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Iodosobenzene diacetate-Iodine and IBX-Iodine: Reagent systems for the synthesis of diastereomerically enriched 2-deoxy-2-iodoglycosyl acetates and 2-deoxy-2-iodoglycosyl *ortho*-iodobenzoates from protected glycals

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ABSTRACT

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1. Introduction

The biological significance of many natural products has been found to be due to the presence of 2-deoxy and 2,6-dideoxy glycosides.¹ These are also structurally important components for the stereoselective synthesis of glycosides found in several important natural products such as the angucycline family of antibiotics (landomycin A),² aureolic acid antibiotics (olivomycin chromomycin A3),³ enediynes (calicheamycin γ_1^{I} , A. esperamicins A1 and C),⁴ antiparacital glycosides, avermectins (avermectin B1a, ivermectin),⁵ some cholestane glycosides (OSW-1),⁶ and cardiac glycosides $(digitoxine)^7$ (Fig. 1). Removing of these deoxy sugars from the above clinically important molecules often harshly decreases their efficacy and/or specificity. 2-Deoxysugars also play a key role in glycolipids, glycoproteins, and lipopolysaccharides, where they act as ligands for cell-cell interactions or as targets for toxins, antibodies, and microorganisms.8 The above compounds contain monosaccharide units belonging to the both D and L series with all possible configurations (Figure 1).

The stereo controlled construction of glycosidic linkage in the absence of a stereo directing group at C-2 position in 2-deoxyoligosaccharides becomes one of the most challenging tasks in glycosylation reactions.⁹ This problem can be overcome by using electron donating groups (such as iodo, phenylselenyl¹⁰ and phenylsulfanyl¹¹) as stereo directing groups at position 2 of glycosyl donor in glycosylation step. The 2-heteroatomic-substituted glycosides can be further reduced to deliver corresponding 2-deoxyglycosides.¹² In this regard, iodoglycosyl derivatives are very important in preparation of oligosaccharides,

Two efficient, metal free reagent systems, PhI(OAc)₂-I₂ (method A) and IBX-I₂ (method B), for stereoselective synthesis of *trans*-2-deoxy-2-iodoglycosylacetates and *O*-iodobenzoates respectively from differently protected glycals have been developed. They are compatible with a variety of protecting groups and various functional groups at 2*C*-position. Hexose-3,2-enolone **8** is obtained directly from 2-acetoxy glycal **5** by method A. An application to modified method B has been shown by synthesis of a diastereomerically pure α -glycosyl *ortho*-hexynylbenzoate **12**, a glycosyl donor from 3,4,6-tri-*O*-acetyl-D-glucal in two steps that has been further utilized in the synthesis of glycosides **13-18**.

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because of the green nature of the iodine over the others. Moreover, as a radical precursor it also provides the basis for introduction of alkenyl substituents.¹³ The stereoselective preparation of 2-deoxy-2-iodoglycopyranosyl acetates can be accomplished in three different ways. The first one involves nucleophilic displacement of 2-triflates with any suitable nucleophile.¹⁴ Second approach proceeds through the formation of halohydrins from protected glycals followed by acetylation to give isomeric mixtures. The low diastereoselectivity of halohydrin formation demerits this method.¹⁵ Formation of haloacetates from protected glycals directly falls under the third category.¹⁶ Among them, last one continues to attract many carbohydrate chemists because the formation of desired product takes place with high yields and excellent stereoselectivity.



Figure 1: Some biologically important 2-deoxyoligosaccharides containing configurationally different 2-deoxy sugars.

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Kirschning et al reported the reactivity of hypervalent iodine and its potential applications in the 1,2-cohalogenation of C-C multiple bonds and glycal substrates.^{16a,17} Hotha and his coworkers investigated the regioselective 1,2-functionalization of glycals using cetylammonium bromide (CTAB) in the presence of critical micelle concentration conditions in combination with trivalent iodine PhI(OAc)₂ (BAIB).^{16f} The hypervalent iodine compound, BAIB along with phosphinic acid^{16a} or trimethylsilyl iodide^{16j} were used together for iodophosphoryloxylation and iodoacetoxylation of glycals respectively. Other reagents that include CAN (ceric ammonium nitrate)/NaI/AcOH,16e IDCP (iodonium dicollidine perchlorate)/NIS (N-iodosuccinimide), . 18h KIO₃/AcOH,^{18f} NH₄I/H₂O₂/Ac₂O,^{16d} and $I_2/Cu(OAc)_2$ CuI/NaIO₄^{16h} promoted the iodoacetoxylation of glycals and alkenes.

During the past two decades, the versatility of hypervalent iodine or organo iodine reagents in organic synthesis has been well recognized owing to their mildness and selectively effecting a number of oxidative transformations.¹⁹ Currently, both iodine (III) and iodine (V) are widely used in organic synthesis (fig.2). An important feature of these molecules is their ability to transfer ligands that are attached to central iodine atom onto appropriate electrophiles. The electrophilic halogenation of olefins by the combination of these reagents with halide salts, followed by nucleophilic-assisted halonium ion ring opening has been well documented in the literature.²⁰ The application of organo iodine reagents (fig. 2) on fully protected glycals has been shown for selective C3-*O*-oxidation, C-2 heteroatom substitution and oxidative glycosidation.²¹ Herein, we have demonstrated a new method for the synthesis of 2-deoxy-2-iodoglycosyl acetate and 2-iodobenzoates using BAIB-I₂ and IBX-I₂ systems respectively.



Figure.2: Hypervalent iodine $(I^{III} \text{ and } I^{V})$ reagents.

2. Results and Discussion

We initiated our work with an aim to search for a suitable reagent system for iodoacetoxylation of globally protected glycals. In our initial experiments, 1 mmol of per-O-acetyl glucal 1a was treated with 1.2 mmol of $PhI(OAc)_2$ BAIB or ([bis(acetoxy)iodo]benzene,), 1.2 mmol of iodine (I₂) and 0.2 mmol of t-butyl hydroperoxide (TBHP, for radical initiation) in 5 mL of dichloromethane at 0 °C. We observed the formation of a complex mixture of pyranosyl acetates α -manno 2a and β -gluco 3a and 2-iodoglucal 4 by their ¹H NMR and MS analyses (Scheme 1). On replacement of more reactive molecular iodine with NIS in the above reaction, we observed that **1a** was not consumed at 0°C. However, performing the reaction at refluxing temperature led to the formation of chromatographically inseparable materials.



Scheme 1: Iodoacetoxylation of glycal 1a using BAIB-I2-TBHP.

Next, we used BAIB-I2 system in the absence of TBHP and gratifyingly the reaction was found to be clean (TLC) due to complete consumption of 1a in just 30 min to afford separable diastereomeric mixture of 2a and 3a in a ratio of 95:5 with 93% yield. We carried out several pilot experiments to optimize the reaction conditions by screening different solvents at various temperatures with varying ratios of 1a and BAIB-I2. The most satisfactory yield of the desired products 2a and 3a with a 95:5 ratio of manno-gluco isomers was 93% when 1.0 mmol of 1a was treated with 0.6 mmol of BAIB and 1.2 mmol of I2 at 25 °C for 30 min (Table 1, entries 1-5). It was found that the reaction in DCM at room temperature proceeded smoothly without formation of any side products whereas the reaction in THF and acetonitrile took more time (30-90 min) to complete the reaction with poor yield of 2a and 3a. The reaction in solvents like toluene and DMF was unsuccessful (Table 1, entries 5-9). Having established optimized conditions (Table 1 entry 3), we further proceeded to examine the scope of differently protected glycals including pentose sugars and with variable 2C-branched hex-2-enopyranosides to obtain the corresponding isomeric iodoacetates (Table 2). As expected, we found that a wide array of masked glycals bearing different protecting groups (acetyl, benzyl, sillyl, MOM) showed good compatibility in this transformation. The complete conversion of each glycal was noticed in just 30 min and their corresponding products 2a-20 were obtained in good to excellent yields with varying α/β ratios under the optimized condition (Table 2, entries 1-11).

Table 1: Optimization of reaction condition.

Entry	BAIB (eq)	I ₂ (eq)	Temp	Solvent	yield (%) and ratio (manno:gluco) ^a
1	1.2	1.5	rt	DCM	93%, 95:5
2	1.0	1.2	rt	DCM	93%, 95:5
3	0.6	1.2	rt	DCM	93%, 95:5
4	0.6	1.2	0 °C	DCM	93%, 95:5
5	0.6	1.2	reflux	DCM	80%, 90:10
6	0.6	12	rt	MeCN	85%, 90:10
7	0.6	1.2	rt	THF	70%, 90:10
8	0.6	1.2	rt	Toluene	-
9	0.6	1.2	rt	DMF	-
a		•		1 0 1	

^ayields and ratios are calculated after column purification

In the case of 6-*O*-*t*-butyldiphenyl silyl protected glycals **1e** and **1f**, the α/β diastereomeric ratios of the desired products were slightly lower than those derived from acetyl (**1a**, **1c**) and benzyl (**1b**, **1d**) protected glycals. Here we wish to mention that the title reaction with **1g** and **1h** (D-arabinals) led to the formation of their respective α/β anomers 96% and 90% yields with diastereomeric ratios 88:12 and 86:14. The ${}^{1}C_{4}$ conformation of the major 1,2- dieqatorial isomer 2h was established by its detailed 1 H and NOESY spectroscopy. Here the anomeric proton appeared at δ 5.89 ppm (d, $J_{1,2}$ = 8.5 Hz), H2 at δ 4.33 ppm (dd, $J_{2,1}$ = 8.7 Hz and $J_{2,3}$ = 10.0 Hz) ,H3 at δ 3.55 ppm (dd, $J_{2,3}$ = 10.0 Hz and $J_{3,4}$ = 3.0 Hz) and its NOESY experiment showed correlation between H1-H3, H1-H5 (*C*5 axial proton), and H3-

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Entry	Substrate	Product	^b Yield & ^c ratios (α/β)	Entry	Substrate	Product	^b Yield & ^c ratios $(\alpha/\beta)^{b}$				
1	Aco OAc Aco 1a	Aco Aco 2a OAc	93% 95:5	10	Aco Aco 1j	Aco Aco 2j I	95% 90:10				
2	BnO BnO 1b	BnO BnO 2b OAc	95% 90:10	11	Bno D	BnO 2k I	98% 80:20				
3		AcO OAc AcO 2c OAc	96% 92:8	12		AcO AcO 21 IOAc	95% 96:4				
4	BnO 1d	BnO OBn BnO 2d OAc	97% 90:10	13	AcO AcO 1m NO ₂	no reaction					
5	TBDPSO MOMO MOMO 1e	TBDPSO MOMO 2e OAc	90% 85:15	14	BnO BnO 1n CO ₂ Me	BnO BnO BnO MeO ₂ C 2n	75% 80:20				
6		MOMO OTBDPS MOMO 2f OAc	87% 89:11	15	AcO AcO 10 CN	AcO AcO NC 20 OAc	85% 85:15				
7	Aco o Aco 1g	OAc OAc 2g	96% 88:12	16	O 1p	O OAc 2p	97%				
8	BnO O BnO1h	OBn 2h	90% 86:14	17	lq	OAc 2q	81%				
9	Aco Aco 1i	Ac0	90% 80:20								



H5 protons. Similarly the identification of **2g** was established by analogy. The title reaction with acetylated L-rhamnal **1i** prepared from L-rhamnose, furnished the α/β anomers in the ratio of 80:20 (90%). Here the major isomer 1,2-diaxial iodoacetate **2i** with ¹C₄ conformation was established on the basis of its proton NMR spectra (1H appeared singlet at δ 6.27 ppm) and previous reports.^{16b} The reaction with D-ribose derived furanoid glycals **1j** and **1k**²² gave their respective iodoacetates **2j** and **2k** with excellent yields and diastereomeric ratios. We have also executed the title reaction with different 2-substituted glycals (**1I-10**).²³ While the reaction was successful with the 2-iodoglucal²³ **11** to give 2-deoxy-2,2-diiodoglycosyl acetate **2l** in 95% yield, iodoacetoxylation of 2*C*-pseudoglycals **1n** and **1o**, took place regioselectively at endocyclic glycosyl 1,2-double bond to furnish the corresponding 1-acetoxy-2-iododerivatives **2n** and **2o** in moderate yields. We also fruitfully applied this reagent system on 3,4-dihydropyran 1p and cyclohexene 1q to accesses their respective derivatives 2p (97%) and 2q (81%). Unfortunately the reaction was futile with 2-nitroglycals²⁴ 1m both at room temperature and with heating.



Scheme 2: Synthesis of enolone 8 from 2-acetoxyglycal 5.

In addition, when 2-acetoxy-peracetylated-D-glucal 5^{25} was subjected to this reaction, in contrast to above examples (Table

2), it took more equivalents of BAIB (1.2 equiv) for complete consumption of the starting material. The purification of the crude product mixture with silica gel column chromatography afforded an unexpected 3,2-enolone **8** (Scheme 2). After thorough literature search,²⁶ we assumed that **8** was obtained through an expected iodoacetoxylated intermediate **6**, which on β -elimintion via a corresponding enolate derivative of **7**. Our assumption was based on its crude HRMS spectrometry which showed m/z peak at 346.²⁶ Finally, the intermediate **7** on silica gel column chromatography gave pyranoid enolone **8** in 72% yield. It was characterized by its NMR and HRMS spectrometry and the data were found to be consistent with the reported.^{26c}



Scheme 3: Reactions of tri-O-acetylated D-glucal with different hypervalent iodine reagents.

Encouraged by the above findings, our attention turned toward to realize the scope of different hypervalent iodine (both I^{III} and I^V) reagents on peracetylated-D-glucal **1a** (Scheme 3). Thus, the reaction of **1a** with BTI and I₂ at room temperature furnished an inseparable mixture of α -manno and β -gluco isomers **9** and **10** in 85% with 90:10 ratio (HPLC). But the reaction of **1a** with Koser's reagent (HTI) and I₂ was futile and the starting material was remain unchanged. Dess-Martin periodinane (DMP) mediated oxidation of **1a** furnished a separable mixture of **2a** and **3a** (52%) along with a considerable amount of 2-iodo-2-deoxy-glycosylester of 2-iodobenzoic acid **11a** in 25% yield (Scheme 3). It was obtained by stereoselective opening of iodonium intermediate by nucleophilic attack of a bidentate ligand 2-iodobenzoic acid.

Table 3: Reactions of various glycals with the reagent system IBX-I2^a





^aReaction conditions: glycals (1 eq), IBX (1.5 eq), I_2 (1.2 eq), dry DCM, 25 °C, 45 min, ^bisomeric ratios were determined by ¹H NMR of the crude sample.

Next, when we attempted the oxidation of **1a** with IBX-I₂ which does not contain any acetoxy functional ligands, α -manno isomer **11a** was obtained exclusively in 74% yield (98:2, α/β ratio) in 45 min. To test the susceptibility of the reaction with different protecting groups, the reaction was further extended to other differently protected pyranoid glycals **1b**,**1c**, **1f**, **1g** and furanoid glycal **1k** to obtain their respective 2-deoxy-2-iodo-(2-iodobenzyloxy) glycosylates (**11b-11f**) in good yields and with excellent α -manno selectivity (Table 3).

To the best of our knowledge, this is the first report on transfer of bidentate ligand of hypervalent iodine reagent (I^V, DMP or IBX) to electron rich double bond in molecules like glycals. To exemplify the synthetic utility of 2-deoxy-2-iodo glycosyl benzoates 11, we chose 11a as an example which was subjected to palladium catalyzed (PdCl₂(PPh₃)₂) Sonogashira coupling with *n*-hexyne to obtain glycosyl *ortho*-hexynyl benzoate **12** in 85%.²⁷ These *n*-hexynyl benzoates can be used as a glycosyl donor for the complex oligosaccharide synthesis by using Gold (I) catalyst.²⁸ In contrast to previous reports²⁸ where they used three step process *i.e.*, Sonogashira coupling of *n*-hexyne with methyl 2-iodobenzoate followed by ester hydrolysis and condensation of the resulting acid with globally protected lactol derivatives to prepare racemic mixture of α/β glycosyl ortho-hexenyl benzoates, herein we synthesized the diastereometically pure α glycosyl ortho-hexenyl benzoate 12 in two steps (Scheme 4) in stereoselective manner. The benzoate 12 was tested for glycosylation with different acceptors like benzyl alcohol, sugar (glucose)²⁹ and amino acid (Phenylglycine)³⁰ derived primary alcohols in presence of catalyst PPh₃AuNTf₂ (0.1 equiv) in DCM at -78 °C to rt to obtain their respective glycoside.^{28c} The glycosylation reaction was also successful with acceptors like 4methoxyphenol and secondary alcohols isopropanol and glucose derived acceptors (4-methoxyphenyl 2,4.6-tri-O-benzyl-a-Dgucopyranoside) to produce the α -glycosides 16, 17 and 18 respectively. In all the cases, we observed only α -diastereomer of the corresponding glycosides 13-18 in 85-92% yields (Scheme 4).



Scheme 4: Synthesis of *ortho*-hexynyl benzoates by Sonogashira coupling and its glycosylation reaction. **Reagents and conditions:** (a) IBX, I₂, dry DCM, rt, 45 min, 74%; (b) n-hexyne, PdCl₂(PPh₃)₂, CuI, *i*Pr₂NH, PPh₃, rt, 85%; (c) ROH, PPh₃AuNTf₂, dry DCM, 4A° MS, -78 °C- rt.

A plausible mechanistic explanation is proposed based on our results and other literature reports as well to understand course of the reaction process, (Scheme 5).³¹⁻³³ Molecular iodine readily undergoes oxidation reaction with hypervalent iodine reagent (BAIB or IBX) to generate two molecules of hypoiodite (CH₃COOI or *O*-IPhCOOI).³¹ This in situ generated I^+ (from IOOCR) forms two types of iodonium ions (π -complexes) i.e., α and β 1,2-iodonium ions similar to the 1,2-episilinoniumion with electron rich double bond of glycals.³² In contrast to 1,2epoxides³³ of glycals, β -iodonium ion **A** is more stable than α iodonium ion C due to non-covalent interaction between spatially closed β -iodonium ion and lone pair of electrons or non-bonded electrons of ring oxygen. In this situation, the nucleophilic ligand $(R'COO^{-})$ attacks iodonium ion in concerted manner $(S_N 2)$ to give corresponding diaxial product **B** in a major amount.³³ D-arabinal (1g or 1h) also followed the same mechanistic path but finally delivered the corresponding product in ¹C₄ conformation as discussed above.^{16b, 34} However, in the case of L-rhamnal, it

dominantly adopts the ${}^{5}H_{4}$ half-chair conformation, from which the formation of the α -iodonium ion is more favoured. The 1,2trans- α -rhamnoside **2i** can only be formed via the α -iodonium ion intermediate.

3. Conclusion

In conclusion, we have developed two new methods for iodoacetoxylation and iodobenzoylation of protected glycals using hypervalent iodine reagents i.e., BAIB/I2 and IBX/I2 respectively. The present methods avoids the expensive halide sources (NIS, KI, etc.) and are also economically useful because of minimum reagents loading (0.6 equiv of BAIB and 1.2 equiv of I₂) compared to previous reports, less reaction times, mild reaction conditions. Here, we have also synthesized a chiral building block 3,2-enolone 8 in a single step by using the method A that could be used as a dienophile partner of Diels-Alder reaction.^{35,36} We have also disclosed preparation of diastereomerically enriched a-glycosyl ortho-hexynylbenzoate 12, a glycosyl donor in a two-step process from D-glucal 1a and which was successfully utilized for glycosylation reaction to obtain glycosides 13-15 in very good yields and with very high α -selectivity (>99%).

4. Experimental Section

4.1. General

The organic solvents were made anhydrous by standard methods before their use. Silica gel (60F-254) 2.5 × 5 cm TLC plates coated with a 0.25 mm thickness were used to monitor the progress of the reaction. Visualization of the spots was done by spraying the plate with Ce(SO₄)₂ (1% in 2N H₂SO₄) and subsequent charring over hot plate. Silica gel (60–120 mesh) and silica gel (230-400 mesh) were used for column chromatography. All the intermediates were characterized by NMR, IR, ESI-HRMS and the identifications of known compounds were done by comparing their optical rotation with those reported in the literature. NMR experiments were recorded in CDCl₃ at 25 °C. Chemical shift values are given on δ scale with reference to TMS at 0.00 ppm for proton and carbon. The reference CDCl₃ appeared at 77.26 ppm for ¹³C NMR. NMR spectra were recorded on Bruker Avance 400 MHz spectrometer at 400 MHz (¹H) and 100 MHz (¹³C).



Scheme 5: Plausible mechanism for synthesis of major products 2 and 11a.

Optical rotations were determined on HORIBA, high sensitive polarimeter, SEPA-300 using a 1 dm cell at 17 °C-32 °C in chloroform; concentrations mentioned are in g/100 mL. For IR spectra were recorded on Perkin–Elmer 881 and FTIR-8210 PC Shimadzu Spectrophotometers. Mass spectra were recorded on a JEOL JMS-600H high resolution spectrometer using EI mode at 70 eV. ESI-HRMS were recorded on a JEOL-AccuTOF, JMS-T100LC spectrometer.

(I). General procedure for the synthesis of 2-deoxy-2iodoglycosylacetates: To a stirred solution of glycal in dry DCM (5 mL), were added BAIB (0.6 equiv.), and iodine (1.2 equiv.) at room temperature and allow the stirring for 30 min. After consumption of the starting material observed by TLC, the reaction mixture was quenched with saturated solution of sodium thiosulfate ($Na_2S_2O_3.5H_2O$). The two layers were separated and aqueous layer was extracted 2-3 times with DCM. The combined organic layers were dried over sodium sulphate and the solvent was evaporated in vacuum. The crude was subjected to column chromatography to obtain the pure compound.

Compound 2a and 3a: These compound were synthesized by adopting the general procedure I using tri-*O*-acetyl-D-glucal **1a** (100 mg, 0.368 mmol) as the starting material. Yield: 0.341 mmol, 93% overall yield (α : β : 148:9 mg, *dr* 95:5).

2a (α -manno diastereomer): $[a]_D^{22} = +31.5$ (*c* 0.1, CHCl₃); R_f: 0.42 (1:5, EtOAc/Hexane); IR (Neat): v_{max} 3015, 2930, 2856, 1722, 1656, 1462, 1253, 1122, 1063, 755, 665 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 6.37 (d, *J*=1.16 Hz, 1H), 5.43 (t, *J*=9.72 Hz, 1H), 4.57 (dd, *J*₁=4.38, *J*₂=9.39 Hz, 1H), 4.51 (dd, *J*₁=1.52, *J*₂=4.38 Hz, 1H), 4.21 (dd, *J*₁=4.47, *J*₂=12.25 Hz, 1H), 4.08-4.12 (m, 2H), 2.14 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H); ¹³C (100 MHz, CDCl₃): δ 170.80, 170.04, 169.43, 168.29, 94.86, 71.59, 68.79, 67.20, 62.00, 27.32, 21.04, 20.98, 20.86, 20.76. ESI-HRMS: *m*/z [M+H]⁺ calcd for C₁₄H₂₀IO₉⁺ 459.0152, measured 459.0144.

3a (β-gluco diastereomer): $[a]_D^{22}$ +61.8 (*c* 0.2, CHCl₃); R_f: 0.50 (1:5, EtOAc/Hexane); IR (Neat): v_{max} 3018, 2931, 2858, 1702, 1584, 1427, 1253, 1122, cm⁻¹; ¹H (400 MHz, CDCl₃): δ 5.80 (d, *J*=9.69 Hz, 1H), 5.27 (dd, *J*₁=9.07, *J*₂=11.08 Hz, 1H), 4.94 (dd, *J*₁=9.26, *J*₂=10.1 Hz, 1H), 4.25 (dd, *J*₁=4.53, *J*₂=12.53 Hz, 1H), 4.03 (dd, *J*₁=2.09, *J*₂=12.53 Hz, 1H), 3.92 (dd, *J*₁=9.57, *J*₂=11.14 Hz, 1H), 3.79-3.83 (m, 1H), 2.10 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.95 (s, 3H); ¹³C (100 MHz, CDCl₃): δ 170.77, 169.73, 169.72, 168.76, 94.22, 75.79, 73.26, 68.77, 61.73, 29.93, 25.94, 20.91, 20.78. ESI-HRMS: *m*/*z* [M+H]⁺ calcd for C₁₄H₂₀IO₉⁺ 459.0152, measured 459.0144.

(2R,3S,4S,5R,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-3iodotetrahydro-2H-pyran-2-yl acetate 2b: This compound was prepared by following the above mentioned general procedure I using tri-O-benzyl-D-glucal 1b (200 mg, 0.481 mmol) as the starting material. Yield: (274 mg, 0.456 mmol, 95%, α:β: 90:10). **\alpha-manno:** $[\alpha]_D^{22} = +7.6$ (*c* 0.2, CHCl₃); R_f: 0.32 (1:9, EtOAc/Hexane); IR (Neat): v_{max} 3019, 2931, 1720, 1638, 1428, 1109, 669 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 7.18-7.33 (m, 13 H), 7.10-7.12 (m, 2H), 6.33 (s, 1H), 4.79 (d, J=10.55 Hz, 1H), 4.63 (d, J=11.77 Hz, 2H), 4.44-4.48 (m, 3H), 4.37-4.38 (m, 1H), 3.86-3.95 (m, 2H), 3.69-3.73 (m, 1H), 3.59-3.62 (m, 1H), 3.13-3.16 (m, 1H) 1.96 (s, 3H). 13 C (100 MHz, CDCl₃): δ 168.78, 138.48, 138.22, 137.55, 128.72, 128.63, 128.56, 128.35, 128.26, 128.05, 127.97, 127.78, 95.76, 76.42, 75.64, 75.07, 73.77, 71.31, 68.81, 31.24, 21.07; ESI-HRMS: m/z [M+Na]⁺ calcd for C₂₉H₃₁INaO₆⁺ 625.1063, measured 625.1045.

(2R,3S,4S,5S,6R)-6-(acetoxymethyl)-3-iodotetrahydro-2H-

pyran-2,4,5-triyl triacetate 2c: This compound was synthesized by adopting the general procedure I using tri-*O*-acetyl-D-galactal **1c** (100 mg, 0.368 mmol) as the starting material. Yield: (162 mg, 0.352 mmol, 96%, α : β : 92:8).

α-manno isomer: $[a]_{D}^{22} = +42.0$ (*c* 0.1, CHCl₃); R_j: 0.42 (1:5, EtOAc/Hexane); IR (Neat): v_{max} 3010, 2920, 2756, 1722, 1655, 1362, 1253, 1120, 1063, 755, 665 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 6.44 (d, *J*=1.04 Hz, 1H), 5.36-5.37 (m, 1H), 4.82-4.84 (m, 1H), 4.34 (td, *J*₁=2.01, *J*₂=6.64 Hz, 1H), 4.21-4.22 (m, 1H), 4.11-4.13 (m, 2H), 2.12 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H); ¹³C (100 MHz, CDCl₃): δ 170.68, 170.22, 169.80, 168.43, 96.26, 69.30, 65.09, 65.05, 61.71, 29.90, 21.16, 21.06, 20.88, 19.14; ESI-HRMS: m/z [M+Na]⁺ calcd for C₁₄H₁₉INaO₉⁺ 480.9971, measured 480.9960.

(2*R*,3*S*,4*S*,5*S*,6*R*)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-3iodotetrahydro-2*H*-pyran-2-yl acetate 2d: This compound was prepared by using the above mentioned general procedure I using tri-*O*-benzyl-D-galactal 1d (250 mg, 0.601 mmol) as the starting material. Yield: (351 mg, 0.583 mmol, 97%, α : β : 90:10).

material. Yield: (351 mg, 0.583 mmol, 97%, α:β: 90:10). **α-manno isomer:** $[α]_D^{22}$ +53.2 (*c* 0.1, CHCl₃); R_{*j*}: 0.32 (1:9, EtOAc/Hexane); IR (Neat): v_{max},3017, 2926, 1725, 1635, 1418, 1207, 1109, 752, 665 cm¹; ¹H (400 MHz, CDCl₃): δ 7.19-7.33 (m, 14H), 7.09-7.11 (m, 2H), 6.33 (d, *J*=1.6 Hz, 1H), 4.79 (d, *J*=10.6 Hz, 1H), 4.63 (d, *J*=11.8 Hz, 2H), 4.38-4.47 (m, 3H), 4.36-4.38 (m, 1H), 3.90-3.92 (m, 2H), 3.69-3.70 (m, 1H), 3.62-3.69 (m, 1H), 3.15-3.36 (m, 1H), 1.95 (s, 3H); ¹³C (100 MHz, CDCl₃): δ 168.77, 138.48, 138.22, 137.55, 128.72, 128.62, 128.55, 128.35, 128.33, 128.25, 128.05, 127.96, 127.77, 95.76, 76.42, 75.64, 75.63, 75.07, 73.77, 71.31, 68.82, 31.24, 21.06; ESI-HRMS: *m*/*z* [M+Na]⁺ calcd for C₂₉H₃₁INaO₆⁺ 625.1063, measured 625.1059.

(2R,3S,4S,5R,6R)-6-(((tert-butyldiphenylsilyl)oxy)methyl)-3iodo-4,5-bis(methoxymethoxy)tetrahydro-2*H*-pyran-2-yl

acetate 2e: This compound was prepared by using the above mentioned general procedure I using (((2R,3S,4R)-3,4-bis(methoxymethoxy)-3,4-dihydro-2H-pyran-2-yl)methoxy)(tert-butyl)diphenylsilane (glucal derived)**1e** $(200 mg, 0.424 mmol) as the starting material. Yield: (250 mg, 0.381 mmol, 90%, <math>\alpha$: β : 85:15).

α-manno isomer: $[α]_D^{22} = -47.5$ (*c* 0.2, CHCl₃); R_j: 0.50 (1:4, EtOAc/Hexane); IR (Neat): v_{max} 3009, 2925, 2846, 1723, 1656, 1460, 1253, 1130, 1063, 750, 660 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 7.56-7.58 (m, 4H), 7.28-7.35 (m, 6H), 6.42 (bs, 1H), 4.82-4.84 (m, 1H), 4.73-4.75 (m, 1H), 4.59-4.63 (m, 2H), 3.83-3.91 (m, 2H), 3.75-3.77 (m, 2H), 3.73-3.74 (m, 1H) 3.49-3.51 (m, 1H), 3.38 (s, 3H), 3.28 (s, 3H), 1.97 (s, 3H), 0.98 (s, 9H); ¹³C (100 MHz, CDCl₃): δ 168.53, 135.80, 135.76, 133.56, 133.46, 130.02, 127.94, 97.12, 96.71, 94.89, 74.10, 70.22, 70.07, 62.50, 56.70, 56.46, 29.90, 27.06, 22.88, 21.07, 19.40; ESI-HRMS: *m/z* [M+Na]⁺ calcd for C₂₈H₃₉INaO₈Si ⁺ 681.1357, measured 681.1330.

(2R,3S,4S,5S,6R)-6-(((tert-butyldiphenylsilyl)oxy)methyl)-3iodo-4,5-bis(methoxymethoxy)tetrahydro-2*H*-pyran-2-yl

acetate 2f: This compound was prepared by using the above mentioned general procedure I using (((2R,3S,4R)-3,4-bis(methoxymethoxy)-3,4-dihydro-2*H*-pyran-2-yl)methoxy)(tert-butyl)diphenylsilane (galactal derived) **1f** (300 mg, 0.635 mmol) as the starting material. Yield: (364 mg, 0.553 mmol, 87%, α : β : 89:11).

α-manno isomer: $[a]_D^{22}$ = -75.5 (*c* 0.38, CHCl₃); R_f: 0.50 (1:4, EtOAc/Hexane); IR (Neat): v_{max} 3117, 2986, 1721, 1630, 1415, 1205, 1120, 750, 660 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 7.56-7.58 (m, 4H), 7.28-7.35 (m, 6H), 6.42 (bs, 1H), 4.82-4.84 (m, 1H),

4.67-4.77 (m, 2H), 4.60-4.63 (m, 1H), 4.08-4.10 (m, 1H), 4.14- M 4.15 (m, 1H), 3.83-3.91 (m, 2H), 3.73-3.77 (m, 1H), 3.49-3.51 (m, 1H), 3.38 (s, 3H), 3.28 (s, 3H), 1.98 (s, 3H), 0.98 (s, 9H); 13 C (100 MHz, CDCl₃): δ 168.55, 137.78, 135.82, 133.59, 133.49, 130.04, 128.15, 127.96, 97.15, 96.74, 94.91, 74.12, 70.24, 70.09, 62.52, 56.72, 56.48, 27.07, 22.89, 21.09, 19.42; ESI-HRMS: *m/z* [M+Na]⁺ calcd for C₂₈H₃₉INaO₈ Si⁺ 681.1357, measured 681.1350.

(2*R*,4*R*,5*R*)-3-iodotetrahydro-2*H*-pyran-2,4,5-triyl triacetate 2g: This compound was prepared by following the above mentioned general procedure I using 3,4-di-*O*-acetyl-D-arabinal 1g (100 mg, 0.5 mmol) as the starting material. Yield: (185 mg, 0.48 mmol, 96%, α : β : 88:12); %).

α-manno isomer: $[a]_D^{22} = +73.7$ (*c* 0.2, CHCl₃); R_f: 0.50 (1:4, EtOAc/Hexane); IR (Neat): v_{max} 3016, 2937, 1717, 1540, 1215, 1205, 1120, 1025 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 5.94 (d, *J*=8.49 Hz, 1H), 5.50 (t, *J*=2.58 Hz, 1H), 5.08-5.12 (m, 1H), 5.03-5.06 (m, 1H), 4.16 (dd, *J*₁=3.10, *J*₂=8.51Hz, 1H), 3.91-3.94 (m, 1H), 2.13 (s, 3H), 2.07 (s, 3H), 1.95 (s, 3H); ¹³C (100 MHz, CDCl₃): δ 169.83, 169.71, 169.11, 93.12, 70.12, 66.33, 62.96, 24.23, 21.03, 20.93, 20.83; ESI-HRMS: *m/z* [M+Na]⁺ calcd for C₁₁H₁₅INaO₇⁺ 408.9760, measured 408.9741.

(2R,3S,4R,5R)-4,5-bis(benzyloxy)-3-iodotetrahydro-2H-

pyran-2-yl acetate 2h: This compound was prepared by adopting the above mentioned general procedure I using (3R,4R)-3,4-bis(benzyloxy)-3,4-dihydro-2*H*-pyran **1h** (150 mg, 0.507 mmol) as the starting material. Yield: (220 mg, 0.456 mmol, 90%, α : β : 86:14).

α-manno isomer: $[a]_D^{22} = +36.9$ (*c* 0.18, CHCl₃); R_j: 0.23 (1:2, EtOAc/Hexane); IR (Neat): v_{max} 3239, 2930, 2399, 1732, 1638, 1403, 1215, 1063, 669 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 7.18-7.35 (m, 10 H), 5.72 (d, *J*=8.35, 1H), 4.48-4.65 (m, 4H), 4.33 (dd, *J*₁=8.37, *J*₂=10.03 Hz, 1H), 4.07 (dd, *J*₁=3.23, *J*₂=12.75 Hz, 1H), 3.62-3.64 (m, 1H), 3.56 (dd, *J*₁=3.13, *J*₂=10Hz, 1H), 3.44 (dd, *J*₁=1.36, *J*₂=12.71 Hz, 1H), 2.06 (s, 3H); ¹³C (100 MHz, CDCl₃): δ 169.44, 137.93, 137.41, 128.71, 128.38, 128.30, 128.23, 128.15, 95.44, 81.15, 72.46, 71.70, 71.59, 64.55, 29.47, 21.05; ESI-HRMS: *m*/z [M+Na]⁺ calcd for C₂₁H₂₃INaO₅ ⁺ 505.0488, measured 505.0472.

(2*S*,3*R*,4*R*,5*S*,6*S*)-3-iodo-6-methyltetrahydro-2*H*-pyran-2,4,5triyl triacetate 2i: This compound was prepared by adopting the above mentioned general procedure I using (3*R*,4*R*)-3,4bis(benzyloxy)-3,4-dihydro-2*H*-pyran 1i (100 mg, 0.467 mmol) as the starting material. Yield: (168 mg, 0.42 mmol, 90%, α : β : 80:20).

α-manno isomer: $[a]_{D}^{22} = +25.3$ (*c* 1.0, CHCl₃); R_f: 0.23 (1:3.5, EtOAc/Hexane); IR (Neat): v_{max} 3110, 2942, 2856, 1722, 1656, 1462, 1253, 1122, 1063, 755, 665 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 6.27 (s, 1H), 5.10-5.15 (m, 1H), 4.44-4.47 (m, 2H), 3.92-3.99 (m, 1H), 2.08 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.18 (d, *J*=6.25 Hz, 3H); ¹³C (100 MHz, CDCl₃): δ 170.24, 169.82, 168.67, 95.07, 72.31, 69.76, 69.03, 28.23, 21.20, 21.12, 20.96, 17.83; ESI-HRMS: *m/z* [M+Na]⁺ calcd for C₈H₁₃INaO₂⁺ 422.9917, measured 422.9905.

(2*R*,3*S*,4*R*,5*R*)-5-(acetoxymethyl)-3-iodotetrahydrofuran-2,4diyl diacetate 2j: This compound was prepared by using the above mentioned general procedure I using ((2*R*,3*S*)-3-acetoxy-2,3-dihydrofuran-2-yl)methyl acetate 1j (200 mg, 1mmol) as the starting material. Yield: (366 mg, 0.95mmol, 95%, α:β: 90:10). α-manno isomer: $[\alpha]_D^{22} = -20.3$ (*c* 0.2, CHCl₃); R_j: 0.5 (1:3, EtOAc/Hexane); IR (Neat): v_{max} 3018, 2931, 1742, 1684, 1471, 1216, 1032, 750, 660 cm⁻¹; ⁻¹H (400 MHz, CDCl₃): δ 6.02 (d, J=8.56 Hz, 1H), 5.60 (t, J=2.76 Hz, 1H), 5.12-5.16 (m, 1H), 4.22-4.26 (m, 1H), 3.96-4.0 (m, 1H), 3.85-3.89 (m, 1H), 2.16 (s, 6H), 2.06 (s, 3H); ¹³C (100 MHz, CDCl₃): δ 170.21, 169.62, 168.86, 94.95, 73.44, 67.80, 65.66, 25.37, 21.03, 20.93, 20.83; ESI-HRMS: *m*/z [M+H]⁺ calcd for C₁₁H₁₆IO₇⁺ 386.9941, measured 386.9935.

(2R,3S,4R,5R)-4-(benzyloxy)-5-((benzyloxy)methyl)-3-

iodotetrahydrofuran-2-yl acetate 2k: This compound was prepared by following the above mentioned general procedure I using (2R,3S)-3-(benzyloxy)-2-((benzyloxy)methyl)-2,3dihydrofuran 1k (200 mg, 0.676 mmol) as the starting material. Yield: (318 mg, 0.661 mmol, 98%, α : β : 80:20).

α-manno isomer: $[a]_D^{22} = +5.43$ (*c* 0.81, CHCl₃); R_j: 0.23 (1:9, EtOAc/Hexane); IR (Neat): v_{max} 3125, 3018, 2925, 1715, 1605, 1453, 1216, 1073, 769, 668 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 7.38-7.39 (M, 2H), 7.22-7.29 (m, 8H), 5.89 (d, *J*=9.25 Hz, 1H), 4.86-4.89 (m, 1H), 4.70-4.72 (m, 1H), 4.50-4.58 (m, 2H), 4.08 (bs, 1H), 3.96-4.01 (m, 2H), 3.83-3.87 (m, 1H), 3.68-3.72 (m, 1H), 2.02 (s, 3H); ¹³C (100 MHz, CDCl₃): δ 169.17, 138.25, 137.87, 128.81, 128.44, 128.25, 127.92, 127.74, 93.00, 78.30, 75.59, 75.47, 72.08, 63.65, 29.03, 21.02. ESI-HRMS: *m*/z [M+Na]⁺ calcd for C₂₁H₂₃INaO₅⁺ 505.0488, measured 505.0481.

(2R,4S,5R,6R)-6-(acetoxymethyl)-3,3-diiodotetrahydro-2H-

pyran-2,4,5-triyl triacetate 21: This compound was prepared by using the above mentioned general procedure I using (2*R*,3*R*,4*S*)-2-(acetoxymethyl)-5-iodo-3,4-dihydro-2*H*-pyran-3,4-diyl

diacetate **11** (200 mg, 0.503 mmol) as the starting material. Yield: (278 mg, 0.477 mmol, 95%, α : β : 96:4).

α-manno isomer: $[a]_D^{22} = -8.62$ (*c* 0.32, CHCl₃); R_f: 0.23 (1:3.5, EtOAc/Hexane); IR (Neat): v_{max} 3055, 2830, 2156, 1722, 1650, 1253, 1063, 755, 665 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 6.55 (s, 1H), 5.26 (t, *J*=9.49 Hz, 1H), 4.90 (d, *J*=8.95 Hz, 1H), 4.03-4.15 (m, 3H), 2.15 (s, 3H), 2.15 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H); ¹³C (100 MHz, CDCl₃): δ 170.76, 169.83, 169.43, 168.03, 96.22, 75.81, 71.12, 68.71, 61.70, 21.11, 20.91, 20.80, 20.72, 0.90; ESI-HRMS: m/z [M+Na]⁺ calcd for C₁₄H₁₈I₂NaO₉⁺ 606.8938, measured 606.8905.

Methyl (*E*)-3-((2*R*,3*S*,4*S*,5*R*,6*R*)-2-acetoxy-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-3-iodotetrahydro-2*H*-pyran-3-

yl)acrylate 2n: This compound was prepared by adopting the above mentioned general procedure I using (E)-methyl 3-((2R,3S,4R)-3,4-bis(benzyloxy)-2-((benzyloxy)methyl)-3,4dihydro-2H-pyran-5-yl)acrylate 1n (100 mg, 0.20 mmol) as the starting material. Yield: (103 mg, 0.150 mmol, 75%, α:β: 80:20). **\alpha-manno isomer:** $[\alpha]_{D}^{22} = -37.0$ (*c* 0.21, CHCl₃); R_f: 0.40 (1:9, EtOAc/Hexane); IR (Neat): v_{max} 3010, 2940, 2856, 1722, 1656, 1462, 1253, 1122, 1063, 755, 665 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 7.10-7.41 (m, 15H), 6.49-6.53 (d, J=16.27 Hz, 1H), 6.32 (s, 1H), 5.98 (s, 1H), 4.67-4.76 (m, 2H), 4.55-4.58 (m, 1H), 4.39-4.47 (m, 3H), 4.09-4.14 (m, 1H), 3.93-3.95 (m, 1H), 3.66-3.75 (m, 5H), 3.58-3.61 (m, 1H), 2.09 (s, 3H); ^{13}C (100 MHz, CDCl₃): δ 168.62, 166.53, 142.27, 138.22, 137.83, 133.42, 130.63, 128.84, 128.80, 128.64, 128.36, 128.22, 128.07, 127.94, 127.89, 127.39, 126.60, 106.27, 91.28, 81.23, 80.11, 75.27, 75.09, 73.80, 72.51, 68.19, 52.08, 29.94, 21.14; ESI-HRMS: m/z [M+Na]⁺ calcd for C₃₃H₃₅INaO₈⁺ 709.1274, measured 709.1264.

(2R,3S,4S,5R,6R)-6-(acetoxymethyl)-3-((E)-2-cyanovinyl)-3-

iodotetrahydro-2H-pyran-2,4,5-triyl triacetate 20: This compound was prepared by using the above mentioned general procedure I using (2R,3S,4R)-2-(acetoxymethyl)-5-((*E*)-2-cyanovinyl)-3,4-dihydro-2*H*-pyran-3,4-diyl diacetate **10** (200

mmol, 85%, α:β: 85:15). **α-manno isomer:** $[\alpha]_D^{22} = -26.0$ (*c* 0.18, CHCl₃); R_j: 0.23 (1:2, EtOAc/Hexane); IR (Neat): v_{max} 3125, 3018, 2925, 1715, 1605, 1453, 1216, 1073, 769, 668 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 6.73 (d, J=17.06 Hz, 1H), 5.98-6.02 (m, 2H), 5.46 (d, J=9.88 Hz, 1H), 4.98 (t, J=.9.60 Hz, 1H), 4.04-4.16 (m, 2H), 3.84-3.88 (m, 1H), 2.16 (s, 3H), 2.10 (s, 3H), 2.01 (s, 3H), 1.95 (s, 3H); ¹³C (100 MHz, CDCl₃): δ 170.65, 169.46, 169.02, 168.14, 147.83, 116.53, 105.49, 95.93, 77.99, 74.33, 66.22, 61.38, 43.11, 20.88, 20.67; ESI-HRMS: m/z [M+Na]⁺ calcd for C₁₇H₂₀INNaO₉⁺ 532.0080, measured 532.0075.

3-iodotetrahydro-2H-pyran-2-yl acetate 2p: This compound was prepared by using the above mentioned general procedure I using 3,4-dihydro-2H-pyran 1p (200 mg, 2.38 mmol) as the starting material. Yield: (624 mg, 2.31 mmol, 97%); Rf: 0.50 (Pure Hexane); IR (Neat): v_{max} 3427, 3015, 2930, 1641, 1427, 1217, 1106, 919, 764 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 5.82 (d, J=5.80 Hz, 1H), 5.24 (s, 1H), 4.04-4.09 (m, 1H), 3.94-3.99 (m, 1H), 3.65-3.71 (m, 1H), 2.28-2.36 (m, 1H), 2.01-2.04 (m, 4H), 1.74-1.78 (m, 1H), 1.56-1.61 (m, 1H); 13 C (100 MHz, CDCl₃): δ 169.20, 95.61, 65.17, 32.68, 26.40, 25.40, 21.08. ESI-HRMS: m/z $[M+Na]^+$ calcd for C₇H₁₁INaO₃⁺ 292.9651, measured 292.9645.

2-iodocyclohexyl acetate 2q: This compound was prepared by using the above mentioned general procedure I using cyclohexene 1q (200 mg, 2.43 mmol) as the starting material. Yield: (595 mg, 2.22 mmol, 91%); Rf: 0.50 (20:1, EtOAc/Hexane); IR (Neat): v_{max} 3427, 3015, 2930, 1641, 1427, 1217, 1106, 919, 764 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 4.80-4.86 (m, 1H), 3.96-4.02 (m, 1H), 2.34-2.41 (m, 1H), 1.91-2.07 (m, 5H), 1.73-1.76 (m, 1H), 1.48-1.55 (m, 1H), 1.19-1.42 (m, 3H); $^{13}\mathrm{C}$ (100 MHz, CDCl₃): δ 170.16, 76.95, 38.12, 31.98, 31.84, 27.31, 23.82, 21.45; ESI-HRMS: *m/z* [M+Na]⁺ calcd for $C_8H_{13}INaO_2^+$ 290.9858, measured 290.9838.

1,3,6-Tri-O-acetyl-4-deoxy-u-~glycero-hex-3-enopyranos-2-

ulose (Compound 8): This compound was prepared by using the above mentioned general procedure I using 2-acetoxy-D-glucal 5 (100 mg, 0.3027 mmol) as the starting material. The crude mixture was subjected to flash column chromatography. In the column the intermediate 6 was converted into 7. Yield: (62 mg, 0.216 mmol, 72%)^{19c}; $[\alpha]_D^{22} = +32.4$ (c 0.3, CHCl₃); R_f : 0.40 (1:9, EtOAc/Hexane); IR (Neat): v_{max} 3015, 2930, 2856, 1722, 1656, 1462, 1253, 1122, 1063, 755, 665 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 6.62 (d, J=1.93 Hz, 1H), 6.23 (s, 1H), 4.95 (dt, J_1 =1.88, J_2 =4.86 Hz, 1H), 4.39 (dd, J_1 =5.11, J_2 =11.73 Hz, 1H), 4.14 (dd, J₁=4.73, J₂=11.73 Hz, 1H), 2.20 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H); 13 C (100 MHz, CDCl₃): δ 181.32, 170.85, 168.94, 168.00, 142.27, 133.20, 90.27, 69.23, 64.46, 20.97, 20.90, 20.52; ESI-HRMS: m/z [M+H]⁺ calcd for C₁₂H₁₅O₈ 287.0767, measured 287.0753.

Compound 9 and 10: Bis[(trifluoroacetoxy)iodo] benzene (94 mg, 0.218 mmol) and I₂ (102 mg, 0.4 mmol) were added to the stirred solution of tri-O-acetoxy-D-glucal (100 mg, 0.3676) in dry DCM (5 mL) at rt and continues the stirring at the same temperature for 30 min Then the reaction was quenched with the saturated solution of Na₂S₂O₃5H₂O (5 mL) and the two layers were separated. The aqueous layer was extracted with DCM (2X5 mL) and combined organic layers were dried over sodium sulphate and concentrated in vacuum to obtain a residue. Its silica gel column chromatography led to give an inseparable mixture of 9 and 10 (α : β : 90:10) in 85% yield (159 mg, 0.312 mmol); R_f. 0.45 (1:2, EtOAc/Hexane); IR (Neat): v_{max} 3020, 2959, 2400,

mg, 0.619 mmol) as the starting material. Yield: (268 mg, 0.526 \land 1746, 1521; 668 cm⁻¹; ESI-HRMS: m/z [M+H]⁺ calcd for $C_{14}H_{17}F_{3}IO_{9}^{+}$ 512.9869, measured 512.9853.

> (II) General procedure for the synthesis of 2-deoxy-2iodoglycosyl ortho-iodobenzoates: To a stirred solution of glycal in dry DCM (5 mL), were added IBX (1.5 equiv.) and iodine (1.2 equiv.) in equivalent amounts at room temperature and allow the stirring for 30 to 45 min. After consumption of the starting material (monitored by TLC), the reaction mixture was quenched with saturated solution of Na₂S₂O₃5H₂O. The two layers were separated and aqueous layer was extracted 2-3 times with DCM. The combined organic layers were dried over sodium sulphate and the solvent was evaporated in vacuum. The crude was subjected to column chromatography to obtain pure compound.

(2R,3R,4S,5S,6R)-2-(acetoxymethyl)-5-iodo-6-((2-

iodobenzoyl)oxy)tetrahydro-2H-pyran-3,4-diyl diacetate 11a: This compound was prepared by using the above mentioned general procedure II using tri-O-acetyl-D-glucal 1a (100 mg, 0.3676 mmol) as the starting material. Yield: (176 mg, 0.272 mmol, 74%, α:β: 98:2).

α-manno isomer: $[\alpha]_D^{22} = +25$ (*c* 0.5, CHCl₃); R_f: 0.23 (1:3.5, EtOAc/Hexane); IR (Neat): v_{max} 3015, 2930, 2856, 1722, 1656, 1462, 1253, 1122, 1063, 755, 665 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 7.96 (dd, $J_1=1$, $J_2=7.97$ Hz, 1H), 7.76 (dd, $J_1=1.69$, $J_2=7.80$ Hz, 1H), 7.39 (td, J_1 =1.16, J_2 =7.55 Hz, 1H), 7.15 (td, J_1 =1.52, J_2 =7.74 Hz, 1H), 6.59 (s, 1H), 5.43-5.48 (m, 1H), 4.67-4.71 (m, 1H), 4.13-4.22 (m, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H); ¹³C (100 MHz, CDCl₃): δ 170.92, 170.09, 169.57, 164.16, 141.87, 134.21, 133.67, 131.82, 128.41, 96.34, 94.18, 72.27, 69.10, 67.25, 62.07, 27.24, 21.14, 20.99, 20.87; ESI-HRMS: m/z $[M+Na]^+$ calcd for $C_{19}H_{20}I_2NaO_9^+$ 668.9094, measured 668.9085.

(2R,3S,4S,5R,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-3iodotetrahydro-2H-pyran-2-yl 2-iodobenzoate 11b: This compound was prepared by using the above mentioned general procedure II using tri-O-benzyl-D-glucal 1b (150 mg, 0.360 mmol) as the starting material. Yield: (224 mg, 0.283 mmol, 79%, α:β: 98:2).

\alpha-manno isomer: $[\alpha]_D^{22} = +36$ (c 1.0, CHCl₃); R_f: 0.23 (1:3.5, EtOAc/Hexane); IR (Neat): v_{max} 3015, 2930, 2856, 1722, 1656, 1462, 1253, 1122, 1063, 755, 665 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 7.89 (dd, J₁=0.96, J₂=7.93 Hz,1H), 7.59 (dd, J₁=1.60, J2=7.81 Hz, 1H), 7.20-7.36 (m, 15H), 7.06-7.13 (m, 3H), 6.61 (d, J=1.23 Hz, 1H), 4.81-4.84 (m, 1H), 4.64-4.69 (m, 2H), 4.57-4.59 (m, 1H), 4.44-4.54 (m, 2H), 3.96-4.02 (m, 2H), 3.72-3.77 (m, 2H), 3.62-3.65 (m, 1H), 3.29-3.32 (m, 1H); $^{13}\mathrm{C}$ (100 MHz, CDCl₃): δ 164.36, 141.69, 138.50, 138.23, 137.61, 134.32, 133.41, 131.64, 128.78, 128.63, 128.56, 128.41, 128.32, 128.26, 127.97, 127.77, 97.20, 94.21, 76.24, 75.74, 75.73, 75.63, 73.80, 71.26, 68.78, 31.16; ESI-HRMS: m/z [M+NH₄]⁺ calcd for C₃₄H₃₆I₂NO₆⁺ 813.0632, measured 808.0651.

(2R,3S,4S,5S,6R)-2-(acetoxymethyl)-5-iodo-6-((2-

iodobenzoyl)oxy)tetrahydro-2H-pyran-3,4-diyl diacetate 11c: This compound was prepared by using the above mentioned general procedure II using tri-O-acetyl-D-galactal 1c (100 mg, 0.3676 mmol) as the starting material. Yield: (173 mg, 0.268

mmol, 73%, α:β: 98:2). **α-manno isomer:** $[\alpha]_D^{22} = -24.8$ (*c* 1.0, CHCl₃); R_{*f*}: 0.23 (1:3.5, EtOAc/Hexane); IR (Neat): v_{max} 3015, 2930, 2856, 1722, 1656, 1462, 1253, 1122, 1063, 755, 665 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 7.95 (d, J=7.85 Hz, 1H), 7.74 (d, J=7.85 Hz, 1H), 7.39 (t, J=7.48 Hz, 1H), 7.15 (t, J=7.48 Hz, 1H), 6.72 (s, 1H), 5.42 (bs, 1H), 4.99-5.00 (m, 1H), 4.49-4.52 (m, 1H), 4.42-4.43 (m, 1H), 4.104.16 (m, 2H), 2.15 (s, 3H), 2.02 (s, 3H), 1.96 (s, 3H); 13 C (100 MHz, CDCl₃): δ 170.58, 170.17, 169.68, 164.09, 141.79, 134.17, 133.63, 131.77, 128.38, 97.83, 94.06, 69.92, 65.09, 65.02, 61.74, 21.15, 21.03, 20.88, 18.77; ESI-HRMS: m/z [M+Na]⁺ calcd for C₁₉H₂₀L₅NaO₉⁺ 668.9094, measured 668.9091.

(2R,3S,4S,5S,6R)-6-(((tert-butyldiphenylsilyl)oxy)methyl)-3-

iodo-4,5-bis(methoxymethoxy)tetrahydro-2*H*-pyran-2-yl 2iodobenzoate 11d: This compound was prepared by using the above mentioned general procedure II using (((2R,3S,4R)-3,4bis(methoxymethoxy)-3,4-dihydro-2*H*-pyran-2-yl)methoxy)(tertbutyl)diphenylsilane 1f (200 mg, 0.422 mmol) as the starting material. Yield: (246 mg, 0.291 mmol, 69%, α : β : 90:10).

material. Yield: (246 mg, 0.291 mmol, 69%, α;β: 90:10). **α-manno isomer:** $[a]_D^{22} = +15.2$ (*c* 0.3, CHCl₃); R_j: 0.23 (1:3.5, EtOAc/Hexane); IR (Neat): v_{max} 3015, 2930, 2856, 1722, 1656, 1462, 1253, 1122, 1063, 755, 665 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 7.95 (d, *J*=8.04 Hz, 1H), 7.64 (dd, *J*₁=1.66, *J*₂=7.74 Hz, 1H), 7.52-7.56 (m, 4H), 7.21-7.39 (m, 7H), 7.14 (td, *J*₁=1.78, *J*₂=7.73 Hz, 1H), 6.71 (s, 1H), 4.86-4.88 (m, 1H), 4.75-4.77 (m, 1H), 4.61-4.71 (m, 2H), 4.38-4.40 (m, 1H), 4.16 (bs, 1H), 4.05-4.08 (m, 1H), 3.85-3.90 (m, 1H), 3.76-3.80 (m, 1H), 3.68-3.70 (m, 1H), 3.37 (s, 3H), 3.29 (s, 3H), 0.96 (s, 9H); ¹³C (100 MHz, CDCl₃): δ 164.51, 141.60, 135.78, 135.10, 133.48, 133.44, 133.31, 131.73, 130.04, 128.29, 128.16, 127.98, 127.95, 98.70, 97.25, 94.80, 93.90, 74.76, 70.18, 69.96, 62.65, 56.70, 56.53, 29.94, 27.11, 22.32; ESI-HRMS: *m*/z [M+Na]⁺ calcd for C₃₃H₄₀I₂NaO₈Si⁺ 869.0480, measured 869.0470.

(3R,4R,5S,6R)-5-iodo-6-((2-iodobenzoyl)oxy)tetrahydro-2H-

pyran-3,4-diyl diacetate 11e: This compound was prepared by using the above mentioned general procedure II using (3R,4S)-3,4-dihydro-2*H*-pyran-3,4-diyl diacetate **1g** (100 mg, 0.5 mmol) as the starting material. Yield: (186 mg, 0.324 mmol, 65%, α : β : 92:8).

α-manno isomer: $[a]_D^{22} = +155.3$ (*c* 0.15, CHCl₃); R_f: 0.23 (1:4, EtOAc/Hexane);); IR (Neat): v_{max} 3019, 2927, 2400, 1751, 1637, 1453, 1371, 1216, 1063, cm⁻¹; ¹H (400 MHz, CDCl₃): δ 7.9 (d, *J*=8.07 Hz, 1H), 7.88 (dd, *J*₁=1.39, *J*₂=7.72 Hz, 1H), 7.36-7.40 (m, 1H), 7.12-7.16 (m, 1H), 6.22 (d, *J*=8.06 Hz, 1H), 5.55-5.56 (m, 1H), 5.09-5.13 (m, 1H), 4.32-4.35 (m, 1H), 3.93-4.03 (m, 2H), 2.15 (s, 3H), 1.98 (s, 3H); ¹³C (100 MHz, CDCl₃): δ 170.58, 169.68, 164.09, 141.79, 134.17, 133.63, 131.77, 128.38, 97.83, 94.06, 69.92, 65.02, 61.74, 21.15, 20.89, 18.77; ESI-HRMS: *m/z* [M+Na]⁺ calcd for C₁₆H₁₆J₂NaO₇ 596.8883, measured 596.8870.

(2R,3S,4R,5R)-4-(benzyloxy)-5-((benzyloxy)methyl)-3-

iodotetrahydrofuran-2-yl 2-iodobenzoate 11f : This compound was prepared by using the above mentioned general procedure II using (2R,3S)-3-(benzyloxy)-2-((benzyloxy)methyl)-2,3dihydrofuran 1j (200 mg, 0.5 mmol) as the starting material. Yield: (339 mg, 0.506 mmol, 75%, α : β : 93:7).

α-manno isomer: $[α]_D^{22} = +80.7$ (c 0.2, CHCl₃); R_j: 0.4 (1:9, EtOAc/Hexane);); IR (Neat): v_{max} 3023, 2931, 2856, 1752, 1642, 1372, 1218, 1122, 1071, cm⁻¹; ¹H (400 MHz, CDCl₃): δ 7.94 (d, J=7.92 Hz, 1H), 7.90 (dd, J₁=1.58 J₂=7.82 Hz, 1H), 7.37 (d, 7.50 Hz, 1H), 7.22-7.31 (m, 10H), 7.06-7.10 (m, 1H), 6.01 (d, J=6.75, 1H), 4.61-4.62 (m, 1H), 4.48-4.59 (m, 4H), 4.16 (dd, J₁=4.93, J₂=12.26 Hz, 1H), 3.83-3.84 (m, 1H), 3.74 (dd, J₁=2.91, J₂=8.47, 1H); ¹³C (100 MHz, CDCl₃): δ 164.04, 142.02, 137.92, 137.46, 133.59, 132.84, 132.26, 102.69, 96.28, 81.79, 80.27, 72.69, 71.75, 71.30, 32.40; ESI-HRMS: m/z [M+Na]⁺ calcd for C₂₆H₂₄I₂NaO₅⁺ 692.9611, measured 692.9600.

$\label{eq:synthesis} Synthesis of (2R, 3R, 4S, 5S, 6R) - 2-(acetoxymethyl) - 6-((2-(hex-1-yn-1-yl)benzoyl)oxy) - 5-iodotetrahydro-2H-pyran-3, 4-diyl$

diacetate 12: $[PdCl_2(PPh_3)_2]$ (54 mg, 0.08 mmol), CuI (14 mg, 0.07 mmol), and PPh₃ (20 mg, 0.08 mmol) were added to 2-

deoxy-2-iodo-(2-iodobenzyloxy) glycosylacetate 11a (500 mg, 0.773 mmol) in dry iPr₂NH (1.5 mL) and then degassed the resulting solution. After stirring at rt for 1 h under a nitrogen atmosphere, 1-hexyne (0.132 mL, 1.16 mmol) was slowly added at 0°C. The mixture was allowed to stir at rt for 18 h and saturated NH₄Cl was added. After vigorously stirring for 30 min petroleum ether (10 mL) was added and the two phases were separated. The aqueous layer was extracted with EtOAc (10 mL), the combined organic layers were washed with H₂O and brine, dried over Na₂SO₄, then concentrated. The crude product was subjected to silica gel column chromatography (hexane/ EtOAc 90:10) to provide pure glycosyl 2-hex-1-ynyl benzoate **12** in 85% (394 mg, 0.66 mmol); $[\alpha]_D^{22} = +73.2$ (*c* 0.2, CHCl₃); R_f : 0.23 (1:5, EtOAc/Hexane); IR (Neat): v_{max} 3022, 2929, 2402, 2250, 1749, 1584, 1427, 1068, 761, 670 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 7.93-7.95 (m, 1H), 7.47-7.50 (m, 1H), 7.39-7.43 (m, 1H), 7.28 (dd, J₁=7.61, J₂=15.46 Hz, 1H), 6.05 (d, J=9.39 Hz, 1H), 5.31-5.36 (m, 1H), 4.98-5.02 (m, 1H), 4.04-4.08 (m, 3H), 3.88-3.92 (m, 1H), 2.43 (t, J=7.19 Hz, 2H), 2.05 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H), 1.53-1.61 (m, 2H), 1.38-1.49 (m, 2H), 0.89 (t, J=7.23 Hz, 3H). ¹³C (100 MHz, CDCl₃): δ 171.34, 170.78, 169.75, 163.40, 134.91, 132.76, 131.07, 129.64, 127.36, 126.07, 97.52, 94.68, 79.26, 75.63, 73.25, 68.82, 61.77, 30.90, 25.86, 22.31, 21.25, 20.94, 20.80, 19.85, 13.89; ESI-HRMS: m/z [M+Na]⁺ calcd for $C_{25}H_{29}INaO_9^+$ 623.0754, measured 623.0737.

(III) General procedure for the glycosylation with glycosyl ortho-hexenylbenzoates 12 as donors: A solution of PPh₃AuNTf₂ in DCM was added at -78 °C to a mixture of ortho-hexenylbenzoates 12 (0.218 mmol), acceptors and 4 Å MS in dry DCM (5 mL). The mixture was allowed to stir at the same temperature for 2-3 h. Then the reaction shifted to room temperature and it was filtered through celite bed and the filterate was concentrated. The residue was purified by silica gel column chromatography to provide pure compounds.

(2R,3R,4S,5S,6S)-2-(acetoxymethyl)-6-(benzyloxy)-5-

iodotetrahydro-2H-pyran-3,4-diyl diacetate 13: This compound was synthesized by above mentioned general procedure III using benzyl alcohol (0.24 mmol) as an acceptor; Yield: (96 mg, 0.189 mmol, 92%); R_f: 0.23 (1:3, EtOAc/Hexane); $[\alpha]_D^{22} = +40.3$ (c 0.3, CHCl₃); IR (Neat): ν_{max} 3015, 2930, 2856, 1722, 1656, 1462, 1253, 1122, 1063, 755, 665 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 7.31-7.39 (m, 5H), 5.39 (t, J=9.33 Hz, 1H), 5.25 (s, 1H), 4.65-4.71 (m, 2H), 4.54-4.57 (m, 2H), 4.22 (dd, J₁=4.77, J₂=12.20 Hz, 1H), 4.08(dd, J₁=2.41, J₂=12.19 Hz, 1H), 4.01-4.05 (m, 1H), 2.12 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H); ¹³C (100 MHz, $CDCl_3$): δ 170.91, 170.05, 169.70, 136.57, 128.84, 128.51, 128.42, 100.77, 70.26, 69.57, 69.34, 67.80, 62.40, 29.75, 21.17, 20.99, 20.87; ESI-HRMS: m/z [M+Na]⁺ calcd for C₁₉H₂₃INaO₈⁺ 529.0335, measured 529.0335.

(2*R*,3*R*,4*S*,5*S*,6*S*)-2-(acetoxymethyl)-5-iodo-6-(((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-(4methoxyphenoxy)tetrahydro-2*H*-pyran-2-

yl)methoxy)tetrahydro-2*H***-pyran-3,4-diyl diacetate 14:** This compound was synthesized by above mentioned general procedure III using glucose derived alcohol (133 mg, 0.24 mmol) as an acceptor; Yield: (145 mg, 0.175 mmol, 85%); R_{f} : 0.23 (1:3, EtOAc/Hexane); $[\alpha]_D^{22} = +29.4$ (*c* 0.1, CHCl₃); IR (Neat): v_{max} 3012, 2830, 1722, 1556, 1362, 1250, 1022, 1063, 755, 665 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 7.27-7.36 (m, 15H), 7.00 (d, *J*=9 Hz, 2H), 6.86 (d, *J*=9.34 Hz, 2H), 5.34 (t, J=9.47 Hz, 1H), 5.19 (s, 1H), 5.04-5.07 (m, 1H), 4.89-4.98 (m, 3H), 4.79-4.83 (m, 2H), 4.57-4.63 (m, 3H), 3.99-4.08 (m, 2H), 3.91-3.95 (m, 1H), 3.69-3.77 (m, 8H), 3.59-3.63 (m, 1H), 3.46-3.51 (m, 1H), 2.09 (s, 3H),

2.07 (s, 3H), 1.92 (s, 3H); ¹³C (100 MHz, CDCl₃); δ 170.88, M 169.99, 169.72, 155.48, 151.59, 138.56, 138.42, 138.05, 128.76, 128.68, 128.45, 128.15, 128.05, 118.18, 115.02, 102.61, 101.69, 84.89, 82.24, 77.92, 76.03, 75.26, 74.27, 69.35, 69.26, 67.41, 62.11, 55.77, 29.53, 21.21, 20.98, 20.66; ESI-HRMS: *m*/z [M+Na]⁺ calcd for C₃₉H₄₄INaO₁₂⁺ 977.2221, measured 977.2190.

(2R,3R,4S,5S,6S)-2-(acetoxymethyl)-6-((R)-2-((tertbutoxycarbonyl)amino)-2-phenylethoxy)-5-iodotetrahydro-

2*H***-pyran-3,4-diyl diacetate 15:** This compound was synthesized by above mentioned general procedure III using unnatural amino acid phenylglycine derived alcohol (57 mg, 0.24 mmol) as an acceptor; Yield: (118 mg, 0.186 mmol, 87%); R_f: 0.25 (1:3, EtOAc/Hexane); $[a]_D^{22} = +27.4$ (*c* 0.25, CHCl₃); IR (Neat): v_{max} 3052, 2720, 1719, 1686, 1272, 1370, 1032, 675 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 7.17-7.30 (m, 5H), 5.27 (bs, 1H), 5.19 (t, J=9.63 Hz, 1H), 5.06 (s, 1H), 4.86 (bs, 1H), 4.44-4.45 (m, 1H), 4.36-4.39 (m, 1H), 3.86-3.90 (m, 1H), 3.68-3.51 (m, 3H), 3.03 (bs, 1H), 2.01 (s, 3H), 2.01 (s, 3H), 1.94 (s, 3H), 1.37 (s, 9H); ¹³C (100 MHz, CDCl₃): δ 170.82, 170.10, 169.54, 155.40, 128.87, 127.75, 126.64, 100.71, 80.22, 71.08, 69.24, 69.16, 67.27, 62.03, 29.05, 28.57, 21.17, 20.93, 20.80; ESI-HRMS: *m*/z [M+Na]⁺ calcd for C₂₅H₃₄INNaO₁₀⁺ 658.1125, measured 658.1138.

(2R,3R,4S,5S,6R)-2-(acetoxymethyl)-5-iodo-6-(4-

methoxyphenoxy)tetrahydro-2*H***-pyran-3,4-diyl diacetate 16:** This compound was prepared by following above mentioned general procedure III using isopropyl alcohol (0.05 mL, 0.24 mmol) as an acceptor; Yield: (95 mg, 0.186 mmol, 90%); R_j: 0.30 (1:3, EtOAc/Hexane); $[\alpha]_D^{22} = +5.6$ (*c* 0.1, CHCl₃); IR (Neat): v_{max} 3015, 2930, 2856, 1722, 1656, 1462, 1253, 1122, 1063, 755, 665 cm⁻¹; ¹H (400 MHz, CDCl₃): δ 6.94 (d, *J*=9.64 Hz, 2H), 6.75 (d, *J*=9.64, 2H), 5.67 (s, 1H), 5.37 (t, *J*=9.64, 1H), 4.76 (dd, *J*₁=4.48, *J*₂=9.41 Hz, 1H), 4.66 (dd, *J*₁=1.35, *J*₂=4.43 Hz, 1H), 4.05-4.15 (m, 3H), 3.70 (s, 3H), 2.05 (s, 3H), 2.0 (s, 3H), 1.99 (s, 3H); ¹³C (100 MHz, CDCl₃): δ 170.80, 170.11, 169.72, 155.70, 149.84, 118.04, 114.89, 100.76, 69.93, 69.20, 67.62, 62.24, 55.88, 29.16, 21.18, 20.91, 20.87 ESI-HRMS: *m/z* [M+H]⁺ calcd for C₁₉H₂₄IO₉⁺ 523.0465, measured 523.0450.

(2R,3R,4S,5S,6S)-2-(acetoxymethyl)-5-iodo-6-

isopropoxytetrahydro-2*H***-pyran-3,4-diyl diacetate 17:** This compound was prepared by adopting the above mentioned general procedure III using 4-methoxyphenol (28 mg, 0.24 mmol) as an acceptor; Yield: (105 mg, 0.19 mmol, 90%); R_f : 0.30 (1:3, EtOAc/Hexane); $[\alpha]_D^{22} = +32.4$ (*c* 0.3, CHCl₃); IR (Neat): v_{max} 3021, 2992, 2812, 1720, 1556, 1462, 1253, 1122, cm⁻¹; ¹H (400 MHz, CDCl₃): δ 5.35 (t, *J*=10 Hz, 1H), 5.25 (s, 1H), 4.64 (dd, J_1 =4.39, J_2 =9.40 Hz, 1H), 4.47 (dd, J_1 =1.31, J_2 =4.33 Hz, 1H), 4.20 (dd, J_1 =5.10, J_2 =12.38 Hz, 1H), 4.05-4.14 (m, 2H), 3.85-3.94 (m, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.22 (d, *J*=6.19 Hz, 3H), 1.16 (d, *J*=5.83 Hz, 3H); ¹³C (100 MHz, CDCl₃): δ 170.90, 170.06, 169.73, 99.90, 71.35, 69.36, 69.32, 68.04, 62.57, 30.79, 23.28, 21.85, 21.18, 20.93, 20.88; ESI-HRMS: m/z [M+Na]⁺ calcd for C₁₅H₂₃INaO₈⁺ 481.0335, measured 481.0342.

(2R, 3R, 4S, 5S, 6R) - 2 - (acetoxymethyl) - 6 - (((2R, 3R, 5R, 6S) - 3, 5-bis(benzyloxy) - 2 - ((benzyloxy)methyl) - 6 - (4 - bis(benzyloxy) - 2 - (benzyloxy) - 2 - (benzy

methoxyphenoxy)tetrahydro-2H-pyran-4-yl)oxy)-5-

iodotetrahydro-2*H*-pyran-3,4-diyl diacetate 18: This compound was prepared by adopting the above mentioned general procedure III using glucose derived acceptor (120 mg, 0.24 mmol) as an acceptor; Yield: (170 mg, 0.19 mmol, 85%); R_{f} : 0.2 (1:3, EtOAc/Hexane); $[a]_{D}^{22} = -20.3$ (*c* 0.2, CHCl₃); IR (Neat): v_{max} 3427, 3015, 2930, 1702, 1427, 1217, 1106, 919, 764

cm⁻¹: ¹H (400 MHz, CDCl₃): δ 7.13-7.36 (m, 16H), 6.89 (d, *J*=8.89 Hz, 2H), 6.72 (d, *J*=9.13 Hz, 2H), 5.46-5.48 (m, 2H), 5.24-5.29 (m, 1H) 4.76-4.79 (m, 1H), 4.58-4.65 (m, 4H), 4.48-4.51 (m, 1H), 4.38-4.41 (m, 2H), 4.19-4.22 (m, 1H), 3.88-4.12 (m, 6H), 3.78-3.81 (m, 1H), 3.68-3.74 (m, 4H), 3.59-3.62 (m, 1H), 2.02 (s, 3H), 1.98 (s, 3H), 1.95 (s, 3H);¹³C (100 MHz, CDCl₃): δ 170.83, 169.95, 169.65, 155.32, 150.33, 138.35, 138.09, 138.0, 128.78, 128.54, 128.05, 128.01, 127.84, 127.79, 118.03, 114.88, 103.47, 96.47, 79.47, 75.39, 75.10, 73.65, 72.74, 72.47, 69.75, 69.11, 69.02, 68.0, 62.57, 55.87, 29.93, 21.18, 20.92, 20.91; ESI-HRMS: *m/z* [M+Na]⁺ calcd for C₄₆H₅₁INaO₁₄⁺ 977.2221, measured 977.2220.

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