

SUBSTITUTED NUCLEOSIDES, NUCLEOTIDES AND ANALOGS THEREOF**INCORPORATION BY REFERENCE TO ANY PRIORITY APPLICATIONS**

[0001] Any and all applications for which a foreign or domestic priority claim is identified in the Application Data Sheet as filed with the present application, are hereby incorporated by reference under 37 CFR 1.57.

REFERENCE TO SEQUENCE LISTING

[0002] The present application is being filed along with a Sequence Listing in electronic format. The Sequence Listing is provided as a file entitled SEQLISTING_065.TXT, created December 19, 2013, which is 1 Kb in size. The information in the electronic format of the Sequence Listing is incorporated herein by reference in its entirety.

BACKGROUNDField

[0003] The present application relates to the fields of chemistry, biochemistry and medicine. More particularly, disclosed herein are nucleotide analogs, pharmaceutical compositions that include one or more nucleotide analogs and methods of synthesizing the same. Also disclosed herein are methods of treating diseases and/or conditions with a nucleotide analog, alone or in combination therapy with one or more other agents.

Description

[0004] Nucleoside analogs are a class of compounds that have been shown to exert antiviral and anticancer activity both in vitro and in vivo, and thus, have been the subject of widespread research for the treatment of viral infections. Nucleoside analogs are usually therapeutically inactive compounds that are converted by host or viral enzymes to their respective active anti-metabolites, which, in turn, may inhibit polymerases involved in viral or cell proliferation. The activation occurs by a variety of mechanisms, such as the addition of one or more phosphate groups and, or in combination with, other metabolic processes.

SUMMARY

[0005] Some embodiments disclosed herein relate to a compound of Formula (I) or a pharmaceutically acceptable salt thereof.

[0006] Some embodiments disclosed herein relate to a method of ameliorating and/or treating a hepatitis C viral (HCV) infection that can include administering to a subject identified as suffering from the HCV infection an effective amount of one or more compounds of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes one or more compounds of Formula (I), or a pharmaceutically acceptable salt thereof. Other embodiments described herein relate to using one or more compounds of Formula (I), or a pharmaceutically acceptable salt thereof, in the manufacture of a medicament for ameliorating and/or treating a HCV infection. Still other embodiments described herein relate to one or more compounds of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes one or more compounds of Formula (I), or a pharmaceutically acceptable salt thereof, that can be used for ameliorating and/or treating a HCV infection.

[0007] Some embodiments disclosed herein relate to a method of ameliorating and/or treating a HCV infection that can include contacting a cell infected with the hepatitis C virus with an effective amount of one or more compounds described herein, or a pharmaceutically acceptable salt of one or more compounds described herein, or a pharmaceutical composition that includes one or more compounds described herein, or a pharmaceutically acceptable salt thereof. Other embodiments described herein relate to using one or more compounds described herein, or a pharmaceutically acceptable salt of one or more compounds described herein, in the manufacture of a medicament for ameliorating and/or treating a HCV infection that can include contacting a cell infected with the hepatitis C virus with an effective amount of said compound(s). Still other embodiments described herein relate to one or more compounds described herein, or a pharmaceutically acceptable salt of one or more compounds described herein, or a pharmaceutical composition that includes one or more compounds described herein, or a pharmaceutically acceptable salt thereof, that can be used for ameliorating and/or treating a HCV infection by contacting a cell infected with the hepatitis C virus with an effective amount of said compound(s).

[0008] Some embodiments disclosed herein relate to a method of inhibiting replication of a hepatitis C virus that can include contacting a cell infected with the hepatitis C virus with an effective amount of one or more compounds described herein, or a pharmaceutically acceptable salt of one or more compounds described herein, or a pharmaceutical composition that includes one or more compounds described herein, or a pharmaceutically acceptable salt thereof. Other embodiments described herein relate to using one or more compounds described herein, or a pharmaceutically acceptable salt of one or more compounds described herein, in the manufacture of a medicament for inhibiting replication of a

hepatitis C virus that can include contacting a cell infected with the hepatitis C virus with an effective amount of said compound(s). Still other embodiments described herein relate to one or more compounds described herein, or a pharmaceutically acceptable salt of one or more compounds described herein, or a pharmaceutical composition that includes one or more compounds described herein, or a pharmaceutically acceptable salt thereof, that can be used for inhibiting replication of a hepatitis C virus by contacting a cell infected with the hepatitis C virus with an effective amount of said compound(s).

[0009] Some embodiments disclosed herein relate to a method of ameliorating and/or treating a HCV infection that can include administering to a subject identified as suffering from the HCV infection an effective amount of a compound described herein or a pharmaceutically acceptable salt thereof (for example, one or more compounds of Formula (I), or a pharmaceutically acceptable salt thereof), or a pharmaceutical composition that includes a compound described herein, or a pharmaceutically acceptable salt thereof, in combination with an agent selected from an interferon, ribavirin, a HCV protease inhibitor, a HCV polymerase inhibitor, a NS5A inhibitor, an other antiviral compound, a compound of Formula (AA), a compound of Formula (BB) and a compound of Formula (CC), or a pharmaceutically acceptable salt of any of the foregoing. Some embodiments disclosed herein relate to a method of ameliorating and/or treating a HCV infection that can include contacting a cell infected with the HCV infection with an effective amount of a compound described herein or a pharmaceutically acceptable salt thereof (for example, one or more compounds of Formula (I), or a pharmaceutically acceptable salt thereof), or a pharmaceutical composition that includes a compound described herein, in combination with an agent selected from an interferon, ribavirin, a HCV protease inhibitor, a HCV polymerase inhibitor, a NS5A inhibitor, an other antiviral compound, a compound of Formula (AA), a compound of Formula (BB) and a compound of Formula (CC), or a pharmaceutically acceptable salt of any of the foregoing. Some embodiments disclosed herein relate to a method of inhibiting replication of a hepatitis C virus that can include administering to a subject identified as suffering from a HCV infection an effective amount of a compound described herein or a pharmaceutically acceptable salt thereof (for example, a compound of Formula (I), or a pharmaceutically acceptable salt thereof), or a pharmaceutical composition that includes a compound described herein, or a pharmaceutically acceptable salt thereof, in combination with an agent selected from an interferon, ribavirin, a HCV protease inhibitor, a HCV polymerase inhibitor, a NS5A inhibitor, another antiviral compound, a compound of Formula (AA), a compound of Formula (BB) and a compound of Formula (CC), or a pharmaceutically acceptable salt of any of the foregoing. In some

embodiments, the agent can be a compound, or a pharmaceutically acceptable salt thereof, selected from Compound 1001-1016, 2001-2012, 3001-3014, 4001-4012, 5001-5012, 6001-6078, 7000-7027 and 8000-8016, or a pharmaceutical composition that includes one or more of the aforementioned compounds, or a pharmaceutically acceptable salt of the foregoing. In some embodiments, the method can include administering a second agent selected from an interferon, ribavirin, a HCV protease inhibitor, a HCV polymerase inhibitor, a NS5A inhibitor, an other antiviral compound, a compound of Formula (AA), a compound of Formula (BB) and a compound of Formula (CC), or a pharmaceutically acceptable salt of any of the foregoing.

BRIEF DESCRIPTION OF THE DRAWINGS

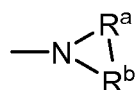
- [0010]** Figure 1 shows example HCV protease inhibitors.
- [0011]** Figure 2 shows example nucleoside HCV polymerase inhibitors.
- [0012]** Figure 3 shows example non-nucleoside HCV polymerase inhibitors.
- [0013]** Figure 4 shows example NS5A inhibitors.
- [0014]** Figure 5 shows example other antivirals.
- [0015]** Figure 6 shows example compounds of Formula (CC) and alpha-thiotriphosphates thereof, wherein Formula (CC) and alpha-thiotriphosphates thereof are described herein.
- [0016]** Figure 7 shows example compounds of Formula (AA), wherein Formula (AA) is described herein.
- [0017]** Figure 8 shows example compounds of Formula (BB), wherein Formula (BB) is described herein.
- [0018]** Figure 9 shows example compounds of Formula (I), wherein Formula (I) is described herein.
- [0019]** Figure 10 shows the gels from the assessment of incorporation of several compound with a uracil base by the human mitochondrial RNA polymerase.
- [0020]** Figure 11 shows the gels from the assessment of incorporation of several compounds with a guanine base by the human mitochondrial RNA polymerase.
- [0021]** Figures 12A-D shows the results of the inhibition of mitochondrial protein synthesis assays.

DETAILED DESCRIPTION

Definitions

[0022] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as is commonly understood by one of ordinary skill in the art. All patents, applications, published applications and other publications referenced herein are incorporated by reference in their entirety unless stated otherwise. In the event that there are a plurality of definitions for a term herein, those in this section prevail unless stated otherwise.

[0023] As used herein, any "R" group(s) such as, without limitation, R^1 , R^2 , R^3 , R^4 , R^{5A} , R^{5B} , R^{6A} , R^{6B} , R^{6C} , R^{6D} , R^{6E} , R^{6F} , R^{6G} , R^{6H} , R^{7A} , R^{7B} , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , R^{17} , R^{18} , R^{A1} , R^{A2} , R^{A3} and R^{A4} represent substituents that can be attached to the indicated atom. An R group may be substituted or unsubstituted. If two "R" groups are described as being "taken together" the R groups and the atoms they are attached to can form a cycloalkyl, cycloalkenyl, aryl, heteroaryl or heterocycle. For example, without limitation, if R^a and R^b of an NR^aR^b group are indicated to be "taken together," it means that they are covalently bonded to one another to form a ring:



In addition, if two "R" groups are described as being "taken together" with the atom(s) to which they are attached to form a ring as an alternative, the R groups are not limited to the variables or substituents defined previously.

[0024] Whenever a group is described as being "optionally substituted" that group may be unsubstituted or substituted with one or more of the indicated substituents. Likewise, when a group is described as being "unsubstituted or substituted" if substituted, the substituent(s) may be selected from one or more the indicated substituents. If no substituents are indicated, it is meant that the indicated "optionally substituted" or "substituted" group may be substituted with one or more group(s) individually and independently selected from alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, heteroaryl, heterocyclyl, aryl(alkyl), heteroaryl(alkyl), (heterocyclyl)alkyl, hydroxy, alkoxy, acyl, cyano, halogen, thiocarbonyl, O-carbamyl, N-carbamyl, O-thiocarbamyl, N-thiocarbamyl, C-amido, N-amido, S-sulfonamido, N-sulfonamido, C-carboxy, O-carboxy, isocyanato, thiocyanato, isothiocyanato, nitro, silyl, sulfenyl, sulfinyl, sulfonyl, haloalkyl, haloalkoxy, trihalomethanesulfonyl, trihalomethanesulfonamido, an amino, a mono-substituted amino group and a di-substituted amino group.

[0025] As used herein, “C_a to C_b” in which “a” and “b” are integers refer to the number of carbon atoms in an alkyl, alkenyl or alkynyl group, or the number of carbon atoms in the ring of a cycloalkyl, cycloalkenyl, aryl, heteroaryl or heterocyclyl group. That is, the alkyl, alkenyl, alkynyl, ring of the cycloalkyl, ring of the cycloalkenyl, ring of the aryl, ring of the heteroaryl or ring of the heterocyclyl can contain from “a” to “b”, inclusive, carbon atoms. Thus, for example, a “C₁ to C₄ alkyl” group refers to all alkyl groups having from 1 to 4 carbons, that is, CH₃-, CH₃CH₂-, CH₃CH₂CH₂-, (CH₃)₂CH-, CH₃CH₂CH₂CH₂-, CH₃CH₂CH(CH₃)- and (CH₃)₃C-. If no “a” and “b” are designated with regard to an alkyl, alkenyl, alkynyl, cycloalkyl cycloalkenyl, aryl, heteroaryl or heterocyclyl group, the broadest range described in these definitions is to be assumed.

[0026] As used herein, “alkyl” refers to a straight or branched hydrocarbon chain that comprises a fully saturated (no double or triple bonds) hydrocarbon group. The alkyl group may have 1 to 20 carbon atoms (whenever it appears herein, a numerical range such as “1 to 20” refers to each integer in the given range; *e.g.*, “1 to 20 carbon atoms” means that the alkyl group may consist of 1 carbon atom, 2 carbon atoms, 3 carbon atoms, *etc.*, up to and including 20 carbon atoms, although the present definition also covers the occurrence of the term “alkyl” where no numerical range is designated). The alkyl group may also be a medium size alkyl having 1 to 10 carbon atoms. The alkyl group could also be a lower alkyl having 1 to 6 carbon atoms. The alkyl group of the compounds may be designated as “C₁-C₄ alkyl” or similar designations. By way of example only, “C₁-C₄ alkyl” indicates that there are one to four carbon atoms in the alkyl chain, *i.e.*, the alkyl chain is selected from methyl, ethyl, propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl and t-butyl. Typical alkyl groups include, but are in no way limited to, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tertiary butyl, pentyl and hexyl. The alkyl group may be substituted or unsubstituted.

[0027] As used herein, “alkenyl” refers to an alkyl group that contains in the straight or branched hydrocarbon chain one or more double bonds. An alkenyl group may be unsubstituted or substituted.

[0028] As used herein, “alkynyl” refers to an alkyl group that contains in the straight or branched hydrocarbon chain one or more triple bonds. An alkynyl group may be unsubstituted or substituted.

[0029] As used herein, “cycloalkyl” refers to a completely saturated (no double or triple bonds) mono- or multi- cyclic hydrocarbon ring system. When composed of two or more rings, the rings may be joined together in a fused fashion. Cycloalkyl groups can contain 3 to 10 atoms in the ring(s) or 3 to 8 atoms in the ring(s). A cycloalkyl group may be unsubstituted or

substituted. Typical cycloalkyl groups include, but are in no way limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl.

[0030] As used herein, “cycloalkenyl” refers to a mono- or multi- cyclic hydrocarbon ring system that contains one or more double bonds in at least one ring; although, if there is more than one, the double bonds cannot form a fully delocalized pi-electron system throughout all the rings (otherwise the group would be “aryl,” as defined herein). When composed of two or more rings, the rings may be connected together in a fused fashion. A cycloalkenyl can contain 3 to 10 atoms in the ring(s) or 3 to 8 atoms in the ring(s). A cycloalkenyl group may be unsubstituted or substituted.

[0031] As used herein, “aryl” refers to a carbocyclic (all carbon) monocyclic or polycyclic aromatic ring system (including fused ring systems where two carbocyclic rings share a chemical bond) that has a fully delocalized pi-electron system throughout all the rings. The number of carbon atoms in an aryl group can vary. For example, the aryl group can be a C₆-C₁₄ aryl group, a C₆-C₁₀ aryl group, or a C₆ aryl group. Examples of aryl groups include, but are not limited to, benzene, naphthalene and azulene. An aryl group may be substituted or unsubstituted.

[0032] As used herein, “heteroaryl” refers to a monocyclic, bicyclic and tricyclic aromatic ring system (a ring system with fully delocalized pi-electron system) that contain(s) one or more heteroatoms (for example, 1 to 5 heteroatoms), that is, an element other than carbon, including but not limited to, nitrogen, oxygen and sulfur. The number of atoms in the ring(s) of a heteroaryl group can vary. For example, the heteroaryl group can contain 4 to 14 atoms in the ring(s), 5 to 10 atoms in the ring(s) or 5 to 6 atoms in the ring(s). Furthermore, the term “heteroaryl” includes fused ring systems where two rings, such as at least one aryl ring and at least one heteroaryl ring, or at least two heteroaryl rings, share at least one chemical bond. Examples of heteroaryl rings include, but are not limited to, furan, furazan, thiophene, benzothiophene, phthalazine, pyrrole, oxazole, benzoxazole, 1,2,3-oxadiazole, 1,2,4-oxadiazole, thiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, benzothiazole, imidazole, benzimidazole, indole, indazole, pyrazole, benzopyrazole, isoxazole, benzoisoxazole, isothiazole, triazole, benzotriazole, thiadiazole, tetrazole, pyridine, pyridazine, pyrimidine, pyrazine, purine, pteridine, quinoline, isoquinoline, quinazoline, quinoxaline, cinnoline and triazine. A heteroaryl group may be substituted or unsubstituted.

[0033] As used herein, “heterocyclyl” or “heteroalicyclyl” refers to three-, four-, five-, six-, seven-, eight-, nine-, ten-, up to 18-membered monocyclic, bicyclic and tricyclic ring system wherein carbon atoms together with from 1 to 5 heteroatoms constitute said ring system.

A heterocycle may optionally contain one or more unsaturated bonds situated in such a way, however, that a fully delocalized pi-electron system does not occur throughout all the rings. The heteroatom(s) is an element other than carbon including, but not limited to, oxygen, sulfur and nitrogen. A heterocycle may further contain one or more carbonyl or thiocarbonyl functionalities, so as to make the definition include oxo-systems and thio-systems such as lactams, lactones, cyclic imides, cyclic thioimides and cyclic carbamates. When composed of two or more rings, the rings may be joined together in a fused fashion. Additionally, any nitrogens in a heteroalicyclic may be quaternized. Heterocyclyl or heteroalicyclic groups may be unsubstituted or substituted. Examples of such “heterocyclyl” or “heteroalicyclic” groups include but are not limited to, 1,3-dioxin, 1,3-dioxane, 1,4-dioxane, 1,2-dioxolane, 1,3-dioxolane, 1,4-dioxolane, 1,3-oxathiane, 1,4-oxathiin, 1,3-oxathiolane, 1,3-dithiole, 1,3-dithiolane, 1,4-oxathiane, tetrahydro-1,4-thiazine, 2H-1,2-oxazine, maleimide, succinimide, barbituric acid, thiobarbituric acid, dioxopiperazine, hydantoin, dihydrouracil, trioxane, hexahydro-1,3,5-triazine, imidazoline, imidazolidine, isoxazoline, isoxazolidine, oxazoline, oxazolidine, oxazolidinone, thiazoline, thiazolidine, morpholine, oxirane, piperidine *N*-Oxide, piperidine, piperazine, pyrrolidine, pyrrolidone, pyrrolidione, 4-piperidone, pyrazoline, pyrazolidine, 2-oxopyrrolidine, tetrahydropyran, 4H-pyran, tetrahydrothiopyran, thiamorpholine, thiamorpholine sulfoxide, thiamorpholine sulfone and their benzo-fused analogs (e.g., benzimidazolidinone, tetrahydroquinoline and 3,4-methylenedioxyphenyl).

[0034] As used herein, “aralkyl” and “aryl(alkyl)” refer to an aryl group connected, as a substituent, via a lower alkylene group. The lower alkylene and aryl group of an aryl(alkyl) may be substituted or unsubstituted. Examples include but are not limited to benzyl, 2-phenylalkyl, 3-phenylalkyl and naphthylalkyl.

[0035] As used herein, “heteroaralkyl” and “heteroaryl(alkyl)” refer to a heteroaryl group connected, as a substituent, via a lower alkylene group. The lower alkylene and heteroaryl group of heteroaralkyl may be substituted or unsubstituted. Examples include but are not limited to 2-thienylalkyl, 3-thienylalkyl, furylalkyl, thienylalkyl, pyrrolylalkyl, pyridylalkyl, isoxazolylalkyl, imidazolylalkyl and their benzo-fused analogs.

[0036] A “(heteroalicyclyl)alkyl” and “(heterocyclyl)alkyl” refer to a heterocyclic or a heteroalicyclic group connected, as a substituent, via a lower alkylene group. The lower alkylene and heterocyclyl of a (heteroalicyclyl)alkyl may be substituted or unsubstituted. Examples include but are not limited tetrahydro-2H-pyran-4-yl)methyl, (piperidin-4-yl)ethyl, (piperidin-4-yl)propyl, (tetrahydro-2H-thiopyran-4-yl)methyl and (1,3-thiazinan-4-yl)methyl.

[0037] “Lower alkylene groups” are straight-chained $-CH_2-$ tethering groups, forming bonds to connect molecular fragments via their terminal carbon atoms. Examples include but are not limited to methylene ($-CH_2-$), ethylene ($-CH_2CH_2-$), propylene ($-CH_2CH_2CH_2-$) and butylene ($-CH_2CH_2CH_2CH_2-$). A lower alkylene group can be substituted by replacing one or more hydrogen of the lower alkylene group with a substituent(s) listed under the definition of “substituted.”

[0038] As used herein, “alkoxy” refers to the formula $-OR$ wherein R is an alkyl, an alkenyl, an alkynyl, a cycloalkyl, a cycloalkenyl, aryl, heteroaryl, heterocyclyl, aryl(alkyl), (heteroaryl)alkyl or (heterocyclyl)alkyl is defined herein. A non-limiting list of alkoxy groups are methoxy, ethoxy, n-propoxy, 1-methylethoxy (isopropoxy), n-butoxy, iso-butoxy, sec-butoxy, tert-butoxy, phenoxy and benzyloxy. An alkoxy may be substituted or unsubstituted.

[0039] As used herein, “acyl” refers to a hydrogen, alkyl, alkenyl, alkynyl, or aryl connected, as substituents, via a carbonyl group. Examples include formyl, acetyl, propanoyl, benzoyl and acryl. An acyl may be substituted or unsubstituted.

[0040] As used herein, “hydroxyalkyl” refers to an alkyl group in which one or more of the hydrogen atoms are replaced by a hydroxy group. Exemplary hydroxyalkyl groups include but are not limited to, 2-hydroxyethyl, 3-hydroxypropyl, 2-hydroxypropyl and 2,2-dihydroxyethyl. A hydroxyalkyl may be substituted or unsubstituted.

[0041] As used herein, “haloalkyl” refers to an alkyl group in which one or more of the hydrogen atoms are replaced by a halogen (e.g., mono-haloalkyl, di-haloalkyl and tri-haloalkyl). Such groups include but are not limited to, chloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, 1-chloro-2-fluoromethyl and 2-fluoroisobutyl. A haloalkyl may be substituted or unsubstituted.

[0042] As used herein, “haloalkoxy” refers to an $-O$ -alkyl group in which one or more of the hydrogen atoms are replaced by a halogen (e.g., mono-haloalkoxy, di-haloalkoxy and tri-haloalkoxy). Such groups include but are not limited to, chloromethoxy, fluoromethoxy, difluoromethoxy, trifluoromethoxy, 1-chloro-2-fluoromethoxy and 2-fluoroisobutoxy. A haloalkoxy may be substituted or unsubstituted.

[0043] A “sulfenyl” group refers to an “ $-SR$ ” group in which R can be hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, heteroaryl, heterocyclyl, aryl(alkyl), (heteroaryl)alkyl or (heterocyclyl)alkyl. A sulfenyl may be substituted or unsubstituted.

[0044] A “sulfinyl” group refers to an “ $-S(=O)-R$ ” group in which R can be the same as defined with respect to sulfenyl. A sulfinyl may be substituted or unsubstituted.

[0045] A “sulfonyl” group refers to an “SO₂R” group in which R can be the same as defined with respect to sulfenyl. A sulfonyl may be substituted or unsubstituted.

[0046] An “O-carboxy” group refers to a “RC(=O)O-” group in which R can be hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, heteroaryl, heterocyclyl, aryl(alkyl), (heteroaryl)alkyl or (heterocyclyl)alkyl, as defined herein. An O-carboxy may be substituted or unsubstituted.

[0047] The terms “ester” and “C-carboxy” refer to a “-C(=O)OR” group in which R can be the same as defined with respect to O-carboxy. An ester and C-carboxy may be substituted or unsubstituted.

[0048] A “thiocarbonyl” group refers to a “-C(=S)R” group in which R can be the same as defined with respect to O-carboxy. A thiocarbonyl may be substituted or unsubstituted.

[0049] A “trihalomethanesulfonyl” group refers to an “X₃CSO₂-” group wherein each X is a halogen.

[0050] A “trihalomethanesulfonamido” group refers to an “X₃CS(O)₂N(R_A)-” group wherein each X is a halogen, and R_A is hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, heteroaryl, heterocyclyl, aryl(alkyl), (heteroaryl)alkyl or (heterocyclyl)alkyl.

[0051] The term “amino” as used herein refers to a -NH₂ group.

[0052] As used herein, the term “hydroxy” refers to a -OH group.

[0053] A “cyano” group refers to a “-CN” group.

[0054] The term “azido” as used herein refers to a -N₃ group.

[0055] An “isocyanato” group refers to a “-NCO” group.

[0056] A “thiocyanato” group refers to a “-CNS” group.

[0057] An “isothiocyanato” group refers to an “-NCS” group.

[0058] A “mercapto” group refers to an “-SH” group.

[0059] A “carbonyl” group refers to a C=O group.

[0060] An “S-sulfonamido” group refers to a “-SO₂N(R_AR_B)” group in which R_A and R_B can be independently hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, heteroaryl, heterocyclyl, aryl(alkyl), (heteroaryl)alkyl or (heterocyclyl)alkyl. An S-sulfonamido may be substituted or unsubstituted.

[0061] An “N-sulfonamido” group refers to a “RSO₂N(R_A)-” group in which R and R_A can be independently hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, heteroaryl, heterocyclyl, aryl(alkyl), (heteroaryl)alkyl or (heterocyclyl)alkyl. An N-sulfonamido may be substituted or unsubstituted.

[0062] An “O-carbamyl” group refers to a “-OC(=O)N(R_AR_B)” group in which R_A and R_B can be independently hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, heteroaryl, heterocyclyl, aryl(alkyl), (heteroaryl)alkyl or (heterocyclyl)alkyl. An O-carbamyl may be substituted or unsubstituted.

[0063] An “N-carbamyl” group refers to an “ROC(=O)N(R_A)-” group in which R and R_A can be independently hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, heteroaryl, heterocyclyl, aryl(alkyl), (heteroaryl)alkyl or (heterocyclyl)alkyl. An N-carbamyl may be substituted or unsubstituted.

[0064] An “O-thiocarbamyl” group refers to a “-OC(=S)-N(R_AR_B)” group in which R_A and R_B can be independently hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, heteroaryl, heterocyclyl, aryl(alkyl), (heteroaryl)alkyl or (heterocyclyl)alkyl. An O-thiocarbamyl may be substituted or unsubstituted.

[0065] An “N-thiocarbamyl” group refers to an “ROC(=S)N(R_A)-” group in which R and R_A can be independently hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, heteroaryl, heterocyclyl, aryl(alkyl), (heteroaryl)alkyl or (heterocyclyl)alkyl. An N-thiocarbamyl may be substituted or unsubstituted.

[0066] A “C-amido” group refers to a “-C(=O)N(R_AR_B)” group in which R_A and R_B can be independently hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, heteroaryl, heterocyclyl, aryl(alkyl), (heteroaryl)alkyl or (heterocyclyl)alkyl. A C-amido may be substituted or unsubstituted.

[0067] An “N-amido” group refers to a “RC(=O)N(R_A)-” group in which R and R_A can be independently hydrogen, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, heteroaryl, heterocyclyl, aryl(alkyl), (heteroaryl)alkyl or (heterocyclyl)alkyl. An N-amido may be substituted or unsubstituted.

[0068] The term “halogen atom” or “halogen” as used herein, means any one of the radio-stable atoms of column 7 of the Periodic Table of the Elements, such as, fluorine, chlorine, bromine and iodine.

[0069] Where the numbers of substituents is not specified (e.g. haloalkyl), there may be one or more substituents present. For example “haloalkyl” may include one or more of the same or different halogens. As another example, “C₁-C₃ alkoxyphenyl” may include one or more of the same or different alkoxy groups containing one, two or three atoms.

[0070] As used herein, the abbreviations for any protective groups, amino acids and other compounds, are, unless indicated otherwise, in accord with their common usage,

recognized abbreviations, or the IUPAC-IUB Commission on Biochemical Nomenclature (See, Biochem. 11:942-944 (1972)).

[0071] The term “nucleoside” is used herein in its ordinary sense as understood by those skilled in the art, and refers to a compound composed of an optionally substituted pentose moiety or modified pentose moiety attached to a heterocyclic base or tautomer thereof via a N-glycosidic bond, such as attached via the 9-position of a purine-base or the 1-position of a pyrimidine-base. Examples include, but are not limited to, a ribonucleoside comprising a ribose moiety and a deoxyribonucleoside comprising a deoxyribose moiety. A modified pentose moiety is a pentose moiety in which an oxygen atom has been replaced with a carbon and/or a carbon has been replaced with a sulfur or an oxygen atom. A “nucleoside” is a monomer that can have a substituted base and/or sugar moiety. Additionally, a nucleoside can be incorporated into larger DNA and/or RNA polymers and oligomers. In some instances, the nucleoside can be a nucleoside analog drug.

[0072] The term “nucleotide” is used herein in its ordinary sense as understood by those skilled in the art, and refers to a nucleoside having a phosphate ester bound to the pentose moiety, for example, at the 5'-position.

[0073] As used herein, the term “heterocyclic base” refers to an optionally substituted nitrogen-containing heterocyclyl that can be attached to an optionally substituted pentose moiety or modified pentose moiety. In some embodiments, the heterocyclic base can be selected from an optionally substituted purine-base, an optionally substituted pyrimidine-base and an optionally substituted triazole-base (for example, a 1,2,4-triazole). The term “purine-base” is used herein in its ordinary sense as understood by those skilled in the art, and includes its tautomers. Similarly, the term “pyrimidine-base” is used herein in its ordinary sense as understood by those skilled in the art, and includes its tautomers. A non-limiting list of optionally substituted purine-bases includes purine, adenine, guanine, hypoxanthine, xanthine, alloxanthine, 7-alkylguanine (e.g. 7-methylguanine), theobromine, caffeine, uric acid and isoguanine. Examples of pyrimidine-bases include, but are not limited to, cytosine, thymine, uracil, 5,6-dihydrouracil and 5-alkylcytosine (e.g., 5-methylcytosine). An example of an optionally substituted triazole-base is 1,2,4-triazole-3-carboxamide. Other non-limiting examples of heterocyclic bases include diaminopurine, 8-oxo-N⁶-alkyladenine (e.g., 8-oxo-N⁶-methyladenine), 7-deazaxanthine, 7-deazaguanine, 7-deazaadenine, N⁴,N⁴-ethanocytosin, N⁶,N⁶-ethano-2,6-diaminopurine, 5-halouracil (e.g., 5-fluorouracil and 5-bromouracil), pseudoisocytosine, isocytosine, isoguanine, and other heterocyclic bases described in U.S. Patent Nos. 5,432,272 and 7,125,855, which are incorporated herein by reference for the limited

purpose of disclosing additional heterocyclic bases. In some embodiments, a heterocyclic base can be optionally substituted with an amine or an enol protecting group(s).

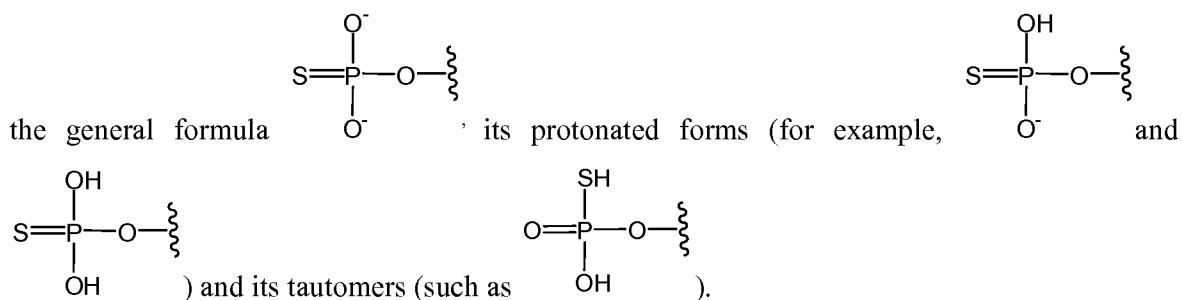
[0074] The term “–N–linked amino acid” refers to an amino acid that is attached to the indicated moiety via a main-chain amino or mono-substituted amino group. When the amino acid is attached in an –N–linked amino acid, one of the hydrogens that is part of the main-chain amino or mono-substituted amino group is not present and the amino acid is attached via the nitrogen. N-linked amino acids can be substituted or unsubstituted.

[0075] The term “–N–linked amino acid ester derivative” refers to an amino acid in which a main-chain carboxylic acid group has been converted to an ester group. In some embodiments, the ester group has a formula selected from alkyl-O-C(=O)-, cycloalkyl-O-C(=O)-, aryl-O-C(=O)- and aryl(alkyl)-O-C(=O)-. A non-limiting list of ester groups include substituted and unsubstituted versions of the following: methyl-O-C(=O)-, ethyl-O-C(=O)-, n-propyl-O-C(=O)-, isopropyl-O-C(=O)-, n-butyl-O-C(=O)-, isobutyl-O-C(=O)-, tert-butyl-O-C(=O)-, neopentyl-O-C(=O)-, cyclopropyl-O-C(=O)-, cyclobutyl-O-C(=O)-, cyclopentyl-O-C(=O)-, cyclohexyl-O-C(=O)-, phenyl-O-C(=O)-, benzyl-O-C(=O)- and naphthyl-O-C(=O)-. N-linked amino acid ester derivatives can be substituted or unsubstituted.

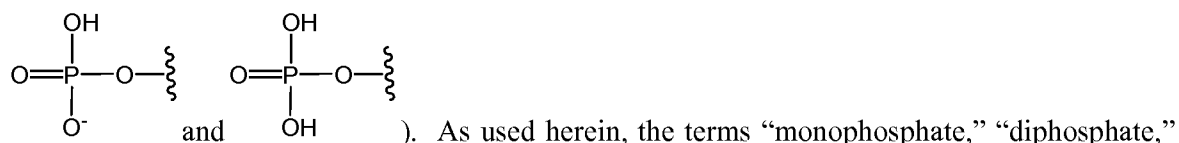
[0076] The term “–O–linked amino acid” refers to an amino acid that is attached to the indicated moiety via the hydroxy from its main-chain carboxylic acid group. When the amino acid is attached in an –O–linked amino acid, the hydrogen that is part of the hydroxy from its main-chain carboxylic acid group is not present and the amino acid is attached via the oxygen. O-linked amino acids can be substituted or unsubstituted.

[0077] As used herein, the term “amino acid” refers to any amino acid (both standard and non-standard amino acids), including, but not limited to, α -amino acids, β -amino acids, γ -amino acids and δ -amino acids. Examples of suitable amino acids include, but are not limited to, alanine, asparagine, aspartate, cysteine, glutamate, glutamine, glycine, proline, serine, tyrosine, arginine, histidine, isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan and valine. Additional examples of suitable amino acids include, but are not limited to, ornithine, hypusine, 2-aminoisobutyric acid, dehydroalanine, gamma-aminobutyric acid, citrulline, beta-alanine, alpha-ethyl-glycine, alpha-propyl-glycine and norleucine.

[0078] The terms “phosphorothioate” and “phosphothioate” refer to a compound of



[0079] As used herein, the term “phosphate” is used in its ordinary sense as understood by those skilled in the art, and includes its protonated forms (for example,



and “triphosphate” are used in their ordinary sense as understood by those skilled in the art, and include protonated forms.

[0080] The terms “protecting group” and “protecting groups” as used herein refer to any atom or group of atoms that is added to a molecule in order to prevent existing groups in the molecule from undergoing unwanted chemical reactions. Examples of protecting group moieties are described in T. W. Greene and P. G. M. Wuts, *Protective Groups in Organic Synthesis*, 3. Ed. John Wiley & Sons, 1999, and in J.F.W. McOmie, *Protective Groups in Organic Chemistry* Plenum Press, 1973, both of which are hereby incorporated by reference for the limited purpose of disclosing suitable protecting groups. The protecting group moiety may be chosen in such a way, that they are stable to certain reaction conditions and readily removed at a convenient stage using methodology known from the art. A non-limiting list of protecting groups include benzyl; substituted benzyl; alkylcarbonyls and alkoxycarbonyls (e.g., t-butoxycarbonyl (BOC), acetyl, or isobutyryl); arylalkylcarbonyls and arylalkoxycarbonyls (e.g., benzyloxycarbonyl); substituted methyl ether (e.g. methoxymethyl ether); substituted ethyl ether; a substituted benzyl ether; tetrahydropyranyl ether; silyls (e.g., trimethylsilyl, triethylsilyl, triisopropylsilyl, t-butyl dimethylsilyl, tri-*iso*-propylsilyloxymethyl, [2-(trimethylsilyl)ethoxy]methyl or t-butyl diphenylsilyl); esters (e.g. benzoate ester); carbonates (e.g. methoxymethylcarbonate); sulfonates (e.g. tosylate or mesylate); acyclic ketal (e.g. dimethyl acetal); cyclic ketals (e.g., 1,3-dioxane, 1,3-dioxolanes and those described herein); acyclic acetal; cyclic acetal (e.g., those described herein); acyclic hemiacetal; cyclic hemiacetal; cyclic dithioketals (e.g., 1,3-dithiane or 1,3-dithiolane); orthoesters (e.g., those described herein) and triarylmethyl groups (e.g., trityl; monomethoxytrityl (MMTr); 4,4'-dimethoxytrityl (DMTr); 4,4',4''-trimethoxytrityl (TMTr); and those described herein).

[0081] The term “pharmaceutically acceptable salt” refers to a salt of a compound that does not cause significant irritation to an organism to which it is administered and does not abrogate the biological activity and properties of the compound. In some embodiments, the salt is an acid addition salt of the compound. Pharmaceutical salts can be obtained by reacting a compound with inorganic acids such as hydrohalic acid (e.g., hydrochloric acid or hydrobromic acid), sulfuric acid, nitric acid and phosphoric acid. Pharmaceutical salts can also be obtained by reacting a compound with an organic acid such as aliphatic or aromatic carboxylic or sulfonic acids, for example formic, acetic, succinic, lactic, malic, tartaric, citric, ascorbic, nicotinic, methanesulfonic, ethanesulfonic, p-toluenesulfonic, salicylic or naphthalenesulfonic acid. Pharmaceutical salts can also be obtained by reacting a compound with a base to form a salt such as an ammonium salt, an alkali metal salt, such as a sodium or a potassium salt, an alkaline earth metal salt, such as a calcium or a magnesium salt, a salt of organic bases such as dicyclohexylamine, N-methyl-D-glucamine, tris(hydroxymethyl)methylamine, C₁-C₇ alkylamine, cyclohexylamine, triethanolamine, ethylenediamine, and salts with amino acids such as arginine and lysine.

[0082] Terms and phrases used in this application, and variations thereof, especially in the appended claims, unless otherwise expressly stated, should be construed as open ended as opposed to limiting. As examples of the foregoing, the term ‘including’ should be read to mean ‘including, without limitation,’ ‘including but not limited to,’ or the like; the term ‘comprising’ as used herein is synonymous with ‘including,’ ‘containing,’ or ‘characterized by,’ and is inclusive or open-ended and does not exclude additional, unrecited elements or method steps; the term ‘having’ should be interpreted as ‘having at least;’ the term ‘includes’ should be interpreted as ‘includes but is not limited to;’ the term ‘example’ is used to provide exemplary instances of the item in discussion, not an exhaustive or limiting list thereof; and use of terms like ‘preferably,’ ‘preferred,’ ‘desired,’ or ‘desirable,’ and words of similar meaning should not be understood as implying that certain features are critical, essential, or even important to the structure or function, but instead as merely intended to highlight alternative or additional features that may or may not be utilized in a particular embodiment. In addition, the term “comprising” is to be interpreted synonymously with the phrases “having at least” or “including at least”. When used in the context of a process, the term “comprising” means that the process includes at least the recited steps, but may include additional steps. When used in the context of a compound, composition or device, the term “comprising” means that the compound, composition or device includes at least the recited features or components, but may also include additional features or components. Likewise, a group of items linked with the conjunction ‘and’

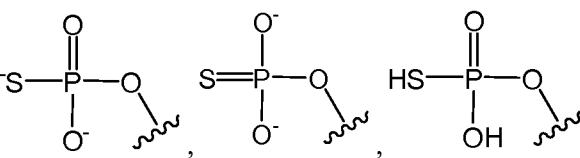
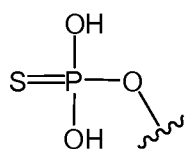
should not be read as requiring that each and every one of those items be present in the grouping, but rather should be read as 'and/or' unless expressly stated otherwise. Similarly, a group of items linked with the conjunction 'or' should not be read as requiring mutual exclusivity among that group, but rather should be read as 'and/or' unless expressly stated otherwise.

[0083] With respect to the use of substantially any plural and/or singular terms herein, those having skill in the art can translate from the plural to the singular and/or from the singular to the plural as is appropriate to the context and/or application. The various singular/plural permutations may be expressly set forth herein for sake of clarity. The indefinite article "a" or "an" does not exclude a plurality. A single processor or other unit may fulfill the functions of several items recited in the claims. The mere fact that certain measures are recited in mutually different dependent claims does not indicate that a combination of these measures cannot be used to advantage. Any reference signs in the claims should not be construed as limiting the scope.

[0084] It is understood that, in any compound described herein having one or more chiral centers, if an absolute stereochemistry is not expressly indicated, then each center may independently be of R-configuration or S-configuration or a mixture thereof. Thus, the compounds provided herein may be enantiomerically pure, enantiomerically enriched, racemic mixture, diastereomerically pure, diastereomerically enriched, or a stereoisomeric mixture. In addition it is understood that, in any compound described herein having one or more double bond(s) generating geometrical isomers that can be defined as E or Z, each double bond may independently be E or Z a mixture thereof.

[0085] Likewise, it is understood that, in any compound described, all tautomeric forms are also intended to be included. For example all tautomers of a phosphate and a phosphorothioate groups are intended to be included. Examples of tautomers of a

phosphorothioate include the following:

. Furthermore, all tautomers of heterocyclic bases known in the art are intended to be included, including tautomers of natural and non-natural purine-bases and pyrimidine-bases.

[0086] It is to be understood that where compounds disclosed herein have unfilled valencies, then the valencies are to be filled with hydrogens or isotopes thereof, e.g., hydrogen-1 (protium) and hydrogen-2 (deuterium).

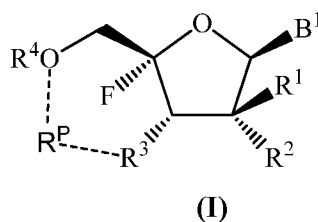
[0087] It is understood that the compounds described herein can be labeled isotopically. Substitution with isotopes such as deuterium may afford certain therapeutic advantages resulting from greater metabolic stability, such as, for example, increased *in vivo* half-life or reduced dosage requirements. Each chemical element as represented in a compound structure may include any isotope of said element. For example, in a compound structure a hydrogen atom may be explicitly disclosed or understood to be present in the compound. At any position of the compound that a hydrogen atom may be present, the hydrogen atom can be any isotope of hydrogen, including but not limited to hydrogen-1 (protium) and hydrogen-2 (deuterium). Thus, reference herein to a compound encompasses all potential isotopic forms unless the context clearly dictates otherwise.

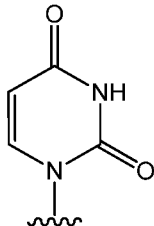
[0088] It is understood that the methods and combinations described herein include crystalline forms (also known as polymorphs, which include the different crystal packing arrangements of the same elemental composition of a compound), amorphous phases, salts, solvates and hydrates. In some embodiments, the compounds described herein exist in solvated forms with pharmaceutically acceptable solvents such as water, ethanol, or the like. In other embodiments, the compounds described herein exist in unsolvated form. Solvates contain either stoichiometric or non-stoichiometric amounts of a solvent, and may be formed during the process of crystallization with pharmaceutically acceptable solvents such as water, ethanol, or the like. Hydrates are formed when the solvent is water, or alcoholates are formed when the solvent is alcohol. In addition, the compounds provided herein can exist in unsolvated as well as solvated forms. In general, the solvated forms are considered equivalent to the unsolvated forms for the purposes of the compounds and methods provided herein.

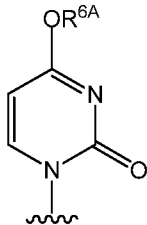
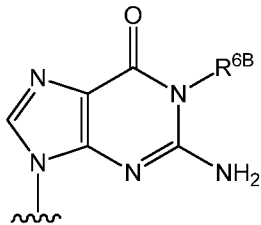
[0089] Where a range of values is provided, it is understood that the upper and lower limit, and each intervening value between the upper and lower limit of the range is encompassed within the embodiments.

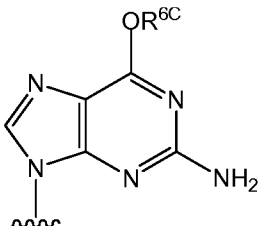
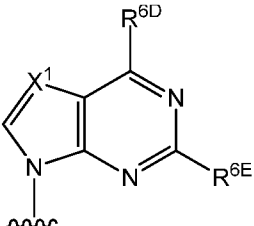
Compounds

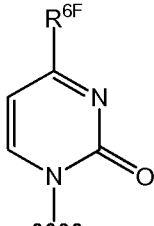
[0090] Some embodiments disclosed herein relate to a compound of Formula (I) or a pharmaceutically acceptable salt thereof:



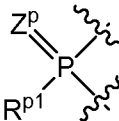
wherein: B¹ can be selected from an optionally substituted , an optionally

substituted , an optionally substituted , an optionally

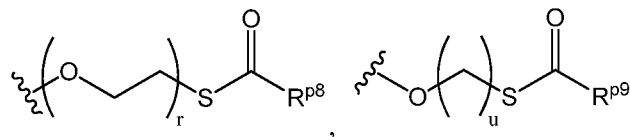
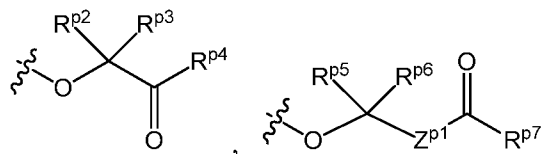
substituted , an optionally substituted  and an

optionally substituted ; R¹ can be selected from an optionally substituted C₁₋₆ alkyl, an optionally substituted C₂₋₆ alkenyl, an optionally substituted C₂₋₆ alkynyl and an optionally substituted C₃₋₆ cycloalkyl; each ----- can be absent or a single bond, provided that both -----

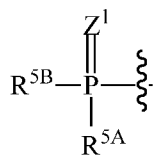
- are each absent or both ----- are each a single bond; when both ----- are each a single bond, then R² can be halo, N₃, -OR^{7A} or -N(R^{7B}R^{7C}); R⁴ can be absent; R³ can be oxygen (O); and R^P

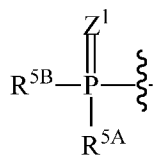
can be , wherein Z^P can be oxygen (O) or sulfur (S) and R^{P1} can be selected from O⁻,

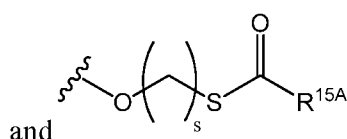
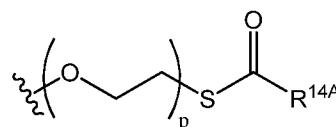
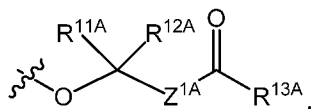
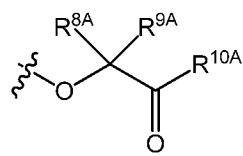
OH, an -O-optionally substituted C₁₋₆ alkyl.

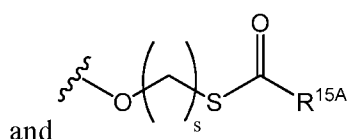


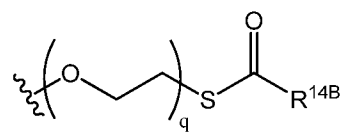
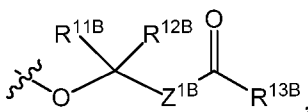
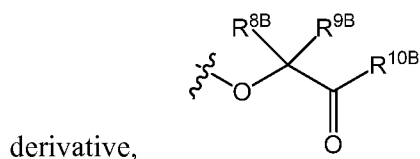
, an optionally substituted N-linked amino acid and an optionally substituted N-linked amino acid ester derivative; when both ----- are each absent, then R^p can be absent; R² can be halo, N₃, -OR^{7A} or -N(R^{7B}R^{7C}); R³ can be -OH or -OC(=O)R⁸; or R² and R³ can be each an oxygen atom which are linked together by a carbonyl



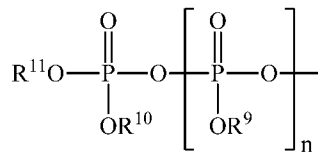
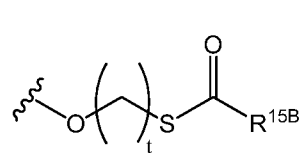
group; and R⁴ can be hydrogen or ; R^{5A} can be selected from O⁻, OH, an optionally substituted N-linked amino acid, an optionally substituted N-linked amino acid ester derivative,

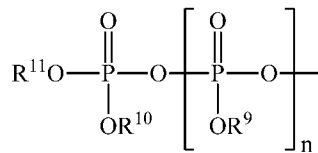


and ; R^{5B} can be selected from O⁻, OH, an -O-optionally substituted aryl, an -O-optionally substituted heteroaryl, an -O-optionally substituted heterocyclyl, an optionally substituted N-linked amino acid, an optionally substituted N-linked amino acid ester

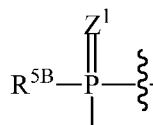


derivative,

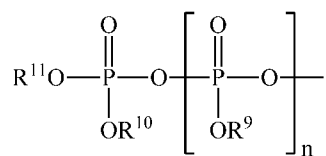


and ; R^{6A} can be an optionally substituted C₁₋₆ alkyl or an optionally substituted C₃₋₆ cycloalkyl; R^{6B} and R^{6C} can be independently selected from hydrogen, an unsubstituted C₁₋₆ alkyl, an unsubstituted C₃₋₆ alkenyl, an unsubstituted C₃₋₆ alkynyl and an unsubstituted C₃₋₆ cycloalkyl; R^{6D} can be NHR^{6G}; R^{6E} can be hydrogen, halogen or NHR^{6H}; R^{6F} can be NHR^{6I}; R^{6G} can be selected from hydrogen, an optionally substituted C₁₋₆ alkyl, an optionally substituted C₃₋₆ alkenyl, an optionally substituted C₃₋₆ cycloalkyl, -C(=O)R^{A1} and -C(=O)OR^{A2}; R^{6H} can be selected from hydrogen, an optionally substituted C₁₋₆

alkyl, an optionally substituted C₃₋₆ alkenyl, an optionally substituted C₃₋₆ cycloalkyl, –C(=O)R^{A3} and –C(=O)OR^{A4}; R^{6I} can be selected from hydrogen, an optionally substituted C₁₋₆ alkyl, an optionally substituted C₃₋₆ alkenyl, an optionally substituted C₃₋₆ cycloalkyl, –C(=O)R^{A5} and –C(=O)OR^{A6}; X¹ can be N (nitrogen) or –CR^{6J}, R^{6J} can be selected from hydrogen, halogen, an optionally substituted C₁₋₆ alkyl, an optionally substituted C₂₋₆ alkenyl and an optionally substituted C₂₋₆ alkynyl; R^{A1}, R^{A2}, R^{A3}, R^{A4}, R^{A5} and R^{A6} can be independently selected from C₁₋₆ alkyl, C₂₋₆ alkenyl, C₂₋₆ alkynyl, C₃₋₆ cycloalkyl, C₃₋₆ cycloalkenyl, C₆₋₁₀ aryl, heteroaryl, heterocyclyl, aryl(C₁₋₆ alkyl), heteroaryl(C₁₋₆ alkyl) and heterocyclyl(C₁₋₆ alkyl); R^{7A} can be hydrogen or –C(=O)R¹²; R^{7B} and R^{7C} can be independently hydrogen or an optionally substituted C₁₋₆ alkyl; R⁸ and R¹² can be independently an optionally substituted C₁₋₆ alkyl or an optionally substituted C₃₋₆ cycloalkyl; R⁹, R¹⁰ and R¹¹ can be independently absent or hydrogen; R^{8A}, R^{9A}, R^{11A}, R^{12A}, R^{8B}, R^{9B}, R^{11B}, R^{12B}, R^{p2}, R^{p3}, R^{p5} and R^{p6} can be independently selected from hydrogen, an optionally substituted C₁₋₂₄ alkyl and an optionally substituted aryl; R^{10A}, R^{10B}, R^{13A}, R^{13B}, R^{p4} and R^{p7} can be independently selected from hydrogen, an optionally substituted C₁₋₂₄ alkyl, an optionally substituted aryl, an optionally substituted –O–C₁₋₂₄ alkyl, an optionally substituted –O–aryl, an optionally substituted –O–heteroaryl and an optionally substituted –O–monocyclic heterocyclyl; R^{14A}, R^{14B}, R^{15A}, R^{15B}, R^{p8} and R^{p9} can be independently selected from hydrogen, an optionally substituted C₁₋₂₄ alkyl and an optionally substituted aryl; n can be 0 or 1; p, q, and r can be independently 1 or 2; s, t and u can be independently 3, 4 or 5; Z¹, Z^{1A}, Z^{1B} and Z^{p1} can be independently O (oxygen) or S (sulfur); and



provided that when R⁴ is $\begin{array}{c} Z^1 \\ \parallel \\ R^{5B}-P-\xi \\ | \\ R^{5A} \end{array}$; and R^{5A} is O[–] or OH, then R^{5B} is O[–], OH,



, an optionally substituted N-linked amino acid or an optionally substituted N-linked amino acid ester derivative.

[0091] The substituents attached to the 2'-carbon can vary. In some embodiments, R² can be halo. For example, R² can be fluoro or chloro. In other embodiments, R² can be N₃. In some embodiments, R² can be –OH. In other embodiments, R² can be OR^{7A}, wherein R^{7A} can be –C(=O)R¹², and R¹² can be an optionally substituted C₁₋₆ alkyl. Suitable alkyl groups include, but are not limited to optionally substituted variants of the following: methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, pentyl (branched and straight-chained) and hexyl (branched and straight-chained). In yet still other embodiments, R² can be OR^{7A}, wherein R^{7A}

can be $-C(=O)R^{12}$, and R^{12} can be an optionally substituted C_{3-6} cycloalkyl. Suitable cycloalkyl groups include, but are not limited to optionally substituted variants of the following: cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl. In some embodiment, R^2 can be $-N(R^{7B}R^{7C})$, wherein R^{7B} and R^{7C} can be independently hydrogen or an optionally substituted C_{1-6} alkyl. In some embodiments, R^{7B} and R^{7C} can be both hydrogen, such that R^2 can be $-NH_2$. In other embodiments, at least one of R^{7B} and R^{7C} can be an optionally substituted C_{1-6} alkyl. In some embodiments, R^{7B} and R^{7C} can be both an optionally substituted C_{1-6} alkyl. In some embodiments, R^{7B} and R^{7C} can be the same. In other embodiments, R^{7B} and R^{7C} can be different.

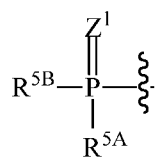
[0092] Various substituents can be attached to the 3'-carbon of the pentose ring. In some embodiments, R^3 can be $-OH$. In other embodiments, R^3 can be $-OC(=O)R^8$, wherein R^8 can be an optionally substituted C_{1-6} alkyl such as those described herein. In still other embodiments, R^3 can be $-OC(=O)R^8$, wherein R^8 can be an optionally substituted C_{3-6} cycloalkyl. Examples of suitable optionally substituted C_{3-6} cycloalkyl groups are described herein.

[0093] In some embodiments, R^2 and R^3 can each be an oxygen atom and the oxygen atoms can be linked together by a carbonyl group. In other embodiments, R^2 and R^3 can be both $-OH$. In other embodiments, R^2 can be halo and R^3 can be $-OH$. In still other embodiments, R^2 can be halo and R^3 can be $-OC(=O)R^8$.

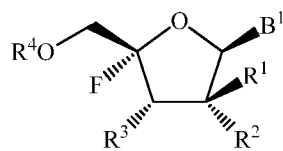
[0094] In some embodiments, R^1 can be an optionally substituted C_{1-6} alkyl. In some embodiments, R^1 can be an unsubstituted C_{1-6} alkyl. For example, R^1 can be unsubstituted methyl, unsubstituted ethyl, unsubstituted n-propyl, unsubstituted isopropyl, unsubstituted n-butyl, unsubstituted isobutyl, unsubstituted tert-butyl, unsubstituted pentyl (branched and straight-chained) or unsubstituted hexyl (branched and straight-chained). In some embodiments, R^1 can be a substituted C_{1-6} alkyl. Suitable substitutions are described herein. As an example, R^1 can be a halo-substituted C_{1-6} alkyl (such as $-CF_3$ or $-CH_2CH_2F$). In other embodiments, R^1 can be an optionally substituted C_{2-6} alkenyl. Suitable alkenyl groups include, but are not limited to optionally substituted variants of the following: ethenyl, n-propenyl, isopropenyl, n-butenyl, isobutenyl, tert-butenyl, pentenyl (branched and straight-chained), hexenyl (branched and straight-chained), vinyl and allenyl. In still other embodiments, R^1 can be an optionally substituted C_{2-6} alkynyl. In yet still other embodiments, R^1 can be an optionally substituted C_{3-6} cycloalkyl, such as those described herein.

[0095] In some embodiments, both ----- can be each absent, R^p can be absent; R^2 can be halo, N_3 , $-OR^{7A}$ or $-N(R^{7B}R^{7C})$; R^3 can be $-OH$ or $-OC(=O)R^8$; or R^2 and R^3 can be each

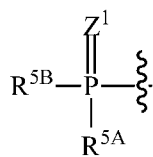
an oxygen atom which are linked together by a carbonyl group; and R^4 can be hydrogen or



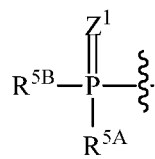
When both ----- are absent, Formula (I) can have the structure:



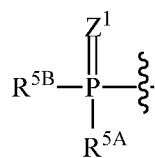
. In some embodiments, R^4 can be hydrogen. In other embodiments, R^4



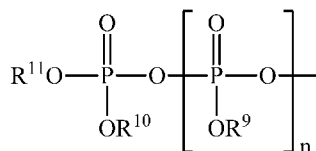
can be R^{5A} . In some embodiments, the compound of Formula (I) can be a monophosphate. In other embodiments, the compound of Formula (I) can be a thiomonophosphate. In some embodiments, the compound of Formula (I) can be a diphosphate. In other embodiments, the compound of Formula (I) can be an alpha-thiodiphosphate. In some embodiments, the compound of Formula (I) can be a triphosphate. In other embodiments, the compound of Formula (I) can be an alpha-thiotriphosphate. In some embodiments, R^4 can be



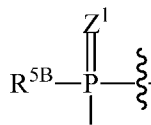
; R^{5A} can be O^- or OH ; and R^{5B} can be O^- or OH . In other embodiments, R^4 can be



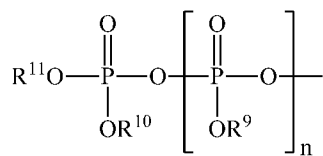
; R^{5A} can be O^- or OH ; R^{5B} can be



; and n can be 0. In



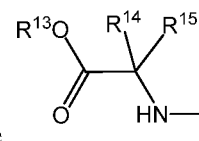
still other embodiments, R^4 can be R^{5A} ; R^{5A} can be O^- or OH ; R^{5B} can be

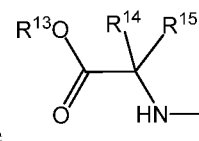


; and n can be 1. The substituents attached to the phosphorus can

vary. In some embodiments, a compound of Formula (I) can be a phosphoroamidate. In other embodiments, a compound of Formula (I) can be a thiophosphoroamidate. In still other embodiments, a compound of Formula (I) can be a phosphorbisamidate. In yet still other embodiments, a compound of Formula (I) can be a thiophosphorbisamidate.

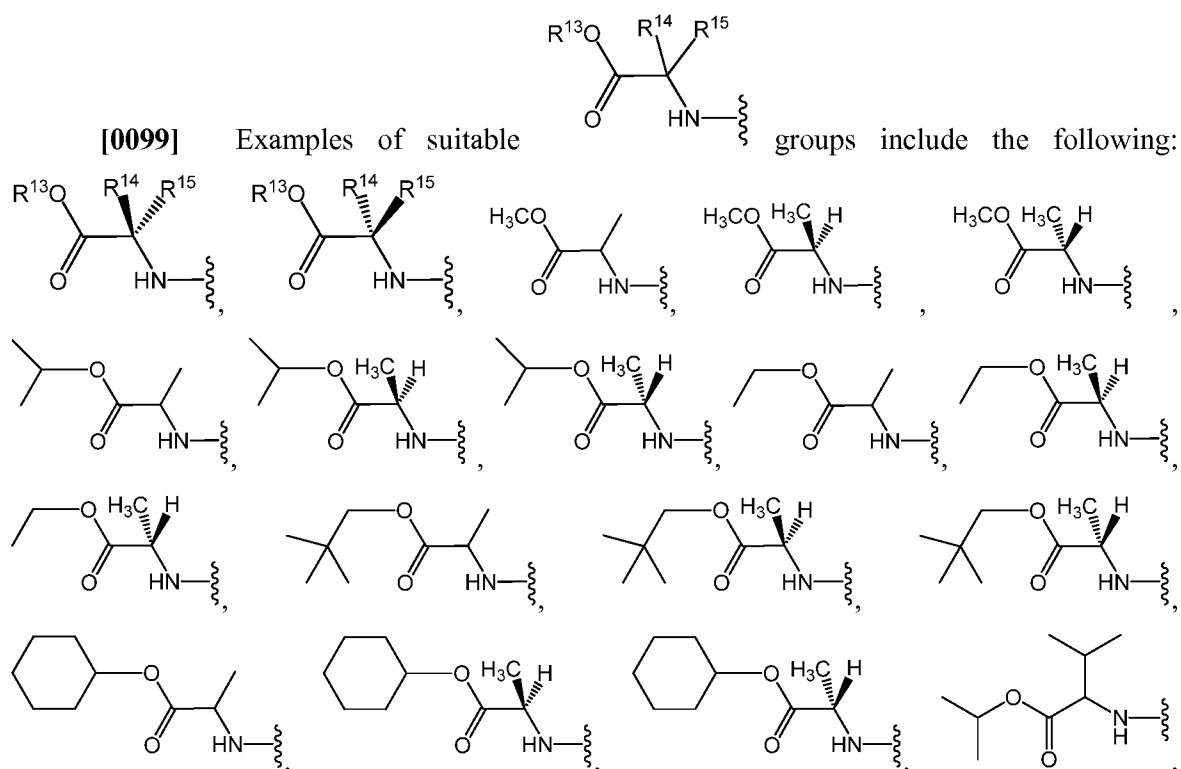
[0096] In some embodiments, R^{5A} can be an optionally substituted N-linked amino acid. Various amino acids are suitable, including those described herein. Examples of suitable amino acids include, but are not limited to, alanine, asparagine, aspartate, cysteine, glutamate, glutamine, glycine, proline, serine, tyrosine, arginine, histidine, isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan and valine. In other embodiments, R^{5A} can be an optionally substituted N-linked amino acid ester derivative. Examples of N-linked amino acid ester derivatives include, but are not limited to, ester derivatives of any of the following amino acids: alanine, asparagine, aspartate, cysteine, glutamate, glutamine, glycine, proline, serine, tyrosine, arginine, histidine, isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan and valine. Additional examples of N-linked amino acid ester derivatives include, but are not limited to, an ester derivative of any of the following amino acids: alpha-ethyl-glycine, alpha-propyl-glycine and beta-alanine. In some embodiments, the N-linked amino acid ester derivative can be a C_{1-6} alkyl ester derivative, for example, an isopropyl ester of alanine. In other embodiments, the N-linked amino acid ester derivative can be a C_{3-6} cycloalkyl ester derivative, such as a cyclohexyl ester of alanine.

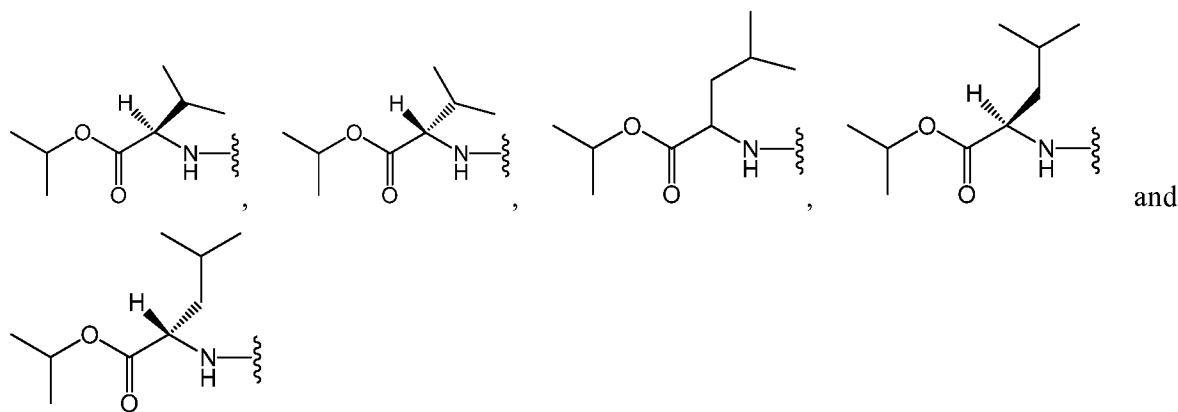


[0097] In some embodiments, R^{5A} can have the structure  wherein R^{13} can be selected from hydrogen, an optionally substituted C_{1-6} -alkyl, an optionally substituted C_{3-6} cycloalkyl, an optionally substituted aryl, an optionally substituted aryl(C_{1-6} alkyl) and an optionally substituted haloalkyl; R^{14} can be selected from hydrogen, an optionally substituted C_{1-6} alkyl, an optionally substituted C_{1-6} haloalkyl, an optionally substituted C_{3-6} cycloalkyl, an optionally substituted C_6 aryl, an optionally substituted C_{10} aryl and an optionally substituted aryl(C_{1-6} alkyl); and R^{15} can be hydrogen or an optionally substituted C_{1-4} -alkyl; or R^{14} and R^{15} can be taken together to form an optionally substituted C_{3-6} cycloalkyl.

[0098] When R^{14} is substituted, R^{14} can be substituted with one or more substituents selected from N-amido, mercapto, alkylthio, an optionally substituted aryl, hydroxy, an optionally substituted heteroaryl, O-carboxy and amino. In some embodiments, R^{14} can be an unsubstituted C_{1-6} -alkyl, such as those described herein. In some embodiments, R^{14} can be hydrogen. In other embodiments, R^{14} can be methyl. In some embodiments, R^{13} can be an optionally substituted C_{1-6} alkyl. Examples of optionally substituted C_{1-6} -alkyls include optionally substituted variants of the following: methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, pentyl (branched and straight-chained) and hexyl (branched and straight-chained). In some embodiments, R^{13} can be methyl or isopropyl. In some embodiments, R^{13}

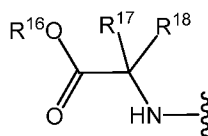
can be ethyl or neopentyl. In other embodiments, R^{13} can be an optionally substituted C_{3-6} cycloalkyl. Examples of optionally substituted C_{3-6} cycloalkyl include optionally substituted variants of the following: cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl. In some embodiments, R^{13} can be an optionally substituted cyclohexyl. In still other embodiments, R^{13} can be an optionally substituted aryl, such as phenyl and naphthyl. In yet still other embodiments, R^{13} can be an optionally substituted aryl(C_{1-6} alkyl). In some embodiments, R^{13} can be an optionally substituted benzyl. In some embodiments, R^{13} can be an optionally substituted C_{1-6} haloalkyl, for example, CF_3 . In some embodiments, R^{15} can be hydrogen. In other embodiments, R^{15} can be an optionally substituted C_{1-4} alkyl, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl or tert-butyl. In some embodiments, R^{15} can be methyl. In some embodiments, R^{14} and R^{15} can be taken together to form an optionally substituted C_{3-6} cycloalkyl. Examples of optionally substituted C_{3-6} cycloalkyl include optionally substituted variants of the following: cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl. Depending on the groups that are selected for R^{14} and R^{15} , the carbon to which R^{14} and R^{15} are attached may be a chiral center. In some embodiment, the carbon to which R^{14} and R^{15} are attached may be a (R)-chiral center. In other embodiments, the carbon to which R^{14} and R^{15} are attached may be a (S)-chiral center.





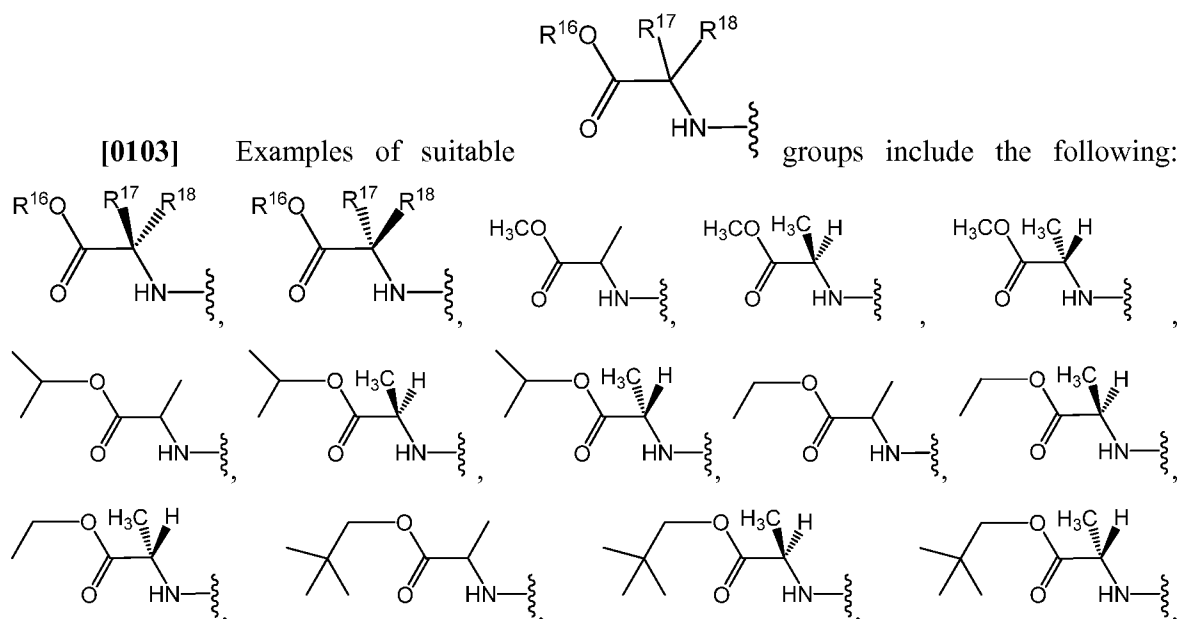
[0100] In some embodiments, R^{5B} can be an $-O$ -optionally substituted aryl. For example, R^{5B} can be an $-O$ -optionally substituted phenyl. When the phenyl is substituted, the ring can be substituted 1, 2, 3 or more than 3 times. Suitable mono-substituted phenyl groups include, ortho-substituted phenyl, meta-substituted phenyl and para-substituted phenyl. In other embodiments, R^{5B} can be an $-O$ -unsubstituted aryl. Alternatively, R^{5B} can be an $-O$ -optionally substituted naphthyl. In other embodiments, R^{5B} can be an $-O$ -optionally substituted heteroaryl. For example, R^{5B} can be an $-O$ -optionally substituted quinoliny. In still other embodiments, R^{5B} can be an $-O$ -optionally substituted heterocyclyl.

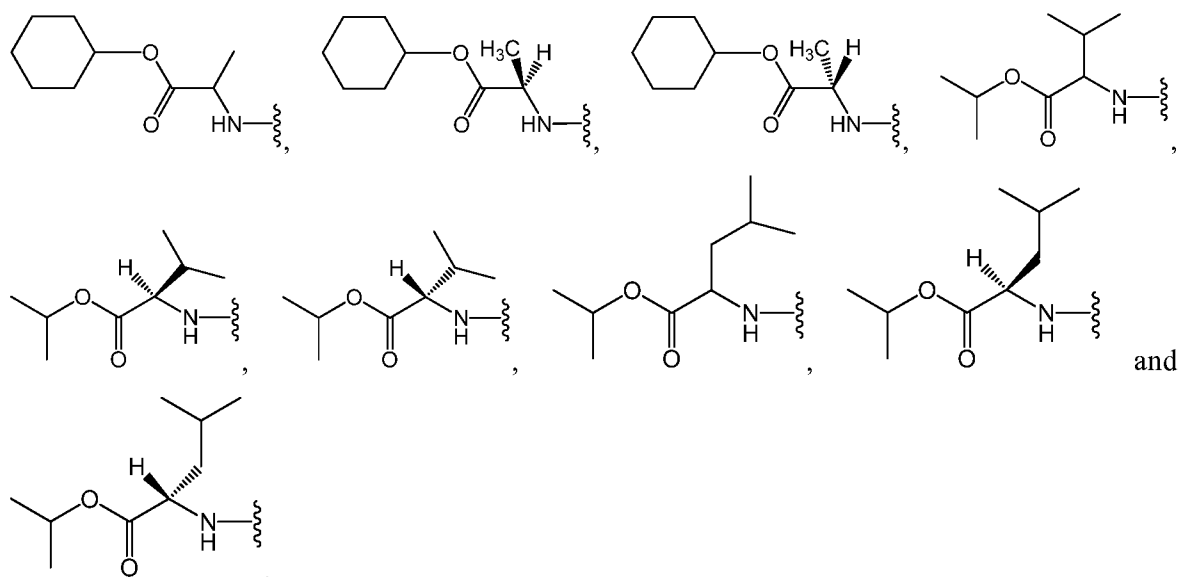
[0101] In some embodiments, R^{5B} is an optionally substituted N-linked amino acid, such as those described for R^{5A} . In other embodiments, R^{5B} is an optionally substituted N-linked amino acid ester derivative, for example, those described herein. In some embodiments,

R^{5B} can have the structure  wherein R^{16} can be selected from hydrogen, an optionally substituted C_{1-6} -alkyl, an optionally substituted C_{3-6} cycloalkyl, an optionally substituted aryl, an optionally substituted aryl(C_{1-6} alkyl) and an optionally substituted haloalkyl; R^{17} can be selected from hydrogen, an optionally substituted C_{1-6} alkyl, an optionally substituted C_{1-6} haloalkyl, an optionally substituted C_{3-6} cycloalkyl, an optionally substituted C_6 aryl, an optionally substituted C_{10} aryl and an optionally substituted aryl(C_{1-6} alkyl); and R^{18} can be hydrogen or an optionally substituted C_{1-4} -alkyl; or R^{17} and R^{18} can be taken together to form an optionally substituted C_{3-6} cycloalkyl.

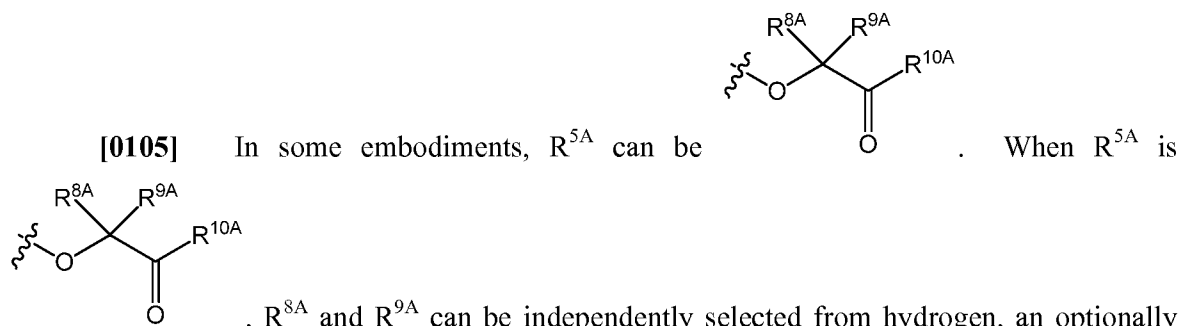
[0102] When R^{17} is substituted, R^{17} can be substituted with one or more substituents selected from N-amido, mercapto, alkylthio, an optionally substituted aryl, hydroxy, an optionally substituted heteroaryl, O-carboxy and amino. In some embodiments, R^{17} can be an unsubstituted C_{1-6} -alkyl, such as those described herein. In some embodiments, R^{17} can be hydrogen. In other embodiments, R^{17} can be methyl. In some embodiments, R^{16} can be an

optionally substituted C₁₋₆ alkyl. Examples of optionally substituted C₁₋₆-alkyls include optionally substituted variants of the following: methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, pentyl (branched and straight-chained) and hexyl (branched and straight-chained). In some embodiments, R¹⁶ can be methyl or isopropyl. In some embodiments, R¹⁶ can be ethyl or neopentyl. In other embodiments, R¹⁶ can be an optionally substituted C₃₋₆ cycloalkyl. Examples of optionally substituted C₃₋₆ cycloalkyl include optionally substituted variants of the following: cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl. In some embodiments, R¹⁶ can be an optionally substituted cyclohexyl. In still other embodiments, R¹⁶ can be an optionally substituted aryl, such as phenyl and naphthyl. In yet still other embodiments, R¹⁶ can be an optionally substituted aryl(C₁₋₆ alkyl). In some embodiments, R¹⁶ can be an optionally substituted benzyl. In some embodiments, R¹⁶ can be an optionally substituted C₁₋₆ haloalkyl, for example, CF₃. In some embodiments, R¹⁸ can be hydrogen. In other embodiments, R¹⁸ can be an optionally substituted C₁₋₄-alkyl, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl or tert-butyl. In some embodiments, R¹⁸ can be methyl. In some embodiments, R¹⁷ and R¹⁸ can be taken together to form an optionally substituted C₃₋₆ cycloalkyl. Examples of optionally substituted C₃₋₆ cycloalkyl include optionally substituted variants of the following: cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl. Depending on the groups that are selected for R¹⁷ and R¹⁸, the carbon to which R¹⁷ and R¹⁸ are attached may be a chiral center. In some embodiment, the carbon to which R¹⁷ and R¹⁸ are attached may be a (R)-chiral center. In other embodiments, the carbon to which R¹⁷ and R¹⁸ are attached may be a (S)-chiral center.

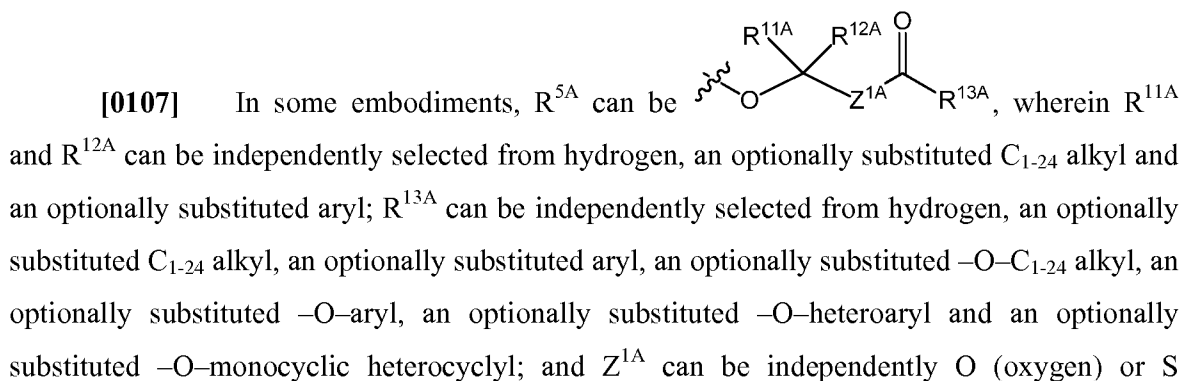
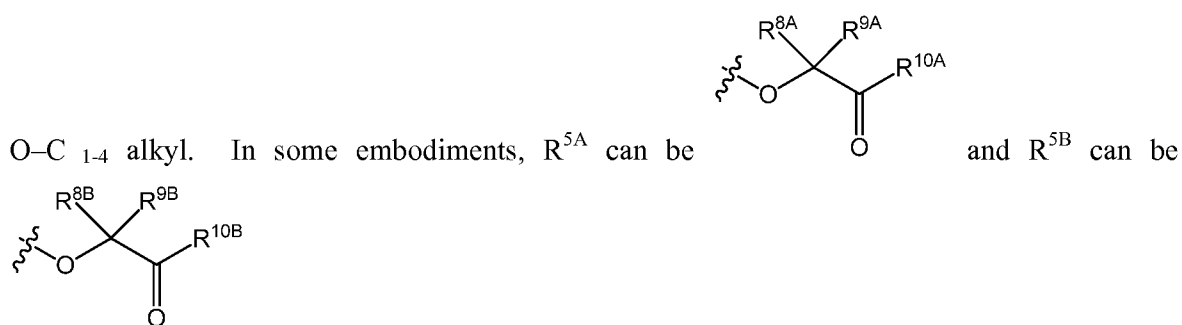
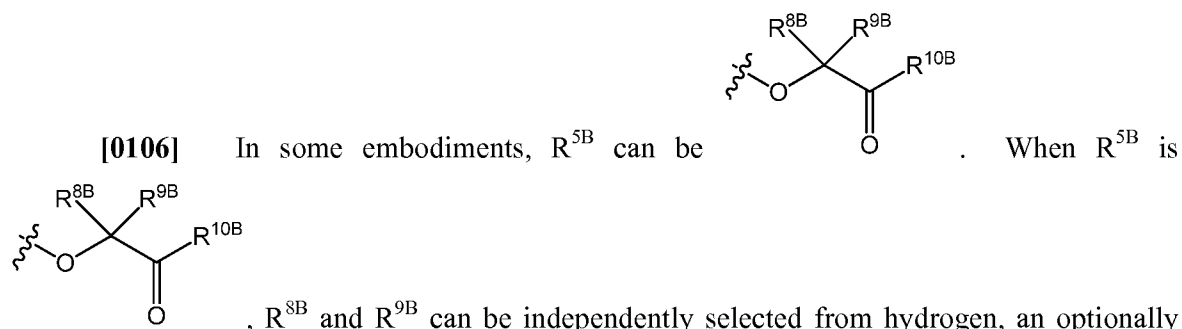




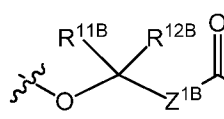
[0104] In some embodiments, R^{5A} can be an optionally substituted N-linked amino acid or an optionally substituted N-linked amino acid ester derivative and R^{5B} can be an $-O-$ optionally substituted aryl. In other embodiments, R^{5A} can be an optionally substituted N-linked amino acid or an optionally substituted N-linked amino acid ester derivative and R^{5B} can be an $-O-$ optionally substituted heteroaryl. In some embodiments, R^{5A} can be an optionally substituted N-linked amino acid or an optionally substituted N-linked amino acid ester derivative and R^{5A} can be an optionally substituted N-linked amino acid or an optionally substituted N-linked amino acid ester derivative.

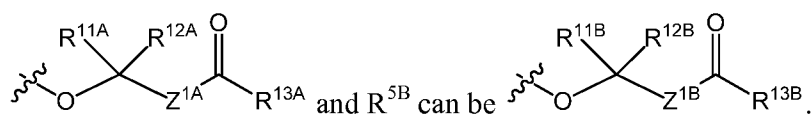


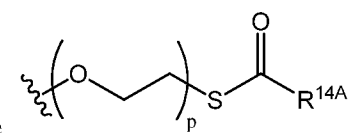
an optionally substituted --O--aryl , an optionally substituted --O--heteroaryl or an optionally substituted $\text{--O--monocyclic heterocyclyl}$. In some embodiments, $\text{R}^{10\text{A}}$ can be an unsubstituted --O--C_{1-4} alkyl.



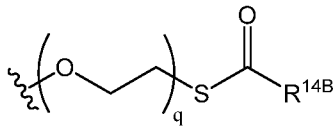
(sulfur). In some embodiments, R^{11A} and R^{12A} can be hydrogen. In other embodiments, at least one of R^{11A} and R^{12A} can be an optionally substituted C_{1-24} alkyl or an optionally substituted aryl. In some embodiments, R^{13A} can be an optionally substituted C_{1-24} alkyl. In some embodiments, R^{13A} can be an unsubstituted C_{1-4} alkyl. In other embodiments, R^{13A} can be an optionally substituted aryl. In still other embodiments, R^{13A} can be an optionally substituted $-O-C_{1-24}$ alkyl, an optionally substituted $-O$ -aryl, an optionally substituted $-O$ -heteroaryl or an optionally substituted $-O$ -monocyclic heterocyclyl. In some embodiments, R^{13A} can be an unsubstituted $-O-C_{1-4}$ alkyl. In some embodiments, Z^{1A} can be O (oxygen). In other embodiments, Z^{1A} can be or S (sulfur).

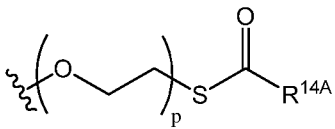
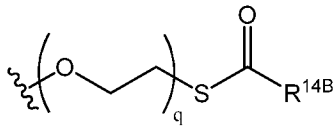
[0108] In some embodiments, R^{5B} can be , wherein R^{11B} and R^{12B} can be independently selected from hydrogen, an optionally substituted C_{1-24} alkyl and an optionally substituted aryl; R^{13B} can be independently selected from hydrogen, an optionally substituted C_{1-24} alkyl, an optionally substituted aryl, an optionally substituted $-O-C_{1-24}$ alkyl, an optionally substituted $-O$ -aryl, an optionally substituted $-O$ -heteroaryl and an optionally substituted $-O$ -monocyclic heterocyclyl; and Z^{1B} can be independently O (oxygen) or S (sulfur). In some embodiments, R^{11B} and R^{12B} can be hydrogen. In other embodiments, at least one of R^{11B} and R^{12B} can be an optionally substituted C_{1-24} alkyl or an optionally substituted aryl. In some embodiments, R^{13B} can be an optionally substituted C_{1-24} alkyl. In some embodiments, R^{13B} can be an unsubstituted C_{1-4} alkyl. In other embodiments, R^{13B} can be an optionally substituted aryl. In still other embodiments, R^{13B} can be an optionally substituted $-O-C_{1-24}$ alkyl, an optionally substituted $-O$ -aryl, an optionally substituted $-O$ -heteroaryl or an optionally substituted $-O$ -monocyclic heterocyclyl. In some embodiments, R^{13B} can be an unsubstituted $-O-C_{1-4}$ alkyl. In some embodiments, Z^{1B} can be O (oxygen). In other embodiments, Z^{1B} can be or S (sulfur). In some embodiments, R^{5A} can be

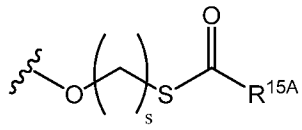


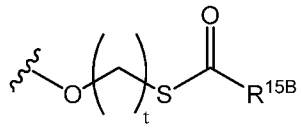
[0109] In some embodiments, R^{5A} can be . In some embodiments, R^{14A} can be hydrogen. In other embodiments, R^{14A} can be an optionally substituted C_{1-24} alkyl. In still other embodiments, R^{14A} can be an optionally substituted aryl. In some embodiments, R^{14A} can be a C_{1-6} alkyl, for example, methyl, ethyl, n-propyl, isopropyl, n-

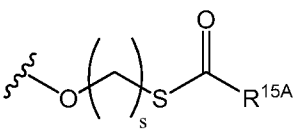
butyl, isobutyl, tert-butyl, pentyl (branched and straight-chained), and hexyl (branched and straight-chained). In some embodiments, p can be 1. In other embodiments, p can be 2.

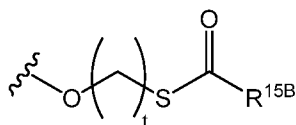
[0110] In some embodiments, R^{5B} can be . In some embodiments, R^{14B} can be hydrogen. In other embodiments, R^{14B} can be an optionally substituted C_{1-24} alkyl. In still other embodiments, R^{14B} can be an optionally substituted aryl. In some embodiments, R^{14B} can be a C_{1-6} alkyl, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, pentyl (branched and straight-chained), and hexyl (branched and straight-chained). In some embodiments, q can be 1. In other embodiments, q can be 2. In

some embodiments, R^{5A} can be  and R^{5B} can be .

[0111] In some embodiments, R^{5A} can be . In some embodiments, R^{15A} can be hydrogen. In other embodiments, R^{15A} can be an optionally substituted C_{1-24} alkyl. In still other embodiments, R^{15A} can be an optionally substituted aryl, for example, an optionally substituted phenyl. In some embodiments, R^{15A} can be an optionally substituted C_{1-6} alkyl. In some embodiments, R^{15A} can be an unsubstituted C_{1-6} alkyl. In some embodiments, s can be 3. In other embodiments, s can be 4. In still other embodiments, s can be 5.

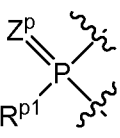
[0112] In some embodiments, R^{5B} can be . In some embodiments, R^{15B} can be hydrogen. In other embodiments, R^{15B} can be an optionally substituted C_{1-24} alkyl. In still other embodiments, R^{15B} can be an optionally substituted aryl, for example, an optionally substituted phenyl. In some embodiments, R^{15B} can be an optionally substituted C_{1-6} alkyl. In some embodiments, R^{15B} can be an unsubstituted C_{1-6} alkyl. In some embodiments, t can be 3. In other embodiments, t can be 4. In still other embodiments, t can be

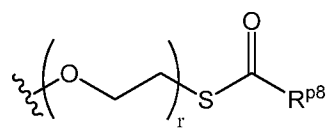
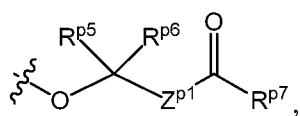
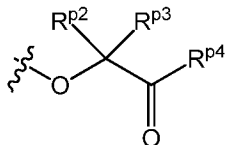
5. In some embodiments, R^{5A} can be  and R^{5B} can be



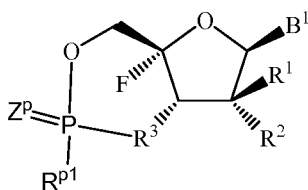
[0113] In some embodiments, R^{5A} and/or R^{5B} can be isopropoxyloxycarbonyloxymethoxy (POC) group. In some embodiments, R^{5A} and/or R^{5B} can be pivaloyloxymethoxy (POM) group. In some embodiments, R^{5A} and R^{5B} can be both a isopropoxyloxycarbonyloxymethoxy (POC) group, and form a bis(isopropoxyloxycarbonyloxymethoxy) (bis(POC)) prodrug. In other embodiments, R^{5A} and R^{5B} can be both a pivaloyloxymethoxy (POM) group, and form a bis(pivaloyloxymethoxy) (bis(POM)) prodrug. In still other embodiments, R^{5A} and R^{5B} can be both a S-acylthioethyl (SATE)-O- group and form a SATE ester prodrug. In some embodiments, R^{5A} and R^{5B} can be the same. In other embodiments, R^{5A} and R^{5B} can be different.

[0114] In some embodiments, both ----- can be each a single bond; R^4 can be

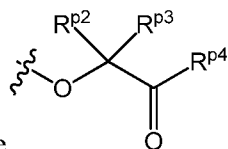
absent; R^3 can be oxygen (O); and R^p can be , wherein Z^p can be oxygen (O) or sulfur (S) and R^{p1} can be selected from O^- , OH, an -O-optionally substituted C_{1-6} alkyl.



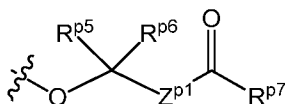
, an optionally substituted N-linked amino acid and an optionally substituted N-linked amino acid ester derivative. When both ----- are each a single bond, Formula (I) can have the structure:



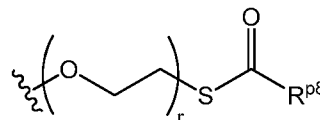
[0115] In some embodiments, R^{p1} can be O^- . In other embodiments, R^{p1} can be OH. In other embodiments, R^{p1} can be an -O-optionally substituted C_{1-6} alkyl. For example, R^{p1} can be a substituted or an unsubstituted version of the following: methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, iso-butoxy, tert-butoxy, pentoxy (branched or straight chained) and hexoxy (branched or straight chained).



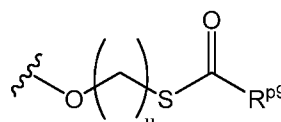
[0116] In some embodiments, R^{p1} can be wherein R^{p2} and R^{p3} can be independently selected from hydrogen, an optionally substituted C_{1-24} alkyl and an optionally substituted aryl; and R^{p4} can be selected from hydrogen, an optionally substituted C_{1-24} alkyl, an optionally substituted aryl, an optionally substituted $-O-C_{1-24}$ alkyl, an optionally substituted $-O$ -aryl, an optionally substituted $-O$ -heteroaryl and an optionally substituted $-O$ -monocyclic heterocyclyl. In some embodiments, R^{p2} and R^{p3} can be hydrogen. In other embodiments, at least one of R^{p2} and R^{p3} can be an optionally substituted C_{1-24} alkyl or an optionally substituted aryl. In some embodiments, R^{p4} can be an optionally substituted C_{1-24} alkyl. In some embodiments, R^{p4} can be an unsubstituted C_{1-4} alkyl. In other embodiments, R^{p4} can be an optionally substituted aryl. In still other embodiments, R^{p4} can be an optionally substituted $-O-C_{1-24}$ alkyl, an optionally substituted $-O$ -aryl, an optionally substituted $-O$ -heteroaryl or an optionally substituted $-O$ -monocyclic heterocyclyl. In some embodiments, R^{p4} can be an unsubstituted $-O-C_{1-4}$ alkyl.



[0117] In some embodiments, R^{p1} can be wherein R^{p5} and R^{p6} can be independently selected from hydrogen, an optionally substituted C_{1-24} alkyl and an optionally substituted aryl; R^{p7} can be independently selected from hydrogen, an optionally substituted C_{1-24} alkyl, an optionally substituted aryl, an optionally substituted $-O-C_{1-24}$ alkyl, an optionally substituted $-O$ -aryl, an optionally substituted $-O$ -heteroaryl and an optionally substituted $-O$ -monocyclic heterocyclyl; and Z^{p1} can be independently O (oxygen) or S (sulfur). In some embodiments, R^{p5} and R^{p6} can be hydrogen. In other embodiments, at least one of R^{p5} and R^{p6} can be an optionally substituted C_{1-24} alkyl or an optionally substituted aryl. In some embodiments, R^{p7} can be an optionally substituted C_{1-24} alkyl. . In some embodiments, R^{p7} can be an unsubstituted C_{1-4} alkyl. In other embodiments, R^{p7} can be an optionally substituted aryl. In still other embodiments, R^{p7} can be an optionally substituted $-O-C_{1-24}$ alkyl, an optionally substituted $-O$ -aryl, an optionally substituted $-O$ -heteroaryl or an optionally substituted $-O$ -monocyclic heterocyclyl. In some embodiments, R^{p7} can be an unsubstituted $-O-C_{1-4}$ alkyl. In some embodiments, Z^{p1} can be O (oxygen). In other embodiments, Z^{p1} can be or S (sulfur). In some embodiments, R^{p1} can be isopropoxyloxycarbonyloxymethoxy (POC) group. In some embodiments, R^{p1} can be pivaloxyloxymethoxy (POM) group.

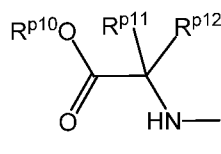


[0118] In some embodiments, R^{p1} can be . In some embodiments, R^{p8} can be hydrogen. In other embodiments, R^{p8} can be an optionally substituted C_{1-24} alkyl. In still other embodiments, R^{p8} can be an optionally substituted aryl. In some embodiments, R^{p8} can be a C_{1-6} alkyl, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, pentyl (branched and straight-chained), and hexyl (branched and straight-chained). In some embodiments, r can be 1. In other embodiments, r can be 2.



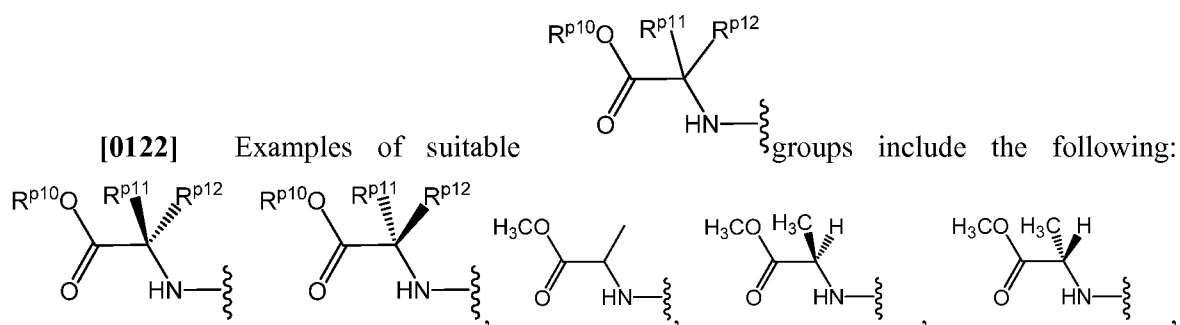
[0119] In some embodiments, R^{p1} can be . In some embodiments, R^{p9} can be hydrogen. In other embodiments, R^{p9} can be an optionally substituted C_{1-24} alkyl. In still other embodiments, R^{p9} can be an optionally substituted aryl, for example, an optionally substituted phenyl. In some embodiments, R^{p9} can be an optionally substituted C_{1-6} alkyl. In some embodiments, R^{p9} can be an unsubstituted C_{1-6} alkyl. In some embodiments, u can be 3. In other embodiments, u can be 4. In still other embodiments, u can be 5. In some embodiments, R^{p1} can be a S-acylthioethyl (SATE) group and form a SATE ester prodrug.

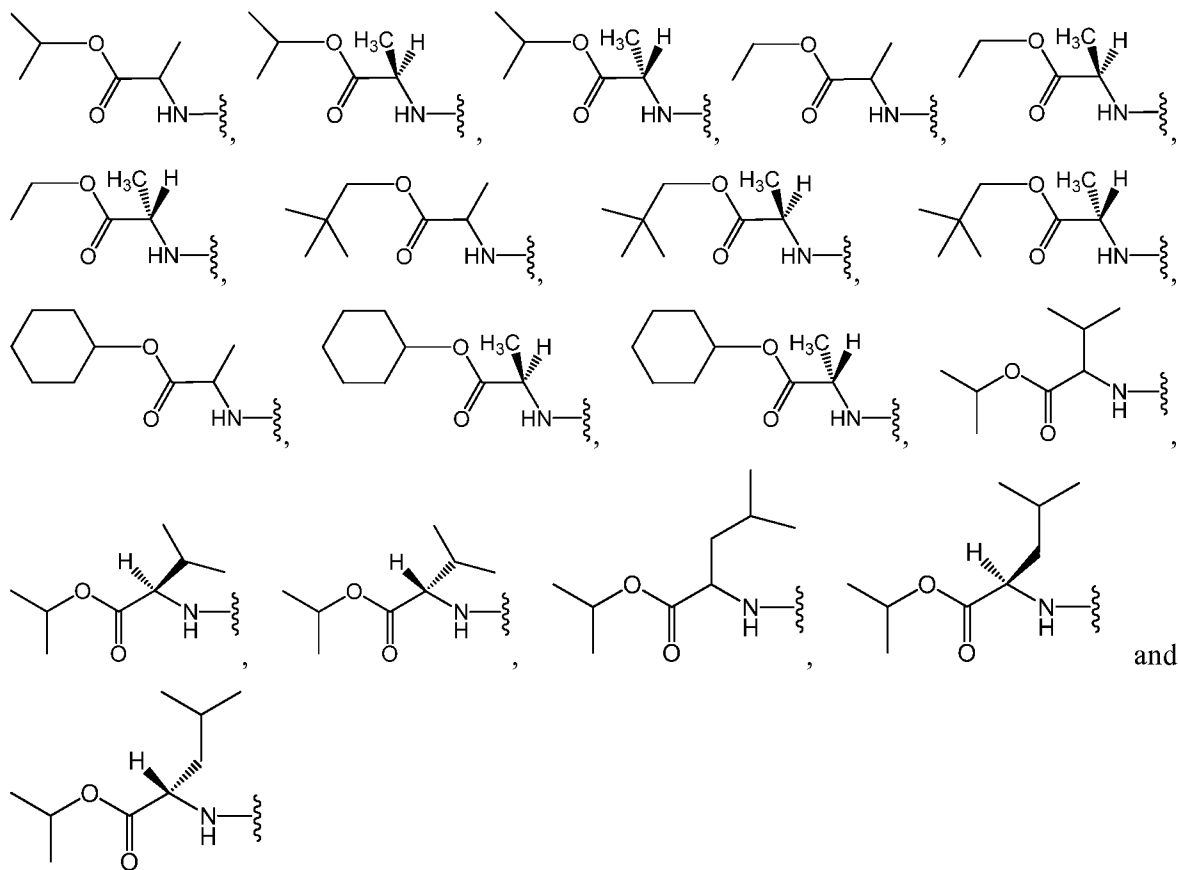
[0120] In some embodiments, R^{p1} can be an optionally substituted N-linked amino acid or an optionally substituted N-linked amino acid ester derivative. For example, R^{p1} can be optionally substituted version of the following: alanine, asparagine, aspartate, cysteine, glutamate, glutamine, glycine, proline, serine, tyrosine, arginine, histidine, isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, valine and ester derivatives thereof. In some embodiments, R^{p1} can be selected from N-alanine isopropyl ester, N-alanine cyclohexyl ester, N-alanine neopentyl ester, N-valine isopropyl ester and N-leucine isopropyl ester. In



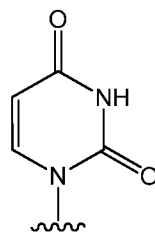
some embodiments, R^{p1} can have the structure , wherein R^{p10} can be selected from hydrogen, an optionally substituted C_{1-6} -alkyl, an optionally substituted C_{3-6} cycloalkyl, an optionally substituted aryl, an optionally substituted aryl(C_{1-6} alkyl) and an optionally substituted haloalkyl; R^{p11} can be selected from hydrogen, an optionally substituted C_{1-6} alkyl, an optionally substituted C_{1-6} haloalkyl, an optionally substituted C_{3-6} cycloalkyl, an optionally substituted C_6 aryl, an optionally substituted C_{10} aryl and an optionally substituted aryl(C_{1-6} alkyl); and R^{p12} can be hydrogen or an optionally substituted C_{1-4} -alkyl; or R^{p11} and R^{p12} can be taken together to form an optionally substituted C_{3-6} cycloalkyl.

[0121] When R^{p11} is substituted, R^{p11} can be substituted with one or more substituents selected from N-amido, mercapto, alkylthio, an optionally substituted aryl, hydroxy, an optionally substituted heteroaryl, O-carboxy, and amino. In some embodiments, R^{p11} can be an unsubstituted C_{1-6} -alkyl, such as those described herein. In some embodiments, R^{p11} can be hydrogen. In other embodiments, R^{p11} can be methyl. In some embodiments, R^{p10} can be an optionally substituted C_{1-6} alkyl. Examples of optionally substituted C_{1-6} -alkyls include optionally substituted variants of the following: methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, pentyl (branched and straight-chained), and hexyl (branched and straight-chained). In some embodiments, R^{p10} can be methyl or isopropyl. In some embodiments, R^{p10} can be ethyl or neopentyl. In other embodiments, R^{p10} can be an optionally substituted C_{3-6} cycloalkyl. Examples of optionally substituted C_{3-6} cycloalkyl include optionally substituted variants of the following: cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl. In some embodiments, R^{p10} can be an optionally substituted cyclohexyl. In still other embodiments, R^{p10} can be an optionally substituted aryl, such as phenyl and naphthyl. In yet still other embodiments, R^{p10} can be an optionally substituted aryl(C_{1-6} alkyl). In some embodiments, R^{p10} can be an optionally substituted benzyl. In some embodiments, R^{p10} can be an optionally substituted C_{1-6} haloalkyl, for example, CF_3 . In some embodiments, R^{p12} can be hydrogen. In other embodiments, R^{p12} can be an optionally substituted C_{1-4} -alkyl, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and tert-butyl. In some embodiments, R^{p12} can be methyl. In some embodiments, R^{p11} and R^{p12} can be taken together to form an optionally substituted C_{3-6} cycloalkyl. Examples of optionally substituted C_{3-6} cycloalkyl include optionally substituted variants of the following: cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl. Depending on the groups that are selected for R^{p11} and R^{p12} , the carbon to which R^{p11} and R^{p12} are attached may be a chiral center. In some embodiment, the carbon to which R^{p11} and R^{p12} are attached may be a (*R*)-chiral center. In other embodiments, the carbon to which R^{p11} and R^{p12} are attached may be a (*S*)-chiral center.

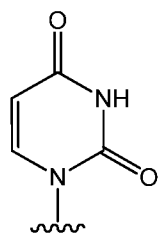




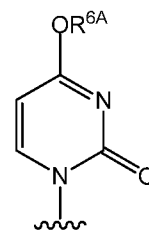
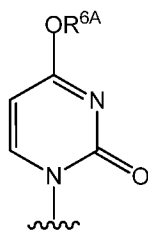
[0123] The nucleobase can vary. In some embodiments, B¹ can be uracil. In some



embodiments, B¹ can be an optionally substituted . In some embodiments, B¹ can



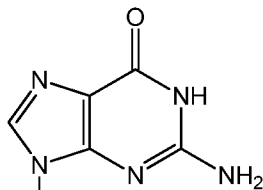
be unsubstituted . In other embodiments, B¹ can be an optionally substituted



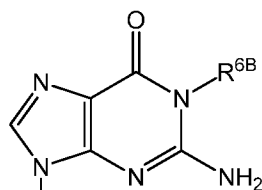
In some embodiments, B¹ can be unsubstituted . In some embodiments, R^{6A} can be an optionally substituted C₁₋₆ alkyl. For example, R^{6A} can be methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, pentyl (branched and straight-chained) or

hexyl (branched and straight-chained). In other embodiments, R^{6A} can be an optionally substituted C_{3-6} cycloalkyl, for example, optionally substituted variants of the following: cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl.

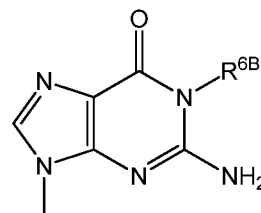
[0124] In some embodiments, B^1 can be guanine. In some embodiments, B^1 can be



an optionally substituted . In other embodiments, B^1 can be an optionally

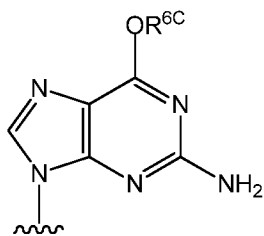


substituted  wherein R^{6B} can be selected from hydrogen, an unsubstituted C_{1-6} alkyl, an unsubstituted C_{3-6} alkenyl, an unsubstituted C_{3-6} alkynyl and an unsubstituted C_{3-6}

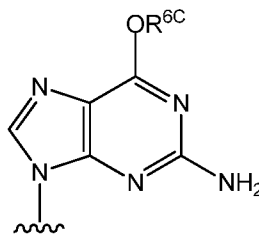


cycloalkyl. In some embodiments, B^1 can be unsubstituted . In some embodiments, R^{6B} can be an unsubstituted C_{1-6} alkyl. For example, R^{6B} can be methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, pentyl (branched and straight-chained) or hexyl (branched and straight-chained). In some embodiments, R^{6B} can be an unsubstituted C_{3-6} alkenyl. In other embodiments, R^{6B} can be an unsubstituted C_{3-6} alkynyl. In still other embodiments, R^{6B} can be an unsubstituted C_{3-6} cycloalkyl, for example, cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl.

[0125] In some embodiments, B^1 can be an optionally substituted

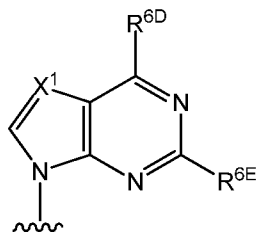


wherein R^{6C} can be selected from hydrogen, an unsubstituted C_{1-6} alkyl, an unsubstituted C_{3-6} alkenyl, an unsubstituted C_{3-6} alkynyl and an unsubstituted C_{3-6} cycloalkyl.



In some embodiments, B¹ can be unsubstituted . In some embodiments, R^{6C} can be hydrogen. In some embodiments, R^{6C} can be an unsubstituted C₁₋₆ alkyl. For example, R^{6C} can be methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, pentyl (branched and straight-chained) or hexyl (branched and straight-chained). In some embodiments, R^{6C} can be an ethyl. In some embodiments, R^{6C} can be an unsubstituted C₃₋₆ alkenyl. In other embodiments, R^{6C} can be an unsubstituted C₃₋₆ alkynyl. In other embodiments, R^{6C} can be an unsubstituted C₃₋₆ cycloalkyl, for example, cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl.

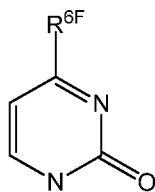
[0126] In some embodiments, B¹ can be adenine. In some embodiments, B¹ can be



an optionally substituted  wherein X¹ can be N (nitrogen) or -CR^{6J}; R^{6J} can be selected from hydrogen, halogen, an optionally substituted C₁₋₆ alkyl, an optionally substituted C₂₋₆ alkenyl and an optionally substituted C₂₋₆ alkynyl; R^{6D} can be NHR^{6G}; R^{6E} can be hydrogen, halogen or NHR^{6H}; R^{6G} can be selected from hydrogen, an optionally substituted C₁₋₆ alkyl, an optionally substituted C₃₋₆ alkenyl, an optionally substituted C₃₋₆ cycloalkyl, -C(=O)R^{A1} and -C(=O)OR^{A2}; R^{6H} can be selected from hydrogen, an optionally substituted C₁₋₆ alkyl, an optionally substituted C₃₋₆ alkenyl, an optionally substituted C₃₋₆ cycloalkyl, -C(=O)R^{A3} and -C(=O)OR^{A4}; R^{A1}, R^{A2}, R^{A3} and R^{A4} can be independently selected from C₁₋₆ alkyl, C₂₋₆ alkenyl, C₂₋₆ alkynyl, C₃₋₆ cycloalkyl, C₃₋₆ cycloalkenyl, C₆₋₁₀ aryl, heteroaryl, heterocyclyl, aryl(C₁₋₆ alkyl), heteroaryl(C₁₋₆ alkyl) and heterocyclyl(C₁₋₆ alkyl). In some embodiments, X¹ can be N (nitrogen). In other embodiments, X¹ can be -CR^{6I}, wherein CR^{6I} can be selected from hydrogen, halogen, an optionally substituted C₁₋₆ alkyl, an optionally substituted C₂₋₆ alkenyl and an optionally substituted C₂₋₆ alkynyl. In some embodiments, X¹ can be CH. In some embodiments, R^{6D} and R^{6E} can be both NH₂. In other embodiments, at least one of R^{6D} and R^{6E} can be NH₂. In some embodiments, R^{6D} can be NHR^{6G}, wherein R^{6G} can be an optionally substituted C₁₋₆ alkyl. In some embodiments, R^{6E} can be hydrogen. In other embodiments, R^{6E} can be halogen. In still other embodiments, R^{6E} can be NHR^{6H}, wherein R^{6H} can be an optionally substituted C₁₋₆ alkyl. In other embodiments, R^{6D} can be NHR^{6G}, wherein

R^{6G} can be selected from an optionally substituted C_{3-6} alkenyl, an optionally substituted C_{3-6} cycloalkyl, $-C(=O)R^{A1}$ and $-C(=O)OR^{A2}$. In other embodiments, R^{6E} can be NHR^{6H} , wherein R^{6H} can be selected from an optionally substituted C_{3-6} alkenyl, an optionally substituted C_{3-6} cycloalkyl, $-C(=O)R^{A3}$ and $-C(=O)OR^{A4}$. In some embodiments, R^{6D} and R^{6E} can be the same. In other embodiments, R^{6D} and R^{6E} can be different.

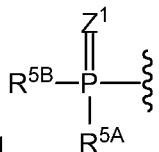
[0127] In some embodiments, B^1 can be cytosine. In some embodiments, B^1 can be

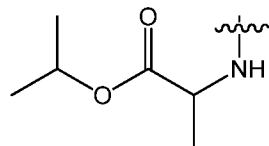


an optionally substituted  wherein R^{6F} can be NHR^{6I} ; R^{6I} can be selected hydrogen, an optionally substituted C_{1-6} alkyl, an optionally substituted C_{3-6} alkenyl, an optionally substituted C_{3-6} cycloalkyl, $-C(=O)R^{A5}$ and $-C(=O)OR^{A6}$; and R^{A5} and R^{A6} are independently selected from the group consisting of C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{3-6} cycloalkyl, C_{3-6} cycloalkenyl, C_{6-10} aryl, heteroaryl, heterocyclyl, aryl(C_{1-6} alkyl), heteroaryl(C_{1-6} alkyl) and heterocyclyl(C_{1-6} alkyl). In some embodiments, R^{6F} can be NH_2 . In other embodiments, R^{6F} can be NHR^{6I} , wherein R^{6I} can be an optionally substituted C_{1-6} alkyl, an optionally substituted C_{3-6} alkenyl or an optionally substituted C_{3-6} cycloalkyl. In still other embodiments, R^{6F} can be NHR^{6I} , wherein R^{6I} can be $-C(=O)R^{A5}$ or $-C(=O)OR^{A6}$. When R^{6I} is $-C(=O)R^{A5}$ or $-C(=O)OR^{A6}$, R^{A5} and R^{A6} can be C_{1-6} alkyl, C_{2-6} alkenyl or C_{2-6} alkynyl. R^{A5} and R^{A6} can also be C_{3-6} cycloalkyl, C_{3-6} cycloalkenyl, C_{6-10} aryl or heteroaryl, heterocyclyl. Additionally, R^{A5} and R^{A6} can be aryl(C_{1-6} alkyl), heteroaryl(C_{1-6} alkyl) or heterocyclyl(C_{1-6} alkyl).

[0128] In some embodiments, Z^1 can be O (oxygen). In other embodiments, Z^1 can be S (sulfur).

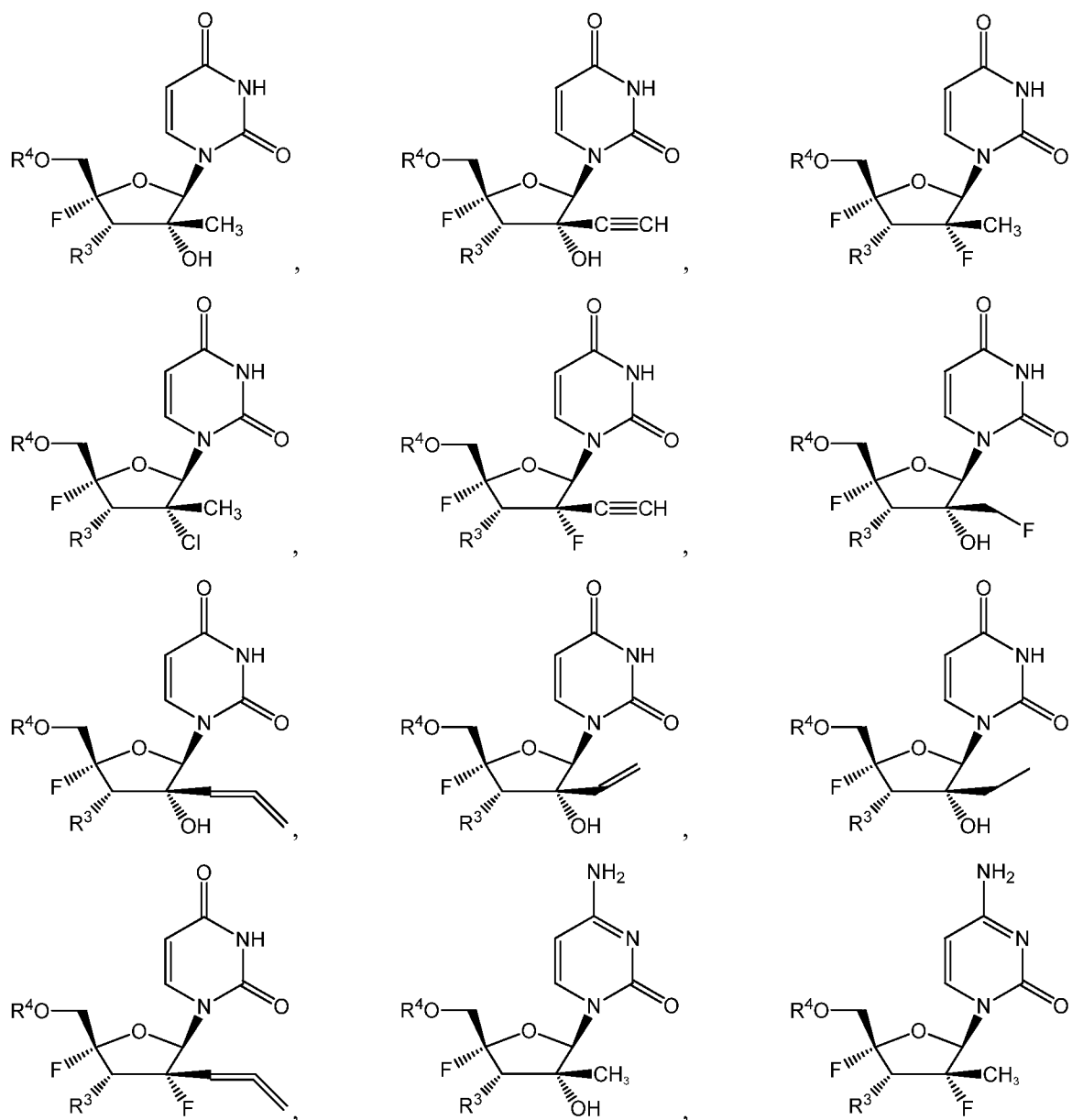
[0129] In some embodiments, R^2 is not halo. In some embodiments, R^2 is not fluoro. In some embodiments, R^{5B} is not an $-O$ -optionally substituted aryl. In some embodiments, R^{5B} is not an $-O$ -unsubstituted aryl. In some embodiments, R^{5A} is not N-alanine isopropyl ester. In some embodiments, R^1 is not an optionally substituted C_{1-6} alkyl. For example, R^1 is not an unsubstituted C_{1-6} alkyl, such as methyl. In some embodiments, B^1 is not an optionally substituted uracil, for example, a halo-substituted uracil. In some embodiment, when both -----
- are each absent; R^P is absent; R^3 is OH or $-OC(=O)R^8$; R^2 is F; and R^1 is methyl, ethyl or

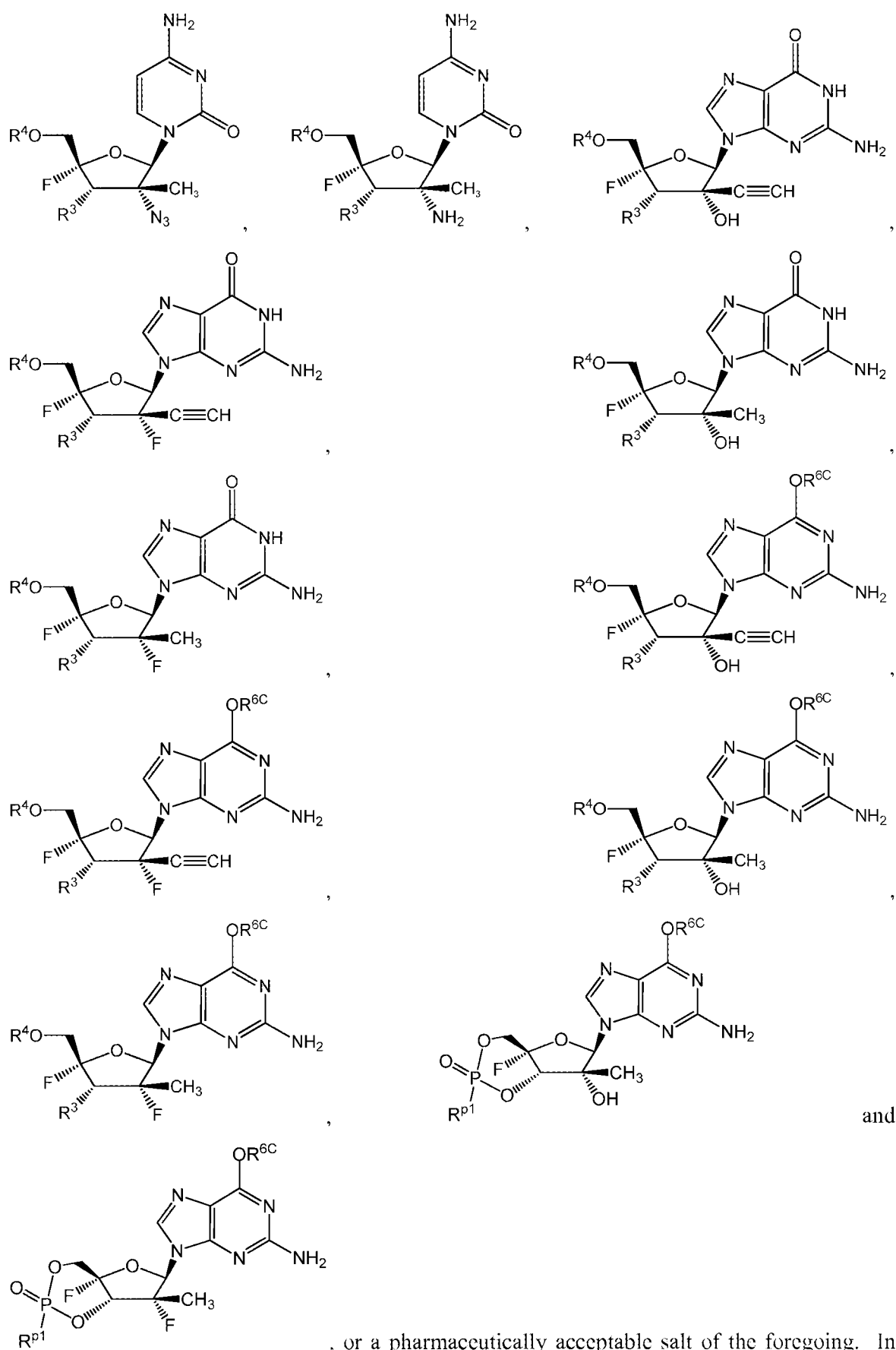
ethenyl; then R^4 cannot be selected from H and , wherein R^{5B} is an $-O$ -unsubstituted



aryl; R^{5A} is and Z^1 is oxygen. In some embodiments, R^2 is not halo (such as fluoro) when B^1 is uracil. In some embodiments, a compound of Formula (I) is not a compound in WO 2013/092481 (filed December 17, 2012).

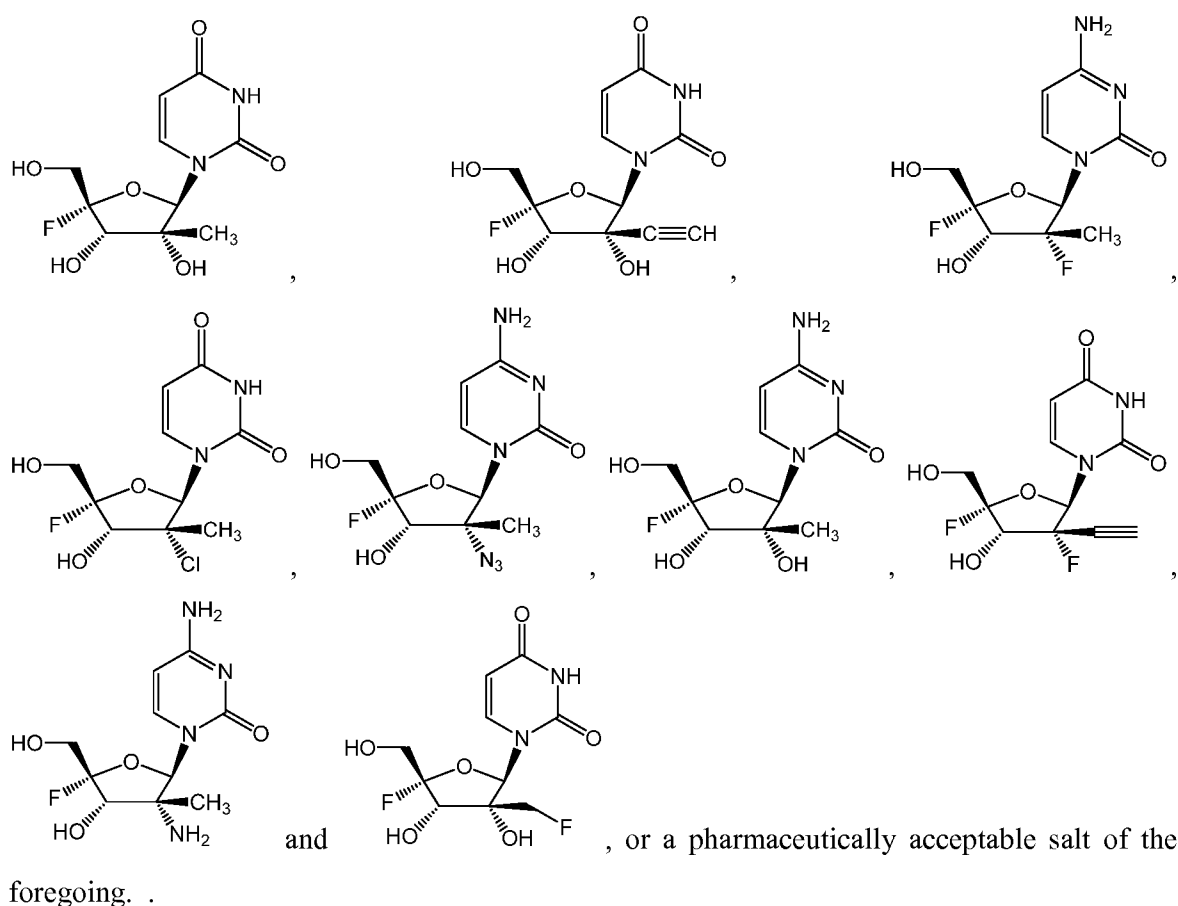
[0130] Example structures of a compound of Formula (I) include the following:



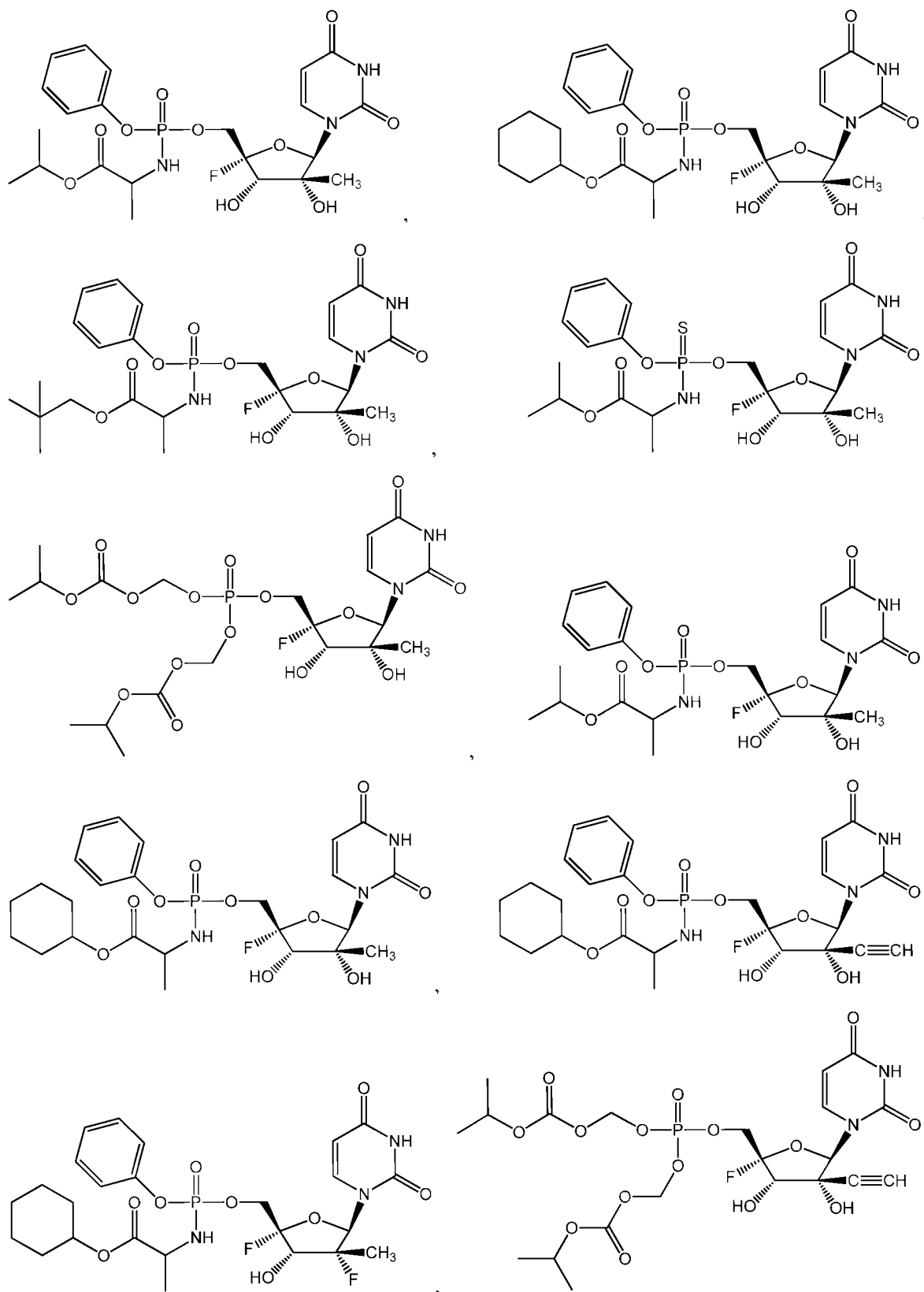


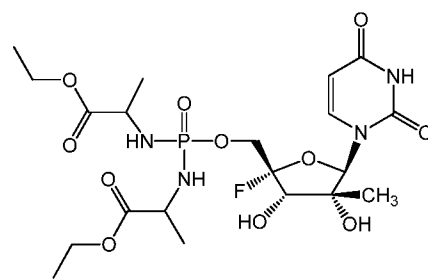
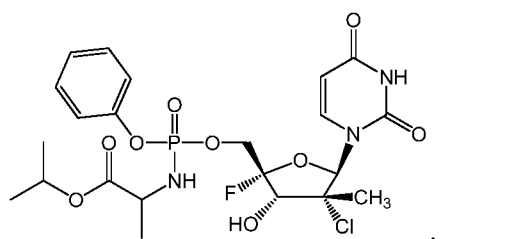
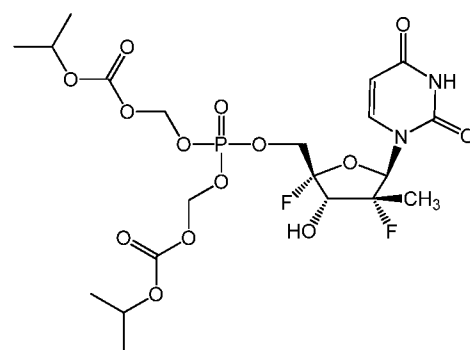
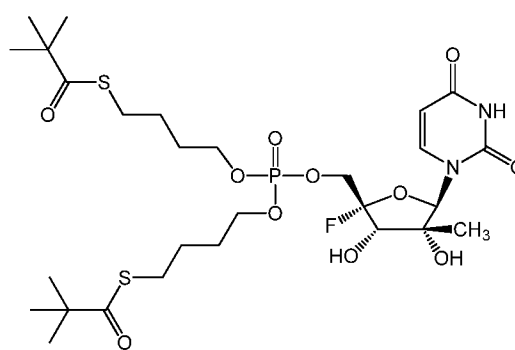
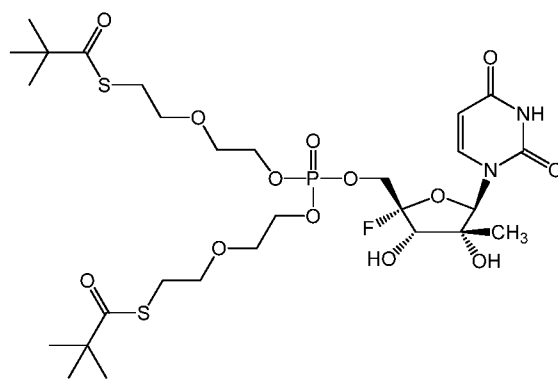
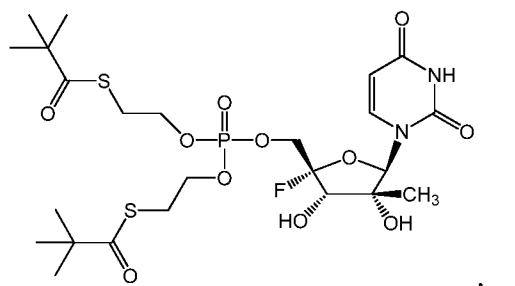
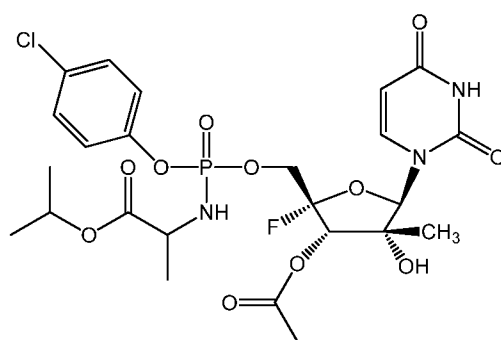
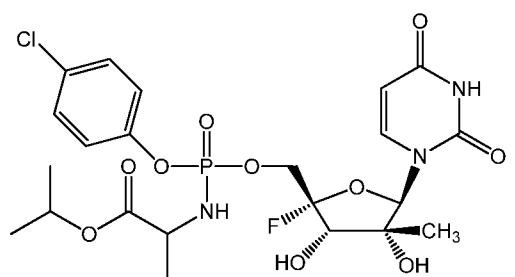
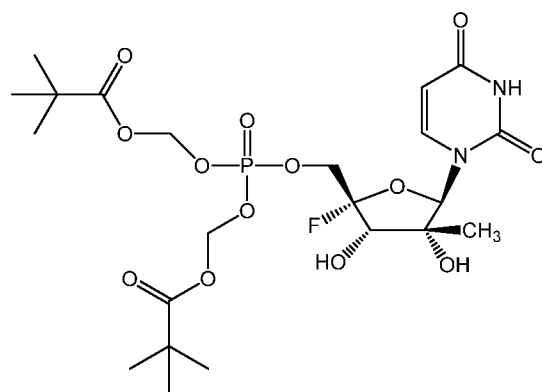
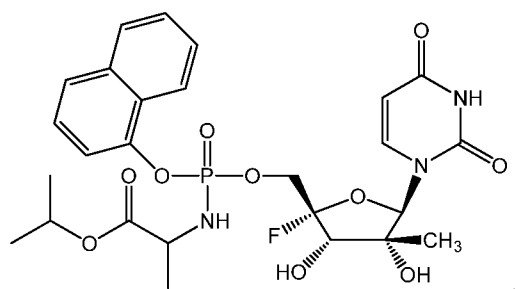
some embodiments of this paragraph, R^3 can be OH. In some embodiments of this paragraph, R^{6C} can be an unsubstituted C_{1-6} alkyl, such as CH_2CH_3 . In some embodiments of this paragraph, R^{P1} can be -O-unsubstituted C_{1-6} alkyl. In some embodiments, of this paragraph, R^4 can be H. In other embodiments, of this paragraph, R^4 can be a phosphoramidate group. In still other embodiments, of this paragraph, R^4 can be a phosphate group (such as a mono-, di- or tri-phosphate). In yet still other embodiments, of this paragraph, R^4 can be a thiophosphoramidate group. In some embodiments, of this paragraph, R^4 can be thiophosphate group (such as an alpha-thiomono-, alpha-thiodi- or alpha-thiotri-phosphate). In some embodiments of this paragraph, R^{P1} can be -O-ethyl, -O-isopropyl or -O-isobutyl.

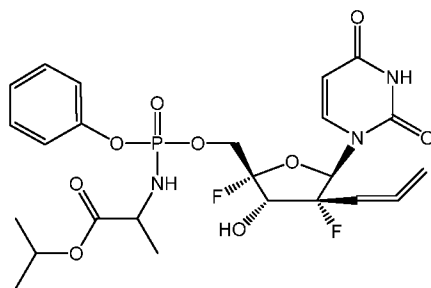
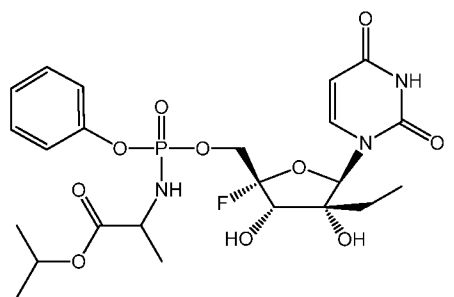
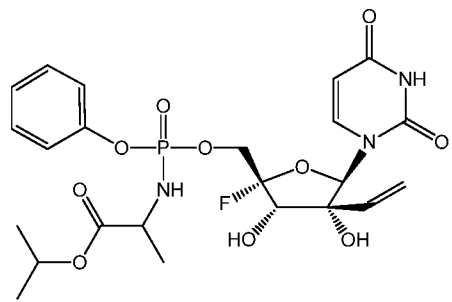
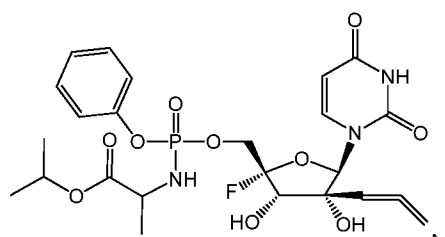
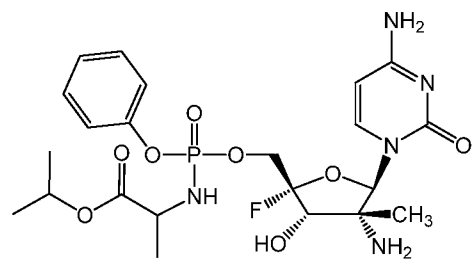
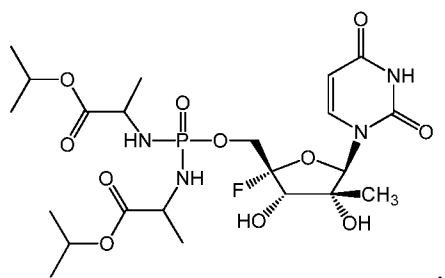
[0131] Examples of compounds of Formula (I) include the following:



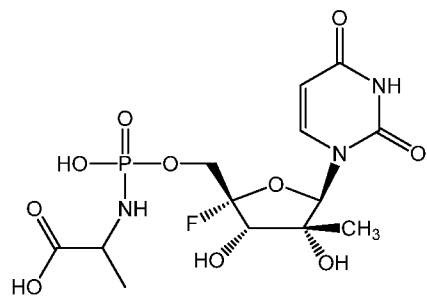
[0132] Additional examples of compounds of Formula (1) include the following:





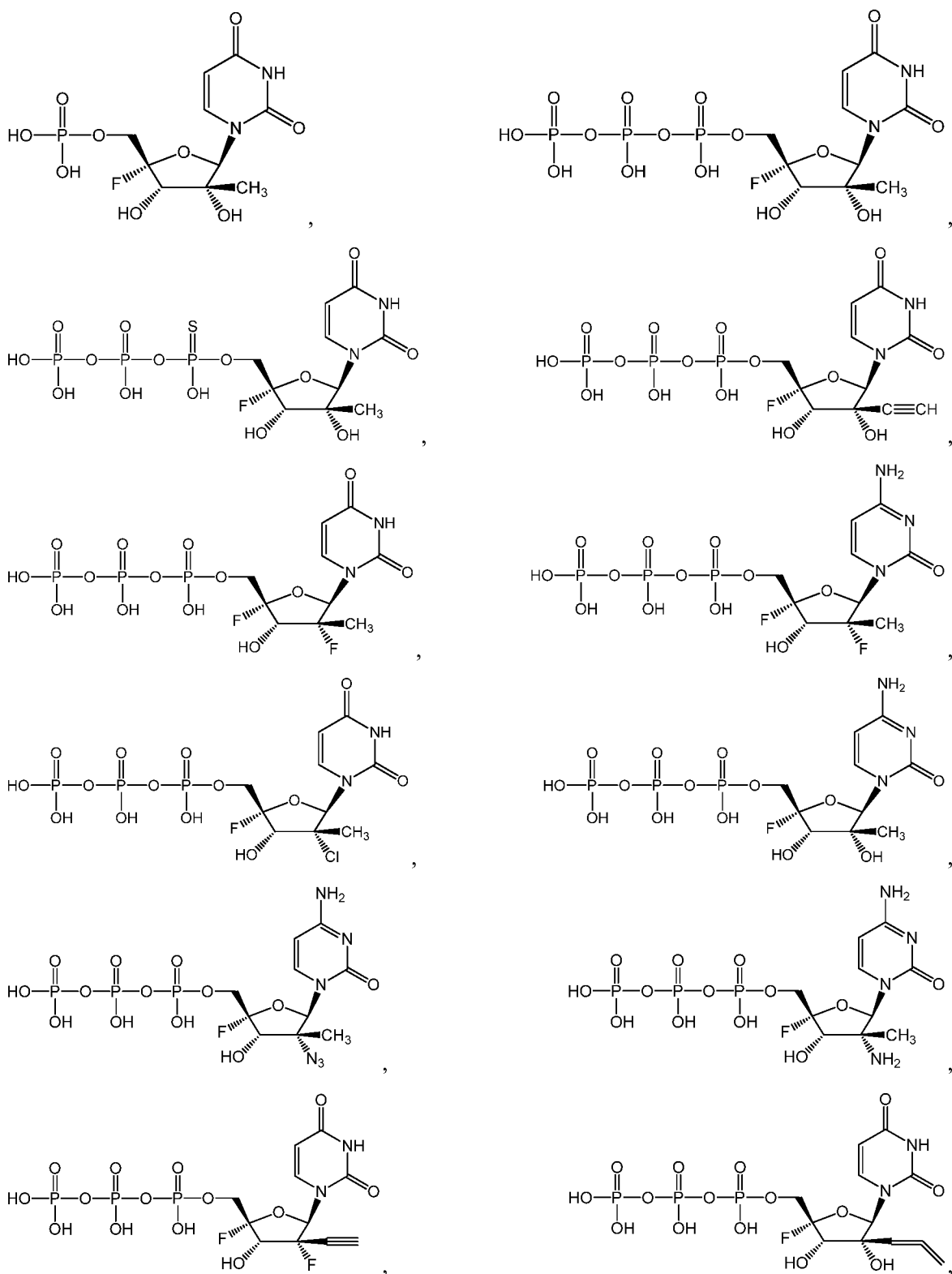


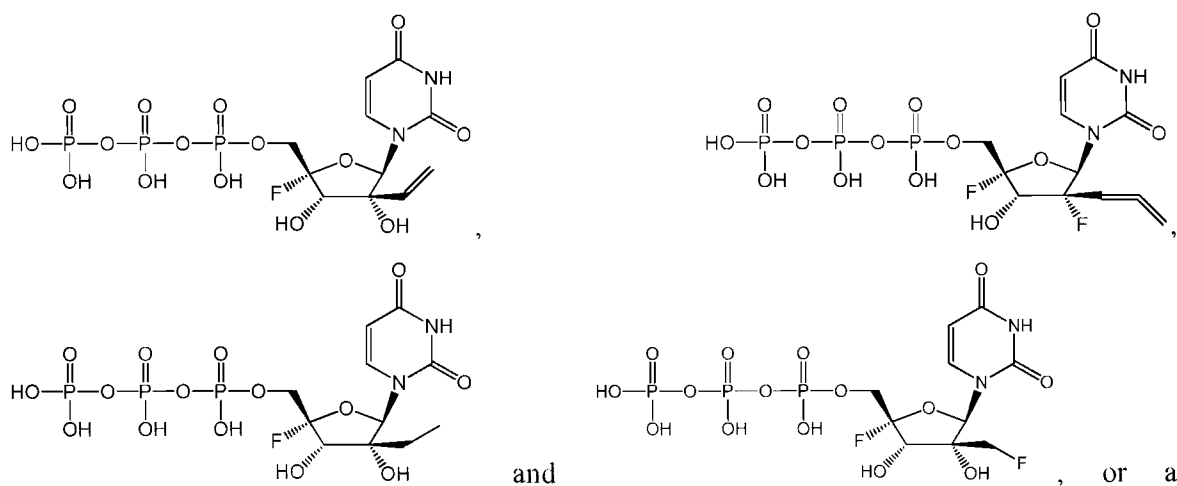
and



, or a pharmaceutically acceptable salt of the foregoing.

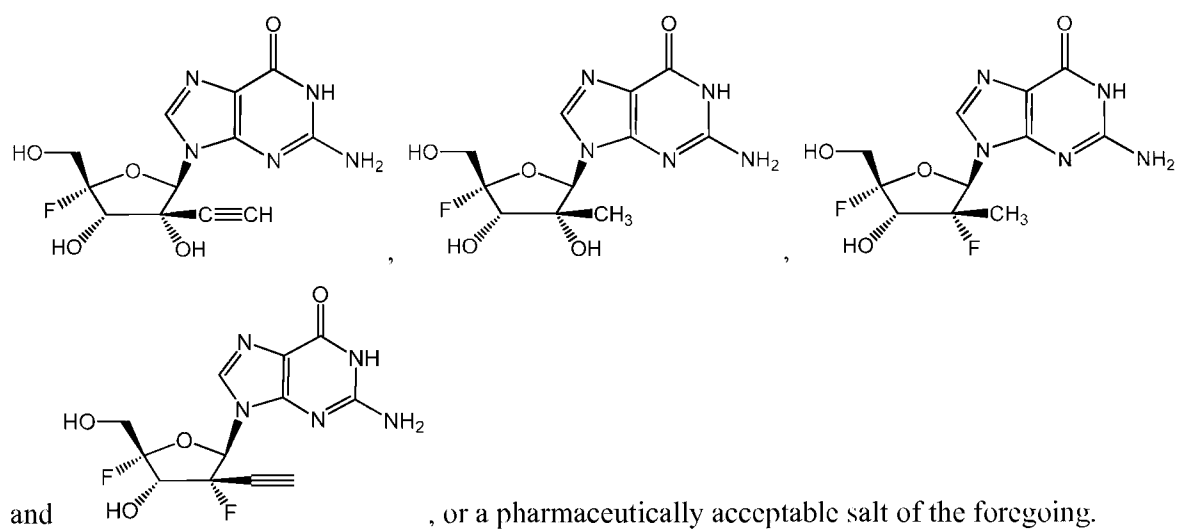
[0133] Still further examples of compounds of Formula (I) include the following:



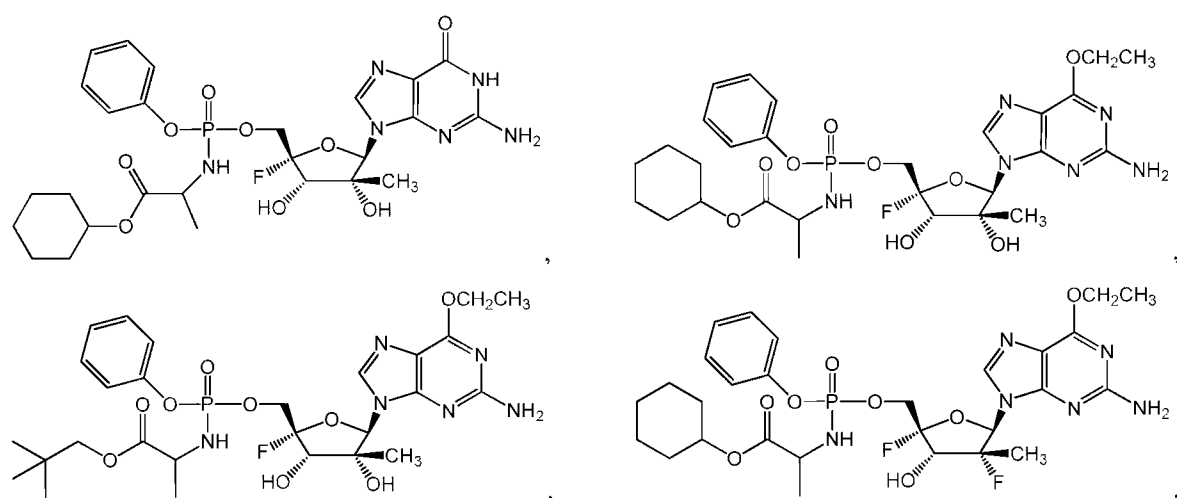


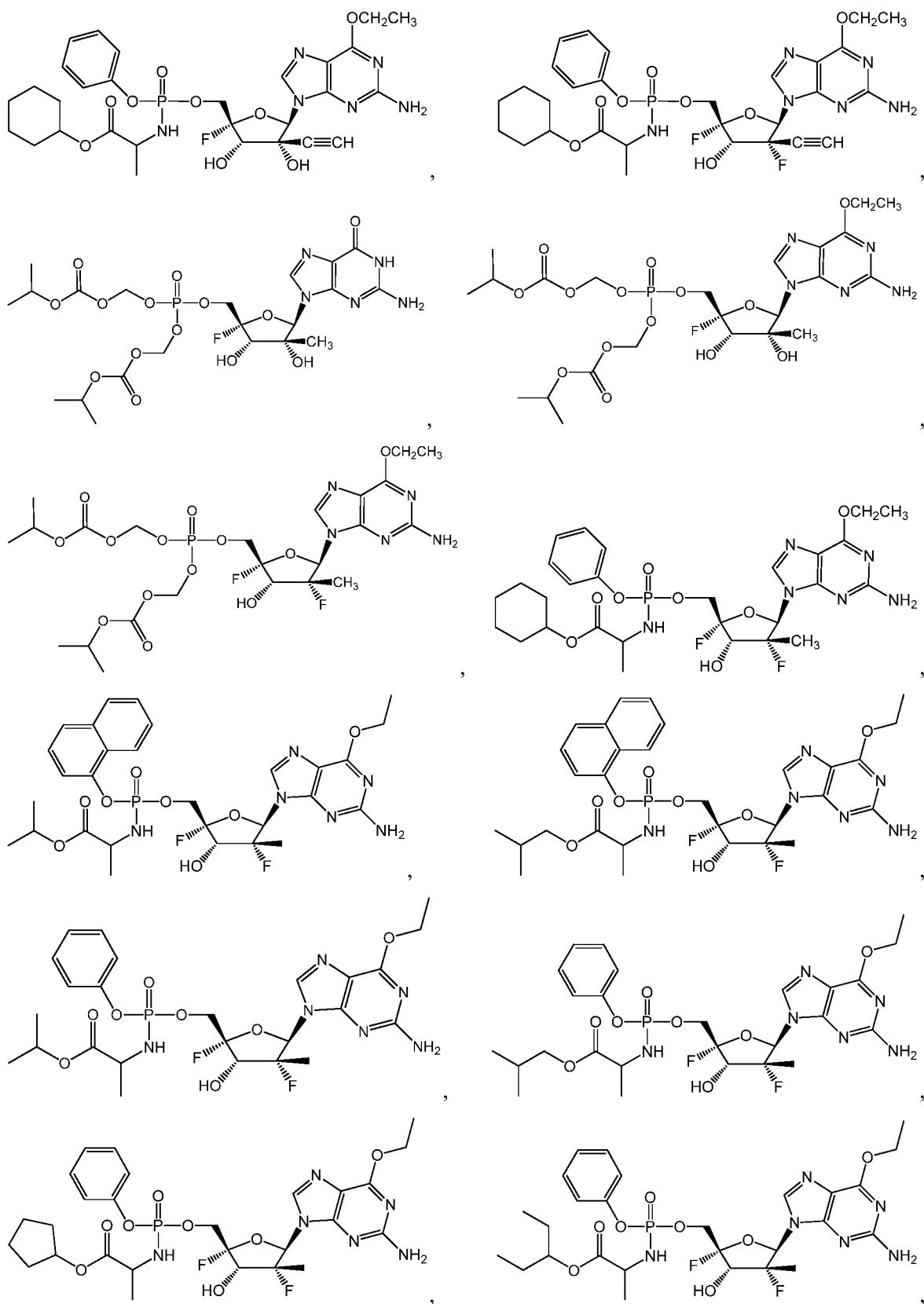
pharmaceutically acceptable salt of the foregoing.

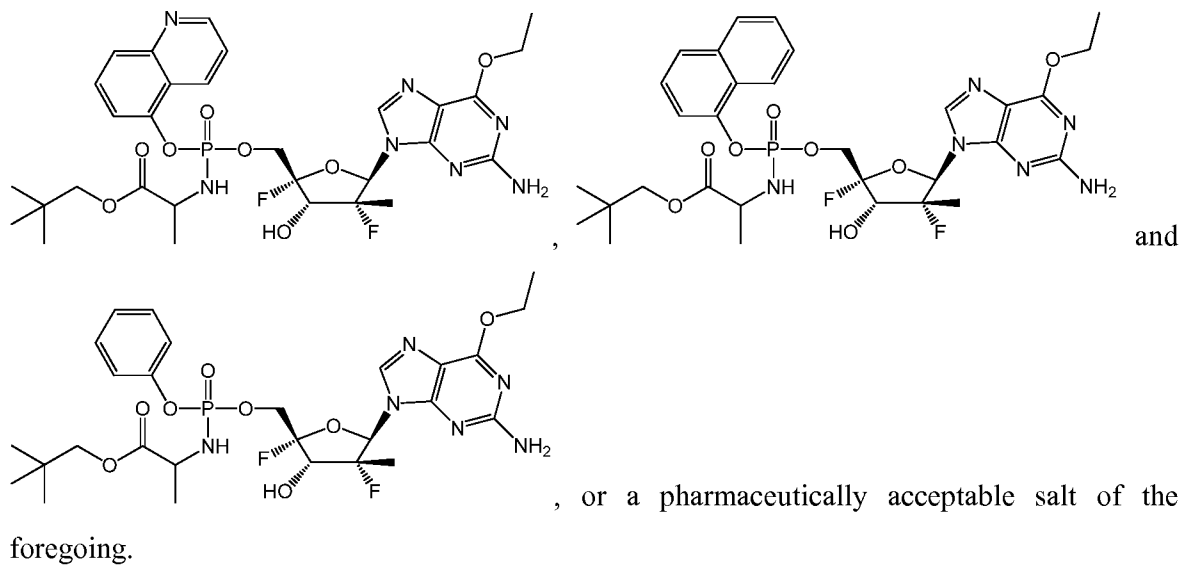
[0134] Examples of compounds of Formula (I) include the following:



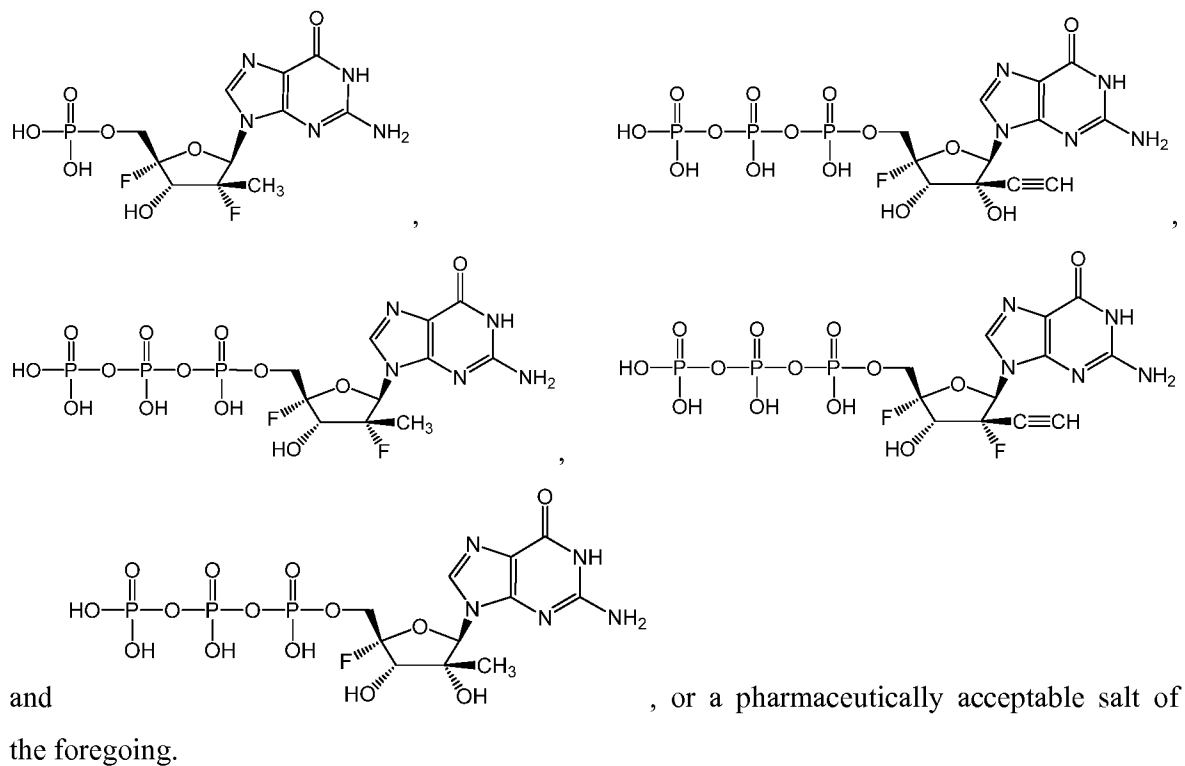
[0135] Further examples of compounds of Formula (I) include the following:



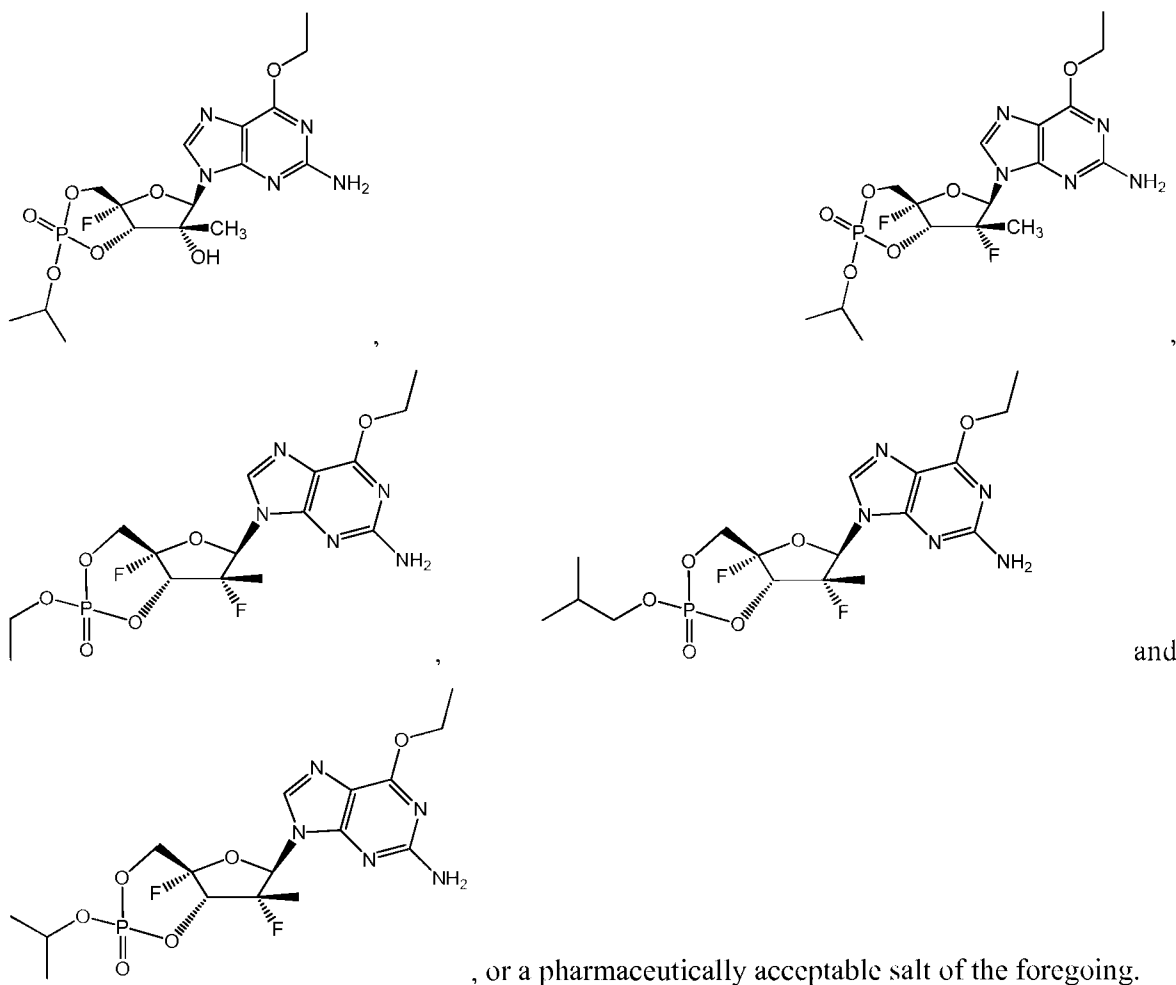




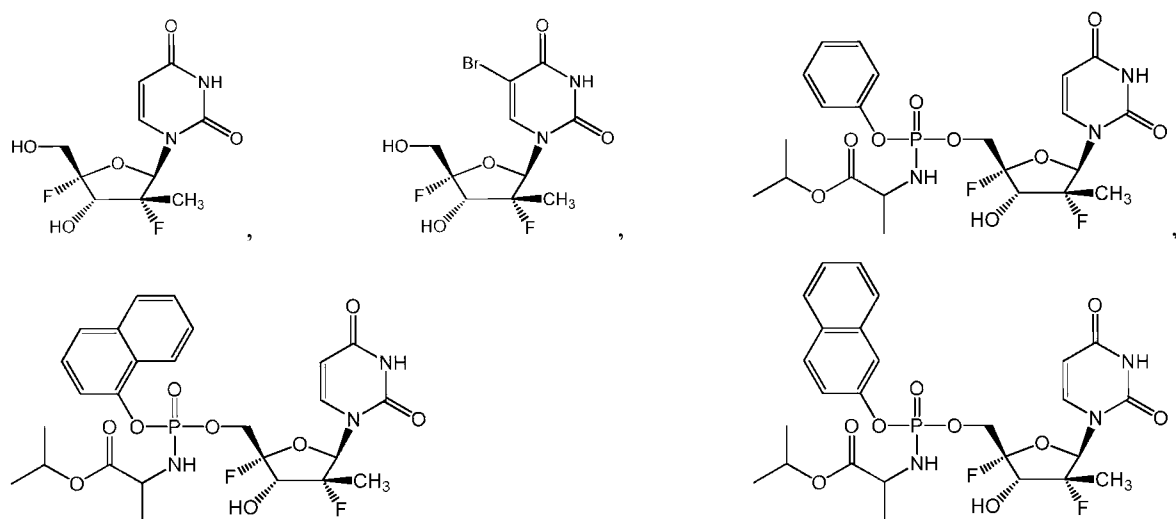
[0136] Further examples of compounds of Formula (I) include the following:

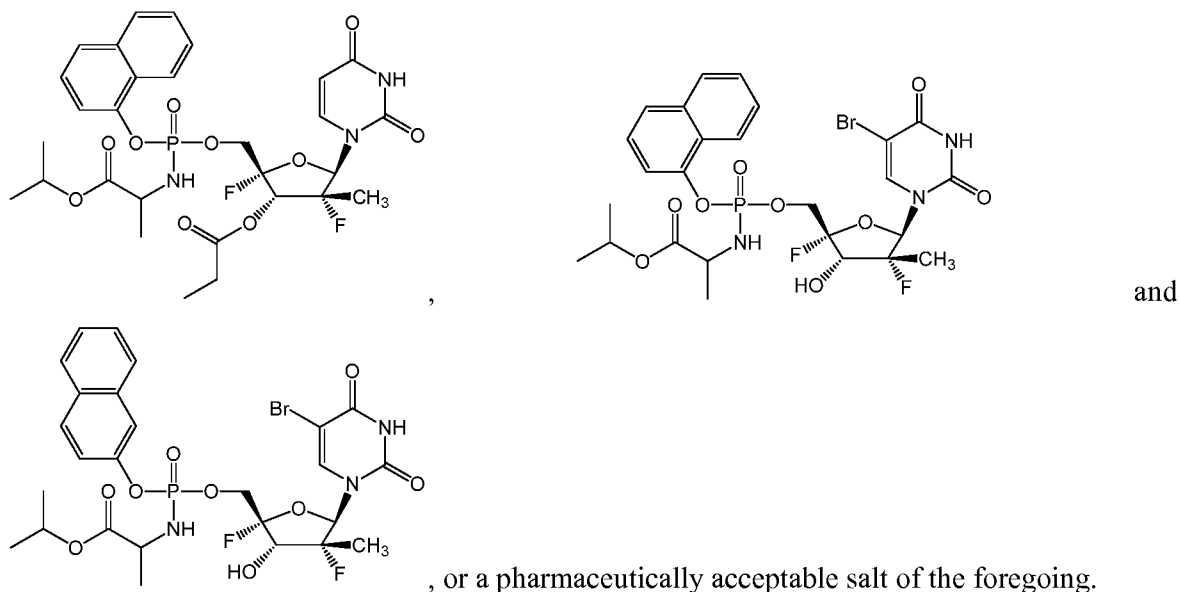


[0137] Additional examples of compounds of Formula (1) include the following:

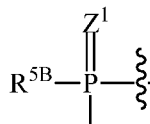


[0138] In some embodiments, a compound of Formula (1) cannot be selected from:





[0139] As described herein, a compound of Formula (I), or a pharmaceutically



acceptable salt thereof, can have R^4 being R^{5A} ; R^{5A} being an optionally substituted N-linked amino acid or an optionally substituted N-linked amino acid ester derivative; and R^{5B} being an $-O$ -optionally substituted aryl, an $-O$ -optionally substituted heteroaryl, an $-O$ -optionally substituted heterocyclyl, an optionally substituted N-linked amino acid or an optionally substituted N-linked amino acid ester derivative. By neutralizing the charge on the phosphate or thiophosphate, penetration of the cell membrane may be facilitated as a result of the increased lipophilicity of the compound. Once absorbed and taken inside the cell, the groups attached to the phosphorus can be easily removed by esterases, proteases and/or other enzymes. In some embodiments, the groups attached to the phosphorus can be removed by simple hydrolysis. Inside the cell, the phosphate thus released may then be metabolized by cellular enzymes to the diphosphate or the active triphosphate. Likewise, the thio-phosphate may be metabolized to the alpha-thiodiphosphate or the alpha-thiotriphosphate. Furthermore, in some embodiments, varying the substituents on a compound described herein, such as compound of Formula (I), can help maintain the efficacy of such the compound by reducing undesirable effects, such as isomerization.

[0140] In some embodiments, the phosphorylation of a thio-monophosphate of a compound of Formula (I), or pharmaceutically acceptable salt thereof, can be stereoselective. For example, a thio-monophosphate of a compound of Formula (I) can be phosphorylated to give an alpha-thiodiphosphate and/or an alpha-thiotriphosphate compound that can be enriched in the (*R*) or (*S*) diastereomer with respect to the 5'-O-phosphorous atom. For example, one of

the (*R*) and (*S*) configuration with respect to the 5'-O-phosphorous atom of the alpha-thiodiphosphate and/or the alpha-thiotriphosphate compound can be present in an amount > 50%, $\geq 75\%$, $\geq 90\%$, $\geq 95\%$ or $\geq 99\%$ compared to the amount of the other of the (*R*) or (*S*) configuration with respect to the 5'-O-phosphorous atom. In some embodiments, phosphorylation of a compound of Formula (I), or pharmaceutically acceptable salt thereof, can result in the formation of a compound that has the (*R*)-configuration at the 5'-O-phosphorous atom. In some embodiments, phosphorylation of a compound of Formula (I), or pharmaceutically acceptable salt thereof, can result in formation of a compound that has the (*S*)-configuration at the 5'-O-phosphorous atom.

[0141] In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can act as a chain terminator of HCV replication. For example, compounds of Formula (I) can contain a moiety at the 2'-carbon position such that once the compound is incorporated into an RNA chain of HCV no further elongation is observed to occur. For example, a compound of Formula (I) can contain a 2'-carbon modification wherein R^1 is a non-hydrogen group selected from an optionally substituted C_{1-6} alkyl, an optionally substituted C_{2-6} alkenyl, an optionally substituted C_{2-6} alkynyl and an optionally substituted C_{3-6} cycloalkyl.

[0142] In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can have increased metabolic and/or plasma stability. In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be more resistant to hydrolysis and/or more resistant to enzymatic transformations. For example, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can have increased metabolic stability, increased plasma stability, can be more resistant to hydrolysis and/or can be more resistant to enzymatic transformations compared to a compound that is identical in structure but for having a hydrogen in place of the fluoro at the 4'-position. In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can have improved properties. A non-limiting list of example properties include, but are not limited to, increased biological half-life, increased bioavailability, increase potency, a sustained in vivo response, increased dosing intervals, decreased dosing amounts, decreased cytotoxicity, reduction in required amounts for treating disease conditions, reduction in viral load, reduction in time to seroconversion (i.e., the virus becomes undetectable in patient serum), increased sustained viral response, a reduction of morbidity or mortality in clinical outcomes, increased subject compliance, decreased liver conditions (such as liver fibrosis, liver cirrhosis and/or liver cancer), and compatibility with other medications. In some embodiments, a compound of

Formula (I), or a pharmaceutically acceptable salt thereof, can have a biological half-life of greater than 24 hours. In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can have a biological half-life greater than a compound that is identical in structure but for having a hydrogen in place of the fluoro at the 4'-position. In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can have more potent antiviral activity (for example, a lower EC₅₀ in an HCV replicon assay) as compared to the current standard of care. In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, does not significantly inhibit mitochondrial function of the mitochondrial RNA polymerase. For example, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, is incorporated in the human mitochondrial RNA polymerase less than 10% compared to the natural 5'-triphosphate nucleotide with the same B¹.

[0143] Additionally, in some embodiments, the presence of a thiophosphoroamidate, phosphoroamidate, thiophosphorbisamidate or phosphorbisamidate in a compound of Formula (I) can increase the stability of the compound by inhibiting its degradation. Also, in some embodiments, the presence of a thiophosphoroamidate, phosphoroamidate, thiophosphorbisamidate or phosphorbisamidate can make the compound more resistant to cleavage *in vivo* and provide sustained, extended efficacy. In some embodiments, a thiophosphoroamidate, phosphoroamidate, thiophosphorbisamidate or phosphorbisamidate can facilitate the penetration of the cell membrane by a compound of Formula (I) by making the compound more lipophilic. In some embodiments, a thiophosphoroamidate, phosphoroamidate, thiophosphorbisamidate or phosphorbisamidate can have improved oral bioavailability, improved aqueous stability and/or reduced risk of byproduct-related toxicity. In some embodiments, for comparison purposes, a compound of Formula (I) can be compared to a compound that is identical in structure but for having a hydrogen in place of the fluoro at the 4'-position.

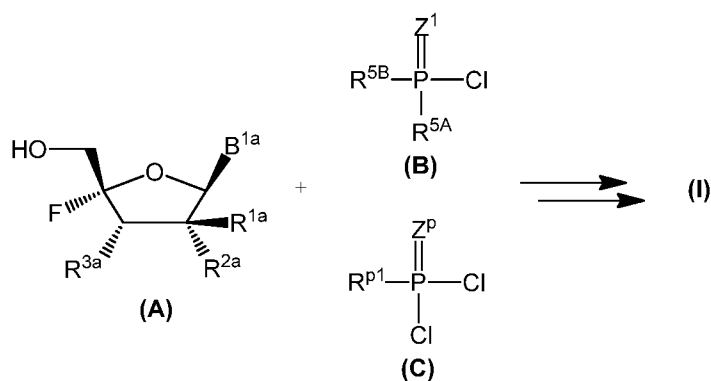
Synthesis

[0144] Compounds of Formula (I) and those described herein may be prepared in various ways. General synthetic routes to the compound of Formula (I), and some examples of starting materials used to synthesize the compounds of Formula (I) are shown in Scheme 1 and 2, and described herein. The routes shown and described herein are illustrative only and are not intended, nor are they to be construed, to limit the scope of the claims in any manner whatsoever. Those skilled in the art will be able to recognize modifications of the disclosed

syntheses and to devise alternate routes based on the disclosures herein; all such modifications and alternate routes are within the scope of the claims.

[0145] Compounds of Formula (I) can be prepared using various methods known to those skilled in the art. Examples of methods are shown in Schemes 1 and 2. Suitable phosphorus containing precursors can be commercially obtained or prepared by synthetic methods known to those skilled in the art. Examples of general structures of phosphorus containing precursors are shown in Schemes 1 and 2, and include phosphorochloridates and thiophosphorochloridates. Suitable phosphorochloridates and thiophosphorochloridates are commercially available and/or can be synthetically prepared.

Scheme 1



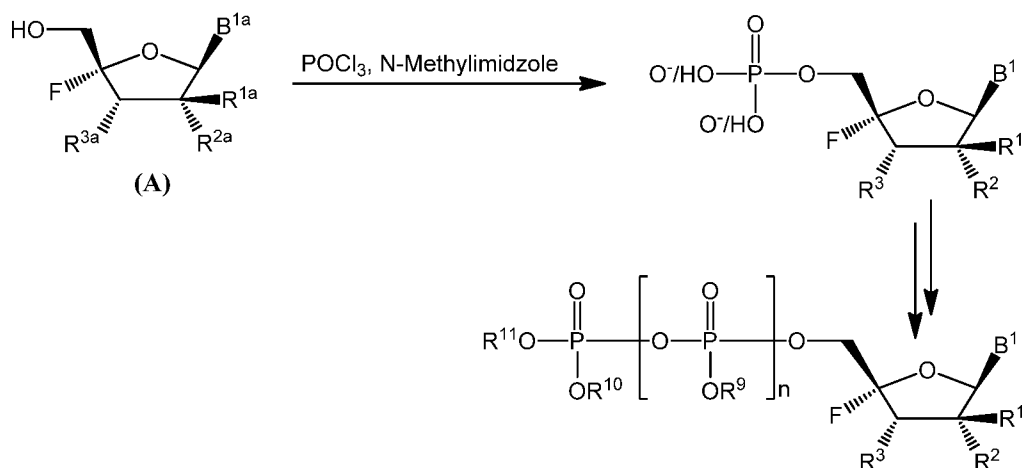
[0146] One method for forming a compound of Formula (I) is shown in Scheme 1. In Scheme 1, R^{1a}, R^{2a}, R^{3a} and B^{1a} can be the same as R¹, R², R³ and B¹ as described herein for Formula (I). In some embodiments, a compound of Formula (I) can be generated from a compound of Formula (A) and a compound of Formula (B) or a compound of Formula (A) and a compound of Formula (C) using an organometallic reagent, such as a Grignard reagent. Suitable Grignard reagents are known to those skilled in the art and include, but are not limited to, alkylmagnesium chlorides and alkylmagnesium bromides. In other embodiments, an appropriate base can be used to form a compound of Formula (I). Examples of suitable bases include, but are not limited to, an amine base, such as an alkylamine (including mono-, di- and tri-alkylamines (e.g., triethylamine)), optionally substituted pyridines (e.g. collidine) and optionally substituted imidazoles (e.g., N-methylimidazole)).

[0147] When compounds of Formula (I) has Z¹ being sulfur, the sulfur can be added in various manners. In some embodiments, the sulfur can be part of the phosphorus containing

precursor, for example, $\begin{array}{c} \text{S} \\ \parallel \\ \text{R}^{5\text{B}}-\text{P}-\text{Cl} \\ | \\ \text{R}^{5\text{A}} \end{array}$. Alternatively, one of the oxygens attached to the

phosphorus can be exchanged with a sulfur using a sulfurization reagent. Suitable sulfurization agents are known to those skilled in the art, and include, but are not limited to, elemental sulfur, Lawesson's reagent, cyclooctasulfur, 3H-1,2-Benzodithiole-3-one-1,1-dioxide (Beaucage's reagent), 3-((N,N-dimethylaminomethylidene)amino)-3H-1,2,4-dithiazole-5-thione (DDTT) and bis(3-triethoxysilyl)propyl-tetrasulfide (TEST).

Scheme 2



[0148] A phosphorus containing precursor can be coupled to the nucleoside, for example, a compound of Formula (A). Following the coupling of the phosphorus containing precursor, any leaving groups can be cleaved under suitable conditions, such as hydrolysis. In Scheme 2, R^{1a} , R^{2a} , R^{3a} and B^{1a} can be the same as R^1 , R^2 , R^3 and B^1 as described herein for Formula (I). Further phosphorus containing groups can be added using methods known to those skilled in the art, for example using a pyrophosphate. If desired, one or more bases can be used during the addition of each phosphorus-containing group. Examples of suitable bases are described herein.

[0149] As described herein, in some embodiments, R^2 and R^3 can be each an oxygen atom, wherein the oxygen atoms are linked together by a carbonyl groups. The $-O-C(=O)-O-$ group can be formed using methods known to those skilled in the art. For example, a compound of Formula (I), wherein R^2 and R^3 are both hydroxy groups, can be treated with 1,1'-carbonyldiimidazole (CDI).

[0150] In some embodiments, R^2 and/or R^3 can be $-OC(=O)R^{12}$ and $-OC(=O)R^8$, respectively. The $-OC(=O)R^{12}$ and $-OC(=O)R^8$ groups can be formed at the 2'- and 3'-positions using various methods known to those skilled in the art. As an example, a compound of Formula (I), wherein R^2 and R^3 are both hydroxy groups, can be treated with an alkyl anhydride (e.g., acetic anhydride and propionic anhydride) or an alkyl acid chloride (e.g., acetylchloride).

If desired, a catalyst can be used to facilitate the reaction. An example of suitable catalyst is 4-dimethylaminopyridine (DMAP). Alternatively, the $-\text{OC}(=\text{O})\text{R}^{12}$ and $-\text{OC}(=\text{O})\text{R}^8$ groups can be formed at the 2'- and 3'-positions by reacting an alkyl acid (e.g. acetic acid and propionic acid) in the presences of a carbodiimide or a coupling reagent. Examples of carbodiimides include, but are not limited to, N,N'-dicyclohexylcarbodiimide (DCC), N,N'-diisopropylcarbodiimide (DIC) and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC).

[0151] To reduce the formation of side products, one or more the groups attached to the pentose ring can be protected with one or more suitable protecting groups. As an example, if R^2 and/or R^3 is/are hydroxy group(s), the hydroxy group(s) can be protected with suitable protecting groups, such as triarylmethyl and/or silyl groups. Examples of triarylmethyl groups include but are not limited to, trityl, monomethoxytrityl (MMTr), 4,4'-dimethoxytrityl (DMTr), 4,4',4''-trimethoxytrityl (TMTr), 4,4',4''-tris- (benzoyloxy) trityl (TBTr), 4,4',4''-tris (4,5-dichlorophthalimido) trityl (CPTr), 4,4',4''-tris (levulinyloxy) trityl (TLTr), p-anisyl-1-naphthylphenylmethyl, di-o-anisyl-1-naphthylmethyl, p-tolyldipheylmethyl, 3-(imidazolylmethyl)-4,4'-dimethoxytrityl, 9-phenylxanthen-9-yl (Pixyl), 9-(p-methoxyphenyl)xanthen-9-yl (Mox), 4-decyloxytrityl, 4-hexadecyloxytrityl, 4,4'-dioctadecyltrityl, 9-(4-octadecyloxyphenyl)xanthen-9-yl, 1,1'-bis-(4-methoxyphenyl)-1'-pyrenylmethyl, 4,4',4''-tris-(tert-butylphenyl)methyl (TTTr) and 4,4'-di-3,5-hexadienoxytrityl. Examples of suitable silyl groups are described herein and include trimethylsilyl (TMS), *tert*-butyldimethylsilyl (TBDMS), triisopropylsilyl (TIPS), *tert*-butyldiphenylsilyl (TBDPS), tri-*iso*-propylsilyloxymethyl and [2-(trimethylsilyl)ethoxy]methyl. Alternatively, R^2 and/or R^3 can be protected by a single achiral or chiral protecting group, for example, by forming an orthoester, a cyclic acetal or a cyclic ketal. Suitable orthoesters include methoxymethylene acetal, ethoxymethylene acetal, 2-oxacyclopentylidene orthoester, dimethoxymethylene orthoester, 1-methoxyethylidene orthoester, 1-ethoxyethylidene orthoester, methylidene orthoester, phthalide orthoester 1,2-dimethoxyethylidene orthoester, and alpha-methoxybenzylidene orthoester; suitable cyclic acetals include methylene acetal, ethylidene acetal, *t*-butylmethylidene acetal, 3-(benzyloxy)propyl acetal, benzylidene acetal, 3,4-dimethoxybenzylidene acetal and *p*-acetoxybenzylidene acetal; and suitable cyclic ketals include 1-*t*-butylethylidene ketal, 1-phenylethylidene ketal, isopropylidene ketal, cyclopentylidene ketal, cyclohexylidene ketal, cycloheptylidene ketal and 1-(4-methoxyphenyl)ethylidene ketal.

Pharmaceutical Compositions

[0152] Some embodiments described herein relates to a pharmaceutical composition, that can include an effective amount of one or more compounds described herein (e.g., a compound of Formula (I)), or a pharmaceutically acceptable salt thereof) and a pharmaceutically acceptable carrier, diluent, excipient or combination thereof. In some embodiments, the pharmaceutical composition can include a single diastereomer of a compound of Formula (I), or a pharmaceutically acceptable salt thereof, (for example, a single diastereomer is present in the pharmaceutical composition at a concentration of greater than 99% compared to the total concentration of the other diastereomers). In other embodiments, the pharmaceutical composition can include a mixture of diastereomers of a compound of Formula (I), or a pharmaceutically acceptable salt thereof. For example, the pharmaceutical composition can include a concentration of one diastereomer of $> 50\%$, $\geq 60\%$, $\geq 70\%$, $\geq 80\%$, $\geq 90\%$, $\geq 95\%$, or $\geq 98\%$, as compared to the total concentration of the other diastereomers. In some embodiments, the pharmaceutical composition includes a 1:1 mixture of two diastereomers of a compound of Formula (I), or a pharmaceutically acceptable salt thereof.

[0153] The term “pharmaceutical composition” refers to a mixture of one or more compounds disclosed herein with other chemical components, such as diluents or carriers. The pharmaceutical composition facilitates administration of the compound to an organism. Pharmaceutical compositions can also be obtained by reacting compounds with inorganic or organic acids such as hydrochloric acid, hydrobromic acid, sulfuric acid, nitric acid, phosphoric acid, methanesulfonic acid, ethanesulfonic acid, p-toluenesulfonic acid and salicylic acid. Pharmaceutical compositions will generally be tailored to the specific intended route of administration. A pharmaceutical composition is suitable for human and/or veterinary applications.

[0154] The term “physiologically acceptable” defines a carrier, diluent or excipient that does not abrogate the biological activity and properties of the compound.

[0155] As used herein, a “carrier” refers to a compound that facilitates the incorporation of a compound into cells or tissues. For example, without limitation, dimethyl sulfoxide (DMSO) is a commonly utilized carrier that facilitates the uptake of many organic compounds into cells or tissues of a subject.

[0156] As used herein, a “diluent” refers to an ingredient in a pharmaceutical composition that lacks pharmacological activity but may be pharmaceutically necessary or desirable. For example, a diluent may be used to increase the bulk of a potent drug whose mass is too small for manufacture and/or administration. It may also be a liquid for the dissolution of

a drug to be administered by injection, ingestion or inhalation. A common form of diluent in the art is a buffered aqueous solution such as, without limitation, phosphate buffered saline that mimics the composition of human blood.

[0157] As used herein, an “excipient” refers to an inert substance that is added to a pharmaceutical composition to provide, without limitation, bulk, consistency, stability, binding ability, lubrication, disintegrating ability etc., to the composition. A “diluent” is a type of excipient.

[0158] The pharmaceutical compositions described herein can be administered to a human patient *per se*, or in pharmaceutical compositions where they are mixed with other active ingredients, as in combination therapy, or carriers, diluents, excipients or combinations thereof. Proper formulation is dependent upon the route of administration chosen. Techniques for formulation and administration of the compounds described herein are known to those skilled in the art.

[0159] The pharmaceutical compositions disclosed herein may be manufactured in a manner that is itself known, *e.g.*, by means of conventional mixing, dissolving, granulating, dragee-making, levigating, emulsifying, encapsulating, entrapping or tableting processes. Additionally, the active ingredients are contained in an amount effective to achieve its intended purpose. Many of the compounds used in the pharmaceutical combinations disclosed herein may be provided as salts with pharmaceutically compatible counterions.

[0160] Multiple techniques of administering a compound exist in the art including, but not limited to, oral, rectal, topical, aerosol, injection and parenteral delivery, including intramuscular, subcutaneous, intravenous, intramedullary injections, intrathecal, direct intraventricular, intraperitoneal, intranasal and intraocular injections.

[0161] One may also administer the compound in a local rather than systemic manner, for example, via injection of the compound directly into the infected area, often in a depot or sustained release formulation. Furthermore, one may administer the compound in a targeted drug delivery system, for example, in a liposome coated with a tissue-specific antibody. The liposomes will be targeted to and taken up selectively by the organ.

[0162] The compositions may, if desired, be presented in a pack or dispenser device which may contain one or more unit dosage forms containing the active ingredient. The pack may for example comprise metal or plastic foil, such as a blister pack. The pack or dispenser device may be accompanied by instructions for administration. The pack or dispenser may also be accompanied with a notice associated with the container in form prescribed by a governmental agency regulating the manufacture, use, or sale of pharmaceuticals, which notice

is reflective of approval by the agency of the form of the drug for human or veterinary administration. Such notice, for example, may be the labeling approved by the U.S. Food and Drug Administration for prescription drugs, or the approved product insert. Compositions that can include a compound described herein formulated in a compatible pharmaceutical carrier may also be prepared, placed in an appropriate container, and labeled for treatment of an indicated condition.

Methods of Use

[0163] Some embodiments disclosed herein relate to a method of treating and/or ameliorating a disease or condition that can include administering to a subject an effective amount of one or more compounds described herein, such as a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound described herein, or a pharmaceutically acceptable salt thereof. Other embodiments disclosed herein relate to a method of treating and/or ameliorating a disease or condition that can include administering to a subject identified as suffering from the disease or condition an effective amount of one or more compounds described herein, such as a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound described herein, or a pharmaceutically acceptable salt thereof.

[0164] Some embodiments disclosed herein relates to a method of ameliorating or treating a HCV infection that can include administering to a subject identified as suffering from a HCV infection an effective amount of one or more compounds described herein (for example, a compound of Formula (I)), or a pharmaceutical composition that includes one or more compounds described herein, or a pharmaceutically acceptable salt thereof. Other embodiments described herein relate to using one or more compounds described herein, or a pharmaceutically acceptable salt of a compound described herein, in the manufacture of a medicament for ameliorating and/or treating a HCV infection that can include administering to a subject identified as suffering from a HCV infection an effective amount of one or more compounds described herein. Still other embodiments described herein relate to one or more compounds described herein, or a pharmaceutically acceptable salt of a compound described herein, that can be used for ameliorating and/or treating a HCV infection by administering to a subject identified as suffering from a HCV infection an effective amount of one or more compounds described herein.

[0165] Some embodiments disclosed herein relate to methods of ameliorating and/or treating a HCV infection that can include contacting a cell infected with the hepatitis C virus

with an effective amount of one or more compounds described herein, or a pharmaceutically acceptable salt of a compound described herein, or a pharmaceutical composition that includes one or more compounds described herein, or a pharmaceutically acceptable salt thereof. Other embodiments described herein relate to using one or more compounds described herein, or a pharmaceutically acceptable salt of a compound described herein, in the manufacture of a medicament for ameliorating and/or treating a HCV infection that can include contacting a cell infected with the hepatitis C virus with an effective amount of said compound(s). Still other embodiments described herein relate to one or more compounds described herein, or a pharmaceutically acceptable salt of a compound described herein, that can be used for ameliorating and/or treating a HCV infection by contacting a cell infected with the hepatitis C virus with an effective amount of said compound(s).

[0166] Some embodiments disclosed herein relate to methods of inhibiting replication of a hepatitis C virus that can include contacting a cell infected with the hepatitis C virus with an effective amount of one or more compounds described herein, or a pharmaceutically acceptable salt of a compound described herein, or a pharmaceutical composition that includes one or more compounds described herein, or a pharmaceutically acceptable salt thereof. Other embodiments described herein relate to using one or more compounds described herein, or a pharmaceutically acceptable salt of a compound described herein, in the manufacture of a medicament for inhibiting replication of a hepatitis C virus that can include contacting a cell infected with the hepatitis C virus with an effective amount of said compound(s). Still other embodiments described herein relate to a compound described herein, or a pharmaceutically acceptable salt of a compound described herein, that can be used for inhibiting replication of a hepatitis C virus by contacting a cell infected with the hepatitis C virus with an effective amount of said compound(s).

[0167] In some embodiments, the compound can be a compound of Formula (I), or a pharmaceutical acceptable salt thereof, wherein R^4 is hydrogen. In other embodiments, the compound can be a compound of Formula (I), wherein compound of Formula (I) is a mono, di, or triphosphate, or a pharmaceutically acceptable salt of the foregoing. In still other embodiments, the compound can be a compound of Formula (I), wherein compound of Formula (I) is a thiomonophosphate, alpha-thiodiphosphate, or alpha-thiotriphosphate, or a pharmaceutically acceptable salt of the foregoing. In yet still other embodiments, the compound can be a compound of Formula (I), wherein compound of Formula (I) is phosphoramidate or phosphorabisamidate, or a pharmaceutically acceptable salt of the foregoing. In some embodiments, the compound can be a compound of Formula (I), wherein compound of Formula

(I) is thiophosphoroamidate or thiophosphorbisamidate, or a pharmaceutically acceptable salt of the foregoing. In some embodiments, the compound of Formula (I), or a pharmaceutical acceptable salt thereof, that can be used to ameliorating and/or treating a viral infection (for example, a HCV infection) and/or inhibit replication of a virus (such as a HCV virus) can be any of the embodiments provided in any of the embodiments described in paragraphs [0090]-[0138].

[0168] HCV is an enveloped positive strand RNA virus in the Flaviviridae family. There are various nonstructural proteins of HCV, such as NS2, NS3, NS4, NS4A, NS4B, NS5A and NS5B. NS5B is believed to be an RNA-dependent RNA polymerase involved in the replication of HCV RNA.

[0169] Some embodiments described herein relate to a method of inhibiting NS5B polymerase activity that can include contacting a cell infected with hepatitis C virus with an effective amount of a compound of Formula (I), or a pharmaceutical acceptable salt thereof. Some embodiments described herein relate to a method of inhibiting NS5B polymerase activity that can include administering to a subject infected with hepatitis C virus an effective amount of a compound of Formula (I), or a pharmaceutical acceptable salt thereof. In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can inhibit a RNA dependent RNA polymerase, and thus, inhibit the replication of HCV RNA. In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can inhibit a HCV polymerase (for example, NS5B polymerase).

[0170] Some embodiments described herein relate to a method of treating a condition selected from liver fibrosis, liver cirrhosis and liver cancer in a subject suffering from one or more of the aforementioned liver conditions that can include administering to the subject an effective amount of a compound or a pharmaceutical composition described herein (for example, a compound of Formula (I), or a pharmaceutical acceptable salt thereof), wherein the liver condition is caused by a HCV infection. Some embodiments described herein relate to a method of increasing liver function in a subject having a HCV infection that can include administering to the subject an effective amount of a compound or a pharmaceutical composition described herein (for example, a compound of Formula (I), or a pharmaceutical acceptable salt thereof). Also contemplated is a method for reducing or eliminating further virus-caused liver damage in a subject having an HCV infection by administering to the subject an effective amount of a compound or a pharmaceutical composition described herein (for example, a compound of Formula (I), or a pharmaceutical acceptable salt thereof). In some embodiments, this method can include slowing or halting the progression of liver disease. In other embodiments, the course of the disease can be reversed, and stasis or improvement in liver function is

contemplated. In some embodiments, liver fibrosis, liver cirrhosis and/or liver cancer can be treated; liver function can be increased; virus-caused liver damage can be reduced or eliminated; progression of liver disease can be slowed or halted; the course of the liver disease can be reversed and/or liver function can be improved or maintained by contacting a cell infected with hepatitis C virus with an effective amount of a compound described herein (for example, a compound of Formula (I), or a pharmaceutically acceptable salt thereof.)

[0171] There are a variety of genotypes of HCV, and a variety of subtypes within each genotype. For example, at present it is known that there are eleven (numbered 1 through 11) main genotypes of HCV, although others have classified the genotypes as 6 main genotypes. Each of these genotypes is further subdivided into subtypes (1a-1c; 2a-2c; 3a-3b; 4a-4e; 5a; 6a; 7a- 7b; 8a-8b; 9a; 10a; and 11a). In some embodiments, an effective amount of a compound of Formula (I), or a pharmaceutical acceptable salt thereof, or a pharmaceutical composition that includes an effective amount of a compound of Formula (I), or a pharmaceutical acceptable salt thereof, can be effective to treat at least one genotype of HCV. In some embodiments, a compound described herein (for example, a compound of Formula (I), or a pharmaceutical acceptable salt thereof) can be effective to treat all 11 genotypes of HCV. In some embodiments, a compound described herein (for example, a compound of Formula (I), or a pharmaceutical acceptable salt thereof) can be effective to treat 3 or more, 5 or more, 7 or more, or 9 or more genotypes of HCV. In some embodiments, a compound of Formula (I), or a pharmaceutical acceptable salt thereof can be more effective against a larger number of HCV genotypes than the standard of care. In some embodiments, a compound of Formula (I), or a pharmaceutical acceptable salt thereof, can be more effective against a particular HCV genotype than the standard of care (such as genotype 1, 2, 3, 4, 5 and/or 6).

[0172] Various indicators for determining the effectiveness of a method for treating a HCV infection are known to those skilled in the art. Examples of suitable indicators include, but are not limited to, a reduction in viral load, a reduction in viral replication, a reduction in time to seroconversion (virus undetectable in patient serum), an increase in the rate of sustained viral response to therapy, a reduction of morbidity or mortality in clinical outcomes, a reduction in the rate of liver function decrease; stasis in liver function; improvement in liver function; reduction in one or more markers of liver dysfunction, including alanine transaminase, aspartate transaminase, total bilirubin, conjugated bilirubin, gamma glutamyl transpeptidase and/or other indicator of disease response. Similarly, successful therapy with an effective amount of a compound or a pharmaceutical composition described herein (for example, a compound of

Formula (I), or a pharmaceutical acceptable salt thereof) can reduce the incidence of liver cancer in HCV infected subjects.

[0173] In some embodiments, an effective amount of a compound of Formula (I), or a pharmaceutically acceptable salt thereof, is an amount that is effective to reduce HCV viral titers to undetectable levels, for example, to about 100 to about 500, to about 50 to about 100, to about 10 to about 50, or to about 15 to about 25 international units/mL serum. In some embodiments, an effective amount of a compound of Formula (I), or a pharmaceutically acceptable salt thereof, is an amount that is effective to reduce HCV viral load compared to the HCV viral load before administration of the compound of Formula (I), or a pharmaceutically acceptable salt thereof. For example, wherein the HCV viral load is measured before administration of the compound of Formula (I), or a pharmaceutically acceptable salt thereof, and again after completion of the treatment regime with the compound of Formula (I), or a pharmaceutically acceptable salt thereof (for example, 1 month after completion). In some embodiments, an effective amount of a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be an amount that is effective to reduce HCV viral load to lower than about 25 international units/mL serum. In some embodiments, an effective amount of a compound of Formula (I), or a pharmaceutically acceptable salt thereof, is an amount that is effective to achieve a reduction in HCV viral titer in the serum of the subject in the range of about 1.5-log to about a 2.5-log reduction, about a 3-log to about a 4-log reduction, or a greater than about 5-log reduction compared to the viral load before administration of the compound of Formula (I), or a pharmaceutically acceptable salt thereof. For example, the HCV viral load can be measured before administration of the compound of Formula (I), or a pharmaceutically acceptable salt thereof, and again after completion of the treatment regime with the compound of Formula (I), or a pharmaceutically acceptable salt thereof (for example, 1 month after completion).

[0174] In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can result in at least a 1, 2, 3, 4, 5, 10, 15, 20, 25, 50, 75, 100-fold or more reduction in the replication of the hepatitis C virus relative to pre-treatment levels in a subject, as determined after completion of the treatment regime (for example, 1 month after completion). In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can result in a reduction of the replication of the hepatitis C virus relative to pre-treatment levels in the range of about 2 to about 5 fold, about 10 to about 20 fold, about 15 to about 40 fold, or about 50 to about 100 fold. In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can result in a reduction of the

hepatitis C virus replication in the range of 1 to 1.5 log, 1.5 log to 2 log, 2 log to 2.5 log, 2.5 to 3 log, 3 log to 3.5 log or 3.5 to 4 log more reduction of the hepatitis C virus replication compared to the reduction of the hepatitis C virus reduction achieved by pegylated interferon in combination with ribavirin, administered according to the standard of care, or may achieve the same reduction as that standard of care therapy in a shorter period of time, for example, in one month, two months, or three months, as compared to the reduction achieved after six months of standard of care therapy with ribavirin and pegylated interferon.

[0175] In some embodiments, an effective amount of a compound of Formula (I), or a pharmaceutically acceptable salt thereof, is an amount that is effective to achieve a sustained viral response, for example, non-detectable or substantially non-detectable HCV RNA (e.g., less than about 500, less than about 200, less than about 100, less than about 25, or less than about 15 international units per milliliter serum) is found in the subject's serum for a period of at least about one month, at least about two months, at least about three months, at least about four months, at least about five months, or at least about six months following cessation of therapy.

[0176] In some embodiments, an effective amount of a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can reduce a level of a marker of liver fibrosis by at least about 10%, at least about 20%, at least about 25%, at least about 30%, at least about 35%, at least about 40%, at least about 45%, at least about 50%, at least about 55%, at least about 60%, at least about 65%, at least about 70%, at least about 75%, or at least about 80%, or more, compared to the level of the marker in an untreated subject, or to a placebo-treated subject. Methods of measuring serum markers are known to those skilled in the art and include immunological-based methods, e.g., enzyme-linked immunosorbent assays (ELISA), radioimmunoassays, and the like, using antibody specific for a given serum marker. A non-limiting list of examples of markers includes measuring the levels of serum alanine aminotransferase (ALT), aspartate aminotransferase (AST), alkaline phosphatase (ALP), gamma-glutamyl transpeptidase (GGT) and total bilirubin (TBIL) using known methods. In general, an ALT level of less than about 45 IU/L (international units/liter), an AST in the range of 10-34 IU/L, ALP in the range of 44-147 IU/L, GGT in the range of 0-51 IU/L, TBIL in the range of 0.3-1.9 mg/dL is considered normal. In some embodiments, an effective amount of a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be an amount effective to reduce ALT, AST, ALP, GGT and/or TBIL levels to with what is considered a normal level.

[0177] Subjects who are clinically diagnosed with HCV infection include "naïve" subjects (e.g., subjects not previously treated for HCV, particularly those who have not

previously received IFN-alpha-based and/or ribavirin-based therapy) and individuals who have failed prior treatment for HCV ("treatment failure" subjects). Treatment failure subjects include "non-responders" (i.e., subjects in whom the HCV titer was not significantly or sufficiently reduced by a previous treatment for HCV (≤ 0.5 log IU/mL), for example, a previous IFN-alpha monotherapy, a previous IFN-alpha and ribavirin combination therapy, or a previous pegylated IFN-alpha and ribavirin combination therapy); and "relapsers" (i.e., subjects who were previously treated for HCV, for example, who received a previous IFN-alpha monotherapy, a previous IFN-alpha and ribavirin combination therapy, or a previous pegylated IFN-alpha and ribavirin combination therapy, whose HCV titer decreased, and subsequently increased).

[0178] In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be administered to a treatment failure subject suffering from HCV. In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be administered to a non-responder subject suffering from HCV. In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be administered to a relapsed subject suffering from HCV.

[0179] After a period of time, infectious agents can develop resistance to one or more therapeutic agents. The term "resistance" as used herein refers to a viral strain displaying a delayed, lessened and/or null response to a therapeutic agent(s). For example, after treatment with an antiviral agent, the viral load of a subject infected with a resistant virus may be reduced to a lesser degree compared to the amount in viral load reduction exhibited by a subject infected with a non-resistant strain. In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be administered to a subject infected with an HCV strain that is resistant to one or more different anti-HCV agents (for example, an agent used in a conventional standard of care). In some embodiments, development of resistant HCV strains is delayed when a subject is treated with a compound of Formula (I), or a pharmaceutically acceptable salt thereof, compared to the development of HCV strains resistant to other HCV drugs (such as an agent used in a conventional standard of care).

[0180] In some embodiments, an effective amount of a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be administered to a subject for whom other anti-HCV medications are contraindicated. For example, administration of pegylated interferon alpha in combination with ribavirin is contraindicated in subjects with hemoglobinopathies (e.g., thalassemia major, sickle-cell anemia) and other subjects at risk from the hematologic side effects of current therapy. In some embodiments, a compound of Formula (I), or a

pharmaceutically acceptable salt thereof, can be provided to a subject that is hypersensitive to interferon and/or ribavirin.

[0181] Some subjects being treated for HCV experience a viral load rebound. The term "viral load rebound" as used herein refers to a sustained ≥ 0.5 log IU/mL increase of viral load above nadir before the end of treatment, where nadir is a ≥ 0.5 log IU/mL decrease from baseline. In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be administered to a subject experiencing viral load rebound, or can prevent such viral load rebound when used to treat the subject.

[0182] The standard of care for treating HCV has been associated with several side effects (adverse events). In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can decrease the number and/or severity of side effects that can be observed in HCV patients being treated with ribavirin and pegylated interferon according to the standard of care. Examples of side effects include, but are not limited to fever, malaise, tachycardia, chills, headache, arthralgias, myalgias, fatigue, apathy, loss of appetite, nausea, vomiting, cognitive changes, asthenia, drowsiness, lack of initiative, irritability, confusion, depression, severe depression, suicidal ideation, anemia, low white blood cell counts, and thinning of hair. In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be provided to a subject that discontinued a HCV therapy because of one or more adverse effects or side effects associated with one or more other HCV agents (for example, an agent used in a conventional standard of care).

[0183] Table 1 provides some embodiments of the percentage improvement obtained using a compound of Formula (I), or a pharmaceutically acceptable salt thereof, as compared to the standard of care. Examples include the following: in some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, results in a percentage of non-responders that is 10% less than the percentage of non-responders receiving the standard of care; in some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, results in a number of side effects that is in the range of about 10% to about 30% less than compared to the number of side effects experienced by a subject receiving the standard of care; and in some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, results in a severity of a side effect (such as one of those described herein) that is 25% less than compared to the severity of the same side effect experienced by a subject receiving the standard of care. Methods of quantifying the severity of a side effect are known to those skilled in the art.

Table 1

Percentage of non-responders	Percentage of relapsers	Percentage of resistance	Percentage of viral load rebound	Number of side effects	Severity of side effects
10% less	10% less	10% less	10% less	10% less	10% less
25% less	25% less	25% less	25% less	25% less	25% less
40% less	40% less	40% less	40% less	40% less	40% less
50% less	50% less	50% less	50% less	50% less	50% less
60% less	60% less	60% less	60% less	60% less	60% less
70% less	70% less	70% less	70% less	70% less	70% less
80% less	80% less	80% less	80% less	80% less	80% less
90% less	90% less	90% less	90% less	90% less	90% less
about 10% to about 30% less	about 10% to about 30% less	about 10% to about 30% less	about 10% to about 30% less	about 10% to about 30% less	about 10% to about 30% less
about 20% to about 50% less	about 20% to about 50% less	about 20% to about 50% less	about 20% to about 50% less	about 20% to about 50% less	about 20% to about 50% less
about 30% to about 70% less	about 30% to about 70% less	about 30% to about 70% less	about 30% to about 70% less	about 30% to about 70% less	about 30% to about 70% less
about 20% to about 80% less	about 20% to about 80% less	about 20% to about 80% less	about 20% to about 80% less	about 20% to about 80% less	about 20% to about 80% less

[0184] As used herein, a “subject” refers to an animal that is the object of treatment, observation or experiment. “Animal” includes cold- and warm-blooded vertebrates and invertebrates such as fish, shellfish, reptiles and, in particular, mammals. “Mammal” includes, without limitation, mice, rats, rabbits, guinea pigs, dogs, cats, sheep, goats, cows, horses, primates, such as monkeys, chimpanzees, and apes, and, in particular, humans. In some embodiments, the subject is human.

[0185] As used herein, the terms “treating,” “treatment,” “therapeutic,” or “therapy” do not necessarily mean total cure or abolition of the disease or condition. Any alleviation of any undesired signs or symptoms of a disease or condition, to any extent can be considered treatment and/or therapy. Furthermore, treatment may include acts that may worsen the patient's overall feeling of well-being or appearance.

[0186] The terms “therapeutically effective amount” and “effective amount” are used to indicate an amount of an active compound, or pharmaceutical agent, that elicits the biological or medicinal response indicated. For example, an effective amount of compound can be the amount needed to prevent, alleviate or ameliorate symptoms of disease or prolong the survival of the subject being treated. This response may occur in a tissue, system, animal or human and includes alleviation of the signs or symptoms of the disease being treated. Determination of an

effective amount is well within the capability of those skilled in the art, in view of the disclosure provided herein. The effective amount of the compounds disclosed herein required as a dose will depend on the route of administration, the type of animal, including human, being treated, and the physical characteristics of the specific animal under consideration. The dose can be tailored to achieve a desired effect, but will depend on such factors as weight, diet, concurrent medication and other factors which those skilled in the medical arts will recognize.

[0187] As will be readily apparent to one skilled in the art, the useful *in vivo* dosage to be administered and the particular mode of administration will vary depending upon the age, weight, the severity of the affliction, and mammalian species treated, the particular compounds employed, and the specific use for which these compounds are employed. The determination of effective dosage levels, that is the dosage levels necessary to achieve the desired result, can be accomplished by one skilled in the art using routine methods, for example, human clinical trials and *in vitro* studies.

[0188] The dosage may range broadly, depending upon the desired effects and the therapeutic indication. Alternatively dosages may be based and calculated upon the surface area of the patient, as understood by those of skill in the art. Although the exact dosage will be determined on a drug-by-drug basis, in most cases, some generalizations regarding the dosage can be made. The daily dosage regimen for an adult human patient may be, for example, an oral dose of between 0.01 mg and 3000 mg of each active ingredient, preferably between 1 mg and 700 mg, e.g. 5 to 200 mg. The dosage may be a single one or a series of two or more given in the course of one or more days, as is needed by the subject. In some embodiments, the compounds will be administered for a period of continuous therapy, for example for a week or more, or for months or years. In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be administered less frequently compared to the frequency of administration of an agent within the standard of care. In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be administered one time per day. For example, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be administered one time per day to a subject suffering from a HCV infection. In some embodiments, the total time of the treatment regime with a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can less compared to the total time of the treatment regime with the standard of care.

[0189] In instances where human dosages for compounds have been established for at least some condition, those same dosages may be used, or dosages that are between about 0.1% and 500%, more preferably between about 25% and 250% of the established human

dosage. Where no human dosage is established, as will be the case for newly-discovered pharmaceutical compositions, a suitable human dosage can be inferred from ED₅₀ or ID₅₀ values, or other appropriate values derived from *in vitro* or *in vivo* studies, as qualified by toxicity studies and efficacy studies in animals.

[0190] In cases of administration of a pharmaceutically acceptable salt, dosages may be calculated as the free base. As will be understood by those of skill in the art, in certain situations it may be necessary to administer the compounds disclosed herein in amounts that exceed, or even far exceed, the above-stated, preferred dosage range in order to effectively and aggressively treat particularly aggressive diseases or infections.

[0191] Dosage amount and interval may be adjusted individually to provide plasma levels of the active moiety which are sufficient to maintain the modulating effects, or minimal effective concentration (MEC). The MEC will vary for each compound but can be estimated from *in vitro* data. Dosages necessary to achieve the MEC will depend on individual characteristics and route of administration. However, HPLC assays or bioassays can be used to determine plasma concentrations. Dosage intervals can also be determined using MEC value. Compositions should be administered using a regimen which maintains plasma levels above the MEC for 10-90% of the time, preferably between 30-90% and most preferably between 50-90%. In cases of local administration or selective uptake, the effective local concentration of the drug may not be related to plasma concentration.

[0192] It should be noted that the attending physician would know how to and when to terminate, interrupt, or adjust administration due to toxicity or organ dysfunctions. Conversely, the attending physician would also know to adjust treatment to higher levels if the clinical response were not adequate (precluding toxicity). The magnitude of an administered dose in the management of the disorder of interest will vary with the severity of the condition to be treated and to the route of administration. The severity of the condition may, for example, be evaluated, in part, by standard prognostic evaluation methods. Further, the dose and perhaps dose frequency, will also vary according to the age, body weight, and response of the individual patient. A program comparable to that discussed above may be used in veterinary medicine.

[0193] Compounds disclosed herein can be evaluated for efficacy and toxicity using known methods. For example, the toxicology of a particular compound, or of a subset of the compounds, sharing certain chemical moieties, may be established by determining *in vitro* toxicity towards a cell line, such as a mammalian, and preferably human, cell line. The results of such studies are often predictive of toxicity in animals, such as mammals, or more specifically, humans. Alternatively, the toxicity of particular compounds in an animal model,

such as mice, rats, rabbits, or monkeys, may be determined using known methods. The efficacy of a particular compound may be established using several recognized methods, such as *in vitro* methods, animal models, or human clinical trials. When selecting a model to determine efficacy, the skilled artisan can be guided by the state of the art to choose an appropriate model, dose, route of administration and/or regime.

Combination Therapies

[0194] In some embodiments, the compounds disclosed herein, such as a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound described herein, or a pharmaceutically acceptable salt thereof, can be used in combination with one or more additional agent(s). Examples of additional agents that can be used in combination with a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (I), or a pharmaceutically acceptable salt thereof, include, but are not limited to, agents currently used in a conventional standard of care for treating HCV, HCV protease inhibitors, HCV polymerase inhibitors, NS5A inhibitors, other antiviral compounds, compounds of Formula (AA), (including pharmaceutically acceptable salts and pharmaceutical compositions that can include a compound of Formula (AA), or a pharmaceutically acceptable salt thereof), compounds of Formula (BB) (including pharmaceutically acceptable salts and pharmaceutical compositions that can include a compound of Formula (BB), or a pharmaceutically acceptable salt thereof), compounds of Formula (CC) (including pharmaceutically acceptable salts and pharmaceutical compositions that can include a compound of Formula (CC), or a pharmaceutically acceptable salt thereof), and/or combinations thereof. In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be used with one, two, three or more additional agents described herein. A non-limiting list of examples of combinations of a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (I), or a pharmaceutically acceptable salt thereof, is provided in Tables A, B, C, D and E.

[0195] In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be used in combination with an agent(s) currently used in a conventional standard of care therapy. For example, for the treatment of HCV, a compound disclosed herein can be used in combination with Pegylated interferon-alpha-

2a (brand name PEGASYS®) and ribavirin, Pegylated interferon-alpha-2b (brand name PEG-INTRON®) and ribavirin, Pegylated interferon-alpha-2a, Pegylated interferon-alpha-2b, or ribavirin.

[0196] In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be substituted for an agent currently used in a conventional standard of care therapy. For example, for the treatment of HCV, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be used in place of ribavirin.

[0197] In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be used in combination with an interferon, such as a pegylated interferon. Examples of suitable interferons include, but are not limited to, Pegylated interferon-alpha-2a (brand name PEGASYS®), Pegylated interferon-alpha-2b (brand name PEG-INTRON®), interferon alfacon-1 (brand name INFERGEN®), pegylated interferon lambda and/or a combination thereof.

[0198] In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be used in combination with a HCV protease inhibitor. A non-limiting list of example HCV protease inhibitors include the following: VX-950 (TELAPREVIR®), MK-5172, ABT-450, BILN-2061, BI-201335, BMS-650032, SCH 503034 (BOCEPREVIR®), GS-9256, GS-9451, IDX-320, ACH-1625, ACH-2684, TMC-435, ITMN-191 (DANOPREVIR®) and/or a combination thereof. Additional HCV protease inhibitors suitable for use in combination with a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (I), or a pharmaceutically acceptable salt thereof, include VP-19744, PSI-879, VCH-759/VX-759, HCV-371, IDX-375, GL-60667, JTK-109, PSI-6130, R1479, R-1626, R-7182, MK-0608, INX-8014, INX-8018, A-848837, A-837093, BILB-1941, VCH-916, VCH-716, GSK-71185, GSK-625433, XTL-2125 and those disclosed in PCT Publication No. WO 2012/142085, which is hereby incorporated by reference for the limited purpose of its disclosure of HCV protease inhibitors, HCV polymerase inhibitors and NS5A inhibitors. A non-limiting list of example HCV protease inhibitors includes the compounds numbered 1001-1016 in Figure 1.

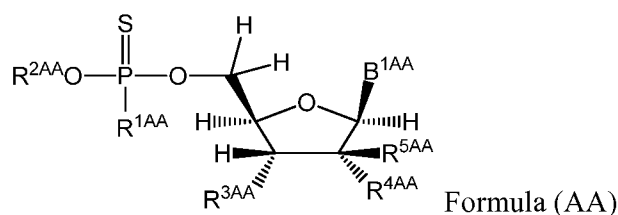
[0199] In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be used in combination with a HCV polymerase inhibitor. In some embodiments, the HCV polymerase inhibitor can be a nucleoside inhibitor. In other embodiments, the HCV polymerase inhibitor can be a non-nucleoside inhibitor. Examples of suitable nucleoside inhibitors include, but are not limited to, RG7128, PSI-7851, PSI-7977, INX-189, PSI-352938, PSI-661, 4'-azidouridine (including known prodrugs of 4'-azidouridine), GS-6620, IDX-184, and TMC649128 and/or combinations thereof. A non-limiting list of example nucleoside inhibitors includes compounds numbered 2001-2012 in Figure 2. Examples of suitable non-nucleoside inhibitors include, but are not limited to, ABT-333, ANA-598, VX-222, HCV-796, BI-207127, GS-9190, PF-00868554 (FILIBUVIR®), VX-497 and/or combinations thereof. A non-limiting list of example non-nucleoside inhibitors includes the compounds numbered 3001-3014 in Figure 3. Further HCV polymerase inhibitors suitable for use in combination with a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (I), or a pharmaceutically acceptable salt thereof, include VX-500, VX-813, VBY-376, TMC-435350, EZ-058, EZ-063, GS-9132, ACH-1095, IDX-136, IDX-316, ITMN-8356, ITMN-8347, ITMN-8096, ITMN-7587, VX-985, and those disclosed in PCT Publication No. WO 2012/142085.

[0200] In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be used in combination with a NS5A inhibitor. Examples of NS5A inhibitors include BMS-790052, PPI-461, ACH-2928, GS-5885, BMS-824393 and/or combinations thereof. A non-limiting list of example NS5A inhibitors includes the compounds numbered 4001-4012 in Figure 4. Additional NS5A inhibitors suitable for use in combination with a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (I), or a pharmaceutically acceptable salt thereof, include A-832, PPI-1301 and those disclosed in PCT Publication No. WO 2012/142085.

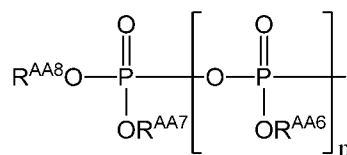
[0201] In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be used in combination with other antiviral compounds. Examples of other antiviral compounds include, but are not limited to, Debio-025,

MIR-122, cyclosporin A and/or combinations thereof. A non-limiting list of example other antiviral compounds includes the compounds numbered 5001-5012 in Figure 5.

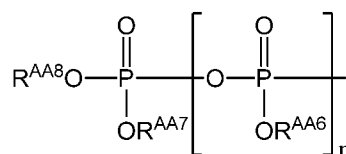
[0202] In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be used in combination with a compound of Formula (AA), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (AA), or a pharmaceutically acceptable salt thereof (see, U.S. Publication No. 2013/0164261, published June 27, 2013, the contents of which are incorporated by reference in its entirety):



wherein: B^{AA1} can be an optionally substituted heterocyclic base or an optionally substituted heterocyclic base with a protected amino group; R^{AA1} can be selected from O^- , OH, an optionally substituted N-linked amino acid and an optionally substituted N-linked amino acid ester derivative; R^{AA2} can be absent or selected from hydrogen, an optionally substituted aryl, an optionally substituted heteroaryl, an optionally substituted heterocyclyl and



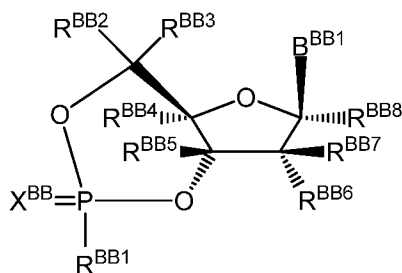
, wherein R^{AA6} , R^{AA7} and R^{AA8} can be independently absent or hydrogen, and n^{AA} can be 0 or 1; provided that when R^{AA1} is O^- or OH, then R^{AA2} is absent,



hydrogen or R^{AA3} can be selected from hydrogen, halogen, $-OR^{AA9}$ and $-OC(=O)R^{AA10}$; R^{AA4} can be selected from halogen, $-OR^{AA11}$ and $-OC(=O)R^{AA12}$; or R^{AA3} and R^{AA4} can be both an oxygen atom which are linked together by a carbonyl group; R^{AA5} can be selected from an optionally substituted C_{2-6} alkyl, an optionally substituted C_{2-6} alkenyl, an optionally substituted C_{2-6} alkynyl and an optionally substituted C_{3-6} cycloalkyl; or R^{AA4} and R^{AA5} together can form $-(C_{1-6} \text{ alkyl})-O-$ or $-O-(C_{1-6} \text{ alkyl})-$; R^{AA9} and R^{AA11} can be independently hydrogen or an optionally substituted C_{1-6} alkyl; and R^{AA10} and R^{AA12} can be independently an optionally substituted C_{1-6} alkyl or an optionally substituted C_{3-6} cycloalkyl. A

non-limiting list of examples of compounds of Formula (AA) includes the compounds numbered 7000-7027 in Figure 7.

[0203] In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be used in combination with a compound of Formula (BB), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (BB), or a pharmaceutically acceptable salt thereof (see, U.S. Publication No. 2012/0165286, published June 28, 2012, the contents of which are incorporated by reference in their entireties):

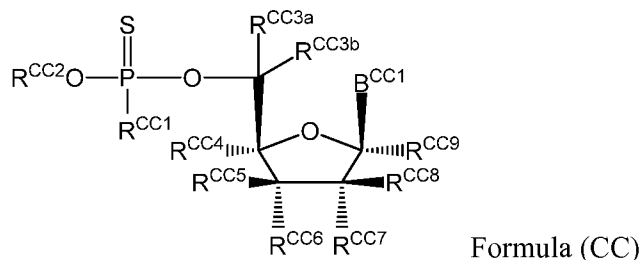


Formula (BB)

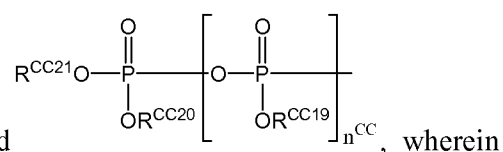
wherein B^{BB1} can be an optionally substituted heterocyclic base or an optionally substituted heterocyclic base with a protected amino group; X^{BB} can be O (oxygen) or S (sulfur); R^{BB1} can be selected from -Z^{BB}-R^{BB9}, an optionally substituted N-linked amino acid and an optionally substituted N-linked amino acid ester derivative; Z^{BB} can be selected from O (oxygen), S (sulfur) and N(R^{BB10}); R^{BB2} and R^{BB3} can be independently selected from hydrogen, an optionally substituted C₁₋₆ alkyl, an optionally substituted C₂₋₆ alkenyl, an optionally substituted C₂₋₆ alkynyl, an optionally substituted C₁₋₆ haloalkyl and an optionally substituted aryl(C₁₋₆ alkyl); or R^{BB2} and R^{BB3} can be taken together to form a group selected from an optionally substituted C₃₋₆ cycloalkyl, an optionally substituted C₃₋₆ cycloalkenyl, an optionally substituted C₃₋₆ aryl and an optionally substituted C₃₋₆ heteroaryl; R^{BB4} can be selected from hydrogen, halogen, azido, cyano, an optionally substituted C₁₋₆ alkyl, an optionally substituted C₂₋₆ alkenyl, an optionally substituted C₂₋₆ alkynyl and an optionally substituted allenyl; R^{BB5} can be hydrogen or an optionally substituted C₁₋₆ alkyl; R^{BB6} can be selected from hydrogen, halogen, azido, amino, cyano, an optionally substituted C₁₋₆ alkyl, -OR^{BB11} and -OC(=O)R^{BB12}; R^{BB7} can be selected from hydrogen, halogen, azido, cyano, an optionally substituted C₁₋₆ alkyl, -OR^{BB13} and -OC(=O)R^{BB14}; R^{BB8} can be selected from hydrogen, halogen, azido, cyano, an optionally substituted C₁₋₆ alkyl, -OR^{BB15} and -OC(=O)R^{BB16}; R^{BB9} can be selected from an optionally substituted alkyl, an optionally substituted alkenyl, an optionally substituted alkynyl, an optionally substituted cycloalkyl, an optionally substituted cycloalkenyl, an optionally substituted aryl, an optionally substituted heteroaryl, an optionally substituted heterocyclyl, an

optionally substituted aryl(C₁₋₆alkyl), an optionally substituted heteroaryl(C₁₋₆alkyl) and an optionally substituted heterocyclyl(C₁₋₆alkyl); R^{BB10} can be selected from hydrogen, an optionally substituted alkyl, an optionally substituted alkenyl, an optionally substituted alkynyl, an optionally substituted cycloalkyl, an optionally substituted cycloalkenyl, an optionally substituted aryl, an optionally substituted heteroaryl, an optionally substituted heterocyclyl, an optionally substituted aryl(C₁₋₆alkyl), an optionally substituted heteroaryl(C₁₋₆alkyl) and an optionally substituted heterocyclyl(C₁₋₆alkyl); R^{BB11}, R^{BB13} and R^{BB15} can be independently hydrogen or an optionally substituted C₁₋₆ alkyl; and R^{BB12}, R^{BB14} and R^{BB16} can be independently an optionally substituted C₁₋₆ alkyl or an optionally substituted C₃₋₆ cycloalkyl. In some embodiments, at least one of R^{BB2} and R^{BB3} is not hydrogen. A non-limiting list of example compounds of Formula (BB) includes the compound numbered 8000-8016 in Figure 8.

[0204] In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be used in combination with a compound of Formula (CC), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (CC), or a pharmaceutically acceptable salt thereof (see, U.S. Publication No. 2012/0071434, published March 22, 2012, the contents of which are incorporated by reference in its entirety):

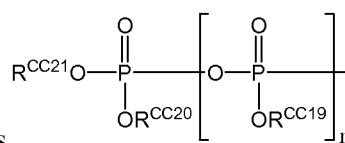


wherein B^{CC1} can be an optionally substituted heterocyclic base or an optionally substituted heterocyclic base with a protected amino group; R^{CC1} can be selected from O⁻, OH, an optionally substituted N-linked amino acid and an optionally substituted N-linked amino acid ester derivative; R^{CC2} can be selected from an optionally substituted aryl, an optionally substituted



heteroaryl, an optionally substituted heterocyclyl and

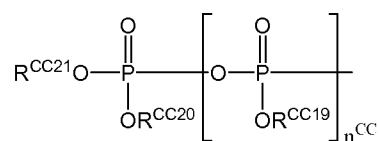
R^{CC19}, R^{CC20} and R^{CC21} can be independently absent or hydrogen, and n^{CC} can be 0 or 1;



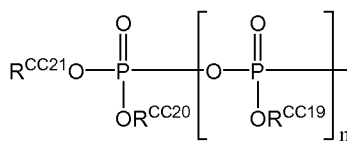
provided that when R^{CC1} is O⁻ or OH, then R^{CC2} is

R^{CC3a} and

R^{CC3b} can be independently selected from hydrogen, deuterium, an optionally substituted C₁₋₆ alkyl, an optionally substituted C₂₋₆ alkenyl, an optionally substituted C₂₋₆ alkynyl, an optionally substituted C₁₋₆ haloalkyl and aryl(C₁₋₆ alkyl); or R^{CC3a} and R^{CC3b} can be taken together to form an optionally substituted C₃₋₆ cycloalkyl; R^{CC4} can be selected from hydrogen, azido, an optionally substituted C₁₋₆ alkyl, an optionally substituted C₂₋₆ alkenyl and an optionally substituted C₂₋₆ alkynyl; R^{CC5} can be selected from hydrogen, halogen, azido, cyano, an optionally substituted C₁₋₆ alkyl, -OR^{CC10} and -OC(=O)R^{CC11}; R^{CC6} can be selected from hydrogen, halogen, azido, cyano, an optionally substituted C₁₋₆ alkyl, -OR^{CC12} and -OC(=O)R^{CC13}; R^{CC7} can be selected from hydrogen, halogen, azido, cyano, an optionally substituted C₁₋₆ alkyl, -OR^{CC14} and -OC(=O)R^{CC15}; or R^{CC6} and R^{CC7} can be both oxygen atoms and linked together by a carbonyl group; R^{CC8} can be selected from hydrogen, halogen, azido, cyano, an optionally substituted C₁₋₆ alkyl, -OR^{CC16} and -OC(=O)R^{CC17}; R^{CC9} can be selected from hydrogen, azido, cyano, an optionally substituted C₁₋₆ alkyl and -OR^{CC18}; R^{CC10}, R^{CC12}, R^{CC14}, R^{CC16} and R^{CC18} can be independently selected from hydrogen and an optionally substituted C₁₋₆ alkyl; and R^{CC11}, R^{CC13}, R^{CC15} and R^{CC17} can be independently selected from an optionally substituted C₁₋₆ alkyl and an optionally substituted C₃₋₆ cycloalkyl. In some embodiments, when R^{CC3a}, R^{CC3b}, R^{CC4}, R^{CC5}, R^{CC7}, R^{CC8} and R^{CC9} are all hydrogen, then R^{CC6} is



not azido. In some embodiments, R^{CC2} cannot be $OR^{CC20}[OR^{CC19}]_{n^{CC}}$ when R^{CC3a} is hydrogen, R^{CC3b} is hydrogen, R^{CC4} is H, R^{CC5} is OH or H, R^{CC6} is hydrogen, OH, or $-OC(=O)CH_3$, R^{CC7} is hydrogen, OH, OCH_3 or $-OC(=O)CH_3$, R^{CC8} is hydrogen, OH or OCH_3 , R^{CC9} is H and B^{CC1} is an optionally substituted adenine, an optionally substituted guanine, an optionally substituted uracil or an optionally substituted hypoxanthine. In some embodiments,



R^{CC2} cannot be $OR^{CC20} [OR^{CC19}]_n^{CC}$. A non-limiting list of examples of compounds of Formula (CC) includes the compounds numbered 6000-6078 in Figure 6.

[0205] Some embodiments described herein relate to a method of ameliorating or treating a HCV infection that can include contacting a cell infected with the HCV infection with an effective amount of a compound of Formula (I), or a pharmaceutically acceptable salt thereof, in combination with one or more agents selected from an interferon, ribavirin, a HCV protease inhibitor, a HCV polymerase inhibitor, a NS5A inhibitor, an antiviral compound, a compound of

Formula (AA), a compound of Formula (BB) and a compound of Formula (CC), or a pharmaceutically acceptable salt of any of the aforementioned compounds.

[0206] Some embodiments described herein relate to a method of ameliorating or treating a HCV infection that can include administering to a subject suffering from the HCV infection an effective amount of a compound of Formula (I), or a pharmaceutically acceptable salt thereof, in combination with one or more agents selected from an interferon, ribavirin, a HCV protease inhibitor, a HCV polymerase inhibitor, a NS5A inhibitor, an antiviral compound, a compound of Formula (AA), a compound of Formula (BB) and a compound of Formula (CC), or a pharmaceutically acceptable salt of any of the aforementioned compounds.

[0207] Some embodiments described herein relate to a method of inhibiting the replication of a hepatitis C virus that can include contacting a cell infected with the hepatitis C virus with an effective amount of a compound of Formula (I), or a pharmaceutically acceptable salt thereof, in combination with one or more agents selected from an interferon, ribavirin, a HCV protease inhibitor, a HCV polymerase inhibitor, a NS5A inhibitor, an antiviral compound, a compound of Formula (AA), a compound of Formula (BB) and a compound of Formula (CC), or a pharmaceutically acceptable salt of any of the aforementioned compounds.

[0208] Some embodiments described herein relate to a method of inhibiting the replication of a hepatitis C virus that can include administering to a subject infected with the hepatitis C virus an effective amount of a compound of Formula (I), or a pharmaceutically acceptable salt thereof, in combination with one or more agents selected from an interferon, ribavirin, a HCV protease inhibitor, a HCV polymerase inhibitor, a NS5A inhibitor, an antiviral compound, a compound of Formula (AA), a compound of Formula (BB) and a compound of Formula (CC), or a pharmaceutically acceptable salt of any of the aforementioned compounds.

[0209] In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be administered with one or more additional agent(s) together in a single pharmaceutical composition. In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be administered with one or more additional agent(s) as two or more separate pharmaceutical compositions. For example, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be administered in one pharmaceutical composition, and at least one of the additional agents can be administered in a second pharmaceutical composition. If there are at least two additional agents, one or more of the additional agents can be in a first pharmaceutical composition that includes a compound of Formula (I), or a pharmaceutically acceptable salt thereof, and at least one of the other additional agent(s) can be in a second pharmaceutical composition.

[0210] The dosing amount(s) and dosing schedule(s) when using a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (I), or a pharmaceutically acceptable salt thereof, and one or more additional agents are within the knowledge of those skilled in the art. For example, when performing a conventional standard of care therapy using art-recognized dosing amounts and dosing schedules, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be administered in addition to that therapy, or in place of one of the agents of a combination therapy, using effective amounts and dosing protocols as described herein.

[0211] The order of administration of a compound of Formula (I), or a pharmaceutically acceptable salt thereof, with one or more additional agent(s) can vary. In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be administered prior to all additional agents. In other embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be administered prior to at least one additional agent. In still other embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be administered concomitantly with one or more additional agent(s). In yet still other embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be administered subsequent to the administration of at least one additional agent. In some embodiments, a compound of Formula (I), or a pharmaceutically acceptable salt thereof, can be administered subsequent to the administration of all additional agents.

[0212] In some embodiments, the combination of a compound of Formula (I), or a pharmaceutically acceptable salt thereof, in combination with one or more additional agent(s) in Figures 1-8 (including pharmaceutically acceptable salts and prodrugs thereof) can result in an additive effect. In some embodiments, the combination of a compound of Formula (I), or a pharmaceutically acceptable salt thereof, in combination with one or more additional agent(s) in Figures 1-8 (including pharmaceutically acceptable salts and prodrugs thereof) can result in a synergistic effect. In some embodiments, the combination of a compound of Formula (I), or a pharmaceutically acceptable salt thereof, in combination with one or more additional agent(s) in Figures 1-8 (including pharmaceutically acceptable salts and prodrugs thereof) can result in a strongly synergistic effect. In some embodiments, the combination of a compound of Formula (I), or a pharmaceutically acceptable salt thereof, in combination with one or more additional agent(s) in Figures 1-8 (including pharmaceutically acceptable salts and prodrugs thereof) is not antagonistic.

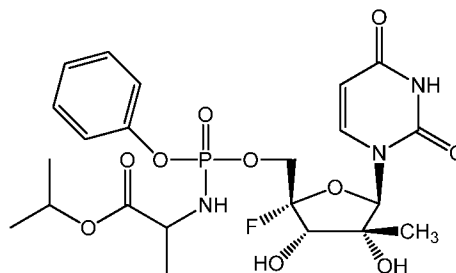
[0213] As used herein, the term “antagonistic” means that the activity of the combination of compounds is less compared to the sum of the activities of the compounds in combination when the activity of each compound is determined individually (i.e. as a single compound). As used herein, the term “synergistic effect” means that the activity of the combination of compounds is greater than the sum of the individual activities of the compounds in the combination when the activity of each compound is determined individually. As used herein, the term “additive effect” means that the activity of the combination of compounds is about equal to the sum of the individual activities of the compound in the combination when the activity of each compound is determined individually.

[0214] A potential advantage of utilizing a compound of Formula (I), or a pharmaceutically acceptable salt thereof, in combination with one or more additional agent(s) in Figures 1-8 (including pharmaceutically acceptable salts thereof) may be a reduction in the required amount(s) of one or more compounds of Figures 1-8 (including pharmaceutically acceptable salts thereof) that is effective in treating a disease condition disclosed herein (for example, HCV), as compared to the amount required to achieve same therapeutic result when one or more compounds of Figures 1-8 (including pharmaceutically acceptable salts thereof) are administered without a compound of Formula (I), or a pharmaceutically acceptable salt thereof. For example, the amount of a compound in Figures 1-8 (including a pharmaceutically acceptable salt thereof), can be less compared to the amount of the compound in Figures 1-8 (including a pharmaceutically acceptable salt thereof), needed to achieve the same viral load reduction when administered as a monotherapy. Another potential advantage of utilizing a compound of Formula (I), or a pharmaceutically acceptable salt thereof, in combination with one or more additional agent(s) in Figures 1-8 (including pharmaceutically acceptable salts thereof) is that the use of two or more compounds having different mechanism of actions can create a higher barrier to the development of resistant viral strains compared to the barrier when a compound is administered as monotherapy.

[0215] Additional advantages of utilizing a compound of Formula (I), or a pharmaceutically acceptable salt thereof, in combination with one or more additional agent(s) in Figures 1-8 (including pharmaceutically acceptable salts thereof) may include little to no cross resistance between a compound of Formula (I), or a pharmaceutically acceptable salt thereof, and one or more additional agent(s) in Figures 1-8 (including pharmaceutically acceptable salts thereof) thereof; different routes for elimination of a compound of Formula (I), or a pharmaceutically acceptable salt thereof, and one or more additional agent(s) in Figures 1-8 (including pharmaceutically acceptable salts thereof); little to no overlapping toxicities between

a compound of Formula (I), or a pharmaceutically acceptable salt thereof, and one or more additional agent(s) in Figures 1-8 (including pharmaceutically acceptable salts thereof); little to no significant effects on cytochrome P450; little to no pharmacokinetic interactions between a compound of Formula (I), or a pharmaceutically acceptable salt thereof, and one or more additional agent(s) in Figures 1-8 (including pharmaceutically acceptable salts thereof); greater percentage of subjects achieving a sustained viral response compared to when a compound is administered as monotherapy and/or a decrease in treatment time to achieve a sustained viral response compared to when a compound is administered as monotherapy.

[0216] A non-limiting list of example combination of compounds of Formula (I), or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition that includes a compound described herein, with one or more additional agent(s) are provided in Tables A, B, C, D and E. Each numbered X and Y compound in Tables A, B, C, D and E has a corresponding name and/or structure provided in Figures 1-8. The numbered compounds in Tables A, B, C, D and E includes pharmaceutically acceptable salts of the compounds and pharmaceutical compositions containing the compounds or a pharmaceutically acceptable salt thereof. For example, 1001 includes the compound corresponding to 1001, pharmaceutically acceptable salts thereof, and pharmaceutical compositions that include compound 1001 and/or a pharmaceutically acceptable salt thereof. The combinations exemplified in Tables A, B, C, D and E are designated by the formula X:Y, which represents a combination of a compound X with a compound Y. For example, the combination designated as 1001:9004 in Table A represents a combination of compound 1001 with compound 9004, including pharmaceutically acceptable salts of compound 1001 and/or 9004, and pharmaceutical compositions including compound 1001 and 9004 (including pharmaceutical compositions that include pharmaceutically acceptable salts of compound 1001 and/or compound 9004). Thus, the combination designated as 1001:9004 in Table A represents the combination of Telaprevir



(compound 1001, as shown in Figure 1) and (compound 9004, as shown in Figure 9), including pharmaceutically acceptable salts of compound 1001 and/or 9004, and pharmaceutical compositions including compound 1001 and 9004 (including pharmaceutical compositions that include pharmaceutically acceptable salts of compound 1001 and/or compound 9004). Each of the combinations provided in Tables A, B, C, D and E can be

used with one, two, three or more additional agents described herein. In some embodiments described herein, the combination of agents can be used to treat, ameliorate and/or inhibit a virus and/or a viral infection, wherein the virus can be HCV and the viral infection can be an HCV viral infection.

Table A: Example combinations of a compound X with a compound Y.

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
1001 : 9000	1001 : 9001	1001 : 9002	1001 : 9003	1001 : 9004	1001 : 9005
1002 : 9000	1002 : 9001	1002 : 9002	1002 : 9003	1002 : 9004	1002 : 9005
1003 : 9000	1003 : 9001	1003 : 9002	1003 : 9003	1003 : 9004	1003 : 9005
1004 : 9000	1004 : 9001	1004 : 9002	1004 : 9003	1004 : 9004	1004 : 9005
1005 : 9000	1005 : 9001	1005 : 9002	1005 : 9003	1005 : 9004	1005 : 9005
1006 : 9000	1006 : 9001	1006 : 9002	1006 : 9003	1006 : 9004	1006 : 9005
1007 : 9000	1007 : 9001	1007 : 9002	1007 : 9003	1007 : 9004	1007 : 9005
1008 : 9000	1008 : 9001	1008 : 9002	1008 : 9003	1008 : 9004	1008 : 9005
1009 : 9000	1009 : 9001	1009 : 9002	1009 : 9003	1009 : 9004	1009 : 9005
1010 : 9000	1010 : 9001	1010 : 9002	1010 : 9003	1010 : 9004	1010 : 9005
1011 : 9000	1011 : 9001	1011 : 9002	1011 : 9003	1011 : 9004	1011 : 9005
1012 : 9000	1012 : 9001	1012 : 9002	1012 : 9003	1012 : 9004	1012 : 9005
1013 : 9000	1013 : 9001	1013 : 9002	1013 : 9003	1013 : 9004	1013 : 9005
1014 : 9000	1014 : 9001	1014 : 9002	1014 : 9003	1014 : 9004	1014 : 9005
1015 : 9000	1015 : 9001	1015 : 9002	1015 : 9003	1015 : 9004	1015 : 9005
1016 : 9000	1016 : 9001	1016 : 9002	1016 : 9003	1016 : 9004	1016 : 9005
2001 : 9000	2001 : 9001	2001 : 9002	2001 : 9003	2001 : 9004	2001 : 9005
2002 : 9000	2002 : 9001	2002 : 9002	2002 : 9003	2002 : 9004	2002 : 9005
2003 : 9000	2003 : 9001	2003 : 9002	2003 : 9003	2003 : 9004	2003 : 9005
2004 : 9000	2004 : 9001	2004 : 9002	2004 : 9003	2004 : 9004	2004 : 9005
2005 : 9000	2005 : 9001	2005 : 9002	2005 : 9003	2005 : 9004	2005 : 9005
2006 : 9000	2006 : 9001	2006 : 9002	2006 : 9003	2006 : 9004	2006 : 9005
2007 : 9000	2007 : 9001	2007 : 9002	2007 : 9003	2007 : 9004	2007 : 9005
2008 : 9000	2008 : 9001	2008 : 9002	2008 : 9003	2008 : 9004	2008 : 9005
2009 : 9000	2009 : 9001	2009 : 9002	2009 : 9003	2009 : 9004	2009 : 9005
2010 : 9000	2010 : 9001	2010 : 9002	2010 : 9003	2010 : 9004	2010 : 9005
2011 : 9000	2011 : 9001	2011 : 9002	2011 : 9003	2011 : 9004	2011 : 9005
2012 : 9000	2012 : 9001	2012 : 9002	2012 : 9003	2012 : 9004	2012 : 9005

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
1001 : 9006	1001 : 9007	1001 : 9008	1001 : 9009	1001 : 9010	1001 : 9011
1002 : 9006	1002 : 9007	1002 : 9008	1002 : 9009	1002 : 9010	1002 : 9011
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2003 : 9054	2003 : 9055	2003 : 9056	2003 : 9057	2003 : 9058	2003 : 9059
2004 : 9054	2004 : 9055	2004 : 9056	2004 : 9057	2004 : 9058	2004 : 9059
2005 : 9054	2005 : 9055	2005 : 9056	2005 : 9057	2005 : 9058	2005 : 9059
2006 : 9054	2006 : 9055	2006 : 9056	2006 : 9057	2006 : 9058	2006 : 9059
2007 : 9054	2007 : 9055	2007 : 9056	2007 : 9057	2007 : 9058	2007 : 9059
2008 : 9054	2008 : 9055	2008 : 9056	2008 : 9057	2008 : 9058	2008 : 9059
2009 : 9054	2009 : 9055	2009 : 9056	2009 : 9057	2009 : 9058	2009 : 9059
2010 : 9054	2010 : 9055	2010 : 9056	2010 : 9057	2010 : 9058	2010 : 9059
2011 : 9054	2011 : 9055	2011 : 9056	2011 : 9057	2011 : 9058	2011 : 9059
2012 : 9054	2012 : 9055	2012 : 9056	2012 : 9057	2012 : 9058	2012 : 9059

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
1001 : 9060	1001 : 9061	1001 : 9062	1001 : 9063	1001 : 9064	1001 : 9065
1002 : 9060	1002 : 9061	1002 : 9062	1002 : 9063	1002 : 9064	1002 : 9065
1003 : 9060	1003 : 9061	1003 : 9062	1003 : 9063	1003 : 9064	1003 : 9065
1004 : 9060	1004 : 9061	1004 : 9062	1004 : 9063	1004 : 9064	1004 : 9065
1005 : 9060	1005 : 9061	1005 : 9062	1005 : 9063	1005 : 9064	1005 : 9065
1006 : 9060	1006 : 9061	1006 : 9062	1006 : 9063	1006 : 9064	1006 : 9065
1007 : 9060	1007 : 9061	1007 : 9062	1007 : 9063	1007 : 9064	1007 : 9065
1008 : 9060	1008 : 9061	1008 : 9062	1008 : 9063	1008 : 9064	1008 : 9065
1009 : 9060	1009 : 9061	1009 : 9062	1009 : 9063	1009 : 9064	1009 : 9065
1010 : 9060	1010 : 9061	1010 : 9062	1010 : 9063	1010 : 9064	1010 : 9065
1011 : 9060	1011 : 9061	1011 : 9062	1011 : 9063	1011 : 9064	1011 : 9065
1012 : 9060	1012 : 9061	1012 : 9062	1012 : 9063	1012 : 9064	1012 : 9065
1013 : 9060	1013 : 9061	1013 : 9062	1013 : 9063	1013 : 9064	1013 : 9065
1014 : 9060	1014 : 9061	1014 : 9062	1014 : 9063	1014 : 9064	1014 : 9065
1015 : 9060	1015 : 9061	1015 : 9062	1015 : 9063	1015 : 9064	1015 : 9065
1016 : 9060	1016 : 9061	1016 : 9062	1016 : 9063	1016 : 9064	1016 : 9065
2001 : 9060	2001 : 9061	2001 : 9062	2001 : 9063	2001 : 9064	2001 : 9065
2002 : 9060	2002 : 9061	2002 : 9062	2002 : 9063	2002 : 9064	2002 : 9065
2003 : 9060	2003 : 9061	2003 : 9062	2003 : 9063	2003 : 9064	2003 : 9065
2004 : 9060	2004 : 9061	2004 : 9062	2004 : 9063	2004 : 9064	2004 : 9065
2005 : 9060	2005 : 9061	2005 : 9062	2005 : 9063	2005 : 9064	2005 : 9065
2006 : 9060	2006 : 9061	2006 : 9062	2006 : 9063	2006 : 9064	2006 : 9065
2007 : 9060	2007 : 9061	2007 : 9062	2007 : 9063	2007 : 9064	2007 : 9065
2008 : 9060	2008 : 9061	2008 : 9062	2008 : 9063	2008 : 9064	2008 : 9065
2009 : 9060	2009 : 9061	2009 : 9062	2009 : 9063	2009 : 9064	2009 : 9065
2010 : 9060	2010 : 9061	2010 : 9062	2010 : 9063	2010 : 9064	2010 : 9065
2011 : 9060	2011 : 9061	2011 : 9062	2011 : 9063	2011 : 9064	2011 : 9065
2012 : 9060	2012 : 9061	2012 : 9062	2012 : 9063	2012 : 9064	2012 : 9065

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
1001 : 9066	1001 : 9067	1001 : 9068	1001 : 9069	1001 : 9070	1001 : 9071
1002 : 9066	1002 : 9067	1002 : 9068	1002 : 9069	1002 : 9070	1002 : 9071
1003 : 9066	1003 : 9067	1003 : 9068	1003 : 9069	1003 : 9070	1003 : 9071
1004 : 9066	1004 : 9067	1004 : 9068	1004 : 9069	1004 : 9070	1004 : 9071
1005 : 9066	1005 : 9067	1005 : 9068	1005 : 9069	1005 : 9070	1005 : 9071
1006 : 9066	1006 : 9067	1006 : 9068	1006 : 9069	1006 : 9070	1006 : 9071
1007 : 9066	1007 : 9067	1007 : 9068	1007 : 9069	1007 : 9070	1007 : 9071
1008 : 9066	1008 : 9067	1008 : 9068	1008 : 9069	1008 : 9070	1008 : 9071
1009 : 9066	1009 : 9067	1009 : 9068	1009 : 9069	1009 : 9070	1009 : 9071
1010 : 9066	1010 : 9067	1010 : 9068	1010 : 9069	1010 : 9070	1010 : 9071
1011 : 9066	1011 : 9067	1011 : 9068	1011 : 9069	1011 : 9070	1011 : 9071
1012 : 9066	1012 : 9067	1012 : 9068	1012 : 9069	1012 : 9070	1012 : 9071
1013 : 9066	1013 : 9067	1013 : 9068	1013 : 9069	1013 : 9070	1013 : 9071
1014 : 9066	1014 : 9067	1014 : 9068	1014 : 9069	1014 : 9070	1014 : 9071
1015 : 9066	1015 : 9067	1015 : 9068	1015 : 9069	1015 : 9070	1015 : 9071
1016 : 9066	1016 : 9067	1016 : 9068	1016 : 9069	1016 : 9070	1016 : 9071
2001 : 9066	2001 : 9067	2001 : 9068	2001 : 9069	2001 : 9070	2001 : 9071
2002 : 9066	2002 : 9067	2002 : 9068	2002 : 9069	2002 : 9070	2002 : 9071
2003 : 9066	2003 : 9067	2003 : 9068	2003 : 9069	2003 : 9070	2003 : 9071
2004 : 9066	2004 : 9067	2004 : 9068	2004 : 9069	2004 : 9070	2004 : 9071
2005 : 9066	2005 : 9067	2005 : 9068	2005 : 9069	2005 : 9070	2005 : 9071
2006 : 9066	2006 : 9067	2006 : 9068	2006 : 9069	2006 : 9070	2006 : 9071
2007 : 9066	2007 : 9067	2007 : 9068	2007 : 9069	2007 : 9070	2007 : 9071
2008 : 9066	2008 : 9067	2008 : 9068	2008 : 9069	2008 : 9070	2008 : 9071
2009 : 9066	2009 : 9067	2009 : 9068	2009 : 9069	2009 : 9070	2009 : 9071
2010 : 9066	2010 : 9067	2010 : 9068	2010 : 9069	2010 : 9070	2010 : 9071
2011 : 9066	2011 : 9067	2011 : 9068	2011 : 9069	2011 : 9070	2011 : 9071
2012 : 9066	2012 : 9067	2012 : 9068	2012 : 9069	2012 : 9070	2012 : 9071

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
1001 : 9072	1001 : 9073	1001 : 9074	1001 : 9075	1001 : 9076	1001 : 9077
1002 : 9072	1002 : 9073	1002 : 9074	1002 : 9075	1002 : 9076	1002 : 9077
1003 : 9072	1003 : 9073	1003 : 9074	1003 : 9075	1003 : 9076	1003 : 9077
1004 : 9072	1004 : 9073	1004 : 9074	1004 : 9075	1004 : 9076	1004 : 9077
1005 : 9072	1005 : 9073	1005 : 9074	1005 : 9075	1005 : 9076	1005 : 9077
1006 : 9072	1006 : 9073	1006 : 9074	1006 : 9075	1006 : 9076	1006 : 9077
1007 : 9072	1007 : 9073	1007 : 9074	1007 : 9075	1007 : 9076	1007 : 9077
1008 : 9072	1008 : 9073	1008 : 9074	1008 : 9075	1008 : 9076	1008 : 9077
1009 : 9072	1009 : 9073	1009 : 9074	1009 : 9075	1009 : 9076	1009 : 9077
1010 : 9072	1010 : 9073	1010 : 9074	1010 : 9075	1010 : 9076	1010 : 9077
1011 : 9072	1011 : 9073	1011 : 9074	1011 : 9075	1011 : 9076	1011 : 9077
1012 : 9072	1012 : 9073	1012 : 9074	1012 : 9075	1012 : 9076	1012 : 9077
1013 : 9072	1013 : 9073	1013 : 9074	1013 : 9075	1013 : 9076	1013 : 9077
1014 : 9072	1014 : 9073	1014 : 9074	1014 : 9075	1014 : 9076	1014 : 9077
1015 : 9072	1015 : 9073	1015 : 9074	1015 : 9075	1015 : 9076	1015 : 9077
1016 : 9072	1016 : 9073	1016 : 9074	1016 : 9075	1016 : 9076	1016 : 9077
2001 : 9072	2001 : 9073	2001 : 9074	2001 : 9075	2001 : 9076	2001 : 9077
2002 : 9072	2002 : 9073	2002 : 9074	2002 : 9075	2002 : 9076	2002 : 9077
2003 : 9072	2003 : 9073	2003 : 9074	2003 : 9075	2003 : 9076	2003 : 9077
2004 : 9072	2004 : 9073	2004 : 9074	2004 : 9075	2004 : 9076	2004 : 9077
2005 : 9072	2005 : 9073	2005 : 9074	2005 : 9075	2005 : 9076	2005 : 9077
2006 : 9072	2006 : 9073	2006 : 9074	2006 : 9075	2006 : 9076	2006 : 9077
2007 : 9072	2007 : 9073	2007 : 9074	2007 : 9075	2007 : 9076	2007 : 9077
2008 : 9072	2008 : 9073	2008 : 9074	2008 : 9075	2008 : 9076	2008 : 9077
2009 : 9072	2009 : 9073	2009 : 9074	2009 : 9075	2009 : 9076	2009 : 9077
2010 : 9072	2010 : 9073	2010 : 9074	2010 : 9075	2010 : 9076	2010 : 9077
2011 : 9072	2011 : 9073	2011 : 9074	2011 : 9075	2011 : 9076	2011 : 9077
2012 : 9072	2012 : 9073	2012 : 9074	2012 : 9075	2012 : 9076	2012 : 9077

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
1001 : 9078	1001 : 9079	1001 : 9080	1001 : 9081	1001 : 9082	1001 : 9083
1002 : 9078	1002 : 9079	1002 : 9080	1002 : 9081	1002 : 9082	1002 : 9083
1003 : 9078	1003 : 9079	1003 : 9080	1003 : 9081	1003 : 9082	1003 : 9083
1004 : 9078	1004 : 9079	1004 : 9080	1004 : 9081	1004 : 9082	1004 : 9083
1005 : 9078	1005 : 9079	1005 : 9080	1005 : 9081	1005 : 9082	1005 : 9083
1006 : 9078	1006 : 9079	1006 : 9080	1006 : 9081	1006 : 9082	1006 : 9083
1007 : 9078	1007 : 9079	1007 : 9080	1007 : 9081	1007 : 9082	1007 : 9083
1008 : 9078	1008 : 9079	1008 : 9080	1008 : 9081	1008 : 9082	1008 : 9083
1009 : 9078	1009 : 9079	1009 : 9080	1009 : 9081	1009 : 9082	1009 : 9083
1010 : 9078	1010 : 9079	1010 : 9080	1010 : 9081	1010 : 9082	1010 : 9083
1011 : 9078	1011 : 9079	1011 : 9080	1011 : 9081	1011 : 9082	1011 : 9083
1012 : 9078	1012 : 9079	1012 : 9080	1012 : 9081	1012 : 9082	1012 : 9083
1013 : 9078	1013 : 9079	1013 : 9080	1013 : 9081	1013 : 9082	1013 : 9083
1014 : 9078	1014 : 9079	1014 : 9080	1014 : 9081	1014 : 9082	1014 : 9083
1015 : 9078	1015 : 9079	1015 : 9080	1015 : 9081	1015 : 9082	1015 : 9083
1016 : 9078	1016 : 9079	1016 : 9080	1016 : 9081	1016 : 9082	1016 : 9083
2001 : 9078	2001 : 9079	2001 : 9080	2001 : 9081	2001 : 9082	2001 : 9083
2002 : 9078	2002 : 9079	2002 : 9080	2002 : 9081	2002 : 9082	2002 : 9083
2003 : 9078	2003 : 9079	2003 : 9080	2003 : 9081	2003 : 9082	2003 : 9083
2004 : 9078	2004 : 9079	2004 : 9080	2004 : 9081	2004 : 9082	2004 : 9083
2005 : 9078	2005 : 9079	2005 : 9080	2005 : 9081	2005 : 9082	2005 : 9083
2006 : 9078	2006 : 9079	2006 : 9080	2006 : 9081	2006 : 9082	2006 : 9083
2007 : 9078	2007 : 9079	2007 : 9080	2007 : 9081	2007 : 9082	2007 : 9083
2008 : 9078	2008 : 9079	2008 : 9080	2008 : 9081	2008 : 9082	2008 : 9083
2009 : 9078	2009 : 9079	2009 : 9080	2009 : 9081	2009 : 9082	2009 : 9083
2010 : 9078	2010 : 9079	2010 : 9080	2010 : 9081	2010 : 9082	2010 : 9083
2011 : 9078	2011 : 9079	2011 : 9080	2011 : 9081	2011 : 9082	2011 : 9083
2012 : 9078	2012 : 9079	2012 : 9080	2012 : 9081	2012 : 9082	2012 : 9083

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
1001 : 9084	1001 : 9085	1001 : 9086	1001 : 9087	1001 : 9088	1001 : 9089
1002 : 9084	1002 : 9085	1002 : 9086	1002 : 9087	1002 : 9088	1002 : 9089
1003 : 9084	1003 : 9085	1003 : 9086	1003 : 9087	1003 : 9088	1003 : 9089
1004 : 9084	1004 : 9085	1004 : 9086	1004 : 9087	1004 : 9088	1004 : 9089
1005 : 9084	1005 : 9085	1005 : 9086	1005 : 9087	1005 : 9088	1005 : 9089
1006 : 9084	1006 : 9085	1006 : 9086	1006 : 9087	1006 : 9088	1006 : 9089
1007 : 9084	1007 : 9085	1007 : 9086	1007 : 9087	1007 : 9088	1007 : 9089
1008 : 9084	1008 : 9085	1008 : 9086	1008 : 9087	1008 : 9088	1008 : 9089
1009 : 9084	1009 : 9085	1009 : 9086	1009 : 9087	1009 : 9088	1009 : 9089
1010 : 9084	1010 : 9085	1010 : 9086	1010 : 9087	1010 : 9088	1010 : 9089
1011 : 9084	1011 : 9085	1011 : 9086	1011 : 9087	1011 : 9088	1011 : 9089
1012 : 9084	1012 : 9085	1012 : 9086	1012 : 9087	1012 : 9088	1012 : 9089
1013 : 9084	1013 : 9085	1013 : 9086	1013 : 9087	1013 : 9088	1013 : 9089
1014 : 9084	1014 : 9085	1014 : 9086	1014 : 9087	1014 : 9088	1014 : 9089
1015 : 9084	1015 : 9085	1015 : 9086	1015 : 9087	1015 : 9088	1015 : 9089
1016 : 9084	1016 : 9085	1016 : 9086	1016 : 9087	1016 : 9088	1016 : 9089
2001 : 9084	2001 : 9085	2001 : 9086	2001 : 9087	2001 : 9088	2001 : 9089
2002 : 9084	2002 : 9085	2002 : 9086	2002 : 9087	2002 : 9088	2002 : 9089
2003 : 9084	2003 : 9085	2003 : 9086	2003 : 9087	2003 : 9088	2003 : 9089
2004 : 9084	2004 : 9085	2004 : 9086	2004 : 9087	2004 : 9088	2004 : 9089
2005 : 9084	2005 : 9085	2005 : 9086	2005 : 9087	2005 : 9088	2005 : 9089
2006 : 9084	2006 : 9085	2006 : 9086	2006 : 9087	2006 : 9088	2006 : 9089
2007 : 9084	2007 : 9085	2007 : 9086	2007 : 9087	2007 : 9088	2007 : 9089
2008 : 9084	2008 : 9085	2008 : 9086	2008 : 9087	2008 : 9088	2008 : 9089
2009 : 9084	2009 : 9085	2009 : 9086	2009 : 9087	2009 : 9088	2009 : 9089
2010 : 9084	2010 : 9085	2010 : 9086	2010 : 9087	2010 : 9088	2010 : 9089
2011 : 9084	2011 : 9085	2011 : 9086	2011 : 9087	2011 : 9088	2011 : 9089
2012 : 9084	2012 : 9085	2012 : 9086	2012 : 9087	2012 : 9088	2012 : 9089

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
1001 : 9090	1001 : 9091	1001 : 9092	1001 : 9093	1001 : 9094	1001 : 9095
1002 : 9090	1002 : 9091	1002 : 9092	1002 : 9093	1002 : 9094	1002 : 9095
1003 : 9090	1003 : 9091	1003 : 9092	1003 : 9093	1003 : 9094	1003 : 9095
1004 : 9090	1004 : 9091	1004 : 9092	1004 : 9093	1004 : 9094	1004 : 9095
1005 : 9090	1005 : 9091	1005 : 9092	1005 : 9093	1005 : 9094	1005 : 9095
1006 : 9090	1006 : 9091	1006 : 9092	1006 : 9093	1006 : 9094	1006 : 9095
1007 : 9090	1007 : 9091	1007 : 9092	1007 : 9093	1007 : 9094	1007 : 9095
1008 : 9090	1008 : 9091	1008 : 9092	1008 : 9093	1008 : 9094	1008 : 9095
1009 : 9090	1009 : 9091	1009 : 9092	1009 : 9093	1009 : 9094	1009 : 9095
1010 : 9090	1010 : 9091	1010 : 9092	1010 : 9093	1010 : 9094	1010 : 9095
1011 : 9090	1011 : 9091	1011 : 9092	1011 : 9093	1011 : 9094	1011 : 9095
1012 : 9090	1012 : 9091	1012 : 9092	1012 : 9093	1012 : 9094	1012 : 9095
1013 : 9090	1013 : 9091	1013 : 9092	1013 : 9093	1013 : 9094	1013 : 9095
1014 : 9090	1014 : 9091	1014 : 9092	1014 : 9093	1014 : 9094	1014 : 9095
1015 : 9090	1015 : 9091	1015 : 9092	1015 : 9093	1015 : 9094	1015 : 9095
1016 : 9090	1016 : 9091	1016 : 9092	1016 : 9093	1016 : 9094	1016 : 9095
2001 : 9090	2001 : 9091	2001 : 9092	2001 : 9093	2001 : 9094	2001 : 9095
2002 : 9090	2002 : 9091	2002 : 9092	2002 : 9093	2002 : 9094	2002 : 9095
2003 : 9090	2003 : 9091	2003 : 9092	2003 : 9093	2003 : 9094	2003 : 9095
2004 : 9090	2004 : 9091	2004 : 9092	2004 : 9093	2004 : 9094	2004 : 9095
2005 : 9090	2005 : 9091	2005 : 9092	2005 : 9093	2005 : 9094	2005 : 9095
2006 : 9090	2006 : 9091	2006 : 9092	2006 : 9093	2006 : 9094	2006 : 9095
2007 : 9090	2007 : 9091	2007 : 9092	2007 : 9093	2007 : 9094	2007 : 9095
2008 : 9090	2008 : 9091	2008 : 9092	2008 : 9093	2008 : 9094	2008 : 9095
2009 : 9090	2009 : 9091	2009 : 9092	2009 : 9093	2009 : 9094	2009 : 9095
2010 : 9090	2010 : 9091	2010 : 9092	2010 : 9093	2010 : 9094	2010 : 9095
2011 : 9090	2011 : 9091	2011 : 9092	2011 : 9093	2011 : 9094	2011 : 9095
2012 : 9090	2012 : 9091	2012 : 9092	2012 : 9093	2012 : 9094	2012 : 9095

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
1001 : 9096	1001 : 9097	1001 : 9098	1001 : 9099	1001 : 9100	1001 : 9101
1002 : 9096	1002 : 9097	1002 : 9098	1002 : 9099	1002 : 9100	1002 : 9101
1003 : 9096	1003 : 9097	1003 : 9098	1003 : 9099	1003 : 9100	1003 : 9101
1004 : 9096	1004 : 9097	1004 : 9098	1004 : 9099	1004 : 9100	1004 : 9101
1005 : 9096	1005 : 9097	1005 : 9098	1005 : 9099	1005 : 9100	1005 : 9101
1006 : 9096	1006 : 9097	1006 : 9098	1006 : 9099	1006 : 9100	1006 : 9101
1007 : 9096	1007 : 9097	1007 : 9098	1007 : 9099	1007 : 9100	1007 : 9101
1008 : 9096	1008 : 9097	1008 : 9098	1008 : 9099	1008 : 9100	1008 : 9101
1009 : 9096	1009 : 9097	1009 : 9098	1009 : 9099	1009 : 9100	1009 : 9101
1010 : 9096	1010 : 9097	1010 : 9098	1010 : 9099	1010 : 9100	1010 : 9101
1011 : 9096	1011 : 9097	1011 : 9098	1011 : 9099	1011 : 9100	1011 : 9101
1012 : 9096	1012 : 9097	1012 : 9098	1012 : 9099	1012 : 9100	1012 : 9101
1013 : 9096	1013 : 9097	1013 : 9098	1013 : 9099	1013 : 9100	1013 : 9101
1014 : 9096	1014 : 9097	1014 : 9098	1014 : 9099	1014 : 9100	1014 : 9101
1015 : 9096	1015 : 9097	1015 : 9098	1015 : 9099	1015 : 9100	1015 : 9101
1016 : 9096	1016 : 9097	1016 : 9098	1016 : 9099	1016 : 9100	1016 : 9101
2001 : 9096	2001 : 9097	2001 : 9098	2001 : 9099	2001 : 9100	2001 : 9101
2002 : 9096	2002 : 9097	2002 : 9098	2002 : 9099	2002 : 9100	2002 : 9101
2003 : 9096	2003 : 9097	2003 : 9098	2003 : 9099	2003 : 9100	2003 : 9101
2004 : 9096	2004 : 9097	2004 : 9098	2004 : 9099	2004 : 9100	2004 : 9101
2005 : 9096	2005 : 9097	2005 : 9098	2005 : 9099	2005 : 9100	2005 : 9101
2006 : 9096	2006 : 9097	2006 : 9098	2006 : 9099	2006 : 9100	2006 : 9101
2007 : 9096	2007 : 9097	2007 : 9098	2007 : 9099	2007 : 9100	2007 : 9101
2008 : 9096	2008 : 9097	2008 : 9098	2008 : 9099	2008 : 9100	2008 : 9101
2009 : 9096	2009 : 9097	2009 : 9098	2009 : 9099	2009 : 9100	2009 : 9101
2010 : 9096	2010 : 9097	2010 : 9098	2010 : 9099	2010 : 9100	2010 : 9101
2011 : 9096	2011 : 9097	2011 : 9098	2011 : 9099	2011 : 9100	2011 : 9101
2012 : 9096	2012 : 9097	2012 : 9098	2012 : 9099	2012 : 9100	2012 : 9101

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
1001 : 9102	1001 : 9103	1001 : 9104	1001 : 9105	--	--
1002 : 9102	1002 : 9103	1002 : 9104	1002 : 9105		
1003 : 9102	1003 : 9103	1003 : 9104	1003 : 9105		
1004 : 9102	1004 : 9103	1004 : 9104	1004 : 9105		
1005 : 9102	1005 : 9103	1005 : 9104	1005 : 9105		
1006 : 9102	1006 : 9103	1006 : 9104	1006 : 9105		
1007 : 9102	1007 : 9103	1007 : 9104	1007 : 9105		
1008 : 9102	1008 : 9103	1008 : 9104	1008 : 9105		
1009 : 9102	1009 : 9103	1009 : 9104	1009 : 9105		
1010 : 9102	1010 : 9103	1010 : 9104	1010 : 9105		
1011 : 9102	1011 : 9103	1011 : 9104	1011 : 9105		
1012 : 9102	1012 : 9103	1012 : 9104	1012 : 9105		
1013 : 9102	1013 : 9103	1013 : 9104	1013 : 9105		
1014 : 9102	1014 : 9103	1014 : 9104	1014 : 9105		
1015 : 9102	1015 : 9103	1015 : 9104	1015 : 9105		
1016 : 9102	1016 : 9103	1016 : 9104	1016 : 9105		
2001 : 9102	2001 : 9103	2001 : 9104	2001 : 9105		
2002 : 9102	2002 : 9103	2002 : 9104	2002 : 9105		
2003 : 9102	2003 : 9103	2003 : 9104	2003 : 9105		
2004 : 9102	2004 : 9103	2004 : 9104	2004 : 9105		
2005 : 9102	2005 : 9103	2005 : 9104	2005 : 9105		
2006 : 9102	2006 : 9103	2006 : 9104	2006 : 9105		
2007 : 9102	2007 : 9103	2007 : 9104	2007 : 9105		
2008 : 9102	2008 : 9103	2008 : 9104	2008 : 9105		
2009 : 9102	2009 : 9103	2009 : 9104	2009 : 9105		
2010 : 9102	2010 : 9103	2010 : 9104	2010 : 9105		
2011 : 9102	2011 : 9103	2011 : 9104	2011 : 9105		
2012 : 9102	2012 : 9103	2012 : 9104	2012 : 9105		

Table B: Example combinations of a compound X with a compound Y.

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
3001 : 9000	3001 : 9001	3001 : 9002	3001 : 9003	3001 : 9004	3001 : 9005
3002 : 9000	3002 : 9001	3002 : 9002	3002 : 9003	3002 : 9004	3002 : 9005
3003 : 9000	3003 : 9001	3003 : 9002	3003 : 9003	3003 : 9004	3003 : 9005
3004 : 9000	3004 : 9001	3004 : 9002	3004 : 9003	3004 : 9004	3004 : 9005
3005 : 9000	3005 : 9001	3005 : 9002	3005 : 9003	3005 : 9004	3005 : 9005
3006 : 9000	3006 : 9001	3006 : 9002	3006 : 9003	3006 : 9004	3006 : 9005
3007 : 9000	3007 : 9001	3007 : 9002	3007 : 9003	3007 : 9004	3007 : 9005
3008 : 9000	3008 : 9001	3008 : 9002	3008 : 9003	3008 : 9004	3008 : 9005
3009 : 9000	3009 : 9001	3009 : 9002	3009 : 9003	3009 : 9004	3009 : 9005
3010 : 9000	3010 : 9001	3010 : 9002	3010 : 9003	3010 : 9004	3010 : 9005
3011 : 9000	3011 : 9001	3011 : 9002	3011 : 9003	3011 : 9004	3011 : 9005
3012 : 9000	3012 : 9001	3012 : 9002	3012 : 9003	3012 : 9004	3012 : 9005
3013 : 9000	3013 : 9001	3013 : 9002	3013 : 9003	3013 : 9004	3013 : 9005
3014 : 9000	3014 : 9001	3014 : 9002	3014 : 9003	3014 : 9004	3014 : 9005
4001 : 9000	4001 : 9001	4001 : 9002	4001 : 9003	4001 : 9004	4001 : 9005
4002 : 9000	4002 : 9001	4002 : 9002	4002 : 9003	4002 : 9004	4002 : 9005
4003 : 9000	4003 : 9001	4003 : 9002	4003 : 9003	4003 : 9004	4003 : 9005
4004 : 9000	4004 : 9001	4004 : 9002	4004 : 9003	4004 : 9004	4004 : 9005
4005 : 9000	4005 : 9001	4005 : 9002	4005 : 9003	4005 : 9004	4005 : 9005
4006 : 9000	4006 : 9001	4006 : 9002	4006 : 9003	4006 : 9004	4006 : 9005
4007 : 9000	4007 : 9001	4007 : 9002	4007 : 9003	4007 : 9004	4007 : 9005
4008 : 9000	4008 : 9001	4008 : 9002	4008 : 9003	4008 : 9004	4008 : 9005
4009 : 9000	4009 : 9001	4009 : 9002	4009 : 9003	4009 : 9004	4009 : 9005
4010 : 9000	4010 : 9001	4010 : 9002	4010 : 9003	4010 : 9004	4010 : 9005
4011 : 9000	4011 : 9001	4011 : 9002	4011 : 9003	4011 : 9004	4011 : 9005
4012 : 9000	4012 : 9001	4012 : 9002	4012 : 9003	4012 : 9004	4012 : 9005
5001 : 9000	5001 : 9001	5001 : 9002	5001 : 9003	5001 : 9004	5001 : 9005
5002 : 9000	5002 : 9001	5002 : 9002	5002 : 9003	5002 : 9004	5002 : 9005
5003 : 9000	5003 : 9001	5003 : 9002	5003 : 9003	5003 : 9004	5003 : 9005
5004 : 9000	5004 : 9001	5004 : 9002	5004 : 9003	5004 : 9004	5004 : 9005
5005 : 9000	5005 : 9001	5005 : 9002	5005 : 9003	5005 : 9004	5005 : 9005
5006 : 9000	5006 : 9001	5006 : 9002	5006 : 9003	5006 : 9004	5006 : 9005
5007 : 9000	5007 : 9001	5007 : 9002	5007 : 9003	5007 : 9004	5007 : 9005
5008 : 9000	5008 : 9001	5008 : 9002	5008 : 9003	5008 : 9004	5008 : 9005
5009 : 9000	5009 : 9001	5009 : 9002	5009 : 9003	5009 : 9004	5009 : 9005
5010 : 9000	5010 : 9001	5010 : 9002	5010 : 9003	5010 : 9004	5010 : 9005
5011 : 9000	5011 : 9001	5011 : 9002	5011 : 9003	5011 : 9004	5011 : 9005
5012 : 9000	5012 : 9001	5012 : 9002	5012 : 9003	5012 : 9004	5012 : 9005

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
3001 : 9036	3001 : 9037	3001 : 9038	3001 : 9039	3001 : 9040	3001 : 9041
3002 : 9036	3002 : 9037	3002 : 9038	3002 : 9039	3002 : 9040	3002 : 9041
3003 : 9036	3003 : 9037	3003 : 9038	3003 : 9039	3003 : 9040	3003 : 9041
3004 : 9036	3004 : 9037	3004 : 9038	3004 : 9039	3004 : 9040	3004 : 9041
3005 : 9036	3005 : 9037	3005 : 9038	3005 : 9039	3005 : 9040	3005 : 9041
3006 : 9036	3006 : 9037	3006 : 9038	3006 : 9039	3006 : 9040	3006 : 9041
3007 : 9036	3007 : 9037	3007 : 9038	3007 : 9039	3007 : 9040	3007 : 9041
3008 : 9036	3008 : 9037	3008 : 9038	3008 : 9039	3008 : 9040	3008 : 9041
3009 : 9036	3009 : 9037	3009 : 9038	3009 : 9039	3009 : 9040	3009 : 9041
3010 : 9036	3010 : 9037	3010 : 9038	3010 : 9039	3010 : 9040	3010 : 9041
3011 : 9036	3011 : 9037	3011 : 9038	3011 : 9039	3011 : 9040	3011 : 9041
3012 : 9036	3012 : 9037	3012 : 9038	3012 : 9039	3012 : 9040	3012 : 9041
3013 : 9036	3013 : 9037	3013 : 9038	3013 : 9039	3013 : 9040	3013 : 9041
3014 : 9036	3014 : 9037	3014 : 9038	3014 : 9039	3014 : 9040	3014 : 9041
4001 : 9036	4001 : 9037	4001 : 9038	4001 : 9039	4001 : 9040	4001 : 9041
4002 : 9036	4002 : 9037	4002 : 9038	4002 : 9039	4002 : 9040	4002 : 9041
4003 : 9036	4003 : 9037	4003 : 9038	4003 : 9039	4003 : 9040	4003 : 9041
4004 : 9036	4004 : 9037	4004 : 9038	4004 : 9039	4004 : 9040	4004 : 9041
4005 : 9036	4005 : 9037	4005 : 9038	4005 : 9039	4005 : 9040	4005 : 9041
4006 : 9036	4006 : 9037	4006 : 9038	4006 : 9039	4006 : 9040	4006 : 9041
4007 : 9036	4007 : 9037	4007 : 9038	4007 : 9039	4007 : 9040	4007 : 9041
4008 : 9036	4008 : 9037	4008 : 9038	4008 : 9039	4008 : 9040	4008 : 9041
4009 : 9036	4009 : 9037	4009 : 9038	4009 : 9039	4009 : 9040	4009 : 9041
4010 : 9036	4010 : 9037	4010 : 9038	4010 : 9039	4010 : 9040	4010 : 9041
4011 : 9036	4011 : 9037	4011 : 9038	4011 : 9039	4011 : 9040	4011 : 9041
4012 : 9036	4012 : 9037	4012 : 9038	4012 : 9039	4012 : 9040	4012 : 9041
5001 : 9036	5001 : 9037	5001 : 9038	5001 : 9039	5001 : 9040	5001 : 9041
5002 : 9036	5002 : 9037	5002 : 9038	5002 : 9039	5002 : 9040	5002 : 9041
5003 : 9036	5003 : 9037	5003 : 9038	5003 : 9039	5003 : 9040	5003 : 9041
5004 : 9036	5004 : 9037	5004 : 9038	5004 : 9039	5004 : 9040	5004 : 9041
5005 : 9036	5005 : 9037	5005 : 9038	5005 : 9039	5005 : 9040	5005 : 9041
5006 : 9036	5006 : 9037	5006 : 9038	5006 : 9039	5006 : 9040	5006 : 9041
5007 : 9036	5007 : 9037	5007 : 9038	5007 : 9039	5007 : 9040	5007 : 9041
5008 : 9036	5008 : 9037	5008 : 9038	5008 : 9039	5008 : 9040	5008 : 9041
5009 : 9036	5009 : 9037	5009 : 9038	5009 : 9039	5009 : 9040	5009 : 9041
5010 : 9036	5010 : 9037	5010 : 9038	5010 : 9039	5010 : 9040	5010 : 9041
5011 : 9036	5011 : 9037	5011 : 9038	5011 : 9039	5011 : 9040	5011 : 9041
5012 : 9036	5012 : 9037	5012 : 9038	5012 : 9039	5012 : 9040	5012 : 9041

[illegible]

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
3001 : 9048	3001 : 9049	3001 : 9050	3001 : 9051	3001 : 9052	3001 : 9053
3002 : 9048	3002 : 9049	3002 : 9050	3002 : 9051	3002 : 9052	3002 : 9053
3003 : 9048	3003 : 9049	3003 : 9050	3003 : 9051	3003 : 9052	3003 : 9053
3004 : 9048	3004 : 9049	3004 : 9050	3004 : 9051	3004 : 9052	3004 : 9053
3005 : 9048	3005 : 9049	3005 : 9050	3005 : 9051	3005 : 9052	3005 : 9053
3006 : 9048	3006 : 9049	3006 : 9050	3006 : 9051	3006 : 9052	3006 : 9053
3007 : 9048	3007 : 9049	3007 : 9050	3007 : 9051	3007 : 9052	3007 : 9053
3008 : 9048	3008 : 9049	3008 : 9050	3008 : 9051	3008 : 9052	3008 : 9053
3009 : 9048	3009 : 9049	3009 : 9050	3009 : 9051	3009 : 9052	3009 : 9053
3010 : 9048	3010 : 9049	3010 : 9050	3010 : 9051	3010 : 9052	3010 : 9053
3011 : 9048	3011 : 9049	3011 : 9050	3011 : 9051	3011 : 9052	3011 : 9053
3012 : 9048	3012 : 9049	3012 : 9050	3012 : 9051	3012 : 9052	3012 : 9053
3013 : 9048	3013 : 9049	3013 : 9050	3013 : 9051	3013 : 9052	3013 : 9053
3014 : 9048	3014 : 9049	3014 : 9050	3014 : 9051	3014 : 9052	3014 : 9053
4001 : 9048	4001 : 9049	4001 : 9050	4001 : 9051	4001 : 9052	4001 : 9053
4002 : 9048	4002 : 9049	4002 : 9050	4002 : 9051	4002 : 9052	4002 : 9053
4003 : 9048	4003 : 9049	4003 : 9050	4003 : 9051	4003 : 9052	4003 : 9053
4004 : 9048	4004 : 9049	4004 : 9050	4004 : 9051	4004 : 9052	4004 : 9053
4005 : 9048	4005 : 9049	4005 : 9050	4005 : 9051	4005 : 9052	4005 : 9053
4006 : 9048	4006 : 9049	4006 : 9050	4006 : 9051	4006 : 9052	4006 : 9053
4007 : 9048	4007 : 9049	4007 : 9050	4007 : 9051	4007 : 9052	4007 : 9053
4008 : 9048	4008 : 9049	4008 : 9050	4008 : 9051	4008 : 9052	4008 : 9053
4009 : 9048	4009 : 9049	4009 : 9050	4009 : 9051	4009 : 9052	4009 : 9053
4010 : 9048	4010 : 9049	4010 : 9050	4010 : 9051	4010 : 9052	4010 : 9053
4011 : 9048	4011 : 9049	4011 : 9050	4011 : 9051	4011 : 9052	4011 : 9053
4012 : 9048	4012 : 9049	4012 : 9050	4012 : 9051	4012 : 9052	4012 : 9053
5001 : 9048	5001 : 9049	5001 : 9050	5001 : 9051	5001 : 9052	5001 : 9053
5002 : 9048	5002 : 9049	5002 : 9050	5002 : 9051	5002 : 9052	5002 : 9053
5003 : 9048	5003 : 9049	5003 : 9050	5003 : 9051	5003 : 9052	5003 : 9053
5004 : 9048	5004 : 9049	5004 : 9050	5004 : 9051	5004 : 9052	5004 : 9053
5005 : 9048	5005 : 9049	5005 : 9050	5005 : 9051	5005 : 9052	5005 : 9053
5006 : 9048	5006 : 9049	5006 : 9050	5006 : 9051	5006 : 9052	5006 : 9053
5007 : 9048	5007 : 9049	5007 : 9050	5007 : 9051	5007 : 9052	5007 : 9053
5008 : 9048	5008 : 9049	5008 : 9050	5008 : 9051	5008 : 9052	5008 : 9053
5009 : 9048	5009 : 9049	5009 : 9050	5009 : 9051	5009 : 9052	5009 : 9053
5010 : 9048	5010 : 9049	5010 : 9050	5010 : 9051	5010 : 9052	5010 : 9053
5011 : 9048	5011 : 9049	5011 : 9050	5011 : 9051	5011 : 9052	5011 : 9053
5012 : 9048	5012 : 9049	5012 : 9050	5012 : 9051	5012 : 9051	5012 : 9053

[illegible]

[illegible]

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
3001 : 9066	3001 : 9067	3001 : 9068	3001 : 9069	3001 : 9070	3001 : 9071
3002 : 9066	3002 : 9067	3002 : 9068	3002 : 9069	3002 : 9070	3002 : 9071
3003 : 9066	3003 : 9067	3003 : 9068	3003 : 9069	3003 : 9070	3003 : 9071
3004 : 9066	3004 : 9067	3004 : 9068	3004 : 9069	3004 : 9070	3004 : 9071
3005 : 9066	3005 : 9067	3005 : 9068	3005 : 9069	3005 : 9070	3005 : 9071
3006 : 9066	3006 : 9067	3006 : 9068	3006 : 9069	3006 : 9070	3006 : 9071
3007 : 9066	3007 : 9067	3007 : 9068	3007 : 9069	3007 : 9070	3007 : 9071
3008 : 9066	3008 : 9067	3008 : 9068	3008 : 9069	3008 : 9070	3008 : 9071
3009 : 9066	3009 : 9067	3009 : 9068	3009 : 9069	3009 : 9070	3009 : 9071
3010 : 9066	3010 : 9067	3010 : 9068	3010 : 9069	3010 : 9070	3010 : 9071
3011 : 9066	3011 : 9067	3011 : 9068	3011 : 9069	3011 : 9070	3011 : 9071
3012 : 9066	3012 : 9067	3012 : 9068	3012 : 9069	3012 : 9070	3012 : 9071
3013 : 9066	3013 : 9067	3013 : 9068	3013 : 9069	3013 : 9070	3013 : 9071
3014 : 9066	3014 : 9067	3014 : 9068	3014 : 9069	3014 : 9070	3014 : 9071
4001 : 9066	4001 : 9067	4001 : 9068	4001 : 9069	4001 : 9070	4001 : 9071
4002 : 9066	4002 : 9067	4002 : 9068	4002 : 9069	4002 : 9070	4002 : 9071
4003 : 9066	4003 : 9067	4003 : 9068	4003 : 9069	4003 : 9070	4003 : 9071
4004 : 9066	4004 : 9067	4004 : 9068	4004 : 9069	4004 : 9070	4004 : 9071
4005 : 9066	4005 : 9067	4005 : 9068	4005 : 9069	4005 : 9070	4005 : 9071
4006 : 9066	4006 : 9067	4006 : 9068	4006 : 9069	4006 : 9070	4006 : 9071
4007 : 9066	4007 : 9067	4007 : 9068	4007 : 9069	4007 : 9070	4007 : 9071
4008 : 9066	4008 : 9067	4008 : 9068	4008 : 9069	4008 : 9070	4008 : 9071
4009 : 9066	4009 : 9067	4009 : 9068	4009 : 9069	4009 : 9070	4009 : 9071
4010 : 9066	4010 : 9067	4010 : 9068	4010 : 9069	4010 : 9070	4010 : 9071
4011 : 9066	4011 : 9067	4011 : 9068	4011 : 9069	4011 : 9070	4011 : 9071
4012 : 9066	4012 : 9067	4012 : 9068	4012 : 9069	4012 : 9070	4012 : 9071
5001 : 9066	5001 : 9067	5001 : 9068	5001 : 9069	5001 : 9070	5001 : 9071
5002 : 9066	5002 : 9067	5002 : 9068	5002 : 9069	5002 : 9070	5002 : 9071
5003 : 9066	5003 : 9067	5003 : 9068	5003 : 9069	5003 : 9070	5003 : 9071
5004 : 9066	5004 : 9067	5004 : 9068	5004 : 9069	5004 : 9070	5004 : 9071
5005 : 9066	5005 : 9067	5005 : 9068	5005 : 9069	5005 : 9070	5005 : 9071
5006 : 9066	5006 : 9067	5006 : 9068	5006 : 9069	5006 : 9070	5006 : 9071
5007 : 9066	5007 : 9067	5007 : 9068	5007 : 9069	5007 : 9070	5007 : 9071
5008 : 9066	5008 : 9067	5008 : 9068	5008 : 9069	5008 : 9070	5008 : 9071
5009 : 9066	5009 : 9067	5009 : 9068	5009 : 9069	5009 : 9070	5009 : 9071
5010 : 9066	5010 : 9067	5010 : 9068	5010 : 9069	5010 : 9070	5010 : 9071
5011 : 9066	5011 : 9067	5011 : 9068	5011 : 9069	5011 : 9070	5011 : 9071
5012 : 9066	5012 : 9067	5012 : 9068	5012 : 9069	5012 : 9070	5012 : 9071

[illegible]

[illegible]

[illegible]

[illegible]

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
3001 : 9096	3001 : 9097	3001 : 9098	3001 : 9099	3001 : 9100	3001 : 9101
3002 : 9096	3002 : 9097	3002 : 9098	3002 : 9099	3002 : 9100	3002 : 9101
3003 : 9096	3003 : 9097	3003 : 9098	3003 : 9099	3003 : 9100	3003 : 9101
3004 : 9096	3004 : 9097	3004 : 9098	3004 : 9099	3004 : 9100	3004 : 9101
3005 : 9096	3005 : 9097	3005 : 9098	3005 : 9099	3005 : 9100	3005 : 9101
3006 : 9096	3006 : 9097	3006 : 9098	3006 : 9099	3006 : 9100	3006 : 9101
3007 : 9096	3007 : 9097	3007 : 9098	3007 : 9099	3007 : 9100	3007 : 9101
3008 : 9096	3008 : 9097	3008 : 9098	3008 : 9099	3008 : 9100	3008 : 9101
3009 : 9096	3009 : 9097	3009 : 9098	3009 : 9099	3009 : 9100	3009 : 9101
3010 : 9096	3010 : 9097	3010 : 9098	3010 : 9099	3010 : 9100	3010 : 9101
3011 : 9096	3011 : 9097	3011 : 9098	3011 : 9099	3011 : 9100	3011 : 9101
3012 : 9096	3012 : 9097	3012 : 9098	3012 : 9099	3012 : 9100	3012 : 9101
3013 : 9096	3013 : 9097	3013 : 9098	3013 : 9099	3013 : 9100	3013 : 9101
3014 : 9096	3014 : 9097	3014 : 9098	3014 : 9099	3014 : 9100	3014 : 9101
4001 : 9096	4001 : 9097	4001 : 9098	4001 : 9099	4001 : 9100	4001 : 9101
4002 : 9096	4002 : 9097	4002 : 9098	4002 : 9099	4002 : 9100	4002 : 9101
4003 : 9096	4003 : 9097	4003 : 9098	4003 : 9099	4003 : 9100	4003 : 9101
4004 : 9096	4004 : 9097	4004 : 9098	4004 : 9099	4004 : 9100	4004 : 9101
4005 : 9096	4005 : 9097	4005 : 9098	4005 : 9099	4005 : 9100	4005 : 9101
4006 : 9096	4006 : 9097	4006 : 9098	4006 : 9099	4006 : 9100	4006 : 9101
4007 : 9096	4007 : 9097	4007 : 9098	4007 : 9099	4007 : 9100	4007 : 9101
4008 : 9096	4008 : 9097	4008 : 9098	4008 : 9099	4008 : 9100	4008 : 9101
4009 : 9096	4009 : 9097	4009 : 9098	4009 : 9099	4009 : 9100	4009 : 9101
4010 : 9096	4010 : 9097	4010 : 9098	4010 : 9099	4010 : 9100	4010 : 9101
4011 : 9096	4011 : 9097	4011 : 9098	4011 : 9099	4011 : 9100	4011 : 9101
4012 : 9096	4012 : 9097	4012 : 9098	4012 : 9099	4012 : 9100	4012 : 9101
5001 : 9096	5001 : 9097	5001 : 9098	5001 : 9099	5001 : 9100	5001 : 9101
5002 : 9096	5002 : 9097	5002 : 9098	5002 : 9099	5002 : 9100	5002 : 9101
5003 : 9096	5003 : 9097	5003 : 9098	5003 : 9099	5003 : 9100	5003 : 9101
5004 : 9096	5004 : 9097	5004 : 9098	5004 : 9099	5004 : 9100	5004 : 9101
5005 : 9096	5005 : 9097	5005 : 9098	5005 : 9099	5005 : 9100	5005 : 9101
5006 : 9096	5006 : 9097	5006 : 9098	5006 : 9099	5006 : 9100	5006 : 9101
5007 : 9096	5007 : 9097	5007 : 9098	5007 : 9099	5007 : 9100	5007 : 9101
5008 : 9096	5008 : 9097	5008 : 9098	5008 : 9099	5008 : 9100	5008 : 9101
5009 : 9096	5009 : 9097	5009 : 9098	5009 : 9099	5009 : 9100	5009 : 9101
5010 : 9096	5010 : 9097	5010 : 9098	5010 : 9099	5010 : 9100	5010 : 9101
5011 : 9096	5011 : 9097	5011 : 9098	5011 : 9099	5011 : 9100	5011 : 9101
5012 : 9096	5012 : 9097	5012 : 9098	5012 : 9099	5012 : 9100	5012 : 9101

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
3001 : 9102	3001 : 9103	3001 : 9104	3001 : 9105		
3002 : 9102	3002 : 9103	3002 : 9104	3002 : 9105		
3003 : 9102	3003 : 9103	3003 : 9104	3003 : 9105		
3004 : 9102	3004 : 9103	3004 : 9104	3004 : 9105		
3005 : 9102	3005 : 9103	3005 : 9104	3005 : 9105		
3006 : 9102	3006 : 9103	3006 : 9104	3006 : 9105		
3007 : 9102	3007 : 9103	3007 : 9104	3007 : 9105		
3008 : 9102	3008 : 9103	3008 : 9104	3008 : 9105		
3009 : 9102	3009 : 9103	3009 : 9104	3009 : 9105		
3010 : 9102	3010 : 9103	3010 : 9104	3010 : 9105		
3011 : 9102	3011 : 9103	3011 : 9104	3011 : 9105		
3012 : 9102	3012 : 9103	3012 : 9104	3012 : 9105		
3013 : 9102	3013 : 9103	3013 : 9104	3013 : 9105		
3014 : 9102	3014 : 9103	3014 : 9104	3014 : 9105		
4001 : 9102	4001 : 9103	4001 : 9104	4001 : 9105		
4002 : 9102	4002 : 9103	4002 : 9104	4002 : 9105		
4003 : 9102	4003 : 9103	4003 : 9104	4003 : 9105		
4004 : 9102	4004 : 9103	4004 : 9104	4004 : 9105		
4005 : 9102	4005 : 9103	4005 : 9104	4005 : 9105		
4006 : 9102	4006 : 9103	4006 : 9104	4006 : 9105	--	--
4007 : 9102	4007 : 9103	4007 : 9104	4007 : 9105		
4008 : 9102	4008 : 9103	4008 : 9104	4008 : 9105		
4009 : 9102	4009 : 9103	4009 : 9104	4009 : 9105		
4010 : 9102	4010 : 9103	4010 : 9104	4010 : 9105		
4011 : 9102	4011 : 9103	4011 : 9104	4011 : 9105		
4012 : 9102	4012 : 9103	4012 : 9104	4012 : 9105		
5001 : 9102	5001 : 9103	5001 : 9104	5001 : 9105		
5002 : 9102	5002 : 9103	5002 : 9104	5002 : 9105		
5003 : 9102	5003 : 9103	5003 : 9104	5003 : 9105		
5004 : 9102	5004 : 9103	5004 : 9104	5004 : 9105		
5005 : 9102	5005 : 9103	5005 : 9104	5005 : 9105		
5006 : 9102	5006 : 9103	5006 : 9104	5006 : 9105		
5007 : 9102	5007 : 9103	5007 : 9104	5007 : 9105		
5008 : 9102	5008 : 9103	5008 : 9104	5008 : 9105		
5009 : 9102	5009 : 9103	5009 : 9104	5009 : 9105		
5010 : 9102	5010 : 9103	5010 : 9104	5010 : 9105		
5011 : 9102	5011 : 9103	5011 : 9104	5011 : 9105		
5012 : 9102	5012 : 9103	5012 : 9104	5012 : 9105		

Table C: Example combinations of a compound X with a compound Y.

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
9000 : 7000	9001 : 7000	9002 : 7000	9003 : 7000	9004 : 7000	9005 : 7000
9000 : 7001	9001 : 7001	9002 : 7001	9003 : 7001	9004 : 7001	9005 : 7001
9000 : 7002	9001 : 7002	9002 : 7002	9003 : 7002	9004 : 7002	9005 : 7002
9000 : 7003	9001 : 7003	9002 : 7003	9003 : 7003	9004 : 7003	9005 : 7003
9000 : 7004	9001 : 7004	9002 : 7004	9003 : 7004	9004 : 7004	9005 : 7004
9000 : 7005	9001 : 7005	9002 : 7005	9003 : 7005	9004 : 7005	9005 : 7005
9000 : 7006	9001 : 7006	9002 : 7006	9003 : 7006	9004 : 7006	9005 : 7006
9000 : 7007	9001 : 7007	9002 : 7007	9003 : 7007	9004 : 7007	9005 : 7007
9000 : 7008	9001 : 7008	9002 : 7008	9003 : 7008	9004 : 7008	9005 : 7008
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9090 : 7016	9091 : 7016	9092 : 7016	9093 : 7016	9094 : 7016	9095 : 7016
9090 : 7017	9091 : 7017	9092 : 7017	9093 : 7017	9094 : 7017	9095 : 7017
9090 : 7018	9091 : 7018	9092 : 7018	9093 : 7018	9094 : 7018	9095 : 7018
9090 : 7019	9091 : 7019	9092 : 7019	9093 : 7019	9094 : 7019	9095 : 7019
9090 : 7020	9091 : 7020	9092 : 7020	9093 : 7020	9094 : 7020	9095 : 7020
9090 : 7021	9091 : 7021	9092 : 7021	9093 : 7021	9094 : 7021	9095 : 7021
9090 : 7022	9091 : 7022	9092 : 7022	9093 : 7022	9094 : 7022	9095 : 7022
9090 : 7023	9091 : 7023	9092 : 7023	9093 : 7023	9094 : 7023	9095 : 7023
9090 : 7024	9091 : 7024	9092 : 7024	9093 : 7024	9094 : 7024	9095 : 7024
9090 : 7025	9091 : 7025	9092 : 7025	9093 : 7025	9094 : 7025	9095 : 7025
9090 : 7026	9091 : 7026	9092 : 7026	9093 : 7026	9094 : 7026	9095 : 7026
9090 : 7027	9091 : 7027	9092 : 7027	9093 : 7027	9094 : 7027	9095 : 7027

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
9096 : 7000	9097 : 7000	9098 : 7000	9099 : 7000	9100 : 7000	9101 : 7000
9096 : 7001	9097 : 7001	9098 : 7001	9099 : 7001	9100 : 7001	9101 : 7001
9096 : 7002	9097 : 7002	9098 : 7002	9099 : 7002	9100 : 7002	9101 : 7002
9096 : 7003	9097 : 7003	9098 : 7003	9099 : 7003	9100 : 7003	9101 : 7003
9096 : 7004	9097 : 7004	9098 : 7004	9099 : 7004	9100 : 7004	9101 : 7004
9096 : 7005	9097 : 7005	9098 : 7005	9099 : 7005	9100 : 7005	9101 : 7005
9096 : 7006	9097 : 7006	9098 : 7006	9099 : 7006	9100 : 7006	9101 : 7006
9096 : 7007	9097 : 7007	9098 : 7007	9099 : 7007	9100 : 7007	9101 : 7007
9096 : 7008	9097 : 7008	9098 : 7008	9099 : 7008	9100 : 7008	9101 : 7008
9096 : 7009	9097 : 7009	9098 : 7009	9099 : 7009	9100 : 7009	9101 : 7009
9096 : 7010	9097 : 7010	9098 : 7010	9099 : 7010	9100 : 7010	9101 : 7010
9096 : 7011	9097 : 7011	9098 : 7011	9099 : 7011	9100 : 7011	9101 : 7011
9096 : 7012	9097 : 7012	9098 : 7012	9099 : 7012	9100 : 7012	9101 : 7012
9096 : 7013	9097 : 7013	9098 : 7013	9099 : 7013	9100 : 7013	9101 : 7013
9096 : 7014	9097 : 7014	9098 : 7014	9099 : 7014	9100 : 7014	9101 : 7014
9096 : 7015	9097 : 7015	9098 : 7015	9099 : 7015	9100 : 7015	9101 : 7015
9096 : 7016	9097 : 7016	9098 : 7016	9099 : 7016	9100 : 7016	9101 : 7016
9096 : 7017	9097 : 7017	9098 : 7017	9099 : 7017	9100 : 7017	9101 : 7017
9096 : 7018	9097 : 7018	9098 : 7018	9099 : 7018	9100 : 7018	9101 : 7018
9096 : 7019	9097 : 7019	9098 : 7019	9099 : 7019	9100 : 7019	9101 : 7019
9096 : 7020	9097 : 7020	9098 : 7020	9099 : 7020	9100 : 7020	9101 : 7020
9096 : 7021	9097 : 7021	9098 : 7021	9099 : 7021	9100 : 7021	9101 : 7021
9096 : 7022	9097 : 7022	9098 : 7022	9099 : 7022	9100 : 7022	9101 : 7022
9096 : 7023	9097 : 7023	9098 : 7023	9099 : 7023	9100 : 7023	9101 : 7023
9096 : 7024	9097 : 7024	9098 : 7024	9099 : 7024	9100 : 7024	9101 : 7024
9096 : 7025	9097 : 7025	9098 : 7025	9099 : 7025	9100 : 7025	9101 : 7025
9096 : 7026	9097 : 7026	9098 : 7026	9099 : 7026	9100 : 7026	9101 : 7026
9096 : 7027	9097 : 7027	9098 : 7027	9099 : 7027	9100 : 7027	9101 : 7027

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
9102 : 7000	9103 : 7000	9104 : 7000	9105 : 7000		
9102 : 7001	9103 : 7001	9104 : 7001	9105 : 7001		
9102 : 7002	9103 : 7002	9104 : 7002	9105 : 7002		
9102 : 7003	9103 : 7003	9104 : 7003	9105 : 7003		
9102 : 7004	9103 : 7004	9104 : 7004	9105 : 7004		
9102 : 7005	9103 : 7005	9104 : 7005	9105 : 7005		
9102 : 7006	9103 : 7006	9104 : 7006	9105 : 7006		
9102 : 7007	9103 : 7007	9104 : 7007	9105 : 7007		
9102 : 7008	9103 : 7008	9104 : 7008	9105 : 7008		
9102 : 7009	9103 : 7009	9104 : 7009	9105 : 7009		
9102 : 7010	9103 : 7010	9104 : 7010	9105 : 7010		
9102 : 7011	9103 : 7011	9104 : 7011	9105 : 7011		
9102 : 7012	9103 : 7012	9104 : 7012	9105 : 7012		
9102 : 7013	9103 : 7013	9104 : 7013	9105 : 7013		
9102 : 7014	9103 : 7014	9104 : 7014	9105 : 7014	--	--
9102 : 7015	9103 : 7015	9104 : 7015	9105 : 7015		
9102 : 7016	9103 : 7016	9104 : 7016	9105 : 7016		
9102 : 7017	9103 : 7017	9104 : 7017	9105 : 7017		
9102 : 7018	9103 : 7018	9104 : 7018	9105 : 7018		
9102 : 7019	9103 : 7019	9104 : 7019	9105 : 7019		
9102 : 7020	9103 : 7020	9104 : 7020	9105 : 7020		
9102 : 7021	9103 : 7021	9104 : 7021	9105 : 7021		
9102 : 7022	9103 : 7022	9104 : 7022	9105 : 7022		
9102 : 7023	9103 : 7023	9104 : 7023	9105 : 7023		
9102 : 7024	9103 : 7024	9104 : 7024	9105 : 7024		
9102 : 7025	9103 : 7025	9104 : 7025	9105 : 7025		
9102 : 7026	9103 : 7026	9104 : 7026	9105 : 7026		
9102 : 7027	9103 : 7027	9104 : 7027	9105 : 7027		

Table D: Example combinations of a compound X with a compound Y.

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
6000 : 9000	6040 : 9000	6000 : 9001	6040 : 9001	6000 : 9002	6040 : 9002
6001 : 9000	6041 : 9000	6001 : 9001	6041 : 9001	6001 : 9002	6041 : 9002
6002 : 9000	6042 : 9000	6002 : 9001	6042 : 9001	6002 : 9002	6042 : 9002
6003 : 9000	6043 : 9000	6003 : 9001	6043 : 9001	6003 : 9002	6043 : 9002
6004 : 9000	6044 : 9000	6004 : 9001	6044 : 9001	6004 : 9002	6044 : 9002
6005 : 9000	6045 : 9000	6005 : 9001	6045 : 9001	6005 : 9002	6045 : 9002
6006 : 9000	6046 : 9000	6006 : 9001	6046 : 9001	6006 : 9002	6046 : 9002
6007 : 9000	6047 : 9000	6007 : 9001	6047 : 9001	6007 : 9002	6047 : 9002
6008 : 9000	6048 : 9000	6008 : 9001	6048 : 9001	6008 : 9002	6048 : 9002
6009 : 9000	6049 : 9000	6009 : 9001	6049 : 9001	6009 : 9002	6049 : 9002
6010 : 9000	6050 : 9000	6010 : 9001	6050 : 9001	6010 : 9002	6050 : 9002
6011 : 9000	6051 : 9000	6011 : 9001	6051 : 9001	6011 : 9002	6051 : 9002
6012 : 9000	6052 : 9000	6012 : 9001	6052 : 9001	6012 : 9002	6052 : 9002
6013 : 9000	6053 : 9000	6013 : 9001	6053 : 9001	6013 : 9002	6053 : 9002
6014 : 9000	6054 : 9000	6014 : 9001	6054 : 9001	6014 : 9002	6054 : 9002
6015 : 9000	6055 : 9000	6015 : 9001	6055 : 9001	6015 : 9002	6055 : 9002
6016 : 9000	6056 : 9000	6016 : 9001	6056 : 9001	6016 : 9002	6056 : 9002
6017 : 9000	6057 : 9000	6017 : 9001	6057 : 9001	6017 : 9002	6057 : 9002
6018 : 9000	6058 : 9000	6018 : 9001	6058 : 9001	6018 : 9002	6058 : 9002
6019 : 9000	6059 : 9000	6019 : 9001	6059 : 9001	6019 : 9002	6059 : 9002
6020 : 9000	6060 : 9000	6020 : 9001	6060 : 9001	6020 : 9002	6060 : 9002
6021 : 9000	6061 : 9000	6021 : 9001	6061 : 9001	6021 : 9002	6061 : 9002
6022 : 9000	6062 : 9000	6022 : 9001	6062 : 9001	6022 : 9002	6062 : 9002
6023 : 9000	6063 : 9000	6023 : 9001	6063 : 9001	6023 : 9002	6063 : 9002
6024 : 9000	6064 : 9000	6024 : 9001	6064 : 9001	6024 : 9002	6064 : 9002
6025 : 9000	6065 : 9000	6025 : 9001	6065 : 9001	6025 : 9002	6065 : 9002
6026 : 9000	6066 : 9000	6026 : 9001	6066 : 9001	6026 : 9002	6066 : 9002
6027 : 9000	6067 : 9000	6027 : 9001	6067 : 9001	6027 : 9002	6067 : 9002
6028 : 9000	6068 : 9000	6028 : 9001	6068 : 9001	6028 : 9002	6068 : 9002
6029 : 9000	6069 : 9000	6029 : 9001	6069 : 9001	6029 : 9002	6069 : 9002
6030 : 9000	6070 : 9000	6030 : 9001	6070 : 9001	6030 : 9002	6070 : 9002
6031 : 9000	6071 : 9000	6031 : 9001	6071 : 9001	6031 : 9002	6071 : 9002
6032 : 9000	6072 : 9000	6032 : 9001	6072 : 9001	6032 : 9002	6072 : 9002
6033 : 9000	6073 : 9000	6033 : 9001	6073 : 9001	6033 : 9002	6073 : 9002
6034 : 9000	6074 : 9000	6034 : 9001	6074 : 9001	6034 : 9002	6074 : 9002
6035 : 9000	6075 : 9000	6035 : 9001	6075 : 9001	6035 : 9002	6075 : 9002
6036 : 9000	6076 : 9000	6036 : 9001	6076 : 9001	6036 : 9002	6076 : 9002
6037 : 9000	6077 : 9000	6037 : 9001	6077 : 9001	6037 : 9002	6077 : 9002
6038 : 9000	6078 : 9000	6038 : 9001	6078 : 9001	6038 : 9002	6078 : 9002
6039 : 9000		6039 : 9001		6039 : 9002	

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
6000 : 9003	6040 : 9003	6000 : 9004	6040 : 9004	6000 : 9005	6040 : 9005
6001 : 9003	6041 : 9003	6001 : 9004	6041 : 9004	6001 : 9005	6041 : 9005
6002 : 9003	6042 : 9003	6002 : 9004	6042 : 9004	6002 : 9005	6042 : 9005
6003 : 9003	6043 : 9003	6003 : 9004	6043 : 9004	6003 : 9005	6043 : 9005
6004 : 9003	6044 : 9003	6004 : 9004	6044 : 9004	6004 : 9005	6044 : 9005
6005 : 9003	6045 : 9003	6005 : 9004	6045 : 9004	6005 : 9005	6045 : 9005
6006 : 9003	6046 : 9003	6006 : 9004	6046 : 9004	6006 : 9005	6046 : 9005
6007 : 9003	6047 : 9003	6007 : 9004	6047 : 9004	6007 : 9005	6047 : 9005
6008 : 9003	6048 : 9003	6008 : 9004	6048 : 9004	6008 : 9005	6048 : 9005
6009 : 9003	6049 : 9003	6009 : 9004	6049 : 9004	6009 : 9005	6049 : 9005
6010 : 9003	6050 : 9003	6010 : 9004	6050 : 9004	6010 : 9005	6050 : 9005
6011 : 9003	6051 : 9003	6011 : 9004	6051 : 9004	6011 : 9005	6051 : 9005
6012 : 9003	6052 : 9003	6012 : 9004	6052 : 9004	6012 : 9005	6052 : 9005
6013 : 9003	6053 : 9003	6013 : 9004	6053 : 9004	6013 : 9005	6053 : 9005
6014 : 9003	6054 : 9003	6014 : 9004	6054 : 9004	6014 : 9005	6054 : 9005
6015 : 9003	6055 : 9003	6015 : 9004	6055 : 9004	6015 : 9005	6055 : 9005
6016 : 9003	6056 : 9003	6016 : 9004	6056 : 9004	6016 : 9005	6056 : 9005
6017 : 9003	6057 : 9003	6017 : 9004	6057 : 9004	6017 : 9005	6057 : 9005
6018 : 9003	6058 : 9003	6018 : 9004	6058 : 9004	6018 : 9005	6058 : 9005
6019 : 9003	6059 : 9003	6019 : 9004	6059 : 9004	6019 : 9005	6059 : 9005
6020 : 9003	6060 : 9003	6020 : 9004	6060 : 9004	6020 : 9005	6060 : 9005
6021 : 9003	6061 : 9003	6021 : 9004	6061 : 9004	6021 : 9005	6061 : 9005
6022 : 9003	6062 : 9003	6022 : 9004	6062 : 9004	6022 : 9005	6062 : 9005
6023 : 9003	6063 : 9003	6023 : 9004	6063 : 9004	6023 : 9005	6063 : 9005
6024 : 9003	6064 : 9003	6024 : 9004	6064 : 9004	6024 : 9005	6064 : 9005
6025 : 9003	6065 : 9003	6025 : 9004	6065 : 9004	6025 : 9005	6065 : 9005
6026 : 9003	6066 : 9003	6026 : 9004	6066 : 9004	6026 : 9005	6066 : 9005
6027 : 9003	6067 : 9003	6027 : 9004	6067 : 9004	6027 : 9005	6067 : 9005
6028 : 9003	6068 : 9003	6028 : 9004	6068 : 9004	6028 : 9005	6068 : 9005
6029 : 9003	6069 : 9003	6029 : 9004	6069 : 9004	6029 : 9005	6069 : 9005
6030 : 9003	6070 : 9003	6030 : 9004	6070 : 9004	6030 : 9005	6070 : 9005
6031 : 9003	6071 : 9003	6031 : 9004	6071 : 9004	6031 : 9005	6071 : 9005
6032 : 9003	6072 : 9003	6032 : 9004	6072 : 9004	6032 : 9005	6072 : 9005
6033 : 9003	6073 : 9003	6033 : 9004	6073 : 9004	6033 : 9005	6073 : 9005
6034 : 9003	6074 : 9003	6034 : 9004	6074 : 9004	6034 : 9005	6074 : 9005
6035 : 9003	6075 : 9003	6035 : 9004	6075 : 9004	6035 : 9005	6075 : 9005
6036 : 9003	6076 : 9003	6036 : 9004	6076 : 9004	6036 : 9005	6076 : 9005
6037 : 9003	6077 : 9003	6037 : 9004	6077 : 9004	6037 : 9005	6077 : 9005
6038 : 9003	6078 : 9003	6038 : 9004	6078 : 9004	6038 : 9005	6078 : 9005
6039 : 9003		6039 : 9004		6039 : 9005	

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
6000 : 9006	6040 : 9006	6000 : 9007	6040 : 9007	6000 : 9008	6040 : 9008
6001 : 9006	6041 : 9006	6001 : 9007	6041 : 9007	6001 : 9008	6041 : 9008
6002 : 9006	6042 : 9006	6002 : 9007	6042 : 9007	6002 : 9008	6042 : 9008
6003 : 9006	6043 : 9006	6003 : 9007	6043 : 9007	6003 : 9008	6043 : 9008
6004 : 9006	6044 : 9006	6004 : 9007	6044 : 9007	6004 : 9008	6044 : 9008
6005 : 9006	6045 : 9006	6005 : 9007	6045 : 9007	6005 : 9008	6045 : 9008
6006 : 9006	6046 : 9006	6006 : 9007	6046 : 9007	6006 : 9008	6046 : 9008
6007 : 9006	6047 : 9006	6007 : 9007	6047 : 9007	6007 : 9008	6047 : 9008
6008 : 9006	6048 : 9006	6008 : 9007	6048 : 9007	6008 : 9008	6048 : 9008
6009 : 9006	6049 : 9006	6009 : 9007	6049 : 9007	6009 : 9008	6049 : 9008
6010 : 9006	6050 : 9006	6010 : 9007	6050 : 9007	6010 : 9008	6050 : 9008
6011 : 9006	6051 : 9006	6011 : 9007	6051 : 9007	6011 : 9008	6051 : 9008
6012 : 9006	6052 : 9006	6012 : 9007	6052 : 9007	6012 : 9008	6052 : 9008
6013 : 9006	6053 : 9006	6013 : 9007	6053 : 9007	6013 : 9008	6053 : 9008
6014 : 9006	6054 : 9006	6014 : 9007	6054 : 9007	6014 : 9008	6054 : 9008
6015 : 9006	6055 : 9006	6015 : 9007	6055 : 9007	6015 : 9008	6055 : 9008
6016 : 9006	6056 : 9006	6016 : 9007	6056 : 9007	6016 : 9008	6056 : 9008
6017 : 9006	6057 : 9006	6017 : 9007	6057 : 9007	6017 : 9008	6057 : 9008
6018 : 9006	6058 : 9006	6018 : 9007	6058 : 9007	6018 : 9008	6058 : 9008
6019 : 9006	6059 : 9006	6019 : 9007	6059 : 9007	6019 : 9008	6059 : 9008
6020 : 9006	6060 : 9006	6020 : 9007	6060 : 9007	6020 : 9008	6060 : 9008
6021 : 9006	6061 : 9006	6021 : 9007	6061 : 9007	6021 : 9008	6061 : 9008
6022 : 9006	6062 : 9006	6022 : 9007	6062 : 9007	6022 : 9008	6062 : 9008
6023 : 9006	6063 : 9006	6023 : 9007	6063 : 9007	6023 : 9008	6063 : 9008
6024 : 9006	6064 : 9006	6024 : 9007	6064 : 9007	6024 : 9008	6064 : 9008
6025 : 9006	6065 : 9006	6025 : 9007	6065 : 9007	6025 : 9008	6065 : 9008
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6027 : 9006	6067 : 9006	6027 : 9007	6067 : 9007	6027 : 9008	6067 : 9008
6028 : 9006	6068 : 9006	6028 : 9007	6068 : 9007	6028 : 9008	6068 : 9008
6029 : 9006	6069 : 9006	6029 : 9007	6069 : 9007	6029 : 9008	6069 : 9008
6030 : 9006	6070 : 9006	6030 : 9007	6070 : 9007	6030 : 9008	6070 : 9008
6031 : 9006	6071 : 9006	6031 : 9007	6071 : 9007	6031 : 9008	6071 : 9008
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6033 : 9006	6073 : 9006	6033 : 9007	6073 : 9007	6033 : 9008	6073 : 9008
6034 : 9006	6074 : 9006	6034 : 9007	6074 : 9007	6034 : 9008	6074 : 9008
6035 : 9006	6075 : 9006	6035 : 9007	6075 : 9007	6035 : 9008	6075 : 9008
6036 : 9006	6076 : 9006	6036 : 9007	6076 : 9007	6036 : 9008	6076 : 9008
6037 : 9006	6077 : 9006	6037 : 9007	6077 : 9007	6037 : 9008	6077 : 9008
6038 : 9006	6078 : 9006	6038 : 9007	6078 : 9007	6038 : 9008	6078 : 9008
6039 : 9006		6039 : 9007		6039 : 9008	

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
6000 : 9009	6040 : 9009	6000 : 9010	6040 : 9010	6000 : 9011	6040 : 9011
6001 : 9009	6041 : 9009	6001 : 9010	6041 : 9010	6001 : 9011	6041 : 9011
6002 : 9009	6042 : 9009	6002 : 9010	6042 : 9010	6002 : 9011	6042 : 9011
6003 : 9009	6043 : 9009	6003 : 9010	6043 : 9010	6003 : 9011	6043 : 9011
6004 : 9009	6044 : 9009	6004 : 9010	6044 : 9010	6004 : 9011	6044 : 9011
6005 : 9009	6045 : 9009	6005 : 9010	6045 : 9010	6005 : 9011	6045 : 9011
6006 : 9009	6046 : 9009	6006 : 9010	6046 : 9010	6006 : 9011	6046 : 9011
6007 : 9009	6047 : 9009	6007 : 9010	6047 : 9010	6007 : 9011	6047 : 9011
6008 : 9009	6048 : 9009	6008 : 9010	6048 : 9010	6008 : 9011	6048 : 9011
6009 : 9009	6049 : 9009	6009 : 9010	6049 : 9010	6009 : 9011	6049 : 9011
6010 : 9009	6050 : 9009	6010 : 9010	6050 : 9010	6010 : 9011	6050 : 9011
6011 : 9009	6051 : 9009	6011 : 9010	6051 : 9010	6011 : 9011	6051 : 9011
6012 : 9009	6052 : 9009	6012 : 9010	6052 : 9010	6012 : 9011	6052 : 9011
6013 : 9009	6053 : 9009	6013 : 9010	6053 : 9010	6013 : 9011	6053 : 9011
6014 : 9009	6054 : 9009	6014 : 9010	6054 : 9010	6014 : 9011	6054 : 9011
6015 : 9009	6055 : 9009	6015 : 9010	6055 : 9010	6015 : 9011	6055 : 9011
6016 : 9009	6056 : 9009	6016 : 9010	6056 : 9010	6016 : 9011	6056 : 9011
6017 : 9009	6057 : 9009	6017 : 9010	6057 : 9010	6017 : 9011	6057 : 9011
6018 : 9009	6058 : 9009	6018 : 9010	6058 : 9010	6018 : 9011	6058 : 9011
6019 : 9009	6059 : 9009	6019 : 9010	6059 : 9010	6019 : 9011	6059 : 9011
6020 : 9009	6060 : 9009	6020 : 9010	6060 : 9010	6020 : 9011	6060 : 9011
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6024 : 9009	6064 : 9009	6024 : 9010	6064 : 9010	6024 : 9011	6064 : 9011
6025 : 9009	6065 : 9009	6025 : 9010	6065 : 9010	6025 : 9011	6065 : 9011
6026 : 9009	6066 : 9009	6026 : 9010	6066 : 9010	6026 : 9011	6066 : 9011
6027 : 9009	6067 : 9009	6027 : 9010	6067 : 9010	6027 : 9011	6067 : 9011
6028 : 9009	6068 : 9009	6028 : 9010	6068 : 9010	6028 : 9011	6068 : 9011
6029 : 9009	6069 : 9009	6029 : 9010	6069 : 9010	6029 : 9011	6069 : 9011
6030 : 9009	6070 : 9009	6030 : 9010	6070 : 9010	6030 : 9011	6070 : 9011
6031 : 9009	6071 : 9009	6031 : 9010	6071 : 9010	6031 : 9011	6071 : 9011
6032 : 9009	6072 : 9009	6032 : 9010	6072 : 9010	6032 : 9011	6072 : 9011
6033 : 9009	6073 : 9009	6033 : 9010	6073 : 9010	6033 : 9011	6073 : 9011
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6008 : 9093	6048 : 9093	6008 : 9094	6048 : 9094	6008 : 9095	6048 : 9095
6009 : 9093	6049 : 9093	6009 : 9094	6049 : 9094	6009 : 9095	6049 : 9095
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6023 : 9093	6063 : 9093	6023 : 9094	6063 : 9094	6023 : 9095	6063 : 9095
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6034 : 9093	6074 : 9093	6034 : 9094	6074 : 9094	6034 : 9095	6074 : 9095
6035 : 9093	6075 : 9093	6035 : 9094	6075 : 9094	6035 : 9095	6075 : 9095
6036 : 9093	6076 : 9093	6036 : 9094	6076 : 9094	6036 : 9095	6076 : 9095
6037 : 9093	6077 : 9093	6037 : 9094	6077 : 9094	6037 : 9095	6077 : 9095
6038 : 9093	6078 : 9093	6038 : 9094	6078 : 9094	6038 : 9095	6078 : 9095
6039 : 9093		6039 : 9094		6039 : 9095	

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
6000 : 9096	6040 : 9096	6000 : 9097	6040 : 9097	6000 : 9098	6040 : 9098
6001 : 9096	6041 : 9096	6001 : 9097	6041 : 9097	6001 : 9098	6041 : 9098
6002 : 9096	6042 : 9096	6002 : 9097	6042 : 9097	6002 : 9098	6042 : 9098
6003 : 9096	6043 : 9096	6003 : 9097	6043 : 9097	6003 : 9098	6043 : 9098
6004 : 9096	6044 : 9096	6004 : 9097	6044 : 9097	6004 : 9098	6044 : 9098
6005 : 9096	6045 : 9096	6005 : 9097	6045 : 9097	6005 : 9098	6045 : 9098
6006 : 9096	6046 : 9096	6006 : 9097	6046 : 9097	6006 : 9098	6046 : 9098
6007 : 9096	6047 : 9096	6007 : 9097	6047 : 9097	6007 : 9098	6047 : 9098
6008 : 9096	6048 : 9096	6008 : 9097	6048 : 9097	6008 : 9098	6048 : 9098
6009 : 9096	6049 : 9096	6009 : 9097	6049 : 9097	6009 : 9098	6049 : 9098
6010 : 9096	6050 : 9096	6010 : 9097	6050 : 9097	6010 : 9098	6050 : 9098
6011 : 9096	6051 : 9096	6011 : 9097	6051 : 9097	6011 : 9098	6051 : 9098
6012 : 9096	6052 : 9096	6012 : 9097	6052 : 9097	6012 : 9098	6052 : 9098
6013 : 9096	6053 : 9096	6013 : 9097	6053 : 9097	6013 : 9098	6053 : 9098
6014 : 9096	6054 : 9096	6014 : 9097	6054 : 9097	6014 : 9098	6054 : 9098
6015 : 9096	6055 : 9096	6015 : 9097	6055 : 9097	6015 : 9098	6055 : 9098
6016 : 9096	6056 : 9096	6016 : 9097	6056 : 9097	6016 : 9098	6056 : 9098
6017 : 9096	6057 : 9096	6017 : 9097	6057 : 9097	6017 : 9098	6057 : 9098
6018 : 9096	6058 : 9096	6018 : 9097	6058 : 9097	6018 : 9098	6058 : 9098
6019 : 9096	6059 : 9096	6019 : 9097	6059 : 9097	6019 : 9098	6059 : 9098
6020 : 9096	6060 : 9096	6020 : 9097	6060 : 9097	6020 : 9098	6060 : 9098
6021 : 9096	6061 : 9096	6021 : 9097	6061 : 9097	6021 : 9098	6061 : 9098
6022 : 9096	6062 : 9096	6022 : 9097	6062 : 9097	6022 : 9098	6062 : 9098
6023 : 9096	6063 : 9096	6023 : 9097	6063 : 9097	6023 : 9098	6063 : 9098
6024 : 9096	6064 : 9096	6024 : 9097	6064 : 9097	6024 : 9098	6064 : 9098
6025 : 9096	6065 : 9096	6025 : 9097	6065 : 9097	6025 : 9098	6065 : 9098
6026 : 9096	6066 : 9096	6026 : 9097	6066 : 9097	6026 : 9098	6066 : 9098
6027 : 9096	6067 : 9096	6027 : 9097	6067 : 9097	6027 : 9098	6067 : 9098
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6029 : 9096	6069 : 9096	6029 : 9097	6069 : 9097	6029 : 9098	6069 : 9098
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6031 : 9096	6071 : 9096	6031 : 9097	6071 : 9097	6031 : 9098	6071 : 9098
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6033 : 9096	6073 : 9096	6033 : 9097	6073 : 9097	6033 : 9098	6073 : 9098
6034 : 9096	6074 : 9096	6034 : 9097	6074 : 9097	6034 : 9098	6074 : 9098
6035 : 9096	6075 : 9096	6035 : 9097	6075 : 9097	6035 : 9098	6075 : 9098
6036 : 9096	6076 : 9096	6036 : 9097	6076 : 9097	6036 : 9098	6076 : 9098
6037 : 9096	6077 : 9096	6037 : 9097	6077 : 9097	6037 : 9098	6077 : 9098
6038 : 9096	6078 : 9096	6038 : 9097	6078 : 9097	6038 : 9098	6078 : 9098
6039 : 9096		6039 : 9097		6039 : 9098	

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
6000 : 9099	6040 : 9099	6000 : 9100	6040 : 9100	6000 : 9101	6040 : 9101
6001 : 9099	6041 : 9099	6001 : 9100	6041 : 9100	6001 : 9101	6041 : 9101
6002 : 9099	6042 : 9099	6002 : 9100	6042 : 9100	6002 : 9101	6042 : 9101
6003 : 9099	6043 : 9099	6003 : 9100	6043 : 9100	6003 : 9101	6043 : 9101
6004 : 9099	6044 : 9099	6004 : 9100	6044 : 9100	6004 : 9101	6044 : 9101
6005 : 9099	6045 : 9099	6005 : 9100	6045 : 9100	6005 : 9101	6045 : 9101
6006 : 9099	6046 : 9099	6006 : 9100	6046 : 9100	6006 : 9101	6046 : 9101
6007 : 9099	6047 : 9099	6007 : 9100	6047 : 9100	6007 : 9101	6047 : 9101
6008 : 9099	6048 : 9099	6008 : 9100	6048 : 9100	6008 : 9101	6048 : 9101
6009 : 9099	6049 : 9099	6009 : 9100	6049 : 9100	6009 : 9101	6049 : 9101
6010 : 9099	6050 : 9099	6010 : 9100	6050 : 9100	6010 : 9101	6050 : 9101
6011 : 9099	6051 : 9099	6011 : 9100	6051 : 9100	6011 : 9101	6051 : 9101
6012 : 9099	6052 : 9099	6012 : 9100	6052 : 9100	6012 : 9101	6052 : 9101
6013 : 9099	6053 : 9099	6013 : 9100	6053 : 9100	6013 : 9101	6053 : 9101
6014 : 9099	6054 : 9099	6014 : 9100	6054 : 9100	6014 : 9101	6054 : 9101
6015 : 9099	6055 : 9099	6015 : 9100	6055 : 9100	6015 : 9101	6055 : 9101
6016 : 9099	6056 : 9099	6016 : 9100	6056 : 9100	6016 : 9101	6056 : 9101
6017 : 9099	6057 : 9099	6017 : 9100	6057 : 9100	6017 : 9101	6057 : 9101
6018 : 9099	6058 : 9099	6018 : 9100	6058 : 9100	6018 : 9101	6058 : 9101
6019 : 9099	6059 : 9099	6019 : 9100	6059 : 9100	6019 : 9101	6059 : 9101
6020 : 9099	6060 : 9099	6020 : 9100	6060 : 9100	6020 : 9101	6060 : 9101
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6023 : 9099	6063 : 9099	6023 : 9100	6063 : 9100	6023 : 9101	6063 : 9101
6024 : 9099	6064 : 9099	6024 : 9100	6064 : 9100	6024 : 9101	6064 : 9101
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6026 : 9099	6066 : 9099	6026 : 9100	6066 : 9100	6026 : 9101	6066 : 9101
6027 : 9099	6067 : 9099	6027 : 9100	6067 : 9100	6027 : 9101	6067 : 9101
6028 : 9099	6068 : 9099	6028 : 9100	6068 : 9100	6028 : 9101	6068 : 9101
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6034 : 9099	6074 : 9099	6034 : 9100	6074 : 9100	6034 : 9101	6074 : 9101
6035 : 9099	6075 : 9099	6035 : 9100	6075 : 9100	6035 : 9101	6075 : 9101
6036 : 9099	6076 : 9099	6036 : 9100	6076 : 9100	6036 : 9101	6076 : 9101
6037 : 9099	6077 : 9099	6037 : 9100	6077 : 9100	6037 : 9101	6077 : 9101
6038 : 9099	6078 : 9099	6038 : 9100	6078 : 9100	6038 : 9101	6078 : 9101
6039 : 9099		6039 : 9100		6039 : 9101	

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
6000 : 9102	6040 : 9102	6000 : 9103	6040 : 9103	6000 : 9104	6040 : 9104
6001 : 9102	6041 : 9102	6001 : 9103	6041 : 9103	6001 : 9104	6041 : 9104
6002 : 9102	6042 : 9102	6002 : 9103	6042 : 9103	6002 : 9104	6042 : 9104
6003 : 9102	6043 : 9102	6003 : 9103	6043 : 9103	6003 : 9104	6043 : 9104
6004 : 9102	6044 : 9102	6004 : 9103	6044 : 9103	6004 : 9104	6044 : 9104
6005 : 9102	6045 : 9102	6005 : 9103	6045 : 9103	6005 : 9104	6045 : 9104
6006 : 9102	6046 : 9102	6006 : 9103	6046 : 9103	6006 : 9104	6046 : 9104
6007 : 9102	6047 : 9102	6007 : 9103	6047 : 9103	6007 : 9104	6047 : 9104
6008 : 9102	6048 : 9102	6008 : 9103	6048 : 9103	6008 : 9104	6048 : 9104
6009 : 9102	6049 : 9102	6009 : 9103	6049 : 9103	6009 : 9104	6049 : 9104
6010 : 9102	6050 : 9102	6010 : 9103	6050 : 9103	6010 : 9104	6050 : 9104
6011 : 9102	6051 : 9102	6011 : 9103	6051 : 9103	6011 : 9104	6051 : 9104
6012 : 9102	6052 : 9102	6012 : 9103	6052 : 9103	6012 : 9104	6052 : 9104
6013 : 9102	6053 : 9102	6013 : 9103	6053 : 9103	6013 : 9104	6053 : 9104
6014 : 9102	6054 : 9102	6014 : 9103	6054 : 9103	6014 : 9104	6054 : 9104
6015 : 9102	6055 : 9102	6015 : 9103	6055 : 9103	6015 : 9104	6055 : 9104
6016 : 9102	6056 : 9102	6016 : 9103	6056 : 9103	6016 : 9104	6056 : 9104
6017 : 9102	6057 : 9102	6017 : 9103	6057 : 9103	6017 : 9104	6057 : 9104
6018 : 9102	6058 : 9102	6018 : 9103	6058 : 9103	6018 : 9104	6058 : 9104
6019 : 9102	6059 : 9102	6019 : 9103	6059 : 9103	6019 : 9104	6059 : 9104
6020 : 9102	6060 : 9102	6020 : 9103	6060 : 9103	6020 : 9104	6060 : 9104
6021 : 9102	6061 : 9102	6021 : 9103	6061 : 9103	6021 : 9104	6061 : 9104
6022 : 9102	6062 : 9102	6022 : 9103	6062 : 9103	6022 : 9104	6062 : 9104
6023 : 9102	6063 : 9102	6023 : 9103	6063 : 9103	6023 : 9104	6063 : 9104
6024 : 9102	6064 : 9102	6024 : 9103	6064 : 9103	6024 : 9104	6064 : 9104
6025 : 9102	6065 : 9102	6025 : 9103	6065 : 9103	6025 : 9104	6065 : 9104
6026 : 9102	6066 : 9102	6026 : 9103	6066 : 9103	6026 : 9104	6066 : 9104
6027 : 9102	6067 : 9102	6027 : 9103	6067 : 9103	6027 : 9104	6067 : 9104
6028 : 9102	6068 : 9102	6028 : 9103	6068 : 9103	6028 : 9104	6068 : 9104
6029 : 9102	6069 : 9102	6029 : 9103	6069 : 9103	6029 : 9104	6069 : 9104
6030 : 9102	6070 : 9102	6030 : 9103	6070 : 9103	6030 : 9104	6070 : 9104
6031 : 9102	6071 : 9102	6031 : 9103	6071 : 9103	6031 : 9104	6071 : 9104
6032 : 9102	6072 : 9102	6032 : 9103	6072 : 9103	6032 : 9104	6072 : 9104
6033 : 9102	6073 : 9102	6033 : 9103	6073 : 9103	6033 : 9104	6073 : 9104
6034 : 9102	6074 : 9102	6034 : 9103	6074 : 9103	6034 : 9104	6074 : 9104
6035 : 9102	6075 : 9102	6035 : 9103	6075 : 9103	6035 : 9104	6075 : 9104
6036 : 9102	6076 : 9102	6036 : 9103	6076 : 9103	6036 : 9104	6076 : 9104
6037 : 9102	6077 : 9102	6037 : 9103	6077 : 9103	6037 : 9104	6077 : 9104
6038 : 9102	6078 : 9102	6038 : 9103	6078 : 9103	6038 : 9104	6078 : 9104
6039 : 9102		6039 : 9103		6039 : 9104	

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
6000 : 9105	6040 : 9105				
6001 : 9105	6041 : 9105				
6002 : 9105	6042 : 9105				
6003 : 9105	6043 : 9105				
6004 : 9105	6044 : 9105				
6005 : 9105	6045 : 9105				
6006 : 9105	6046 : 9105				
6007 : 9105	6047 : 9105				
6008 : 9105	6048 : 9105				
6009 : 9105	6049 : 9105				
6010 : 9105	6050 : 9105				
6011 : 9105	6051 : 9105				
6012 : 9105	6052 : 9105				
6013 : 9105	6053 : 9105				
6014 : 9105	6054 : 9105				
6015 : 9105	6055 : 9105				
6016 : 9105	6056 : 9105				
6017 : 9105	6057 : 9105				
6018 : 9105	6058 : 9105				
6019 : 9105	6059 : 9105				
6020 : 9105	6060 : 9105	--	--	--	--
6021 : 9105	6061 : 9105				
6022 : 9105	6062 : 9105				
6023 : 9105	6063 : 9105				
6024 : 9105	6064 : 9105				
6025 : 9105	6065 : 9105				
6026 : 9105	6066 : 9105				
6027 : 9105	6067 : 9105				
6028 : 9105	6068 : 9105				
6029 : 9105	6069 : 9105				
6030 : 9105	6070 : 9105				
6031 : 9105	6071 : 9105				
6032 : 9105	6072 : 9105				
6033 : 9105	6073 : 9105				
6034 : 9105	6074 : 9105				
6035 : 9105	6075 : 9105				
6036 : 9105	6076 : 9105				
6037 : 9105	6077 : 9105				
6038 : 9105	6078 : 9105				
6039 : 9105					

Table E: Example combinations of a compound X with a compound Y.

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
8000 : 9000	8000 : 9001	8000 : 9002	8000 : 9003	8000 : 9004	8000 : 9005
8001 : 9000	8001 : 9001	8001 : 9002	8001 : 9003	8001 : 9004	8001 : 9005
8002 : 9000	8002 : 9001	8002 : 9002	8002 : 9003	8002 : 9004	8002 : 9005
8003 : 9000	8003 : 9001	8003 : 9002	8003 : 9003	8003 : 9004	8003 : 9005
8004 : 9000	8004 : 9001	8004 : 9002	8004 : 9003	8004 : 9004	8004 : 9005
8005 : 9000	8005 : 9001	8005 : 9002	8005 : 9003	8005 : 9004	8005 : 9005
8006 : 9000	8006 : 9001	8006 : 9002	8006 : 9003	8006 : 9004	8006 : 9005
8007 : 9000	8007 : 9001	8007 : 9002	8007 : 9003	8007 : 9004	8007 : 9005
8008 : 9000	8008 : 9001	8008 : 9002	8008 : 9003	8008 : 9004	8008 : 9005
8009 : 9000	8009 : 9001	8009 : 9002	8009 : 9003	8009 : 9004	8009 : 9005
8010 : 9000	8010 : 9001	8010 : 9002	8010 : 9003	8010 : 9004	8010 : 9005
8011 : 9000	8011 : 9001	8011 : 9002	8011 : 9003	8011 : 9004	8011 : 9005
8012 : 9000	8012 : 9001	8012 : 9002	8012 : 9003	8012 : 9004	8012 : 9005
8013 : 9000	8013 : 9001	8013 : 9002	8013 : 9003	8013 : 9004	8013 : 9005
8014 : 9000	8014 : 9001	8014 : 9002	8014 : 9003	8014 : 9004	8014 : 9005
8015 : 9000	8015 : 9001	8015 : 9002	8015 : 9003	8015 : 9004	8015 : 9005
8016 : 9000	8016 : 9001	8016 : 9002	8016 : 9003	8016 : 9004	8016 : 9005
8000 : 9006	8000 : 9007	8000 : 9008	8000 : 9009	8000 : 9010	8000 : 9011
8001 : 9006	8001 : 9007	8001 : 9008	8001 : 9009	8001 : 9010	8001 : 9011
8002 : 9006	8002 : 9007	8002 : 9008	8002 : 9009	8002 : 9010	8002 : 9011
8003 : 9006	8003 : 9007	8003 : 9008	8003 : 9009	8003 : 9010	8003 : 9011
8004 : 9006	8004 : 9007	8004 : 9008	8004 : 9009	8004 : 9010	8004 : 9011
8005 : 9006	8005 : 9007	8005 : 9008	8005 : 9009	8005 : 9010	8005 : 9011
8006 : 9006	8006 : 9007	8006 : 9008	8006 : 9009	8006 : 9010	8006 : 9011
8007 : 9006	8007 : 9007	8007 : 9008	8007 : 9009	8007 : 9010	8007 : 9011
8008 : 9006	8008 : 9007	8008 : 9008	8008 : 9009	8008 : 9010	8008 : 9011
8009 : 9006	8009 : 9007	8009 : 9008	8009 : 9009	8009 : 9010	8009 : 9011
8010 : 9006	8010 : 9007	8010 : 9008	8010 : 9009	8010 : 9010	8010 : 9011
8011 : 9006	8011 : 9007	8011 : 9008	8011 : 9009	8011 : 9010	8011 : 9011
8012 : 9006	8012 : 9007	8012 : 9008	8012 : 9009	8012 : 9010	8012 : 9011
8013 : 9006	8013 : 9007	8013 : 9008	8013 : 9009	8013 : 9010	8013 : 9011
8014 : 9006	8014 : 9007	8014 : 9008	8014 : 9009	8014 : 9010	8014 : 9011
8015 : 9006	8015 : 9007	8015 : 9008	8015 : 9009	8015 : 9010	8015 : 9011
8016 : 9006	8016 : 9007	8016 : 9008	8016 : 9009	8016 : 9010	8016 : 9011

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
8000 : 9012	8000 : 9013	8000 : 9014	8000 : 9015	8000 : 9016	8000 : 9017
8001 : 9012	8001 : 9013	8001 : 9014	8001 : 9015	8001 : 9016	8001 : 9017
8002 : 9012	8002 : 9013	8002 : 9014	8002 : 9015	8002 : 9016	8002 : 9017
8003 : 9012	8003 : 9013	8003 : 9014	8003 : 9015	8003 : 9016	8003 : 9017
8004 : 9012	8004 : 9013	8004 : 9014	8004 : 9015	8004 : 9016	8004 : 9017
8005 : 9012	8005 : 9013	8005 : 9014	8005 : 9015	8005 : 9016	8005 : 9017
8006 : 9012	8006 : 9013	8006 : 9014	8006 : 9015	8006 : 9016	8006 : 9017
8007 : 9012	8007 : 9013	8007 : 9014	8007 : 9015	8007 : 9016	8007 : 9017
8008 : 9012	8008 : 9013	8008 : 9014	8008 : 9015	8008 : 9016	8008 : 9017
8009 : 9012	8009 : 9013	8009 : 9014	8009 : 9015	8009 : 9016	8009 : 9017
8010 : 9012	8010 : 9013	8010 : 9014	8010 : 9015	8010 : 9016	8010 : 9017
8011 : 9012	8011 : 9013	8011 : 9014	8011 : 9015	8011 : 9016	8011 : 9017
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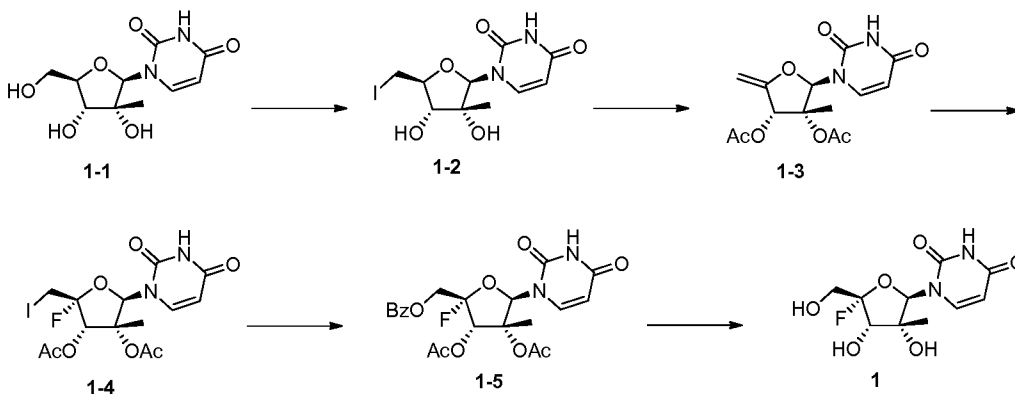
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8008 : 9090	8008 : 9091	8008 : 9092	8008 : 9093	8008 : 9094	8008 : 9095
8009 : 9090	8009 : 9091	8009 : 9092	8009 : 9093	8009 : 9094	8009 : 9095
8010 : 9090	8010 : 9091	8010 : 9092	8010 : 9093	8010 : 9094	8010 : 9095
8011 : 9090	8011 : 9091	8011 : 9092	8011 : 9093	8011 : 9094	8011 : 9095
8012 : 9090	8012 : 9091	8012 : 9092	8012 : 9093	8012 : 9094	8012 : 9095
8013 : 9090	8013 : 9091	8013 : 9092	8013 : 9093	8013 : 9094	8013 : 9095
8014 : 9090	8014 : 9091	8014 : 9092	8014 : 9093	8014 : 9094	8014 : 9095
8015 : 9090	8015 : 9091	8015 : 9092	8015 : 9093	8015 : 9094	8015 : 9095
8016 : 9090	8016 : 9091	8016 : 9092	8016 : 9093	8016 : 9094	8016 : 9095

X : Y	X : Y	X : Y	X : Y	X : Y	X : Y
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8008 : 9096	8008 : 9097	8008 : 9098	8008 : 9099	8008 : 9100	8008 : 9101
8009 : 9096	8009 : 9097	8009 : 9098	8009 : 9099	8009 : 9100	8009 : 9101
8010 : 9096	8010 : 9097	8010 : 9098	8010 : 9099	8010 : 9100	8010 : 9101
8011 : 9096	8011 : 9097	8011 : 9098	8011 : 9099	8011 : 9100	8011 : 9101
8012 : 9096	8012 : 9097	8012 : 9098	8012 : 9099	8012 : 9100	8012 : 9101
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8016 : 9096	8016 : 9097	8016 : 9098	8016 : 9099	8016 : 9100	8016 : 9101
8000 : 9102	8000 : 9103	8000 : 9104	8000 : 9105	--	--
8001 : 9102	8001 : 9103	8001 : 9104	8001 : 9105		
8002 : 9102	8002 : 9103	8002 : 9104	8002 : 9105		
8003 : 9102	8003 : 9103	8003 : 9104	8003 : 9105		
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8007 : 9102	8007 : 9103	8007 : 9104	8007 : 9105		
8008 : 9102	8008 : 9103	8008 : 9104	8008 : 9105		
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8014 : 9102	8014 : 9103	8014 : 9104	8014 : 9105		
8015 : 9102	8015 : 9103	8015 : 9104	8015 : 9105		
8016 : 9102	8016 : 9103	8016 : 9104	8016 : 9105		

EXAMPLES

[0217] Additional embodiments are disclosed in further detail in the following examples, which are not in any way intended to limit the scope of the claims.

EXAMPLE 1
2'-C-METHYL-4'-FLUOROURIDINE 1



[0218] To a stirred suspension of **1-1** (20 g, 77.5 mmol), PPh₃ (30 g, 114.5 mmol), imidazole (10 g, 147 mmol) and pyridine (90 mL) in anhydrous THF (300 mL) was added a solution of I₂ (25 g, 98.4 mmol) in THF (100 mL) dropwise at 0°C. The mixture was warmed to room temperature (R.T.) and stirred at R.T. for 10 h. The reaction was quenched by MeOH (100 mL). The solvent was removed, and the residue was re-dissolved in a mixture ethyl acetate (EA) and THF (2 L, 10:1). The organic phase was washed with saturated Na₂S₂O₃ aq., and the aqueous phase was extracted with a mixture of EA and THF (2 L, 10:1). The organic layer was combined and concentrated to give a residue, which was purified on a silica gel column (0-10% MeOH in DCM) to give **1-2** (22.5 g, 78.9%) as a white solid. ¹H NMR: (DMSO-*d*₆, 400 MHz) δ 11.42 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 5.82 (s, 1H), 5.63 (d, *J* = 8.0 Hz, 1H), 5.50 (s, 1H), 5.23 (s, 1H), 3.77-3.79 (m, 1H), 3.40-3.62 (m, 3H), 0.97 (s, 3H).

[0219] To a stirred solution of **1-2** (24.3 g, 66.03 mmol) in anhydrous MeOH (240 mL) was added NaOMe (10.69 g, 198.09 mmol) at R.T. under N₂. The mixture was refluxed for 3 h. The solvent was removed, and the residue was re-dissolved in anhydrous pyridine (200 mL). To the mixture was added Ac₂O (84.9 g, 833.3 mmol) at 0°C. The mixture was warmed to 60 °C and stirred for 10 h. The solvent was removed, and the residue was diluted with DCM, washed with saturated NaHCO₃ and brine. The organic layer was concentrated and purified on a silica gel column (10-50% EA in PE) to give **1-3** (15 g, 70.1%) as a white solid. ¹H NMR: (CDCl₃, 400 MHz) δ 8.82 (s, 1H), 7.23 (d, *J* = 2.0 Hz, 1H), 6.54 (s, 1H), 5.85 (s, 1H), 5.77 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.69 (d, *J* = 2.4 Hz, 1H), 4.58 (d, *J* = 2.8 Hz, 1H), 2.07 (d, *J* = 5.2 Hz, 6H), 1.45 (s, 3H).

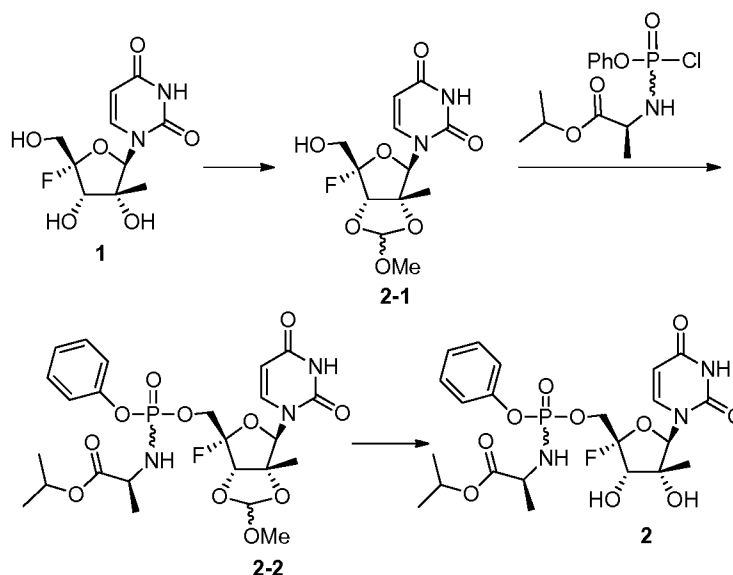
[0220] To an ice-cooled solution of **1-3** (15 g, 46.29 mmol) in anhydrous DCM (300 mL) was added AgF (29.39 g, 231.4 mmol). I₂ (23.51 g, 92.58 mmol) in anhydrous DCM (1.0 L) was added dropwise to the solution. The reaction mixture was stirred at R.T. for 5 h. The reaction was quenched with saturated Na₂S₂O₃ and NaHCO₃, and extracted with DCM. The

organic layer was separated, dried and evaporated to dryness. The residue was purified on a silica gel column (10-30% EA in PE) to give **1-4** (9.5 g, 43.6%) as a white solid. ^1H NMR: (Methanol- d_4 , 400 MHz) δ 7.52 (d, J = 8.0 Hz, 1H), 6.21 (s, 1H), 5.80 (d, J = 17.2 Hz, 1H), 5.73 (d, J = 8.0 Hz, 1H), 3.58 (s, 1H), 3.54 (d, J = 6.8 Hz, 1H), 2.17 (s, 3H), 2.09 (s, 3H), 1.58 (s, 3H).

[0221] To a solution of **1-4** (7.0 g, 14.89 mmol) in anhydrous DMF (400 mL) were added NaOBz (21.44 g, 148.9 mmol) and 15-crown-5 (32.75 g, 148.9 mmol). The reaction mixture was stirred at 130 °C for 6 h. The solvent was removed, diluted with EA and washed with water and brine. The organic layer was evaporated and purified on a silica gel column (10-30% EA in PE) to give **1-5** (2.8 g, 40.5%). ^1H NMR: (CDCl_3 , 400 MHz) δ 8.84 (s, 1H), 8.04-8.06 (m, 2H), 7.59 (t, J = 7.2 Hz, 1H), 7.44-7.47 (m, 2H), 7.21-7.26 (m, 1H), 6.21 (s, 1H), 5.85 (d, J = 18 Hz, 1H), 5.67 (d, J = 8.0 Hz, 1H), 4.59-4.72 (m, 2H), 2.14 (s, 6H), 1.64 (d, J = 6.0 Hz, 3H). ESI-MS: m/z 444.9 $[\text{M-F+H}]^+$.

[0222] A mixture of **1-5** (4.0 g; 8.6 mmol) and liquid ammonia was kept overnight at R. T. in a high-pressure stainless-steel vessel. Ammonia was then evaporated, and the residue purified on silica (50g column) with a $\text{CH}_2\text{Cl}_2/\text{MeOH}$ solvent mixture (4-12% gradient) to yield compound **1** as a colorless foam (2.0 g; 84% yield). ESI-MS: m/z 275.1 $[\text{M-H}]^-$.

EXAMPLE 2 COMPOUND 2



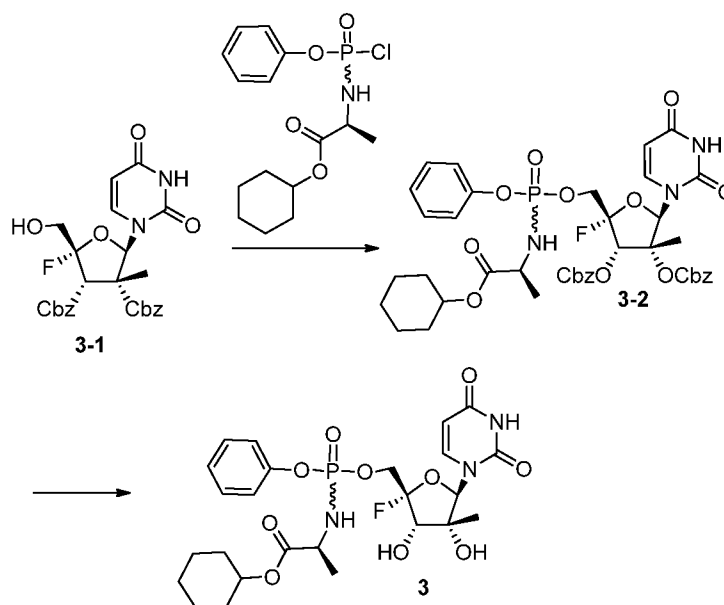
[0223] To a solution of **1** (1.2 g; 4.3 mmol) in dioxane (30 mL) were added p-toluenesulphonic acid monohydrate (820 mg; 1 eq.) and trimethyl orthoformate (14 mL; 30 eq.). The mixture was stirred overnight at R.T. The mixture was then neutralized with methanolic

ammonia and the solvent evaporated. Purification on silica gel column with CH₂Cl₂-MeOH solvent system (4-10% gradient) yielded **2-1** (1.18 g, 87%).

[0224] To an ice cold solution of **2-1** (0.91 g; 2.9 mmol) in anhydrous THF (20 mL) was added iso-propylmagnesium chloride (2.1 mL; 2 M in THF). The mixture was stirred at 0 °C for 20 mins. A solution of phosphorochloridate reagent (2.2 g; 2.5 eq.) in THF (2 mL) was added dropwise. The mixture was stirred overnight at R.T. The reaction was quenched with saturated aq. NH₄Cl solution and stirred at R.T. for 10 mins. The mixture was then diluted with water and CH₂Cl₂, and the two layers were separated. The organic layer was washed with water, half saturated aq. NaHCO₃ and brine, and dried with Na₂SO₄. The evaporated residue was purified on silica gel column with CH₂Cl₂-iPrOH solvent system (4-10% gradient) to yield Rp/Sp-mixture of **2-2** (1.59 g; 93%).

[0225] A mixture of **2-2** (1.45 g; 2.45 mmol) and 80% aq. HCOOH (7 mL) was stirred at R.T. for 1.5 h. The solvent was evaporated and coevaporated with toluene. The obtained residue was dissolved in MeOH, treated with Et₃N (3 drops) and the solvent was evaporated. Purification on silica gel column with CH₂Cl₂-MeOH solvent system (4-10% gradient) yielded Rp/Sp-mixture of compound **2** (950 mg; 70%). ³¹P-NMR (DMSO-d₆): δ 3.52, 3.47. MS: m/z = 544 [M-1]⁻.

EXAMPLE 3 **COMPOUND 3**

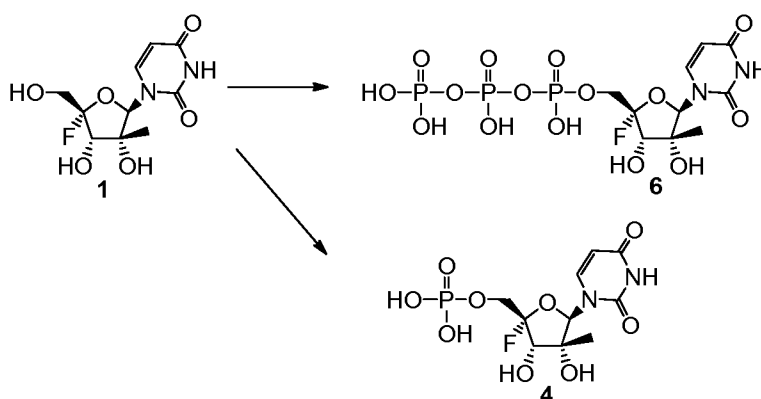


[0226] To an ice cold solution of **3-1** (80 mg; 0.15 mmol) in anhydrous THF (2 mL) was added isopropylmagnesium chloride (0.22 mL; 2 M in THF). The mixture was stirred at 0 °C for 20 mins. A solution of the phosphorochloridate reagent (0.16 g; 0.45 mmol) in THF (0.5 mL) was added dropwise. The mixture was stirred overnight at R.T. The reaction was

quenched with saturated aq. NH_4Cl solution and stirred at R.T. for 10 mins. The mixture was diluted with water and CH_2Cl_2 , and the two layers were separated. The organic layer was washed with water, half saturated aq. NaHCO_3 and brine, and dried with Na_2SO_4 . The evaporated residue was purified on silica gel column with CH_2Cl_2 -MeOH solvent system (2-10% gradient) to yield Rp/Sp-mixture of **3-2** (102 mg; 80%).

[0227] A mixture of **3-2** (100 mg; 0.12 mmol) in EtOH (3 mL) and 10% Pd/C (10 mg) was stirred under the H_2 atmosphere for 1.5 h. The mixture was filtered through a Celite pad, evaporated and purified on silica gel column with CH_2Cl_2 -MeOH solvent system (4-10% gradient) to yield Rp/Sp-mixture of compound **3** (52 mg, 74%). ^{31}P -NMR (DMSO-d_6): δ 3.51, 3.48. MS: m/z = 584 $[\text{M}-1]^-$.

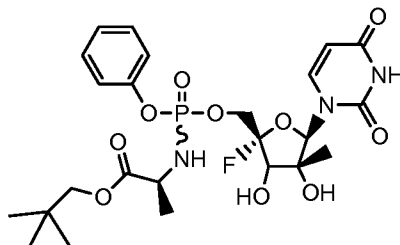
EXAMPLE 4 COMPOUNDS 4 and 6



[0228] Dry **1** (14 mg, 0.05 mmol) was dissolved in the mixture of $\text{PO}(\text{OMe})_3$ (0.750 mL) and pyridine (0.5 mL). The mixture was evaporated in vacuum for 15 mins at bath temperature 42°C , and then cooled down to R.T. N-Methylimidazole (0.009 mL, 0.11 mmol) was added followed by POCl_3 (0.009 mL, 0.1 mmol). The mixture was kept at R.T. for 45 mins. Tributylamine (0.065 mL, 0.3 mmol) and N-tetrabutyl ammonium salt of pyrophosphate (100 mg) was added. About 1 mL of dry DMF was added to get a homogeneous solution. In 1 h, the reaction was quenched with 2M ammonium acetate buffer (1 mL, $\text{pH} = 7.5$), diluted water (10 mL) and loaded on a column HiLoad 16/10 with Q Sepharose High Performance. The separation was done in linear gradient of NaCl from 0 to 1N in 50mM TRIS-buffer ($\text{pH} 7.5$). The fractions eluted at 60% buffer B contained Compound **4** and at 80% buffer B contained Compound **6**. The corresponding fractions were concentrated, and the residue purified by RP HPLC on Synergy 4 micron Hydro-RP column (Phenomenex). A linear gradient of methanol from 0 to 30% in 50mM triethylammonium acetate buffer ($\text{pH} 7.5$) was used for elution. The corresponding fractions were combined, concentrated and lyophilized 3 times to remove excess

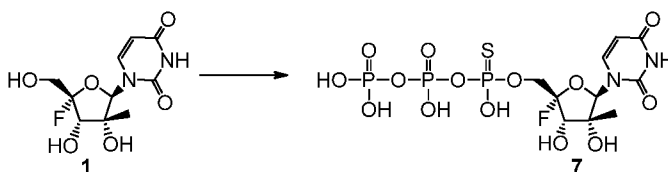
of buffer. Compound **4**: ^{31}P -NMR (D_2O): -3.76 (s); MS: m/z 355.3 $[\text{M}-\text{H}]^-$. Compound **6**: ^{31}P -NMR (D_2O): -9.28(d, 1H, $\text{P}\alpha$), -12.31(d, 1H, $\text{P}\gamma$), -22.95(t, 1H, $\text{P}\beta$); MS: m/z 515.0 $[\text{M}-1]^-$.

EXAMPLE 5
COMPOUND 5



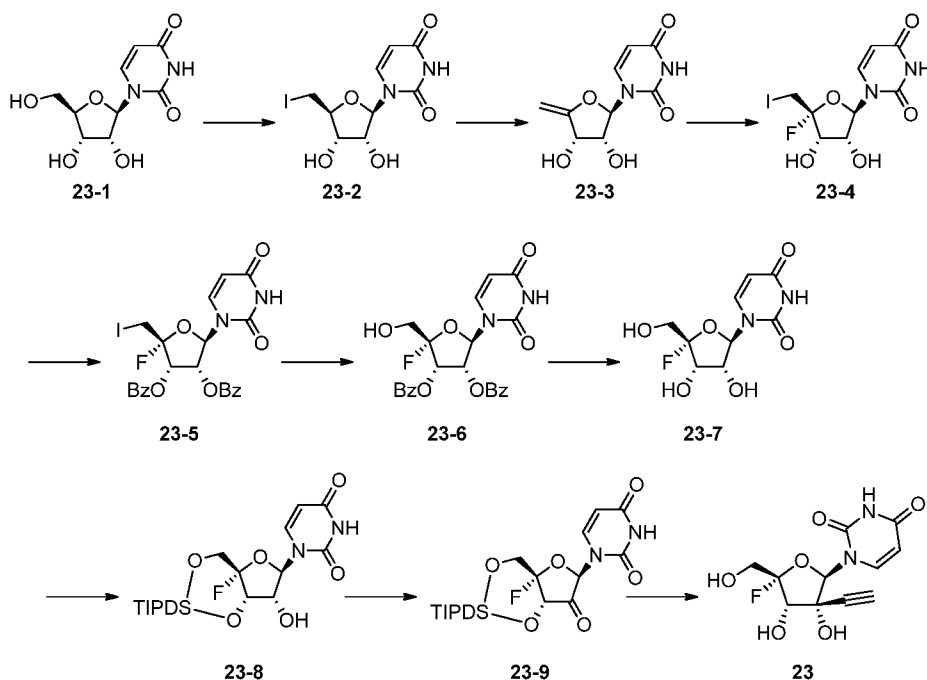
[0229] Compound **5** was synthesized as described for **2** on 0.1 mmol scale and with neopentyl ester of phosphorochloridate reagent. Yield was 36 mg (63%). ^{31}P -NMR (CDCl_3): δ 2.57 (s), 2.43 (s). MS: 572.6 $[\text{M}-1]^-$.

EXAMPLE 6
COMPOUND 7



[0230] Dry **1** (14 mg, 0.05 mmol) was dissolved in the mixture of $\text{PO}(\text{OMe})_3$ (0.750 mL) and pyridine (0.5 mL). The mixture was evaporated in vacuum for 15 mins at bath temperature 42°C , and then cooled down to R.T. N-Methylimidazole (0.009 mL, 0.11 mmol) was added followed by PSCl_3 (0.01 mL, 0.1 mmol). The mixture was kept at R.T. for 1 h. Tributylamine (0.065 mL, 0.3 mmol) and N-tetrabutyl ammonium salt of pyrophosphate (200 mg) was added. About 1 mL of dry DMF was added to get a homogeneous solution. In 2 h, the reaction was quenched with 2M ammonium acetate buffer (1 mL, $\text{pH} = 7.5$), diluted with water (10 mL) and loaded on a column HiLoad 16/10 with Q Sepharose High Performance. Separation was done in linear gradient of NaCl from 0 to 1N in 50mM TRIS-buffer ($\text{pH} 7.5$). The fractions eluted at 80% buffer B contained **7** (compounds **7a** and **7b**). The corresponding fractions were concentrated, and the residue purified by RP HPLC on Synergy 4 micron Hydro-RP column (Phenomenex). A linear gradient of methanol from 0 to 20% in 50mM triethylammonium acetate buffer ($\text{pH} 7.5$) was used for elution. Two peaks were collected. The corresponding fractions were combined, concentrated and lyophilized 3 times to remove excess of buffer. Peak 1 (more polar): ^{31}P -NMR (D_2O): +42.68(d, 1H, $\text{P}\alpha$), -9.05(d, 1H, $\text{P}\gamma$), -22.95(t, 1H, $\text{P}\beta$); MS 530.90 $[\text{M}-1]^-$. Peak 2 (less polar): ^{31}P -NMR (D_2O): +42.78(d, 1H, $\text{P}\alpha$), -10.12(bs, 1H, $\text{P}\gamma$), -23.94(t, 1H, $\text{P}\beta$); and MS 530.90 $[\text{M}-1]^-$.

EXAMPLE 7
COMPOUND 23



[0231] To a stirred suspension of **23-1** (20.0 g, 81.3 mmol), imidazole (15.9 g, 234.0 mmol), PPh_3 (53.5 g, 203.3 mmol) and pyridine (90 mL) in anhydrous THF (100 mL) was added a solution of I_2 (41.3 g, 162.6 mmol) in THF (150 mL) dropwise at 0°C . The mixture was slowly warmed to R.T. and stirred for 14 h. The reaction was quenched with sat. aq. $\text{Na}_2\text{S}_2\text{O}_3$ (150 mL) and extracted with THF/EA (1/1) (100 mL x 3). The organic layer was dried over Na_2SO_4 and concentrated at a low pressure. The residue was recrystallized from EtOH to afford pure **23-2** (23 g, 79%) as a white solid.

[0232] To a stirred solution of **23-2** (23 g, 65 mmol) in anhydrous MeOH (200 mL) was added NaOCH_3 (10.5 g, 195 mmol) in MeOH (50 mL) at R.T. The mixture was stirred at 60°C for 3 h, and quenched with dry ice. A solid precipitated and removed by filtration. The filtrate was concentrated at a low pressure. The residue was purified on column silica gel column (MeOH in DCM from 1% to 10%) to provide **23-3** (13.1 g, 92.5%) as a white foam solid.

[0233] To a stirred solution of **23-3** (12.0 g, 53 mmol) in anhydrous CH_3CN was added $\text{TEA} \cdot 3\text{HF}$ (8.5 g, 53 mmol) and NIS (10.2 g, 63.6 mmol) at 0°C . The mixture was stirred for 30 mins, and slowly warmed to R.T. The mixture was stirred for another 30 mins. The solid was removed by filtration, and washed with DCM to give **23-4** (14 g, 73%) as a yellow solid. ESI-MS: m/z 373.0 $[\text{M}+\text{H}]^+$.

[0234] To a stirred solution of **23-4** (12.0 g, 32 mmol) and DMAP (1.2 g, 9.6 mmol) in pyridine (100 mL) was added Bz₂O (21.7 g, 96 mmol) at R.T. The mixture was stirred at 50 °C for 16 h. The resulting solution was quenched with water, and concentrated to dryness at low pressure. The crude was purified on silica gel column (50% EA in PE) to give **23-5** (15 g, 81%) as a white solid. ESI-TOF-MS: m/z 581.0 [M+H]⁺.

[0235] Tetra-butylammonium hydroxide (288 mL as 54-56% aqueous solution, 576 mmol) was adjusted to pH~4 by adding TFA (48 mL). The resulting solution was treated with a solution of **23-5** (14 g, 24 mmol) in DCM (200 mL). *m*-Cloroperbenzoic acid (30 g, 60-70%, 120 mmol) was added portion wise with vigorous stirring, and the mixture was stirred overnight. The organic layer was separated and washed with brine. The resulting solution was dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography to give **23-6** (7.5 g, 68%)

[0236] Compound **23-6** (5.0 g, 10.6 mmol) was treated with 7N NH₃•MeOH (100 mL), and the mixture was stirred for 5 h. The mixture was then concentrated to dryness at low pressure. The residue was washed with DCM, and the solid was filtered to give **23-7** (2.1 g, 75%) as a white foam. ESI-MS: m/z 263.0 [M+H]⁺.

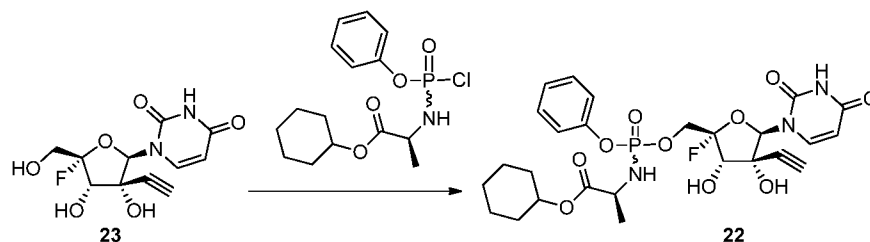
[0237] To a solution of **23-7** (2.1 g, 8.0 mmol) in pyridine was added TIDPSCI (2.5 g, 8.0 mmol) dropwise at 0 °C, and stirred for 12 h. at R.T. The solution was quenched with water, and concentrated to dryness at low pressure. The crude was purified by column chromatography (EA in PE from 10% to 50%) to give pure **23-8** (1.6 g, 40%) as a white foam.

[0238] A solution of **23-8** (1.5 g, 3.0 mmol) and IBX (1.69 g, 6.0 mmol) in anhydrous CH₃CN (10 mL) was stirred at 80 °C for 3 h. The mixture was cooled down to R.T. and filtered. The filtrate was concentrated to dryness at low pressure. The residue was purified by column chromatography (EA in PE from 2% to 50%) to give pure **23-9** (1.2 g, 80%) as a white foam. ESI-MS: m/z 503.0 [M+H]⁺

[0239] Compound **23-9** (500 mg, 1 mmol) was dissolved in dry THF (8 mL). Ethynyl magnesium bromide (8 mL of 0.5M solution in cyclohexane) was added at R.T. After 30 mins, additional ethynyl magnesium bromide (8 mL) was added. The mixture was left for 30 mins, and then quenched with sat. solution of ammonium chloride. The product was extracted with EA. The organic extracts were washed with brine, dried, and concentrated. The residue was purified by flash chromatography on silica gel in EA to remove the dark color. The yellow compound was dissolved in THF (3 mL) and treated with TBAF (1mL, 2M solution in THF) for 30 mins. The solvent was evaporated, and the residue was subjected to silica gel chromatography on a Biotage cartridge (25g). EA saturated with water was used for isocratic

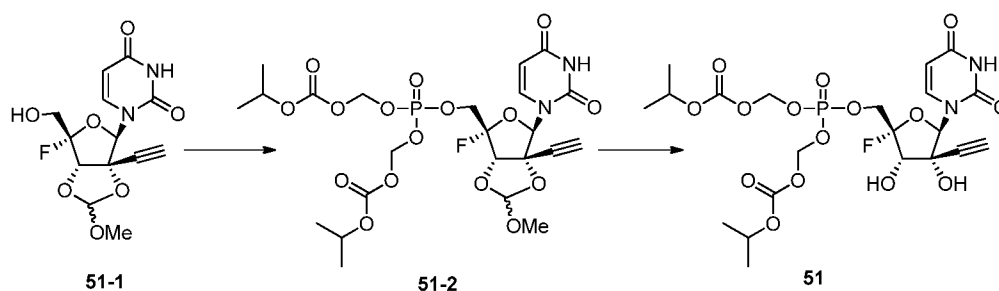
elution. Each fractions were analyzed by TLC in DCM-MeOH (9:1 v/v). Fractions containing only the isomer with a high R_f were concentrated to give pure compound **23** (110 mg). MS: 285.1 [M-1]⁻.

EXAMPLE 8 **COMPOUND 22**



[0240] Compound **23** (57 mg, 0.2 mmol) was dissolved in CH₃CN (2 mL), containing N-methylimidazole (40 μ L). The phosphorochloridate (207 mg, 0.6 mmol) was added, and the mixture was kept overnight at 40 °C. The mixture was distributed between water and EA. The organic layer was separated, washed with brine, dried and evaporated. The product was isolated by silica gel chromatography in gradient of methanol in DCM from 0% to 15%. Compound **22** was obtained (46 mg, 39%). MS: m/z 593.9 [M-1]⁻.

EXAMPLE 9 **COMPOUND 51**

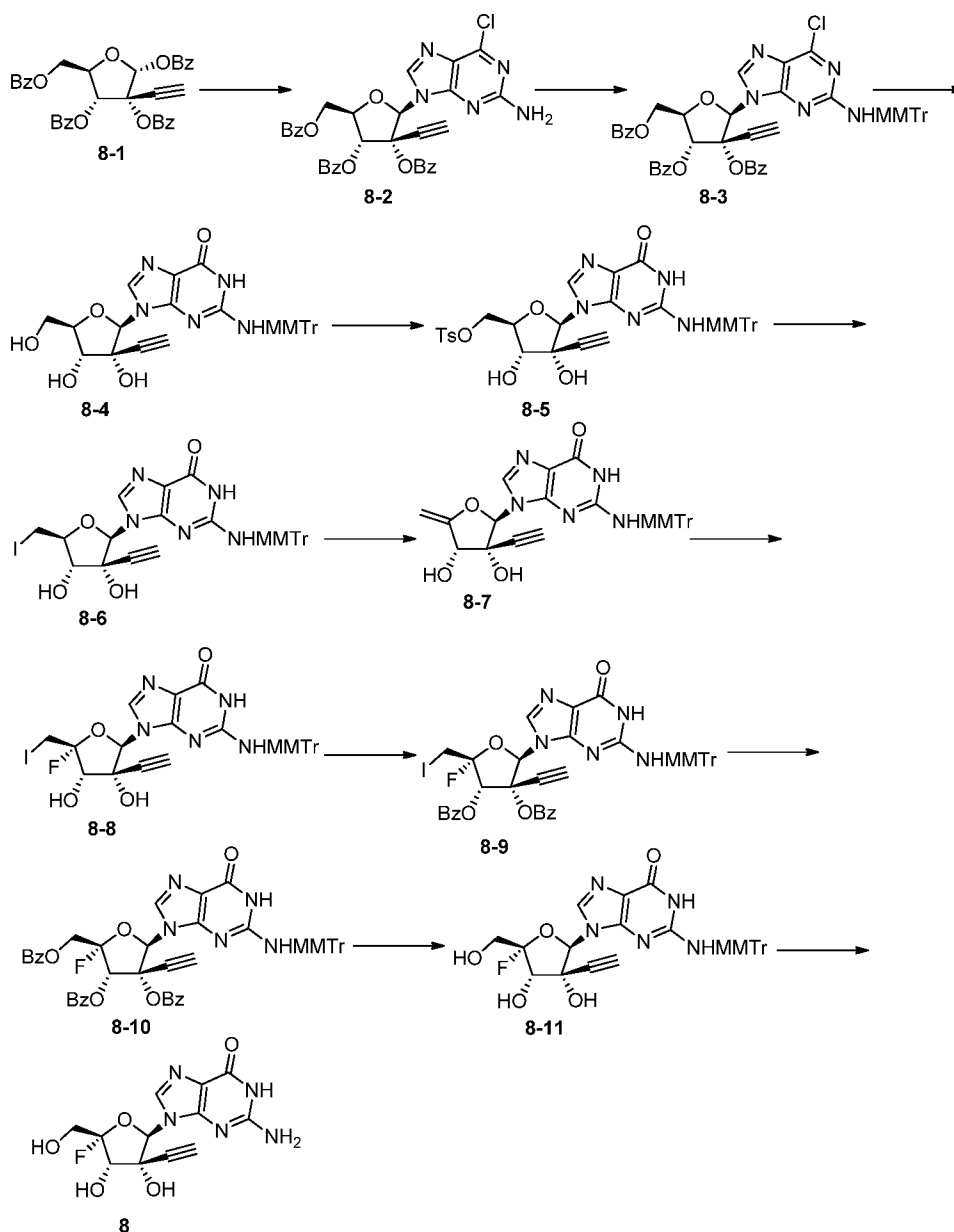


[0241] To a solution of triethylammonium bis(isopropoxycarbonyloxymethyl)phosphate (0.74 mmol) in THF was added **51-1** (0.16g; 0.49 mmol). The mixture evaporated and rendered anhydrous by coevaporating with pyridine follow by toluene. The residue was dissolved in anhydrous THF and cooled in an ice-bath. Diisopropylethyl amine (0.34 mL) was added, followed by BOP-Cl (250 mg) and 3-nitro-1,2,4-triazole (112 mg) in THF (5 mL). The mixture was stirred at 0 °C for 90 mins, diluted with EtOAc, washed with sat. aq. NaHCO₃ and brine, and dried (Na₂SO₄). The residue was purified on silica column with 3-10% i-PrOH in DCM to give **51-2** (0.2 g, 64%).

[0242] A solution of **51-2** (0.20 g; 0.31 mmol) in 80% aq. HCOOH was stirred at R.T. for 2 h, and then concentrated. The residue was coevaporated with toluene and then with MeOH containing a small amount of Et₃N (2 drops). Purification on silica gel (10 g column)

with CH₂Cl₂/MeOH (4-10% gradient) was followed by RP-HPLC purification in 5 runs on a Synergi Hydro RP column 250 x 30 mm (Phenomenex P/N 00G-4375-U0-AX) using H₂O and ACN both 50mM TEAA. The Gradient was 25-75% ACN in 20 mins at 24mL/mins, 254nm detection. The compound eluted at 16.0 minutes; and the pure fractions were pooled and lyophilized. TEAA was removed by dissolving the compound in DMSO (2 mL) and using the same column and same gradient, using only H₂O and ACN. Pure fractions were pooled and lyophilized to give compound **51** (18 mg). MS: m/z = 1197 [2M+1]⁺.

EXAMPLE 10
COMPOUND 8



[0243] Compound **8-1** (5.0 g, 8.5 mmol) and 2-amino-6-chloropurine (3.0 g, 17.7 mmol) were co-concentrated with anhydrous toluene for 3 times. To a stirred suspension of the

above mixtures in anhydrous MeCN (50 mL) was added DBU (7.5 g, 49 mmol) at 0°C. The mixture was stirred at 0 °C for 15 mins, and then TMSOTf (15 g, 67.6 mmol) was added dropwise at 0°C. The mixture was stirred at 0 °C for 15 mins. The mixture was heated at 70°C overnight. The mixture was cooled to R.T., and diluted with EA (100 mL). The solution was washed with sat. NaHCO₃ solution and brine. The organic layer was dried over Na₂SO₄ and concentrated at low pressure. The residue was purified by column on silica gel (PE/EA: from 15/1 to 3/1) to give **8-2** (2.5 g, 46.3%) as a white foam.

[0244] To a solution of **8-2** (10 g, 15.7 mmol), AgNO₃ (8.0g, 47 mmol) and collidine (10 mL) in anhydrous DCM (20 mL) was added MMTTrCl (14.5 g, 47 mmol) in small portions under N₂. The mixture was stirred at R.T. overnight. The mixture was filtered, and the filtrate was washed with sat. aq. NaHCO₃ and brine. The organic layer was dried over anhydrous Na₂SO₄ and concentrated at low pressure. The residue was purified by silica gel column (PE/ME = 20/1 to 8/1) to give **8-3** (10 g, 70 %) as a yellow solid.

[0245] To a solution of 3-hydroxy-propionitrile (3.51 g, 49.4 mmol) in anhydrous THF (100 mL) was added NaH (2.8 g, 70 mmol) at 0°C, and the mixture was stirred at R.T. for 30 mins. A solution of **8-3** (8.5 g, 9.35 mmol) in anhydrous THF (100 mL) at 0 °C was added, and the mixture was stirred at R.T. overnight. The reaction was quenched with water, and extracted with EA (100 mL). The organic layer was dried over anhydrous Na₂SO₄ and concentrated at low pressure. The residue was purified by silica gel column (DCM/MeOH = 100/1 to 20/1) to give **8-4** (4.5 g, 83%) as a white solid.

[0246] Compound **8-4** (1.5g, 2.6 mmol) was co-concentrated with anhydrous pyridine 3 times. To an ice-cooled solution of **8-4** in anhydrous pyridine (30 mL) was added TsCl (1.086 g, 5.7 mmol), and the mixture was stirred at 0 °C for 1 h. The reaction was quenched with water, and extracted with EA (80 mL). The organic layer was dried over anhydrous Na₂SO₄ and concentrated at low pressure. The residue was purified by silica gel column (DCM/MeOH = 100/1 to 15/1) to give **8-5** (1.4 g, 73%) as a white solid.

[0247] To a solution of **8-5** (4.22 g, 5.7 mmol) in acetone (60 mL) was added NaI (3.45 g, 23 mmol), and the mixture was refluxed overnight. The reaction was quenched with sat. aq. Na₂S₂O₃ and extracted with EA (100 mL). The organic layer was dried over anhydrous Na₂SO₄ and concentrated at low pressure. The residue was purified by silica gel column (DCM/MeOH = 100/1 to 15/1) to give **8-6** (4 g, 73%) as a white solid.

[0248] To a solution of **8-6** (4.0 g, 5.8 mmol) in anhydrous THF (60 mL) was added DBU (3.67 g, 24 mmol), and the mixture was stirred at 60 °C overnight. The mixture was diluted with EA (80 mL), and the solution was washed with brine. The organic layer was dried

over anhydrous Na₂SO₄, and concentrated at low pressure. The residue was purified by silica gel column (DCM/MeOH = 100/1 to 20/1) to give **8-7** (2 g, 61%) as a white solid.

[0249] To an ice-cooled solution of **8-7** (500 mg, 0.89 mmol) in anhydrous DCM (20 mL) was added AgF (618 mg, 4.9 mmol) and a solution of I₂ (500 mg, 1.97 mmol) in anhydrous DCM (20 mL). The mixture was stirred at R.T. for 3 h. The reaction was quenched with sat Na₂S₂O₃ and NaHCO₃ aqueous, and the mixture was extracted with DCM (50 mL). The organic layer was separated, dried over anhydrous Na₂SO₄, and concentrated to give the crude **8-8** (250 mg) as a yellow solid.

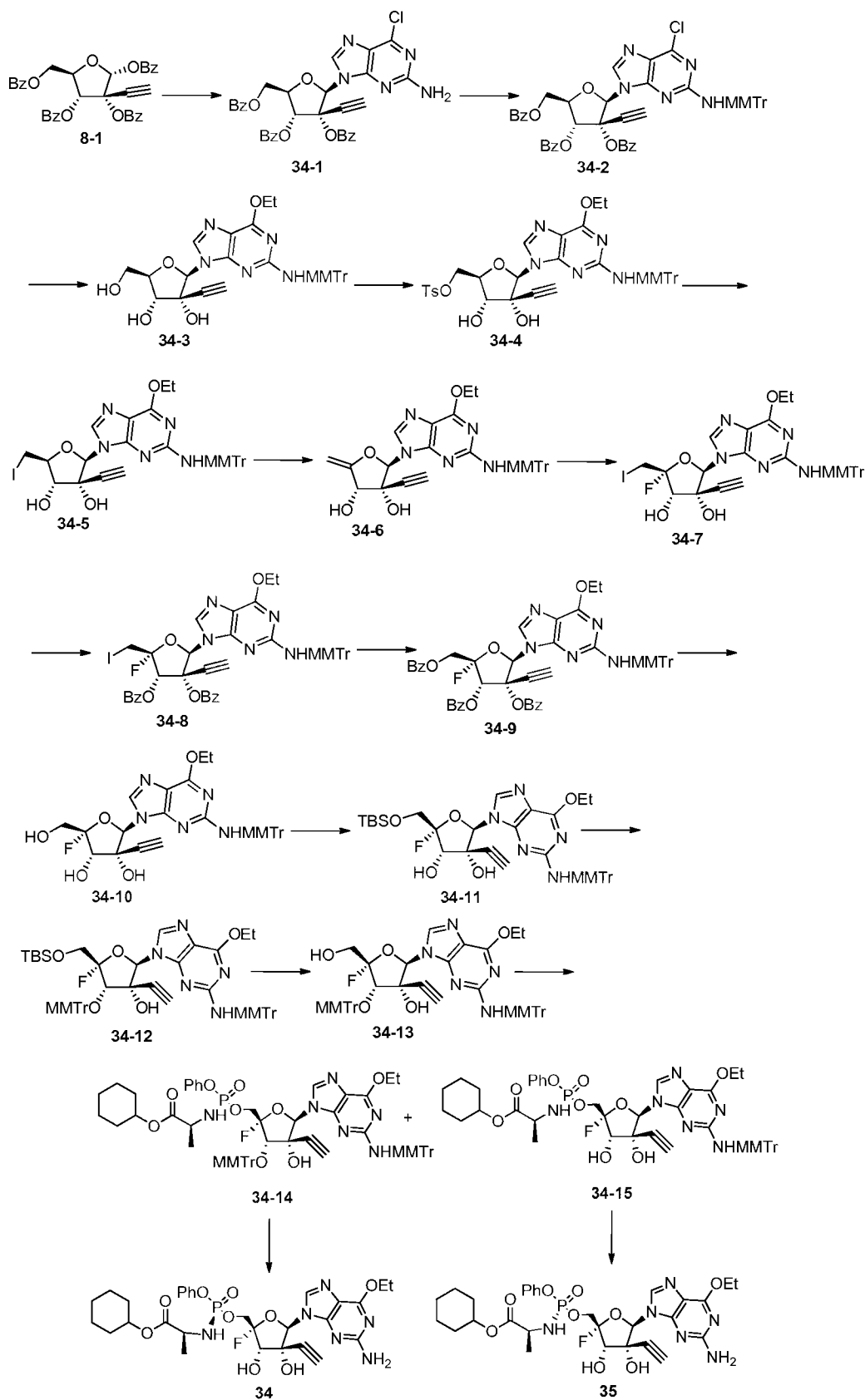
[0250] To a solution of crude **8-8** (900 mg, 1.28 mmol) in anhydrous DCM (50 mL) was added DMAP (1.0g, 8.2 mmol) and BzCl (795 mg, 5.66 mmol). The mixture was stirred at R.T. overnight. The mixture was washed with sat. aq. NaHCO₃ and brine. The organic layer was dried over anhydrous Na₂SO₄, and concentrated at low pressure. The residue was purified by prep-TLC (DCM/MeOH = 15:1) to give **8-9** (300 mg, 26%) as a white solid.

[0251] To a solution of crude **8-9** (750 mg, 0.82 mmol) in anhydrous HMPA (20 mL) was added NaOBz (1.2 g, 8.3 mmol) and 15-crown-5 (1.8 g, 8.3 mmol). The mixture was stirred at 60 °C for 2 d. The mixture was diluted with EA, and the solution was washed with brine. The organic layer was dried over anhydrous Na₂SO₄, and concentrated at low pressure. The residue was purified by prep-TLC (PE/EA = 1:1) to give crude **8-10** (550 mg, 73%) as a white solid.

[0252] The crude **8-10** (550 mg, 0.6 mmol) was dissolved in NH₃/MeOH (7N, 50 mL). The mixture was stirred at R.T. overnight. The mixture was concentrated, and the residue was purified by silica gel column (DCM/MeOH from 100/1 to 20/1) to give **8-11** (62 mg, 17%) as a white solid. ESI-MS: m/z 598.0 [M+H]⁺

[0253] A solution of **8-11** (12 mg) in 80% formic acid (0.5 mL) stood at R.T. for 3.5 h and then was concentrated. The residue was co-evaporated with MeOH/toluene 4 times in a vial, and triturated with EtOAc at 40°C. The EtOAc solution removed with pipet. The trituration step was repeated several times, and the remaining solid was dissolved in MeOH. The solution was concentrated and dried to give compound **8** as off white solid (4.7 mg). ESI-MS: m/z 326.6 [M+H]⁺.

EXAMPLE 11
COMPOUNDS 34 and 35



[0254] To a stirred suspension of **8-1** (50 g, 84.8 mmol) and 2-amino-6-chloropurine (28.6 g, 169.2 mmol) in anhydrous MeCN (500 mL) was added DBU (77.8 g, 508 mmol) at 0°C. The mixture was stirred at 0 °C for 30 mins, and TMSOTf (150.5 g, 678 mmol) was added dropwise at 0°C. The mixture was stirred at R.T. for 20 mins until a clear solution was formed. The mixture was stirred at 90-110°C overnight. The mixture was cooled to R.T., and diluted with EA. The solution was washed with sat. NaHCO₃ solution and brine. The organic layer was dried over Na₂SO₄ and then concentrated at low pressure. The residue was purified by silica gel column (PE/EA = 2/1) to give **34-1** (30 g, 55.5%) as a white solid.

[0255] To a solution of **34-1** (30 g, 47.1 mmol) in anhydrous DCM (300 mL) was added collidine (30 mL), AgNO₃ (24 g, 141.4 mmol) and MMTrCl (43.6 g, 141.4 mmol). The mixture was stirred at R.T. overnight. The mixture was filtered, and the filtrate was washed with water and brine. The organic layer was dried over anhydrous Na₂SO₄, and concentrated at low pressure. The residue was purified by silica gel column (PE/EA= 4/1) to give **34-2** (35 g, 82%) as a white solid.

[0256] To a stirred solution of **34-2** (35 g, 38.5 mmol) in anhydrous EtOH (150 mL) was added a solution of EtONa in EtOH (2N, 150 mL). The mixture was stirred at R.T. overnight, and then concentrated at low pressure. The residue was dissolved in EA (200 mL) and the solution was washed with water and brine. The organic layer was dried over Na₂SO₄, and concentrated at low pressure. The residue was purified by silica gel column (DCM/MeOH = 100/2) to give **34-3** (19 g, 81%) as a white solid.

[0257] Compound **34-3** (19 g, 31.3 mmol) was co-concentrated with anhydrous pyridine for 3 times. To an ice-cooled solution of **34-3** in anhydrous pyridine (120 mL) was added a solution of TsCl (6.6 g, 34.6 mmol) in pyridine (40 mL) dropwise at 0°C. The mixture was stirred at 0 °C for 16 h. The mixture was quenched with water, and the reaction mixture was concentrated. The residue was re-dissolved in EA (200 mL). The solution was washed with sat. aq. NaHCO₃ and brine. The organic layer was dried over anhydrous Na₂SO₄ and filtered, and the filtrate was concentrated. The residue was purified by silica gel column (DCM/MeOH = 100/1) to give **34-4** (16 g, 67 %) as a yellow solid.

[0258] To a solution of **34-4** (15 g, 19.7 mmol) in acetone (100 mL) was added NaI (30 g, 197 mmol). The mixture was refluxed overnight, and then concentrated at low pressure. The residue was purified by silica gel column (DCM/MeOH = 100/1) to give **34-5** (9 g, 63.7%) as a white solid.

[0259] To a solution of **34-5** (8 g, 11.2 mmol) in anhydrous THF (60 mL) was added DBU (5.12 g, 33.5 mmol), and the mixture was heated at 60°C overnight. The mixture was

diluted with EA, and washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated. The residue was purified by silica gel column (PE/acetone = 4/1) to give **34-6** (5.7 g, 86%) as a white solid. $^1\text{H-NMR}$ (CD_3OH , 400MHz) δ = 8.18 (s, 1H), 7.17-7.33 (m, 12H), 6.80 (d, J = 8.8 Hz, 2H), 5.98 (s, 1H), 5.40 (d, J = 8.6 Hz, 1H), 3.87 (m, 5H), 3.75 (s, 3H), 2.69 (s, 1H), 1.05 (s, 3H).

[0260] To an ice-cooled solution of **34-6** (4.44 g, 7.5 mmol) in anhydrous MeCN (45 mL) was added TEA•3HF (1.23 g, 7.6 mmol) and NIS (2.16 g, 9.5 mmol). The mixture was stirred at R.T. for 2-3 h. The reaction was quenched with sat. Na_2SO_3 and NaHCO_3 solution. The mixture was extracted with EA (3 x 100 mL). The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated at low pressure. The residue was purified by silica gel column (DCM/acetone = 100/2) to give **34-7** (4.4 g, 79.8%) as a white solid.

[0261] To a solution of **34-7** (5.36 g, 7.3 mmol) in anhydrous DCM (50 mL) was added DMAP (3.6 g, 29.8 mmol) and BzCl (3.1 g, 22.1 mmol) at 0°C. The mixture was stirred at R.T. overnight. The mixture was washed with sat. aq. NaHCO_3 and brine. The organic layer was concentrated, and the residue was purified by silica gel column (PE/EA = 5/1) to give **34-8** (5.6 g, 81.3%) as a white solid.

[0262] To a solution of **34-8** (5.0 g, 5.3 mmol) in anhydrous DMF (150 mL) was added NaOBz (7.64 g, 53 mmol) and 15-crown-5 (14 g, 68 mmol). The mixture was stirred at 90-100 °C for 48 h. The mixture was diluted with EA, and washed with water and brine. The organic layer was concentrated, and the residue was purified by silica gel column (PE/EA = 5/1) to give **34-9** (3.9 g, 78.5%) as a white solid.

[0263] Compound **34-9** in NH_3 in MeOH (7N, 60 mL) was stirred at R.T. for 18 h. The mixture was concentrated at low pressure. The residue was purified by silica gel column (DCM/acetone = 50/1) to give **34-10** (500 mg, 74.7%) as a white solid. ESI-MS: m/z 626.3 $[\text{M}+\text{H}]^+$.

[0264] To a solution of **34-10** (350 mg, 0.56 mmol) in anhydrous pyridine (4 mL) was added imidazole (50 mg, 0.72 mmol) and TBSCl (108 mg, 0.72 mmol) at 0 to 5 °C, and stirred at R.T. for 15 h. The reaction was quenched with absolute EtOH (0.5 mL). The solution was concentrated to dryness under reduced pressure. The residue was dissolved in EA (150 mL), and washed with water, sat. NaHCO_3 and brine. The combined organic layers were dried over Na_2SO_4 , filtered and evaporated at low pressure. The residue was purified by silica gel column (10-30% EA in hexanes) to give **34-11** (338 mg, 81.8%) as a white solid.

[0265] To a solution of compound **34-11** (328 mg, 0.44 mmol), AgNO_3 (226 mg, 1.33 mmol) and collidine (0.59 mL, 4.84 mmol) in anhydrous DCM (4 mL) was added MMTTrCl (410

mg, 1.33 mmol) under N₂. The mixture was stirred at R.T. overnight under N₂, and monitored by TLC to completion. The mixture was filtered through pre-packed Celite filter, and the filtrate was washed with water, 50% aqueous citric acid, and brine. The organic layer was separated, dried over anhydrous Na₂SO₄, filtered and concentrated at low pressure. The residue was purified by silica gel column (EA in hexanes from 0% to 30%) to give **34-12** (337 mg).

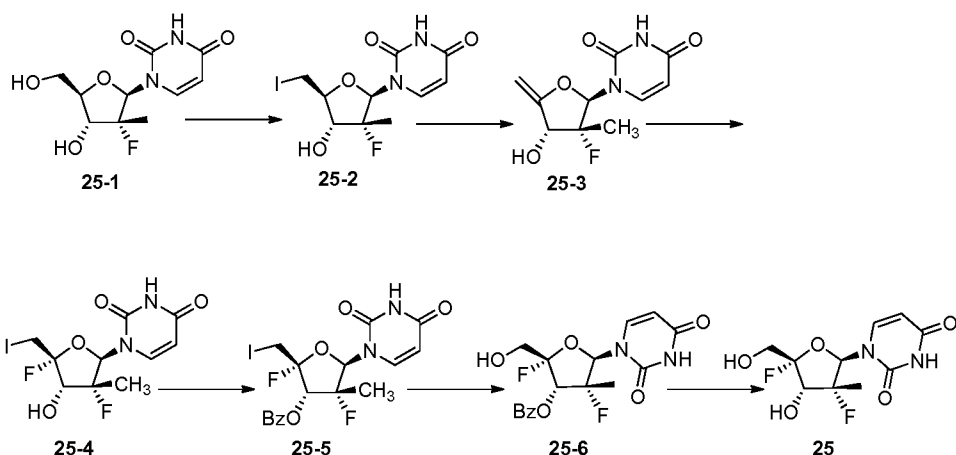
[0266] To a solution of **34-12** (337 mg, 0.33 mmol) in anhydrous THF (4 mL) was added 1.0 M solution of TBAF (0.66 mL, 0.66 mmol) at 0 to 5°C. The reaction was slowly warmed to R.T., and stirred for 1 h. The mixture was quenched with silica gel, and filtered. The solvents were evaporated to give the crude product, which was purified by silica gel column (EA in hexanes from 0% to 50%) to give **34-13** (188 mg).

[0267] To a stirred solution of **34-13** (180 mg, 0.16 mmol) in anhydrous CH₃CN (2.5 mL) was added N-methylimidazole (132 µL, 1.6 mmol) at 0-5 °C (ice/water bath) followed by solution of phenyl (cyclohexanoxo-L-alaninyl) phosphorochloridate (207 mg, 0.6 mmol, dissolved in 2mL of CH₃CN). The solution was stirred at R.T. for 2.5 h, and the mixture was diluted with EA followed by addition of water (15 mL). The solution was washed H₂O, 50 % aqueous citric acid solution and brine. The organic layer was separated, dried over anhydrous MgSO₄ and filtered. The filtrate was concentrated in vacuum to give a residue, which was purified on silica gel with 0 to 40% EA/hexanes to give **34-14** (75.8 mg) and **34-15** (108 mg) as a slower eluting isomer.

[0268] Compound **34-14** (76 mg, 0.063 mmol) was dissolved in anhydrous CH₃CN (0.5 mL), and 4N HCl in dioxane (47 µL) was added at 0 to 5 °C (ice/ water bath). The mixture was stirred at R.T. for 40 mins, and anhydrous EtOH (200 µL) was added. The solvents were evaporated at R.T. and co-evaporated with toluene 3 times. The residue was dissolved in 50% CH₃CN/ H₂O, purified on a reverse-phase HPLC (C18) using acetonitrile and water, and lyophilized to give compound **34** (26.6 mg). ESI-LCMS: m/z = 663.3 [M+H]⁺.

[0269] Compound **34-15** (108 mg, 0.089 mmol) was dissolved in anhydrous CH₃CN (0.7 mL), and 4N HCl in dioxane (67 µL) was added at 0 to 5 °C (ice/ water bath). The mixture was stirred at R.T. for 60 mins, and anhydrous EtOH (200 µL) was added. The solvents were evaporated at R.T. and co-evaporated with toluene 3 times. The residue was dissolved in 50% CH₃CN/ H₂O, purified on a reverse-phase HPLC (C18) using acetonitrile and water, and lyophilized to give compound **35** (40.3 mg). ESI-LCMS: m/z = 663.2 [M+H]⁺.

EXAMPLE 12
COMPOUND 25



[0270] To a solution of **25-1** (260 mg, 1 mmol), PPh₃ (780 mg, 3 mmol) and pyridine (0.5 mL) in anhydrous THF (8 mL) were added I₂ (504 mg, 2 mmol) at R.T., and the mixture was stirred at R.T. for 12 h. The mixture was diluted with EtOAc and washed with 1M HCl solution. The organic layer was dried over Na₂SO₄, filtered and concentrated at low pressure. The residue was purified by silica gel column (5% MeOH in DCM) to give **25-2** (190 mg, 85%) as a white solid.

[0271] To a solution of **25-2** (190 mg, 0.52 mmol) in THF (4 mL) was added DBU (760 mg, 5 mmol) at R.T., and the mixture was heated at 50 °C overnight. The mixture was diluted with EtOAc, and washed with water. The organic layer was dried over anhydrous Na₂SO₄ and concentrated at low pressure. The residue was purified by silica gel column (30% EA in PE) to give **25-3** (75 mg, 52%) as a white solid.

[0272] To a solution of **25-3** (200 mg, 0.82 mmol) in MeCN (anhydrous, 4 mL) was added NIS (337 mg, 1.5 mmol) and TEA•3HF (213 mg, 1.25 mmol) at R.T., and the mixture was stirred at R.T. for 7 h. The reaction was quenched with sat. Na₂SO₃ solution and sat. aq. NaHCO₃ solution. The mixture was extracted with EA. The organic layer was separated, dried over anhydrous Na₂SO₄, and concentrated at low pressure. The residue was purified by silica gel column (20% EA in PE) to give **25-4** (300 mg, 62%) as a white solid.

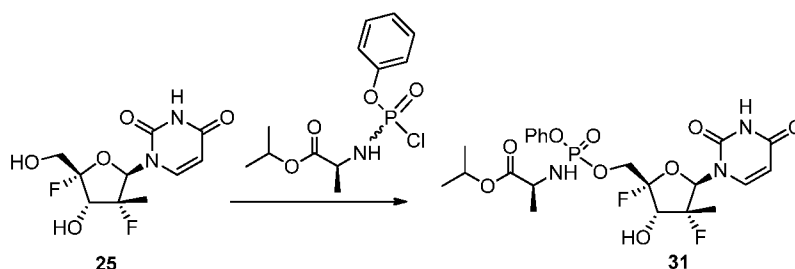
[0273] To a solution of **25-4** (194 mg, 0.5 mmol) in pyridine (5 mL) was added BzCl (92 mg, 0.55 mmol) at 0°C. The mixture was stirred at R.T. for 5 h, and the reaction was quenched with water. The mixture was concentrated at low pressure, and the residue was purified by silica gel column (20% EA in PE) to give **25-5** (397 mg, 81%) as a white solid.

[0274] To a solution of **25-5** (1.05 g, 2.13 mmol) in DCM (12 mL) was added a mixture of TFA (0.5 mL) and Bu₄NOH (1 mL), followed by addition of *m*-CPBA (1.3 g, 6 mmol) at R.T. The mixture was stirred at R.T. for 5 h. The mixture was washed with sat.

Na₂SO₃ solution and aq. NaHCO₃ solution. The organic layer was dried over anhydrous Na₂SO₄, and concentrated at low pressure. The residue was purified by silica gel column (30% EA in PE) to give **25-6** (450 mg, 63%) as a white solid.

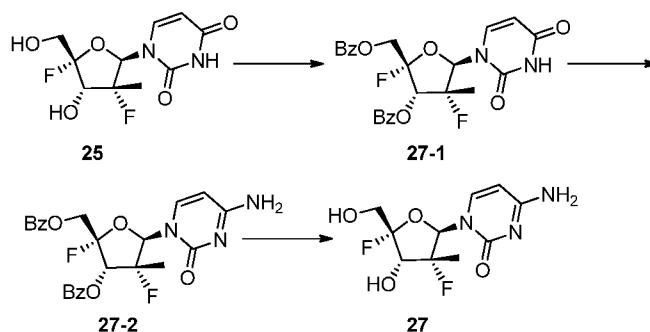
[0275] Compound **25-6** (250 mg, 0.65 mmol) was dissolved in NH₃/MeOH (5 mL). The mixture was stirred at R.T. for 5 h, and then concentrated at low pressure. The residue was purified by silica gel column (5% MeOH in DCM) to give compound **25** (120 mg, 66%) as a white powder. ESI-MS: m/z 279.0 [M+H]⁺.

EXAMPLE 13 **COMPOUND 31**



[0276] To a stirred solution of compound **25** (100 mg, 0.36 mmol) in anhydrous THF (3.0 mL) was added N-methylimidazole (236 μ L, 2.87 mmol) at 0 °C (dry ice/acetone bath) followed by a solution of the phosphorochloridate (329 mg, 1.08 mmol, dissolved in 2 mL of THF). The solution was stirred at 0 °C for 1 h, the reaction temperature was raised up-to 10 °C during the next 1 h, and the solution was left at 10 °C for the next 4 h. The mixture was cooled to 0 to 5 °C, diluted with EA, and water was added (15 mL). The solution was washed H₂O, 50 % aqueous citric acid solution and brine. The organic layer was separated, dried over anhydrous MgSO₄ and filtered. The filtrate was concentrated in vacuum to give a residue, which dissolved in 25% CH₃CN/ H₂O. The residue was purified on a reverse-phase HPLC (C18) using acetonitrile and water, followed by lyophilization to give a mixture of two isomers of compound **31** (17.5 mg). MS: m/z 546.05 [M-H]⁻.

EXAMPLE 14 **COMPOUND 27**

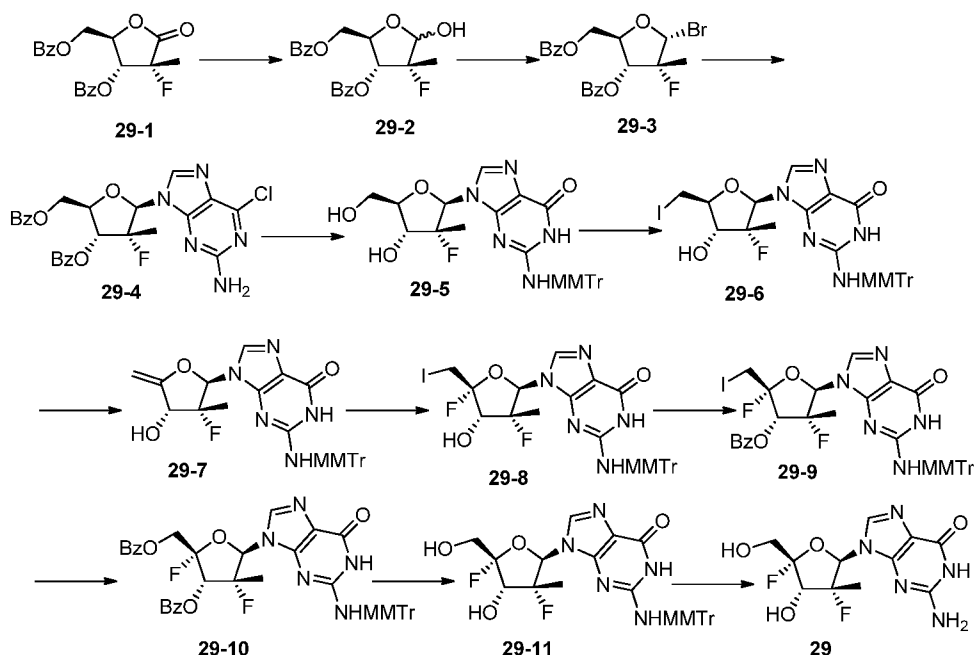


[0277] To a solution of compound **25** (139 mg, 0.5 mmol) in pyridine (5 mL) was added BzCl (92 mg, 0.55 mmol) at 0°C. The mixture was stirred at R.T. for 5 h, diluted with EtOAc and washed with 1N HCl solution. The organic layer was dried over anhydrous Na₂SO₄, and concentrated at low pressure. The residue was purified by silica gel column (20% EA in PE) to give **27-1** (274 mg, 79%) as a white solid.

[0278] To a solution of **27-1** (490 mg, 1 mmol), DMAP (244 mg, 2 mmol) and TEA (205 mg, 2.1 mmol) in MeCN (10 mL) were added TPSCl (604 mg, 2 mmol) at 0°C. The mixture was stirred at R.T. for 2 h., and then NH₄OH aq. was added at R.T. The mixture was stirred for 0.5 h, diluted with EtOAc and washed with sat. aq. NaHCO₃ and brine. The organic layer was dried over anhydrous Na₂SO₄, and concentrated at low pressure. The residue was purified by silica gel column (30% EA in PE) to give **27-2** (250 mg, 41%) as a white solid.

[0279] Compound **27-2** (250 mg, 0.51 mmol) was dissolved in NH₃/MeOH (15 mL). The mixture was stirred at R.T. for 5 h. and then concentrated at low pressure. The residue was purified by silica gel column (5% DCM in DCM) to give compound **27** (95 mg, 66%) as a white powder. ESI-MS: m/z 278.1 [M+H]⁺.

EXAMPLE 15 COMPOUND 29



[0280] To a solution of compound **29-1** (30 g, 0.08 mol) in anhydrous THF (300 mL) was added a solution of lithium tri-tert-butoxyaluminumhydride (120 mL, 0.12 mol) dropwise at -78 °C under N₂. The mixture was stirred at -20 °C for 1 h. The reaction was quenched with sat. aq. NH₄Cl and then filtered. The filtrate was extracted with EA (3 x 300 mL). The organic

layer was dried over anhydrous Na_2SO_4 , and concentrated at low pressure. The residue was purified by silica gel column (10% EA in PE) to give **29-2** (26 g, 86%) as a colorless oil.

[0281] To a stirred solution of PPh_3 (37.7 g, 0.144 mol) in DCM (100 mL) was added compound **29-2** (27 g, 0.072 mol) at -20°C under N_2 . After the mixture was stirred at R.T. for 15 mins, CBr_4 (42 g, 0.129 mol) was added while maintaining the reaction temperature between -25 and -20°C under N_2 . The mixture was then stirred below -17°C for 20 mins. Silica gel was added into the solution, and then purified by flash silica gel column separation to give the crude oil product. The crude was purified by silica gel column (EA in PE from 2% to 20%) to give **29-3** (α -isomer, 17 g, 55%) as a colorless oil.

[0282] A mixture of 6-Cl-guanine (11.6 g, 68.8 mmol) and t-BuOK (8.2 g, 73 mmol) in t-BuOH (200 mL) and MeCN (150 mL) was stirred at 35°C for 30 mins, and then **29-3** (10 g, 22.9 mmol) in MeCN (100 mL) was added at R.T. The mixture was heated at 50°C overnight. The reaction was quenched with a solution of NH_4Cl (5 g) in water (40 mL), and the mixture was filtered. The filtrate was evaporated at low pressure. The residue was purified by silica gel column (20% EA in PE) to give **29-4** (6 g, 42%) as a yellow solid.

[0283] To a solution of **29-4** (12.5 g, 23.8 mmol) in DCM (50 mL) was added AgNO_3 (8.1 g, 47.6 mmol), collidine (5.77 g, 47.6 mmol) and MMTrCl (11 g, 35.7 mmol). The mixture was stirred at R.T. overnight. The reaction was quenched with MeOH (5 mL), filtered and concentrated at low pressure. The residue was purified by silica gel column (5% MeOH in DCM) to give the intermediate (16 g, 86%) as a yellow solid. To a solution of $\text{HOCH}_2\text{CH}_2\text{CN}$ (4.7 g, 66 mmol) in THF (200 mL) was added NaH (3.7 g, 92 mmol) at 0°C . The mixture was stirred at R.T. for 30 mins. A solution of the intermediate (10.5 g, 13 mmol) in THF (50 mL) was added, and the reaction mixture was stirred at R.T. for 12 h. The reaction was quenched with MeOH (2 mL), diluted with EA (100 mL), and washed with brine. The organic layer was dried over anhydrous Na_2SO_4 , and concentrated at low pressure. The residue was purified by silica gel column (5% MeOH in DCM) to give **29-5** (5.8 g, 77%) as a yellow solid.

[0284] To a solution of PPh_3 (7.0 g, 26.6 mmol) in anhydrous pyridine (100 mL) was added I_2 (6.3 g, 24.9 mmol), and stirred at R.T. for 30 mins. The mixture was treated with a solution of **29-5** (9.5 g, 16.6 mmol) in pyridine (40 mL). The mixture was stirred at R.T. overnight. The reaction was quenched with sat. $\text{Na}_2\text{S}_2\text{O}_3$ solution, and the mixture was extracted with EA. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 , and concentrated at low pressure. The residue was purified by silica gel column (30% EA in PE) to give **29-6** (7 g, 66%) as a yellow solid.

[0285] To a solution of **29-6** (7.5 g, 11 mmol) in dry THF (50 mL) was added DBU (5.4 g, 33 mmol), and the mixture was heated to reflux for 4 h. The mixture was diluted with EA (3 x 100 mL), and washed with brine. The organic layer was dried over anhydrous Na₂SO₄, and concentrated at low pressure. The residue was purified by silica gel column (30% EA in PE) to give **29-7** (4.0 g, 67%) as a white solid.

[0286] To an ice-cooled solution of **29-7** (3.0 g, 5.4 mmol) in anhydrous MeCN (20 mL) was added TEA•3HF (0.65 g, 4.1 mmol) and NIS (1.53 g, 6.78 mmol) at R.T., and the reaction mixture was stirred at R.T. for 2 h. The mixture was diluted with EA (50 mL), and washed with sat. Na₂S₂O₃ solution and NaHCO₃ aq. The organic layer was dried over anhydrous Na₂SO₄, and concentrated to dryness at low pressure. The residue was purified by prep-HPLC (0.1% HCOOH in water and MeCN) to separate the two isomers (about 1:1). NOE showed the polar one was **29-8** (0.6 g, 16%) as a white solid.

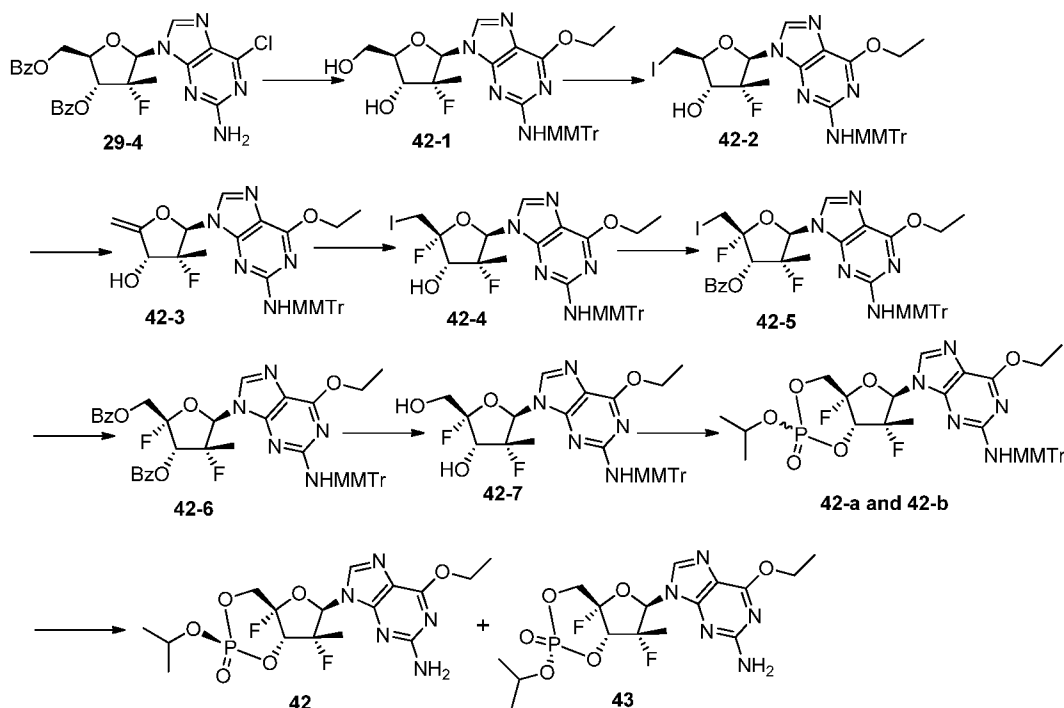
[0287] To a solution of **29-8** (0.7 g, 1 mmol) in dry pyridine (10 mL) was added BzCl (147 mg, 1.05 mmol) at 0°C. The mixture was stirred at R.T. for 3 h. The mixture was then diluted with EA, and washed with sat. NaHCO₃ aq. and brine. The organic layer was dried over Na₂SO₄, and evaporated at low pressure. The residue was purified by silica gel column (20% EA in PE) to give **29-9** (0.65 g, 81%) as a white solid.

[0288] To a solution of **29-9** (0.65 g, 0.8 mmol) in dry DMF (40 mL) was added NaOBz (1.15 g, 8 mmol) and 15-crown-5 (1.77 g, 8 mmol). The mixture was stirred at 100 °C for 48 h. The solvent was evaporated at low pressure, and the residue was dissolved in EA (30 mL), and washed with water and brine. The organic layer was dried over Na₂SO₄ and concentrated at low pressure. The residue was purified by silica gel column (20% EA in PE) to give **29-10** (500 mg, 78%) as a white solid.

[0289] Compound **29-10** (400 mg, 0.5 mmol) in NH₃/MeOH (7N, 100 mL) was stirred at R.T. for 18 h. The mixture was concentrated at low pressure, and the residue was purified by silica gel column (5% MeOH in DCM) to give **29-11** (220 mg, 63%) as a white solid. ESI-MS: m/z 590.3 [M+H]⁺.

[0290] Compound **29-11** (59 mg, 0.1 mmol) was dissolved in 50% TFA in methanol (10 mL), and the mixture was kept at R.T. for 2 h. The solvent was evaporated and co-evaporated with a methanol/toluene mixture to remove traces of the acid. The residue was suspended in CH₃CN (1 mL) and centrifuged. The precipitate was washed with CH₃CN (1mL) and dried. Compound **29** was obtained as a colorless solid (21 mg, 65%. MS: m/z 316.2 [M-1]).

EXAMPLE 16
COMPOUNDS 42 AND 43



[0291] A freshly prepared EtONa in dry EtOH (2N, 150 mL) was added to a solution of **29-4** (13.67 g, 17.15 mmol) in EtOH (50 mL) at 0°C. The mixture was stirred at R.T. for 1 h, and then concentrated at low pressure. The residue was purified by silica gel column (5% MeOH in DCM) to give **42-1** (10 g, 98%) as a yellow solid.

[0292] To a solution of PPh₃ (2.73 g, 10.4 mol) in anhydrous pyridine (60 mL) was added I₂ (2.48 g, 9.76 mmol) at R.T., and the reaction mixture was stirred R.T. for 30 mins. A solution of **42-1** (3.9 g, 6.51 mmol) in pyridine (10 mL) was added. The mixture was stirred at R.T. overnight. The reaction was quenched with sat. Na₂S₂O₃ solution and NaHCO₃ aq., and then extracted with EA (100 mL). The organic layer was dried over anhydrous Na₂SO₄, and evaporated at low pressure. The residue was purified by silica gel column (2% MeOH in DCM) to give **42-2** (3.0 g, 75%) as a yellowed solid.

[0293] To a solution of **42-2** in dry THF (300 mL) was added DBU (14.0 g, 91.8 mmol), and the mixture was heated to reflux for 3 h. The mixture was concentrated at low pressure. The residue was dissolved in EA (100 mL), and washed with brine. The organic layer was dried over anhydrous Na₂SO₄, and evaporated at low pressure. The residue was purified by silica gel column (20% EA in PE) to give **42-3** (0.6 g, 37.5%) as a white solid.

[0294] To an ice-cooled solution of **42-3** (2.0 g, 3.44 mmol) in anhydrous MeCN (20 mL) was added NIS (0.975 g, 4.3 mmol) and TEA•3HF (0.82 g, 5.16 mmol) at 0°C. The mixture was stirred at R.T. for 2 h. The reaction was quenched with sat. Na₂SO₃ and NaHCO₃

aqueous solution, and then concentrated at low pressure. The residue was dissolved in EA (50 mL), washed with brine, dried over anhydrous Na₂SO₄, and evaporated at low pressure. The residue was purified by silica gel column (20% EA in PE) to give **42-4** (1.5 g, 60%) as a white solid.

[0295] To a solution of **42-4** (1 g, 1.37 mmol) in dry pyridine (100 mL) was added BzCl (0.23 g, 1.65 mmol) at 0°C. The reaction was stirred for 30 mins and checked by LCMS. The mixture was concentrated at low pressure, and the residue was dissolved in EA (50 mL). The solution was washed with brine. The organic layer was dried over MgSO₄, and evaporated at low pressure. The residue was purified by silica gel column chromatography (10% EA in PE) to give **42-5** (0.9 g, 78%) as a white solid.

[0296] To a solution of **42-5** (2 g, 2.4 mmol) in dry DMF (40 mL) was added NaOBz (3.46 g, 24 mmol) and 15-crown-5 (4.5 mL). The mixture was stirred at 95 °C for 72 h. The mixture was then diluted with EA (100 mL), and washed with water and brine. The organic phase was dried over MgSO₄, and concentrated at low pressure. The residue was purified by silica gel column (15% EA in PE) to give **42-6** (1.5 g, 75%) as a white solid.

[0297] Compound **42-6** (1.35 g, 1.64 mmol) in NH₃/MeOH (150 mL) was stirred at R.T. for 18 h. The mixture was concentrated at low pressure, and the residue was purified by silica gel column (5% MeOH in DCM) to give **42-7** (0.9 g, 90%) as a white solid. ESI-MS: m/z 618.3 [M+H]⁺.

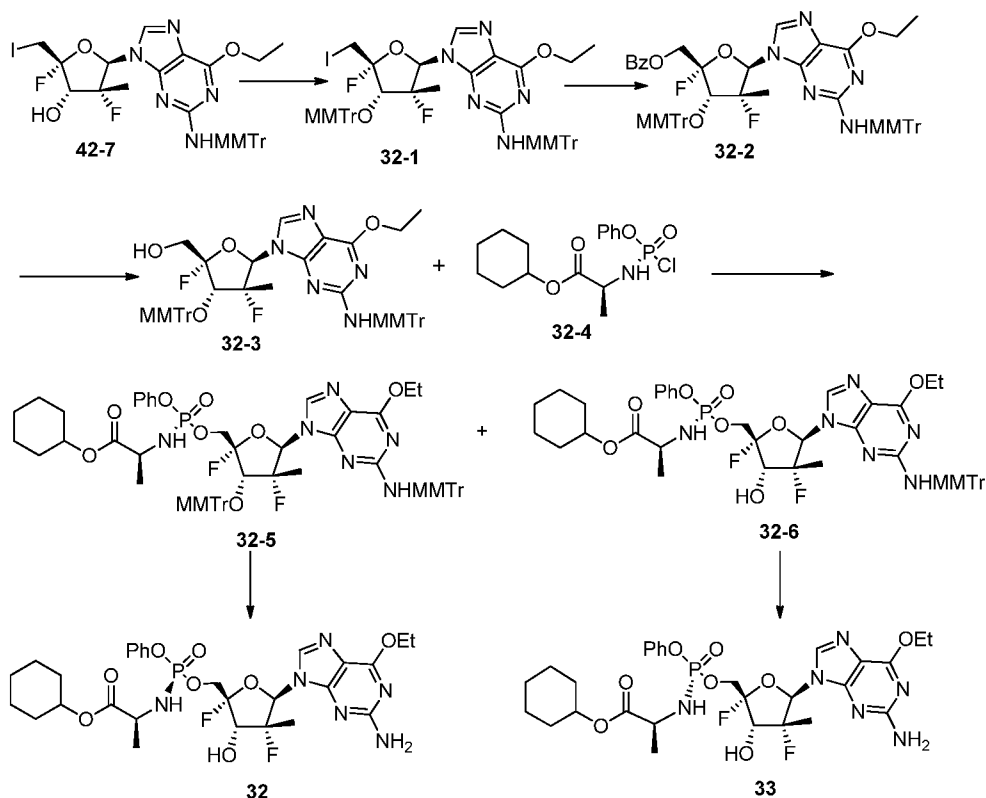
[0298] To a solution of **42-7** (99 mg, 0.16 mmol) in DCM (1.0 mL), triethylamine (92.7 µL, 0.64 mmol) was added at R.T. The mixture was cooled to 0 to 5°C (ice/water bath), and freshly prepared and distilled isopropyl phosphorodichloridate (36.6 µL, 0.2 mmol, prepared according to a procedure, Reddy *et al. J. Org. Chem.* **2011**, 76 (10), 3782-3790) was added to the mixture. The mixture was stirred 0 to 5°C (ice/ water bath) for 15 mins, followed by addition of N-methylimidazole (26.3 µL, 0.32 mmol). The mixture was then stirred for 1 h at 0 to 5°C. TLC showed absence of **42-7**. EA (100 mL) was added, followed by water. The organic layer was washed H₂O, saturated aqueous NH₄Cl solution and brine. The organic layer was separated, dried over anhydrous MgSO₄ and filtered. The filtrate was concentrated in vacuum to give a residue, which was purified on silica gel with 0 to 10% iPrOH/ DCM to give a mixture of **42-a** and **42-b** (61.5 mg).

[0299] A mixture of **42-a** and **42-b** (61.5mg, 0.085 mmol) was dissolved in anhydrous CH₃CN (0.5 mL), and 4N HCl in dioxane (64 µL) was added at 0 to 5 °C (ice/ water bath). The mixture was stirred at R.T. for 40 mins, and anhydrous EtOH (200 µL) was added. The solvents were evaporated at R.T. and co-evaporated with toluene 3 times. The residue was

dissolved in 50% CH₃CN/H₂O, was purified on a reverse-phase HPLC (C18) using acetonitrile and water, followed by lyophilization to give compound **42** (1.8 mg) and compound **43** (14.5 mg).

[0300] Compound **42**: ¹H NMR (CD₃OD-d₄, 400 MHz) δ 8.0 (s, 1H), 6.69 (d, *J* = 16.0 Hz, 1H), 5.9-5.6 (br s, 1H), 4.94-4.85 (m, 1H), 4.68-4.52 (m, 3H), 1.49-1.3 (m, 12H); ¹⁹F NMR (CD₃OD-d₄) δ -122.8 (s), -160.06 (s); ³¹P NMR (CD₃OD-d₄) δ -7.97 (s). ESI-LCMS: *m/z* = 450.1 [M+H]⁺; Compound **43**: ¹H NMR (CD₃OD-d₄, 400 MHz) δ 7.96 (s, 1H), 6.68 (s, 1H), 6.69 (d, *J* = 16.8 Hz, 1H), 6.28-6.1 (br s, 1H), 4.81-4.5 (m, 4H), 1.45-1.39 (m, 12H); ³¹P NMR (CD₃OD-d₄) δ -5.84 (s). ESI-LCMS: *m/z* = 450.0 [M+H]⁺.

EXAMPLE 17 COMPOUNDS 32 AND 33



[0301] To a solution of **42-7** (0.47 g, 0.65 mmol) in DCM (3 mL) was added AgNO₃ (0.22 g, 1.29 mmol), collidine (0.15 g, 1.29 mmol) and MMTTrCl (0.3 g, 0.974 mmol) at 0°C. The mixture was stirred at R.T. overnight. The mixture was filtered, and the filter was washed with sat. aq. NaHCO₃ solution and brine. The organic layer was separated, dried over anhydrous Na₂SO₄ and concentrated at low pressure. The residue was purified by silica gel column to give **32-1** (0.55, 85%) as a white solid.

[0302] To a solution of **32-1** (0.5 g, 0.5 mmol) in dry DMF (10 mL) was added NaOBz (0.72 g, 5 mmol) and 15-crown-5 (0.9 mL). The mixture was stirred at 95 °C for 72 h.

The mixture was diluted with EA, and washed with water and brine. The organic phase was dried over MgSO_4 and concentrated at low pressure. The residue was purified by silica gel column (10% EA in PE) to give **32-2** (0.3 g, 60%) as a white solid.

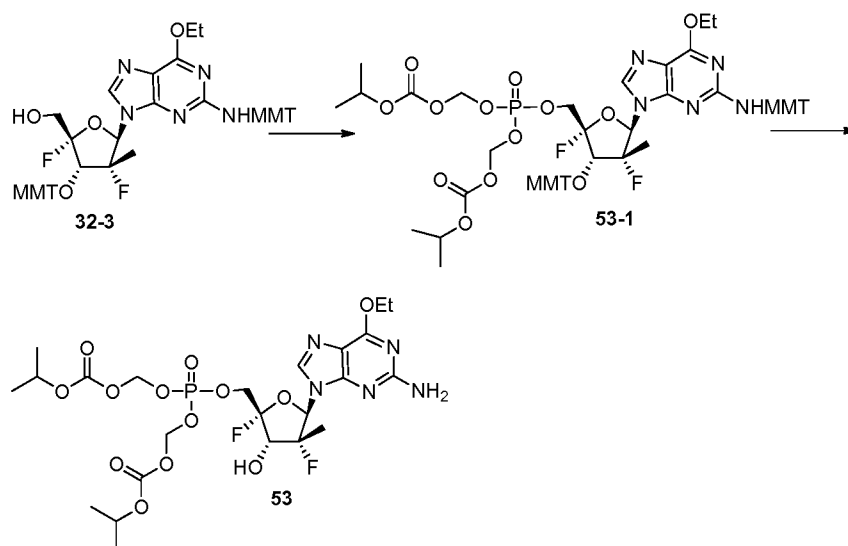
[0303] Compound **32-2** (0.3 g, 0.3 mmol) in NH_3/MeOH (30 mL) was stirred at R.T. for 18 h. The mixture was concentrated at low pressure, and the residue was purified by silica gel column (20% EA in PE) to give **32-3** (145 mg, 56%) as a white solid. ESI-LCMS: m/z 890.5 $[\text{M}+\text{H}]^+$.

[0304] To a stirred solution of **32-3** (161 mg, 0.16 mmol) in anhydrous CH_3CN (2.0 mL) was added N-methylimidazole (118 μL , 2.87 mmol) at 0 to 5 $^\circ\text{C}$ (ice/water bath) followed by solution of **32-4** (186 mg, 0.54 mmol, dissolved in 2 mL of CH_3CN). The solution was stirred at 0 to 5 $^\circ\text{C}$ for 4 h. The mixture was diluted with EA, and water was added (15 mL). The solution was washed H_2O , 50 % aqueous citric acid solution and brine. The organic layer was separated, dried over anhydrous MgSO_4 and filtered. The filtrate was concentrated in vacuum to give a residue, which was purified on silica gel with 0 to 40% EA/hexanes to give as **32-5** (82.6 mg) as the faster eluting isomer and **32-6** (106 mg) as the slower eluting isomer.

[0305] Compound **32-5** (82.6 mg, 0.07 mmol) was dissolved in anhydrous CH_3CN (0.5 mL), and 4N HCl in dioxane (35 μL) was added at 0 to 5 $^\circ\text{C}$. The mixture was stirred at R.T. for 1 h, and anhydrous EtOH (100 μL) was added. The solvents were evaporated at R.T. and co-evaporated with toluene 3 times. The residue was dissolved in 50% $\text{CH}_3\text{CN}/\text{H}_2\text{O}$, and purified on a reverse-phase HPLC (C18) using acetonitrile and water, followed by lyophilization to give compound **32** (19.4 mg). ^1H NMR ($\text{CD}_3\text{OD}-d_4$, 400 MHz) δ 7.9 (s, 1H), 7.32-7.28 (t, J = 8.0 Hz, 2H), 7.2-7.12 (m, 3H), 6.43 (d, J = 17.6 Hz, 1H), 4.70-4.63 (m, 2H), 4.55-4.4 (m, 3H), 3.94-3.9 (m, 1H), 1.79-1.67 (m, 4H), 1.53-1.49 (m, 1H), 1.45-1.22 (m, 15H); ^{31}P NMR ($\text{CD}_3\text{OD}-d_4$) δ 4.06 (s); ESI-LCMS: m/z = 655.2 $[\text{M}+\text{H}]^+$, 653.15 $[\text{M}-\text{H}]^-$.

[0306] Compound **32-6** (100 mg, 0.083 mmol) was dissolved in anhydrous CH_3CN (0.5 mL), and 4N HCl in dioxane (50 μL) was added at 0 to 5 $^\circ\text{C}$. Following the procedure for obtaining compound **32**, compound **33** (31.8 mg) was obtained. ^1H NMR ($\text{CD}_3\text{OD}-d_4$, 400 MHz) δ 7.93 (s, 1H), 7.33-7.29 (m, 2H), 7.24-7.14 (m, 3H), 6.41 (d, J = 17.6 Hz, 1H), 4.70-4.60 (m, 2H), 4.54-4.49 (m, 2H), 4.44-4.39 (m, 1H), 3.92-3.89 (m, 1H), 1.77-1.66 (m, 4H), 1.54-1.24 (m, 16H); ^{31}P NMR ($\text{CD}_3\text{OD}-d_4$) δ 3.91 (s); ESI-LCMS: m/z = 655.2 $[\text{M}+\text{H}]^+$, 653.1 $[\text{M}-\text{H}]^-$.

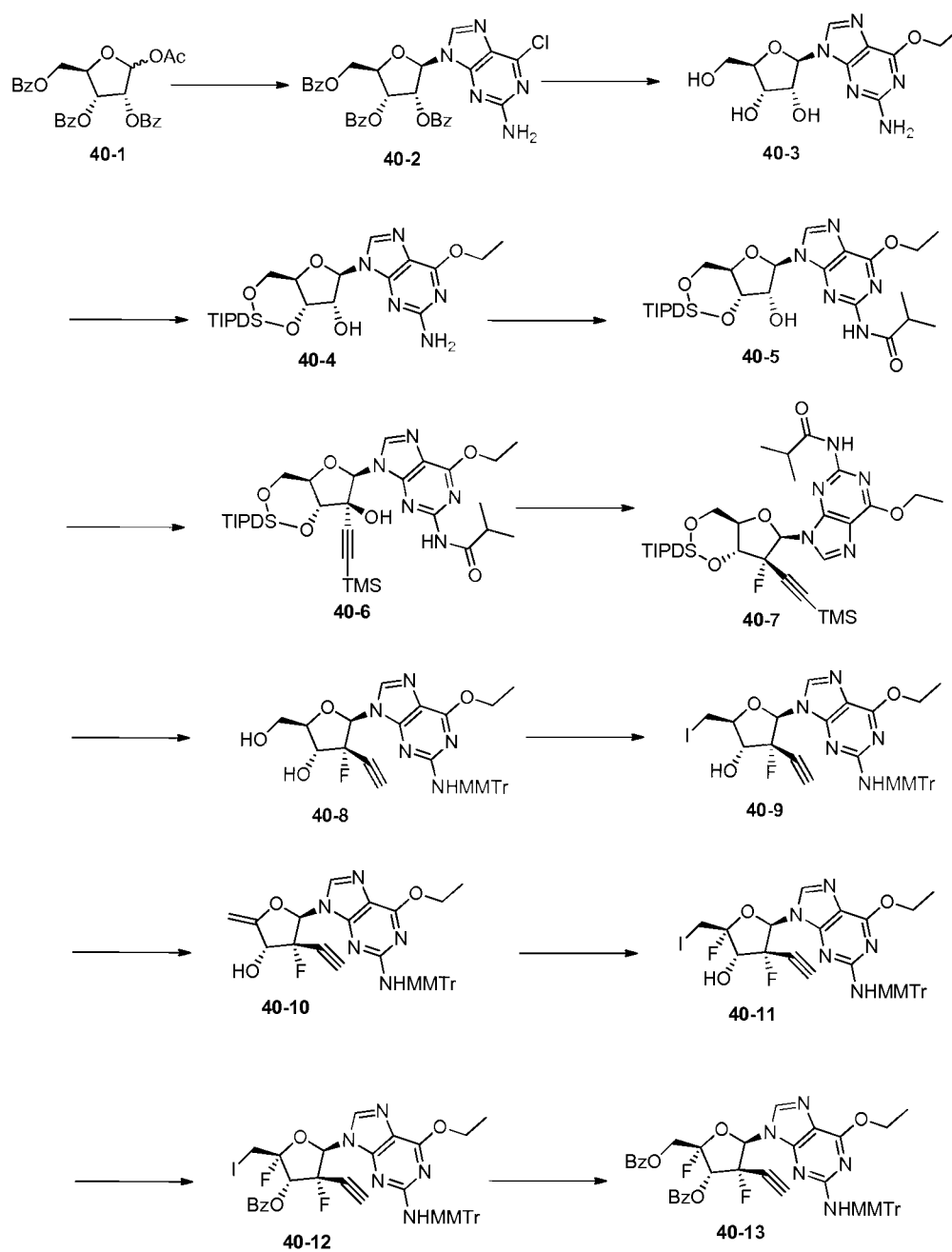
EXAMPLE 18
COMPOUND 53

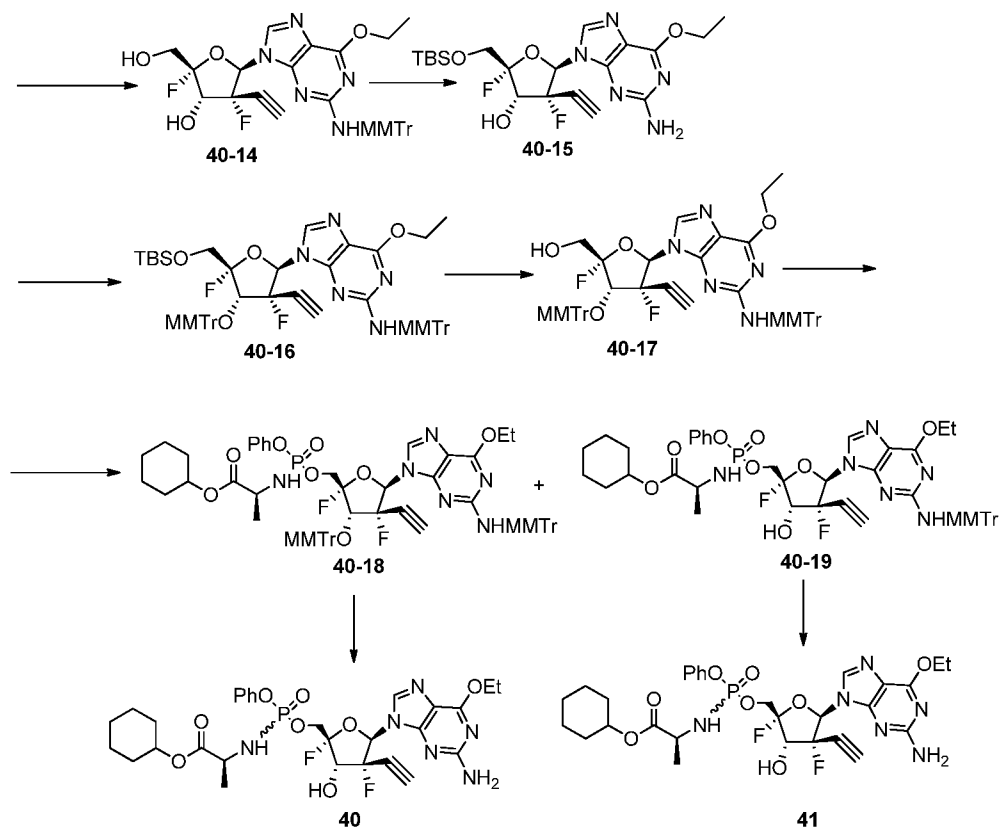


[0307] Compound **53-1** (70 mg, 58%) was prepared from **32-3** (90 mg; 0.1 mmol) and triethylammonium bis(isopropoxyloxycarbonyloxymethyl)phosphate (0.2 mmol) with DIPEA (87 μ L), BopCl (44 mg), and 3-nitro-1,2,4-triazole (29 mg) in THF (2 mL) according to a method described for compound 51-2. Purification was done with hexanes/EtOAc solvent system, 20-80% gradient.

[0308] Compound **53** (25 mg, 64%) was prepared from **53-1** (70 mg) in acetonitrile (0.6 mL) and 4 N HCl/dioxane (50 μ L) according to a method described for compound 51. MS: $m/z = 658 [M+1]^+$.

EXAMPLE 19
COMPOUNDS 40 AND 41





[0309] To a mixture of pre-silylated 6-Cl-guanine (using HMDS and $(\text{NH}_4)_2\text{SO}_4$) (25.2 g, 150 mmol) in DCE (300 mL) was added **40-1** (50 g, 100 mmol) and TMSOTf (33.3 g, 150 mmol) at 0°C. The mixture was stirred at 70 °C for 16 h, and then concentrated at low pressure. The residue was re-dissolved in EA, and washed with sat. aq. NaHCO_3 and brine. The organic layer was dried over anhydrous Na_2SO_4 , and concentrated at low pressure. The residue was purified on silica gel column (PE/EA = 2/1) to give pure **40-2** (45 g, 73%) as a white solid.

[0310] To a solution of **40-2** (45 g, 73.4 mmol) in EtOH (73 mL) was added with EtONa (1N in EtOH, 360 mL). The mixture was stirred at R.T. for 16 h. The mixture was then concentrated to give a residue, which was purified by silica gel column (DCM/MeOH = 10/1) to give pure **40-3** (19 g, 83%) as a white solid.

[0311] To a solution of **40-3** (19 g, 61.1 mmol) in pyridine (120 mL) was added with TIPDSCl₂ (19.2 g, 61 mmol) dropwise at 0°C. The mixture was stirred at R.T. for 16 h, and then concentrated at low pressure. The residue was re-dissolved in EA, and washed with sat. aq. NaHCO₃. The organic layer was dried over anhydrous Na₂SO₄, and concentrated at low pressure. The residue was purified by silica gel column (DCM/MeOH = 20/1) to give pure **40-4** (22 g, 65%) as a white solid.

[0312] To a solution of **40-4** (22 g, 39.8 mmol) in DMF/pyridine (5/1, 100 mL) was added TMSCl (12.9 g, 119 mmol) dropwise at 0°C. The mixture was stirred at R.T. for 1 h and

then treated with isobutryl chloride (5.4 g, 50 mmol). The mixture was stirred at R.T. for 3 h and then quenched by NH_4OH . The mixture was concentrated at low pressure. The residue was dissolved in EA (200 mL). The solution was washed with sat. aq. NaHCO_3 , and then the organic layer was dried and concentrated at low pressure. The residue was purified by silica gel column (DCM/MeOH = 50/1) to give pure **40-5** (15 g, 60%) as a white solid.

[0313] To a solution of **40-5** (15 g, 24.1 mmol) in DCM (100 mL) was added PDC (13.5 g, 26 mmol) and Ac_2O (9.8 g, 96 mmol) at 0°C . The mixture was stirred at R.T. for 16 h. The reaction was quenched by sat. aq. NaHCO_3 , and then extracted with EA. The organic layer was dried over anhydrous Na_2SO_4 , and concentrated at low pressure. The residue was dissolved in anhydrous THF (100 mL). To a solution of TMSCH (12 g, 112 mmol) in THF (200 mL) was added n-BuLi (2.5 N, 44 mL) at -78°C . The mixture was stirred at -78°C for 15 mins and 0°C for 15 mins. The mixture was treated with a solution of crude ketone in THF at -78°C and stirred at -30°C for 2 h. The reaction was quenched by sat. aq. NH_4Cl , and then extracted by EA. The combined organic layer was dried over anhydrous Na_2SO_4 , and concentrated at low pressure. The residue was purified by silica gel column (PE/EA = 10/1) to give pure **40-6** (3.1 g, 18%) as a white solid.

[0314] To a solution of **40-6** (7 g, 7.5 mmol) and pyridine (1.4 g, 17 mmol) in DCM (35 mL) was added with DAST (5.6 g, 35 mmol) at -78°C . The mixture was stirred at -78°C for 3 h. The reaction was quenched by sat. aq. NaHCO_3 , and then extracted with EA. The combined organic layer was dried over anhydrous, and concentrated at low pressure. The residue was purified by silica gel column (PE/EA = 10/1) to give pure **40-7** (3.1 g, 18%) as a white solid.

[0315] Compound **40-7** (4.1 g, 5.7 mmol) in sat. NH_3/MeOH (100 mL) was stirred at R.T. for 16 h, and concentrated at low pressure. The residue was re-dissolved in anhydrous DCM (300 mL), and was treated with AgNO_3 (27.0 g, 160 mmol), collidine (22 mL) and MMTrCl (23.0 g, 75.9 mmol) in small portions under N_2 . The mixture was stirred at R.T. for 16 h. The mixture was filtered, and the filtrate was washed with sat. NaHCO_3 solution and brine. The organic layer was separated, dried over anhydrous Na_2SO_4 , and concentrated at low pressure. The residue was purified by silica gel column (PE/EA = 10/1) to give the pure intermediate. The intermediate was dissolved in a solution of TBAF/THF (1N, 20 mL). The mixture was stirred at R.T. for 2 h and then concentrated at low pressure. The residue was purified by silica gel column (DCM/MeOH = 50/1) to give pure **40-8** (3.0 g, 86%) as a white solid.

[0316] To a solution of **40-8** (3.0 g, 4.9 mmol) in THF (50 mL) was added imidazole (840 mg, 12 mmol), PPh₃ (3.2 g, 12 mmol), and I₂ (2.4 g, 9.2 mmol) at 0°C. The mixture was stirred at R.T. for 16 h. The reaction was quenched by sat. aq. Na₂S₂O₃, and then extracted with EA. The combined organic layer was dried over anhydrous Na₂SO₄, and concentrated at low pressure. The residue was purified by silica gel column (PE/EA= 2/1) to give crude **40-9** (4.2 g, >100%, containing TPPO) as a white solid.

[0317] To a solution of crude **40-9** in anhydrous THF (30 mL) was added DBU (2.7 g, 18 mmol), and heated to 80°C. The mixture was stirred for 1 h and checked by LCMS. The mixture was quenched by water, and extracted with EA. The organic layer was dried over anhydrous Na₂SO₄ and filtered, and the filtrate was concentrated at low pressure. The residue was purified by silica gel column (PE/EA= 2/1) to give **40-10** (2.0 g, 69%) as a white solid.

[0318] To an ice-cooled solution of **40-10** (2.0 g, 3.38 mmol) in anhydrous MeCN (15 mL) was added NIS (777 mg, 3.5 mmol) and NEt₃•3HF (536 g, 3.3 mmol) at 0°C. The mixture was stirred at R.T. for 16 h and checked by LCMS. After completion, the mixture was quenched by sat. Na₂SO₃ and sat. NaHCO₃ solution, and extracted with EA. The organic layer was separated, dried over anhydrous Na₂SO₄ and concentrated at low pressure. The residue was purified by silica gel column chromatography (PE/EA=10/1 to 3/1) to give **40-11** (2.1 g, 84.0%) as a white solid.

[0319] To a solution of crude **40-11** (2.1 g, 2.85 mmol) in anhydrous DCM (100 mL) was added DMAP (490 mg, 4 mmol), and BzCl (580 mg, 4 mmol) at 0°C. The mixture was stirred overnight and checked by LCMS. The reaction was washed with sat. NaHCO₃ solution. The organic layer was dried over anhydrous Na₂SO₄, and concentrated at low pressure. The residue was purified by silica gel column chromatography (PE/EA = 8/1 to 3/1) to give **40-12** (2.0 g, 83.4%) as a white solid.

[0320] To a solution of **40-12** (2.0 g, 2.4 mmol) in anhydrous DMF (60 mL) was added NaOBz (3.3 g, 23.0 mmol) and 15-crown-5 (5.11 g, 23 mmol). The mixture was stirred at 110 °C for 36 h. The reaction was quenched by water, and the mixture was extracted with EA. The organic layer was dried over anhydrous Na₂SO₄, and concentrated at low pressure. The residue was purified by silica gel column (PE/EA= 5/1 to 3/1) to give **40-13** (830 mg, 42.0%) as a white solid. ESI-MS: m/z 836.11 [M+H]⁺.

[0321] A solution of **40-13** (831mg, 1.0 mmol) in anhydrous n-butylamine (4 mL) was stirred at R.T. for 3 h under N₂ atmosphere. The reaction was monitored by TLC. The solvent was evaporated in vacuo, and the residue was purified by silica gel column (MeOH in

DCM from 0% to 10%) to give the crude product, which as re-purified using silica gel column to give **40-14** as a light pink solid (563 mg).

[0322] To a solution of **40-14** (560 mg, 0.89 mmol) in anhydrous pyridine (5 mL) was added imidazole (78.6 mg, 1.16 mmol) and TBSCl (202 mg, 1.34 mmol) at 0 to 5°C. The mixture was stirred at R.T. for 15 h. The reaction was quenched by adding absolute EtOH (0.3 mL). The solution was concentrated to dryness under reduced pressure, and co-evaporated with toluene 3 times. The residue was dissolved in EA (150 mL), and washed with water, sat. NaHCO₃, and brine. The combined organic layer was dried over Na₂SO₄, filtered and evaporated at low pressure. The residue was purified by silica gel column (0-20% EA in hexanes) to give **40-15** (303 mg) as a white solid.

[0323] To a solution of **40-15** (303 mg, 0.41 mmol), AgNO₃ (208 mg, 1.23 mmol) and collidine (0.55 mL, 4.51 mmol) in anhydrous DCM (4 mL) was added MMTrCl (378 mg, 1.3 mmol) under N₂. The mixture was stirred at R.T. overnight under N₂, and monitored by TLC. The mixture was filtered through pre-packed celite filter, and the filtrate was washed with water and, 50% aqueous citric acid, and brine. The organic layer was separated, dried over anhydrous Na₂SO₄, filtered and concentrated at low pressure. The residue was purified by silica gel column (EA in hexanes from 0% to 30%) to give **40-16** (374 mg, 90%).

[0324] To a solution of **40-16** (374 mg, 0.37 mmol) in anhydrous THF (4 mL) was added 1.0 M solution of TBAF (0.74 mL, 0.74 mmol) at 0 to 5°C. The mixture was stirred at R.T. for 1 h. The mixture was quenched with silica gel, and filtered. The solvents were evaporated to give the crude product, which was purified by silica gel column (EA in hexanes from 0% to 50%) to give **40-17** (265 mg).

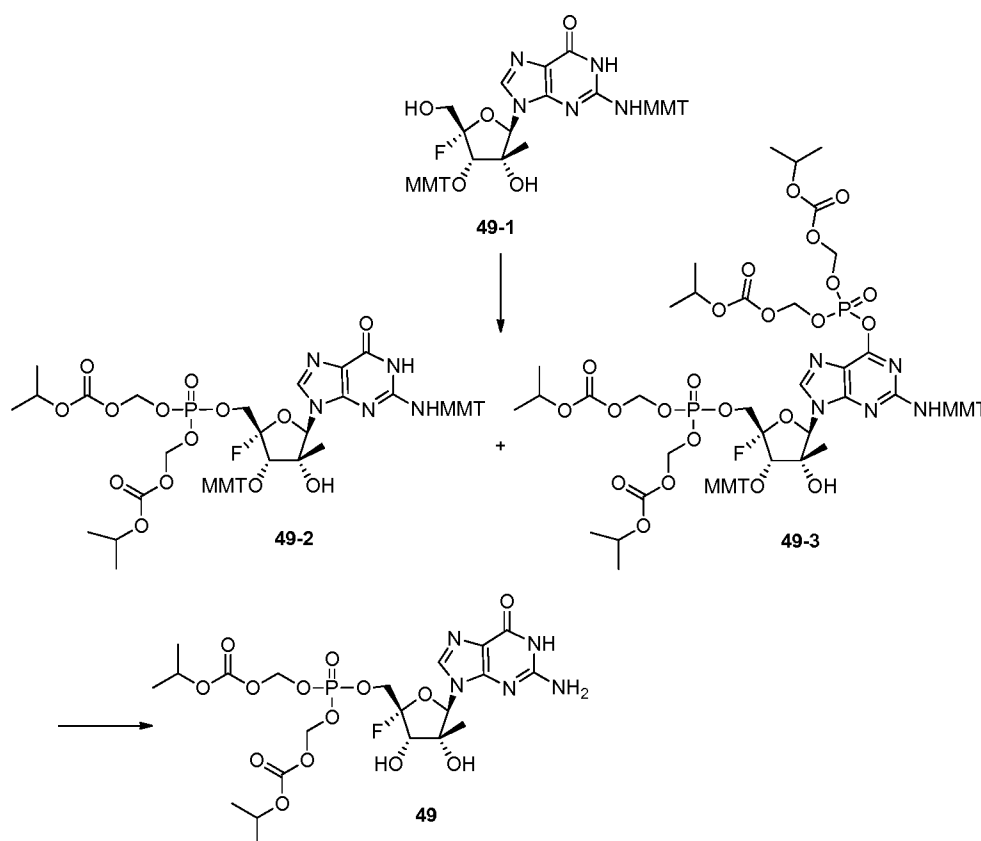
[0325] To a stirred solution of **40-17** (187.5 mg, 0.16 mmol) in anhydrous CH₃CN (2.5 mL) was added N-methylimidazole (136 µL, 1.66 mmol) at 0-5 °C (ice/water bath) followed by solution of phenyl (cyclohexanoxo-L-alaninyl) phosphorochloridate (214 mg, 0.62 mmol, dissolved in 0.5 mL of CH₃CN). The solution was stirred at R.T. for 3 h, and then diluted with EA followed by the addition of water (15 mL). The solution was washed with H₂O, 50 % aqueous citric acid solution and brine. The organic layer was separated, dried over anhydrous MgSO₄ and filtered. The filtrate was concentrated in vacuum to give a residue, which was purified on silica gel with 0 to 40% EA/hexanes to give (single isomers) of **40-18** (108 mg) Elution of the latter fraction gave (single isomers) of **40-19** (120 mg) as glassy solid.

[0326] Compound **40-18** (108mg, 0.089 mmol) was dissolved in anhydrous CH₃CN (0.5 mL), and 4N HCl in dioxane (67 µL) was added at 0 to 5 °C (ice/ water bath). The mixture was stirred at R.T. for 40 mins, and anhydrous EtOH (200 µL) was added. The solvents were

evaporated at R.T. and co-evaporated with toluene 3 times. The residue was dissolved in 50% CH₃CN/H₂O, was purified on a reverse-phase HPLC (C18) using acetonitrile and water, followed by lyophilization to give compound **40** (26.6 mg) as a white foam. ¹H NMR (CD₃OD-d₄, 400 MHz) δ 7.89 (s, 1H), 7.33-7.29 (m, 2H), 7.20-7.13 (m, 3H), 7.17 (m, 1H), 6.62 (d, J = 15.6 Hz, 1H), 5.39 (t, J = 25.2 Hz, 1H), 4.75-4.42 (m, 6H), 3.92 (t, J = 8.8 Hz, 1H), 3.24 (d, J = 5.6 Hz, 1H), 1.76-1.51 (m, 5H), 1.45-1.25 (m, 12H); ³¹P NMR (CD₃OD-d₄) δ 4.04 (s); ESI-LCMS: m/z = 665.2 [M+H]⁺.

[0327] Compound **41** (44.4 mg, single isomer) was obtained according to the procedure described for compound **40** using **40-19**. ¹H NMR (CD₃OD-d₄, 400 MHz) δ 7.93 (s, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.24 (d, J = 7.6 Hz, 2H), 7.16 (t, J = 7.6 Hz, 1H), 6.61 (d, J = 16.0 Hz, 1H), 4.68-4.60 (m, 2H), 4.54-4.39 (m, 3H), 3.93-3.89 (m, 1H), 3.24 (d, J = 5.6 Hz, 1H), 1.75-1.5 (m, 5H), 1.48-1.23 (m, 12H); ¹⁹F NMR (CD₃OD-d₄) δ -122.95 (s), -155.84-155.99 (m); ³¹P NMR (CD₃OD-d₄) δ 3.94 (s); ESI-LCMS: m/z = 665.15 [M+H]⁺.

EXAMPLE 20 COMPOUND 49

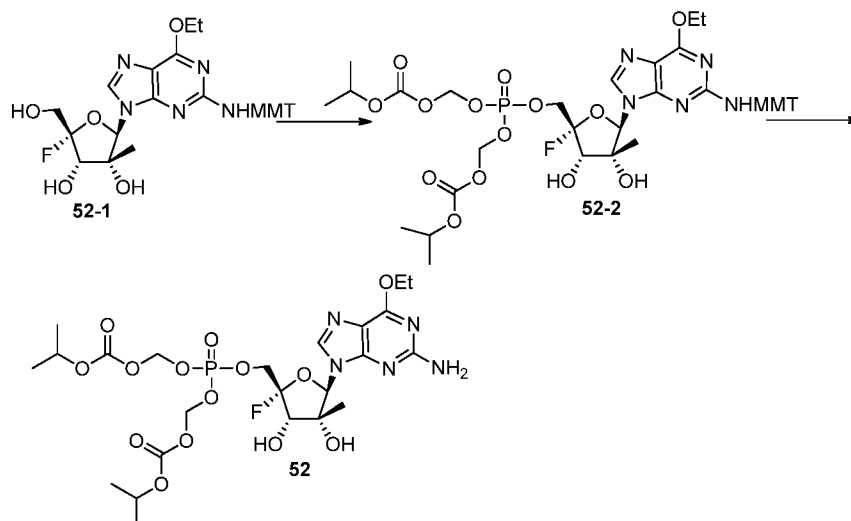


[0328] To a solution of triethylammonium bis(isopropoxycarbonyloxymethyl)phosphate (0.33 mmol, prepared from 110 mg of bis(POC)phosphate and 46 μ L of Et₃N) in THF was added **49-1** (91 mg, 0.11 mmol). The

mixture evaporated and rendered anhydrous by co-evaporating with pyridine follow by toluene. The residue was dissolved in anhydrous THF (1.5 mL) and cooled in an ice-bath. Diisopropylethyl amine (0.19 mL, 10 eq.) was added, followed by BOP-Cl (0.14 g, 5 eq.), and 3-nitro-1,2,4-triazole (63 mg, 5 eq.). The mixture was stirred 0 °C for 90 mins, diluted with EtOAc (30 mL), washed with sat. aq. NaHCO₃, brine, and dried (Na₂SO₄). The residue was purified on silica (10 g column) with CH₂Cl₂/i-PrOH solvent system (2-10% gradient) to obtain **49-2** (13 mg, 10%) and **49-3** (95 mg, 58%).

[0329] A solution of **49-2** and **49-3** (13 mg and 95 mg, respectively) in 80% aq. HCOOH (3 mL) was stirred at R.T. for 3 h, then evaporated and co-evaporated with toluene. The residue was purified on silica (10 g column) with CH₂Cl₂/MeOH (4-10% gradient) to obtain compound **49** in (42 mg, 94%) yield. MS: m/z=628 [M+1]⁺.

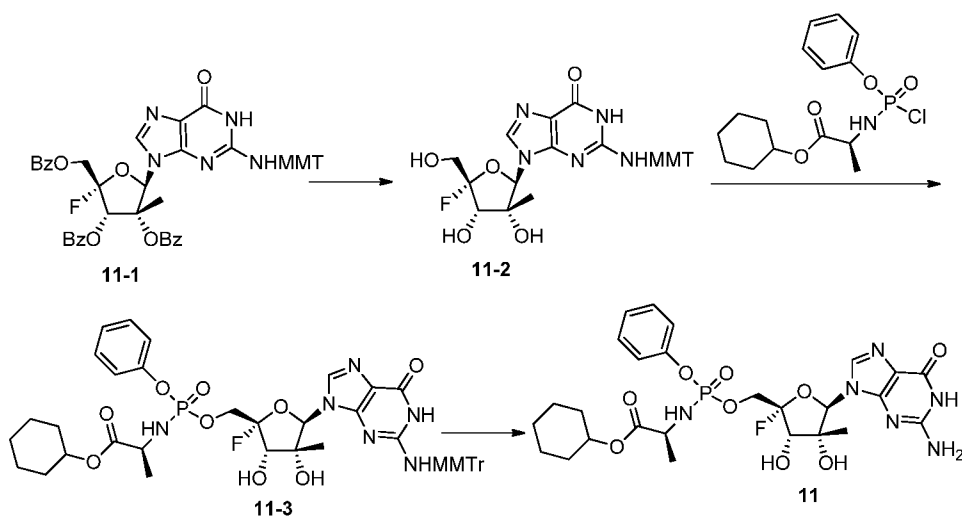
EXAMPLE 21 **COMPOUND 52**



[0330] Compound **52-2** (158 mg, 50%) was from **52-1** (0.21 g; 0.35 mmol) and triethylammonium bis(isopropoxyloxycarbonyloxymethyl)phosphate (0.54 mmol) with DIPEA (0.18 mL), BopCl (178 mg), and 3-nitro-1,2,4-triazole (80 mg) in THF (4 mL).

[0331] A solution of **52-2** (158 mg) in acetonitrile (1 mL) and HCl (4 N/dioxane; 85 µL) was stirred at R.T. for 30 mins. The reaction was quenched with MeOH and concentrated. The residue was purified on silica gel (10 g column) with CH₂Cl₂ /i-PrOH (3-10% gradient) to give compound **52** (85 mg, 76%). MS: m/z = 656 [M+1]⁺.

EXAMPLE 22
COMPOUND 11

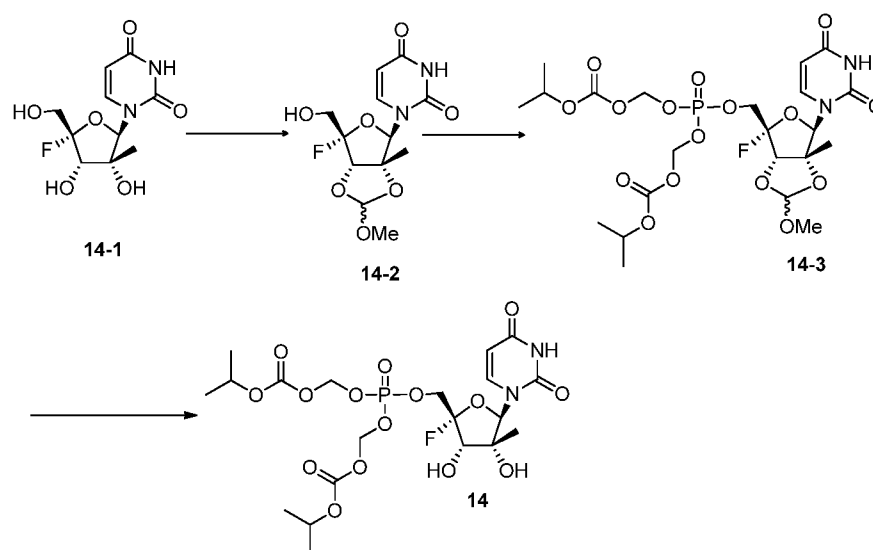


[0332] A mixture of **11-1** (170 mg, 0.19 mmol) and methanolic ammonia (7 N; 3 mL) was stirred at R.T. for 8 h, concentrated and purified on silica gel (10 g column) with CH₂Cl₂/MeOH (4-11% gradient) to give **11-2** (100 mg, 90%).

[0333] Compound **11-2** was rendered anhydrous by co-evaporating with pyridine, followed by toluene. To a solution of **11-2** (24 mg, 0.04 mmol), and N-methylimidazole (17 μ L, 5 eq.) in acetonitrile (1 mL) was added the phosphorochloridate (50 mg, 3.5 eq.) in 2 portions in 6 h intervals. The mixture was stirred at R.T. for 1 d and evaporated. Purification on silica (10 g column) with CH₂Cl₂/MeOH (4-12% gradient) yielded **11-3** (10 mg, 28%).

[0334] A solution of **11-3** (9 mg, 0.01 mmol) in 80% formic acid was stirred 3 h at R.T. The mixture was evaporated and purified on silica (10 g column) with CH₂Cl₂/MeOH (5-15% gradient) to give compound **11** (3 mg, 50%). MS: m/z = 624 [M-1].

EXAMPLE 23
COMPOUND 14

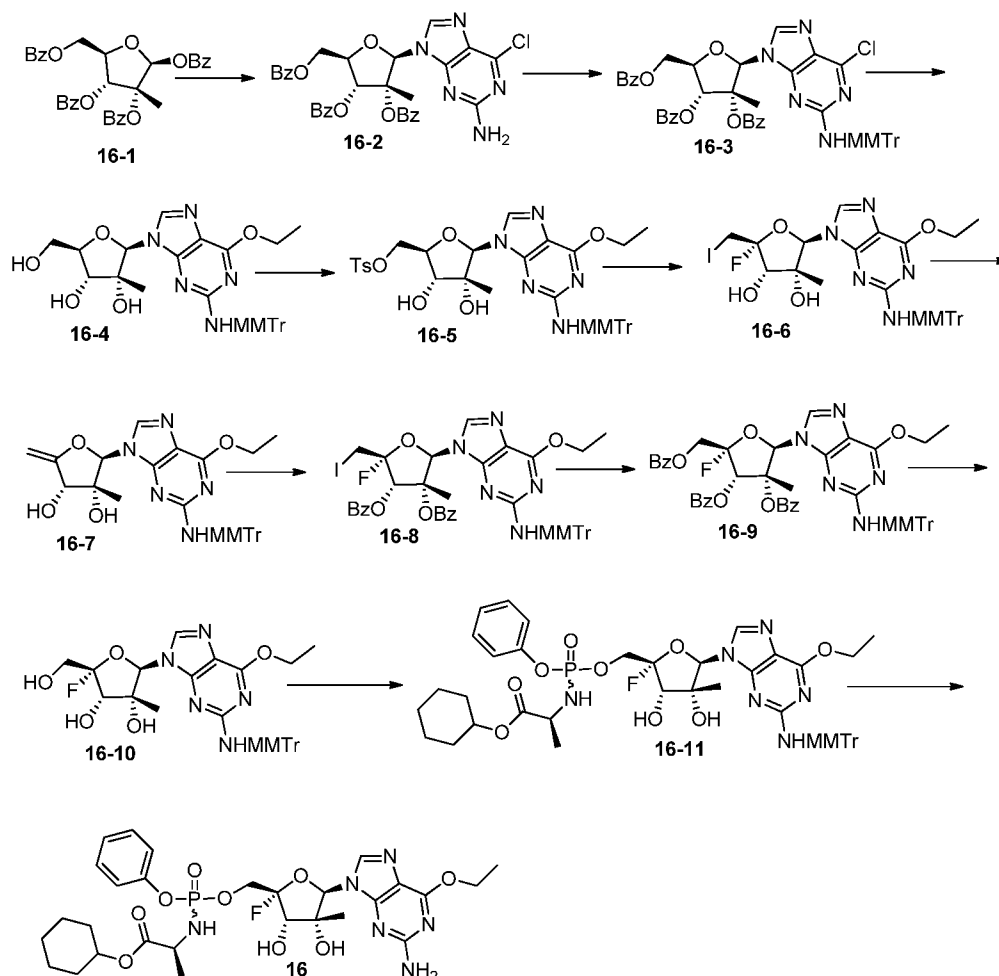


[0335] A mixture of **14-1** (1.2 g, 4.3 mmol), PTSA monohydrate (0.82 g, 1 eq.), and trimethyl orthoformate (14 mL, 30 eq.) in dioxane (30 mL) was stirred overnight at R.T. The reaction was neutralized with 7 N NH_3/MeOH and a white solid removed by filtration. The residue was dissolved in THF (10 mL) and treated with 80% aq. AcOH (5 mL). The mixture was kept at R.T. for 45 mins and then evaporated. The residue was purified on silica gel (25 g column) with $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (4-10% gradient) to give **14-2** (1.18 g, 87%).

[0336] Compound **14-3** (137 mg, 75%) was prepared from **14-2** (93 mg, 0.29 mmol) and triethylammonium bis(isopropoxyloxycarbonyloxymethyl)phosphate (0.44 mmol) with DIPEA (0.2 mL), BopCl (147 mg), and 3-nitro-1,2,4-triazole (66 mg) in THF (3 mL). Purification was done with CH_2Cl_2 /i-PrOH solvent system (3-10% gradient).

[0337] A solution of **14-3** (137 mg) in 80% aq. HCOOH was stirred at R.T. for 2 h, and then concentrated. The residue was co-evaporated with toluene and then MeOH containing a small amount of a small amount of Et_3N (2 drops). Purification on silica (25 g column) with $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (4-10% gradient) gave compound **14** (100 mg, 77%). MS: $m/z = 1175$ [2M-1].

EXAMPLE 24
COMPOUND 16



[0338] Compound **16-1** (50 g, 86.0 mmol) and 6-Cl-guanine (16.1 g, 98.2 mmol) were co-evaporated with anhydrous toluene 3 times. To a solution of **10-1** in MeCN (200 mL) was added DBU (39.5 g, 258.0 mmol) at 0 °C. The mixture was stirred at 0 °C for 30 mins, and then TMSOTf (95.5 g, 430.0 mmol) was added dropwise at 0 °C. The mixture was stirred at 0 °C for 30 mins. The mixture was heated to 70 °C, and stirred overnight. The solution was cooled to R.T. and diluted with EA (100 mL). The solution was washed with sat. NaHCO₃ solution and brine. The organic layer was dried over Na₂SO₄, and concentrated at low pressure. The residue was purified by column on silica gel (EA in PE from 10% to 40%) to give **16-2** (48.0 g, yield: 88.7%) as a yellow foam. ESI-MS: m/z 628 [M+H]⁺.

[0339] To a solution of **16-2** (48.0 g, 76.4 mol), AgNO₃ (50.0 g, 294.1 mmol) and collidine (40 mL) in anhydrous DCM (200 mL) was added MMTrCl (46.0 g, 149.2 mmol) in small portions under N₂. The mixture was stirred at R.T. for 3 h under N₂. The reaction was monitored by TLC. The mixture was filtered, and the filter was washed with sat. NaHCO₃ solution and brine. The organic layer was dried over anhydrous Na₂SO₄, and concentrated at

low pressure. The residue was purified by silica gel column (EA in PE from 5% to 50%) to the give crude **16-3** (68 g, 98%). ESI-MS: m/z 900.1 $[M+H]^+$.

[0340] Sodium (8.7 g, 378.0 mmol) was dissolved in dry EtOH (100 mL) at 0 °C, and slowly warmed to R.T. Compound **16-3** (68.0 g, 75.6 mmol) was treated with freshly prepared NaOEt solution, and stirred overnight at R.T. The reaction was monitored by TLC, and the mixture was concentrated at low pressure. The mixture was diluted with H₂O (100 mL), and extracted with EA (3 x 100 mL). The organic layer was dried over anhydrous Na₂SO₄, and evaporated at low pressure. The residue was purified by silica gel column chromatography (MeOH in DCM from 1% to 5%) to give **16-4** (34.0 g, 75.2%) as a yellow solid. ESI-MS: m/z 598 $[M+H]^+$.

[0341] Compound **16-4** (32.0 g, 53.5 mmol) was co-evaporated with anhydrous pyridine 3 times. To an ice-cooled solution of **16-4** in anhydrous pyridine (100 mL) was added TsCl (11.2 g, 58.9 mmol) in pyridine (50 mL) dropwise at 0°C. The mixture was stirred for 18 h. at 0°C. The reaction was checked by LCMS (about 70% was the desired product). The reaction was quenched with H₂O, and the solution was concentrated at low pressure. The residue was dissolved in EA (100 mL), and washed with sat. NaHCO₃ solution. The organic layer was dried over anhydrous Na₂SO₄, and evaporated at low pressure. The residue was purified by silica gel column chromatography (MeOH in DCM from 1% to 5%) to give crude **16-5** (25.0 g, 62.2%) as a yellow solid. ESI-MS: m/z 752 $[M+H]^+$.

[0342] To a solution of **16-5** (23.0 g, 30.6 mmol) in acetone (150 mL) was added NaI (45.9 g, 306.0 mmol) and TBAI (2.0 g), and refluxed overnight. The reaction was monitored by LCMS. After the reaction was complete, the mixture was concentrated at low pressure. The residue was dissolved in EA (100 mL), washed with brine, and dried over anhydrous Na₂SO₄. The organic solution was evaporated at low pressure. The residue was purified by silica gel column chromatography (DCM: MeOH=100:1 to 20:1) to give the crude product. To a solution of the crude product in dry THF (200 mL) was added DBU (14.0 g, 91.8 mmol), and heated to 60°C. The mixture was stirred overnight, and checked by LCMS. The reaction was quenched with sat. NaHCO₃, and the solution was extracted with EA (100 mL). The organic layer was dried over anhydrous Na₂SO₄, and evaporated at low pressure. The residue was purified by silica gel column chromatography (MeOH in DCM from 1% to 5%) to give **16-6** (12.0 g, 67.4%) as a yellow solid. ESI-MS: m/z 580 $[M+H]^+$.

[0343] To an ice-cooled solution of **16-6** (8.0 g, 13.8 mmol) in dry MeCN (100mL) was added NIS (3.9 g, 17.2 mmol) and TEA•3HF (3.3 g, 20.7 mmol) at 0°C. The mixture was stirred at R.T. for 18 h and checked by LCMS. After the reaction was complete, the reaction

was quenched with sat Na_2SO_3 and sat. NaHCO_3 solution. The solution was extracted with EA. The organic layer was dried over anhydrous Na_2SO_4 , and evaporated at low pressure. The residue was purified by silica gel column chromatography (EA in PE from 10% to 50%) to give **16-7** (7.2 g, 72.0%) as a solid. ESI-MS: m/z 726 $[\text{M}+\text{H}]^+$.

[0344] To a solution of crude **16-7** (7.2 g, 9.9 mmol) in dry DCM (100 mL) was added DMAP (3.6 g, 29.8 mmol), and BzCl (2.8 g, 19.8 mmol) at 0°C . The mixture was stirred overnight, and checked by LCMS. The mixture was washed with sat. NaHCO_3 solution. The organic layer was dried over anhydrous Na_2SO_4 , and evaporated at low pressure. The residue was purified by silica gel column chromatography (EA in PE from 10% to 30%) to give **16-8** (8.0 g, 86.4%) as a solid. ESI-MS: m/z 934 $[\text{M}+\text{H}]^+$.

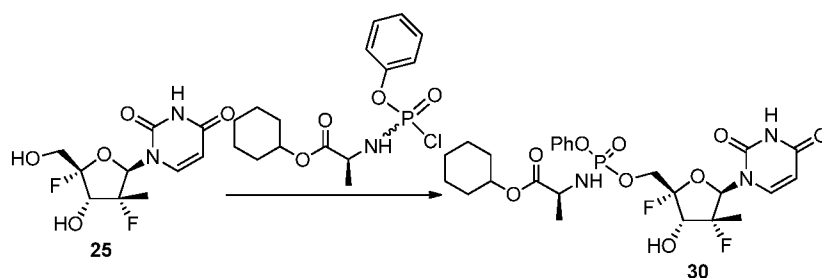
[0345] To a solution of **16-8** (7.5 g, 8.0 mmol) in dry DMF (100 mL) was added NaOBz (11.5 g, 80.0 mmol) and 15-crown-5 (15.6 mL). The mixture was stirred for 36 h. at 90°C . The mixture was diluted with H_2O (100 mL), and extracted with EA (3x150 mL). The organic layer was dried over anhydrous Na_2SO_4 , and evaporated at low pressure. The residue was purified by silica gel column chromatography (EA in PE from 10% to 30%) to give crude **16-9** (6.0 g, 80.0%) as a solid. ESI-MS: m/z 928 $[\text{M}+\text{H}]^+$.

[0346] Compound **16-9** (4.0 g, 4.3 mmol) was co-evaporated with anhydrous toluene 3 times, and treated with NH_3/MeOH (50 mL, 4N) at R.T. The mixture was stirred for 18 h at R.T. The reaction was monitored by LCMS, and the mixture was concentrated at low pressure. The residue was purified by silica gel column chromatography (EA in PE from 30% to 50%) to give **16-10** (1.9 g, 71.7%) as a solid. ESI-MS: m/z 616 $[\text{M}+\text{H}]^+$.

[0347] Compound **16-10** (300.0 mg, 0.49 mmol) was co-evaporated with anhydrous toluene 3 times, and was dissolved in MeCN (2 mL). The mixture was treated with NMI (120.5 mg, 1.47 mmol) and the phosphorochloridate reagent (338.1 mg, 0.98 mmol) in MeCN (1 mL) at 0°C . The mixture was stirred for 18 h at R.T. The reaction was monitored by LCMS. The mixture was diluted with 10% NaHCO_3 solution, and extracted with EA. The residue was purified by silica gel column chromatography (EA in PE from 30% to 50%) to give **16-11** (240 mg, 53.3%) as a solid. ESI-MS: m/z 925 $[\text{M}+\text{H}]^+$.

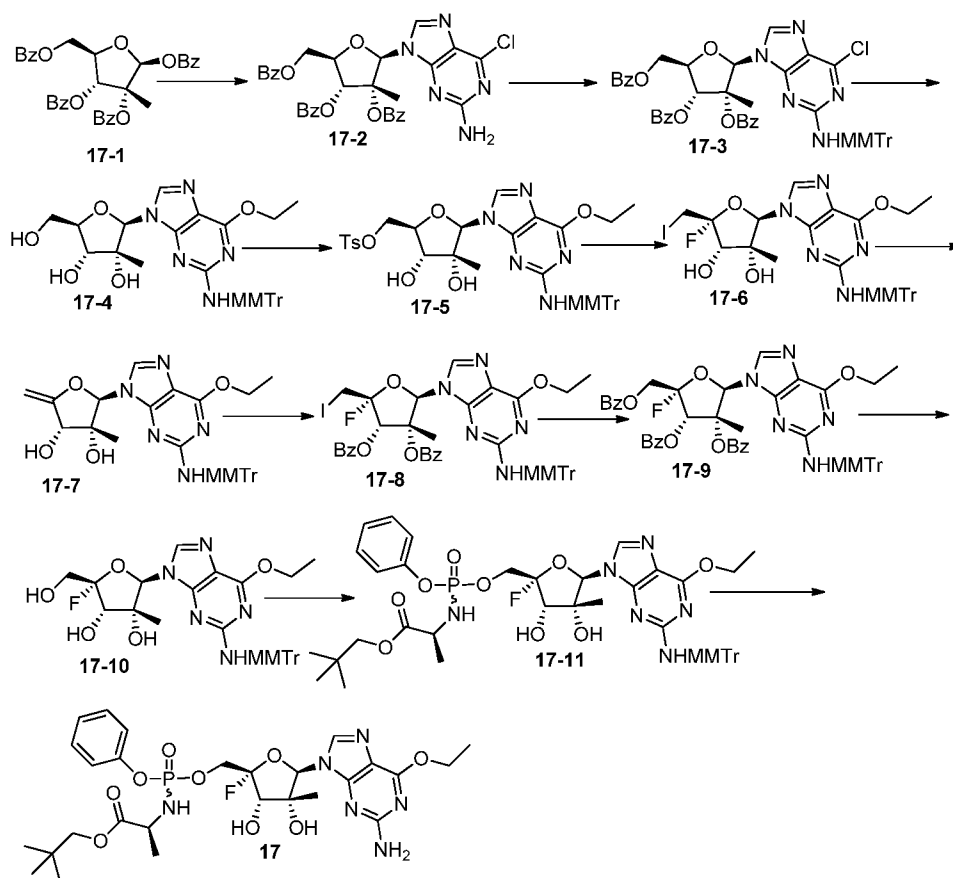
[0348] Compound **16-11** (240.0 mg, 0.26 mmol) was treated with 80% AcOH (10 mL), and the mixture was stirred for 18 h at R.T. The reaction was monitored by LCMS. The mixture was concentrated at low pressure. The residue was purified by silica gel column chromatography (MeOH in DCM from 1% to 3%) to give compound **16** (87.6 mg, 51.7%) as a solid. ESI-MS: m/z 653 $[\text{M}+\text{H}]^+$.

EXAMPLE 25
COMPOUND 30



[0349] To a stirred solution of compound **25** (60 mg, 0.22 mmol) in anhydrous THF (2.0 mL) was added N-methylimidazole (0.142 mL, 1.73 mmol) at 0 °C (dry ice/acetone bath) followed by solution of phenyl (cyclohexanoxy-L-alaninyl) phosphorochloridate (235 mg, 0.68 mmol, dissolved in THF (2 mL)). The resulting solution was stirred at 0 °C for 1 h, and the temperature was raised up-to 10 °C over the next 1 h. The reaction left at 10 °C for 3 h. The mixture was cooled to 0 to 5 °C, diluted with EA, and water (5 mL) was added. The solution was washed with H₂O and brine. The organic layer was separated, dried over anhydrous Na₂SO₄ and filtered. The filtrate was concentrated in vacuum to give a residue, which dissolved in 25% CH₃CN/H₂O. The compound was purified on a reverse-phase HPLC (C18) using acetonitrile and water, followed by lyophilization gave a white foam. The produce was re-dissolved in EtOAc, washed with 50 % aqueous citric acid solution, dried over anhydrous MgSO₄ and filtered. The filtrate was concentrated in vacuum, and lyophilized to give two isomers (*Rp/Sp*) of compound **30** (6.3 mg). MS: m/z 586.05 [M-H]⁻.

EXAMPLE 26
COMPOUND 17



[0350] Compound **17-1** (50 g, 86.0 mmol) and 6-Cl-guanine (16.1 g, 98.2 mmol) were co-evaporated with anhydrous toluene 3 times. To a solution of **17-1** (50 g, 86.0 mmol) and 6-Cl-guanine (16.1 g, 98.2 mmol) in MeCN (200 mL) was added DBU (39.5 g, 258.0 mmol) at 0°C. The mixture was stirred at 0 °C for 30 mins, and TMSOTf (95.5 g, 430.0 mmol) was added dropwise at 0°C. The mixture was stirred at 0 °C for 30 mins until a clear solution was observed. The mixture was heated to 70 °C, and stirred overnight. The solution was cooled to R.T., and diluted with EA (100 mL). The solution was washed with sat. NaHCO₃ solution and brine. The organic layer was dried over Na₂SO₄, and concentrated at low pressure. The residue was purified by column on silica gel (EA in PE from 10% to 40%) to give **17-2** (48.0 g, 88.7%) as a yellow foam. ESI-MS: m/z 628 [M+H]⁺.

[0351] To a solution of **17-2** (48.0 g, 76.4 mol), AgNO₃ (50.0 g, 294.1 mmol) and collidine (40 mL) in anhydrous DCM (200 mL) was added MMTrCl (46.0 g, 149.2 mmol) in small portions under N₂. The mixture was stirred at R.T. for 3 h under N₂. Completion of the reaction was determined by TLC. After filtration, the filtrate was washed with sat. NaHCO₃ solution and brine. The organic layer was dried over anhydrous Na₂SO₄, and concentrated at

low pressure. The residue was purified by silica gel column (EA in PE from 5% to 50%) to the give crude **17-3** (68 g, 98%). ESI-MS: m/z 900.1 $[M+H]^+$.

[0352] Sodium (8.7 g, 378.0 mmol) was dissolved in dry EtOH (100 mL) at 0 °C, and slowly warmed to R.T. Compound **17-3** (68.0 g, 75.6 mmol) was treated with freshly prepared NaOEt solution, and stirred overnight at R.T. Completion of the reaction was determined by TLC and LCMS. The mixture was concentrated at a low pressure, diluted with H₂O (100 mL), and extracted with EA (3 x 100 mL). The organic layer was dried over anhydrous Na₂SO₄, and evaporated at low pressure. The residue was purified by silica gel column chromatography (MeOH in DCM from 1% to 5%) to give **17-4** (34.0 g, 75.2%) as a yellow solid. ESI-MS: m/z 598 $[M+H]^+$.

[0353] Compound **17-4** (32.0 g, 53.5 mmol) was co-evaporated with anhydrous pyridine 3 times. To an ice-cooled solution of **17-4** (32.0 g, 53.5 mmol) in anhydrous pyridine (100 mL) was added a solution of TsCl (11.2 g, 58.9 mmol) in pyridine (50 mL) dropwise at 0°C. The mixture was stirred for 18 h. at 0°C. The reaction was monitored by LCMS, and quenched with H₂O. The solution was concentrated at low pressure, and the residue was dissolved in EA (100 mL), and washed with sat. NaHCO₃ solution. The organic layer was dried over anhydrous Na₂SO₄, and evaporated at a low pressure. The residue was purified by silica gel column chromatography (MeOH in DCM from 1% to 5%) to give crude **17-5** (25.0 g, 62.2%) as a yellow solid. ESI-MS: m/z 752 $[M+H]^+$.

[0354] To a solution of **17-5** (23.0 g, 30.6 mmol) in acetone (150 mL) was added NaI (45.9 g, 306.0 mmol) and TBAI (2.0 g), and the mixture was refluxed overnight. Completion of the reaction was determined by LCMS. The mixture was concentrated at low pressure, and the residue was dissolved in EA (100 mL). The solution was washed with brine, and dried over anhydrous Na₂SO₄. The organic solution was evaporated at low pressure, and the residue was purified by silica gel column chromatography (DCM: MeOH=100:1 to 20:1) to give a crude product. To a solution of the crude product in dry THF (200 mL) was added DBU (14.0 g, 91.8 mmol), and the mixture was heated to 60 °C and stirred overnight. The reaction was monitored by LCMS. The reaction was quenched with sat. NaHCO₃ solution, and the solution was extracted with EA (100 mL). The organic layer was dried over anhydrous Na₂SO₄, and evaporated at low pressure. The residue was purified by silica gel column chromatography (MeOH in DCM from 1% to 5%) to give **17-6** (12.0 g, 67.4%) as a yellow solid. ESI-MS: m/z 580 $[M+H]^+$.

[0355] To an ice-cooled solution of **17-6** (8.0 g, 13.8 mmol) in anhydrous MeCN (100mL) was added NIS (3.9 g, 17.2 mmol) and TEA•3HF (3.3 g, 20.7 mmol) at 0°C. The

mixture was stirred at R.T. for 18 h, and the reaction was checked by LCMS. After the reaction was completed, the reaction was quenched with sat. Na₂SO₃ solution and sat. NaHCO₃ solution. The solution was extracted with EA (3 x 100 mL). The organic layer was dried over anhydrous Na₂SO₄, and evaporated at low pressure. The residue was purified by silica gel column chromatography (EA in PE from 10% to 50%) to give **17-7** (7.2 g, 72.0%) as a solid. ESI-MS: m/z 726 [M+H]⁺.

[0356] To a solution of **17-7** (7.2 g, 9.9 mmol) in dry DCM (100 mL) was added DMAP (3.6 g, 29.8 mmol), and BzCl (2.8 g, 19.8 mmol) at 0°C. The mixture was stirred overnight, and checked by LCMS. The mixture was washed with sat. NaHCO₃ solution. The organic layer was dried over anhydrous Na₂SO₄, and evaporated at low pressure. The residue was purified by silica gel column chromatography (EA in PE from 10% to 30%) to give **17-8** (8.0 g, 86.4%) as a solid. ESI-MS: m/z 934 [M+H]⁺.

[0357] To a solution of **17-8** (7.5 g, 8.0 mmol) in dry DMF (100 mL) was added NaOBz (11.5 g, 80.0 mmol) and 15-crown-5 (15.6 mL). The mixture was stirred for 36 h. at 90°C. The mixture was diluted with H₂O (100 mL), and extracted with EA (3 x 150 mL). The organic layer was dried over anhydrous Na₂SO₄, and evaporated at low pressure. The residue was purified by silica gel column chromatography (EA in PE from 10% to 30%) to give crude **17-9** (6.0 g, 80.0%) as a solid. ESI-MS: m/z 928 [M+H]⁺.

[0358] Compound **17-9** (4.0 g, 4.3 mmol) was co-evaporated with anhydrous toluene 3 times, and treated with NH₃/MeOH (50 mL, 4N) at R.T. The mixture was stirred for 18 h. at R.T. Completion of the reaction was determined by LCMS. The mixture was concentrated at low pressure, and the residue was purified by silica gel column chromatography (EA in PE from 30% to 50%) to give product **17-10** (1.9 g, 71.7%) as a solid. ESI-MS: m/z 616 [M+H]⁺.

[0359] Compound **17-10** (300.0 mg, 0.49 mmol) was co-evaporated with anhydrous toluene 3 times, and was dissolved in MeCN (2 mL). The mixture was treated with NMI (120.5 mg, 1.47 mmol) and the phosphorochloridate reagent (326.3 mg, 0.98 mmol) in MeCN (1 mL) at 0°C. The mixture was stirred for 18 h at R.T. and monitored by LCMS. The mixture was diluted with 10% NaHCO₃ solution, and extracted with EA (3 x 30 mL). The residue was purified by silica gel column chromatography (EA in PE from 30% to 50%) to give **17-11** (210 mg, 47.5%) as a solid. ESI-MS: m/z 913.0 [M+H]⁺.

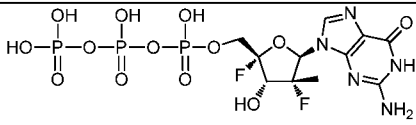
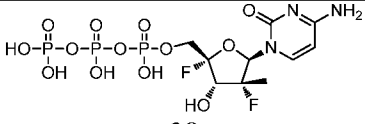
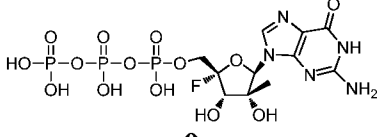
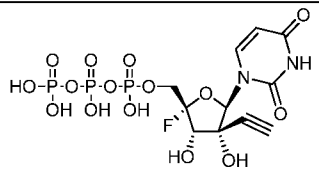
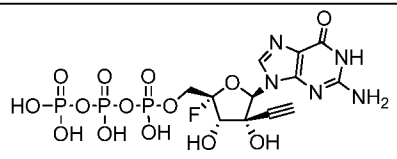
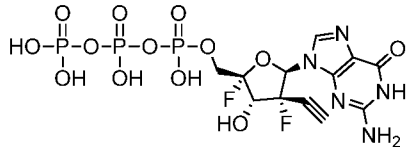
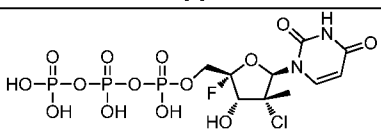
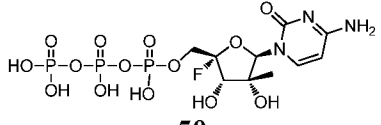
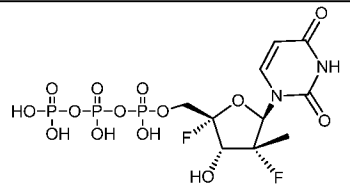
[0360] Compound **17-11** (210 mg, 0.26 mmol) was treated with 80% of AcOH (15 mL), and the mixture was stirred for 18 h at R.T. Completion of the reaction was determined by LCMS. The mixture was concentrated at low pressure, and the residue was purified by silica gel

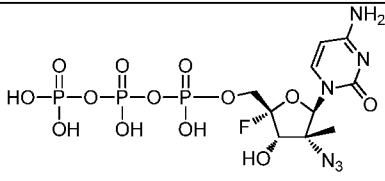
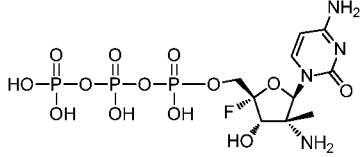
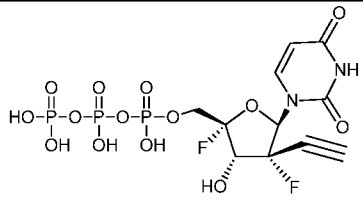
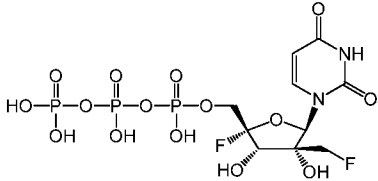
column chromatography (MeOH in DCM from 1% to 3%) to give compound **17** (71.8 mg, 48.7%) as a solid. ESI-MS: m/z 641.3 $[M+H]^+$.

EXAMPLE 27

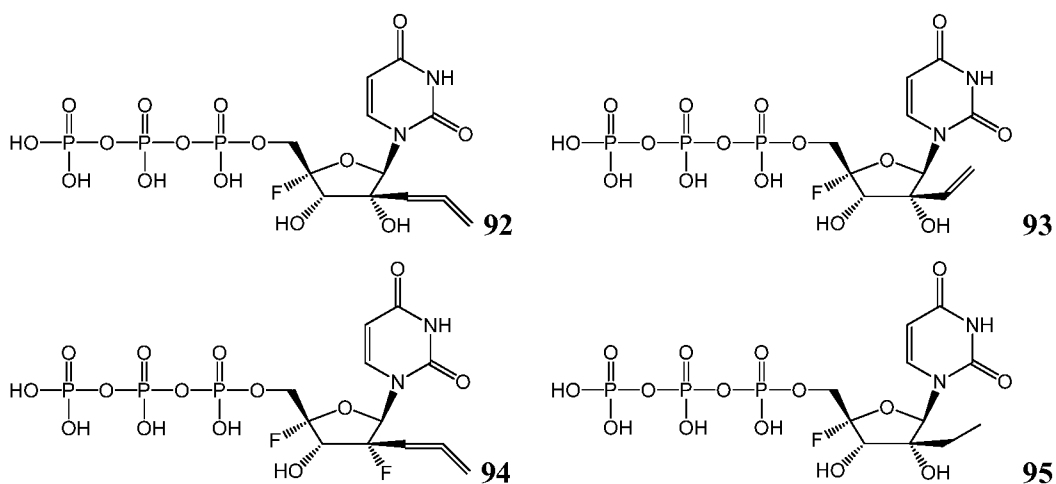
COMPOUNDS 9, 12, 15, 26, 28, 38, 44, 46, 50, 63, 64, 69 and 76

[0361] Compounds **9, 12, 15, 26, 28, 38, 44, 46, 50, 63, 64, 69** and **76** were prepared in a manner similar to method for preparing compound **6**. After the addition of $POCl_3$, the mixture was kept at R.T. for 20-40 mins. The reaction was controlled by LCMS and monitored by the appearance of corresponding nucleoside 5'-monophosphate. After completion of the reaction, tetrabutylammonium salt of pyrophosphate (150 mg) was added, followed by DMF (0.5 mL) to get a homogeneous solution. After 1.5 h at ambient temperature, the reaction was diluted with water (10 mL). The triphosphate (eluted at 75-80%B) were obtained as described for compound **6**.

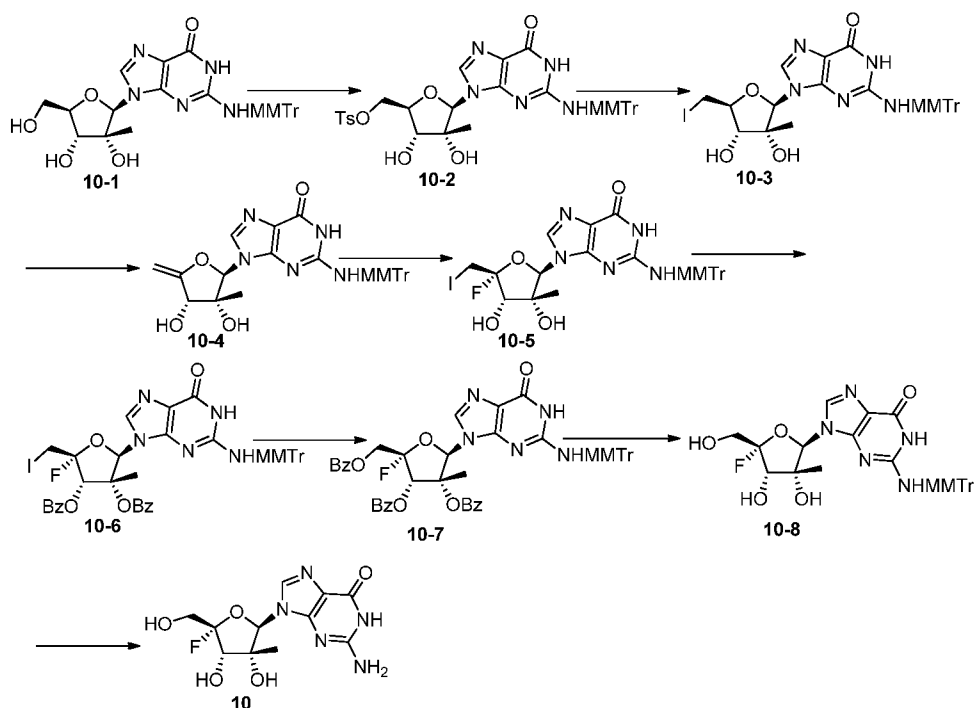
Structure	MS [M-1] ⁻	³¹ P NMR		
		P(α)	P(β)	P(γ)
 28	556.2	-10.92 -11.03(d)	- 23.18(t)	-11.86 -11.98(d)
 38	516.1	-7.49 -7.61(d)	- 22.42(t)	-12.17 -12.30(d)
 9	554.0	-10.94 -11.06(d)	- 23.25(t)	-11.85 -11.97(d)
 12	525.2	-8.53(bs)	-22.61 (bs)	-12.17 -12.29(d)
 15	564.4	-11.05 (bs)	-23.25 (bs)	-11.96 -12.08(d)
 44	566.0	-10.92 -11.04(d)	- 23.18(t)	-11.93 -1(d)
 46	533.3	-10.89 -11.01(d)	- 23.31(t)	-12.49 -1(d)
 50	513.8	-8.66(bs)	- 22.80(t)	-12.17 -12.29(d)
 26	517.7	-13.73 -13.60(d)	- 25.98(t)	-15.18 -15.06(d)

Structure	MS [M-1] ⁻	³¹ P NMR		
		P(α)	P(β)	P(γ)
 63	539.5	-7.42 (br.s)	- 22.57(t)	-12.23 -12.34(d)
 64	513.1	-6.36 -6.49(d)	- 22.49(t)	-12.20 -12.33(d)
 69	526.8	-10.96 -11.08(d)	- 23.33(t)	-12.41 -12.53(d)
 76	533.4	-10.78 (br.s)	- 23.22(t)	-12.24 -12.36(d)

[0362] The following compounds can also be prepared using a method similar to the method described in Example 27:



EXAMPLE 28
COMPOUND 10



[0363] Compound **10-1** (5 g, 8.79 mmol) was co-evaporated with anhydrous pyridine. To an ice-cooled solution of **10-1** in anhydrous pyridine (15 mL) was added TsCl (3.43 g, 17.58 mmol), and stirred for 1 h at 0°C. The reaction was checked by LCMS and TLC. The reaction was quenched with H₂O, and extracted with EA. The organic phase was dried over anhydrous Na₂SO₄, and evaporated at low pressure. Compound **10-2** (6.35 g, 100%) was used for next step directly.

[0364] To a solution of **10-2** (31.77g, 43.94 mmol) in acetone (300 mL) was added NaI (65.86 g, 439.4 mmol), and heated to reflux overnight. The reaction was checked by LCMS. The reaction was quenched with sat. Na₂S₂O₃ solution, and extracted with EA. The organic layer was dried over anhydrous Na₂SO₄, and evaporated at low pressure. The residue was purified by silica gel column chromatography (MeOH in DCM from 1% to 6%) to give **10-3** (11.5g, 38%) as a white solid.

[0365] To a solution of **10-3** (11.5 g, 16.94 mmol) in dry THF (120 mL) was added DBU (12.87 g, 84.68 mmol), and heated to 60°C. The reaction was stirred overnight and checked by LCMS. The reaction was quenched with sat. NaHCO₃ solution, and extracted with EA. The organic phase was dried over anhydrous Na₂SO₄, and evaporated at low pressure. The residue was purified by silica gel column chromatography (MeOH in DCM from 1% to 5%) to give **10-4** (5.5 g, 54%) as a white solid.

[0366] To an ice-cooled solution of **10-4** (500 mg, 0.90 mmol) in dry DCM (20ml) was added AgF (618 mg, 4.9 mmol) and a solution of I₂ (500 mg, 1.97 mmol) in dry DCM (20 mL). The reaction was stirred for 3 h., and checked by LCMS. The reaction was quenched with sat Na₂S₂O₃ solution and sat. NaHCO₃ solution, and the mixture was extracted with DCM. The organic layer was dried by anhydrous Na₂SO₄, and evaporated at low pressure to give crude **10-5** (420 mg, 66%).

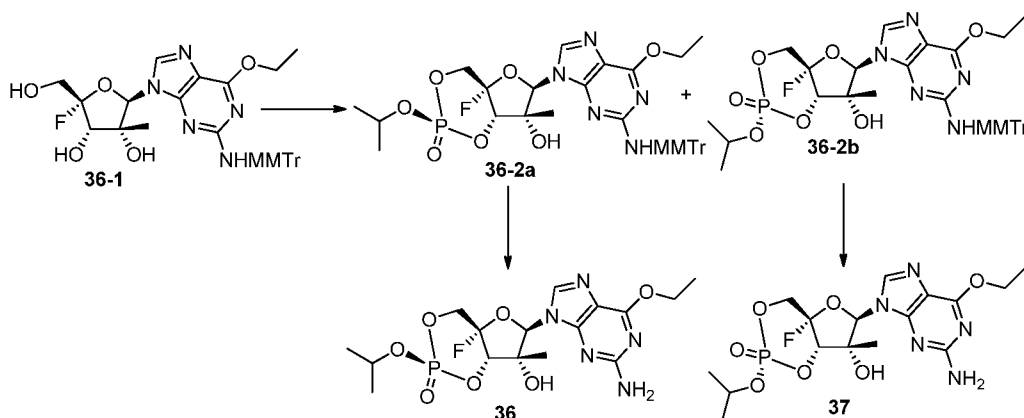
[0367] To a solution of crude **10-5** (250 mg, 0.36 mmol) in dry DCM (8 mL) was added DMAP (0.28 g, 2.33 mmol), TEA (145 mg, 1.44mmol) and BzCl (230 mg, 1.62 mmol) in a solution of DCM (2 mL). The reaction was stirred overnight, and checked by LCMS. The mixture was washed with sat. NaHCO₃ solution and brine. The organic layer was evaporated at low pressure. The residue was purified by prep-TLC to give crude **10-6** (150 mg, 46%).

[0368] To a solution of crude **10-6** (650 mg, 0.72 mmol) in dry HMPA (20 mL) was added NaOBz (1.03 g, 7.2 mmol) and 15-crown-5 (1.59 g, 7.2 mmol). The reaction was stirred for 2 d at 60°C. The mixture was diluted with H₂O, and extracted with EA. The organic layer was evaporated at low pressure. The residue was purified by prep-TLC to give **10-7** (210 mg, 32.4%). ESI-MS: m/z: 900.4 [M+H]⁺.

[0369] A mixture of **10-7** (25 mg) and BuNH₂ (0.8 mL) was stirred overnight at R.T. The mixture was evaporated and purified on silica gel (10 g column) with CH₂Cl₂/MeOH (4-15% gradient) to yield **10-8** (15 mg, 91%).

[0370] A mixture of **10-8** (15 mg, 0.02 mmol) in ACN (0.25 mL) and 4 N HCL/dioxane (19 uL) was stirred at R.T. for 45 mins. The mixture was diluted with MeOH and evaporated. The crude residue was treated with MeCN, and the solid was filtered to yield compound **10** (7 mg). MS: m/z = 314 [M-1]⁻.

EXAMPLE 29 COMPOUNDS 36 AND 37

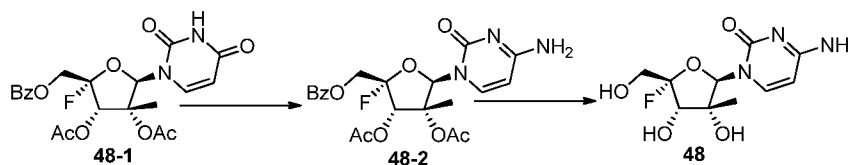


[0371] To a solution of **36-1** (150 mg, 0.24 mmol) in DCM (2.0 mL), triethylamine (141 μ L, 2.0 mmol) was added at R.T. The mixture was cooled to 0 to 5°C (ice/water bath), and freshly prepared and distilled isopropyl phosphorodichloridate (45 μ L, 0.26 mmol, prepared according to a procedure, Reddy *et al. J. Org. Chem.* **2011**, 76 (10), 3782-3790) was added. The mixture was stirred at 0 to 5°C (ice/water bath) for 15 mins, followed by N-methylimidazole (40 μ L, 0.49 mmol). The mixture was stirred for 1 h at 0 to 5°C. TLC showed the absence of starting material **36-1**. EA (100 mL) was added, followed by water. The organic layer was washed with H₂O, sat. aq. NH₄Cl solution and brine. The organic layer was separated, dried over anhydrous MgSO₄ and filtered. The filtrate was concentrated in vacuum to give a residue, which was purified on silica gel with 0 to 10% iPrOH/ DCM to give **36-2a** (16.9 mg, faster eluting isomer) and **36-2b** (72.7 mg, slower eluting isomer).

[0372] Compounds **36-2a** and **36-2b** were deprotected using a procedure described herein. Compound **36** (7.3 mg, single isomers from **36-2a** (16.5 mg, 0.0235 mmol)) and compound **37** (29.0 mg, single isomers from **36-2b** (72.7 mg, 0.1 mmol)) were obtained.

[0373] Compound **36**: ¹H NMR (CD₃OD-d₄, 400 MHz) δ 7.94 (s, 1H), 6.32 (s, 1H), 6.00-5.9 (br s, 1H), 4.9-4.487 (m, 1H), 4.83-4.77 (m, 1H), 4.65-4.50 (m, 3H), 1.45-1.39 (s, 9H), 1.2 (s, 3H); ¹⁹F NMR (CD₃OD-d₄) δ -120.3 (s); ³¹P NMR (CD₃OD-d₄) δ -5.19 (s); ESI-LCMS: m/z = 448.05 [M+H]⁺. Compound **37**: ¹H NMR (CD₃OD-d₄, 400 MHz) δ 7.98 (s, 1H), 6.34 (s, 1H), 5.78-5.64 (br s, 1H), 4.95-4.48 (m, 2H), 4.62-4.52 (m, 3H), 1.48-1.42 (s, 9H), 1.1 (s, 3H); ¹⁹F NMR (CD₃OD-d₄) δ -121.3 (s); ³¹P NMR (CD₃OD-d₄) δ -7.38 (s); ESI-LCMS: m/z = 448.05 [M+H]⁺.

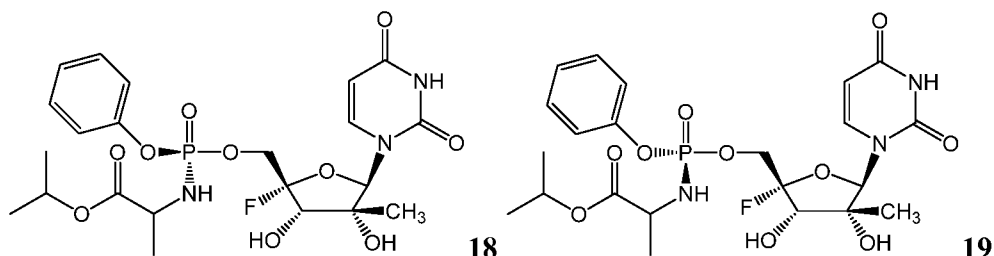
EXAMPLE 30 COMPOUND 48



[0374] To a solution of **48-1** (600 mg, 1.29 mmol) in anhydrous CH₃CN (4 mL) was added DMAP (315 mg, 2.59 mmol), TEA (391 mg, 3.87 mmol) and TPSCl (782 mg, 2.58 mmol). The mixture was stirred for 3 h. under N₂. A solution of NH₃ in THF (2 mL) was added, and stirred for 1 h. The reaction was quenched with sat. NH₄Cl solution, and extracted with EA. The organic layer was dried over anhydrous Na₂SO₄, and concentrated to dryness at low pressure. The residue was purified by column chromatography to provide **48-2** (370 mg, 62%) as a white foam solid.

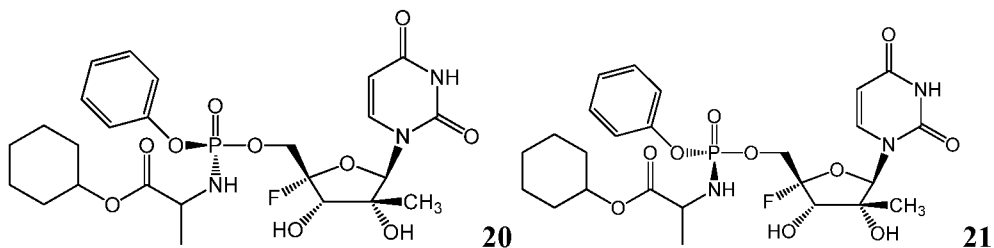
[0375] Compound **48-2** (370 mg, 1.48 mmol) in methanolic ammonium was stirred at R.T. for 4 h. The solution was concentrated to dryness to give compound **48** (200 mg, 91%) as a white solid. ESI-MS: m/z 275.9 $[M+H]^+$.

EXAMPLE 31
COMPOUNDS 18 AND 19



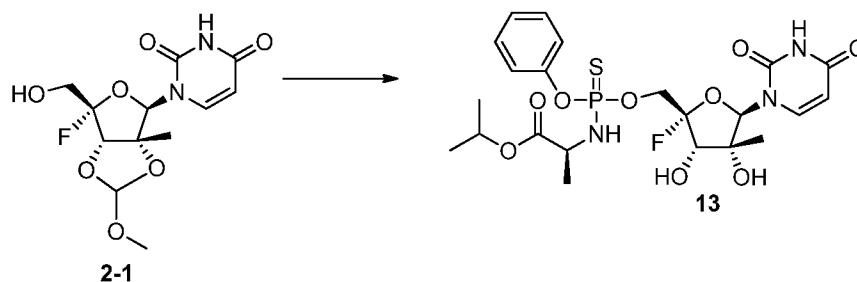
[0376] The diastereomers of compound **2** were separated by RP-HPLC. A gradient of 10-43%ACN in H₂O over 26 mins on a Synergi Hydro RP 30 x 250 m 4u particle column (Phenomenex PN 00G-4375-U0-AX) eluted compound **19** (29.5 mins) and compound **18** (30.1 mins). Pure fractions were lyophilized to produce a white powder. Compound **19**: ³¹P-NMR (DMSO-d₆) 3.448 ppm; MS: m/z : 544 $[M-1]^-$; Compound **18**: ³¹P-NMR (DMSO-d₆) 3.538 ppm; MS: m/z : 544 $[M-1]^-$.

EXAMPLE 32
COMPOUNDS 20 AND 21



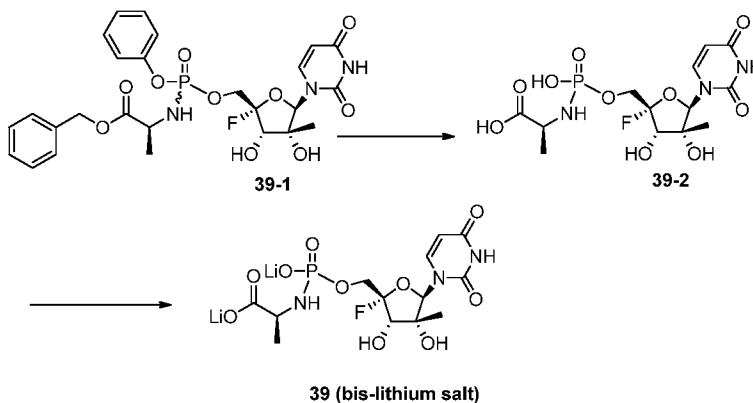
[0377] The diastereomers of compound **3** were separated by RP-HPLC. A gradient of 25-52%ACN in H₂O over 26 mins on a Synergi Hydro RP 30x250m 4u particle column (Phenomenex PN 00G-4375-U0-AX) eluted compound **21** (24.8 mins) and compound **20** (25.3 mins). Pure fractions were lyophilized to produce a white powder. Compound **21**: ³¹P-NMR (DMSO-d₆) 3.492 ppm; MS: m/z : 584 $[M-1]^-$. Compound **20**: ³¹P-NMR (DMSO-d₆) 3.528 ppm; MS: m/z : 584 $[M-1]^-$.

EXAMPLE 33
COMPOUND 13



[0378] Compound **2-1** (32 mg, 0.1 mmol) was dissolved in dry THF (3 mL) and 2M solution of isopropylmagnesium bromide in THF (0.1 mL) was added at 0°C. The reaction was left for 1 h at R.T., and phenyl(isopropyl-L-alaninyl) thiophosphorochloridate was added (0.3 mmol). The mixture was left overnight at R.T. LSMS analysis showed about 20% of unreacted starting material. The same amount of Grignard reagent and thiophosphorochloridate were added, and the mixture was heated at 37°C for 4 h. The reaction was quenched with NH₄Cl. The product was extracted with EA, washed with brine, dried over Na₂SO₄, and evaporated. The resulting oil was dissolved in 80% formic acid (4 mL) and in 1 h evaporated. Compound **13** was purified by RP HPLC in gradient of methanol in water from 30% to 95% on Synergy 4u Hydro-RP column (Phenomenex) yielding a colorless solid. Compound **13** (7 mg, yield 12.5%). MS: m/z: 560.0 [M-1].

EXAMPLE 34
COMPOUND 39, Bis-lithium Salt

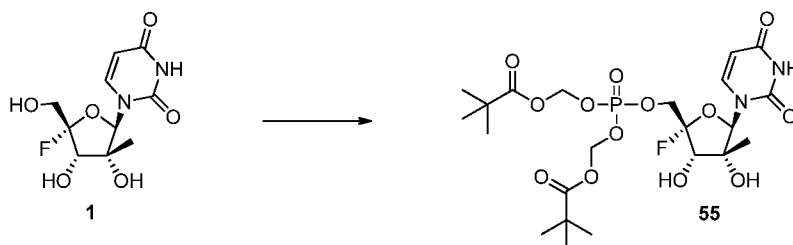


[0379] Compound **39-1** was synthesized using a procedure similar for preparing compound **2** using alanine benzyl ester hydrochloride. LCMS: m/z 592 [M-1].

[0380] To a solution of **39-1** (1.1 g, 1.85 mmol) in dioxane (15 mL) and water (3 mL) was added aqueous triethylammonium acetate (2M, 2 mL, 4 mmol) followed by Pd-C (10%, 100 mg). The mixture was hydrogenated (balloon) for 2 h, and monitored by HPLC. The catalyst was filtered off, and the filtrate was concentrated to dryness. The residue was

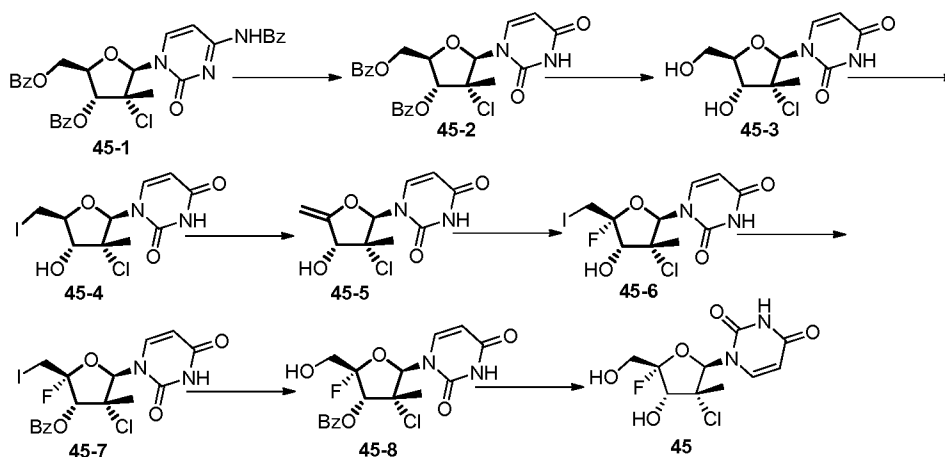
suspended in 3% solution of lithium perchlorate in acetone (25 mL). The solid was isolated by filtration, rinsed with acetone and dried under vacuum to give compound **39** (bis-lithium salt) (731 mg, 90%). LCMS: m/z 426 $[M-1]^-$.

EXAMPLE 35 **COMPOUND 55**



[0381] Compound **1** (40 mg, 0.14 mmol) and triethylammonium bis(pivaloyloxymethyl)phosphate (0.21 mmol, prepared from 80 mg of bis(pivaloyloxymethyl)phosphate and 30 μ L of Et_3N) were rendered anhydrous by coevaporating with pyridine, followed by toluene. The evaporated residue was dissolved in anhydrous THF (2 mL) and cooled in an ice-bath. Diisopropylethyl amine (73 μ L, 3 eq.), BopCl (71 mg, 2 eq.), and 3-nitro-1,2,4-triazole (32 mg, 2 eq.) were added. The mixture was stirred at 0°C for 90 mins. The mixture was then diluted with EtOAc, washed with sat. aq. NaHCO_3 and brine, and dried (Na_2SO_4). Purification on silica gel column with $\text{CH}_2\text{Cl}_2/\text{i-PrOH}$ solvent system (4-10% gradient) followed by RP-HPLC purification (A: water, B: MeCN) yielded compound **55** (13 mg, 16%). MS: m/z = 1167 $[2M-1]$.

EXAMPLE 36 **COMPOUND 45**



[0382] Compound **45-1** (15.0 g, 25.55 mmol) was treated with 90% HOAc (150 mL) at R.T. The mixture was stirred at 110°C for 12 h, and then concentrated at a low pressure. The residue was dissolved in DCM, and the solution was washed with brine. The organic phase was

dried over anhydrous Na_2SO_4 , and then concentrated at a low pressure. The residue was purified by column chromatography (5% MeOH in DCM) to give **45-2** (11.0 g, 88.9%) as a white solid.

[0383] Compound **45-2** (12.0 g, 24.79 mmol) was treated with NH_3 in MeOH (200 mL, 7 M) at R.T. The solution was stirred at R.T. for 12 h, and then concentrated at a low pressure. The residue was purified by column chromatography (10% MeOH in DCM) to give **45-3** (6.5 g, 95.0%) as a white solid.

[0384] To a stirred suspension of **45-3** (4.3 g, 15.58 mmol), PPh_3 (8.16 g, 31.15 mmol), imidazole (2.11 g, 31.15 mmol) and pyridine (15 mL) in anhydrous THF (45 mL) was added a solution of I_2 (7.91 g, 31.15 mmol) in THF (100 mL) dropwise at 0°C . The mixture was slowly warmed to R.T. and stirred overnight. The mixture was quenched with MeOH (100 mL). The solvent was removed at a low pressure, and the residue was re-dissolved in a mixture of EA and THF (0.2 L, 10:1). The organic phase was washed with sat. $\text{Na}_2\text{S}_2\text{O}_3$ aq. (2x). The aqueous phase was extracted with a mixture of EA and THF (0.2 L, 10:1, 2x). The concentrated organic phase was dried over anhydrous Na_2SO_4 . The residue was purified on a silica gel column (0-10% MeOH in DCM) to afford **45-4** (5.1 g, 85.0%) as a white solid.

[0385] Compound **45-4** (800 mg, 2.07 mmol) was dissolved in a mixture of DBU (4 mL) and THF (4 mL) at R.T. under N_2 . The solution was stirred at R.T. for 1 h. The mixture was neutralized with HOAc, and extracted with a mixture of EA and THF (10:1, 40 mL). The organic phase was washed with brine, and dried over anhydrous Na_2SO_4 . The concentrated organic phase was purified by column chromatography (0-10% MeOH in DCM) to give **45-5** (240 mg, 44.9%) as a white solid.

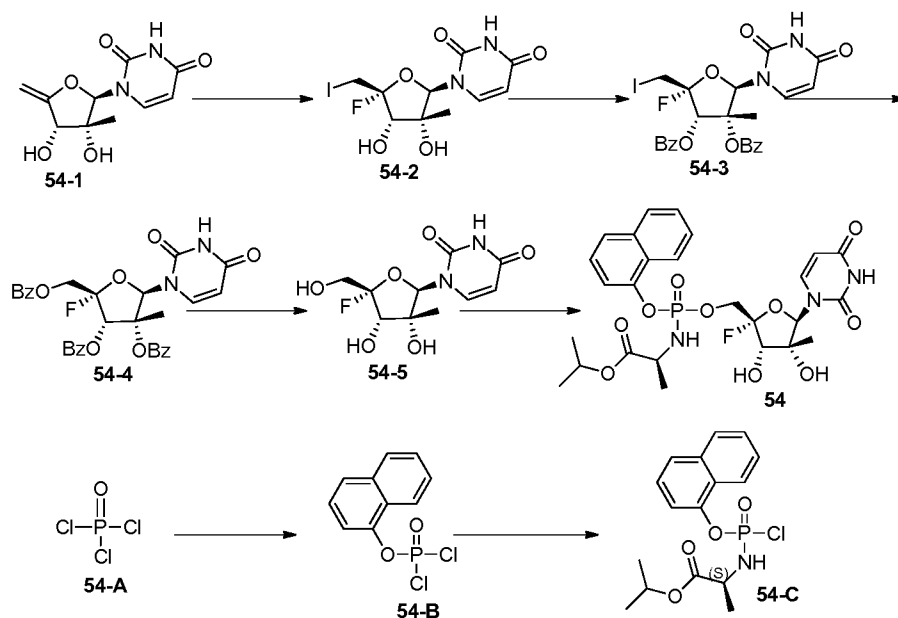
[0386] To an ice-cooled solution of **45-5** (1.20 g, 4.65 mmol) in anhydrous MeCN (12 mL) was added NIS (1.57 g, 6.97 mmol) and TEA $\cdot$ 3HF (1.12 g, 6.97 mmol) under N_2 . The mixture was stirred at R.T. for 5 h. The reaction was quenched with sat. NaHCO_3 solution, and extracted with EA (3 x 100 mL). The organic phase was dried over anhydrous Na_2SO_4 , and evaporated to dryness at low pressure. The residue was purified on a silica gel column (0-5% MeOH in DCM) to give **45-6** (0.91 g, 48.6%) as a white solid.

[0387] To a stirred solution of **45-6** (1.2 g, 2.97 mmol) in anhydrous DCM (12 mL) was added BzCl (0.83 g, 5.94 mmol), TEA (0.6 g, 5.94 mmol) and DMAP (0.72 g, 5.94 mmol) successively at R.T. The mixture was stirred at R.T. for 12 h. The reaction was quenched with water, and extracted with EA (3 x 60 mL). The organic phase was concentrated at low pressure. The residue was purified by column chromatography (0-5% MeOH in DCM) to give **45-7** (1.2 g, 66.2%) as a white solid.

[0388] Tetra-butyl ammonium hydroxide (25.78 mL, 51.78 mmol) was neutralized with TFA (4.3 mL) to pH=4, and the solution was added to a solution of **45-7** (1.09 g, 2.14 mmol) in DCM (30 mL). *m*-CPBA (1.85 g, 10.74 mmol) was added portion-wise under vigorous stirring, and the mixture was stirred for 12 h. The mixture was diluted with EA (100 mL), and washed with sat. sodium bicarbonate. The organic phase was concentrated at low pressure. The residue was purified by column chromatography (50% EA in PE) to give **45-8** (350 mg, 41.1%) as a white solid.

[0389] Compound **45-8** (280 mg, 0.704 mmol) was treated with NH₃ in MeOH (10 mL, 7 M) at R.T. The mixture was stirred at R.T. for 2 h. The mixture was concentrated at a low pressure. The residue was purified by column chromatography (0-10% MeOH in DCM) to give compound **45** (110 mg, 53.1%) as a white solid. ESI-LCMS: *m/z* 295.1 [M+H]⁺.

EXAMPLE 37 COMPOUND 54



[0390] To an ice-cooled solution of **54-1** (10 g, 42 mmol) in anhydrous MeCN (200 mL) was added TEA•3HF (10 g, 62.5 mmol) and NIS (28 g, 126 mmol). The mixture was stirred at R.T. for 1.5 h, and monitored by LCMS. After the reaction was completed, the mixture was concentrated at a low pressure. The residue was purified by silica gel column chromatography (15% MeCN in DCM) to give **54-2** (12 g, 74%) as a yellow solid.

[0391] To a solution of **54-2** (22 g, 57 mmol) in anhydrous DCM (200 mL) was added DMAP (21 g, 171 mmol) and BzCl (17.6 g, 125 mol). The mixture was stirred for 5 h at R.T., and monitored by LCMS. The solution was washed with sat. NaHCO₃ solution, brine and extracted with EA. The organic phase was dried over anhydrous Na₂SO₄ and filtered. The

filtrate was concentrated at low pressure. The residue was purified by silica gel column chromatography (20% EA in PE) to give **54-3** (30 g, 88%) as a white foam.

[0392] To a solution of **54-3** (6.5 g, 11 mmol) in anhydrous DMF (270 mL) was added NaOBz (15.8 g, 110 mmol) and 15-crown-5 (29 g, 132 mmol). The mixture was stirred at 95°C for 48 h. The precipitate was removed by filtration, and the organic solvent was removed at low pressure. The residue was dissolved in EA (200 mL), and the solution was washed with sat. NaHCO₃ solution, and brine. The organic layer was dried over anhydrous Na₂SO₄ and filtered. The filtrate was concentrated at low pressure. The residue was purified by silica gel column chromatography (20% EA in PE) to give **54-4** (3 g crude, 46.1%) as an oil.

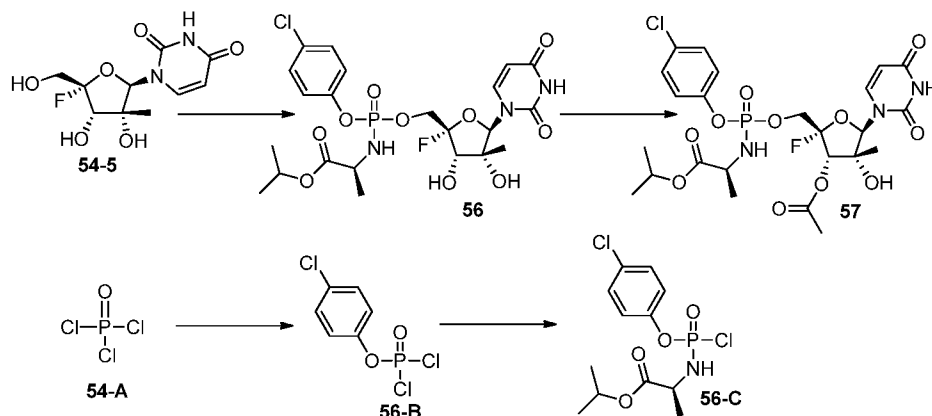
[0393] Compound **54-4** (3 g, crude) was treated with NH₃ in MeOH (120 mL, 7 M). The mixture was stirred for 3 h and monitored by TLC. The solution was concentrated at low pressure. The residue was purified by silica gel column chromatography (10% isopropanol in DCM) to give **54-5** (1.0 g, 67%) as a white solid. ¹H-NMR (CD₃OD, 400MHz) δ = 1.19(s, 3H), 3.76-3.82 (m, 2H), 4.02 (d, *J* = 19.8 Hz, 1H), 5.70 (d, *J* = 8.07 Hz, 1H), 6.27 (s, 1H), 7.89 (d, *J* = 8.07 Hz, 1H).

[0394] Compound **54-5** (100 mg, 0.36 mmol) was co-evaporated with toluene 3 times. To a stirred solution of **54-5** (100 mg, 0.36 mmol) in a mixture of MeCN (1.0 mL) and NMI (295 mg, 3.6 mmol) was added a solution of **54-C** (255.6 mg, 0.72 mmol, preparation described below) in MeCN (0.5 mL) at 0 °C. The mixture was stirred at R.T. overnight. The reaction was quenched with water, and diluted with EA (20 mL). The organic layer was washed with water and brine. The organic layer was dried over anhydrous Na₂SO₄. The organic phase was concentrated at low pressure. The residue was purified on a silica gel column (5% *i*-PrOH in DCM) to give the crude product. The product was purified by prep-HPLC (0.1% HCOOH in water and MeCN) to give compound **54** (46.7 mg, 23.3%) as a white solid. ESI-LCMS: *m/z* 618 [M+Na]⁺.

[0395] To a stirred solution of **54-A** (2.0 g, 13.16 mmol) and naphthalen-1-ol (1.89 g, 13.16 mmol) in anhydrous DCM (100 mL) was added a solution of TEA (1.33 g, 13.16 mmol) in DCM (20 mL) dropwise at -78°C. After addition, the mixture was gradually warmed to R.T., and stirred for 2 h. The solution was cooled to -78°C, and (S)-isopropyl 2-aminopropanoate hydrochloride (2.20 g, 13.16 mmol) in DCM (20 mL) was added, followed by TEA (2.66 g, 26.29 mmol) in DCM (20 mL) dropwise. The mixture was gradually warmed to R.T., and stirred for 2 h. The organic solvent was removed at low pressure. The residue was dissolved in methyl-butyl ether. The precipitate was filtered, and the filtrate was concentrated at low

pressure. The residue was purified on a silica gel column (anhydrous DCM) to give **54-C** (1.0 g, 24.8%) as a colorless oil.

EXAMPLE 38
COMPOUNDS 56 AND 57

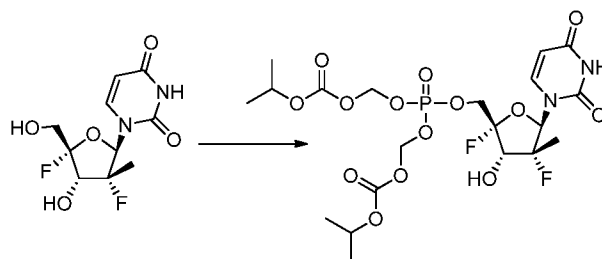


[0396] To a solution of **54-5** (300 mg, 1.08 mmol) and NMI (892 mg, 10 mmol) in anhydrous MeCN (4 mL) was added a solution of **57-C** (736 mg, 2.17 mmol, preparation described below) in anhydrous MeCN (1 mL) dropwise at 0°C. The mixture was stirred at R.T. overnight. The reaction was quenched with water, and diluted with EA (30 mL). The organic layer was washed with water and brine. The organic phase was dried over anhydrous Na₂SO₄ and concentrated at low pressure. The residue was purified by a silica gel column (iPrOH in DCM from 1% to 5%) to give crude compound **56** (276 mg, crude). Crude compound **56** (96 mg) was purified by prep-HPLC (0.1% HCOOH in water and MeCN) to give pure compound **56** (46 mg, 47.9%) as a white solid. ESI-LCMS: m/z 560 [M - F]⁺.

[0397] To a solution of compound **56** (180 mg, 0.31 mmol) in anhydrous pyridine (6 mL) was added acetic anhydride (158 mg, 1.54 mmol) dropwise at 0°C. The mixture was stirred at R.T. overnight. The solution was quenched with water and concentrated at a low pressure. The residue was dissolved in EA (10 mL), and washed with brine. The organic layer was dried over anhydrous Na₂SO₄. The organic phase was concentrated at low pressure. The residue was purified by silica gel column (i-PrOH in DCM from 1% to 3%) to give crude compound **57** (172 mg). Crude compound **57** was purified by prep-HPLC (0.1% HCOOH in water and MeCN) to give pure compound **57** (46 mg, 23.8%) as a white solid. ESI-LCMS: m/z 602.3 [M-F]⁺.

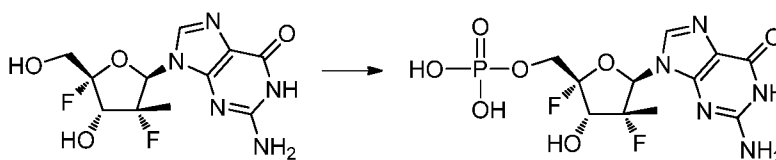
[0398] Compound **56-C** (1.02 g, 23%, a colorless oil) was prepared using a procedure similar to the preparation of **54-C** using **54-A** (2.00 g, 13.16 mmol) and 4-chlorophenol (1.68 g, 13.16 mmol).

EXAMPLE 39
COMPOUND 61



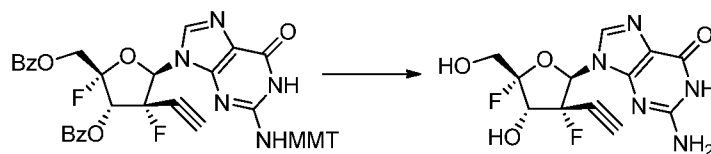
[0399] Compound **25** (109 mg, 0.39 mmol) and triethylammonium bis(isopropoxyloxycarbonyloxymethyl)phosphate (0.6 mmol, prepared from 195 mg of bis(isopropoxyloxycarbonyloxymethyl)phosphate and 85 μ L of Et₃N) were rendered anhydrous by coevaporating with pyridine, followed by toluene. The residue was dissolved in anhydrous THF (3 mL) and cooled in an ice-bath. Diisopropylethyl amine (0.2 mL, 3 eq.), BopCl (190 mg, 2 eq.), and 3-nitro-1,2,4-triazole (81 mg, 2 eq.) were added, and the mixture was stirred at 0°C for 90 mins. The mixture was diluted with EtOAc, washed with sat. aq. NaHCO₃ and brine, and dried (Na₂SO₄). Purification on silica gel column with CH₂Cl₂/i-PrOH (4-10% gradient) followed by RP-HPLC purification (A: 0.1% HCOOH in water, B: 0.1% HCOOH in MeCN) yielded compound **61** (28 mg, 12%). ¹H-NMR (CDCl₃): δ 7.24 (d, 1H), 6.6 (br, 1H), 5.84 (d, 1H), 5.65-5.73 (m, 4H), 4.94 (m, 2H), 4.38 (m, 2H), 4.1 (b, 1H), 2.88 (d, 1H), 1.47 (d, 3H), 1.33 (m, 12H).

EXAMPLE 40
COMPOUND 74



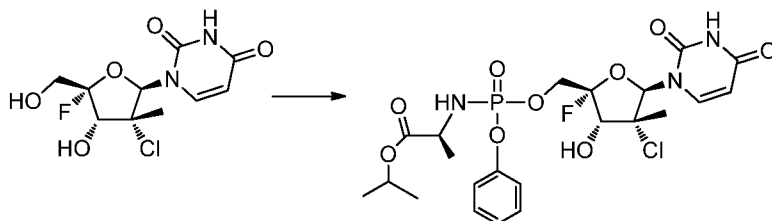
[0400] Dry nucleoside (0.05 mmol) was dissolved in a mixture of PO(OMe)₃ (0.7 mL) and pyridine (0.3 mL). The mixture was evaporated in vacuum for 15 mins. at 42°C, then cooled to R.T. N-Methylimidazole (0.009 mL, 0.11 mmol) was added followed by POCl₃ (0.009 mL, 0.11 mmol). The mixture was kept at R.T. for 20-40 mins and monitored for the formation of compound **74** by LCMS. The reaction was quenched with water and isolated by RP HPLC on Synergy 4 micron Hydro-RP column (Phenomenex). A linear gradient of methanol from 0 to 30% in 50mM triethylammonium acetate buffer (pH 7.5) was used for elution. The corresponding fractions were combined, concentrated and lyophilized 3 times to remove excess of buffer. MS: m/z 396.5 [M-1].

EXAMPLE 41
COMPOUND 68



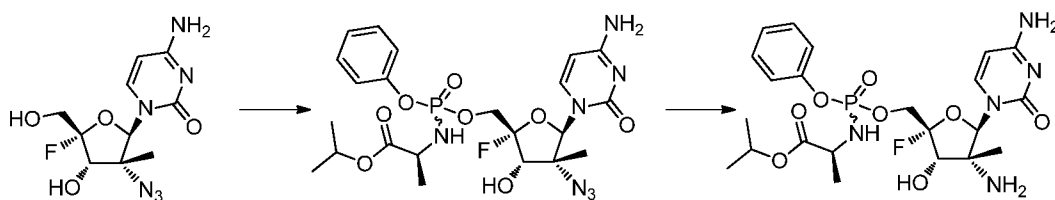
[0401] The nucleoside (140 mg, 0.42 mmol) was dissolved in n-butylamine (0.5 mL). The mixture was kept for 2 h at R.T., and the amine was then evaporated. The residue was dissolved in EtOAc, and the organic layer was washed twice with 10% citric acid, dried over Na₂SO₄, and evaporated. The residue purified by column chromatography on silica gel in linear gradient of methanol in DCM from 0% to 12% over 10 column volumes. The fractions containing the product were concentrated and treated with 80% HCOOH for 1 h at R.T. The mixture was evaporated to dryness, and suspended in CH₃CN. The precipitate was separated, washed with CH₃CN (1 mL) and dried to yield compound **68** (27 mg, 50%). MS: m/z 326.5 [M-1].

EXAMPLE 42
COMPOUND 62



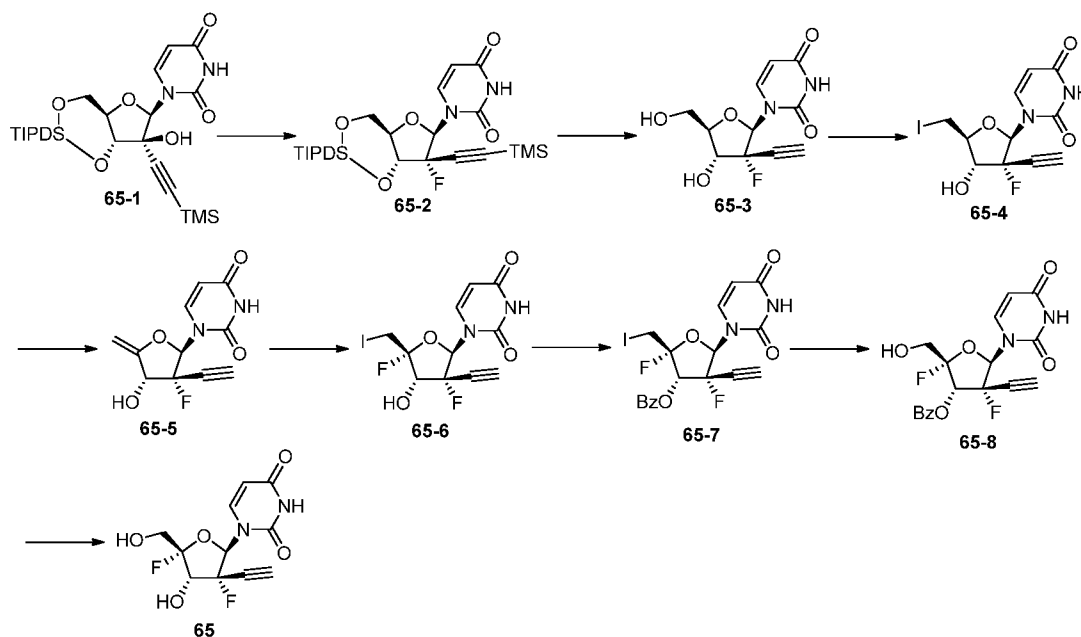
[0402] Compound **45** (30 mg, 0.1 mmol) was dissolved in a mixture of CH₃CN (2 mL) and N-methylimidazole (200 uL). Phosphorochloridate (100 mg, 0.3 mmol) was added, and the mixture was kept for 5 d at R.T. The mixture was distributed between water and EA. The organic layer was separated, washed with brine, dried and evaporated. The phosphoroamidate was isolated by silica gel chromatography in a gradient of methanol in DCM from 3% to 10%. The corresponding fractions were concentrated and re-purified by RP HPLC on Synergy 4 micron Hydro-RP column (Phenomenex). A linear gradient of methanol in DCM from 3% to 95% containing 0.1% formic acid was used for elution. Compound **62** was obtained as a mixture Rp and Rs isomers (9 mg, 16%). MS: m/z 562.1[M-1].

EXAMPLE 43
COMPOUND 72



[0403] Compound **47** (30 mg, 0.1 mmol) was dissolved in a mixture of CH₃CN (2 mL) and N-methylimidazole (200 μ L). Phosphorochloridate (100 mg, 0.3 mmol) was added, and the mixture was kept overnight at 40°C. The temperature was increased to 65°C and heated for 1 h. The mixture was distributed between water and EA. The organic layer was separated, washed with brine, dried and evaporated. The azido-phosphoramidate was purified by RP HPLC on Synergy 4 micron Hydro-RP column (Phenomenex). A linear gradient of methanol from 30% to 100% in 50mM triethylammonium acetate buffer (pH 7.5) was used for elution. The azido-phosphoramidate (8 mg) was dissolved in pyridine/Et₃N (3 mL, 8:1 v/v) and cooled to 0°C. H₂S gas was bubbled through the solution for 10 min, and the reaction was kept for 1 h at R.T. The solvents were evaporated, and the residue isolated by RP HPLC. The corresponding fractions were combined, concentrated and lyophilized 3 times to remove excess of buffer, to provide compound **72** (1.2 mg) as mixture Rp and Rs isomers. MS: m/z 544.1 [M+1]⁺.

EXAMPLE 44 COMPOUND 65



[0404] To a solution of **65-1** (23.0 g, 39.5 mmol) in anhydrous toluene (200 mL) was added DAST (31.9 g, 198 mmol) dropwise at -78°C, and the solution was stirred at -78°C for 3 h. The mixture was quenched with sat. NaHCO₃, extracted with EA (2 x 200 mL) and dried over with anhydrous Na₂SO₄. The solution was concentrated to dryness under low pressure. The residue was purified on a silica gel column (50% EA in PE) to give **65-2** (16.5 g, 71%) as a yellow foam.

[0405] A mixture of **65-2** (16.0 g, 27.4 mmol) and NH_4F (3.0 g, 82.2 mmol) in methanol (100 mL) was stirred at 70°C for 12 h. The reaction was cooled, and the salt was removed by filtration. The filtrate was concentrated to dryness at low pressure. The residue was purified on a silica gel column (3% MeOH in DCM) to give **65-3** (5.1 g, 69.0%) as a white foam.

[0406] To a stirred suspension of **65-3** (4.1 g, 15.2 mmol), PPh_3 (8.0 g, 30.4 mmol), imidazole (2.1 g, 30.4 mmol) and pyridine (18.2 mL) in anhydrous THF (40 mL) was added dropwise a solution of I_2 (5.8 g, 22.8 mmol) in THF (20 mL) at 0°C. The mixture was stirred at R.T. for 12 h. The reaction was quenched with MeOH (100 mL), and the solvent was removed under reduced pressure. The residue was purified on a silica gel column (4% MeOH in DCM) to give pure **65-4** (4.4 g, 77%) as a white solid. ESI-MS: m/z 381.1 $[\text{M}+1]^+$.

[0407] To a stirred solution of **65-4** (2.5 g, 0.7 mmol) in anhydrous THF (3 mL) was added DBU (2.1 g, 14 mmol) at R.T., and the mixture was stirred at R.T. for 1 h. The reaction was quenched with HOAc, and diluted with 2-Me-tetrahydrofuran. The solution was washed with brine, dried over with anhydrous Na_2SO_4 and concentrated to dryness at low pressure. The residue was purified on a silica gel column (MeOH 5% in DCM) to give **65-5** (1.1 g, 68.9%) as a white foam.

[0408] To a stirred solution of **65-5** (800 mg, 3.17 mmol) in anhydrous CH_3CN (10 mL) was added TEA•3HF (510 mg, 3.17 mmol) and NIS (785 mg, 3.49 mmol) at 0°C. The mixture was stirred for 30 mins, gradually warmed to R.T., and stirred for 1 h. The mixture was quenched with sat. NaHCO_3 solution and $\text{Na}_2\text{S}_2\text{O}_3$ solution, and extracted with EA (2 x 20 mL). The organic layer was dried over with anhydrous Na_2SO_4 , and concentrated to dryness at low pressure. The residue was purified on a silica gel column to give pure **65-6** (695 mg, 57.9%) as a yellow solid.

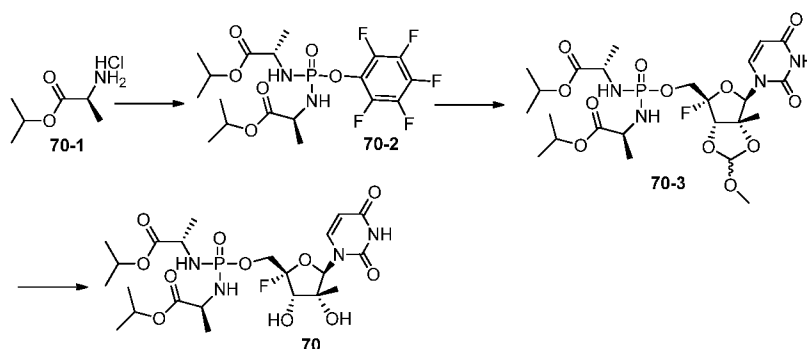
[0409] To a stirred solution of **65-6** (650 mg, 1.63 mmol) in pyridine (3 mL) was added BzCl (507 mg, 3.59 mmol) at 0°C, and stirred at R.T. for 12 h. The mixture was quenched with water, and concentrated to dryness under reducing pressure. The residue was purified on a silica gel column (EA 50% in PE) to yield **65-7** (550 mg, 67%) as a white foam.

[0410] Tetra-butylammonium hydroxide (9 mL as 54-56% aqueous solution, 72 mmol) was neutralized with TFA to pH~4 (1.5 mL), and the mixture was added to a solution of **65-7** (375 mg, 0.75 mmol) in DCM (9 mL). *m*-Chloroperbenzoic acid (924 mg, 60-70%, 3.75 mmol) was added in portions with vigorous stirring, and the mixture was stirred overnight. The mixture was washed with brine, dried over magnesium sulfate and concentrated under reduced

pressure. The residue was purified by column chromatography (EA 50% in PE) to give **65-8** (230 mg, 78.8%) as a white foam. ESI-MS: m/z 393.1 $[M+1]^+$.

[0411] Compound **65-8** (120 mg, 0.24 mmol) was treated with 7N $\text{NH}_3 \cdot \text{MeOH}$ (20 mL), and stirred for 5 h. The mixture was concentrated to dryness at low pressure. The residue was purified on a silica gel column (propan-2-ol 15% in DCM) to yield compound **65** (53 mg, 60.2%) as a white solid. ESI-MS: m/z 288.8 $[M+1]^+$.

EXAMPLE 45 **COMPOUND 70**



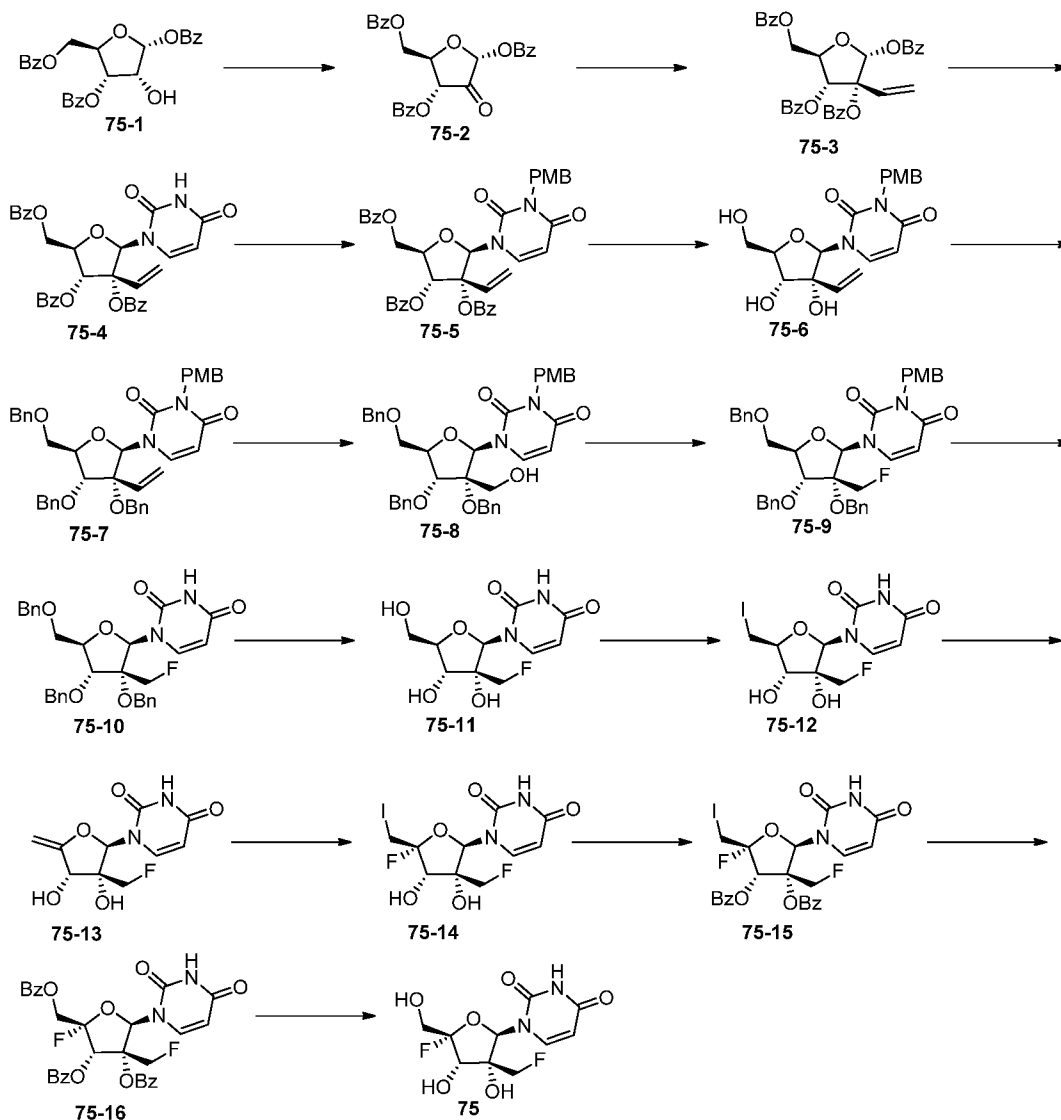
[0412] To a solution of **70-1** (3.0 g, 18.0 mmol) and POCl_3 (1.35 g, 9.0 mmol) in DCM (80 mL) was added TEA (3.6 g, 36.0 mmol) in DCM (20 mL) dropwise at 0°C . The mixture was stirred at 0°C for 2 h. A solution of pentafluorophenol (1.65 g, 9.0 mmol) and TEA (0.9 g, 9.0 mmol) in DCM (20 mL) was added dropwise at 0°C , and the mixture was stirred at 0°C for 15 h. After the reaction was completed, the mixture was concentrated under reduced pressure. The residue was washed by TBME and filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (20% EA in PE) to give **70-2** (2.7 g, 62.7%) as a white solid. ESI-MS: m/z 491.1 $[M+1]^+$.

[0413] To a stirred solution of 1-((3aR,4R,6S,6aS)-6-fluoro-6-(hydroxymethyl)-2-methoxy-3a-methyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)pyrimidine-2,4(1H,3H)-dione (150 mg, 0.47 mmol) in anhydrous THF (2 mL) was added a solution of $t\text{-BuMgCl}$ (0.46 mL, 1M in THF) dropwise at 0°C . The mixture was stirred at R.T. for 40 mins, and re-cooled to 0°C . A solution of **70-2** (462 mg, 0.94 mmol) was added, and the mixture was stirred at R.T. for 4 h. The mixture was quenched with H_2O , and extracted with EA. The organic layer was dried over Na_2SO_4 and concentrated under reducing pressure. The residue was purified on a silica gel column (50% EA in PE) to give **70-3** as a white foam (230 mg, 78%).

[0414] Compound **70-3** (230 mg, 0.37 mmol) was dissolved in 80% HCOOH aqueous solution (20 mL), and the mixture was stirred at R.T. for 24 h. The solvent was removed at low pressure. The residue was purified on a silica gel column to give the crude

product, which was purified by RP HPLC (HCOOH system) to give compound **70** as a mixture of two P-isomers (75 mg, 33%). ESI-TOF-MS: m/z 583.0 $[M+H]^+$.

EXAMPLE 46
COMPOUND 75



[0415] To a solution of **75-1** (120 g, 0.26 mol) in CH_3CN (2.0 L) was added IBX (109 g, 0.39 mol), and refluxed for 12 h. The reaction was monitored by TLC and LCMS. After cooling to R.T., the mixture was filtered, and the filtrate was concentrated at low pressure. The crude product was used directly for the next step.

[0416] Compound **75-2** (130 g, 0.26 mol) was co-evaporated with anhydrous toluene three times to remove H_2O . To a solution of **75-2** in THF (300 mL) was added dropwise vinyl magnesium bromide (700 mL, 0.78 mol, 1N in THF) over 30 min at $-78^\circ C$. The mixture was stirred for about 1 h at R.T. After the starting material was consumed, the mixture was poured into a sat. NH_4Cl solution. The organic layer was washed with brine, dried with anhydrous

Na₂SO₄ and filtered. The solution was concentrated at low pressure to get the crude product. To a solution of this crude product (170 g, 0.346 mol) in anhydrous CH₂Cl₂ was added TEA (105 g, 1.04 mol) and DMAP (84 g, 0.69 mol). Benzoyl chloride (146 g, 1.04 mol) was added slowly at R.T. for 12 h. The mixture was diluted with CH₂Cl₂ and then washed with sat. aq. NaHCO₃. The combined aq. phase was extracted with DCM (100 mL), and the combined organic phase was dried with Na₂SO₄. After filtration, the solution was evaporated to dryness under reduced pressure, and the residue was purified by column chromatography to give **75-3** (107 g, 52%).

[0417] Uracil (44.8 g, 0.4 mol) (co-evaporated with toluene twice) and NOBSA (81.4 g, 0.4 mol) were dissolved in CH₃CN (500 mL). The mixture was refluxed for 1.5 h and then slowly cooled to R.T. The mixture was treated with **75-3** (59 g, 0.1 mol) and TMSOTf (155 g, 0.7 mol), and then warmed to 60-70°C for 12 h. The mixture was neutralized with a sat. NaHCO₃ solution, and extracted with EA (3 x 1000 mL). The solution was dried over anhydrous MgSO₄, and evaporated at low pressure. The residue was purified using a silica gel column to give pure **75-4** (40 g, 69%) as a white solid.

[0418] To a solution of **75-4** (50 g, 0.086 mol) in DMF was added PMBCl (16 g, 0.1 mol) and K₂CO₃ (17.8 g, 0.13 mol) at 0°C, and the mixture was stirred at R.T. for 12 h. The mixture was quenched with water (100 mL), and extracted with EA (3 x 200 mL). The organic phase was concentrated at low pressure to give crude **75-5** (65 g) which was used in the next step without further purification.

[0419] To a solution of crude **75-5** (65 g, 0.086 mol) in MeOH/DCM (4/1) (200 mL) was added NaOMe (16.8 g, 0.3 mol), and the mixture was stirred at R.T. for 2.5 h. The reaction was quenched with dry ice, and then concentrated at low pressure. The residue was dissolved in EA (200 mL) and washed with brine. The organic layer was concentrated at low pressure, and the residue was purified using a silica gel column using 1% MeOH in CH₂Cl₂ to give **75-6** as a yellow foam (25 g, 75%).

[0420] To a solution of **75-6** (25.5 g, 0.065 mol) in DMF was added NaH (10.5 g, 0.26 mol) slowly at 0°C, and the mixture was stirred for 30 mins. BnBr (36.3 g, 0.21 mol) was added, and the mixture was stirred at R.T. for 12 h. The reaction was quenched with sat. NH₄Cl (aq.), and then extracted with EA (3 x 100 mL). The solution was dried over anhydrous MgSO₄, and evaporated at low pressure. The residue was purified by a silica gel column using 10% EA in PE to give **75-7** (20 g, 46%) as a white solid.

[0421] To a solution of **75-7** (20 g, 0.03 mol) and NMMO (7 g, 0.06 mol) in THF:H₂O (5:1) (100 mL) was added OsO₄ (2.6 g, 0.01 mol) at R.T., and the mixture was stirred

at R.T. for 24 h. The mixture was quenched with a sat. $\text{Na}_2\text{S}_2\text{O}_3$ solution, and extracted with EA (3 x 100 mL). The organic layer was washed with brine, and dried over anhydrous MgSO_4 . The solution was evaporated at low pressure to give the crude compound, which was used in the next step without further purification.

[0422] To a solution of the crude diol (0.03 mol) in $\text{MeOH}:\text{H}_2\text{O}:\text{THF}$ (170 mL:30 mL:50 mL) was added NaIO_4 (9.6 g, 0.045 mol), and the mixture was stirred at R.T. for 2 h. After filtration, the filtrate was used directly in the next step. This solution was treated with NaBH_4 (1.8 g, 0.048 mol) at 0°C , and the mixture was stirred at R.T. for 30 mins. The mixture was quenched with MeOH , and evaporated at low pressure. The residue was dissolved in EA (100 mL), and washed with brine. The solution was evaporated at low pressure, and the residue was purified by a silica gel column using 20% EA in EA to give **75-8** (12 g, 61% over three steps).

[0423] To a solution of **75-8** (14 g, 21 mmol) and DMAP (5.1 g, 42 mmol) in DCM (100 mL) was added MsCl (3.1 g, 27 mmol) at 0°C , and the mixture was stirred at R.T. for 40 mins. The reaction was quenched with sat. NaHCO_3 (aq.), and washed with HCl (0.2 N) solution. The organic phase was dried over anhydrous MgSO_4 , and evaporated at low pressure. The residue was purified by a silica gel column using 5% EA in PE to give mysolate product (14 g, 90%). The MsO -product (41 g, 55 mmol) was treated with TBAF (1 N in THF, 500 mL), and the mixture was stirred at $70\text{--}80^\circ\text{C}$ for 3 d. The mixture was concentrated at low pressure, and the residue was dissolved in EA (200 mL). The solution was washed with brine, dried over anhydrous MgSO_4 and evaporated at low pressure. The residue was purified by chromatography using 10% EA in PE to give **75-9** (9.9 g, 27%).

[0424] To a solution of **75-9** (6.3 g, 9.45 mmol) in $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (3:1, 36 mL:12 mL) was added CAN (15.5 g, 28.3 mmol), and the mixture was stirred at R.T. overnight. The mixture was extracted with EA (3 x 50 mL). The solution was dried over anhydrous MgSO_4 , and evaporated at low pressure. The residue was purified by chromatography using 20% EA in PE to give **75-10** (3.6 g, 71%) as a white solid.

[0425] To a solution of **75-10** (2.4 g, 4.4 mmol) in anhydrous DCM (10 mL) was added slowly BCl_3 (1 N, 30 mL CH_2Cl_2) at -70°C , and the mixture was stirred for 2 h. at -70°C . The mixture was quenched with the slow addition of MeOH at -70°C , and the mixture was concentrated at low pressure. The residue was purified by chromatography using 50% EA in PE to give **75-11** (1.2 g, 86%) as a white solid. ESI-MS: m/z 277.1 $[\text{M}+\text{H}]^+$.

[0426] To a solution of PPh_3 (3.37 g, 12.8 mmol) in pyridine (15 mL) was added I_2 (3.06 g, 12 mmol) at 0°C , and the mixture was stirred at R.T. for 30-40 mins. The mixture was

cooled to 0°C, and then treated with **75-11** (2.2 g, 8 mmol) in Py. (5 mL). The mixture was stirred at R.T. under N₂ for 12 h. The mixture was quenched with sat. Na₂S₂O₃ (aq.) and extracted with CH₂Cl₂ (3 x 50 mL). The organic phase was dried over anhydrous MgSO₄, and then concentrated at low pressure. The residue was purified by chromatography using 1-2% MeOH in CH₂Cl₂ to yield **75-12** (1.8 g, 58%) as a white solid.

[0427] To a solution of **75-12** (1.35 g, 3.5 mmol) in THF:CH₃CN (10 mL:5 mL) was added DBU (1.06 g, 7 mmol), and the mixture was stirred at 60-70°C for 2 h. The mixture was concentrated at low pressure, and the residue was dissolved in EA (20 mL). The solution was washed with 10% HCl solution and brine. The organic phase was dried over anhydrous MgSO₄ and concentrated at low pressure. The residue was purified by chromatography using 30% EA in PE to give **75-13** (0.5 g, 55%).

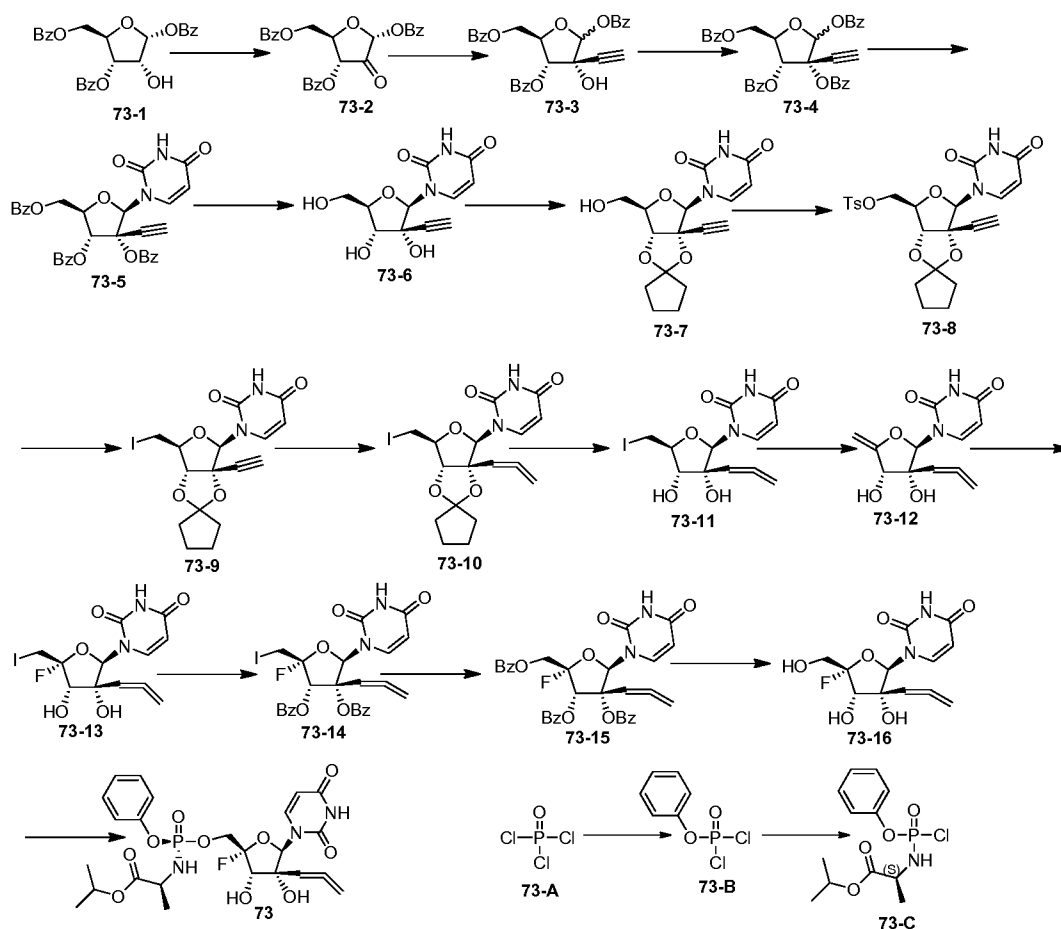
[0428] To a solution of **75-13** (670 mg, 2.6 mmol) in CH₃CN (6 mL) was added NIS (730 mg, 3.25 mmol) and 3HF•TEA (335 mg, 2.1 mmol) at 0°C, and the mixture was stirred at R.T. for 2 h. The mixture was quenched with sat. NaHCO₃ (aq.) and Na₂S₂O₃ (aq.) solution. The mixture was extracted with EA (3 x 20 mL), dried over anhydrous MgSO₄ and concentrated at low pressure. The residue was purified by chromatography using 1-2% MeOH in CH₂Cl₂ to give **75-14** (1.2 g, 80%).

[0429] To a solution of **75-14** (1.0 g, 2.47 mmol), DMAP (0.75 g, 6.2 mmol) and TEA (0.75 g, 7.42 mmol) in DCM (10 mL) was added BzCl (1.15 g, 8.16 mmol) in DCM (1 mL) at 0°C, and the mixture was stirred at R.T. for 12 h. The mixture was diluted with CH₂Cl₂ (10 mL), and then washed with HCl (0.1 N, 20 mL) solution and brine. The organic phase was dried over anhydrous MgSO₄, and concentrated at low pressure. The residue was purified by chromatography using 20% EA in PE to afford **75-15** (850 mg, purity~80%).

[0430] To a solution of **75-15** (600 mg, 1 mmol) in DMF (25 mL) was added BzONa (1.45 g, 10 mmol), 15-crown-5 (2.2 g, 10 mmol), and the mixture was stirred at 90-100°C for 24 h. The mixture was concentrated at low pressure, and the residue was dissolved in EA (20 mL), and washed with brine. The organic phase was dried over anhydrous MgSO₄, and then concentrated at low pressure. The residue was purified by chromatography using 15% EA in PE to give **75-16** (275 mg, 37%) as a light yellow foam.

[0431] Compound **75-16** (250 mg, 0.41 mmol) was treated with NH₃•MeOH (7 N, 5 mL), and the mixture stirred at R.T. for 15 h. The mixture was concentrated at low pressure, and the residue was purified by prep-HPLC to give compound **75** (33 mg, 25%) as a white solid. ESI-MS: m/z 295.1 [M+H]⁺.

EXAMPLE 47
COMPOUND 73



[0432] To a solution of IBX (133.33 g, 476 mmol) in dry CH₃CN (2 L) was added **73-1** (100.0 g, 216 mol) at R.T. The mixture was refluxed and stirred for 12 h. The mixture was filtered, and the filtrate was concentrated at low pressure to give **73-2** as a yellow oil (90.0 g, 90.4%).

[0433] Compound **73-2** (50.0 g, 108.70 mmol) was coevaporated with anhydrous toluene twice to remove H₂O. Ethynyl magnesium bromide, (800 mL, 400.0 mmol) was added dropwise into a solution of **73-2** in THF (500 mL) over 20 mins at -78°C. The mixture was stirred for about 10 mins at -78°C. When the starting material was consumed, the ice–acetone cooling bath was removed. The mixture was quenched with a sat. NH₄Cl solution with stirring, and then warmed to R.T. The mixture was extracted with EA, filtered through Celite and washed with brine. The combined organic phase was dried over anhydrous Na₂SO₄, filtered and concentrated at low pressure to give crude **73-3** as a deep yellow oil (48.0g, yield: 90.8%).

[0434] Compound **73-3** (200.0 g, 411.52 mmol) was dissolved in anhydrous CH₂Cl₂ (2000 mL) and then DMAP (100.41 g, 823.05 mmol) and Et₃N (124.94 g, 1.23 mol) were added at R.T. The mixture was treated with benzoyl chloride (173.46 g, 1.23 mol) at 0°C. After

stirring for 12 h at R.T., the reaction was quenched with H₂O. The combined aq. phase was extracted with DCM. The combined organic phase was dried over anhydrous Na₂SO₄, filtered and evaporated to dryness under reduced pressure to give a black oil. The oil was purified by column chromatography using 7%-20% EA in PE as the eluent to give a yellow oil. The residue triturated with CH₃OH and filtered. The filter cake was concentrated in vacuo to give **73-4** as a white solid (30.0 g, 36.4%).

[0435] Uracil (34.17 g, 305.08 mmol) were coevaporated with anhydrous toluene twice to remove H₂O. To a stirred suspension of uracil in anhydrous MeCN (150 mL) was added N,O-BSA (123.86 g, 610.17 mmol) at R.T. The mixture was refluxed for 1.5 h and then cooled to R.T. Compound **73-4** (90 g, 152.54 mmol, which were coevaporated with anhydrous toluene twice to remove H₂O) was added. TMSOTf (237.05 g, 1.07 mol) was then added at R.T. The mixture was heated to 70°C, and then stirred overnight and then monitored by LCMS. The mixture was cooled to R.T., and quenched with a sat. NaHCO₃ solution. The solution was extracted with EA. The organic layer was dried over Na₂SO₄, and then concentrated at low pressure. The residue was purified using a silica gel column eluted with 10%-50% EA in PE to give **73-5** as a white solid (45 g, 50.9%).

[0436] Compound **73-5** (50 g, 86.21 mmol) was treated with NH₃ in MeOH (1 L) at R.T., and then stirred for 48 h. The mixture was concentrated at low pressure, and the residue was purified by column chromatography (10% MeOH in DCM) to give **73-6** (12.6 g, 54.55%) as a white solid.

[0437] To a solution of cyclopentanone (100 g, 1.189 mmol) and trimethyl orthoformate (150 mL) in MeOH (600 mL) was added TsOH·H₂O (1.13 g, 5.9 mmol), and the mixture was stirred at R.T. for 30 mins. The reaction was quenched with NaOMe (0.32 g, 5.9 mmol) and H₂O, and the solution was extracted by n-hexane. The organic layer was dried over anhydrous Na₂SO₄, and then concentrated at low pressure. The cyclopentyl dimethoxy acetal and **73-6** (20 g, 74.63 mmol) was dissolved in DCE (200 mL), and then treated with TsOH·H₂O (0.71 g, 3.73 mmol). The mixture was stirred at 50°C for 12 h, and then concentrated at low pressure. The residue was purified by silica gel column chromatography (1-10% MeOH in DCM) to give **73-7** (15.4 g, 61.8%) as a white solid.

[0438] Compound **73-7** (20.0 g, 0.06 mol) was coevaporated with anhydrous pyridine three times to remove H₂O. To an ice-cold solution of **73-7** in anhydrous pyridine (100 ml) was added TsCl (22.8 g, 0.12 mol) at 0°C, and the mixture was stirred overnight and monitored by LCMS and TLC. The reaction was quenched with H₂O and extracted with EA. The organic phase was dried over anhydrous NaSO₄ and evaporated at low pressure. The

residue was purified by silica gel column chromatography (DCM: MeOH=100:1 to 15:1) to give **78-8** (20.0 g, 69.0%) as a white solid.

[0439] To a solution of **73-8** (20.0 g, 0.04 mol) in acetone (200 ml) was added NaI (31.0 g, 0.2 mol) and heated to reflux overnight and monitored by LCMS. The mixture was quenched with a sat. Na₂S₂O₃ solution, and extracted with EA. The organic phase was dried over anhydrous Na₂SO₄ and evaporated at low pressure. The residue was purified by silica gel column chromatography (DCM: MeOH=100:1 to 15:1) to give **73-9** (15.0 g, 83.3%) as a white solid.

[0440] To **73-9** (30.0 g, 0.068 mol) in dioxane (60 mL) in sealed tube was added CuBr (4.9 g, 0.034 mol), *i*-Pr₂NH (13.6 g, 0.135 mol) and (CH₂O)_n (5.1 g, 0.17 mol) under N₂. The mixture was heated at reflux for 16 h. The mixture was diluted with EtOAc, and washed with a sat. NH₄Cl solution and brine. The solution was dried over anhydrous MgSO₄, and concentrated under reduced pressure. The residue was purified by column chromatography (DCM: MeOH=100:1 to 15:1) to give **73-10** (10.0 g, 32.3%) as a white solid.

[0441] Compound **73-10** (10 g, 21.83 mmol) was treated with HCOOH (80%) in H₂O at R.T. The solution was stirred at 60°C for 2 h, and then concentrated at a low pressure. The residue was purified by column chromatography (1%-10% MeOH in DCM) to give **73-11** (5.1 g, 58.55%) as a white solid.

[0442] Compound **73-11** (5 g, 12.79 mmol) was dissolved in anhydrous MeOH (100 mL) and treated with NaOMe (4.83 g, 89.5 mmol) at R.T. The solution was stirred at 60°C for 36 h. The mixture was quenched with CO₂ and then concentrated at low pressure. The residue was purified by column chromatography (0-10% MeOH in DCM) to give **73-12** (2.3 g, 68.05%) as a yellow solid. ¹H-NMR (CDCl₃, 400 MHz) δ = 7.29 (d, *J* = 8 Hz 1H), 6.10 (s, 1H), 5.71 (d, *J* = 8.0 Hz 1H), 5.18 (t, *J* = 6.4 Hz, 1H), 4.79-4.84 (m, 1H), 4.61 (d, *J* = 8.0 Hz, 2H), 4.39 (s, 1H), 3.45 (s, 1H).

[0443] To an ice-cold solution of **73-12** (1.5 g, 5.68 mmol) in anhydrous MeCN (15 mL) was added NIS (1.66 g, 7.39 mmol) and TEA•3HF (0.73 g, 4.55 mmol) under N₂. The mixture was stirred at R.T. for 1 h. The reaction was quenched with sat. NaHCO₃ and sat. Na₂SO₃ solution, and extracted with EA (3 x 100 mL). The organic phase was dried over anhydrous Na₂SO₄, and evaporated to dryness at low pressure. The residue was purified on a silica gel column (0-5% MeOH in DCM) to give **73-13** (1.08 g, 46.2%) as a yellow solid.

[0444] To a stirred solution of **73-13** (1 g, 2.44 mmol) in anhydrous DCM (10 mL) was added DMAP (0.60 g, 4.88 mmol) and Et₃N (0.74g, 7.32 mmol) at R.T. The mixture was treated with benzoyl chloride (0.79 g, 5.61 mmol) at 0°C and then stirred at R.T. for 3 h. The

reaction was quenched with water, and extracted with EA (3 x 60 mL). The organic phase was concentrated at low pressure, and the residue was purified by column chromatography (0-10% MeOH in DCM) to give **73-14** (0.9 g, 59.6%) as a white solid.

[0445] Bu₄NOH (55% in H₂O, 13.74 mL) was treated with TFA (to adjust pH=3-4). The mixture was cooled to R.T. To a solution of **73-14** (0.9 g, 1.46 mmol) in DCM (9 mL) was added m-CPBA (80%, 1.57 g, 7.28 mmol) at R.T. The mixture was stirred at 25°C for 48 h. The mixture was washed with sat. aq. NaHCO₃. The organic layer was passed through an anhydrous Al₂O₃ column, and the solution was concentrated at low pressure. The residue was purified by a silica gel column (30% EA in PE) to give **73-15** (0.26 g, 35.1%) as a yellow solid.

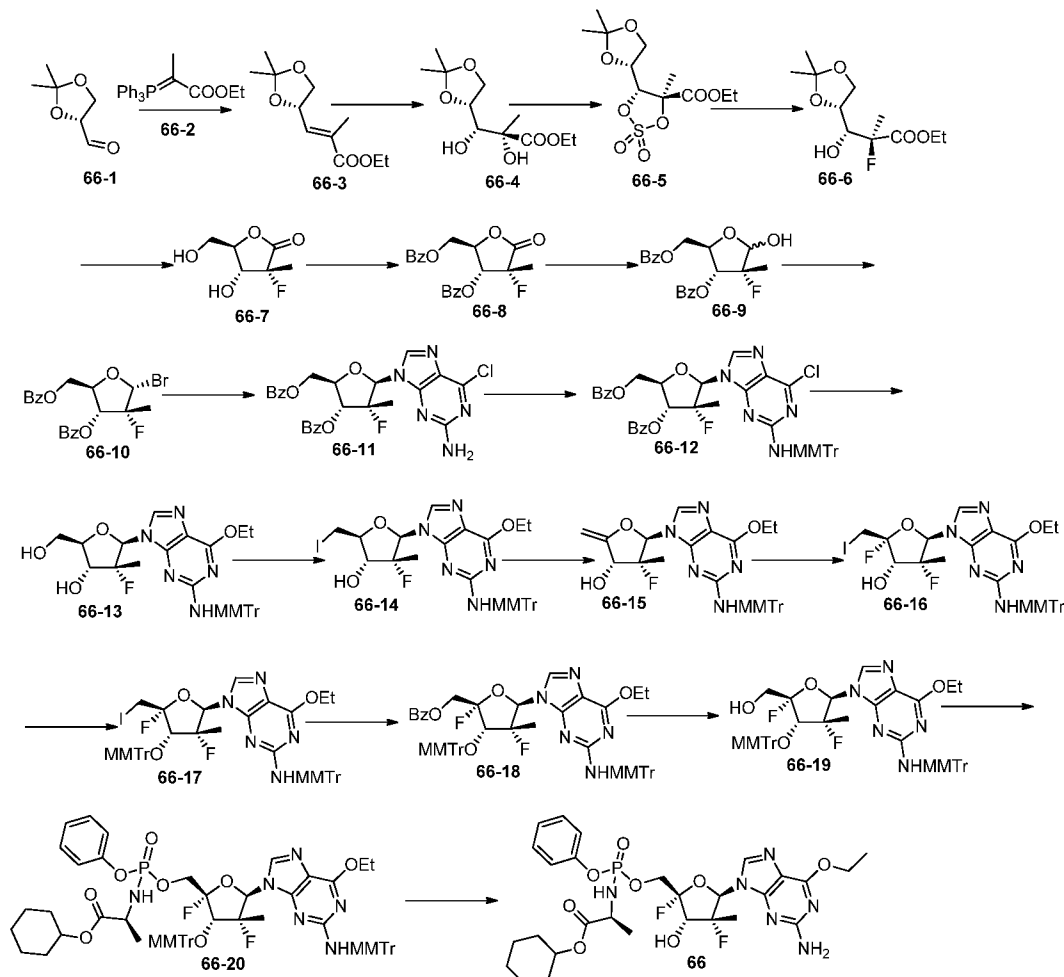
[0446] Compound **73-15** (0.25 g, 0.49 mmol) was dissolved in NH₃/MeOH (5 mL, 7 M), and the mixture was stirred at R.T. for 24 h under N₂. The mixture was concentrated at low pressure at R.T., and the residue was purified by a silica gel column (5% MeOH in DCM) to give **73-16** (100 g, 67.75%) as a white solid. ¹H-NMR (CD₃OD, 400 MHz) δ = 7.83 (d, *J* = 8 Hz 1H), 6.29 (s, 1H), 5.67 (d, *J* = 6.0 Hz 1H), 5.12 (t, *J* = 6.8 Hz, 1H), 4.99-5.01 (m, 1H), 4.38 (d, *J* = 19.6 Hz 1H), 3.74-3.81 (m, 2H), 3.35 (s, 1H).

[0447] Compound **73-16** (100 mg, 0.33 mmol) was co-evaporated with toluene three times to remove H₂O. To a stirred solution of **73-16** (100 mg, 0.33 mmol) in a mixture of MeCN (1.0 mL) and NMI (271 mg, 3.3 mmol) was added a solution of **73-C** (216.5 mg, 0.66 mmol) in MeCN (0.5 mL) at 0 °C. The mixture was stirred at R.T. overnight and then reaction was quenched with water. The mixture was diluted with EA (20 mL), and the organic layer was washed with water and brine, and dried over anhydrous Na₂SO₄. The organic phase was concentrated at low pressure, and the residue was purified on a silica gel column (5% *i*-PrOH in DCM) to give the crude product. The crude product was purified by prep-HPLC (0.1% HCOOH in water and MeCN) to give compound **73** (35.6 mg, 19.0%) as a white solid. ESI-LCMS: *m/z* 592 [M+Na]⁺.

[0448] To a stirred solution of **73-A** (2.0 g, 13.16 mmol) and phenol (1.22 g, 13.16 mmol) in anhydrous DCM (100 mL) was added a solution of TEA (1.33 g, 13.16 mmol) in DCM (20 mL) dropwise at -78°C. The mixture was warmed gradually to R.T., and then stirred for 2 h. The solution was re-cooled to -78°C, and (S)-isopropyl 2-aminopropanoate hydrochloride (2.20 g, 13.16 mmol) in DCM (20 mL) was added, followed by the dropwise addition of TEA (2.66 g, 26.29 mmol) in DCM (20 mL). The mixture was warmed gradually to R.T., and then stirred for 2 h. The organic solvent was removed at low pressure, and the residue was dissolved in methyl-butyl ether. The precipitate was filtered, and the filtrate was

concentrated at low pressure. The residue was purified on a silica gel column (anhydrous DCM) to give **73-C** (0.9 g, 22.3%) as a colorless oil.

EXAMPLE 48
COMPOUND 66



[0449] Compound **66-2** (2648 g, 7.3 mol) was dissolved in anhydrous dichloromethane (10 L), and the solution was cooled to -40 °C with stirring under N₂. Compound **66-1** (1 kg, 7.69 mol) was dissolved in anhydrous CH₂Cl₂ (3 L) and added to the solution of **66-2** over 30 mins at -40 °C. The stirred mixture was allowed to warm to R.T. overnight. The mixture was concentrated under reduced pressure to dryness, and the residue was suspended in TMBE (6 L). The suspension was filtered to remove Ph₃PO, and the filtrate was concentrated under reduced pressure to afford crude **66-3** (1230 g, 78.6%). ¹H NMR (400 Hz) (CDCl₃): δ 6.65 (dt, *J* = 7.6 Hz, 1H), 4.82 (dd, *J* = 14.8, 7.6 Hz, 1H), 4.20-4.10 (m, 3H), 3.59 (t, *J* = 8.0 Hz, 1H), 1.86 (d, *J* = 1.2 Hz, 3H), 1.41 (s, 3H), 1.37 (s, 3H), 1.26 (t, *J* = 6.8 Hz, 3H).

[0450] Crude **66-3** (1230 g, 5.74 mol) was dissolved in acetone (30 L) at 0-5 °C. KMnO₄ (1107 g, 5.17 mol) was added in one portion. After being stirred at 0-5 °C for 5 h, the

reaction was quenched with sat. aq. sodium sulfite (20 L). After 30 mins, a colorless suspension was formed. The solid was removed by filtration and washed with EA (6 L). The filtrate was extracted with EA (3 x 2 L). The combined extracts were dried over Na₂SO₄, filtered, and concentrated under reduced pressure to give a white solid residue. The residue was dissolved in EA, and PE was added to give a precipitate. The solid was collected by filtration and recrystallization was 3 times to give **66-4** (770 g, 53.6%) as a white solid.

[0451] To a stirred solution of **66-4** (770 g, 3.1 mol) in anhydrous DCM (5 L) and triethylamine (1.1 L, 8.05 mol) at 0°C was added slowly sulfuryl chloride (300 mL, 3.6 mmol). The mixture was stirred at R.T. for 2 h, diluted with DCM (3 L), and washed with sat. NaHCO₃ aq. and brine. The organic phase was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by a silica gel column using PE:EA = 1:0 to 10:1 as the eluent to give **66-5** (490 g, 50.6%) as an oil.

[0452] Tetraethylammonium fluoride hydrate (650 g, 3.7 mol) was added into a solution of **66-5** (490 g, 1.6 mol) in anhydrous dioxane (3 L), and the mixture was heated to 120°C for 16 h. The mixture was then cooled to ambient temperature. 2,2-Dimethoxypropane (3 L) was added followed by conc. aq hydrochloric acid (200 mL). The mixture was stirred for 3 h at ambient temperature. The solvent was concentrated to 1/3 of the original volume, and then diluted with EA (3 L). The mixture was washed with cold sat. aq. sodium bicarbonate and brine. The combined aqueous layer was back-extracted with EA (1 L). The combined organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated at low pressure to give crude **66-6** (220 g, 70.8%).

[0453] Crude **66-6** (220 g, 0.89mol) was dissolved in ethanol (2 L) and conc. aq. HCl (60 mL). The solution was stirred at ambient temperature for 48 h. and then concentrated under reduced pressure followed by co-evaporations with toluene 3 times to give **66-7** as a pale yellow solid (110 g).

[0454] Compound **66-7** (110 g) was dissolved in anhydrous pyridine (1 L). Benzoyl chloride (200 mL, 1.67 mol) was added slowly at 0-5°C. The mixture was stirred at ambient temperature for 45 mins. The reaction was quenched with ice and MeOH to form a precipitate. After filtration, the filtrate was washed with MeOH to give **66-8** (200 g, 61.2%) as a white solid.

[0455] To a solution of **66-8** (100 g, 269 mmol) in anhydrous THF (1000 ml) was added dropwise a solution of lithium tri-tert-butoxyaluminumhydride (400 ml, 1M, 0.4 mol) at -78°C under N₂ for 30 mins. The solution was stirred at -20°C for 1 h, and TLC (PE: EA= 3:1) showed that the reaction was complete. The mixture was quenched with sat.NH₄Cl, and diluted with EA. After filtration, the filtrate was extracted with EA. The combined layers were dried

over Na₂SO₄, and concentrated at low pressure. The residue was purified by a silica column gel (PE: EA=20:1) to give **66-9** (100 g, 100%) as a colorless oil.

[0456] To a stirred solution of PPh₃ (140 g, 382 mol) in CH₂Cl₂ (1000 ml) was added **66-9** (100 g, 269 mmol) at -20 °C under N₂. After stirring for 15 mins, CBr₄ (177 g, 382 mol) was added dropwise while maintaining the temperature between -25 and -20 °C under N₂. The mixture was stirred below -17 °C for 20 mins. Silica gel was added to the mixture. The mixture was filtered through cold silica column gel and washed with PE: EA (50:1 to 4:1). The combined filtrates were concentrated under reduced pressure at R.T. to give the crude oil product. The residue was purified by a silica column gel a second time (PE: EA=50:1 to 4:1) to give **66-10** (α -isomer, 64 g, yield: 55%) as a colorless oil.

[0457] A mixture of 6-chloro-guanine (55.8 g, 316.5 mol) and t-BuOK (39.5 g, 352.7 mmol) in t-BuOH (500 mL) and MeCN (280 mL) was stirred for 30 mins. Compound **66-10** (48 g, 105.5 mmol) was added at R.T., and the mixture was heated to 50 °C and stirred overnight. The reaction was monitored by TLC (PE:EA=2:1). The mixture was quenched with solid NH₄Cl. After stirring for 1 h, the mixture was filtered and washed with MeCN. The filtrate was evaporated at low pressure, and the residue was purified by a silica gel column to give **66-11** (33 g, 57%).

[0458] To a solution of **66-11** (49 g, 93.1 mol) in CH₂Cl₂ (200 mL) was added AgNO₃ (31.7 g, 186 mmol), collidine (22.5 g, 186 mmol) and MMTrCl (43 g, 140 mmol) in small portions under N₂ at 0°C. The mixture was stirred at R.T., and monitored by TLC (PE:EA=4:1). After filtration, the organic phase was washed with NaHCO₃ aqueous and brine. The organic layer was dried over anhydrous Na₂SO₄ and concentrated at low pressure. The residue was purified by a silica gel column (PE:ME= 20:1 to 1:1) to give **66-12** (70 g, 94.2%).

[0459] Sodium (10.1 g, 439 mmol) was dissolved in dry EtOH (600 mL) at 70°C and then cooled to 0 °C. To a solution of **66-12** (70 g, 87.7 mmol) was added a freshly prepared NaOEt solution in portions at 0°C, and the mixture was stirred for 1 h. at R.T. After TLC and LCMS showed the reaction was completed, the reaction was quenched with carbon dioxide. The mixture was evaporated at low pressure, and the residue was purified using silica gel column chromatography (DCM: MeOH=100:1 to 20:1) to give **66-13** (50 g, yield 5%) as a yellow solid.

[0460] A mixture of PPh₃ (35 g, 133.5 mol) and I₂ (31.75 g, 125 mmol) in anhydrous pyridine (600 mL) was stirred for 30 mins, and then a solution of **66-13** (50 g, 83.3 mmol) in pyridine (100 mL) was added at 0°C. The mixture was stirred overnight at R.T. and monitored by TLC (DCM:MeOH=50:1). The reaction was quenched with a sat. NaHCO₃ solution, and

extracted with DCM (3 x 50 mL). The organic phase was dried over anhydrous MgSO_4 , and evaporated at low pressure. The residue was purified using silica gel column chromatography (DCM: MeOH=200:1 to 50:1) to give **66-14** (50 g, 84.7%).

[0461] To a solution of **66-14** (37 g, 52.1 mmol) in dry THF (400 mL) was added DBU (16 g, 105 mmol). The mixture was heated to reflux and stirred for 3 h. The reaction was monitored by LCMS. The reaction was quenched with a sat. NaHCO_3 solution, and extracted with EA. The combined organic layers were dried over anhydrous Na_2SO_4 , and evaporated at low pressure. The residue was purified using silica gel column chromatography (PE:EA=10:1 to 5:1) to give **66-15** (25 g, 61.1%) as a white solid.

[0462] To an ice-cold solution of **66-15** (26 g, 44.6 mmol) in dry MeCN (300 mL) was added NIS (12.68 g, 56 mmol) and $\text{NEt}_3 \cdot 3\text{HF}$ (10.6 g, 67 mmol) at 0 °C. The reaction was stirred at R.T. for 2 h. and monitored by LCMS. After the reaction was completed, the reaction was quenched with a sat Na_2SO_3 and sat. NaHCO_3 solution, and extracted with EA. The organic layer was separated, dried over anhydrous Na_2SO_4 , and evaporated at low pressure. The residue was purified using silica gel column chromatography (PE: EA=8:1 to 1:1) to give **66-16** (21 g, 64.4%) as a white solid.

[0463] To a solution of **66-16** (21 g, 28.8 mol) in CH_2Cl_2 (150 mL) was added AgNO_3 (9.8 g, 59.6 mmol) and collidine (7 g, 59.8 mmol) and MMTrCl (13.1 g, 42.5 mmol) in small portions under N_2 at 0°C. The mixture was stirred at R.T., and the reaction was monitored by TLC (PE:EA=2:1). After filtration, the solution was washed with sat. aq. NaHCO_3 and brine. The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated at low pressure. The residue was purified by a silica gel column to give **66-17** (25 g, yield 86.5%).

[0464] To a solution of **66-17** (22 g, 22 mmol) in dry DMF (500 mL) was added NaOBz (31.9 g, 220 mmol) and 15-crown-5 (48.4 g, 220 mmol), and the mixture was stirred for 72 h. at 95°C. The mixture was diluted with EA, washed with water and brine, and dried over MgSO_4 . The organic layer was evaporated at low pressure, and the residue was purified using a silica gel column chromatography to give **66-18** (15 g, 68.8%) as a white solid.

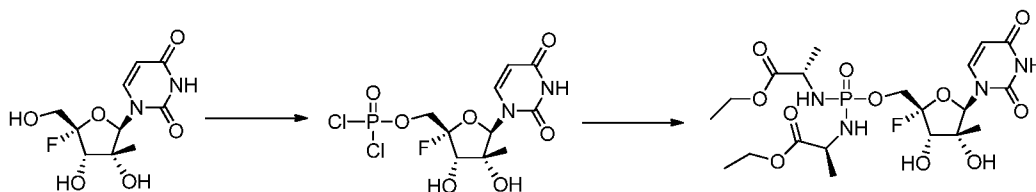
[0465] Compound **66-18** (15.2 g, 15.3 mmol) was co-evaporated with anhydrous toluene 3 times to remove H_2O . The compound was treated with NH_3 in MeOH (7 N, 200 mL) at R.T. The mixture was stirred for 18 h at R.T., and the reaction was monitored by LCMS. The residue was concentrated at low pressure, and purified using silica gel column chromatography to give **66-19** (11 g, 81%) as a white solid.

[0466] To a stirred solution of **66-20** (14 g, 15.73 mmol) in anhydrous CH_3CN (150 mL) was added N-methylimidazole (23.5 g, 283.9 mmol) at 0 to 5°C (ice/water bath) followed

by a solution of phenyl(cyclohexanoxo-L-alaninyl)phosphorochloridate (16.33 g, 47.2 mmol, dissolved in 50 mL of CH₃CN). The solution was stirred at 0 to 5°C for 12 h and then diluted with EA. The solution was washed 50 % aqueous citric acid solution and brine. The organic layer was separated, dried over anhydrous MgSO₄ and filtered. The filtrate was concentrated at low pressure, and the residue was purified on silica gel with PE: EA=5:1 as the eluent to give **66-20** (17.62 g, 93.4%) as a white solid.

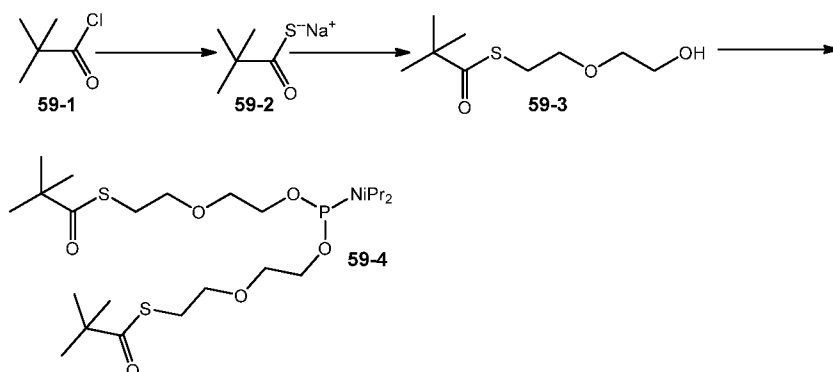
[0467] Compound **66-20** (17.62 g, 14.7 mmol) was dissolved in 80% AcOH (200 mL), and the mixture was stirred overnight at R.T. After removal of the solvents, the residue was purified on silica gel using PE:EA=2:1 to eluent to give the crude product, which was purified on via reverse-phase HPLC using acetonitrile and water to give compound **66** (5.25 g, yield 66%) as a white solid. ESI-LCMS: m/z 655 [M+H]⁺.

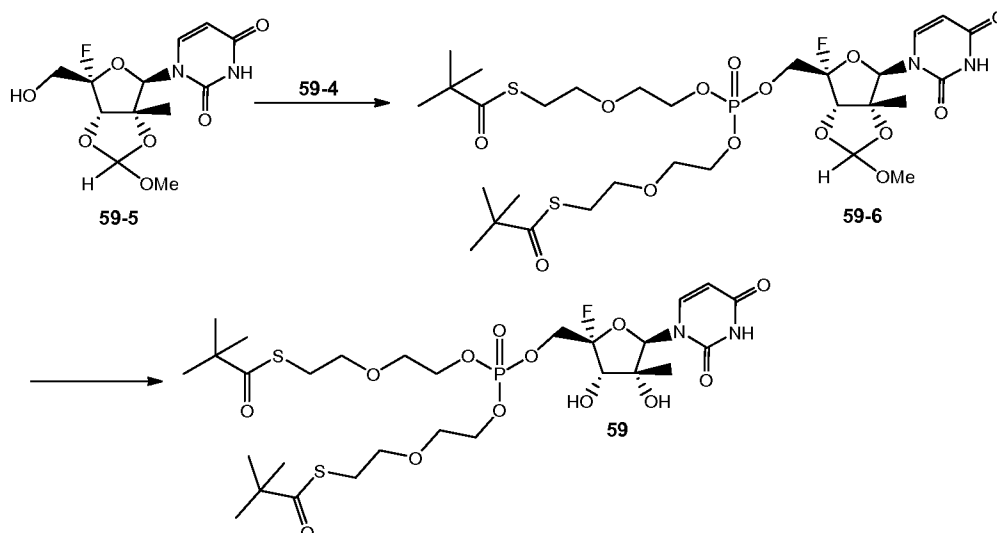
EXAMPLE 49 **COMPOUND 67**



[0468] To a solution of the nucleoside (300 mg, 1.09 mmol) and proton-sponge (467 mg, 2.18 mmol) in anhydrous CH₃CN (5 mL) at 0°C under N₂ was added dropwise a solution of phosphorus oxychloride (330 mg, 2.18 mmol) in anhydrous CH₃CN (1 mL). The mixture was stirred at 0°C for 30 mins, and the hydrogen chloride salt of (S)-ethyl 2-aminopropanoate (998 mg, 6.52 mmol) and triethylamine (1.5 mL, 10.87 mmol) at 0°C were added. The mixture was stirred overnight at 30°C. The reaction was quenched with water, and extracted with EA (3 x 20 mL). The organic layer was concentrated at low pressure, and the residue was purified by reverse phase HPLC to give compound **67** (20 mg, 3%) as a white solid. ESI-LCMS: m/z 535 [M-F]⁺.

EXAMPLE 50 **COMPOUND 59**





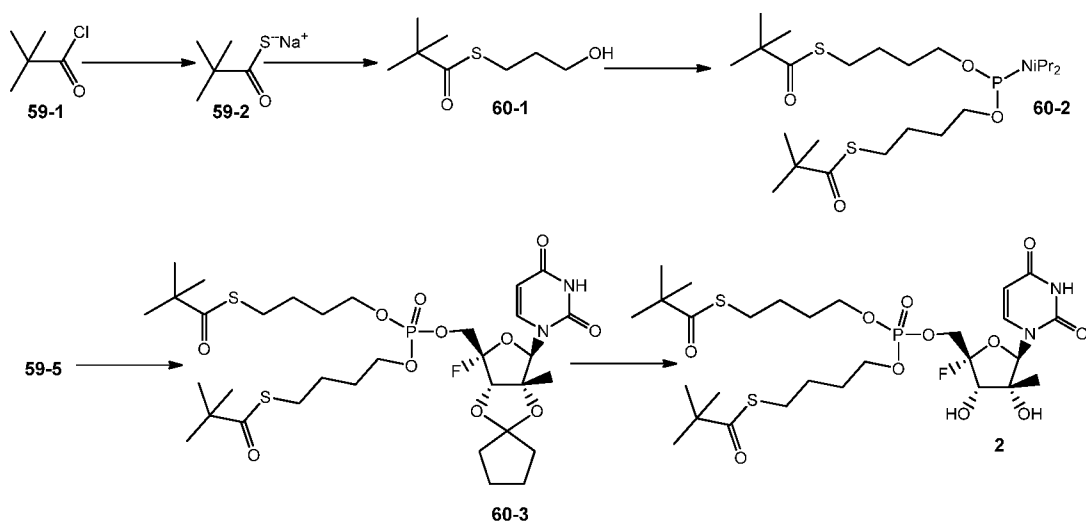
[0469] To a solution of sodium hydrosulfide (4.26 g, 76.0 mmol) in EtOH (100 mL) was added t-butyryl chloride (76.2 mmol; 9.35 mL) dropwise at 0 °C, and the mixture was stirred at R.T. for 1 h. A solution of 2-(2-chloroethoxy)ethanol (57 mmol; 6.0 mL) and TEA (21 mL, 120 mmol) was added, and the mixture was heated at reflux for 60 h. The mixture was filtered, and then concentrated to a small volume. The residue was dissolved in EA, and then washed with water, sat. aq. NaHCO₃ and brine. The organic phase was dried over Na₂SO₄, filtered and concentrated in vacuo. The crude product (10.0 g) was isolated and 5 grams were purified by silica gel flash column chromatography using a gradient of 0 to 100% EA in hexane to give **59-3** (4.5 g, 22 mmol) as a clear, colorless oil. ¹H-NMR (CDCl₃): 3.70-3.74 (m, 2H), 3.5-3.65 (m, 4H), 3.1 (t, 2H), 1.25 (s, 9H).

[0470] A solution **59-3** (4.5 g; 21.8 mmol) and triethylamine (6.7 mL, 87.2 mmol) in tetrahydrofuran (50 mL) was added dropwise over 1 h to a stirred solution of N,N-diisopropylphosphorodichloridite (2.0 mL, 10.9 mmol) in THF (50 mL) under argon at -78°C. The mixture was stirred at R.T. for 2 h, and then diluted with EA (200 mL). The mixture was washed with sat. aq. NaCl and dried over Na₂SO₄. After filtration, the filtrate was evaporated under reduced pressure to give a pale yellow oil. Purification by flash column chromatography using a gradient of EA (0-5%) in hexane containing 5% triethylamine afforded **59-4** (2.5 g, 4.25 mmol) as a clear, colorless oil. ¹H-NMR (CDCl₃): 3.70-3.82 (m, 4H), 3.57-3.65 (m, 10H), 3.1 (t, 4H), 1.25 (s, 18H), 1.17 (t, 12H); ³¹P-NMR (CDCl₃): 148.0 ppm.

[0471] Compound **59-5** (285 mg, 0.9 mmol) and DCI (175 mg, 1.5 mmol) were coevaporated twice with ACN and then dissolved in ACN (5 mL). Compound **59-4** (790 mg, 1.35 mmol) in ACN (4 mL) was added, and the reaction was monitored by TLC. After 15 mins, tert-butylhydroperoxide (0.5 mL of 5.5M solution in decane) was added, and the mixture was stirred for 10 mins. The mixture was diluted with EA (25 mL), washed with sat. aq. NaHCO₃

and sat. aq. NaCl solution, dried over Na₂SO₄, filtered and concentrated. Purification by flash column chromatography using a gradient of EA (0-100%) in hexane afforded **59-6** (0.17 g, 0.22 mmol) as a white solid. Compound **59-6** was dissolved in 80% aq. HCOOH (5 mL). After 30 mins at R.T., the solvent was removed and coevaporated twice with toluene. The residue was dissolved in methanol (10 mL) and TEA (0.2 mL) was added. After 2 mins at R.T., the solvent was removed in vacuo. Purification by flash column chromatography using a gradient of methanol (0-15%) in DCM afforded compound **59** (90 mg). ¹H-NMR (CDCl₃): 7.40 (d, 1H), 6.1 (s, 1H), 5.83 (d, 1H), 4.3 (t, 2H), 4.1-4.2 (m, 6H), 3.70-3.82 (m, 4H), 3.57-3.65 (m, 4H), 3.1 (t, 4H) 1.61 (s, 8H), 1.3 (s, 3H), 1.23 (s, 18H). ³¹P-NMR (CDCl₃): -1.55 ppm.

EXAMPLE 51 COMPOUND 60

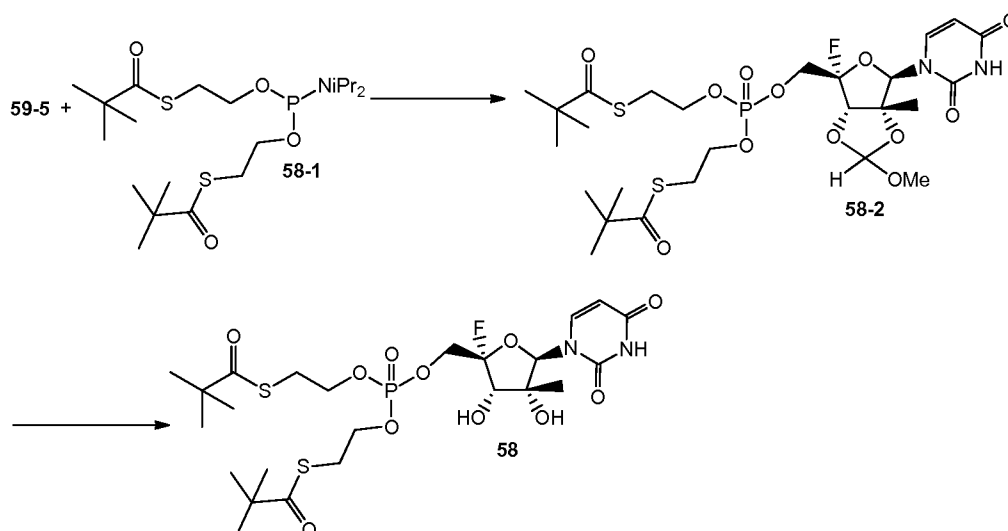


[0472] Compound **60-1** (6.0 g, 31.6 mmol) was prepared using a similar procedure to the one used to prepared **59-3** using 4-chlorobutanol. Compound **60-1** was obtained as a clear, colorless oil. ¹H-NMR (CDCl₃): 3.67 (s, 2H), 2.86 (m, 2H), 1.65 (m, 4H), 1.25 (s, 9H).

[0473] Compound **60-2** (2.14 g, 4.0 mmol) was prepared using a similar procedure to the one used to prepared **59-4**. Compound **60-2** was obtained as a clear, colorless oil. ¹H-NMR (CDCl₃): 3.67 (m, 6H), 2.86 (t, 4H), 1.65 (m, 8H), 1.25 (s, 18H), 1.17 (t, 12H). ³¹P-NMR (CDCl₃): 143.7 ppm.

[0474] Compound **60-3** (0.23 g, 0.22 mmol) was prepared using a similar procedure to the one used to prepared **59-6** using **59-5** and **60-2**. Compound **60-3** was obtained as a white solid. Using a similar procedure to the one used to prepared compound **59**, **60-3** was used to prepare compound **60** (170 mg). ¹H-NMR (CDCl₃): 7.40 (d, 1H), 6.1 (s, 1H), 5.83 (d, 1H), 4.3 (t, 2H), 4.1-4.2 (m, 6H), 2.8 (t, 4H), 1.78 (m, 4H), 1.69 (s, 8H), 1.3 (s, 3H), 1.23 (s, 18H). ³¹P-NMR (CDCl₃): -1.56 ppm.

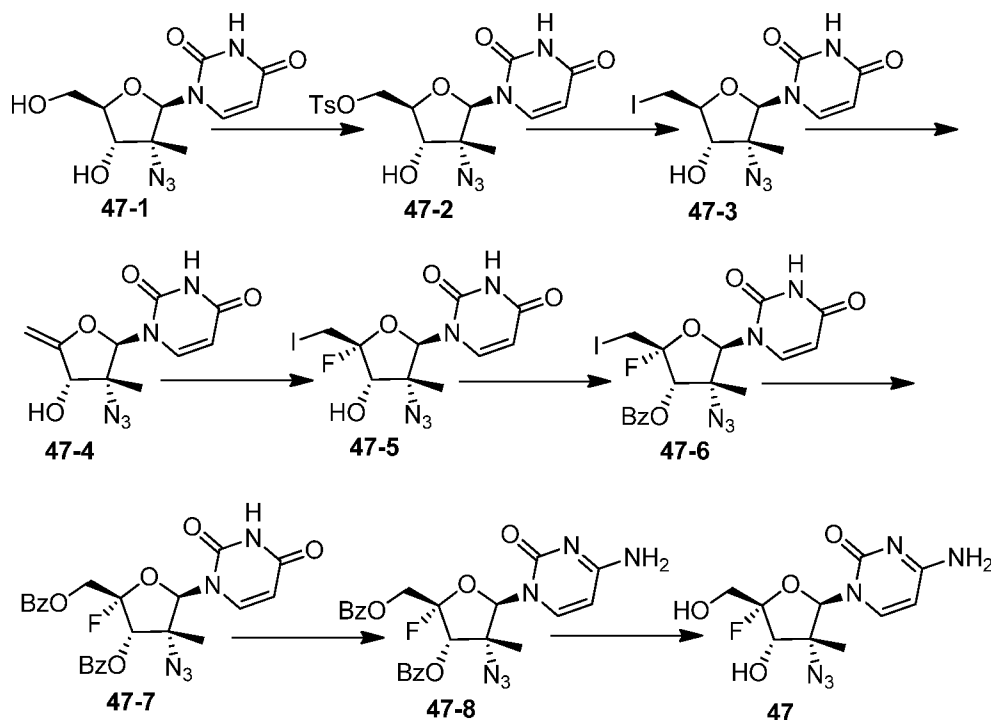
EXAMPLE 52
COMPOUND 58



[0475] Compound **58-1** was prepared according to the procedure described in Lefebvre et al. J. Med. Chem. (1995) 38:3941-3950, which is hereby incorporated by reference for the limited purpose of its description of the preparation of **58-1**.

[0476] Compound **58-2** (0.33 g, 0.5 mmol) was prepared using a similar procedure to the one used to prepared **59-6** using **59-5** and **58-1**. Compound **58-2** was obtained as a white solid. Using a similar procedure to the one used to prepared compound **59**, **58-2** was used to prepare compound **58** (130 mg). $^1\text{H-NMR}$ (CDCl_3): 7.40 (d, 1H), 6.1 (s, 1H), 5.83 (d, 1H), 4.3 (t, 2H), 4.1-4.2 (m, 6H), 3.2 (t, 4H), 1.69 (s, 4H), 1.3 (s, 3H), 1.23 (s, 18H); $^{31}\text{P-NMR}$ (CDCl_3): -2.4 ppm.

EXAMPLE 53
COMPOUND 47



[0477] Compound **47-1** (1.0 g, 3.53 mmol) was coevaporated with anhydrous pyridine 3 times to remove H₂O. To an ice-cold solution of **47-1** in anhydrous pyridine (9 mL) was added TsCl (808 mg, 4.24 mmol) in pyridine (3 mL) drop-wise at 0°C, and the mixture was stirred for 18 h. at 0°C. The reaction was monitored by LCMS, and then quenched with H₂O. After concentration at low pressure, the residue was dissolved in EA (50 mL). The solution was washed with sat. NaHCO₃ solution and brine. The organic layer was dried over anhydrous Na₂SO₄ and filtered. The filtrate was evaporated at low pressure, and the residue was purified by silica gel column chromatography (1% MeOH in DCM) to give **47-2** (980 mg, 63 %) as a white solid.

[0478] To a solution of **47-2** (980 mg, 2.24 mmol) in acetone (10 mL) was added NaI (1.01 g, 6.73 mmol), and the mixture was heated to reflux overnight. The reaction was monitored by LCMS. After the reaction was completed, the mixture was concentrated at low pressure. The residue was dissolved in EA (50 mL). The solution was washed with brine, and dried over anhydrous Na₂SO₄. The solution was evaporated at low pressure, and the residue was purified by silica gel column chromatography (1% MeOH in DCM) to give **47-3** (700 mg, 79 %) as a solid.

[0479] To a solution of **47-3** (700 mg, 1.78 mmol) in dry THF (9 mL) was added DBU (817 mg, 5.34 mmol), and the mixture was heated to 60°C. The mixture was stirred overnight, and monitored by LCMS. The reaction was quenched with sat. NaHCO₃ and

extracted with EA (3 x 50 mL). The organic phase was dried over anhydrous Na₂SO₄, and filtered. The filtrate was evaporated at low pressure, and the residue was purified by silica gel column chromatography (1% MeOH in DCM) to give **47-4** (250 mg, 53 %) as a white solid.

[0480] To an ice-cold solution of **47-4** (250 mg, 0.94 mmol) in dry MeCN (5 mL) was added NEt₃·3HF (151 mg, 0.94 mmol) and NIS (255 mg, 1.13 mmol). The mixture was stirred at R.T., for 3 h., and checked by LCMS. The reaction was quenched with sat Na₂S₂O₃ and sat. NaHCO₃ solution, and extracted with EA (3 x 50 mL). The organic layer was separated, dried over anhydrous Na₂SO₄, and evaporated at low pressure. The residue was purified by silica gel column chromatography (2% acetone in DCM) to give **47-5** (170 mg, 44 %).

[0481] To a solution of **47-5** (270 mg, 0.65 mmol) in dry DCM (4 mL) was added DMAP (158.6 mg, 1.3 mmol), and BzCl (137 mg, 0.98 mmol). The mixture was stirred for 4-5 h. at R.T., and checked by LCMS. The mixture was diluted with CH₂Cl₂, and washed with sat. NaHCO₃ solution and brine. The organic layer was evaporated at low pressure, and the residue was purified by silica gel column chromatography (20% EA in PE) to give **47-6** (290 mg, 86 %) as a solid.

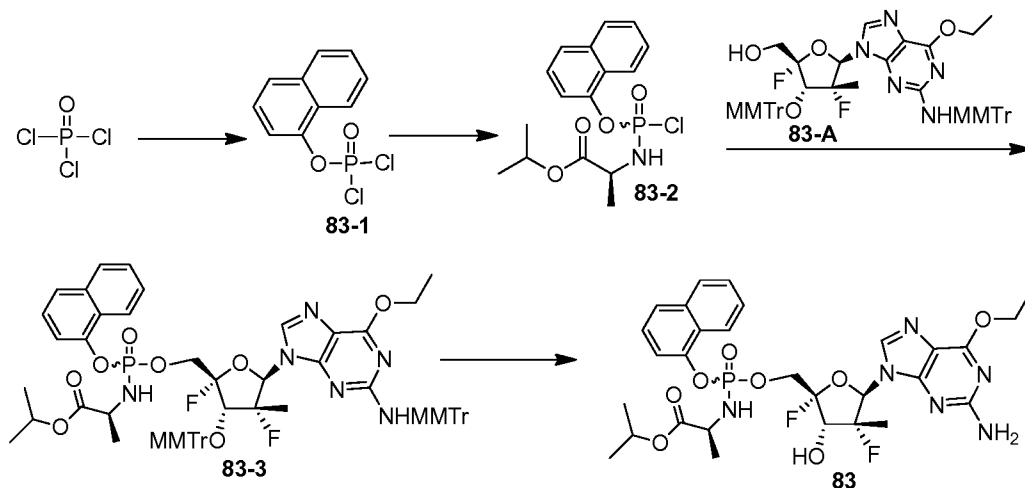
[0482] To a solution of **47-6** (900 mg, 1.74 mmol) in dry DMF (45 mL) was added NaOBz (2.5 g, 17.4 mmol) and 15-crown-5 (4.5 g, 20.9 mmol). The mixture was stirred for 48 h at 90-100°C. The mixture was diluted with EA (100 mL), and washed with brine. The organic layer was evaporated at low pressure, and the residue was purified by silica gel column chromatography (20% EA in PE) to give **47-7** (500 mg, 56 %) as a solid.

[0483] To a solution of **47-7** (500 mg, 0.98 mmol) in anhydrous CH₃CN (5 mL) was added TPSCl (741 mg, 2.45 mmol), DMAP (299.6 mg, 2.45 mmol) and NEt₃ (248 mg, 2.45 mmol) at R.T., and the mixture was stirred overnight. The mixture was then treated with NH₃ in THF (5 mL) and then stirred for another 30 mins. The mixture was diluted with EA (100 mL). The solution was washed with 0.5% AcOH solution. The organic solvent was dried over anhydrous MgSO₄, and concentrated at low pressure. The crude product was purified by silica gel column chromatography (2% Acetone in DCM) to give **47-8** (257 mg, 51.6 %) as a white solid. ESI-MS: m/z 509 [M+H]⁺.

[0484] Compound **47-8** (80 mg, 0.16 mmol) was dissolved in n-butylamine (3 mL). The mixture was kept overnight at R.T. and evaporated. The residue was crystallized from methanol to give compound **47** (30 mg). The mother liquor was purified by RP HPLC on Synergy 4 micron Hydro-RP column (Phenomenex). A linear gradient of methanol from 0 to 30% in 50mM triethylammonium acetate buffer (pH 7.5) was used for elution. The

corresponding fractions were combined, concentrated and lyophilized 3 times to remove excess of buffer to yield additional compound **47** (13 mg). Compound **47** (total yield 43 mg, 73%). MS: m/z 299.7 $[M-1]^-$.

EXAMPLE 54 COMPOUND 83



[0485] To a stirred solution of POCl₃ (2.0 g, 13 mmol) in anhydrous DCM (10 mL) was added 1-naphthol (1.88 g, 13 mmol) at -70°C, and TEA (1.31 g, 13 mmol) in DCM (3 mL) dropwise at -70°C. The mixture was gradually warmed to R.T. and stirred for 1 h. Crude **83-1** was obtained.

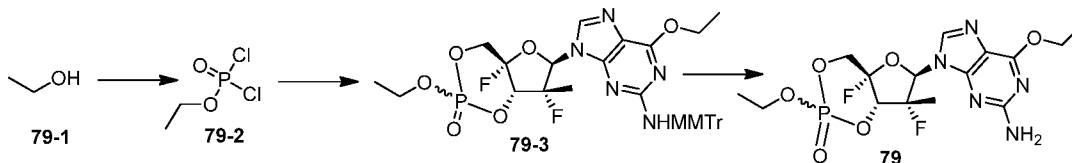
[0486] To a stirred solution of (S)-isopropyl 2-aminopropanoate hydrochloride (2.17 g, 13 mmol) in DCM (10 mL) was added crude **83-1** at -70°C. TEA (2.63 g, 26 mmol) was added to the stirred solution dropwise at -70°C. The mixture was gradually warmed to R.T. and stirred for 2 h. The reaction was monitored by LCMS and quenched with n-propylamine. The mixture was concentrated at low pressure, and the residue was purified by a silica gel column (PE:MTBE = 5:1~1:1) to give pure **83-2** (1.6 g, 35%).

[0487] To a solution of **83-A** (300 mg, 0.337 mmol) and NMI (276 mg, 3.37 mmol) in anhydrous CH₃CN (4 mL) was added **83-2** (240 mg, 0.674 mmol, in DCM (5 mL)) at 0°C. The mixture was stirred at R.T. for 10 h. The reaction was monitored by LCMS. The reaction was quenched with water, and extracted with CH₂Cl₂ (3 x 20 mL). The organic phase was dried over anhydrous MgSO₄, and concentrated at low pressure. The residue was purified by sil-gel (PE:EA = 5:1~2:1) to give **83-3** (380 mg, 93%).

[0488] Compound **83-3** (380 mg, 0.314 mmol) was dissolved in CH₃COOH (80%, 8 mL), and stirred at 40-50°C for 2.5 h. The reaction was monitored by LCMS. The mixture was concentrated at low pressure, and the residue was purified by chromatography (PE:EA = 1:1~EA) to give crude compound **83**. The crude product was purified by prep-HPLC (neutral

system, NH_4HCO_3) to give pure compound **83** (70 mg, 80%) as a white solid. ESI-MS: m/z 665.1 $[\text{M}+\text{H}]^+$.

EXAMPLE 55
COMPOUND 79

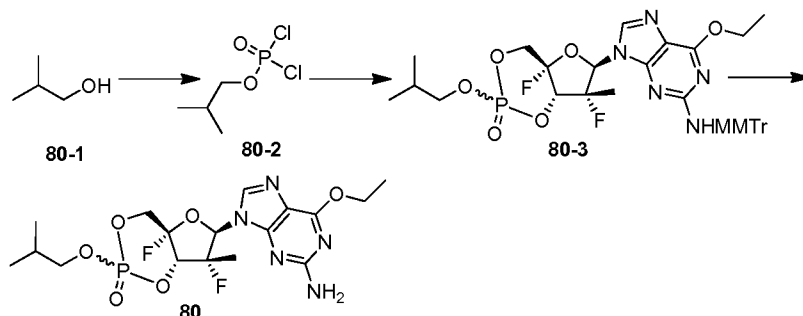


[0489] A solution of **79-1** (16.70 g, 0.363 mol) and TEA (36.66 g, 0.363 mol) in CH_2Cl_2 (150 mL) was added dropwise to a stirred solution of POCl_3 (55.65 g, 0.363 mol) in DCM (100 mL) over 25 mins at -78°C . After the mixture was stirred for 2 h. at R.T., the triethylamine hydrochloride salt was filtered, and washed with CH_2Cl_2 (100 mL). The filtrate was concentrated at low pressure, and the residue was distilled under high vacuum (~ 10 mm Hg) with a cow-head fraction collector. The product was collected between 45°C (distillation head temperature) as a colorless liquid (30.5 g, 50% yield). ^1H -NMR (400 MHz, CDCl_3) δ = 4.44 (dq, J =10.85, 7.17 Hz, 2 H), 1.44 - 1.57 (m, 3 H); ^{31}P -NMR (162 MHz, CDCl_3) δ = 6.75 (br. s., 1 P).

[0490] To a stirred suspension of **83-A** (93 mg, 0.15 mmol) in CH_2Cl_2 (1 mL) was added TEA (61 mg, 0.15 mmol) at R.T. The mixture was cooled to -20°C , and then was treated with a **79-2** (35 mg, 0.21 mmol) solution dropwise over a period of 10 mins. The mixture was stirred at this temperature for 15 min., and then was treated with NMI (27 mg, 0.33 mmol). The mixture was stirred at -20°C , and then slowly warmed to R.T. The mixture was stirred overnight. The mixture was suspended in EA (15 mL), washed with brine (10 mL) and dried over anhydrous sodium sulfate. The solution was concentrated at low pressure, and the residue was purified by chromatography (DCM: MeOH=100:1) to give **79-3** (60 mg, yield: 56%) as a solid.

[0491] A solution of **79-3** (60 mg, 0.085 mmol) in 80% AcOH aqueous (2 mL) was stirred at R.T. for 2 h. The mixture was concentrated under reduced pressure, and the residue was purified by a silica gel column eluting DCM/MeOH = 50/1 and prep-HPLC to give compound **79** (23 mg, 62%) as a white solid. ESI-MS: m/z 436.3 $[\text{M}+\text{H}]^+$.

EXAMPLE 56
COMPOUND 80

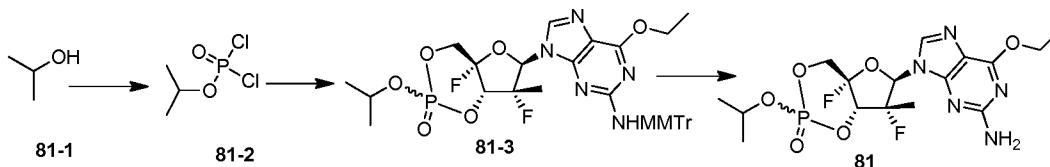


[0492] Compound **80-2** was prepared using a similar procedure as for the preparation of **79-2** using a solution of iso-butanol (23.9 g, 322.98 mmol) and POCl_3 (49.5 g, 322.98 mmol). Compound **80-2** (26 g, 42% yield) was obtained as a colorless liquid. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 4.10 (dd, J =9.04, 6.39 Hz, 2 H), 2.09 (dq, J =13.24, 6.67, 6.67, 6.67 Hz, 1 H), 1.01 (d, J =6.62 Hz, 6 H); $^{31}\text{P-NMR}$ (162 MHz, CDCl_3) δ = 7.06 (br. s., 1 P).

[0493] To a stirred suspension of **83-A** (310 mg, 0.5 mmol) in CH_2Cl_2 (3 mL) was added TEA (202 mg, 2 mmol) at R.T. The mixture was cooled to -20°C , and then was treated with **80-2** (134 mg, 0.7 mmol). The mixture was stirred at this temperature for 15 mins and then was treated with NMI (90 mg, 1.1 mmol). The mixture was stirred at -20°C for 1 h., and then slowly warmed to R.T. overnight. The mixture was suspended in EA (15 mL), washed with brine (10 mL), and dried over anhydrous sodium sulfate. The organic phase was concentrated at low pressure, and the residue was purified by silica column gel (DCM: MeOH=100:1) to give **80-3** (310 mg, yield: 84%) as a solid.

[0494] A solution of **80-3** (310 mg, 0.43 mmol) in 80% AcOH aqueous (4 mL) was stirred at R.T. for 2 h. The mixture was concentrated at low pressure, and the residue was purified by a silica gel column eluting DCM/MeOH = 50/1 and prep-HPLC to give compound **80** (79 mg, 50%) as a white solid. ESI-MS: m/z 464.0 $[\text{M}+\text{H}]^+$.

EXAMPLE 57
COMPOUND 81



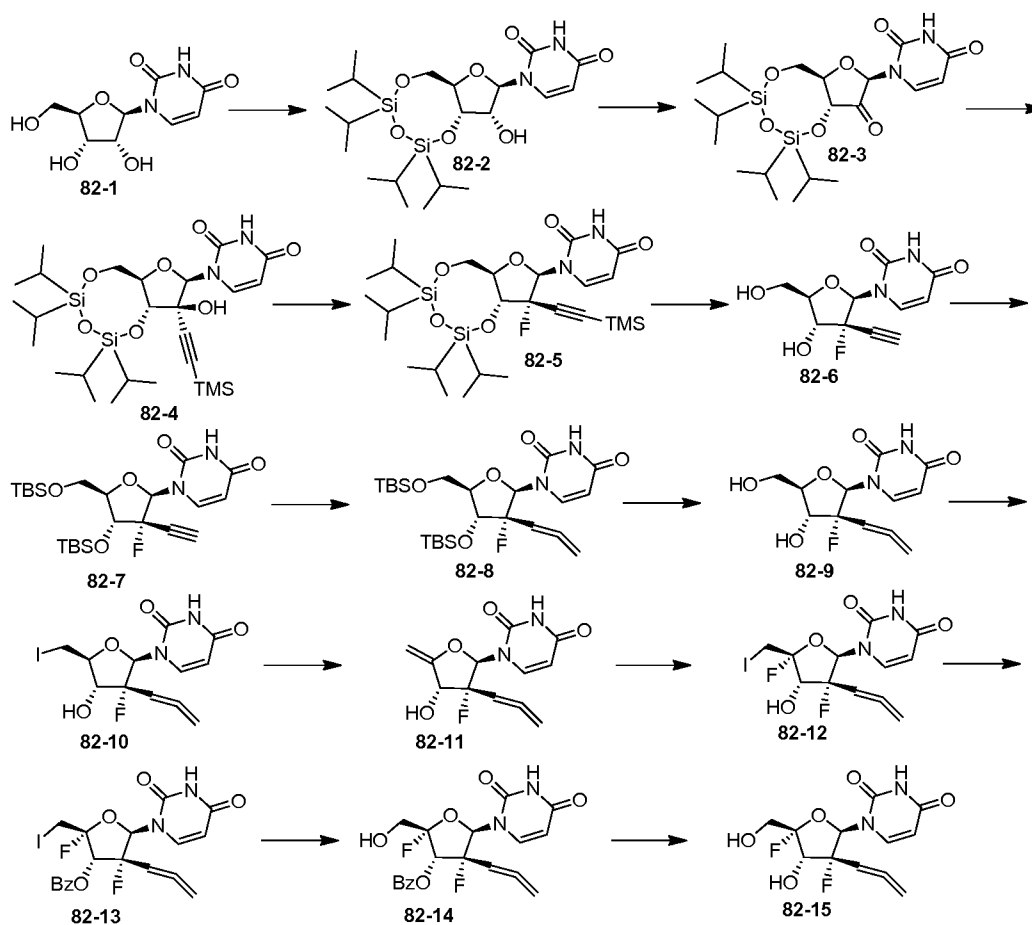
[0495] Compound **81-2** was prepared using a similar procedure as for the preparation of **79-2** using a solution of isopropyl alcohol (21 g, 350 mmol) and POCl_3 (53.6 g, 350 mmol). Compound **81-2** (40.5 g, 65% yield) was obtained as a colorless liquid. $^1\text{H-NMR}$ (400 MHz,

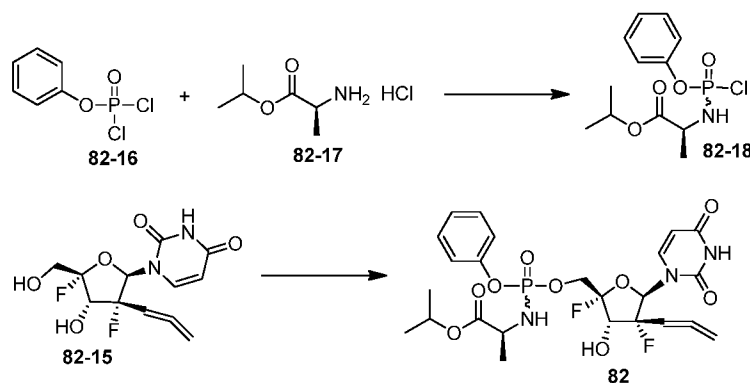
CDCl_3) δ = 4.94 - 5.10 (m, 1 H), 1.48 (d, J =6.17 Hz, 6 H); ^{31}P - NMR (162 MHz, CDCl_3) δ = 5.58 (br. s., 1 P).

[0496] Compound **81-3** was prepared using a similar procedure as for the preparation of **80-3** using **81-2** (124 mg, 0.7 mmol) and **83-A** (310 mg, 0.5 mmol). Compound **81-3** (300 mg, 83%) was obtained as a solid.

[0497] Compound **81** was prepared using a similar procedure as for the preparation of compound **80** using **81-3** (300 mg, 0.41 mmol) in 80% AcOH aqueous (4 mL). Compound **81** (80 mg, 43%) was obtained as a white solid. ESI-MS: m/z 450.0 $[\text{M}+\text{H}]^+$.

EXAMPLE 58 COMPOUND 82





[0498] To an ice cooled solution of **82-1** (50 g, 204.9 mmol) in dry Py (400 mL) was added TIPDSCl (70.78 g, 225.4 mmol) dropwise. The mixture was stirred at R.T. for 16 h, and then concentrated at low pressure. The residue was purified by chromatography using 20% EA in PE to generate **82-2** (111.5 g, 100%) as a white solid.

[0499] To a solution of **82-2** (50 g, 103 mmol) in anhydrous CH₃CN (400 mL) was added IBX (43 g, 153 mmol) at R.T. The mixture was refluxed overnight and monitored by TLC (PE:EA=1:1). The precipitate was filtered off, and the filtrate was concentrated to give the crude **82-3** (50 g, 99%) as a white solid.

[0500] To a solution of trimethylsilylacetylene (20 g, 200 mmol) in anhydrous THF (400 mL) was added dropwise *n*-BuLi (80 mL, 200 mmol) at -78°C. The mixture was stirred at -78°C for 30 mins, and then warmed to R.T for 10 mins. Compound **82-3** (30 g, 60 mmol) in THF (100 mL) was added to the mixture dropwise at -78°C. The mixture was stirred at -78°C for 1 h and then slowly warmed to R.T. The mixture was stirred for 20 mins, and then the reaction was quenched with a sat. NH₄Cl solution at -78°C. The mixture was diluted with EA. The organic phase was washed with brine, dried over anhydrous Na₂SO₄, and concentrated at low pressure. The residue was purified by silica gel column chromatography (15% EA in PE) to give **82-4** as a white solid (14 g, 50 %).

[0501] Compound **82-4** (14 g, 24 mmol) was dissolved in anhydrous toluene (100 mL) under N₂ and cooled to -78°C. DAST (19 g, 120 mmol) was added dropwise at -78°C and stirring was continued for 1.5 h. The mixture was diluted with EA and poured into a sat. NaHCO₃ solution. The organic layer was washed with brine, dried over anhydrous Na₂SO₄, and concentrated at low pressure. The residue was purified by silica gel chromatography (20% EA in PE) to give **82-5** as a white solid (12 g, 81 %).

[0502] A mixture of **82-5** (12 g, 20 mmol) and NH₄F (11 g, 30 mmol) in MeOH (150 mL) was refluxed for 2 h. After cooling to R.T, the mixture was concentrated at low pressure, and the residue was purified by silica gel column chromatography (5% MeOH in DCM) to give **82-6** (3.1 g, 58%) as a white solid.

[0503] To a solution of **82-6** (3.1 g, 11.6 mmol) in dry Py (50 mL) was added imidazole (3.1 g, 46.4 mmol) and TBSCl (5.2 g, 34.8 mmol). The mixture was stirred at 50-60°C for 3 h. The mixture was concentrated at low pressure, and the residue was dissolved in EA (100 mL). The solution was washed with brine, dried over anhydrous Na₂SO₄, and concentrated at low pressure. The residue was purified by silica gel chromatography (20% EA in PE) to give **82-7** as a white solid (5 g, 86%).

[0504] To a solution of **82-7** (4.5 g, 9 mmol) in 1,4-dioxane (45 mL) was added CuBr (643 mg, 4.5 mmol), dicyclohexylamine (3.3 g, 18 mmol) and paraformaldehyde (675 mg, 22.5 mmol). The mixture was refluxed for 24 h and then cooled to R.T. The reaction was quenched with a sat. NH₄Cl solution. The mixture was extracted with EA (3 x 100 mL). The organic layer was washed with brine, dried over anhydrous Na₂SO₄, and concentrated at low pressure. The residue was purified by silica gel column chromatography (15% EA in PE) to give **82-8** as a white solid (2.0 g, 43%).

[0505] A mixture of **82-8** (2 g, 4 mmol) and NH₄F (2.2 g, 60 mmol) in MeOH (20 mL) was refluxed overnight. After cooling to R.T., the mixture was concentrated at low pressure, and the residue was purified by silica gel column chromatography (5% MeOH in DCM) to give **82-9** (946 mg, 83%) as a white solid.

[0506] To a stirred suspension of **82-9** (946 mg, 3.33 mmol), PPh₃ (1.3 g, 5 mmol), imidazole (453 mg, 6.66 mmol) and pyridine (3 mL) in anhydrous THF (12 mL) was added a solution of I₂ (1 g, 4.33 mmol) in THF (4 mL) dropwise at 0°C. The mixture was warmed to R.T. and stirred for 16 h. The reaction was quenched with a sat. Na₂S₂O₃ aq. solution and extracted with EA (3 x 60 mL). The organic layer was dried over Na₂SO₄ and concentrated at low pressure. The residue was purified on a silica gel column (2% MeOH in DCM to 5% MeOH in DCM) to afford **82-10** (2.1 g, crude) as a white solid.

[0507] To a solution of **82-10** (2.1 g, 5.3 mmol) in THF (15 mL) was added DBU (15 g, 100 mmol) and the mixture stirred for 30 mins. The mixture was diluted with EA and neutralized with acetic acid. The solution was washed with brine, dried over anhydrous Na₂SO₄, and concentrated at low pressure. The residue was purified by silica gel column chromatography (1.5% MeOH in DCM) to give **82-11** as a white solid (800 mg, 90%).

[0508] To an ice-cooled solution of **82-11** (800 mg, 3 mmol) in dry MeCN (1.5 mL) was added NEt₃•3HF (484 mg, 3 mmol) and NIS (1.68 g, 7.5 mmol). The mixture was stirred at R.T. for 30 mins., and the reaction was monitored by LCMS. The reaction was quenched with sat. Na₂S₂O₃ and sat. NaHCO₃ solution, and extracted with EA (3 x 50 mL). The organic

layer was dried over anhydrous Na₂SO₄, and concentrated at low pressure. The residue was purified by a silica gel column (25% EA in PE) to afford **82-12** (850 mg, 68%) as a white solid.

[0509] To a solution of **82-12** (850 mg, 2 mmol) in dry DCM (10 mL) was added DMAP (488 mg, 4 mmol) and BzCl (422 mg, 3 mol). The mixture was stirred for 4-5 h at R.T., and the reaction was monitored by LCMS. The mixture was diluted with CH₂Cl₂ (40 mL), and washed with a sat. NaHCO₃ solution. The organic layer was dried over anhydrous Na₂SO₄, and filtered. The filtrate was evaporated at low pressure, and the residue was purified by silica gel column chromatography (20% EA in PE) to give **82-13** (900 mg, 87%) as a white foam.

[0510] Tetra-butylammonium hydroxide (21 mL as 54-56% aqueous solution, ~ 42 mmol, 24 eq.) was adjusted with TFA to pH ~ 4 (~ 3.5 mL), and the solution was treated with a solution of **82-13** (900 mg, 1.7 mmol) in DCM (21 mL). *m*-Chloroperbenzoic acid (2.1 g, 60-70%, ~ 8.75 mmol, ~ 5 eq.) was added portionwise under vigorous stirring, and the mixture was stirred overnight. The mixture was diluted with CH₂Cl₂ (30 mL), and washed with a saturated NaHCO₃ solution. The organic layer was washed with brine, dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography in (40-70% EA in PE) to give **82-14** as an oil. The residue was purified by TLC (50% EA in PE) to give pure **82-14** (350 mg 50%).

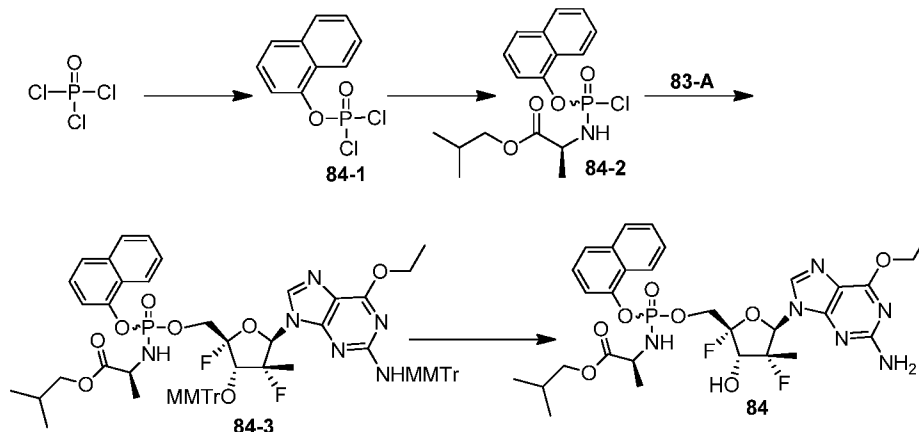
[0511] Compound **82-14** (350 mg, 0.86 mg) was treated with 7N NH₃ in MeOH (15 mL). The mixture was stirred for 2-3 h and monitored by TLC. The mixture was concentrated at low pressure, and the residue was purified by silica gel column chromatography (5% isopropanol in DCM) to give **82-15** (250 mg, 96%) as a white solid. ¹H NMR (CD₃OD, 400 M Hz) δ = 7.75 (d, *J* = 7.9 Hz, 1H), 6.60-6.35 (m, 1H), 5.72 (d, *J* = 8.2 Hz, 1H), 5.37-5.25 (m, 1H), 5.17-5.06 (m, 1H), 5.04-4.94 (m, 1H), 4.59-4.29 (m, 1H), 3.87-3.70 (m, 2H) .

[0512] To a stirred solution of **82-16** (3.79 g, 18 mmol) and **82-17** (3 g, 18 mmol) in anhydrous DCM (60 mL) was added with a solution of TEA (4 g, 39 mmol) in DCM (40 mL) dropwise at -78°C, and the mixture was stirred for 2 h. The mixture was concentrated at low pressure, and the residue was dissolved in methyl-butyl ether. The precipitate was removed by filtration, and the filtrate was concentrated to give the crude product. The residue was purified by dry column chromatography (anhydrous DCM) to give pure **82-18** as a colorless oil (3 g, 54 %).

[0513] Compound **82-15** (200 mg, 0.66 mmol) was coevaporated with toluene 3 times to remove H₂O. Compound **82-15** was treated with MeCN (1.5 mL) and NMI (541 mg, 6.6 mmol). The mixture was stirred at R.T., and then **82-18** (403 mg, 1.32 mmol) in MeCN (0.5 mL) was added. The residue was purified by a silica gel column (5% iPrOH in DCM) to give

the crude product, which was purified by HPLC (0.1% HCOOH in water and MeCN) to give compound **82** (33 mg, 9%). ESI-LCMS: m/z 594 $[M+Na]^+$.

EXAMPLE 59
COMPOUND 84



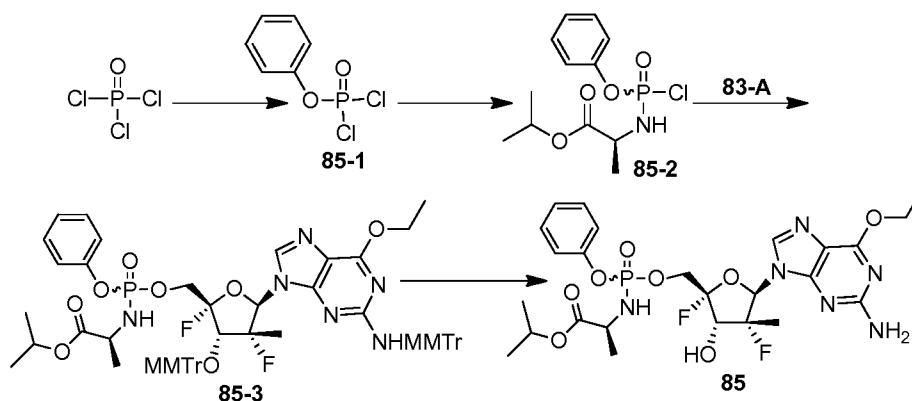
[0514] To a stirred solution of POCl₃ (2.0 g, 13 mmol) in anhydrous DCM (10 mL) was added 1-naphthol (1.88 g, 13 mmol) at -70°C and TEA (1.31 g, 13 mmol) in DCM (3 mL) dropwise at -70°C. The mixture was gradually warmed to R.T., and stirred for 1 h. A crude solution of **84-1** was obtained.

[0515] To a stirred solution of (S)-isobutyl 2-aminopropanoate hydrochloride (2.35 g, 13 mmol) in DCM (20 mL) was added TEA (2.63 g, 26 mmol) and a crude solution of **84-1** at -70°C. The mixture was gradually warmed to R.T., and stirred for 2 h. The reaction was monitored by LCMS and quenched with n-propylamine. The solvent was evaporated at low pressure, and the residue was purified by chromatography (PE:MTBE = 5:1~1:1) to give pure **84-2** (1.8 g, 37%).

[0516] To a solution of **83-A** (300 mg, 0.337 mmol) and NMI (276 mg, 3.37 mmol) in anhydrous CH₃CN (4 mL) was added **84-2** (249 mg, 0.674 mmol, in DCM (5 mL)) at 0°C. The mixture was stirred at R.T. for 10 h. The reaction was monitored by LCMS, and then quenched with H₂O. The mixture was extracted with CH₂Cl₂ (3 x 20 mL). The organic phase was dried over anhydrous MgSO₄, and concentrated at low pressure. The residue was purified by chromatography using PE:EA = 5:1~2:1 as the eluent to give **84-3** (360 mg, 87%).

[0517] Compound **84-3** (360 mg, 0.294 mmol) was dissolved in CH₃COOH (80%, 8 mL), and stirred at 40-50°C for 2.5 h. The reaction was monitored by LCMS and then quenched with MeO. The mixture was concentrated at low pressure, and the residue was purified by chromatography using PE:EA = 1:1 as the eluent to generate crude compound **84**. The product purified by prep-HPLC (neutral system, NH₄HCO₃) to give compound **84** (70 mg, 75%) as a white solid. ESI-MS: m/z 679.2 $[M+H]^+$.

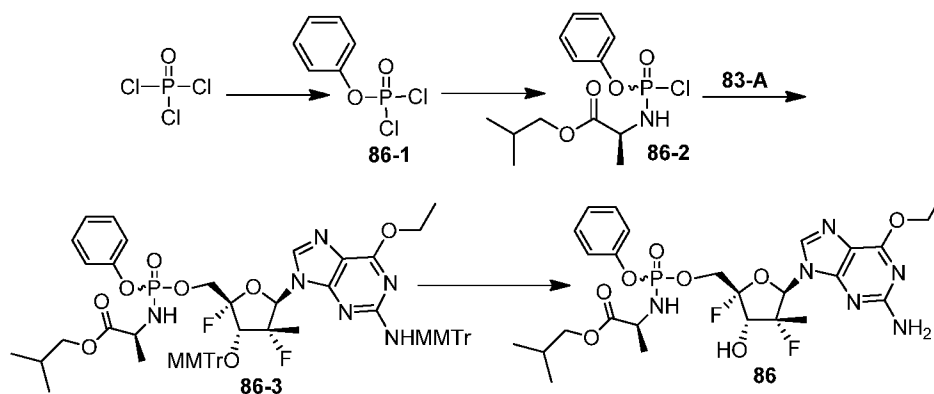
EXAMPLE 60
COMPOUND 85



[0518] To a stirred solution of POCl_3 (2.0 g, 13 mmol) in anhydrous DCM (10 mL) was added phenol (1.22 g, 13 mmol) at -70°C and TEA (1.31 g, 13 mmol) in DCM (3 mL) dropwise at -70°C . The mixture was gradually warmed to R.T., and stirred for 1 h. A crude solution of **85-1** was obtained.

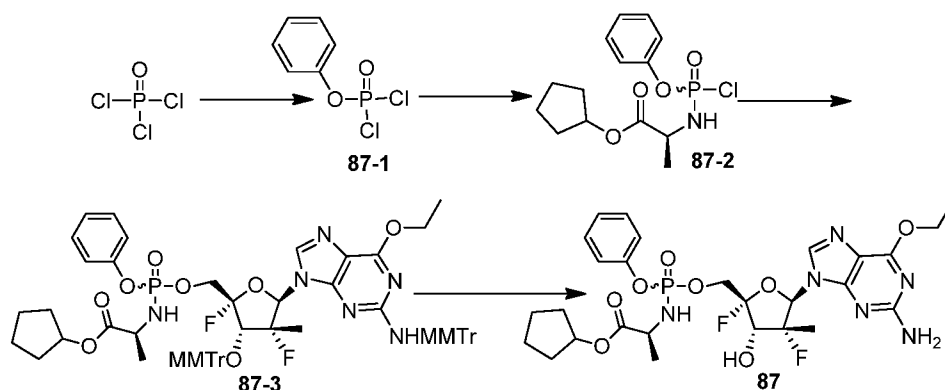
[0519] Compound **85** was prepared using a similar procedure as for the preparation of compound **84** using **85-2** (205 mg, 0.674 mmol, in DCM (5 mL) obtained from (S)-isopropyl 2-aminopropanoate hydrochloride and **85-1**) and **83-A** (300 mg, 0.337 mmol). Compound **85** (50 mg, 74%) was obtained as a white solid. ESI-MS: m/z 615.2 $[\text{M}+\text{H}]^+$.

EXAMPLE 61
COMPOUND 86



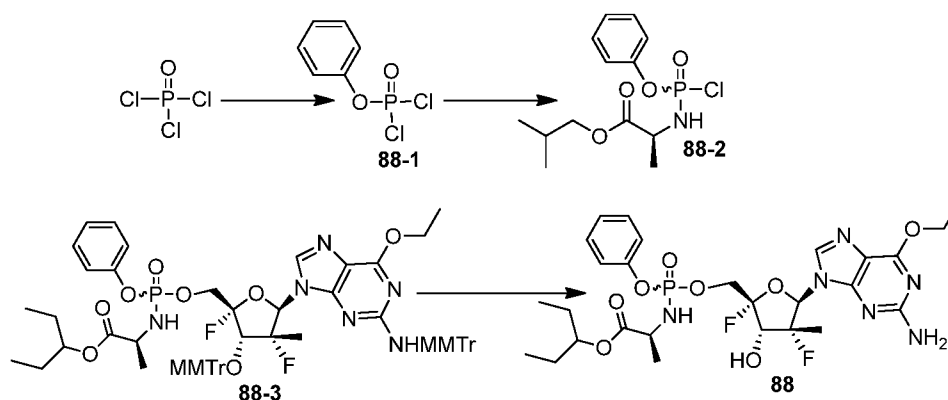
[0520] Compound **86** was prepared using a similar procedure as for the preparation of compound **84** using **86-2** (214 mg, 0.674 mmol, in DCM (5 mL) obtained from (S)-isobutyl 2-aminopropanoate hydrochloride and **86-1**) and **83-A** (300 mg, 0.337 mmol). Compound **86** (70 mg, 87%) was obtained as a white solid. ESI-MS: m/z 629.2 $[\text{M}+\text{H}]^+$.

EXAMPLE 62
COMPOUND 87



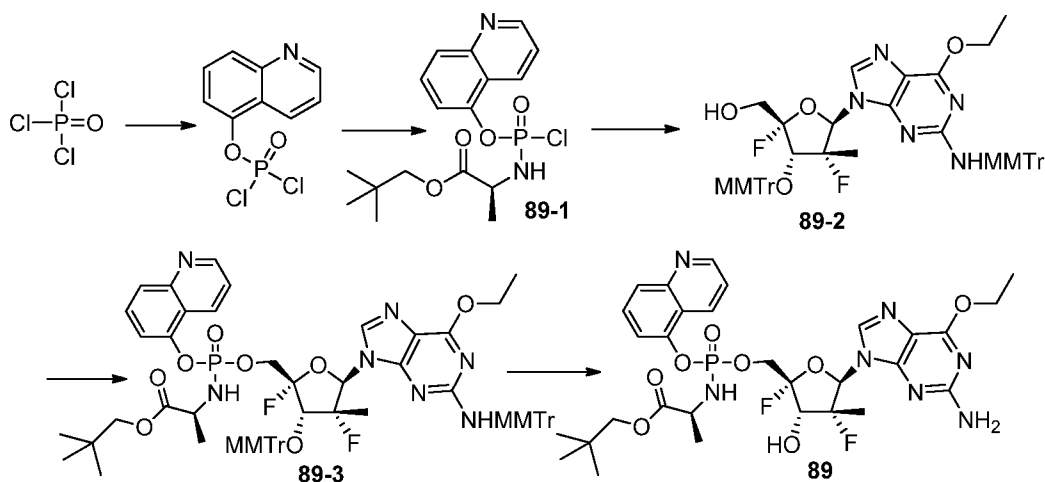
[0521] Compound **87** was prepared using a similar procedure as for the preparation of compound **84** using **87-2** (223 mg, 0.674 mol, DCM (5 mL) obtained from (S)-cyclopentyl 2-aminopropanoate hydrochloride and **87-1**) and **83-A** (300 mg, 0.337 mmol). Compound **87** (62 mg, 71%) was obtained as a white solid. ESI-MS: m/z 641.2 $[\text{M}+\text{H}]^+$.

EXAMPLE 63
COMPOUND 88



[0522] Compound **88** was prepared using a similar procedure as for the preparation of compound **84** using **88-2** (223 mg, 0.674 mol, DCM (5 mL), obtained from (S)-3-pentyl 2-aminopropanoate hydrochloride and **88-1**) and **83-A** (300 mg, 0.337 mmol). Compound **88** (42 mg, 60%) was obtained as a white solid. ESI-MS: m/z 643.2 $[\text{M}+\text{H}]^+$.

EXAMPLE 64
COMPOUND 89

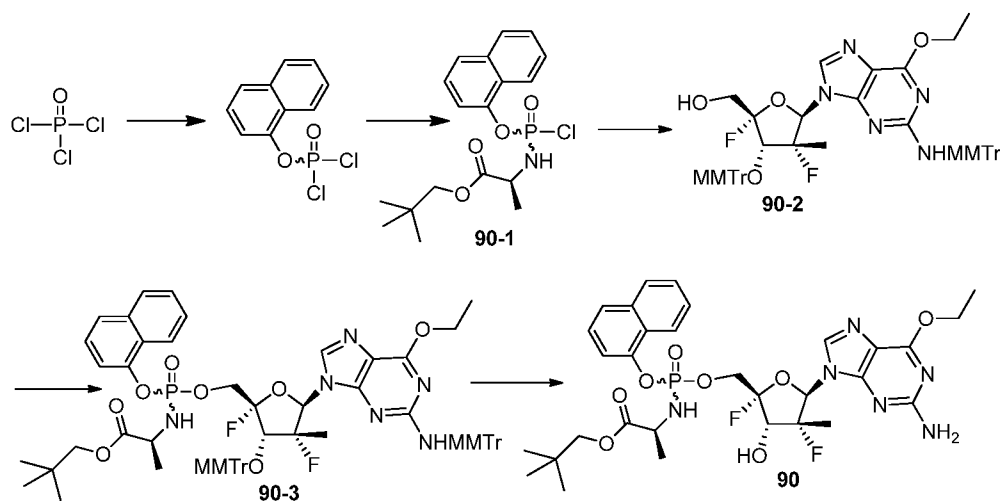


[0523] A stirred solution of phosphoryl trichloride (1.00 g, 6.58 mmol) and 5-quinoline (955 mg, 6.58 mmol) in anhydrous DCM (50 mL) was treated with a solution of TEA (665 mg, 6.58 mmol) in DCM (10 mL) at -78°C . The mixture was gradually warmed to R.T., and stirred for 2 h. The solution was cooled to -78°C and then treated with (*S*)-neopentyl 2-aminopropanoate hydrochloride (1.28 g, 6.58 mmol). TEA (1.33 g, 13.16 mmol) was added dropwise at -78°C . The mixture was gradually warmed to R.T., and stirred for 2 h. The mixture was concentrated at low pressure, and the residue was dissolved in methyl-butyl ether. The precipitate was filtered off, and the filtrate was concentrated at low pressure. The residue was purified by a silica gel column (pure AcOEt) to give **89-1** as colorless oil (500 mg, 20%).

[0524] To a solution of **89-2** (300 mg, 0.337 mmol) and NMI (276.6 mg, 3.37 mmol) in anhydrous CH_3CN (0.9 mL) was added **89-1** (388 mg, 1.011 mmol) in CH_3CN (0.3 mL) dropwise at 0°C . The mixture was stirred at R.T. overnight. The reaction was quenched with water, and extracted with AcOEt. The organic phase was washed with brine, dried over anhydrous sodium sulfate, and concentrated at low pressure. The residue was purified by silica gel column (33% EA in PE) to give **89-3** as a yellow powder (300 mg, 71.9%).

[0525] Compound **89-3** (300 mg, 0.243 mmol) was dissolved in 80% CH_3COOH (3 mL), and the mixture was stirred at 60°C for 2.5 h. The mixture was partitioned between AcOEt and water. The organic layer phase was washed by brine, dried over sodium sulfate and concentrated at low pressure. The residue was purified by silica gel column (50% EA in PE) to give compound **89** as a yellow powder (81 mg, crude product). The crude product (81 mg) was purified by RP HPLC to give compound **89** as a white solid. (28.7 mg, 17.1%). ESI-LCMS: m/z 694.1 $[\text{M}+\text{H}]^+$.

EXAMPLE 65
COMPOUND 90

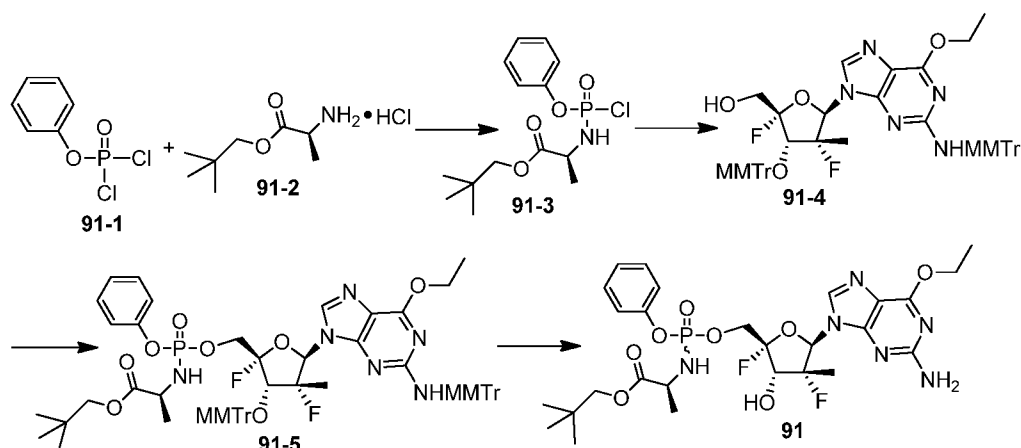


[0526] Compound **90-1** was prepared using a similar procedure as for the preparation of compound **89-1** using phosphoryl trichloride (2.00 g, 13.16 mmol), 1-naphthol (1.882 g, 13.16 mmol) and (*S*)-neopentyl 2-aminopropanoate hydrochloride (2.549 g, 13.16 mmol). Compound **90-1** (600 mg, 12%) was obtained as a colorless oil.

[0527] A solution of **90-2** (230 mg 0.26 mmol) and NMI (212 mg 2.60 mmol) in anhydrous CH_3CN (1 mL) was treated with a solution of **90-1** (300 mg 0.78 mmol) in anhydrous CH_3CN (0.5 mL) at R.T. The mixture was stirred at R.T. overnight. The reaction was quenched with water, and extracted with EA (3 x 20 mL). The organic layer was washed with brine, dried by anhydrous sodium sulfate, and concentrated at low pressure. The residue was purified by a silica gel column (CH_3OH in CH_2Cl_2 from 1% to 5%) to give **90-3** (300 mg, 93%) as a white solid.

[0528] Compound **90-3** (300 mg, 0.24 mmol) was dissolved in CH_3COOH (80%, 5 mL). The mixture was stirred at 60°C for 2.5 h. The mixture was diluted with EA (30 mL) and washed with brine. The organic phase was dried over anhydrous sodium sulfate, and concentrated at low pressure. The residue was purified by a silica gel column (CH_3OH in CH_2Cl_2 from 1% to 5%) to give crude compound **90** (105 mg). The crude product was purified by HPLC (0.1% NH_4HCO_3 in water and CH_3CN) to give compound **90** (45 mg, 26%) as a white solid. ESI-LCMS: m/z 693.2 $[\text{M}+\text{H}]^+$.

EXAMPLE 66
COMPOUND 91

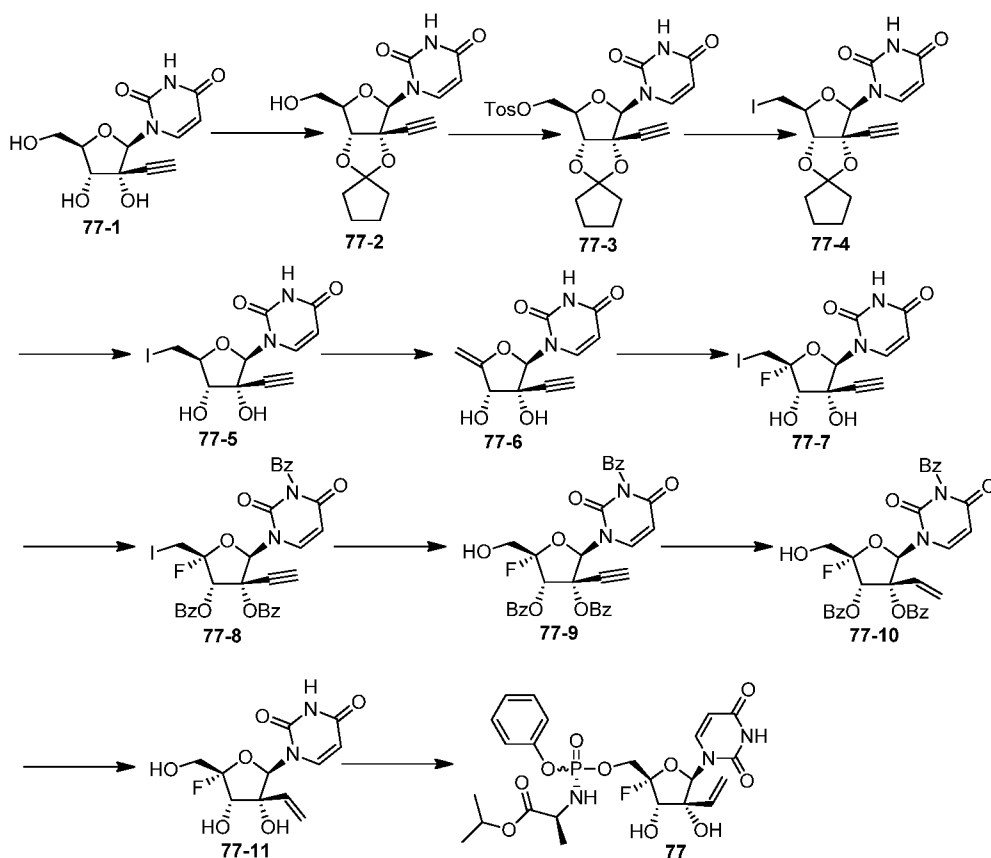


[0529] A stirred solution of **91-1** (2.00 g, 13.99 mmol) and **91-2** (2.00 g, 13.99 mmol) in anhydrous DCM (8 mL) was treated with a solution of TEA (3.11 g, 30.8 mmol) in DCM (20 mL) dropwise at -78°C. The mixture was stirred for 2 h. at -78 °C and then gradually warmed to R.T. The organic solvent was removed at low pressure, and the residue was dissolved in methyl-butyl ether. The precipitate was filtered off, and the filtrate was concentrated at low pressure. The residue was purified on a silica gel column (dry DCM) to give **91-3** as colorless oil (1 g, 20.96%).

[0530] Compound **91-4** (260 mg, 0.29 mmol) was coevaporated with toluene 3 times to remove H₂O. Dried **91-4** was treated with MeCN (0.8 mL) and NMI (240 mg, 2.9 mmol) and then stirred for 10 mins. The mixture was treated with a solution of **91-3** (291 mg, 0.87 mmol) in MeCN (0.4 mL), and then concentrated at low pressure. The residue was purified on a silica gel column (75% EA in PE)) to give **91-5** (300 mg, 86%) as a white solid.

[0531] Compound **91-5** (300 mg, 0.25 mmol) was treated with CH₃COOH (5 mL, 80%), and stirred at 50 °C for 3 h. The mixture was diluted with EA. The solution was washed with brine, dried over anhydrous Na₂SO₄, and concentrated at low pressure. The residue was purified by silica gel column chromatography (67% EA in PE) to give crude compound **91**, which was purified by HPLC. The product was dried by lyophilization to give compound **91** (30 mg, 18.5%) as a white solid. ESI-LCMS: m/z 643 [M+H]⁺.

EXAMPLE 67
COMPOUND 77



[0532] To a solution of 1,1-dimethoxycyclopentane (19.3 g, 148.52 mmol) and **77-1** (10.0 g, 37.13 mmol) in DCE (100 mL) was added TsOH·H₂O (0.7 g, 3.71 mmol). The mixture was stirred at 50°C for 12 h. The mixture was neutralized with Et₃N, and concentrated at low pressure. The residue was purified by silica gel column chromatography (1-10% MeOH in DCM) to give **77-2** (8.7 g, 70.1%) as a white solid.

[0533] Compound **77-2** (20.0 g, 0.06 mol) was coevaporated with anhydrous pyridine 3 times to remove H₂O. To an ice-cold solution of **77-2** in anhydrous pyridine (100 mL) was added TsCl (22.8 g, 0.12 mol) at 0°C, and the mixture was stirred overnight. The reaction was monitored by LCMS and TLC. The reaction was quenched with H₂O, and the mixture extracted with EA (3 x 200 mL). The solution was dried over anhydrous Na₂SO₄ and evaporated at low pressure. The residue was purified by silica gel column chromatography (DCM: MeOH=100:1 to 15:1) to give **77-3** (20.0 g, 69.0%) as a white solid.

[0534] To a solution of **77-3** (20.0 g, 0.04 mol) in acetone (200 mL) was added NaI (31.0 g, 0.2 mol), and the mixture was heated to reflux overnight. The reaction was monitored by LCMS. The reaction was quenched with a sat. Na₂S₂O₃ solution. The solution was extracted with EA (3 x 200 mL). The organic layer was dried over anhydrous Na₂SO₄, and evaporated at

low pressure. The residue was purified by silica gel column chromatography (DCM: MeOH=100:1 to 15:1) to give **77-4** (15.0 g, 83.3%) as a white solid.

[0535] Compound **77-4** (13.4 g, 30.16 mmol) was treated with HCOOH (80%) in H₂O at R.T. The solution was stirred at 60 °C for 2 h. The mixture was concentrated at low pressure. The residue was purified by column chromatography (1%-10% MeOH in DCM) to give **77-5** (9.1 g, 80.0%) as a white solid.

[0536] To a solution of **77-5** (5.0 g, 13.22 mmol) in anhydrous CH₃CN/THF (50 mL, 1:1, v:v) was added DBU (6.0 g, 39.66 mmol) at R.T. The solution was stirred at 50°C for 1.5 h. The reaction was quenched with HCOOH at 0°C, and then concentrated at low pressure. The residue was purified by column chromatography (50%-70% EA in PE) to give **77-6** (3.3 g, 48.1%) as a white solid.

[0537] To an ice-cold solution of **77-6** (2.1 g, 8.39 mmol) in anhydrous MeCN (21 mL) was added NIS (2.4 g, 10.49 mmol) and TEA•3HF (1.0 g, 6.29 mmol) under N₂. The mixture was stirred at R.T. for 1 h. The reaction was quenched with sat. NaHCO₃ and sat. Na₂SO₃ solution, and extracted with EA (3 x 100 mL). The organic phase was dried over anhydrous Na₂SO₄, and evaporated to dryness at low pressure. The residue was purified on a silica gel column (30%-50% EA in PE) to give **77-7** (1.3 g, 39.3%) as a light yellow solid.

[0538] To a stirred solution of **77-7** (3.2 g, 8.08 mmol) in anhydrous DCM (32 mL) was added DMAP (2.5 g, 20.20 mmol) and Et₃N (2.5 g, 24.24 mmol) at R.T. The mixture was treated with BzCl (3.7 g, 26.66 mmol) at 0°C and then stirred at R.T. overnight. The reaction was quenched with water, and extracted with EA (3 x 60 mL). The organic phase was concentrated at low pressure, and the residue was purified by column chromatography (20%-30% EA in PE) to give **77-8** (1.8 g, 31.6 %) as a white solid.

[0539] Bu₄NOH (8.0 g, 13.74 mL, 55% in H₂O) was adjusted to pH=3-4 with TFA, and then cooled to R.T. To a solution of **77-8** (600 mg, 0.85 mmol) in DCM (10 mL) was added the Bu₄NOH solution and *m*-CPBA (917 mg, 4.25 mmol, 80%) at R.T. The mixture was stirred at 25 °C for 48 h and then washed with a sat. NaHCO₃ solution. The organic layer was directly passed through basic Al₂O₃ column, and the solvent was concentrated at low pressure. The residue was purified by a silica gel column (20%-30% EA in PE) to give **77-9** (123 mg, 24.3%) as a white solid.

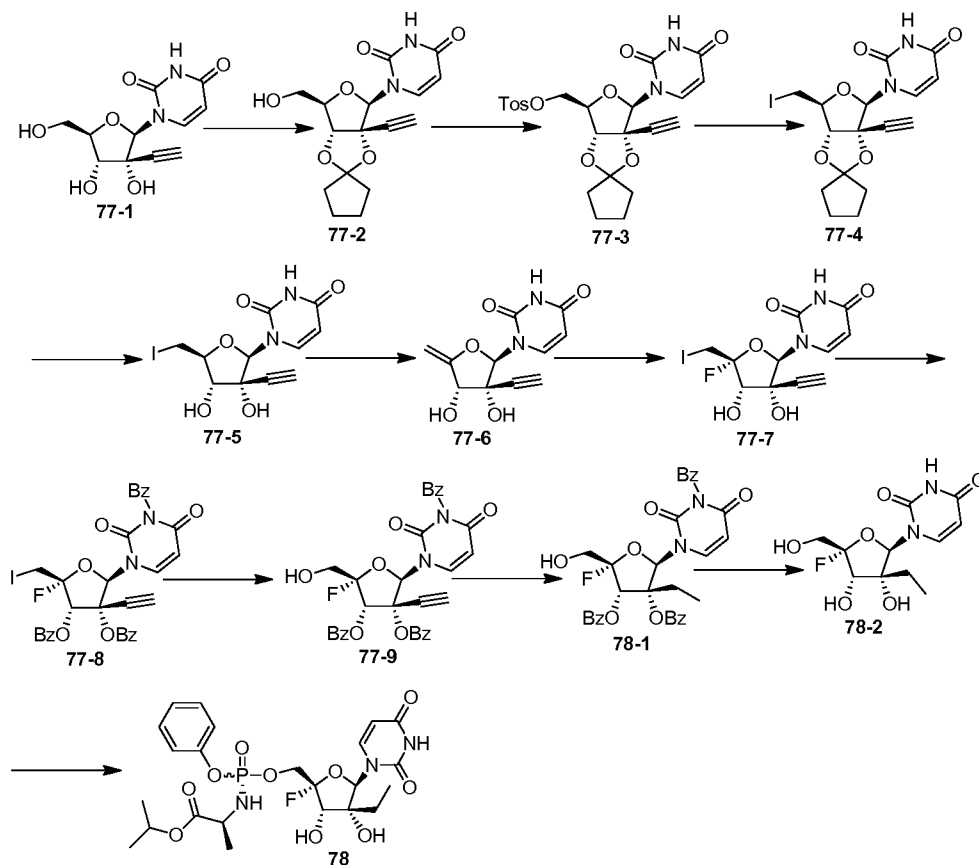
[0540] To a solution of **77-9** (300 mg, 0.50 mmol) in EA/hexane (20 mL, 1:1, v:v) was added Lindlar catalyst (200 mg) under N₂. The mixture was stirred under H₂ (40 Psi) at 2 °C for 1.5 h. The suspension was filtered, and the filtrate was treated with Lindlar catalyst (200

mg) under N₂, and stirred under H₂ (40 Psi) at 25 °C for 1.5 h. The mixture was filtered, and the filtrate was concentrated at low pressure to give crude **77-10** (287 mg) as a white solid.

[0541] Compound **77-10** (287 mg, 0.48 mmol) was dissolved in NH₃/MeOH (30 mL, 7 M). The mixture was stirred at R.T. for 24 h under N₂ and then concentrated at low pressure. The residue was purified by prep-HPLC (0.1% HCOOH in water and MeCN) to give **77-11** (50 mg, 34.7% over two steps) as a white solid. ¹H-NMR (CD₃OD, 400 MHz) δ = 7.86 (d, J = 8.0 Hz 1H), 6.26 (s, 1H), 5.62-5.86 (m, 1H), 5.49 (d, J = 17.1 Hz, 1 H), 5.30 (d, J = 10.5 Hz, 1H), 4.41 (d, J = 19.3 Hz, 1 H), 3.71-3.86 (m, 1H).

[0542] Compound **77-11** (113 mg, 0.39 mmol) was co-evaporated with toluene 3 times to remove H₂O. To a stirred solution of **77-11** (113 mg, 0.39 mmol) in a mixture of MeCN (0.5 mL) and NMI (320 mg, 3.90 mmol) was added a solution of **73-C** (256 mg, 0.66 mmol) in MeCN (0.5 mL) at 0°C. The mixture was stirred at R.T. overnight and then concentrated at low pressure. The residue was purified on a silica gel column (5% MeOH in DCM) to give crude compound **77**, which purified by prep-HPLC (0.1% HCOOH in water and MeCN) to give compound **77** (45 mg, 20.1%) as a white solid. ESI-MS: m/z 538.2 [M-F]⁺ ESI-MS: m/z 580.2 [M+Na]⁺.

EXAMPLE 68 COMPOUND 78



[0543] To a solution of **77-9** (300 mg, 0.50 mmol) in MeOH (30 mL) was added wet Pd/C (300 mg, 10%) under N₂. The mixture was stirred under H₂ (1 atm) at 25°C for 1.5 h. The suspension was filtered, and then concentrated at low pressure to give crude **78-1** (307 mg) as a white solid.

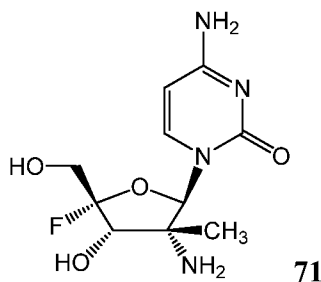
[0544] Compound **78-1** (307 mg, 0.48 mmol) was dissolved in NH₃/MeOH (30 mL, 7 M). The mixture was stirred at R.T. for 24 h under N₂ then concentrated at low pressure. The residue was purified by prep-HPLC (0.1% HCOOH in water and MeCN) to give **78-2** (30 mg, 21% over two steps) as a white solid.

[0545] Compound **78-2** (91 mg, 0.31 mmol) was co-evaporated with toluene 3 times to remove H₂O. To a stirred solution of **78-2** (91 mg, 0.31 mmol) in a mixture of MeCN (0.5 mL) and NMI (254 mg, 3.90 mmol) was added a solution **73-C** (203 mg, 0.66 mmol) in MeCN (0.5 mL) at 0°C. The mixture was stirred at R.T. overnight and then concentrated at low pressure. The residue was purified on a silica gel column (5% MeOH in DCM) to the crude compound **78**, which purified by prep-HPLC (0.1% HCOOH in water and MeCN) to give compound **78** (30 mg, 17%) as a white solid. ESI-MS: m/z 540.1 [M-F]⁺.

EXAMPLE 69

ADDITIONAL COMPOUNDS OF FORMULA (I)

[0546] The foregoing syntheses are exemplary and can be used as a starting point to prepare a large number of additional compounds. Examples of compounds of Formula (I) that can be prepared in various ways, including those synthetic schemes shown and described herein, are provided below. Those skilled in the art will be able to recognize modifications of the disclosed syntheses and to devise routes based on the disclosures herein; all such modifications and alternate routes are within the scope of the claims.



EXAMPLE 70

HCV Replicon Assay

Cells

[0547] Huh-7 cells containing the self-replicating, subgenomic HCV replicon with a stable luciferase (LUC) reporter were cultured in Dulbecco's modified Eagle's medium (DMEM) containing 2mM L-glutamine and supplemented with 10% heat-inactivated fetal

bovine serum (FBS), 1% penicillin-streptomycin, 1% nonessential amino acids, and 0.5 mg/mL G418.

Determination of anti-HCV activity

[0548] Determination of 50% inhibitory concentration (EC_{50}) of compounds in HCV replicon cells were performed by the following procedure. On the first day, 5,000 HCV replicon cells were plated per well in a 96-well plate. On the following day, test compounds were solubilized in 100% DMSO to 100x the desired final testing concentration. Each compound was then serially diluted (1:3) up to 9 different concentrations. Compounds in 100% DMSO are reduced to 10% DMSO by diluting 1:10 in cell culture media. The compounds were diluted to 10% DMSO with cell culture media, which were used to dose the HCV replicon cells in 96-well format. The final DMSO concentration was 1%. The HCV replicon cells were incubated at 37 °C for 72 h. At 72 h, cells were processed when the cells are still subconfluent. Compounds that reduce the LUC signal are determined by Bright-Glo Luciferase Assay (Promega, Madison, WI). % Inhibition was determined for each compound concentration in relation to the control cells (untreated HCV replicon) to calculate the EC_{50} .

[0549] Compounds of Formula (I) are active in the replicon assay. The antiviral activity of exemplary compounds is shown in Table 2, where 'A' indicates an $EC_{50} < 1 \mu M$, 'B' indicates an $EC_{50} \geq 1 \mu M$ and $< 10 \mu M$, and 'C' indicates an $EC_{50} \geq 10 \mu M$ and $< 100 \mu M$.

Table 2

Compound #	EC ₅₀
2	A
3	A
5	A
11	A
13	B
14	A
16	A
17	A
18	A
19	A
20	A
21	A
22	A
27	C
28	A
29	C
30	A
31	A
32	A
33	A
34	A
35	A
36	A
37	A
40	B
41	B
42	A
43	A
49	A
51	B
52	A
53	A
54	A
55	A
56	A
57	A
58	A
59	C
60	C
61	A
62	A
66	A
67	B
70	B
73	B
77	B
79	A
80	B
81	A
83	A
84	A
85	A
86	A
87	A
88	A
89	A
90	A
91	A

EXAMPLE 71
NS5B Inhibition Assay

[0550] The enzyme activity of NS5B570-Con1 (Delta-21) was measured as an incorporation of tritiated NTP into acid-insoluble RNA products. The complementary IRES (cIRES) RNA sequence was used as a template, corresponding to 377 nucleotides from the 3'-end of HCV (–) strand RNA of the Con-1 strain, with a base content of 21% Ade, 23% Ura, 28% Cyt, and 28% Gua. The cIRES RNA was transcribed *in vitro* using a T7 transcription kit (Ambion, Inc.) and purified using the Qiagen RNeasy maxi kit. HCV polymerase reactions contained 50 nM NS5B570-Con1, 50 nM cIRES RNA, about 0.5 μ Ci tritiated NTP, 1 μ M of competing cold NTP, 20 mM NaCl, 40 mM Tris-HCl (pH 8.0), 4 mM dithiothreitol, and 4 mM $MgCl_2$. Standard reactions were incubated for 2 h at 37°C, in the presence of increasing concentration of inhibitor. At the end of the reaction, RNA was precipitated with 10% TCA, and acid-insoluble RNA products were filtered on a size exclusion 96-well plate. After washing of the plate, scintillation liquid was added and radio labeled RNA products were detected according to standard procedures with a Trilux Topcount scintillation counter. The compound concentration at which the enzyme-catalyzed rate was reduced by 50% (IC_{50}) was calculated by fitting the data to a non-linear regression (sigmoidal). The IC_{50} values were derived from the mean of several independent experiments and are shown in Table 3. Compounds of Formula (I) showed activity in this assay. A value of 'A' in the table below indicates an IC_{50} of < 1 μ M, a value of 'B' indicates an $IC_{50} \geq 1 \mu$ M and < 10 μ M, and a value of 'C' indicates an IC_{50} value of $\geq 10 \mu$ M and < 100 μ M.

Table 3

Compound #	IC ₅₀
6	A
7a	A
7b	B
9	A
12	A
15	A
26	A
28	A
38	A
44	A
46	A
50	A
63	A
64	A
69	A
76	A

EXAMPLE 72

Assessment of inhibition of mitochondrial function

[0551] Drug-associated dysfunction of mitochondria is believed to play a role in the etiology of the various adverse symptoms that occur in patients treated with antiviral nucleoside/nucleotides. For this reason, evaluation of compounds for their potential to inhibit mitochondrial function is useful. To assess the potential for nucleotide/nucleoside analogs to interfere with normal mitochondrial functions and exhibit mitochondrial toxicity, the following were measured: (1) the ability of nucleotides to be incorporated by human mitochondrial RNA polymerase in vitro and (2) the cellular inhibition of the synthesis of the mitochondrial DNA (mtDNA)-encoded protein, cytochrome c oxidase (COX-I), relative to the nuclear DNA (nDNA)-encoded mitochondrial protein succinate dehydrogenase subunit A (SDH-A) in HepG2 cells. Control compounds and compounds of Formula (I) were studied in these assays.

Biochemical assay

[0552] Arnold et al. "Sensitivity of Mitochondrial Transcription and Resistance of RNA Polymerase II Dependent Nuclear Transcription to Antiviral Ribonucleosides" PLoS Pathog (2012) 8(11): e1003030. doi:10.1371/journal.ppat.1003030, which is hereby incorporated by reference in its entirety.

Assessment of incorporation of nucleotides by human mitochondrial RNA polymerase (HMRP)

DdRp assay with human mitochondrial RNA polymerase

[0553] The DdRp assay with human mitochondrial RNA polymerase was performed under single turnover conditions where enzyme concentration is in excess of the

primer/template. The ^{33}P -RNA/DNA primer/template was used at a concentration of 100 nM, together with 320 nM enzyme. The standard 10- μL reactions were carried out at 30°C for 1 minute with 100 μM of each nucleotide 5'-triphosphate (NTP), 10 mM MgCl_2 , 50 mM NaCl, 40 mM Tris, pH 7.5, and 1 mM DTT. The reaction was stopped by adding 20 μL of formamide loading dye containing 50 mM EDTA. RNA products were resolved by electrophoresis on 22.5% TBE Urea polyacrylamide sequencing gels that were scanned using a TYPHOON PhosphorImager.

Results

[0554] As shown in both Figures 10 and 11, the appropriate natural nucleotides were shown to be good substrates for incorporation by HMRP in each template. The template in Figure 10 was designed to measure incorporation of UTP analogs. Primer/Template: (SEQ ID NO: 1) UUUUGCCGCGCC and (SEQ ID NO: 2) GGGAATGCTAGGCGCGGC. In the control water lanes, wherein no nucleotides were added, no incorporation was observed as indicated by the lack of product band. As shown in Figure 10, UTP and 3'-deoxy-UTP were efficient substrates for incorporation as indicated by the prominent product band. The potential for misincorporation was assessed using the control nucleotide CTP. As provided in Figure 10, CTP was incorporated to a lesser extent relative to UTP. In contrast to UTP and 3'-deoxy-UTP, compounds of Formula (I) and 2'-Me-2'-F-UTP were not efficient substrates for incorporation by HMRP as demonstrated by the lack of product band.

[0555] The template strand shown in Figure 11 was designed to measure the incorporation of GTP analogs. Primer/Template: (SEQ ID NO: 3) UUUUGCCGCGCC and (SEQ ID NO: 4) GGGAATGCACGGCGCGGC. In the control water lanes, no incorporation was observed as indicated by the lack of product band. GTP and 3'-deoxy-GTP were found to be efficient substrates for incorporation as demonstrated by the significant product bands. The potential for misincorporation was assessed using the control nucleotide ATP. As shown by the lack of product band in Figure 11, control ATP was a poor substrate for incorporation. Nucleotide analog 2'-Me-GTP (the nucleotide metabolite of monophosphate prodrug INX-0189/BMS-986094) was tested and found to be a good substrate for incorporation by HMRP as indicated by the product band. Nucleotide analog 2'-Me-2'-F-GTP (nucleotide metabolite of monophosphate prodrug GS-938) was tested and also found to be incorporated by HMRP. In contrast, compounds of Formula (I) were not efficient substrates for incorporation into the template strand by HMRP as indicated by the lack of product bands in Figure 11.

Assessment of inhibition of mitochondrial protein synthesis - Cell Based Assay**Assay Principle**

[0556] MitoBiogenesis™ In Cell ELISA kits (Cat. #MS643) were obtained from Mitosciences, OR, USA. The MitoBiogenesis™ In Cell ELISA kit is a duplexing 96 well assay that ratios both an mtDNA and an nDNA encoded mitochondrial protein. Cells were seeded in 96 microplates and after exposure to compounds for several cell doublings, the levels of the two mitochondrial proteins were measured simultaneously in each well. The two proteins assayed were each subunits of different oxidative phosphorylation enzyme complexes, one protein being subunit I of Complex IV (cytochrome c oxidase; COX I) that is mtDNA encoded and the other being the 70 kDa subunit of Complex II (succinate dehydrogenase subunit A; SDH A) that is nDNA encoded. Complex IV includes several proteins that are encoded by the mtDNA while the proteins of Complex II are entirely encoded by nDNA. To control for the density of cells present at the end of the culture period, the number of cells were assessed by staining with Janus Green and the levels of COX I/SDH A normalized to the final cell density.

96 Well Plate Assay Format for HepG2 Cells

[0557] On the first day, 1000 HepG2 cells per well were plated in a 96 well plate. On the following day, compounds to be tested were solubilized in 100% DMSO to 100 x the desired final testing concentration. Each compound was serially diluted (1:3) up to 9 distinct concentrations. Compounds in 100% DMSO were reduced to 10% (v/v) DMSO by diluting 1:10 in cell culture media. A 10 µL aliquot of the compounds diluted to 10% (v/v) DMSO with cell culture media was used to dose the cells in duplicate. The final DMSO concentration was 1% (v/v). Untreated cells and wells containing no cells were included on the plate to serve as controls. Cells were then incubated with compounds and observed for 8 days at 37°C and 5% CO₂. Plates were processed as described below in the assay procedure.

Batch Assay Format for HepG2 Cells

[0558] An alternate cell culture procedure was employed to test the potential to mediate mitochondrial toxicity at higher concentrations than achievable in the 96 well plate format. HepG2 cells were grown either in media/DMSO alone or in a series of compound concentrations in 15 cm² dishes or 6 well plates at an initial cell seeding density of 5 x 10⁶ and 5 x 10⁴ cells/mL, respectively. Cells were then incubated and observed for 8 days at 37°C and 5% CO₂. After 8 days, the cells were harvested by trypsinization, counted, and seeded in 96 well plates at a density of 25,000 cells/well in 16 replicate wells. Cells were allowed to adhere overnight and then the plates were processed as described below in the assay procedure.

Assay Procedure

[0559] The assay was performed according to the manufacturer's instructions. Briefly, after the end of the culture period the cell culture media was gently aspirated from the wells of the plate and replaced with 100 μ L of 4% (v/v) paraformaldehyde solution in phosphate buffered saline (PBS, Electron Microscopy Sciences Cat. #15713). After a 20 mins incubation at R.T., the solution was removed and the wells washed 3 x with 300 μ L of PBS. After the final wash, the PBS was removed and the wells overlayed with 100 μ L PBS. The plates were then sealed and stored at 4°C until used. To perform the assay, the PBS overlay was removed by blotting on a paper towel and 100 μ L of 0.5% (v/v) acetic acid added to each well to block endogenous alkaline phosphatase activity. After a 5 mins incubation at R.T., the acetic acid solution was removed and the cells washed once with 200 μ L PBS. Then, 100 μ L of permeabilization buffer (0.1% (v/v) Triton X 100) was added to each well. After 30 mins incubation at R.T., the permeabilization buffer was removed and each well was blocked with 200 μ L of 2 x blocking solution for 2 h at R.T. The 2 x blocking solution was then removed and 100 μ L of primary antibody solution containing anti COX I and anti SDH A antibodies in 1 x blocking solution was added to each well. Plates were then sealed and incubated overnight at 4°C. The primary antibody/blocking solution was removed and the plate washed 3 x with 250 μ L 0.05% (v/v) Tween 20 in PBS. Then, 100 μ L of secondary antibody solution containing alkaline phosphatase (AP) labeled anti SDH A antibody and horseradish peroxidase (HRP) labeled anti COX I antibody was added and incubated for 1 h at R.T. The plate was then washed 4 x with 250 μ L 0.05% (v/v) Tween 20 in PBS. After blotting the plate dry 100 μ L of AP detection reagent was added to each well, and the plate incubated in the dark for 30 mins at R.T. The optical density of each well was then measured at 405 nm. The AP detection reagent was then removed and replaced with 100 μ L of HRP detection reagent, and the plate incubated in the dark for a further 30 mins at R.T. The optical density of each well was then measured at 600 nm. The HRP detection reagent was then removed and each well was then stained with 50 μ L of 1 x Janus Green Stain for 5 mins at R.T. After removal of the dye, the plates were washed 5 x in ultrapure water to remove any remaining dye. The Janus Green stain was then solubilized by the addition of 100 μ L of 0.5 M HCl and incubated for 10 mins. The optical density of each well was then measured at 595 nm.

Data Analysis

[0560] The average of all replicate background measurements from each experimental condition was calculated and subtracted from the experimental values of the same

condition. The SDH A and COX I signals were then plotted as a ratio (COX I/SDH A) and normalized to the Janus Green staining intensity to correct for differences in cell density.

Results

[0561] Control compound d4T was tested and found not to inhibit mitochondrial protein synthesis at concentrations up to 100 μ M as shown in Figures 12A-D. Control compound ddC was tested and found to strongly inhibit mitochondrial protein synthesis. See Figures 12A-D. As demonstrated in Figure 12A, nucleoside monophosphate prodrug INX-08189/BMS-986094 (which delivers 2'-Me-GTP) was tested in the assay and found to strongly inhibit mitochondrial protein synthesis. In contrast, compounds of Formula (I) were tested and found to not inhibit mitochondrial protein synthesis at concentrations up to 100 μ M as shown in Figures 12B-D.

EXAMPLE 73

Combination of Compounds

Combination Testing

[0562] Two or more test compounds were tested in combination with each other using an HCV genotype 1b HCV replicon harbored in Huh7 cells with a stable luciferase (LUC) reporter. Cells were cultured under standard conditions in Dulbecco's modified Eagle's medium (DMEM; Mediatech Inc, Herndon, VA) containing 10% heat-inactivated fetal bovine serum (FBS; Mediatech Inc, Herndon, VA) 2mM L-glutamine, and nonessential amino acids (JRH Biosciences). HCV replicon cells were plated in a 96-well plate at a density of 10^4 cells per well in DMEM with 10% FBS. On the following day, the culture medium was replaced with DMEM containing either no compound as a control, the test compounds serially diluted in the presence of 2% FBS and 0.5% DMSO, or a combination of compound 18 with one or more test compounds serially diluted in the presence of 2% FBS and 0.5% DMSO. The cells were incubated with no compound as a control, with the test compounds, or the combination of compounds for 72 h. The direct effects of the combination of the test compounds were examined using a luciferase (LUC) based reporter as determined by the Bright-Glo Luciferase Assay (Promega, Madison, WI). Dose-response curves were determined for individual compounds and fixed ratio combinations of two or more test compounds.

[0563] The method utilized for evaluating combination effects used a program called MacSynergy II. MacSynergy II software was kindly provided by Dr. M. Prichard (University of Michigan). The Prichard Model allows for a three-dimensional examination of drug interactions and a calculation of the synergy volume (units: μ M²%) generated from running the replicon assay using a checkerboard combination of two or more inhibitors. The volumes of synergy (positive volumes) or antagonism (negative volumes) represent the relative quantity of

synergism or antagonism per change in the concentrations of the two drugs. Synergy and antagonism volumes are defined based on the Bliss independence model. In this model, synergy volumes of less than -25 indicate antagonistic interactions, volumes in the -25 – 25 range indicate additive behavior, volumes in the 25 – 100 range indicate synergistic behavior and volumes >100 indicate strong synergistic behavior. Determination of in vitro additive, synergistic and strongly synergistic behavior for combinations of compounds can be of utility in predicting therapeutic benefits for administering the combinations of compounds in vivo to infected patients.

[0564] The synergy volume results for the combinations are provided in Table 4.

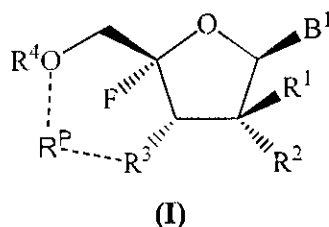
Table 4

Combination Compound	Synergy Volume ($\mu\text{M}^2\%$)	Determination
ANA-598 (3002)	29.46	Synergistic
HCV-796 (3004)	81.72	Synergistic
Ribavirin (5012)	6.77	Additive
Filibuvir (3007)	23.51	Additive
VX-222 (3003)	32.35	Synergistic
BMS-790052 (4001)	38.01	Synergistic
VX-950 (1001)	32.28	Synergistic
TMC-435 (1013)	97.17	Synergistic

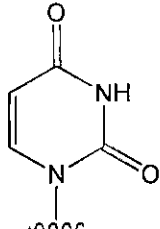
[0565] Although the foregoing has been described in some detail by way of illustrations and examples for purposes of clarity and understanding, it will be understood by those of skill in the art that numerous and various modifications can be made without departing from the spirit of the present disclosure. Therefore, it should be clearly understood that the forms disclosed herein are illustrative only and are not intended to limit the scope of the present disclosure, but rather to also cover all modification and alternatives coming within the true scope and spirit of the invention.

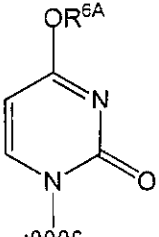
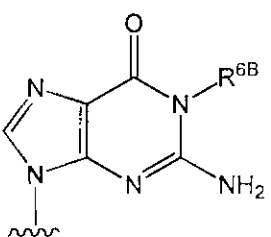
WHAT IS CLAIMED IS:

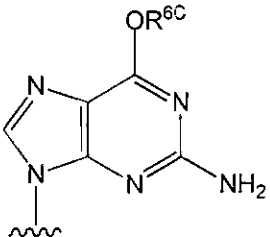
1. A compound of Formula (I), or a pharmaceutically acceptable salt thereof, having the structure:

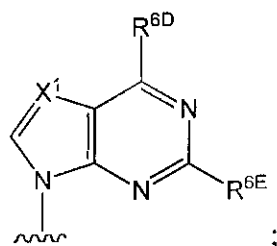


wherein:

B¹ is selected from the group consisting of an optionally substituted ,

an optionally substituted , an optionally substituted , an

optionally substituted  and an optionally substituted

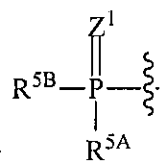


R¹ is selected from the group consisting of an optionally substituted C₁₋₆ alkyl, an optionally substituted C₂₋₆ alkenyl, an optionally substituted C₂₋₆ alkynyl and an optionally substituted C₃₋₆ cycloalkyl;

each ----- is absent and R^P is absent;

R² is -OR^{7A} or -N(R^{7B}R^{7C});

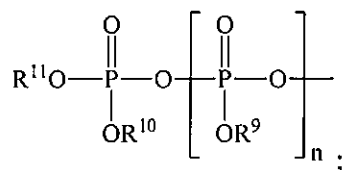
R³ is -OH or -OC(=O)R⁸; or R² and R³ are each an oxygen atom which are linked together by a carbonyl group;



R⁴ is hydrogen or

R^{5A} is selected from the group consisting of O⁻, OH, an optionally substituted N-linked amino acid and an optionally substituted N-linked amino acid ester;

R^{5B} is selected from the group consisting of O⁻, OH, an -O-optionally substituted aryl, an -O-optionally substituted heteroaryl, an -O-optionally substituted heterocyclyl, an optionally substituted N-linked amino acid, an optionally substituted N-linked amino



acid ester and

R^{6A} is an optionally substituted C₁₋₆ alkyl or an optionally substituted C₃₋₆ cycloalkyl;

R^{6B} and R^{6C} are independently selected from the group consisting of hydrogen, an unsubstituted C₁₋₆ alkyl, an unsubstituted C₃₋₆ alkenyl, an unsubstituted C₃₋₆ alkynyl and an unsubstituted C₃₋₆ cycloalkyl;

R^{6D} is NHR^{6G};

R^{6E} is hydrogen, halogen or NHR^{6H};

R^{6G} is selected from the group consisting of hydrogen, an optionally substituted C₁₋₆ alkyl, an optionally substituted C₃₋₆ alkenyl, an optionally substituted C₃₋₆ cycloalkyl, -C(=O)R^{A1} and -C(=O)OR^{A2};

R^{6H} is selected from the group consisting of hydrogen, an optionally substituted C₁₋₆ alkyl, an optionally substituted C₃₋₆ alkenyl, an optionally substituted C₃₋₆ cycloalkyl, -C(=O)R^{A3} and -C(=O)OR^{A4};

X¹ is N or -CR^{6J},

R^{6J} is selected from the group consisting of hydrogen, halogen, an optionally substituted C_{1-6} alkyl, an optionally substituted C_{2-6} alkenyl and an optionally substituted C_{2-6} alkynyl;

R^{A1} , R^{A2} , R^{A3} and R^{A4} are independently selected from the group consisting of C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{3-6} cycloalkyl, C_{3-6} cycloalkenyl, C_{6-10} aryl, heteroaryl, heterocyclyl, aryl(C_{1-6} alkyl), heteroaryl(C_{1-6} alkyl) and heterocyclyl(C_{1-6} alkyl);

R^{7A} is hydrogen or $-C(=O)R^{12}$;

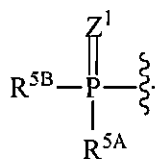
R^{7B} and R^{7C} are independently hydrogen or an optionally substituted C_{1-6} alkyl;

R^8 and R^{12} are independently an optionally substituted C_{1-6} alkyl or an optionally substituted C_{3-6} cycloalkyl;

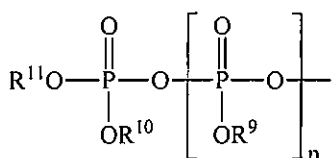
R^9 , R^{10} and R^{11} are independently absent or hydrogen;

n is 0 or 1;

Z^1 is O or S; and



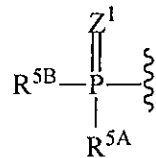
provided that when R^4 is R^{5B} ; and R^{5A} is O^- or OH , then R^{5B} is O^- , OH , or



2. The compound of Claim 1, wherein R^2 is $-OR^{7A}$.
3. The compound of Claim 2, wherein R^{7A} is hydrogen.
4. The compound of Claim 1, wherein R^2 is selected from the group consisting of $-N(R^{7B}R^{7C})$ and $-NH_2$.
5. The compound of any one of Claims 1-4, wherein R^1 is an optionally substituted C_{1-6} alkyl.
6. The compound of any one of Claims 1-4, wherein R^1 is selected from the group consisting of an optionally substituted C_{2-6} alkenyl, an optionally substituted C_{2-6} alkynyl and an optionally substituted C_{3-6} cycloalkyl.
7. The compound of any one of Claims 1- 6, wherein R^3 is $-OH$.

8. The compound of any one of Claims 1-6, wherein R^3 is $-\text{OC}(=\text{O})R^8$.

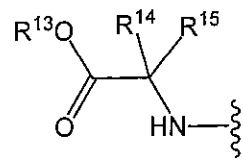
9. The compound of any one of Claims 1-8, wherein R^4 is hydrogen.



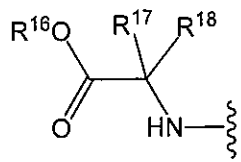
10. The compound of any one of Claims 1-8, wherein R^4 is

11. The compound of Claim 10, wherein R^{5A} is an optionally substituted N-linked amino acid or is an optionally substituted N-linked amino acid ester; and R^{5B} is an optionally substituted N-linked amino acid or is an optionally substituted N-linked amino acid ester.

12. The compound of Claim 10, wherein R^{5A} is selected from the group consisting of alanine isopropyl ester, alanine cyclohexyl ester, alanine neopentyl ester, valine isopropyl ester, isoleucine isopropyl ester, methionine isopropyl ester and leucine isopropyl ester; and R^{5B} is selected from the group consisting of alanine isopropyl ester, alanine cyclohexyl ester, alanine neopentyl ester, valine isopropyl ester, isoleucine isopropyl ester, methionine isopropyl ester and leucine isopropyl ester.



13. The compound of Claim 10, wherein R^{5A} has the structure wherein R^{13} is selected from the group consisting of hydrogen, an optionally substituted C_{1-6} -alkyl, an optionally substituted C_{3-6} cycloalkyl, an optionally substituted aryl, an optionally substituted aryl(C_{1-6} alkyl) and an optionally substituted haloalkyl; R^{14} is selected from the group consisting of hydrogen, an optionally substituted C_{1-6} alkyl, an optionally substituted C_{1-6} haloalkyl, an optionally substituted C_{3-6} cycloalkyl, an optionally substituted C_6 aryl, an optionally substituted C_{10} aryl and an optionally substituted aryl(C_{1-6} alkyl); and R^{15} is hydrogen or an optionally substituted C_{1-4} -alkyl; or R^{14} and R^{15} is taken together to form an optionally substituted C_{3-6} cycloalkyl; and



R^{5B} has the structure wherein R^{16} is selected from the group consisting of hydrogen, an optionally substituted C_{1-6} -alkyl, an optionally substituted C_{3-6} cycloalkyl, an optionally substituted aryl, an optionally substituted aryl(C_{1-6} alkyl) and an

optionally substituted haloalkyl; R^{17} is selected from the group consisting of hydrogen, an optionally substituted C_{1-6} alkyl, an optionally substituted C_{1-6} haloalkyl, an optionally substituted C_{3-6} cycloalkyl, an optionally substituted C_6 aryl, an optionally C_{10} aryl and an optionally substituted aryl(C_{1-6} alkyl); and R^{18} is hydrogen or an optionally substituted C_{1-4} -alkyl; or R^{17} and R^{18} is taken together to form an optionally substituted C_{3-6} cycloalkyl.

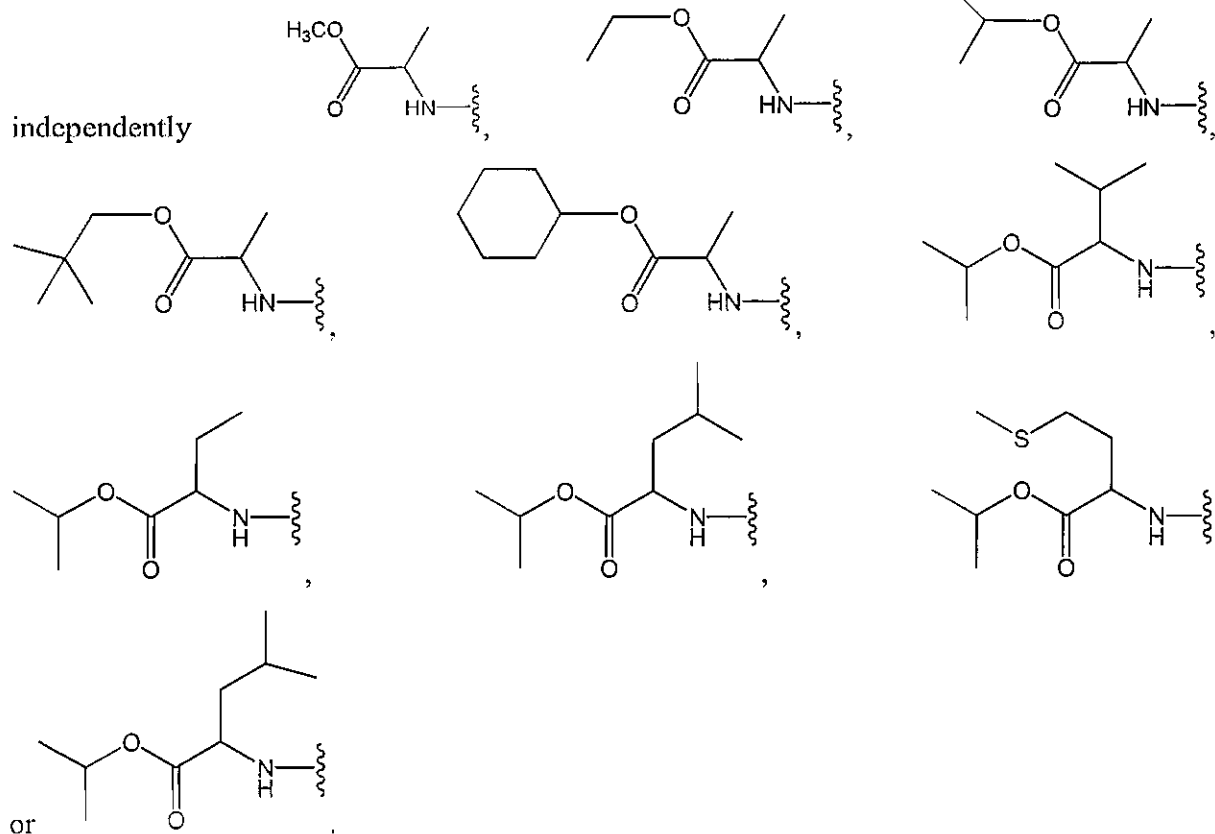
14. The compound of Claim 13, wherein R^{14} , R^{15} , R^{17} and R^{18} are independently hydrogen or an optionally substituted C_{1-6} -alkyl.

15. The compound of any one of Claims 13-14, wherein R^{13} and R^{16} are independently an optionally substituted C_{1-6} alkyl or an optionally substituted C_{3-6} cycloalkyl.

16. The compound of Claim 13, wherein

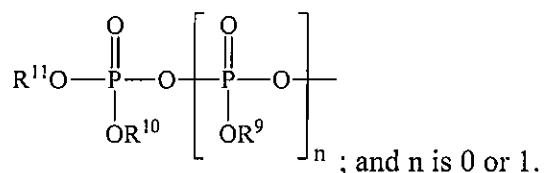
and

independently



17. The compound of Claim 10, wherein R^{5A} is an optionally substituted N-linked amino acid ester; and R^{5B} is selected from the group consisting of an -O-optionally substituted aryl, an -O-optionally substituted heteroaryl and an -O-optionally substituted heterocyclyl.

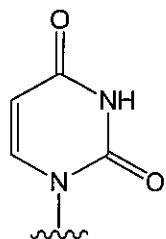
18. The compound of Claim 10, wherein R^{5A} is O^- or OH ; R^{5B} is O^- , OH or



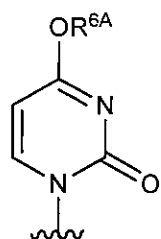
19. The compound of any one of Claims 1-18, wherein Z^1 is O.

20. The compound of any one of Claims 1-18, wherein Z^1 is S.

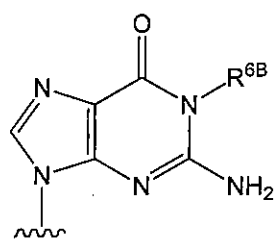
21. The compound of any one of Claims 1-20, wherein B^1 is an optionally substituted



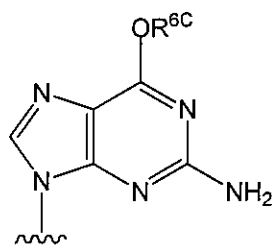
22. The compound of any one of Claims 1-20, wherein B^1 is an optionally substituted



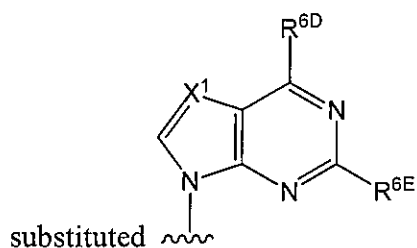
23. The compound of any one of Claims 1-20, wherein B¹ is an optionally substituted



, an optionally substituted

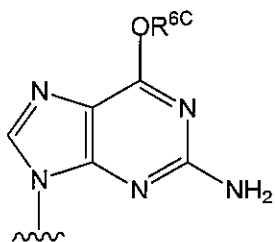


or an optionally

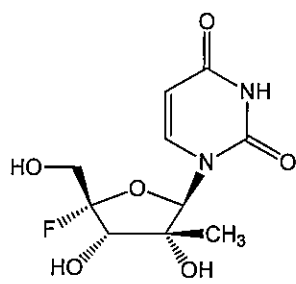


substituted

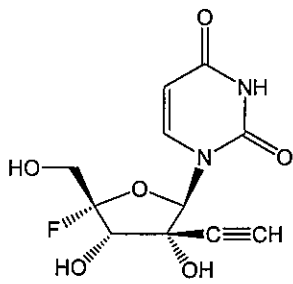
24. The compound of Claim 23, wherein B¹ is an optionally substituted



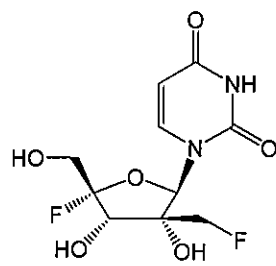
25. The compound of Claim 1 selected from the group consisting of:



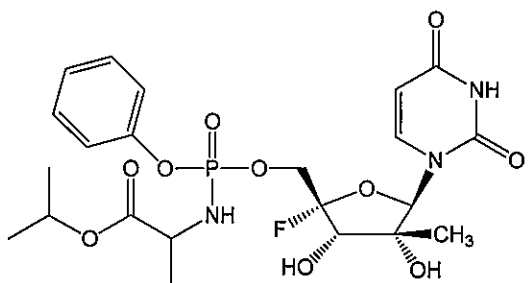
,



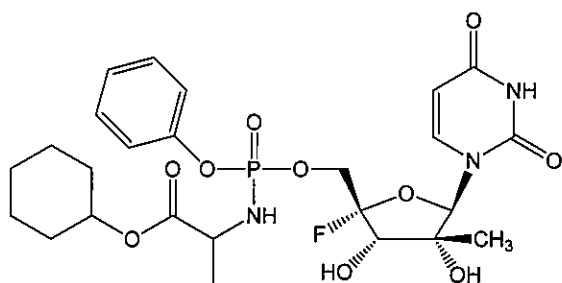
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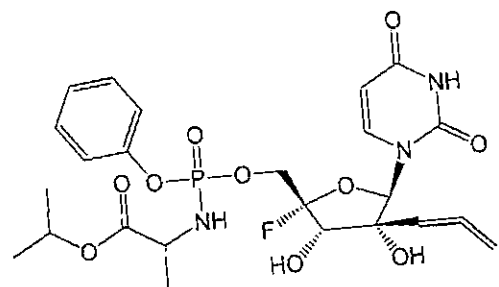
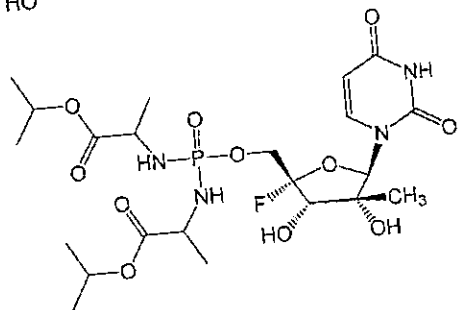
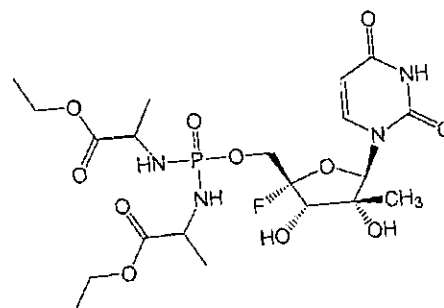
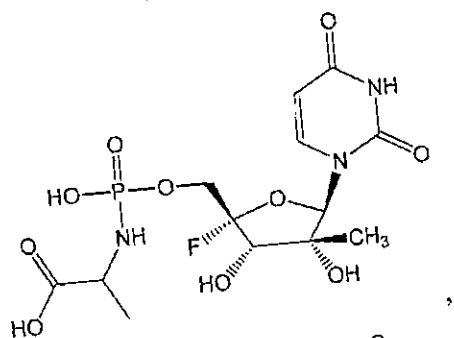
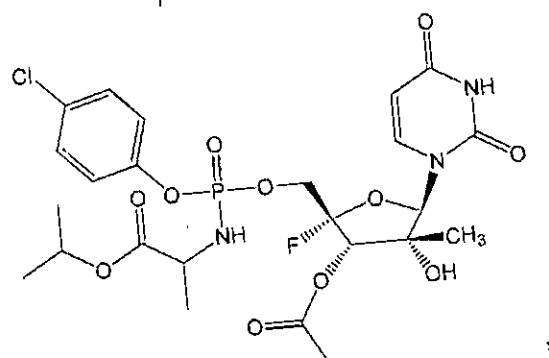
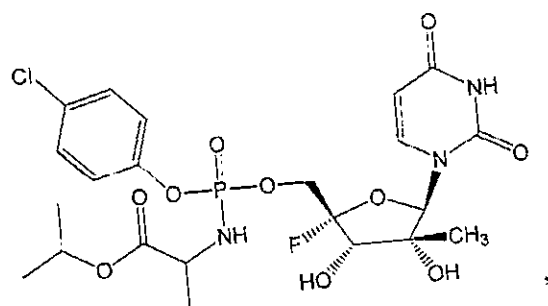
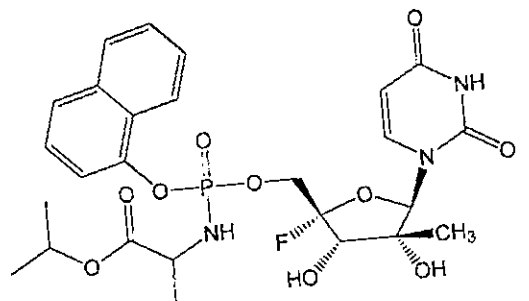
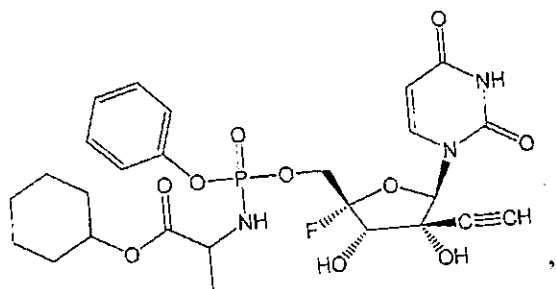
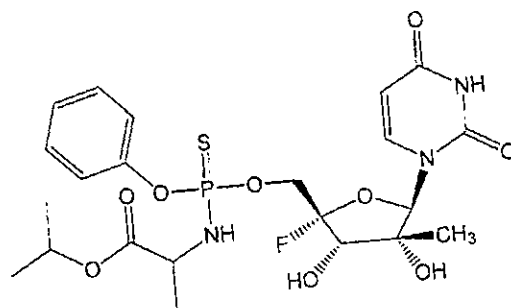
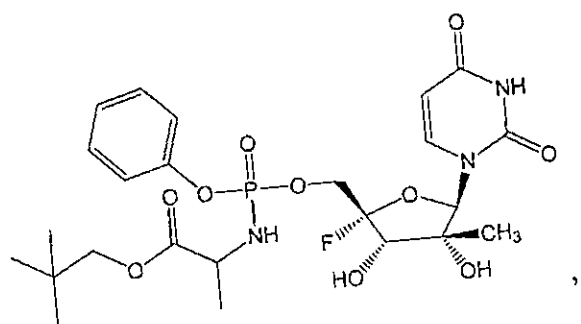
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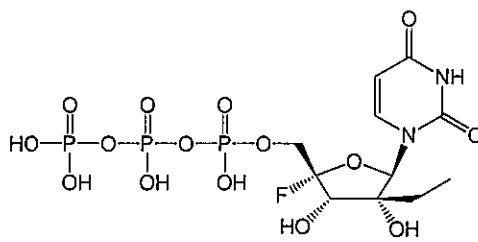
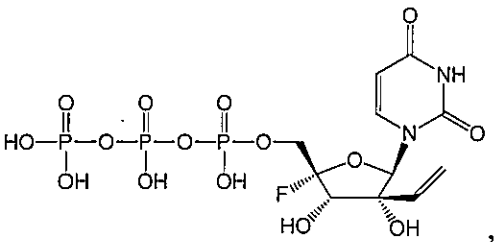
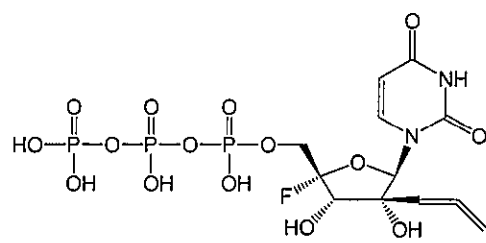
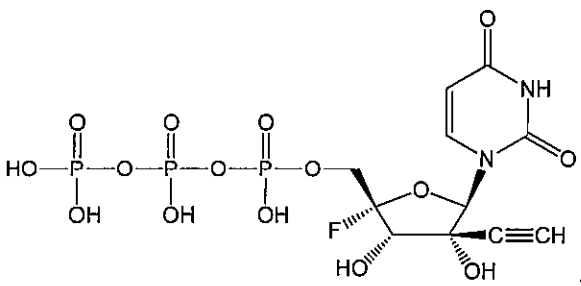
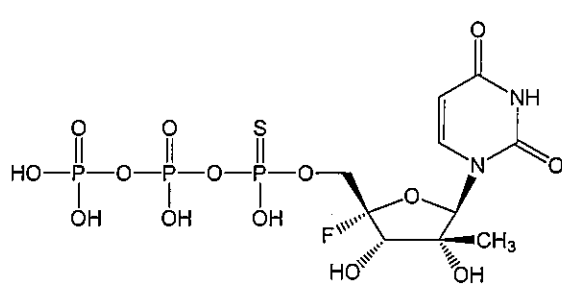
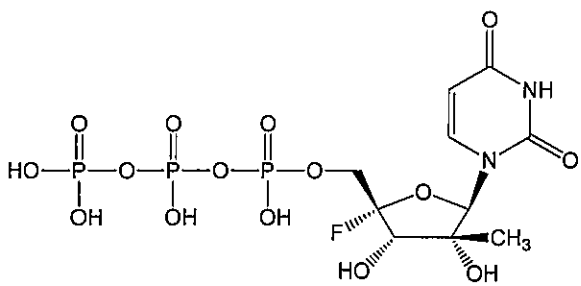
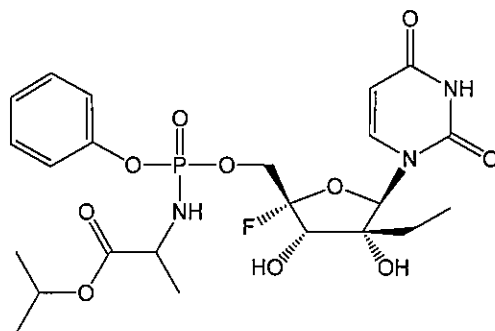
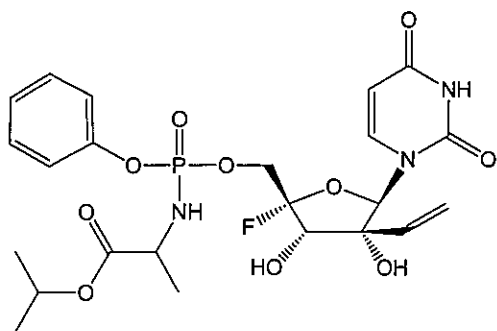


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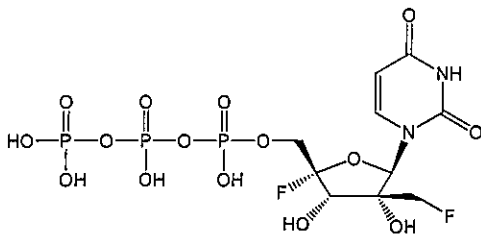


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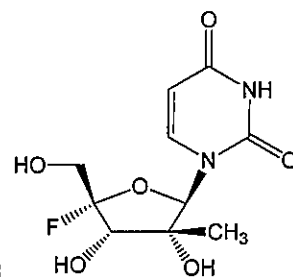
and



, or a pharmaceutically acceptable salt of the foregoing.

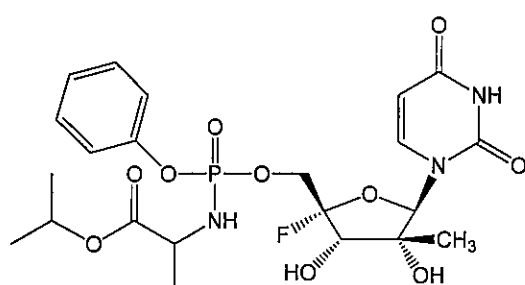
[illegible]

, or a pharmaceutically acceptable salt of the



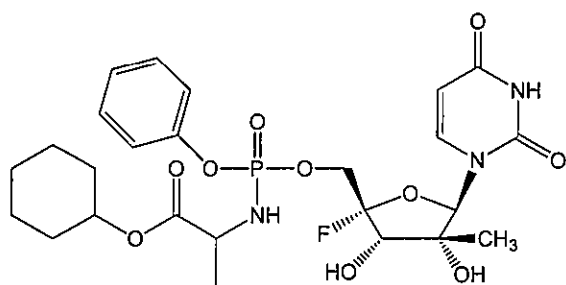
27. The compound of Claim 1, wherein the compound is pharmaceutically acceptable salt thereof.

28. The compound of Claim 1, wherein the compound is



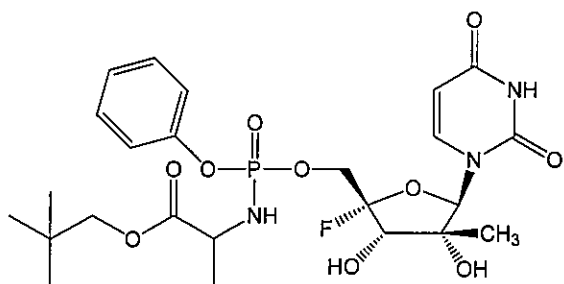
, or a pharmaceutically acceptable salt thereof.

29. The compound of Claim 1, wherein the compound is



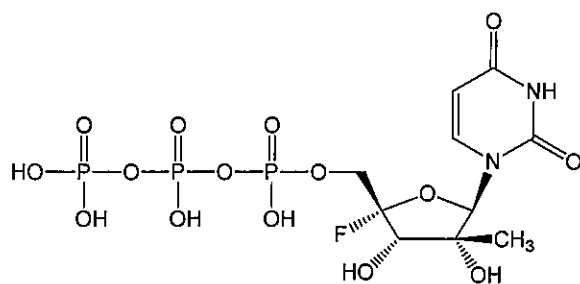
, or a pharmaceutically acceptable salt thereof.

30. The compound of Claim 1, wherein the compound is



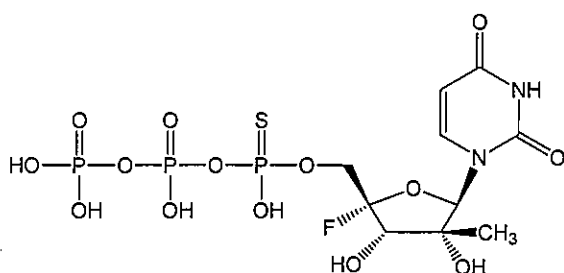
, or a pharmaceutically acceptable salt thereof.

31. The compound of Claim 1, wherein the compound is



, or a pharmaceutically acceptable salt thereof.

32. The compound of Claim 1, wherein the compound is



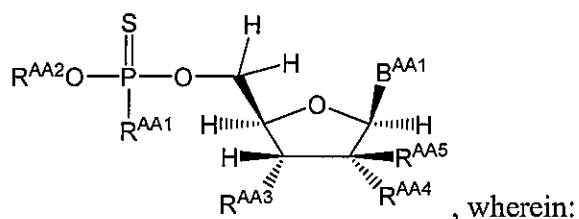
, or a pharmaceutically acceptable salt thereof.

33. A pharmaceutical composition comprising an effective amount of a compound of any one of Claims 1-32, or a pharmaceutically acceptable salt thereof, and a pharmaceutically acceptable carrier, diluent, excipient or combination thereof.

34. Use of a compound of any one of Claims 1-32, or a pharmaceutically acceptable salt thereof, or a pharmaceutical composition of Claim 33 in the manufacture of a medicament for ameliorating or treating a HCV infection.

35. Use of a compound of any one of Claims 1-32 in the preparation of a medicament for ameliorating or treating a HCV infection, wherein the medicament is manufactured for use in combination with one or more agents, or pharmaceutically acceptable salts thereof, selected from the group consisting of an interferon, ribavirin, a HCV protease inhibitor, a HCV polymerase inhibitor, a NS5A inhibitor, an antiviral compound, a compound of Formula (AA), a compound of Formula (BB) and a compound of Formula (CC), wherein:

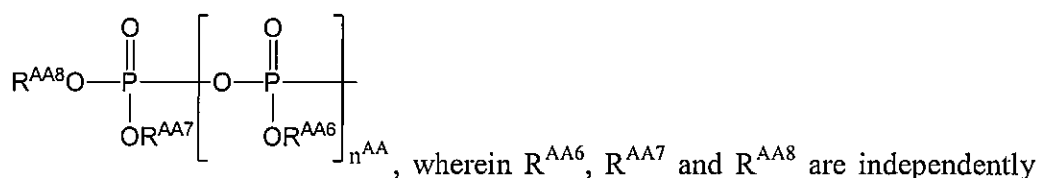
Formula (AA) has the structure:



B^{AA1} is an optionally substituted heterocyclic base or an optionally substituted heterocyclic base with a protected amino group;

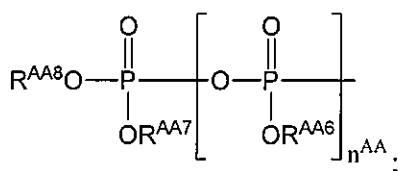
R^{AA1} is selected from O⁻, OH, an optionally substituted N-linked amino acid and an optionally substituted N-linked amino acid ester;

R^{AA2} is absent or selected from hydrogen, an optionally substituted aryl, an optionally substituted heteroaryl, an optionally substituted heterocyclyl and



absent or hydrogen, and n^{AA} is 0 or 1;

provided that when R^{AA1} is O⁻ or OH, then R^{AA2} is absent, hydrogen or



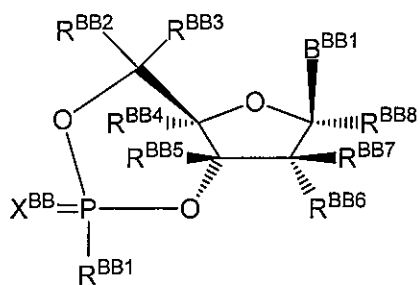
R^{AA3} is selected from hydrogen, halogen, -OR^{AA9} and -OC(=O)R^{AA10};

R^{AA4} is selected from halogen, -OR^{AA11} and -OC(=O)R^{AA12}; or R^{AA3} and R^{AA4} are both an oxygen atom which are linked together by a carbonyl group;

R^{AA5} is selected from an optionally substituted C₂₋₆ alkyl, an optionally substituted C₂₋₆ alkenyl, an optionally substituted C₂₋₆ alkynyl and an optionally substituted C₃₋₆ cycloalkyl; or R^{AA4} and R^{AA5} together form -(C₁₋₆ alkyl)-O- or -O-(C₁₋₆ alkyl)-;

R^{AA9} and R^{AA11} are independently hydrogen or an optionally substituted C₁₋₆ alkyl; and R^{AA10} and R^{AA12} are independently an optionally substituted C₁₋₆ alkyl or an optionally substituted C₃₋₆ cycloalkyl;

Formula (BB) has the structure:



, wherein:

B^{BB1} is an optionally substituted heterocyclic base or an optionally substituted heterocyclic base with a protected amino group;

X^{BB} is O (oxygen) or S (sulfur);

R^{BB1} is selected from $-Z^{BB}-R^{BB9}$, an optionally substituted N-linked amino acid and an optionally substituted N-linked amino acid ester;

Z^{BB} is selected from O (oxygen), S (sulfur) and $N(R^{BB10})$;

R^{BB2} and R^{BB3} are independently selected from hydrogen, an optionally substituted C_{1-6} alkyl, an optionally substituted C_{2-6} alkenyl, an optionally substituted C_{2-6} alkynyl, an optionally substituted C_{1-6} haloalkyl and an optionally substituted aryl(C_{1-6} alkyl); or R^{BB2} and R^{BB3} are taken together to form a group selected from an optionally substituted C_{3-6} cycloalkyl, an optionally substituted C_{3-6} cycloalkenyl, an optionally substituted C_{3-6} aryl and an optionally substituted C_{3-6} heteroaryl;

R^{BB4} is selected from hydrogen, halogen, azido, cyano, an optionally substituted C_{1-6} alkyl, an optionally substituted C_{2-6} alkenyl, an optionally substituted C_{2-6} alkynyl and an optionally substituted allenyl;

R^{BB5} is hydrogen or an optionally substituted C_{1-6} alkyl;

R^{BB6} is selected from hydrogen, halogen, azido, amino, cyano, an optionally substituted C_{1-6} alkyl, $-OR^{BB11}$ and $-OC(=O)R^{BB12}$;

R^{BB7} is selected from hydrogen, halogen, azido, cyano, an optionally substituted C_{1-6} alkyl, $-OR^{BB13}$ and $-OC(=O)R^{BB14}$;

R^{BB8} is selected from hydrogen, halogen, azido, cyano, an optionally substituted C_{1-6} alkyl, $-OR^{BB15}$ and $-OC(=O)R^{BB16}$;

R^{BB9} is selected from an optionally substituted alkyl, an optionally substituted alkenyl, an optionally substituted alkynyl, an optionally substituted cycloalkyl, an

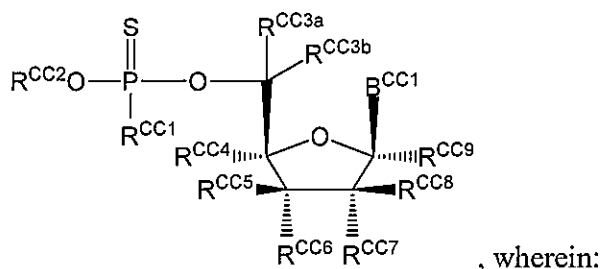
optionally substituted cycloalkenyl, an optionally substituted aryl, an optionally substituted heteroaryl, an optionally substituted heterocyclyl, an optionally substituted aryl(C₁₋₆alkyl), an optionally substituted heteroaryl(C₁₋₆alkyl) and an optionally substituted heterocyclyl(C₁₋₆alkyl);

R^{BB10} is selected from hydrogen, an optionally substituted alkyl, an optionally substituted alkenyl, an optionally substituted alkynyl, an optionally substituted cycloalkyl, an optionally substituted cycloalkenyl, an optionally substituted aryl, an optionally substituted heteroaryl, an optionally substituted heterocyclyl, an optionally substituted aryl(C₁₋₆alkyl), an optionally substituted heteroaryl(C₁₋₆alkyl) and an optionally substituted heterocyclyl(C₁₋₆alkyl);

R^{BB11}, R^{BB13} and R^{BB15} are independently hydrogen or an optionally substituted C₁₋₆ alkyl; and

R^{BB12}, R^{BB14} and R^{BB16} are independently an optionally substituted C₁₋₆ alkyl or an optionally substituted C₃₋₆ cycloalkyl; and

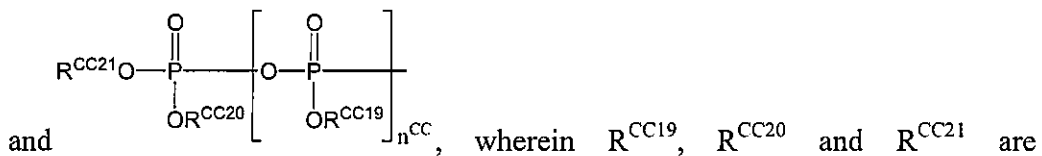
Formula (CC) has the structure:



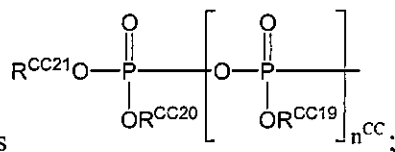
B^{CC1} is an optionally substituted heterocyclic base or an optionally substituted heterocyclic base with a protected amino group;

R^{CC1} is selected from O⁻, OH, an optionally substituted N-linked amino acid and an optionally substituted N-linked amino acid ester;

R^{CC2} is selected from an optionally substituted aryl, an optionally substituted heteroaryl, an optionally substituted heterocyclyl



independently absent or hydrogen, and n^{CC} is 0 or 1; provided that when R^{CC1} is



O^- or OH , then R^{CC2} is

R^{CC3a} and R^{CC3b} are independently selected from hydrogen, deuterium, an optionally substituted C_{1-6} alkyl, an optionally substituted C_{2-6} alkenyl, an optionally substituted C_{2-6} alkynyl, an optionally substituted C_{1-6} haloalkyl and aryl(C_{1-6} alkyl); or R^{CC3a} and R^{CC3b} are taken together to form an optionally substituted C_{3-6} cycloalkyl;

R^{CC4} is selected from hydrogen, azido, an optionally substituted C_{1-6} alkyl, an optionally substituted C_{2-6} alkenyl and an optionally substituted C_{2-6} alkynyl;

R^{CC5} is selected from hydrogen, halogen, azido, cyano, an optionally substituted C_{1-6} alkyl, $-OR^{CC10}$ and $-OC(=O)R^{CC11}$;

R^{CC6} is selected from hydrogen, halogen, azido, cyano, an optionally substituted C_{1-6} alkyl, $-OR^{CC12}$ and $-OC(=O)R^{CC13}$;

R^{CC7} is selected from hydrogen, halogen, azido, cyano, an optionally substituted C_{1-6} alkyl, $-OR^{CC14}$ and $-OC(=O)R^{CC15}$; or R^{CC6} and R^{CC7} are both oxygen atoms and linked together by a carbonyl group;

R^{CC8} is selected from hydrogen, halogen, azido, cyano, an optionally substituted C_{1-6} alkyl, $-OR^{CC16}$ and $-OC(=O)R^{CC17}$;

R^{CC9} is selected from hydrogen, azido, cyano, an optionally substituted C_{1-6} alkyl and $-OR^{CC18}$;

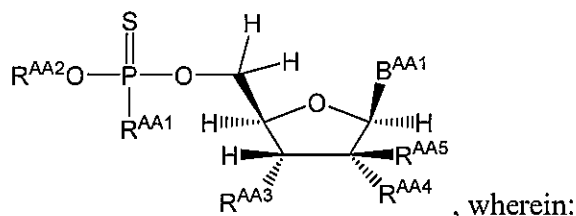
R^{CC10} , R^{CC12} , R^{CC14} , R^{CC16} and R^{CC18} are independently selected from hydrogen and an optionally substituted C_{1-6} alkyl; and

R^{CC11} , R^{CC13} , R^{CC15} and R^{CC17} are independently selected from an optionally substituted C_{1-6} alkyl and an optionally substituted C_{3-6} cycloalkyl.

36. Use of a compound of any one of Claims 1-32 in the preparation of a medicament for contacting a cell infected with a hepatitis C virus, wherein the medicament is manufactured for use in combination with one or more agents, or pharmaceutically acceptable salts thereof, selected from the group consisting of an interferon, ribavirin, a HCV protease inhibitor, a HCV

polymerase inhibitor, a NS5A inhibitor, an antiviral compound, a compound of Formula (AA), a compound of Formula (BB) and a compound of Formula (CC), wherein

Formula (AA) has the structure:



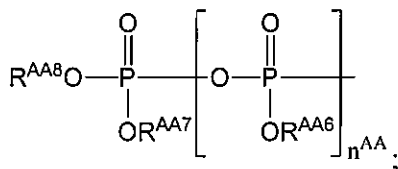
B^{AA1} is an optionally substituted heterocyclic base or an optionally substituted heterocyclic base with a protected amino group;

R^{AA1} is selected from O^- , OH, an optionally substituted N-linked amino acid and an optionally substituted N-linked amino acid ester;

R^{AA2} is absent or selected from hydrogen, an optionally substituted aryl, an optionally substituted heteroaryl, an optionally substituted heterocyclyl and

$R^{AA8}O-P(=O)(OR^{AA7})-O-P(=O)(OR^{AA6})_n$, wherein R^{AA6} , R^{AA7} and R^{AA8} are independently absent or hydrogen, and n^{AA} is 0 or 1;

provided that when R^{AA1} is O^- or OH, then R^{AA2} is absent, hydrogen or



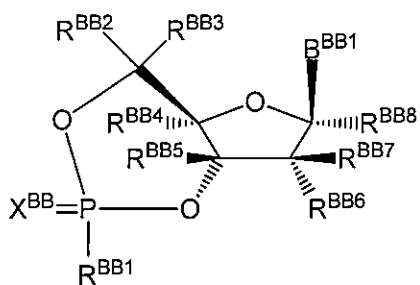
R^{AA3} is selected from hydrogen, halogen, $-OR^{AA9}$ and $-OC(=O)R^{AA10}$;

R^{AA4} is selected from halogen, $-OR^{AA11}$ and $-OC(=O)R^{AA12}$; or R^{AA3} and R^{AA4} are both an oxygen atom which are linked together by a carbonyl group;

R^{AA5} is selected from an optionally substituted C_{2-6} alkyl, an optionally substituted C_{2-6} alkenyl, an optionally substituted C_{2-6} alkynyl and an optionally substituted C_{3-6} cycloalkyl; or R^{AA4} and R^{AA5} together form $-(C_{1-6} \text{ alkyl})-O-$ or $-O-(C_{1-6} \text{ alkyl})-$;

R^{AA9} and R^{AA11} are independently hydrogen or an optionally substituted C_{1-6} alkyl; and R^{AA10} and R^{AA12} are independently an optionally substituted C_{1-6} alkyl or an optionally substituted C_{3-6} cycloalkyl;

Formula (BB) has the structure:



, wherein:

B^{BB1} is an optionally substituted heterocyclic base or an optionally substituted heterocyclic base with a protected amino group;

X^{BB} is O (oxygen) or S (sulfur);

R^{BB1} is selected from $-Z^{BB}-R^{BB9}$, an optionally substituted N-linked amino acid and an optionally substituted N-linked amino acid ester;

Z^{BB} is selected from O (oxygen), S (sulfur) and $N(R^{BB10})$;

R^{BB2} and R^{BB3} are independently selected from hydrogen, an optionally substituted C_{1-6} alkyl, an optionally substituted C_{2-6} alkenyl, an optionally substituted C_{2-6} alkynyl, an optionally substituted C_{1-6} haloalkyl and an optionally substituted aryl(C_{1-6} alkyl); or R^{BB2} and R^{BB3} are taken together to form a group selected from an optionally substituted C_{3-6} cycloalkyl, an optionally substituted C_{3-6} cycloalkenyl, an optionally substituted C_{3-6} aryl and an optionally substituted C_{3-6} heteroaryl;

R^{BB4} is selected from hydrogen, halogen, azido, cyano, an optionally substituted C_{1-6} alkyl, an optionally substituted C_{2-6} alkenyl, an optionally substituted C_{2-6} alkynyl and an optionally substituted allenyl;

R^{BB5} is hydrogen or an optionally substituted C_{1-6} alkyl;

R^{BB6} is selected from hydrogen, halogen, azido, amino, cyano, an optionally substituted C_{1-6} alkyl, $-OR^{BB11}$ and $-OC(=O)R^{BB12}$;

R^{BB7} is selected from hydrogen, halogen, azido, cyano, an optionally substituted C_{1-6} alkyl, $-OR^{BB13}$ and $-OC(=O)R^{BB14}$;

R^{BB8} is selected from hydrogen, halogen, azido, cyano, an optionally substituted C_{1-6} alkyl, $-OR^{BB15}$ and $-OC(=O)R^{BB16}$;

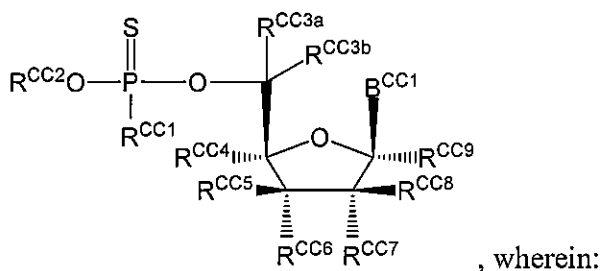
R^{BB9} is selected from an optionally substituted alkyl, an optionally substituted alkenyl, an optionally substituted alkynyl, an optionally substituted cycloalkyl, an optionally substituted cycloalkenyl, an optionally substituted aryl, an optionally substituted heteroaryl, an optionally substituted heterocyclyl, an optionally substituted aryl(C_{1-6} alkyl), an optionally substituted heteroaryl(C_{1-6} alkyl) and an optionally substituted heterocyclyl(C_{1-6} alkyl);

R^{BB10} is selected from hydrogen, an optionally substituted alkyl, an optionally substituted alkenyl, an optionally substituted alkynyl, an optionally substituted cycloalkyl, an optionally substituted cycloalkenyl, an optionally substituted aryl, an optionally substituted heteroaryl, an optionally substituted heterocyclyl, an optionally substituted aryl(C_{1-6} alkyl), an optionally substituted heteroaryl(C_{1-6} alkyl) and an optionally substituted heterocyclyl(C_{1-6} alkyl);

R^{BB11} , R^{BB13} and R^{BB15} are independently hydrogen or an optionally substituted C_{1-6} alkyl; and

R^{BB12} , R^{BB14} and R^{BB16} are independently an optionally substituted C_{1-6} alkyl or an optionally substituted C_{3-6} cycloalkyl; and

Formula (CC) has the structure:



B^{CC1} is an optionally substituted heterocyclic base or an optionally substituted heterocyclic base with a protected amino group;

R^{CC1} is selected from O^- , OH , an optionally substituted N-linked amino acid and an optionally substituted N-linked amino acid ester;

R^{CC2} is selected from an optionally substituted aryl, an optionally substituted heteroaryl, an optionally substituted heterocyclyl

and
$$\text{R}^{\text{CC}21}\text{O}-\text{P}\left(\text{O}\right)\left(\text{OR}^{\text{CC}20}\right)\left[\text{O}-\text{P}\left(\text{O}\right)\left(\text{OR}^{\text{CC}19}\right)\right]_{n^{\text{CC}}}$$
, wherein $\text{R}^{\text{CC}19}$, $\text{R}^{\text{CC}20}$ and $\text{R}^{\text{CC}21}$ are independently absent or hydrogen, and n^{CC} is 0 or 1; provided that when $\text{R}^{\text{CC}1}$ is

O^- or OH , then $\text{R}^{\text{CC}2}$ is
$$\text{R}^{\text{CC}21}\text{O}-\text{P}\left(\text{O}\right)\left(\text{OR}^{\text{CC}20}\right)\left[\text{O}-\text{P}\left(\text{O}\right)\left(\text{OR}^{\text{CC}19}\right)\right]_{n^{\text{CC}}}$$
, $\text{R}^{\text{CC}3a}$ and $\text{R}^{\text{CC}3b}$ are independently selected from hydrogen, deuterium, an optionally substituted C_{1-6} alkyl, an optionally substituted C_{2-6} alkenyl, an optionally substituted C_{2-6} alkynyl, an optionally substituted C_{1-6} haloalkyl and aryl(C_{1-6} alkyl); or $\text{R}^{\text{CC}3a}$ and $\text{R}^{\text{CC}3b}$ are taken together to form an optionally substituted C_{3-6} cycloalkyl;

$\text{R}^{\text{CC}4}$ is selected from hydrogen, azido, an optionally substituted C_{1-6} alkyl, an optionally substituted C_{2-6} alkenyl and an optionally substituted C_{2-6} alkynyl;

$\text{R}^{\text{CC}5}$ is selected from hydrogen, halogen, azido, cyano, an optionally substituted C_{1-6} alkyl, $-\text{OR}^{\text{CC}10}$ and $-\text{OC}(=\text{O})\text{R}^{\text{CC}11}$;

$\text{R}^{\text{CC}6}$ is selected from hydrogen, halogen, azido, cyano, an optionally substituted C_{1-6} alkyl, $-\text{OR}^{\text{CC}12}$ and $-\text{OC}(=\text{O})\text{R}^{\text{CC}13}$;

$\text{R}^{\text{CC}7}$ is selected from hydrogen, halogen, azido, cyano, an optionally substituted C_{1-6} alkyl, $-\text{OR}^{\text{CC}14}$ and $-\text{OC}(=\text{O})\text{R}^{\text{CC}15}$; or $\text{R}^{\text{CC}6}$ and $\text{R}^{\text{CC}7}$ are both oxygen atoms and linked together by a carbonyl group;

$\text{R}^{\text{CC}8}$ is selected from hydrogen, halogen, azido, cyano, an optionally substituted C_{1-6} alkyl, $-\text{OR}^{\text{CC}16}$ and $-\text{OC}(=\text{O})\text{R}^{\text{CC}17}$;

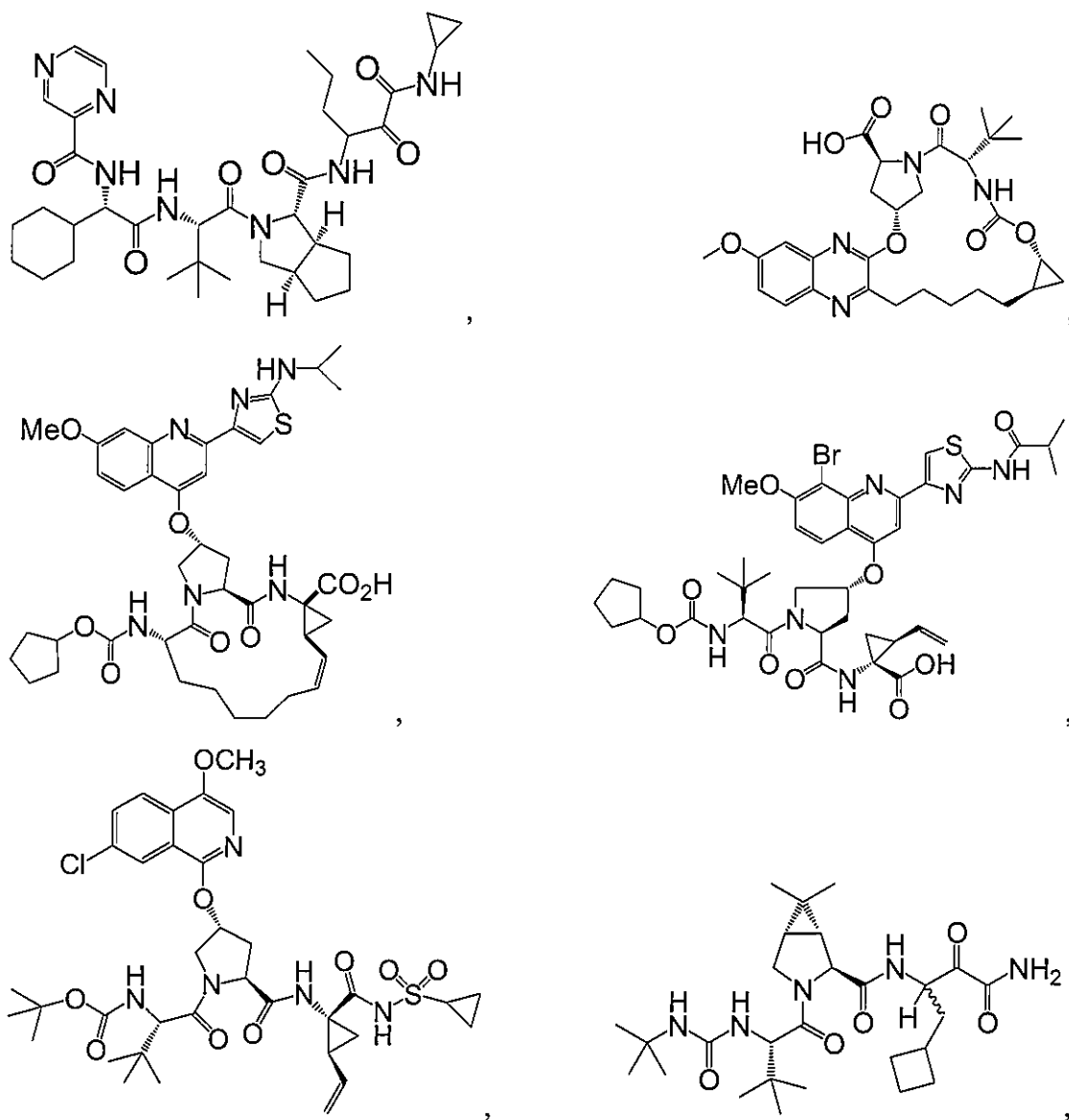
$\text{R}^{\text{CC}9}$ is selected from hydrogen, azido, cyano, an optionally substituted C_{1-6} alkyl and $-\text{OR}^{\text{CC}18}$;

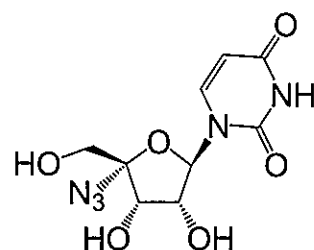
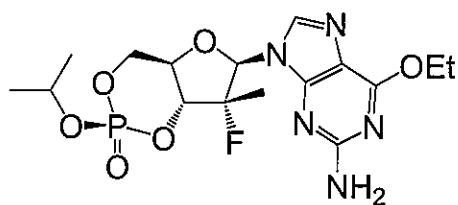
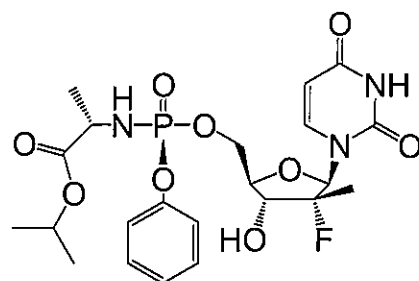
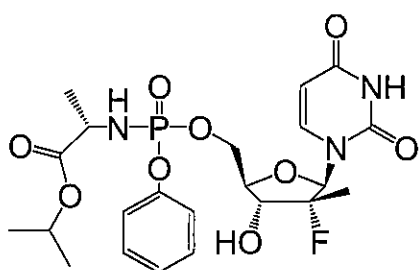
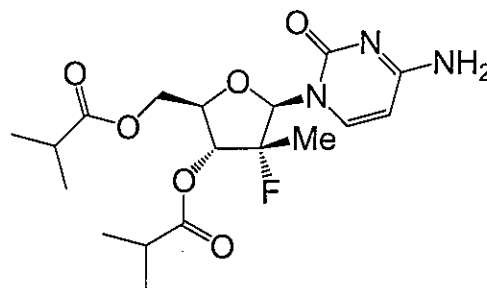
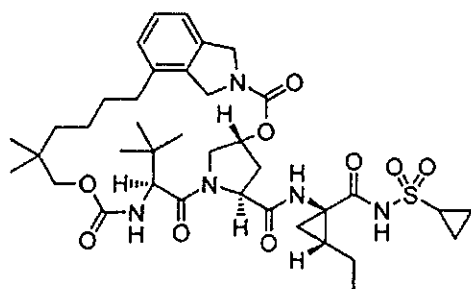
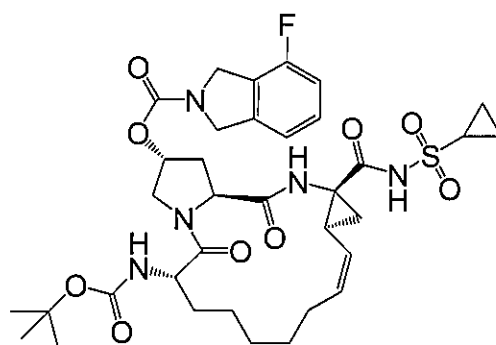
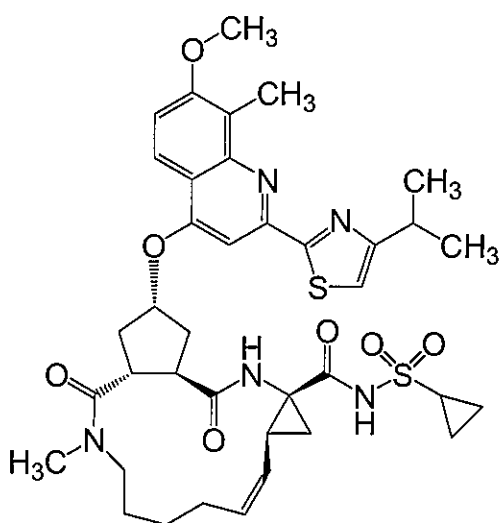
$\text{R}^{\text{CC}10}$, $\text{R}^{\text{CC}12}$, $\text{R}^{\text{CC}14}$, $\text{R}^{\text{CC}16}$ and $\text{R}^{\text{CC}18}$ are independently selected from hydrogen and an optionally substituted C_{1-6} alkyl; and

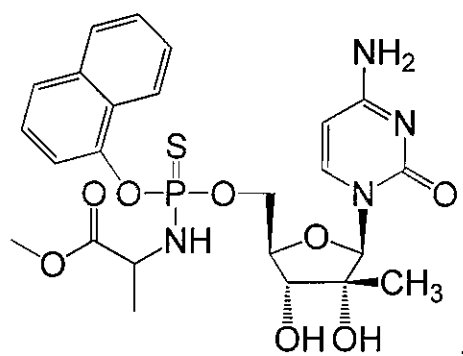
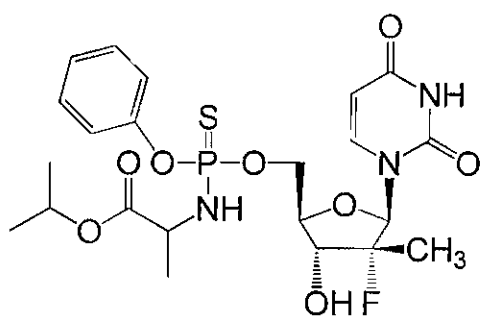
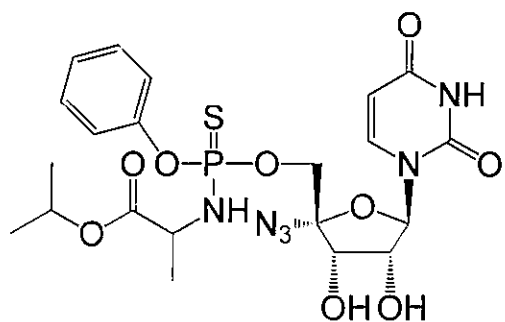
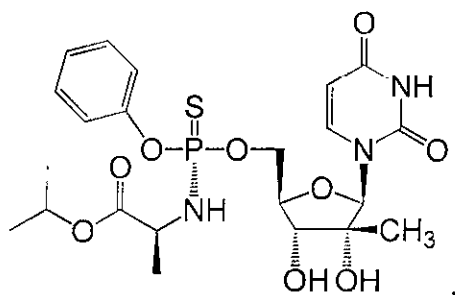
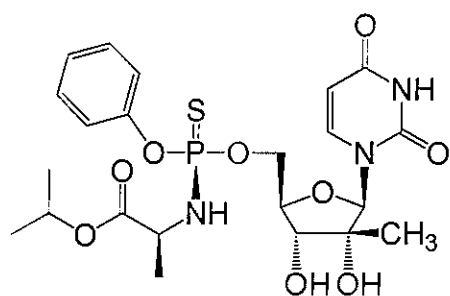
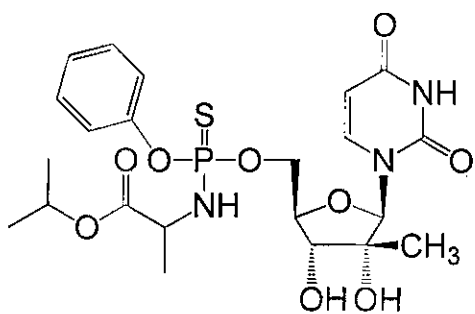
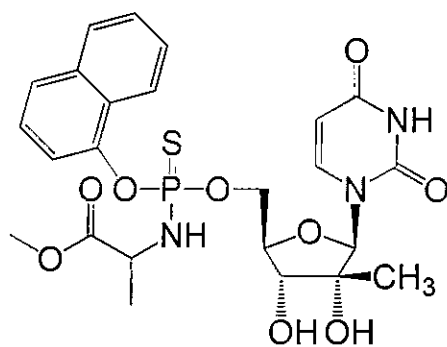
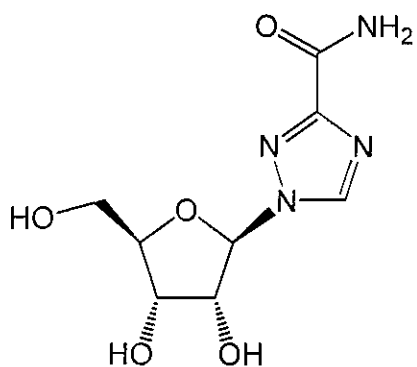
$\text{R}^{\text{CC}11}$, $\text{R}^{\text{CC}13}$, $\text{R}^{\text{CC}15}$ and $\text{R}^{\text{CC}17}$ are independently selected from an optionally substituted C_{1-6} alkyl and an optionally substituted C_{3-6} cycloalkyl.

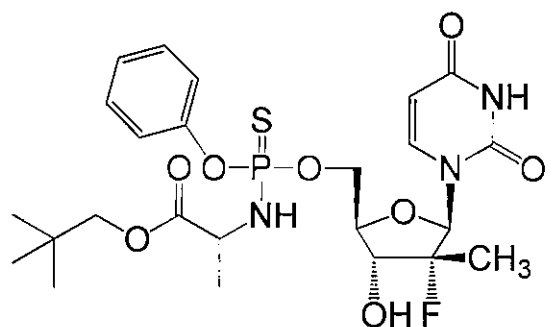
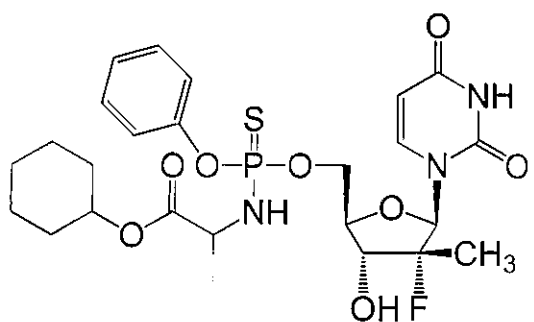
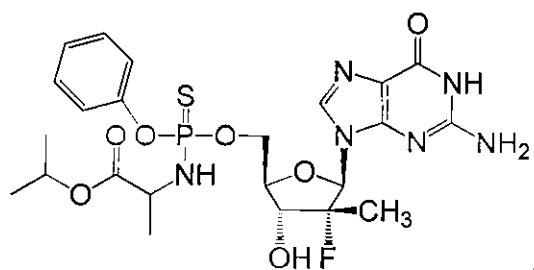
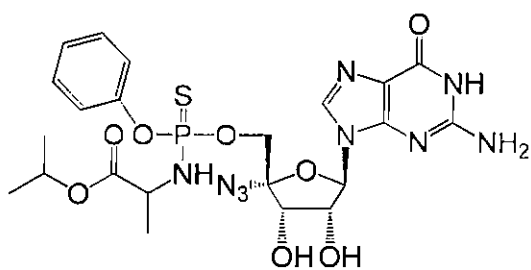
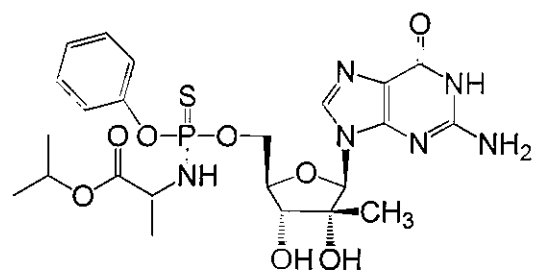
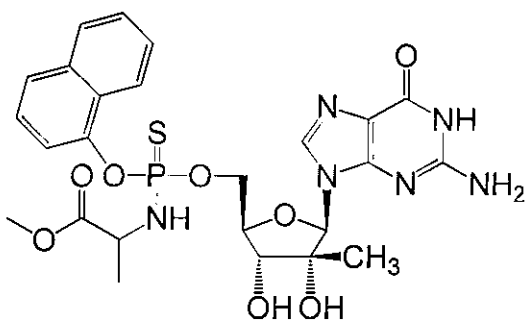
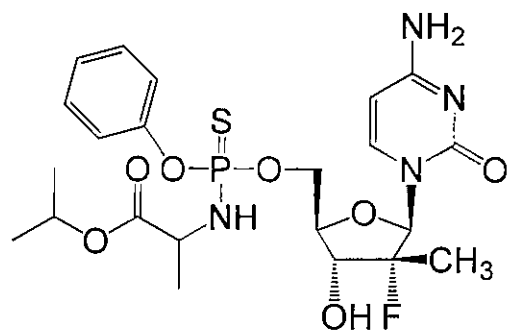
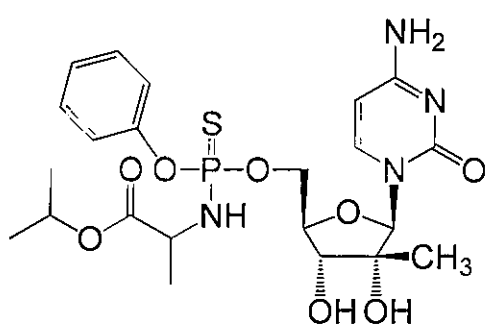
37. The use of any one of Claims 35-36, wherein the one or more agents, or pharmaceutically acceptable salts thereof, are selected from the group consisting of

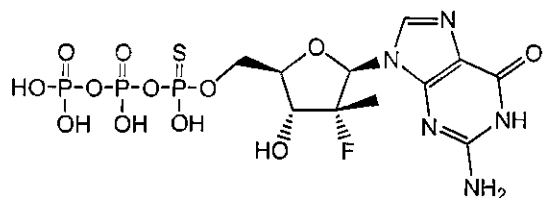
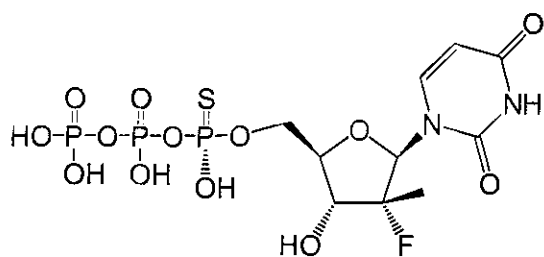
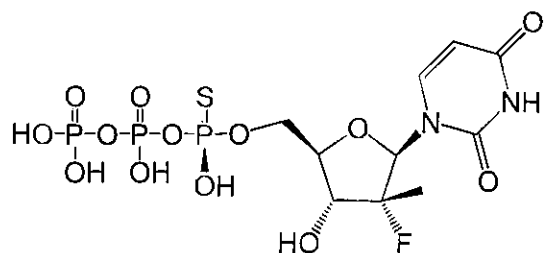
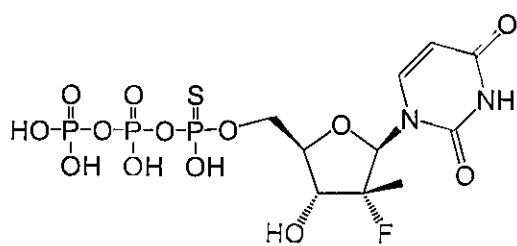
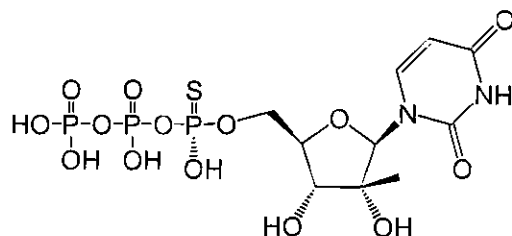
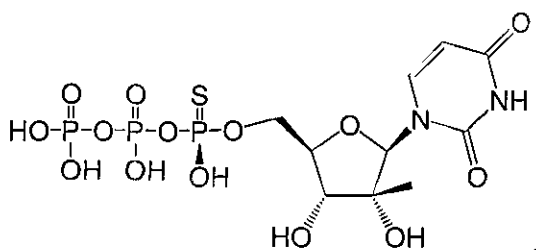
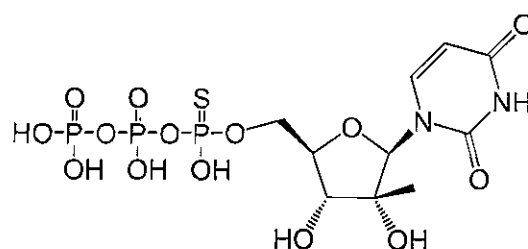
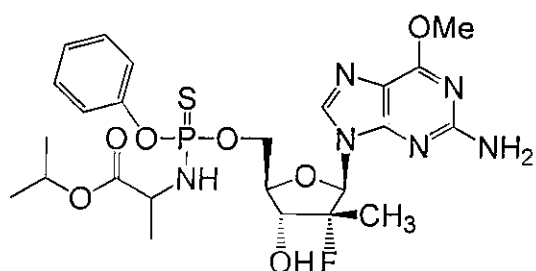
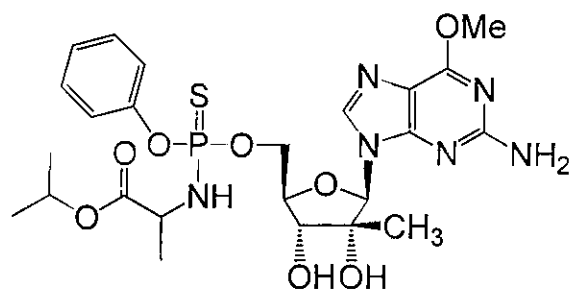
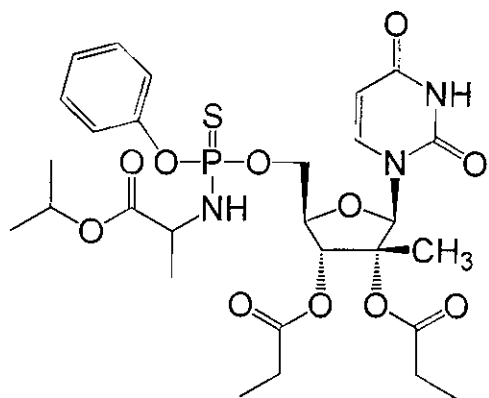
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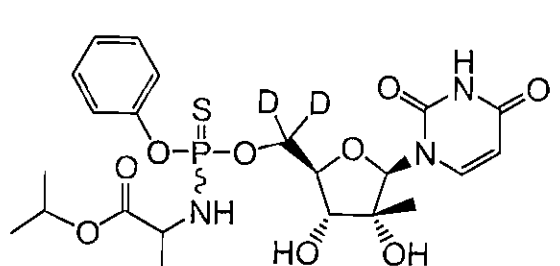
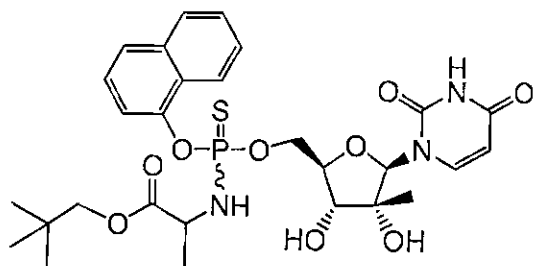
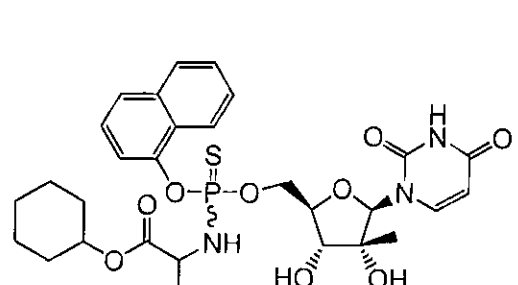
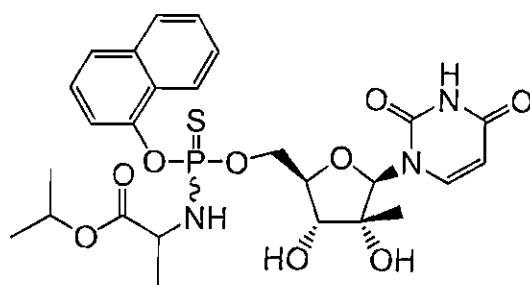
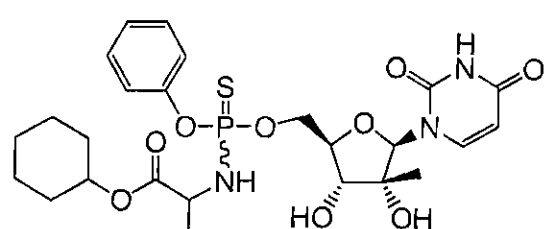
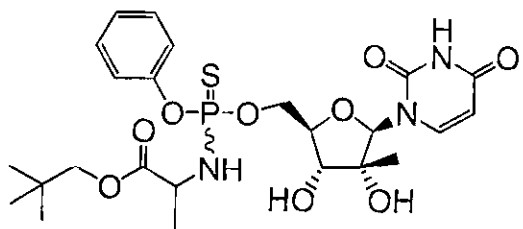
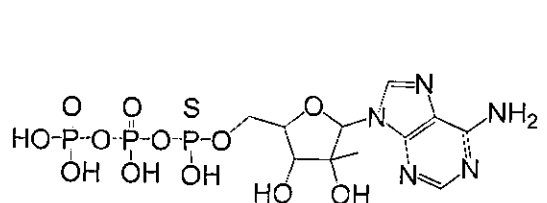
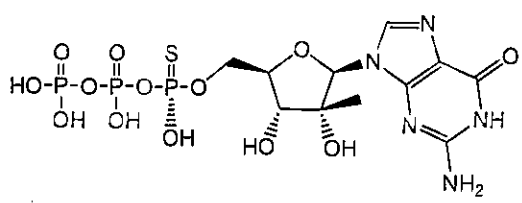
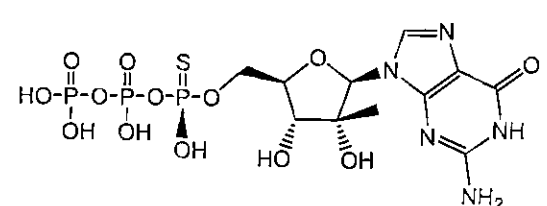
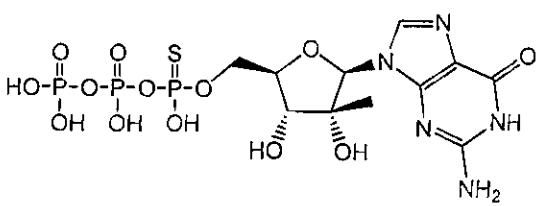
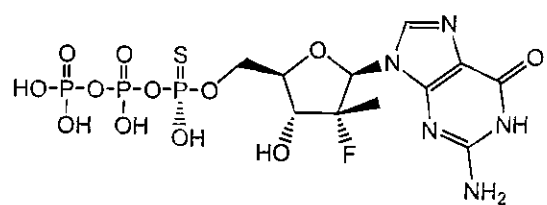
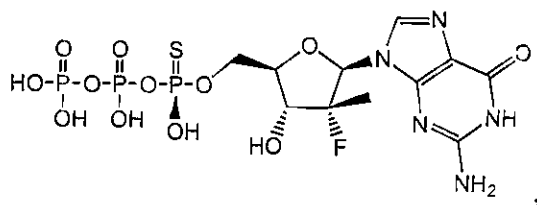


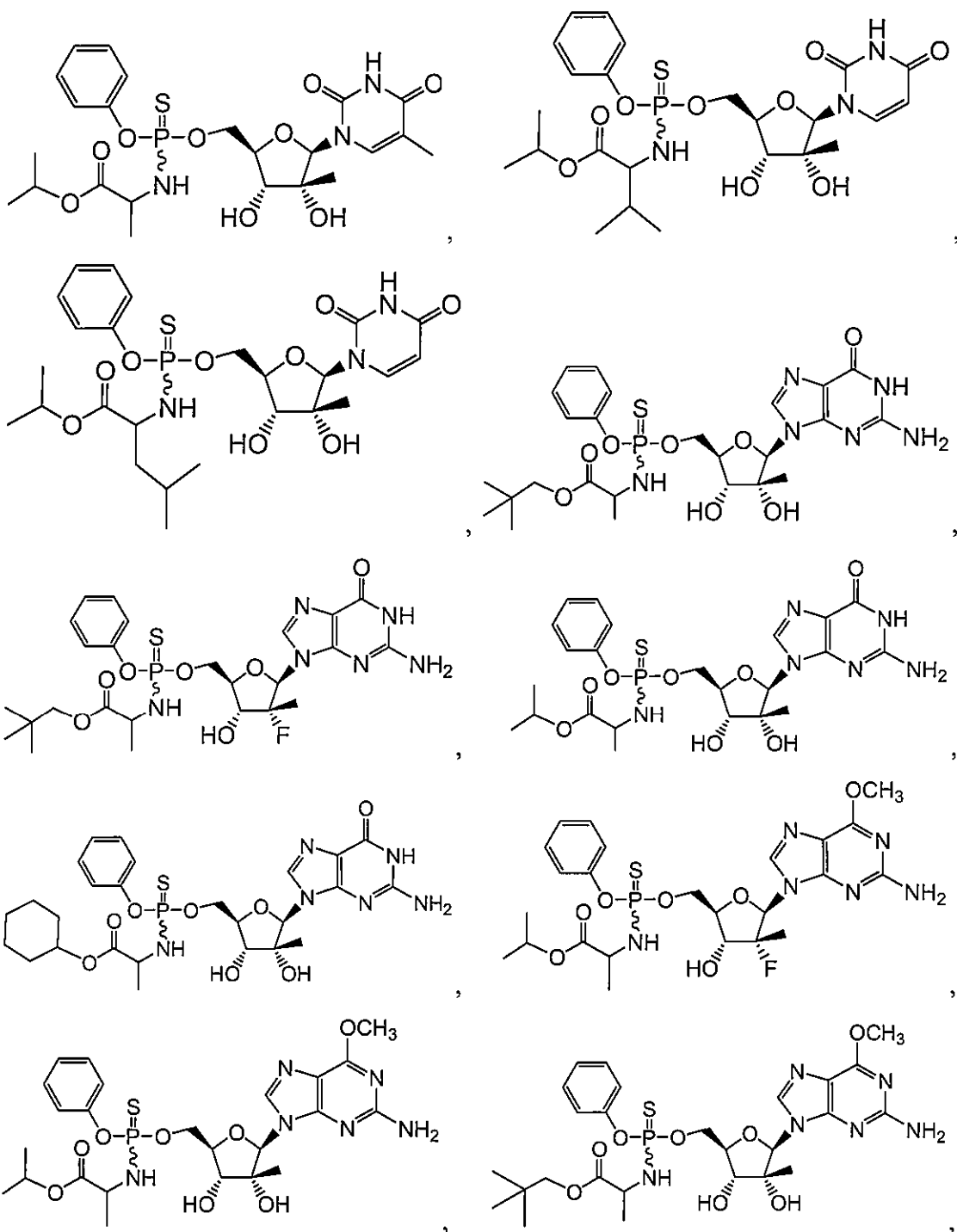


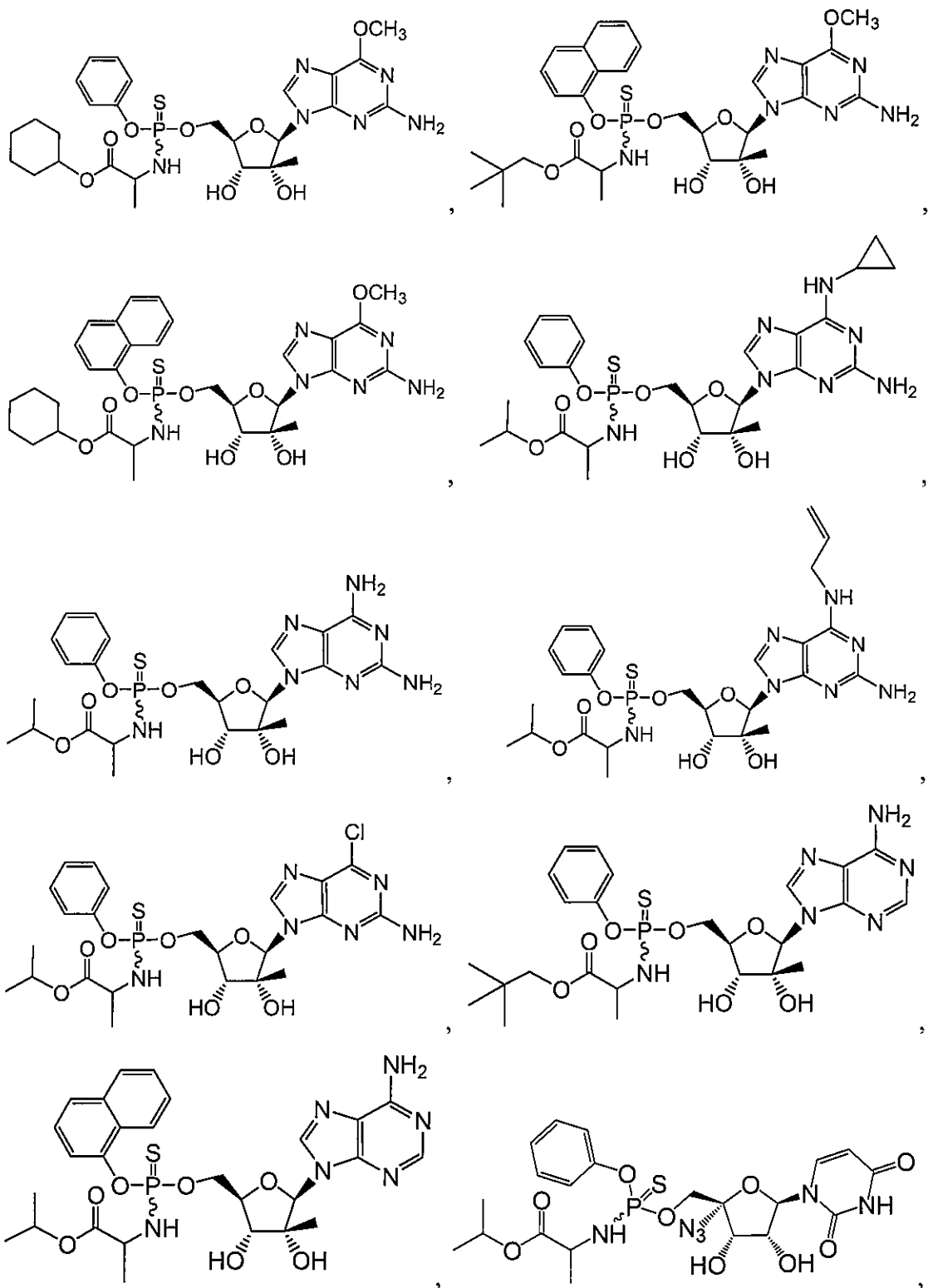


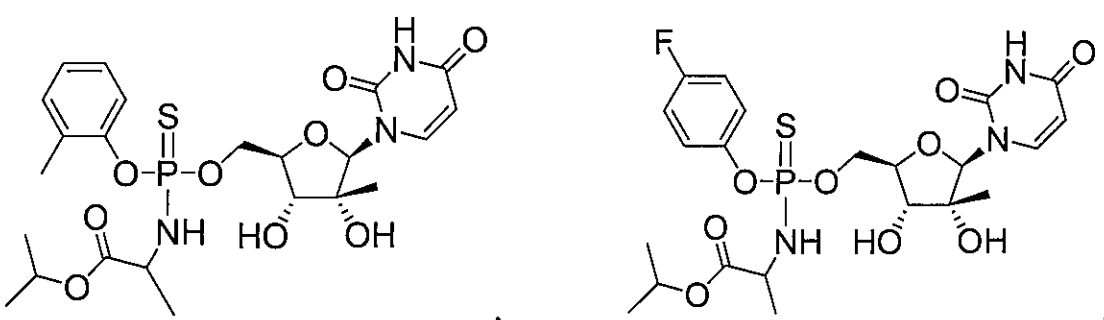
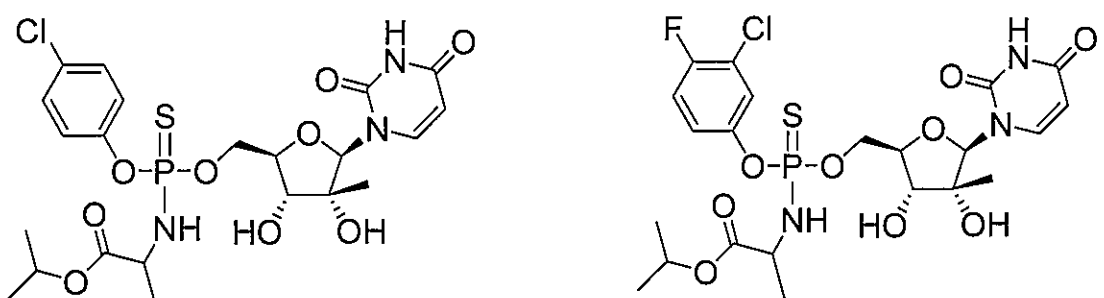
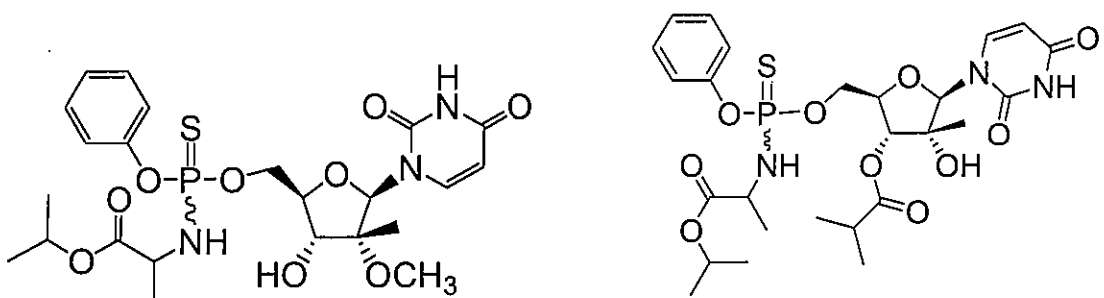
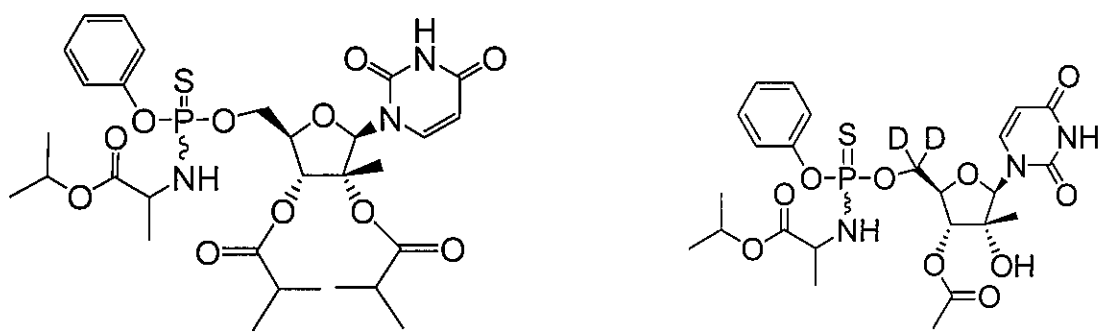
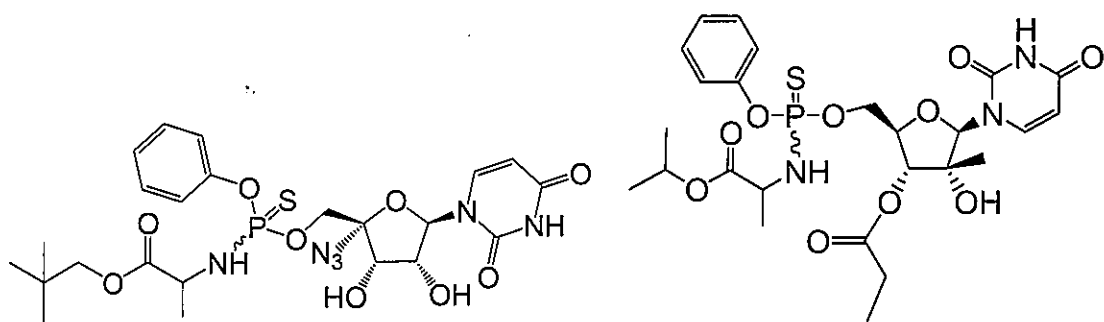


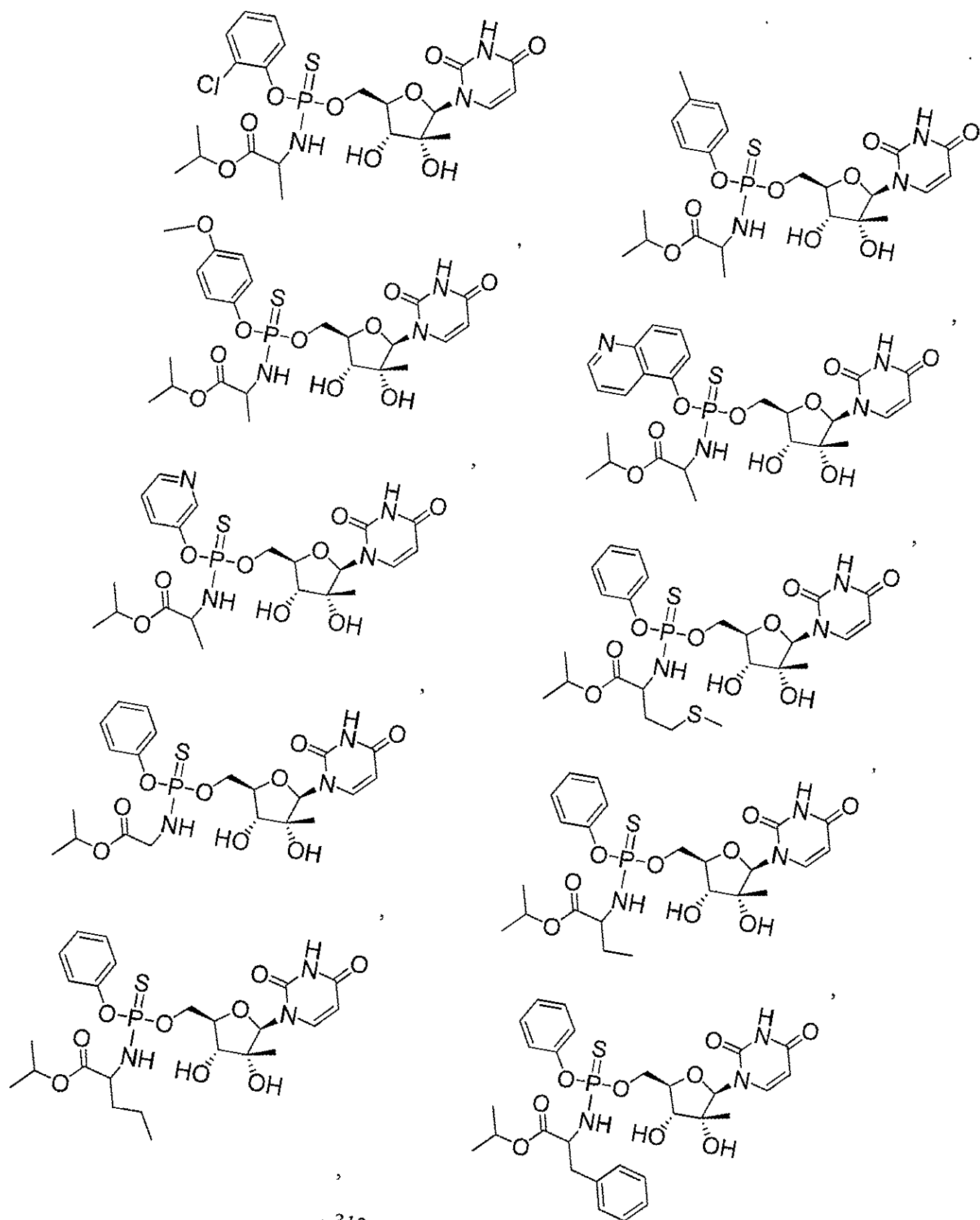


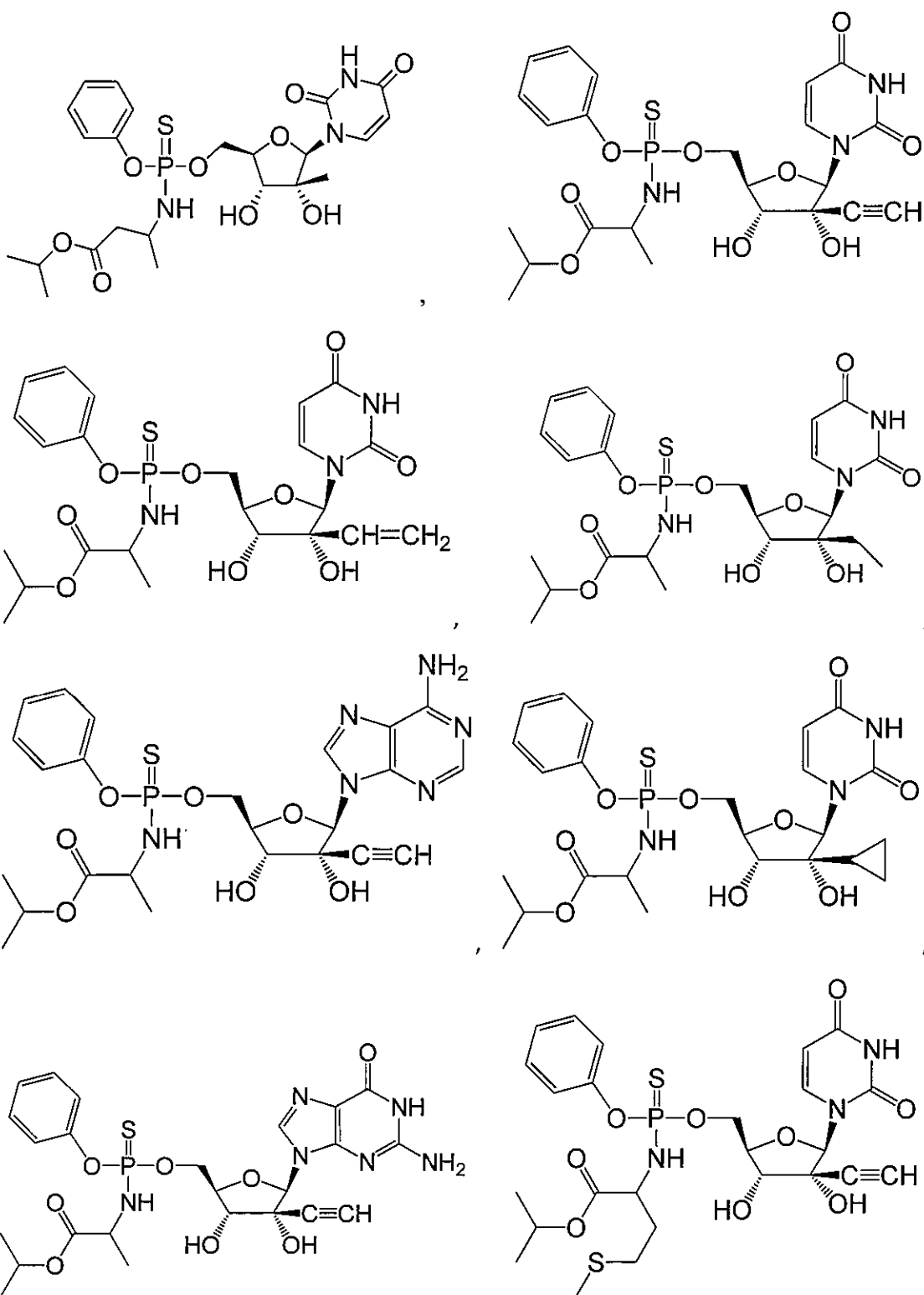


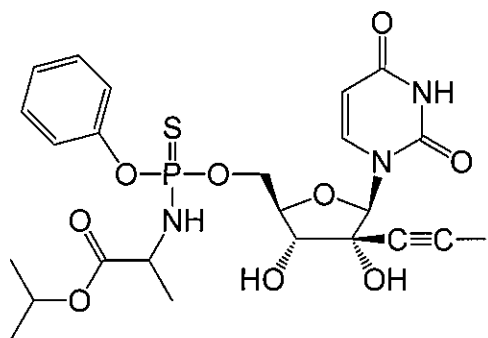
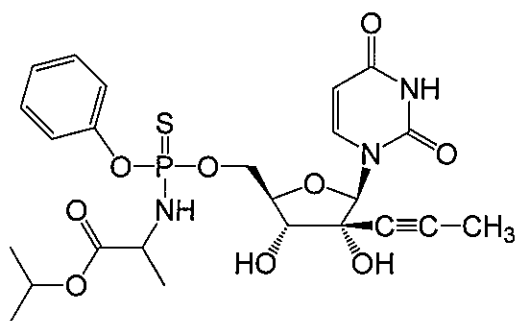
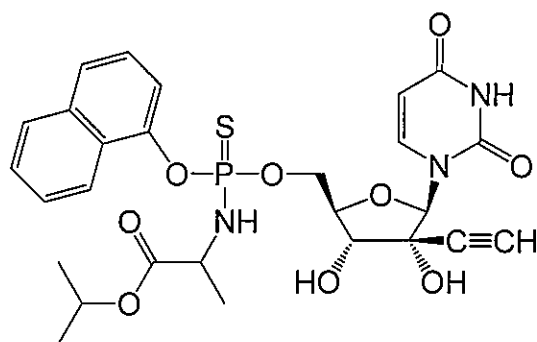
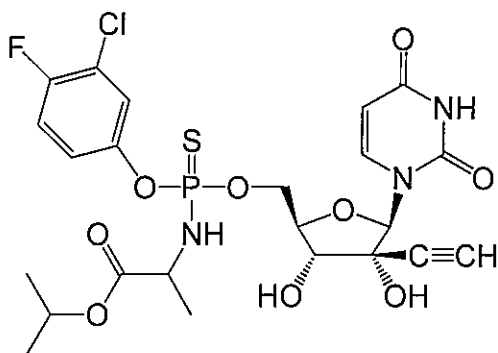
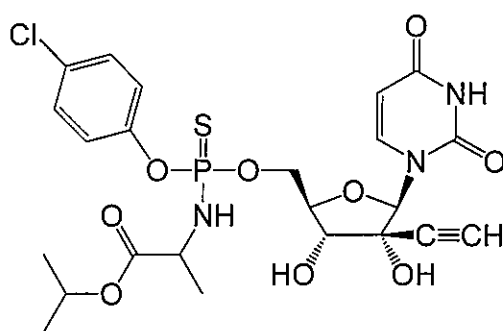
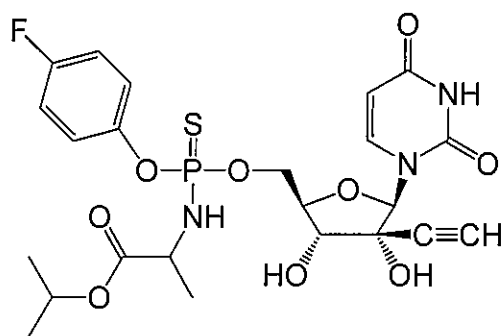
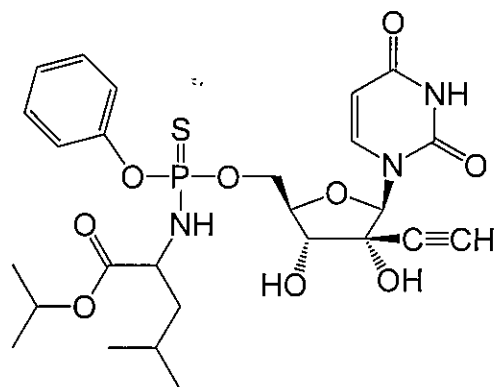
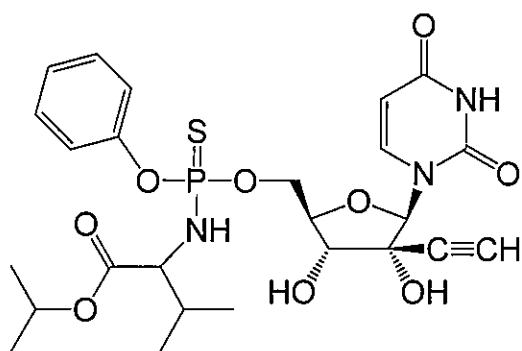


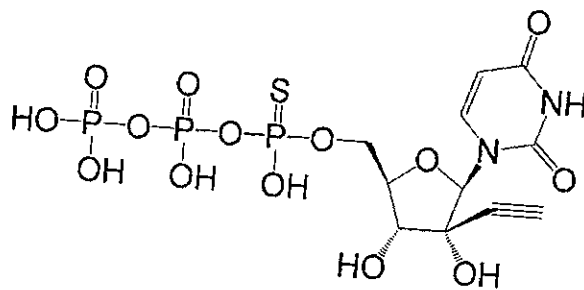
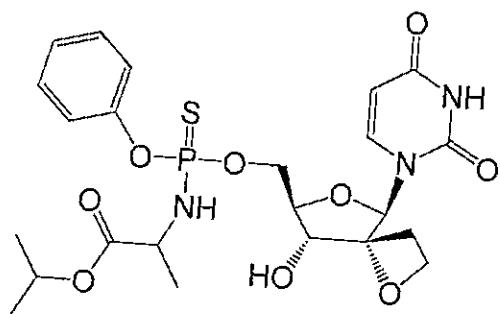
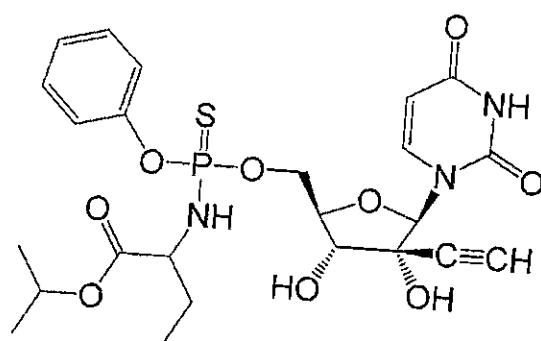
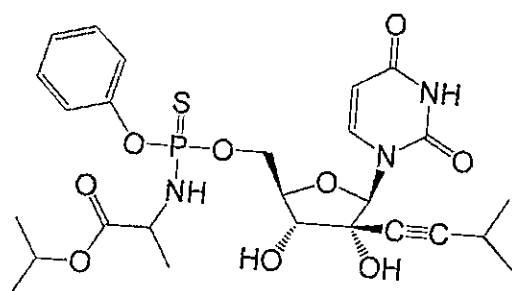
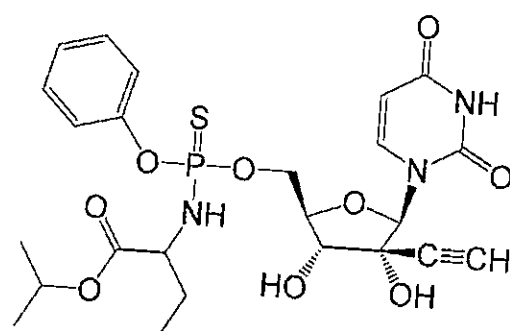
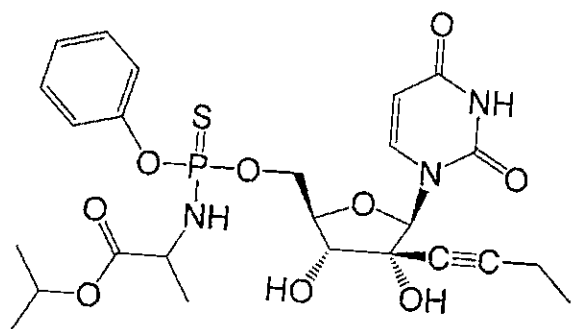
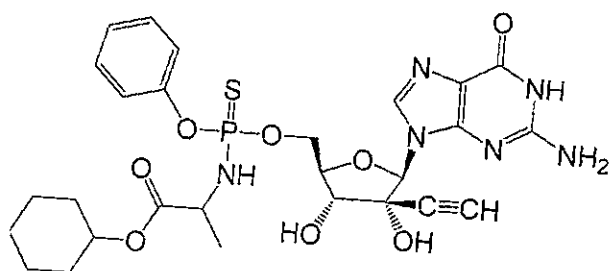
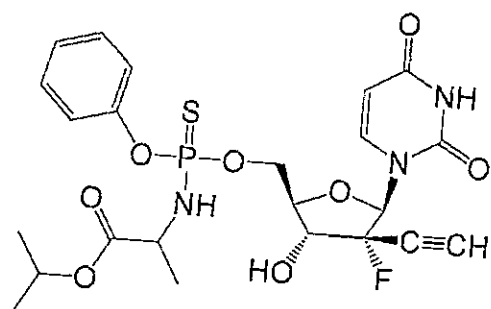


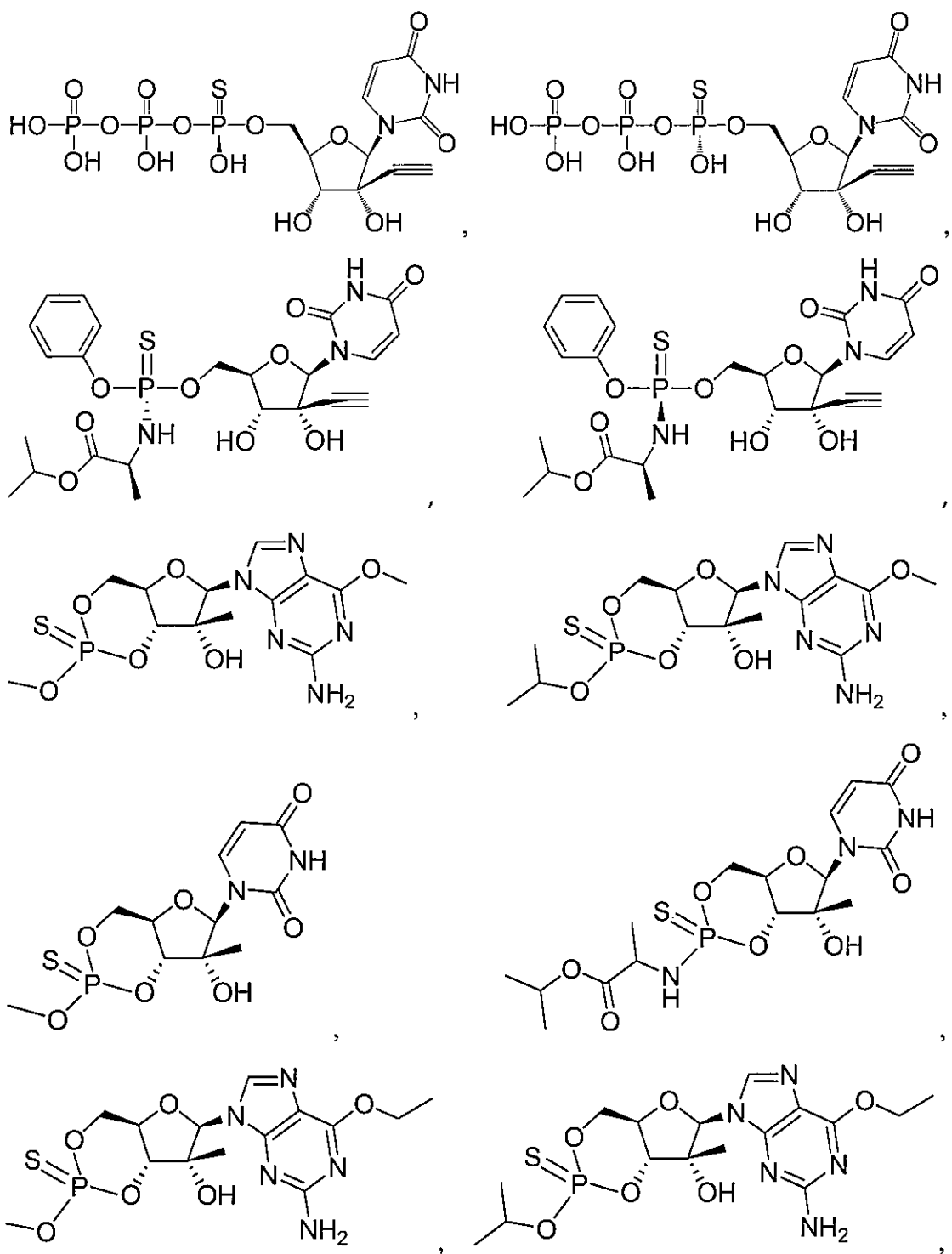


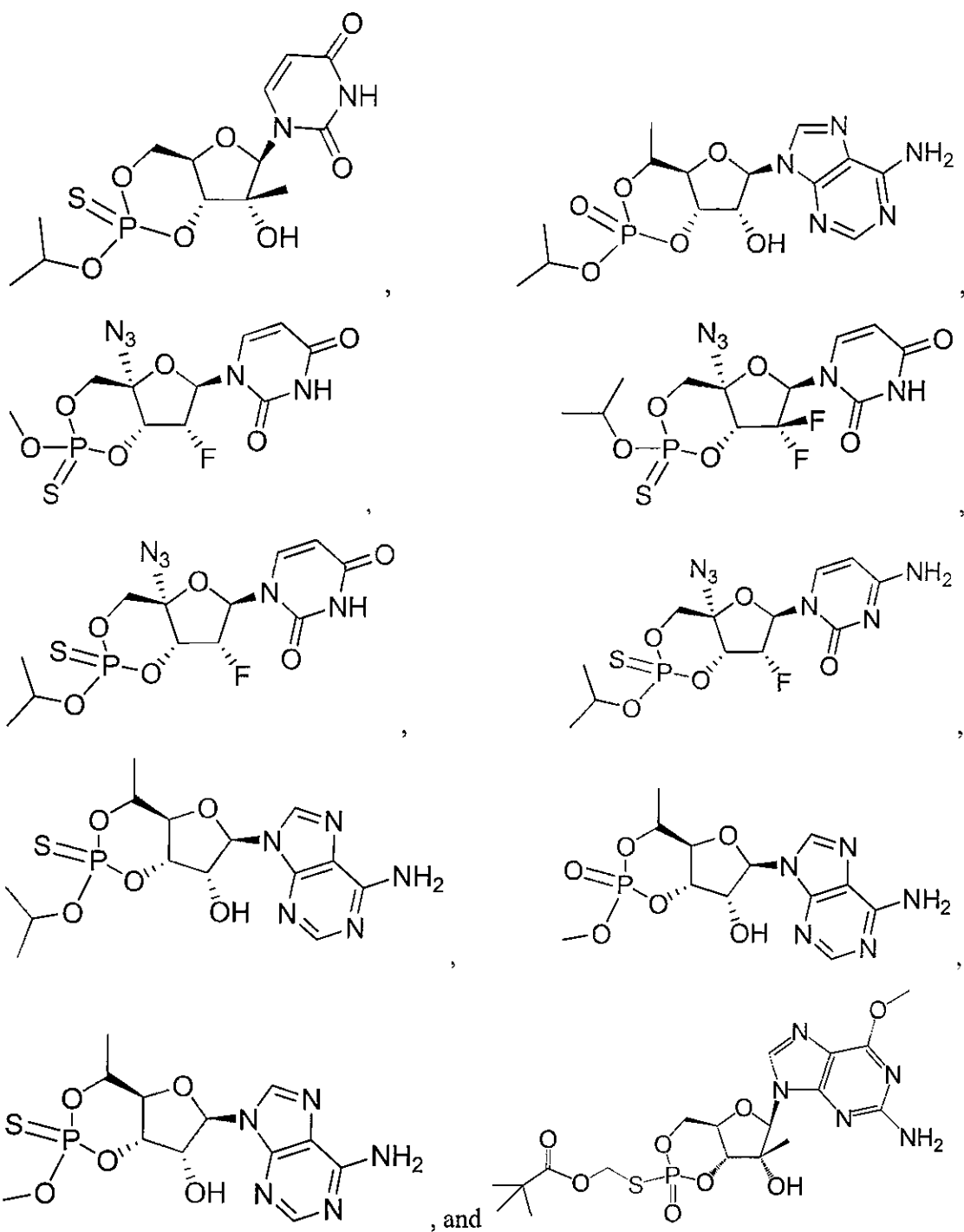












, or a pharmaceutically acceptable salt of any of the aforementioned compounds.