- 15 μ -oxo-bis[bis(4-methyl-*N*-tosylbenzenesulfonamide)(4-trifluoromethyl-phenyl)iodine(III)];
- μ -oxo-[bis(4-methyl-*N*-tosylbenzenesulfonamide)(biphenyl-2,2'-yl)-bis-iodine(III)];
- μ -oxo-bis[bis(4-methyl-*N*-tosylbenzenesulfonamide)(4-methylphenyl)iodine(III)];
- 20 μ -oxo-bis[bis(*N*-mesylmethanesulfonamide)(phenyl)iodine(III)];
- μ -oxo-bis[bis(4-methyl-*N*-mesylbenzenesulfonamide)(phenyl)iodine(III)];
- μ -oxo-bis[bis(4-nitro-*N*-mesylbenzenesulfonamide)(phenyl)iodine(III)];
- μ -oxo-bis[bis(4-methyl-*N*-tosylbenzenesulfonamide)(1,3-bis(*O*-((*R*)-2-methyl propionate))phen-2-yl]iodine(III)];
- 25 μ -oxo-bis[bis(*N*-mesylmethanesulfonamide)(1,3-bis(*O*-((*R*)-2-methyl propionate))phen-2-yl]iodine(III)];
- μ -oxo-[bis(4-methyl-*N*-tosylbenzenesulfonamide)(1,1'-binaphthyl-2,2'-yl)-bis-iodine(III)];
- 30 μ -oxo-[bis(*N*-mesylmethanesulfonamide)(1,1'-binaphthyl-2,2'-yl)-bis-iodine(III)];
- μ -oxo-[bis(*N*-mesylmethanesulfonamide)(7,7'-(2,2',3,3'-tetrahydro)1,1'-spirobi[indene])-bis-iodine(III)];
- μ -oxo-[bis(4-methyl-*N*-tosylbenzenesulfonamide)(7,7'-(2,2',3,3'-tetrahydro)1,1'-spirobi[indene])-bis-iodine(III)];
- 35 bis(4-methyl-*N*-tosylbenzenesulfonamide)iodobenzene;
- bis(*N*-mesyl-methanesulfonamide)iodobenzene;

- tetrakis(4-methyl-*N*-tosylbenzenesulfonamide)-2,2'-dioiodobiphenyl;
 acetoxy(4-methyl-*N*-tosylbenzenesulfonamide)iodo benzene;
 acetoxy(*N*-mesyl-methanesulfonamide)iodobenzene;
 acetoxy(4-methyl-*N*-tosylbenzenesulfonamide)iodo-4-methyl-benzene;
 5 acetoxy(4-methyl-*N*-mesyl-benzenesulfonamide) iodobenzene;
 acetoxy((*N*-mesylmethanesulfonamide)iodo-(2*R*,2'*R*)-dimethyl-2,2'-(1,3-phenylenebis(oxy))dipropanoate;
 acetoxy((*N*-mesylmethanesulfonamide)iodo-dimethyl-(1,3-phenylenebis(oxy))diacetate;
 10 methoxy(4-methyl-*N*-tosylbenzenesulfonamide)iodo-4-methyl-benzene;
 μ -oxo-bis[bis(4-methyl-*N*-tosylbenzenesulfonamide)(1,3-bis(*O*-((*R*)-2-(*N*,*N*-2,6-diisopropylphenyl) propanamide))phen-2-yl]iodine(III)];
 μ -oxo-bis[bis(4-methyl-*N*-tosylbenzenesulfonamide)(1,3-bis(*O*-((*R*)-2-isopropyl propionate))phen-2-yl]iodine(III)]; and
 15 μ -oxo-bis[bis(*N*-mesylmethanesulfonamide)(1,3-bis(*O*-((*R*)-2-methyl 3-methylbutanoate))phen-2-yl]iodine(III)].

In an embodiment of the first aspect, the present invention provides a iodine compound of formula (I) wherein each one of the rings, forming Y_1 and Y_2 ring
 20 systems, is isolated or, alternatively, Y_1 and Y_2 are C-radicals, as defined above, which are bound via a bond between one of the atoms forming part of the ring system of Y_1 and one of the atoms forming part of the ring system of Y_2 , thus forming a ring with the moiety -I-O-I- of the compound of formula (I), with the proviso that X is a radical of formula (II).

25 In a preferred embodiment, Y_1 and Y_2 are C-radicals, same or different, of one of the known ring systems with 1-4 rings, wherein each one of the rings forming said ring system

- 30 has 3-7 members, each member being independently selected from C, CH, and CH₂
 is saturated, partially unsaturated or aromatic, and
 is isolated; and

$R_1, R_1', R_2, R_2', R_3, R_3', R_7$ and R_8 are radicals, same or different,
 independently selected from the group consisting of (C₁-C₁₂)-alkyl; halo(C₁-
 35 C₁₂)-alkyl; phenyl; phenyl substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and nitro; (C₁-C₃)-alkylphenyl; and (C₁-C₄)-alkyl-tri-(C₁-C₄)-alkyl silane;

and

R_4 is a radical selected from the group consisting of (C₁-C₁₂)-alkylcarbonyl; halo(C₁-C₁₂)-alkylcarbonyl; phenylcarbonyl; phenylcarbonyl, being the phenyl moiety substituted by at least a radical selected from the group consisting of
 5 halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and nitro; (C₁-C₃)-alkylphenylcarbonyl; (C₁-C₁₂)-alkyl; halo(C₁-C₁₂)-alkyl; phenyl; phenyl substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and nitro; and (C₁-C₃)-alkylphenyl.

10

In a preferred embodiment of the iodine compound of the first aspect of the invention, Y_1 and Y_2 are radicals, same or different, of one of the known ring systems with 1-2 rings, wherein each one of the rings forming said ring system

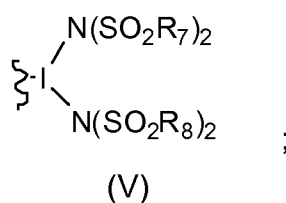
15

has 5-6 members, each member being independently selected from C, CH, and CH₂,
 is saturated, partially unsaturated or aromatic, and
 is isolated;

20

being each ring forming part of the ring system optionally substituted by at least one radical selected from the group consisting of: halogen, nitro, (C₁-C₁₂)-alkyl, halo(C₁-C₁₂)-alkyl, -OCH(R₅)C(O)Z, and a iodine-radical of formula (V)

25

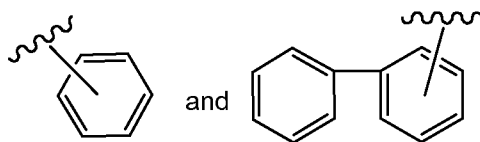


wherein Z, R₅, R₇, and R₈ are as defined above.

30

In a further embodiment of the first aspect of the invention, Y_1 and Y_2 are known ring systems selected from the group consisting of:

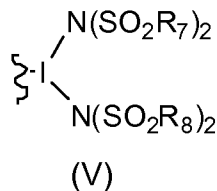
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wherein the wavy line indicates the position through which the ring radical

binds to the iodine atom of the compound of formula (I),
said ring systems being optionally substituted by at least one radical selected
from the group consisting of: methyl, $-\text{CF}_3$, nitro, $-\text{OCH}(\text{R}_5)\text{C}(\text{O})\text{Z}$, and a
iodine-radical of formula (V)

5



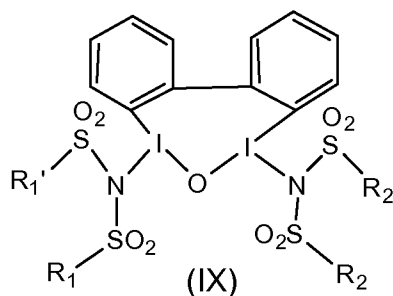
wherein

- 10 Z is selected from the group consisting of $-\text{OR}_6$;
 R_5 is selected from the group consisting of: hydrogen, methyl, ethyl, i-
 propyl and t-butyl;
 R_6 is selected from the group consisting of: methyl, ethyl, i-propyl and t-
 butyl; and
 15 R_7 and R_8 are methyl.

In a further embodiment of the first aspect, the present invention provides the
iodine compound of formula (VI) as defined above, wherein:

- 20 Y_1 and Y_2 are phenyl radicals and are bound via a bond from one of the
 atoms forming the phenyl ring of Y_1 to one of the atoms forming the phenyl
 ring of Y_2 , thus forming a compound of formula (IX)

25



- 30 wherein R_1 , R_1' , R_2 , and R_2' are as defined above.

In a still more preferred embodiment of the first aspect of the invention, the
iodine compound is selected from the group consisting of:

- 35 μ -oxo-bis[bis(4-methyl-N-tosylbenzenesulfonamide)(phenyl)iodine(III)];
 μ -oxo-bis[bis(4-methyl-N-tosylbenzenesulfonamide)(4-nitro-
 phenyl)iodine(III)];
 μ -oxo-bis[bis(4-methyl-N-tosylbenzenesulfonamide)(4-trifluoromethyl-

phenyl)iodine(III)];
 μ -oxo-[bis(4-methyl-*N*-tosylbenzenesulfonamide)(biphenyl-2,2'-yl)-bis-
 iodine(III)];
 bis(4-methyl-*N*-tosylbenzenesulfonamide)iodobenzene;
 5 bis(*N*-mesyl-methanesulfonamide)iodobenzene;
 tetrakis(4-methyl-*N*-tosylbenzenesulfonamide)-2,2'-dioiodobiphenyl;
 acetoxy(4-methyl-*N*-tosylbenzenesulfonamide)iodo benzene;
 acetoxy(*N*-mesyl-methanesulfonamide)iodobenzene;
 acetoxy(4-methyl-*N*-tosylbenzenesulfonamide)iodo-4-methyl-benzene;
 10 acetoxy((*N*-mesylmethanesulfonamide)iodo-(2*R*,2'*R*)-dimethyl-2,2'-(1,3-
 phenylenebis(oxy))dipropanoate;
 acetoxy((*N*-mesylmethanesulfonamide)iodo-dimethyl-(1,3-
 phenylenebis(oxy))diacetate; and
 methoxy(4-methyl-*N*-tosylbenzenesulfonamide)iodo-4-methyl-benzene.

15

In another embodiment of the first aspect of the invention, the compound of formula (I) is methoxy(4-methyl-*N*-tosylbenzenesulfonamide)iodobenzene.

20 In a preferred embodiment of the process of the second, third, fourth, seventh, eighth and ninth aspects of the invention, the solvent is an organic solvent, either protic or aprotic or a mixture thereof.

25 In a preferred embodiment of the process of the second, third, fourth, seventh, eighth and ninth aspects of the invention, the solvent is selected from the group consisting of: water, an aprotic solvent, and a mixture thereof.

In still a further preferred embodiment of the process of the second, third, fourth, seventh, eighth and ninth aspects of the invention, the solvent is an aprotic solvent.

30

The term "aprotic solvent" is to be understood as any solvent that lacks an acidic hydrogen. Common characteristics of aprotic solvents are: (1) they do not display hydrogen bonding, (2) and they do not have an acidic hydrogen. Illustrative non-limitative examples of aprotic solvents are chloroform,
 35 dichloromethane (DCM), tetrahydrofuran (THF), ethyl acetate, acetone, dimethylformamide (DMF), acetonitrile (MeCN), dimethyl sulfoxide, toluene, chlorobenzene, and diethyl ether, among others.

In a preferred embodiment of the processes of the second, third, fourth, seventh, eighth and ninth aspects of the invention, the aprotic solvent is an halogenated aprotic solvent.

5

In a preferred embodiment of the process of the tenth and eleventh aspects of the invention, the solvent is an aprotic solvent, more preferably an halogenated aprotic solvent.

10 The term "halogenated aprotic solvent" is to be understood as an aprotic organic solvent, molecules of which contain halogen atoms: chlorine, fluorine, bromine or iodine. Accordingly to the type of halogen, halogenated solvents are classified into the following categories: chlorinated solvents (trichlorethylene, perchlorethylene, methylene chloride, carbon tetrachloride, 15 chloroform, dichloroethane and 1,1,1-trichloroethane); fluorocarbon solvents (dichlorofluoromethane, trichlorofluoromethane, tetrafluoromethane, difluorodichloromethane, and hydrochlorofluorocarbon); brominated solvents (ethylene dibromide, methylene chlorobromide, and methyl bromine); iodinated solvents (n-butyl iodide, methyl iodide, ethyl iodide, and n- 20 propyl iodide). In a more preferred embodiment of the processes of the second, third and fourth aspects of the invention, the aprotic solvent is selected from the group consisting of: dichlorometane, chlorobenzene, chloroform, and mixtures thereof.

25 In another embodiment, the halogenated aprotic solvent is dichloroethane.

In a further preferred embodiment of the process of the second, third, fourth and fifth aspect, the reaction takes place at a temperature ranging from -30 °C to 100 °C, more preferably from 0 °C to 80 °C.

30

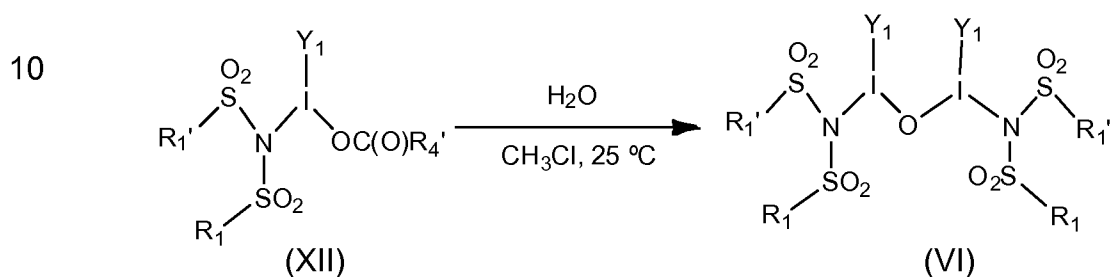
In an embodiment of the process of tenth aspect, the reaction takes place at a temperature ranging from -30 °C to 100 °C, more preferably from 20 °C to 100°C.

35 In an embodiment of the process of eleventh aspect, the reaction takes place at a temperature ranging from -30 °C to 100 °C, more preferably from 20 °C to 100 °C.

The compounds (VI)-(VIII) of the present invention can be obtained following several synthetic methods.

- 5 Particular embodiments of the process of the second aspect of the invention are summarized in schemes 1 to 3 below.

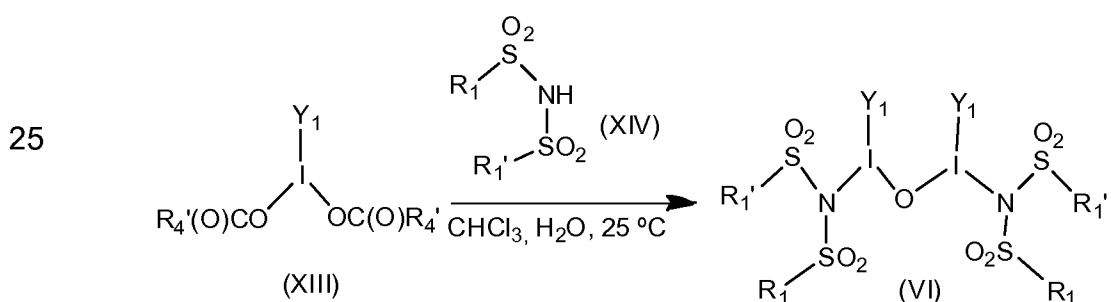
Scheme 1: when Y_1 is the same as Y_2



Briefly, to a solution of a compound of formula (XII) (1 mmol), in $CHCl_3$ (2 mL) was added H_2O (2mL). The reaction was stirred 1h at room temperature, after that time the solvents were removed under vacuum and compound (VI) was isolated.

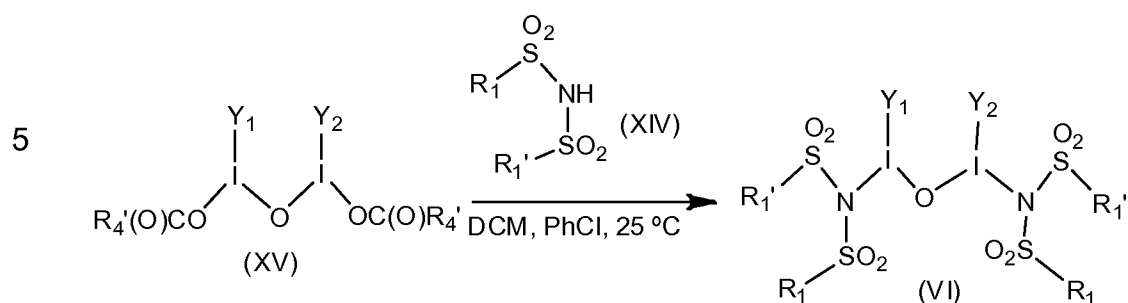
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Scheme 2: alternative process when Y_1 is the same as Y_2



- 30 Briefly, to a solution of a compound of formula (XIII) (1.0 mmol) in a mixture of $CHCl_3$ (1 mL) and H_2O (1 mL) was added the compound of formula (XIV) (1.0 mmol). The reaction was stirred over 2h at room temperature, after that time the solvents were removed under vacuum and compound (VI) was isolated.

Scheme 3: when Y₁ and Y₂ can be the same or different



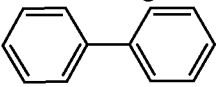
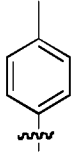
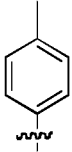
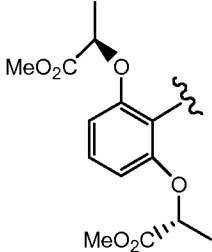
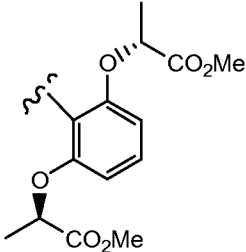
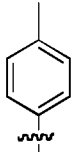
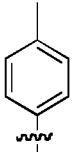
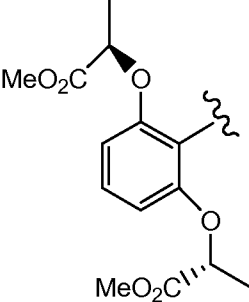
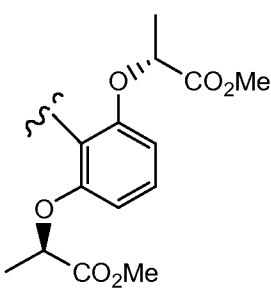
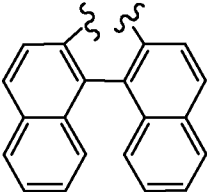
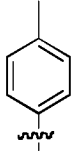
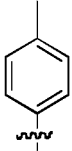
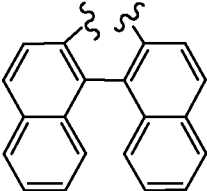
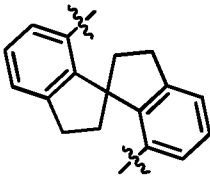
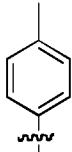
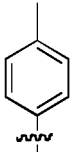
- 10 Briefly, to a solution of a compound of formula (XV) (1.0 mmol) in a mixture of dichloromethane (1 mL) was added the compound of formula (XIV) (2.0 mmol). Then, PhCl (5 mL) was added for the azeotropic distillation of formed acetic acid, and solvents and the acetic acid formed were removed under reduced pressure and compound (VI) was isolated.

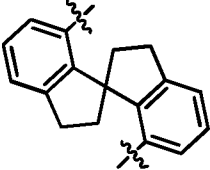
15

In this way, the compounds listed in Table 1 below were obtained:

TABLE 1

Reference Compound	Y ₁	Y ₂	R ₁ =R ₂	R ₁ '=R ₂ '
(VIa)	Ph	Ph		
(VIb)	Ph	Ph	-CH ₃	-CH ₃
(VIc)	4-nitrophenyl	4-nitrophenyl		
(VId)				
(VIe)	4-trifluoromethylphenyl	4-trifluoromethylphenyl		
(VI f)	Ph	Ph		-CH ₃

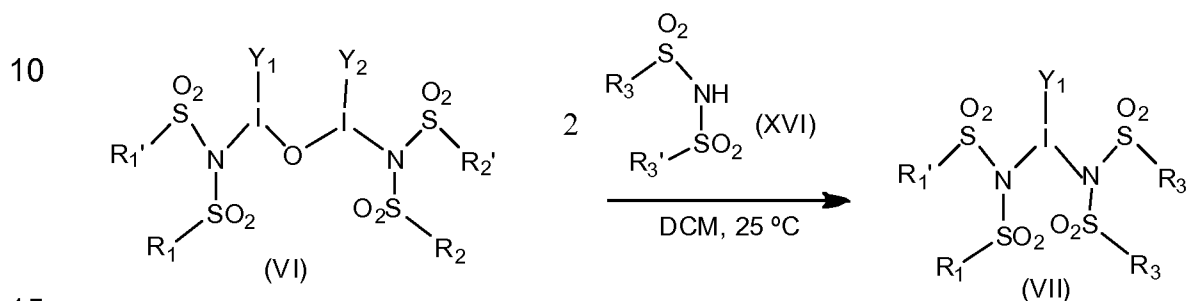
(VIg)	Ph	Ph	-PhNO ₂	-CH ₃
(VIh)	Y ₁ and Y ₂ are phenyl radicals which are bound forming: 			
(VIi)				
(VIj)			-CH ₃	-CH ₃
(VIk)	Both Y ₁ and Y ₂ are naphthalene ring systems, said systems being bound, thus forming: 			
(VII)	Both Y ₁ and Y ₂ are naphthalene ring systems, said systems being bound, thus forming: 		-CH ₃	-CH ₃
(VIIm)	Both Y ₁ and Y ₂ are 2,3-dihydro-1H-indenyl ring systems, said systems sharing one carbon atom, thus forming: 			

(VIn)	Both Y_1 and Y_2 are 2,3-dihydro-1<i>H</i>-indenyl ring systems, said systems sharing one carbon atom, thus forming: 	-CH ₃	-CH ₃
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The wavy line specifies the position through which the radical is bound to the backbone of the iodine compound of formula (I)

Particular embodiments of the process of the third aspect of the invention are summarized in schemes 4 to 6 below.

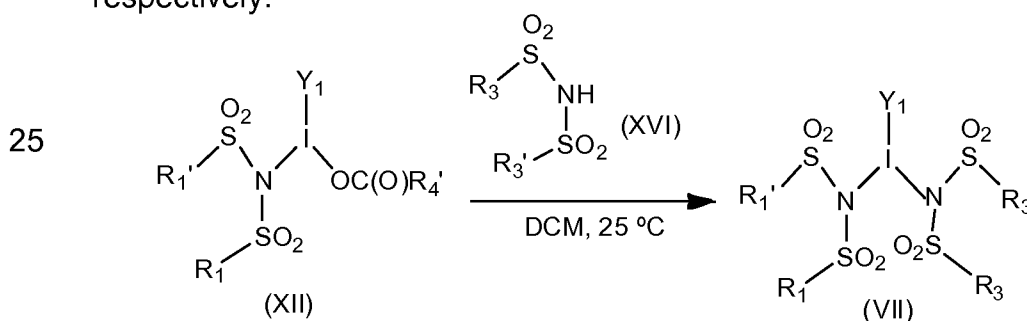
Scheme 4: R_1 and R_1' can be the same or different than R_3 and R_3' , respectively.



Briefly, to a solution of a compound of formula (VI) (1 mmol) in dichloromethane (10 mL) was added the compound of formula (XVI) (2 mmol). The reaction was stirred at room temperature 3h, the solvent was removed under reduced pressure and the compound of formula (VII) was isolated.

20

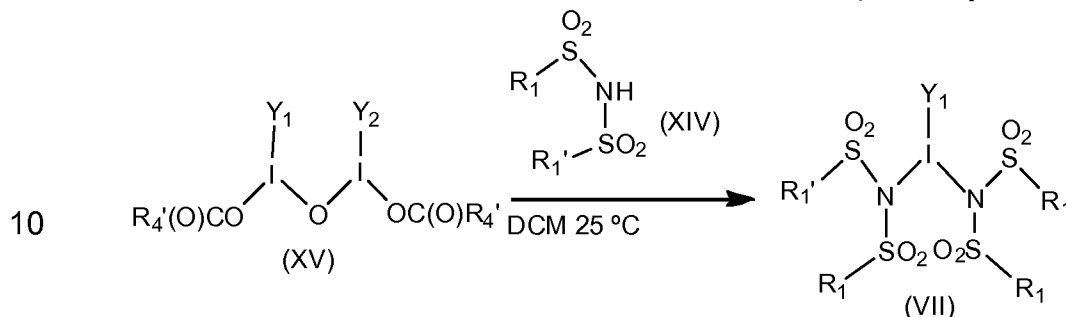
Scheme 5: R_1 and R_1' can be the same or different than R_3 and R_3' , respectively.



Briefly, to a solution of a compound of formula (XII) (1 mmol) in dichloromethane (10 mL) was added the compound of formula (XVI) (1.0

mmol) and the reaction was stirred 12h at room temperature. Chlorobenzene (5 mL) was added, the solvent was removed under reduced pressure and the compound of formula (VII) was isolated.

5 Scheme 6: R_1 and R_1' are the same as R_3 and R_3' , respectively .



Briefly, to a solution of a compound (XV) (1.0 mmol) in a mixture of DCM (1 mL) was added the compound of formula (XIV) (4.0 mmol). PhCl (5 mL) was added for the azeotropic distillation of formed AcOH, and the solvents and the acetic acid formed were removed under reduced pressure. The compound of formula (VII) was isolated.

15

In this way, the compounds listed in Table 2 below were obtained:

20

Table 2

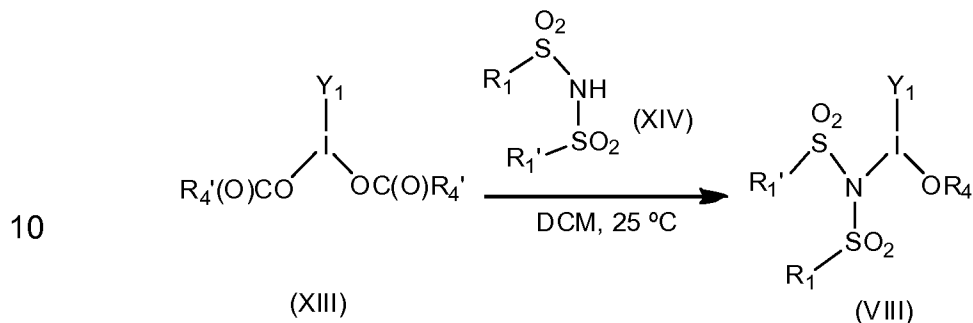
Reference compound	Y_1	$R_1 = R_3$	$R_1' = R_3'$
(VIIa)	Ph		
(VIIb)	Ph	-CH ₃	-CH ₃
(VIIc)			

The wavy line specifies the position through which the radical is bound to the backbone of the iodine compound of formula (I)

25

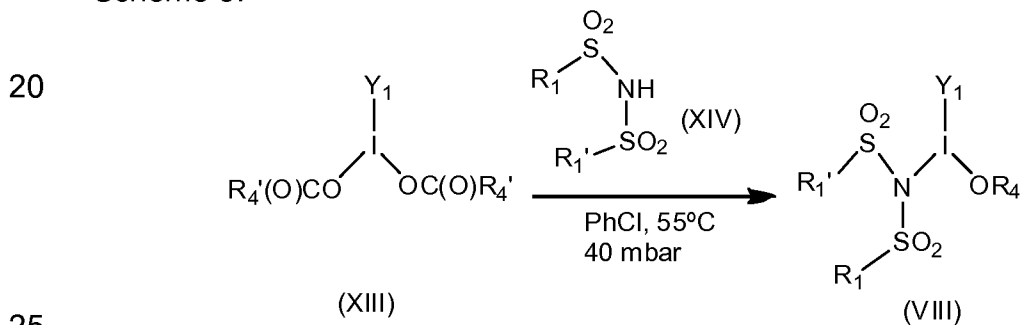
In a preferred embodiment of the process of the fourth aspect of the invention, the compounds of formula (VIII) can be obtained following the process summarized in schemes 7 and 8.

5 Scheme 7:



Briefly, to a solution of a compound of formula (XIII) (1 mmol), in DCM (10 mL), was added the compound of formula (XIV) (1 mmol). The reaction was stirred at room temperature 3h. After that time, solvent was removed under vacuum and the compound of formula (VIII) was isolated.

Scheme 8:

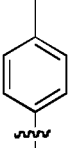
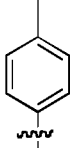
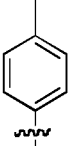
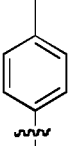
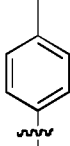
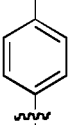
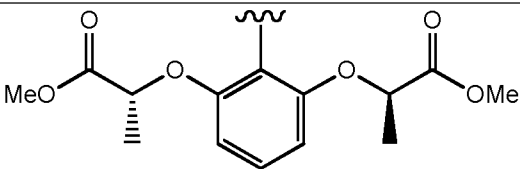
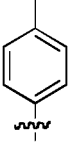
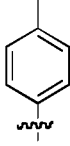
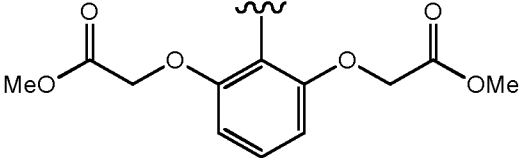


Briefly, to a solution of a compound of formula (XIII) (1 mmol) in PhCl (10 mL) was added a compound of formula (XIV) (1 mmol) and the solvent and the acetic acid formed were removed under reduced pressure. The compound of formula (VIII) was isolated.

30

In this way, the compounds listed in Table 3 below were obtained:

Table 3

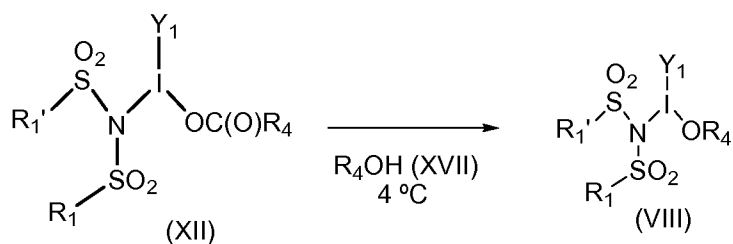
Reference compound	Y ₁	R ₁	R ₁ '	R ₄
(VIIIa)	Ph			-C(O)CH ₃
(VIIIb)	Ph	-CH ₃	-CH ₃	-C(O)CH ₃
(VIIIc)				-C(O)CH ₃
(VIId)	Ph		-CH ₃	-C(O)CH ₃
(VIIIe)				-C(O)CH ₃
(VIIIf)		-CH ₃	-CH ₃	-C(O)CH ₃

The wavy line specifies the position through which the radical is bound to the backbone of the iodine compound of formula (I)

- 5 In a preferred embodiment of the fifth aspect of the invention, the compounds of formula (VIII) can be obtained following the process summarized in Scheme 9.

Scheme 9:

10



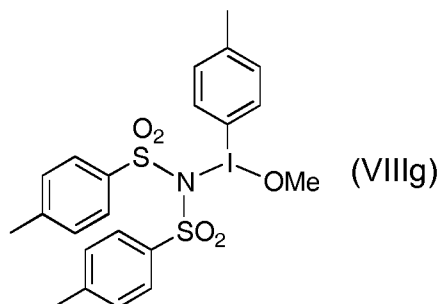
15

Briefly, the compound of formula (VIII) was obtained by crystallization at 4 °C of the compound of formula (XII), using the organic alcohol of formula R₄OH (XVII) as a crystallization solvent.

31

In this way, compound (VIIIg) was obtained.

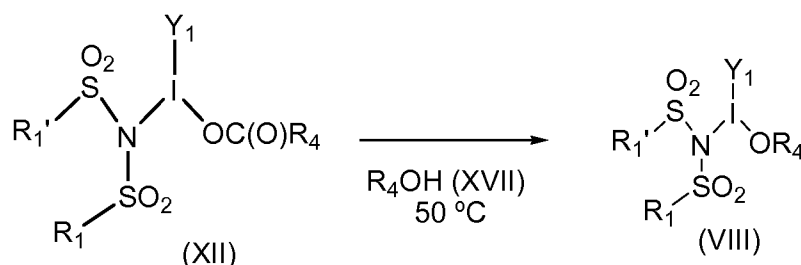
5



In another preferred embodiment of the fifth aspect of the invention, the compounds of formula (VIII) can be obtained following the process summarized in Scheme 10.

Scheme 10:

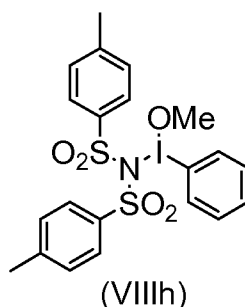
15



20

Briefly, the compound of formula (VIII) was obtained by heating a solution of a compound formula (XII) in R_4OH (XVII) at 50°C . Then the solvent was evaporated. In this way, compound (VIIIh) was obtained:

25



30

Illustrative, non-limitative examples of organic alcohols of formula (XVII) are methanol, ethanol, propanol, *iso*-propanol, butanol, *tert*-butanol, isobutanol, pentanol, *neo*-pentanol, hexanol, heptanol, octanol, phenol, *o*-toluol, 4-nitrophenol, 3-methoxyphenol, phenylmethanol, trifluoroethanol, polyethyleneglycol PEG400.

35

As it has been stated above, the iodine compounds of formula (I) of the

present invention are useful as amination agent.

In the present invention the term "amination" includes any reaction wherein a carbon-nitrogen bond is generated under oxidative conditions. This comprises
5 reactions using alkenes, alkynes and/or alkanes as carbon component, either functionalized or non-functionalized and includes oxidation of pi-bonds as well as C-H to C-N transformations. Examples of this type of transformation include diamination of alkenes (including dienes and trienes) as well as C-H
activation/amination reactions of allylic, acetylenic or aromatic positions and
10 positions alpha to a carbonyl.

In the present invention, the term "alkene" is to be understood as an unsaturated chemical compound containing at least one carbon-to-carbon double bond. Preferably, the alkene is selected from the group consisting of:
15 1,3-dienes, 1,3,5-trienes, terminal alkenes and internal alkenes.

In the present invention, the term "alkyne" is to be understood as an unsaturated chemical compound containing at least one carbon-to-carbon triple bond. Illustrative non-limitative examples of alkynes are the terminal and
20 internal alkynes.

In the present invention, the term "enolizable ketone compound" is to be understood as a ketone whose molecule has one or more alpha hydrogens.

25 In the present invention, the term "allyl compound" is to be understood as any compound including the substituent with the structural formula $\text{XYC}=\text{CH}-\text{CH}_2\text{Z}$, where X, Y and Z are the positions through which the substituent binds to the rest of the compound.

30 In the present invention, the term "bissulfonylimide compound" is to be understood as a compound of formula (XIV) or (XVI) defined above. Preferably, the bissulfonylimide compound is selected from the group consisting of: HNTs_2 , HNMs_2 , *N*-(phenylsulfonyl)benzenesulfonamide, 4-nitro-*N*-((4-nitrophenyl)sulfonyl)benzenesulfonamide, *N*-(benzylsulfonyl)-1-phenylmethanesulfonamide, 1,1,1-trifluoro-*N*-((trifluoromethyl)sulfonyl)
35 methanesulfonamide, 4-chloro-*N*-((4-chlorophenyl)sulfonyl)benzenesulfonamide, 4-methoxy-*N*-((4-methoxyphenyl)sulfonyl)benzenesulfonamide

and 2-(trimethylsilyl)-*N*-((2-(trimethylsilyl)ethyl)sulfonyl)ethanesulfonamide. Unless otherwise stated, "Ts" and "Tos" are interchangeable and means "tosyl"; Ns means "Nosyl" and "Ms" means "Mesyl".

- 5 In the present invention, the term "aryl" referred in the process of the eleventh aspect of the invention, is to be understood as a compound including a known ring system with 1-4 rings, wherein each one of the rings forming said ring system
- 10 has 3-20 members, each member being independently selected from C, N, O, S, CH, CH₂, and NH,
is saturated, partially unsaturated or aromatic, with the proviso that at least one ring is aromatic, and
is isolated, partially or totally fused;
being each ring forming part of the ring system optionally substituted by at
- 15 least one radical selected from the group consisting of: (C₁-C₁₂)-alkyl, halo (C₁-C₁₂)-alkyl, (C₁-C₁₂)-alkyloxy, (C₁-C₁₂)-alkylcarbonyl, aryloxy, (C₁-C₁₂)-alkyloxycarbonyl, (C₁-C₁₂)-alkylcarbonyloxy, (C₂-C₁₂)-tri(C₁-C₆)-alkylsilylalkynyl, aryloxycarbonyl, arylcarbonyloxy, arylcarbonyl, nitro, cyano, halogen, hydroxy, (C₁-C₁₂)-alkylaminocarbonyl, arylaminocarbonyl, (C₁-C₁₂)-
- 20 alkylamidyl, and arylamidyl. Preferably, the aryl compound is one including as known ring system one ring, more preferably a phenyl group.

- The term "aryloxy" refers to an -O-aryl radical, wherein the aryl moiety is a known ring system with 1-4 rings, wherein each one of the rings forming said
- 25 ring system
has 3-20 members, each member being independently selected from C, N, O, S, CH, CH₂, and NH,
is saturated, partially unsaturated or aromatic, and
is isolated, partially or totally fused,
- 30 being each ring forming part of the ring system optionally substituted by at least one radical selected from the group consisting of: (C₁-C₁₂)-alkyl, halo (C₁-C₁₂)-alkyl, (C₁-C₁₂)-alkyloxy, cyano, nitro, hydroxy and halogen.

- The term "aryloxycarbonyl" refers to a -C(O)-O-aryl radical, wherein the aryl moiety is is a known ring system with 1-4 rings, wherein each one of the rings forming said ring system
- 35 has 3-20 members, each member being independently selected from C,

N, O, S, CH, CH₂, and NH,
is saturated, partially unsaturated or aromatic, and
is isolated, partially or totally fused,
being each ring forming part of the ring system optionally substituted by at
5 least one radical selected from the group consisting of: (C₁-C₁₂)-alkyl, halo
(C₁-C₁₂)-alkyl, (C₁-C₁₂)-alkyloxy, cyano, nitro, hydroxy and halogen.

The term "arylcarbonyloxy" refers to an -O-C(O)-aryl radical, wherein the aryl
moiety is a known ring system with 1-4 rings, wherein each one of the rings
10 forming said ring system
has 3-20 members, each member being independently selected from C,
N, O, S, CH, CH₂, and NH,
is saturated, partially unsaturated or aromatic, and
is isolated, partially or totally fused,
15 being each ring forming part of the ring system optionally substituted by at
least one radical selected from the group consisting of: (C₁-C₁₂)-alkyl, halo
(C₁-C₁₂)-alkyl, (C₁-C₁₂)-alkyloxy, cyano, nitro, hydroxy and halogen.

The term "arylcarbonyl" refers to a -C(O)-aryl radical, wherein the aryl moiety
20 is a known ring system with 1-4 rings, wherein each one of the rings forming
said ring system
has 3-20 members, each member being independently selected from C,
N, O, S, CH, CH₂, and NH,
is saturated, partially unsaturated or aromatic, and
25 is isolated, partially or totally fused,
being each ring forming part of the ring system optionally substituted by at
least one radical selected from the group consisting of: (C₁-C₁₂)-alkyl, halo
(C₁-C₁₂)-alkyl, (C₁-C₁₂)-alkyloxy, cyano, nitro, hydroxy and halogen.

30 The term "arylamino carbonyl" refers to a -C(O)-NH₂-aryl radical, wherein the
aryl moiety is a known ring system with 1-4 rings, wherein each one of the
rings forming said ring system
has 3-20 members, each member being independently selected from C,
N, O, S, CH, CH₂, and NH,
35 is saturated, partially unsaturated or aromatic, and
is isolated, partially or totally fused,
being each ring forming part of the ring system optionally substituted by at

least one radical selected from the group consisting of: (C₁-C₁₂)-alkyl, halo (C₁-C₁₂)-alkyl, (C₁-C₁₂)-alkyloxy, cyano, nitro, hydroxy and halogen.

The term "arylamidyl" refers to a -NH-aryl radical, wherein the aryl moiety is
 5 is a known ring system with 1-4 rings, wherein each one of the rings forming said ring system

has 3-20 members, each member being independently selected from C, N, O, S, CH, CH₂, and NH,

is saturated, partially unsaturated or aromatic, and

10 is isolated, partially or totally fused,

being each ring forming part of the ring system optionally substituted by at least one radical selected from the group consisting of: (C₁-C₁₂)-alkyl, halo (C₁-C₁₂)-alkyl, (C₁-C₁₂)-alkyloxy, cyano, nitro, hydroxy and halogen.

15 In an embodiment of the process of the eleventh aspect of the invention, the ring(s) is/are optionally substituted by one or more radicals selected from (C₁-C₁₂)-alkyl, halo (C₁-C₁₂)-alkyl, (C₁-C₁₂)-alkyloxy, (C₁-C₁₂)-alkylcarbonyl, (C₅-C₇)aryloxy, (C₁-C₁₂)-alkyloxycarbonyl, (C₁-C₁₂)-alkylcarbonyloxy, (C₂-C₁₂)-tri(C₁-C₆)-alkylsilylalkynyl, (C₅-C₇)aryloxycarbonyl, (C₅-C₇)arylcarbonyloxy,
 20 (C₅-C₇)arylcarbonyl, nitro, cyano, (C₁-C₁₂)-alkylaminocarbonyl, (C₅-C₇)arylaminocarbonyl, (C₁-C₁₂)-alkylamidyl, and (C₅-C₇)arylamidyl, more preferably by one or more radicals selected from (C₂-C₁₂)-tri(C₁-C₆)-alkylsilylalkynyl and (C₅-C₇)arylamidyl.

25 In another embodiment of the process of the eleventh aspect of the invention, the aryl compound corresponds to phenyl substituted by at least one radical selected from trimethylsilylethynyl and phenylamidyl.

In another embodiment of the process of the eleventh aspect of the invention,
 30 the aryl compound corresponds to phenyl substituted by trimethylsilylethynyl and phenylamidyl radicals.

In a preferred embodiment of the process of the seventh aspect of the invention, the process comprises:

35

a) when the compound of formula (I) is one where X is a radical of formula (II), and Y₁ is the same as Y₂, then the process comprises any of the steps

(a.1) or (a.2):

5 (a.1) mixing the substrate with a compound of formula (XII), as defined above, in a solvent selected from the group consisting of: a protic solvent, an aprotic solvent and a mixture thereof,

10 (a.2) mixing the substrate with a compound of formula (XIII) with a compound of formula (XIV), as defined above, in a solvent selected from the group consisting of: a protic solvent, an aprotic solvent and a mixture thereof;

or, alternatively,

15 (b) when the compound of formula (I) is one where X is a radical of formula (II) and Y_1 and Y_2 are the same or different, then the process comprises the step of mixing the substrate with a compound of formula (XV) and a compound of formula (XIV), both as defined above, in a solvent selected from the group consisting of: a protic solvent, an aprotic solvent, and a mixture thereof;

20

or, alternatively,

25 (c) when the compound of formula (I) is one where X is a radical of formula (III), and R_1 and R_1' are the same or different than R_3 and R_3' , respectively, then the process comprises the step of mixing the substrate with a compound of formula (VI) or of formula (XII), as defined above, a compound of formula (XVI), and a solvent selected from the group consisting of: a protic solvent, an aprotic solvent, and a mixture thereof;

30 or, alternatively,

35 (d) when the compound of formula (I) is one where X is a radical of formula (III), and R_1 is the same as R_3 and R_1' is the same as R_3' , then the process comprises the step of mixing the substrate with a compound of formula (XV), a compound of formula (XIV) and a solvent selected from the group consisting of: a protic solvent, an aprotic solvent, and a mixture thereof;

or, alternatively,

(e) when the compound of formula (I) is one where X is a radical of formula (IV), being R_4 a radical selected from the group consisting of (C₁-C₁₂)-alkylcarbonyl; halo(C₁-C₁₂)-alkylcarbonyl; phenylcarbonyl; phenylcarbonyl, the phenyl moiety being substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and nitro; (C₁-C₃)-alkylphenylcarbonyl; (C₁-C₃)-alkylphenylcarbonyl being the phenyl moiety substituted by at least a radical selected from the group consisting of (C₁-C₆)-alkyl and (C₁-C₆)-alkoxy; then, the process comprises the step of mixing the substrate with a compound of formula (XIII) and a compound of formula (XIV), both as defined above, and a solvent selected from the group consisting of: a protic solvent, an aprotic solvent, and a mixture thereof;

15

or, alternatively,

(f) when the compound of formula (I) is one where X is a radical of formula (IV), being R_4 a radical selected from the group consisting of (C₁-C₁₂)-alkyl; halo(C₁-C₁₂)-alkyl; phenyl; phenyl substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and nitro; (C₁-C₃)-alkylphenyl; (C₁-C₃)-alkylphenyl being the phenyl moiety substituted by at least a radical selected from the group consisting of (C₁-C₆)-alkyl and (C₁-C₆)-alkoxy and a radical of formula -CH₂-CH₂-(O-CH₂-CH₂)_n-OH wherein n is an integer from 1 to 30; then, the process comprises the step of mixing the substrate with:

(f.1) a compound of formula (XIII), a compound of formula (XIV), an organic alcohol of formula (XVII), and a solvent selected from the group consisting of: a protic solvent, an aprotic solvent, and a mixture thereof; or, alternatively,

(f.2) a compound of formula (VI), an organic alcohol of formula (XVII), and a solvent selected from the group consisting of: a protic solvent, an aprotic solvent, and a mixture thereof;

35 wherein R_1 , R_1' , R_2 , R_2' , R_3 , R_3' , R_4' , Y_1 , and Y_2 are as defined above.

Preferably, the solvent is selected from the group consisting of: water, an

aprotic solvent, and a mixture thereof, more preferably the solvent is an aprotic solvent.

5 In a further preferred embodiment of the process of the seventh aspect of the invention:

a) when the compound of formula (I) is one where X is a radical of formula (II), as defined above, and Y_1 is the same as Y_2 , then the process comprises the step of mixing the substrate with:

10 (i) a compound of formula (XII), as defined above, in a solvent selected from the group consisting of: water, an aprotic solvent and a mixture thereof; and in a stoichiometric ratio substrate/compound (XII) of about 1/2;

15 or

(ii) a compound of formula (XIII), and a compound of formula (XIV), both compounds as defined above, in a solvent selected from the group consisting of: water, an aprotic solvent and a mixture thereof; and in a
20 stoichiometric ratio substrate/compound (XIII)/compound (XIV) of about 1/1/2;

or, alternatively,

25 (b) when the compound of formula (I) is one where X is a radical of formula (II), and Y_1 and Y_2 are the same or different, then the process comprises the step of mixing the substrate with a compound of formula (XIV), and a compound of formula (XV), both compounds as defined above, in a solvent selected from the group consisting of: water, an aprotic solvent and a mixture
30 thereof; and in a stoichiometric ratio substrate/compound (XIV)/compound (XV) of about 1/2/1;

(c) when the compound of formula (I) is one where X is a radical of formula (III), as defined above, and R_1 and R_1' are the same or different than R_3 and
35 R_3' , respectively, then the process comprises the step of mixing the substrate with:

(i) a compound of formula (VI), and a compound of formula (XVI), both as

defined above, in a solvent selected from the group consisting of: water, an aprotic solvent and a mixture thereof, and in a stoichiometric ratio substrate/compound (VI) /compound (XVI) of about 2/1/2;

5 or

(ii) a compound of formula (XII), and a compound of formula (XVI), both as defined above, in a solvent selected from the group consisting of: water, an aprotic solvent and a mixture thereof, and in a stoichiometric ratio
10 substrate/compound (XII)/compound (XVI) of about 1/1/1;

or alternatively,

(d) when the compound of formula (I) is one where X is a radical of formula
15 (III), as defined above, and R_1 and R_1' are the same as R_3 and R_3' , respectively, then the process comprises the step of mixing the substrate with a compound of formula (XV), a compound of formula (XIV), all of them as defined above, in a solvent selected from the group consisting of: water, an aprotic solvent and a mixture thereof, and in a stoichiometric ratio
20 substrate/compound of formula (XV)/compound of formula (XIV) of about 2/1/4;

or alternatively,

(e) when the compound of formula (I) is one where X is a radical of formula
25 (IV), being R_4 a radical selected from the group consisting of (C₁-C₁₂)-alkylcarbonyl; halo(C₁-C₁₂)-alkylcarbonyl; phenylcarbonyl; phenylcarbonyl, the phenyl moiety being substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and
30 nitro; (C₁-C₃)-alkylphenylcarbonyl; (C₁-C₃)-alkylphenylcarbonyl being the phenyl moiety substituted by at least a radical selected from the group consisting of (C₁-C₆)-alkyl and (C₁-C₆)-alkoxy; then the process comprises the step of mixing the substrate with a compound of formula (XIII) and a compound of formula (XIV), as defined above, in a solvent selected from the group consisting of: water, an aprotic solvent and a mixture thereof, and in a
35 stoichiometric ratio substrate/compound (XIII)/compound (XIV) of about 1/1/2;

or, alternatively,

- (f) when the compound of formula (I) is one where X is a radical of formula (IV), being R₄ a radical selected from the group consisting of (C₁-C₁₂)-alkyl; halo(C₁-C₁₂)-alkyl; phenyl; phenyl substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and nitro; (C₁-C₃)-alkylphenyl; (C₁-C₃)-alkylphenyl being the phenyl moiety substituted by at least a radical selected from the group consisting of (C₁-C₆)-alkyl and (C₁-C₆)-alkoxy and a radical of formula -CH₂-CH₂-(O-CH₂-CH₂)_n-OH wherein n is an integer from 1 to 30; then the process comprises the step of mixing the substrate with:
- i) a compound of formula (XIII), and a compound of formula (XIV), and an organic alcohol of formula (XVII), as defined above, in a solvent selected from the group consisting of: water, an aprotic solvent and a mixture thereof, and in a stoichiometric ratio substrate/compound (XIII)/compound (XIV) of about 1/1/2; or
- ii) a compound of formula (VI), and an organic alcohol of formula (XVII), as defined above, in a solvent selected from the group consisting of: water, an aprotic solvent and a mixture thereof, and in a stoichiometric ratio substrate/compound (VI) of about 1/1.

In a preferred embodiment of the seventh aspect of the invention, the process is performed at a temperature ranging from -30 °C to 100 °C.

In a preferred embodiment of the seventh aspect of the invention, the solvent is an aprotic solvent.

In a more preferred embodiment of the seventh aspect, the process for the amination of the substrate comprises the step of mixing the substrate, a compound of formula (XIII) and a compound of formula (XIV) as defined above, in an aprotic solvent, at a temperature ranging from -30 °C to 100 °C, and in a stoichiometric ratio substrate/compound (XIII)/compound (XIV) of 1/1/2.

In a preferred embodiment of the eighth aspect of the invention:

(a) when the iodine compound of formula (I) is one wherein X is a radical of formula (II) or (III) as defined above, then the diamination process comprises the step of mixing the alkene with the iodine compound as defined in the first aspect of the invention, in a stoichiometric ratio alkene/iodine compound of 1:1, in the presence of a solvent selected from the group consisting of: water, an aprotic solvent and a mixture thereof;

(b) when the iodine compound of formula (I) is one wherein X is a radical of formula (IV), then the process comprises the step of mixing the alkene, with the iodine compound of formula (I) as defined in the first aspect of the invention, and a bissulfonylimide compound, in a stoichiometric ratio alkene/iodine compound/bissulfonylimide compound of 1/1/1, and in the presence of a solvent selected from the group consisting of: water, an aprotic solvent and a mixture thereof.

In a preferred embodiment of the eighth aspect of the invention, the process is carried out at a temperature ranging from -30 °C to 100 °C, more preferably from 0 °C to 30 °C.

In a preferred embodiment of the eighth aspect of the invention, the solvent is an aprotic solvent.

In a preferred embodiment of the process of the ninth aspect of the invention:

(a) when the iodine compound of formula (I) is one wherein X is a radical of formula (II) or (III) as defined above, then the α -amination process comprises the step of mixing the ketone compound with the iodine compound (I) as defined in the first aspect of the invention, in a stoichiometric ratio ketone compound/iodine compound of 1:1, in the presence of a solvent selected from the group consisting of: water, an aprotic solvent and a mixture thereof;

or, alternatively,

(b) when the iodine compound of formula (I) is one wherein X is a radical of formula (IV), then the process comprises the step of mixing the ketone compound, with the iodine compound of formula (I), as defined in the first aspect of the invention, and the bissulfonylimide compound in a

stoichiometric ratio alkene/iodine compound/bissulfonylimide compound of 1/1/1, and in the presence of a solvent selected from the group consisting of: water, an aprotic solvent, and a mixture thereof.

- 5 In a preferred embodiment, the process of the ninth aspect of the invention is performed at a temperature ranging from -30 °C to 100 °C.

In a preferred embodiment, the process of the ninth aspect of the invention is performed in an aprotic solvent.

10

In a further embodiment, the iodine compound of formula (I) can be used in the amination of alkynes, allylic substrates and electron-deficient C-H bonds.

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In a preferred embodiment, process of the tenth and eleventh aspects of the invention, the amination of the alkyne is performed in the presence of dichloroethane at 80°C.

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Once the desired aminated product is obtained, the person skilled in the art will be able to perform the deprotection step of the bissulfonylimide groups transferred to achieve the free corresponding amine groups. Examples of deprotection steps of sulfonamide and bissulfonylimide groups are well known in the art (see for example Wuts P.G.M and Greene T.W., "Greene's Protective Groups in Organic Synthesis", John Wiley & Sons, 4th edition, 2006, p. 848-868).

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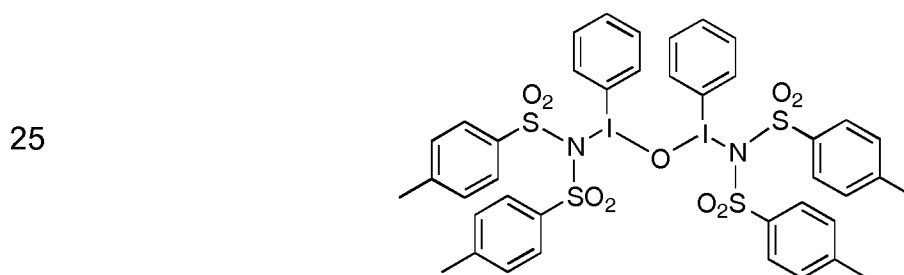
Throughout the description and claims the word "comprise" and variations of the word, are not intended to exclude other technical features, additives, components, or steps. Additional objects, advantages and features of the invention will become apparent to those skilled in the art upon examination of the description or may be learned by practice of the invention. The following examples are provided by way of illustration, and they are not intended to be limiting of the present invention. Furthermore, the present invention covers all possible combinations of particular and preferred embodiments described herein.

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EXAMPLES

Unless otherwise stated, NMR spectra were recorded on a Bruker Avance 400 Ultrashield NMR spectrometer or on a Bruker Avance 500 Ultrashield
5 NMR spectrometer using the residual solvent peak as internal standard. Column chromatography was done using silica gel by SDS (Chromagel 60 ACC, 40-60 μm mesh) following known procedures. Melting points were recorded on a Büchi B-540 apparatus. Optical rotations were determined on a Perkin-Elmer 241 MC polarimeter (Na_D 589 nm). Mass spectra were recorded
10 on a Waters LCT Premier spectrometer using ESI technique or on a Bruker Autoflex MALDI-TOF instrument. The conversion was calculated by integration of the peaks corresponding to the amination substrate on the ^1H NMR spectrum (MestreNova Version 6.1.0). The enantiomeric excesses were determined on an analytical HPLC with a chiral stationary phase, a Chiralpak
15 IB column (250x4.6 mm, 5 μm particle size) using mixtures of Hept/EtOH 80:20, Hex/EtOH 80:20 or 90:10 or Hept/THF 80:20 as mobile phases under a flow of 0.7-1 mL/min. The values were determined by area integration of the correspondent peaks using the ChromGate Client software.

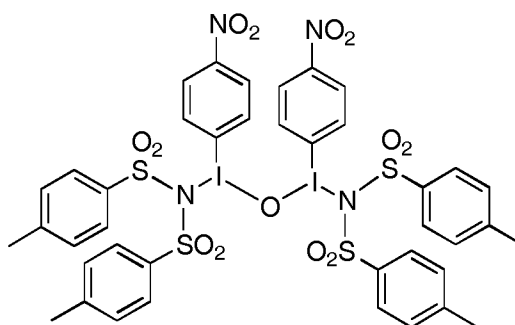
20 Example 1: Preparation of μ -oxo-bis[bis(4-methyl-*N*-tosylbenzene sulfonamide) (phenyl)iodine(III)] (VIa)



This compound was obtained following Scheme 2 above. The compounds of
30 formula (XIII) and (XIV) were, respectively, iodosobenzene diacetate and 4-methyl-*N*-tosylbenzenesulfonamide. The solvents were removed under reduced pressure and (VIa) was isolated as a yellow solid with a yield of 90%.

^1H -NMR (400MHz, d -DMSO): δ = 2.32 (s, 12H), 7.16 (d, J = 8.1 Hz, 8H), 7.1-
35 7.2 (m, 4H), 7.40 (t, J = 7.5 Hz, 2H), 7.52 (d, J = 7.5 Hz, 2H), 7.52 (d, J = 8.2 Hz, 8H), 7.74 (d, J = 7.2 Hz, 4H). IR (solid): 3062, 2922, 1594, 1470, 1441, 1367, 1308, 1141, 1079, 942, 813, 763, 739, 659, 546 cm^{-1}

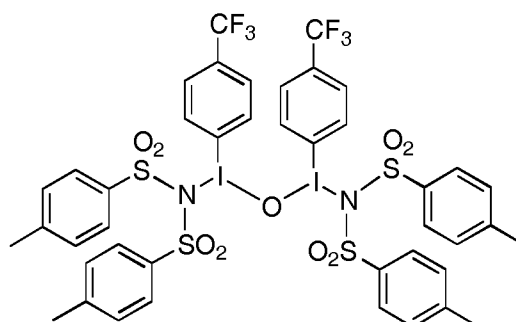
Example 2: Preparation of μ -oxo-bis[bis(4-methyl-*N*-tosylbenzene sulfonamide)(4-nitro-phenyl)iodine(III)] (VIc)



This compound was obtained following Scheme 2 above. The compounds of formula (XIII) and (XIV) were, respectively, 4-nitroiodosobenzene diacetate and 4-methyl-*N*-tosylbenzenesulfonamide. The solvents were removed under reduced pressure and (VIc) was isolated as a yellow solid with a yield of 93%.

$^1\text{H-NMR}$ (400MHz, *d*-DMSO): δ = 2.31 (s, 12H), 7.1-7.2 (m, 8H), 7.5-7.6 (m, 8H), 7.97 (d, J = 8.9 Hz, 4H), 8.06 (d, J = 8.9 Hz, 4H). IR (solid): 3095, 3048, 2924, 1595, 1398, 1335, 1316, 1142, 1081, 1065, 938, 812, 766, 660, 548, 519 cm^{-1} .

Example 3: Preparation of μ -oxo-bis[bis(4-methyl-*N*-tosylbenzenesulfonamide)(4-trifluoromethyl-phenyl)iodine(III)] (VIe)



This compound was obtained following Scheme 2 above. The compounds of formula (XIII) and (XIV) were, respectively, 4-trifluoromethyliodosobenzene diacetate and 4-methyl-*N*-tosylbenzenesulfonamide. The solvents were removed under reduced pressure and (VIe) was isolated as a yellow solid with a yield of 93%.

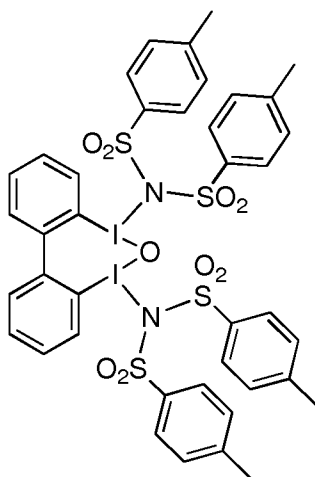
$^1\text{H-NMR}$ (400MHz, *d*-DMSO): δ = 2.31 (s, 12H), 7.15 (d, J = 8.0 Hz, 8H), 7.51 (d, J = 8.1 Hz, 8H), 8.00 (d, J = 8.3 Hz, 4H), 8.39 (d, J = 8.1 Hz, 4H). IR (solid): 3095, 3048, 2924, 1595, 1398, 1335, 1316, 1142, 1081, 1065, 938, 812, 766, 660, 548, 519 cm^{-1}

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Example 4: Preparation of μ -oxo-[bis(4-methyl-*N*-tosylbenzenesulfonamide) (biphenyl-2,2'-yl)-bis-iodine(III)] (VIh)

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This compound was obtained following Scheme 3 above. The compounds of formula (XV) and (XVI) were, respectively, μ -oxo-[bis(diacetoxy)(biphenyl-2,2'-yl)-bis-iodine(III)] and 4-methyl-*N*-tosylbenzenesulfonamide. The solvents and the acetic acid formed were removed under reduced pressure. The compound was isolated as a yellow solid in 92% yield.

25 Melting point: 152°C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 2.37 (s, 12H), 7.12 (d, J = 7.1 Hz, 8H), 7.40 (d, J = 7.1 Hz, 8H), 7.61 (m, 2H), 7.82 (dd, J = 7.6 and 1.7 Hz, 2H), 7.89 (ddd, J = 7.6 and 0.9 Hz, 2H), 8.54 (d, J = 8.1 Hz, 2H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ = 21.6, 127.4, 128.4, 129.3, 132.8, 133.2, 133.6, 136.0, 138.7, 143.4, 143.5. IR (film): 1597, 1451, 1327, 1141, 1080, 930, 817, 804, 770, 754, 730 cm^{-1} . MS (MALDI+): 745.7 (M-NTs₂).

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Example 5: Diamination of styrenes with iodine compound VIa VIe, and VIc

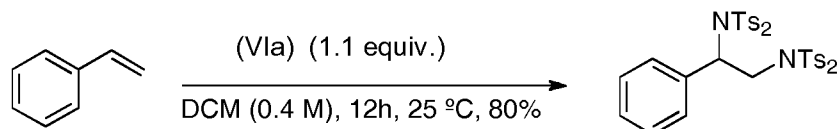
To a solution of styrene (1 mmol) and HNTs₂ or HNMs₂ (1.2 mmol) in DCM (2.6 mL) was added iodine compound VIa, VIe or VIc (1.1 mmol) and the reaction was stirred at room temperature overnight. The solvent was removed under reduced pressure and the resulting compound, N,N'-(1-phenylethane-

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1,2-diyl)bis(4-methyl-N-tosylbenzenesulfonamide), was purified to obtain the corresponding diamination product as a white solid.

A similar reactivity was observed with compounds VIe and VIc.

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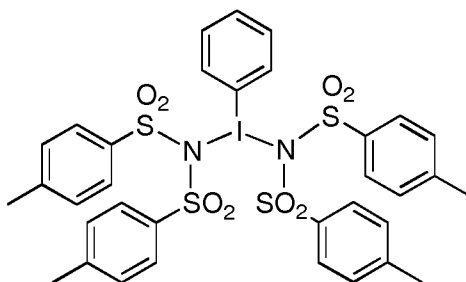


10 *Characterization of N,N'-(1-phenylethane-1,2-diyl)bis(4-methyl-N-tosylbenzenesulfonamide):*

¹H-NMR (400MHz, CDCl₃): δ = 2.41 (s, 12H), 3.74 (dd, *J* = 14.5, 3.9 Hz, 1H), 5.57 (dd, *J* = 14.3, 11.4 Hz, 1H), 6.09 (dd, *J* = 11.3, 3.8 Hz, 1H), 7.0-8.0 (bs, 8H), 7.2-7.1 (m, 7H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 4H). HRMS: 15 calcd for C₃₆H₃₆N₂O₈NaS₄: 775.1252, found 775.1262. IR (solid): 3056, 2964, 2924, 1595, 1493, 1458, 1445, 1372, 1351, 1328, 1164, 1081, 809, 759, 714 cm⁻¹.

20 Example 6: Preparation of bis(4-methyl-N-tosylbenzenesulfonamide)iodo benzene (VIIa)

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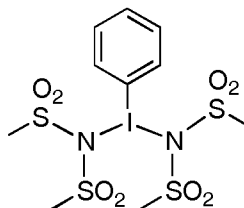


This compound was obtained following Scheme 4 above. The compounds of formula (VI) and (XVI) were, respectively, μ-oxo-bis[bis(4-methyl-N-tosylbenzenesulfonamide) (phenyl)iodine(III)] and 4-methyl-N-tosylbenzenesulfonamide. The solvent (DCM) was removed under reduced pressure. The compound was isolated as a white solid with a 97% yield.

35 ¹H-NMR (400MHz, *d*-DMSO): δ 2.32 (s, 12H), 7.16 (d, *J* = 8.0 Hz, 8H), 7.52 (d, *J* = 8.2 Hz, 8H), 7.62 (pseudo triplet, *J* = 7.6, 7.6 Hz, 2H), 7.6-7.7 (m, 1H), 8.22 (dd, *J* = 8.3 and 1.1 Hz, 2H). IR (solid): 3154, 3080, 2992, 2926, 1595, 1493, 1327, 1306, 1151, 1081, 987, 900, 809, 759, 633, 541 cm⁻¹.

Example 7: Preparation of bis(*N*-mesyl-methanesulfonamide)iodobenzene (VIIb)

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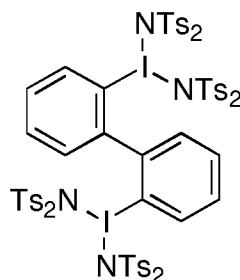


This compound was obtained following Scheme 5 above. The compounds of formula (VIII) and (XVI) were, respectively, acetoxy(*N*-mesylmethanesulfonamide)iodo benzene and *N*-mesylmethanesulfonamide. The solvent (DCM) was removed under reduced pressure. The compound was isolated as a white solid with 98% yield.

¹H-NMR (400MHz, *d*-DMSO): δ = 2.92 (s, 12H), 7.62 (dd, *J* = 7.6, 7.3 Hz, 2H), 7.71 (t, *J* = 7.3 Hz, 1H), 8.22 (d, *J* = 7.6 Hz, 2H). IR (solid): 3024, 2940, 1340, 1311, 1133, 973, 921, 901, 801, 762, 740, 725, 536, 505 cm⁻¹.

Example 8: Preparation of tetrakis(4-methyl-*N*-tosylbenzenesulfonamide)-2,2'-diodobiphenyl (VIIc)

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This compound was obtained following Scheme 6 above. The compounds of formula (XV) and (XIV) were, respectively, μ -oxo-[bis(diacetoxy)(biphenyl-2,2'-yl)-bis-iodine(III)] and 4-methyl-*N*-tosylbenzenesulfonamide. The mixture of solvents, DCM (1 mL) and PhCl (5 mL), and the acetic acid formed were removed at 55 °C under reduced pressure. The compound was isolated as a yellow solid with 98% yield.

¹H NMR (500 MHz, CDCl₃): δ = 2.39 (s, 24H), 7.19 (d, *J* = 7.9 Hz, 16H), 7.53-7.66 (m, 18H), 7.82 (dd, *J* = 7.6 and 1.6 Hz, 2H), 7.89 (ddd, *J* = 7.6 and 0.9 Hz, 2H), 8.60 (dd, *J* = 8.3 and 0.9 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 21.7, 127.7, 128.4, 129.6, 132.9, 133.2, 133.6, 136.0, 137.7, 143.4, 144.3.

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IR (film): 3093, 3067, 1597, 1367, 1332, 1161, 1146, 1083, 932, 915, 859, 812 cm^{-1} . MS (MALDI+): 1378 (M-NTs₂).

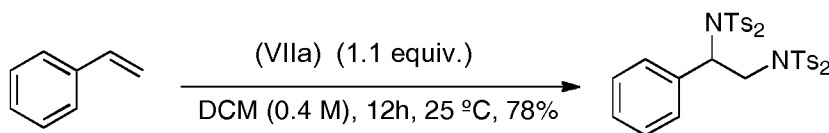
Example 9: Amination methods with the iodine compound (VIIa)

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A) Diamination of styrenes.

To a solution of styrene (1 mmol) in DCM (2.6 mL) was added the iodine compound (VIIa) (1.1 mmol) and the reaction was stirred at room temperature overnight. The DCM solvent was removed under reduced pressure and the resulting compound (N,N'-(1-phenylethane-1,2-diyl)bis(4-methyl-N-tosylbenzenesulfonamide)) was purified to obtain the corresponding diamination product as a white solid.

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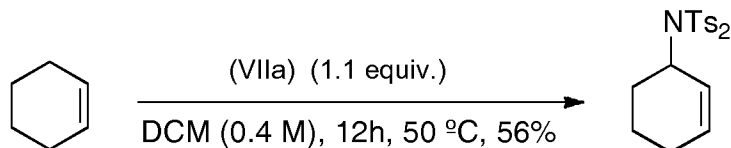


B) Conversion of alkenes into allylic amines.

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To a solution of the cyclohexene (1 mmol) in DCM (2.6 mL) was added the iodine compound (VIIa) (1.1 mmol) and the reaction was stirred at 50 °C overnight. The solvent was removed under reduced pressure and the compound was purified to obtain the corresponding amination product as a white solid.

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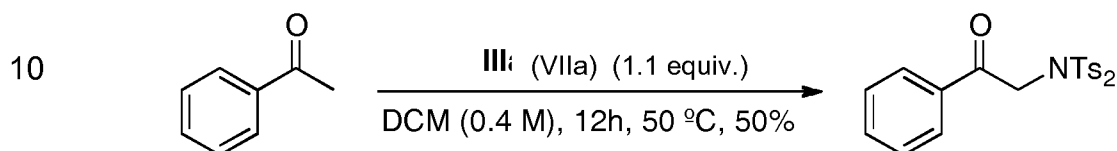


¹H-NMR (400MHz, CDCl₃): δ = 1.6-1.7 (m, 2H), 1.8-1.9 (m, 2H), 1.9-2.0 (m, 1H), 2.1-2.2 (m, 1H), 2.50 (s, 6H), 4.7-4.8 (m, 1H), 5.43 (d, J = 10.2 Hz, 1H), 5.7-5.8 (m, 1H), 7.38 (d, J = 8.0 Hz, 4H), 7.97 (d, J = 8.4 Hz, 4H). ¹³C-NMR (100MHz, CDCl₃): δ = 21.6, 22.8, 24.0, 28.4, 60.6, 127.2, 128.1, 128.3, 129.5, 137.9, 144.6.

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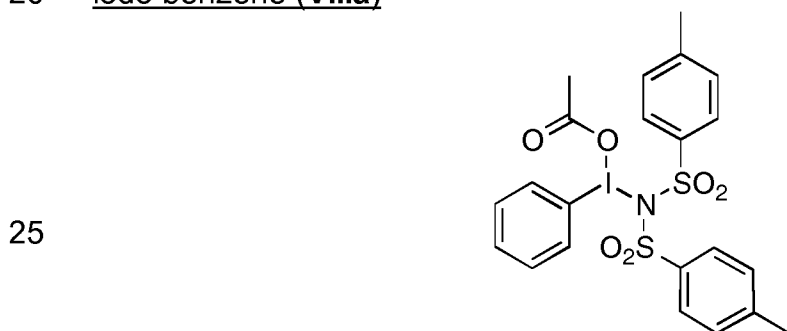
C) α -amination of ketones.

To a solution of acetophenone (1 mmol) in DCM (2.6 mL) was added the iodine compound (VIIa) (1.1 mmol) and the reaction was stirred at 50 °C overnight. The solvent was removed under reduced pressure and the compound was purified to obtain the corresponding amination product as a white solid in 50% yield.



$^1\text{H-NMR}$ (400MHz, CDCl_3): δ = 2.46 (s, 6H), 5.15 (s, 2H), 7.35 (d, J = 8.1 Hz, 4H), 7.48 (dd, J = 8.3, 7.4 Hz, 2H), 7.61 (tt, J = 7.4, 1.2 Hz, 1H), 7.88 (dd, J = 8.4 and 1.2 Hz, 2H), 7.95 (d, J = 8.3 Hz, 4H). $^{13}\text{C-NMR}$ (100MHz, CDCl_3): δ = 21.7, 53.5, 128.0, 128.8, 128.9, 129.5, 133.8, 134.5, 136.4, 145.1, 191.0.

20 Example 10: Preparation of acetoxy(4-methyl-*N*-tosylbenzenesulfonamide)
iodo benzene (VIIIa)

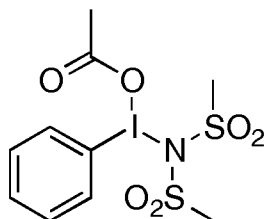


This compound was obtained following Scheme 7 above. The compounds of formula (XIII) and (XIV) were, respectively, iodosobenzene diacetate and 4-methyl-*N*-tosylbenzenesulfonamide. The solvent (DCM) was removed under reduced pressure. The compound was isolated as a white solid with 93% yield.

$^1\text{H-NMR}$ (400MHz, d -DMSO): δ = 1.91 (s, 3H), 2.31 (s, 6H), 7.14 (d, J = 7.9 Hz, 4H), 7.51 (d, J = 8.2 Hz, 4H), 7.62 (pseudo triplet, J = 7.4, 7.4 Hz, 2H), 7.71 (tt, J = 7.4, 1.1 Hz, 1H), 8.22 (dd, J = 7.3, 1.1 Hz, 2H). $^{13}\text{C-NMR}$ (100MHz, CDCl_3): δ = 20.8, 21.0, 123.4, 126.2, 128.2, 131.2, 132.5, 134.5,

139.8, 143.5, 172.0. IR (solid): 3097, 3084, 3066, 1663, 1594, 1443, 1363, 1264, 1149, 1082, 911, 814, 803, 657 cm^{-1} .

Example 11: Preparation of acetoxy(*N*-mesyl-methanesulfonamide)iodo
benzene (VIIIb)



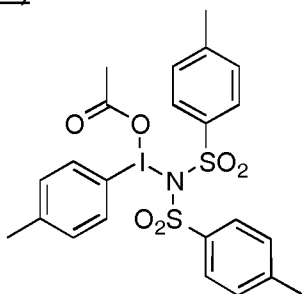
This compound was obtained following Scheme 8 above. The compounds of formula (XIII) and (XIV) were, respectively, iodosobenzene diacetate and *N*-mesylmethanesulfonamide. The compound was isolated as a white solid with 92% yield.

$^1\text{H-NMR}$ (400MHz, *d*-DMSO): δ = 1.91 (s, 3H), 2.73 (s, 3H), 2.74 (s, 3H), 7.62 (t, *J* = 7.6 Hz, 2H), 7.72 (t, *J* = 7.3 Hz, 1H), 8.22 (d, *J* = 7.4 Hz, 2H).

$^{13}\text{C-NMR}$ (100MHz, CDCl_3): δ = 21.1, 42.2, 123.5, 131.2, 132.5, 134.5, 172.0.

IR (solid): 3023, 1632, 1311, 971, 904, 804, 762, 741, 680, 537, 505 cm^{-1} .

Example 12: Preparation of acetoxy(4-methyl-*N*-tosylbenzenesulfonamide)
iodo-4-methyl-benzene (VIIIc)



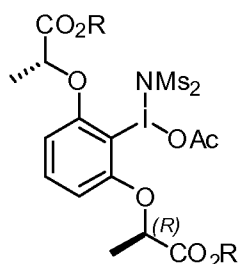
This compound was obtained following Scheme 7 above. The compounds of formula (XIII) and (XIV) were, respectively, (4-methylphenyl)-diacetoxyiodine (III) and 4-methyl-*N*-tosylbenzenesulfonamide. The solvent (DCM) was removed under reduced pressure. The compound was isolated as a white solid with 95% yield.

^1H -NMR (400MHz, *d*-DMSO): δ = 1.91 (s, 3H), 2.31 (s, 6H), 7.14 (d, J = 8.2 Hz, 4H), 7.43 (d, J = 8.1 Hz, 2H), 7.51 (d, J = 8.2 Hz, 4H), 8.11 (d, J = 8.3 Hz, 2H). IR (solid): 3055, 2923, 1649, 1596, 1340, 1305, 1266, 1119, 1001, 913, 802, 771, 657, 545 cm^{-1} .

5

Example 13: Preparation of acetoxy((*N*-mesylmethanesulfonamide) iodo-(2*R*,2'*R*)-dimethyl-2,2'-(1,3-phenylenebis(oxy))dipropanoate (VIIIe)

10

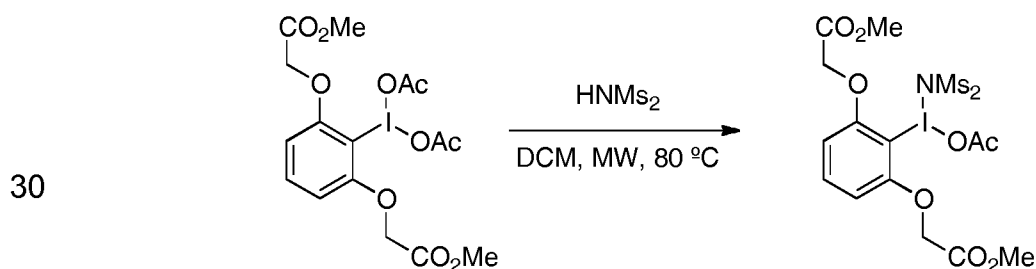


15 This compound was obtained following Scheme 8 above. The compounds of formula (XIII) and (XIV) were, respectively, diacetoxy(iodo-(2*R*,2'*R*)-dimethyl-2,2'-(1,3-phenylenebis(oxy))dipropanoate and *N*-mesylmethanesulfonamide. The compound was isolated as a white solid with 10% yield.

20 ^1H NMR (400 MHz, CDCl_3): δ = 1.60-1.90 (bs, 6H), 1.90-2.15 (bs, 3H), 2.99 (s, 6H), 3.63-3.96 (bs, 6H), 4.75-5.07 (bs, 2H), 6.51 (d, J = 8.3 Hz, 2H), 7.43 (t, J = 8.4 Hz, 1H).

Example 14: Preparation of acetoxy((*N*-mesylmethanesulfonamide)iodo-dimethyl-(1,3-phenylenebis(oxy))diacetate (VIIIf)

25



30

The bisacetate iodine derivative (1 mmol) was dissolved in DCM (2mL), HNMs₂ (1mmol) was added and the reaction was stirred at 80 °C for 15 minutes under microwave irradiation. The solvent was removed and the compound was isolated as a white solid in 90 % yield.

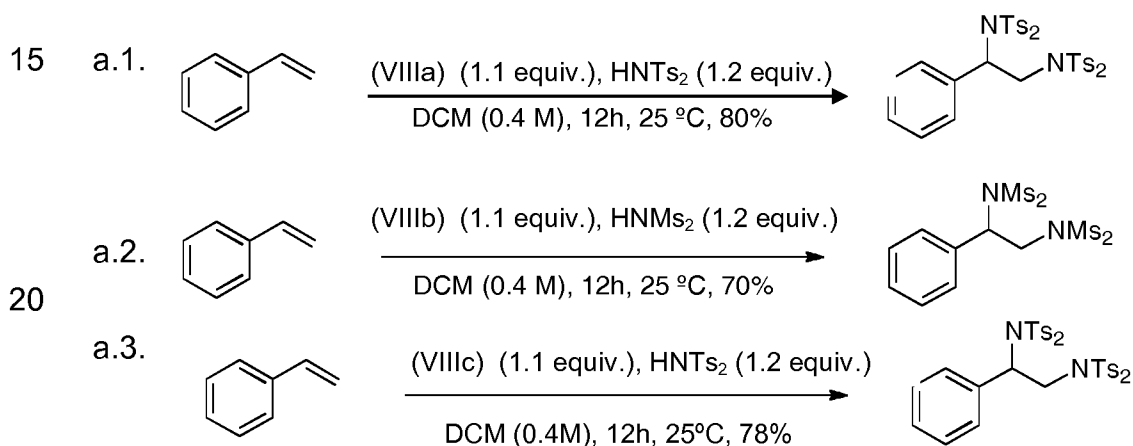
35

$^1\text{H-NMR}$ (400MHz, CDCl_3): δ = 2.08 (s, 3H), 3.10 (s, 6H), 3.82 (s, 6H), 4.90 (s, 4H), 6.66 (d, J = 8.4 Hz, 2H), 7.49 (t, J = 8.4 Hz, 1H).

Example 15: Amination methods with iodine compounds (VIIIa), (VIIIb) and (VIIIc)

A) Diamination of styrenes.

To a solution of styrene (1 mmol) and HNTs_2 or HNMs_2 (1.2 mmol) in DCM (2.6 mL) was added the iodine compound VIIIa, VIIIb or VIIIc (1.1 mmol) and the reaction was stirred at room temperature overnight. The solvent was removed under reduced pressure and the compound was purified to obtain the corresponding diamination product as a white solid.



25 Characterization of *N,N'*-(1-phenylethane-1,2-diyl)bis(*N*-(methanesulfonyl) methanesulfonamide)

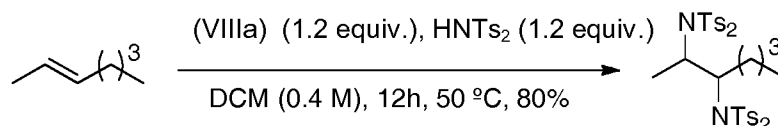
$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 2.2-3.0 (bs, 3H), 3.0-3.8 (bs, 3H), 3.24 (s, 6H), 4.57 (dd, J = 15.3, 6.8 Hz, 1H), 4.79 (dd, J = 15.3, 5.3 Hz, 1H), 5.90 (dd, J = 6.8, 5.3 Hz, 1H), 7.4-7.5 (m, 3H), 7.62 (d, J = 6.5 Hz, 2H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ = 43.2, 44.5 (bs), 50.7, 63.4, 129.1, 129.8, 130.2, 133.8. HRMS: calcd for $\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}_8\text{NaS}_4$: 471.0000, found 471.0019.

B) Diamination of internal alkenes and 1,3-dienes.

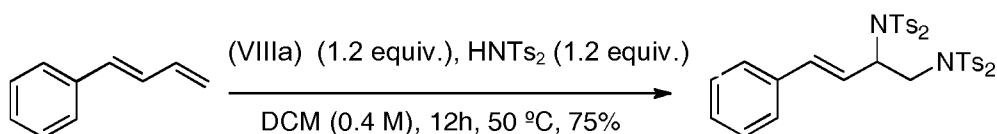
To a solution of alkene (1 mmol) and HNTs_2 or HNMs_2 (1.2 mmol) in DCM (2.6 mL) was added the iodine compound (VIIIa) or (VIIIb) (1.2 mmol) and the

reaction was stirred at 50 °C overnight. The solvent was removed under reduced pressure and the compound was purified to obtain the corresponding diamination product as a white solid.

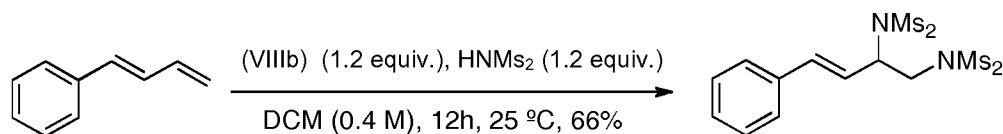
5 b.1.



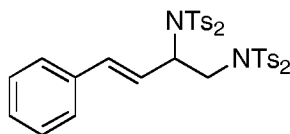
10 b.2.



15 b.3.

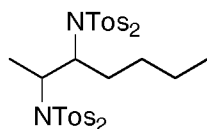


Characterization data of



20 ¹H-NMR (400 MHz, CDCl₃): δ = 2.37 (s, 6H), 2.39 (s, 6H), 3.66 (dd, *J* = 14.7, 4.0 Hz, 1H), 4.97 (dd, *J* = 14.7, 11.4 Hz, 1H), 5.21 (ddd, *J* = 11.1, 9.3, 4.0 Hz, 1H), 5.69 (d, *J* = 16.0 Hz, 1H), 6.52 (dd, *J* = 16.0, 9.0 Hz, 1H), 7.1-7.4 (m, 13H), 7.8-7.9 (m, 8H). ¹³C-NMR (100 MHz, CDCl₃): δ = 21.7, 21.8, 50.3, 62.5, 123.3, 126.9, 128.4, 128.5, 128.6, 128.7, 128.8, 129.6, 135.8, 136.2, 138.1, 145.1. HRMS (ESI-MS): calculated for C₃₈H₃₈N₂O₈NaS₄: 801.1409; found: 801.1392.

Characterization data of



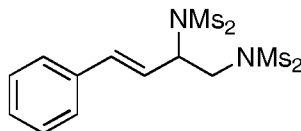
30

¹H NMR (500 MHz, CDCl₃): δ = 0.63 (t, *J* = 7.2 Hz, 3H), 0.75 (d, *J* = 7.0 Hz, 3H), 0.8-1.0 (m, 4H), 1.6-1.8 (m, 2H), 2.41 (s, 3H), 2.42 (s, 3H), 2.46 (s, 6H), 4.85 (dq, *J* = 7.0, 10.3 Hz, 1H), 5.0-5.1 (m, 1H), 7.3-7.4 (m, 8H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H), 8.03 (d, *J* = 8.4 Hz, 2H), 8.05 (d, *J* = 8.4 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃): δ = 13.9, 16.9, 21.6, 21.7, 21.8, 22.6, 28.6, 29.9, 62.5, 65.4, 128.7, 128.9, 129.2, 129.3, 129.4, 129.5, 129.7, 129.8, 135.7,

136.3, 138.3, 138.7, 144.8, 144.9, 145.2, 145.4. IR: 3031, 2955, 2928, 2873, 1741, 1596, 1493, 1465, 1366, 1308, 1292, 1248, 1187, 1159, 1122, 1082, 1046, 1018, 1003, 977, 953, 933, 859, 814, 754, 708, 689, 658, 623, 547, 480. HRMS: calcd for $C_{35}H_{42}N_2O_8S_4Na$: 769.1722, found: 769.1706.

5

Characterization data of



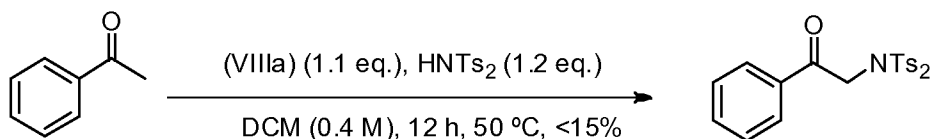
m.p. 112-114 °C.

- 10 1H -NMR (400 MHz, $CDCl_3$): δ = 3.34 (s, 6H), 3.37 (s, 6H), 4.31 (d, J = 6.1 Hz, 2H), 5.29 (dt, J = 9.0, 6.1 Hz, 1H), 6.58 (dd, J = 15.9, 9.0 Hz, 1H), 6.88 (d, J = 15.9 Hz, 1H), 7.25-7.45 (m, 3H), 7.40-7.50 (m, 2H). ^{13}C -NMR (100 MHz, $CDCl_3$): δ = 43.3, 51.6, 64.2, 123.1, 127.1, 129.1, 129.3, 135.0, 138.6. FTIR: $\nu_{max}(cm^{-1})$ = 3043, 3022, 2921, 2850, 1413, 1342, 1320, 1158, 1103, 1063, 1017, 989, 964, 911, 897, 850, 794, 781, 754, 709, 689, 536. HRMS: calcd for $C_{14}H_{22}N_2O_8NaS_4$: 497.0157, found 497.0139.
- 15

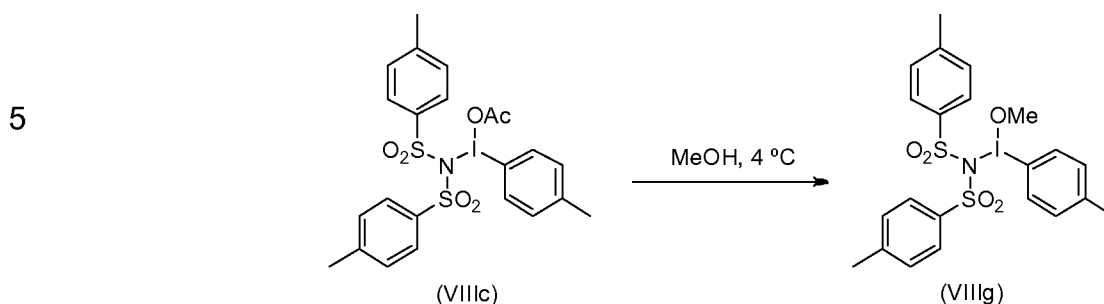
C) α -amination of ketones.

- 20 To a solution of acetophenone (1 mmol) and HNTs₂ (1.2 mmol) in DCM (2.6 mL) was added iodine compound VIIIa (1.1 mmol) and the reaction was stirred at 50 °C overnight. The solvent was removed under reduced pressure and the compound was purified to obtain the corresponding amination product as a white solid.

25



Example 16: Preparation of methoxy(4-methyl-*N*-tosylbenzenesulfonamide) iodo-4-methyl-benzene (VIIIg)

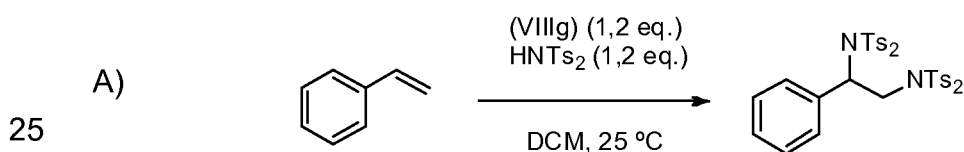


- 10 This compound was obtained following scheme 9 above by crystallization of compound (VIIIc) in methanol at 4 °C, which afforded the isolation of (VIIIg) in 34% yield.

¹H NMR (400 MHz, CDCl₃): δ = 2.32 (s, 6H), 2.42 (s, 3H), 3.17 (s, 3H), 7.16 (d, *J* = 8.0 Hz, 4H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 4H), 8.11 (d, *J* = 8.2 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 20.9, 21.1, 48.6, 126.2, 128.3, 131.5, 131.7, 134.8, 136.9, 139.9, 143.1. IR: 3026, 2957, 2921, 1597, 1482, 1447, 1399, 1317, 1283, 1138, 1079, 960, 805, 771, 664, 547, 506, 483.

20

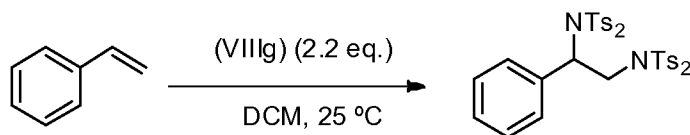
Example 17: Amination methods with iodine compound (VIIIg)



- To a solution of iodine compound (VIIIg) (0.069 g, 0.12 mmol) in DCM (0.50 mL) was added subsequently HNTs₂ (0.039 g, 0.12 mmol) and styrene (0.011 mL, 0.10 mmol) and the reaction was stirred overnight at 25 °C. Solvent was removed under vacuum and the residue was dissolved in MeOH. The insoluble solid was filtered and washed with MeOH to obtain 46 mg (61% yield) of a white solid identified as the desired diaminated product.
- 30

56

B)

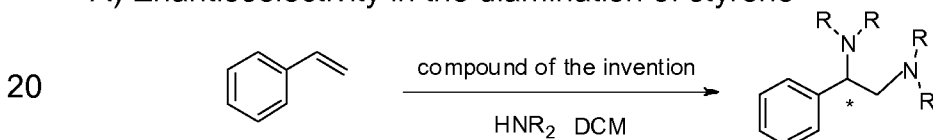


- 5 To a solution of hypervalent iodine (VIIIlg) (0.10 g, 0.18 mmol) in DCM (1.0 mL) was added styrene (0.090 mL, 0.080 mmol) and the reaction was stirred overnight at 25 °C. Then solvent was removed and the residue was dissolved in MeOH. The insoluble solid was filtered and washed with MeOH to obtain
10 30 mg (50% yield) of a white solid identified as the desired diaminated product.

Example 18: Enantioselective diamination in one-pot reactions

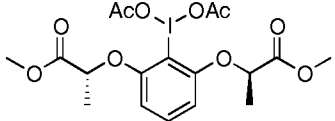
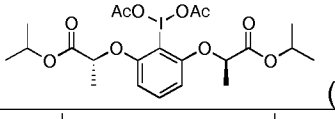
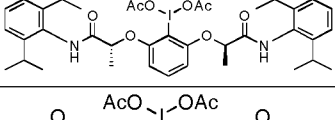
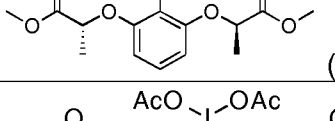
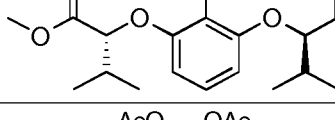
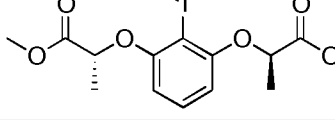
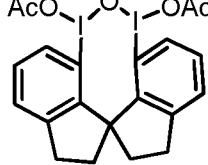
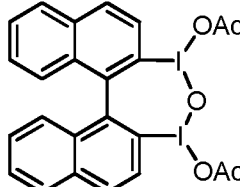
- Several diamination reactions were performed in order to determine whether
15 the iodine compound of formula (I) of the present invention confers selectivity to the amination reaction:

A) Enantioselectivity in the diamination of styrene



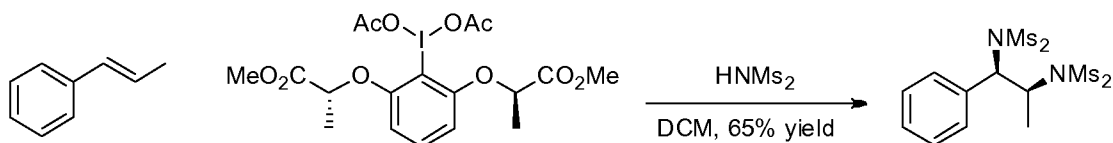
- To a solution of alkene (1 mmol) and HNTs₂ or HNMs₂ (2.4 mmol) in DCM (2.6 mL) was added the compound of formula (XIII) (1.2 mmol) and the reaction was stirred overnight at the indicated temperature. The reaction was
25 quenched by addition of a saturated aqueous solution of Na₂S₂O₃. Aqueous phase was extracted with DCM (3x), dried with anhydrous sodium sulfate, filtered and solvent was removed under reduced pressure. The crude was purified to obtain the corresponding diamination product as a white solid. ees were determined by chromatographic methods (chiral HPLC).
- 30 The results are summarized in Table 4:

Table 4

Iodine compound (XIII) (equiv.)	HNR ₂ (equiv.)	T (°C)	yield (%)	ee (%)
 (1.2)	HNTs ₂ (2.4)	25	53	50
 (1.2)	HNTs ₂ (2.4)	25	43	58
 (1.2)	HNTs ₂ (2.4)	25	21	24
 (1.2)	HNMs ₂ (2.4)	25	50	73
 (1.2)	HNMs ₂ (2.4)	0	30	84
 (1.5)	HNMs ₂ (2.4)	0	82	85
 (1.2)	HNTs ₂ (2.4)	25	55	32
 (1.2)	HNTs ₂ (2.4)	25	30	14

ee: enantiomeric excess

Following a similar procedure, *trans*- β -methylstyrene was diaminated
 5 successfully in 65% yield and 90% ee (99% ee after recrystallization in
 DCM/MeOH).



Example 19: Diamination reactions of one-pot type

A) Examples of styrene diamination:

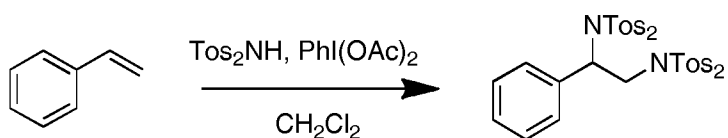
5

General procedure 1: To a solution of the alkene (0.5 mmol) and compound of formula (XIV) (1.2 mmol) in dichloromethane (1.3 mL) was added the compound of formula (XIII) (0.6 mmol) and the reaction was stirred at room temperature over the course of 15 h. After that, the solvent was removed by evaporation and the crude reaction product was taken up in MeOH and stirred over 5 min.

15

Following the general procedure 1 wherein the alkene is styrene, the compound of formula (XIII) is iodosobenzenediacetate and the compound of formula (XIV) is bis-*p*-toluenesulfonylimide, an insoluble white solid was obtained, which was filtered and washed with MeOH to give *N,N'*-(1-phenylethane-1,2-diyl)bis(4-methyl-*N*-tosylbenzenesulfonamide) as analytically pure material (80% yield).

20



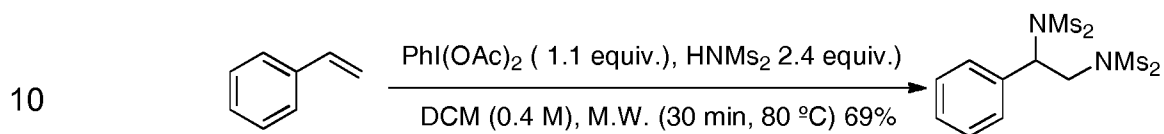
25

The diamination reaction was carried out in different solvents, observing that appropriate yields were achieved.

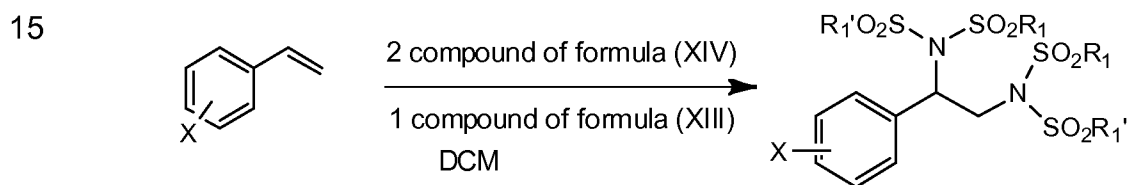
Table 5

solvent	T (°C)	t (h)	yield (%)
DCM	25	15	80
Dioxane	25	15	24
CHCl ₃	25	15	27
Et ₂ O	25	15	24
EtOAc	25	96	68
H ₂ O	25	15	>10

Alternatively, to a suspension of $\text{PhI}(\text{OAc})_2$ (1.2 mmol) in DCM (2 mL), HNMs_2 (2.4 mmol), styrene (0.5 mmol) was added. The reaction mixture was stirred under microwave irradiation (80 °C) for 30 min. The solvent was removed under reduced pressure and the residue was purified by column chromatography.



A.1. Substituted Styrenes: a) Ring Substitution



20 Following the general procedure 1 and using the corresponding styrene derivative as the alkene, iodosobenzenediacetate as the compound of formula (XIII) and the corresponding compound of formula (XIV) as the compound of formula (XIV), at the indicated temperature, the results of Table 6 were achieved.

25

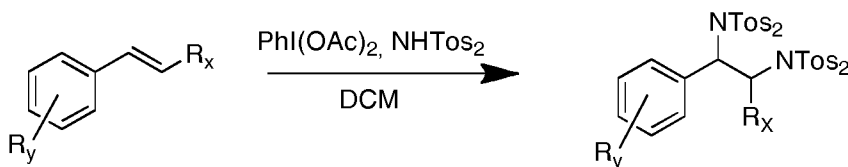
Table 6

X	T (°C)	t (h)	R ₁ , R ₁ '	yield (%)
H	25	12	Ts, Ts	80
3-OPh	50	18	Ts, Ts	81

3-OMe	50	15	Ts, Ts	77
3-NO ₂	50	96	Ts, Ts	77
4-F	25	18	Ts, Ts	66
4-Cl	25	18	Ts, Ts	69
4-Br	25	18	Ts, Ts	80
4-CF ₃	25	18	Ts, Ts	79
4-NO ₂	50	96	Ts, Ts	70
H	25	18	Ms, Ms	49
H	25	18	Ms, Ts	20
H	25	18	Ms, Ns	20

The reaction of styrene was also scaled up to 10 mmol of starting material with no change in isolated yield of the diamination product.

5 A.2. Substituted Styrenes: b) Alkene Substitution



- 10 Following the general procedure 1 and using the corresponding styrene derivative as the alkene, iodosobenzenediacetate as the compound of formula (XIII) and di-*p*-toluenesulfonylamine as the compound of formula (XIV), the results of Table 7 were achieved.

15

Table 7

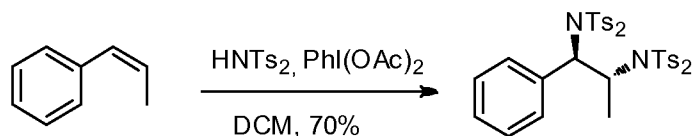
R _y	R _x	T (°C)	t (h)	Yield (%)
H	Ph	50	60	56
H	Me	25	18	70
4-Cl		50	18	67

A.3 Diamination of *cis*-β-methylstyrene

- 20 To a solution of *cis*-β-methylstyrene (1 mmol) and di-*p*-toluenesulfonamide (6.6 mmol) in DCM (2.6 mL) was added iodobenzene diacetate (3.3 mmol)

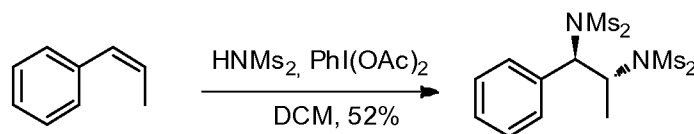
and the reaction was stirred at room temperature over the course of 15 h. After that, the solvent was removed by evaporation and the crude reaction product was purified by silica gel column chromatography.

5



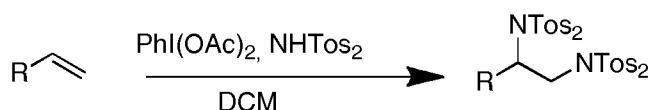
Alternatively, to a suspension of PhI(OAc)_2 (1.2 mmol) in DCM (2 mL), and HNMs_2 (2.4 mmol), *cis*- β -methyl styrene (0.5 mmol) was added. The reaction mixture was stirred under microwave irradiation (80 °C), and the conversion was followed by TLC. The solvent was removed under reduced pressure and the residue was purified by column chromatography:

15



B) Examples of diamination of Aliphatic Terminal Alkenes

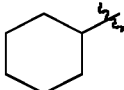
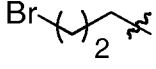
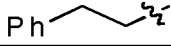
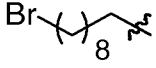
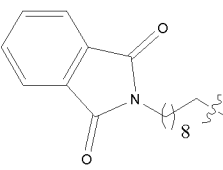
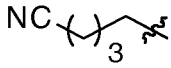
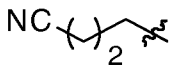
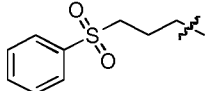
20



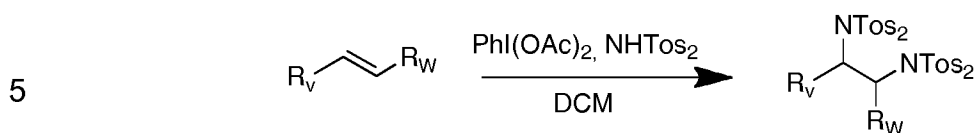
To a solution of olefin (0.5 mmol) and di-*p*-toluensulfonylamide (0.39 g, 1.2 mmol) in dichloromethane (1.3 mL) was added iodobenzene diacetate (0.19 g, 0.6 mmol) and the reaction was stirred at 50 °C during 18 h unless otherwise indicated. Conversion was followed by peak integration of the ^1H NMR of the reaction crude. After that time the solvent was removed by evaporation and the crude was purified by column chromatography (silicagel, hexane/EtOAc 90:10). The pure diamine was obtained as a white solid.

Table 8

R	T (°C)	t (h)	Conversion (%)	yield (%)
C_6H_{13}	50	18	90	80
C_8H_{17}	50	18	90	80
$\text{C}_{10}\text{H}_{21}$	25	72	80	68

	50	15	60	53
	50	24	95	88
$(\text{CH}_2)_8\text{CO}_2\text{Et}$	50	24	85	70
	50	40	85	72
	25	15	80	74
	50	18	100	89
	50	18	100	67
	50	18	100	91
	50	18	100	82
	50	18	100	69

C) Examples of diamination of Internal alkenes:



To a solution of olefin (0.5 mmol) and di-*p*-toluensulfonylamide (0.39 g, 1.2 mmol) in dichloromethane (1.3 mL) was added iodobenzene diacetate (0.19 g, 0.6 mmol) and the reaction was stirred at 50 °C during the indicated time.

10 After that time the solvent was removed by evaporation and the crude was purified by column chromatography (silica gel, hexane/EtOAc 90:10). The pure diamine was obtained as a white solid.

Table 9

R_v	R_w	T (°C)	t (h)	yield (%)
C ₄ H ₉	C ₄ H ₉	50	36	41
CH ₃	C ₅ H ₁₁	50	36	68
C ₃ H ₇	C ₃ H ₇	50	15	54

D) Diamination of butadienes

5

General procedure 2: Dissolved in dichloromethane (1ml) bistosylamide (358 mg, 1.2 mmol) and iodosobenzenediacetate (177mg, 0.6 mmol). The white precipitate was formed immediately, and the suspension was stirred for 5 min. The solution of diene (0.5 mmol) in 1 ml was added then. The mixture was then stirred for 18 h at rt. Conversion was determined by peak integration of the ¹H NMR of the reaction crude.

10

The crude product was purified by silica gel column chromatography (ethyl acetate/hexane) to afford the product as white solid

15

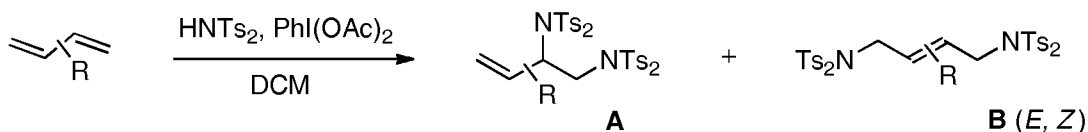
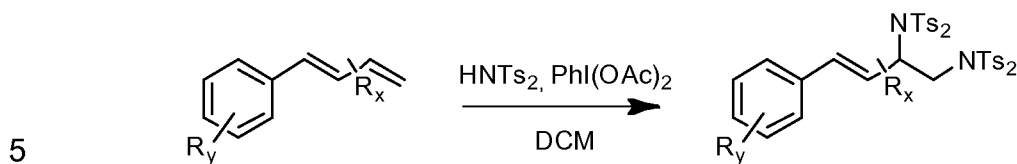


Table 10

Substrate	Product	T (°C)	Conversion (%)	A (%)	B (%)	E/Z
	 	25	100	0	74	1:1
	 	25	100	0	78	2:1

E) Diamination of aromatic 1,3-dienes using HNTs₂

Following the general procedure 2 with the corresponding aromatic diene derivative and stirring the mixture at the indicated temperature for the indicated time, results of Table 11 were obtained. Conversion was determined thanks to peak integration of the ¹H NMR of the reaction crude.

10

Table 11

Substrate	Product	T (°C)	Time (h)	Conversion (%)	yield %
		25	18	100	75
		25	18	100	73
		25	18	100	72
		25	18	100	40
		50	72	>95	64
		25	24	100	50
		25	24	>90	67

- Characterization of aromatic 1,3-dienes

- 15 (E)-N,N'-(4-Phenylbut-3-ene-1,2-diyl)bis(4-methyl-N-tosylbenzene sulfonamide): Isolated as a white solid (292 mg, 75%). m.p. 181-183 °C. IR:

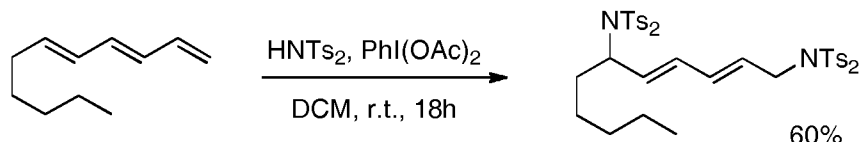
$\nu_{\text{max}}(\text{cm}^{-1}) = 3067, 3031, 2923, 1593, 1492, 1448, 1367, 1350, 1305, 1292, 1186, 1160, 1122, 1082, 1050, 1012, 1000, 970, 930, 909, 896, 848, 815, 805, 787, 755, 735, 711, 694, 655, 624, 539.$

- 5 (E)-N,N'-(4-(4-Fluorophenyl)but-3-ene-1,2-diyl)bis(4-methyl-N-tosylbenzene sulfonamide): Isolated as a white solid (287 mg, 72%). m.p. 176-178 °C. IR: $\nu_{\text{max}}(\text{cm}^{-1}) = 2969, 1596, 1508, 1450, 1373, 1309, 1227, 1163, 1083, 1062, 995, 972, 919, 891, 851, 826, 715, 690, 656, 540.$
- (E)-N,N'-(4-(4-Chlorophenyl)but-3-ene-1,2-diyl)bis(4-methyl-N-tosylbenzene sulfonamide): Isolated as a white solid (297 mg, 73%). m.p. 171-173 °C. IR: $\nu_{\text{max}}(\text{cm}^{-1}) = 3067, 1595, 1490, 1372, 1306, 1165, 1083, 1061, 1008, 975, 919, 850, 811, 784, 730, 714, 702, 659, 549.$
- 10
- (E)-N,N'-(4-(p-Tolyl)but-3-ene-1,2-diyl)bis(4-methyl-N-tosylbenzene sulfonamide): Isolated as a white solid (159 mg, 40%). m.p. 159-161 °C. IR: $\nu_{\text{max}}(\text{cm}^{-1}) = 2923, 1595, 1493, 1448, 1373, 1307, 1163, 1083, 1054, 999, 974, 897, 845, 811, 714, 691, 657, 543.$
- 15
- (E)-Ethyl 4,5-bis(4-methyl-N-tosylphenylsulfonamido)-5-phenylpent-2-enoate: Isolated as a white solid (272 mg, 64%). m.p. 208-210 °C. IR: $\nu_{\text{max}}(\text{cm}^{-1}) = 2960, 2919, 1722, 1595, 1493, 1451, 1369, 1355, 1327, 1301, 1275, 1236, 1188, 1162, 1081, 1021, 998, 988, 894, 841, 824, 811, 764, 747, 701, 687, 655, 577.$
- 20
- (E)-N,N'-(4-(Naphthalen-2-yl)but-3-ene-1,2-diyl)bis(4-methyl-N-tosylbenzene sulfonamide): Isolated as a white solid (278 mg, 67%). m.p. 160-162 °C. IR: $\nu_{\text{max}}(\text{cm}^{-1}) = 3033, 2956, 2922, 1595, 1492, 1450, 1373, 1358, 1346, 1308, 1292, 1187, 1163, 1104, 1082, 1063, 1015, 972, 903, 890, 862, 832, 819, 809, 752, 737, 726, 711, 702, 692, 658, 624, 577.$
- 25
- (E)-N,N'-(5-Phenylpent-4-ene-2,3-diyl)bis(4-methyl-N-tosylbenzene sulfonamide): Isolated as a white solid (282 mg, 71%). m.p. 176-178 °C. IR: $\nu_{\text{max}}(\text{cm}^{-1}) = 2979, 1594, 1490, 1448, 1390, 1359, 1308, 1179, 1164, 1080, 1010, 980, 912, 865, 811, 762, 728, 702, 683, 657, 629, 546.$
- 30
- 35

F) 1,6-diamination of trienes

Following the general procedure 2 and using undec-1,3,5-triene as the alkene, the following diamination product could be obtained in 60% yield.

5

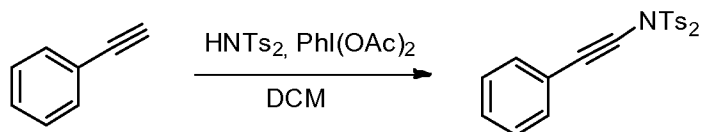


G) Amination of alkynes

10

Following the general procedure 1 and using ethynylbenzene as the alkyne, the following diamination product could be obtained in 52% yield.

15



Example 20: Preparation of acetoxymethanesulfonamido-phenylacetylene (VIIIId)

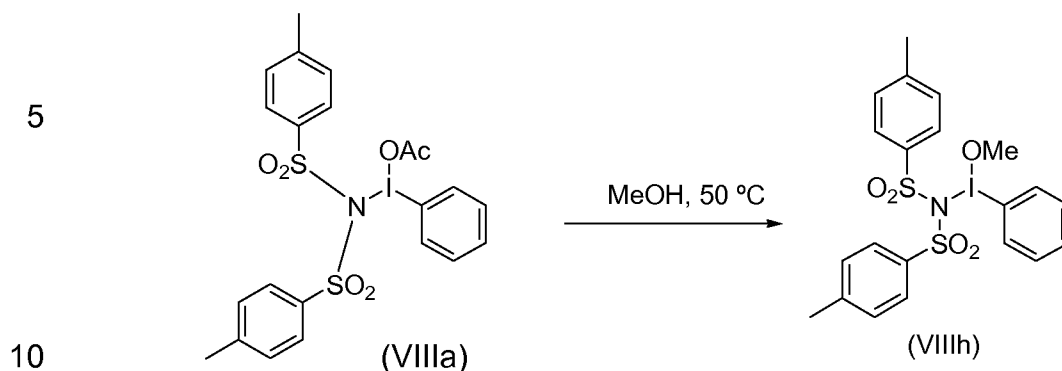
20 This compound was alternatively obtained (in addition to the way illustrated in Scheme 8 above) by dissolving the compound of formula (VIa) in 10 mL methanol. The resulting mixture was stirred at 50°C for 5 minutes. Solvent was then eliminated under vacuum, to yield the compound of formula VIIIId in quantitative yield.

25

$^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ = 1.92 (s, 3H), 2.33 (s, 3H), 2.77 (s, 3H), 7.21 (d, J = 8.0 Hz, 2H), 7.41-7.67 (m, 4H), 7.71 (t, J = 7.4 Hz, 1H), 8.22 (d, J = 7.5 Hz, 2H). $^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO-}d_6$): δ = 20.9, 21.1, 42.8, 126.4, 128.4, 131.2, 132.5, 134.6, 140.0, 143.4, 172.1. IR: $\nu_{\text{max}}(\text{cm}^{-1})$ = 3022, 2926, 1655, 1596, 1472, 1443, 1368, 1328, 1308, 1263, 1187, 1138, 1080, 1015, 976, 907, 850, 836, 809, 790, 739, 705, 678, 653, 595.

30

Example 21: Preparation of methoxy(4-methyl-*N*-tosylbenzene sulfonamide) iodobenzene (VIIIh)



This compound was obtained following Scheme 10 by heating a solution of the compound of formula (VIIIa) in methanol at 50°C. The solvent was evaporated, which afforded the isolation of (VIIIh) in quantitative yield.

15 ^1H NMR (400 MHz, CDCl_3): δ = 2.31 (s, 6H), 3.17 (s, 3H), 7.15 (d, J = 8.0 Hz, 4H), 7.52 (d, J = 8.2 Hz, 4H), 7.62 (dd, J = 7.0, 8.4 Hz, 2H), 7.6-7.7 (m, 1H), 8.22 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 20.9, 48.6, 123.4, 126.2, 128.2, 131.2, 132.5, 134.5, 139.7, 143.7. MS (MALDI⁺): 528.1 (M^+ -NTs₂).

20

Example 22: Alkyne amination

General Procedure:

25 To a solution of $\text{PhI}(\text{OAc})(\text{NTs}_2)$ (0.117 g, 0.200 mmol) in dichloroethane (DCE) (2.000 mL) was added the corresponding alkyne (0.204 mmol) and the reaction mixture was stirred at 80 °C. After 15 min. (unless otherwise stated) the solution was quenched by addition of a 10% aqueous solution of sodium thiosulfate. Aqueous phase was extracted with dichloromethane (DCM) (3x).

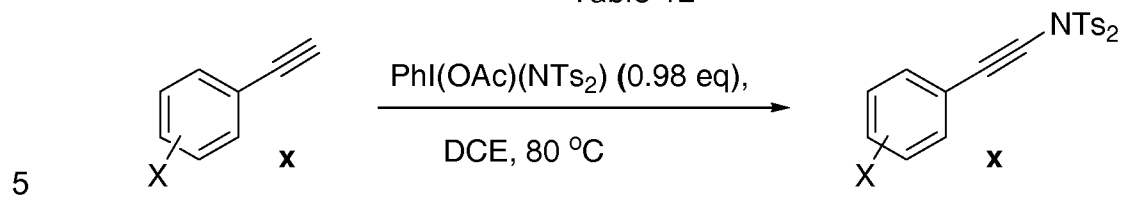
30 Combined organic layers were washed with brine (2x), dried and solvents were removed under reduced pressure. Unless otherwise stated the product was obtained pure and no further purification was required.

In this way, the aminated compounds listed in Tables 12-13 were obtained.

35

68

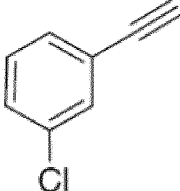
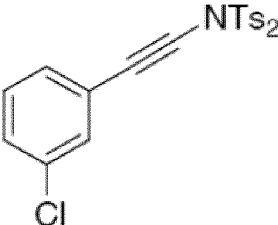
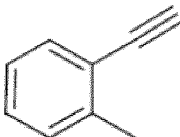
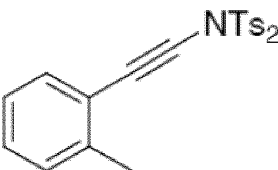
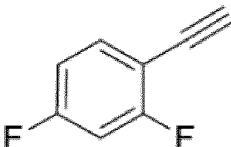
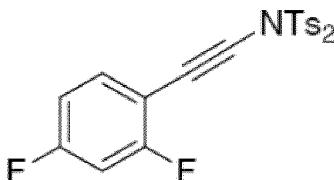
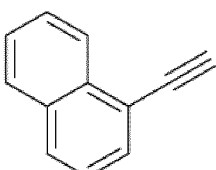
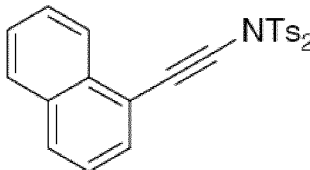
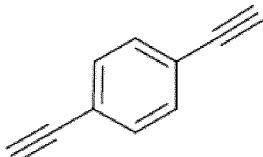
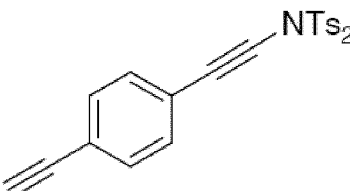
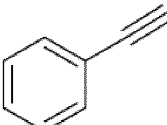
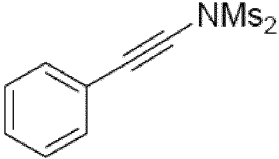
Table 12



	Alkyne	Amine	Yield [%] ^a	t (min)
10			84	20
15			91	10
20			83	15
25			89	120

30

35

5			59(92) ^b	15
10			62	120
15			72	15
			65	15
			66 ^c	15
			37 ^d	20min

^a Isolated yield after purification. Scale, 0.2 mmol.

^b Between brackets yield based on recovered starting material.

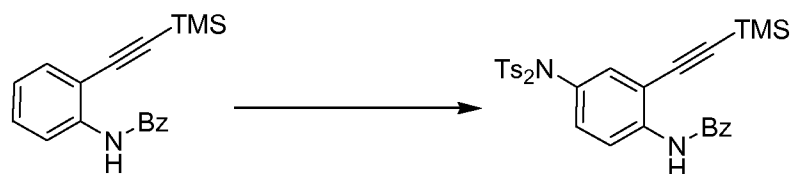
^c 2 equiv of alkyne. ^d PhI(OAc)(NMs₂) (0.98 eq.), DCE, 80 °C, 20 min, 0.1M

Table 13

		Alkyne $\xrightarrow[\text{DCE, 80 } ^\circ\text{C}]{\text{PhI(OAc)(NTs}_2\text{)} (0.98 \text{ eq})}$ Amine		
5	Entry	Alkyne	Amine	Yield [%] ^a t (h)
	1 ^b			78 1
	2			47 0.25
10	3 ^c			45 0.25
	4 ^c			40 10

^a Isolated yield after purification. Scale, 0.2 mmol. ^b 5 equiv of alkyne.^c 2 eq of PhI(OAc)NTs₂.Example 23: aromatic amination

2U



25

Conditions	Yield [%] ^a
1.5 equiv. of PhI(OAc)NTs ₂ , DCE, 80°C, 14h	65

30

(^aIsolated yield after purification. Scale, 0.2 mmol)
 Bz: benzyl; TMS: trimethylsilylethynyl

N-(4-(4-methyl-*N*-tosylphenylsulfonamido)-2-((trimethylsilyl)ethynyl)phenyl) benzamide: synthesized according to the general procedure as described above in Example 22. The crude was purified by column chromatography (silicagel, hexanes/EtOAc, 9:1, v/v). Isolated as a yellow solid. ¹H-NMR (400 MHz, CDCl₃): δ = 0.31 (s, 9H), 2.48 (s, 6H), 6.94 (dd, *J* = 2.5, 8.9 Hz, 1H), 7.23 (d, *J* = 2.5 Hz, 1H), 7.35 (m, 4H), 7.52 (m, 2H), 7.60 (m, 1H), 7.81 (d, *J* = 8.3 Hz, 4H), 7.93 (dd, *J* = 1.3, 8.3 Hz, 2H), 8.61 (d, *J* = 8.9 Hz, 1H), 9.02 (s,

1H). ¹³C-NMR (100 MHz, CDCl₃): δ = -0.2, 21.7, 98.8, 104.2, 112.9, 118.9, 127.1, 128.6, 128.8, 128.9, 129.6, 132.4, 133.3, 134.4, 134.5, 136.4, 141.0, 145.1, 165.0.

5 - Characterization of amines listed in Tables 12-13

4-Methyl-*N*-(phenylethynyl)-*N*-tosylbenzenesulfonamide: m.p. = 127-129 °C.
IR ν_{max}(cm⁻¹): 3065, 2923, 1595, 1382, 1365, 1169, 1082, 848, 808, 765, 656, 530.

10

4-Methyl-*N*-(*p*-tolylethynyl)-*N*-tosylbenzenesulfonamide: m.p. = 141-142 °C.
IR ν_{max}(cm⁻¹): 3012, 2920, 1594, 1509, 1387, 1369, 1172, 1081, 841, 811, 656, 542.

15 *N*-((4-(*tert*-Butyl)phenyl)ethynyl)-4-methyl-*N*-tosylbenzenesulfonamide: m.p. = 144-145 °C. IR ν_{max}(cm⁻¹): 3035, 2962, 1596, 1378, 1158, 1112, 1085, 833, 811, 658, 543.

20 *N*-((4-Bromophenyl)ethynyl)-4-methyl-*N*-tosylbenzenesulfonamide: m.p. = 143-145 °C. IR ν_{max}(cm⁻¹): 3072, 2923, 1594, 1384, 1368, 1167, 1081, 1010, 809, 659, 536.

25 *N*-((3-Methoxyphenyl)ethynyl)-4-methyl-*N*-tosylbenzenesulfonamide: m.p. = 141-143 °C. IR ν_{max}(cm⁻¹): 3070, 2940, 1595, 1390, 1171, 1083, 1039, 845, 657, 615, 539.

30 *N*-((3-Chlorophenyl)ethynyl)-4-methyl-*N*-tosylbenzenesulfonamide: m.p. = 110-112 °C. IR ν_{max}(cm⁻¹): 2955, 2921, 2851, 1594, 1387, 1368, 1163, 1082, 832, 810, 787, 656, 537.

30

4-Methyl-*N*-(*o*-tolylethynyl)-*N*-tosylbenzenesulfonamide: m.p. = 149-152 °C
IR ν_{max}(cm⁻¹): 3027, 2922, 1595, 1388, 1171, 1083, 1038, 842, 811, 657, 540.

35 *N*-((2,4-Difluorophenyl)ethynyl)-4-methyl-*N*-tosylbenzenesulfonamide: m.p. = 130-132 °C. IR ν_{max}(cm⁻¹): 3078, 2925, 1594, 1506, 1396, 1375, 1169, 1083, 847, 809, 747, 725, 656, 540.

4-Methyl-*N*-(naphthalen-1-ylethynyl)-*N*-tosylbenzenesulfonamide: m.p. = 133-137 °C. IR $\nu_{\text{max}}(\text{cm}^{-1})$: 3058, 2922, 1594, 1373, 1168, 1083, 847, 798, 769, 657, 540.

5

N-((4-Ethynylphenyl)ethynyl)-4-methyl-*N*-tosylbenzenesulfonamide:

Synthesized according to the general procedure as described above. The crude was purified by column chromatography (silicagel, hexanes/EtOAc, 9:1, v/v). Isolated as a white solid. m.p. = 125-127 °C. IR $\nu_{\text{max}}(\text{cm}^{-1})$: 3266, 2922, 1702, 1596, 1385, 1369, 1169, 1083, 838, 810, 661, 541.

10

N-(Methylsulfonyl)-*N*-(phenylethynyl)methanesulfonamide: Synthesized according to the general procedure as described above. The crude was purified by column chromatography (silicagel, hexanes/EtOAc, 9:1, v/v). Isolated as a white solid. m.p. = 150-151 °C. IR $\nu_{\text{max}}(\text{cm}^{-1})$: 3025, 2930, 1360, 1328, 1168, 1085, 966, 846, 786, 690, 502.

15

4-Methyl-*N*-(3-propylcyclopent-1-en-1-yl)-*N*-tosylbenzenesulfonamide:

Synthesized according to the general procedure as described above. The crude was purified by column chromatography (silicagel, hexanes/EtOAc, 9:1, v/v). Isolated as a white solid. m.p. = 92-94 °C. IR $\nu_{\text{max}}(\text{cm}^{-1})$: 3060, 2927, 1596, 1510, 1365, 1340, 1161, 1111, 856, 669, 546.

20

Ferrocene derivative: Synthesized according to the general procedure as described above. The crude was purified by column chromatography (silicagel, hexanes/EtOAc, 9:1, v/v). Isolated as a purple solid. m.p. = 131-134 °C. IR $\nu_{\text{max}}(\text{cm}^{-1})$: 2920, 2852, 1595, 1372, 1355, 1165, 930, 911, 808, 657, 543.

25

N-(3-(But-3-yn-1-yl)cyclopent-1-en-1-yl)-4-methyl-*N*-tosylbenzenesulfonamide: Synthesized according to the general procedure as described above. The crude was purified by column chromatography (silicagel, hexanes/EtOAc, 9:1, v/v). Isolated as a purple solid. m.p. = 103-105 °C. IR $\nu_{\text{max}}(\text{cm}^{-1})$: 3289, 2929, 2859, 1595, 1373, 1354, 1167, 1085, 908, 840, 657, 545.

30

35

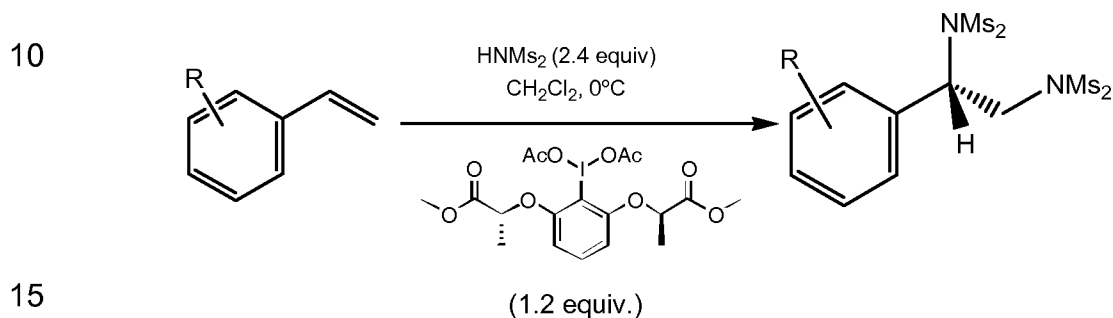
N,N'-(Spiro[4.4]nona-1,6-diene-2,7-diyl)bis(4-methyl-*N*-tosylbenzene

sulfonamide): Synthesized according to the general procedure a described above. The crude was purified by column chromatography (silicagel, hexanes/EtOAc, 9:1, v/v). Isolated as a purple solid. m.p. = 104-106 °C. IR $\nu_{\text{max}}(\text{cm}^{-1})$: 2926, 1596, 1372, 1164, 1084, 909, 655, 547.

5

Example 24: Diamination of styrenes

Table 14. Intermolecular enantioselective diamination of styrenes [a]



20

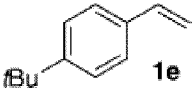
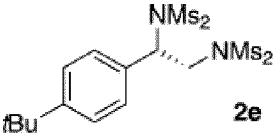
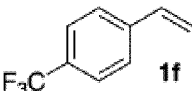
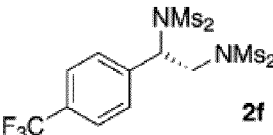
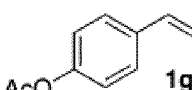
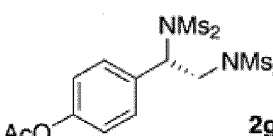
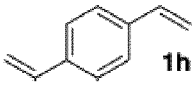
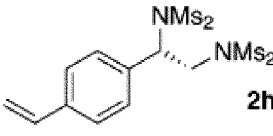
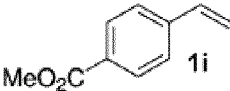
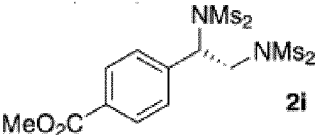
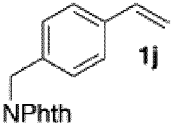
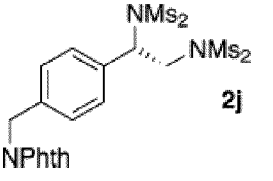
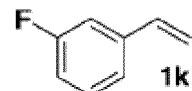
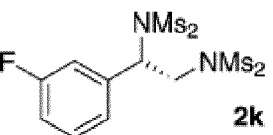
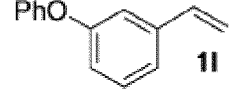
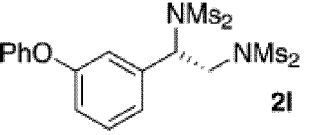
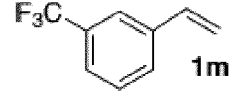
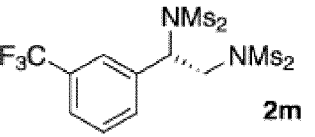
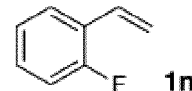
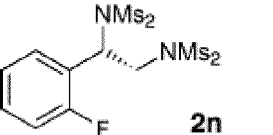
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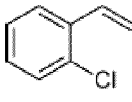
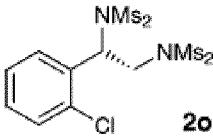
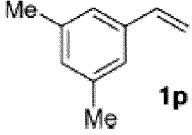
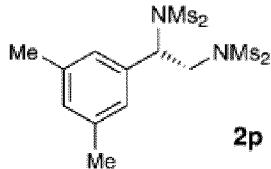
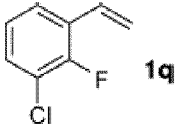
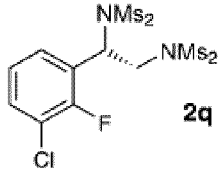
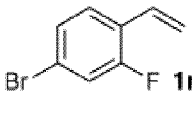
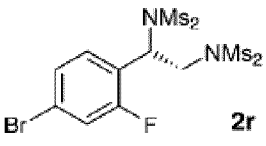
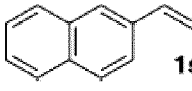
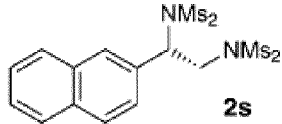
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Styrene	Diamine	Yield [%] ^[b]	ee [%] ^[c,d]
		67	91 (99)
		66	82 (99)
		75	88 (99)

74

5			72	78 (99)
			50	86 (99)
10			72	88 (99)
15			44	74 (99)
			60	79 (99)
20			64	90 (99)
25			73	90
			60	86
30			55	88
35			64	86 (99)

75

5			71	95 (99)
10			70	78 (99)
15			65	92 (99)
20			69	85 (99)
25			64	86 (99)

[a] Reaction carried out on a 0.5 mmol scale. [b] Yield of isolated product after purification. [c] Determined by HPLC on a chiral stationary phase. [d] The ee values obtained after crystallization are in brackets. [e] With HNMs2 (3.6

25

- Characterization of diaminated styrenes

N,N'-(1-(4-Fluorophenyl)ethane-1,2-diyl)bis(*N*-(methylsulfonyl)methanesulfonamide) 2b: m.p. = 237-239 °C. IR ν (cm⁻¹): 2955, 2916, 2848, 1754, 1641, 1591, 1469, 1377, 1217, 1123, 776, 719, 540.

N,N'-(1-(4-Chlorophenyl)ethane-1,2-diyl)bis(*N*-(methylsulfonyl)methanesulfonamide) 2c: m.p. = 212-213 °C. IR ν (cm⁻¹): 3023, 2915, 2848, 1750, 1592, 1493, 1469, 1371, 1357, 1326, 1218, 1156, 1121, 1092, 1045, 1016, 987, 967, 897, 856, 836, 818, 796, 757, 722, 705, 617, 555, 538, 511.

N,N'-(1-(4-Bromophenyl)ethane-1,2-diyl)bis(*N*-(methylsulfonyl)methane sulfonamide) 2d: m.p. = 208-210°C. IR $\nu(\text{cm}^{-1})$: 3022, 2938, 1491, 1413, 1353, 1315, 1152, 1094, 1074, 1046, 1013, 966, 899, 854, 815, 792, 753, 693, 537, 508.

5

(1-(4-(*tert*-Butyl)phenyl)ethane-1,2-diyl)bis(*N*-(methylsulfonyl)methane sulfonamide) 2e: m.p. = 153-155°C. IR $\nu(\text{cm}^{-1})$: 3020, 2963, 1416, 1355, 1329, 1153, 1096, 1052, 969, 900, 859, 828, 795, 755, 577, 539, 509.

10 *N,N'*-(1-(4-(Trifluoromethyl)phenyl)ethane-1,2-diyl)bis(*N*-(methylsulfonyl) methanesulfonamide) 2f: m.p. = 223-225°C. IR $\nu(\text{cm}^{-1})$: 3022, 2923, 1737, 1418, 1357, 1324, 1152, 1110, 1068, 1020, 974, 947, 903, 858, 845, 830, 791, 753, 684, 628, 598, 536, 509.

15 *N,N'*-(1-(4-(Acetoxy)phenyl)ethane-1,2-diyl)bis(*N*-(methylsulfonyl) methanesulfonamide) 2g: m.p. = 137-139°C. IR $\nu(\text{cm}^{-1})$: 3019, 2398, 1758, 1510, 1361, 1322, 1207, 1153, 1057, 966, 896, 855, 805, 782, 759, 537, 508.

N,N'-(1-(4-Vinylphenyl)ethane-1,2-diyl)bis(*N*-(methylsulfonyl)methane sulfonamide) 2h: m.p. = 199-201 °C. IR $\nu(\text{cm}^{-1})$: 3020, 1514, 1416, 1367, 1348, 1315, 1151, 1096, 1034, 963, 943, 922, 901, 857, 839, 803, 754, 657, 614, 538.

N,N'-(1-(4-Methoxycarbonyl)phenyl)ethane-1,2-diyl)bis(*N*-(methylsulfonyl) methanesulfonamide) 2i: m.p. = 225-227 °C with decomposition. IR $\nu(\text{cm}^{-1})$: 3022, 2939, 1720, 1611, 1438, 1413, 1359, 1323, 1283, 1154, 1108, 1053, 955, 900, 848, 825, 787, 757, 708, 665, 618, 535, 506.

N,N'-(1-(4-((1,3-dioxoisindolin-2-yl)methyl)phenyl)ethane-1,2-diyl)bis(*N*-(methylsulfonyl)methanesulfonamide) 2j: m.p. = 215°C. IR $\nu(\text{cm}^{-1})$: 3039, 1771, 1711, 1394, 1350, 1154, 964, 905, 726.

N,N'-(1-(3-Fluorophenyl)ethane-1,2-diyl)bis(*N*-(methylsulfonyl)methane sulfonamide) 2k: m.p. = 162-164 °C. IR $\nu(\text{cm}^{-1})$: 2958, 2918, 2850, 1462, 1364, 1260, 1156, 1017, 865, 795, 540, 508.

35

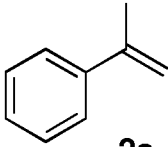
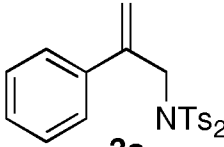
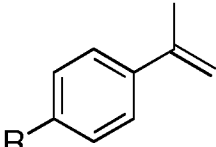
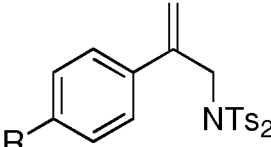
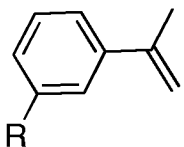
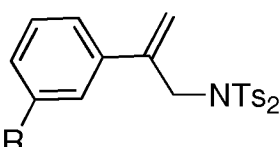
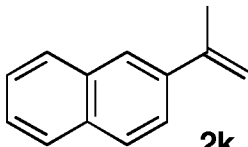
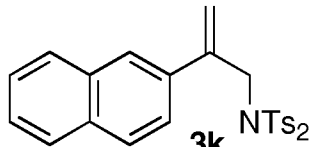
- N,N'*-(1-(3-Phenoxyphenyl)ethane-1,2-diyl)bis(*N*-(methylsulfonyl)methane sulfonamide) 2l: m.p. = 128-130 °C. IR $\nu(\text{cm}^{-1})$: 3020, 2933, 1583, 1487, 1447, 1413, 1349, 1321, 1236, 1211, 1153, 1048, 964, 870, 843, 754, 693, 538, 507.
- 5 *N,N'*-(1-(3-(Trifluoromethyl)phenyl)ethane-1,2-diyl)bis(*N*-(methylsulfonyl)methanesulfonamide) 2m: m.p. = 104-106°C. IR $\nu(\text{cm}^{-1})$: 3025, 2962, 1738, 1415, 1351, 1321, 1260, 1153, 1117, 1076, 966, 858, 804, 760, 704, 664, 539, 508.
- 10 *N,N'*-(1-(2-Fluorophenyl)ethane-1,2-diyl)bis(*N*-(methylsulfonyl)methane sulfonamide) 2n: m.p. = 224-226 °C. IR $\nu(\text{cm}^{-1})$: 3015, 1618, 1495, 1460, 1360, 1317, 1232, 1151, 1088, 1045, 964, 908, 849, 819, 754, 623, 540, 505.
- 15 *N,N'*-(1-(2-Chlorophenyl)ethane-1,2-diyl)bis(*N*-(methylsulfonyl)methane sulfonamide) 2o: m.p. = 222-224°C. IR $\nu(\text{cm}^{-1})$: 2935, 1743, 1587, 1495, 1460, 1361, 1317, 1261, 1230, 1152, 1121, 1088, 1045, 964, 947, 908, 865, 849, 818, 779, 766, 731, 623, 557, 540, 518, 505.
- 20 *N,N'*-(1-(3,5-Dimethylphenyl)ethane-1,2-diyl)bis(*N*-(methylsulfonyl)methane sulfonamide) 2p: m.p. = 222-224 °C. IR $\nu(\text{cm}^{-1})$: 3018, 1603, 1417, 1347, 1321, 1153, 1106, 1044, 973, 928, 876, 855, 821, 759, 725, 638, 573.
- N,N'*-(1-(4-Bromo-2-fluorophenyl)ethane-1,2-diyl)bis(*N*-(methylsulfonyl)methanesulfonamide) 2q: m.p. = 234-236 °C. IR $\nu(\text{cm}^{-1})$: 3023, 2938, 1603, 1575, 1489, 1403, 1372, 1351, 1318, 1222, 1151, 1094, 1043, 967, 943, 907, 871, 847, 825, 783, 751, 621, 580.
- 25 *N,N'*-(1-(3-chloro-2-fluorophenyl)ethane-1,2-diyl)bis(*N*-(methylsulfonyl)methanesulfonamide) 2r: m.p. = 228-230 °C. IR $\nu(\text{cm}^{-1})$: 3085, 3049, 3027, 2923, 2853, 1738, 1461, 1352, 1154, 1102, 1082, 1049, 958, 857, 810, 792, 761, 735, 627, 533, 503.
- 30 *N,N'*-(1-(Naphthalen-2-yl)ethane-1,2-diyl)bis(*N*-(methylsulfonyl)methane sulfonamide) 2s: m.p. = 166-168 °C. IR $\nu(\text{cm}^{-1})$: 3043, 3020, 2936, 1416, 1347, 1315, 1152, 1095, 1036, 962, 941, 873, 859, 814, 785, 752, 667, 607, 537.
- 35

Example 25: Allylic amination

Table 15. Metal-free allylic amination of α -methyl styrenes. ^a Isolated yield after purification.

5

10

Alkene	Product	Reaction Time [h]	Yield [%] ^a
 2a	 3a	20	87
 2b : R = NO ₂	 3b	20	70
2c : R = CF ₃	3c	20	43
2d : R = Cl	3d	20	67
2e : R = F	3e	20	61
2f : R = Me	3f	6	79
2g : R = <i>t</i> Bu	3g	6	80
2h : R = OMe	3h	0.25	32
 2i : R = Me	 3i	1	75
2j : R = Br	3j	20	81
 2k	 3k	20	73

20

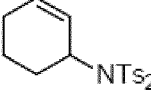
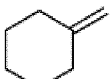
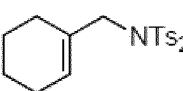
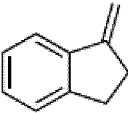
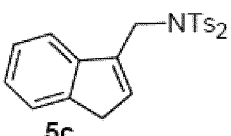
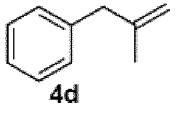
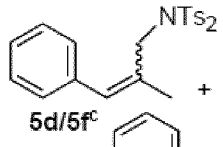
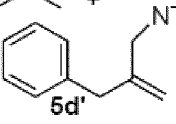
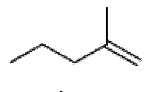
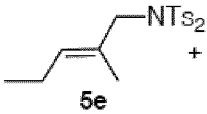
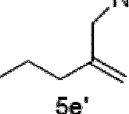
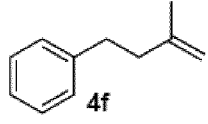
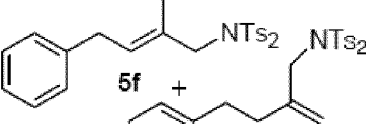
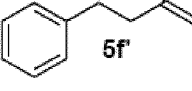
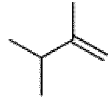
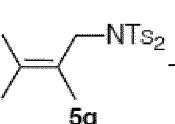
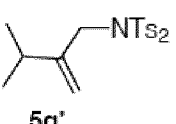
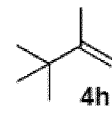
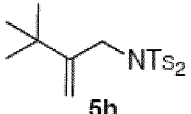
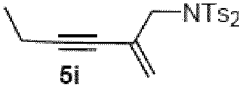
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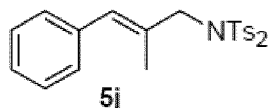
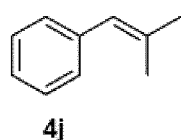
Table 16: Metal-free allylic amination

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$$\begin{array}{c}
 \text{R}'' \\
 | \\
 \text{R}-\text{C}=\text{C}-\text{R}' \\
 \xrightarrow[\text{CH}_2\text{Cl}_2, 25^\circ\text{C}, 20\text{h}]{\text{PhI(OAc)(NTs}_2\text{)} (1.4 \text{ equiv.}), \text{HNTs}_2 (1.5 \text{ equiv.})} \\
 \text{R}-\text{C}(\text{R}'')=\text{C}(\text{NTs}_2)-\text{R}'
 \end{array}$$

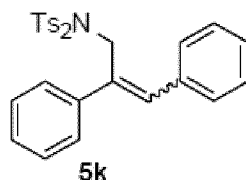
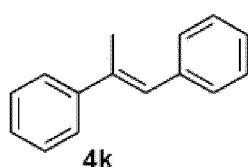
	Alkene	Product	Yield [%] ^a
10	 4a	 5a	65
	 4b	 5b	99
15	 4c	 5c	53
20	 4d	 5d/5f ^c +  5d'	73 ^d
25	 4e	 5e +  5e'	36 ^{c,d}
	 4f	 5f +  5f'	58 ^{c,d}
30	 4g	 5g +  5g'	65 ^{c,d}
	 4h	 5h	24
35	 4i	 5i	67

80

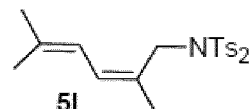
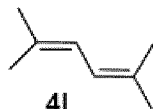


94

5

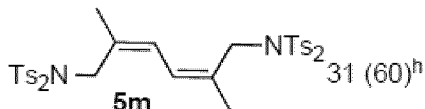
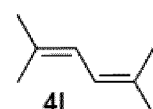
77^d

10



92

15

31 (60)^h

^a Isolated yield after purification. ^b 5 minutes reaction time. ^c ratio **5d/5f** = 1/2; ratio **5e/5e'** = 2/1; ratio **5f/5f'** = 1/1; ratio **5g/5g'** = 3/1. ^d Combined yield of isomers. ^e 14h reaction time. ^f 10h reaction time. ^g 3 equivalents alkene, 12h reaction time. ^h Yield from crude reaction mixture in brackets.

20

- Characterization of allylic amines

4-Methyl-*N*-(2-phenylallyl)-*N*-tosylbenzenesulfonamide: Isolated as a white solid. ¹H-NMR (400 MHz, CDCl₃): δ = 2.45 (s, 6H), 4.78 (s, 2H), 5.14 (s, 1H), 5.31 (s, 1H), 7.2-7.4 (m, 9H), 7.88 (d, *J* = 8.3 Hz, 4H). ¹³C-NMR (100 MHz, CDCl₃): δ = 21.8, 52.2, 116.0, 126.7, 128.1, 128.5, 128.6, 128.9, 129.6, 137.0, 138.9, 142.1, 145.0. IR: ν(cm⁻¹) = 3057, 2996, 2947, 1595, 1368, 1343, 1162, 814, 666, 543.

4-Methyl-*N*-(2-(4-nitrophenyl)allyl)-*N*-tosylbenzenesulfonamide: Isolated as a white solid. ¹H-NMR (400MHz, CDCl₃): δ = 2.45 (s, 6H), 4.79 (s, 2H), 5.38 (s, 1H), 5.45 (s, 1H), 7.30 (d, *J* = 8.2 Hz, 4H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 4H), 8.12 (d, *J* = 8.6 Hz, 2H). ¹³C-NMR (100MHz, CDCl₃): δ = 21.6, 51.7, 119.8, 123.5, 127.4, 128.4, 129.5, 136.7, 140.6, 144.9, 145.2, 147.3. IR: ν(cm⁻¹) = 3060, 2927, 1596, 1510, 1365, 1340, 1161, 1111, 856, 669, 546.

4-Methyl-*N*-tosyl-*N*-(2-(4-(trifluoromethyl)phenyl)allyl)benzene sulfonamide: Isolated as a white solid. ¹H-NMR (400MHz, CDCl₃): δ = 2.44 (s, 6H), 4.78 (s, 2H), 5.28 (s, 1H), 5.38 (s, 1H), 7.28 (d, *J* = 8.3 Hz, 4H), 7.40 (d, *J* = 8.2 Hz,

2H), 7.54 (d, $J = 8.2$ Hz, 2H), 7.84 (d, $J = 8.4$ Hz, 4H). ^{13}C -NMR (100MHz, CDCl_3): $\delta = 21.6, 51.9, 118.3, 124.0, (q, {}^1J_{\text{CF}} = 272.1$ Hz), 125.2 (q, ${}^3J_{\text{CF}} = 3.8$ Hz), 126.9, 128.4, 129.5, 129.9 (q, ${}^2J_{\text{CF}} = 32.6$ Hz), 136.8, 136.9, 141.1, 142.1, 145.0. ^{19}F -NMR (376MHz, CDCl_3): $\delta = -62.68$. IR: $\nu(\text{cm}^{-1}) = 2945,$
5 1596, 1577, 1365, 1323, 1164, 1111, 812, 664, 540.

N-(2-(4-Chlorophenyl)allyl)-4-methyl-*N*-tosylbenzenesulfonamide: Isolated as a white solid. ^1H -NMR (400MHz, CDCl_3): $\delta = 2.46$ (s, 6H), 4.77 (s, 2H), 5.21 (s, 1H), 5.32 (s, 1H), 7.2-7.4 (m, 8H), 7.88 (d, $J = 8.3$ Hz, 4H). ^{13}C -NMR
10 (100MHz, CDCl_3): $\delta = 21.6, 51.9, 116.8, 127.9, 128.4, 128.7, 129.4, 133.8, 136.8, 137.0, 141.0, 144.9$. IR: $\nu(\text{cm}^{-1}) = 2956, 2925, 1594, 1493, 1360, 1345, 1164, 1082, 907, 803, 793, 656, 539$.

N-(2-(4-Fluorophenyl)allyl)-4-methyl-*N*-tosylbenzenesulfonamide: Isolated as a white solid. ^1H -NMR (400MHz, CDCl_3): $\delta = 2.44$ (s, 6H), 4.75 (s, 2H), 5.16 (s, 1H), 5.26 (s, 1H), 6.98 (pst, $J = 8.7$ Hz, 2H), 7.2-7.3 (m, 6H), 7.86 (d, $J = 7.9$ Hz, 4H). ^{13}C -NMR (100MHz, CDCl_3): $\delta = 21.7, 52.1, 115.2$ (d, ${}^2J_{\text{CF}} = 21.2$ Hz), 116.4, 128.3 (d, ${}^3J_{\text{CF}} = 8.1$ Hz), 128.5, 129.5, 134.7, 136.9, 141.1, 145.0, 162.6 (d, ${}^1J_{\text{CF}} = 247.1$ Hz). ^{19}F -NMR (376MHz, CDCl_3): $\delta = -113.99$.
15
20 IR $\nu(\text{cm}^{-1})$: 3046, 2957, 1598, 1494, 1345, 1161, 804, 662, 535.

4-Methyl-*N*-(2-(*p*-tolyl)allyl)-*N*-tosylbenzenesulfonamide: Isolated as a white solid. ^1H -NMR (400 MHz, CDCl_3): $\delta = 2.35$ (s, 3H), 2.45 (s, 6H), 4.74 (s, 2H), 5.07 (s, 1H), 5.26 (s, 1H), 7.12 (d, $J = 8.2$ Hz, 2H), 7.22 (d, $J = 8.2$ Hz, 2H),
25 7.29 (d, $J = 8.1$ Hz, 4H), 7.87 (d, $J = 8.3$ Hz, 4H). ^{13}C -NMR (100 MHz, CDCl_3): $\delta = 21.1, 21.7, 52.1, 115.2, 126.4, 128.5, 129.0, 129.4, 135.9, 137.0, 137.8, 141.7, 144.8$. IR: $\nu(\text{cm}^{-1}) = 2922, 1597, 1370, 1164, 811, 660, 548$.

N-(2-(4-(*tert*-Butyl)phenyl)allyl)-4-methyl-*N*-tosylbenzenesulfonamide:
30 Isolated as a white solid. ^1H -NMR (400 MHz, CDCl_3): $\delta = 1.33$ (s, 9H), 2.44 (s, 6H), 4.76 (s, 2H), 5.06 (s, 1H), 5.29 (s, 1H), 7.2-7.3 (m, 6H), 7.3-7.4 (m, 2H), 7.87 (d, $J = 8.4$ Hz, 4H). ^{13}C -NMR (100 MHz, CDCl_3): $\delta = 21.7, 31.3, 34.5, 52.0, 115.2, 125.2, 126.1, 128.5, 128.8, 129.4, 137.0, 141.5, 144.8, 151.1$. IR: $\nu(\text{cm}^{-1}) = 2960, 1597, 1366, 1350, 1162, 808, 658, 545$.

35 *N*-(2-(4-Methoxyphenyl)allyl)-4-methyl-*N*-tosylbenzenesulfonamide: Isolated as a white solid. ^1H -NMR (400 MHz, CDCl_3): $\delta = 2.47$ (s, 6H), 3.84 (s, 3H),

4.76 (s, 2H), 5.07 (s, 1H), 5.24 (s, 1H), 6.85 (d, $J = 8.8$ Hz, 2H), 7.2-7.3 (m, 6H), 7.8-7.9 (m, 2H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): $\delta = 21.7, 52.1, 55.3, 113.7, 114.7, 127.7, 128.5, 129.4, 131.1, 137.0, 141.2, 144.8, 159.5$. IR: $\nu(\text{cm}^{-1}) = 2997, 2958, 2836, 1573, 1493, 1402, 1364, 1161, 808, 660, 544$.

5

4-Methyl-*N*-(2-(*m*-tolyl)allyl)-*N*-tosylbenzenesulfonamide: Isolated as a white solid. $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 2.33$ (s, 3H), 2.45 (s, 6H), 4.75 (s, 2H), 5.09 (s, 1H), 5.27 (s, 1H), 7.0-7.1 (m, 3H), 7.1-7.2 (pst, $J = 7.5$ Hz, 1H), 7.30 (d, $J = 8.2$ Hz, 4H), 7.88 (d, $J = 8.1$ Hz, 4H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): $\delta =$
10 21.4, 21.7, 52.1, 115.7, 123.7, 127.3, 128.2, 128.5, 128.7, 129.4, 137.0, 137.9, 138.7, 142.0, 144.8. IR: $\nu(\text{cm}^{-1}) = 3025, 2996, 2923, 1595, 1370, 1344, 1161, 810, 666, 545$.

N-(2-(3-Bromophenyl)allyl)-4-methyl-*N*-tosylbenzenesulfonamide: Isolated as
15 a white solid. $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 2.46$ (s, 6H), 4.75 (s, 2H), 5.21 (s, 1H), 5.30 (s, 1H), 7.18 (pst, $J = 7.8$ Hz, 1H), 7.2-7.3 (m, 1H), 7.3-7.4 (m, 5H), 7.40 (d, $J = 7.9$ Hz, 1H), 7.85 (d, $J = 8.4$ Hz, 4H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): $\delta = 21.7, 52.0, 117.8, 122.4, 125.1, 128.4, 129.5, 129.7, 129.8, 130.9, 136.9, 140.6, 140.8, 145.0$. IR: $\nu(\text{cm}^{-1}) = 2998, 2944, 1593, 1341, 1158, 812,$
20 665, 544.

4-Methyl-*N*-(2-(naphthalen-2-yl)allyl)-*N*-tosylbenzenesulfonamide: Isolated as a white solid. $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 2.43$ (s, 6H), 4.91 (s, 2H), 5.26 (s, 1H), 5.45 (s, 1H), 7.28 (d, $J = 8.4$ Hz, 4H), 7.4-7.5 (m, 2H), 7.72 (s, 1H),
25 7.8-7.9 (m, 4H), 7.90 (d, $J = 8.1$ Hz, 4H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): $\delta = 21.6, 52.2, 116.7, 124.7, 125.4, 126.1, 126.2, 127.5, 127.9, 128.2, 128.5, 128.8, 129.4, 132.9, 133.1, 135.9, 136.9, 141.8, 144.8$. IR: $\nu(\text{cm}^{-1}) = 2919, 1595, 1350, 1306, 1162, 1084, 810, 660, 545$.

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N-(Cyclohex-2-en-1-yl)-4-methyl-*N*-tosylbenzenesulfonamide: Isolated as a white solid. $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 1.5$ -1.9 (m, 2H), 1.8-2.0 (m, 3H), 2.1-2.2 (m, 1H), 2.48 (s, 6H), 4.8-4.9 (m, 1H), 5.40 (d, $J = 10.3$ Hz, 1H), 5.7-5.8 (m, 1H), 7.36 (d, $J = 8.0$ Hz, 4H), 7.95 (d, $J = 8.4$ Hz, 4H). $^{13}\text{C-NMR}$ (100
35 MHz, CDCl_3): $\delta = 21.7, 22.8, 24.0, 28.5, 60.6, 127.2, 128.2, 128.3, 129.6, 137.9, 144.6$. IR: $\nu(\text{cm}^{-1}) = 2925, 1596, 1363, 1307, 1161, 1083, 1039, 1018, 938, 923, 855, 808, 735, 703, 658, 618, 580, 547$.

N-(Cyclohex-1-en-1-ylmethyl)-4-methyl-*N*-tosylbenzenesulfonamide: Isolated as a white solid. ¹H-NMR (400 MHz, CDCl₃) δ = 1.3-1.4 (m, 4H), 1.7-1.8 (m, 2H), 1.8-1.9 (m, 2H), 2.47 (s, 6H), 4.35 (s, 2H), 5.6-5.7 (m, 1H), 7.34 (d, *J* = 8.6 Hz, 4H), 7.92 (d, *J* = 8.4 Hz, 4H). ¹³C-NMR (100 MHz, CDCl₃): δ = 21.6, 21.8, 22.0, 25.2, 25.4, 55.7, 128.3, 128.5, 129.4, 131.2, 137.7, 144.5. IR: ν(cm⁻¹) = 2927, 1595, 1367, 1265, 1161, 1084, 1027, 998, 915, 839, 803, 787, 722, 703, 662, 588, 541.

10 *N*-((1*H*-Inden-3-yl)methyl)-4-methyl-*N*-tosylbenzenesulfonamide: Isolated as a white solid. ¹H-NMR (400 MHz, CDCl₃): δ = 2.39 (s, 6H), 3.15 (s, 2H), 4.97 (s, 2H), 6.25 (s, 1H), 7.2-7.3 (m, 6H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 8.40 (d, *J* = 7.8 Hz, 4H). ¹³C-NMR (100 MHz, CDCl₃): δ = 21.6, 37.7, 46.9, 119.3, 123.5, 124.9, 126.2, 128.2, 129.2, 133.5, 137.2, 137.8, 142.9, 15 143.8, 144.6. IR: ν(cm⁻¹) = 3068, 2923, 1596, 1367, 1160, 810, 659, 542.

(*Z*)-4-Methyl-*N*-(2-methyl-3-phenylallyl)-*N*-tosylbenzenesulfonamide: Isolated as a white solid. ¹H-NMR signals assigned from the mixture of isomers. ¹H-NMR (400 MHz, CDCl₃): δ = 1.68 (s, 3H), 2.44 (s, 6H), 4.64 (s, 2H), 6.45 (s, 20 1H), 7.1-7.4 (m, 9H), 7.76 (d, *J* = 8.3 Hz, 4H).

N-(2-Benzylallyl)-4-methyl-*N*-tosylbenzenesulfonamide: Isolated as a white solid. ¹H-NMR signals assigned from the mixture of isomers. ¹H-NMR (400 MHz, CDCl₃): δ = 2.46 (s, 6H), 3.24 (s, 2H), 4.78 (s, 1H), 5.05 (s, 1H), 7.03 (d, 25 *J* = 7.7 Hz, 2H), 7.2-7.3 (m, 7H), 7.88 (d, *J* = 8.4 Hz, 4H).

(*E*)-4-Methyl-*N*-(2-methylpent-2-en-1-yl)-*N*-tosylbenzenesulfonamide: Isolated as a white solid. ¹H-NMR signals assigned from the mixture of isomers. ¹H-NMR (400 MHz, CDCl₃): δ = 0.93 (t, *J* = 7.5 Hz, 3H), 1.34 (s, 3H), 1.9-2.0 (m, 30 2H), 2.44 (s, 6H), 4.34 (s, 2H), 5.43 (t, *J* = 7.6 Hz, 1H), 7.3-7.4 (m, 4H), 7.8-7.9 (m, 4H).

4-Methyl-*N*-(2-methylenepentyl)-*N*-tosylbenzenesulfonamide: Isolated as a white solid. ¹H-NMR signals assigned from the mixture of isomers. ¹H-NMR (400 MHz, CDCl₃): δ = 0.84 (t, *J* = 7.3 Hz, 3H), 0.9-1.0 (m, 2H), 1.8-2.0 (m, 35 2H), 2.44 (s, 6H), 4.32 (s, 2H), 4.87 (s, 1H), 4.95 (s, 1H), 7.3-7.4 (m, 4H), 7.8-7.9 (m, 4H).

(*E*)-4-Methyl-*N*-(2-methyl-4-phenylbut-2-en-1-yl)-*N*-tosylbenzene

sulfonamide: Isolated as a white solid. ¹H-NMR signals assigned from the mixture of isomers. ¹H-NMR (400 MHz, CDCl₃): δ = 1.50 (s, 3H), 2.43 (s, 6H),
5 3.30 (d, *J* = 7.4 Hz, 2H), 4.37 (s, 2H), 5.68 (t, *J* = 7.9 Hz, 1H), 7.1-8.1 (m, 13H).

4-Methyl-*N*-(2-methylene-4-phenylbutyl)-*N*-tosylbenzenesulfonamide: Isolated as a white solid. ¹H-NMR signals assigned from the mixture of isomers. ¹H-
10 NMR (400 MHz, CDCl₃): δ = 2.1-2.2 (m, 2H), 2.6-2.7 (m, 2H), 4.37 (s, 2H), 4.95 (s, 1H), 5.02 (s, 1H), 7.1-8.1 (m, 13H).

N-(2,3-Dimethylbut-2-en-1-yl)-4-methyl-*N*-tosylbenzenesulfonamide: Isolated as a white solid. ¹H-NMR signals assigned from the mixture of isomers. ¹H-
15 NMR (400 MHz, CDCl₃): δ = 1.21 (s, 3H), 1.54 (s, 3H), 1.81 (s, 3H), 2.45 (s, 6H), 4.53 (s, 2H), 7.3-7.4 (m, 4H), 7.90 (d, *J* = 8.3 Hz, 4H). MS (ESI-MS): 430.1 [M⁺ + Na].

4-Methyl-*N*-(3-methyl-2-methylenebutyl)-*N*-tosylbenzenesulfonamide: Isolated as a white solid. ¹H-NMR signals assigned from the mixture of isomers. ¹H-
20 NMR (400 MHz, CDCl₃): δ = 0.96 (d, *J* = 6.8 Hz, 6H), 2.1-2.2 (m, 1H), 2.45 (s, 6H), 4.38 (s, 1H), 4.53 (s, 2H), 4.87 (s, 1H), 7.3-7.4 (m, 4H), 7.86 (d, *J* = 8.4 Hz, 4H). MS (ESI-MS): 430.1 [M⁺ + Na].

N-(3,3-Dimethyl-2-methylenebutyl)-4-methyl-*N*-tosylbenzenesulfonamide: Isolated as a white solid. ¹H-NMR (400MHz, CDCl₃): δ = 1.10 (s, 9H), 2.45 (s, 6H), 4.42 (s, 2H), 4.69 (s, 1H), 4.86 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 4H), 7.90 (d, *J* = 8.2 Hz, 4H). ¹³C-NMR (100MHz, CDCl₃): δ = 21.7, 29.0, 35.1, 50.2, 109.0, 128.6, 129.4, 137.0, 144.8, 149.7. IR: ν(cm⁻¹) = 2973, 1596, 1369, 1351,
25 1083, 810, 658, 543.

4-Methyl-*N*-(2-methylenehex-3-yn-1-yl)-*N*-tosylbenzenesulfonamide: Isolated as a white solid. ¹H-NMR (400MHz, CDCl₃): δ = 1.06 (t, *J* = 7.5 Hz, 3H), 2.20 (q, *J* = 7.5 Hz, 2H), 2.44 (s, 6H), 4.40 (s, 2H), 5.24 (s, 1H), 5.33 (s, 1H), 7.32 (d, *J* = 8.1 Hz, 4H), 7.92 (d, *J* = 8.3 Hz, 4H). ¹³C-NMR (100MHz, CDCl₃): δ =
35 12.9, 13.4, 21.6, 53.0, 94.5, 122.1, 126.3, 128.5, 129.4, 129.6, 137.1, 144.7. IR: ν(cm⁻¹) = 2973, 1596, 1369, 1351, 1163, 1083, 810, 658, 543.

(*E*)-4-Methyl-*N*-(2-methyl-3-phenylallyl)-*N*-tosylbenzenesulfonamide: Isolated as a white solid. ¹H-NMR (400MHz, CDCl₃): δ = 1.62 (s, 3H), 2.41 (s, 6H), 4.53 (s, 2H), 6.48 (s, 1H), 7.10 (d, *J* = 7.6 Hz, 2H), 7.2-7.3 (m, 7H), 7.92 (d, *J* = 8.2 Hz, 4H). ¹³C-NMR (100MHz, CDCl₃): δ = 15.1, 21.6, 57.3, 126.8, 128.1, 128.2, 128.8, 129.4, 130.5, 131.4, 136.8, 137.4, 144.6. IR: ν_{max}(cm⁻¹) = 2975, 2939, 2923, 1594, 1396, 1372, 1164, 810, 658, 544.

(*E*)-*N*-(2,3-Diphenylallyl)-4-methyl-*N*-tosylbenzenesulfonamide: Separated from the mixture of isomers by preparative HPLC (Chiralpak IC 250x4.6mm, 5μm, 1 mL/min, hexanes/DCM/EtOH 90/9/1, v/v, t_R = 12.9 min). Isolated as a white solid. ¹H-NMR (400 MHz, CDCl₃): δ = 2.36 (s, 6H), 4.97 (s, 2H), 6.76 (s, 1H), 7.02 (d, *J* = 8.2 Hz, 4H), 7.17 (d, *J* = 8.4 Hz, 4H), 7.3-7.4 (m, 5H), 7.4-7.5 (m, 3H), 7.5-7.6 (m, 2H). IR: ν(cm⁻¹) = 3057, 1595, 1493, 1429, 1187, 1120, 886, 697, 657, 549.

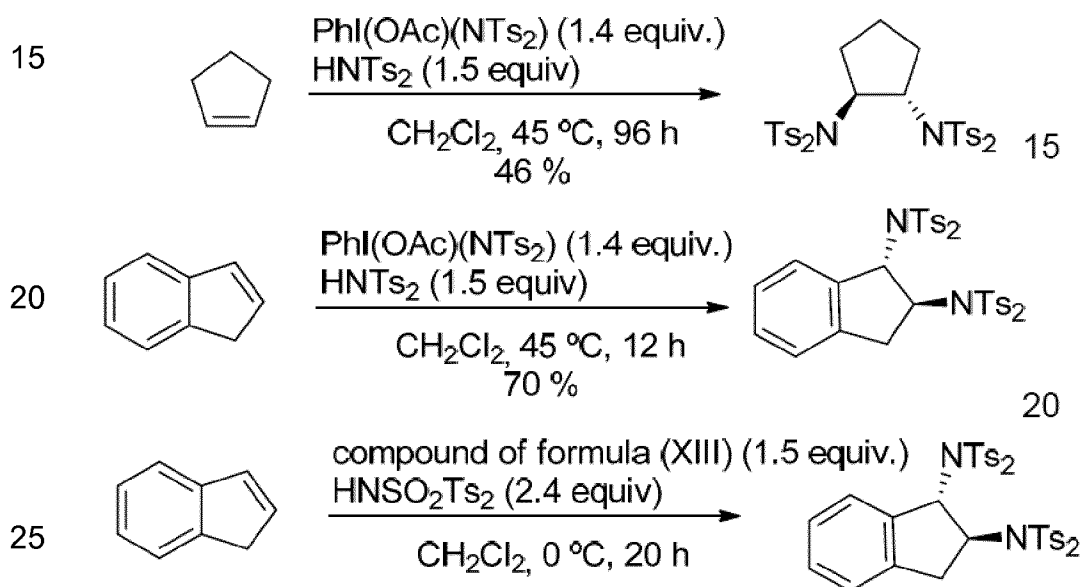
(*Z*)-*N*-(2,3-diphenylallyl)-4-methyl-*N*-tosylbenzenesulfonamide: Isolated as a white solid. Separated from the mixture of isomers by preparative HPLC (Chiralpak IC 250x4.6mm, 5μm, 1 mL/min, hexanes/DCM/EtOH 90/9/1, v/v, t_R = 14.9 min). Isolated as a white solid. ¹H-NMR (400 MHz, CDCl₃): δ = 2.39 (s, 6H), 4.72 (s, 2H), 6.36 (s, 1H), 6.6-6.7 (m, 2H), 7.0-7.3 (m, 12H), 7.88 (d, *J* = 8.3 Hz, 4H). IR: ν(cm⁻¹) = 3057, 1595, 1493, 1429, 1187, 1120, 886, 697, 657, 549.

(*Z*)-*N*-(2,5-Dimethylhexa-2,4-dien-1-yl)-4-methyl-*N*-tosylbenzene sulfonamide: To a solution of PhI(OAc)(NTs₂) 1 [2] (0.18 g, 0.35 mmol) in CH₂Cl₂ (1.00 mL) were added HNTs₂ (0.11 g, 0.35 mmol) and 2,5-dimethylhexa-2,4-diene 4h (1.05 mmol). The reaction mixture was stirred at 25 °C and the conversion followed by TLC. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silicagel, hexanes/EtOAc, 9:1, v/v). ¹H-NMR (400 MHz, CDCl₃): δ = 1.46 (s, 3H), 1.70 (s, 3H), 1.82 (s, 3H), 2.43 (s, 6H), 4.42 (s, 2H), 5.84 (d, *J* = 11.2 Hz, 1H), 6.19 (d, *J* = 11.0 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 4H), 7.87 (d, *J* = 8.4 Hz, 4H). ¹³C-NMR (100 MHz, CDCl₃): δ = 13.7, 18.3, 21.6, 26.4, 57.1, 120.3, 126.7, 127.3, 128.2, 129.3, 129.4, 137.4, 144.5. IR: ν(cm⁻¹) = 2923, 1595, 1368, 1161, 805, 659, 542.

N,N'-((2*Z*,4*Z*)-2,5-Dimethylhexa-2,4-diene-1,6-diyl)bis(4-methyl-*N*-tosyl

benzenesulfonamide): To a solution of $\text{PhI}(\text{OAc})(\text{NTs}_2)$ 1 [2] (0.15 g, 0.30 mmol) in CH_2Cl_2 (0.50 mL) were added HNTs_2 (0.10 g, 0.30 mmol) and 2,5-dimethylhexa-2,4-diene 4h (0.10 mmol). The reaction mixture was stirred at 25 °C and the conversion followed by TLC. The solvent was removed under reduced pressure and the yield calculated by ^1H -NMR using 1,3,5-trimethoxy benzene as internal standard. The residue was purified by recrystallization from MeOH at 0 °C. ^1H -NMR (400 MHz, CDCl_3): δ = 1.43 (s, 6H), 2.43 (s, 12H), 4.40 (s, 4H), 6.10 (s, 2H), 7.31 (d, J = 8.3 Hz, 8H), 7.87 (d, J = 8.4 Hz, 8H). ^{13}C -NMR (100 MHz, CDCl_3): δ = 14.1, 21.7, 56.5, 124.8, 128.3, 129.5, 132.2, 137.2, 144.8. IR: $\nu(\text{cm}^{-1})$ = 2923, 1595, 1368, 1161, 805, 659, 542.

Example 26: Diamination of intermolecular alkenes



- Characterization of the resulting diaminated products

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N,N'-(cyclopentane-1,2-diyl)bis(4-methyl-*N*-tosylbenzenesulfonamide): ^1H -NMR (400 MHz, CDCl_3) δ = 1.5-1.6 (m, 2H), 1.6-1.7 (m, 2H), 1.7-1.8 (m, 2H), 2.46 (s, 12H), 5.55 (q, J = 6.3 Hz, 2H), 7.36 (d, J = 10.4 Hz, 8H), 7.94 (d, J = 7.8 Hz, 4H), 8.22 (d, J = 6.2 Hz, 4H). ^{13}C -NMR (100 MHz, CDCl_3): δ = 21.67, 21.73, 22.9, 29.8, 66.2, 128.8, 129.2, 129.5, 129.7, 134.8, 138.7, 144.7, 145.3. IR: $\nu(\text{cm}^{-1})$: 2957, 1596, 1493, 1371, 1333, 1156, 1082, 1036, 1002, 916, 867, 806, 747, 703, 655, 591, 539

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N,N'-((1*S*,2*S*)-2,3-dihydro-1*H*-indene-1,2-diyl)bis(4-methyl-*N*-tosylbenzene sulfonamide): ¹H-NMR (500 MHz, CDCl₃): δ = 2.4-2.5 (m, 12H), 2.85 (dd, *J* = 4.0, 17.2 Hz, 1H), 3.22 (dd, *J* = 10.3, 17.1 Hz, 1H), 5.75 (dt, *J* = 3.9, 10.2 Hz, 1H), 6.71 (d, *J* = 4.0 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 6.8-6.9 (m, 1H), 7.0-7.1 (m, 3H), 7.2-7.3 (m, 5H), 7.4-7.5 (m, 4H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H), 8.07 (d, *J* = 8.1 Hz, 2H). ¹³C-NMR (125 MHz, CDCl₃): δ = 21.5, 21.6, 21.7, 21.8, 37.9, 66.2, 72.4, 124.2, 125.2, 126.5, 128.3, 128.6, 128.7, 128.9, 128.9, 129.0, 129.5, 129.7, 129.8, 135.4, 136.1, 137.0, 137.5, 138.0, 142.6, 144.3, 144.7, 145.1, 145.3. IR ν(cm⁻¹): 3031, 2923, 1597, 1371, 1349, 1159, 1083, 861, 655, 546.

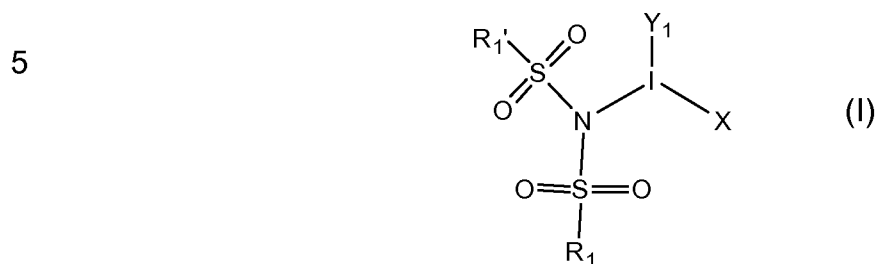
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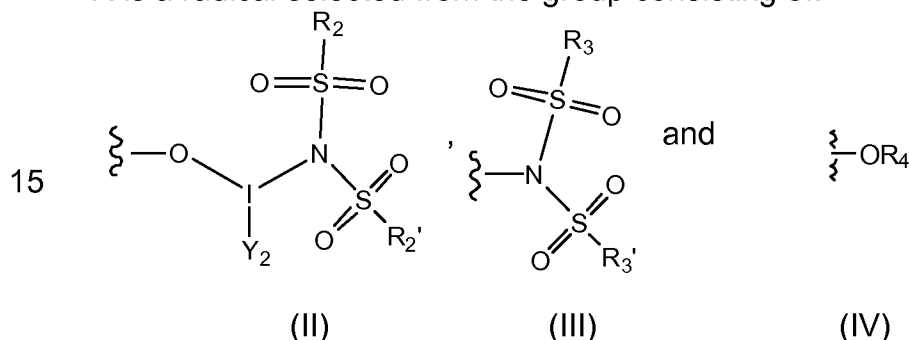
CLAIMS

1. An iodine compound of formula (I)



10 wherein:

X is a radical selected from the group consisting of:



20 wherein the wavy line indicates the position through which the X radical binds to the iodine atom of the compound of formula (I);

Y₁ and Y₂ are C-radicals, same or different, of one of the known ring systems with 1-4 rings, wherein each one of the rings forming said ring system has 3-20 members, each member being independently selected from C, N, O, S, CH, CH₂, and NH, is saturated, partially unsaturated or aromatic, and is isolated, partially or totally fused; being each ring forming part of the ring system optionally substituted by at least one radical selected from the group consisting of: halogen, nitro, (C₁-C₁₂)-alkyl, (C₁-C₁₂)-alkoxy, halo(C₁-C₁₂)-alkyl, -OCH(R₅)C(O)Z, and a iodine-radical of formula (V)



wherein the wavy line indicates the position through which the radical binds to the ring; and

Z is selected from the group consisting of -OR₆ and -NR₉R₁₀;
 with the proviso that when one or more of the rings forming part of the
 ring system is substituted by at least one iodine-radical of formula (V),
 then X is a radical of formula (III) or (IV);

5

or, alternatively, Y₁ and Y₂ are C-radicals, as defined above, which are bound
 via a bond between one of the atoms forming part of the ring system of Y₁ and
 one of the atoms forming part of the ring system of Y₂, thus forming a ring with
 the moiety -I-O-I- of the compound of formula (I), with the proviso that X is a
 radical of formula (II);

10

or, alternatively, Y₁ and Y₂ are C-radicals, as defined above, which are bound
 via a common atom shared by the ring systems of Y₁ and Y₂, thus forming a
 ring with the moiety -I-O-I- of the compound of formula (I), with the proviso
 that X is a radical of formula (II); and

15

R₁, R₁', R₂, R₂', R₃, R₃', R₇ and R₈ are radicals independently selected from the
 group consisting of (C₁-C₁₂)-alkyl; halo(C₁-C₁₂)-alkyl; phenyl; phenyl
 substituted by at least a radical selected from the group consisting of halo(C₁-
 C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and nitro;
 (C₁-C₃)-alkylphenyl; (C₁-C₃)-alkylphenyl being the phenyl moiety substituted
 by at least a radical selected from the group consisting of (C₁-C₆)-alkyl and
 (C₁-C₆)-alkoxy; (C₁-C₄)-alkyl-tri-(C₁-C₄)-alkyl silane; and (C₁-C₄)-alkyl-
 diphenyl-(C₁-C₄)-alkylsilane; and

20

R₄ is a radical selected from the group consisting of (C₁-C₁₂)-alkylcarbonyl;
 halo(C₁-C₁₂)-alkylcarbonyl; phenylcarbonyl; phenylcarbonyl, the phenyl
 moiety being substituted by at least a radical selected from the group
 consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and
 nitro; (C₁-C₃)-alkylphenylcarbonyl; (C₁-C₃)-alkylphenylcarbonyl being the
 phenyl moiety substituted by at least a radical selected from the group
 consisting of (C₁-C₆)-alkyl and (C₁-C₆)-alkoxy; (C₁-C₁₂)-alkyl; halo(C₁-C₁₂)-
 alkyl; phenyl; phenyl substituted by at least a radical selected from the group
 consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and
 nitro; (C₁-C₃)-alkylphenyl; (C₁-C₃)-alkylphenyl, being the phenyl moiety
 substituted by at least a radical selected from the group consisting of (C₁-C₆)-
 alkyl and (C₁-C₆)-alkoxy; and a radical of formula -CH₂-CH₂-(O-CH₂-CH₂)_n-OH
 wherein n is an integer from 1 to 30;

30

35

$R_1, R_1', R_3, R_3', R_7$ and R_8 are the same or different;

R_1 and R_1' are the same as R_2 and R_2' , respectively;

5

R_5 is selected from the group consisting of H and (C₁-C₁₂)-alkyl;

R_6 is selected from the group consisting of (C₁-C₁₂)-alkyl and (C₁-C₃)-alkylphenyl; and

10

R_9 is selected from the group consisting of hydrogen and (C₁-C₁₂)-alkyl; and

R_{10} is selected from the group consisting of (C₁-C₁₂)-alkyl; phenyl; phenyl substituted by at least a radical selected from the group consisting of

15

halogen, (C₁-C₆)-alkyl, halo(C₁-C₆)-alkyl, nitro and (C₁-C₆)-alkoxy; (C₁-C₃)-alkylphenyl and (C₁-C₃)-alkylphenyl being the phenyl moiety substituted by at least a radical selected from the group consisting of (C₁-C₆)-alkyl and (C₁-C₆)-alkoxy.

20

2. The iodine compound according to claim 1, wherein

Y_1 and Y_2 are C-radicals, same or different, of one of the known ring systems with 1-4 rings, wherein each one of the rings forming said ring system

25

has 3-7 members, each member being independently selected from C, CH, and CH₂

is saturated, partially unsaturated or aromatic, and is isolated, partially or totally fused; and

$R_1, R_1', R_2, R_2', R_3, R_3', R_7$ and R_8 are radicals, same or different, independently selected from the group consisting of (C₁-C₁₂)-alkyl; halo(C₁-C₁₂)-alkyl; phenyl; phenyl substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and nitro; (C₁-C₃)-alkylphenyl; and (C₁-C₄)-alkyl-tri-(C₁-C₄)-alkyl silane; and

30

R_4 is a radical selected from the group consisting of (C₁-C₁₂)-alkylcarbonyl; halo(C₁-C₁₂)-alkylcarbonyl; phenylcarbonyl; phenylcarbonyl, being the phenyl moiety substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and nitro;

35

(C₁-C₃)-alkylphenylcarbonyl; (C₁-C₁₂)-alkyl; halo(C₁-C₁₂)-alkyl; phenyl; phenyl substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and nitro; and (C₁-C₃)-alkylphenyl.

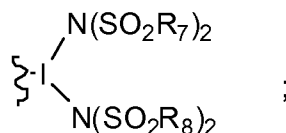
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3. The iodine compound according to any one of the preceding claims, wherein Y₁ and Y₂ are radicals, same or different, of one of the known ring systems with 1-2 rings, wherein each one of the rings forming said ring system

10 has 5-6 members, each member being independently selected from C, CH, and CH₂, is saturated, partially unsaturated or aromatic, and is isolated, partially or totally fused;

15 being each ring forming part of the ring system optionally substituted by at least one radical selected from the group consisting of: halogen, nitro, (C₁-C₁₂)-alkyl, halo(C₁-C₁₂)-alkyl, -OCH(R₅)C(O)Z, and a iodine-radical of formula (V).

20

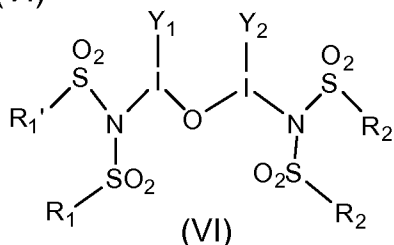


(V)

wherein Z, R₅, R₇, and R₈ are as defined in claim 1.

25 4. The iodine compound according to any one of the preceding claims, which is one of formula (VI)

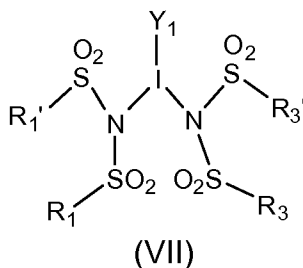
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wherein Y₁, Y₂, R₁, R₁', R₂ and R₂' are as defined in claim 1.

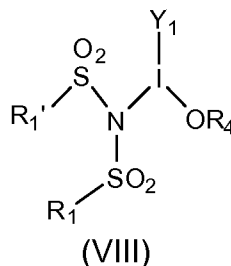
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5. The iodine compound according to any one of the claims 1-3, of formula (VII)



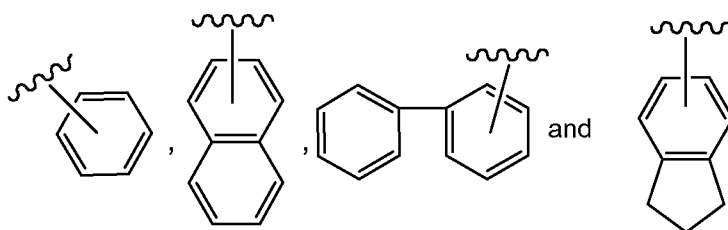
wherein Y_1 , R_1 , R_1' , R_3 and R_3' are as defined in claim 1.

6. The iodine compound according to any one of the claims 1-3, of formula (VIII)



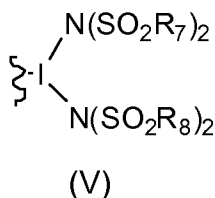
wherein Y_1 , R_1 , R_1' and R_4 are as defined in claim 1.

7. The iodine compound according to any one of the preceding claims , wherein Y_1 and Y_2 are known ring systems selected from the group consisting of:



wherein the wavy line indicates the position through which the ring radical binds to the iodine atom of the compound of formula (I),

said ring systems being optionally substituted by at least one radical selected from the group consisting of: methyl, $-CF_3$, nitro, $-OCH(R_5)C(O)Z$, and a iodine-radical of formula (V)



wherein

Z is selected from the group consisting of $-OR_6$ and $-NR_9R_{10}$; and

R_5 is selected from the group consisting of: hydrogen, methyl, ethyl, i-propyl and t-butyl;

R_6 is selected from the group consisting of: methyl, ethyl, i-propyl and t-butyl; and

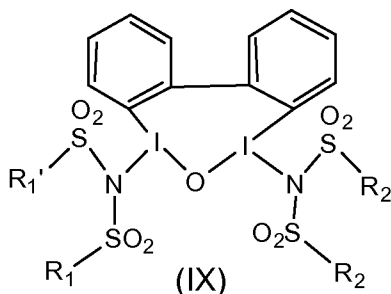
R_7 and R_8 are methyl; and

R_9 is hydrogen; and

R_{10} is 2,6-diisopropylphenyl.

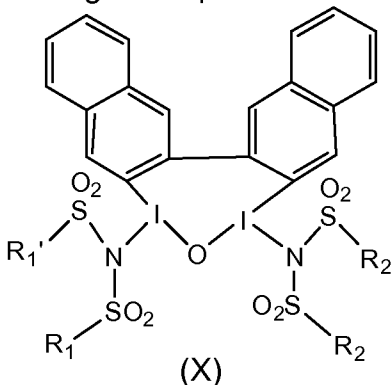
8. The iodine compound of formula (VI) according to any of the claims 1-4, wherein

Y_1 and Y_2 are phenyl radicals and are bound via a bond from one of the atoms forming the phenyl ring of Y_1 to one of the atoms forming the phenyl ring of Y_2 , thus forming a compound of formula (IX)



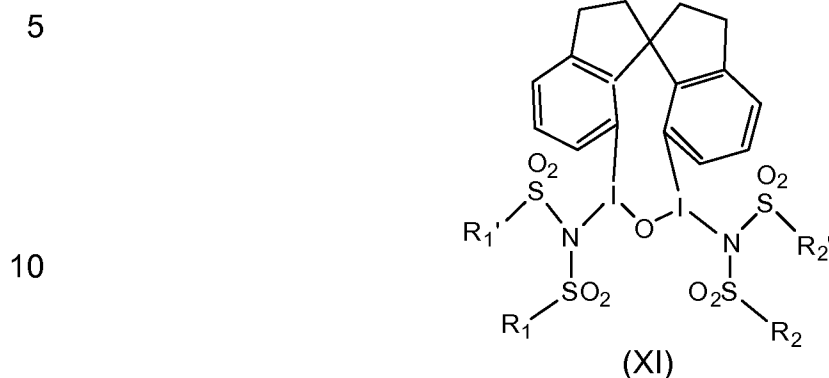
or,

Y_1 and Y_2 are naphthyl radicals and are bound via a bond from one of the atoms forming the naphthyl ring of Y_1 to one of the atoms forming the naphthyl ring of Y_2 , thus forming a compound of formula (X)



or,

Y_1 and Y_2 are 2,3-dihydro-1*H*-indenyl radicals and are bound via a common atom shared by both ring systems, thus forming a compound of formula (XI)



wherein R_1 , R_1' , R_2 and R_2' are as defined in claim 1.

- 15 9. The iodine compound according to any one of the preceding claims, wherein R_1 , R_1' , R_2 , R_2' , R_3 , and R_3' are radicals, independently selected from the group consisting of methyl, 4-nitrophenyl, triethylsilylethyl, and 4-methylphenyl; and R_4 is a radical selected from the group consisting of methylcarbonyl, trifluoromethylcarbonyl, ethylcarbonyl, isopropylcarbonyl, tert-butylcarbonyl, methyl, ethyl, isopropyl and tert-butyl.
- 20

10. The iodine compound according to any of the preceding claims, which is selected from the group consisting of:
- 25 μ -oxo-bis[bis(4-methyl-*N*-tosylbenzenesulfonamide)(phenyl)iodine(III)];
- μ -oxo-bis[bis(4-methyl-*N*-tosylbenzenesulfonamide)(4-nitrophenyl)iodine(III)];
- μ -oxo-bis[bis(4-methyl-*N*-tosylbenzenesulfonamide)(4-trifluoromethylphenyl)iodine(III)];
- 30 μ -oxo-[bis(4-methyl-*N*-tosylbenzenesulfonamide)(biphenyl-2,2'-yl)-bisiodine(III)];
- μ -oxo-bis[bis(4-methyl-*N*-tosylbenzenesulfonamide)(4-methylphenyl)iodine(III)];
- μ -oxo-bis[bis(*N*-mesylmethanesulfonamide)(phenyl)iodine(III)];
- μ -oxo-bis[bis(4-methyl-*N*-mesylbenzenesulfonamide)(phenyl)iodine(III)];
- 35 μ -oxo-bis[bis(4-nitro-*N*-mesylbenzenesulfonamide)(phenyl)iodine(III)];
- μ -oxo-bis[bis(4-methyl-*N*-tosylbenzenesulfonamide)(1,3-bis(*O*-((*R*)-2-methyl propionate))phen-2-yl]iodine(III)];

- μ -oxo-bis[bis(*N*-mesylmethanesulfonamide)(1,3-bis(*O*-((*R*)-2-methyl propionate))phen-2-yl]iodine(III)];
 μ -oxo-[bis(4-methyl-*N*-tosylbenzenesulfonamide)(1,1'-binaphthyl-2,2'-yl)-bis-iodine(III)];
 5 μ -oxo-[bis(*N*-mesylmethanesulfonamide)(1,1'-binaphthyl-2,2'-yl)-bis-iodine(III)];
 μ -oxo-[bis(*N*-mesylmethanesulfonamide)(7,7'-(2,2',3,3'-tetrahydro)1,1'-spirobi[indene])-bis-iodine(III)];
 10 μ -oxo-[bis(4-methyl-*N*-tosylbenzenesulfonamide)(7,7'-(2,2',3,3'-tetrahydro)1,1'-spirobi[indene])-bis-iodine(III)];
 bis(4-methyl-*N*-tosylbenzenesulfonamide)iodobenzene;
 bis(*N*-mesyl-methanesulfonamide)iodobenzene;
 tetrakis(4-methyl-*N*-tosylbenzenesulfonamide)-2,2'-diiodobiphenyl;
 acetoxy(4-methyl-*N*-tosylbenzenesulfonamide)iodo benzene;
 15 acetoxy(*N*-mesyl-methanesulfonamide)iodobenzene;
 acetoxy(4-methyl-*N*-tosylbenzenesulfonamide)iodo-4-methyl-benzene;
 acetoxy(4-methyl-*N*-mesyl-benzenesulfonamide) iodobenzene;
 acetoxy((*N*-mesylmethanesulfonamide)iodo-(2*R*,2'*R*)-dimethyl-2,2'-(1,3-phenylenebis(oxy))dipropanoate;
 20 acetoxy((*N*-mesylmethanesulfonamide)iodo-dimethyl-(1,3-phenylenebis(oxy))diacetate;
 methoxy(4-methyl-*N*-tosylbenzenesulfonamide)iodo-4-methyl-benzene; μ -oxo-bis[bis(4-methyl-*N*-tosylbenzenesulfonamide)(1,3-bis(*O*-((*R*)-2-(*N*, *N*-2,6-diisopropylphenyl) propanamide))phen-2-yl]iodine(III)];
 25 μ -oxo-bis[bis(4-methyl-*N*-tosylbenzenesulfonamide)(1,3-bis(*O*-((*R*)-2-isopropyl propionate))phen-2-yl]iodine(III)]; and
 μ -oxo-bis[bis(*N*-mesylmethanesulfonamide)(1,3-bis(*O*-((*R*)-2-methyl 3-methylbutanoate))phen-2-yl]iodine(III)].

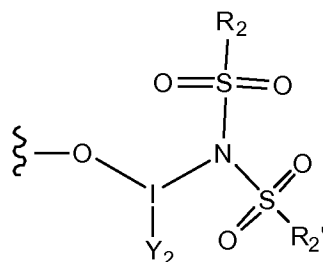
- 30 11. The iodine compound according to any of the preceding claims, which is methoxy(4-methyl-*N*-tosylbenzene sulfonamide)iodobenzene.

12. A process for the preparation of a iodine compound of formula (I) as defined in claim 1,

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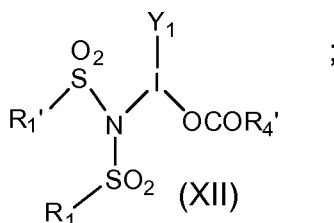
wherein:

a) when the compound of formula (I) is one where X is a radical of formula (II), and Y_1 is the same as Y_2 ,

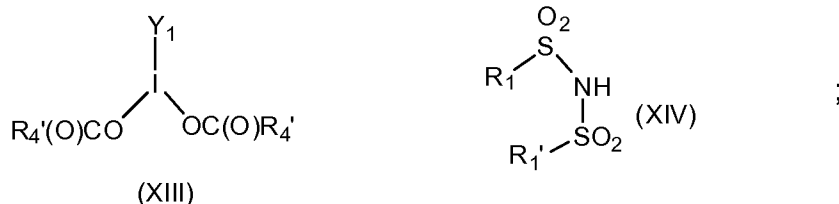


then the process comprises any of the steps (a.1) or (a.2):

(a.1) mixing a compound of formula (XII) with a solvent selected from the group consisting of: a protic solvent, an aprotic solvent and a mixture thereof,

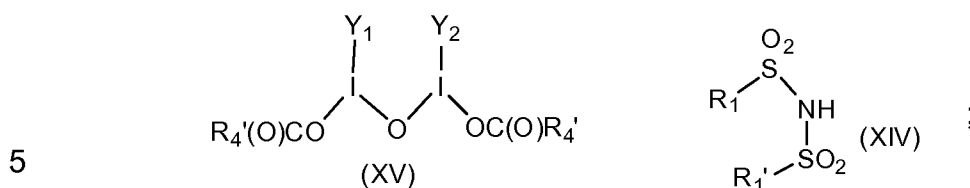


(a.2) mixing a compound of formula (XIII) with a compound of formula (XIV), in a solvent selected from the group consisting of: a protic solvent, an aprotic solvent and a mixture thereof



or, alternatively,

(b) when the compound of formula (I) is one where X is a radical of formula (II) and Y_1 and Y_2 are the same or different, then the process comprises the step of mixing a compound of formula (XV) with a compound of formula (XIV) and with a solvent selected from the group consisting of: a protic solvent, an aprotic solvent, and a mixture thereof;

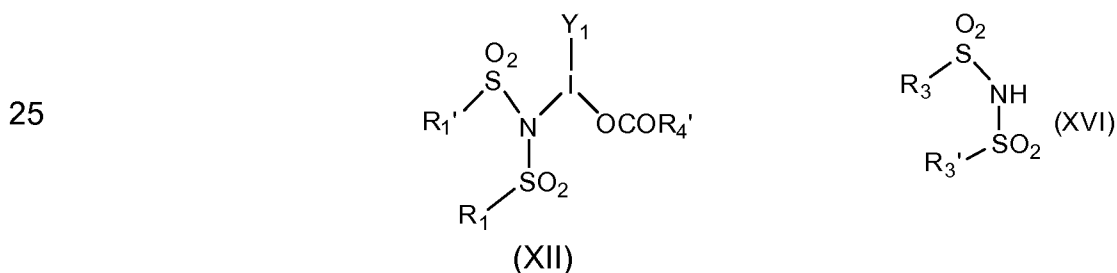


or, alternatively,

10 (c) when the compound of formula (I) is one where X is a radical of formula (III), and R_1 and R_1' are the same or different than R_3 and R_3' , respectively,



20 then the process comprises the step of mixing a compound of formula (VI) as defined in claim 5 or of formula (XII), with a compound of formula (XVI), with a solvent selected from the group consisting of: a protic solvent, an aprotic solvent, and a mixture thereof;

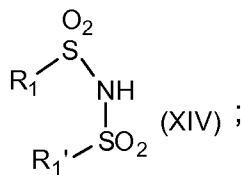
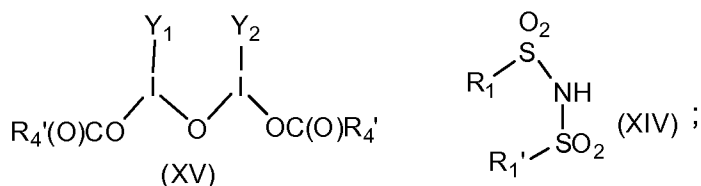


30 or, alternatively,

(d) when the compound of formula (I) is one where X is a radical of formula (III), and R_1 is the same as R_3 and R_1' is the same as R_3' , then the process comprises the step of mixing a compound of formula (XIV) with a compound of formula (XV) and a solvent selected from the group consisting of: a protic solvent, an aprotic solvent, and a mixture thereof;

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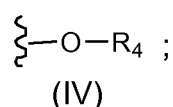
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or, alternatively,

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(e) when the compound of formula (I) is one where X is a radical of formula (IV),



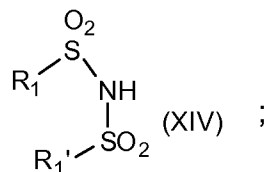
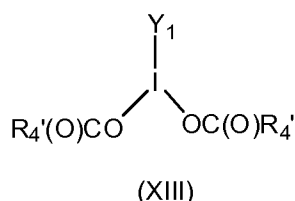
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wherein R_4 is selected from the group consisting of (C₁-C₁₂)-alkylcarbonyl; halo(C₁-C₁₂)-alkylcarbonyl; phenylcarbonyl; phenylcarbonyl, the phenyl moiety being substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and nitro; (C₁-C₃)-alkylphenylcarbonyl; and (C₁-C₃)-alkylphenylcarbonyl, being the phenyl moiety substituted by at least a radical selected from the group consisting of (C₁-C₆)-alkyl and (C₁-C₆)-alkoxy;

20

then the process comprises the step of mixing a compound of formula (XIII) with a compound of formula (XIV), and a solvent selected from the group consisting of: a protic solvent, an aprotic solvent, and a mixture thereof;

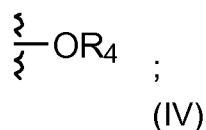
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or, alternatively,

30

(f) when the compound of formula (I) is one where X is a radical of formula (IV),



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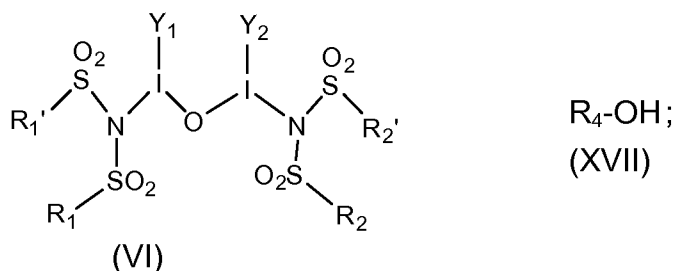
wherein R_4 is a radical selected from the group consisting of (C₁-C₁₂)-alkyl; halo(C₁-C₁₂)-alkyl; phenyl; phenyl substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl,

(C₁-C₆)-alkoxy, and nitro; (C₁-C₃)-alkylphenyl; (C₁-C₃)-alkylphenyl being the phenyl moiety substituted by at least a radical selected from the group consisting of (C₁-C₆)-alkyl and (C₁-C₆)-alkoxy; and a radical of formula -CH₂-CH₂-(O-CH₂-CH₂)_n-OH wherein n is an integer from 1 to 30;

5

then, the process comprises the step of mixing a compound of formula (VI), as defined above, with an organic alcohol of formula (XVII)

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15 wherein:

in the organic alcohol of formula (XVII), the R₄ radical is selected from the group consisting of: (C₁-C₁₂)-alkyl; halo(C₁-C₁₂)-alkyl; phenyl; phenyl substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and nitro;

(C₁-C₃)-alkylphenyl; (C₁-C₃)-alkylphenyl being the phenyl moiety substituted by at least a radical selected from the group consisting of (C₁-C₆)-alkyl and (C₁-C₆)-alkoxy and a radical of formula -CH₂-CH₂-(O-CH₂-CH₂)_n-OH wherein n is an integer from 1 to 30;

R₁, R₁', R₂, R₂', R₃, R₃', Y₁ and Y₂ are as defined in claim 1; and R₄' is a radical selected from the group consisting of (C₁-C₁₂)-alkyl; halo(C₁-C₁₂)-alkyl; phenyl; phenyl substituted by at least a radical selected from the group consisting of halo(C₁-C₆)-alkyl, halogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy, and nitro; (C₁-C₃)-alkylphenyl; and (C₁-C₃)-alkylphenyl being the phenyl moiety substituted by at least a radical selected from the group consisting of (C₁-C₆)-alkyl and (C₁-C₆)-alkoxy.

13. Use of a compound as defined in any one of the claims 1-11 as amination agent.

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14. A process for the amination of a substrate, the process comprising the step of adding the substrate to the mixing step comprised in any of the

processes defined in claim 12, and wherein

the substrate is selected from the group consisting of an alkene, an alkyne, an enolizable ketone compound and an allyl derivative; and

the amination is carried out in the absence of a catalyst.

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15. A process for the diamination of an alkene, the process comprising the step of mixing the alkene with a iodine compound of formula (I) as defined in any of the claims 1-11, in the presence of a solvent selected from the group consisting of: a protic solvent, an aprotic solvent, and a mixture thereof.

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16. A process for the α -amination of a ketone compound, the process comprising the step of mixing the ketone compound with a iodine compound of formula (I) as defined in any of the claims 1-11, and with a bissulfonylimide compound when X is a radical of formula (IV), in the presence of a solvent
15 selected from the group consisting of: a protic solvent, an aprotic solvent, and a mixture thereof.

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17. A process for the amination of an alkyne, the process comprising the step of mixing the alkyne with a iodine compound as defined in any one of the claims 1-11 which corresponds to a compound of formula VIII, in the presence of a solvent selected from the group consisting of: a protic solvent, an aprotic solvent, and a mixture thereof.

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18. A process for the amination of an aryl substrate, the process comprising the step of adding the substrate to the mixing step comprised in any of the processes defined in claim 12.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/059638

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D209/48 C07D347/00 C07C209/60 C07C311/48 C07C315/04
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D C07C

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

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

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	HYUN JIN KIM ET AL: "Intermolecular Oxidative C-N Bond Formation under Metal-Free Conditions: Control of Chemoselectivity between Aryl sp² and Benzylic sp³ C-H Bond Imidation", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 133, no. 41, 20 September 2011 (2011-09-20), pages 16382-16385, XP055014610, ISSN: 0002-7863, DOI: 10.1021/ja207296y table 4 ----- -/--	18



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

13 June 2012

Date of mailing of the international search report

26/06/2012

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/059638

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ÁLVARO IGLESIAS ET AL: "An Intermolecular Palladium-Catalyzed Diamination of Unactivated Alkenes", ANGEWANDTE CHEMIE. INTERNATIONAL EDITION, WILEY VCH VERLAG, WEINHEIM, vol. 49, no. 44, 25 October 2010 (2010-10-25), pages 8109-8111, XP002620150, ISSN: 1433-7851, DOI: 10.1002/ANIE.201003653 [retrieved on 2010-09-22] tables 1,2	1-18
A	----- KILIAN MUÑIZ ET AL: "Intermolecular Regioselective 1,2-Diamination of Allylic Ethers", ADVANCED SYNTHESIS & CATALYSIS, vol. 353, no. 5, 15 March 2011 (2011-03-15), pages 689-694, XP055014613, ISSN: 1615-4150, DOI: 10.1002/adsc.201000813 the whole document -----	14,15,18