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WO 03/022860 A1

(54) Title: SYNTHETIC HEPARIN PENTASACCHARIDES

(57) Abstract: Preparation of synthetic monosaccharides, disaccharides, trisaccharides, tetrasaccharides and pentasaccharides for use in the preparation of synthetic heparinoids.

# TITLE

# Synthetic Heparin Pentasaccharides

## Field of the Invention

This invention is directed to intermediates, and a processes for the chemical synthesis of AT-III binding heparin or heparinoid, pentasaccharides.

## Background Art

Vascular thrombosis is a cardiovascular disease indicated by the partial or total occlusion of a blood vessel by a clot containing blood cells and fibrin. In arteries, it results predominantly from platelet activation and leads to heart attack, angina or stroke, whereas venous thrombosis results in inflammation and pulmonary emboli. The coagulation of blood is the result of a cascade of events employing various enzymes collectively known as activated blood-coagulation factors. Heparin, a powerful anticoagulant has been used since the late 1930's in the treatment of thrombosis. In its original implementation, tolerance problems were noted and so reduced dosage was suggested to reduce bleeding and improve efficacy. In the early 1970's, clinical trials did indeed indicate acceptable tolerance was obtainable whilst still preserving antithrombotic activity. Unfractioned heparin (UFH) is primarily used as an anticoagulant for both therapeutic and surgical indications, and is usually derived from either bovine lung or porcine mucosa. Amongst the modern uses of unfractioned heparin are the management of unstable angina, an adjunct to chemotherapy and anti-inflammatory treatment, and as a modulation agent for growth factors and treatment of haemodynamic disorders.

In the late 1980's, the development of low molecular weight heparins (LMWHs) led to improvements in antithrombotic therapy. LMWHs are derived from UFH by such processes as; chemical degradation, enzymatic depolymerisation and $\gamma$-radiation cleavage. This class of heparins have recently been used for treatment of trauma related thrombosis. Of particular interest is the fact that their relative effects on platelets are minimal compared

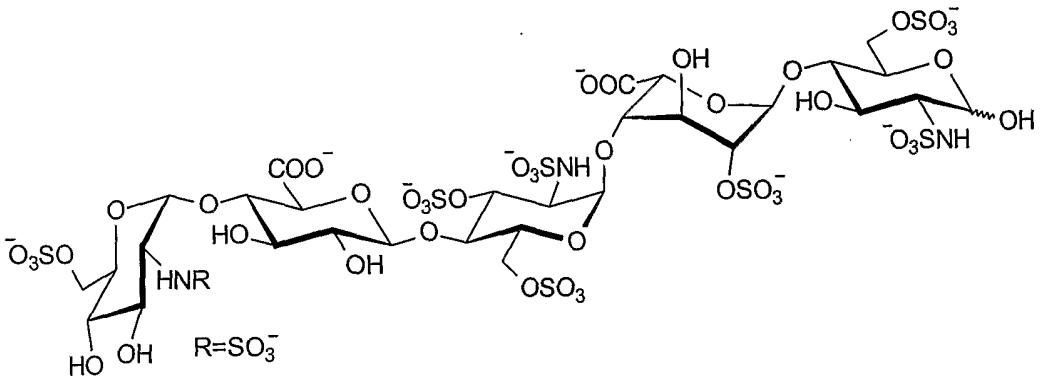
to heparin, providing an immediate advantage when treating platelet compromised patients. The degree of depolymerisation of UFH can be controlled to obtain LMWH of different lengths. Dosage requirements for the treatment of deep vein thrombosis (DVT) are significantly reduced when employing LMWH as opposed to UFH, although in general the efficacy of both therapeutics seems to be comparable. In addition, LMWH can be effective as an alternative therapeutic for patients who have developed a sensitivity to UFH. Unfortunately, there has recently been a great deal of concern in the use of LMWH due to the perceived potential for cross-species viral contamination as a result of the animal source of the parent UFH.

One way of avoiding the possibility of cross-species contamination, is to prepare heparins by chemical synthesis. This method would also provide the opportunity to develop second generation heparins or heparinoids, that can be tailored to target particular biological events in the blood coagulation cascade.

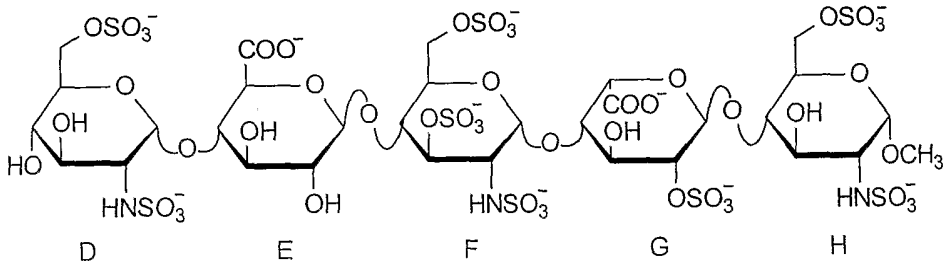
An investigation to determine the critical structural motif required for an important binding event in a coagulation cascade involving heparin, dates back to the 1970's. Some structural features of heparin were defined, but the binding domains of interest remained essentially undefined. Research conducted by Lindahl and co-workers[1] and separately by Choay and co-workers[2] eventually led to the determination that a pentasaccharide sequence constituted the critical binding domain for the pro-anticoagulant cofactor, antithrombin III (AT-III). After determination of the critical heparin sugar sequence, complete chemical syntheses were embarked upon to further prove the theories. Complete syntheses of the pentasaccharide binding domain were completed at similar times by Sinay and co-workers[3] and by Van Boeckel and co-workers[4].

Significant difficulties were encountered during both these reported syntheses. The synthesis by Van Boeckel and co-workers provided a method on reasonable scale (156mg's of final product) and with improved yields compared to the Sinay synthesis, but still only provided an overall yield of 0.22%, (compared with 0.053% for the Sinay synthesis). One particular problem encountered during the final deprotection, was the intermolecular reaction of the hemiacetal (the reducing end functionality of the sugar), which

led to the formation dimers and trimers. To reduce the likelihood of this occuring, an α-methyl glycoside of the pentasaccharide was synthesised. The structures of interest are represented in **Figure 1**, wherein **I** represents the hemiacetal form, and **II** represents the α-methylglycoside form.




I




II

**Figure I**

As mentioned, studies have determined that the significant biological event in preventing thrombosis is the binding of a pentasaccharide sequence[5] of heparin, to heparin cofactor antithrombin III (AT-III). As well as pentasaccharide **I**, the important derivative **II** has also been prepared by total synthesis[6]. Compound **II** has recently completed phase III clinical trials for the treatment of deep-vein thrombosis. The following patents display some relevance to the present invention. Patent US 4,401,662 claims composition of matter on the pentasaccharide AT-III binding sequence of heparin as does US 4,496,550. Patents EP 0,084,999 and US 4,818,816 detail synthetic methodologies towards pentasaccharide **I**, and derivative **II**.

Object of the Invention

It is an object of the invention to provide a synthetic preparation for heparin pentasaccharides, and intermediates thereof, and to novel intermediates for heparin pentasaccharides, and to novel heparin pentasaccharides.

The present invention provides composition of matter of intermediates, and a process for the synthesis, of AT-III binding heparins and heparinoids. What this entails is a stepwise synthetic process employing monosaccharide building blocks.

The nature of the AT-III binding pentasaccharide is such, that under cursory analysis of the individual monomeric units constituting the pentasaccharide, we note that each is distinct from the others. Secondly, we can see that there is an alternating stereospecificity in regard to the glycosidic linkages (**Fig. 1**).

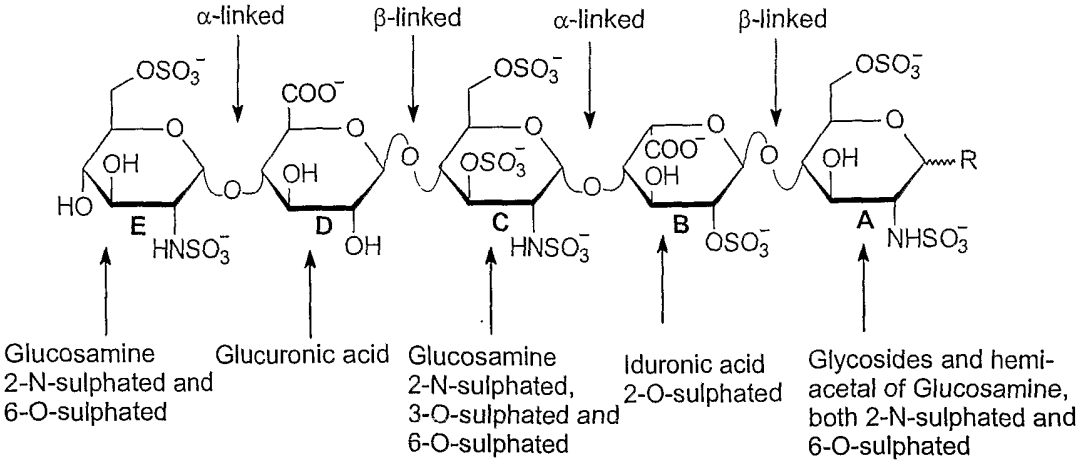



**Fig. 1**

In a synthesis, the difference evident in each block requires that each individual monomer used in the synthesis will need a different protecting group pattern. In light of this, it is essential in the synthesis of the above pentasaccharide that a protecting group strategy is carefully conceived. As can be seen, the pentasaccharide displays *O*-sulphation, *N*-sulphation, there are free hydroxyl groups, and there are stereospecific glycosidic linkages.

Therefore, a protection strategy is required such that (1) sulphation can be effected at the required sites, whilst leaving some hydroxyl groups unsulphated (note that due to the chemical lability of *N*- and *O*-sulphates, sulphation needs to be effected late in the synthesis), (2) a protection strategy is required that assists in effecting the appropriate glycosidic linkage and (3) a protection strategy is required that enables the correct (in terms of regio- and stereoisomerism) glycosidic linkages to be formed. α-Glycosidic linkages are typically generated by the use of what are known as non-participating protecting groups, whilst β-linkages are effected by participating protecting groups. Some *N*- and *O*-participating and non-participating protecting groups are known to the art (the art being considered carbohydrate chemistry). It is also well known to the art that the kind of protecting groups employed can effect the reactivity of the building block. The culmination of these requirements are demonstrated in the exemplary building block in **Fig. 2** below, which displays the kind of characteristics required to effect the synthesis of heparin oligosaccharides.

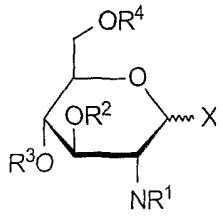



**Fig. 2, Exemplary Building Block C**

In exemplary building block **C**, X is a leaving group suitable of reacting with another monomer or acceptor, to form an interglycosidic linkage; $R^1$ is a non-participating amino protecting group so as to effect an α-linkage upon activation of X followed by coupling to an appropriate acceptor; $R^2$ and $R^4$ can be similarly protected to allow for eventual *O*-sulphation, whilst $R^3$ is required to be differentially protected so as to allow the formation of an acceptor hydroxyl group to couple this block to the next in the chain. The building blocks in **Fig. 3** exemplify the kind of derivatised monosaccharides required to effect the synthesis of heparin AT-III binding pentasaccharides.

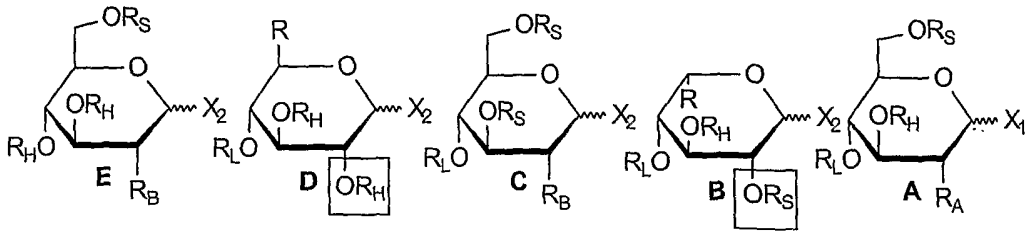


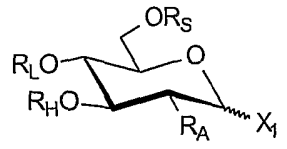

**Fig. 3**

The protecting groups represented by '$R_S$' in **Fig. 3** are sites that will eventually require *O*-sulphation, the protecting groups represented by '$R_H$' need to be orthogonal to '$R_S$' and represents sites that will eventually become hydroxyl groups. The substituents '$X_1$' and '$X_2$' represent leaving groups that are activated to react with another suitable protected building block to form a glycosidic linkage, and,in the case of $X_1$, may also be derivatised as alkyl glycosides or substituted with a group suitable to allow conjugation to a support for drug delivery. The '$R_L$' groups are protecting groups orthogonal to both '$R_S$' and '$R_H$', and represent sites through which chain elongation *via* glycosylation occurs. 'R' is representative of either a protected or latent carboxylate function. The '$R_A$' groups are non-participating amino protecting groups that enable α-linkages to be formed while the '$R_B$' groups may be either a participating or non-participating amino protecting group. There is another level of complexity to be added to the synthesis in as much as the protecting groups in blocks **D** and **B** that are indicated by the boxes, need to be such that they allow for the formation of a β-glycosidic linkage. This may require a two stage protection at the indicated sites, ie. a protection followed by deprotection and subsequent reprotection with a different protecting group. The initial protection is required to effect the correct stereochemistry in a glycosylation, and second stage protection to allow for the correct sulphation pattern.

As is evident, the pentasaccharide can be constructed in a variety of different ways; blocks B and A can be coupled, blocks E and D can be coupled, block C can be coupled to either, and the resulting dimer and trimer can finally be coupled to form the pentasaccharide. Alternatively, each block can be added sequentially and so on. There are a number of alternative

coupling sequences that can be easily conceived and the choice made in regard to this, in itself, has a marked effect on the synthetic methodologies that will finally be employed, and therefore impacts on the overall success of the synthesis.

In one aspect the invention provides for a monosaccharide building block in the D-glucopyrano configuration, for the preparation of synthetic heparinoids, said building block of General Formula I,




General Formula I (Block A)

Wherein $X_1$ includes but is not limited to: hydroxy, alkoxy, aryloxy, benzyloxy, substituted benzyloxy; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, or other suitable leaving group; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; a lipoaminoacid or other such group suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta; other suitable groups will be known to those skilled in the art,

$R_A$ includes but is not limited to: an azido function, an amine; an *N*H-Dde, *N*H-DTPM, *N*H-Fmoc, *N*H-Boc, NH-Cbz, *N*H-Troc, *N*-phthalimido; or, other such suitable protected amino functions known to those skilled in the art,

$R_H$ is a benzyl or substituted benzyl protecting group,

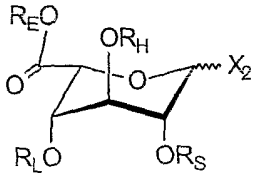
$R_L$ includes but is not limited to: a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; γ-aminobutyryl, 4-*N*-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-*N*-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-*N*-Alloc-butyryl, 4-*N*-Fmoc-

butyryl, 4-*N*-Boc-butyryl type protecting groups; or, other such suitable protecting groups as known to those skilled in the art, and

$R_S$ includes but is not limited to: 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; or, other suitable protecting groups as known to those skilled in the art.

Alternatively $R_L$ and $R_S$ can combine to form a benzylidene or substituted benzylidene ring.

In a second aspect the invention provides for a monosaccharide building block in the L-idopyrano conformation, for the preparation of synthetic heparinoids, said building block of General Formula II,




General Formula II (Block B)

Wherein $X_2$ includes but is not limited to: a hydroxyl group; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, or other suitable leaving group; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta; other suitable groups will be known to those skilled in the art,

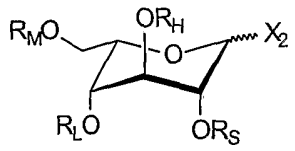
$R_S$ is defined as in General Formula I,

$R_H$ is defined as in General Formula I,

$R_L$ is defined as in General Formula I, and

$R_E$ includes but is not limited to: methyl, $C_2$-$C_5$ alkyl; substituted alkyl; or, benzyl and substituted benzyl groups; other suitable groups will be known to those skilled in the art.

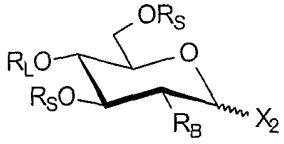
In a third aspect the invention provides for a monosaccharide building block in the L-idopyrano configuration, for the preparation of synthetic heparinoids, said building block of General Formula III,




General Formula III (Alternate Block B)

Wherein $X_2$ is defined as in General Formula II,
$R_S$ is defined as in General Formula II,
$R_H$ is defined as in General Formula I,
$R_L$ is defined as in General Formula I, and
$R_M$ includes but is not limited to a *p*-methoxyphenyl protecting group or other suitable oxidatively labile protecting group; a trityl group; or, other such suitable protecting groups as known to those skilled in the art.

In a fourth aspect the invention provides for a monosaccharide building block in the D-glucopyrano configuration for the preparation of synthetic heparinoids, said building block of General Formula IV,

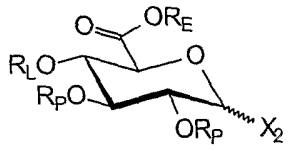



General Formula IV (Block C)

Wherein $X_2$ is defined as in General Formula II,
$R_B$ includes but is not limited to: an azido function, an amine; an *N*H-Dde or *N*H-DTPM group; or other suitably protected amino functions as known to those skilled in the art,
$R_L$ is defined as in General Formula I, and

$R_S$ is defined as in General Formula I.

In a fifth aspect the invention provides for a monosaccharide building block in the D-glucuronate configuration for the preparation of synthetic heparinoids, said building block of General Formula V,



General Formula V (Block D)

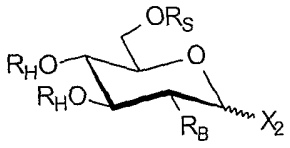
Wherein $X_2$ is as defined in General Formula II,

$R_P$ includes but is not limited to: 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups; carbonate protecting groups; or, other suitable protecting groups as known to those skilled in the art.

$R_L$ is defined as in General Formula I, and

$R_E$ is defined as in General Formula II.

In a sixth aspect the invention provides for a monosaccharide building block in the D-glucopyrano configuration for the preparation of synthetic heparinoids, said building block of General Formula VI,



General Formula VI (Block E)

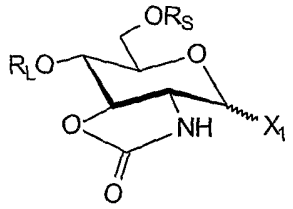
Wherein $X_2$ is as defined as in General Formula II,

$R_B$ is defined as in General Formula IV,

$R_H$ may be selected independently and are defined as in General Formula I, and

$R_S$ is defined as in General Formula I.

In a seventh aspect the invention provides for a monosaccharide building block in the D-glucopyrano configuration for the preparation of synthetic heparinoids, said building block of General Formula VII,




General Formula VII (Common Intermediate for Blocks A, C and E)

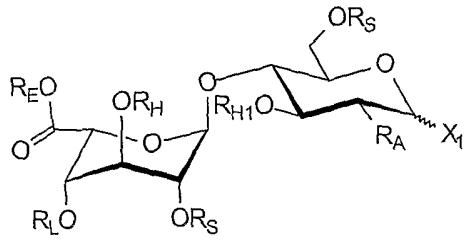
Wherein $X_1$ is defined as in General Formula I,

$R_L$ is defined as in General Formula I, and

$R_S$ is defined as in General Formula I.

$R_L$ and $R_S$ may also together combine to form a benzylidene or substituted benzylidene ring.

In an eighth aspect the invention provides for a disaccharide building block for the preparation of synthetic heparinoids, said building block of General Formula VIII,




General Formula VIII (Block B-A)

Wherein $X_1$ is defined as in General Formula I,

$R_{H1}$ is defined as being selected from $R_H$ of General Formula I, with the addition that $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate,

$R_A$ is defined as in General Formula I, with the addition that $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate

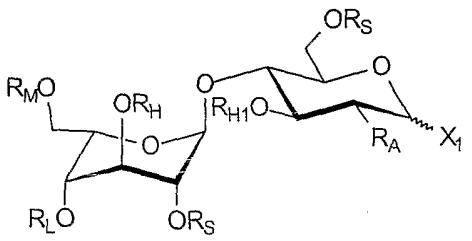
$R_S$ is defined as in General Formula I,

$R_H$ is defined as in General Formula I,

$R_L$ is defined as in General Formula I, and

$R_E$ is defined as in General Formula II.

In a ninth aspect the invention provides for a disaccharide building block for the preparation of synthetic heparinoids, said building block of General Formula IX,




General Formula IX (Alternate Block B-A)

Wherein $X_1$ is as defined as in General Formula I,

$R_A$ is defined as in General Formula XIII,

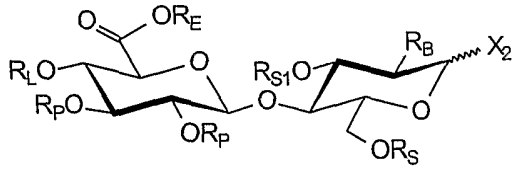
$R_{H1}$ is defined as in General Formula XIII,

$R_S$ is defined as in General Formula I,

$R_L$ is defined as in General Formula I, and

$R_M$ is defined as in General Formula III.

In a tenth aspect the invention provides for a disaccharide building block for the preparation of synthetic heparinoids, said building block of General Formula X,



General Formula X (Block D-C)

Wherein $X_2$ is as defined in General Formula II,

$R_{S1}$ is defined as being selected from $R_S$ of General Formula I, with the addition that $R_{S1}$ and $R_B$ can combine together to form a cyclic carbamate.

$R_B$ is defined as in General Formula IV, with the addition that $R_{S1}$ and $R_B$ can combine together to form a cyclic carbamate.

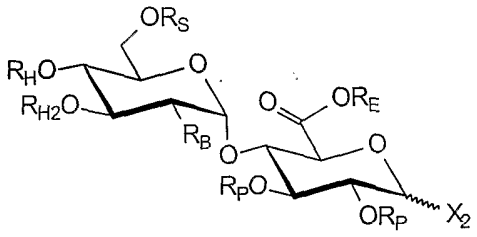
$R_S$ is defined as in General Formula I,

$R_P$ are defined as in General Formula V,

$R_L$ is defined as in General Formula I, and

$R_E$ is defined as in General Formula II.

In an eleventh aspect the invention provides for a disaccharide building block for the preparation of synthetic heparinoids, said building block of General Formula XI,



General Formula XI (Block E-D)

Wherein $X_2$ is as defined in General Formula II,

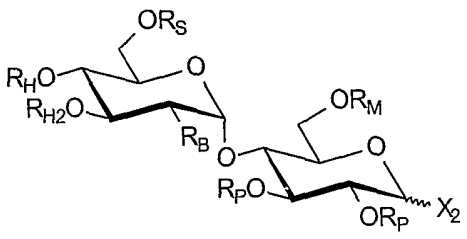
$R_P$ are defined as in General Formula V,

$R_E$ is defined as in General Formula II,

$R_B$ is defined as in General Formula IV, with the addition that $R_B$ and $R_{H2}$ can combine to form a cyclic carbamate,

$R_{H2}$ is defined as being selected from $R_H$ of General Formula I, with the addition that $R_B$ and $R_{H2}$ can combine to form a cyclic carbamate,
$R_H$ is defined as in General Formula I, and
$R_S$ is defined as in General Formula I.

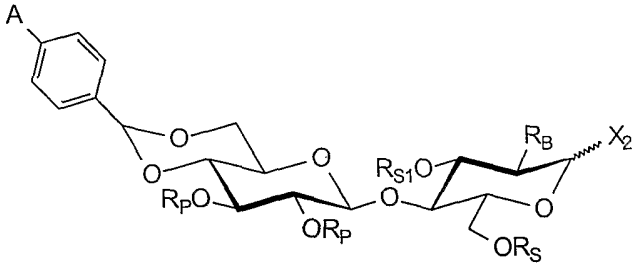
In a twelfth aspect the invention provides for a disaccharide building block for the preparation of synthetic heparinoids, said building block of General Formula XII,




General Formula XII (Alternate Block E-D)

Wherein $X_2$ is as defined in General Formula II,
$R_P$ are defined as in General Formula V,
$R_M$ is defined as in General Formula III,
$R_B$ and $R_{H2}$ are as defined in General Formula XI,
$R_H$ isdefined as in General Formula I, and
$R_S$ is defined as in General Formula I.

In a thirteenth aspect the invention provides for a disaccharide building block for the preparation of synthetic heparinoids, said building block of General Formula XIII,



General Formula XIII (Alternate Block D-C)

Wherein $X_2$ is defined as in General Formula II,

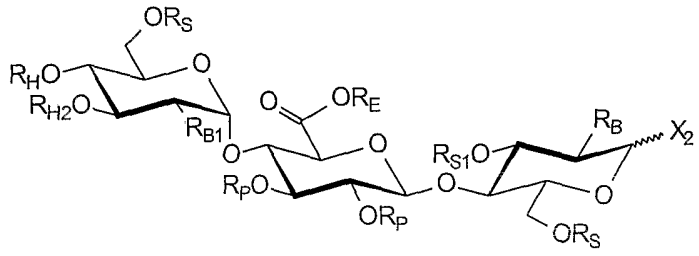
$R_B$ and $R_{S1}$ are defined as in General Formula X,

$R_S$ is defined as in General Formula I,

$R_P$ is defined as in General Formula V, and

A includes but is not limited to; H, Methoxy, Methyl; other suitable substituents will be known to those in the art.

In a fourteenth aspect the invention provides for a trisaccharide building block for the preparation of synthetic heparinoids, said building block of General Formula XIV,




General Formula XIV (Block E-D-C)

Wherein $X_2$ is defined as in General Formula II,

$R_B$ and $R_{S1}$ are defined as in General Formula X,

$R_S$ is defined as in General Formula I,

$R_P$ is defined as in General Formula V,

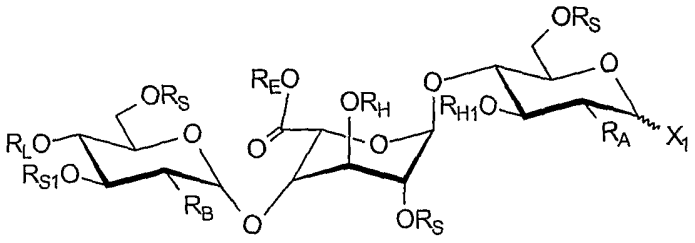
$R_E$ is defined as in General Formula II,

$R_{B1}$ is defined as being selected from $R_B$ of General Formula IV, with the addition that $R_{B1}$ can combine together with $R_{H2}$ to form a cyclic carbamate,

$R_{H2}$ is defined as being selected from $R_H$ of General Formula I, with the addition that $R_{H2}$ can combine together with $R_{B1}$to form a cyclic carbamate, and

$R_H$ is defined as in General Formula I.

In a fifteenth aspect the invention provides for a trisaccharide building block for the preparation of synthetic heparinoids, said building block of General Formula XV,



General Formula XV (Block C-B-A)

Wherein $X_1$ is defined as in General Formula I

$R_A$ and $R_{H1}$ are defined as in General Formula VIII,

$R_S$ is defined as in General Formula I,

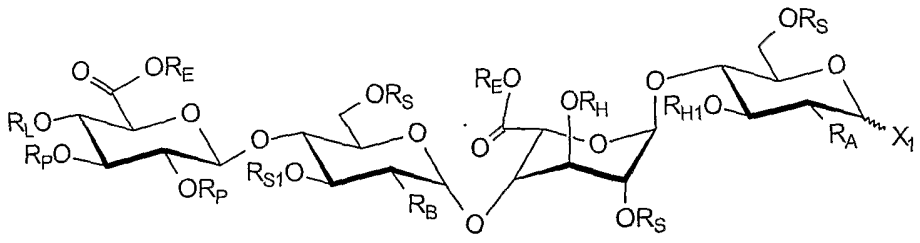
$R_H$ is defined as in General Formula I,

$R_E$ is defined as in General Formula II,

$R_B$ and $R_{S1}$ are defined as in General Formula X, and

$R_L$ is defined as in General Formula I.

In a sixteenth aspect the invention provides for a tetrasaccharide building block for the preparation of synthetic heparinoids, said building block of General Formula XVI,



General Formula XVI (Block D-C-B-A)

Wherein $X_1$ is defined as in General Formula I

$R_A$ and $R_{H1}$ are defined as in General Formula VIII,

$R_S$ is defined as in General Formula I,

$R_H$ is defined as in General Formula I,

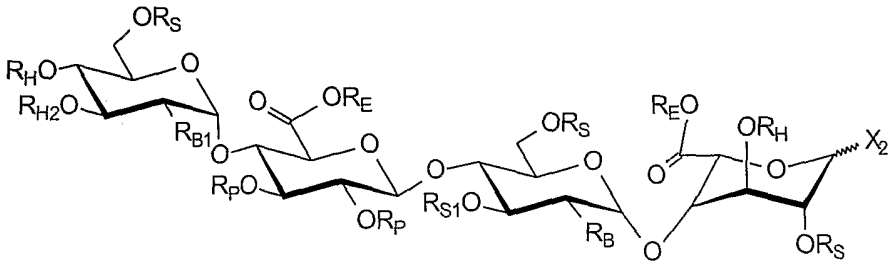
$R_E$ is defined as in General Formula II,

$R_B$ and $R_{S1}$ are defined as in General Formula X,

$R_P$ is as defined in General Formula V, and

$R_L$ is as defined in General Formula I.

In an seventeenth aspect the invention provides for a tetrasaccharide building block for the preparation of synthetic heparinoids, said building block of General Formula XVII,



General Formula XVII (Block E-D-C-B)

Wherein $X_2$ is defined as in General Formula IV,

$R_H$ is defined as in General Formula I,

$R_E$ is defined as in General Formula II,

$R_B$ and $R_{S1}$ are defined as in General Formula X,

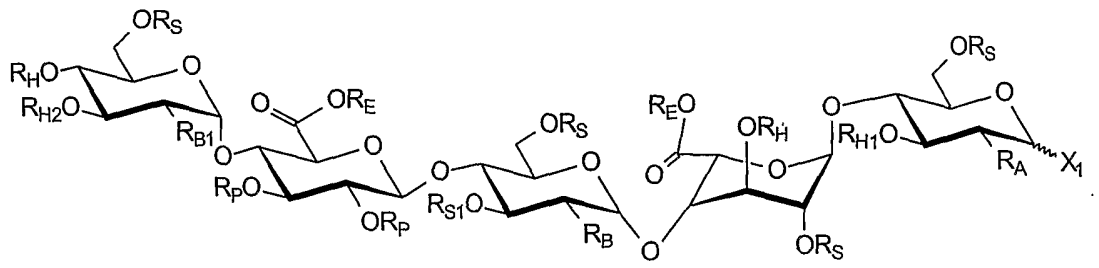
$R_S$ is defined as in General Formula I,

$R_P$ is defined as in General Formula V,

$R_L$ is defined as in General Formula I, and

$R_{B1}$ and $R_{H2}$ are defined as in General Formula XIV.

In a eighteenth aspect the invention provides for a pentasaccharide building block for the preparation of synthetic heparinoids, said building block of General Formula XIII,



General Formula XVIII (Block E-D-C-B-A)

Wherein $X_1$ is defined as in General Formula I

$R_A$ and $R_{H1}$ are defined as in General Formula VIII,

$R_S$ is defined as in General Formula I,

$R_H$ is defined as in General Formula I,

$R_E$ is defined as in General Formula II,

$R_B$ and $R_{S1}$ are defined as in General Formula X,

$R_P$ is defined as in General Formula V, and

$R_{B1}$ and $R_{H2}$ are defined as in General Formula XIV.

In a nineteenth aspect, the invention provides a method for the preparation of compounds of the eighth aspect, involving the step of reacting a compound of the second or third aspect with a compound of the first or seventh aspect to form a new glycosidic bond.

In a twentieth aspect, the invention provides a method for the preparation of compounds of the eighth aspect, involving the step of selectively removing the protecting group $R_M$ from compounds of the ninth aspect and oxidizing the product of said deprotection.

In a twenty first aspect, the invention provides a method for the preparation of compounds of the tenth aspect, involving the step of reacting a compound of the fifth aspect with a compound of the fourth or seventh aspect to form a new glycosidic bond.

In a twenty second aspect, the invention provides a method for the preparation of compounds of the eleventh aspect, involving the step of reacting a compound of the fifth aspect with a compound of the sixth or seventh aspect to form a new glycosidic bond.

In a twenty third aspect, the invention provides a method for preparation of compounds of the thirteenth aspect involving the reaction of a compound of the fourth or seventh aspect with a suitable donor molecule, to form a new glycosidic bond.

In a twenty fourth aspect, the invention provides a method for the preparation of compounds of the fourteenth aspect involving the step of using any one or more of the compounds of the fourth, fifth, sixth, seventh, tenth, eleventh, twelfth or thirteenth aspect in a glycosidic bond forming reaction.

In a twenty fifth aspect, the invention provides a method for the preparation of compounds of the fifteenth aspect involving the step of using any one or more compounds of the first, second, third, fourth, seventh, eighth and ninth aspects in a glycosidic bond forming reaction.

In a twenty sixth aspect, the invention provides a method for the preparation of compounds of the sixteenth aspect involving the step of using any one or more of the compounds of the first, second third, fourth, fifth, seventh, eighth, ninth, tenth, thirteenth or fifteenth aspect in a glycosidic bond forming reaction.

In a twenty seventh aspect, the invention provides a method for the preparation of compounds of the seventeenth aspect involving the step of using any one or more of the compounds of the second, third, fourth, fifth, seventh, tenth, eleventh, twelth, thirteenth or fourteenth aspect in a glycosidic bond forming reaction.

In a twenty eighth aspect, the invention provides a method for the preparation of compounds of the eighteenth aspect involving the step of using any one or

more of the compounds of the 1,2,3,4,5,7, 8, 9, 10, 11, 12, 13, 14, or 15, 16 or 17th aspect in a glycosidic bond forming reaction.

Best Mode

**Embodiments of the invention will be described with reference to the following examples: Standard operating protocols are provided for many of the examples.**

**List of Abbrevations:**

**AcO:** Acetyl,

**All:** Allyl,

**Alloc:** Allyloxycarbonyl,

**Bn:** Benzyl,

**Bz:** Benzoyl,

**CAN:** $(NH_4)_2Ce^{IV}(NO_3)_6$, ceric ammonium (IV) nitrate,

**ClAc:** Monochloroacetyl,

**Cres:** p-Tolyl,

**DCC:** Dicyclohexylcarbodiimide,

**Dde:** 1-(4,4-**d**imethyl-2,6-**d**ioxocyclohex-ylidene)**e**thyl,

**DEAD:** Diethyl azodicarboxylate,

**DIPEA:** Diisopropylethylamine,

**DMAP:** 4-*N,N*-dimethylaminopyridine,

**DMF:** *N,N*-Dimethylformamide,

**DMTST:** Dimethyl (methylthio)sulfoniumtetrafluoromethansulfonate,

**DTPM:** (1,3-**d**imethyl-2,4,6 (1H, 3H, 5H)-**t**rioxo**p**yrimidin-5-ylidene) **m**ethyl,

**Lev:** 4-Oxopentanoyl,

**MCPBA:** 3-chloroperbenzoic acid,

**Mes:** Methanesulfonyl,

**Mp:** 4-Methoxyphenyl,

**Mpm:** 4-methoxybenzyl,

**NBS:** *N*-Bromosuccinimide,

**NIS:** *N*-Iodosuccinimide,

**NMP:** *N*-Methylpyrollidone

**NPht:** *N*-Phthaloyl

**PDC:** Pyridiniumdichromate,

**Pent:** *n*-Pentenyl,

**$Ph_3P$**: Triphenylphosphine,

**Piv:** Pivaloyl,

**TBAF**: Tetrabutylammoniumfluoride,

**TBDMS:** *tert*-Butyldimethylsilyl,

**TBDPS**: *tert*-Butyldiphenylsilyl,

**TCA:** Trichloroacetimidyl,

**TEMPO:** 2,2,6,6-Tetramethyl-1-piperidinyloxyl,

**TFA:** Trifluoroacetic acid,

**TFAA:** Trifluoroacetic acid anhydride,

**Tf:** Trifluoromethanesulfonyl,

**$TfN_3$**: Trifluoromethanesulfonyl azide, prepared from $NaN_3$ and $Tf_2O$,

**TfOH**: Trifluoromethanesulfonic acid,

**THF**: Terahydrofuran,

**TMS:** Trimethylsilyl,

**Tos:** p-Toluenesulfonyl,

**p-TosOH**: *p*-Toluenesulfonic acid,

**Trit:** Triphenylmethyl.

**Standard Operating Procedures**

Standard Operating Procedure **1**: Formation of Benzylidene acetals

Standard Operating Procedure **2**: Formation of p-Methoxybenzylidene acetals

Standard Operating Procedure **3**: Formation of isopropylidene acetals:

Standard Operating Procedure **4**: Dealkylidenation (Removal of isopropylidene, benzylidene and p-methoxybenzylidene)

Standard Operating Procedure **5**: Regioselective opening of the p-methoxy-benzyliden acetal to a 6-O-*pMethoxybenzyl ether*

Standard Operating Procedure **6**: Regioselective opening of a benzylidene ring to a 4-O-benzyl ether

Standard Operating Procedure **7**: Introduction of a benzyl or *p*-methoxybenzyl ether

Standard Operating Procedure **8**:Introdution of a *tert*-butyldiphenylsilyl ether

Standard Operating Procedure **9**: Cleavage of a *tert*-Butyl-diphenylsilyl ether

Standard Operating Procedure **10**:Introduction of a *N*-DTPM-group

Standard Operating Procedure **11**:Cleavage of a N-DTPM-group

Standard Operating Procedure **12**: Introduction of an azide group via diazo transfer reaction

Standard Operating Procedure **13**: Hydrolysis of thioglycosides (NBS)

Standard Operating Procedure **14**: Hydrolysis of thioglycosides (NIS)

Standard Operating Procedure **15**:Chemoselective Oxidation to Uronic acids

Standard Operating Procedure **16**: Methyl ester formation on the Uronic acids

Standard Operating Procedure **17**: Regioselective 6-O-Benzoylation

Standard Operating Procedure **18**: Common procedure for O-Benzoylation

Standard Operating Procedure **19**:Common procedure for O-Acetylation

Standard Operating Procedure **20**: PDC-oxidation of alcohols to carboxylic acids

Standard Operating Procedure **21**:Chemoselective 1-O-Benzoyl cleavage

Standard Operating Procedure **22**: Deacylation under Zemplen conditions

Standard Operating Procedure **23**: Introduction of the 4-Oxopentanoyl (=Levulinoyl) group

Standard Operating Procedure **24**:Cleavage of the 4-Oxopentanoyl (= Levulinoyl) group

Standard Operating Procedure **25**: Formation of Trichloroacetimidates

Standard Operating Procedure **26**: Regioselective introduction of a 6-O-*p*Methoxyphenyl group under Mitsunobu conditions

Standard Operating Procedure **27**: Cleavage of the *p*-Methoxyphenyl ether

Standard Operating Procedure **28**: Cleavage of p-Methoxybenzyl ethers

Standard Operating Procedure **29**: Formation of a 2,3-cyclic carbamate

Standard Operating Procedure **30**: Cleavage of the N-phthaloyl group

Standard Operating Procedure **31**: Introduction of a thiocresyl ether at the reducing end

Standard Operating Procedure **32**: Glycosylation with thioglycosides

a) NIS-promoted glycosylation

b) DMTST promoted glycosylations:

Standard Operating Procedure **33**: Glycosylations with trichloroacetimidates

Standard Operating Procedure **34**: Glycosylations using 2,3-cyclocarbamoyl protected *p*Thiocresyl glycosides as glycosyl donors

Standard Operating Procedure **35**: Introduction of an Alloc-group

Standard Operating Procedure **36**: Cleavage of an Alloc-group

Standard Operating Procedure **37**: Lewis acid mediated benzylation
Standard Operating Procedure ***38***: benzylation under mild basic conditions
Standard Operating Procedure **39**: Ester cleavage under very mild conditions

**Standard Operating Procedure 1: Formation of Benzylidene acetals**

The starting material (47.5 mmol) was dissolved in acetonitrile (100 – 200 ml) and reacted with benzaldehyde dimethyl acetal (1.2 equiv.) and a catalytic amount of *p*-toluenesulphonic acid monohydrate (0.01-0.1 equiv). The reaction was stirred at 50°C under reduced pressure (350 mbar) until the TLC shows completion. Subsequently, the mixture was neutralized with triethylamine (pH ≈ 9) and concentrated in vacuo. The remaining residue was dissolved in an organic solvent (e.g. dichloromethane or ethyl acetate) and extracted with $H_2O$, saturated brine solution, dried over $Na_2SO_4$ and concentrated. Final purification was achieved either by crystallization or by silica gel chromatography. The typical yields for the product formation varied between 70 and 95 %.

**Standard Operating Procedure 2: Formation of p-Methoxybenzylidene acetals**

The starting material (47.5 mmol) was dissolved in DMF/acetonitrile (1/1, 100 – 200 ml) and reacted with p-methoxybenzaldehyde dimethyl acetal (1.2 equiv.) and a catalytic amount of *p*-toluenesulphonic acid monohydrate (0.01-0.1 equiv). The reaction was stirred between 50 - 60 °C under reduced pressure (350 mbar) until the TLC shows completion. Subsequently, the mixture was neutralized with triethylamine (pH ≈ 9) and concentrated in vacuo. The remaining residue was dissolved in an organic solvent (e.g. dichloromethane or ethyl acetate) and extracted with $H_2O$, saturated brine solution, dried over $Na_2SO_4$ and concentrated. Final purification was achieved either by crystallization or by silica gel chromatography. The typical yields for the product formation varied between 70 and 85 %.

**Standard Operating Procedure 3: Formation of isopropylidene acetals:**

A solution of starting material (10 mmol) and catalytic amounts of camphorsulfonic acid (0.01-0.1 equiv) in 2,2-dimethoxypropane (50 ml) was stirred at 25 °C until completion, neutralized with triethylamine and concentrated. The remaining residue was dissolved in an organic solvent (e.g. dichloromethane or ethyl acetate) and extracted with $H_2O$ and saturated brine solution. The organic layer was dried over $Na_2SO_4$ and concentrated. Final purification was achieved either by crystallization or by silica gel chromatography. The typical yields for the product formation varied between 75 and 93 %.

**Standard Operating Procedure 4:**
**Dealkylidenation (Removal of isopropylidene, benzylidene and p-methoxybenzylidene)**

A solution of the acetal (31 mmol) in 150 ml dichloromethane was cooled to 0°C and reacted with 80 % aqueous TFA (20.0 ml, cooled to 0°C). After stirring at 0°C until completion, the reaction mixture was neutralized with 30 % NaOH solution and extracted with water and saturated brine solution. The organic layer was dried over $Na_2SO_4$ and concentrated. Final purification was achieved either by crystallization or by silica gel chromatography. The typical yields for the product formation varied between 70 and 95 %.

Modification using *p*-TosOHxOH$_2$ in MeOH/$CH_3CN$ for cleavage:

The acetal (16.6 mmol) was dissolved in 100mL of dry acetonitrile and 25 mL MeOH and the solution was reacted with catalytic amounts of *p*-TosOHxOH$_2$. The reaction mixture was heated at elevated Temperature (between 40 and 60 °C) until completion and then neutralized with $Et_3N$, concentrated *in vacuo* and purified either by crystallization or by silica gel chromatography. The typical yields for the product formation varied between 70 and 95 %.

**Standard Operating Procedure 5: Regioselective opening of the p-methoxybenzyliden acetal to a 6-O-*pMethoxybenzyl ether***

A suspension of the starting sugar (10.2 mmol), molecular sieves 3Å (6.5 g, freshly activated) and $Na(CN)BH_3$ (3.85 g, 61.2 mmol) in dry DMF (90 ml) was stirred for 1 hr at r.t. and cooled down to 0°C. Subsequently, a solution of TFA (11.2 mL, 122.4 mmol in 51 mL dry DMF) was added dropwise and stirring continued at 50 to 60°C until completion of the reaction. The reaction mixture was cooled to 20°C, diluted with ethyl acetate and extracted with a saturated aqueous $NaHCO_3$ solution and filtered through a celite pad. The combined organic layers were washed with saturated brine solution, dried over $MgSO_4$ and concentrated. Final purification was achieved either by crystallization or by silica gel chromatography. The typical yields for the product formation varied between 70 and 90 %.

**Standard Operating Procedure 6: Regioselective opening of a benzylidene ring to a 4-O-benzyl ether**

A solution of the starting material (3.4 mmol) in 25 mL dichloromethane is cooled to 0°C and to it is added of a solution of $BH_3$ in THF (1 M, 34 ml) and a solution of $Bu_2BOTf$ in dichloromethane (1 M, 3.7 ml). The reaction is stirred at 0°C till completion and then quenched with 10 ml $Et_3N$ and 10 ml MeOH, concentrated and coevaporated three times with toluene. Final purification was achieved either by crystallization or by silica gel chromatography. The typical yield for the product formation varied between 75 and 90 %.

**Standard Operating Procedure 7: Introduction of a benzyl or *p*-methoxybenzyl ether**

The starting material (40.2 mmol) was dissolved in dry *N,N'*-dimethylformamide (100 mL) at 0°C and reacted with NaH (48.24 mmol, 1.2 eq .per OH to be benzylated). Then benzyl bromide (1.1 eq per OH to be benzylated) was added dropwise and stirring continued at 0°C until completion. The same conditions were applied for the introduction of an allyl ether (Allylbromide served as allylating reagent).

The excess of NaH was neutralized by careful addition of acetic acid, followed by concentration of the reaction mixture *in vacuo*. The residue was dissolved

in ethyl acetate and subsequently washed with water, 10 % aqueous HCl solution, saturated aqueous $NaHCO_3$ solution, saturated brine solution, dried over $Na_2SO_4$ and concentrated *in vacuo*. Final purification was achieved either by crystallization or by silica gel chromatography. The typical yield for the product formation varied between 70 and 92 %.

The same procedure was followed for the formation of the *p*-methoxybenzyl ether except that *p*-methoxybenzyl chloride was added to the reaction instead of benzyl bromide and the reaction was performed between 50 and 60°C.

**Standard Operating Procedure 8:**

**Introdution of a *tert*-butyldiphenylsilyl ether**

A mixture of the starting material (29.0 mmol) and imidazole (70.1 mmol) was dissolved in 80 mL anhydrous DMF and heated to 55 °C. To the solution was added *tert*-butyldiphenylchlorosilane (8.30 mL, 31.9 mmol) and stirring continued at 55 °C until completion. The reaction mixture was then cooled to 20 °C and quenched with aqueous $NaHCO_3$ solution. After concentration *in vacuo*, the residue was taken up in ethyl acetate and the organic phase washed successively with water, 10% aqueous citric acid, water, saturated brine solution, dried over $Na_2SO_4$ and evaporated. Final purification was achieved either by crystallization or by silica gel chromatography. The typical yields for the product formation varied between 85 and 95 %.

**Standard Operating Procedure 9: Cleavage of a *tert*-Butyl-diphenylsilyl ether**

To a solution of the silyl ether (2.15 mmol) in 2.5 mL dry THF and acetic acid (3.44 mmol) was added 1M TBAF solution in THF (3.22 mL) and stirring continued till completion of the reaction. Subsequently, the reaction mixture was concentrated *in vacuo*. Final purification was achieved either by crystallization or by silica gel chromatography. The typical yields for the product formation varied between 85 and 97 %.

**Standard Operating Procedure 10:Introduction of a *N*-DTPM-group**

To a solution of the starting amine (24.5 mmol) in methanol (60 ml) is added a solution of the DTPM reagent (5.43 g, 25.7 mmol) in methanol (60 ml) at 60 °C. After completion of the reaction, the reaction mixture was concentrated *in vacuo*, taken up in dichloromethane, extracted with water and saturated brine solution, dried over $MgSO_4$ and evaporated. Final purification was achieved either by crystallization or by silica gel chromatography. The typical yields for the product formation varied between 85 and 97 %.

**Standard Operating Procedure 11:Cleavage of a N-DTPM-group**

The starting material (40.94 mmol) was dissolved in dry DMF (50ml) and reacted with ethylene diamine (20 ml) at room temperature until completion. The reaction mixture was concentrated *in vacuo* and coevaporated with toluene. The residue was suspended in $CHCl_3$ and filtered through a Celite pad. The filtrate was evaporated and final purification of the residue was achieved either by crystallization or by silica gel chromatography. The typical yields for the product formation varied between 85 and 92 %.

**Standard Operating Procedure 12: Introduction of an azide group via diazo transfer reaction**

a) Preparation of a trifluoromethansulfonylazide solution:

A solution of sodium azide (492mmol) in water (80mL) was prepared under $N_2$-atmosphere. To this stirred solution was added dichloromethane (100mL) at 0°C, followed by the addition of triflic anhydride (16.5 ml) over 10 min. The mixture was further stirred for 2 hours at 0°C, the organic layer was separated and the aqueous layer was extracted with dichloromethane (2x40 mL). The combined organic layers were washed with saturated, aqueous $NaHCO_3$ solution (80 mL), water (80 mL) and dried over $Na_2SO_4$. After filtration, this solution was directly used for the diazotransfer reaction.

b) Diazotransfer reaction:

To a solution of the starting material (26.0 mmol) and 4-*N,N'*-(dimethylamino)pyridine (14.5g) in acetonitrile (100mL) was added dropwise $TfN_3$-solution (85ml) at room temperature within 10 min. The reaction was stirred till complete conversion of the starting material into the product. The reaction mixture was concentrated *in vacuo* to 30 ml and suspended in chloroform. After filtration through a Celite pad, the filtrate was concentrated and the residue was purified by filtration through a short silica gel pad. The typical yields for the product formation varied between 85 and 95 %.

**Standard Operating Procedure 13: Hydrolysis of thioglycosides (NBS)**

The starting thioglycoside (33.4 mmol) was suspended in 240 ml Acetone and 18 ml of distilled water and stirred for 45 min at –20°C. After addition of NBS (155 mmol) stirring was continued at –20°C. After completion, the reaction was stopped by addition of $NaS_2O_3$ /$NaHCO_3$ (20 % aqueous solution , 1/1) and the mixture diluted with ethyl acetate, subsequently washed with water and saturated brine solution. The organic layer was dried over $Na_2SO_4$ and concentrated *in vacuo*. Final purification was achieved either by crystallization or by silica gel chromatography. The typical yields for the product formation varied between 75 and 90 %.

**Standard Operating Procedure 14: Hydrolysis of thioglycosides (NIS)**

The starting thioglycoside (33.4 mmol) was suspended in 240 ml Acetone and 18 ml of distilled water and stirred for 45 min at –20°C. After addition of NIS (56.8 mmol) and TMSOTf (2.84 mmol) stirring was continued until completion. The reaction was stopped by addition of $NaS_2O_3$ /$NaHCO_3$ (20 % aqueous solution , 1/1), diluted with ethyl acetate and washed with water and saturated brine solution. The organic layer was dried over $Na_2SO_4$ and concentrated *in vacuo*. Final purification was achieved either by crystallization (e.g. petroleum spirit/ ethylacetate) or by silica gel chromatography. The typical yields for the product formation varied between 79 and 92 %.

**Standard Operating Procedure 15: Chemoselective Oxidation to Uronic acids**

A solution of the starting material (20.0 mmol) in dichloromethane (141 ml) was cooled to 0°C and subsequently mixed with TEMPO (0.205 mmol in 12.8 ml dichloromethane), Aliquat 336 (12.8 ml of a 0.08 M solution in dichloromethane) and KBr (2.08 mmol in 4.17 ml $H_2O$) and stirring continued at 0°C. After 5 mins, a suspension of $Ca(OCl)_2$ (43.6 mmol) and $NaHCO_3$ (43.6 mmol) in 135 ml $H_2O$ was added within 15 mins to the reaction mixture and stirring at 0°C was continued till completion. The reaction was concentrated *in vacuo* and freeze dried. The crude residue was used as such for the next reactions.

**Standard Operating Procedure 16: Methyl ester formation on the Uronic acids**

The crude residue of the oxidation to the uronic acid was dissolved in 50 ml Toluene and 50 ml Methanol and titurated with $TMSCHN_2$-solution (2M in hexane) until completion. The reaction mixture was quenched with acetic acid to destroy excess of esterification reagent and evaporated *in vacuo*. Final purification was achieved by silica gel chromatography. The typical yields for the product formation varied between 65 and 80 % over the steps oxidation and esterification.

**Standard Operating Procedure 17: Regioselective 6-O-Benzoylation**

The starting material (32.04 mmol) was dissolved in dry dichloromethane (50 mL) and dry pyridine (10 mL) and cooled down to - 45°C. Benzoyl chloride ( 32.04 mmol) was added dropwise and stirring continued at - 45°C till completion. The reaction was concentrated *in vacuo* and coevaporated with toluene three times. The remaining residue was dissolved in dichloromethane and washed with 10% aqueous citric acid solution, saturated aqueous $NaHCO_3$ solution and saturated brine solution, dried over $Na_2SO_4$ and evaporated *in vacuo*. Final purification was achieved either by crystallization or by silica gel chromatography. The typical yields for the product formation varied between 75 and 94 %.

**Standard Operating Procedure 18: Common procedure for O-Benzoylation**

To a solution of the starting material (11.9mmol) and DMAP (13.6mmol) in 1,2-dichloroethane was added dropwise benzoylchloride (1.7g, 12.1mmol). at 0°C. The mixture was then left to stir until completion (dependent on the substrate between 20 to 55°C). Subsequently, the reaction mixture was diluted with dichloromethane and washed with water, 5% $NaHSO_4$ solution, saturated aqueous $NaHCO_3$ solution and saturated brine solution. The organic layer was dried over $MgSO_4$ followed by removal of the solvent *in vacuo* to give a crude residue. Final purification was achieved either by crystallization or by silica gel chromatography. The typical yields for the product formation varied between 80 and 96 %.

**Standard Operating Procedure 19:Common procedure for O-Acetylation**

To a suspension of the starting material (235 mmol, 3 acetylation sites) in pyridine (350 ml) at 0°C was added dropwise acetic anhydride (175 ml). After completion of the addition, the reaction was allowed to return to room temperature and stirred until completion. The reaction mixture was evaporated to dryness and 3x coevaporated with toluene. The residue was taken up in dichloromethane and washed with 5 % aqueous $NaHSO_4$-solution, saturated aqueous $NaHCO_3$-solution, water and saturated brine solution. The organic layer was dried over $MgSO_4$ and evaporated. Final purification of the residue

was achieved either by crystallization or by silica gel chromatography. The typical yields for the product formation varied between 88 and 98 %.

**Standard Operating Procedure 20: PDC-oxidation of alcohols to carboxylic acids**

The starting material (1.15 mol) was dissolved in anhydrous DMF (7.0 ml) and reacted with PDC (11.5 mmol) under stirring at room temperature until complete conversion into the uronic acid. The reaction mixture was subsequently poured into 50 ml water and the whole extracted with diethyl ether. The combined ether layers were washed with 10 % aqueous citric acid solution, filtered through a short silica gel pad, dried over $MgSO_4$, evaporated and dried under high vacuum.

**Standard Operating Procedure 21:Chemoselective 1-O-Benzoyl cleavage**

The starting material (36.8 mmol) was dissolved in dry DMF (80 ml) and cooled to 0°C. Subsequently, hydrazine acetate (44.06 mmol) was added and stirring continued until completion. After addition of acetone and acetic acid the reaction mixture was concentrated *in vacuo*. The residue was dissolved in dichloromethane and extracted with 10% aqueous citric acid solution, saturated $NaHCO_3$ solution, water and saturated brine solution, dried over $MgSO_4$, evaporated and dried under high vaccuum. Final purification was achieved either by crystallization or by silica gel chromatography. The typical yields for the product formation varied between 72 and 88 %.

**Standard Operating Procedure 22: Deacylation under Zemplen conditions**

The starting material (23.7 mmol) was suspended in dry MeOH (70 ml) and stirred for 30 mins at 0 °C. Subsequently, NaOMe (0.1 equiv. / O-Acyl group) was added (positive flush of $N_2$) and stirring was continued at 0° C until completion. Finally, the reaction was neutralized with 10 % aqueous HCl and the solvent evaporated. Final purification was achieved either by crystallization or by silica gel chromatography. The typical yield for the product formation varied between 90 and 98 %.

**Standard Operating Procedure 23: Introduction of the 4-Oxopentanoyl (=Levulinoyl) group**

a) Preparation of the $Lev_2O$ solution:

To a solution of DCC (31.2 mmol) in 100 mL dichloromethane was added levulinic acid (62.4 mmol) and DIPEA (62.42 mmol). The supernatant was used as such for the levulination reaction.

*Reaction*

The above $Lev_2O$ solution was added to a solution of the starting sugar (15.6 mmol) dissolved in 25 mL of dry dichloromethane and stirring was continued until completion. Subsequently, the reaction mixture was filtered through a Celite pad and all combined organic layers were extracted with 10 % aqueous citric acid solution, saturated aqueous brine solution, dried with $Na_2SO_4$ and concentrated. Final purification was achieved either by crystallization or by silica gel chromatography. The typical yields for the product formation varied between 85 and 96 %.

**Standard Operating Procedure 24:Cleavage of the 4-Oxopentanoyl (= Levulinoyl) group**

A solution of the starting sugar (1.28 mmol) and acetic acid (1.35 mL) in pyridine (5.0 mL) was cooled to 0 °C followed by addition of hydrazine hydrate (200 µL). Stirring at 0 °C was continued until completion and the reaction mixture diluted with dichloromethane, subsequently extracted with 10% aqueous citric acid, 10 % aqueous $NaHCO_3$ solution, saturated brine solution, dried over $Na_2SO_4$, filtered and concentrated. Final purification was achieved either by crystallization or silica gel chromatography. The typical yields for the product formation varied between 80 and 95 %.

**Standard Operating Procedure 25: Formation of Trichloroacetimidates**

a) with DBU:

A solution of the starting sugar (1.99 mmol) and trichloroacetonitrile (601 µL, 5.99 mmol) in 5 mL dry dichloromethane was stirred at room temperature for

30 min. The reaction mixture was then cooled to 0°C and DBU (100 μmol) added. Stirring was continued until completion (dependent on the substrate, stirring was performed from 0°C to 20°C). The reaction mixture was concentrated to one half of its volume and directly loaded on a short plug of silica gel and purified via silica gel chromatography. The typical yields for the product formation varied between 78 and 95 %.

b) with $K_2CO_3$:

A solution of the starting sugar (1.99 mmol) and trichloroacetonitrile (601 μL, 5.99 mmol) in 5 mL dry dichloromethane is stirred at rt for 30 min. The reaction mixture was then cooled down to 0°C and anhydrous $K_2CO_3$ (19.9 mmol) added. The reaction was stirred at 0°C till completion and then filtered through a celite pad. The filtrate was dried over $Na_2SO_4$ and evaporated. Final purification was achieved either by crystallization or by silica gel chromatography. The typical yield for the product formation varied between 78 and 95 %.

**Standard Operating Procedure 26: Regioselective introduction of a 6-O-*p*Methoxyphenyl group under Mitsunobu conditions**

A solution of the starting sugar (13.52 mmol), 4-methoxyphenol (20.3 mmol) and triphenylphosphine (20.3 mmol) in 85 ml dry dichloromethane was stirred at 0°C for 45 min. After addition of DEAD-reagent (22.9 mmol) at 0°C, the reaction mixture was further stirred at room temperature until completion, filtered through a celite pad, diluted with dichloromethane and extracted with 10 % aqueous $NaHCO_3$/NaOH solution (1/1), 10 % aqueous citric acid solution and aqueous saturated brine solution. The organic layer was dried over $Na_2SO_4$ and concentrated. Final purification was achieved by silica gel chromatography. The typical yield for the product formation varied between 70 and 89 %.

**Standard Operating Procedure 27: Cleavage of the *p*-Methoxyphenyl ether**

The starting material (1.18 mmol) was dissolved in 30 ml acetonitrile and 7.5 ml water and cooled to 0°C. Subsequently, CAN (3.83 mmol) was added and stirring continued at 0°C until completion. The reaction mixture was diluted with ethyl acetate and extracted with water. The aqueous layer was made alkaline by addition of solid $NaHCO_3$ and back extracted with ethyl acetate. The combined organic layers were extracted with saturated aqueous $NaHCO_3$ solution and saturated brine solution, dried over $MgSO_4$ and evaporated. Final purification was achieved by silica gel chromatography. The typical yields for the product formation varied between 73 and 89 %.

**Standard Operating Procedure 28: Cleavage of p-Methoxybenzyl ethers**

The starting material (0.60 mmol) was dissolved in 27 ml acetonitrile and 3.0 ml water and cooled to 0°C. Subsequently, CAN (4.5 equiv.) was added and stirring continued from 0°C to room temperature until completion. The reaction mixture was diluted with ethyl acetate and extracted with water. The aqueous layer was made alkaline by addition of solid $NaHCO_3$ and back extracted with ethyl acetate. The combined organic layers were extracted with saturated aqueous $NaHCO_3$ solution and saturated brine solution, dried over $MgSO_4$ and evaporated. Final purification was achieved by silica gel chromatography. The typical yields for the product formation varied between 73 and 85 %.

**Standard Operating Procedure 29: Formation of a 2,3-cyclic carbamate**

To a stirred solution of the starting material (3.56 mmol) in dichloromethane (100 ml) and 10% aqueous solution of $NaHCO_3$ (75 ml) was added a solution of triphosgene (1.25 mmol) in 10 ml dry dichloromethane. The reaction was stirred at room temperature till completion. The organic phase was washed with water, dried over $Na_2SO_4$, filtered and concentrated. Final purification was achieved either by crystallization or silica gel chromatography. The typical yield for the product formation varied between 75 and 95 %.

**Standard Operating Procedure 30: Cleavage of the N-phthaloyl group**

The N-phthaloylated starting material (45.9 mmol) was dissolved in *n*-butanol (200 ml) and treated with 1,2-diaminoethane (50 ml) at 100°C. After stirring at 100°C until completion, the reaction mixture was concentrated *in vacuo*, coevaporated with toluene three times and dried under high vacuum. Final purification was achieved by silica gel chromatography. The typical yield for the product formation varied between 78 and 92 %.

**Standard Operating Procedure 31: Introduction of a thiocresyl ether at the reducing end**

A solution of the 1-*O*-glycosyl acetate (10.48 mmol) and *p*-thiocresol (12.58 mmol) in dry dichloromethane (30ml) was stirred at 0°C and subsequently activated by the addition of boron trifluoride diethylether complex (12.58mmol) over 5 min. Stirring was continued (0°C → 20°C) until completion and the reaction stopped by the addition of triethyl amine (14.0 mmol). The reaction mixture was diluted with dichloromethane and extracted with saturated $NaHCO_3$-solution, water and saturated brine solution, dried over $MgSO_4$ and evaporated *in vacuo*. Final purification was achieved by crystallization or silica gel chromatography. The typical yield for the product formation varied between 81 and 92 %.

**Standard Operating Procedure 32: Glycosylation with thioglycosides**

**a) NIS-promoted glycosylation**

A mixture of glycosyl acceptor (1 mmol), thioglycoside (1 mmol) and 1.0 g of freshly activated molecular sieves in 20 ml of a dry solvent (e.g. $CH_3CN$, $CH_2Cl_2$, Toluene, Ether) was stirred for 45 min at r.t and cooled down to the reaction temperature. Subsequently, *N*-Iodosuccinimide (1.7 mmol) was added and stirring continued for 20 min at the reaction temperature. After the addition of a Lewis acid as promotor (e.g. TfOH, 85-170 µmol), stirring was continued at the reaction temperature until completion. The reaction mixture was quenched with triethyl amine, filtered through a celite pad and extracted with a 10 % aqueous $KHCO_3/Na_2S_2O_3$ solution, water and saturated brine solution, dried over $MgSO_4$ and evaporated. Final purification was achieved

by silica gel column chromatography. The typical yields for the product formation varied between 65 and 85 %.

**b) DMTST promoted glycosylations:**

A mixture of glycosyl acceptor (1 mmol), thioglycoside (1 mmol) and 1.0 g of freshly activated molecular sieves in 20 ml of a dry solvent (e.g. $CH_3CN$, $CH_2Cl_2$, Toluene, Ether) was stirred for 45 min at r.t and cooled down to the reaction temperature. Subsequently, DMTST (3-5 equiv.) was added stirring continued at the reaction temperature until completion. The reaction mixture was quenched with triethyl amine, filtered through a celite pad and extracted with aqueous $NaHCO_3$-solution, water and saturated brine solution, dried over $Na_2SO_4$, concentrated *in vacuo* and purified by silica gel column chromatography. The typical yields for the product formation varied between 50 and 85 %.

**Standard Operating Procedure 33:**

Glycosylations with trichloroacetimidates

A suspension of the trichloroacetimidate (1.54 mmol), glycosyl acceptor (11.3 mmol) and freshly activated molecular sieves (1.0 g) in an anhydrous solvent (e.g. $CH_3CN$, $CH_2Cl_2$, Toluene, Ether, 20 mL) was stirred at rt for 1 h and then cooled to reaction temperature. Subsequently, a catalytic amount of a promotor (e.g. TMSOTf, 0.01-0.1 equiv.) was added and stirring continued at reaction temperature until completion. The reaction was quenched with triethylamine) and filtered through a Celite pad. The combined organic layers were washed with aqueous $NaHCO_3$-solution and saturated brine solution, dried over $Na_2SO_4$, concentrated *in vacuo* and purified by silica gel column chromatography. The typical yields for the product formation varied between 50 and 85 %.

**Standard Operating Procedure 34:**
**Glycosylations using 2,3-cyclocarbamoyl protected *p*Thiocresyl glycosides as glycosyl donors**

PhSCl (0.2 mmol, 2 equiv.) in dry dichloromethane (1 ml) was added dropwise to a mixture of AgOTf (0.2 mmol) in dry dichloromethane (2 ml) at –78°C containing freshly activated molecular sieves 3 Å. After stirring for 15 mins at –78°C, a solution of the thioglycoside (0.1 mmol, 1 equiv.) and DTBMP (0.2 mmol, 2 equiv.) in dry dichloromethane (2 ml) was slowly added. After further stirring for 15 mins at –78°C, the glycosyl acceptor (0.2 mmol, 2 equiv.) in dry dichloromethane (1 ml) was slowly added and stirring continued until completion. The reaction was quenched with saturated aqueous $NaHCO_3$ solution (1 ml), warmed to rt and diluted with dichloromethane. The organic layer was dried over $MgSO_4$, filtered and evaporated. Final purification was achieved by silica gel chromatography. The typical yields for the product formation varied between 60 and 90 %.

**Standard Operating Procedure 35: Introduction of an Alloc-group**

A solution of starting material (2 mmol), dry pyridine (5 mmol) and dry THF (5 ml) was cooled to 0oC. Subsequently, Allylchloroformate (2.2 mmol) were added dropwise and stirring was continued until completion. The reaction mixture was diluted with dichloromethane and subsequently washed with 10 % aqueous citric acid solution, saturated $NaHCO_3$ solution, water and saturated brine solution. The organic layer was dried over $Na_2SO_4$, filtered and evaporated. Final purification was achieved either by crystallization or by silica gel chromatography. The typical yields for the product formation varied between 80 and 95 %.

**Standard Operating Procedure 36: Cleavage of an Alloc-group**

A mixture of the Allyloxycarbonate (1.17 mmol), dimedone (1.33 mmol) and $Pd(Ph_3P)_4$ (0.30 mmol) was dissolved in dry THF (60 ml) and stirred under Ar atmosphere until completion of the reaction. The reaction mixture was

concentrated in vacuo and purified by silica gel chromatography. The typical yields for the product formation varied between 78 and 97 %.

**Standard Operating Procedure 37: Lewis acid mediated benzylation**

To a stirred mixture of the starting material (1 mmol) and benzyl trichloroacetimidate in dry hexane/dichloromethane (10 ml, 2/1) was added Lewis acid (0.01-0.05 equiv., e.g. TMSOTf, TfOH) and stirring was continued at rt until completion. The reaction was quenched with triethyl amine and concentrated. Final purification was achieved by silica gel chromatography. The typical yields for the product formation varied between 50 and 92 %.

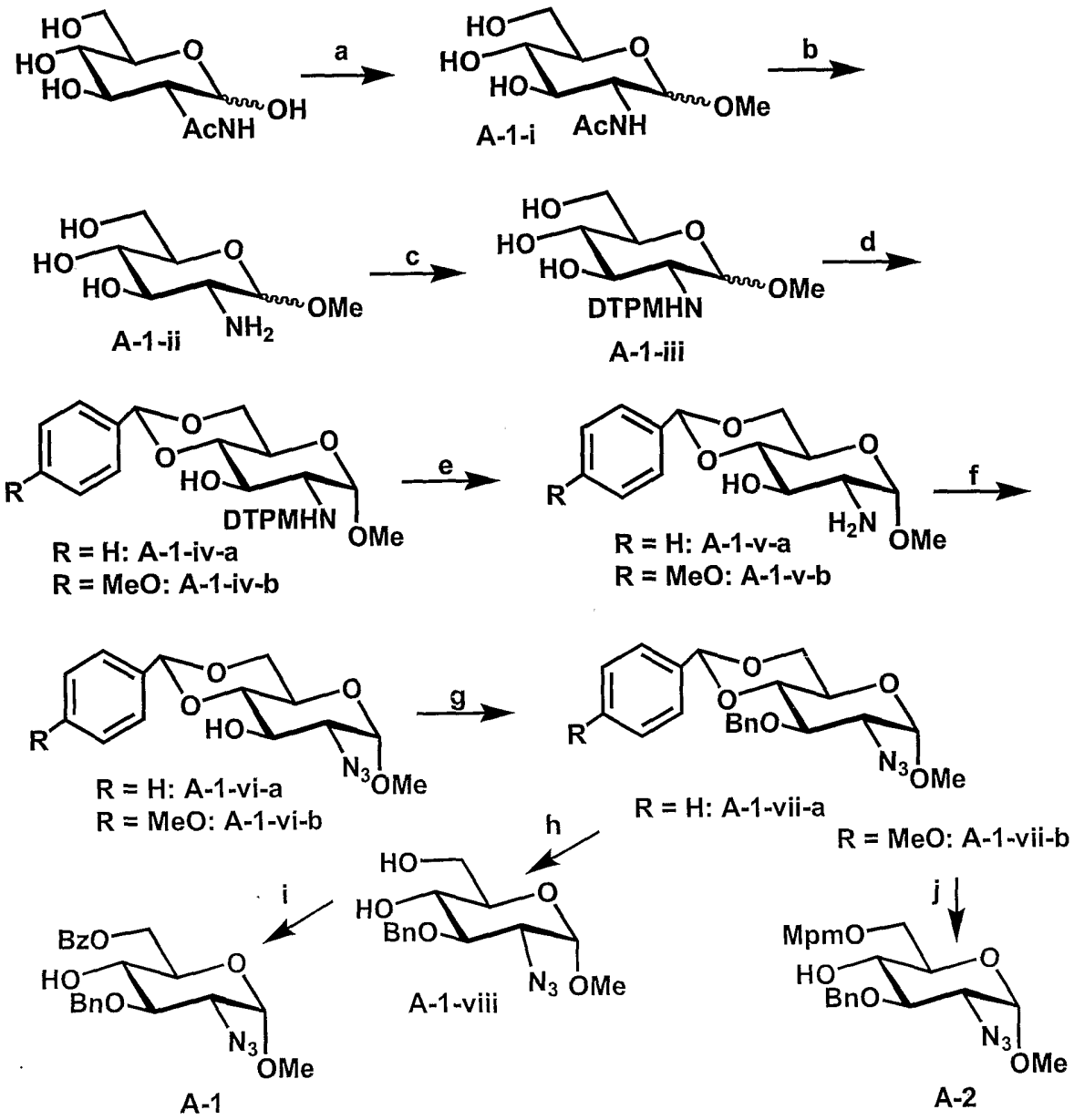
**Standard Operating Procedure 38: benzylation under mild basic conditions**

The starting material (3.49 mmol) was dissolved in dry DMSO (20 ml) and cooled to 0°C. To the stirred solution were added successively benzyl bromide (3.5 equiv./OH-group), barium oxide (1.5 equiv/OH-group), catalytic amounts of TBAI ( 0.05 eqiv./OH-group) and potassium hydroxide (3.5 equiv./ OH-group). Stirring was continued from 0°C to rt until completion. The reaction was quenched with methanol, and further stirred for 30 min. After dilution with ether, the organic layer was washed with water and brine solution, dried over $MgSO_4$ and concentrated in vacuo. Final purification was achieved by silica gel chromatography.

**Standard Operating Procedure 39: Ester cleavage under aqueous conditions**

The starting material (0.3mmol ester groups) was dissolved in 11.8 ml of a mixture of water and THF (3:7), cooled to 0°C and reacted with 1M aqueous NaOH-solution (5.0 ml). Stirring was continued until completion and the reaction mixture titurated with 10 % aqueous HCl-solution to a pH of 9.5. After evaporation of the THF, the mixture was freeze dried and the remaining residue purified by silica gel chromatography to yield the product. The typical yields for the product formation varied between 85 and 95 %.

Example 1: Synthesis of Building Blocks **A-1** and **A-2** from *N*-Acetyl Glucosamine




Example 1: Synthesis of building blocks **A-1** and **A-2** from *N*-Acetyl glucosamine, yields are reported for R=H, conditions; a) Amberlyte IR 120 ($H^+$), MeOH, 60 °C, (70 %); b) 1M NaOH, 120°C; c) 1. SOP 10; 2. $Ac_2O$, pyridine; 3. NaOMe, MeOH (70 %, 4 steps); d) SOP 1 (80 % for R=H) or SOP 2 for R = OMe; e) SOP 11; f) SOP 12, (85 %, 2 steps); g) SOP 7, (92 %); h) SOP 4, (91 %); i) SOP 17, (85 %); j) SOP 5.

Preparation of **A-1-i:**

*N*-Acetyl-2-deoxy-α/β-D-glucopyranoside (8.5 g, 38.4mmol) was suspended in 100 ml dry methanol. Subsequently, 12.0 g Amberlite IR 120 iron exchange resin ($H^+$-form) was added and the reaction mixture refluxed for 70 hrs at 65°C. After cooling to 25 °C, the iron exchange resin was removed by filtration and several times extracted with methanol. The combined methanol layers were neutralized with triethyl amine and concentrated *in vacuo*. The crude residue was purified by crystallization to furnish the title compound in 70 % yield (α/β -mixture).

Preparation of **A-1-iii**:

Methyl glycoside **A-1-i** (20.6 mmol) was suspended in 100 ml aqueous NaOH solution (1 M) and stirred under reflux at 120°C until completion. After cooling and neutralization with 10 % aqueous HCl, the mixture was concentrated *in vacuo* and crude **A-1-ii** suspended in 200 ml methanol and reacted with *N*-[(1,3-dimethyl-2,4,6 (1H,3H,5H)-trioxopyrimidin-5-ylidene) methyl]-*N',N''*-dimethylamine (23.6 mmol) at 50°C (pH ~ 9.0) until completion. After evaporation and drying, crude **A-1-iii** was reacted with 150 mL acetylation mixture (pyridine/$Ac_2O$, 2/1, v/v) until completion, concentrated in vacuo, coevaporated with toluene and dried. The residue was suspended in ethyl acetate and extracted with water, 10 % aqueous HCl, saturated, aqueous $NaHCO_3$ solution and $H_2O$, dried over $Na_2SO_4$ and concentrated. The crude residue was dissolved in dry methanol and reacted with a catalytic amount of NaOMe. After completion, the reaction was neutralized with Amberlite IR 120 and filtered. The organic layer was evaporated and dried to furnish the title compound **A-1-iii** in 70 % yield (over 4 steps).

Preparation of **A-1-iva**:

Methyl-2-deoxy-2-N-[1-(1,3-dimethyl-2,4,6(1H, 3H, 5H)-trioxopyrimidin-5-ylidene) methyl]-α-D-glucopyranoside **A-1-iii** (16.0 g, 44.5mmol) in acetonitrile (200ml) was reacted with benzaldehyde dimethyl acetal (14.0 ml, 89.0 mmol) and a catalytic amount of *p*-toluenesulphonic acid monohydrate. After 2 hours at 55° C, the mixture was neutralized and evaporated. The remaining residue

was extracted, washed and evaporated. Yield: 18.3 g (92 %), $R_f$ = 0.20 (1,2-dichloroethane/ ethylacetate = 7/3).

Preparation of **A-1-va**:

Methyl-4,6-O-benzylidene-2-deoxy-2-N-[1-(1,3-dimethyl-2,4,6(1H, 3H, 5H)-trioxopyrimidin-5-ylidene) methyl]-α-D-glucopyranoside **A-1-iva** (18.30 g, 40.94 mmol) in DMF (50ml) was reacted with ethylenediamine (20ml) at room temperature. After stirring for 35 minutes, the mixture was concentrated. Yield: 10.90 g (94.7 %), $R_f$ = 0.18 (chloroform/methanol = 9/1).

Preparation of **A-1-via**:

To a solution of methyl-2-amino-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (7.5 g, 26.0 mmol) and 4-*N,N'*-(dimethylamino)pyridine (14.5g) in acetonitrile (100mL) was added $TfN_3$-solution (85ml) at room temperature. The reaction mixture was concentrated and the residue was purified by filtration through a short silica gel pad. Yield: 7.00 g (85.3 %), $R_f$ = 0.18 (chloroform/ methanol = 9/1).

Preparation of **A-1-viia**:

Methyl 2-azido-2-*deoxy*-4,6-benzylidene-α-D-glucopyranoside **A-1-via** (10.87g, 35.41mmol) in *N,N'*-dimethylformamide (50mL) was reacted with NaH (95 %, 0.92g, 42.49mmol) and benzyl bromide (5.47 ml, 45.9 mmol). After completion, the excess of NaH was quenched, followed by concentration. The residue was extracted, washed and concentrated. Yield: 12.93 g (92.0 %), $R_f$ = 0.37 (petroleum spirit/ethyl acetate = 3/1).

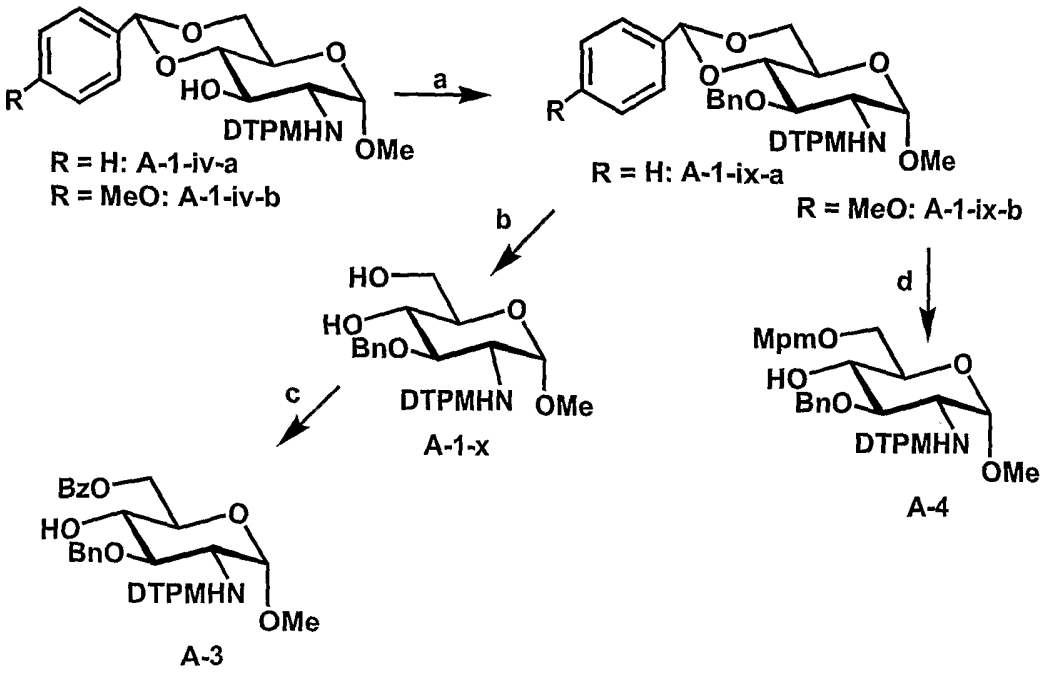
Preparation of **A-1**:

Methyl-2-azido-3-O-benzyl-2-deoxy-α-D-glucopyranoside (9.87g, 32.04mmol) in dichloromethane (50 mL) and pyridine (10 mL) was treated with benzoyl chloride (3.72mL, 32.04 mmol) at - 45°C for 2 hours. The reaction was concentrated and the residue extracted, washed and evaporated. Yield: 10.78 g (81.7 %), $R_f$ = 0.31 (petroleum spirit/ ethylacetate = 1/1).

Compound **A-1**:

$^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 8.03 (d, 2 H, Aryl), 7.57 (m, 1H, Aryl), 7.45-7.29 (m, 7H, Aryl), 4.93 (d, 1H, $J_{gem}$ = 10.8 Hz, $OCH_2$), 4.82 (d, 1H, $J_{gem}$ = 10.8 Hz, $OCH_2$), 4.81 ( d, 1H, $J_{1,2}$ = 3.6 Hz, H-1$\alpha$), 4.73 (dd, 1H, $J_{5,6a}$ = 4.4 Hz, $J_{gem}$ = 12.0 Hz, H-6a), 4.47 (dd, 1H, $J_{5,6b}$ = 2.0 Hz, H-6b), 3.85 ( dd, 1H, $J_{3,4}$ = 8.8 Hz, H-3), 3.57 ( ddd, 1H, $J_{4,5}$ = 10.0 Hz, H-4), 3.45 (s, 3H, OMe), 3.37 ( dd, 1H, $J_{2,3}$ = 10.0 Hz, H-2), 2.80 (bs, 1H, 4-OH).

Example 2: Synthesis of Building Blocks **A-3** and **A-4**

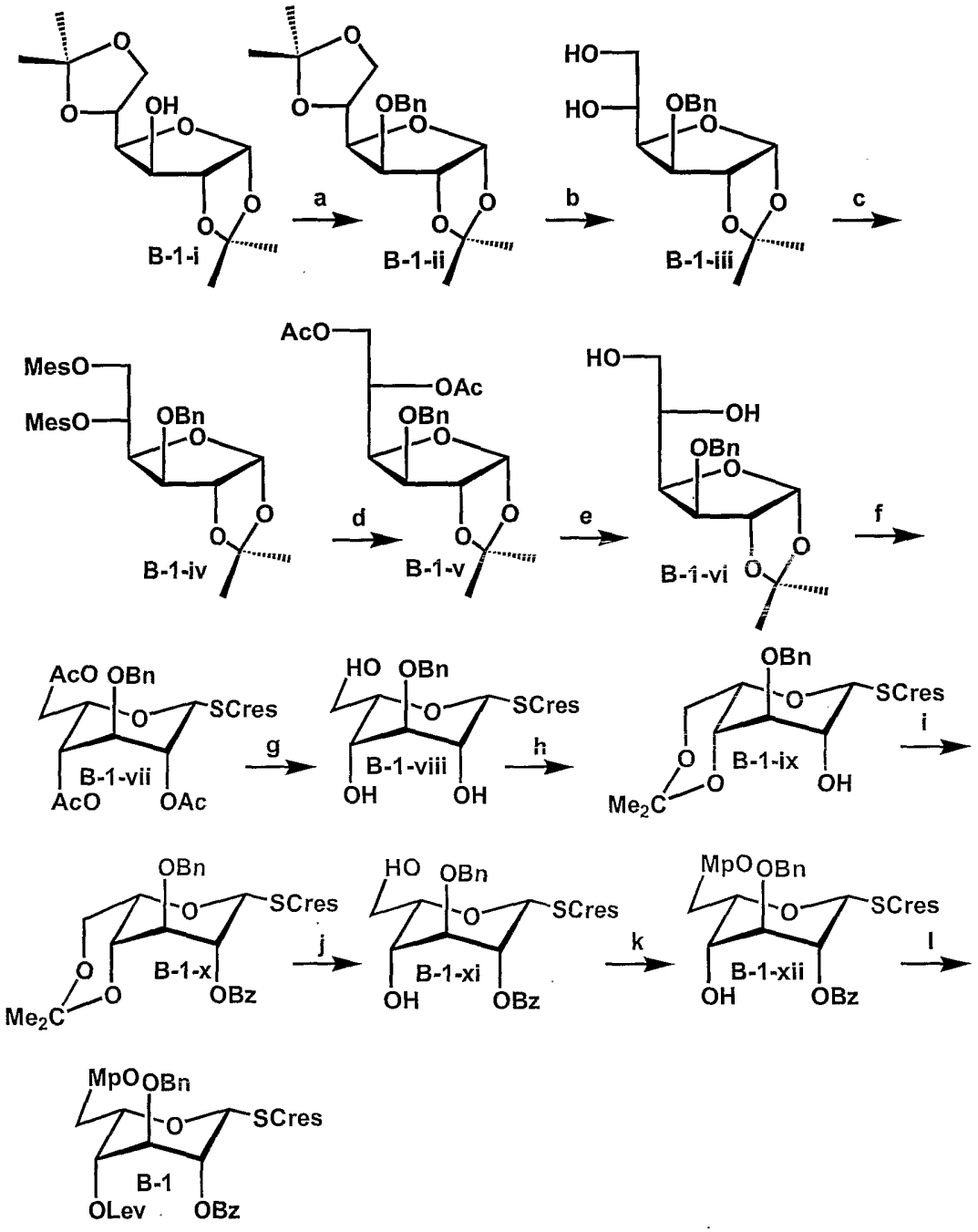



Example 2: Synthesis of building block **A-3** and **A-4**, conditions: a) SOP 7, (72 % for R = H); b) SOP 4, (82 %); c) SOP 17, (84 %); d) SOP 5.

Compound **A-3**:

$^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 10.16 (dd, 1 H, $J_{NH,2}$ = 9.4 Hz, $J_{NH,=C-H}$ = 14.0 Hz, NH), 8.11 (d, 1H, =C-H), 7.68-7.22 (3m, 8H, Aryl), 4.84 ( d, 1H, $J_{1,2}$ = 3.5 Hz, H-1$\alpha$), 4.83 (dd, 1H, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6a}$ = 3.5 Hz, H-6a), 4.73 (d, 1H, $J_{gem}$ = 11.7 Hz, $OCH_2$), 4.46 (dd, 1H, $J_{5,6b}$ = 2.1 Hz, H-6b), 3.91 (m, 1H, H-5), 3.72 (dd, 1H, $J_{3,4} \approx J_{2,3}$ = 8.8 Hz, H-3), 3.57 (ddd, 1H, $J_{4,5}$ = 9.5 Hz, H-4), 3.48 (s, 3H, OMe), 3.38 (ddd, 1H, $J_{2,3}$ = 10.5 Hz, H-2), 3.32 (s, 3H, NMe), 3.31 (s, 3H, NMe), 3.05 (bs, 1H, 4-OH).

Example 3: Synthesis of L-ido configured glycosyl donor **B-1**




Example 3: Synthesis of Building Block **B-1**, conditions: a) SOP 7, (95%); b) 60% aqueous Acetic acid, 60°C (90%); c) Methanesulfonyl chloride, Pyridine, 0°C-RT (87 %); d) Cesium Acetate, $Ac_2O$, 120°C (95%); e) SOP 22, (92%); f) 1. 90% TFA, O°C; 2. $Ac_2O$, Pyridine; 3. SOP 31, (73%, 3 steps); g) SOP 22, (98%); h) SOP 3, (92%); i) SOP 18, (98%); j) 80% acetic acid, 100°C (98%); k) SOP 26, (89%); l) SOP 23, (98%).

Preparation of **B-1-iii**:

**B-1-ii** (15.60 mmol) was dissolved in 60 % aqueous acetic acid (50 ml) and stirred at 60 °C until completion. After neutralization with solid $NaHCO_3$, the mixture was evaporated and co evaporated with toluene. Crude **B-1-iii** was dissolved in $CHCl_3/H_2O$, the organic layer separated, dried over $Na_2SO_4$ and evaporated. The remaining residue was purified by a short silica gel chromatography to yield **B-1-iii** in 90 % (4.43 g).

Preparation of **B-1-iv**:

17.72 mmol of **B-1-iii** was dissolved in 25 ml dry pyridine, to which mesyl chloride (methylsulfonyl chloride, 42.5 mmol) was added dropwise at 0°C. The mixture was stirred at 4°C until completion and was subsequently poured into warm water (50°C, 90 ml), cooled and the precipitate isolated by filtration. **B-1-iv** was obtained after drying in 87 % yield (7.23 g).

Preparation of **B-1-v**:

**B-1-iv** (6.43 mmol) and cesium acetate (64.3 mmol) were suspended in 25 ml acetic anhydride and refluxed at 125 °C until completion. The reaction mixture was concentrated *in vacuo,* co evaporated with toluene and the residue extracted from ethyl acetate/$H_2O$ (1/1). The organic layer was collected and washed with saturated aqueous $NaHCO_3$ solution and saturated brine solution, dried over $Na_2SO_4$ and evaporated. Purification was achieved by silica gel chromatography. Yield: 2.68 g (95 %).

Preparation of **B-1-vii**:

**B-1-vi** (5.61 mmol) was dissolved in aqueous TFA (90 %, 15 ml) and further stirred at 0°C until completion. The reaction mixture was neutralized with aqueous NaOH solution at 0°C, concentrated *in vacuo* and dried. The residue was suspended in 90 ml acetylation mixture (pyridine/acetic anhydride = 2/1) and 50 ml dichloromethane at 0°C and further stirred until completion. After concentration *in vacuo* and co evaporation with toluene, the residue was dissolved in ethyl acetate/$H_2O$ (1/1), the organic layer collected and washed

with 10 % aqueous citric acid solution, saturated aqueous $NaHCO_3$ solution and brine solution, dried over $Na_2SO_4$ and evaporated. The crude residue and *p*-thiocresol (6.0 mmol) were dissolved in 40 ml anhydrous dichloromethane and cooled to 0°C, reacted with $BF_3xOEt_2$ (8.41 mmol) and further stirred at rt until completion. The reaction was stopped with saturated $NaHCO_3$ solution and the organic layer was washed with water, dried over $Na_2SO_4$ and evaporated. Final purification was achieved by silica gel chromatography to yield **B-1-vii** in 73 % over 3 steps.

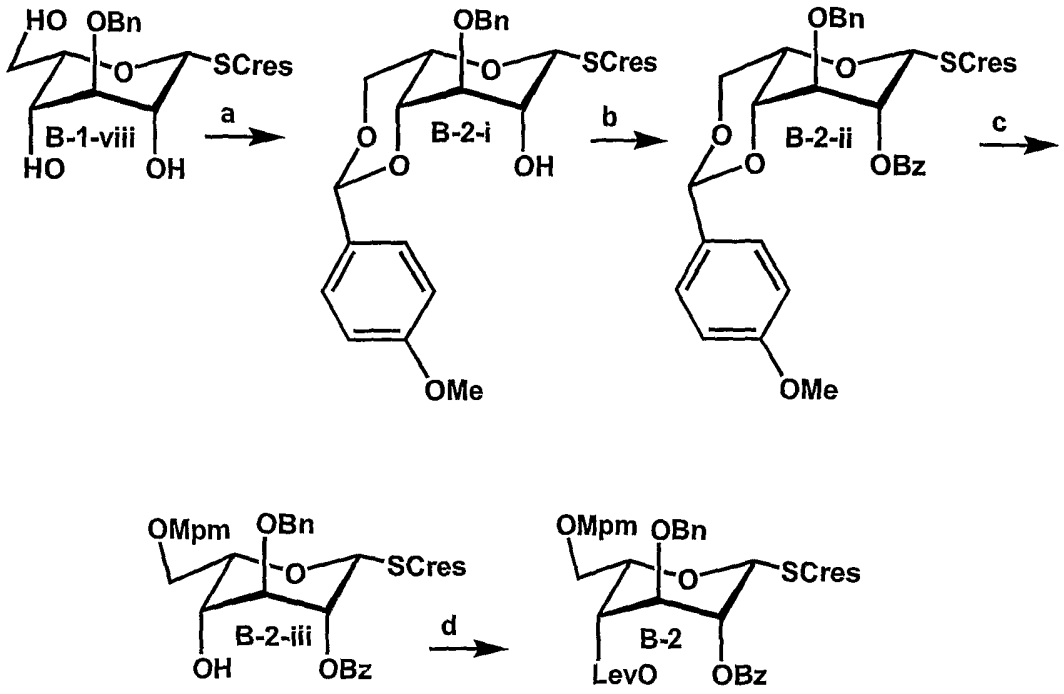
Preparation of **B-1-xi**:

**B-1-x** (8.0 mmol) was dissolved in 80 % aqueous AcOH and heated at 100°C until completion. The mixture was cooled to rt, neutralized with solid $NaHCO_3$ and dissolved in ethyl acetate/water (1/1). After removal of the aqueous layer, the organic layer was dried over $MgSO_4$ and evaporated to dryness furnishing **B-1-xi** in 98 % yield.

Compound **B-1**:

$^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 8.07 (d, 2H, Aryl), 7.57-7.30 (m, 10H, Aryl), 7.10 (d, 2 H, Aryl), 6.88-6.81 (m, 4H, Mp), 5.55 (d, 1H, $J_{1,2}$ < 1.5 Hz,H-1β), 5.45 (m, 1H, H-2), 5.26 (ddd, 1H, H-5), 5.13 (m, 1H, H-4), 4.91 (d, 1H, $J_{gem}$ = 12.1 Hz, $OCH_2$), 4.78 (d, 1H, $J_{gem}$ = 12.1 Hz, $OCH_2$), 4.16 (dd, 1H, $J_{gem}$ = 9.6 Hz, $J_{5,6a}$ = 7.6 Hz, H-6a), 4.08 (dd, 1H, $J_{5,6b}$ = 5.2 Hz, H-6b), 3.93 (m, 1H, H-3), 3.77 (s, 3H, $OCH_3$), 2.58-2.36 (m, 4H, $(CH_2)_2$ Lev), 2.32 (s, 3H, $SCH_3$), 2.05 (s, 3H, $CH_3C$=O).

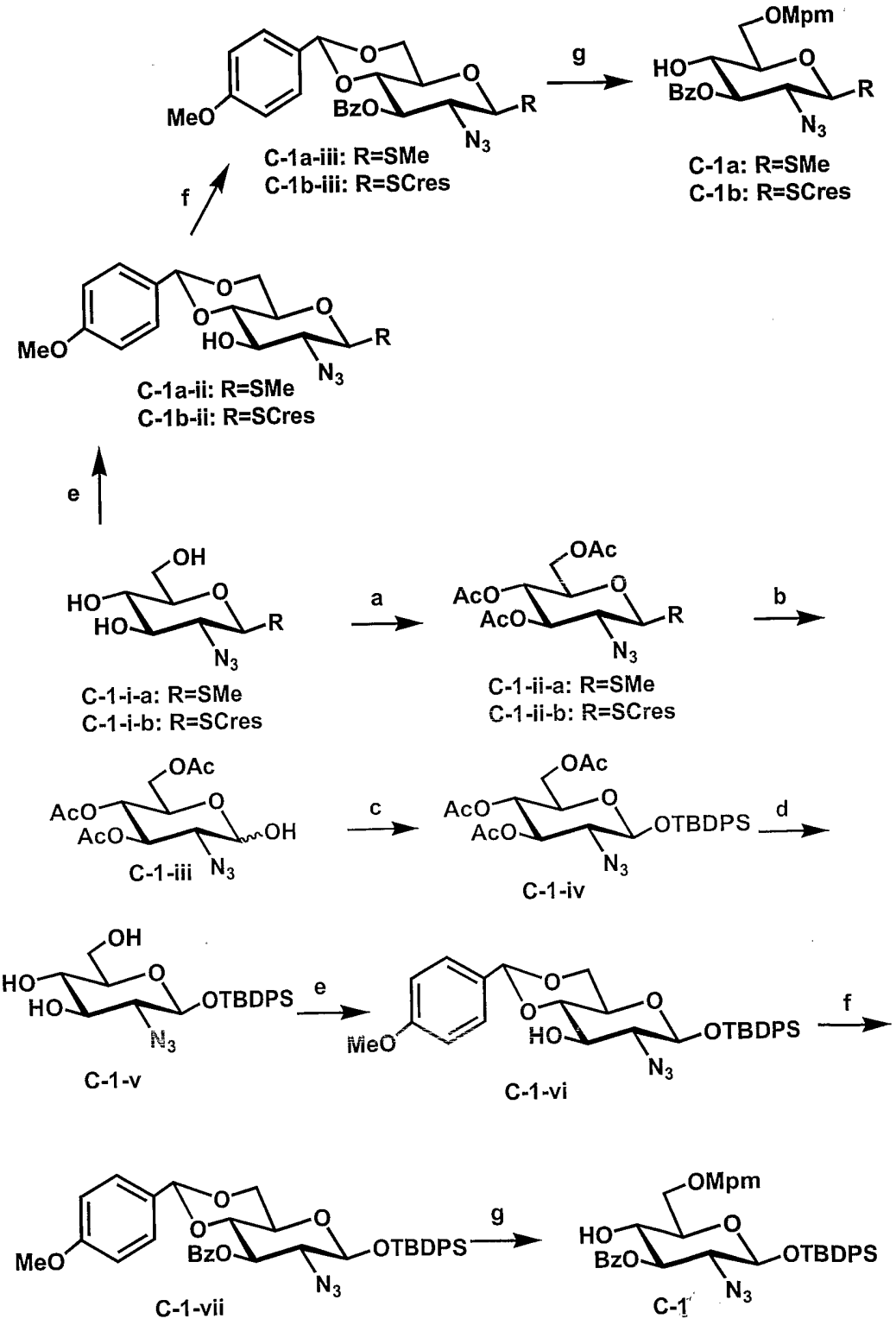
Example 4: Synthesis of L-ido configured glycosyl donor **B-2**.




Example 4: Synthesis of L-ido configured glycosyl donor **B-2**; a) SOP 2; b) SOP 18; c) SOP 5; d) SOP 23.

5

Example 5: Synthesis of Building Block **C-1, C-1a** and **C-1b**



Example 5: Synthesis of Building Blocks **C-1**, **C-1a** and **C-1b**, conditions: a) SOP 19; b) SOP 13, (78 %, 2 steps); c) SOP 8, (91 %); d) SOP 22; e) SOP 2, (85%, 2 steps for **C-1-vi** ); f) SOP 18; g) SOP 5, (75 %, 2 steps for **C-1**).

Preparation of **C-1-iia**:

To methyl 2-azido-2-deoxy-1-thio-β-D-glucopyranoside. (10g, 42.55 mmol) in pyridine (50ml) at O°C was added acetic anhydride (20g) and the reaction stirred for 1 hour. The reaction mixture was evaporated to dryness and the residue extracted to give the title triacetate (15.23g, quantitative,), $R_f$=0.7 ($CHCl_3$/Petroleum ethers, 1 :1).

Preparation of **C-1-iii**:

To a solution of methyl 3,4,6-tri-O-acetyl-2-azido-2-deoxy-1-thio-β-D-glucopyranoside in wet acetone (200ml) was added NBS (3 equiv.). The resulting mixture was allowed to stir for 2h. The mixture was then quenched, concentrated and the residue purified by silica gel chromatography to give the title hemiacetal as an oil (10.1g, 78%), $R_f$ = 0.5 (EtOAc/Petroleum ether, 1:1).

Preparation of **C-1-vi**:

A mixture of 2-azido-2-deoxy-β-D-glucopyranosyl *tert*-butyldiphenylsilane (5.5g,12.42 mmol), 4-methoxybenzaldehyde dimethylacetal (4.4g, 24mmol), and 4-toluenesulphonic acid (100mg, ) in acetonitrile/DMF (200ml, 5:3) were heated at 60°C for 1 hour. The reaction mixture was then neutralized and evaporated to give the crude compound as an oil. The residue was purified by silica chromatography to give the product (6.7g, 96%, 85% from C-1-iv); $R_f$ = 0.8 (dichloromethane/Petroleum ethers; 10:2).

Preparation of **C-1-vii**:

A mixture of DMAP (1.63, 13.6mmol) and benzoyl chloride (1.7g, 12.1mmol) and 2-azido-2-deoxy-4,6-O-(4-methoxybenzylidene)-β-D-glucopyranosyl *tert*-butyldiphenylsilane (6.7g, 11.9mmol) in 1,2-dichloroethane (100ml) was stirred at 60°C for 1h. The reaction mixture was quenched, extracted, washed and concentrated to give a crude residue. The residue was passed through a plug of silica to give the product (5.5g, 69%); $R_f$ = 0.7 (dichloromethane/Petroleum ethers; 4:1).

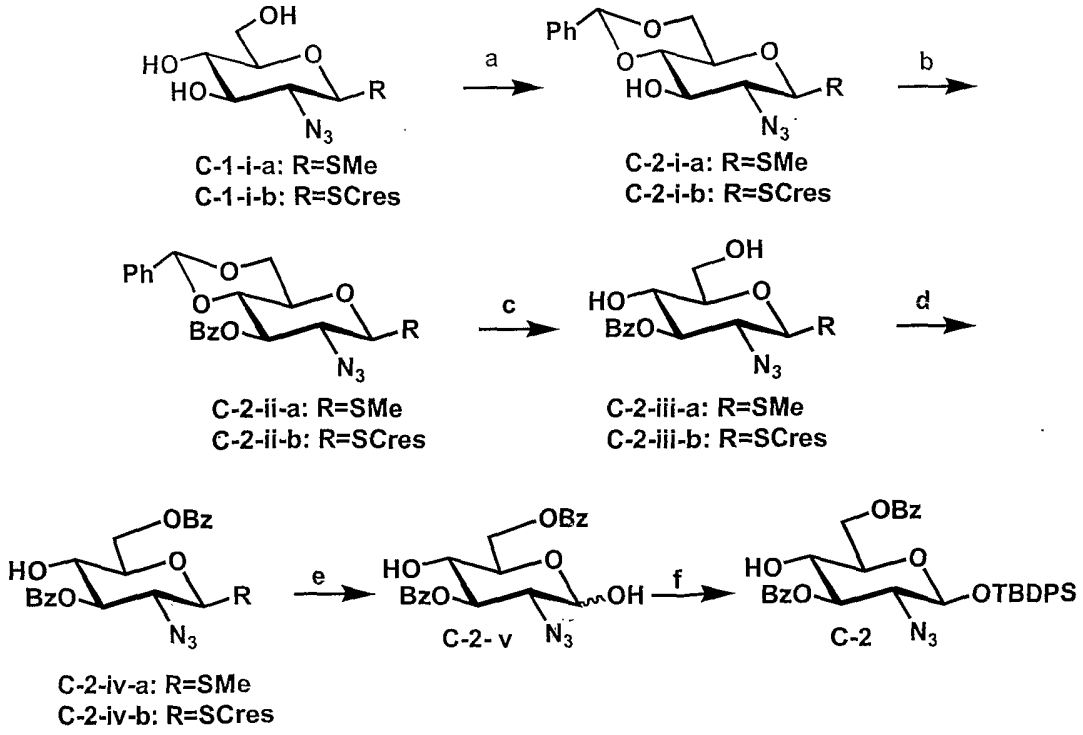
Preparation of **C-1**:

To a mixture of 2-azido-2-deoxy-3-O-benzoyl-4,6-O-(4-methoxybenzylidene)-β-D-glucopyranosyl *tert*-butyldiphenylsilane (10g, 15mmol), sodiumcyanoborohydride (5g, 80mmol) and molecular sieves in DMF (200ml) at 0°C was added trifluoroacetic acid (28g, 247mmol) at 0°C and then left to run overnight at rt. The reaction mixture was quenched, filtered and concentrated and the residue purified by column chromatography to give the title compound (7.0g, 70% ), $R_f$ = 0.4 (ethylacetate/petroleum ethers, 3:7).

Compound **C-1**:

$^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 8.08 (d, 2 H, Aryl), 7.72 (m, 4 H, Aryl), 7.59 (m, 1 H, Aryl), 7.47 (m, 3 H, Aryl), 7.42 (m, 2 H, Aryl), 7.34 (m, 3 H, Aryl), 7.13 (d, 2 H, Mpm) 6.83 (d, 2H, Mpm), 4.96 (dd, 1 H, $J_{2,3} \approx J_{3,4}$ = 9.7 Hz, H-3), 4.53 (d, 1 H, $J_{1,2}$ = 7.6 Hz, H-1β), 4.37 (2d, 2 H, $OCH_2$), 3.83 (ddd, 1 H, H-4), 3.79 (s, 3 H, $OCH_3$), 3.65 (dd, 1 H, H-2), 3.53 (dd, 1 H, $J_{gem}$ = 10.8 Hz, $J_{5,6a}$ = 4.1 Hz, H-6a), 3.46 (dd, 1 H, $J_{5,6b}$ = 4.1 Hz, H-6b), 3.12 (m, 1 H, H-5), 3.02 (d, 1 H, $J_{4,OH}$ = 3.5 Hz, 4-OH), 1.12 (s, 9 H, $C(CH_3)_3$).

Example 6: Synthesis of Building Block **C-2**

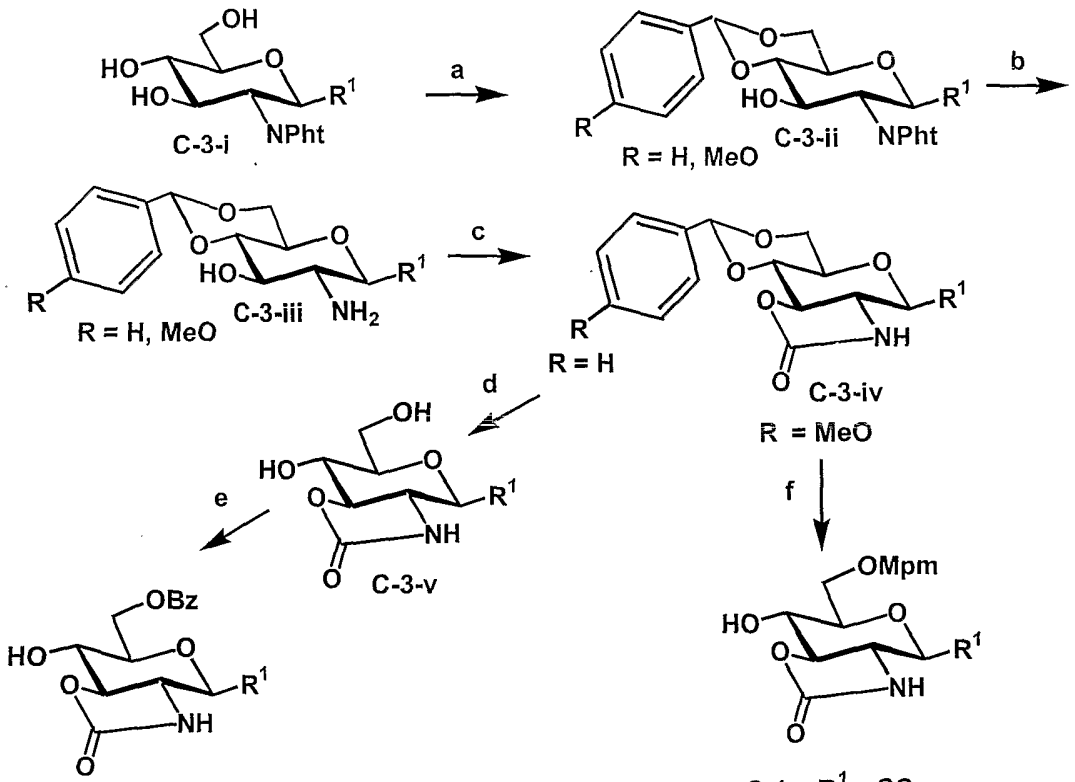


Example 6: Synthesis of Building Block **C-2**, conditions: a) SOP 1, (90% for R=SMe); b) SOP 18, (87% for R=SMe); c) SOP 4, p-TosOH, MeOH, $CH_3CN$ (86% for R=SMe); d) SOP 17, (92% for R=SMe); e) SOP 13, (94%); f) SOP 8, (82%).

Compound **C-2**:

$^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 8.09 (d, 2 H, Aryl), 7.97 (d, 2 H, Aryl), 7.72 (m, 4 H, Aryl), 7.60 (m, 1 H, Aryl), 7.50-7.27 (m, 11 H, Aryl), 4.98 (dd, 1 H, $J_{2,3} \approx J_{3,4}$ = 9.7 Hz, H-3), 4.58 (d, 1 H, $J_{1,2}$ = 7.8 Hz, H-1β), 4.51 (dd, 1 H, $J_{gem}$ = 11.3 Hz, $J_{5,6a}$ = 4.7 Hz, H-6a), 4.36 (dd, 1 H, $J_{5,6b}$ = 2.2 Hz, H-6b), 3.72-3.68 (m, 2 H, H-2, H-4), 3.31 (m, 1 H, H-5), 3.23 (d, 1 H, $J_{4,OH}$ = 4.5 Hz, 4-OH), 1.13 (s, 9 H, $C(CH_3)_3$).

Example 7: Synthesis of several carbamoylated Building Blocks **C-3a** to **C-3d** and **C-4a** to **C-4d**, containing a 6-O benzoyl or 6-O-p-methoxybenzyl protection

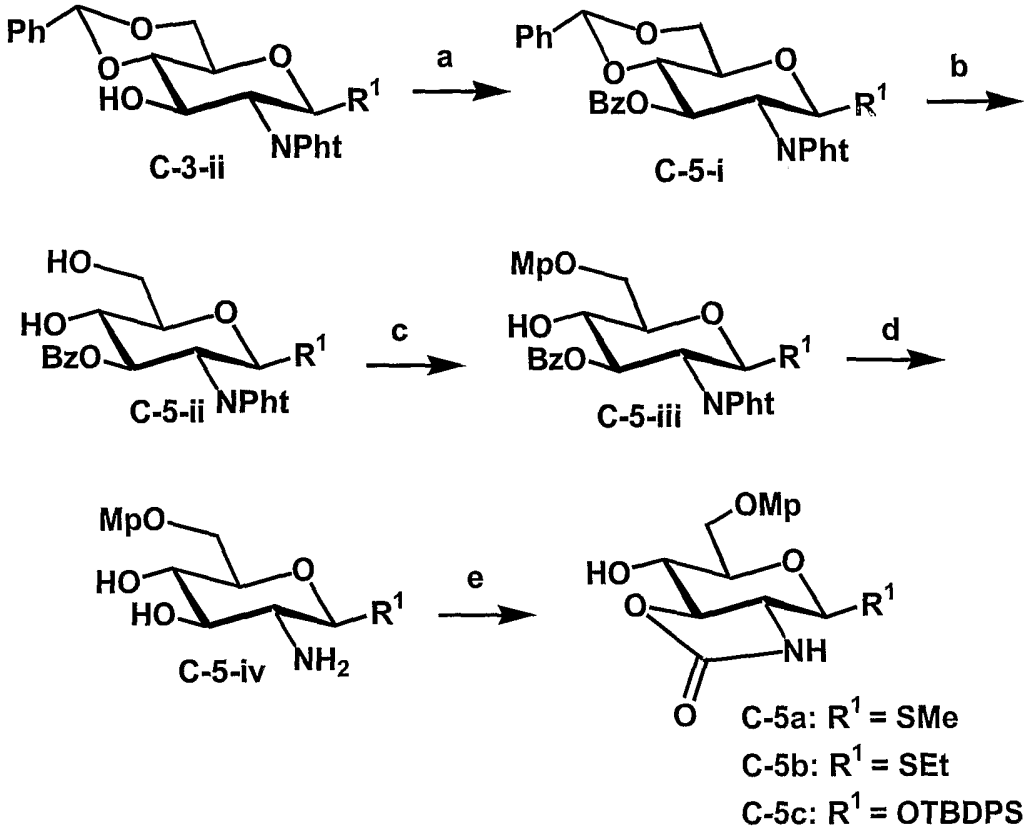


Example 7: Synthesis of several carbamoylated building blocks **C-3a** to **C-3d** and **C-4a** to **C-4d**, containing a 6-O-benzoyl or 6-O-p-methoxybenzyl protection, conditions: a) R = MeO: SOP 2; R = H: SOP 1, (82 %, $R^1$ = SCres, R = H); b) SOP 30, (87 %, $R^1$ = SCres, R = H); c) SOP 29, (95 %, $R^1$ = Scres, R = H); d) SOP 4, (72 %, $R^1$ = SCres); e) SOP 17, (85 %); f) SOP 5.

Compound **C-3a**:

$^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 8.06 (d, 2 H, Aryl), 7.62 (m, 1 H, Aryl), 7.48 (t, 2 H, Aryl), 7.38 (d, 2 H, Aryl), 6.97 (d, 2 H, Aryl), 5.06 (bs, 1H, NH), 4.79 (dd, 1H, $J_{gem}$ = 12.0 Hz, $J_{5,6a}$= 3.6 Hz, H-6a), 4.70 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1β), 4.63 (dd, 1H, $J_{5,6b}$ = 2.0 Hz, H-6b), 4.18 (dd, 1H, $J_{2,3} \approx J_{3,4}$ = 10.4 Hz, H-3), 3.89 (dd, 1H, $J_{4,5}$ = 9.2 Hz, H-4), 3.72 (m, 1H, H-5), 3.23 (ddd, 1H, H-2), 3.12 (bs, 1H, 4-OH), 2.29 (s, 3H, $SCH_3$).

Example 8: Synthesis of several 6-OMp and cyclic 2,3-carbamoyl protected building blocks **C-5a** to **C-5c**

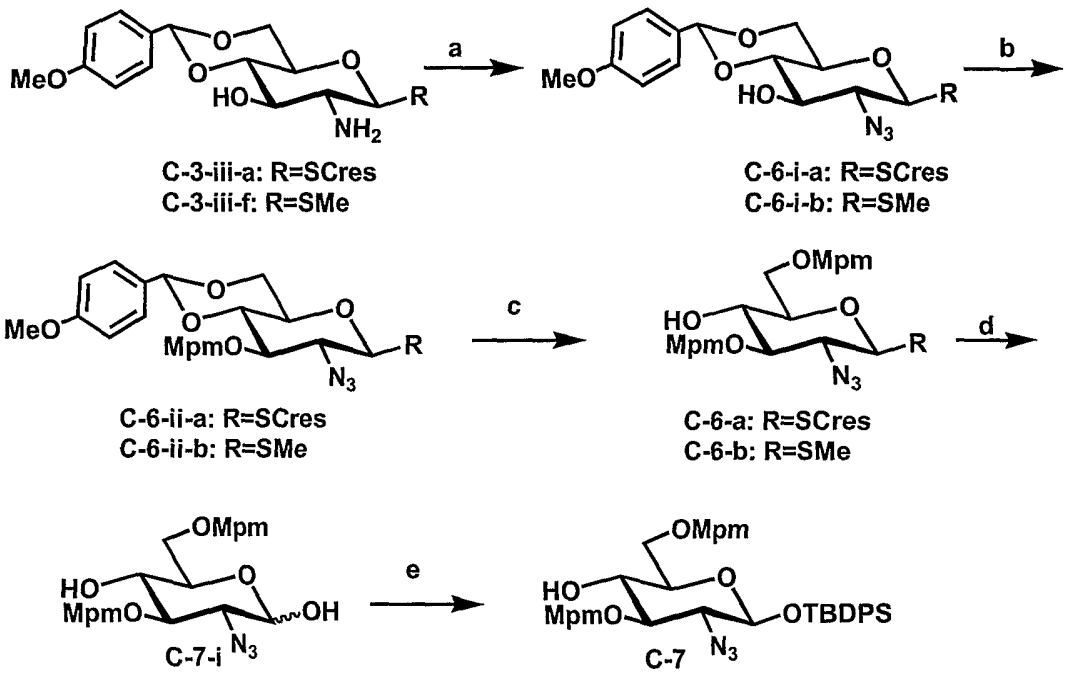



Example 8: Synthesis of several 6-OMp and cyclic 2,3-carbamoyl protected building blocks **C-5a** to **C-5c**, conditions: a) SOP 18, (92 % for $R^1$ = OTBDPS); b) SOP 4, (82 %); c) SOP 26, (75 % for $R^1$ = OTBDPS); d) SOP 30, (87 %); e) SOP 29, (95 %).

Compound **C-5c**:

$^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 7.69 (m, 2 H, Aryl), 7.63 (m, 2H, Aryl), 7.46-7.31 (m, 6H, Aryl), 6.82 (bs, 4H, Mp), 5.04 ( bs, 1H, NH), 4.78 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1β), 4.15-4.10 (m, 3H, H's not assigned), 3.97 (dd, 1H, J =11.6 Hz, J = 9.6 Hz, H not assigned), 3.78 (s, 3H, OMe), 3.56 (m, 1H, H not assigned), 3.48 (m, 1H, H not assigned), 2.80 (bs, 1H, 4-OH), 1.08 (s, 9H, C-$(CH_3)_3$).

Example 9: Synthesis of Building Blocks **C-6-a** and **C-6-b** and **C-7**




Example 9: Synthesis of building blocks **C-6-a, C-6-b** and **C-7**, conditions; a) SOP 12, (83 %); b) SOP 7; c) SOP 5, (75 %, 2steps); d) SOP 14 ( 82 %); e) SOP 8 (91 %).

Compound **C-6-a**:

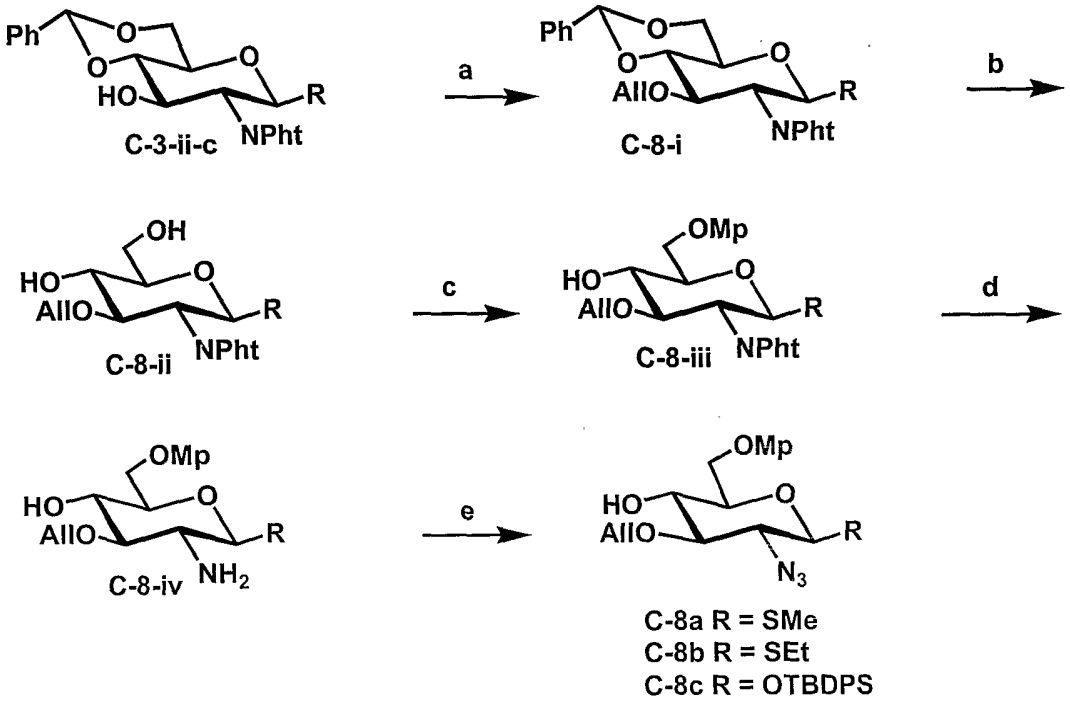
$^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 7.43 (d, 2 H, Aryl), 7.25 (m, 4 H, Aryl), 7.08 (d, 2 H, Aryl), 6.88 (m, 4 H, Aryl), 4.81 (d, 1 H, $J_{gem}$ = 10.8 Hz, $OCH_2$), 4.74 (d, 1 H, $J_{gem}$ = 10.8 Hz, $OCH_2$), 4.53 (d, 1 H, $J_{gem}$ = 11.1 Hz, $OCH_2$), 4.48 (d, 1 H, $J_{gem}$ = 10.8 Hz, $OCH_2$), 4.35 (d, 1 H, $J_{1,2}$ = 10.0 Hz, H-1β), 3.82 (s, 3 H, $OCH_3$), 3.79 (s, 3 H, $OCH_3$), 3.76 (dd, 1 H, $J_{gem}$ = 10.5 Hz, $J_{5,6a}$ = 5.4 Hz, H-6a), 3.70 (dd, 1 H, $J_{5,6b}$ = 5.4 Hz, H-6b), 3.56 (ddd, 1 H, H-4), 3.42 (m, 1 H, H-5), 3.34 (dd, 1 H, $J_{3,4}$ = 8.8 Hz, H-3), 3.24 (dd, 1 H, $J_{2,3}$ = 9.4 Hz, H-2), 2.72 (d, 1 H, $J_{4,OH}$ = 3.5 Hz, 4-OH), 2.38 (s, 3 H, $SCH_3$).

Compound **C-7**:

$^1$H-NMR (400 MHz, $CDCl_3$): 7.63 (d, 4 H, Aryl), 7.35-7.21 (m, 8H, Aryl), 7.08 (m, 2 H, Aryl), 6.83-6.78 (m, 4 H, Aryl), 4.72 (d, 1H, $J_{gem}$ = 11.0 Hz, $OCH_2$), 4.59 (d, 1H, $J_{gem}$ = 11.0 Hz, $OCH_2$), 4.29 (d, 1 H, $J_{1,2}$ = 7.8 Hz, H-1β), 4.27 (d, 1H, $J_{gem}$ = 11.7 Hz, $OCH_2$), 4.21 (d, 1H, $J_{gem}$ = 11.7 Hz, $OCH_2$), 3.72 (s, 3 H, $OCH_3$), 3.71 (s, 3 H, $OCH_3$), 3.51 (ddd, 1 H, $J_{3,4} \approx J_{4,5}$ = 8.6 Hz, H-4), 3.40-

3.32 (m, 3 H, H-6a, H-6b, H-2), 3.05 (dd, 1 H, $J_{2,3}$ = 9.8 Hz, H-3), 2.90 (m, 1 H, H-5), 2.51 (d, 1 H, $J_{4,OH}$ = 2.2 Hz, 4-OH), 1.12 (s, 9 H, $C(CH_3)_3$).

Example 10: Synthesis of building block **C-8a** to **C-8c**



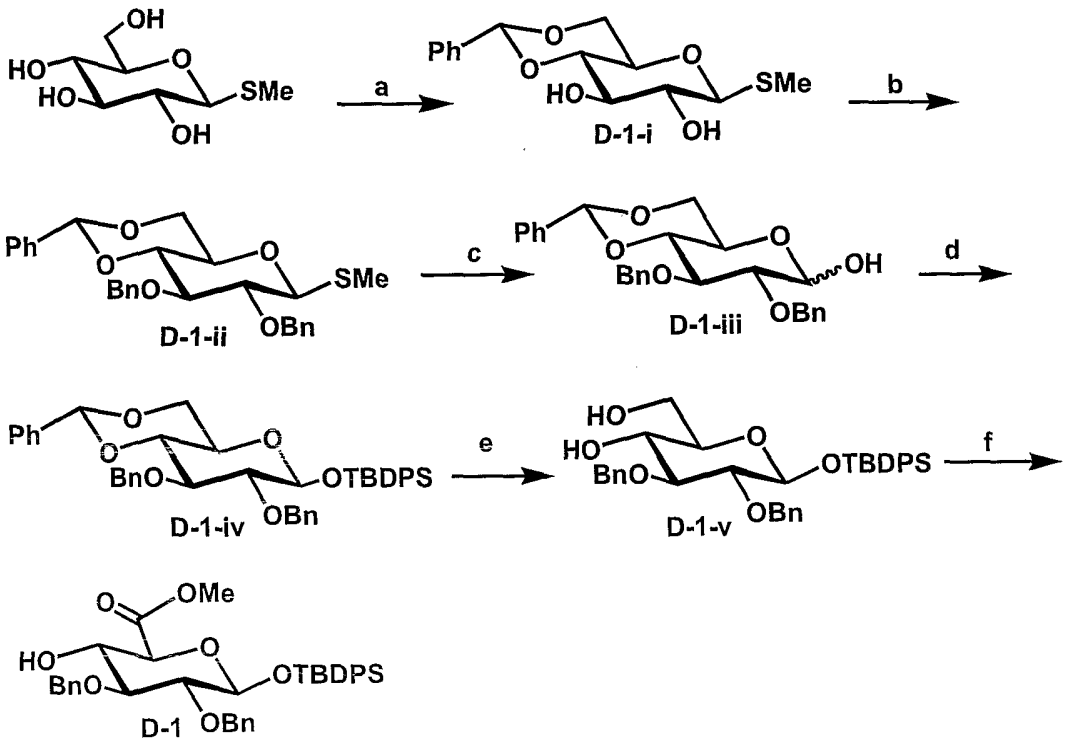

Example 10: Synthesis of building blocks **C-8a to C-8c**, conditions: a) SOP 7, AllBr, DMF (65 %, R=OTBDPS); b) SOP 4, (86 %, R=OTBDPS); c) SOP 26, (70 %, R=OTBDPS); d) SOP-30; e) SOP 12, (70 %, 2 steps for R=OTBDPS).

Compound **C-8c**:

$^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 7.72 (m, 4 H, Aryl), 7.43-7.16 (m, 6 H, Aryl), 6.76 (m, 4H, Mp), 5.96 (m, 1 H, =CH Allyl), 5.31 (m, 1 H, =CH Allyl), 5.22 (m, 1 H, =CH Allyl), 4.42 (d, 1 H, $J_{1,2}$ = 7.6 Hz, H-1β), 4.39 (m, 1 H, $OCH_2$ Allyl), 4.23 (m, 1 H, $OCH_2$ Allyl), 3.97 (dd, 1 H, $J_{gem}$ = 10.0 Hz, $J_{5,6a}$ = 3.6 Hz, H-6a), 3.92 (dd, 1 H, $J_{5,6b}$ = 5.2 Hz, H-6b), 3.77 (s, 3 H, $OCH_3$), 3.66 (ddd, 1 H, $J_{4,5} \approx J_{3,4}$ = 9.4 Hz, H-4), 3.42 ( dd, 1 H, J = 9.8 Hz and J = 7.8 Hz, H not assigned),

3.22 (m, 1 H, H-5), 3.09 (dd, 1 H, J = 8.4 Hz and J = 9.6 Hz, H not assigned), 2.48 (d, 1 H, $J_{4,OH}$ = 2.8 Hz, 4-OH), 1.12 (s, 9 H, $C(CH_3)_3$).

Example 11: Synthesis of Building Block **D-1**:

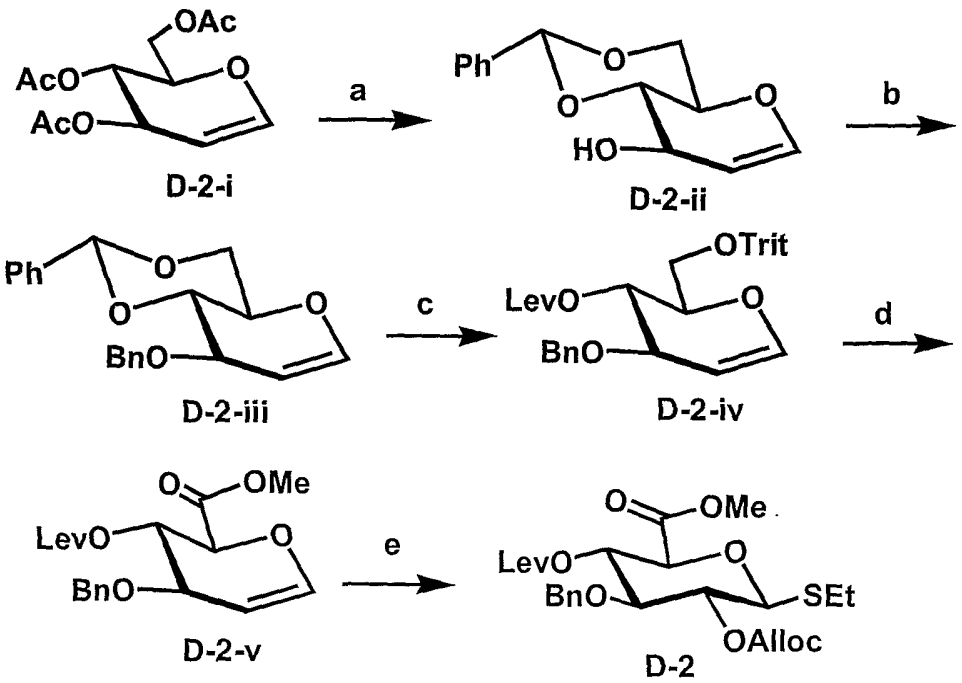



Example 11: Synthesis of building block **D-1**; a) SOP 1, (95 %); b) SOP 7, (85 %); c) SOP 13, (92 %); d) SOP 8; e) SOP 4, (70 %, 2 steps); f) 1. SOP 15; 2. SOP 16, (75 %, 2 steps).

Compound **D-1**:

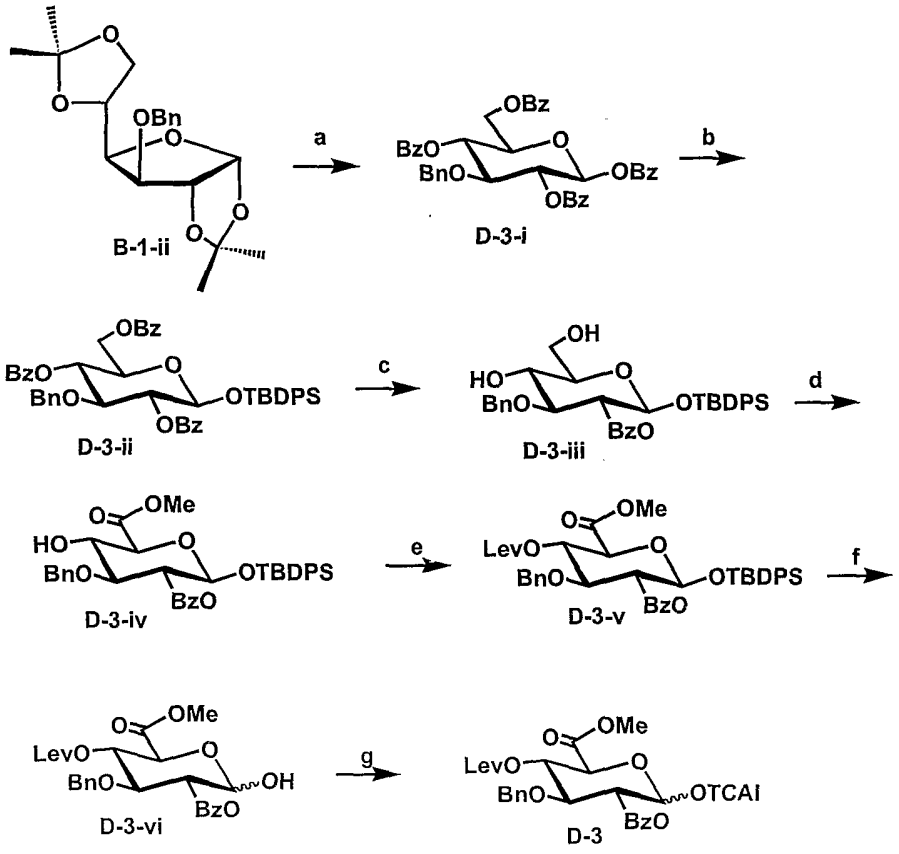
$^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 7.72 (m, 4 H, Aryl), 7.41 (m, 2 H, Aryl), 7.32 – 7.25 (m, 14 H, Aryl), 5.04 (d, 1 H, $J_{gem}$ = 11.0 Hz, $OCH_2$), 4.81 (m, 3 H, $OCH_2$), 4.63 (d, 1 H, $J_{1,2}$ = 7.4 Hz, H-1β), 3.88 (ddd, 1 H, $J_{3,4} \approx J_{4,5}$ = 9.2 Hz, H-4), 3.70 (s, 3 H, $OCH_3$), 3.53 (dd, 1H, J = 7.5 Hz, J = 9.0 Hz, H not assigned), 3.47 (d, 1 H, $J_{4,5}$ = 9.8 Hz, H-5), 3.42 (dd, 1 H, J = 8.9 Hz and J = 8.9 Hz, H not assigned), 2.87 (d, 1 H, $J_{4,OH}$ = 2.4 Hz, 4-OH), 1.11 (s, 9 H, $C(CH_3)_3$).

Example 12: Synthesis of Building Block **D-2**, a 2-O-Allyloxycarbonyl protected thioethyl glycoside




Example 12: Synthesis of Building Block **D-2**, conditions: a) 1. SOP 22; 2. SOP 1; b) SOP 7; c) 1. SOP 4; 2. TritCl, Pyridine, $(ClCH_2)_2$; 3. SOP 23; d) 1. $CrO_3$, $H_2SO_4$, Acetone, 0°C, 2. SOP 16; e) 1. Dimethyl dioxirane , Acetone; 2. EtSH, TFAA, $CH_2Cl_2$, 3. SOP 35.

Example 13: Synthesis of Building Block **D-3**




Example 13: Synthesis of Building Block **D-3**, conditions: a) 1. SOP 4, Amberlite IR 120, $H_2O$, 80°C; 2. SOP 18, (85 %, 2 steps) b) 1. SOP 21; 2. SOP 8, ( 70 %, 2 steps); c) SOP 22, (96 %); d) 1. SOP 15; 2. SOP 16, (80 %, 2 steps); e) SOP 23, (92 %); f) SOP 9, (95 %); g) SOP 25a, (91 %).

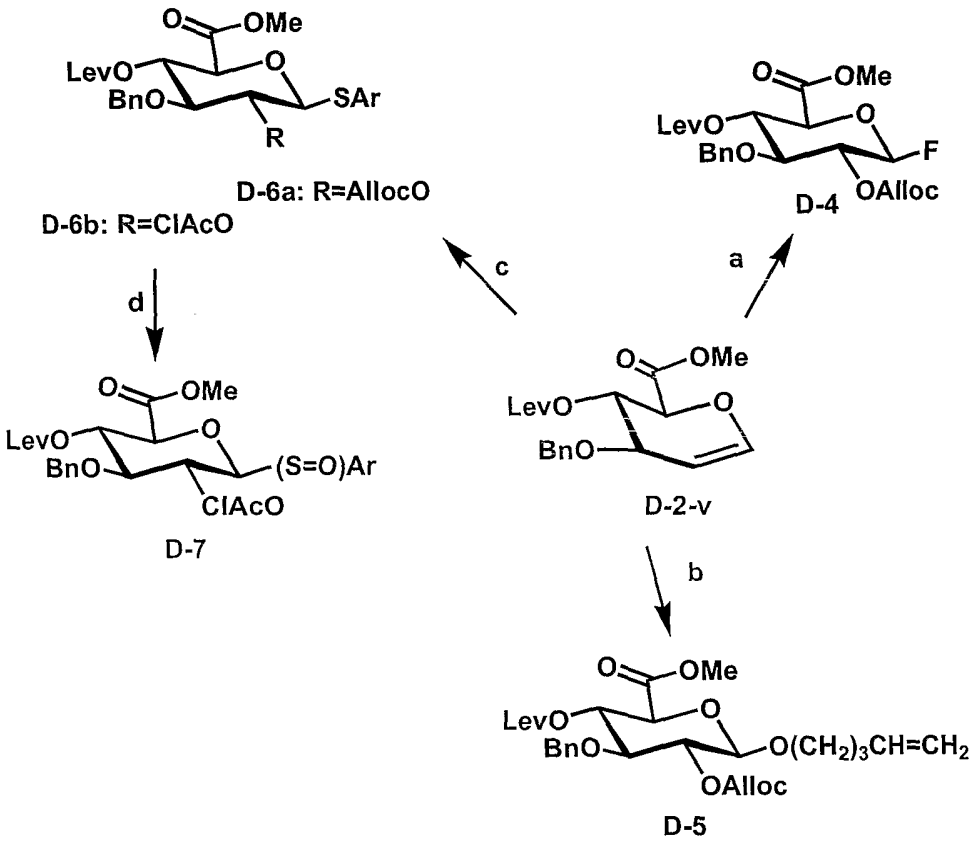
Preparation of **D-3-i**, step 1:

The starting material (57 mmol) and Amberlite IR 120 iron exchange resin ($H^+$-form, 20 g) were suspended in water (180 ml) and stirred at 80 °C until completion. The iron exchange resin was removed by filtration and extracted with water The combined aqueous layers were neutralized with triethyl amine and freeze dried.

Compound **D-3-v**:

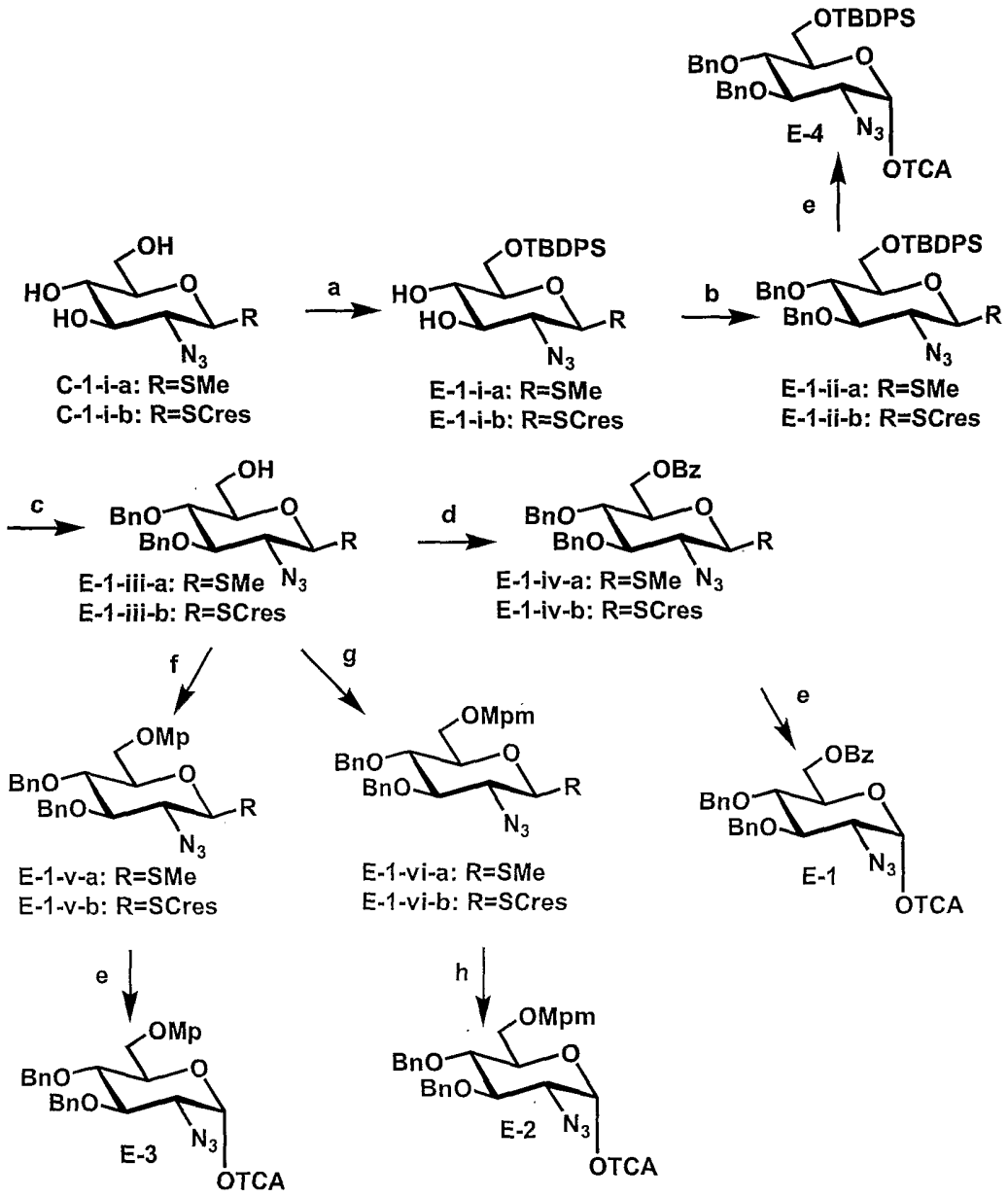
$^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 7.95 (m, 2 H, Aryl), 7.68 (m, 2 H, Aryl), 7.58 – 7.12 (m, 16 H, Aryl), 5.47 (dd, $J_{1,2}$ = 7.6 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 5.31 (dd, $J_{3,4}$ = 9.6 Hz, H-4), 4.64 (d, 1H, 7.6 Hz, H-1β), 4.60 (d, 1H, $J_{gem}$ = 12.0 Hz, $OCH_2$), 4.55 (d, 1H, $J_{gem}$ = 12.0 Hz, $OCH_2$), 3.74 (dd, 1H, H-3), 3.70 (s, 3H, $OCH_3$), 3.63 (d, 1H, $J_{4,5}$ = 9.6 Hz, H-5), 2.68 – 2.16 (m, 4H, $(CH_2)_2$-Lev), 2.15 (s, 3H, $CH_3$), 0.96 (s, 9H, $C(CH_3)_3$).

Example 14: Syntheses of a range of block D donor sugars **D-4** to **D-7** from a common intermediate, a 4-O-levulinoyl glucal.




Example 14: Syntheses of **D-4** to **D-7** as donor sugars, conditions: a) 1. Dimethyl dioxirane, Acetone; 2. TBAF, THF; 3. SOP 35; b) 1. Dimethyl dioxirane, Acetone; 2. 4-penten-1-ol, $ZnCl_2$, $CH_2Cl_2$; 3. SOP 35; c) 1. Dimethyl dioxirane, Acetone; 2. ArSH, TFAA, $CH_2Cl_2$, (Ar = Ph, *p*-Tol); 3. SOP 35 or $(ClAc)_2O$, Pyridine, $CH_2Cl_2$ (for **D-6b**); d) MCPBA, $CH_2Cl_2$ (for **D-6b** as substrate).

Example 15: Synthesis of Building Block **E-1** to **E-4**




Example 15: Synthesis of Building Block **E-1** to **E-4**, conditions: a) SOP 8; b) SOP 7; c) SOP 9, (84% over 3 steps, R=SMe); d) SOP 18, (86%, R=SMe); e) 1. SOP 13, (75%, for **E-1-iv-a** as starting material); 2. SOP 25b, (88%); f) 1. TosCl, Pyridine; 2. p-MeO-$C_6H_4$-ONa, NMP, 60°C; g) SOP 7, (78 %, R=SMe); h) 1. SOP 14; 2. SOP 25b, (79 %, 2 steps, R=SMe).

Preparation of **E-1-i-a**:

A mixture of methyl 2-azido-2-deoxy-thio-β-D-glucopyranoside (10g, 42.5mmol) and imidazole (4.9g, 72.25 mmol) in 20 mL DMF was treated with *tert*-butyldiphenylchlorosilane (11.6mL, 44.63mmol) for 2h. The reaction mixture was concentrated, extracted, washed and dried. yield: 23g (crude light yellow syrup), $R_f$ = 0.74 ($CHCl_3$/methanol = 9/1).

Preparation of **E-1-ii-a**:

The silyl ether from the previous step in 50 mL DMF, was treated with 2.68g of 95% NaH (106.25 mmol) and 12.64 mL (106.25 mmol) of benzyl bromide at 0 °C. After 1h the excess NaH was quenched and the reaction concentrated, extracted, washed and concentrated to afford a yellow syrup yield: 28.5g (crude yellow syrup), $R_f$ = 0.80 (hexane/ethyl acetate =7/3).

Preparation of **E-1-iii-a**:

The crude yellow syrup from the above reaction was treated with 36.5 mL AcOH and 106.3 mL (106.25 mmol) of 1M solution of TBAF in THF overnight. The reaction was concentrated and purified by chromatography to afford the title compound. 14.9g (84%, 3 steps ) $R_f$= 0.36 (petroleum spirit/ethyl acetate = 7/3)

Preparation of **E-1-iv-a**:

Methyl 2-azido-2,3 di-O-benzyl-2-deoxy-thio-β-D-glucopyranoside (14.5 g, 34.9 mmol) in dichloromethane (200 ml) and anhydrous pyridine (8.6 ml, 106.2 mmol) was treated with benzoylchloride (4.93 ml, 42.5 mmol) at 0°C for 1 hour. The reaction mixture was quenched, extracted, washed and evaporated. The residue was purified by silica gel column chromatography to afford the title compound as a white solid.

Yield: 14.9 g (86 %), $R_f$ = 0.82 (Petroleum spirit/Ethyl acetate = 7/3).

Preparation of **E-1**:

Methyl 2-azido-6-O-benzoyl-2,3di-O-benzyl-2-deoxy-thio-□-D-glucopyranoside (8.68 g, 16.7 mmol) in acetone (50 ml) was treated with *N*-bromosuccinimide (8.92 g, 50.12 mmol) at 0°C for 1 hour. The reaction mixture was then quenched, extracted, washed and evaporated, furnishing a yellow syrup which was purified by chromatography. Yield: 6.13 g (75%), $R_f$ = 0.57 (Petroleum spirit/Ethyl acetate = 7/3). A cooled mixture of 2-azido-6-O-

benzoyl-2,3 di-O-benzyl- 2-deoxy-α/β-D-glucopyranose (5g, 10.2 mmol), $K_2CO_3$ (7.0 g , 51 mmol) and trichloroacetonitrile (5.1ml, 51 mmol) in 30 ml of dichloromethane was stirred for 2h. The mixture was then filtered through celite and the filtrate was concentrated and purified on a short column of silica gel to obtain the title compound as an amorphous white solid. Yield 5.69 g (88%), $R_f$ = 0.85 (Petroleum spirit/Ethyl acetate = 7/3).

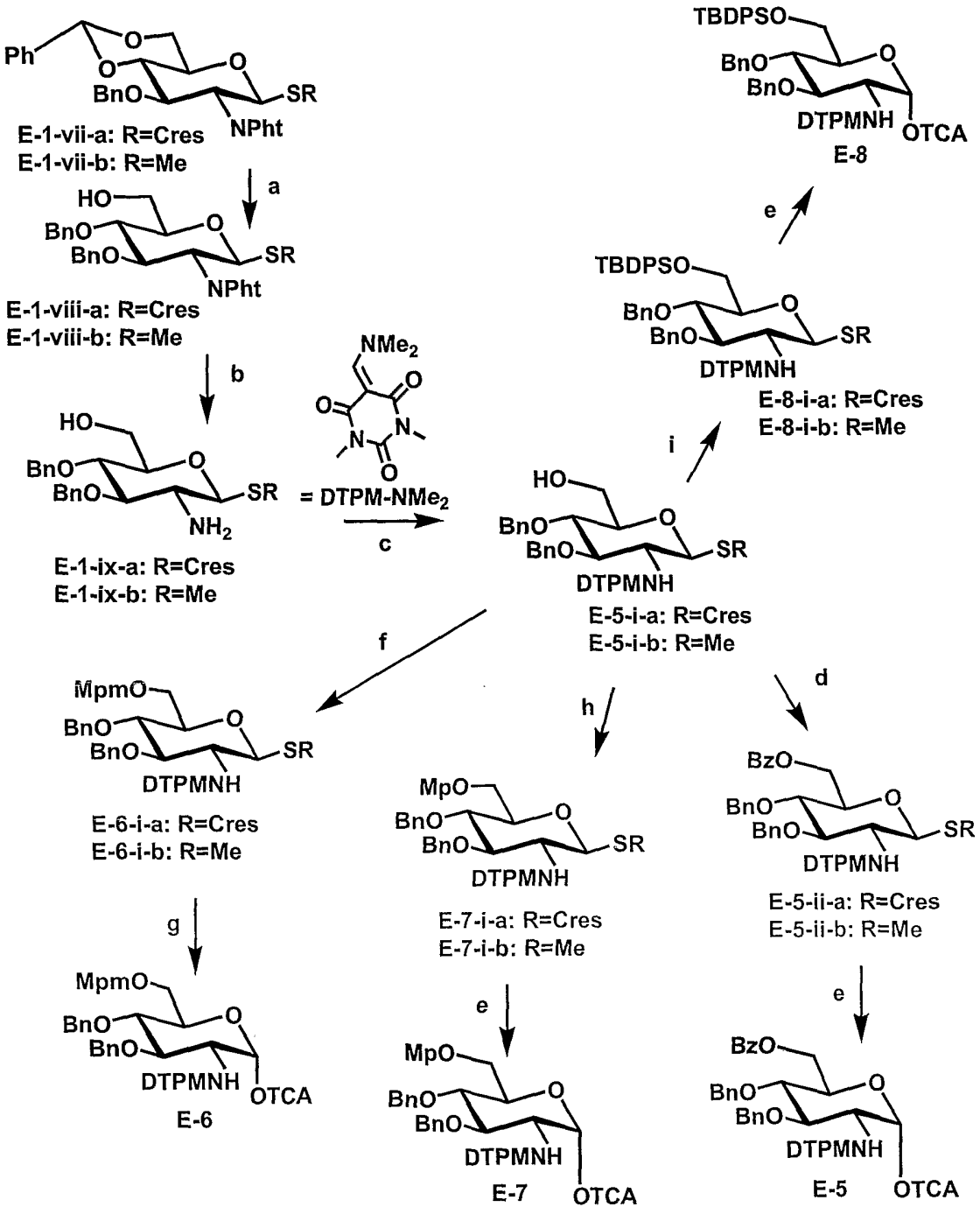
Compound **E-1**:

$^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 8.73 (s, 1 H, C=NH), 8.00 (m, 2 H, Aryl), 7.56 (m, 1 H, Aryl), 7.43-7.25 (m, 12 H, Aryl), 5.66 (d, 1H, J = 8.4 Hz, H-1β), 4.95 (d, 1H, $J_{gem}$ = 10.8 Hz, $OCH_2$), 4.87 (d, 2H, J = 10.8 Hz , $OCH_2$), 4.62 (d, 2H, $J_{gem}$ = 10.8 Hz, $OCH_2$), 4.58 (dd, 1H, $J_{gem}$= 12.4 Hz, $J_{5,6a}$ = 2.0 Hz, H-6a), 4.46 (dd, 1H, $J_{5,6b}$ = 3.6 Hz, H-6b), 3.77-3.72 (m, 3H, H-5, 2H not assigned), 3.62 (dd, 1H, J = 8.3 Hz, J = 9.7 Hz, H not assigned).

Compound **E-2**:

$^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 8.70 (s, 1 H, C=NH), 7.38-7.22 (m, 10H, Aryl), 7.13 (m, 2H, Aryl), 6.83 (d, 2H, Mpm), 6.44 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1α), 4.93 (d, 1H, $J_{gem}$ = 10.5 Hz, $OCH_2$), 4.89 (d, 1H, $J_{gem}$ = 10.5 Hz, $OCH_2$), 4.78 (d, 1H, $J_{gem}$ = 10.5 Hz, $OCH_2$), 4.57 (d, 1H, $J_{gem}$ = 11.7 Hz, $OCH_2$), 4.51 (d, 1H, $J_{gem}$ = 11.7 Hz, $OCH_2$), 4.39 (d, 1H, $J_{gem}$ = 11.7 Hz, $OCH_2$), 4.02 (dd, 1H, $J_{3,4} \approx J_{2,3}$ = 9.5 Hz, H-3), 3.98 (m, 1H, H-5), 3.86 (dd, 1H, $J_{4,5}$ = 9.6 Hz, H-4), 3.76 (dd, 1H, H-2), 3.75 (s, 3H, $OCH_3$), 3.69 (dd, 1H, $J_{5,6a}$ = 3.5 Hz, $J_{gem}$ = 10.5 Hz, H-6a), 3.63 (dd, 1H, $J_{5,6b}$ = 1.8 Hz, H-6b).

Example 16: Synthesis of Building Blocks **E-5** to **E-8**

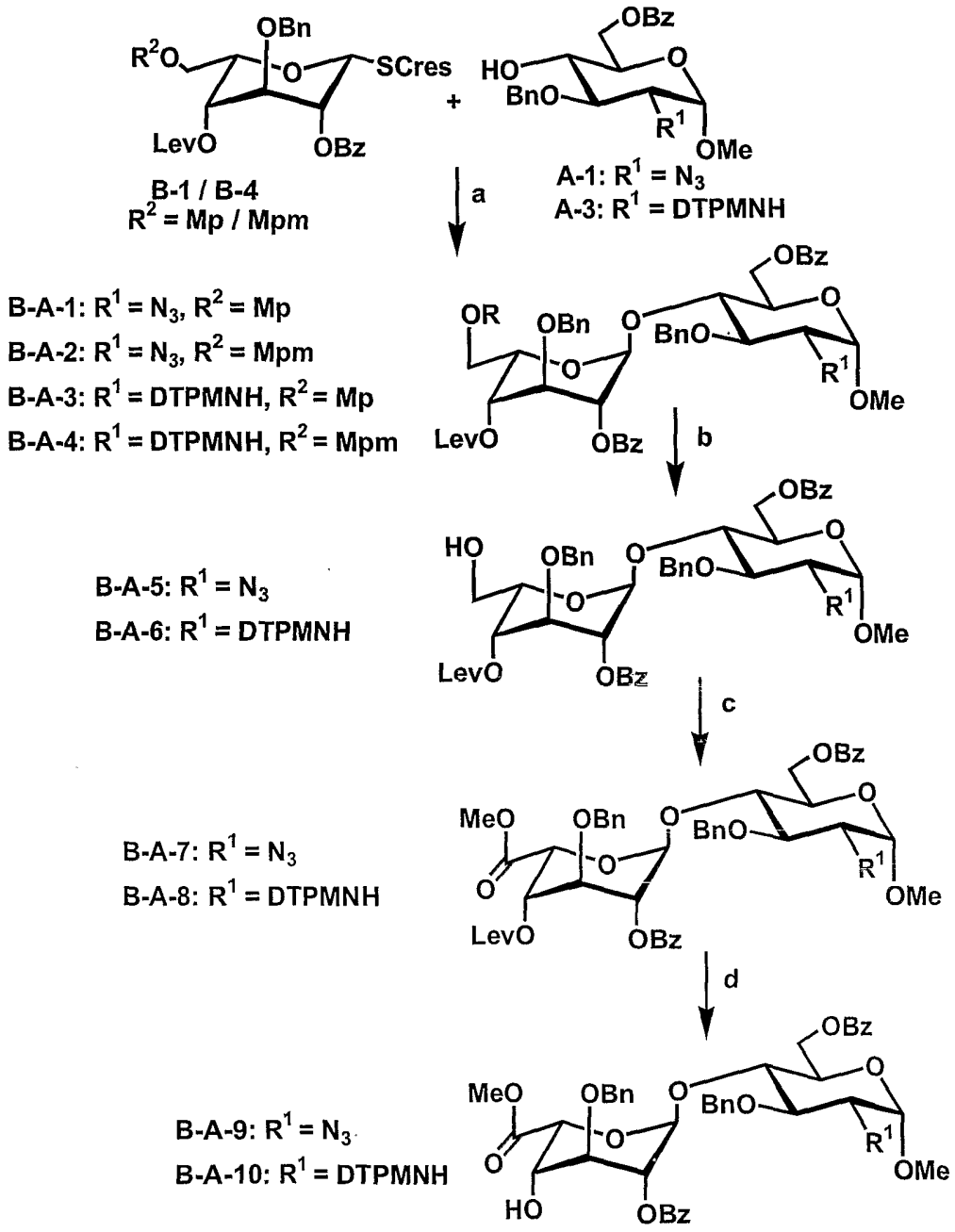



Example 16: Syntheses of Building Blocks **E-5 to E-8**, conditions: a) SOP 6, (85 %, R=SMe); b). SOP 30, (86 %, R=SMe); c) SOP 10, (88 %, R=SMe); d) SOP 18, (92 %, R=SMe); e) 1. SOP 13; 2. SOP 25b, (85 %, 2 steps, R=SMe); f) SOP 7; g) 1. SOP 14; 2. SOP 25b; h) 1. TsCl, DMF; 2. p-MeO-$C_6H_4$-ONa, NMP, 60°C; i) SOP 8.

Compound **E-5**:

$^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 10.20 (dd, 1 H, $J_{NH,=C-H}$ = 14.0 Hz, $J_{NH,H-2}$ = 9.9 Hz, NH), 8.80 (s, 1 H, C=NH), 8.16 (d, 1H, =C-H), 7.99 (m, 2H, Aryl) 7.58 (m, 1 H, Aryl), 7.45 (m, 2 H, Aryl), 7.30-7.17 (m, 10H, Aryl), 6.42 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1$\alpha$), 4.89 (d, 1H, $J_{gem}$ = 8.4 Hz, $OCH_2$), 4.68-4.60 (m, 3H, $OCH_2$), 4.58 (dd, 1H, $J_{5,6a}$ = 2.0 Hz, $J_{gem}$ = 12.4 Hz, H-6a), 4.51 (dd, 1 H, $J_{5,6b}$ = 4.0 Hz, H-6b), 4.22 (m, 1 H, H-5), 4.03 (dd, 1 H, $J_{3,4} \approx J_{2,3}$ = 9.6 Hz, H-3), 3.80 (dd, 1 H, $J_{4,5}$ = 9.4 Hz, H-4), 3.70 (ddd, 1 H, H-2), 3.32 (s, 3 H, $NCH_3$), 3.25 (s, 3 H, $NCH_3$).

Example 17: Preparation of L-iduronic acid containing disaccharides **B-A-1** to **B-A-10**




Example 17: Preparation L-iduronic acid containing disaccharides **B-A-1** to **B-A-10**; a) SOP 32a, (80 %, for **B-A-1**); b) SOP 27, (88 %, for **B-A-5**); c) 1.SOP 20; 2. SOP 16, (84 % for **B-A-7**, 2 steps); d) SOP 24, (94 %, for **B-A-9**).

Formation of disaccharide **B-A-1 (step a)**

A suspension of **A-1** (410 mg, 990 µmol), **B-1** (680 mg, 990 µmol) and freshly activated molecular sieves 4 Å (1.0 g) in dry $CH_2Cl_2$ (20 mL) was stirred for 90 min at 0°C. *N*-Iodosuccinimide (405 mg, 1.8 mmol) was added and stirring

continued for 20 min. After addition of trifluoromethanesulfonic acid (10.6 µl, 119.7 µmol), the reaction mixture was further stirred until completion (from 0°C to 25 °C) and quenched with aqueous $NaHCO_3$-solution (10 %). The mixture was diluted with $CH_2Cl_2$ and filtered through a celite pad. The filtrate was washed with a 10 % $KHCO_3/Na_2S_2O_3$ solution, water and saturated brine solution, dried over $MgSO_4$ and evaporated. Final purification was achieved by silica gel column chromatography. Yield: 730 mg (80 %).

Formation of disaccharide **B-A-7(step c)**

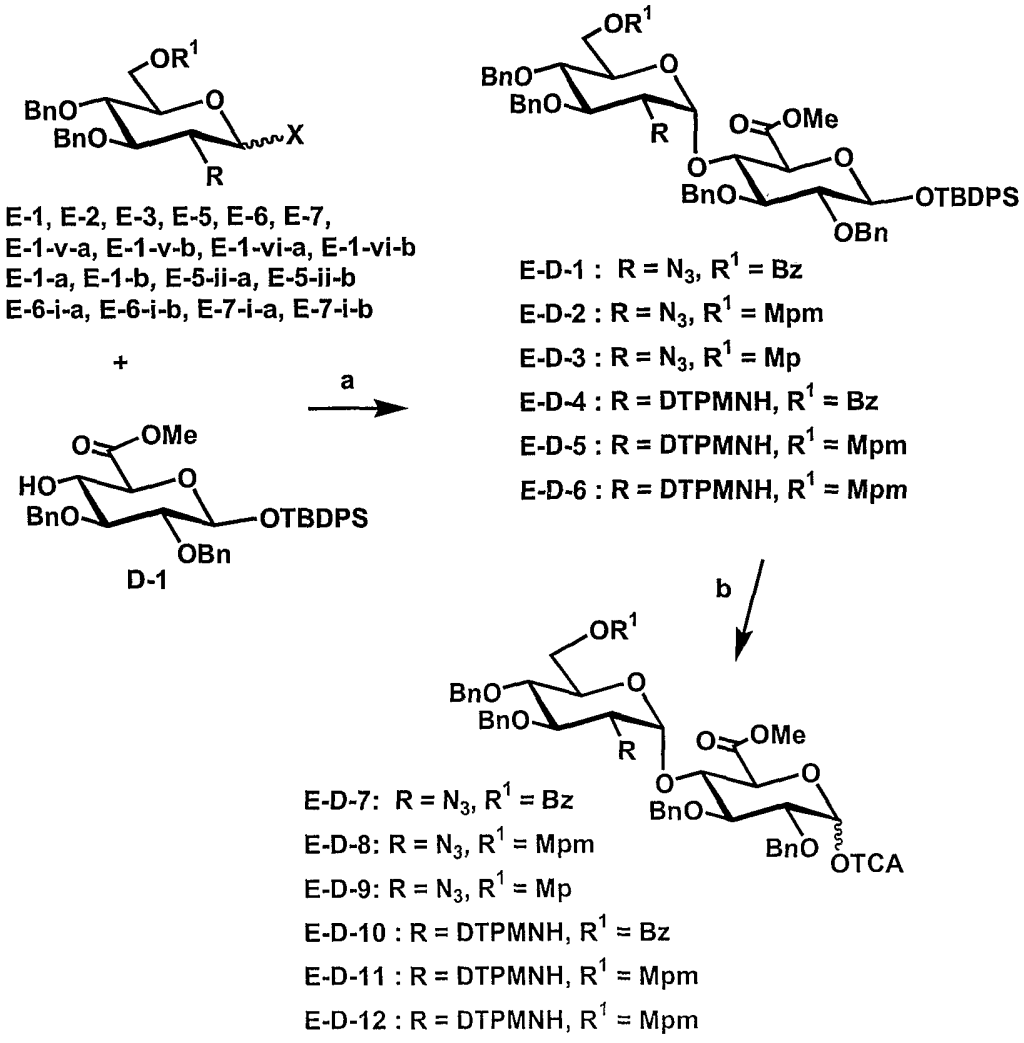
Disaccharide **B-A-5** (1.00 g, 1.15 mol) was dissolved in anhydrous DMF (7.0 ml) and reacted with pyridinium dichromate (4.33 g, 11.5 mmol) under stirring at room temperature until complete conversion into the uronic acid. The reaction mixture was subsequently poured into 50 ml water and the whole extracted with diethyl ether. The combined ether layers were washed with 10 % aqueous citric acid solution, filtered through a short silica gel pad, dried over $MgSO_4$, evaporated and dried under high vacuum. The crude residue was dissolved in Toluene (3 ml) and methanol (3 ml) and titurated with $TMSCHN_2$ solution (2M in hexane) until completion. The excess of $TMSCHN_2$ was destroyed by addition of acetic acid and the mixture evaporated. Final purification was achieved via silica gel chromatography. Yield: 871 mg (84 %).

Compound **B-A-9**:

$^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 8.03 (m, 2H, Aryl), 7.91 (m, 2H, Aryl), 7.53 (m, 2H, Aryl), 7.42-7.23 (m, 14H, Aryl), 5.37 (d, 1H, $J_{1,2}$ < 1.5 Hz, H-1'α), 5.21 (m, 1H, H-2'), 4.97 (d, 1H, $J_{4,5}$ = 2.3 Hz, H-5'), 4.84 (d, 2H, $J_{gem}$ = 10.8 Hz, $OCH_2$), 4.81 (d, 1H, $J_{gem}$ = 10.8 Hz, $OCH_2$), 4.80 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1α), 4.77 (1H, $J_{5,6a}$ = 1.8 Hz, H-6a), 4.70 (m, 2H, $OCH_2$), 4.47 (dd, 1H, $J_{5,6b}$ = 4.2 Hz, $J_{gem}$ = 12.3 Hz, H-6b), 4.05-3.97 (m, 3H, H-4', H-4, H-5), 3.91-3.87 (m, 2H, H-3', H-3), 3.49 (s, 3H, $OCH_3$), 3.44 (m, 1H, H-2), 3.43 (s, 3H, $OCH_3$).

Selected $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ = 98.73 C-1 ($J_{CH}$ = 172.5 Hz), 98.35 C-1' ($J_{CH}$ = 171.8 Hz).

Example 18: Syntheses of Building Blocks **E-D-1** to **E-D-12**




Example 18 : Syntheses of disaccharides **E-D-1** to **E-D-12**, conditions: a) SOP 32 a/b for X =SMe/ Scres or SOP 33 for X = OTCA, (86 % for **E-D-1 via E-1,** 84% for **E-D-4 via E-5,** as α/β̃ mixtures), b) 1. SOP 9; 2. SOP 25a, (90 % for **E-D-7** over 2 steps).

Preparation of **E-D-1**:Methyl (2-azido-6-O-benzoyl-3,4-di-O-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-tert-butyldiphenylsilyl 2,3-di-O-benzyl-β–D-glucopyranosid)uronate

A mixture of 2-azido-6-O-benzoyl-2,3 di-O-benzyl- 2-deoxy-α/β-D-glucopyranosyl trichloroacemidate (2.5 g, 3.94 mmol), and methyl (*tert*-butyldiphenylsilyl 2,3-di-O-benzyl-β-D-glucopyranoside) uronate (1.6 g, 2.629

mmol) and molecular sieves 4A (2.5 g) in 50 ml diethyl ether was treated with TBDMSOTf (180 µl, 788.76 µmol) at -20°C for 1h. The reaction was quenched filtered, concentrated and the residue purified by silica gel column chromatography to obtain the desired disaccharide 2.48 g, 86%. $R_f$= 0.67 (toluene/ethyl acetate 9/1)

Compound **E-D-1**:

**E-D-1** was formed according to SOP 33 with ether as solvent at -30°C and TBDMSOTf as promotor in 86 % yield (α/β-mixture).

$^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 8.00 (m, 2H, Aryl), 7.68 (m, 4H, Aryl), 7.56 (m, 1H, Aryl), 7.42 (m, 4H, Aryl), 7.36-7.17 (m, 24H, Aryl), 5.47 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1'α), 5.02 (d, 1H, $J_{gem}$ = 11.4 Hz, $OCH_2$), 4.97 (d, 1H, $J_{gem}$ = 11.0 Hz, $OCH_2$), 4.84 (m, 4H, $OCH_2$), 4.75 (d, 1H, $J_{gem}$ = 11.4 Hz, $OCH_2$), 4.66 (d, 1H, $J_{1,2}$ = 7.5 Hz, H-1β), 4.57 (d, 1H, $J_{gem}$ = 10.9 Hz, $OCH_2$), 4.45 (m, 2H, H-6'a, H-6'b), 4.15 (dd, J = 8.8 Hz and J = 9.6 Hz), 3.86 (m, 1H), 3.65 (s, 3H, $OCH_3$, 3.68-3.58 (m, 3H), 3.55 (d, 1H, $J_{4,5}$ = 10.0 Hz, H-5), 3.31 (dd, 1H, $J_{2,3}$ = 10.2 Hz, H-2'), 1.12 (s, 9H, $C(CH_3)_3$).

Compound **E-D-4**:

**E-D-4** was formed according to SOP 33 with ether as solvent at -30°C and TBDMSOTf as promotor in 84 % yield (α/β-mixture).

Selected $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 10.02 (dd, 1 H, $J_{NH,=C-H}$ = 14.4 Hz, $J_{NH,H-2}$ = 9.6 Hz, N-H), 8.02 (m, 2 H, Aryl), 7.79 (d, 1H, =C-H), 7.72-6.93 (m, 33 H, Aryl), 5.60 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1'α), 4.49 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1β), 3.66 (s, 3 H, $OCH_3$), 3.29 (s, 3 H, $NCH_3$), 3.28 (s, 3 H, $NCH_3$), 1.14 (s, 9 H, $C(CH_3)_3$).

Preparation of **E-D-7**: *Methyl (2-azido-6-O-benzoyl-3,4-di-O-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-2,3-di-O-benzyl-β-D-glucopyranosyl trichloroacetimidyl)uronate*

A solution of methyl (2-azido-6-O-benzoyl-3,4-di-O-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-*tert*-butyldiphenylsilyl 2,3-di-O-benzyl-β-D-glucopyranoside)

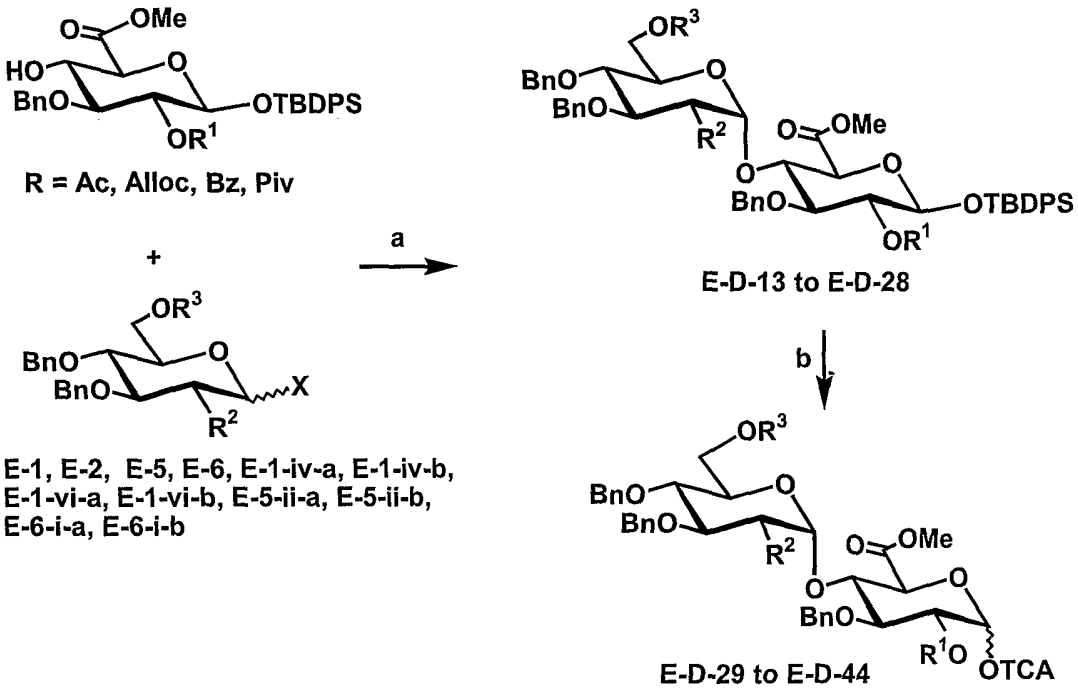
uronate (2.09 g, 1.903 mmol) in acetic acid (1.74 ml, 30.45 mmol) and 1 M solution of tetrabutylammoniumfluoride (7.6 ml, 7.61 mmol) was stirred at room temperature overnight. The reaction mixture was then concentrated and the residual syrup was purified by silica gel column chromatography to obtain the desired hemiacetal. Yield: 1.57 g (95.8%), $R_f$= 0.21 (toluene/ethyl acetate 9/1).

A mixture of methyl (2-azido-6-O-benzoyl-3,4-di-O-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-2,3-di-O-benzyl-β-D-glucopyranosyl)uronate (594 mg, 690.76 μmol), trichloroacetonitrile (280 μl , 2.79 mmol) and DBU (31 μl, 209.3 μmol) in 8.0 ml dichloromethane was stirred at 0°C for 1 h. The mixture was then concentrated and purified on a short column of silica gel to obtain the title compound as an amorphous white solid. Yield: 662 mg (95.3 %), $R_f$= 0.46 (toluene/ethyl acetate 9/1).

Compound **E-D-7**:

Selected $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 8.68 (s, 1H, C=NH), 8.00 (m, 2H, Aryl), 7.56 (m, 2H, Aryl), 7.43-7.23 (m, 22H, Aryl), 6.48 (d, 1H, $J_{1,2}$ = 4.3 Hz, H-1α), 5.59 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1'α), 5.03 (1H, $J_{gem}$ = 10.8 Hz, $OCH_2$), 4.93-4.83 (m, 4H, $OCH_2$), 4.70 (d, 1H, $J_{gem}$= 12.0 Hz, $OCH_2$), 4.64 (d, 1H, $J_{gem}$ = 12.0 Hz, $OCH_2$), 4.60 (d, 1H, $J_{gem}$= 11.2 Hz, $OCH_2$), 4.47 (m, 2H, H-6'a, H-6'b), 4.42 (m, 1H, not assigned), 4.15 (m, 2H, not assigned), 3.97 (dd, 1H, J = 8.2 Hz and J = 10.2 Hz, not assigned), 3.80 (m, 1H, not assigned), 3.76 (m, 3H, $OCH_3$), 3.72-3.64 (m, 2H, not assigned), 3.30 (dd, 1H, $J_{2,3}$ = 10.4 Hz, H-2').

Example 19: Syntheses of disaccharides **E-D-13** to **E-D-44**




E-D-13 & E-D-29: $R^3$= Bz, $R^2$ = $N_3$, $R^1$ = Alloc
E-D-14 & E-D-30: $R^3$= Bz, $R^2$ = NHDTPM, $R^1$ = Alloc
E-D-15 & E-D-31 : $R^3$ = Mpm, $R^2$ = $N_3$, $R^1$ = Alloc
E-D-16 & E-D-32 : $R^3$ = Mpm, $R^2$ = NHDTPM, $R^1$ = Alloc
E-D-17 & E-D-33 : $R^3$ = Bz, $R^2$ = $N_3$, $R^1$ = Piv
E-D-18 & E-D-34: $R^3$ = Bz, $R^2$ = NHDTPM, $R^1$ = Piv
E-D-19 & E-D-35 : $R^3$ = Mpm, $R^2$ = $N_3$, $R^1$ = Piv
E-D-20 & E-D-36: $R^3$ = Mpm, $R^2$ = NHDTPM, $R^1$ = Piv

E-D-21 & E-D-37: $R^3$= Bz, $R^2$ = $N_3$, $R^1$ = Bz
E-D-22 & E-D-38: $R^3$= Bz, $R^2$ = NHDTPM, $R^1$ = Bz
E-D-23 & E-D-39: $R^3$ = Mpm, $R^2$ = $N_3$, $R^1$ = Bz
E-D-24 & E-D-40: $R^3$ = Mpm, $R^2$ = NHDTPM, $R^1$ = Bz
E-D-25 & E-D-41: $R^3$ = Bz, $R^2$ = $N_3$, $R^1$ = Ac
E-D-26 & E-D-42: $R^3$ = Bz, $R^2$ = NHDTPM, $R^1$ = Ac
E-D-27 & E-D-43: $R^3$ = Mpm, $R^2$ = $N_3$, $R^1$ = Ac
E-D-28 & E-D-44: $R^3$ = Mpm, $R^2$ = NHDTPM, $R^1$ = Ac

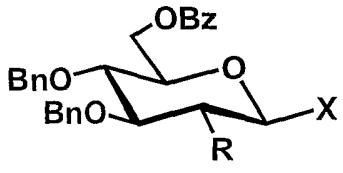
Example 19: Syntheses of disaccharides **E-D-13** to **E-D-44**, conditions: a) SOP 32 a/b for X = SMe/ Scres or SOP 33 for X = OTCA ( 70 % for **E-D-23**, α/β mixture); b) 1. SOP 9; 2. SOP 25a.

Compound **E-D-27:**

**E-D-27** was formed according to SOP 33 with ether as solvent at -20°C and TBDMSOTf as promotor in 70 % yield (α/β-mixture).

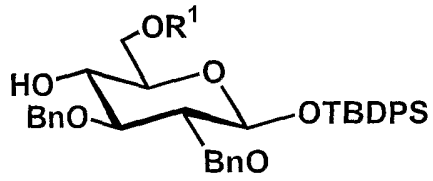
Selected $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 7.58 (m, 2H, Aryl), 7.54 (m, 2H, Aryl), 7.36 – 7.00 (m, 23 H, Aryl), 6.73 (m, 2H, Aryl), 5.37 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-1'α), 5.12 (dd, 1H, $J_{2,3}$ = 8.8 Hz, H-2), 4.63 (d, 1H, $J_{gem}$ = 11.2 Hz, $OCH_2$), 4.58 (d, 1H, $J_{gem}$ = 11.2 Hz, $OCH_2$), 4.48 (d, 1H, $J_{1,2}$ = 7.3 Hz, H-1β), 3.66 (s, 3 H, $OCH_3$), 3.55 (s, 3 H, $OCH_3$), 3.34 (m, 1H), 3.22 (dd, 1H, J = 3.4 Hz, J = 10.7 Hz), 1.81 (s, 3 H, OAc), 0.98 (s, 9H, $C(CH_3)_3$).

Example 20 : Synthesis of alternative E-D-disaccharides **E-D-45** to **E-D-50**

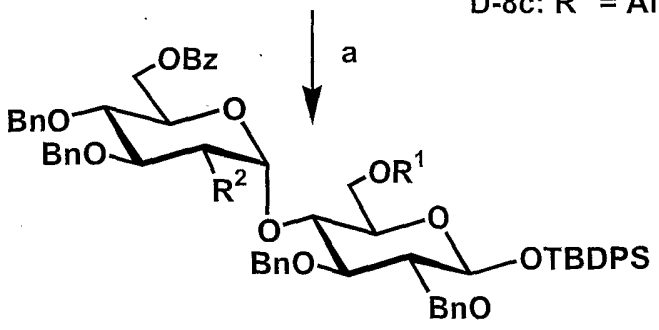



**E-1, E-5, E-1-iv-a, E-1-iv-b, E-5-ii-a, E-5-ii-b**

+



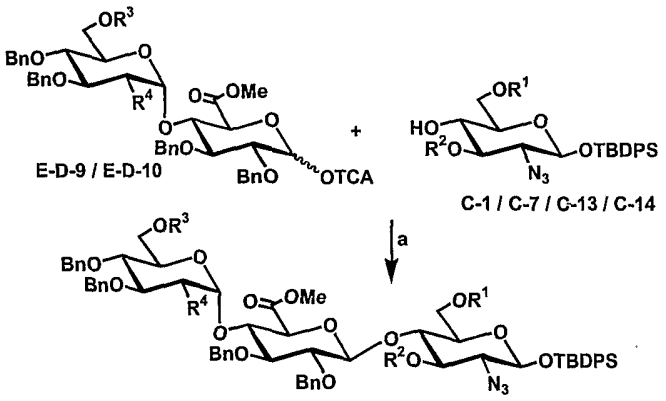

**D-8a: $R^1$ = Mp**
**D-8b: $R^1$ = Mpm**
**D-8c: $R^1$ = All**




**E-D-45: $R^1$ = Mp, $R^2$ = $N_3$**
**E-D-46: $R^1$ = Mp, $R^2$ = NHDTPM**
**E-D-47: $R^1$ = Mpm, $R^2$ = $N_3$**
**E-D-48: $R^1$ = Mpm, $R^2$ = NHDTPM**
**E-D-49: $R^1$ = All, $R^2$ = $N_3$**
**E-D-50: $R^1$ = All, $R^2$ = NHDTPM**

Example 20 : Synthesis of alternative E-D-disaccharides **E-D-45** to **E-D-50**, conditions: a) SOP 32a/b for X = SMe/SCres or SOP 33 for X = OTCA, diethyl ether, TBDMS-OTf, -20 deg. C (75 % for **E-D-45** as α/β-mixture).

Example 21: Synthesis of trisaccharides **E-D-C-1** to **E-D-C-16**




E-D-C-1 : $R^1$ = Mpm, $R^2$ = Mpm, $R^3$ = Mpm, $R^4$ = NHDTPM
E-D-C-2 : $R^1$ = Mp, $R^2$ = Mpm, $R^3$ = Mpm, $R^4$ = NHDTPM
E-D-C-3 : $R^1$ = Mpm, $R^2$ = Mpm, $R^3$ = Bz, $R^4$ = NHDTPM
E-D-C-4 : $R^1$ = Mp, $R^2$ = Mpm, $R^3$ = Bz, $R^4$ = NHDTPM
E-D-C-5 : $R^1$ = Mpm, $R^2$ =Bz, $R^3$ = Mpm, $R^4$ = NHDTPM
E-D-C-6 : $R^1$ = Mp, $R^2$ =Bz, $R^3$ = Mpm, $R^4$ = NHDTPM
E-D-C-7 : $R^1$ = Mpm, $R^2$ =Bz, $R^3$ = Bz, $R^4$ = NHDTPM
E-D-C-8 : $R^1$ = Mp, $R^2$ =Bz, $R^3$ = Bz, $R^4$ = NHDTPM

E-D-C-9 : $R^1$ = Mpm, $R^2$ = Mpm, $R^3$ = Mpm, $R^4$ = $N_3$
E-D-C-10 : $R^1$ = Mp, $R^2$ = Mpm, $R^3$ = Mpm, $R^4$ = $N_3$
E-D-C-11: $R^1$ = Mpm, $R^2$ = Mpm, $R^3$ = Bz, $R^4$ = $N_3$
E-D-C-12: $R^1$ = Mp, $R^2$ = Mpm, $R^3$ = Bz, $R^4$ = $N_3$
E-D-C-13: $R^1$ = Mpm, $R^2$ =Bz, $R^3$ = Mpm, $R^4$ = $N_3$
E-D-C-14: $R^1$ = Mp, $R^2$ =Bz, $R^3$ = Mpm, $R^4$ = $N_3$
E-D-C-15: $R^1$ = Mpm, $R^2$ =Bz, $R^3$ = Bz, $R^4$ = $N_3$
E-D-C-16: $R^1$ = Mp, $R^2$ =Bz, $R^3$ = Bz, $R^4$ = $N_3$

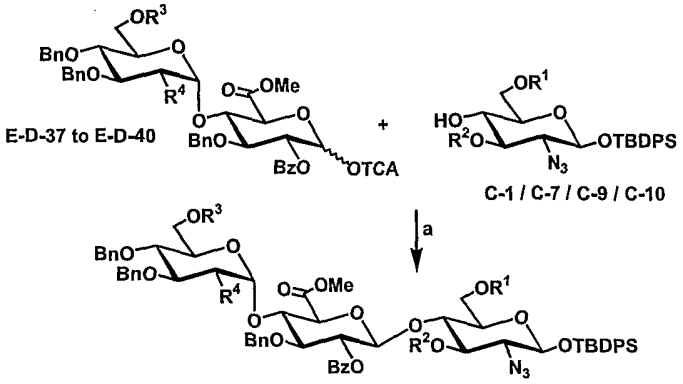
Example 21: Synthesis of trisaccharide **E-D-C-1** to **E-D-C-16**, conditions: a) SOP 33, (70 % for **E-D-C 15** as an α/β mixture).

Compound **E-D-C-15**:

**E-D-C-15** was formed according to SOP 33 with dichloromethane as solvent at 0 to 20°C and TBDMSOTf as promotor in 70 % yield (α/β-mixture).

$^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 7.93 (m, 2H, Aryl), 7.87 (m, 2H, Aryl), 7.66 (m, 2H, Aryl), 7.61 (m, 2H, Aryl), 7.46 (m, 2H, Aryl), 7.38-6.99 (m, 32 H, Aryl), 6.79 (m, 2H, Aryl), 5.27 (d, 1 H, $J_{1,2}$ = 3.8 Hz, H-1"α), 4.99 (dd, 1 H, $J_{3,4} \approx J_{2,3}$ = 9.5 Hz, H-3), 4.80-4.69 (m, 6 H, $OCH_2$), 4.52 (m, 3 H, $OCH_2$), 4.40 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1β), 4.38-4.32 (m, 2 H, not assigned), 4.29 (d, 1 H, $J_{1,2}$ = 7.5 Hz, H-1'β), 4.15 (m, 1 H, $J_{gem}$ = 12.0 Hz, $OCH_2$), 4.02 (dd, 1 H, $J_{4,5}$ = 9.6 Hz, H-4), 3.80 (2 dd, 2 H, H-3", H-4'), 3.71, (s, 3 H, $OCH_3$), 3.67 (m, 1 H, not assigned), 3.61-3.53 (m, 2 H, H-5', H-2'), 3.46 (dd, 1 H, $J_{gem}$ = 11.2 Hz, $J_{5,6a}$ = 2.4 Hz, H-6a), 3.41 (dd, 1H, $J_{2,3} \approx J_{3,4}$ = 9.0 Hz, H-3'), 3.27 (s, 3 H, $OCH_3$), 3.21 (dd, 1 H, $J_{2,3}$ = 10.0 Hz, H-2"), 3.14 (dd, 1 H, H-2'), 3.00 (dd, 1 H, $J_{5,6b}$ <2.0 Hz, H-6b), 2.75 (m, 1 H, H-5) 1.05 (s, 9H,$C(CH_3)_3$).

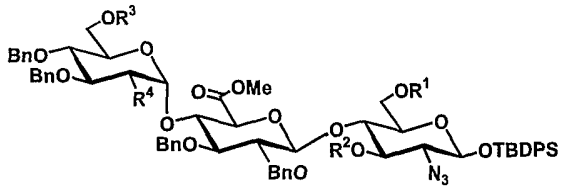
Example 22: Synthesis of trisaccharides **E-D-C-17** to **E-D-C-32**



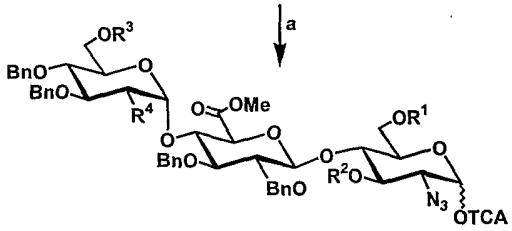

E-D-C-17 : $R^1$ = Mpm, $R^2$ = Mpm, $R^3$ = Mpm, $R^4$ = NHDTPM
E-D-C-18 : $R^1$ = Mp, $R^2$ = Mpm, $R^3$ = Mpm, $R^4$ = NHDTPM
E-D-C-19 : $R^1$ = Mpm, $R^2$ = Mpm, $R^3$ = Bz, $R^4$ = NHDTPM
E-D-C-20 : $R^1$ = Mp, $R^2$ = Mpm, $R^3$ = Bz, $R^4$ = NHDTPM
E-D-C-21: $R^1$ = Mpm, $R^2$ =Bz, $R^3$ = Mpm, $R^4$ = NHDTPM
E-D-C-22: $R^1$ = Mp, $R^2$ =Bz, $R^3$ = Mpm, $R^4$ = NHDTPM
E-D-C-23: $R^1$ = Mpm, $R^2$ =Bz, $R^3$ = Bz, $R^4$ = NHDTPM
E-D-C-24: $R^1$ = Mp, $R^2$ =Bz, $R^3$ = Bz, $R^4$ = NHDTPM
E-D-C-25: $R^1$ = Mpm, $R^2$ = Mpm, $R^3$ = Mpm, $R^4$ = $N_3$
E-D-C-26: $R^1$ = Mp, $R^2$ = Mpm, $R^3$ = Mpm, $R^4$ = $N_3$
E-D-C-27: $R^1$ = Mpm, $R^2$ = Mpm, $R^3$ = Bz, $R^4$ = $N_3$
E-D-C-28: $R^1$ = Mp, $R^2$ = Mpm, $R^3$ = Bz, $R^4$ = $N_3$
E-D-C-29: $R^1$ = Mpm, $R^2$ =Bz, $R^3$ = Mpm, $R^4$ = $N_3$
E-D-C-30: $R^1$ = Mp, $R^2$ =Bz, $R^3$ = Mpm, $R^4$ = $N_3$
E-D-C-31: $R^1$ = Mpm, $R^2$ =Bz, $R^3$ = Bz, $R^4$ = $N_3$
E-D-C-32: $R^1$ = Mp, $R^2$ =Bz, $R^3$ = Bz, $R^4$ = $N_3$

Example 22: Synthesis of trisaccharide **E-D-C-17** to **E-D-C-32**, conditions: a) SOP 33.

Example 23: Formation of trisaccharidic Trichloroacetimidates **E-D-C-33** to **E-D-C-48**



E-D-C-1 to E-D-C-16

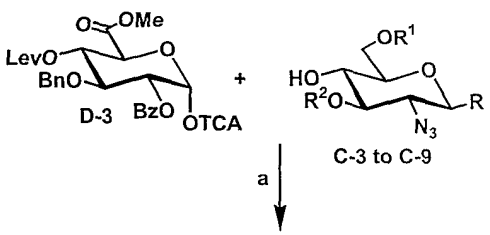


E-D-C-33 : $R^1$ = Mpm, $R^2$ = Mpm, $R^3$ = Mpm, $R^4$ = NHDTPM
E-D-C-34 : $R^1$ = Mp, $R^2$ = Mpm, $R^3$ = Mpm, $R^4$ = NHDTPM
E-D-C-35 : $R^1$ = Mpm, $R^2$ = Mpm, $R^3$ = Bz, $R^4$ = NHDTPM
E-D-C-36 : $R^1$ = Mp, $R^2$ = Mpm, $R^3$ = Bz, $R^4$ = NHDTPM
E-D-C-37 : $R^1$ = Mpm, $R^2$ =Bz, $R^3$ = Mpm, $R^4$ = NHDTPM
E-D-C-38 : $R^1$ = Mp, $R^2$ =Bz, $R^3$ = Mpm, $R^4$ = NHDTPM
E-D-C-39 : $R^1$ = Mpm, $R^2$ =Bz, $R^3$ = Bz, $R^4$ = NHDTPM
E-D-C-40 : $R^1$ = Mp, $R^2$ =Bz, $R^3$ = Bz, $R^4$ = NHDTPM

E-D-C-41 : $R^1$ = Mpm, $R^2$ = Mpm, $R^3$ = Mpm, $R^4$ = $N_3$
E-D-C-42 : $R^1$ = Mp, $R^2$ = Mpm, $R^3$ = Mpm, $R^4$ = $N_3$
E-D-C-43 : $R^1$ = Mpm, $R^2$ = Mpm, $R^3$ = Bz, $R^4$ = $N_3$
E-D-C-44 : $R^1$ = Mp, $R^2$ = Mpm, $R^3$ = Bz, $R^4$ = $N_3$
E-D-C-45 : $R^1$ = Mpm, $R^2$ =Bz, $R^3$ = Mpm, $R^4$ = $N_3$
E-D-C-46 : $R^1$ = Mp, $R^2$ =Bz, $R^3$ = Mpm, $R^4$ = $N_3$
E-D-C-47 : $R^1$ = Mpm, $R^2$ =Bz, $R^3$ = Bz, $R^4$ = $N_3$
E-D-C-48 : $R^1$ = Mp, $R^2$ =Bz, $R^3$ = Bz, $R^4$ = $N_3$

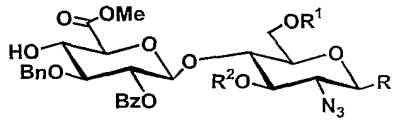
Example 23: Formation of trisaccharidic Trichloroacetimidates **E-D-C-33** to **E-D-C-48,** conditions: a) 1. SOP 9; 2. SOP 25, (82% over 2 steps for **E-D-C-47**

Example 24: Syntheses of trisaccharides **E-D-C-9** to **E-D-C-12** and **E-D-C-49** to **E-D-C-60**

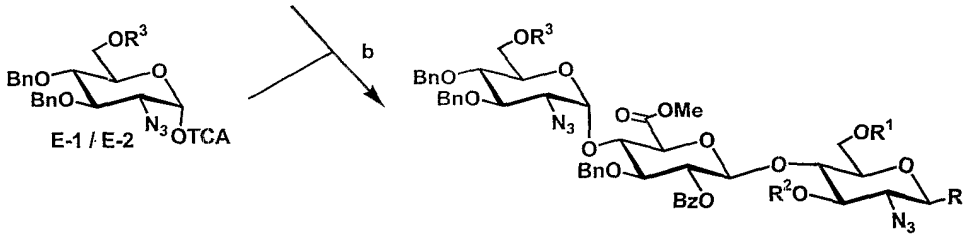



C-6a : R = SCres, $R^1$ = Mpm, $R^2$ = Mpm
C-7 : R = OTBDPS, $R^1$ = Mpm, $R^2$ = Mpm
C-8c : R = OTBDPS, $R^1$ = Mp, $R^2$ = All
C-10 : R = SCres, $R^1$ = Mp, $R^2$ = Mpm
C-11 : R = SCres, $R^1$ = Mpm, $R^2$ = All
C-12 : R = OTBDPS, $R^1$ = Mpm, $R^2$ = All
C-13 : R = SCres, $R^1$ = Mp, $R^2$ =All
C-14 : R = OTBDPS, $R^1$ = Mp, $R^2$ = Mpm

D-C-1 : R = SCres, $R^1$ = Mpm, $R^2$ = Mpm
D-C-2 : R = SCres, $R^1$ = Mpm, $R^2$ = All
D-C-3 : R = SCres, $R^1$ = Mp, $R^2$ = Mpm
D-C-4 : R = SCres, $R^1$ = Mp, $R^2$ = All




D-C-5 : R = OTBDPS, $R^1$ = Mpm, $R^2$ = Mpm
D-C-6 : R = OTBDPS, $R^1$ = Mpm, $R^2$ = All
D-C-7 : R = OTBDPS, $R^1$ = Mp, $R^2$ = Mpm
D-C-8 : R = OTBDPS, $R^1$ = Mp, $R^2$ = All




E-D-C-49 : R = SCres, $R^1$ = Mpm, $R^2$ = Mpm, $R^3$ = Bz
E-D-C-50 : R = SCres, $R^1$ = Mpm, $R^2$ =All, $R^3$ = Bz
E-D-C-51 : R = SCres, $R^1$ = Mp, $R^2$ = Mpm, $R^3$ = Bz
E-D-C-52 : R = SCres, $R^1$ = Mp, $R^2$ = All, $R^3$ = Bz
E-D-C-53 : R = SCres, $R^1$ = Mpm, $R^2$ = Mpm, $R^3$ = Mpm
E-D-C-54 : R = SCres, $R^1$ = Mpm, $R^2$ = All, $R^3$ = Mpm
E-D-C-55 : R = SCres, $R^1$ = Mp, $R^2$ = Mpm, $R^3$ = Mpm
E-D-C-56 : R = SCres, $R^1$ = Mp, $R^2$ = All, $R^3$ = Mpm

E-D-C-11 : R = OTBDPS, $R^1$ = Mpm, $R^2$ = Mpm, $R^3$ = Bz
E-D-C-57 : R = OTBDPS, $R^1$ = Mpm, $R^2$ = All, $R^3$ = Bz
E-D-C-12 : R = OTBDPS, $R^1$ = Mp, $R^2$ = Mpm, $R^3$ = Bz
E-D-C-58 : R = OTBDPS, $R^1$ = Mp, $R^2$ = All, $R^3$ = Bz
E-D-C-9 : R = OTBDPS, $R^1$ = Mpm, $R^2$ = Mpm, $R^3$= Mpm
E-D-C-59 : R = OTBDPS, $R^1$ = Mpm, $R^2$ = All, $R^3$= Mpm
E-D-C-10 : R = OTBPS, $R^1$ = Mp, $R^2$ = Mpm, $R^3$ = Mpm
E-D-C-60 : R = OTBPS, $R^1$ = Mp, $R^2$ = All, $R^3$ = Mpm

Example 24: Syntheses of trisaccharides **E-D-C-9** to **E-D-C-12** and **E-D-C-49** to **E-D-C-60**, conditions: a) 1. SOP 33; 2. SOP 24; b) SOP 33. (for **D-C-5:** 70 %, 2 steps); b) SOP 33, ( 78 % for **E-D-C-9** as an α/β mixture).

Compound **D-C-5**:

**D-C-5** was formed according to SOP 33 with ether as solvent at -20°C and TMSOTf as promotor, followed by SOP 24 in 70 % yield (over 2 steps as α/β-mixture).

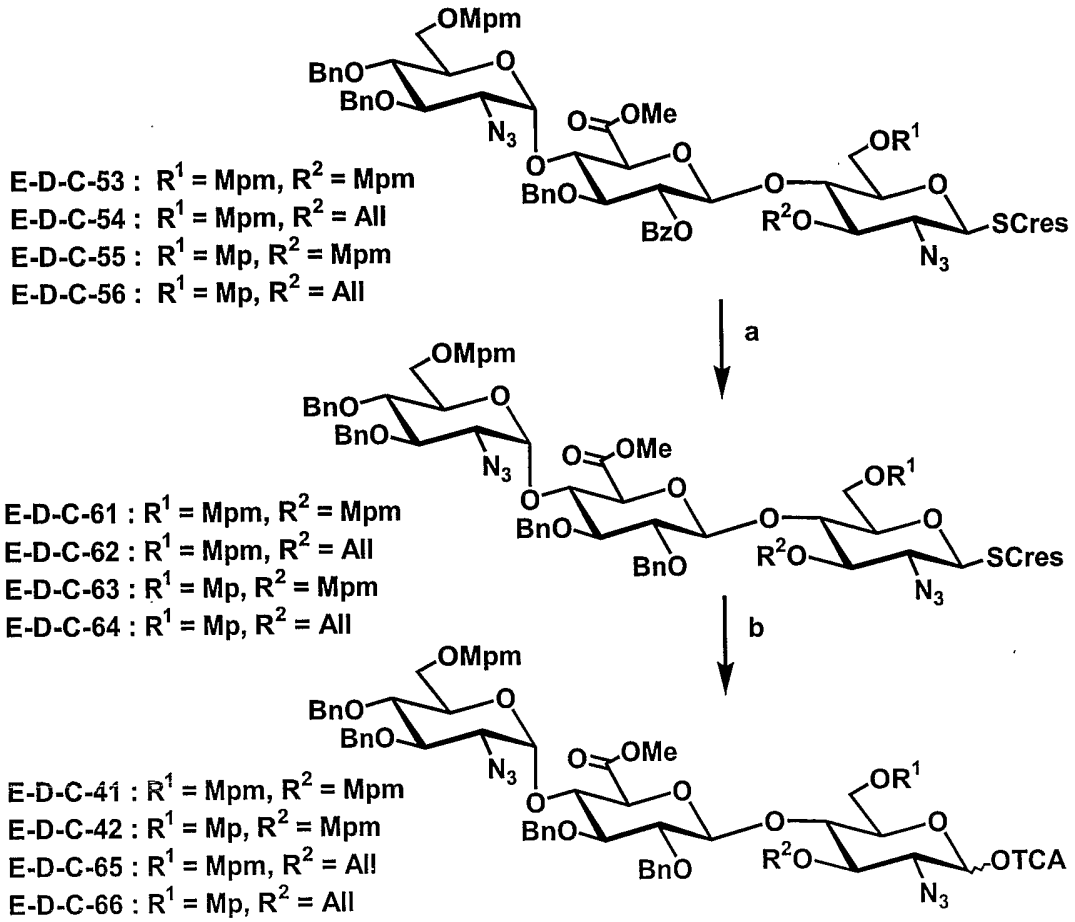
Selected $^1$H-NMR (400 MHz in $CDCl_3$): $\delta$ = 7.88 (m, 2H, Ar), 7.67- 7.58 (m, 5H, Ar), 7.42 (m, 2H, Ar), 7.37-7.12 (m, 16H, Aryl), 6.84 (m, 3H, Ar), 5.14 (dd, 1H, $J_{1,2}$ = 8.2 Hz, $J_{2,3}$ = 9.5Hz, H-2'), 4.90 (d, 1H, $J_{gem}$ = 10.7 Hz, $OCH_2$), 4.73 (d, 1H, $J_{gem}$ = 11.5 Hz, $OCH_2$), 4.65 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1'β), 4.63 – 4.58 (m, 2H, $OCH_2$), 4.51 (d, 1H, $J_{gem}$ = 12.0 Hz, $OCH_2$), 4.20 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1 β ), 4.05 (d, 1H, $J_{gem}$ = 11.9 Hz, $OCH_2$), 4.02 – 3.95 (m, 2H, not assigned), 3.81 (s, 3H, $OCH_3$), 3.80 (s, 3H, $OCH_3$), 3.71 (d, 1H, $J_{4,5}$ = 9.9 Hz, H-5'), 3.67 (s, 3H, $OCH_3$), 3.47 - 3.40 (m, 3H, not assigned), 3.21 (dd, 1 H, J = 9.0 Hz, J = 9.8 Hz, not assigned), 3.00 (dd, 1 H, $J_{5,6b}$ = 1.4 Hz, $J_{gem}$ = 10.5 Hz, H-6b), 2.63 (m, 1 H, H-5), 2.35 (bs, 1 H, 4-OH), 1.07 (s, 9H, $C(CH_3)_3$).

Compound **E-D-C-9**:

**E-D-C-9** was formed according to SOP 33 with ether as solvent at -20°C and TBDMSOTf as promotor in 78 % yield (α/β-mixture).

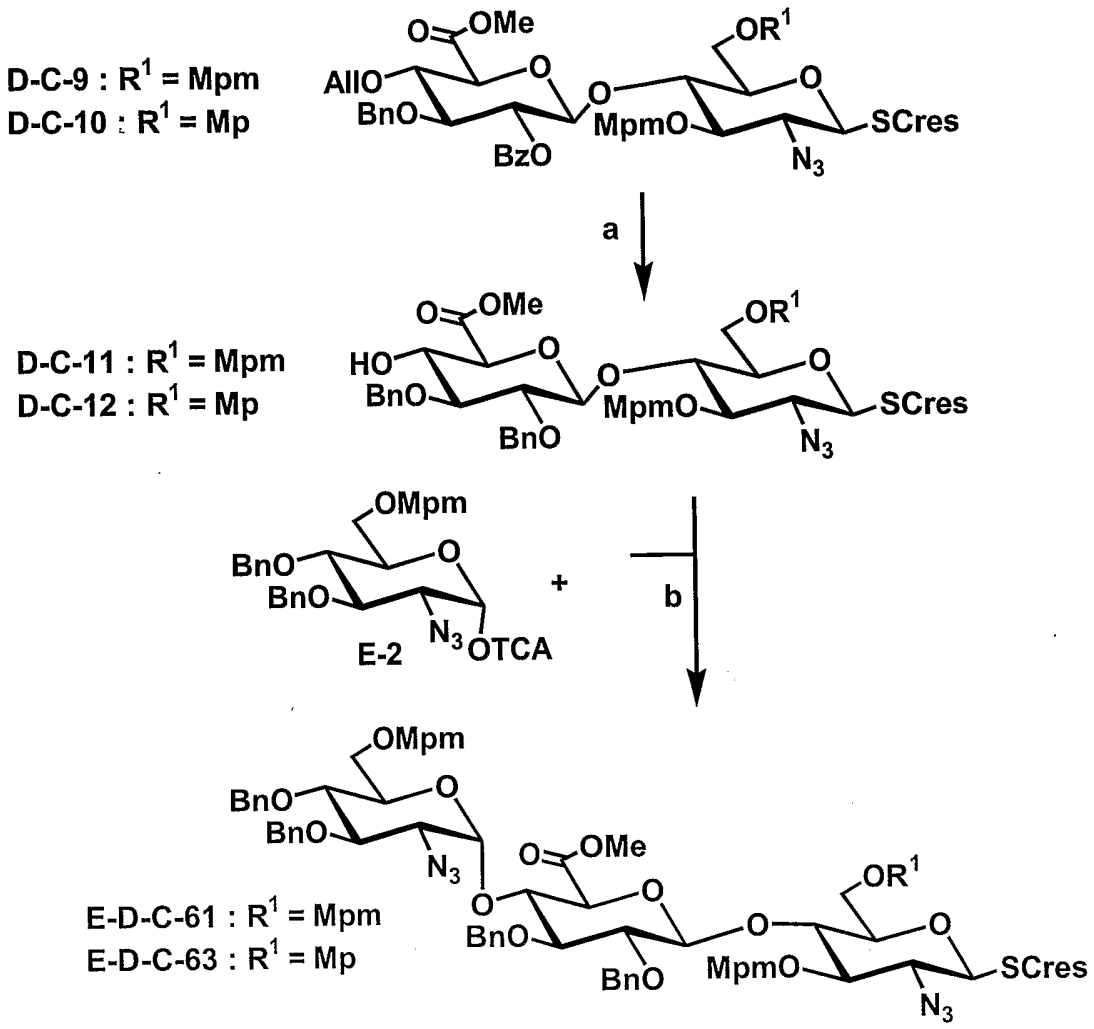
Selected $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 7.77 (m, 2H, Aryl), 7.59, 7.54 (2m, 2 x 2H, Aryl), 7.35 – 7.00 (m, 30 H, Aryl), 6.88 (m, 2H, Aryl), 6.82 (m, 2H, Aryl), 6.73 (m, 2H, Aryl), 5.41 (d, 1 H, $J_{1,2}$ = 3.5 Hz, H-1"α), 5.19 (dd, 1 H, $J_{2,3} \approx J_{1,2}$ = 9.6 Hz, H-2'), 4.85 - 4.78 (m, 4 H, $OCH_2$), 4.67 (m, 2H, $OCH_2$), 4.65 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1β, not assigned), 4.38 (d, 1 H, $J_{gem}$ = 11.1 Hz, $OCH_2$), 4.29 (d, 1 H, $J_{gem}$ = 11.7 Hz, $OCH_2$), 4.17 (dd, 1H, not assigned), 4.11 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1β not assigned), 4.03 (d, 1 H, $J_{gem}$ = 12.0 Hz, $OCH_2$), 3.90 - 3.76 (m, 3H, not assigned), 3.730, 3.727 (2s, 2 x 3H, $OCH_3$), 3.65 (s, 3H, $OCH_3$), 3.54 (s, 3H, $OCH_3$), 2.89 (dd, 1 H, $J_{gem}$ = 10.5 Hz, $J_{5,6b}$ < 2.0 Hz, H-6b), 2.52 (m, 1H, H-5), 1.02 (s, 9 H, $C(CH_3)_3$).

**Example 25:** Synthesis of trisaccharides **E-D-C-41, E-D-C-42** and **E-D-C-61 to E-D-C-66**



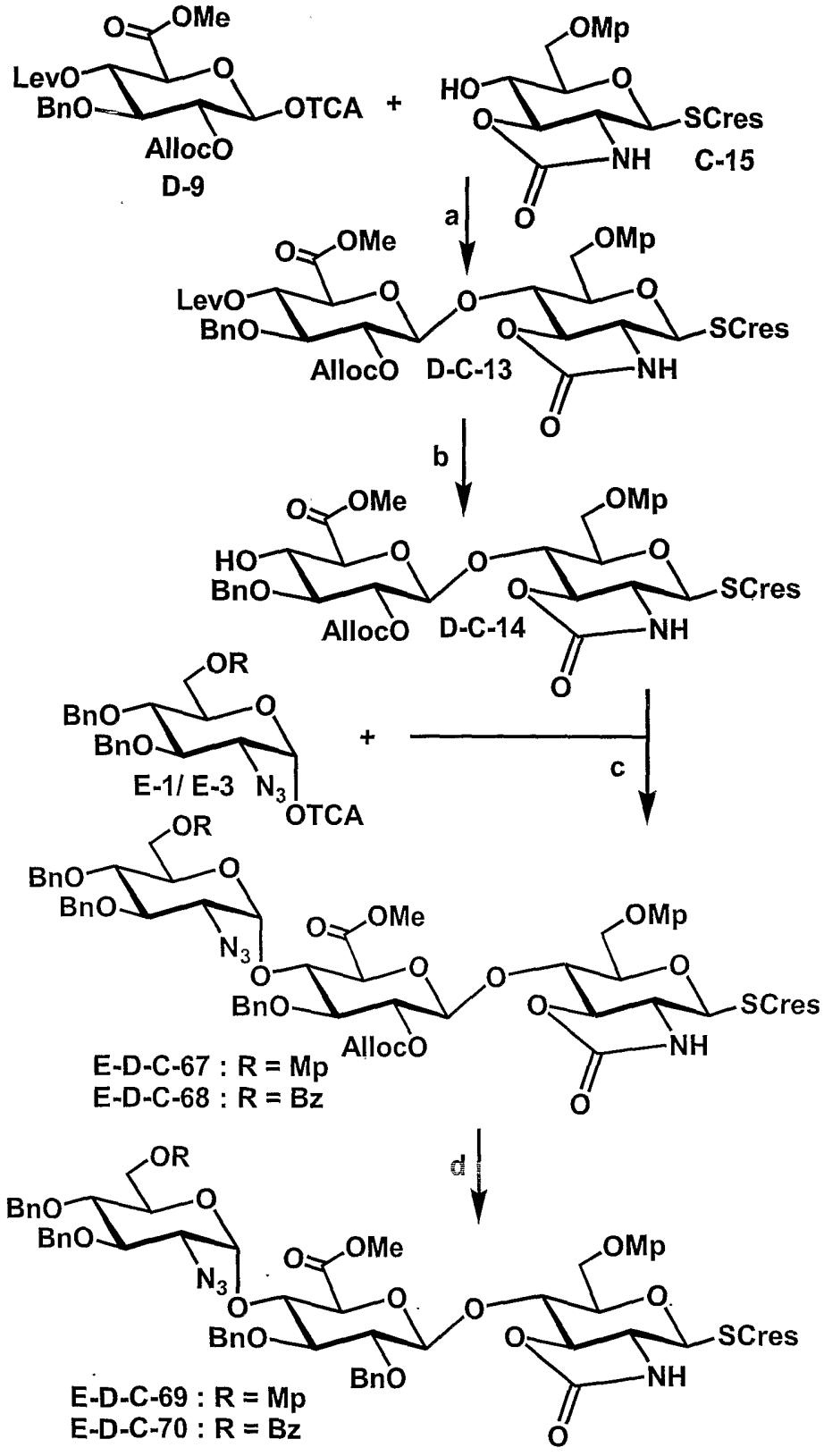

Example 25: Synthesis of trisaccharides **E-D-C-41**, **E-D-C-42** and **E-D-C-61** to **E-D-C-66**, conditions: a) 1. SOP 39; 2. SOP 38; 3. SOP 16; b) 1. SOP 14; 2. SOP 25a.

Example 26: An alternative route to the trisaccharides **E-D-C-61** and **E-D-C-63**



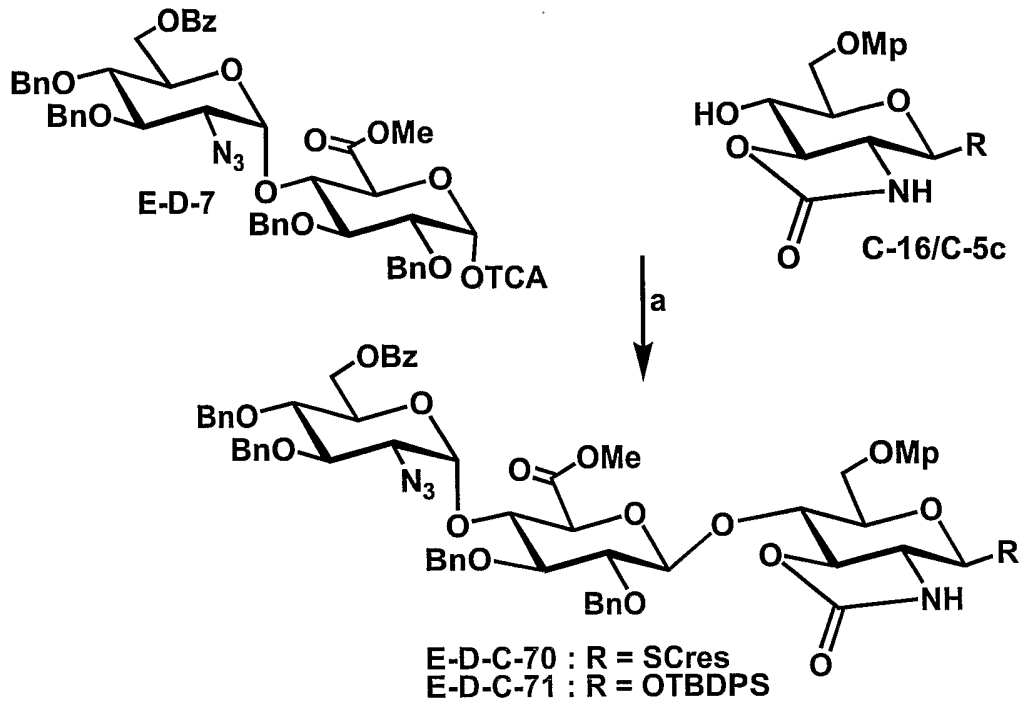

Example 26: An alternative route to the trisaccharides **E-D-C-61** and **E-D-C-63**, conditions: a) 1. SOP 39; 2. SOP 38; 3. SOP 16; 4. $Pd(Ph_3P)_4$, p-TolSO$_2$Na, THF, MeOH; b) SOP 33.

Example 27: Syntheses of blocks **E-D-C-67** to **E-D-C-70**




Example 27 : Syntheses of trisaccharides **E-D-C-67** to **E-D-C-70**, conditions: a) SOP 33; b) SOP 24; c) SOP 33; d) 1. SOP 36; 2. SOP 37.

Example 28: Synthesis of trisaccharides **E-D-C-70** and **E-D-C-71**




Example 28: Synthesis of trisaccharides **E-D-C-70** and **E-D-C-71**, conditions: a) SOP 33, (55% for **E-D-C-71**, α/β mixture).

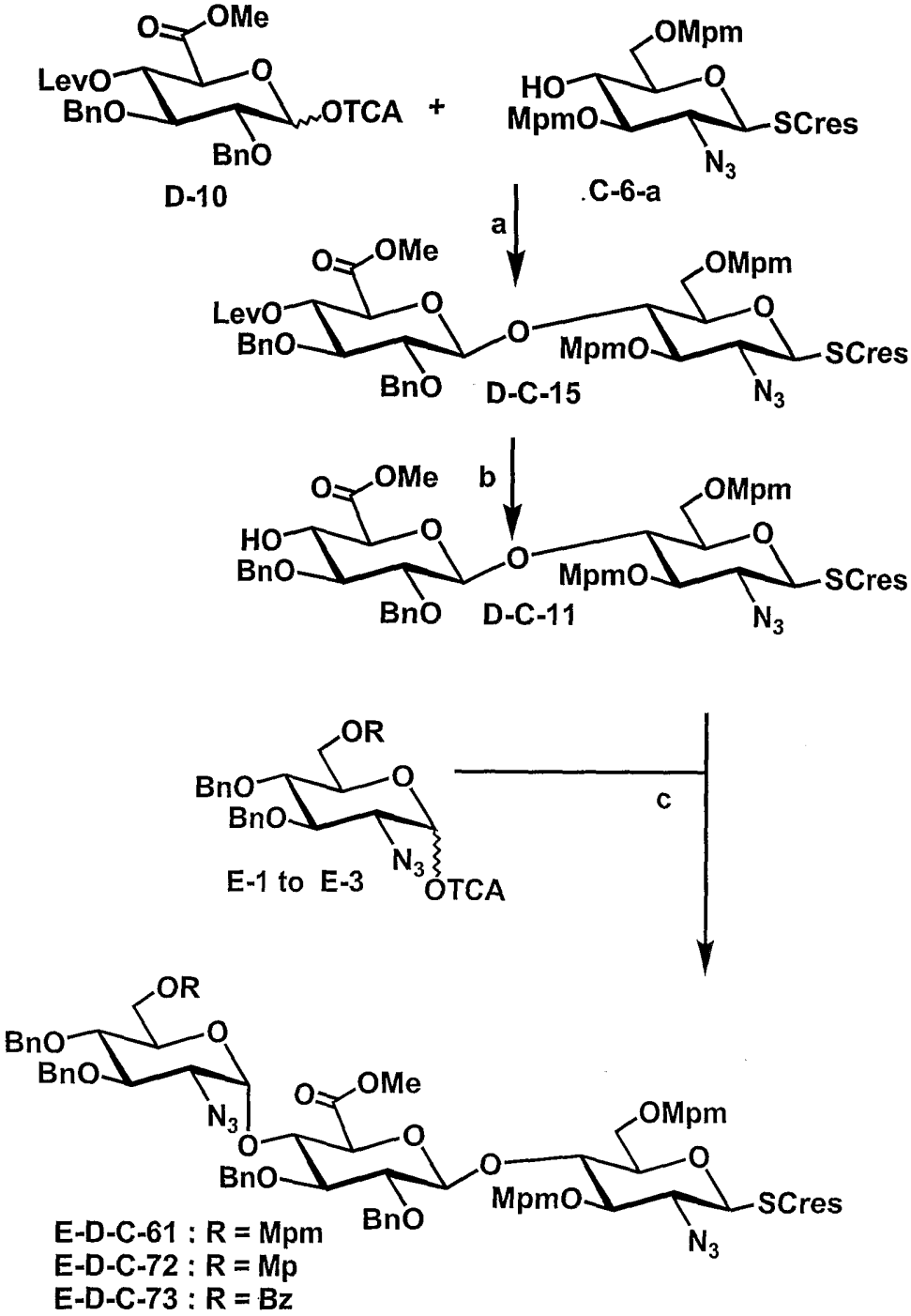
Compound **E-D-C-71**:

**E-D-C-71** was formed according to SOP 33 with dichloromethane as solvent at 40°C and TBDMSOTf as promotor in 55 % yield (as α/β-mixture).

Selected $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ = 7.91 (m, 2H, Aryl), 7.61 (m, 2H, Aryl), 7.55 (m, 2H, Aryl), 7.50 – 7.02 (m, 29 H, Aryl), 6.65 (m, 4H, Mp), 5.38 (d, 1 H, $J_{1,2}$ = 3.9 Hz, H-1"α), 5.22 (bs, 1 H, NH), 4.67 (d, 1H, $J_{1,2}$ = 7.4 Hz, H-1β, not assigned), 4.50 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1β, not assigned), 3.92 (d, 1 H, $J_{4,5}$ = 9.8 Hz, H-5'), 3.698 (s, 3 H, $OCH_3$), 3.693 (s, 3 H, $OCH_3$), 1.03 (s, 9 H, $C(CH_3)_3$).

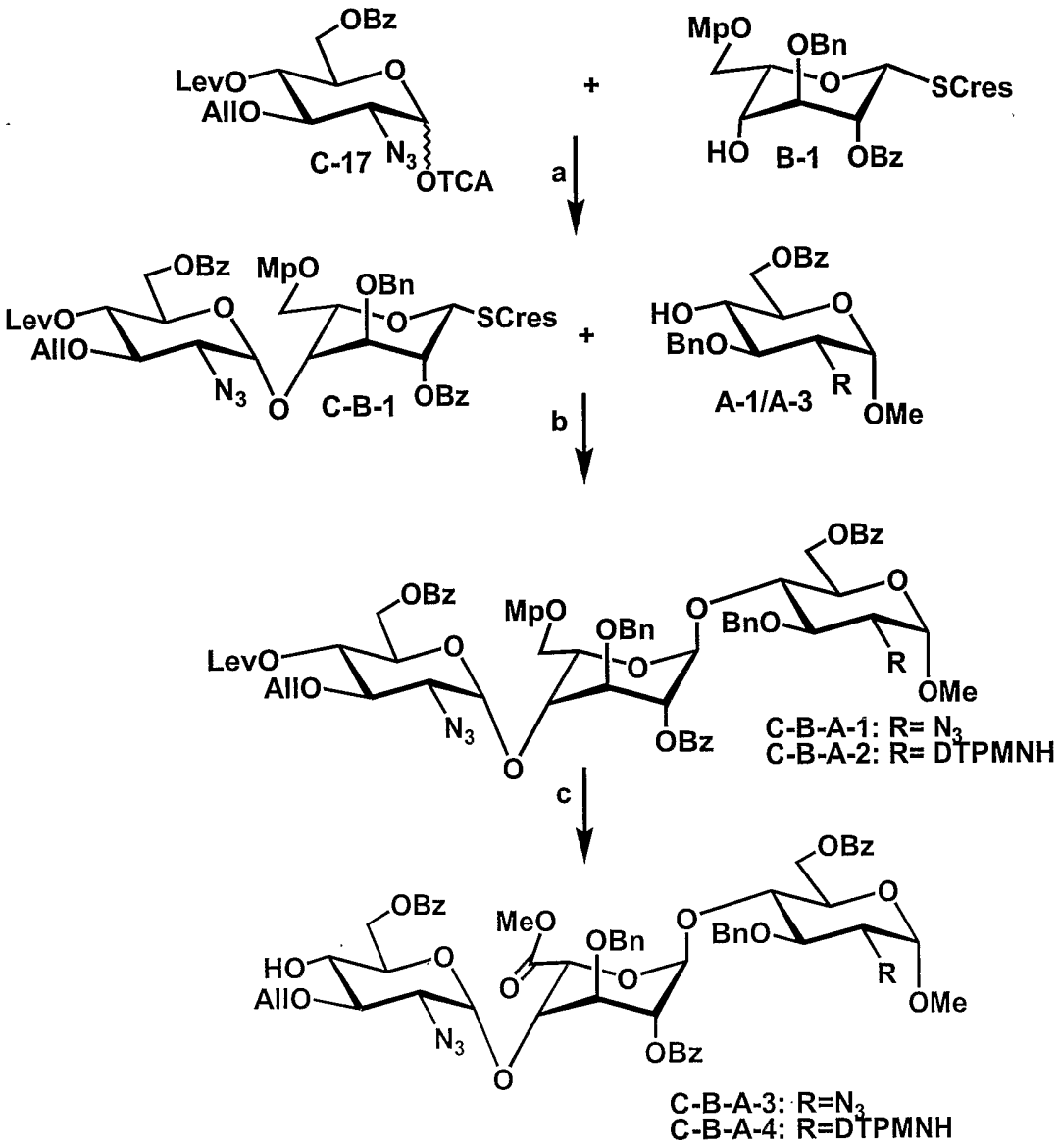
$M_{found}$ = 1408.52 $(M+H_2O)^+$, $M_{calc}$ = 1390.54 ($M^+$).

Example 29: Syntheses of trisaccharides **E-D-C-61**, **E-D-C-72** and **E-D-C-73**

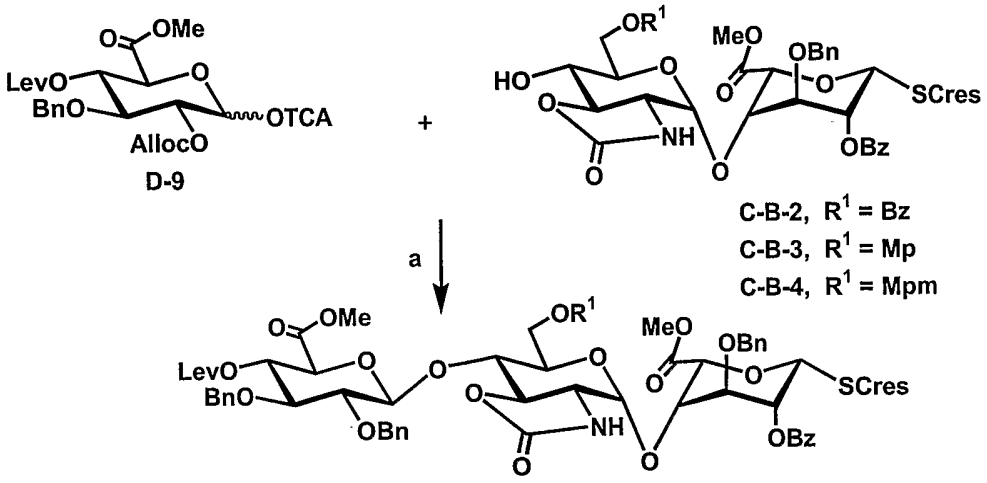



Example 29: Syntheses of trisaccharides **E-D-C-72** to **E-D-C-73** and **E-D-C-61**, conditions: a) SOP 33; b) SOP 24; c) SOP 33.

Example 30: Syntheses of trisaccharides **C-B-A-1** to **C-B-A-4**



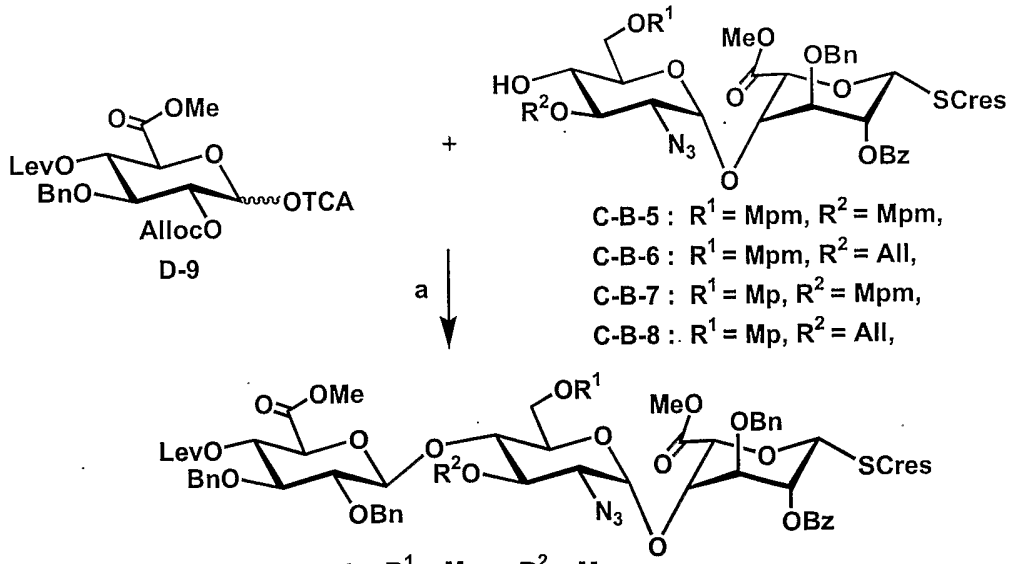

Example 30: Syntheses of trisaccharides **C-B-A-1** to **C-B-A-4**, conditions: a) SOP 33; b) SOP 32a; c) 1. SOP 27; 2. SOP 20; 3. SOP 16; 4. SOP 24.




D-C-B-1, $R^1$ = Bz
D-C-B-2, $R^1$ = Mp
D-C-B-3, $R^1$ = Mpm

Example 32: Syntheses of D-C-B-trisaccharides **D-C-B-1** to **D-C-B-3**, conditions: a) 1. SOP 33; 2. SOP 36; 3. SOP 37.

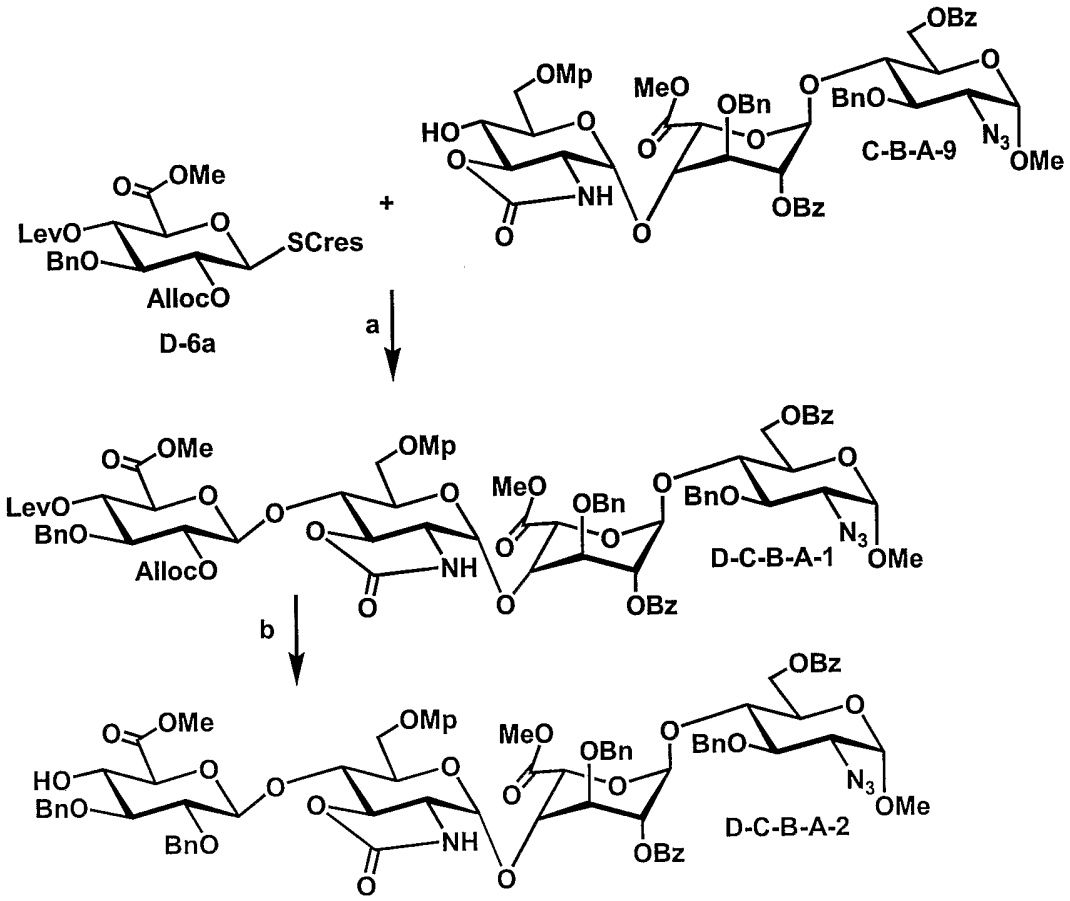
Example 33: Syntheses of D-C-B trisaccharides **D-C-B-4** to **D-C-B-7**.




D-C-B-4 : $R^1$ = Mpm, $R^2$ = Mpm,
D-C-B-5 : $R^1$ = Mpm, $R^2$ = All,
D-C-B-6 : $R^1$ = Mp, $R^2$ = Mpm,
D-C-B-7 : $R^1$ = Mp, $R^2$ = All,

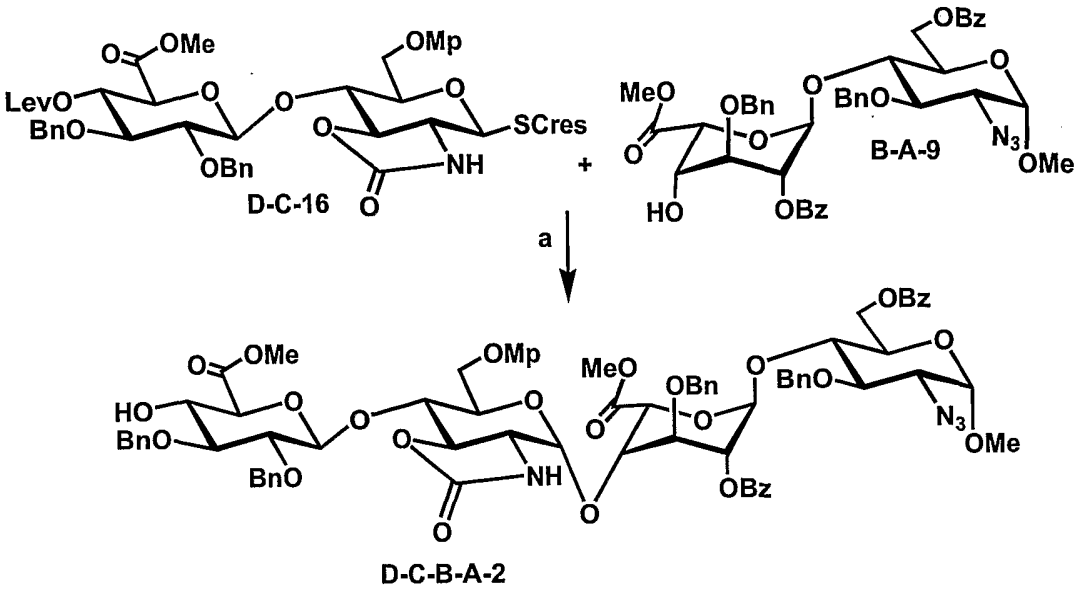
Example 33: Syntheses of D-C-B-trisaccharides **D-C-B-4** to **D-C-B-7**, conditions: a) 1. SOP 33; 2. SOP 36; 3. SOP 37.

Example 34: Syntheses of tetrasaccharides **D-C-B-A-1** to **D-C-B-A-2**



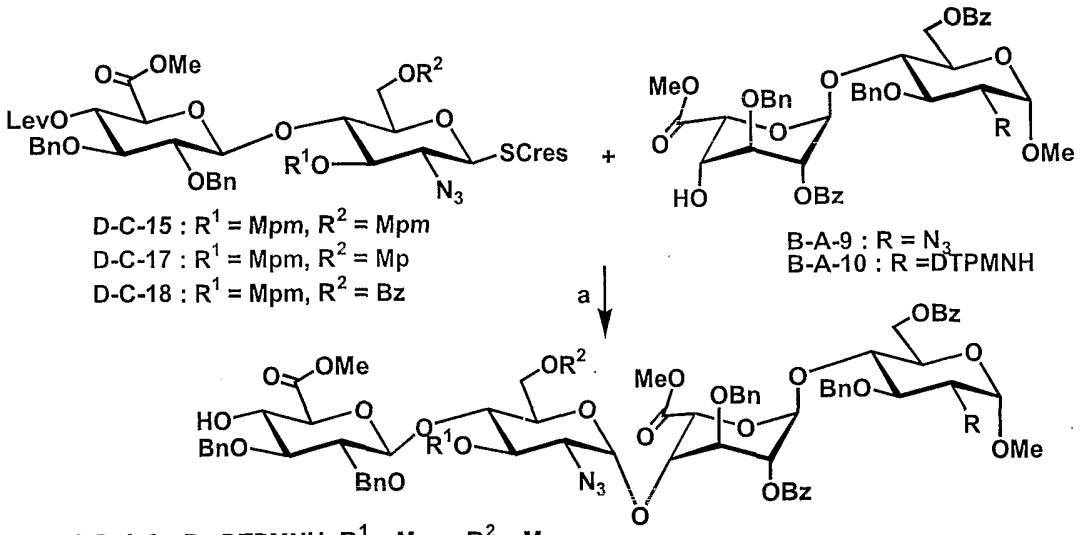

Example 34: Syntheses of tetrasaccharides **D-C-B-A-1** and **D-C-B-A-2**, conditions: a) SOP 32a; b)1. SOP 36; 2. SOP 37; 3. SOP 24.

Example 35: Alternative syntheses of tetrasaccharides **D-C-B-A-2**




Example 35: Alternative synthesis of tetrasaccharide **D-C-B-A-2**, conditions: a) 1. SOP 34; 2. SOP 24.

Example 36: Syntheses of tetrasaccharides **D-C-B-A-3** to **D-C-B-A-8**



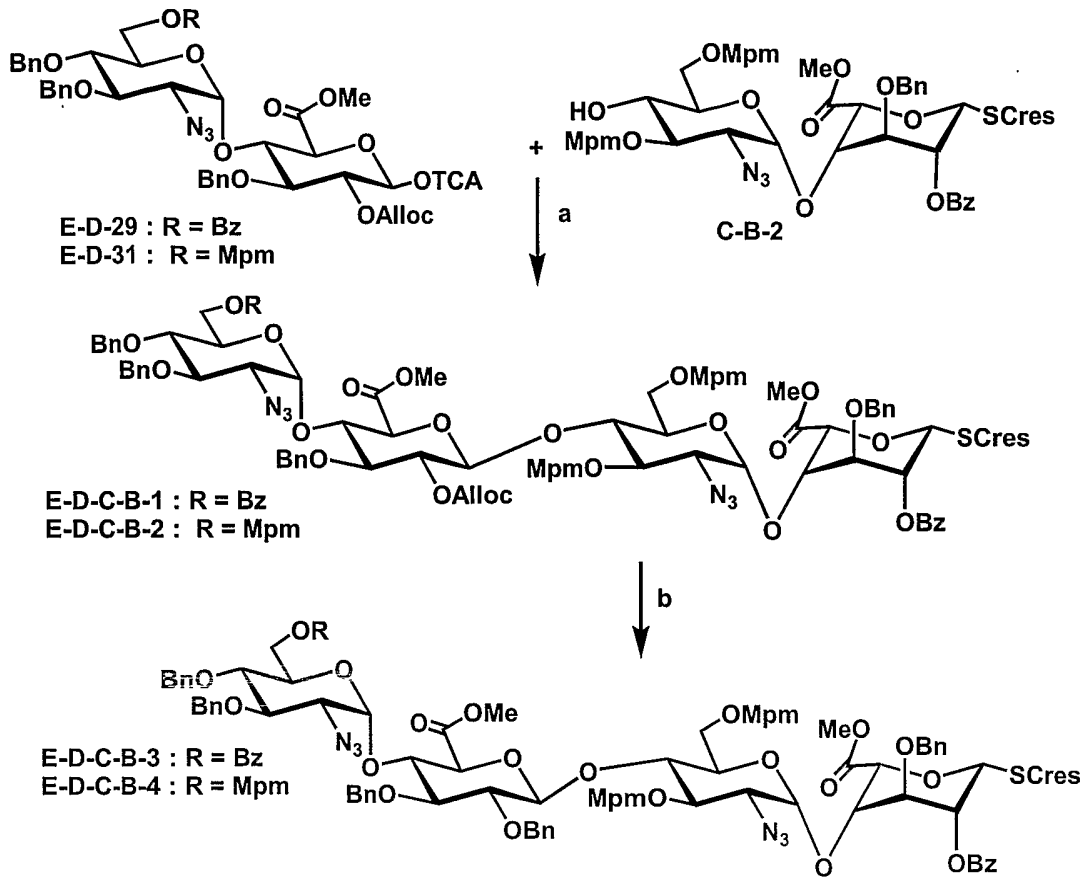

D-C-15 : $R^1$ = Mpm, $R^2$ = Mpm
D-C-17 : $R^1$ = Mpm, $R^2$ = Mp
D-C-18 : $R^1$ = Mpm, $R^2$ = Bz

B-A-9 : R = $N_3$
B-A-10 : R =DTPMNH

D-C-B-A-3 : R= DTPMNH, $R^1$ = Mpm, $R^2$ = Mpm,
D-C-B-A-4 : R= DTPMNH, $R^1$ = Mpm, $R^2$ = Bz
D-C-B-A-5 : R= DTPMNH, $R^1$ = Mpm, $R^2$ = Mp
D-C-B-A-6 : R= $N_3$, $R^1$ = Mpm, $R^2$ = Mpm,
D-C-B-A-7 : R= $N_3$, $R^1$ = Mpm, $R^2$ = Bz
D-C-B-A-8 :R= $N_3$, $R^1$ = Mpm, $R^2$ = Mp

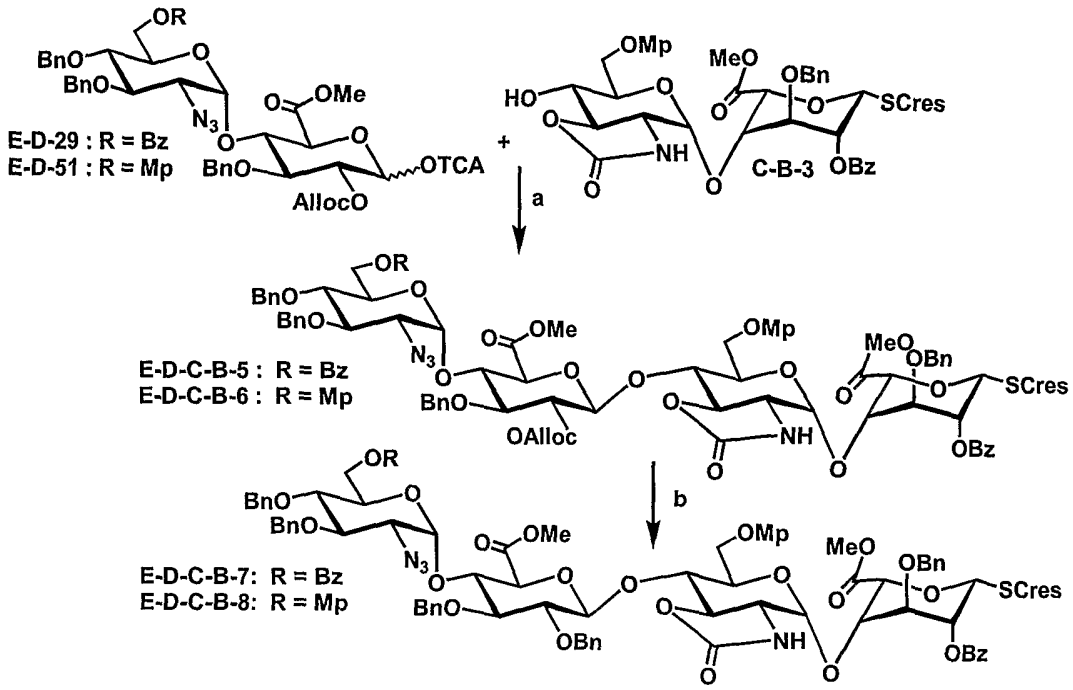
Example 36: Syntheses of tetrasaccharides **D-C-B-A-3** to **D-C-B-A-8**, conditions: a) 1 SOP 32b; 2. SOP 24.

Example 37: Syntheses of tetrasaccharides **E-D-C-B-1** to **E-D-C-B-4**



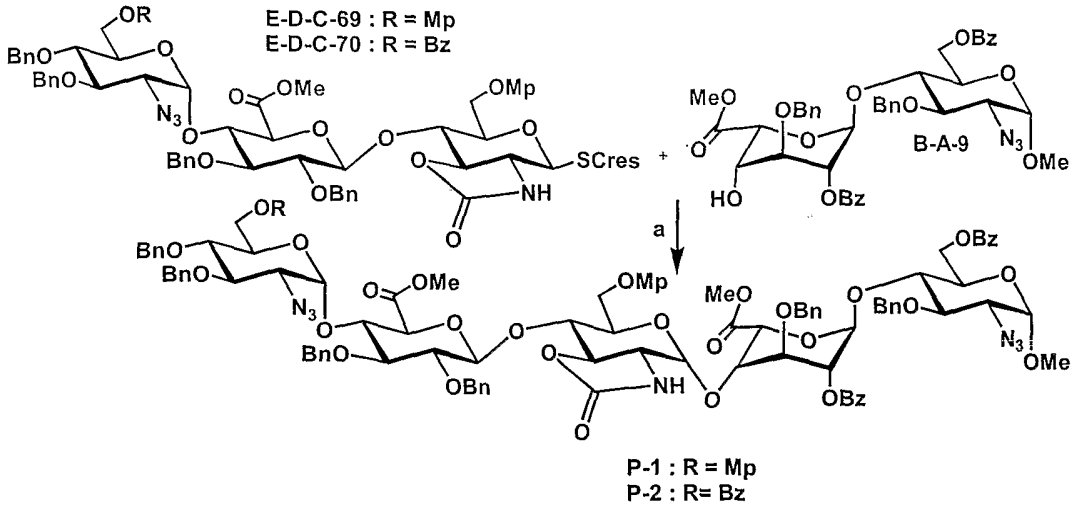

Example 37: Syntheses of tetrasaccharides **E-D-C-B-1** to **E-D-C-B-4**, conditions: a) SOP 33; b) 1. SOP 36; 2. SOP 37.

Example 38: Syntheses of blocks **E-D-C-B-5** to **E-D-C-B-8**



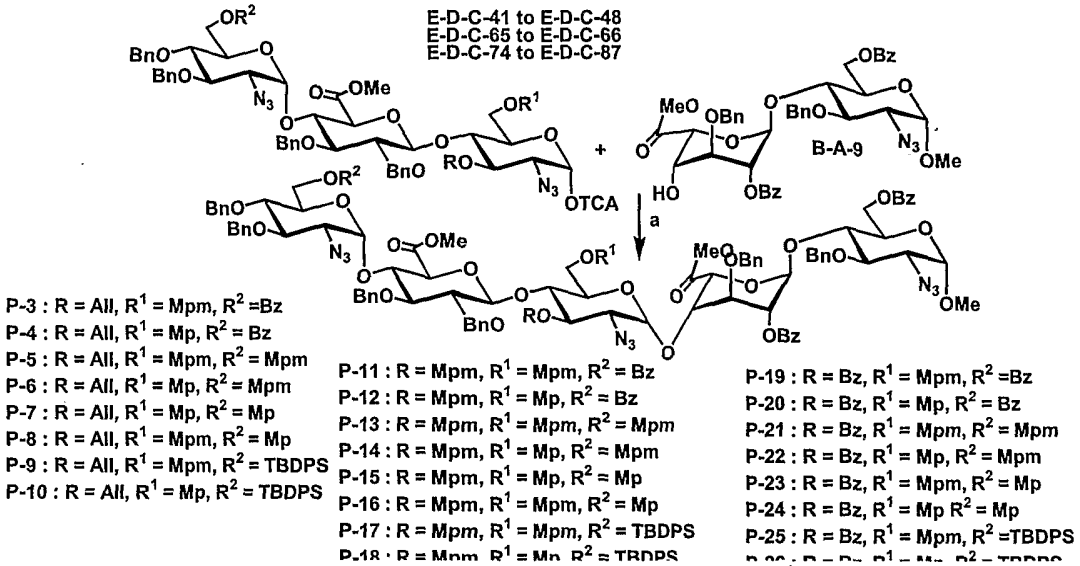

Example 38: Syntheses of tetrasaccharides **E-D-C-B-5** to **E-D-C-B-8**, conditions: a) SOP 33; b) 1. SOP 36; 2. SOP 37.

Example 39 : Syntheses of E-D-C-B-A pentasaccharides **P-1** and **P-2**




Example 39: Syntheses of E-D-C-B-A pentasaccharides **P-1** and **P-2**, conditions: a) SOP 34.

Example 40: Synthesis of E-D-C-B-A pentasaccharides **P-3** to **P-26**



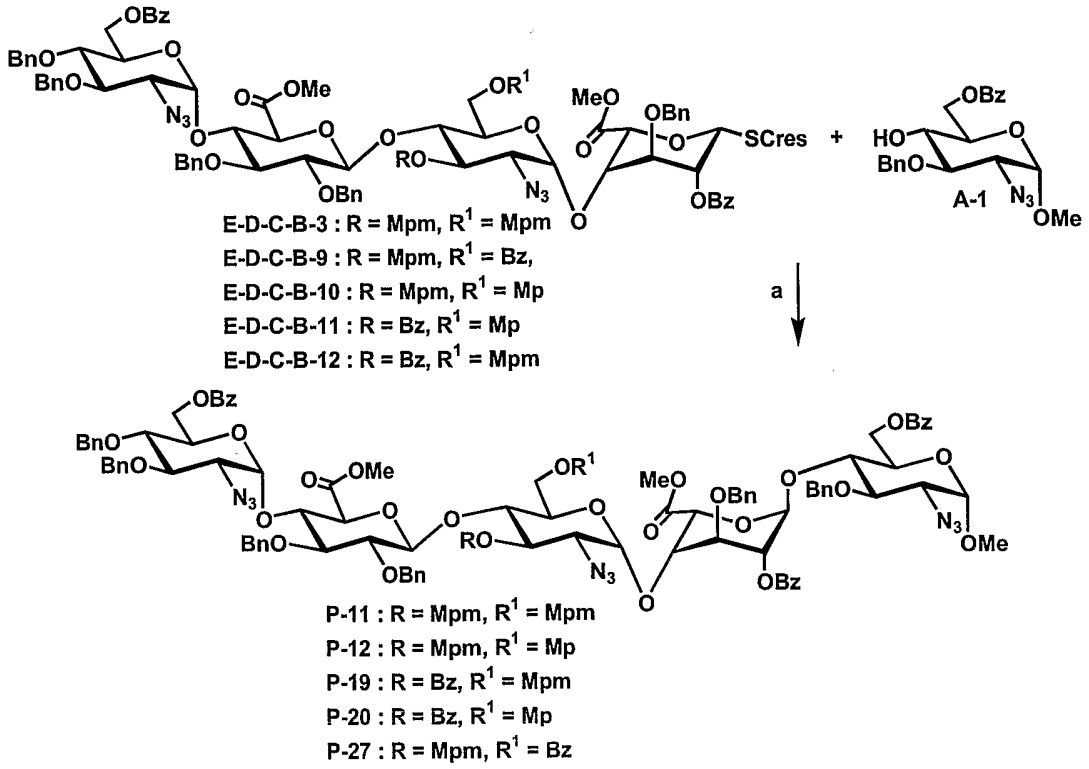

Example 40: Synthesis of E-D-C-B-A pentasaccharide **P-3** to **P-26**, conditions: a) SOP 33 (75 % for **P-19** as an α/β mixture).

Compound **P-19**:

**P-19** was formed according to SOP 33 with dichloromethane as solvent at - 20°C and TMSOTf as promotor;

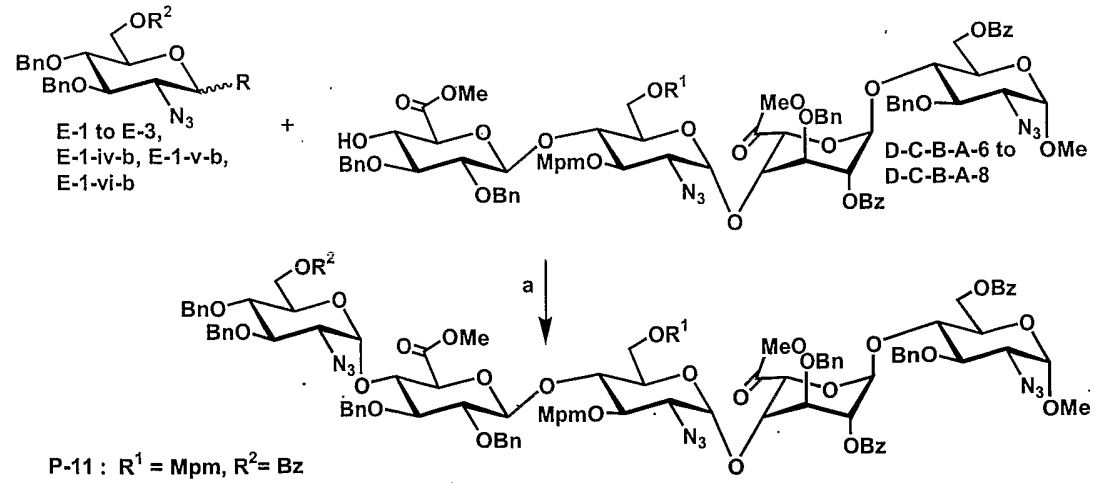
$M_{found}$ = 2068.76 $(M+H+H_2O)^+$, $M_{calc}$ = 2049.74 $(M^+)$.

Example 41: Alternative syntheses of E-D-C-B-A pentasaccharides **P-11, P-12, P-19, P-20** and **P-27**



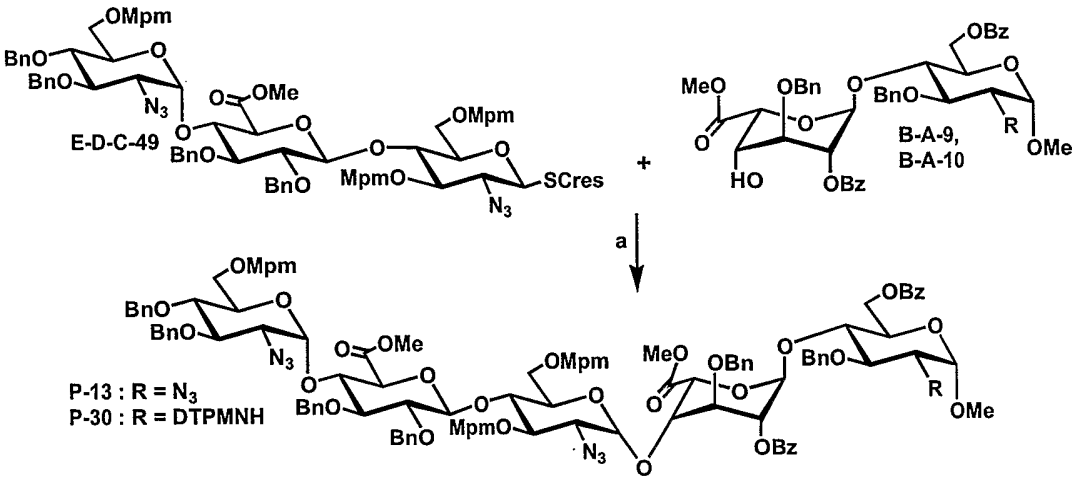

Example 41: Alternative syntheses of E-D-C-B-A pentasaccharides **P-11, P-12, P-19, P-20** and **P-27**, conditions: a) SOP 32a.

Example 42: Alternative syntheses of some E-D-C-B-A pentasaccharides



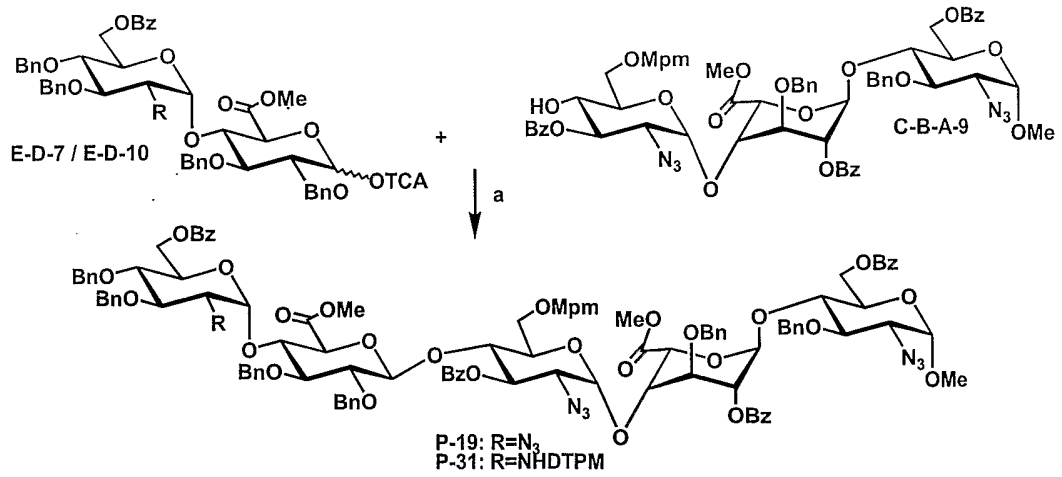

Example 42: Alternative syntheses of some E-D-C-B-A pentasaccharides, conditions: a) SOP 32a (for R = SCres) or SOP 33 ( for R = OTCA).

Example 43:Synthesis of pentasaccharide **P-13** and **P-30**




Example 43: Formation of pentasaccharides **P-13** and **P-30**, conditions: a) SOP 32a.

Example 44: Formation of pentasaccharide **P-19** and **P-31**

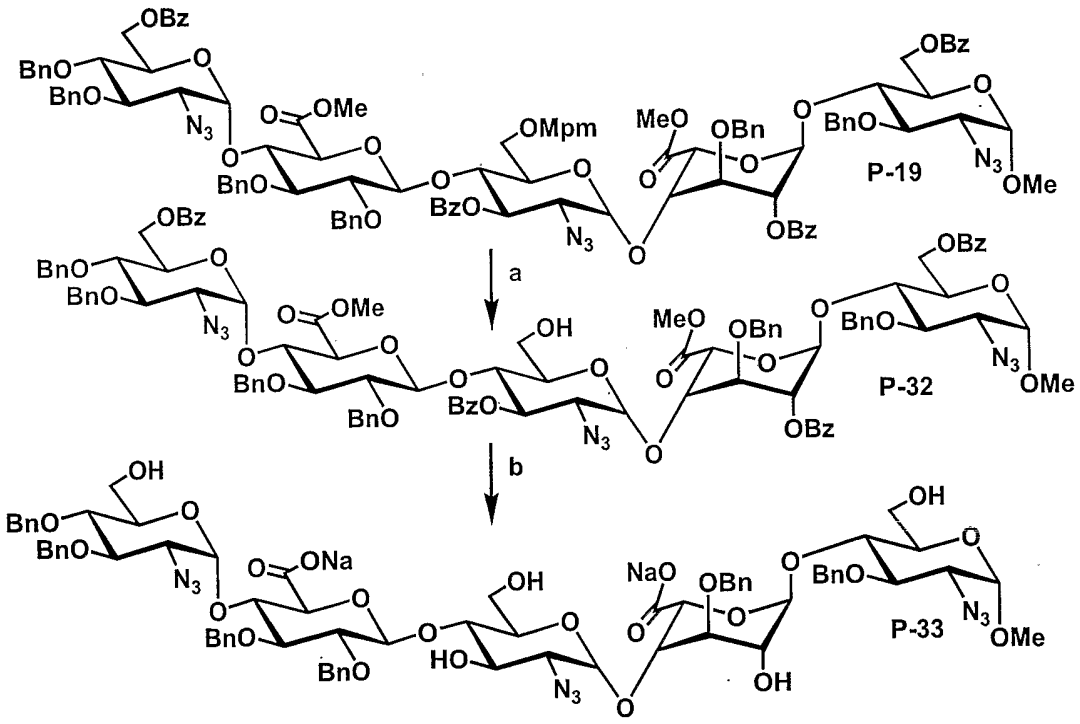



Example 45: Partial deprotection of pentasaccharide **P-19**, conditions: a) SOP 28, 84%; b) SOP 39, 86%.

Example preparation of **P19** :

A mixture of O-(2-azido-6-O-benzoyl-3,4-di-O-benzyl-2-deoxy–α-D-glucopyranosyl)-(1→4)-(methyl 2,3-di-O-benzyl-β-D-glucopyranosyluronate)-(1→4)-2-azido-3-O-benzoyl-2-deoxy-6-O-*p*-methoxybenzyl–α-D-glucopyranosyltrichloroacetimidate (30.0 mg, 21.2 μmol) and methyl (methyl 2-O-benzoyl-3-O-benzyl-α-L-idupyranosyluronate)-(1→4)-2-azido-3-O-benzyl-6-O-benzoyl-2-deoxy-α-D-glucopyranoside (15.4 mg 19.3 μmol) and 100 mg of molecular sieves 4Å in 1.5 ml dry dichloromethane was treated with TBDMSOTf (0.97 μl, 4.24 μmol) at -20°C for 20 hours. The reaction was quenched, filtered and concentrated. Further purification of the title compound was achieved by silica gel chromatography Yield: 15.83 mg (40%), $R_f$= 0.30 (toluene/ethyl acetate = 9/1).

Example 45: Partial deprotection of pentasaccharide **P-19**




Example 45: Partial deprotection of pentasaccharide **P-19**, conditions: a) SOP 28, 84%; b) SOP 39, 86%.

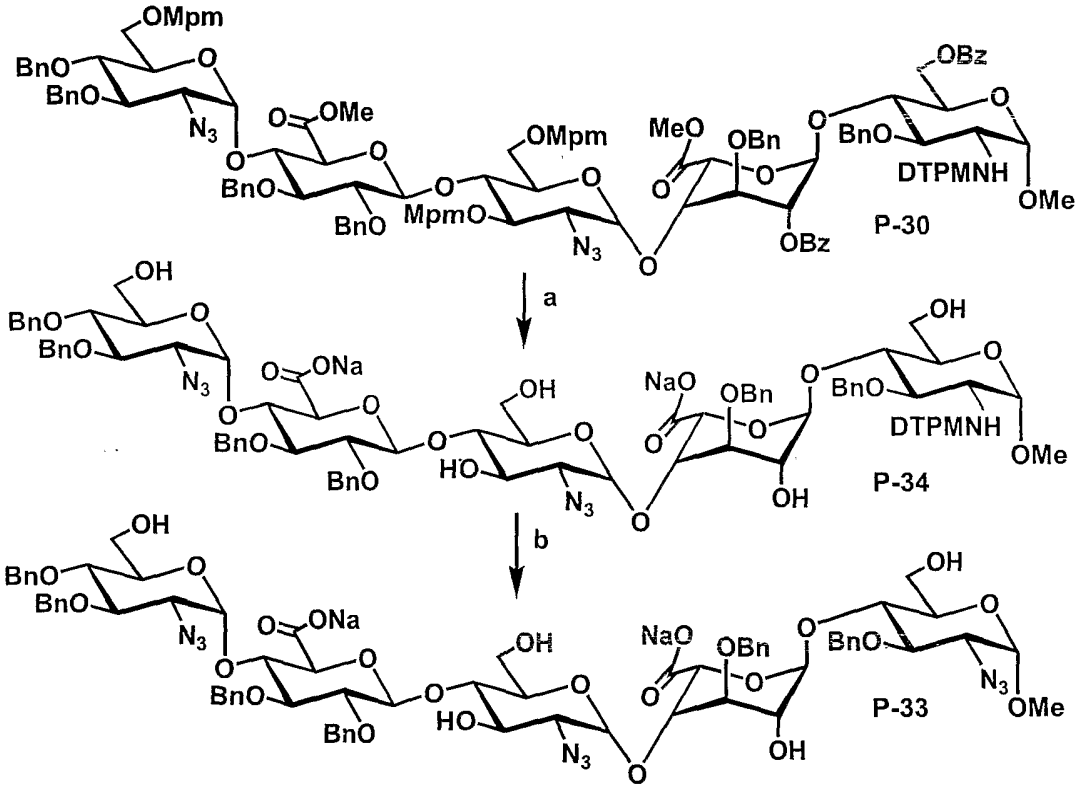
Compound **P-33**:

$M_{found}$ = 1503.5 $(M-N_2+2H)^+$, $M_{calc}$ = 1529.51 $(M^+)$.

To ease the structural proof, a small part of **P-33** was transformed into the bis methyl uronurate derivative and characterized via NMR-spectroscopy. Characteristic $^1$H-NMR-spectral regions are shown in figure 1.

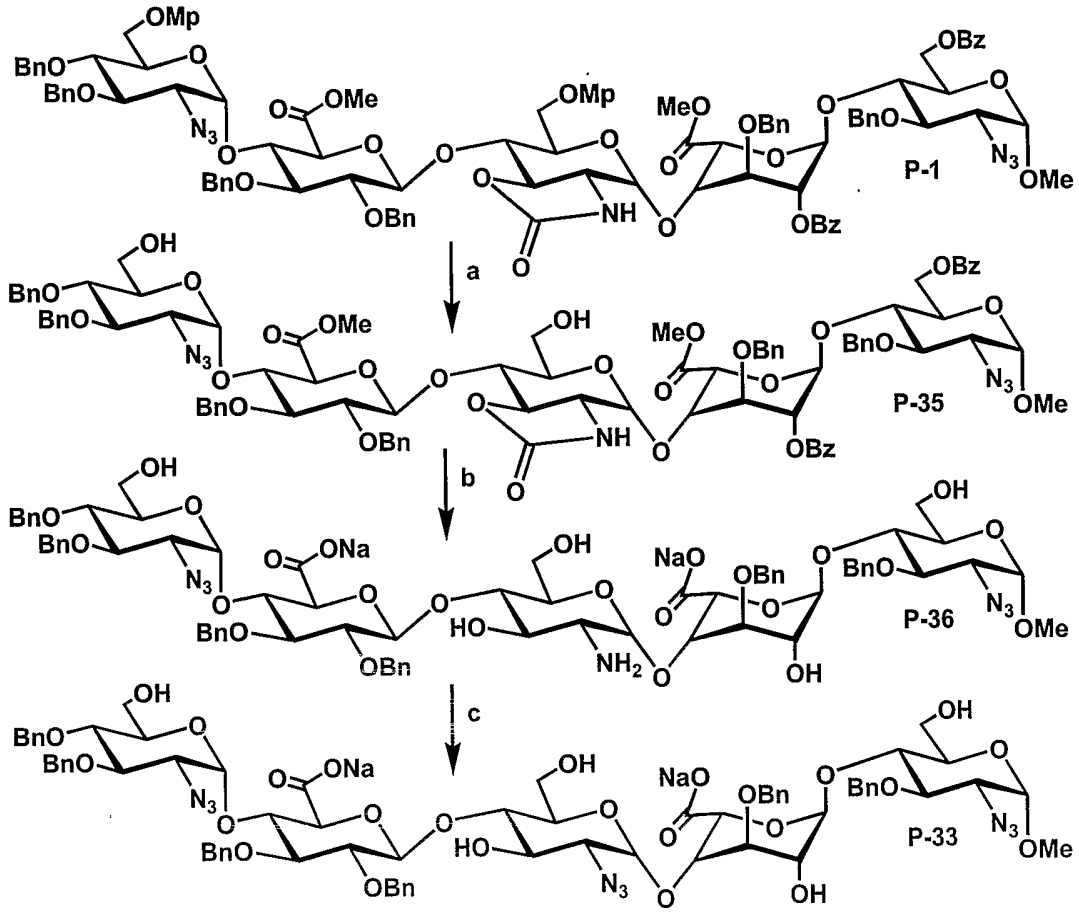
$M_{found}$ = 1514.62 $(M+H)^+$, $M_{calc}$ = 1513.58 $(M^+)$.

Example 46: Partial deprotection of pentasaccharide **P-30**, containing a DTPM-group as amino protection



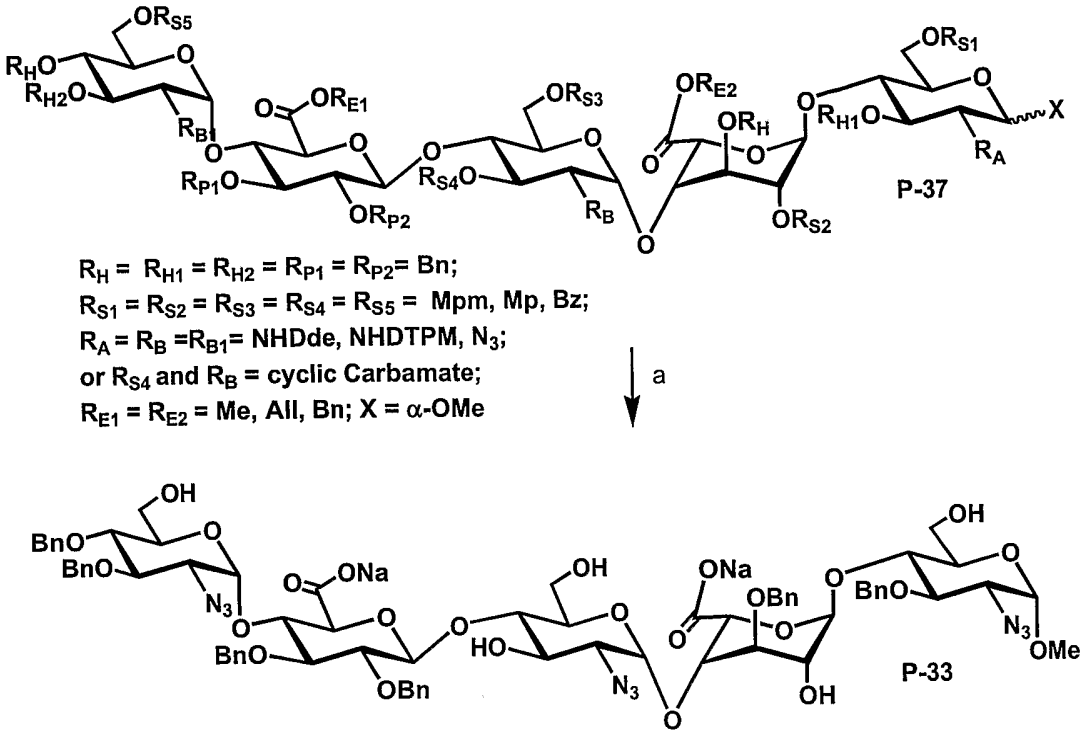

Example 46: Partial deprotection of pentasaccharide **P-30**, containing a DTPM-group as amino protection, conditions: a) 1. SOP 28; 2. SOP 39; b) 1. SOP 11 with $MeNH_2$ as primary amine and MeOH as solvent; 2. SOP 12.

Example 47: Partial deprotection of pentasaccharide **P-1**, containing a cyclic carbamate as amino protection



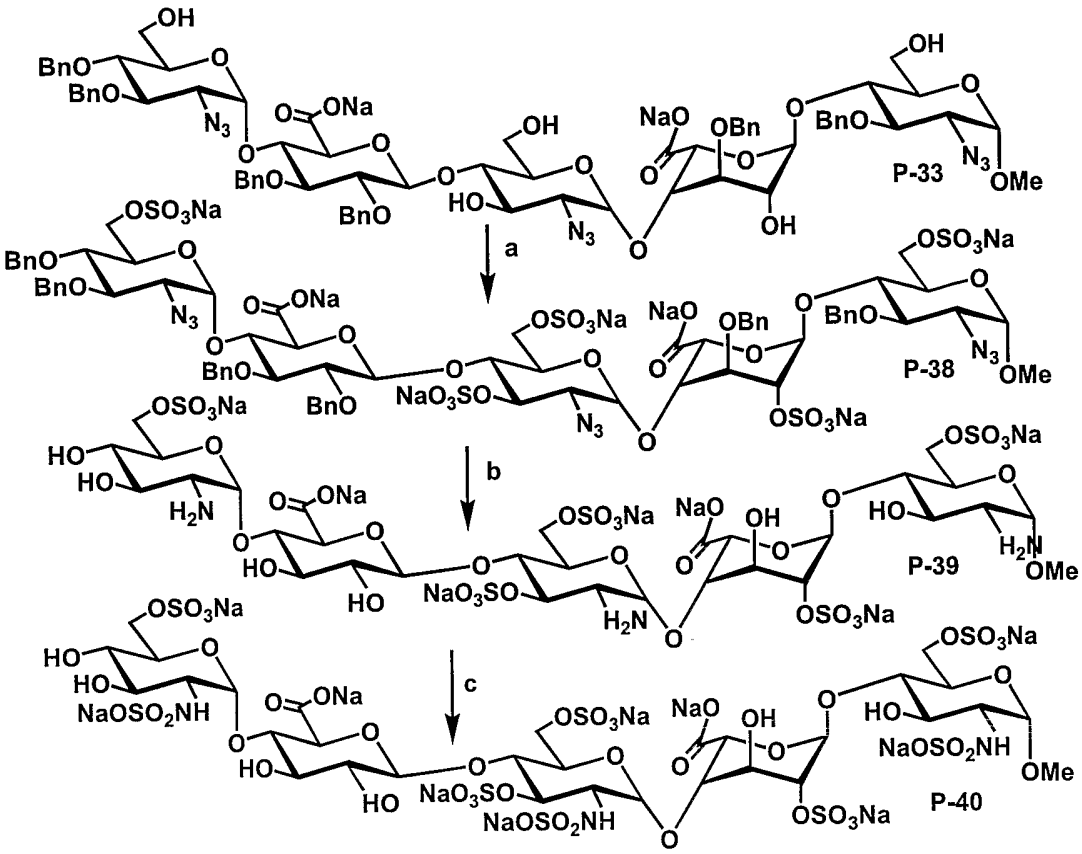

Example 47: Partial deprotection of pentasaccharide **P-1**, containing a cyclic carbamate as amino protection, conditions: a) SOP 27; b) SOP 39; c) SOP 12.

Example 48: Deprotection protocol for pentasaccharides **P-37** of claim 4




Example 48: Deprotection protocol for pentasaccharides **P-37** of claim 4, conditions: a) 1. SOP 27 and 28; 2. SOP 39; 3. SOP 11 with $MeNH_2$ as primary amine and MeOH as solvent; 4. SOP 12.

Example 49: Transformation of pentasaccharide **P-33** into the *O*-and *N*-sulfated pentasaccharide **P-35**




Example 49: Transformation of pentasaccharide **P-33** into the *O*-and *N*-sulfated pentasaccharide **P-40**, conditions: a) $SO_3$xNMe$_3$, DMF, 50°C; b) $H_2$ (70 psi), Pd/C, $H_2O$; c) $SO_3$xPyridine, $H_2O$, pH = 9.5. The transformation of **P-33** into **P-40** has been performed according to literature: Petitou et al., *Carbohydr. Res.* **1987**, *167*, 67-75.

The $^1$H-NMR (400 MHz, $D_2O$) of **P-40** is shown in figure 2.

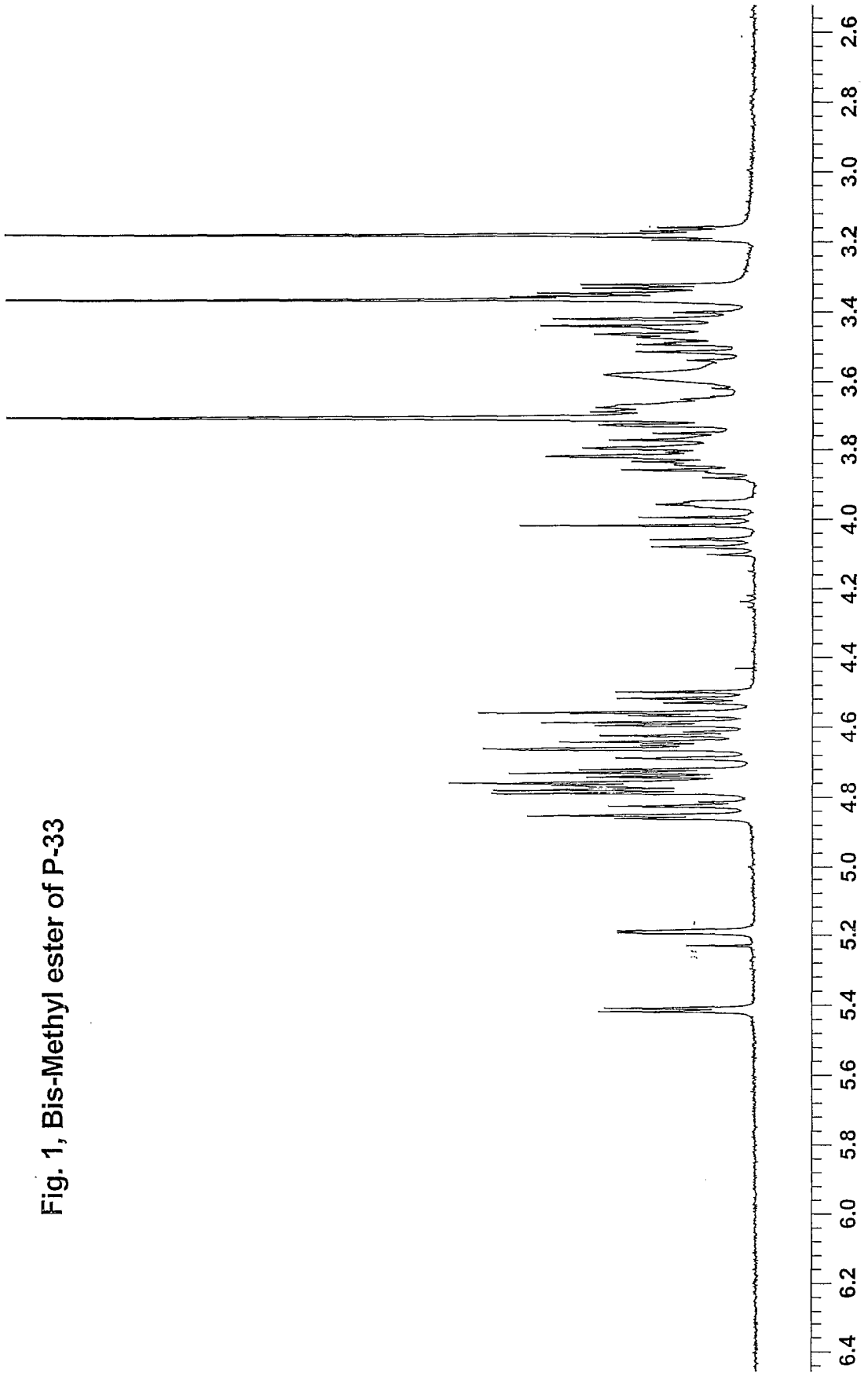



Fig. 1, Bis-Methyl ester of P-33

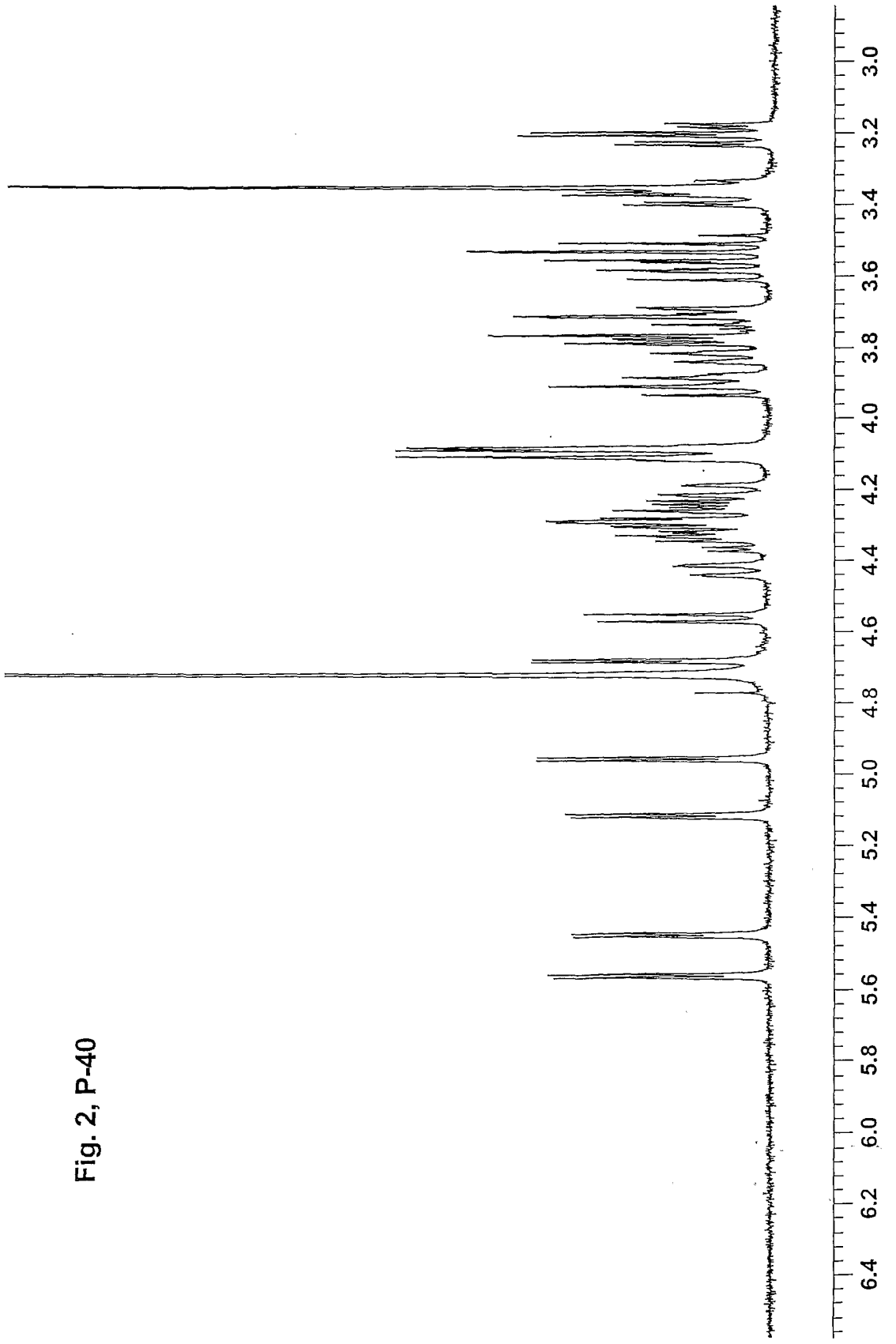
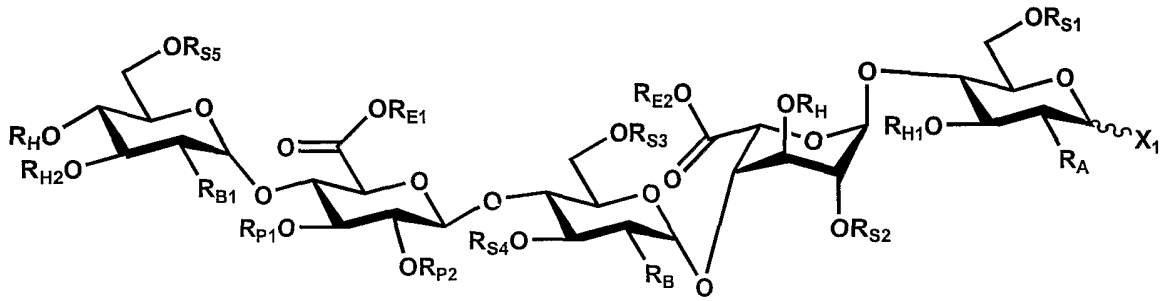



Fig. 2, P-40

## Claims

**1.** A pentasaccharide building block for the preparation of synthetic heparinoids, said building block being of General Formula I,




General Formula I (Block E-D-C-B-A)

In which the configuration of the monosaccharidic units and the stereochemistry of the internal linkages is defined as D-gluco-alpha-1,4-D-glucurono-beta-1,4-D-Gluco-alpha-1,4-L-idurono-beta-1,4-D-gluco, and the substituents are defined as;

**$X_1$** is selected from the group consisting of hydroxy, alkenyloxy, alkoxy, aryloxy, benzyloxy, substituted benzyloxy; thioalkyl, thioaryl, halogen, imidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; a lipoaminoacid or other such group suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl;

$R_{H1}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_{H2}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl, or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_A$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde, *N*H-DTPM, *N*H-Fmoc, *N*H-Boc, NH-Cbz, *N*H-Troc, *N*-phthalimido, NH-Ac, NH-Allyloxycarbonyl; or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_{S1}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

$R_{S2}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; allyl, methoxymethyl, methoxyethyl , benzyloxymethyl;

$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; allyl, methoxymethyl, methoxyethyl, benzyloxymethyl,

or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{S5}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

Or $R_{S5}$ and $R_H$ can be combined to form a cyclic acetal or ketal moiety;

$R_{E1}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl,$C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups;

$R_{E2}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl,$C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups;

$R_B$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

$R_{B1}$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate;

$R_{P1}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or

substituted alkylacyl, arylacyl and alkylarylacyl protecting groups; carbonate protecting groups;

$R_{P2}$ is selected from the group consisting of 4-methoxyphenyl;benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups, silyl protecting groups, carbamate protecting groups, C3-C5 alkenyl.

**2** The pentasaccharide building block of claim 1,

In which the configuration of the monosacharidic units and the stereochemistry of the internal linkages is defined as D-gluco-alpha-1,4-D-glucurono-beta-1,4-D-Gluco-alpha-1,4-L-idurono-beta-1,4-D-gluco, and ,

Wherein:

$X_1$ is selected from the group consisting of hydroxy, alkoxy, aryloxy, benzyloxy, substituted benzyloxy; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; a lipoaminoacid suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_H$, $R_{H1}$,and $R_{H2}$ are independently selected from a benzyl or substituted benzyl protecting group, or $R_{H1}$ and $R_A$ or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_A$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde, *N*H-DTPM, *N*H-Fmoc, *N*H-Boc, NH-Cbz, *N*H-Troc, *N*-phthalimido; or other such suitable protected amino functions or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_{S1}$, $R_{S2}$, $R_{S3}$, $R_{S4}$ and $R_{S5}$ are independently selected from: 4-methoxyphenyl; 4-methoxybenzyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, benzoyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{E1}$ and $R_{E2}$ are independently selected from methyl, $C_2$-$C_5$ alkyl; substituted alkyl; or, benzyl and substituted benzyl groups;

$R_B$ and $R_{B1}$ are independently selected from an azido function, an amine; an *N*H-Dde or *N*H-DTPM group; additionally $R_{S4}$ and $R_B$ or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_{P1}$ and $R_{P2}$ are independently selected from benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl, and alkylarylacyl protecting groups; and carbonate protecting groups.

**3.** The pentasaccharide building block of claim 1,

$X_1$ is selected from the group consisting of hydroxy, methoxy, ethoxy, allyloxy, n-pentenyloxy, C1-5 alkoxy, C3-7 alkenyloxy, benzyloxy, substituted benzyloxy; thiomethyl, thioethyl, thiocresyl, thiophenyl, chloro, bromo, fluoro, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy, 2-trimethylsilyloxyethoxy (SEM), or other such substituted silyloxy protecting group; a lipoaminoacid or other such group suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group;

$R_{H1}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_{H2}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_A$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde, *N*H-DTPM, *N*H-Fmoc, *N*H-Boc, NH-Cbz, *N*H-Troc, *N*-phthalimido, NH-Ac, NH-Alloc; or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_{S1}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, substituted benzyl groups; alkylacyl, benzoyl, arylacyl or alkylarylacyl, and substituted alkylacyl, 4-chlorobenzoyl, arylacyl or alkylarylacy protecting groups; allyloxycarbonyl, ethoxycarbonyl, tertbutoxycarbonyl, carbonate protecting groups; tert-butyldiphenylsilyl, allyl, tert-butyldimethylsilyl, methoxymethyl, methoxyethyl, trimethylsiloxyethyl (SEM), benzyloxymethyl;

$R_{S2}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, substituted benzyl groups; alkylacyl, benzoyl, arylacyl or alkylarylacyl, and substituted alkylacyl, 4-chlorobenzoyl, arylacyl or alkylarylacy protecting groups; allyloxycarbonyl, ethoxycarbonyl, tertbutoxycarbonyl, carbonate protecting groups; tert-butyldiphenylsilyl, allyl, tert-butyldimethylsilyl, methoxymethyl, methoxyethyl, trimethylsiloxyethyl, benzyloxymethyl;

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, substituted benzyl groups; alkylacyl, benzoyl, arylacyl or alkylarylacyl, and substituted alkylacyl, 4-chlorobenzoyl, arylacyl or alkylarylacy protecting groups; allyloxycarbonyl, ethoxycarbonyl, tertbutoxycarbonyl, carbonate protecting groups; tert-butyldiphenylsilyl, allyl,

tert-butyldimethylsilyl, methoxymethyl, methoxyethyl, trimethylsiloxyethyl, benzyloxymethyl;

$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, substituted benzyl groups; alkylacyl, benzoyl, arylacyl or alkylarylacyl, and substituted alkylacyl, 4-chlorobenzoyl, arylacyl or alkylarylacy protecting groups; allyloxycarbonyl, ethoxycarbonyl, tertbutoxycarbonyl, carbonate protecting groups; tert-butyldiphenylsilyl, allyl, tert-butyldimethylsilyl, methoxymethyl, methoxyethyl, trimethylsiloxyethyl, benzyloxymethyl, or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{S5}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, substituted benzyl groups; alkylacyl, benzoyl, arylacyl or alkylarylacyl, and substituted alkylacyl, 4-chlorobenzoyl, arylacyl or alkylarylacy protecting groups; allyloxycarbonyl, ethoxycarbonyl, tertbutoxycarbonyl, carbonate protecting groups; tert-butyldiphenylsilyl, allyl, tert-butyldimethylsilyl, methoxymethyl, methoxyethyl, trimethylsiloxyethyl, benzyloxymethyl;

$R_{E1}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl; or, benzyl and substituted benzyl groups;

$R_{E2}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl; or, benzyl and substituted benzyl groups;

$R_B$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

$R_{B1}$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate;

$R_{P1}$ is selected from the group consisting of benzyl; 4-methoxybenzyl, substituted benzyl groups; allyloxycarbonyl, ethoxycarbonyl, tertbutoxycarbonyl, carbonate protecting groups;

$R_{P2}$ is selected from the group consisting of benzyl; 4-methoxybenzyl, substituted benzyl groups; benzoyl, 4-chlorobenzoyl, chloroacetyl, acetyl, levulinoyl, pivaloyl, 4-methoxybenzoyl, 4-azidobenzoyl, alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups; allyloxycarbonyl, ethoxycarbonyl, tertbutoxycarbonyl, carbonate protecting groups.

**4.** The pentasaccharide building block of claim 1,

In which the configuration of the monosacharidic units and the stereochemistry of the internal linkages is defined as D-gluco-alpha-1,4-D-glucurono-beta-1,4-D-Gluco-alpha-1,4-L-idurono-beta-1,4-D-gluco, and ,

Wherein:

$X_1$ is selected from the group consisting of hydroxy, methoxy, thiomethyl, thioethyl, thiocresyl, thiophenyl, trichloroacetimidoyl, a $^t$butyldiphenylsilyloxy a lipoaminoacid suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_H$, $R_{H1}$,and $R_{H2}$ are independently selected from a benzyl or substituted benzyl protecting group, or $R_{H1}$ and $R_A$ or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_A$ is selected from the group consisting of an azido function, an *N*H-Dde, *N*H-DTPM, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate,

$R_{S1}$,$R_{S2}$,$R_{S3}$,$R_{S4}$ and $R_{S5}$ are independently selected from: 4-methoxyphenyl; 4-methoxybenzyl; benzoyl, or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{E1}$ and $R_{E2}$ are independently selected from methyl, allyl or, benzyl and substituted benzyl groups;

$R_B$ and $R_{B1}$ are independently selected from an azido function; an *N*H-Dde or *N*H-DTPM group; additionally $R_{S4}$ and $R_B$ or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_{P1}$ is benzyl;

$R_{P2}$ is selected from the group consisting of benzyl; benzoyl, allyloxycarbonyl.

**5.** The pentasaccharide building block of claim 1, wherein $X_1$ is C1 to C5 alkoxy.

**6.** The pentasaccharide building block of claim 1, wherein $R_A$ is azido or –*N*H-DTPM.

**7.** The pentasaccharide building block of claim 1, wherein $R_{P1}$, $R_H$ and $R_{H1}$ is benzyl.

**8** The pentasaccharide building block of claim 1, wherein $R_{S1}$,$R_{S2}$,$R_{S3}$,$R_{S4}$ and $R_{S5}$ are independently selected from benzoyl, 4-methoxybenzyl, 4-methoxyphenyl, 4-chlorobenzoyl,or tert-butyldiphenylsilyl, allyl, trimethylsiloxyethyl.

**9** The pentasaccharide building block of claim 1, wherein $R_{P1}$ and $R_{P2}$ is benzyl or substituted benzyl.

**10** The pentasaccharide building block of claim 1, wherein $R_{E2}$ is methyl.

**11** The pentasaccharide building block of claim 1, wherein $R_B$ is azido or $R_B$ and $R_{S4}$ combine to form a cyclic carbamate.

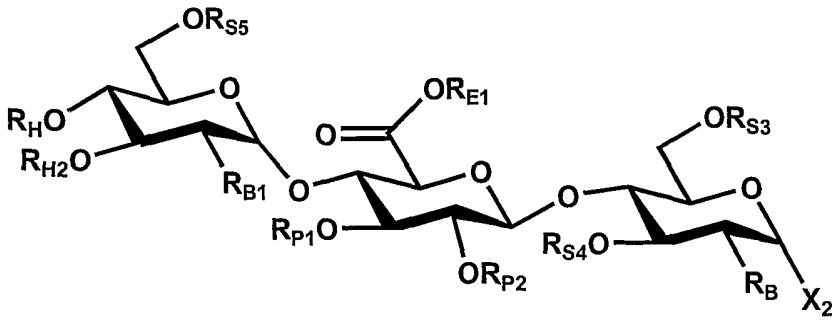
**12** The pentasaccharide building block of claim 1, wherein $R_{S1}$ and $R_{S2}$ is benzoyl, and $R_A$ is azido or -*N*H-DTPM or $R_A$ and $R_{H1}$ together combine to form a cyclic carbamate.

**13** The pentasaccharide building block of claim 1, wherein $R_{P2}$ is selected from benzyl, chloroacetyl, acetyl, benzoyl, substituted benzoyl, pivaloyl, levulinyl or allyloxycarbonyl.

**14** The pentasaccharide building block of claim 1, wherein $R_{B1}$ is azido or -*N*H-DTPM.

**15** The pentasaccharide building block of claim 1, wherein $X_1$ is C1-C5 alkoxy, $R_{S1}$ and $R_{S2}$ is benzoyl, $R_{S3}$, $R_{S4}$ and $R_{S5}$ are independently selected from benzoyl, 4-methoxybenzyl, 4-methoxypheyl, 4-chlorobenzoyl, tert-butyldiphenylsilyl, allyl, $R_{E2}$ is methyl, $R_{P1}$, $R_H$, $R_{H1}$ and $R_{H2}$ is benzyl and $R_{P2}$ is selected from benzyl, chloroacetyl, acetyl, benzoyl, substituted benzoyl, pivaloyl, levulinyl or allyloxycarbonyl.

**16** A method of synthesizing the pentasaccharide of claim 1, comprising the steps of forming a trisaccharide EDC of formula II,




E D C

Formula II

wherein

$X_2$ is selected from thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, n-pentenyl and the stereochemistry may be alpha or beta;

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl;

$R_{H2}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl, or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl , benzyloxymethyl;

$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting

group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl, or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{S5}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting groups, allyl, methoxymethyl, methoxyethyl, benzyloxymethyl, carbamate protecting groups, trityl,or $R_{S5}$ and $R_H$ can be combined to form a cyclic acetal or ketal moiety;

$R_{E1}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl,$C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups;

$R_B$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

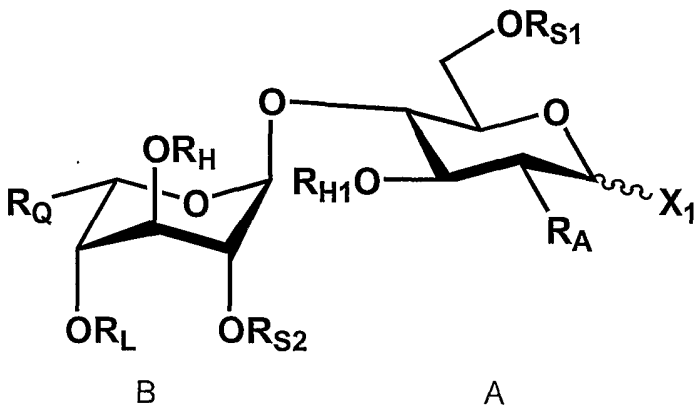
$R_{B1}$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate;

$R_{P1}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups;

$R_{P2}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate

protecting groups, silyl protecting groups, carbamate protecting groups, C3-C5 alkenyl;

and forming a disaccharide BA of formula III




Formula III

Wherein

$X_1$ is selected from the group consisting of alkoxy, alkenyloxy, aryloxy, benzyloxy, substituted benzyloxy; thioalkyl, thioaryl, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; a lipoaminoacid or other such group suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta ;

$R_{H1}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_A$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde, *N*H-DTPM, *N*H-Fmoc, *N*H-Boc, NH-Cbz, *N*H-Troc, *N*-phthalimido, NH-Alloc, NH-Ac; or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_{S1}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

$R_{S2}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

$R_Q$ is either a) **–(C=O)-$OR_{E2}$** wherein $R_{E2}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl,$C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups;
or b) **–($CH_2$)-$OR_M$** wherein $R_M$ is selected from *p*-methoxyphenyl, p-methoxybenzyl, a trityl group, allyl, levulinoyl;

$R_L$ is H;

and linking the trisaccharide to the disaccharide to form the pentasaccharide.

**17** A method of of claim 16, wherein:

wherein

$X_1$ is selected from the group consisting of hydroxy, methoxy, thiomethyl, thioethyl, thiocresyl, trichloroacetimidoyl, a $^t$butyldiphenylsilyloxy a lipoaminoacid suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_H$,$R_{H1}$,and $R_{H2}$ are independently selected from a benzyl or substituted benzyl protecting group, or $R_{H1}$ and $R_A$ or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_A$ is selected from the group consisting of an azido function, an *N*H-Dde, *N*H-DTPM, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate,

$R_{S1}$,$R_{S2}$,$R_{S3}$,$R_{S4}$ and $R_{S5}$ are independently selected from: 4-methoxyphenyl; 4-methoxybenzyl; benzoyl, or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{E1}$ and $R_{E2}$ are independently selected from methyl, allyl or, benzyl and substituted benzyl groups;

$R_B$ and $R_{B1}$ are independently selected from an azido function; an *N*H-Dde or *N*H-DTPM group; additionally $R_{S4}$ and $R_B$ or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_{P1}$ is benzyl;

$R_{P2}$ is selected from the group consisting of benzyl; benzoyl, allyloxycarbonyl.

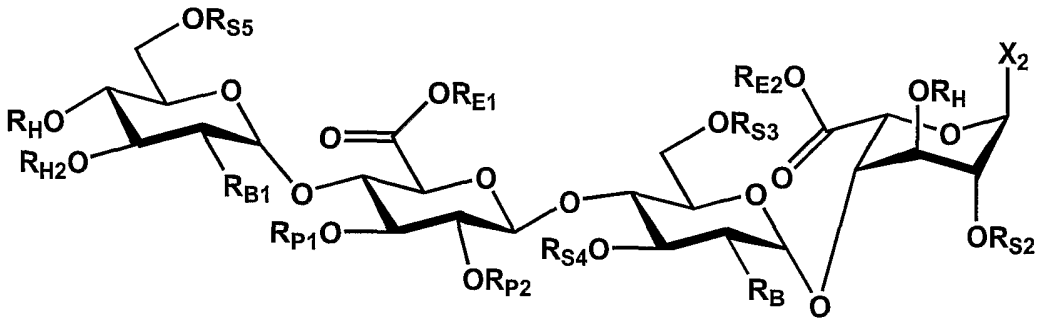
$X_2$ is selected from thiomethyl, thiocresyl, or trichloroacetimidoyl, and the stereochemistry may be alpha or beta,

$R_Q$ is either a) $-(C=O)-OR_{E2}$ wherein $R_{E2}$ is methyl, allyl or benzyl;
or b) $-(CH_2)-OR_M$ wherein $R_M$ is selected from *p*-methoxyphenyl, p-methoxybenzyl, a trityl group,

$R_L$ is H,

and linking the trisaccharide to the disaccharide to form the pentasaccharide.

18 A method of synthesizing the pentasaccharide of claim1 comprising the step of synthesizing a tetrasaccharide EDCB (formula IV),




E D C B

Formula IV

Wherein:

$X_2$ is selected from a thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, and the stereochemistry may be alpha or beta;

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl;

$R_{H2}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl, or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_{S2}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting

groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl , benzyloxymethyl;

$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl, or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{S5}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, substituted benzyl groups; alkylacyl, benzoyl, arylacyl or alkylarylacyl, and substituted alkylacyl, 4-chlorobenzoyl; arylacyl or alkylarylacy protecting groups; allyloxycarbonyl, ethoxycarbonyl, tertbutoxycarbonyl, carbonate protecting groups; is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl; or $R_{S5}$ and $R_H$ can be combined to form a cyclic acetal or ketal moiety;

$R_{E1}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl, $C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups;

$R_{E2}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl,$C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups;

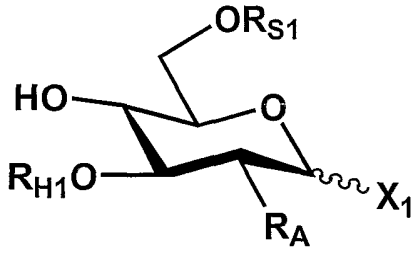
$R_B$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

$R_{B1}$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate;

$R_{P1}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups;

$R_{P2}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups, silyl protecting groups, carbamate protecting groups, C3-C5 alkenyl;

and linking the tetrasaccharide to a monosaccharide of formula V




A

Formula V

Wherein:

$X_1$ is selected from alkoxy, aryloxy, benzyloxy, substituted benzyloxy; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta;

$R_{H1}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_A$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde, *N*H-DTPM, *N*H-Fmoc, *N*H-Boc, NH-Cbz, *N*H-Troc, *N*-phthalimido, NH-Ac, NH-Allyloxycarbonyl; or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate,

$R_{S1}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl,

**19** The method of claim 18 wherein:

$X_1$ is selected from the group consisting of hydroxy, methoxy, thiomethyl, thioethyl, thiocresyl, trichloroacetimidoyl, a $^t$butyldiphenylsilyloxy a lipoaminoacid suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_H$,$R_{H1}$,and $R_{H2}$ are independently selected from a benzyl or substituted benzyl protecting group, or $R_{H1}$ and $R_A$ or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_A$ is selected from the group consisting of an azido functionan *N*H-Dde, *N*H-DTPM, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate,

$R_{S1}$,$R_{S2}$,$R_{S3}$,$R_{S4}$ and $R_{S5}$ are independently selected from: 4-methoxyphenyl; 4-methoxybenzyl; benzoyl, or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{E1}$ and $R_{E2}$ are independently selected from methyl, allyl or, benzyl and substituted benzyl groups;

$R_B$ and $R_{B1}$ are independently selected from an azido function; an *N*H-Dde or *N*H-DTPM group; additionally $R_{S4}$ and $R_B$ or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

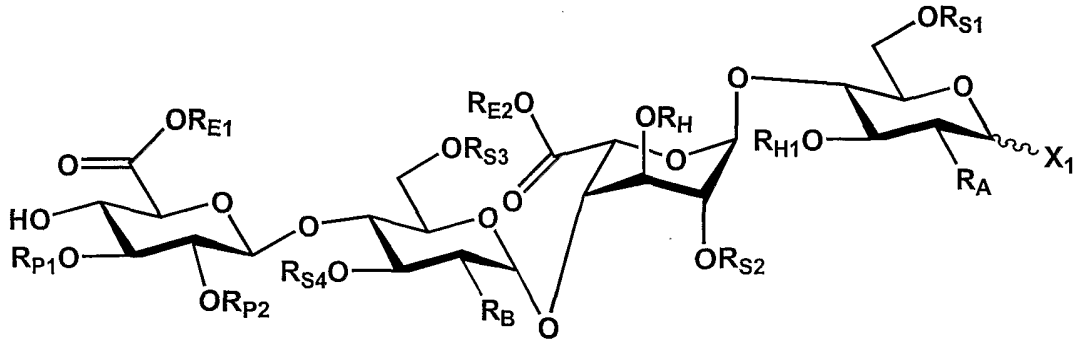
$R_{P1}$ is benzyl;

$R_{P2}$ is selected from the group consisting of benzyl; benzoyl, allyloxycarbonyl.

$X_2$ is selected from thiomethyl, thiocresyl, or trichloroacetimidoyl, and the stereochemistry may be alpha or beta,

$R_{E2}$ is methyl, allyl or benzyl;

**20** A method of synthesizing the pentasaccharide of claim 1 comprising synthesizing a tetrasaccharide DCBA of formula VI



D C B A

Formula VI

$X_1$ is selected from the group consisting of hydroxy, alkenyloxy, alkoxy, aryloxy, benzyloxy, substituted benzyloxy; thioalkyl, thioaryl, halogen, imidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; a lipoaminoacid or other such group suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta,

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl;

$R_{H1}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_A$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde, *N*H-DTPM, *N*H-Fmoc, *N*H-Boc, NH-Cbz, *N*H-Troc, *N*-phthalimido, NH-Ac, NH-Allyloxycarbonyl; or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate,

$R_{S1}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl,

$R_{S2}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl,

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl , benzyloxymethyl,

$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl,
or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate,

$R_{E1}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl, $C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups;

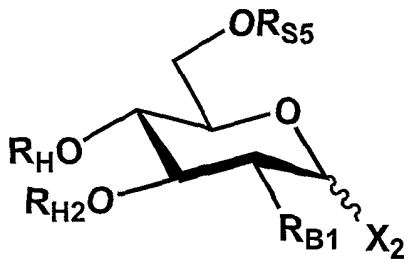
$R_{E2}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl,$C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups,

$R_B$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate,

$R_{P1}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups;

$R_{P2}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups, silyl protecting groups, carbamate protecting groups, C3-C5 alkenyl;

and linking the tetrasaccharide to a monosaccharide of formula VII




formula VII

wherein

$X_2$ is selected from a thioalkyl, thioaryl, trichloroacetimidoyl; and the stereochemistry may be alpha or beta;

$R_{S5}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, substituted benzyl groups; alkylacyl, benzoyl, arylacyl or alkylarylacyl, and substituted alkylacyl, 4-chlorobenzoyl, arylacyl or alkylarylacy protecting groups; allyloxycarbonyl, ethoxycarbonyl, tertbutoxycarbonyl, carbonate protecting groups; is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^{t}$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;or $R_{S5}$ and $R_H$ can be combined to form a cyclic acetal or *ketal moiety*;

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl;

$R_{H2}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl, or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_{B1}$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate.

**21** The method of claim 20 wherein:

$X_1$ is selected from the group consisting of hydroxy, methoxy, thiomethyl, thioethyl, thiocresyl, trichloroacetimidoyl, a $^t$butyldiphenylsilyloxy a lipoaminoacid suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_H$,$R_{H1}$,and $R_{H2}$ are independently selected from a benzyl or substituted benzyl protecting group, or $R_{H1}$ and $R_A$ or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_A$ is selected from the group consisting of an azido functionan *N*H-Dde, *N*H-DTPM, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate,

$R_{S1}$,$R_{S2}$,$R_{S3}$,$R_{S4}$ and $R_{S5}$ are independently selected from: 4-methoxyphenyl; 4-methoxybenzyl; benzoyl, or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{E1}$ and $R_{E2}$ are independently selected from methyl, allyl or, benzyl and substituted benzyl groups;

$R_B$ and $R_{B1}$ are independently selected from an azido function; an *N*H-Dde or *N*H-DTPM group; additionally $R_{S4}$ and $R_B$ or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

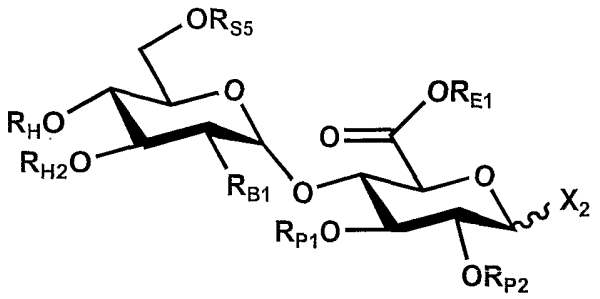
$R_{P1}$ is benzyl;

$R_{P2}$ is selected from the group consisting of benzyl; benzoyl, allyloxycarbonyl.

$X_2$ is selected from thiomethyl, thiocresyl, or trichloroacetimidoyl, and the stereochemistry may be alpha or beta,

$R_{E2}$ is methyl, allyl or benzyl;

**22** A method of synthesizing the pentasaccharide of claim 1 comprising the steps of forming a disaccharide ED of formula VIII,




E D

Formula VIII

wherein

$X_2$ is selected from thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, and the stereochemistry may be alpha or beta;

$R_{S5}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, substituted benzyl groups; alkylacyl, benzoyl, arylacyl or alkylarylacyl, and substituted alkylacyl, 4-chlorobenzoyl, arylacyl or alkylarylacy protecting groups; allyloxycarbonyl, ethoxycarbonyl, tertbutoxycarbonyl, carbonate protecting groups; is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^{t}$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;or $R_{S5}$ and $R_H$ can be combined to form a cyclic acetal or ketal moiety;

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl;

$R_{H2}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl, or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

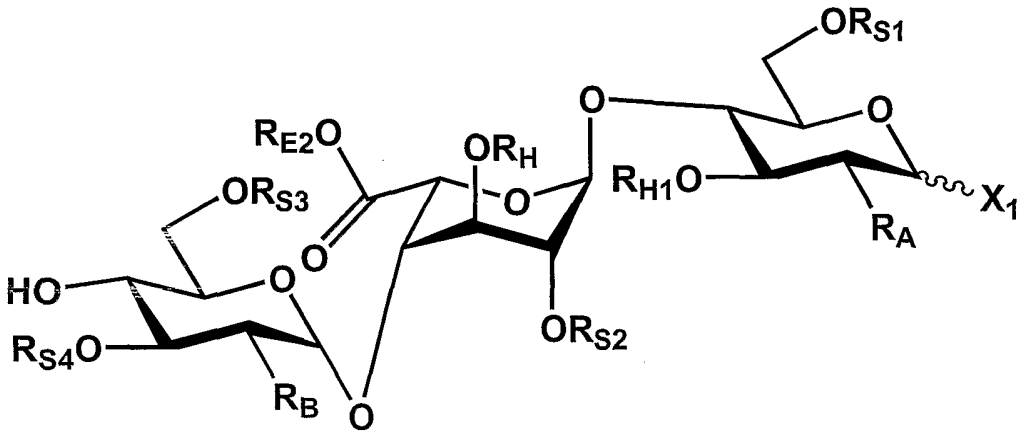
$R_{B1}$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate.

$R_{E2}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl,$C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups,

$R_{P1}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups;

$R_{P2}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups, silyl protecting groups, carbamate protecting groups, C3-C5 alkenyl;

and forming a trisaccharide CBA of formula IX




C B A

Formula IX

wherein

$X_1$ is selected from the group consisting of alkoxy, aryloxy, benzyloxy, substituted benzyloxy; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; a lipoaminoacid or other such group suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta with the proviso that when $X_1$ is a halogen, trichloroacetimidoyl, phosphate or related phosphate ester type leaving group, $X_2$ may not be the same;

$R_B$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

$R_A$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde, *N*H-DTPM, *N*H-Fmoc, *N*H-Boc, NH-Cbz, *N*H-Troc, *N*-phthalimido, NH-Ac, NH-Allyloxycarbonyl; or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_{S1}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

$R_{S2}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl , benzyloxymethyl;

$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting

group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl,or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl;

$R_{H1}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_{E2}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl,$C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups;

and linking the disaccharide to the trisaccharide.

**23** The method of claim 22 wherein:

$X_1$ is selected from the group consisting of hydroxy, methoxy, thiomethyl, thioethyl, thiocresyl, trichloroacetimidoyl, a $^t$butyldiphenylsilyloxy a lipoaminoacid suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_H$,$R_{H1}$,and $R_{H2}$ are independently selected from a benzyl or substituted benzyl protecting group, or $R_{H1}$ and $R_A$ or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_A$ is selected from the group consisting of an azido functionan *N*H-Dde, *N*H-DTPM, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate,

$R_{S1}$,$R_{S2}$,$R_{S3}$,$R_{S4}$ and $R_{S5}$ are independently selected from: 4-methoxyphenyl; 4-methoxybenzyl; benzoyl, or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{E1}$ and $R_{E2}$ are independently selected from methyl, allyl or, benzyl and substituted benzyl groups;

$R_B$ and $R_{B1}$ are independently selected from an azido function; an *N*H-Dde or *N*H-DTPM group; additionally $R_{S4}$ and $R_B$ or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_{P1}$ is benzyl;

$R_{P2}$ is selected from the group consisting of benzyl; benzoyl, allyloxycarbonyl.

$X_2$ is selected from thiomethyl, thiocresyl, or trichloroacetimidoyl, and the stereochemistry may be alpha or beta,

$R_{E2}$ is methyl, allyl or benzyl;

**24** A pentasaccharide of claim 1

wherein

$X_1$ is selected from the group consisting of alpha or beta thiomethyl or thiocresyl or trichloroacetimidoyl or (t-butyldiphenylsilyloxy), alpha methoxy;

$R_{H1}$ is selected from the group consisting of benzyl or substituted benzyl protecting group;

$R_A$ is selected from the group consisting of an azido function, an *N*H-Dde, *N*H-DTPM, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_{S1}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, benzoyl, 4-chlorobenzoyl.

**25** A pentasaccharide of claim 1

Wherein:

$X_1$ is selected from the group consisting of alpha or beta thiomethyl or thiocresyl or trichloroacetimidoyl or (t-butyldiphenylsilyloxy), alpha methoxy;

$R_{H1}$ is selected from the group consisting of benzyl or substituted benzyl protecting group;

$R_A$ is selected from the group consisting of an azido function, an *N*H-Dde, *N*H-DTPM, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_{S1}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, benzoyl, 4-chlorobenzoyl;

$R_H$ is selected from the group consisting of benzyl;

$R_{S2}$ is selected from the group consisting of benzoyl, substituted arylacyl protecting groups;

$R_{E2}$ is methyl or allyl or benzyl.

**26** A pentasaccharide of claim 1

Wherein:

$X_1$ is selected from the group consisting of alpha or beta thiomethyl or thiocresyl or trichloroacetimidoyl or (t-butyldiphenylsilyloxy), alpha methoxy;

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, benzoyl, 4-chlorobenzoyl, allyl, allyloxycarbonyl,;

$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, benzoyl, 4-chlorobenzoyl, allyl, or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_B$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate.

**27** A pentasaccharide of claim 1

Wherein:

$X_1$ is selected from the group consisting of alpha or beta thiomethyl or thiocresyl or trichloroacetimidoyl or (t-butyldiphenylsilyloxy), alpha methoxy;

$R_{E1}$ is selected from the group consisting of methyl, allyl, benzyl;

$R_{P1}$ is benzyl;

$R_{P2}$ is selected from the group consisting of benzyl; benzoate; or allyloxycarbonyl.

**28** A pentasaccharide of claim 1

Wherein:

$X_1$ is selected from the group consisting of alpha or beta thiomethyl or thiocresyl or trichloroacetimidoyl or (t-butyldiphenylsilyloxy), alpha methoxy;

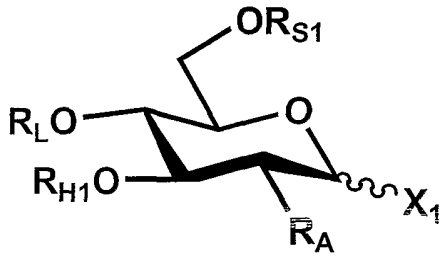
$R_H$ is benzyl;

$R_{H2}$ is benzyl;

$R_{S5}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, benzoyl, tert-butyldiphenylsilyl;

$R_{B1}$ is selected from the group consisting of an azido function, an *N*H-Dde or *N*H-DTPM group, or $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate.

**29** A monosaccharide of General Formula X




General Formula X (Block A)

Wherein

$X_1$ is selected from the group consisting of hydroxy, alkenyloxy, alkoxy, aryloxy, benzyloxy, substituted benzyloxy; thioalkyl, thioaryl, halogen,

imidoyl, phosphate and related phosphate ester type leaving groups, a $^{t}$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; a lipoaminoacid or other such group suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_{H1}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_A$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde, *N*H-DTPM, *N*H-Fmoc, *N*H-Boc, NH-Cbz, *N*H-Troc, *N*-phthalimido, NH-Ac, NH-Allyloxycarbonyl; or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_{S1}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^{t}$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl , benzyloxymethyl;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; γ-aminobutyryl, 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting groups; allyloxycarbonyl, allyl ether, carbonate type protecting groups; or $R_L$ and $R_{S1}$can combine to form a benzylidene or substituted benzylidene ring.

**30** A monosaccharide of claim 29

Wherein

$X_1$ is selected from the group consisting of hydroxy, alkoxy, aryloxy, benzyloxy, substituted benzyloxy; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; a lipoaminoacid or other such group suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_{H1}$ is selected from the group consisting of benzyl or substituted benzyl protecting group;

$R_A$ is selected from the group consisting of an azido function, an *N*H-Dde, *N*H-DTPM, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_{S1}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, substituted benzyl groups; benzoyl, arylacyl or alkylarylacyl, 4-chlorobenzoyl, allyloxycarbonyl, ethoxycarbonyl, tertbutoxycarbonyl, carbonate protecting groups;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; γ-aminobutyryl, 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting groups; or $R_L$ **and** $R_{S1}$can combine to form a benzylidene or substituted benzylidene ring.

**31** A monosaccharide of claim 29

Wherein

$X_1$ is selected from the group consisting of alpha or beta thiomethyl or thiocresyl or trichloroacetimidoyl or (t-butyldiphenylsilyloxy), alpha methoxy;

$R_{H1}$ is selected from the group consisting of benzyl or substituted benzyl protecting group;

$R_A$ is selected from the group consisting of an azido function, an *N*H-Dde, *N*H-DTPM, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_{S1}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, benzoyl, 4-chlorobenzoyl;

$R_L$ is a H atom or (levulinoyl).

**32** The monosaccharide as claimed in claimed 29,

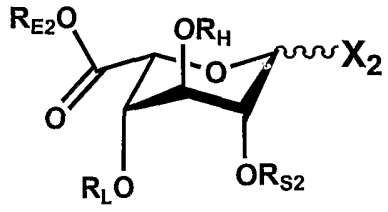
Wherein:

$R_A$ is azido or $R_A$ and $R_{H1}$ combine to form a cyclic carbamate.

**33** The monosaccharide as claimed in claim 29, wherein $R_{H1}$ is benzyl.

**34** The monosaccharide as claimed in claim 29, wherein $R_{S1}$ is selected from benzoyl, 4-methoxybenzyl, 4-methoxyphenyl, 4-chlorobenzoyl.

**35** A monosaccharide of General Formula XI,




General Formula XI (Block B)

Wherein,

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl;

$R_{S2}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

$R_{E2}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl,$C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; γ-aminobutyryl, 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting groups; allyloxycarbonyl, allyl ether, carbonate type protecting groups;

$X_2$ is selected from a hydroxyl group; thioalkyl, thioaryl, halogen, imidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta.

**36** A monosaccharide of claim 35,

Wherein,

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group;

$R_{S2}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, substituted benzyl groups; alkylacyl, benzoyl, arylacyl or alkylarylacyl, and substituted alkylacyl, 4-chlorobenzoyl, arylacyl or alkylarylacy protecting groups; allyloxycarbonyl, ethoxycarbonyl, tertbutoxycarbonyl, carbonate protecting groups;

$R_{E2}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl; or, benzyl and substituted benzyl groups;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; -aminobutyryl,γ– 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting group;

$X_2$ is selected from a hydroxyl group; thioalkyl, thioaryl, trichloroacetimidoyl, and the stereochemistry may be alpha or beta.

**37** A monosaccharide of claim 35,

Wherein,

$R_H$ is selected from the group consisting of benzyl;

$R_{S2}$ is selected from the group consisting of benzoyl, substituted arylacyl protecting groups;

$R_{E2}$ is methyl, (search others allyl benzyl);

$R_L$ is selected from a H atom; a levulinoyl;

$X_2$ is selected from a t-butyldiphenylsiloxy, trichloroacetimidoyl, and the stereochemistry may be alpha or beta. Search these

**38** A monosaccharide of claim 35,

Wherein,

$R_H$ is selected from the group consisting of benzyl;

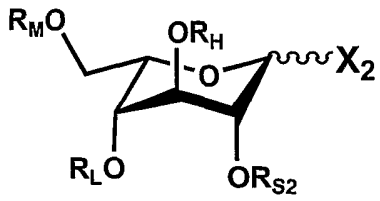
$R_{S2}$ is selected from the group consisting of benzoyl, substituted arylacyl protecting groups;

$R_{E2}$ is methyl, (search others allyl benzyl);

$R_L$ is selected from a H atom; a levulinoyl;

$X_2$ is selected from a thiomethyl or thiocresyl, and the stereochemistry may be alpha or beta. Search these

**39** A monosaccharide of General Formula XII,




General Formula XII (Alternate Block B)

Wherein:

$X_2$ is selected from a hydroxyl group; thioalkyl, thioaryl, halogen, imidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta;

$R_{S2}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; γ-aminobutyryl, 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-

(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting groups; allyloxycarbonyl, allyl ether, carbonate type protecting groups;

$R_M$ is selected from a p-methoxyphenyl or p-methoxybenzyl protecting group or other suitable oxidatively labile protecting group; a trityl group;

or $R_M$ and $R_L$ are combined together to form an cyclic acetal or ketal.

**40** A monosaccharide of claim 39,

Wherein:

$X_2$ is selected from a hydroxyl group; thioalkyl, thioaryl, trichloroacetimidoyl, and the stereochemistry may be alpha or beta;

$R_{S2}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, substituted benzyl groups; alkylacyl, benzoyl, arylacyl or alkylarylacyl, and substituted alkylacyl, 4-chlorobenzoyl, arylacyl or alkylarylacy protecting groups; allyloxycarbonyl, ethoxycarbonyl, tertbutoxycarbonyl, carbonate protecting groups;

$R_H$ is benzyl or a substituted benzyl protecting group;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; -aminobutyryl,γ 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-

trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting group;

$R_M$ is selected from a p-methoxyphenyl or p-methoxybenzyl protecting group or other suitable oxidatively labile protecting group; a trityl group;

or $R_M$ and $R_L$ are combined together to for an isopropylidene, benzylidene, 4-methoxybenzylidene, substituted benzylidene, cyclohexylidene or other alkylidene protecting group.

**41** A monosaccharide of claim 39,

Wherein:

$X_2$ is selected from a thiomethyl or thiocresyland the stereochemistry may be alpha or beta;

$R_{S2}$ is benzoyl;

$R_H$ is benzyl;

$R_L$ is selected from a H atom; a levulinoyl;

$R_M$ is selected from a p-methoxyphenyl or p-methoxybenzyl protecting group; or $R_M$ and $R_L$ are combined together to for an isopropylidene, (benzylidene), (4-methoxybenzylidene).

**42** A monosaccharide of claim 39,

Wherein:

$X_2$ is selected from a trichloroacetimidoyl or t-butyldiphenylsilyloxy and the stereochemistry may be alpha or beta;

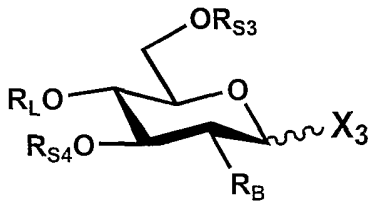
$R_{S2}$ is benzoyl;

$R_H$ is benzyl;

$R_L$ is selected from a H atom; a levulinoyl;

$R_M$ is selected from a p-methoxyphenyl or p-methoxybenzyl protecting group; or $R_M$ and $R_L$ are combined together to for an isopropylidene, (benzylidene), (4-methoxybenzylidene).

**43** A monosaccharide of General Formula XIII,




General Formula XIII (Block C)

Wherein:

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl , benzyloxymethyl;

$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting

group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl, or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_B$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; γ-aminobutyryl, 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting groups; allyloxycarbonyl, allyl ether, carbonate type protecting groups;

$X_3$ is selected from a hydroxyl group; thioalkyl, thioaryl, halogen, imidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta.

**44** A monosaccharide of claim 43,

Wherein:

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; tert-Butyldiphenylsilyl;

$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting

groups; tert-Butyldiphenylsilyl, or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_B$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; -aminobutyryl,γ 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting group;

$X_3$ is selected from a hydroxyl group; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta.

**45** A monosaccharide of claim 43,

Wherein:

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, benzoyl, 4-chlorobenzoyl, allyl, allyloxycarbonyl;

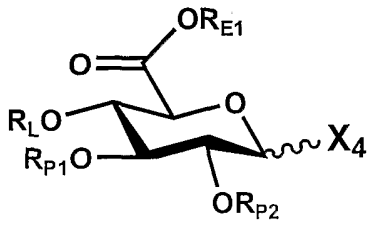
$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, benzoyl, 4-chlorobenzoyl, allyl, or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_B$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

$R_L$ is selected from a H atom or a levulinoyl group;

$X_3$ is selected from a thiomethyl, thioethyl, thiophenyl, thiocresyl, trichloroacetimidoyl, tert-butyldiphenylsilyloxy and the stereochemistry may be alpha or beta.

46 A monosaccharide of General Formula XIV,




General Formula XIV (Block D)

wherein,

$R_{E1}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl,$C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups;

$R_{P1}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups; carbonate protecting groups:

$R_{P2}$ is selected from the group consisting of 4-methoxyphenyl;benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting

groups;, carbonate protecting groups, silyl protecting groups, carbamate protecting groups, C3-C5 alkenyl;

$X_4$ is selected from a hydroxyl group; thioalkyl, thioaryl, halogen, imidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; γ-aminobutyryl, 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting groups; allyloxycarbonyl, allyl ether, carbonate type protecting groups.

47 A monosaccharide of claim 46,

wherein,

$R_{E1}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl; or, benzyl and substituted benzyl groups;

$R_{P1}$ is selected from the group consisting of 4-methoxyphenyl; benzyl; substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups; carbonate protecting groups including allyloxycarbonyl;

$R_{P2}$ is selected from the group consisting of 4-methoxyphenyl; benzyl; substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups; carbonate protecting groups including allyloxycarbonyl;

$X_4$ is selected from a hydroxyl group; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; -aminobutyryl,γ 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting group.

48 A monosaccharide of claim 46,

wherein,

$R_{E1}$ is selected from the group consisting of methyl, allyl, benzyl;

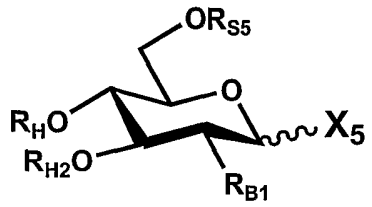
$R_{P1}$ is benzyl;

$R_{P2}$ is selected from the group consisting of benzyl; benzoate; or allyloxycarbonyl;

$X_4$ is selected from tertbutyldiphenylsilyloxy , trichloroacetimidoyl or fluoro and the stereochemistry may be alpha or beta;

$R_L$ is selected from a H atom; a levulinoyl, pivaloyl, benzoyl, allyl.

49 A monosaccharide of General Formula XV,




General Formula XV

Wherein:

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl;

$R_{H2}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl, or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_{S5}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, substituted benzyl groups; alkylacyl, benzoyl, arylacyl or alkylarylacyl, and substituted alkylacyl, 4-chlorobenzoyl, arylacyl or alkylarylacy protecting groups; allyloxycarbonyl, ethoxycarbonyl, tertbutoxycarbonyl, carbonate protecting groups; is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl,or $R_{S5}$ and $R_H$ can be combined to form a cyclic acetal or ketal moiety;

$R_{B1}$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate;

$X_5$ is selected from a hydroxyl group; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta.

50 A monosaccharide of claim 49,

Wherein:

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group;

$R_{H2}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_{S5}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; tert-Butyldiphenylsilyl;

$R_{B1}$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate;

$X_5$ is selected from a hydroxyl group; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta.

51 A monosaccharide of claim 49,

Wherein:

$R_H$ is benzyl;

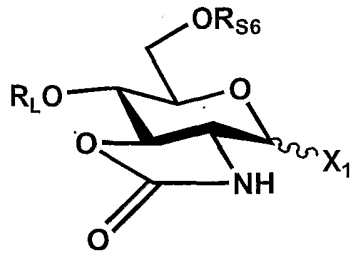
$R_{H2}$ is benzyl;

$R_{S5}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, benzoyl, tert-butyldiphenylsilyl;

$R_{B1}$ is selected from the group consisting of an azido function, an *N*H-Dde or *N*H-DTPM group, or $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate;

$X_5$ is selected from a thiomethyl, thiocresyl, trichloroacetimidate and the stereochemistry may be alpha or beta, with the proviso that $X_5$ may not be trichloroacetimidate when all of $R_{B1}$ is azido and $R_{H2}$ is unsubstituted benzyl and $R_{S5}$ is unsubstituted benzoyl.

52 A monosaccharide of General Formula XVI,




General Formula XVI (Common Intermediate for Blocks A, C and E)

Wherein

$X_1$ is selected from the group consisting of hydroxy, alkoxy, aryloxy, benzyloxy, substituted benzyloxy; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; a lipoaminoacid or other such group suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; γ-aminobutyryl, 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting groups; allyloxycarbonyl, allyl ether, carbonate type protecting groups.

$R_{S6}$ is selected from the group consisting of 4-methoxyphenyl, 4-methoxybenzyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; tert-Butyldiphenylsilyl;

$R_L$ and $R_{S6}$ may also together combine to form an alkylidene, isopropylidene, benzylidene or substituted benzylidene ring.

53 A monosaccharide of claim 52,

Wherein

**X1** is selected from the group consisting of hydroxy, alkoxy, aryloxy, benzyloxy, substituted benzyloxy; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving

groups, a $^{t}$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; γ-aminobutyryl, 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting groups;

$R_{S6}$ is selected from the group consisting of 4-methoxyphenyl, 4-methoxybenzyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; tert-Butyldiphenylsilyl;

$R_L$ and $R_{S6}$ may also together combine to form an alkylidene, isopropylidene, benzylidene or substituted benzylidene ring.

**54** A monosaccharide of claim 52,

Wherein

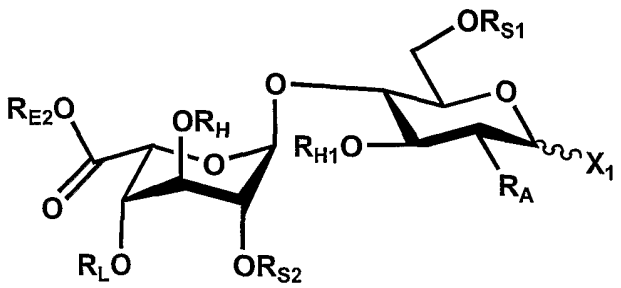
**X1** is selected from the group consisting of thiomethyl, thiocresyl, trichloroacetimidoyl, or a $^{t}$butyldiphenylsilyloxy and the stereochemistry may be alpha or beta;

$R_L$ is selected from a H atom; a levulinoyl;

$R_{S6}$ is selected from the group consisting of 4-methoxyphenyl, 4-methoxybenzyl; benzoyl, 4-chlorobenzoyl, or tert-Butyldiphenylsilyl;

$R_L$ and $R_{S6}$ may also together combine to form an isopropylidene, benzylidene or 4-methoxybenzylidene ring.

55 A disaccharide of formula XVII




General Formula XVII Intermediate B-A disaccharide

Wherein,

$X_1$ is selected from the group consisting of hydroxy, alkenyloxy, alkoxy, aryloxy, benzyloxy, substituted benzyloxy; thioalkyl, thioaryl, halogen, imidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; a lipoaminoacid or other such group suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl;

$R_{H1}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_A$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde, *N*H-DTPM, *N*H-Fmoc, *N*H-Boc, NH-Cbz, *N*H-Troc, *N*-

phthalimido, NH-Ac, NH-Allyloxycarbonyl; or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_{S1}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

$R_{S2}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

$R_{E2}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl,$C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; γ-aminobutyryl, 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting groups; allyloxycarbonyl, allyl ether, carbonate type protecting groups.

56 A disaccharide of claim 55

Wherein,

$X_1$ is selected from the group consisting of hydroxy, alkoxy, aryloxy, benzyloxy, substituted benzyloxy; thioalkyl, thioaryl, halogen,

trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, a $^{t}$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; a lipoaminoacid or other such group suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group;

$R_{H1}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_A$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde, *N*H-DTPM, *N*H-Fmoc, *N*H-Boc, NH-Cbz, *N*H-Troc, *N*-phthalimido; or, other such suitable protected amino functions, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_{S1}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; tert-Butyldiphenylsilyl;

$R_{S2}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; tert-Butyldiphenylsilyl;

$R_{E2}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl; or, benzyl and substituted benzyl groups;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting

group; -aminobutyryl,γ 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting group.

57 A disaccharide of claim 55

Wherein,

$X_1$ is selected from the group consisting of alpha or beta thiomethyl or thiocresyl or trichloroacetimidoyl or (t-butyldiphenylsilyloxy), alpha methoxy;

$R_{H1}$ is selected from the group consisting of benzyl or substituted benzyl protecting group;

$R_A$ is selected from the group consisting of an azido function, an *N*H-Dde, *N*H-DTPM, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_{S1}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, benzoyl, 4-chlorobenzoyl;

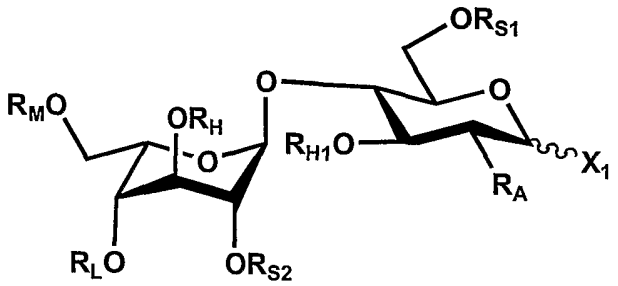
$R_H$ is selected from the group consisting of benzyl;

$R_{S2}$ is selected from the group consisting of benzoyl, substituted arylacyl protecting groups;

$R_{E2}$ is methyl, (search others allyl benzyl);

$R_L$ is selected from a H atom; a levulinoyl.

58 A disaccharide building block, said building block of General Formula XVIII,




General Formula XVIII (Alternate Block B-A)

Wherein

$X_1$ is selected from the group consisting of hydroxy, alkenyloxy, alkoxy, aryloxy, benzyloxy, substituted benzyloxy; thioalkyl, thioaryl, halogen, imidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; a lipoaminoacid or other such group suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_A$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde, *N*H-DTPM, *N*H-Fmoc, *N*H-Boc, NH-Cbz, *N*H-Troc, *N*-phthalimido, NH-Ac, NH-Allyloxycarbonyl; or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_{S1}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

$R_{S2}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^{t}$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl;

$R_{H1}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_M$ is selected from a p-methoxyphenyl or p-methoxybenzyl protecting group or other suitable oxidatively labile protecting group; a trityl group;

or $R_M$ and $R_L$ are combined together to form an isopropylidene, benzylidene, substituted benzylidene, cyclohexylidene or other acetal or ketal protecting group;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; γ-aminobutyryl, 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting groups; allyloxycarbonyl, allyl ether, carbonate type protecting groups.

59 A disaccharide building block, of claim 58 wherein:

$X_1$ is selected from the group consisting of hydroxy, alkenyloxy, alkoxy, aryloxy, benzyloxy, substituted benzyloxy; thioalkyl, thioaryl, halogen, imidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; a lipoaminoacid or other such group suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_A$ is selected from the group consisting of an azido function, an *N*H-Dde, *N*H-DTPM, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_{S1}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group;

$R_{S2}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group;

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group,;

$R_{H1}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_M$ is selected from a p-methoxyphenyl or p-methoxybenzyl protecting group or other suitable oxidatively labile protecting group; a trityl group;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; -aminobutyryl,γ 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting group.

60 A disaccharide building block, of claim 58 wherein:

$X_1$ is selected from the group consisting of alpha or beta thiomethyl or thiocresyl or trichloroacetimidoyl or (t-butyldiphenylsilyloxy), alpha methoxy;

$R_{H1}$ is selected from the group consisting of benzyl or substituted benzyl protecting group;

$R_A$ is selected from the group consisting of an azido function, an *N*H-Dde, *N*H-DTPM, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_{S1}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, benzoyl, 4-chlorobenzoyl;

$R_H$ is selected from the group consisting of benzyl;

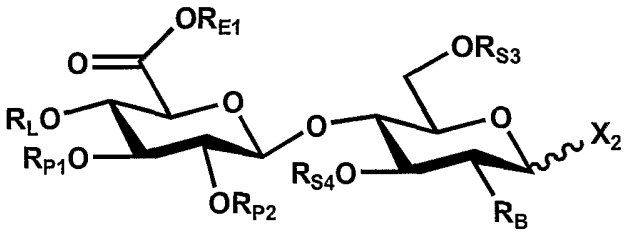
$R_{S2}$ is selected from the group consisting of benzoyl, substituted arylacyl protecting groups;

$R_{E2}$ is methyl, (search others allyl benzyl);

$R_L$ is selected from a H atom; a levulinoyl;

$R_M$ is selected from a p-methoxyphenyl or p-methoxybenzyl protecting group or a trityl group;

61 A disaccharide building block of General Formula XIX,




General Formula XIX (Block D-C)

Wherein,

$X_2$ is selected from the group consisting of hydroxy, alkenyloxy, alkoxy, aryloxy, benzyloxy, substituted benzyloxy; thioalkyl, thioaryl, halogen, imidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; a lipoaminoacid or other such group suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl , benzyloxymethyl;

$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting

group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl, or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{E1}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl,$C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups;

$R_B$ is selected from the group consisting of an azido function, an *N*H-Dde or *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

$R_{P1}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups;

$R_{P2}$ is selected from the group consisting of hydroxy, 4-methoxyphenyl;benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups, silyl protecting groups, carbamate protecting groups, C3-C5 alkenyl;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; γ-aminobutyryl, 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting groups; allyloxycarbonyl, allyl ether, carbonate type protecting groups.

62 A disaccharide building block of claim 61

Wherein,

$X_2$ is selected from the group consisting of hydroxy, alkenyloxy, alkoxy, aryloxy, benzyloxy, substituted benzyloxy; thiomethyl, thioethyl, thiocresyl, thiophenyl, chloro, bromo, fluoro, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; a lipoaminoacid or other such group suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, benzoyl, substituted benzyl groups; substituted arylacyl protecting groups; allyloxycarbonyl, 9-fluorenylmethoxycarbonyl, carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl , benzyloxymethyl;

$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; allyloxycarbonyl, carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl, or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{E1}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl,$C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups;

$R_B$ is selected from the group consisting of an azido function, an *N*H-Dde or *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

$R_{P1}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups;

$R_{P2}$ is selected from the group consisting of hydroxy, 4-methoxyphenyl;benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups, silyl protecting groups, carbamate protecting groups, C3-C5 alkenyl;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; -aminobutyryl,γ 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting group;

63 A disaccharide building block of claim 61

Wherein:

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, benzoyl, 4-chlorobenzoyl, allyl, allyloxycarbonyl;

$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, benzoyl, 4-chlorobenzoyl, allyl, or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_B$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

$X_3$ is selected from a thiomethyl, thioethyl, thiophenyl, thiocresyl, trichloroacetimidoyl, tert-butyldiphenylsilyloxy and the stereochemistry may be alpha or beta;

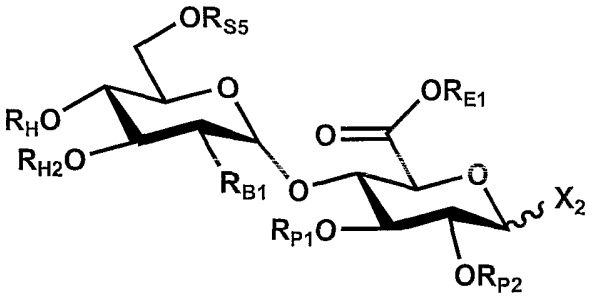
$R_{E1}$ is selected from the group consisting of methyl, allyl, benzyl;

$R_{P1}$ is benzyl;

$R_{P2}$ is selected from the group consisting of benzyl; benzoate; or allyloxycarbonyl;

$R_L$ is selected from a H atom; a levulinoyl, pivaloyl, benzoyl, allyl;

64 A disaccharide building block of General Formula XX,




General Formula XX (Block E-D)

Wherein:

$X_2$ is selected from a hydroxyl group; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving

groups, a $^{t}$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta;

$R_{P1}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups;

$R_{P2}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups, silyl protecting groups, carbamate protecting groups, C3-C5 alkenyl;

$R_{E1}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl, $C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups;

$R_{B1}$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate;

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl;

$R_{H2}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl, or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_{S5}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, substituted benzyl groups; alkylacyl, benzoyl, arylacyl or alkylarylacyl, and substituted alkylacyl, 4-chlorobenzoyl, arylacyl or alkylarylacy protecting groups; allyloxycarbonyl, ethoxycarbonyl, tertbutoxycarbonyl, carbonate protecting groups; is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl

or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^{t}$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

Or $R_{S5}$ and $R_H$ can be combined to form a cyclic acetal or ketal moiety;

65 A disaccharide building block of claim 64

Wherein:

**$X_2$** is selected from a hydroxyl group; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, a $^{t}$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta;

**$R_{P2}$** is selected from the group consisting of 4-methoxyphenyl; benzyl; substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups; carbonate protecting groups including allyloxycarbonyl;

**$R_{P1}$** is selected from the group consisting of 4-methoxyphenyl; benzyl; substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups; carbonate protecting groups including allyloxycarbonyl;

**$R_{E1}$** is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl; or, benzyl and substituted benzyl groups;

**$R_{B1}$** is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or **$R_{H2}$** and **$R_{B1}$** can combine together to form a cyclic carbamate;

$R_{H2}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group;

$R_{S5}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; tert-Butyldiphenylsilyl.

66 A disaccharide building block of claim 64
Wherein:

is selected from tertbutyldiphenylsilyloxy , trichloroacetimidoyl or fluoro and the stereochemistry may be alpha or beta;

$R_{E1}$ is selected from the group consisting of methyl, allyl, benzyl;

$R_{P1}$ is benzyl;

$R_{P2}$ is selected from the group consisting of benzyl; benzoate; or allyloxycarbonyl;

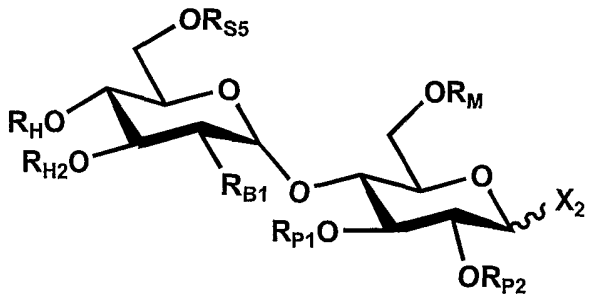
$R_H$ is benzyl;

$R_{H2}$ is benzyl;

$R_{S5}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, benzoyl, tert-butyldiphenylsilyl;

$R_{B1}$ is selected from the group consisting of an azido function, an *N*H-Dde or *N*H-DTPM group, or $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate.

67 A disaccharide building block of General Formula XXI,




General Formula XXI (Alternate Block E-D)

Wherein:

$X_2$ is selected from a hydroxyl group; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta;

$R_{P1}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups; carbonate protecting groups;

$R_{P2}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups, silyl protecting groups, carbamate protecting groups, C3-C5 alkenyl;

$R_{B1}$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate;

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl;

$R_{H2}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl, or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_{S5}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, substituted benzyl groups; alkylacyl, benzoyl, arylacyl or alkylarylacyl, and substituted alkylacyl, 4-chlorobenzoyl, arylacyl or alkylarylacy protecting groups; allyloxycarbonyl, ethoxycarbonyl, tertbutoxycarbonyl, carbonate protecting groups; is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

Or $R_{S5}$ and $R_H$ can be combined to form a cyclic acetal or ketal moiety;

**RM** is selected from the group consisting of a *p*-methoxyphenyl protecting group or other suitable oxidatively labile protecting group; a trityl group.

68 A disaccharide building block of claim 67,

Wherein:

$X_2$ is selected from a hydroxyl group; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta;

$R_{P2}$ is selected from the group consisting of 4-methoxyphenyl; benzyl; substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups; carbonate protecting groups including allyloxycarbonyl;

$R_{P1}$ is selected from the group consisting of 4-methoxyphenyl; benzyl; substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups; carbonate protecting groups including allyloxycarbonyl;

$R_{B1}$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate;

$R_{H2}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group;

$R_{S5}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; tert-Butyldiphenylsilyl;

$R_M$ is selected from the group consisting of a *p*-methoxyphenyl protecting group or other suitable oxidatively labile protecting group; a trityl group.

69 A disaccharide building block of claim 67,

Wherein:

$X_2$ is selected from a thiomethyl, thiocresyl, trichloroacetimidoyl and tert-butyldiphenylsilyl, and the stereochemistry may be alpha or beta;

$R_{P1}$ is benzyl;

$R_{P2}$ is selected from the group consisting of benzyl; benzoate; or allyloxycarbonyl;

$R_{B1}$ is selected from the group consisting of an azido function, an *N*H-DTPM group, or $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate.

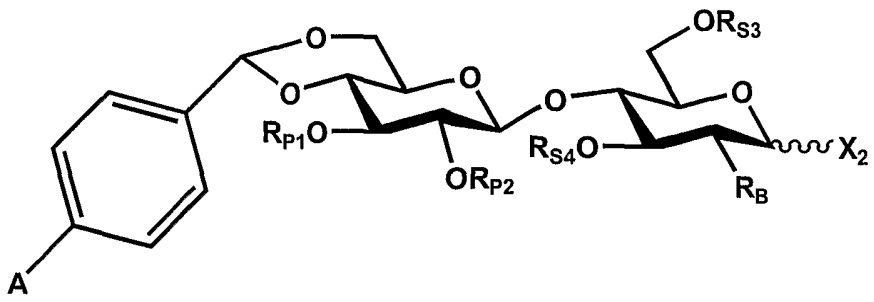
$R_{H2}$ is benzyl;

$R_H$ is benzyl;

$R_{S5}$ is selected from the group consisting of 4-methoxyphenyl, 4-methoxybenzyl, benzoyl, tert-butyldiphenylsilyl;

$R_M$ is selected from the group consisting of a *p*-methoxyphenyl, 4-methoxybenzyl and a trityl group.

70 A disaccharide building block of General Formula XXII,




General Formula XXII (Alternate Block D-C)

Wherein:

$X_2$ is selected from a hydroxyl group; thioalkyl, thioaryl, halogen, imidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta;

$R_B$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl , benzyloxymethyl;

$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;
or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{P1}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or

substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups;

$R_{P2}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups, silyl protecting groups, carbamate protecting groups, C3-C5 alkenyl;

A includes but is not limited to; H, Methoxy, Methyl; other suitable substituents will be known to those in the art.

71 A disaccharide building block of claim 70,

Wherein:

$X_2$ is selected from a hydroxyl group; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta;

$R_B$ is selected from the group consisting of an azido function, an *N*H-Dde or *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups;

$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{P1}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups; carbonate protecting groups;

$R_{P2}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups, silyl protecting groups, carbamate protecting groups, C3-C5 alkenyl;

A includes but is not limited to; H, Methoxy, Methyl; other suitable substituents will be known to those in the art.

**72** A disaccharide building block of claim 70,

Wherein:

$X_2$ is selected from a hydroxyl group; thiomethyl, thiocresyl, trichloroacetimidoyl or a $^t$butyldiphenylsilyloxy; and the stereochemistry may be alpha or beta;

$R_B$ is selected from the group consisting of an azido function, an *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, benzoyl, allyloxycarbonyl;

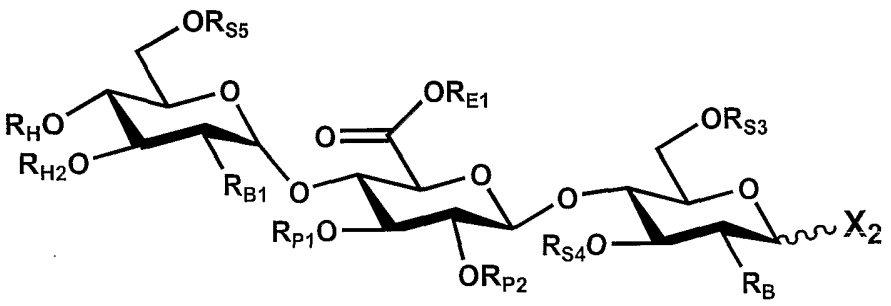
$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, benzoyl, allyloxycarbonyl; or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{P1}$ is benzyl;

$R_{P2}$ is selected from the group consisting of benzyl; benzoate; or allyloxycarbonyl;

**A** is H or Methoxy.

**73** A trisaccharide building block of General Formula XXIII,




General Formula XXIII (Block E-D-C)

Wherein:

$X_2$ is selected from a hydroxyl group; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta;

$R_{P1}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups;

$R_{P2}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate

protecting groups, silyl protecting groups, carbamate protecting groups, C3-C5 alkenyl;

$R_{E1}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl, $C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups;

$R_{B1}$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate;

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl;

$R_{H2}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl, or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_{S5}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, substituted benzyl groups; alkylacyl, benzoyl, arylacyl or alkylarylacyl, and substituted alkylacyl, 4-chlorobenzoyl, arylacyl or alkylarylacy protecting groups; allyloxycarbonyl, ethoxycarbonyl, tertbutoxycarbonyl, carbonate protecting groups; is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

Or $R_{S5}$ and $R_H$ can be combined to form a cyclic acetal or ketal moiety;

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting

groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl , benzyloxymethyl;

$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_B$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

74 A trisaccharide building block of claim 73,

Wherein:

$X_2$ is selected from a hydroxyl group; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta;

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; tert-Butyldiphenylsilyl;

$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted

alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; tert-Butyldiphenylsilyl, or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_B$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

$R_{P2}$ is selected from the group consisting of 4-methoxyphenyl; benzyl; substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups; carbonate protecting groups including allyloxycarbonyl;

$R_{P1}$ is selected from the group consisting of 4-methoxyphenyl; benzyl; substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups; carbonate protecting groups including allyloxycarbonyl;

$R_{E1}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl; or, benzyl and substituted benzyl groups;

$R_{B1}$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate;

$R_{H2}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group;

$R_{S5}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted

alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; tert-butyldiphenylsilyl.

**75** A trisaccharide building block of claim 73,

Wherein:

$X_2$ is selected from a hydroxyl group; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta;

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; tert-Butyldiphenylsilyl;

$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; tert-Butyldiphenylsilyl, or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_B$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

$R_{P2}$ is selected from the group consisting of 4-methoxyphenyl; benzyl; substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups; carbonate protecting groups including allyloxycarbonyl;

$R_{P1}$ is selected from the group consisting of 4-methoxyphenyl; benzyl; substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or

substituted alkylacyl, arylacyl and alkylarylacyl protecting groups; carbonate protecting groups including allyloxycarbonyl;

$R_{E1}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl; or, benzyl and substituted benzyl groups;

$R_{B1}$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate;

$R_{H2}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group;

$R_{S5}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; tert-Butyldiphenylsilyl;

**76** A trisaccharide building block of claim 73,

Wherein:

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, benzoyl, 4-chlorobenzoyl, allyl, allyloxycarbonyl;

$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, benzoyl, 4-chlorobenzoyl, allyl, or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_B$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

$X_2$ is selected from a thiomethyl, thioethyl, thiophenyl, thiocresyl, trichloroacetimidoyl, tert-butyldiphenylsilyloxy and the stereochemistry may be alpha or beta;

$R_{E1}$ is selected from the group consisting of methyl, allyl, benzyl;

$R_{P1}$ is benzyl;

$R_{P2}$ is selected from the group consisting of benzyl; benzoate; or allyloxycarbonyl;

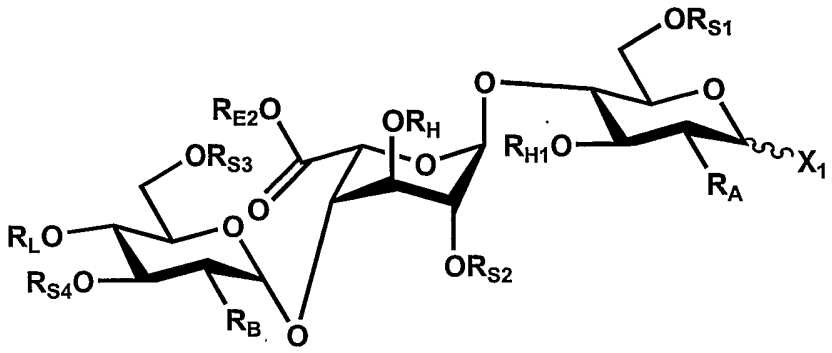
$R_H$ is benzyl;

$R_{H2}$ is benzyl;

$R_{S5}$ is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, benzoyl, tert-butyldiphenylsilyl;

$R_{B1}$ is selected from the group consisting of an azido function, an *N*H-Dde or *N*H-DTPM group, or $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate.

**77** A trisaccharide building block of General Formula XXIV,




General Formula XXIV (Block C-B-A)

Wherein:

$X_1$ is selected from the group consisting of hydroxy, alkenyloxy, alkoxy, aryloxy, benzyloxy, substituted benzyloxy; thioalkyl, thioaryl, halogen, imidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; a lipoamincacid or other such group suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_{H1}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl;

$R_A$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde, *N*H-DTPM, *N*H-Fmoc, *N*H-Boc, NH-Cbz, *N*H-Troc, *N*-phthalimido, NH-Ac, NH-Allyloxycarbonyl; or $R_H$ and $R_A$ can combine together to form a cyclic carbamate;

$R_{S1}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

$R_{S2}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted

alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^{t}$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^{t}$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl , benzyloxymethyl;

$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^{t}$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl,
or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{E2}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl,$C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups;

$R_B$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; γ-aminobutyryl, 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl,

4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting groups; allyloxycarbonyl, allyl ether, carbonate type protecting groups;

**78** A trisaccharide building block of claim 77,

Wherein:

$X_1$ is selected from the group consisting of hydroxy, alkoxy, aryloxy, benzyloxy, substituted benzyloxy; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; a lipoaminoacid suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_H$ and $R_{H1}$ are independently selected from a benzyl or substituted benzyl protecting group, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_A$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde, *N*H-DTPM, *N*H-Fmoc, *N*H-Boc, NH-Cbz, *N*H-Troc, *N*-phthalimido; or other such suitable protected amino functions or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate,

$R_{S1}$,$R_{S2}$,$R_{S3}$, and $R_{S4}$ are independently selected from: 4-methoxyphenyl; 4-methoxybenzyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, benzoyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{E2}$ is selected from methyl, $C_2$-$C_5$ alkyl; substituted alkyl; or, benzyl and substituted benzyl groups;

$R_B$ is selected from an azido function, an amine; an *N*H-Dde or *N*H-DTPM group; additionally $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; -aminobutyryl,γ 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting group.

**79** A trisaccharide building block of claim 77,

Wherein:

$X_1$ is selected from the group consisting of hydroxy, methoxy, thiomethyl, thioethyl, thiocresyl, trichloroacetimidoyl, a $^t$butyldiphenylsilyloxy a lipoaminoacid suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_H$ and $R_{H1}$ are independently selected from a benzyl or substituted benzyl protecting group, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_A$ is selected from the group consisting of an azido function an *N*H-Dde, *N*H-DTPM, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

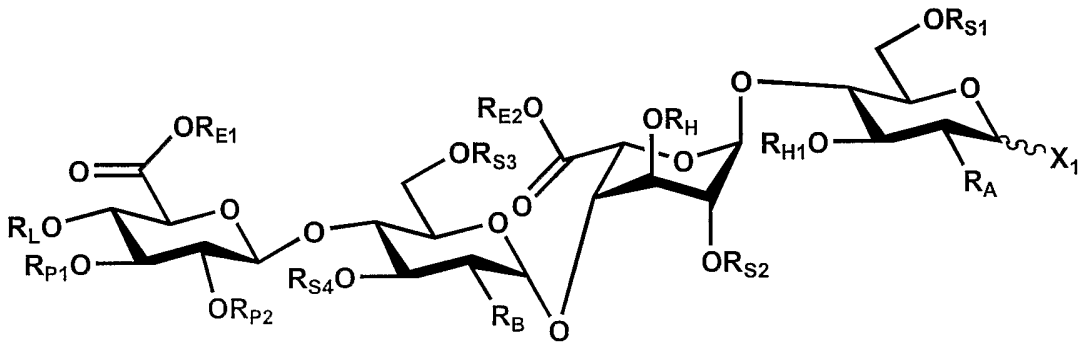
$R_{S1}$,$R_{S2}$,$R_{S3}$ and $R_{S4}$ are independently selected from: 4-methoxyphenyl; 4-methoxybenzyl; benzoyl, or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{E2}$ is selected from methyl, allyl or, benzyl and substituted benzyl groups;

$R_B$ is selected from an azido function; an *N*H-Dde or *N*H-DTPM group; additionally $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

$R_L$ is selected from a H atom; a levulinoyl.

**80** A tetrasaccharide building block of General Formula XXV,




General Formula XXV (Block D-C-B-A)

Wherein,

$X_1$ is selected from the group consisting of hydroxy, alkenyloxy, alkoxy, aryloxy, benzyloxy, substituted benzyloxy; thioalkyl, thioaryl, halogen, imidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; a lipoaminoacid or other such group suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta,

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl;

$R_{H1}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_A$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde, *N*H-DTPM, *N*H-Fmoc, *N*H-Boc, NH-Cbz, *N*H-Troc, *N*-phthalimido, NH-Ac, NH-Allyloxycarbonyl; or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate,

$R_{S1}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl,

$R_{S2}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl,

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl , benzyloxymethyl,

$R_{S4}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl,
or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate,

$R_{E1}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl, $C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups;

$R_{E2}$ is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl,$C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups,

$R_B$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate,

$R_{P1}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups;

$R_{P2}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups, silyl protecting groups, carbamate protecting groups, C3-C5 alkenyl;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; γ-aminobutyryl, 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting groups; allyloxycarbonyl, allyl ether, carbonate type protecting groups;

**81** A tetrasaccharide building block of claim 80,

Wherein,

$X_1$ is selected from the group consisting of hydroxy, alkoxy, aryloxy, benzyloxy, substituted benzyloxy; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; a lipoaminoacid suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_H$ and $R_{H1}$ are independently selected from a benzyl or substituted benzyl protecting group, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_A$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde, *N*H-DTPM, *N*H-Fmoc, *N*H-Boc, NH-Cbz, *N*H-Troc, *N*-phthalimido; or other such suitable protected amino functions or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_{S1}$,$R_{S2}$,$R_{S3}$ and $R_{S4}$ are independently selected from: 4-methoxyphenyl; 4-methoxybenzyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, benzoyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{E1}$ and $R_{E2}$ are independently selected from methyl, $C_2$-$C_5$ alkyl; substituted alkyl; or, benzyl and substituted benzyl groups;

$R_B$ is selected from an azido function, an amine; an *N*H-Dde or *N*H-DTPM group; additionally $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

$R_L$ is selected from a H atom; a levulinoyl, chloroacetyl, 4-acetoxybenzoyl, 4-acetamidobenzoyl, 4-azidobenzoyl, or other substituted

benzoyl type protecting group; a benzyl group, a 4-acetoxybenzyl, 4-acetamidobenzyl or other such suitable substituted benzyl type protecting group; -aminobutyryl,γ 4-N-[1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)ethylamino]-butyryl, 4-N-[1-(1,3-dimethyl-2,4,6(1H,3H,5H)-trioxopyrimidin-5-ylidene)methylamino]-butyryl, 4-N-Alloc-butyryl, 4-N-Fmoc-butyryl, 4-N-Boc-butyryl type protecting group.

**82** A tetrasaccharide building block of claim 80,

Wherein,

$X_1$ is selected from the group consisting of hydroxy, methoxy, thiomethyl, thioethyl, thiocresyl, trichloroacetimidoyl, a $^t$butyldiphenylsilyloxy a lipoaminoacid suitable for conjugation to delivery systems or solid supports; and the stereochemistry may be alpha or beta;

$R_H$ and $R_{H1}$ are independently selected from a benzyl or substituted benzyl protecting group, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

$R_A$ is selected from the group consisting of an azido functionan *N*H-Dde, *N*H-DTPM, or $R_{H1}$ and $R_A$ can combine together to form a cyclic carbamate;

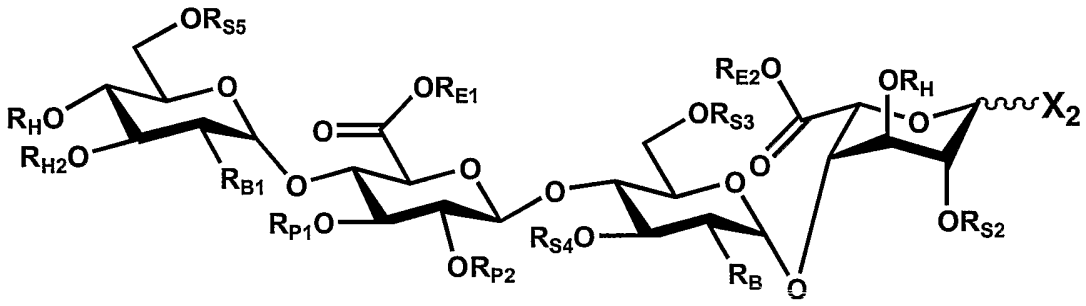
$R_{S1}$,$R_{S2}$,$R_{S3}$ and $R_{S4}$ are independently selected from: 4-methoxyphenyl; 4-methoxybenzyl; benzoyl, or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{E1}$ and $R_{E2}$ are independently selected from methyl, allyl or, benzyl and substituted benzyl groups;

$R_B$ is selected from an azido function; an *N*H-Dde or *N*H-DTPM group; additionally $R_{S4}$ and $R_B$ can combine together to form a cyclic carbamate;

$R_L$ is selected from a H atom; a levulinoyl.

83 A tetrasaccharide building block of General Formula XXVI,




E D C B

General Formula XXVI (Block E-D-C-B)

Wherein:

$R_H$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl;

$R_{H2}$ is selected from the group consisting of benzyl or substituted benzyl protecting group, allyl, allyloxycarbonyl, or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_{S2}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

$R_{S3}$ is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted

alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^{t}$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl , benzyloxymethyl;

**$R_{S4}$** is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^{t}$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl,
or **$R_{S4}$** and **$R_B$** may be combined to form a cyclic carbamate,

**$R_{S5}$** is selected from the group consisting of 4-methoxyphenyl; 4-methoxybenzyl, substituted benzyl groups; alkylacyl, benzoyl, arylacyl or alkylarylacyl, and substituted alkylacyl, 4-chlorobenzoyl, arylacyl or alkylarylacy protecting groups; allyloxycarbonyl, ethoxycarbonyl, tertbutoxycarbonyl, carbonate protecting groups; is selected from the group consisting of 4-methoxyphenyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; a $^{t}$butyldiphenylsilyloxy or other such substituted silyloxy protecting group allyl, methoxymethyl, methoxyethyl, benzyloxymethyl;

Or $R_{S5}$ and $R_H$ can be combined to form a cyclic acetal or ketal moiety;

**$R_{E1}$** is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl, $C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups;

**$R_{E2}$** is selected from the group consisting of methyl, $C_2$-$C_5$ alkyl; substituted alkyl,$C_3$-$C_5$ alkenyl; or, benzyl and substituted benzyl groups;

**$R_B$** is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or **$R_{S4}$** and **$R_B$** can combine together to form a cyclic carbamate;

$R_{B1}$ is selected from the group consisting of an azido function, an amine; an *N*H-Dde or *N*H-DTPM group, or $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate;

$R_{P1}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups;

$R_{P2}$ is selected from the group consisting of 4-methoxyphenyl; benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl and alkylarylacyl protecting groups;, carbonate protecting groups, silyl protecting groups, carbamate protecting groups, C3-C5 alkenyl;

$X_2$ is selected from a hydroxyl group; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta

Claim 84 A tetrasaccharide building block of claim 83,

Wherein:

$R_H$ and $R_{H2}$ are independently selected from a benzyl or substituted benzyl protecting group, $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate;

$R_{S2}$,$R_{S3}$,$R_{S4}$ and $R_{S5}$ are independently selected from: 4-methoxyphenyl; 4-methoxybenzyl; substituted benzyl groups; alkylacyl, arylacyl or alkylarylacyl, and substituted alkylacyl, benzoyl, arylacyl or alkylarylacy protecting groups; carbonate protecting groups; or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{E1}$ and $R_{E2}$ are independently selected from methyl, $C_2$-$C_5$ alkyl; substituted alkyl; or, benzyl and substituted benzyl groups;

$R_B$ and $R_{B1}$ are independently selected from an azido function, an amine; an *N*H-Dde or *N*H-DTPM group; additionally $R_{S4}$ and $R_B$ or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_{P1}$ and $R_{P2}$ are independently selected from benzyl, substituted benzyl groups; alkylacyl, arylacyl and alkylarylacyl, or substituted alkylacyl, arylacyl, and alkylarylacyl protecting groups; and carbonate protecting groups;

$X_2$ is selected from a hydroxyl group; thioalkyl, thioaryl, halogen, trichloroacetimidoyl, phosphate and related phosphate ester type leaving groups, a $^t$butyldiphenylsilyloxy or other such substituted silyloxy protecting group; and the stereochemistry may be alpha or beta.

85 A tetrasaccharide building block of claim 83,

Wherein:

$R_H$ and $R_{H2}$ are independently selected from a benzyl or substituted benzyl protecting group, or $R_{H2}$ and $R_{B1}$ can combine together to form a cyclic carbamate;

$R_{S2}$,$R_{S3}$,$R_{S4}$ and $R_{S5}$ are independently selected from: 4-methoxyphenyl; 4-methoxybenzyl; benzoyl, or $R_{S4}$ and $R_B$ may be combined to form a cyclic carbamate;

$R_{E1}$ and $R_{E2}$ are independently selected from methyl, allyl or, benzyl and substituted benzyl groups;

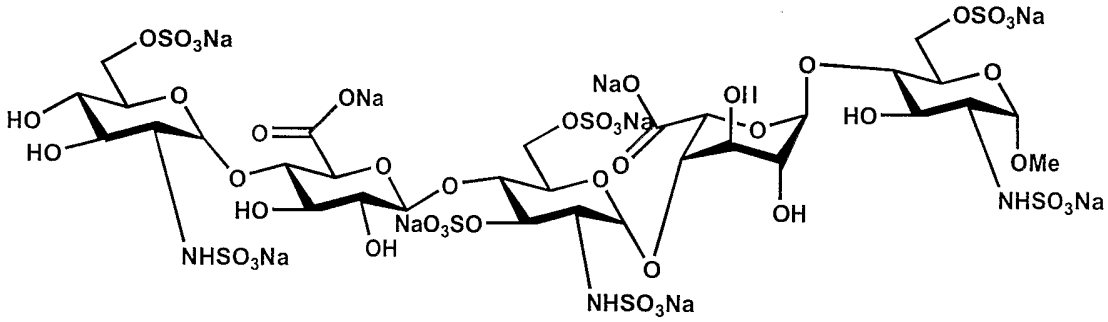
$R_B$ and $R_{B1}$ are independently selected from an azido function; an *N*H-Dde or *N*H-DTPM group; additionally $R_{S4}$ and $R_B$ or $R_{H2}$ and $R_{B1}$ independently can combine together to form a cyclic carbamate;

$R_{P1}$ is benzyl;

$R_{P2}$ is selected from the group consisting of benzyl; benzoyl, allyloxycarbonyl;.

$X_2$ is selected from a hydroxyl group; thiomethyl, thiocresyl trichloroacetimidoyl, or $^t$butyldiphenylsilyloxy; and the stereochemistry may be alpha or beta.

86 A pentasaccharide of the formula




formed by deprotection of the pentasaccharide of claim

87. A monosaccharide of claim 44,

wherein,

$R_{E1}$ is selected from the group consisting of methyl, allyl, benzyl,;

$R_{P1}$ is benzyl;

$R_{P2}$ is selected from the group consisting of benzyl; benzoate; or allyloxycarbonyl;

$X_4$ is selected from a thiomethyl, thiocresyl and the stereochemistry may be alpha or beta;

$R_L$ is selected from a H atom; a levulinoyl, pivaloyl, benzoyl, allyl.

Claim 88 A pharmaceutical preparation comprising a pharmaceutically effective amount of the pentasaccharide of claim 86 together with a pharmaceutical carrier.

REFERENCES

[1] Lindahl, U., Backdtrom, G., Thunberg, L., Leder, I.G., *Proc. Natl. Acad. Sci. USA*, **1980**, *Vol. 77, No. 11*, 6551-6555; Reisenfeld, J., Thunberg, L., Hook, M., & Lindahl, U., *J. Biol. Chem.*, **1981**, *Vol. 256, No. 5*, 2389-2394.
[2] Choay, J., Lormeau, J-C., Petitou, M., Sinay, P., and Fareed, J., *Annals New York Academy of Sciences*, **1981**, *370*, 644-649.
[3] Pierre Sinaÿ, Jean-Claude Jacquinet, *Carbohydrate Research*, 132, (1984), C5-C9.
[4] C.A.A. van Boeckel, T. Beetz, J.N. Vos, A.J.M. de Jong, S.F. van Aelst, R.H. van den Bosch, J.M.R. Mertens and F.A. van der Vlugt., *J. Carbohydrate Chemistry*, 4(3), 1985, 293-321.
[5]. J. Choay, M. Petitou, J.C. Lormeau, P. Sinäy, J. Fareed, *Ann. NY Acad. Sci.*, **1981**, 370, 644-649.
[6]. J. Choay *et. al.*, *Biochem. Biophys. Res. Commun.*, **1983**, 116, 492-499.

CORRECTED VERSION

# INTERNATIONAL SEARCH REPORT

International application No.
**PCT/AU02/01228**

**A. CLASSIFICATION OF SUBJECT MATTER**

Int. Cl. [7]: C07H 3/02, 3/04, 3/06; A61K 31/702; A61P 7/02

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

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
See electronic database below

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

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

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | STN File CA Abstract Accession No. 136:70031<br>& Love K R et al., "Linear synthesis of a protected H-type II pentasaccharide using glycosyl phosphate building blocks". Journal of Organic Chemistry, 2001 66(24) pages 8165-8176.<br>See RN 385422-04-8 (regarding: Block Alt B) | 29-34<br>Block A |
| X | JP 10-182576 A (WAKO PURE CHEM IND LTD) 7 July 1998<br>See page 9 compound 9 (re: Block Alt B) | 39-42<br>Block Alt B |
| X | WO 95/03316 A2 (HANESSIAN, S) 2 February 1995<br>See page 26 Schemes I and II (re: Blocks A, C, E); page 27 (re: Block A); page 44 Table XXVIII (re: Block Alt B); page 54 Table XXXVIII (re: Block A). | 29-34; 43-45, 87; 49-51; 39-42; Blocks A, C, E, Alt B |

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 10 December 2002 | 13 JAN 2003 |
| Name and mailing address of the ISA/AU | Authorized officer |
| AUSTRALIAN PATENT OFFICE<br>PO BOX 200, WODEN ACT 2606, AUSTRALIA<br>E-mail address: pct@ipaustralia.gov.au<br>Facsimile No. (02) 6285 3929 | **CHRISTINE BREMERS**<br>Telephone No : (02) 6283 2313 |

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## INTERNATIONAL SEARCH REPORT

International application No.
**PCT/AU02/01228**

**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | JP 3-237101 A (KYOWA HAKKO KOGYO KK (RIKA)) 23 October 1991<br>See page 8 compounds 21-25 (re: Block Alt B); compound 18 (re: Blocks A, C, E); page 11 compounds 29, 50-53 (re: alt Block B-A) | 39-42; 29-34,43-45, 87, 49-51; 58-60; Blocks A, C, E, Alt B, Alt BA |
| X | EP 0333243 A2 (AZKO N.V.) 20 September 1989<br>See Formula Sheet (page 8?) compound 1(re: Blocks A, C, E), compounds 2 and 3 (re: Block D-C) | 29-34, 43-45, 87, 49-51, 61-63; Blocks A, C, E, DC |
| X | JP 63-218691 A (KODAMA KK (RIKA)) 12 September 1988<br>See page 704 compound 23 (re: Block E-D-C-B); page 704 compound 24 (re: Block A); 704 page 705 compound 25 (re: Block E-D-C-B-A); page 709 compounds 17-19 (re: Block B-A); page 709 compound 21 (re: Block D-C); page 709 compounds 22-23 (re: Block D-C-B-A) | 83-85; 29-24; 1-15; 55-57; 61-63; 80-82; Blocks EDCB, A, EDCBA, BA, DC, DCBA |
| X | STN File CA Abstract Accession No. 104:130179<br>& Ichikawa, Y et al, "Synthetic studies on mucopolysaccharides. Part III. Synthesis, from cellobiose of a trisaccharide closely related to the GlcNAc → GlcA → GlcN segment of the antithrombin-binding sequence of heparin".<br>Carbohydrate Research 1985, 141(2) pages 272-282.<br>See formula III (re: Block A) | 29-34<br>Block A |
| X | AU 42637/85 A (CHOAY SA) 21 November 1985<br>See page 24 example 2, compound 6 and last compound on first formula sheet (re: E-D-C-B); page 29 example 4 compound 27 (re: Block E-D-C-B-A); first formula sheet compound 1 (re: Block D-C); first formula sheet compound 2 (re: Block B); second formula sheet compound (Block D); second formula sheet compounds 18-19 (re: Block D-C); third formula sheet compound 20 (re: Block B-A); third formula sheet compound 21 (re: Block D-C-B-A); third formula sheet compounds 22-23 (re: Block E-D-C-B-A) | 83-85; 1-15; 61-63; 35-38; 46-48; 55-57; 80-82; Blocks EDCB, EDCBA, DC, B, D, BA, DCBA |
| X | FR 2531436 A1 (CHOAY SA) 10 February 1984<br>See page 8 formula (III) (re: Blocks A, C, E); page 8 formula (IV) (re: Block D-C-B-A); page 13 formulas (V)-(VI) (re: Block D-C); page 13 formula (VII) (re: Block D); page 14 formula (VIII) (re: Blocks A, C, E); Figure 1 compounds 14 and 16-18 (re: Block D); figure 2 compounds 2-3 (re: Block D-C); Figure 2 compounds 5-6 (re: D-C-B-A); Figure 3 compound 7 (re: Block E); Figure 3 compound 8 (re: E-D-C-B-A) | 29-34, 43-45, 87, 49-51; 80-82; 61-63; 46-48; 1-15; Blocks A, C, E, DCBA, DC, D, E, EDCBA |
| X | EP 0082793 B1 (CHOAY SA) 10 May 1989<br>See page 21 compound 87 (re: Block B); page 28 formula (IV) (re: Block D); page 29 formula (V) (re: Block B); Fig. 14. compound 80 (re: Block A) | 35-38; 46-48; 29-34; Blocks B, D, A |

CORRECTED VERSION

# INTERNATIONAL SEARCH REPORT

International application No.
**PCT/AU02/01228**

**C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | AU 83955/82 A1 (CHOAY SA) 24 November 1982<br>See page 13 formula (V) and Fig. 1. Compound (1) (re: Blocks A, E) | 29-34; 49-51<br>Blocks A, E |
| X | AU 10397/83 (CHOAY SA) 3 August 1983<br>See Fig. 3. compound (16) (re: Block D); Fig. 4. compound (20) (re: Block D-C); Fig. 5. compound (22) (re: Block A); Fig. 7. compound (36) (re: Block B); Fig. 8. compound (22) (re: Block A); Fig. 8. compounds (40)-(41) (re: Block B-A); Fig. 9. compound (20) (re: Block D-C); Fig. 9 compound (41) (re: Block B-A); Fig 9. compounds (42)-(43) (re: Bock D-C-B-A); Fig. 10. compound (44) (re: Block E); Fig. 10 compound (45) (re: Block E-D-C-B-A); Fig. 12. compounds (52)-(54) (re: Block E-D); Fig. 13. compound (55) (re: Block D); Fig. 13a. compound (55) (re: Block Alt B); Fig. 14. compound (63) (re: Block E-D-C); Fig. 15. compounds (65), (67) and (68) (re Block A); Fig. 15. compound (69) (re: Block B); Fig. 15. compound (70) (re: Block B-A); Fig. 16 compounds (75) and (77) (re: Block A); Fig. 16. compound (36) (re: Block B); Fig. 17. compounds (81)-(83) (re: Block B-A); Fig. 18. compound (84) (re: Block C); Fig. 18. compound (41) (re: Block B-A); Fig. 18. compound (85) (re: Block C-B-A); Fig. 19. compound (90) (re: Block D); Fig. 20. compound (97) (re: Block D-C); Fig. 20. compound (98) (re: Block D-C-B-A); Fig. 24 compound (124) (re: Block Alt B); Fig. 27. compound (141) (re: Block D-C); Fig. 28. compound (97) (re: Block D-C) | 46-48; 61-63; 29-34; 35-38; 55-57; 80-82; 49-51; 1-15; 64-66; 39-42; 73-76; 43-45, 87; 77-79; Blocks D, DC, A, B, BA, DCBA, EDCBA, ED, Alt B, EDC, C, CBA |

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# INTERNATIONAL SEARCH REPORT

International application No.
**PCT/AU02/01228**

**Box I** **Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

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

1. ☐ Claims Nos :

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

2. ☒ Claims Nos : **1-88**

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

For economic reasons, the search was broadly based on the examples.

3. ☐ Claims Nos :

because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

**Box II** **Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

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

See Supplemental Sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

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## INTERNATIONAL SEARCH REPORT

International application No.
**PCT/AU02/01228**

**Supplemental Box**
(To be used when the space in any of Boxes I to VIII is not sufficient)

**Continuation of Box No: II**

The international application does not comply with the requirements of unity of invention because it does not relate to one invention only or to a group of inventions so linked as to form a single general inventive concept. In coming to this conclusion the International Searching Authority has found that there are three different groups of inventions as follows:

1. Claims 1-34, 43-45, 49-88 are directed to the pentasaccharide of General Formula I; monosaccharides A, C and E and their di-, tri- and tetra-saccharides; and the intermediate of General Formula XVI.

2. Claims 1-29, 35-42, 55-60, 77-86 and 88 are directed to the pentasaccharide of General Formula I; monosaccharides B and alternate B and their di-, tri- and tetra-saccharides.

3. Claims 1-29, 46-48, 61-76, 80-86 and 88 are directed to the pentasaccharide of General Formula I, monosaccharide D and its di-, tri- and tetra-saccharides; and disaccharides that have alternate D ie E-alternate D and alternate D-C.

These groups of inventions are not so linked to form a single general inventive concept.

The pentasaccharide (final product) has unity with each of the monosaccharides in accordance with PCT/AI/1g (ii) (A).

However, the monosaccharides A, B, C, D and E (and their corresponding di-, tri- and tetra-saccharides) which are the intermediates for the pentasaccharide, lack unity. The PCT Administrative Instructions Annex B Part 1(g) (vi) for determination of compliance with unity of invention under Rule 13.2 states that if the same application claims different intermediates for different structural parts of the final product, unity is not present between the intermediates. Therefore the monosaccharides do not have unity among themselves except between monosaccharides A, C and E which have a common intermediate.

Furthermore, these groups of claims will require distinct search strategies and therefore it is considered that because of these distinct search strategies, these inventions could not be searched without involving significant extra effort.

Also with regard to searching, the economic feasibility for the search of each invention, including the searches that would pertain to blocks B and D and their alternates, may force restrictions on any search that is carried out.

CORRECTED VERSION

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
**PCT/AU02/01228**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

| Patent Document Cited in Search Report | | Patent Family Member | | | | | |
|---|---|---|---|---|---|---|---|
| WO | 9503316 | AU | 72620/94 | CA | 2100821 | US | 5767256 |
| AU | 42637/85 | CA | 1265792 | DK | 2159/85 | EP | 165134 |
| | | FR | 2564468 | JP | 60260590 | NZ | 212094 |
| | | US | 4801583 | ZA | 8503694 | AU | 10397/83 |
| | | AU | 21285/83 | CA | 1258452 | CA | 1265132 |
| | | DK | 3135/84 | EP | 84999 | EP | 113599 |
| | | ES | 527144 | ES | 8501414 | FR | 2535324 |
| | | JP | 58170797 | JP | 5262783 | JP | 5331182 |
| | | US | 4803265 | US | 4818816 | US | 4943630 |
| | | WO | 8401777 | CA | 1247608 | EP | 82793 |
| | | FR | 2533219 | JP | 59010599 | LU | 90928 |
| | | US | 4987223 | FR | 2533220 | FR | 2531436 |
| | | SU | 1694065 | FR | 2529557 | DK | 143/83 |
| | | FR | 2528854 | FR | 2528853 | FR | 2527614 |
| | | ES | 519232 | ES | 8402844 | FR | 2521566 |
| | | FR | 2520744 | FR | 2519987 | WO | 8203863 |
| | | AU | 83955/82 | DK | 5756/82 | US | 4774231 |
| | | SU | 1470196 | CA | 1263381 | EP | 64012 |
| | | ES | 512381 | ES | 8303444 | FR | 2504535 |
| | | US | 4607025 | FR | 2535323 | FR | 2518550 |
| | | BE | 898096 | FR | 2535306 | IT | 1175140 |
| JP | 10182576 | NONE | | | | | |
| JP | 3237101 | NONE | | | | | |
| JP | 63218691 | NONE | | | | | |
| FR | 2531436 | AU | 42637/85 | SEE | FAMILY | LIST | ABOVE |
| EP | 82793 | AU | 42637/85 | SEE | FAMILY | LIST | ABOVE |
| AU | 83955/82 | AU | 42637/85 | SEE | FAMILY | LIST | ABOVE |
| AU | 10397/83 | AU | 42637/85 | SEE | FAMILY | LIST | ABOVE |
| EP | 333243 | NONE | | | | | |

END OF ANNEX