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INCREASING PLANT VIGOR

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority from U.S. Provisional Application 60/961,319, filed July 20, 2007.

FIELD OF THE INVENTION

The invention disclosed in this document is related to the field of pesticides, their use to control pests and their use to increase plant vigor.

BACKGROUND OF THE INVENTION

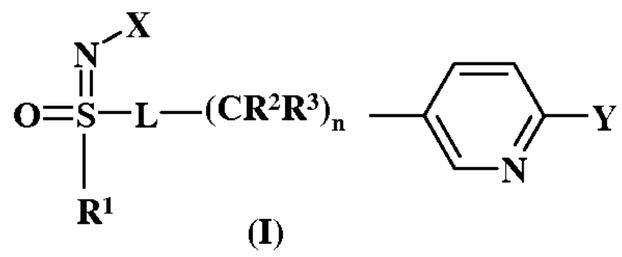
Pests cause millions of human deaths around the world each year. Furthermore, there are more than ten thousand species of pests that cause losses in agriculture. **These agricultural losses amount to billions of U.S. dollars each year**. Termites cause damage to various structures such as homes. **These termite damage losses amount to billions of U.S. dollars each year.** As final note, many stored food pests eat and adulterate stored food. **These stored food losses amount to billions of U.S. dollars each year, but more importantly, deprive people of needed food.**

There is an acute need for new pesticides. Insects are developing resistance to pesticides in current use. Hundreds of insect species are resistant to one or more pesticides. The development of resistance to some of the older pesticides, such as DDT, the carbamates, and the organophosphates, is well known. But resistance has even developed to some of the newer pesticides. Therefore, a need exists for new pesticides and particularly for pesticides that have

new modes of action. Furthermore, pesticides that can increase plant vigor are especially needed.

SUMMARY OF THE INVENTION

The invention concerns compounds of the formula (I)



(I)

wherein

X represents NO_2, CN or $COOR^4$;

L represents a single bond or R^1, S and L taken together represents a 4-, 5- or 6-membered ring;

R^1 represents (C_1-C_4) alkyl;

R^2 and R^3 independently represent hydrogen, methyl, ethyl, fluoro, chloro or bromo;

n is an integer from 0-3;

Y represents (C_1-C_4) haloalkyl; and

R^4 represents (C_1-C_3) alkyl.

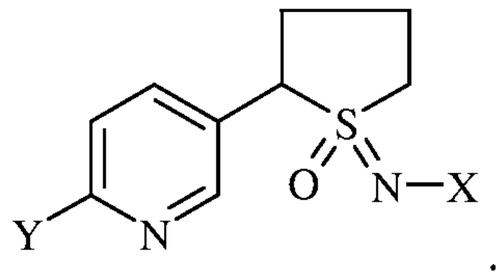
Preferred compounds of formula (I) include the following classes:

(1) Compounds of formula (I) wherein X is NO_2 or CN, most preferably CN.

(2) Compounds of formula (I) wherein Y is CF_3.

(3) Compounds of formula (I) wherein R^2 and R^3 independently represent hydrogen, methyl or ethyl.

(4) Compounds of formula (I) wherein R^1, S and L taken together form a saturated 5-membered ring, and n is 0, i.e., having the structure



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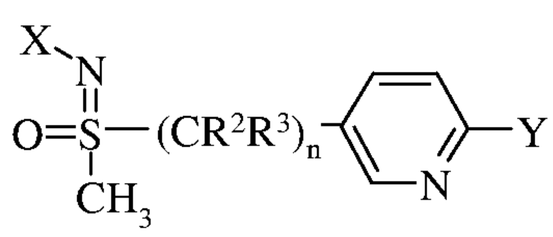
(5) Compounds of formula (I) wherein R^1 represents CH_3 and L represents a single bond, i.e., having the structure



wherein n=1-3, most preferably n=1.

It will be appreciated by those skilled in the art that the most preferred compounds are generally those which are comprised of combinations of the above preferred classes.

The invention also provides new processes for preparing compounds of formula (I) as well as new compositions and methods of use, which will be described in detail hereinafter.

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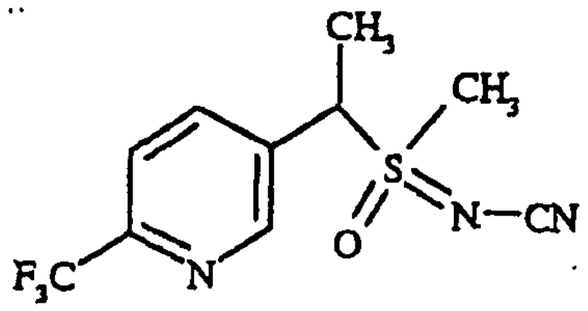
In one aspect, the invention provides a process to increase the weight of that portion of a plant that is above the ground said process comprising soaking a seed, which can germinate and begin to grow into said plant, in a solution that comprises a compound having the following formula



,

5

wherein said soaking occurs before said seed is planted.

DETAILED DESCRIPTION OF THE INVENTION

The compounds disclosed herein are disclosed in U.S. patent application serial number 11/704,842 filed on February 9, 2007, (publication no 2007-0203191A1).

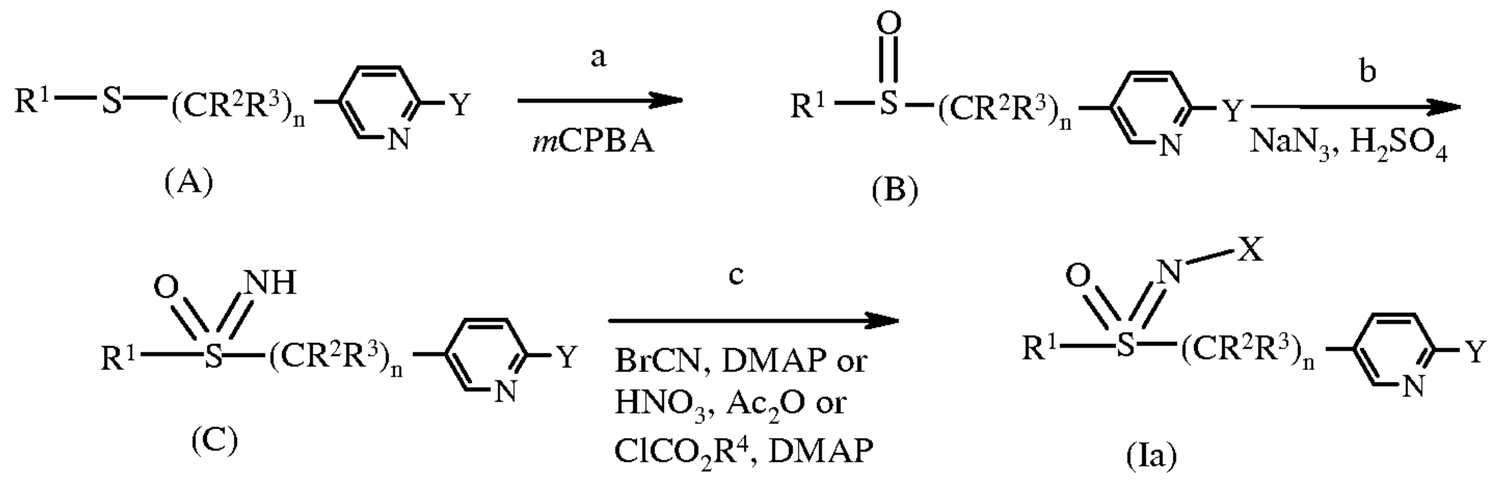
Throughout this document, all temperatures are given in degrees Celsius, and all percentages are weight percentages unless otherwise stated.

Unless specifically limited otherwise, the term alkyl (including derivative terms such as alkoxy), as used herein, include straight chain, branched chain, and cyclic groups. Thus, typical alkyl groups are methyl, ethyl, 1-methylethyl, propyl, 1,1-dimethylethyl, and cyclopropyl. The term haloalkyl includes alkyl groups substituted with from one to the maximum possible number of halogen atoms, all combinations of halogens included. The term halogen includes fluorine, chlorine, bromine and iodine, with fluorine being preferred.

The compounds of this invention can exist as one or more stereoisomers. The various stereoisomers include geometric isomers, diastereomers and enantiomers. Thus the compounds of the present invention include racemic mixtures, individual stereoisomers and optically active mixtures. It will be appreciated by those skilled in the art that one stereoisomer may be more active than the others. Individual stereoisomers and optically active mixtures may be obtained by selective synthetic procedures, by conventional synthetic procedures using resolved starting materials or by conventional resolution procedures.

The compounds of formula (Ia), wherein R^1, R^2, R^3, R^4, X, and Y are as previously defined and L is a single bond, can be prepared by the methods illustrated in Scheme A:

Scheme A



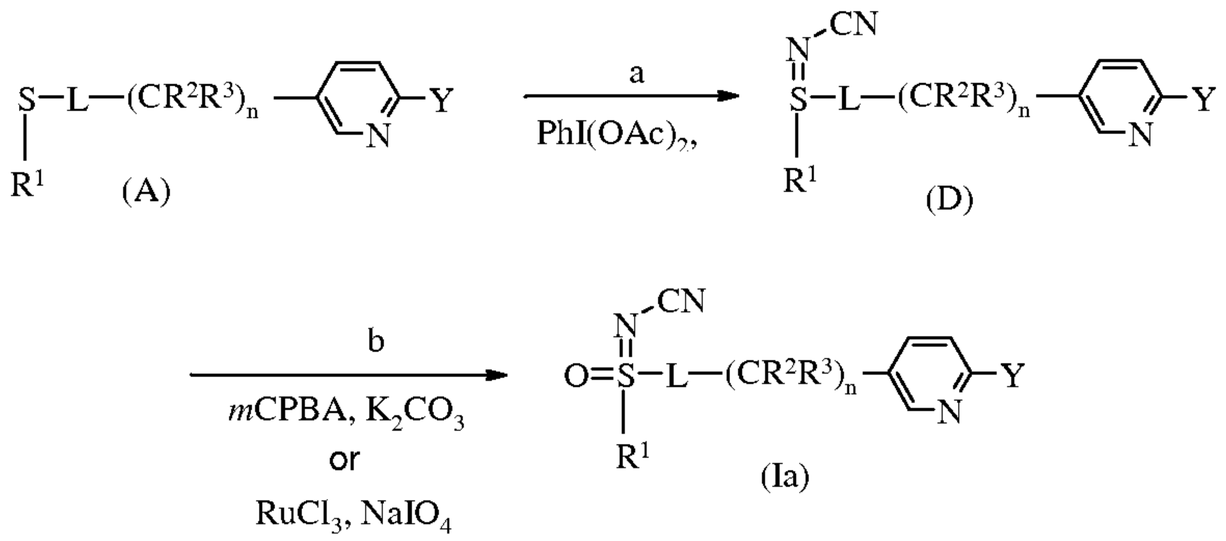
In step ***a*** of Scheme A, sulfide of formula (A) is oxidized with *meta*-chloroperoxybenzoic acid (*m*CPBA) in a polar solvent below 0 °C to provide sulfoxide of formula (B). In most cases, dichloromethane is the preferred solvent for oxidation.

In step ***b*** of Scheme A, sulfoxide (B) is iminated with sodium azide in the presence of concentrated sulfuric acid in an aprotic solvent under heating to provide sulfoximine of formula (C). In most cases, chloroform is the preferred solvent for this reaction.

In step ***c*** of Scheme A, the nitrogen of sulfoximine (C) can be either cyanated with cyanogen bromide in the presence of a base, or nitrated with nitric acid in the presence of acetic anhydride under mildly elevated temperature, or carboxylated with alkyl (R^4) chloroformate in the presence of base such as 4-dimethylaminopyridine (DMAP) to provide *N*-substituted sulfoximine (Ia). Base is required for efficient cyanation and carboxylation and the preferred base is DMAP, whereas sulfuric acid is used as catalyst for efficient nitration reaction.

The compounds of formula (Ia), wherein X represents CN and R^1, R^2, R^3, R^4 and Y are as previously defined, can be prepared by the mild and efficient method illustrated in Scheme B.

Scheme B



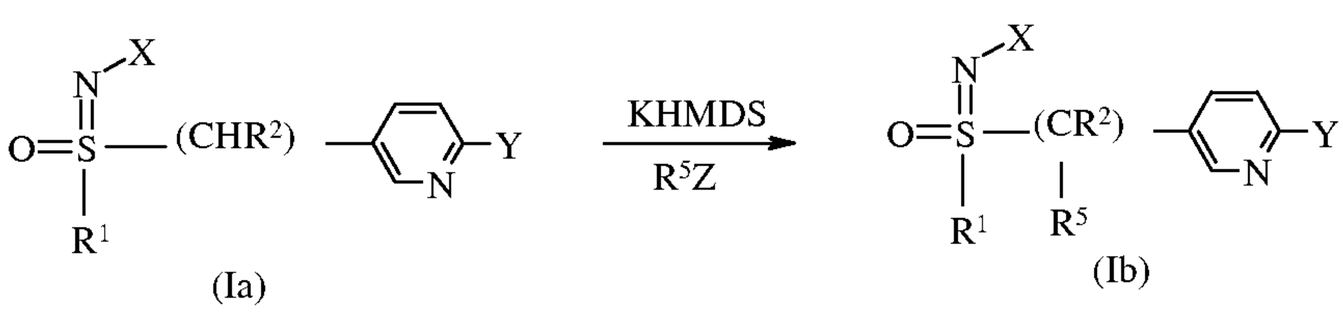
In step ***a*** of Scheme B, sulfide is oxidized with iodobenzene diacetate in the presence of cyanamide at 0 °C to give sulfilimine (D). The reaction can be carried out in a polar aprotic solvent like CH_2Cl_2.

In step ***b*** of Scheme B, the sulfilimine (D) is oxidized with *m*CPBA. A base such as potassium carbonate is employed to neutralize the acidity of *m*CPBA. Protic polar solvents such as ethanol and water are used to increase the solubility of the sulfilimine starting material and the base employed. The sulfilimine (**D**) can also be oxidized with aqueous sodium or potassium periodinate solution in the presence of catalyst ruthenium trichloride hydrate or similar catalyst. The organic solvent for this catalysis can be polar aprotic solvent such as CH_2Cl_2, chloroform, or acetonitrile.

The α-carbon of the *N*-substituted sulfoximine of formula (Ia), i.e., n=1, R^3 = H in the (CR^2R^3) group adjacent to the *N*-substituted sulfoximine function can be further alkylated or halogenated (R^5) in the presence of a base such as potassium hexamethyldisilamide (KHMDS) to give *N*-substituted sulfoximines of formula (Ib), wherein R^1, R^2, R^3, R^4, X, L and Y are as previously defined and Z is an appropriate leaving group, as illustrated in Scheme C. The preferred leaving

groups are iodide (R^5 = alkyl), benzenesulfonimide (R^5 = F), tetrachloroethene (R^5 = Cl), and tetrafluoroethene (R^5 = Br).

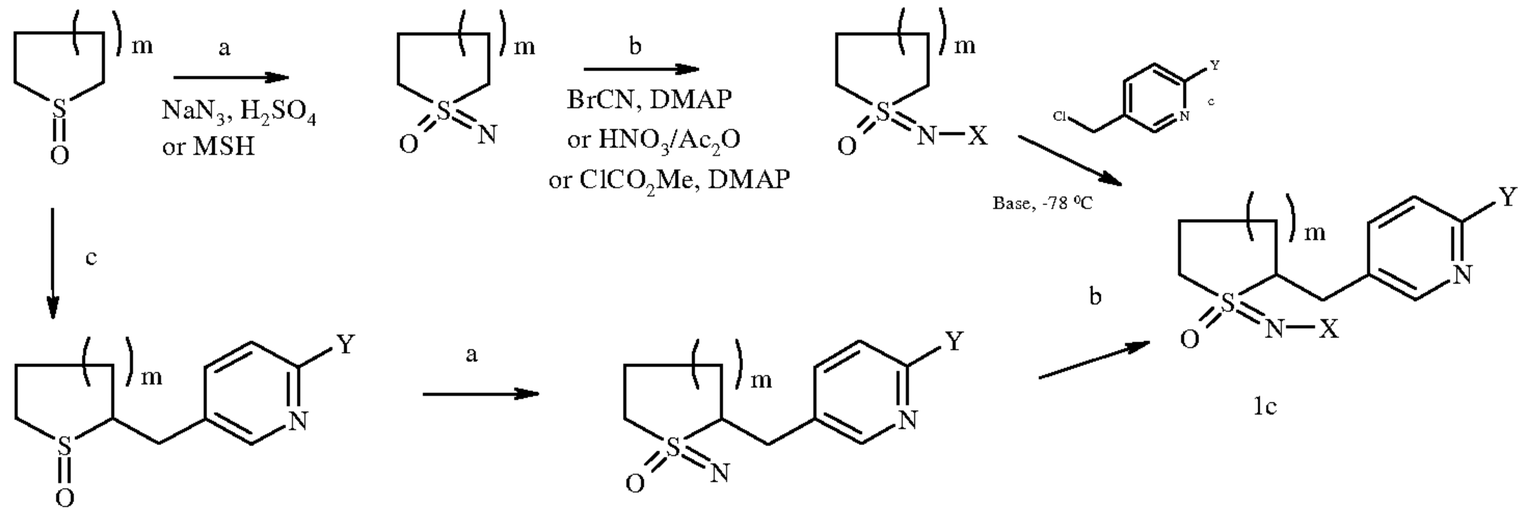
Scheme C



(Ia) (Ib)

Sulfoximine compounds of formula (Ic) wherein R^1, S and L taken together form a saturated 4-, 5- or 6-membered ring and n=1 can be prepared by the methods illustrated in Scheme D wherein X and Y are as previously defined and m is 0, 1, or 2.

Scheme D



In step ***a*** of Scheme D, which is similar to step ***b*** of Scheme A, sulfoxide is iminated with sodium azide in the presence of concentrated sulfuric acid or with *O*-mesitylsulfonylhydroxylamine in a polar aprotic solvent to provide sulfoximine. Chloroform or dichloromethane are the preferred solvents.

In step ***b*** of Scheme D, similar to step ***c*** of Scheme A, the nitrogen of sulfoximine can be either cyanated with cyanogen bromide, or nitrated with nitric acid followed by treatment with acetic anhydride under refluxing conditions, or

carboxylated with methyl chloroformate in the presence of base such as DMAP to provide *N*-substituted cyclic sulfoximine. Base is required for efficient cyanation and carboxylation and the preferred base is DMAP, whereas sulfuric acid is used as catalyst for efficient nitration reaction.

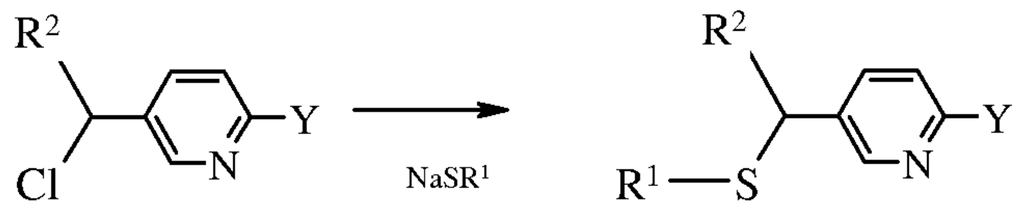
In step ***c*** of Scheme D, the α-carbon of *N*-substituted sulfoximine can be alkylated with a heteroaromatic methyl halide in the presence of a base such as KHMDS or butyl lithium (BuLi) to give the desired *N*-substituted sulfoximines. The preferred halide can be bromide, chloride or iodide.

Alternatively, the compounds of formula (Ic) can be prepared by a first α-alkylation of sulfoxides to give α-substituted sulfoxides and then an imination of the sulfoxide followed by *N*-substitution of the resulting sulfoximine by using the steps ***c*** , ***a*** and ***b*** respectively as described above for Scheme D.

The starting sulfides (A) in Scheme A can be prepared in different ways as illustrated in Schemes E, F G, H, I and J.

In Scheme E, the sulfide of formula (A_1), wherein R^1, R^2 and Y are as previously defined, n=1, and R^3 = H, can be prepared from the chloride of formula (E) by nucleophilic substitution with the sodium salt of an alkyl thiol.

Scheme E

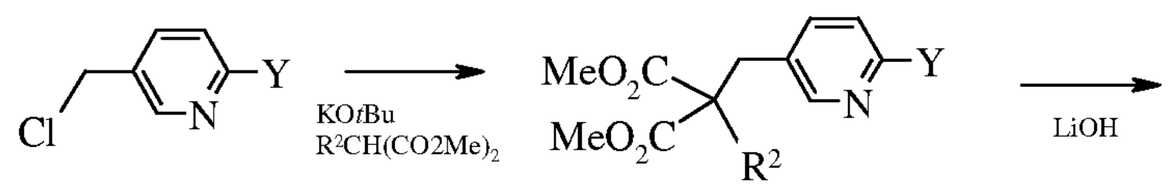


(E) (A_1)

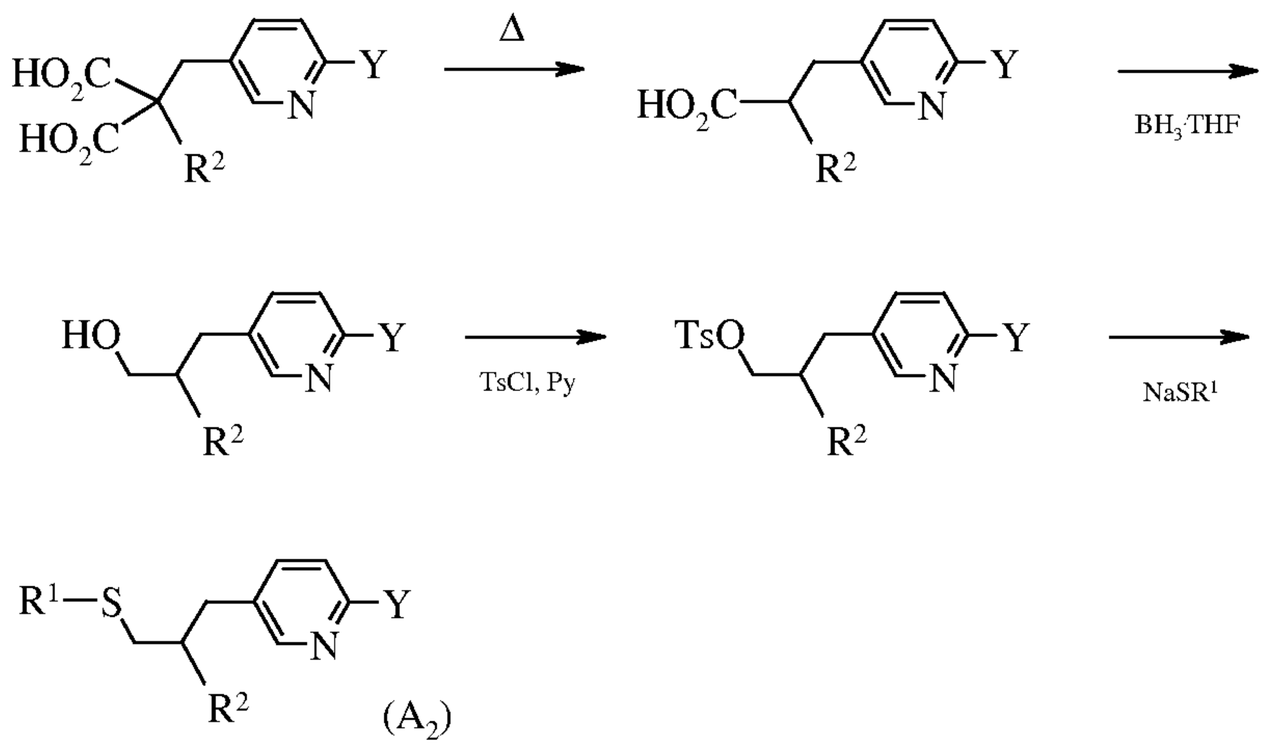
In Scheme F, the sulfide of formula (A_2), wherein R^1, R^2 and Y are as previously defined, n=3, and R^3 = H, can be prepared from the chloride of formula

(F) by reacting with a 2-mono substituted methyl malonate in the presence of base such as potassium *tert*-butoxide to provide 2,2-disubstitued malonate, hydrolysis under basic conditions to form a diacid, decarboxylation of the diacid by heating to give a monoacid, reduction of the monoacid with borane-tetrahyrofuran complex to provide an alcohol, tosylation of the alcohol with toluenesulfonyl chloride (tosyl chloride) in the presence of a base like pyridine to give a tosylate and replacement of the tosylate with the sodium salt of the desired thiol.

Scheme F



(F)

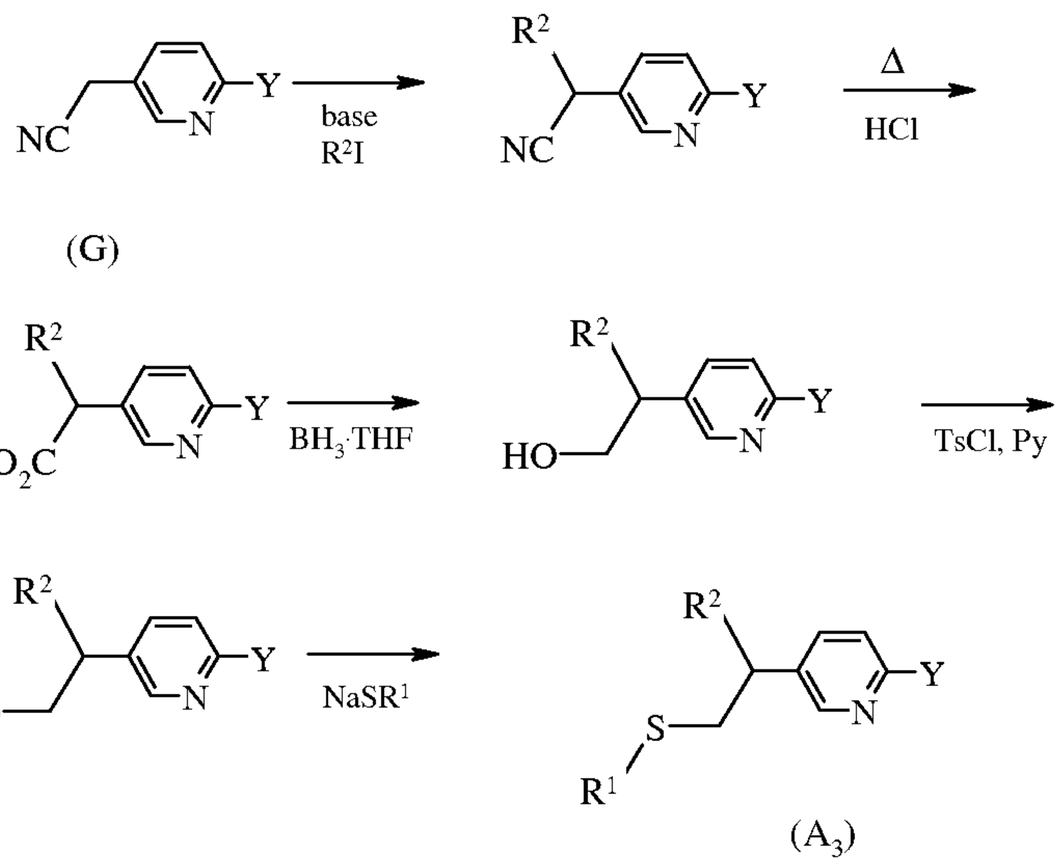


(A_2)

In Scheme G, the sulfide of formula (A_3), wherein R^1, R^2 and Y are as previously defined, n=2, and R^3 = H, can be prepared from the nitrile of formula (G) by deprotonation with a strong base and alkylation with an alkyl iodide to give α-alkylated nitrile, hydrolysis of the α-alkylated nitrile in the presence of a strong acid like HCl to give an acid, reduction of the acid with borane-tetrahyrofuran

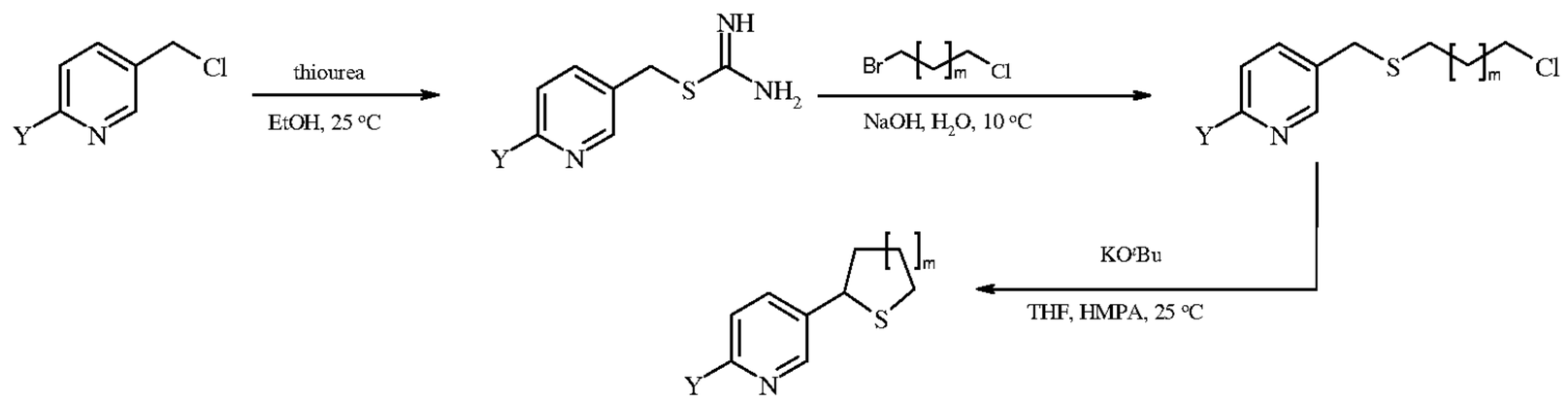
complex to provide an alcohol, tosylation of the alcohol with tosyl chloride in the presence of a base like pyridine to give a tosylate and replacement of the tosylate with the sodium salt of the desired thiol.

Scheme G



In Scheme H, the sulfide of formula (A_4), wherein R^1, S and L taken together represents a 4-, 5- or 6-membered ring (m = 0, 1, or 2) and n is 0 can be prepared from the corresponding substituted chloromethyl pyridine by treatment with thiourea, hydrolysis and subsequent alkylation with the appropriate bromo chloroalkane (m = 0, 1, or 2) under aqueous base conditions, and cyclization in the presence of a base like potassium-*t*-butoxide in a polar aprotic solvent such as THF.

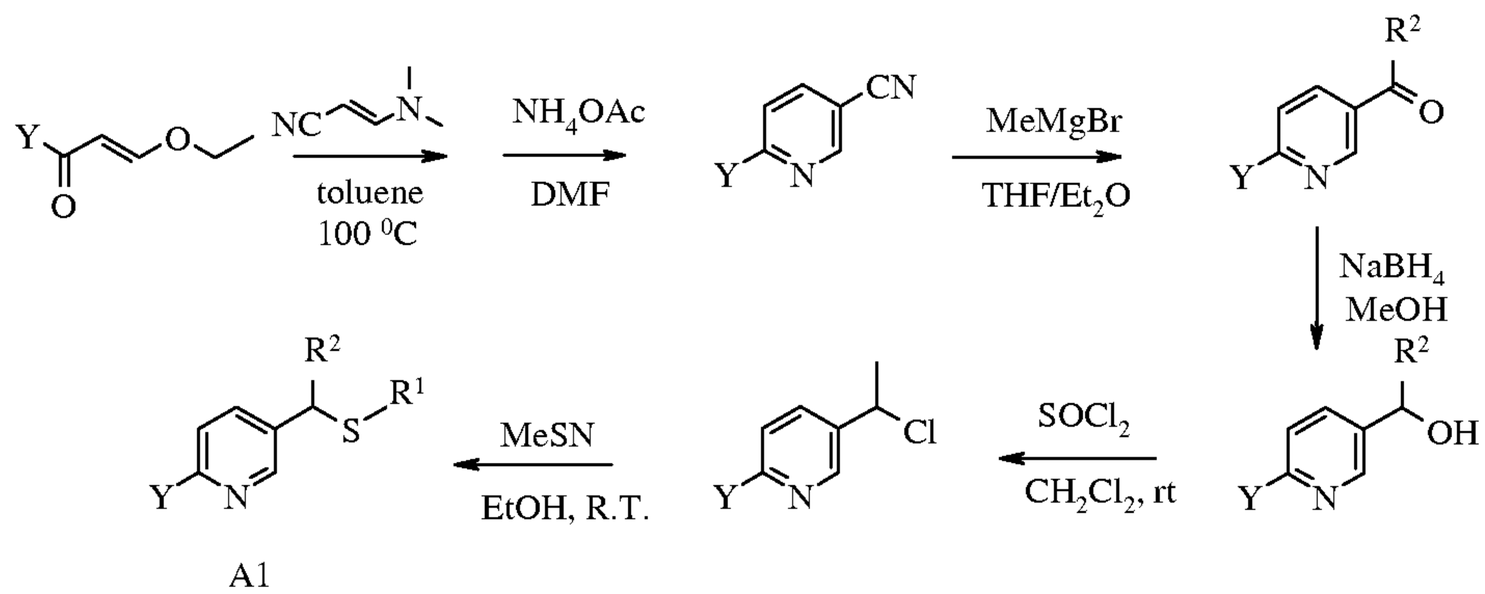
Scheme H



A_4 where n = 0, 1, 2

Sulfides of formula (A_1), wherein R^1, R^2 = CH_3, Y as previously defined, and R^3 = H, can be prepared alternatively via methods illustrated in Scheme I. Accordingly, the appropriate enone is coupled with dimethyl-aminoacrylonitrile and cyclized with ammonium acetate in DMF to yield the corresponding 6-substituted nicotinonitrile. Treatment with methylmagnesium bromide, reduction with sodium borohydride, chlorination with thionyl chloride, and nucleophilic substitution with the sodium salt of an alkyl thiol provide desired sulfides (A_1).

Scheme I

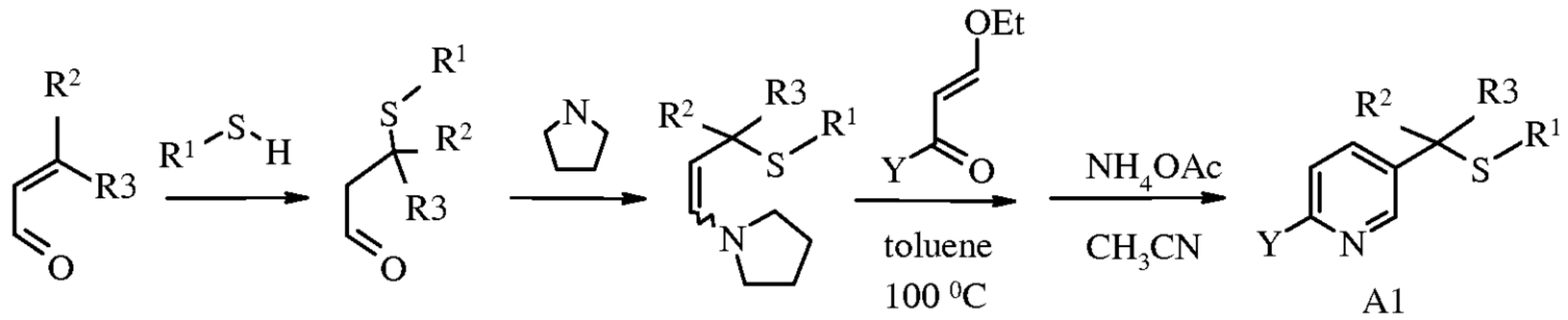


A1

Sulfides of formula (A_1), wherein R^1 = methyl or ethyl, R^2 and R^3 independently represent hydrogen, methyl or ethyl, and Y is as previously defined can be prepared via a variation of Scheme I, depicted in Scheme J, wherein enamines, formed from the addition of an amine, e.g., pyrrolidine, with the

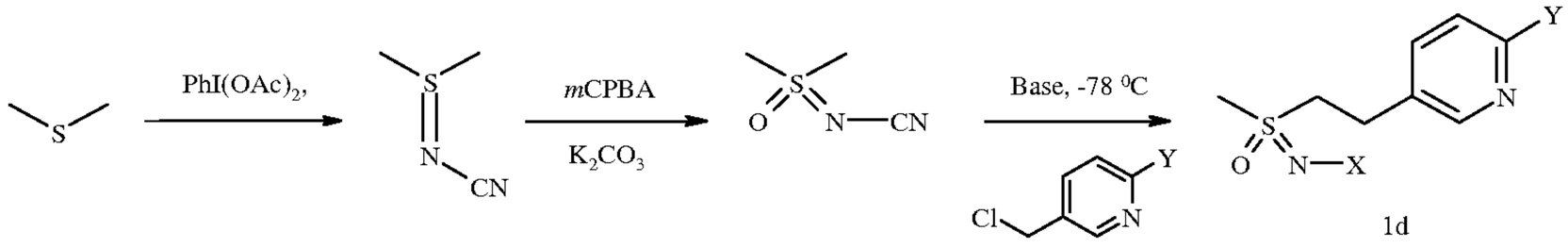
Michael adduct of certain sulfides with appropriately substituted α,β-unsaturated aldehydes, are coupled with substituted enones and cyclized with ammonium acetate in acetonitrile to yield the desired sulfides (A_1).

Scheme J



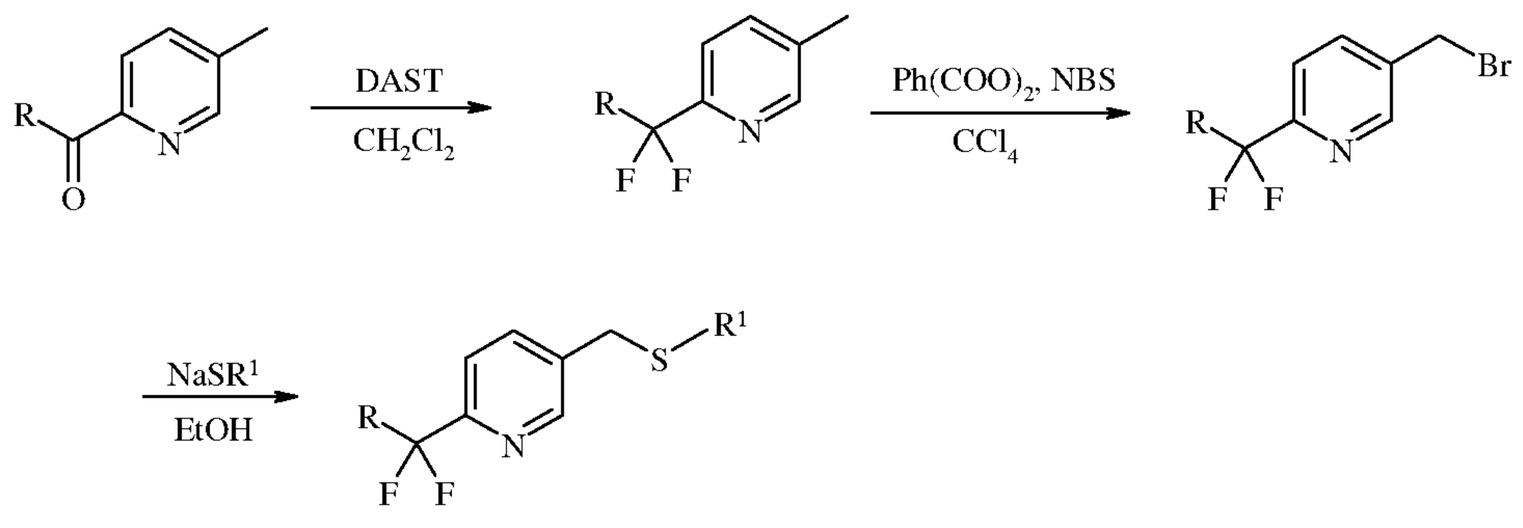
Sulfoximine compounds of the formula (Id) wherein n = 2, R^1 and R^2 are hydrogen, L is a single bond, and X and Y are as previously defined can be prepared by the method illustrated in Scheme K. Dimethylsulfide is oxidized with iodobenzene diacetate in the presence of cyanamide at 0 °C to give the corresponding sulfilimine. The reaction can be carried out in a polar aprotic solvent like CH_2Cl_2 or THF. The sulfilimine is then oxidized with *m*CPBA. A base such as potassium carbonate is employed to neutralize the acidity of *m*CPBA. Protic polar solvents such as ethanol and water are used to increase the solubility of the sulfilimine starting material and the base employed. The α-carbon of the *N*-substituted sulfoximine can be alkylated with a heteroaromatic methyl halide in the presence of a base such as KHMDS or butyl lithium (BuLi) to give the desired *N*-substituted sulfoximine. The preferred halide can be bromide, chloride or iodide.

Scheme K



In Scheme L, sulfides of formula (A_1), wherein Y is a fluoroalkyl group, R^1 is as previously defined, and n=1 can be prepared from the 6- acylpyridine or 6-formyl pyridine by reaction with diethylaminosulfur trifluoride (DAST). Subsequent halogenation of the 3-methyl group with NBS followed by nucleophilic substitution with the sodium salt of an alkyl thiol furnishes the desired sulfide.

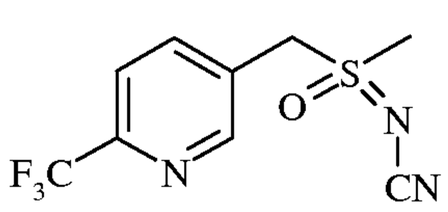
Scheme L



EXAMPLES

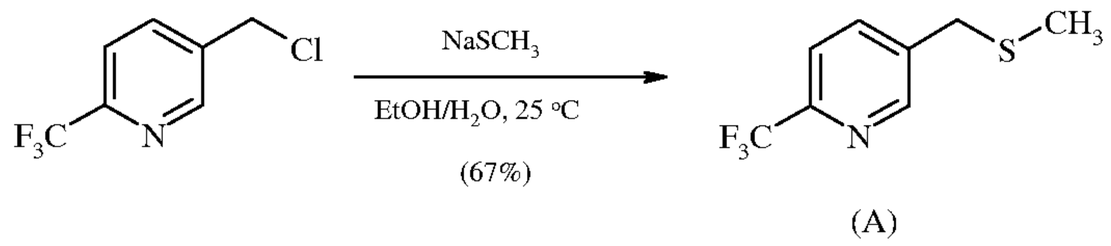
The examples are for illustration purposes and are not to be construed as limiting the invention disclosed in this document to only the embodiments disclosed in these examples.

Example I. Preparation of [(6-trifluoromethylpyridin-3-yl)methyl](methyl)-oxido- λ^4-sulfanylidenecyanamide (**1**)



(1)

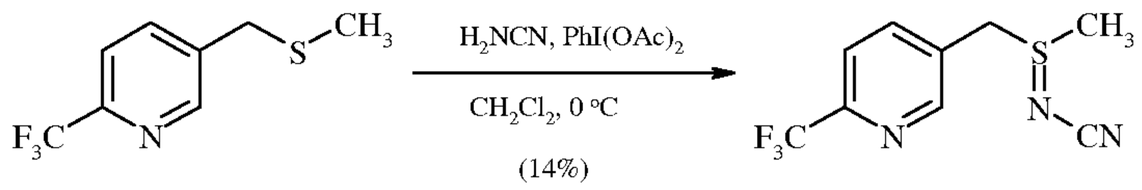
(A)



(A)

To a solution of 3-chloromethyl-6-(trifluoromethyl)pyridine (5.1 g, 26 mmol) in dimethyl sulfoxide (DMSO; 20 mL) was added in one portion sodium thiomethoxide (1.8 g, 26 mmol). A violent exothermic reaction was observed which resulted in the reaction turning dark. The reaction was stirred for 1 hr, then additional sodium thiomethoxide (0.91 g, 13 mmol) was added slowly. The reaction was stirred overnight, after which it was poured into H_2O and several drops of conc. HCl were added. The mixture was extracted with Et_2O (3 x 50 mL) and the organic layers combined, washed with brine, dried over $MgSO_4$ and concentrated. The crude product was purified by chromatography (Prep 500, 10% acetone/hexanes) to furnish the sulfide (A) as a pale yellow oil (3.6 g, 67%). ^1H NMR (300 MHz, $CDCl_3$) δ 8.6 (s, 1H), 7.9 (d, 1H), 7.7 (d, 1H), 3.7 (s, 2H), 2.0 (s, 3H); GC-MS: mass calcd for $C_8H_8F_3NS$ $[M]^+$ 207. Found 207.

(B)

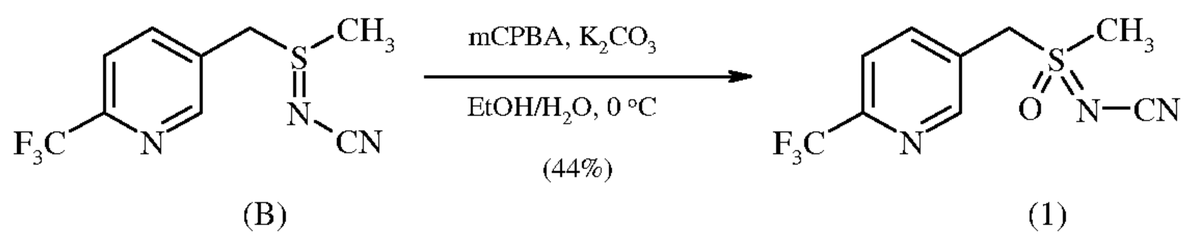


(A) (B)

To a solution of sulfide (A) (3.5 g, 17 mmol) and cyanamide (1.4 mg, 34 mmol) in CH_2Cl_2 (30 mL) at 0 °C was added iodobenzenediacetate (11.0 g, 34 mmol) all at once. The reaction was stirred for 30 min, then allowed to warm to room temperature overnight. The mixture was diluted with CH_2Cl_2 (50 mL) and washed with H_2O. The aqueous layer was extracted with ethyl acetate (4 x 50 mL), and the combined CH_2Cl_2 and ethyl acetate layers dried over $MgSO_4$ and concentrated. The crude product was triturated with hexanes and purified by

chromatography (chromatotron, 60% acetone/hexanes) to furnish the sulfilimine (B) as a yellow gum (0.60 g, 14%). IR (film) 3008, 2924, 2143, 1693 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.8 (s, 1H), 8.0 (d, 1H), 7.8 (d, 1H), 4.5 (d, 1H), 4.3 (d, 1H), 2.9 (s, 3H); LC-MS (ESI): mass calcd for $C_9H_9F_3N_3S$ $[M+H]^+$ 248.04. Found 248.

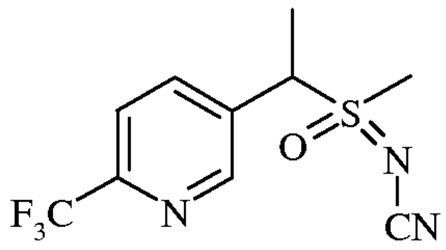
(C)



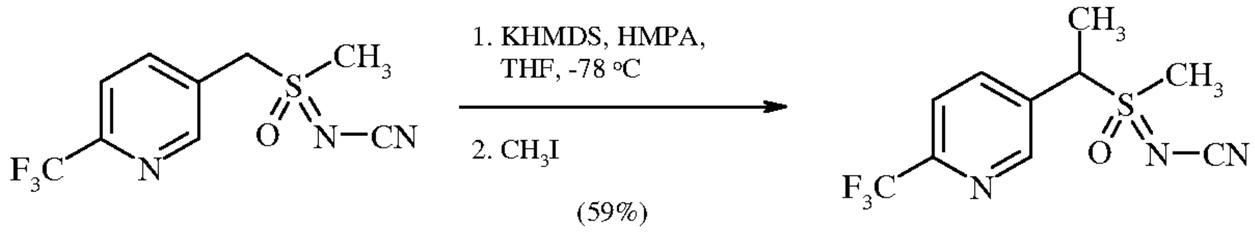
(B) (1)

To a solution of *m*-chloroperbenzoic acid (mCPBA; 80%, 1.0 g, 4.9 mmol) in EtOH (10 mL) at 0 °C was added a solution of K_2CO_3 (1.4 g, 10 mmol) in H_2O (7 mL). The solution was stirred for 20 min, then a solution of sulfilimine (B) (0.60 g, 2.4 mmol) in EtOH (20 mL) was added all at once. The reaction was stirred at 0 °C for 30 min, then allowed to warm to room temperature over the course of 1 hr. The reaction was then quenched with aq. sodium bisulfite and the mixture was concentrated to remove ethanol. The resulting mixture was extracted with CH_2Cl_2 and the combined organic layers dried over $MgSO_4$ and concentrated. The crude product was purified by chromatography (chromatotron, 50% acetone/hexanes) to furnish the sulfoximine (**1**) as an off-white solid (0.28 g, 44%). Mp = 135-137 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.8 (s, 1H), 8.1 (d, 1H), 7.8 (d, 1H), 4.7 (m, 2H), 3.2 (s, 3H); LC-MS (ELSD): mass calcd for $C_9H_9F_3N_3OS$ $[M+H]^+$ 264.04. Found 263.92.

Example II. Preparation of [1-(6-trifluoromethylpyridin-3-yl)ethyl](methyl)-oxido-λ^4-sulfanylidenecyanamide (**2**).



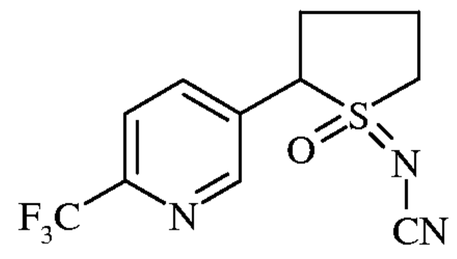
(2)



(1) (2)

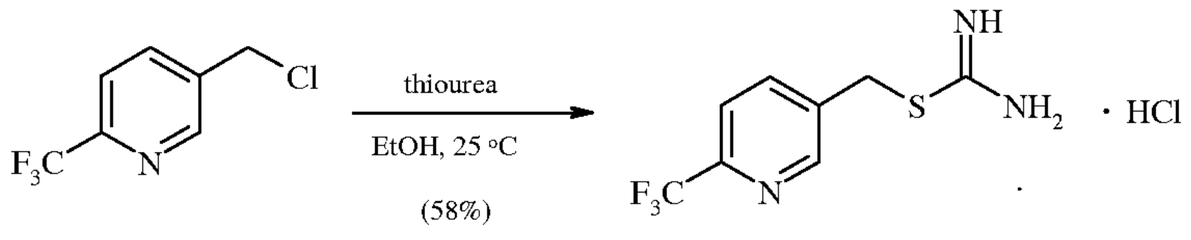
To a solution of sulfoximine **(1)** (50 mg, 0.19 mmol) and hexamethylphosphoramide (HMPA; 17 μL, 0.10 mmol) in tetrahydrofuran (THF; 2 mL) at -78 °C was added potassium hexamethyldisilazane (KHMDS; 0.5 M in toluene, 420 μL, 0.21 mmol) dropwise. The solution was stirred at -78 °C for an additional 20 min, after which iodomethane (13 μL, 0.21 mmol) was added. The reaction was allowed to warm to room temperature over the course of 1 hr, after which it was quenched with satd. aq. NH_4Cl and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, concentrated, and the crude product purified by chromatography (chromatotron, 70% acetone/CH_2Cl_2) to furnish the sulfoximine (**2**) as a 2:1 mixture of diastereomers (colorless oil; 31 mg, 59%). ^1H NMR (300 MHz, $CDCl_3$) δ (major diastereomer) 8.8 (s, 1H), 8.1 (d, 1H), 7.8 (d, 1H), 4.6 (q, 1H), 3.0 (s, 3H), 2.0 (d, 3H); (minor diastereomer) 8.8 (s, 1H), 8.1 (d, 1H), 7.8 (d, 1H), 4.6 (q, 1H), 3.1 (s, 3H), 2.0 (d, 3H); LC-MS (ELSD): mass calcd for $C_{10}H_{10}F_3N_3OS$ $[M+H]^+$ 278.06. Found 278.05.

Example III. Preparation of 2-(6-trifluoromethylpyridin-3-yl)-1-oxido-tetrahydro-1*H*-1λ^4-thien-1-ylidenecyanamide (**3**)



(3)

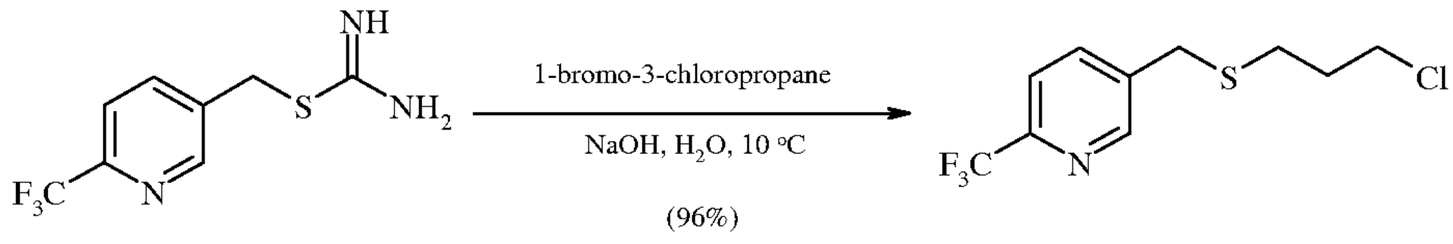
(A)



(A)

To a suspension of thiourea (1.2 g, 16 mmol) in EtOH (25 mL) was added a solution of 3-chloromethyl-6-(trifluoromethyl)pyridine in EtOH (10 mL). The suspension was stirred at room temperature for 2 days, during which a white precipitated formed. The precipitate was filtered to give the desired amidine hyrdochloride as a white solid (2.4 g, 58%). Mp = 186-188 °C. No further attempt was made to purify the product. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.9 (bs, 4H), 8.4 (s, 1H), 7.6 (d, 1H), 7.3 (d, 1H), 4.2 (s, 2H); LC-MS (ELSD): mass calcd for $C_8H_8F_3N_3S$ $[M+H]^+$ 236.05. Found 236.01.

(B)

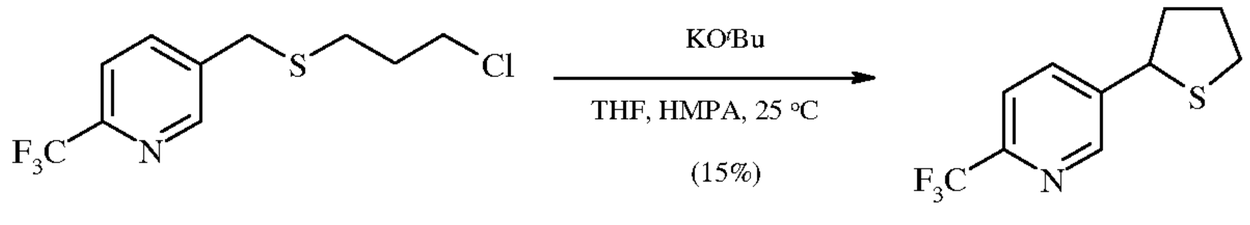


(A) (B)

To a solution of amidine hydrochloride (A) (1.8 g, 6.8 mmol) in H_2O (12 mL) at 10 °C was added 10 N NaOH (0.68 mL, 6.8 mmol), which resulted in the formation of a white precipitate. The suspension was heated at 100 °C for 30 min,

then cooled back down to 10 °C. Additional 10 N NaOH (0.68 mL, 6.8 mmol) was then added, followed by 1-bromo-3-chloropropane (0.67 mL, 6.8 mmol) all at once. The reaction was stirred at room temperature overnight, then extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated to furnish the sulfide (B) as a colorless oil (1.7 g, 96%). No further attempt was made to purify the product. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.6 (s, 1H), 7.8 (d, 1H), 7.6 (d, 1H), 3.8 (s, 2H), 3.6 (t, 2H), 2.6 (t, 2H), 2.0 (quint, 2H).

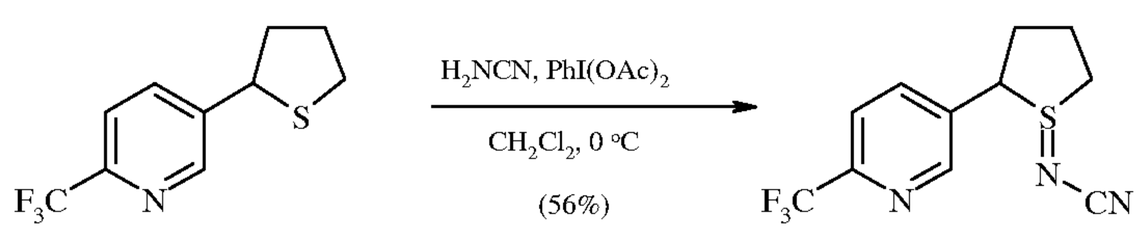
(C)



(B) (C)

To a suspension of potassium *tert*-butoxide (1.5 g, 13 mmol) in THF (12 mL) was added HMPA (1.7 mL, 10 mmol) followed by a solution of sulfide (B) (1.8 g, 6.7 mmol) in THF (3 mL) dropwise. The reaction was allowed to stir at room temperature overnight, followed by concentration and purification by chromatography (Biotage, 40% EtOAc/hexanes) to furnish cyclized product (C) as an orange oil (230 mg, 15%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.7 (s, 1H), 8.0 (d, 1H), 7.6 (d, 1H), 4.6 (dd, 1H), 3.2 (m, 1H), 3.1 (m, 1H), 2.5 (m, 1H), 2.3 (m, 1H), 2.1-1.9 (m, 2H).

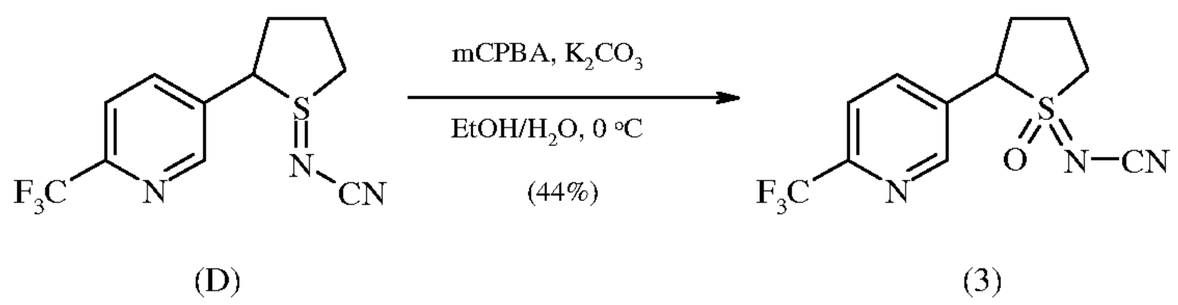
(D)



(C) (D)

To a solution of sulfide (C) (230 mg, 0.99 mmol) and cyanamide (83 mg, 2.0 mmol) in CH_2Cl_2 (5 mL) at 0 °C was added iodobenzenediacetate (350 mg, 1.1 mmol) all at once. The reaction was stirred for 3 hr, then concentrated and the crude product purified by chromatography (chromatotron, 50% acetone/hexanes) to furnish the sulfilimine (D) as an orange oil (150 mg, mixture of diastereomers, 56%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.8 (s, 1H), 7.9 (d, 1H), 7.8 (d, 1H), 4.8 (dd, 1H), 3.5 (m, 2H), 2.9-2.7 (m, 2H), 2.6 (m, 1H), 2.3 (m, 1H).

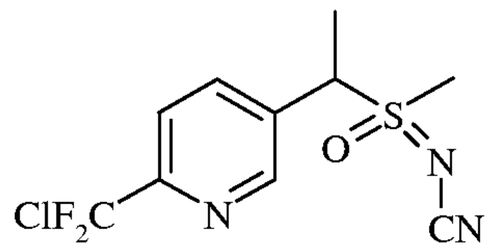
(E)



(D) (3)

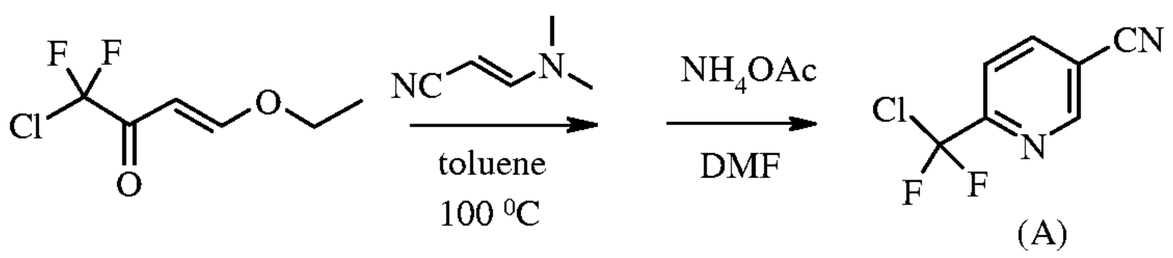
To a solution of mCPBA (80%, 180 mg, 0.82 mmol) in EtOH (3 mL) at 0 °C was added a solution of K_2CO_3 (230 mg, 1.7 mmol) in H_2O (1.5 mL). The solution was stirred for 20 min, then a solution of sulfilimine (D) (150 mg, 0.55 mmol) in EtOH (2 mL) was added all at once. The reaction was stirred at 0 °C for 45 min, after which the solvent was decanted into a separate flask and concentrated to give a white solid. The solid was slurried in $CHCl_3$, filtered, and concentrated to furnish pure sulfoximine (**3**) as a colorless oil (72 mg, 44%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (1.5:1 mixture of diastereomers) 8.8 (s, 2H), 8.0 (d, 2H), 7.8 (d, 2H), 4.7 (q, 1H), 4.6 (q, 1H), 4.0-3.4 (m, s, 4H), 3.0-2.4 (m, 8 H); LC-MS (ELSD): mass calcd for $C_{11}H_{11}F_3N_3OS$ $[M+H]^+$ 290.06. Found 289.99.

Example IV. Preparation of (1-{6-[chloro(difluoro)methyl]pyridin-3-yl}ethyl)(methyl)-oxido- λ^4-sulfanylidenecyanamide (**4**).



(4)

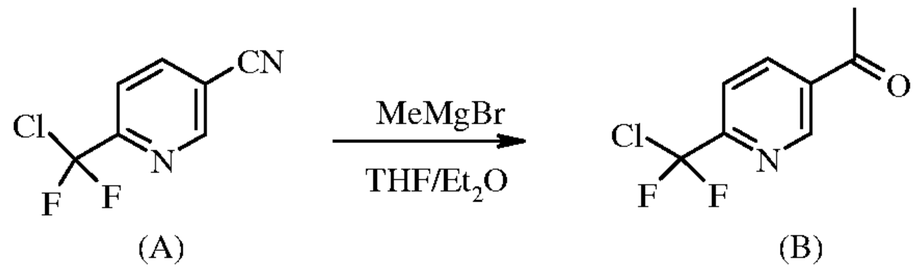
(A)



(A)

(3E)-1-Chloro-4-ethoxy-1,1-difluorobut-3-en-2-one (7.36 g, 40 mmol) was dissolved in dry toluene (40 mL) and treated with 3-dimethylaminoacrylonitrile (4.61 g, 48 mmol) at room temperature. The solution was heated at about 100 °C for 3.5 hr. The solvent was then removed under reduced pressure and the remaining mixture was re-dissolved in DMF (20 mL), treated with ammonium acetate (4.62 g, 60 mmol) and stirred at room temperature overnight. Water was added to the reaction mixture and the resulting mixture was extracted with ether-CH_2CH_2 (1 : 2, v/v) twice. The combined organic layer was washed with brine, dried, filtered and concentrated. The residue was purified on silica gel to give 3.1 g of 6-[chloro(difluoro)methyl]nicotinonitrile (A) as light colored oil in 41% yield. GC-MS: mass calcd for $C_7H_3ClF_2N_2$ $[M]^+$ 188. Found 188.

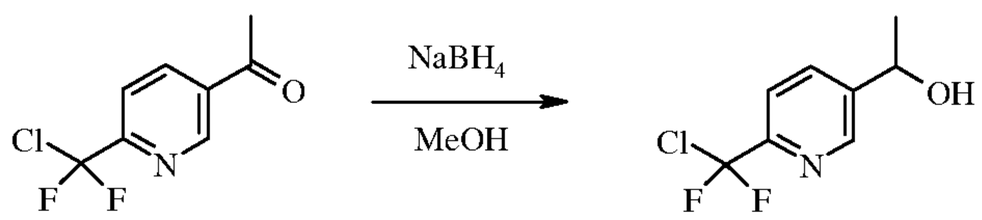
(B)



(A) (B)

6-[Chloro(difluoro)methyl]nicotinonitrile (A) (3.0 g, 15.8 mmol) was dissolved in anhydrous ether (25 mL) and cooled in an ice-water bath. A solution of 3 M of methylmagnesium bromide in hexane (6.4 mL, 19 mmol) was added through a syringe. After the addition was over, the mixture was stirred at 0 °C for 5 hr and then at room temperature for 10 hr. The reaction was quenched slowly with 1 N citric acid aqueous solution at 0 °C and the resulting mixture was stirred at room temperature for 1 hr. The pH was adjusted back to pH 7 with saturated $NaHCO_3$ aqueous solution. The two phases were separated and the aqueous phase was extracted with ethyl acetate twice. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The remaining mixture was purified on silica gel eluted with 15% acetone in hexane to give 0.88 g of the desired product 1-{6-[chloro(difluoro)methyl]pyridin-3-yl}-ethanone (B) as brownish oil in 30% yield. GC-MS: mass calcd for $C_8H_6ClF_2NO$ $[M]^+$ 205. Found 205.

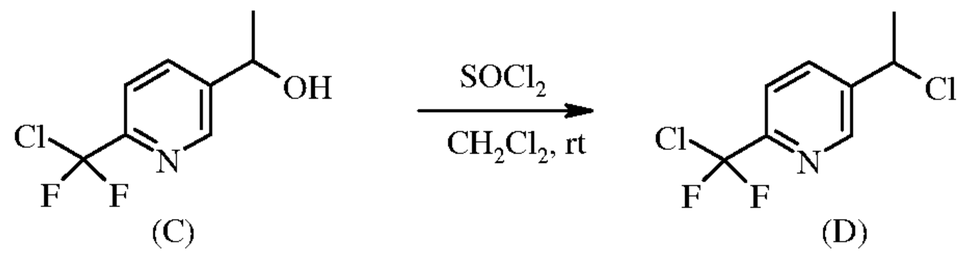
(C)



(B) (C)

To a solution of 1-{6-[chloro(difluoro)methyl]pyridin-3-yl}ethanone (B) (0.85 g, 4.14 mmol) in MeOH (10 mL) at 0 °C was added $NaBH_4$ (0.16 g, 4.14 mmol). The mixture was stirred for 30 min and 2 M HCl aqueous solution was added until pH reached 7. Solvent was removed under reduced pressure and the remaining mixture was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, concentrated, and dried *in vacuo* to give 0.798 g of analytically pure 1-{6-[chloro(difluoro)methyl]-pyridin-3-yl}ethanol (C) on GC-MS as a light yellow oil in 93% yield. GC-MS: mass calcd for $C_8H_6ClF_2NO$ $[M]^+$ 207. Found 207.

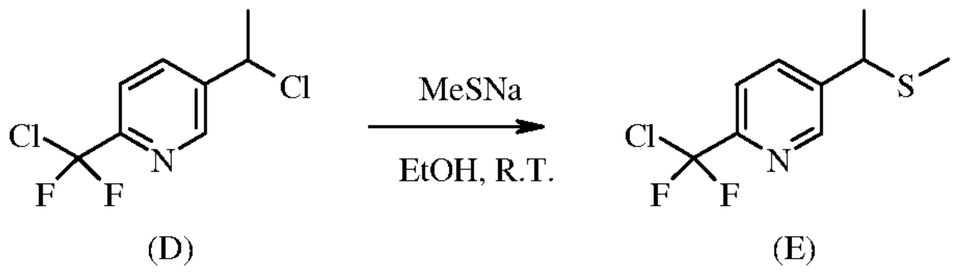
(D)



(C) (D)

To a solution of 1-{6-[chloro(difluoro)methyl]-pyridin-3-yl}ethanol (0.78 g, 3.77 mmol) in CH_2Cl_2 (40 mL) was added thionyl chloride (0.54 mL, 7.54 mmol) dropwise at room temperature. After 1hr, the reaction was quenched slowly with saturated $NaHCO_3$ aqueous solution and the two phases were separated. The organic layer was dried over Na_2SO_4, filtered, concentrated, and dried in vacuum to give 0.83 g of the crude 2-[chloro(difluoro)methyl]-5-(1-chloroethyl)pyridine (D) as brown oil in 98% yield, which was directly used for the next step reaction. GC-MS: mass calcd for $C_8H_7Cl_2F_2N$ $[M]^+$ 225. Found 225.

(E)

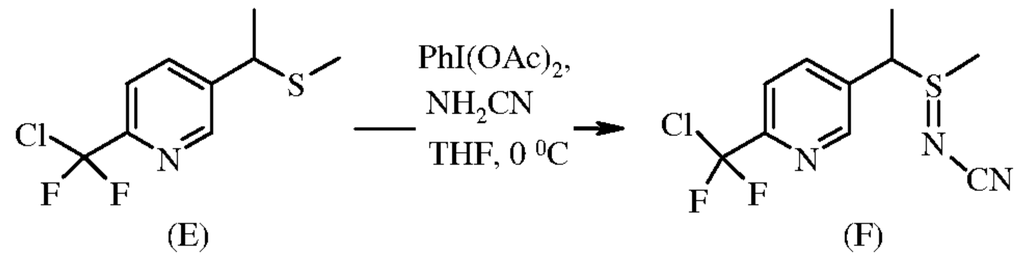


(D) (E)

To a solution of 2-[chloro(difluoro)methyl]-5-(1-chloroethyl)pyridine (D) (0.81 g, 3.6 mmol) in ethanol (10 mL) was added sodium thiomethoxide (0.52 g, 7.4 mmol) under stirring in one portion at 0 °C. After 10 min, the mixture was allowed to warm to room temperature and stirred overnight. The solvent ethanol was then removed under reduced pressure and the residue was re-taken into ether/CH_2Cl_2 and brine. The two phases were separated and the organic layer was extracted with CH_2Cl_2 one more time. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, concentrated, purified on silica gel using 5% ethyl acetate in hexane to give 0.348 g of the 2-[chloro(difluoro)methyl]-5-[1-

(methylthio)ethyl]pyridine (E) in 40% yield GC-MS: mass calcd for $C_9H_{10}ClF_2NS$ $[M]^+$ 237. Found 237.

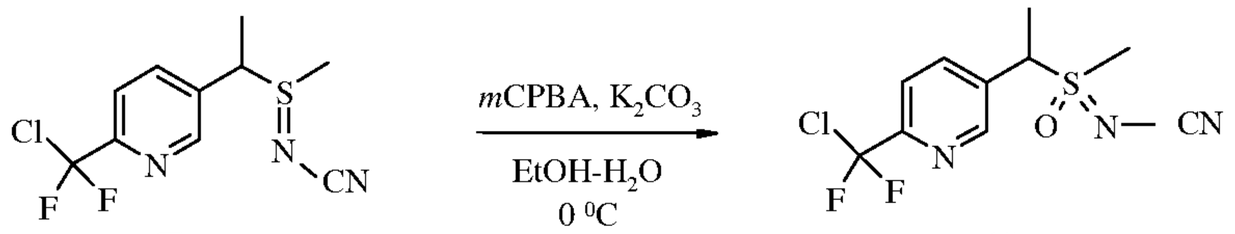
(F)



(E) (F)

To a stirred solution of 2-[chloro(difluoro)methyl]-5-[1-(methylthio)-ethyl]pyridine (E) (0.32 g, 1.35 mmol) and cyanamide (0.058 g, 1.35 mmol) in THF (7 mL) was added iodobenzene diacetate (0.44 g, 1.35 mmol) in one portion at 0 °C and the resulting mixture was stirred at this temperature for 1 hr and then at room temperature for 2 hr. The solvent was then removed under reduced pressure and the resulting mixture was dissolved in CH_2Cl_2, washed with half-saturated brine, dried over anhydrous Na_2SO_4, filtered, concentrated, and purified on silica gel using 50% acetone in hexane to give 0.175 g of (1-{6-[chloro-(difluoro)methyl]pyridin-3-yl}ethyl)(methyl)-λ^4-sulfanylidenecyanamide (F) as light-yellow oil in 48% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71 (d, J = 1.8 Hz, 1H), 7.91 (dd, J = 8.4, 1.8 Hz, 1H) 7.78 (d, J = 8.4 Hz, 1H), 4.42 (q, J = 6.9 Hz, 1H), 2.64 (s, 3H), 1.92 (d, J = 6.9 Hz, 3H); LC-MS: mass calcd for $C_{10}H_{10}ClF_2N_3S$ $[M+1]^+$ 278. Found 278.

(G)

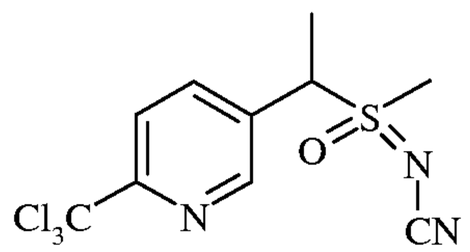


(F) (4)

To a stirred solution of (1-{6-[chloro(difluoro)methyl]pyridin-3-yl}ethyl)-(methyl)-λ^4-sulfanylidenecyanamide (F) (0.16 g, 0.6 mmol) in ethanol (10 mL) was added 20% potassium carbonate aqueous solution (1.24 g, 1.8 mmol) at 0 °C

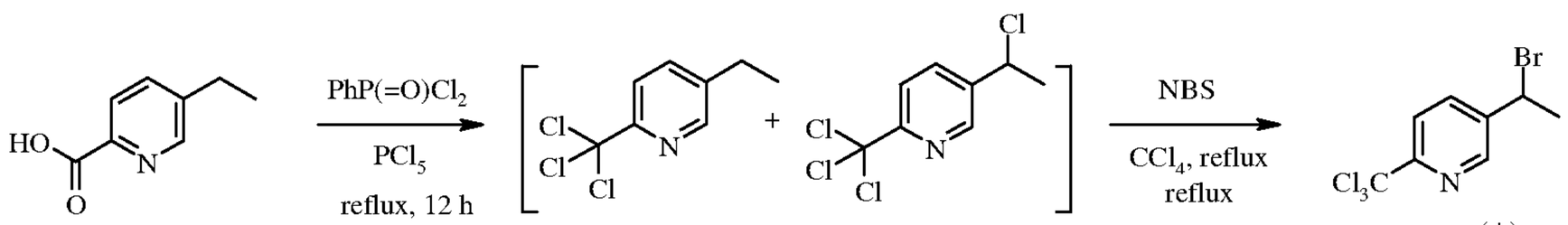
under stirring. After 10 min stirring, 80% mCPBA (0.19 g, ca 0.9 mmol) was added to the mixture, which was stirred at 0 °C for 2 hr after which the reaction was quenched with a spatula of solid sodium thiosulfate. Most of the solvent ethanol was removed under reduced pressure and an aqueous saturated $NaHCO_3$ - brine (1 : 1, v/v) solution was added and the mixture extracted with chloroform three times. The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified on silica gel using 35-50% acetone in hexane as eluent to give 0.092 g of the product (1-{6-[chloro(difluoro)-methyl]pyridin-3-yl}ethyl)(methyl)oxido-λ^4-sulfanylidenecyanamide (**4**) as colorless oil in 57% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.09 (d, J = 8.1 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 4.73 (q, J = 7.2 Hz, 1H), 3.16 and 3.11 (2 s, 3H, a mixture of two diastereomeric α-CH_3 groups between the sulfoximine and the pyridine tail), 2.00 (d, J = 7.2 Hz, 3H); LC-MS: mass calcd for $C_{10}H_{10}ClF_2N_3OS$ $[M-1]^+$ 292. Found 292.

Example V. Preparation of [1-(6-trichloromethylpyridin-3-yl)ethyl](methyl)-oxido- λ^4-sulfanylidenecyanamide (**5**).



(5)

(A)

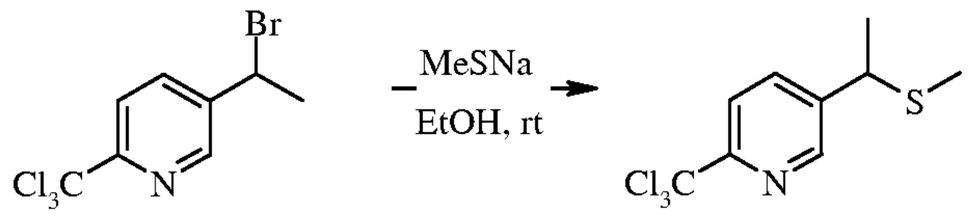


(A)

A mixture of 5-ethylpyridine-2-carboxylic acid (1.98 g, 13 mmol), phenylphosphonic dichloride (2.8 g, 14.3 mmol), phosphorus pentachloride (7.7 g, 32 mmol) was stirred and slowly heated. Once a clear yellow liquid was formed, the mixture was heated to reflux overnight. After cooling, the volatiles were removed under reduced pressure. The residue was carefully poured into saturated sodium carbonate aqueous solution cooled in an ice-water bath. The aqueous phase was then extracted with CH_2Cl_2 two times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, concentrated, and partially purified on silica gel eluted with 10% EtOAc in hexane to give 2.7 g of crude product containing both 5-ethyl-2-(trichloromethyl)pyridine and 5-(1-chloroethyl)-2-(trichloromethyl)pyridine in an approximate 3:1 ratio (GC data, masses calcd for $C_8H_8Cl_3N$ and $C_8H_7Cl_4N$ $[M]^+$ 223 and 257 respectively. Found 223 and 257 respectively).

A mixture of the above-mentioned crude product (2.6 g) in carbon tetrachloride (100 mL) was then treated with 80% of *N*-bromosuccinimide (1.9 g, 11 mmol) and benzoylperoxide (0.66 g, 0.275 mmol) and then refluxed overnight. The solid was filtered off, the filtrate concentrated and the resulting residue purified on silica gel using 4% EtOAc in hexane to give 1.0 g of the desired product 5-(1-bromoethyl)-2-(trichloromethyl)pyridine (A) as a yellow solid. The combined yield for the two steps was 25%. GC-MS: mass calcd for $C_8H_7BrCl_3N$ $[M\text{-}1\text{-}Cl]^+$ 266. Found 266.

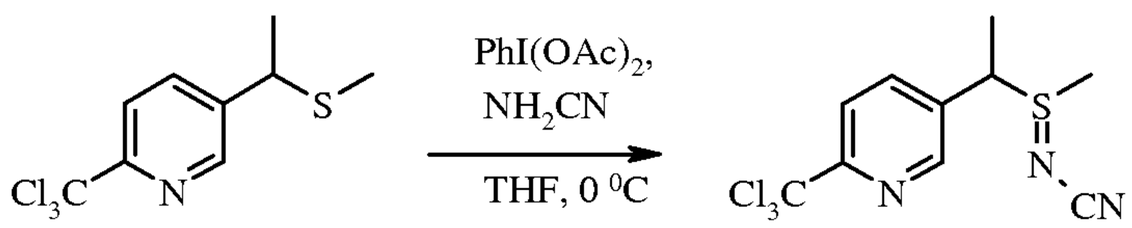
(B)



(A) (B)

A solution of 5-(1-bromoethyl)-2-(trichloromethyl)pyridine (A) (0.95 g, 3.14 mmol) in ethanol (15 mL) was treated with sodium thiomethoxide (0.44 g, 6.29 mmol) portion wise at 0 °C. The mixture was stirred at room temperature overnight. The solvent ethanol was then removed under a reduced pressure and the residue was re-taken into CH_2Cl_2 and brine. The two phases were separated and the organic layer was dried over anhydrous Na_2SO_4, filtered, concentrated. The residue was purified on silica gel using 5% EtOAc in hexane to give 0.57 g of the partially pure 5-[1-(methylthio)ethyl]-2-(trichloromethyl)pyridine (B) in 67% crude yield. GC-MS: mass calcd for $C_9H_{10}Cl_3NS$ $[M]^+$ 269. Found 269.

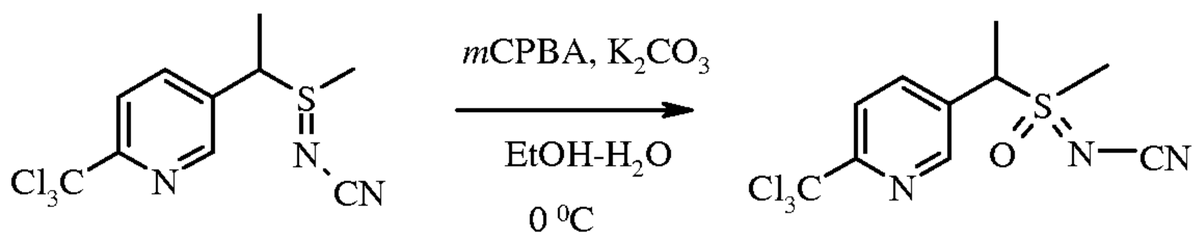
(C)



(B) (C)

To a stirred solution of 5-[1-(methylthio)ethyl]-2-(trichloromethyl)-pyridine (B) (0.55 g, 2.3 mmol) and cyanamide (0.097 g, 2.3 mmol) in THF (7 mL) cooled to 0 °C was added iodobenzene diacetate (0.75 g, 2.3 mmol) in one portion. The resulting mixture was stirred at 0 °C for 1 hr and then at room temperature for 2 hr. The solvent was removed *in vacuo* and the resulting mixture was purified on silica gel using 50% acetone in hexane to give 0.254 g of (1E)-methyl{1-[6-(trichloromethyl)pyridin-3-yl]ethyl}-λ^4-sulfanylidenecyanamide (C) as an off-white solid in 40% yield. ^{1}H NMR for the diastereomeric mixture (300 MHz, d_6-acetone) δ 8.87 (s, 1H), 8.21-8.25 (m, 2H), 4.65-4.76 (m, 1H), 2.86-2.66 (m, 3H), 1.88-1.92 (m, 3H).

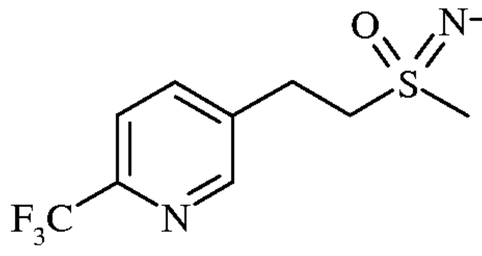
(D)



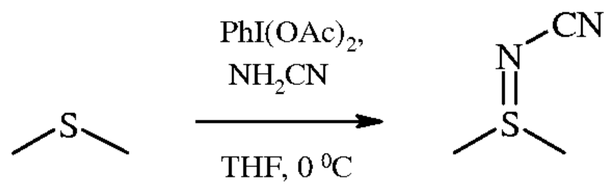
(C) *(5)*

To a stirred solution of (1E)-methyl{1-[6-(trichloromethyl)pyridin-3-yl]ethyl}-λ^4-sulfanylidenecyanamide (C) (0.20 g, 0.65 mmol) in ethanol (15 mL) was added 20% aqueous potassium carbonate solution (1.3 mL) at 0 °C, followed by addition of 80% mCPBA. The resulting mixture was stirred for 2 hr at 0 °C and then quenched with solid sodium thiosulfate. Most of the solvent was evaporated and 1:1 aqueous saturated $NaHCO_3$-brine (v/v) was added and the mixture was extracted with chloroform three times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified on silica gel using 40% acetone in hexane to give 0.10 g of [1-(6-trichloromethylpyridin-3-yl)ethyl](methyl)-oxido- λ^4-sulfanylidene-cyanamide (**5**) as colorless oil in 50% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.12-8.23 (m, 1H), 5.15(q, 1H), 3.37 and 3.28 (2 s, 3H, a mixture of two diastereomeric α-CH_3 groups between the sulfoximine and the pyridine tail), 2.03 (d, 3H); LC-MS: mass calcd for $C_{10}H_{12}Cl_3N_3OS$ $[M+1]^+$ 328. Found 328.

Example VI. Preparation of [2-(6-trifluoromethylpyridin-3-yl)ethyl](methyl)-oxido- λ^4-sulfanylidenecyanamide (**6**).



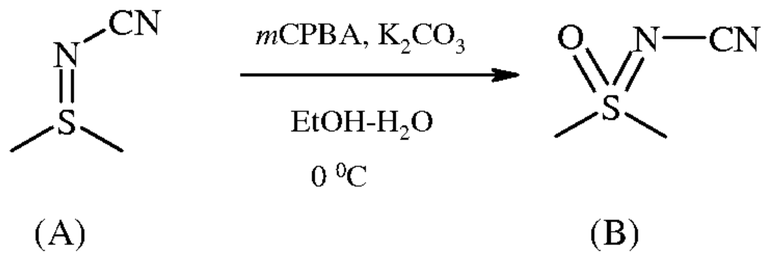
(A) (6)



(A)

To a solution of dimethylsulfide (10.0 g, 161 mmol) and cyanamide (6.7 g, 161 mmol) in THF (500 mL) at 0 °C was added iodobenzenediacetate (51.8 g, 161 mmol) all at once. Let stir at 0 °C for 30 min, then allowed reaction to warm to room temperature overnight. The reaction was concentrated and purified by passing through a silica gel plug, first with 100% hexanes, then with 100% acetone, furnishing sulfilimine (A) as a colorless oil = 13.4 g (82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.8 (s, 6H); GC-MS: mass calcd for $C_3H_6N_2S$ $[M]^+$, 102. Found 102.

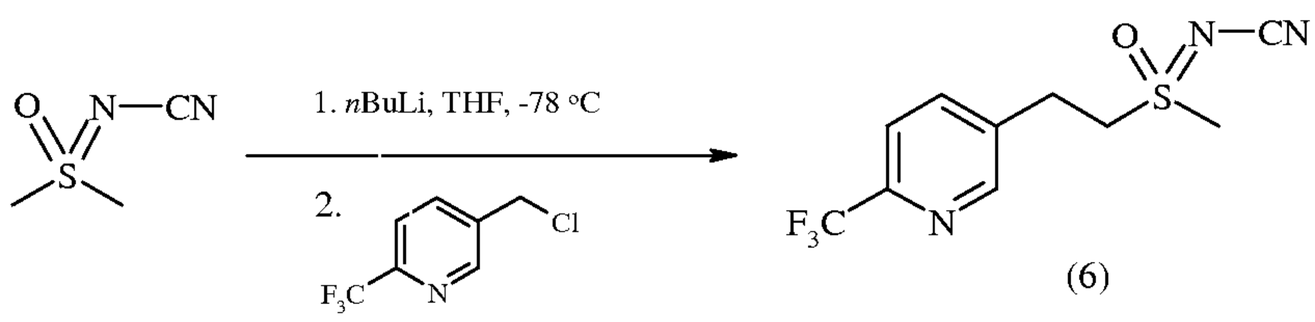
(B)



(A) (B)

To a solution mCPBA (80%, 25.3 g, 147 mmol) in EtOH (450 mL) at 0 °C was added solution of K_2CO_3 (40.6 g, 294 mmol) in H_2O (340 mL). After 20 min, sulfilimine (10.0 g, 98 mmol) in EtOH (150 mL) was added all at once. The suspension was stirred at 0 °C for 90 min, after which the crude reaction mixture was concentrated to remove EtOH, then extracted with CH_2Cl_2 (3x). The combined organic layers were washed with satd aq $NaHCO_3$ soln (3x), dried over Na_2SO_4 and concentrated to furnish sulfoximine (B) as a yellow solid = 1.310 g (10%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.4 (s, 6H); GC-MS: mass calcd for $C_3H_6N_2OS$ $[M]^+$, 118. Found 118.

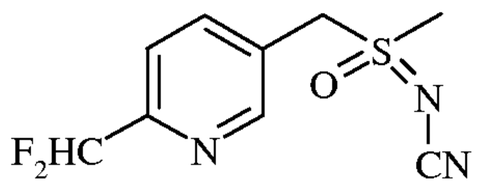
(C)



(6)

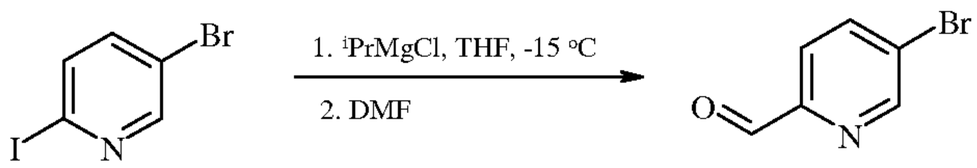
To a solution of sulfoximine (100 mg, 0.85 mmol) in THF (2 mL) at -78 °C was added nBuLi (2.5 M, 340 µL, 0.85 mmol) dropwise. The solution was let solution stir for 20 min, then 5-(chloromethyl)-2-trifluoromethyl pyridine (170 mg, 0.85 mmol) was added. The solution was let solution stir at -78 °C for additional 2 h, then quenched with satd aq ammonium chloride and extracted with CH_2Cl_2. The combined organic extracts were dried over sodium sulfate, concentrated and purified by flash chromatography (40% EtOAc/ 80% hexanes) to furnish [2-(6-trifluoromethylpyridin-3-yl)ethyl](methyl)-oxido- λ^4-sulfanylidene-cyanamide (**6**) as a yellow solid = 14.5 mg (6%); mp = 83-87 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69 (d, 1H), 7.85 (dd, 1H), 7.74 (d, 1H), 3.58-3.79 (m, 2H), 3.38-3.46 (m, 2H), 3.30 (s, 3H); LC-MS (ELSD): mass calcd for $C_{10}H_{11}F_3N_3OS$ $[M+H]^+$, 278. Found 278.

Example VII. <u>Preparation of [(6-difluoromethylpyridin-3-yl)methyl](methyl)-oxido- λ^4-sulfanylidenecyanamide (**7**)</u>



(7)

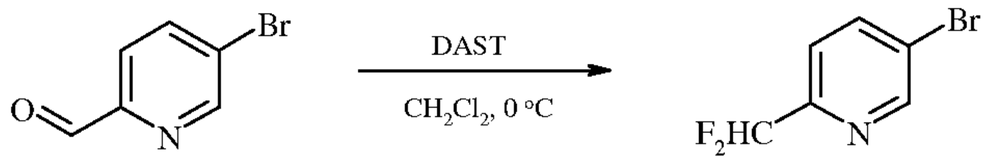
(A)



(A)

To a solution of 2-iodo-5-bromopyridine (18.4 g, 65 mmol) in THF (100 mL) at -15 °C was added isopropylmagnesium chloride (2M, 35 mL, 70 mmol) dropwise at a rate such that the temperature of the reaction did not exceed 0 °C. The reaction was stirred at -15 °C for 1 h, then DMF (7.5 mL, 97 mmol) was added dropwise at a rate such that the temperature of the reaction did not exceed 0 °C. The reaction was stirred for 30 min, then warmed to room temperature for an additional 1 h. The reaction was cooled back down to 0 °C and 2 N HCl (80 mL) was added dropwise, maintaining the temperature below 20 °C. After stirring for 30 min, 2 N NaOH was added until pH 7 was reached. The organic layer was then separated and the aqueous layer extracted with CH_2Cl_2 (3x). The combined organic layers were dried over $MgSO_4$, concentrated and purified by flash chromatography (SiO_2, 10% EtOAc/hexanes) to furnish 5-bromopyridine-2-carbaldehyde (A) as a white solid (7.3g, 60%). ^1H NMR (300 MHz, $CDCl_3$) δ 10.0 (s, 1H), 8.9 (s, 1H), 8.0 (d, 1H), 7.8 (d, 1H).

(B)

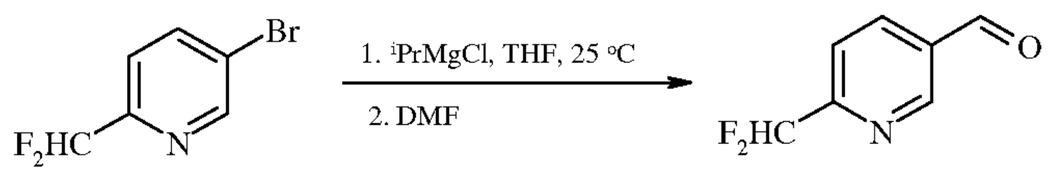


(A) (B)

To a cooled solution of 5-bromopyridine-2-carbaldehyde (A) (7.0 g, 38 mmol) in CH_2Cl_2 (300 mL) at -78 °C was added diethylaminosulfur trifluoride (DAST, 10.8 mL, 83 mmol). The reaction was allowed to warm to room temperature over the course of 6 h, then it was quenched slowly with H_2O, washed with saturated aqueous $NaHCO_3$ and dried over Na_2SO_4. Concentration and

purification by silica gel plug (CH_2Cl_2 eluent) furnished 5-bromo-2-difluoromethylpyridine (B) as brown crystals (5.3g, 67%). ^1H NMR (300 MHz, $CDCl_3$) δ 8.8 (s, 1H), 8.0 (d, 1H), 7.6 (d, 1H), 6.6 (t, 1H).

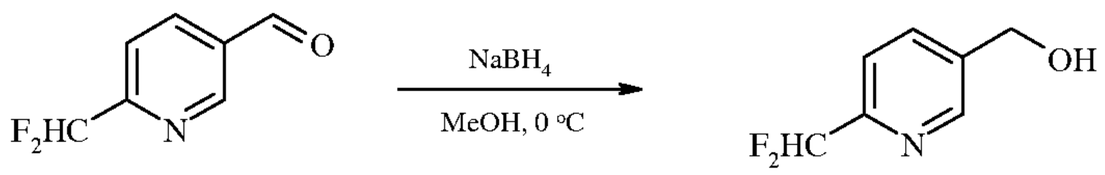
(C)



(B) (C)

To a solution of 5-bromo-2-difluoromethylpyridine (B) (1.8 g, 8.6 mmol) in THF (40 mL) at 25 °C was added isopropylmagnesium chloride (2M, 8.6 mL, 17 mmol) dropwise. The reaction was allowed to stir for 2 h, then DMF (660 µL, 8.6 mmol) was added and the reaction was stirred for an additional 22 h. The reaction was quenched with 2M HCl and basified with 1M NaOH until pH 7 reached. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, concentrated and purified by flash chromatography (10% EtOAc/hexanes) to furnish 6-difluoromethylpyridine-3-carbaldehyde (C) as an orange oil (320 mg, 24%).

(D)

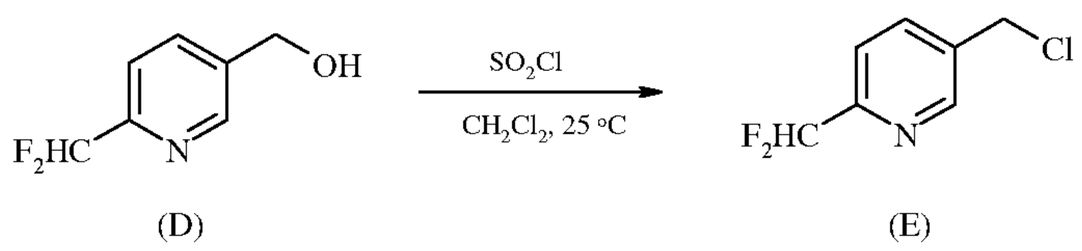


(C) (D)

To a solution of 6-difluoromethylpyridine-3-carbaldehyde (C) (500 mg, 3.2 mmol) in MeOH (10 mL) at 0 °C was added $NaBH_4$ (60 mg, 1.6 mmol). The reaction was allowed to stir for 30 min, then 2M HCl was added until pH 2 was reached. The resulting solution was extracted with CH_2Cl_2 (3x) and the combined organic layers dried over Na_2SO_4 and concentrated to furnish (6-difluoromethyl-pyridin-3-yl)methanol (D) as an orange oil (420 mg, 82%) which was used in the

next step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.6 (s, 1H), 7.9 (d, 1H), 7.6 (d, 1H), 6.6 (t, 1H), 4.8 (s, 2H).

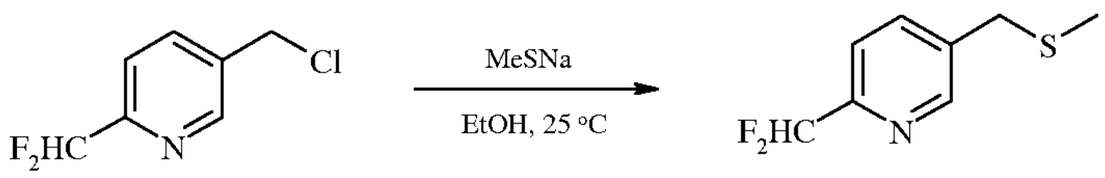
(E)



(D) (E)

To a solution of (6-difluoromethylpyridin-3-yl)methanol (D) (450 mg, 2.8 mmol) in CH_2Cl_2 (10 mL) at room temperature was $SOCl_2$ (230 μL, 3.1 mmol). The reaction was allowed to stir for 1 h, then the reaction was quenched slowly with saturated aqueous $NaHCO_3$. The aqueous phase was extracted with CH_2Cl_2 (3x) and the combined organic layers were dried over Na_2SO_4 and concentrated to furnish the resulting solution was extracted with CH_2Cl_2 (3x) and the combined organic layers dried over Na_2SO_4 and concentrated to furnish 5-chloromethyl-2-difluoromethylpyridine (E) as a reddish brown oil (490 mg, 98%) which was used in the next step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.7 (s, 1H), 7.9 (d, 1H), 7.6 (d, 1H), 6.6 (t, 1H), 4.6 (s, 2H).

(F)

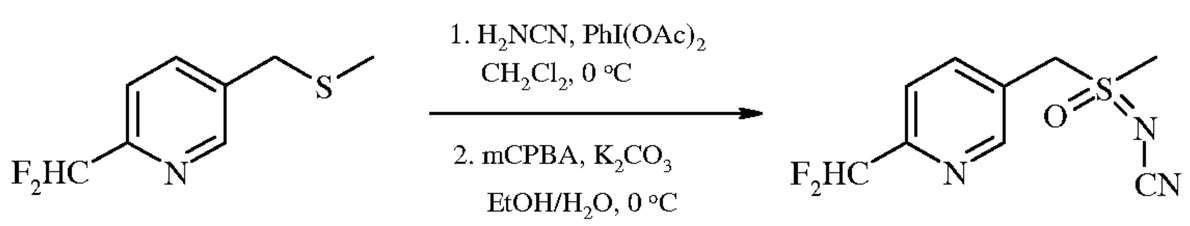


(E) (F)

To a solution of sodium thiomethoxide (240 mg, 3.3 mmol) in EtOH (10 ml) at room temperature was added a solution of 5-chloromethyl-2-difluoromethylpyridine (E) (490 mg, 2.8 mmol) in EtOH (3 mL). The reaction was allowed to stir for 9 h, then the reaction was concentrated, taken up in Et_2O, and washed with H_2O. The organic phase was dried over Na_2SO_4 and concentrated to furnish 2-difluoromethyl-5-methylthiomethyl-pyridine (F) as an orange oil (422 mg, 81%) which was used in the next step without further purification. ^{1}H NMR

(300 MHz, $CDCl_3$) δ 8.6 (s, 1H), 7.8 (d, 1H), 7.6 (d, 1H), 6.6 (t, 1H), 3.7 (s, 2H), 2.0 (s, 3H).

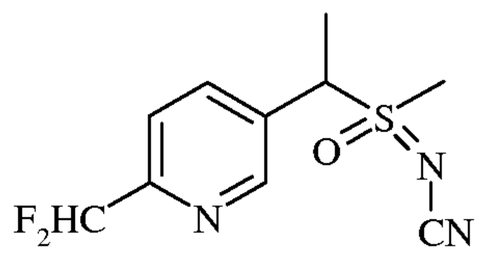
(G)



(F) (7)

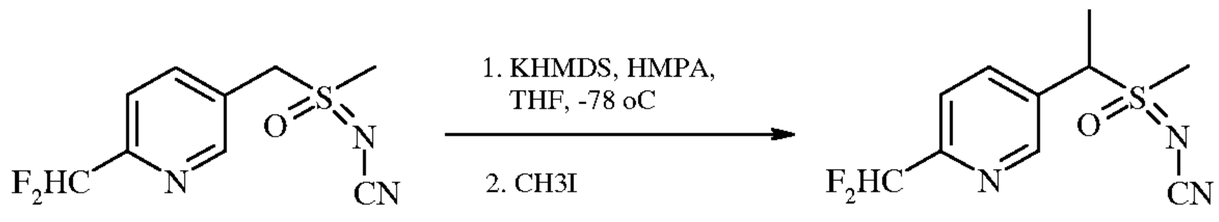
[(6-Difluoromethylpyridin-3-yl)methyl](methyl)-oxido- λ^4-sulfanylidenecyanamide (**7**) was synthesized from 2-difluoromethyl-5-methylthiomethylpyridine (F) in two steps as described in Examples I-B and I-C. Isolated as a white solid (51% yield). ^1H NMR (300 MHz, $CDCl_3$) δ 8.7 (s, 1H), 8.0 (d, 1H), 7.8 (d, 1H), 6.7 (t, 1H), 4.7 (dd, 2H), 3.2 (s, 3H); LC-MS (ELSD): mass calcd for $C_9H_{10}F_2N_3OS$ $[M+H]^+$, 246. Found 246.

Example VIII. Preparation of [1-(6-difluoromethylpyridin-3-yl)ethyl](methyl)-oxido- λ^4-sulfanylidenecyanamide (**8**)



(8)

(A)

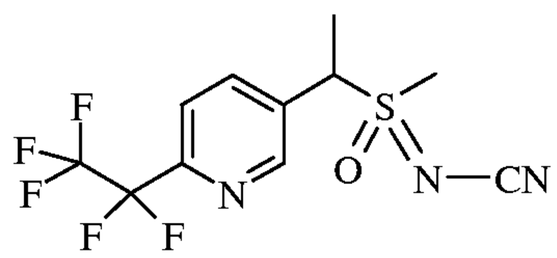


(7) (8)

[1-(6-difluoromethylpyridin-3-yl)ethyl](methyl)-oxido- λ^4-sulfanylidene cyanamide (**8**) was synthesized from [(6-difluoromethylpyridin-3-

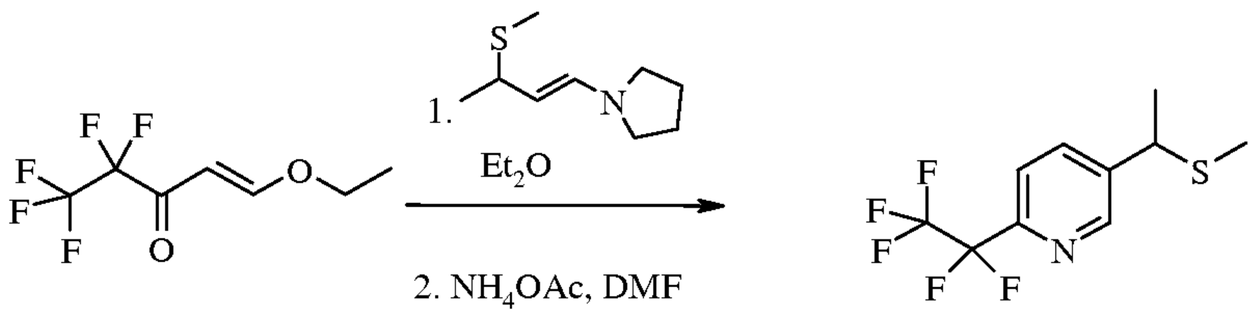
yl)methyl](methyl)-oxido- λ^4-sulfanylidenecyanamide (**7**) in one step as described in Example II. Isolated as a colorless oil (74% yield) and a 1:1 mixture of diastereomers. ^{1}H NMR (300 MHz, $CDCl_3$) δ (mixture of two diastereomers) 8.7 (s, 2H), 8.0 (d, 2H), 7.8 (d, 2H), 6.7 (t, 2H), 4.6 (q, 2H), 3.1 (s, 3H), 3.0 (s, 3H), 2.0 (d, 6H); LC-MS (ELSD): mass calcd for $C_{10}H_{12}F_2N_3OS$ $[M+H]^+$, 260. Found 260.

Example IX. Preparation of [1-(6-pentafluoroethylpyridin-3-yl)ethyl](methyl)-oxido- λ^4-sulfanylidenecyanamide (**9**)



(9)

(A)

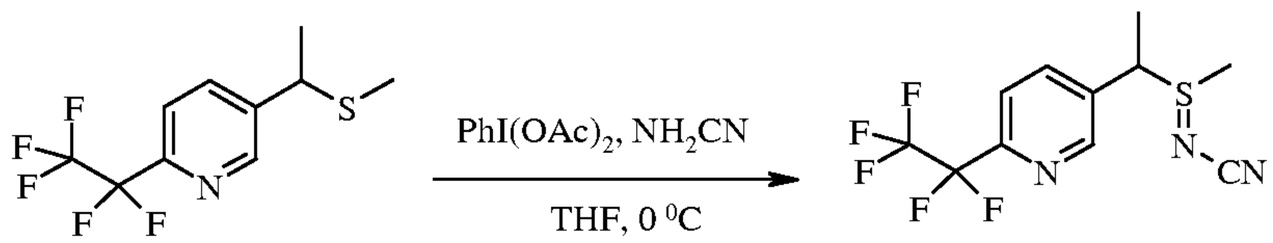


(A)

(E)-1-Ethoxy-4,4,5,5,5-pentafluoropent-1-en-3-one (1.09 g, 5 mmol) in anhydrous ethyl ether (5 mL) was treated with 1-((E)-3-methylthiobut-1-enyl)pyrrolidine (0.85 g, 5 mmol) in 2 mL dry ether at -15 °C over a period of 5 min and the reaction was continued for 20 min. Then the temperature was allowed to rise to room temperature and the reaction continued for 3 h. The solvent was removed under reduced pressure and the residue re-dissolved in anhydrous DMF (5 mL). Ammonium acetate (0.58 g, 7.5 mmol) was added and the mixture stirred at room temperature over a weekend. Water was added and mixture extracted with

ether three times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, concentrated, and purified on silica gel eluted with 8% EtOAc in hexane (v/v) to give 0.16 g of the desired 5-(1-methylthioethyl)-2-pentafluoroethylpyridine (A) as brownish colored oil in 12% yield. GC-MS: mass calcd for $C_{10}H_{11}F_2N_3S$ $[M]^+$ 271. Found 271.

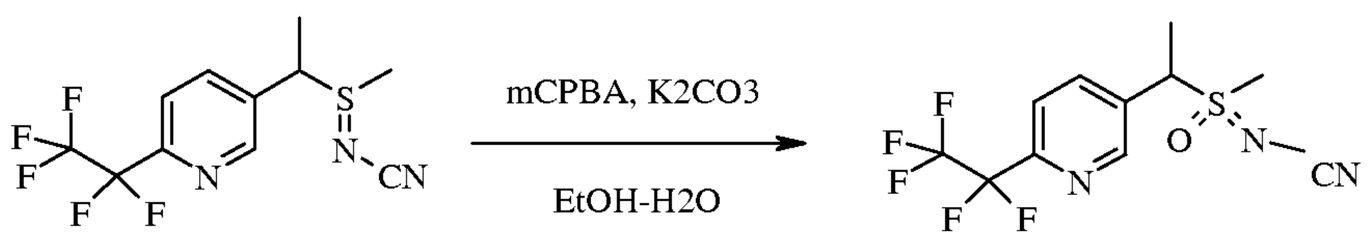
(B)



(A) (B)

To a stirred solution of the 5-(1-methylthioethyl)-2-pentafluoroethylpyridine (A) (0.16 g, 0.6 mmol) and cyanamide (0.025 g, 0.6 mmol) in THF (3 mL) cooled to 0 °C was added iodobenzene diacetate (0.19 g, 0.6 mmol) in one portion and the resulting mixture was stirred at 0 °C for 2 h and then at room temperature overnight. The solvent was removed *in vacuo* and the resulting mixture was suspended in brine-saturated $NaHCO_3$ (9:1), which was then extracted with CH_2Cl_2-EtOAc (1:1, v/v) two times. The combined organic layer was dried over Na_2SO_4, filtered, concentrated, and dried to give 0.16 g of (1-{6-[pentafluoroethyl]pyridin-3-yl}ethyl)(methyl)-λ^4-sulfanylidenecyanamide (B) as a brownish oil in 85% yield. LC-MS: mass calcd for $C_{11}H_{10}F_5N_3S$ $[M]^+$ 311.28. Found $[M-1]^+$ 309.84

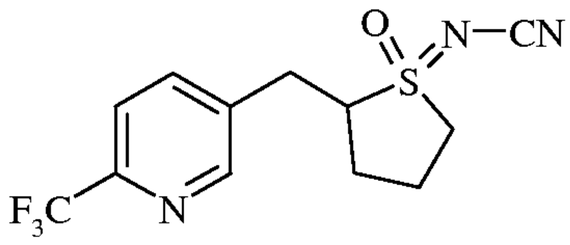
(C)



(B) (9)

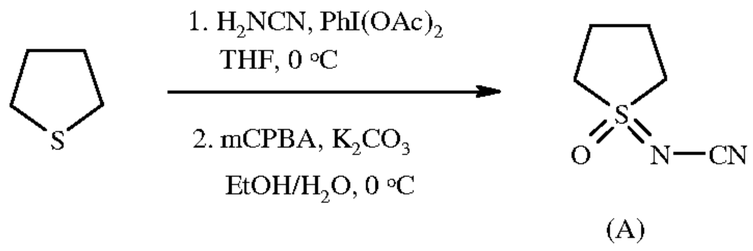
To a stirred solution of the 80% 3-chloroperoxybenzoic acid (0.17 g, *ca* 0.8 mmol) in ethanol (3 mL) cooled to 0 ^{0}C was added 20% aqueous potassium carbonate (1.0 mL, 1.5 mmol and the resulting mixture was stirred at 0 ^{o}C for 20 min. Then (1-{6-[pentafluoroethyl]pyridin-3-yl}ethyl)(methyl)-λ^4-sulfanylidene-cyanamide (B) was added at once and the mixture was stirred at 0 ^{0}C for 1 h. The reaction was quenched with a small spatula of solid sodium thiosulfate. Most of the solvent was evaporated and brine solution was added and the mixture extracted with CH_2Cl_2 three times. The combined organic layer was dried over Na_2SO_4, filtered and concentrated and the residue was purified on silica gel using 10% acetone in CH_2Cl_2 (v/v) to give 0.089 g of [1-(6-pentafluoroethylpyridin-3-yl)ethyl](methyl)-oxido- λ^4-sulfanylidenecyanamide (**9**) as a white solid in 54% yield. LC-MS: mass calcd for $C_{10}H_{10}F_5N_3OS$ $[M]^+$ 327.28. Found $[M-1]^+$ 325.83.

Example X. <u>Preparation of 2-[(6-trifluoromethylpyridin-3-yl)methyl]-1-oxidotetrahydro-1H-1λ^4-thien-1-ylidenecyanamide (**10**)</u>



(10)

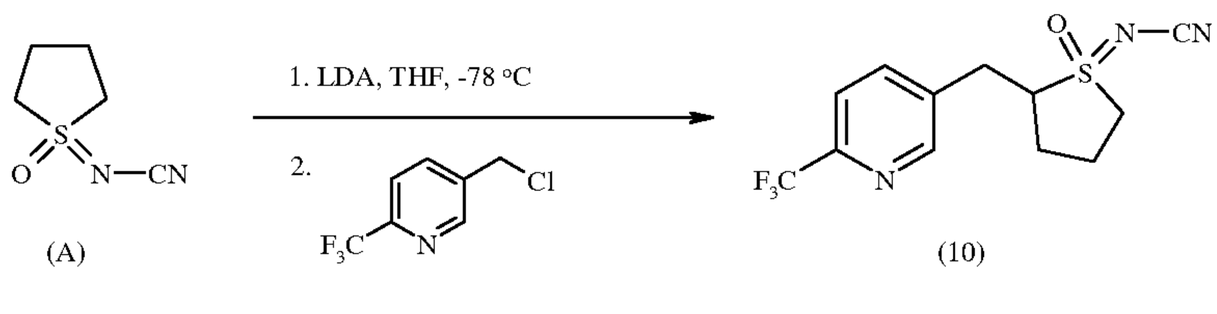
(A)



(A)

1-Oxidotetrahydro-1H-1λ^4-thien-1-ylidenecyanamide (A) was prepared from tetrahydrothiophene by a two step procedure as described in Examples VI-A and VI-B (69% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.5 (m, 2H), 3.3 (m, 2H), 2.3-2.5 (m, 4H); GC-MS: mass calcd for $C_5H_8N_2OS$ $[M+H]^+$, 144. Found 144.

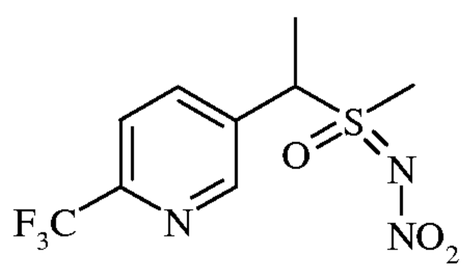
(B)



(A) (10)

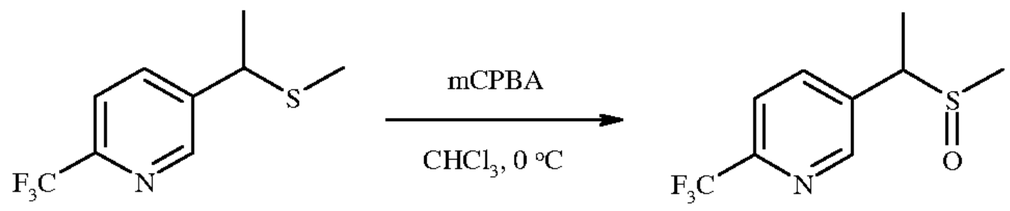
To a solution of 1-oxidotetrahydro-1H-1λ^4-thien-1-ylidenecyanamide (A) (200 mg, 1.4 mmol) in THF (10 ml) at -78 °C was added LDA solution in THF (1.8M, 850 µL, 1.5 mmol). The reaction was allowed to stir for 45 min, then 5-chloromethyl-2-trifluoromethylpyridine (300 mg, 1.5 mmol) was added dropwise. The solution was allowed to stir at -78 °C for 1 h, then it was warmed to 0 °C for an additional 2 h. The reaction was then quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, concentrated, and purified by flash chromatography to furnish 2-[(6-trifluoromethylpyridin-3-yl)methyl]-1-oxidotetrahydro-1H-1λ^4-thien-1-ylidenecyanamide (**10**) as a yellow oil (41 mg, 9%). IR (film) 2946, 2194, 1339 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ (mixture of two diastereomers) 8.6 (s, 2H), 7.8 (m, 2H), 7.7 (d, 1H), 7.6 (d, 1H), 3.4 - 3.8 (m, 7H), 3.3 (m, 1H), 3.0 - 3.2 (m, 2H), 1.9-2.6 (m, 8H); LC-MS (ELSD): mass calcd for $C_{12}H_{13}F_3N_3OS$ $[M+H]^+$, 304. Found 304.

Example XI. <u>Preparation of 2-trifluoromethyl-5-(1-{methyl(oxido)[oxido(oxo)hydrazono]- λ^4-sulfanyl}ethyl)pyridine (**11**)</u>



(11)

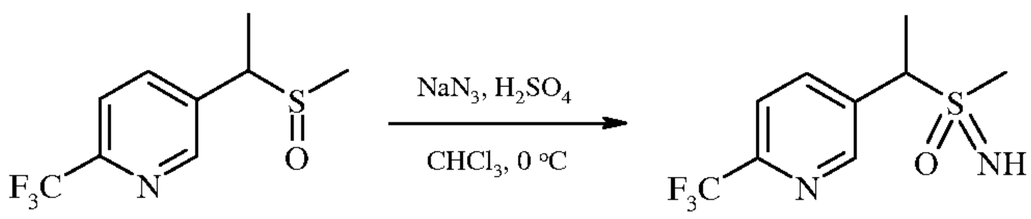
(A)



(A)

To a solution of 5-(1-methylthioethyl)-2-trifluoromethylpyridine (2.0 g, 9 mmol) in $CHCl_3$ (20 mL) at 0 °C was added solution of mCPBA (2.1 g, 10 mmol) in $CHCl_3$ (25 mL) over the course of 1.5 h. The solution was stirred an additional 2 h, then it was concentrated and purified by flash chromatography (10% MeOH/ CH_2Cl_2) to furnish 5-(1-methylsulfinylethyl)-2-trifluoromethylpyridine (A) as a yellow oil (710 mg, 33%) and a ~2:1 mixture of diastereomers. ^1H NMR (300 MHz, $CDCl_3$) δ (major diastereomer) 8.7 (s, 1H), 7.8 (d, 1H), 7.7 (d, 1H), 4.0 (q, 1H), 2.4 (s, 3H), 1.75 (d, 3H); (minor diastereomer) 8.6 (s, 1H), 7.9 (d, 1H), 7.7 (d, 1H), 3.8 (q, 1H), 2.3 (s, 3H), 1.8 (d, 3H); LC-MS (ELSD): mass calcd for $C_9H_{11}F_3NOS$ $[M+H]^+$, 238. Found 238.

(B)

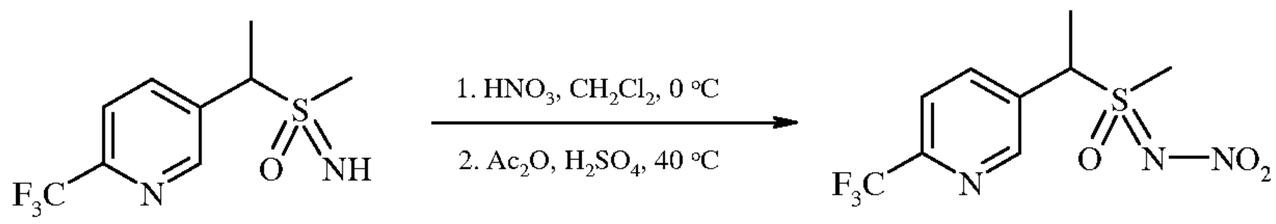


(A) (B)

To a solution of 5-(1-methylsulfinylethyl)-2-trifluoromethylpyridine (A) (600 mg, 2.5 mmol) in $CHCl_3$ (5 mL) at 0 °C was added sodium azide (260 mg, 4.0 mmol) and H_2SO_4 (1 mL). The reaction was warmed to 55 °C until gas evolution was observed, then it was cooled back down to room temperature overnight. The liquid was decanted into a separate flask and the residual syrup was dissolved in H_2O, basified with Na_2CO_3 and extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, concentrated and purified by flash chromatography to furnish 5-[1-(methylsulfonimidoyl)ethyl]-2-

trifluoromethylpyridine (B) as a yellow oil (130 mg, 20%) and a ~1:1 mixture of diastereomers. ^{1}H NMR (300 MHz, $CDCl_3$) δ (mixture of diastereomer) 8.8 (d, 2H), 8.0 (dd, 2H), 7.8 (d, 2H), 4.4 (m, 2H), 2.9 (s, 3H), 2.85 (s, 3H), 1.8 (m, 6H); LC-MS (ELSD): mass calcd for $C_9H_{11}F_3N_2OS$ $[M]^+$, 252. Found 252.

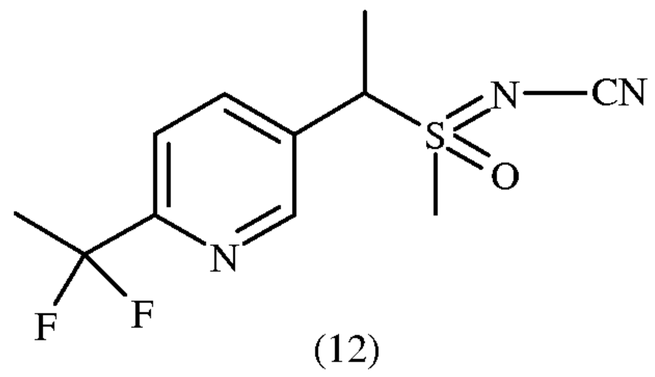
(C)



(B) (11)

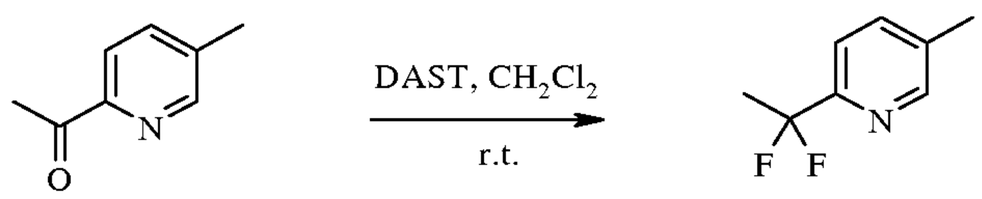
To a solution of 5-[1-(methylsulfonimidoyl)ethyl]-2-trifluoromethylpyridine (B) (100 mg, 0.4 mmol) in CH_2Cl_2 (2 mL) at 0 °C was added HNO_3 (16 μL, 0.4 mmol) dropwise. To the resulting suspension was added acetic anhydride (750 μL) and concentrated H_2SO_4 (5 μL) and the mixture was heated to 40 °C. The suspension slowly became homogeneous over the course of 15 min. The solvent was then removed and the crude residue was dissolved in H_2O. Solid Na_2CO_3 was added until pH 8 was reached and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, concentrated and purified by flash chromatography to furnish 2-trifluoromethyl-5-(1-{methyl(oxido)-[oxido(oxo)hydrazono]- λ^4-sulfanyl}ethyl)pyridine (**11**) as a yellow oil (22 mg, 19%) and a 1:1 mixture of diastereomers. ^{1}H NMR (300 MHz, $CDCl_3$) δ (mixture of diastereomers) 8.8 (d, 2H), 8.1 (m, 2H), 7.8 (m, 2H), 5.1 (q, 1H), 5.0 (q, 1H), 3.3 (s, 3H), 3.25 (s, 3H), 2.0 (m, 6H); LC-MS (ELSD): mass calcd for $C_9H_{11}F_3N_3O_3S$ $[M+H]^+$, 298. Found 298.

Example XII. Preparation of [6-(1,1-difluoroethyl)pyridin-3-yl)ethyl](methyl)-oxido- λ4-sulfanylidenecyanamide (**12**)



(12)

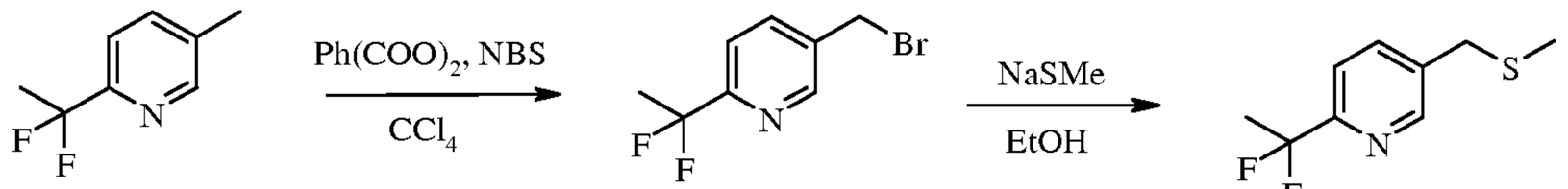
(A)



(A)

To a solution 5-methyl-2-acetylpyridine (9.9 g, 73.3 mmol) in molecule sieves-dried CH_2Cl_2 (150 mL) was added diethylamino sulfolnyltrifluoride (DAST) (25.8 g, 260 mmol) at room temperature and the mixture was stirred at room temperature overnight. More DAST (12 g, 74 mmol) was added and the reaction continued for two more days after which an additional DAST (3.8 g, 23 mmol) was added and the reaction continued for another 3 days. After the reaction was quenched slowly with saturated $NaHCO_3$ at 0 °C, the organic phase was separated, dried over Na_2SO_4, filtered, and concentrated. The residue was purified on silica gel eluted with 8% EtOAc in hexane to give 3.91 g of 2-(1,1-difluoroethyl)-5-methylpyridine (A) as a light brownish oil in 34% yield. GC-MS: mass calcd for $C_8H_9F_2N$ $[M]^+$ 157. Found 157.

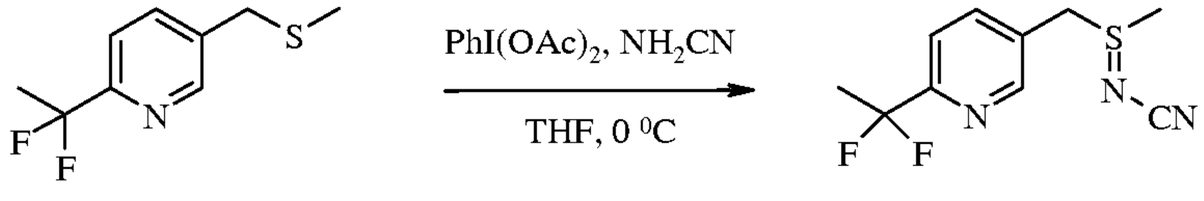
(B)



(A) (B)

A mixture of 2-(1,1-difluoroethyl)-5-methylpyridine (A) (2.0 g, 12.7 mmol), N-bromosuccinimide (2.2 g, 12.7 mmol) and benzoylperoxide (0.15 g, 0.63 mmol) in carbon tetrachloride (100 mL) was refluxed overnight. After the solid was removed by filtration, the filtrate was concentrated. The residue was re-dissolved in ethanol (40 mL) and sodium thiomethoxide (1.33 g, 19 mmol) was added at room temperature and stirred for 3 h. The solvent was removed under reduced pressure and the remaining mixture was dissolved in CH_2Cl_2 and water. After separation, the organic layer was dried over Na_2SO_4, filtered and concentrated. The crude product 2-(1,1-difluoroethyl)-5-methylthiomethyl-pyridine (B) was 94% pure on GC/MS, which was used directly for the next reaction without further purification. GC-MS: mass calcd for $C_9H_{11}F_2NS$ $[M]^+$ 203. Found 203.

(C)

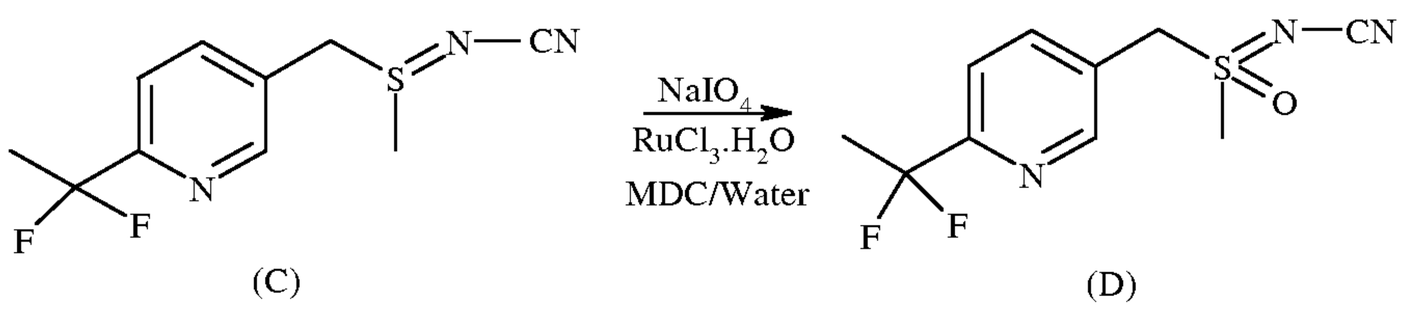


(B) (C)

To a stirred solution of 2-(1,1-difluoroethyl)-5-methylthiomethylpyridine (B) (1.22 g. 6.0 mmol) and cyanamide (0.25 g, 6.0 mmol) in THF (7 mL) cooled to 0 °C was added iodobenzene diacetate (1.93 g, 6.0 mmol) in one portion and the resulting mixture was stirred at 0 °C for 1 h and then at room temperature for 2

h. The solvent was removed *in vacuo* and the resulting mixture was purified on silica gel using 60% acetone in hexane (v/v) to give 1.22 g of [(6-(1,1-difluoroethylpyridin-3-yl)methyl](methyl)-λ^4-sulfanylidenecyanamide (C) (84% yield) as brownish oil which turned into a brownish solid after standing in the refrigerator overnight. LC-MS: mass calcd for $C_{10}H_{11}F_2N_3S$ $[M]^+$ 243.28. Found $[M+1]^+$ 244.11.

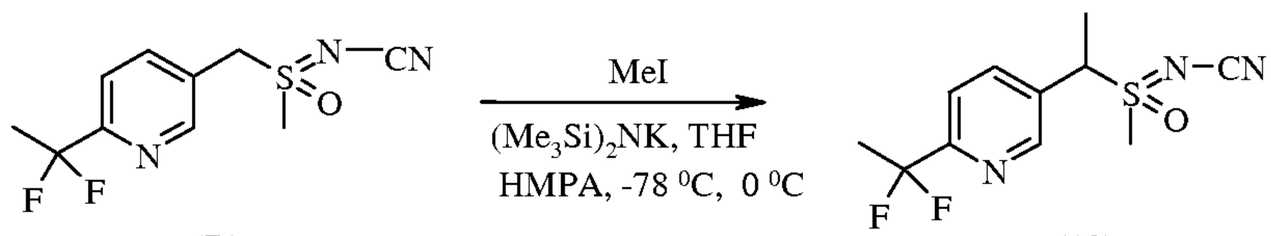
(D)



(C) (D)

To a 100 ml round bottom flask equipped with magnetic stirrer, addition funnel, and thermometer was charged the sodium periodate (0.95 g, 4.44 mmol) and water (12 mL). After the solid had dissolved, 15 mL of CH_2Cl_2 was added followed by the ruthenium trichloride hydrate (0.033 g, 0.15 mmol). [(6-(1,1-difluoroethylpyridin-3-yl)methyl](methyl)-λ^4-sulfanylidenecyanamide (C) (0.72 g, 2.96 mmol) dissolved in 5 mL of CH_2Cl_2 was added dropwise over a period of 30 min. The mixture was stirred rapidly at room temperature for 1.5 h and then filtered through a filtering paper to remove some insolubles. The mixture was then separated in separation funnel after ethyl acetate was added to facilitate the separation. The aqueous phase was extracted with CH_2Cl_2 twice. The combined organics was washed with brine, dried over dry Na_2SO_4, filtered, concentrated, and briefly purified on silica gel with 70% acetone in hexane to give 0.652 g of the desired product [(6-(1,1-difluoroethylpyridin-3-yl)methyl](methyl)-oxido λ^4-sulfanylidenecyanamide (D) as a white solid in 87% yield. LC-MS: mass calcd for $C_{10}H_{11}F_2N_3OS$ $[M]^+$ 259.28. Found $[M+1]^+$ 260.02.

(E)

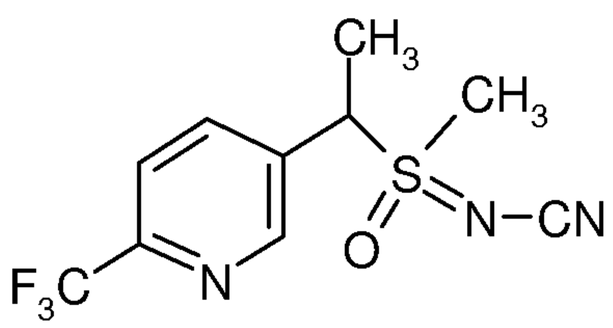


(D) (12)

To a solution of [(6-(1,1-difluoroethylpyridin-3-yl)methyl](methyl)-oxido λ^4-sulfanylidenecyanamide (D) (0.55 g, 2.0 mmol) and HMPA (0.09 mL, 0.55 mmol) in 20 mL anhydrous THF was added 0.5 M potassium bis(trimethylsilyl)amide in toluene (4.4 mL, 2.2 mmol) at –78 °C dropwise. After 45 min, iodomethane (0.14 mL, 2.2 mmol) was added in one portion via a syringe. Ten minutes later, the temperature was allowed to rise to 0 °C and mixture continued to stir for 1.5 h. The reaction was quenched with saturated aqueous NH_4Cl, diluted with brine, extracted once each with EtOAc and CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by preparative HPLC to give 0.15 g of the desired [6-(1,1-difluoroethyl)pyridin-3-yl)ethyl](methyl)-oxido- λ^4-sulfanylidenecyanamide (**12**) in 26% yield. LC-MS: mass calcd for $C_{11}H_{13}F_2N_3OS$ $[M]^+$ 273.31. Found $[M+1]^+$ 274.21.

<u>Increasing Plant Vigor.</u>

Compound A



73776-279

Test 1

Seeds were soaked beginning on T = 0 days in solutions of either Compound A, imidacloprid, or plain water containing 0.125% (v:v) Tween™ 20 (check treatment). Compounds were formulated as technical material in water containing 0.125% Tween 20. The high rate solution was prepared first by weighing each material into a container and then adding water and Tween 20 (0.125%) so that a concentration of 0.05 mg/ml (50 ppm) of solution was made. This high rate solution was serially diluted in 10 fold increments with water containing Tween 20 (0.125%) to achieve successively lower concentrations. Solution concentrations were 50, 5, 0.5, 0.05 and 0.005 ppm. No evaporation was possible and a significant excess of solution was present to ensure abundant availability of either Compound A or imidacloprid from each solution. On average 20 ml of solution was used to soak groups of seed needed for the seed soaking phase of this test. Seeds were removed from these solutions on T = 2 days and planted. Seeds exposed to each unique treatment were germinated as a groups in dedicated shallow plastic cups filled with white sand and containing plain water. Planting of these seeds occurred on T = 2 days and the seeds were grown in these shallow cups until T = 10 days. Initially 70 ml of water was added to each shallow cup at planting and additional water was added to the cups as needed to keep the sand moist. On T = 10 days germinating seedlings were transplanted from the shallow germination cups to individual containers (plastic cups -6 reps per treatment) filled with white sand. Thirty ml of water was used to water the plants following transplanting. After the initial treatment water was added to cups as needed to maintain moisture for plant development. An outline of the treatments is presented in Table 1. On T = 14 days each plant was infested with cotton aphid (CA) *Aphis gossypii* by transferring a small piece of infested foliage to each test plant. The number of aphids transferred to each plant was uniform based on visual

estimation. Plants were rated on T = 17 days and T = 18 days by counting the number of CA and taking the weight of the each plant. The plant part weighed was the aerial portion of the plant cut off at the surface of the sand. Data were analyzed using analysis of variance with an LSD means separation test (Minitab).

Table 1. Treatment outline, aphid counts and plant weights.

No.	Compound	Rate (ppm)	Aphids (#/plant)						Plant Weight (g)					
			Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6
1	A	50	4	2	2	12	18	2	2.29	2.22	2.12	1.87	1.87	2.14
2	A	5	23	25	33	65	25	32	2.23	2.1	1.79	2.53	1.87	1.9
3	A	0.5	55	75	65	40	45	30	1.84	1.88	2.04	2.13	1.96	1.8
4	A	0.05	70	80	60	35	NR	NR	0.73	1.35	1.2	1.1	NR	NR
5	A	0.005	72	110	35	70	55	15	2.36	1.76	2.09	2.22	1.92	1.93
6	Imidacloprid	50	0	0	4	7	4	1	1.47	2.05	1.73	1.84	2.02	1.86
7	Imidacloprid	5	33	37	17	18	30	34	1.64	1.44	1.91	1.44	1.75	2.05
8	Imidacloprid	0.5	25	44	43	70	80	30	1.61	1.82	1.73	2.05	1.66	1.95
9	Imidacloprid	0.05	95	60	65	95	75	50	1.38	1.37	1.65	1.57	1.72	1.62
10	Imidacloprid	0.005	45	125	55	75	80	35	2.07	1.59	2.01	1.67	1.86	1.68
11	Check		80	85	65	45	60	60	1.6	1.13	1.37	1.5	1.63	1.36
12	Check		25	60	50	50	65	75	1.41	1.37	2.04	1.56	1.4	1.42

NR= plants not rated due to plant death

Test 2

Technical samples of Compound A and imidacloprid were dissolved in water containing 0.125% Tween 20 (V:V). The high rate solution for each material was 50 ppm and lower rates were generated for each material by 4 fold dilution with additional volumes of 0.125% Tween 20 in water. The treatment concentrations for Compound A and imidacloprid were 50, 12.5, 3.125, 0.78 and 0.19 ppm. Solutions were prepared in excess and 40 ml was added to 50 ml centrifuge tubes. Corn (*Zea mays* 'M2T783') seeds were inspected for uniform size and undamaged condition and were placed into each centrifuge tube containing specific compound by rate solutions. A treatment of only 0.125% aqueous Tween 20 was used to soak corn seeds and served as the untreated check. Tubes containing seeds and compound solutions were held at room temperature

and after 48 the seeds were removed from each solution, rinsed and planted into sand in 7.5 cm^2 pots. Tissue paper was placed into the bottom of each pot to keep sand from leaching from the pot. A total of 8 reps of each compound by rate combination were planted for both corn. Eight replicate pots of compound by rate combination were arranged in a completely randomized design on greenhouse carts. This arrangement of treated seeds in pots was placed into the greenhouse and watered over the top as needed. Each cart was equipped with a plastic rack that served to raise the pots up off the cart surface and away from any standing water. The carts were placed in the center of the greenhouse and were rotated 180 degrees daily. After 13 days the carts were moved to the laboratory and the plants were cut off at the soil surface and weighed. Fresh plant weight data were analyzed for homogeneity of variance using Levene's test and further evaluated using one way analysis of variance of individual treatment combinations (compound by rate) and pooled by compound across rates. Means were separated using Tukey's mean separation test with a family-wise error rate of 0.05. All analyses were conducted using Minitab

Results

Test 1

Analysis of Plant Weights

Plant weights are summarized in Table 1. Treatment number 4 experienced some negative effects associated with excess watering during the phase when these plants were being germinated. As a result the plants were undersized and many seeds did not germinate. Only four replicate plants were able to be planted to individual growing cups. An analysis of data homogeneity was performed on the plant weight by No (Treatment number) data (Table 1) using Levene's test

(Minitab) and the resulting test statistic of 0.399 indicated that the data were homogeneous (P-value 0.951). Prior to conducting an analysis of individual treatment effects (factorial analysis of variance, LSD means separation test P=0.05, Minitab) on weight Treatment 4 (Compound A 0.05 ppm) was removed from the analysis because it was judged to be an outlier based on poor growth as described above. The paired imidacloprid rate (0.05 ppm, No. 9) was also removed to keep the data balanced.

Analysis of Aphid Count Data

Raw data were not homogeneous and so replicate aphid counts were transformed using a square root count + 0.5 transformation. These data were homogeneous (Levene's test P=0.438) and were analyzed using a factorial analysis of compound (imidacloprid or Compound A) by rate (excluding the 0.05 ppm rates for both imidacloprid and Compound A as described previously). This analysis indicates that there was no interaction between compound and rate and that only the rate factor was a significant contributor to difference. An analysis of the compound main effect including the Check indicates that there were significantly more aphids in the check treatment compared to Compound A or imidacloprid but that there was not a difference between Compound A and imidacloprid main effects.

Test 2

Corn data were homogeneous based on Levene's test for homgeneity of variance (p=0.116 and p=0.69 respectively). AOV of corn data did indicate a difference (F=3.22, P=0.045, df=2) for pooled compound effects but not for individual treatment effects. Tukey's pair-wise comparison of compound factors indicated that only the comparison of Compound A and the untreated Tween 20 water check was significantly different (Table 2). This significant increase in

seedling corn plant weight following exposure to Compound A represented a 38.9% increase in seedling weight compared to the untreated Tween 20 water check treatment. Other pair-wise comparisons (imidacloprid vs. Compound A and imidacloprid vs. the untreated check) were not significantly different.

Table 2. Effect of treatment on corn plant weights.

Compound	Reps	Plant Weight (g)		
		Mean	SE Mean	% increase
Imidacloprid	37	2.841	0.172	24.8
Tween 20 Water check	8	2.275	0.169	
Compound A	38	3.162	0.148	38.9*
* Significant increase over Tween 20 Water check (Tukey's pairwise comparisons P=0.05)				

Conclusions

Test 1

Compound A when applied to seeds caused a significant increase in plant weight. This effect was significantly greater than was observed for imidacloprid. Both imidacloprid and Compound A resulted in increased plant weights compared to the check plants. On average, Compound A and imidacloprid reduced the number of aphids on plants however these effects were not statistically different and so this result does not correlate with the growth effects measured. Plant weight increases are related to exposure to Compound A and are not explained by other factors such as insect density resulting from compound treatment or rate.

Test 2

Exposure of corn seeds to solutions of Compound A resulted in significantly increased plant weight (38.9%) compared to the check treatment of 0.125% Tween 20 in water.

PESTS

In another embodiment, the invention disclosed in this document can be used to control pests.

In another embodiment, the invention disclosed in this document can be used to control pests of the Phylum Nematoda.

In another embodiment, the invention disclosed in this document can be used to control pests of the Phylum Arthropoda.

In another embodiment, the invention disclosed in this document can be used to control pests of the Subphylum Chelicerata.

In another embodiment, the invention disclosed in this document can be used to control pests of the Class Arachnida.

In another embodiment, the invention disclosed in this document can be used to control pests of the Subphylum Myriapoda.

In another embodiment, the invention disclosed in this document can be used to control pests of the Class Symphyla.

In another embodiment, the invention disclosed in this document can be used to control pests of the Subphylum Hexapoda.

In another embodiment, the invention disclosed in this document can be used to control pests of the Class Insecta.

In another embodiment, the invention disclosed in this document can be used to control **Coleoptera (beetles)**. A non-exhaustive list of these pests includes, but is not limited to, *Acanthoscelides* spp. (weevils), *Acanthoscelides*

obtectus (common bean weevil), *Agrilus planipennis* (emerald ash borer), *Agriotes* spp. (wireworms), *Anoplophora glabripennis* (Asian longhorned beetle), *Anthonomus* spp. (weevils), *Anthonomus grandis* (boll weevil), *Aphidius* spp., *Apion* spp. (weevils), *Apogonia* spp. (grubs), *Ataenius spretulus* (Black Turgrass Ataenius), *Atomaria linearis* (pygmy mangold beetle), *Aulacophore* spp., *Bothynoderes punctiventris* (beet root weevil), *Bruchus* spp. (weevils), *Bruchus pisorum* (pea weevil), *Cacoesia* spp., *Callosobruchus maculatus* (southern cow pea weevil), *Carpophilus hemipteras* (dried fruit beetle), *Cassida vittata*, *Cerosterna* spp, *Cerotoma* spp. (chrysomeids), *Cerotoma trifurcata* (bean leaf beetle), *Ceutorhynchus* spp. (weevils), *Ceutorhynchus assimilis* (cabbage seedpod weevil), *Ceutorhynchus napi* (cabbage curculio), *Chaetocnema* spp. (chrysomelids), *Colaspis* spp. (soil beetles), *Conoderus scalaris*, *Conoderus stigmosus*, *Conotrachelus nenuphar* (plum curculio), *Cotinus nitidis* (Green June beetle), *Crioceris asparagi* (asparagus beetle), *Cryptolestes ferrugineus* (rusty grain beetle), *Cryptolestes pusillus* (flat grain beetle), *Cryptolestes turcicus* (Turkish grain beetle), *Ctenicera* spp. (wireworms), *Curculio* spp. (weevils), *Cyclocephala* spp. (grubs), *Cylindrocpturus adspersus* (sunflower stem weevil), *Deporaus marginatus* (mango leaf-cutting weevil), *Dermestes lardarius* (larder beetle), *Dermestes maculates* (hide beetle), *Diabrotica* spp. (chrysolemids), *Epilachna varivestis* (Mexican bean beetle), *Faustinus cubae, Hylobius pales* (pales weevil), *Hypera* spp. (weevils), *Hypera postica* (alfalfa weevil), *Hyperdoes* spp. (Hyperodes weevil), *Hypothenemus hampei* (coffee berry beetle), *Ips* spp. (engravers), *Lasioderma serricorne* (cigarette beetle), *Leptinotarsa decemlineata* (Colorado potato beetle), *Liogenys fuscus, Liogenys suturalis, Lissorhoptrus oryzophilus* (rice water weevil), *Lyctus* spp. (wood beetles/powder post beetles), *Maecolaspis joliveti, Megascelis* spp., *Melanotus communis, Meligethes* spp., *Meligethes aeneus* (blossom beetle), *Melolontha melolontha* (common European cockchafer), *Oberea brevis, Oberea linearis, Oryctes rhinoceros* (date palm

beetle), *Oryzaephilus mercator* (merchant grain beetle), *Oryzaephilus surinamensis* (sawtoothed grain beetle), *Otiorhynchus* spp. (weevils), *Oulema melanopus* (cereal leaf beetle), *Oulema oryzae, Pantomorus* spp. (weevils), *Phyllophaga* spp. (May/June beetle), *Phyllophaga cuyabana, Phyllotreta* spp. (chrysomelids), *Phynchites* spp., *Popillia japonica* (Japanese beetle), *Prostephanus truncates* (larger grain borer), *Rhizopertha dominica* (lesser grain borer), *Rhizotrogus* spp. (Eurpoean chafer), *Rhynchophorus* spp. (weevils), *Scolytus* spp. (wood beetles), *Shenophorus* spp. (Billbug), *Sitona lineatus* (pea leaf weevil), *Sitophilus* spp. (grain weevils), *Sitophilus granaries* (granary weevil), *Sitophilus oryzae* (rice weevil), *Stegobium paniceum* (drugstore beetle), *Tribolium* spp. (flour beetles), *Tribolium castaneum* (red flour beetle), *Tribolium confusum* (confused flour beetle), *Trogoderma variabile* (warehouse beetle), and *Zabrus tenebioides.*

In another embodiment, the invention disclosed in this document can be used to control **Dermaptera (earwigs)**.

In another embodiment, the invention disclosed in this document can be used to control **Dictyoptera (cockroaches)**. A non-exhaustive list of these pests includes, but is not limited to, *Blattella germanica* (German cockroach), *Blatta orientalis* (oriental cockroach), *Parcoblatta pennylvanica, Periplaneta americana* (American cockroach), *Periplaneta australoasiae* (Australian cockroach), *Periplaneta brunnea* (brown cockroach), *Periplaneta fuliginosa* (smokybrown cockroach), *Pyncoselus suninamensis* (Surinam cockroach), and *Supella longipalpa* (brownbanded cockroach).

In another embodiment, the invention disclosed in this document can be used to control **Diptera (true flies)**. A non-exhaustive list of these pests includes, but is not limited to, *Aedes* spp. (mosquitoes), *Agromyza frontella* (alfalfa blotch

leafminer), *Agromyza* spp. (leaf miner flies), *Anastrepha* spp. (fruit flies), *Anastrepha suspensa* (Caribbean fruit fly), *Anopheles* spp. (mosquitoes), *Batrocera* spp. (fruit flies), *Bactrocera cucurbitae* (melon fly), *Bactrocera dorsalis* (oriental fruit fly), *Ceratitis* spp. (fruit flies), *Ceratitis capitata* (Mediterranea fruit fly), *Chrysops* spp. (deer flies), *Cochliomyia* spp. (screwworms), *Contarinia* spp. (Gall midges), *Culex* spp. (mosquitoes), *Dasineura* spp. (gall midges), *Dasineura brassicae* (cabbage gall midge), *Delia* spp., *Delia platura* (seedcorn maggot), *Drosophila* spp. (vinegar flies), *Fannia* spp. (filth flies), *Fannia canicularis* (little house fly), *Fannia scalaris* (latrine fly), *Gasterophilus intestinalis* (horse bot fly), *Gracillia perseae, Haematobia irritans* (horn fly), *Hylemyia* spp. (root maggots), *Hypoderma lineatum* (common cattle grub), *Liriomyza* spp. (leafminer flies), *Liriomyza brassica* (serpentine leafminer), *Melophagus ovinus* (sheep ked), *Musca spp.* (muscid flies), *Musca autumnalis* (face fly), *Musca domestica* (house fly), *Oestrus ovis* (sheep bot fly), *Oscinella frit* (frit fly), *Pegomyia betae* (beet leafminer), *Phorbia spp., Psila rosae* (carrot rust fly), *Rhagoletis cerasi* (cherry fruit fly), *Rhagoletis pomonella* (apple maggot), *Sitodiplosis mosellana* (orange wheat blossom midge), *Stomoxys calcitrans* (stable fly), *Tabanus* spp. (horse flies), and *Tipula* spp. (crane flies).

In another embodiment, the invention disclosed in this document can be used to control **Hemiptera (true bugs)**. A non-exhaustive list of these pests includes, but is not limited to, *Acrosternum hilare* (green stink bug), *Blissus leucopterus* (chinch bug), *Calocoris norvegicus* (potato mirid), *Cimex hemipterus* (tropical bed bug), *Cimex lectularius* (bed bug), *Dagbertus fasciatus, Dichelops furcatus, Dysdercus suturellus* (cotton stainer), *Edessa meditabunda, Eurygaster maura* (cereal bug), *Euschistus heros, Euschistus servus* (brown stink bug), *Helopeltis antonii, Helopeltis theivora* (tea blight plantbug), *Lagynotomus* spp. (stink bugs), *Leptocorisa oratorius, Leptocorisa varicornis, Lygus* spp. (plant

bugs), *Lygus hesperus* (western tarnished plant bug), *Maconellicoccus hirsutus, Neurocolpus longirostris, Nezara viridula* (southern green stink bug), *Phytocoris* spp. (plant bugs), *Phytocoris californicus, Phytocoris relativus, Piezodorus guildingi, Poecilocapsus lineatus* (fourlined plant bug), *Psallus vaccinicola, Pseudacysta perseae, Scaptocoris castanea,* and *Triatoma* spp. (bloodsucking conenose bugs/kissing bugs).

In another embodiment, the invention disclosed in this document can be used to control **Homoptera (aphids, scales, whiteflies, leafhoppers)**. A non-exhaustive list of these pests includes, but is not limited to, *Acrythosiphon pisum* (pea aphid), *Adelges* spp. (adelgids), *Aleurodes proletella* (cabbage whitefly), *Aleurodicus disperses, Aleurothrixus floccosus* (woolly whitefly), *Aluacaspis* spp., *Amrasca bigutella bigutella, Aphrophora* spp. (leafhoppers), *Aonidiella aurantii* (California red scale), *Aphis* spp. (aphids), *Aphis gossypii* (cotton aphid), *Aphis pomi* (apple aphid), *Aulacorthum solani* (foxglove aphid), *Bemisia spp.* (whiteflies), *Bemisia argentifolii, Bemisia tabaci* (sweetpotato whitefly), *Brachycolus noxius* (Russian aphid), *Brachycorynella asparagi* (asparagus aphid), *Brevennia rehi, Brevicoryne brassicae* (cabbage aphid), *Ceroplastes* spp.(scales), *Ceroplastes rubens* (red wax scale), *Chionaspis* spp.(scales), *Chrysomphalus* spp. (scales), *Coccus* spp. (scales), *Dysaphis plantaginea* (rosy apple aphid), *Empoasca* spp. (leafhoppers), *Eriosoma lanigerum* (woolly apple aphid), *Icerya purchasi* (cottony cushion scale), *Idioscopus nitidulus* (mango leafhopper), *Laodelphax striatellus* (smaller brown planthopper), *Lepidosaphes* spp., *Macrosiphum* spp., *Macrosiphum euphorbiae* (potato aphid), *Macrosiphum granarium* (English grain aphid), *Macrosiphum rosae* (rose aphid), *Macrosteles quadrilineatus* (aster leafhopper), *Mahanarva frimbiolata, Metopolophium dirhodum* (rose grain aphid), *Mictis longicornis, Myzus persicae* (green peach aphid), *Nephotettix* spp. (leafhoppers), *Nephotettix cinctipes* (green leafhopper), *Nilaparvata lugens*

(brown planthopper), *Parlatoria pergandii* (chaff scale), *Parlatoria ziziphi* (ebony scale), *Peregrinus maidis* (corn delphacid), *Philaenus* spp. (spittlebugs), *Phylloxera vitifoliae* (grape phylloxera), *Physokermes piceae* (spruce bud scale), *Planococcus* spp. (mealybugs), *Pseudococcus* spp. (mealybugs), *Pseudococcus brevipes* (pine apple mealybug), *Quadraspidiotus perniciosus* (San Jose scale), *Rhapalosiphum* spp. (aphids), *Rhapalosiphum maida* (corn leaf aphid), *Rhapalosiphum padi* (oat bird-cherry aphid), *Saissetia* spp. (scales), *Saissetia oleae* (black scale), *Schizaphis graminum* (greenbug), *Sitobion avenae* (English grain aphid), *Sogatella furcifera* (white-backed planthopper), *Therioaphis* spp. (aphids), *Toumeyella* spp. (scales), *Toxoptera* spp. (aphids), *Trialeurodes* spp. (whiteflies), *Trialeurodes vaporariorum* (greenhouse whitefly), *Trialeurodes abutiloneus* (bandedwing whitefly), *Unaspis* spp. (scales), *Unaspis yanonensis* (arrowhead scale), and *Zulia entreriana.*

In another embodiment, the invention disclosed in this document can be used to control **Hymenoptera (ants, wasps, and bees)**. A non-exhaustive list of these pests includes, but is not limited to, *Acromyrrmex* spp., *Athalia rosae, Atta* spp. (leafcutting ants), *Camponotus* spp. (carpenter ants), *Diprion* spp. (sawflies), *Formica* spp. (ants), *Iridomyrmex humilis* (Argentine ant), *Monomorium* ssp., *Monomorium minumum* (little black ant), *Monomorium pharaonis* (Pharaoh ant), *Neodiprion* spp. (sawflies), *Pogonomyrmex* spp. (harvester ants), *Polistes* spp. (paper wasps), *Solenopsis* spp. (fire ants), *Tapoinoma sessile* (odorous house ant), *Tetranomorium* spp. (pavement ants), *Vespula* spp. (yellow jackets), and *Xylocopa* spp. (carpenter bees).

In another embodiment, the invention disclosed in this document can be used to control **Isoptera (termites)**. A non-exhaustive list of these pests includes, but is not limited to, *Coptotermes* spp., *Coptotermes curvignathus, Coptotermes*

frenchii, Coptotermes formosanus (Formosan subterranean termite), *Cornitermes* spp. (nasute termites), *Cryptotermes* spp. (drywood termites), *Heterotermes* spp. (desert subterranean termites), *Heterotermes aureus, Kalotermes* spp. (drywood termites), *Incistitermes* spp. (drywood termites), *Macrotermes* spp. (fungus growing termites), *Marginitermes* spp. (drywood termites), *Microcerotermes* spp. (harvester termites), *Microtermes obesi, Procornitermes* spp., *Reticulitermes* spp. (subterranean termites), *Reticulitermes banyulensis, Reticulitermes grassei, Reticulitermes flavipes* (eastern subterranean termite), *Reticulitermes hageni, Reticulitermes hesperus* (western subterranean termite), *Reticulitermes santonensis, Reticulitermes speratus, Reticulitermes tibialis, Reticulitermes virginicus, Schedorhinotermes* spp., and *Zootermopsis* spp. (rotten-wood termites).

In another embodiment, the invention disclosed in this document can be used to control **Lepidoptera (moths and butterflies)**. A non-exhaustive list of these pests includes, but is not limited to, *Achoea janata, Adoxophyes* spp., *Adoxophyes orana*, *Agrotis* spp. (cutworms), *Agrotis ipsilon* (black cutworm), *Alabama argillacea* (cotton leafworm), *Amorbia cuneana, Amyelosis transitella* (navel orangeworm), *Anacamptodes defectaria, Anarsia lineatella* (peach twig borer), *Anomis sabulifera* (jute looper), *Anticarsia gemmatalis* (velvetbean caterpillar), *Archips argyrospila* (fruittree leafroller), *Archips rosana* (rose leaf roller), *Argyrotaenia spp.* (tortricid moths), *Argyrotaenia citrana* (orange tortrix), *Autographa gamma, Bonagota cranaodes, Borbo cinnara* (rice leaf folder), *Bucculatrix thurberiella* (cotton leafperforator), *Caloptilia* spp. (leaf miners), *Capua reticulana, Carposina niponensis* (peach fruit moth), *Chilo* spp., *Chlumetia transversa* (mango shoot borer), *Choristoneura rosaceana* (obliquebanded leafroller), *Chrysodeixis* spp., *Cnaphalocerus medinalis* (grass leafroller), *Colias* spp., *Conpomorpha cramerella, Cossus cossus* (carpenter moth), *Crambus* spp.

(Sod webworms), *Cydia funebrana* (plum fruit moth), *Cydia molesta* (oriental fruit moth), *Cydia nignicana* (pea moth), *Cydia pomonella* (codling moth), *Darna diducta, Diaphania* spp. (stem borers), *Diatraea* spp. (stalk borers), *Diatraea saccharalis* (sugarcane borer), *Diatraea graniosella* (southwester corn borer), *Earias* spp. (bollworms), *Earias insulata* (Egyptian bollworm), *Earias vitella* (rough northern bollworm), *Ecdytopopha aurantianum, Elasmopalpus lignosellus* (lesser cornstalk borer), *Epiphysias postruttana* (light brown apple moth), *Ephestia* spp. (flour moths), *Ephestia cautella* (almond moth), *Ephestia elutella* (tobbaco moth), *Ephestia kuehniella* (Mediterranean flour moth), *Epimeces* spp., *Epinotia aporema, Erionota thrax* (banana skipper), *Eupoecilia ambiguella* (grape berry moth), *Euxoa auxiliaris* (army cutworm), *Feltia* spp. (cutworms), *Gortyna* spp. (stemborers), *Grapholita molesta (*oriental fruit moth), *Hedylepta indicata* (bean leaf webber), *Helicoverpa* spp. (noctuid moths), *Helicoverpa armigera* (cotton bollworm), *Helicoverpa zea* (bollworm/corn earworm), *Heliothis* spp. (noctuid moths), *Heliothis virescens* (tobacco budworm), *Hellula undalis* (cabbage webworm), *Indarbela* spp. (root borers), *Keiferia lycopersicella* (tomato pinworm), *Leucinodes orbonalis* (eggplant fruit borer), *Leucoptera malifoliella, Lithocollectis* spp., *Lobesia botrana* (grape fruit moth), *Loxagrotis* spp. (noctuid moths), *Loxagrotis albicosta* (western bean cutworm), *Lymantria dispar* (gypsy moth), *Lyonetia clerkella* (apple leaf miner), *Mahasena corbetti* (oil palm bagworm), *Malacosoma* spp. (tent caterpillars), *Mamestra brassicae* (cabbage armyworm), *Maruca testulalis* (bean pod borer), *Metisa plana* (bagworm), *Mythimna unipuncta* (true armyworm), *Neoleucinodes elegantalis* (small tomato borer), *Nymphula depunctalis* (rice caseworm), *Operophthera brumata* (winter moth), *Ostrinia nubilalis* (European corn borer), *Oxydia vesulia, Pandemis cerasana* (common currant tortrix), *Pandemis heparana* (brown apple tortrix), *Papilio demodocus, Pectinophora gossypiella* (pink bollworm), *Peridroma* spp. (cutworms), *Peridroma saucia* (variegated cutworm), *Perileucoptera coffeella*

(white coffee leafminer), *Phthorimaea operculella* (potato tuber moth), *Phyllocnisitis citrella*, *Phyllonorycter* spp. (leafminers), *Pieris rapae* (imported cabbageworm), *Plathypena scabra, Plodia interpunctella* (Indian meal moth), *Plutella xylostella* (diamondback moth), *Polychrosis viteana* (grape berry moth), *Prays endocarpa,Prays oleae* (olive moth), *Pseudaletia* spp. (noctuid moths), *Pseudaletia unipunctata* (armyworm), *Pseudoplusia includens* (soybean looper), *Rachiplusia nu*, *Scirpophaga incertulas, Sesamia* spp. (stemborers), *Sesamia inferens* (pink rice stem borer), *Sesamia nonagrioides, Setora nitens, Sitotroga cerealella* (Angoumois grain moth), *Sparganothis pilleriana, Spodoptera* spp. (armyworms), *Spodoptera exigua* (beet armyworm), *Spodoptera fugiperda* (fall armyworm), *Spodoptera oridania* (southern armyworm), *Synanthedon* spp. (root borers), *Thecla basilides, Thermisia gemmatalis, Tineola bisselliella* (webbing clothes moth), *Trichoplusia ni* (cabbage looper), *Tuta absoluta, Yponomeuta* spp., *Zeuzera coffeae* (red branch borer), and *Zeuzera pyrina* (leopard moth).

In another embodiment, the invention disclosed in this document can be used to control **Mallophaga (chewing lice)**. A non-exhaustive list of these pests includes, but is not limited to, *Bovicola ovis* (sheep biting louse), *Menacanthus stramineus* (chicken body louse), and *Menopon gallinea* (common hen house).

In another embodiment, the invention disclosed in this document can be used to control **Orthoptera (grasshoppers, locusts, and crickets)**. A non-exhaustive list of these pests includes, but is not limited to, *Anabrus simplex* (Mormon cricket), Gryllotalpidae (mole crickets), *Locusta migratoria,* Melanoplus spp.(grasshoppers), *Microcentrum retinerve* (angularwinged katydid), *Pterophylla* spp. (kaydids), *chistocerca gregaria, Scudderia furcata* (forktailed bush katydid), and *Valanga nigricorni.*

In another embodiment, the invention disclosed in this document can be used to control **Phthiraptera (sucking lice)**. A non-exhaustive list of these pests includes, but is not limited to, *Haematopinus* spp. (cattle and hog lice), *Linognathus ovillus* (sheep louse), *Pediculus humanus capitis* (human body louse), *Pediculus humanus humanus* (human body lice), and *Pthirus pubis* (crab louse),

In another embodiment, the invention disclosed in this document can be used to control **Siphonaptera (fleas)**. A non-exhaustive list of these pests includes, but is not limited to, *Ctenocephalides canis* (dog flea), *Ctenocephalides felis* (cat flea), and *Pulex irritans* (human flea).

In another embodiment, the invention disclosed in this document can be used to control **Thysanoptera (thrips)**. A non-exhaustive list of these pests includes, but is not limited to, *Frankliniella fusca* (tobacco thrips), *Frankliniella occidentalis* (western flower thrips), *Frankliniella shultzei Frankliniella williamsi* (corn thrips), *Heliothrips haemorrhaidalis* (greenhouse thrips), *Riphiphorothrips cruentatus, Scirtothrips* spp., *Scirtothrips citri* (citrus thrips), *Scirtothrips dorsalis* (yellow tea thrips), *Taeniothrips rhopalantennalis,* and *Thrips* spp.

In another embodiment, the invention disclosed in this document can be used to control **Thysanura (bristletails)**. A non-exhaustive list of these pests includes, but is not limited to, *Lepisma* spp. (silverfish) and *Thermobia* spp. (firebrats).

In another embodiment, the invention disclosed in this document can be used to control **Acarina (mites and ticks)**. A non-exhaustive list of these pests includes, but is not limited to, *Acarapsis woodi* (tracheal mite of honeybees), *Acarus* spp. (food mites), *Acarus siro* (grain mite), *Aceria mangiferae* (mango bud

mite), *Aculops* spp., *Aculops lycopersici* (tomato russet mite), *Aculops pelekasi, Aculus pelekassi*, *Aculus schlechtendali* (apple rust mite), *Amblyomma americanum* (lone star tick), *Boophilus* spp. (ticks), *Brevipalpus obovatus* (privet mite), *Brevipalpus phoenicis* (red and black flat mite), *Demodex* spp. (mange mites), *Dermacentor* spp. (hard ticks), *Dermacentor variabilis* (american dog tick), *Dermatophagoides pteronyssinus* (house dust mite), *Eotetranycus* spp., *Eotetranychus carpini* (yellow spider mite), *Epitimerus* spp., *Eriophyes* spp., *Ixodes* spp. (ticks), *Metatetranycus* spp., *Notoedres cati, Oligonychus* spp., *Oligonychus coffee,Oligonychus ilicus* (southern red mite), *Panonychus* spp., *Panonychus citri* (citrus red mite), *Panonychus ulmi* (European red mite), *Phyllocoptruta oleivora* (citrus rust mite), *Polyphagotarsonemun latus* (broad mite), *Rhipicephalus sanguineus* (brown dog tick), *Rhizoglyphus* spp. (bulb mites), *Sarcoptes scabiei* (itch mite), *Tegolophus perseaflorae, Tetranychus* spp., *Tetranychus urticae* (twospotted spider mite), and *Varroa destructor* (honey bee mite).

In another embodiment, the invention disclosed in this document can be used to control **Nematoda (nematodes)**. A non-exhaustive list of these pests includes, but is not limited to, *Aphelenchoides* spp. (bud and leaf & pine wood nematodes), *Belonolaimus* spp. (sting nematodes), *Criconemella* spp. (ring nematodes), *Dirofilaria immitis* (dog heartwom), *Ditylenchus* spp. (stem and bulb nematodes), *Heterodera* spp. (cyst nematodes), *Heterodera zeae* (corn cyst nematode), *Hirschmanniella* spp. (root nematodes), *Hoplolaimus* spp. (lance nematodes), *Meloidogyne* spp. (root knot nematodes), *Meloidogyne incognita* (root knot nematode), *Onchocerca volvulus* (hook-tail worm), *Pratylenchus* spp. (lesion nematodes), *Radopholus* spp. (burrowing nematodes), and *Rotylenchus reniformis* (kidney-shaped nematode).

In another embodiment, the invention disclosed in this document can be used to control **Symphyla (symphylans)**. A non-exhaustive list of these pests includes, but is not limited to, *Scutigerella immaculata.*

For more detailed information consult "Handbook of Pest Control – The Behavior, Life Histroy, and Control of Household Pests" by Arnold Mallis, 9th Edition, copyright 2004 by GIE Media Inc.

MIXTURES

Some of the pesticides that can be employed beneficially in combination with the invention disclosed in this document include, but are not limited to the following:

1,2 dichloropropane, 1,3 dichloropropene,

abamectin, acephate, acequinocyl, acetamiprid, acethion, acetoprole, acrinathrin, acrylonitrile, alanycarb, aldicarb, aldoxycarb, aldrin, allethrin, allosamidin, allyxycarb, alpha cypermethrin, alpha ecdysone, amidithion, amidoflumet, aminocarb, amiton, amitraz, anabasine, arsenous oxide, athidathion, azadirachtin, azamethiphos, azinphos ethyl, azinphos methyl, azobenzene, azocyclotin, azothoate,

barium hexafluorosilicate, barthrin, benclothiaz, bendiocarb, benfuracarb, benomyl, benoxafos, bensultap, benzoximate, benzyl benzoate, beta cyfluthrin, beta cypermethrin, bifenazate, bifenthrin, binapacryl, bioallethrin, bioethanomethrin, biopermethrin, bistrifluron, borax, boric acid, bromfenvinfos, bromo DDT, bromocyclen, bromophos, bromophos ethyl, bromopropylate, bufencarb, buprofezin, butacarb, butathiofos, butocarboxim, butonate, butoxycarboxim,

cadusafos, calcium arsenate, calcium polysulfide, camphechlor, carbanolate, carbaryl, carbofuran, carbon disulfide, carbon tetrachloride, carbophenothion, carbosulfan, cartap, chinomethionat, chlorantraniliprole, chlorbenside, chlorbicyclen, chlordane, chlordecone, chlordimeform, chlorethoxyfos, chlorfenapyr, chlorfenethol, chlorfenson, chlorfensulphide, chlorfenvinphos, chlorfluazuron, chlormephos, chlorobenzilate, chloroform, chloromebuform, chloromethiuron, chloropicrin, chloropropylate, chlorphoxim, chlorprazophos, chlorpyrifos, chlorpyrifos methyl, chlorthiophos, chromafenozide, cinerin I, cinerin II, cismethrin, cloethocarb, clofentezine, closantel, clothianidin, copper acetoarsenite, copper arsenate, copper naphthenate, copper oleate, coumaphos, coumithoate, crotamiton, crotoxyphos, cruentaren A &B, crufomate, cryolite, cyanofenphos, cyanophos, cyanthoate, cyclethrin, cycloprothrin, cyenopyrafen, cyflumetofen, cyfluthrin, cyhalothrin, cyhexatin, cypermethrin, cyphenothrin, cyromazine, cythioate,

d-limonene, dazomet, DBCP, DCIP, DDT, decarbofuran, deltamethrin, demephion, demephion O, demephion S, demeton, demeton methyl, demeton O, demeton O methyl, demeton S, demeton S methyl, demeton S methylsulphon, diafenthiuron, dialifos, diamidafos, diazinon, dicapthon, dichlofenthion, dichlofluanid, dichlorvos, dicofol, dicresyl, dicrotophos, dicyclanil, dieldrin, dienochlor, diflovidazin, diflubenzuron, dilor, dimefluthrin, dimefox, dimetan, dimethoate, dimethrin, dimethylvinphos, dimetilan, dinex, dinobuton, dinocap, dinocap 4, dinocap 6, dinocton, dinopenton, dinoprop, dinosam, dinosulfon, dinotefuran, dinoterbon, diofenolan, dioxabenzofos, dioxacarb, dioxathion, diphenyl sulfone, disulfiram, disulfoton, dithicrofos, DNOC, dofenapyn, doramectin,

ecdysterone, emamectin, EMPC, empenthrin, endosulfan, endothion, endrin, EPN, epofenonane, eprinomectin, esfenvalerate, etaphos, ethiofencarb,

ethion, ethiprole, ethoate methyl, ethoprophos, ethyl DDD, ethyl formate, ethylene dibromide, ethylene dichloride, ethylene oxide, etofenprox, etoxazole, etrimfos, EXD,

famphur, fenamiphos, fenazaflor, fenazaquin, fenbutatin oxide, fenchlorphos, fenethacarb, fenfluthrin, fenitrothion, fenobucarb, fenothiocarb, fenoxacrim, fenoxycarb, fenpirithrin, fenpropathrin, fenpyroximate, fenson, fensulfothion, fenthion, fenthion ethyl, fentrifanil, fenvalerate, fipronil, flonicamid, fluacrypyrim, fluazuron, flubendiamide, flubenzimine, flucofuron, flucycloxuron, flucythrinate, fluenetil, flufenerim, flufenoxuron, flufenprox, flumethrin, fluorbenside, fluvalinate, fonofos, formetanate, formothion, formparanate, fosmethilan, fospirate, fosthiazate, fosthietan, fosthietan, furathiocarb, furethrin, furfural,

gamma cyhalothrin, gamma HCH,

halfenprox, halofenozide, HCH, HEOD, heptachlor, heptenophos, heterophos, hexaflumuron, hexythiazox, HHDN, hydramethylnon, hydrogen cyanide, hydroprene, hyquincarb,

imicyafos, imidacloprid, imiprothrin, indoxacarb, iodomethane, IPSP, isamidofos, isazofos, isobenzan, isocarbophos, isodrin, isofenphos, isoprocarb, isoprothiolane, isothioate, isoxathion, ivermectin

jasmolin I, jasmolin II, jodfenphos, juvenile hormone I, juvenile hormone II, juvenile hormone III,

kelevan, kinoprene,

lambda cyhalothrin, lead arsenate, lepimectin, leptophos, lindane, lirimfos, lufenuron, lythidathion,

malathion, malonoben, mazidox, mecarbam, mecarphon, menazon, mephosfolan, mercurous chloride, mesulfen, mesulfenfos, metaflumizone, metam, methacrifos, methamidophos, methidathion, methiocarb, methocrotophos, methomyl, methoprene, methoxychlor, methoxyfenozide, methyl bromide, methyl isothiocyanate, methylchloroform, methylene chloride, metofluthrin, metolcarb, metoxadiazone, mevinphos, mexacarbate, milbemectin, milbemycin oxime, mipafox, mirex, MNAF, monocrotophos, morphothion, moxidectin,

naftalofos, naled, naphthalene, nicotine, nifluridide, nikkomycins, nitenpyram, nithiazine, nitrilacarb, novaluron, noviflumuron,

omethoate, oxamyl, oxydemeton methyl, oxydeprofos, oxydisulfoton,

paradichlorobenzene, parathion, parathion methyl, penfluron, pentachlorophenol, permethrin, phenkapton, phenothrin, phenthoate, phorate, phosalone, phosfolan, phosmet, phosnichlor, phosphamidon, phosphine, phosphocarb, phoxim, phoxim methyl, pirimetaphos, pirimicarb, pirimiphos ethyl, pirimiphos methyl, potassium arsenite, potassium thiocyanate, pp' DDT, prallethrin, precocene I, precocene II, precocene III, primidophos, proclonol, profenofos, profluthrin, promacyl, promecarb, propaphos, propargite, propetamphos, propoxur, prothidathion, prothiofos, prothoate, protrifenbute, pyraclofos, pyrafluprole, pyrazophos, pyresmethrin, pyrethrin I, pyrethrin II, pyridaben, pyridalyl, pyridaphenthion, pyrifluquinazon, pyrimidifen, pyrimitate, pyriprole, pyriproxyfen,

quassia, quinalphos, quinalphos, quinalphos methyl, quinothion, quantifies,

rafoxanide, resmethrin, rotenone, ryania,

sabadilla, schradan, selamectin, silafluofen, sodium arsenite, sodium fluoride, sodium hexafluorosilicate, sodium thiocyanate, sophamide, spinetoram,

spinosad, spirodiclofen, spiromesifen, spirotetramat, sulcofuron, sulfiram, sulfluramid, sulfotep, sulfur, sulfuryl fluoride, sulprofos,

tau fluvalinate, tazimcarb, TDE, tebufenozide, tebufenpyrad, tebupirimfos, teflubenzuron, tefluthrin, temephos, TEPP, terallethrin, terbufos, tetrachloroethane, tetrachlorvinphos, tetradifon, tetramethrin, tetranactin, tetrasul, theta cypermethrin, thiacloprid, thiamethoxam, thicrofos, thiocarboxime, thiocyclam, thiodicarb, thiofanox, thiometon, thionazin, thioquinox, thiosultap, thuringiensin, tolfenpyrad, tralomethrin, transfluthrin, transpermethrin, triarathene, triazamate, triazophos, trichlorfon, trichlormetaphos 3, trichloronat, trifenofos, triflumuron, trimethacarb, triprene,

vamidothion, vamidothion, vaniliprole, vaniliprole,

XMC, xylylcarb,

zeta cypermethrin and zolaprofos.

Additionally, any combination of the above pesticides can be used.

The invention disclosed in this document can also be used with herbicides and fungicides, both for reasons of economy and synergy.

The invention disclosed in this document can be used with antimicrobials, bactericides, defoliants, safeners, synergists, algaecides, attractants, desiccants, pheromones, repellants, animal dips, avicides, disinfectants, semiochemicals, and molluscicides (these categories not necessarily mutually exclusive) for reasons of economy, and synergy.

For more information consult "Compendium of Pesticide Common Names" located at http://www.alanwood.net/pesticides/index.html as of the filing

date of this document. Also consult "The Pesticide Manual" 14th Edition, edited by C D S Tomlin, copyright 2006 by British Crop Production Council.

SYNERGISTIC MIXTURES

The invention disclosed in this document can be used with other compounds such as the ones mentioned under the heading "Mixtures" to form synergistic mixtures where the mode of action of the compounds in the mixtures are the same, similar, or different.

Examples of mode of actions include, but are not limited to: acetyl choline esterase inhibitor; sodium channel modulator; chitin biosynthesis inhibitor; GABA-gated chloride channel antagonist; GABA and glutamate-gated chloride channel agonist; acetyl choline receptor agonist; MET I inhibitor; Mg-stimulated ATPase inhibitor; nicotinic acetylcholine receptor; Midgut membrane disrupter; and oxidative phosphorylation disrupter.

Additionally, the following compounds are known as synergists and can be used with the invention disclosed in this document: piperonyl butoxide, piprotal, propyl isome, sesamex, sesamolin, and sulfoxide.

FORMULATIONS

A pesticide is rarely suitable for application in its pure form. It is usually necessary to add other substances so that the pesticide can be used at the required concentration and in an appropriate form, permitting ease of application, handling, transportation, storage, and maximum pesticide activity. Thus, pesticides are formulated into, for example, baits, concentrated emulsions, dusts, emulsifiable concentrates, fumigants, gels, granules, microencapsulations, seed treatments, suspension concentrates, suspoemulsions, tablets, water soluble liquids, water

dispersible granules or dry flowables, wettable powders, and ultra low volume solutions.

For further information on formulation types see "Catalogue of pesticide formulation types and international coding system" Technical Monograph n°2, 5th Edition by CropLife International (2002).

Pesticides are applied most often as aqueous suspensions or emulsions prepared from concentrated formulations of such pesticides. Such water-soluble, water-suspendable, or emulsifiable formulations, are either solids, usually known as wettable powders, or water dispersible granules, or liquids usually known as emulsifiable concentrates, or aqueous suspensions. Wettable powders, which may be compacted to form water dispersible granules, comprise an intimate mixture of the pesticide, a carrier, and surfactants. The concentration of the pesticide is usually from about 10% to about 90% by weight. The carrier is usually chosen from among the attapulgite clays, the montmorillonite clays, the diatomaceous earths, or the purified silicates. Effective surfactants, comprising from about 0.5% to about 10% of the wettable powder, are found among sulfonated lignins, condensed naphthalenesulfonates, naphthalenesulfonates, alkylbenzenesulfonates, alkyl sulfates, and nonionic surfactants such as ethylene oxide adducts of alkyl phenols.

Emulsifiable concentrates of pesticides comprise a convenient concentration of a pesticide, such as from about 50 to about 500 grams per liter of liquid dissolved in a carrier that is either a water miscible solvent or a mixture of water-immiscible organic solvent and emulsifiers. Useful organic solvents include aromatics, especially xylenes and petroleum fractions, especially the high-boiling naphthalenic and olefinic portions of petroleum such as heavy aromatic naphtha. Other organic solvents may also be used, such as the terpenic solvents including

rosin derivatives, aliphatic ketones such as cyclohexanone, and complex alcohols such as 2-ethoxyethanol. Suitable emulsifiers for emulsifiable concentrates are chosen from conventional anionic and nonionic surfactants.

Aqueous suspensions comprise suspensions of water-insoluble pesticides dispersed in an aqueous carrier at a concentration in the range from about 5% to about 50% by weight. Suspensions are prepared by finely grinding the pesticide and vigorously mixing it into a carrier comprised of water and surfactants. Ingredients, such as inorganic salts and synthetic or natural gums, may also be added, to increase the density and viscosity of the aqueous carrier. It is often most effective to grind and mix the pesticide at the same time by preparing the aqueous mixture and homogenizing it in an implement such as a sand mill, ball mill, or piston-type homogenizer.

Pesticides may also be applied as granular compositions that are particularly useful for applications to the soil. Granular compositions usually contain from about 0.5% to about 10% by weight of the pesticide, dispersed in a carrier that comprises clay or a similar substance. Such compositions are usually prepared by dissolving the pesticide in a suitable solvent and applying it to a granular carrier which has been pre-formed to the appropriate particle size, in the range of from about 0.5 to 3 mm. Such compositions may also be formulated by making a dough or paste of the carrier and compound and crushing and drying to obtain the desired granular particle size.

Dusts containing a pesticide are prepared by intimately mixing the pesticide in powdered form with a suitable dusty agricultural carrier, such as kaolin clay, ground volcanic rock, and the like. Dusts can suitably contain from about 1% to about 10% of the pesticide. They can be applied as a seed dressing, or as a foliage application with a dust blower machine.

It is equally practical to apply a pesticide in the form of a solution in an appropriate organic solvent, usually petroleum oil, such as the spray oils, which are widely used in agricultural chemistry.

Pesticides can also be applied in the form of an aerosol composition. In such compositions the pesticide is dissolved or dispersed in a carrier, which is a pressure-generating propellant mixture. The aerosol composition is packaged in a container from which the mixture is dispensed through an atomizing valve.

Pesticide baits are formed when the pesticide is mixed with food or an attractant or both. When the pests eat the bait they also consume the pesticide. Baits may take the form of granules, gels, flowable powders, liquids, or solids. They are use in pest harborages.

Fumigants are pesticides that have a relatively high vapor pressure and hence can exist as a gas in sufficient concentrations to kill pests in soil or enclosed spaces. The toxicity of the fumigant is proportional to its concentration and the exposure time. They are characterized by a good capacity for diffusion and act by penetrating the pest's respiratory system or being absorbed through the pest's cuticle. Fumigants are applied to control stored product pests under gas proof sheets, in gas sealed rooms or buildings or in special chambers.

Pesticides can be microencapsulated by suspending the pesticide particles or droplets in plastic polymers of various types. By altering the chemistry of the polymer or by changing factors in the processing, microcapsules can be formed of various sizes, solubility, wall thicknesses, and degrees of penetrability. These factors govern the speed with which the active ingredient within is released, which. in turn, affects the residual performance, speed of action, and odor of the product.

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Oil solution concentrates are made by dissolving pesticide in a solvent that will hold the pesticide in solution. Oil solutions of a pesticide usually provide faster knockdown and kill of pests than other formulations due to the solvents themselves having pesticidal action and the dissolution of the waxy covering of the integument increasing the speed of uptake of the pesticide. Other advantages of oil solutions include better storage stability, better penetration of crevices, and better adhesion to greasy surfaces.

Another embodiment is an oil-in-water emulsion, wherein the emulsion comprises oily globules which are each provided with a lamellar liquid crystal coating and are dispersed in an aqueous phase, wherein each oily globule comprises at least one compound which is agriculturally active, and is individually coated with a monolamellar or oligolamellar layer comprising: (1) at least one non-ionic lipophilic surface-active agent, (2) at least one non-ionic hydrophilic surface-active agent and (3) at least one ionic surface-active agent, wherein the globules having a mean particle diameter of less than 800 nanometers. Further information on the embodiment is disclosed in U.S. patent publication 20070027034 published February 1, 2007, having Patent Application serial number 11/495,228. For ease of use this embodiment will be referred to as "OIWE".

For further information consult "Insect Pest Management" 2nd Edition by D. Dent, copyright CAB International (2000). Additionally, for more detailed information consult "Handbook of Pest Control – The Behavior, Life Histroy, and Control of Household Pests" by Arnold Mallis, 9th Edition, copyright 2004 by GIE Media Inc.

OTHER FORMULATION COMPONENTS

Generally, the invention disclosed in this document when used in a formulation, such formulation can also contain other components. These components include, but are not limited to, (this is a non-exhaustive and non-mutually exclusive list) wetters, spreaders, stickers, penetrants, buffers, sequestering agents, drift reduction agents, compatibility agents, anti-foam agents, cleaning agents, and emulsifiers. A few components are described forthwith.

A wetting agent is a substance that when added to a liquid increases the spreading or penetration power of the liquid by reducing the interfacial tension between the liquid and the surface on which it is spreading. Wetting agents are used for two main functions in agrochemical formulations: during processing and manufacture to increase the rate of wetting of powders in water to make concentrates for soluble liquids or suspension concentrates; and during mixing of a product with water in a spray tank to reduce the wetting time of wettable powders and to improve the penetration of water into water-dispersible granules. Examples of wetting agents used in wettable powder, suspension concentrate, and water-dispersible granule formulations are: sodium lauryl sulphate; sodium dioctyl sulphosuccinate; alkyl phenol ethoxylates; and aliphatic alcohol ethoxylates.

A dispersing agent is a substance which adsorbs onto the surface of a particles and helps to preserve the state of dispersion of the particles and prevents them from reaggregating. Dispersing agents are added to agrochemical formulations to facilitate dispersion and suspension during manufacture, and to ensure the particles redisperse into water in a spray tank. They are widely used in wettable powders, suspension concentrates and water-dispersible granules. Surfactants that are used as dispersing agents have the ability to adsorb strongly

onto a particle surface and provide a charged or steric barrier to reaggregation of particles. The most commonly used surfactants are anionic, non-ionic, or mixtures of the two types. For wettable powder formulations, the most common dispersing agents are sodium lignosulphonates. For suspension concentrates, very good adsorption and stabilization are obtained using polyelectrolytes, such as sodium naphthalene sulphonate formaldehyde condensates. Tristyrylphenol ethoxylate phosphate esters are also used. Non-ionics such as alkylarylethylene oxide condensates and EO-PO block copolymers are sometimes combined with anionics as dispersing agents for suspension concentrates, In recent years, new types of very high molecular weight polymeric surfactants have been developed as dispersing agents. These have very long hydrophobic 'backbones' and a large number of ethylene oxide chains forming the 'teeth' of a 'comb' surfactant. These high molecular weight polymers can give very good long-term stability to suspension concentrates because the hydrophobic backbones have many anchoring points onto the particle surfaces. Examples of dispersing agents used in agrochemical formulations are: sodium lignosulphonates; sodium naphthalene sulphonate formaldehyde condensates; tristyrylphenol ethoxylate phosphate esters; aliphatic alcohol ethoxylates; alky ethoxylates; EO-PO block copolymers; and graft copolymers.

An emulsifying agent is a substance which stabilizes a suspension of droplets of one liquid phase in another liquid phase. Without the emulsifying agent the two liquids would separate into two immiscible liquid phases. The most commonly used emulsifier blends contain alkylphenol or aliphatic alcohol with 12 or more ethylene oxide units and the oil-soluble calcium salt of dodecylbenzene sulphonic acid. A range of hydrophile-lipophile balance ("HLB") values from 8 to 18 will normally provide good stable emulsions. Emulsion stability can sometimes

be improved by the addition of a small amount of an EO-PO block copolymer surfactant.

A solubilizing agent is a surfactant which will form micelles in water at concentrations above the critical micelle concentration. The micelles are then able to dissolve or solubilized water-insoluble materials inside the hydrophobic part of the micelle. The type of surfactants usually used for solubilization are non-ionics: sorbitan monooleates; sorbitan monooleate ethoxylates; and methyl oleate esters.

Surfactants are sometimes used, either alone or with other additives such as mineral or vegetable oils as adjuvants to spray-tank mixes to improve the biological performance of the pesticide on the target. The types of surfactants used for bioenhancement depend generally on the nature and mode of action of the pesticide. However, they are often non-ionics such as: alky ethoxylates; linear aliphatic alcohol ethoxylates; aliphatic amine ethoxylates.

A carrier or diluent in an agricultural formulation is a material added to the pesticide to give a product of the required strength. Carriers arc usually materials with high absorptive capacities, while diluents are usually materials with low absorptive capacities. Carriers and diluents are used in the formulation of dusts, wettable powders, granules and water-dispersible granules.

Organic solvents are used mainly in the formulation of emulsifiable concentrates, ULV formulations, and to a lesser extent granular formulations. Sometimes mixtures of solvents are used. The first main groups of solvents are aliphatic paraffinic oils such as kerosene or refined paraffins. The second main group and the most common comprises the aromatic solvents such as xylene and higher molecular weight fractions of C_9 and C_{10} aromatic solvents. Chlorinated hydrocarbons are useful as cosolvents to prevent crystallization of pesticides when

the formulation is emulsified into water. Alcohols are sometimes used as cosolvents to increase solvent power.

Thickeners or gelling agents are used mainly in the formulation of suspension concentrates, emulsions and suspoemulsions to modify the rheology or flow properties of the liquid and to prevent separation and settling of the dispersed particles or droplets. Thickening, gelling, and anti-settling agents generally fall into two categories, namely water-insoluble particulates and water-soluble polymers. It is possible to produce suspension concentrate formulations using clays and silicas. Examples of these types of materials, include, but are limited to, montmorillonite, e.g. bentonite; magnesium aluminum silicate; and attapulgite. Water-soluble polysaccharides have been used as thickening-gelling agents for many years. The types of polysaccharides most commonly used are natural extracts of seeds and seaweeds or are synthetic derivatives of cellulose. Examples of these types of materials include, but are not limited to, guar gum; locust bean gum; carrageenam; alginates; methyl cellulose; sodium carboxymethyl cellulose (SCMC); hydroxyethyl cellulose (HEC). Other types of anti-settling agents are based on modified starches, polyacrylates, polyvinyl alcohol and polyethylene oxide. Another good anti-settling agent is xanthan gum.

Microorganisms which cause spoilage of formulated products. Therefore preservation agents are used to eliminate or reduce their effect. Examples of such agents include, but are limited to. propionic acid and its sodium salt; sorbic acid and its sodium or potassium salts; benzoic acid and its sodium salt; p-hydroxy benzoic acid sodium salt; methyl p-hydroxy benzoate; and 1,2-benzisothiazalin-3-one (BIT).

The presence of surfactants, which lower interfacial tension, often causes water-based formulations to foam during mixing operations in production and in

application through a spray tank. In order to reduce the tendency to foam, anti-foam agents are often added either during the production stage or before filling into bottles. Generally, there are two types of anti-foam agents, namely silicones and non-silicones. Silicones are usually aqueous emulsions of dimethyl polysiloxane while the non-silicone anti-foam agents are water-insoluble oils, such as octanol and nonanol, or silica. In both cases, the function of the anti-foam agent is to displace the surfactant from the air-water interface.

For further information see "Chemistry and Technology of Agrochemical Formulations" edited by D.A. Knowles, copyright 1998 by Kluwer Academic Publishers. Also see "Insecticides in Agriculture and Environment – Retrospects and Prospects" by A.S. Perry, I. Yamamoto, I. Ishaaya, and R. Perry, copyright 1998 by Springer-Verlag.

APPLICATIONS

The actual amount of pesticide to be applied to loci of pests is not critical and can readily be determined by those skilled in the art. In general, concentrations from about 0.01 grams of pesticide per hectare to about 5000 grams of pesticide per hectare are expected to provide good control.

The locus to which a pesticide is applied can be any locus inhabited by an pest, for example, vegetable crops, fruit and nut trees, grape vines, ornamental plants, domesticated animals, the interior or exterior surfaces of buildings, and the soil around buildings.

Generally, with baits, the baits are placed in the ground where, for example, termites can come into contact with the bait. Baits can also be applied to a surface of a building, (horizontal, vertical, or slant, surface) where, for example, ants, termites, cockroaches, and flies, can come into contact with the bait.

Because of the unique ability of the eggs of some pests to resist pesticides repeated applications may be desirable to control newly emerged larvae.

Systemic movement of pesticides in plants may be utilized to control pests on one portion of the plant by applying the pesticides to a different portion of the plant. For example, control of foliar-feeding insects can be controlled by drip irrigation or furrow application, or by treating the seed before planting. Seed treatment can be applied to all types of seeds, including those from which plants genetically transformed to express specialized traits will germinate. Representative examples include those expressing proteins toxic to invertebrate pests, such as Bacillus thuringiensis or other insecticidal toxins, those expressing herbicide resistance, such as "Roundup Ready" seed, or those with "stacked" foreign genes expressing insecticidal toxins, herbicide resistance, nutrition-enhancement or any other beneficial traits. Furthermore, such seed treatments with the invention disclosed in this document can further enhance the ability of a plant to better withstand stressful growing conditions. This results in a healthier, more vigorous plant, which can lead to higher yields at harvest time.

The invention disclosed in this document is suitable for controlling endoparasites and ectoparasites in the veterinary medicine sector or in the field of animal keeping. Compounds according to the invention are applied here in a known manner, such as by oral administration in the form of, for example, tablets, capsules, drinks, granules, by dermal application in the form of, for example, dipping, spraying, pouring on, spotting on, and dusting, and by parenteral administration in the form of, for example, an injection.

The invention disclosed in this document can also be employed advantageously in livestock keeping, for example, cattle, sheep, pigs, chickens, and geese. Suitable formulations are administered orally to the animals with the

drinking water or feed. The dosages and formulations that are suitable depend on the species.

The invention disclosed in this document can also be used

Before a pesticide can be used or sold commercially, such pesticide undergoes lengthy evaluation processes by various governmental authorities (local, regional, state, national, international). Voluminous data requirements are specified by regulatory authorities and must be addressed through data generation and submission by the product registrant or by another on the product registrant's behalf. These governmental authorities then review such data and if a determination of safety is concluded, provide the potential user or seller with product registration approval. Thereafter, in that locality where the product registration is granted and supported, such user or seller may use or sell such pesticide.

The headings in this document are for convenience only and must not be used to interpret any portion thereof.

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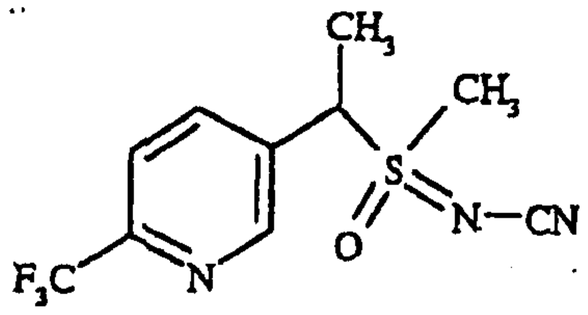
CLAIMS:

1. A process to increase the weight of that portion of a plant that is above the ground said process comprising soaking a seed, which can germinate and begin to grow into said plant, in a solution that comprises a compound having the following formula



,

wherein said soaking occurs before said seed is planted.

2. A process according to claim 1 wherein said seed is a corn seed.