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Note

An efficient method for the selective synthesis of 2-deoxy-2-iodo-glycosides by O-glycosidation of D-glucal using I_2–$Cu(OAc)_2$

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ABSTRACT

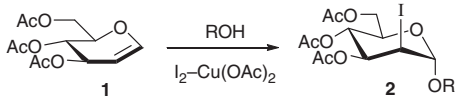
An efficient and convenient method for the synthesis of 2-deoxy-2-iodo-O-glycosides from tri-*O*-acetyl-D-glucal with various alcohols by using I_2–$Cu(OAc)_2$ is described. The 21 examples of corresponding glycosides were obtained in high yields, with good anomeric selectivity.

2-Deoxy-glycosides are important structural units in many biologically significant natural products[1] such as aureolic acid, anthracycline, cardiac glycosides, avermectins, erythromycins, mitemcinal fumarate, and steroidal glycoside PP57.2. The presence of 2-deoxy-glycosides is found as important components in glycoproteins, glycolipids, and a great variety of secondary metabolites. In some cases, the presence of these sugars is crucial for recognition, binding, and activity.[2] As the biological importance of 2-deoxy-glycosides has increased, the investigation of potential methods for the synthesis of these glycosides becomes a challenging target for glycoside chemists.[3]

The most extensive synthetic methods of 2-deoxy-glycosides utilize glycoside donors with C-2 heteroatom substituents[4] such as -Br, -SR, -SeR, -OAc, and -I, which are removed reductively after the glycosylation step by radical-induced reductive cleavage to give 2-deoxy-glycosides. Among these glycoside donors, 2-deoxy-2-iodo-glycosides have been widely investigated and employed in the preparation of 2-deoxy-glycosides as versatile synthetic intermediates.[5] Moreover, 2-deoxy-2-iodo-glycosides have been alternatively used as novel potential imaging or therapeutic imagine agents.[6]

The synthesis of 2-deoxy-2-iodo-glycosides from D-glucal has been reported by the glycosylation reactions using iodonium ion (I+) equivalent reagents such as *N*-iodosuccinimide (NIS)[7] or iodonium-*sym*-collidine perchlorate (IDCP),[5d,8] polymer-supported iodate reagent,[9] hypervalent iodine,[10] and recently NH_4I–H_2O_2–Ac_2O.[11] However, most of these catalysts were not used for wide variety in organic reactions. In the search for a versatile reagent to generate an iodonium ion source for the synthesis of 2-deoxy-2-iodo-glycosides, molecular iodine has received considerable attention due to its ready availability, low cost, easy handling, high efficiency, and environmentally benign nature. Recently, our group has reported a convenient procedure using iodine catalyst in place of Lewis acid in the C-glycosidation of D-glucal with silylacetylenes, which provided α-glycosyl-acetylene products in high yield and high selectivity.[12] Therefore, to continue our interest in the use of iodine for glycoside synthesis, we report herein an efficient method for the synthesis of various 2-deoxy-2-iodo-glycosides as precursors for 2-deoxy-glycoside, via glycosidation of D-glucal employing a combination of iodine and cupric acetate (Scheme 1).

The synthesis of 2-deoxy-2-iodo-glycosides was investigated by O-glycosidation of D-glucal (**1**) with 1.5 equiv of iodine and 1.5 equiv of cupric acetate. Cupric acetate has been reported to be used with iodine for cohalogenation reactions of alkenes in the presence of water to generate iodohydrins.[13] For application to the glycosylation reaction, we first examined suitable conditions as shown in Table 1. The glycosylation of D-glucal with ethanol was



Scheme 1.

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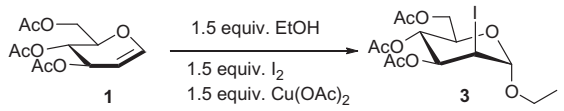
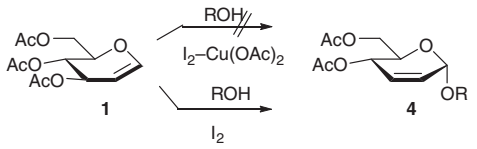
Table 1
O-Glycosidation of D-glucal 1 under various conditions



Entry	Solvent	Condition	Time (h)	Yield (%)
1	CH3CN	a	2	49
2	THF	a	2	40
3	DMF	a	48	0
4	Acetone	a	48	0
5	CH_2Cl_2	a	1	72
6	CH_2Cl_2	b	1	82
7	CH_2Cl_2	c	1	95

Condition a room temperature 30 °C, b 10–20 °C, c 10–20 °C and 4 Å MS.



Scheme 2.

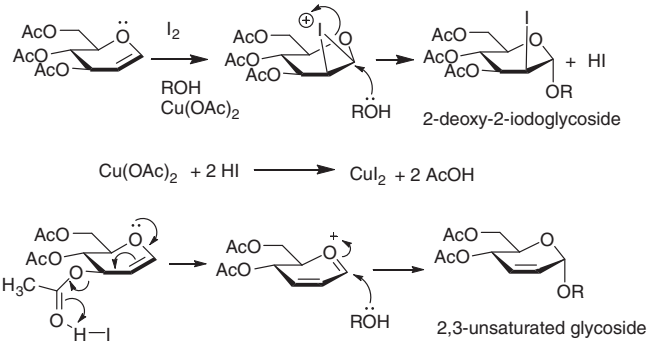


Figure 1. Proposed mechanism.

selected as the model reaction to examine reaction conditions in various solvents such as CH_2Cl_2, CH_3CN, THF, DMF, and acetone. In all cases studied, glycoside **3** was obtained; the best yield was obtained when CH_2Cl_2 was used as the solvent. The yield of product was significantly increased to nearly quantitative yield when the reaction was performed at lower temperature (10–20 °C) and the addition of 4 Å molecular sieves (entry 6 and 7). The use of CH_3CN or THF delivered 40–49% yields of desired product (entries 1and 2), and no reaction was observed when DMF and acetone were employed as solvents (entries 3 and 4).

It is interesting to note that this glycosylation method using $Cu(OAc)_2$ did not produce any of other glycoside product, compared to iodine-catalyzed O-glycosylation, which is known to provide 2,3-unsaturated glycoside **4** (Scheme 2).[14] Thus, the selective formation of 2-deoxy-2-iodo-glycoside can be successfully achieved in the presence of additives such as $Cu(OAc)_2$.

A proposed mechanism for the glycosylation is summarized in Figure 1. The reaction of D-glucal and an alcohol in the presence of iodine without an additive can produce HI, which is believed to promote Ferrier rearrangement leading to the formation of the 2,3-unsaturated glycoside. However, in the presence of cupric acetate, hydroiodic acid (HI) will generate AcOH and CuI_2. Without HI, the reaction proceeds exclusively through the cyclic iodonium intermediate, resulting in the formation of the 2-deoxy-2-iodo-glycoside.

With the optimized conditions in hand (Table 1, entry 7), a number of alcohols were investigated to react with D-glucal to examine the efficiency, scope, and limitations of this method. The results are summarized in Table 2. The first set of experiments were conducted on primary alcohols (entries 1–6), which afforded 2-deoxy-2-iodo-glycosides in excellent yields with high α-stereoselectivity.

To further study the reaction, we carried out the experiments using secondary and tertiary alcohols such as 2-propanol, 2-butanol, cyclohexanol, *tert*-butanol, and menthol (entries 7–10, 21). The desired products were afforded in good yields (80–84%) with higher stereoselectivity than primary alcohols. In comparison with the secondary alcohols, the reaction of the tertiary alcohol (entry 10) afforded the product in lower yield (51%) but provided improved stereoselectivity. While the glycosylation with phenol (entry 11) yielded glycoside **14** in low yield (10%), the reactions of benzyl alcohol and derivatives smoothly produced the corresponding glycosides in excellent yields (entries 12–17). Glycoside derivative **25** (entry 20) was also subjected to the O-glycosylation as the alcohol nucleophile, which smoothly produced the pure α-anomer **23** in 82% yield. Alcohols with functional groups such as propargyl alcohol and 2-bromoethanol (entries 18 and 19) were also examined in the present conditions. It was found that the alkyne and halogen-functionality were retained under these conditions. In all cases, a noteworthy point is that the α-anomer is the predominant product, which can be attributed to the anomeric effect and the size of alcohol; the selectivity is particularly high when a bulky alcohol was used as the nucleophile.

In conclusion, we have developed an efficient method for selective synthesis of 2-deoxy-2-iodo-glycosides. Attractive features of this method are the simple experimental procedure, good yields, high stereoselectivity, and its adaptability for the synthesis of a diverse set of 2-deoxy-2-iodo-glycosides. This approach can be further applied to the synthesis of 2-deoxy-glycosides, which are the units of biologically important natural products and they could be potential imaging or therapeutic imaging agents.

1. Experimental

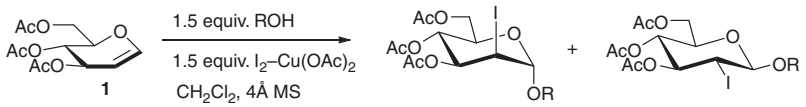
1.1. General methods

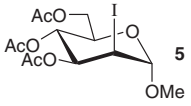
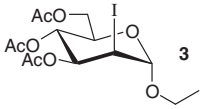
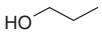
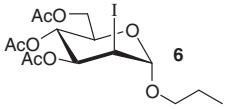
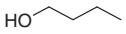
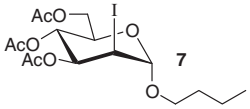
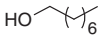
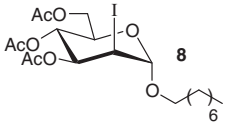
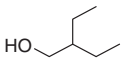
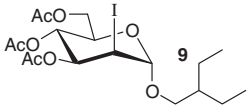
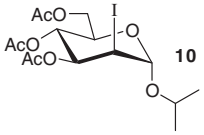
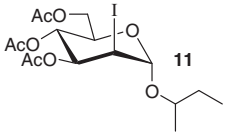
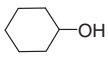
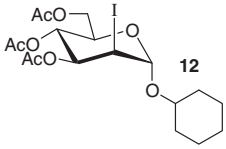
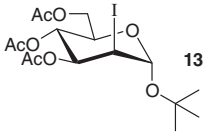
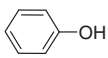
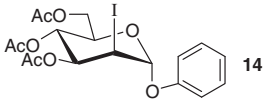
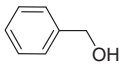
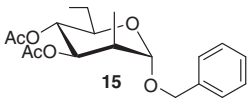
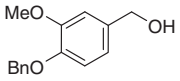
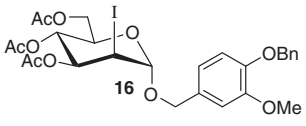
Proton NMR spectra were recorded on a BRUKER AVANC (400 MHz). All spectra were measured in $CDCl_3$ solvent and chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane (δ 0.00) or $CDCl_3$ (δ 7.26) as the internal standard. Data are reported as follows: chemical shift (multiplicity, integration intensity, coupling constants in Hz, assignment). Carbon NMR spectra were recorded on a BRUKER AVANC (100 MHz). All spectra were measured in $CDCl_3$ solvent and chemical shifts are reported as δ values in parts per million (ppm) relative to $CDCl_3$ (δ 77.0) as internal standard. High-resolution FAB mass spectra were obtained with a Finnigan MAT 95. Infrared spectra were determined on a PERKIN ELMER FT/IR-2000S spectrophotometer and are reported in wave number (cm^{-1}). Optical rotation was determined with a JASCO P-1020 digital polarimeter. Analytical thin-layer chromatography (tlc) was conducted on precoated tlc plates; Silica Gel 60F-254 [E. Merck, Darmstadt, Germany]. Silica gel columns for open-column chromatography utilized Silica Gel 60 PF254 [E. Merck, Darmstadt, Germany].

1.2. General procedure for synthesis of 2-deoxy-2-iodo-glycosides

To a solution of 3,4,6-tri-*O*-acetoxy-D-glucal (**1**, 0.1354 g, 0.50 mmol), alcohol (0.75 mmol), cupric acetate (0.1360 g,

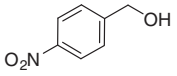
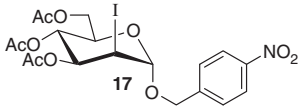
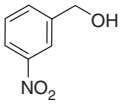
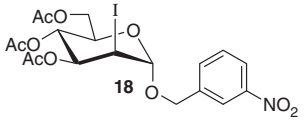
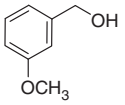
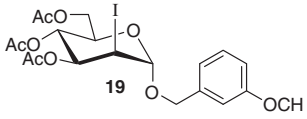
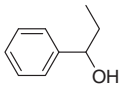
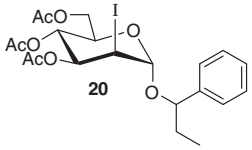
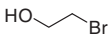
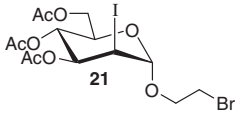
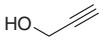
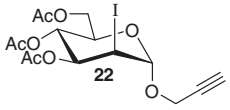
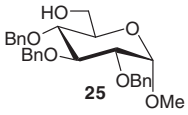
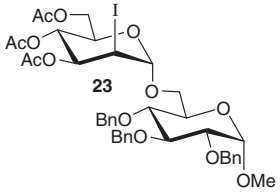
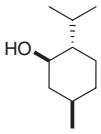
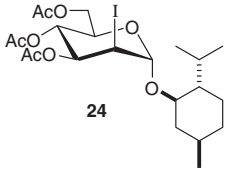
Table 2
O-Glycosylation of D-glucal **1** with various alcohols using $Cu(OAc)_2$



Entry	Nucleophile	Time (h)	Major products[c]	Yield[a] (%) (α:β)[b]
1	MeOH	1	 **5**	98 (5:1)
2		1	 **3**	95 (7:1)
3		2	 **6**	92 (7:1)
4		2	 **7**	90 (7:1)
5		2	 **8**	90 (6:1)
6		2	 **9**	85 (7:1)
7		2	 **10**	80 (9:1)
8		3	 **11**	80 (9:1)[d]
9		3	 **12**	84 (8:1)
10		3	 **13**	51 (14:1)
11		24	 **14**	10 (only α)
12		5	 **15**	76 (9:1)
13		24	 **16**	80 (7:1)

(*continued on next page*)

Table 2 (*continued*)

Entry	Nucleophile	Time (h)	Major products[c]	Yield[a] (%) (α:β)[b]
14		12	 **17**	88 (9:1)
15		6	 **18**	98 (6:1)
16		3	 **19**	98 (11:1)
17		3	 **20**	95 (8:1)[d]
18		2	 **21**	60 (12:1)
19		3	 **22**	57 (9:1)
20	 **25**	24	 **23**	82 (only α)
21		5	 **24**	64 (12:1)

[a] Isolated yields as diastereomeric mixtures.
[b] Determined by ^{1}H NMR spectroscopy.
[c] Major product can be separated by simple column chromatography.
[d] Diastereomeric mixture from racemic alcohol.

0.75 mmol), and molecular sieves 4 Å (0.1354 g) in anhydrous CH_2Cl_2 (5.0 mL) was added iodine powder (0.1900 g, 0.75 mmol) at 10–20 °C. The mixture was stirred for 1 h. After TLC showed the complete conversion, the molecular sieves were removed by filtration. The filtrate solution was diluted with dichloromethane, washed with satd aq $Na_2S_2O_3$, then dried over with Na_2SO_4 anhydrous, and concentrated in vacuo. The residue was purified by silica gel column chromatography to give the 2-deoxy-2-iodo-glycoside product.

1.3. Ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo–D-mannopyranoside (3)

$[\alpha]_D^{28}$ +7.89 (*c* 1.02, $CHCl_3$). IR ($CHCl_3$): 2980, 2930, 1748, 1370, 1231, 1052 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (t, 3H, *J* = 7.0 Hz, H-2′), 2.07 (s, 3H, Ac), 2.10 (s, 3H, Ac), 2.14 (s, 3H, Ac), 3.56 (dq, 1H, *J* = 10.0, 7.0 Hz, H-1′a), 3.75 (dq, 1H, *J* = 10.0, 7.0 Hz, H-1′b), 4.05 (ddd, 1H, *J* = 9.5, 5.0, 2.5 Hz, H-5), 4.16 (dd, 1H, *J* = 12.0, 2.5 Hz, H-6a), 4.25 (dd, 1H, *J* = 12.0, 5.0 Hz, H-6b), 4.54 (dd, 1H, *J* = 4.5, 1.0 Hz, H-2), 4.68 (dd, 1H, *J* = 9.5, 4.5 Hz, H-3), 5.20 (br s, 1H, H-1), 5.39 (t, 1H, *J* = 9.5 Hz, H-4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.98, 20.67, 20.75, 20.97, 29.80, 62.29, 64.11, 67.66, 69.05, 69.12, 101.10, 169.53, 169.89, 170.75. HRMS: $C_{14}H_{21}IO_8$ (M^++Na), Calcd 467.0175, Found 467.0183.

1.4. Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo–D-mannopyranoside (5)

IR ($CHCl_3$): 2940, 2838, 1747, 1369, 1231, 1052, 967, 902, 602 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.02 (s, 3H, Ac), 2.05 (s, 3H, Ac), 2.09 (s, 3H, Ac), 3.38 (s, 3H, H-1′), 3.97 (ddd, 1H, *J* = 9.5, 5.0, 2.5 Hz, H-5), 4.13 (dd, 1H, *J* = 12.0, 2.5 Hz, H-6a), 4.20 (dd, 1H, *J* = 12.0, 5.0 Hz, H-6b), 4.50 (dd, 1H, *J* = 4.5, 1.0 Hz, H-2), 4.59 (dd, 1H, *J* = 9.5, 4.5 Hz, H-3), 5.05 (br s, 1H, H-1), 5.33 (t, 1H,

J = 9.5 Hz, H-4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.60, 20.69, 20.88, 29.22, 55.38, 62.25, 67.52, 69.0, 69.18, 102.28, 169.48, 169.81, 170.68. HRMS: $C_{13}H_{19}IO_8$ (M^++Na), Calcd 453.0022, Found. 453.0031.

1.5. Propyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo–D-mannopyranoside (6)

$[\alpha]_D^{28}$ +1.64 (c 1.01, $CHCl_3$). IR ($CHCl_3$): 2959, 2936, 1745, 1432, 1366, 1220, 1019, 743 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (t, 3H, J = 7.4 Hz, H-3′), 1.57–1.73 (m, 2H, H-2′), 2.07 (s, 3H, Ac), 2.10 (s, 3H, Ac), 2.13 (s, 3H, Ac), 3.45 (dt, 1H, J = 9.6, 6.8 Hz, H-1′a), 3.64 (dt, 1H, J = 9.6, 6.8 Hz, H-1′b), 4.04 (ddd, 1H, J = 9.6, 5.0, 2.8 Hz, H-5), 4.16 (dd, 1H, J = 12.0, 2.8 Hz, H-6a), 4.24 (dd, 1H, J = 12.0, 5.0 Hz, H-6b), 4.55 (dd, 1H, J = 4.4, 1.2 Hz, H-2), 4.66 (dd, 1H, J = 9.6, 4.4 Hz, H-3), 5.19 (br s, 1H, H-1), 5.38 (t, 1H, J = 9.6 Hz, H-4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.60, 20.67, 20.75, 20.97, 22.65, 29.78, 62.30, 67.65, 69.07, 69.16, 70.25, 101.29, 169.54, 169.88, 170.73. HRMS: $C_{15}H_{23}IO_8$ (M^++Na), Calcd 481.0336, Found. 481.0339.

1.6. Butyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo–D-mannopyranoside (7)

$[\alpha]_D^{28}$ +14.75 (c 1.08, $CHCl_3$). IR ($CHCl_3$): 2959, 2874, 1742, 1433, 1366, 1219, 1117, 1038, 673 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, 3H, J = 7.1 Hz, H-4′), 1.34–1.45 (m, 2H, H-3′), 1.54–1.65 (m, 2H, H-2′), 2.06 (s, 3H, Ac), 2.09 (s, 3H, Ac), 2.12 (s, 3H, Ac), 3.47 (dt, 1H, J = 9.0, 6.6 Hz, H-1′a), 3.68 (dt, 1H, J = 9.0, 6.7 Hz, H-1′b), 4.02 (ddd, 1H, J = 9.5, 4.5, 2.0 Hz, H-5), 4.15 (dd, 1H, J = 12.1, 2.0 Hz, H-6a), 4.23 (dd, 1H, J = 12.1, 4.5 Hz, H-6b), 4.53 (d, 1H J = 4.0 Hz, H-2), 4.65 (dd, 1H, J = 9.5, 4.0 Hz, H-3), 5.17 (br s, 1H, H-1), 5.37 (t, 1H, J = 9.5 Hz, H-4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.79, 19.29, 20.67, 20.75, 20.97, 29.79, 31.40, 62.31, 67.63, 69.41, 69.07, 69.14, 101.29, 169.52, 169.86, 170.70. HRMS: $C_{16}H_{25}IO_8$ (M^++Na), Calcd 495.0492, Found. 495.0481.

1.7. Octyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo–D-mannopyranoside (8)

$[\alpha]_D^{28}$ +16.79 (c 1.02, $CHCl_3$). IR ($CHCl_3$): 3056, 2929, 1748, 1455, 1423, 1368, 1265, 1229, 1047, 739 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, 3H, J = 6.8 Hz, H-8′), 1.22–1.40 (m, 10H, H-3′, H-4′, H-5′, H-6′, H-7′), 1.57–1.64 (m, 2H, H-2′), 2.06 (s, 3H, Ac), 2.09 (s, 3H, Ac), 2.12 (s, 3H, Ac), 3.45 (ddd, 1H, J = 13.2, 6.0, 3.0 Hz, H-1a′), 3.67 (ddd, 1H, J = 13.2, 6.0, 3.0 Hz, H-1b′), 4.02 (ddd, 1H, J = 9.8, 4.8, 2.4 Hz, H-5), 4.15 (dd, 1H, J = 12.1, 2.4 Hz, H-6a), 4.23 (dd, 1H, J = 12.1, 4.8 Hz, H-6b), 4.54 (dd, 1H, J = 4.4, 1.1 Hz, H-2), 4.65 (dd, 1H, J = 9.8, 4.4 Hz, H-3), 5.17 (br s, 1H, H-1), 5.37 (t, 1H, J = 9.8 Hz, H-4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.08, 20.67, 20.75, 20.97, 22.63, 26.06, 29.18, 29.29, 29.33, 29.80, 31.79, 62.29, 67.63, 68.74, 69.06, 69.15, 101.29, 169.52, 169.86, 170.71. HRMS: $C_{20}H_{33}IO_8$ (M^++Na), Calcd 551.1118, Found. 551.0984.

1.8. 3′-Ethyl-butyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo–D-mannopyranoside (9)

$[\alpha]_D^{28}$ +2.03 (c 1.06, $CHCl_3$). IR ($CHCl_3$): 3056, 2964, 1747, 1458, 1368, 1266, 1229, 1045, 738 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, 6H, J = 7.2 Hz, H-4′, H-6′), 1.34–1.41 (m, 4H, H-3′, H-5′), 1.40–1.50 (m, 1H, H-2′), 2.07 (s, 3H, Ac), 2.10 (s, 3H, Ac), 2.12 (s, 3H, Ac), 3.36 (dd, 1H, J = 9.4, 5.6 Hz, H-1′a), 3.61 (dd, 1H, J = 9.4, 5.6 Hz, H-1′b), 4.01 (ddd, 1H, J = 9.8, 5.0, 2.4 Hz, H-5), 4.16 (dd, 1H, J = 12.2, 2.4 Hz, H-6a), 4.23 (dd, 1H, J = 12.2, 5.0 Hz, H-6b), 4.55 (d, 1H, J = 4.4 Hz, H-2), 4.64 (dd, 1H, J = 9.8, 4.3 Hz, H-3), 5.16 (br s, 1H, H-1), 5.37 (t, 1H, J = 9.8 Hz, H-4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.02, 11.12, 20.68, 20.74, 20.97, 23.23, 23.30, 29.77, 40.93, 62.35, 67.62, 69.19, 69.20, 70.97, 101.55, 169.55, 169.88, 170.71. HRMS: $C_{18}H_{29}IO_8$ (M^++Na), Calcd 523.0805, Found. 523.0687.

1.9. *i*-Propyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo–D-mannopyranoside (10)

$[\alpha]_D^{28}$ +1.83 (c 1.01, $CHCl_3$), IR ($CHCl_3$): 2972, 2925, 1742, 1433, 1367, 1220, 1113, 1032, 736 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17 (d, 3H, J = 6.0 Hz, H-2′a), 1.23 (d, 3H, J = 6.0 Hz, H-2′b), 2.05 (s, 3H, Ac), 2.08 (s, 3H, Ac), 2.10 (s, 3H, Ac), 3.80–4.00 (m, 1H, H-1′), 4.08 (ddd, 1H, J = 9.5, 5.0, 2.4 Hz, H-5), 4.14 (dd, 1H, J = 12.0, 2.4 Hz, H-6a), 4.22 (dd, 1H, J = 12.2, 5.0 Hz, H-6b), 4.48 (d, 1H, J = 4.3 Hz, H-2), 4.66 (dd, 1H, J = 9.5, 4.3 Hz, H-3), 5.26 (br s, 1H, H-1), 5.36 (t, 1H, J = 9.7 Hz, H-4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.62, 20.68, 20.92, 21.60, 23.03, 30.56, 62.30, 67.75, 69.05, 69.08, 71.06, 99.61, 169.47, 169.77, 170.60. HRMS: $C_{15}H_{23}IO_8$ (M^++Na), Calcd 481.0336, Found. 481.0324.

1.10. *s*-Butyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo–D-mannopyranoside (12) (mixture of diastereomers)

$[\alpha]_D^{28}$ +1.90 (c 1.05, $CHCl_3$), IR ($CHCl_3$): 2970, 2936, 1748, 1369, 1230, 1040, 599 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.77–0.93 (m, 6H, H-4′, isomer A, isomer B), 1.07 (d, 3H, J = 5.0 Hz, H-2′, isomer A), 1.14 (d, 3H, J = 5.3 Hz, H-2′, isomer B), 1.31–1.63 (m, 4H, H-3′, isomer A, isomer B), 1.99 (s, 3H, Ac), 2.01 (s, 3H, Ac), 2.04 (s, 3H, Ac), 3.55–3.68 (m, 2H, H-1′, isomer A, isomer B), 3.98–4.19 (m, 6H, H-5, H-6, isomer A, isomer B), 4.42 (d, 1H, J = 4.5 Hz, H-2, isomer A), 4.41 (d, 1H, J = 4.5 Hz, H-2, isomer B), 4.53–4.63 (m, 2H, H-3, isomer A, isomer B), 5.19 (br s, 1H, H-1, isomer A), 5.21 (br s, 1H, H-1, isomer B), 5.29 (t, 2H, J = 9.7 Hz, H-4, isomer A, isomer B). ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.57, 10.17, 18.59, 20.45, 20.65, 20.69, 20.94, 28.99, 29.76, 30.42, 30.65, 62.37, 67.74, 67.82, 69.13, 69.19, 69.25, 75.22, 77.68, 98.92, 101.00, 169.51, 169.80, 170.63. HRMS: $C_{16}H_{25}IO_8$ (M^++Na), Calcd 495.0492, Found. 495.0499.

1.11. Cylohexyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo–D-mannopyranoside (12)

$[\alpha]_D^{28}$ +22.03 (c 1.05, $CHCl_3$), IR ($CHCl_3$): 2933, 2857, 1743, 1449, 1366, 1219, 1114, 1033, 672 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05–1.55 (m, 6H, H-3′, H-4′, H-5′), 1.60–1.85 (m, 4H, H-2′, H-6′), 1.99 (s, 3H, Ac), 2.01 (s, 3H, Ac), 2.04 (s, 3H, Ac), 3.52 (tt, 1H, J = 9.3, 3.9 Hz, H-1′), 4.04 (ddd, 1H, J = 9.6, 4.9, 2.5 Hz, H-5), 4.08 (dd, 1H, J = 12.1, 2.5 Hz, H-6a), 4.14 (dd, 1H, J = 12.1, 4.9 Hz, H-6b), 4.42 (dd, 1H, J = 4.3, 1.2 Hz, H-2), 4.60 (dd, 1H, J = 9.5, 4.3 Hz, H-3), 5.23 (br s, 1H, H-1), 5.29 (t, 1H, J = 9.6 Hz, H-4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.68, 20.74, 20.99, 23.84, 24.10, 25.44, 30.68, 31.58, 33.19, 62.37, 67.84, 69.14, 69.20, 76.93, 99.58, 169.57, 169.90, 170.72. HRMS: $C_{18}H_{27}IO_8$ (M^++Na), Calcd 521.0649, Found. 521.0643.

1.12. *t*-Butyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo–D-mannopyranoside (13)

$[\alpha]_D^{28}$ +18.19 (c 1.02, $CHCl_3$), IR ($CHCl_3$): 2977, 2937, 1748, 1370, 1231, 1046, 882, 602 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (s, 9H, H-2′), 2.06 (s, 3H, Ac), 2.09 (s, 3H, Ac), 2.10 (s, 3H, Ac), 4.09–4.26 (m, 3H, H-5, H-6), 4.41 (d, 1H, J = 4.0 Hz, H-2), 4.70 (dd, 1H, J = 9.5, 4.0 Hz, H-3), 5.36 (t, 1H, J = 9.5 Hz, H-4), 5.42 (br s, 1H, H-1). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.66, 20.71, 20.97, 28.38, 32.03, 62.47, 67.98, 68.74, 69.19, 76.86, 96.21, 169.55, 169.90, 170.70. HRMS: $C_{16}H_{25}IO_8$ (M^++Na), Calcd 495.0492, Found. 495.0490.

1.13. Phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo–D-mannopyranoside (14)

$[\alpha]_D^{28}$ +39.49 (*c* 1.04, $CHCl_3$), IR ($CHCl_3$): 2922, 2852, 1743, 1596, 1493, 1367, 1211, 1115, 1059, 691 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.07 (s, 3H, Ac), 2.08 (s, 3H, Ac), 2.15 (s, 3H, Ac), 4.10–4.19 (m, 2H, H-5, H-6a), 4.23 (dd, 1H, *J* = 12.1, 4.9 Hz, H-6b), 4.76 (dd, 1H, *J* = 4.5, 1.3 Hz, H-2), 4.87 (dd, 1H, *J* = 9.5, 4.5 Hz, H-3), 5.47 (t, 1H, *J* = 9.5 Hz, H-4), 5.87 (br s, 1H, H-1), 7.05–7.15 (m, 3H, Ph), 7.32 (dd, 2H, *J* = 8.8, 7.3 Hz, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.66, 20.68, 20.99, 28.81, 61.93, 67.30, 68.96, 69.78, 99.70, 116.48, 123.06, 129.66, 155.53, 169.53, 169.94, 170.62. HRMS: $C_{18}H_{21}IO_8$ (M^++Na), Calcd 515.0179, Found. 515.0167.

1.14. Benzyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo–D-mannopyranoside (15)

$[\alpha]_D^{28}$ +35.76 (*c* 1.09, $CHCl_3$), IR ($CHCl_3$): 3055, 2986, 1746, 1455, 1422, 1368, 1265, 1121, 1042, 896, 738 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.06 (s, 3H, Ac), 2.10 (s, 3H, Ac), 2.14 (s, 3H, Ac), 4.05 (ddd, 1H, *J* = 9.5, 4.7, 2.4 Hz, H-5), 4.10 (dd, 1H, *J* = 12.2, 2.4 Hz, H-6a), 4.24 (dd, 1H, *J* = 12.2, 4.7 Hz, H-6b), 4.57 (d, 1H, *J* = 11.8 Hz, H-1′a), 4.58 (dd, 1H, *J* = 4.4, 1.0 Hz, H-2), 4.69 (dd, 1H, *J* = 9.5, 4.4 Hz, H-3), 4.72 (d, 1H, *J* = 11.8 Hz, H-1′b), 5.27 (br s, 1H, H-1), 5.41 (t, 1H, *J* = 9.5 Hz, H-4), 7.29–7.50 (m, 5H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.67, 20.78, 20.96, 29.55, 62.16, 67.55, 69.10, 69.33, 70.03, 100.53, 128.21, 128.30, 128.62, 136.34, 169.50, 169.85, 170.71. HRMS: $C_{19}H_{23}IO_8$ (M^++Na), Calcd 529.0335, Found. 529.0323.

1.15. 4-Benzyloxy-3-methoxy-benzyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo–D-mannopyranoside (16)

$[\alpha]_D^{28}$ +42.06 (*c* 0.98, $CHCl_3$), IR ($CHCl_3$): 3055, 2988, 1749, 1605, 1590, 1421, 1369, 1266, 1122, 1037, 735 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.07 (s, 3H, Ac), 2.10 (s, 3H, Ac), 2.15 (s, 3H, Ac), 3.93 (s, 3H, OMe), 4.05 (ddd, 1H, *J* = 9.5, 4.7, 2.4 Hz, H-5), 4.13 (dd, 1H, *J* = 12.2, 2.4 Hz, H-6a), 4.25 (dd, 1H, *J* = 12.2, 4.7 Hz, H-6b), 4.49 (d, 1H, *J* = 11.6 Hz, H-1′a), 4.55 (dd, 1H, *J* = 4.3, 1.0 Hz, H-2), 4.64 (d, 1H, *J* = 11.6 Hz, H-1′b), 4.69 (dd, 1H, *J* = 9.5, 4.3 Hz, H-3), 5.18 (s, 2H, OCH_2Ph), 5.23 (br s, 1H, H-1), 5.41 (t, 1H, *J* = 9.5 Hz, H-4), 6.83 (dd, 1H, *J* = 8.0, 2.0 Hz, Ph), 6.88 (d, 1H, *J* = 8.0 Hz, Ph), 6.90 (d, 1H, *J* = 2 Hz, Ph), 7.25–7.34 (m, 1H, Ph), 7.39 (t, 2H, *J* = 7.2 Hz, Ph), 7.45 (d, 2H, *J* = 7.2 Hz, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.67, 20.79, 20.97, 29.62, 56.09, 62.19, 67.59, 69.11, 69.30, 69.80, 71.05, 100.07, 112.12, 113.78, 121.02, 127.25, 127.90, 128.59, 129.27, 136.98, 148.26, 149.77, 169.52, 169.89, 170.73. HRMS: $C_{27}H_{31}IO_{10}$ (M^++Na), Calcd 665.0860, Found. 665.0841.

1.16. 4-Nitro-benzyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo–D-mannopyranoside (17)

$[\alpha]_D^{28}$ +35.57 (*c* 1.08, $CHCl_3$), IR ($CHCl_3$): 3055, 2987, 1748, 1607, 1522, 1348, 1265, 1230, 1047, 738 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.08 (s, 3H, Ac), 2.12 (s, 3H, Ac), 2.15 (s, 3H, Ac), 4.05 (ddd, 1H, *J* = 9.7, 4.7, 2.5 Hz, H-5), 4.16 (dd, 1H, *J* = 12.3, 2.5 Hz, H-6b), 4.26 (dd, 1H, *J* = 12.3, 4.7 Hz, H-6a), 4.63 (d, 1H, *J* = 4.4 Hz, H-2), 4.65 (d, 1H, *J* = 13.0 Hz, H-1a′), 4.66 (dd, 1H, *J* = 9.7, 4.4 Hz, H-3), 4.84 (d, 1H, *J* = 13.0 Hz, H-1b′), 5.29 (br s, 1H, H-1), 5.43 (t, 1H, *J* = 9.7 Hz, H-4), 7.54 (d, 2H, *J* = 8.4 Hz, Ph), 8.26 (d, 2H, *J* = 8.4 Hz, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.63, 20.74, 20.93, 28.59, 62.12, 67.41, 68.53, 68.95, 69.69, 100.97, 123.87, 128.17, 143.62, 148.13, 169.42, 169.89, 170.61. HRMS: $C_{19}H_{22}INO_{10}$ (M^++Na), Calcd 574.0186, Found. 573.9964.

1.17. 3-Nitro-benzyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo–D-mannopyranoside (18)

$[\alpha]_D^{28}$ +27.45 (*c* 1.02, $CHCl_3$), IR ($CHCl_3$): 3055, 2986, 1747, 1607, 1532, 1351, 1265, 1230, 1045, 738 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.07 (s, 3H, Ac), 2.11 (s, 3H, Ac), 2.15 (s, 3H, Ac), 4.05 (ddd, 1H, *J* = 9.7, 5.0, 2.4 Hz, H-5), 4.16 (dd, 1H, *J* = 12.2, 2.4 Hz, H-6b), 4.26 (dd, 1H, *J* = 12.2, 5.0 Hz, H-6a), 4.62 (d, 1H, *J* = 4.4 Hz, H-2), 4.64 (d, 1H, *J* = 12.5 Hz, H-1a′), 4.66 (dd, 1H, *J* = 9.7, 4.3 Hz, H-3), 4.82 (d, 1H, *J* = 12.5 Hz, H-1b′), 5.29 (br s, 1H, H-1), 5.42 (t, 1H, *J* = 9.7 Hz, H-4), 7.59 (t, 1H, *J* = 8.6 Hz, Ph), 7.71 (d, 1H, *J* = 8.6 Hz, Ph), 8.21 (s, 1H, Ph), 8.22 (d, 1H, *J* = 8.6 Hz, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.63, 20.74, 20.91, 28.70, 62.15, 67.44, 68.69, 68.93, 69.66, 100.89, 122.79, 123.26, 129.71, 133.82, 138.40, 148.39, 169.43, 169.82, 170.62. HRMS: $C_{19}H_{22}INO_{10}$ (M^++Na), Calcd 574.0186, Found. 574.0034.

1.18. 3-Methoxy-benzyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo–D-mannopyranoside (19)

$[\alpha]_D^{28}$ +33.04 (*c* 1.08, $CHCl_3$), IR ($CHCl_3$): 3055, 2986, 1747, 1588, 1490, 1457, 1368, 1265, 1231, 1042, 738 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.07 (s, 3H, Ac), 2.10 (s, 3H, Ac), 2.15 (s, 3H, Ac), 3.84 (s, 3H, H-8′), 4.06 (ddd, 1H, *J* = 9.8, 4.6, 2.3 Hz, H-5), 4.12 (dd, 1H, *J* = 12.2, 2.3 Hz, H-6b), 4.24 (dd, 1H, *J* = 12.2, 4.6 Hz, H-6a), 4.54 (d, 1H, *J* = 12.0 Hz, H-1′a), 4.58 (dd, 1H, *J* = 4.3, 1.2 Hz, H-2), 4.69 (d, 1H, *J* = 12.0 Hz, H-1′b), 4.70 (dd, 1H, *J* = 9.8, 4.3 Hz, H-3), 5.26 (br s, 1H, H-1), 5.41 (t, 1H, *J* = 9.8 Hz, H-4), 6.88 (d, 1H, *J* = 7.6 Hz, Ph), 6.90 (s, 1H, Ph), 6.93 (d, 1H, *J* = 7.6 Hz, Ph), 7.30 (t, 1H, *J* = 7.6 Hz, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.67, 20.78, 20.96, 29.50, 55.28, 62.19, 67.56, 69.10, 69.35, 69.81, 100.43, 113.65, 113.76, 120.39, 129.68, 137.86, 159.80, 169.52, 169.85, 170.74. HRMS: $C_{20}H_{25}IO_9$ (M^++Na), Calcd 559.0441, Found. 559.0309.

1.19. 2-Phenyl-propyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo–D-mannopyranoside (20) (mixture of isomers)

$[\alpha]_D^{29}$ +20.28 (*c* 1.01, $CHCl_3$), IR ($CHCl_3$): 3058, 2967, 2938, 1747, 1493, 1455, 1368, 1266, 1230, 1117, 1040, 738 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.77 (t, 3H, *J* = 7.4 Hz, H-3′, isomer A), 0.84 (t, 3H, *J* = 7.4 Hz, H-3′, isomer B), 1.66 (m, 2H, H-2′, isomer B), 1.84 (m, 2H, H-2′, isomer B), 1.90, 1.95, 2.00, 2.01, 2.05 (6s, 18H, Ac, isomer A and B), 3.39 (dd, 1H, *J* = 12.5, 2.0 Hz, H-6a, isomer A), 3.49 (m, 1H, H-5, isomer A), 3.84 (dd, 1H, *J* = 12.5, 4.0 Hz, H-6b, isomer A), 4.08 (m, 1H, H-5, isomer B), 4.12 (dd, 1H, *J* = 12.5, 2.0 Hz, H-6a, isomer B), 4.18 (dd, 1H, *J* = 12.5, 5.0 Hz, H-6b, isomer B), 4.30 (t, 1H, *J* = 6.5, H-1′, isomer A), 4.37 (m, 1H, H-2, isomer A), 4.39 (t, 1H, *J* = 6.5, H-1′, isomer B), 4.55 (m, 1H, H-2, isomer B), 4.52–4.56 (m, 1H, H-3, isomer B), 4.65 (dd, 1H, *J* = 9.5, 4.5 Hz, H-3, isomer A), 4.86 (br s, 1H, H-1, isomer B), 5.24 (t, 1H, *J* = 10.0, H-4, isomer B), 5.30 (br s, 1H, H-1, isomer A), 5.31 (t, 1H, *J* = 9.5, H-4, isomer A), 7.16–7.31 (m, 5H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.99, 10.05, 10.62, 20.56, 20.70, 20.91, 20.96, 29.79, 30.00, 30.70, 61.48, 62.45, 67.32, 67.81, 69.23, 69.33, 69.38, 69.46, 80.67, 84.13, 98.34, 102.11, 102.16, 126.68, 127.00, 127.87, 128.21, 128.37, 128.64, 140.16, 141.65, 169.29, 169.45, 169.81, 170.51, 170.55. HRMS: $C_{21}H_{27}IO_8$ (M^++Na), Calcd 557.0648, Found. 557.0511.

1.20. 2-Bromoethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo–D-mannopyranoside (21)

$[\alpha]_D^{29}$ +20.33 (*c* 0.97, $CHCl_3$), IR ($CHCl_3$): 3056, 2985, 1735, 1373, 1266, 1244, 1046, 909, 738 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.05 (s, 3H, Ac), 2.08 (s, 3H, Ac), 2.11 (s, 3H, Ac), 3.50 (t, 1H, *J* = 5.0 Hz, H-2′), 3.86 (dt, 1H, *J* = 11.0, 5.0 Hz, H-1′a), 3.97 (dt, 1H, *J* = 11.0, 5.0 Hz, H-1′b), 4.15 (m, 1H, H-5), 4.16 (dd, 1H, *J* = 12.0, 2.5 Hz, H-6a), 4.21

(dd, 1H, J = 12.0, 5.0 Hz, H-6b), 4.55 (dd, 1H, J = 4.4, 1.2 Hz, H-2), 4.66 (dd, 1H, J = 9.5, 4.5 Hz, H-3), 5.23 (br s, 1H, H-1), 5.36 (t, 1H, J = 9.5 Hz, H-4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.63, 20.72, 20.91, 28.95, 29.72, 62.15, 67.40, 68.44, 68.94, 69.64, 101.54, 169.47, 169.78, 170.61. HRMS: HRMS: $C_{14}H_{20}BrIO_8$ (M^++Na), Calcd 544.9284, Found. 544.9145.

1.21. Propargyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo–D-mannopyranoside (22)

$[\alpha]_D^{28}$ +38.19 (c 1.01, $CHCl_3$), IR ($CHCl_3$): 3301, 3056, 2986, 2123, 1748, 1423, 1368, 1227, 1124, 1046, 970, 897, 738 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.06 (s, 3H, Ac), 2.09 (s, 3H, Ac), 2.12 (s, 3H, Ac), 2.50 (t, 1H, J = 2.4 Hz, H-3′), 4.06 (ddd, 1H, J = 10.0, 4.5, 2.0 Hz, H-5), 4.15 (dd, 1H, J = 12.0, 2.0 Hz, H-6b), 4.23 (dd, 1H, J = 12.0, 4.5 Hz, H-6a), 4.27 (d, 1H, J = 2.3 Hz, H-1′a), 4.28 (d, 1H, J = 2.3 Hz, H-1′b), 4.56 (dd, 1H, J = 4.4, 1.2 Hz, H-2), 4.63 (dd, 1H, J = 10.0, 4.5 Hz, H-3), 5.38 (br s, 1H, H-1), 5.40 (t, 1H, J = 10.0 Hz, H-4). ^{13}C NMR (100 MHZ, $CDCl_3$): δ 20.58, 20.69, 20.86, 28.81, 54.95, 62.00, 67.37, 68.78, 69.56 , 75.59, 78.01, 99.92, 169.37, 169.71, 170.60. HRMS: $C_{15}H_{19}IO_8$ (M^++Na), Calcd 477.0022, Found. 476.9917.

1.22. Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo–D-mannopyranosyl-(1→6)-3,4,6-tri-*O*-benzyl–D-glucopyranoside (23)

$[\alpha]_D^{28}$ +52.41 (c 1.08, $CHCl_3$), IR ($CHCl_3$): 2925, 2850, 1744, 1600, 1496, 1454, 1366, 1223, 1086, 1028, 697 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.94 (s, 3H, Ac), 1.97 (s, 3H, Ac), 2.00 (s, 3H, Ac), 3.30 (s, 3H, OMe), 3.40 (t, 1H, J = 9.4 Hz, H-4′), 3.47 (dd, 1H, J = 9.6, 3.6 Hz, H-2′), 3.57 (d, 1H, J = 10.1 Hz, H-6′a), 3.65–3.78 (m, 2H, H-6′b, H-5′), 3.83–4.00 (m, 3H, H-5, H-6, H-3′), 4.43–4.55 (m, 4H, H-2, H-3, H-1′, O-CH_2Ph), 4.60 (d, 1H, J = 12.0 Hz, O-CH_2Ph), 4.72 (d, 2H, J = 11.5 Hz, 2 × O-CH_2Ph), 4.90 (d, 1H, J = 11.2 Hz, O-CH_2Ph), 4.92 (d, 1H, J = 10.8 Hz, O-CH_2Ph), 5.13 (br s, 1H, H-1), 5.26 (t, 1H, J = 9.6 Hz, H-4), 7.00–7.50 (m, 15H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.66, 20.73, 20.97, 29.27, 55.24, 62.01, 66.74, 67.40, 69.00, 69.19, 69.69, 73.42, 74.91, 75.82, 77.58, 80.08, 82.12, 97.97, 101.42, 127.46, 127.69, 127.79, 127.98, 128.04, 128.13, 128.44, 128.45, 128.52, 138.08, 138.20, 138.57, 169.45, 169.79, 170.67. HRMS: $C_{40}H_{47}IO_{13}$ (M^++Na), Calcd 885.1959, Found. 885.1980.

1.23. Menthyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo–D-mannopyranoside (24)

$[\alpha]_D^{28}$ +64.18 (c 1.01, $CHCl_3$), IR ($CHCl_3$): 3055, 2959, 1748, 1456, 1369, 1233, 1115, 1032, 896, 738 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.70 (d, 3H, J = 7.0 Hz, H-9′), 0.73–1.05 (m, 10H, menthol ring, H-8′, H-8″), 1.15–1.39 (m, 2H, menthol ring), 1.48–1.75 (m, 3H, menthol ring), 1.99 (s, 3H, Ac), 2.01 (s, 3H, Ac), 2.04 (s, 3H, Ac), 3.30 (dt, 1H, J = 10.6, 4.2 Hz, H-1′), 4.02–4.18 (m, 3H, H-5, H-6), 4.44 (d, 1H, J = 4.1 Hz, H-2), 4.59 (dd, 1H, J = 9.1, 4.1 Hz, H-3), 5.18 (br s, 1H, H-1), 5.27 (t, 1H, J = 9.0 Hz, H-4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.33, 20.67, 20.76, 20.92, 20.95, 22.29, 23.33, 25.96, 30.28, 31.60, 34.15, 42.48, 48.26, 62.59, 67.87, 69.12, 69.32, 82.77, 103.03, 169.56, 169.91, 170.69. HRMS: $C_{22}H_{35}IO_8$ (M^++Na), Calcd 577.1274, Found. 577.1274.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2010.08.020.

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