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(54) Title: METHOD FOR PREPARATION OF CYANO COMPOUNDS OF BORON WITH A BRONSTEDT ACID

(57) Abstract: The invention discloses a method for preparation of cyano compounds of boron with 1, 2, 3 or 4 cyano residues, represented by formula (I): $[Cat^{n+}]\ [(BF_{4-m}(CN)m)^{-}]_n$ by a reaction of compound of formula (A1) with trimethylsilylcyanide in the presence of a Bronstedt acid; $[Cat^{n+}]\ [(BF_4)^{-}]_n$ (A1); n+ Cat is a cation, m is 1, 2, 3 or 4 and n is 1, 2, 3 or 4. In a specific embodiment, the method is for prepration of the following three compounds: $[(n\text{-}Bu)_4N][BF(CN)_3]$ (1), $[(n\text{-}Pr)_3NH][BF(CN)_3]$ (2), $[(n\text{-}Pr)_3NH][B(CN)_4]$ (3).

METHOD FOR PREPARATION OF CYANO COMPOUNDS OF BORON WITH A BRONSTEDT ACID

The invention discloses a method for preparation of cyano compounds of boron with 1, 2, 3 or 4 cyano residues, represented by formula (I),

$$[Cat^{n+}]\,[(BF_{4-m}(CN)_m)^-]_n \qquad (I)$$

by a reaction of compound of formula (A1) with trimethylsilylcyanide in the presence of a Bronstedt acid;

$$[Cat^{n+}]\,[(BF_4)^-]_n \qquad (A1)$$

Cat^{n+} is a cation, m is 1, 2, 3 or 4 and n is 1, 2, 3 or 4.

BACKGROUND OF THE INVENTION

The term "ionic liquid" (IL) is usually used to refer to a salt which is liquid at temperatures below 100°C, in particular at room temperature. Such liquid salts typically comprise organic cations and organic or inorganic anions, and are described inter alia in P. Wasserscheid et al., Angew. Chem., 2000, 112, 3926-3945.

Ionic liquids have a series of interesting properties: Usually, they are thermally stable, relatively non-flammable and have a low vapor pressure. They show good solvability for numerous organic and inorganic substances. In addition, ionic liquids have interesting electrochemical properties, for example electrical conductivity which is often accompanied by a high electrochemical stability.

These attributes give rise to many applications of ionic liquids: They can be used for example as solvent in synthesis, as electrolyte, as lubricant and as hydraulic fluid. Moreover they serve as phase-transfer catalyst, as extraction medium, as heat-transfer medium, as surface-active substance, as plasticizer, as conductive salt, organic salt or additive in electrochemical cells, as electrolyte, as component in electrolyte formulations, wherein such electrolyte formulation comprising an ionic liquid is preferably used in electrochemical and/or optoelectronic device such as a photovoltaic cell, a light emitting device, an electrochromic or photo-electrochromic device, an electrochemical sensor and/or biosensor, particularly preferred in a dye sensitized solar cell.

Therefore, there is a fundamental need for ionic liquids having a variety of properties which open up additional opportunities for their use.

An interesting family of ionic liquids contains tetravalent boron anions. Tetrafluoroborate containing ionic liquids were among the first of this new generation of compounds and 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm][BF_4]) was prepared via metathesis of [EMIm]I with Ag[BF_4] in methanol as disclosed by J. S. Wilkes et al., J. Chem. Soc. Chem. Commun. 1990, 965.

WO 2014/029833 A1 a method for the preparation of tetra alkylammonium and tetra alkylphosphonium tricyanidofluoroborate starting from tetraalkylammonium or tetra alkylphosphonium tetrafluoroborate and trimethylsilylcyanide. Exemplified are inter alia [$(nBu)_4N$], [Me_4N] and [$(nOct)_4N$] as ammonium ions. Bronstedt acid is not disclosed.

EP 2772495 A1 discloses a method for the preparation of tricyanidofluoroborate in two steps via tetra alkylammonium and tetra alkylphosphonium tricyanidofluoroborate, starting from tetraalkylammonium or tetra alkylphosphonium tetrafluoroborate and trimethylsilylcyanide in the first step and exchanging the cation in the second step. Exemplified are inter alia [(nBu)4N], [Me4N] and [(nOct)4N] as ammonium ions. Bronstedt acid is not disclosed.

WO 2014/029834 A1 discloses a method for the preparation of tetra alkylammonium tetracyanidoborate starting from tetraalkylammonium tetrafluoroborate and trimethylsilylcyanide. Exemplified are inter alia [(nBu)4N] and [(nOct)4N] as ammonium ions. Bronstedt acid is not disclosed.

Jan A. P. Sprenger et al., Inorg. Chem. 2015, 54, 3403-3412, discloses a method for producing K[$BF(CN)_3$] from Na[BF_4] and TMS-CN using TMS-Cl as catalyst, see scheme 2. lt discloses that TMS-Cl plays the role of a catalysts that enables a cleaner reaction, page 3406, right column. Bronstedt acid is not disclosed.

E. Bernhardt, Z. Anorg. Allg. Chem. 2003, 629, 677-685, discloses the reaction of M[BF_4] (M = Li, K) with $(CH_3)_3SiCN$ (TMSCN). The preparation of Li[$BF(CN)_3$] is disclosed to take 7 days, that of K[$BF(CN)_3$] takes one month. The yield of K[$BF(CN)_3$] was 60%, the product

contained 5% $K[BF_2(CN)_2]$. The molar ratio of $[BF_4]^-$: TMSCN was 1 : 7.8. Bronstedt acid is not disclosed.

Darrick Williams et al., J. Am. Chem. Soc. 2000, 122, 7735-7741, discloses a method for producing $Li[B(CN)_4]$ from $Li[BF_4]$ and TMS-CN, see page 7740, compound 1. Bronstedt acid is not disclosed.

E. Bernhardt et al., Z. Anorg. Allg. Chem. 2003, 629, 1229-1234, discloses a sintering process for the preparation of $LiB(CN)_4$ and $KB(CN)_4$ at temperatures of 280 to 340°C; other cations can be introduced starting from e.g. $KB(CN)_4$ by metathesis. Bronstedt acid is not disclosed.

T. Kueppers et al., Inorg. Chem. 2005, 44, 1015-1022, discloses also teh use of teh sintering process, which is disclosed in E. Bernhardt et al., Z. Anorg. Allg. Chem. 2003, 629, 1229-1234, for teh preparation of $KB(CN)_4$. Bronstedt acid is not disclosed.

EP 2 327 707 A claims in claim 7 a method for producing an ionic compound represented by the general formula (I), comprising a step of reacting starting materials containing a cyanide and a boron compound. General formula (I) is a salt of a cation Kt^{m+} with $[B(CN)_4]^-$.

The examples disclose various methods for preparing tetrabutylammonium tetracyanoborate, for example:

1) Example 1-1 of EP 2 327 707 A discloses a reaction of tetrabutylammonium bromide, zinc (II) cyanide and boron tribromide in toluene at 130°C for 2 days, with a yield of 35%. The molar ratio of boron compound : TMSCN was 1 : 5.5.

2) Example 2-1 of EP 2 327 707 A discloses a reaction of tetrabutylammonium bromide, tetrabutylammonium cyanide and boron tribromide in toluene at 130°C for 2 days, with a yield of 77%. The molar ratio of boron compound : tetrabutylammonium cyanide was 1 : 7.1.

3) Example 3-3 of EP 2 327 707 A discloses a reaction of tetrabutylammonium bromide, trimethylsilyl cyanide and boron trichloride in p-xylene at 150°C for 30 hours, with a yield of 98%. The molar ratio of boron compound : TMSCN was 1 : 5.5.

4) Example 3-11 of EP 2 327 707 A discloses a reaction of boron trifluoride diethyl ether, tetrabutylammonium bromide and trimethylsilylcyanide at 170°C for 30 hours, with a yield of 75%.

But not all embodiments which fall under claim 7 actually work well: Example 3 of the instant invention shows one embodiment also starting with boron trifluoride diethyl ether,

which falls under claim 7, but produces the desired $[B(CN)_4]$ salt only as a by-product in negligible amounts, the main product is a $[BF(CN)_3]$ salt.

There was a need for a simplified method with high yield and satisfactory purity for the preparation of fluoro cyanide compounds of boron with the anion having the general formula $[(BF_{4-m}(CN)_m)^-]$ with m being 1, 2, 3 or 4. The boron source should be a readily available compound with low costs. The cyanide source should not be a metal cyanide to avoid its negative impact on the environment. The number of reactants should be small and the method should allow the conversion without the presence of a solvent. The content of Cl and Br in the final product should be low. Also the content of Si and cyanide in the final product should be low. The method should require as few steps as possible. The method should allow also the preparation of compounds with m being 1, 2, 3 or 4 and not only of either a compound with m being 3 or a compound with m being 4. The method should avoid the use of Cl_2, AgCN or $AgBF_4$. The method should provide stable compounds of said formula which can be used as ionic liquids or as precursors of ionic liquids and can be used e.g. in electrolyte formulations and in electrochemical or optoelectronic devices. These compounds should be able to be disposed of in an environmentally friendly manner after use.
The method should allow the preparation of the desired compounds in high yields and under mild conditions with respect to methods disclosed in the prior art.

This object is achieved by a method using trimethylsilylcyanide as CN source and by doing the reaction in the presence of a Bronstedt acid. No Cl_2, AgCN or $AgBF_4$ is required. The content of Cl, Br, Si and cyanide in the final product is low. Another advantage is that the reaction does not require mandatorily an extra solvent. The method has a reduced number of steps compared to the methods known from the prior art. The method allows for the preparation not only of compounds with m being only 3 or only 4, but for compounds with n being 1, 2, 3 or 4. These compounds can be prepared specifically and individually, and not only as mixtures. The reaction can be done under milder conditions than those used in the methods of the prior art, the reaction can be done at lower temperature or in shorter time.

In this text, the following meanings are used, if not otherwise stated:

alkyl	linear or branched alkyl;
C_{1-q} alkyl	refers to any alkyl residue which contains from 1 to q carbon atoms; for example C_{1-6} alkyl encompasses inter alia methyl, ethyl, propyl, isopropyl, n-

butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl (3-methylbutyl), neopentyl (2,2-dimethylpropyl), n-hexyl and isohexyl (4-methylpentyl);

C_{2-q} alkenyl refers to an alkenyl residue which contains from 2 to q carbon atoms and contains at least one double bond, the carbon chain can be linear or branched; for example C_{2-4} alkenyl encompasses inter alia ethenyl, 1-methylethenyl, prop-1-enyl, prop-2-enyl, 2-methylprop-2-enyl and buta-1,3-dienyl;

C_{2-q} alkynyl refers to an alkynyl residue which contains from 2 to q carbon atoms and contains at least one triple bond, the carbon chain can be linear or branched; for example C_{2-4} alkynyl encompasses inter alia ethynyl, prop-1-ynyl and prop-2-ynyl;

C_{6-10} aryl refers to an aryl residue which has from 6 to 10 carbon atoms and is unsubstituted or substituted by 1, 2, 3 or 4 identical or different substituents independently from each other selected from the group consisting of C_{1-4} alkyl and C_{1-4} alkoxy; for example C_{6-10} aryl encompasses inter alia phenyl, methylphenyl, methoxyphenyl, dimethylphenyl, ethylmethylphenyl, diethylphenyl and naphthyl;

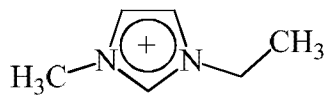
cyclic alkyl or cycloalkyl include cyclo and polycyclo, such as bicyclo or tricyclo, aliphatic residues;

C_{3-q} cycloalkyl refers to a cycloalkyl group having from 3 to q carbon atoms; for example C_{3-10} cycloalkyl encompasses inter alia cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl and cyclodecyl;

C_{1-q} alkoxy refers to an linear or branched alkoxy group having from 1 to q carbon atoms; for example C_{1-20} alkoxy encompasses inter alia methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy, sec-butoxy, tert-butoxy, pentyloxy, 1,4-dimethylpentyloxy, hexyloxy, heptyloxy, octyloxy, 1,5-dimethylhexyloxy, nonyloxy, decyloxy, 4-ethyl-1,5-dimethylhexyloxy, undecyloxy, dodecyloxy, tridecyloxy, tetradecyloxy and eicosyloxy;

alkylene means a linear or branched alkylene group; e.g. propylene, and e.g. propylene can be connected via its C1 and C2 carbon atoms (a branched alkylene group), or via its C1 and C3 carbon atoms (linear alkylene group);

DCM dichloromethane;

EMIm 1-ethyl-3-methylimidazolium 

eq. molar equivalent;

halide F^-, Cl^-, Br^- or I^-, preferably F^-, Cl^- or Br^-, more preferably Cl^-;

halogen F, Cl, Br or I; preferably F, Cl or Br;

IL ionic liquid;

"linear" and "n-" are used synonymously with respect to the respective isomers of alkanes;

RT room temperature, it is used synonymously with the expression ambient temperature;

T_{dec} decomposition temperature;

THF tetrahydrofuran;

TMSCN $(CH_3)_3SiCN$, i.e. trimethylsilylcyanide;

triflic acid trifluoromethanesulfonic acid, CF_3SO_3H;

Trityl means the trityl cation, i.e. $[Ph_3C]^+$;

"wt%", "% by weight" and "weight-%" are used synonymously and mean percent by weight.

The expressions dye sensitized solar cell and photosensitized solar cell are used synonymously.

SUMMARY OF THE INVENTION

Subject of the invention is a method for the preparation of compound of formula (I);

$$[Cat^{n+}]\,[(BF_{4-m}(CN)_m)^-]_n \qquad (I)$$

the method comprises a step STEP1;

STEP1 comprises a reaction REAC1, wherein compound of formula (A1)

$$[Cat^{n+}]\,[(BF_4)^-]_n \qquad (A1)$$

is reacted with trimethylsilylcyanide in the presence of a compound CATACID;

CATACID is selected from the group consisting of HF, HCl, HBr, HI, HNO_3, H_2SO_3, H_2SO_4, $NaHSO_4$, Oleum, $KHSO_4$, $NaHCO_3$, $KHCO_3$, H_3PO_4, H_3PO_3, HSO_3F, HSO_3Cl, CH_3COOH, CF_3COOH, $C(Cl_3)COOH$, methansulfonic acid, HCOOH, AR-COOH, AR-SO_3H, $C(OH)(COOH)_3$, CF_3SO_3H, HCN, HOCN, HSCN, HSeCN, HNCO, HNCS, HN_3, HQ20(X1)4, polymolybdate, polytungstate, $HQ21(X1)_6$, and mixtures thereof;

AR is Phe or Phe substituted with 1, 2 or 3 identical or different residues selected from the group consisting of halogen and CH_3;

Q20 is B, Al, Ga, In or Th;

Q21 is P, As, Sb or Bi;

X1 is halogen;

m is 1, 2, 3 or 4;

n is 1, 2, 3 or 4;

Cat^{n+} is selected from the group consisting of inorganic cation $CatINORG^{n+}$ and organic cation $CatORG^{n+}$;

$CatINORG^{n+}$ is a cation selected from the 1., 2., 3., 4., 5., 6., 7., 8., 9., 10., 11., 12., 13., 14., 15. or 16. group of the periodic table, or is a cation from the lanthanides or is a cation from the actinides or is NH_4^+;

$CatORG^{n+}$ is selected from the group consisting of CatORG-A^+, CatORG-B^+, CatORG-C^+, $[(CH_3)_3SiFSi(CH_3)_3]^+$, Ph_3C^+, guanidinium and $(H_2(R18)N\text{-}R16\text{-}N(R19)H_2)^{2+}$;

CatORG-A^+ is $(WR2R3R4R5)^+$,

wherein

W is a nitrogen or phosphorus; and

(i) R2, R3, R4 and R5 are identical or different and independently from each other selected from the group consisting of H, C_{1-20} alkyl, C_{1-20} perfluoroalkyl, C_{3-10} cycloalkyl and C_{6-10} aryl, with the proviso, that at least one of the residues R2, R3, R4 and R5 is not H; or

(ii) R2 and R3 together are a hydrocarbon chain and form together with W a 5- to 7-membered saturated or unsaturated heterocyclic ring,

R4 and R5 are identical or different and independently from each other selected from the group consisting of H, C_{1-20} alkyl, C_{1-20} perfluoroalkyl, C_{3-10} cycloalkyl and C_{6-10} aryl; or

(iii) R2 and R3 together are a hydrocarbon chain and form together with W, and R4 and R5 together are a hydrocarbon chain and form together with W, independently from each other, 5- to 7-membered saturated or unsaturated heterocyclic rings;

CatORG-B^+ is $(XR6R7R8)^+$,

wherein

X is nitrogen,

R6 and R7 together are a hydrocarbon chain and form together with X a 5- to 7-membered unsaturated heterocyclic ring in which X is connected by a single bond and a double bond to R6 and R7 respectively,

R8 is selected from the group consisting of H, C_{1-20} alkyl, C_{2-8} alkenyl, C_{1-20} perfluoroalkyl, C_{3-10} cycloalkyl or C_{6-10} aryl;

CatORG-C^+ is $(YR9R10R11)^+$,

wherein

Y is sulphur;

(i) R9, R10 and R11 are identical or different and independently from each other selected from the group consisting of H, C_{1-20} alkyl, C_{1-20} perfluoroalkyl, C_{3-10} cycloalkyl and C_{6-10} aryl; or

(ii) R9 and R10 together are a hydrocarbon chain and form together with Y a 5- to 7-membered saturated or unsaturated ring,

R11 is selected from the group consisting of H, C_{1-20} alkyl, C_{1-20} perfluoroalkyl, C_{3-10} cycloalkyl and C_{6-10} aryl;

the residues R2, R3, R4, R5, R6, R7, R8, R9, R10 and R11 are, independently from each other, unsubstituted or, where applicable, substituted by 1, 2, 3, 4, 5 or 6 substituents selected from the group consisting of C_{1-4} alkyl, C_{3-10} cycloalkyl, C_{2-8} alkenyl, phenyl, benzyl, halogen, cyano and C_{1-4} alkoxy;

in any of said hydrocarbon chains formed by R2 and R3, by R4 and R5, by R6 and R7, and by R9 and R10, 1 or 2 carbon atoms of said hydrocarbon chains can be exchanged for 1 or 2 heteroatoms respectively, said one or two heteroatoms being selected from the group consisting of O, N and S; in case of an exchange for N, this N is unsubstituted or

substituted by a residue selected from the group consisting of C_{1-8} alkyl, C_{3-10} cycloalkyl, C_{2-8} alkenyl and C_{1-8} perfluoroalkyl;

R16 is selected from the group consisting of C_{2-8} alkylen, C_{3-8} cycloalkylen, phenylen, C(H)(phenyl), $R17(-O-R17)_{n1}$;

R17 is selected from the group consisting of CH_2-CH_2, CH_2-CH_2-CH_2, CH_2-$C(H)(CH_3)$-CH_2, CH_2-CH_2-$C(H)(CH_3)$ and CH_2-CH_2-CH_2-CH_2;

R18 and R19 are identical or different and independently from each other selected from the group consisting of H, C_{1-8} alkyl, C_{3-8} cycloalkyl, phenyl and benzyl;

n1 is an integer from 1 to 20.

DETAILED DESCRIPTION OF THE INVENTION

Preferably, m is 2, 3 or 4;

more preferably, m is 3 or 4;

also in connection with any of the embodiments disclosed in the specification.

Preferably, n is 1 or 2, also in connection with any of the embodiments disclosed in the specification.

Preferably, CATACID is selected from the group consisting of HF, HCl, HBr, H_2SO_4, $NaHSO_4$, Oleum, $KHSO_4$, H_3PO_4, HSO_3F, HSO_3Cl, CH_3COOH, CF_3COOH, $C(Cl_3)COOH$, methansulfonic acid, HCOOH, AR-SO_3H, $C(OH)(COOH)_3$, CF_3SO_3H, HCN, HQ20(X1)4, polymolybdate, polytungstate, $HQ21(X1)_6$, and mixtures thereof;

AR is Phe or Phe substituted with 1, 2 or 3 identical or different residues selected from the group consisting of halogen and CH_3;

Q20 is B, Al or Ga;

Q21 is P, Sb or Bi;

X1 is F, Cl or Br.

More preferably, CATACID is selected from the group consisting of HF, HCl, HBr, H_2SO_4, Oleum, H_3PO_4, HSO_3F, HSO_3Cl, CH_3COOH, CF_3COOH, methansulfonic acid, AR-SO_3H, CF_3SO_3H, HCN, HQ20(X1)4, polymolybdate, polytungstate, and mixtures thereof;

AR is Phe substituted with 1 residue selected from the group consisting of F, Cl and CH_3;

Q20 is B, Al or Ga;

X1 is F, Cl or Br.

Even more preferably, CATACID is selected from the group consisting of HF, HCl, H_2SO_4, Oleum, H_3PO_4, HSO_3F, HSO_3Cl, CH_3COOH, CF_3COOH, methansulfonic acid, AR-SO_3H, CF_3SO_3H, HCN, HQ20(X1)4, and mixtures thereof;

AR is Phe substituted with 1 residue selected from the group consisting of F, Cl and CH_3;

Q20 is B, Al or Ga;

X1 is F or Cl.

Especially, CATACID is selected from the group consisting of HF, HCl, H_2SO_4, Oleum, HSO_3F, HSO_3Cl, CF_3COOH, methansulfonic acid, AR-SO_3H, CF_3SO_3H, and mixtures thereof;

AR is Phe substituted with CH_3.

More especially, CATACID is CF_3SO_3H.

Preferably, $CatINORG^{n+}$ is a cation selected from the 1., 2., 3., 4., 5., 6., 7., 8., 9., 10., 11., 12., 13., 14. or 15. group of the periodic table or is a cation from the lanthanides or is NH_4^+;

more preferably, $CatINORG^{n+}$ is a cation selected from the 1., 2., 4., 5., 6., 7., 8., 9., 10., 11., 12., 13., 14. or 15. group of the periodic table or is a cation from the lanthanides or NH_4^+;

even more preferably, $CatINORG^{n+}$ is selected from the group consisting of Li^+, Na^+, K^+, Rb^+, Cs^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ti^{4+}, Ti^{3+}, Zr^{4+}, Zr^{3+}, Hf^{4+}, Hf^{3+}, V^{4+}, V^{3+}, V^{2+}, Nb^{4+}, Ta^{4+}, Cr^{3+}, Mo^{4+}, Mo^{3+}, Mo^{2+}, W^{4+}, W^{3+}, W^{2+}, Mn^{4+}, Mn^{3+}, Mn^{2+}, Fe^{4+}, Fe^{3+}, Fe^{2+}, Ru^{4+}, Ru^{3+}, Ru^{2+}, Os^{4+}, Os^{3+}, Os^{2+}, Co^{4+}, Co^{3+}, Co^{2+}, Rh^{4+}, Rh^{3+}, Ir^{4+}, Ir^{3+}, Ni^{4+}, Ni^{3+}, Ni^{2+}, Pd^{4+}, Pd^{3+}, Pd^{2+}, Pt^{4+}, Pt^{3+}, Pt^{2+}, Cu^{4+}, Cu^{3+}, Cu^{2+}, Cu^+, Ag^{4+}, Ag^{3+}, Ag^{2+}, Ag^+, Au^{3+}, Au^{2+}, Au^+, Zn^{2+}, Zn^+, Cd^{2+}, Cd^+, Hg^{2+}, Hg^+, B^{3+}, Al^{3+}, Ga^{3+}, Ga^+, In^{3+}, In^+, Tl^{3+}, Tl^+, Ge^{4+},Ge^{2+}, Sn^{4+},Sn^{2+}, Pb^{4+}, Pb^{2+}, As^{3+}, Sb^{3+}, Bi^{3+}, Bi^{1+}, La^{3+}, Nb^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, and NH_4^+;

especially, $CatINORG^{n+}$ is selected from the group consisting of Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ti^{4+}, Ti^{3+}, Zr^{4+}, Zr^{3+}, V^{4+}, V^{3+}, V^{2+}, Cr^{3+}, Mo^{4+}, Mo^{3+}, Mo^{2+}, W^{4+}, W^{3+}, W^{2+}, Mn^{4+}, Mn^{3+}, Mn^{2+}, Fe^{4+}, Fe^{3+}, Fe^{2+}, Ru^{4+}, Ru^{3+}, Ru^{2+}, Co^{4+}, Co^{3+}, Co^{2+}, Rh^{4+}, Rh^{3+}, Ir^{4+}, Ir^{3+}, Ni^{4+},

Ni^{3+}, Ni^{2+}, Pd^{4+}, Pd^{3+}, Pd^{2+}, Pt^{4+}, Pt^{3+}, Pt^{2+}, Cu^{4+}, Cu^{3+}, Cu^{2+}, Cu^{+}, Ag^{4+}, Ag^{3+}, Ag^{2+}, Ag^{+}, Zn^{2+}, Zn^{+}, Al^{3+}, Ga^{3+}, Ga^{+}, In^{3+}, In^{+}, Sn^{4+},Sn^{2+}, Pb^{4+}, Pb^{2+}, Sb^{3+}, Nb^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, and NH_4^{+};

more especially, $CatINORG^{n+}$ is selected from the group consisting of Li^{+}, Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Ti^{4+}, V^{4+}, V^{3+}, V^{2+}, Cr^{3+}, Fe^{4+}, Fe^{3+}, Fe^{2+}, Co^{4+}, Co^{3+}, Co^{2+}, Cu^{4+}, Cu^{3+}, Cu^{2+}, Cu^{+}, Ag^{2+}, Ag^{+}, Zn^{2+}, Zn^{+}, Al^{3+}, Sn^{4+},Sn^{2+}, Pb^{4+}, Pb^{2+}, Sb^{3+}, Eu^{3+}, Gd^{3+}, and NH_4^{+};

even more especially, $CatINORG^{n+}$ is selected from the group consisting of Li^{+}, Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Ti^{4+}, V^{4+}, V^{3+}, Cr^{3+}, Fe^{4+}, Fe^{3+}, Fe^{2+}, Co^{4+}, Co^{3+}, Co^{2+}, Cu^{4+}, Cu^{3+}, Cu^{2+}, Cu^{+}, Ag^{+}, Zn^{2+}, Al^{3+}, Sn^{4+},Sn^{2+}, Pb^{4+}, Pb^{2+}, Gd^{3+}, and NH_4^{+};

in particular, $CatINORG^{n+}$ is selected from the group consisting of Li^{+}, Na^{+}, K^{+}, NH_4^{+}, Ag^{+}, Mg^{2+}, Ca^{2+}, Zn^{2+} and Cu^{2+};

more in particular, $CatINORG^{n+}$ is selected from the group consisting of Li^{+}, Na^{+}, K^{+}, NH_4^{+}, Ag^{+}, Mg^{2+}, Ca^{2+} and Zn^{2+};

even more in particular, $CatINORG^{n+}$ is Li^{+}, Na^{+}, K^{+}, Ag^{+}, Mg^{2+}, or Zn^{2+};

especially in particular, $CatINORG^{n+}$ is Li^{+}, K^{+}, Ag^{+}, Mg^{2+}, or Zn^{2+};

more especially in particular, $CatINORG^{n+}$ is Li^{+}, K^{+} or Ag^{+}.

Preferably, n in $CatInORG^{n+}$ is 1 or 2.

The term "where applicable" in the definition of $CatORG^{n+}$ means, that any of the optional substituents of the residues R2 to R11 requires a respective site, and e.g. in case of R2 being a perfluorinated side chain no respective site is available any more for a substituent.

Preferably, $CatORG^{n+}$ contains a heteroatom selected from the group consisting of nitrogen, phosphorus, sulfur and oxygen;

more preferably, $CatORG^{n+}$ contains a heteroatom selected from the group consisting of nitrogen and phosphorus.

Preferably,

R16 is selected from the group consisting of C_{2-6} alkylen, C_{5-6} cycloalkylen, phenylen, C(H)(phenyl), $R17(-O-R17)_{n1}$;

R17 is selected from the group consisting of CH_2-CH_2, CH_2-CH_2-CH_2 and CH_2-CH_2-CH_2-CH_2;

R18 and R19 are identical or different and independently from each other selected from the group consisting of H, C_{1-4} alkyl, C_{5-6} cycloalkyl, phenyl and benzyl;

n1 is an integer from 1 to 10;

more preferably,

R16 is selected from the group consisting of C_{2-4} alkylen, C_6 cycloalkylen, phenylen, C(H)(phenyl), R17(-O-R17)$_{n1}$;

R17 is selected from the group consisting of CH_2-CH_2 and CH_2-CH_2-CH_2;

R18 and R19 are identical and selected from the group consisting of H, C_{1-4} alkyl, C_{5-6} cycloalkyl, phenyl and benzyl;

n1 is an integer from 1 to 6;

even more preferably, for n being 2 $CatORG^{n+}$ is $(H_2(R18)N\text{-}R16\text{-}N(R19)H_2)^{2+}$;

R16 is selected from the group consisting of C_{2-4} alkylen, phenylen and C(H)(phenyl);

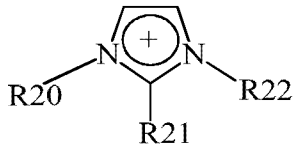
R18 and R19 are identical and selected from the group consisting of H, C_{1-4} alkyl, C_{5-6} cycloalkyl, phenyl and benzyl;

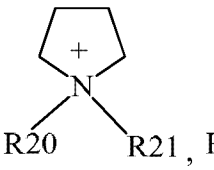
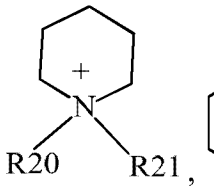
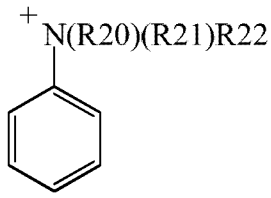
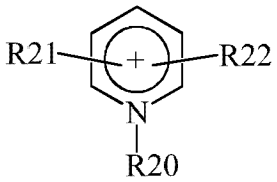
especially, when n is 2, then $CatORG^{n+}$ is $(H_3N\text{-}CH_2\text{-}CH_2\text{-}NH_3)^{2+}$.

Preferably, n in $CatORG^{n+}$ is 1.

Preferably, $CatORG^{n+}$ is selected from the group consisting of ammonium, phosphonium, sulfonium, pyrrolidinium, pyrrolinium, pyrrolium, pyrazolium, pyrazolinium, imidazolium, imidazolinium, triazolium, oxazolium, thiazolium, piperidinium, piperazinium, morpholinium, pyridinium, pyridazinium, pyrimidinium, pyrazinium, 1,3-dioxolium, pyrylium, thiopyrylium, quinoxalinium, indolinium, indolium, $[(CH_3)_3SiFSi(CH_3)_3]^+$, Ph_3C^+, and mixtures thereof;

more preferably from the group consisting of ammonium, phosphonium, sulfonium, pyrrolidinium, pyrrolinium, pyrrolium, pyrazolium, imidazolium, triazolium, oxazolium, thiazolium, piperidinium, piperazinium, morpholinium, pyridinium, pyridazinium, pyrimidinium, pyrazinium, 1,3-dioxolium, pyrylium, thiopyrylium, $[(CH_3)_3SiFSi(CH_3)_3]^+$, Ph_3C^+, and mixtures thereof.

More preferably, $CatORG^{n+}$ is selected from the group consisting of  ,

 ,  ,  ,  ,

$[N(R20)(R21)(R22)R23]^+$, $[P(R20)(R21)(R22)R23]^+$, $[(CH_3)_3SiFSi(CH_3)_3]^+$, Ph_3C^+, and mixtures thereof;

wherein

R20, R21, R23 are identical or different and independently from each other selected from the group consisting of H, C_{1-20} alkyl, C_{3-10} cycloalkyl and allyl;

R22 is C_{1-20} alkyl, C_{3-10} cycloalkyl or allyl;

preferably,

R20, R21, R23 are identical or different and independently from each other selected from the group consisting of H, C_{1-14} alkyl, C_{5-8} cycloalkyl and allyl;

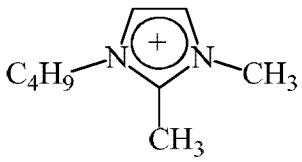
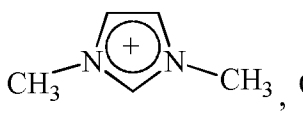
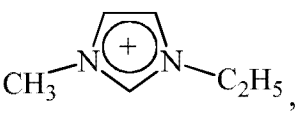
R22 is C_{1-14} alkyl, C_{5-8} cycloalkyl or allyl;

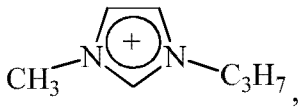
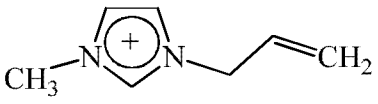
more preferably,

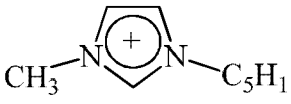
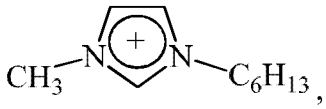
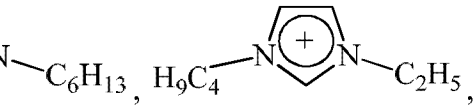
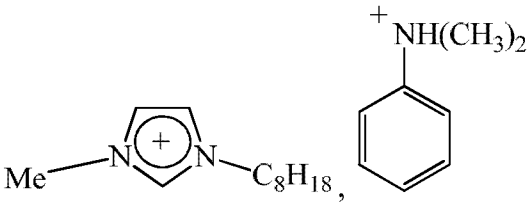
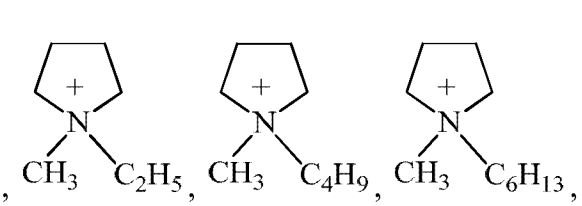
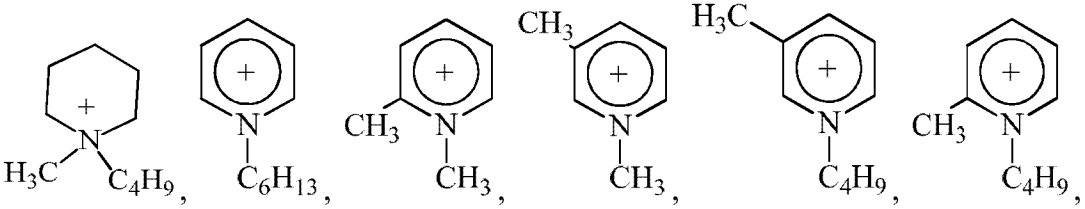
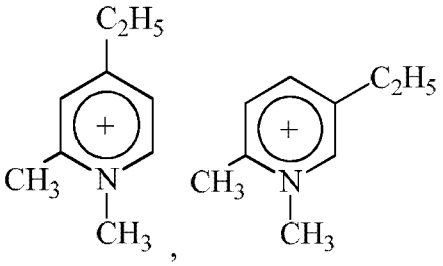
R20, R21, R23 are identical or different and independently from each other selected from the group consisting of H, C_{1-8} alkyl, C_{5-7} cycloalkyl and allyl;

R22 is C_{1-8} alkyl, C_{5-7} cycloalkyl or allyl;

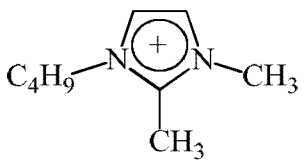
even more preferably, $CatORG^{n+}$ is selected from the group consisting of

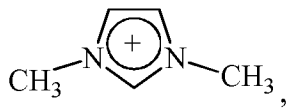
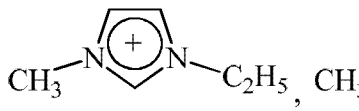
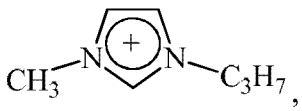
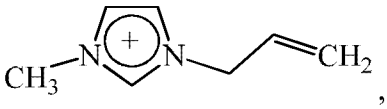
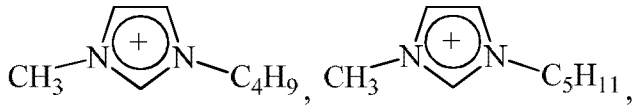
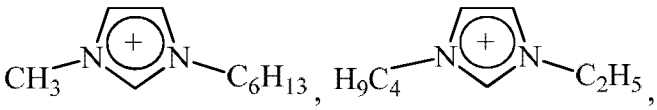
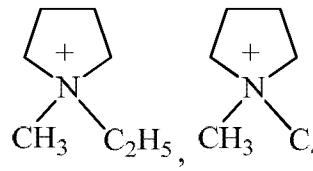
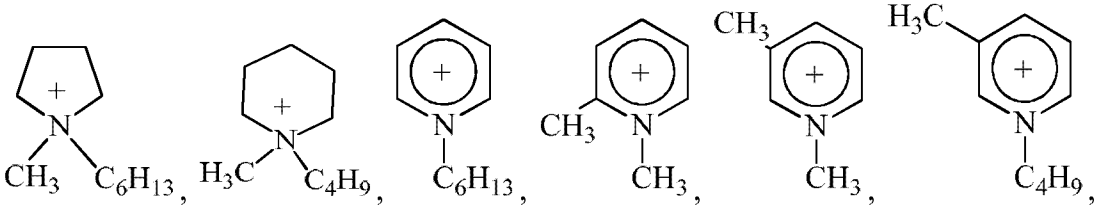
 ,  ,  ,  ,

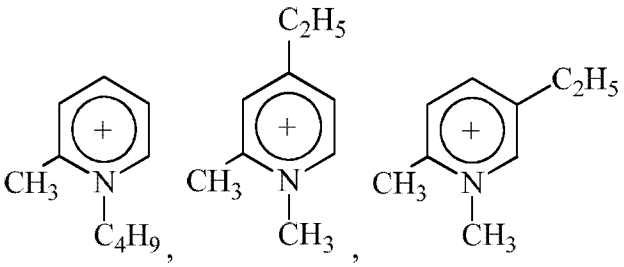
 ,  ,  ,

, $[NH(C_2H_5)_3]^+$, $[NH(C_3H_7)_3]^+$, $[NH(C_4H_9)_3]^+$, $[N(C_2H_5)_4]^+$, $[N(C_3H_7)_4]^+$, $[N(C_4H_9)_4]^+$, $[P(C_2H_5)_4]^+$, $[P(C_3H_7)_4]^+$, $[P(C_4H_9)_4]^+$, $[P(C_6H_{13})_3(C_{14}H_{29})]^+$, $[(CH_3)_3SiFSi(CH_3)_3]^+$, Ph_3C^+, and mixtures thereof;

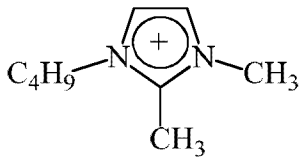
especially, $CatORG^{n+}$ is selected from the group consisting of  ,



, $[NH(C_2H_5)_3]^+$, $[NH(C_3H_7)_3]^+$, $[NH(C_4H_9)_3]^+$, $[N(C_2H_5)_4]^+$, $[N(C_3H_7)_4]^+$, $[N(C_4H_9)_4]^+$, $[P(C_2H_5)_4]^+$, $[P(C_3H_7)_4]^+$, $[P(C_4H_9)_4]^+$, $[(CH_3)_3SiFSi(CH_3)_3]^+$, Ph_3C^+, and mixtures thereof.

more especially, $CatORG^{n+}$ is selected from the group consisting of



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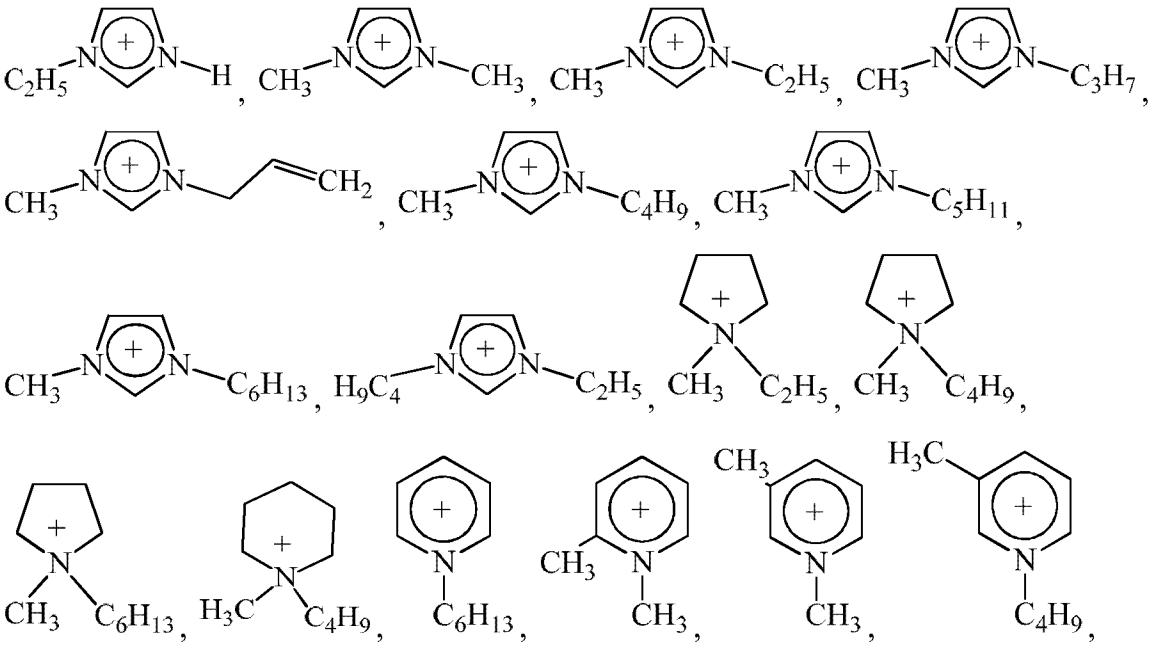
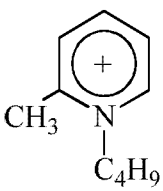




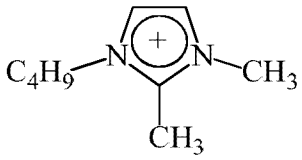
, $[NH(C_2H_5)_3]^+$, $[NH(C_3H_7)_3]^+$, $[NH(C_4H_9)_3]^+$, $[N(C_2H_5)_4]^+$, $[N(C_3H_7)_4]^+$, $[N(C_4H_9)_4]^+$, $[P(C_2H_5)_4]^+$, $[P(C_3H_7)_4]^+$, $[P(C_4H_9)_4]^+$, $[(CH_3)_3SiFSi(CH_3)_3]^+$, Ph_3C^+, and mixtures thereof.

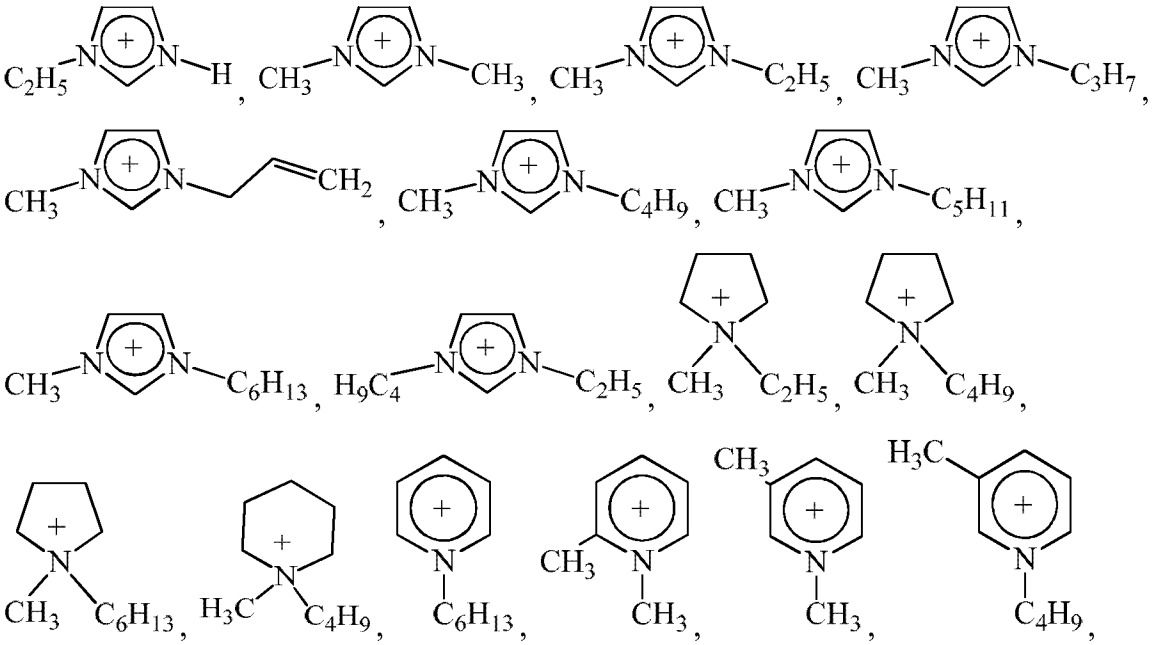
In particular, Cat^{n+} is a cation (Cat-Part1);

cation (Cat-Part1) is $CatINORG^{n+}$ or $CatORG^{n+}$,

with $CatINORG^{n+}$ selected from the group consisting of Li^+, Na^+, K^+, NH_4^+, Ag^+, Mg^{2+}, Ca^{2+} and Zn^{2+};

and

with $CatORG^{n+}$ selected from the group consisting of  ,



$[NH(C_2H_5)_3]^+$, $[NH(C_3H_7)_3]^+$, $[NH(C_4H_9)_3]^+$, $[N(C_2H_5)_4]^+$, $[N(C_3H_7)_4]^+$, $[N(C_4H_9)_4]^+$, $[P(C_2H_5)_4]^+$, $[P(C_3H_7)_4]^+$, $[P(C_4H_9)_4]^+$, $[(CH_3)_3SiFSi(CH_3)_3]^+$, Ph_3C^+, and mixtures thereof.

Even more preferably, compound of formula (I) is compound (Group-I),

compound (Group-I) is selected from the group consisting of compound of formula (Ia) and compound of formula (Ib);

$$[Cat^{n+}]\,[(BF(CN)_3)^-]_n \qquad \text{(Ia)}$$

$$[Cat^{n+}]\,[(B(CN)_4)^-]_n \qquad \text{(Ib)}$$

Cat^{n+} and n are as defined above, also with all their embodiments,

preferably Cat^{n+} is cation (Cat-Part1).

In particular, compound of formula (I) is selected from the group consisting of compound of formula (1), compound of formula (2), compound of formula (3), and mixtures thereof.

$[(n\text{-}Bu)_4N][BF(CN)_3]$ (1)

$[(n\text{-}Pr)_3NH][BF(CN)_3]$ (2)

$[(n\text{-}Pr)_3NH][B(CN)_4]$ (3)

Preferably, from 1 to 40 mol equivalents, more preferably 4 to 35 mol equivalents, even more preferably from 5 to 25 mol equivalents, especially from 5 to 15 mol equivalents, of trimethylsilylcyanide are used in REAC1, the mol equivalents being based on the molar amount of the anion $[(BF_4)^-]$ of compound of formula (A1).

The reaction temperatures of REAC1 is preferably from -75 to 150°C, more preferably from -50 to 120°C, more preferably from -50 to 100°C, even more preferably -50 to 80°C.

Another possible range of the reaction temperatures of REAC1 is preferably from -10 to 150°C, more preferably from -10 to 120°C, more preferably from 0 to 100°C, even more preferably 10 to 80°C.

REAC1 can be done in a closed system and at the pressure caused by the chosen temperature.

The reaction time of REAC1 is preferably from 15 min to 96 h, more preferably from 20 min to 84 h, even more preferably from 20 min to 48 h, especially from 20 min to 24 h, more especially from 20 min to 12 h, even more especially from 20 min to 6 h.

Preferably, REAC1 is done under inert atmosphere. Preferably, the inert atmosphere is achieved by the use if an inert gas preferably selected from the group consisting of argon, another noble gas, lower boiling alkane, nitrogen and mixtures thereof.

The lower boiling alkane is preferably a C_{1-3} alkane, i.e. methane, ethane or propane.

After the reaction, compound of formula (I) can be isolated by standard methods such as evaporation of volatile components, extraction, washing, drying, concentration, crystallization, chromatography and any combination thereof, which are known per se to the person skilled in the art.

Preferably, after the reaction the reaction product is treated with hydrogen peroxide, preferably with aqueous hydrogen peroxide.

More preferably for isolation, the reaction product is mixed with aqueous hydrogen peroxide to provide a mixture MIXT.
Preferably, the concentration of the aqueous hydrogen peroxide is from 10 to 40 wt% hydrogen peroxide, the wt% based on the total weight of the aqueous hydrogen peroxide.

Preferably, from 1 to 30 mol equivalents, more preferably from 1 to 20 mol equivalents, of hydrogen peroxide are used, the mol equivalents being based on the molar amount of compound of formula (A1).

Preferably MIXT is stirred for 5 min to 24 h, more preferably for 10 min to 20 h.

Preferably MIXT is stirred at a temperature TEMPMIXT, TEMPMIXT is preferably from ambient temperature to 100°C.

After treatment with hydrogen peroxide, MIXT is preferably filtrated. The residue of the filtration is preferably washed with a solvent WASHMIXT, WASHMIXT is preferably water or an ether such as diethylether or dichloromethane.

REAC1 can be done in the presence of a compound CAT;
CAT is a Lewis Acid selected from the group consisting of Lewis Acids derived , that is based on, the 1., 2., 3., 4., 5., 6., 7., 8., 9., 10., 11., 12., 13., 14., 15. and 16. group of the periodic table, zeolite, guanidinium[ANIO] and mixtures thereof;
more preferably, CAT is selected from the group consisting of $[(CH_3)_3SiFSi(CH_3)_3][ANIO]$, $Q1(R27)_3$, guanidinium[ANIO], $(R26)_3C[ANIO]$, adamantyl[ANIO], $[(R24)_3O][ANIO]$,

$[(R25)_3Si][ANIO]$, $Q2(R36)(R28)_3$, $Q3(R29)_3$, $Q4(R30)_5$, $Q5(R32)_3$, $Q6(R33)_2$, $Q7(R31)$, $Q8(R34)_2$, $Q9(R35)_3$, $Q10(R37)_2$, $Q11(R38)$, zeolite and mixtures thereof;

even more preferably, CAT is selected from the group consisting of $[(CH_3)_3SiFSi(CH_3)_3][ANIO]$, $Si(Cl)(C_6H_5)_3$, $B(R27)_3$, $Al(R27)_3$, GaF_3, $GaCl_3$, guanidinium[ANIO], $(R26)_3C[ANIO]$, $[(R24)_3O][ANIO]$, $[(R25)_3Si][ANIO]$, $Si(R28)_4$, TiF_4, $TiCl_4$, $Q3(halogen)_3$, $Q3(CN)_3$, $Q3(C_{1-4}\ alkyl)_3$, $Q4(halogen)_5$, $Q4(C_{1-10}\ alkyl)_5$, $Cr(Cl)_3$, $Fe(halogen)_3$, $Mn(Cl)_2$, $Fe(halogen)_2$, $Pd(halogen)_2$, $Pt(halogen)_2$, $Pd(CN)_2$, $Pt(CN)_2$, $Pd(SCN)_2$, $Pt(SCN)_2$, AgCl, AgCN, CuCl, $CuCl_2$, CuF, CuBr, CuCN, CuF_2, $CuBr_2$, $Cu(CN)_2$, ZnF_2, $ZnCl_2$, $ZnBr_2$, $Zn(CN)_2$, ScF_3, $ScCl_3$, $ScBr_3$, LnF_3, $LnCl_3$, $LnBr_3$, $CaCl_2$, KF, zeolite and mixtures thereof;

especially, CAT is selected from the group consisting of $[(CH_3)_3SiFSi(CH_3)_3][ANIO]$, $Si(Cl)(C_6H_5)_3$, $B(R27)_3$, $Al(R27)_3$, GaF_3, $GaCl_3$, $(R26)_3C[ANIO]$, $[(R24)_3O][ANIO]$, $[(R25)_3Si][ANIO]$, $Si(halogen)_4$, $Si(C_{1-10}\ alkyl)_4$, TiF_4, $TiCl_4$, $P(halogen)_3$, $P(CN)_3$, $Sb(halogen)_3$, $Bi(halogen)_3$, $Bi(CN)_3$, $P(halogen)_5$, $P(C_{1-10}\ alkyl)_5$, $Sb(halogen)_5$, $Nb(halogen)_5$, $CrCl_3$, FeF_3, $FeCl_3$, $FeBr_3$, $MnCl_2$, FeF_2, $FeCl_2$, $FeBr_2$, PdF_2, $PdCl_2$, $PdBr_2$, PtF_2, $PtCl_2$, $PtBr_2$, AgCN, CuCl, $CuCl_2$, CuF, CuBr, CuCN, CuF_2, ZnF_2, $ZnCl_2$, $ZnBr_2$, $Zn(CN)_2$, ScF_3, $ScCl_3$, LnF_3, $LnCl_3$, $CaCl_2$, KF, zeolite and mixtures thereof;

more especially, CAT is selected from the group consisting of $[(CH_3)_3SiFSi(CH_3)_3][ANIO]$, $Si(Cl)(C_6H_5)_3$, BF_3, BCl_3, BBr_3, $B(C_{1-4}\ alkyl)_3$, $B(C_6F_5)_3$, AlF_3, $AlCl_3$, $Al(C_{1-4}\ alkyl)_3$, $Al(C_6F_5)_3$, GaF_3, $GaCl_3$, $(Ph)_3C[ANIO]$, $(CH_3)_3C[ANIO]$, $[(C_{1-3}\ alkyl)_3O][ANIO]$, $[(C_{1-4}\ alkyl)_3Si][ANIO]$, $Si(halogen)_4$, $Si(C_{1-10}\ alkyl)_4$, TiF_4, $TiCl_4$, $P(halogen)_3$, $P(CN)_3$, SbF_3, SbI_3, BiF_3, BiI_3, $Bi(CN)_3$, $P(halogen)_5$, SbF_5, NbF_5, $NbCl_5$, $CrCl_3$, $FeCl_3$, $FeBr_3$, $MnCl_2$, $FeCl_2$, $FeBr_2$, $PdCl_2$, $PdBr_2$, $PtCl_2$, $PtBr_2$, AgCN, CuCl, $CuCl_2$, CuF, CuF_2, ZnF_2, $ZnCl_2$, $ZnBr_2$, $Zn(CN)_2$, ScF_3, $ScCl_3$, LnF_3, $LnCl_3$, $CaCl_2$, KF, zeolite and mixtures thereof;

even more especially, CAT is selected from the group consisting of $[(CH_3)_3SiFSi(CH_3)_3][ANIO]$, $Si(Cl)(C_6H_5)_3$, BF_3, BCl_3, $B(C_{1-4}\ alkyl)_3$, $B(C_6F_5)_3$, $AlCl_3$, GaF_3, $GaCl_3$, $(Ph)_3C[ANIO]$, $(CH_3)_3C[ANIO]$, $[(C_{1-4}\ alkyl)_3Si][ANIO]$, SiF_4, $SiCl_4$, $Si(C_{1-8}\ alkyl)_4$, TiF_4, $TiCl_4$, PCl_3, PBr_3, PI_3, $P(CN)_3$, SbF_3, SbI_3, $Bi(CN)_3$, PF_5, PCl_5, PBr_5, PI_5, SbF_5, $NbCl_5$, $CrCl_3$, $FeCl_3$, $FeBr_3$, $MnCl_2$, $FeCl_2$, $FeBr_2$, $PdCl_2$, $PdBr_2$, $PtCl_2$, $PtBr_2$, AgCN, CuCl, $CuCl_2$, CuF, CuF_2, ZnF_2, $Zn(CN)_2$, ScF_3, $ScCl_3$, LnF_3, $LnCl_3$, $CaCl_2$, KF, zeolite and mixtures thereof;

in particular, CAT is selected from the group consisting of $[(CH_3)_3SiFSi(CH_3)_3][ANIO]$, $Si(Cl)(C_6H_5)_3$, BF_3, BCl_3, $B(C_6F_5)_3$, $AlCl_3$, GaF_3, $GaCl_3$, $Ph_3C[ANIO]$, $[(C_{1-4}\ alkyl)_3Si][ANIO]$, SiF_4, $SiCl_4$, $Si(C_{1-4}\ alkyl)_4$, TiF_4, $TiCl_4$, PCl_3, PBr_3, PI_3, $P(CN)_3$, SbF_3,

SbI_3, $Bi(CN)_3$, PF_5, PCl_5, PBr_5, PI_5, SbF_5, $NbCl_5$, $CrCl_3$, $FeCl_3$, $FeBr_3$, $MnCl_2$, $FeCl_2$, $FeBr_2$, $PdCl_2$, $PdBr_2$, $PtCl_2$, $PtBr_2$, AgCN, CuCl, $CuCl_2$, CuF, CuF_2, ZnF_2, ScF_3, $ScCl_3$, LnF_3, $LnCl_3$, $CaCl_2$, KF, zeolite and mixtures thereof;

more in particular, CAT is selected from the group consisting of $[(CH_3)_3SiFSi(CH_3)_3][ANIO]$, $Si(Cl)(C_6H_5)_3$, BF_3, BCl_3, $B(C_6F_5)_3$, $AlCl_3$, GaF_3, $GaCl_3$, $Ph_3C[ANIO]$, $SiCl_4$, TiF_4, $TiCl_4$, $P(CN)_3$, SbF_3, $Bi(CN)_3$, PF_5, PCl_5, SbF_5, $NbCl_5$, $CrCl_3$, $FeCl_3$, $MnCl_2$, AgCN, CuCl, $CuCl_2$, ZnF_2, $CaCl_2$, KF, zeolite and mixtures thereof;

even more in particular, CAT is selected from the group consisting of $[(CH_3)_3SiFSi(CH_3)_3][ANIO]$, $Si(Cl)(C_6H_5)_3$, BF_3, $B(C_6F_5)_3$ GaF_3, $GaCl_3$, $Ph_3C[ANIO]$, $SiCl_4$, TiF_4, $TiCl_4$, $P(CN)_3$, PF_5, PCl_5, SbF_5, $NbCl_5$, $CrCl_3$, $FeCl_3$, $MnCl_2$, AgCN, $CaCl_2$, KF, $SiCl_4$, zeolite and mixtures thereof;

very even more in particular, CAT is selected from the group consisting of $[(CH_3)_3SiFSi(CH_3)_3][ANIO]$, $Si(Cl)(C_6H_5)_3$, BF_3, $B(C_6F_5)_3$ GaF_3, $GaCl_3$, $Ph_3C[ANIO]$, $SiCl_4$, TiF_4, $TiCl_4$, $P(CN)_3$, PF_5, PCl_5, SbF_5, $NbCl_5$, $CrCl_3$, $FeCl_3$, $MnCl_2$, $SiCl_4$, zeolite and mixtures thereof;

in a very preferred embodiment, CAT is selected from the group consisting of BF_3, $B(C_6F_5)_3$ GaF_3, $GaCl_3$, TiF_4, $TiCl_4$, PF_5, PCl_5, SbF_5, $[(CH_3)_3SiFSi(CH_3)_3]$ [ANIO], $Ph_3C[ANIO]$, SbF_5, zeolite and mixtures thereof;

in a more very preferred embodiment, CAT is $[(CH_3)_3SiFSi(CH_3)_3][ANIO]$, $B(C_6F_5)_3$ GaF_3, $GaCl_3$, TiF_4, $TiCl_4$, PF_5, PCl_5, SbF_5, $Ph_3C[ANIO]$, zeolite or mixtures thereof;

in an even more very preferred embodiment, CAT is $[(CH_3)_3SiFSi(CH_3)_3][ANIO]$, $B(C_6F_5)_3$ GaF_3, $GaCl_3$, TiF_4, $TiCl_4$, PF_5, PCl_5, SbF_5, $Ph_3C[ANIO]$, zeolite or mixtures thereof;

in an especially very preferred embodiment, CAT is $B(C_6F_5)_3$ GaF_3, $GaCl_3$, TiF_4, $TiCl_4$, PF_5, PCl_5, SbF_5, $Ph_3C[ANIO]$, zeolite or mixtures thereof;

Q1 is selected from the group consisting of B, Al and Ga;

R27 is selected from the group consisting of C_{1-10} alkoxy, halogen, C_{1-10} alkyl, CN, SCN and C_6F_5;

R24 is C_{1-10} alkyl;

R25 is C_{1-10} alkyl;

R26 is selected from the group consisting of CN, SCN, Ph and C_{1-10} alkyl;

Q2 is selected from the group consisting of Si and Ti;

R28 and R36 are identical or different and independently from each other selected from the group consisting of C_{1-10} alkoxy, halogen, C_{1-10} alkyl, CN, SCN and C_6F_5;

Q3 is selected from the group consisting of P, Sb and Bi;

R29 is selected from the group consisting of C_{1-10} alkoxy, halogen, CN, SCN, C_{1-10} alkyl and C_6F_5;

Q4 is selected from the group consisting of P, Sb and Nb;

R30 is selected from the group consisting of C_{1-10} alkoxy, halogen, CN, SCN, C_{1-10} alkyl and C_6F_5;

Q5 is selected from the group consisting of Cr and Fe;

R32 is selected from the group consisting of halogen, CN and SCN;

Q6 is selected from the group consisting of Mn, Fe, Pd and Pt;

R33 is selected from the group consisting of halogen, CN and SCN;

Q7 is Cu or Ag;

R31 is selected from the group consisting of halogen, CN and SCN;

Q8 is selected from the group consisting of Cu, Zn, Cd and Hg;

R34 is selected from the group consisting of halogen, CN, and SCN;

Q9 Sc or Ln;

R35 is selected from the group consisting of halogen, CN, and SCN;

Q10 Ca;

R37 is halogen;

Q11 K;

R38 is halogen;

ANIO is selected from the group consisting of $[P(R40)_{6-m1}(R41)_{m1}]^-$, $[B(R42)_{4-m2}(R43)_{m2}]^-$, F^-, Cl^-, Br^-, I^-, CN^- and SCN^-;

R40 and R41 are identical of different in independently from each other selected from the group consisting of CN, SCN, F, Cl, Br and I;

m1 is 0, 1, 2, 3, 4 or 5;

R42 and R43 are identical of different in independently from each other selected from the group consisting of C_6F_5, CN, SCN, F, Cl, Br and I;

m2 is 0, 1, 2 or 3;

preferably, ANIO is selected from the group consisting of $P(R40)_6^-$, $B(R42)_4^-$, F^-, Cl^-, Br^-, I^-, CN^- and SCN^-;

R40 is selected from the group consisting of CN, SCN, F, Cl, Br and I;

R42 is selected from the group consisting of C_6F_5, CN, SCN, F, Cl, Br and I;

more preferably, ANIO is selected from the group consisting of $P(R40)_6^-$, $B(R42)_4^-$, F^-, Cl^-, Br^-, CN^- and SCN^-;

R40 is selected from the group consisting of CN, SCN, F, Cl and Br;

R42 is selected from the group consisting of C_6F_5, CN, SCN, F, Cl and Br.

Preferably,

Q1 is B.

Preferably,

R24 is C_{1-4} alkyl;

R25 is C_{1-7} alkyl;

R26 is selected from the group consisting of Ph and C_{1-4} alkyl;

R27 is selected from the group consisting of C_{1-7} alkoxy, Cl, F, Br, C_{1-7} alkyl and C_6F_5;

more preferably,

R24 is C_{1-3} alkyl;

R25 is C_{1-5} alkyl;

R26 is selected from the group consisting of Ph and C_{1-2} alkyl;

R27 is selected from the group consisting of C_{1-4} alkoxy, Cl, F, C_{1-4} alkyl and C_6F_5;

even more preferably,

R24 is methyl or ethyl;

R25 is C_{1-4} alkyl;

R26 is Ph or methyl;

R27 is selected from the group consisting of C_{1-3} alkoxy, Cl, F, C_{1-3} alkyl and C_6F_5.

Preferably, [ANIO] is $[B(C_6F_5)_4]$ or $[BF_4]$.

In a special embodiments, CAT is selected from the group consisting of $[(CH_3)_3SiFSi(CH_3)_3][B(C_6F_5)_4]$, $Si(Cl)(C_6H_5)_3$, BF_3, BCl_3, $B(C_6F_5)_3$, $AlCl_3$, GaF_3, $GaCl_3$, $Ph_3C[BF_4]$, $SiCl_4$, TiF_4, $TiCl_4$, $P(CN)_3$, SbF_3, $Bi(CN)_3$, PF_5, PCl_5, SbF_5, $NbCl_5$, $CrCl_3$, $FeCl_3$, $MnCl_2$, AgCN, CuCl, $CuCl_2$, ZnF_2, $CaCl_2$, KF, zeolite, and mixtures thereof;

preferably, CAT is selected from the group consisting of $[(CH_3)_3SiFSi(CH_3)_3][B(C_6F_5)_4]$, $Si(Cl)(C_6H_5)_3$, BF_3, $B(C_6F_5)_3$, GaF_3, $GaCl_3$, $Ph_3C[BF_4]$, $SiCl_4$, TiF_4, $TiCl_4$, $P(CN)_3$, PF_5, PCl_5, SbF_5, $NbCl_5$, $CrCl_3$, $FeCl_3$, $MnCl_2$, $SiCl_4$, zeolite, and mixtures thereof;

more preferably, CAT is selected from the group consisting of $[(CH_3)_3SiFSi(CH_3)_3][B(C_6F_5)_4]$, BF_3, $B(C_6F_5)_3$ GaF_3, $GaCl_3$, $Ph_3C[BF_4]$, TiF_4, $TiCl_4$, PF_5, PCl_5, SbF_5, zeolite, and mixtures thereof;

even more preferably, CAT is $[(CH_3)_3SiFSi(CH_3)_3][B(C_6F_5)_4]$, $B(C_6F_5)_3$ GaF_3, $GaCl_3$, TiF_4, $TiCl_4$, PF_5, PCl_5, SbF_5, $Ph_3C[BF_4]$, zeolite or mixtures thereof;

especially, CAT is $B(C_6F_5)_3$, GaF_3, $GaCl_3$, TiF_4, $TiCl_4$, PF_5, PCl_5, SbF_5, $Ph_3C[BF_4]$, zeolite or mixtures thereof.

In another preferred embodiment, CAT is selected from the group consisting of $(CH_3)_3SiFSi(CH_3)_3[B(C_6F_5)_4]$, $[Ph_3C][BF_4]$, $B(C_6F_5)_3$ and mixtures thereof;

more preferably, CAT is $[Ph_3C][BF_4]$.

CAT can be used in immobilized form on a carrier CARR;

CARR is a carrier conventionally used for immobilizing catalysts in heterogeneously catalyzed reactions;

preferably, CARR is seleceted from the group consisting of epoxide, polystyrene, zeolite, activated carbon and metal oxide;

said metal oxide is preferably selected from the group consisting of MnO_2, Fe_2O_3, Co_3O_4, NiO, CuO, $CuMnO_2$, MgO, Al_2O_3, SiO_2, V_2O_5, MoO_3, WO_3 and mixed oxides thereof.

Zeolite can be any zeolite, preferably montmorrilonte or bentonite, more preferably Montmorillonite K10®, BASF, Germany (also available at Sigma Aldrich, CAS Number 1318-93-0).

Compound of formula (A1) and CAT can be one and the same compound, therefore

in one preferred embodiment, compound of formula (A1) is different from CAT;

in another preferred embodiment, compound of formula (A1) is identical with CAT.

Preferably, from 0.0001 to 40 mol equivalents, more preferably 0.001 to 35 mol equivalents, even more preferably from 0.005 to 25 mol equivalents, especially from 0.005 to 25 mol equivalents, more especially from 0.005 to 15 mol equivalents, even more especially from 0.005 to 5 mol equivalents, of CAT are used in REAC1, the mol equivalents being based on the combined molar amount of the anion $[(BF_4)^-]$ of compound of formula (A1), CATACID and CAT.

In another preferable embodiment, from 0.01 to 40 mol%, more preferably 0.1 to 35 mol%, even more preferably 0.1 to 25 mol%, especially from 0.5 to 15 mol%, more especially from 0.5 to 10 mol%, even more especially from 0.5 to 5 mol%, of CAT are used in REAC1, the mol% being based on the combined molar amount of the anion $[(BF_4)^-]$ of compound of formula (A1), CATACID and CAT.

Preferably, from 0.01 to 40 mol%, more preferably 0.1 to 35 mol%, even more preferably 0.1 to 25 mol%, especially from 0.5 to 17.5 mol%, more especially from 0.5 to 12.5 mol%, even more especially from 0.5 to 10 mol%, of CATACID are used in REAC1, the mol% being based on the combined molar amount of of the anion $[(BF_4)^-]$ compound of formula (A1), CATACID and, if present, CAT.

Preferably, the method comprises additionally to STEP1 a step STEP2, STEP2 is done after STEP1;

STEP2 comprises a reaction REAC2, REAC2 is a metathesis reaction wherein cation Cat^{n+} in compound of formula (I) is exchanged for a cation different from Cat^{n+};

compound of formula (I) having been prepared in STEP1;

Cat^{n+}, n, compound of formula (I) and STEP1 are as defined above, also with all their embodiments.

REAC2 is a metathesis reaction, also called a salt-exchange reaction. In a metathesis reaction such as REAC2 a first cation in a first salt is exchanged for a second cation, said second cation coming from a second salt.

Preferably, REAC2 provides for the preparation of a compound of formula (I-Cat-r);

$$[Cat\text{-}r^{r+}]\ [(BF_{4-m}(CN)_m)^-]_r \qquad \text{(I-Cat-r)}$$

$Cat\text{-}r^{r+}$ is selected from the group consisting of $CatINORG^{n+}$ and $CatORG^{n+}$ and is different from Cat^{n+};

r is 1, 2, 3 or 4;

with STEP1, m, $CatINORG^{n+}$ and $CatORG^{n+}$ as defined above, also with all their embodiments.

Preferably, in REAC2 Cat^{n+} is exchanged for $Cat\text{-}r^{r+}$ from a compound of formula (I-Cat-n);

$$(Cat\text{-}r^{r+})_{t1}\ (AnINORG^{q-})_{t2} \qquad \text{(I-Cat-n)}$$

q is 1 or 2;

t1 is 1 or2;

t2 is 1, 2, 3 or 4;

when r is 1 and q is 1, then t1 is 1 and t2 is 1;

when r is 2 and q is 1, then t1 is 1 and t2 is 2;

when r is 3 and q is 1, then t1 is 1 and t2 is 3;

when r is 4 and q is 1, then t1 is 1 and t2 is 4;

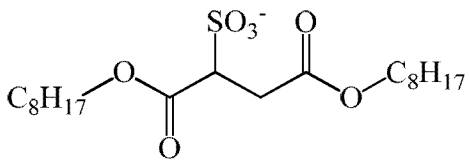
when r is 1 and q is 2, then t1 is 2 and t2 is 1;

when r is 2 and q is 2, then t1 is 1 and t2 is 1;

when r is 3 and q is 2, then t1 is 2 and t2 is 3;

when r is 4 and q is 2, then t1 is 1 and t2 is 2;

$AnINORG^{q-}$ is an anion selected from the group consisting of halide, OH^-, CN^-, OCN^-, SCN^-, N_3^-, sulfate, hydrogensulfate, nitrate, CO_3^{2-}, HCO_3^-, BF_4^-, PF_6^-, SbF_6^-, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, $(FSO_2)_2N^-$, C_{1-6} alkyl-SO_3^-, C_{1-6} alkyl-O-SO_3^-,



, anions of C_{1-20} monocarboxylic aliphatic acids, mono- and dianions of C_{2-6} dicarboxylic aliphatic acids, anions of benzoic acids, mono- and dianions of phthalic acids, of isophthalic acids and of terephthalic acids, $N(CN)_2^-$, $C(CN)_3^-$, $B(CN)_4^-$, $P(CN)_6^-$, $Sb(CN)_6^-$, and mixtures thereof;

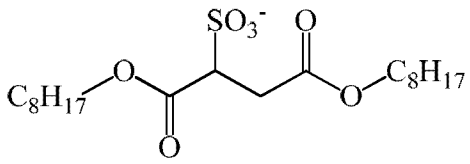
$Cat\text{-}r^{r+}$, r, $CatINORG^{n+}$ and $CatORG^{n+}$ are as defined above, also with all their embodiments.

Preferably, $AnINORG^{q-}$ is an anion selected from the group consisting of halide, OH^-, CN^-, sulfate, hydrogensulfate, nitrate, CO_3^{2-}, HCO_3^-, BF_4^-, PF_6^-, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, $(FSO_2)_2N^-$, $H_3C\text{-}SO_3^-$, $H_3C\text{-}CH_2\text{-}SO_3^-$, $H_3C\text{-}O\text{-}SO_3^-$, $H_3C\text{-}CH_2\text{-}O\text{-}SO_3^-$, acetate, oleate, fumarate, maleate, oxalate, benzoate, $N(CN)_2^-$, and mixtures thereof;

more preferably, $AnINORG^{q-}$ is an anion selected from the group consisting of Br^-, Cl^-, OH^-, CN^-, sulfate, hydrogensulfate, CO_3^{2-}, HCO_3^-, acetate, and mixtures thereof;

even more preferably, $AnINORG^{q-}$ is an anion selected from the group consisting of Cl^-, OH^-, CN^-, sulfate, hydrogensulfate, CO_3^{2-}, HCO_3^-, acetate, and mixtures thereof.

In another preferred embodiment, $AnINORG^{q-}$ is an anion selected from the group consisting of halide, OH^-, CN^-, OCN^-, SCN^-, N_3^-, sulfate, hydrogensulfate, nitrate, CO_3^{2-}, HCO_3^-, BF_4^-, PF_6^-, SbF_6^-, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, $(FSO_2)_2N^-$, $C_{1\text{-}6}$ alkyl-SO_3^-, $C_{1\text{-}6}$ alkyl-O-SO_3^-,



, anions of $C_{1\text{-}20}$ monocarboxylic aliphatic acids, anions of $C_{2\text{-}6}$ dicarboxylic aliphatic acids, benzoate, phthalates, $N(CN)_2^-$, $C(CN)_3^-$, $B(CN)_4^-$, $P(CN)_6^-$, $Sb(CN)_6^-$, and mixtures thereof.

Preferably, r is 1 or 2.

In case of REAC2, preferably a compound of formula (I-Cat-r) with $Cat\text{-}r^{r+}$ being $CatORG^{n+}$ is prepared by exchange of a Cat^{n+} being a $CatINORG^{n+}$ in compound of formula (I) for a $CatORG^{n+}$.

Said $CatORG^{n+}$ is provided in REAC2 preferably in form of a compound of formula (I-CatORG)

$(CatORG^{n+})_q(AnINORG^{q-})_n$ (I-CatORG)

wherein

Cat^{n+}, n, $CatORG^{n+}$, $CatINORG^{n+}$, q and $AnINORG^{q-}$ are as defined above, also with all their embodiments.

Preferably, in REAC2 the cation different from Cat^{n+}, that is preferably Cat-r^{r+}, is present in at least such a molar amount relative to the molar amount of Cat^{n+} as required for a stoichiometric exchange of said two cations;

more preferably, compound of formula (I) and compound of formula (I-Cat-n) are present in at least such a molar amount relative to each other, that Cat^{n+} is stoichiometrically exchanged for Cat-r^{r+};

even more preferably, the molar amount of compound of formula (I-Cat-n) is such, that from 1 to 1.5, even more preferably from 1 to 1.2, required equivalents of Cat-r^{r+} relative to the equivalents of Cat^{n+} are present.

The reaction temperatures of REAC2 is preferably from 0 to 250 °C, more preferably from 10 to 200 °C, even more preferably from 10 to 150 °C, especially from 10 to 100°C, more especially from 10 to 50°C.

The REAC2 is preferably carried out in a solvent SOLV2, SOLV2 is preferably selected from the group consisting of water, DCM, ethyl acetate, C_{5-10} alkane, and mixtures thereof. C_{5-10} alkane is preferably pentane, hexane or heptane.
In a more preferred embodiment, REAC2 is done in DCM or in a biphasic solvent system of water and DCM.

As an alternative, REAC2 can also be carried out in the absence of a solvent or in a solvent in which the inorganic salt formed as side product is sparingly soluble or insoluble. As a further alternative, it is also possible to carry out the reaction in an aqueous solution using an ion exchanger loaded with the desired cation Cat^{n+}.

The amount of solvent is preferably from 2 to 40 fold, more preferably from 3 to 20 fold, of the weight of compound of formula (I).

REAC2 can be done in a closed system and at the pressure caused by the chosen temperature.

The reaction time of REAC2 is preferably from 15 min to 96 h, more preferably from 15 min to 48 h, even more preferably from 15 min to 24 h.

Preferably, REAC2 is done under inert atmosphere. Preferably, the inert atmosphere is achieved by the use if an inert gas preferably selected from the group consisting of argon, another noble gas, lower boiling alkane, nitrogen and mixtures thereof.
The lower boiling alkane is preferably a C_{1-3} alkane, i.e. methane, ethane or propane.

Subsequent to REAC2 there can be a further metathesis reaction or further metathesis reactions.

After REAC2, compound of formula (I) can be isolated from the reaction mixture by standard methods such as filtration, evaporation of volatile components, extraction, washing, drying, concentration, crystallization, chromatography and any combination thereof, which are known per se to the person skilled in the art.

For example, when REAC2 was done in a biphasic solvent system of water and DCM, the aqueous and organic phases are separated, the organic phase is preferably washed, preferably with water, then preferably dried, preferably with Na_2SO_4, K_2CO_3, $CaCl_2$ or $MgSO_4$, and finally evaporated.

Or as another example, when REAC2 was done in DCM and a suspension was formed, filtration and evaporation of the solvent will isolate the product.

It is possible use compound of formula (I), which was obtained by the method of instant invention, as substrate in a similar reaction with trimethylsilylcyanide.
Therefore the method of instant invention can comprise additionally to STEP1 a
step STEP1-1, STEP1-1 is done after STEP1;

STEP1-1 comprises a reaction REAC1-1, wherein compound of formula (I), obtained in STEP1, is reacted with trimethylsilylcyanide;

preferably, REAC1-1 is done in the presence of CATACID, in the presence of CAT, or in the presence of both CATACID and CAT;

with CAT and CATACID as defined above, also in all their embodiments.

CATACID is commercially available compounds or can be prepared according to known methods. Compounds of formula (A1) are commercially available depending on the cation Cat^{n+}, e.g. $[(n\text{-}Bu_4)N][BF_4]$ and $K[BF_4]$, as well as CAT are commercially available. Other compounds of formula (A1) with cations Cat^{n+} different from K^+ and $(n\text{-}Bu_4)N^+$, and which are not commercially available, can be prepared by conventional metathesis reaction, i.e. substitution of the respective cation K^+ or $(n\text{-}Bu_4)N^+$ against another cation, or by reaction of tetrafluoroboric acid with a respective compound, such as exemplified herein.

EXAMPLES

Methods

^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker AVANCE 300 and Bruker AVANCE 250 instruments in CD_3CN, $CDCl_3$, D_6-DMSO, D_2O or CD_2Cl_2. Chemical shifts are expressed in parts per million referred to TMS in case of ^{1}H and ^{13}C, $C^{19}FCl_3$ in case of ^{19}F, and $H_3{}^{31}PO_4$ in case of ^{31}P, and coupling constants (J) in Hertz. When a % value for the amount of compounds is stated based on NMR measurement, the % value represents an area-%, the area-% being based on the total area of peaks in the spectrum. In case of the individual amount of a component in a mixture the stated % value for the amount of the component in the mixture represents an area-%, this area-% being based on the combined area of peaks of all components of the mixture; if not stated otherwise.

IR-spectra were recorded on a Nicolet 380 FT-IR spectrometer. Measurements were done at room temperature.

RAMAN-spectra were recorded on a LabRAM HR 800 Horiba Jobin YVON. Measurements were done at room temperature.

The C/H/N-analyses were measured on a C/H/N/S-Analysator (Thermoquest Flash EA 1112).

Melting points and temperature of decomposition T_{dec} were measured on a DSC 823e from Mettler-Toledo. The calibration was carried out with the melting points of In (156.6 ± 0.3°C) and Zn (419.6 ± 0.7°C) with an heating rate of 5 K per min.

TGA/DSC measurements were conducted on a Setaram Labsys TGA / DSC 1600. The measurements were carried out under argon atmosphere with a heating rate of 5 K per min, corrected via a blank measurement.

Preparation description A: Synthesis of $[(n\text{-}Bu)_4N][BF_4]$

A solution of $[(n\text{-}Bu_4)N]Br$ (8.05 g, 24.98 mmol) in 50 ml of CH_2Cl_2 was added to a solution of $K[BF_4]$ (3.12 g, 24.78 mmol) in 30 ml of H_2O. After stirring for 24 h at ambient temperature the phases were separated. The organic phase was washed three times with 10 ml of water, dried over anhydrous Mg_2SO_4 and filtered. The filtrate was concentrated on a rotary

evaporator to obtain a white solid. The obtained solid was dried at 90°C in vacuo for 15 hours. The yield of $[(n\text{-}Bu_4)N][BF_4]$ was 7.83 g (96%, 23.8 mmol).

DSC (10 $Kmin^{-1}$): m.p. = 153°C

C/H/N Analysis calc. % (found): C 58.36 (58.48), H 11.02 (10.84), N 4.25 (4.13)

^{1}H NMR (25°C, CD_3CN, 300.13 MHz, delta in ppm): 0.96 (t, 12H, CH_3), 1.35 (m, 8H, CH_3-CH_2, 1.61 (m, 8H, CH_2-CH_2N), 3.11 (m, 8H, NCH_2)

^{13}C NMR (25 °C, CD_3CN, 75.47 MHz, delta in ppm): 14.4 (s, 4C, CH_3), 20.9 (m, 4C, CH_3-CH_2), 25.0 (m, 4C, CH_2-CH_2N), 59.9 (m, 4C, NCH_2)

^{11}B NMR (25°C, CD_3CN, 96.29 MHz, delta in ppm): −1.2 (s, 1B, BF_4)

^{19}F NMR (25°C, CD_3CN, 282.40 MHz, delta in ppm): −151.6 (s, 4F, BF_4)

IR (ATR, 32 scans, ν in cm^{-1}): 2960 (m), 2935 (w), 2875 (w), 1486 (m), 1468 (w), 1382 (w), 1285 (w), 1152 (w), 1093 (m), 1047 (s), 1034 (s), 881 (w), 800 (w), 739 (w)

RAMAN (460 mW, 150 scans, ν in cm^{-1}): 2964 (7), 2933 (10), 2876 (10), 2746 (1), 1453 (4), 1327(2), 1153(1), 1137 (2), 911 (2), 880 (1), 766 (1), 256 (2), 79 (1)

Preparation description B: Synthesis of $[(n\text{-}Pr)_3NH][BF_4]$

Tetrafluoroboric acid (18 mL, 35 wt% aqueous solution, 88 mmol) was cooled to ca. 0 °C. $n\text{-}Pr_3N$ (17 ml, 89 mmol) was added dropwise to the aqueous solution. After 30 min of stirring the product was extracted with CH_2Cl_2 (three times a 50 ml). The combined organic phases were dried over anhydrous Na_2SO_4 and filtered After evaporating the solvent and drying the white solid in vacuo 18.9 g (93 %, 82 mmol) of $[(n\text{-}Pr)_3NH][BF_4]$ were obtained.

C/H/N Analysis % calc. (found): C 46.78 (47.05) H 9.60 (10.01) N 6.06 (6.36)

^{1}H NMR (300 K, CD_2Cl_2, 300.13 MHz, delta in ppm): 1.00 (t, 9H, CH_3), 1.77 (m, 6H., CH_2-CH_3), 3.05 (m, 6H, NCH_2), 7.25 (br, 1H, NH)

^{11}B NMR (25°C, CD_2Cl_2, 96.29 MHz, delta in ppm): −1.2 (s, 1B, BF_4)

IR (25 °C, ATR, 32 scans, cm^{-1}): 756 (m), 764 (m), 993 (s), 1036 (s), 1051 (s), 1246 (w), 1284 (w), 1387 (w), 1425 (m), 1462 (m), 1477 (m), 2885 (w), 2945 (w), 2978 (w), 3161 (w)

Example 1: Synthesis of compound of formula 1

$[(n\text{-}Bu)_4N][BF_4]$ (764 mg, 2.32 mmol), prepared according to Preparation Description A, triflic acid (34 mol%, the mol% being based on the combined molar amount of

$[(n\text{-}Bu)_4N][BF_4]$ and triflic acid, 177 mg, 1.18 mmol) and $(CH_3)_3SiCN$ (2.30 g, 23 mmol) were stirred under argon atmosphere at ambient temperature. After 2 hours of stirring an ^{11}B NMR spectrum was measured. According to the ^{11}B NMR spectrum the reaction mixture contained only compound of formula (1).

^{11}B NMR (300 K, CD_3CN, 96.29 MHz, delta in ppm): −17.9 (d, 1B, $BF(CN)_3$, $^1J(^{11}B–^{19}F)$ = 44 Hz, $^1J(^{11}B–^{13}C)$ = 75 Hz)

Example 2: Synthesis of compound of formula 2

$[(n\text{-}Pr)_3NH][BF_4]$ (681 mg, 2.95 mmol), prepared according to Preparation Description B, triflic acid (21 mol%, the mol% being based on the combined molar amount of $[(n\text{-}Pr)_3NH][BF_4]$ and triflic acid, 122 mg, 0.81 mmol) and $(CH_3)_3SiCN$ (2.9 g, 29 mmol) were stirred under argon atmosphere at ambient temperature. After 2 hours of stirring an ^{11}B NMR spectrum was measured. According to ^{11}B NMR the reaction mixture contained only compound of formula (2).

^{11}B NMR (300 K, CD_3CN, 96.29 MHz, delta in ppm): −17.9 (d, 1B, $BF(CN)_3$, $^1J(^{11}B–^{19}F)$ = 44 Hz, $^1J(^{11}B–^{13}C)$ = 75 Hz)

Example 3:

$[(n\text{-}Pr)_3NH][BF_4]$ (922 mg, 3.99 mmol), prepared according to Preparation Description B, triflic acid (15 mol%, the mol% being based on the combined molar amount of $[(n\text{-}Pr)_3NH][BF_4]$ and triflic acid, 108 mg, 0.72 mmol) and $(CH_3)_3SiCN$ (4.0 g, 40 mmol) were refluxed under argon atmosphere. After 3 hours of refluxing an ^{11}B NMR spectrum was measured. According to the ^{11}B NMR spectrum the reaction mixture contained 76 % of compound of formula (2) and 24 % compound of formula (3). After a total of 31.5 hours of refluxing again an ^{11}B NMR spectrum was measured. According to the ^{11}B NMR spectrum the reaction mixture contained 29 % of compound of formula (2) and 71 % compound of formula (3).

^{11}B NMR (300 K, CD_3CN, 96.29 MHz, delta in ppm): −17.9 (d, 1B, $BF(CN)_3$, $^1J(^{11}B–^{19}F)$ = 44 Hz, $^1J(^{11}B–^{13}C)$ = 75 Hz), −38.6 (s, 1B, $B(CN)_4$, $^1J(^{11}B–^{13}C)$ = 70 Hz)

Example 4:

$[(n\text{-}Bu)_4][BF_4]$ (618 mg, 1.88 mmol), prepared according to Preparation Description A, triflic acid, $TiCl_4$ (7 mol%, 25 mg, 0,17 mol triflic acid and 9 mol%, 40 mg, 0.21 mol $TiCl_4$, the mol% being based on the combined molar amount of $[(n\text{-}Bu)_4N][BF_4]$, triflic acid and $TiCl_4$) and $(CH_3)_3SiCN$ (1.9 g, 19 mmol) were stirred under argon atmosphere and ambient temperature. After 3 hours of stirring an ^{11}B NMR spectrum was measured. According to ^{11}B NMR the reaction mixture contained only compound of formula (1).

NMR data was the same as in example 1.

Example 5:

Example 4 was repeated with the differences:

$GaCl_3$ was used instead of $TiCl_4$ (7 mol% $GaCl_3$, the mol% being based on the combined molar amount of $[(n\text{-}Bu)_4N][BF_4]$, $GaCl_3$, and triflic acid (15 mol% instead of 9 mol%)).

After the stirring for 3 h an ^{11}B NMR spectrum were measured. In accordance to ^{11}B NMR the product contained 100% of compound of formula (1).

NMR data was the same as in example 1.

Example 6:

Example 4 was repeated with the difference:

SbF_5 was used instead of $TiCl_4$ (7 mol% SbF_5, the mol% being based on the combined molar amount of $[(n\text{-}Bu)_4N][BF_4]$, SbF_5, and triflic acid (10 mol% instead of 9 mol%).

After the stirring for 3 h an ^{11}B NMR spectrum were measured. In accordance to ^{11}B NMR the product contained 100% of compound of formula (1).

NMR data was the same as in example 1.

Comparative Example 1: No CATACID

$[(n\text{-}Bu)_4N][BF_4]$ (0.491 g, 1.49 mmol), prepared according to Preparation Description A, and $(CH_3)_3SiCN$ (1.58 g, 1.59 mmol) were stirred under argon atmosphere at ambient temperature for 100 h.

After the stirring at ambient temperature for 100 h an ^{11}B and ^{19}F NMR spectra were measured. In accordance to ^{19}F and ^{11}B NMR the product contained about 82% of compound of formula (4) and 18% of compound of formula (5).

$[(n\text{-}Bu)_4N][BF_3(CN)]$ (4)

$[(n\text{-}Bu)_4N][BF_2(CN)_2]$ (5)

^{1}H NMR (25°C, $CDCl_3$, 300.13 MHz, delta in ppm): 0.98 (t, 12H, CH_3), 1.41 (m, 8H, CH_3-CH_2), 1.61 (m, 8H, CH_2-CH_2N), 3.16 (m, 8H, NCH_2)

^{11}B NMR (25°C, $CDCl_3$, 300.13 MHz, delta in ppm): -3.6 (q, 1B, $BF_3(CN)$, $^1J(^{11}B\text{-}^{19}F)$ = 28 Hz), -7.2 (q, 1B, $BF_2(CN)_2$, $^1J(^{11}B\text{-}^{19}F)$ = 42 Hz)

^{13}C NMR (25°C, $CDCl_3$, 300.13 MHz, delta in ppm): 13.4 (s, 4C, CH_3), 19.5 (t, 4C, CH_2-CH_3), 23.7 (s, 4C, N-CH_2-CH_2), 58.5 (t, 4C, NCH_2)

^{19}F NMR (25°C, $CDCl_3$, 300.13 MHz, delta in ppm): -137.0 (q, 3F, $BF_3(CN)$, $^1J(^{11}B\text{-}^{19}F)$ = 28 Hz), -153.1 (q, 2F, $BF_2(CN)_2$, $^1J(^{11}B\text{-}^{19}F)$ = 42 Hz)

IR (ATR, 32 scans, ν in cm^{-1}): 2964 (m), 2937 (m), 2877 (m), 2206 (w), 1474 (m), 1383 (m), 1261 (w), 1106 (s), 1058 (s), 990 (m), 952 (s), 881 (m), 799 (m), 738 (m), 681 (m), 532 (w)

Comparative Example 2:

$[(n\text{-}Bu)_4N][BF_4]$ (0.498 g, 1.41 mmol), prepared according to Preparation Description A, and $(CH_3)_3SiCN$ (1.58 g, 1.59 mmol) were stirred under argon atmosphere at ambient temperature for 3 h. An ^{11}B NMR was then measured and revealed 1 % of $[(n\text{-}Bu)_4N][BF_4]$, 79 % of compound of formula (4) ($[(n\text{-}Bu)_4N][BF_3(CN)]$), and 20 % of compound of formula (5) ($[(n\text{-}Bu)_4N][BF_2(CN)_2]$).

CLAIMS

1. Method for the preparation of compound of formula (I);

$$[Cat^{n+}]\,[(BF_{4-m}(CN)_m)^-]_n \qquad (I)$$

the method comprises a step STEP1;

STEP1 comprises a reaction REAC1, wherein compound of formula (A1)

$$[Cat^{n+}]\,[(BF_4)^-]_n \qquad (A1)$$

is reacted with trimethylsilylcyanide in the presence of a compound CATACID;

CATACID is selected from the group consisting of HF, HCl, HBr, HI, HNO_3, H_2SO_3, H_2SO_4, $NaHSO_4$, Oleum, $KHSO_4$, $NaHCO_3$, $KHCO_3$, H_3PO_4, H_3PO_3, HSO_3F, HSO_3Cl, CH_3COOH, CF_3COOH, $C(Cl_3)COOH$, methansulfonic acid, HCOOH, AR-COOH, AR-SO_3H, $C(OH)(COOH)_3$, CF_3SO_3H, HCN, HOCN, HSCN, HSeCN, HNCO, HNCS, HN_3, HQ20(X1)4, polymolybdate, polytungstate, $HQ21(X1)_6$, and mixtures thereof;

AR is Phe or Phe substituted with 1, 2 or 3 identical or different residues selected from the group consisting of halogen and CH_3;

Q20 is B, Al, Ga, In or Th;

Q21 is P, As, Sb or Bi;

X1 is halogen;

m is 1, 2, 3 or 4;

n is 1, 2, 3 or 4;

Cat^{n+} is selected from the group consisting of inorganic cation $CatINORG^{n+}$ and organic cation $CatORG^{n+}$;

$CatINORG^{n+}$ is a cation selected from the 1., 2., 3., 4., 5., 6., 7., 8., 9., 10., 11., 12., 13., 14., 15. or 16. group of the periodic table, or is a cation from the lanthanides or is a cation from the actinides or is NH_4^+;

$CatORG^{n+}$ is selected from the group consisting of $CatORG\text{-}A^+$, $CatORG\text{-}B^+$, $CatORG\text{-}C^+$, $[(CH_3)_3SiFSi(CH_3)_3]^+$, Ph_3C^+, guanidinium and $(H_2(R18)N\text{-}R16\text{-}N(R19)H_2)^{2+}$;

$CatORG\text{-}A^+$ is $(WR2R3R4R5)^+$,

wherein

W is a nitrogen or phosphorus; and

(i) R2, R3, R4 and R5 are identical or different and independently from each other selected from the group consisting of H, C_{1-20} alkyl, C_{1-20} perfluoroalkyl, C_{3-10} cycloalkyl and C_{6-10} aryl, with the proviso, that at least one of the residues R2, R3, R4 and R5 is not H; or

(ii) R2 and R3 together are a hydrocarbon chain and form together with W a 5- to 7-membered saturated or unsaturated heterocyclic ring,
R4 and R5 are identical or different and independently from each other selected from the group consisting of H, C_{1-20} alkyl, C_{1-20} perfluoroalkyl, C_{3-10} cycloalkyl and C_{6-10} aryl; or

(iii) R2 and R3 together are a hydrocarbon chain and form together with W, and R4 and R5 together are a hydrocarbon chain and form together with W, independently from each other, 5- to 7-membered saturated or unsaturated heterocyclic rings;

$CatORG\text{-}B^+$ is $(XR6R7R8)^+$,

wherein

X is nitrogen,

R6 and R7 together are a hydrocarbon chain and form together with X a 5- to 7-membered unsaturated heterocyclic ring in which X is connected by a single bond and a double bond to R6 and R7 respectively,

R8 is selected from the group consisting of H, C_{1-20} alkyl, C_{2-8} alkenyl, C_{1-20} perfluoroalkyl, C_{3-10} cycloalkyl or C_{6-10} aryl;

CatORG-C^+ is $(YR9R10R11)^+$,

wherein

Y is sulphur;

(i) R9, R10 and R11 are identical or different and independently from each other selected from the group consisting of H, C_{1-20} alkyl, C_{1-20} perfluoroalkyl, C_{3-10} cycloalkyl and C_{6-10} aryl; or

(ii) R9 and R10 together are a hydrocarbon chain and form together with Y a 5- to 7-membered saturated or unsaturated ring,

R11 is selected from the group consisting of H, C_{1-20} alkyl, C_{1-20} perfluoroalkyl, C_{3-10} cycloalkyl and C_{6-10} aryl;

the residues R2, R3, R4, R5, R6, R7, R8, R9, R10 and R11 are, independently from each other, unsubstituted or, where applicable, substituted by 1, 2, 3, 4, 5 or 6 substituents selected from the group consisting of C_{1-4} alkyl, C_{3-10} cycloalkyl, C_{2-8} alkenyl, phenyl, benzyl, halogen, cyano and C_{1-4} alkoxy;

in any of said hydrocarbon chains formed by R2 and R3, by R4 and R5, by R6 and R7, and by R9 and R10, 1 or 2 carbon atoms of said hydrocarbon chains can be exchanged for 1 or 2 heteroatoms respectively, said one or two heteroatoms being selected from the group consisting of O, N and S; in case of an exchange for N, this N is unsubstituted or substituted by a residue selected from the group consisting of C_{1-8} alkyl, C_{3-10} cycloalkyl, C_{2-8} alkenyl and C_{1-8} perfluoroalkyl;

R16 is selected from the group consisting of C_{2-8} alkylen, C_{3-8} cycloalkylen, phenylen, C(H)(phenyl), R17(-O-R17)$_{n1}$;

R17 is selected from the group consisting of CH_2-CH_2, CH_2-CH_2-CH_2, CH_2-C(H)(CH_3)-CH_2, CH_2-CH_2-C(H)(CH_3) and CH_2-CH_2-CH_2-CH_2;

R18 and R19 are identical or different and independently from each other selected from the group consisting of H, C_{1-8} alkyl, C_{3-8} cycloalkyl, phenyl and benzyl;

n1 is an integer from 1 to 20.

2. Method according to claim 1, wherein

m is 2, 3 or 4.

3. Method according to claim 1 or 2, wherein

n is 1 or 2.

4. Method according to one or more of claims 1 to 3, wherein

CATACID is selected from the group consisting of HF, HCl, HBr, H_2SO_4, $NaHSO_4$, Oleum, $KHSO_4$, H_3PO_4, HSO_3F, HSO_3Cl, CH_3COOH, CF_3COOH, $C(Cl_3)COOH$, methansulfonic acid, HCOOH, AR-SO_3H, $C(OH)(COOH)_3$, CF_3SO_3H, HCN, HQ20(X1)4, polymolybdate, polytungstate, $HQ21(X1)_6$, and mixtures thereof;

AR is Phe or Phe substituted with 1, 2 or 3 identical or different residues selected from the group consisting of halogen and CH_3;

Q20 is B, Al or Ga;

Q21 is P, Sb or Bi;

X1 is F, Cl or Br.

5. Method according to one or more of claims 1 to 4, wherein

$CatINORG^{n+}$ is a cation selected from the 1., 2., 3., 4., 5., 6., 7., 8., 9., 10., 11., 12., 13., 14. or 15. group of the periodic table or is a cation from the lanthanides or is NH_4^+.

6. Method according to one or more of claims 1 to 5, wherein

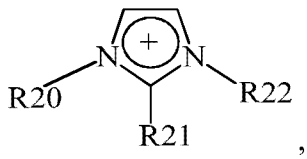
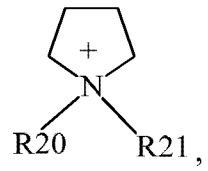
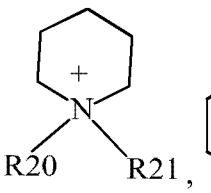
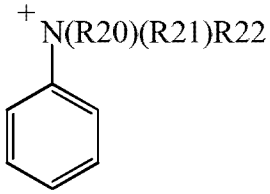
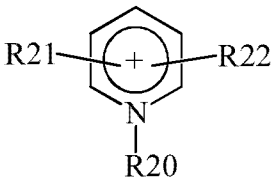
$CatINORG^{n+}$ is selected from the group consisting of Li^+, Na^+, K^+, Rb^+, Cs^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ti^{4+}, Ti^{3+}, Zr^{4+}, Zr^{3+}, Hf^{4+}, Hf^{3+}, V^{4+}, V^{3+}, V^{2+}, Nb^{4+}, Ta^{4+}, Cr^{3+}, Mo^{4+}, Mo^{3+}, Mo^{2+}, W^{4+}, W^{3+}, W^{2+}, Mn^{4+}, Mn^{3+}, Mn^{2+}, Fe^{4+}, Fe^{3+}, Fe^{2+}, Ru^{4+}, Ru^{3+}, Ru^{2+}, Os^{4+}, Os^{3+}, Os^{2+}, Co^{4+}, Co^{3+}, Co^{2+}, Rh^{4+}, Rh^{3+}, Ir^{4+}, Ir^{3+}, Ni^{4+}, Ni^{3+}, Ni^{2+}, Pd^{4+}, Pd^{3+}, Pd^{2+}, Pt^{4+}, Pt^{3+}, Pt^{2+}, Cu^{4+}, Cu^{3+}, Cu^{2+}, Cu^+, Ag^{4+}, Ag^{3+}, Ag^{2+}, Ag^+, Au^{3+}, Au^{2+}, Au^+, Zn^{2+}, Zn^+, Cd^{2+}, Cd^+, Hg^{2+}, Hg^+, B^{3+}, Al^{3+}, Ga^{3+}, Ga^+, In^{3+}, In^+, Tl^{3+}, Tl^+, Ge^{4+},Ge^{2+}, Sn^{4+},Sn^{2+}, Pb^{4+}, Pb^{2+}, As^{3+}, Sb^{3+}, Bi^{3+}, Bi^{1+}, La^{3+}, Nb^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, and NH_4^+.

7. Method according to one or more of claims 1 to 6, wherein

$CatORG^{n+}$ is selected from the group consisting of ammonium, phosphonium, sulfonium, pyrrolidinium, pyrrolinium, pyrrolium, pyrazolium, pyrazolinium, imidazolium, imidazolinium, triazolium, oxazolium, thiazolium, piperidinium, piperazinium, morpholinium, pyridinium, pyridazinium, pyrimidinium, pyrazinium, 1,3-dioxolium,

pyrylium, thiopyrylium, quinoxalinium, indolinium, indolium, $[(CH_3)_3SiFSi(CH_3)_3]^+$, Ph_3C^+, and mixtures thereof.

8. Method according to one or more of claims 1 to 7, wherein

$CatORG^{n+}$ is selected from the group consisting of  ,  ,  ,  ,  , $[N(R20)(R21)(R22)R23]^+$, $[P(R20)(R21)(R22)R23]^+$, $[(CH_3)_3SiFSi(CH_3)_3]^+$, Ph_3C^+, and mixtures thereof;

wherein

R20, R21, R23 are identical or different and independently from each other selected from the group consisting of H, C_{1-20} alkyl, C_{3-10} cycloalkyl and allyl;

R22 is C_{1-20} alkyl, C_{3-10} cycloalkyl or allyl.

9. Method according to one or more of claims 1 to 8, wherein

compound of formula (I) is compound (Group-I),

compound (Group-I) is selected from the group consisting of compound of formula (Ia) and compound of formula (Ib).

$$[Cat^{n+}]\,[(BF(CN)_3)^-]_n \qquad \text{(Ia)}$$

$$[Cat^{n+}]\,[(B(CN)_4)^-]_n \qquad \text{(Ib)}$$

10. Method according to one or more of claims 1 to 9, wherein

compound of formula (I) is selected from the group consisting of compound of formula (1), compound of formula (2), compound of formula (3), and mixtures thereof.

$$[(n\text{-}Bu)_4N][BF(CN)_3] \qquad (1)$$

$[(n\text{-}Pr)_3NH][BF(CN)_3]$ (2)

$[(n\text{-}Pr)_3NH][B(CN)_4]$ (3)

11. Method according to one or more of claims 1 to 10, wherein

REAC1 is done in the presence of a compound CAT;

CAT is a Lewis Acid selected from the group consisting of Lewis Acids derived , that is based on, the 1., 2., 3., 4., 5., 6., 7., 8., 9., 10., 11., 12., 13., 14., 15. and 16. group of the periodic table, zeolite, guanidinium[ANIO] and mixtures thereof.

12. Method according to claims 11, wherein

CAT is selected from the group consisting of $[(CH_3)_3SiFSi(CH_3)_3][ANIO]$, $Q1(R27)_3$, guanidinium[ANIO], $(R26)_3C[ANIO]$, adamantyl[ANIO], $[(R24)_3O][ANIO]$, $[(R25)_3Si][ANIO]$, $Q2(R36)(R28)_3$, $Q3(R29)_3$, $Q4(R30)_5$, $Q5(R32)_3$, $Q6(R33)_2$, $Q7(R31)$, $Q8(R34)_2$, $Q9(R35)_3$, $Q10(R37)_2$, $Q11(R38)$, zeolite and mixtures thereof;

Q1 is selected from the group consisting of B, Al and Ga;

R27 is selected from the group consisting of $C_{1\text{-}10}$ alkoxy, halogen, $C_{1\text{-}10}$ alkyl, CN, SCN and C_6F_5;

R24 is $C_{1\text{-}10}$ alkyl;

R25 is $C_{1\text{-}10}$ alkyl;

R26 is selected from the group consisting of CN, SCN, Ph and $C_{1\text{-}10}$ alkyl;

Q2 is selected from the group consisting of Si and Ti;

R28 and R36 are identical or different and independently from each other selected from the group consisting of $C_{1\text{-}10}$ alkoxy, halogen, $C_{1\text{-}10}$ alkyl, CN, SCN and C_6F_5;

Q3 is selected from the group consisting of P, Sb and Bi;

R29 is selected from the group consisting of $C_{1\text{-}10}$ alkoxy, halogen, CN, SCN, $C_{1\text{-}10}$ alkyl and C_6F_5;

Q4 is selected from the group consisting of P, Sb and Nb;

R30 is selected from the group consisting of $C_{1\text{-}10}$ alkoxy, halogen, CN, SCN, $C_{1\text{-}10}$ alkyl and C_6F_5;

Q5 is selected from the group consisting of Cr and Fe;

R32 is selected from the group consisting of halogen, CN and SCN;

Q6 is selected from the group consisting of Mn, Fe, Pd and Pt;

R33 is selected from the group consisting of halogen, CN and SCN;

Q7 is Cu or Ag;

R31 is selected from the group consisting of halogen, CN and SCN;

Q8 is selected from the group consisting of Cu, Zn, Cd and Hg;

R34 is selected from the group consisting of halogen, CN, and SCN;

Q9 Sc or Ln;

R35 is selected from the group consisting of halogen, CN, and SCN;

Q10 Ca;

R37 is halogen;

Q11 K;

R38 is halogen;

ANIO is selected from the group consisting of $[P(R40)_{6-m1}(R41)_{m1}]^-$, $[B(R42)_{4-m2}(R43)_{m2}]^-$, F^-, Cl^-, Br^-, I^-, CN^- and SCN^-;

R40 and R41 are identical of different in independently from each other selected from the group consisting of CN, SCN, F, Cl, Br and I;

m1 is 0, 1, 2, 3, 4 or 5;

R42 and R43 are identical of different in independently from each other selected from the group consisting of C_6F_5, CN, SCN, F, Cl, Br and I;

m2 is 0, 1, 2 or 3.

13. Method according to one or more of claims 1 to 12, wherein

the method comprises additionally to STEP1 a step STEP2, STEP2 is done after STEP1;

STEP2 comprises a reaction REAC2, REAC2 is a metathesis reaction wherein cation Cat^{n+} in compound of formula (I) is exchanged for a cation different from Cat^{n+};

compound of formula (I) having been prepared in STEP1.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/057584

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07F9/02 C01B25/00 C09K19/00 H01M10/0568
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)
C07F C01B C09K H01M

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2014/029833 A1 (LONZA AG [CH]) 27 February 2014 (2014-02-27) Method for producing [(nBu)4N][BF(CN)3] from [(nBu)4N][BF4] and TMS-CN: examples 1-5; analogous method for producing [Me4N][BF(CN)3]: example 6; analogous method for producing [(nOct)4N][BF(CN)3]: example 7 ----- -/--	1-13

[X] Further documents are listed in the continuation of Box C.

[X] 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

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 June 2016	11/07/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Lange, Tim

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 2 772 495 A1 (LONZA AG [CH]) 3 September 2014 (2014-09-03) Method for producing [(nBu)4N][BF(CN)3] from [(nBu)4N][BF4] and TMS-CN: examples 1-5; analogous method for producing [Me4N][BF(CN)3]: example 6; analogous method for producing [(nOct)4N][BF(CN)3]: example 7	1-13
A	WO 2014/029834 A1 (LONZA AG [CH]) 27 February 2014 (2014-02-27) Method for producing [(nBu)4N][BF(CN)4] from [(nBu)4N][BF4] and TMS-CN: example 1, page 8; analogous method for producing [(nOct)4N][B(CN)4]: example 9	1-13
A	JAN A. P. SPRENGER ET AL: "Syntheses of Tricyanofluoroborates M[BF(CN) 3] (M = Na, K): (CH 3) 3 SiCl Catalysis, Countercation Effect, and Reaction Intermediates", INORGANIC CHEMISTRY, vol. 54, no. 7, 6 April 2015 (2015-04-06), pages 3403-3412, XP055214264, ISSN: 0020-1669, DOI: 10.1021/ic503077c Method for producing K[BF(CN)3] from Na[BF4] and TMS-CN using TMS-Cl as catalyst: scheme 2 TMS-Cl plays the role of a catalysts that enables a cleaner reaction: Page 3406, right column	1-13
A	EDUARD BERNHARDT ET AL: "Die Reaktionen von M[BF4] (M = Li, K) und (C2H5)2O.BF3 mit (CH3)3SiCN. Bildung von M[BFx>(CN)4-x] (M = Li, K; x = 1, 2) und (CH3)3SiNCBFx(CN)3-x, (x = 0, 1)", ZEITSCHRIFT F&#XFFFD;R ANORGANISCHE UND ALLGEMEINE CHEMIE, vol. 629, no. 4, 2003, pages 677-685, XP055043104, ISSN: 0044-2313, DOI: 10.1002/zaac.200390115 Method for producing Li[BF2(CN)2] from Li[BF4] and TMS-CN: equation (1) on page 678 and paragraph 2) on page 684; analogous method for producingLi[BF(CN)3]: equation 2, same page; analogous method for producing K[BF(CN)3]: equation 4, page 678	1-13

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WILLIAMS D ET AL: "Synthesis of LiBC4N4, BC3N3, and Related C-N Compounds of Boron: New Precursors to Light Element Ceramics", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, AMERICAN CHEMICAL SOCIETY, US, vol. 122, 2000, pages 7735-7741, XP002278152, ISSN: 0002-7863, DOI: 10.1021/JA0006752 Method for producing Li[B(CN)4] from Li[BF4] and TMS-CN: page 7740, compound 1	1-13
A	BERNHARDT E ET AL: "EINE EFFIZIENTE SYNTHESE VON TETRACYANOBORATEN DURCH SINTERPROZESSE//AN EFFICIENT SYNTHESIS FOR TETRACYANOBORATES BY SINTER PROCESSES", ZEITSCHRIFT FUR ANORGANISCHE UND ALLGEMEINE CHEMIE, WILEY - V C H VERLAG GMBH & CO. KGAA, DE, vol. 629, no. 7/08, 2003, pages 1229-1234, XP009030008, ISSN: 0044-2313, DOI: 10.1002/ZAAC.200300047 disclosure of [NPr3H][B(CN)4] : page 1232	10
A	TORSTEN KÜPPERS ET AL: "Tetracyanoborate Salts M[B(CN) 4] with M = Singly Charged Cations: Properties and Structures", INORGANIC CHEMISTRY, vol. 44, no. 4, 2005, pages 1015-1022, XP055214417, ISSN: 0020-1669, DOI: 10.1021/ic048780q disclosure of [NPr3H][B(CN)4] and method to make it from KBF4, LiCl and KCN: page 1018 last paragraph	10
X,P	WO 2015/067405 A1 (LONZA AG [CH]) 14 May 2015 (2015-05-14) method of claim 1, using Lewis acid to catalyze conversion of Tetrafluoroborates with TMS-CN into mixed fluoro-cyano-boranates of type [BF4-m(CN)m]-	1-13
X,P	KEVIN BLÄSING ET AL: "Lewis Acid Catalyzed Synthesis of Cyanidoborates", EUROPEAN JOURNAL OF INORGANIC CHEMISTRY., vol. 2016, no. 8, 18 March 2016 (2016-03-18), pages 1175-1183, XP055283519, DE ISSN: 1434-1948, DOI: 10.1002/ejic.201501485 the whole document	1-13

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/057584

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2014029833 A1	27-02-2014	NONE	
EP 2772495 A1	03-09-2014	NONE	
WO 2014029834 A1	27-02-2014	NONE	
WO 2015067405 A1	14-05-2015	CA 2926010 A1	14-05-2015
		EP 3039740 A1	06-07-2016
		TW 201522223 A	16-06-2015
		WO 2015067405 A1	14-05-2015