CHAPTER-2

A Highly Efficient TEMPO Mediated Oxidation of Sugar Primary Alcohols into Uronic Acids using 1-chloro-1,2-benziodoxol-3-one at Room Temperature

2.1 Introduction

Uronic acid containing polysaccharides are widespread in nature and involved in many biological processes (Figure 2.1) [1]. For instance, glycosaminoglycans (GAGs) such as heparin sulphate, dermatan sulphate, chondroitin sulphate and hyaluronan are made up of uronic acids (Figure 2.1) [2]. In addition, capsular polysaccharides of various bacteria, marine polysaccharides, homoglycuronans, saponinsas, etc. possess uronic acid units [1a–c, 3]. A typical route for the preparation of uronic acid involves the direct oxidation of primary alcohols in a pyranose sugar [1a, 1b].

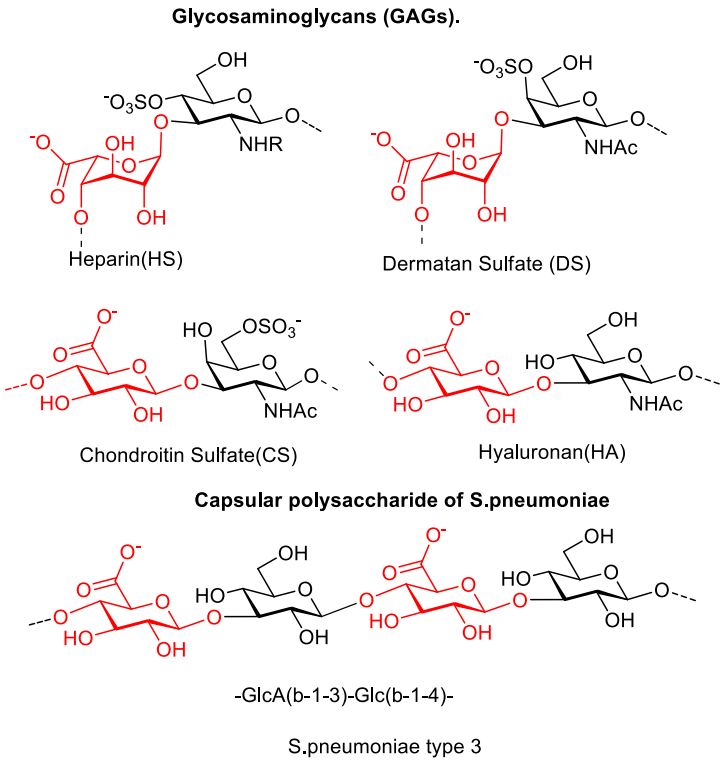


Figure 2.1 Structures of uronic acid containing polysaccharides

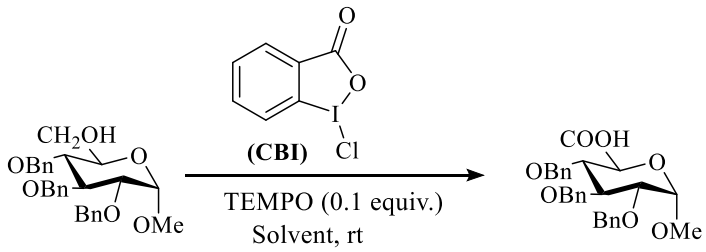
Nevertheless, de novo synthesis was also developed for the preparation of some rare uronic acids (e.g., L-iduronic acid, L-altruronic acid, etc.) [4]. Although numerous oxidants have been developed for the oxidation of simple aryl and aliphatic alcohols, only a few of them have proved to be efficient for the oxidation of sugar primary alcohols into corresponding uronic acids [5]. In general, TEMPO mediated oxidations in the presence of different co-oxidants such as NaOCl, $Ca(OCl)_2$, $PhI(OAc)_2$, *t*-BuOCl, TCC, etc. have shown high efficiency and selectivity for oxidation of sugar primary alcohols[5a, 6]. Nevertheless, each method of alcohol oxidation has its own advantages and limitations. It is also often noticed that direct oxidation of alcohol to carboxylic acid is accompanied by a few other disadvantages like the use of unstable and toxic oxidants, inconvenient reaction conditions, formation of undesired products, low yield, etc. For example, the use of NaOCl as a co-oxidant requires pH maintenance to obtain a good conversion in alcohol oxidation [5a, 6a]. On the other hand, different side reactions have been observed during the oxidation of allyl, thioacetal and methoxybenzyl groups functionalized alcohols [7]. Therefore, the development of a simple and efficient method for the direct oxidation of alcohols to corresponding uronic acids is of great interest. Recently, the hypervalent iodine compound, 1-chloro-1, 2-benziodoxol-3-one (CBI) has proved as an important reagent in organic synthesis [8]. In this context, CBI is also reported for the oxidation of aryl and alkyl alcohols to corresponding aldehydes in the presence of TEMPO [8d]. However, to our surprise, it has not been investigated for the oxidation of primary alcohols to carboxylic acids. This bench stable compound is commercially available and also easy to prepare which can be stored for a long time.

As part of our continuing investigation on carbohydrate synthesis and oxidation reactions, [9] here we report an efficient and practical method for the conversion of sugar primary alcohols into uronic acids using CBI/TEMPO at room temperature.

2.2 Results and Discussion

At the outset, methyl 2, 3, 4-tri-*O*-benzyl-α-D-glucopyranoside (**1a**) was chosen as a model substrate and oxidized using CBI with a catalytic amount of TEMPO (10 mol%) in different solvents at room temperature (Table 2.1). In most of the solvents, including acetonitrile, tetrahydrofuran, diethyl ether and dichloromethane the corresponding uronic acid 2a was obtained only in an insignificant amount (Table 2.1, entries 1–4). In fact, the reagent CBI was found to be insoluble in diethyl ether while sparingly soluble in DCM, THF and acetonitrile. In all these reactions, starting material 1a was recovered in >80% (Table 2.1, entries 1–4). However, in the presence of water, the reaction proceeds better where the uronic acid **2a** was obtained in 13–43% yields (Table 2.1, entries 5–7). Among the different water mixed solvents, DCM-water (2:1 ratio) provides the maximum yield of **2a** (i.e., 43%) after 12 h at room temperature (Table 2.1, entry 7). Further, the oxidation reaction was investigated with an increased amount of CBI in DCM-water (Table 2.1, entries 8–9). To our delight, the desired uronic acid was obtained in 93% yield in the presence of two equiv. of CBI at room temperature within 2.0 h (Table 2.1, entry 9). It is also important to note that in the absence of TEMPO, no reaction takes place (Table 2.1, entry 10). Further, to realize the efficiency of CBI, other halogen mediated oxidants such as molecular iodine (I_2), *t*-butyl hypochlorite (*t*-BuOCl), Dess-Martin periodinane (DMP), cyanuric chloride and $PhI(OAc)_2$ were evaluated for the oxidation under the same condition (Table 2.1, entries 11–15).

Table 2.1 Oxidation of benzyl protected glucopyranoside primary alcohol under various reaction conditions[a]



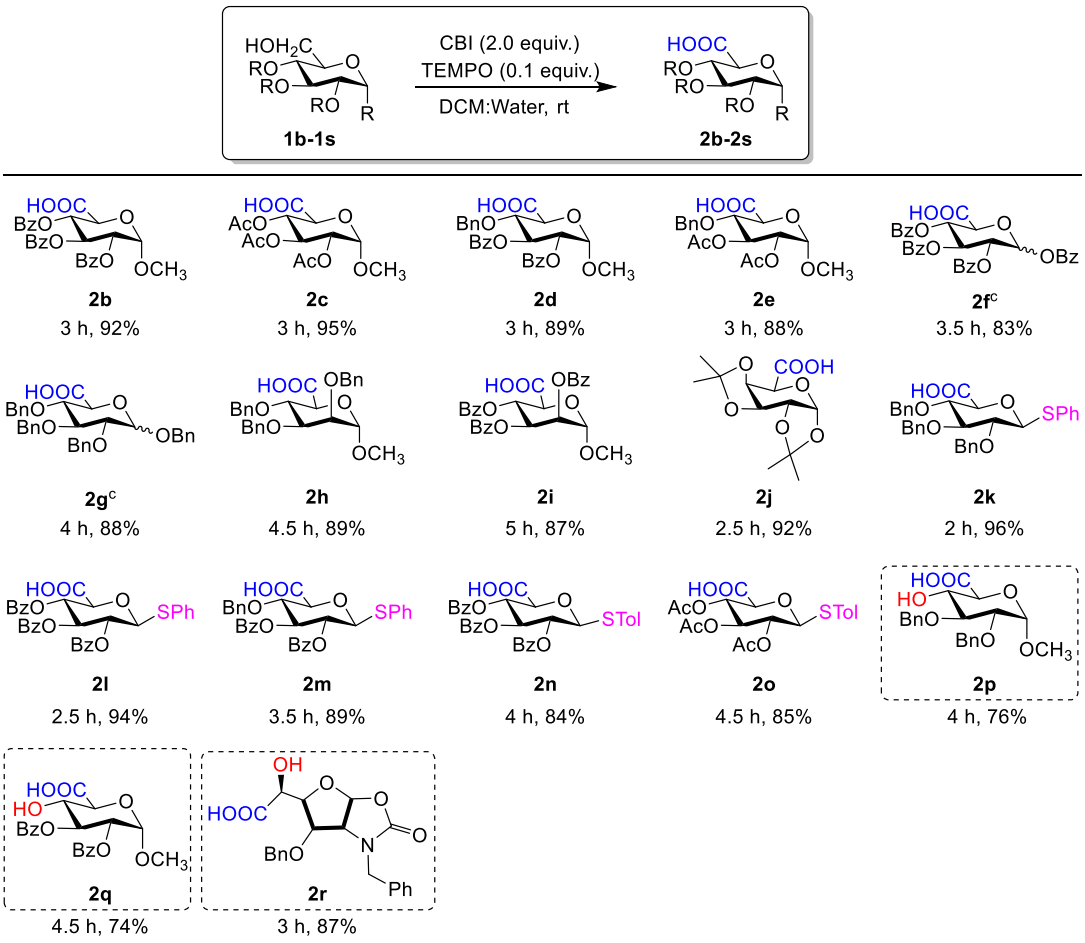
1a **2a**

S.No.	Reagents (equiv.)	Solvents	Time (h)	Yield (%)[b]
1.	CBI (1.0)	CH_3CN	12	<5
2.	CBI (1.0)	THF	12	<5
3.	CBI (1.0)	Diethyl ether	12	NR
4.	CBI (1.0)	DCM	12	<5
5.	CBI (1.0)	CH_3CN:H_2O	12	22
6.	CBI (1.0)	THF:H_2O	12	13
7.	CBI (1.0)	DCM:H_2O	12	43
8.	CBI (1.5)	DCM:H_2O	4.0	71
9.	CBI (2.0)	DCM:H_2O	2.0	93
10	CBI (2.0)	DCM:H_2O	2.0	<5[c]
11	I_2 (2.0)	DCM:H_2O	2.0	20
12	*t*-BuOCl (2.0)	DCM:H_2O	2.0	79
13	Cyanuric Chloride (2.0)	DCM:H_2O	2.0	52
14	DMP (2.0)	DCM:H_2O	2.0	<10
15	$PhI(OAc)_2$ (2.0)	DCM:H_2O	2.5	75

[a]Reaction Conditions: Alcohol (0.3 mmol), oxidant and TEMPO (0.1 equiv.) were stirred together in different solvents (3.0 mL) for appropriate time at room temperature. [b]Isolated yield. [c]Reaction was carried out in the absence of TEMPO.

Among them, *t*-BuOCl and $PhI(OAc)_2$ showed a comparable reactivity to that of CBI and gave 75–79% yield of desired uronic acid (Table 2.1, entries 12 and 15). However, *t*-butyl hypochlorite is very unstable and light-sensitive which requires extra care for the preparation and usage.

Table 2.2 Oxidation of various monosaccharide primary alcohols to corresponding uronic acids under optimized conditions.[a,b]



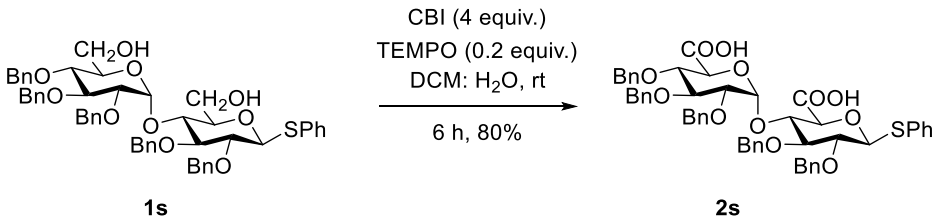
[a]Reaction Conditions: Alcohol (0.3 mmol), oxidant (2.0 equiv.) and TEMPO (0.1 equiv.) were stirred in DCM-water mixture (3.0 mL, 2:1) at room temperature. [b]Isolated yield. [c]Anomeric mixture (**1f**: α:β=2:3 and **1g**: α:β=2:5) was taken as the starting material.

After establishing the optimized condition (Table 2.1, entry 9), the direct oxidation of various sugar primary alcohols was investigated (Table 2.2). For this study, a series of monosaccharides possessing primary alcohols (**1b–1r**) were prepared with structurally diverse moieties in different positions. Acetyl, benzoyl and benzyl protected glucopyranoside primary alcohols were efficiently oxidized to corresponding uronic acids **2b–2g** in excellent yields (i.e., >83%) within 3 h at room temperature. Similar to glucopyranoside, oxidation of primary alcohols in various mannopyranosides was successfully accomplished with good to excellent yields (Table 2.2, **2h**, **i**).

Moreover, this method was also found to be suitable for the oxidation of acid-labile group protected monosaccharide such as 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside. It provides the corresponding uronic acid **2j** in 92% yield under optimized conditions.

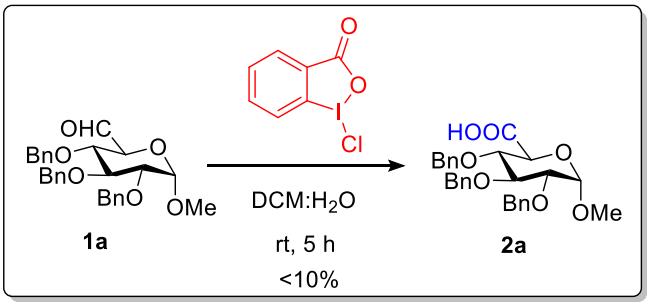
Thioglycopyranoside uronic acids are important building blocks in the synthesis of uronic acid containing oligosaccharides [1a, b]. Therefore, the oxidation of primary alcohols in various thioglycosides was investigated under optimized conditions (Table 2.2). All these substrates produced the corresponding uronic acids in 84-96% yields while the sulfides were found to be intact during the oxidation (Table 2.2, **2k-o**). Selective oxidation of primary alcohol over secondary alcohol plays an important role in organic synthesis. To test this, primary as well as secondary alcohol containing glucopyranoside was prepared and subjected to oxidation under optimized conditions. To our delight, this protocol selectively oxidizes the primary alcohol without affecting the secondary alcohol (Table 2.2, **2p-r**).

The efficiency of the developed method was further investigated for the oxidation of disaccharides having two primary hydroxyl groups. The reaction proceeds with the same efficiency to that of monosaccharides and gave the corresponding uronic acid **2s** in 80% yield (Scheme 2.1).



Scheme 2.1 Oxidation of primary alcohols in a disaccharide

The mechanism of the oxidation of primary alcohol into uronic acid by CBI/TEMPO is not clear to us. In general, TEMPO-mediated alcohol oxidations are known to take place under strongly basic conditions (pH >9) through a formation of *N*-oxoammonium salt [10].

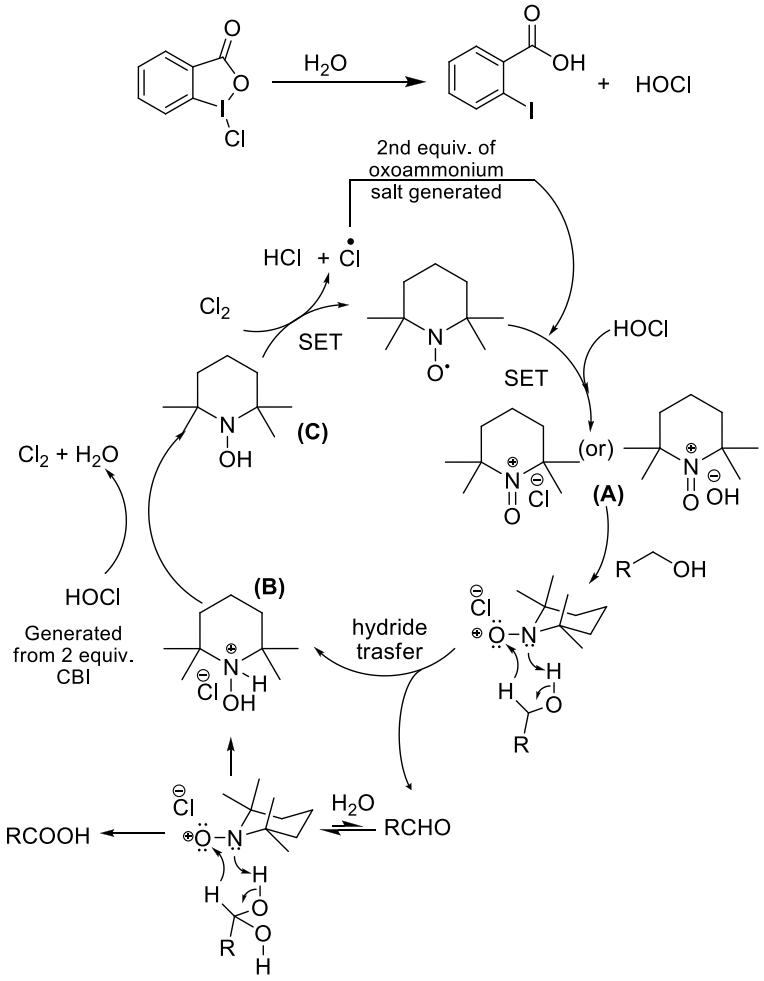


Scheme 2.2 Oxidation of aldehyde using CBI in the absence of TEMPO

Nevertheless, it has been recently reported that TEMPO catalyzed oxidation can take place under mild basic (or) neutral (or) acidic conditions *via* hydride transfer to the *N*-oxoammonium salt [11]. The following observations were made during our experiments: i) in the absence of TEMPO (or) water, alcohol oxidation did not take place (Table 2.1,

entries 4 and 10), ii) aldehyde intermediate was not observed under non-aqueous reaction conditions and iii) CBI alone is not capable of oxidizing the aldehyde into acid in the absence of TEMPO (Scheme 2.2). Based on these observations, a plausible mechanism for alcohol oxidation is illustrated in Scheme 2.3.

2.3 Plausible reaction mechanism



Scheme 2.3 Plausible mechanism for the alcohol oxidation

Initially, the reagent CBI dissociates into hypochlorous acid and 2-iodobenzoic acid in the presence of water. Subsequently, TEMPO is converted to oxoammonium salt by the

hypochlorous acid. This oxoammonium salt oxidizes the alcohol through hydride transfer mechanism to yield the aldehyde and intermediate **B.** The resulted aldehyde undergoes formation of gem-diol in the presence of water and gets oxidized to corresponding carboxylic acid by the oxoammonium salt. The intermediate **B** is converted to hydroxylamine **C** by hypochlorous acid resulting into the formation of chlorine. Finally, the regeneration of TEMPO is achieved from hydroxylamine **C** by the chlorine as shown mechanism (Scheme 2.3). The second equivalent of oxoammonium salt is generated by the reaction of chlorine radical with TEMPO.

2.4 Summary

In summary, a highly efficient TEMPO-catalyzed alcohol oxidation protocol is developed using 1-chloro-1,2-benziodoxol-3(1H)-one as the terminal oxidant. This protocol provides various uronic acids in excellent yields from corresponding alcohols under mild reaction conditions. Moreover, primary alcohols were selectively oxidized over the secondary alcohols making this protocol potentially useful in the complex oligosaccharide synthesis.

2.5 Experimental Section

2.5.1 Preparation of 1-Chloro-1,2-benziodoxol-3-(1H)-one [12]

A 500 mL three-necked, round-bottom flask equipped with a magnetic stirring bar, condenser, and dropping funnel was charged under argon with solid 2-iodobenzoic acid (20 g, 0.0790 mol, 1.0 equiv.), and anhydrous MeCN (150 mL) was added. The resulting stirred mixture was heated to 75 ^{o}C in an oil bath. The dropping funnel was charged with a

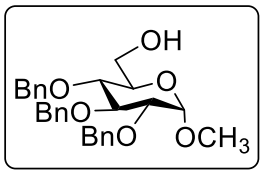
solution of trichloroisocyanuric acid (6.37 g, 0.0266 mol) in 30 mL of anhydrous MeCN. The solution of trichloroisocyanuric acid was dropped into the reaction mixture within 5 min. During the addition of the trichloroisocyanuric acid solution, insoluble isocyanuric acid becomes apparent. The dropping funnel was washed with further anhydrous MeCN (10 mL). After the addition was finished, the reaction mixture was refluxed for another 5 min. The reaction mixture was filtered over a funnel with a pad of Celite, and the filter cake was washed with hot MeCN (20 mL). The combined organic phase was evaporated, and the resulting yellow solid was filtered over a funnel and washed with cold MeCN (10 mL). The mother liquor from filtration was partially concentrated on a rotavapor, and the yellow solid was filtered and washed with cold MeCN, giving the yellow crystals. The combined two crystals were dried 2 h under a high vacuum to give the light-yellow crystals 21 g. Yield: 95 %.

2.5.2 General Procedure for the TEMPO/CBI Mediated Oxidation:

To a vigorously stirred solution of 0.3 mmol monosaccharide alcohol in DCM-water (3 mL, 2:1) was added TEMPO (0.03 mmol, 0.1 equiv.) and 0.6 mmol CBI (2.0 equiv.). Stirring was allowed until TLC indicated complete conversion of the starting material. The reaction mixture was quenched by the addition of 10 ml $Na_2S_2O_3$ solution (10% in H2O). The mixture was then extracted twice with EtOAc (10 ml) and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. Flash column chromatography using EtOAc/petroleum ether afforded the pure uronic acids. The same procedure was followed for the oxidation of disaccharide (0.1 mmol) using TEMPO (0.2 equiv.) and CBI (4.0 equiv.).

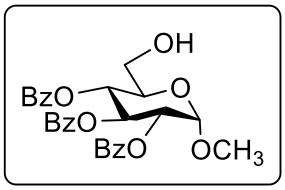
2.6 Analytical data of monosaccharide primary alcohols

2.6.1 Methyl 2,3,4-tri-*O*-benzyl-α-*D*-glucopyranoside (1a) [13]



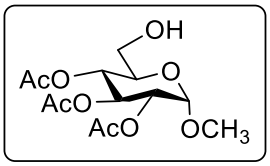
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.27 (m, 15H), 4.97 (d, J = 10.9 Hz, 1H), 4.88-4.77 (m, 3H), 4.64 (t, J = 11.1 Hz, 2H), 4.56 (d, J =3.5 Hz, 1H), 3.99 (t, J = 9.3 Hz, 1H)), 3.78-3.74 (m, 1H), 3.69-3.62 (m, 2H), 3.53-3.47 (m, 2H), 3.35 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 138.1, 138.1, 128.4, 128.3, 128.0, 128.0, 127.9, 127.9, 127.8, 127.5, 98.1, 81.9, 79.9, 77.4, 75.7, 75.0, 73.4, 70.6, 61.8, 55.1.

2.6.2 Methyl 2, 3, 4-tri-*O*-benzoyl-α-*D*-glucopyranoside (1b) [13]



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04-7.80 (m , 6H), 7.47-7.19 (m, 9H), 6.16 (t, J = 9.8 Hz, 1H), 5.44 (t, J = 9.9 Hz, 1H), 5.24-5.19 (m, 2H), 3.99-3.96 (m, 1H), 3.78- 3.75 (m, 1H), 3.69-3.66 (m, 1H), 3.41 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 165.8 (2C), 133.6, 133.3, 133.1, 130.1, 129.9, 129.8, 129.6, 129.1, 129.0, 128.5, 128.4, 128.4, 128.4, 128.2, 97.1, 72.0, 70.1, 69.7, 69.5, 61.0, 55.6.

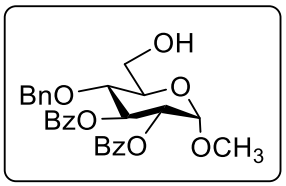
2.6.3 Methyl 2, 3, 4-tri-*O*-acetyl- α-D-glucopyranoside (1c) [14]



^{1}H NMR (500 MHz, $CDCl_3$) δ 5.49-5.22 (m, 1H), 4.98-4.78 (m, 3H), 4.42-4.23 (m, 2H), 3.78-3.71 (m, 1H), 3.67-

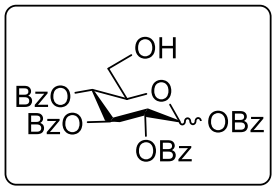
3.64 (m, 1H), 3.55-3.48 (m, 1H), 3.34 (s, 3H), 2.06-1.96 (m, 9H).^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 170.2, 170.0, 96.7, 70.9, 69.7, 69.2, 68.8, 60.9, 55.4, 20.8, 20.7, 20.6.

2.6.4 Methyl 2, 3-di-*O*-benzoyl-4-benzyl- α -D-glucopyranoside (1d) [15]



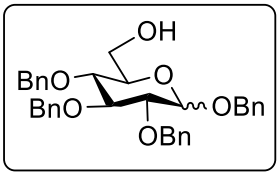
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15-8.02 (m, 4H), 7.56-7.30 (m, 11H), 5.81 (dd, *J* = 10.1, 8.6 Hz, 1H), 5.31 (dd, *J* = 10.2, 3.7 Hz, 1H), 5.18 (d, *J* = 3.7 Hz, 1H), 4.69 (q, *J* = 12.1 Hz, 2H), 4.06-3.99 (m, 2H), 3.92-3.85 (m, 2H), 3.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 165.9, 137.7, 133.2, 133.2, 129.8, 129.8, 129.2, 129.1, 128.4, 128.3, 128.3, 127.7, 127.6, 97.0, 74.0, 73.7, 71.4, 70.5, 70.2, 69.4, 55.3.

2.6.5 1, 2, 3, 4-tetra-*O*-benzoyl-D-glucopyranoside (1f) (α:β =2:3) [16]



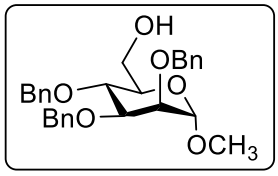
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22-7.92 (m, 8H), 7.54-7.28 (m, 12H), 6.45-6.35 (m, 1H), 6.45-6.16 (m, 1H), 5.94-5.70 (m, 2H), 4.38-3.80 (m, 3H), 3.02. (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 165.7, 165.1, 164.8, 133.8, 133.7, 133.4, 133.3, 130.2, 130.0, 130.0, 129.8, 129.8, 129.7, 129.7, 129.0, 128.8, 128.5, 128.4, 128.4, 92.8, 75.6, 72.8, 70.9, 69.2, 61.0.

2.6.6 1, 2, 3, 4-Tetra-*O*-benzoyl-D-glucopyranoside (1g) (α:β=2:5) [17]



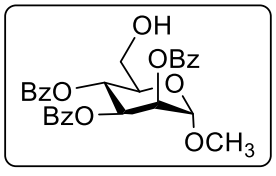
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.20 (m, 20H), 4.94-4.92 (m, 1H), 4.88-4.72 (m, 3H), 4.66-4.55 (m, 3H), 4.50-4.46 (m, 2H), 4.01-3.97 (m, 1H), 3.64-3.41 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 138.1 (2C), 137.0, 128.5, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 95.6, 84.5, 82.3, 81.9, 80.0, 77.4, 75.6, 75.0, 73.0, 70.9, 69.2, 61.7.

2.6.7 Methyl 2, 3, 4-tri-*O*-benzyl-α-D-mannopyranoside (1h) [15]



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.31 (m, 15H), 4.98 (d, J = 10.9 Hz, 1H), 4.82 (d, J = 12.3 Hz, 1H), 4.74-4.67 (m, 5H), 4.00 (t, J = 9.5 Hz, 1H), 3.95-3.92 (m, 1H), 3.89-3.86 (m, 1H), 3.83-3.79 (m, 2H), 3.67-3.64 (m, 1H), 3.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 138.3, 138.2, 128.3, 128.3, 128.3, 127.9, 127.8, 127.6, 127.5, 99.3, 80.1, 75.1, 74.8, 74.6, 72.9, 72.1, 71.9, 62.3, 54.7.

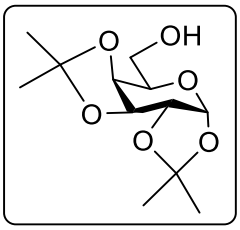
2.6.8 Methyl 2, 3, 4-tri-*O*-benzoyl-*α*-D-mannopyranoside (1i) [18]



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14-8.12 (m, 2H), 8.01-7.99 (m, 2H), 7.86-7.84 (m, 2H), 7.65-7.40 (m, 7H), 7.29-7.26 (m, 2H), 6.00 (dd, J = 10.1, 3.4 Hz, 1H), 5.87 (t, J = 10.1 Hz, 1H), 5.71-5.70 (m, 1H), 5.03 (s, 1H), 4.10-4.07 (m, 1H), 3.89-3.79 (m, 2H), 3.55 (s, 3H). ^{13}C NMR (125

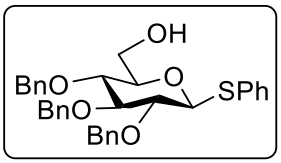
MHz, $CDCl_3$) δ 166.5, 165.5, 165.4, 133.6, 133.5, 133.1, 129.9, 129.9, 129.7, 129.3, 129.1, 128.7, 128.6, 128.5, 128.2, 98.7, 70.8, 70.5, 69.6, 67.3, 61.4, 55.5.

2.6.9 1, 2, 3, 4-Di-*O*-isopropylidene-α-D-galactopyranoside (1j) [14]



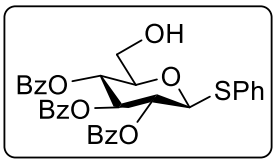
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.57 (d, J = 5.0 Hz, 1H), 4.62 (dd, J = 7.9, 2.4 Hz, 1H), 4.34 (dd, J = 5.0, 2.4 Hz, 1H), 4.28 (dd, J = 7.9, 1.6 Hz, 1H), 3.88-3.83 (m, 2H), 3.75-3.73 (m, 1H), 1.54 (s, 3H), 1.46 (s, 3H), 1.34 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 109.4, 108.6, 96.2, 71.5, 70.7, 70.5, 68.1, 62.2, 26.0, 25.9, 24.9, 24.3.

2.6.10 Phenyl-2, 3, 4-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (1k) [13]



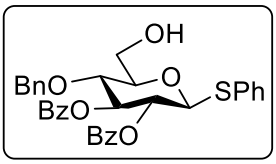
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.43 (m, 2H), 7.32-7.17 (m, 18H), 4.85-4.77 (m, 4H), 4.69 (d, J = 10.2 Hz, 1H, 4.64 (d, J = 9.8 Hz, 1H), 4.58 (d, J = 10.9 Hz, 1H), 3.82-3.78 (m, 1H), 3.67-3.59 (m, 2H), 3.50 (t, J = 9.4 Hz, 1H), 3.41 (t, J = 9.3 Hz, 1H), 3.33-3.30 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 137.8, 137.8, 133.4, 131.8, 129.0, 128.5, 128.4, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 127.6, 87.5, 86.5, 81.0, 79.3, 77.5, 75.8, 75.5, 75.1, 62.1.

2.6.11 Phenyl 2, 3, 4-tri-*O*-benzoyl-1-thio-*β*-D-glucopyranoside (1l) [13]



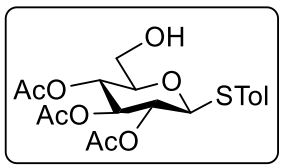
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05-7.72 (m, 6H), 7.45-7.18 (m, 14H), 5.86 (t, J = 9.5 Hz, 1H), 5.43-5.38 (m, 2H), 4.98 (d, J = 10.0 Hz, 1H), 3.81-3.75 (m, 2H), 3.69-3.65 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 165.7, 165.0, 133.6, 133.3, 133.2, 133.1, 131.7, 130.1, 129.9, 129.8, 129.7, 129.1, 129.0, 128.7, 128.5, 128.4, 128.4, 128.3, 128.2, 86.1, 78.8, 74.0, 70.6, 69.2, 61.6.

2.6.12 Phenyl 2,3-di-*O*-benzoyl-4-*O*-benzyl-1-thio-*β*-D-glucopyranoside (1m) [19]



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89-7.82 (m, 4H), 7.44-7.04 (m, 16H), 5.67 (t, J = 9.4 Hz, 1H), 5.28 (t, J = 9.8 Hz, 1H), 4.90 (d, J = 10.0 Hz, 1H), 4.58-4.48 (m, 2H), 3.91-3.65 (m, 3H), 3.57-3.54 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6, 165.2, 137.0, 133.2, 133.1, 132.6, 132.5, 129.9, 129.8, 129.6, 129.0, 128.8, 128.4, 128.3, 128.1, 128.1, 127.9, 127.6, 86.1, 79.5, 76.1, 75.3, 74.8, 70.8, 61.6.

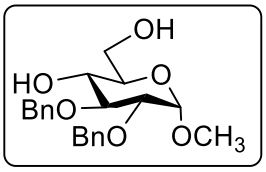
2.6.13 Tolyl 2, 3, 4-tri-*O*-acetyl-1-thio-*β*-D-glucopyranoside (1o) [20]



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 5.22 (t, J = 9.4 Hz, 1H), 5.04 (t, J = 9.8 Hz, 1H), 4.97-4.93 (m, 1H), 4.65 (d, J = 10.1 Hz, 1H), 4.25-4.17 (m, 2H), 3.73-3.70 (m, 1H), 2.37 (s, 3H), 2.11 (s, 3H), 2.10 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H). ^{13}C

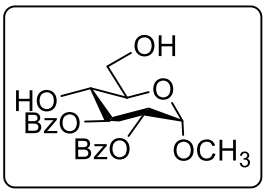
NMR (125 MHz, $CDCl_3$) δ 170.5, 170.2, 169.3, 169.2, 138.8, 133.8, 129.6, 127.5, 85.8, 75.7, 74.0, 69.9, 68.1, 62.1, 21.1, 20.7, 20.7, 20.6, 20.5.

2.6.14 Methyl- 2, 3-di-*O*-benzyl-α-D-glucopyranoside (1p) [13]



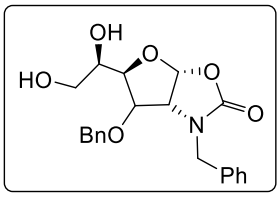
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.33 (m, 10H), 5.05 (d, J = 11.5 Hz, 1H), 4.80-4.67 (m, 3H), 4.62 (d, J = 3.3 Hz, 1H), 3.83-3.75 (m, 3H), 3.65-3.61 (m, 1H), 3.56-3.50 (m, 2H), 3.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 137.9, 128.6, 128.5, 128.1, 128.0, 127.9, 127.9, 98.2, 81.3, 79.8, 75.4, 73.1, 70.7, 70.4, 62.4, 55.2.

2.6.15 Methyl- 2, 3-di-*O*-benzoyl-α-D-glucopyranoside (1q) [21]



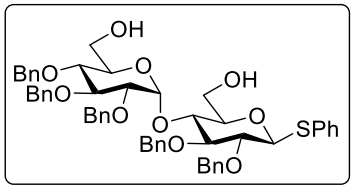
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00-7.96 (m, 4H), 7.51-7.45 (m, 2H), 7.37- 7.32 (m, 4H), 5.82 (t, J = 9.6 Hz, 1H)5.21 (dd, J = 10.1, 3.6 Hz, 1H), 5.15 (d, J = 3.6 Hz, 1H), 4.01 (t, J = 9.5 Hz, 1H), 3.96 (d, J = 3.3 Hz, 2H), 3.89-3.86 (m, 1H), 3.43 (s, 3H), 2.96 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 166.1, 133.3, 133.3, 129.8, 129.8, 129.3, 129.0, 128.4, 128.4, 97.1, 73.8, 71.8, 71.4, 69.4, 61.8, 55.4.

2.6.16 1-benzyl-6-(benzyloxy)-5-((R)-1,2-dihydroxyethyl)tetrahydrofuro[3,2-d]oxazol-2(3aH)-one (1r) [22]



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.21 (m, 10H), 6.02 (s, 1H), 4.78 (d, J = 14.9 Hz, 1H), 4.49-4.43 (m, 2H), 4.07-4.02 (m, 5H), 3.85-3.74 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.9, 137.0, 134.9, 129.1, 128.7, 128.5, 128.3, 128.3, 127.8, 100.9, 80.3, 78.3, 72.4, 68.4, 64.2, 63.8, 47.4.

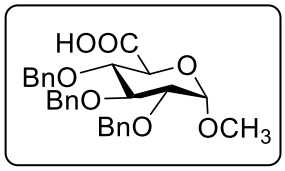
2.6.17 Phenylthio-2,3,4-tri-*O*-benzyl- 6-hydroxy-*α*-*D*-glucopyranosyl-(1→4)-2,3- di-*O*-benzyl-6-hydroxy-*β*-*D*-glucopyranoside (1s) (unknown compound)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J=7.2 Hz, 2H), 7.28–6.98 (m, 28H), 5.61 (d, J =3.8 Hz, 1H), 4.84 (d, J=11.9 Hz, 1H), 4.74 (m, 5H), 4.64 (t, J = 11.2 Hz, 1H), 4.50 (m, 3H), 4.37 (d, J = 11.8 Hz, 1H), 4.02 (t, J = 9.3 Hz, 1H), 3.89 – 3.71 (m, 5H), 3.70 – 3.62 (m, 1H), 3.54 (dd, J = 11.6, 5.8 Hz, 1H), 3.45 – 3.35 (m, 3H), 3.32 (t, J = 9.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 138.5, 137.9, 137.9, 137.7, 134.9, 133.7, 131.8, 129.6, 129.2, 128.6, 128.4, 128.4, 128.4, 128.4, 128.3, 128.2, 128.0, 128.0, 127.8, 127.7, 127.6, 127.6, 127.6, 127.2, 126.2, 97.2, 87.7, 86.7, 81.9, 81.3, 79.3, 78.8, 78.2, 75.6, 75.5, 75.2, 74.2, 73.7, 72.4, 71.7, 62.1, 61.4. HRMS: Calc. for: $C_{53}H_{57}O_{10}S$ $[M+H]^+$: 885.3669, obser.885.3672.

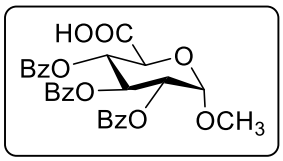
2.7 Analytical data for the uronic acids (2a-2r)

2.7.1 Methyl 2, 3, 4-tri-*O*-benzyl-D-glucopyranosiduronic acid (2a) [23]



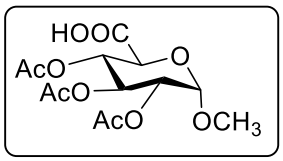
Oily syrup (134 mg, 93%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.61 (s, 1H), 7.43 –7.33 (m, 15H), 5.06 (d, J = 10.8 Hz, 1H), 4.93 –4.88 (m, 3H), 4.73 (d, J = 11.8 Hz, 3H), 4.33 (d, J = 10.0 Hz, 1H), 4.13 (t, J = 9.2 Hz, 1H), 3.82 (t, J = 9.4 Hz, 1H), 3.69 (d, J = 9.3 Hz, 1H), 3.48 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 174.6, 138.4, 137.8, 137.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.8, 98.7, 81.4, 79.2, 79.2, 77.5, 75.2, 73.7, 69.8, 55.8. HRMS: Calc. for $C_{28}H_{30}O_7Na$ $[M+Na]^+$:501.1889, Obser. 501.1900.

2.7.2 Methyl 2, 3, 4-tri-*O*-benzoyl-D-glucopyranosiduronic acid (2b) [24]



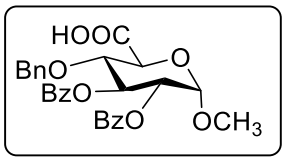
Colourless Oily syrup (143 mg, 92%);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91–7.79 (m, 6H), 7.43–7.18 (m, 9H), 6.10 (t, J = 9.7 Hz, 1H), 5.66 (t, J = 9.8 Hz, 1H), 5.24 (dd, J = 13.8, 3.7 Hz, 2H), 4.55 (d, J = 10.1 Hz, 1H), 3.43 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 165.7, 165.6, 165.3, 133.4, 133.2, 133.1, 129.9, 129.8, 129.6, 129.0, 128.9, 128.8, 128.4, 128.3, 128.2, 97.3, 71.4, 69.8, 69.8, 68.2, 56.2. HRMS: Calc. for $C_{28}H_{25}O_{10}[M+H]^+$: 521.1448, Obser. 521.1474.

2.7.3 Methyl 2, 3, 4-tri-*O*-acetyl-D-glucopyranosiduronic acid (2c) [25]



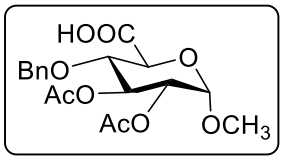
Oily syrup (yield = 95.2 mg, 95%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.47 (t, J = 9.9 Hz, 1H), 5.12 (t, J = 9.9 Hz, 1H), 4.97 (d, J = 3.1 Hz, 1H), 4.85 (dd, J = 10.2, 3.1 Hz, 1H), 4.05 (d, J = 10.2 Hz, 1H), 3.34 (s, 3H), 1.99 (s, 3H), 1.95 (s, 3H), 1.92 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 170.5, 170.3, 169.7, 96.6, 70.8, 70.3, 69.6, 69.2, 55.4, 20.7, 20.6, 20.5. HRMS: Calc. for $C_{13}H_{18}O_{10}Na$ $[M+Na]^+$:357.0798, Obser.357.0812.

2.7.4 Methyl 2, 3-di-*O*-benzoyl-4-benzyl-D-glucopyranosiduronic acid (2d)



Oily syrup (yield = 135 mg, 89 %);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J = 7.3Hz, 4H), 7.53–7.16 (m, 11H), 6.08 (t, J = 9.6 Hz, 1H), 5.26–5.20 (m, 2H), 4.69-4.47 (m, 2H), 4.48 (d, J = 9.9Hz, 1H), 4.15 (t, J = 9.5 Hz, 1H), 3.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 165.9, 165.5, 136.9, 133.3, 133.2, 129.9, 127.9, 97.4, 74.7, 71.8, 71.7, 69.7, 55.9. HRMS: Calc. for $C_{28}H_{27}O_9$ $[M+H]^+$: 507.1655, Obser.507.1622.

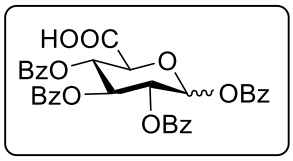
2.7.5 Methyl 2, 3-di-*O*-acetyl-4-benzyl-D-glucopyranosiduronic acid (2e)



Colourless oily syrup (yield = 101 mg, 88 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.26 (m, 5H), 5.65–5.57 (m, 3H), 5.00 (d, J = 3.5 Hz, 1H), 4.90 (dd, J = 10.2, 3.6 Hz,

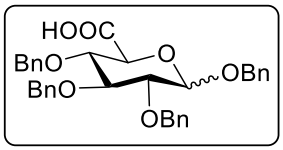
1H), 4.40 (d, *J* = 9.9 Hz, 1H), 3.96 (t, *J* = 9.6 Hz, 1H), 3.48 (s, 3H), 2.10 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ171.7, 170.3, 169.7, 137.2, 128.4, 128.0, 128.0, 127.7, 97.3, 74.7, 71.3, 70.8, 69.3, 55.8, 20.7, 20.7, 14.1. HRMS: Calc. for $C_{18}H_{23}O_9$ $[M+H]^+$: 383.1342, Obser. 383.1340.

2.7.6 1, 2, 3, 4-tetra-*O*-benzoyl-D-glucopyranosiduronic acid (2f) [26] (α:β =2:3)



Colourless oily syrup (yield =152 mg, 83%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18–7.28 (m, 20H), 6.41–6.31 (m, 2H), 6.03–5.81 (m, 2H) 4.77 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 169.9, 165.7, 165.4, 165.3, 165.2, 165.2, 165.0, 164.5, 164.2, 134.0, 133.8, 133.5, 130.2, 130.1, 129.9, 129.9, 129.9, 129.8, 129.7, 128.8, 128.7, 128.6, 128.6, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 91.9, 89.6, 72.8, 70.9, 70.7, 69.7, 69.7, 69.4, 68.8. HRMS: Calc. for $C_{34}H_{26}O_{11}Na$ $[M+Na]^+$:633.1373, Obser.633.1369.

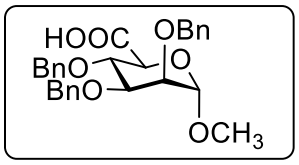
2.7.7 1, 2, 3, 4-Tetra-*O*-benzoyl-D-glucopyranosiduronic acid (2g) [27] (α:β=2:5)



Colourless oily syrup (yield = 146 mg, 88%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (s, 20H), 4.97-4.50 (m, 9H), 3.94–3.57 (m, 3H), 3.08 (dd, *J* = 14.2, 7.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 172.9, 138.7, 138.4, 138.2, 138.1, 138.0, 138.0, 137.2, 136.8, 128.3, 128.2,

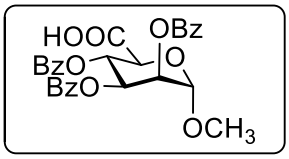
128.2, 127.9, 127.9, 127.8, 127.8, 127.7, 127.5, 102.5, 95.6, 81.8, 81.3, 80.0, 79.7, 79.4, 75.6, 75.4, 74.9, 74.7, 74.6, 72.9, 71.3, 69.0, 45.0. HRMS: Calc. for $C_{34}H_{35}O_7$ $[M+H]^+$: 555.2383, Obser. 555.2387.

2.7.8 Methyl 2, 3, 4-tri-*O*-benzyl-D-mannopyranosiduronic acid (2h) [28]



Colourless oily syrup (yield = 128 mg, 89%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.18 (m, 15H), 4.82 (d, J = 2.7 Hz, 1H), 4.73–4.59 (m, 4H), 4.54–4.48 (m, 2H), 4.17-4.07 (m, 2H), 3.81 (dd, J = 8.1, 3.0 Hz, 1H), 3.68 (t, J = 3.0 Hz, 1H), 3.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 138.0, 138.0, 137.6, 128.3, 128.0, 127.8, 127.8, 127.7, 127.6, 127.6, 99.5, 75.6, 74.6, 74.4, 72.9, 72.3, 71.1, 55.6. HRMS: Calc. for $C_{28}H_{30}O_7Na$ $[M+Na]^+$: 501.1889, Obser. 501.1914.

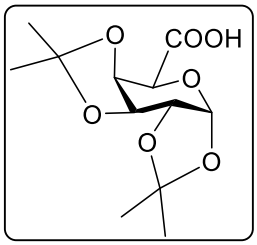
2.7.9 Methyl 2, 3, 4-tri-*O*-benzoyl-D-mannopyranosiduronic acid (2i) [29]



Colourless oily syrup (yield = 135 mg, 87%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.11 (d, J = 7.2 Hz, 2H), 7.98 (d, J = 7.3 Hz, 2H), 7.88 (d, J = 7.3 Hz, 2H), 7.62 (t, J = 6.9 Hz, 1H), 7.53 –7.29 (m, 9H), 6.06 (t, J = 9.1 Hz, 1H), 5.94 (d, J = 9.4 Hz, 1H), 5.71 (s, 1H), 5.16 (s, 1H), 4.71 (d, J = 9.1 Hz, 1H), 3.59 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 172.4, 165.6, 165.5, 165.3, 133.6, 133.4, 133.3, 130.0,

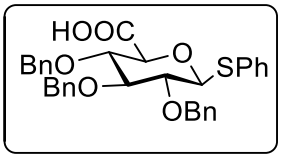
129.8, 129.8, 129.0, 128.9, 128.9, 128.6, 128.4, 128.4, 98.8, 77.3, 77.1, 76.8, 69.8, 69.4, 69.3, 67.4, 56.2. HRMS: Calc. for $C_{28}H_{25}O_{10}$ $[M+H]^+$: 521.1448, Obser. 521.1440.

2.7.10 1, 2, 3, 4-Di-*O*-isopropylidene-α-D-galactopyranosiduronic acid (2j) [30]



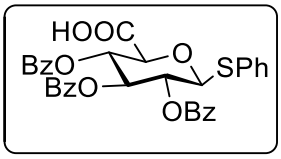
Colourless oily syrup (yield = 76 mg, 92%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.67 (d, J = 4.9 Hz, 1H), 4.71-4.64 (m, 2H), 4.48–4.40 (m, 2H), 1.55 (s, 3H), 1.47 (s, 3H), 1.37 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 110.1, 109.4, 96.3, 71.6, 70.5, 70.4, 68.2, 25.9, 25.8, 24.7, 24.4. HRMS: Calc. for $C_{12}H_{19}O_7$ $[M+H]^+$: 275.1131, Obser. 275.1124.

2.7.11 Phenyl 2, 3, 4-tri-*O*-benzyl-1-thio-β-D-glucopyranosyduronic acid (2k) [31]



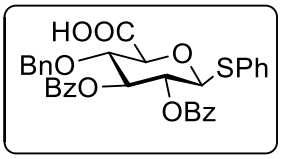
Colourless oily syrup (yield = 160 mg, 96%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49–7.15 (m, 20H), 4.82–4.59 (m, 7H), 3.90 (d, J = 9.2 Hz, 1H), 3.75 (t, J = 9.0 Hz, 1H), 3.65 (t, J = 8.6 Hz, 1H), 3.46 (t, J= 10.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 137.9, 137.7, 137.2, 132.9, 132.3, 129.0, 128.4, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 127.8, 114.0, 88.0, 85.3, 80.2, 78.6, 75.7, 75.3, 75.0. HRMS: Calc. for $C_{33}H_{33}O_6S$ $[M+H]^+$:557.1998,Obser. 557.2028.

2.7.12 Phenyl 2, 3, 4-tri-*O*-benzoyl-1-thio-β-D-glucopyranosyduronic acid (2l) [32]



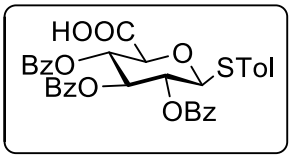
Colourless oily syrup (yield = 168 mg, 94 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90–7.18 (m, 20H), 5.83 (t, J = 9.3 Hz, 1H), 5.61 (t, J = 9.6 Hz, 1H), 5.42 (t, J = 9.6 Hz, 1H), 5.01 (d, J = 9.9 Hz, 1H), 4.32 (d, J = 9.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 165.8, 165.4, 165.1, 133.8, 133.6, 133.5, 131.3, 130.3, 130.0, 130.0, 129.4, 129.3, 129.2, 128.9, 128.9, 128.8, 128.6, 128.6, 128.5, 86.6, 76.1, 73.6, 70.2, 69.9. HRMS: Calc. for $C_{33}H_{27}O_9S$ $[M+H]^+$: 599.1376, Obser. 599.1407.

2.7.13 Phenyl 2,3-di-*O*-benzoyl-4-O-benzyl-1-thio-β-D-glucopyranosyduronic acid (2m) [19]



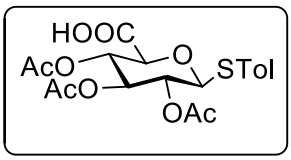
Colourless oily syrup (yield = 155 mg, 89%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99-7.91 (dd, J = 28.9, 7.5 Hz, 4H), 7.56–7.13 (m, 16H), 5.78 (t, J = 8.9 Hz, 1H), 5.45 (t, J = 9.5 Hz, 1H), 5.06 (d, J = 9.9 Hz, 1H), 4.68 (d, J = 10.0 Hz, 1H), 4.57 (d, J=15.0 Hz, 1H), 4.28–4.19 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5, 165.5, 165.2, 136.9, 133.3, 133.2, 132.9, 132.0, 129.9, 129.8, 129.2, 129.1, 129.0, 128.4, 128.2, 128.2, 128.1, 127.9, 127.9, 86.7, 75.3, 74.6, 70.4, 66.4. HRMS: Calc. for $C_{33}H_{29}O_8S$ $[M+H]^+$: 585.1583, Obser. 585.1589.

2.7.14 Tolyl 2,3,4-tri-*O*-benzoyl-1-thio- β -D-glucopyranosyduronic acid (2n) [32]



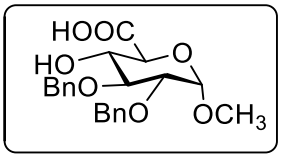
Pale yellow oily syrup (yield = 154 mg, 84%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98–7.08 (m, 19H), 5.91 (t, J = 8.9 Hz, 1H), 5.70 (s, 1H), 5.55 (s, 1H), 5.01 (d, J = 9.3 Hz, 1H), 4.28 (d, J = 6.9 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 165.7, 165.6, 164.8, 138.7, 133.7, 133.2, 133.1, 132.2, 130.0, 129.8, 129.8, 129.6, 129.2, 128.7, 128.6, 128.3, 128.2, 128.1, 123.3, 114.0, 87.0, 73.4, 70.3, 69.4, 21.1. HRMS: Calc. for $C_{34}H_{29}O_9S$ $[M+H]^+$: 613.1532, Obser.613.1539.

2.7.15 Tolyl 2, 3, 4-tri-*O*-acetyl-1-thio- β -D-glucopyranosyduronic acid (2o)



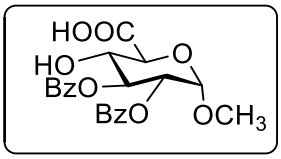
Pale yellow oily syrup (yield =108 mg, 85%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 7.7 Hz, 1H), 7.96 (d, J = 7.0 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 5.58–5.54 (m, 2H), 5.49 (d, J = 3.6 Hz, 1H), 5.30–5.26 (m, 1H), 4.77 (d, J = 8.1 Hz, 1H), 2.13 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 170.8, 170.2, 170.1, 141.6, 133.0, 131.5, 128.0, 90.1, 71.0, 69.9, 68.5, 67.3, 22.7, 20.8, 20.7, 20.7. HRMS: Calc. for $C_{19}H_{23}O_9S$ $[M+H]^+$: 427.1063, Obser. 427.1059.

2.7.16 Methyl- 2, 3-di-*O*-benzyl-α-D-glucopyranosiduronic acid (2p) [33]



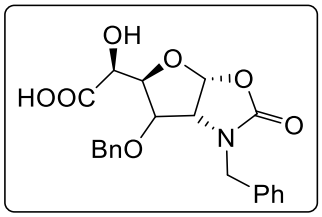
Colourless oil (yield = 88 mg, 76 %); 1H NMR (500MHz, CD_3OD) δ 7.28-7.15 (m, 10H), 4.68 (m, 3H), 4.57 (m, 2H), 3.90 (d, J = 9.7 Hz, 1H), 3.61 (m, 2H), 3.42 (dd, J = 9.3, 3.5 Hz, 1H), 3.30 (s, 3H). ^{13}C NMR (125 MHz, CD_3OD) δ 171.5, 138.3, 137.7, 127.5, 127.3, 127.2, 127.1, 127.0, 126.6, 97.8, 80.5, 78.7, 74.6, 72.3, 71.5, 70.6, 54.0. HRMS: Calc. for $C_{21}H_{24}O_7$ $[M+Na]^+$: 411.1420, Obser. 411.1431.

2.7.17 Methyl- 2, 3-di-*O*-benzoyl-α-D-glucopyranosiduronic acid (2q) [34]



Colourless oil (yield = 92 mg, 74 %); ^1H NMR (500 MHz, CD_3OD) δ 7.99–7.97 (m, 2H), 7.92 (dd, J = 8.1, 0.9 Hz, 2H), 7.56–7.52 (m, 2H), 7.40 (dd, J = 14.6, 7.3 Hz, 4H), 5.82 (t, J = 9.8 Hz, 1H), 5.20 (d, J = 7.0 Hz, 2H), 4.15 (d, J = 10.0 Hz, 1H), 4.01 (t, J = 9.6 Hz, 1H), 3.49 (s, 3H).^{13}C NMR (125 MHz, MeOD) δ 172.5, 166.3, 165.7, 133.2, 132.9, 129.7, 129.3, 129.2, 129.0, 128.1, 128.0, 97.2, 72.8, 71.9, 70.8, 70.5, 54.7. HRMS: Calc. for $C_{21}H_{21}O_9$ $[M+H]^+$: 417.1186, Obser. 416.1190.

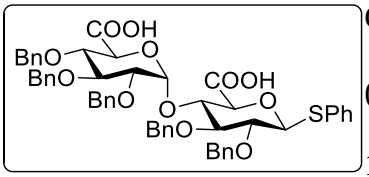
2.7.18 2-(1-benzyl-6-(benzyloxy)-2-oxohexahydrofuro[3,2-d]oxazol-5-yl)-2-hydroxyacetic acid (2r)



Colourless oily syrup (yield = 104 mg, 87%); ^1H NMR (500 MHz, DMSO-d_6) δ 7.39–7.27 (m, 10H), 6.13 (d, J = 5.6 Hz, 1H), 4.56 (d, J = 15.3 Hz, 1H), 4.42 (s, 2H), 4.34 (d, J = 15.3 Hz, 1H), 4.17-4.13 (m, 2H), 4.03–4.01 (m,

2H). ^{13}C NMR (125 MHz, DMSO) δ 173.9, 156.8, 138.0, 136.3, 129.7, 129.3, 129.2, 129.1, 128.7, 128.5, 128.4, 128.2, 128.1, 128.0, 101.1, 81.3, 78.4, 71.9, 67.8, 64.3, 47.0. HRMS: Calc. for $C_{21}H_{22}NO_7$ $[M+H]^+$: 400.1396, Obser. 400.1401.

2.7.19 *α*-D-Glucopyranosiduronic acid, phenyl 2,3-di-*O*-(benzyl)-1-thio-4-*O*-[2, 3,4-tri-*O*-(benzyl)-*β*-D-glucopyranosiduronic acid] (2s)



Colourless oily syrup (yield =73 mg, 80%); ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.44 –7.10 (m, 30H), 6.22 (s, 1H), 5.54 (d, J = 3.3 Hz, 1H), 4.82 –4.66 (m, 4H), 4.66 –4.48 (m, 7H), 4.29 (d, J = 9.9 Hz, 1H), 4.13 (s, 1H), 3.85 –3.78 (m, 2H), 3.66 (m, 2H), 3.59 (dd, J = 9.6, 3.3 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-D_6) δ 170.8, 170.3, 139.0, 138.7, 138.6, 138.2, 137.8, 128.7, 128.6, 128.6, 128.6, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 102.0, 97.7, 80.8, 79.3, 79.2, 75.0, 74.9, 74.6, 72.8, 72.6, 72.3, 71.7, 71.2, 71.2, 70.9. HRMS: Calc. for $C_{53}H_{53}O_{12}S$ $[M+H]^+$: 913.3258, Obser. 913.3250.

2.8 Spectral Data of few products

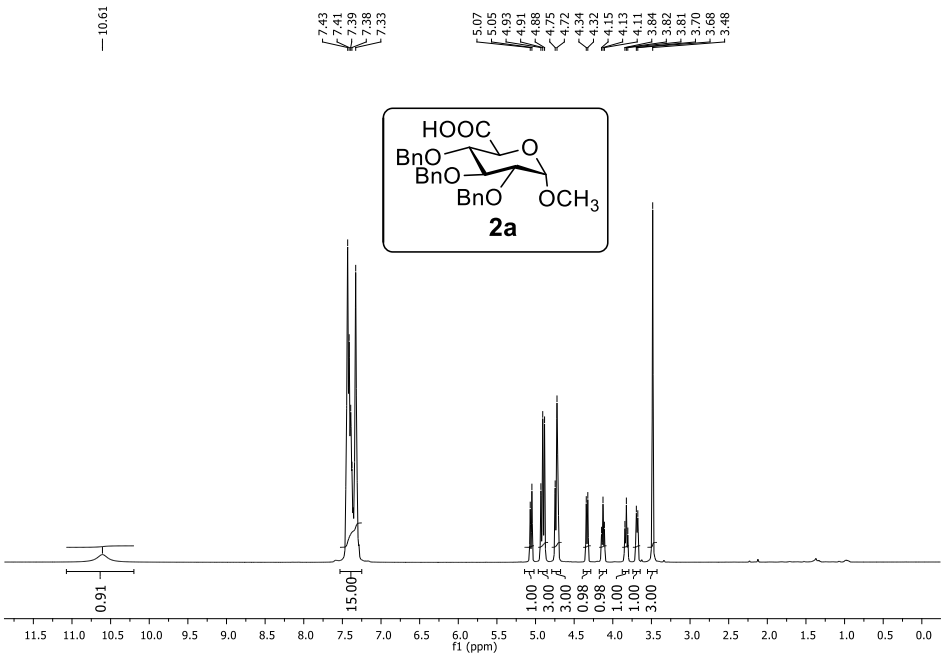


Figure 2.2 ^{1}H-NMR spectrum of compound **2a** in $CDCl_3$

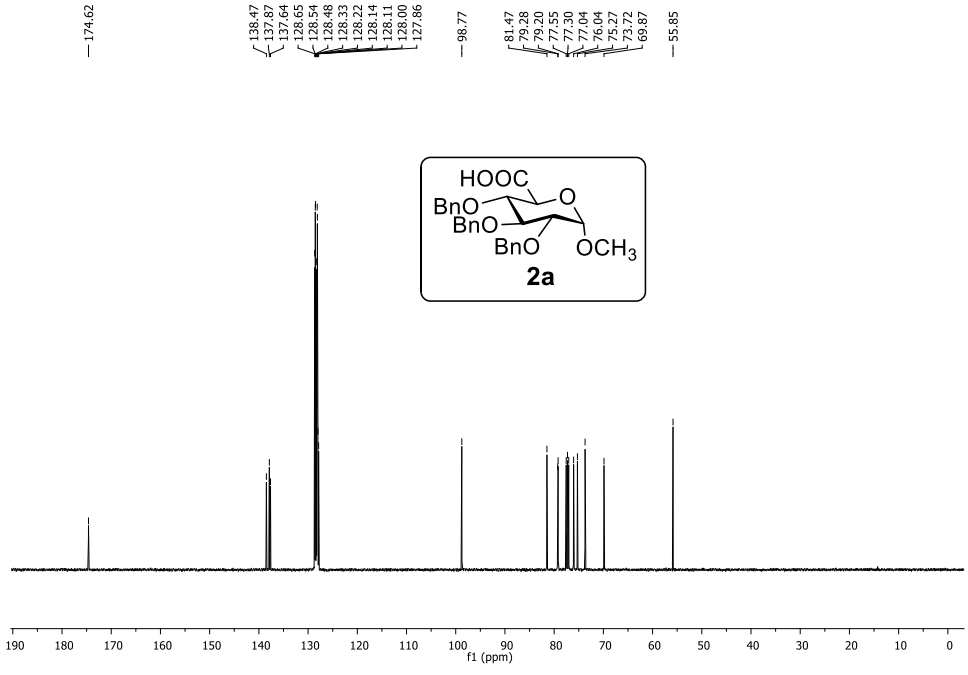


Figure 2.3 ^{13}C-NMR spectrum of compound **2a** in $CDCl_3$

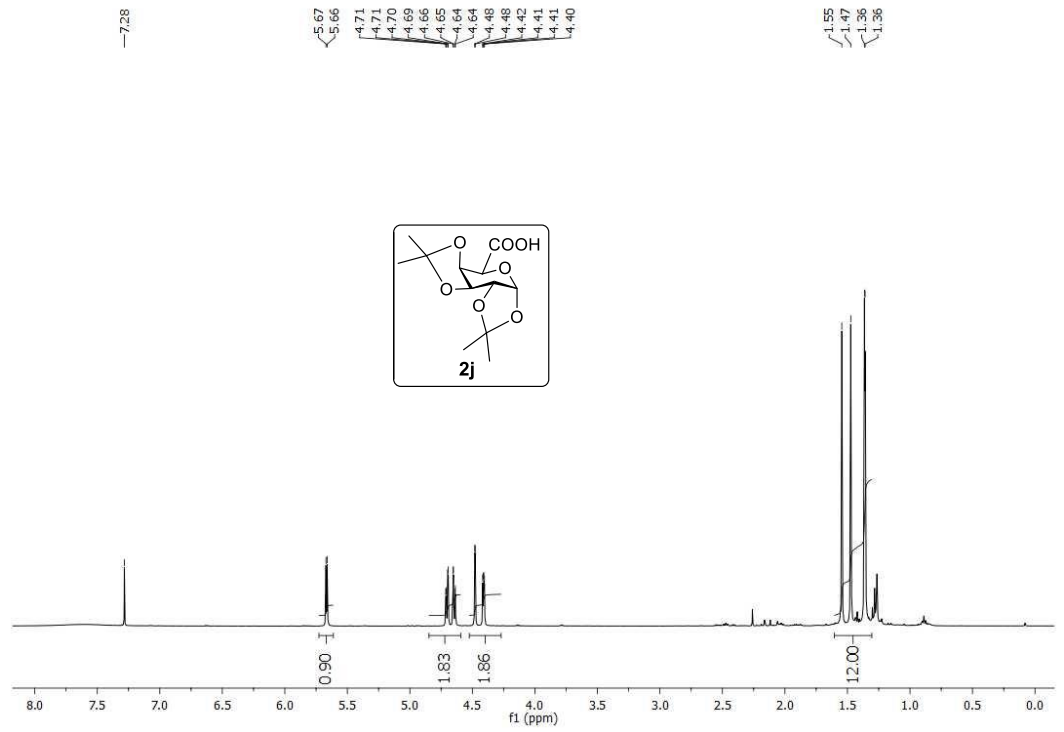


Figure 2.4 ^{1}H-NMR spectrum of compound **2j** in $CDCl_3$

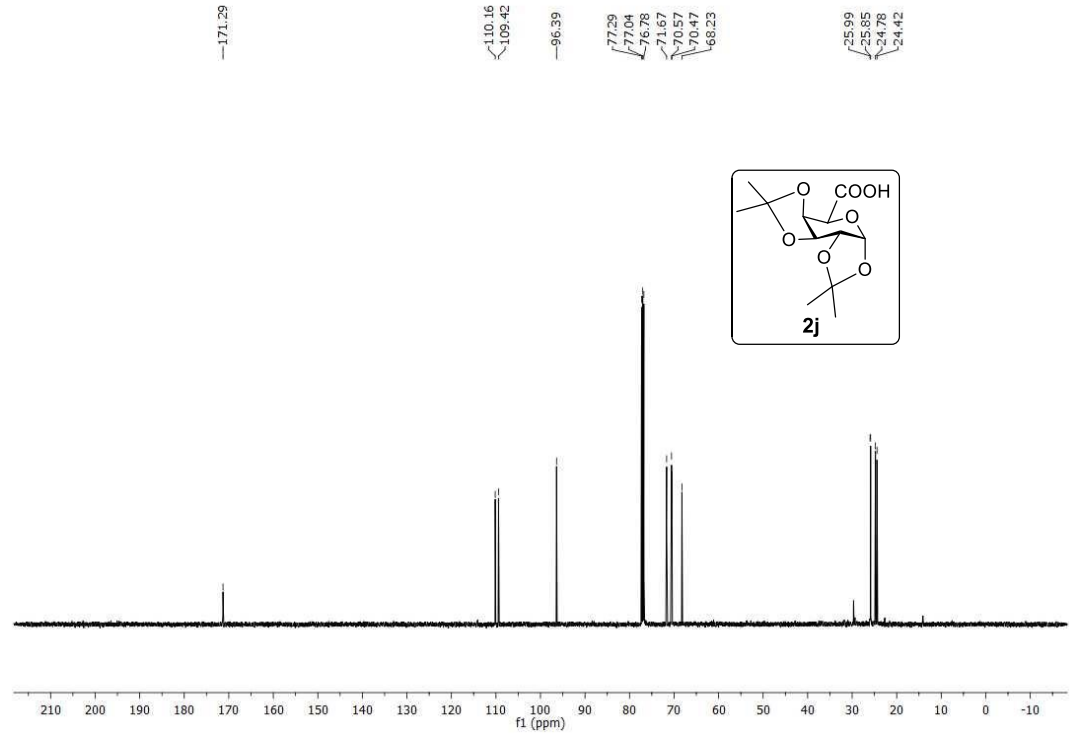


Figure 2.5 ^{13}C-NMR spectrum of compound **2j** in $CDCl_3$

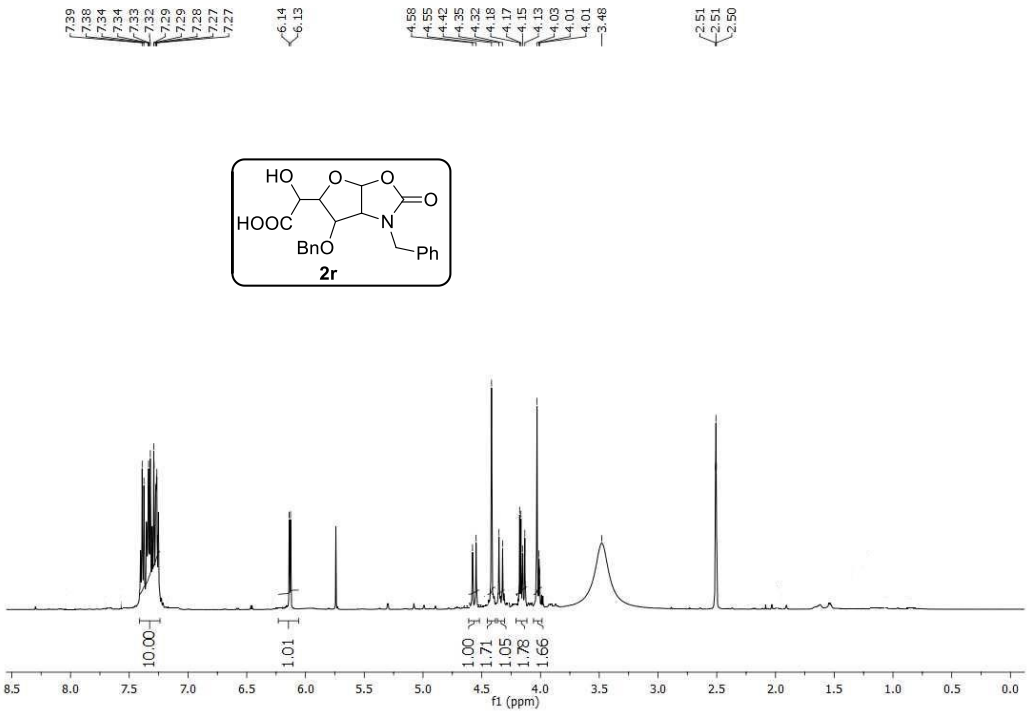


Figure 2.6 ^{1}H-NMR spectrum of compound **2r** in $CDCl_3$

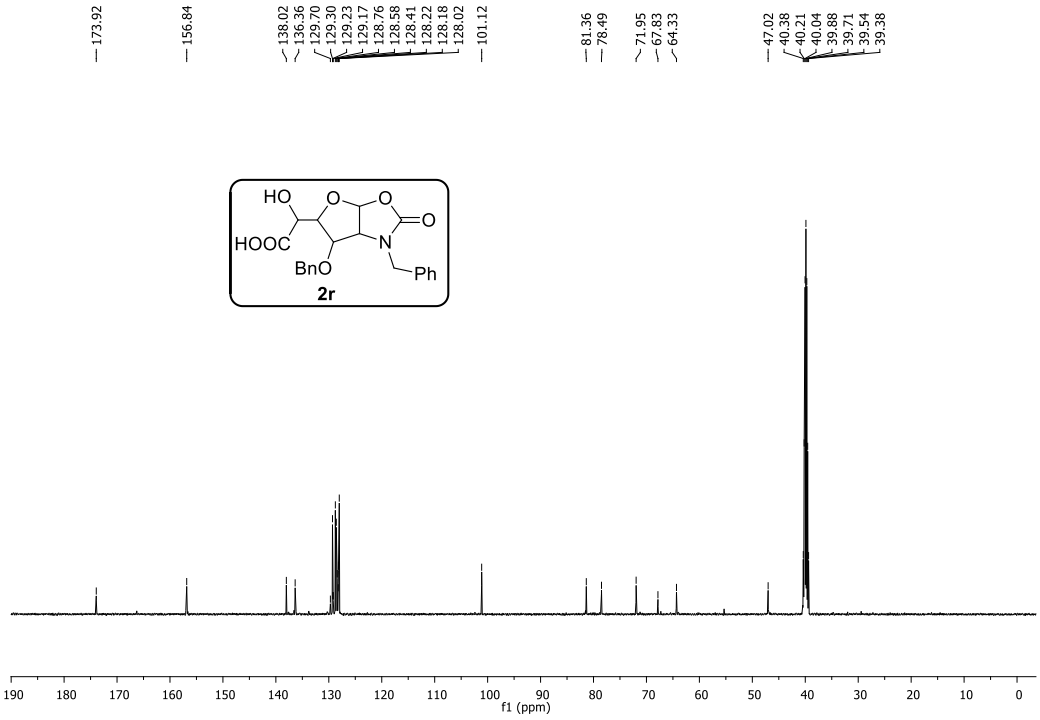


Figure 2.7 ^{13}C-NMR spectrum of compound **2r** in $CDCl_3$

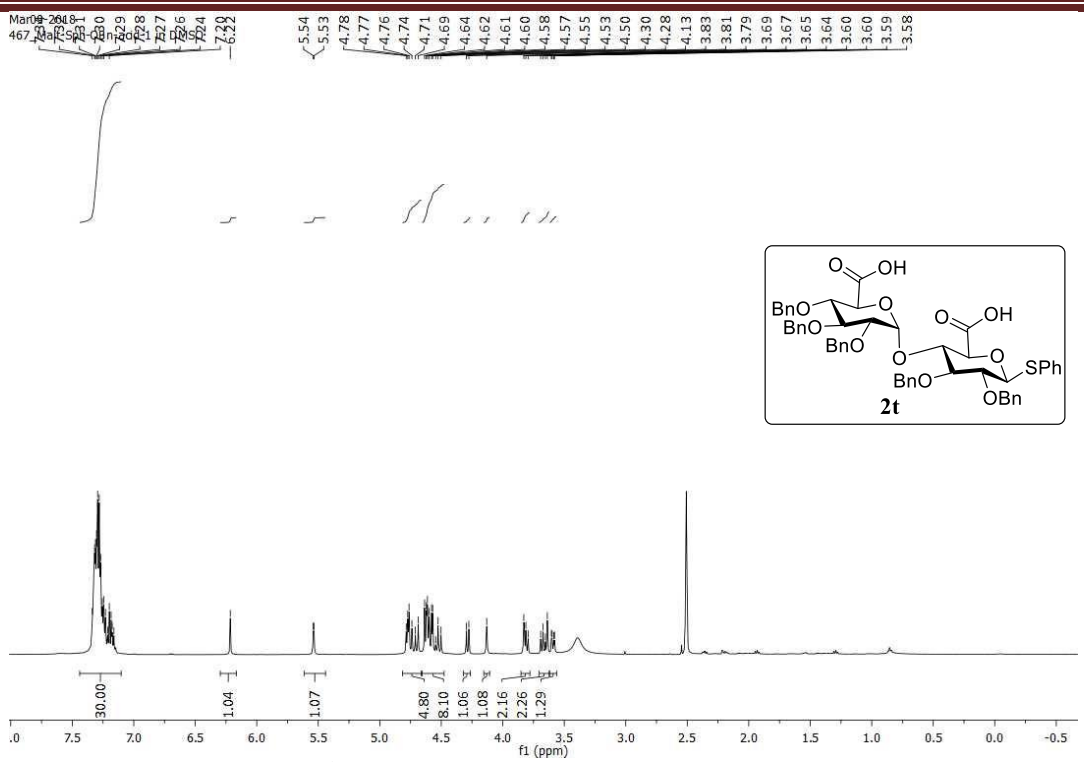


Figure 2.8 ^{1}H-NMR spectrum of compound **2t** in $CDCl_3$

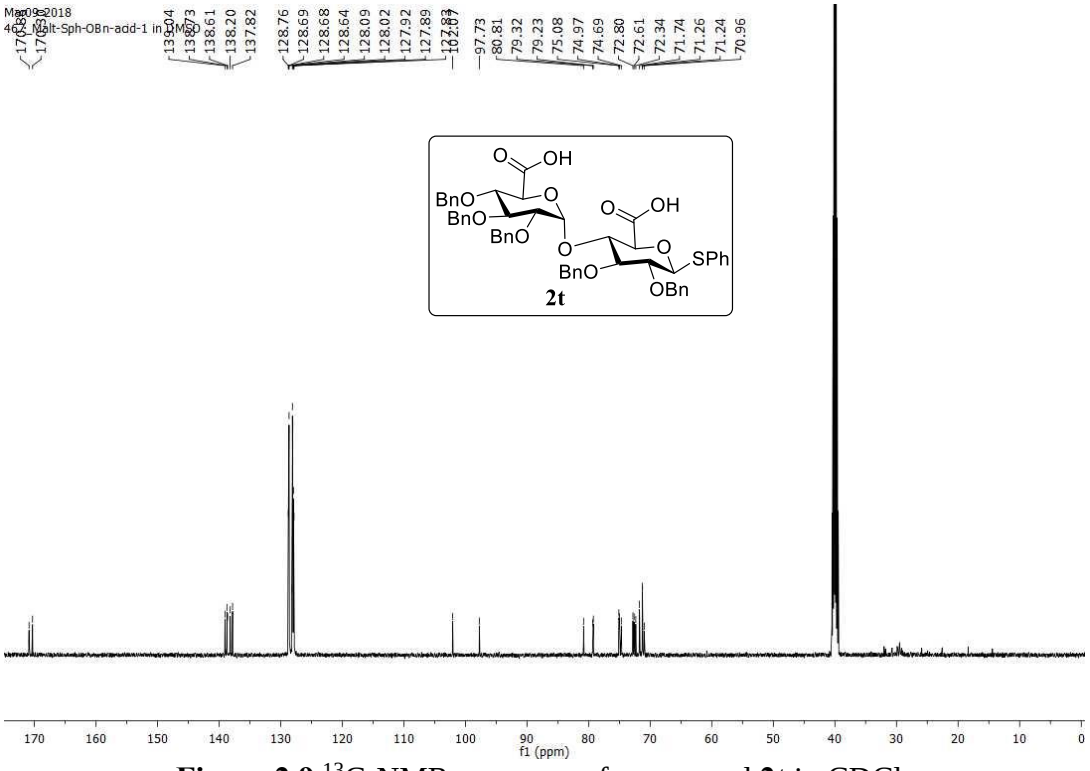


Figure 2.9 ^{13}C-NMR spectrum of compound **2t** in $CDCl_3$

2.9 References

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