JOC The Journal of Organic Chemistry

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/jo501488x • Publication Date (Web): 22 Sep 2014

Synthesis of substituted momo- and di-indole *C*-nucleoside analogs from terminal sugar alkynes by sequential Sonogashira/ heteroannulation reaction

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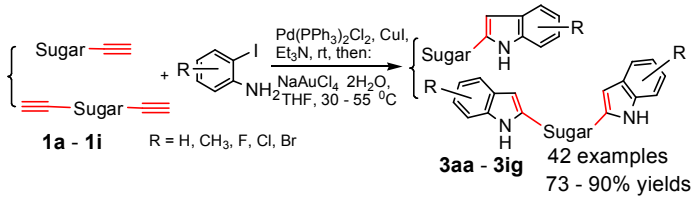


ABSTRACT: The synthesis of substituted mono- and di-indole *C*-nucleoside analogs has been achieved in good to excellent yields by sequential Sonogashira coupling/$NaAuCl_4$ catalyzed heteroannulation reactions of substituted 2-iodoanilines with various sugar terminal alkynes in one pot. The method is general, mild and efficient and suitable for a wide range of sugar substrates, and forty two examples are given. The amino group of the substituted 2-iodoanilines is unprotected. The sugar terminal alkynes include furanosides,

pyranosides and acyclic glycosides with free hydroxyl groups, sensitive functional subtituents and various protected groups having different steric hindrance.

INTRODUCTION

Heteroaryl *C*-nucleosides have received much attention due to their interesting biological activities and their use in the extension of the genetic alphabet.[1] Indole represents an important artificial DNA base because of its structural similarity with guanine and adenine.[1g,2] It is also a very crucial charge transport trap in DNA, especially for *C*-2 or *C*-3 substituted indole *C*-nucleosides.[3] Figure 1 shows α-*C*-mannosyltryptophan discovered in Trp7 of ribonuclease 2[4] and two *C*-2 substituted indole *C*-nucleoside analogs isolated recently from the roots of *Isatis indigotica*, which display significant cytotoxic activities against human liver cancer HepG2 cells, human myeloid leukemia HL-60 and human myeloid leukemia Mata.[5] The methods for the synthesis of *C*-2 and *C*-3 substituted indole derivatives are well documented.[6] Catalytic heteroannulation of functionalized 2-alkynylaniline derivatives is the most efficient approach for the synthesis of *C*-2 substituted indole derivatives.[6a-6j,7] Many kinds of catalysts were reported for these cyclizations, and transition-metal-promoted heteroannulations have been achieved.[6g−6j,8] Base-promoted heteroannulations of 2-alkynylphenylamines and their *N*-protected derivatives have also been established.[6i,6k,9] I_2 and iodinating reagent were successfully used for electrophilic cyclizations to synthesize *C*-2 substituted 3-iodoindoles.[10]

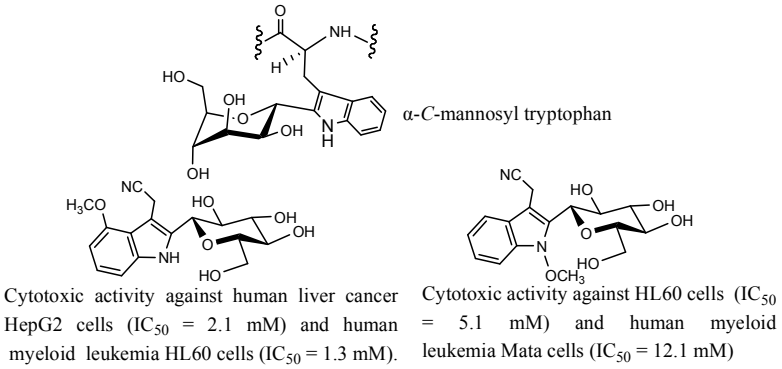


Figure 1. Examples of naturally occurring indole *C*-nucleoside analogs.

Among the approaches used for the synthesis of *C*-2 and *C*-3 substituted indole *C*-nucleoside analogs, the most common method is the addition of *N*-protected lithio-indoles onto sugar lactones or lactols followed by reduction.[11] *C*-glycosylation of indole derivatives with glycosyl donors promoted by boron trifluoride–diethyl etherate[12] or trifluoromethanesulfonic anhydride[13] has also been employed. Recently, catalytic heteroannulation of sugar 2-alkynylanilines has been developed. Minehan and co-workers reported a concise route to a natural indole *C*-nucleoside analog[5] by Sonogashira coupling of sugar alkyne with 2-iodo-3-nitrophenol, nitro group reduction, and subsequent heteroannulation of sugar 2-alkynylaniline promoted by potassium *tert*-butoxide.[14] Hocek's group synthesized 1-α- and 1-β-(indol-2-yl)-2′-deoxyribose *C*-nucleosides based on the Sonogashira reaction of 1α- and 1β-ethynyldeoxyribose and 2-haloanilines followed by a Pd-complex catalyzed cyclization.[15] Isobe reported the synthesis of *C*-2 substituted indole *C*-nucleoside analogs by a Pd-mediated Sonogashira coupling of sugar alkynes with *N*-tosyl-2-iodoaniline, a Cu-mediated Castro cyclization, and subsequent removal of *N*-tosyl group by tetrabutylammonium fluoride.[16] In view of

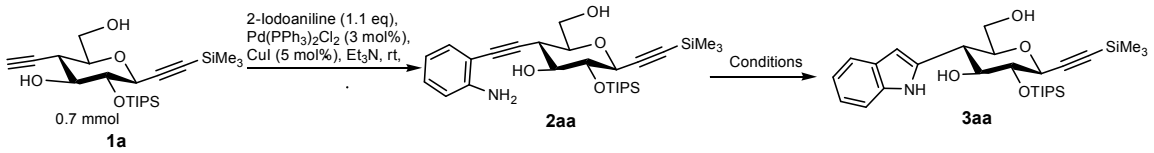
the biological importance of *C*-2 substituted indole *C*-nucleoside analogs, and our interest in the syntheses of biologically active carbohydrate analogues[17] as well as *C*-substituted sugar analogues,[18] we describe herein a general, mild and efficient synthesis of *C*-2 substituted mono- and di-indole *C*-nucleoside analogs from various sugar alkynes.

RESULTS AND DISCUSSION

Terminal alkynes serving as building blocks for the synthesis of substituted indoles by Sonogashira coupling with substituted 2-haloanilines have been reported and most substrates were phenylacetylene.[6e–6o] In order to find a general reaction system tolerant of various functional groups and structural diversity of sugar alkynes in one pot, at the outset, **1a**[19] (Scheme 1) with sterically bulky triisopropylsilyl, unprotected hydroxyl groups and sensitive trimethylsilylethynyl group was deliberately used as a model to perform the Sonogashira coupling/heteroannulation reaction. In the optimization studies, the two-step reactions were examined, respectively. Sonogashira coupling reaction of **1a** with 2-iodoaniline was performed under classical conditions in the presence of $Pd(PPh_3)_2Cl_2$, CuI and Et_3N in degassed solvent. The influence of solvent, the amount of the catalyst and temperature on the reaction was examined in detail. When the reaction was carried out in THF, the coupling product sugar substituted 2-ethynylaniline **2aa** (Scheme 1) was obtained in 85% yield. The change of a solvent to MeCN and CH_2Cl_2 gave rise to **2aa** in 80% and 88% yield, respectively. In these cases, the undesired homocoupling product 1,3-diyne was not observed. The best result was obtained using

1.1 equiv of 2-iodoaniline, 1.0 equiv of **1a**, 3 mol% of $Pd(PPh_3)_2Cl_2$ and 5 mol% of CuI in pure degassed Et_3N. The coupling reaction was complete within 5 h at rt and **2aa** was attained in 95% isolated yield. Heteroannulation product **3aa** was not obtained under these conditions. After the coupling reaction of **1a** with 2-iodoaniline was accomplished, an attempt to carry out a tandem reaction by increasing the temperature to 60 ^{0}C gave **3aa** only in 18% yield.

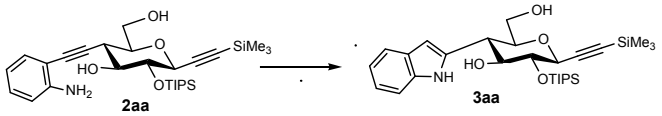
Scheme 1. Synthesis of 2aa and 3aa



The second task was the development of the high yielding heteroannulation of **2aa** (Table 1). Although many examples for the intramolecular heteroannulation of 2-alkynylaniline to indole were reported,[6a-6j,7] elevated temperature, prolonged reaction time in strong basic or Lewis acidic media are not suitable for the sugar substituted alkynylaniline possessing complex structures and sensitive functional substituents. In order to get a general and efficient catalytic system for heteroannulation of various sugar 2-ethynylanilines, many catalysts were scanned using isolated **2aa** as starting material and some results are listed in Table 1. Strong bases such as t-BuOK in THF and $NaNH_2$ in DMF at 50 ^{0}C gave **3aa** in very low yields of 12% and 15% (entries 1 and 2). In the two cases, TLC indicated most of **2aa** decomposed. The change of catalyst to a Lewis acid gave better results. The use of $ZnCl_2$ in toluene at 80 ^{0}C afforded **3aa** in 20% yield, and $InBr_3$ gave the similar result (entries 3 and 4). A slight increase in yield of 28% was

obtained in toluene by the use of $Cu(OTf)_2$ (entry 5). When $Pd(MeCN)_2Cl_2$ was used in MeCN at 60 ^{0}C, **3aa** was obtained in 38%, which was better than that using $PdCl_2$ (entries 7 and 8). Fortunately, $NaAuCl_4 \cdot 2H_2O$ was found to be an efficient catalyst for heteroannulation of **2aa** to indole *C*-nucleoside. In the presence of 3 mol % of $NaAuCl_4 \cdot 2H_2O$, the best yield of **3aa** (86%) was achieved in THF at 50 ^{0}C (entry 9).

Table 1. Heteroannulation of Sugar 2-Ethynylaniline 2aa under Various Conditions[a]



Entry	Catalyst	Solvent	T (^{0}C)	Time (h)	Yield (%)[b]
1	t–BuOK	THF	50	6	12
2	$NaNH_2$	DMF	50	5	15
3	$ZnCl_2$	Toluene	80	4.5	20
4	$InBr_3$	Toluene	80	3	22
5	$Cu(OTf)_2$	Toluene	80	3	28
6	$CuCl_2$	$(CH_2Cl)_2$	80	3.5	20
7	$Pd(MeCN)_2Cl_2$	MeCN	60	5	38
8	$PdCl_2$	DMF	60	5.5	30
9	**$NaAuCl_4 \cdot 2H_2O$**[c]	**THF**	**50**	**4.5**	**86**
10	$NaAuCl_4 \cdot 2H_2O$	EtOH	50	5	70

[a]Conditions: 0.4 mmol sugar 2–ethynylaniline **2aa**, 5 mol % catalyst, 6 mL solvent. [b]Isolated yield. [c]3 mol %.

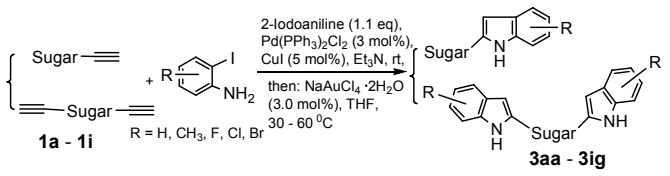
After obtaining the optimal conditions for the two steps, we carried out Sonogashira coupling/heteroannulation reaction in one pot. When the coupling of **1a** with 2-iodoaniline was finished under the optimal conditions, Et_3N was removed; THF and 3 mol % of $NaAuCl_4 \cdot 2H_2O$ were then added and the mixture stirred for 4.5 h at 50 ^{0}C to afford **3aa** in 83% yield. In order to examine the electronic effect of the substituents of 2-iodoaniline on the reactions and to obtain different substituted indole patterns for

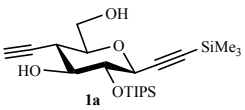
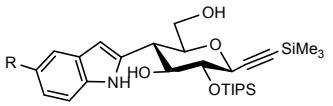
nucleobase surrogate, 2-iodoanilines with electron-donating, electron-neutral, and electron-withdrawing substituents were used to react with **1a**. Fortunately, all cases the sequence proceeded smoothly to give the corresponding products in high yields (Table 2, entry 1). Next, terminal sugar diyne **1b** (entry 2) having a sterically bulky triisopropylsilyl group and two unprotected hydroxyl groups was used to react with some substituted 2-iodoaniline to test this protocol. The corresponding di-indole *C*-nucleoside analogs with electron-neutral, electron-donating and electron-withdrawing substituents in the indole rings were afforded in high yields.

To investigate the scope and generality of this method further, different other sugar alkynes including sugars in furanose, pyranose and acyclic forms with various protected groups and free hydroxyl groups having different steric hindrance were employed in reactions with various substituted 2-iodoanilines. The results are also summarized in Table 2. The substituted 2-iodoaniline having electron-donating substituent gave a slightly higher yield than that having an electron-neutral or electron-withdrawing substituent. This is the same as the cases for **1a** and **1b** described. The steric hindrance of the sugar alkynes also affects the Sonogashira coupling/heteroannulation reaction. For the furanoside alkynes **1c**−**1e** (Table 2, entries 3−5), **1c** with *trans* isopropylidene next to ethynyl exhibited clean reaction and afforded *C*-nucleoside analogs **3ca**−**3ce** in excellent yields (83−90%). Alkynes **1d** and **1e** (entries 4 and 5) with *cis* isopropylidene and benzyloxy next to ethynyl respectively gave the corresponding products in slightly lower yields (73−78%), probably due to increased steric hindrance. In these two cases, the

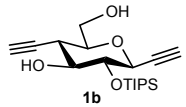
starting material can't be converted completely. Increasing the temperature and prolonged reaction time caused the decomposition of the starting material. However, the pyranoside alkynes **1f** and **1g** (entries 6 and 7) with *cis* and *trans* isopropylidenes next to ethynyl respectively, proceeded very smoothly and the corresponding products were obtained in 80−88% yields. Then we turned our attention to acyclic alkynes. Alkynes **1h** and **1i** (entries 8 and 9) were used to perform the Sonogashira coupling/heteroannulation reactions. Both acyclic alkynes are much more reactive than the furanoside and pyranoside ones, probably because the acyclic chains are more flexible and have less steric hindrance, leading to the corresponding substituted indole acyclic *C*-nucleoside analogs in excellent yields. The structures of all the new compounds (**3aa**−**3ig**) were characterized by ^{1}H NMR, ^{13}C NMR, DEPT-135, ^{19}F NMR, 2D NMR, HRMS and IR spectra.

Table 2. Synthesis of mono- and di-indole *C*-nucleoside analogs *via* sequential Sonogashira coupling/heteroannulation reactions of various terminal sugar alkynes with substituted 2-iodoanilines

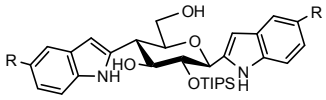


Entry	Terminal sugar alkynes	Product, Temperature, Time, Yield[a]
1		 **3aa**: R = H, 50 ^{0}C, 5.0 h, 83% **3ab**: R = CH_3,50 ^{0}C, 4.0 h, 87% **3ac**: R = F, 50 ^{0}C, 10.0 h, 78% **3ad**: R = Cl, 50 ^{0}C, 8.0 h, 80% **3ae**, R = Br, 50 ^{0}C, 7.5 h, 85%

2

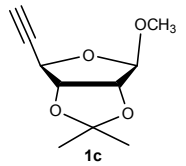


1b

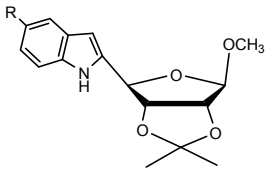


3ba: R = H, 50 ^{0}C, 5.0 h, 88%
3bb: R = CH_3,50 ^{0}C, 4.0 h, 90%
3bc: R = F, 50 ^{0}C, 8.0 h, 84%
3bd: R = Cl, 50 ^{0}C, 7.5 h, 87%
3be, R = Br, 50 ^{0}C, 6 h, 85%

3

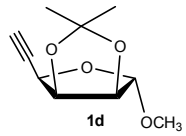


1c

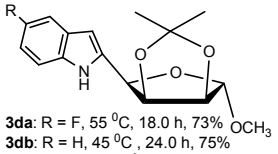


3ca: R = Cl, 50 ^{0}C, 8.0 h, 83%
3cb: R = H, 50 ^{0}C, 4.0 h, 85%
3cc: R = CH_3, 50 ^{0}C, 3.0 h, 90%
3cd: R= F, 50 ^{0}C, 10.0 h, 80%
3ce: R= Br, 50 ^{0}C, 7.5 h, 83%

4

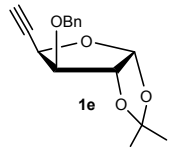


1d

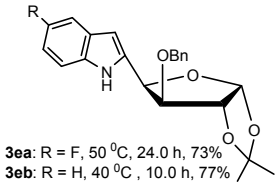


3da: R = F, 55 ^{0}C, 18.0 h, 73%
3db: R = H, 45 ^{0}C , 24.0 h, 75%
3dc: R = CH_3, 50 ^{0}C, 24.0 h, 78%

5

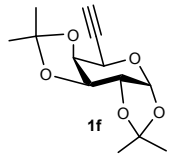


1e

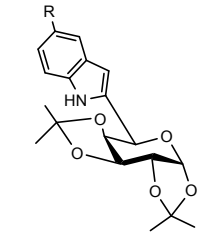


3ea: R = F, 50 ^{0}C, 24.0 h, 73%
3eb: R = H, 40 ^{0}C , 10.0 h, 77%

6

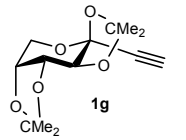


1f

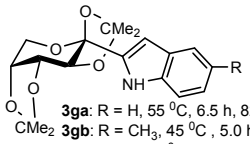


3fa: R = H, 45 ^{0}C, 8.0 h, 82%
3fb: R = CH_3, 45 ^{0}C , 5.0 h, 85%
3fc: R = F, 55 ^{0}C, 9.0 h, 80%
3fd: R = Cl, 55 ^{0}C, 8.0 h, 84%
3fe: R = Br, 50 ^{0}C, 7.5 h, 87%

7

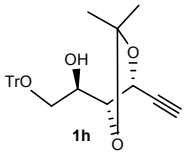


1g

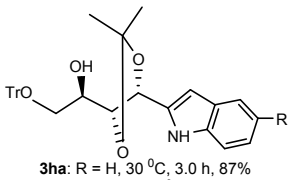


3ga: R = H, 55 ^{0}C, 6.5 h, 82%
3gb: R = CH_3, 45 ^{0}C , 5.0 h, 88%
3gc: R = F, 55 ^{0}C, 9.0 h, 80%
3gd: R = Cl, 55 ^{0}C, 8.0 h, 85%
3ge: R = Br, 55 ^{0}C, 7.5 h, 85%

8

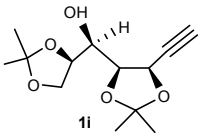


1h

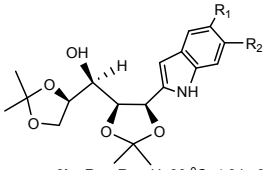


3ha: R = H, 30 ^{0}C, 3.0 h, 87%
3hb: R = CH_3, 45 ^{0}C , 5.0 h, 90%
3hc: R = F, 45 ^{0}C, 4.0 h, 83%
3hd: R = Cl, 35 ^{0}C, 4.0 h, 89%
3he: R = Br, 30 ^{0}C, 5.0 h, 87%

9



1i



3ia: R_1 = R_2 = H, 30 ^{0}C, 4.0 h, 88%
3ib: R_1 = CH_3, R_2 = H, 25 ^{0}C, 3.0 h, 90%
3ic: R_1 = F, R_2 = H, 45 ^{0}C, 5.0 h, 86%
3id: R_1 = H, R_2 = F, 55 ^{0}C, 3.5 h, 84%
3ie: R_1 = Cl, R_2 = H, 35 ^{0}C, 5.0 h, 85%
3if: R_1 = H, R_2 = Cl, 50 ^{0}C, 4.0 h, 90%
3ig: R_1 = Br, R_2 = H, 30 ^{0}C, 5.0 h, 88%

[a]Isolated yield

CONCLUSIONS

We have developed a new approach to synthesize substituted mono- and di-indole *C*-nucleoside analogs by the sequential Sonogashira coupling/heteroannulation reactions of substituted 2-iodoanilines with terminal sugar alkynes. Various substituted indoles as the isosterical surragates of the structurally similar guanine and adenine have been coupled in the sugars. This method is simple, mild and efficient and the desired products were obtained in good to excellent yields. The scope and generality have been examined and forty two examples are given. The sugar alkynes include furanosides, pyranosides, and acyclic glycosides derived from various cheap and abundant natural sugars. The reaction conditions are tolerant of various structurally complex sugars having sterically bulky groups, unprotected hydroxyl groups, sensitive substituents, as well as various protecting groups. The modification and biological study of these *C*-nucleoside analogs

are in progress.

EXPERIMENTAL SECTION

Synthesis of 3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-6-*C*-ethynyl-4-*O*-(triisopropylsily1)-1-*C*-(trimethylsilyl)-D-glycero-D-gulo-octitol (1a).[19] A solution of $AgNO_2$ (10.7 g, 69.5 mmol) in MeOH/H_2O 25:8 (33 mL) was added to a solution of protected 1,4-dideoxy-1,4-diethyny1-β-D-glucopyranose[19] (11.6 g, 23.3 mmol) in MeOH (120 mL). The mixture was stirred at rt for 4 h. Then it was cooled to 0 ^{0}C, treated with saturated KCN solution (18 mL), carefully neutralized with 2 N HCl *(ca.* 35 mL) and evaporated to remove MeOH. The residue was dissolved in EtOAc (80 mL), washed with water (2 × 15 mL). The organic phase was dried over Na_2SO_4 and evaporated to dryness to give **1a** (8.9 g, 90%) as a white solid. R_f = 0.5 (silica gel F_{254}, 3:1, petroleum ether/EtOAc); Mp: 136−138 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (d, 1H, J = 9.2 Hz), 3.94−3.93 (m, 1H), 3.77−3.71 (m, 1H), 3.63 (t, 1H, J = 8.4 Hz), 3.57−3.51 (m, 1H), 3.48−3.44 (m, 1H), 2.58−2.52 (m, 1H), 2.47 (s, 1H), 2.22 (d, 1H, J = 2.4 Hz), 2.08 (s, 1H), 1.30−1.10 (m, 21H), 0.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 102.3, 91.4, 80.2, 79.0, 77.0, 75.3, 73.0, 72.1, 63.6, 37.6, 18.5, 13.2, 0.3.

Synthesis of 3,7-Anhydro-l,1,2,2-tetradehydro-l,2,6-trideoxy-6-*C*-ethynyl-4-*O*-(triisopropylsilyl)-D-glycero-D-gulo-octitol (1b).[19] A 0.5 N NaOH solution (3 mL) was added to a solution of protected 1,4-dideoxy-1,4-diethyny1-β-D-glucopyranose[19] (1.0 g, 2.0 mmol) in MeOH (30 mL). The mixture was stirred at rt until TLC indicated the

completion of the reaction. Then it was neutralized with 1 N HCl (1.5 mL) and evaporated to remove MeOH. The residue was dissolved in EtOAc (30 mL), washed with water (2 × 5 mL). The organic phase was dried over Na_2SO_4 and evaporated to dryness to give **1b** (0.64 g, 90%) as a white solid. R_f = 0.5 (silica gel F_{254}, 3:1, petroleum ether/EtOAc); Mp: 113−115 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (dd, 1H, J = 9.2 Hz, J = 2.2 Hz), 3.94−3.91 (m, 1H), 3.82−3.71 (m, 1H), 3.66 (t, 1H, J = 9.0 Hz), 3.58−3.53 (m, 1H), 3.50−3.46 (m, 1H), 2.60−2.54 (m, 1H), 2.50 (s, 1H), 2.49 (d, 1H, J = 2.1 Hz), 2.23 (d, 1H, J = 2.4 Hz), 2.09 (s, 1H), 1.26−1.09 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 81.1, 80.2, 79.0, 76.7, 75.1, 74.8, 73.1, 71.3, 63.4, 37.7, 18.4, 13.0.

General procedure for the preparation of 1c−1g. [20]

A solution of CBr_4 (2 equiv) in dry CH_2Cl_2 was added to a mixture of zinc (3 equiv), PPh_3 (3 equiv) and dry CH_2Cl_2 at 0 ^{0}C. Then sugar aldehyde[20c−20i] (1.0 equiv) in dry CH_2Cl_2 was added dropwise for 10 min. The mixture was stirred at rt until TLC indicated the complete conversion of sugar aldehyde. Then it was evaporated and the residue was purified by column chromatography (silica gel, 6:1−3:1, petroleum ether/EtOAc) to give a syrup.

A 2.5 M *n*-butyllithium solution in dry THF (2.5 equiv) was added to a solution of the syrup (1.0 equiv) in dry THF at −45 ^{0}C. The mixture was stirred until TLC indicated the completion of the reaction. It was quenched by water (*ca*. 2.5 equiv) and evaporated. The residue was dissolved in EtOAc, washed with water. The organic phase was dried over Na_2SO_4 and evaporated. The residue was purified by column chromatography (silica gel,

5:1−3:1, petroleum ether/EtOAc) to give **1c**−**1g**.

1-O-Methyl-5,6-dideoxy-2,3-O-isopropylidene-β-D-ribo-hex-5-ynofuranoside ***(1c)***.[20c,20d] White solid, 457 mg, 68% yield; R_f = 0.5 (silica gel F_{254}, 6:1, petroleum ether/EtOAc); Mp: 63−64 ^{0}C ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.97 (s,1H), 4.78 (d, 1H, $J_{3,2}$ = 6.0 Hz), 4.68 (d, 1H, J = 2.8 Hz), 4.58 (d, 1H, J = 6.0 Hz), 3.27 (s, 3H), 1.34, 1.20 (2s, each 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.5, 109.2, 85.3, 85.1, 81.5, 74.6, 74.1, 54.1 , 26.2, 24.8.

1-O-Methyl-5,6-dideoxy-2,3-O-isopropylidene-α-D-lyxo-hex-5-ynofuranoside ***(1d)***. [20c,20d] Yellow solid, 486 mg, 74% yield; R_f = 0.5 (silica gel F_{254}, 6:1, petroleum ether/EtOAc); Mp: 45−46 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 (s, 1H), 4.72 (d, 1H, J = 4.0 Hz), 4.60 (dd, 1H, J = 5.6 Hz, J = 4.0 Hz), 4.53 (d, 1H, J = 5.6 Hz), 3.32 (s, 3H), 1.50, 1.32 (2s, each 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.4, 107.2, 84.8, 80.6, 77.4, 76.6, 70.6, 55.0, 26.3, 25.3.

3-O-Benzyl-5,6-dideoxy-1,2-O-isopropylidene-α-D-xylo-hex-5-ynofuranose ***(1e)***.[20c−20g] Colourless oil, 438 mg, 72% yield; R_f = 0.6 (silica gel F_{254}, 4:1, petroleum ether/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.27 (m, 5H), 5.96 (d, 1H, J = 3.6 Hz), 4.83 (t, 1H, J = 2.4 Hz, J = 2.8 Hz), 4.81 (d, 1H, J = 12.4 Hz), 4.74 (d, 1H, J = 12.4 Hz), 4.58 (d, 1H, J = 3.6 Hz), 4.02 (d, 1H, J = 2.8 Hz), 2.64 (d, 1H, J = 2.4 Hz), 1.49, 1.31 (2s, each 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 128.5, 128.0, 127.8, 112.0, 104.7, 82.8, 82.4, 77.6, 76.6, 72.6, 70.7, 26.8, 26.2.

6,7-Dideoxy-1,2:3,4-di-O-isopropylidene-α-D-galacto-hept-6-ynopyranose

(1f).[20c,20d,20g] Colourless oil, 583 mg, 76% yield; R_f= 0.7 (silica gel F_{254}, 4:1, petroleum ether/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 (d, 1H, J= 4.8 Hz), 4.60−4.58 (m, 2H), 4.29−4.25 (m, 2H), 2.51 (d, 1H, J = 2.0 Hz), 1.48, 1.47, 1.32, 1.27 (4s, each 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.9, 108.9, 96.4, 78.8, 74.5, 72.6, 70.6, 70.1, 60.0, 26.1, 25.9, 24.7, 24.3.

1,2-Dideoxy-3,4:5,6-di-O-isopropylidene-β-D-arabino-hept-1-yn-3-ulo-3,7-pyranose ***(1g)***.[20h,20i] Colourless oil, 532 mg, 80% yield; R_f= 0.7 (silica gel F_{254}, 4:1, petroleum ether/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53 (dd, 1H, J= 2.0 Hz, J= 8.0 Hz), 4.43 (d, 1H, J = 2.0 Hz), 4.18−4.15 (m, 1H), 3.73−3.67 (m, 2H), 2.58 (s, 1H), 1.46, 1.45, 1.40, 1.29 (4s, each 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.6, 109.5, 95.8, 81.8, 75.7, 72.4, 70.4, 70.2, 61.2, 26.1, 26.0, 24.6, 24.2.

General procedure for the preparation of 1h and 1i.[21,22] A mixture of sugar hemiacetal (10.0 mmol), anhydrous K_2CO_3 (4.1 g, 30.0 mmol) and dry MeOH (20 mL) was refluxed, to which Ohira's reagent (6.7 g, 35.0 mmol) in dry MeOH (20 mL) was added dropwise for 6−8 h. TLC indicated completion of the reaction. The mixture was evaporated to dryness and water (30 ml) was added. The solution was extracted with EtOAc (4 × 10 mL). The combined organic phases were dried over Na_2SO_4 and evaporated. The residue was purified by column chromatography (silica gel, 6:1−4:1, petroleum ether/EtOAc) to give **1g** or **1i**.

3,4-Isopropylidene-6-O-triphenylmethyl-1,2-dideoxy-D-ribo-hex-1-ynitol ***(1h)***.[22,23] Colourless oil, 3.6 g, 85% yield; R_f= 0.6 (silica gel F_{254}, 4:1, petroleum ether/EtOAc); ^{1}H

NMR (400MHz, $CDCl_3$) δ 7.50−7.28 (m, 15H), 4.73−4.71 (dd, J = 6.4 Hz, 1H), 4.25−4.22 (t, J = 6.0 Hz, 1H), 3.91 (s, 1H), 3.35−3.34 (d, J = 5.2 Hz, 2H), 2.53 (d, J = 3.6 Hz, 1H), 2.49 (d, J = 2.0 Hz), 1.52 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 128.7, 127.9, 127.2, 110.8, 99.8, 87.1, 82.0, 74.4, 70.9, 66.9, 64.4, 26.9, 26.1.

3,4:6,7-Di-O-isopropylidene-1,2-dideoxy-D-manno-hex-1-ynitol ***(1i)****.*[22–24] Colourless oil, 2.2 g, 86% yield; R_f = 0.7 (silica gel F_{254}, 5:1, petroleum ether/EtOAc); ^{1}H NMR (400 Hz, $CDCl_3$) δ 4.68 (dd, 1H, J = 1.4 Hz, J = 7.6Hz), 4.30 (dd, 1H, J = 7.6 Hz, J = 1.6 Hz), 4.02−4.14 (m, 3H), 3.58 (br s, 1H), 2.56 (d, 1H, J = 1.4 Hz), 2.23 (d, 1H, J = 7.6Hz), 1.53, 1.45, 1.44, 1.38 (s, each 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.1, 109.5, 80.8, 80.6, 76.2, 74.9, 69.8, 66.8, 66.6, 26.8, 26.6, 26.2, 25.3.

Synthesis of 3,7-Anhydro-1,1,2,2-tetradehydro-1,2,6-trideoxy-6-C-[(2-aminophenyl)ethynyl]-4-*O*-(triisopropylsily1)-1-*C*-(trimethylsilyl)-D-glycero-D-gulo-octitol (2aa). A mixture of 2-iodoaniline (90 mg, 0.77 mmol), $Pd(PPh_3)_2Cl_2$ (15 mg, 0.021 mmol), CuI (7 mg, 0.035 mmol), and Et_3N (3 mL) was degassed. Then sugar alkyne **1a** (297 mg, 0.70 mmol) in Et_3N (3 mL) was injected with syringe. The mixture was stirred at room temperature until TLC indicated completion of the reaction. It was evaporated to remove Et_3N. The residue was purified by column chromatography (silica gel, 3:1, petroleum ether/EtOAc) to give **2aa** (342 mg, 95%) as a brown oil: R_f = 0.5 (silica gel F_{254}, 3:1, petroleum ether/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, 1H, J = 1.1 Hz, J = 7.6 Hz, H−6'), 7.11−7.07 (m, 1H, H−5'), 6.68 (d, 1H, J = 7.9 Hz, H−4'), 6.65 (d, 1H, J = 7.4 Hz, H−7'), 3.99 (d, 1H, J = 9.3 Hz, H−3), 3.97 (d, 1H, J = 2.4 Hz,

H−8a), 3.78 (dd, 1H, J = 5.8 Hz, J = 11.7 Hz, H−8b), 3.68 (t, J = 8.5 Hz, J = 10.2 Hz, H−5), 3.54−3.49 (m, 1H, H−7), 2.78 (t, 1H, J = 10.3 Hz, H−6), 1.29−1.10 (m, 21H, $Si(CH(CH_3)_2)_3$), 0.18 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.04 (C−8'), 132.21 (C−6'), 129.79 (C−5'), 118.14 (C−4'), 114.67 (C−7'), 107.64 (C−3'), 102.61 (C−2), 90.66 (C−1), 91.23 (C−1'), 81.59 (C−2'), 79.30 (C−7), 77.20 (C−5), 75.36 (C−4), 72.12 (C−3), 63.77 (C−8), 38.84 (C−6), 18.47 ($Si(CH(\mathit{C}H_3)_2)_3$), 13.17 ($Si(\mathit{C}H(CH_3)_2)_3$), −0.28 ($Si(\mathit{C}H_3)_3$) ppm; HRMS (ESI) calcd. for $C_{28}H_{46}NO_4Si_2$ $[M+H]^+$ 516.2965, found: 516.2960.

General procedure for the synthesis of 3aa−3ig. A mixture of substituted 2-iodoaniline (0.77 mmol), $Pd(PPh_3)_2Cl_2$ (0.021 mmol), CuI (0.035 mmol) and Et_3N (3 mL) was degassed. Then sugar alkyne (0.70 mmol) in Et_3N (3 mL) was injected with syringe. The mixture was stirred at room temperature until TLC indicated the completion of the reaction. It was evaporated to remove Et_3N. THF (8 mL) and $NaAuCl_4{\cdot}2H_2O$ (0.021 mmol) were then added, and the mixture was stirred at 25−55 ^{0}C. After TLC indicated completion of the reaction, the mixture was evaporated. The residue was purified by column chromatography (silica gel, 3:1−1:1, petroleum ether/EtOAc) to give the products **3aa−3ig**.

*3,7-Anhydro-6-C-(indol-2-yl)-1,1,2,2-tetradehydro-1,2,6-trideoxy-4-O-(triisopropylsilyl)-1-C-(trimethylsilyl)-D-glycero-D-gulo-octitol (**3aa**)*. Brown foam, 299 mg, 83% yield; Mp: 56−57 ^{0}C; R_f= 0.7 (silica gel F_{254}, 1:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -26.3^0$ (*c* 0.66, $CHCl_3$); IR (KBr): 3421, 3133, 2963, 2865, 1664, 1622, 1455, 1290, 1253, 1141,

1112, 1070, 1021, 883, 803 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H, NH), 7.56 (d, 1H, $J_{4', 5'}$ = 8.0 Hz, H−4'), 7.31 (d, 1H, $J_{7', 6'}$ = 8.0 Hz, H−7'), 7.18−7.08 (m, 2H, H−5', H−6'), 6.34 (s, 1H, H−3'), 4.12 (d, 1H, $J_{3, 4}$ = 8.4 Hz, H−3), 3.82−3.80 (m, 2H, H−4, H−5), 3.70 (d, 1H, $J_{8a, 8b}$ = 12.0 Hz, H−8a), 3.58(br d, J = 10.4 Hz, H−7), 3.37 (dd, 1H, $J_{8b, 7}$ = 4.0 Hz, $J_{8b, 8a}$ = 12.0 Hz, H−8b), 3.06 (t, 1H, $J_{6, 7} = J_{6, 5}$ = 10.0 Hz, H−6), 2.38 (s, 2H, 2OH), 1.30−1.11 (m, 21H, $Si(CH(CH_3)_2)_3$), 0.21 (s, 9H, $Si(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8 (C−7a'), 135.0 (C−2'), 128.5 (C−3a'), 122.0 (C−6'), 120.3 (C−4'), 120.2 (C−5'), 111.0 (C−7'), 102.7 (C−2), 99.4 (C−3'), 91.3 (C−1), 80.0 (C−7), 77.4 (C−5), 75.7 (C−4), 72.2 (C−3), 63.2 (C−8), 44.4 (C−6), 18.5 ($Si(CH(CH_3)_2)_3$), 13.2 ($Si(CH(CH_3)_2)_3$), −0.2 ($Si(CH_3)_3$) ppm; HRMS (ESI) calcd. for $C_{28}H_{46}NO_4Si_2$ $[M+H]^+$ 516.2965, found: 516.2962.

*3,7-Anhydro-6-C-(5-methylindol-2-yl)-1,1,2,2-tetradehydro-1,2,6-trideoxy-4-O-(triisopropylsilyl)-1-C-(trimethylsilyl)-D-glycero-D-gulo-octitol (**3ab**).* Brown foam, 322 mg, 87% yield; Mp: 92−93 ^{0}C; R_f= 0.7 (silica gel F_{254}, 1:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -30.8^0$ (*c* 0.50, $CHCl_3$); IR (KBr) 3425, 3132, 2966, 2864, 1664, 1623, 1400, 1293, 1254, 1141, 1071, 1023, 882, 778 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.34 (s, 1H), 7.20 (d, 1H, J = 8.4 Hz), 6.98(d, 1H, J = 8.4 Hz), 6.25 (s, 1H), 4.12 (d, 1H, J = 8.8 Hz), 3.81−3.78 (m, 2H), 3.70 (d, 1H, J = 12.0 Hz), 3.60−3.56 (m, 1H), 3.37 (br d, 1H, J = 8.4 Hz), 3.03 (t, 1H, J= 10.2 Hz), 2.43 (s, 3H), 2.33, 2.27 (2br s, each 1H), 1.28−1.11 (m, 21H), 0.20 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 134.2, 129.4, 128.8, 123.6, 120.0, 110.7, 102.8, 99.0, 91.2, 80.0, 77.4, 75.7, 72.2, 63.3, 44.5, 21.5, 18.5, 13.2, −0.2 ppm;

HRMS (ESI) calcd. for $C_{29}H_{48}NO_4Si_2$ $[M+H]^+$ 530.3122, found: 530.3125.

*3,7-Anhydro-6-C-(5-fluoroindol-2-yl)-1,1,2,2-tetradehydro-1,2,6-trideoxy-4-O-(triisopropylsilyl)-1-C-(trimethylsilyl)-D-glycero-D-gulo-octitol (**3ac**).* Brown foam, 291 mg, 78% yield; Mp: 63−64 ^{0}C; R_f= 0.7 (silica gel F_{254}, 1:1, petroleum ether/EtOAc); $[\alpha]^{20}_D$ = −30.7^0 (*c* 0.52, $CHCl_3$); IR (KBr) 3422, 3335, 3133, 2961, 2865, 1626, 1487, 1454, 1400, 1291, 1253, 1119, 1069, 1022, 849, 813 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.22−7.17 (m, 2H), 6.92−6.86 (m, 1H), 6.30 (s, 1H), 4.12 (d, 1H, *J*= 8.4 Hz), 3.82−3.79 (m, 2H), 3.74 (d, 1H, *J*= 11.4 Hz), 3.61−3.58 (m, 1H), 3.38 (dd, *J*= 3.6 Hz, *J*= 11.4 Hz), 3.08 (t, 1H, *J*= 10.2 Hz), 2.36 (s, 1H), 2.26 (s, 1H), 1.29−1.11 (m, 21H), 0.20 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2 (d, $^1J_{C-F}$ = 233.0 Hz), 137.0, 132.3, 128.9 (d, $^3J_{C-F}$ = 10.0 Hz), 111.6 (d, $^3J_{C-F}$= 10.0 Hz), 110.3 (d, $^2J_{C-F}$= 26.0 Hz), 105.1 (d, $^2J_{C-F}$= 24.0 Hz), 102.6, 99.5 (d, $^4J_{C-F}$ = 4.0 Hz), 91.4, 80.0, 77.4, 75.8, 72.2, 63.2, 44.2, 18.5, 13.2, −0.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −124.4 (dt, J_1 = 9.2 Hz, J_2 = 4.1 Hz) ppm; HRMS (ESI) calcd. for $C_{28}H_{45}FNO_4Si_2$ $[M+H]^+$ 534.2871, found 534.2869.

*3,7-Anhydro-6-C-(5-chloroindol-2-yl)-1,1,2,2-tetradehydro-1,2,6-trideoxy-4-O-(triisopropylsilyl)-1-C-(trimethylsilyl)-D-glycero-D-gulo-octitol (**3ad**).* Brown foam, 308 mg, 80% yield; Mp: 39−40 ^{0}C; R_f= 0.7 (silica gel F_{254}, 1:1, petroleum ether/EtOAc); $[\alpha]^{20}_D$ = −39.0^0 (*c* 0.54, $CHCl_3$); IR (KBr) 3413, 3335, 3134, 2927, 2863, 1665, 1618, 1583, 1464, 1311, 1252, 1140, 1113, 1065, 1022, 848, 805 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H, NH), 7.51 (d, 1H, *J*= 1.6 Hz), 7.22 (d, 1H, *J* = 8.4 Hz), 7.10 (dd, 1H, *J* = 1.6 Hz, *J* = 8.4 Hz), 6.28 (s, 1H), 4.12 (d, 1H, *J* = 8.8 Hz), 3.84−3.80 (m, 2H), 3.76 (d, 1H, *J* = 13.2 Hz),

3.60 (dd, 1H, J = 2.8 Hz, J = 10.4 Hz), 3.39 (dd, 1H, J = 3.4 Hz, J = 12.0 Hz), 3.60 (dd, 1H, J = 2.8 Hz, J_7 = 10.4 Hz), 3.39 (dd, 1H, J = 3.4 Hz, J = 12.0 Hz), 3.10 (t, 1H, J = 10.4 Hz), 2.34 (s, 1H), 2.22 (s, 1H), 1.28−1.11 (m, 21H), 0.20 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 134.2, 129.6, 125.8, 122.3, 119.7, 112.0, 102.5, 99.0, 91.5, 80.0, 77.4, 75.9, 72.2, 63.2, 44.1, 18.5, 13.2, −0.2 ppm; HRMS (ESI) calcd. for $C_{28}H_{45}ClNO_4Si_2$ $[M+H]^+$ 550.2576, found 550.2579.

3,7-Anhydro-6-C-(5-bromoindol-2-yl)-1,1,2,2-tetradehydro-1,2,6-trideoxy-4-O-(triisopropylsilyl)-1-C-(trimethylsilyl)-D-glycero-D-gulo-octitol ***(3ae)***. Brown foam, 353 mg, 85% yield; Mp: 96−97 ^{0}C; R_f = 0.7 (silica gel F_{254}, 1:1, petroleum ether/EtOAc); $[\alpha]^{20}_D$ = −34.4^0 (*c* 0.50, $CHCl_3$); IR (KBr) 3423, 3134, 2964, 2864, 1664, 1621, 1449, 1400, 1312, 1256, 1141, 1109, 1070, 1022, 882, 802 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.66 (s, 1H), 7.23 (dd, 1H, J = 1.6 Hz, J = 8.6 Hz), 7.17 (d, 1H, J = 8.6 Hz), 6.28 (s, 1H), 4.12 (d, 1H, J = 8.4 Hz), 3.81−3.79 (m, 2H), 3.74 (d, 1H, J = 12.4 Hz), 3.60−3.58 (m, 1H), 3.36 (br d, 1H, J = 9.2 Hz), 3.09 (t, 1H, J = 10.0 Hz), 2.36 (s, 1H), 2.26 (s, 1H), 1.27−1.11 (m, 21H), 0.20 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 134.4, 130.3, 124.8, 122.8, 113.3, 112.4, 102.5, 98.9, 91.5, 80.0, 77.4, 75.8, 72.2, 63.2, 44.0, 18.5, 13.2, −0.2 ppm; HRMS (ESI) calcd. for $C_{28}H_{45}BrNO_4Si_2$ $[M+H]^+$ 594.2070, found 594.2072.

2-[4-deoxy-2-O-triisopropylsilyl-4-C-(indol-2-yl)-β-D-glucopyranosyl]indole ***(3ba)***. Brown foam, 329 mg, 88% yield; Mp: 74−75 ^{0}C; R_f = 0.7 (silica gel F_{254}, 1:1, petroleum ether/EtOAc); $[\alpha]^{20}_D$ = −20.2^0 (*c* 0.53, $CHCl_3$); IR (KBr) 3556, 3409, 2962, 2864, 1664, 1619, 1545, 1455, 1400, 1291, 1262, 1130, 1070, 1017, 848, 792 cm^{-1}; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 8.91, 8.74 (2s, each 1H, 2NH), 7.64−7.59 (m, 2H, H−4, H−4''), 7.31−7.28 (m, 2H, H−7, H−7''), 7.23−7.11 (m, 4H, H−5, H−5'', H−6, H−6''), 6.54 (s, 1H, H−3), 6.35 (s, 1H, H−3''), 4.45 (d, 1H, $J_{1', 2'}$ = 8.8 Hz, H−1'), 4.06 (t, 1H, $J_{2', 1'} = J_{2', 3'}$ = 8.8 Hz, H−2'), 3.96−3.91 (m, 1H, H−3'), 3.67−3.59 (m, 2H, H−5', H−6'a), 3.33 (dd, 1H, $J_{6'b, 5'}$ = 2.8 Hz, $J_{6'b, 6'a}$ =11.6 Hz, H−6'b), 3.21 (t, 1H, $J_{4', 3'} = J_{4', 5'}$ = 10.4 Hz, H−4'), 2.50 (s, 1H, OH), 0.88−0.80 (m, 21H, $Si(CH(CH_3)_2)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 135.9, 135.6, 135.4 (C−2, C−7a, C−2'', C−7a''), 128.6, 128.0 (C−3a, C−3a''), 122.3, 122.0 (C−6, C−6''), 120.8, 120.3, 120.2, 119.9 (C−4, C−5, C−4'', C−5''), 111.1, 111.0 (C−7, C−7''), 102.9 (C−3), 99.4 (C−3''), 79.7 (C−5'), 78.7 (C−3'), 77.4 (C−1'), 75.9 (C−2'), 62.9 (C−6'), 45.0 (C−4'), 18.1 ($Si(CH(\mathit{C}H_3)_2)_3$), 13.1 ($Si(\mathit{C}H(CH_3)_2)_3$) ppm; HRMS (ESI) calcd. for $C_{31}H_{43}N_2O_4Si$ $[M+H]^+$ 535.2992, found 535.2993.

*5-Methyl-2- [4-deoxy-2-O-triisopropylsilyl-4-C-(5-methylindol-2-yl)-β-D-glucopyranosyl] indole (**3bb**)*. Brown foam, 354 mg, 90% yield; Mp: 97−100 ^{0}C; R_f = 0.7 (silica gel F_{254}, 1:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -23.6^0$ (*c* 1.61, $CHCl_3$); IR (KBr) 3405, 3165, 3018, 2942, 2864, 1665, 1623, 1458, 1400, 1314, 1258, 1129, 1063, 883, 794 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81, 8.68 (2s, each 1H), 7.43, 7.41 (2s, each 1H), 7.21−7.18 (m, 2H), 7.05−7.02 (m, 2H), 6.46 (s, 1H), 6.25 (s, 1H), 4.36 (d, 1H, *J* = 8.6 Hz, 4.05 (t, 1H, *J* = 8.6 Hz), 3.88 (br t, 1H, *J* = 9.2 Hz), 3.56−3.48 (m, 2H), 3.24 (br d, 1H, *J* = 9.6 Hz), 3.11 (t, 1H, *J* = 10.4 Hz), 2.49, 2.48 (2s, each 3H), 0.91−0.83 (m, 21H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 135.5, 134.5, 134.1, 129.4, 128.89, 128.88, 128.3, 123.8, 123.5, 120.4, 119.8, 110.8, 110.7, 102.4, 98.8, 79.6, 78.8, 77.4, 75.6, 62.7, 45.0, 21.64, 21.57, 18.1, 13.0 ppm; HRMS (ESI)

calcd. for $C_{33}H_{46}N_2O_4Si$ $[M+H]^+$ 562.3227, found 562.3228.

*5-Fluoro-2-[4-deoxy-2-O-triisopropylsilyl-4-C-(5-fluorolindol-2-yl)-β-D-glucopyranosyl]indole (**3bc**).* Brown foam, 335 mg, 84% yield; Mp: 95−97 ^{0}C; R_f = 0.7 (silica gel F_{254}, 1:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -21.9^0$ (*c* 1.48, $CHCl_3$); IR (KBr) 3405, 3165, 3018, 2942, 2864, 1665, 1623, 1458, 1400, 1314, 1258, 1129, 1063, 883, 794 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10, 8.95 (2s, each 1H), 7.25−7.22 (m, 2H), 7.15−7.11 (m, 2H), 6.93−6.88 (m, 2H), 6.48 (s, 1H), 6.29 (s, 1H), 4.46 (d, 1H, J = 8.8 Hz), 4.05 (t, 1H, J = 8.8 Hz), 3.95 (br t, 1H, J = 8.8 Hz), 3.73−3.64 (m, 2H), 3.37 (br d, 1H, J = 9.6 Hz), 3.28 (t, 1H, J = 10.4 Hz), 2.65 (s, 1H), 0.88−0.84 (m, 21H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2 (2d, $^1J_{C-F}$ = 232.0 Hz), 158.0 (2d, $^1J_{C-F}$ = 232.0 Hz), 137.25, 137.19, 132.7, 132.3, 129.0 (2d, $^3J_{C-F}$ = 10.0 Hz), 128.2 (2d, $^3J_{C-F}$ = 10.0 Hz), 111.65 (2d, $^3J_{C-F}$ = 9.0 Hz), 111.56 (2d, $^3J_{C-F}$ = 10.0 Hz), 110.8(2d, $^2J_{C-F}$ = 26.0 Hz), 110.3 (2d, $^2J_{C-F}$ = 26.0 Hz), 105.4 (2d, $^2J_{C-F}$ = 23.0 Hz), 105.1 (2d, $^2J_{C-F}$ = 23.0 Hz), 103.3, 103.2, 99.43, 99.39, 79.5, 78.8, 77.4, 75.9, 62.8, 44.8, 18.1, 13.1 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −124.1 (dt, J_1 = 9.0 Hz, J_2 = 4.9 Hz); −124.5 (dt, J_1 = 9.4 Hz, J_2 = 4.5 Hz) ppm; HRMS (ESI) calcd. for $C_{31}H_{41}F_2N_2O_4Si$ $[M+H]^+$ 571.2804, found 571.2803.

*5-Chloro-2-[4-deoxy-2-O-triisopropylsilyl-4-C-(5-chloroindol-2-yl)-β-D-glucopyranosyl]indole (**3bd**).* Brown foam, 367 mg, 87% yield; Mp: 49−50 ^{0}C; R_f = 0.7 (silica gel F_{254}, 1:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -16.5^0$ (*c* 0.51, $CHCl_3$); IR (KBr) 3405, 3165, 3018, 2942, 2864, 1665, 1623, 1458, 1400, 1314, 1258, 1129, 1063, 883, 794 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94, 8.86 (2s, each 1H), 7.55, 7.54 (2s, each 1H), 7.18−7.09 (m,

4H), 6.46 (s, 1H), 6.31 (s, 1H), 4.51 (d, 1H, J= 8.4 Hz), 4.04−3.96 (m, 2H), 3.78−3.72 (m, 2H), 3.40 (dd, 1H, J= 2.8 Hz, J= 9.2 Hz), 3.29 (t, 1H, J = 10.0 Hz), 0.87−0.84 (m, 21H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 136.8, 134.5, 134.2, 129.7, 129.0, 126.0, 125.5, 122.7, 122.4, 120.1, 119.8, 112.0, 111.9, 102.6, 99.1, 79.7, 78.5, 77.4, 76.2, 63.0, 44.8, 18.1, 13.1 ppm; HRMS (ESI) calcd. for $C_{31}H_{41}Cl_2N_2O_4Si$ $[M+H]^+$ 603.2213, found 603.2215.

*5-Bromo-2-[4-deoxy-2-O-triisopropylsilyl-4-C-(5-bromoindol-2-yl)-β-D-glucopyranosyl]indole (**3be**).* Brown foam, 412 mg, 85% yield; Mp: 95−97 ^{0}C; R_f= 0.7 (silica gel F_{254}, 1:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -25.8^0$ (c 1.04, $CHCl_3$); IR (KBr) 3405, 3165, 3018, 2942, 2864, 1665, 1623, 1457, 1400, 1314, 1258, 1129, 1063, 883, 794 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11, 8.98 (2s, each 1H), 7.71, 7.70 (2s, each 1H), 7.25−7.21 (m, 2H), 7.11−7.08 (m, 2H), 6.43 (s, 1H), 6.26 (s, 1H), 4.43 (d, 1H, J = 8.8 Hz), 4.03 (t, 1H, J = 8.8 Hz), 3.96−3.91 (m, 1H), 3.69−3.62 (m, 2H), 3.32 (br d, 1H, J = 12.0 Hz), 3.26 (t, 1H, J = 10.4 Hz), 2.64 (br s, 1H), 0.86−0.83 (m, 21H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.74, 136.69, 134.7, 134.4, 130.3, 129.6, 125.2, 124.9, 123.2, 122.8, 113.4, 113.1, 112.5, 112.4, 102.6, 98.9, 79.5, 78.8, 77.3, 75.8, 62.8, 44.7, 18.1, 13.1 ppm; HRMS (ESI) calcd. for $C_{31}H_{40}Br_2N_2O_4Si$ $[M]^+$ 690.1124, found 690.1123.

*Methyl 4S-4-C-(5-chloroindol-2-yl)-2,3-O-isopropylidene-β-D-erythrofuranoside (**3ca**).* Brown oil, 188 mg, 83% yield; R_f= 0.6 (silica gel F_{254}, 3:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -45.1^0$ (c 0.56, $CHCl_3$); IR (KBr) 3389, 3046, 2960, 1629, 1599, 1556, 1489, 1459, 1377, 1209, 1096, 799 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.56 (s,

1H), 7.27 (d, 1H, $J_{7,6}$ = 8.4 Hz), 7.15 (d, 1H, $J_{6,7}$ = 8.4 Hz), 6.42 (s, 1H), 5.48 (s, 1H), 5.20 (s, 1H), 4.87 (d, 1H, $J_{3',2'}$ = 4.8 Hz), 4.28 (br s, 1H), 3.47 (s, 3H), 1.60, 1.37 (2s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 135.2, 129.3, 125.6, 122.6, 120.2, 113.0, 112.1, 110.5, 101.0, 85.6, 85.2, 84.00, 55.8, 26.6, 25.1 ppm; HRMS (ESI) calcd. for $C_{16}H_{19}ClNO_4$ $[M+H]^+$ 324. 1003, found: 324.1006.

*Methyl 4S-4-C-(indol-2-yl)-2,3-O-isopropylidene-β-D-erythrofuranoside (**3cb**).* Brown oil, 172 mg, 85% yield; R_f = 0.6 (silica gel F_{254}, 3:1, petroleum ether/EtOAc); $[\alpha]^{20}_D$ = −45.1^0 (*c* 1.25, $CHCl_3$); IR (KBr) 3444, 3062, 2939, 1625, 1589, 1550, 1491, 1455, 1377, 1207, 1097, 799 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.60 (d, 1H, *J* = 8.0 Hz), 7.35 (d, 1H, *J* = 8.0 Hz), 7.20 (t, 1H, *J* = 7.6 Hz), 7.11 (t, 1H, *J* =7.6 Hz), 6.47 (s, 1H), 5.50 (s, 1H), 5.19 (s, 1H), 4.88 (d, 1H, *J* = 5.8 Hz), 4.82 (d, 1H, *J* = 5.8 Hz), 3.46 (s, 3H), 1.59, 1.36 (2s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 136.5, 128.3, 122.4, 120.9, 120.0, 112.9, 115.2, 110.5, 101.6, 85.8, 85.3, 84.2, 55.7, 26.6, 25.1 ppm; HRMS (ESI) calcd. for $C_{16}H_{20}NO_4$ $[M+H]^+$ 290.1392, found 290.1390.

*Methyl 4S-4-C-(5-methylindol-2-yl)-2,3-O-isopropylidene-β-D-erythrofuranoside (**3cc**).* Brown oil, 191 mg, 90% yield; R_f = 0.6 (silica gel F_{254}, 3:1, petroleum ether/EtOAc); $[\alpha]^{20}_D$ = −46.8^0 (*c* 1.23, $CHCl_3$); IR (KBr) 3387, 3029, 2939, 1627, 1596, 1555, 1492, 1458, 1377, 1212, 1097, 795 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 7.37 (s, 1H), 7.23 (d, 1H, *J* = 8.2 Hz), 7.01 (d, 1H, *J* = 8.2 Hz), 6.37 (s, 1H), 5.46 (s, 1H), 5.16 (s, 1H), 4.86 (d, 1H, *J* = 6.0 Hz), 4.80 (d, 1H, *J* = 6.0 Hz), 3.44 (s, 3H), 2.44 (s, 3H), 1.57, 1.34 (2s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 135.2, 129.1, 128.5, 123.9,

120.5, 112.8, 110.8, 110.4, 101.0, 85.7, 85.2, 84.2, 55.5, 26.6, 25.1, 21.5 ppm; HRMS (ESI) calcd. for $C_{17}H_{22}NO_4$ $[M+H]^+$ 304.1549, found 304.1550.

*Methyl 4S-4-C-(5-fluoroindol-2-yl)-2,3-O-isopropylidene-β-D-erythrofuranoside (**3cd**).* Brown oil, 172 mg, 80% yield; R_f = 0.6 (silica gel F_{254}, 3:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -38.2^0$ (*c* 1.52, $CHCl_3$); IR (KBr) 3413, 3045, 2957, 1629, 1588, 1553, 1489, 1452, 1377, 1212, 1095, 797 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.25−7.21 (m, 2H), 6.96−6.91 (m, 1H), 6.42 (s, 1H), 5.47 (s, 1H), 5.18 (s, 1H), 4.86 (d, 1H, J = 6.0 Hz), 4.80 (d, 1H, J = 6.0 Hz), 3.46 (s, 3H), 1.58, 1.35 (2s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0 (d, $^1J_{C-F}$ = 233.0 Hz), 138.3, 133.4, 128.6 (d, $^3J_{C-F}$ = 10.0 Hz), 113.0, 111.7 (d, $^3J_{C-F}$ = 9.0 Hz), 110.7 (d, $^2J_{C-F}$ = 26.0 Hz), 110.5, 105.6 (d, $^2J_{C-F}$ = 24.0 Hz), 101.5 (d, $^4J_{C-F}$ = 4.0 Hz), 85.7, 85.2, 84.0, 55.7, 26.6, 25.0 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −124.9 (dt, J_1 = 9.3 Hz, J_2 = 4.1 Hz) ppm; HRMS (ESI) calcd. for $C_{16}H_{19}FNO_4$ $[M+H]^+$ 308.1294, found 308.1296.

*Methyl 4S-4-C-(5-bromoindol-2-yl)-2,3-O-isopropylidene-β-D-erythrofuranoside (**3ce**).* Brown oil, 213 mg, 83% yield; R_f = 0.6 (silica gel F_{254}, 3:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -39.3^0$ (c 1.15, $CHCl_3$); IR (KBr) 3406, 3056, 2958, 1624, 1598, 1579, 1485, 1456, 1378, 1096, 1055, 795 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.70 (s, 1H), 7.27−7.20 (m, 2H), 6.39 (s, 1H), 5.45 (s, 1H), 5.17 (s, 1H), 4.84 (d, 1H, J = 5.8 Hz), 4.79 (d, 1H, J = 5.8 Hz), 3.45 (s, 3H), 1.56, 1.34 (2s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 135.4, 130.0, 125.1, 123.3, 113.1, 113.0, 112.6, 110.5, 100.9, 85.6, 85.2, 83.9, 55.7, 26.6, 25.0 ppm; HRMS (ESI) calcd. for $C_{16}H_{19}BrNO_4$ $[M+H]^+$ 368.0497,

found 368. 0499.

*Methyl 4S-4-C-(5-fluoroindol-2-yl)-2,3-O-isopropylidene-α-L-erythrofuranoside (**3da**).* Pale yellow oil, 165 mg, 78% yield; R_f = 0.6 (silica gel F_{254}, 3:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -23^0$ (*c* 0.50, $CHCl_3$); IR (KBr) 3337, 3048, 2926, 1626, 1586, 1542, 1485, 1457, 1380, 1090, 1026, 800 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H, NH), 7.30−7.22 (m, 2H, H−4, H−7), 6.96−6.91 (m, 1H, H−6), 6.52 (s, 1H, H−3), 5.15 (d, 1H, $J_{4',3'}$ = 3.2 Hz, H−4'), 5.00 (s, 1H, H−1'), 4.86 (dd, 1H, $J_{3',4'}$ = 3.2 Hz, $J_{3',2'}$ = 5.6 Hz, H−3'), 4.69 (d, 1H, $J_{2',3'}$ = 5.6 Hz, H−2'), 3.40 (s, 3H, OCH_3), 1.60, 1.34 (2s, each 3H, 2CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0 (C−5, d, $^1J_{C-F}$ = 232.0 Hz), 134.2 (C−2), 133.2 (C−7a), 127.9 (C−3a, d, $^3J_{C-F}$ = 10.0 Hz), 113.0 (isopropylidene−*C*), 111.9 (C−7, d, $^3J_{C-F}$ = 9.6 Hz), 110.9 (C−6, d, $^2J_{C-F}$ = 26.3 Hz), 107.1 (C−1'), 105.5 (C−4, d, $^2J_{C-F}$ = 23.3 Hz), 103.3 (C−3, d, $^4J_{C-F}$ = 4.5 Hz), 85.5 (C−2'), 81.7 (C−3'), 75.2 (C−4'), 55.2 (O*C*H_3), 26.4, 24.6 (2*C*H_3) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −124.9 (dt, J_1 = 9.3 Hz, J_2 = 4.1 Hz) ppm; HRMS (ESI) calcd. for $C_{16}H_{19}FNO_4$ $[M+H]^+$ 308.1294, found 308.1292.

*Methyl 4S-4-C-(indol-2-yl)-2,3-O-isopropylidene-α-L-erythrofuranoside (**3db**).* Brown oil, 157 mg, 73% yield; R_f = 0.6 (silica gel F_{254}, 3:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -25.0^0$ (*c* 0.5, $CHCl_3$); IR (KBr) 3447, 3032, 2926, 1624, 1591, 1557, 1491, 1450, 1378, 1231, 1096, 802 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.60 (d, 1H, *J* = 7.6 Hz), 7.37 (dd, 1H, *J* = 8.0 Hz, *J* = 0.8 Hz), 7.18 (dt, 1H, *J* = 8.0 Hz, *J* = 0.9 Hz), 7.08 (dt, 1H, *J* = 8.0 Hz, *J* = 0.8 Hz), 6.56 (s, 1H), 5.18 (d, 1H, *J* = 3.4 Hz), 5.00 (s, 1H), 4.86 (dd, 1H, *J* = 3.4 Hz, *J* = 5.6 Hz), 4.69 (d, 1H, *J* = 5.6 Hz), 3.40 (s, 3H), 1.60, 1.34 (2s, each 3H)

ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 132.4, 127.6, 122.4, 120.9, 119.8, 112.9, 111.3, 107.1, 103.3, 85.5, 81.8, 75.4, 55.1, 26.4, 24.6 ppm; HRMS (ESI) calcd. for $C_{16}H_{20}NO_4$ $[M+H]^+$ 290.1392, found 290.1391.

*Methyl 4S-4-C-(5-methylindol-2-yl)-2,3-O-isopropylidene-α-L-erythrofuranoside (**3dc**).* Yellow oil, 151 mg, 75% yield; R_f = 0.6 (silica gel F_{254}, 3:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -9.0^0$ (*c* 0.50, $CHCl_3$); IR (KBr) 3457, 3048, 2925, 1627, 1589, 1556, 1483, 1459, 1379, 1163, 1100, 1020, 801 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.37 (s, 1H), 7.25 (d, *J* = 8.0 Hz), 7.00 (d, 1H, *J* = 8.0 Hz), 6.47 (s, 1H), 5.15 (d, 1H, *J* = 3.2 Hz), 4.99 (s, 1H), 4.85 (dd, 1H, *J* = 3.2 Hz, *J* = 5.6 Hz), 4.68 (d, 1H, *J* = 5.6 Hz), 3.40 (s, 3H), 2.43 (s, 3H), 1.60, 1.33 (2s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 132.4, 128.9, 127.9, 124.1, 120.5, 112.7, 110.9, 107.1, 102.8, 85.5, 81.8, 75.4, 55.1, 26.4, 24.6, 21.6 ppm; HRMS (ESI) calcd. for $C_{17}H_{22}NO_4$ $[M+H]^+$ 304.1549, found 304.1548.

*4S-4-C-(5-fluoroindol-2-yl)-3-O-benzyl-1,2-O-isopropylidene-α-L-threofuranoside (**3ea**).* Pale yellow oil, 195 mg, 73% yield; R_f = 0.6 (silica gel F_{254}, 3:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -55.0^0$ (*c* 0.48, $CHCl_3$); IR (KBr) 3442, 3058, 2926, 1625, 1589, 1549, 1488, 1456, 1378, 1261, 1081, 801 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H, NH), 7.36−7.18 (m, 5H, H−4, H−7, 3Ar*H*), 7.01 (d, 2H, *J* = 6.8 Hz, 2Ar*H*), 6.93 (t, 1H, *J* = 9.2 Hz, H−7), 6.48 (s, 1H, H−3), 6.06 (d, 1H, $J_{1',2'}$ = 3.4 Hz, H−1'), 5.39 (s, 1H, H−4'), 4.75 (d, 1H, $J_{2',1'}$ = 3.4 Hz, H−2'), 4.44 (d, B of AB, 1H, *J* = 11.2 Hz, Ph−CH_B), 4.18 (d, A of AB, 1H, *J* = 11.2 Hz, Ph−CH_A), 4.08 (s, 1H, H−3'), 1.59, 1.38 (2s, each 3H, 2CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0 (C−5, d, $^1J_{C-F}$ = 232.0 Hz), 137.0

(aromatic−*C*), 134.2 (C−2), 133.0 (C−7a), 128.6, 128.3, 128.01 (5 aromatic−*C*H), 127.95 (C−3a, d, $^{3}J_{C-F}$ = 11.2 Hz), 112.1 (isopropylidene−*C*), 111.7 (C−7, d, $^{3}J_{C-F}$ = 10.0 Hz), 110.7 (C−6, d, $^{2}J_{C-F}$ = 26.0 Hz), 105.5 (C−4, d, $^{2}J_{C-F}$ = 23.0 Hz), 104.8 (C−1'), 102.3 (C−3, d, $^{4}J_{C-F}$ = 5.0 Hz), 84.2 (C−3'), 83.1 (C−2'), 76.2 (C−4'), 72.9 (Ph*C*H$_2$O), 27.0, 26.3 (2*C*H$_3$) ppm; ^{19}F NMR (376 MHz, CDCl$_3$) δ −125.0 (dt, J_1 = 9.2 Hz, J_2 = 4.1 Hz) ppm; HRMS (ESI) calcd. for $C_{21}H_{21}FNO_4$ $[M+H]^+$ 370.1455, found 370.1452.

*4S-4-C-(indol-2-yl)-3-O-benzyl-1,2-O-isopropylidene-α-L-threofuranoside (**3eb**).* Pale yellow oil, 196 mg, 77% yield; R_f = 0.6 (silica gel F_{254}, 3:1, petroleum ether/EtOAc); $[\alpha]^{20}_D$ = −31.0^0 (*c* 0.52, CHCl$_3$); IR (KBr) 3395, 3055, 2940, 1646, 1597, 1561, 1523, 1492, 1374, 1214, 1086, 803 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.76 (s, 1H), 7.62 (d, 1H, *J* = 7.6 Hz), 7.31−6.39 (m, 8H), 6.54 (s, 1H), 6.08 (d, 1H, *J* = 3.2 Hz), 5.42 (br s, 1H), 4.76 (s, 1H, *J* = 3.2 Hz), 4.42 (d, 1H, *J* = 11.2 Hz), 4.20 (d, 1H, *J* = 11.2 Hz), 4.08 (d, 1H, *J* = 2.0 Hz), 1.60, 1.38 (2s, each 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 137.0, 136.5, 132.4, 128.6, 128.2, 128.0, 127.7, 122.2, 120.8, 119.7, 112.0, 115.2, 104.7, 102.4, 84.3, 83.2, 76.4, 72.9, 27.0, 26.3 ppm; HRMS (ESI) calcd. for $C_{21}H_{22}NO_4$ $[M+H]^+$ 352.1549, found 352.1547.

*5R-5-C-(indol-2-yl)-1,2;3,4-di-O-isopropylidene-β-L-arabinopyranose (**3fa**).* Pale yellow oil, 198 mg, 82% yield; R_f = 0.6 (silica gel F_{254}, 3:1, petroleum ether/EtOAc); $[\alpha]^{20}_D$ = −123.0^0 (*c* 0.50, CHCl$_3$); IR (KBr) 3473, 3030, 2927, 1619, 1601, 1558, 1498, 1458 , 1381, 1260, 1093, 800 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.79 (s, 1H,NH), 7.58 (d, 1H, $J_{4,5}$ = 7.6 Hz, H−4), 7.37 (d, 1H, $J_{7,6}$ = 7.6 Hz, H−7), 7.17 (t, 1H, $J_{6,5}$ = $J_{6,7}$ = 7.6

Hz, H−6), 7.08 (t, 1H, $J_{5,4} = J_{5,6} = 7.6$ Hz, H−5), 6.48 (s, 1H, H−3), 5.66 (d, 1H, $J_{1',2'} = 4.8$ Hz, H−1'), 5.11 (s, 1H, H−5'), 4.73 (d, 1H, $J_{3',4'} = 7.6$ Hz, H−3'), 4.52 (d, 1H, $J_{4',3'} = 7.6$ Hz, H−4'), 4.39 (br d , 1H, H−2'), 1.63, 1.59, 1.39, 1.38 (4s, each 3H, 4 CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2 (C−7a), 134.6 (C−2), 127.8 (C−3a), 122.1 (C−6), 120.8 (C−4), 119.7 (C−5), 111.3 (C−7), 109.6, 108.9 (2 isopropylidene−*C*), 101.7 (C−3), 96.8 (C−1'), 73.8 (C−4'), 71.1 (C−3'), 70.9 (C−2'), 64.4 (C−5'), 26.4, 26.2, 25.1, 24.1 (4 *C*H_3) ppm; HRMS (ESI) calcd. for $C_{19}H_{24}NO_5$ $[M+H]^+$ 346.1654, found 346.1652.

5R-5-C-(5-methylindol-2-yl)-1,2;3,4-di-O-isopropylidene-β-L-arabinopyranose ***(3fb)***. Pale yellow oil, 213 mg, 85% yield; $R_f = 0.6$ (silica gel F_{254}, 3:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -168.0^0$ (*c* 0.46, $CHCl_3$); IR (KBr) 3454, 3024, 2926, 1613, 1588, 1568, 1464, 1456, 1380, 1212, 1068, 800 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.36 (d, 1H), 7.25 (d, 1H, $J = 8.8$ Hz), 6.99 (d, 1H, $J = 8.8$ Hz), 6.39 (s, 1H), 5.65 (d, 1H, $J = 4.8$ Hz), 5.08 (s, 1H), 4.72 (d, 1H, $J = 8.0$ Hz), 4.50 (d, 1H, $J = 8.0$ Hz), 4.38 (d, 1H, $J = 4.8$ Hz), 2.43 (s, 3H), 1.63, 1.58, 1.39, 1.37 (4s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.7, 134.6, 128.8, 128.0, 123.8, 120.4, 110.9, 109.5, 108,9, 101.3, 96.8, 73.8, 71.1, 70.9, 64.4, 26.5, 26.2, 25.1, 24.1, 21.6 ppm; HRMS (ESI) calcd. for $C_{20}H_{26}NO_5$ $[M+H]^+$ 360.1811, found 360.1814.

5R-5-C-(5-fluoroindol-2-yl)-1,2;3,4-di-O-isopropylidene-β-L-arabinopyranose ***(3fc)***. Pale yellow oil, 203 mg, 80% yield; $R_f = 0.6$ (silica gel F_{254}, 3:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -131.2^0$ (*c* 1.39, $CHCl_3$); IR (KBr) 3472, 3032, 2929, 1623, 1589, 1548, 1487, 1456, 1380, 1212, 1070, 800 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 7.29−7.22

(m, 2H), 6.95−6.90 (m, 1H), 6.45 (s, 1H), 5.67 (d, 1H, J = 4.8 Hz), 5.10 (br s, 1H), 4.74 (dd, 1H, J = 2.2 Hz, J = 8.0 Hz), 4.51 (dd, 1H, J = 1.2 Hz, J = 8.0 Hz), 4.41 (dd, 1H, J = 4.8 Hz, J = 2.2 Hz), 1.63, 1.58, 1.40, 1.38 (4s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9 (d, $^{1}J_{C-F}$ = 233.0 Hz), 136.4, 133.0, 128.0 (d, $^{3}J_{C-F}$ = 10.0 Hz), 111.8 (d, $^{3}J_{C-F}$ = 9.0 Hz), 110.5 (d, $^{2}J_{C-F}$ = 26.0 Hz), 109.6, 109.0, 105.4 (d, $^{2}J_{C-F}$ = 23.0 Hz), 101.6 (d, $^{4}J_{C-F}$ = 5.0 Hz), 96.8, 73.6, 71.0, 70.8, 64.3, 26.4, 26.1, 25.0, 24.0 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −125.0 (dt, J_1 = 9.3 Hz, J_2 = 4.1 Hz) ppm; HRMS (ESI) calcd. for $C_{19}H_{23}FNO_5$ $[M+H]^+$ 364.1560, found 364.1563.

5R-5-C-(5-chloroindol-2-yl)-1,2;3,4-di-O-isopropylidene-β-L-arabinopyranose ***(3fd)***. Brown oil, 223 mg, 84% yield; R_f = 0.6 (silica gel F_{254}, 3:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -174.4^0$ (c 0.83, $CHCl_3$); IR (KBr) 3458, 3054, 2929, 1613, 1580, 1553, 1482, 1463, 1381, 1212, 1069, 801 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 7.52 (d, 1H, J = 1.4 Hz), 7.25 (d, 1H, J = 8.8 Hz), 7.09 (dd, 1H, J = 2.0 Hz, J = 8.8 Hz), 6.40 (s, 1H), 5.63 (d, 1H, J = 4.8 Hz), 5.06 (s, 1H), 4.70 (dd, 1H, J = 2.1 Hz, J = 8.0 Hz), 4.48 (dd, 1H, J = 8.0 Hz, J = 1.6 Hz), 4.38 (dd, 1H, J = 4.8 Hz, J = 2.1 Hz), 1.60, 1.55, 1.36, 1.35 (4s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 134.5, 128.8, 125.3, 122.4, 120.0, 112.2, 109.6, 109.0, 101.2, 96.8, 73.5, 71.0, 70.8, 64.3, 26.4, 26.2, 25.0, 24.0 ppm; HRMS (ESI) calcd. for $C_{19}H_{23}ClNO_5$ $[M+H]^+$ 380.1265, found 380.1268.

5R-5-C-(5-bromoindol-2-yl)-1,2;3,4-di-O-isopropylidene-β-L-arabinopyranose ***(3fe)***. Yellow oil, 258 mg, 87% yield; R_f = 0.6 (silica gel F_{254}, 3:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -137.8^0$ (c 0.54, $CHCl_3$); IR (KBr) 3452, 3058, 2928, 1649, 1577, 1542, 1486,

1460, 1380, 1211, 1070, 804 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.69 (s, 1H), 7.31−7.24 (m, 2H), 6.41 (s, 1H), 5.65 (d, 1H, J = 4.8 Hz), 5.08 (s, 1H), 4.72 (d, 1H, J = 7.8 Hz), 4.50 (d, 1H, J = 7.8 Hz), 4.40 (d, 1H, J = 4.8 Hz), 1.62, 1.57, 1.38, 1.37 (4s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0, 134.8, 129.6, 125.0, 123.2, 112.9, 112.7, 109.7 ,109.0, 101.1, 96.8, 73.6, 71.0, 70.9, 64.3, 26.4, 26.2, 25.0, 24.1 ppm; HRMS (ESI) calcd. for $C_{19}H_{23}BrNO_5$ $[M+H]^+$ 424.0760, found 424.0763.

*1-C-(indol-2-yl)-1,2;3,4-di-O-isopropylidene-β-D-arabinopyranose (**3ga**).* Brown oil, 198 mg, 82% yield; R_f = 0.6 (silica gel F_{254}, 2:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -26.2^0$ (c 1.74, $CHCl_3$); IR (KBr) 3433, 3061, 2925, 1625, 1598, 1561, 1494, 1456, 1379, 1079, 1026, 801 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H, NH), 7.62 (d, 1H, J = 7.6 Hz, H−4), 7.33 (d, 1H, $J_{7,6}$ = 7.8 Hz, H−7), 7.19 (dt, 1H, $J_{6,4}$ = 1.0 Hz, $J_{6,5}$ = $J_{6,7}$ = 7.8 Hz, H−6), 7.10 (t, 1H, J = 7.8 Hz, H−5), 6.67 (s, 1H, H−3), 4.73 (dd, 1H, $J_{3',2'}$ = 2.7 Hz, $J_{3',4'}$ = 8.0 Hz, H−3'), 4.54 (d, 1H, $J_{2',3'}$ = 2.7 Hz, H−2'), 4.35 (dd, 1H, $J_{4',5'a}$ = 1.8 Hz , $J_{4',3'}$ = 8.0 Hz, H−4'), 4.05 (dd, 1H, $J_{5'a,4'}$ = 1.8 Hz, $J_{5'a,5'b}$ = 13.2 Hz, H−5'a), 3.87 (d, 1H, $J_{5'b,5'a}$ = 13.2 Hz, H−5'b), 1.69, 1.67, 1.45, 1.44 (4s, each 3H, 4CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3 (C−2), 136.0 (C−7a), 127.7 (C−3a), 122.3 (C−6), 121.1 (C−4), 119.8 (C−5), 111.1 (C−7), 109.4 (2 isopropylidene−*C*), 100.9 (C−1'), 100.3 (C−3), 74.5 (C−2'), 70.7 (C−4'), 70.4 (C−3'), 61.7 (C−5'), 26.1, 26.0, 24.8, 24.3 (4*C*H_3) ppm; HRMS (ESI) calcd. for $C_{19}H_{24}NO_5$ $[M+H]^+$ 346.1654, found 346.1653.

*1-C-(5-methylindol-2-yl)-1,2;3,4-di-O-isopropylidene-β-D-arabinopyranose (**3gb**).* Brown oil, 221 mg, 88% yield; R_f = 0.6 (silica gel F_{254}, 2:1, petroleum ether/EtOAc);

$[\alpha]^{20}_{D} = -18.6^{0}$ (*c* 0.53, $CHCl_3$); IR (KBr) 3414, 3021, 2926, 1621, 1585, 1564, 1487, 1458, 1379, 1211, 1067, 799 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.39 (s, 1H), 7.20 (d, 1H, J = 7.8 Hz), 7.50 (d, 1H, J= 7.8 Hz), 6.56 (s, 1H), 4.71 (d, 1H, J= 7.8 Hz), 4.51 (s, 1H), 4.33 (d, 1H, J= 7.8 Hz), 4.03 (d, 1H, J= 13.4 Hz), 3.85 (d, 1H, J= 13.4 Hz), 2.43 (s, 3H), 1.67, 1.65, 1.44, 1.42 (4s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 134.4, 129.0, 128.0, 124.0, 120.8, 110.8, 109.5, 109.4, 101.0, 100.0, 74.6, 70.8, 70.5, 61.7, 26.1, 24.8, 24.3, 21.5 ppm; HRMS (ESI) calcd. for $C_{20}H_{26}NO_5$ $[M+H]^+$ 360.1811, found 360.1810.

*1-C-(5-fluoroindol-2-yl)-1,2;3,4-di-O-isopropylidene-β-D-arabinopyranose (**3gc**).* Pale yellow oil, 203 mg, 80% yield; R_f= 0.6 (silica gel F_{254}, 2:1, petroleum ether/EtOAc); $[\alpha]^{20}_{D} = -30.1^{0}$ (*c* 0.56, $CHCl_3$); IR (KBr) 3391, 3068, 2926, 1619, 1589, 1592, 1548, 1454, 1209, 1069, 801 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 7.24−7.21 (m, 2H), 6.95−6.90 (m, 1H), 6.62 (s, 1H), 4.73 (dd, 1H, J= 2.8 Hz, J= 8.0 Hz), 4.51 (d, 1H, J= 2.8 Hz), 4.34 (br d, J = 7.6 Hz), 4.04 (dd, 1H, J= 1.6 Hz, J= 13.2 Hz), 3.86 (d, 1H, J = 13.2 Hz), 1.67, 1.66, 1.44. 1.43 (4s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0 (d, $^1J_{C-F}$= 232.6 Hz), 140.1, 132.6, 128.1 (d, $^3J_{C-F}$= 10.2 Hz), 111.7 (d, $^3J_{C-F}$= 9.5 Hz), 110.8 (d, $^2J_{C-F}$= 26.2 Hz), 109.6, 109.5, 105.9 (d, $^2J_{C-F}$= 23.2 Hz), 100.8, 100.5 ($^4J_{C-F}$ = 4.7 Hz), 74.6, 70.8, 70.4, 61.8, 26.1, 24.9, 24.3 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −124.8 (dt, J_1 = 9.3 Hz, J_2 = 4.5 Hz) ppm; HRMS (ESI) calcd. for $C_{19}H_{23}FNO_5$ $[M+H]^+$ 364.1560, found 364.1559.

*1-C-(5-chloroindol-2-yl)-1,2;3,4-di-O-isopropylidene-β-D-arabinopyranose (**3gd**).*

Brown oil, 225 mg, 85% yield; R_f = 0.6 (silica gel F_{254}, 2:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -26.6^0$ (*c* 0.45, $CHCl_3$); IR (KBr) 3383, 3067, 2927, 1628, 1599, 1549, 1515, 1463, 1379, 1212, 1067, 798 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.61 (s, 1H), 7.29 (d, 1H, *J* = 8.7 Hz), 7.17 (dd, 1H, *J*=1.6 Hz, *J*= 8.7 Hz), 6.64 (s, 1H), 4.77 (dd, 1H, *J*= 2.4 Hz, *J* = 7.4 Hz), 4.55 (d, 1H, *J*= 2.4 Hz), 4.38 (d, 1H, *J*= 7.4 Hz), 4.08 (dd, 1H, *J*= 0.9 Hz, *J*= 12.8 Hz), 3.90 (d, 1H, *J*= 12.8 Hz), 1.71, 1.70, 1.49, 1.47 (4 s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 134.4, 128.8, 125.5, 122.8, 120.6, 112.2, 109.7, 109.5, 100.8, 100.1, 74.6, 70.8, 70.4, 61.8, 26.1, 24.9, 24.3 ppm; HRMS (ESI) calcd. for $C_{19}H_{23}ClNO_5$ $[M+H]^+$ 380.1265, found 380.1264.

1-C-(5-bromoindol-2-yl)-1,2;3,4-di-O-isopropylidene-β-D-arabinopyranose ***(3ge)***. Brown oil, 252 mg, 85% yield; R_f = 0.6 (silica gel F_{254}, 2:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -21.5^0$ (*c* 0.66, $CHCl_3$); IR (KBr) 3396, 3061, 2927, 1629, 1586, 1564, 1496, 1462, 1379, 1212, 1068, 798 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.72 (s, 1H), 7.25 (dd, 1H, *J*= 1.6 Hz, *J*= 8.6 Hz), 7.18 (d, 1H, *J* = 8.6 Hz), 6.59 (s, 1H), 4.72 (dd, 1H, *J*= 2.7 Hz, *J* = 7.6 Hz), 4.50 (d, 1H, *J*= 2.7 Hz), 4.34 (dd, 1H, *J*= 1.8 Hz , *J*= 7.6 Hz), 4.03 (dd, 1H, *J* = 1.8 Hz, *J*= 13.2 Hz), 3.85 (d, 1H, *J*= 13.2 Hz), 1.66, 1.65, 1.44, 1.42 (4s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 134.7, 129.5, 125.3, 123.7, 113.0, 112.6, 109.7, 109.5, 100.7, 99.9, 74.5, 70.7, 70.4, 61.8, 26.1, 24.8, 24.3 ppm; HRMS (ESI) calcd. for $C_{19}H_{23}BrNO_5$ $[M+H]^+$ 424.0760, found 424.0761.

1R-1-C-(indol-2-yl)-1,2-O-ispropylidene-4-O-trityl-D-erythritol ***(3ha)***. Yellow oil, 316 mg, 87% yield; R_f = 0.6 (silica gel F_{254}, 1:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = +9.1^0$ (*c*

0.48, $CHCl_3$); IR (KBr) 3460, 3046, 2926, 1624, 1605, 1572, 1490, 1449, 1377, 1210, 1023, 801 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H, NH), 7.55 (d, 1H, J = 8.0 Hz, H−4), 7.45−7.20 (m, 16H, Ar*H*, H−7), 7.14 (t, 1H, J = 7.2 Hz, H−6), 7.07 (t, 1H, J = 7.2 Hz, H−5), 6.42 (s, 1H, H−3), 5.20 (d, 1H, $J_{1', 2'}$ = 7.2 Hz, H−1'), 4.05 (t, 1H, $J_{2', 3'} = J_{2', 1'}$ = 7.2 Hz, H−2'), 3.98−3.94 (m, 1H, H−3'), 3.40 (dd, 1H, $J_{4'a, 3'}$ = 3.6 Hz, $J_{4'a, 4'b}$ = 10.0 Hz, H−4'a), 3.30 (dd, 1H, $J_{4'b, 3'}$ = 7.2 Hz, $J_{4'b, 4'a}$ = 9.6 Hz, H−4'b), 1.46, 1.44 (2s, each 3H, 2CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7 (Ar*C*), 137.4 (C−2), 136.2 (C−7a), 128.7, 128.1, 127.4 (Ar*C*), 127.0 (C−3a), 121.8 (C−6), 120.6 (C−4), 119.8 (C−5), 111.0 (C−7), 110.2 (isopropylidene−*C*), 99.7 (C−3), 87.4 (ph_3C−O), 81.0 (C−2'), 75.9 (C−1'), 72.4 (C−3'), 65.2 (C−4'), 27.0, 26.6 (2*C*H_3) ppm; HRMS (ESI) calcd. for $C_{34}H_{34}NO_4$ $[M+H]^+$ 520.2488, found 520.2487.

*1R-1-C-(5-methylindol-2-yl)-1,2-O-ispropylidene-4-O-trityl-D-erythritol (**3hb**).* Pale yellow oil, 336 mg, 90% yield; R_f = 0.5 (silica gel F_{254}, 2:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -2.0^0$ (*c* 0.50, $CHCl_3$); IR (KBr) 3422, 3012, 2924, 1628, 1598, 1542, 1489, 1453, 1380, 1095, 1025, 802 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.42−7.06 (m, 18H), 6.43 (s, 1H), 5.21 (d, 1H, J = 7.2 Hz), 4.05 (t, 1H, J = 7.2 Hz), 3.98−3.94 (m, 1H), 3.40 (dd, 1H, J = 3.6 Hz, J = 10.0 Hz), 3.30 (dd, 1H, J = 6.8 Hz, J = 10.0 Hz), 2.45 (s, 3H), 1.46, 1.45 (2s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 137.3, 134.4, 128.7, 128.5, 127.9, 127.2, 127.8, 123.2, 120.1, 110.4, 109.9, 99.0 (C−3), 87.2, 80.8, 75.7, 72.2, 65.0, 26.8, 26.4, 21.4 ppm; HRMS (ESI) calcd. for $C_{35}H_{36}NO_4$ $[M+H]^+$ 534.2644, found 534.2643.

*1R-1-C-(5-fluoroindol-2-yl)-1,2-O-ispropylidene-4-O-trityl-D-erythritol (**3hc**).* Pale yellow oil, 312 mg, 83% yield; R_f = 0.5 (silica gel F_{254}, 2:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -5.0^0$ (*c* 0.50, $CHCl_3$); IR (KBr) 3398, 3021, 2924, 1627, 1593, 1548, 1489, 1449, 1260, 1095, 801 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.41−6.85 (m, 18H), 6.38 (s, 1H), 5.18 (d, 1H, *J* = 7.2 Hz), 4.02 (t, 1H, *J* = 7.2 Hz), 3.95 (d, 1H, *J* = 3.4 Hz), 3.41 (dd, 1H, *J* = 3.4 Hz, *J* = 9.6 Hz), 3.29 (dd, 1H, *J* = 7.0 Hz, *J* = 9.6 Hz), 1.46, 1.44 (2s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0 (d, $^1J_{C-F}$ = 232.4 Hz), 143.6, 139.4, 132.7, 128.7, 128.1, 128.0 (d, $^3J_{C-F}$ = 7.8 Hz), 127.4, 111.5 (d, $^3J_{C-F}$ = 9.5 Hz), 110.3, 110.0 (d, $^2J_{C-F}$ = 26.2 Hz), 105.4 (d, $^2J_{C-F}$ = 23.2 Hz), 99.8 (d, $^4J_{C-F}$ = 4.4 Hz), 87.4, 81.0, 75.9, 72.4, 65.3, 26.9, 26.6 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −125.0 (dt, J_1 = 9.3 Hz, J_2 = 4.1 Hz) ppm; HRMS (ESI) calcd. for $C_{34}H_{33}FNO_4$ $[M+H]^+$ 538.2394, found 538.2396.

*1R-1-C-(5-chloroindol-2-yl)-1,2-O-ispropylidene-4-O-trityl-D-erythritol (**3hd**).* Pale yellow oil, 345 mg, 89% yield; R_f = 0.5 (silica gel F_{254}, 2:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -8.5^0$ (*c* 0.50, $CHCl_3$); IR (KBr) 3396, 3020, 2923, 1626, 1591, 1546, 1484, 1447, 1262, 1097, 800 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.33−6.97 (m, 18H), 6.28 (s, 1H), 5.09(d, 1H, *J* = 7.2 Hz), 3.94 (t, 1H, *J* = 7.2 Hz), 3.87−3.82 (m, 1H), 3.29 (dd, 1H, *J* = 3.6 Hz, *J* = 10.0 Hz), 3.18 (dd, 1H, *J* =7.2 Hz, *J* = 9.6 Hz), 1.35, 1.33 (2s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 139.1, 134.3, 129.4, 128.7, 128.1, 127.9, 127.4, 122.0, 119.9, 112.0, 110.3, 99.2, 87.4, 80.9, 75.9, 72.4, 65.3, 26.9, 26.5 ppm; HRMS (ESI) calcd. for $C_{34}H_{33}ClNO_4$ $[M+H]^+$ 554.2098, found 554.2099.

*1R-1-C-(5-bromoindol-2-yl)-1,2-O-ispropylidene-4-O-trityl-D-erythritol (**3he**).* Pale yellow oil, 364 mg, 87% yield; R_f = 0.5 (silica gel F_{254}, 2:1, petroleum ether/EtOAc); $[\alpha]^{20}_D$ = −10.8^0 (*c* 0.50, $CHCl_3$); IR (KBr) 3392, 3018, 2921, 1623, 1590, 1543, 1482, 1448, 1260, 1090, 800 cm^{-1}; ^{1}H NMR (400 MHz, DMSO) δ 11.29 (s, 1H), 7.64 (s, 1H), 7.33−7.18 (m, 17H), 6.35 (s, 1H), 5.36 (d, 1H, *J* = 6.0 Hz), 4.25 (t, 1H, *J* = 6.0 Hz), 3.91−3.88 (m, 1H), 2.98 (dd, 1H, *J* = 8.0 Hz, *J* = 16.0 Hz), 2.89 (dd, 1H, *J* = 4.4 Hz, *J* = 4.8 Hz), 1.39, 1.34 (2s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 138.3, 135.2, 129.4, 128.3, 127.7, 126.9, 123.6, 122.2, 113.3, 111.4, 108.9, 100.1, 86.0, 80.9, 73.2, 69.8, 65.4, 27.0, 26.9 ppm; HRMS (ESI) calcd. for $C_{34}H_{33}BrNO_4$ $[M+H]^+$ 598.1593, found 598.1595.

*1R-1-C-(indol-2-yl)-1,2;4,5-di-O-isopropylidene-D-arabinitol (**3ia**).* Pale yellow oil, 213 mg, 88% yield; R_f = 0.6 (silica gel F_{254}, 1:1, petroleum ether/EtOAc). $[\alpha]^{20}_D$ = −6^0 (*c* 0.50, $CHCl_3$); IR (KBr) 3420, 3058, 2925, 1627, 1582, 1553, 1501, 1460, 1380, 1217, 1095, 801 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H, NH), 7.58 (d, 1H, $J_{4,5}$ = 7.6 Hz, H−4), 7.38 (d, $J_{7,6}$ = 8.0 Hz, H−7), 7.19 (t, 1H, $J_{5,4} = J_{5,6}$ = 7.6 Hz, H−6), 7.10 (t, 1H, $J_{6,5} = J_{6,7}$ = 7.6 Hz, H−5), 6.48 (s, 1H, H−3), 5.26 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H−1'), 4.24 (dd, 1H, $J_{2',3'}$ = 1.6 Hz, $J_{2',1'}$ = 8.0 Hz, H−2'), 4.12−4.02 (m, 3H, H−4', H−5'), 3.62−3.60 (m, 1H, H−3'), 1.56, 1.54, 1.34, 1.31 (4s, each 3H, 4 C*H*$_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2 (C−7a), 135.0 (C−2), 128.4 (C−3a), 122.3 (C−6), 120.8 (C−4), 120.1 (C−5), 111.1 (C−7), 110.2, 109.7 (2 isopropylidene−*C*), 100.6 (C−3), 80.6 (C−2'), 76.5 (C−4'), 73.7 (C−1'), 70.0 (C−3'), 67.1 (C−5'), 27.3, 27.1, 26.8, 25.4 (4 *C*H$_3$) ppm; HRMS (ESI)

calcd. for $C_{19}H_{25}NO_5$ $[M+H]^+$ 347.1733, found 347.1734.

*1R-1-C-(5-methylindol-2-yl)-1,2;4,5-di-O-isopropylidene-D-arabinitol (**3ib**).* Brown oil, 227 mg, 90% yield; R_f = 0.5 (silica gel F_{254}, 1:1, petroleum ether/EtOAc); $[\alpha]^{20}_D$ = −5.6^0 (*c* 0.48, $CHCl_3$); IR (KBr) 3420, 3064, 2987, 1625, 1597, 1558, 1482, 1456, 1372, 1260, 1060, 800 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.36 (s, 1H), 7.23 (d, 1H, *J* = 8.8 Hz), 7.01 (dd, 1H, *J* = 8.4 Hz, *J* = 1.2 Hz), 6.40 (s, 1H), 5.24 (d, 1H, *J* = 8.4 Hz), 4.24 (dd, 1H, *J* = 2.0 Hz, *J* = 8.4 Hz), 4.07−4.04 (m, 3H), 3.60 (dd, 1H, *J* = 2.0 Hz, *J* = 7.6 Hz), 2.44 (s, 3H), 1.56, 1.54, 1.34, 1.32 (4s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 134.6, 129.3, 128.7, 123.9, 120.4, 110.7, 110.1, 109.7, 100.2, 80.5, 76.5, 73.7, 70.0, 67.0, 27.3, 27.0, 26.8, 25.4, 21.5 ppm; HRMS (ESI) calcd. for $C_{20}H_{27}NO_5$[M+H]$^+$ 361.1889, found 361.1888.

*1R-1-C-(5-fluoroindol-2-yl)-1,2;4,5-di-O-isopropylidene-D-arabinitol (**3ic**).* Pale yellow oil, 219 mg, 86% yield; R_f = 0.5 (silica gel F_{254}, 1:1, petroleum ether/EtOAc); $[\alpha]^{20}_D$ = −1.5^0 (*c* 0.50, $CHCl_3$); IR (KBr) 3418, 3015, 2925, 1615, 1582, 1553, 1487, 1457, 1378, 1217, 1086, 803 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.22−7.20 (m, 2H), 6.95−6.90 (m, 1H), 6.43 (s, 1H), 5.23 (d, 1H, *J* = 8.0 Hz), 4.21 (dd, 1H, *J* = 2.0 Hz, *J* = 8.0 Hz), 4.11−4.05 (m, 3H), 3.59 (dd, 1H, *J* = 2.0 Hz, *J* = 6.8), 1.56, 1.54, 1.34, 1.31 (4s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1 (d, $^1J_{C-F}$ = 233.0 Hz), 137.0, 132.7, 128.8 (d, $^3J_{C-F}$ = 10.2 Hz), 111.6 (d, $^3J_{C-F}$ = 9.6 Hz), 110.7 ($^2J_{C-F}$ = 26.3 Hz), 110.3, 109.7, 105.5 (d, $^2J_{C-F}$ = 23.5 Hz), 100.6 (d, $^4J_{C-F}$ = 4.6 Hz,), 80.7, 76.5, 73.6, 70.1, 67.1, 27.3, 27.1, 26.9, 25.5 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −125.1 (dt, J_1 = 9.3 Hz, J_2 =

4.5 Hz) ppm; HRMS (ESI) calcd. for $C_{19}H_{24}FNO_5$ $[M+H]^+$ 365.1639, found 365.1640.

*1R-1-C-(6-fluoroindol-2-yl)-1,2;4,5-di-O-isopropylidene-D-arabinitol (**3id**).* Pale yellow oil, 214 mg, 84% yield; R_f = 0.6 (silica gel F_{254}, 1:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -17.6^0$ (*c* 0.42, $CHCl_3$); IR (KBr) 3362, 3061, 2926, 1627, 1599, 1560, 1499, 1457, 1377, 1221, 1063, 809 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.49 (dd, 1H, J = 5.6 Hz, J = 8.4 Hz), 7.05 (dd, 1H, J = 2.0 Hz, $J_{H,F}$ = 9.5 Hz), 6.91−6.86 (m, 1H), 6.47 (s, 1H), 5.24(d, 1H, J = 8.0 Hz), 4.25 (dd, 1H, J = 2.0 Hz, J = 8.0 Hz), 4.14−4.05 (m, 3H), 3.61 (br d, 1H, J = 6.4 Hz), 1.58, 1.56, 1.36, 1.32 (4s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0 ($^1J_{C-F}$ = 236.4 Hz), 136.2 (d, $^3J_{C-F}$ = 12.4 Hz), 135.3, 124.8, 121.4 (d, $^3J_{C-F}$ = 10.1 Hz), 110.2, 109.7, 108.8 (d, $^2J_{C-F}$ = 24.2 Hz), 100.7, 97.5 (d, $^2J_{C-F}$ = 26.0 Hz), 80.4, 76.5, 73.5, 69.9, 67.1, 27.3, 27.0, 26.8, 25.4 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −120.6 (dt, J_1 = 9.5 Hz, J_2 = 5.6 Hz) ppm; HRMS (ESI) calcd. for $C_{19}H_{24}FNO_5$ $[M+H]^+$ 365.1639, found 365.1638.

*1R-1-C-(5-chloroindol-2-yl)-1,2;4,5-di-O-isopropylidene-D-arabinitol (**3ie**).* Brown oil, 227 mg, 85% yield; R_f = 0.6 (silica gel F_{254}, 1:1, petroleum ether/EtOAc). $[\alpha]^{20}_D = -12.7^0$ (*c* 0.50, $CHCl_3$); IR (KBr) 3420, 3053, 2959, 1624, 1581, 1510, 1462, 1378, 1217, 1061, 799 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.53 (s, 1H), 7.29 (d, 1H, J = 8.0 Hz), 7.13 (d, 1H, J = 8.0 Hz), 6.41 (s, 1H), 5.24 (d, 1H, J = 8.4 Hz), 4.21 (dd, 1H, J = 1.6 Hz, J = 8.4 Hz), 4.08−4.04 (m, 3H), 3.60−3.57 (m, 1H), 1.55, 1.54, 1.34, 1.30 (4s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 134.8, 129.8, 126.1, 123.0, 120.5, 112.4, 110.7, 110.1, 110.4, 81.0 , 76.8, 73.8, 70.4, 67.4, 27.6, 27.3, 27.2, 25.8 ppm; HRMS (ESI)

calcd. for $C_{19}H_{24}ClNO_5$ $[M+H]^+$ 381.1343, found 381.1345.

*1R-1-C-(6-choroindol-2-yl)-1,2;4,5-di-O-isopropylidene-D-arabinitol (**3if**).* Pale yellow oil, 240 mg, 90% yield; R_f = 0.6 (silica gel F_{254}, 1:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -25.3^0$ (*c* 0.52, $CHCl_3$); IR (KBr) 3362, 3063, 2928, 1616, 1598, 1576, 1506, 1456, 1377, 1217, 1061, 814 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.46 (d, 1H , J = 8.4 Hz), 7.33 (s, 1H), 7.06 (dd, 1H, J = 8.4 Hz, J = 1.6 Hz), 6.44 (s, 1H), 5.23 (d, 1H, J = 8.4 Hz), 4.22 (dd, 1H, J = 2.4 Hz, J = 8.4 Hz), 4.10−4.05 (m, 3H), 3.59 (br s, lH), 1.55, 1.53, 1.34, 1.30 (4s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 135.9, 128.0, 126.9, 121.5, 120.8, 111.0, 110.3, 109.7, 100.6, 80.6, 76.4, 73.5, 70.0, 67.0, 27.2, 27.0, 26.8, 25.4 ppm; HRMS (ESI) calcd. for $C_{19}H_{24}ClNO_5$ $[M+H]^+$ 381.1343, found 381.1344.

*1R-1-C-(5-bromoindol-2-yl)-1,2;4,5-di-O-isopropylidene-D-arabinitol (**3ig**).* Brown oil, 262 mg, 88% yield; R_f = 0.6 (silica gel F_{254}, 1:1, petroleum ether/EtOAc); $[\alpha]^{20}_D = -30.5^0$ (*c* 0.54, $CHCl_3$); IR (KBr) 3360, 3061, 2925, 1612, 1596, 1573, 1501, 1451, 1378, 1213, 1060, 810 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.70 (s, 1H), 7.28−7.20 (m, 2H), 6.41 (s, 1H), 5.23 (d, 1H, J = 8.4 Hz), 4.21 (dd, 1H, J = 2.0 Hz, J = 8.4 Hz), 4.15−4.02 (m, 3H), 3.59 (dd, 1H, J = 2.0 Hz, J = 7.6 Hz), 1.56, 1.54, 1.35, 1.31 (4s, each 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 134.7, 130.2, 125.2, 123.2, 113.3, 112.5, 110.4, 109.8, 100.0, 80.7, 76.4, 73.4, 70.1, 67.1, 27.3, 27.0, 26.9, 25.4 ppm; HRMS (ESI) calcd. for $C_{19}H_{24}BrNO_5$ $[M+H]^+$ 425.0838, found 425. 0839.

ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, DEPT−135, and 2D NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (21272219, 20972142), the National Basic Research Program of China (973 program, 2013CB910700), and the State Key Laboratory of Bio−organic and Natural Products Chemistry, CAS (08417).

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