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Facile Preparation of Peracetates and Per-3-bromobenzoates of α-Mono- and Disaccharides

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Abstract: A simple and convenient method for the preparation of fully acetylated and (3-bromo)benzoylated α-monosaccharides and disaccharides through vigorous mechanical mixing of solid reactants on a high speed shaker is described. Using this technique a variety of α-acylated sugars are prepared, including penta-*O*-acetyl-α-D-galactopyranose, penta-*O*-acetyl-α-D-glucopyranose, penta-*O*-acetyl-α-D-mannopyranose, octa-*O*-acetyl-α-lactose, penta-*O*-(3-bromo)benzoyl-α-D-galactopyranose, penta-*O*-(3-bromo)benzoyl-α-D-gluco-pyranose, penta-*O*-(3-bromo)benzoyl-α-D-mannopyranose, and octa-*O*-(3-bromo)benzoyl-α-lactose.

Keywords: α-Galactose, α-glucose, α-mannose, lactose, mechanochemical mixing

Introduction

Mechanochemical methods have recently attracted much attention because of their inherent advantages, including less secondary reactions [1], high conversion yield within short reaction time [2], reduced pollution, low costs, and simplicity in processing and handling [3]. So far, mechanochemical methods have been successfully applied to areas such as decomposition of organic polymer wastes [1], degradation of organic compounds [4], single-crystal polymer synthesis [5], reduction of metal oxides in solid state [6], etc. More importantly, mechanochemical treatments have made many classic organic reactions which have traditionally been carried out in liquid phase possible

in the solid state [7]. All these processes or reactions are carried out either by cogrinding [2], high energy impact ball milling [5b], ball milling [5d], mechanical milling [8], or high-speed vibration milling [7d].

On the other hand, per-*O*-acetyl and per-*O*-benzoyl derivatives of sugars are important intermediates in carbohydrate transformation and synthesis [9], as indicated by the following observations: 1) acetylation and benzoylation of carbohydrates will convert unprotected and polar sugars into substances soluble in many organic solvents and the resulting sugar peracetates and perbenzoates have been utilized as glycosyl donors in monosaccharide transformations and oligosaccharide syntheses [10]; 2) sugar peracetates and perbenzoates, especially the latter, often show favorable crystalline properties, thus the purification of products by crystallization is practical and convenient; in addition, the resulting products can also be purified through column chromatography due to the lower polarity of acylated sugars; 3) more importantly, both the acetyl and benzoyl groups are very cheap protecting groups that can be easily removed and the parent alcoholic components can be recovered under basic or acidic conditions [11], e.g., via the application of Zemplen's reagent [12].

In comparison with sugar peracetates, sugar perbenzoates even possess some additional advantages. For example, benzoylated sugar derivatives are significantly less reactive than their acetylated analogues and tend to be more bench-stable [9,13]. Thus, many glycosyl chlorides of sugar benzoates can be easily prepared and extracted by methylene chloride in water, whereas acetylated glycosyl chlorides are rather difficult to prepare in this manner. As a result of all these factors the acetylation and benzoylation of sugars are very common transformations in monosaccharide and carbohydrate syntheses.

During the acetylation of glucose, acetic anhydride is almost always the reagent of choice, and the catalysts most frequently employed are zinc chloride [14] (or other Lewis acids), sodium acetate [15] and pyridine [16]. The acetylation of other sugars can be carried out under similar conditions. In contrast, benzoylation of sugars are commonly carried out in pyridine using benzoyl chlorides. However, in many cases, such normal acetylations and benzoylations of sugars produce mixtures of sugar peracetates and perbenzoates, including the α and β anomeric forms [14]. For example, acetylation of mannose in acetic anhydride with NaOAc at high temperature gives a mixture of four products, i.e., mannofuranose and mannopyranose peracetates in either the α or β forms; similarly, acetylation of mannose in pyridine with acetic anhydride also produces four products and these four sugar products cannot be separated by simple crystallization or column chromatography. The presence of undesired sugar peracetate and perbenzoate derivatives often complicates the subsequent carbohydrate transformations and result in difficulties in product purification. To date some methods have been developed to prepare pure α- or β-glucose peracetate [19] or the four isomers of galactose peracetates [20], while some other methods have been used to produce pure sugar perbenzoates [21], such as the application of high pressure [22].

In this paper, we wish to report a general and convenient method to prepare the fully acylated α-sugars by high-speed vibration of sugars and acylation reagent mixture on a shaker at very low temperature.

Results and Discussion

One of our projects is to prepare carbohydrate-containing polymers, if which the fully acetylated or benzoylated glucose, galactose and mannose are chosen as glycosyl donors to react with polymerizable monomers. We have observed that the peracetates of glucose and galactose in β-form can be conveniently prepared from the corresponding monosaccharide and acetic anhydride at 110°C in the presence of NaOAc, according to the reported method [15a]. This is because that sodium acetate causes a rapid anomerization of the free sugar and the more reactive anomer is then acetylated preferentially [9,15a]. However, when mannose is acetylated under similar condition, a mixture of four products, including α- and β-furanomannose and pyranomannose peracetates are formed, which could not be isolated from either crystallization or column chromatography.

On the other hand, it is known that reactions in pyridine generally give the same anomer of the peracetates as found in the parent free sugars [15a,23], and because of the anomeric effect, the pyranose peracetates or perbenzoates having axial anomeric ester groups are generally formed in the largest proportions. Unfortunately, the acetylation of mannose in pyridine at room temperature also affords a mixture of four products. In addition, it is observed that the benzoylation or acetylation of sugar in pyridine from corresponding acyl chloride at room temperature often results in dark mixtures, although this can be circumvented to a certain extent by lowering the reaction temperature. However, further decreasing the temperature of reaction system, such as using dry ice, results in a solid block of reagents and prevents mixing by magnetic stirring. To solve this problem, we have applied a high speed shaker to vibrate the reactant mixture vigorously in the solid state, to adapt the advantages of solid state reaction as mentioned previously, while keeping the reaction system cooled at -78°C. 3-bromobenzoyl chloride is used in this study instead of benzoyl chloride, as the former has a higher melting point and turns into solid when temperature is close to 0°C. In this case, the solid state reaction is guaranteed. Under these conditions, pyridine was used as catalyst, acid scavenger and reactant dispersant. When acyl chlorides (i.e., acetyl chloride and 3-bromobenzoyl chloride) are applied as acylation reagents, only single products are isolated from flash column chromatography via a 10 cm silica gel column, which are shown to be fully acylated α-sugars; however, the acetylation of sugars from acetic anhydride results in the products containing about 10% of sugar peracetate in β-form. We rationalize these results as follows, at very low temperature (e.g., -78°C), the quick anomerization of sugar is probably impossible, and the mechanical energy is transferred to the reacting system through vigorous shaking and vibration, that produces the highly activated local sites of the reacting species and gives the product in one form, and the α-form is preferred in pyridine, especially at very low temperature. For the case of acetic anhydride, the reaction is much slower than that with acetyl chloride and 3-bromobenzoyl chloride, so that some anomerization might have occurred prior to the actual acylation and produced about 10% of sugar peracetate in β-form as the minor product.

The fully acylated α-sugar derivatives prepared in this study using the mechanochemical force method are shown in Figure 1, and the experimental details from different acylation reagents are summarized in Table 1.

Conclusions

In summary, acetylation and (3-bromo)benzoylation of glucose, mannose, galactose and lactose in cold pyridine with acyl chlorides provides a means of obtaining good yields of esters of the α-pyranoid

sugars. This transformation is driven by mechanochemical force through vigorous shaking of solid mixtures at low temperature.

Figure 1. The structure of fully acetylated and 3-bromobenzoylated sugars.

1 R = Ac	
2 R = 3-bromobenzoyl	
3 R = Ac	
4 R = 3-bromobenzoyl	
5 R = Ac	
6 R = 3-bromobenzoyl	
7 R = Ac	
8 R = 3-bromobenzoyl	
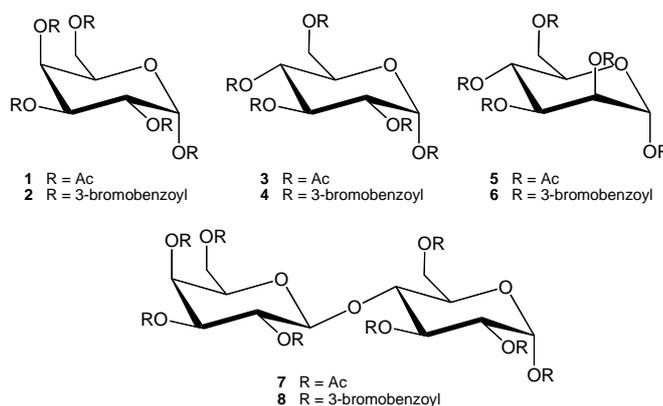
Table 1. The experimental details of the acetylation and (3-bromo)benzoylation of sugars

Entry	Sugar	Amount (g)	Acylation Reagent	Amount (mL)	Product [a]	R_f	Yield(%)[b]
1	Galactose	0.313 (1.74 mmol)	AcCl	0.68 (5.5 eq)	0.468	0.64 [c]	69.0
2	Glucose	0.237 (1.32 mmol)	AcCl	0.51 (5.4 eq)	0.391	0.61 [c]	76.3
3	Mannose	0.158 (0.88 mmol)	AcCl	0.34 (5.4 eq)	0.249	0.63 [c]	72.9
4	Lactose	0.257 (0.75 mmol)	AcCl	0.54 (10.1 eq)	0.367	0.43 [c]	71.9
5	Galactose	0.328 (1.82 mmol)	Ac$_2$O	0.94 (5.5 eq)	0.518		72.7
6	Glucose	0.164 (0.91 mmol)	Ac$_2$O	0.47 (5.5 eq)	0.257		72.3
7	Mannose	0.159 (0.88 mmol)	Ac$_2$O	0.46 (5.5 eq)	0.296		85.8
8	Galactose	0.505 (2.81 mmol)	3-bromo-BzCl	2.10 (6.1 eq)	2.463	0.37 [d]	80.2
9	Glucose	0.509 (2.83 mmol)	3-bromo-BzCl	2.10 (6.1 eq)	2.310	0.45 [d]	74.7
10	Mannose	0.504 (2.80 mmol)	3-bromo-BzCl	2.10 (6.1 eq)	2.173	0.26 [d]	70.9
11	Lactose	0.503 (1.47 mmol)	3-bromo-BzCl	1.80 (10.0 eq)	1.815	0.25 [d]	68.4

a. in grams; b. isolated yield after extraction and column chromatography; c. using hexane- EtOAc (1:2) as eluent; d. using hexane-EtOAc (3:1) as eluent.

Experimental

General

The high speed shaker used in this study was a Wrist Action™ Shaker (Model 75) purchased from Burrell Scientific (Pittsburg, PA, USA). High resolution mass spectra (HRMS) were recorded in MALDI mode with a Voyager-DE STR 4160, using α-cyano-4-hydroxycinnamic acid as matrix, at the Department of Chemistry, University of Houston. ^{1}H- and ^{13}C-NMR were recorded in CDCl$_3$ with a Bruker Avance 600 MHz NMR spectrometer (at 600 Mz for ^{1}H and 150 MHz for ^{13}C, respectively, TMS as internal standard) at the Keck/IMD NMR center founded by the W. M. Keck Foundation and the University of Houston. Column chromatography was carried out on silica gel using hexane-EtOAc mixtures as eluents (6:1 for per-(3-bromo)benzoate derivatives and 4:1 to 3:1 for peracetate analogues). Thin-layer chromatography (TLC) was performed on silica gel (precoated silica gel plate F$_{254}$, Merck) and detected both by UV and heating with 1.5% H$_2$SO$_4$ in EtOH.

General Experimental Procedure

A general experimental procedure is represented by the preparation of penta-3-bromobenzoyl-α-D-galactopyranose. To a 25 mL of round-bottomed flask was added galactose (0.505 gram, 2.81 mmol) and pyridine (3 mL), and the flask was sealed by a rubber septum. The flask was connected to a vacuum source (< 5 mmHg) through a needle to remove the air inside the flask for 10 minutes and during that period the flask was shaken by hand. Then the flask was put into a plastic box and covered with dry ice blocks (ca. 25 g) and the mixture turned into solid after five minutes. After 30 minutes, 3-bromobenzoyl chloride (2.10 mL, 17.2 mmol, 6.1 equivalent) was transferred into the cold flask via syringe, and the added 3-bromobenzoyl chloride suddenly solidified. Then the cold flask was mounted onto the high speed shaker along with the plastic box filled with dry ice and vibrated vigorously at full scale. The shaker was stopped during addition of additional dry ice into the plastic box, in order to maintain the cooling for three hours while shaking; then the shaking was continued until all dry ice evaporated and the flask reached the room temperature. At this moment, the reaction mixture was still in solid form, as the formed pyridinium chloride and galactose per(3-bromo)benzoate were all solids at room temperature. The reaction mixture was then transferred to a separatory funnel with EtOAc (50 mL) and washed extensively with 1 N HCl (3 × 25 mL), saturated aqueous NaHCO$_3$ (2 × 25 mL) and brine (25 mL). Rotatory evaporation of the EtOAc gave a light yellow residue that was quickly passed through a 10 cm silica gel column (eluent hexane-EtOAc = 6:1) to afford penta-*O*-(3-bromo)benzoyl α-D-galactopyranose (2.463 g, 2.25 mmol, 80.2% yield). It should be pointed out that such (3-bromo)benzoylation at room temperature resulted in a dark mixture. Likewise, the 3-bromo-benzoylation of the other sugars listed in Table 1 was carried out under similar conditions. The

acetylation of sugars was also performed similarly using acetyl chloride or acetic anhydride as acetylation reagents. Nevertheless, only a single product was found in the reaction of sugars with acetyl chloride and 3-bromobenzoyl chloride; whereas about 10% of the resulting sugar peracetates were identified as β-anomers by NMR from the reaction with acetic anhydride after short column purification (hexane-EtOAc = 4:1 to 3:1), indicating that acetic anhydride was not a good acetylation reagent under this condition.

Spectral Data

The ^{1}H-NMR data for penta-*O*-acetyl-α-D-glucopyranose [24a] and penta-*O*-acetyl-α-D-mannopyranose [24b] reported in the cited literature matches with our values. ^{13}C-NMR data for penta-*O*-acetyl-α-D-glucopyranose, penta-*O*-acetyl-α-D-galactopyranose and penta-*O*-acetyl-α-D-mannopyranose have been previously reported [24c], therefore, the spectral data for these monosaccharide peracetates are omitted here. The HRMS measurements for all the monosaccharide peracetates could not be obtained with the Voyager-DE STR 4160 equipment, due to the instrumental MS measurement limitation of > 500 au.

Octa-O-α-acetyl-lactose: ^{1}H-NMR (600 MHz, CDCl$_3$), δ (ppm): 1.97 (s, 3H, Ac), 2.02 (s, 3H, Ac), 2.06 (s, 3H, Ac), 2.07 (s, 6H, 2Ac), 2.12 (s, 3H, Ac), 2.16 (s, 3H, Ac), 2.18 (s, 3H, Ac), 3.85 (dd, $J_{3,4}$ = 9.73 Hz, $J_{4,5}$ = 9.64 Hz, 1H, H-4, Glc), 3.94 (dd, $J_{5,6}$ = 6.77 Hz, $J_{5,6'}$ = 6.64 Hz, 1H, H-5, Gal), 4.09 – 4.17 (m, 3H, H-6, Glc, H-6, Gal, H-6', Gal), 4.44 (d, J = 11.60 Hz, 1H, H-6', Glc), 4.53 (d, J = 7.89 Hz, 1H, H-1, Gal), 4.98 (dd, $J_{2,3}$ = 10.33 Hz, $J_{3,4}$ = 3.20 Hz, 1H, H-3, Gal), 5.00 (dd, $J_{2,3}$ = 10.22 Hz, $J_{1,2}$ = 3.58 Hz, 1H, H-2, Glc), 5.11 (dd, $J_{2,3}$ = 10.18 Hz, $J_{1,2}$ = 8.08 Hz, 1H, H-2, Gal), 5.36 (d, J = 3.19 Hz, 1H, H-4, Gal), 5.46 (dd, $J_{2,3}$ = 9.77 Hz, $J_{3,4}$ = 9.74 Hz, 1H, H-3, Glc), 6.25 (d, J = 3.55 Hz, 1H, H-1, Glc); ^{13}C-NMR (150 MHz, CDCl$_3$), δ (ppm): 20.17 (2Ac), 20.32 (3Ac), 20.49 (Ac), 20.52 (Ac), 20.60 (Ac), 60.63 (C-6, Gal), 61.27 (C-6, Glc), 66.44 (C-4, Gal), 68.88 (C-2, Gal), 69.14 (C-2, Glc), 69.32 (C-3, Glc), 70.41 (C-5, Gal, C-5, Glc), 70.70 (C-3, Gal), 75.45 (C-4, Glc), 88.64 (C-1, Glc), 100.81 (C-1, Gal), 168.66, 168.87, 169.36, 169.65, 169.75, 169.87, 170.04 (2Ac); HRMS calc. for C$_{28}$H$_{38}$O$_{19}$Na: 701.1906, found: 701.2351.

Penta-O-(3-bromo)benzoyl-α-D-galactopyranose: ^{1}H-NMR δ (ppm): 4.47 (dd, $J_{6,6'}$ = 11.32 Hz, $J_{5,6}$ = 6.53 Hz, 1H, H-6), 4.63 (dd, $J_{6,6'}$ = 11.37 Hz, $J_{5,6'}$ = 6.65 Hz, 1H, H-6'), 4.84 (d, $J_{5,6}$ = 5.77 Hz, 1H, H-5), 5.94 (dd, $J_{2,3}$ = 10.24 Hz, $J_{1,2}$ = 4.31 Hz, 1H, H-2), 6.05 (dd, $J_{2,3}$ = 10.43 Hz, $J_{3,4}$ = 3.22 Hz, 1H, H-3), 6.14 (s, 1H, H-4), 6.94 (d, $J_{1,2}$ = 3.41 Hz, 1H, H-1), 7.17 – 7.22 (m, 2H), 7.28 (td, J = 7.94 Hz, J = 2.58 Hz, 1H), 7.41 (t, J = 7.86 Hz, 2H), 7.60 (d, J = 7.82 Hz, 2H), 7.66 (d, J = 7.72 Hz, 1H), 7.74 (d, J = 7.87 Hz, 1H), 7.78 (t, J = 8.74 Hz, 3H), 7.88 (d, J = 7.76 Hz, 1H), 7.89 (s, 1H), 7.97 (t, J = 1.53 Hz, 1H), 8.04 – 8.07 (m, 3H), 8.20 (dt, J = 9.56 Hz, J = 1.57 Hz, 2H); ^{13}C-NMR δ (ppm): 62.06 (C-6), 67.86 (C-2), 68.68 (C-3, C-4), 69.28 (C-5), 90.88 (C-1), 122.50, 122.94, 128.20, 128.33, 128.39, 129.98, 130.37, 130.47, 130.64, 130.98, 132.68, 132.82, 136.29, 136.52, 136.58, 136.92, 136.99, 163.28, 164.11, 164.20, 164.32, 164.52; HRMS calc. for C$_{41}$H$_{27}$Br$_5$O$_{11}$Na: 1116.7328, found: 1116.7801.

Penta-O-(3-bromo)benzoyl-α-D-glucopyranose: ^{1}H-NMR δ (ppm): 4.53 (dd, $J_{6,6'}$ = 12.48 Hz, $J_{5,6}$ = 4.73 Hz, 1H, H-6), 4.59 – 4.63 (m, 2H, H-5, H-6'), 5.65 (dd, $J_{2,3}$ = 10.16 Hz, $J_{1,2}$ = 3.92 Hz, 1H, H-2), 5.77 (dd, $J_{3,4}$ = 9.93 Hz, $J_{4,5}$ = 9.92 Hz, 1H, H-4), 6.20 (dd, $J_{3,4}$ = 9.97 Hz, $J_{2,3}$ = 9.91 Hz, 1H, H-3), 6.82 (d, $J_{1,2}$ = 3.74 Hz, 1H, H-1), 7.22 (t, J = 7.90 Hz, 2H), 7.26 (t, J = 6.42 Hz, 2H), 7.32 (t, J = 7.87 Hz, 1H), 7.46 (t, J = 7.90 Hz, 1H), 7.62 (td, J_1 = 8.17 Hz, J_2 = 0.92 Hz, 2H), 7.66 (dt, J_1 = 7.99 Hz, J_2 = 0.94 Hz, 1H), 7.69 (dt, J_1 = 7.91 Hz, J2 = 0.96 Hz, 1H), 7.78 – 7.83 (m, 3H), 7.87 (d, J = 7.81 Hz, 1H), 7.95 (d, J = 7.78 Hz, 1H), 7.98 (t, J = 1.62 Hz, 1H), 8.01 (t, J = 1.57 Hz, 1H), 8.10 (td, J_1 = 7.81 Hz, J_2 = 1.60 Hz, 2H), 8.25 (t, J = 1.60 Hz, 1H); ^{13}C-NMR δ (ppm): 62.88 (C-6), 79.08 (C-4), 70.23 (C-5), 70.55 (C-2), 70.78 (C-3), 90.28 (C-1), 122.63, 122.98, 128.27, 128.44, 130.10, 130.46, 131.22, 132.74, 133.00, 136.28, 136.61, 136.68, 136.74, 137.08, 137.65, 163.24, 163.84, 163.93, 164.53, 164.68; HRMS calc. for $C_{41}H_{27}Br_5O_{11}Na$: 1118.7307, found: 1118.7327.

Penta-O-(3-bromo)benzoyl-α-D-mannopyranose: ^{1}H-NMR δ (ppm): 4.55 – 4.59 (m, 2H, H-5, H-6), 4.66 (dd, $J_{6,6'}$ = 12.07 Hz, $J_{5,6'}$ = 2.72 Hz, 1H, H-6'), 5.89 (dd, $J_{2,3}$ = 3.11 Hz, $J_{1,2}$ = 1.97 Hz, 1H, H-2), 5.97 (dd, $J_{3,4}$ = 10.13 Hz, $J_{2,3}$ = 3.32 Hz, 1H, H-3), 6.07 (dd, $J_{3,4}$ = 10.05 Hz, $J_{4,5}$ = 9.98 Hz, 1H, H-4), 6.59 (d, $J_{1,2}$ = 1.52 Hz, 1H, H-1), 7.20 (t, J = 7.89 Hz, 1H), 7.26 (t, J = 8.15 Hz, 1H), 7.28 (t, J = 7.99 Hz, 2H), 7.33 (t, J = 7.90 Hz, 1H), 7.46 (t, J = 7.87 Hz, 1H), 7.62 (dd, J_1 = 7.95 Hz, J_2 = 0.87 Hz, 1H), 7.65 (dd, J_1 = 7.97 Hz, J_2 = 0.86 Hz, 1H), 7.68 (dd, J_1 = 7.90 Hz, J_2 = 0.86 Hz, 1H); ^{13}C-NMR δ (ppm): 62.86 (C-6), 66.76 (C-4), 69.57 (C-2), 70.13 (C-3), 70.88 (C-5), 91.71 (C-1). 122.58, 122.64, 122.92, 128.14, 128.19, 128.40, 128.62, 130.06, 130.39, 132.71, 133.02, 133.07, 136.19, 136.59, 136.71, 136.89, 137.18, 162.60, 164.00 (2C), 164.21, 164.64; HRMS calc. for $C_{41}H_{27}Br_5O_{11}Na$: 1118.7307, found: 1118.7250.

Octa-O-(3-bromo)benzoyl-α-lactose: ^{1}H-NMR δ (ppm): 3.80 – 3.84 (m, 1H, H-6, Gal), 3.88 (dd, $J_{6,6'}$ = 11.26 Hz, $J_{5,6'}$ = 6.18 Hz, 1H, H-6', Gal), 4.00 (s, br, 1H, H-5, Gal), 4.30 – 4.32 (br, 2H, H-4, Glc, H-5, Glc), 4.56 (br, 2H, H-6, Glc, H-6', Glc), 5.00 (d, $J_{1,2}$ = 5.86 Hz, 1H, H-1, Gal), 5.46 (dd, $J_{2,3}$ = 9.92 Hz, $J_{3,4}$ = 2.71 Hz, 1H, H-3, Gal), 5.60 (dd, $J_{2,3}$ = 10.11 Hz, $J_{1,2}$ = 3.75 Hz, 1H, H-2, Glc), 5.69 (dd, $J_{2,3}$ = 10.12 Hz, $J_{1,2}$ = 7.93 Hz, 1H, H-2, Gal), 5.75 (d, $J_{3,4}$ = 2.42 Hz, 1H, H-4, Gal), 6.13 (dd, $J_{2,3}$ = 9.58 Hz, $J_{3,4}$ = 8.57 Hz, 1H, H-3, Glc), 6.73 (d, $J_{1,2}$ = 3.64 Hz, 1H, H-1, Glu), 7.12 – 7.20 (m, 4H), 7.30 – 7.33 (m, 2H), 7.41 – 7.44 (m, 2H), 7.52 (t, J = 7.83 Hz, 1H), 7.56 (t, J = 7.81 Hz, 2H), 7.60 (d, J = 7.03 Hz, 2H), 7.69 (t, J = 7.91 Hz, 2H), 7.78 (t, J = 7.75 Hz, 3H), 7.81 (s, 1H), 7.86 (t, J = 8.35 Hz, 2H), 7.90 (t, J = 5.20 Hz, 2H), 7.97 (s, 1H), 7.99 (d, J = 7.83 Hz, 1H), 8.04 – 8.09 (m, 5H), 8.18 (d, J = 1.47 Hz, 2H); ^{13}C-NMR δ (ppm): 60.89 (C-6, Gal), 62.05 (C-6, Glc), 67.62 (C-4, Gal), 70.33 (C-2, Gal, C-2, Glc), 70.86 (C-3, Glc), 71.11 (C-5, Glc, C-5, Gal), 71.89 (C-3, Gal), 75.68 (C-4, Glc), 90.07 (C-1, Glc), 101.00 (C-1, Gal), 122.48, 122.56, 122.61, 122.68, 122.87, 128.10, 128.17, 128.33, 128.37, 129.92, 130.08, 130.19, 130.38, 130.50, 130.97, 131.11, 132.44, 132.64, 132.77, 132.92, 136.36, 136.39, 136.46, 136.57, 136.84, 136.97, 163.23, 163.58, 163.97, 164.38; HRMS calc. for $C_{68}H_{46}Br_8O_{19}Na$: 1828.5917, found: 1828.3177.

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