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(54) Title: PROCESS FOR THE SELECTIVE CLEAVAGE OF C-SCF₃ BONDS AND ANALOGUES

(57) Abstract: The invention relates to a process for the preparation of a compound A-R, by reacting a compound A-X, in the presence of a metallic complex comprising nickel, palladium or rhodium (I), a ligand, a nucleophile carrying one group R, and a solvent, R being a hydrocarbon group, optionally including at least one heteroatom and/or at least one atom other than C or H, A being selected from the group consisting of: (C₆-C₁₀)aryl groups, heteroaryl groups, and a vinyl compound, and X being selected from the group consisting of: YCF₃, Y(O)_nCF₃, YCF₂SO₂Ph, Y(O)_nCF₂SO₂Ph, Y(O)_nCF₂COOR, Y(O)_nCF₂CONR₂, Y(O)_nCF₂CH₂OH, Y(O)_nCN, Y(O)_nCHF₂, Y(O)_nCF₂H, Y(O)_nCF₂C_nF_{2n+1}, Y(O)_nCF₂COR, Y being S or Se, n being 1 or 2, and R being (C₁-C₆)alkyl.



PROCESS FOR THE SELECTIVE CLEAVAGE OF C-SCF₃ BONDS AND ANALOGUES

5 The present invention concerns a process for the selective cleavage of C-SCF₃ bonds and analogues of such bonds.

10 In a society concerned about the environment, earth and aquatic systems pollution and circular economy, development of new technologies to meet such objectives is nowadays a real challenge and a hot topic across the whole chemical industry.

15 The field of organofluorine chemistry is unavoidable and fluorinated compounds are highly represented in many fields such as materials science, pharmaceutical and agrochemical industries. Indeed, the incorporation of a fluorine atom or a fluorinated unit can modify the physico-chemical properties of organic molecules in a significant way explaining the interest of the scientific community regarding this research area. However, the prevalence of these compounds raises the question of their fate and degradation. Recently, there has been a strong awareness from the scientific community and society regarding chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs) and per- and poly-fluoroalkyl substances (PFAs). It is now important to go even further and to look at the fate of emerging fluorinated groups that have become essential, such as derivatives containing a SCF₃ unit (eg. Toltrazuril and Fipronil).

20 In this context, the development of tools allowing to valorize these fluorinated derivatives, which, once used, are then considered as waste by converting them into compounds with high added value would have an undeniable ecological impact and allow for cost reduction. It is therefore essential to develop innovative tools to meet this challenge and to remove this synthetic lock.

25 There is currently no technology allowing to selectively cleave C(sp²)-SRf bonds on (hetero)aromatic derivatives or vinyl positions or C(sp³)-SRf bonds and any progress would have a major impact from a scientific and environmental point of view.

30 N. Barbero *et al.*, Organic Letters, 2012, 14, 796-799 (Supporting Information, S1-S78) relates to catalytic reductive cleavage of unactivated C-SMe bonds. As shown on page 797, left column, last paragraph, the SMe group, namely an electron-donating group on the sulfur atom, was reported as the most efficient in the reductive cleavage of C-S bond. The optimization process reported in Tables 1 to 6 of the supporting information (p. S3 to S5) was carried out for this specific thioether only.

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Table 7 (p. S5) of this document confirms that SMe group raises the highest yield with respect to cleavage of the C-S bond, while electron-attracting groups, such as Ac and CONMe₂, were inefficient.

Surprisingly, it has now been found that it was possible to selectively cleave C-S bonds and analogues of such bonds on organic molecules in the presence of an electron-attracting fluorinated group, such as CF₃ or analogous fluorine-containing groups.

One aim of the present invention is thus to provide a tool for the de-fluorination of fluorinated compounds.

One aim of the present invention is to provide a process for the de-fluorination of fluorinated compounds, for example through the cleavage of C-SCF₃ bonds, or analogues of such bonds.

The present invention relates to a process for the preparation of a compound having the formula (I):



by reacting a compound having the formula (II):



in the presence of a metallic complex comprising nickel, palladium or rhodium(I), a ligand, a nucleophile carrying one group R, and a solvent,

R being a hydrocarbon group, optionally including at least one heteroatom such as S, N or O, and/or at least one atom other than C or H, such as Se, Si, B, or P,

wherein:

- A is selected from the group consisting of:

. (C₆-C₁₀)aryl groups,

said aryl groups being optionally substituted with at least one substituent preferably selected from the group consisting of: halogen, (C₁-C₆)alkyl, (C₁-C₆)alkoxy, -CN, -CF₃, -OCF₃, -NR_aR_b, -SiR_aR_bR_c, -BR_aR_b, (C₂-C₆)alkenyl, (C₂-C₆)alkynyl, -C(=O)-NR_aR_b, and -C(=O)-O(C₁-C₆)alkyl;

R_a and R_b being independently from each other H or a (C₁-C₆)alkyl group; R_c being a (C₁-C₆)alkyl group;

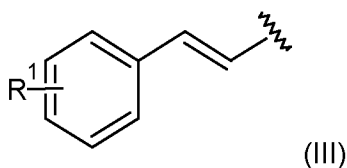
. heteroaryl groups comprising from 5 to 10 atoms and including at least one heteroatom selected from O, N, and S,

said heteroaryl groups being optionally substituted with at least one substituent preferably selected from: halogen, (C₁-C₆)alkyl, (C₁-C₆)alkoxy,

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-CN, -CF₃, -OCF₃, -NR_aR_b, -Si(R_c)₃, -BR_aR_b, (C₂-C₆)alkenyl, (C₂-C₆)alkynyl, -C(=O)-NR_aR_b, and -C(=O)-O(C₁-C₆)alkyl, R_a, R_b and R_c being as defined above; and

. a vinyl compound having the following formula (III):



R¹ being selected from the group consisting of: halogen, (C₁-C₆)alkyl, (C₁-C₆)alkoxy, -CN, -CF₃, -OCF₃, -NR_aR_b, -Si(R_c)₃, -BR_aR_b, (C₂-C₆)alkenyl, (C₂-C₆)alkynyl, -C(=O)-NR_aR_b, and -C(=O)-O(C₁-C₆)alkyl, R_a, R_b and R_c being as defined above; and

- X is selected from the group consisting of: YCF₃, YOCF₃, YO₂CF₃, YCF₂SO₂Ph, YOCF₂SO₂Ph, YO₂CF₂SO₂Ph, Y(O)_nCF₂COOR', Y(O)_nCF₂CONR'₂, Y(O)_nCF₂CH₂OH, Y(O)_nCN, Y(O)_nCHF₂, Y(O)_nCF₂H, Y(O)_nCF₂C_nF_{2n+1}, Y(O)_nCF₂COR', Y being S or Se, n being 1 or 2, and R' being (C₁-C₆)alkyl.

Thus, the present invention relates to a process for the preparation of a compound having the formula (I):

A-R

by reacting a compound having the formula (II):

A-X

in the presence of a metallic complex comprising nickel, a ligand, a nucleophile carrying one group R, and a solvent,

R being a hydrocarbon group, optionally including at least one heteroatom such as S, N or O, and/or at least one atom other than C or H, such as Se, Si, B, or P,

wherein:

- A is selected from the group consisting of:

. (C₆-C₁₀)aryl groups,

said aryl groups being optionally substituted with at least one substituent preferably selected from the group consisting of: halogen, (C₁-C₆)alkyl, (C₁-

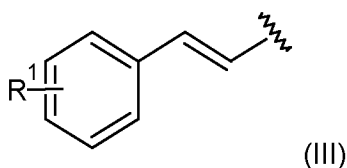
C₆)alkoxy, -CN, -CF₃, -OCF₃, -NR_aR_b, -SiR_aR_bR_c, -BR_aR_b, (C₂-C₆)alkenyl, (C₂-C₆)alkynyl, -C(=O)-NR_aR_b, and -C(=O)-O(C₁-C₆)alkyl;

R_a and R_b being independently from each other H or a (C₁-C₆)alkyl group; R_c being a (C₁-C₆)alkyl group;

heteroaryl groups comprising from 5 to 10 atoms and including at least one heteroatom selected from O, N, and S,

said heteroaryl groups being optionally substituted with at least one substituent preferably selected from: halogen, (C₁-C₆)alkyl, (C₁-C₆)alkoxy, -CN, -CF₃, -OCF₃, -NR_aR_b, -Si(R_c)₃, -BR_aR_b, (C₂-C₆)alkenyl, (C₂-C₆)alkynyl, -C(=O)-NR_aR_b, and -C(=O)-O(C₁-C₆)alkyl, R_a, R_b and R_c being as defined above; and

a vinyl compound having the following formula (III):



R¹ being selected from the group consisting of: halogen, (C₁-C₆)alkyl, (C₁-C₆)alkoxy, -CN, -CF₃, -OCF₃, -NR_aR_b, -Si(R_c)₃, -BR_aR_b, (C₂-C₆)alkenyl, (C₂-C₆)alkynyl, -C(=O)-NR_aR_b, and -C(=O)-O(C₁-C₆)alkyl, R_a, R_b and R_c being as defined above; and

- X is selected from the group consisting of: YCF₃, YO CF₃, YO₂CF₃, YCF₂SO₂Ph, YO CF₂SO₂Ph, YO₂CF₂SO₂Ph, Y(O)_nCF₂COOR', Y(O)_nCF₂CONR'₂, Y(O)_nCF₂CH₂OH, Y(O)_nCN, Y(O)_nCHF₂, Y(O)_nCF₂H, Y(O)_nCF₂C_nF_{2n+1}, Y(O)_nCF₂COR', Y being S or Se, n being 1 or 2, and R' being (C₁-C₆)alkyl.

According to an embodiment, in formula (II) above, X is selected from the group consisting of: SCF₃, SOCF₃, SO₂CF₃, SCF₂SO₂Ph, SOCF₂SO₂Ph, SO₂CF₂SO₂Ph, S(O)_nCF₂COOR, S(O)_nCF₂CONR₂, S(O)_nCF₂CH₂OH, S(O)_nCN, S(O)_nCHF₂, S(O)_nCF₂H, S(O)_nCF₂C_nF_{2n+1}, S(O)_nCF₂COR, and all analogues of this list in the selenium series, R and n being as defined above.

According to an embodiment, in formula (II) above, X is selected from the group consisting of: SCF₃, SOCF₃, SO₂CF₃, SCF₂SO₂Ph, SOCF₂SO₂Ph, SO₂CF₂SO₂Ph, S(O)_nCF₂COOR, S(O)_nCF₂CONR₂, S(O)_nCF₂CH₂OH, S(O)_nCN, S(O)_nCHF₂, S(O)_nCF₂H, S(O)_nCF₂C_nF_{2n+1}, S(O)_nCF₂COR, and SeCF₃.

According to an embodiment, in formula (II) above, X is selected from the group consisting of: SCF₃, SOCF₃, SO₂CF₃, SCF₂SO₂Ph, SO₂CF₂SO₂Ph, and SeCF₃.

The following definitions are set forth to illustrate and define the meaning and scope of the various terms used to describe the invention herein.

The expression "C_t-C_z" means a carbon-based chain which can have from t to z carbon atoms, for example C₁-C₃ means a carbon-based chain which can have from 1 to 3 carbon atoms.

The term "alkyl group" means: a linear or branched, saturated, hydrocarbon-based aliphatic group comprising, unless otherwise mentioned, from 1 to 12 carbon atoms. By way of examples, mention may be made of methyl, ethyl, n-propyl, isopropyl, butyl, isobutyl, tert-butyl or pentyl groups.

The term "aryl group" means: a cyclic aromatic group comprising between 6 and 10 carbon atoms. By way of examples of aryl groups, mention may be made of phenyl or naphthyl groups.

The term "heteroaryl group" means: a 5- to 10-membered aromatic monocyclic or bicyclic group containing from 1 to 4 heteroatoms selected from O, S or N. By way of examples, mention may be made of imidazolyl, thiazolyl, oxazolyl, furanyl, thiophenyl, pyrazolyl, oxadiazolyl, tetrazolyl, pyridinyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolyl, benzofuranyl, benzothiophenyl, benzoxazolyl, benzimidazolyl, indazolyl, benzothiazolyl, isobenzothiazolyl, benzotriazolyl, quinolinyl and isoquinolinyl groups.

By way of a heteroaryl comprising 5 to 6 atoms, including 1 to 4 nitrogen atoms, mention may in particular be made of the following representative groups: pyrrolyl, pyrazolyl, 1,2,3-triazolyl, 1,2,4-triazolyl, tetrazolyl and 1,2,3-triazinyl.

Mention may also be made, by way of heteroaryl, of thiophenyl, oxazolyl, furazanyl, 1,2,4-thiadiazolyl, naphthyridinyl, quinoxalinyl, phthalazinyl, imidazo[1,2-a]pyridine, imidazo[2,1-b]thiazolyl, cinnolinyl, benzofurazanyl, azaindolyl, benzimidazolyl, benzothiophenyl, thienopyridyl, thienopyrimidinyl, pyrrolopyridyl, imidazopyridyl, benzoazaindole, 1,2,4-triazinyl, indoliziny, isoxazolyl, isoquinolinyl, isothiazolyl, purinyl, quinazolinyl, quinolinyl, isoquinolyl, 1,3,4-thiadiazolyl, thiazolyl, isothiazolyl, carbazolyl, and also the corresponding groups resulting from their fusion or from fusion with the phenyl nucleus.

When an alkyl group is substituted with an aryl group, the term "arylalkyl" or "aralkyl" group is used. The "arylalkyl" or "aralkyl" groups are aryl-alkyl- groups, the

aryl and alkyl groups being as defined above. Among the arylalkyl groups, mention may in particular be made of the benzyl or phenethyl groups.

The term "halogen" means: a fluorine, a chlorine, a bromine or an iodine.

The term "alkoxy group" means: an -O-alkyl group where the alkyl group is as previously defined. By way of examples, mention may be made of -O-(C₁-C₄)alkyl groups, and in particular the -O-methyl group, the -O-ethyl group, as -O-C₃alkyl group, the -O-propyl group, the -O-isopropyl group, and as -O-C₄alkyl group, the -O-butyl, -O-isobutyl or -O-tert-butyl group.

The term "alkynyl" as employed herein includes unsaturated, nonaromatic, hydrocarbon groups having 2 to 6 carbons, and comprising at least one triple bond. Preferably, the alkynyl group is linear. Preferably, the alkynyl group is a -(CH₂)_m-C≡CH group, m being an integer comprised from 1 to 4.

The term "alkenyl" as employed herein includes unsaturated, nonaromatic, hydrocarbon groups having 2 to 6 carbons, and comprising at least one double bond. Preferably, the alkenyl group is linear. Preferably, the alkenyl group is a -(CH₂)_m-CH=CH₂ group, m being an integer comprised from 1 to 4.

The abovementioned "alkyl", "aryl", and "heteroaryl" groups can be substituted with one or more substituents. Among these substituents, mention may be made of the following groups: amino, amide, hydroxyl, thiol, oxo, halogen, alkyl, alkoxy, alkylthio, alkylamino, aryloxy, arylalkoxy, cyano, trifluoromethyl, carboxy or carboxyalkyl.

The term "alkylthio" means: an -S-alkyl group, the alkyl group being as defined above.

The term "alkylamino" means: an -NH-alkyl group, the alkyl group being as defined above.

The term "aryloxy" means: an -O-aryl group, the aryl group being as defined above.

The term "arylalkoxy" means: an aryl-alkoxy- group, the aryl and alkoxy groups being as defined above.

The term "carboxyalkyl" means: an HOOC-alkyl- group, the alkyl group being as defined above. As examples of carboxyalkyl groups, mention may in particular be made of carboxymethyl or carboxyethyl.

The term "haloalkyl group" means: an alkyl group as defined above, in which one or more of the hydrogen atoms is(are) replaced with a halogen atom. By way of example, mention may be made of fluoroalkyls, in particular CF₃ or CHF₂.

The term "carboxyl" means: a COOH group.

The term "oxo" means: " $=O$ ".

The term "hydrocarbon group" means a group comprising hydrogen and carbon atoms. As mentioned above, R is a group comprising at least one carbon atom and at least one hydrogen atom. This group may also include at least one heteroatom, such as O, N or S, and/or at least one atom other than C or H, such as Se, Si, B or P.

In one embodiment of the process according to the invention, the nucleophile is selected from the group consisting of: alkyl amines, cycloalkyl amines, aryl amines, alkyl thiols, thiophenol compounds, aryl selenol compounds, phosphine oxides, Grignard reagents, alcohols, esters and phosphorus derivatives. The alkyl amines, cycloalkyl amines and aryl amines can be either primary or secondary amines. The terms "alkyl", "cycloalkyl", and "aryl" are as defined above.

Preferably, the nucleophile is a RH group, wherein R is selected from the group consisting of: (C_1-C_6) alkyl, heterocycloalkyl, $-S-cyclo(C_3-C_{10})$ alkyl, $-O-(C_1-C_{12})$ alkyl, an optionally substituted heteroaryl, $-NR^1R^2$, $-P(=O)-R^1R^2$, $-X^1-Ar^1$, $-X^1-(C_1-C_{12})$ alkyl- Ar^1 , $-X^1-Het^1$, $-X^1-(C_1-C_{12})$ alkyl- Het^1 , X^1 being S, Se, NH or N-alkyl, Ar^1 being an optionally substituted (C_6-C_{10}) aryl group, Het^1 being an optionally substituted heteroaryl group and R^1 and R^2 being, independently from each other, a (C_1-C_6) alkyl group or a (C_6-C_{10}) aryl group.

In particular, when the nucleophile is a cycloalkyl amine, R can be a $cyclo(C_3-C_{10})$ alkylamino group as defined above.

In particular, when the nucleophile is a thiol, R can be $-S-(C_1-C_6)$ alkyl ("alkylthio" as defined above), the alkyl being optionally substituted as defined above.

In particular, R can be (C_1-C_6) alkyl, $S-cyclo(C_3-C_{10})$ alkyl, $O-(C_1-C_{12})$ alkyl ("alkoxy" as defined above), $-X^1-(C_1-C_{12})$ alkyl- Ar^1 , $X^1-(C_1-C_{12})$ alkyl- Het^1 , where $-X^1$, Ar^1 and Het^1 are as defined above, and where the alkyl is optionally substituted by at least one substituent as defined above.

The terms "alkyl", "aryl", "heterocycloalkyl", heteroaryl" and their optional substituents are as defined above.

Preferably, R is selected from the group consisting of: (C_1-C_6) alkyl, heterocycloalkyl, $-S-cyclo(C_3-C_{10})$ alkyl, $-P(=O)-R^1R^2$, and $-X^1-Ar^1$, X^1 being S, Se or NH, and Ar^1 being an optionally substituted (C_6-C_{10}) aryl group, and R^1 and R^2 being, independently from each other, a (C_1-C_6) alkyl group or a (C_6-C_{10}) aryl group.

More preferably, the nucleophile is selected from the group consisting of: heterocycloalkyl groups comprising at least one nitrogen and/or sulfur atom such as

morpholine, aniline groups and derivatives thereof, such as 4-methylaniline, H-S-(cyclo)alkyl groups, such as CySH, H-S-aryl groups, such as 4-methylthiophenol, H-Se-aryl groups, such as benzene selenol, phosphine oxides such as HP(=O)Ph₂, Grignard reagents such as Alk-MgBr, in particular iPrMgBr and phosphorus derivatives such as HPPH₂ where Ph is phenyl.

In one embodiment, in formula (I) and in formula (II) as defined above, A is selected from the heteroaryl groups comprising from 5 to 10 atoms and including at least one heteroatom selected from O, N, and S, said heteroaryl groups being optionally substituted with at least one substituent selected from: halogen, (C₁-C₆)alkyl, (C₁-C₆)alkoxy, -CN, -CF₃, -OCF₃, -NR_aR_b, -Si(R_c)₃, -BR_aR_b, (C₂-C₆)alkenyl, (C₂-C₆)alkynyl, -C(=O)-NR_aR_b, and -C(=O)-O(C₁-C₆)alkyl, R_a, R_b and R_c being as defined above.

According to one embodiment, the process of the invention as defined above further comprises the use of a hydride compound, such as LiHMDS. In this embodiment, the compound having the formula (II) is reacted with the nucleophile in the presence of the metallic complex comprising nickel, palladium or rhodium (I) the ligand, and the solvent, and also with a hydride compound.

In this embodiment, the nucleophile is in particular a Grignard reactant.

According to one embodiment, in the process according to the invention, the ligand is selected from the group consisting of: 1,5-cyclooctadiene (COD), 1,2-Bis(dicyclohexylphosphino)ethane (dcype), 1,1'-Bis(diphenylphosphino)ferrocene (dppf), 1,1'-Bis(di-*tert*-butylphosphino)ferrocene (DTBPF), 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene (XantPhos), triphenylarsine (AsPh₃) and triphenylphosphane (PPh₃).

The term "ligand" refers to a chemical component that is able to bind to the metal of the metallic complex. The initial state of a metallic complex is the state where the metallic complex is used in the reaction medium. In the initial state of the metallic complex, the ligand can be bound to the metal.

Alternatively, the ligand can be added to the reaction medium in addition to the metallic complex. In such case, the ligand will bind to the metal in the reaction medium.

According to an embodiment of the process, the ligand is bound to the metal in the initial state of the metallic complex.

According to another embodiment of the process, the ligand is added to the reaction medium in addition to the metallic complex.

According to a further embodiment of the process, at least one first ligand is bound to the metal in the initial state of the metallic complex and at least one second ligand is added to the reaction medium in addition to the metallic complex, wherein the first and second ligands are identical or different.

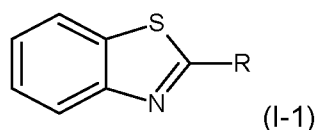
Preferably, the metallic complex is a Ni(0) complex such as bis(1,5-cyclooctadiene)nickel (Ni[cod]₂) or bis(triphenylphosphine)nickel (Ni[PPh₃]₂).

According to another embodiment, the metallic complex comprises nickel, palladium or rhodium(I). For example, the metallic complex can be a Pd(0) complex such as tris(dibenzylideneacetone)dipalladium(0) of formula Pd₂dba₃ or tetrakis(triphenylphosphine)palladium(0) of formula Pd(PPh₃)₄. In particular, the metallic complex can be a Pd(II) complex such as, for example, [1,3-Bis(2,6-Diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride (PEPPSITM-SIPr catalyst, 905459-27-0), palladium(II) acetate of formula Pd(OAc)₂ or allylpalladium(II) chloride dimer of formula [Pd(π-allyl)Cl]₂. Alternatively, the metallic complex can be a Rh(I) complex such as, for example, rhodium carbonyl chloride of formula [Rh(CO)₂Cl]₂ or a hydroxy(cyclooctadiene)rhodium(I) dimer of formula [Rh(OH)COD]₂.

According to one embodiment, the solvent used in the process according to the invention is selected from the usual solvents used in the field. Preferably, the solvent for the process according to the invention is toluene.

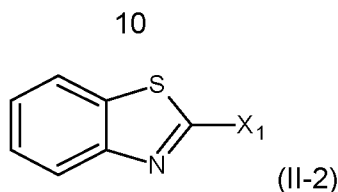
According to one embodiment of the process according to the invention, the reaction is carried out a temperature from 90°C to 140°C. Preferably, the reaction may be carried out at 90°C, 110°C, 120°C, and 140°C.

The present invention also relates to the process as defined above, for the preparation of a compound having the formula (I-1):



R being as defined above,

from a compound having the formula (II-1):



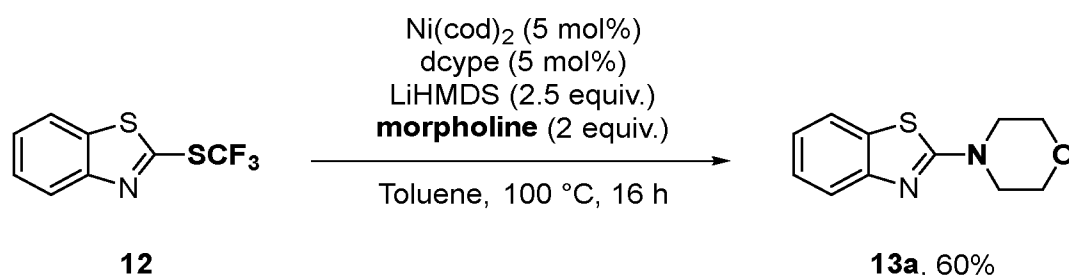
X_1 being selected from the group consisting of: SCF_3 , SOCF_3 , SO_2CF_3 , $\text{SCF}_2\text{SO}_2\text{Ph}$, $\text{SOCF}_2\text{SO}_2\text{Ph}$, $\text{SO}_2\text{CF}_2\text{SO}_2\text{Ph}$, and SeCF_3 .

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EXAMPLES

Example 1: Selective cleavage of C- SCF_3 bond in the presence of an alkyl amine as a nucleophile

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Scheme 1: Reaction conditions: **12** (0.5 mmol, 1 equiv.), Ni(cod)_2 (5 mol%), dcype (5 mol%), LiHMDS (2.5 equiv.), morpholine (2 equiv.), toluene (0.4M), 100°C, 16 h. Yield shown is the isolated yield.

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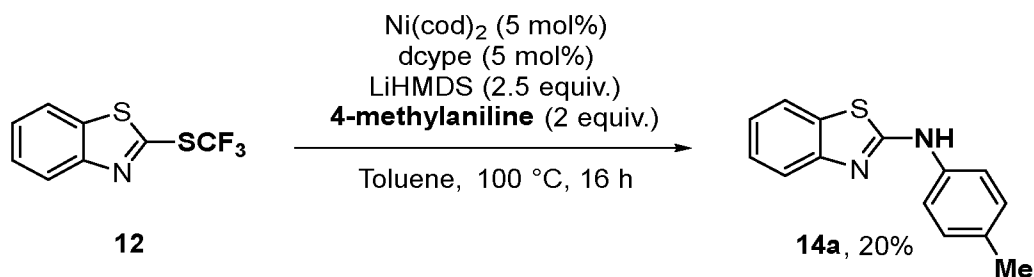
An oven-dried 10 mL tube equipped with a stirring bar was charged with Ni(cod)_2 (7 mg, 0.025 mmol, 5 mol%), dcype (11 mg, 0.025 mmol, 5 mol%), LiHMDS (209 mg, 1.25 mmol, 2.5 equiv.), 2-((trifluoromethylthio)benzo[d]thiazole **12** (118 mg, 0.5 mmol, 1 equiv.), alkyl amine (1.25 mmol, 2 equiv.) and toluene (1.25 mL) under argon. The resulting solution was stirred at 100 °C for 16 h. The mixture was allowed to cool down to 21 °C. EtOAc (10 mL) was added in the mixture and the resulting solution was washed with an aqueous solution of NaOH (1M, 10 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried over MgSO_4 and concentrated under vacuum. The residue was purified by silica gel flash column chromatography to isolate the desired product **13a**.

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The result shows that the cleavage of the C-S bond in the presence of a CF_3 group is achieved with a good yield when using an alkylamine as a nucleophile.

Example 2: Selective cleavage of C- SCF_3 bond in the presence of an aryl amine as a nucleophile

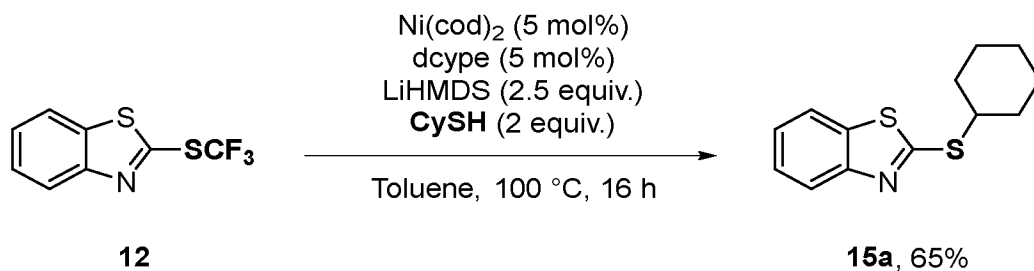


Scheme 2: Reaction conditions: **12** (0.5 mmol, 1 equiv.), $\text{Ni}(\text{cod})_2$ (5 mol%), dcype (5 mol%), LiHMDS (2.5 equiv.), 4-methylaniline (2 equiv.), toluene (0.4M), 100°C, 16 h. Yield shown is the isolated yield.

An oven-dried 10 mL tube equipped with a stirring bar was charged with $\text{Ni}(\text{cod})_2$ (7 mg, 0.025 mmol, 5 mol%), dcype (11 mg, 0.025 mmol, 5 mol%), LiHMDS (209 mg, 1.25 mmol, 2.5 equiv.), 2-((trifluoromethylthio)benzo[d]thiazole **12** (118 mg, 0.5 mmol, 1 equiv.), aryl amine (1.25 mmol, 2 equiv.) and toluene (1.25 mL) under argon. The resulting solution was stirred at 100 °C for 16 h. The mixture was allowed to cooled down to 21 °C. EtOAc (10 mL) was added in the mixture and the resulting solution was washed with an aqueous solution of NaOH (1M, 10 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried over MgSO_4 and concentrated under vacuum. The residue was purified by silica gel flash column chromatography to afford the desired product **14a**.

The result shows that primary and aromatic amines are suitable nucleophiles in this Ni-catalyzed transformation allowing the cleavage of the C-S bond in the presence of a CF_3 group.

Example 3: Selective cleavage of C-SCF₃ bond in the presence of an alkyl thiol as a nucleophile

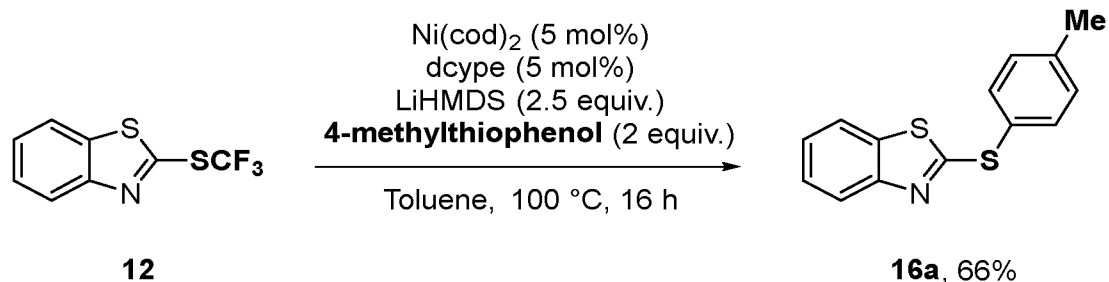


Scheme 3: Reaction conditions: **12** (0.5 mmol, 1 equiv.), Ni(cod)₂ (5 mol%), dcype (5 mol%), LiHMDS (2.5 equiv.), CySH (2 equiv.), toluene (0.4M), 100 °C, 16 h. Yield shown is the isolated yield.

An oven-dried 10 mL tube equipped with a stirring bar was charged with Ni(cod)₂ (7 mg, 0.025 mmol, 5 mol%), dcype (11 mg, 0.025 mmol, 5 mol%), LiHMDS (209 mg, 1.25 mmol, 2.5 equiv.), 2-((trifluoromethyl)thio)benzo[d]thiazole **12** (118 mg, 0.5 mmol, 1 equiv.), alkyl thiol (1.25 mmol, 2 equiv.) and toluene (1.25 mL) under argon. The resulting solution was stirred at 100 °C for 16 h. The mixture was allowed to cooled down to 21 °C. EtOAc (10 mL) was added in the mixture and the resulting solution was washed with an aqueous solution of NaOH (1M, 10 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried over MgSO₄ and concentrated under vacuum. The residue was purified by silica gel flash column chromatography to afford the desired product **15a**.

The result shows that the SCF₃ group was selectively replaced by a group consisting of a sulfur atom linked to an alkyl (SAlkyl group) with a high yield.

Example 4: Selective cleavage of C-SCF₃ bond in the presence of a thiophenol derivative as a nucleophile



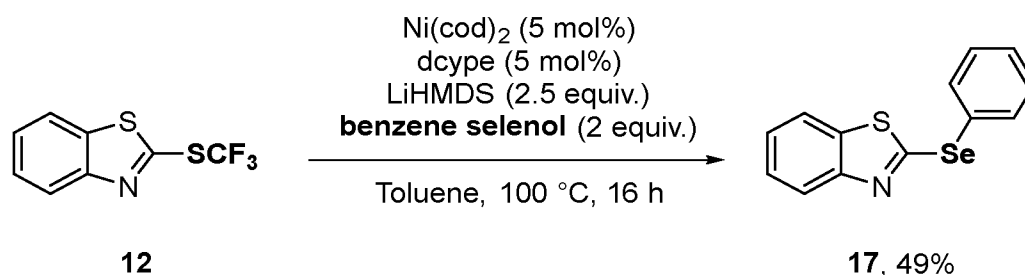
Scheme 4: Reaction conditions: **12** (0.5 mmol, 1 equiv.), Ni(cod)₂ (5 mol%), dcype (5 mol%), LiHMDS (2.5 equiv.), 4-methylthiophenol (2 equiv.), toluene (0.4M), 100°C, 16 h. Yield shown is the isolated yield.

An oven-dried 10 mL tube equipped with a stirring bar was charged with Ni(cod)₂ (7 mg, 0.025 mmol, 5 mol%), dcype (11 mg, 0.025 mmol, 5 mol%), LiHMDS (209 mg, 1.25 mmol, 2.5 equiv.), 2-((trifluoromethyl)thio)benzo[d]thiazole **12** (118 mg, 0.5 mmol, 1 equiv.), aryl thiol (1.25 mmol, 2 equiv.) and toluene (1.25 mL) under argon. The resulting solution was stirred at 100 °C for 16 h. The mixture was allowed to cooled down to 21 °C. EtOAc (10 mL) was added in the mixture and the resulting

solution was washed with an aqueous solution of NaOH (1M, 10 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried over MgSO₄ and concentrated under vacuum. The residue was purified by silica gel flash column chromatography to isolate the desired product **16a**.

The SCF₃ moiety was also successfully replaced by a group consisting of a sulfur atom linked to an aryl (SAr group). These results showed that chalcogens are well compatible as class of nucleophiles.

Example 5: Selective cleavage of C-SCF₃ bond in the presence of an aryl selenol as a nucleophile

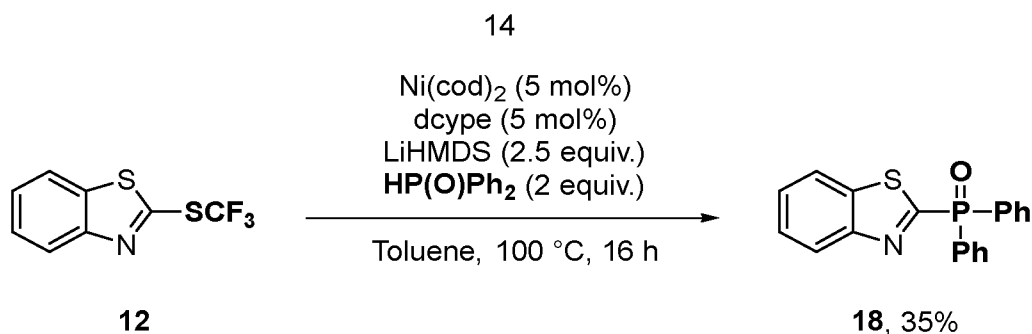


Scheme 5: Reaction conditions: **12** (0.5 mmol, 1 equiv.), Ni(cod)₂ (5 mol%), dcype (5 mol%), LiHMDS (2.5 equiv.), benzene selenol (2 equiv.), toluene (0.4M), 100 °C, 16 h. Yield shown is the isolated yield.

An oven-dried 10 mL tube equipped with a stirring bar was charged with Ni(cod)₂ (7 mg, 0.025 mmol, 5 mol%), dcype (11 mg, 0.025 mmol, 5 mol%), LiHMDS (209 mg, 1.25 mmol, 2.5 equiv.), 2-((trifluoromethyl)thio)benzo[d]thiazole **12** (118 mg, 0.5 mmol, 1 equiv.), aryl selenol (1.25 mmol, 2 equiv.) and toluene (1.25 mL) under argon. The resulting solution was stirred at 100 °C for 16 h. The mixture was allowed to cooled down to 21 °C. EtOAc (10 mL) was added in the mixture and the resulting solution was washed with an aqueous solution of NaOH (1M, 10 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried over MgSO₄ and concentrated under vacuum. The residue was purified by silica gel flash column chromatography to isolate the desired product **17**.

The results show that an aryl selenol is also a suitable nucleophile.

Example 6: Selective cleavage of C-SCF₃ bond in the presence of a phosphine oxide as nucleophile:

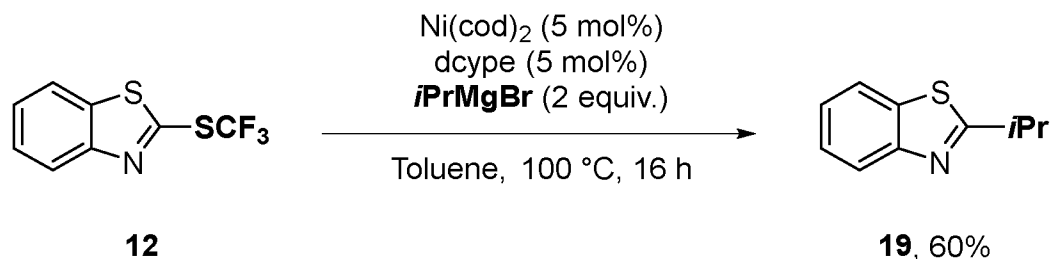


Scheme 6: Reaction conditions: **12** (0.5 mmol, 1 equiv.), Ni(cod)_2 (5 mol%), dcype (5 mol%), LiHMDS (2.5 equiv.), diphenylphosphine oxide (2 equiv.), toluene (0.4M), 100°C, 16 h. Yield shown is the isolated yield.

An oven-dried 10 mL tube equipped with a stirring bar was charged with Ni(cod)_2 (7 mg, 0.025 mmol, 5 mol%), dcype (11 mg, 0.025 mmol, 5 mol%), LiHMDS (209 mg, 1.25 mmol, 2.5 equiv.), 2-((trifluoromethyl)thio)benzo[d]thiazole **12** (118 mg, 0.5 mmol, 1 equiv.), phosphine oxide (1.25 mmol, 2 equiv.) and toluene (1.25 mL) under argon. The resulting solution was stirred at 100 °C for 16 h. The mixture was allowed to cooled down to 21 °C. EtOAc (10 mL) was added in the mixture and the resulting solution was washed with an aqueous solution of NaOH (1M, 10 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried over MgSO_4 and concentrated under vacuum. The residue was purified by silica gel flash column chromatography to afford the desired product **18**.

The result shows that phosphine oxides are suitable nucleophiles in this Ni-catalyzed transformation.

Example 7: Selective cleavage of C-SCF₃ bond in the presence of a Grignard reagent as a nucleophile

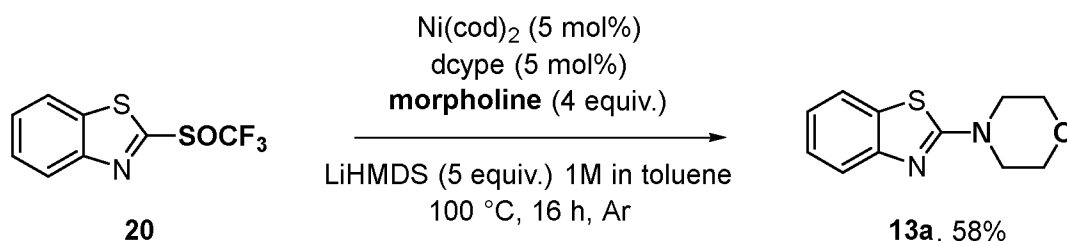


Scheme 7: Reaction conditions: **12** (0.5 mmol, 1 equiv.), Ni(cod)_2 (5 mol%), dcype (5 mol%), $i\text{PrMgBr}$ (2 equiv.), toluene (0.4M), 100°C, 16 h. Yield shown is the isolated yield.

An oven-dried 10 mL tube equipped with a stirring bar was charged with Ni(cod)₂ (7 mg, 0.025 mmol, 5 mol%), dcype (11 mg, 0.025 mmol, 5 mol%), 2-((trifluoromethyl)thio)benzo[d]thiazole **12** (118 mg, 0.5 mmol, 1 equiv.), Grignard reagent (1.25 mmol, 2 equiv.) and toluene (1.25 mL) under argon. The resulting solution was stirred at 100 °C for 16 h. The mixture was allowed to cool down to 21 °C. The residue was concentrated under vacuum and purified by silica gel flash column chromatography to isolate the desired product **19**.

The result shows that a Grignard reagent is a suitable nucleophile for the replacement of a SCF₃ group by an alkyl.

Example 8: Selective cleavage of C-SOCF₃ bond

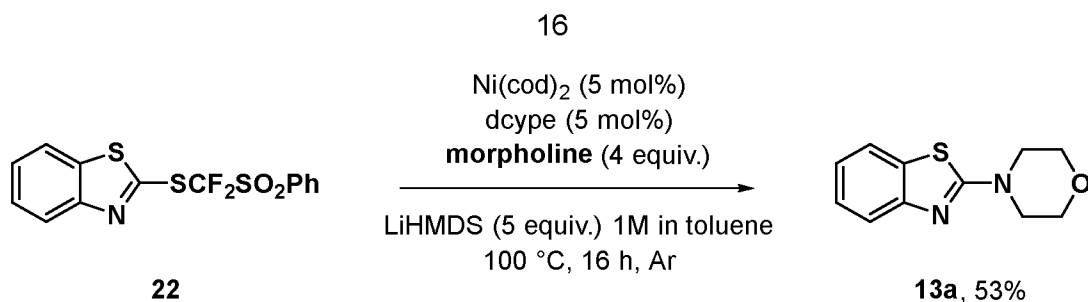


Scheme 8: Reaction conditions: **20** (0.5 mmol, 1 equiv.), Ni(cod)₂ (5 mol%), dcype (5 mol%), LiHMDS (5 equiv.), morpholine (4 equiv.), toluene, 100°C, 16 h, under Argon. Yield shown is the isolated yield.

An oven-dried 10 mL tube equipped with a stirring bar was charged with Ni(cod)₂ (7 mg, 0.025 mmol, 5 mol%), dcype (11 mg, 0.025 mmol, 5 mol%), LiHMDS in toluene (2.5 mL, 1M, 418 mg, 2.5 mmol, 5 equiv.), **20** (0.5 mmol, 1 equiv.) and morpholine (2 mmol, 4 equiv.) under argon. The resulting solution was stirred at 100 °C for 16 h. The mixture was allowed to cooled down to 21 °C. EtOAc (10 mL) was added in the mixture and the resulting solution was washed with an aqueous solution of NaOH (1M, 10 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried over MgSO₄ and concentrated under vacuum. The residue was purified by silica gel flash column chromatography to afford the desired product **13a**.

The result shows that when using an aliphatic amine (morpholine) as a nucleophile, the cleavage of the C-S(O)SCF₃ bond, where the carbon atom is linked to a sulfoxide, is achieved with a good yield.

Example 9: Selective cleavage of C-SCF₂SO₂Ph bond

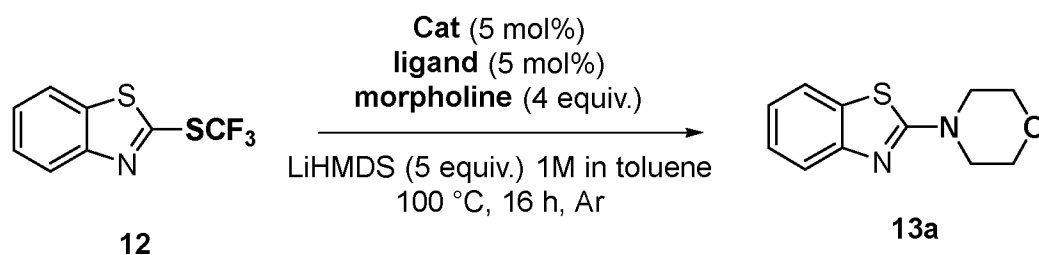


Scheme 9 Reaction conditions: **22** (0.5 mmol, 1 equiv.), Ni(cod)₂ (5 mol%), dcype (5 mol%), LiHMDS (5 equiv.), morpholine (4 equiv.), toluene, 100°C, 16 h, under Argon. Yield shown is the isolated yield.

An oven-dried 10 mL tube equipped with a stirring bar was charged with Ni(cod)₂ (4 mg, 0.015 mmol, 5 mol%), dcype (6 mg, 0.015 mmol, 5 mol%), LiHMDS in toluene (1.5 mL, 1M, 251 mg, 1.5 mmol, 5 equiv.), **22** (107 mg, 0.3 mmol, 1 equiv.) and morpholine (1.2 mmol, 4 equiv.) under argon. The resulting solution was stirred at 100 °C for 16 h. The mixture was allowed to cool down to 21 °C. EtOAc (10 mL) was added in the mixture and the resulting solution was washed with an aqueous solution of NaOH (1M, 10 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried over MgSO₄ and concentrated under vacuum. The residue was purified by silica gel flash column chromatography to isolate the desired product **13a**. The product and the corresponding yield are reported in scheme 9.

The result shows that the process according to the invention allows the cleavage of a C-S bond bearing another fluorinated functional group, namely CF₂SO₂Ph group, using an amine (morpholine) as a nucleophile.

Example 10: Selective cleavage of C-SCF₃ bond in the presence of various metallic complexes and various ligands



Scheme 10 Reaction conditions: **12** (0.5 mmol, 1 equiv.), Cat (5 mol%), ligand (5 mol%), LiHMDS (5 equiv.), morpholine (4 equiv.), toluene, 100°C, 16 h, under Argon. The yield shown is the isolated yield. "Cat" denotes the metallic complex.

For 10-A and 10-C, an oven-dried 10 mL tube equipped with a stirring bar was charged with Ni(cod)₂ (7 mg, 0.025 mmol, 5 mol%) or Ni(PPh₃)₂ (14.6 mg, 0.025 mmol, 5 mol%), dcype (11 mg, 0.025 mmol, 5 mol%), LiHMDS in toluene (2.5 mL, 1M, 418 mg, 2.50 mmol, 5 equiv.), 2-((trifluoromethyl)thio)benzo[d]thiazole **12** (118 mg, 0.5 mmol, 1 equiv.), morpholine (2.5 mmol, 4 equiv.) under argon. The resulting solution was stirred at 100 °C for 16 h. The mixture was allowed to cool down to 21 °C. EtOAc (10 mL) was added in the mixture and the resulting solution was washed with an aqueous solution of NaOH (1M, 10 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried over MgSO₄ and concentrated under vacuum.

In the case of 10-A, the residue was purified by silica gel flash column chromatography to isolate the desired product **13a**. For 10-B, 10-C and 10-D, yields were determined by ¹H NMR with 1,3,5-Trimethoxybenzene as an internal standard. The product obtained and the corresponding yields are reported in scheme 10 and Table 1, respectively.

The same procedure was followed for 10-B and 10-D except that dcype was not added to the solution.

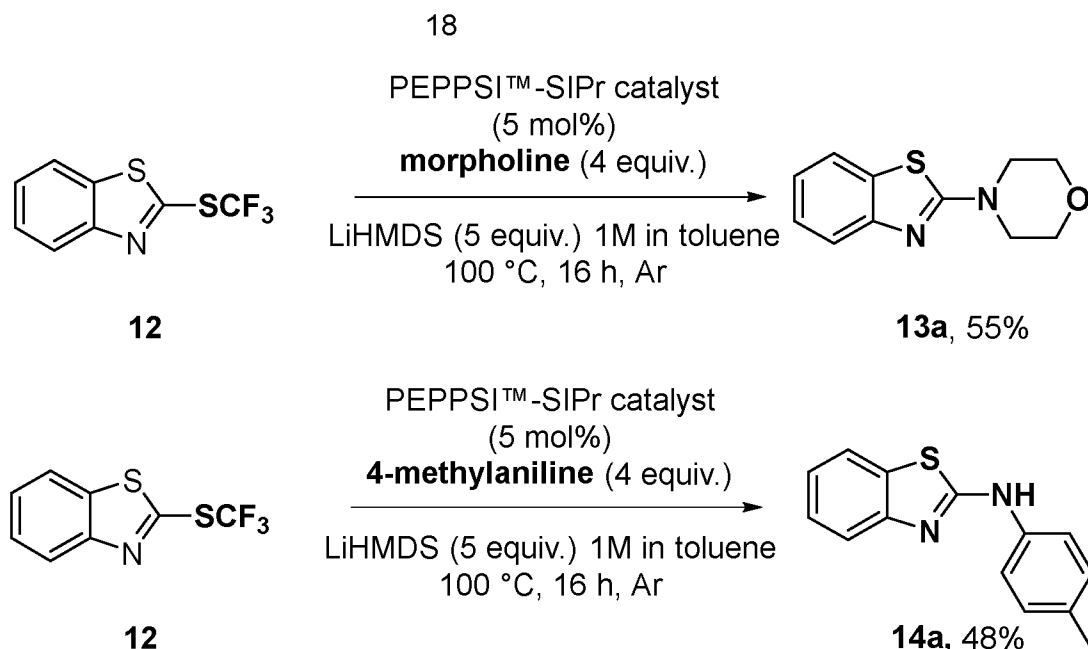
The metallic complexes, ligands and reaction yields are reported in Table 1.

Table 1

Entry	Metallic complex (cat)	Ligand	Reaction yield
10-A	Ni(cod) ₂	dcype	71% (isolated yield)
10-B	Ni(cod) ₂	-	49% (¹ H NMR)
10-C	Ni(PPh ₃) ₂	dcype	47% (¹ H NMR)
10-D	Ni(PPh ₃) ₂	-	53% (¹ H NMR)

The results show that the reaction was smoothly conducted using the metallic complexes with or without the addition of dcype as a ligand.

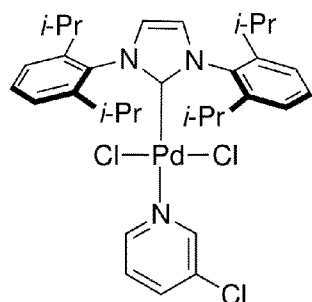
Example 11: Selective cleavage of C-SCF₃ bond in the presence of a Pd complex



Scheme 11 Reaction conditions: **12** (0.5 mmol, 1 equiv.), PEPPSI™-SIPr catalyst (5 mol%), LiHMDS (5 equiv.), HNR³R⁴ (4 equiv.), toluene, 100°C, 16 h, under Argon. The yield shown is the isolated yield.

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An oven-dried 10 mL tube equipped with a stirring bar was charged with [1,3-Bis(2,6-Diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride (PEPPSI™-SIPr catalyst, 905459-27-0, 17 mg, 0.025 mmol, 5 mol%) of formula :



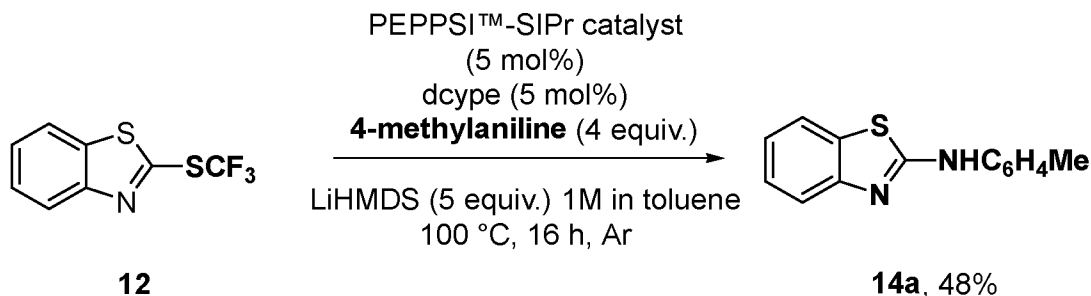
10

with LiHMDS 1M in Toluene (2.5mL, 418 mg, 2.50 mmol, 5 equiv., 1M), 2-((trifluoromethyl)thio)benzo[d]thiazole **12** (118 mg, 0.5 mmol, 1 equiv.) and morpholine or 4-methylaniline (2 mmol, 4 equiv.) under argon. The resulting solution was stirred at 100 °C for 16 h. The mixture was allowed to cool down to 21 °C. EtOAc (10 mL) was added in the mixture and the resulting solution was washed with an aqueous solution of NaOH (1M, 10 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried over MgSO₄ and concentrated under vacuum. The residue was purified by silica gel flash column chromatography to isolate the desired product **13a** or **14a**.

15

The result shows that the C-SCF₃ bond cleavage can be achieved when using a Pd-catalyst in the presence of a secondary aliphatic amine or an aniline derivative.

Example 12: selective cleavage of C-SCF₃ bond in the presence of a ligand and a Pd complex

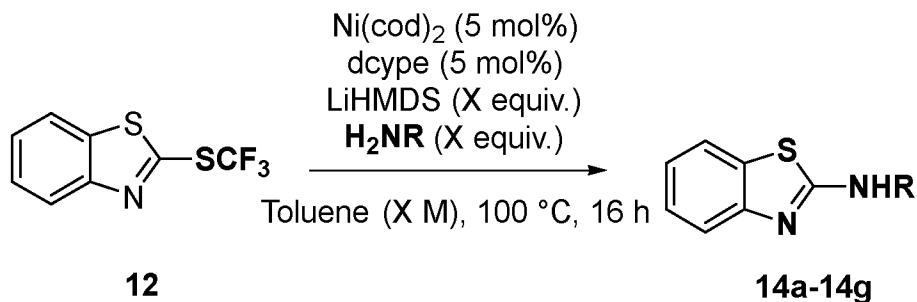


Scheme 12 Reaction conditions: **12** (0.5 mmol, 1 equiv.), PEPPSITM-SIPr catalyst (5 mol%), dcype (5 mol%), LiHMDS (5 equiv.), 4-methylaniline (4 equiv.), toluene, 100°C, 16 h, under Argon. The yield shown is the isolated yield.

An oven-dried 10 mL tube equipped with a stirring bar was charged with [1,3-Bis(2,6-Diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride (PEPPSITM-SIPr catalyst, 905459-27-0, 17 mg, 0.025 mmol, 5 mol%), dcype (11 mg, 0.025 mmol, 5 mol%), LiHMDS 1M in toluene (2.5 mL, 418 mg, 2.50 mmol, 5 equiv., 1M), 2-((trifluoromethyl)thio)benzo[d]thiazole **12** (118 mg, 0.5 mmol, 1 equiv.) and 4-methylaniline (2 mmol, 4 equiv.) under argon. The resulting solution was stirred at 100 °C for 16 h. The mixture was allowed to cooled down to 21 °C. EtOAc (10 mL) was added in the mixture and the resulting solution was washed with an aqueous solution of NaOH (1M, 10 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic phase were dried over MgSO₄ and concentrated under vacuum. The residue was purified by silica gel flash column chromatography to isolate the desired product **14a**.

The results show that the C-S bond cleavage of **12** is achieved whether the ligand is bound to the metal in the initial state of the metallic complex) (Example 11) or when the ligand is added to the reaction medium in addition to the metallic complex (Example 12).

Example 13: Selective cleavage of C-SCF₃ bond in the presence of a primary amine as a nucleophile

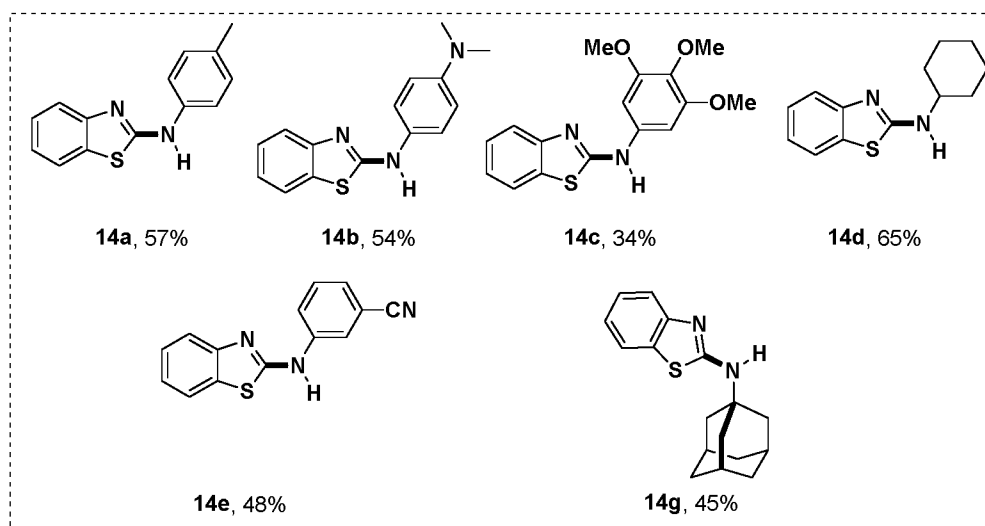


Scheme 13: Reaction conditions: **12** (0.5 mmol, 1 equiv.), Ni(cod)_2 (5 mol%), dcype (5 mol%), LiHMDS (X equiv.), primary amine of formula H_2NR (X equiv.), toluene, 100°C, 16 h, under Argon.

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An oven-dried 10 mL tube equipped with a stirring bar was charged with Ni(cod)_2 (7 mg, 0.025 mmol, 5 mol%), dcype (11 mg, 0.025 mmol, 5 mol%), LiHMDS (209mg, 1.25mmol, 2.5 equiv.; or 418 mg, 2.5 mmol, 5 equiv.), 2-((trifluoromethyl)thio)benzo[d]thiazole **12** (118 mg, 0.5 mmol, 1 equiv.), primary amine of formula H_2NR (2 mmol, 4 equiv.) and toluene under argon. The reaction conditions are reported in Table 2 below. The resulting solution was stirred at 100 °C for 16 h. The mixture was allowed to cool down to 21 °C. EtOAc (10 mL) was added in the mixture and the resulting solution was washed with an aqueous solution of NaOH (1M, 10 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried over MgSO_4 and concentrated under vacuum. The residue was purified by silica gel flash column chromatography to afford the desired products. The products and the corresponding isolated yields are reported in scheme 14 and in Table 2 below.

15



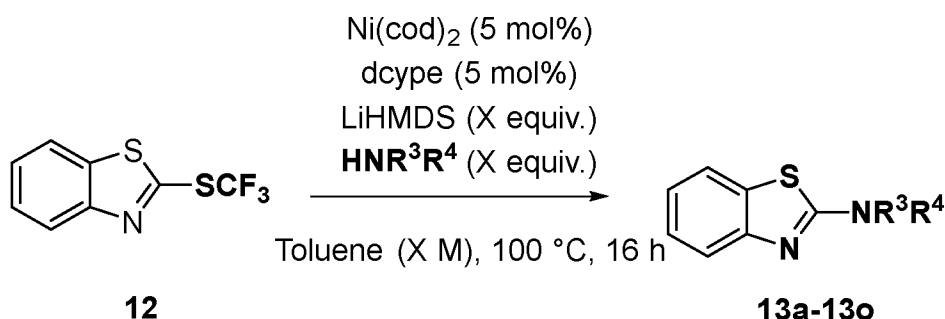
Scheme 14: Products obtained by the selective cleavage of **12** in the presence of various primary amines. Yield shown is the isolated yield.

20

Table 2

Product	H ₂ NR (X eq)	LiHMDS (X eq)	Toluene (X M)	Yield (%)
14-a	4	5	0.4	57
14-b	4	5	0.4	54
14-c	2	2.5	0.4	34
14-d	4	5	0.4	65
14-e	4	5	0.4	48
14-g	4	5	0.2	45

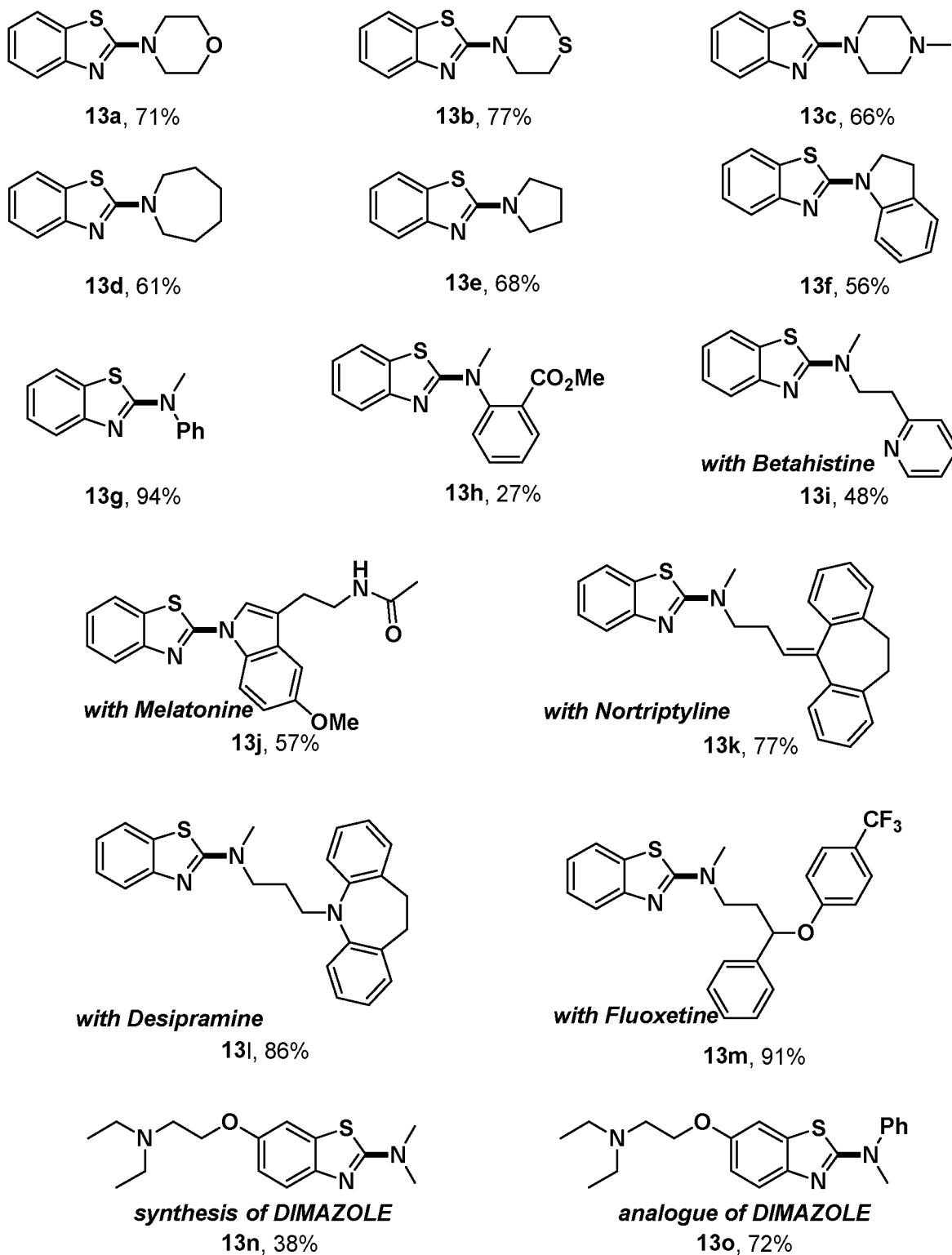
Example 14: Selective cleavage of C-SCF₃ bond in the presence of a secondary amine as a nucleophile:



Scheme 15: Reaction conditions: **12** (0.5 mmol, 1 equiv.), Ni(cod)₂ (5 mol%), dcype (5 mol%), LiHMDS (X equiv.), secondary amine of formula HNR¹R² (X equiv.), toluene, 100°C, 16 h, under Argon. R³ and R⁴, identical or different, represent an alkyl or an aryl, or are linked together with the nitrogen atom.

An oven-dried 10 mL tube equipped with a stirring bar was charged with Ni(cod)₂ (7 mg, 0.025 mmol, 5 mol%), dcype (11 mg, 0.025 mmol, 5 mol%), LiHMDS (209mg, 1.25mmol, 2.5 equiv.; or 418 mg, 2.5 mmol, 5 equiv.), 2-((trifluoromethyl)thio)benzo[d]thiazole **12** (118 mg, 0.5 mmol, 1 equiv.), secondary amine of formula HNR¹R² (2 mmol, 4 equiv.) and toluene under argon. The reaction conditions are reported in Table 3 below. The resulting solution was stirred at 100 °C for 16 h. The mixture was allowed to cooled down to 21 °C. EtOAc (10 mL) was added in the mixture and the resulting solution was washed with an aqueous solution of NaOH (1M, 10 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic phase were dried over MgSO₄ and concentrated under vacuum. The residue was purified by silica gel flash column chromatography to isolate the

desired products. The products and the corresponding yields are reported in scheme 16 and in Table 3 below.

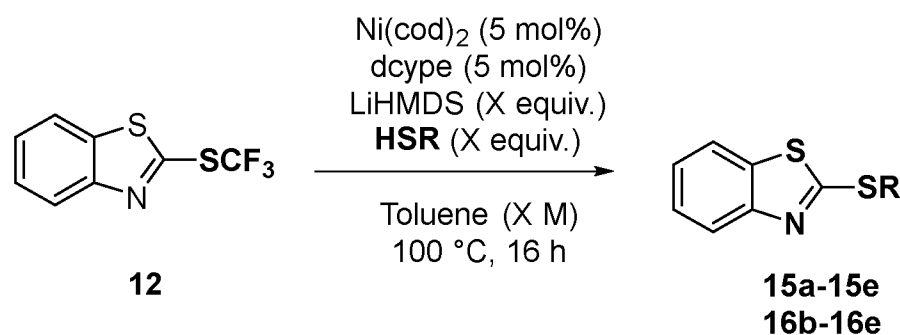


Scheme 16: Products obtained by the selective cleavage of **12** in the presence of various secondary amines. Isolated yields are depicted.

Table 3

Product	12 (X mmol)	HNR ¹ R ² (X eq)	LiHMDS (X eq)	Toluene (X M)	Yield (%)
13-a	0.5	4	5	0.2	71
13-b	0.5	2	2.5	0.4	77
13-c	0.5	2	2.5	0.4	66
13-d	0.5	2	2.5	0.4	61
13-e	0.5	4	5	0.4	66
13-f	0.5	2	2.5	0.4	56
13-g	0.5	4	5	0.2	94
13-h	0.5	4	5	0.4	27
13-i	0.5	4	5	0.2	48
13-j	0.5	4	5	0.4	57
13-k	0.5	4	5	0.2	77
13-l	0.5	4	5	0.2	86
13-m	0.5	4	5	0.2	91
13-n	0.5	4	5	0.2	38
13-o	0.2	4	5	0.2	72

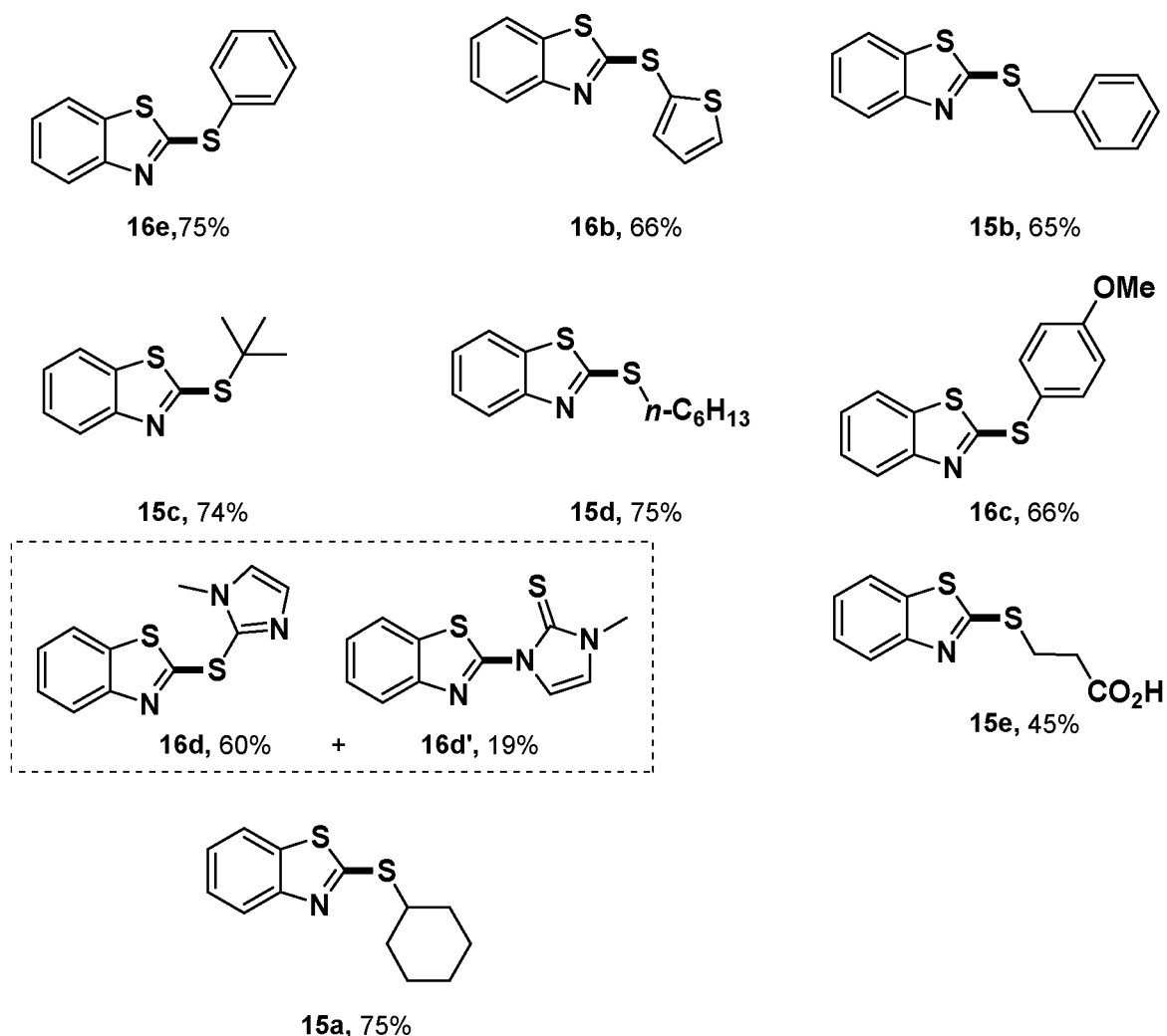
Example 15: Selective cleavage of C-SCF₃ bond in the presence of a thiol as a nucleophile:



Scheme 17: Reaction conditions: **12** (0.5 mmol, 1 equiv.), Ni(cod)₂ (5 mol%), dcype (5 mol%), LiHMDS (X equiv.), a thiol **15** or **16** of formula HSR (X equiv.), toluene, 100°C, 16 h, under Argon.

An oven-dried 10 mL tube equipped with a stirring bar was charged with Ni(cod)₂ (7 mg, 0.025 mmol, 5 mol%), dcype (11 mg, 0.025 mmol, 5 mol%), LiHMDS (209mg, 1.25mmol, 2.5 equiv.; or 418 mg, 2.5 mmol, 5 equiv.), 2-

((trifluoromethyl)thio)benzo[d]thiazole **12** (118 mg, 0.5 mmol, 1 equiv.), a thiol **15** or **16** of formula HSR (2 mmol, 4 equiv.), and toluene under argon. The reaction conditions are reported in Table 4 below. The resulting solution was stirred at 100 °C for 16 h. The mixture was allowed to cool down to 21 °C. EtOAc (10 mL) was added in the mixture and the resulting solution was washed with an aqueous solution of NaOH (1M, 10 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic phase were dried over MgSO₄ and concentrated under vacuum. The residue was purified by silica gel flash column chromatography to afford the desired products. The products and the corresponding yields are reported in scheme 18 and in Table 4 below.

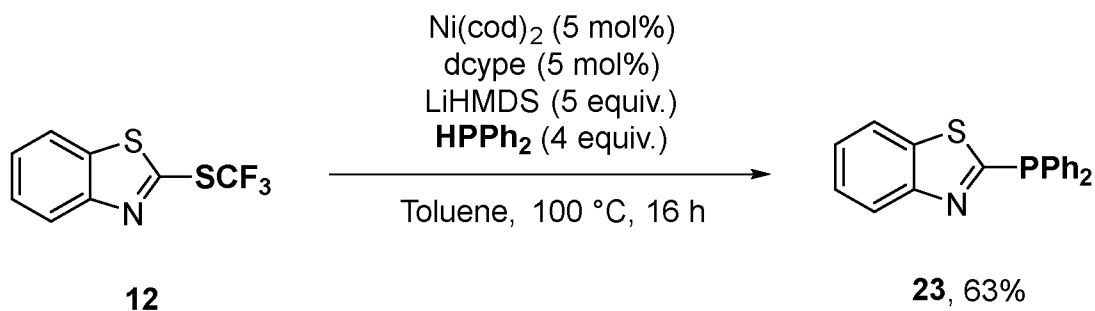


Scheme 18: Products obtained by the selective cleavage of **12** in the presence of various thiols as nucleophiles. Yield shown is the isolated yield.

Table 4

Product	12 (X mmol)	Thiol (X eq)	LiHMDS (X eq)	Toluene (X M)	Yield (%)
16e	0.5	4	5	0.4	75
16b	0.5	4	5	0.4	66
15b	0.5	4	5	0.4	65
15c	0.5	4	5	0.4	74
15d	0.5	4	5	0.4	75
16c	0.5	4	5	0.4	66
16d	0.5	4	5	0.4	60
16d'					19
15e	0.5	4	5	0.4	45
15a	0.5	4	5	0.2	75

Example 16: Selective cleavage of C-SCF₃ bond in the presence of a phosphorus derivate as a nucleophile



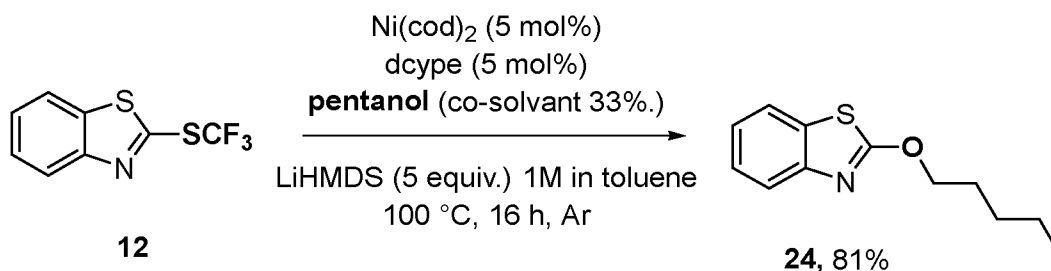
Schema 19: Reaction conditions: **12** (0.5 mmol, 1 equiv.), Ni(cod)_2 (5 mol%), dcype (5 mol%), LiHMDS (5 equiv.), HPPH_2 (4 equiv.), toluene, 100°C, 16 h, under Argon. Yield shown is the isolated yield.

An oven-dried 10 mL tube equipped with a stirring bar was charged with Ni(cod)_2 (7 mg, 0.025 mmol, 5 mol%), dcype (11 mg, 0.025 mmol, 5 mol%), LiHMDS (418 mg, 2.5 mmol, 5 equiv.), 2-((trifluoromethyl)thio)benzo[d]thiazole **12** (118 mg, 0.5 mmol, 1 equiv.), HPPH_2 (2 mmol, 4 equiv.), and toluene under argon. The resulting solution was stirred at 100 °C for 16 h. The mixture was allowed to cool down to 21 °C. EtOAc (10 mL) was added in the mixture and the resulting solution was washed with an aqueous solution of NaOH (1M, 10 mL). The aqueous phase was extracted with

EtOAc (3 x 20 mL) and the combined organic phase were dried over MgSO₄ and concentrated under vacuum. The residue was purified by silica gel flash column chromatography to isolate the desired product **23**.

This result shows that the cleavage of **12** is achieved with a high yield in presence of a phosphorus nucleophile and shows an interesting swap between S- and P-containing groups.

Example 17: Selective cleavage of C-SCF₃ bond in the presence of an alcohol as a nucleophile



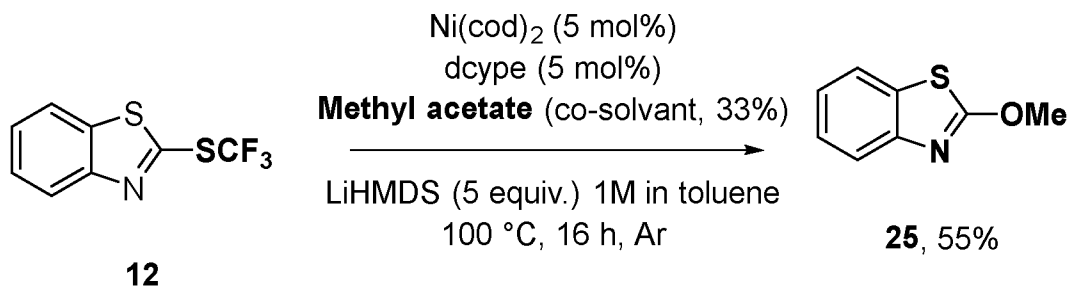
Schema 20: Reaction conditions: **12** (0.5 mmol, 1 equiv.), Ni(cod)₂ (5 mol%), dcype (5 mol%), LiHMDS (5 equiv.), pentanol (4 equiv.), toluene, 100°C, 16 h, under Argon. Yield shown is the isolated yield.

An oven-dried 10 mL tube equipped with a stirring bar was charged with Ni(cod)₂ (7 mg, 0.025 mmol, 5 mol%), dcype (11 mg, 0.025 mmol, 5 mol%), LiHMDS in toluene (2.5 mL, 1M, 418 mg, 2.5 mmol, 5 equiv.), 2-((trifluoromethyl)thio)benzo[d]thiazole **12** (118 mg, 0.5 mmol, 1 equiv.) and pentanol as co-solvent (1.25 mL, 33%) under argon. The resulting solution was stirred at 100 °C for 16 h. The mixture was allowed to cool down to 21 °C. EtOAc (10 mL) was added in the mixture and the resulting solution was washed with an aqueous solution of NaOH (1M, 10 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried over MgSO₄ and concentrated under vacuum. The residue was purified by silica gel flash column chromatography to isolate the desired product **24**.

This result shows that the cleavage of **12** is achieved with a high yield in presence of an alcohol nucleophile.

Example 18: Selective cleavage of C-SCF₃ bond in the presence of an ester as a nucleophile

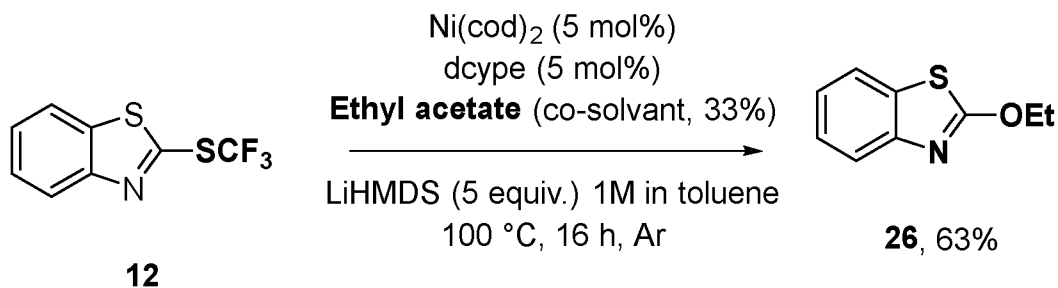
27



Schema 21: Reaction conditions: **12** (0.5 mmol, 1 equiv.), $\text{Ni}(\text{cod})_2$ (5 mol%), dcype (5 mol%), LiHMDS (5 equiv.), methyl acetate (4 equiv.), toluene, 100°C , 16 h, under Argon. Yield shown is the isolated yield.

An oven-dried 10 mL tube equipped with a stirring bar was charged with $\text{Ni}(\text{cod})_2$ (7 mg, 0.025 mmol, 5 mol%), dcype (11 mg, 0.025 mmol, 5 mol%), LiHMDS in toluene (2.5 mL, 1M, 418 mg, 2.5 mmol, 5 equiv.), 2-((trifluoromethyl)thio)benzo[d]thiazole **12** (118 mg, 0.5 mmol, 1 equiv.), and methyl acetate (1.25 mL, 33%) under argon. The resulting solution was stirred at 100°C for 16 h. The mixture was allowed to cooled down to 21°C . EtOAc (10 mL) was added in the mixture and the resulting solution was washed with an aqueous solution of NaOH (1M, 10 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried over MgSO_4 and concentrated under vacuum. The residue was purified by silica gel flash column chromatography to isolate the desired product **25**.

Example 19: Selective cleavage of C- SCF_3 bond in the presence of an ester as nucleophile

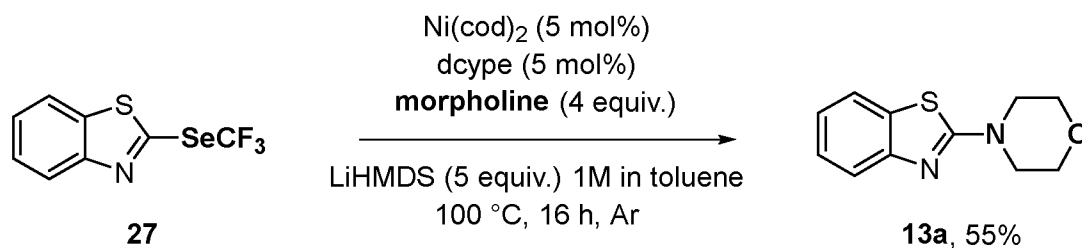


Schema 22: Reaction conditions: **12** (0.5 mmol, 1 equiv.), $\text{Ni}(\text{cod})_2$ (5 mol%), dcype (5 mol%), LiHMDS (5 equiv.), ethyl acetate (4 equiv.), toluene, 100°C , 16 h, under Argon. Yield shown is the isolated yield.

An oven-dried 10 mL tube equipped with a stirring bar was charged with Ni(cod)₂ (7 mg, 0.025 mmol, 5 mol%), dcype (11 mg, 0.025 mmol, 5 mol%), LiHMDS in toluene (2.5 mL, 1M, 418 mg, 2.5 mmol, 5 equiv.), 2-((trifluoromethyl)thio)benzo[d]thiazole **12** (118 mg, 0.5 mmol, 1 equiv.), and ethyl acetate (1.25 mL, 33%) under argon. The resulting solution was stirred at 100 °C for 16 h. The mixture was allowed to cool down to 21 °C. EtOAc (10 mL) was added in the mixture and the resulting solution was washed with an aqueous solution of NaOH (1M, 10 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried over MgSO₄ and concentrated under vacuum. The residue was purified by silica gel flash column chromatography to isolate the desired product **26**.

Examples 17, 18 and 19 illustrated the possibility of forming a C-O bond from the cleavage of **12** using different nucleophiles.

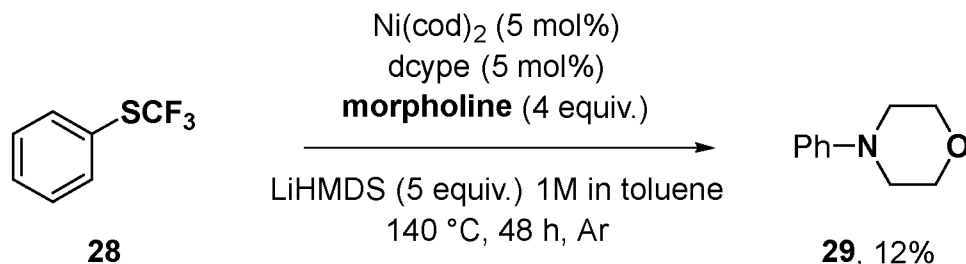
Example 20: Selective cleavage of C-SeCF₃ bond



Scheme 23: Reaction conditions: **27** (0.5 mmol, 1 equiv.), Ni(cod)₂ (5 mol%), dcype (5 mol%), LiHMDS (5 equiv.), morpholine (4 equiv.), toluene, 100°C, 16 h, under Argon. Yield shown is the isolated yield.

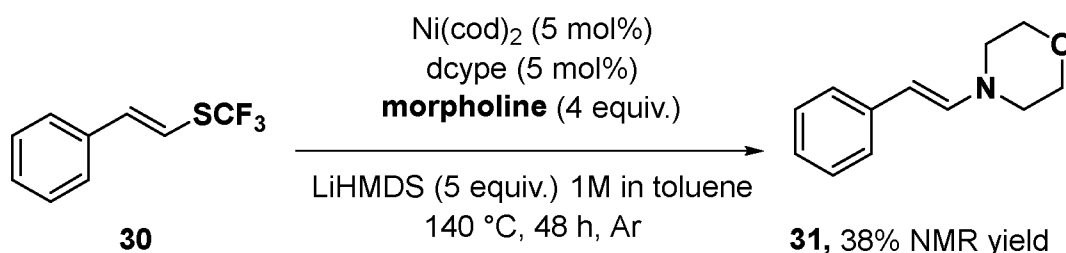
An oven-dried 10 mL tube equipped with a stirring bar was charged with Ni(cod)₂ (7 mg, 0.025 mmol, 5 mol%), dcype (11 mg, 0.025 mmol, 5 mol%), LiHMDS in toluene (2.5 mL, 1M, 418 mg, 2.5 mmol, 5 equiv.), **27** (142 mg, 0.5 mmol, 1 equiv.) and morpholine (2 mmol, 4 equiv.) under argon. The resulting solution was stirred at 100 °C for 16 h. The mixture was allowed to cooled down to 21 °C. EtOAc (10 mL) was added in the mixture and the resulting solution was washed with an aqueous solution of NaOH (1M, 10 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried over MgSO₄ and concentrated under vacuum. The residue was purified by silica gel flash column chromatography to isolate the desired product **13a**.

This result shows that the selective cleavage of the C-SeCF₃ bond is achieved in the presence of an amine as a nucleophile.

Example 21: Selective cleavage of C-SCF₃ bond on an aryl group

Scheme 24: Reaction conditions: **28** (0.5 mmol, 1 equiv.), Ni(cod)_2 (5 mol%), dcype (5 mol%), LiHMDS 1M solution in toluene (5 equiv.), morpholine (4 equiv.), $140\text{ }^\circ\text{C}$, 48 h, under Argon. Yield shown is the isolated yield.

An oven-dried 10 mL tube equipped with a stirring bar was charged with Ni(cod)_2 (7 mg, 0.025 mmol, 5 mol%), dcype (11 mg, 0.025 mmol, 5 mol), LiHMDS in toluene (2.5 mL, 1M, 418 mg, 2.5 mmol, 5 equiv), **28** (0.5 mmol, 1 equiv.) and morpholine (2 mmol, 4 equiv.) under argon. The resulting solution was stirred at $140\text{ }^\circ\text{C}$ for 48 h. The mixture was allowed to cool down to $21\text{ }^\circ\text{C}$. EtOAc (10 mL) was added in the mixture and the resulting solution was washed with an aqueous solution of NaOH (1M, 10 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried over MgSO_4 and concentrated under vacuum. The residue was purified by silica gel flash column chromatography to isolate the desired product **29**.

Example 22: Selective cleavage of C-SCF₃ bond on a vinyl group

Scheme 25: Reaction conditions: **30** (0.3 mmol, 1 equiv.), Ni(cod)_2 (5 mol%), dcype (5 mol%), LiHMDS 1M solution in toluene (5 equiv.), morpholine (4 equiv.), $140\text{ }^\circ\text{C}$, 48 h, under Argon. Yields were determined by ^1H NMR using Nitromethane as an internal standard.

An oven-dried 10 mL tube equipped with a stirring bar was charged with Ni(cod)_2 (4 mg, 0.015 mmol, 5 mol%), dcype (6 mg, 0.015 mmol, 5 mol%), LiHMDS in toluene (1.5 mL, 1M, 251 mg, 1.5 mmol, 5 equiv.), **30** (0.3 mmol, 1 equiv.) and morpholine (1.2 mmol, 4 equiv.) under argon. The resulting solution was stirred at $140\text{ }^\circ\text{C}$ for 48

h. The mixture was allowed to cool down to 21 °C. EtOAc (10 mL) was added in the mixture and the resulting solution was washed with an aqueous solution of NaOH (1M, 10 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried over MgSO₄ and concentrated under vacuum. The yield of **31** was determined by ¹H NMR using Nitromethane as an internal standard.

CLAIMS

1. A process for the preparation of a compound having the formula (I):



by reacting a compound having the formula (II):



in the presence of a metallic complex comprising nickel, palladium or rhodium(I),
a ligand, a nucleophile carrying one group R, and a solvent,

R being a hydrocarbon group, optionally including at least one heteroatom
and/or at least one atom other than C or H,

wherein:

- A is selected from the group consisting of:

. (C₆-C₁₀)aryl groups,

said aryl groups being optionally substituted with at least one substituent
preferably selected from the group consisting of: halogen, (C₁-C₆)alkyl, (C₁-
C₆)alkoxy, -CN, -CF₃, -OCF₃, -NR_aR_b, -SiR_aR_bR_c, -BR_aR_b, (C₂-C₆)alkenyl,
(C₂-C₆)alkynyl, -C(=O)-NR_aR_b, and -C(=O)-O(C₁-C₆)alkyl;

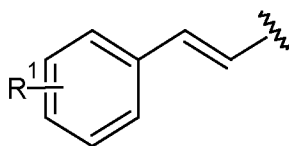
R_a and R_b being independently from each other H or a (C₁-C₆)alkyl group;

R_c being a (C₁-C₆)alkyl group;

. heteroaryl groups comprising from 5 to 10 atoms and including at least one
heteroatom selected from O, N, and S,

said heteroaryl groups being optionally substituted with at least one
substituent preferably selected from: halogen, (C₁-C₆)alkyl, (C₁-C₆)alkoxy,
-CN, -CF₃, -OCF₃, -NR_aR_b, -Si(R_c)₃, -BR_aR_b, (C₂-C₆)alkenyl, (C₂-C₆)alkynyl,
-C(=O)-NR_aR_b, and -C(=O)-O(C₁-C₆)alkyl, R_a, R_b and R_c being as defined
above; and

. a vinyl compound having the following formula (III):



(III)

R¹ being selected from the group consisting of: halogen, (C₁-C₆)alkyl, (C₁-
C₆)alkoxy, -CN, -CF₃, -OCF₃, -NR_aR_b, -Si(R_c)₃, -BR_aR_b, (C₂-C₆)alkenyl, (C₂-

C_6)alkynyl, $-C(=O)-NR_aR_b$, and $-C(=O)-O(C_1-C_6)$ alkyl, R_a , R_b and R_c being as defined above; and

- X is selected from the group consisting of: YCF_3 , $YOCF_3$, YO_2CF_3 , YCF_2SO_2Ph , $YOCF_2SO_2Ph$, $YO_2CF_2SO_2Ph$, $Y(O)_nCF_2COOR'$, $Y(O)_nCF_2CONR'_2$, $Y(O)_nCF_2CH_2OH$, $Y(O)_nCN$, $Y(O)_nCHF_2$, $Y(O)_nCF_2H$, $Y(O)_nCF_2C_nF_{2n+1}$, $Y(O)_nCF_2COR'$, Y being S or Se, n being 1 or 2, and R' being (C_1-C_6) alkyl.

2. The process of claim 1, wherein the metallic complex comprises nickel.

3. The process of claim 1 or 2, wherein the ligand is bound to the metal in the initial state of the metallic complex and/or the ligand is added to a reaction medium in addition to the metallic complex.

4. The process of any one of claims 1 to 3, wherein the nucleophile is selected from the group consisting of: alkyl amines, cycloalkyl amines, aryl amines, alkyl thiols, thiophenol compounds, aryl selenol compounds, phosphine oxides, Grignard reagents, alcohols, esters and phosphorus derivatives.

5. The process of any one of claims 1 to 4, wherein the nucleophile is a RH group, wherein R is selected from the group consisting of: (C_1-C_6) alkyl, heterocycloalkyl, $-S-cyclo(C_3-C_{10})$ alkyl, $-O-(C_1-C_{12})$ alkyl, an optionally substituted heteroaryl, a $cyclo(C_3-C_{10})$ alkylamino group, a $-S-(C_1-C_6)$ alkyl where the alkyl is optionally substituted, $-NR^1R^2$, $-P(=O)-R^1R^2$, $-X^1-Ar^1$, $-X^1-(C_1-C_{12})$ alkyl- Ar^1 , $-X^1-Het^1$, $-X^1-(C_1-C_{12})$ alkyl- Het^1 , X^1 being S, Se or NH, Ar^1 being an optionally substituted (C_6-C_{10}) aryl group, Het^1 being an optionally substituted heteroaryl group and R^1 and R^2 being, independently from each other, a (C_1-C_6) alkyl group or a (C_6-C_{10}) aryl group.

6. The process of any one of claims 1 to 4, wherein the nucleophile is a RH group, wherein R is selected from the group consisting of: (C_1-C_6) alkyl, heterocycloalkyl, $-S-cyclo(C_3-C_{10})$ alkyl, $-P(=O)-R^1R^2$, and $-X^1-Ar^1$, X^1 being S, Se or NH, and Ar^1 being an optionally substituted (C_6-C_{10}) aryl group, and R^1 and R^2 being, independently from each other, a (C_1-C_6) alkyl group or a (C_6-C_{10}) aryl group.

7. The process of any one of claims 1 to 6, wherein A is selected from the heteroaryl groups comprising from 5 to 10 atoms and including at least one heteroatom selected from O, N, and S, said heteroaryl groups being optionally substituted with at least one substituent selected from: halogen, (C₁-C₆)alkyl, (C₁-C₆)alkoxy, -CN, -CF₃, -OCF₃, -NR_aR_b, -Si(R_c)₃, -BR_aR_b, (C₂-C₆)alkenyl, (C₂-C₆)alkynyl, -C(=O)-NR_aR_b, and -C(=O)-O(C₁-C₆)alkyl, R_a, R_b and R_c being as defined in claim 1.

8. The process of any one of claim 1 to 7, further comprising the use of a hydride compound, such as LiHMDS.

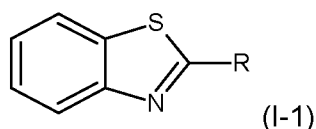
9. The process of any one of claims 1 to 8, wherein the ligand is selected from the group consisting of: 1,5-cyclooctadiene (COD), 1,2-Bis(dicyclohexylphosphino)ethane (dcype), 1,1'-Bis(diphenylphosphino)ferrocene (dppf), 1,1'-Bis(di-*tert*-butylphosphino)ferrocene (DTBPF), 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene (XantPhos), triphenylarsine (AsPh₃) and triphenylphosphane (PPh₃).

10. The process of any one of claims 1 to 9, wherein the solvent is toluene.

11. The process of any one of claims 1 to 10, wherein the reaction is carried out at a temperature from 90°C to 140°C.

12. The process of any one of the p claims 1 to 11, wherein the metallic complex is a Ni(0) complex such as bis(1,5-cyclooctadiene)nickel.

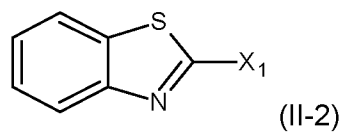
13. The process of any one of claims 1 to 12, for the preparation of a compound having the formula (I-1):



R being as defined above in any one of claims 1 to 6,

from a compound having the formula (II-1):

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X₁ being selected from the group consisting of: SCF₃, SOCF₃, SO₂CF₃, SCF₂SO₂Ph, SOCF₂SO₂Ph, SO₂CF₂SO₂Ph, and SeCF₃.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/064950

A. CLASSIFICATION OF SUBJECT MATTER		
INV. C07D277/64 C07D277/68 C07D277/74 C07D277/82		
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		
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		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	BOUKOUVALAS JOHN ET AL: "Unified route to asymmetrically substituted butenolide, maleic anhydride, and maleimide constituents ofAntrodia camphorata", TETRAHEDRON, vol. 68, no. 47, 2012, pages 9592-9597, XP028945132, ISSN: 0040-4020, DOI: 10.1016/J.TET.2012.09.064 scheme 3; compounds 16, 17	1 - 13
Y	EP 3 431 462 A1 (DAINIPPON INK & CHEMICALS [JP]) 23 January 2019 (2019-01-23) page 16, paragraph 102; compounds 101-1, 101	1 - 13
	- / - -	
☒ 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 25 July 2024		Date of mailing of the international search report 19/08/2024
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Seelmann, Marielle

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2024/064950

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2004/087145 A2 (GLAXO GROUP LTD [GB]; HENNESSY ALAN J [GB] ET AL.) 14 October 2004 (2004-10-14) examples 3, 36, 40, 41(b), 42 -----	1-13
A	JUN WEI ET AL: "Transition-Metal-Free Electrophilic Fluoroalkanesulfinylation of Electron-Rich (Het)Arenes with Fluoroalkyl Heteroaryl Sulfones via C(Het)-S and S=O Bond Cleavage", ADVANCED SYNTHESIS AND CATALYSIS, JOHN WILEY & SONS, INC, HOBOKEN, USA, vol. 361, no. 24, 6 November 2019 (2019-11-06), pages 5528-5533, XP072359563, ISSN: 1615-4150, DOI: 10.1002/ADSC.201900959 scheme 4; table 2 -----	1-13
X	FUKUDA JUN-ICHI ET AL: "Cross-Coupling of Aryl Trifluoromethyl Sulfones with Arylboronates by Cooperative Palladium/Rhodium Catalysis", ORGANIC LETTERS, vol. 21, no. 22, 24 October 2019 (2019-10-24), pages 8987-8991, XP93189403, US ISSN: 1523-7060, DOI: 10.1021/acs.orglett.9b03393 -----	1-3,7,9
Y	scheme 1;	4-6,8,
A	figures 1(c),1(d), 2, 3; tables 1-2	10-12
A	-----	13
X	PAUL CHATELAIN ET AL: "Suzuki-Miyaura Coupling of (Hetero)Aryl Sulfones: Complementary Reactivity Enables Iterative Polyaryl Synthesis", ANGEWANDTE CHEMIE INTERNATIONAL EDITION, VERLAG CHEMIE, HOBOKEN, USA, vol. 58, no. 42, 12 September 2019 (2019-09-12), pages 14959-14963, XP072098524, ISSN: 1433-7851, DOI: 10.1002/ANIE.201908336 -----	1-3,7,9
Y	scheme 2;	4-6,8,
A	tables 1-2	10-12
A	----- -/-	13

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2024/064950

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Chatelain Paul ET AL: "Suzuki-Miyaura Coupling of (Hetero)Aryl Sulfones: Complementary Reactivity Enables Iterative Polyaryl Synthesis**", , 9 December 2019 (2019-12-09), pages S1-S84, XP93189527, Retrieved from the Internet: URL: https://onlinelibrary.wiley.com/action/downloadSupplement?doi=10.1002%2Fanie.201908336&file=anie201908336-sup-0001-misc_information.pdf	1-3,7,9
Y	supplementary information of D6	4-6,8, 10-12
A	-----	13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2024/064950

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EP 3431462	A1	23-01-2019	CN 108495833 A	04-09-2018
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			US 2006189601 A1	24-08-2006
			WO 2004087145 A2	14-10-2004
