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(54) Title: USE OF MACROCYCLIC PICOLINAMIDES AS FUNGICIDES

(57) Abstract: The invention relates to macrocyclic picolinamides of Formula I and their use as fungicides. Fungicides are compounds, of natural or synthetic origin, which act to protect and/or cure plants against damage caused by agriculturally relevant fungi. Generally, no single fungicide is useful in all situations. Consequently, research is ongoing to produce fungicides that may have better performance, are easier to use, and cost less. The present disclosure relates to macrocyclic picolinamides and their use as fungicides. The compounds of the present disclosure may offer protection against ascomycetes, basidiomycetes, deuteromycetes and oomycetes.



USE OF MACROCYCLIC PICOLINAMIDES AS FUNGICIDES

CROSS REFERENCE TO RELATED APPLICATIONS

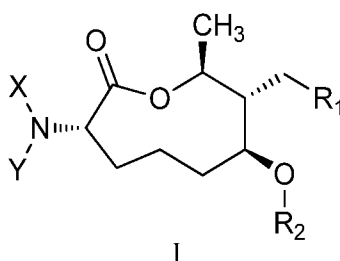
[0001] This application claims the benefit of U.S. Provisional Patent Application Serial Numbers 61/920,962 and 61/920,966, each filed December 26, 2013, the disclosures of which are hereby incorporated by reference in their entireties.

BACKGROUND & SUMMARY

[0002] Fungicides are compounds, of natural or synthetic origin, which act to protect and/or cure plants against damage caused by agriculturally relevant fungi. Generally, no single fungicide is useful in all situations. Consequently, research is ongoing to produce fungicides that may have better performance, are easier to use, and cost less.

[0003] The present disclosure relates to macrocyclic picolinamides and their use as fungicides. The compounds of the present disclosure may offer protection against ascomycetes, basidiomycetes, deuteromycetes and oomycetes.

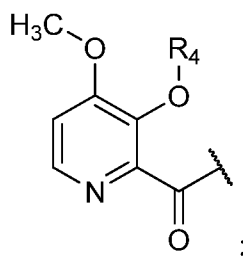
[0004] One embodiment of the present disclosure may include compounds of Formula I:



X is hydrogen or C(O)R₃;

Y is hydrogen, C(O)R₃, or Q;

Q is



[0005] R₁ is hydrogen, alkyl, acyl, alkenyl, aryl, or alkoxy, each optionally substituted with 0, 1 or multiple R₆;

[0006] R₂ is hydrogen, alkyl, acyl, alkenyl, aryl, or -Si(R₅)₃, each optionally substituted with 0, 1 or multiple R₆;

[0007] R₃ alkoxy or benzyloxy, each optionally substituted with 0, 1, or multiple R₆;

[0008] R₄ is hydrogen, -C(O)R₅, or -CH₂OC(O)R₅;

[0009] R₅ is alkyl, alkoxy, or aryl, each optionally substituted with 0, 1, or multiple R₆;

[0010] R₆ is hydrogen, alkyl, aryl, halo, acyl, alkenyl, alkoxy, heteroaryl, heterocyclyl, or thioalkyl, each optionally substituted with 0, 1, or multiple R₇; and

[0011] R₇ is hydrogen, alkyl, aryl, or halo.

[0012] Another embodiment of the present disclosure may include a fungicidal composition for the control or prevention of fungal attack comprising the compounds described above and a phytolegically acceptable carrier material.

[0013] Yet another embodiment of the present disclosure may include a method for the control or prevention of fungal attack on a plant, the method including the steps of applying a fungicidally effective amount of one or more of the compounds described above to at least one of the fungus, the plant, and an area adjacent to the plant.

[0014] It will be understood by those skilled in the art that the following terms may include generic "R"-groups within their definitions, e.g., "the term alkoxy refers to an -OR substituent". It is also understood that within the definitions for the following terms, these "R" groups are included for illustration purposes and should not be construed as limiting or being limited by substitutions about Formula I.

[0015] The term "alkyl" refers to a branched, unbranched, or saturated cyclic carbon chain, including, but not limited to, methyl, ethyl, propyl, butyl, isopropyl, isobutyl, tertiary butyl, pentyl, hexyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and the like. In some exemplary embodiments, the term "alkyl" refers to a branched, unbranched, or saturated cyclic carbon chain, including containing from 1 to 12 carbon atoms, from 1 to 6 carbons, or from 1 to 4 carbons.

[0016] The term "alkenyl" refers to a branched, unbranched or cyclic carbon chain containing one or more double bonds including, but not limited to, ethenyl, propenyl, butenyl, isopropenyl, isobutenyl, cyclobutenyl, cyclopentenyl, cyclohexenyl, and the like. In some exemplary

embodiments, the term "alkenyl" refers to a branched, unbranched, or saturated cyclic carbon chain, including containing from 1 to 12 carbon atoms, from 1 to 6 carbons, or from 1 to 4 carbons.

[0017] The term "alkynyl" refers to a branched or unbranched carbon chain containing one or more triple bonds including, but not limited to, propynyl, butynyl and the like. In some exemplary embodiments, the term "alkynyl" refers to a branched, unbranched, or saturated cyclic carbon chain, including containing from 1 to 12 carbon atoms, from 1 to 6 carbons, or from 1 to 4 carbons.

[0018] The term "aryl" refers to any aromatic, mono- or bi-cyclic ring, containing 0 heteroatoms.

[0019] The term "heterocycle" refers to any aromatic or non-aromatic ring, mono- or bi-cyclic, containing one or more heteroatoms. In some exemplary embodiments, the one or more heteroatoms are independently selected from nitrogen, oxygen, phosphorous, and sulfur.

[0020] The term "alkoxy" refers to an –OR substituent.

[0021] The term "cyano" refers to a –C≡N substituent.

[0022] The term "hydroxyl" refers to an –OH substituent.

[0023] The term "amino" refers to a –NH₂ substituent.

[0024] The term "arylalkoxy" refers to –O(CH₂)_nAr where n is an integer selected from the list 1, 2, 3, 4, 5, or 6.

[0025] The term "haloalkoxy" refers to an –OR–X substituent, wherein X is Cl, F, Br, or I, or any combination thereof.

[0026] The term "haloalkyl" refers to an alkyl, which is substituted with Cl, F, I, or Br or any combination thereof.

[0027] The term "halogen" or "halo" refers to one or more halogen atoms, defined as F, Cl, Br, and I.

[0028] The term "nitro" refers to a –NO₂ substituent.

[0029] The term thioalkyl refers to an –SR substituent.

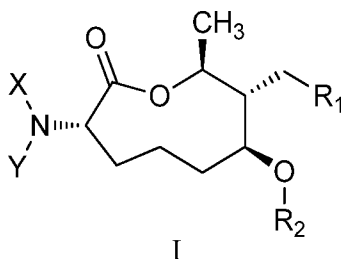
[0030] Throughout the disclosure, reference to the compounds of Formula I is read as also including diastereomers, enantiomers, and mixtures thereof. In another embodiment, Formula (I) is read as also including salts or hydrates thereof. Exemplary salts include, but are not limited to: hydrochloride, hydrobromide, and hydroiodide.

[0031] It is also understood by those skilled in the art that additional substitution is allowable, unless otherwise noted, as long as the rules of chemical bonding and strain energy are satisfied and the product still exhibits fungicidal activity.

[0032] Another embodiment of the present disclosure is a use of a compound of Formula I, for protection of a plant against attack by a phytopathogenic organism or the treatment of a plant infested by a phytopathogenic organism, comprising the application of a compound of Formula I, or a composition comprising the compound to soil, a plant, a part of a plant, foliage, and/or roots.

[0033] Additionally, another embodiment of the present disclosure is a composition useful for protecting a plant against attack by a phytopathogenic organism and/or treatment of a plant infested by a phytopathogenic organism comprising a compound of Formula I and a phytolegically acceptable carrier material.

[0034] In one exemplary embodiment, a composition for the control of a fungal pathogen is provided. The composition at least one of the compounds of Formula 1:

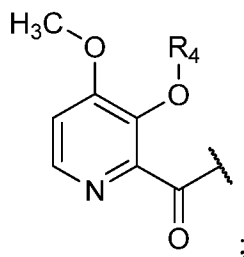


wherein

X is hydrogen or C(O)R₃;

Y is hydrogen, C(O)R₃, or Q;

Q is



R₁ is hydrogen, alkyl, alkenyl, aryl, alkoxy, or acyl, each optionally substituted with 0, 1 or multiple R₆;

R₂ is hydrogen, alkyl, acyl, aryl, alkenyl, or -Si(R₅)₃, each optionally substituted with 0, 1 or multiple R₆;

R₃ is alkoxy or benzyloxy, each optionally substituted with 0, 1, or multiple R₆;

R₄ is hydrogen, -C(O)R₅, or -CH₂OC(O)R₅;

R₅ is alkyl, alkoxy, or aryl, each optionally substituted with 0, 1, or multiple R₆;

R₆ is hydrogen, alkyl, aryl, acyl, halo, alkenyl, alkoxy, heteroaryl, heterocyclyl, or thioalkyl, each optionally substituted with 0, 1, or multiple R₇; and

R₇ is hydrogen, alkyl, aryl, or halo.

[0035] In a one more particular embodiment, X is hydrogen and Y is Q. In another more particular embodiment of any of the above embodiments, R₄ is hydrogen. In another more particular embodiment of any of the above embodiments, R₁ is chosen from alkyl and aryl, each optionally substituted with 0, 1 or multiple R₆. In another more particular embodiment of any of the above embodiments, R₂ is chosen from alkyl, aryl, and acyl, each optionally substituted with 0, 1 or multiple R₆. In another more particular embodiment of any of the above embodiments, R₁ is chosen from alkyl and aryl, each optionally substituted with 0, 1 or multiple R₆, and R₂ is chosen from alkyl, aryl, and acyl, each optionally substituted with 0, 1 or multiple R₆. In another more particular embodiment of any of the above embodiments, R₄ is -C(O)R₅ or -CH₂OC(O)R₅. In another more particular embodiment of any of the above embodiments, R₅ is chosen from alkyl and alkoxy, each optionally substituted with 0, 1, or multiple R₆. In another more particular embodiment of any of the above embodiments, R₁ is chosen from alkyl and aryl, each optionally substituted with 0, 1 or multiple R₆. In another more particular embodiment of any of the above embodiments, R₂ is chosen from alkyl, aryl, and acyl, each optionally substituted with 0, 1 or multiple R₆. In another more particular embodiment of any of the above embodiments, R₁ is chosen from alkyl and aryl, each optionally substituted with 0, 1 or multiple R₆, and R₂ is chosen from alkyl, aryl, and acyl, each optionally substituted with 0, 1 or multiple R₆. In another more particular embodiment of any of the above embodiments, R₅ is chosen from -CH₃ and -CH₂OCH₂CH₃.

[0036] In another more particular embodiment of any of the above embodiments, the composition further includes a phytolegically acceptable carrier material.

[0037] In another more particular embodiment of any of the above embodiments, the composition further includes another pesticide. Exemplary pesticides include fungicides, insecticides, nematocides, miticides, arthropodocides, bactericides and combinations thereof.

[0038] In another more particular embodiment of any of the above embodiments, the fungal pathogen is one of Leaf Blotch of Wheat (*Mycosphaerella graminicola*; anamorph: *Septoria tritici*), Wheat Brown Rust (*Puccinia triticina*), Stripe Rust (*Puccinia striiformis*), Scab of Apple (*Venturia inaequalis*), Blister Smut of Maize (*Ustilago maydis*), Powdery Mildew of Grapevine (*Uncinula necator*), Barley scald (*Rhynchosporium secalis*), Blast of Rice (*Magnaporthe grisea*), Rust of Soybean (*Phakopsora pachyrhizi*), Glume Blotch of Wheat (*Leptosphaeria nodorum*), Powdery Mildew of Wheat (*Blumeria graminis f. sp. tritici*), Powdery Mildew of Barley (*Blumeria graminis f. sp. hordei*), Powdery Mildew of Cucurbits (*Erysiphe cichoracearum*), Anthracnose of Cucurbits (*Glomerella lagenarium*), Leaf Spot of Beet (*Cercospora beticola*), Early Blight of Tomato (*Alternaria solani*), and Net Blotch of Barley (*Pyrenophora teres*). In an even more particular embodiment, the fungal pathogen is one of Leaf Blotch of Wheat (*Septoria tritici*), Wheat Brown Rust (*Puccinia triticina*), and Rust of Soybean (*Phakopsora pachyrhizi*).

[0039] In another embodiment, a method for the control and prevention of fungal attack on a plant is provided. The method includes applying a fungicidally effective amount of at least one of any of the above compositions to at least one of the plant, an area adjacent to the plant, soil adapted to support growth of the plant, a root of the plant, and foliage of the plant.

DETAILED DESCRIPTION

[0040] The compounds of the present disclosure may be applied by any of a variety of known techniques, either as the compounds or as formulations comprising the compounds. For example, the compounds may be applied to the roots or foliage of plants for the control of various fungi, without damaging the commercial value of the plants. The materials may be applied in the form of any of the generally used formulation types, for example, as solutions, dusts, wettable powders, flowable concentrate, or emulsifiable concentrates.

[0041] Preferably, the compounds of the present disclosure are applied in the form of a formulation, comprising one or more of the compounds of Formula I with a phytologically acceptable carrier. Concentrated formulations may be dispersed in water, or other liquids, for

application, or formulations may be dust-like or granular, which may then be applied without further treatment. The formulations can be prepared according to procedures that are conventional in the agricultural chemical art.

[0042] The present disclosure contemplates all vehicles by which one or more of the compounds may be formulated for delivery and use as a fungicide. Typically, formulations are applied as aqueous suspensions or emulsions. Such suspensions or emulsions may be produced from water-soluble, water-suspendible, or emulsifiable formulations which are solids, usually known as wettable powders; or liquids, usually known as emulsifiable concentrates, aqueous suspensions, or suspension concentrates. As will be readily appreciated, any material to which these compounds may be added may be used, provided it yields the desired utility without significant interference with the activity of these compounds as antifungal agents.

[0043] Wettable powders, which may be compacted to form water-dispersible granules, comprise an intimate mixture of one or more of the compounds of Formula I, an inert carrier and surfactants. The concentration of the compound in the wettable powder may be from about 10 percent to about 90 percent by weight based on the total weight of the wettable powder, more preferably about 25 weight percent to about 75 weight percent. In the preparation of wettable powder formulations, the compounds may be compounded with any finely divided solid, such as prophyllite, talc, chalk, gypsum, Fuller's earth, bentonite, attapulgite, starch, casein, gluten, montmorillonite clays, diatomaceous earths, purified silicates or the like. In such operations, the finely divided carrier and surfactants are typically blended with the compound(s) and milled.

[0044] Emulsifiable concentrates of the compounds of Formula I may comprise a convenient concentration, such as from about 1 weight percent to about 50 weight percent of the compound, in a suitable liquid, based on the total weight of the concentrate. The compounds may be dissolved in an inert carrier, which is either a water-miscible solvent or a mixture of water-immiscible organic solvents, and emulsifiers. The concentrates may be diluted with water and oil to form spray mixtures in the form of oil-in-water emulsions. Useful organic solvents include aromatics, especially the high-boiling naphthalenic and olefinic portions of petroleum such as heavy aromatic naphtha. Other organic solvents may also be used, for example, terpenic solvents, including rosin derivatives, aliphatic ketones, such as cyclohexanone, and complex alcohols, such as 2-ethoxyethanol.

[0045] Emulsifiers which may be advantageously employed herein may be readily determined by those skilled in the art and include various nonionic, anionic, cationic and amphoteric emulsifiers, or a blend of two or more emulsifiers. Examples of nonionic emulsifiers useful in preparing the emulsifiable concentrates include the polyalkylene glycol ethers and condensation products of alkyl and aryl phenols, aliphatic alcohols, aliphatic amines or fatty acids with ethylene oxide, propylene oxides such as the ethoxylated alkyl phenols and carboxylic esters solubilized with the polyol or polyoxyalkylene. Cationic emulsifiers include quaternary ammonium compounds and fatty amine salts. Anionic emulsifiers include the oil-soluble salts (e.g., calcium) of alkylaryl sulphonic acids, oil-soluble salts or sulfated polyglycol ethers and appropriate salts of phosphated polyglycol ether.

[0046] Representative organic liquids which may be employed in preparing the emulsifiable concentrates of the compounds of the present disclosure are the aromatic liquids such as xylene, propyl benzene fractions; or mixed naphthalene fractions, mineral oils, substituted aromatic organic liquids such as dioctyl phthalate; kerosene; dialkyl amides of various fatty acids, particularly the dimethyl amides of fatty glycols and glycol derivatives such as the *n*-butyl ether, ethyl ether or methyl ether of diethylene glycol, the methyl ether of triethylene glycol, petroleum fractions or hydrocarbons such as mineral oil, aromatic solvents, paraffinic oils, and the like; vegetable oils such as soy bean oil, rape seed oil, olive oil, castor oil, sunflower seed oil, coconut oil, corn oil, cotton seed oil, linseed oil, palm oil, peanut oil, safflower oil, sesame oil, tung oil and the like; esters of the above vegetable oils; and the like. Mixtures of two or more organic liquids may also be employed in the preparation of the emulsifiable concentrate. Organic liquids include xylene, and propyl benzene fractions, with xylene being most preferred in some cases. Surface-active dispersing agents are typically employed in liquid formulations and in an amount of from 0.1 to 20 percent by weight based on the combined weight of the dispersing agent with one or more of the compounds. The formulations can also contain other compatible additives, for example, plant growth regulators and other biologically active compounds used in agriculture.

[0047] Aqueous suspensions comprise suspensions of one or more water-insoluble compounds of Formula I, dispersed in an aqueous vehicle at a concentration in the range from about 1 to about 50 weight percent, based on the total weight of the aqueous suspension. Suspensions are prepared by finely grinding one or more of the compounds, and vigorously mixing the ground

material into a vehicle comprised of water and surfactants chosen from the same types discussed above. Other components, such as inorganic salts and synthetic or natural gums, may also be added to increase the density and viscosity of the aqueous vehicle.

[0048] The compounds of Formula I can also be applied as granular formulations, which are particularly useful for applications to the soil. Granular formulations generally contain from about 0.5 to about 10 weight percent, based on the total weight of the granular formulation of the compound(s), dispersed in an inert carrier which consists entirely or in large part of coarsely divided inert material such as attapulgite, bentonite, diatomite, clay or a similar inexpensive substance. Such formulations are usually prepared by dissolving the compounds in a suitable solvent and applying it to a granular carrier which has been preformed to the appropriate particle size, in the range of from about 0.5 to about 3 mm. A suitable solvent is a solvent in which the compound is substantially or completely soluble. Such formulations may also be prepared by making a dough or paste of the carrier and the compound and solvent, and crushing and drying to obtain the desired granular particle.

[0049] Dusts containing the compounds of Formula I may be prepared by intimately mixing one or more of the compounds in powdered form with a suitable dusty agricultural carrier, such as, for example, kaolin clay, ground volcanic rock, and the like. Dusts can suitably contain from about 1 to about 10 weight percent of the compounds, based on the total weight of the dust.

[0050] The formulations may additionally contain adjuvant surfactants to enhance deposition, wetting and penetration of the compounds onto the target crop and organism. These adjuvant surfactants may optionally be employed as a component of the formulation or as a tank mix. The amount of adjuvant surfactant will typically vary from 0.01 to 1.0 percent by volume, based on a spray-volume of water, preferably 0.05 to 0.5 volume percent. Suitable adjuvant surfactants include, but are not limited to ethoxylated nonyl phenols, ethoxylated synthetic or natural alcohols, salts of the esters or sulphosuccinic acids, ethoxylated organosilicones, ethoxylated fatty amines, blends of surfactants with mineral or vegetable oils, crop oil concentrate (mineral oil (85%) + emulsifiers (15%)); nonylphenol ethoxylate; benzylcocoalkyldimethyl quaternary ammonium salt; blend of petroleum hydrocarbon, alkyl esters, organic acid, and anionic surfactant; C₉–C₁₁ alkylpolyglycoside; phosphated alcohol ethoxylate; natural primary alcohol (C₁₂–C₁₆) ethoxylate; di-*sec*-butylphenol EO-PO block copolymer; polysiloxane-methyl cap; nonylphenol ethoxylate +

urea ammonium nitrate; emulsified methylated seed oil; tridecyl alcohol (synthetic) ethoxylate (8EO); tallow amine ethoxylate (15 EO); PEG(400) dioleate-99. The formulations may also include oil-in-water emulsions such as those disclosed in U.S. Patent Application Serial No. 11/495,228, the disclosure of which is expressly incorporated by reference herein.

[0051] The formulations may optionally include combinations that contain other pesticidal compounds. Such additional pesticidal compounds may be fungicides, insecticides, herbicides, nematocides, miticides, arthropodocides, bactericides or combinations thereof that are compatible with the compounds of the present disclosure in the medium selected for application, and not antagonistic to the activity of the present compounds. Accordingly, in such embodiments, the other pesticidal compound is employed as a supplemental toxicant for the same or for a different pesticidal use. The compounds of Formula I and the pesticidal compound in the combination can generally be present in a weight ratio of from 1:100 to 100:1.

[0052] The compounds of the present disclosure may also be combined with other fungicides to form fungicidal mixtures and synergistic mixtures thereof. The fungicidal compounds of the present disclosure are often applied in conjunction with one or more other fungicides to control a wider variety of undesirable diseases. When used in conjunction with other fungicide(s), the presently claimed compounds may be formulated with the other fungicide(s), tank-mixed with the other fungicide(s) or applied sequentially with the other fungicide(s). Such other fungicides may include 2-(thiocyanatomethylthio)-benzothiazole, 2-phenylphenol, 8-hydroxyquinoline sulfate, ametoctradin, amisulbrom, antimycin, *Ampelomyces quisqualis*, azaconazole, azoxystrobin, *Bacillus subtilis*, *Bacillus subtilis* strain QST713, benalaxyl, benomyl, benthiavalicarb-isopropyl, benzovindiflupyr, benzylaminobenzene-sulfonate (BABS) salt, bicarbonates, biphenyl, bismethiazol, bitertanol, bixafen, blasticidin-S, borax, Bordeaux mixture, boscalid, bromuconazole, bupirimate, calcium polysulfide, captafol, captan, carbendazim, carboxin, carpropamid, carvone, chlazafenone, chloroneb, chlorothalonil, chlozolinate, *Coniothyrium minitans*, copper hydroxide, copper octanoate, copper oxychloride, copper sulfate, copper sulfate (tribasic), cuprous oxide, cyazofamid, cyflufenamid, cymoxanil, cyproconazole, cyprodinil, dazomet, debacarb, diammonium ethylenebis-(dithiocarbamate), dichlofluanid, dichlorophen, diclocymet, diclomezine, dichloran, diethofencarb, difenoconazole, difenzoquat ion, diflumetorim, dimethomorph, dimoxystrobin, diniconazole, diniconazole-M, dinobuton, dinocap, diphenylamine, dithianon, dodemorph,

dodemorph acetate, dodine, dodine free base, edifenphos, enestrobina, enestrobina, epoxiconazole, ethaboxam, ethoxyquin, etridiazole, famoxadone, fenamidone, fenarimol, fenbuconazole, fenfuram, fenhexamid, fenoxanil, fenciclonil, fenpropidin, fenpropimorph, fenpyrazamine, fentin, fentin acetate, fentin hydroxide, ferbam, ferimzone, fluazinam, fludioxonil, flumorph, fluopicolide, fluopyram, fluoroimide, fluoxastrobin, fluquinconazole, flusilazole, flusulfamide, flutianil, flutolanil, flutriafol, fluxapyroxad, folpet, formaldehyde, fosetyl, fosetyl-aluminium, fuberidazole, furalaxyl, furametpyr, guazatine, guazatine acetates, GY-81, hexachlorobenzene, hexaconazole, hymexazol, imazalil, imazalil sulfate, imibenconazole, iminoctadine, iminoctadine triacetate, iminoctadine tris(albesilate), iodocarb, ipconazole, ipfenpyrazolone, iprobenfos, iprodione, iprovalicarb, isoprothiolane, isopyrazam, isotianil, kasugamycin, kasugamycin hydrochloride hydrate, kresoxim-methyl, laminarin, mancozeb, mancozeb, mandipropamid, maneb, mefenoxam, mepanipyrim, mepronil, meptyl-dinocap, mercuric chloride, mercuric oxide, mercurous chloride, metalaxyl, metalaxyl-M, metam, metam-ammonium, metam-potassium, metam-sodium, metconazole, methasulfocarb, methyl iodide, methyl isothiocyanate, metiram, metominostrobin, metrafenone, mildiomyacin, myclobutanil, nabam, nitrothal-isopropyl, nuarimol, octhilinone, ofurace, oleic acid (fatty acids), oryastrobin, oxadixyl, oxine-copper, oxpoconazole fumarate, oxycarboxin, pefurazoate, penconazole, pencycuron, penflufen, pentachlorophenol, pentachlorophenyl laurate, penthiopyrad, phenylmercury acetate, phosphonic acid, phthalide, picoxystrobin, polyoxin B, polyoxins, polyoxorim, potassium bicarbonate, potassium hydroxyquinoline sulfate, probenazole, prochloraz, procymidone, propamocarb, propamocarb hydrochloride, propiconazole, propineb, proquinazid, prothioconazole, pyraclostrobin, pyrametostrobin, pyraoxystrobin, pyrazophos, pyribencarb, pyributicarb, pyrifenoxy, pyrimethanil, pyriofenone, pyroquilon, quinochloramine, quinoxifen, quintozone, *Reynoutria sachalinensis* extract, sedaxane, silthiofam, simeconazole, sodium 2-phenylphenoxide, sodium bicarbonate, sodium pentachlorophenoxide, spiroxamine, sulfur, SYP-Z048, tar oils, tebuconazole, tebufloquin, tecnazene, tetraconazole, thiabendazole, thifluzamide, thiophanate-methyl, thiram, tiadinil, tolclofos-methyl, tolylfluanid, triadimefon, triadimenol, triazoxide, tricyclazole, tridemorph, trifloxystrobin, triflumizole, triforine, triticonazole, validamycin, valifenalate, valiphenal, vinclozolin, zineb, ziram, zoxamide, *Candida oleophila*, *Fusarium oxysporum*, *Gliocladium* spp., *Phlebiopsis gigantea*, *Streptomyces griseoviridis*, *Trichoderma* spp., (RS)-N-(3,5-dichlorophenyl)-

2-(methoxymethyl)-succinimide, 1,2-dichloropropane, 1,3-dichloro-1,1,3,3-tetrafluoroacetone hydrate, 1-chloro-2,4-dinitronaphthalene, 1-chloro-2-nitropropane, 2-(2-heptadecyl-2-imidazolin-1-yl)ethanol, 2,3-dihydro-5-phenyl-1,4-dithi-ine 1,1,4,4-tetraoxide, 2-methoxyethylmercury acetate, 2-methoxyethylmercury chloride, 2-methoxyethylmercury silicate, 3-(4-chlorophenyl)-5-methylrhodanine, 4-(2-nitroprop-1-enyl)phenyl thiocyanateme, ampropylfos, anilazine, azithiram, barium polysulfide, Bayer 32394, benodanil, benquinox, bentaluron, benzamacril; benzamacril-isobutyl, benzamorf, binapacryl, bis(methylmercury) sulfate, bis(tributyltin) oxide, buthiobate, cadmium calcium copper zinc chromate sulfate, carbamorph, CECA, chlobenthiazone, chloraniformethan, chlorfenazole, chlorquinox, climbazole, copper bis(3-phenylsalicylate), copper zinc chromate, cufraneb, cupric hydrazinium sulfate, cuprobam, cyclafuramid, cypendazole, cyprofuram, decafentin, dichlone, dichlozoline, diclobutrazol, dimethirimol, dinocton, dinosulfon, dinoterbon, dipyrithione, ditalimfos, dodicin, drazoxolon, EBP, ESBP, etaconazole, etem, ethirim, fenaminosulf, fenapanil, fenitropan, fluotrimazole, furcarbanil, furconazole, furconazole-cis, furmecyclox, furophanate, glyodine, griseofulvin, halacrinat, Hercules 3944, hexylthiofos, ICIA0858, isopamphos, isovalledione, mebenil, mecarbinzid, metazoxolon, methfuroxam, methylmercury dicyandiamide, metsulfovax, milneb, mucochloric anhydride, myclozolin, *N*-3,5-dichlorophenyl-succinimide, *N*-3-nitrophenylitaconimide, natamycin, *N*-ethylmercurio-4-toluenesulfonanilide, nickel bis(dimethyldithiocarbamate), OCH, phenylmercury dimethyldithiocarbamate, phenylmercury nitrate, phosdiphen, prothiocarb; prothiocarb hydrochloride, pyracarbolid, pyridinitril, pyroxychlor, pyroxyfur, quinacetol; quinacetol sulfate, quinazamid, quinconazole, rabenzazole, salicylanilide, SSF-109, sultropen, tecoram, thiadifluor, thicyofen, thiochlorfenphim, thiophanate, thioquinox, tioxymid, triamiphos, triarimol, triazbutil, trichlamide, urbacid, zarilamid, and any combinations thereof.

[0053] Additionally, the compounds described herein may be combined with other pesticides, including insecticides, nematocides, miticides, arthropodicides, bactericides or combinations thereof that are compatible with the compounds of the present disclosure in the medium selected for application, and not antagonistic to the activity of the present compounds to form pesticidal mixtures and synergistic mixtures thereof. The fungicidal compounds of the present disclosure may be applied in conjunction with one or more other pesticides to control a wider variety of undesirable

pests. When used in conjunction with other pesticides, the presently claimed compounds may be formulated with the other pesticide(s), tank-mixed with the other pesticide(s) or applied sequentially with the other pesticide(s). Typical insecticides include, but are not limited to: 1,2-dichloropropane, abamectin, acephate, acetamiprid, acethion, acetoprole, acrinathrin, acrylonitrile, alanycarb, aldicarb, aldoxycarb, aldrin, allethrin, allosamidin, allyxycarb, alpha-cypermethrin, alpha-ecdysone, alpha-endosulfan, amidithion, aminocarb, amiton, amiton oxalate, amitraz, anabasine, athidathion, azadirachtin, azamethiphos, azinphos-ethyl, azinphos-methyl, azothoate, barium hexafluorosilicate, barthrin, bendiocarb, benfuracarb, bensultap, beta-cyfluthrin, beta-cypermethrin, bifenthrin, bioallethrin, bioethanomethrin, biopermethrin, bistrifluron, borax, boric acid, bromfenvinfos, bromocyclen, bromo-DDT, bromophos, bromophos-ethyl, bufencarb, buprofezin, butacarb, butathiofos, butocarboxim, butonate, butoxycarboxim, cadusafos, calcium arsenate, calcium polysulfide, camphechlor, carbanolate, carbaryl, carbofuran, carbon disulfide, carbon tetrachloride, carbophenothion, carbosulfan, cartap, cartap hydrochloride, chlorantraniliprole, chlorbicyclen, chlordane, chlordecone, chlordimeform, chlordimeform hydrochloride, chlorethoxyfos, chlorfenapyr, chlorfenvinphos, chlorfluazuron, chlormephos, chloroform, chloropicrin, chlorphoxim, chlorprazophos, chlorpyrifos, chlorpyrifos-methyl, chlorthiophos, chromafenozide, cinerin I, cinerin II, cinerins, cismethrin, cloethocarb, closantel, clothianidin, copper acetoarsenite, copper arsenate, copper naphthenate, copper oleate, coumaphos, coumithoate, crotamiton, crotoxyphos, crufomate, cryolite, cyanofenphos, cyanophos, cyanthoate, cyantraniliprole, cyclethrin, cycloprothrin, cyfluthrin, cyhalothrin, cypermethrin, cyphenothrin, cyromazine, cythioate, 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, diatomaceous earth, diazinon, dicapthon, dichlofenthion, dichlorvos, dicresyl, dicrotophos, dicyclanil, dieldrin, diflubenzuron, dilor, dimefluthrin, dimefox, dimetan, dimethoate, dimethrin, dimethylvinphos, dimetilan, dinex, dinex-diclexine, dinoprop, dinosam, dinotefuran, diofenolan, dioxabenzofos, dioxacarb, dioxathion, disulfoton, dithicrofos, d-limonene, DNOC, DNOC-ammonium, DNOC-potassium, DNOC-sodium, doramectin, ecdysterone, emamectin, emamectin benzoate, EMPC, empenthrin, endosulfan, endothion, endrin, EPN, epofenonane, eprinomectin, esdepalléthrine, esfenvalerate, etaphos, ethiofencarb, ethion, ethiprole, ethoate-methyl, ethoprophos, ethyl formate, ethyl-DDD, ethylene dibromide, ethylene

dichloride, ethylene oxide, etofenprox, etrimfos, EXD, famphur, fenamiphos, fenazaflor, fenchlorphos, fenethacarb, fenfluthrin, fenitrothion, fenobucarb, fenoxacrim, fenoxycarb, fenpirithrin, fenpropathrin, fensulfothion, fenthion, fenthion-ethyl, fenvalerate, fipronil, flonicamid, flubendiamide, flucofuron, flucyclohexuron, flucythrinate, flufenerim, flufenoxuron, flufenprox, fluvalinate, fonofos, formetanate, formetanate hydrochloride, formothion, formparanate, formparanate hydrochloride, fosmethilan, fospirate, fosthietan, furathiocarb, furethrin, gamma-cyhalothrin, gamma-HCH, halfenprox, halofenozide, HCH, HEOD, heptachlor, heptenophos, heterophos, hexaflumuron, HHDN, hydramethylnon, hydrogen cyanide, hydroprene, hyquincarb, imidacloprid, imiprothrin, indoxacarb, iodomethane, IPSP, isazofos, isobenzan, isocarbophos, isodrin, isofenphos, isofenphos-methyl, 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, mesulfenfos, metaflumizone, 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, molosultap, monocrotophos, monomehypo, monosultap, morphothion, moxidectin, naftalofos, naled, naphthalene, nicotine, nifluridide, nitenpyram, nithiazine, nitrilacarb, novaluron, noviflumuron, omethoate, oxamyl, oxydemeton-methyl, oxydeprofos, oxydisulfoton, para-dichlorobenzene, parathion, parathion-methyl, penfluron, pentachlorophenol, permethrin, phenkapton, phenothrin, phenthoate, phorate, phosalone, phosfolan, phosmet, phosnichlor, phosphamidon, phosphine, phoxim, phoxim-methyl, pirimetaphos, pirimicarb, pirimiphos-ethyl, pirimiphos-methyl, potassium arsenite, potassium thiocyanate, pp'-DDT, prallethrin, precocene I, precocene II, precocene III, primidophos, profenofos, profluralin, promacyl, promecarb, propaphos, propetamphos, propoxur, prothidathion, prothiofos, prothoate, protrifenbute, pyraclofos, pyrafluprole, pyrazophos, pyresmethrin, pyrethrin I, pyrethrin II, pyrethrins, pyridaben, pyridalyl, pyridaphenthion, pyrifluquinazon, pyrimidifen, pyrimitate, pyriprole, pyriproxyfen, quassia, quinalphos, quinalphos-methyl, quinothion, rafoxanide, resmethrin, rotenone, ryania, sabadilla, schradan, selamectin, silafluofen, silica gel, sodium arsenite,

sodium fluoride, sodium hexafluorosilicate, sodium thiocyanate, sophamide, spinetoram, spinosad, spiromesifen, spirotetramat, sulcofuron, sulcofuron-sodium, sulfluramid, sulfotep, sulfoxaflor, sulfuryl fluoride, sulprofos, tau-fluvalinate, tazimcarb, TDE, tebufenozide, tebufenpyrad, tebupirimfos, teflubenzuron, tefluthrin, temephos, TEPP, terallethrin, terbufos, tetrachloroethane, tetrachlorvinphos, tetramethrin, tetramethylfluthrin, theta-cypermethrin, thiacloprid, thiamethoxam, thiofufos, thiocarboxime, thiocyclam, thiocyclam oxalate, thiodicarb, thiofanox, thiometon, thiosultap, thiosultap-disodium, thiosultap-monosodium, thuringiensin, tolfenpyrad, tralomethrin, transfluthrin, transpermethrin, triarathene, triazamate, triazophos, trichlorfon, trichlormetaphos-3, trichloronat, trifenofos, triflumuron, trimethacarb, triprene, vamidothion, vaniliprole, XMC, xylylcarb, zeta-cypermethrin, zolaprofos, and any combinations thereof.

[0054] Additionally, the compounds described herein may be combined with herbicides that are compatible with the compounds of the present disclosure in the medium selected for application, and not antagonistic to the activity of the present compounds to form pesticidal mixtures and synergistic mixtures thereof. The fungicidal compounds of the present disclosure may be applied in conjunction with one or more herbicides to control a wide variety of undesirable plants. When used in conjunction with herbicides, the presently claimed compounds may be formulated with the herbicide(s), tank-mixed with the herbicide(s) or applied sequentially with the herbicide(s). Typical herbicides include, but are not limited to: 4-CPA; 4-CPB; 4-CPP; 2,4-D; 3,4-DA; 2,4-DB; 3,4-DB; 2,4-DEB; 2,4-DEP; 3,4-DP; 2,3,6-TBA; 2,4,5-T; 2,4,5-TB; acetochlor, acifluorfen, aclonifen, acrolein, alachlor, allidochlor, alloxydim, allyl alcohol, alorac, ametrudione, ametryn, amibuzin, amicarbazone, amidosulfuron, aminocyclopyrachlor, aminopyralid, amiprofos-methyl, amitrole, ammonium sulfamate, anilofos, anisuron, asulam, atraton, atrazine, azafenidin, azimsulfuron, aziprotryne, barban, BCPC, beflubutamid, benazolin, bencarbazon, benfluralin, benfuresate, bensulfuron, bensulide, bentazone, benzadox, benzfendizone, benzipram, benzobicyclon, benzofenap, benzofluor, benzoylprop, benzthiazuron, bicyclopyrone, bifenox, bilanafos, bispyribac, borax, bromacil, bromobonil, bromobutide, bromofenoxim, bromoxynil, brompyrazon, butachlor, butafenacil, butamifos, butenachlor, buthidazole, buthiuron, butralin, butroxydim, buturon, butylate, cacodylic acid, cafenstrole, calcium chlorate, calcium cyanamide, cambendichlor, carbasulam, carbetamide, carboxazole chlorprocarb, carfentrazone, CDEA, CEPC, chlomethoxyfen, chloramben, chloranocryl, chlorazifop, chlorazine, chlorbromuron, chlorbufam, chloreturon,

chlorfenac, chlorfenprop, chlorflurazole, chlorflurenol, chloridazon, chlorimuron, chlornitrofen, chloropon, chlorotoluron, chloroxuron, chloroxynil, chlorpropham, chlorsulfuron, chlorthal, chlorthiamid, cinidon-ethyl, cinmethylin, cinosulfuron, cisanilide, clethodim, cliodinate, clodinafop, clofop, clomazone, clomeprop, cloprop, cloproxydim, clopyralid, cloransulam, CMA, copper sulfate, CPMF, CPPC, credazine, cresol, cumyluron, cyanatryn, cyanazine, cycloate, cyclosulfamuron, cycloxydim, cycluron, cyhalofop, cyperquat, cyprazine, cyprazole, cypromid, daimuron, dalapon, dazomet, delachlor, desmedipham, desmetryn, di-allate, dicamba, dichlobenil, dichloralurea, dichlormate, dichlorprop, dichlorprop-P, diclofop, diclosulam, diethamquat, diethatyl, difenopenten, difenoxuron, difenzoquat, diflufenican, diflufenzopyr, dimefuron, dimepiperate, dimethachlor, dimethametryn, dimethenamid, dimethenamid-P, dimexano, dimidazon, dinitramine, dinofenate, dinoprop, dinosam, dinoseb, dinoterb, diphenamid, dipropetryn, diquat, disul, dithiopyr, diuron, DMPA, DNOC, DSMA, EBEP, eglinazine, endothal, epronaz, EPTC, erbon, esprocarb, ethalfluralin, ethametsulfuron, ethidimuron, ethiolate, ethofumesate, ethoxyfen, ethoxysulfuron, etinofen, etnipromid, etobenzanid, EXD, fenasulam, fenoprop, fenoxaprop, fenoxaprop-P, fenoxasulfone, fenteracol, fenthiaprop, fentrazamide, fenuron, ferrous sulfate, flamprop, flamprop-M, flazasulfuron, florasulam, fluazifop, fluazifop-P, fluazolate, flucarbazone, flucetosulfuron, fluchloralin, flufenacet, flufenican, flufenpyr, flumetsulam, flumezin, flumiclorac, flumioxazin, flumipropyn, fluometuron, fluorodifen, fluoroglycofen, fluoromidine, fluoronitrofen, fluothiuron, flupoxam, flupropacil, flupropanate, flupyrsulfuron, fluridone, flurochloridone, fluroxypry, flurtamone, fluthiacet, fomesafen, foramsulfuron, fosamine, furyloxyfen, glufosinate, glufosinate-P, glyphosate, halauxifen, halosafen, halosulfuron, haloxydine, haloxyfop, haloxyfop-P, hexachloroacetone, hexaflurate, hexazinone, imazamethabenz, imazamox, imazapic, imazapyr, imazaquin, imazethapyr, imazosulfuron, indanofan, indaziflam, iodobonil, iodomethane, iodosulfuron, ioxynil, ipazine, ipfencarbazone, iprymidam, isocarbamid, isocil, isomethiozin, isonoruron, isopolinate, isopropalin, isoproturon, isouron, isoxaben, isoxachlortole, isoxaflutole, isoxapyrifop, karbutilate, ketospiradox, lactofen, lenacil, linuron, MAA, MAMA, MCPA, MCPA-thioethyl, MCPB, mecoprop, mecoprop-P, medinoterb, mefenacet, mefluidide, mesoprazine, mesosulfuron, mesotrione, metam, metamifop, metamitron, metazachlor, metazosulfuron, metflurazon, methabenzthiazuron, methalpropalin, methazole, methiobencarb, methiozolin, methiuron, methometon, methoprotryne, methyl bromide, methyl isothiocyanate, methylmymron,

metobenzuron, metobromuron, metolachlor, metosulam, metoxuron, metribuzin, metsulfuron, molinate, monalide, monisouron, monochloroacetic acid, monolinuron, monuron, morfamquat, MSMA, naproanilide, napropamide, naptalam, neburon, nicosulfuron, nipyraclufen, nitralin, nitrofen, nitrofluorfen, norflurazon, noruron, OCH, orbencarb, *ortho*-dichlorobenzene, orthosulfamuron, oryzalin, oxadiargyl, oxadiazon, oxapyrazon, oxasulfuron, oxaziclomefone, oxyfluorfen, parafluron, paraquat, pebulate, pelargonic acid, pendimethalin, penoxsulam, pentachlorophenol, pentanochlor, pentoxazone, perfluidone, pethoxamid, phenisopham, phenmedipham, phenmedipham-ethyl, phenobenzuron, phenylmercury acetate, picloram, picolinafen, pinoxaden, piperophos, potassium arsenite, potassium azide, potassium cyanate, pretilachlor, primisulfuron, procyazine, prodiamine, profluazol, profluralin, profoxydim, proglinazine, prometon, prometryn, propachlor, propanil, propaquizafof, propazine, propham, propisochlor, propoxycarbazone, propyrisulfuron, propyzamide, prosulfalin, prosulfocarb, prosulfuron, proxan, prynachlor, pydanon, pyraclonil, pyraflufen, pyrasulfotole, pyrazolynate, pyrazosulfuron, pyrazoxyfen, pyribenzoxim, pyributicarb, pyriclor, pyridafol, pyridate, pyrifthalid, pyriminobac, pyrimisulfan, pyriothiobac, pyroxasulfone, pyroxsulam, quinclorac, quinmerac, quinochloramine, quinonamid, quizalofop, quizalofop-P, rhodethanil, rimsulfuron, saflufenacil, S-metolachlor, sebuthylazine, secbumeton, sethoxydim, siduron, simazine, simeton, simetryn, SMA, sodium arsenite, sodium azide, sodium chlorate, sulcotrione, sulfallate, sulfentrazone, sulfometuron, sulfosulfuron, sulfuric acid, sulglycapin, swep, TCA, tebutam, tebuthiuron, tefuryltrione, tembotrione, tepraloxydim, terbacil, terbucarb, terbuchlor, terbumeton, terbuthylazine, terbutryn, tetrafluron, thenylchlor, thiazafluron, thiazopyr, thidiazimin, thidiazuron, thiencarbazone-methyl, thifensulfuron, thiobencarb, tiocarbazil, tioclorim, topramezone, tralkoxydim, triafamone, tri-allate, triasulfuron, triaziflam, tribenuron, tricamba, triclopyr, tridiphane, trietazine, trifloxysulfuron, trifluralin, triflusulfuron, trifop, trifopsime, trihydroxytriazine, trimeturon, tripropindan, tritac, tritosulfuron, vernolate, and xylachlor.

[0055] Another embodiment of the present disclosure is a method for the control or prevention of fungal attack. This method comprises applying to the soil, plant, roots, foliage, or locus of the fungus, or to a locus in which the infestation is to be prevented (for example applying to cereal or grape plants), a fungicidally effective amount of one or more of the compounds of Formula

I. The compounds are suitable for treatment of various plants at fungicidal levels, while exhibiting low phytotoxicity. The compounds may be useful both in a protectant and/or an eradicant fashion.

[0056] The compounds have been found to have significant fungicidal effect particularly for agricultural use. Many of the compounds are particularly effective for use with agricultural crops and horticultural plants.

[0057] It will be understood by those in the art that the efficacy of the compound for the foregoing fungi establishes the general utility of the compounds as fungicides.

[0058] The compounds have broad ranges of activity against fungal pathogens. Exemplary pathogens may include, but are not limited to, causing agent of wheat leaf blotch (*Mycosphaerella graminicola*; impect stage: *Septoria tritici*), wheat brown rust (*Puccinia triticina*), wheat stripe rust (*Puccinia striiformis*), scab of apple (*Venturia inaequalis*), powdery mildew of grapevine (*Uncinula necator*), barley scald (*Rhynchosporium secalis*), blast of rice (*Magnaporthe grisea*), rust of soybean (*Phakopsora pachyrhizi*), glume blotch of wheat (*Leptosphaeria nodorum*), powdery mildew of wheat (*Blumeria graminis f. sp. tritici*), powdery mildew of barley (*Blumeria graminis f. sp. hordei*), powdery mildew of cucurbits (*Erysiphe cichoracearum*), anthracnose of cucurbits (*Glomerella lagenarium*), leaf spot of beet (*Cercospora beticola*), early blight of tomato (*Alternaria solani*), and spot blotch of barley (*Cochliobolus sativus*). The exact amount of the active material to be applied is dependent not only on the specific active material being applied, but also on the particular action desired, the fungal species to be controlled, and the stage of growth thereof, as well as the part of the plant or other product to be contacted with the compound. Thus, all the compounds, and formulations containing the same, may not be equally effective at similar concentrations or against the same fungal species.

[0059] The compounds are effective in use with plants in a disease-inhibiting and phytologically acceptable amount. The term "disease-inhibiting and phytologically acceptable amount" refers to an amount of a compound that kills or inhibits the plant disease for which control is desired, but is not significantly toxic to the plant. This amount will generally be from about 0.1 to about 1000 ppm (parts per million), with 1 to 500 ppm being preferred. The exact concentration of compound required varies with the fungal disease to be controlled, the type of formulation employed, the method of application, the particular plant species, climate conditions, and the like. A

suitable application rate is typically in the range from about 0.10 to about 4 pounds/acre (about 0.01 to 0.45 grams per square meter, g/m²).

[0060] Any range or desired value given herein may be extended or altered without losing the effects sought, as is apparent to the skilled person for an understanding of the teachings herein.

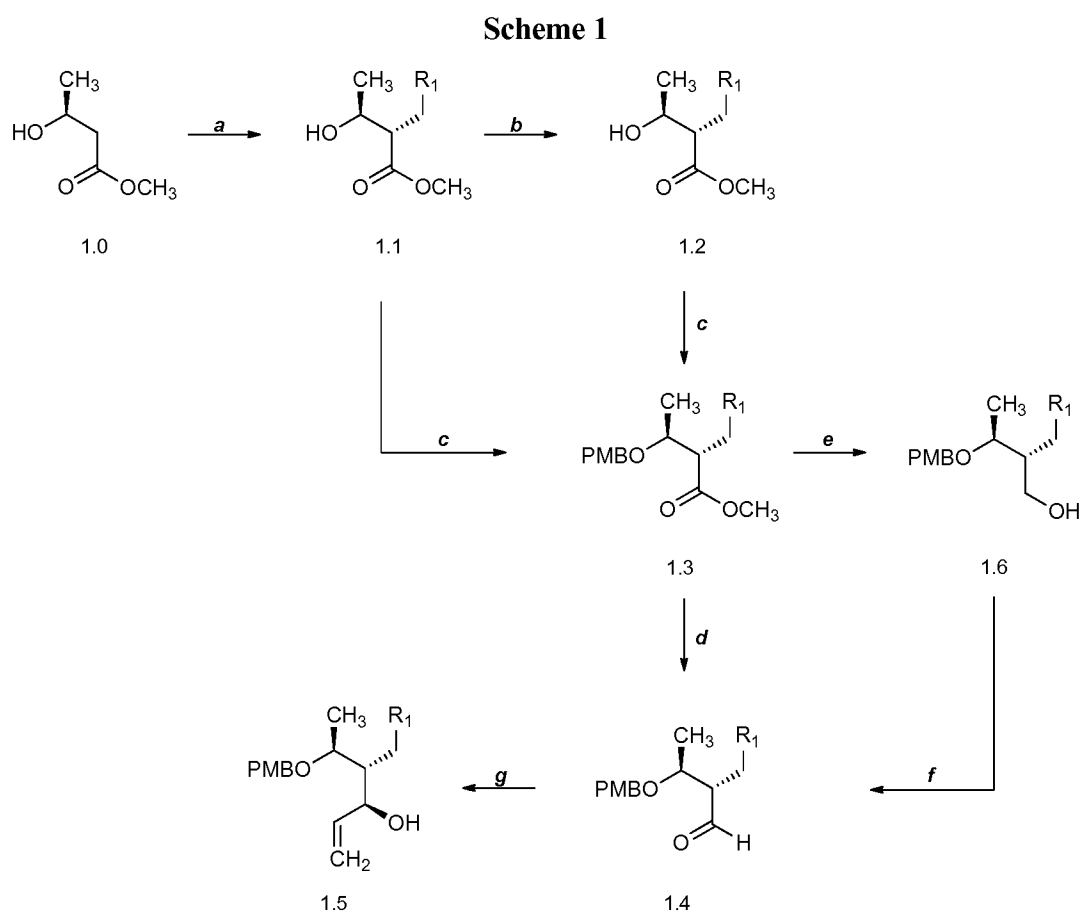
[0061] The compounds of Formula I may be made using well-known chemical procedures. Intermediates not specifically mentioned in this disclosure are either commercially available, may be made by routes disclosed in the chemical literature, or may be readily synthesized from commercial starting materials utilizing standard procedures.

GENERAL SCHEMES

[0062] The following schemes illustrate approaches to generating picolinamide compounds of Formula (I). The following descriptions and examples are provided for illustrative purposes and should not be construed as limiting in terms of substituents or substitution patterns.

[0063] Compounds of Formula 1.5, where R₁ is as originally defined, can be prepared according to the methods outlined in **Scheme 1, steps a – g**. Compounds of Formula 1.1, where R₁ is as originally defined, can be obtained by reaction of the dianion of an ester of Formula 1.0 formed by treatment with lithium diisopropyl amide (LDA) at -50 °C, with an alkyl halide or allyl halide in a solvent such as tetrahydrofuran (THF) at cryogenic temperatures such as -78 °C, as shown in **a**. Compounds of Formula 1.2, where R₁ is as originally defined, can be obtained by treating compounds of Formula 1.1, where R₁ is an alkenyl functionality, with hydrogen gas in the presence of a catalyst such as palladium on carbon (Pd/C) in a solvent such as ethyl acetate (EtOAc), as shown in **b**. Compounds of Formula 1.3, where R₁ is as originally defined can be prepared from compounds of Formula 1.1, where R₁ is as defined above, and Formula 1.2, where R₁ is as defined above, by treating with an alkylating agent such as 4-methoxybenzyl 2,2,2-trichloroacetimidate in the presence of an acid such as camphor sulfonic acid (CSA) in a solvent such as dichloromethane (DCM), as depicted in **c**. Aldehydes of Formula 1.4, where R₁ is as originally defined, can be obtained by the reduction of esters of Formula 1.3, where R₁ is as defined above, using a catalyst such as chlorobis(cyclooctene)iridium(I) dimer in the presence of a reducing agent such as diethylsilane (Et₂SiH) in a solvent such as DCM, as shown in **d**. Aldehydes of Formula 1.4, where R₁ is as originally defined, can also be obtained by reduction of esters of Formula 1.3, where R₁ is

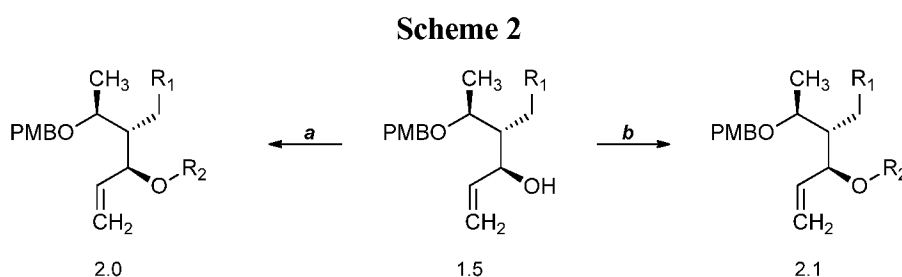
as defined above, using hydride reducing agents, such as lithium aluminum hydride (LiAlH_4 , LAH) in ethereal solvents, giving alcohols of Formula 1.6, where R_1 is as defined above, as depicted in *e*. Oxidation of alcohols of Formula 1.6, where R_1 is as defined above, using oxidation reagents such as sulfur trioxide-pyridine complex (SO_3 -pyridine/dimethyl sulfoxide (DMSO)) in solvents such as DCM, furnish the aldehydes of Formula 1.4, where R_1 is as originally defined, as depicted in *f*. The addition of metallated alkenes such as vinyl magnesium bromide to aldehydes of Formula 1.4, where R_1 is as defined above, in a solvent such as THF at -78°C affords allylic alcohols of Formula 1.5, where R_1 is as originally defined, as depicted in *g*.



[0064] Compounds of Formulas 2.0 and 2.1, where R_1 and R_2 are as originally defined, but R_2 is not acyl or hydrogen, can be prepared as shown in **Scheme 2**, steps *a-b*. Alcohols of Formula 1.5, where R_1 is as originally defined, can be alkylated to give compounds of Formula 2.0, where R_1 and

R₂ are as defined above, by deprotonation with a base such as sodium hydride (NaH) in an aprotic solvent such as *N,N*-dimethylformamide (DMF), followed by treatment with an alkylating agent, such as cyclopropylmethyl bromide, at an elevated temperature such as 50 °C, as shown in **a**.

Alternatively, alcohols of Formula 1.5, where R₁ is as defined above, can be arylated by treating with an arylating agent such as triphenylbismuth(V)diacetate in the presence of a copper catalyst such as diacetylcopper and a base such as *N,N*-dicyclohexyl-*N*-methylamine in a solvent such as toluene at an elevated temperature such as 60 °C to give compounds of Formula 2.1, where R₁ and R₂ are as defined above, as depicted in **b**.

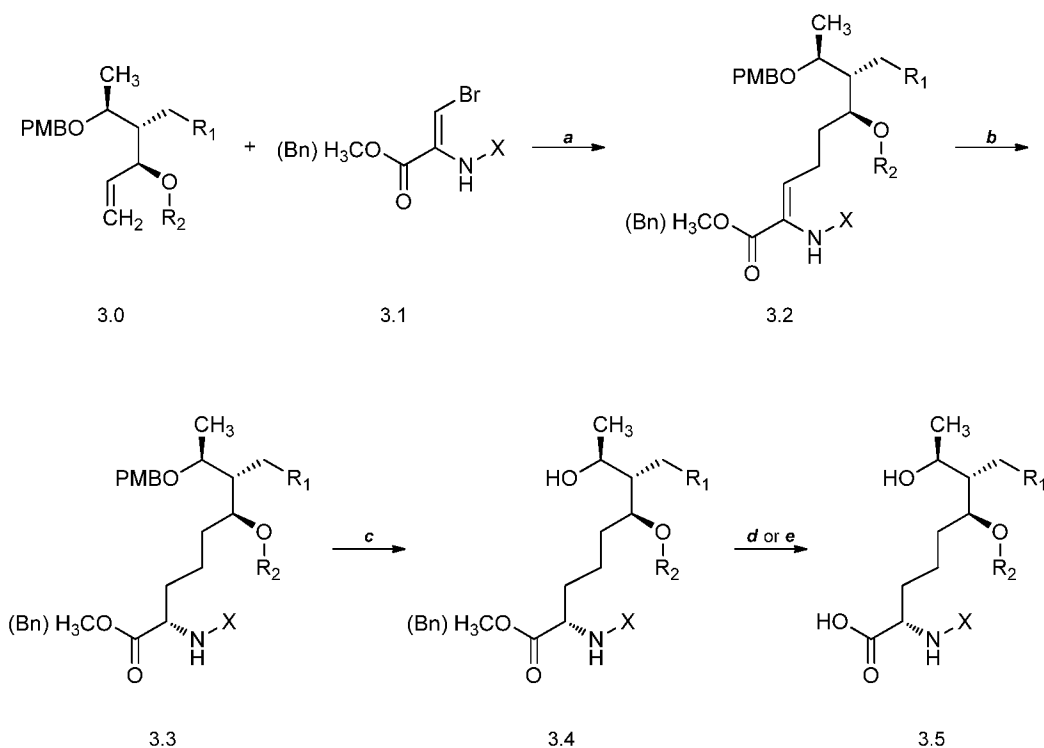


[0065] Compounds of Formula 3.5, where both R₁ and R₂ are as originally defined, but R₂ is not acyl or hydrogen, and X is Boc, can be prepared as outlined in **Scheme 3, steps a-e**.

Compounds of Formula 3.2, where R₁, R₂ and X are as defined above, can be prepared from compounds of Formula 3.0, where R₁ is as originally defined, R₂ is not acyl or alkenyl, and X is Boc, by treatment with an alkylborane reagent, such as 9-borabicyclo[3.3.1]nonane (9-BBN), in a solvent such as THF, at a temperature between ambient room temperature and about 50 °C. Then, the mixture can be treated with an aqueous basic solution, such as potassium phosphate (K₃PO₄), a brominated olefin, such as a compound of Formula 3.1, where X is Boc (prepared as in Singh et al. *Org. Lett.* **2003**, *17*, 3155-3158), and a catalyst, such as [1,1-bis(diphenylphosphino)ferrocene] dichloropalladium(II) (PdCl₂(dppf)) at ambient room temperature to about 55 °C to produce a compound of Formula 3.2 as shown in **step a**. Compounds of the Formula 3.3, where R₁, R₂ and X are as defined above, can be prepared from enamides, generalized by Formula 3.2, where R₁, R₂, and X are as defined above, using an asymmetric hydrogenation reaction employing a catalyst such as (+)-1,2-bis((2*S*,5*S*)-2,5-diethylphospholano)benzene(1,5-cyclooctadiene) rhodium(I)

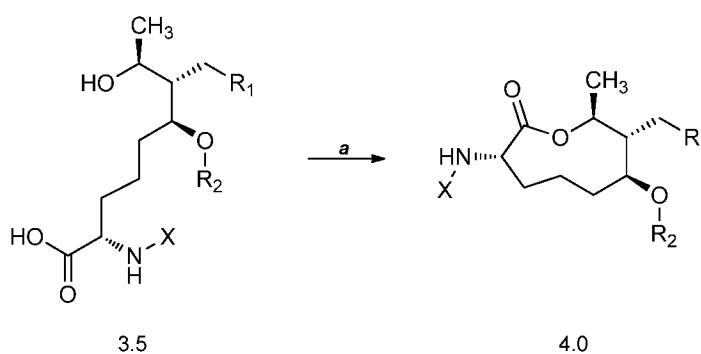
trifluoromethanesulfonate ((*S,S*)-Et-DuPHOS-Rh) under a hydrogen atmosphere at a pressure between 40 and 200 pounds per square inch (psi) in a solvent such as methanol (MeOH) as shown in *step b*. As shown in *step c*, compounds of Formula 3.3 can be converted to compounds of Formula 3.4, where R₁, R₂ and X are as defined above, by removing the *para*-methoxybenzyl (PMB) protecting group using an oxidant such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in an aqueous DCM solvent mixture at a temperature of about 0 °C. Compounds of Formula 3.5, where R₁, R₂, and X are as defined above, can be prepared from compounds of Formula 3.4, where R₁, R₂, and X are as defined above and the carboxylic acid is protected as either the methyl (Me) or benzyl (Bn) ester, by treating with a hydroxide base, such as lithium hydroxide (LiOH), in an aqueous THF solvent mixture, as shown in *step d*. Additionally, compounds of Formula 3.5, where R₁ and X are as defined above and R₂ is as originally defined, but not benzyl, acyl, or hydrogen, can be prepared from compounds of Formula 3.4 wherein the carboxylic acid is protected as the Bn ester and R₁, R₂, and X are as defined above by treatment with hydrogen gas in the presence of a catalyst such as Pd/C, in a solvent such as EtOAc, as shown in *step e*.

Scheme 3



[0066] Compounds of Formula 4.0, where R_1 and R_2 are as originally defined, but R_2 is not acyl or hydrogen, and X is Boc, can be prepared according to the methods outlined in **Scheme 4**. Compounds of Formula 4.0, can be obtained from compounds of Formula 3.5, where R_1 and R_2 are as defined above and X is Boc, by the addition of a solution of compounds of Formula 3.5 in a halogenated solvent such as DCM or an aromatic solvent such as toluene to a mixture of a base, such as 4-dimethylaminopyridine (DMAP), and a mixed anhydride, such as 2-methyl-6-nitrobenzoic anhydride (MNBA), in either a halogenated solvent such as DCM or an aromatic solvent such as toluene at a temperature between about 21 °C and about 60 °C over a period of 4 – 12 hours (h), as shown in *a*.

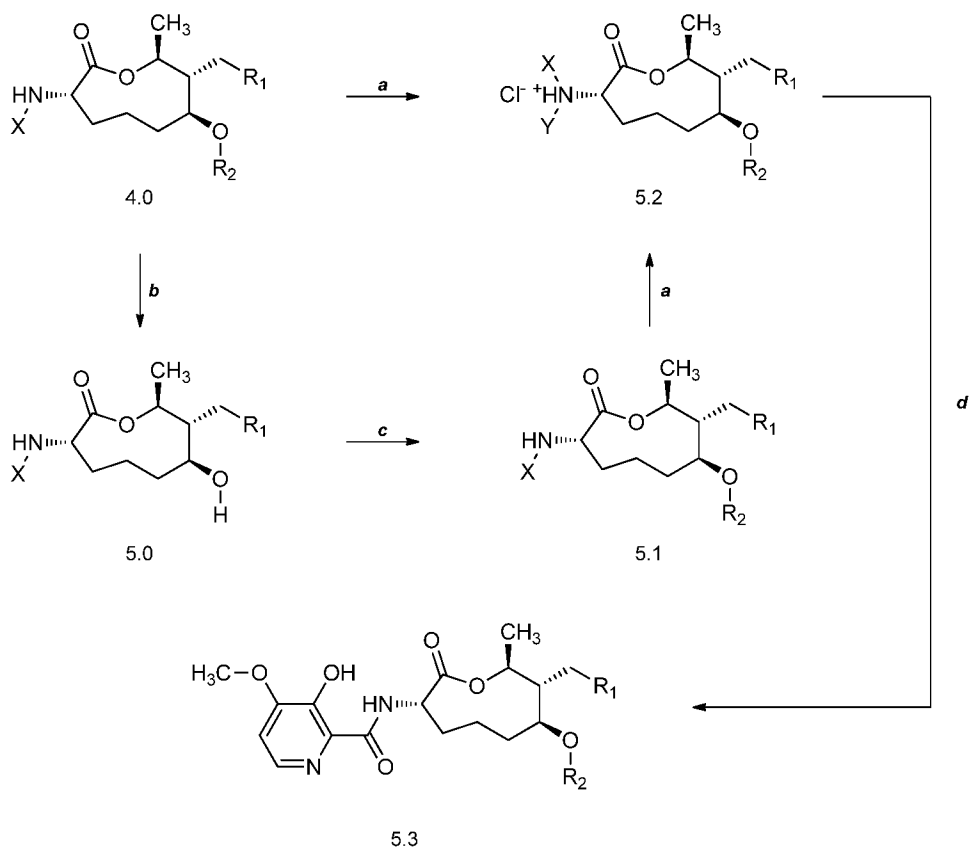
Scheme 4



[0067] Compounds of Formulas 5.2 and 5.3 can be prepared through the methods shown in **Scheme 5, steps a – d**. Alcohols of Formula 5.0 are accessed from compounds of Formula 4.0, where R_1 is as originally defined, R_2 is benzyl, and X is Boc, by treatment with hydrogen gas in the presence of a catalyst such as Pd/C, in a solvent such as THF, as shown in *b*. Compounds of Formula 5.1, where R_1 is as originally defined, R_2 is acyl, and X is Boc, can be prepared from compounds of Formula 5.0, where R_1 and X are as defined above, by treating with a carbonyl chloride such as cyclopropanecarbonyl chloride in the presence of an amine base such as DMAP, in a mixed solvent system such as pyridine and DCM, as shown in *step c*. Compounds of Formula 5.2, where R_1 and R_2 are as originally defined and X and Y are hydrogen, can be obtained from compounds of Formula 4.0 or 5.1, where R_1 and R_2 are as originally defined, and X is Boc, by

treating with an acid, such as a 4.0 Molar (M) hydrogen chloride (HCl) solution in dioxane, in a solvent such as DCM, as shown in *a*. The resulting hydrochloride salt may be neutralized prior to use to give the free amine or neutralized *in situ* in step *d*. Compounds of Formula 5.3, where R₁ and R₂ are as originally defined, can be prepared from compounds of Formula 5.2 by treatment with 3-hydroxy-4-methoxypicolinic acid in the presence of a base, such as 4-methylmorpholine, and a peptide coupling reagent, such as *O*-(7-azabenzotriazol-1-yl)-*N,N,N',N'*-tetramethyluronium hexafluorophosphate (HATU) or benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate (PyBOP), in an aprotic solvent such as DCM, as shown in *d*.

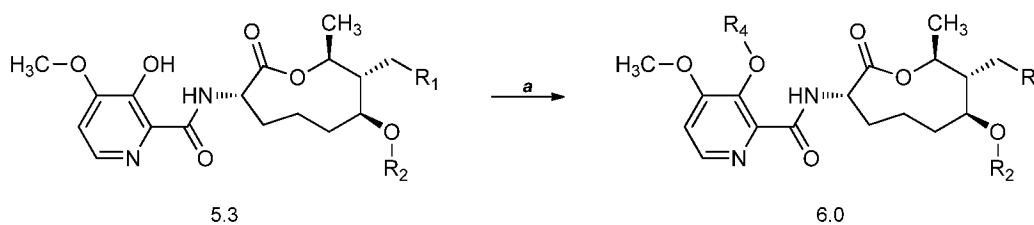
Scheme 5



[0068] Compounds of Formula 6.0, where R₁, R₂ and R₄ are as originally defined, can be prepared by the method shown in **Scheme 6**. Compounds of Formula 6.0 can be prepared from compounds of Formula 5.3, where R₁ and R₂ are as originally defined, by treatment with the

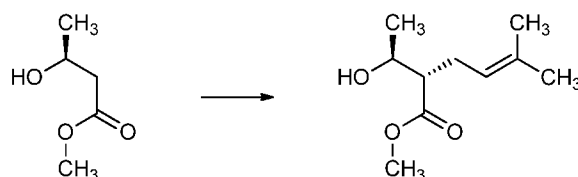
appropriate alkyl halide with or without a reagent such as sodium iodide (NaI) and an alkali carbonate base such as sodium carbonate (Na_2CO_3) or potassium carbonate (K_2CO_3) in a solvent such as acetone or by treatment with an acyl halide in the presence of an amine base, such as pyridine, triethylamine (TEA), DMAP, or mixtures thereof in an aprotic solvent such as DCM, as shown in *step a*.

Scheme 6



EXAMPLES

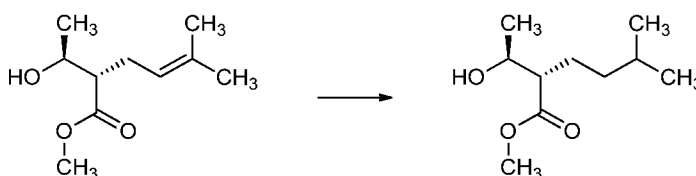
[0069] Example 1, Step 1: Preparation of (*S*)-methyl 2-((*S*)-1-hydroxyethyl)-5-methylhex-4-enoate:



[0070] To a solution of diisopropylamine (19.93 milliliters (mL), 142 millimoles (mmol)) in anhydrous THF (99 mL) at $-50\text{ }^\circ\text{C}$ (deficient dry ice/acetone bath) was added *n*-butyllithium (*n*-BuLi; 54.3 mL, 130 mmol, 2.5 M in hexanes). This solution was removed from the cold bath for 15 minutes (min), then re-cooled to $-50\text{ }^\circ\text{C}$. To the lithium diisopropylamide (LDA) was added a solution of (*S*)-methyl 3-hydroxybutanoate (6.64 mL, 59.3 mmol) in THF (20.0 mL) dropwise over 15 min using a cannula. This solution was allowed to warm to $-30\text{ }^\circ\text{C}$ over 30 min, stirred at $-30\text{ }^\circ\text{C}$ for 1 h, and re-cooled to $-78\text{ }^\circ\text{C}$. To the enolate was added a solution of 1-bromo-3-methylbut-2-ene (13.7 mL, 119 mmol) in anhydrous 1,2-dimethoxyethane (20.0 mL, 193 mmol) dropwise over 15 min. The cold bath was at $-60\text{ }^\circ\text{C}$ after 1 h at which time the reaction flask was removed from the bath and stirred without cooling for 1.5 h. The reaction was quenched by the addition of sat. aq. ammonium chloride (NH_4Cl ; 50 mL), diluted with EtOAc (50 mL), and the phases were separated.

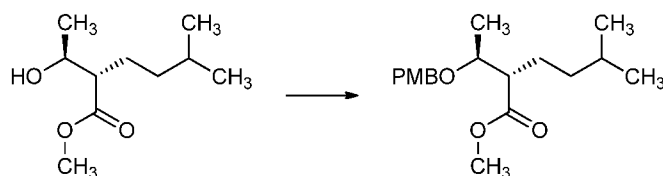
The aqueous phase was further extracted with EtOAc (2 x 50 mL) and the combined organic extracts were washed with sat. aq. sodium chloride (NaCl, brine; 50 mL), dried over sodium sulfate Na₂SO₄, filtered, and concentrated to dryness. The crude residue was purified by flash column chromatography (120 grams (g) silica gel (SiO₂), 0→40% EtOAc/hexanes) to afford the title compound (9.5 g, 51.0 mmol, 86%) as a slightly yellow oil: IR (thin film) 3452, 2971, 2929, 1730, 1437, 1198, 1160 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.11 – 5.01 (m, 1H), 3.92 (p, *J* = 6.3 Hz, 1H), 3.70 (s, 3H), 2.78 (s, 1H), 2.46 – 2.28 (m, 3H), 1.69 (d, *J* = 1.4 Hz, 3H), 1.62 (s, 3H), 1.23 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 175.54, 134.14, 120.30, 67.78, 52.72, 51.52, 27.90, 25.73, 21.46, 17.64.

[0071] Example 1, Step 2: Preparation of (*S*)-methyl 2-((*S*)-1-hydroxyethyl)-5-methylhexanoate:



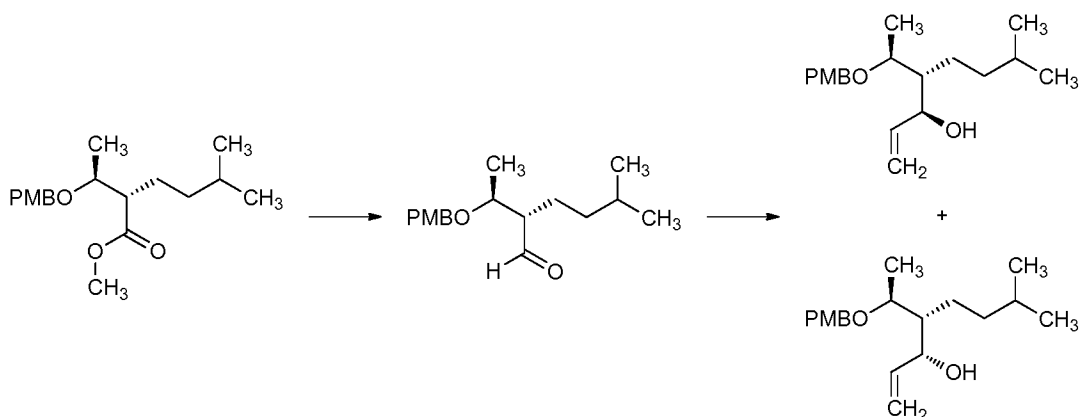
[0072] To a well stirred solution of (*S*)-methyl 2-((*S*)-1-hydroxyethyl)-5-methylhex-4-enoate (9.5 g, 51.0 mmol) in MeOH (51 mL) was added 10% Pd/C (0.543 g, 5.10 mmol). The reaction was put under a hydrogen atmosphere (balloon) and stirred at room temperature for 20 h. The mixture was filtered through a plug of Celite[®] and the plug was washed with MeOH (20 mL). The filtrate and washes were combined, the solvent was removed under reduced pressure, and the residue was dissolved in DCM (50 mL). The solution was passed through a phase separator to remove residual water (H₂O), and the solvent was removed under reduced pressure to afford the title compound (9.45 g, 50.2 mmol, 98%) as a slightly yellow oil: IR (thin film) 3451, 2954, 2871, 1736, 1719, 1169 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.91 (p, *J* = 6.4 Hz, 1H), 3.72 (s, 3H), 2.77 (s, 1H), 2.36 (ddd, *J* = 9.2, 6.3, 5.0 Hz, 1H), 1.72 – 1.45 (m, 3H), 1.28 – 1.05 (m, 5H), 0.88 (dd, *J* = 6.6, 3.2 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 176.13, 68.55, 53.29, 51.67, 36.55, 28.16, 27.37, 22.74, 22.44, 21.68.

[0073] Example 1, Step 3: Preparation of (*S*)-methyl 2-((*S*)-1-((4-methoxybenzyl)oxy)ethyl)-5-methylhexanoate:



[0074] To a solution of (*S*)-methyl 2-((*S*)-1-hydroxyethyl)-5-methylhexanoate (5.00 g, 26.6 mmol) and ((1*S*,4*R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonic acid (camphorsulfonic acid, CSA; 0.617 g, 2.66 mmol) in DCM (53.1 mL) was added 4-methoxybenzyl 2,2,2-trichloroacetimidate (8.27 mL, 39.8 mmol) at 0 °C. The reaction mixture was removed from the cold bath and stirred at room temperature for 17 h. Hexane (50 mL) was added to the reaction and the precipitate was removed by filtration. The solids were washed with hexanes (2 x 10 mL), Celite[®] (2 scoopula tip-fulls) was added to the combined filtrate and washes, and the solvent was removed under reduced pressure. The resulting adsorbed material was directly loaded onto a column and purified using flash column chromatography (80 g SiO₂, 0→35% EtOAc/hexanes) to afford the title compound (6.3 g, 20.4 mmol, 77%) as a colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.16 (m, 2H), 6.89 – 6.79 (m, 2H), 4.49 (d, *J* = 11.2 Hz, 1H), 4.33 (d, *J* = 11.1 Hz, 1H), 3.75 (s, 3H), 3.74 – 3.62 (m, 4H), 2.49 (ddd, *J* = 10.7, 8.2, 4.0 Hz, 1H), 1.62 – 1.40 (m, 3H), 1.23 – 1.16 (m, 3H), 1.16 – 1.03 (m, 2H), 0.87 (d, *J* = 3.9 Hz, 3H), 0.85 (d, *J* = 3.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 175.03, 159.10, 130.63, 129.14, 113.62, 76.16, 70.71, 55.11, 52.64, 51.25, 36.58, 27.97, 26.00, 22.69, 22.17, 17.08; ESIMS *m/z* 331 ([M+Na]⁺).

[0075] Example 1, Steps 4 and 5: Preparation of (3*S*,4*R*)-4-((*S*)-1-((4-methoxybenzyl)oxy)ethyl)-7-methyloct-1-en-3-ol and (3*R*,4*R*)-4-((*S*)-1-((4-methoxybenzyl)oxy)ethyl)-7-methyloct-1-en-3-ol:



Step 4

[0076] To a solution of (*S*)-methyl 2-((*S*)-1-((4-methoxybenzyl)oxy)ethyl)-5-methylhexanoate (6.00 g, 19.5 mmol) and chlorobis(cyclooctene)-iridium(I) dimer (0.349 g, 0.389 mmol) in dry DCM (19.5 mL) was slowly added Et₂SiH (3.76 mL, 29.2 mmol) at 0 °C. The flask was removed from the cold bath and the reaction was stirred at room temperature for 20 h under nitrogen (N₂). The reaction mixture was transferred via cannula to an ice-cooled mixture of diethyl ether (Et₂O; 60 mL) and 2 Normal (N) HCl (20 mL) over 15 min. The mixture was removed from the cold bath and stirred at room temperature for 30 min. The phases were separated and the aq. phase was further extracted with Et₂O (2 x 50 mL). The organics were combined, washed with sat. aq. sodium bicarbonate (NaHCO₃; 25 mL) and brine (25 mL), dried over Na₂SO₄, filtered, and the filtrate treated with Celite[®] (5 scoopula tip-fulls). The solvent was removed under reduced pressure and the resulting adsorbed material was directly loaded onto a column and purified using flash column chromatography (120 g SiO₂, 0→75% EtOAc/hexanes) to afford the intermediate aldehyde, (*S*)-2-((*S*)-1-((4-methoxybenzyl)oxy)ethyl)-5-methylhexanal.

Step 5

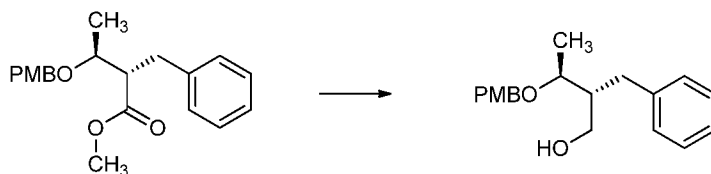
[0077] The intermediate aldehyde was dissolved in THF (30 mL), the mixture was cooled to -78 °C, vinylmagnesium bromide (29.2 mL, 29.2 mmol, 1M in THF) was slowly added, and the resulting solution was stirred for 30 min. The reaction was removed from the cold bath, stirred at room temperature for 30 min, and quenched by the addition of sat. aq. NH₄Cl (30 mL). The phases were separated, and the aq. phase was further extracted with Et₂O (3 x 50 mL). The combined organics were dried over Na₂SO₄, filtered, and concentrated to dryness. The residue was dissolved in DCM (20 mL) and the resulting solution was treated with Celite[®] (5 scoopula tip-fulls). The

solvent was removed under reduced pressure and the resulting adsorbed material was directly loaded onto a column and purified using flash column chromatography (220 g SiO₂, 0→15% acetone/hexanes) to afford the individual diastereomers as colorless oils:

[0078] (3*S*,4*R*)-4-((*S*)-1-((4-methoxybenzyl)oxy)ethyl)-7-methyloct-1-en-3-ol (2.35 g, 7.67 mmol, 39%): ¹H NMR (400 MHz, CDCl₃) δ 7.27 – 7.19 (m, 2H), 6.91 – 6.82 (m, 2H), 5.84 (ddd, *J* = 17.2, 10.6, 4.7 Hz, 1H), 5.29 (app dt, *J* = 17.2, 1.9 Hz, 1H), 5.16 (app dt, *J* = 10.6, 1.9 Hz, 1H), 4.58 (d, *J* = 11.0 Hz, 1H), 4.53 – 4.45 (m, 1H), 4.27 (d, *J* = 10.9 Hz, 1H), 3.83 (d, *J* = 4.3 Hz, 1H), 3.79 (s, 3H), 3.76 – 3.65 (m, 1H), 1.52 – 1.26 (m, 7H), 1.20 – 1.06 (m, 2H), 0.85 (app dd, *J* = 6.6, 2.2 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 159.33, 139.16, 130.02, 129.54, 114.61, 113.88, 76.55, 72.08, 70.65, 55.26, 49.31, 37.35, 28.25, 23.51, 22.63, 22.52, 17.71; ESIMS *m/z* 329 ([M+Na]⁺).

[0079] (3*R*,4*R*)-4-((*S*)-1-((4-methoxybenzyl)oxy)ethyl)-7-methyloct-1-en-3-ol (1.48 g, 4.83 mmol, 25%): ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.22 (m, 2H), 6.91 – 6.83 (m, 2H), 5.89 (ddd, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.24 (ddd, *J* = 17.2, 1.8, 1.2 Hz, 1H), 5.12 (ddd, *J* = 10.4, 1.8, 1.1 Hz, 1H), 4.58 (d, *J* = 11.1 Hz, 1H), 4.35 (d, *J* = 11.1 Hz, 1H), 4.22 – 4.13 (m, 1H), 3.80 (s, 3H), 3.70 (p, *J* = 6.3 Hz, 1H), 3.66 (d, *J* = 3.2 Hz, 1H), 1.56 (tt, *J* = 6.8, 5.2 Hz, 1H), 1.49 – 1.24 (m, 6H), 1.19 – 1.08 (m, 2H), 0.84 (dd, *J* = 6.7, 2.0 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 159.24, 140.20, 130.22, 129.41, 115.17, 113.87, 78.10, 75.83, 70.43, 55.28, 48.98, 36.07, 28.53, 26.08, 22.52, 17.93; ESIMS *m/z* 329 ([M+Na]⁺).

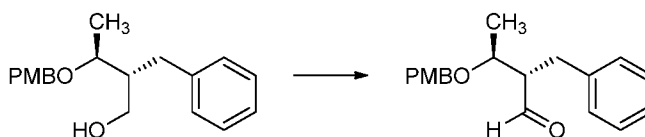
[0080] Example 1, Step 6: Preparation of (2*R*,3*S*)-2-benzyl-3-((4-methoxybenzyl)-oxy)butan-1-ol:



[0081] To a stirred suspension of LAH (2.77 g, 73.1 mmol) in anhydrous Et₂O (140 mL) was added (2*S*,3*S*)-methyl 2-benzyl-3-((4-methoxybenzyl)oxy)butanoate (8.0 g, 24.36 mmol) dissolved in Et₂O (104 mL) dropwise at 0 °C. The reaction was stirred at 0 °C for 15 min, followed by warming to room temperature and stirring for 1 h. The reaction was recooled to 0 °C and carefully quenched by the simultaneous dropwise addition of H₂O (2.8 mL) and 1N sodium hydroxide

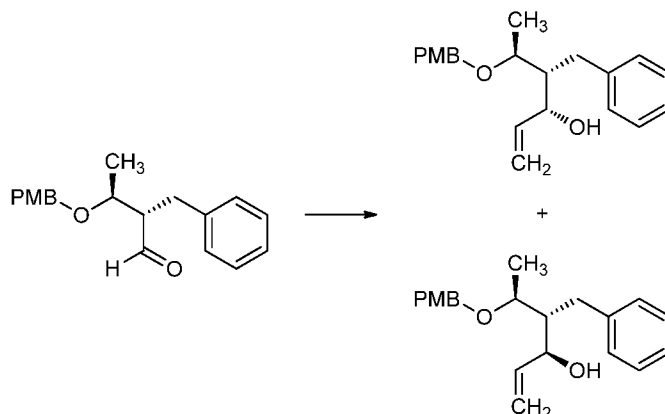
(NaOH; 2.8 mL). The mixture was filtered and the aluminum salts were washed with Et₂O (50 mL). The filtrate was treated with Celite[®] (20 g) and concentrated to give a solid. The adsorbed material was purified using flash column chromatography (120 g SiO₂ column, 0→60% EtOAc/hexane) to afford the title compound (5.38 g, 74%) as a clear oil: ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.10 (m, 7H), 6.93 – 6.84 (m, 2H), 4.59 (d, *J* = 11.2 Hz, 1H), 4.30 (d, *J* = 11.2 Hz, 1H), 3.89 (app dt, *J* = 11.4, 2.9 Hz, 1H), 3.80 (s, 3H), 3.66 (app qd, *J* = 6.2, 4.3 Hz, 1H), 3.50 (ddd, *J* = 11.5, 6.9, 4.7 Hz, 1H), 2.93 – 2.85 (m, 1H), 2.75 (app qd, *J* = 13.7, 7.5 Hz, 2H), 1.76 (dddt, *J* = 10.9, 6.6, 4.3, 2.3 Hz, 1H), 1.29 (d, *J* = 6.3 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 159.32, 140.61, 130.35, 129.39, 129.20, 128.36, 125.97, 113.93, 70.70, 62.36, 55.31, 47.81, 35.11, 17.67; ESIMS *m/z* 323 ([M+Na]⁺).

[0082] Example 1, Step 7: (2*S*,3*S*)-2-benzyl-3-((4-methoxybenzyl)oxy)butanal:



[0083] To a solution of (2*R*,3*S*)-2-benzyl-3-((4-methoxybenzyl)oxy)butan-1-ol (5.38 g, 17.91 mmol) in CH₂Cl₂ (90 mL) in a nitrogen flushed 250 mL round bottomed flask was added DMSO (17.9 mL, 25.24 mmol) and TEA (12.5 mL, 90 mmol) via syringe followed by sulfur trioxide-pyridine complex (8.55 g, 53.7 mmol) in three equal portions at 0 °C under N₂. The reaction was removed from the cold bath and allowed to warm to room temperature, and stirred for 2 h. The reaction was diluted with ice cold 0.5 N HCl (100 mL) and EtOAc (150 mL). The phases were separated and the organic phase was washed with sat. aq. NaHCO₃ (50 mL) and brine (50 mL). The solution was dried over magnesium sulfate (MgSO₄), filtered, and concentrated to afford the title compound (5.3 g, 96%) as a yellow oil: ¹H NMR (400 MHz, CDCl₃) δ 9.78 (d, *J* = 2.8 Hz, 1H), 7.29 – 7.09 (m, 7H), 6.89 (d, *J* = 8.7 Hz, 2H), 4.56 (d, *J* = 11.3 Hz, 1H), 4.34 (d, *J* = 11.3 Hz, 1H), 3.82 (s, 3H), 3.03 (dd, *J* = 14.0, 8.2 Hz, 1H), 2.87 (dd, *J* = 14.0, 6.4 Hz, 2H), 2.78 – 2.55 (m, 1H), 1.29 (d, *J* = 6.4 Hz, 3H); ESIMS *m/z* 321.3 ([M+Na]⁺).

[0084] Example 1, Step 8: Preparation of (3*S*,4*R*,5*S*)-4-benzyl-5-((4-methoxybenzyl)oxy)-hex-1-en-3-ol:



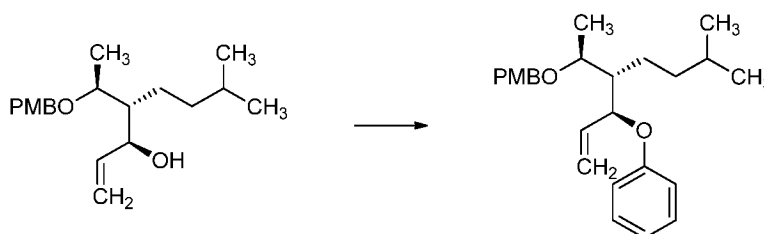
[0085] To a 200 mL round-bottomed flask equipped with a magnetic stir bar were added (2*S*,3*S*)-2-benzyl-3-((4-methoxybenzyl)oxy)butanal (5.34 g, 17.90 mmol) and THF (36 mL). The flask was cooled to -78 °C and vinylmagnesium bromide (1.0 M in THF, 36 mL, 36 mmol) was added *via* a syringe. The reaction was maintained at -78 °C for 1.5 h, quenched with sat. aq. NH₄Cl (25 mL) at -78 °C, and then removed from the cold bath. After warming to room temperature, the biphasic mixture was diluted with EtOAc (100 mL), and the phases were separated. The organic phase was washed with brine (30 mL), dried over MgSO₄, filtered, and concentrated. The oil was purified by flash column chromatography (120 g SiO₂ column, 0→100% EtOAc/hexanes) to afford the pure desired isomer (1.18 g), and a mixture of the isomers (2.53 g). The mixture was re-purified by flash column chromatography (80 g SiO₂ column, 0→15% acetone/hexanes) to afford clean separation of the isomers in a 2.23:1 ratio of diastereomers.

[0086] (3*S*,4*R*,5*S*)-4-Benzyl-5-((4-methoxybenzyl)oxy)hex-1-en-3-ol (2.88 g, 49%): ¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.17 (m, 5H), 7.05 – 6.98 (m, 2H), 6.92 – 6.84 (m, 2H), 5.91 (ddd, *J* = 17.1, 10.6, 4.4 Hz, 1H), 5.36 (dt, *J* = 17.2, 1.9 Hz, 1H), 5.23 (dt, *J* = 10.6, 1.8 Hz, 1H), 4.65 – 4.59 (m, 1H), 4.56 (d, *J* = 10.9 Hz, 1H), 4.21 (d, *J* = 11.0 Hz, 1H), 3.89 (d, *J* = 2.7 Hz, 1H), 3.78 (s, 3H), 3.65 (qd, *J* = 6.3, 3.7 Hz, 1H), 2.72 (d, *J* = 7.3 Hz, 2H), 1.78 – 1.70 (m, 1H), 1.25 (d, *J* = 6.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 159.46, 141.10, 139.22, 130.09, 129.57, 129.23, 128.39, 125.91, 115.02, 114.01, 75.38, 70.99, 70.74, 55.33, 50.95, 31.46, 17.72; ESIMS *m/z* 349 ([M+Na]⁺).

[0087] (3*R*,4*R*,5*S*)-4-Benzyl-5-((4-methoxybenzyl)oxy)hex-1-en-3-ol (1.3 g, 22%): ¹H NMR (300 MHz, CDCl₃) δ 7.33 – 7.04 (m, 7H), 6.96 – 6.78 (m, 2H), 5.96 (ddd, *J* = 17.2, 10.4, 5.5 Hz, 1H), 5.25 (dt, *J* = 17.2, 1.7 Hz, 1H), 5.11 (dt, *J* = 10.5, 1.6 Hz, 1H), 4.56 (d, *J* = 11.4 Hz, 1H), 4.31

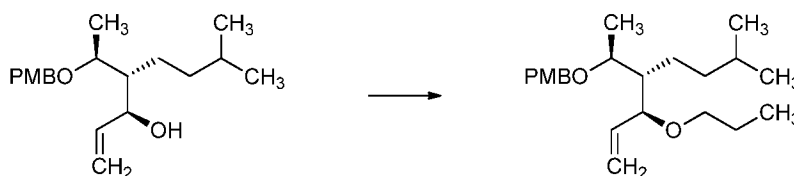
(d, $J = 11.4$ Hz, 1H), 4.28 – 4.22 (m, 1H), 3.82 (s, 3H), 3.72 – 3.65 (m, 1H), 2.86 – 2.87 (m, 3H), 2.06 – 1.96 (m, 1H), 1.27 (d, $J = 6.4$ Hz, 3H): ESIMS m/z 349.3 ($[M+Na]^+$).

[0088] Example 2, Step 1: Preparation of 1-methoxy-4-((((2*S*,3*S*)-6-methyl-3-((*S*)-1-phenoxymethyl)heptan-2-yl)oxy)methyl)benzene:



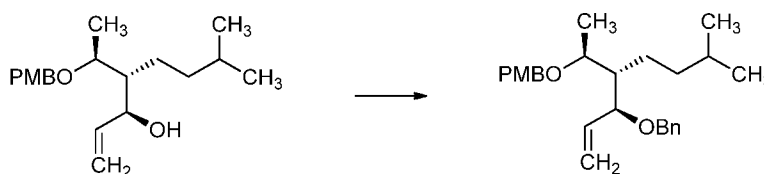
[0089] A toluene (12.0 mL) solution of (3*S*,4*R*)-4-(((*S*)-1-((4-methoxybenzyl)oxy)ethyl)-7-methyloct-1-en-3-ol (1.10 g, 3.59 mmol), *N*-cyclohexyl-*N*-methylcyclohexanamine (1.14 mL, 5.38 mmol), triphenylbismuth diacetate (3.01 g, 5.38 mmol), and copper(II) acetate (0.130 g, 0.718 mmol) was heated to 50 °C and stirred at this temperature for 16 h. Additional triphenylbismuth diacetate (1.00 g) was added to push the reaction to completion, and after a total reaction time of 38 h, the reaction mixture was cooled to room temperature, loaded onto a Celite[®] plug and purified by flash column chromatography (40 g SiO₂, 0 → 15% EtOAc/hexanes) to afford the title compound (1.10 g, 2.30 mmol, 64%): ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.20 (m, 3H), 6.99 – 6.86 (m, 4H), 6.76 – 6.68 (m, 2H), 5.85 (ddd, $J = 17.4, 10.8, 4.8$ Hz, 1H), 5.27 – 5.16 (m, 2H), 5.09 (ddt, $J = 4.8, 3.2, 1.7$ Hz, 1H), 4.39 (d, $J = 10.6$ Hz, 1H), 4.09 (d, $J = 10.6$ Hz, 1H), 3.76 (s, 3H), 3.64 (dq, $J = 8.0, 6.2$ Hz, 1H), 1.68 – 1.56 (m, 2H), 1.55 – 1.42 (m, 1H), 1.41 – 1.17 (m, 6H), 0.88 (app dd, $J = 6.6, 1.4$ Hz, 6H); ESIMS m/z 405 ($[M+Na]^+$).

[0090] Example 2, Step 2: Preparation of 1-methoxy-4-((((2*S*,3*S*)-6-methyl-3-((*S*)-1-propoxymethyl)heptan-2-yl)oxy)methyl)benzene:



[0091] To a solution of (3*S*,4*R*)-4-((*S*)-1-((4-methoxybenzyl)oxy)ethyl)-7-methyloct-1-en-3-ol (1.40 g, 4.57 mmol) and potassium 2-methylpropan-2-olate (0.564 g, 5.03 mmol) in THF (30.5 mL) was added propyl 4-methylbenzenesulfonate (2.15 mL, 11.4 mmol). The reaction was stirred at room temperature for 72 h, diluted with H₂O (15 mL), and the phases were separated. The aq. phase was further extracted with Et₂O (3 x 25 mL), and the combined organics were washed with brine (15 mL), dried over Na₂SO₄, filtered, and the filtrate was treated with Celite[®] (4 scoopula tip-fulls). The solvent was removed under reduced pressure and the resulting adsorbed material was directly loaded onto a column and purified using flash column chromatography (80 g SiO₂, 0→15% EtOAc/hexanes) to afford the title compound (1.30 g, 3.36 mmol, 74%) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.22 (m, 2H), 6.91 – 6.83 (m, 2H), 5.77 – 5.63 (m, 1H), 5.20 – 5.14 (m, 1H), 5.13 (d, *J* = 1.1 Hz, 1H), 4.50 – 4.35 (m, 2H), 3.85 – 3.77 (m, 4H), 3.61 (p, *J* = 6.3 Hz, 1H), 3.43 (app tt, *J* = 9.8, 6.6 Hz, 1H), 3.12 (app dt, *J* = 9.1, 6.6 Hz, 1H), 1.69 – 1.20 (m, 8H), 1.15 (d, *J* = 6.3 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.87 (app dd, *J* = 6.6, 1.1 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 158.98, 138.54, 131.33, 129.16, 116.04, 113.69, 81.66, 75.17, 70.57, 70.12, 55.26, 47.97, 38.70, 28.65, 23.69, 23.24, 22.63, 16.76, 10.90; ESIMS *m/z* 371 ([M+Na]⁺).

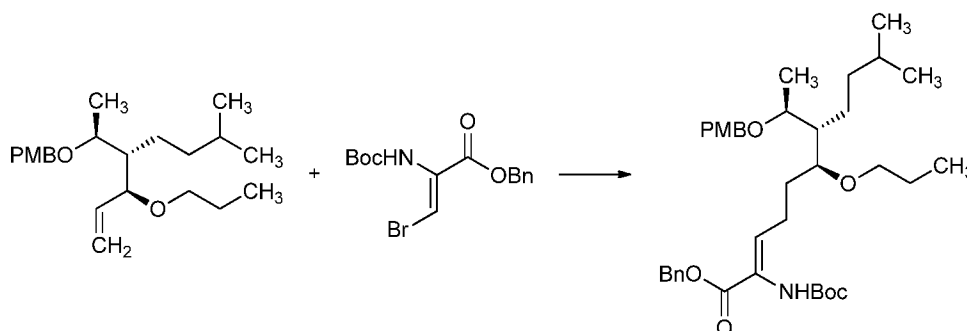
[0092] Example 2, Step 3: Preparation of 1-(((2*S*,3*S*)-3-((*S*)-1-(benzyloxy)allyl)-6-methylheptan-2-yl)oxy)methyl)-4-methoxybenzene:



[0093] To a solution of (3*S*,4*R*)-4-((*S*)-1-((4-methoxybenzyl)oxy)ethyl)-7-methyloct-1-en-3-ol (2.34 g, 7.64 mmol) in DMF (15.3 mL) was added NaH (0.611 g, 15.3 mmol, 60% dispersion in mineral oil) at 0 °C. After 20 min, benzyl bromide (2.27 mL, 19.1 mmol) was added and the reaction was stirred at 0 °C for 20 min, warmed to 45 °C, and stirred at this temperature for 16 h. The reaction was cooled to room temperature and quenched with sat. aq. NH₄Cl (40 mL). The mixture was extracted with Et₂O (3 x 50 mL), and the combined organics were washed with brine (40 mL), dried over Na₂SO₄, filtered, and concentrated to dryness. The residue was purified using flash column chromatography (120 g SiO₂, 0→20% EtOAc/hexanes) to afford the title compound

(2.75 g, 6.93 mmol, 91%) as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.34 (m, 2H), 7.32 – 7.25 (m, 3H), 7.22 – 7.17 (m, 2H), 6.87 – 6.78 (m, 2H), 5.78 (ddd, $J = 17.4, 9.9, 7.3$ Hz, 1H), 5.27 – 5.18 (m, 2H), 4.58 (d, $J = 12.4$ Hz, 1H), 4.42 (d, $J = 11.2$ Hz, 1H), 4.29 (d, $J = 11.2$ Hz, 1H), 4.26 (d, $J = 11.9$ Hz, 1H), 4.04 – 3.96 (m, 1H), 3.77 (s, 3H), 3.64 (p, $J = 6.3$ Hz, 1H), 1.73 – 1.63 (m, 1H), 1.55 – 1.42 (m, 2H), 1.43 – 1.21 (m, 3H), 1.15 (d, $J = 6.3$ Hz, 3H), 0.86 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.92, 139.07, 137.94, 131.19, 129.17, 128.19, 127.77, 127.47, 116.82, 113.65, 81.13, 75.03, 70.36, 70.07, 55.22, 48.17, 38.66, 28.62, 23.67, 22.61, 16.84; ESIMS m/z 419 ($[\text{M}+\text{Na}]^+$).

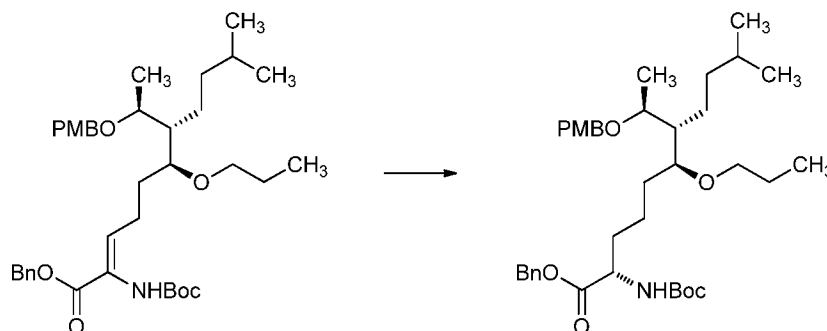
[0094] Example 3, Step 1: Preparation of (6*S*,7*S*,*Z*)-benzyl 2-((*tert*-butoxycarbonyl)amino)-7-((*S*)-1-((4-methoxybenzyl)oxy)ethyl)-10-methyl-6-propoxyundec-2-enoate:



[0095] To a solution of 1-methoxy-4-(((2*S*,3*S*)-6-methyl-3-((*S*)-1-propoxyallyl)heptan-2-yl)oxy)methyl)benzene (1.25 g, 3.59 mmol) in THF (3 mL) was added 9-BBN (10.8 mL, 5.38 mmol, 0.5 M in THF) dropwise, and the reaction was stirred at room temperature for 6 h. The reaction mixture was carefully treated with an aq. solution of K_3PO_4 (3 M, 2.152 mL, 6.46 mmol; gas evolution), followed by a solution of (*Z*)-benzyl 3-bromo-2-((*tert*-butoxycarbonyl)amino)acrylate (1.30 g, 3.66 mmol) in DMF (3.59 mL), and $\text{PdCl}_2\text{-dppf}$ (0.262 g, 0.359 mmol). The reaction vessel was fitted with an air condenser and slowly warmed to 55 °C. The solution became homogeneous and bright orange after 30 min. The reaction was maintained at this temperature for 20 h, at which point the color had turned a very dark red (almost black). The reaction was cooled to room temperature, diluted with H_2O (30 mL), and the phases were separated. The aq. phase was extracted with Et_2O (3 x 50 mL), and the combined organics were washed with

brine (15 mL), dried over Na₂SO₄, filtered, and the filtrate was treated with Celite[®] (2 scoopula tip-fulls). The solvent was removed under reduced pressure and the resulting adsorbed material was directly loaded onto a column and purified using flash column chromatography (80 g SiO₂, 0→25% acetone/hexanes) to afford the title compound (1.50 g, 2.397 mmol, 67%) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.29 (m, 5H), 7.25 – 7.20 (m, 2H), 6.88 – 6.80 (m, 2H), 6.59 (app t, *J* = 7.5 Hz, 1H), 6.15 (s, 1H), 5.20 (app d, *J* = 2.2 Hz, 2H), 4.48 (d, *J* = 11.4 Hz, 1H), 4.34 (d, *J* = 11.4 Hz, 1H), 3.78 (s, 3H), 3.57 (p, *J* = 6.2 Hz, 1H), 3.36 (ddd, *J* = 7.3, 5.3, 3.7 Hz, 1H), 3.33 – 3.19 (m, 2H), 2.36 – 2.16 (m, 2H), 1.72 – 1.38 (m, 16H), 1.38 – 1.13 (m, 6H), 0.91 – 0.82 (m, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 164.82, 158.99, 153.42, 137.06, 135.73, 131.13, 129.21, 128.52, 128.24, 128.22, 113.70, 80.33, 79.43, 74.78, 71.76, 69.86, 67.00, 55.25, 46.35, 38.73, 30.64, 28.68, 28.19, 25.39, 23.88, 23.47, 22.64, 22.61, 17.08, 10.79; ESIMS *m/z* 648 ([M+Na]⁺).

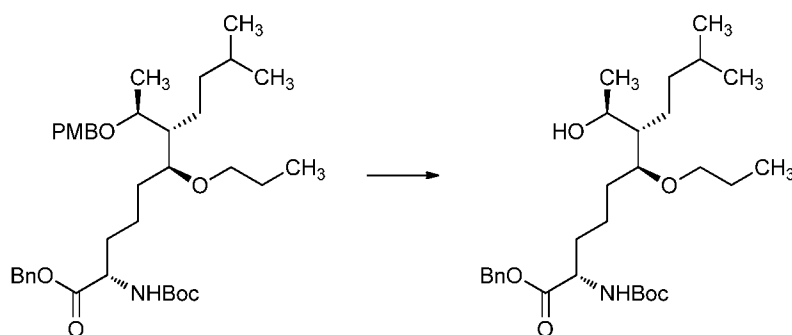
[0096] Example 3, Step 2: Preparation of (2*S*,6*S*,7*S*)-benzyl 2-((*tert*-butoxycarbonyl)-amino)-7-((*S*)-1-((4-methoxybenzyl)oxy)ethyl)-10-methyl-6-propoxyundecanoate:



[0097] A solution of (6*S*,7*S*,*Z*)-benzyl 2-((*tert*-butoxycarbonyl)amino)-7-((*S*)-1-((4-methoxybenzyl)oxy)ethyl)-10-methyl-6-propoxyundec-2-enoate (1.50 g, 2.40 mmol) in MeOH (9.59 mL) was added to a 45 mL pressure reactor. The system was purged with N₂ for 5 min and then (+)-1,2-bis((2*S*,5*S*)-2,5-diethylphospholano)benzene(1,5-cyclooctadiene)rhodium (I) trifluoromethanesulfonate (0.0170 g, 0.0240 mmol) was added. The system was purged with hydrogen gas (200 psi) 3 times, charged to 200 psi with hydrogen gas, and stirred at room temperature for 24 h. The hydrogen was evacuated and the solution was transferred to a round bottom flask rinsing with EtOAc (10 mL), and the solvent was removed under reduced pressure. The residue was dissolved in DCM (10 mL) and the resulting solution was treated with Celite[®] (3

scoopula tip-fulls). The solvent was removed under reduced pressure and the resulting adsorbed material was directly loaded onto a column and purified using flash column chromatography (40 g SiO₂, 0→40% EtOAc/hexanes) to afford the title compound (1.10 g, 1.752 mmol, 73%) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.27 (m, 5H), 7.29 – 7.21 (m, 2H), 6.90 – 6.83 (m, 2H), 5.21 – 5.09 (m, 2H), 5.04 (d, *J* = 8.4 Hz, 1H), 4.47 (d, *J* = 11.3 Hz, 1H), 4.41 – 4.27 (m, 2H), 3.78 (s, 3H), 3.63 – 3.52 (m, 1H), 3.38 – 3.26 (m, 3H), 1.87 – 1.74 (m, 1H), 1.70 – 1.17 (m, 22H), 1.16 (d, *J* = 6.2 Hz, 3H), 0.92 – 0.83 (m, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 172.75, 158.98, 155.35, 135.47, 131.30, 129.09, 128.57, 128.35, 128.20, 113.70, 79.78, 75.02, 71.89, 69.98, 66.92, 55.24, 53.59, 46.51, 38.66, 32.83, 31.98, 28.69, 28.33, 23.83, 23.54, 22.66, 22.64, 22.22, 17.13, 10.84; ESIMS *m/z* 650 ([M+Na]⁺).

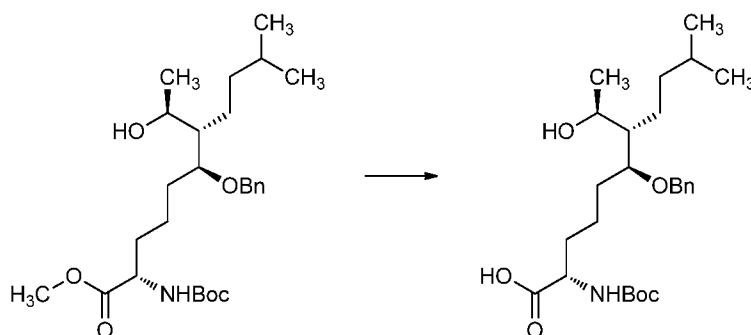
[0098] Example 3, Step 3: Preparation of (2*S*,6*S*,7*S*)-benzyl 2-((*tert*-butoxycarbonyl)amino)-7-((*S*)-1-hydroxyethyl)-10-methyl-6-propoxyundecanoate:



[0099] To a solution of (2*S*,6*S*,7*S*)-benzyl 2-((*tert*-butoxycarbonyl)amino)-7-((*S*)-1-((4-methoxybenzyl)oxy)-ethyl)-10-methyl-6-propoxyundecanoate (1.10 g, 1.75 mmol) in H₂O (0.531 mL) and DCM (5.31 mL) was added DDQ (0.418 g, 1.84 mmol) at 0 °C. The mixture was stirred vigorously at this temperature for 1 h and then 1N NaOH (1.84 mL, 1.84 mmol) and H₂O (20 mL) were added. The phases were separated and the aqueous phase was extracted with DCM (3 x 15 mL). The combined organic extracts were washed with brine (8 mL), dried over Na₂SO₄, filtered, and the filtrate was treated with Celite[®] (2 scoopula tip-fulls). The solvent was removed under reduced pressure and the resulting adsorbed material was directly loaded onto a column and purified using flash column chromatography (40 g SiO₂, 0→60% EtOAc/hexanes) to afford the title compound (815 mg, 1.61 mmol, 92%) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.30

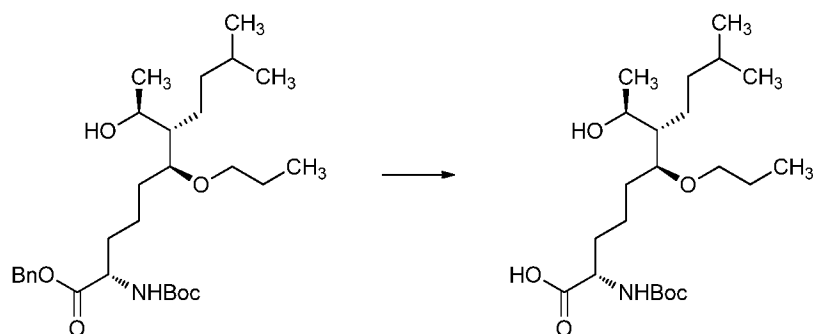
(m, 5H), 5.17 (app q, $J = 12.4$ Hz, 2H), 5.07 (d, $J = 8.5$ Hz, 1H), 4.44 – 4.39 (m, 1H), 4.39 – 4.30 (m, 1H), 3.87 – 3.75 (m, 1H), 3.54 (app dt, $J = 9.0, 6.6$ Hz, 1H), 3.42 – 3.33 (m, 1H), 3.26 (app dt, $J = 8.9, 6.6$ Hz, 1H), 1.87 – 1.76 (m, 1H), 1.72 – 1.37 (m, 17H), 1.35 – 1.07 (m, 7H), 1.04 – 0.93 (m, 1H), 0.93 – 0.84 (m, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.66, 155.32, 135.39, 128.59, 128.42, 128.24, 82.50, 79.89, 71.42, 69.10, 66.99, 53.52, 45.46, 37.47, 32.82, 28.82, 28.31, 28.28, 25.27, 23.20, 22.68, 22.54, 22.44, 22.06, 10.66; ESIMS m/z 530 ($[\text{M}+\text{Na}]^+$).

[00100] Example 3, Step 4: Preparation of (2*S*,6*S*,7*S*)-6-(benzyloxy)-2-((*tert*-butoxycarbonyl)amino)-7-((*S*)-1-hydroxyethyl)-10-methylundecanoic acid:



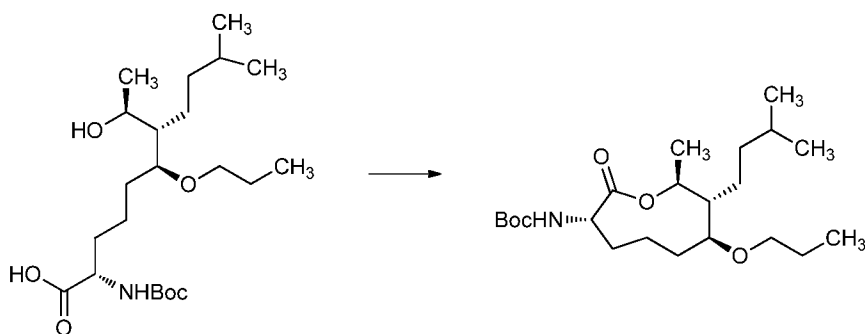
[00101] To a solution of (2*S*,6*S*,7*S*)-methyl 6-(benzyloxy)-2-((*tert*-butoxycarbonyl)amino)-7-((*S*)-1-hydroxyethyl)-10-methylundecanoate (700 mg, 1.46 mmol) in THF (9.73 mL) and H_2O (4.87 mL) was added $\text{LiOH} \cdot \text{H}_2\text{O}$ (184 mg, 4.38 mmol), and the reaction was stirred at room temperature for 4 h. The reaction was diluted with EtOAc (15 mL) and 0.2 M HCl (15 mL), the phases were separated, and the aq. phase was further extracted with EtOAc (3 x 15 mL). The combined organic extracts were washed with brine (8 mL), dried over Na_2SO_4 , filtered, and concentrated to dryness to afford the title compound (600 mg, 1.289 mmol, 88 %) as a white solid: ^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.21 (m, 5H), 5.63 (s, 1H), 4.57 – 4.45 (m, 2H), 3.89 – 3.74 (m, 2H), 3.59 – 3.52 (m, 1H), 1.92 – 1.63 (m, 2H), 1.63 – 0.94 (m, 22H), 0.83 (app dd, $J = 6.6, 2.1$ Hz, 6H) (carboxylic acid and alcohol peaks are very broad (not listed)); ^{13}C NMR (101 MHz, CDCl_3) δ 179.67, 156.76, 138.11, 128.33, 128.05, 127.64, 80.99, 79.27, 71.52, 68.79, 56.30, 46.67, 37.81, 32.72, 29.56, 28.48, 28.27, 25.15, 23.19, 22.63, 22.50, 22.21; ESIMS m/z 464 ($[\text{M}-\text{H}]^-$).

[00102] Example 3, Step 5: Preparation of (2*S*,6*S*,7*S*)-2-((*tert*-butoxycarbonyl)amino)-7-((*S*)-1-hydroxyethyl)-10-methyl-6-propoxyundecanoic acid:



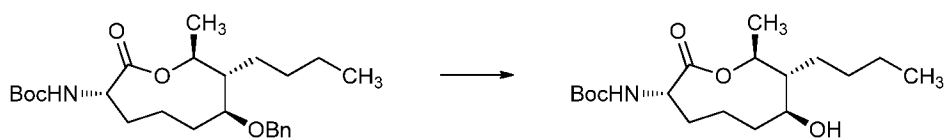
[00103] A solution of (2*S*,6*S*,7*S*)-benzyl 2-((*tert*-butoxycarbonyl)amino)-7-((*S*)-1-hydroxyethyl)-10-methyl-6-propoxyundecanoate (815 mg, 1.61 mmol) and 10% Pd/C (85 mg, 0.803 mmol) in THF (5.35 mL) was stirred under a hydrogen atmosphere (balloon pressure) at room temperature for 4 h. The hydrogen was removed using a stream of N₂ and the reaction was filtered through a plug of Celite[®]. The plug was washed with DCM (2 x 5 mL) and the combined filtrate and washes were concentrated to dryness under reduced pressure to afford the title compound (660 mg, 1.58 mmol, 98%) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 5.14 (d, *J* = 8.2 Hz, 1H), 4.36 – 4.26 (m, 1H), 3.95 – 3.83 (m, 1H), 3.63 – 3.52 (m, 1H), 3.49 – 3.41 (m, 1H), 3.37 – 3.27 (m, 1H), 1.93 – 1.81 (m, 2H), 1.79 – 0.80 (m, 33H) (carboxylic acid peak is very broad (not listed) and alcohol proton is not visible); ¹³C NMR (101 MHz, CDCl₃) δ 175.98, 155.52, 82.43, 79.93, 71.50, 69.42, 53.26, 45.32, 37.36, 32.61, 28.69, 28.31, 28.26, 25.17, 23.16, 22.66, 22.39, 21.82, 10.63; ESIMS *m/z* 416 ([M-H]⁻).

[00104] Example 4: Preparation of *tert*-butyl ((3*S*,7*S*,8*S*,9*S*)-8-isopentyl-9-methyl-2-oxo-7-propoxyoxonan-3-yl)carbamate (**18**):



[00105] A solution of (2*S*,6*S*,7*S*)-2-((*tert*-butoxycarbonyl)amino)-7-((*S*)-1-hydroxyethyl)-10-methyl-6-propoxyundecanoic acid (627 mg, 1.50 mmol) in anhydrous DCM (80 mL) was added over 12 h using a syringe pump to a stirred solution of MNBA (1.03 g, 3.00 mmol) and DMAP (1.10 g, 9.01 mmol) in DCM (150 mL) at room temperature. Stirring was continued for an additional 7 h then the reaction mixture was treated with Celite[®] (5 scoopula tip-fulls). The solvent was removed under reduced pressure and the resulting adsorbed material was directly loaded onto a column and purified using flash column chromatography (80 g SiO₂, 0→30% EtOAc/hexanes) to afford the title compound (355 mg, 0.888 mmol, 59%) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 5.06 (d, *J* = 8.2 Hz, 1H), 4.70 (dq, *J* = 10.1, 6.4 Hz, 1H), 4.24 – 4.14 (m, 1H), 3.50 (app dt, *J* = 9.0, 6.4 Hz, 1H), 3.28 – 3.19 (m, 1H), 3.13 (app dt, *J* = 8.8, 6.6 Hz, 1H), 2.30 – 2.18 (m, 1H), 2.11 (dddd, *J* = 15.6, 10.1, 7.9, 5.2 Hz, 1H), 1.87 (app dq, *J* = 13.1, 4.6 Hz, 1H), 1.78 – 1.35 (m, 16H), 1.31 (d, *J* = 6.3 Hz, 3H), 1.24 – 1.03 (m, 3H), 0.96 – 0.75 (m, 10H); ¹³C NMR (101 MHz, CDCl₃) δ 173.11, 154.94, 79.93, 79.70, 73.53, 70.41, 52.46, 46.66, 34.41, 33.63, 29.03, 28.75, 28.33, 26.26, 23.30, 22.61, 22.44, 19.26, 17.80, 10.88; ESIMS *m/z* 422 ([M+Na]⁺).

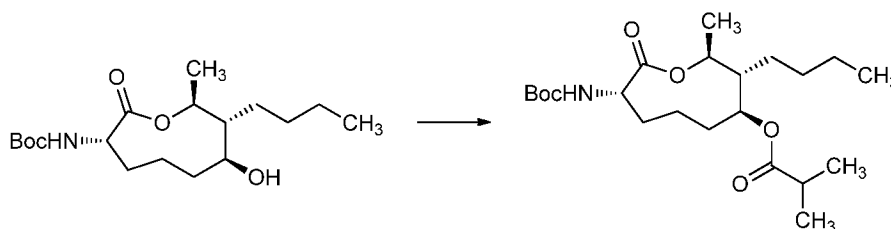
[00106] Example 5, Step 1: Preparation of *tert*-butyl ((3*S*,7*S*,8*R*,9*S*)-8-butyl-7-hydroxy-9-methyl-2-oxooxonan-3-yl)carbamate (**21**):



[00107] To a solution of *tert*-butyl ((3*S*,7*S*,8*S*,9*S*)-7-(benzyloxy)-8-butyl-9-methyl-2-oxooxonan-3-yl)carbamate (0.600 g, 1.38 mmol) in EtOAc (15 mL) was added 10% Pd/C (0.0740 g, 0.0690 mmol). The reaction flask was placed under 1 atm. of hydrogen (balloon) and stirred vigorously for 72 h. The reaction was filtered through a pad of celite and the pad was washed with EtOAc. The filtrate was concentrated and the residue purified by flash chromatography (SiO₂; EtOAc/ hexanes) to give the title compound as a colorless oil (0.405g, 1.18 mmol, 85%): ¹H NMR (400 MHz, CDCl₃) δ 5.11 (d, *J* = 8.3 Hz, 1H), 4.71 (dq, *J* = 10.0, 6.4 Hz, 1H), 4.26 – 4.15 (m, 1H), 3.69 (ddd, *J* = 8.7, 5.7, 2.2 Hz, 1H), 2.34 – 2.22 (m, 1H), 1.97 (dddd, *J* = 15.5, 10.1, 7.7, 5.2 Hz, 1H), 1.87 – 1.76 (m, 1H), 1.75 – 1.53 (m, 5H), 1.52 – 1.46 (m, 1H), 1.44 (s, 9H), 1.40 – 1.34 (m,

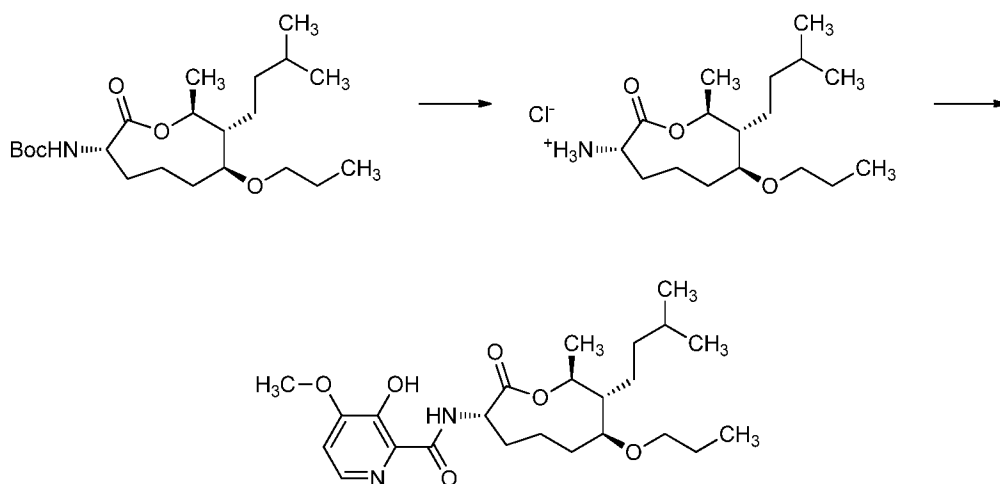
1H), 1.33 (d, $J = 6.3$ Hz, 3H), 1.30 (d, $J = 7.1$ Hz, 1H), 1.23 – 1.13 (m, 2H), 1.10 – 1.00 (m, 1H), 0.90 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 173.03, 154.09, 79.78, 73.54, 72.41, 52.43, 48.04, 34.24, 33.60, 28.31, 28.26, 27.61, 23.41, 19.21, 17.61, 13.97; ESIMS m/z 407 ($[\text{M}+\text{Na}+\text{CH}_3\text{CN}]^+$).

[00108] Example 5, Step 2: Preparation of (2*S*,3*S*,4*S*,8*S*)-8-((*tert*-butoxycarbonyl)amino)-3-butyl-2-methyl-9-oxooxonan-4-yl isobutyrate (**14**):



[00109] To a solution of *tert*-butyl ((3*S*,7*S*,8*R*,9*S*)-8-butyl-7-hydroxy-9-methyl-2-oxooxonan-3-yl)carbamate (0.405 g, 1.179 mmol) in pyridine (3.4 mL) was added DMAP (0.029 g, 0.236 mmol) followed by the slow addition of isobutyryl chloride (0.247 ml, 2.36 mmol) at room temperature. The reaction was warmed to 50 °C and stirred for 3 h, at which point additional isobutyryl chloride (0.247 ml, 2.36 mmol) was added. The reaction was stirred at 50 °C for an additional 14 h, cooled to room temperature, quenched with sat. aq. NH_4Cl (5ml), and extracted with EtOAc (3 x 10ml). The combined organic extracts were dried over MgSO_4 , filtered, and concentrated to dryness. The crude residue was purified by flash chromatography (SiO_2 ; EtOAc/hexanes) to give the title compound (0.274 g, 0.663 mmol, 56%) as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 5.15 (d, $J = 8.3$ Hz, 1H), 4.91 – 4.84 (m, 1H), 4.79 (dq, $J = 10.0, 6.3$ Hz, 1H), 4.27 – 4.16 (m, 1H), 2.60 – 2.44 (m, 1H), 2.23 (dt, $J = 13.8, 7.1$ Hz, 1H), 2.15 – 1.99 (m, 3H), 1.73 (tdd, $J = 13.0, 7.3, 2.3$ Hz, 1H), 1.57 – 1.46 (m, 1H), 1.44 (s, 9H), 1.34 (d, $J = 6.4$ Hz, 4H), 1.33 – 1.19 (m, 5H), 1.18 – 1.12 (m, 6H), 1.04 – 0.94 (m, 1H), 0.87 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 175.41, 172.91, 154.98, 79.76, 74.44, 73.12, 52.42, 45.44, 34.24, 33.73, 33.32, 30.88, 28.29, 27.38, 23.25, 19.19, 19.03, 18.88, 18.79, 18.02, 13.82; ESIMS m/z 436 ($[\text{M}+\text{Na}]^+$).

[00110] Example 6, Steps 1 and 2: Preparation of: 3-hydroxy-*N*-((3*S*,7*S*,8*S*,9*S*)-8-isopentyl-9-methyl-2-oxo-7-propoxyoxonan-3-yl)-4-methoxypicolinamide (**31**):



Step 1

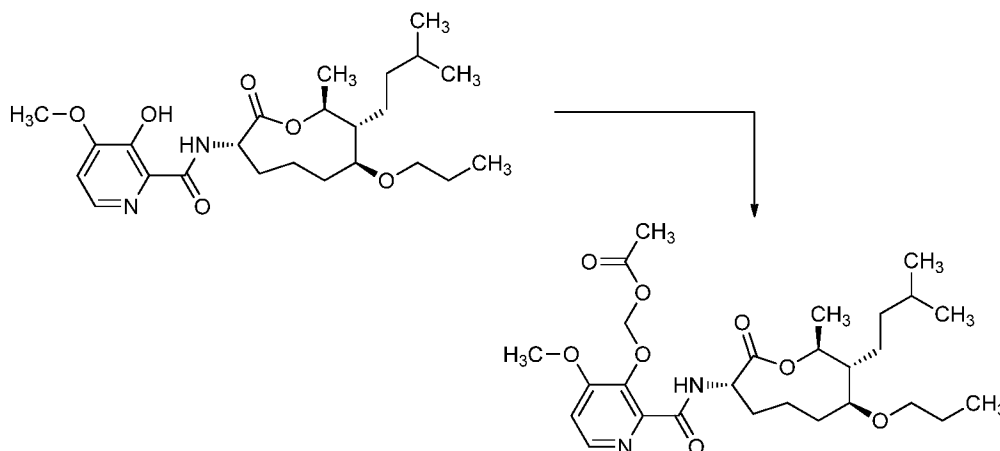
[00111] To a solution of *tert*-butyl ((3*S*,7*S*,8*S*,9*S*)-8-isopentyl-9-methyl-2-oxo-7-propoxyoxonan-3-yl)carbamate (330 mg, 0.826 mmol) in DCM (3 mL) was added a solution of HCl in dioxane (2.07 mL, 8.26 mmol, 4M) under N₂ and the resulting solution was stirred at room temperature for 2 h. The solvent was removed under a stream of N₂, which afforded a white solid. This solid was triturated with Et₂O (3 x 3 mL) and the resulting powder was dried under high vacuum for 1 h to give (3*S*,7*S*,8*S*,9*S*)-8-isopentyl-9-methyl-2-oxo-7-propoxyoxonan-3-aminium chloride (**59**): ESIMS *m/z* 300 ([M+H]⁺).

Step 2

[00112] To the reaction flask containing the hydrochloride salt as a solution in DCM (3 mL) were added PyBop (473 mg, 0.908 mmol) and 3-hydroxy-4-methoxypicolinic acid (154 mg, 0.908 mmol), followed by *N*-ethyl-*N*-isopropylpropan-2-amine (475 microliters (μL), 2.73 mmol). After 10 min, everything had solubilized and stirring was continued for 3 h (turned pink). The reaction was treated with Celite[®] (2 scoopula tip-fulls) and the solvent was removed under reduced pressure. The resulting adsorbed material was purified using flash column chromatography (40 g SiO₂, 0→100% EtOAc/hexanes) to provide the title compound (250 mg, 0.555 mmol, 67%) as a white powder: mp: 45 – 49 °C; IR (thin film): 3368, 2954, 2872, 1739, 1651, 1529 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 12.14 (d, *J* = 0.6 Hz, 1H), 8.48 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 5.2 Hz, 1H), 6.87 (d, *J* = 5.3 Hz, 1H), 4.76 (dq, *J* = 10.1, 6.3 Hz, 1H), 4.59 (ddd, *J* = 10.7, 8.2, 7.3 Hz, 1H), 3.94 (s, 3H), 3.52 (app dt, *J* = 8.9, 6.4 Hz, 1H), 3.32 – 3.23 (m, 1H), 3.16 (app dt, *J* = 8.9, 6.6 Hz, 1H),

2.44 – 2.31 (m, 1H), 2.25 – 2.10 (m, 1H), 1.98 – 1.86 (m, 1H), 1.86 – 1.72 (m, 1H), 1.67 – 1.36 (m, 7H), 1.34 (d, $J = 6.3$ Hz, 3H), 1.27 – 1.03 (m, 2H), 0.98 – 0.83 (m, 10H); HRMS–ESI m/z $[M+H]^+$ calcd for: $C_{24}H_{39}N_2O_6$, 451.2803; found, 451.2804.

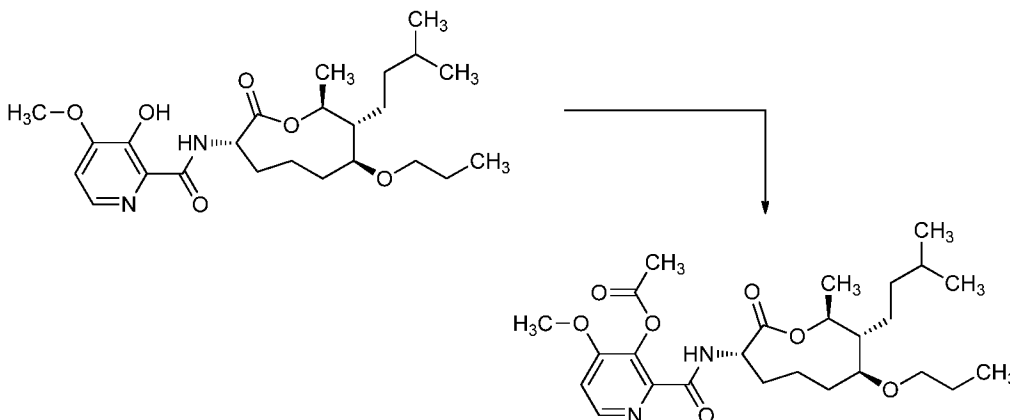
[00113] Example 7: Preparation of ((2-(((3*S*,7*S*,8*S*,9*S*)-8-isopentyl-9-methyl-2-oxo-7-propoxyoxonan-3-yl)carbamoyl)-4-methoxypyridin-3-yl)oxy)methyl acetate (**25**):



[00114] To a solution of 3-hydroxy-*N*-((3*S*,7*S*,8*S*,9*S*)-8-isopentyl-9-methyl-2-oxo-7-propoxyoxonan-3-yl)-4-methoxypyridin-3-yl)carbamamide (125 mg, 0.277 mmol) and K_2CO_3 (77 mg, 0.555 mmol) in acetone (2.77 mL) was added bromomethyl acetate (54.4 μ L, 0.555 mmol). The reaction was sealed, heated to 50 °C, stirred at this temperature for 6 h, and then cooled to room temperature. The mixture was diluted with DCM (4 mL) and treated with Celite[®] (3 scoopula tip-fulls). The solvent was removed under reduced pressure and the resulting adsorbed material was directly loaded onto a column and purified using flash column chromatography (24 g SiO_2 , 0 \rightarrow 100% EtOAc/hexanes) to afford the title compound (112 mg, 0.214 mmol, 77%) as a sticky, slightly yellow oil: IR (thin film): 3378, 2954, 2872, 1740, 1677, 1504, 1202 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, $J = 8.1$ Hz, 1H), 8.28 (d, $J = 5.4$ Hz, 1H), 6.95 (d, $J = 5.4$ Hz, 1H), 5.74 (s, 2H), 4.74 (dq, $J = 10.1, 6.3$ Hz, 1H), 4.61 (app dt, $J = 10.7, 7.6$ Hz, 1H), 3.91 (s, 3H), 3.52 (app dt, $J = 8.9, 6.4$ Hz, 1H), 3.31 – 3.22 (m, 1H), 3.15 (app dt, $J = 8.9, 6.6$ Hz, 1H), 2.45 – 2.33 (m, 1H), 2.21 – 2.09 (m, 1H), 2.07 (s, 3H), 1.98 – 1.86 (m, 1H), 1.85 – 1.70 (m, 1H), 1.67 – 1.28 (m, 10H), 1.24 –

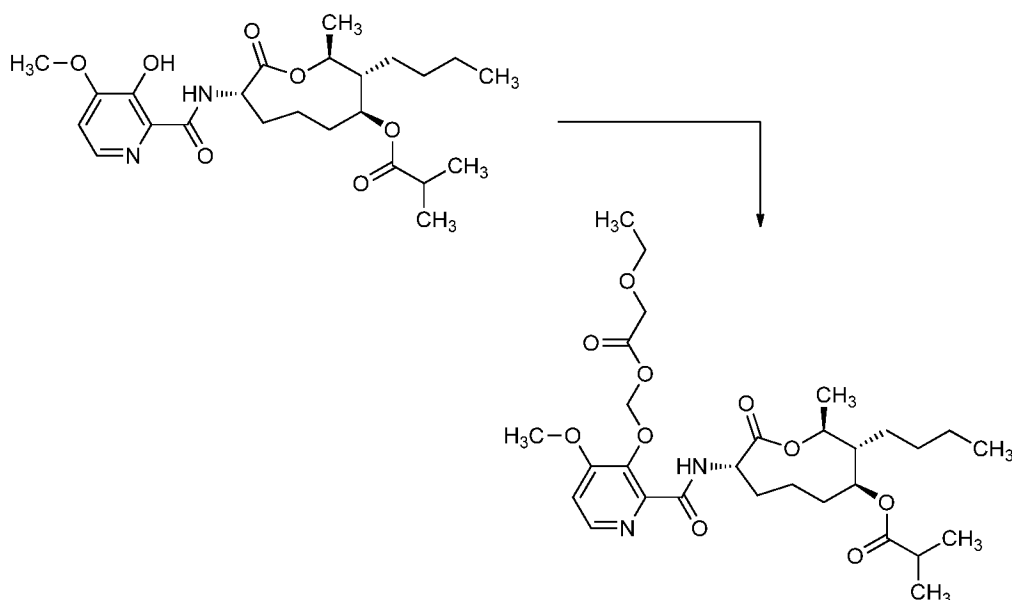
1.03 (m, 2H), 0.97 – 0.84 (m, 10H); HRMS–ESI m/z $[M+Na]^+$ calcd for: $C_{27}H_{42}N_2NaO_8$, 545.2833; found, 545.2853.

[00115] Example 8: Preparation of 2-(((3*S*,7*S*,8*S*,9*S*)-8-isopentyl-9-methyl-2-oxo-7-propoxyoxonan-3-yl)carbamoyl)-4-methoxypyridin-3-yl acetate (**74**):



[00116] To a solution of 3-hydroxy-*N*-(((3*S*,7*S*,8*S*,9*S*)-8-isopentyl-9-methyl-2-oxo-7-propoxyoxonan-3-yl)-4-methoxypicolinamide (75 mg, 0.166 mmol) were added TEA (34.8 μ L, 0.250 mmol) and acetyl chloride (17.8 μ L, 0.250 mmol) in DCM (0.832 mL). The reaction was stirred at room temperature for 4 h and then treated with Celite[®] (3 scoopula tip-fulls). The solvent was removed under reduced pressure and the resulting adsorbed material was directly loaded onto a column and purified using flash column chromatography (24 g SiO₂, 0 \rightarrow 100% EtOAc/hexanes) to afford the title compound (74 mg, 0.150 mmol, 90%) as a white powder (hygroscopic): IR (thin film): 3383, 2953, 2871, 1772, 1737, 1678, 1506, 1197, 1173 cm^{-1} ; ¹H NMR (400 MHz, CDCl₃) δ 8.53 (d, J = 8.2 Hz, 1H), 8.33 (d, J = 5.4 Hz, 1H), 7.00 (d, J = 5.4 Hz, 1H), 4.74 (dq, J = 9.9, 6.3 Hz, 1H), 4.65 – 4.53 (m, 1H), 3.90 (s, 3H), 3.52 (app dt, J = 8.9, 6.4 Hz, 1H), 3.31 – 3.22 (m, 1H), 3.15 (app dt, J = 8.9, 6.6 Hz, 1H), 2.43 – 2.30 (m, 4H), 2.22 – 2.07 (m, 1H), 1.96 – 1.84 (m, 1H), 1.83 – 1.69 (m, 1H), 1.68 – 0.98 (m, 12H), 0.96 – 0.84 (m, 10H); HRMS–ESI m/z $[M+H]^+$ calcd for: $C_{26}H_{41}N_2O_7$, 493.2908; found 493.2936.

[00117] Example 9: Preparation of (2*S*,3*S*,4*S*,8*S*)-3-butyl-8-(3-((2-ethoxyacetoxy)methoxy)-4-methoxypicolinamido)-2-methyl-9-oxooxonan-4-yl isobutyrate (**71**):



[00118] To a solution of (2*S*,3*S*,4*S*,8*S*)-3-butyl-8-(3-hydroxy-4-methoxypicolinamido)-2-methyl-9-oxooxonan-4-yl isobutyrate (45 mg, 0.097 mmol), Na₂CO₃ (20.5 mg, 0.194 mmol), and NaI (22.2 mg, 0.145 mmol) in acetone (2.0 mL) was added chloromethyl 2-ethoxyacetate (22.2 mg, 0.145 mmol). The sealed reaction was warmed to 45 °C and stirred for 16 h. The reaction was cooled to room temperature and concentrated under a stream of N₂. The resulting residue was purified by flash column chromatography (4g SiO₂, 0→100% EtOAc/hexanes) to afford the title compound (23.2 mg, 0.040 mmol, 41 %) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, *J* = 8.1 Hz, 1H), 8.28 (d, *J* = 5.4 Hz, 1H), 6.95 (d, *J* = 5.4 Hz, 1H), 5.82 (s, 2H), 4.90 (ddd, *J* = 9.1, 5.6, 1.9 Hz, 1H), 4.83 (dq, *J* = 10.0, 6.4 Hz, 1H), 4.62 (ddd, *J* = 10.7, 8.1, 7.1 Hz, 1H), 4.10 (s, 2H), 3.90 (s, 3H), 3.59 (q, *J* = 7.0 Hz, 2H), 2.53 (hept, *J* = 7.0 Hz, 1H), 2.36 (dt, *J* = 13.7, 6.8 Hz, 1H), 2.21 – 2.03 (m, 2H), 1.87 – 1.76 (m, 1H), 1.60 – 1.51 (m, 1H), 1.41 – 1.32 (m, 5H), 1.32 – 1.25 (m, 3H), 1.23 (t, *J* = 7.0 Hz, 4H), 1.17 (dd, *J* = 7.0, 0.8 Hz, 7H), 1.05 (ddt, *J* = 15.9, 7.5, 2.2 Hz, 1H), 0.88 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 176.48, 172.33, 170.05, 162.94, 160.18, 145.80, 143.89, 142.32, 109.69, 89.56, 74.52, 73.29, 67.80, 67.19, 56.22, 51.32, 45.49, 34.29, 32.91, 30.88, 28.17, 27.45, 23.30, 19.22, 19.09, 18.94, 18.14, 15.01, 13.88; HRMS–ESI *m/z* [M+H]⁺ calcd for: C₂₉H₄₄N₂O₁₀, 581.3069; found 581.3073.

[00119] Example A: Evaluation of Fungicidal Activity: Leaf Blotch of Wheat (*Mycosphaerella graminicola*; Anamorph: *Septoria tritici*; Bayer code SEPTTR):

[00120] Technical grades of materials were dissolved in acetone, which were then mixed with nine volumes of water containing 110 ppm Triton X-100. The fungicide solutions were applied onto wheat seedlings using an automated booth sprayer to run-off. All sprayed plants were allowed to air dry prior to further handling. All fungicides were evaluated using the aforementioned method for their activity vs. all target diseases. Wheat leaf blotch and brown rust activity were also evaluated using track spray applications, in which case the fungicides were formulated as EC formulations, containing 0.1% Trycol 5941 in the spray solutions.

[00121] Wheat plants (variety Yuma) were grown from seed in a greenhouse in 50% mineral soil/50% soil-less Metro mix until the first leaf was fully emerged, with 7-10 seedlings per pot. These plants were inoculated with an aqueous spore suspension of *Septoria tritici* either prior to or after fungicide treatments. After inoculation the plants were kept in 100% relative humidity (one day in a dark dew chamber followed by two to three days in a lighted dew chamber at 20 °C) to permit spores to germinate and infect the leaf. The plants were then transferred to a greenhouse set at 20 °C for disease to develop. When disease symptoms were fully expressed on the 1st leaves of untreated plants, infection levels were assessed on a scale of 0 to 100 percent disease severity. Percent disease control was calculated using the ratio of disease severity on treated plants relative to untreated plants.

[00122] Example B: Evaluation of Fungicidal Activity: Wheat Brown Rust (*Puccinia triticina*; Synonym: *Puccinia recondita f. sp. tritici*; Bayer code PUCCRT):

[00123] Wheat plants (variety Yuma) were grown from seed in a greenhouse in 50% mineral soil/50% soil-less Metro mix until the first leaf was fully emerged, with 7-10 seedlings per pot. These plants were inoculated with an aqueous spore suspension of *Puccinia triticina* either prior to or after fungicide treatments. After inoculation the plants were kept in a dark dew room at 22 °C with 100% relative humidity overnight to permit spores to germinate and infect the leaf. The plants were then transferred to a greenhouse set at 24 °C for disease to develop. Fungicide formulation, application and disease assessment followed the procedures as described in the Example A.

[00124] Example C: Evaluation of Fungicidal Activity: Wheat Glume Blotch (*Leptosphaeria nodorum*; Bayer code LEPTNO):

[00125] Wheat plants (variety Yuma) were grown from seed in a greenhouse in 50% mineral soil/50% soil-less Metro mix until the first leaf was fully emerged, with 7-10 seedlings per pot. These plants were inoculated with an aqueous spore suspension of *Leptosphaeria nodorum* 24 hr after fungicide treatments. After inoculation the plants were kept in 100% relative humidity (one day in a dark dew chamber followed by two days in a lighted dew chamber at 20 °C) to permit spores to germinate and infect the leaf. The plants were then transferred to a greenhouse set at 20 °C for disease to develop. Fungicide formulation, application and disease assessment followed the procedures as described in the Example A.

[00126] Example D: Evaluation of Fungicidal Activity: Apple Scab (*Venturia inaequalis*; Bayer code VENTIN):

[00127] Apple seedlings (variety McIntosh) were grown in soil-less Metro mix, with one plant per pot. Seedlings with two expanding young leaves at the top (older leaves at bottom of the plants were trimmed) were used in the test. Plants were inoculated with a spore suspension of *Venturia inaequalis* 24 hr after fungicide treatment and kept in a 22 °C dew chamber with 100% RH for 48 hr, and then moved to a greenhouse set at 20 °C for disease to develop. Fungicide formulation, application and disease assessment on the sprayed leaves followed the procedures as described in the Example A.

[00128] Example E: Evaluation of Fungicidal Activity: Grape Powdery Mildew (*Uncinula necator*; Bayer code UNCINE):

[00129] Grape seedlings (variety Carignane) were grown in soil-less Metro mix, with one plant per pot, and used in the test when approximately one month old. Plants were inoculated 24 hr after fungicide treatment by shaking spores from infected leaves over test plants. Plants were maintained in a greenhouse set at 20 °C until disease was fully developed. Fungicide formulation, application and disease assessment on the sprayed leaves followed the procedures as described in the Example A.

[00130] Example F: Evaluation of Fungicidal Activity: Powdery Mildew of Cucumber (*Erysiphe cichoracearum*; Bayer code ERYSCI):

[00131] Cucumber seedlings (variety Bush Pickle) were grown in soil-less Metro mix, with one plant per pot, and used in the test when 12 to 14 days old. Plants were inoculated with a spore suspension 24 hr following fungicide treatments. After inoculation the plants remained in the greenhouse set at 20 °C until disease was fully expressed. Fungicide formulation, application and disease assessment on the sprayed leaves followed the procedures as described in the Example A.

[00132] Example G: Evaluation of Fungicidal Activity: Leaf Spot of Sugar Beets (*Cercospora beticola*; Bayer code CERCBE):

[00133] Sugar beet plants (variety HH88) were grown in soil-less Metro mix and trimmed regularly to maintain a uniform plant size prior to test. Plants were inoculated with a spore suspension 24 hr after fungicide treatments. Inoculated plants were kept in a dew chamber at 22 °C for 48 hr then incubated in a greenhouse set at 24 °C under a clear plastic hood with bottom ventilation until disease symptoms were fully expressed. Fungicide formulation, application and disease assessment on the sprayed leaves followed the procedures as described in the Example A.

[00134] Example H: Evaluation of Fungicidal Activity: Asian Soybean Rust (*Phakopsora pachyrhizi*; Bayer code PHAKPA):

[00135] Technical grades of materials were dissolved in acetone, which were then mixed with nine volumes of water containing 0.011% Tween 20. The fungicide solutions were applied onto soybean seedlings using an automated booth sprayer to run-off. All sprayed plants were allowed to air dry prior to further handling.

[00136] Soybean plants (variety Williams 82) were grown in soil-less Metro mix, with one plant per pot. Two weeks old seedlings were used for testing. Plants were inoculated either 3 days prior to or 1 day after fungicide treatments. Plants were incubated for 24 h in a dark dew room at 22 °C and 100 % RH then transferred to a growth room at 23 °C for disease to develop. Disease severity was assessed on the sprayed leaves.

[00137] Example I: Evaluation of Fungicidal Activity: Wheat Powdery Mildew (*Blumeria graminis f.sp. tritici*; Synonym: *Erysiphe graminis f.sp. tritici*; Bayer code ERYSGT):

[00138] Wheat plants (variety Yuma) were grown from seed in a greenhouse in 50% mineral soil/50% soil-less Metro mix until the first leaf was fully emerged, with 7-10 seedlings per pot. These plants were inoculated by dusting with infected stock plants 24 hr after fungicide treatments. After inoculation the plants were kept in a greenhouse set at 20 °C for disease to develop. Fungicide formulation, application and disease assessment on the sprayed leaves followed the procedures as described in the Example A.

[00139] Example J: Evaluation of Fungicidal Activity: Barley Powdery Mildew (*Blumeria graminis f.sp. hordei*; Synonym: *Erysiphe graminis f.sp. hordei*; Bayer code ERYSGH):

[00140] Barley seedlings (variety Harrington) were propagated in soil-less Metro mix, with each pot having 8 to 12 plants, and used in the test when first leaf was fully emerged. Test plants were inoculated by dusting with infected stock plants 24 hr after fungicide treatments. After inoculation the plants were kept in a greenhouse set at 20 °C for disease to develop. Fungicide formulation, application and disease assessment on the sprayed leaves followed the procedures as described in the Example A.

[00141] Example K: Evaluation of Fungicidal Activity: Barley Scald (*Rhynchosporium secalis*; Bayer code RHYNSE):

[00142] Barley seedlings (variety Harrington) were propagated in soil-less Metro mix, with each pot having 8 to 12 plants, and used in the test when first leaf was fully emerged. Test plants were inoculated by an aqueous spore suspension of *Rhynchosporium secalis* 24 hr after fungicide treatments. After inoculation the plants were kept in a dew room at 20 °C with 100% relative humidity for 48 hr. The plants were then transferred to a greenhouse set at 20 °C for disease to develop. Fungicide formulation, application and disease assessment on the sprayed leaves followed the procedures as described in the Example A.

[00143] Example L: Evaluation of Fungicidal Activity: Rice Blast (*Magnaporthe grisea*; Anamorph: *Pyricularia oryzae*; Bayer code PYRIOR):

[00144] Rice seedlings (variety Japonica) were propagated in soil-less Metro mix, with each pot having 8 to 14 plants, and used in the test when 12 to 14 days old. Test plants were inoculated with an aqueous spore suspension of *Pyricularia oryzae* 24 hr after fungicide treatments. After inoculation the plants were kept in a dew room at 22 °C with 100% relative humidity for 48 hr to permit spores to germinate and infect the leaf. The plants were then transferred to a greenhouse set at 24 °C for disease to develop. Fungicide formulation, application and disease assessment on the sprayed leaves followed the procedures as described in the Example A.

[00145] Example M: Evaluation of Fungicidal Activity: Tomato Early Blight (*Alternaria solani*; Bayer code ALTESO):

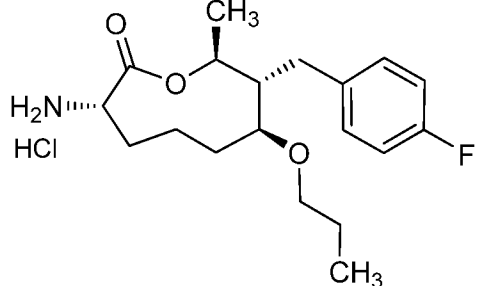
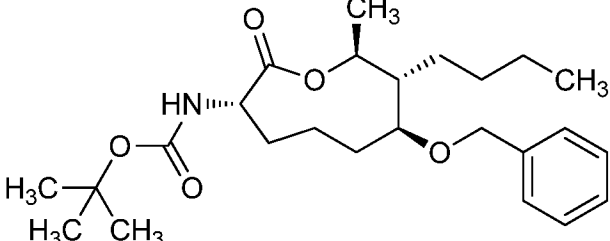
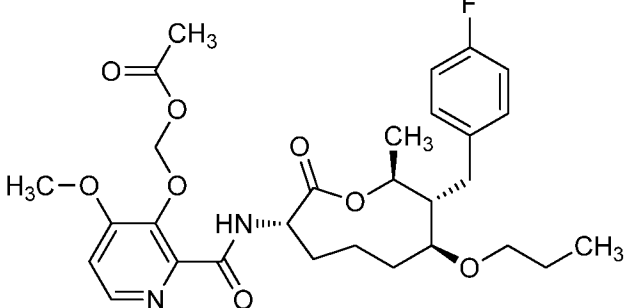
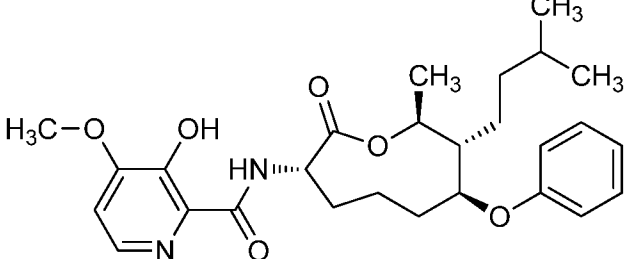
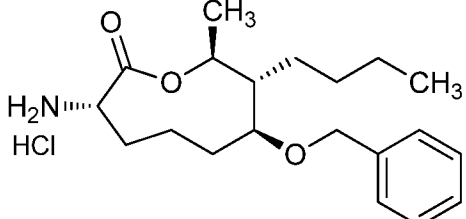
[00146] Tomato plants (variety Outdoor girl) were propagated in soil-less Metro mix, with each pot having one plant, and used when 12 to 14 days old. Test plants were inoculated with an aqueous spore suspension of *Alternaria solani* 24 hr after fungicide treatments. After inoculation the plants were kept in 100% relative humidity (one day in a dark dew chamber followed by two to three days in a lighted dew chamber at 20 °C) to permit spores to germinate and infect the leaf. The plants were then transferred to a growth room at 22 °C for disease to develop. Fungicide formulation, application and disease assessment on the sprayed leaves followed the procedures as described in the Example A.

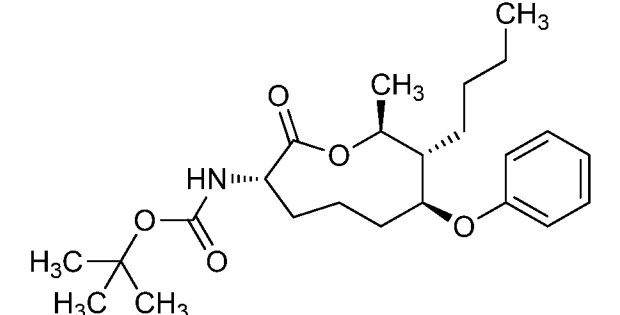
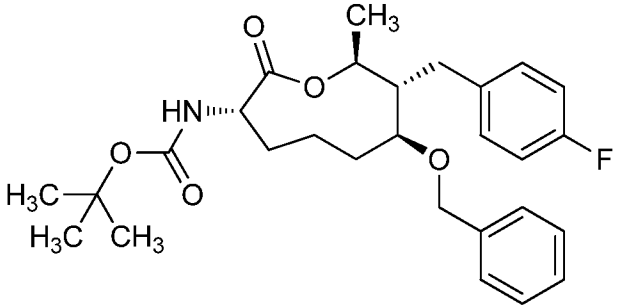
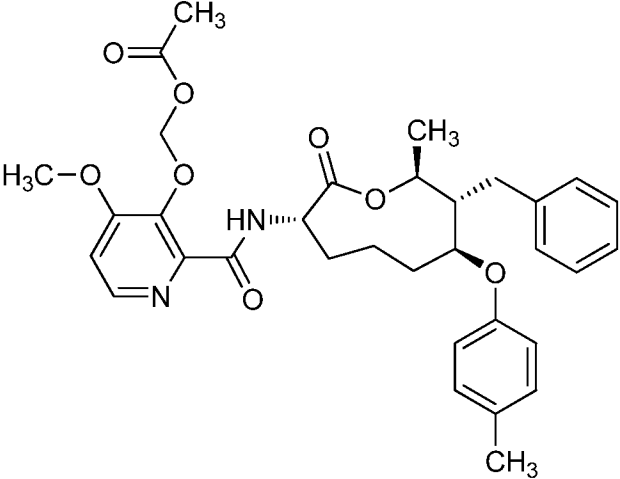
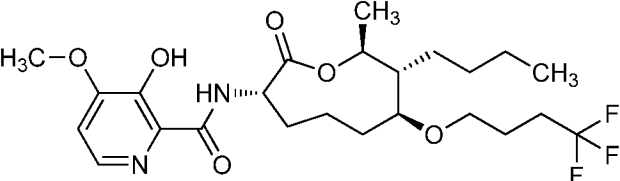
[00147] Example N: Evaluation of Fungicidal Activity: Cucumber Anthracnose (*Glomerella lagenarium*; Anamorph: *Colletotrichum lagenarium*; Bayer code COLLLA):

[00148] Cucumber seedlings (variety Bush Pickle) were propagated in soil-less Metro mix, with each pot having one plant, and used in the test when 12 to 14 days old. Test plants were inoculated with an aqueous spore suspension of *Colletotrichum lagenarium* 24 hr after fungicide treatments. After inoculation the plants were kept in a dew room at 22 °C with 100% relative humidity for 48 hr to permit spores to germinate and infect the leaf. The plants were then transferred to a growth room set at 22 °C for disease to develop. Fungicide formulation, application and disease assessment on the sprayed leaves followed the procedures as described in the Example A.

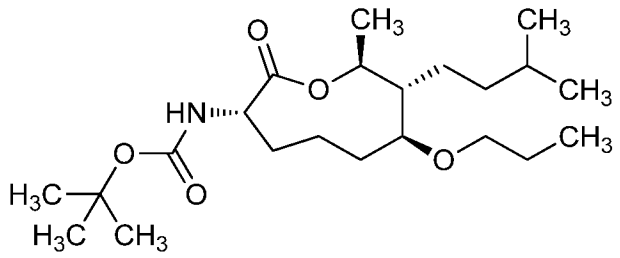
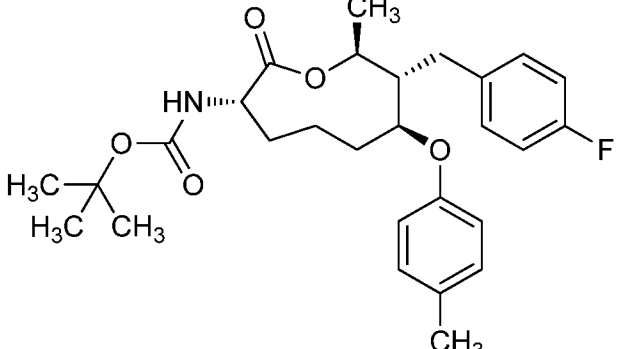
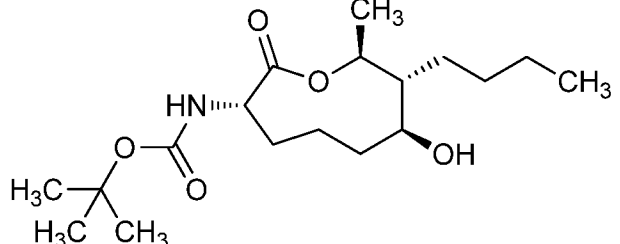
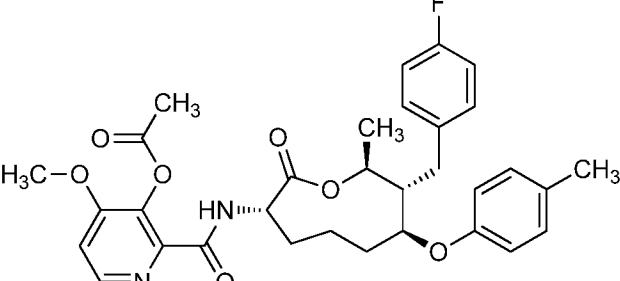
Table 1. Compound Structure and Appearance

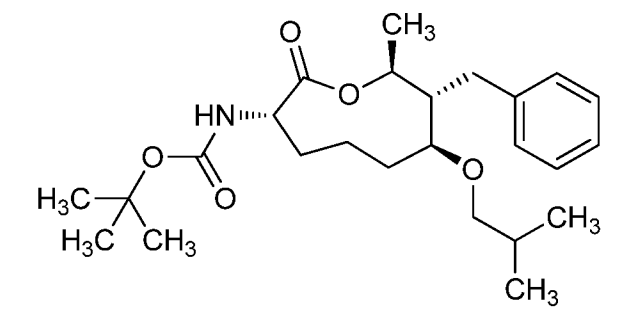
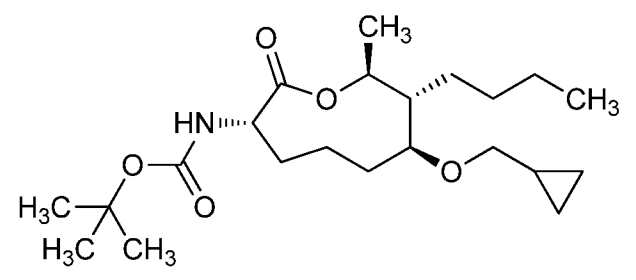
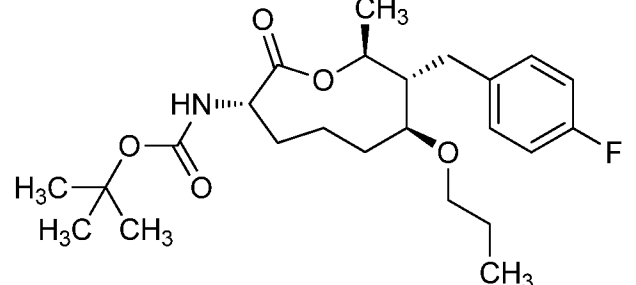
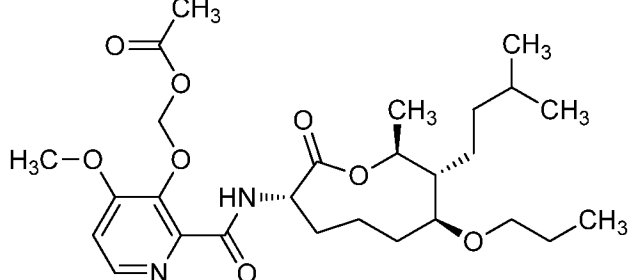
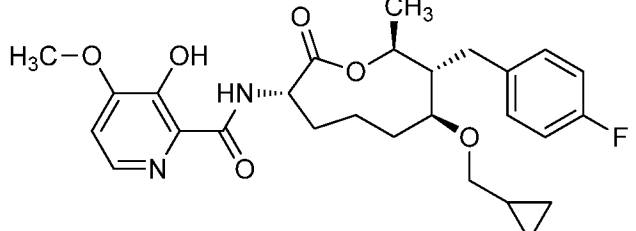
Cmpd. No.	Structure	Prepared According To Example	Appearance
1		Example 7.	Sticky White Solid
2		Example 6, Step 2.	White Foam
3		Example 1, Steps 1,3,6,7,8; Example 2, Step 1; Example 3, Steps 1,2,3,5; Example 4.	Clear Oil
4		Example 5, Step 1.	White Solid

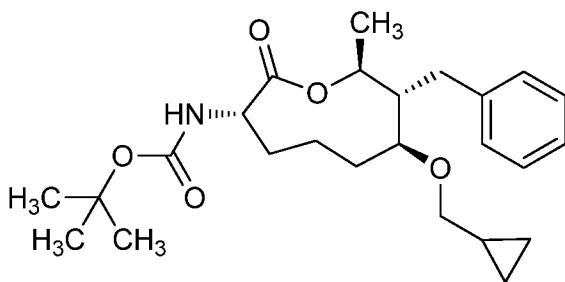
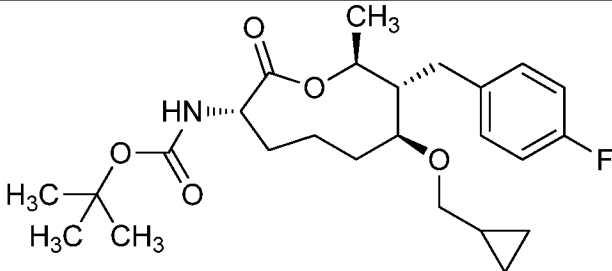
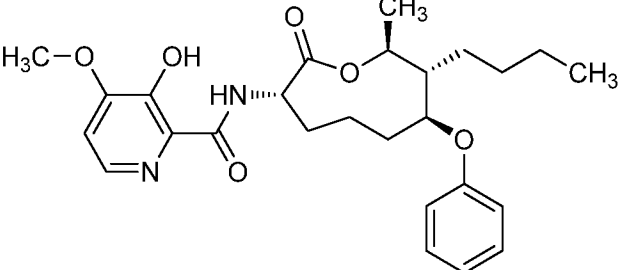
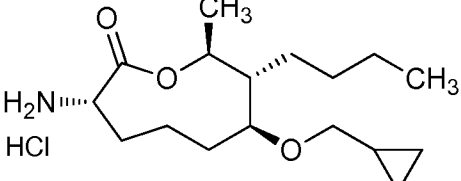
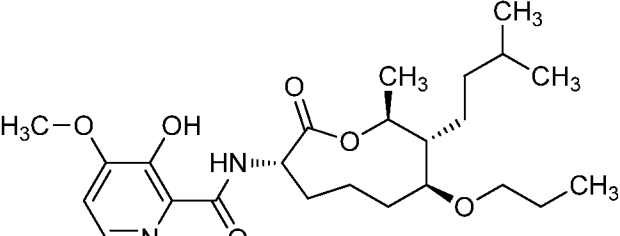
Cmpd. No.	Structure	Prepared According To Example	Appearance
5		Example 6, Step 1.	White Solid
6		Example 1, Steps 1-5; Example 2, Step 3; Example 3, Steps 1-4; Example 4.	Colorless Oil
7		Example 7.	White Foam
8		Example 6, Step 2.	White Powder
9		Example 6, Step 1.	White Solid

Cmpd. No.	Structure	Prepared According To Example	Appearance
10		Example 1, Steps 1-5; Example 2, Step 1; Example 3, Steps 1-3,5; Example 4.	Colorless Oil
11		Example 1, Steps 1, 3-5; Example 2, Step 3; Example 3, Steps 1-4; Example 4.	White Foam
12		Example 7.	Clear Oil
13		Example 6, Step 2.	White Solid

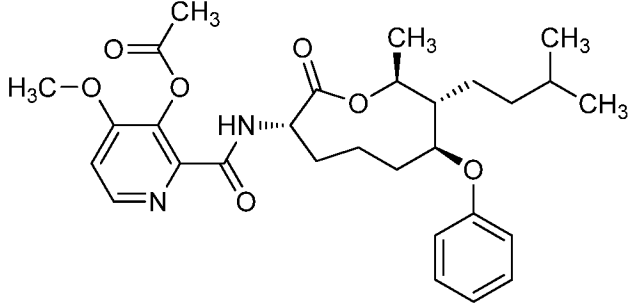
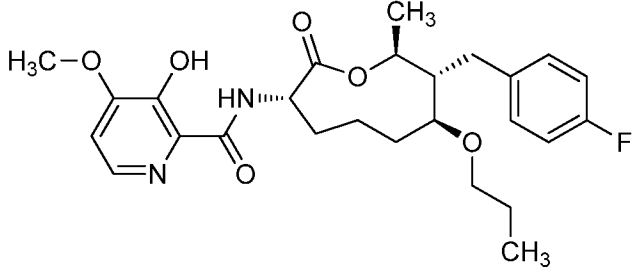
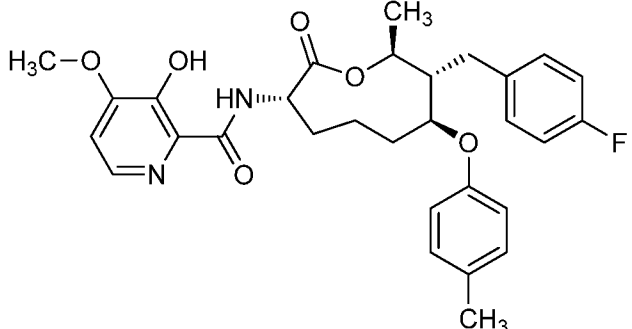
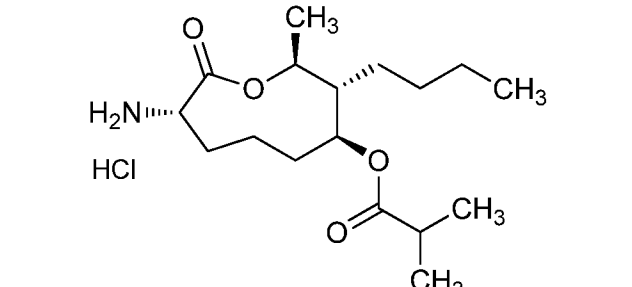
Cmpd. No.	Structure	Prepared According To Example	Appearance
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15		Example 7.	Colorless Oil
16		Example 6, Step 1.	White Powder
17		Example 8.	White Powder

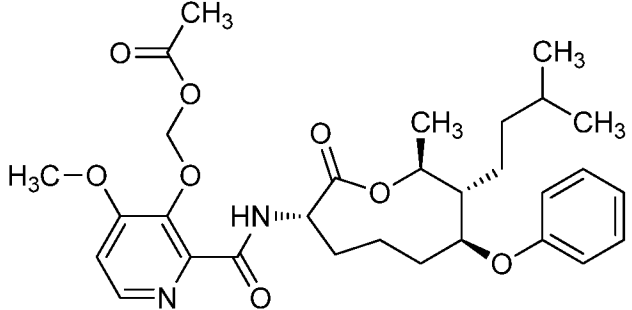
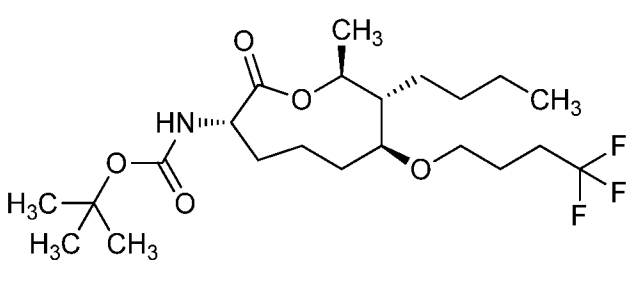
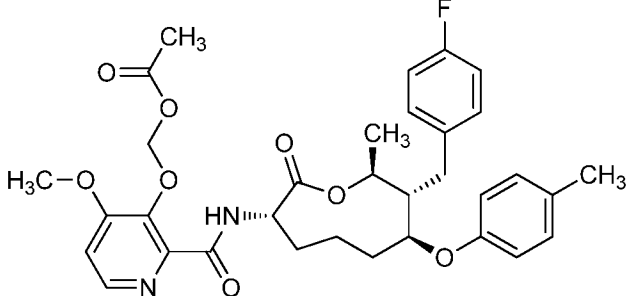
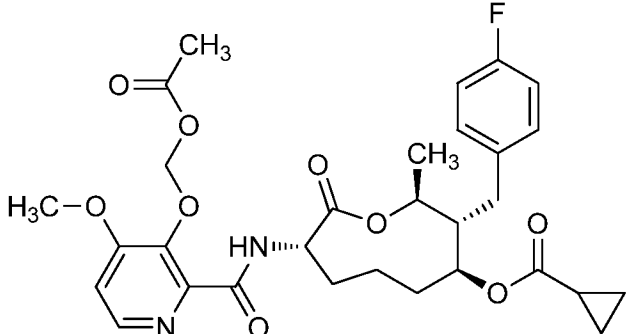
Cmpd. No.	Structure	Prepared According To Example	Appearance
18		Example 1, Steps 1-5; Example 2, Step 2; Example 3, Steps 1-3, 5; Example 4.	Colorless Oil
19		Example 1, Steps 1, 3-5; Example 2, Step 1; Example 3, Steps 1-4; Example 4.	Colorless Oil
20		Example 5, Step 1.	Colorless Oil
21		Example 8.	White Foam

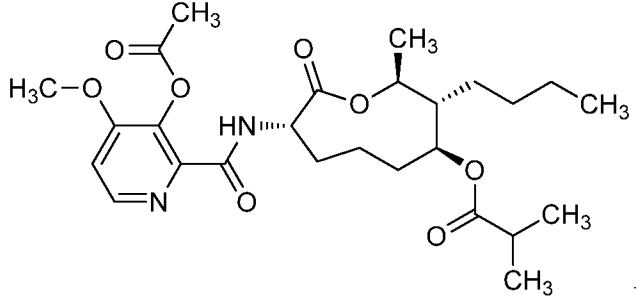
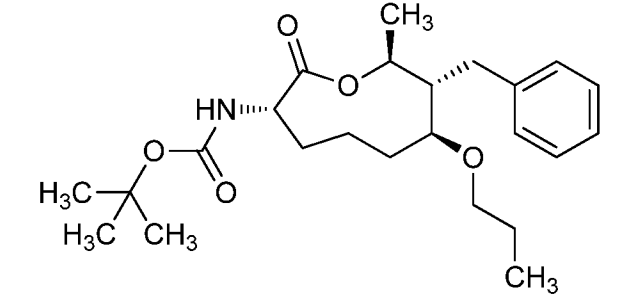
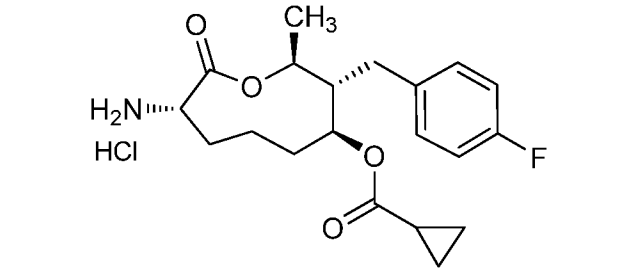
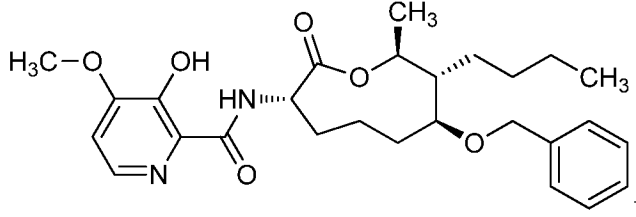
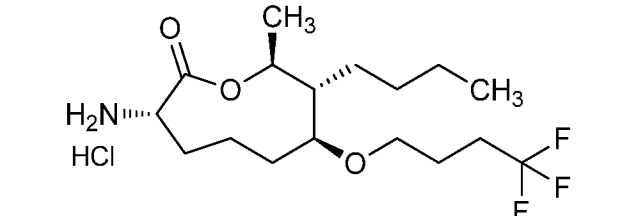
Cmpd. No.	Structure	Prepared According To Example	Appearance
22		Example 1, Steps 1,3,6,7,8; Example 2, Step 2; Example 3, Steps 1,2,3,5; Example 4.	Clear Oil
23		Example 1, Steps 1-5; Example 2, Step 2; Example 3, Steps 1-3,5; Example 4.	Colorless Oil
24		Example 1, Steps 1, 3-5; Example 2, Step 2; Example 3, Steps 1-4; Example 4.	Pale Yellow Oil
25		Example 7.	Sticky Slightly Yellow Oil
26		Example 6, Step 2.	White Solid

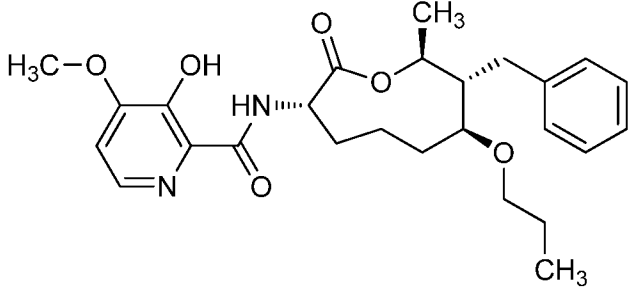
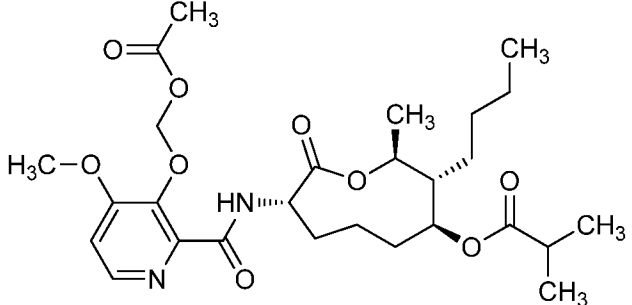
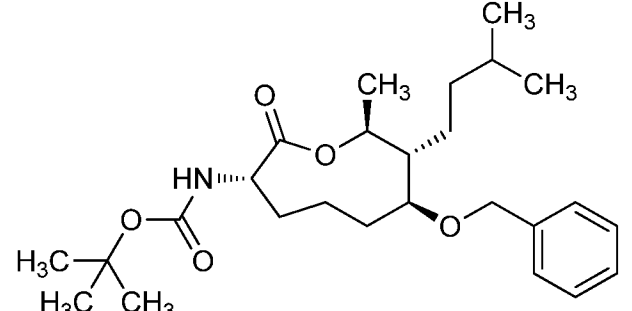
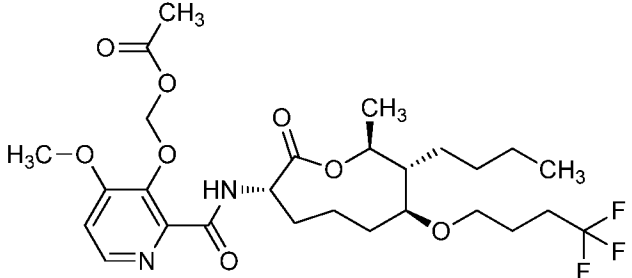
Cmpd. No.	Structure	Prepared According To Example	Appearance
27		Example 1, Steps 1,3,6,7,8; Example 2, Step 3; Example 3, Steps 1,2,3,5; Example 4.	Clear Oil
28		Example 1, Steps 1, 3-5; Example 2, Step 3; Example 3, Steps 1-4; Example 4.	Pale Yellow Oil
29		Example 6, Step 2.	White Solid
30		Example 6, Step 1.	White Solid
31		Example 6, Step 2.	White Powder

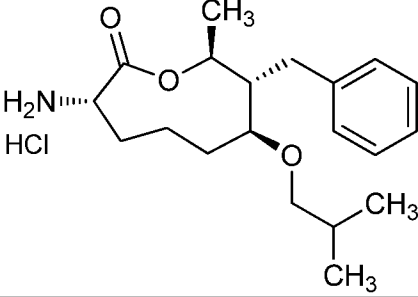
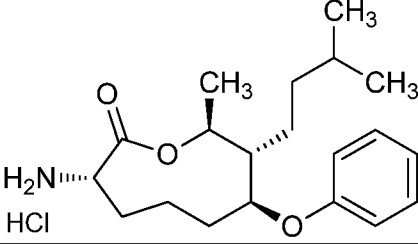
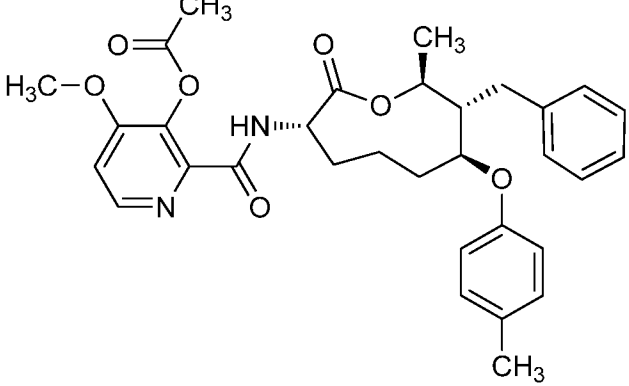
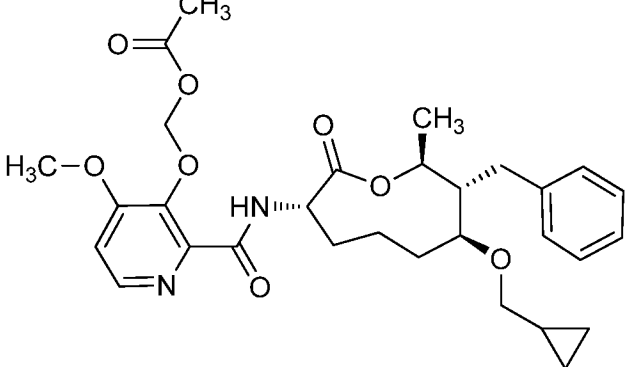
Cmpd. No.	Structure	Prepared According To Example	Appearance
32		Example 6, Step 2.	White Solid
33		Example 7.	White Foam
34		Example 6, Step 1.	White Powder
35		Example 9.	White Foam

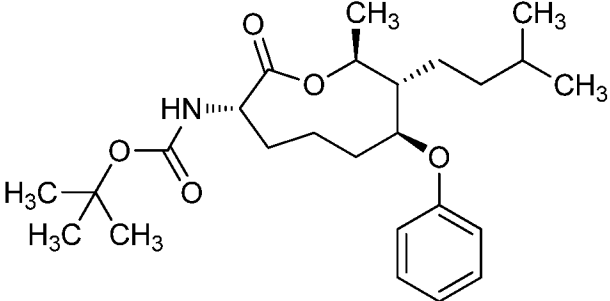
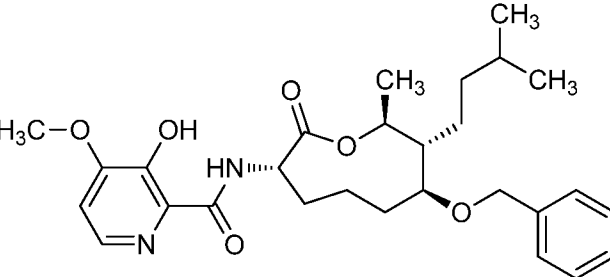
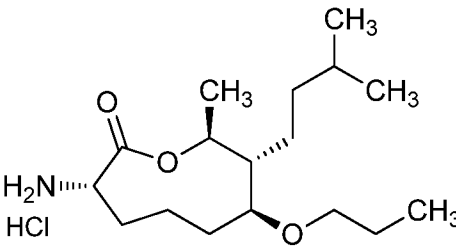
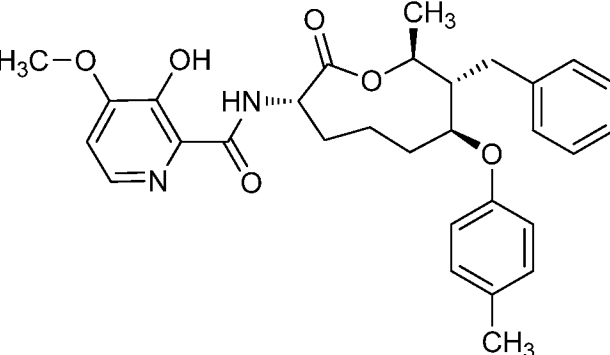
Cmpd. No.	Structure	Prepared According To Example	Appearance
36		Example 8.	White Powder
37		Example 6, Step 2.	White Solid
38		Example 6, Step 2.	White Solid
39		Example 6, Step 1.	White Solid

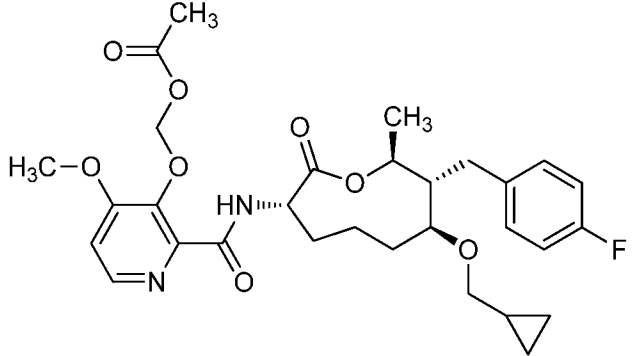
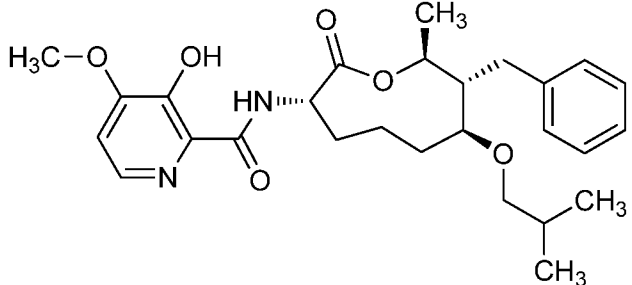
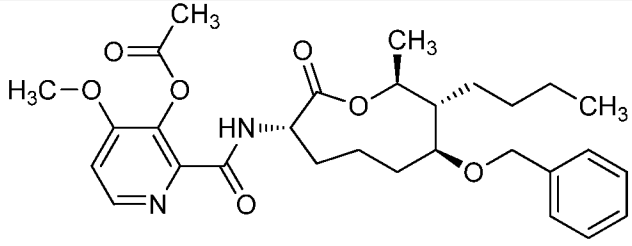
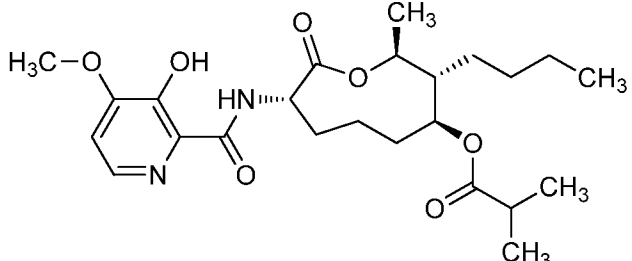
Cmpd. No.	Structure	Prepared According To Example	Appearance
40		Example 7.	White Powder
41		Example 1, Steps 1-5; Example 2, Step 2; Example 3, Steps 1-3,5; Example 4.	Slight Yellow Oil
42		Example 7.	White Foam
43		Example 7.	White Foam

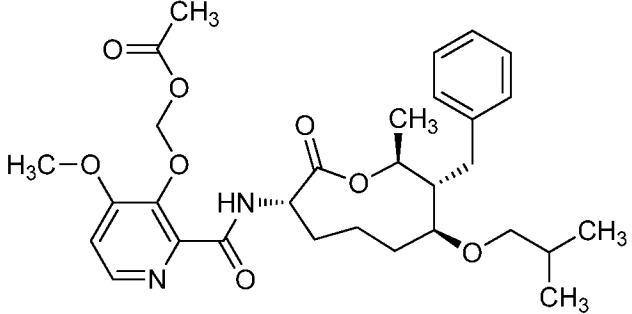
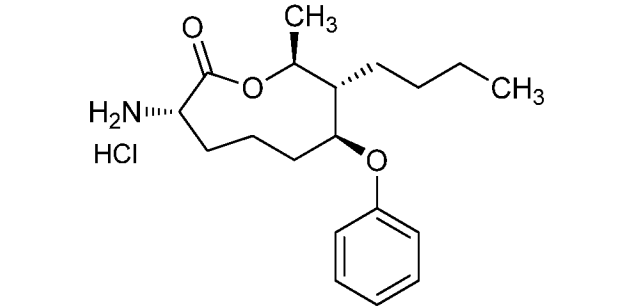
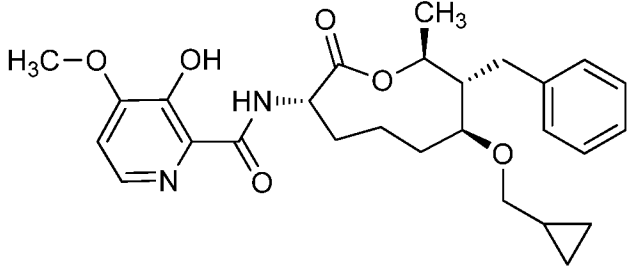
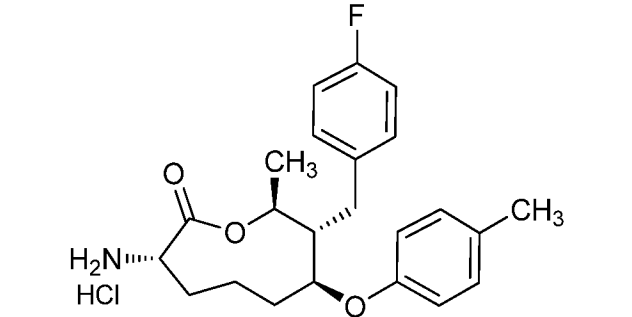
Cmpd. No.	Structure	Prepared According To Example	Appearance
44		Example 8.	Yellow Foam
45		Example 1, Steps 1, 3–5; Example 2, Step 2; Example 3, Steps 1–3, 5; Example 4.	Colorless Oil
46		Example 6, Step 1.	White Solid
47		Example 6, Step 2.	Clear Glass
48		Example 6, Step 1.	White Solid

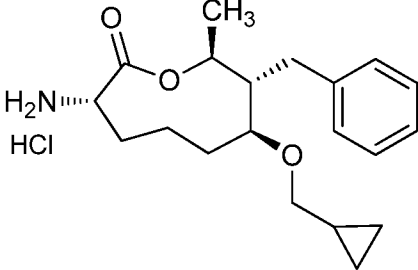
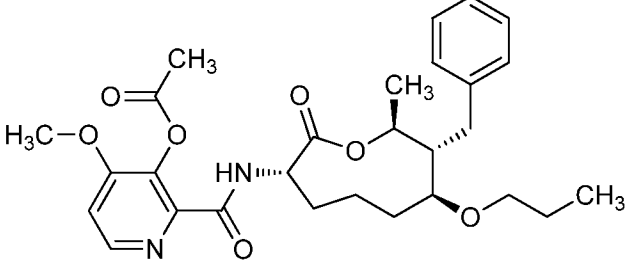
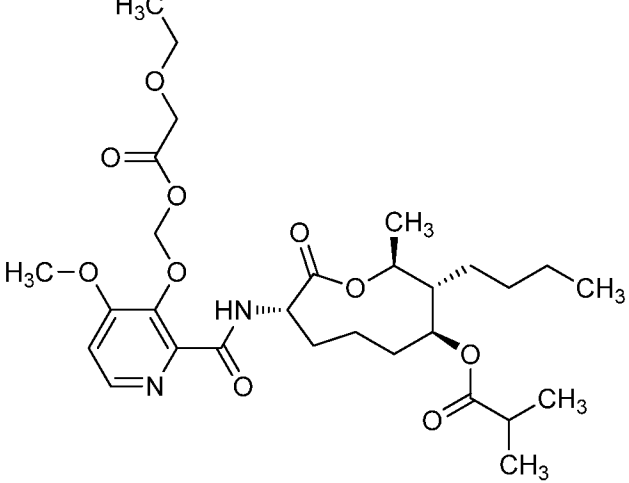
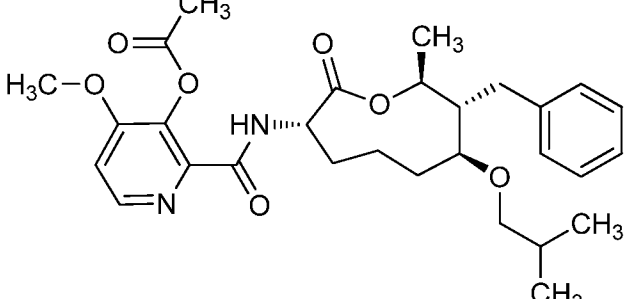
Cmpd. No.	Structure	Prepared According To Example	Appearance
49		Example 6, Step 2.	White Powder
50		Example 7.	Colorless Oil
51		Example 1, Steps 1-5; Example 2, Step 3; Example 3, Steps 1-4; Example 4.	White Powder
52		Example 7.	Colorless Glass

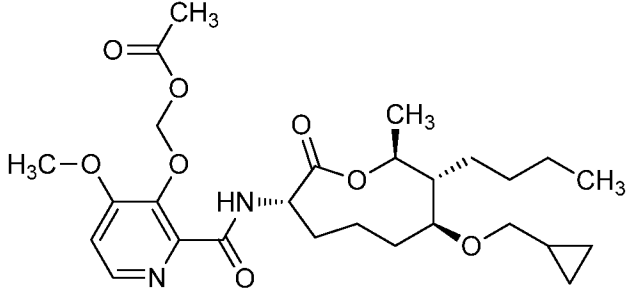
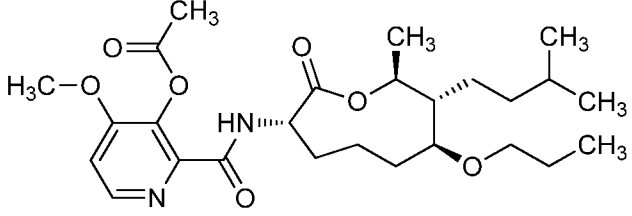
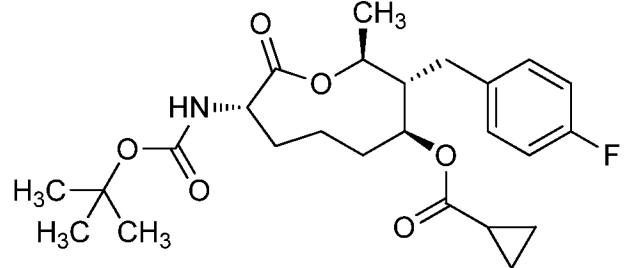
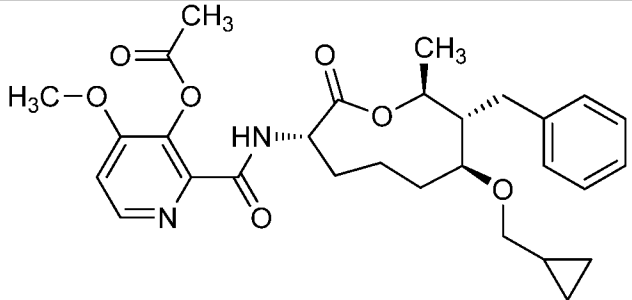
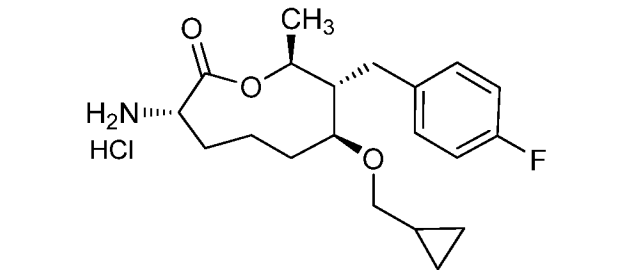
Cmpd. No.	Structure	Prepared According To Example	Appearance
53		Example 6, Step 1.	White Solid
54		Example 6, Step 1.	White Powder
55		Example 8.	White Solid
56		Example 7.	White Foam

Cmpd. No.	Structure	Prepared According To Example	Appearance
57		Example 1, Steps 1–5; Example 2, Step 1; Example 3, Steps 1–3, 5; Example 4.	Colorless Oil
58		Example 6, Step 2.	White Powder
59		Example 6, Step 1.	White Powder
60		Example 6, Steps 1,2.	White Solid

Cmpd. No.	Structure	Prepared According To Example	Appearance
61		Example 7.	White Foam
62		Example 6, Steps 1,2.	Clear Oil
63		Example 8.	Yellow Oil
64		Example 6, Step 2.	Clear Glass

Cmpd. No.	Structure	Prepared According To Example	Appearance
65		Example 7.	Clear Gel
66		Example 6, Step 1.	White Solid
67		Example 6, Steps 1,2.	Clear Gel
68		Example 6, Step 1.	White Solid

Cmpd. No.	Structure	Prepared According To Example	Appearance
69		Example 6, Step 1.	White Solid
70		Example 8.	White Powder
71		Example 9.	Colorless Oil
72		Example 8.	Clear Gel

Cmpd. No.	Structure	Prepared According To Example	Appearance
73		Example 7.	Colorless Oil
74		Example 8.	White Powder
75		Example 5, Step 2.	Colorless Oil
76		Example 8.	White Foam
77		Example 6, Step 1.	White Solid

Cmpd. No.	Structure	Prepared According To Example	Appearance
78		Example 6, Step 1.	White Solid

Table 2. Analytical Data

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
1	---	(Thin Film) 3380, 2951, 2869, 1739, 1676, 1502, 1201	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₃₁ H ₄₃ N ₂ O ₈ , 571.3014; found, 571.3024	¹ H NMR (CDCl ₃) δ 8.32 (d, <i>J</i> = 8.1 Hz, 1H), 8.28 (d, <i>J</i> = 5.4 Hz, 1H), 7.39 – 7.24 (m, 5H), 6.95 (d, <i>J</i> = 5.4 Hz, 1H), 5.74 (s, 2H), 4.74 (dq, <i>J</i> = 10.1, 6.3 Hz, 1H), 4.67 – 4.56 (m, 2H), 4.32 (d, <i>J</i> = 11.4 Hz, 1H), 3.90 (s, 3H), 3.47 – 3.39 (m, 1H), 2.46 – 2.34 (m, 1H), 2.33 – 2.16 (m, 1H), 2.07 (s, 3H), 2.04 – 1.93 (m, 1H), 1.90 – 1.77 (m, 1H), 1.70 – 1.52 (m, 2H), 1.48 – 1.29 (m, 6H), 1.12 – 0.87 (m, 3H), 0.84 (app dd, <i>J</i> = 10.7, 6.6 Hz, 6H)	---
2	---	---	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₂₇ H ₃₂ FN ₂ O ₇ , 515.2188; found, 515.2188	¹ H NMR (CDCl ₃) δ 12.08 (s, 1H), 8.51 (d, <i>J</i> = 8.1 Hz, 1H), 7.98 (d, <i>J</i> = 5.2 Hz, 1H), 7.15 (dd, <i>J</i> = 8.5, 5.5 Hz, 2H), 6.97 (t, <i>J</i> = 8.6 Hz, 2H), 6.87 (d, <i>J</i> = 5.2 Hz, 1H), 4.93 – 4.86 (m, 1H), 4.83 (ddd, <i>J</i> =	¹⁹ F NMR (CDCl ₃) δ -117.10

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				8.1, 6.0, 1.8 Hz, 1H), 4.62 (dt, <i>J</i> = 10.5, 7.5 Hz, 1H), 3.93 (s, 3H), 2.76 (dd, <i>J</i> = 13.9, 5.4 Hz, 1H), 2.57 – 2.41 (m, 2H), 2.36 (dt, <i>J</i> = 13.8, 7.0 Hz, 1H), 2.23 – 2.06 (m, 1H), 1.88 – 1.72 (m, 1H), 1.69 – 1.53 (m, 1H), 1.48 – 1.38 (m, 1H), 1.36 (d, <i>J</i> = 6.4 Hz, 3H), 1.33 – 1.22 (m, 1H), 1.07 (ddt, <i>J</i> = 16.1, 7.3, 2.1 Hz, 1H), 0.84 – 0.78 (m, 2H), 0.77 – 0.71 (m, 2H)	
3	---	--	ESIMS <i>m/z</i> 490.5 ([M+Na] ⁺)	¹ H NMR (CDCl ₃) δ 7.32 – 7.10 (m, 6H), 7.03 (d, <i>J</i> = 8.2 Hz, 2H), 6.70 (d, <i>J</i> = 8.5 Hz, 2H), 5.06 (d, <i>J</i> = 8.1 Hz, 1H), 4.99 – 4.80 (m, 1H), 4.22 (q, <i>J</i> = 7.9 Hz, 1H), 4.18 – 4.03 (m, 1H), 2.98 (dd, <i>J</i> = 14.8, 3.1 Hz, 1H), 2.72 (dd, <i>J</i> = 14.8, 7.3 Hz, 1H), 2.61 – 2.50 (m, 1H), 2.26 (s, 3H), 2.23 – 1.99 (m, 3H), 1.85 – 1.76 (m, 1H), 1.43 (s, 9H), 1.35 (d, <i>J</i> = 6.4 Hz, 3H), 0.98 – 0.81 (m, 1H)	¹³ C NMR (CDCl ₃) δ 172.99, 155.23, 139.95, 130.34, 129.93, 129.21, 128.36, 126.11, 116.27, 79.81, 79.12, 77.28, 73.68, 52.44, 48.36, 35.41, 33.51, 29.16, 28.35, 20.51, 20.32, 17.83
4	---	---	ESIMS <i>m/z</i> 418 ([M+Na] ⁺)	¹ H NMR (CDCl ₃) δ 7.25 – 7.14 (m, 2H), 6.99 (t, <i>J</i> = 8.6 Hz, 2H), 5.07 (d, <i>J</i> = 8.3 Hz, 1H), 4.75 (dq, <i>J</i> = 9.8, 6.4 Hz, 1H), 4.19 (dt, <i>J</i> = 10.6, 7.5 Hz, 1H), 3.64 (dd, <i>J</i> = 8.3, 5.0 Hz, 1H), 2.88 – 2.64 (m, 2H), 2.25 (dt, <i>J</i> = 14.1, 7.5 Hz, 1H), 2.17 (ddt, <i>J</i> = 9.8, 8.4, 6.3 Hz, 1H), 1.99 – 1.86 (m, 1H), 1.78 – 1.67	¹⁹ F NMR (CDCl ₃) δ -116.54

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				(m, 1H), 1.67 – 1.55 (m, 1H), 1.43 (s, 9H), 1.35 (d, <i>J</i> = 4.3 Hz, 1H), 1.31 (d, <i>J</i> = 6.4 Hz, 3H), 1.28 – 1.13 (m, 1H), 1.11 – 1.00 (m, 1H)	
5	---	---	ESIMS <i>m/z</i> 338 ([M+H] ⁺)	---	---
6	---	---	ESIMS <i>m/z</i> 334 ([M-Boc+H] ⁺)	¹ H NMR (CDCl ₃) δ 7.37 – 7.26 (m, 5H), 5.06 (d, <i>J</i> = 8.3 Hz, 1H), 4.69 (dq, <i>J</i> = 9.8, 6.3 Hz, 1H), 4.60 (d, <i>J</i> = 11.5 Hz, 1H), 4.30 (d, <i>J</i> = 11.5 Hz, 1H), 4.19 (dt, <i>J</i> = 10.0, 7.4 Hz, 1H), 3.39 (ddd, <i>J</i> = 8.8, 5.3, 1.6 Hz, 1H), 2.33 – 2.14 (m, 2H), 1.99 – 1.87 (m, 1H), 1.75 (td, <i>J</i> = 13.3, 8.0 Hz, 1H), 1.56 (dddd, <i>J</i> = 18.2, 11.1, 5.5, 3.1 Hz, 3H), 1.44 (s, 9H), 1.42 – 1.33 (m, 1H), 1.30 (d, <i>J</i> = 6.4 Hz, 3H), 1.24 – 1.14 (m, 3H), 1.15 – 1.03 (m, 2H), 0.84 (t, <i>J</i> = 7.2 Hz, 3H)	¹³ C NMR (CDCl ₃) δ 173.10, 154.94, 138.40, 128.35, 127.99, 127.63, 79.74, 78.84, 73.49, 70.34, 52.45, 46.47, 33.59, 28.62, 28.34, 28.17, 27.31, 23.39, 19.25, 17.83, 13.94
7	---	---	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₂₉ H ₃₈ FN ₂ O ₈ , 561.2607; found, 561.2615	¹ H NMR (CDCl ₃) δ 8.33 (d, <i>J</i> = 8.0 Hz, 1H), 8.27 (d, <i>J</i> = 5.3 Hz, 1H), 7.19 (dd, <i>J</i> = 8.5, 5.5 Hz, 2H), 6.99 – 6.94 (m, 3H), 5.74 (s, 2H), 4.81 (dq, <i>J</i> = 9.8, 6.4 Hz, 1H), 4.60 (dt, <i>J</i> = 10.7, 7.5 Hz, 1H), 3.90 (s, 3H), 3.45 (dt, <i>J</i> = 8.7, 6.6 Hz, 1H), 3.23 – 3.08 (m, 1H), 2.98 (dt, <i>J</i> = 8.7, 6.5 Hz, 1H), 2.84 (dd, <i>J</i> = 14.7, 4.1 Hz, 1H), 2.63 (dd, <i>J</i> = 14.7, 7.4 Hz, 1H), 2.39 (dt, <i>J</i> = 13.7, 7.1 Hz,	¹⁹ F NMR (CDCl ₃) δ -117.66

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				1H), 2.33 – 2.21 (m, 1H), 2.06 (s, 3H), 1.81 (td, <i>J</i> = 13.5, 12.6, 7.8 Hz, 1H), 1.65 – 1.53 (m, 1H), 1.55 – 1.41 (m, 3H), 1.42 – 1.29 (m, 1H), 1.25 (d, <i>J</i> = 6.5 Hz, 3H), 0.98 – 0.90 (m, 1H), 0.88 (t, <i>J</i> = 7.4 Hz, 3H)	
8	55-60	---	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₂₇ H ₃₇ N ₂ O ₆ , 485.2646; found, 485.2651	¹ H NMR (CDCl ₃) δ 12.11 (s, 1H), 8.47 (d, <i>J</i> = 8.1 Hz, 1H), 7.99 (d, <i>J</i> = 5.2 Hz, 1H), 7.32 – 7.23 (m, 2H), 6.99 – 6.83 (m, 4H), 4.89 (app dq, <i>J</i> = 9.9, 6.3 Hz, 1H), 4.63 (app dt, <i>J</i> = 10.7, 7.7 Hz, 1H), 4.37 – 4.28 (m, 1H), 3.94 (s, 3H), 2.42 – 2.29 (m, 1H), 2.29 – 2.13 (m, 2H), 1.97 – 1.83 (m, 1H), 1.71 – 1.29 (m, 8H), 1.27 – 1.10 (m, 2H), 1.08 – 0.98 (m, 1H), 0.84 (app dd, <i>J</i> = 13.9, 6.6 Hz, 6H)	---
9	---	---	ESIMS <i>m/z</i> 334 ([M+H] ⁺)	¹ H NMR (CDCl ₃) δ 8.71 (bs, 3H), 7.38 – 7.26 (m, 5H), 4.77 – 4.67 (m, 1H), 4.58 (d, <i>J</i> = 11.5 Hz, 1H), 4.30 (d, <i>J</i> = 11.5 Hz, 1H), 4.01 (t, <i>J</i> = 8.7 Hz, 1H), 3.38 (dd, <i>J</i> = 8.8, 4.8 Hz, 1H), 2.61 – 2.49 (m, 1H), 2.25 (d, <i>J</i> = 15.1 Hz, 1H), 1.90 (td, <i>J</i> = 9.2, 4.6 Hz, 1H), 1.74 (q, <i>J</i> = 10.9, 10.1 Hz, 2H), 1.64 (s, 1H), 1.58 – 1.48 (m, 1H), 1.36 (dd, <i>J</i> = 10.5, 5.3 Hz, 1H), 1.31 (d, <i>J</i> = 6.3 Hz, 3H), 1.19 (dh, <i>J</i> = 12.3, 6.4 Hz, 2H), 1.06 (dq, <i>J</i> =	---

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				12.0, 5.3 Hz, 2H), 0.88 (d, <i>J</i> = 8.1 Hz, 1H), 0.83 (t, <i>J</i> = 7.2 Hz, 3H)	
10	---	---	ESIMS <i>m/z</i> 442 ([M+Na] ⁺)	¹ H NMR (CDCl ₃) δ 7.33 – 7.21 (m, 2H), 6.99 – 6.90 (m, 1H), 6.90 – 6.82 (m, 2H), 5.07 (d, <i>J</i> = 8.2 Hz, 1H), 4.83 (dq, <i>J</i> = 10.0, 6.3 Hz, 1H), 4.33 – 4.18 (m, 2H), 2.28 – 2.08 (m, 3H), 1.91 – 1.71 (m, 1H), 1.68 – 1.54 (m, 1H), 1.52 – 1.46 (m, 1H), 1.44 (s, 9H), 1.38 (d, <i>J</i> = 6.3 Hz, 3H), 1.33 – 1.20 (m, 4H), 1.19 – 1.05 (m, 1H), 1.01 – 0.91 (m, 1H), 0.90 – 0.79 (m, 4H)	¹³ C NMR (CDCl ₃) δ 173.09, 157.74, 154.94, 129.54, 121.00, 116.32, 79.77, 78.50, 73.34, 52.45, 46.44, 33.45, 29.50, 28.33, 28.29, 27.75, 23.23, 19.31, 17.74, 13.91
11	---	---	ESIMS <i>m/z</i> 508 ([M+Na] ⁺)	¹ H NMR (CDCl ₃) δ 7.35 – 7.19 (m, 5H), 7.12 (dd, <i>J</i> = 8.5, 5.4 Hz, 2H), 6.92 (t, <i>J</i> = 8.7 Hz, 2H), 5.09 (d, <i>J</i> = 8.2 Hz, 1H), 4.78 (dq, <i>J</i> = 9.9, 6.4 Hz, 1H), 4.53 (d, <i>J</i> = 11.3 Hz, 1H), 4.24 – 4.17 (m, 1H), 4.15 (d, <i>J</i> = 11.2 Hz, 1H), 3.32 (ddd, <i>J</i> = 8.6, 5.3, 1.6 Hz, 1H), 2.84 (dd, <i>J</i> = 15.1, 4.3 Hz, 1H), 2.61 (dd, <i>J</i> = 14.8, 7.4 Hz, 1H), 2.37 – 2.07 (m, 3H), 1.87 – 1.70 (m, 1H), 1.65 – 1.50 (m, 1H), 1.43 (s, 9H), 1.24 (d, <i>J</i> = 6.4 Hz, 3H), 1.23 – 1.11 (m, 1H), 0.99 – 0.83 (m, 1H)	¹⁹ F NMR (CDCl ₃) δ -117.36
12	---	---	HRMS–ESI <i>m/z</i> [M+H] ⁺ calcd for C ₃₃ H ₃₈ N ₂ O ₈ ,	¹ H NMR (CDCl ₃) δ 8.38 – 8.18 (m, 1H), 7.37 – 7.10 (m, 5H), 7.04 (d, <i>J</i> = 8.2 Hz, 2H), 6.94 (d, <i>J</i> = 4.9 Hz, 1H), 6.72 (d, <i>J</i> =	---

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
			560.2628; found, 560.2642	8.5 Hz, 2H), 5.73 (s, 2H), 5.02 – 4.88 (m, 1H), 4.62 (d, <i>J</i> = 7.7 Hz, 1H), 4.18 (dd, <i>J</i> = 8.5, 4.3 Hz, 1H), 3.90 (s, 3H), 3.01 (dd, <i>J</i> = 14.8, 3.3 Hz, 1H), 2.74 (dd, <i>J</i> = 14.8, 7.4 Hz, 1H), 2.63 – 2.56 (m, 1H), 2.39 – 2.37 (m, 1H), 2.27 (s, 3H), 2.20 – 2.09 (m, 2H), 2.06 (s, 3H), 1.97 – 1.84 (m, 1H), 1.58 – 1.44 (m, 2H), 1.37 (d, <i>J</i> = 6.4 Hz, 3H)	
13	---	(Thin Film) 3369, 2944, 2897, 1739, 1641	ESIMS <i>m/z</i> 505 ([M+H] ⁺)	¹ H NMR (CDCl ₃) δ 12.12 (d, <i>J</i> = 0.6 Hz, 1H), 8.48 (d, <i>J</i> = 8.1 Hz, 1H), 7.99 (d, <i>J</i> = 5.2 Hz, 1H), 6.87 (d, <i>J</i> = 5.2 Hz, 1H), 4.76 (dq, <i>J</i> = 10.1, 6.3 Hz, 1H), 4.59 (dt, <i>J</i> = 10.7, 7.7 Hz, 1H), 3.94 (s, 3H), 3.61 (dt, <i>J</i> = 9.0, 5.9 Hz, 1H), 3.27 (ddt, <i>J</i> = 15.1, 9.0, 3.8 Hz, 2H), 2.38 (ddd, <i>J</i> = 12.2, 7.5, 6.3 Hz, 1H), 2.27 – 2.09 (m, 3H), 1.94 – 1.87 (m, 1H), 1.86 – 1.72 (m, 3H), 1.62 – 1.48 (m, 2H), 1.46 – 1.36 (m, 2H), 1.35 (d, <i>J</i> = 6.3 Hz, 3H), 1.33 – 1.23 (m, 4H), 1.19 (ddt, <i>J</i> = 16.7, 10.0, 3.8 Hz, 1H), 0.91 (t, <i>J</i> = 7.0 Hz, 3H)	---
14	---	---	ESIMS <i>m/z</i> 436 ([M+Na] ⁺)	¹ H NMR (CDCl ₃) δ 5.15 (d, <i>J</i> = 8.3 Hz, 1H), 4.91 – 4.84 (m, 1H), 4.79 (dq, <i>J</i> = 10.0, 6.3 Hz, 1H), 4.27 – 4.16 (m, 1H), 2.60 – 2.44 (m, 1H), 2.23 (dt, <i>J</i> = 13.8, 7.1 Hz, 1H), 2.15 – 1.99 (m, 3H), 1.73 (tdd, <i>J</i>	¹³ C NMR (CDCl ₃) δ 175.41, 172.91, 154.98, 79.76, 74.44, 73.12, 52.42, 45.44, 34.24, 33.32, 30.88, 28.29, 27.38, 23.25,

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				= 13.0, 7.3, 2.3 Hz, 1H), 1.57 – 1.46 (m, 1H), 1.44 (s, 9H), 1.34 (d, <i>J</i> = 6.4 Hz, 4H), 1.33 – 1.19 (m, 5H), 1.18 – 1.12 (m, 6H), 1.04 – 0.94 (m, 1H), 0.87 (t, <i>J</i> = 7.0 Hz, 3H)	19.19, 19.03, 18.88, 18.79, 18.02, 13.82
15	---	(Thin Film) 3382, 2938, 2870, 1738, 1675	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₃₀ H ₄₀ N ₂ O ₈ , 557.2857; found, 557.2864	¹ H NMR (CDCl ₃) δ 8.31 (d, <i>J</i> = 8.1 Hz, 1H), 8.28 (d, <i>J</i> = 5.4 Hz, 1H), 7.38 – 7.27 (m, 5H), 6.94 (d, <i>J</i> = 5.4 Hz, 1H), 5.74 (s, 2H), 4.74 (dq, <i>J</i> = 10.2, 6.3 Hz, 1H), 4.66 – 4.57 (m, 2H), 4.32 (d, <i>J</i> = 11.5 Hz, 1H), 3.91 (s, 3H), 3.42 (ddd, <i>J</i> = 8.8, 5.3, 1.6 Hz, 1H), 2.46 – 2.35 (m, 1H), 2.32 – 2.18 (m, 1H), 2.07 (s, 3H), 1.97 (ddd, <i>J</i> = 13.3, 8.9, 4.6 Hz, 1H), 1.90 – 1.77 (m, 1H), 1.67 – 1.52 (m, 2H), 1.45 – 1.35 (m, 2H), 1.32 (d, <i>J</i> = 6.3 Hz, 3H), 1.29 – 1.15 (m, 2H), 1.15 – 1.05 (m, 2H), 0.99 – 0.88 (m, 1H), 0.84 (t, <i>J</i> = 7.2 Hz, 3H)	---
16	---	---	ESIMS <i>m/z</i> 348 ([M+H] ⁺)	---	---
17	58-62	---	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₃₀ H ₄₁ N ₂ O ₇ , 541.2908; found, 541.2924	¹ H NMR (CDCl ₃) δ 8.57 – 8.50 (m, 1H), 8.33 (d, <i>J</i> = 5.5 Hz, 1H), 7.38 – 7.24 (m, 5H), 6.99 (d, <i>J</i> = 5.5 Hz, 1H), 4.79 – 4.67 (m, 1H), 4.66 – 4.54 (m, 2H), 4.31 (d, <i>J</i> = 11.5 Hz, 1H), 3.89 (s, 3H), 3.47 – 3.38 (m, 1H), 2.44 – 2.32 (m, 4H), 2.32 – 2.17 (m, 1H), 2.03 – 1.91 (m, 1H), 1.88	---

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				- 1.75 (m, 1H), 1.68 – 1.51 (m, 2H), 1.47 – 1.23 (m, 6H), 1.08 – 0.79 (m, 9H)	
18	---	---	ESIMS <i>m/z</i> 422 ([M+Na] ⁺)	¹ H NMR (CDCl ₃) δ 5.06 (d, <i>J</i> = 8.2 Hz, 1H), 4.70 (dq, <i>J</i> = 10.1, 6.4 Hz, 1H), 4.24 – 4.14 (m, 1H), 3.50 (app dt, <i>J</i> = 9.0, 6.4 Hz, 1H), 3.28 – 3.19 (m, 1H), 3.13 (app dt, <i>J</i> = 8.8, 6.6 Hz, 1H), 2.30 – 2.18 (m, 1H), 2.11 (dddd, <i>J</i> = 15.6, 10.1, 7.9, 5.2 Hz, 1H), 1.87 (app dq, <i>J</i> = 13.1, 4.6 Hz, 1H), 1.78 – 1.35 (m, 16H), 1.31 (d, <i>J</i> = 6.3 Hz, 3H), 1.24 – 1.03 (m, 3H), 0.96 – 0.75 (m, 10H)	¹³ C NMR (CDCl ₃) δ 173.11, 154.94, 79.93, 79.70, 73.53, 70.41, 52.46, 46.66, 34.41, 33.63, 29.03, 28.75, 28.33, 26.26, 23.30, 22.61, 22.44, 19.26, 17.80, 10.88
19	---	---	ESIMS <i>m/z</i> 508 ([M+Na] ⁺)	¹ H NMR (CDCl ₃) δ 7.12 (dd, <i>J</i> = 8.5, 5.5 Hz, 2H), 7.02 (d, <i>J</i> = 8.3 Hz, 2H), 6.90 (t, <i>J</i> = 8.7 Hz, 2H), 6.67 (d, <i>J</i> = 8.2 Hz, 2H), 5.08 (d, <i>J</i> = 7.8 Hz, 1H), 4.89 (dq, <i>J</i> = 9.8, 6.4 Hz, 1H), 4.28 – 4.18 (m, 1H), 4.12 (ddd, <i>J</i> = 8.0, 5.7, 1.7 Hz, 1H), 2.90 (dd, <i>J</i> = 14.9, 3.9 Hz, 1H), 2.70 (dd, <i>J</i> = 14.9, 7.1 Hz, 1H), 2.56 – 2.43 (m, 1H), 2.26 (s, 3H), 2.24 – 2.03 (m, 2H), 1.88 – 1.74 (m, 1H), 1.52 – 1.45 (m, 1H), 1.43 (s, 9H), 1.34 (d, <i>J</i> = 6.4 Hz, 3H), 1.12 (q, <i>J</i> = 11.8 Hz, 1H), 0.97 (ddt, <i>J</i> = 13.2, 6.7, 2.1 Hz, 1H)	¹³ C NMR (CDCl ₃) δ 172.95, 161.36 (d, <i>J</i> = 244.1 Hz), 155.15, 154.93, 135.63 (d, <i>J</i> = 3.3 Hz), 130.50 (d, <i>J</i> = 7.8 Hz), 130.39, 129.96, 116.13, 115.10 (d, <i>J</i> = 21.1 Hz), 79.79, 79.13, 73.45, 52.49, 48.69, 34.77, 33.47, 29.35, 28.34, 20.48, 20.28, 17.92
20	---	---	ESIMS <i>m/z</i> 407 ([M+Na+CH ₃ CN] ⁺)	¹ H NMR (CDCl ₃) δ 5.11 (d, <i>J</i> = 8.3 Hz, 1H), 4.71 (dq, <i>J</i> = 10.0, 6.4 Hz, 1H),	¹³ C NMR (CDCl ₃) δ 173.03, 154.09, 79.78, 73.54,

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				4.26 – 4.15 (m, 1H), 3.69 (ddd, <i>J</i> = 8.7, 5.7, 2.2 Hz, 1H), 2.34 – 2.22 (m, 1H), 1.97 (dddd, <i>J</i> = 15.5, 10.1, 7.7, 5.2 Hz, 1H), 1.87 – 1.76 (m, 1H), 1.75 – 1.53 (m, 5H), 1.52 – 1.46 (m, 1H), 1.44 (s, 9H), 1.40 – 1.34 (m, 1H), 1.33 (d, <i>J</i> = 6.3 Hz, 3H), 1.30 (d, <i>J</i> = 7.1 Hz, 1H), 1.23 – 1.13 (m, 2H), 1.10 – 1.00 (m, 1H), 0.90 (t, <i>J</i> = 7.1 Hz, 3H)	72.41, 52.43, 48.04, 34.24, 33.60, 28.31, 28.26, 27.61, 23.41, 19.21, 17.61, 13.97
21	---	---	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₃₂ H ₃₆ FN ₂ O ₇ , 579.2501; found, 579.2508	¹ H NMR (CDCl ₃) δ 8.51 (d, <i>J</i> = 7.5 Hz, 1H), 8.32 (d, <i>J</i> = 5.5 Hz, 1H), 7.14 (dd, <i>J</i> = 8.4, 5.5 Hz, 2H), 7.04 (d, <i>J</i> = 8.6 Hz, 2H), 6.99 (d, <i>J</i> = 5.5 Hz, 1H), 6.92 (t, <i>J</i> = 8.7 Hz, 2H), 6.75 – 6.64 (m, 2H), 4.92 (dq, <i>J</i> = 9.7, 6.4 Hz, 1H), 4.63 (dt, <i>J</i> = 10.5, 7.7 Hz, 1H), 4.26 – 4.04 (m, 1H), 3.89 (d, <i>J</i> = 1.7 Hz, 3H), 2.92 (dd, <i>J</i> = 14.8, 3.8 Hz, 1H), 2.72 (dd, <i>J</i> = 14.8, 7.2 Hz, 1H), 2.58 – 2.47 (m, 1H), 2.39 (s, 3H), 2.37 – 2.29 (m, 1H), 2.27 (s, 3H), 2.22 – 2.08 (m, 1H), 1.93 – 1.79 (m, 1H), 1.57 – 1.42 (m, 1H), 1.34 (d, <i>J</i> = 6.4 Hz, 3H), 1.33 – 1.21 (m, 1H), 1.02 (ddt, <i>J</i> = 16.0, 7.6, 2.1 Hz, 1H)	¹⁹ F NMR (CDCl ₃) δ -117.18
22	---	---	ESIMS <i>m/z</i> 456.4 ([M+Na] ⁺)	¹ H NMR (CDCl ₃) δ 7.22 (tt, <i>J</i> = 21.8, 7.2 Hz, 6H), 5.07 (d, <i>J</i> = 8.0 Hz, 1H), 4.87 – 4.70 (m, 1H), 4.18 (q, <i>J</i> = 7.9 Hz, 1H), 3.25	¹³ C NMR (CDCl ₃) δ 173.04, 154.93, 140.90, 129.86, 129.10, 128.27, 125.84, 113.68,

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				(dd, <i>J</i> = 8.4, 6.5 Hz, 1H), 3.15 (dd, <i>J</i> = 8.1, 4.6 Hz, 1H), 2.93 (dd, <i>J</i> = 14.7, 3.3 Hz, 1H), 2.88 – 2.75 (m, 1H), 2.60 (dd, <i>J</i> = 14.7, 7.8 Hz, 1H), 2.37 – 2.19 (m, 2H), 2.19 – 2.01 (m, 1H), 1.78 – 1.67 (m, 2H), 1.55 – 1.48 (m, 1H), 1.43 (s, 9H), 1.30 – 1.25 (m, 1H), 1.22 (d, <i>J</i> = 6.4 Hz, 3H), 0.87 (d, <i>J</i> = 7.3 Hz, 6H)	81.16, 75.36, 74.15, 52.47, 48.77, 36.03, 28.86, 28.34, 22.66, 20.22, 19.60, 17.83
23	---	---	ESIMS <i>m/z</i> 420 ([M+Na] ⁺)	¹ H NMR (CDCl ₃) δ 5.07 (d, <i>J</i> = 7.9 Hz, 1H), 4.70 (dq, <i>J</i> = 10.1, 6.3 Hz, 1H), 4.24 – 4.14 (m, 1H), 3.32 (dd, <i>J</i> = 10.0, 6.9 Hz, 1H), 3.27 (ddd, <i>J</i> = 8.8, 5.4, 1.6 Hz, 1H), 3.11 (dd, <i>J</i> = 10.0, 6.7 Hz, 1H), 2.23 (dq, <i>J</i> = 10.3, 5.0, 3.2 Hz, 1H), 2.14 – 2.02 (m, 1H), 1.90 (ddt, <i>J</i> = 10.2, 8.8, 4.4 Hz, 1H), 1.78 – 1.66 (m, 1H), 1.65 – 1.54 (m, 1H), 1.54 – 1.46 (m, 1H), 1.45 (m, 10H), 1.37 (m, 1H), 1.31 (m, 5H), 1.23 – 1.10 (m, 2H), 1.07 – 0.96 (m, 1H), 0.90 (t, <i>J</i> = 7.0 Hz, 3H), 0.82 (ddt, <i>J</i> = 16.1, 8.1, 1.6 Hz, 1H), 0.59 – 0.44 (m, 2H), 0.17 (qd, <i>J</i> = 4.8, 2.0 Hz, 2H)	¹³ C NMR (CDCl ₃) δ 173.07, 154.91, 79.69, 73.56, 73.26, 52.48, 46.67, 33.57, 29.06, 28.42, 28.31, 27.65, 23.40, 19.26, 17.88, 13.93, 10.85, 3.01, 2.89
24	---	---	ESIMS <i>m/z</i> 460 ([M+Na] ⁺)	¹ H NMR (CDCl ₃) δ 7.17 (dd, <i>J</i> = 8.4, 5.5 Hz, 2H), 6.96 (t, <i>J</i> = 8.7 Hz, 2H), 5.07 (d, <i>J</i> = 8.1 Hz, 1H), 4.77 (dq, <i>J</i> = 9.8, 6.5 Hz, 1H), 4.18 (dt, <i>J</i> = 10.6, 7.7 Hz, 1H), 3.43 (dt, <i>J</i> = 8.6,	¹³ C NMR (CDCl ₃) δ 173.02, 161.24 (d, <i>J</i> = 243.9 Hz), 154.92, 136.45 (d, <i>J</i> = 3.2 Hz), 130.36 (d, <i>J</i> = 7.7 Hz), 114.98 (d, <i>J</i> = 21.0

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				6.6 Hz, 1H), 3.14 (ddd, <i>J</i> = 8.6, 5.4, 1.6 Hz, 1H), 3.02 – 2.90 (m, 1H), 2.82 (dd, <i>J</i> = 14.8, 4.2 Hz, 1H), 2.61 (dd, <i>J</i> = 14.7, 7.4 Hz, 1H), 2.33 – 2.16 (m, 2H), 2.17 – 2.02 (m, 1H), 1.72 (td, <i>J</i> = 13.3, 12.8, 7.9 Hz, 1H), 1.60 – 1.44 (m, 3H), 1.43 (s, 9H), 1.24 (d, <i>J</i> = 6.4 Hz, 3H), 1.21 – 1.07 (m, 1H), 0.87 (t, <i>J</i> = 7.4 Hz, 3H), 0.83 (q, <i>J</i> = 3.6, 1.9 Hz, 1H)	Hz), 81.21, 79.75, 73.90, 70.13, 52.46, 48.89, 35.36, 33.60, 28.75, 28.32, 23.23, 20.19, 17.87, 10.82
25	---	(Thin Film) 3378, 2954, 2872, 1740, 1677, 1504, 1202	HRMS–ESI <i>m/z</i> [M+Na] ⁺ calcd for C ₂₇ H ₄₂ N ₂ NaO ₈ , 545.2833; found, 545.2853	¹ H NMR (CDCl ₃) δ 8.31 (d, <i>J</i> = 8.1 Hz, 1H), 8.28 (d, <i>J</i> = 5.4 Hz, 1H), 6.95 (d, <i>J</i> = 5.4 Hz, 1H), 5.74 (s, 2H), 4.74 (dq, <i>J</i> = 10.1, 6.3 Hz, 1H), 4.61 (app dt, <i>J</i> = 10.7, 7.6 Hz, 1H), 3.91 (s, 3H), 3.52 (app dt, <i>J</i> = 8.9, 6.4 Hz, 1H), 3.31 – 3.22 (m, 1H), 3.15 (app dt, <i>J</i> = 8.9, 6.6 Hz, 1H), 2.45 – 2.33 (m, 1H), 2.21 – 2.09 (m, 1H), 2.07 (s, 3H), 1.98 – 1.86 (m, 1H), 1.85 – 1.70 (m, 1H), 1.67 – 1.28 (m, 10H), 1.24 – 1.03 (m, 2H), 0.97 – 0.84 (m, 10H)	---
26	---	---	HRMS–ESI <i>m/z</i> [M+H] ⁺ calcd for C ₂₇ H ₃₄ FN ₂ O ₆ , 501.2395; found, 501.2408	¹ H NMR (CDCl ₃) δ 12.12 (s, 1H), 8.49 (d, <i>J</i> = 8.1 Hz, 1H), 7.98 (d, <i>J</i> = 5.2 Hz, 1H), 7.21 (dd, <i>J</i> = 8.5, 5.5 Hz, 2H), 6.97 (t, <i>J</i> = 8.7 Hz, 2H), 6.86 (d, <i>J</i> = 5.2 Hz, 1H), 4.83 (dq, <i>J</i> = 9.8, 6.4 Hz, 1H), 4.59 (dt, <i>J</i> = 10.6, 7.6 Hz, 1H), 3.93 (s, 3H), 3.30 – 3.13	¹⁹ F NMR (CDCl ₃) δ -117.48

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				(m, 2H), 3.00 (dd, <i>J</i> = 9.8, 6.3 Hz, 1H), 2.85 (dd, <i>J</i> = 14.7, 4.4 Hz, 1H), 2.67 (dd, <i>J</i> = 14.7, 7.3 Hz, 1H), 2.44 – 2.34 (m, 1H), 2.34 – 2.25 (m, 1H), 2.21 – 2.06 (m, 1H), 1.91 – 1.78 (m, 1H), 1.68 – 1.53 (m, 1H), 1.40 (q, <i>J</i> = 11.8 Hz, 1H), 1.28 (d, <i>J</i> = 6.4 Hz, 3H), 0.99 – 0.85 (m, 2H), 0.55 – 0.42 (m, 2H), 0.19 – 0.06 (m, 2H)	
27	---	---	ESIMS <i>m/z</i> 454.4 ([M+Na] ⁺)	¹ H NMR (CDCl ₃) δ 7.34 – 7.10 (m, 6H), 5.08 (d, <i>J</i> = 8.0 Hz, 1H), 4.78 (dq, <i>J</i> = 12.8, 6.3 Hz, 1H), 4.19 (q, <i>J</i> = 7.9 Hz, 1H), 3.19 (q, <i>J</i> = 9.6, 7.6 Hz, 2H), 3.00 – 2.84 (m, 2H), 2.68 (dd, <i>J</i> = 14.6, 7.3 Hz, 1H), 2.35 – 2.21 (m, 2H), 2.17 – 1.97 (m, 1H), 1.88 – 1.64 (m, 1H), 1.58 – 1.45 (m, 1H), 1.43 (s, 9H), 1.26 (d, <i>J</i> = 6.3 Hz, 3H), 0.93 – 0.81 (m, 2H), 0.52 – 0.40 (m, 2H), 0.14 – 0.07 (m, 2H)	¹³ C NMR (CDCl ₃) δ 173.03, 154.93, 140.62, 129.16, 128.28, 125.88, 80.77, 79.73, 74.06, 73.05, 52.47, 48.56, 36.10, 33.58, 28.33, 20.21, 17.95, 10.78, 3.09, 2.82
28	---	---	ESIMS <i>m/z</i> 472 ([M+Na] ⁺)	¹ H NMR (CDCl ₃) δ 7.19 (dd, <i>J</i> = 8.4, 5.6 Hz, 2H), 6.96 (t, <i>J</i> = 8.7 Hz, 2H), 5.04 (d, <i>J</i> = 8.2 Hz, 1H), 4.76 (dq, <i>J</i> = 9.9, 6.4 Hz, 1H), 4.19 (q, <i>J</i> = 8.3 Hz, 1H), 3.23 – 3.11 (m, 2H), 2.97 (dd, <i>J</i> = 9.8, 6.4 Hz, 1H), 2.82 (dd, <i>J</i> = 14.7, 4.5 Hz, 1H), 2.65 (dd, <i>J</i> = 14.7, 7.2 Hz, 1H), 2.37 – 2.15 (m, 2H), 2.12 – 1.98 (m, 1H), 1.81 – 1.64 (m,	¹⁹ F NMR (CDCl ₃) δ -117.59

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				1H), 1.55 – 1.47 (m, 1H), 1.43 (s, 9H), 1.25 (d, <i>J</i> = 6.4 Hz, 3H), 1.21 – 1.10 (m, 1H), 0.95 – 0.75 (m, 2H), 0.53 – 0.41 (m, 2H), 0.17 – 0.04 (m, 2H)	
29	---	(Thin Film) 3366, 2938, 2871, 1737, 1649	ESIMS <i>m/z</i> 471 ([M+H] ⁺)	¹ H NMR (CDCl ₃) δ 12.11 (s, 1H), 8.47 (d, <i>J</i> = 8.1 Hz, 1H), 7.98 (d, <i>J</i> = 5.2 Hz, 1H), 7.41 – 7.14 (m, 2H), 6.99 – 6.92 (m, 1H), 6.92 – 6.84 (m, 3H), 4.88 (dq, <i>J</i> = 10.1, 6.3 Hz, 1H), 4.63 (dt, <i>J</i> = 10.7, 7.7 Hz, 1H), 4.32 (ddd, <i>J</i> = 8.6, 5.6, 1.7 Hz, 1H), 3.93 (s, 3H), 2.41 – 2.31 (m, 1H), 2.21 (m, 2H), 1.97 – 1.84 (m, 1H), 1.73 – 1.45 (m, 3H), 1.41 (d, <i>J</i> = 6.3 Hz, 3H), 1.39 – 1.30 (m, 2H), 1.26 (td, <i>J</i> = 7.1, 4.8 Hz, 3H), 1.03 (ddt, <i>J</i> = 16.0, 7.8, 1.9 Hz, 1H), 0.86 (t, <i>J</i> = 6.9 Hz, 3H)	---
30	223-224	---	ESIMS <i>m/z</i> 298 ([M+H] ⁺)	¹ H NMR (CDCl ₃) δ 8.68 (bs, 3H), 4.72 (dd, <i>J</i> = 10.2, 6.1 Hz, 1H), 3.99 (t, <i>J</i> = 8.5 Hz, 1H), 3.38 – 3.24 (m, 2H), 3.10 (dd, <i>J</i> = 10.0, 6.7 Hz, 1H), 2.59 – 2.44 (m, 1H), 2.22 – 2.04 (m, 1H), 1.88 (dq, <i>J</i> = 9.1, 4.7 Hz, 1H), 1.79 – 1.65 (m, 2H), 1.64 – 1.51 (m, 2H), 1.46 – 1.24 (m, 7H), 1.22 – 1.11 (m, 1H), 1.08 – 0.96 (m, 1H), 0.90 (t, <i>J</i> = 7.0 Hz, 3H), 0.82 (dd, <i>J</i> = 15.8, 7.6 Hz, 1H), 0.56 – 0.47 (m, 2H), 0.23 – 0.13 (m, 2H)	---

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
31	45-49	---	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₂₄ H ₃₉ N ₂ O ₆ , 451.2803; found, 451.2804	¹ H NMR (CDCl ₃) δ 12.14 (d, <i>J</i> = 0.6 Hz, 1H), 8.48 (d, <i>J</i> = 8.1 Hz, 1H), 7.99 (d, <i>J</i> = 5.2 Hz, 1H), 6.87 (d, <i>J</i> = 5.3 Hz, 1H), 4.76 (dq, <i>J</i> = 10.1, 6.3 Hz, 1H), 4.59 (ddd, <i>J</i> = 10.7, 8.2, 7.3 Hz, 1H), 3.94 (s, 3H), 3.52 (app dt, <i>J</i> = 8.9, 6.4 Hz, 1H), 3.32 – 3.23 (m, 1H), 3.16 (app dt, <i>J</i> = 8.9, 6.6 Hz, 1H), 2.44 – 2.31 (m, 1H), 2.25 – 2.10 (m, 1H), 1.98 – 1.86 (m, 1H), 1.86 – 1.72 (m, 1H), 1.67 – 1.36 (m, 7H), 1.34 (d, <i>J</i> = 6.3 Hz, 3H), 1.27 – 1.03 (m, 2H), 0.98 – 0.83 (m, 10H)	---
32	---	(Thin Film) 3331, 3078, 2948, 2868, 1728	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₂₄ H ₃₆ N ₂ O ₆ , 449.2646; found, 449.2666	¹ H NMR (CDCl ₃) δ 12.14 (d, <i>J</i> = 0.6 Hz, 1H), 8.47 (d, <i>J</i> = 8.1 Hz, 1H), 7.99 (d, <i>J</i> = 5.2 Hz, 1H), 6.86 (d, <i>J</i> = 5.3 Hz, 1H), 4.76 (dq, <i>J</i> = 10.1, 6.3 Hz, 1H), 4.59 (dt, <i>J</i> = 10.7, 7.7 Hz, 1H), 3.94 (s, 3H), 3.39 – 3.29 (m, 2H), 3.13 (dd, <i>J</i> = 10.0, 6.7 Hz, 1H), 2.38 (dt, <i>J</i> = 13.7, 7.1 Hz, 1H), 2.22 – 2.08 (m, 1H), 1.95 (tt, <i>J</i> = 9.1, 4.4 Hz, 1H), 1.87 – 1.75 (m, 1H), 1.68 – 1.52 (m, 3H), 1.47 – 1.37 (m, 1H), 1.34 (d, <i>J</i> = 6.3 Hz, 3H), 1.33 – 1.29 (m, 3H), 1.24 – 1.15 (m, 1H), 1.09 – 0.99 (m, 1H), 0.91 (t, <i>J</i> = 7.0 Hz, 3H), 0.89 – 0.85 (m, 1H), 0.58 – 0.48 (m, 2H), 0.18 (qd, <i>J</i> = 4.7, 1.6 Hz, 2H)	---

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
33	---	(Thin Film) 3377, 2938, 2871, 1740, 1676	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₂₉ H ₃₈ N ₂ O ₈ , 543.2701; found, 543.2706	¹ H NMR (CDCl ₃) δ 8.31 (d, <i>J</i> = 8.1 Hz, 1H), 8.28 (d, <i>J</i> = 5.4 Hz, 1H), 7.32 – 7.23 (m, 2H), 6.98 – 6.92 (m, 2H), 6.91 – 6.87 (m, 2H), 5.74 (s, 2H), 4.86 (dq, <i>J</i> = 10.1, 6.3 Hz, 1H), 4.65 (dt, <i>J</i> = 10.7, 7.6 Hz, 1H), 4.31 (ddd, <i>J</i> = 8.7, 5.6, 1.7 Hz, 1H), 3.90 (s, 3H), 2.36 (dtd, <i>J</i> = 13.7, 7.6, 1.3 Hz, 1H), 2.27 – 2.14 (m, 2H), 2.07 (s, 3H), 1.96 – 1.84 (m, 1H), 1.69 – 1.57 (m, 1H), 1.57 – 1.44 (m, 2H), 1.39 (d, <i>J</i> = 6.3 Hz, 3H), 1.37 – 1.17 (m, 5H), 1.03 (ddt, <i>J</i> = 15.9, 7.7, 1.9 Hz, 1H), 0.86 (d, <i>J</i> = 6.9 Hz, 3H)	---
34	---	---	ESIMS <i>m/z</i> 320 ([M+H] ⁺)	---	---
35	---	---	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₃₅ H ₄₂ FN ₂ O ₉ , 653.2869; found, 653.2876	¹ H NMR (CDCl ₃) δ 8.31 (d, <i>J</i> = 8.0 Hz, 1H), 8.26 (d, <i>J</i> = 5.3 Hz, 1H), 7.15 (dd, <i>J</i> = 8.5, 5.5 Hz, 2H), 7.07 – 7.01 (m, 2H), 6.97 – 6.89 (m, 3H), 6.70 (d, <i>J</i> = 8.5 Hz, 2H), 5.81 (s, 2H), 4.93 (dq, <i>J</i> = 9.6, 6.4 Hz, 1H), 4.63 (dt, <i>J</i> = 10.5, 7.6 Hz, 1H), 4.16 (ddd, <i>J</i> = 8.0, 5.6, 1.7 Hz, 1H), 4.09 (s, 2H), 3.89 (s, 3H), 3.58 (q, <i>J</i> = 7.0 Hz, 2H), 2.93 (dd, <i>J</i> = 14.8, 3.8 Hz, 1H), 2.73 (dd, <i>J</i> = 14.8, 7.2 Hz, 1H), 2.60 – 2.47 (m, 1H), 2.41 – 2.30 (m, 1H), 2.27 (s, 3H), 2.26 – 2.10 (m, 1H), 1.97	¹⁹ F NMR (CDCl ₃) δ -117.21

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				- 1.81 (m, 1H), 1.60 – 1.43 (m, 1H), 1.36 (d, <i>J</i> = 6.4 Hz, 3H), 1.32 – 1.27 (m, 1H), 1.22 (t, <i>J</i> = 7.0 Hz, 3H), 1.03 (ddt, <i>J</i> = 15.7, 7.2, 1.9 Hz, 1H)	
36	73-77	---	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₂₉ H ₃₉ N ₂ O ₇ , 527.2752; found, 527.2757	¹ H NMR (CDCl ₃) δ 8.56 – 8.49 (m, 1H), 8.33 (d, <i>J</i> = 5.4 Hz, 1H), 7.31 – 7.22 (m, 2H), 6.99 (d, <i>J</i> = 5.4 Hz, 1H), 6.97 – 6.91 (m, 1H), 6.91 – 6.84 (m, 2H), 4.86 (dq, <i>J</i> = 10.0, 6.3 Hz, 1H), 4.64 (app dt, <i>J</i> = 10.6, 7.7 Hz, 1H), 4.35 – 4.26 (m, 1H), 3.89 (s, 3H), 2.43 – 2.28 (m, 4H), 2.26 – 2.10 (m, 2H), 1.94 – 1.80 (m, 1H), 1.68 – 1.58 (m, 1H), 1.57 – 1.41 (m, 3H), 1.38 (d, <i>J</i> = 6.3 Hz, 3H), 1.33 – 1.09 (m, 3H), 1.06 – 0.97 (m, 1H), 0.83 (app dd, <i>J</i> = 13.9, 6.6 Hz, 6H)	---
37	---	---	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₂₆ H ₃₄ FN ₂ O ₆ , 489.2395; found, 489.2404	¹ H NMR (CDCl ₃) δ 12.12 (s, 1H), 8.49 (d, <i>J</i> = 8.1 Hz, 1H), 8.02 – 7.92 (m, 1H), 7.19 (dd, <i>J</i> = 9.4, 4.7 Hz, 2H), 6.97 (t, <i>J</i> = 7.7 Hz, 2H), 6.86 (d, <i>J</i> = 5.3 Hz, 1H), 4.89 – 4.75 (m, 1H), 4.63 – 4.51 (m, 1H), 3.93 (s, 3H), 3.45 (td, <i>J</i> = 8.8, 7.9, 5.5 Hz, 1H), 3.18 (dd, <i>J</i> = 8.6, 4.9 Hz, 1H), 2.99 (td, <i>J</i> = 6.7, 4.4 Hz, 1H), 2.89 – 2.79 (m, 1H), 2.63 (dd, <i>J</i> = 14.7, 7.8 Hz, 1H), 2.38 (dt, <i>J</i> = 13.8, 7.1 Hz, 1H), 2.33 – 2.22 (m, 1H), 2.22 – 2.09 (m, 1H),	¹⁹ F NMR (CDCl ₃) δ -117.55

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				1.89 – 1.74 (m, 1H), 1.67 – 1.52 (m, 1H), 1.54 – 1.42 (m, 2H), 1.43 – 1.34 (m, 1H), 1.26 (d, <i>J</i> = 4.4 Hz, 3H), 0.98 – 0.92 (m, 1H), 0.88 (t, <i>J</i> = 7.4 Hz, 3H)	
38	---	---	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₃₀ H ₃₄ FN ₂ O ₆ , 537.2395; found, 537.2410	¹ H NMR (CDCl ₃) δ 12.08 (d, <i>J</i> = 0.6 Hz, 1H), 8.45 (d, <i>J</i> = 8.1 Hz, 1H), 7.98 (d, <i>J</i> = 5.2 Hz, 1H), 7.19 – 7.10 (m, 2H), 7.05 (d, <i>J</i> = 8.7 Hz, 2H), 6.99 – 6.88 (m, 2H), 6.86 (d, <i>J</i> = 5.3 Hz, 1H), 6.70 (d, <i>J</i> = 8.5 Hz, 2H), 4.95 (dq, <i>J</i> = 9.7, 6.4 Hz, 1H), 4.63 (dt, <i>J</i> = 10.6, 7.7 Hz, 1H), 4.17 (ddd, <i>J</i> = 8.7, 5.5, 1.7 Hz, 1H), 3.93 (s, 3H), 2.94 (dd, <i>J</i> = 14.7, 4.0 Hz, 1H), 2.74 (dd, <i>J</i> = 14.8, 7.3 Hz, 1H), 2.61 – 2.49 (m, 1H), 2.41 – 2.29 (m, 1H), 2.28 (s, 3H), 2.25 – 2.12 (m, 1H), 1.96 – 1.82 (m, 1H), 1.63 – 1.46 (m, 2H), 1.37 (d, <i>J</i> = 6.4 Hz, 3H), 1.04 (ddt, <i>J</i> = 13.6, 7.6, 2.2 Hz, 1H)	¹⁹ F NMR (CDCl ₃) δ -117.15
39	---	---	ESIMS <i>m/z</i> 314 ([M+H] ⁺)	¹ H NMR (CDCl ₃) δ 8.70 (s, 3H), 4.92 – 4.85 (m, 1H), 4.82 (dd, <i>J</i> = 10.1, 6.2 Hz, 1H), 4.05 (t, <i>J</i> = 8.5 Hz, 1H), 2.61 – 2.46 (m, 2H), 2.23 – 1.98 (m, 2H), 1.71 (t, <i>J</i> = 10.1 Hz, 2H), 1.67 – 1.53 (m, 1H), 1.36 (d, <i>J</i> = 6.3 Hz, 3H), 1.34 – 1.29 (m, 3H), 1.30 – 1.21 (m, 3H), 1.15 (dd, <i>J</i> = 6.9, 0.9 Hz, 6H), 1.04	---

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				- 0.93 (m, 1H), 0.87 (t, <i>J</i> = 7.1 Hz, 3H)	
40	47-51	---	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₃₀ H ₄₁ N ₂ O ₈ , 557.2857; found, 557.2865	¹ H NMR (CDCl ₃) δ 8.31 (d, <i>J</i> = 8.1 Hz, 1H), 8.27 (d, <i>J</i> = 5.4 Hz, 1H), 7.32 – 7.23 (m, 2H), 6.98 – 6.85 (m, 4H), 5.74 (s, 2H), 4.87 (dq, <i>J</i> = 10.0, 6.4 Hz, 1H), 4.65 (app dt, <i>J</i> = 10.7, 7.6 Hz, 1H), 4.36 – 4.27 (m, 1H), 3.90 (s, 3H), 2.42 – 2.30 (m, 1H), 2.28 – 2.11 (m, 2H), 2.07 (s, 3H), 1.96 – 1.83 (m, 1H), 1.69 – 1.37 (m, 7H), 1.35 – 1.09 (m, 3H), 1.08 – 0.98 (m, 1H), 0.84 (app dd, <i>J</i> = 13.9, 6.6 Hz, 6H)	---
41	---	---	ESIMS <i>m/z</i> 476 ([M+Na] ⁺)	¹ H NMR (CDCl ₃) δ 5.07 (d, <i>J</i> = 8.2 Hz, 1H), 4.70 (dq, <i>J</i> = 10.1, 6.3 Hz, 1H), 4.24 – 4.12 (m, 1H), 3.59 (dt, <i>J</i> = 9.0, 5.8 Hz, 1H), 3.24 (tt, <i>J</i> = 10.4, 3.8 Hz, 2H), 2.31 – 2.06 (m, 4H), 1.82 (dddd, <i>J</i> = 22.2, 12.6, 7.6, 2.9 Hz, 3H), 1.73 – 1.63 (m, 1H), 1.59 – 1.47 (m, 1H), 1.44 (s, 9H), 1.42 – 1.35 (m, 1H), 1.32 (d, <i>J</i> = 6.3 Hz, 3H), 1.30 – 1.25 (m, 3H), 1.23 – 1.10 (m, 2H), 0.94 – 0.77 (m, 5H)	¹³ C NMR (CDCl ₃) δ 173.07, 154.94, 127.27 (q, <i>J</i> = 276.1 Hz), 80.42, 79.76, 73.48, 66.54, 52.43, 46.58, 33.53, 30.83 (q, <i>J</i> = 28.9 Hz), 28.94, 28.51, 28.31, 27.79, 23.34, 22.83 (q, <i>J</i> = 2.8 Hz), 19.24, 17.74, 13.91
42	---	---	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₃₃ H ₃₈ FN ₂ O ₈ , 609.2607; found, 609.2615	¹ H NMR (CDCl ₃) δ 8.30 (d, <i>J</i> = 8.0 Hz, 1H), 8.26 (d, <i>J</i> = 5.4 Hz, 1H), 7.15 (dd, <i>J</i> = 8.5, 5.5 Hz, 2H), 7.07 – 7.01 (m, 2H), 6.97 – 6.89 (m, 3H), 6.73 – 6.66 (m, 2H), 5.73 (s, 2H), 4.93 (dq, <i>J</i> = 9.7, 6.4	¹⁹ F NMR (CDCl ₃) δ -117.21

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				Hz, 1H), 4.64 (dt, <i>J</i> = 10.5, 7.6 Hz, 1H), 4.16 (ddd, <i>J</i> = 8.7, 5.6, 1.8 Hz, 1H), 3.89 (s, 3H), 2.93 (dd, <i>J</i> = 14.9, 3.8 Hz, 1H), 2.73 (dd, <i>J</i> = 14.8, 7.2 Hz, 1H), 2.60 – 2.48 (m, 1H), 2.40 – 2.30 (m, 1H), 2.27 (s, 3H), 2.23 – 2.10 (m, 1H), 2.06 (s, 3H), 1.95 – 1.83 (m, 1H), 1.58 – 1.43 (m, 1H), 1.36 (d, <i>J</i> = 6.4 Hz, 3H), 1.32 – 1.23 (m, 1H), 1.03 (ddt, <i>J</i> = 15.9, 7.6, 2.1 Hz, 1H)	
43	---	---	HRMS–ESI <i>m/z</i> [M+H] ⁺ calcd for C ₃₀ H ₃₆ FN ₂ O ₉ , 587.2399; found, 587.2399	¹ H NMR (CDCl ₃) δ 8.34 (d, <i>J</i> = 8.0 Hz, 1H), 8.27 (d, <i>J</i> = 5.3 Hz, 1H), 7.14 (dd, <i>J</i> = 8.5, 5.5 Hz, 2H), 7.01 – 6.91 (m, 3H), 5.74 (s, 2H), 4.93 – 4.77 (m, 2H), 4.64 (dt, <i>J</i> = 10.7, 7.4 Hz, 1H), 3.91 (s, 3H), 2.76 (dd, <i>J</i> = 14.0, 5.5 Hz, 1H), 2.57 – 2.29 (m, 3H), 2.21 – 2.09 (m, 1H), 2.07 (s, 3H), 1.86 – 1.72 (m, 1H), 1.65 – 1.46 (m, 1H), 1.35 (d, <i>J</i> = 6.3 Hz, 3H), 1.33 – 1.21 (m, 2H), 1.06 (ddt, <i>J</i> = 16.3, 7.6, 2.2 Hz, 1H), 0.83 – 0.77 (m, 2H), 0.77 – 0.69 (m, 2H)	¹⁹ F NMR (CDCl ₃) δ -117.20
44	---	(Thin Film) 3385, 2938, 2873, 1772, 1728	HRMS–ESI <i>m/z</i> [M+H] ⁺ calcd for C ₂₆ H ₃₈ N ₂ O ₈ , 507.2701; found, 507.2705	¹ H NMR (CDCl ₃) δ 8.54 (d, <i>J</i> = 8.2 Hz, 1H), 8.34 (d, <i>J</i> = 5.4 Hz, 1H), 7.00 (d, <i>J</i> = 5.5 Hz, 1H), 4.89 (ddd, <i>J</i> = 9.0, 5.7, 1.9 Hz, 1H), 4.83 (dq, <i>J</i> = 10.0, 6.4 Hz, 1H), 4.62 (ddd, <i>J</i> = 10.7, 8.4, 7.2 Hz, 1H), 3.90 (s, 3H), 2.53 (hept, <i>J</i>	¹³ C NMR (CDCl ₃) δ 176.47, 172.23, 168.89, 162.42, 159.42, 146.71, 141.42, 137.46, 109.78, 74.50, 73.29, 56.28, 51.06, 45.47, 34.28, 33.09,

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				= 7.0 Hz, 1H), 2.40 (s, 3H), 2.37 – 2.30 (m, 1H), 2.19 – 2.02 (m, 2H), 1.86 – 1.66 (m, 2H), 1.63 – 1.48 (m, 1H), 1.41 – 1.30 (m, 5H), 1.27 (ddt, <i>J</i> = 16.9, 9.5, 5.5 Hz, 3H), 1.17 (s, 6H), 1.05 (ddt, <i>J</i> = 16.1, 7.9, 2.5 Hz, 1H), 0.88 (t, <i>J</i> = 7.1 Hz, 3H), 0.91 – 0.83 (m, 1H)	30.88, 28.15, 27.44, 23.30, 20.74, 19.19, 19.08, 18.94, 18.09, 13.87
45	---	---	ESIMS <i>m/z</i> 442 ([M+Na] ⁺)	¹ H NMR (CDCl ₃) δ 7.31 – 7.13 (m, 5H), 5.07 (d, <i>J</i> = 8.2 Hz, 1H), 4.85 – 4.72 (m, 1H), 4.24 – 4.12 (m, 1H), 3.43 (app dt, <i>J</i> = 8.5, 6.6 Hz, 1H), 3.16 (ddd, <i>J</i> = 8.4, 5.4, 1.6 Hz, 1H), 3.03 – 2.93 (m, 1H), 2.89 (dd, <i>J</i> = 14.7, 4.0 Hz, 1H), 2.64 (dd, <i>J</i> = 14.7, 7.5 Hz, 1H), 2.34 – 2.19 (m, 2H), 2.18 – 2.05 (m, 1H), 1.80 – 1.67 (m, 1H), 1.57 – 1.41 (m, 12H), 1.29 – 1.11 (m, 4H), 0.92 – 0.79 (m, 4H)	¹³ C NMR (CDCl ₃) δ 173.03, 154.93, 140.77, 129.11, 128.25, 125.85, 81.19, 79.73, 74.09, 70.16, 52.48, 48.68, 36.08, 33.65, 28.75, 28.33, 23.24, 20.22, 17.88, 10.84
46	---	---	ESIMS <i>m/z</i> 364 ([M+H] ⁺)	---	---
47	---	(Thin Film) 3368, 2937, 2870, 1736, 1649	ESIMS <i>m/z</i> 485 ([M+H] ⁺)	¹ H NMR (CDCl ₃) δ 12.14 (d, <i>J</i> = 0.6 Hz, 1H), 8.49 (d, <i>J</i> = 8.1 Hz, 1H), 7.99 (d, <i>J</i> = 5.2 Hz, 1H), 7.39 – 7.27 (m, 5H), 6.86 (dd, <i>J</i> = 5.2, 0.7 Hz, 1H), 4.76 (dq, <i>J</i> = 10.1, 6.3 Hz, 1H), 4.66 – 4.54 (m, 2H), 4.32 (d, <i>J</i> = 11.5 Hz, 1H), 3.93 (s, 3H), 3.43 (ddd, <i>J</i> = 9.1, 5.4, 1.6 Hz, 1H), 2.39 (ddd, <i>J</i> = 12.5, 7.6, 6.4	---

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				Hz, 1H), 2.26 (dddd, <i>J</i> = 15.7, 10.1, 8.0, 5.2 Hz, 1H), 2.03 – 1.93 (m, 1H), 1.92 – 1.78 (m, 1H), 1.71 – 1.51 (m, 2H), 1.46 – 1.36 (m, 2H), 1.33 (d, <i>J</i> = 6.3 Hz, 3H), 1.30 – 1.15 (m, 2H), 1.16 – 1.04 (m, 2H), 0.99 – 0.88 (m, 1H), 0.85 (t, <i>J</i> = 7.2 Hz, 3H)	
48	196-198	---	ESIMS <i>m/z</i> 395 ([M+CH ₃ CN] ⁺)	¹ H NMR (CD ₃ OD) δ 4.78 (ddd, <i>J</i> = 12.7, 8.2, 4.9 Hz, 1H), 3.90 (dd, <i>J</i> = 10.7, 7.4 Hz, 1H), 3.66 (dt, <i>J</i> = 9.7, 5.9 Hz, 1H), 3.36 – 3.29 (m, 2H), 2.23 (m, 4H), 1.91 – 1.81 (m, 1H), 1.81 – 1.68 (m, 3H), 1.67 – 1.51 (m, 2H), 1.51 – 1.38 (m, 2H), 1.39 – 1.28 (m, 5H), 1.27 – 1.17 (m, 1H), 0.92 (t, <i>J</i> = 7.0 Hz, 3H), 0.89 – 0.80 (m, 2H)	---
49	59-64	---	HRMS–ESI <i>m/z</i> [M+H] ⁺ calcd for C ₂₆ H ₃₅ N ₂ O ₆ , 471.2490; found, 471.2492	¹ H NMR (CDCl ₃) δ 12.12 (d, <i>J</i> = 0.6 Hz, 1H), 8.49 (d, <i>J</i> = 8.1 Hz, 1H), 7.99 (d, <i>J</i> = 5.2 Hz, 1H), 7.33 – 7.14 (m, 5H), 6.86 (d, <i>J</i> = 5.2 Hz, 1H), 4.85 (dq, <i>J</i> = 9.8, 6.4 Hz, 1H), 4.59 (app dt, <i>J</i> = 10.6, 7.6 Hz, 1H), 3.93 (s, 3H), 3.45 (app dt, <i>J</i> = 8.6, 6.5 Hz, 1H), 3.21 (ddd, <i>J</i> = 8.7, 5.3, 1.6 Hz, 1H), 3.00 (app dt, <i>J</i> = 8.7, 6.6 Hz, 1H), 2.91 (dd, <i>J</i> = 14.7, 4.0 Hz, 1H), 2.66 (dd, <i>J</i> = 14.7, 7.6 Hz, 1H), 2.44 – 2.27 (m, 2H), 2.25 – 2.10 (m, 1H), 1.83 (td, <i>J</i> =	---

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				13.0, 7.5 Hz, 1H), 1.67 – 1.32 (m, 4H), 1.27 (d, <i>J</i> = 6.4 Hz, 3H), 0.98 – 0.84 (m, 4H)	
50	---	(Thin Film) 3379, 2938, 2873, 1729, 1676	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₂₇ H ₄₀ N ₂ O ₉ , 537.2807; found, 537.2814	¹ H NMR (CDCl ₃) δ 8.33 (d, <i>J</i> = 8.1 Hz, 1H), 8.28 (d, <i>J</i> = 5.4 Hz, 1H), 6.95 (d, <i>J</i> = 5.4 Hz, 1H), 5.74 (s, 2H), 4.90 (ddd, <i>J</i> = 9.0, 5.6, 1.9 Hz, 1H), 4.83 (dq, <i>J</i> = 10.0, 6.4 Hz, 1H), 4.63 (ddd, <i>J</i> = 10.7, 8.1, 7.1 Hz, 1H), 3.91 (s, 3H), 2.54 (hept, <i>J</i> = 7.0 Hz, 1H), 2.43 – 2.32 (m, 1H), 2.14 – 2.09 (m, 1H), 2.07 (s, 3H), 1.82 (dtd, <i>J</i> = 17.5, 9.7, 8.7, 4.9 Hz, 1H), 1.65 – 1.50 (m, 1H), 1.38 (d, <i>J</i> = 1.8 Hz, 1H), 1.35 (d, <i>J</i> = 6.3 Hz, 4H), 1.33 – 1.23 (m, 5H), 1.17 (dd, <i>J</i> = 6.9, 0.8 Hz, 6H), 1.10 – 1.01 (m, 1H), 0.88 (t, <i>J</i> = 7.1 Hz, 3H), 0.90 – 0.83 (m, 1H)	---
51	97-100	---	ESIMS <i>m/z</i> 470 ([M+Na] ⁺)	¹ H NMR (CDCl ₃) δ 7.37 – 7.23 (m, 5H), 5.12 (d, <i>J</i> = 8.3 Hz, 1H), 4.74 – 4.65 (m, 1H), 4.59 (d, <i>J</i> = 11.5 Hz, 1H), 4.30 (d, <i>J</i> = 11.5 Hz, 1H), 4.25 – 4.13 (m, 1H), 3.43 – 3.35 (m, 1H), 2.31 – 2.14 (m, 2H), 2.00 – 1.88 (m, 1H), 1.82 – 1.68 (m, 1H), 1.63 – 1.50 (m, 2H), 1.49 – 1.33 (m, 11H), 1.30 (d, <i>J</i> = 6.3 Hz, 3H), 1.25 – 1.11 (m, 1H), 1.08 – 0.91 (m, 2H), 0.90 – 0.78 (m, 7H)	---
52	---	(Thin	ESIMS	¹ H NMR (CDCl ₃) δ 8.31	---

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
		Film) 3379, 2939, 2873, 1740, 1676	<i>m/z</i> 577 ([M+H] ⁺)	(d, <i>J</i> = 8.1 Hz, 1H), 8.28 (d, <i>J</i> = 5.4 Hz, 1H), 6.95 (d, <i>J</i> = 5.4 Hz, 1H), 5.74 (s, 2H), 4.74 (dq, <i>J</i> = 10.1, 6.3 Hz, 1H), 4.61 (dt, <i>J</i> = 10.7, 7.6 Hz, 1H), 3.91 (s, 3H), 3.60 (dt, <i>J</i> = 9.1, 5.9 Hz, 1H), 3.32 – 3.20 (m, 2H), 2.39 (ddd, <i>J</i> = 12.5, 7.6, 6.3 Hz, 1H), 2.29 – 2.09 (m, 4H), 2.07 (s, 3H), 1.95 – 1.86 (m, 1H), 1.86 – 1.70 (m, 3H), 1.60 – 1.46 (m, 2H), 1.45 – 1.37 (m, 1H), 1.35 (m, 7H), 1.24 – 1.13 (m, 1H), 0.90 (t, <i>J</i> = 7.0 Hz, 3H)	
53	---	---	ESIMS <i>m/z</i> 334.4 ([M-Cl] ⁺)	---	---
54	---	---	ESIMS <i>m/z</i> 334 ([M+H] ⁺)	---	---
55	83-86	---	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₃₂ H ₃₆ N ₂ O ₇ , 560.2523; found, 560.2523	¹ H NMR (CDCl ₃) δ 8.51 (d, <i>J</i> = 7.0 Hz, 1H), 8.32 (d, <i>J</i> = 5.4 Hz, 1H), 7.30 – 7.11 (m, 5H), 7.04 (d, <i>J</i> = 8.3 Hz, 2H), 6.99 (d, <i>J</i> = 5.5 Hz, 1H), 6.71 (d, <i>J</i> = 8.5 Hz, 2H), 4.94 (dq, <i>J</i> = 9.9, 6.3 Hz, 1H), 4.63 (dt, <i>J</i> = 10.5, 7.8 Hz, 1H), 4.23 – 4.12 (m, 1H), 3.89 (s, 3H), 3.00 (dd, <i>J</i> = 14.8, 3.3 Hz, 1H), 2.73 (dd, <i>J</i> = 14.8, 7.4 Hz, 1H), 2.63 – 2.54 (m, 1H), 2.39 (s, 3H), 2.37 – 2.29 (m, 2H), 2.27 (s, 3H), 2.19 – 2.11 (m, 1H), 1.94 – 1.82 (m, 1H), 1.78 – 1.63 (m, 1H), 1.59 – 1.47 (m, 1H), 1.35	---

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				(d, <i>J</i> = 6.4 Hz, 3H)	
56	---	---	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₃₀ H ₃₈ N ₂ O ₈ , 554.2628; found, 554.2644	¹ H NMR (CDCl ₃) δ 8.29 (dd, <i>J</i> = 15.0, 6.6 Hz, 2H), 7.36 – 7.12 (m, 5H), 6.94 (d, <i>J</i> = 5.4 Hz, 1H), 5.74 (s, 2H), 4.91 – 4.73 (m, 1H), 4.61 (dt, <i>J</i> = 10.6, 7.6 Hz, 1H), 3.90 (s, 3H), 3.35 – 3.12 (m, 2H), 2.99 (dd, <i>J</i> = 9.8, 6.4 Hz, 1H), 2.91 (dd, <i>J</i> = 14.6, 4.2 Hz, 1H), 2.70 (dd, <i>J</i> = 14.7, 7.4 Hz, 1H), 2.48 – 2.26 (m, 2H), 2.14 – 2.09 (m, 1H), 2.07 (s, 3H), 1.91 – 1.76 (m, 1H), 1.58 (dt, <i>J</i> = 15.3, 7.0 Hz, 1H), 1.45 – 1.30 (m, 1H), 1.28 (d, <i>J</i> = 6.4 Hz, 3H), 0.92 (dd, <i>J</i> = 14.7, 7.7 Hz, 2H), 0.62 – 0.40 (m, 2H), 0.16 – 0.07 (m, 2H)	¹³ C NMR (CDCl ₃) δ 172.51, 170.27, 162.96, 160.26, 145.72, 140.65, 129.17, 128.28, 125.88, 109.56, 89.56, 80.83, 74.21, 73.08, 56.18, 51.39, 48.55, 36.11, 33.06, 28.72, 20.87, 20.20, 18.04, 14.20, 10.78, 3.10, 2.82
57	---	---	ESIMS <i>m/z</i> 456 ([M+Na] ⁺)	¹ H NMR (CDCl ₃) δ 7.28 – 7.24 (m, 2H), 6.98 – 6.90 (m, 1H), 6.90 – 6.83 (m, 2H), 5.04 (d, <i>J</i> = 8.3 Hz, 1H), 4.83 (dq, <i>J</i> = 9.9, 6.4 Hz, 1H), 4.32 – 4.17 (m, 2H), 2.28 – 2.07 (m, 3H), 1.87 – 1.73 (m, 1H), 1.67 – 1.56 (m, 1H), 1.52 – 1.42 (m, 12H), 1.38 (d, <i>J</i> = 6.3 Hz, 3H), 1.30 – 1.05 (m, 3H), 1.01 – 0.87 (m, 1H), 0.83 (app dd, <i>J</i> = 14.0, 6.6 Hz, 6H)	¹³ C NMR (CDCl ₃) δ 173.05, 157.77, 154.93, 129.51, 121.01, 116.37, 79.67, 78.39, 73.18, 52.46, 46.53, 34.45, 33.38, 29.62, 28.55, 28.32, 26.15, 22.54, 22.41, 19.28, 17.78
58	---	(Thin Film) 3367, 2951, 2869, 1736,	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₂₈ H ₃₉ N ₂ O ₆ , 499.2803;	¹ H NMR (CDCl ₃) δ 12.14 (s, 1H), 8.49 (d, <i>J</i> = 8.1 Hz, 1H), 7.99 (d, <i>J</i> = 5.2 Hz, 1H), 7.39 – 7.24 (m, 5H), 6.86 (d, <i>J</i> = 5.2 Hz, 1H), 4.76 (dq, <i>J</i> = 10.0,	---

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
		1649, 1527, 1264	found, 499.2814	6.3 Hz, 1H), 4.65 – 4.54 (m, 2H), 4.32 (d, <i>J</i> = 11.5 Hz, 1H), 3.93 (s, 3H), 3.44 (ddd, <i>J</i> = 8.8, 5.2, 1.6 Hz, 1H), 2.45 – 2.33 (m, 1H), 2.33 – 2.19 (m, 1H), 2.05 – 1.93 (m, 1H), 1.92 – 1.78 (m, 1H), 1.71 – 1.52 (m, 2H), 1.47 – 1.30 (m, 6H), 1.13 – 0.88 (m, 3H), 0.84 (app dd, <i>J</i> = 10.8, 6.6 Hz, 6H)	
59	---	---	ESIMS <i>m/z</i> 300 ([M+H] ⁺)	---	---
60	68-71	---	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₃₀ H ₃₄ N ₂ O ₆ , 518.2417; found, 518.2417	¹ H NMR (CDCl ₃) δ 12.10 (s, 1H), 8.47 (d, <i>J</i> = 8.1 Hz, 1H), 7.97 (d, <i>J</i> = 5.2 Hz, 1H), 7.36 – 7.12 (m, 5H), 7.04 (d, <i>J</i> = 8.2 Hz, 2H), 6.84 (d, <i>J</i> = 5.2 Hz, 1H), 6.72 (d, <i>J</i> = 8.5 Hz, 2H), 5.03 – 4.89 (m, 1H), 4.62 (dt, <i>J</i> = 10.6, 7.7 Hz, 1H), 4.24 – 4.14 (m, 1H), 3.91 (s, 3H), 3.01 (dd, <i>J</i> = 14.8, 3.3 Hz, 1H), 2.74 (dd, <i>J</i> = 14.8, 7.5 Hz, 1H), 2.64 – 2.56 (m, 1H), 2.35 (dt, <i>J</i> = 13.7, 7.1 Hz, 1H), 2.27 (s, 3H), 2.21 – 2.14 (m, 1H), 1.99 – 1.82 (m, 1H), 1.53 (dq, <i>J</i> = 15.8, 7.9 Hz, 1H), 1.37 (d, <i>J</i> = 6.4 Hz, 3H), 1.30 – 1.20 (m, 1H), 1.02 (dd, <i>J</i> = 15.9, 7.5 Hz, 1H)	---
61	---	---	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₃₀ H ₃₈ FN ₂ O ₈ ,	¹ H NMR (CDCl ₃) δ 8.33 (d, <i>J</i> = 8.0 Hz, 1H), 8.27 (d, <i>J</i> = 5.3 Hz, 1H), 7.21 (dd, <i>J</i> = 8.4, 5.5 Hz, 2H), 7.00 – 6.93 (m, 3H), 5.74	¹⁹ F NMR (CDCl ₃) δ -117.58

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
			573.2607; found, 573.2621	(s, 2H), 4.81 (dq, <i>J</i> = 10.0, 6.4 Hz, 1H), 4.61 (dt, <i>J</i> = 10.6, 7.5 Hz, 1H), 3.90 (s, 3H), 3.21 (ddd, <i>J</i> = 9.9, 6.5, 3.3 Hz, 2H), 3.00 (dd, <i>J</i> = 9.8, 6.3 Hz, 1H), 2.85 (dd, <i>J</i> = 14.7, 4.4 Hz, 1H), 2.67 (dd, <i>J</i> = 14.7, 7.3 Hz, 1H), 2.39 (dt, <i>J</i> = 13.7, 7.0 Hz, 1H), 2.34 – 2.25 (m, 1H), 2.19 – 2.08 (m, 1H), 2.06 (s, 3H), 1.90 – 1.77 (m, 1H), 1.64 – 1.48 (m, 1H), 1.42 – 1.29 (m, 1H), 1.27 (d, <i>J</i> = 6.3 Hz, 3H), 0.99 – 0.81 (m, 2H), 0.53 – 0.42 (m, 2H), 0.20 – 0.08 (m, 2H)	
62	---	---	HRMS–ESI <i>m/z</i> [M+H] ⁺ calcd for C ₂₇ H ₃₆ N ₂ O ₆ , 484.2573; found, 484.2571	¹ H NMR (CDCl ₃) δ 12.13 (s, 1H), 8.49 (d, <i>J</i> = 8.1 Hz, 1H), 7.98 (d, <i>J</i> = 5.2 Hz, 1H), 7.41 – 7.07 (m, 5H), 6.85 (d, <i>J</i> = 5.2 Hz, 1H), 4.94 – 4.74 (m, 1H), 4.58 (dt, <i>J</i> = 10.7, 7.6 Hz, 1H), 3.92 (s, 3H), 3.27 (dd, <i>J</i> = 8.4, 6.5 Hz, 1H), 3.23 – 3.15 (m, 1H), 2.95 (dd, <i>J</i> = 14.7, 3.4 Hz, 1H), 2.85 (dd, <i>J</i> = 8.4, 6.3 Hz, 1H), 2.62 (dd, <i>J</i> = 14.7, 7.9 Hz, 1H), 2.44 – 2.27 (m, 2H), 2.25 – 2.09 (m, 1H), 1.88 – 1.70 (m, 2H), 1.65 – 1.55 (m, 1H), 1.40 (q, <i>J</i> = 11.7 Hz, 1H), 1.25 (d, <i>J</i> = 6.4 Hz, 3H), 0.99 – 0.91 (m, 1H), 0.89 (dd, <i>J</i> = 6.7, 1.8 Hz, 6H)	¹³ C NMR (CDCl ₃) δ 171.89, 168.63, 155.34, 148.72, 140.87, 140.48, 130.44, 129.10, 128.30, 125.88, 109.45, 81.15, 75.39, 74.58, 56.06, 51.08, 48.78, 36.05, 33.02, 28.87, 28.51, 20.22, 19.62, 17.85
63	---	(Thin Film) 3380,	HRMS–ESI <i>m/z</i> [M+H] ⁺	¹ H NMR (CDCl ₃) δ 8.53 (d, <i>J</i> = 8.4 Hz, 1H), 8.34 (d, <i>J</i> = 5.4 Hz, 1H), 7.42 –	---

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
		2937, 2870, 1771, 1677	calcd for C ₂₉ H ₃₉ N ₂ O ₇ , 527.2752; found, 527.2758	7.27 (m, 5H), 7.00 (d, <i>J</i> = 5.5 Hz, 1H), 4.73 (dq, <i>J</i> = 10.2, 6.3 Hz, 1H), 4.67 – 4.55 (m, 2H), 4.31 (d, <i>J</i> = 11.5 Hz, 1H), 3.91 (s, 3H), 3.42 (dd, <i>J</i> = 8.6, 4.9 Hz, 1H), 2.40 (s, 4H), 2.32 – 2.19 (m, 1H), 2.01 – 1.92 (m, 1H), 1.88 – 1.76 (m, 1H), 1.66 – 1.50 (m, 3H), 1.44 – 1.33 (m, 1H), 1.31 (d, <i>J</i> = 6.3 Hz, 3H), 1.28 – 1.16 (m, 2H), 1.14 – 1.04 (m, 2H), 0.97 – 0.87 (m, 1H), 0.84 (t, <i>J</i> = 7.2 Hz, 3H)	
64	---	(Thin Film) 3369, 2938, 2873, 1728, 1649	ESIMS <i>m/z</i> 465 ([M+H] ⁺)	¹ H NMR (CDCl ₃) δ 12.10 (d, <i>J</i> = 0.6 Hz, 1H), 8.51 (d, <i>J</i> = 8.2 Hz, 1H), 7.98 (d, <i>J</i> = 5.2 Hz, 1H), 6.88 (dd, <i>J</i> = 5.3, 0.6 Hz, 1H), 4.96 – 4.80 (m, 2H), 4.61 (ddd, <i>J</i> = 10.8, 8.2, 7.1 Hz, 1H), 3.94 (s, 3H), 2.54 (p, <i>J</i> = 7.0 Hz, 1H), 2.42 – 2.31 (m, 1H), 2.16 – 2.04 (m, 2H), 2.02 – 1.77 (m, 2H), 1.67 – 1.52 (m, 1H), 1.49 – 1.39 (m, 1H), 1.37 (d, <i>J</i> = 6.3 Hz, 3H), 1.36 – 1.21 (m, 5H), 1.17 (dd, <i>J</i> = 7.0, 0.8 Hz, 6H), 1.07 (ddt, <i>J</i> = 16.1, 7.7, 2.3 Hz, 1H), 0.88 (t, <i>J</i> = 7.1 Hz, 3H)	---
65	---	---	HRMS–ESI <i>m/z</i> [M+H] ⁺ calcd for C ₃₀ H ₄₀ N ₂ O ₈ , 556.2785; found,	¹ H NMR (CDCl ₃) δ 8.29 (dd, <i>J</i> = 14.8, 6.6 Hz, 2H), 7.33 – 7.12 (m, 5H), 6.94 (d, <i>J</i> = 4.9 Hz, 1H), 5.73 (s, 2H), 4.91 – 4.75 (m, 1H), 4.60 (dt, <i>J</i> = 10.5, 7.6 Hz, 1H), 3.90 (s, 3H),	¹³ C NMR (CDCl ₃) δ 172.52, 170.28, 162.96, 160.25, 145.73, 140.94, 129.11, 128.27, 125.84, 109.56, 89.54, 81.21,

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
			556.2801	3.27 (dd, <i>J</i> = 8.4, 6.6 Hz, 1H), 3.18 (dd, <i>J</i> = 8.4, 4.4 Hz, 1H), 2.95 (dd, <i>J</i> = 14.7, 3.2 Hz, 1H), 2.84 (dd, <i>J</i> = 8.4, 6.4 Hz, 1H), 2.61 (dd, <i>J</i> = 14.7, 7.9 Hz, 1H), 2.43 – 2.29 (m, 2H), 2.19 – 2.10 (m, 1H), 2.06 (s, 3H), 1.88 – 1.67 (m, 3H), 1.62 – 1.57 (m, 1H), 1.35 (q, <i>J</i> = 11.6 Hz, 1H), 1.24 (d, <i>J</i> = 6.4 Hz, 3H), 0.88 (dd, <i>J</i> = 6.7, 1.1 Hz, 6H) ¹³ C NMR (CDCl ₃) δ 172.52, 170.28, 162.96, 160.25, 145.73, 140.94, 129.11, 128.27, 125.84, 109.56, 89.54, 81.21, 77.26, 75.38, 74.30, 60.39, 56.18, 51.41, 48.78, 36.04, 33.13, 28.86, 28.63, 20.87, 20.21, 19.60, 17.92	77.26, 75.38, 74.30, 60.39, 56.18, 51.41, 48.78, 36.04, 33.13, 28.86, 28.63, 20.87, 20.21, 19.60, 17.92
66	---	---	ESIMS <i>m/z</i> 320 ([M+H] ⁺)	¹ H NMR (CD ₃ OD) δ 7.30 – 7.22 (m, 2H), 6.95 – 6.88 (m, 3H), 4.97 – 4.89 (m, 1H), 4.40 (ddd, <i>J</i> = 8.5, 5.6, 1.7 Hz, 1H), 3.97 (dd, <i>J</i> = 10.7, 7.5 Hz, 1H), 2.26 (tt, <i>J</i> = 9.8, 6.6, 5.8, 1.8 Hz, 2H), 2.21 – 2.12 (m, 1H), 1.95 – 1.83 (m, 1H), 1.68 – 1.45 (m, 3H), 1.42 (d, <i>J</i> = 6.4 Hz, 4H), 1.40 – 1.35 (m, 1H), 1.28 (qdd, <i>J</i> = 9.6, 5.2, 2.0 Hz, 3H), 0.99 (ddt, <i>J</i> = 16.2, 7.7, 2.1 Hz, 1H), 0.85 (t, <i>J</i> = 7.0 Hz, 3H)	¹³ C NMR (CD ₃ OD) δ 171.05, 159.10, 130.68, 122.17, 117.20, 79.56, 76.15, 52.61, 47.90, 31.47, 30.48, 29.55, 29.08, 24.23, 19.60, 18.43, 14.22
67	---	---	HRMS–ESI <i>m/z</i> [M+H] ⁺	¹ H NMR (CDCl ₃) δ 12.13 (s, 1H), 8.49 (d, <i>J</i> = 8.1 Hz, 1H), 7.98 (d, <i>J</i> = 5.2	¹³ C NMR (CDCl ₃) δ 171.88, 168.65, 155.33, 148.71,

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
			calcd for C ₂₇ H ₃₄ N ₂ O ₆ , 482.2417; found, 482.2424	Hz, 1H), 7.36 – 7.10 (m, 5H), 6.86 (d, <i>J</i> = 5.2 Hz, 1H), 4.95 – 4.73 (m, 1H), 4.59 (dt, <i>J</i> = 10.7, 7.6 Hz, 1H), 3.93 (s, 3H), 3.26 – 3.15 (m, 2H), 2.99 (dd, <i>J</i> = 9.8, 6.4 Hz, 1H), 2.91 (dd, <i>J</i> = 14.7, 4.2 Hz, 1H), 2.70 (dd, <i>J</i> = 14.7, 7.4 Hz, 1H), 2.46 – 2.29 (m, 2H), 2.23 – 2.06 (m, 1H), 1.91 – 1.80 (m, 1H), 1.64 – 1.53 (m, 1H), 1.39 (q, <i>J</i> = 11.4 Hz, 1H), 1.29 (d, <i>J</i> = 6.4 Hz, 3H), 0.92 (dd, <i>J</i> = 15.0, 7.8 Hz, 2H), 0.52 – 0.41 (m, 2H), 0.19 – 0.05 (m, 2H)	140.58, 130.42, 129.15, 128.30, 125.92, 109.46, 80.76, 74.50, 73.09, 56.06, 51.07, 48.55, 36.11, 32.93, 28.61, 20.21, 17.97, 10.78, 3.11, 2.83
68	---	---	ESIMS <i>m/z</i> 386 ([M+H] ⁺)	---	---
69	---	---	ESIMS <i>m/z</i> 332.4 ([M-Cl] ⁺)	---	---
70	56-61	---	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₂₈ H ₃₇ N ₂ O ₇ , 513.2595; found, 513.2601	¹ H NMR (CDCl ₃) δ 8.53 (d, <i>J</i> = 8.3 Hz, 1H), 8.33 (d, <i>J</i> = 5.4 Hz, 1H), 7.32 – 7.14 (m, 5H), 6.99 (d, <i>J</i> = 5.5 Hz, 1H), 4.82 (dq, <i>J</i> = 9.8, 6.4 Hz, 1H), 4.59 (ddd, <i>J</i> = 10.6, 8.3, 7.2 Hz, 1H), 3.90 (s, 3H), 3.44 (app dt, <i>J</i> = 8.6, 6.5 Hz, 1H), 3.19 (ddd, <i>J</i> = 8.6, 5.3, 1.6 Hz, 1H), 2.99 (app dt, <i>J</i> = 8.7, 6.6 Hz, 1H), 2.90 (dd, <i>J</i> = 14.7, 4.0 Hz, 1H), 2.65 (dd, <i>J</i> = 14.7, 7.5 Hz, 1H), 2.43 – 2.25 (m, 5H), 2.22 – 2.07 (m, 1H), 1.86 – 1.73 (m, 1H), 1.63 – 1.40 (m, 3H),	---

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				1.40 – 1.21 (m, 4H), 0.98 – 0.83 (m, 4H)	
71	---	(Thin Film) 3380, 2937, 2873, 1729, 1676	HRMS–ESI <i>m/z</i> [M+H] ⁺ calcd for C ₂₉ H ₄₄ N ₂ O ₁₀ , 581.3069; found, 581.3073	¹ H NMR (CDCl ₃) δ 8.34 (d, <i>J</i> = 8.1 Hz, 1H), 8.28 (d, <i>J</i> = 5.4 Hz, 1H), 6.95 (d, <i>J</i> = 5.4 Hz, 1H), 5.82 (s, 2H), 4.90 (ddd, <i>J</i> = 9.1, 5.6, 1.9 Hz, 1H), 4.83 (dq, <i>J</i> = 10.0, 6.4 Hz, 1H), 4.62 (ddd, <i>J</i> = 10.7, 8.1, 7.1 Hz, 1H), 4.10 (s, 2H), 3.90 (s, 3H), 3.59 (q, <i>J</i> = 7.0 Hz, 2H), 2.53 (hept, <i>J</i> = 7.0 Hz, 1H), 2.36 (dt, <i>J</i> = 13.7, 6.8 Hz, 1H), 2.21 – 2.03 (m, 2H), 1.87 – 1.76 (m, 1H), 1.60 – 1.51 (m, 1H), 1.41 – 1.32 (m, 5H), 1.32 – 1.25 (m, 3H), 1.23 (t, <i>J</i> = 7.0 Hz, 4H), 1.17 (dd, <i>J</i> = 7.0, 0.8 Hz, 7H), 1.05 (ddt, <i>J</i> = 15.9, 7.5, 2.2 Hz, 1H), 0.88 (t, <i>J</i> = 7.1 Hz, 3H)	---
72	---	---	HRMS–ESI <i>m/z</i> [M+H] ⁺ calcd for C ₂₉ H ₃₈ N ₂ O ₇ , 526.2679; found, 526.2693	¹ H NMR (CDCl ₃) δ 8.52 (d, <i>J</i> = 7.0 Hz, 1H), 8.33 (d, <i>J</i> = 5.4 Hz, 1H), 7.35 – 7.13 (m, 5H), 6.99 (d, <i>J</i> = 5.5 Hz, 1H), 4.90 – 4.76 (m, 1H), 4.59 (dt, <i>J</i> = 10.6, 7.6 Hz, 1H), 3.90 (s, 3H), 3.26 (dd, <i>J</i> = 8.4, 6.5 Hz, 1H), 3.21 – 3.14 (m, 1H), 2.95 (dd, <i>J</i> = 14.7, 3.4 Hz, 1H), 2.84 (dd, <i>J</i> = 8.4, 6.4 Hz, 1H), 2.61 (dd, <i>J</i> = 14.7, 7.9 Hz, 1H), 2.39 (s, 3H), 2.37 – 2.28 (m, 2H), 2.20 – 2.10 (m, 1H), 1.84 – 1.51 (m, 4H), 1.39 – 1.26 (m, 1H), 1.22 (d, <i>J</i> = 6.4 Hz, 3H), 0.88	¹³ C NMR (CDCl ₃) δ 172.42, 168.93, 162.38, 159.43, 146.68, 141.54, 140.93, 137.47, 129.12, 128.28, 125.84, 109.74, 81.21, 75.40, 74.32, 56.28, 51.14, 48.78, 36.04, 33.33, 28.86, 28.65, 20.75, 20.20, 19.61, 17.89

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				(d, <i>J</i> = 6.7 Hz, 6H)	
73	---	(Thin Film) 3379, 2937, 2870, 1738, 1676	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₂₄ H ₃₆ N ₂ O ₆ , 521.2857; found, 521.2872	¹ H NMR (CDCl ₃) δ 8.38 – 8.22 (m, 2H), 6.94 (d, <i>J</i> = 5.4 Hz, 1H), 5.74 (s, 2H), 4.74 (dq, <i>J</i> = 10.0, 6.3 Hz, 1H), 4.61 (dt, <i>J</i> = 10.7, 7.6 Hz, 1H), 3.91 (s, 3H), 3.39 – 3.26 (m, 2H), 3.12 (dd, <i>J</i> = 10.0, 6.7 Hz, 1H), 2.38 (dt, <i>J</i> = 13.8, 7.0 Hz, 1H), 2.19 – 2.09 (m, 1H), 2.07 (s, 3H), 2.00 – 1.90 (m, 1H), 1.86 – 1.73 (m, 1H), 1.68 – 1.49 (m, 3H), 1.47 – 1.35 (m, 1H), 1.33 (d, <i>J</i> = 6.4 Hz, 3H), 1.32 – 1.28 (m, 3H), 1.24 – 1.14 (m, 1H), 1.10 – 0.99 (m, 1H), 0.91 (t, <i>J</i> = 7.0 Hz, 3H), 0.88 – 0.84 (m, 1H), 0.59 – 0.46 (m, 2H), 0.18 (qd, <i>J</i> = 4.6, 1.2 Hz, 2H)	---
74	46-50	---	HRMS-ESI <i>m/z</i> [M+H] ⁺ calcd for C ₂₆ H ₄₁ N ₂ O ₇ , 493.2908; found, 493.2936	¹ H NMR (CDCl ₃) δ 8.53 (d, <i>J</i> = 8.2 Hz, 1H), 8.33 (d, <i>J</i> = 5.4 Hz, 1H), 7.00 (d, <i>J</i> = 5.4 Hz, 1H), 4.74 (dq, <i>J</i> = 9.9, 6.3 Hz, 1H), 4.65 – 4.53 (m, 1H), 3.90 (s, 3H), 3.52 (app dt, <i>J</i> = 8.9, 6.4 Hz, 1H), 3.31 – 3.22 (m, 1H), 3.15 (app dt, <i>J</i> = 8.9, 6.6 Hz, 1H), 2.43 – 2.30 (m, 4H), 2.22 – 2.07 (m, 1H), 1.96 – 1.84 (m, 1H), 1.83 – 1.69 (m, 1H), 1.68 – 0.98 (m, 12H), 0.96 – 0.84 (m, 10H)	---
75	---	---	ESIMS <i>m/z</i> 486 ([M+Na] ⁺)	¹ H NMR (CDCl ₃) δ 7.13 (dd, <i>J</i> = 8.5, 5.5 Hz, 2H), 6.96 (t, <i>J</i> = 8.7 Hz, 2H),	¹⁹ F NMR (CDCl ₃) δ -117.15

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS	¹ H NMR	¹³ C or ¹⁹ F NMR
				5.12 (d, <i>J</i> = 8.2 Hz, 1H), 4.88 – 4.75 (m, 2H), 4.21 (dt, <i>J</i> = 10.9, 7.7 Hz, 1H), 2.74 (dd, <i>J</i> = 14.3, 5.7 Hz, 1H), 2.49 (dd, <i>J</i> = 14.3, 7.3 Hz, 1H), 2.44 – 2.35 (m, 1H), 2.23 (dt, <i>J</i> = 13.8, 7.2 Hz, 1H), 2.17 – 2.01 (m, 1H), 1.78 – 1.64 (m, 1H), 1.57 – 1.46 (m, 1H), 1.43 (s, 9H), 1.33 (d, <i>J</i> = 6.4 Hz, 3H), 1.25 – 1.32 (m, 1H), 1.24 – 1.13 (m, 1H), 1.05 – 0.94 (m, 1H), 0.78 (dt, <i>J</i> = 4.5, 2.7 Hz, 2H), 0.75 – 0.68 (m, 2H)	
76	---	---	HRMS–ESI <i>m/z</i> [M+H] ⁺ calcd for C ₂₉ H ₃₆ N ₂ O ₇ , 524.2523; found, 524.2534	¹ H NMR (CDCl ₃) δ 8.52 (d, <i>J</i> = 6.8 Hz, 1H), 8.33 (d, <i>J</i> = 5.4 Hz, 1H), 7.35 – 7.12 (m, 5H), 6.99 (d, <i>J</i> = 5.5 Hz, 1H), 4.89 – 4.75 (m, 1H), 4.59 (dt, <i>J</i> = 10.6, 7.6 Hz, 1H), 3.90 (s, 3H), 3.32 – 3.11 (m, 2H), 2.98 (dd, <i>J</i> = 9.8, 6.4 Hz, 1H), 2.90 (dd, <i>J</i> = 14.7, 4.3 Hz, 1H), 2.69 (dd, <i>J</i> = 14.7, 7.3 Hz, 1H), 2.39 (s, 3H), 2.38 – 2.30 (m, 1H), 2.16 – 2.05 (m, 1H), 1.87 – 1.75 (m, 1H), 1.68 – 1.48 (m, 2H), 1.38 – 1.26 (m, 1H), 1.25 (s, 3H), 0.99 – 0.77 (m, 2H), 0.54 – 0.38 (m, 2H), 0.17 – 0.05 (m, 2H)	¹³ C NMR (CDCl ₃) δ 172.42, 168.91, 162.38, 159.43, 146.68, 141.52, 140.64, 129.18, 128.29, 125.88, 109.75, 80.85, 74.23, 73.12, 56.28, 51.12, 48.55, 36.12, 29.71, 28.74, 20.75, 20.18, 18.01, 10.78, 3.12, 2.83
77	---	---	ESIMS <i>m/z</i> 350 ([M+H] ⁺)	---	---
78	---	---	ESIMS <i>m/z</i> 368.4	---	---

Cmpd. No.	MP (°C)	IR (cm ⁻¹)	MASS ([M-Cl] ⁺)	¹ H NMR	¹³ C or ¹⁹ F NMR
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*¹H NMR were run at 400 MHz unless noted otherwise

*¹³C NMR were run at 101 MHz unless noted otherwise

*¹⁹F NMR were run at 376 MHz unless noted otherwise

Table 3. Biological Testing Rating Scale

Rating Table for Fungal Pathogens	
% Control	Rating
> 70	A
≤ 70	B
Not Tested	C

Table 4. Biological Activity – Disease Control in High and Low Volume Applications

Cmpd. No.	PUCCRT*				SEPTTR*			
	1DP*		3DC*		1DP*		3DC*	
	Rate				Rate			
	121.5 g/H*	100 ppm*	121.5 g/H*	100 ppm*	121.5 g/H*	100 ppm*	121.5 g/H*	100 ppm*
1	A	C	A	C	A	C	A	C
2	C	A	C	A	C	A	C	B
7	A	C	A	C	A	C	A	C
8	C	A	C	A	C	A	C	A
12	C	C	C	C	C	C	C	C
13	C	A	C	B	C	A	C	B
15	A	C	A	C	A	C	A	C
17	A	C	A	C	A	C	A	C

Cmpd. No.	PUCCRT*				SEPTTR*			
	1DP*		3DC*		1DP*		3DC*	
	Rate				Rate			
	121.5 g/H*	100 ppm*	121.5 g/H*	100 ppm*	121.5 g/H*	100 ppm*	121.5 g/H*	100 ppm*
21	A	C	B	C	A	C	B	C
25	A	C	A	C	B	C	A	C
26	C	A	C	A	C	A	C	B
29	C	A	C	A	C	A	C	B
31	C	A	C	B	C	B	C	B
32	C	A	C	A	C	A	C	A
33	A	C	A	C	A	C	A	C
35	A	C	B	C	B	C	B	C
36	A	C	B	C	A	C	A	C
37	C	A	C	A	C	A	C	B
38	C	A	C	B	C	A	C	B
40	A	C	A	C	A	C	A	C
42	A	C	B	C	A	C	A	C
43	A	C	A	C	A	C	A	C
44	A	C	A	C	A	C	A	C
47	C	A	C	A	C	A	C	B
49	C	A	C	A	C	A	C	A
50	A	C	A	C	A	C	A	C
52	A	C	A	C	A	C	A	C

Cmpd. No.	PUCCRT*				SEPTTR*			
	1DP*		3DC*		1DP*		3DC*	
	Rate				Rate			
	121.5 g/H*	100 ppm*	121.5 g/H*	100 ppm*	121.5 g/H*	100 ppm*	121.5 g/H*	100 ppm*
55	A	C	A	C	A	C	B	C
56	C	A	C	A	C	A	C	A
58	C	A	C	A	C	B	C	B
60	C	A	C	A	C	A	C	A
61	A	C	A	C	A	C	A	C
62	C	C	C	C	C	C	C	C
63	A	C	A	C	A	C	A	C
64	C	A	C	B	C	A	C	A
65	A	C	A	C	A	C	A	C
67	C	A	C	A	C	A	C	A
70	A	A	A	A	A	A	A	A
71	A	C	A	C	A	C	A	C
72	A	C	A	C	A	C	A	C
73	A	C	A	C	A	C	A	C
74	A	C	A	C	A	C	A	C
76	C	A	C	A	C	A	C	A

*PUCCRT – Wheat Brown Rust (*Puccinia triticina*)

*SEPTTR – Wheat Leaf Blotch (*Septoria tritici*)

*1DP – 1 Day Protectant

*3DC – 3 Day Curative

*g/H – Grams Per Hectare

*ppm – Parts Per Million

Table 5. Biological Activity – Disease Control at 100 ppm

Cmpd. No.	ALTESO*	CERCBE*	COLLLA*	ERYSCI*	ERYSGH*
	1DP*				
25	A	A	A	B	A
33	A	A	A	A	A
36	A	A	A	A	A
40	A	A	A	A	A
61	B	A	A	B	B
70	A	A	A	B	B
73	B	A	A	B	A
74	A	A	A	A	B

* ALTESO – Tomato Early Blight (*Alternaria solani*)

* CERCBE – Leaf Spot of Sugar Beets (*Cercospora beticola*)

* COLLLA – Cucumber Anthracnose (*Glomerella lagenarium*; Anamorph: *Colletotricum lagenarium*)

* ERYSCI – Powdery Mildew of Cucumber (*Erysiphe cichoracearum*)

* ERYSGH – Barley Powdery Mildew (*Blumeria graminis f.sp. hordei*; Synonym: *Erysiphe graminis f.sp. hordei*)

* 1DP – 1 Day Protectant

Table 6. Biological Activity – Disease Control at 100 ppm

Compound Number	LEPTNO*	PYRIOR*	RHYNSE*	UNCINE*	VENTIN*
	1DP*				
25	A	C	A	A	A
33	A	A	A	A	C

Compound. Number	LEPTNO*	PYRIOR*	RHYNSE*	UNCINE*	VENTIN*
	1DP*				
36	A	C	A	A	B
40	A	A	A	A	A
61	A	A	A	A	C
70	A	A	A	A	A
73	A	A	A	A	C
74	A	A	A	A	A

* LEPTNO – Wheat Glume Blotch (*Leptosphaeria nodorum*)

* PYRIOR – Rice Blast (*Magnaporthe grisea*; Anamorph: *Pyricularia oryzae*)

* RHYNSE – Barley Scald (*Rhynchosporium secalis*)

* UNCINE – Grape Powdery Mildew (*Uncinula necator*)

* VENTIN – Apple Scab (*Venturia inaequalis*)

* 1DP – 1 Day Protectant

Table 7. Biological Activity – Disease Control at 25 ppm

Cmpd. No.	PHAKPA*	
	1DP*	3DC*
25	A	B
36	A	B
40	A	B
70	A	B
74	A	B

* PHAKPA – Asian Soybean Rust (*Phakopsora pachyrhizi*)

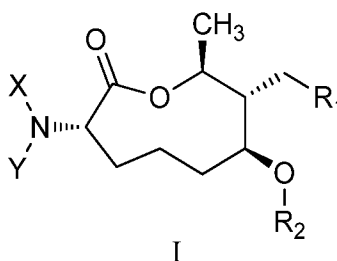
* 1DP – 1 Day Protectant

* 3DC – 3 Day Curative

CLAIMS

What is claimed is:

1. A composition for the control of a fungal pathogen including mixtures of at least one of the compounds of Formula 1

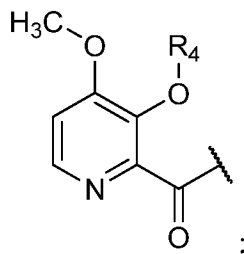


wherein

X is hydrogen or C(O)R₃;

Y is hydrogen, C(O)R₃, or Q;

Q is



R₁ is hydrogen, alkyl, alkenyl, aryl, alkoxy, or acyl, each optionally substituted with 0, 1 or multiple R₆;

R₂ is hydrogen, alkyl, acyl, aryl, alkenyl, or -Si(R₅)₃, each optionally substituted with 0, 1 or multiple R₆;

R₃ is alkoxy or benzyloxy, each optionally substituted with 0, 1, or multiple R₆;

R₄ is hydrogen, -C(O)R₅, or -CH₂OC(O)R₅;

R₅ is alkyl, alkoxy, or aryl, each optionally substituted with 0, 1, or multiple R₆;

R₆ is hydrogen, alkyl, aryl, acyl, halo, alkenyl, alkoxy, heteroaryl, heterocyclyl, or thioalkyl, each optionally substituted with 0, 1, or multiple R₇; and
R₇ is hydrogen, alkyl, aryl, or halo.

2. A composition according to Claim 1, wherein X is hydrogen and Y is Q.
3. A composition according to Claim 2, wherein R₄ is hydrogen.
4. A composition according to Claim 3, wherein R₁ is chosen from alkyl and aryl, each optionally substituted with 0, 1 or multiple R₆.
5. A composition according to Claim 3, wherein R₂ is chosen from alkyl, aryl, and acyl, each optionally substituted with 0, 1 or multiple R₆.
6. A composition according to Claim 3, wherein R₁ is chosen from alkyl and aryl, each optionally substituted with 0, 1 or multiple R₆, and R₂ is chosen from alkyl, aryl, and acyl, each optionally substituted with 0, 1 or multiple R₆.
7. A composition according to Claim 2, wherein R₄ is $-C(O)R_5$ or $-CH_2OC(O)R_5$.
8. A composition according to Claim 7, wherein R₅ is chosen from alkyl and alkoxy, each optionally substituted with 0, 1, or multiple R₆.
9. A composition according to Claim 8, wherein R₁ is chosen from alkyl and aryl, each optionally substituted with 0, 1 or multiple R₆.
10. A composition according to Claim 8, wherein R₂ is chosen from alkyl, aryl, and acyl, each optionally substituted with 0, 1 or multiple R₆.
11. A composition according to Claim 8, wherein R₁ is chosen from alkyl and aryl, each optionally substituted with 0, 1 or multiple R₆, and R₂ is chosen from alkyl, aryl, and acyl, each optionally substituted with 0, 1 or multiple R₆.

12. A composition according to Claim 11, wherein R₅ is chosen from –CH₃ and –CH₂OCH₂CH₃.
13. A composition for the control of a fungal pathogen including at least one of the compositions of Claims 1 – 12 and a phytologically acceptable carrier material.
14. A composition for the control of a fungal pathogen including mixtures of at least one of the compositions of Claims 1 – 13 and another pesticide including fungicides, insecticides, nematocides, miticides, arthropodicides, bactericides and combinations thereof.
15. The composition according to at least one of Claims 1 – 14 wherein the fungal pathogen is one of Leaf Blotch of Wheat (*Mycosphaerella graminicola*; anamorph: *Septoria tritici*), Wheat Brown Rust (*Puccinia triticina*), Stripe Rust (*Puccinia striiformis*), Scab of Apple (*Venturia inaequalis*), Blister Smut of Maize (*Ustilago maydis*), Powdery Mildew of Grapevine (*Uncinula necator*), Barley scald (*Rhynchosporium secalis*), Blast of Rice (*Magnaporthe grisea*), Rust of Soybean (*Phakopsora pachyrhizi*), Glume Blotch of Wheat (*Leptosphaeria nodorum*), Powdery Mildew of Wheat (*Blumeria graminis f. sp. tritici*), Powdery Mildew of Barley (*Blumeria graminis f. sp. hordei*), Powdery Mildew of Cucurbits (*Erysiphe cichoracearum*), Anthracnose of Cucurbits (*Glomerella lagenarium*), Leaf Spot of Beet (*Cercospora beticola*), Early Blight of Tomato (*Alternaria solani*), and Net Blotch of Barley (*Pyrenophora teres*).
16. The composition according to Claim 15 wherein the fungal pathogen is one of Leaf Blotch of Wheat (*Septoria tritici*), Wheat Brown Rust (*Puccinia triticina*), and Rust of Soybean (*Phakopsora pachyrhizi*).
17. A method for the control and prevention of fungal attack on a plant, the method including the step of: Applying a fungicidally effective amount of at least one of the

compositions of Claims 1 – 14 to at least one of the plant, an area adjacent to the plant, soil adapted to support growth of the plant, a root of the plant, and foliage of the plant.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2014/071695

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - A01N 43/22 (2015.01)

CPC - A01N 43/22 (2015.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8) - A01N 43/00, 43/04, 43/22, 43/40 (2015.01)

CPC - A01N 43/00, 43/04, 43/22, 43/40 (2015.01) (keyword delimited)

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

USPC - 514/336, 450; 546/281.7; 549/346 (keyword delimited)

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

Orbit, Google Patents, STN, Google, PubChem, SureChem, ChemSpider

Search terms used: Macrocyclic, picolinamide, fungicide, ascomycetes, basidiomycetes, deuteromycetes, oomycetes.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2013/0296373 A1 (DOW AGROSCIENCES LLC) 07 November 2013 (07.11.2013) entire document	1-13
A	US 2013/0296371 A1 (DOW AGROSCIENCES LLC) 07 November 2013 (07.11.2013) entire document	1-13
A	US 7,250,389 B1 (SAKANAKA et al) 31 July 2007 (31.07.2007) entire document	1-13
A	US 2006/0167281 A1 (MEIJER et al) 27 July 2006 (27.07.2006) entire document	1-13
A, P	US 2014/0187588 A1 (DOW AGROSCIENCES LLC) 03 July 2014 (03.07.2014) entire document	1-13

Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

24 February 2015

Date of mailing of the international search report:

17 APR 2015

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Blaine R. Copenheaver

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2014/071695

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.: 14-17
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

- Remark on Protest**
- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
 - The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
 - No protest accompanied the payment of additional search fees.