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— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(H))*
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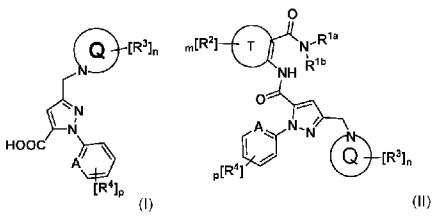
(54) Title: A NOVEL PROCESS FOR THE PREPARATION OF ANTHRANILIC DIAMIDES



(I) (II)

(57) Abstract: The present invention relates to a novel process for the preparation of a compound of formula (II) and anthranilic diamides of formula (I) therefrom: wherein, R^{1a}, R^{1b}, R^2, R^3, R^4, A, m, n, p, Q, and T are as defined in the description.

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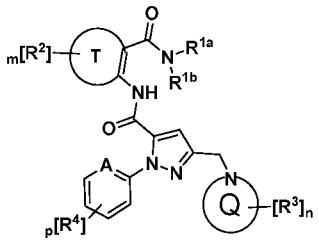
TITLE: A NOVEL PROCESS FOR THE PREPARATION OF ANTHRANILIC DIAMIDES

FIELD OF THE INVENTION:

The present invention relates to a novel process for the preparation of anthranilic diamides of formula I



I

wherein, R^{1a}, R^{1b}, R^2, R^3, R^4, A, m, n, p, Q, and T are as defined in the description, which can be used as insecticides.

BACKGROUND OF THE INVENTION AND PROBLEM TO BE SOLVED

l-Heteroarylpyrazole-5 -carboxylic acids are known to be important intermediates in the agrochemical industry, e. g. for the synthesis of anthranilic diamides which are useful to protect crops against harmful pests. Several methods have been disclosed in literature, by which these intermediates can be obtained.

The formation of pyrazoles by the reaction of 1,3-dicarbonyls or of corresponding l,3-bis-electrophilic compounds with hydrazines has been described in Synthesis 2004, pages 43-52. However, according to other references, namely W02003016282, and Tetrahedron (2003), vol. 59, pages 2197-2205, the product formed in such reactions consists of a mixture of regioisomeric pyrazoles, meaning that the selectivity in the synthesis of the desired product is a challenge.

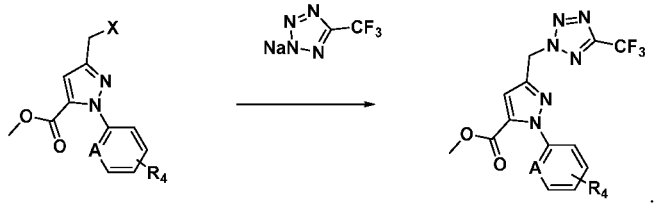
W02007144100 describes a process for preparing tetrazolyl substituted N-(aryl or heteroaryl) pyrazole-5-carboxylic acid in which diisobutylaluminium hydride (DIBAL) or lithium aluminium hydride ($L1AIH_4$) is used. Typical shortcomings of this process are that it requires very low temperature conditions and that the use of DIBAL as a reagent is uneconomical.

W02010069502 describes that tetrazolyl substituted anthranilic diamides can be prepared by reacting tetrazolyl substituted N-heteroaryl pyrazole acid with anthranilamides. It also describes that tetrazolyl substituted anthranilic diamides can be prepared by reacting tetrazolyl substituted benzoxazinones with appropriate amines. However, both the processes rarely offer good yield.

WO20101 12178 describes a method for producing l-pyridinylpyrazole-5 -carboxylic acids or esters by the reaction of trihalo substituted acetylene ketones with pyridinyl hydrazines to first obtain an intermediate having a trihalomethyl substituent on the dihydro pyrazole ring, followed by dehydration and an oxidation

step. However, trihalo substituted acetylene ketones are expensive starting materials which make this process economically unviable.

WO201 1157664 and W02013030100 disclose the following process for preparing tetrazolyl substituted l-heteroarylpyrazole-5-carboxylic acid esters or l-arylpyrazole-5 -carboxylic acid esters:



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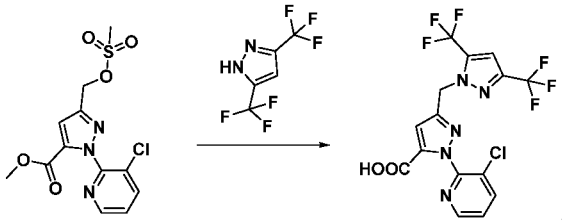
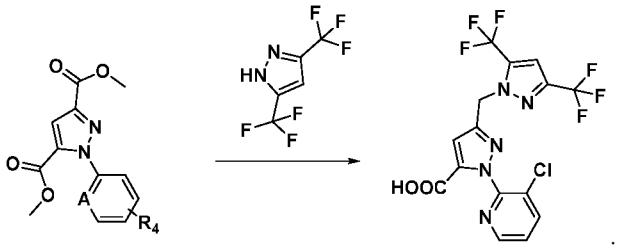
W02013030100 additionally discloses a method for the preparation of tetrazolyl substituted anthranilic diamides from tetrazolyl substituted pyrazole carboxylic acids.

W02011073101 describes a process for the preparation of l-alkyl- or 1-aryl-substituted 5-pyrazole-carboxylic acids which involves the steps of converting substituted l,3-dioxolanes or l,4-dioxanes into 1-alkyl- or 1-aryl-substituted dihydro- lH-pyrazoles by reaction with alkyl or aryl hydrazines, and further converting said pyrazoles into l-alkyl- or 1-aryl-substituted 5-pyrazole carboxylic acids.

Another prior art, DE 102006032 168 discloses the following two processes for the preparation of 1-heteroarylpyrazole-5 -carboxylic acids as key intermediates:



; and



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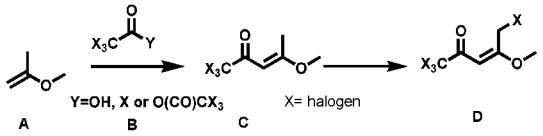
WO20 11009551 describes a process for the preparation of l-heteroaryl substituted pyrazole-5 -carboxylic acids by reacting trihalo substituted alkoxy enones or enaminoketones with hydrazines to obtain 1-heteroaryl substituted dihydro- lH-pyrazoles as intermediates, followed by eliminating water and subsequent oxidation.

WO20 13007604 describes a method for the preparation of tetrazolyl substituted anthranilic diamides by reacting pyrazole carboxylic acids with anthranilic esters, followed by hydrolysis to obtain acid intermediates which are then reacted with an appropriate amine.

An article published in SYNLETT 2005, No. 20, pp 3079-3082 discloses a method for the synthesis of useful intermediates as 1-phenyl-N-pyrazolylmethylpyrimidinones from 5-bromo-l,l,l-trichloro(fluoro)-4-methoxypent-3-en-2-ones with a moderate yield of 60-70%.

These processes described in the prior art have shortcomings such as poor yields of the desired intermediates or products, or synthetic procedures being not amenable to commercial scale, or of involving extreme reaction conditions or of lengthy reaction sequences making them uneconomical.

Further, l,l,l,5-Tetrahalo-4-alkoxypent-3-en-2-ones are also key precursors in the synthesis of 1-heteroarylpyrazole-5 -carboxylic acids. Several methods for preparing the key precursors (D) have been disclosed in prior art documents such as Journal of Heterocyclic Chemistry, 50(1), pp. 71-77; Tetrahedron Letters, 51(35), pp. 4623-4626; Journal of F Chemistry, 128(10), pp. 1264-1270; Synthesis, (16), pp. 2353-2358; Synthesis, (13), pp. 1959-1964; and Synthesis (3), pp. 431-436; by acylating enol ether (A) or acetal with trihaloacetic anhydride or trihaloacetic acid or trihaloacetyl halide (B) and then halogenating the intermediate (C).



However, in these processes the isolation of the intermediate (C) is inevitable thereby making them uneconomical.

Thus, there is still a need for a process that obviates at least one shortcomings associated with the known processes.

OBJECT AND SUMMARY OF THE INVENTION

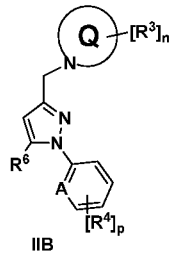
It was therefore an objective to provide a novel and economically viable process for the preparation of anthranilic diamides of formula I.

It is also an objective of the present invention to provide a novel and economically advantageous process for the preparation of l,l,l,5-tetrahalo-4-alkoxypent-3-en-2-ones.

Another objective was to provide novel intermediates for the preparation of anthranilic diamides of formula I.

Surprisingly, the present invention provides a solution to these objectives by offering a novel high yielding and economically attractive process that allows the preparation of anthranilic diamides and / or novel key intermediates to prepare such anthranilic diamides, overcoming at least one of the shortcomings of the processes described in the prior art.

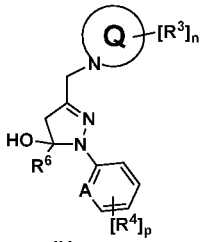
The objectives were achieved according to the present invention by finding a process for preparing anthranilic diamides in which a compound of formula IIB



IIB

wherein, R^3, R^4, R^6, A, n, p, and Q are each as defined in the description,

is obtained from a compound of formula IIA

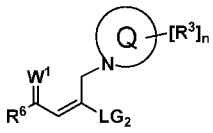


IIA

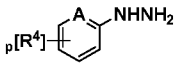
wherein, R^3, R^4, R^6, A, n, p, and Q are each as defined in the description,

by elimination of water.

The compound of formula IIA is obtained by reacting a compound of formula III with a compound of formula VIII



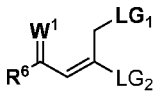
III



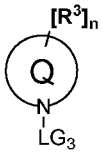
VIII

wherein, R^3, R^4, R^6, A, n, p, Q, W^1, and LG2 are each as defined in the description.

The compound of formula III in turn is obtained by reacting a compound of formula IV with a compound of formula VII



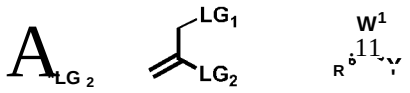
IV



VII

wherein, R^3, R^6, n, Q, W^1, LGi, LG_2, and LG3 are each as defined in the description.

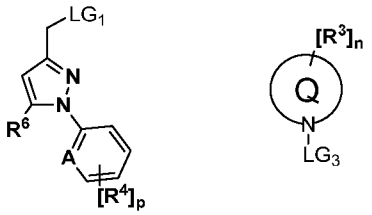
The compound of formula IV is obtained by converting a compound of formula IV-A into a compound of formula IV-B and then reacting the compound of formula IV-B with a compound of formula IV-C.



IV-A IV-B IV-C

wherein, R^6, W^1, Y, LGi, and LG2 are each as defined in the description.

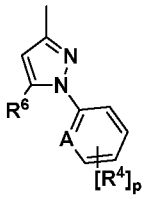
Alternatively, the compound of formula IIB is obtained by a novel process in which a compound of formula XIV and the compound of formula VII are reacted.



XIV VII

wherein, R^3, R^4, R^6, A, n, p, Q, LGi, and LG_3 are each as defined in the description.

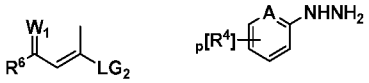
The compound of formula XIV is obtained from a compound of formula XV



XV

wherein, R^4, R^6, A, and p are each as defined in the description.

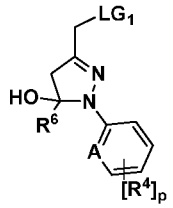
The compound of formula XV is obtained by reacting a compound of formula XVII with the compound of formula VIII



XVII VIII

wherein, R^4, R^6, A, p, W^1 and LG2 are each as defined in the description.

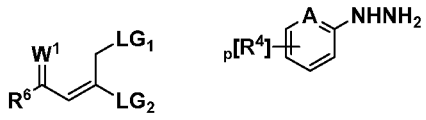
Alternatively, the compound of formula XIV is obtained from XVIII by elimination of water



XVIII

wherein, R^4, R^6, A, p, and LGi are each as defined in the description.

The compound of formula XVIII is obtained by reacting a compound IV with the compound of formula VIII



IV VIII

wherein, R^4, R^6, A, p, W^1, LGi and LG_2 are each as defined in the description.

Finally, the compound of formula IIB is converted into anthranilic diamides of formula I by the processes known in the prior art documents.

DETAILED DESCRIPTION OF THE INVENTION

GENERAL DEFINITIONS

The definitions provided herein for the terminologies used in the present disclosure are for illustrative purpose only and in no manner limit the scope of the present invention disclosed in the present disclosure.

As used herein, the terms "comprises", "comprising", "includes", "including", "has", "having", "contains", "containing", "characterized by" or any other variation thereof, are intended to cover a non-exclusive inclusion, subject to any limitation explicitly indicated. For example, a composition, mixture, process or method that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such composition, mixture, process or method.

The transitional phrase "consisting of' excludes any element, step or ingredient not specified. If in the claim, such would close the claim to the inclusion of materials other than those recited except for impurities ordinarily associated therewith. When the phrase "consisting of' appears in a clause of the body of a claim, rather than immediately following the preamble, it limits only the element set forth in that clause; other elements are not excluded from the claim as a whole.

The transitional phrase "consisting essentially of' is used to define a composition or method that includes materials, steps, features, components or elements, in addition to those literally disclosed, provided that these additional materials, steps, features, components or elements do not materially affect the basic and novel characteristic(s) of the claimed invention. The term "consisting essentially of' occupies a middle ground between "comprising" and "consisting of'.

Further, unless expressly stated to the contrary, "or" refers to an inclusive "or" and not to an exclusive "or". For example, a condition A "or" B is satisfied by any one of the following: A is true (or present) and

B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

Also, the indefinite articles “a” and “an” preceding an element or component of the present invention are intended to be nonrestrictive regarding the number of instances (i.e. occurrences) of the element or component. Therefore “a” or “an” should be read to include one or at least one, and the singular word form of the element or component also includes the plural unless the number is obviously meant to be singular.

Compounds of the present disclosure may be present either in pure form or as mixtures of different possible isomeric forms such as stereoisomers or constitutional isomers. The various stereoisomers include enantiomers, diastereomers, chiral isomers, atropisomers, conformers, rotamers, tautomers, optical isomers, polymorphs, and geometric isomers. Any desired mixtures of these isomers fall within the scope of the claims of the present disclosure. One skilled in the art will appreciate that one stereoisomer may be more active and/or may exhibit beneficial effects when enriched relative to the other isomer(s) or when separated from the other isomer(s). Additionally, the person skilled in the art knows processes or methods or technology to separate, enrich, and/or to selectively prepare said isomers.

The meaning of various terms used in the description shall now be illustrated.

The term “alkyl”, used either alone or in compound words such as “alkylthio” or “haloalkyl” or -N(alkyl) or alkylcarbonylalkyl or alkylsuphonylamino includes straight-chain or branched C_i to C_{24} alkyl, preferably C_i to C_{15} alkyl, more preferably C_i to C_{10} alkyl, most preferably C_i to G, alkyl. Non-limiting examples of alkyl include methyl, ethyl, propyl, l-methylethyl, butyl, l-methylpropyl, 2-methylpropyl, l,l-dimethylethyl, pentyl, l-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, hexyl, l,l-dimethylpropyl, l,2-dimethylpropyl, l-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, l,l-dimethylbutyl, l,2-dimethylbutyl, l,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, l-ethylbutyl, 2-ethylbutyl, l,l,2-trimethylpropyl, l,2,2-trimethylpropyl, 1-ethyl-l-methylpropyl and l-ethyl-2-methylpropyl or the different isomers. If the alkyl is at the end of a composite substituent, as, for example, in alkylcycloalkyl, the part of the composite substituent at the start, for example the cycloalkyl, may be mono- or polysubstituted identically or differently and independently by alkyl. The same also applies to composite substituents in which other radicals, for example alkenyl, alkynyl, hydroxyl, halogen, carbonyl, carbonyloxy and the like, are at the end.

The term “alkenyl”, used either alone or in compound words includes straight-chain or branched C_2 to C_{24} alkenes, preferably C_2 to C_{15} alkenes, more preferably C_2 to C_{10} alkenes, most preferably C_2 to G, alkenes. Non-limiting examples of alkenes include ethenyl, l-propenyl, 2-propenyl, l-methylethenyl, l-butenyl, 2-butenyl, 3-butenyl, 1-methyl-l-propenyl, 2-methyl-l-propenyl, 1-methyl-2-propenyl, 2-methyl-2-propenyl,

l-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1-methyl-l-butenyl, 2-methyl-l-butenyl, 3-methyl-l-butenyl, l-methyl-2-butenyl, 2-methyl-2-butenyl, 3-methyl-2-butenyl, l-methyl-3-butenyl, 2-methyl-3-butenyl, 3-methyl-3-butenyl, 1,1-dimethyl-2-propenyl, l,2-dimethyl-l-propenyl, 1,2-dimethyl-2-propenyl, 1-ethyl-1-propenyl, l-ethyl-2-propenyl, l-hexenyl, 2-hexenyl, 3-hexenyl, 4-hexenyl, 5-hexenyl, 1-methyl-l-pentenyl, 2-methyl-l-pentenyl, 3-methyl-l-pentenyl, 4-methyl-l-pentenyl, l-methyl-2-pentenyl, 2-methyl-2-pentenyl, 3-methyl-2-pentenyl, 4-methyl-2-pentenyl, l-methyl-3-pentenyl, 2-methyl-3-pentenyl, 3-methyl-3-pentenyl, 4-methyl-3-pentenyl, 1-methyl-4-pentenyl, 2-methyl-4-pentenyl, 3-methyl-4-pentenyl, 4-methyl-4-pentenyl, l,l-dimethyl-2-butenyl, l,l-dimethyl-3-butenyl, l,2-dimethyl-l-butenyl, 1,2-dimethyl-2-butenyl, l,2-dimethyl-3-butenyl, 1,3-dimethyl-l-butenyl, l,3-dimethyl-2-butenyl, 1,3-dimethyl-3-butenyl, 2,2-dimethyl-3-butenyl, 2,3-dimethyl-l-butenyl, 2,3-dimethyl-2-butenyl, 2,3-dimethyl-3-butenyl, 3,3-dimethyl-l-butenyl, 3,3-dimethyl-2-butenyl, 1-ethyl-l-butenyl, l-ethyl-2-butenyl, l-ethyl-3-butenyl, 2-ethyl- l-butenyl, 2-ethyl-2-butenyl, 2-ethyl-3-butenyl, 1,1,2-trimethyl-2-propenyl, 1-ethyl-l-methyl-2-propenyl, l-ethyl-2-methyl-l-propenyl and l-ethyl-2-methyl-2-propenyl and the different isomers. “Alkenyl” also includes polyenes such as l,2-propadienyl and 2,4-hexadienyl. This definition also applies to alkenyl as a part of a composite substituent, for example haloalkenyl and the like, unless defined specifically elsewhere.

Non-limiting examples of alkynes include ethynyl, l-propynyl, 2-propynyl, l-butynyl, 2-butynyl, 3-butynyl, 1-methyl-2-propynyl, l-pentynyl, 2-pentynyl, 3-pentynyl, 4-pentynyl, l-methyl-2-butynyl, 1-methyl-3-butynyl, 2-methyl-3-butynyl, 3-methyl-l-butynyl, 1,1-dimethyl-2-propynyl, l-ethyl -2-propynyl, 1-hexynyl, 2-hexynyl, 3-hexynyl, 4-hexynyl, 5-hexynyl, 1-methyl-2-pentynyl, l-methyl-3-pentynyl, 1-methyl-4-pentynyl, 2-methyl-3-pentynyl, 2-methyl-4-pentynyl, 3-methyl-l-pentynyl, 3-methyl-4-pentynyl, 4-methyl-l-pentynyl, 4-methyl-2-pentynyl, 1,1-dimethyl-2-butynyl, l,l-dimethyl-3-butynyl, 1,2-dimethyl-3-butyny1, 2,2-dimethyl-3-butynyl, 3,3-dimethyl-l-butynyl, l-ethyl-2-butynyl, l-ethyl-3-butynyl, 2-ethyl-3-butynyl and 1-ethyl-1-methyl-2-propynyl and the different isomers. This definition also applies to alkynyl as a part of a composite substituent, for example haloalkynyl etc., unless specifically defined elsewhere. “Alkynyl” can also include moieties comprised of multiple triple bonds such as 2,5-hexadiynyl.

The term “cycloalkyl” means alkyl closed to form a ring. Non-limiting examples include cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl. This definition also applies to cycloalkyl as a part of a composite substituent, for example cycloalkylalkyl etc., unless specifically defined elsewhere.

Cycloalkenyl means alkenyl closed to form a ring including monocyclic, partially unsaturated hydrocarbyl groups. Non-limiting examples include cyclopentenyl and cyclohexenyl. This definition also applies to cycloalkenyl as a part of a composite substituent, for example cycloalkenylalkyl etc., unless specifically defined elsewhere.

Cycloalkynyl means alkynyl closed to form a ring including monocyclic, partially unsaturated groups. This definition also applies to cycloalkynyl as a part of a composite substituent, for example cycloalkynylalkyl etc., unless specifically defined elsewhere.

The term “cycloalkoxy”, “cycloalkenyloxy” and the like are defined analogously. Non limiting examples of cycloalkoxy include cyclopropyloxy, cyclopentyloxy and cyclohexyloxy. This definition also applies to cycloalkoxy as a part of a composite substituent, for example cycloalkoxy alkyl etc., unless specifically defined elsewhere.

The term “halogen”, either alone or in compound words such as “haloalkyl”, includes F, Cl, Br or I. Further, when used in compound words such as “haloalkyl”, said alkyl may be partially or fully substituted with halogen atoms which may be the same or different.

Non-limiting examples of “haloalkyl” include chloromethyl, bromomethyl, dichloromethyl, trichloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, chlorofluoromethyl, dichlorofluoromethyl, chlorodifluoromethyl, l-chloroethyl, l-bromoethyl, l-fluoroethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2-chloro-2-fluoroethyl, 2-chloro-2,2-difluoroethyl, 2,2-dichloro-2-fluoroethyl, 2,2,2-trichloroethyl, pentafluoroethyl, l,l-dichloro-2,2,2-trifluoroethyl, and 1,1,1-trifluoroprop-2-yl. This definition also applies to haloalkyl as a part of a composite substituent, for example haloalkylaminoalkyl etc., unless specifically defined elsewhere.

The terms “haloalkenyl” and “haloalkynyl” are defined analogously except that, instead of alkyl groups, alkenyl and alkynyl groups are present as a part of the substituent.

The term “haloalkoxy” means straight-chain or branched alkoxy groups where some or all of the hydrogen atoms in these groups may be replaced by halogen atoms as specified above. Non-limiting examples of haloalkoxy include chloromethoxy, bromomethoxy, dichloromethoxy, trichloromethoxy, fluoromethoxy, difluoromethoxy, trifluoromethoxy, chlorofluoromethoxy, dichlorofluoromethoxy, chlorodifluoromethoxy, l-chloroethoxy, l-bromoethoxy, l-fluoroethoxy, 2-fluoroethoxy, 2,2-difluoroethoxy, 2,2,2-trifluoroethoxy, 2-chloro-2-fluoroethoxy, 2-chloro-2,2-difluoroethoxy, 2,2-dichloro-2-fluoroethoxy, 2,2,2-trichloroethoxy, pentafluoroethoxy and l,l,l-trifluoroprop-2-oxy. This definition also applies to haloalkoxy as a part of a composite substituent, for example haloalkoxyalkyl etc., unless specifically defined elsewhere.

The term “haloalkylthio” means straight-chain or branched alkylthio groups where some or all of the hydrogen atoms in these groups may be replaced by halogen atoms as specified above. Non-limiting examples of haloalkylthio include chloromethylthio, bromomethylthio, dichloromethylthio, trichloromethylthio, fluoromethylthio, difluoromethylthio, trifluoromethylthio, chlorofluoromethylthio, dichlorofluoromethylthio, chlorodifluoromethylthio, l-chloroethylthio, l-bromoethylthio, 1-fluoroethylthio, 2-fluoroethylthio, 2,2-difluoroethylthio, 2,2,2-trifluoroethylthio, 2-chloro-2-

fluoroethylthio, 2-chloro-2,2-difluoroethylthio, 2,2-dichloro-2-fluoroethylthio, 2,2,2-trichloroethylthio, pentafluoroethylthio and l,l,l-trifluoroprop-2-ylthio. This definition also applies to haloalkylthio as a part of a composite substituent, for example haloalkylthioalkyl etc., unless specifically defined elsewhere.

Examples of "haloalkylsulfmyl" include $CF_3S(0)$, CCbS(O), $CF_3CH_2S(0)$ and $CF_3CF_2S(0)$. Examples of "haloalkylsulfonyl" include $CF_3S(0)_2$, $CCl_3S(0)_2$, $CF_3CH_2S(0)_2$ and $CF_3CF_2S(0)_2$.

Hydroxy means -OH, Amino means -NRR, wherein R can be H or any possible substituent such as alkyl. Carbonyl means -C(O)- , carbonyloxy means -OC(O)-, sulfinyl means SO, sulfonyl means $S(0)_2$.

The term "alkoxy" used either alone or in compound words included Ci to C_{24} alkoxy, preferably Ci to C_{15} alkoxy, more preferably Ci to Cio alkoxy, most preferably Ci to O, alkoxy. Examples of alkoxy include methoxy, ethoxy, propoxy, l-methylethoxy, butoxy, l-methylpropoxy, 2-methylpropoxy, 1,1-dimethylethoxy, pentoxy, l-methylbutoxy, 2-methylbutoxy, 3-methylbutoxy, 2,2-dimethylpropoxy, 1-ethylpropoxy, hexoxy, l,l-dimethylpropoxy, l,2-dimethylpropoxy, l-methylpentoxy, 2-methylpentoxy, 3-methylpentoxy, 4-methylpentoxy, l,l-dimethylbutoxy, l,2-dimethylbutoxy, l,3-dimethylbutoxy, 2,2-dimethylbutoxy, 2,3-dimethylbutoxy, 3,3-dimethylbutoxy, l-ethylbutoxy, 2-ethylbutoxy, 1,1,2-trimethylpropoxy, l,2,2-trimethylpropoxy, 1-ethyl-l-methylpropoxy and 1-ethyl-2-methylpropoxy and the different isomers. This definition also applies to alkoxy as a part of a composite substituent, for example haloalkoxy, alkynylalkoxy, etc., unless specifically defined elsewhere.

"Alkoxyalkyl" denotes alkoxy substitution on alkyl. Non-limiting examples of "alkoxyalkyl" include CH_3OCH_2, $CH_3OCH_2CH_2$, $CH_3CH_2OCH_2$, $CH_3CH_2CH_2CH_2OCH_2$ and $CH_3CH_2OCH_2CH_2$.

The term "alkoxyalkoxy" denotes alkoxy substitution on alkoxy.

The term "alkylthio" includes branched or straight-chain alkylthio moieties such as methylthio, ethylthio, propylthio, l-methylethylthio, butylthio, l-methylpropylthio, 2-methylpropylthio, l,l-dimethylethylthio, pentylthio, l-methylbutylthio, 2-methylbutylthio, 3-methylbutylthio, 2,2-dimethylpropylthio, 1-ethylpropylthio, hexylthio, l,l-dimethylpropylthio, l,2-dimethylpropylthio, l-methylpentylthio, 2-methylpentylthio, 3-methylpentylthio, 4-methylpentylthio, l,l-dimethylbutylthio, l,2-dimethylbutylthio, l,3-dimethylbutylthio, 2,2-dimethylbutylthio, 2,3-dimethylbutylthio, 3,3-dimethylbutylthio, 1-ethylbutylthio, 2-ethylbutylthio, l,l,2-trimethylpropylthio, l,2,2-trimethylpropylthio, 1-ethyl-1-methylpropylthio and l-ethyl-2-methylpropylthio and the different isomers.

Halocycloalkyl, halocycloalkenyl, alkylcycloalkyl, cycloalkylalkyl, cycloalkoxyalkyl, alkylsulfinylalkyl, alkylsulfonylalkyl, haloalkylcarbonyl, cycloalkylcarbonyl, haloalkoxylalkyl, and the like, are defined analogously to the above examples.

The term "alkylthioalkyl" denotes alkylthio substitution on alkyl. Non-limiting examples of "alkylthioalkyl" include CH_2SCH_2, $CH_2SCH_2CH_2$, $CH_3CH_2SCH_2$, $CH_3CH_2CH_2CH_2SCH_2$ and

$CH_3CH_2SCH_2CH_2$. "Alkylthioalkoxy" denotes alkylthio substitution on alkoxy. The term "cycloalkylalkylamino" denotes cycloalkyl substitution on alkyl amino.

The terms alkoxyalkoxyalkyl, alkylaminoalkyl, dialkylaminoalkyl, cycloalkylaminoalkyl, cycloalkylaminocarbonyl and the like, are defined analogously to "alkylthioalkyl" or cycloalkylalkylamino .

The term "alkoxycarbonyl" is an alkoxy group bonded to a skeleton via a carbonyl group (-CO-). This definition also applies to alkoxycarbonyl as a part of a composite substituent, for example cycloalkylalkoxycarbonyl and the like, unless specifically defined elsewhere.

The term "alkoxycarbonylalkylamino" denotes alkoxy carbonyl substitution on alkyl amino.

"Alkylcarbonylalkylamino" denotes alkyl carbonyl substitution on alkyl amino. The terms alkylthioalkoxycarbonyl, cycloalkylalkylaminoalkyl and the like are defined analogously.

Non-limiting examples of "alkylsulfinyl" include methylsulphinyl, ethylsulphinyl, propylsulphinyl, 1-methylethylsulphinyl, butylsulphinyl, l-methylpropylsulphinyl, 2-methylpropylsulphinyl, 1,1-dimethylethylsulphinyl, pentylsulphinyl, l-methylbutylsulphinyl, 2-methylbutylsulphinyl, 3-methylbutylsulphinyl, 2,2-dimethylpropylsulphinyl, l-ethylpropylsulphinyl, hexylsulphinyl, 1,1-dimethylpropylsulphinyl, l,2-dimethylpropylsulphinyl, l-methylpentylsulphinyl, 2-methylpentylsulphinyl, 3-methylpentylsulphinyl, 4-methylpentylsulphinyl, 1,1-dimethylbutylsulphinyl, 1.2-dimethylbutylsulphinyl, l,3-dimethylbutylsulphinyl, 2,2-dimethylbutylsulphinyl, 2,3-dimethylbutylsulphinyl, 3,3-dimethylbutylsulphinyl, l-ethylbutylsulphinyl, 2-ethylbutylsulphinyl, 1,1,2-trimethylpropylsulphinyl, l,2,2-trimethylpropylsulphinyl, 1-ethyl-l-methylpropylsulphinyl and l-ethyl-2-methylpropylsulphinyl and the different isomers. The term "arylsulfinyl" includes Ar-S(O), wherein Ar can be any carbocyle or heterocylcle. This definition also applies to alkylsulphinyl as a part of a composite substituent, for example haloalkylsulphinyl etc., unless specifically defined elsewhere.

Non-limiting examples of "alkylsulfonyl" include methylsulphonyl, ethylsulphonyl, propylsulphonyl, 1-methylethylsulphonyl, butylsulphonyl, l-methylpropylsulphonyl, 2-methylpropylsulphonyl, 1,1-dimethylethylsulphonyl, pentylsulphonyl, l-methylbutylsulphonyl, 2-methylbutylsulphonyl, 3-methylbutylsulphonyl, 2,2-dimethylpropylsulphonyl, l-ethylpropylsulphonyl, hexylsulphonyl, 1,1-dimethylpropylsulphonyl, l,2-dimethylpropylsulphonyl, l-methylpentylsulphonyl, 2-methylpentylsulphonyl, 3-methylpentylsulphonyl, 4-methylpentylsulphonyl, 1,l-dimethylbutylsulphonyl, 1.2-dimethylbutylsulphonyl, l,3-dimethylbutylsulphonyl, 2,2-dimethylbutylsulphonyl, 2,3-dimethylbutylsulphonyl, 3,3-dimethylbutylsulphonyl, l-ethylbutylsulphonyl, 2-ethylbutylsulphonyl, 1.1.2-trimethylpropylsulphonyl, l,2,2-trimethylpropylsulphonyl, 1-ethyl-l-methylpropylsulphonyl and 1-ethyl-2-methylpropylsulphonyl and the different isomers. The term "arylsulfonyl" includes Ar-$S(0)_2$,

wherein Ar can be any carbocyle or heterocylcle. This definition also applies to alkylsulphonyl as a part of a composite substituent, for example alkylsulphonylalkyl etc., unless defined elsewhere.

"Alkylamino", "dialkylamino", and the like, are defined analogously to the above examples.

The term "carbocycle or carbocyclic" includes "aromatic carbocyclic ring system" and "nonaromatic carbocybc ring system" or polycyclic or bicycbc (spiro, fused, bridged, nonfused) ring compounds in which ring may be aromatic or non-aromatic (where aromatic indicates that the Huckel's rule is satisfied and non-aromatic indicates that the Huckel's rule is not statisfied).

The term "heterocycle" or "heterocyclic" includes "aromatic heterocycle" or "heteroaryl ring system" and "nonaromatic heterocycle ring system" or polycyclic or bicyclic (spiro, fused, bridged, non-fused) ring compounds in which ring may be aromatic or non-aromatic, wherein the heterocycle ring contains at least one heteroatom selected from N, O, S(0)o-$_2$, and or C ring member of the heterocycle may be replaced by C(=0), C(=S), C(=CR*R*) and C=NR*, * indicates integers.

The term "non-aromatic heterocycle" or "non-aromatic heterocyclic" means three- to fifteen-membered, preferably three- to twelve-membered, saturated or partially unsaturated heterocycle containing one to four heteroatoms from the group of oxygen, nitrogen and sulphur: mono, bi- or tricyclic heterocycles which contain, in addition to carbon ring members, one to three nitrogen atoms and/or one oxygen or sulphur atom or one or two oxygen and/or sulphur atoms; if the ring contains more than one oxygen atom, they are not directly adjacent; for example (but not limited to) oxetanyl, oxiranyl, aziridinyl, 2-tetrahydrofuranyl, 3-tetrahydrofuranyl, 2-tetrahydrothienyl, 3-tetrahydrothienyl, l-pyrrolidinyl, 2-pyrrolidinyl, 3-pyrrolidinyl, 3-isoxazolidinyl, 4-isoxazolidinyl, 5-isoxazolidinyl, 3-isothiazolidinyl, 4-isothiazolidinyl, 5-isothiazolidinyl, l-pyrazolidinyl, 3-pyrazolidinyl, 4-pyrazolidinyl, 5-pyrazolidinyl, 2-oxazolidinyl, 4-oxazolidinyl, 5-oxazolidinyl, 2-thiazolidinyl, 4-thiazolidinyl, 5-thiazolidinyl, 1-imidazolidinyl, 2-imidazolidinyl, 4-imidazolidinyl, l,2,4-oxadiazolidin-3-yl, l,2,4-oxadiazolidin-5-yl, l,2,4-thiadiazolidin-3-yl, l,2,4-thiadiazolidin-5-yl, 1,2,4-triazolidin-l-yl, l,2,4-triazolidin-3-yl, 1,3,4-oxadiazolidin-2-yl, l,3,4-thiadiazolidin-2-yl, l,3,4-triazolidin-l-yl, l,3,4-triazolidin-2-yl, 2,3-dihydrofur-2-yl, 2,3-dihydrofur-3-yl, 2,4-dihydrofur-2-yl, 2,4-dihydrofur-3-yl, 2,3-dihydrothien-2-yl, 2,3-dihydrothien-3-yl, 2,4-dihydrothien-2-yl, 2,4-dihydrothien-3-yl, pyrrolinyl, 2-pyrrolin-2-yl, 2-pyrrolin-3-yl, 3-pyrrolin-2-yl, 3-pyrrolin-3-yl, 2-isoxazolin-3-yl, 3-isoxazolin-3-yl, 4-isoxazolin-3-yl, 2-isoxazolin-4-yl, 3-isoxazolin-4-yl, 4-isoxazolin-4-yl, 2-isoxazolin-5-yl, 3-isoxazolin-5-yl, 4-isoxazolin-5-yl, 2-isothiazolin-3-yl, 3-isothiazolin-3-yl, 4-isothiazolin-3-yl, 2-isothiazolin-4-yl, 3-isothiazolin-4-yl, 4-isothiazolin-4-yl, 2-isothiazolin-5-yl, 3-isothiazolin-5-yl, 4-isothiazolin-5-yl, 2,3-dihydropyrazol-l-yl, 2,3-dihydropyrazol-2-yl, 2,3-dihydropyrazol-3-yl, 2,3-dihydropyrazol-4-yl, 2,3-dihydropyrazol-5-yl, 3,4-dihydropyrazol-l-yl, 3,4-dihydropyrazol-3-yl, 3,4-dihydropyrazol-4-yl, 3,4-dihydropyrazol-5-yl, 4,5-dihydropyrazol-l-yl, 4,5-dihydropyrazol-3-yl, 4,5-dihydropyrazol-4-yl, 4,5-dihydropyrazol-5-yl, 2,3-

dihydrooxazol-2-yl, 2,3-dihydrooxazol-3-yl, 2,3-dihydrooxazol-4-yl, 2,3-dihydrooxazol-5-yl, 3,4-dihydrooxazol-2-yl, 3,4-dihydrooxazol-3-yl, 3,4-dihydrooxazol-4-yl, 3,4-dihydrooxazol-5-yl, 3,4-dihydrooxazol-2-yl, 3,4-dihydrooxazol-3-yl, 3,4-dihydrooxazol-4-yl, piperidinyl, 2-piperidinyl, 3-piperidinyl, 4-piperidinyl, pyrazynyl, morpholinyl, thiomorphlinyl, l,3-dioxan-5-yl, 2-tetrahydropyranyl, 4-tetrahydropyranyl, 2-tetrahydrothienyl, 3-hexahydropyridazinyl, 4-hexahydropyridazinyl, 2-hexahydropyrimidinyl, 4-hexahydropyrimidinyl, 5-hexahydropyrimidinyl, 2-piperazinyl, 1,3,5-hexahydrotriazin-2-yl, l,2,4-hexahydrotriazin-3-yl, cycloserines, 2,3,4,5-tetrahydro[lH]azepin-l- or -2- or -3- or -4- or -5- or -6- or -7- yl, 3,4,5,6-tetra-hydro[2H]azepin-2- or -3- or -4- or -5- or -6- or-7-yl, 2,3,4,7-tetrahydro[lH]azepin-l- or -2- or -3- or -4- or -5- or -6- or-7- yl, 2,3,6,7-tetrahydro[lH]azepin-l- or -2- or -3- or -4- or -5- or -6- or -7- yl, hexahydroazepin-l- or -2- or -3- or -4- yl, tetra- and hexahydrooxepinyl such as 2,3,4,5-tetrahydro[l H]oxepin-2- or -3- or -4- or -5- or -6- or -7- yl, 2,3,4,7-tetrahydro[lH]oxepin-2- or -3- or -4- or -5- or -6- or -7- yl, 2,3,6,7-tetrahydro[lH]oxepin-2- or -3- or -4- or -5- or -6- or -7- yl, hexahydroazepin-l- or -2- or -3- or -4- yl, tetra- and hexahydro-l,3-diazepinyl, tetra- and hexahydro-l,4-diazepinyl, tetra- and hexahydro-l,3-oxazepinyl, tetra- and hexahydro-l,4-oxazepinyl, tetra- and hexahydro-l,3-dioxepinyl, tetra- and hexahydro-l,4-dioxepinyl. This definition also applies to heterocyclyl as a part of a composite substituent, for example heterocyclylalkyl etc., unless specifically defined elsewhere.

The term “heteroaryl” means 5 or 6-membered, fully unsaturated monocyclic ring system containing one to four heteroatoms from the group of oxygen, nitrogen and sulphur; if the ring contains more than one oxygen atom, they are not directly adjacent; 5-membered heteroaryl containing one to four nitrogen atoms or one to three nitrogen atoms and one sulphur or oxygen atom: 5-membered heteroaryl groups which, in addition to carbon atoms, may contain one to four nitrogen atoms or one to three nitrogen atoms and one sulphur or oxygen atom as ring members, for example (but not limited thereto) furyl, thienyl, pyrrolyl, isoxazolyl, isothiazolyl, pyrazolyl, oxazolyl, thiazolyl, imidazolyl, l,2,4-oxadiazolyl, l,2,4-thiadiazolyl, l,2,4-triazolyl, l,3,4-oxadiazolyl, l,3,4-thiadiazolyl, l,3,4-triazolyl, tetrazolyl; nitrogen-bonded 5-membered heteroaryl containing one to four nitrogen atoms, or benzofused nitrogen-bonded 5-membered heteroaryl containing one to three nitrogen atoms: 5-membered heteroaryl groups which, in addition to carbon atoms, may contain one to four nitrogen atoms or one to three nitrogen atoms as ring members and in which two adjacent carbon ring members or one nitrogen and one adjacent carbon ring member may be bridged by a buta-l,3-diene-l,4-diyl group in which one or two carbon atoms may be replaced by nitrogen atoms, where these rings are attached to the skeleton via one of the nitrogen ring members, for example (but not limited to) l-pyrrolyl, l-pyrazolyl, l,2,4-triazol-l- yl, l-imidazolyl, l,2,3-triazol-l-yl and 1,3,4-triazol-l-yl.

6-membered heteroaryl which contains one to four nitrogen atoms: 6-membered heteroaryl groups which, in addition to carbon atoms, may contain, respectively, one to three and one to four nitrogen atoms as ring members, for example (but not limited thereto) 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, 3-pyridazinyl, 4-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl, 2-pyrazinyl, l,3,5-triazin-2-yl, l,2,4-triazin-3-yl and l,2,4,5-tetrazin-3-yl; benzofused 5-membered heteroaryl containing one to three nitrogen atoms or one nitrogen atom and one oxygen or sulphur atom: for example (but not limited to) indol-l-yl, indol-2-yl, indol-3-yl, indol-4-yl, indol-5-yl, indol-6-yl, indol-7-yl, benzimidazol-l-yl, benzimidazol-2-yl, benzimidazol-4-yl, benzimidazol-5-yl, indazol-l-yl, indazol-3-yl, indazol-4-yl, indazol-5-yl, indazol-6-yl, indazol-7-yl, indazol-2-yl, l-benzofuran-2-yl, l-benzofuran-3-yl, l-benzofuran-4-yl, l-benzofuran-5-yl, 1-benzofuran- 6-yl, l-benzofuran-7-yl, l-benzothiophen-2-yl, l-benzothiophen-3-yl, l-benzothiophen-4-yl, 1-benzothiophen-5-yl, l-benzothiophen-6-yl, l-benzothiophen-7-yl, l,3-benzothiazol-2-yl, 1,3- benzothiazol-4-yl, l,3-benzothiazol-5-yl, l,3-benzothiazol-6-yl, l,3-benzothiazol-7-yl, l,3-benzoxazol-2-yl, 1,3-benzoxazol-4-yl, l,3-benzoxazol-5-yl, l,3-benzoxazol-6-yl and l,3-benzoxazol-7-yl; benzofused 6-membered heteroaryl which contains one to three nitrogen atoms: for example (but not limited to) quinolin-2-yl, quinolin-3-yl, quinolin-4-yl, quinolin-5-yl, quinolin-6-yl, quinolin-7-yl, quinolin-8-yl, isoquinolin-l-yl, isoquinolin-3-yl, isoquinolin-4-yl, isoquinolin-5-yl, isoquinolin-6-yl, isoquinolin-7-yl and isoquinolin-8-yl.

This definition also applies to heteroaryl as a part of a composite substituent, for example heteroarylalkyl etc., unless specifically defined elsewhere.

"Trialkylsilyl" includes 3 branched and/or straight-chain alkyl radicals attached to and linked through a silicon atom such as trimethylsilyl, triethylsilyl and t-butyl-dimethylsilyl. "Halotrialkylsilyl" denotes at least one of the three alkyl radicals is partially or fully substituted with halogen atoms which may be the same or different. "Alkoxytrialkylsilyl" denotes at least one of the three alkyl radicals is substituted with one or more alkoxy radicals which may be the same or different. "Trialkylsilyloxy" denotes a trialkylsilyl moiety attached through oxygen.

Non-limiting examples of "alkylcarbonyl" include C(0)CH $_3$, C(O)$CH_2CH_2CH_3$ and C(0)CH$(CH_3)_2$. Non-limiting examples of "alkoxycarbonyl" include CH30C(=0), $CH_3CH_2OC(=O)$, $CH_3CH_2CH_2OC(=O)$, $(CH_3)_2$CH0C(=0) and the different butoxy or pentoxycarbonyl isomers. Non-limiting examples of "alkylaminocarbonyl" include CH_3NHC(=0), CH_3CHf NHC(=O), $CH_3CH_2CH_2NHC(=O)$, $(CH_3)_2$CHNHC(=0) and the different butylamino -or pentylaminocarbonyl isomers. Non-limiting examples of "dialkylaminocarbonyl" include (CH3)2NC(=0), (CHf $CH_2)_2$NC(=O), CH3CH2(CH3)NC(=0), CH3CH_2CH_2(CH3)NC(=0) and $(CH3)_2$CHN(CH3)C(=0). Non-limiting examples of "alkoxy alkylcarbonyl" include $CH_3$0CH $_2$C(=0), $CH_3$0CH $_2CH_2$C(=0), $CH_3CH_2$0CH $_2$C(=0), $CH_3CH_2CH_2CH_2OCH_2C(=O)$ and $CH_3CH_2OCH_2CH_2C(=O)$. Non-limiting examples of

"alkylthioalkylcarbonyl" include $CH_3SCH_2C(=0)$, $CH_3SCH_2CH_2C(=0)$, $CH_3CH_2SCH_2C(=0)$, $CH_3CH_2CH_2CH_2SCH_2C(=0)$ and $CH_3CH_2SCH_2CH_2C(=0)$. The term haloalkylsufonylaminocarbonyl, alkylsulfonylaminocarbonyl, alkylthioalkoxycarbonyl, alkoxycarbonylalkyl amino and the like are defined analogously.

Non-limiting examples of "alkylaminoalkylcarbonyl" include $CH_3NHCH_2C(=0)$, $CH_3NHCH_2CH_2C(=0)$, $CH_3CH_2NHCH_2C(=0)$, $CH_3CH_2CH_2CH_2NHCH_2C(=0)$ and $CH_3CH_2NHCH_2CH_2C(=0)$.

The term "amide" means A-R'C=ONR"-B, wherein R and R" indicates substituents and A and B indicate any group.

The term "thioamide" means A-R'C=SNR"-B, wherein R and R" indicates substituents and A and B indicate any group.

The total number of carbon atoms in a substituent group is indicated by the "C_i C_j" prefix where i and j are numbers from 1 to 21. For example, Ci-C_3 alkylsulfonyl designates methylsulfonyl through propylsulfonyl; C_2 alkoxyalkyl designates CH_3OCH_2; C_3 alkoxyalkyl designates, for example, $CH_3CH(OCH_3)$, $CH_3OCH_2CH_2$ or $CH_3CH_2OCH_2$; and C_4 alkoxyalkyl designates the various isomers of an alkyl group substituted with an alkoxy group containing a total of four carbon atoms, examples including $CH_3CH_2CH_2OCH_2$ and $CH_3CH_2OCH_2CH_2$. In the above recitations, when a compound of Formula I is comprised of one or more heterocyclic rings, all substituents are atached to these rings through any available carbon or nitrogen by replacement of a hydrogen on said carbon or nitrogen.

When a compound is substituted with a substituent bearing a subscript that indicates the number of said substituents can exceed 1, said substituents (when they exceed 1) are independently selected from the group of defined substituents. Further, when the subscript m in $(R)_m$ indicates an integer ranging from for example 0 to 4 then the number of substituents may be selected from the integers between 0 and 4 inclusive.

When a group contains a substituent which can be hydrogen, then, when this substituent is taken as hydrogen, it is recognized that said group is being un-substituted.

The embodiments herein and the various features and advantageous details thereof are explained with reference to the non-limiting embodiments in the description. Descriptions of well-known components and processing techniques are omited so as to not unnecessarily obscure the embodiments herein. The examples used herein are intended merely to facilitate an understanding of ways in which the embodiments herein may be practiced and to further enable those of skilled in the art to practice the embodiments herein. Accordingly, the examples should not be construed as limiting the scope of the embodiments herein.

The description of the specific embodiments will so fully reveal the general nature of the embodiments herein that others can, by applying current knowledge, readily modify and/or adapt for various

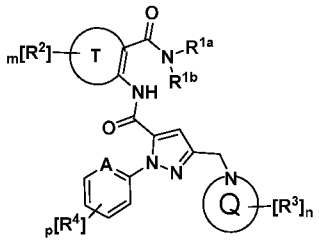
applications such specific embodiments without departing from the generic concept, and, therefore, such adaptations and modifications should and are intended to be comprehended within the meaning and range of equivalents of the disclosed embodiments. It is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation. Therefore, while the embodiments herein have been described in terms of preferred embodiments, those skilled in the art will recognize that the embodiments herein can be practiced with modification within the spirit and scope of the embodiments as described herein.

Any discussion of documents, acts, materials, devices, articles and the like that has been included in this specification is solely for the purpose of providing a context for the disclosure. It is not to be taken as an admission that any or all of these matters form a part of the prior art base or were common general knowledge in the field relevant to the disclosure as it existed anywhere before the priority date of this application.

The numerical values mentioned in the description and the description/claims though might form a critical part of the present invention of the present disclosure, any deviation from such numerical values shall still fall within the scope of the present disclosure if that deviation follows the same scientific principle as that of the present invention disclosed in the present disclosure.

The compounds synthesized by the novel and inventive process of the present invention may, if appropriate, be present as mixtures of different possible isomeric forms, especially of stereoisomers, for example E and Z, threo and erythro, and also optical isomers, but if appropriate also of tautomers. Both the E and the Z isomers, and also the threo and erythro isomers, and the optical isomers, any desired mixtures of these isomers and the possible tautomeric forms are disclosed and claimed.

The present invention relates to a novel process for preparing a compound of formula I;



I

wherein,

R^{1a} and R^{1b} are independently selected from the group consisting of hydrogen, Ci-Ce-alkyl, Ci-Ce-haloalkyl, C_3-C_6-cycloalkyl, (Ci-C_6-alkyl)-C_3-C_6-cycloalkyl, or (C_3-C_6-cycloalkyl)-Ci-C_6-alkyl; or

R^{1a} and R^{1b} together with the N atom to which they are attached form N=S(=0)o-$_2$(Ci-C_6-alkyl)$_2$;

T is an aryl or a heteroaryl ring or a fused or a bicyclic aryl or heteroaryl ring or ring system;

R^2 is selected from the group consisting of hydrogen, halogen, cyano, nitro, G-G, -alkyl. Ci-G,-haloalkyl, or C3-C6-cycloalkyl;

A is N or C;

R^3 and R^4 are independently selected from the group consisting of hydrogen, halogen, cyano, nitro, hydroxy, G-G, -alkyl. G-G,-haloalkyl. C_3-C_6-cycloalkyl, C_3-C_6-halocycloalkyl, G-G,-alkoxy, Ci-Ce-haloalkoxy, G-G.-alkylthio. G-G.-alkylsulphinyl. G-G.-alkylsulphonyl. Ci-G,-haloalkylthio, G-G.-haloalkylsulphinyl. G-G.-haloalkylsulphonyl or NR^aR^b, R^a and R^b are independently selected from the group consisting of hydrogen, G-G, -alkyl. C3-C6-cycloalkyl or R^a and R^b together with the N atom to which they are attached form a substituted or unsubstituted 3- to 6- membered heterocyclic ring;

Q is a 3-, 4- or 5 membered heterocyclic ring;

n is an integer 0 to 4;

m is an integer 0 to 6; and

p is an integer 0 to 5.

The substituents on the 3- to 6- membered heterocyclic ring are selected from the group consisting of halogen, cyano, nitro, hydroxy, G-G, -alkyl. G-G,-haloalkyl. C3-C6-cycloalkyl, C3-C6-halocycloalkyl, Ci-Ce-alkoxy, G-G,-haloalko\y. G-G.-alkylthio. G-G,-alkylsulphinyl. G-G,-alkylsulphonyl. Ci-G,-haloalkylthio, Ci-G,-haloalkylsulphinyl or Ci-G,-haloalkyl sulphonyl.

In one of the particular embodiments the present invention relates to a novel process for preparing a compound of formula I;

wherein,

R^{la} is hydrogen; R^{lb} is selected from the group consisting of hydrogen, G-G, -alkyl and (C_3-C_6-cycloalkyl)-Ci-C_6-alkyl; T is a phenyl ring; R^2 is selected from the group consisting of halogen, cyano, and G-G, -alkyl: A is N; R^3 is G-G, -haloalkyl: R^4 is halogen; Q is a 5 membered heterocyclic ring; n is an integer 1; m is an integer 2; and p is an integer 1 or 2.

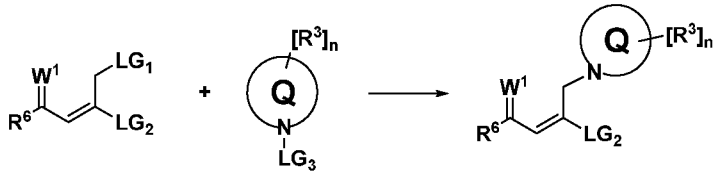
In another particular embodiment the present invention relates to a novel process for preparing a compound of formula I;

wherein,

R^{1a} is hydrogen; R^{1b} is G-G,-alkyl: T is a phenyl ring; $\mathbf{R}_2$ is selected from the group consisting of Cl, cyano and methyl; A is N; $\mathbf{R}_3$ is trifluoro alkyl or difluoro alkyl; $\mathbf{R}_4$ is Cl; Q is a tetrazole ring; n is an integer $_1$; m is an integer $_2$; and p is an integer $_1$ or $_2$.

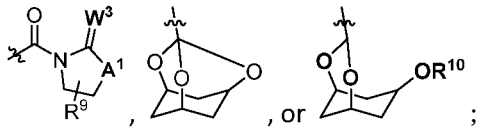
The process for preparing the compound of formula I is described herein after.

PROCESS STEP (a): In the step (a) of the process, a compound of formula IV is reacted with a compound of formula VII to obtain a compound of formula III;



IV VII III

wherein,

$\mathbf{R}_6$ is selected from the group consisting of CX_3, $COW^2(R^7)$, $C(W^4R_7)_3$, $CH(W_4R^7)_2$, allylic group, substituted or unsubstituted furanyl,  ;

wherein,

W^1, W^2, W^3, $\mathbf{W}_4$ and $\mathbf{A}_1$ are independently O, S or NR^{1c}; wherein R^{1c} is hydrogen, G-G,-alkyl, or C_3-C_6-cycloalkyl;

$\mathbf{R}_7$ is selected from the group consisting of hydrogen, substituted or unsubstituted $C_{:1}$-G,-alkyl, substituted or unsubstituted C_3-C_6-cycloalkyl, substituted or unsubstituted aryl and substituted or unsubstituted arylalkyl groups; or

two R^7 together with the atom to which they are attached form a substituted or unsubstituted $_3$- to 6- membered carbocyclic or heterocyclic ring; and

R^9 and R^{10} are independently selected from the group consisting of hydrogen, halogen, cyano, substituted or unsubstituted G-G,-alkyl. substituted or unsubstituted G-G,-alkoxy, substituted or unsubstituted C_3-C_6-cycloalkyl, substituted or unsubstituted $C_{:1}$-G,-alkylthio, substituted or unsubstituted G-G.-alkylsulphinyl. substituted or unsubstituted Ci-Ce-alkylsulphonyl, substituted or unsubstituted aryl and substituted or unsubstituted arylalkyl groups;

LGi is selected from the group consisting of X, OR^5, and $OSi(R^{11})_3$;

R^5 is selected from the group consisting of hydrogen, substituted or unsubstituted Ci-G,-alkyl, substituted or unsubstituted aryl-G-G, -alkyl. substituted or unsubstituted aryl, -(C=0)-Ci-C $_6$-alkyl, -(C=0)-Ci-C $_6$-haloalkyl, -(C=0)0-Ci-C $_6$-alkyl, -(C=0)0-haloCi-C $_6$-alkyl, SCh-G-G, -alkyl. SCh-G-G, -haloalkyl or substituted or unsubstituted S0 $_2$-aryl;

R^{11} is selected from the group consisting of hydrogen, halogen, substituted or unsubstituted G-G, -alkyl, substituted or unsubstituted aryl-G-G, -alkyl, substituted or unsubstituted aryl, -(C=0)-Ci-C $_6$-alkyl, -(C=0)-Ci-C $_6$-haloalkyl, -(C=0)0-Ci-C $_6$-alkyl, -(C=0)0-haloCi-C $_6$-alkyl, SCT-G-G, -alkyl. SO_2-G-G, -haloalkyl and substituted or unsubstituted SCh-aryl;

LG2 is X, OR^{12}; R^{12} is selected from the group consisting of hydrogen, substituted or unsubstituted G-G, -alkyl, substituted or unsubstituted aryl-G-G, -alkyl, substituted or unsubstituted aryl, -(C=0)-Ci-C $_6$-alkyl, -(C=0)-Ci-C $_6$-haloalkyl, -(C=0)0-Ci-C $_6$-alkyl, -(C=0)0-haloCi-C $_6$-alkyl, SCh-Ci-Ce-alkyl, SCh-Ci-Ce-haloalkyl, substituted or unsubstituted SCh-aryl, alkylthio and NR^aR^b; R^a and R^b are independently selected from the group consisting of hydrogen, G-G, -alkyl. C3-C6-cycloalkyl; or R^a and R^b together with the N atom to which they are attached form a substituted or unsubstituted 3- to 6- membered heterocyclic ring;

LG_3 is selected from the group consisting of hydrogen, alkali metal, halogen and $Si(R^{11})_3$;

each X is independently hydrogen, F, Cl, Br or I;

R^3, n, and Q are each as defined above.

The substitution on furanyl group is selected from the group consisting of halogen, cyano, nitro, hydroxy, C_1-G,-alkyl. G-G,-haloalkyl. C_3-C_6-cycloalkyl, C_3-C_6-halocycloalkyl, G-G,-alko\y. G-G,-haloalko\y. C_1-G,-alkylthio. G-G,-alkylsulphinyl. G-G,-alkylsulphonyl. Ci-G,-haloalkylthio. C_1-G,-haloalkylsulphinyl, and Ci-G,-haloalkylsulphonyl.

The substitution on G-G, -alkyl. C3-C6-cycloalkyl, aryl, arylalkyl groups of R^7 and carbocyclic or heterocyclic ring formed by two R^7 are independently selected from the group consisting of halogen, cyano, nitro, hydroxy, G-G, -alkyl. G-G,-haloalkyl. C3-C6-cycloalkyl, C3-C6-halocycloalkyl, C_1-G,-alkoxy, Ci-G,-haloalkoxy. Ci-G,-alkylthio. G-G,-alkylsulphinyl. Ci-G,-alkylsulphonyl. C_1-G,-haloalkylthio, Ci-G,-haloalkylsulphinyl. and Ci-G,-haloalkylsulphonyl.

The substitution on G-G, -alkyl. Ci-Ce-alkoxy, C3-C6-cycloalkyl, G-G, -alkylthio. G-G,-alkylsulphinyl. C_1-G,-alkylsulphonyl, aryl, and arylalkyl groups of R^9 and R^{10} is selected from the group consisting of halogen, cyano, nitro, hydroxy, G-G, -alkyl. G-G,-haloalkyl. C3-C6-cycloalkyl, C3-C6-halocycloalkyl, Ci-

G.-alkoxy. G-C,-haloalkoxy. G-G.-alkylthio. Ci-G,-alkylsulphinyl. Ci-G,-alkylsulphonyl. Ci-G,-haloalkylthio, G-G.-haloalkylsulphinyl. and G-G.-haloalkylsulphonyl.

The substitution on G-G, -alkyl, aryl-G-G, -alkyl, aryl, and S0 $_2$-aryl of LGi and LG_2 group is selected from the group consisting of halogen, cyano, nitro, hydroxy, Ci-Ce-alkyl, Ci-Ce-haloalkyl, C3-C6-cycloalkyl, C3-C6-halocycloalkyl, Ci-Ce-alkoxy, Ci-Ce-haloalkoxy, Ci-Ce-alkylthio, Ci-Ce-alkylsulphinyl, Ci-Ce-alkylsulphonyl, Ci-Ce-haloalkylthio, Ci-Ce-haloalkylsulphinyl, and Ci-Ce-haloalkylsulphonyl.

Particularly, definitions of the substituents of the compounds of formula IV and VII used in the process step (a) and the compound of formula III obtained in the process step (a) are as follows:

R^6 is CX_3 or $C(=0)W^2R^7$,

wherein, R^7 is selected from the group consisting of hydrogen, Ci-Ce-alkyl, C_3-C_6-cycloalkyl, aryl and arylalkyl groups;

W^1 and W^2 are O; LGi is X; LG2 is X or OR^{12}; R^{12} is Ci-Ce-alkyl; each X is independently F, Cl, Br or I; LG3 is hydrogen or alkali metal; R^3 is G-G.-haloalkyl: n is an integer 1; and Q is a 3-, 4- or 5 membered heterocyclic ring.

More particularly, definitions of the substituents of the compounds of formula IV and VII used in the process step (a) and the compound of formula III obtained in the process step (a) are as follows:

R^6 is CCT, CBr_3, $C(=0)W^2CH_3$, $C(=0)W^2C_2H_5$; W^1 and W^2 are O; LGi is Cl, Br or I, preferably Br; LG_2 is Cl, Br, I, OCH_3, or OC_2H_5; LG_3 is sodium metal ion; R^3 is trifluoro methyl; n is an integer 1; and Q is a tetrazole ring.

The process step (a) is carried out in the presence of one or more suitable solvent and optionally, in the presence of one or more suitable reagent and or one or more suitable catalyst and or reagent under particular reaction conditions.

The suitable solvent useful for the purpose of the process step (a) is preferably selected from the group consisting of acetone, acetonitrile, methyl tert-butyl ether, chlorobenzene, dichloroethane, dichloromethane, dioxane, ethyl acetate, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, 2-methyltetrahydrofuran, tetrahydrofuran, l,2-dimethoxyether, toluene, p-xylene and N-methyl-2-pyrrolidone.

The suitable catalyst for the purpose of the process step (a) is selected from the group consisting of potassium iodide, sodium iodide, copper iodide, cupric iodide.

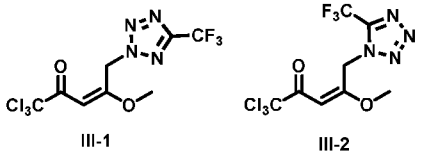
The process step (a) of the present invention can be performed particularly within a temperature range from 20 °C to 150 °C.

The reaction time is not critical and depends on the batch size, temperature, reagent and solvent employed. Typically, the reaction time may vary from few minutes to several hours.

The process step (a) of the present invention is usually performed under standard pressure conditions. It is, however, also possible to perform the process step (a) under reduced pressure conditions to effect complete conversion of the reactants into the product.

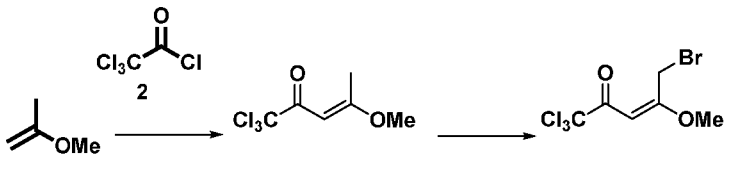
It has been found that the replacement of LGi by the compound of formula VII in the process step (a) is critical to the present invention as none of the prior art discloses or suggests to couple the compound of formula IV and the compound of formula VII.

It is also found that the reaction is highly regioselective. For example, when R^6 is CCT, W^1 is O, Q is tetrazole, R^3 is trifluoro methyl, LG2 is OMe and n is an integer 1, the product III-1 is formed in higher percentage than that of the product III-2:



III-1 III-2

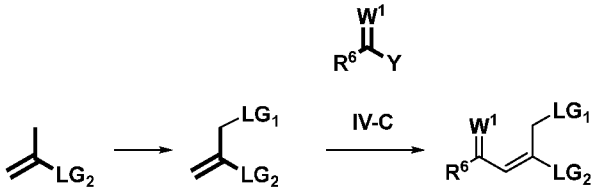
The process to obtain the compound of formula IV is known in the prior art. One of the methods involves reacting a compound 1 and 2 and then the obtained intermediate XVII-1 is converted into the compound of formula IV-1. The known reaction is depicted below:



1 XVII-1 IV-1

Alternatively, the compound of formula IV can be prepared by the novel process of the present invention. It has also been found, surprisingly, that if the conversion of IV-A to IV-B is carried out first followed by coupling with IV-C, then the intermediate IV-B may not be isolated and the process can be carried out in one pot.

Consequently, it is considered to be surprising that the compound of formula IV can be obtained by one pot process as depicted herein below, as pre-step of step (a), in accordance with the present invention:



IV-A IV-B IV

wherein, Y is OR^5, X, or -0(C=0)CX_3; R^5, R^6, W^1, X, LGi, and LG_2, are as defined herein above.

In another embodiment the compound of formula IV-B may optionally be isolated if required.

Alternatively, the compound of formula IV may also be procured commercially or can be obtained by various methods known in the prior art documents, for example, Synthesis (16), pp. 2353-2358, 2002.

Particularly, definitions of the substituents of the compounds of formula IV-A, IV-B and IV-C used and the compound of formula IV obtained are as follows:

R^6 is CX_3 or C(=0)W^2R^7,

wherein, R^7 is selected from the group consisting of hydrogen, G-G, -alkyl. G-Ce-cycloalkyl, aryl and arylalkyl groups;

W^1 and W^2 are O; LGi is X; LG_2 is X or OR^{12}; R^{12} is G-G, -alkyl: and each X is independently F, Cl, Br or I.

More particularly, definitions of the substituents of the compounds of formula IV-A, IV-B and IV-C used and the compound of formula IV are as follows:

R^6 is CCl_3, CBr_3, C(=0)W^2CH_3, C(=0)$W^2C_2¾$; W^1 and W^2 are O; LGi is Cl, Br or I; LG_2 is Cl, Br, I, OCH_3, or $OC_2¾$.

In accordance with the present invention, the conversion of the compound of formula IV-A into the compound of formula IV-B is carried out using one or more suitable reagent and one or more suitable solvent under particular reaction conditions. For example, if LGi is halogen then the suitable reagent is a halogenating reagent selected from the group consisting of HX, NaX, KX, CuX2, MgX2, CsX, ZnX2, SOCh, SO2CI2, COCI2, X2, 0(=0)(0(¾) 2, f-BuOCl, NaOCl, chloramine-T, A'-halosuccinimidcs, N-halosaccharine, halohydantoines, POX3, PX3 and PX5; wherein X or halo is Cl, Br, I or F. The preference is given to SOCF, COCF, X2. and A'-halosuccinimidcs.

The suitable solvent, used in the conversion of the compound of formula IV-A into the compound of formula IV-B, is selected preferably from the group consisting of acetone, acetonitrile, methyl tert-butyl ether, chlorobenzene, dichloroethane, dichloromethane, dioxane, ethyl acetate, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, 2-methyltetrahydrofuran, tetrahydrofuran, l,2-dimethoxyether, toluene, p-xylene andN-methyl-2-pyrrolidone.

The conversion of the compound of formula IV-A into the compound of formula IV, without isolating the compound of formula IV-B and in the same pot, is carried out using one or more suitable reagent and one or more suitable solvent under particular reaction conditions.

The suitable reagent used for assisting the conversion of formula IV-B into the compound of formula IV is selected preferably from the group consisting of pyridine, 1- or 2- or 3-picoline, triethyl amine, *N,N*-Diisopropylethylamine, 2,6-Di-tert-butylpyridine, l,5-Diazabicyclo(4.3.0)non-5-ene, 1,8-Diazabicycloundec-7-ene, lithium diisopropylamide, sodium bis(trimethylsilyl)amide, and potassium bis(trimethylsilyl)amide .

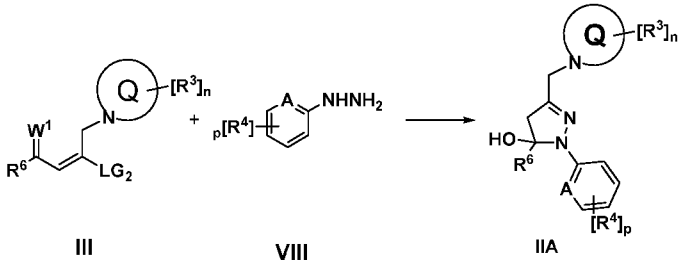
The suitable solvent in which the conversion of formula IV-B into the compound of formula IV is preferably selected from the group consisting of acetone, acetonitrile, methyl tert-butyl ether, chlorobenzene, dichloroethane, dichloromethane, dioxane, ethyl acetate, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, 2-methyltetrahydrofuran, tetrahydrofuran, l,2-dimethoxyether, toluene, p-xylene andN-methyl-2-pyrrolidone.

The temperature conditions employed for obtaining the compound of formula IV-B and the compound of formula IV range from 20 °C to 100 °C.

The reaction time is not critical and depends on the batch size, temperature, reagent and solvent employed. Typically, the reaction time may vary from few minutes to several hours.

This process step is usually performed under standard pressure conditions. It is, however, also possible to perform this process step under reduced pressure conditions to achieve complete conversion of the reactants into the product.

PROCESS STEP (b): In the step (b) of the process, the compound of formula III is cyclized with hydrazine of formula VIII to obtain a compound of formula IIA;



III VIII IIA

wherein, R^3, R^4, R^6, A, n, p, Q, W^1, and LG2 are each as defined herein above.

Consequently, the process of the present invention is non-obvious and inventive in light of the technical as well as economical advantage of first attaching the compound of formula VII with the compound of formula IV as shown in the process step (a) and then executing cyclization reaction as shown in the process step (b) not only reduces the number of steps but also facilitates the synthesis of the compound of formula I in a single pot. By virtue of reduction in number of steps for the synthesis of the compound of formula I in a single pot or multi pot the overall yield obtained is higher with reduced time, labor and operational cost.

Thus, though the compound of formula III formed in the process step (a) or the compound of formula IIA formed in the process step (b) can be isolated by suitable workup and optionally further purification, it is also possible to proceed without these compounds being isolated for the reason of yield and operational efficacy.

Particularly, definitions of the substituents of the compounds of formula III and VIII used in the process step (b) and the compound of formula IIA obtained in the process step (b) are as follows:

R^6 is CX_3 or $C(=0)W^2R^7$,

wherein, R^7 is selected from the group consisting of hydrogen, Ci-C_6-alkyl. C3-C6-cycloalkyl, aryl and arylalkyl groups;

W^1 and W^2 are O; LG2 is X or OR^{12}; R^{12} is Ci-Ce-alkyl; R^3 is Ci-Ce-haloalkyl; n is an integer 1; Q is a 3-, 4- or 5 membered heterocyclic ring; A is N; R^4 is X; p is an integer 1 or 2; and each X is independently F, Cl, Br or I.

More particularly, definitions of the substituents of the compounds of formula III and VIII used in the process step (b) and the compound of formula IIA obtained in the process step (b) are as follows:

R^6 is CCT, CBr_3, $C(=0)W^2CH_3$, $C(=0)W^2C_2¾$; W^1 and W^2 are O; LG_2 is Cl, Br, I, OCH_3, or $OC_2¾$; R^3 is trifluoro alkyl; n is an integer 1; Q is a tetrazole ring; A is N; R^4 is Cl; and p is an integer 1. The process step (b) is carried out in the presence of one or more suitable solvent and optionally, in the presence of one or more suitable reagent and or one or more suitable catalyst under particular reaction conditions.

The wordings "n is an integer 1" and "p is an integer 1" are sounding strange.

The suitable solvent useful for the purpose of the process step (b) is preferably selected from the group consisting of acetone, acetonitrile, ethyl alcohol, acetic acid, methyl tert-butyl ether, chlorobenzene, dichloroethane, dichloromethane, dioxane, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, ethyl acetate, 2-metyltetrahedrafuran, tetrahydrofuran, l,2-dimethoxyether, toluene, xylene andN-methyl-2-pyrrolidone.

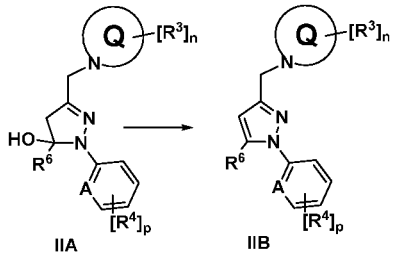
The suitable reagent useful for the purpose of the process step (b) is preferably selected from the group consisting of acetic acid, trifluoroacetic acid, hydrochloric acid, hydrobromic acid, sulphuric acid, methanesulfonic acid, triflic acid, phosphoric acid and p-toluenesulfonic acid.

The process step (b) of the present invention can be performed particularly within a temperature range from 20 °C to 150 °C.

The reaction time is not critical and depends on the batch size, temperature, reagent and solvent employed. Typically, the reaction time may vary from few minutes to several hours.

The process step (b) of the present invention is usually performed under standard pressure conditions. It is, however, also possible to perform the process step (b) under reduced pressure conditions for regioselective cyclization proceeding into the compound of formula IIA.

PROCESS STEP (c): In the process step (c) of the present invention, the compound of formula IIA is converted into the compound of formula IIB by eliminating water in one or more suitable dehydrating reagent;



wherein, R^3, R^4, R^6, A, n, p, and Q are each as defined above.

For elimination of water leading to the formation of the compound of formula IIB from the compound of formula IIA the following dehydrating reagents are useful: sulphuric acid, trifluoroacetic acid, phosphorous trichloride, phosphorous oxychloride, thionyl chloride, acetic anhydride, trifluoroacetic anhydride, oxalyl chloride, phosgene, diphosgene, methanolic hydrochloric acid, hydrogen chloride gas, acetic acid, hydrogen bromide, triflic acid, methanesulfonic acid, p-toluenesulfonic acid, hydrogen chloride-1,4-dioxane and silica gel.

Particularly, sulphuric acid, trifluoroacetic acid, thionyl chloride, trifluoroacetic anhydride, oxalyl chloride, methanolic hydrochloric acid, hydrogen chloride gas, acetic acid, hydrogen bromide, triflic acid, methanesulfonic acid, p-toluenesulfonic acid, hydrogen chloride-1,4-dioxane and silica gel are used for elimination of water from the compound of formula IIA.

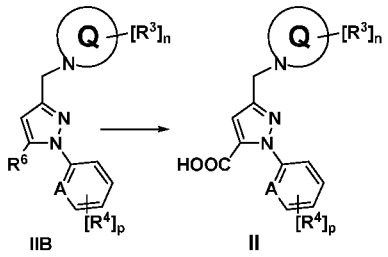
The suitable solvent useful for the purpose of step (c) is preferably 1selected from the group consisting of acetonitrile, methyl tert-butyl ether, dichloromethane, dioxane, thionyl chloride, acetic acid, methyl alcohol, ethyl alcohol, tetrahydrofuran, isopropyl alcohol and tert-butyl alcohol.

The elimination of water is performed within a temperature range of 20 °C to 150 °C, more preferably to 25 °C to 100 °C.

The reaction time is not critical and depends on the batch size, temperature, reagent and solvent employed. Typically, the reaction time may vary from few minutes to several hours.

The process of elimination of water is usually performed under standard pressure conditions. It is, however, also possible to perform elimination of water under reduced pressure or elevated pressure conditions. The water can also be eliminated thermally.

PROCESS STEP (d): In the process step (d), the compound of formula IIB, obtained after elimination of water from the compound of formula IIA, is converted into the compound of formula II;



wherein, R^3, R^4, R^6, A, n, p, and Q are each as defined above.

The process step (d) can be performed in water only, without addition of acid or base. The process step (d) can also be performed under acidic or basic conditions.

Acidic condition is maintained by using mineral for example acids such as sulphuric acid, chlorosulphuric acid, hydrochloric acid, hydrofluoric acid, hydroboric acid, and phosphoric acid; or organic acids such as acetic acid, trifluoroacetic acid,p-toluenesulphonic acid, methanesulphonic acid, and trifluoromethanesulphonic acid.

Basic condition is maintained by using organic bases such as trialkylamines, pyridine, alkylpyridines, phosphazines and l,8-diazabicyclo[5.4.0]undecene (DBU) or by using inorganic bases such as alkali metal hydroxides, for example lithium, sodium or potassium hydroxide; alkali metal carbonates such as sodium carbonate, and potassium carbonate; acetates such as sodium acetate, potassium acetate, and lithium acetate; and alkoxides such as sodium methoxide, sodium ethoxide, sodium tert-butoxide, and potassium tert-butoxide.

This reaction can be accelerated by the addition of catalysts such as ferric chloride (FcCT), aluminum chloride (AICT), boron trifluoride (BF_3), antimony trichloride (SbCT) and monosodium phosphate (NaH_2P0_4).

The suitable solvent useful for the purpose of the process step (d) is selected from the group consisting of water, acetonitrile, dioxane, acetic acid, methyl alcohol, ethyl alcohol, tetrahydrofuran, isopropyl alcohol and tert-butyl alcohol.

This reaction is performed within a temperature range of 20 °C to 150 °C, more preferably to 25 °C to 100 °C.

The reaction time is not critical and depends on the batch size, temperature, reagent and solvent employed. Typically, the reaction time may vary from few minutes to several hours.

This reaction is usually performed under standard pressure conditions. It is, however, also possible to perform this reaction under reduced pressure or elevated pressure conditions.

Though the compounds of formula IIA obtained in step (b), IIB in step (c), and II obtained in step (d) can be isolated by suitable workup and optionally further purification, it is also possible to proceed without these compounds being isolated for the reason of yield and operational efficacy.

Particularly, definitions of the substituents of the compounds of formula IIA used in the process step (c) and the compounds of formula IIB and II obtained in the process step (c) are as follows:

R^6 is CX_3 or $C(=0)W^2R^7$,

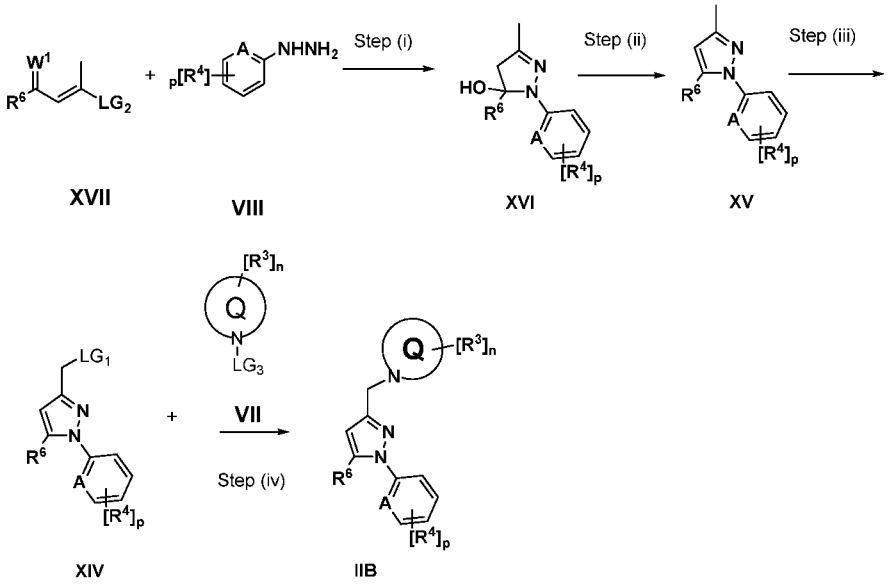
wherein, R^7 is selected from the group consisting of hydrogen, G-G, -alkyl. C3-C6-cycloalkyl, aryl and arylalkyl groups;

W^2 is O; R^3 is Ci-G.-haloalkyl: n is an integer 1; Q is a 3-, 4- or 5 membered heterocyclic ring; A is N; R^4 is X; p is an integer 1 or 2; and each X is independently F, Cl, Br or I.

More particularly, definitions of the substituents of the compounds of formula III and VIII used in the process step (b) and the compound of formula IIA obtained in the process step (b) are as follows:

R^6 is CCb, CBr_3, $C(=0)W^2CH3$, $C(=0)W^2C_2H_5$; W^2 is O; R^3 is trifluoro alkyl; n is an interger 1; Q is a tetrazole ring; A is N; R^4 is Cl; and p is an integer 1.

Alternatively, the compound of formula IIB can be prepared according to the reaction scheme depicted below:



wherein, the definition of R^3, R^4, R^6, R^7, R^9, R^{10}, A, A^1, n, p, Q, W^1, W^2, W^3, W^4, X, LGi, LG_2 and LG_3 are each as defined above.

Particularly, definitions of the substituents of the compounds of formula in the above reaction scheme are as follows:

R^6 is CX_3 or $C(=0)W^2R^7$,

wherein, R^7 is selected from the group consisting of hydrogen, G-G, -alkyl. C3-C6-cycloalkyl, aryl and arylalkyl groups;

W^1 and W^2 are O; LG_2 is X or OR^{12}; R^{12} is G-G, -alkyl: LG_3 is hydrogen or alkali metal; R^3 is Ci-Ce-haloalkyl; n is an integer 1; Q is a 3-, 4- or 5 membered heterocyclic ring; A is N; R^4 is X; p is an integer 1 or 2; and each X is independently F, Cl, Br or I.

More particularly, definitions of the substituents of the compounds of formula in the above reaction scheme are as follows:

R^6 is CCh, CBr_3, $C(=0)W^2CH_3$, $C(=0)W^2C_2¾$; W^1 and W^2 are O; LG_2 is Cl, Br, I, OCH_3, or OGFfi; LG_3 is hydrogen or sodium metal ion; R^3 is trifluoro alkyl; n is an integer 1; Q is a tetrazole ring; A is N; R^4 is Cl; and p is an integer 1.

PROCESS STEP (i): The process step (i) is carried out in the presence of one or more suitable solvent and optionally, in the presence of one or more suitable reagent and or one or more suitable catalyst under particular reaction conditions.

The suitable solvent useful for the purpose of the process step (i) is selected preferably from the group consisting of acetone, acetonitrile, ethyl alcohol, methyl tert-butyl ether, chlorobenzene, dichloroethane, dichloromethane, dioxane, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, ethyl acetate, 2-metyltetrahedrafuran, tetrahydrofuran, l,2-dimethoxyether, toluene, xylene and N-methyl-2-pyrrolidone.

The suitable reagent useful for the purpose of the process step (i) is selected preferably from the group consisting of acetic acid, trifluoroacetic acid, hydrochloric acid, hydrobromic acid, sulphuric acid, methanesulfonic acid, triflic acid, phosphoric acid and p-toluenesulfonic acid.

The process step (i) of the present invention can be performed particularly within a temperature range from 20 °C to 150 °C.

The reaction time is not critical and depends on the batch size, temperature, reagent and solvent employed. Typically, the reaction time may vary from few minutes to several hours.

The process step (i) of the present invention is usually performed under standard pressure conditions. It is, however, also possible to perform the process step (i) under reduced pressure conditions for regioselective cyclization proceeding into the compound of formula XVI.

PROCESS STEP (ii): The compound of formula XVI is converted into the compound of formula XV by elimination of water in the process step (ii).

For elimination of water the reagent/s selected preferably from the group consisting of sulphuric acid, trifluoroacetic acid, phosphorous trichloride, phosphorous oxychloride, thionyl chloride, acetic anhydride, trifluoroacetic anhydride, oxalyl chloride, phosgene and diphosgene is/are useful.

Particularly, trifluoroacetic anhydride, thionyl chloride, oxalyl chloride and phosgene are used for elimination of water from the compound of formula XVI.

The suitable solvent useful for the purpose of step (ii) is selected preferably from the group consisting of acetonitrile, methyl tert-butyl ether, dichloromethane, dioxane, thionyl chloride, acetic acid, methyl alcohol, ethyl alcohol, tetrahydrofuran, isopropyl alcohol and tert-butyl alcohol.

The elimination of water is performed within a temperature range of 20 °C to 150 °C, more preferably to 25 °C to 100 °C.

The reaction time is not critical and depends on the batch size, temperature, reagent and solvent employed. Typically, the reaction time may vary from few minutes to several hours.

The process of elimination of water is usually performed under standard pressure conditions. It is, however, also possible to perform elimination of water under reduced pressure or elevated pressure conditions. The water can also be eliminated thermally.

PROCESS STEP (iii): In the process step (iii), the compound of formula XIV is obtained from the compound of formula XV.

For instance, XIV wherein LGi is halogen, is obtained by halogenating the compound of formula XV using one or more halogenating agent selected from the group consisting of N-halosuccinimide, X2, X2/I1V, N-halosaccharine, and halohydantoine, optionally in the presence of a radical initiator.
X2is Cl_2, Br2 or I_2 and hv indicates that the halogenating reaction is carried out in the presence of light.
N-halosuccinimide is selected from the group consisting of N-chlorosuccinimide, N-bromosuccinimide andN-iodosuccinimide. Preferably, N-halosuccinimide is N-chlorosuccinimide and N-bromosuccinimide.
N-halosaccharine is selected from the group consisting of N-chlorosaccharine, N-bromosaccharine and N-iodosaccharine. Preferably, N-halosaccharine is N-chlorosaccharine and N-bromosaccharine.
N-halohydantoine is selected from the group consisting of N-chlorohydantoine, N-bromohydantoine and N-iodohydantoine. Preferably, N-halohydantoine is N-chlorohydantoine and N-bromohydantoine.

Non-limiting examples of radical initiators useful for halogenating the compound of formula XV include dibenzoyl peroxide, hydrogen peroxide, di(n-propyl)peroxydicarbonate, t-butyl peroxybenzoate, methyl ethyl ketone peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy)-3-hexyne, di(t-butyl)peroxide, acetone peroxide, dicumyl peroxide, azobisisobutyronitrile, bis(2-ethylhexyl)peroxydicarbonate, (peroxybis(propane-2,2-diyl))dibenzene, peracetic acid, metachloroperbenzoic acid, Payne's reagent,

magnesium monoperphthalate, trifluoroperacetic acid, trichloroperacetic acid, 2, 4-dinitorperbenzoic acid, Caro's Acid and potassium caroate.

The process step (iii) is carried out in the presence of one or more suitable solvent(s) and optionally, in the presence of one or more suitable reagent(s) and or one or more suitable catalyst(s) under particular reaction conditions.

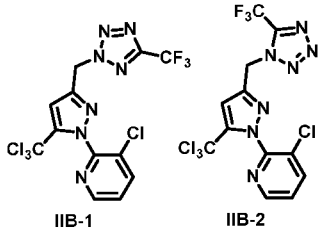
The suitable solvent useful for the purpose of step (iii) is selected from the group consisting of acetone, acetonitrile, ethyl alcohol, methyl tert-butyl ether, chlorobenzene, dichloroethane, dichloromethane, dioxane, ethyl acetate, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, 2-methyltetrahydrofuran, tetrahydrofuran, l,2-dimethoxyether, toluene, p-xylene and N-methyl-2-pyrrolidone.

The process step (iii) of the present invention can be performed particularly within a temperature range from 20 °C to 150 °C.

The reaction time is not critical and depends on the batch size, temperature, reagent and solvent employed. Typically, the reaction time may vary from few minutes to several hours.

The process step (iii) is usually performed under standard pressure conditions. It is, however, also possible to perform the process step (iii) under reduced pressure or elevated pressure conditions.

PROCESS STEP (iv): The process step (iv) is carried out in the presence of one or more suitable solvent(s) and optionally, in the presence of one or more suitable reagent(s) and or one or more suitable catalyst(s) under particular reaction conditions. The process step (iv) is highly regioselective. For example, the product IIB-l is regioselectively formed over the product IIB-2.



IIB-1 IIB-2

The suitable solvent useful for the purpose of step (iv) is selected preferably from the group consisting of acetone, acetonitrile, methyl tert-butyl ether, chlorobenzene, dichloroethane, dichloromethane, dioxane,

ethyl acetate, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, 2-methyltetrahydrofuran, tetrahydrofuran, l,2-dimethoxy ether, toluene, p-xylene andN-methyl-2-pyrrolidone.

The suitable catalyst for the purpose of step (iv) is preferably selected from the group consisting of potassium iodide, sodium iodide, copper iodide and cupric iodide.

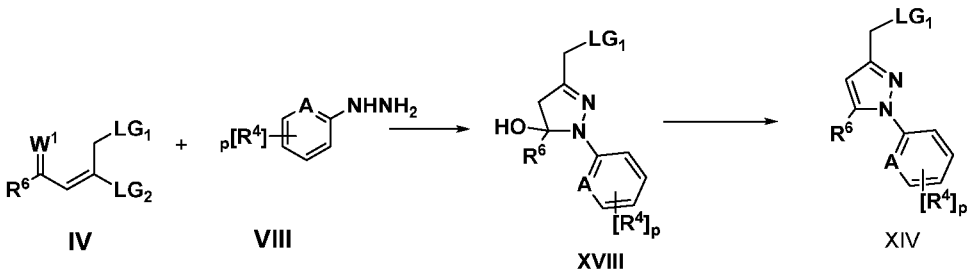
The process step (iv) of the present invention can be performed particularly within a temperature range from 20 °C to 150 °C.

The reaction time is not critical and depends on the batch size, temperature, reagent and solvent employed. Typically, the reaction time may vary from few minutes to several hours.

The process step (iv) of the present invention is usually performed under standard pressure conditions. It is, however, also possible to perform the process step (iv) under reduced pressure conditions to effect complete conversion of the reactants into the product.

The compound of formula XIV, wherein LGi is Cl can alternatively be prepared by regioselectively cyclizing a compound of formula IV and the compound of formula VIII to provide XVIII using the process, reagent/catalyst, solvent and reaction conditions similar to that for preparing the compound of formula IIA. It is surprisingly and unexpectedly observed that the compound of formula IV and the compound of formula VIII do not cyclize to produce XVIII when LGi is Br or I.

Subsequently, the compound of formula XVIII is converted into the compound of formula XIV by elimination of water. The water is eliminated according to the process described for the preparation of IIB from IIA.



wherein, the definition of R^4, R^6, A, p, W^1, LGi, and LG2 are each as defined above.

Particularly, definitions of the substituents of the compounds of formula IV, VIII, XVIII and XIV are as follows:

R^6 is CX_3 or $C(=0)W^2R^7$,

wherein, R^7 is selected from the group consisting of hydrogen, Ci-Ce-alkyl, C3-C6-cycloalkyl, aryl and arylalkyl groups;

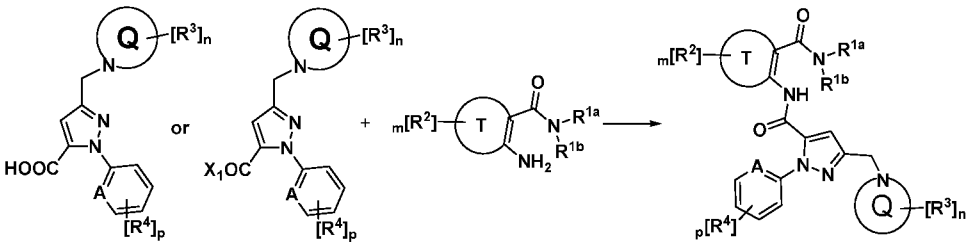
W^1 and W^2 are O; LGi is Cl; LG2 is X or OR^{12}; R^{12} is Ci-Ce-alkyl; A is N; R^4 is X; p is an integer 1 or 2; and each X is independently F, Cl, Br or I.

More particularly, definitions of the substituents of the compounds of formula IV and VII used in the process step (a) and the compound of formula III obtained in the process step (a) are as follows:

R^6 is CCh, CBr_3, $C(=0)W^2CH_3$, $C(=0)W^2C_2¾$; W^1 and W^2 are O; LG_2 is Cl, Br, I, OCH_3, or $OC_{2]}¾$; A is N; R^4 is Cl; and p is an integer 1.

Though the compounds of formula XVI, XV, XIV and XVIII prepared according to shown reaction scheme can be isolated by suitable workup steps and optionally further purification, it is also possible to prepare the compound of formula IIB without these compounds being isolated for the reason of yield and operational efficacy.

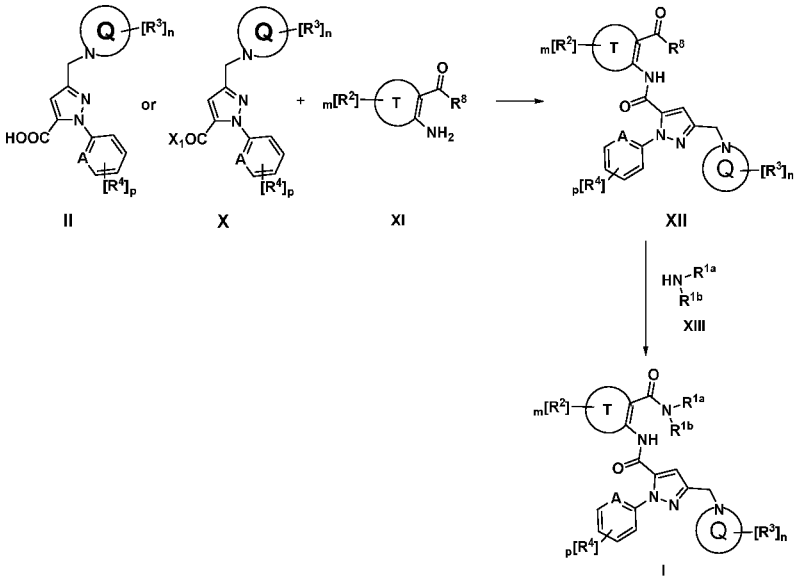
PROCESS STEP (e): In the process step (e) of the present invention, the compound of formula II, optionally after converting into a compound of formula X using a halogenating agent, is reacted with a compound of formula IX to obtain the compound of formula I;



II X IX I

wherein, Xi is Cl or Br; R^{la}, R^{lb}, R^2, R^3, R^4, A, m, n, p, Q, and T are each as defined above.

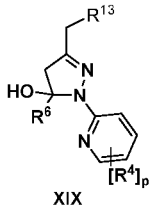
Alternatively, the compound of formula II, optionally after converting into a compound of formula X using halogenating agent, is reacted with a compound of formula XI to obtain a compound of formula XII, and then the compound of formula XII, optionally after hydrolyzing, is reacted with an amine of formula XIII to obtain a compound of formula I,

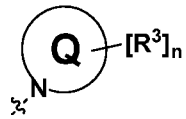


wherein, R^8 is selected from the group consisting of hydroxy, Cl and OR^7; R^{1a}, R^{1b}, R^2, R^3, R^4, R^7, A, m, n, p, Q, T and Xi are each as defined hereinabove.

The present invention also relates to novel and inventive intermediates formed in the process of the instant invention.

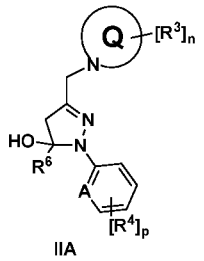
The present invention relates to a compound of formula XIX,



wherein, R^{13} is  or LG_1; R^3, R^4, R^6, n, p, and Q are each as defined herein above,

with the proviso that when R^{13} is LGi then R^6 is CX_3, wherein LGi is Cl, Br or I; and X is F, Cl, Br, or I.

In one embodiment, the compound of formula XIX is the compound of formula IIA,



IIA

wherein, R^3, R^4, R^6, A, n, p, and Q are each as defined hereinabove.

Particularly, definitions of the substituents of the compounds of formula IIA are as follows:

R^6 is CX_3 or $C(=0)W^2R^7$,

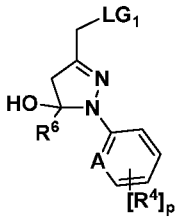
wherein, R^7 is selected from the group consisting of hydrogen, G-G, -alkyl. C3-C6-cycloalkyl, aryl and arylalkyl groups;

W^2 is O; R^3 is G-C,-haloalkyl: n is an integer 1; Q is a 5 membered heterocyclic ring; A is N; R^4 is X; p is an integer 1 or 2; and each X is independently F, Cl, Br or I.

More particularly, definitions of the substituents of the compounds of formula IIA are as follows:

R^6 is CCI_3, CBr_3, $C(=0)W^2CH_3$, $C(=0)W^2C_2H_5$; W^2 is O; R^3 is trifluoro alkyl; n is an integer 1; Q is a tetrazole ring; A is N; R^4 is Cl; and p is an integer 1.

In second embodiment, the compound of formula XIX is the compound of formula XVIII,



XVIII

wherein, R^4, R^6, A, p, and LGi are each as defined above.

Particularly, definitions of the substituents of the compounds of formula XVIII are as follows:

R^6 is CX_3, or $C(=0)W^2R^7$,

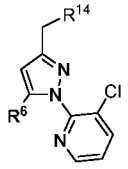
wherein, R^7 is selected from the group consisting of hydrogen, G-G,-alkyl. C_3-C_6-cycloalkyl, aryl and arylalkyl groups;

W^2 is O; LGi is X; A is N; R^4 is X; p is an integer 1 or 2; and each X is independently F, Cl, Br or I.

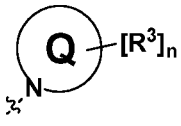
More particularly, definitions of the substituents of the compounds of formula XVIII are as follows:

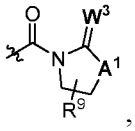
R^6 is CCl_3 or CBr_3; W^2 is O; LGi is Cl, Br or I, preferably Br; A is N; R^4 is Cl; and p is an integer 1.

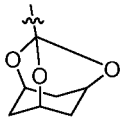
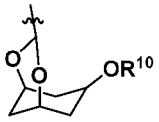
The present invention also relates to a compound of formula XX,



XX

wherein, R^{14} is  or LG_1 or hydrogen;

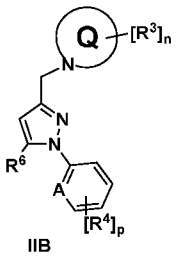
R^6 is CX_3, $C(W^4R^7)_3$, $CH(W^4R^7)_2$, allylic group, substituted or unsubstituted furanyl,  ,

 , and  ;

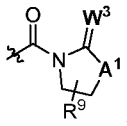
R^3, R^4, R^7, R^9, R^{10}, LGi, A, A^1, n, p, Q, W^3, W^4, X and the substituents on furanyl are each as defined herein above,

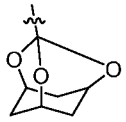
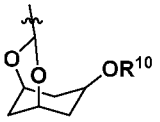
with the proviso that when R^{14} is LGi or hydrogen then R^6 is CX_3, wherein LGi and X are Cl, Br, or I.

In one embodiment, the compound of formula XX is the compound of formula IIB,



IIB



wherein, R^6 is CX_3, $C(W^4R_7)_3$, $CH(W^4R_7)_2$, allylic group, substituted or unsubstituted furanyl, ,  , or  ; R^3, R^4, R^7, R^9, R^{10}, A, A^1, n, p, Q, W^3, W^4, and X are each as defined hereinabove.

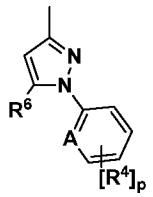
Particularly, definitions of the substituents of the compounds of formula IIA are as follows:

R^6 is CX_3, R^3 is Ci-Ce-haloalkyl; n is an integer 1; Q is a 5 membered heterocyclic ring; A is N; R^4 is X; p is an integer 1 or 2; and each X is independently F, Cl, Br or I.

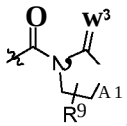
More particularly, definitions of the substituents of the compounds of formula IIA are as follows:

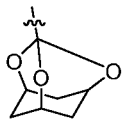
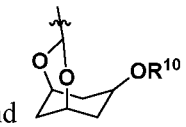
R^6 is CCI3 or CBr3; R^3 is trifluoro alkyl; n is an integer 1; Q is a tetrazole ring; A is N; R^4 is Cl; and p is an integer 1.

In second embodiment, the compound of formula XX is the compound of formula XV,



XV



wherein, R_6 is CX_3, $C(W_4R^7)_3$, $CH(W_4R^7)_2$, allylic group, substituted or unsubstituted furanyl, ,  , and  ; A is N; and R^4, R^7, R^9, R^{10}, A^1, p, W^3, W^4, and X are each as defined hereinabove.

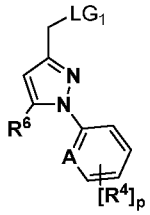
Particularly, definitions of the substituents of the compounds of formula XV are as follows:

R^6 is CX3, A is N; R^4 is X; p is an integer 1 or 2; and each X is independently F, Cl, Br or I.

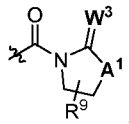
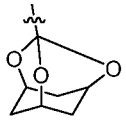
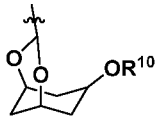
More particularly, definitions of the substituents of the compounds of formula XV are as follows:

R^6 is CCl_3 or CBr_3; A is N; R^4 is Cl; and p is an integer 1.

In third embodiment, the compound of formula XX is the compound of formula XIV,



XIV

wherein, R^6 is CX_3, $C(W^4R^7)_3$, $CH(W^4R^7)_2$, allylic group, substituted or unsubstituted furanyl,  ,  , and  ; and R^4, R^7, R^9, R^{10}, A, A^1, p, W^3, W^4 , X and LG_1 are each as defined hereinabove.

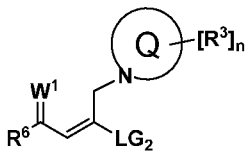
Particularly, definitions of the substituents of the compounds of formula XIV are as follows:

R^6 is CX_3, W^2 is O; LGi is X; A is N; R^4 is X; p is an integer 1 or 2; and each X is independently F, Cl, Br or I.

More particularly, definitions of the substituents of the compounds of formula XIV are as follows:

R^6 is CCl_3 or CBr_3; W^2 is O; LGi is Cl, Br or I, preferably Br; A is N; R^4 is Cl; and p is an integer 1.

The present invention further relates to the compound of formula III,



III ;

wherein, Q is a 3-, 4- or 5 membered heterocyclic ring excluding triazole ring; R^3, R^6, n, W^1, and LG2 are each as defined in herein above.

Particularly, definitions of the substituents of the compounds of formula III are as follows:

R^6 is CX_3 or $C(=O)W^2R^7$,

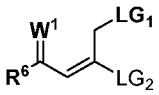
wherein, R^7 is selected from the group consisting of hydrogen, G-G, -alkyl. C3-C6-cycloalkyl, aryl and arylalkyl groups;

W^1 & W^2 are O; LG2 is X or OR^{12}; R^{12} is G-G, -alkyl: R^3 is Ci-G,-haloalkyl: n is an integer 1; Q is a 5 membered heterocyclic ring; and each X is independently F, Cl, Br or I.

More particularly, definitions of the substituents of the compounds of formula III are as follows:

R^6 is CCh, CBr_3, C(=0)W $^2CH_3$, C(=0)W $^2C_2¾$; W^1 and W^2 are O; LG_2 is Cl, Br, I, OCH_3, or OGFfi; R^3 is trifluoro alkyl; n is an integer 1; and Q is a tetrazole ring.

The present invention still further relates to the compound of formula IV,



IV

wherein, R^6, W^1, LGi and LG_2 are each as defined hereinabove, proviso that when LG_2 is OR^{12}, LGi is not Br or I.

Particularly, definitions of the substituents of the compound of formula IV are as follows:

R^6 is CX_3 or C(=0)W $^2R^7$,

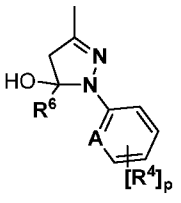
wherein, R^7 is selected from the group consisting of hydrogen, G-G,-alkyl. C3-C6-cycloalkyl, aryl and arylalkyl groups;

W^1 and W^2 are O; LGi is X; LG_2 is X or OR^{12}; R^{12} is G-G,-alkyl: and each X is independently F, Cl, Br or I.

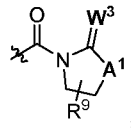
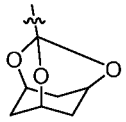
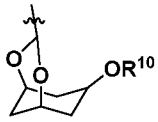
More particularly, definitions of the substituents of the compound of formula IV are as follows:

R^6 is CCT, CBr3, C(=0)W $^2CH_3$, C(=0)W $^2C_2H_5$; W^1 and W^2 are O; LGi is Cl, Br or I, preferably Br; and LG_2 is Cl, Br, I, OCH3, or OGFfi.

The present invention still further relates to the compound of formula XVI,



XVI

wherein, R^6 is CX_3, $C(W^4R^7)_3$, $CH(W^4R^7)_2$, allylic group, substituted or unsubstituted furanyl,  ,  , and  ; A is N; and R^4, R^7, R^9, R^{10}, A^1, p, W^3, W^4, and X are each as defined hereinabove.

Particularly, definitions of the substituents of the compounds of formula XVI are as follows:

R^6 is CX3; A is N; R^4 is X; p is an integer 1 or 2; and each X is independently F, Cl, Br or I.

More particularly, definitions of the substituents of the compounds of formula XVI are as follows:

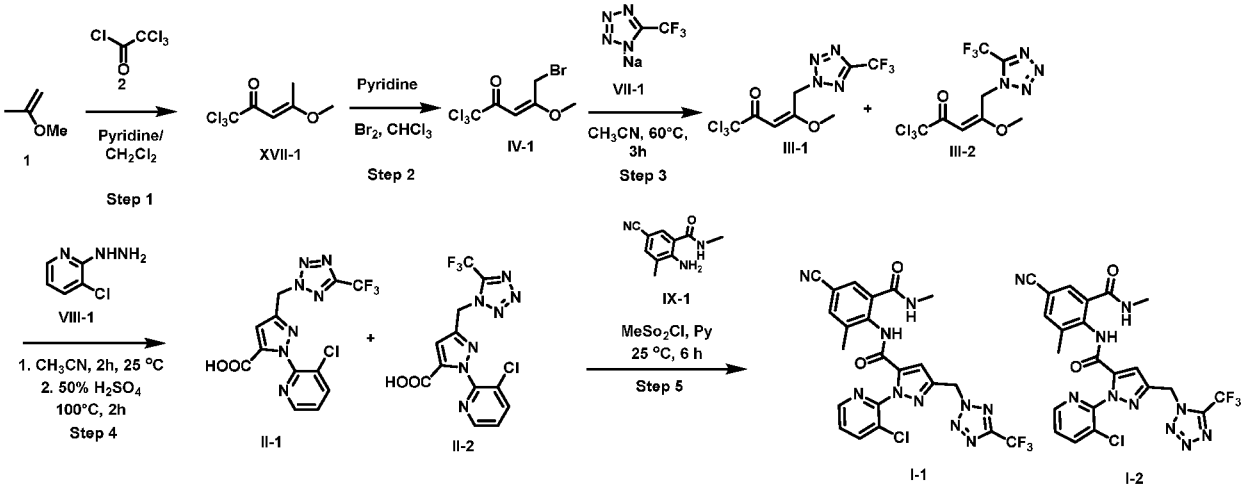
R^6 is CCl_3 or CBr3; A is N; R^4 is Cl; and p is an integer 1.

In absence of specific mention of a solvent in a process step, the following solvents are useful in the process of the present invention aliphatic, alicyclic or aromatic hydrocarbons, for example petroleum ether, n-hexane, n-heptane, cyclohexane, methylcyclohexane, benzene, toluene, xylene or decalin; halogenated hydrocarbons, for example chlorobenzene, dichlorobenzene, dichloromethane, chloroform, tetrachloromethane, dichloroethane or trichloroethane; ethers such as diethyl ether, diisopropyl ether, methyl tert-butyl ether, methyl tert-amyl ether, dioxane, tetrahydrofuran, 2-methyl tetrahydrofuran, 1,2-dimethoxyethane, l,2-diethoxyethane or anisole; nitriles such as acetonitrile, propionitrile, n- or isobutyronitrile or benzonitrile; amides such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methylformanilide, N-methylpyrrolidone or hexanlethylphosphoranlide; sulphoxides such as dimethyl sulphoxide; sulphones such as sulpholane; alcohols such as methyl alcohol, ethyl alcohol, or isopropyl alcohol.

The present invention is further described in detail as illustrated in the non-limiting examples. It should be understood that variations and modifications of the processes are possible within the ambit of the invention broadly disclosed herein.

PREPARATION EXAMPLES

Example 1:



Step-1: Synthesis of l,l,l-trichloro-4-methoxypent-3-en-2-one (XVII-1) (ref: Synthesis 12, 1013-14, 1986)

A solution of 2,2,2-trichloroacetyl chloride (9.75 mL, 86 mmol) in dichloromethane (30 mL) was added to a stirred solution of 2-methoxyprop-l-ene (9.4 mL, 100 mmol) and pyridine (9.0 mL, 112 mmol) in dichloromethane (60 mL) at 0 °C over 30 min. The resultant mixture was stirred at 25 °C for 16 h and then diluted with dichloromethane (200 mL), washed with 10% hydrogen chloride (50 mL) and finally twice with water (200 mL). The dichloromethane layer was dried over anhydrous sodium sulphate and concentrated under reduced pressure to give crude product l,l,l-trichloro-4-methoxypent-3-en-2-one (18 g, 83 mmol, 96 % yield).

¾-NMR (400 MHz, CDCL) δ 6.00 (s, 1H), 3.79 (s, 3H), 2.40 (s, 3H)

Step-2: Synthesis of (E/Z)-5-bromo-l,l,l-trichloro-4-methoxypent-3-en-2-one (IV-1) (ref: Synthesis 16, 2353-2358, 2002; WO201 1009551)

A solution of Br (1.9 mL, 37 mmol) in dichloromethane (10 mL) was added drop wise to a stirred solution of l,l,l-trichloro-4-methoxypent-3-en-2-one (8 g, 37 mmol) in dichloromethane (50 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 15 min followed by addition of a solution of pyridine (3 mL, 37 mmol) in dichloromethane (10 mL) at 0 °C. After completion of the reaction, the reaction mixture was partitioned between water (100 mL) and dichloromethane (100 mL). The dichloromethane layer was washed twice with 2N aqueous hydrogen chloride (50 mL) and then with water (100 mL). The dichloromethane layer was dried over anhydrous sodium sulphate and concentrated under reduced pressure to get crude product, which was purified by flash chromatography using 10% ethyl acetate in

hexane as eluent to afford desired product 5-bromo-l,l,l-trichloro-4-methoxypent-3-en-2-one (6.6 g, 22 mmol, 60 % yield).

¾-NMR (400 MHz, $CDCl_3$) δ 6.09 (s, 1H), 4.50 (s, 2H), 3.90 (s, 3H)

Step-3: Synthesis of l,l,l-trichloro-4-methoxy-5-(5-(trifluoromethyl)-2H-tetrazol-2-yl)pent-3-en-2-one (III-l) and l,l,l-trichloro-4-methoxy-5-(5-(trifluoromethyl)-lH-tetrazol-l-yl)pent-3-en-2-one (III-2)

Sodium 5-(trifluoromethyl)tetrazol-l-ide (1.3 g, 8.0 mmol) was added at once to a stirred solution of 5-bromo-l,l,l-trichloro-4-methoxypent-3-en-2-one (2.0 g, 6.7 mmol) in acetonitrile (30 mL) at 25 °C. The reaction mixture was heated to 60 °C for 3 h under stirring. After completion of the reaction, the reaction mixture was cooled to 25 °C and was partitioned between water (20 mL) and ethyl acetate (50 mL). The ethyl acetate layer was washed subsequently with water (25 mL) and brine solution (25 mL), dried over anhydrous sodium sulphate and concentrated under reduced pressure to get the crude product which was purified by flash chromatography using 20% ethyl acetate in hexane as eluent to get pure desired product 1,1,1-trichloro-4-methoxy-5-(5-(trifluoromethyl)-2H-tetrazol-2-yl)pent-3-en-2-one and 1,1,1-trichloro-4-methoxy-5-(5-(trifluoromethyl)-lH-tetrazol-l-yl)pent-3-en-2-one (1.7 g, 5.0 mmol, 81% yield).

¾-NMR (400 MHz, CDCL) δ 6.28 (s, 1H), 6.15 (d, J = 0.7 Hz, 2H), 3.84 (s, 3H); LCMS: $[352.80]^{M+H}$

Step-4: Synthesis of l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazole-5-carboxylic acid (II-l) and l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-lH-tetrazol-l-yl)methyl)-lH-pyrazole-5-carboxylic acid (II-2)

3-Chloro-2-hydrazinylpyridine (0.2 g, 1.4 mmol) was added to a stirred solution of l,l,l-trichloro-4-methoxy-5-(5-(trifluoromethyl)-2H-tetrazol-2-yl)pent-3-en-2-one (0.5 g, 1.4 mmol) in acetonitrile (5 mL) at 25 °C. The reaction mixture was stirred for 2 h at the same temperature. Then the reaction mixture was cooled to 0 °C and 50% aqueous sulphuric acid solution (6 mL) was added. The reaction mixture was heated with stirring to 100 °C for 2 h, cooled to 25 °C and then poured into ice-cold water. The mixture was extracted twice with ethyl acetate (20 mL), dried over anhydrous sodium sulphate and concentrated under reduced pressure to obtain the crude product, which was triturated with hexane and dried under reduced pressure to obtain l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazole-5-carboxylic acid and l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-lH-tetrazol-l-yl)methyl)-lH-pyrazole-5-carboxylic acid (0.44 g, 1.2 mmol, 89% yield).

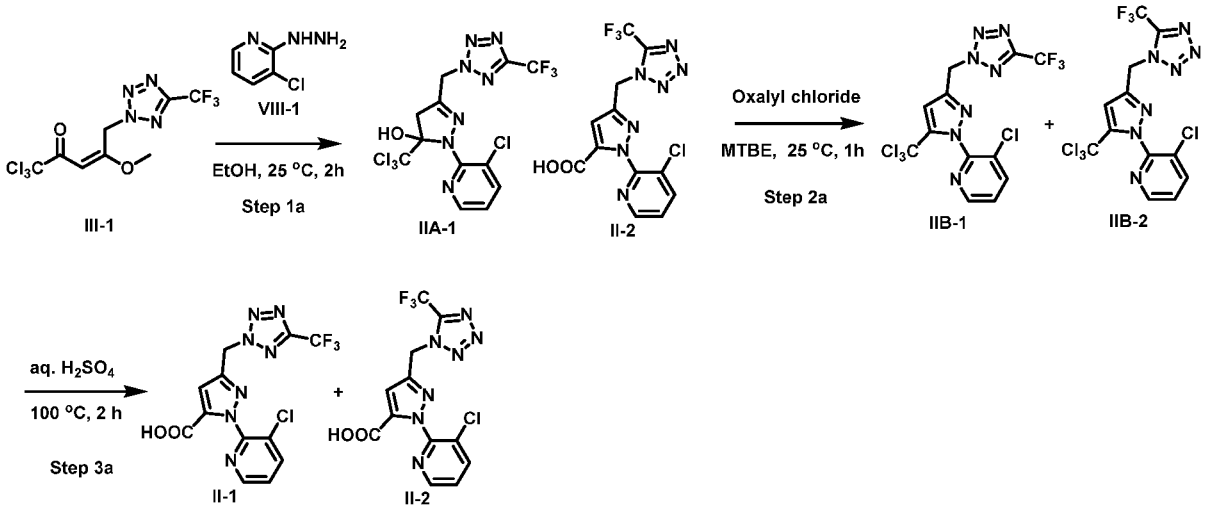
¾-NMR (400 MHz, DMSO-D_6) δ 8.55 (dd, J = 4.6, 1.5 Hz, 1H), 8.23-8.28 (m, 1H), 7.68 (dd, J = 8.1, 4.6 Hz, 1H), 7.20 (s, 1H), 6.25 (s, 2H); LCMS: $[373.90]^{M+H}$

Step-5: Preparation of mixture of l-(3-chloropyridin-2-yl)-N-(4-cyano-2-methyl-6-(methylcarbamoyl)phenyl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyr azole-5-

carboxamide (1-1) and l-(3-chloropyridin-2-yl)-N-(4-cyano-2-methyl-6-(methylcarbamoyl)phenyl)-3-((5-(trifluoromethyl)-lH-tetrazol-l-yl)methyl)-lH-pyrazole-5-carboxamide (1-2):

Methanesulfonyl chloride (CH3SO2CI; 520 mg, 4 mmol) was added drop wise to a solution containing the compound II-1, the compound II-2 (1.0 g, 2.7 mmol) and pyridine (570 mg, 7.2 mmol) in dimethyl acetamide (10 mL) at 0 °C. Then, a compound IX-l was added portion wise over 2 min to the reaction mixture. The resulting reaction mixture was heated to 50 °C with stirring for 4 h. The reaction mixture was then cooled to 25 °C and was poured on to crushed ice (50 mL). The precipitate was filtered and washed with cold water (50 mL) to get a mixture of products 1-1 and 1-2 (1.38 g, 2.56 mmol, 95%).

Example 2:



Step-la: l-(3-chloropyridin-2-yl)-5-(trichloromethyl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-4,5-dihydro-lH-pyrazol-5-ol (IIA-1)

A solution of 3-chloro-2-hydrazinylpyridine (0.2 g, 1.4 mmol) and l,l,l-trichloro-4-methoxy-5-(5-(trifluoromethyl)-2H-tetrazol-2-yl)pent-3-en-2-one (0.5 g, 1.4 mmol) in ethyl alcohol (10 mL) was stirred at 25 °C for 2 h. After completion of the reaction, ethyl alcohol was removed under reduced pressure to get a crude product, which was purified by flash chromatography using 30% ethyl acetate in hexane as eluent, to get the desired product l-(3-chloropyridin-2-yl)-5-(trichloromethyl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-4,5-dihydro-lH-pyrazol-5-ol (0.57 g, 1.2 mmol, 87% yield).

¾-NMR (400 MHz, CDCb) δ 9.80-9.08 (1H), 8.17 (dd, J = 4.9, 1.7 Hz, 1H), 7.86 (dd, J = 8.1, 1.7 Hz, 1H), 7.13-7.17 (m, 1H), 5.71 (s, 2H), 3.84 (d, J = 19.1 Hz, 1H), 3.34 (d, J = 19.1 Hz, 1H); LCMS: [463.8]$^{M-H}$

Step-2a: 3-chloro-2-(5-(trichloromethyl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazol-l-yl)pyridine (IIB-1)

Oxalyl chloride (0.17 mL, 1.9 mmol) was added drop wise to a solution of l-(3-chloropyridin-2-yl)-5-(trichloromethyl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-4, 5-dihydro-1H-pyrazol-5-ol (0.3 g, 0.6 mmol) in methyl tert-butyl ether (3 mL) at 25 °C. The reaction mixture was stirred for 1 h at 25 °C. After completion of the reaction, volatiles were removed from the reaction mixture under reduced pressure to get a crude product, which was purified by flash chromatography using 20% ethyl acetate in hexane as eluent to get the desired product 3-chloro-2-(5-(trichloromethyl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazol-l-yl)pyridine (0.27 g, 0.6 mmol, 94% yield).

¾-NMR (400 MHz, CDCb) δ 8.57 (dd, J = 4.6, 1.7 Hz, 1H), 7.97 (dd, J = 8.1, 1.7 Hz, 1H), 7.50-7.54 (m, 1H), 7.03 (s, 1H), 5.98 (s, 2H); LCMS: $[448]^{M+H}$

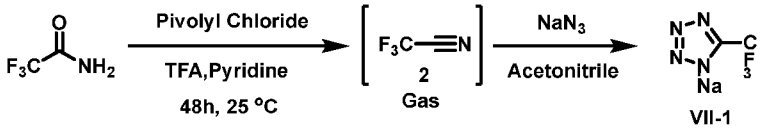
Step-3a: l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazole-5-carboxylic acid (II-l)

A suspension of 3-chloro-2-(5-(trichloromethyl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazol-l-yl)pyridine (0.25 g, 0.56 mmol) in 50% aqueous sulphuric acid solution (5 mL) was heated at 100 °C with stirring for 2 h. After completion of the reaction, the reaction mixture was cooled to 0 °C, and was diluted with ice-cold water (10 mL) to get a precipitate, which was filtered and dried to get the desired product 1-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)- 1H-pyrazole-5-carboxylic acid (140 mg, 0.4 mmol, 67.0% yield).

¾-NMR (400 MHz, DMSO-D_6) δ 8.55 (dd, J = 4.6, 1.5 Hz, 1H), 8.23-8.28 (m, 1H), 7.68 (dd, J = 8.1, 4.6 Hz, 1H), 7.20 (s, 1H), 6.25 (s, 2H); LCMS: $[373.9]^{M-H}$

Example 3:

Synthesis of sodium 5-(trifluoromethyl)tetrazol-l-ide (VII-1)



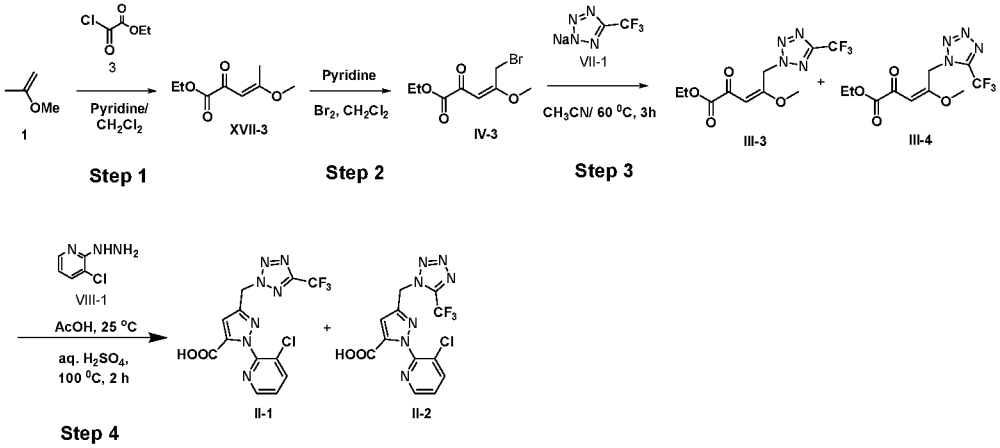
To a solution of trifluoroacetic acid (4.8 mL, 62 mmol) in pyridine (72 mL, 890 mmol) was added 2,2,2-trifluoroacetamide (20 g, 177 mmol). Subsequently, trimethylacetyl chloride (47 g, 391 mmol) was added drop wise at 25 °C to this solution over 3 h. The gaseous trifluoroacetonitrile formed in the course of drop wise addition was purged into another container containing a solution of sodium azide (17 g, 260 mmol) in acetonitrile (100 mL) at 25 °C. The reaction mixture was allowed to stir for 24 h. The resultant solids

were filtered and washed with acetonitrile (50 mL), the filtrate was concentrated under reduced pressure to obtain sodium 5-(trifhioromethyl)tetrazol-l-ide (15 g, 94 mmol, 53.0% yield).

^{9}F-NMR (400 MHz, DMSO-D_6) δ -59.60 (s, 3F)

A similar process is also disclosed in an article by Crawford, Margaret-J. et al., Journal of F Chemistry, 129(12), 1199-1205; 2008.

Example 4:



Step-1: Synthesis of ethyl 4-methoxy-2-oxopent-3-enoate (XVII-2).

To a stirred solution of 2-methoxyprop-l-ene (13.0 mL, 139 mmol) in dichloromethane (170 mL), was added pyridine (11 mL, 139 mmol) at 0 °C, followed by addition of a solution of ethyl 2-chloro-2-oxoacetate (15.5 mL, 139 mmol) in dichloromethane (30 mL) at 0 °C. The reaction mixture was stirred at 25 °C for 12 h. After the completion of the reaction, the reaction mixture was diluted with dichloromethane (200 mL) and washed successively with water (100 mL), 10% hydrogen chloride (50 mL) and brine solution (50 mL). The dichloromethane layer was dried over anhydrous sodium sulphate and concentrated under reduced pressure to obtain ethyl 4-methoxy-2-oxopent-3-enoate (22.0 g, 128 mmol, 93% yield).

¾-NMR (400 MHz, CDCL) δ 6.22 (s, 1H), 4.25-4.38 (m, 2H), 3.76 (s, 3H), 2.36 (s, 3H), 1.25-1.40 (m, 3H); LCMS: [173.15]$^{M+H}$

Step-2: Synthesis of ethyl 5-bromo-4-methoxy-2-oxopent-3-enoate (IV-3).

A solution of Br (1.5 mL, 29.0 mmol) in dichloromethane (20 mL) was added to a stirred solution of ethyl 4-methoxy-2-oxopent-3-enoate (5.0 g, 29.0 mmol) in dichloromethane (50 mL) at 0 °C and was stirred at 0 °C for 15 min. Then, a solution of pyridine (2.3 mL, 29.0 mmol) in dichloromethane (20 mL) was added drop wise to the reaction mixture. After completion of the reaction, the reaction mixture was diluted with dichloromethane (100 mL) and washed with 2N hydrogen chloride (40 mL). The dichloromethane layer was dried over anhydrous sodium sulphate and concentrated under reduced pressure to get a crude

product, which was purified by flash chromatography using 10% ethyl acetate in hexane as eluent to afford the desired product ethyl 5-bromo-4-methoxy-2-oxopent-3-enoate (5.0 g, 19.91 mmol, 69% yield).

¾-NMR (400 MHz, CDCb) δ 6.36 (s, 1H), 4.48 (s, 2H), 4.28-4.42 (m, 2H), 3.86 (s, 3H), 1.31-1.48 (m, 3H); LCMS: [252.75]$^{M+2}$

Step-3: Synthesis of ethyl 4-methoxy-2-oxo-5-(5-(trifluoromethyl)-2H-tetrazol-2-yl)pent-3-enoate (III-3) and ethyl 4-methoxy-2-oxo-5-(5-(trifluoromethyl)-lH-tetrazol-l-yl)pent-3-enoate (III-4)

Sodium 5-(trifluoromethyl)tetrazol-l-ide (1.5 g, 9.6 mmol) was added to a stirred solution of ethyl 5-bromo-4-methoxy-2-oxopent-3-enoate (2.0 g, 8.0 mmol) in acetonitrile (20 mL) at 25 °C and the resulting reaction mixture was heated at 60 °C for 3 h. After the completion of the reaction, the reaction mixture was diluted with water and extracted thrice with ethyl acetate (30 mL). The ethyl acetate layer was washed with brine solution (30 mL), dried over anhydrous sodium sulphate and concentrated under reduced pressure to get a crude product, which was purified by flash to obtain the desired product ethyl 4-methoxy-2-oxo-5-(5-(trifluoromethyl)-2H-tetrazol-2-yl)pent-3-enoate (2.0 g, 6.5 mmol, 87% yield).

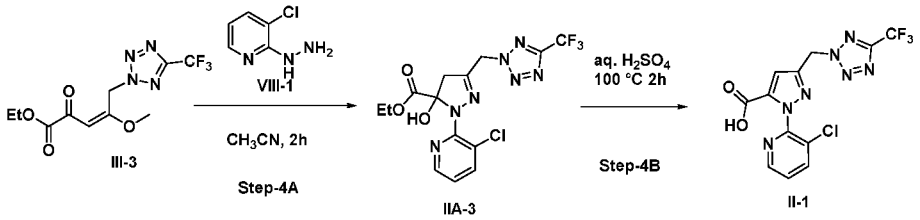
¾-NMR (400 MHz, CDCb) δ 6.55 (s, 1H), 6.10 (s, 2H), 4.34-4.42 (m, 2H), 3.79 (s, 3H), 1.28-1.44 (m, 3H); LCMS: [309.l0] $^{M+H}$

Step-4: Synthesis of l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazole-5-carboxylic acid (II-l) and l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-lH-tetrazol-l-yl)methyl)-lH-pyrazole-5-carboxylic acid (II-2)

A solution of ethyl 4-methoxy-2-oxo-5-(5-(trifluoromethyl)-2H-tetrazol-2-yl)pent-3-enoate (0.2 g, 0.65 mmol) and 3-chloro-2-hydrazinylpyridine (0.1 g, 0.65 mmol) in glacial acetic acid (2 mL) was stirred at 25 °C for 6 h. After completion of the reaction, the reaction mixture was cooled to 0 °C and 50% sulphuric acid (3 mL) was added to it. The reaction mixture was then heated at 100 °C for 2 h. The reaction mixture was then cooled to 25 °C and poured into ice-cold water (20 mL), and was extracted twice with dichloromethane (25 mL). The combined dichloromethane layer was dried over anhydrous sodium sulphate and concentrated under reduced pressure to obtain a crude product, which was triturated with hexane, filtered and dried to obtain l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazole-5-carboxylic acid and l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-lH-tetrazol-l-yl)methyl)-lH-pyrazole-5-carboxylic acid (0.2 g, 0.51 mmol, 84% yield).

¾-NMR (400 MHz, DMSO- D_6) δ 8.55 (dd, J = 4.6, 1.5 Hz, 1H), 8.23-8.28 (m, 1H), 7.68 (dd, J = 8.1, 4.6 Hz, 1H), 7.20 (s, 1H), 6.25 (s, 2H); LCMS: [373.90]$^{M+H}$

Example 5:



Step-4A: Synthesis of ethyl l-(3-chloropyridin-2-yl)-5-hydroxy-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-4,5-dihydro-lH-pyrazole-5-carboxylate (IIA-3).

A solution of ethyl 4-methoxy-2-oxo-5-(5-(trifluoromethyl)-2H-tetrazol-2-yl)pent-3-enoate (0.25 g, 0.8 mmol) and 3-chloro-2-hydrazinylpyridine (0.1 g, 0.8 mmol) in acetonitrile (5 mL) was stirred at 25 °C for 2 h. After the completion of the reaction, the reaction mixture was diluted with water and extracted twice with ethyl acetate (20 mL). The ethyl acetate layers were combined, dried over anhydrous sodium sulphate and concentrated under reduced pressure to obtain ethyl l-(3-chloropyridin-2-yl)-5-hydroxy-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-4,5-dihydro-lH-pyrazole-5-carboxylate (0.3 g, 0.7 mmol, 88% yield).

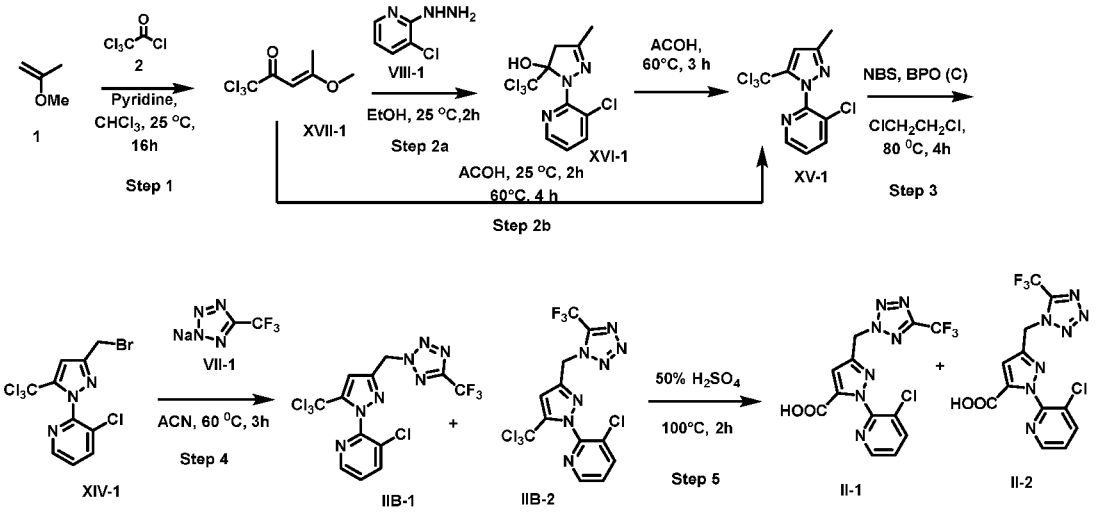
¾-NMR (400 MHz, CDCb) δ 7.96-8.04 (m, 1H), 7.73 (dd, J = 7.9, 1.6 Hz, 1H), 6.88-6.93 (m, 1H), 5.72-5.76 (s, 2H), 4.21-4.29 (m, 2H), 3.30-3.35 (m, 1H), 3.07-3.11 (m, 1H), 1.15-1.20 (m, 3H); LCMS: [4l9] $^{M+H}$

Step-4B: Synthesis of l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazole-5-carboxylic acid (II-l).

A suspension of ethyl l-(3-chloropyridin-2-yl)-5-hyclroxy-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-4,5-dihydro-lH-pyrazole-5-carboxylate (0.3 g, 0.7 mmol) in 50% (v/v) aqueous sulphuric acid (2.5 mL) was heated at 100 °C for 2 h under stirring. After the completion of the reaction, the reaction mixture was cooled to 25 °C and poured in ice-cold water. The resultant solid was filter and washed with water (5 mL) and dried under reduced pressure to obtain l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazole-5-carboxylic acid (0.22 g, 0.6 mmol, 82% yield).

¾-NMR (400 MHz, DMSO-D_6) δ 8.55 (dd, J = 4.6, 1.5 Hz, 1H), 8.23-8.28 (m, 1H), 7.68 (dd, J = 8.1, 4.6 Hz, 1H), 7.20 (s, 1H), 6.25 (s, 2H); LCMS: [373.90] $^{M+H}$

Example 6:



Step-2a: l-(3-chloropyridin-2-yl)-3-methyl-5-(trichloromethyl)-4,5-dihydro-lH-pyrazol-5-ol (XVI-1)

A solution of l,l,l-trichloro-4-methoxypent-3-en-2-one (1.0 g, 4.60 mmol) (prepared in accordance with the process described in Step 1 of scheme 1) and 3-chloro-2-hydrazinylpyridine (0.7 g, 4.6 mmol) in ethyl alcohol (15 mL) was stirred for 1 h at 25 °C. After completion of the reaction, volatiles of reaction mixture were removed under reduced pressure to get a crude product, which was purified by flash chromatography using 10% ethyl acetate in hexane as eluent to get 1-(3-chloropyridin-2-yl)-3 -methyl-5-(trichloromethyl)-4,5-dihydro-lH-pyrazol-5-ol (1.24 g, 3.76 8 mmol, 82% yield).

¾-NMR (400 MHz, CDCI3) δ 8.12 (dd, 1H), 7.82 (dd, 1H), 7.07 (m, 1H), 3.70 (s, 1H), 3.22 (s, 1H), 2.09 (s, 3H)

Step-2b: Synthesis of 3-chloro-2-(3-methyl-5-(trichloromethyl)-lH-pyrazol-l-yl)pyridine (XV-1)

3-Chloro-2-hydrazinylpyridine (0.3 g, 2.3 mmol) was added to a solution of l,l,l-trichloro-4-methoxypent-3-en-2-one (0.5 g, 2.3 mmol) in acetic acid (15 mL) at 25 °C and stirred for 2 h. The reaction mixture was heated at 60 °C for 6 h. The reaction mixture was cooled to 25 °C and partitioned between ethyl acetate (25 mL) and water (20 mL), ethyl acetate layer was washed successively with saturated aqueous sodium bicarbonate solution (25 mL), water (25 mL) and brine solution (20 mL). The ethyl acetate layer was dried over anhydrous sodium sulphate, concentrated under reduced pressure to get the desired product 3-chloro-2-(3-methyl-5-(trichloromethyl)-lH-pyrazol-l-yl)pyridine (0.5 g, 1.64 mmol, 71% yield).

¾-NMR (400 MHz, CDCL) δ 8.52 (dd, 1H), 7.90 (dd, 1H), 7.42 (m, 1H), 6.70 (s, 1H), 2.35 (s, 3H); LCMS: [3ll.9] $^{M+H}$

Step-3: Synthesis of 2-(3-(bromomethyl)-5-(trichloromethyl)-lH-pyrazol-l-yl)-3-chloropyridine (XIV-1)

To a solution of 3-chloro-2-(3-methyl-5-(trichloromethyl)-lH-pyrazol-l-yl)pyridine (0.2 g, 0.6 mmol) in dichloroethane (5 mL) was added N-bromosuccinimide (0. 17 g, 0.96 mmol) and benzoyl peroxide (0. 1 g, 0.3 mmol) and stirred at 80 °C for 4 h. After completion of the reaction, the reaction mixture was diluted with water and extracted thrice with ethyl acetate (20 mL), dried over anhydrous sodium sulphate, concentrated under reduced pressure to get a crude product, which was purified by flash chromatography using 20% ethyl acetate in hexane as eluent to get the desired product 2-(3-(bromomethyl)-5-(trichloromethyl)-lH-pyrazol-l-yl)-3-chloropyridine (0.2 g, 0.4 mmol, 67% yield).

¾-NMR (400 MHz, CDCL) δ 8.53 (dd, 1H), 7.92 (dd, 1H), 7.47 (m, 1H), 6.97 (s, 1H), 4.49 (s, 2H); LCMS: $[389.9]^{M\text{-}H}$

Step-4: 3-chloro-2-(5-(trichloromethyl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazol-l-yl)pyridine (IIB-1) and 3-chloro-2-(5-(trichloromethyl)-3-((5-(trifluoromethyl)-lH-tetrazol-1-yl)methyl)-1H-pyrazol-1-yl)pyridine (IIB-2)

Sodium 5-(trifluoromethyl)tetrazol-l-ide (0.1 g, 0.7 mmol) was added to a stirred solution of 2-(3-(bromomethyl)-5-(trichloromethyl)-lH-pyrazol-l-yl)-3-chloropyridine (0.2 g, 0.6 mmol) in acetonitrile (2 mL) at 25 °C and the resulting reaction mixture was heated with stirring at 60 °C for 3 h. After completion of the reaction, the reaction mixture was diluted with water and extracted thrice with ethyl acetate (20 mL). The combined ethyl acetate layer was washed with brine (25 mL), dried over anhydrous sodium sulphate and concentrated under reduced pressure to get a crude product, which was purified by flash chromatography to get 3-chloro-2-(5-(trichloromethyl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-1H-pyrazol-1-yl)pyridine and 3-chloro-2-(5-(trichloromethyl)-3-((5-(trifluoromethyl)-1H-tetrazol-l-yl)methyl)-lH-pyrazol-l-yl)pyridine (0.2 g, 0.4 mmol, 75% yield).

¾-NMR (400 MHz, CDCL) δ 8.53 (dd, 1H), 7.92 (dd, 1H), 7.48 (m, 1H), 7.0 (s, 1H), 5.96 (s, 2H); LCMS: $[448]^{M+H}$

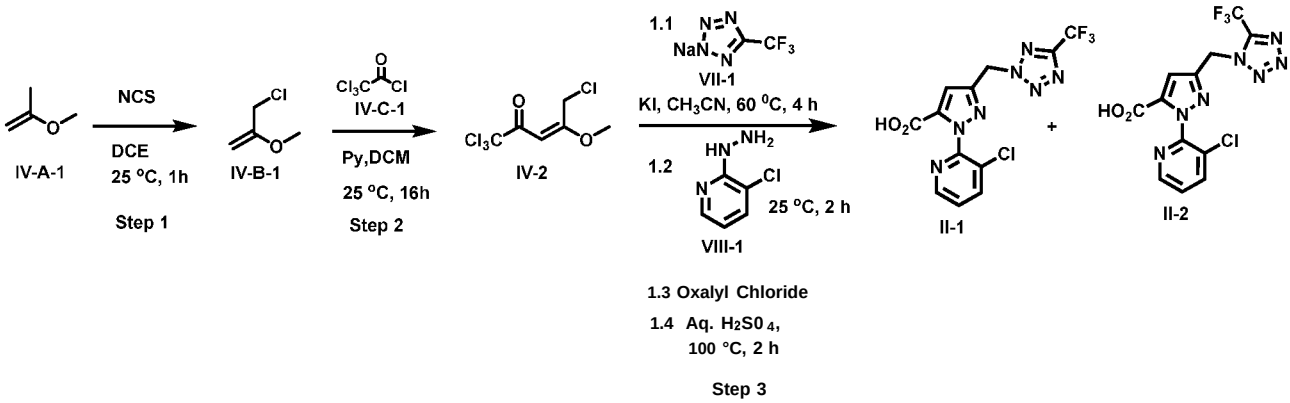
Step-5: l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazole-5-carboxylic acid (II-l) and l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-lH-tetrazol-l-yl)methyl)-lH-pyrazole-5-carboxylic acid (II-2)

A stirred solution of 3-chloro-2-(5-(trichloromethyl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazol-l-yl)pyridine (0.25 g, 0.56 mmol) in 50% (v/v) aqueous sulphuric acid solution (3 mL) was heated with stirring at 100 °C for 2 h. After completion of the reaction, the reaction mixture was cooled to 25 °C and was diluted with ice-cold water to get a precipitate, which was filtered and dried to get the desired product 1-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-1H-pyrazole-5-

carboxylic acid and l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-lH-tetrazol-l-yl)methyl)-lH-pyrazole-5-carboxylic acid (0.2 g, 0.5 mmol, 97% yield).

¾-NMR (400 MHz, DMSO-D_6) δ 8.55 (dd, J = 4.6, 1.5 Hz, 1H), 8.23-8.28 (m, 1H), 7.68 (dd, J = 8.1, 4.6 Hz, 1H), 7.20 (s, 1H), 6.25 (s, 2H); LCMS: $[373.9]^{M-H}$

Example 7:



Step-1

Synthesis of 3-chloro-2-methoxyprop-l-ene

To a solution of 2-methoxyprop-l-ene (3.9 mL, 41.6 mmol) in dichloroethane (50 mL) was added N-chlorosuccinimide (5.6 g, 41.6 mmol) at 0 °C and stirred for 1 h at 0 °C. The temperature of the reaction mixture was allowed to rise to 25 °C and filtered to remove precipitated succinimide. The filtrate was concentrated under reduced pressure to obtain crude 3-chloro-2-methoxyprop-l-ene (50% by GCMS). GC: 106 M+

Step-2

Synthesis of l,l,l,5-tetrachloro-4-methoxypent-3-en-2-one

To a stirred solution of 3-chloro-2-methoxyprop-l-ene (3.4 g, 31.6 mmol) and pyridine (2.9 mL, 35.7 mmol) in dichloromethane (30 mL), 2,2,2-trichloroacetyl chloride (3.1 mL, 27.5 mmol) in dichloromethane (10 mL) was added drop wise over 30 min. The reaction mixture was stirred at 25 °C for 16 h and diluted with dichloromethane (50 mL) washed subsequently with 0.1 M hydrochloric acid (30 mL) and twice with water (50 mL). The dichloromethane layer was dried over anhydrous sodium sulphate and concentrated under reduced pressure to obtain a crude product, which was purified by flash chromatography using 10% ethyl acetate in hexane as eluent to obtain pure product l,l,l,5-tetrachloro-4-methoxypent-3-en-2-one (3 g, 4 mmol, 43% yield).

¾-NMR (400 MHz, CDCL) δ 6.08 (s, 1H), 4.62 (s, 2H), 3.88 (s, 3H)

Step-3

Synthesis of l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazole-5-carboxylic acid (II-1) and l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-lH-tetrazol-l-yl)methyl)-lH-pyrazole-5-carboxylic acid (II-2)

A mixture of l,l,l,5-tetrachloro-4-methoxypent-3-en-2-one (1.0 g, 4.0 mmol), sodium 5-(trifluoromethyl)tetrazol-2-ide (0.7 g, 0.44 mmol) and potassium iodide (0.1 g, 0.8 mmol) in acetonitrile (10 mL) was heated at 60 °C with stirring for 4 h. The reaction mixture was cooled to 25 °C and 3-chloro-2-hydrazinylpyridine (0.6 g, 4.0 mmol) was added to it. The reaction mixture was stirred for 2 h at 25 °C. Then, oxalyl chloride (0.4 mL, 4.6 mmol) was added drop wise to the reaction mixture during 15 min and allowed to stir at 25 °C for 2 h. Volatiles were evaporated from the reaction mixture, then 40% aqueous sulphuric acid was added (3 mL) under cooling (5 °C) and the reaction mixture was heated at 100 °C for 2 h. The reaction mixture was cooled to 25 °C and was poured onto crushed ice to obtain the crude product as a precipitate, which was filtered and triturated with a solution of 10% dichloromethane in hexane to obtain a solid product (1.3 g, 3.4 mmol, 85% yield), which consisted of l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazole-5-carboxylic acid (II-1) and l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-lH-tetrazol-l-yl)methyl)-lH-pyrazole-5-carboxylic acid (II-2) in 93:07 ratio.

II-l: 1H-NMR (400 MHz, DMSO-D6) δ 13.74 (s, 1H), 8.55 (dd, J = 4.6, 1.5 Hz, 1H), 8.23 (dd, J = 8.2, 1.6 Hz, 1H), 7.67 (dd, J = 8.1, 4.6 Hz, 1H), 7.22 (s, 1H), 6.27 (s, 2H)

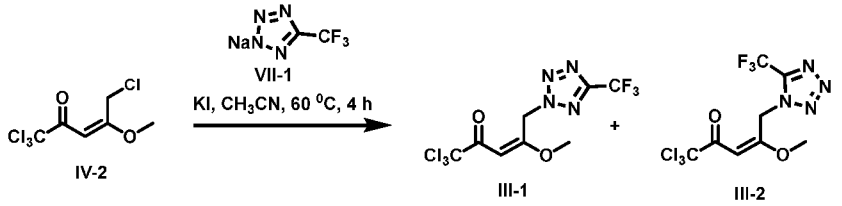
19F NMR:- δ 62.67

II-l: 1H-NMR (400 MHz, DMSO-D6) δ 13.75 (s, 1H), 8.53 (dd, J = 4.8, 1.6 Hz, 1H), 8.21 (dd, J = 8.1, 1.7 Hz, 1H), 7.66 (dd, J = 8.1, 4.9 Hz, 1H), 7.15 (s, 1H), 6.05 (s, 2H)

19F NMR:- δ 60.36

Example 8:

Synthesis of mixture of l,l,l-trichloro-4-methoxy-5-(5-(trifluoromethyl)-2H-tetrazol-2-yl)pent-3-en-2-one (III-l) and l,l,l-trichloro-4-methoxy-5-(5-(trifluoromethyl)-lH-tetrazol-l-yl)pent-3-en-2-one (HI-2)

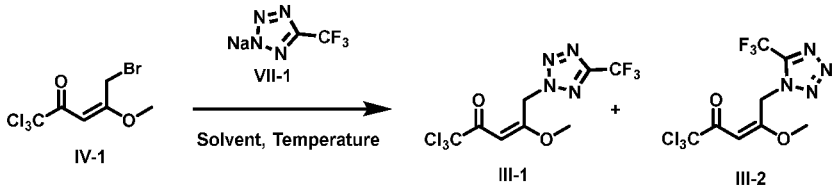


A mixture of l,l,l,5-tetrachloro-4-methoxypent-3-en-2-one (0.5 g, 2.0 mmol), sodium 5-(trifluoromethyl)tetrazol-2-ide (0.4 g, 0.2 mmol) and potassium iodide (0. 1 g, 0.4 mmol) in acetonitrile (10 mL) was heated at 60 °C with stirring for 4 h. After completion of the reaction, the reaction mixture was diluted with water and extracted twice with ethyl acetate (20 mL). Combined ethyl acetate layer was washed with brine solution (20 mL), dried over anhydrous sodium sulphate and concentrated to obtain a crude product, which was purified by flash chromatography using 10% ethyl acetate in hexane as eluent to obtain a mixture of products, consisting of l,l,l-trichloro-4-methoxy-5-(5-(trifluoromethyl)-2H-tetrazol-2-yl)pent-3-en-2-one (III-1) and 1,1,l-trichloro-4-methoxy-5-(5-(trifluoromethyl)-lH-tetrazol-1-yl)pent-3-en-2-one (III-2) in 93:07 ratio (0.6 g, 1.8 mmol, 90% yield).

¾-NMR (400 MHz, CDCL) δ 6.26 (s, 1H), 6.12 (d, J = 0.8 Hz, 2H), 3.82 (s, 3H); LCMS: $[353]^{M-H}$

Example 9:

Synthesis of mixture of (E)-l,l,l-trichloro-4-methoxy-5-(5-(trifluoromethyl)-2H-tetrazol-2-yl)pent-3-en-2-one (III-l) and (E)-l,l,l-trichloro-4-methoxy-5-(5-(trifluoromethyl)-lH-tetrazol-l-yl)pent-3-en-2-one (III-2)



(E)-5-bromo-l,l,l-trichloro-4-methoxypent-3-en-2-one (IV-l; 158 g; 533 mmol) was reacted with 5-(trifluoromethyl)-2H-tetrazole (VII-1; 85 g, 533 mmol) for 5 h in a suitable solvent (460 mL) as shown in Table 1.

Table No.l: The preparation of III-1 and III-2 using different solvents at 50 °C to 80 °C

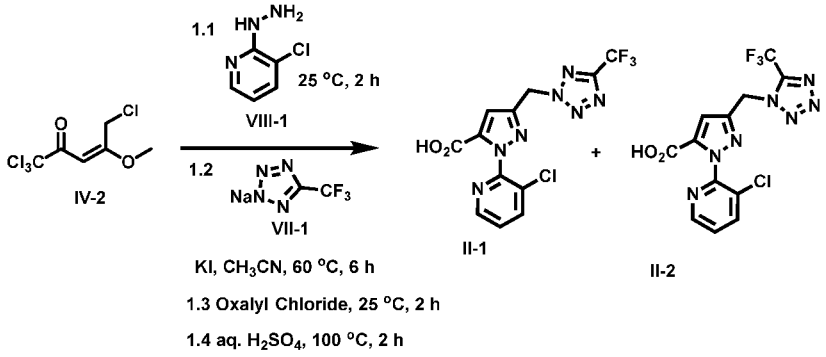
Sr. No.	Solvent
1	Acetone
2	Acetonitrile
3	Methyl tert-butyl ether
4	Chlorobenzene
5	Dichloroethane
6	Dichloromethane
7	Dioxane

8	Ethyl acetate
9	Dimethylformamide
10	Dimethylacetamide
11	Dimethyl sulfoxide
12	2-Methyltetrahydrofuran
13	Tetrahydrofuran
14	1,2-Dimethoxyether
15	Toluene
16	*p*-Xylene
17	N-methyl-2-pyrrolidone

A mixture of III-1+III-2 was obtained in low to high yield.

Example 10:

Synthesis of mixture of l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazole-5-carboxylic acid (II-l) and l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-lH-tetrazol-l-yl)methyl)-lH-pyrazole-5-carboxylic acid (II-2)



A mixture of l,l,l,5-tetrachloro-4-methoxypent-3-en-2-one (1.0 g, 4.0 mmol) and 3-chloro-2-hydrazinylpyridine (0.6 g, 4.0 mmol) in acetonitrile (10 mL) was stirred at 25 °C for 2 h. Then, sodium 5-(trifluoromethyl)tetrazol-2-ide (0.7 g, 4.4 mmol) and potassium iodide (0.1 g, 0.8 mmol) were added, and the reaction mixture was heated at 60 °C under stirring for 6 h. Then, oxalyl chloride (0.4 mL, 4.6 mmol) was added drop wise to the reaction mixture during 5 min at 25 °C, and the resulting mixture was allowed to stir at 25 °C for 2 h. Volatiles were evaporated from the reaction mixture. Then, 40% aqueous sulphuric acid was added (5 ml) to the reaction mixture at 5 °C. Subsequently, the reaction mixture was heated at 100 °C under stirring for 2 h. The reaction mixture was cooled to 25 °C and was poured onto crushed ice

to obtain a crude precipitate, which was filtered and triturated with a solution of 10% dichloromethane in hexane to obtain a solid product (1.10 g, 3 mmol, 75% yield), which consists of l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazole-5-carboxylic acid (II-1) and l-(3-chloropyridin-2-yl)-3 -((5-(trifluoromethyl)- lH-tetrazol- 1-yl)methyl)- 1H-pyrazole-5 -carboxylic acid (II-2) in 84: 16 ratio.

II-l: 1H-NMR (400 MHz, DMSO-D6) δ 13.74 (s, 1H), 8.55 (dd, J = 4.6, 1.5 Hz, 1H), 8.23 (dd, J = 8.2, 1.6 Hz, 1H), 7.67 (dd, J = 8.1, 4.6 Hz, 1H), 7.22 (s, 1H), 6.27 (s, 2H)

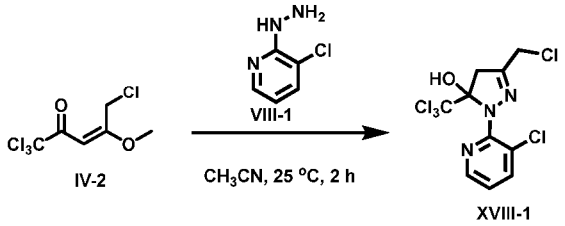
19F NMR:- δ 62.67

II-l: 1H-NMR (400 MHz, DMSO-D6) δ 13.75 (s, 1H), 8.53 (dd, J = 4.8, 1.6 Hz, 1H), 8.21 (dd, J = 8.1, 1.7 Hz, 1H), 7.66 (dd, J = 8.1, 4.9 Hz, 1H), 7.15 (s, 1H), 6.05 (s, 2H)

19F NMR:- δ 60.36

Example 11:

Preparation of 3-(chloromethyl)-l-(3-chloropyridin-2-yl)-5-(trichloromethyl)-4,5-dihydro-lH-pyrazol-5-ol (XVIII-1)

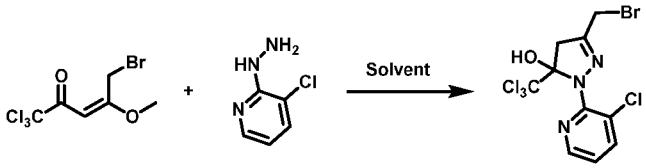


To a stirred solution of l,l,l,5-tetrachloro-4-methoxypent-3-en-2-one (1 g, 4.0 mmol) in acetonitrile (3 mL), 3-chloro-2-hydrazinylpyridine (0.6 g, 4.0 mmol) was added, and stirring was continued at 25 °C for 2 h. After completion of the reaction, the reaction mixture was diluted with water and extracted twice with ethyl acetate (20 mL). The combined ethyl acetate layers were dried over anhydrous sodium sulphate and concentrated under reduced pressure to obtain a crude product, which was purified by flash chromatography using 10% ethyl acetate in hexane as eluent giving the pure product 3-(chloromethyl)-l-(3-chloropyridin-2-yl)-5-(trichloromethyl)-4,5-dihydro-lH-pyrazol-5-ol (0.8 g, 2.2 mmol, 55% yield).

¾-NMR (400 MHz, CDCb) δ 9.48 (bs, 1H), 8.14 (dd, J = 4.9, 1.7 Hz, 1H), 7.83 (dd, J = 8.1, 1.7 Hz, 1H), 7.08-7. 12 (m, 1H), 4.36 (s, 2H), 3.90 (d, J = 18.8 Hz, 1H), 3.45 (d, J = 18.8 Hz, 1H); LCMS: $[363.8]^{M-H}$

Example-12:

Synthesis of 3-(bromomethyl)-l-(3-chloropyridin-2-yl)-5-(trichloromethyl)-4,5-dihydro-lH-pyrazol-5-ol (XVIII-2)



IV-1 VIII-1 XVMI-2

3-chloro-2-hydrazineylpyridine (VIII- 1; 143 mg; 1 mmol) was added to a solution of (E)-5 -bromo- 1,1,1 - trichloro-4-methoxypent-3-en-2-one (IV- 1; 296 mg; 1.0 mmol) in a suitable solvent (5 mL) as shown in Table No. 2 herein below at 25 °C with stirring for 4 h.

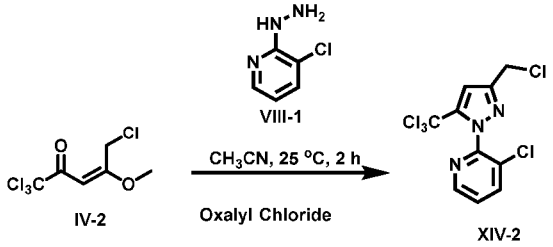
Table No. 2: The preparation of XVIII-2 using different solvents

Sr. No.	Solvent
1	Acetone
2	Acetonitrile
3	Methyl tert-butyl ether
4	Chlorobenzene
5	Dichloroethane
6	Dichloromethane
7	Dioxane
8	Dimethylformamide
9	Dimethylacetamide
10	Dimethylsulfoxide
11	Methanol
12	Ethanol
13	Isopropanol
14	Ethyl acetate
15	2-metyl tetrahydrofuran
16	Tetrahydrofuran
17	1,2-Dimethoxyether
18	Toluene
19	N-methyl-2-pyrrolidone

XVIII -2 formation was not observed.

Example 13:

Preparation of 3-chloro-2-(3-(chloromethyl)-5-(trichloromethyl)-lH-pyrazol-l-yl)pyridine (XIV-2)

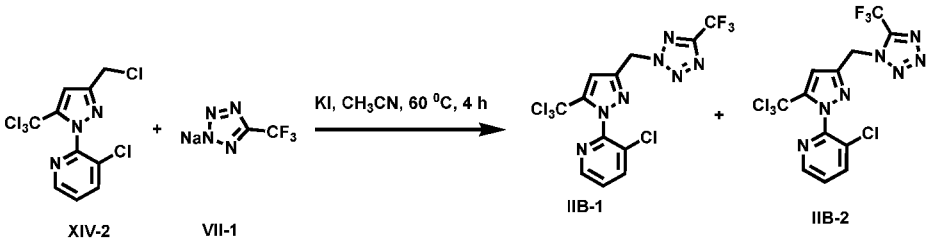


To a stirred solution of l,l,l,5-tetrachloro-4-methoxypent-3-en-2-one (1 g, 4.0 mmol) in acetonitrile (3 mL), 3-chloro-2-hydrazinylpyridine (0.6 g, 4.0 mmol) was added, and stirring was continued at 25 °C for 1 h. After complete consumption of the starting material, oxalyl chloride (1.0 mL, 11.9 mmol) was added to the reaction mixture. Stirring was continued at 25 °C for another 1 h. After completion of reaction, the reaction mixture was concentrated under reduced pressure to obtain a crude product which was purified by combi flash chromatography to obtain 3-chloro-2-(3-(chloromethyl)-5-(trichloromethyl)-lH-pyrazol-l-yl)pyridine (1.2 g, 3.5 mmol, 88% yield).

¾-NMR (400 MHz, DMSO-D6) δ 8.63 (dd, J = 4.6, 1.5 Hz, 1H), 8.31 (dd, J = 8.1, 1.5 Hz, 1H), 7.76 (dd, J = 8.1, 4.6 Hz, 1H), 7.14-7.18 (m, 1H), 4.81 (s, 2H); LCMS: $[345]^{M+H}$

Example 14:

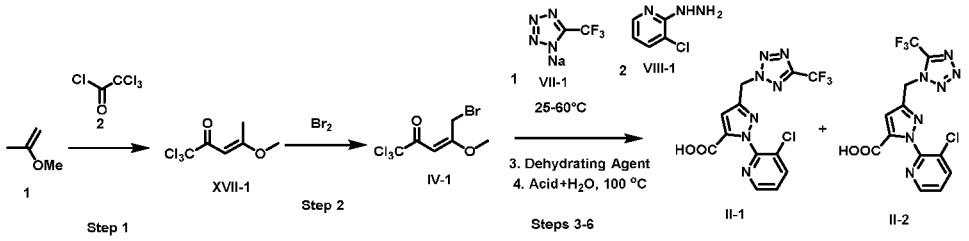
Synthesis of l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazole-5-carboxylic acid (IIB-1) and l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-lH-tetrazol-l-yl)methyl)-lH-pyrazole-5-carboxylic acid (IIB-2)



A mixture of (3-chloro-2-(3-(chloromethyl)-5-(trichloromethyl)-lH-pyrazol-l-yl)pyridine (1.0 g, 2.9 mmol), sodium 5-(trifluoromethyl)tetrazol-2-ide (0.5 g, 3.2 mmol) and potassium iodide (0.1 g, 0.3 mmol) in acetonitrile (10 mL) was heated at 60 °C under stirring for 4 h. The reaction mixture was cooled and was poured onto crushed ice to obtain a precipitate, which was filtered and triturated with hexane to get a crude product (1.3 g, 2.6 mmol, 90 % yield), which consists of l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazole-5-carboxylic acid (IIB-l) and l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-lH-tetrazol-1-yl)methyl)-1H-pyrazole-5-carboxylic acid (IIB-2) in 85:15 ratio.

¾-NMR (400 MHz, DMSO-D6) δ 8.61 (dd, J = 4.6, 1.7 Hz, 1H), 8.29-8.26 (dd, J = 8.1, 1.7 Hz, 1H), 7.52-7.56 (m, 1H), 7.26 (s, 1H), 6.23 (s, 2H); LCMS: [448]$^{M+H}$

Example 15:



Steps- 1 & 2: Synthesis of (E)-5-bromo-l,l,l-trichloro-4-methoxypent-3-en-2-one (IV-1) (ref: Synthesis 12, 1013-14, 1986 and Synthesis 16, 2353-2358, 2002; W02011009551)

A solution of 2,2,2-trichloroacetyl chloride (100 g, 533 mmol) in chlorobenzene (75 mL) was added to a stirred solution of 2-methoxyprop-l-ene (42.5 g, 560 mmol) and 3-picoline (52.7 g, 560 mmol) in chlorobenzene (250 mL) at 0 °C over 1 h. The resultant mixture was stirred at 25 °C for 3 h and which was then filtered and washed with chlorobenzene (150 mL). The resulting filtrate was added drop wise to a solution of Br (87 g, 533 mmol) in chlorobenzene (70 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 20 min followed by addition of a solution of 3-picoline (45.2 g, 480 mmol) in chlorobenzene (30 mL) at 0 °C. The reaction mixture was filtered and the filtrate was washed successively with water (200 mL), aqueous sodium carbonate solution (200 ml) and brine solution (200 mL). Chlorobenzene was distilled out under reduced pressure to obtain desired product IV-l (158 g; 533 mmol, 99% yield).

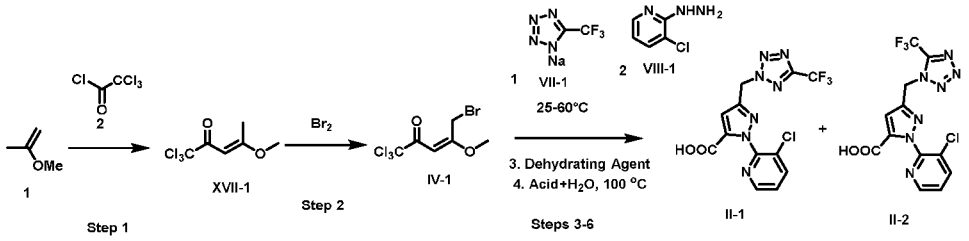
¾-NMR (400 MHz, CDCL) δ 6.07 (s, 1H), 4.46 (s, 2H), 3.87 (s, 3H).

Steps-3 to 6: Synthesis of l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazole-5-carboxylic acid (II-l and II-2)

(E)-5-bromo-l,l,l-trichloro-4-methoxypent-3-en-2-one (IV-l; 158 g; 533 mmol) was added at once to a solution of sodium 5-(trifluoromethyl)-2H-tetrazole (VII-1; 85 g, 533 mmol) in acetonitrile (460 mL) at 25 °C, then heated to 60 °C and stirred for 5 h. After completion of the reaction, the reaction mixture was cooled to 25 °C, and 3-chloro-2-hydrazineylpyridine (74.0 g, 517 mmol) was added to it. The reaction mixture was stirred for 4 h at 25 °C. Hydrogen chloride gas (39 g; 1.1 mol) was bubbled into the reaction mixture and allowed to stir at 75 °C for 4 h. Acetonitrile was distilled out from the reaction mixture. The resulting residue was dissolved in glacial acetic acid (320 mL) and subsequently water (480 mL) was added at 100 °C and allowed it to stir for 8 h. The obtained reaction mixture was allowed to cool to 15 °C with stirring. The resulting precipitated product was filtered and washed successively with water (200 mL) and a solution of 30% methyl alcohol in water (200 mL). The resulting product is air-dried to obtain

150 g of desired product II-1 and II-2. The product was further purified by using a mixture ethyl acetate and hexane.

Example 16:



Steps- 1 & 2: Synthesis of (E)-5-bromo-l,l,l-trichloro-4-methoxypent-3-en-2-one (IV-1) (ref: Synthesis 12, 1013-14, 1986 and Synthesis 16, 2353-2358, 2002; W02011009551)

A solution of 2,2,2-trichloroacetyl chloride (100 g, 533 mmol) in chlorobenzene (75 mL) was added to a stirred solution of 2-methoxyprop-l-ene (42.5 g, 560 mmol) and 3-picoline (52.7 g, 560 mmol) in chlorobenzene (250 mL) at 0 °C over 1 h. The resultant mixture was stirred at 25 °C for 3 h and was then filtered and washed with chlorobenzene (150 mL). The resulting filtrate was added drop wise to a solution of bromine (87 g, 533 mmol) in chlorobenzene (70 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 20 min followed by addition of a solution of 3-picoline (45.2 g, 480 mmol) in chlorobenzene (30 mL) at 0 °C. The reaction mixture was filtered and the filtrate was washed successively with water (200 mL), aqueous sodium carbonate solution (200 mL) and brine solution (200 mL). Chlorobenzene was distilled out under reduced pressure to obtain desired product IV-l (158 g; 533 mmol, 99% yield).

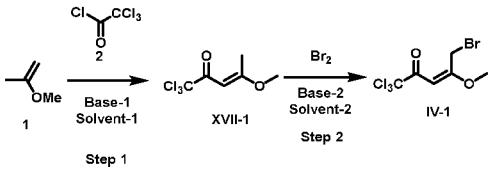
¾-NMR (400 MHz, CDCL) δ 6.07 (s, 1H), 4.46 (s, 2H), 3.87 (s, 3H).

Steps-3 to 6: Synthesis of l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazole-5-carboxylic acid (II-l and II-2)

(E)-5-bromo-l,l,l-trichloro-4-methoxypent-3-en-2-one (IV-l; 158 g; 533 mmol) and a solution of sodium 5-(trifluoromethyl)-2H-tetrazole (VII-1; 85 g, 533 mmol) in acetonitrile (450 mL), separately, were added at a rate of 1:3 respectively to acetonitrile (460 mL) at 60 °C and stirred for 5 h. After completion of the reaction, the reaction mixture was cooled to 25 °C, and 3-chloro-2-hydrazineylpyridine (74.0 g, 517 mmol) was added to it. The reaction mixture was stirred for 4 h at 25 °C. Hydrogen chloride gas (39 g; 1.1 mol) was bubbled into the reaction mixture and allowed to stir at 75 °C for 4 h. Acetonitrile was distilled out from the reaction mixture. The resulting residue was dissolved in glacial acetic acid (320 mL) and subsequently water (480 mL) was added at 100 °C and allowed it to stir for 8 h. The obtained reaction mixture was allowed to cool to 15 °C with stirring. The resulting precipitated product was filtered and washed successively with water (200 mL) and a solution of 20% methyl alcohol in water (200 mL).

The resulting product is air-dried to obtain 150 g of desired product II-1 (97%) and II-2 (3%). The product was further purified by using a mixture ethyl acetate and hexane.

Example 17:



Steps- 1 & 2: Synthesis of (E)-5-bromo-l,l,l-trichloro-4-methoxypent-3-en-2-one (IV-1) (ref: Synthesis 12, 1013-14, 1986 and Synthesis 16, 2353-2358, 2002; W02011009551)

A solution of 2,2,2-trichloroacetyl chloride (100 g, 533 mmol) in solvent-l (75 mL) was added to a stirred solution of 2-methoxyprop-l-ene (42.5 g, 560 mmol) and base-l (52.7 g, 560 mmol) in solvent-l (250 mL) at 0 °C over 1 h. The resultant mixture was stirred at 25 °C for 3 h and which was then filtered and washed with solvent-l (150 mL). The resulting filtrate was added drop wise to a solution of bromine (87 g, 533 mmol) in solvent-2 (70 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 20 min followed by addition of a solution of base-2 (45.2 g, 480 mmol) in solvent-2 (30 mL) at 0 °C. The reaction mixture was filtered and filtrate was washed successively with water (200 mL), aqueous sodium carbonate solution (200 ml) and brine solution (200 mL). Solvent-2 was distilled out under reduced pressure to obtain desired product IV-l. ¾-NMR (400 MHz, $CDCl_3$) δ 6.07 (s, 1H), 4.46 (s, 2H), 3.87 (s, 3H).

The yields are provided in table no. 3 below:

The above reaction was carried out additionally using different bases and solvents as shown in Table No. 3.

Table No. 3: The preparation of IV-1 using different solvents.

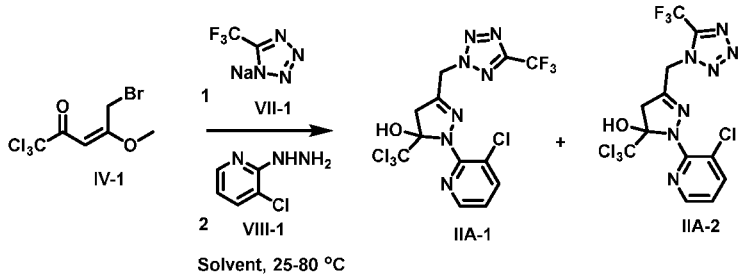
Sr. No.	Base-1 and Solvent-1	Base-2 and Solvent-2
1	Pyridine, Chlorobenzene	Pyridine, Chlorobenzene
2	3-Picoline, Chlorobenzene	3-Picoline, Chlorobenzene
3	Pyridine, Methyl tert-butyl ether	Pyridine, Methyl tert-butyl ether
4	3-Picoline, Methyl tert-butyl ether	3-Picoline, Methyl tert-butyl ether
5	Pyridine, Dichloromethane	Pyridine, Dichloromethane
6	3-Picoline, Dichloromethane	3-Picoline, Dichloromethane

7	Pyridine, Dichloromethane	Sodium carbonate, Dichloromethane
8	Pyridine, Dichloromethane	Sodium bicarbonate, Dichloromethane
9	Pyridine, Dichloromethane	Potassium bicarbonate, Dichloromethane
10	Pyridine, Dichloromethane	Cesium bicarbonate, Dichloromethane
11	Pyridine, Dichloromethane	Sodium carbonate, Acetonitrile
12	Pyridine, Dichloromethane	Sodium bicarbonate, Acetonitrile
13	Pyridine, Dichloromethane	Potassium bicarbonate, Acetonitrile
14	Pyridine, Dichloromethane	Cesium bicarbonate, Acetonitrile
15	Pyridine, Dichloromethane	Sodium hydroxide, Dichloromethane

IV-1 was obtained in moderate to high yield.

Example 18:

Synthesis of mixture of l-(3-chloropyridin-2-yl)-5-(trichloromethyl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-4,5-dihydro-lH-pyrazol-5-ol (IIA-1) and l-(3-chloropyridin-2-yl)-5-(trichloromethyl)-3-((5-(trifluoromethyl)-lH-tetrazol-l-yl)methyl)-4,5-dihydro-lH-pyrazol-5-ol (IIA-2)



(E)-5-bromo-l,l,l-trichloro-4-methoxypent-3-en-2-one (IV-1, 158 g, 533 mmol) was added to a solution of sodium 5-(trifluoromethyl)-2H-tetrazole (VII-1, 85 g, 533 mmol) in a suitable solvent (460 mL) (see Table No. 4 herein below) at 60 °C with stirring for 5 h. The resulting reaction mixture was cooled to 25 °C, and 3-chloro-2-hydrazineylpyridine (VIII-1, 74.0 g, 517 mmol) was added to it. The reaction mixture was stirred for 4 h at 25 °C. The results are provided in Table No. 4 herein below.

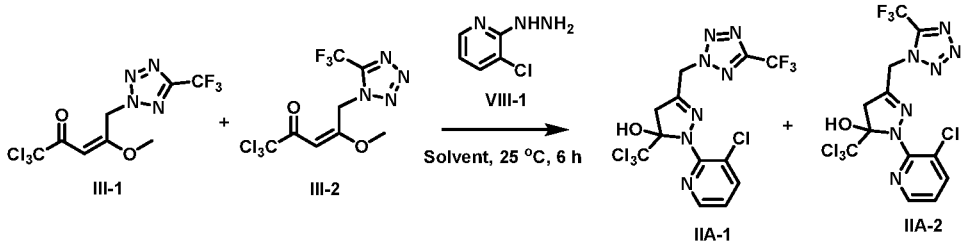
Table No. 4: The preparation of IIA-l and IIA-2 using different solvents

Sr. No.	Solvent

1	Acetone
2	Acetonitrile
3	Methyl tert-butyl ether
4	Chlorobenzene
5	Dichloroethane
6	Dichloromethane
7	Dioxane
8	Ethyl acetate
9	Dimethylformamide
10	Dimethylacetamide
11	Dimethyl sulfoxide
12	2-Methyltetrahydrofuran
13	Tetrahydrofuran
14	1,2-Dimethoxyether
15	Toluene
16	Xylene
17	N-methyl-2-pyrrolidone

A mixture of IIA-l and IIA-2 was obtained in low to high yield.

Example 19:



The above reaction with 1:1 molar ratio of III-1+III-2:VIII-1 was carried out using different solvents as mentioned in Table No. 5 herein below.

Table No. 5: The preparation of IIA-l and IIA-2 using different solvents

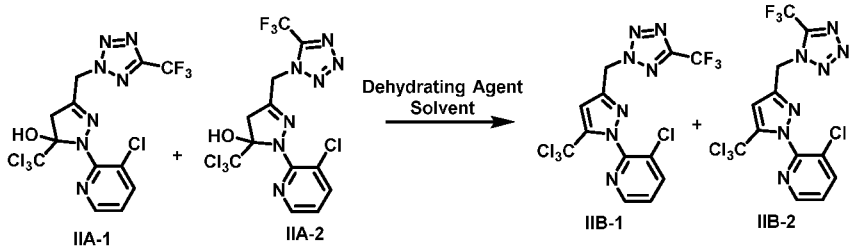
Sr. No.	Solvent
1	Acetone
2	Acetonitrile

3	Methyl tert-butyl ether
4	Chlorobenzene
5	Dichloroethane
6	Dichloromethane
7	Dioxane
8	Dimethylformamide
9	Dimethylacetamide
10	Dimethyl sulfoxide
11	Ethyl acetate
12	2-Metyltetrahedrafuran
13	Tetrahydrofuran
14	1,2-Dimethoxyether
15	Toluene
16	Xylene
17	N-methyl-2-pyrrolidone

A mixture of IIA-l and IIA-2 was obtained in low to high yield.

Example 20:

Synthesis of mixture of 3-chloro-2-(5-(trichloromethyl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazol-l-yl)pyridine (IIB-1) and 3-chloro-2-(5-(trichloromethyl)-3-((5-(trifluoromethyl)-lH-tetrazol-l-yl)methyl)-lH-pyrazol-l-yl)pyridine (IIB-2)



Hydrochloride gas (109 mg, 3 mmol) was bubbled into a solution of a mixture containing l-(3-chloropyridin-2-yl)-5-(trichloromethyl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-4,5-dihydro-lH-pyrazol-5-ol and 1-(3-chloropyridin-2-yl)-5-(trichloromethyl)-3-((5-(trifluoromethyl)-1H-tetrazol-1-yl)methyl)-4,5-dihydro-lH-pyrazol-5-ol (930 mg, 2 mmol) in a suitable solvent and dehydrating agent at 25 °C (see Table No. 6 herein below). The reaction mixture was heated at 65 °C with stirring for 6 h.

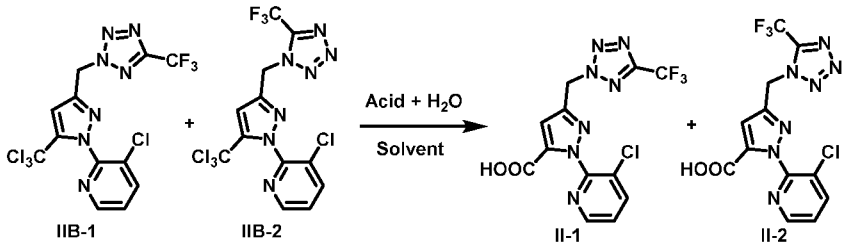
Table No. 6 : The preparation of **IIB-l** and **IIB-2** using different dehydrating agents and solvents

Sr. No.	Dehydrating agent	Solvent
1	Oxalyl chloride	Acetonitrile
2	Oxalyl chloride	Methyl tert-butyl ether
3	Oxalyl chloride	Dichloromethane
4	Oxalyl chloride	Dioxane
5	Thionyl chloride	Thionyl Chloride
6	Thionyl chloride	Dichloromethane
7	Thionyl chloride	Methyl tert-butyl ether
8	Thionyl chloride	Acetic acid
9	Methanolic hydrochloric acid	Methyl alcohol
10	Hydrogen chloride gas	Methyl alcohol
11	Conc. Sulphuric acid (cat)	Ethyl alcohol
12	Conc. Sulphuric acid (cat)	Tetrahydrofuran
13	Conc. Sulphuric acid (cat)	Methyl alcohol
14	Conc. Sulphuric acid (cat)	Dioxane
15	Conc. Sulphuric acid (cat)	Isopropyl alcohol
16	Conc. Sulphuric acid (cat)	tert-Butyl alcohol
17	Conc. Sulphuric acid (cat)	Acetonitrile
18	Conc. Sulphuric acid (cat)	Acetic acid
19	Acetic Acid	Acetonitrile
20	Acetic acid	Acetic acid
21	Hydrogen chloride-1,4-dioxane	Acetic acid
22	Hydrogen chloride gas	Acetic acid
23	Hydrogen bromide (30% in Acetic Acid)	Acetic acid
24	Conc. Sulphuric acid (cat)	Acetic acid
25	Triflic acid(cat)	Acetic acid
26	Trifluoroacetic acid (cat)	Acetic acid
27	Methanesulfonic acid	Acetic acid
28	p-Toluenesulfonic acid	Acetonitrile
29	Methanesulfonic acid	Acetonitrile
30	Silica gel	Acetonitrile
31	Silica gel	Acetic acid

A mixture of IIB-l+IIB-2 was obtained in moderate to high yield.

Example 21:

Synthesis of mixture of l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)-lH-pyrazole-5-carboxylic acid (II-l) and l-(3-chloropyridin-2-yl)-3-((5-(trifluoromethyl)-lH-tetrazol-l-yl)methyl)-lH-pyrazole-5-carboxylic acid (II-2)



A mixture (1.3 g, 3 mmol) of 3-chloro-2-(5-(trichloromethyl)-3-((5-(trifluoromethyl)-2H-tetrazol-2-yl)methyl)- 1H-pyrazol- 1-yl)pyridine (IIB- 1) and 3-chloro-2-(5-(trichloromethyl)-3 -((5 -(trifluoromethyl)-lH-tetrazol-l-yl)methyl)-lH-pyrazol-l-yl)pyridine (IIB-2) was dissolved in a suitable acid and solvent (see Table No. 7 herein below). The reaction mixture was heated at 100 °C with stirring. Water (4 mL) was added drop wise to reaction mixture at 100 °C and continued stirring for 8 h.

Table No. 7: The preparation of II- 1 and II-2 different acids and solvents

Sr. No.	Acid	Solvent
1	50 % sulphuric acid	Acetonitrile
2	50 % sulphuric acid	50 % Sulphuric acid
3	Acetic acid	Water
4	6N Hydrochloric acid	Acetonitrile
5	50% sulphuric acid	Ethyl alcohol
6	50% sulphuric acid	Tetrahydrofuran
7	50% sulphuric acid	Dioxane
8	50% sulphuric acid	Isopropyl alcohol
9	50% sulphuric acid	tert-Butyl alcohol
10	10% sulphuric acid	Acetonitrile
11	20% sulphuric acid	Acetonitrile
12	30% Sulphuric acid	Acetonitrile
13	40% sulphuric acid	Acetonitrile
14	98% sulphuric acid	Acetonitrile

15	10% sulphuric acid	Acetic Acid
16	20% sulphuric acid	Acetic Acid
17	30% sulphuric acid	Acetic Acid
18	40% sulphuric acid	Acetic Acid
19	6N Hydrochloric Acid	Methyl alcohol
20	6N Hydrochloric Acid	Ethyl alcohol
21	6N Hydrochloric Acid	tert-Butyl alcohol
22	6N Hydrochloric Acid	Isopropyl alcohol

A mixture of II-1+II-2 was obtained in moderate to high yield.

Example 22:

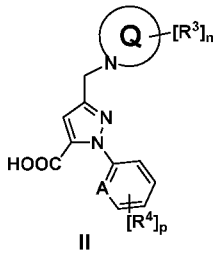
One pot synthesis of 3-chloro-2-methoxyprop-l-ene (3a)

To a solution of 2-methoxyprop-l-ene (670 mg, 9.3 mmol) in dichloroethane (10 mL) was added *N*-chlorosuccinimide (225 mg, 9.3 mmol) at 0 °C and stirred for 1 h at 0 °C. The temperature of the reaction mixture was allowed to rise to 25 °C and filtered to remove precipitated succinimide. The filtrate was taken in a round bottom flask and to it pyridine and a solution of 2,2,2-trichloroacetyl chloride (1.69 g, 9.3 mmol) in dichloroethane (10 mL) was added drop wise over 30 min. The reaction mixture was stirred at 25 °C for 16 h. Then, the reaction mixture was washed subsequently with 0.1 M hydrochloric acid (10 mL) and twice with water (10 mL). The dichloroethane layer was dried over anhydrous sodium sulphate and concentrated under reduced pressure to obtain a crude product, which was purified by flash chromatography to obtain pure product l,l,l,5-tetrachloro-4-methoxypent-3-en-2-one (1.0 g, 1.34 mmol, 15% yield).

¾-NMR (400 MHz, CDCL) δ 6.08 (s, 1H), 4.62 (s, 2H), 3.88 (s, 3H).

CLAIMS:

1. A process for preparing a compound of formula II



II

wherein,

A is N or C;

R^3 and R^4 are independently selected from the group consisting of hydrogen, halogen, cyano, nitro, hydroxy, G-G, -alkyl. G-G,-haloalkyl. C3-C6-cycloalkyl, C3-C6-halocycloalkyl, G-G,-alkoxy, Ci-Ce-haloalkoxy, Ci-Ce-alkylthio, Ci-Ce-alkylsulphinyl, Ci-Ce-alkylsulphonyl, Ci-Ce-haloalkylthio, G-G.-haloalkylsulphinyl. Ci-G,-haloalkylsulphony1 and NR^aR^b; R^a and R^b are independently selected from the group consisting of hydrogen, G-G, -alkyl. C3-C6-cycloalkyl; or R^a and R^b together with the N atom to which they are attached form a substituted or unsubstituted 3- to 6- membered heterocyclic ring,

wherein, the substituents on the 3- to 6- membered heterocyclic ring are selected from the group consisting of halogen, cyano, nitro, hydroxy, G-G, -alkyl. G-G,-haloalkyl. C3-C6-cycloalkyl, C3-C6-halocycloalkyl, G-G,-alko\y. G-G,-haloalko\y. G-G.-alkylthio. Ci-C_6-alkylsulphinyl, Ci-G.-alkylsulphonyl, Ci-Ce-haloalkylthio, Ci-Ce-haloalkylsulphinyl and Ci-G.-haloalkylsulphonyl:

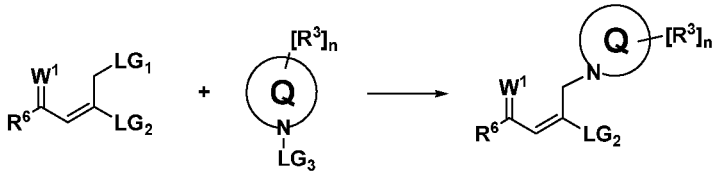
Q is a 3-, 4- or 5 membered heterocyclic ring;

n is an integer 0 to 4; and

p is an integer 0 to 5;

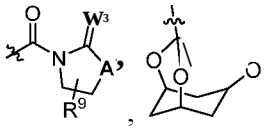
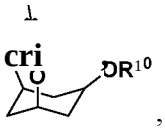
said process comprising the steps of:

a. reacting a compound of formula IV with a compound of formula VII in the presence of one or more suitable solvent and optionally, one or more suitable catalyst and or reagent to obtain a compound of formula III,



IV VII III

wherein,

R_6 is selected from the group consisting of CX_3, $COW^2(R^7)$, $C(W^4R_7)_3$, $CH(W^4R_7)_2$, allylic group, substituted or unsubstituted furanyl.,  , and  ,

wherein, the substitution on furanyl group is selected from the group consisting of halogen, cyano, nitro, hydroxy, G-G, -alkyl. G-G,-haloalkyl. C_3-C_6-cycloalkyl, C_3-C_6-halocycloalkyl, Ci-G,-alkoxy. Ci-Ce-haloalkoxy, Ci-G,-alkylthio. G-G,-alkylsulphinyl. Ci-Ce-alkylsulphonyl, Ci-Ce-haloalkylthio, G-G.-haloalkylsulphinyl. or C_1-G,-haloalkylsulphonyl;

W^1, W^2, W^3, W^4 and A^1 are independently O, S or NR^{1c}; wherein R^{1c} is hydrogen, G-G, -alkyl, or C_3-C_6-cycloalkyl;

R^7 is selected from the group consisting of hydrogen, substituted or unsubstituted G-G, -alkyl, substituted or unsubstituted C_3-C_6-cycloalkyl, substituted or unsubstituted aryl and substituted or unsubstituted arylalkyl, or

two R^7 together with the atom to which they are attached form a substituted or unsubstituted 3- to 6- membered carbocyclic or heterocyclic ring,

wherein, the substitution on G-G, -alkyl. C_3-C_6-cycloalkyl, aryl, and arylalkyl of R^7 and carbocyclic or heterocyclic ring formed by two R^7 are independently selected from the group consisting of halogen, cyano, nitro, hydroxy, G-G, -alkyl. G-G,-haloalkyl. C_3-C_6-cycloalkyl, C_3-C_6-halocycloalkyl, G-G,-alko\y. G-G,-haloalko\y. G-G.-alkylthio. Ci-Ce-alkylsulphinyl, G-G,-alkylsulphonyl. G-G.-haloalkylthio. Ci-G,-haloalkylsulphinyl. and Ci-Ce-haloalkylsulphonyl;

R^9 and R^{10} are independently selected from the group consisting of hydrogen, halogen, cyano, substituted or unsubstituted G-G, -alkyl. substituted or unsubstituted G-G,-alkoxy. substituted or unsubstituted C3-C6-cycloalkyl, substituted or unsubstituted Ci-G,-alkylthio. substituted or unsubstituted G-G.-alkylsulphinyl. substituted or unsubstituted Ci-G,-alkylsul phony 1, substituted or unsubstituted aryl and substituted or unsubstituted arylalkyl,

wherein, the substitution on G-G, -alkyl. Ci-G,-alkoxy. C3-C6-cycloalkyl, G-G,-alkylthio, G-G.-alkylsulphinyl. G-G, -alkyl sulphonyl. aryl, and arylalkyl of R^9 and R^{10} is selected from the group consisting of halogen, cyano, nitro, hydroxy, G-G, -alkyl. C_1-G,-haloalkyl, C3-C6-cycloalkyl, C3-C6-halocycloalkyl, Ci-G,-alkoxy. Ci-G,-haloalkoxy. Ci-Ce-alkylthio, G-G,-alkylsulphinyl. Ci-G.-alkylsulphonyl, Ci-Ce-haloalkylthio, C_1-G,-haloalkylsulphinyl, and Ci-G.-haloalkylsulphonyl:

LGi is selected from the group consisting of X, OR^5, and $OSi(R^{11})_3$,

wherein, R^5 is selected from the group consisting of hydrogen, substituted or unsubstituted G-G, -alkyl, substituted or unsubstituted aryl-G-G, -alkyl, substituted or unsubstituted aryl, -(C=0)-Ci-C_6-alkyl, -(C=0)-Ci-C_6-haloalkyl, -(C=0)0-Ci-C_6-alkyl, -(C=0)0-haloCi-C_6-alkyl, SO2-G-G, -alkyl. SCf-G-G.-haloalkyl and substituted or unsubstituted S0$_2$-aryl,

R^{11} is selected from the group consisting of hydrogen, halogen, substituted or unsubstituted G-G, -alkyl, substituted or unsubstituted aryl-G-G, -alkyl, substituted or unsubstituted aryl, -(C=0)-Ci-C_6-alkyl, -(C=0)-Ci-C_6-haloalkyl, -(C=0)0-Ci-C_6-alkyl, -(C=0)0-haloCi-C_6-alkyl, SO2-G-G, -alkyl. SCf-G-G.-haloalkyl and substituted or unsubstituted S0$_2$-aryl;

LG_2 is X, OR^{12},

wherein, R^{12} is selected from the group consisting of hydrogen, substituted or unsubstituted Ci-Ce-alkyl, substituted or unsubstituted aryl-G-G, -alkyl. substituted or unsubstituted aryl, -(C=0)-Ci-C_6-alkyl, -(C=0)-Ci-C_6-haloalkyl, -(C=0)0-Ci-C_6-alkyl, -(C=0)0-haloCi-C_6-alkyl, SCh-Ci-Ce-alkyl, SCh-Ci-Ce-haloalkyl, substituted or unsubstituted S02-aryl, alkylthio, and NR^aR^b; R^a and R^b are independently selected from the group consisting of hydrogen, Ci-Ce-alkyl, C3-C6-cycloalkyl; or R^a and R^b together

with the N atom to which they are attached form a substituted or unsubstituted 3- to 6-membered heterocyclic ring,

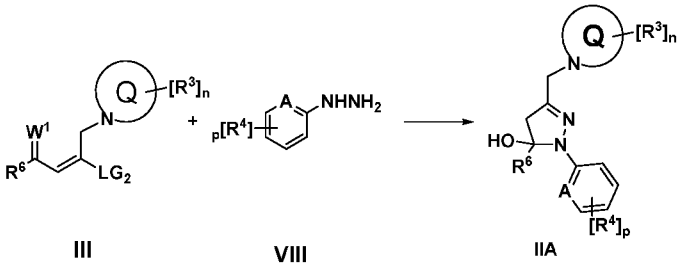
wherein, the substitution on Ci-G,-alkyl. aryl-Ci-Ce-alkyl, aryl, and S0 $_2$-aryl of LGi and LG_2 group is selected from the group consisting of halogen, cyano, nitro, hydroxy, Ci-Ce-alkyl, Ci-Ce-haloalkyl, C_3-C_6-cycloalkyl, C_3-C_6-halocycloalkyl, Ci-Ce-alkoxy, Ci-Ce-haloalkoxy, Ci-Ce-alkylthio, Ci-Ce-alkylsulphinyl, Ci-Ce-alkylsulphonyl, Ci-Ce-haloalkylthio, Ci-Ce-haloalkylsulphinyl, and C_1-G.-haloalkylsulphonyl;

LG_3 is selected from the group consisting of hydrogen, alkali metal, halogen and $Si(R^{11})_3$;

each X is independently hydrogen, F, Cl, Br or I;

R^3, n, and Q are each as defined above;

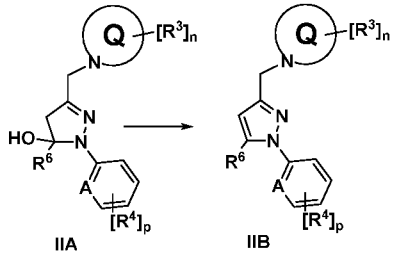
b. cyclizing the compound of formula III with a hydrazine of formula VIII in one or more suitable solvent and optionally, one or more suitable reagent to obtain a compound of formula IIA,



III VIII IIA

wherein, R^3, R^4, R^6, A, n, p, Q, W^1, and LG_2 are each as defined herein above;

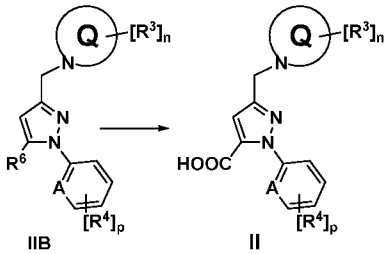
c. eliminating water from the compound of formula IIA by using one or more suitable dehydrating reagent in one or more suitable solvent to obtain a compound of formula IIB,



IIA IIB

wherein, R^3, R^4, R^6, A, n, p, and Q are each as defined herein above; and

d. converting the compound of formula IIB into the compound of formula II using one or more suitable reagent in one or more suitable solvent and optionally, one or more suitable catalyst,



wherein, R^3, R^4, R^6, A, n, p, and Q are each as defined herein above; and

wherein, the compound of formula III obtained in step (a), the compound of formula IIA obtained in step (b) and the compound of formula IIB obtained in step (c) may or may not be isolated.

2. The process as claimed in claim 1, wherein

i. the suitable solvent in the process step (a) is selected from the group consisting of acetone, acetonitrile, methyl tert-butyl ether, chlorobenzene, dichloroethane, dichloromethane, dioxane, ethyl acetate, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, 2-methyltetrahydrofuran, tetrahydrofuran, l,2-dimethoxyether, toluene, p-xylene and N-methyl-2-pyrrolidone;

ii. the suitable catalyst in the process step (a) is selected from the group consisting of potassium iodide, sodium iodide, copper iodide and cupric iodide. and

iii. the process step (a) is performed within a temperature range from 20 °C to 150 °C.

3. The process as claimed in claim 1, wherein

i. the suitable solvent in the process step (b) is selected from the group consisting of acetone, acetonitrile, ethyl alcohol, acetic acid, methyl tert-butyl ether, chlorobenzene, dichloroethane, dichloromethane, dioxane, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, ethyl acetate, 2-metyltetrahedrafuran, tetrahydrofuran, l,2-dimethoxy ether, toluene, xylene and N-methyl-2-pyrrolidone;

ii. the suitable reagent in the process step (b) is selected from the group consisting of acetic acid, trifluoroacetic acid, hydrochloric acid, hydrobromic acid, sulphuric acid, methanesulfonic acid, triflic acid, phosphoric acid and p-toluenesulfonic acid; and

iii. the process step (b) is performed within a temperature range from 20 °C to 150 °C.

4. The process as claimed in claim 1, wherein

i. the suitable solvent in the process step (c) is selected from the group consisting of acetonitrile, methyl tert-butyl ether, dichloromethane, dioxane, thionyl chloride, acetic acid, methyl alcohol, ethyl alcohol, tetrahydrofuran, isopropyl alcohol and tert-butyl alcohol;

ii. the suitable dehydrating reagent in the process step (c) is selected from the group consisting of sulphuric acid, trifluoroacetic acid, phosphorous trichloride, phosphorous oxychloride, thionyl chloride, acetic anhydride, trifluoroacetic anhydride, oxalyl chloride, phosgene, diphosgene, methanolic hydrochloric acid, hydrogen chloride gas, acetic acid, hydrogen bromide, triflic acid, methanesulfonic acid, p-toluenesulfonic acid, hydrogen chloride- 1,4-dioxane and silica gel; and

iii. the process step (c) is performed within a temperature range from 20 °C to 150 °C.

5. The process as claimed in claim 1, wherein

i. the suitable solvent in the process step (d) is selected from the group consisting of water, acetonitrile, dioxane, sulphuric acid, acetic acid, methyl alcohol, ethyl alcohol, tetrahydrofuran, isopropyl alcohol and tert-butyl alcohol;

ii. the suitable reagent in the process step (d) is an acid selected from the group consisting of sulphuric acid, chlorosulphuric acid, hydrochloric acid, hydrofluoric acid, hydroboric acid, phosphoric acid, acetic acid, trifluoroacetic acid, p-toluenesulphonic acid, methanesulphonic acid, and trifluoromethanesulphonic acid; or

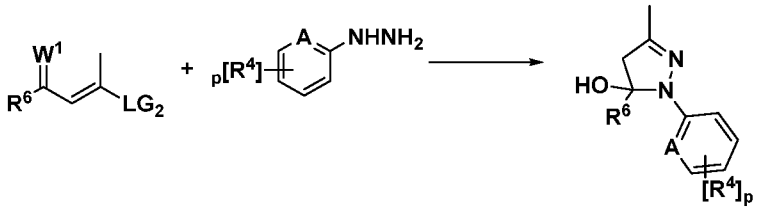
iii. the suitable reagent in the process step (d) is a base selected from the group consisting of trialkylamines, pyridine, alkylpyridines, phosphazines, l,8-diazabicyclo[5.4.0]undecene (DBU), lithium hydroxide, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium acetate, potassium acetate, lithium acetate, sodium methoxide, sodium ethoxide, sodium tert-butoxide, and potassium tert-butoxide;

iv. the catalyst in the process step (d) is selected from the group consisting of ferric chloride (FeCT), aluminum chloride (A1CT), boron trifluoride (BF_3), antimony trichloride ($SbCl_3$) and monosodium phosphate ($NaFl_2PO_4$); and

v. the process step (d) is performed within a temperature range from 20 °C to 150 °C.

6. The process as claimed in claim 1, wherein the compound of formula IIB is alternatively obtained by the process comprising the steps of:

i. cyclizing a compound of formula XVII with the hydrazine of formula VIII in one or more suitable solvent and optionally, one or more suitable reagent to obtain a compound of formula XVI,

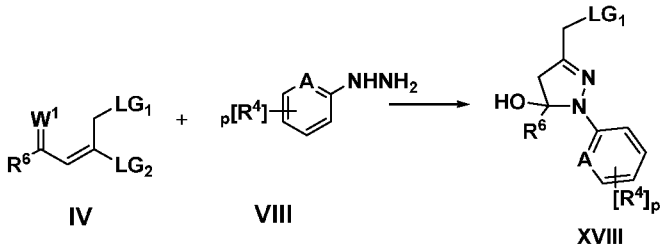


XVII VIII XVI

wherein, $R^6$is CX_3, X is F, Cl, Br and I; R^4, A, p, W^1, and LG_2 are each as defined in claim 1;

or

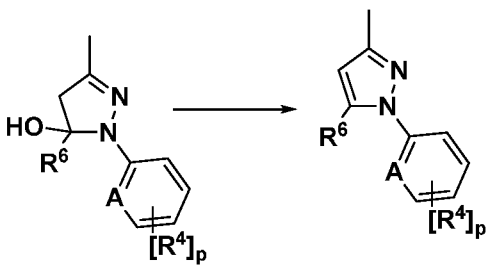
cyclizing the compound of formula IV and the hydrazine of formula VIII in one or more suitable solvent and optionally, one or more suitable reagent to obtain a compound of formula XVIII,



IV VIII XVIII

wherein, $R^6$is CX_3, LGi is Cl; X is F, Cl, Br and I, preferably Cl; R^4, A, p, W^1 and LG2 are each as defined in claim 1;

ii. eliminating water from the compound of formula XVI by using one or more suitable dehydrating reagent in one or more suitable solvent to obtain a compound of formula XV;

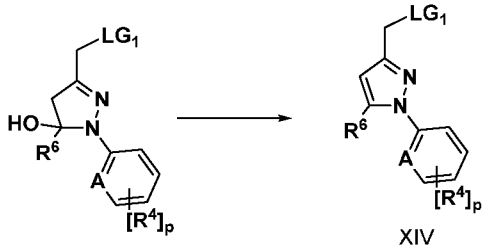


XVI XV

wherein, R^6 is CX_3, X is F, Cl, Br and I; R^4, A, and p are each as defined in claim 1;

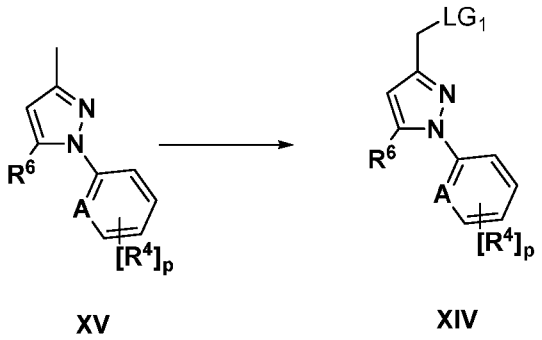
or

eliminating water from the compound of formula XVIII by using one or more suitable dehydrating reagent in one or more suitable solvent to obtain a compound of formula XIV,



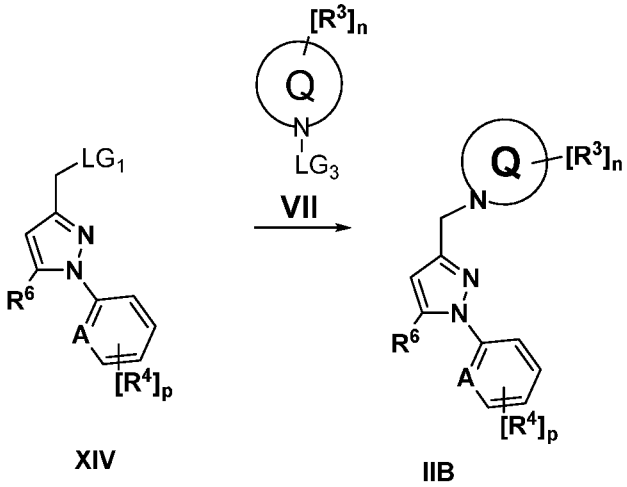
wherein, R^6 is CX_3, LGi is Cl, X is F, Cl, Br and I; R^4, A, and p, are each as defined in claim 1;

iii. halogenating the compound of formula XV using a suitable halogenating agent in one or more suitable solvent and optionally, one or more radical initiator to obtain a compound of formula XIV,



wherein, R^6 is CX3, LGi is X, X is F, Cl, Br and I; R^4, A, and p, are each as defined in claim 1; and

iv. obtaining the compound of formula IIB by reacting the compound of formula XIV with the compound of formula VII,



XIV IIB

wherein, R^6 is CX_3, LGi is X, X is F, Cl, Br and I; R^3, R^4, A, Q, n, p, and LG_3 are each as defined in claim 1; and

the compounds of formula XVI and XVIII obtained in step (i), the compounds of formula XV and XIV obtained in step (ii) and the compound XIV obtained in step (iii) may or may not be isolated.

7. The process as claimed in claim 6, wherein

i. the suitable solvent in the step (i) is selected from the group consisting of acetone, acetonitrile, ethyl alcohol, methyl tert-butyl ether, chlorobenzene, dichloroethane, dichloromethane, dioxane, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, ethyl acetate, 2-metyltetrahedrafuran, tetrahydrofuran, l,2-dimethoxy ether, toluene, xylene and N-methyl-2-pyrrolidone;

ii. the suitable reagent in the step (i) is selected from the group consisting of acetic acid, trifluoroacetic acid, hydrochloric acid, hydrobromic acid, sulphuric acid, methanesulfonic acid, triflic acid, phosphoric acid and p-toluenesulfonic acid; and

iii. the step (i) is performed within a temperature range from 20 °C to 150 °C.

8. The process as claimed in claim 6, wherein

i. the suitable solvent in the step (ii) is selected from the group consisting of water, acetonitrile, methyl tert-butyl ether, dichloromethane, dioxane, thionyl chloride, acetic acid, methyl alcohol, ethyl alcohol, tetrahydrofuran, isopropyl alcohol and tert-butyl alcohol;

ii. the suitable dehydrating reagent in the step (ii) is selected from the group consisting of sulphuric acid, trifluoroacetic acid, phosphorous trichloride, phosphorous oxychloride, thionyl chloride, acetic anhydride, trifluoroacetic anhydride, oxalyl chloride, phosgene,

diphosgene, methanolic hydrochloric acid, hydrogen chloride gas, acetic acid, hydrogen bromide, triflic acid, methanesulfonic acid, p-toluenesulfonic acid and silica gel; and

iii. the step (ii) is performed within a temperature range from 20 °C to 150 °C.

9. The process as claimed in claim 6, wherein

i. the suitable solvent in the step (iii) is selected from the group consisting of acetone, acetonitrile, methyl tert-butyl ether, chlorobenzene, dichloroethane, dichloromethane, dioxane, ethyl acetate, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, 2-methyltetrahydrofuran, tetrahydrofuran, l,2-dimethoxyether, toluene, p-xylene and N-methyl-2-pyrrolidone;

ii. the halogenating agent in the step (iii) is selected from the group consisting of N-halosuccinimide: N-chlorosuccinimide, N-bromosuccinimide and N-iodosuccinimide; X2: Cl_2, Br_2 or I_2; $X_{2/I1V}$: Ch/hv Br_2/hv or I_2/hv; N-halosaccharine: N-chlorosaccharine, N-bromosaccharine and N-iodosaccharine; and halohydantoine: N-chlorohydantoine, N-bromohydantoine and N-iodohydantoine;

iii. the radical initiator in the step (iii) is selected from the group consisting of dibenzoyl peroxide, hydrogen peroxide, di(n-propyl)peroxydicarbonate, t-butyl peroxybenzoate, methyl ethyl ketone peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy)-3-hexyne, di(t-butyl)peroxide, acetone peroxide, dicumyl peroxide, azobisisobutyronitrile, bis(2-ethylhexyl)peroxydicarbonate, (peroxybis(propane-2,2-diyl))dibenzene, peracetic acid, metachloroperbenzoic acid, Payne's reagent, magnesium monoperphthalate, trifluoroperacetic acid, trichloroperacetic acid, 2, 4-dinitorperbenzoic acid, Caro's Acid and potassium caroate; and

iv. the step (iii) is performed within a temperature range from 20 °C to 150 °C.

10. The process as claimed in claim 6, wherein

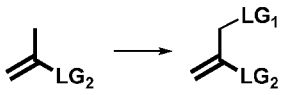
i. the suitable solvent in the step (iv) is selected from the group consisting of acetone, acetonitrile, methyl tert-butyl ether, chlorobenzene, dichloroethane, dichloromethane, dioxane, ethyl acetate, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, 2-methyltetrahydrofuran, tetrahydrofuran, l,2-dimethoxyether, toluene, p-xylene and N-methyl-2-pyrrolidone;

ii. the catalyst in the step (iv) is selected from the group consisting of potassium iodide, sodium iodide, copper iodide and cupric iodide; and

iii. the step (iv) is performed within a temperature range from 20 °C to 150 °C.

11. The process as claimed in claim 1, wherein the compound of formula IV is obtained by the process steps of:

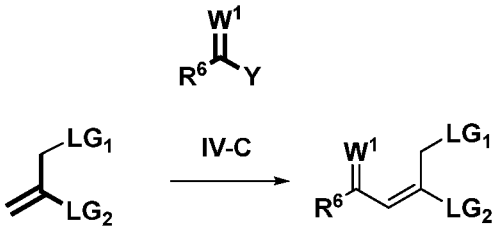
i. converting a compound of formula IV-A into a compound of formula IV-B using a suitable reagent in one or more suitable solvent,



IV-A IV-B

wherein, LGi and LG2 are each as defined in claim 1;

ii. reacting the compound of formula IV-B with a compound of formula IV-C in a suitable solvent and optionally using suitable reagent to obtain the compound of formula IV,



IV-B IV

wherein, Y is OR^5, X, or -0(C=0)CX_3; X is F, Cl, Br or I; R^5, R^6, W^1, LGi and LG2 are each as defined in claim 1,

and

wherein, the compound of formula IV-B may or may not be isolated.

12. The process as claimed in claim 11, wherein

i. the suitable reagent in the step (i), is selected from the group consisting of HX, NaX, KX, CuX_2, MgX_2, CsX, ZnX_2, $SOCl_2$, $S0_2Cl_2$. $COCl_2$, X_2, $C(=0)(0Cl_3)_2$, f-BuOCl, NaOCl, chloramine-T, *N*-halosuccinimidcs., N-halosaccharine, halohydantoine, POX3, PX3 and PX5; wherein, X or halo is Cl, Br, I or F;

ii. the suitable solvent in the step (i) is selected from the group consisting of acetone, acetonitrile, methyl tert-butyl ether, chlorobenzene, dichloroethane, dichloromethane, dioxane, ethyl acetate, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, 2-

methyltetrahydrofuran, tetrahydrofuran, l,2-dimethoxyether, toluene, p-xylene and N-methyl-2-pyrrolidone; and

iii. the step (i) is performed within a temperature range from 20 °C to 100 °C.

13. The process as claimed in claim 11, wherein

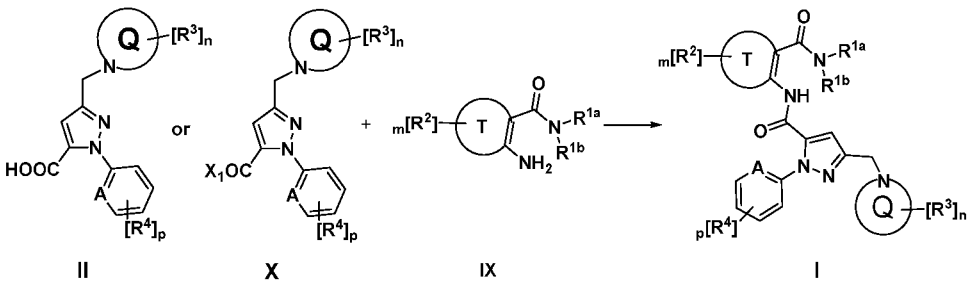
i. the suitable reagent in the step (ii), is selected from the group consisting of pyridine, triethyl amine, *N,N*-Diisopropylethylamine, 2,6-Di-tert-butylpyridine, l,5-Diazabicyclo(4.3.0)non-5-ene, l,8-Diazabicycloundec-7-ene, Lithium diisopropylamide, sodium bis(trimethylsilyl)amide, and potassium bis(trimethylsilyl)amide;

ii. the suitable solvent in the step (ii) is selected from the group consisting of acetone, acetonitrile, methyl tert-butyl ether, chlorobenzene, dichloroethane, dichloromethane, dioxane, ethyl acetate, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, 2-methyltetrahydrofuran, tetrahydrofuran, l,2-dimethoxyether, toluene, p-xylene and N-methyl-2-pyrrolidone; and

iii. the step (ii) is performed within a temperature range from 20 °C to 100 °C.

14. A process for preparing a compound of formula I form the compound of formula II obtained by the process as claimed in claim 1, said process comprising the step of:

reacting the compound of formula II optionally after converting into a compound of formula X with a compound of formula IX to obtain the compound of formula I,



II X IX I

wherein,

X1 is Cl or Br;

R^{1a} and R^{1b} are independently selected from the group consisting of hydrogen, C_1-C_6-alkyl, Ci-Ce-haloalkyl, Cs-Ce-cycloalkyl, (Ci-Ce-alkylJ-Cs-Ce-cycloalkyl, and (C_3-C_6-cycloalkyl)-Ci-C_6-alkyl; or

R^{1a} and R^{1b} together with the N atom to which they are attached form N=S(=0) $_{0-2}$(C_1-C_6-alkyl)$_2$;

T is an aryl or a heteroaryl ring or a fused or a bicyclic aryl or heteroaryl ring or ring system;

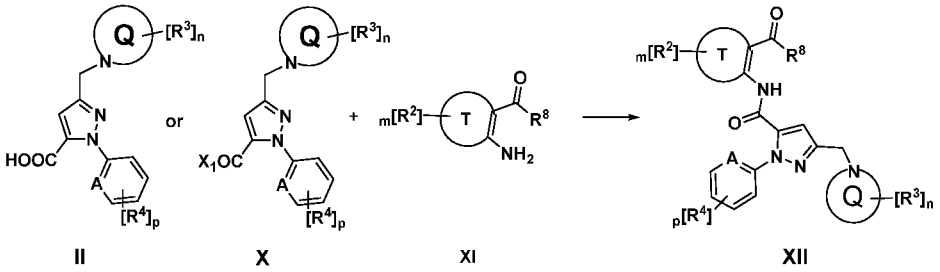
R^2 is selected from the group consisting of hydrogen, halogen, cyano, nitro, Ci-C_6-alkyl. Ci-Ce-haloalkyl, and C_3-C_6-cycloalkyl;

m is an integer 0 to 6; and

R^3, R^4, A, n, p, and Q are each as defined in claim 1;

or

reacting the compound of formula II optionally after converting into a compound of formula X with a compound of formula XI to obtain a compound of formula XII and reacting the compound of formula XII with suitable amine XIII to obtain the compound of formula I,



wherein,

Xi is Cl or Br;

R^{1a} and R^{1b} are independently selected from the group consisting of hydrogen, Ci-C_6-alkyl, Ci-Ce-haloalkyl, Cs-Ce-cycloalkyl, (Ci-Ce-alkylJ-Cs-Ce-cycloalkyl, and (C_3-C_6-cycloalkyl)-Ci-C_6-alkyl; or

R^{1a} and R^{1b} together with the N atom to which they are attached form N=S(=0)O-$_2$(C_1-C6-alkyl)$_2$;

T is an aryl or a heteroaryl ring or a fused or a bicyclic aryl or heteroaryl ring or ring system;

R^2 is selected from the group consisting of hydrogen, halogen, cyano, nitro, G-G, -alkyl. Ci-Ce-haloalkyl, and C3-C6-cycloalkyl;

R^8 is selected from the group consisting of the group consisting of hydroxy, Cl and OR^7;

m is an integer 0 to 6; and

R^3, R^4, R^7, A, n, p, and Q are each as defined in claim 1.

15. The process as claimed in claims 1 and 14, wherein

R^{1a} is hydrogen; R^{1b} is selected from the group consisting of hydrogen, G-G, -alkyl and (C3-C6-cycloalkyl)-Ci-C_6-alkyl;

R^2 is selected from the group consisting of halogen, cyano, and G-G, -alkyl:

R^3 is Ci-Ce-haloalkyl;

R^4 is X;

R^5 is CX_3 or $C(=0)W^2R^7$,

wherein, R^7 is selected from the group consisting of hydrogen, G-G,-alkyl. C3-C6-cycloalkyl, aryl and arylalkyl groups;

W^1 and W^2 are O;

LGi is X;

LG_2 is X or OR^{12}; R^{12} is Ci-C_6-alkyl;

LG_3 is hydrogen or alkali metal;

A is N;

Q is a 3-, 4- or 5 membered heterocyclic ring;

T is a phenyl ring;

Y is X;

n is an integer 1;

m is an integer 2;

p is an integer 1 or 2; and

each X is independently F, Cl, Br or I.

16. The process as claimed in claims 1 and 14, wherein

R^{1a} is hydrogen; R^{1b} is Ci-Ce-alkyl;

R^2 is selected from the group consisting of Cl, cyano, and methyl;

R^3 is trifluoro methyl;

R^4 is Cl;

R^5 is CCl_3, CBr_3, $C(=0)W^2CH_3$, or $C(=0)W^2C_2¾$,

W^1 and W^2 are O;

LGi is Cl, Br or I;

LG_2 is Cl, Br, I, OCH_3 or $OC_2¾$;

LG_3 is alkali metal;

A is N;

Q is a tetrazole ring;

T is a phenyl ring;

Y is Cl;

n is an integer 1;

m is an integer 2; and

p is an integer 1.

17. The process as claimed in claim 6, wherein

R^3 is Ci-Ce-haloalkyl;

R^4 is X;

R^5 is CX_3 or $C(=0)W^2R^7$,

wherein, R^7 is selected from the group consisting of hydrogen, Ci-C_6-alkyl. C_3-Ce-cycloalkyl, aryl and arylalkyl;

W^1 and W^2 are O;

LGi is X;

LG_2 is X or OR^{12}; R^{12} is Ci-C_6-alkyl;

LG_3 is hydrogen or alkali metal;

A is N;

Q is a 3-, 4- or 5 membered heterocyclic ring;

n is an integer 1;

p is an integer 1 or 2; and

each X is independently F, Cl, Br or I.

18. The process as claimed in claim 6, wherein

R^3 is trifluoro methyl;

R^4 is Cl;

R^5 is $CC1_3$, CBr_3, $C(=0)W^2CH_3$, or $C(=0)W^2G¾$,

W^1 and W^2 are O;

LGi is Cl, Br or I;

LG_2 is Cl, Br, I, OCH_3 or $OC_2¾$;

LG_3 is alkali metal;

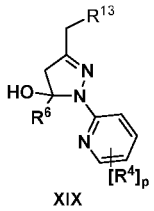
A is N;

Q is a tetrazole ring;

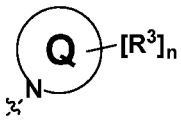
n is an integer 1; and

p is an integer 1.

19. A compound of formula XIX,



XIX

wherein, R^{13} is 

or LGi; R^3, R^4, R^6, n, p, and Q are each as defined in claim 1,

with the proviso that when R^{13} is LGi then R^6 is CX_3, wherein LGi is Cl, Br or I; and X is F, Cl, Br, or I.

20. The compound as claimed in claim 19, wherein

R^6 is CX_3 or $C(=0)W^2R^7$,

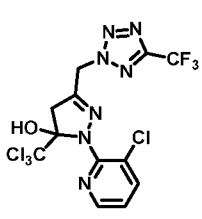
wherein, R^7 is selected from the group consisting of hydrogen, G-G, -alkyl. G-G,-cycloalkyl, aryl and arylalkyl;

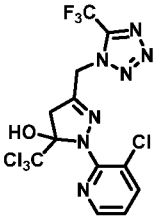
W^2 is O; R^3 is G-G.-haloalkyl: R^4 is X; n is an integer 1; Q is a 5 membered heterocyclic ring; A is N; p is an integer 1 or 2; and each X is independently F, Cl, Br or I.

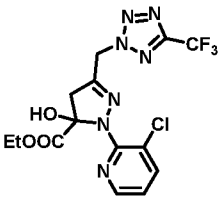
21. The compound as claimed in claim 19, wherein

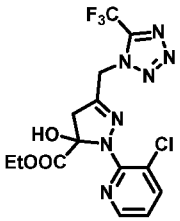
R^6 is $CC1_3$, CBr_3, $C(=0)W^2CH_3$, $C(=0)W^2C_2¾$; W^2 is O; R^3 is trifluoro alkyl; R^4 is Cl; n is an integer 1; Q is a tetrazole ring; A is N; p is an integer 1 and LGi is Cl or Br.

22. The compound as claimed in claim 19, wherein the compound of formula XIX is selected from the group consisting of:

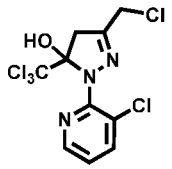

IIA-1


IIA-2


IIA-3

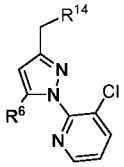

IIA-4

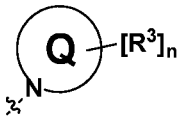
and

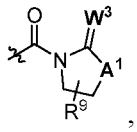

XVIII-1

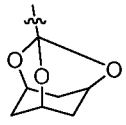
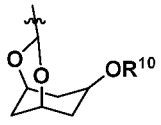
.

23. A compound of formula XX,


XX

wherein, R^{14} is  or LG_1 or hydrogen;

R^6 is CX_3, $C(W^4R^7)_3$, $CH(W^4R^7)_2$, allylic group, substituted or unsubstituted furanyl,  ,

 , and  ;

R^3, R^4, R^7, R^9, R^{10}, LGi, A, A^1, n, p, Q, W^3, W^4, X and the substituents on furanyl are each as defined in claim 1,

with the proviso that when R^{14} is LGi or hydrogen then R^6 is CX_3, wherein LGi and X are Cl, Br, or I.

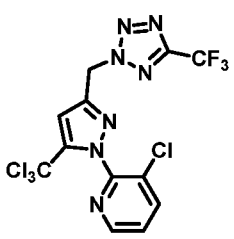
24. The compound as claimed in claim 23, wherein

R^6 is CX3, R^3 is Ci-Ce-haloalkyl; n is an integer 1; Q is a 5 membered heterocyclic ring; A is N; R^4 is X; p is an integer 1 or 2.

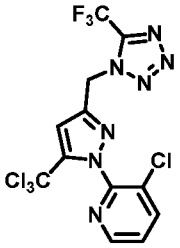
25. The compound as claimed in claim 23, wherein

R^6 is CCl_3 or CBr3; R^3 is trifluoro alkyl; n is an interger 1; Q is a tetrazole ring; A is N; R^4 is Cl; p is an integer 1, and LGi is Cl or Br.

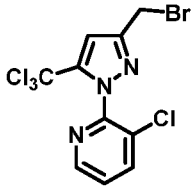
26. The compound as claimed in claim 23, wherein the compound of formula XX is selected from the group consisting of:



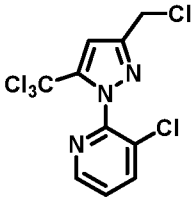
IIB-1



IIB-2

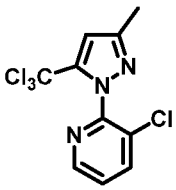


XIV-1



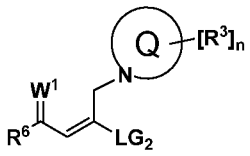
XIV-2

and



XV-1 .

27. A compound of formula III,



III ;

wherein, Q is a 3-, 4- or 5 membered heterocyclic ring excluding triazole ring; R^3, R^6, n, W^1, and LG2 are each as defined in claim 1.

28. The compounds of formula III as claimed in claim 27, wherein

R^6 is CX_3 or $C(=0)W^2R^7$,

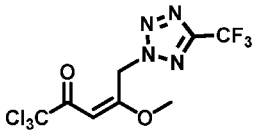
wherein, R^7 is selected from the group consisting of hydrogen, Ci-Ce-alkyl, C3-C6-cycloalkyl, aryl and arylalkyl;

W^1 and W^2 are O; LG_2 is X or OR^{12}; R^{12} is Ci-Ce-alkyl; R^3 is Ci-Ce-haloalkyl; n is an integer 1; Q is a 5 membered heterocyclic ring excluding triazole ring; and each X is independently F, Cl, Br or I.

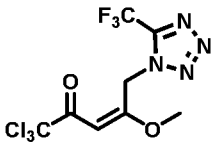
29. The compounds of formula III as claimed in claim 27, wherein

R^6 is CCT, CBr_3, $C(=0)W^2CH_3$, $C(=0)W^2C_2¾$; W^1 and W^2 are O; LG_2 is Cl, Br, I, OCH_3, or OC_2H_5; R^3 is trifluoro alkyl; n is an integer 1; and Q is a tetrazole ring.

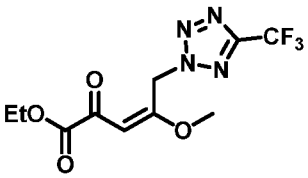
30. The compound as claimed in claim 27, wherein the compound of formula III is selected from the group consisting of:



III-1

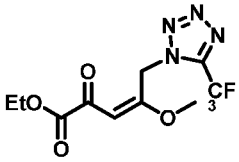


III-2



III-3

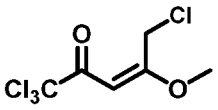
and



III-4

.

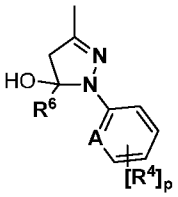
31. A compound of formula IV-2:



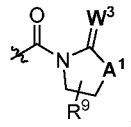
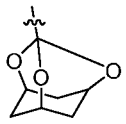
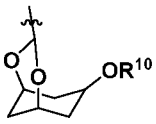
IV-2

.

32. A compound of formula XVI,



XVI

wherein, R^6 is CX_3, $C(W^4R_7)_3$, $CH(W^4R_7)_2$, allylic group, substituted or unsubstituted furanyl,  ,  , and  ; A is N; and R^4, R^7, R^9, R^{10}, A^1, p, W^3, W^4, and X are each as defined in claim 1.

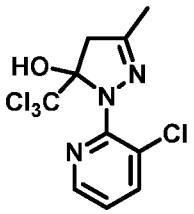
33. The compound of formula XVI as claimed in claim 32, wherein

R^6 is CX3; A is N; R^4 is X; p is an integer 1 or 2; and each X is independently F, Cl, Br or I.

34. The compound of formula XVI as claimed in claim 32, wherein

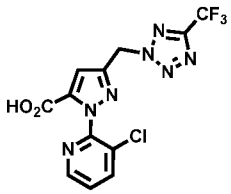
R^6 is CCl_3 or CBr3; A is N; R^4 is Cl; and p is an integer 1.

35. The compound as claimed in claim 32, wherein the compound of formula XVI is XVI-1:



XVI-1

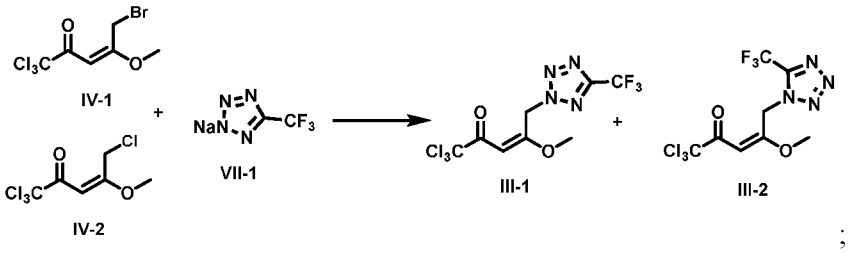
36. A process for preparing a compound of formula II-1



11-1

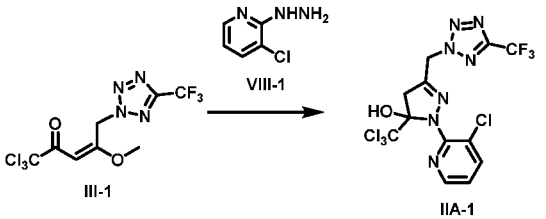
said process comprising the steps of:

a. reacting a compound of formula IV-l or IV-2 with a compound of formula VII-1 in the presence of one or more suitable solvent and optionally, one or more suitable catalyst and or reagent to obtain a mixture of a compound of formula III-1 and a compound of formula III-2,

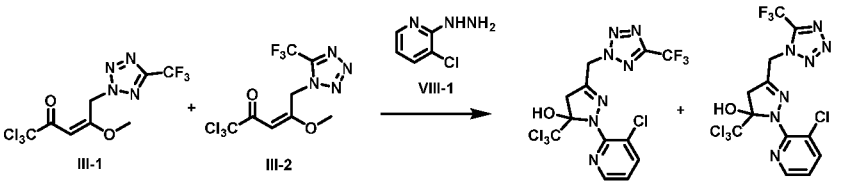


IV-1 + IV-2 + VII-1 → III-1 + III-2;

b. cyclizing the compound of formula III-1, or the compound of formula III-1 and the compound of formula III-2 in the mixture, with a hydrazine of formula VIII-1 in one or more suitable solvent and optionally, one or more suitable reagent to obtain a compound of formula IIA-l or the mixture of the compound of formula IIA-1 and a compound of formula IIA-2 respectively,

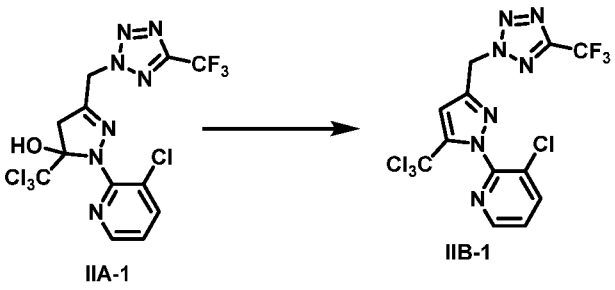


, or

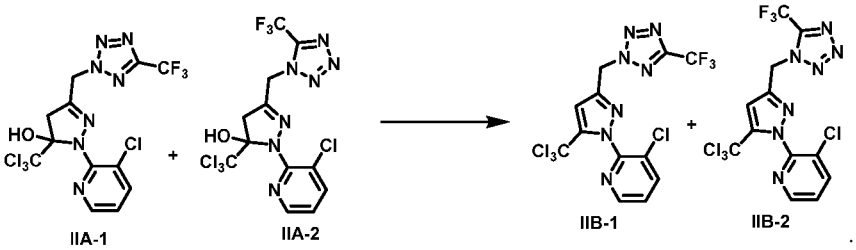


;

c. eliminating water from the compound of formula IIA-l, or the compound of formula IIA-l and the compound of formula IIA-2 in the mixture, by using one or more suitable dehydrating reagent in one or more suitable solvent to obtain a compound of formula IIB-l or the mixture of the compound of formula IIB-1 and a compound of formula IIB-2 respectively,

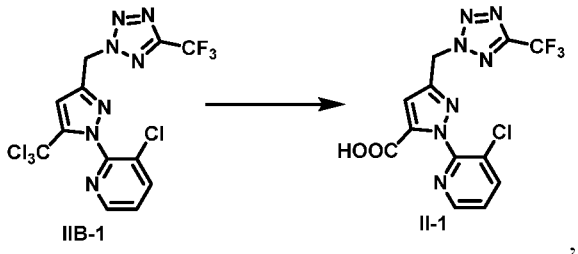


, or

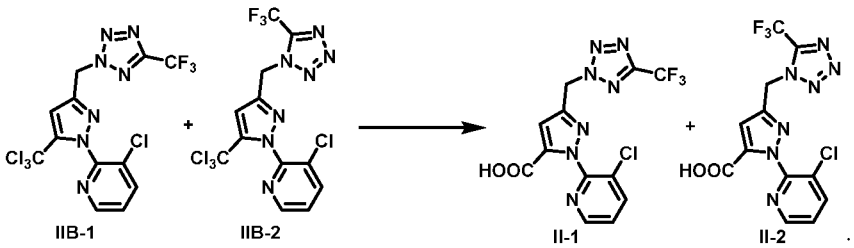


; and

d. converting the compound of formula IIB-l, or the compound of formula IIB-l and the compound of formula IIB-2 in the mixture, into the compound of formula II-1 or the mixture of the compound of formula II-1 and a compound of formula II-2 respectively, using one or more suitable reagent in one or more suitable solvent and optionally, one or more suitable catalyst,



, or



;

and

wherein, the compound of formula III-1 or the mixture of the compounds of formula III-1 and III-2 obtained in step (a), the compound of formula IIA-l or the mixture of the compounds of formula IIA-l and IIA-2 obtained in step (b) and the compound of formula IIB-l or the mixture of the compounds of formula IIB-1 and IIB-2 obtained in step (c) may or may not be isolated.

37. The process as claimed in claim 36, wherein

i. the suitable solvent in the process step (a) is selected from the group consisting of acetone, acetonitrile, methyl tert-butyl ether, ethyl acetate, dioxane, tetrahydrofuran, 1,2-dimethoxyether;

ii. the suitable catalyst in the process step (a) is potassium iodide; and

iii. the process step (a) is performed within a temperature range from 50 °C to 80 °C.

38. The process as claimed in claim 36, wherein

i. the suitable solvent in the process step (b) is selected from the group consisting of acetone, acetonitrile, ethyl alcohol, acetic acid, methyl tert-butyl ether, dichloroethane, dichloromethane, dioxane, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, ethyl acetate, tetrahydrofuran, l,2-dimethoxyether, toluene, xylene and N-methyl-2-pyrrolidone;;

ii. the suitable reagent in the process step (b) is selected from the group consisting of acetic acid, trifluoroacetic acid, and hydrochloric acid; and

iii. the process step (b) is performed within a temperature range from 20 °C to 50 °C.

39. The process as claimed in claim 36, wherein

i. the suitable solvent in the process step (c) is selected from the group consisting of acetonitrile, methyl tert-butyl ether, dichloromethane, dioxane, thionyl chloride, acetic acid, methyl alcohol, ethyl alcohol, tetrahydrofuran, isopropyl alcohol and tert-butyl alcohol;

ii. the suitable dehydrating reagent in the process step (c) is selected from the group consisting of sulphuric acid, trifluoroacetic acid, thionyl chloride, oxalyl chloride, methanolic hydrochloric acid, hydrogen chloride gas, acetic acid, hydrogen bromide, triflic acid, methanesulfonic acid, p-toluenesulfonic acid, hydrogen chloride-1,4-dioxane and silica gel; and

iii. the process step (c) is performed within a temperature range from 20 °C to 80 °C.

40. The process as claimed in claim 36, wherein

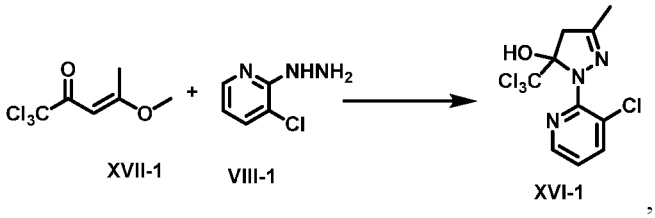
i. the suitable solvent in the process step (d) is selected from the group consisting of water, acetonitrile, dioxane, acetic acid, sulphuric acid, methyl alcohol, ethyl alcohol, tetrahydrofuran, isopropyl alcohol and tert-butyl alcohol;

ii. the suitable reagent in the process step (d) is an acid selected from the group consisting of sulphuric acid, hydrochloric acid, and acetic acid; and

iii. the process step (d) is performed within a temperature range from 50 °C to 120 °C.

41. The process as claimed in claim 36, wherein the compound of formula IIB-1 is alternatively obtained by the process comprising the steps of:

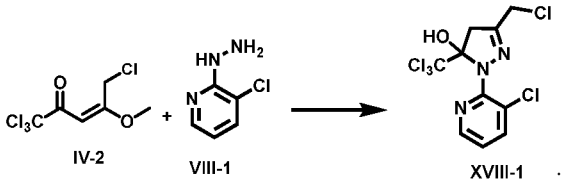
i. cyclizing a compound of formula XVII-1 with the hydrazine of formula VIII-1 in one or more suitable solvent and optionally, one or more suitable reagent to obtain a compound of formula XVI-l,



XVII-1 VIII-1 XVI-1 ,

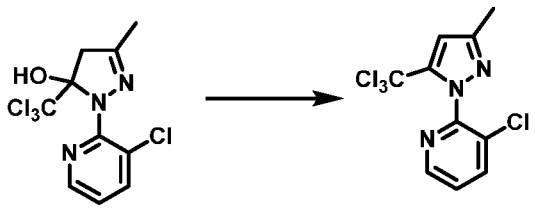
or

cyclizing the compound of formula IV-2 and the hydrazine of formula VIII-1 in one or more suitable solvent and optionally, one or more suitable reagent to obtain a compound of formula XVIII-1,



IV-2 VIII-1 XVIII-1 ;

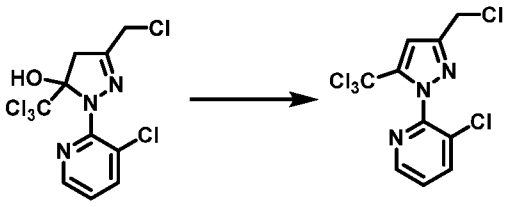
ii. eliminating water from the compound of formula XVI-1 by using one or more suitable dehydrating reagent in one or more suitable solvent to obtain a compound of formula XV-1;



XVI-1 XV-1

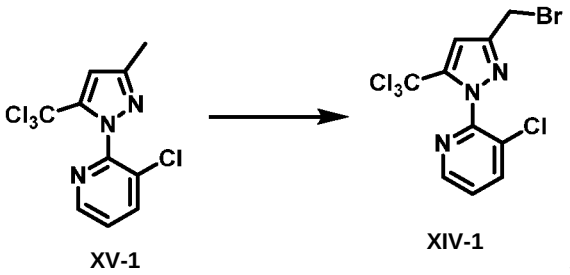
or

eliminating water from the compound of formula XVIII by using one or more suitable dehydrating reagent in one or more suitable solvent to obtain a compound of formula XIV,



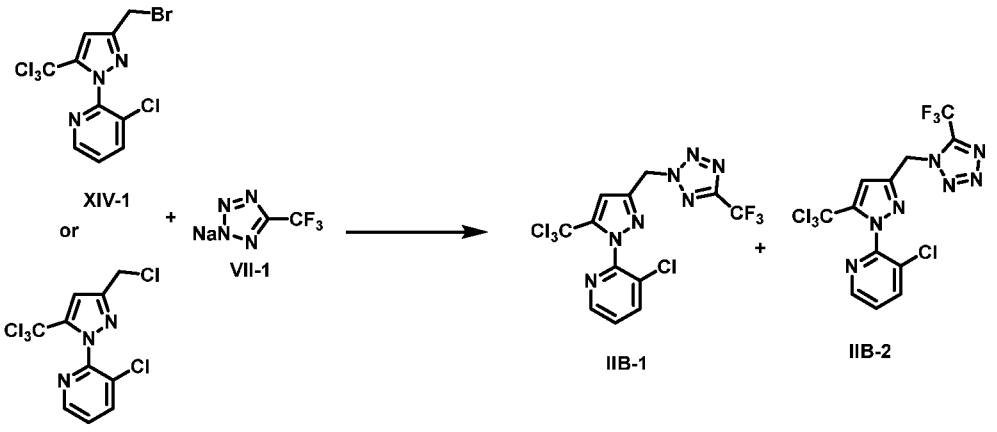
XVIII-1 XIV-2 ;

iii. halogenating the compound of formula XV-1 using a suitable halogenating agent in one or more suitable solvent and optionally, one or more radical initiator to obtain a compound of formula XIV-1,



XV-1 XIV-1 ; and

iv. obtaining the compound of formula IIB-l or a mixture of the compound of formula IIB-l and a compound of formula IIB-2 by reacting the compound of formula XIV-1 or XIV-2 with the compound of formula VII-1,



XIV-2 ,

wherein, the compounds of formula XVI-1 and XVIII-1 obtained in step (i), the compounds of formula XV-1 and XIV-2 obtained in step (ii) and the compound XIV-1 obtained in step (iii) may or may not be isolated.

42. The process as claimed in claim 41, wherein

i. the suitable solvent in the process step (i) is selected from the group consisting of acetone, acetonitrile, ethyl alcohol, acetic acid, methyl tert-butyl ether, dichloroethane, dichloromethane, dioxane, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, ethyl acetate, tetrahydrofuran, l,2-dimethoxyether, toluene, xylene and N-methyl-2-pyrrolidone;;

ii. the suitable reagent in the process step (i) is selected from the group consisting of acetic acid, trifluoroacetic acid, and hydrochloric acid; and

iii. the process step (i) is performed within a temperature range from 20 °C to 50 °C.

43. The process as claimed in claim 41, wherein

i. the suitable solvent in the process step (ii) is selected from the group consisting of acetonitrile, methyl tert-butyl ether, dichloromethane, dioxane, thionyl chloride, acetic acid, methyl alcohol, ethyl alcohol, tetrahydrofuran, isopropyl alcohol and tert-butyl alcohol;

ii. the suitable dehydrating reagent in the process step (ii) is selected from the group consisting of sulphuric acid, trifluoroacetic acid, thionyl chloride, oxalyl chloride, methanolic hydrochloric acid, hydrogen chloride gas, acetic acid, hydrogen bromide, triflic acid, methanesulfonic acid, p-toluenesulfonic acid, hydrogen chloride- l,4-dioxane and silica gel; and

iv. the process step (ii) is performed within a temperature range from 20 °C to 80 °C.

44. The process as claimed in claim 41, wherein

i. the suitable solvent in the step (iii) is selected from the group consisting of acetonitrile, and ethanol;

ii. the halogenating agent in the step (iii) is selected from the group consisting of N-chlorosuccinimide, N-bromosuccinimide and I¾ ;

iii. the radical initiator in the step (iii) is selected from the group consisting of dibenzoyl peroxide, hydrogen peroxide, azobisisobutyronitrile, peracetic acid, metachloroperbenzoic acid, trifluoroperacetic acid, trichloroperacetic acid; and

iv. the step (iii) is performed within a temperature range from 30 °C to 100 °C.

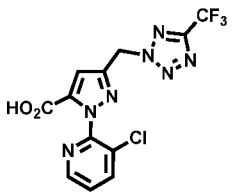
45. The process as claimed in claim 41, wherein

i. the suitable solvent in the step (iv) is selected from the group consisting of acetonitrile, and ethanol;

ii. the catalyst in the step (iv) is potassium iodide; and

iii. the step (iv) is performed within a temperature range from 30 °C to 100 °C.

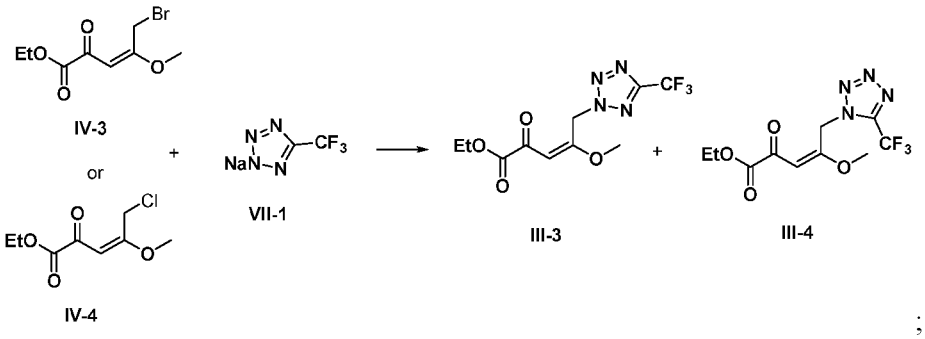
46. A process for preparing a compound of formula II- 1



M-1

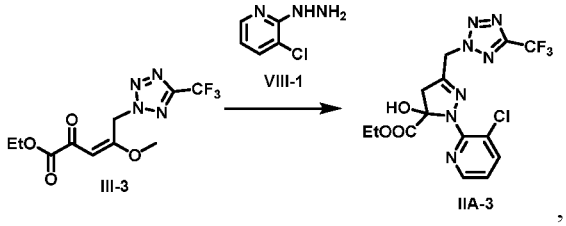
said process comprising the steps of:

a. reacting a compound of formula IV-3 or IV-4 with a compound of formula VII-1 in the presence of one or more suitable solvent and optionally, one or more suitable catalyst and or reagent to obtain a mixture of a compound of formula III-3 and a compound of formula III-4 ,

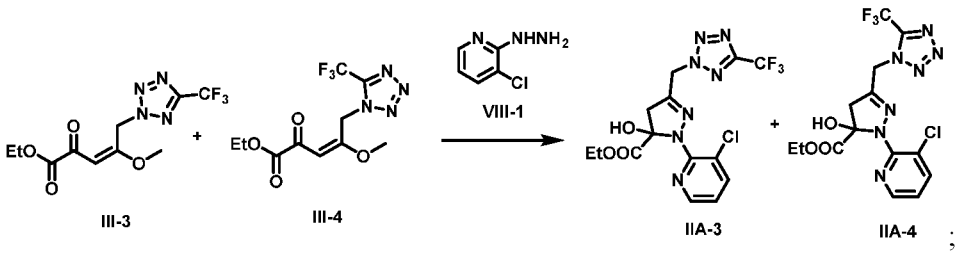


;

b. cyclizing the compound of formula III-3, or the compound of formula III-3 and the compound of formula III-4 in the mixture, with a hydrazine of formula VIII-1 in one or more suitable solvent and optionally, one or more suitable reagent to obtain a compound of formula IIA-3 or the mixture of the compound of formula IIA-3 and a compound of formula IIA-4 respectively,



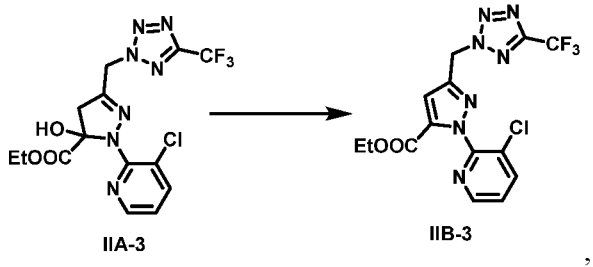
, or



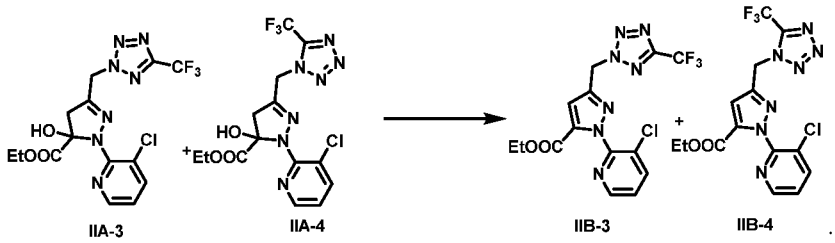
;

c. eliminating water from the compound of formula IIA-3, or the compound of formula IIA-3 and the compound of formula IIA-4 in the mixture, by using one or more suitable dehydrating reagent in one

or more suitable solvent to obtain a compound of formula IIB-3 or the mixture of the compound of formula IIB-3 and a compound of formula IIB-4 respectively,

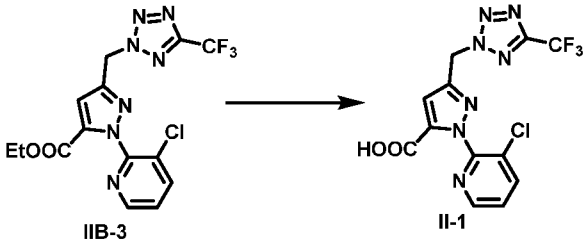


, or

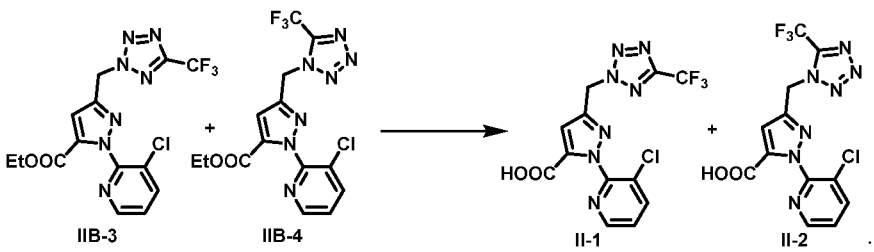


; and

d. converting the compound of formula IIB-3, or the compound of formula IIB-3 and the compound of formula IIB-4 in the mixture, into the compound of formula II-1 or the mixture of the compound of formula II-1 and a compound of formula II-2 respectively, using one or more suitable reagent in one or more suitable solvent and optionally, one or more suitable catalyst,



, or



;

and

wherein, the compound of formula III-3 or the mixture of the compounds of formula III-3 and III-4 obtained in step (a), the compound of formula IIA-3 or the mixture of the compounds of formula IIA-3 and IIA-4 obtained in step (b) and the compound of formula IIB-3 or the mixture of the compounds of formula IIB-3 and IIB-4 obtained in step (c) may or may not be isolated.

47. The process as claimed in claim 46, wherein

i. the suitable solvent in the process step (a) is selected from the group consisting of acetone, acetonitrile, methyl tert-butyl ether, ethyl acetate, dioxane, tetrahydrofuran, 1,2-dimethoxyether;

ii. the suitable catalyst in the process step (a) is potassium iodide; and

iii. the process step (a) is performed within a temperature range from 50 °C to 80 °C.

48. The process as claimed in claim 46, wherein

i. the suitable solvent in the process step (b) is selected from the group consisting of acetone, acetonitrile, ethyl alcohol, acetic acid, methyl tert-butyl ether, dichloroethane, dichloromethane, dioxane, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, ethyl acetate, tetrahydrofuran, l,2-dimethoxyether, toluene, xylene and N-methyl-2-pyrrolidone;;

ii. the suitable reagent in the process step (b) is selected from the group consisting of acetic acid, trifluoroacetic acid, and hydrochloric acid; and

iii. the process step (b) is performed within a temperature range from 20 °C to 50 °C.

49. The process as claimed in claim 46, wherein

i. the suitable solvent in the process step (c) is selected from the group consisting of acetonitrile, methyl tert-butyl ether, dichloromethane, dioxane, thionyl chloride, acetic acid, methyl alcohol, ethyl alcohol, tetrahydrofuran, isopropyl alcohol and tert-butyl alcohol;

ii. the suitable dehydrating reagent in the process step (c) is selected from the group consisting of sulphuric acid, trifluoroacetic acid, thionyl chloride, oxalyl chloride, methanolic hydrochloric acid, hydrogen chloride gas, acetic acid, hydrogen bromide, triflic acid, methanesulfonic acid, p-toluenesulfonic acid, hydrogen chloride- l,4-dioxane and silica gel; and

iii. the process step (c) is performed within a temperature range from 20 °C to 80 °C.

50. The process as claimed in claim 46, wherein

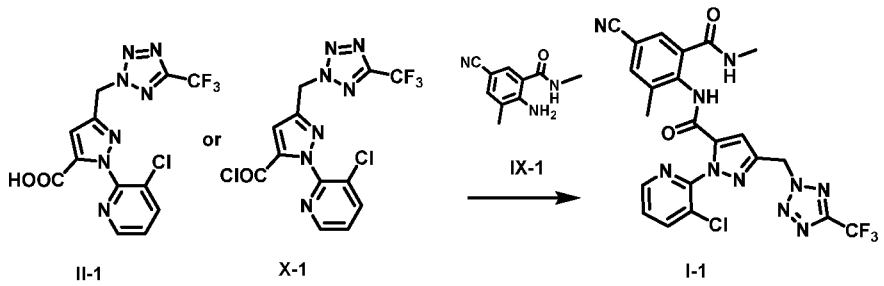
i. the suitable solvent in the process step (d) is selected from the group consisting of water, acetonitrile, dioxane, acetic acid, sulphuric acid, methyl alcohol, ethyl alcohol, tetrahydrofuran, isopropyl alcohol and tert-butyl alcohol;

ii. the suitable reagent in the process step (d) is an acid selected from the group consisting of sulphuric acid, hydrochloric acid, and acetic acid; and

iii. the process step (d) is performed within a temperature range from 50 °C to 120 °C.

51. A process for preparing a compound of formula 1-1 form the compound of formula II-1 obtained by the process as claimed in claim 36, said process comprising the step of:

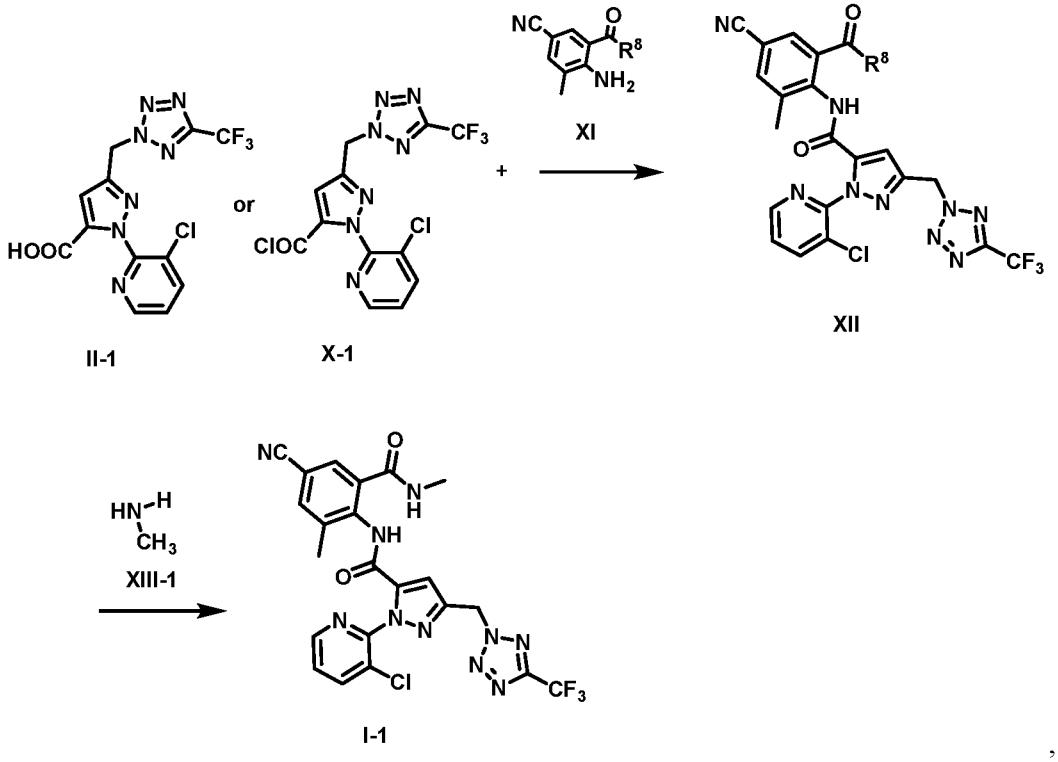
reacting the compound of formula II-1 optionally after converting into a compound of formula X-l with a compound of formula IX-1 to obtain the compound of formula 1-1,



II-1 X-1 I-1

or

reacting the compound of formula II-1 optionally after converting into a compound of formula X-1 with a compound of formula XI to obtain a compound of formula XII and reacting the compound of formula XII with amine XIII-1 to obtain the compound of formula 1-1,

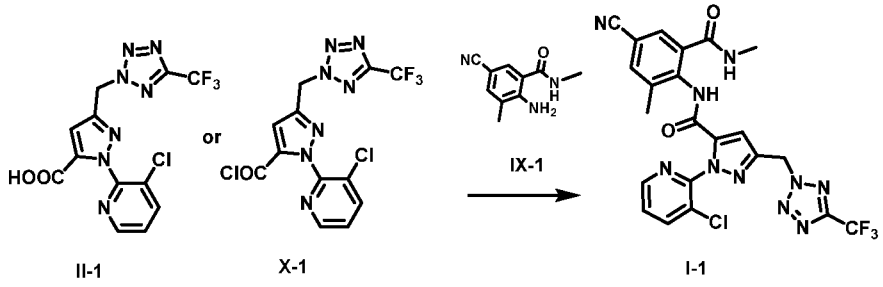


,

wherein, R^8 is hydroxy or Cl.

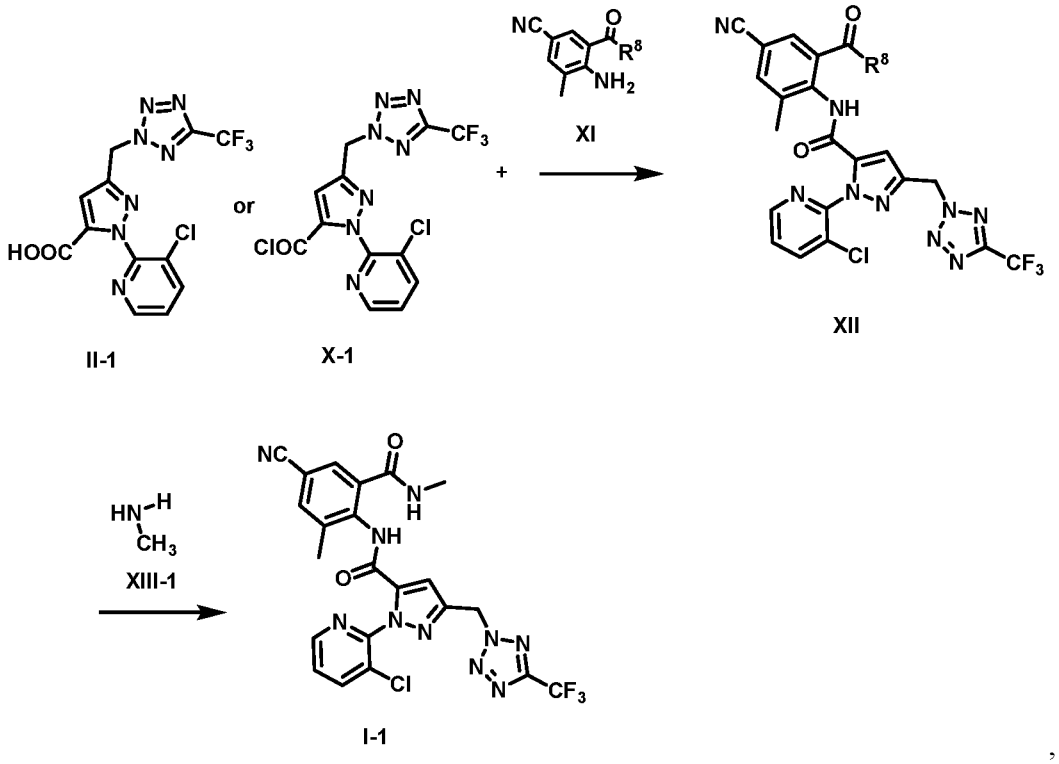
52. A process for preparing a compound of formula 1-1 form the compound of formula II-1 obtained by the process as claimed in claim 46, said process comprising the step of:

reacting the compound of formula II-1 optionally after converting into a compound of formula X-l with a compound of formula IX-1 to obtain the compound of formula 1-1,



or

reacting the compound of formula II-1 optionally after converting into a compound of formula X-1 with a compound of formula XI to obtain a compound of formula XII and reacting the compound of formula XII with amine XIII-1 to obtain the compound of formula 1-1,



wherein, R^8 is hydroxy or Cl.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2019/054120

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D401/14 C07D401/04 C07C49/255
ADD.

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

B. FIELDS SEARCHED

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

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

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

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 10 2006 032168 A1 (BAYER CROPSCIENCE AG [DE]) 20 December 2007 (2007-12-20) cited in the application	14-16, 23-26, 32-35, 51,52
A	Paragraph 36 ("Verfahren B")	1-13, 17-22, 27-31, 36-50

X	WO 2011/157664 A1 (BAYER CROPSCIENCE AG [DE]; PAZENOK SERGII [DE] ET AL.) 22 December 2011 (2011-12-22) cited in the application	14-16, 23-26, 32-35, 51,52
A	p. 14, bottom; example 3	1-13, 17-22, 27-31, 36-50

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"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

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"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	Date of mailing of the international search report
2 September 2019	06/09/2019

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	Fritz, Martin

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2019/054120

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