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(73)专利权人 中国科学院昆明植物研究所
地址 650201 云南省昆明市蓝黑路132号

(72)发明人 肖国志 李朋华 何海清 张云琴

(74)专利代理机构 北京慕达星云知识产权代理事务所(特殊普通合伙) 11465
专利代理师 崔自京

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(56)对比文件

Guthrie, R. D.,等.Synthesis of oligosaccharides on polymer supports. I. 6-O-(p-Vinylbenzoyl) derivatives of glucopyranose and their copolymers with styrene.《Journal of the Chemical Society [Section] C: Organic》.1971,第2690-2696页.

Roy D. Guthrie,等.Synthesis of oligosaccharides on polymer supports.II. Synthesis of β-D-gentiobiose derivatives on soluble support copolymers of styrene and 6-O-(p-vinylbenzoyl) or 6-O-(p-vinylphenylsulfonyl)derivatives of D-glucopyranose.《J.C.S. Perkin I》.1973,第20卷第2414-2417页.

Von Harimut Seliger,等.Spezifische Produktaussonderung bei Trager-Oligonucleotidsynthesen nach dem Triesterverfahren.《Angew. Chem.》.1981,第8卷第709-710页.

Sergey A. Dergunov,等.Functionalization of Imprinted Nanopores in Nanometer-Thin Organic Materials.《Angew. Chem. Int. Ed.》.2008,第47卷第8264-8267页.

Sergey A. Dergunov,等.pH-Mediated Catch and Release of Charged Molecules with Porous Hollow Nanocapsules.《J. Am. Chem. Soc.》.2013,第136卷第2212-2215页.

审查员 臧乐芸

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(54)发明名称

一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体及其制备方法和应用

(57)摘要

本发明公开了一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体,其制备方法及在糖苷化反应中的应用。本发明公开的邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体稳定,容易制备和保存,广泛用于各种氧糖苷和核苷(氮糖苷)糖苷键的构建中。给体的离去基为烯基酯类,活性更高,可以结合硫苷或正戊烯基醚类糖苷进行一锅糖苷化反应合成寡糖。本糖苷化反应条件温和,对酸敏感和对亲电试剂敏感的受体均能耐受。

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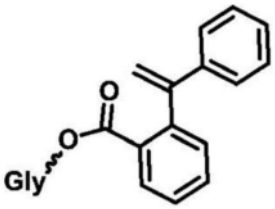
1.一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体,其特征在于,所述糖苷化给体如结构式I所示:



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其中,Gly为取代或非取代的糖基。

2.根据权利要求1所述的一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体,其特征在于,所述Gly选自以下结构中的一种:

其中,PG为一个或多个羟基保护基,糖基或糖链;

所述羟基保护基选自取代或非取代的芳酰基、取代或非取代的C2-C6烷酰基、取代或非取代的硅基、取代或非取代的芳基、取代或非取代的C1-C6烷基中的任意一种。

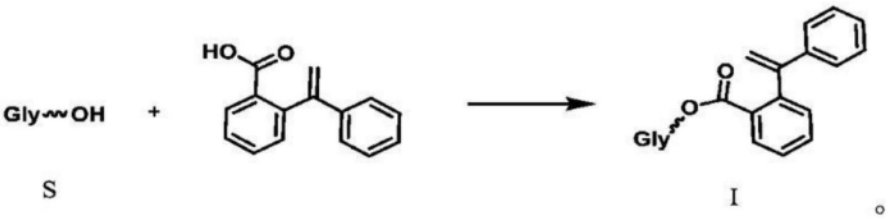
3.一种权利要求1-2任一项所述的邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的制备方法,其特征在于,包括以下步骤:

(1)室温下将式S所示化合物、邻-(1-苯基乙烯基)苯甲酸溶解在有机溶剂中;

(2)在惰性气体气氛下,加入DMAP、EDCI和DIPEA,搅拌至TLC显示反应完全;

(3)将混合物经过稀释、洗涤、干燥、过滤、真空浓缩、纯化后得到结构式I所示的糖苷化给体;

式S所示化合物与邻-(1-苯基乙烯基)苯甲酸进行酯化反应的方程式如下:



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4.根据权利要求3所述的一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的制备方法,其特征在于,步骤(1)中所述有机溶剂选自N,N-二甲基甲酰胺、四氢呋喃、二氯甲烷、丙酮或乙腈中的一种或多种。

5.根据权利要求3所述的一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的制备方法,其特征在于,式S所示化合物、邻-(1-苯基乙烯基)苯甲酸、DMAP、EDCI和DIPEA的摩尔比为1:1～1.2:1:1.5～2:3。

6.一种权利要求1-2任一项所述的邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体在糖苷化反应中的应用,其特征在于,以N-碘代丁二酰亚胺和路易斯酸TMSOTf的组合物为催化剂,所述糖苷化受体与路易斯酸TMSOTf、N-碘代丁二酰亚胺的摩尔比为1:0.1～1:1.2～2.5;所

述糖苷化给体和所述糖苷化受体的摩尔比为1.2～2.5:1～2。

7.根据权利要求6所述的一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的应用,其特征在于,包括以下步骤:

(1)在惰性气体环境中,干燥剂存在下,以N-碘代丁二酰亚胺和路易斯酸的组合物为催化剂,将结构式I所示的糖苷化给体和式Ⅱ所示的糖苷化受体ROH或者RNH在有机溶剂中进行糖苷化反应;

(2)待反应完全后淬灭反应,经过稀释、过滤、减压蒸馏、纯化,得到式P所示的糖苷化产物;

反应方程式如下:

I Ⅱ P

其中,ROH为含有羟基的化合物,RNH为含有肿胺的嘧啶类或者嘌呤类化合物。

8.根据权利要求7所述的一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的应用,其特征在于,所述有机溶剂为芳烃类溶剂、卤代烃类溶剂、酮类溶剂、醇类溶剂、醚类溶剂和腈类溶剂中的一种或多种。

9.根据权利要求7所述的一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的应用,其特征在于,步骤(1)中,所述糖苷化受体ROH与有机溶剂的摩尔体积比为0.01～0.1mol/L;所述糖苷化受体RNH与有机溶剂的摩尔体积比为0.01～0.5mol/L。

一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体及其制备方法和应用

技术领域

[0001] 本发明涉及化学合成技术领域,更具体的说是涉及一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体及其制备方法和应用。

背景技术

[0002] 化学合成是一种有效的,可靠的和可规模化的方法来产生纯的和结构确定的糖类化合物以进行解密它们的功能和开发新的治疗药物。与氧苷的合成方法相比,核苷(氮苷)的合成方法相对有限。目前,还没有一种方法可以普遍适用于所有寡糖的合成,特别是同时适用于氧苷和核苷的合成方案更为稀少。因此,发展同时适用氧糖苷和核苷的糖苷化反应方法是非常必要的,同时也是化学上一直存在的难题。

[0003] Vorbruggen型反应是一种著名的核苷合成方法,其局限性包括:1)使用强路易斯酸官能团兼容性差;2)当使用嘌呤时,偶联产率低,N9/N7区域选择性中等;3)后处理纯化难度增加,特别是在制备规模上。为了克服上述问题,Jamison小组引入了三氟吡啶鎓盐作为有效的bronsted酸催化剂,用于核苷和核苷类似物的合成,尽管他们在核苷合成方面取得了一定的成功,但糖基乙酸酯供体在氧糖苷合成中活性相对较弱。

[0004] 2008年,上海有机化学研究所的俞飚课题组报道了一种新的糖基化方法,以糖基邻炔基苯甲酸酯(ABz)为供体,Au(I)配合物为催化剂,这种俞氏糖基化反应条件非常温和,已经被成功地应用于复杂的氧糖苷天然产物和核苷类抗生素的全合成中,然而,该反应使用了昂贵的金试剂作为糖基化反应中的促进剂。2019年,俞飚课题组报告了另一种高效、通用的糖基化方法,即3,5-二甲基-4-(2'-苯基乙炔基苯基)苯基(EPP)糖苷作为供体,适用于氧糖苷和核苷的有效合成,虽然该糖基化反应使用催化量的路易斯酸,避免了反应体系酸性过强的问题,还降低了反应的成本,但由于该糖基化供体(EPP)的合成步骤增多且复杂,依然使得该反应存在一定的缺陷。

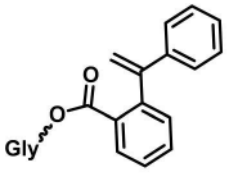
[0005] 因此有必要发展一种新型的糖苷化方法,使用易于制备且稳定的糖基化供体,廉价且容易获得的促进剂,温和的反应条件,普遍适用于各种底物的合成,产率高,反应副产物少,可以组合以实现多步一锅合成寡糖。

发明内容

[0006] 有鉴于此,本发明提供了一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体及其制备方法和糖苷化给体在糖苷化反应中的应用。

[0007] 为了达到上述目的,本发明采用如下技术方案:

[0008] 一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体,所述糖苷化给体如结构式I所示:

[0009] 

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[0010] 其中,Gly为取代或非取代的糖基。

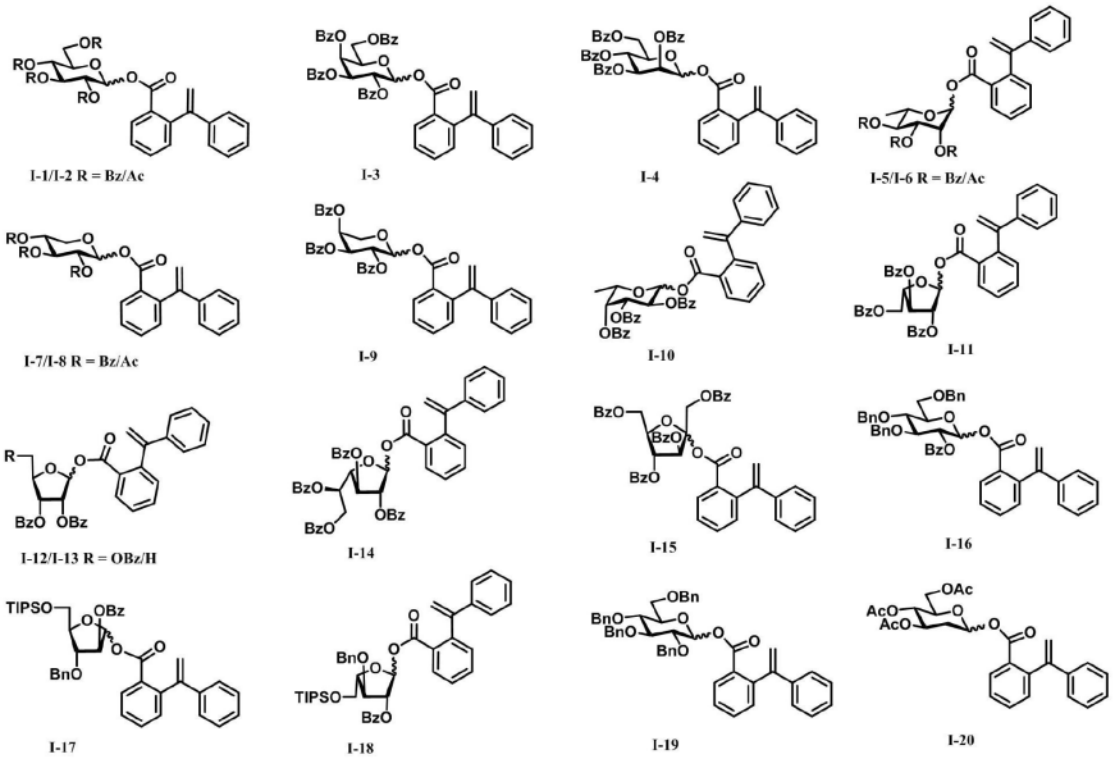
[0011] 优选的,在上述一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体中,所述Gly选自以下结构中的一种:

[0012] 

[0013] 其中,PG为一个或多个羟基保护基,糖基或糖链。

[0014] 优选的,在上述一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体中,所述羟基保护基选自取代或非取代的芳酰基、取代或非取代的C_2-C_6烷酰基、取代或非取代的硅基、取代或非取代的芳基、取代或非取代的C_1-C_6烷基中的任意一种,进一步优选为乙酰基(Ac),苄基(Bn),苯甲酰基(Bz),三异丙基硅烷基(TIPS)中的任意一种。

[0015] 优选的,在上述一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体中,结构式I为以下任一结构的化合物:

[0016] 

[0017] 本发明还公开了一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的制备方法,包括以下步骤:

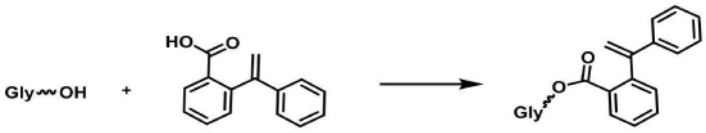
[0018] (1)室温下将式S所示化合物、邻-(1-苯基乙烯基)苯甲酸溶解在有机溶剂中;

[0019] (2)在惰性气体气氛下,加入DMAP、EDCI和DIPEA,搅拌至TLC显示反应完全;

[0020] (3)将混合物用有机溶剂稀释,然后用水和盐水洗涤,经过干燥、过滤、真空浓缩、

纯化后得到结构式I所示的糖苷化给体；

[0021] 式S所示化合物与邻-(1-苯基乙烯基)苯甲酸进行酯化反应的方程式如下：

[0022] 

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[0023] 优选的，在上述一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的制备方法中，步骤(1)中所述有机溶剂选自N,N-二甲基甲酰胺、四氢呋喃、二氯甲烷、丙酮或乙腈中的一种或多种，进一步优选为二氯甲烷。

[0024] 优选的，在上述一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的制备方法中，式S所示化合物、邻-(1-苯基乙烯基)苯甲酸、DMAP、EDCI和DIPEA的摩尔比为1:1～1.2:1:1.5～2:3；进一步优选为1:1.1:1:1.8:3。

[0025] 优选的，在上述一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的制备方法中，式S所示化合物在有机溶剂中的浓度为0.01～1mol/L，进一步优选为0.1～0.5mol/L。

[0026] 以及公开了一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体在糖苷化反应中的应用。

[0027] 优选的，在上述一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的应用中，包括以下步骤：

[0028] (1)在惰性气体环境中，干燥剂存在下，以N-碘代丁二酰亚胺NIS和路易斯酸的组合物为催化剂，将结构式I所示的糖苷化给体和式Ⅱ所示的糖苷化受体ROH或者RNH在有机溶剂中进行糖苷化反应；

[0029] (2)待反应完全后淬灭反应，经过稀释、过滤、减压蒸馏、纯化，得到式P所示的糖苷化产物；

[0030] 反应方程式如下：

[0031] 

I II P

[0032] 其中，ROH为含有羟基的化合物，RNH为含有肿胺的嘧啶类或者嘌呤类化合物。

[0033] 优选的，在上述一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体与糖苷化受体ROH或者嘌呤类化合物RNH反应的应用中，所述步骤(1)包括以下步骤：

[0034] A.将结构式I所示的糖苷化给体和式Ⅱ所示的糖苷化受体ROH或者嘌呤类化合物RNH溶解到有机溶剂中，在惰性气体环境下，加入干燥剂于室温下搅拌30min；

[0035] B.对反应溶液进行冷却后，向其中加入催化剂N-碘代丁二酰亚胺NIS和路易斯酸的组合物，逐渐升至室温，搅拌反应1.5-3h；

[0036] 步骤B中当糖苷化受体为ROH时，反应溶液冷却至0℃；当糖苷化受体为嘌呤类化合物RNH时，反应溶液冷却至-20℃。

[0037] 优选的，在上述一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体与糖苷化受体嘧啶类化合物RNH反应的应用中，所述步骤(1)包括以下步骤：

[0038] A.在惰性气体气氛下,将N,O-双(三甲基硅烷基)三氟乙酰胺加入到糖苷化受体嘧啶类化合物RNH的有机溶剂悬浮液中,在50℃下搅拌反应30min得到混合液;

[0039] B.将混合液添加到已经在室温和惰性气体气氛下搅拌30min的结构式I所示的糖苷化给体和活化的3ÅMS的有机溶液中,室温下继续搅拌10min;

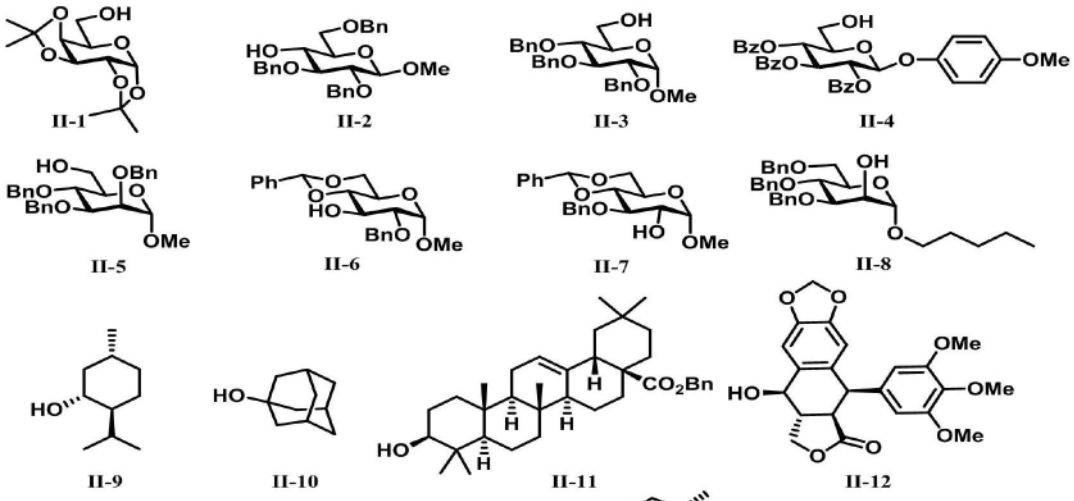
[0040] C.将反应溶液冷却至0℃,向其中加入催化剂N-碘代丁二酰亚胺NIS和路易斯酸的组合物,逐渐升至室温后,搅拌反应3h。

[0041] 优选的,在上述一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的应用中,所述有机溶剂为芳烃类溶剂、卤代烃类溶剂、酮类溶剂、醇类溶剂、醚类溶剂和腈类溶剂中的一种或多种,进一步优选为甲苯、二氯甲烷、乙醚、丙酮、四氢呋喃、乙腈中的一种或多种。

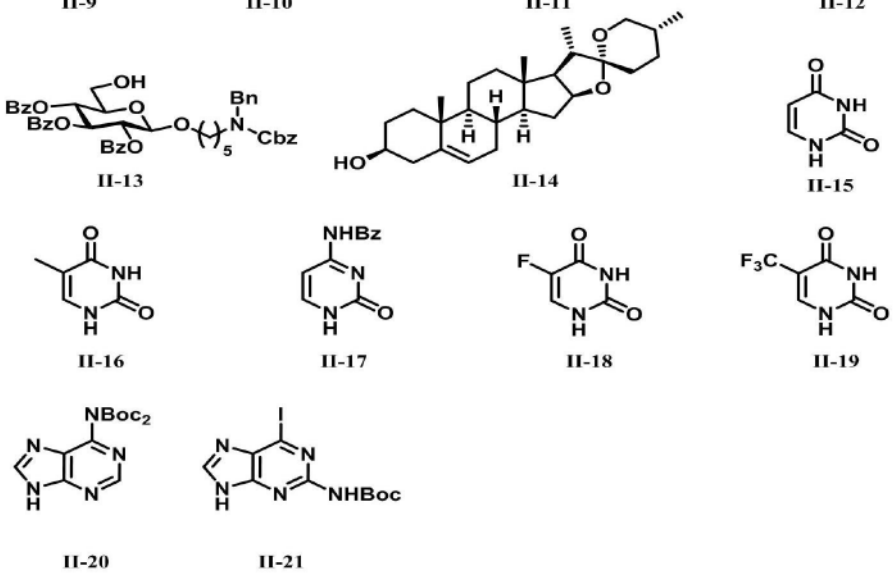
[0042] 优选的,在上述一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的应用中,当糖苷化受体为ROH或嘌呤类化合物RNH时,有机溶剂优选为二氯甲烷;当糖苷化受体为嘧啶类化合物RNHRNH时,有机溶剂优选为乙腈。

[0043] 优选的,在上述一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的应用中,所述路易斯酸为TMSOTf。

[0044] 优选的,在上述一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的应用中,所述糖苷化受体ROH或RNH选自以下所示的任一化合物:



[0045]



[0046] 优选的,在上述一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的应用中,所述糖苷化受体与路易斯酸、NIS的摩尔比为1:0.1～1:1.2～2.5,进一步优选为1:0.3～0.5:1.2～1.5。

[0047] 优选的,在上述一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的应用中,所述受体RNH和N,O-双(三甲基硅烷基)三氟乙酰胺的摩尔比为1:3.6～6,进一步优选为1:4～6。

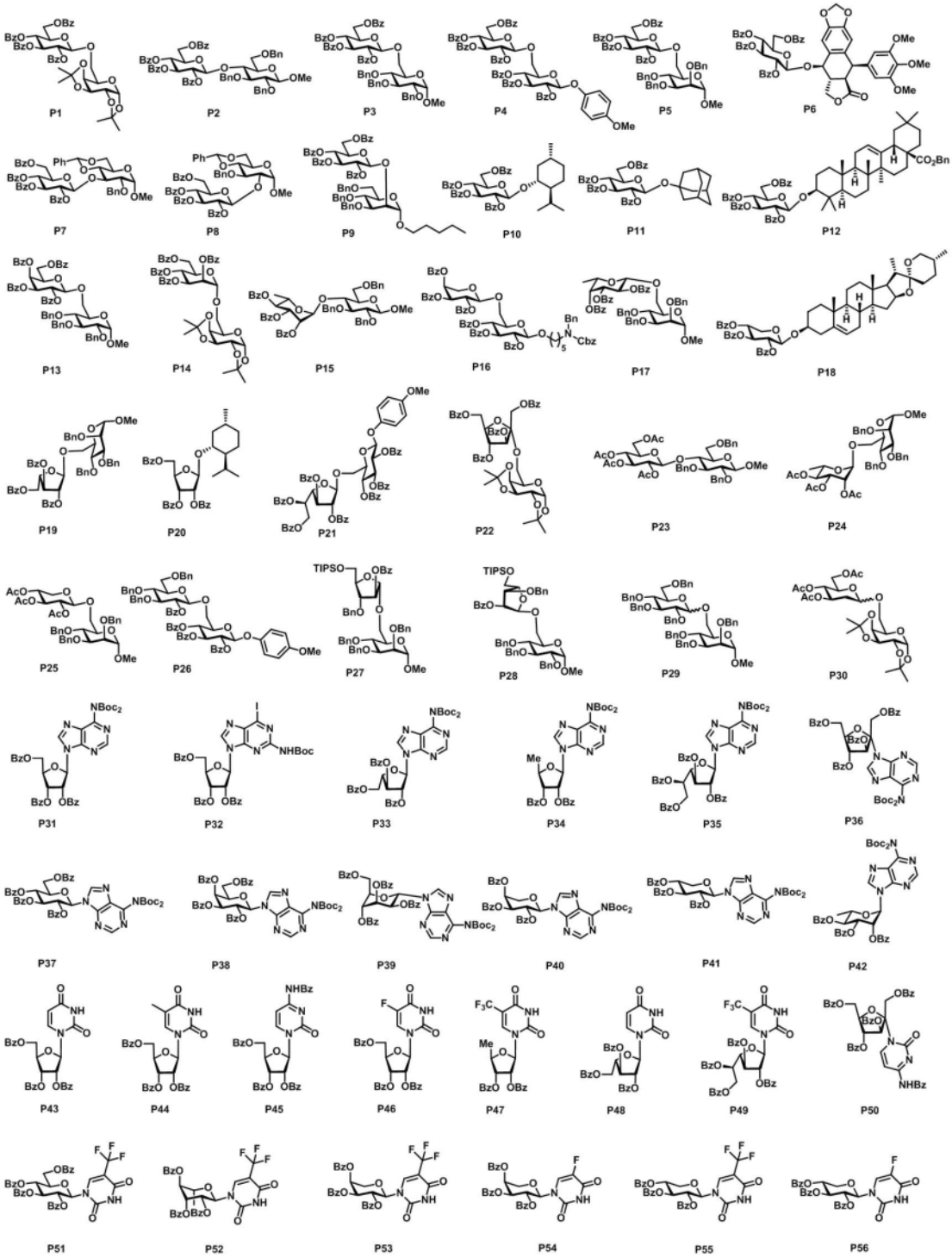
[0048] 优选的,在上述一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的应用中,所述糖苷化给体和所述糖苷化受体的摩尔比为1.2～2.5:1～2,进一步优选为1.2～1.5:1。

[0049] 优选的,在上述一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的应用中,步骤(1)中,所述糖苷化受体ROH与有机溶剂的摩尔体积比为0.01～0.1mol/L,进一步优选为0.003-0.005mol/L;所述糖苷化受体RNH与有机溶剂的摩尔体积比为0.01～0.5mol/L,进一步优选为0.05-0.1mol/L。

[0050] 优选的,在上述一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的应用中,所述惰性气体为高纯氩气或高纯氮气。

[0051] 优选的,在上述一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的应用中,所述干燥剂选自3A分子筛、4A分子筛和5A分子筛中的任意一种或者几种。

[0052] 优选的,在上述一种邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体的应用中,式P所示的糖苷化产物包括以下结构:

[0053] 

[0054] 经由上述的技术方案可知，与现有技术相比，本发明公开提供的邻-(1-苯基乙烯基)苯甲酸酯类糖苷化给体稳定，容易制备和保存，广泛用于各种氧糖苷和核苷(氮糖苷)糖苷键的构建中，给体的离去基为烯基酯类，活性更高，可以结合硫苷或正戊烯基醚类糖苷进行一锅糖苷化反应合成寡糖。本发明的糖苷化反应条件温和，对酸敏感和对亲电试剂敏感的受体均能耐受。

附图说明

[0055] 为了更清楚地说明本发明实施例或现有技术中的技术方案，下面将对实施例或现

有技术描述中所需要使用的附图作简单地介绍，显而易见地，下面描述中的附图仅仅是本发明的实施例，对于本领域普通技术人员来讲，在不付出创造性劳动的前提下，还可以根据提供的附图获得其他的附图。

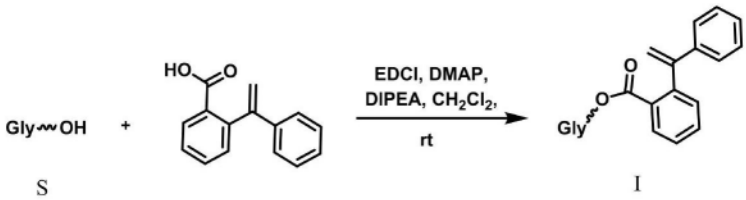
[0056] 图1附图为本发明不同条件下的糖苷化反应，其中NR表示没有反应发生；收率为分离收率；上标c表示反应温度为0℃至室温。

具体实施方式

[0057] 根据下述实施例，可以更好地理解本发明，但并不以此来限定本发明，实施例所描述的内容仅用于说明本发明。在下述说明中，一或多个实施例中的特定特征、结构、或特点可由任何合适形式组合。

[0058] 实施例1：

[0059] 本发明式I中的所有化合物按照下述路线一制备：

[0060] 

S I

[0061] 其中Gly为取代或非取代的糖基。

[0062] 具体步骤如下：将化合物S(1.0当量)和2-(1-苯基乙烯基)苯甲酸(1.1当量)溶解在无水DCM(c＝0.1M)中，加入4-二甲基氨基吡啶(DMAP)(1.0当量)、N-(3-二甲基氨基丙基)-N'-乙基碳二亚胺盐酸盐(EDCI)(1.8当量)和N,N-二异丙基乙胺(DIPEA)(3.0当量)。将混合物在室温下搅拌，直到TLC分析表明反应完成。然后，将混合物用DCM稀释，并用水和盐水洗涤。有机层经无水Na_2SO_4干燥，过滤，并真空浓缩。残余物通过硅胶柱快速纯化，得到糖苷化给体。

[0063] 1、化合物I-1：

[0064] 根据路线一，由S-1(500mg，0.84mmol)制备化合物I-1。将粗产物通过硅胶柱色谱法纯化(石油醚/乙酸乙酯＝3:1)，得到I-1(627mg，93％，α/β＝1:1.2)，为白色固体。α构型：$[\alpha]_D^{25}$＝-2.4(c 0.20,CHCl3)；^{1}H NMR(400MHz,$CDCl_3$)：δ8.02(d,J＝7.7Hz,2H),7.91-7.82(m,7H),7.59-7.20(m,20H),6.74(d,J＝3.8Hz,1H),6.04(s,1H),5.97(t,J＝10.0Hz,1H),5.65(t,J＝10.0Hz,1H),5.52(dd,J＝10.3,3.9Hz,1H),5.25(s,1H),4.29(dd,J＝12.4,3.0Hz,1H),4.11(dd,J＝12.5,3.8Hz,1H),3.73(dt,J＝10.2,3.4Hz,1H)；^{13}C NMR(101MHz,$CDCl_3$)δ166.16,166.04,165.77,165.36,165.01,148.01,142.81,139.81,133.49,133.27,133.15,132.19,131.03,130.71,130.21,129.90,129.85,129.80,129.69,129.58,128.93,128.77,128.71,128.60,128.43,128.40,128.35,128.02,127.71,127.02,114.94,90.22,70.61,70.40,70.35,68.39,62.03；HRMS(ESI)calcd for $C_{49}H_{38}O_{11}Na[M+Na]^+$825.2306,found 825.2317。

[0065] 2、化合物I-2：

[0066] 根据路线一，由S-2(100mg，0.29mmol)制备化合物I-2。将粗产物通过硅胶柱色谱法纯化(石油醚/乙酸乙酯＝3:1)，得到I-2(155mg，97％，α/β＝1:2.4)，为无色糖浆。α构型：$[\alpha]_D^{25}$＝103.6(c 0.13,CHCl3)；^{1}H NMR(400MHz,$CDCl_3$)：δ7.93(d,J＝7.9Hz,1H),7.57(td,J

＝7.5,1.4Hz,1H),7.48(td,J＝7.6,1.4Hz,1H),7.37(d,J＝7.8Hz,2H),7.34-7.24(m,4H),6.41(d,J＝3.7Hz,1H),5.94(s,1H),5.28(t,J＝9.8Hz,1H),5.20(s,1H),5.05(dd,J＝10.2,3.7Hz,1H),4.99(t,J＝9.9Hz,1H),3.96(dd,J＝12.6,3.6Hz,1H),3.74(dd,J＝12.5,2.2Hz,1H),3.41(dt,J＝10.3,2.9Hz,1H),2.05(s,3H),2.00(s,3H),1.98(s,3H),1.92(s,3H);^{13}C NMR(101MHz,$CDCl_3$)δ170.60,170.06,169.72,169.27,165.94,147.92,142.90,139.57,132.27,131.13,130.60,130.00,128.44,127.84,127.72,126.88,114.59,89.92,70.01,69.78,69.39,67.34,61.00,20.68,20.56,20.37;HRMS(ESI)calcd for $C_{29}H_{30}O_{11}Na$[M+Na]$^+$577.1680,found 577.1690。

[0067] 3、化合物I-3：

[0068] 根据路线一，由S-3(100mg,0.17mmol)制备化合物I-3。将粗产物通过硅胶柱色谱法纯化(石油醚/乙酸乙酯＝3:1)，得到I-3(123mg,91％,α/β＝1:1.3)，为白色固体。α构型：$[\alpha]_D^{25}$＝155.6(c 0.17,CHCl3);^{1}H NMR(400MHz,$CDCl_3$):δ7.95(d,J＝7.5Hz,2H),7.89(d,J＝7.4Hz,2H),7.83(d,J＝7.9Hz,1H),7.78(d,J＝7.5Hz,2H),7.71(d,J＝7.6Hz,2H),7.52(t,J＝8.0Hz,1H),7.48(t,J＝8.0Hz,2H),7.43-7.32(m,9H),7.28-7.14(m,7H),7.01(t,J＝7.4Hz,1H),6.74(d,J＝2.2Hz,1H),5.99(s,1H),5.74(d,J＝2.1Hz,2H),5.62(s,1H),5.15(s,1H),4.25(dd,J＝11.2,6.3Hz,1H),3.99(dd,J＝11.3,7.1Hz,1H),3.57(t,J＝6.7Hz,1H);^{13}C NMR(151MHz,$CDCl_3$)δ166.10,165.59,165.49,165.35,147.91,142.64,139.19,133.57,133.38,133.22,133.19,132.29,131.12,130.85,130.01,129.84,129.72,129.70,129.68,129.39,128.94,128.92,128.78,128.61,128.56,128.39,128.36,128.26,128.13,127.65,126.61,114.31,90.80,69.11,68.40,68.16,67.83,61.31;HRMS(ESI)calcd for $C_{49}H_{38}O_{11}Na$[M+Na]$^+$825.2306,found825.2305。

[0069] 4、化合物I-4：

[0070] 根据路线一，由S-4(100mg,0.17mmol)制备化合物I-4。将粗产物通过硅胶柱色谱法纯化(石油醚/乙酸乙酯＝3:1)，得到I-4(131mg,97％,α/β＝1:11.4)，为白色固体。β构型：$[\alpha]_D^{25}$＝-8.2(c 0.17,CHCl3);^{1}H NMR(400MHz,$CDCl_3$):δ8.07(d,J＝7.8Hz,2H),8.03(d,J＝7.8Hz,2H),8.00(d,J＝7.7Hz,1H),7.86(d,J＝7.8Hz,2H),7.82(d,J＝7.7Hz,2H),7.61-7.22(m,20H),6.38(s,1H),6.07(t,J＝8.2Hz,1H),6.04(s,1H),5.68(t,J＝3.6Hz,1H),5.66(s,1H),5.37(s,1H),4.43(dd,J＝12.4,2.6Hz,1H),4.22(dd,J＝12.4,3.5Hz,1H),3.89(dt,J＝10.3,3.2Hz,1H);^{13}C NMR(101MHz,$CDCl_3$)δ166.03,165.68,165.39,165.21,164.99,148.47,142.77,139.86,133.61,133.52,133.29,133.09,132.46,131.20,130.70,130.05,129.91,129.84,129.78,129.74,129.08,128.96,128.88,128.67,128.64,128.45,128.41,128.37,128.12,127.91,126.97,115.06,91.67,71.04,69.90,69.27,66.00,62.16;HRMS(ESI)calcd for $C_{49}H_{38}O_{11}Na$[M+Na]$^+$825.2306,found825.2322。

[0071] 5、化合物I-5：

[0072] 根据路线一，由S-5(100mg,0.21mmol)制备化合物I-5。将粗产物通过硅胶柱色谱法纯化(石油醚/乙酸乙酯＝3:1)，得到I-5(140mg,98％,α/β＝1:3.5)，为白色固体。β构型：$[\alpha]_D^{25}$＝52.8(c 0.16,CHCl3);^{1}H NMR(400MHz,$CDCl_3$):δ8.06(d,J＝7.3Hz,2H),8.00(d,J＝7.5Hz,1H),7.89(d,J＝7.5Hz,2H),7.80(d,J＝7.6Hz,2H),7.63-7.57(m,2H),7.54-7.38(m,10H),7.36(d,J＝5.2Hz,1H),7.33(d,J＝7.7Hz,1H),7.27-7.23(m,3H),6.27(s,1H),

6.02(s,1H),5.61-5.55(m,3H),5.36(s,1H),3.84-3.71(m,1H),1.17(d,J=6.2Hz,3H);^{13}C NMR(101MHz,$CDCl_3$)δ165.70,165.59,165.37,165.17,148.61,142.87,139.93,133.57,133.40,133.17,132.33,131.23,130.61,130.18,129.96,129.78,129.68,129.15,129.09,128.61,128.54,128.39,128.32,127.98,127.83,126.92,114.84,91.63,71.03,69.79,69.56,69.19,17.47;HRMS(ESI)calcd for $C_{42}H_{34}O_9Na[M+Na]^+$705.2095,found 705.2112。

[0073] 6、化合物I-6：

[0074] 根据路线一，由S-6(500mg,0.84mmol)制备化合物I-6。将粗产物通过硅胶柱色谱法纯化(石油醚/乙酸乙酯=3:1)，得到I-6(627mg,93%,α/β=1:1.2)，为白色固体。α构型：$[\alpha]_D^{25}$=-2.4(c 0.20,CHCl3);^{1}H NMR(400MHz,$CDCl_3$):δ8.02(d,J=7.7Hz,2H),7.91-7.82(m,7H),7.59-7.20(m,20H),6.74(d,J=3.8Hz,1H),6.04(s,1H),5.97(t,J=10.0Hz,1H),5.65(t,J=10.0Hz,1H),5.52(dd,J=10.3,3.9Hz,1H),5.25(s,1H),4.29(dd,J=12.4,3.0Hz,1H),4.11(dd,J=12.5,3.8Hz,1H),3.73(dt,J=10.2,3.4Hz,1H);^{13}C NMR(101MHz,$CDCl_3$)δ166.16,166.04,165.77,165.36,165.01,148.01,142.81,139.81,133.49,133.27,133.15,132.19,131.03,130.71,130.21,129.90,129.85,129.80,129.69,129.58,128.93,128.77,128.71,128.60,128.43,128.40,128.35,128.02,127.71,127.02,114.94,90.22,70.61,70.40,70.35,68.39,62.03;HRMS(ESI)calcd for $C_{49}H_{38}O_{11}Na[M+Na]^+$825.2306,found 825.2317。

[0075] 7、化合物I-7：

[0076] 根据路线一，由S-7(75mg,0.16mmol)制备化合物I-7。将粗产物通过硅胶柱色谱法纯化(石油醚/乙酸乙酯=5:1)，得到I-7(108mg,93%,α/β=1:2)，为白色固体。α和β混合构型：^{1}H NMR(400MHz,$CDCl_3$):δ7.87(d,J=7.8Hz,7H),7.83(dd,J=8.0,3.4Hz,6H),7.78(dd,J=7.8,3.6Hz,5H),7.50-7.02(m,54H),6.53(d,J=3.7Hz,1H),5.99(d,J=3.9Hz,1H),5.89(t,J=9.8Hz,1H),5.87(s,1H),5.61(t,J=5.6Hz,2H),5.57(s,2H),5.36(d,J=4.0Hz,1H),5.23-5.19(m,3H),5.14-5.12(m,2H),5.07(s,2H),4.21(dd,J=12.8,3.5Hz,2H),3.85(dd,J=11.2,5.7Hz,1H),3.74(dd,J=12.8,4.8Hz,2H),3.25(t,J=10.9Hz,1H);^{13}C NMR(101MHz,$CDCl_3$)δ166.09,165.77,165.52,165.43,165.41,164.93,164.86,164.85,148.94,148.25,143.51,143.04,140.40,139.86,133.52,133.49,133.45,133.33,132.30,132.18,131.56,131.20,130.59,130.15,130.11,130.02,129.95,129.93,129.84,129.78,129.71,129.68,129.14,129.12,129.07,128.95,128.93,128.91,128.78,128.75,128.43,128.26,128.21,127.86,127.76,127.70,126.97,126.75,114.79,114.65,91.99,90.40,70.48,69.88,69.46,68.28,68.12,67.84,61.48,61.01;HRMS(ESI)calcd for $C_{41}H_{32}O_9Na[M+Na]^+$691.1939,found691.1938。

[0077] 8、化合物I-8：

[0078] 根据路线一，由S-8(90mg,0.22mmol)制备化合物I-8。将粗产物通过硅胶柱色谱法纯化(石油醚/乙酸乙酯=3:1)，得到I-8(154mg,98%,α/β=1:2.1)，为无色糖浆。β构型：$[\alpha]_D^{25}$=-104.0(c 0.10,CHCl3);^{1}H NMR(400MHz,$CDCl_3$):δ7.91(d,J=7.7Hz,1H),7.56(t,J=7.2Hz,1H),7.43(t,J=7.5Hz,1H),7.34(d,J=7.5Hz,1H),7.31-7.20(m,5H),5.73(s,1H),5.72(d,J=5.9Hz,1H),5.18(s,1H),5.16(t,J=8.0Hz,1H),5.05-5.00(m,1H),4.91(td,J=7.7,5.0Hz,1H),4.00(dd,J=12.2,4.8Hz,1H),3.45(dd,J=12.2,7.7Hz,1H),2.05

(s,3H),2.03(s,3H),1.95(s,3H);^{13}C NMR(101MHz,$CDCl_3$)δ169.85,169.73,169.20,164.57,148.96,143.84,140.35,132.57,131.63,130.38,128.84,128.21,127.71,127.63,126.57,114.26,92.42,70.70,69.23,68.36,62.65,20.75,20.69,20.54;HRMS(ESI)calcd for $C_{26}H_{26}O_9Na[M+Na]^+$505.1469,found 505.1473。

[0079] 9、化合物I-9：

[0080] 根据路线一，由S-9(70mg,0.15mmol)制备化合物I-9。将粗产物通过硅胶柱色谱法纯化(石油醚/乙酸乙酯＝5:1)，得到I-9(97mg,96％,α/β＝1:4.6)，为白色固体。α构型：$[\alpha]_D^{25}$＝380.8(c 0.11,CHCl3);^{1}H NMR(400MHz,$CDCl_3$):δ8.06(d,J＝7.7Hz,2H),7.92(d,J＝7.8Hz,1H),7.85(t,J＝8.2Hz,3H),7.63-7.55(m,2H),7.53-7.41(m,7H),7.38-7.24(m,9H),6.68(d,J＝3.5Hz,1H),6.00(s,1H),5.85(dd,J＝10.7,3.6Hz,1H),5.77(dd,J＝10.7,3.4Hz,1H),5.46(d,J＝3.3Hz,1H),5.24(s,1H),3.73(d,J＝12.6Hz,1H),3.43(d,J＝13.3Hz,1H);^{13}C NMR(151MHz,$CDCl_3$)δ166.02,165.66,165.55,165.47,148.18,142.82,139.49,133.46,133.36,133.26,132.28,131.29,130.71,130.01,129.82,129.72,129.68,129.35,129.02,128.89,128.55,128.50,128.37,128.32,128.04,127.66,126.71,114.24,91.25,69.51,67.89,62.77;HRMS(ESI)calcd for $C_{41}H_{32}O_9Na[M+Na]^+$691.1939,found 691.1951。

[0081] 10、化合物I-10：

[0082] 根据路线一，由S-10(100mg,0.20mmol)制备化合物I-10。将粗产物通过硅胶柱色谱法纯化(石油醚/乙酸乙酯＝5:1)，得到I-10(128mg,91％,α/β＝1:3.3)，为白色固体。β构型：$[\alpha]_D^{25}$＝-271.3(c 0.12,CHCl3);^{1}H NMR(400MHz,$CDCl_3$):δ7.98(d,J＝7.3Hz,2H),7.84(dd,J＝7.9,1.4Hz,1H),7.78(d,J＝7.4Hz,2H),7.71(d,J＝7.4Hz,2H),7.55-7.47(m,2H),7.44-7.33(m,7H),7.31-7.23(m,5H),7.21-7.15(m,3H),6.63(d,J＝1.9Hz,1H),5.99(s,1H),5.73-5.67(m,2H),5.34-5.28(m,1H),5.16(s,1H),3.38(q,J＝6.5Hz,1H),0.87(d,J＝6.4Hz,3H);^{13}C NMR(101MHz,$CDCl_3$)δ165.13,164.83,164.56,164.48,147.03,141.65,138.36,132.45,132.29,132.14,131.22,130.19,129.82,129.18,128.84,128.68,128.64,128.18,128.08,127.94,127.57,127.49,127.33,127.25,127.04,126.64,125.66,113.09,90.03,70.34,67.66,66.78,66.58,15.01;HRMS(ESI)calcd for $C_{42}H_{34}O_9Na[M+Na]^+$705.2095,found 705.2105。

[0083] 11、化合物I-11：

[0084] 根据路线一，由S-11(431mg,0.93mmol)制备化合物I-11。将粗产物通过硅胶柱色谱法纯化(石油醚/乙酸乙酯＝5:1)，得到I-11(560mg,91％,α/β＝2.2:1)，为白色固体。α构型：$[\alpha]_D^{25}$＝2.5(c 0.16,CHCl3);^{1}H NMR(400MHz,$CDCl_3$):δ8.00(d,J＝7.8Hz,7H),7.94(d,J＝7.6Hz,2H),7.67-7.51(m,J＝7.2Hz,4H),7.51-7.37(m,9H),7.30-7.23(m,5H),7.15(dd,J＝5.2,2.1Hz,4H),6.36(s,1H),5.75(s,1H),5.53(d,J＝7.1Hz,2H),5.25(s,1H),4.67(dd,J＝12.0,4.0Hz,1H),4.59(dd,J＝12.0,5.0Hz,1H),4.41(t,J＝4.5Hz,1H);^{13}C NMR(101MHz,$CDCl_3$)δ166.12,165.64,165.45,164.99,148.85,143.15,140.26,133.70,133.68,133.10,132.21,131.44,130.20,130.11,129.95,129.75,129.56,128.99,128.73,128.61,128.54,128.50,128.30,128.23,127.73,127.63,126.70,114.60,100.01,83.10,80.99,77.42,63.45;HRMS(ESI)calcd for $C_{41}H_{32}O_9Na[M+Na]^+$691.1939,found 691.1938。

[0085] 12、化合物I-12：

[0086] 根据路线一，由S-12(402mg,0.87mmol)制备化合物I-12。将粗产物通过硅胶柱色谱法纯化(石油醚/乙酸乙酯＝5:1)，得到I-12(560mg,96％,α/β＝1:10)，为糖浆。β构型：$[\alpha]_D^{25}$＝26.7(c 0.14,CHCl3)；^{1}H NMR(400MHz,$CDCl_3$)δ7.91(ddd,J＝35.5,20.8,7.8Hz,9H),7.64-7.17(m,23H),6.30(s,1H),5.89(s,1H),5.62(dd,J＝7.3,4.8Hz,1H),5.52(d,J＝4.8Hz,1H),5.24(s,1H),4.71-4.63(m,1H),4.47-4.30(m,2H)；^{13}C NMR(101MHz,$CDCl_3$)δ166.02,165.77,165.12,164.81,148.86,142.99,139.88,133.61,133.47,133.08,132.37,131.45,130.46,129.84,129.74,129.67,129.47,128.92,128.74,128.53,128.46,128.39,128.26,127.94,127.80,126.59,114.35,99.09,79.64,74.73,71.54,64.23;HRMS(ESI)calcd for$C_{41}H_{32}O_9Na[M+Na]^+$691.1939,found 691.1933。

[0087] 13、化合物I-13：

[0088] 根据路线一，由S-13(184mg,0.53mmol)制备化合物I-13。将粗产物通过硅胶柱色谱法纯化(石油醚/乙酸乙酯＝3:1)，得到I-13(275mg,95％,α/β＝1:4)，为无色糖浆。β构型：$[\alpha]_D^{25}$＝1.19(c 0.24,$CHCl_3$)；^{1}H NMR(400MHz,$CDCl_3$)δ7.96(d,J＝7.7Hz,3H),7.86(d,J＝7.7Hz,2H),7.62-7.20(m,14H),6.26(s,1H),5.90(s,1H),5.46(d,J＝4.8Hz,1H),5.26(d,J＝3.3Hz,2H),4.44(t,J＝6.4Hz,1H),1.28(d,J＝6.5Hz,3H)；^{13}C NMR(100MHz,$CDCl_3$)δ166.07,165.34,164.90,148.89,142.98,139.96,133.49,133.35,132.27,131.41,130.49,129.99,129.82,129.70,129.08,128.48,128.42,128.37,127.87,127.71,126.65,114.21,99.23,78.86,75.75,75.33,19.72;HRMS(ESI)calcd for $C_{34}H_{28}O_7Na[M+Na]^+$571.1727,found 571.1727。

[0089] 14、化合物I-14：

[0090] 根据路线一，由S-14(100mg,0.17mmol)制备化合物I-14。将粗产物通过硅胶柱色谱法纯化(石油醚/乙酸乙酯＝4:1)，得到I-14(108mg,80％,α/β＝1:4.6)，为白色固体。β构型：$[\alpha]_D^{25}$＝-24.4(c 0.10,CHCl3)；^{1}H NMR(400MHz,$CDCl_3$)δ7.92(d,J＝7.8Hz,2H),7.88(d,J＝5.7Hz,1H),7.85(d,J＝7.4Hz,2H),7.78(d,J＝7.8Hz,2H),7.52(d,J＝7.7Hz,1H),7.48(d,J＝7.9Hz,1H),7.45-7.14(m,16H),7.09-7.06(m,2H),6.34(s,1H),5.91(dt,J＝7.4,3.8Hz,1H),5.67(s,1H),5.53(d,J＝4.9Hz,1H),5.42(s,1H),5.16(s,1H),4.59(dd,J＝12.1,4.0Hz,1H),4.53(dd,J＝12.0,7.2Hz,1H),4.38(t,J＝4.3Hz,1H)；^{13}C NMR(101MHz,$CDCl_3$)δ166.07,165.66,165.57,165.39,165.01,148.82,143.15,140.17,133.65,133.49,133.26,133.07,132.25,131.42,130.26,130.05,130.03,129.97,129.95,129.86,129.73,129.54,129.31,128.91,128.56,128.47,128.44,128.39,128.36,128.34,128.28,127.83,127.65,126.68,114.58,99.92,83.62,81.03,69.98,63.67;HRMS(ESI)calcd for$C_{49}H_{38}O_{11}Na[M+Na]^+$825.2306,found 825.2316。

[0091] 15、化合物I-15：

[0092] 根据路线一，由S-15(100mg,0.17mmol)制备化合物I-15。将粗产物通过硅胶柱色谱法纯化(石油醚/乙酸乙酯＝4:1)，得到I-15(115mg,85％,α/β＝1:1)，为白色固体。α和β混合构型：^{1}H NMR(400MHz,$CDCl_3$)δ7.92-7.78(m,17H),7.73(d,J＝7.7Hz,1H),7.50-6.92(m,40H),6.19-6.10(m,2H),6.05(d,J＝2.1Hz,1H),5.55(d,J＝3.5Hz,2H),5.49(d,J＝5.1Hz,1H),5.13(s,1H),4.98(s,1H),4.91(d,J＝12.0Hz,1H),4.64(d,J＝12.1Hz,1H),

4.58-4.38(m,7H),4.03(q,J＝4.3Hz,1H);^{13}C NMR(101MHz,$CDCl_3$)δ166.09,166.06,165.45,165.41,165.32,165.20,164.88,164.73,164.36,149.12,148.89,143.47,143.38,140.70,140.19,133.69,133.64,133.57,133.23,133.20,133.07,133.03,132.32,132.28,131.71,131.67,130.44,130.38,130.27,130.05,130.02,129.95,129.90,129.87,129.75,129.72,129.66,129.52,129.50,129.37,128.98,128.90,128.75,128.69,128.62,128.57,128.50,128.47,128.42,128.39,128.31,128.27,128.18,127.79,127.65,127.56,126.81,126.59,114.78,114.43,109.49,105.48,82.58,80.17,79.95,77.62,77.51,65.05,64.90,63.37,61.96;HRMS(ESI)calcd for $C_{49}H_{38}O_{11}Na[M+Na]^+$825.2306,found 825.2314。

[0093] 16、化合物I-16:

[0094] 根据路线一,由S-16(295mg,0.53mmol)制备化合物I-16。将粗产物通过硅胶柱色谱法纯化(石油醚/乙酸乙酯＝5:1),得到I-16(367mg,91%,α/β＝1:10.6),为白色固体。β构型:$[\alpha]_D^{25}$＝29.6(c 0.11,CHCl3);^{1}H NMR(400MHz,$CDCl_3$)δ7.90(d,J＝7.8Hz,3H),7.54(t,J＝7.5Hz,1H),7.47(t,J＝7.5Hz,1H),7.43-7.06(m,24H),5.77(d,J＝8.2Hz,1H),5.57(s,1H),5.45(t,J＝8.6Hz,1H),5.00(s,1H),4.80(d,J＝10.7Hz,1H),4.73(d,J＝11.1Hz,1H),4.64(d,J＝11.0Hz,1H),4.62-4.54(m,2H),4.47(d,J＝12.1Hz,1H),3.89(t,J＝9.2Hz,1H),3.82(t,J＝8.9Hz,1H),3.75(dd,J＝11.1,3.6Hz,1H),3.68(d,J＝11.8Hz,1H),3.63-3.57(m,1H);^{13}C NMR(101MHz,$CDCl_3$)δ165.12,164.75,149.01,143.91,140.33,138.04,137.94,137.69,133.25,132.39,131.39,130.75,129.86,129.55,128.88,128.49,128.44,128.35,128.33,128.15,128.07,128.03,127.96,127.92,127.81,127.76,127.73,127.70,127.45,126.52,114.02,92.60,82.68,76.03,75.18,75.11,73.64,72.59,68.12;HRMS(ESI)calcd for $C_{49}H_{44}O_8Na[M+Na]^+$783.2928,found 783.2944。

[0095] 17、化合物I-17:

[0096] 根据路线一,由S-17(100mg,0.20mmol)制备化合物I-17。将粗产物通过硅胶柱色谱法纯化(石油醚/乙酸乙酯＝5:1),得到I-17(128mg,91%,α/β＝1:3.3),为白色固体。β构型:$[\alpha]_D^{25}$＝21.3(c 0.16,$CHCl_3$);^{1}H NMR(400MHz,$CDCl_3$)δ7.91(d,J＝7.8Hz,2H),7.83(d,J＝7.7Hz,1H),7.49(t,J＝7.5Hz,1H),7.43(t,J＝7.5Hz,1H),7.35(t,J＝7.7Hz,2H),7.30-7.17(m,9H),7.15-7.08(m,3H),6.12(s,1H),5.64(s,1H),5.30(s,1H),5.15(s,1H),4.69(d,J＝11.9Hz,1H),4.51(d,J＝11.9Hz,1H),4.14(q,J＝4.8Hz,1H),4.08(d,J＝4.4Hz,1H),3.74(dd,J＝10.7,4.3Hz,1H),3.65(dd,J＝10.7,5.6Hz,1H),0.89(s,21H);^{13}C NMR(101MHz,$CDCl_3$)δ166.04,165.21,149.10,143.24,140.54,137.90,133.69,133.57,132.04,131.37,130.55,130.40,129.89,129.35,128.52,128.41,128.25,127.88,127.77,127.68,127.64,126.91,114.51,100.71,86.13,82.73,81.18,72.19,62.56,18.00,17.99,11.96;HRMS(ESI)calcd for $C_{43}H_{50}O_7Si$ Na$[M+Na]^+$729.3218,found729.3191。

[0097] 18、化合物I-18的:

[0098] 根据路线一,由S-18(125mg,0.25mmol)制备化合物I-18。将粗产物通过硅胶柱色谱法纯化(石油醚/乙酸乙酯＝20:1),得到I-18(156mg,88%,α/β＝2.2:1),为白色粉末。α构型:$[\alpha]_D^{25}$＝-55.8(c 0.10,$CHCl_3$);^{1}H NMR(400MHz,$CDCl_3$)δ7.91(d,J＝7.5Hz,2H),7.83(d,J＝7.6Hz,1H),7.49(t,J＝7.3Hz,1H),7.43(t,J＝7.4Hz,1H),7.35(t,J＝7.6Hz,2H),7.29-7.08(m,12H),6.12(s,1H),5.64(s,1H),5.29(s,1H),5.15(s,1H),4.69(d,J＝

11.9Hz,1H),4.51(d,J=11.9Hz,1H),4.17-4.11(m,1H),4.08(d,J=4.0Hz,1H),3.74(dd,J=10.7,4.1Hz,1H),3.69-3.62(m,1H),0.89(s,21H);^{13}C NMR(151MHz,$CDCl_3$)δ166.04,165.21,149.10,143.24,140.54,137.90,133.57,132.04,131.37,130.55,130.39,129.89,129.34,128.52,128.41,128.25,127.88,127.77,127.68,127.64,126.91,114.51,100.70,86.13,82.71,81.17,72.18,62.54,17.99,17.98,11.95;HRMS(ESI)calcd for $C_{43}H_{50}O_7SiNa$[M+Na]$^+$729.3218,found 729.3216。

[0099] 19、化合物I-19：

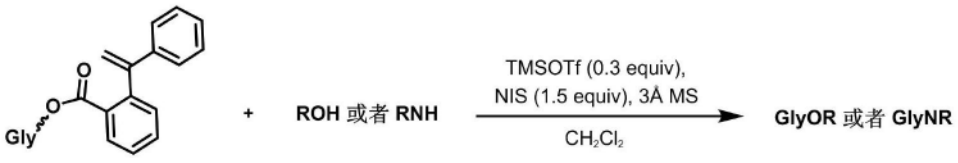
[0100] 根据路线一,由S-19(100mg,0.18mmol)制备化合物I-19。将粗产物通过硅胶柱色谱法纯化(石油醚/乙酸乙酯=3:1),得到I-19(127mg,92%,α/β=1:4),为白色粉末。α和β混合构型:^{1}H NMR(400MHz,$CDCl_3$)δ7.87(d,J=7.8Hz,4H),7.82(d,J=7.7Hz,1H),7.47-7.37(m,6H),7.31(t,J=7.6Hz,6H),7.23-7.06(m,128H),6.32(d,J=3.4Hz,1H),5.61(s,5H),5.55(d,J=7.9Hz,4H),5.08(d,J=7.8Hz,4H),4.75(d,J=10.9Hz,4H),4.73-4.67(m,10H),4.55-4.31(m,27H),3.71-3.33(m,30H);^{13}C NMR(151MHz,$CDCl_3$)δ166.11,164.95,149.08,148.50,143.94,143.11,140.53,140.31,138.80,138.48,138.44,138.17,138.15,138.06,137.96,137.90,132.36,131.86,131.66,131.18,130.82,130.63,130.44,129.49,128.47,128.44,128.43,128.38,128.34,128.27,128.04,127.99,127.94,127.85,127.82,127.76,127.75,127.70,127.64,127.61,127.05,126.63,114.76,114.29,94.60,90.77,84.88,81.65,80.97,78.93,75.72,75.66,75.56,75.07,75.00,74.82,73.60,73.58,73.11,72.86,68.27,68.04;HRMS(ESI)calcd for $C_{49}H_{46}O_7Na$[M+Na]$^+$769.3136,found 769.3142。

[0101] 20、化合物I-20：

[0102] 根据路线一,由S-20(115mg,0.40mmol)制备化合物I-20。将粗产物通过硅胶柱色谱法纯化(石油醚/乙酸乙酯=5:1),得到I-20(156mg,79%,α/β=1:4),为无色糖浆。β构型:$[\alpha]_D^{25}$=-10.7(c 0.16,$CHCl_3$);^{1}H NMR(400MHz,$CDCl_3$)δ7.89(d,J=7.7Hz,1H),7.59-7.52(m,1H),7.43(t,J=7.6Hz,1H),7.37(d,J=7.6Hz,1H),7.25(q,J=4.9Hz,5H),5.73(s,1H),5.64(dd,J=9.9,2.3Hz,1H),5.23(s,1H),4.99-4.93(m,2H),4.26(dd,J=12.3,4.7Hz,1H),4.03(dd,J=12.3,2.3Hz,1H),3.65(td,J=4.7,2.3Hz,1H),2.12-2.08(m,1H),2.06(s,3H),2.02(s,6H),1.70-1.65(m,1H);^{13}C NMR(101MHz,$CDCl_3$)δ170.70,170.01,169.76,164.98,149.01,143.22,140.38,132.33,131.48,130.23,129.50,128.19,127.64,126.67,114.43,91.67,72.72,70.12,68.31,62.02,34.29,20.86,20.77,20.71;HRMS(ESI)calcd for $C_{27}H_{28}O_9Na$[M+Na]$^+$519.1625,found 519.1626。

[0103] 实施例2：

[0104] 本发明式P中的部分化合物按照下述路线二制备：

[0105] 

I II P

[0106] 其中,ROH为任意的含有羟基的化合物,RNH为含有肿胺的嘌呤类化合物。

[0107] 具体步骤如下:室温下,将式I糖苷化给体(1.2当量)和式II受体(1.0当量)溶解到无水DCM(c=0.033M)中,在惰性气体环境下,加入干燥的3ÅMS(3.0g/mmol)于室温搅拌30分钟。然后将反应冷却至0℃(ROH为受体)或者-20℃(嘌呤类化合物RNH为受体),向其中加入NIS(1.5当量)和TMSOTf(0.3当量)。逐渐升至室温后,将反应混合物搅拌1.5-3小时。然后添加Et_3N淬灭反应,DCM稀释,过滤,并在减压蒸馏下除去溶剂。所得残余物通过硅胶柱色谱法纯化,得到式P糖基化产物。

[0108] 糖苷化产物P1:

[0109] 根据路线二,将I-1(65.9mg,0.08mmol)与II-1(17.8mg,0.07mmol)进行糖苷化反应,得到P1(53.5mg,94%),为白色固体:$[\alpha]_D^{25}$=-41.4(c 0.15,CHCl3);^{1}H NMR(400MHz,$CDCl_3$):δ8.03(d,J=7.6Hz,2H),7.97(d,J=7.6Hz,2H),7.90(d,J=7.6Hz,2H),7.83(d,J=7.6Hz,2H),7.56-7.45(m,3H),7.25-7.41(m,9H),5.92(t,J=9.5Hz,1H),5.70(d,J=9.6Hz,1H),5.55(t,J=8.6Hz,1H),5.43(d,J=4.7Hz,1H),5.06(d,J=7.7Hz,1H),4.65(d,J=10.3Hz,1H),4.50(dd,J=12.0,5.0Hz,1H),4.43(d,J=7.5Hz,1H),4.26-4.15(m,2H),4.10(d,J=7.8Hz,1H),4.07-3.98(m,1H),3.93-3.83(m,2H),1.37(s,3H),1.24(s,3H),1.20(s,6H);^{13}C NMR(101MHz,$CDCl_3$)δ166.18,165.82,165.22,165.18,133.43,133.21,133.09,130.03,129.84,129.78,129.65,129.38,128.87,128.84,128.41,128.37,128.29,128.22,109.28,108.50,101.25,96.18,73.05,72.19,71.84,71.01,70.55,70.36,69.84,68.31,67.57,63.27,25.91,25.70,24.88,24.27;HRMS(ESI)calcd for $C_{46}H_{46}O_{15}Na[M+Na]^+$ 861.2729,found 861.2733。

[0110] 糖苷化产物P2:

[0111] 根据路线二,将I-1(62.0mg,0.08mmol)与II-2(29.9mg,0.06mmol)进行糖苷化反应,得到P2(66.4mg,99%),为白色固体:$[\alpha]_D^{25}$=-10.9(c 0.20,CHCl3);^{1}HNMR(400MHz,$CDCl_3$):δ7.96(d,J=7.8Hz,2H),7.90(d,J=7.8Hz,2H),7.86(d,J=7.7Hz,2H),7.80(d,J=7.8Hz,2H),7.54-7.16(m,27H),5.68(t,J=9.6Hz,1H),5.57(t,J=9.6Hz,1H),5.48(t,J=8.9Hz,1H),5.06(d,J=11.2Hz,1H),4.94(d,J=8.1Hz,1H),4.82(d,J=7.5Hz,1H),4.79(d,J=7.7Hz,1H),4.72(d,J=12.1Hz,1H),4.65(d,J=11.1Hz,1H),4.42-4.37(m,2H),4.24(dd,J=12.1,5.0Hz,1H),4.20(d,J=7.8Hz,1H),4.04(t,J=9.3Hz,1H),3.73-3.66(m,2H),3.64-3.56(m,2H),3.49(s,3H),3.37(t,J=8.4Hz,1H),3.23(d,J=9.7Hz,1H);^{13}C NMR(101MHz,$CDCl_3$)δ166.04,165.76,165.11,164.89,139.02,138.55,138.15,133.40,133.21,133.01,129.77,129.72,129.62,129.08,128.89,128.86,128.73,128.52,128.41,128.30,128.24,128.14,128.12,128.09,127.96,127.51,127.43,127.23,104.57,100.38,82.48,81.74,75.23,74.78,74.30,73.54,73.15,72.31,71.96,69.76,67.83,63.06,57.07;HRMS(ESI)calcdfor $C_{62}H_{58}O_{15}Na[M+Na]^+$1065.3668,found 1065.3673。

[0112] 糖苷化产物P3:

[0113] 根据路线二,将I-1(62.0mg,0.08mmol)与II-3(29.9mg,0.06mmol)进行糖苷化反应,得到P3(65.1mg,97%),为白色固体:$[\alpha]_D^{25}$=6.5(c 0.10,CHCl3);^{1}H NMR(400MHz,$CDCl_3$):δ7.91(d,J=7.8Hz,2H),7.81(d,J=7.8Hz,4H),7.74(d,J=7.8Hz,2H),7.45-7.38(m,2H),7.31-7.12(m,23H),7.01-6.94(m,2H),5.81(t,J=9.6Hz,1H),5.60(t,J=9.7Hz,1H),5.52(t,J=8.7Hz,1H),4.81(d,J=10.9Hz,1H),4.74(d,J=7.8Hz,1H),4.65(d,J=

12.1Hz,1H),4.60(d,J=10.9Hz,1H),4.55-4.50(m,2H),4.47-4.40(m,3H),4.20(d,J=11.1Hz,1H),4.07(d,J=9.8Hz,1H),4.02(dd,J=9.7,4.8Hz,1H),3.80(t,J=9.3Hz,1H),3.70-3.61(m,2H),3.35(dd,J=9.7,3.6Hz,1H),3.30(t,J=9.3Hz,1H),3.13(s,3H);^{13}C NMR(101MHz,$CDCl_3$)δ165.07,164.81,164.12,163.89,137.74,137.14,137.09,132.40,132.22,132.11,132.07,128.76,128.70,128.67,128.50,128.11,127.73,127.68,127.39,127.36,127.31,127.29,127.26,127.23,127.07,126.85,126.83,126.56,126.42,100.29,96.90,80.84,78.72,74.50,73.66,72.33,71.82,71.15,70.77,68.74,68.43,67.27,62.21,53.97;HRMS(ESI)calcd for$C_{62}H_{58}O_{15}Na[M+Na]^+$1065.3668,found 1065.3667。

[0114] 糖苷化产物P4:

[0115] 根据路线二,将I-1(56.3mg,0.07mmol)与II-4(35.0mg,0.06mmol)进行糖苷化反应,得到P4(65.4mg,95%),为白色固体:$[\alpha]_D^{25}$=-2.27(c 0.11,CHCl3);^{1}HNMR(400MHz,$CDCl_3$):δ8.04(d,J=7.7Hz,2H),7.95(d,J=7.8Hz,2H),7.90(d,J=7.7Hz,2H),7.87-7.80(m,8H),7.57-7.24(m,21H),6.96(d,J=8.8Hz,2H),6.86(d,J=8.8Hz,2H),5.87(d,J=12.0Hz,1H),5.84(d,J=12.0Hz,1H),5.72-5.60(m,2H),5.51(dd,J=9.7,7.8Hz,1H),5.40(t,J=9.7Hz,1H),5.19(d,J=7.8Hz,1H),5.06(d,J=7.9Hz,1H),4.59(dd,J=12.2,3.0Hz,1H),4.42(dd,J=12.2,5.1Hz,1H),4.18-4.11(m,1H),4.08-3.95(m,3H),3.76(s,3H);^{13}C NMR(101MHz,$CDCl_3$)δ166.09,165.73,165.69,165.39,165.20,165.18,165.08,155.94,150.95,133.57,133.48,133.32,133.27,133.21,129.86,129.81,129.76,129.55,129.24,129.19,128.82,128.80,128.77,128.63,128.48,128.42,128.36,128.32,118.94,114.76,100.75,100.64,74.84,72.96,72.74,72.32,71.97,71.84,69.61,69.50,67.86,62.88,55.67;HRMS(ESI)calcd for $C_{68}H_{56}O_{19}Na[M+Na]^+$1199.3308,found 1199.3307。

[0116] 糖苷化产物P5:

[0117] 根据路线二,将I-1(62.0mg,0.08mmol)与II-5(29.9mg,0.06mmol)进行糖苷化反应,得到P5(63.8mg,95%),为白色固体:$[\alpha]_D^{25}$=4.61(c 0.18,CHCl3);^{1}H NMR(400MHz,$CDCl_3$):δ8.07(d,J=7.7Hz,2H),7.95(d,J=7.8Hz,4H),7.88(d,J=7.7Hz,2H),7.56-7.25(m,27H),5.97(t,J=9.7Hz,1H),5.75(t,J=9.7Hz,1H),5.65(dd,J=9.8,7.8Hz,1H),5.03(d,J=7.8Hz,1H),4.79(d,J=11.1Hz,1H),4.72(s,2H),4.68(dd,J=12.1,3.2Hz,1H),4.63-4.54(m,4H),4.48(d,J=11.1Hz,1H),4.27(d,J=9.7Hz,1H),4.24-4.16(m,1H),3.87-3.69(m,5H),3.03(s,3H);^{13}C NMR(101MHz,$CDCl_3$)δ166.19,165.91,165.19,165.05,138.43,138.35,138.28,133.44,133.25,133.11,133.04,129.84,129.78,129.61,129.48,128.86,128.83,128.43,128.37,128.33,128.31,128.27,127.90,127.75,127.68,127.64,127.56,127.54,101.76,98.66,80.24,75.04,74.92,74.30,73.03,72.67,72.13,72.04,71.98,71.36,69.83,69.62,63.21,54.33;HRMS(ESI)calcd for $C_{62}H_{58}O_{15}Na[M+Na]^+$1065.3668,found 1065.3679。

[0118] 糖苷化产物P6:

[0119] 根据路线二,将I-1(70.1mg,0.08mmol)与II-6(25.0mg,0.07mmol)进行糖苷化反应,得到P6(62.4mg,98%),为白色固体:$[\alpha]_D^{25}$=-40.2(c 0.10,CHCl3);^{1}HNMR(400MHz,$CDCl_3$):δ7.88(t,J=8.4Hz,4H),7.77(d,J=7.7Hz,2H),7.72(d,J=7.7Hz,2H),7.44-7.39(m,3H),7.39-7.34(m,2H),7.32-7.20(m,9H),7.19-7.14(m,6H),7.05-6.99(m,2H),5.80

(t,J＝9.6Hz,1H),5.66-5.54(m,2H),5.48(s,1H),5.17(d,J＝7.9Hz,1H),4.51(d,J＝12.5Hz,1H),4.41(dd,J＝11.9,2.8Hz,1H),4.25-4.16(m,3H),4.16-4.07(m,2H),3.92-3.84(m,1H),3.67(dd,J＝9.6,4.0Hz,1H),3.63-3.56(m,1H),3.53(t,J＝9.2Hz,1H),3.35(dd,J＝9.1,3.5Hz,1H),3.18(s,3H);^{13}C NMR(151MHz,$CDCl_3$)δ166.23,165.97,165.41,165.30,138.20,137.36,133.46,133.33,133.30,133.07,129.96,129.92,129.84,129.73,129.44,129.10,128.99,128.95,128.54,128.51,128.48,128.40,128.36,128.29,128.05,127.95,126.17,101.46,101.24,99.02,79.85,79.56,77.86,74.21,73.38,72.43,71.99,69.95,69.06,63.32,62.37,55.37;HRMS(ESI)calcdfor $C_{55}H_{50}O_{15}Na[M+Na]^+$973.3042,found 973.3030。

[0120] 糖苷化产物P7：

[0121] 根据路线二,将I-1(50.0mg,0.06mmol)与II-7(19.3mg,0.05mmol)进行糖苷化反应,得到P7(46.2mg,94％),为白色固体:$[\alpha]_D^{25}$＝-7.2(c 0.11,CHCl3);^{1}HNMR(400MHz,$CDCl_3$):δ7.97(d,J＝7.7Hz,2H),7.85(d,J＝7.8Hz,2H),7.81(d,J＝7.7Hz,2H),7.73(d,J＝7.8Hz,2H),7.49(t,J＝7.4Hz,1H),7.42(t,J＝7.4Hz,1H),7.35-7.25(m,10H),7.20-7.12(m,5H),7.09-7.03(m,3H),6.91(d,J＝6.5Hz,2H),5.84(t,J＝9.6Hz,1H),5.67-5.59(m,2H),5.42(s,1H),5.12(d,J＝7.8Hz,1H),4.89(d,J＝3.6Hz,1H),4.66(dd,J＝12.2,3.1Hz,1H),4.46(d,J＝11.7Hz,1H),4.38(dd,J＝12.2,5.3Hz,1H),4.32(d,J＝11.7Hz,1H),4.18(dd,J＝10.1,4.7Hz,1H),4.09-4.04(m,1H),3.85(t,J＝9.2Hz,1H),3.75-3.69(m,2H),3.61(t,J＝10.2Hz,1H),3.45(t,J＝9.3Hz,1H),3.29(s,3H);^{13}C NMR(101MHz,$CDCl_3$)δ166.05,165.83,165.23,165.05,138.39,137.31,133.54,133.27,133.19,129.88,129.82,129.78,129.74,129.49,129.13,128.90,128.75,128.73,128.48,128.38,128.31,128.15,128.09,127.41,127.30,126.07,102.38,101.37,100.30,82.07,80.83,74.75,73.14,72.35,72.03,69.56,69.15,62.75,62.11,55.53;HRMS(ESI)calcd for $C_{55}H_{50}O_{15}Na[M+Na]^+$973.3042,found973.3035。

[0122] 糖苷化产物P8：

[0123] 根据路线二,将I-1(67.9mg,0.09mmol)与II-8(40.0mg,0.08mmol)进行糖苷化反应,得到P8(77.7mg,92％),为无色糖浆:$[\alpha]_D^{25}$＝-15.7(c 0.14,CHCl3);^{1}HNMR(400MHz,$CDCl_3$):δ7.90(d,J＝7.6Hz,2H),7.83(t,J＝7.3Hz,4H),7.77(d,J＝7.5Hz,2H),7.45-7.38(m,2H),7.38-7.31(m,2H),7.29-7.05(m,23H),5.84(t,J＝9.6Hz,1H),5.69-5.53(m,2H),5.01-4.92(m,1H),4.70(d,J＝10.6Hz,3H),4.63-4.54(m,1H),4.50-4.40(m,2H),4.31(d,J＝10.8Hz,1H),4.21-4.12(m,2H),4.12-4.05(m,2H),3.81(s,1H),3.57(d,J＝4.5Hz,2H),3.51-3.41(m,2H),3.22(d,J＝6.6Hz,1H),3.18-3.10(m,1H),1.47-1.30(m,2H),1.22-1.11(m,4H),0.79(t,J＝6.8Hz,3H);^{13}C NMR(151MHz,$CDCl_3$)δ166.24,165.95,165.32,165.00,138.68,138.46,138.33,133.54,133.34,133.25,133.11,129.93,129.90,129.86,129.83,129.62,129.54,128.92,128.89,128.52,128.47,128.40,128.37,128.35,128.33,128.27,128.20,128.14,127.65,127.59,127.39,100.29,97.18,78.26,74.93,73.16,73.04,72.53,72.09,72.00,71.36,70.00,69.91,67.83,63.48,29.16,28.34,22.54,14.12;HRMS(ESI)calcd for $C_{66}H_{66}O_{15}Na[M+Na]^+$1121.4294,found 1121.4274。

[0124] 糖苷化产物P9：

[0125] 根据路线二，将I-1(184.9mg,0.23mmol)与II-9(30.0mg,0.19mmol)进行糖苷化反应，得到P9(134.3mg,95%)，为白色固体:$[\alpha]_D^{25}$=-43.2(c 0.10,CHCl3);^{1}H NMR(400MHz,$CDCl_3$):δ8.01(d,J=7.8Hz,2H),7.97(d,J=7.8Hz,2H),7.91(d,J=7.8Hz,2H),7.84(d,J=7.7Hz,2H),7.54-7.45(m,3H),7.42-7.31(m,7H),7.27(t,J=7.5Hz,2H),5.91(t,J=9.7Hz,1H),5.65(t,J=9.7Hz,1H),5.51(dd,J=9.8,7.9Hz,1H),4.94(d,J=7.9Hz,1H),4.64(dd,J=12.0,3.4Hz,1H),4.50(dd,J=12.0,5.7Hz,1H),4.15(ddd,J=9.5,5.6,3.4Hz,1H),3.49(td,J=10.6,4.1Hz,1H),2.26(dtd,J=13.9,7.1,2.6Hz,1H),1.95(d,J=12.5Hz,1H),1.61-1.53(m,2H),1.32-1.23(m,1H),1.22-1.13(m,1H),0.96-0.85(m,1H),0.82(d,J=7.1Hz,3H),0.75(d,J=6.4Hz,3H),0.74-0.65(m,5H);^{13}C NMR(101MHz,$CDCl_3$)δ166.13,165.87,165.32,165.08,133.41,133.19,133.13,133.10,129.84,129.77,129.73,129.63,129.53,128.93,128.87,128.41,128.31,128.29,99.03,79.11,73.24,72.17,72.03,70.21,63.48,47.33,40.79,34.10,31.39,25.15,23.04,22.05,20.82,15.64;HRMS(ESI)calcdfor $C_{44}H_{46}O_{10}Na[M+Na]^+$757.2983,found 757.2988。

[0126] 糖苷化产物P10：

[0127] 根据路线二，将I-1(126.6mg,0.16mmol)与II-10(20.0mg,0.13mmol)进行糖苷化反应，得到P10(91.3mg,95%)，为白色固体:$[\alpha]_D^{25}$=-9.0(c 0.13,CHCl3);^{1}H NMR(400MHz,$CDCl_3$):δ8.02(d,J=7.8Hz,2H),7.96(d,J=7.8Hz,2H),7.92(d,J=7.7Hz,2H),7.83(d,J=7.7Hz,2H),7.56-7.47(m,3H),7.44-7.33(m,7H),7.31-7.25(m,2H),5.93(t,J=9.6Hz,1H),5.56(t,J=9.7Hz,1H),5.50(t,J=8.8Hz,1H),5.13(d,J=7.9Hz,1H),4.59(dd,J=12.0,3.2Hz,1H),4.49(dd,J=11.9,7.1Hz,1H),4.18(ddd,J=12.0,7.3,3.8Hz,1H),2.05-1.99(m,3H),1.82(d,J=11.7Hz,3H),1.67(s,3H),1.59-1.45(m,6H);^{13}C NMR(101MHz,$CDCl_3$)δ166.06,165.86,165.35,164.92,133.44,133.18,133.09,129.85,129.77,129.71,129.66,129.53,128.91,128.81,128.43,128.35,128.31,128.28,94.33,75.88,73.27,72.09,71.93,70.33,63.71,42.36,36.03,30.55;HRMS(ESI)calcd for $C_{44}H_{42}O_{10}Na[M+Na]^+$753.2670,found 753.2665。

[0128] 糖苷化产物P11：

[0129] 根据路线二，将I-1(80.0mg,0.10mmol)与II-11(44.2mg,0.08mmol)进行糖苷化反应，得到P11(78.8mg,87%)，为白色固体:$[\alpha]_D^{25}$=22.3(c 0.10,CHCl3);^{1}H NMR(400MHz,$CDCl_3$):δ8.05(d,J=7.7Hz,2H),8.00-7.93(m,4H),7.86(d,J=7.7Hz,2H),7.59-7.50(m,3H),7.44-7.30(m,14H),5.95(t,J=9.7Hz,1H),5.63(t,J=8.0Hz,1H),5.59(d,J=6.9Hz,1H),5.33(d,J=3.6Hz,1H),5.12(d,J=12.5Hz,1H),5.06(d,J=12.5Hz,1H),4.89(d,J=7.9Hz,1H),4.63(dd,J=12.0,3.5Hz,1H),4.58(dd,J=12.0,6.3Hz,1H),4.18(ddd,J=10.0,6.4,3.5Hz,1H),3.13(dd,J=11.7,4.5Hz,1H),2.94(dd,J=13.7,4.4Hz,1H),2.00(td,J=12.0,2.0Hz,1H),1.88-0.60(m,21H),1.12(s,3H),0.96(s,3H),0.94(s,3H),0.83(s,3H),0.71(s,3H),0.66(s,3H),0.58(s,3H);^{13}C NMR(101MHz,$CDCl_3$)δ177.41,166.03,165.88,165.32,165.02,143.71,136.40,133.47,133.23,133.11,133.09,129.86,129.76,129.74,129.69,129.41,128.85,128.79,128.44,128.41,128.38,128.30,127.99,127.92,122.50,103.32,90.79,72.99,72.16,72.00,70.31,65.95,63.45,55.45,47.56,46.73,45.93,41.63,41.38,39.26,38.74,38.24,36.62,33.88,33.16,32.62,32.39,30.74,

27.68,27.60,25.88,25.84,23.68,23.38,23.04,18.08,16.83,16.21,15.18;HRMS(ESI)calcdfor $C_{71}H_{80}O_{12}Na[M+Na]^+$1147.5542,found 1147.5552。

[0130] 糖苷化产物P12：

[0131] 根据路线二,将I-1(69.7mg,0.09mmol)与II-12(30.0mg,0.07mmol)进行糖苷化反应,得到P12(67.3mg,94%),为白色固体:$[\alpha]_D^{25}$=-80.6(c 0.14,CHCl3);^{1}H NMR(400MHz,$CDCl_3$):δ7.92(t,J=6.8Hz,4H),7.87(d,J=7.7Hz,2H),7.81(d,J=7.6Hz,2H),7.56-7.48(m,3H),7.46-7.31(m,7H),7.27(dd,J=10.3,4.4Hz,2H),7.12(s,1H),6.48(s,1H),6.34(s,2H),5.99-5.88(m,3H),5.72-5.59(m,2H),4.99(d,J=7.6Hz,1H),.4.98(d,J=10.0Hz,1H),4.69(dd,J=12.1,2.0Hz,1H),4.59-4.44(m,3H),4.23-4.14(m,1H),4.07(t,J=9.4Hz,1H),3.73(s,6H),3.67(s,3H),2.99-2.86(m,1H),2.72(dd,J=14.4,4.5Hz,1H);^{13}C NMR(151MHz,$CDCl_3$)δ173.83,166.13,165.88,165.24,165.03,152.69,148.18,147.74,137.48,135.16,133.72,133.48,133.29,132.43,129.91,129.83,129.76,129.72,129.23,129.19,128.75,128.70,128.65,128.64,128.60,128.53,128.44,109.59,108.65,108.08,101.57,99.06,80.04,72.81,72.73,71.83,71.16,69.64,62.97,60.68,56.49,45.51,44.01,38.61;HRMS(ESI)calcd for$C_{56}H_{48}O_{17}Na[M+Na]^+$1015.2784,found 1015.2767。

[0132] 糖苷化产物P13：

[0133] 根据路线二,将I-3(107.8mg,0.13mmol)与II-3(52.0mg,0.11mmol)进行糖苷化反应,得到P13(108.7mg,93%),为白色固体:$[\alpha]_D^{25}$=72.4(c 0.11,CHCl3);^{1}HNMR(400MHz,$CDCl_3$):δ8.08(d,J=7.7Hz,2H),8.02(d,J=7.8Hz,2H),7.89(d,J=7.8Hz,2H),7.77(d,J=7.8Hz,2H),7.60(t,J=7.3Hz,1H),7.53(t,J=7.4Hz,1H),7.46(t,J=7.7Hz,2H),7.39(t,J=7.9Hz,4H),7.34-7.19(m,17H),7.13(d,J=7.4Hz,2H),5.98(d,J=3.5Hz,1H),5.86(dd,J=10.4,7.9Hz,1H),5.61(dd,J=10.4,3.5Hz,1H),4.90(d,J=10.9Hz,1H),4.80-4.65(m,4H),4.62-4.54(m,2H),4.51(d,J=3.5Hz,1H),4.44-4.35(m,2H),4.30-4.18(m,2H),3.91(t,J=9.2Hz,1H),3.82-3.72(m,2H),3.45-3.34(m,2H),3.21(s,3H);^{13}C NMR(101MHz,$CDCl_3$)δ166.05,165.66,165.61,165.18,138.82,138.26,138.18,133.63,133.34,133.19,130.08,129.79,129.73,129.44,129.30,129.04,128.73,128.65,128.51,128.48,128.44,128.41,128.32,128.12,127.93,127.90,127.74,127.59,127.54,102.05,97.93,81.95,79.89,75.57,74.74,73.39,71.67,71.40,69.79,69.64,68.73,68.14,61.94,55.05;HRMS(ESI)calcd for$C_{62}H_{58}O_{15}Na[M+Na]^+$1065.3668,found 1065.3693。

[0134] 糖苷化产物P14：

[0135] 根据路线二,将I-4(132.1mg,0.16mmol)与II-1(35.7mg,0.14mmol)进行糖苷化反应,得到P14(110.5mg,96%),为白色固体:$[\alpha]_D^{25}$=-71.6(c 0.18,CHCl3);^{1}H NMR(400MHz,$CDCl_3$):δ8.13(d,J=7.7Hz,2H),8.06(d,J=7.7Hz,2H),7.96(d,J=7.7Hz,2H),7.84(d,J=7.7Hz,2H),7.58(q,J=7.2Hz,2H),7.50(t,J=7.4Hz,1H),7.44-7.34(m,7H),7.26(t,J=7.7Hz,2H),6.15(t,J=10.1Hz,1H),5.93(dd,J=10.1,3.3Hz,1H),5.80-5.74(m,1H),5.57(d,J=5.0Hz,1H),5.18(d,J=1.8Hz,1H),4.73-4.65(m,2H),4.61(dt,J=10.2,3.2Hz,1H),4.51(dd,J=12.2,3.9Hz,1H),4.38-4.33(m,2H),4.13(td,J=6.1,1.8Hz,1H),3.98(dd,J=10.5,6.4Hz,1H),3.90(dd,J=10.5,5.9Hz,1H),1.64(s,3H),1.44(s,3H),1.36(s,6H);^{13}C NMR(101MHz,$CDCl_3$)δ166.23,165.54,165.42,165.35,133.44,133.39,

133.16,132.99,129.98,129.85,129.81,129.79,129.73,129.38,129.14,129.10,128.59,128.45,128.42,128.30,109.49,108.78,97.88,96.36,70.95,70.67,70.38,70.25,68.83,67.56,66.83,66.75,62.88,26.25,25.99,25.03,24.44;HRMS(ESI)calcd for $C_{46}H_{46}O_{15}Na$[M+Na]$^+$861.2729,found861.2757。

[0136] 糖苷化产物P15：

[0137] 根据路线二,将I-5(100.2mg,0.15mmol)与II-2(56.8mg,0.12mmol)进行糖苷化反应,得到P15(105.4mg,97%),为白色固体:$[\alpha]_D^{25}$=39.1(c 0.17,CHCl3);^{1}H NMR(400MHz,$CDCl_3$):δ7.98(d,J=7.7Hz,2H),7.78(d,J=8.8Hz,2H),7.76(d,J=8.7Hz,2H),7.50(d,J=7.2Hz,1H),7.44-7.10(m,19H),7.08-7.01(m,4H),5.70(dd,J=10.2,3.4Hz,1H),5.55-5.47(m,2H),5.25-5.17(m,1H),5.08(d,J=11.1Hz,1H),4.85(d,J=10.9Hz,1H),4.74(d,J=11.2Hz,1H),4.61(d,J=11.0Hz,1H),4.56-4.48(m,2H),4.34-4.25(m,2H),3.97(t,J=9.4Hz,1H),3.80(dd,J=11.2,3.3Hz,1H),3.74(dd,J=11.3,2.0Hz,1H),3.59(t,J=9.1Hz,1H),3.50(s,3H),3.47(t,J=8.4Hz,1H),3.44-3.39(m,1H),0.81(d,J=6.1Hz,3H);^{13}C NMR(101MHz,$CDCl_3$)δ165.77,138.48,138.34,138.04,133.51,133.28,133.22,129.94,129.73,129.69,129.44,129.24,128.60,128.42,128.36,128.23,128.20,127.74,127.72,127.43,127.36,104.92,97.07,82.56,82.44,75.35,74.89,74.72,74.70,73.19,71.80,71.21,70.10,68.26,67.09,57.12,17.21;HRMS(ESI)calcd for $C_{55}H_{54}O_{13}Na$[M+Na]$^+$945.3457,found 945.3479。

[0138] 糖苷化产物P16：

[0139] 根据路线二,将I-9(65.0mg,0.10mmol)与II-13(65.0mg,0.08mmol)进行糖苷化反应,得到P16(100.2mg,99%),为无色糖浆:$[\alpha]_D^{25}$=35.7(c 0.18,CHCl3);^{1}H NMR(400MHz,$CDCl_3$):δ8.00(t,J=8.1Hz,4H),7.96-7.85(m,6H),7.78(d,J=7.6Hz,2H),7.54(t,J=7.3Hz,1H),7.47(t,J=7.2Hz,3H),7.44-7.17(m,25H),7.15-7.08(m,1H),5.83(t,J=9.6Hz,1H),5.73(dd,J=8.2,6.4Hz,1H),5.67(s,1H),5.62(dd,J=8.4,3.1Hz,1H),5.38(t,J=9.3Hz,2H),5.15(d,J=5.2Hz,2H),4.84(t,J=5.9Hz,1H),4.60(dd,J=19.5,7.1Hz,1H),4.42-4.32(m,2H),4.25(dd,J=12.8,4.0Hz,1H),4.10(d,J=10.9Hz,1H),4.00(d,J=7.9Hz,1H),3.89-3.78(m,2H),3.59-3.48(m,1H),3.21-3.08(m,1H),3.02-2.84(m,2H),1.34-1.21(m,4H),0.98(d,J=16.0Hz,2H);^{13}C NMR(101MHz,$CDCl_3$)δ165.81,165.68,165.58,165.42,165.21,164.99,156.68,156.11,138.05,138.01,136.96,136.92,136.85,133.55,133.44,133.24,133.21,129.92,129.89,129.82,129.77,129.70,129.42,129.37,129.34,129.13,128.88,128.78,128.57,128.53,128.50,128.48,128.37,128.31,127.88,127.78,127.32,127.30,127.16,101.06,100.94,73.92,72.95,71.98,70.42,69.92,69.84,69.67,68.41,68.36,67.15,62.44,50.60,50.28,47.16,46.18,29.76,28.94,27.75,27.37,23.08;HRMS(ESI)calcd for $C_{73}H_{67}NO_{18}Na$[M+Na]$^+$1268.4250,found 1268.4220。

[0140] 糖苷化产物P17：

[0141] 根据路线二,将I-10(74.8mg,0.12mmol)与II-5(42.4mg,0.10mmol)进行糖苷化反应,得到P17(73.5mg,88%),为白色固体:$[\alpha]_D^{25}$=-171.0(c 0.12,CHCl3);^{1}H NMR(400MHz,$CDCl_3$):δ8.09(d,J=7.2Hz,2H),7.94(d,J=7.3Hz,2H),7.79(d,J=7.5Hz,2H),7.57(t,J

＝7.4Hz,1H),7.43(t,J＝7.7Hz,2H),7.41-7.19(m,21H),5.81(dd,J＝10.5,7.9Hz,1H),5.73(d,J＝3.4Hz,1H),5.50(dd,J＝10.5,3.5Hz,1H),5.08(d,J＝8.0Hz,1H),4.68(d,J＝9.2Hz,3H),4.62(d,J＝10.8Hz,1H),4.58-4.52(m,2H),4.47(d,J＝10.8Hz,1H),4.11(dd,J＝12.0,5.6Hz,1H),4.06-3.99(m,2H),3.93(t,J＝9.6Hz,1H),3.81(dd,J＝9.4,3.2Hz,1H),3.75(t,J＝2.4Hz,1H),3.66(dd,J＝10.1,5.3Hz,1H),3.10(s,3H),1.34(d,J＝6.3Hz,3H);^{13}C NMR(101MHz,$CDCl_3$)δ166.12,165.71,165.39,138.64,138.57,138.31,133.40,133.16,132.94,130.06,129.89,129.77,129.55,129.31,129.04,128.55,128.44,128.35,128.33,128.28,127.93,127.81,127.76,127.62,127.53,100.49,98.70,80.10,75.01,74.72,74.64,72.73,72.41,72.04,71.98,71.23,70.03,69.71,67.43,54.51,16.36;HRMS(ESI)calcdfor $C_{55}H_{54}O_{13}Na[M+Na]^+$945.3457,found 945.3479。

[0142] 糖苷化产物P18：

[0143] 根据路线二,将I-7(100.0mg,0.15mmol)与II-14(51.7mg,0.12mmol)进行糖苷化反应,得到P18(98.7mg,92％),为白色固体:$[\alpha]_D^{25}$＝-53.3(c 0.16,CHCl3);^{1}H NMR(400MHz,$CDCl_3$):δ7.99(dd,J＝7.9,3.0Hz,6H),7.56-7.47(m,3H),7.40-7.32(m,6H),5.77(t,J＝7.4Hz,1H),5.35(dd,J＝7.5,5.6Hz,1H),5.33-5.26(m,2H),4.96(d,J＝5.6Hz,1H),4.44(dd,J＝12.1,4.5Hz,1H),4.40(t,J＝8.0Hz,1H),3.69(dd,J＝12.1,7.3Hz,1H),3.58(dt,J＝11.4,6.3Hz,1H),3.47(dd,J＝11.6,5.2Hz,1H),3.37(t,J＝10.9Hz,1H),2.29(dd,J＝13.4,2.9Hz,1H),2.15(dd,J＝13.4,2.9Hz,1H),2.04-0.87(m,22H),0.99-0.95(m,6H),0.80-0.76(m,6H);^{13}C NMR(101MHz,$CDCl_3$)δ165.56,165.44,165.20,140.32,133.36,133.30,133.22,129.89,129.81,129.43,129.24,129.21,128.42,128.35,121.76,109.29,98.63,80.81,78.76,70.71,70.53,69.29,66.85,62.09,61.37,56.47,50.05,41.61,40.26,39.75,38.61,37.23,36.86,32.07,31.85,31.40,30.30,29.54,28.81,20.84,19.36,17.16,16.29,14.55;HRMS(ESI)calcdfor $C_{53}H_{62}O_{10}Na[M+Na]^+$881.4235,found 881.4239。

[0144] 糖苷化产物P19：

[0145] 根据路线二,将I-11(50.0mg,0.07mmol)与II-5(29.0mg,0.06mmol)进行糖苷化反应,得到P19(55.0mg,98％),为无色糖浆:$[\alpha]_D^{25}$＝17.4(c 0.13,$CHCl_3$);^{1}H NMR(400MHz,$CDCl_3$)δ8.06-7.87(m,6H),7.45(dd,J＝24.3,7.8Hz,3H),7.35-7.12(m,20H),5.47(d,J＝3.2Hz,2H),5.29(s,1H),4.84(d,J＝10.9Hz,1H),4.73-4.68(m,1H),4.68-4.59(m,2H),4.59-4.48(m,5H),3.98(d,J＝11.0Hz,1H),3.88(d,J＝9.5Hz,1H),3.81(dd,J＝8.7,3.3Hz,2H),3.73-3.65(m,2H),3.20(s,3H);^{13}C NMR(101MHz,$CDCl_3$)δ166.27,165.85,165.31,138.48,138.43,138.17,133.42,133.39,133.01,130.02,129.88,129.81,129.77,129.16,129.04,128.50,128.43,128.38,128.37,128.32,128.30,128.24,127.96,127.84,127.70,127.68,127.66,127.59,105.86,98.94,82.05,80.81,80.24,77.85,75.17,74.92,74.56,72.72,72.13,71.61,67.08,63.76,54.67;HRMS(ESI)calcdfor $C_{54}H_{52}O_{13}Na[M+Na]^+$931.3300,found 931.3322。

[0146] 糖苷化产物P20：

[0147] 根据路线二,将I-12(43.0mg,0.06mmol)与II-9(8.5mg,0.05mmol)进行糖苷化反应,得到P20(31.0mg,98％),为白色固体:$[\alpha]_D^{25}$＝-26.9(c 0.25,$CHCl_3$);^{1}HNMR(400MHz,

$CDCl_3$)δ8.05-7.92(m,4H),7.87-7.78(m,2H),7.55-7.20(m,9H),5.72(dd,J=7.1,4.7Hz,1H),5.54(d,J=4.7Hz,1H),5.40(s,1H),4.69-4.55(m,2H),4.45(dd,J=11.5,6.4Hz,1H),3.46(td,J=10.6,4.2Hz,1H),2.15(td,J=7.0,2.6Hz,1H),2.10-2.02(m,1H),1.57(dt,J=10.1,3.5Hz,3H),1.36-1.11(m,2H),0.93-0.87(m,3H),0.85(d,J=6.4Hz,3H),0.76(d,J=7.0Hz,3H),0.70(d,J=6.9Hz,3H);^{13}C NMR(101MHz,$CDCl_3$)δ166.20,165.36,165.34,133.43,133.34,133.06,129.80,129.73,129.67,129.33,129.01,128.48,128.34,128.31,102.47,78.07,76.93,76.24,73.09,65.89,47.74,40.04,34.35,31.46,25.23,22.84,22.30,21.02,15.63;HRMS(ESI)calcd for $C_{36}H_{40}O_8Na[M+Na]^+$623.2615,found 623.2617。

[0148] 糖苷化产物P21：

[0149] 根据路线二，将I-14(57.9mg,0.07mmol)与II-4(36.0mg,0.06mmol)进行糖苷化反应，得到P21(70.2mg,99%)，为白色固体：$[\alpha]_D^{25}$=-6.5(c 0.27,$CHCl_3$)；^{1}H NMR(400MHz,$CDCl_3$)δ8.15(d,J=7.5Hz,2H),8.02(d,J=7.5Hz,2H),7.94(d,J=7.7Hz,4H),7.58(t,J=7.3Hz,1H),7.54-7.43(m,5H),7.38-7.31(m,4H),7.24(t,J=7.6Hz,2H),5.92(s,1H),5.56(d,J=4.4Hz,1H),5.50(d,J=4.9Hz,1H),4.97(d,J=12.2Hz,1H),4.85(dd,J=11.5,2.0Hz,1H),4.77-4.66(m,2H),4.53(dd,J=7.6,1.7Hz,1H),4.40(d,J=12.2Hz,1H),4.28(dd,J=9.5,5.0Hz,2H),3.99(t,J=5.3Hz,1H),3.88(t,J=6.4Hz,2H),1.38(s,2H),1.37(s,2H),1.28(s,3H),1.12(s,3H)；^{13}C NMR(151MHz,$CDCl_3$)δ166.25,165.95,165.70,164.79,133.54,133.47,133.13,133.10,130.24,129.83,129.80,129.76,129.53,129.35,129.09,128.62,128.46,128.41,128.37,128.36,109.35,108.55,107.34,96.40,81.52,81.13,78.99,71.15,70.65,70.54,66.96,63.72,60.66,59.63,26.05,25.98,25.02,24.27;HRMS(ESI)calcd for $C_{46}H_{46}O_{15}Na[M+Na]^+$861.2729,found 861.2749。

[0150] 糖苷化产物P22：

[0151] 根据路线二，将I-15(111.0mg,0.14mmol)与II-1(30.0mg,0.12mmol)进行糖苷化反应，得到P22(96.1mg,99%)，为无色糖浆：$[\alpha]_D^{25}$=-5.8(c 0.16,$CHCl_3$)；^{1}H NMR(400MHz,$CDCl_3$)δ8.01(d,J=6.9Hz,2H),7.97-7.81(m,8H),7.75(d,J=6.0Hz,4H),7.49-7.15(m,21H),6.86(d,J=7.9Hz,2H),6.57(d,J=7.9Hz,2H),5.98-5.82(m,2H),5.69-5.60(m,1H),5.60-5.49(m,2H),5.44(s,1H),5.34(s,1H),5.20(d,J=7.2Hz,1H),4.67-4.46(m,3H),4.17-4.05(m,1H),3.96(d,J=10.9Hz,1H),3.90-3.79(m,1H),3.46(s,3H)；^{13}C NMR(151MHz,$CDCl_3$)δ166.17,165.90,165.83,165.75,165.31,165.31,165.17,155.81,151.09,133.63,133.59,133.39,133.28,133.14,130.12,130.02,129.99,129.92,129.82,129.67,129.52,129.33,129.14,128.98,128.91,128.65,128.57,128.52,128.45,128.42,118.91,114.62,106.30,100.97,81.94,81.91,77.62,74.06,73.03,71.99,70.39,69.70,66.29,63.75,55.47;HRMS(ESI)calcd for $C_{68}H_{56}O_{19}Na[M+Na]^+$1199.3308,found1199.3284。

[0152] 糖苷化产物P23：

[0153] 根据路线二，将I-2(50.0mg,0.09mmol)与II-2(34.9mg,0.08mmol)进行糖苷化反应，得到P23(58.7mg,98%)，为白色固体：$[\alpha]_D^{25}$=-19.8(c 0.10,$CHCl_3$)；^{1}HNMR(400MHz,$CDCl_3$)δ7.42-7.36(m,4H),7.35-7.31(m,3H),7.30-7.22(m,8H),5.06-4.99(m,2H),4.96(d,J=11.2Hz,1H),4.91(t,J=8.5Hz,1H),4.83(d,J=11.0Hz,1H),4.76(dd,J=11.7,

7.6Hz,2H),4.68-4.63(m,2H),4.50(d,J=12.1Hz,1H),4.27(d,J=7.7Hz,1H),4.12(dd,J=12.5,4.1Hz,1H),3.94(t,J=9.3Hz,1H),3.87(dd,J=12.4,2.3Hz,1H),3.79-3.71(m,2H),3.61-3.51(m,4H),3.38(d,J=8.0Hz,1H),3.34(dt,J=9.8,3.0Hz,1H),3.29(qd,J=5.8,3.1Hz,1H),1.99(s,3H),1.98(s,3H),1.96(s,3H),1.94(s,3H);^{13}C NMR(151MHz,$CDCl_3$)δ170.65,170.25,169.37,169.15,139.07,138.46,137.94,128.57,128.24,128.10,127.99,127.53,127.30,127.26,104.65,100.00,82.59,81.71,75.06,74.77,74.61,73.64,73.15,71.94,71.57,68.01,67.75,61.57,57.09,20.69,20.64,20.63,20.58;HRMS(ESI)calcd for $C_{42}H_{50}O_{15}Na[M+Na]^+$817.3042,found817.3041。

[0154] 糖苷化产物P24:

[0155] 根据路线二,将I-6(29.0mg,0.06mmol)与II-5(37.2mg,0.07mmol)进行糖苷化反应,得到P24(43.0mg,96%),为无色糖浆:$[\alpha]_D^{25}$=-23.7(c 0.16,$CHCl_3$);^{1}HNMR(400MHz,$CDCl_3$)δ7.44-7.24(m,15H),5.35-5.25(m,2H),5.07(d,J=9.7Hz,1H),4.96(d,J=11.1Hz,1H),4.81(s,1H),4.78-4.67(m,3H),4.64-4.54(m,3H),3.92(ddd,J=17.6,8.8,4.9Hz,3H),3.83-3.71(m,3H),3.69-3.61(m,1H),3.33(s,3H),2.14(s,3H),1.99(d,J=15.2Hz,6H),1.18(d,J=6.2Hz,3H);^{13}C NMR(101MHz,$CDCl_3$)δ170.07,170.05,169.89,138.40,138.37,138.25,128.38,128.37,127.87,127.84,127.67,127.64,127.60,98.81,97.76,80.25,75.11,75.02,74.42,72.68,72.08,71.65,71.16,69.87,69.16,67.35,66.32,54.80,20.95,20.82,20.74,17.37;HRMS(ESI)calcd for $C_{40}H_{48}O_{13}Na[M+Na]^+$759.2987,found759.3010。

[0156] 糖苷化产物P25:

[0157] 根据路线二,将I-8(100.0mg,0.21mmol)与II-5(80.0mg,0.17mmol)进行糖苷化反应,得到P25(123.1mg,99%),为无色糖浆:$[\alpha]_D^{25}$=-24.4(c 0.14,$CHCl_3$);^{1}H NMR(400MHz,$CDCl_3$)δ7.38-7.24(m,15H),5.11(t,J=8.1Hz,1H),4.97-4.87(m,3H),4.73-4.68(m,3H),4.62-4.58(m,2H),4.57(d,J=13.1Hz,1H),4.54(d,J=6.4Hz,0H),4.13(dd,J=11.9,4.9Hz,1H),4.04(dd,J=9.5,4.0Hz,1H),3.87(dd,J=9.1,3.0Hz,1H),3.83(d,J=9.2Hz,1H),3.79-3.76(m,1H),3.75-3.69(m,2H),3.36-3.31(m,1H),3.30(s,3H),2.04(s,3H),2.00(s,6H);^{13}C NMR(101MHz,$CDCl_3$)δ170.13,169.84,169.26,138.44,138.20,128.44,128.38,127.91,127.87,127.72,127.70,127.58,100.55,98.92,80.23,74.99,74.76,74.56,72.80,72.01,71.42,71.12,70.52,68.78,68.48,61.62,54.68,20.81,20.72;HRMS(ESI)calcd for $C_{39}H_{46}O_{13}Na[M+Na]^+$745.2831,found 745.2834。

[0158] 糖苷化产物P26:

[0159] 根据路线二,将I-16(54.6mg,0.07mmol)与II-4(35.8mg,0.06mmol)进行糖苷化反应,得到P26(67.2mg,99%),为无色糖浆:$[\alpha]_D^{25}$=-1.3(c 0.10,$CHCl_3$);^{1}H NMR(400MHz,$CDCl_3$)δ7.93(d,J=8.7Hz,2H),7.91(d,J=7.8Hz,2H),7.87(d,J=7.8Hz,2H),7.80(d,J=7.8Hz,2H),7.55-7.46(m,3H),7.42(t,J=7.4Hz,1H),7.39-7.25(m,17H),7.19-7.11(m,6H),6.90(d,J=8.6Hz,2H),6.74(d,J=8.8Hz,2H),5.83(t,J=9.6Hz,1H),5.63(t,J=8.8Hz,1H),5.39(t,J=9.7Hz,1H),5.26(t,J=8.1Hz,1H),5.11(d,J=7.8Hz,1H),4.78(d,J=10.8Hz,1H),4.71(d,J=11.0Hz,1H),4.67(d,J=7.9Hz,1H),4.62(d,J=10.9Hz,1H),4.54(d,J=10.7Hz,2H),4.43(d,J=12.2Hz,1H),4.08(t,J=8.6Hz,1H),3.97(d,J=

11.0Hz,1H),3.91(dd,J=11.6,7.7Hz,1H),3.77-3.71(m,2H),3.69(s,3H),3.68-3.62(m,2H),3.47(dt,J=9.6,3.2Hz,1H);^{13}C NMR(101MHz,$CDCl_3$)δ165.69,165.40,165.24,165.07,155.76,151.08,138.00,137.92,137.79,133.49,133.27,133.22,133.00,129.93,129.88,129.79,129.76,129.71,129.20,128.81,128.70,128.43,128.40,128.33,128.28,128.25,128.00,127.93,127.83,127.80,127.66,127.63,119.19,114.63,100.97,100.75,83.03,77.81,75.22,75.19,75.01,74.80,73.61,73.53,72.84,71.81,69.61,68.51,67.58,55.58;HRMS(ESI)calcd for $C_{68}H_{62}O_{16}Na[M+Na]^+$1157.3930,found 1157.3972。

[0160] 糖苷化产物P27:

[0161] 根据路线二,将I-17(69.4mg,0.10mmol)与II-5(38.0mg,0.08mmol)进行糖苷化反应,得到P27(69.5mg,90%),为无色糖浆:$[\alpha]_D^{25}$=38.0(c 0.13,$CHCl_3$);^{1}HNMR(400MHz,$CDCl_3$)δ7.94(d,J=7.5Hz,2H),7.49(t,J=7.1Hz,1H),7.35(t,J=7.5Hz,2H),7.29-7.10(m,20H),5.47(s,1H),5.27(s,1H),4.75(t,J=11.9Hz,2H),4.69-4.63(m,3H),4.59(d,J=11.1Hz,1H),4.54-4.46(m,3H),4.17-4.12(m,1H),4.07-4.00(m,2H),3.97(d,J=9.6Hz,1H),3.78(d,J=9.5Hz,1H),3.75-3.63(m,5H),3.20(s,3H),0.95-0.87(m,21H);^{13}C NMR(151MHz,$CDCl_3$)δ165.42,138.99,138.76,138.53,138.11,133.36,129.88,129.81,128.47,128.42,128.41,128.36,128.10,127.95,127.88,127.71,127.65,127.58,127.49,106.38,99.16,84.48,83.48,81.84,80.43,75.08,74.84,74.62,72.65,72.32,72.25,71.34,66.10,63.02,54.81,18.04,18.03,12.02;HRMS(ESI)calcdfor $C_{56}H_{70}O_{11}SiNa[M+Na]^+$969.4580,found 969.4568。

[0162] 糖苷化产物P28:

[0163] 根据路线二,将I-18(54.8mg,0.08mmol)与II-3(30mg,0.06mmol)进行糖苷化反应,得到P28(53.3mg,87%),为无色糖浆:$[\alpha]_D^{25}$=38.0(c 0.13,$CHCl_3$);^{1}HNMR(400MHz,$CDCl_3$)δ7.91(d,J=7.4Hz,2H),7.49(t,J=7.0Hz,1H),7.34(t,J=7.4Hz,2H),7.31-7.09(m,20H),5.34(s,1H),5.04(s,1H),4.90(d,J=10.8Hz,1H),4.80(d,J=11.0Hz,1H),4.74(d,J=10.9Hz,1H),4.72-4.63(m,2H),4.62-4.47(m,4H),4.16(d,J=4.2Hz,1H),4.09(d,J=4.2Hz,1H),3.97-3.85(m,2H),3.78(d,J=3.4Hz,2H),3.75-3.69(m,1H),3.56(m,1H),3.47(t,J=9.3Hz,2H),3.26(s,3H),0.95(s,21H);^{13}C NMR(101MHz,$CDCl_3$)δ165.46,138.97,138.53,138.34,137.97,133.41,129.87,129.67,128.55,128.48,128.42,128.20,128.07,127.96,127.91,127.90,127.74,127.66,106.54,97.99,83.62,83.00,82.27,80.15,78.06,75.82,75.06,73.47,72.35,70.18,66.18,62.82,55.17,18.07,18.06,12.05;HRMS(ESI)calcd for $C_{56}H_{70}O_{11}SiNa[M+Na]^+$969.4580,found 969.4578。

[0164] 糖苷化产物P29:

[0165] 根据路线二,将I-19(120.0mg,0.16mmol)与II-5(62.0mg,0.13mmol)进行糖苷化反应,得到P29(130.8mg,99%,α/β=1:1),为白色固体;α和β混合构型:^{1}H NMR(400MHz,$CDCl_3$)δ7.38-7.10(m,70H),5.11(d,J=3.4Hz,1H),5.06(d,J=10.9Hz,1H),4.95(d,J=7.4Hz,1H),4.93(d,J=4.9Hz,1H),4.91(d,J=8.3Hz,1H),4.84(d,J=5.2Hz,1H),4.81(d,J=6.4Hz,2H),4.76(d,J=11.8Hz,3H),4.69(d,J=9.7Hz,5H),4.67-4.57(m,9H),4.54(d,J=10.5Hz,3H),4.48(d,J=9.1Hz,1H),4.45(d,J=3.4Hz,1H),4.41(d,J=7.3Hz,1H),4.27(d,J=10.5Hz,1H),4.04-3.97(m,2H),3.95(d,J=9.4Hz,1H),3.91-3.44(m,21H),

3.27(s,3H),3.25(s,3H);^{13}C NMR(101MHz,$CDCl_3$)δ138.97,138.82,138.73,138.68,138.66,138.62,138.56,138.35,138.33,138.27,138.11,128.46,128.44,128.41,128.40,128.37,128.35,128.30,128.23,128.09,128.03,128.00,127.99,127.96,127.93,127.87,127.80,127.76,127.70,127.69,127.65,127.63,127.59,127.53,127.48,104.22,99.03,98.98,96.61,84.76,82.25,81.74,80.40,80.31,80.16,77.98,77.73,75.80,75.52,75.13,75.09,75.02,74.95,74.87,74.64,73.55,73.48,72.88,72.84,72.62,72.21,72.08,71.81,71.47,70.19,69.14,68.58,66.04,54.84,54.80;HRMS(ESI)calcd for $C_{62}H_{66}O_{11}Na[M+Na]^+$1009.4497,found1009.4507。

[0166] 糖苷化产物P30：

[0167] 根据路线二,将I-20(53.0mg,0.11mmol)与II-1(23.0mg,0.09mmol)进行糖苷化反应,得到P30(40.0mg,86％,α/β＝3.3:1),为无色糖浆;α和β混合构型:^{1}H NMR(400MHz,$CDCl_3$)δ5.51(d,J＝5.0Hz,1H),5.31(ddd,J＝11.5,9.3,5.4Hz,1H),5.05-4.95(m,2H),4.62(dd,J＝7.9,2.5Hz,1H),4.32(tq,J＝8.9,4.8Hz,3H),4.25(dd,J＝7.9,2.0Hz,1H),4.09-3.99(m,2H),3.99-3.92(m,1H),3.75(dd,J＝10.1,6.3Hz,1H),3.66(dd,J＝10.3,6.8Hz,1H),2.28(dd,J＝13.0,5.4Hz,1H),2.10(s,2H),2.09(s,1H),2.04(s,2H),2.03(s,1H),2.02(s,1H),2.01(s,3H),1.84(dd,J＝12.3,3.7Hz,1H),1.81-1.78(m,1H),1.56(s,3H),1.53(s,1H),1.45(s,1H),1.43(s,3H),1.34(d,J＝2.1Hz,7H),1.26(s,1H);^{13}C NMR(101MHz,$CDCl_3$)δ170.82,170.24,169.95,169.82,109.41,109.30,108.66,100.14,97.08,96.29,71.93,71.61,71.36,70.91,70.69,70.60,70.57,70.36,69.25,69.17,69.12,68.05,67.88,67.72,66.26,66.18,62.46,62.35,62.26,36.07,34.95,26.12,26.03,25.97,24.93,24.51,24.37,24.29,20.99,20.90,20.79,20.75,20.73;HRMS(ESI)calcd for $C_{24}H_{36}O_{13}Na[M+Na]^+$555.2048,found555.2048。

[0168] 糖苷化产物P31：

[0169] 根据路线二,将I-12(40mg,0.06mmol)与II-20(16.8mg,0.05mmol)according进行糖苷化反应,得到P31(33mg,84％),为白色固体:$[\alpha]_D^{25}$＝-89.46(c0.13,$CHCl_3$);^{1}H NMR(400MHz,$CDCl_3$)δ8.76(s,1H),8.24(s,1H),8.17-8.08(m,2H),8.06-7.98(m,2H),7.97-7.86(m,2H),7.58(d,J＝7.9Hz,3H),7.41(ddd,J＝30.7,15.6,7.7Hz,7H),6.50(d,J＝5.3Hz,1H),6.40(d,J＝5.6Hz,1H),6.26(t,J＝5.2Hz,1H),4.96-4.84(m,2H),4.73(dd,J＝12.1,4.2Hz,1H),1.43(s,18H);^{13}C NMR(101MHz,$CDCl_3$)δ166.16,165.33,165.07,152.85,152.46,150.73,150.32,143.30,133.85,133.79,133.49,129.83,129.77,129.31,128.67,128.65,128.59,128.53,128.30,86.99,83.92,80.88,73.87,71.48,63.59,27.78;HRMS(ESI)calcd for $C_{41}H_{41}N_5O_{11}Na[M+Na]^+$802.2695,found 802.2710。

[0170] 糖苷化产物P32：

[0171] 根据路线二,将I-12(40mg,0.06mmol)与II-21(18mg,0.05mmol)进行糖苷化反应,得到P32(38mg,85％),为白色固体:$[\alpha]_D^{25}$＝-46.29(c 0.19,$CHCl_3$);^{1}H NMR(400MHz,$CDCl_3$)δ8.09(s,1H),8.02(t,J＝7.3Hz,4H),7.96-7.91(m,2H),7.62-7.51(m,4H),7.39(ddd,J＝12.6,9.5,6.3Hz,6H),6.64(t,J＝5.8Hz,1H),6.27(d,J＝6.8Hz,2H),4.96(dd,J＝11.8,3.9Hz,1H),4.94-4.86(m,1H),4.79(dd,J＝11.8,5.5Hz,1H),1.46(s,9H);^{13}C NMR(101MHz,$CDCl_3$)δ166.18,165.34,165.15,152.14,149.57,148.12,142.28,135.40,133.80,133.53,

133.30,129.87,129.81,129.63,129.45,128.94,128.52,128.49,128.46,122.59,88.35,81.50,80.86,74.85,71.81,64.00,28.08;HRMS(ESI)calcd for $C_{36}H_{32}N_5O_9INa[M+Na]^+$ 828.1137,found 828.1135。

[0172] 糖苷化产物P33：

[0173] 根据路线二,将I-11(40mg,0.06mmol)与II-20(17mg,0.05mmol)进行糖苷化反应,得到P33(32mg,83%),为白色固体:$[\alpha]_D^{25}$=-13.76(c 0.21,$CHCl_3$);^{1}H NMR(400MHz,$CDCl_3$)δ8.89(s,1H),8.36(s,1H),8.13-8.00(m,4H),7.96-7.86(m,2H),7.68-7.34(m,10H),6.55(dd,J=7.3,2.7Hz,2H),5.93(dd,J=4.6,2.8Hz,1H),5.11(d,J=4.8Hz,1H),4.80(d,J=4.9Hz,2H),1.46(s,18H);^{13}C NMR(101MHz,$CDCl_3$)δ166.14,165.47,165.27,152.82,152.46,150.73,150.37,143.13,134.02,133.94,133.35,130.03,129.83,129.40,129.30,128.75,128.71,128.47,128.41,128.25,89.25,83.89,83.31,80.55,63.59,27.81;HRMS(ESI)calcdfor $C_{41}H_{41}N_5O_{11}Na[M+Na]^+$802.2695,found 802.2693。

[0174] 糖苷化产物P34：

[0175] 根据路线二,将I-13(40mg,0.073mmol)与II-20(21mg,0.061mmol)进行糖苷化反应,得到P34(40mg,83%),为白色固体:$[\alpha]_D^{25}$=-65.02(c 0.20,$CHCl_3$);^{1}HNMR(400MHz,$CDCl_3$)δ8.91(s,1H),8.27(s,1H),8.01(d,J=7.8Hz,2H),7.89(d,J=7.8Hz,2H),7.55(dd,J=18.9,7.4Hz,2H),7.39(dt,J=27.8,7.7Hz,4H),6.39(d,J=4.8Hz,1H),6.31(d,J=5.4Hz,1H),5.83(t,J=5.5Hz,1H),4.69-4.57(m,1H),1.65(d,J=6.4Hz,3H),1.46(s,18H);^{13}C NMR(101MHz,$CDCl_3$)δ165.42,165.10,152.84,152.41,150.68,150.36,143.42,133.74,133.64,129.80,129.77,129.57,128.94,128.54,128.48,87.28,83.89,79.19,75.13,74.10,27.80,18.83;HRMS(ESI)calcd for $C_{34}H_{37}N_5O_9Na[M+Na]^+$:682.2483,found:682.2487。

[0176] 糖苷化产物P35：

[0177] 根据路线二,将I-14(48mg,0.06mmol)与II-20(17mg,0.05mmol)进行糖苷化反应,得到P35(37mg,82%),为白色固体:$[\alpha]_D^{25}$=-19.09(c 0.15,$CHCl_3$);^{1}H NMR(400MHz,$CDCl_3$)δ8.87(s,1H),8.36(s,1H),8.13(d,J=7.7Hz,2H),8.06-7.80(m,7H),7.66-7.32(m,13H),6.64(d,J=3.1Hz,1H),6.44(t,J=2.9Hz,1H),6.14-6.03(m,1H),5.99(t,J=3.4Hz,1H),5.15(t,J=4.5Hz,1H),4.87-4.68(m,2H),1.45(s,18H);^{13}C NMR(101MHz,$CDCl_3$)δ166.04,165.70,165.54,165.32,152.85,152.47,150.71,150.34,143.17,133.93,133.79,133.54,133.24,130.03,129.96,129.88,129.69,129.34,129.26,129.17,128.70,128.57,128.54,128.40,128.09,89.29,83.89,80.76,77.74,70.78,63.20,27.81;HRMS(ESI)calcd for $C_{49}H_{47}N_5O_{13}Na[M+Na]^+$936.3063,found 936.3062。

[0178] 糖苷化产物P36：

[0179] 根据路线二,将I-15(48mg,0.06mmol)与II-20(17mg,0.05mmol)进行糖苷化反应,得到P36(38mg,84%),为白色固体:$[\alpha]_D^{25}$=-2.44(c 0.16,$CHCl_3$);^{1}H NMR(400MHz,$CDCl_3$)δ8.84(s,1H),8.54(s,1H),8.06(dd,J=25.2,7.9Hz,5H),7.77(d,J=7.8Hz,2H),7.56(s,1H),7.48(dt,J=15.2,6.2Hz,6H),7.38-7.28(m,9H),5.77(d,J=3.1Hz,1H),5.08(d,J=2.2Hz,2H),4.85(d,J=5.2Hz,2H),4.83-4.75(m,1H),1.38(s,18H);^{13}C NMR(101MHz,$CDCl_3$)δ166.10,165.23,165.03,164.50,152.64,152.25,150.86,150.33,142.63,134.10,

133.70,133.45,133.29,130.02,129.79,129.70,129.43,129.30,128.89,128.73,128.59,128.42,128.39,128.30,127.95,97.76,84.47,83.78,78.60,77.84,64.49,63.33,27.71;HRMS(ESI)calcd for $C_{49}H_{47}N_5O_{13}Na[M+Na]^+$936.3063,found 936.3066。

[0180] 糖苷化产物P37：

[0181] 根据路线二，将I-1(50.0mg,0.06mmol)与II-20(22.4mg,0.12mmol)进行糖苷化反应，得到P37(41.9mg,89％)，为白色固体:$[\alpha]_D^{25}$＝-16.8(c 0.11,CHCl3)；^{1}HNMR(400MHz,$CDCl_3$):δ8.71(s,1H),8.35(s,1H),7.94(d,J＝7.8Hz,2H),7.87(d,J＝7.8Hz,2H),7.75(d,J＝7.8Hz,2H),7.61(d,J＝7.8Hz,2H),7.51-7.13(m,12H),6.28(d,J＝8.3Hz,1H),6.16-6.03(m,2H),5.86(t,J＝8.9Hz,1H),4.63(d,J＝10.3Hz,1H),4.52-4.38(m,2H),1.25(s,18H)；^{13}CNMR(101MHz,$CDCl_3$)δ166.12,165.67,165.23,164.85,153.21,152.54,150.77,150.11,142.27,133.86,133.83,133.61,133.42,130.01,129.89,129.85,129.40,128.63,128.60,128.55,128.53,128.49,128.44,127.68,83.86,81.14,75.74,73.15,71.14,68.98,62.59,27.73;HRMS(ESI)calcd for $C_{49}H_{47}N_5O_{13}Na[M+Na]^+$936.3063,found936.3064。

[0182] 糖苷化产物P38：

[0183] 根据路线二，将I-3(65.0mg,0.08mmol)与II-20(22.6mg,0.07mmol)进行糖苷化反应，得到P38(41.6mg,67％)，为白色固体:$[\alpha]_D^{25}$＝150.2(c 0.20,CHCl3)；^{1}H NMR(400MHz,$CDCl_3$):δ8.84(s,1H),8.48(s,1H),8.18(d,J＝7.2Hz,2H),7.99(d,J＝6.9Hz,2H),7.79(d,J＝7.2Hz,2H),7.73-7.67(m,3H),7.61-7.53(m,3H),7.49-7.38(m,4H),7.31-7.21(m,4H),6.47(t,J＝9.7Hz,1H),6.28(d,J＝9.4Hz,1H),6.18(d,J＝3.3Hz,1H),5.88(dd,J＝10.1,3.3Hz,1H),4.74-4.61(m,2H),4.51(dd,J＝10.6,5.1Hz,1H),1.35(s,24H)；^{13}C NMR(101MHz,$CDCl_3$)δ166.13,165.47,165.44,165.00,153.26,152.60,150.83,150.19,142.50,134.10,133.90,133.69,133.57,130.14,129.96,129.93,129.83,129.23,129.02,128.95,128.76,128.62,128.55,128.53,128.50,127.83,83.91,81.67,74.72,72.05,68.87,68.11,62.04,27.79;HRMS(ESI)calcd for $C_{49}H_{48}N_5O_{13}[M+H]^+$914.3243,found 914.3238。

[0184] 糖苷化产物P39：

[0185] 根据路线二，将I-4(60.0mg,0.07mmol)与II-20(20.9mg,0.06mmol)进行糖苷化反应，得到P39(43.3mg,76％)，为白色固体:$[\alpha]_D^{25}$＝29.5(c 0.17,CHCl3)；^{1}HNMR(400MHz,$CDCl_3$):δ8.90(s,1H),8.43(s,1H),8.15(d,J＝7.8Hz,2H),8.03(t,J＝8.3Hz,4H),7.86(d,J＝7.8Hz,2H),7.65-7.30(m,12H),6.93(dd,J＝6.4,3.3Hz,1H),6.62(d,J＝6.3Hz,1H),6.24(dd,J＝6.0,3.4Hz,1H),5.88(t,J＝5.7Hz,1H),5.22(dd,J＝12.3,7.7Hz,1H),4.75-4.67(m,1H),4.56(dd,J＝12.3,3.3Hz,1H),1.37(s,18H)；^{13}C NMR(101MHz,$CDCl_3$)δ166.46,165.31,165.14,164.94,153.25,152.72,150.92,150.33,143.92,134.04,133.97,133.89,133.51,130.20,130.00,129.88,129.86,129.42,129.35,128.89,128.81,128.76,128.72,128.66,128.62,128.47,83.93,79.68,74.68,69.38,67.98,67.77,61.31,27.82;HRMS(ESI)calcd for $C_{49}H_{48}N_5O_{13}[M+H]^+$914.3243,found 914.3237。

[0186] 糖苷化产物P40：

[0187] 根据路线二，将I-9(55.0mg,0.08mmol)与II-20(23.0mg,0.07mmol)进行糖苷化反应，得到P40(36.6mg,68％)，为白色固体:$[\alpha]_D^{25}$＝45.4(c 0.12,CHCl3)；^{1}H NMR(400MHz,

$CDCl_3$):δ8.83(s,1H),8.43(s,1H),8.21(d,J=7.4Hz,2H),7.85(d,J=7.4Hz,2H),7.74-7.65(m,3H),7.57(t,J=7.6Hz,2H),7.50-7.40(m,2H),7.32-7.22(m,4H),6.48(t,J=9.7Hz,1H),6.16(d,J=9.3Hz,1H),5.93-5.88(m,1H),5.83(dd,J=10.0,3.4Hz,1H),4.52(dd,J=13.6,2.1Hz,1H),4.25(d,J=13.5Hz,1H),1.32(s,18H);^{13}C NMR(151MHz,$CDCl_3$)δ165.72,165.56,165.06,153.21,152.56,150.83,150.05,142.51,133.96,133.89,133.73,130.08,129.93,129.81,129.34,128.94,128.77,128.64,128.58,128.50,127.89,83.83,82.09,71.87,69.08,69.02,67.72,27.76;HRMS(ESI)calcd for $C_{41}H_{42}N_5O_{11}$[M+H]$^+$780.2875,found 780.2878。

[0188] 糖苷化产物P41:

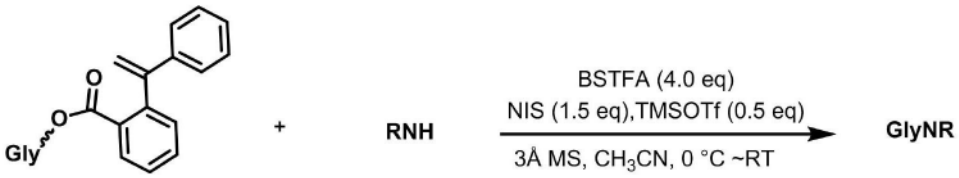
[0189] 根据路线二,将I-7(40mg,0.06mmol)与II-20(17mg,0.05mmol)进行糖苷化反应,得到P41(30mg,76%),为白色固体:[α]$_D^{25}$=-11.75(c 0.17,$CHCl_3$);^{1}H NMR(400MHz,$CDCl_3$)δ8.81(s,1H),8.42(s,1H),8.05-7.94(m,2H),7.94-7.84(m,2H),7.75-7.62(m,2H),7.55(d,J=7.5Hz,2H),7.50-7.22(m,10H),6.26-6.08(m,3H),5.65(td,J=9.8,5.8Hz,1H),4.63(dd,J=11.6,5.6Hz,1H),3.91(t,J=11.0Hz,1H),1.32(s,18H);^{13}C NMR(101MHz,$CDCl_3$)δ165.56,165.47,164.76,153.07,152.44,150.68,149.92,142.24,133.73,133.53,129.89,129.76,129.73,128.60,128.58,128.53,128.43,128.33,127.62,83.72,81.71,72.66,70.89,69.52,66.19,27.62;HRMS(ESI)calcd for $C_{41}H_{41}N_5O_{11}Na$[M+Na]$^+$802.2695,found 802.2694。

[0190] 糖苷化产物P42:

[0191] 根据路线二,将I-5(55.0mg,0.08mmol)与II-20(22.5mg,0.06mmol)进行糖苷化反应,得到P42(35.4mg,66%),为白色固体:[α]$_D^{25}$=-3.0(c 0.13,CHC13);^{1}HNMR(400MHz,$CDCl_3$):δ8.94(s,1H),8.43(s,1H),8.09(d,J=7.5Hz,2H),8.00(d,J=7.5Hz,2H),7.89(d,J=7.5Hz,2H),7.64-7.34(m,9H),6.61(dd,J=5.4,3.7Hz,1H),6.50(d,J=5.6Hz,1H),6.15(dd,J=6.2,3.5Hz,1H),5.63(t,J=6.1Hz,1H),4.46-4.37(m,1H),1.62(d,J=6.6Hz,3H),1.41(s,18H);^{13}C NMR(101MHz,$CDCl_3$)δ165.39,165.16,165.05,153.21,152.63,150.77,150.31,143.07,133.78,133.74,133.67,129.93,129.85,129.83,128.94,128.92,128.83,128.64,128.53,128.38,83.87,78.99,72.11,71.80,69.74,68.62,27.74,16.97;HRMS(ESI)calcd for $C_{42}H_{44}N_5O_{11}$[M+H]$^+$794.3032,found 794.3035。

[0192] 实施例3:

[0193] 本发明式P中的部分化合物按照下述路线三制备:

[0194] 

I II P

[0195] 其中,RNH为含有肿胺的嘧啶类化合物。

[0196] 具体步骤如下:在惰性气体气氛下,将N,O-双(三甲基硅烷基)三氟乙酰胺(BSTFA)(4.0当量)加入到式II受体(2.0当量)的无水CH_3CN(c=0.1M)悬浮液中,将混合物在50℃下搅拌30分钟后,将此溶液添加到已经在室温和惰性气体气氛下搅拌30分钟的式I糖苷化给

体(1.0当量)和活化的3ÅMS(4.0g/mmol)的无水CH_3CN(c＝0.05M)溶液。室温下继续搅拌10分钟,然后将反应冷却至0℃,向其中加入NIS(1.5当量)和TMSOTf(0.5当量)。逐渐升至室温后,将反应混合物搅拌3小时。待反应完全,加入Et_3N淬灭反应,DCM稀释,并在减压蒸馏下除去溶剂。所得残余物通过硅胶柱色谱法纯化,得到式P所示的糖苷化产物。

[0197] 糖苷化产物P43:

[0198] 根据路线三,将I-12(40mg,0.06mmol)与II-15(13.5mg,0.12mmol)进行糖苷化反应,得到P43(31mg,93%),为白色固体:$[\alpha]_D^{25}$＝-56.37(c 0.15,CHCl3);^{1}HNMR(400MHz,$CDCl_3$)δ9.01(s,1H),8.10(d,J＝7.8Hz,2H),7.96(dd,J＝14.9,7.8Hz,4H),7.54(m,5H),7.38(m,5H),6.32(d,J＝5.5Hz,1H),5.89(t,J＝5.3Hz,1H),5.76(t,J＝5.8Hz,1H),5.62(dd,J＝8.2,2.0Hz,1H),4.84(dd,J＝12.1,2.7Hz,1H),4.70(ddd,J＝16.0,9.9,4.0Hz,2H).^{13}C NMR(101MHz,$CDCl_3$)δ166.06,165.34,165.30,162.69,150.01,139.62,133.85,133.79,133.69,129.93,129.84,129.64,129.20,128.79,128.57,128.33,103.41,88.10,80.55,73.75,71.15,63.73;HRMS(ESI)calcd for $C_{30}H_{24}N_2O_9Na[M+Na]^+$579.1374,found 579.1376。

[0199] 糖苷化产物P44:

[0200] 根据路线三,将I-12(40mg,0.06mmol)与II-16(15mg,0.12mmol)进行糖苷化反应,得到P44(28mg,85%),为白色粉末:$[\alpha]_D^{25}$＝-59.58(c 0.20,$CHCl_3$);^{1}H NMR(400MHz,$CDCl_3$)δ8.58(s,1H),8.20-8.12(m,2H),7.97(dd,J＝14.8,7.7Hz,4H),7.66-7.48(m,5H),7.39(dt,J＝15.3,7.7Hz,4H),7.16(s,1H),6.43(d,J＝6.4Hz,1H),5.92(dd,J＝6.0,3.7Hz,1H),5.76(t,J＝6.2Hz,1H),4.89(dd,J＝12.1,2.6Hz,1H),4.74-4.61(m,2H),1.59(s,3H);^{13}C NMR(101MHz,$CDCl_3$)δ166.00,165.42,165.34,163.19,150.23,134.81,133.82,133.79,133.74,129.94,129.84,129.65,129.20,128.89,128.62,128.58,128.55,128.34,112.21,86.89,80.62,73.36,71.44,63.94,12.11;HRMS(ESI)calcd for $C_{31}H_{26}N_2O_9Na[M+Na]^+$593.1531,found 593.1535。

[0201] 糖苷化产物P45:

[0202] 根据路线三,将I-12(40mg,0.06mmol)与II-17(26mg,0.12mmol)进行糖苷化反应,得到P45(38mg,96%),为白色固体:$[\alpha]_D^{25}$＝-42.47(c 0.16,$CHCl_3$);^{1}H NMR(400MHz,$CDCl_3$)δ8.83(s,1H),8.11(d,J＝7.7Hz,2H),8.01-7.87(m,7H),7.66-7.47(m,9H),7.36(t,J＝7.6Hz,4H),6.46(d,J＝4.4Hz,1H),5.91(dt,J＝19.8,5.5Hz,2H),4.92-4.68(m,3H);^{13}C NMR(101MHz,$CDCl_3$)δ166.13,165.28,165.21,133.67,133.25,129.97,129.84,129.67,129.23,129.03,128.78,128.62,128.59,128.49,128.48,89.55,80.64,74.75,70.94,63.60;HRMS(ESI)calcdfor $C_{37}H_{29}N_3O_9Na[M+Na]^+$682.1796,found 682.1796。

[0203] 糖苷化产物P46:

[0204] 根据路线三,将I-12(40mg,0.06mmol)与II-18(16mg,0.12mmol)进行糖苷化反应,得到P46(33mg,96%),为白色固体:$[\alpha]_D^{25}$＝-56.64(c 0.13,$CHCl_3$);^{1}H NMR(400MHz,DMSO-d_6)δ12.04(s,1H),8.23(d,J＝6.8Hz,1H),8.06-7.96(m,2H),7.89(d,J＝7.7Hz,4H),7.72-7.58(m,3H),7.55-7.39(m,6H),6.19(d,J＝3.4Hz,1H),5.93(t,J＝3.3Hz,2H),4.73(ddt,J＝21.1,11.7,4.9Hz,3H);^{13}C NMR(101MHz,DMSO-d_6)δ165.94,165.03,157.66,157.40,149.50,141.82,139.52,134.42,134.31,134.02,129.82,129.77,129.63,129.21,129.16,

128.99,128.89,126.71,126.37,89.35,79.36,73.56,70.72,64.12;HRMS(ESI)calcd for$C_{30}H_{23}N_2O_9FNa$[M+Na]$^+$597.1280,found 597.1285。

[0205] 糖苷化产物P47：

[0206] 根据路线三,将I-13(40mg,0.073mmol)与II-19(26mg,0.146mmol)进行糖苷化反应,得到P47(34mg,93%),为白色固体:$[\alpha]_D^{25}$=-56.37(c 0.13,$CHCl_3$);^{1}HNMR(400MHz,Chloroform-d)δ9.38(s,1H),8.05-7.88(m,4H),7.63-7.49(m,2H),7.49-7.33(m,4H),6.52(d,J=46.7Hz,1H),6.08(d,J=4.6Hz,1H),5.73(t,J=5.3Hz,1H),5.45(t,J=5.9Hz,1H),4.52(t,J=6.2Hz,1H),1.59(d,J=6.4Hz,3H);^{13}C NMR(101MHz,$CDCl_3$)δ165.47,165.41,158.22,149.01,141.27,141.21,133.85,133.72,129.89,129.79,128.72,128.55,128.53,128.31,122.93,106.22,105.89,90.00,78.96,74.67,74.20,18.58;HRMS(ESI)calcd for$C_{24}H_{19}N_2O_7F_3Na$[M+Na]$^+$527.1037,found 527.1034。

[0207] 糖苷化产物P48：

[0208] 根据路线三,将I-11(40mg,0.06mmol)与II-15(13.5mg,0.12mmol)进行糖苷化反应,得到P48(30mg,91%),为白色固体:$[\alpha]_D^{25}$=5.6(c 0.16,$CHCl_3$);^{1}H NMR(400MHz,$CDCl_3$)δ8.80(s,1H),8.13-7.96(m,6H),7.67-7.35(m,12H),6.21(d,J=3.2Hz,1H),5.96(t,J=3.0Hz,1H),5.84-5.71(m,2H),4.97(q,J=4.6Hz,1H),4.81-4.59(m,2H);^{13}C NMR(101MHz,$CDCl_3$)δ166.10,165.37,165.25,162.81,149.95,140.27,134.02,133.97,133.37,130.05,129.86,129.82,129.35,128.72,128.69,128.50,128.42,128.30,102.71,91.75,83.80,80.55,77.23,63.89;HRMS(ESI)calcd for $C_{30}H_{24}N_2O_9Na$[M+Na]$^+$579.1374,found 579.1370。

[0209] 糖苷化产物P49：

[0210] 根据路线三,将I-14(48mg,0.06mmol)与II-19(22mg,0.12mmol)进行糖苷化反应,得到P49(44mg,96%),为白色固体:$[\alpha]_D^{25}$=-5.11(c 0.16,$CHCl_3$);^{1}H NMR(400MHz,$CDCl_3$)δ9.46(d,J=104.4Hz,1H),8.10(d,J=7.7Hz,2H),8.04-7.94(m,3H),7.90(dd,J=10.3,7.7Hz,4H),7.61(d,J=7.4Hz,1H),7.51(t,J=7.4Hz,3H),7.47-7.28(m,8H),6.52(d,J=44.1Hz,1H),6.40(d,J=2.5Hz,1H),6.09-6.01(m,1H),5.86(d,J=2.2Hz,2H),5.03-4.95(m,1H),4.85(dd,J=12.2,4.3Hz,1H),4.70(dd,J=12.2,6.1Hz,1H);^{13}C NMR(101MHz,$CDCl_3$)δ166.09,165.69,165.42,165.30,158.30,148.92,140.80,134.18,133.85,133.64,133.29,130.03,130.00,129.79,129.68,129.21,128.98,128.76,128.62,128.57,128.40,128.05,127.92,122.97,120.29,105.93,105.60,91.81,85.26,80.81,77.60,70.96,63.15;HRMS(ESI)calcd for $C_{39}H_{29}N_2O_{11}F_3Na$[M+Na]$^+$781.1616,found781.1615。

[0211] 糖苷化产物P50：

[0212] 根据路线三,将I-15(48mg,0.06mmol)与II-17(26mg,0.12mmol)进行糖苷化反应,得到P50(45mg,96%),为白色固体:$[\alpha]_D^{25}$=-4.66(c 0.20,$CHCl_3$);^{1}H NMR(400MHz,$CDCl_3$)δ9.69(s,1H),8.23(d,J=7.6Hz,1H),8.07(d,J=7.7Hz,2H),8.04-7.86(m,6H),7.65(d,J=7.6Hz,4H),7.56-7.34(m,11H),7.29(q,J=6.4,4.7Hz,5H),6.81(s,1H),5.61(d,J=2.5Hz,1H),5.30(d,J=11.8Hz,1H),5.18(d,J=11.8Hz,1H),4.71(dt,J=18.4,6.2Hz,3H);^{13}C NMR(101MHz,$CDCl_3$)δ166.06,165.48,164.77,164.27,163.34,144.45,133.91,133.84,133.35,133.23,133.15,130.04,129.77,129.68,129.58,129.29,129.25,128.83,

128.79,128.59,128.55,128.40,128.35,128.13,127.83,99.33,83.86,79.59,77.00,63.37,63.27;HRMS(ESI)calcd for $C_{45}H_{35}N_3O_{11}Na[M+Na]^+$:816.2164,found:816.2165。

[0213] 糖苷化产物P51：

[0214] 根据路线三,将I-1(50.0mg,0.06mmol)与II-19(22.4mg,0.12mmol)进行糖苷化反应,得到P51(41.9mg,89%),为白色固体:$[\alpha]_D^{25}$=3.1(c 0.10,CHC13);^{1}HNMR(600MHz,$CDCl_3$):δ8.03(d,J=7.1Hz,2H),7.98(s,1H),7.93(d,J=7.2Hz,2H),7.87(d,J=7.2Hz,2H),7.81(d,J=7.2Hz,2H),7.58(t,J=7.4Hz,1H),7.55-7.49(m,2H),7.46-7.42(m,3H),7.40-7.34(m,4H),7.30-7.27(m,2H),6.24(d,J=9.4Hz,1H),6.13(t,J=9.7Hz,1H),5.79(t,J=9.9Hz,1H),5.59(t,J=9.5Hz,1H),4.68(dd,J=12.5,2.7Hz,1H),4.51(dd,J=12.5,4.9Hz,1H),4.42(ddd,J=10.0,4.9,2.8Hz,1H);^{13}C NMR(151MHz,$CDCl_3$)δ166.15,165.59,165.51,165.21,157.36,148.99,134.23,133.94,133.74,133.59,130.17,130.04,129.90,129.87,129.31,128.75,128.70,128.66,128.56,128.40,127.67,121.49(q,J=268.5Hz),107.00(q,J=34.5Hz),81.13,75.82,72.50,70.77,68.63,62.43;HRMS(ESI)calcd for $C_{39}H_{29}F_3N_2O_{11}Na[M+Na]^+$781.1616,found 781.1603。

[0215] 糖苷化产物P52：

[0216] 根据路线三,将I-5(50.0mg,0.07mmol)与II-19(26.4mg,0.14mmol)进行糖苷化反应,得到P52(46.5mg,99%),为白色固体:$[\alpha]_D^{25}$=-72.0(c 0.10,CHC13);^{1}H NMR(400MHz,$CDCl_3$):δ9.22(s,1H),8.16-8.07(m,4H),8.03(s,1H),7.82(d,J=7.7Hz,2H),7.67(t,J=7.3Hz,2H),7.58-7.48(m,5H),7.32(t,J=7.6Hz,2H),6.63(d,J=9.4Hz,1H),6.02(t,J=3.5Hz,1H),5.68(dd,J=9.4,3.3Hz,1H),5.40-5.32(m,1H),4.64(q,J=6.8Hz,1H),1.75(d,J=7.2Hz,3H);^{13}C NMR(101MHz,$CDCl_3$)δ165.32,165.19,165.10,159.34,158.27,149.37,141.00,134.17,134.15,134.08,130.01,129.97,129.09,128.94,128.91,128.77,128.74,128.11,119.19,106.50,74.98,74.92,71.77,69.60,67.91,16.14;HRMS(ESI)calcd for $C_{32}H_{25}F_3N_2O_9Na[M+Na]^+$661.1404,found 661.1407。

[0217] 糖苷化产物P53：

[0218] 根据路线三,将I-9(40mg,0.06mmol)与II-19(22mg,0.12mmol)进行糖苷化反应,得到P53(35mg,93%),为白色固体:$[\alpha]_D^{25}$=-117.86(c 0.19,$CHCl_3$);^{1}HNMR(400MHz,$CDCl_3$))δ8.16-8.03(m,3H),7.86(dd,J=17.0,7.8Hz,4H),7.66(d,J=7.4Hz,1H),7.51(dt,J=21.0,7.6Hz,4H),7.45-7.19(m,5H),6.21-6.07(m,1H),5.83(d,J=2.5Hz,3H),4.42(d,J=13.6Hz,1H),4.15(d,J=13.4Hz,1H);^{13}C NMR(101MHz,$CDCl_3$)δ165.72,165.33,157.55,149.16,140.54,134.03,133.95,133.66,129.95,129.78,129.69,129.04,128.88,128.63,128.46,128.44,127.79,122.81,107.04,106.70,81.58,71.00,69.00,68.68,67.32.HRMS(ESI)calcd for $C_{31}H_{23}N_2O_9F_3Na[M+Na]^+$647.1248,found 647.1248。

[0219] 糖苷化产物P54：

[0220] 根据路线三,将I-9(40.0mg,0.06mmol)与II-18(15.6mg,0.12mmol)进行糖苷化反应,得到P54(33.8mg,98%),为白色固体:$[\alpha]_D^{25}$=268.5(c 0.10,CHC13);^{1}H NMR(400MHz,$CDCl_3$):δ9.20(s,1H),8.11(d,J=7.5Hz,2H),7.88(d,J=7.6Hz,2H),7.84(d,J=7.6Hz,2H),7.67(t,J=7.3Hz,1H),7.61-7.53(m,3H),7.52-7.44(m,2H),7.34(t,J=7.8Hz,2H),7.29(t,J=7.8Hz,2H),6.09(d,J=8.6Hz,1H),5.89-5.76(m,3H),4.42(d,J=13.3Hz,1H),

4.15(d,J＝13.6Hz,1H);^{13}C NMR(101MHz,$CDCl_3$)δ165.71,165.64,165.42,156.58,156.31,149.08,142.21,139.82,134.03,133.97,133.71,130.06,129.88,129.26,128.97,128.72,128.64,128.56,128.08,123.85,123.51,81.78,71.35,69.09,68.45,67.54;HRMS(ESI)calcd for $C_{30}H_{23}FN_2O_9Na[M+Na]^+$597.1280,found 597.1280。

[0221] 糖苷化产物P55：

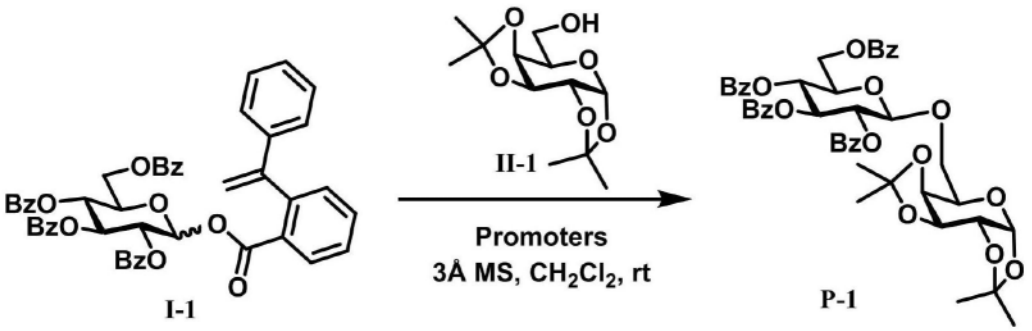
[0222] 根据路线三,将I-7(40mg,0.06mmol)与II-19(22mg,0.12mmol)进行糖苷化反应,得到P55(34mg,92％),为白色固体:$[\alpha]_D^{25}$＝-2.18(c 0.21,$CHCl_3$);^{1}H NMR(400MHz,Chloroform-d)δ9.09(s,1H),8.10-7.85(m,6H),7.57-7.27(m,9H),6.44(d,J＝41.1Hz,1H),6.15(dt,J＝9.9,5.0Hz,2H),5.63-5.45(m,2H),4.56(dd,J＝11.5,5.7Hz,1H),3.82(t,J＝11.1Hz,1H);^{13}C NMR(101MHz,$CDCl_3$)δ165.51,165.45,157.68,149.18,140.70,140.64,134.01,133.79,133.60,129.98,129.89,129.73,128.61,128.58,128.47,128.45,127.61,122.78,120.10,106.92,106.58,81.61,72.07,70.61,69.27,65.98;HRMS(ESI)calcd for $C_{31}H_{23}N_2O_9F_3Na[M+Na]^+$647.1248,found 647.1245。

[0223] 糖苷化产物P56：

[0224] 根据路线三,将I-7(60.0mg,0.09mmol)与II-18(23.3mg,0.18mmol)进行糖苷化反应,得到P56(51.1mg,99％),为白色固体:$[\alpha]_D^{25}$＝14.7(c 0.16,CHCl3);^{1}H NMR(400MHz,$CDCl_3$):δ9.42(s,1H),7.97(d,J＝7.5Hz,2H),7.90-7.82(m,4H),7.61(d,J＝5.6Hz,1H),7.54(t,J＝7.4Hz,1H),7.51-7.38(m,4H),7.35-7.27(m,4H),6.11(dt,J＝9.6,5.2Hz,2H),5.57(t,J＝9.4Hz,1H),5.49(td,J＝10.1,5.7Hz,1H),4.53(dd,J＝11.4,5.6Hz,1H),3.81(t,J＝11.0Hz,1H);^{13}C NMR(101MHz,$CDCl_3$)δ165.67,165.61,165.48,156.77,156.50,149.13,142.16,139.77,134.03,133.87,133.66,130.08,129.99,129.83,128.71,128.67,128.62,128.55,127.91,123.97,123.63,81.76,72.37,70.35,69.49,65.93;HRMS(ESI)calcd for $C_{30}H_{24}FN_2O_9[M+H]^+$575.1460,found 575.1459。

[0225] 本说明书中各个实施例采用递进的方式描述,每个实施例重点说明的都是与其他实施例的不同之处,各个实施例之间相同相似部分互相参见即可。对于实施例公开的装置而言,由于其与实施例公开的方法相对应,所以描述的比较简单,相关之处参见方法部分说明即可。

[0226] 对所公开的实施例的上述说明,使本领域专业技术人员能够实现或使用本发明。对这些实施例的多种修改对本领域的专业技术人员来说将是显而易见的,本文中所定义的一般原理可以在不脱离本发明的精神或范围的情况下,在其它实施例中实现。因此,本发明将不会被限制于本文所示的这些实施例,而是要符合与本文所公开的原理和新颖特点相一致的最宽的范围。



Entry	Promotor (equiv)	Product	Yield
1	$Ph_3PAuOTf$ (0.5)	--	NR
2	AgOTf (1.0)	--	NR
3	$Cu(OTf)_2$ (1.0)	--	NR
4	TMSOTf (0.5)	--	Trace
5	TfOH (0.5)	3a	9%
6	MeOTf (1.0)	--	NR
7	NIS (2.5), TMSOTf (0.3)	3a	97%[c]
8	NIS (1.5), TMSOTf (0.3)	3a	94%[c]

图1