Synthesis and Decomposition of Novel Diazosugars

by

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Thesis Abstract

This thesis deals with the synthesis and decomposition of diazodeoxy furanose sugar derivatives. The decomposition of these diazodeoxy sugars not only led to the desired insertion products, but also novel ketone derivatives and dimeric ethers. Furthermore, a new synthetic pathway was discovered for the synthesis of azidodeoxy compounds through an interesting side-reaction *en route* to one of these diazodeoxy sugars.

Acknowledgements

First off, I would like to thank Dr. Peter Norris, for advising me these past few years. I also want to thank Dr. Matthias Zeller for the X-ray crystal data, Ray Hoff for helping me with all of the instrumentation, and Dr. Roland Riesen for teaching me how to use the mass spectrometer.

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Introduction

Carbohydrates

Carbohydrates are the most abundant organic molecules on earth;[1-4] they are used to store energy and transport energy. Carbohydrates perform other essential biological functions such as cell-cell recognition and cell-external agent interactions.[4] They are also used to carry biological information, for example the body uses carbohydrates to differentiate between the different blood groups A, B, and H (Figure 1). Simple carbohydrates have the empirical formula $C_n(H_2O)_n$, where an oxygen atom is attached to each carbon. Derivatives containing nitrogen and sulfur can be synthesized, altering this empirical formula. Carbohydrates can be broken down into three main groups: monosaccharides, oligosaccharides, and polysaccharides.

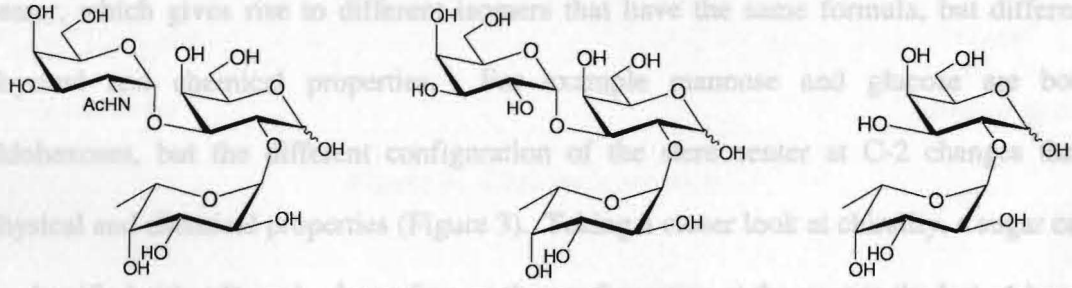


Figure 1: Differentiation of blood groups by oligosaccharide structure.

A monosaccharide is a single carbohydrate unit.[1,2] These sugars can be classified as either aldoses or ketoses (Figure 2). An aldose sugar contains an aldehyde functional group at C-1 while all other carbons have one hydroxyl group attached. A ketose sugar has a ketone functional group within the chain and primary alcohols on either end of the

chain. Monosaccharides can also be classified by the number of carbons in the chain, for example a three carbon chain would be a triose, four carbon chain a tetrose, five carbon chain a pentose and so on. These two classifications can be combined to give a carbohydrate a generic name; for example, glucose is an aldohexose.

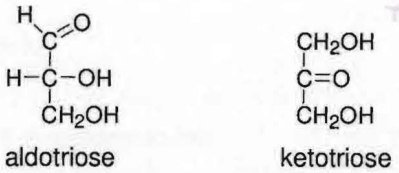


Figure 2: Fischer projections of glyceraldehyde and dihydroxyacetone.

Monosaccharides can be drawn in the Fischer projection,[2] the Haworth projection, and the chair form. A closer look at these depictions reveals that each carbon has a chiral center, which gives rise to different isomers that have the same formula, but different physical and chemical properties. For example mannose and glucose are both aldohexoses, but the different configuration of the stereocenter at C-2 changes their physical and chemical properties (Figure 3). Taking a closer look at chirality, a sugar can be classified either D- or L- depending on the configuration at the next to the last carbon.

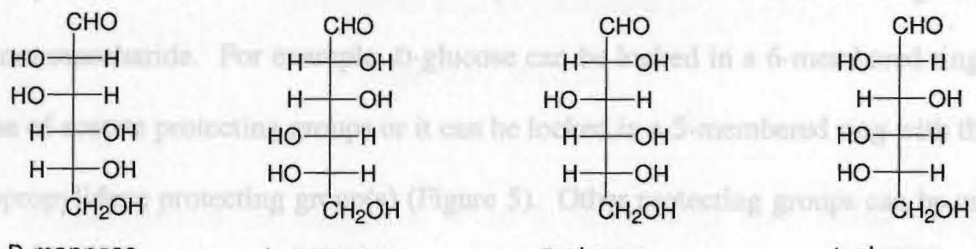


Figure 3: Fischer projections of mannose and glucose.

In solution monosacchrides can adopt different forms and conformations;[2] glucose is depicted below in Figure 4. The acyclic form can cyclize forming a lactol or cyclic hemiacetal. A 5-membered ring is called *furanose*, the 6-membered ring *pyranose*. Glucose can be classified as either the α or β anomer depending on the orientation of the hydroxyl group at the acetal/hemiacetal carbon or the *anomeric* carbon on the ring.

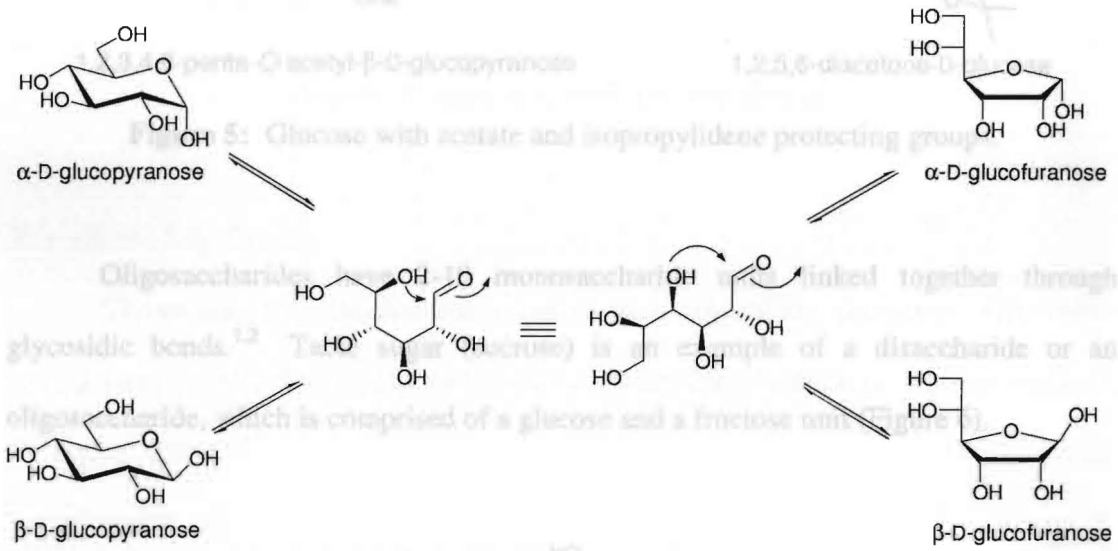


Figure 4: Glucose in solution.

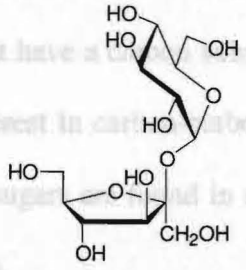
Protecting groups are used to mask part of the carbohydrate,[2,4] allowing access to only a specific area of the molecule, and they can also be used to lock the ring structure of a monosaccharide. For example, D-glucose can be locked in a 6-membered ring with the use of acetate protecting groups or it can be locked in a 5-membered ring with the use of isopropylidene protecting group(s) (Figure 5). Other protecting groups can be used to give similar results. Acetate protecting groups have been known to migrate and their selectivity is unreliable and reagent-specific. Isopropylidene protecting groups are acid-

stable and are used to block pairs of hydroxyls. When choosing protecting groups, one must find a group that is stable to subsequent reaction conditions and that can easily be put onto the molecule or removed.

1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose 1,2;5,6-diacetone-D-glucose

Figure 5: Glucose with acetate and isopropylidene protecting groups.

Oligosaccharides have 2-10 monosaccharide units linked together through glycosidic bonds.[1,2] Table sugar (sucrose) is an example of a disaccharide or an oligosaccharide, which is comprised of a glucose and a fructose unit (Figure 6).

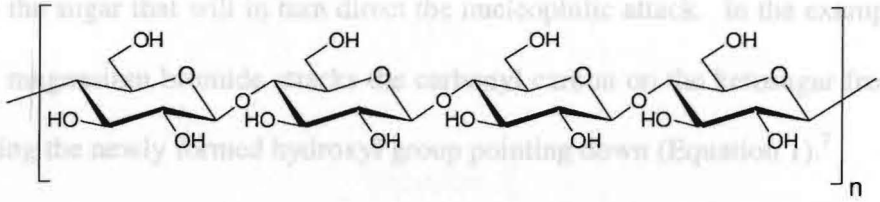


β-D-fructofuranosyl–α-D-glucopyranoside

Figure 6: Sucrose.

Polysaccharides are comprised of 10 or more sugar units linked together.[1,2] Cellulose, found in plants, is an example of a glucopyranose-based polysaccharide

(Figure 7). The units are linked together at C-1 and C-4 through a β-1,4-linkage, hence the name poly [β(1-4)-glucopyranose].



poly [β(1-4)-glucopyranose]

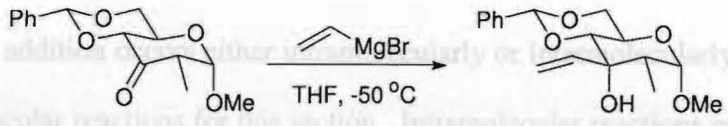
Figure 7: Repeating structure of cellulose.

Branched-chain sugars

Glycosides and branched-chain sugars are carbohydrate derivates.[5] Glycosides have a (non-carbohydrate) group attached to the anomeric carbon of a sugar molecule through a glycosidic bond. This group can be either an -OR, -SR, -NR, or -CR group, thus denoting the compound as an *O*-, *S*-, *N*-, or *C*-glycoside, respectively. Branched-chain sugars are carbohydrates that have a carbon substituent directly attached to a non-terminal carbon. A long-held interest in carbon-carbon bond forming reactions, paired with the fact that branched-chain sugars are found in nature, has sparked our interest in synthesizing branched-chain sugars.

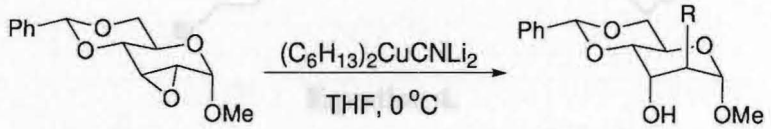
Previously branched-chain sugars have been synthesized using, but not limited to, Grignard reagents, epoxides, 1,4-conjugate addition, radical chemistry, and Wittig reagents, all of which will be discussed here.[6] The main issue in all of these reactions is stereochemical and regiochemical control of the newly formed carbon-carbon bond. This is often solved with the use of appropriate protecting groups.

Organometalics, such as Grignard reagents, are useful in forming carbon-carbon bonds when ketosugars and epoxides are involved. Reactions with Grignard reagents are often stereoselective due to the coordination of the magnesium with another oxygenated group on the sugar that will in turn direct the nucleophilic attack. In the example below, the vinyl magnesium bromide attacks the carbonyl carbon on the ketosugar from the top face leaving the newly formed hydroxyl group pointing down (Equation 1).[7]



Equation 1.

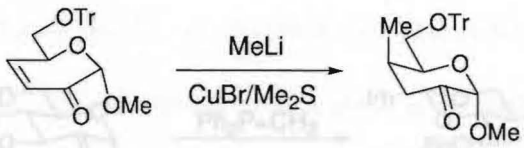
Organocopper reagents are useful for introducing carbon-carbon bonds by opening epoxides. As an example, a combination of Grignard reagents with copper salts and Gilman reagents was used to form the organocopper reagent *in situ*. In the equation below, the nucleophile was introduced at C-2, in the axial position, opening the epoxide giving a "*trans*-diaxial" arrangement (Equation 2).[8]



Equation 2.

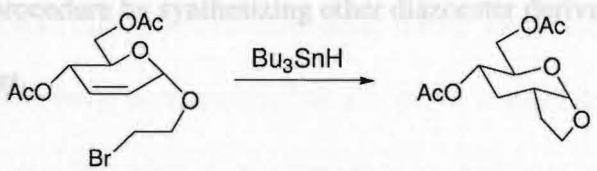
Unsaturated carbohydrates can undergo 1,4-conjugate addition when reacted with organocopper derivatives. The example below is again a pyranosidic ring in which the

addition of the nucleophilic methyl cuprate onto the unsaturated carbohydrate is seen to give the axial product (Equation 3).[9]

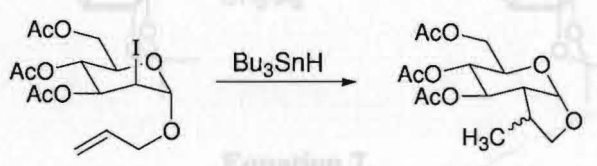


Equation 3.

Radical addition occurs either intramolecularly or intermolecularly; the focus will be on intramolecular reactions for this section. Intramolecular reactions often generate 5-*exo* cyclization products in which either the radical is formed on a tether and added to the double bond within the sugar or *visa versa*. A tin reagent and azo-*bis*-isobutyrolnitrile (AIBN) initiator are often used in these reactions to give a *cis*-fused ring. The first example below has the alkene in the carbohydrate ring and second example has the alkene on the tether (Equation 4 and Equation 5).[10]

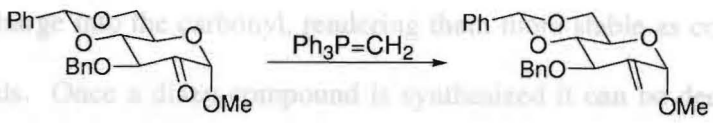


Equation 4.



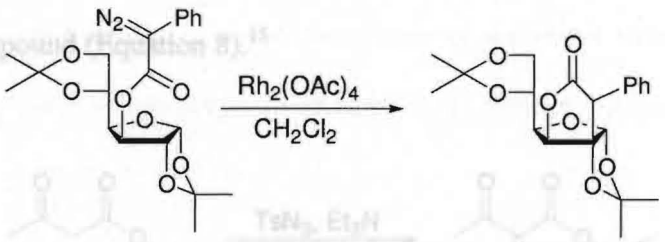
Equation 5.

Wittig and Wittig-like reactions are also useful in synthesizing branched-chain sugars. Under Wittig conditions a carbon-carbon double bond would be formed. Methylenation is common and an example is shown below in Equation 6.[11]



Equation 6.

Our group is interested in finding a new approach for synthesizing branched-chain sugars. Our pathway is similar to that of the radical reaction in that we are interested in metal-catalyzed intramolecular reactions. The basic principle is similar in that the carbohydrate has a tether attached to the ring that can react to form another five-membered ring. We propose to synthesize a diazoester-modified sugar that can be decomposed in the presence of rhodium(II) to yield a branched-chain sugar. This has been accomplished previously by Berndt and Norris (Equation 7),[12] and we will attempt to elaborate on this procedure by synthesizing other diazoester derivatives that can lead to branched-chain sugars.



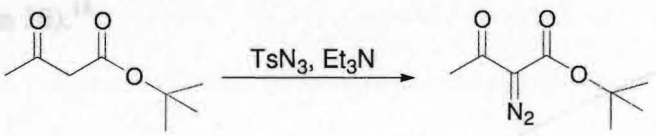
Equation 7.

Diazocarbonyl Compounds

Diazo compounds have the general formula $R_2C{=}N_2$, where a positive charge is located in the central nitrogen and a negative charge is distributed between the terminal nitrogen and carbon (Figure 8).[13,14] α-Diazoketones and α-diazoesters can delocalize their negative charge into the carbonyl, rendering them more stable as compared to alkyl diazo compounds. Once a diazo compound is synthesized it can be decomposed in the presence of a transition metal catalyst generating a metal carbene, which can undergo C-H, O-H, or N-H insertion, amongst others. In the following section the synthesis and decomposition of diazo compounds will be discussed, as well as the choice of transition metal catalyst.[14]

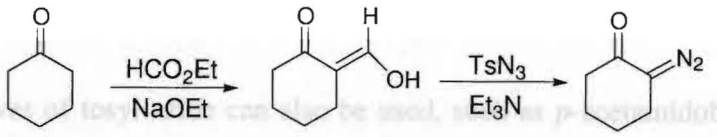
Figure 8: Depiction of a generic diazo compound.

If the α-methylene position is already reactive towards the diazo transfer, an α-diazocarbonyl compound can be synthesized using a base and a sulfonyl azide. In the example below, the *tert*-butyl acetoacetate has a reactive α-methylene position that can be deprotonated by a base like triethylamine and then reacted with tosyl azide to yield the desired diazo compound (Equation 8).[15]



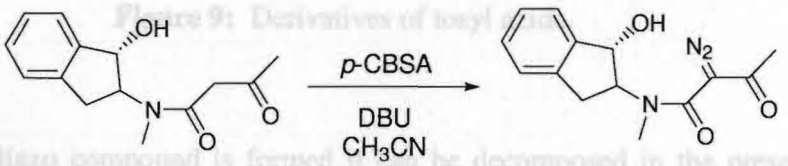
Equation 8.

If the methylene group is activated by only one carbonyl group then the α-methylene position generally needs to be activated further, for example, by placing an acyl aldehyde at this position prior to the diazo transfer (Scheme 1).[16]



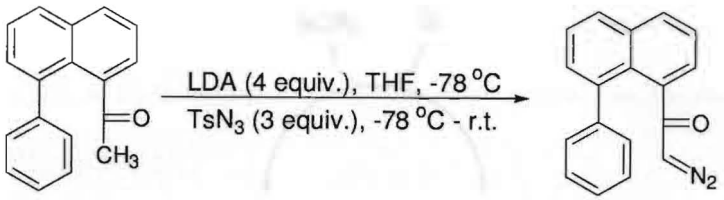
Scheme 1.

In some cases triethylamine is not a strong enough base and the diazo transfer cannot occur. A group from Merck, Sharp & Dohme Research Laboratories encountered this dilemma. The problem was solved when the triethylamine was replaced by a stronger base, 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) (Equation 9).[17]



Equation 9.

When only one carbonyl is present a base of sufficient strength is needed to deprotonate at the α-methylene position. In some cases lithium diisopropylamide is used as a base (Equation 10).[18]



Equation 10.

Derivatives of tosyl azide can also be used, such as *p*-acetamidobenzenesulfonyl azide (*p*-ABSA), *p*-nitrobenzenesulfonyl azide (*p*-NBSA), and *p*-carboxybenzenesulfonyl azide (*p*-CBSA), among others (Figure 9).[14]

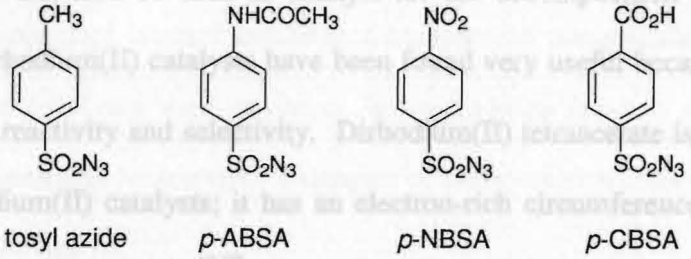


Figure 9: Derivatives of tosyl azide.

Once a diazo compound is formed it can be decomposed in the presence of a metal catalyst; in doing so a metal-stabilized carbene can be formed by displacing N_2. This electrophilic carbene can then be transferred to an electron-rich substrate (S:), regenerating the metal catalyst. The electron-rich substrate (S:) can be double bonds, single C-H, N-H, O-H bonds, carbonyl groups, etc. This cycle is depicted in Figure 10.[14]

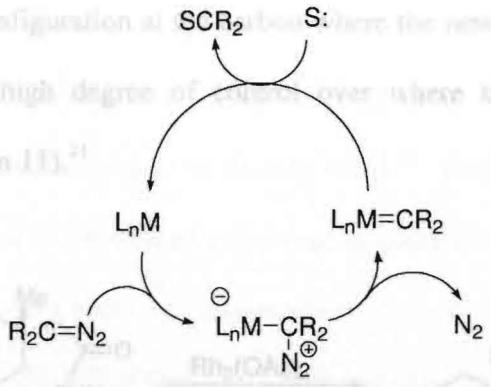


Figure 10: Metal-catalyzed diazo decomposition cycle.

Our research focuses on reactions catalyzed by rhodium(II). Copper and other transition metals can also be used as catalyst for the decomposition of diazocarbonyl compounds. Dirhodium(II) catalysts have been found very useful because they are able to better control reactivity and selectivity. Dirhodium(II) tetraacetate is the most widely used of the rhodium(II) catalysts; it has an electron-rich circumference surrounding an electron-poor center (Figure 11).[19,20]

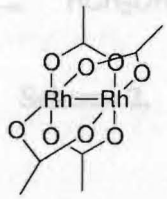
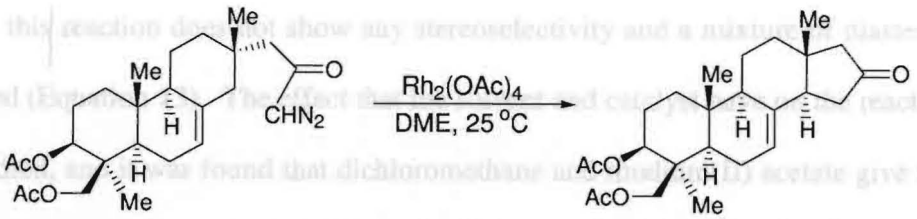


Figure 11: Rhodium(II) acetate.

We are interested in the use of rhodium(II) acetate as a catalyst for the intramolecular C-H insertion reaction, which often results in a five-membered ring. This type of reaction was first reported by Wenkert and co-workers.[21] This insertion occurred

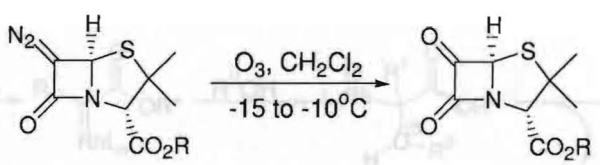
without changing the configuration at the carbon where the new bond was formed. This reaction also shows a high degree of control over where the insertion occurs, i.e. regioselectivity (Equation 11).[21]



Equation 11.

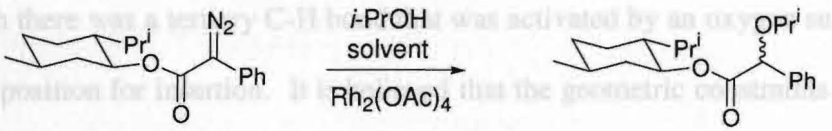
Other reactions of interest involving diazocarbonyl compounds and rhodium(II) catalysts are those involving water or ozone. Water insertion gives an ether product and ozone insertion generates a carbonyl. Examples of these reactions can be seen below in Scheme 2 and Equation 12.[13,22]

Scheme 2.

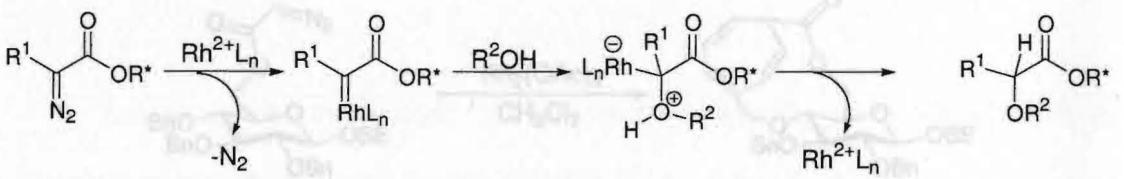


Equation 12.

Since O-H insertion reactions can occur so readily with water, it can be assumed that O-H insertion reactions can also occur with alcohols. These types of alcohol insertion reactions have been explored by Moody *et. al.*[23] Their research has found that an alcohol can indeed react with a diazo compound to yield in an O-H insertion product, but that this reaction does not show any stereoselectivity and a mixture of diastereomers is formed (Equation 13). The effect that the solvent and catalyst have on the reaction was also studied, and it was found that dichloromethane and rhodium(II) acetate give the best results. Other solvents led to an increase in side reaction compared to dichloromethane, and other metal catalysts proved to be less reactive, compared to rhodium(II) acetate. In some cases it was found that the carbenoid was reacting with oxygen thus forming a ketone, even though the reaction was run under nitrogen. A mechanistic pathway was proposed that shows the alcohol attacking the electrophilic rhodium carbenoid (Scheme 3).

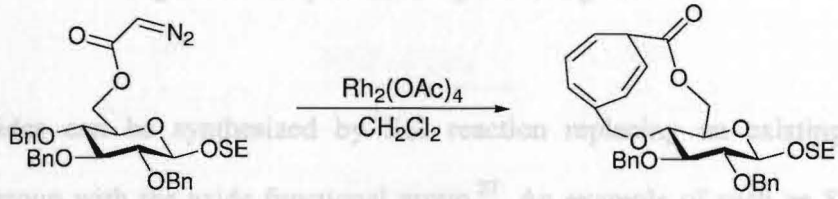


Equation 13.

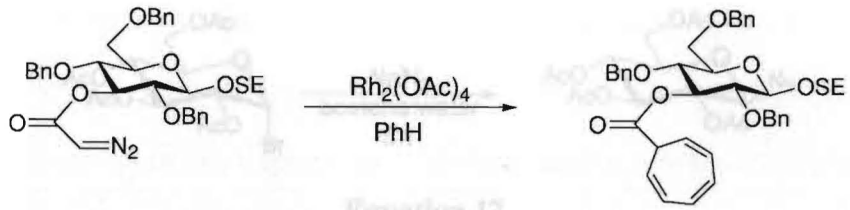


Scheme 3.

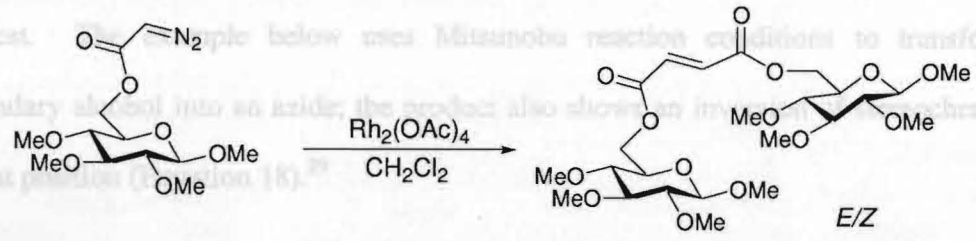
There have been a few research groups that have combined diazo chemistry with carbohydrate chemistry. A group from the Netherlands has been attempting similar intramolecular C-H insertion reactions with little success.[24] D-Glucose derivatives were used in their research and the choice of protecting groups and ring conformation might explain the difficulties they encountered. Their first attempts at intramolecular C-H insertion showed that aromatic cycloaddition was occurring with one of the neighboring benzyl protecting groups (Equation 14). When the position of the diazo group was changed from C-6 to C-3, and the decomposition run in methylene chloride, the isolated and characterized products were found to be of aromatic cycloaddition into neighboring benzyl protecting groups. Since no significant amount of the desired insertion product could be detected, the decomposition was run in benzene to show that an aromatic cylcoaddition was the most likely path (Equation 15). When methyl ether protecting groups were employed carbene dimers were formed (Equation 16). Attempts at producing a five-membered ring *via* an intramolecular C-H insertion were not successful, even though there was a tertiary C-H bond that was activated by an oxygen substituent at the desired position for insertion. It is believed that the geometric constraints of the ring were unfavorable for the desired intramolecular reaction to occur.



Equation 14.



Equation 15.



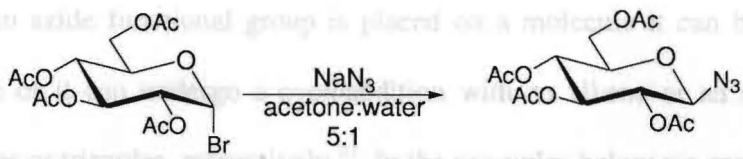
Equation 16.

Azides

Azides have the general formula R-N_3,[25,26] where a formal positive charge is located on the central nitrogen atom and a negative charge is distributed between the first and third nitrogen atoms (Figure 12).

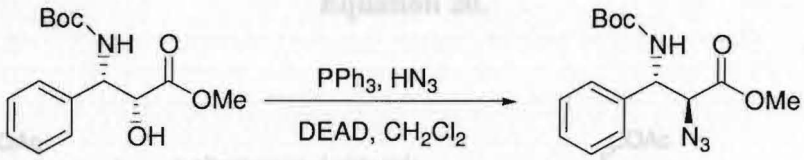
Figure 12: Depiction of a generic organic azide.

Azides can be synthesized by S_N2 reaction replacing an existing halide or sulfonate group with the azide functional group.[27] An example of such an S_N2 reaction can be seen in Equation 17, where 2,3,4-tri-*O*-acetyl-α-D-glucopyranosyl bromide is reacted with sodium azide to form a glucosyl azide.[28]



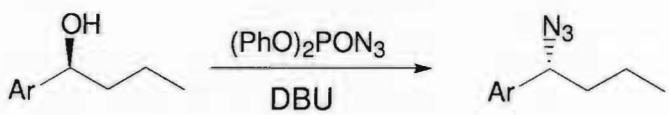
Equation 17.

Organic azides synthesized using alcohols as starting materials are of particular interest. The example below uses Mitsunobu reaction conditions to transform a secondary alcohol into an azide; the product also shows an inversion of stereochemistry at that position (Equation 18).[29]



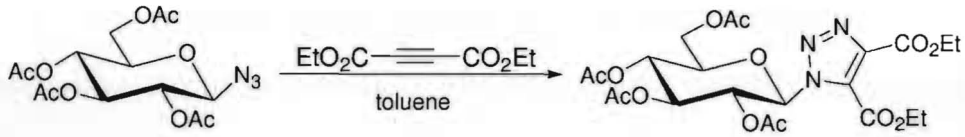
Equation 18.

Chemists from Merck Research Laboratories developed a similar one-pot azide synthesis involving a secondary alcohol and reacting it with diphenyl phosphorazidate (DPPA), and 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) (Equation 19).[30]

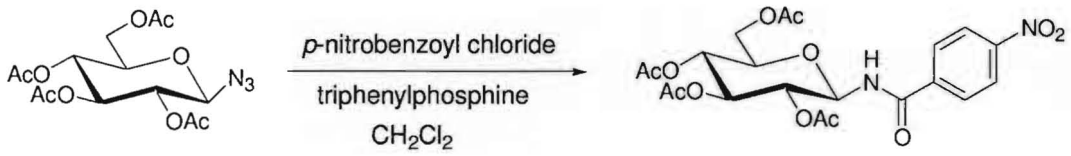


Equation 19.

Once an azide functional group is placed on a molecule it can be reduced to a primary amine or it can undergo a cycloaddition with an alkene or an alkyne to form 1,2,3-triazolines or triazoles, respectively.[27] In the examples below we can see that 2,3,4-tri-*O*-acetyl-α-D-glucopyranuronosyl azide can be reacted with an alkyne to form a 1,2,3-triazole (Equation 20) or it can be reacted with an acid chloride to form an amide (Equation 21).[28]



Equation 20.



Equation 21.

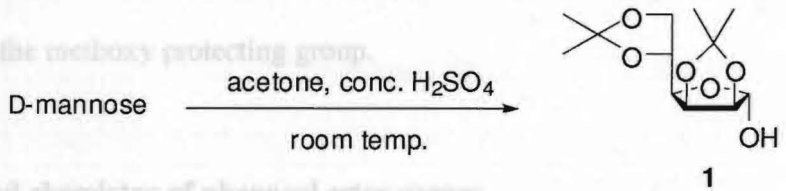
Statement of Problem

Carbon-carbon bond forming reactions are of great interest and useful for the synthesis of branched-chain sugars. The decomposition of a diazodeoxy furanose sugar derivative offers a potentially useful route for the synthesis of branched-chain sugars.

Results and Discussion

Protecting groups

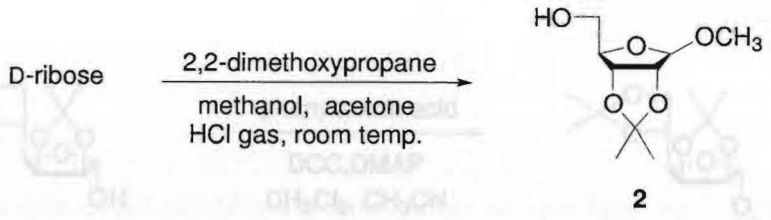
Carbohydrates are able to serve as inexpensive chiral scaffolds; at each chiral center there is a reactive hydroxyl group. The best way to control the reactivity of a carbohydrate is through the use of protecting groups and there is a large variety of such groups, which offer an assortment of selectivity. Isopropylidene protecting groups are of interest in this project because they are selective and do not interfere with the subsequent reactions. These protecting groups can easily be put in place by reacting a carbohydrate with acetone and a catalytic amount of acid (Equation 22). Sugars with isopropylidene protecting groups can also be purchased from Acros or Aldrich. 2,3:5,6-Di-*O*-isopropylidene-α-D-mannofuranose (**1**) and methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (**2**) were both synthesized, while 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**3**) and 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**4**) were purchased.



Equation 22.

D-Mannose was reacted with a catalytic amount of sulfuric acid in an excess amount of acetone to form diacetone-D-mannose (**1**),[31,32] after which, the reaction was neutralized with anhydrous sodium bicarbonate, yielding a solid, which was then recrystallized using methanol. ^{1}H NMR of crystals clearly showed four singlets worth

three hydrogens a piece between 1.0 and 1.5 ppm representing the isopropylidene protecting groups.



2

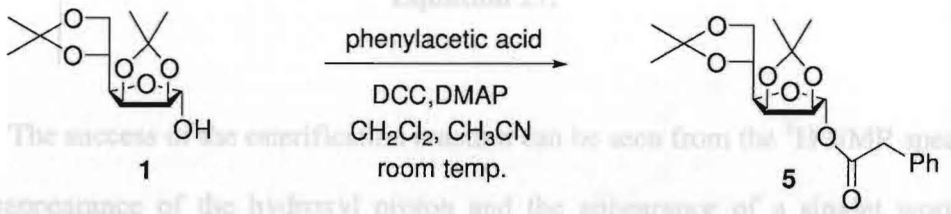
Equation 23.

Methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (**2**) was synthesized by reacting D-ribose with 2,2-dimethoxypropane and hydrogen chloride-saturated methanol in excess acetone (Equation 23).[33] Once the reaction was complete, pyridine was added to neutralize the reaction, and workup gave a yellow oil, which was purified by flash column. ^{1}H NMR of the oil clearly showed three singlets worth three hydrogens each, at 1.32 and 1.49 ppm representing the isopropylidene protecting group and at 3.44 ppm representing the methoxy protecting group.

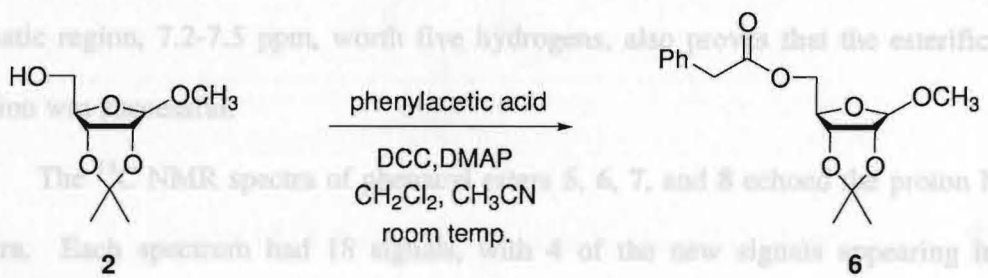
Synthesis and chemistry of phenacyl ester sugars.

With protecting groups in place, now only one reactive hydroxyl group is available for a Steglich esterification (Equations 24-27),[34] which involves reacting an alcohol with a carboxylic acid in the presence of 1,3-dicyclohexylcarbodiimide (DCC) and a catalytic amount of 4-(dimethylamino)pyridine (DMAP). In this case, the alcohol is a protected sugar with one free hydroxyl group and phenylacetic acid is the carboxylic acid. The TLC of the reaction showed the appearance of a spot with a higher R_f value

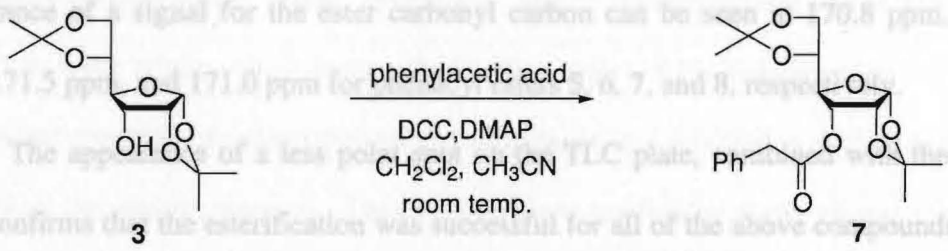
than the starting material. After the workup was completed, ^{1}H NMR was used to check the purity of the compound before proceeding to the diazo transfer reaction.



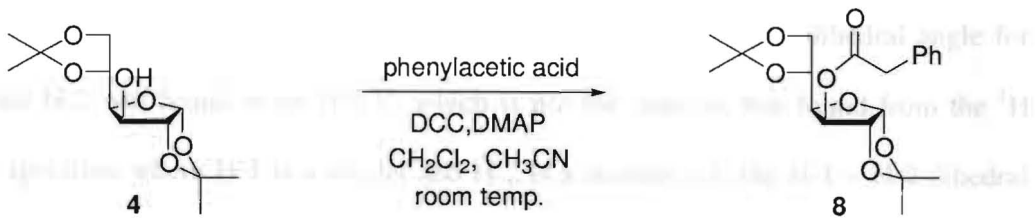
Equation 24.



Equation 25.



Equation 26.



Equation 27.

The success of the esterification reaction can be seen from the ^{1}H NMR spectra by the disappearance of the hydroxyl proton and the appearance of a singlet worth two hydrogens representing the -CH_2- group *alpha* to the carbonyl of the newly formed phenacyl esters **5**, **6**, **7**, and **8**. This singlet can be seen at 3.63 ppm for phenacyl ester **5**, 3.66 ppm for **6**, 3.70 ppm for **7**, and 3.67 ppm for **8**. The appearance of a multiplet in the aromatic region, 7.2-7.5 ppm, worth five hydrogens, also proves that the esterification reaction was successful.

The ^{13}C NMR spectra of phenacyl esters **5**, **6**, **7**, and **8** echoed the proton NMR spectra. Each spectrum had 18 signals, with 4 of the new signals appearing in the aromatic region, 125-140 ppm, showing the symmetry of the benzene ring. The appearance of a signal, for the carbon *alpha* to the ester, can be seen at 42.6 ppm for phenacyl ester **5**, 42.4 ppm for **6**, 42.1 ppm for **7**, and 42.6 ppm for **8**. Also, the appearance of a signal for the ester carbonyl carbon can be seen at 170.8 ppm, 172.0 ppm, 171.5 ppm, and 171.0 ppm for phenacyl esters **5**, **6**, **7**, and **8**, respectively.

The appearance of a less polar spot on the TLC plate, combined with the NMR data, confirms that the esterification was successful for all of the above compounds. The X-ray crystallography data of compound **5** also confirms that the esterification reaction was successful. The crystallography data clearly shows that the protecting groups are

still attached and that the stereochemistry at C-1 was retained. The dihedral angle for H-1 and H-2 was found to be 102.3°, which is not the same as that found from the ^{1}H NMR spectrum where H-1 is a singlet and H-2 is a doublet, i.e. the H-1 – H-2 dihedral angle is close to 90 degrees.

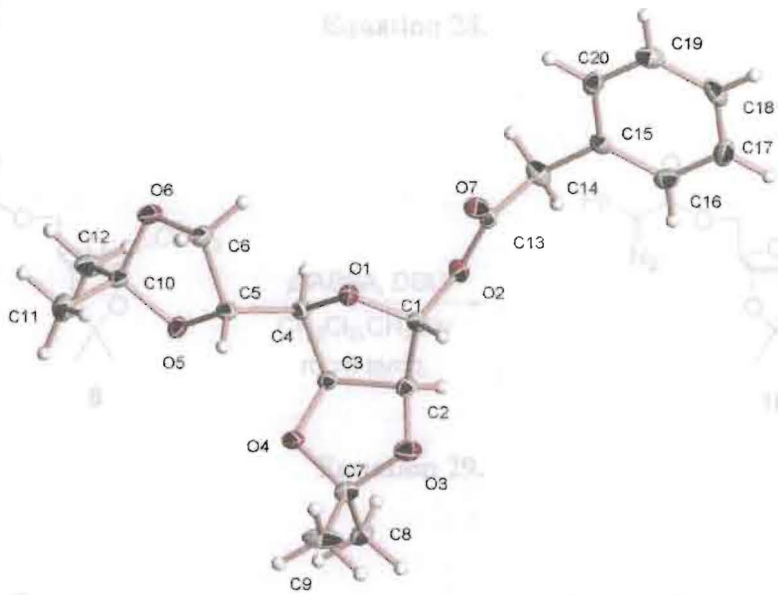
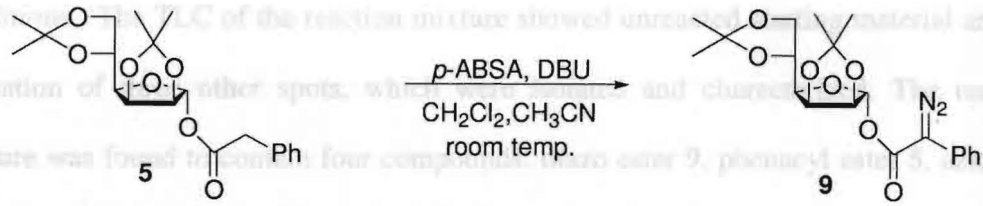


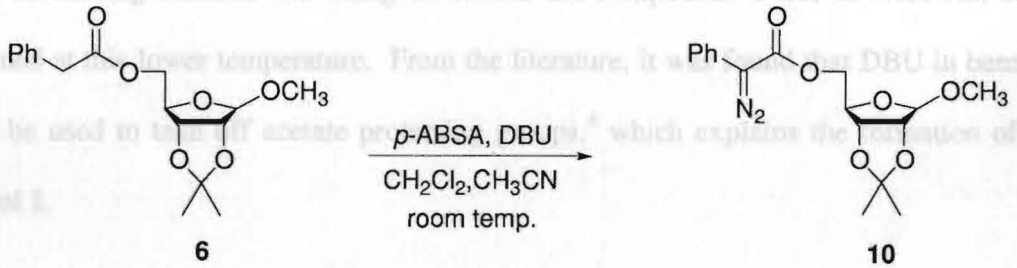
Figure 13: X-Ray crystal structure of phenacyl ester **5**.

Synthesis and chemistry of diazoester sugars

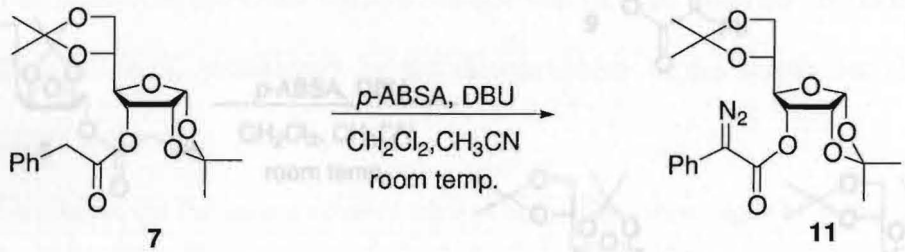
The newly synthesized phenacyl ester sugars 5-8 were then reacted with *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) and 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) to form bright yellow-orange diazo ester sugars 9-12 (Equations 28-31). The TLC of the completed reaction showed the appearance of a spot with a slightly higher R_f value than the starting material. The products were purified by flash column to ensure that a pure diazoester sugar was used in the decompositions to follow. The purity of the diazo ester sugars 9-12 was checked by NMR.



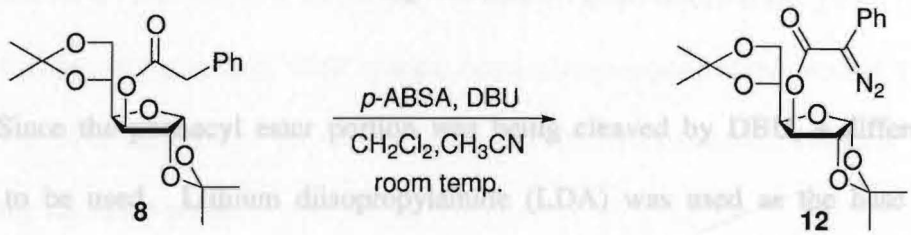
Equation 28.



Equation 29.

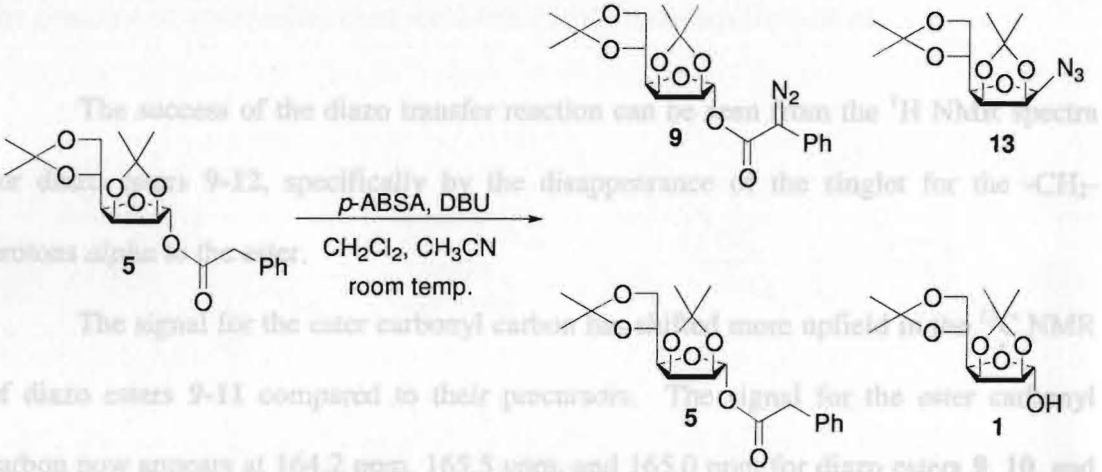


Equation 30.



Equation 31.

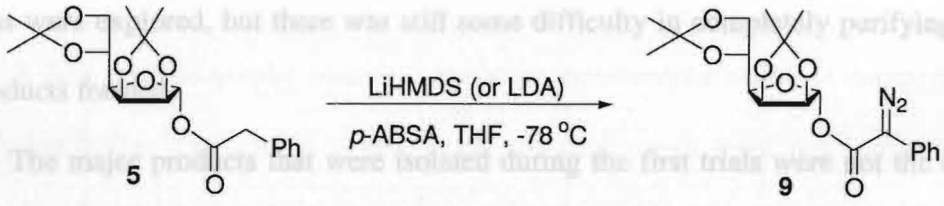
The synthesis of diazo ester **9** was not completely successful under these conditions. The TLC of the reaction mixture showed unreacted starting material and the formation of three other spots, which were isolated and characterized. The reaction mixture was found to contain four compounds: diazo ester **9**, phenacyl ester **5**, azide **13**, and lactol **1** (Equation 32).[37] The same reaction was run in the refrigerator in the hopes of increasing the yield of the desired product **9** and decrease the formation of **1** and **13**. Not all starting material was being consumed and compounds **1** and **13** were still being formed at this lower temperature. From the literature, it was found that DBU in benzene can be used to take off acetate protecting groups,[4] which explains the formation of the lactol **1**.



Equation 32.

Since the phenacyl ester portion was being cleaved by DBU, a different base needed to be used. Lithium diisopropylamide (LDA) was used as the base and the reaction was run in tetrahydrofuran (THF) at -78 °C (Equation 33). This base proved to

be more successful. Though compounds **1** and **13** were still being formed, all of the starting material was consumed, which allowed for easier isolation of the desired diazo compound **9**. Lithium bis(trimethylsilyl)amide (LiHMDS) can also be used for this reaction, and due to convenience is the preferred base for this reaction. LDA and LiHMDS are stronger bases, which offer an irreversible acid-base reaction, thus helping to push the reaction toward the formation of the diazo ester product.



Equation 33.

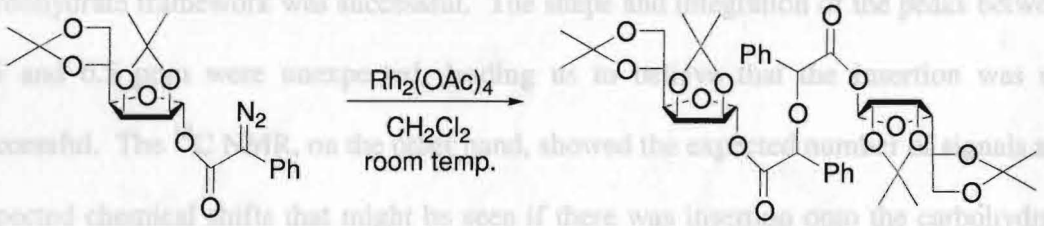
The success of the diazo transfer reaction can be seen from the ^{1}H NMR spectra for diazo esters **9-12**, specifically by the disappearance of the singlet for the $-CH_2-$ protons *alpha* to the ester.

The signal for the ester carbonyl carbon has shifted more upfield in the ^{13}C NMR of diazo esters **9-11** compared to their precursors. The signal for the ester carbonyl carbon now appears at 164.2 ppm, 165.5 ppm, and 165.0 ppm for diazo esters **9**, **10**, and **11**, respectively. The peak for the carbon directly attached to the diazo group cannot be observed in any of the carbon NMR spectra, but a disappearance of the peak at 42 ppm is apparent in all of the spectra. IR spectra showed an absorption band at 2100 cm^{-1}, clearly identifying the diazo group.

Rhodium(II)-catalyzed decomposition of diazo ester sugars

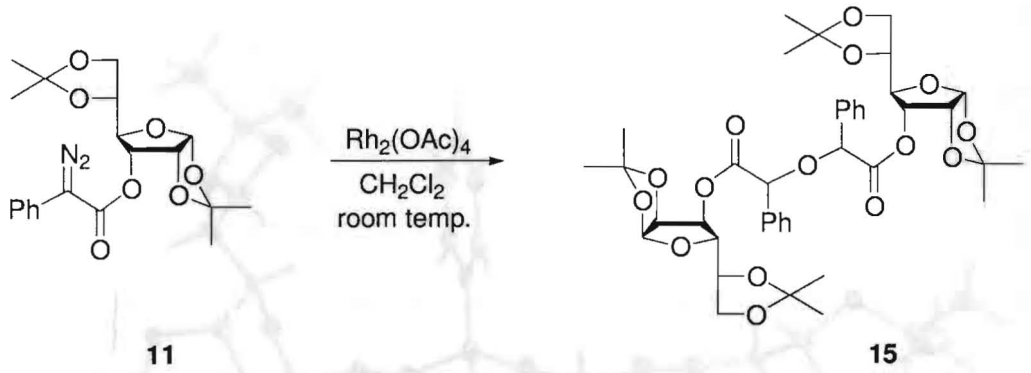
The diazo esters **9-12** were dried using a vacuum pump, characterized, and checked for purity, then dissolved in freshly distilled methylene chloride and degassed. This solution was slowly added by syringe pump to a reaction flask containing rhodium (II) acetate suspended in distilled methylene chloride, which had also been degassed. Column chromatography was used for the purification of these reactions, though this technique was not successful in the isolation of all products formed. Different solvent systems were explored, but there was still some difficulty in completely purifying all of the products formed.

The major products that were isolated during the first trials were not the desired insertion products. Dimeric ethers were formed (Equations 34 and 35), which is due to the presence of water either from the solvent or the rhodium(II) catalyst.



9 **14**

Equation 34.



11 **15**

Equation 35.

X-Ray crystallography was very useful in the characterization of compounds **14** and **15**, but before the crystals were formed, the compounds were characterized using NMR. The ^{1}H NMR spectra for the compounds **14** and **15** showed misleadingly simple sets of signals. The proton NMR of compound **15** showed a singlet at 5.13 ppm for the -CH- proton *alpha* to the ester, which would be expected if the insertion onto the carbohydrate framework was successful. The shape and integration of the peaks between 3.5 and 6.5 ppm were unexpected, leading us to believe that the insertion was not successful. The ^{13}C NMR, on the other hand, showed the expected number of signals and expected chemical shifts that might be seen if there was insertion onto the carbohydrate framework.

The X-ray data of compounds **14** and **15** showed that a dimeric ether had been formed in each case, which are linked through an unexpected C-O-C bond (Figures 14 and 15). One major diastereomer was formed in each case, therefore the reaction leading to these products was diastereoselective. Mass spectrometry data confirmed the formation of the dimeric ether **15**, with a peak at 793.6 *m/z*, which is the calculated mass plus a sodium ion.

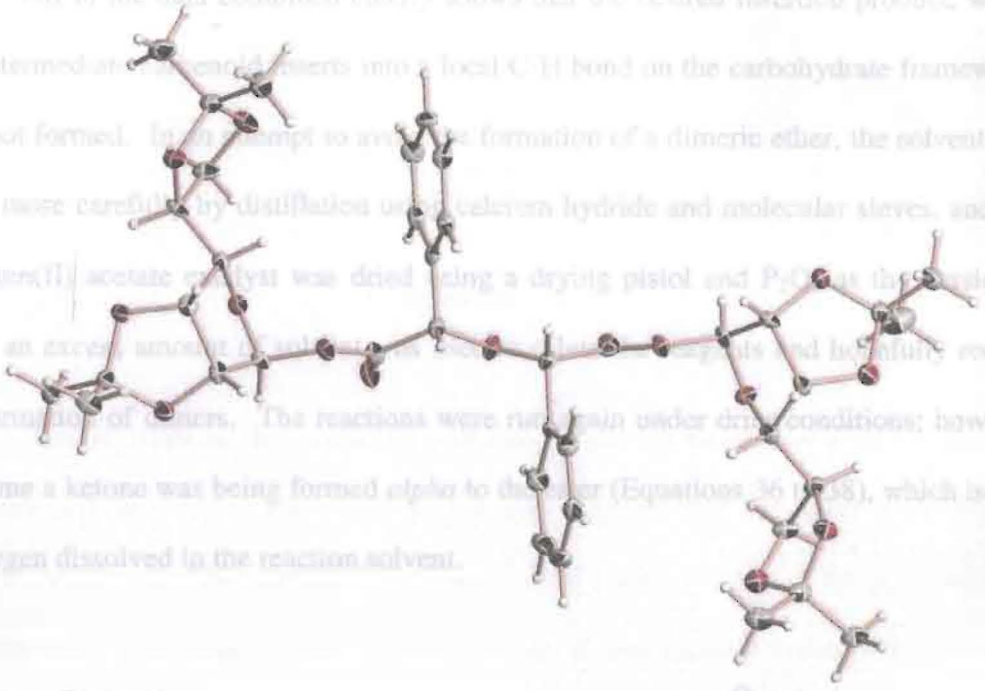


Figure 14: X-Ray crystal structure of dimeric ether **14**.

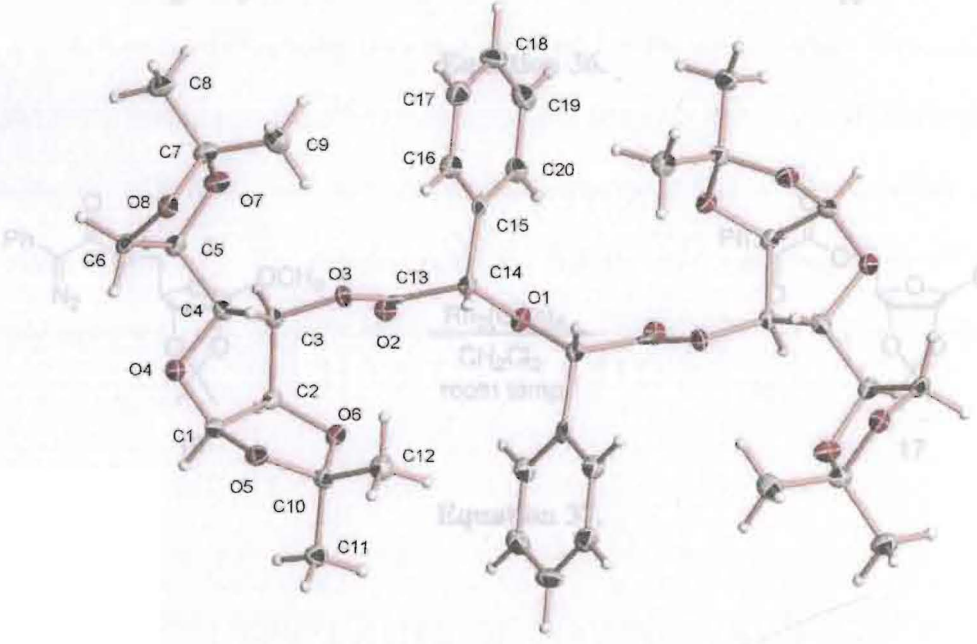
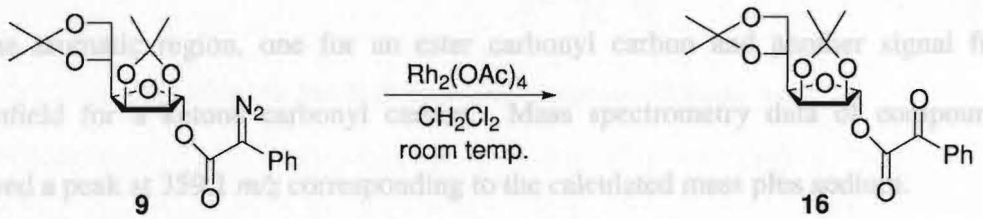
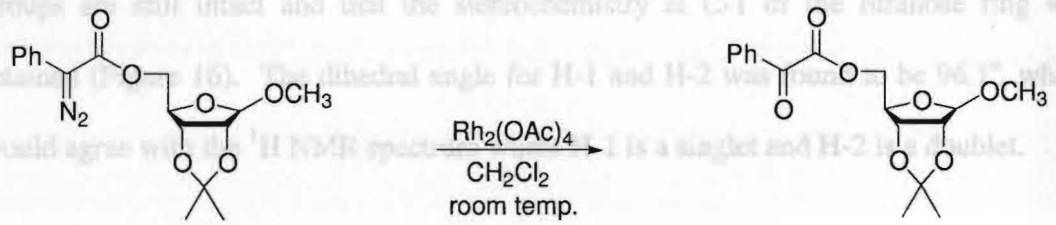


Figure 15: X-Ray crystal structure of dimeric ether **15**.

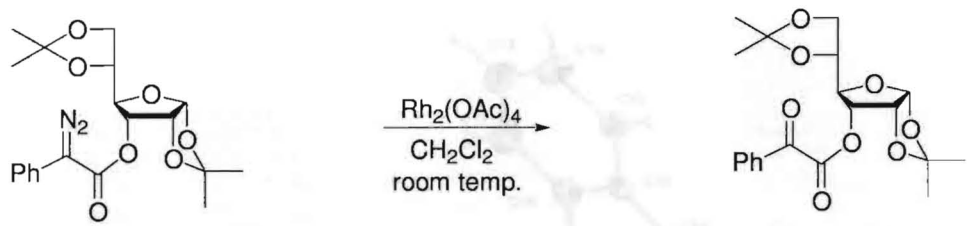
All of the data combined clearly shows that the desired insertion product, where the intermediate carbenoid inserts into a local C-H bond on the carbohydrate framework, was not formed. In an attempt to avoid the formation of a dimeric ether, the solvent was dried more carefully by distillation using calcium hydride and molecular sieves, and the rhodium(II) acetate catalyst was dried using a drying pistol and P_2O_5 as the dessicant. Also, an excess amount of solvent was used to dilute the reagents and hopefully reduce the formation of dimers. The reactions were run again under drier conditions; however this time a ketone was being formed *alpha* to the ester (Equations 36 to 38), which is due to oxygen dissolved in the reaction solvent.



Equation 36.



Equation 37.



11 18

Equation 38.

The ^{1}H NMR of the products **16-18** did not show a singlet for a proton *alpha* to the ester carbonyl. Also, the signal shapes and integration of the peaks were not that expected of an insertion product. The formation of a ketone *alpha* to the ester carbonyl could be seen more easily in the ^{13}C NMR, which clearly showed two signals downfield of the aromatic region, one for an ester carbonyl carbon and another signal further downfield for a ketone carbonyl carbon. Mass spectrometry data of compound **17** showed a peak at 359.1 *m/z* corresponding to the calculated mass plus sodium.

X-Ray crystallography data was obtained for **16,** which clearly shows a carbonyl *alpha* to the ester carbonyl. The crystallography data also shows that all of the protecting groups are still intact and that the stereochemistry at C-1 of the furanose ring was retained (Figure 16). The dihedral angle for H-1 and H-2 was found to be 96.1°, which would agree with the ^{1}H NMR spectrum where H-1 is a singlet and H-2 is a doublet.

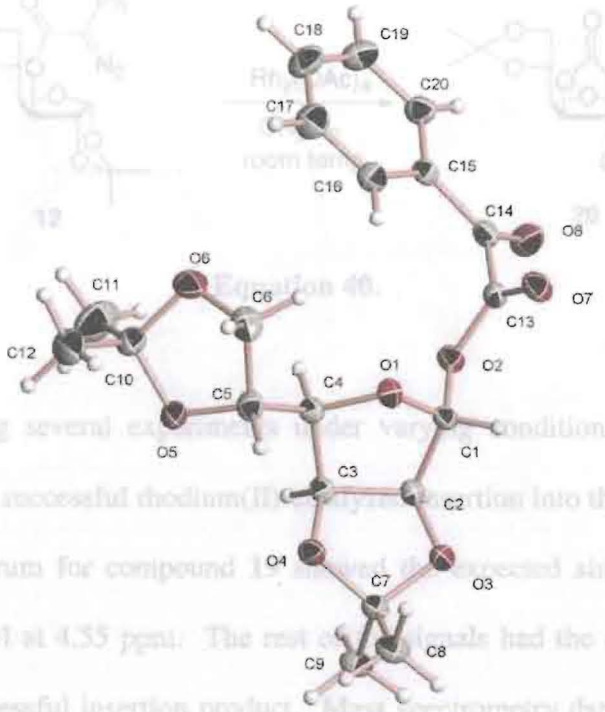
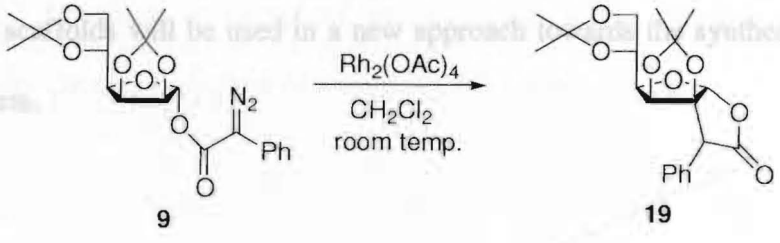


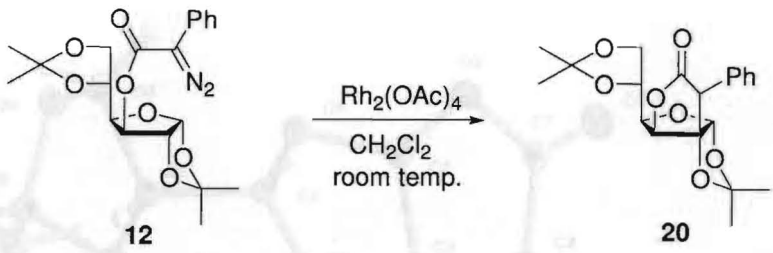
Figure 16: X-Ray crystal structure of ketone **16**.

To avoid the formation of the ketone product, new septa were used, syringe joints were wrapped with Teflon tape, and reaction flasks were degassed for a longer amount of time. Also, the amount of rhodium(II) catalyst used was reduced. The formation of the desired insertion product was successful under these new conditions (Equations 39 and 40).



9 **19**

Equation 39.



12 20

Equation 40.

After running several experiments under varying conditions, data was finally obtained that proved successful rhodium(II)-catalyzed insertion into the sugar framework. The ^{1}H NMR spectrum for compound **19** showed the expected singlet for the proton *alpha* to the carbonyl at 4.55 ppm. The rest of the signals had the expected shape and integration of a successful insertion product. Mass spectrometry data showed a peak at 399.1 *m/z*, which is the mass of the insertion product plus sodium.

NMR data looked very promising, so we diligently tried to recrystallize the compound. X-Ray crystallography data obtained clearly shows the insertion at C-2, as predicted (Figure 17). The crystal structure also shows the retention of stereochemistry at C-1 of the furanose, which directed the insertion at C-2, and that the protecting groups are still intact. The stereochemistry at the carbon *alpha* to the carbonyl needs to be further investigated. Compound **20** was also successfully synthesized, and the data obtained matched the literature data.[35] With the success of this reaction, different carbohydrate scaffolds will be used in a new approach towards the synthesis of various natural products.

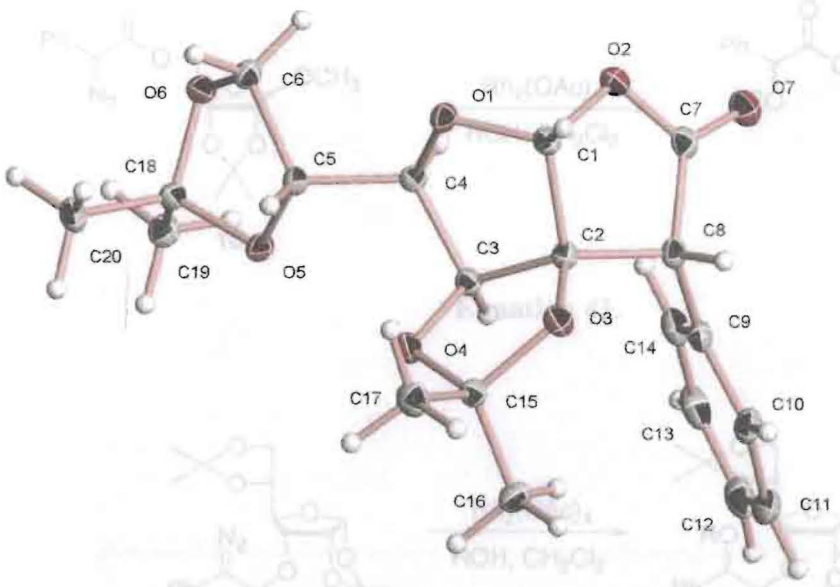
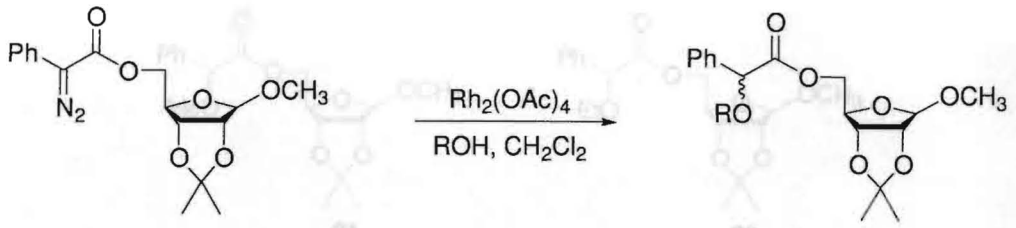


Figure 17: X-Ray crystal structure of insertion product **19**.

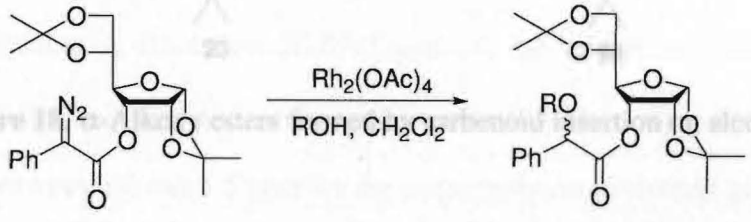
Rhodium(II)-catalyzed decomposition in the presence of alcohols

The stereoselectivity seen in formation of the dimeric ethers gave rise to the following reactions; we were interested to see if the same diasteroselectivity would be observed. The diazo ester compounds **10** and **11** were decomposed in the presence of a simple alcohol (methanol, ethanol, isopropanol, *t*-butanol) (Equations 41 and 42, Table 1). TLC showed the formation of one major product of lower R_f than the starting material in each case. ^{1}H NMR of the column-purified material showed a 50/50 mixture of isomers and mass spectrometry data showed that O-H insertion with the alcohols did indeed occur. This leads us to believe that the water in the previous reactions was coming from the catalyst (i.e. water of hydration) and not the solvent.



10 **21-24**

Equation 41.



11 **25-27**

Equation 42.

Table 1: O-H insertion of alcohols with diazo sugars **10** and **11**.

Starting Material	Alcohol/Amine	Product	% Yield	R_f Value*
10	Methanol	**21**	75	0.47
	Ethanol	**22**	80	0.59
	Isopropanol	**23**	71	0.43
	t-Butanol	**24**	42	0.67
11	Methanol	**25**	59	0.33
	Ethanol	**26**	43	0.35
	Isopropanol	**27**	41	0.44
	n-Butyl amine	**N/R**	-	-

* Solvent system 2:1 hexanes to ethyl acetate

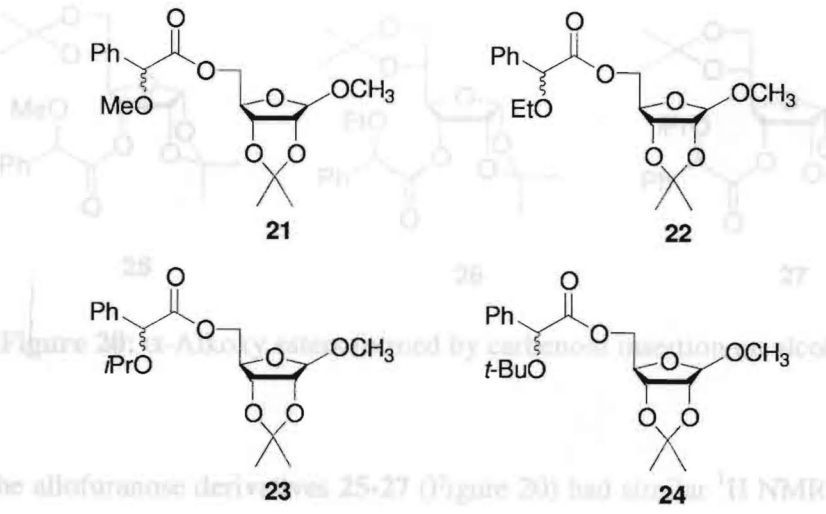


Figure 18. α-Alkoxy esters formed by carbenoid insertion on alcohols.

Compounds **21-24** (Figure 18) have similar ^{1}H NMR spectra. The signal for the proton *alpha* to the ester carbonyl can be seen downfield of H-1. The signals for the methyl protecting groups can be seen at 3.12 ppm and 3.23 ppm, clearly showing that there is a mixture of isomers (~50:50). The alkoxy groups can each be seen in their respective region. Mass spectrometry data collected for compounds **22** and **23** clearly show a peak representing the calculated mass plus sodium.

Ribofuranose-isopropanol derivative **23** had an interesting proton NMR. The two overlapping septets at 3.68 ppm, representing the methyl protons on the newly attached isopropyl group, clearly show that there is a mixture of isomers (Figure 19).

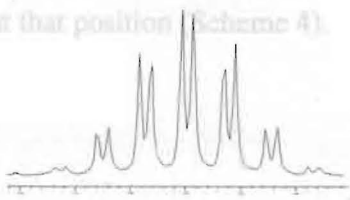
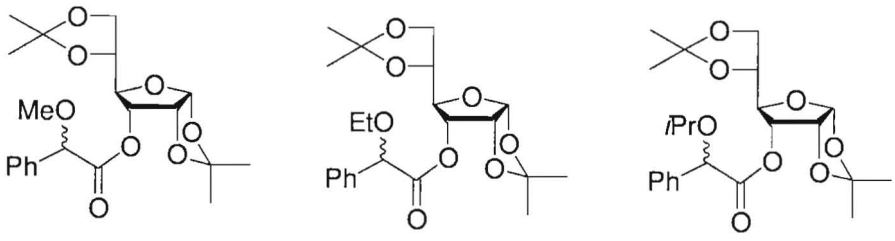


Figure 19: ^{1}H NMR spectrum of ribofuranose derivative **23**.



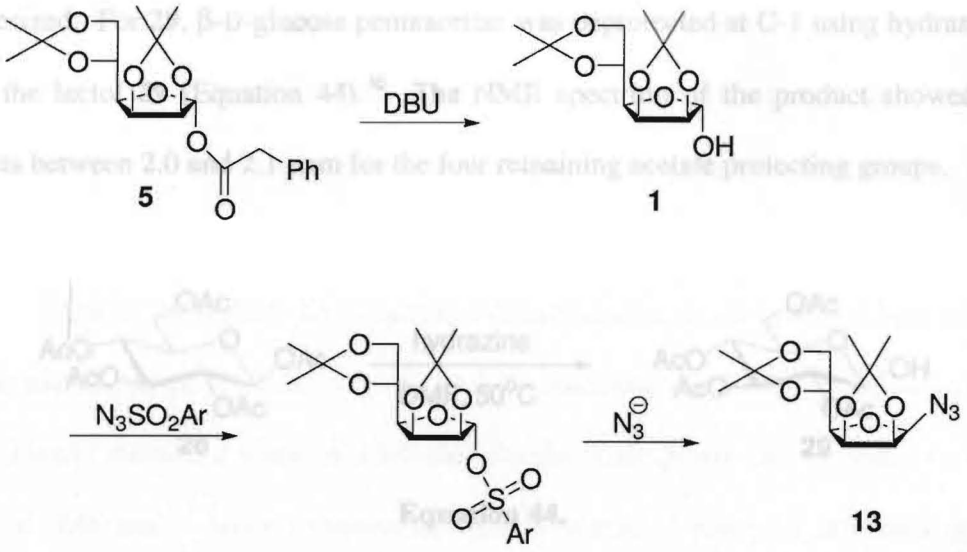
25 26 27

Figure 20: α-Alkoxy esters formed by carbenoid insertion on alcohols.

The allofuranose derivatives **25-27** (Figure 20) had similar ^{1}H NMR spectra. The proton *alpha* to the ester carbonyl can be seen downfield of H-1. Eight peaks can be seen in the region between 1.0 and 1.5 ppm for the isopropylidene protecting groups, showing that there is a mixture of isomers. The alkoxy groups can each be seen in their respective region. Mass spectrometry data collected for compounds **25** and **26** clearly show a peak representing the calculated mass plus sodium.

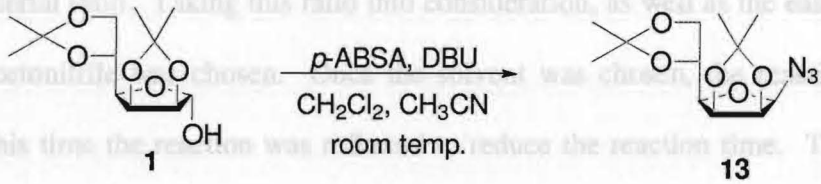
Deprotection

When trying to synthesize diazo ester **9**, azide **13** and lactol **1** were found to be forming as well. This reaction was further investigated and extrapolated. It is believed that the base, DBU, is able to cleave the phenacyl ester leaving a free hydroxyl group. This free hydroxyl then reacts with *p*-ABSA forming a sulfonate ester and displacing the azide portion. The azide generated *in situ* displaces the sulfonate ester in a S_N2 reaction, inverting the stereochemistry at that position (Scheme 4).



Scheme 4.

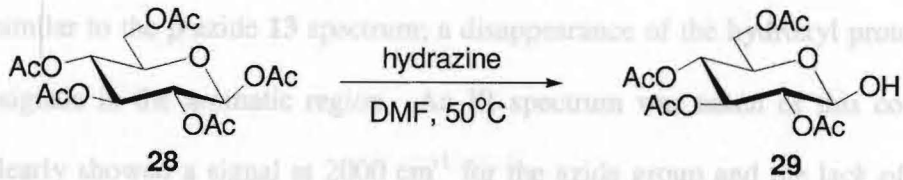
We decided to take lactol **1** and react it with *p*-ABSA and DBU under the same conditions to see if we were able to synthesize compound **13** (Equation 43). This reaction was successful; as a result, we decided to run this reaction with other selectively protected sugars in order to see if we could develop a general one-pot method for the synthesis of azidodeoxy sugars.



Equation 43.

Most of the selectively protected sugars were either purchased or synthesized. In this section sugars **3**, **4**, **31**, and **34** were purchased, while sugars **1**, **2**, and **29** were

synthesized. For **29**, β-D-glucose pentaacetate was deprotected at C-1 using hydrazine to yield the lactol **29** (Equation 44).[36] The NMR spectrum of the product showed four singlets between 2.0 and 2.1 ppm for the four remaining acetate protecting groups.



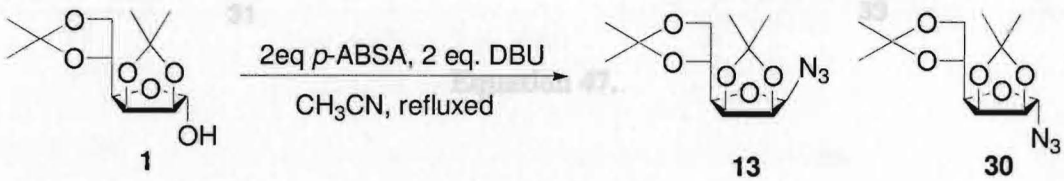
28 **29**

Equation 44.

One-pot azide synthesis

The trial one-pot azide synthesis using *p*-ABSA and DBU to convert lactol **1** to azide **13** looked promising. This same reaction was run in the parallel synthesizer to determine what would be the best solvent for the reaction. The solvents used in this experiment were acetonitrile, tetrahydrofuran (THF), dimethyl formamide (DMF), dioxane, pyridine, and dichloromethane. TLC taken of each reaction showed successful formation of the azide product. From ^{1}H NMR we were able to see the product to starting material ratio. Taking this ratio into consideration, as well as the ease of solvent removal, acetonitrile was chosen. Once the solvent was chosen, the reaction was run again but this time the reaction was refluxed to reduce the reaction time. This reaction proved successful, but the reaction was not going to completion. The ratio of lactol **1** to *p*-ABSA and DBU used to this point was 1:1. Various ratios of lactol **1** to *p*-ABSA/DBU (1:1.2, 1:1.4, 1:1.6, 1:1.8 and 1:2) were explored and it was found that the best ratio was 1:2, even though this is a significant excess of base and source of azide.

When the mannose derivative **1** was refluxed with *p*-ABSA and DBU, we saw that not only was β azide **13** being formed but also a small amount of α azide **30** (Equation 45). When running the reaction, a spot with a higher R_f than the β azide **13** appeared. This compound was isolated by column chromatography and the ^{1}H NMR looked similar to the β azide **13** spectrum; a disappearance of the hydroxyl proton signal and no signals in the aromatic region. An IR spectrum was taken of this compound, which clearly showed a signal at 2000 cm^{-1} for the azide group and the lack of a broad signal at 3000 cm^{-1}. Mass spectrometry data of mannosyl azide **30** showed a peak at 308.1 *m/z*, the calculated mass plus sodium.

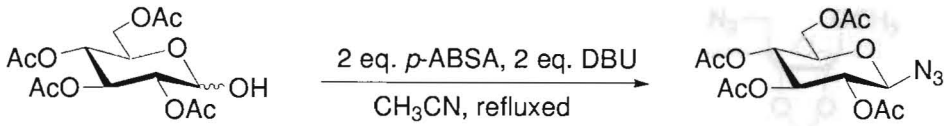


Equation 45.

Once our standard parameters were set, other selectively protected sugars were used as a source of a free hydroxyl group that could be replaced by azide. These sugars were either purchased or synthesized. All of the reactions that were successfully purified, and where the ^{1}H NMR spectra of the azide product could be matched to those published in the literature, will be discussed in this section.

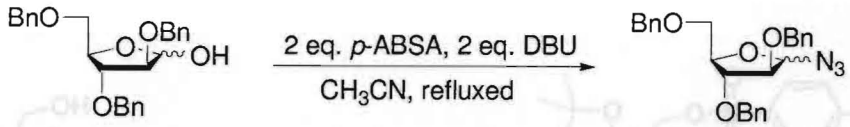
The selectively protected sugars had free hydroxyls at various positions. OH groups at C-1 (or the *anomeric* carbon) were successfully converted to the azide using

this one-pot method (Equations 46 and 47). ^{1}H NMR data of azide products **32** and **33** were verified with those published in the literature.[28,38]



29 **32**

Equation 46.

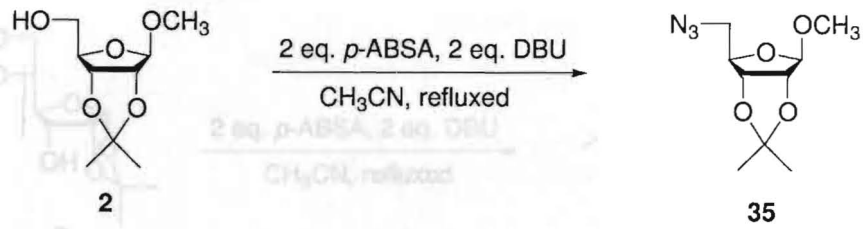


31 **33**

Equation 47.

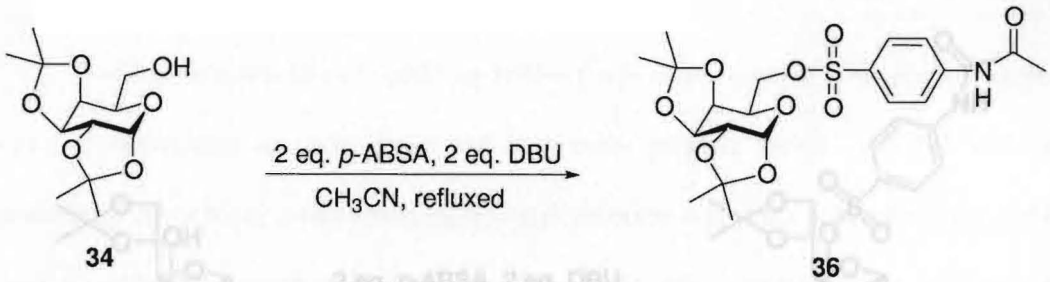
Azidation of carbohydrates **2** and **34,** which have free hydroxyls on the terminal carbon, i.e. at a primary position, were also explored (Equations 48 and 49). These reactions were successful in forming the azide only if the position was sterically unhindered, thus allowing the S_N2 attack of the azide anion formed *in situ.* If the hydroxyl at the primary position was hindered, the sulfonate ester was isolated. The formation of this product gives us a clue to the possible mechanism of the reaction. ^{1}H NMR data of azide **35** was verified with data published in the literature.[39] The spectra of the column-purified sulfonate ester **36** clearly shows signals in the aromatic region, which indicates that the sulfonate ester was formed. The signal at 2.23 ppm can be seen for the protons *alpha* to the carbonyl, which again is an indication that the sulfonate ester

was formed. Also, mass spectrometry data for compound **36** shows a peak at 480.2 *m/z*, which is the calculated mass plus sodium.



2 **35**

Equation 48.

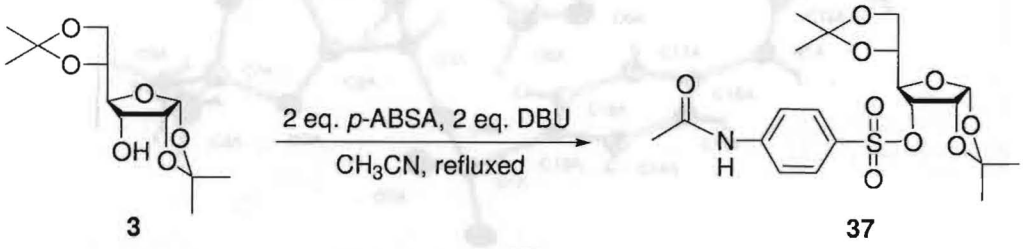


34 **36**

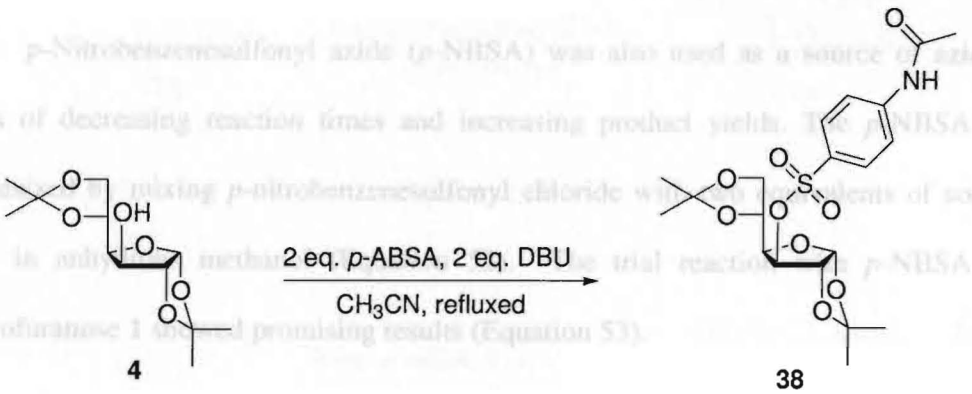
Equation 49.

Hydroxyls on any carbon between the first and the last are at a secondary position. These secondary hydroxyls were not converted to an azide functional group through this one-pot method. The secondary hydroxyls **3** and **4** formed sulfonate esters **37** and **38** (Equations 50 and 51). S_N2 reactions are slower at secondary positions due to steric crowding, and the formation of an azide is not seen in the examples studied here. The ^{1}H NMR data of column-purified products **37** and **38** clearly show signals in the aromatic region and a singlet at 2.23 ppm for protons *alpha* to a carbonyl of the *N*-acetyl group, which indicates that the sulfonate ester was formed. Mass spectrometry data

clearly shows the expected mass 480.2 *m/z*, which is our calculated mass plus sodium, for both **37** and **38**.



Equation 50.



Equation 51.

Allofuranose derivative **38** was recrystallized and the X-ray crystal gives further evidence for the formation of this sulfonate ester product (Figure 21). The crystal structure of **38** clearly shows the retention of stereochemistry at C-3, and that the protecting groups are still intact.

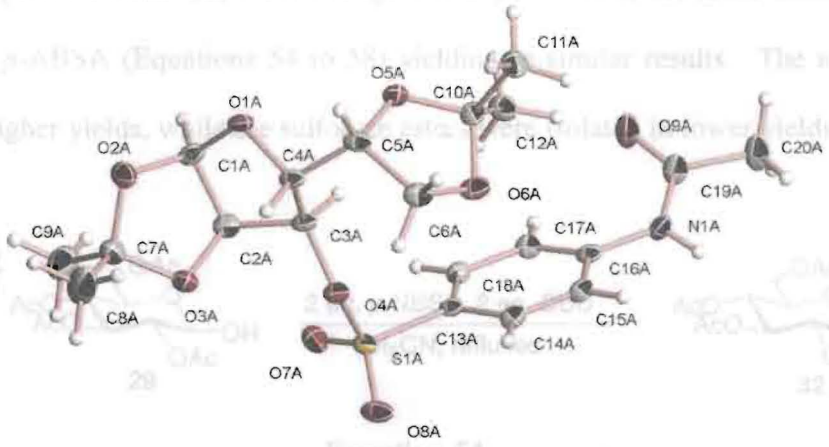
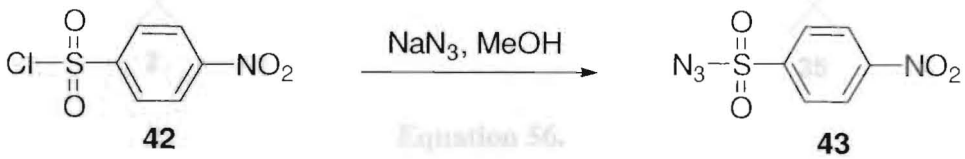


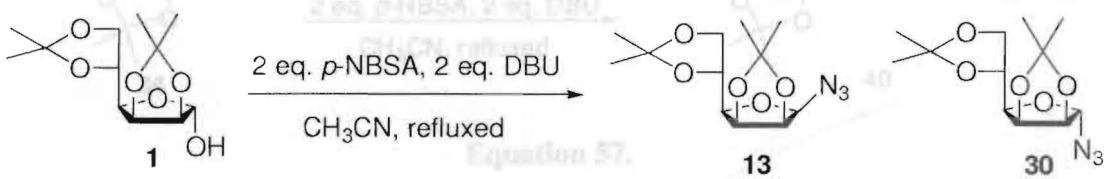
Figure 21: X-Ray crystal structure of allofuranose derivative **38**.

p-Nitrobenzenesulfonyl azide (*p*-NBSA) was also used as a source of azide in hopes of decreasing reaction times and increasing product yields. The *p*-NBSA was synthesized by mixing *p*-nitrobenzenesulfonyl chloride with two equivalents of sodium azide in anhydrous methanol (Equation 52). The trial reaction with *p*-NBSA and mannofuranose **1** showed promising results (Equation 53).



42 **43**

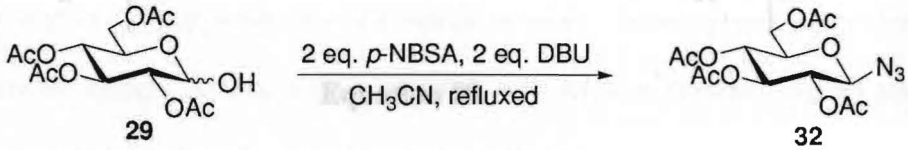
Equation 52.



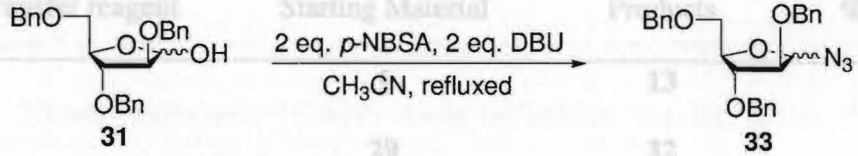
1 **13** **30**

Equation 53.

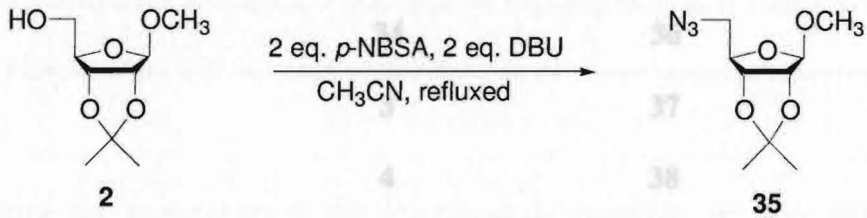
The previous reactions were run again with *p*-NBSA as the azide transfer reagent in place of *p*-ABSA (Equations 54 to 58) yielding in similar results. The azides were formed in higher yields, while the sulfonate esters were isolated in lower yields (Table 2).



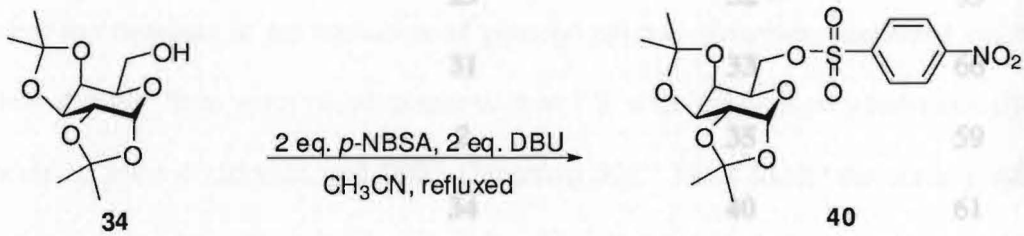
Equation 54.



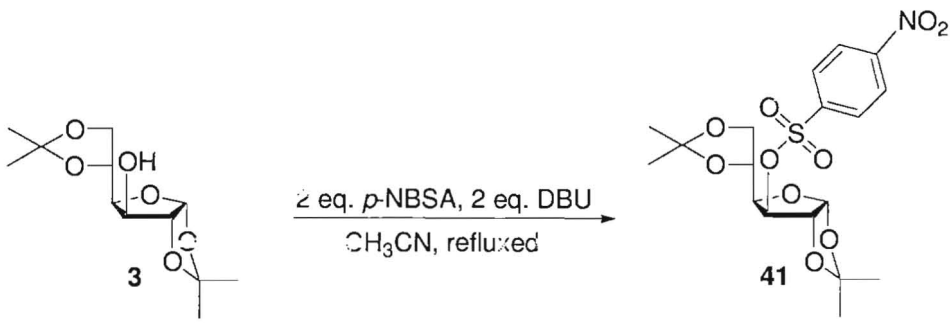
Equation 55.



Equation 56.



Equation 57.



Equation 58.

Table 2: One-pot synthesis of azidodeoxysugars.

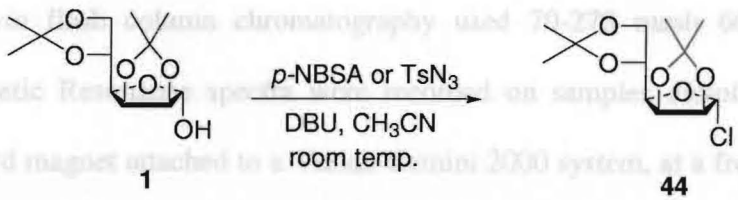
Azide transfer reagent	Starting Material	Products	% Yield
p-ABSA	**1**	**13**	56
	29	**32**	15
	31	**33**	18
	2	**35**	49
	34	**36**	82
	3	**37**	90
	4	**38**	90
p-NBSA	**1**	**13**	44
	29	**32**	33
	31	**33**	66
	2	**35**	59
	34	**40**	61
	3	**41**	25

Spectral data of successfully formed azides matched the literature data. The sulfonate esters **40** and **41** synthesized using *p*-NBSA as the azide transfer reagent had similar spectra to the sulfonate esters **36** and **37**. ^{1}H NMR spectra for sulfonate esters **40** and **41** showed the disappearance of a hydroxyl proton and the appearance of signals in the aromatic region for the newly formed sulfonate ester. Mass spectrometry data of sulfonate ester **40** clearly showed a peak at 468.1 *m/z*, while sulfonate ester **41** clearly showed a peak at 464.1 *m/z*, both of which are the calculated mass plus sodium.

With the success of this preliminary investigation, more research will be done on this one-pot azide synthesis. Future students will be able to use microwave heating to speed up reaction time, in which case different reaction conditions can be more easily explored. Dimethylformamide (DMF) could be another solvent choice if a higher temperature is desired. Also, different bases and azide transfer reagents can be explored more quickly. The ratio of alcohol to transfer reagent and base also needs to be reduced. Also, non-carbohydrate primary alcohols will be explored to find the limitations of this reaction. This reaction will be more useful if it can be run on non-carbohydrate systems as well.

During our exploration of this one-pot azide synthesis, we were interested in seeing if a sulfonate ester at C-1 of a carbohydrate could be isolated since this is the putative intermediate in the formation of glycosyl azides. However, mannosyl chloride **44** was formed from reaction of mannose lactol **1** with either *p*-nitrobenzenesulfonyl chloride or *p*-tosyl chloride and DBU (Equation 59). Most likely the corresponding tosylate is formed but then is displaced by chloride ion; the isolation of only the α-

chloride agrees with other syntheses of this compound in which the α-anomer is thermodynamically favored.[40]



1 44

Equation 59.

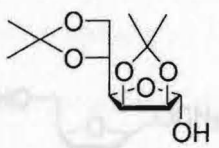
Experimental

General Procedures

Reactions were analyzed by TLC on Whatman aluminum-backed plates. Purifications *via* flash column chromatography used 70-270 mesh 60-Å silica gel. Nuclear Magnetic Resonance spectra were recorded on samples dissolved in $CDCl_3$, using an Oxford magnet attached to a Varian Gemini 2000 system, at a frequency of 400 MHz for ^1H spectra and 100 MHz for ^{13}C spectra. All chemical shifts were recorded in parts per million (ppm). Signals are labeled as follows: s (singlet), d (doublet), dd (doublet of doublets), ddd (doublet of doublet of doublets), m (multiplet) and coupling constants (*J*) are measured in Hertz. All mass spectra were obtained through the use of a Bruker Esquire LC-MS instrument. Infrared spectra were recorded on a Thermo Electron Corporation IR 200 spectrophotometer.

Protecting groups

Synthesis of 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (1) from D-mannose.



1

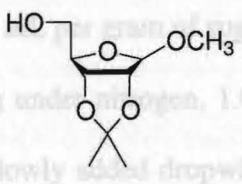
In a flame-dried 2 L Erlenmeyer flask, D-mannose (20.0 g, 0.11 mmol) was dissolved in 750 mL of dry acetone. Concentrated sulfuric acid (7.0 mL) was added in 2 mL portions every 5 min to the solution. A drying tube was connected and the reaction

was stirred at RT until reaction was complete. The reaction was then neutralized with excess sodium carbonate (color lightened) and let stir for 30 min. The reaction was filtered and the filtrate refluxed for 1 h with several grams of sodium carbonate and charcoal. Once cooled, the solution was filtered and evaporated under reduced pressure. The solid residue was recrystalized from methanol to give pure 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (11.2 g, 0.043 mol) (**1**) in 39% yield.

^{1}H NMR: δ 1.31 (s, 3H, -CH_3), 1.37 (s, 3H, -CH_3), 1.44 (s, 3H, -CH_3), 1.45 (s, 3H, -CH_3), 3.35 (d, 1H, -OH, J = 2.6 Hz), 4.02-4.12 (m, 2H, H-6, H-6'), 4.17 (dd, 1H, H-3, J = 3.7, 7.1 Hz), 4.40 (ddd, 1H, H-5, J = 3.9, 5.9, 6.0 Hz,), 4.61 (d, 1H, H-2, J = 6.0 Hz), 4.81 (dd, 1H, H-4, J = 3.7, 5.9 Hz), 5.36 (d, 1H, H-1, J = 2.4 Hz).

Melting point: 120-122 °C

Synthesis of methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (2) from D-ribose.



2

In a flame-dried round bottom flask, dry D-ribose (10.033 g, 33.4 mmol) was dissolved in 200 mL of dry acetone. 2,2-Dimethyoxypropane (20 mL) was added by

syringe, followed by 45 mL of a methanol solution containing 40 mL methanol and 5 mL hydrogen chloride saturated methanol. The reaction was stirred overnight under nitrogen at RT. Pyridine (10 mL) was slowly added to neutralize the reaction (color lightened). The solution was then evaporated under reduced pressure and the resulting residue was partitioned between ethyl acetate (40 mL) and deionized water (100 mL). The aqueous layer was extracted two more times with 40 mL of ethyl acetate. Aqueous NaCl can be added to help separate layers. The organic layer was dried over $MgSO_4$, filtered, and evaporated to give a yellow oil. This oil was purified using a silica gel flash column eluted with 4:1 hexane – ethyl acetate to give 7.89 g (58%) of pure compound **2**.

^{1}H NMR: δ 1.32 (s, 3H, -CH_3), 1.49 (s, 3H, -CH_3), 3.27 (dd, 1H, H-4, J = 2.6, 10.6 Hz), 3.44 (s, 3H, -CH_3), 3.56-3.70 (m, 2H, H-5 and H-5'), 4.44 (s, 1H, -OH), 4.59 (d, 2H, H-2), 4.84 (d, 1H, H-3), 4.98 (s, 1H, H-1).

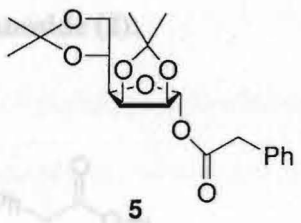
Synthesis of phenacyl ester derivatives

Protected sugars **1-4** (1.0 equivalent), phenylacetic acid (1.1 eq.), and 4-dimethylaminopyridine (0.16 eq.) were added to a flame-dried round-bottom flask and dissolved in anhydrous CH_2Cl_2 (10 mL per gram of sugar) and anhydrous CH_3CN (10 mL per gram of sugar). While stirring under nitrogen, 1.0 M 1,3-dicyclohexylcarbodiimide solution in CH_2Cl_2 (1.1 eq.) was slowly added dropwise resulting in a white precipitate. The reaction mixture was stirred overnight at RT. TLC showed the formation of a spot with a higher R_f value than the starting material in each case. After gravity filtering the mixture, the solvent was removed under reduced pressure and the resultant residue was

dissolved in CH_2Cl_2. The solution was then washed three times with 5% H_2SO_4, followed by two washings with deionized H_2O. After drying with $MgSO_4$, the filtrate was evaporated to give the crude phenacyl ester product.

This general procedure was used for the synthesis of compounds **5**-**8**. In most cases the ^1H NMR spectrum of the crude product was clean, so no further purification was necessary.

2,3:5,6-Di-*O*-isopropylidene-1-*O*-phenacyl-α-D-mannofuranose (5) from 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (1).



5

Prepared from protected mannofuranose **1** (3.049 g, 11.7 mmol), phenylacetic acid (1.756 g, 12.9 mmol), DMAP (0.233 g, 1.9 mmol), and DCC in CH_2Cl_2 (12.9 mL, 12.9 mmol) according to the procedure for the synthesis of ester derivatives described above. TLC (2:1 hexanes – ethyl acetate) showed product at $R_f = 0.51$. The reaction gave 3.99 g of phenacyl ester derivative **5** in 90% yield.

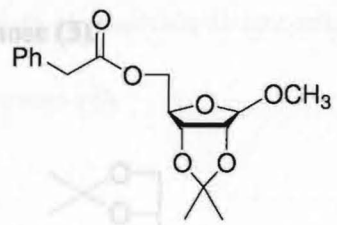
^1H NMR ($CDCl_3$): δ 1.32 (s, 3H, -CH_3), 1.37 (s, 3H, -CH_3), 1.44 (s, 3H, -CH_3), 1.47 (s, 3H, -CH_3), 3.63 (s, 2H, -CH_2-), 3.89 (dd, 1H, H-4, J = 3.7, 8.1 Hz), 3.96 (dd, 1H, H-6, J = 4.2, 8.6 Hz), 4.07 (dd, 1H, H-6', J = 6.2, 8.4 Hz), 4.36 (ddd, 1H,

H-5, J = 4.4, 6.0, 8.1 Hz), 4.66 (d, 1H, H-2, J = 5.5 Hz), 4.81 (dd, 1H, H-3, J = 3.5, 5.7 Hz), 6.13 (s, 1H, H-1), 7.2-7.4 (m, 5H, Ar-H).

^{13}C NMR ($CDCl_3$): δ 25.9, 26.4, 27.1, 28.3, 42.6, 68.0, 73.9, 80.4, 83.4, 86.0, 101.9, 110.4, 114.3, 128.3, 129.7 (double intensity), 130.2 (double intensity), 137.4, 170.8.

Melting point: 70-74 °C

Methyl 2,3-*O*-isopropylidene-5-*O*-phenacyl-β-D-ribofuranoside (6) from methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (2).



6

Prepared from protected ribose **2** (8.0 g, 39.2 mmol), phenylacetic acid (5.876 g, 43.1 mmol), DMAP (0.769 g, 6.3 mmol) and DCC in CH_2Cl_2 (43.1 mL, 43.1 mmol) according to the procedure for the synthesis of ester derivatives described above. TLC (1:1 hexanes – ethyl acetate) showed product at R_f = 0.75. The reaction yielded 11.26 g of phenacyl ester derivative **6** (89% yield).

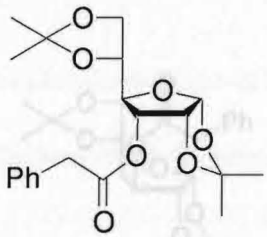
^{1}H NMR: δ 1.31 (s, 3H, -CH_3), 1.49 (s, 3H, -CH_3), 3.26 (s, 3H, -CH_3), 3.66 (s, 2H, -CH_2-), 4.07-4.18 (m, 2H, H-5 and H-5'), 4.38 (t, 1H, H-4, J = 6.9 Hz), 4.56 (d, 1H, H-3, J = 6.2 Hz), 4.62 (d, 1H, H-2, J = 5.8 Hz), 4.96 (s, 1H, H-1), 7.25-7.34 (m, 5H, Ar-H).

^{13}C NMR: δ 26.2, 27.7, 42.4, 56.1, 66.2, 82.9, 85.2, 86.3, 110.5, 113.6, 128.2, 129.6 (double intensity), 130.3 (double intensity), 134.7, 172.0.

MS: Calculated: 322.14 *m/z*, Found: (ESI pos) 345.1 *m/z* ($M+Na^+$).

$[\alpha]_D$= -38.0 °, 150 mg/mL in chloroform.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-phenacyl-α-D-allofuranose (7) from 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (3).



7

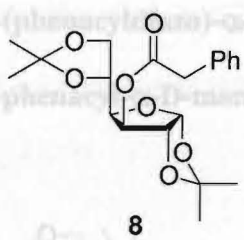
Prepared from protected allofuranose **3** (1.004 g, 3.9 mmol), phenylacetic acid (0.582 g, 4.3 mmol), DMAP (0.085 g, 0.69 mmol), and DCC in CH_2Cl_2 (4.3 mL, 4.3 mmol) according to the procedure for the synthesis of ester derivatives described above.

TLC (1:1 hexanes – ethyl acetate) showed product at $R_f = 0.65$. The reaction resulted in 1.025 g of phenacyl ester derivative **7** (70% yield).

^{1}H NMR: δ1.32 (s, 6H, 2 x -CH_3), 1.34 (s, 3H, -CH_3), 1.50 (s, 3H, -CH_3), 3.70 (s, 2H, -CH_2-), 3.75 (dd, 1H, H-4, J = 6.0, 8.6 Hz), 3.99 (dd, 1H, H-3, J = 6.8, 8.6 Hz), 4.13 (dd, 1H, H-2, J = 4.4, 8.1 Hz), 4.26 (ddd, 1H, H-5, J = 4.2, 6.0, 10.4 Hz), 4.83-4.87 (m, 2H, H-6 and H-6'), 5.85 (d, 1H, H-1, J = 3.7 Hz), 7.25-7.34 (m, 5H, Ar-H).

^{13}C NMR: δ26.3, 27.4, 27.8, 28.0, 42.1, 66.7, 74.0, 76.0, 78.6, 78.7, 105.2, 110.9, 114.1, 128.2, 129.5 (double intensity), 130.4 (double intensity), 134.4, 171.5.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-phenacyl-α-D-glucofuranose (8) from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (4).



8

Prepared from protected glucose **4** (5.012 g, 19.2 mmol), phenylacetic acid (2.883 g, 21.2 mmol), DMAP (0.382 g, 3.1 mmol) and DCC in CH_2Cl_2 (21.2 mL, 21.2 mmol) according to the procedure for the synthesis of ester derivatives described above. TLC

(3:1 hexanes – ethyl acetate) showed product at $R_f = 0.43$. The reaction gave 6.71 g of phenacyl ester derivative **8** (92% yield).

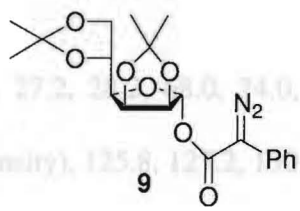
^{1}H NMR: δ 1.26 (s, 3H, -CH_3), 1.28 (s, 3H, -CH_3), 1.39 (s, 3H, -CH_3), 1.51 (s, 3H, -CH_3), 3.67 (s, 2H, -CH_2-), 4.01-3.93 (m, 2H, H-6 and H-6'), 4.08 (ddd, 1H, H-5, J = 5.5, 8.1, 10.9 Hz), 4.18 (dd, 1H, H-4, J = 2.9, 8.1 Hz), 4.42 (d, 1H, H-2, J = 3.7 Hz), 5.27 (d, 1H, H-3, J = 2.9 Hz), 5.82 (d, 1H, H-1, J = 3.7 Hz), 7.25-7.34 (m, 5H, Ar-H).

^{13}C NMR: δ26.4, 27.4, 27.9, 28.0, 42.6, 68.3, 73.4, 77.5, 81.0, 84.3, 106.1, 110.3, 113.4, 128.3, 129.7 (double intensity), 130.2 (double intensity), 134.4, 171.0.

Melting point: 52-54 °C

Synthesis of diazoester sugars

2,3:5,6-Di-*O*-isopropylidene-1-*O*-(phenacyldiazo)-α-D-mannofuranose (9) from 2,3:5,6-Di-*O*-isopropylidene-1-*O*-phenacyl-α-D-mannofuranose (5).



9

A flame-dried round-bottom flask was cooled in a dry ice-acetone bath (-78 °C). To this chilled flask, 1.0 M lithium hexamethyldisilazane (1.16 mL, 1.1 eq.) was added and let chill. Mannofuranosyl ester **5** (0.405 g, 1.0 mmol, 1.0 eq.) in 8 mL of dry THF was added dropwise to the base. This was left to react for 30 min. before *p*-acetamidobenzenesulfonyl azide (0.279 g, 1.1 mmol, 1.1 eq.) in THF (5 mL) was added dropwise. This reaction was allowed to warm to RT. TLC confirmed the complete consumption of starting material, and the appearance of a spot with a slightly higher R_f value (R_f = 0.63 in 2:1 hexanes – ethyl acetate). The reaction mixture was then poured into 50 mL of saturated NH_4Cl, and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were then washed with deionized H_2O (2 x 20 mL). The organic layer was then dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product **9** was purified by flash column (6:1 hexanes – ethyl acetate) to yield 0.146 g of orange syrup in 34% yield.

^{1}H NMR: δ 1.36 (s, 3H, -CH_3), 1.39 (s, 3H, -CH_3), 1.47 (s, 3H, -CH_3), 1.51 (s, 3H, -CH_3), 4.04-4.14 (m, 3H, H-4, H-6, H-6'), 4.43 (ddd, 1H, H-5, J = 4.4, 6.0, 7.8 Hz), 4.78 (d, 1H, H-2, J = 5.9 Hz), 4.89 (dd, 1H, H-3, J = 3.4, 6.0 Hz), 6.32 (s, 1H, H-1), 7.18-7.47 (m, 5H, Ar-H).

^{13}C NMR: δ 26.0, 26.4, 27.2, 28.2, 68.0, 74.0, 80.5, 83.5, 86.2, 102.3, 110.4, 114.4, 125.1 (double intensity), 125.8, 127.2, 130.0 (double intensity), 164.2.

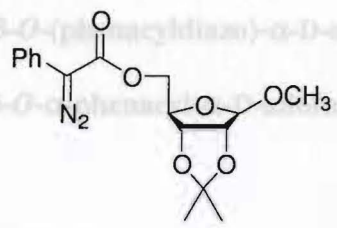
IR absorption: 2095 cm^{-1} for diazo group.

General procedure for other diazoester sugars

In a flame-dried round-bottom flask, phenacyl ester sugar **6-8** (1.0 eq.) and *p*-acetamidobenzenesulfonyl azide (1.0 eq.) were dissolved in dry CH_2Cl_2 (10 mL per gram of sugar) and dry CH_3CN (10 mL per gram of sugar). While stirring at RT, 1,8-diazabicyclo[5.4.0]undec-7-ene (1.1 eq.) was added dropwise over 1-2 h *via* syringe pump producing an orange solution. TLC showed the formation of a spot with a slightly higher R_f value than the starting material. More base and diazo transfer reagent (0.5 eq.) may be added to push the reaction to completion. After stirring for 48 h, the reaction was evaporated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 and washed three times with 5% H_2SO_4, followed two times by deionized H_2O. After drying the organic layers with $MgSO_4$ the filtrate was evaporated to give the crude diazoester sugar. The resulting syrup was purified using a silica gel flash column.

This general procedure was used for the synthesis of compounds **10** to **12**.

Methyl 2,3-*O*-isopropylidene-5-*O*-(phenacyldiazo)-β-D-ribofuranose (10) from methyl 2,3-*O*-isopropylidene-5-*O*-phenacyl-β-D-ribofuranoside (6).



10

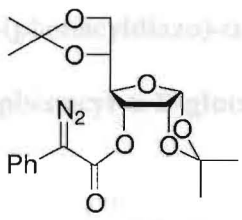
Prepared from ribofuranose-derived phenacylester **6** (1.05 g, 3.2 mmol), *p*-ABSA (0.789 g, 3.3 mmol) and DBU (0.55 mL, 3.6 mmol) according to the general procedure for the synthesis of diazoester sugars above. TLC (3:1 hexanes – ethyl acetate) showed the product at an R_f value of 0.44. The resulting syrup was purified using a silica gel flash column eluted with a 6:1 hexane – ethyl acetate mixture to give 0.559 g of pure product in 67% yield.

^{1}H NMR: δ 1.33 (s, 3H, -CH_3), 1.49 (s, 3H, -CH_3), 3.33 (s, 3H, -CH_3), 4.26 (dd, 1H, H-4, J = 6.2, 10.9 Hz), 4.37-4.46 (m, 2H, H-5 and H-5'), 4.62 (d, 1H, H-3, J = 5.9 Hz), 4.71 (d, 1H, H-2, J = 5.9 Hz), 5.00 (s, 1H, H-1), 7.17-7.49 (m, 5H, Ar-H).

^{13}C NMR: δ 26.2, 27.7, 56.2, 66.0, 82.8, 85.5, 86.4, 110.5, 113.6, 124.9 (double intensity), 126.3, 126.9, 129.9 (double intensity), 165.5.

IR absorption: 2092 cm^{-1} for diazo group.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-(phenacyldiazo)-α-D-allofuranose (11) from 1,2:5,6-di-*O*-isopropylidene-3-*O*-α-phenacyl-α-D-allofuranose (4).



11

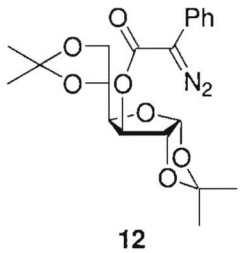
Prepared from allofuranose-derived phenacylester **7** (2.5 g, 6.6 mmol), *p*-ABSA (1.590 g, 6.6 mmol), and DBU (1.10 mL, 7.2 mmol) according to the general procedure for the synthesis of diazoester sugars above. TLC showed the formation of a spot at an R_f value of 0.45 in 2:1 hexanes – ethyl acetate. The resulting syrup was purified using a silica gel flash column eluted with 6:1 hexane – ethyl acetate. The reaction yielded 1.31 g in 49% yield.

^{1}H NMR: δ 1.35 (s, 6H, 2 -CH_3), 1.43 (s, 3H, -CH_3), 1.56 (s, 3H, -CH_3), 3.90 (dd, 1H, H-4, J = 5.3, 8.6 Hz), 4.09 (dd, 1H, H-6, J = 6.6, 8.6 Hz), 4.15 (dd, 1H, H-6', J = 5.9, 8.6 Hz), 4.30 (ddd, 1H, H-5, J = 5.1, 6.6, 10.3 Hz), 4.92 (t, 1H, H-3, J = 4.8 Hz), 5.00 (dd, 1H, H-2, J = 4.9, 8.7 Hz), 5.86 (d, 1H, H-1, J = 4.0 Hz), 7.18-7.50 (m, 5H, Ar-H).

^{13}C NMR: δ 26.2, 27.6, 27.9, 28.0, 67.1, 74.6, 76.4, 78.8, 79.0, 105.3, 111.1, 114.3, 125.0 (double intensity), 126.0, 127.1, 129.9 (double intensity), 165.0.

IR absorption: 2100 cm^{-1} for diazo group.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-(phenacyldiazo)-α-D-glucofuranose (12) from 1,2:5,6-di-*O*-isopropylidene-3-*O*-phenacyl-α-D-glucofuranose (5).



12

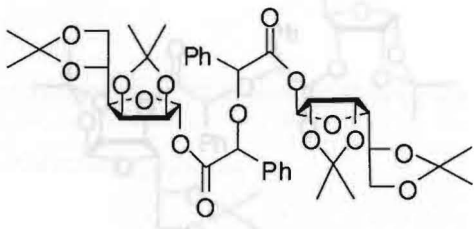
Prepared from glucofuranose-derived phenacylester **7** (2.091 g, 5.5 mmol), *p*-ABSA (1.287 g, 5.4 mmol), and DBU (0.92 mL, 6.0 mmol) according to the general procedure for the synthesis of diazoester sugars above. TLC showed the appearance of a spot at an R_f value of 0.49 in 3:1 hexanes – ethyl acetate. The resulting syrup was purified using a silica gel flash column eluted with 6:1 hexane – ethyl acetate. The reaction yielded 1.45 g of diazo product (65% yield).

^{1}H NMR: δ 1.32 (s, 6H, 2 x -CH_3), 1.42 (s, 3H, -CH_3), 1.54 (s, 3H, -CH_3), 4.02 (dd, 1H, H-6, J = 4.9, 8.8 Hz), 4.10 (dd, 1H, H-6', J = 5.9, 8.4 Hz), 4.19 (ddd, 1H, H-5, J = 5.5, 8.3, 10.8 Hz), 4.27 (dd, 1H, H-4, J = 3.3, 8.1 Hz), 4.67 (d, 1H, H-2, J = 3.7 Hz), 5.38 (d, 1H, H-3, J = 2.9 Hz), 5.91 (d, 1H, H-1, J = 3.7 Hz), 7.19-7.48 (m, 5H, Ar-H).

IR absorption: 2091 cm^{-1} for diazo group.

Rhodium(II)-catalyzed decomposition of diazoester sugars

Rh(II)-catalyzed decomposition of 2,3:5,6-Di-*O*-isopropylidene-1-*O*-(phenacyldiazo)-α-D-mannofuranose (9) to form dimeric ether 14.

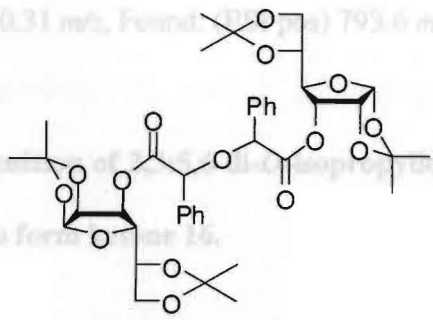


14

In a flame-dried round-bottom flask, rhodium(II) acetate (0.013 g, 0.03 mmol) was stirred in anhydrous CH_2Cl_2 (4 mL) while diazoester **9** (0.097g, 0.239 mmol) was dissolved in anhydrous CH_2Cl_2 (4 mL). After degassing both solutions with N_2, the diazosugar solution was added dropwise to the dirhodium acetate solution over 1 h using a syringe pump. TLC (4:1 hexanes – ethyl acetate) revealed the formation of the product at an R_f value of 0.13. The solution was then filtered with celite and evaporated. The reaction was then purified using a flash column eluted with 4:1 hexanes – ethyl acetate. The isolated solid was then recrystalized using ethanol.

^{1}H NMR: 1.44 (s, 3H, -CH_3), 1.34 (s, 3H, -CH_3), 1.33 (s, 3H, -CH_3), 1.30 (s, 3H, -CH_3), 3.45 (dd, 1H, H-4, J = 3.3, 8.1 Hz), 3.70 (dd, 1H, H-6, J = 4.4, 8.8 Hz), 4.00 (dd, 1H, H-6', J = 6.2, 8.8 Hz), 4.27 (ddd, 1H, H-5, J = 4.4, 6.2, 8.5 Hz), 4.63 (d, 1H, H-2, J = 5.9 Hz), 4.70 (dd, 1H, H-3, J = 3.3, 5.9 Hz), 5.04 (s, 1H, -CH- α to carbonyl), 6.16 (s, 1H, H-1), 7.35-7.42 (m, 5H, Ar-H).

Rh(II)-catalyzed decomposition of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-(phenacyldiazo)-α-D-allofuranose (11) to form dimeric ether 15.



15

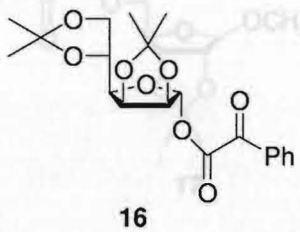
Dirhodium acetate (0.025 g, 0.05 mmol) was stirred in anhydrous CH_2Cl_2 (10 mL) while allofuranose-derived diazo ester **11** (0.400 g, 0.989 mmol) was dissolved in anhydrous CH_2Cl_2 (10 mL). Diazosugar **11** was added dropwise to the dirhodium acetate solution over 1 h using a syringe pump. TLC showed a spot with an R_f value of 0.08 in 3:1 hexanes – ethyl acetate. The reaction was purified using a flash column eluted with 3:1 hexanes – ethyl acetate and recrystalized using ethanol. The reaction gave 0.22 g of product in 58% yield.

^{1}H NMR: 1.19 (s, 3H, -CH_3), 1.26 (s, 3H, -CH_3), 1.32 (s, 3H, -CH_3), 1.48 (s, 3H, -CH_3), 3.42 (dd, 1H, H-6, *J* = 6.6, 8.8 Hz), 3.78 (dd, 1H, H-6', *J* = 6.7, 8.6 Hz), 4.07 (dd, 1H, H-2, *J* = 3.7, 8.4 Hz), 4.16 (ddd, 1H, H-5, *J* = 3.6, 6.8, 10.4 Hz), 4.82 (dd, 1H, H-3, *J* = 5.1, 8.4 Hz), 4.87 (dd, 1H, H-4, *J* = 4.0, 5.1 Hz), 5.13 (s, 1H, -CH-), 5.82 (d, 1H, H-1, *J* = 3.7 Hz), 7.35-7.51 (m, 5H, Ar-H).

^{13}C NMR: δ26.3, 27.2, 27.9, 28.1, 66.2, 74.1, 75.6, 78.6, 78.7, 80.0, 105.2, 110.8, 114.1, 128.8 (double intensity), 129.6 (double intensity), 130.0, 136.1, 170.3.

MS: Calculated: 770.31 *m/z*, Found: (ESI pos) 793.6 *m/z* ($M+Na^+$).

Rh(II)-catalyzed decomposition of 2,3:5,6-di-*O*-isopropylidene-1-*O*-(phenacyldiazo)-α-D-mannofuranose (9) to form ketone 16.



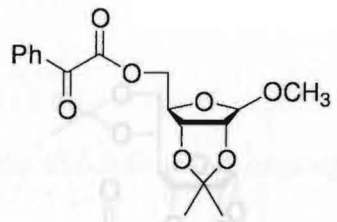
16

In a flame-dried round-bottom flask, dried rhodium(II) acetate (tip of spatula, ~5 mg) was stirred in freshly distilled CH_2Cl_2 (45 mL). Diazo ester **9** (0.140 g, 0.346 mmol) was dissolved in distilled CH_2Cl_2 (5 mL). After degassing both solutions with N_2, the diazosugar solution was added dropwise to the dirhodium acetate solution over 20 h using a syringe pump. TLC showed a spot with an R_f value of 0.58 in 2:1 hexanes – ethyl acetate. The solution was then evaporated and purified using a flash column eluted with 4:1 hexanes – ethyl acetate. The resulting solid was recrystalized using methanol to give 0.030 g of ketone **16** in 22% yield.

^{1}H NMR: 1.37 (s, 3H, -CH_3), 1.39 (s, 3H, -CH_3), 1.45 (s, 3H, -CH_3), 1.52 (s, 3H, -CH_3), 4.06 (dd, 1H, H-4, J = 4.0, 8.8 Hz), 4.10-4.15 (m, 2H, H-6 and H-6'), 4.43

(ddd, 1H, H-5, J = 4.0, 5.8, 7.7 Hz), 4.85 (d, 1H, H-2, J = 5.9 Hz), 4.89 (dd, 1H, H-3, J = 3.7, 5.9 Hz), 6.42 (s, 1H, H-1), 7.53 (t, 2H, Ar-H, J = 7.9 Hz), 7.68 (t, 1H, Ar-H, J = 7.5 Hz), 8.00 (d, 2H, Ar-H, J = 8.5 Hz).

Rh(II)-catalyzed decomposition of methyl 2,3-*O*-isopropylidene-5-*O*-(phenacyl-diazo)-β-D-ribofuranose (10) to form ketone 17.



17

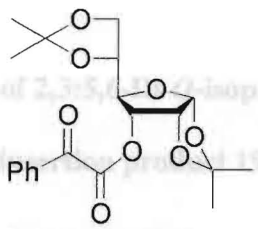
Dried rhodium(II) acetate (0.030 g, 0.067 mmol) was stirred in freshly distilled CH_2Cl_2 (40 mL) while diazo ester **10** (0.740 g, 2.13 mmol) was dissolved in distilled CH_2Cl_2 (18 mL). After degassing both solutions with N_2, the diazosugar solution was added dropwise to the dirhodium acetate solution over 15 h using a syringe pump. TLC showed a spot with an R_f value of 0.36 in 3:1 hexanes – ethyl acetate. A flash column was eluted with 3:1 hexanes – ethyl acetate to give 0.124 g of ketone **17** in 17% yield.

^{1}H NMR: δ 1.32 (s, 3H, -CH_3), 1.49 (s, 3H, -CH_3), 3.34 (s, 3H, -CH_3), 4.36-4.44 (m, 2H, H-5 and H-5'), 4.50 (dd, 2H, H-4, J = 1.1, 7.5 Hz,), 4.63 (d, 1H, H-3, J = 5.9 Hz), 4.72 (d, 1H, H-2, J = 5.9 Hz), 5.01 (s, 1H, H-1), 7.50 (t, 2H, Ar-H, J = 7.8 Hz), 7.65 (t, 1H, Ar-H, J = 7.5 Hz), 8.00 (d, 2H, Ar-H, J = 8.4 Hz).

^{13}C NMR: δ 26.1, 27.6, 56.3, 67.2, 82.7, 84.8, 86.2, 110.7, 113.8, 130.0 (double intensity), 131.1(double intensity), 133.4, 136.1, 164.3, 186.7.

MS: Calculated: 336.12 *m/z*, Found: (ESI pos) 359.1 *m/z* ($M+Na^+$).

Rh(II)-catalyzed decomposition of 1,2:5,6-di-*O*-isopropylidene-3-*O*-(phenacyldiazo)-α-D-allofuranose (11) to form ketone 18.



18

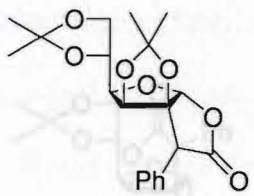
Dried rhodium(II) acetate (0.032 g, 0.07 mmol) was stirred in freshly distilled CH_2Cl_2 (15 mL) while allofuranose diazoester **11** (0.51 g, 1.26 mmol) was dissolved in distilled CH_2Cl_2 (13 mL). Diazosugar **11** was added dropwise to the dirhodium acetate solution over 14 h using a syringe pump. TLC (1:1 hexanes – ethyl acetate) showed the formation of product2 at R_f = 0.56. The solution was then filtered with celite and evaporated. The residue was then purified using a flash column eluted with 3:1 hexanes – ethyl acetate mixture to give 0.27 g of ketone **18** (55% yield).

^{1}H NMR: δ 1.36 (s, 3H, -CH_3), 1.39 (s, 3H, -CH_3), 1.41 (s, 3H, -CH_3), 1.53 (s, 3H, -CH_3), 3.9 (dd, 1H, H-6, J = 5.5, 8.8 Hz), 4.08 (dd, 1H, H-6', J = 6.6, 8.8 Hz),

4.24 (dd, 1H, H-4, J = 4.5, 8.3 Hz), 4.35 (ddd, 1H, H-5, J = 5.3, 6.7, 10.0 Hz), 5.02 (dd, 1H, H-2, J = 3.8, 5.3 Hz), 5.09 (dd, 1H, H-3, J = 5.3, 8.3 Hz), 5.91 (d, 1H, H-1, J = 3.7 Hz), 7.51 (t, 2H, *meta* Ar-H, J = 7.7 Hz), 7.67 (t, 1H, *para* Ar-H, J = 7.5 Hz), 8.09 (d, 2H, *ortho* Ar-H, J = 8.6 Hz).

^{13}C NMR: δ 26.2, 27.5, 27.8, 28.2, 66.91, 75.2, 76.1, 78.6, 79.0, 105.5, 111.2, 114.5, 129.9 (double intensity), 131.4 (double intensity), 133.3, 136.2, 163.8, 186.5.

Rh(II)-catalyzed decomposition of 2,3:5,6-Di-*O*-isopropylidene-1-*O*-(phenacyldiazo)-α-D-mannofuranose (9) to form insertion product 19.



19

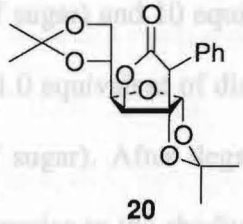
In a flame-dried round-bottom flask, the tip of a spatula (~ 4 mg) of rhodium(II) acetate was stirred in freshly distilled CH_2Cl_2 (40 mL). Diazo ester **19** (0.410 g, 1.01 mmol) was dissolved in distilled CH_2Cl_2 (4 mL). After degassing both solutions with N_2, the diazosugar solution was added dropwise to the dirhodium acetate solution over 16 h using a syringe pump. TLC (2:1 hexanes – ethyl acetate) showed the formation of product with R_f value of 0.56. The solution was then evaporated and purified using a

flash column eluted with 5:1 petroleum ether – ethyl acetate. The isolated solid was then recrystalized using ethyl acetate and hexanes, by the diffusion method, to give 0.060 g of the branched-chain sugar **19** in 16% yield.

^{1}H NMR: δ 1.16 (s, 3H, -CH_3), 1.33 (s, 3H, -CH_3), 1.39 (s, 3H, -CH_3), 1.46 (s, 3H, -CH_3), 4.00-4.37 (m, 5H, H-3, H-4, H-5, H-6, H-6'), 4.34 (s, 1H, -CH- α to carbonyl), 5.86 (s, 1H, H-1), 7.15-7.42 (m, 5H, Ar-H).

MS: Calculated: 376.15 *m/z*, Found: (ESI pos) 399.1 *m/z* ($M+Na^+$).

Rh(II)-catalyzed decomposition of 1,2:5,6-di-*O*-isopropylidene-3-*O*-(phenacyl-diazo)-α-D-glucofuranose (12) to form insertion product 20.



20

Dirhodium acetate (0.020 g, 0.04 mmol) was stirred in anhydrous CH_2Cl_2 (10 mL) while glucofuranose-derived diazoester **12** (0.390 g, 0.96 mmol) was dissolved in anhydrous CH_2Cl_2 (10 mL). The solution of diazosugar **12** was added dropwise to the dirhodium acetate solution over 1 h using a syringe pump. TLC showed a spot with an R_f value of 0.22 in 4:1 hexanes – ethyl acetate. The reaction mixture was filtered through

celite and purified using a flash column eluted with 4:1 hexanes – ethyl acetate. The purification gave 0.070 g of product (19% yield).

^{1}H NMR: δ 1.27 (s, 3H, -CH_3), 1.38 (s, 3H, -CH_3), 1.44 (s, 3H, -CH_3), 1.47 (s, 3H, -CH_3), 3.96 (s, 1H, -CH- α to carbonyl), 4.05 (dd, 1H, H-6, J = 4.4, 8.8 Hz), 4.17 (dd, 1H, H-6', J = 6.2, 8.8 Hz), 4.27 (dd, 1H, H-4, J = 2.6, 8.4 Hz), 4.42 (ddd, 1H, H-5, J = 4.6, 6.0, 10.1 Hz), 4.91 (d, 1H, H-3, J = 2.7 Hz), 5.82 (s, 1H, H-1), 7.17-7.41 (m, 5H, Ar-H).

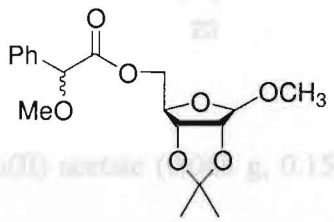
MS: Calculated: 376.15 *m/z*, Found: (ESI pos) 399.2 *m/z* ($M+Na^+$).

Rhodium(II)-catalyzed decomposition of diazoesters in the presence of alcohols

In a flame-dried 100 mL round-bottom flask, rhodium(II) acetate was suspended in dry CH_2Cl_2 (20 mL per gram of sugar) and 10 equivalents of dry alcohol were added. In a separate round-bottom flask, 1.0 equivalent of diazosugar **10** or **11** was dissolved in dry CH_2Cl_2 (20 mL per gram of sugar). After degassing both solutions with N_2, the diazosugar solution was added dropwise to the rhodium(II) acetate solution over a 4-5 h period using a syringe pump. The solution was let stir overnight after which time the TLC showed complete consumption of the starting material and the appearance of a spot with a lower R_f value. The solution was then filtered with celite and evaporated. The reaction was then purified using a flash column.

This general procedure was used to synthesize compounds **21**-**27**.

Methyl 2,3-*O*-isopropylidene-5-*O*-(2-methoxy-2-phenylacetyl)-β-D-ribofuranosides (21) from methyl 2,3-*O*-isopropylidene-5-*O*-(phenacyldiazo)-β-D-ribofuranoside (10).

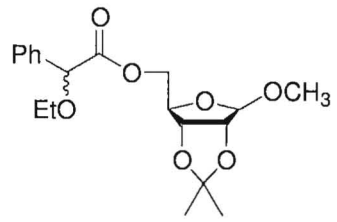


21

Prepared using rhodium(II) acetate (0.068 g, 0.15 mmol), dry methanol (1.3 mL), and ribofuranose-derived diazoester **10** (1.095 g, 3.14 mmol) according to the general procedure above. The reaction was then purified using a flash column, eluted with a 4:1 hexanes – ethyl acetate mixture, to give 0.83 g (75%) of stereoisomers **21**.

^{1}H NMR: δ 1.27, 1.45 (m, 6 H, 2 x -CH_3 protecting group), 3.12, 3.23 (2s, 3H, -OCH_3 protecting group), 3.40 (s, 3H, -OCH_3 methyl group), 4.00-4.55 (multiplets, 5H, H-2, H-3, H-4, H-5, H-5'), 4.80 (s, 1H, -CH- α to C=O), 4.91, 4.92 (2s, 1H, H-1), 7.31-7.48 (m, 5H, Ar-H).

Methyl 2,3-*O*-isopropylidene-5-*O*-(2-ethoxy-2-phenylacetyl)-β-D-ribofuranosides (22) from methyl 2,3-*O*-isopropylidene-5-*O*-(phenacyldiazo)-β-D-ribofuranoside (10).



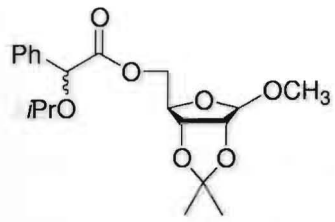
22

Prepared using rhodium(II) acetate (0.068 g, 0.15 mmol), dry ethanol (1.7 mL), and ribofuranose-derived diazoester **10** (1.013 g, 2.91 mmol) according to the general procedure above. The reaction mixture was then purified using a flash column, eluted with a 4:1 hexanes – ethyl acetate mixture, to give 0.85 g (80%) of product mixture **22**.

^{1}H NMR: δ1.27-1.45 (m, 9 H, -CH_3 protecting group and ethyl group), 3.11, 3.23 (2s, 3H, -OCH_3 protecting group), 4.35-4.54 (multiplets, 7H, -CH_2- ethyl group and H-2, H-3, H-4, H-5, H-5'), 4.90 (m, 2H, -CH- α to C=O and H-1), 7.30-7.48 (m, 5H, Ar-H).

MS: Calculated: 366.17 *m/z*, Found: (ESI pos) 389.2 *m/z* ($M+Na^+$).

Methyl 2,3-*O*-isopropylidene-5-*O*-(2-isopropoxy-2-phenylacetyl)-β-D-ribofuranosides (23) from methyl 2,3-*O*-isopropylidene-5-*O*-(phenacyldiazo)-β-D-ribofuranoside (10).



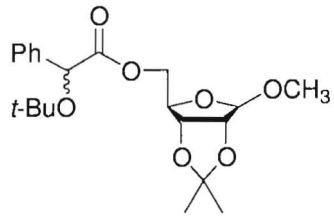
23

Prepared using rhodium(II) acetate (0.04 g, 0.09 mmol), dry isopropanol (1.5 mL), and ribofuranose-derived diazoester **10** (0.641 g, 1.84 mmol) according to the general procedure above. The reaction was then purified using a flash column, eluted with a 5:1 hexanes – ethyl acetate mixture, to give 0.50 g (71%) of stereoisomers **23**.

^{1}H NMR: δ1.27-1.49 (m, 12H, -CH_3 protecting group and isopropyl group), 3.12, 3.24 (2s, 3H, -OCH_3 protecting group), 3.68 (overlapping septet, 1H, -CH- isopropyl group), 4.00-4.53 (multiplets, 5H, H-2, H-3, H-4, H-5, H-5'), 4.91, 4.93 (2s, 1H, H-1), 5.02 (s, 1H, -CH- α to C=O), 7.29-7.48 (m, 5H, Ar-H).

MS: Calculated: 380.18 *m/z*, Found: (ESI pos) 403.2 *m/z* ($M+Na^+$).

Methyl 2,3-*O*-isopropylidene-5-*O*-(2-*t*-butoxy-2-phenylacetyl)-β-D-ribofuranosides (24) from methyl 2,3-*O*-isopropylidene-5-*O*-(phenacyldiazo)-β-D-ribofuranoside (10).

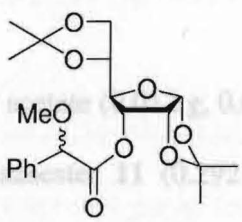


24

Prepared using rhodium(II) acetate (0.075 g, 0.17 mmol), dry *t*-butanol (3.2 mL), and ribofuranose-derived diazoester **10** (1.194 g, 3.42 mmol) according to the general procedure above. The reaction was then purified using a flash column, eluted with a 10:1 hexanes – ethyl acetate mixture, to give 0.563 g (42%) of stereoisomers **24**.

^{1}H NMR: δ 1.22-1.48 (m, 15H, -CH_3 protecting group and *t*-butyl group), 3.15, 3.24 (2s, 3H, -CH_3 protecting group), 4.00-4.54 (multiplets, 5H, H-2, H-3, H-4, H-5, H-5'), 4.94, 4.92 (2s, 1H, H-1), 5.10 (s, 1H, -CH- α to C=O), 7.26-7.48 (m, 5H, Ar-H).

1,2:5,6-Di-*O*-isopropylidene-3-*O*-(2-methoxy-2-phenylacetyl)-α-D-allofuranoses (25) from 1,2:5,6-di-*O*-isopropylidene-3-*O*-(phenacyldiazo)-α-D-allofuranose (11)



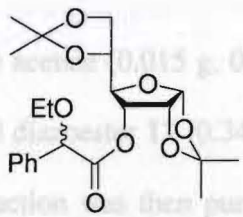
25

Prepared using rhodium(II) acetate (0.034 g, 0.07 mmol), anhydrous methanol (0.55 mL), and allofuranose-derived diazoester **11** (0.548 g, 1.36 mmol) according to the general procedure above. The reaction was then purified using a flash column, eluted with a 6:1 hexanes – ethyl acetate mixture, to give 0.33 g (59%) of products **25**.

^{1}H NMR: δ 1.13-1.48 (m, 12H, -CH_3 protecting groups), 3.42, 3.45 (2s, 3H, -CH_3 methyl group), 3.80-4.89 (multiplets, 7H, -CH- α to C=O and H-2, H-3, H-4, H-5, H-6, H-6'), 5.79, 5.81 (2d, 1H, H-1, J = 4.0, 3.6 Hz), 7.32-7.46 (m, 5H, Ar-H).

MS: Calculated: 408.18 *m/z*, Found: (ESI pos) 431.2 *m/z* ($M+Na^+$).

1,2:5,6-Di-*O*-isopropylidene-3-*O*-(2-ethoxy-2-phenylacetyl)-α-D-allofuranoses (26) from 1,2:5,6-di-*O*-isopropylidene-3-*O*-(phenacyldiazo)-α-D-allofuranose (11)



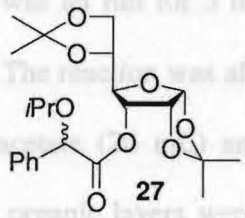
26

Prepared using rhodium(II) acetate (0.012 g, 0.03 mmol), anhydrous ethanol (0.55 mL), and allofuranose-derived diazoester **11** (0.292 g, 0.72 mmol) according to the general procedure above. The reaction was then purified using a flash column, eluted with a 6:1 hexanes – ethyl acetate mixture, to give 0.13 g (43%) of products **26**.

^{1}H NMR: δ1.13-1.48 (m, 15H, -CH_3 protecting group and ethyl group), 3.38-4.89 (multiplets, 8H, -CH_2- ethyl group and H-2, H-3, H-4, H-5, H-6, H-6'), 4.92, 4.93 (2s, 1H, -CH- α to C=O), 5.79, 5.81 (2d, 1H, H-1, J = 4.0, 3.6 Hz), 7.30-7.48 (m, 5H, Ar-H).

MS: Calculated: 422.19 *m/z*, Found: (ESI pos) 445.2 *m/z* ($M+Na^+$).

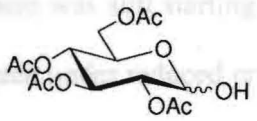
1,2:5,6-Di-*O*-isopropylidene-3-*O*-(2-isopropoxy-2-phenylacetyl)-α-D-allofuranoses (27) from 1,2:5,6-di-*O*-isopropylidene-3-*O*-(phenacyldiazo)-α-D-allofuranose (11).



Prepared using rhodium(II) acetate (0.015 g, 0.03 mmol), anhydrous isopropanol (0.6 mL), and allofuranose-derived diazoester **11** (0.349 g, 0.863 mmol) according to the general procedure above. The reaction was then purified using a flash column, eluted with a 6:1 hexanes – ethyl acetate mixture, to give 0.154 g (41%) of products **27**.

^{1}H NMR: δ1.15-1.45 (m, 18H, -CH_3 protecting group and isopropyl group), 3.39-4.89 (multiplets, 7H, -CH- isopropyl group and H-2, H-3, H-4, H-5, H-6, H-6'), 5.05 (s, 1H, -CH- α to C=O), 5.79, 5.81 (2d, 1H, H-1, J = 4.0, 4.0 Hz), 7.29-7.48 (m, 5H, Ar-H).

Deprotection of 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (28) at C-1 to form 2,3,4,6-tetra-*O*-acetyl-α/β-D-glucopyranose (29).



29

A flame-dried three-neck round-bottom flask was equipped with a reflux condenser and thermometer. β-D-Glucose pentaacetate (0.399 g, 1.0 mmol) was dissolved in DMF (10 mL) and the mixture was brought to 50 °C before hydrazine acetate was added. The reaction was let run for 5 min, after which time TLC showed consumption of starting material. The reaction was allowed to cool to room temperature before being diluted with ethyl acetate (20 mL) and the solution then washed with saturated NaCl (2 x 15 mL). The organic layers were combined, dried over anhydrous $MgSO_4$, filtered, and evaporated to give 0.26 g of tetraacetate **21** in 73% yield.

^{1}H NMR: δ 2.02 (s, 3H, -CH_3), 2.03 (s, 3H, -CH_3), 2.08 (s, 3H, -CH_3), 2.09 (s, 3H, -CH_3), 4.07-4.31 (m, 3H, H-5, H-6, H-6'), 4.90 (dd, 1H, H-2, J = 3.6, 10.2 Hz), 5.08 (t, 1H, H-3, J = 9.5 Hz), 5.46 (d, 1H, H-1, J = 3.6 Hz), 5.53 (t, 1H, H-4, J = 9.9 Hz).

One-pot azide synthesis

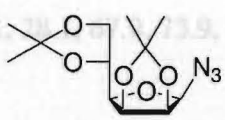
In a flame-dried round-bottom flask, 1.0 equivalent of the sugar with one free hydroxyl group and 2.0 equivalents of *p*-acetamidobenzenesulfonyl azide or 2.0

equivalents of *p*-nitrobenzenesulfonyl azide were dissolved in dry acetonitrile (20 mL per gram of sugar). 2.0 Equivalents of DBU were added to this mixture. The reaction was then refluxed overnight. The progress of the reaction was monitored by TLC and more *p*-ABSA and DBU were added if there was still starting material left. When reaction was complete, the solvent was evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 and washed three times with 5% H_2SO_4 and two times with H_2O. The organic layer was dried over anhydrous $MgSO_4$, filtered, and evaporated. The product was purified by flash column chromatography. This general procedure was used to make the azide and sulfonate ester sugars that follow.

Synthesis of 1-azido-1-deoxy-2,3:5,6-di-*O*-isopropylidene-β- (13) and -α-D-mannofuranose (30) from 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (1).

Prepared from diacetone-D-mannose (**1**) (1.007 g, 3.86 mmol), *p*-ABSA (1.843 g, 7.6 mmol), and DBU (1.16 mL, 7.6 mmol) according to the general procedure described above. The product was purified by flash column (6:1 hexanes – ethyl acetate), to give 0.62 g of azide **13** and **30** in 56% total yield.

1-Azido-1-deoxy-2,3:5,6-di-*O*-isopropylidene-β-D-mannofuranose (13)



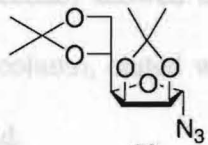
13

^{1}H NMR: δ 1.37 (s, 3H, -CH_3), 1.39 (s, 3H, -CH_3), 1.45 (s, 3H, -CH_3), 1.56 (s, 3H, -CH_3), 3.59 (dd, 1H, H-4, J = 3.5, 7.5 Hz), 4.08-4.16 (m, 2H, H-6, H-6'), 4.42 (d, 1H, H-1, J = 3.6 Hz), 4.46 (ddd, 1H, H-5, J = 4.7, 6.2, 7.7 Hz), 4.68 (dd, 1H, H-2, J = 3.4, 6.0 Hz), 4.78 (dd, 1H, H-3, J = 3.5, 6.0 Hz).

^{13}C NMR: δ25.5, 26.3, 26.4, 28.1, 67.8, 73.9, 79.6, 80.6, 82.2, 90.1, 110.2, 114.5.

R_f: 0.49 in 1:1 hexanes – ethyl acetate.

1-Azido-1-deoxy-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (30)



30

^{1}H NMR: δ 1.32 (s, 3H, -CH_3), 1.39 (s, 3H, -CH_3), 1.47 (s, 6H, 2 x -CH_3), 4.02-4.15 (m, 3H, H-4, H-6, H-6'), 4.42 (ddd, 1H, H-5, J = 4.4, 6.2, 7.7 Hz), 4.48 (d, 1H, H-2, J = 5.9 Hz), 4.79 (dd, 1H, H-3, J = 3.5, 6.0 Hz), 5.45 (s, 1H, H-1).

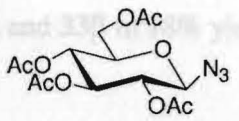
^{13}C NMR: δ25.8, 26.4, 27.1, 28.1, 67.9, 73.9, 80.6, 82.9, 86.1, 96.5, 110.4, 114.2,

MS: Calculated: 285.13 *m/z*, Found: (ESI pos) 308.1 *m/z* ($M+Na^+$).

IR absorption: 2100 cm^{-1} for azide group.

R_f: 0.75 in 1:1 hexanes – ethyl acetate.

Synthesis of 1-azido-1-deoxy-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose (32) from 2,3,4,6-tetra-*O*-acetyl-α/β-D-glucopyranose (29).



32

Prepared from glucopyranose **29** (1.17 g, 3.36 mmol), *p*-ABSA (1.614 g, 6.7 mmol), and DBU (0.88 mL, 5.8 mmol) according to the general procedure described above. TLC (1:1 hexanes – ethyl acetate) showed the formation of product at R_f = 0.5. The product was purified by flash column, eluted with 10:1 hexanes – ethyl acetate, to give 0.116 g of azide **32** in 15% yield.

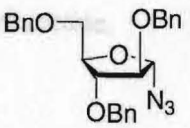
^{1}H NMR: δ 2.01 (s, 3H, -CH_3), 2.03 (s, 3H, -CH_3), 2.08 (s, 3H, -CH_3), 2.11 (s, 3H, -CH_3), 3.79 (ddd, 1H, H-5, J = 2.2, 4.7, 6.9 Hz), 4.17 (dd, 1H, H-6, J = 2.2, 12.5 Hz), 4.27 (dd, 1H, H-6', J = 4.7, 12.4 Hz), 4.65 (d, 1H, H-1, J = 8.8 Hz), 4.96 (t, 1H, H-2, J = 9.2 Hz), 5.11 (t, 1H, H-3, J = 9.9 Hz), 5.22 (t, 1H, H-4, J = 9.5 Hz).

Melting point: 122-124 °C

Synthesis of 2,3,5-tri-*O*-benzyl-α- (33α) and -β- (33β) -D-arabinofuranosyl azides from 2,3,5-tri-*O*-benzyl-β-D-arabinofuranose.

Prepared from arabinofuranose **31** (0.502 g, 1.19 mmol), *p*-ABSA (0.576 g, 2.39 mmol), and DBU (0.58 mL, 3.8 mmol) according to the general procedure described above. The product was purified by flash column, eluted with 2:1 hexanes – ethyl acetate, to give 0.19 g of azide **33α** and **33β** in 18% yield.

2,3,5-Tri-*O*-benzyl-α-D-arabinofuranosyl azide (33α)



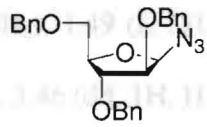
33α

^{1}H NMR: δ3.60 (d, 2H, H-5, H-5', J = 5.1 Hz), 3.90 (dd, 1H, H-2, J = 1.46, 1.83 Hz), 3.97 (dd, 1H, H-3, J = 2.6, 5.5 Hz), 4.36 (dd, 1H, H-4, J = 5.1, 10.6 Hz), 4.43-4.55 (m, 6H, -C$\underline{H}_2$Ph), 5.42 (s, 1H, H-1), 7.24-7.36 (m, 15H, Ar-H).

MS: Calculated: 445.2 *m/z*, Found: (ESI pos) 468.2 *m/z* ($M+Na^+$).

R_f: 0.59 in 4:1 hexanes – ethyl acetate.

2,3,5-Tri-*O*-benzyl-β-D-arabinofuranosyl azide (33β)



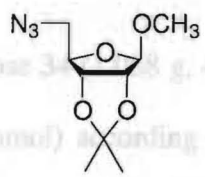
33β

^{1}H NMR: δ 3.59 (d, 2H, H-5, H-5', J = 5.9 Hz), 4.06-4.13 (m, 3H, H-2, H-3, H-4), 4.54-4.65 (m, 6H, 3 x -C$\underline{H}_2$Ph), 5.21 (d, 1H, H-1, J = 4.8 Hz), 7.24-7.37 (m, 15H, Ar-H).

MS: Calculated: 445.2 *m/z*, Found: (ESI pos) 468.2 *m/z* ($M+Na^+$).

R_f: 0.55 in 4:1 hexanes – ethyl acetate.

Synthesis of methyl 5-azido-5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranoside (35) from methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (2).



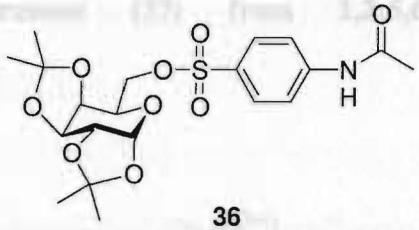
35

Prepared from ribofuranoside **2** (0.416 g, 2.03 mmol), *p*-ABSA (0.989 g, 4.1 mmol), and DBU (0.62 mL, 4.1 mmol) according to the general procedure described above. TLC showed the formation of the product at R_f = 0.31 in 10:1 hexanes – ethyl acetate. The product was purified by flash column eluted with 10:1 hexanes – ethyl acetate, to give 0.23 g of azide **35** in 49% yield.

^{1}H NMR: δ 1.32 (s, 3H, -CH_3), 1.49 (s, 3H, -CH_3), 3.29 (dd, 1H, H-5, J = 6.8, 12.7 Hz), 3.38 (s, 3H, -CH_3), 3.46 (dd, 1H, H-5', J = 7.7, 12.4 Hz), 4.30 (t, 1H, H-4, J = 7.0 Hz), 4.61 (s, 2H, H-2, H-3), 5.00 (s, 1H, H-1).

^{13}C NMR: δ26.2, 27.7, 54.9, 56.5, 83.2, 86.3, 86.6, 110.9, 113.8.

Synthesis of the 6-*O*-(*p*-acetamido)benzenesulfonate ester of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (36) from 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (34).



36

Prepared from galactopyranose **34** (1.088 g, 4.18 mmol), *p*-ABSA (2.036 g, 8.47 mmol), and DBU (0.90 mL, 5.9 mmol) according to the general procedure described above. TLC showed the formation of product at R_f = 0.15 in 1:1 hexanes – ethyl acetate. The product was purified by flash column eluted with 10:1 hexanes – ethyl acetate, to give 1.57 g of sulfonate ester **36** in 82% yield.

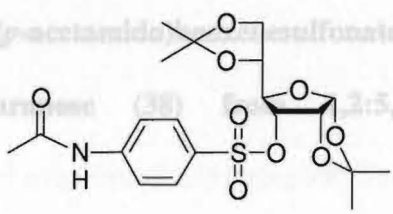
^{1}H NMR: δ 1.27 (s, 3H, -CH_3), 1.29 (s, 3H, -CH_3), 1.32 (s, 3H, -CH_3), 1.35 (s, 3H, -CH_3), 2.23 (s, 3H, -CH_3 α to C=O), 4.07-4.15 (m, 3H, H-6, H-6', H-5), 4.21

(dd, 1H, H-4, J = 4.8, 8.9 Hz), 4.30 (dd, 1H, H-2, J = 2.6, 5.2 Hz), 4.61 (dd, 1H, H-3, J = 5.6, 8.1 Hz), 5.46 (d, 1H, H-1, J = 5.1 Hz), 7.68 (d, 2H, Ar-H, J = 9.1 Hz), 7.81 (d, 2H, Ar-H, J = 9.1 Hz), 7.84 (s, H, N-H).

^{13}C NMR: δ 22.4, 25.5, 26.1, 27.1, 61.7, 67.1, 69.7, 71.4, 71.5, 71.6, 97.2, 110.1, 110.8, 120.4, 130.5, 144.2, 169.9, 172.3.

MS: Calculated: 457.1 *m/z*, Found: (ESI pos) 480.2 *m/z* ($M+Na^+$).

Synthesis of the 3-*O*-(*p*-acetamido)benzenesulfonate ester of 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (37) from 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (3)



37

Prepared from allofuranose **3** (0.303 g, 1.16 mmol), *p*-ABSA (0.564 g, 2.35 mmol), and DBU (0.36 mL, 2.36 mmol) according to the general procedure described above. TLC showed the formation of product at R_f = 0.02 in 1:1 hexanes – ethyl acetate. The product was recrystalized from methanol to give 0.479 g of sulfonate ester **37** in 90% yield.

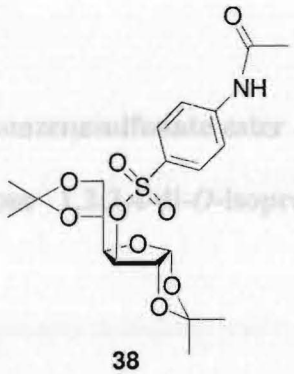
^{1}H NMR: δ 1.29 (s, 9H, 3 x -CH_3), 1.36 (s, 3H, -CH_3), 2.23 (s, 3H, -CH_3 α to C=O), 3.80 (dd, 1H, H-4, J = 6.4, 8.6 Hz), 3.97 (dd, 1H, H-3, J = 6.9, 8.4 Hz), 4.15 (dd, 1H, H-2, J = 4.2, 7.5 Hz), 4.21 (ddd, 1H, H-5, J = 4.2, 6.6, 10.6 Hz), 4.66 (m, 2H, H-6 and H-6'), 5.77 (d, 1H, H-1, J = 3.3 Hz), 7.70 (d, 2H, Ar-H, J = 8.8 Hz), 7.80 (s, H, N-H), 7.89 (d, 2H, Ar-H, J = 9.2 Hz).

^{13}C NMR: δ26.1, 26.3, 27.4, 27.8, 27.9, 66.4, 75.8, 77.8, 78.2, 79.0, 104.9, 111.1, 114.7, 120.1, 130.7, 131.4, 144.3, 169.7.

MS: Calculated: 457.1 *m/z*, Found: (ESI pos) 480.2 *m/z* ($M+Na^+$).

Melting point: 134-140 °C

Synthesis of the 6-*O*-(*p*-acetamido)benzenesulfonate ester of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (38) from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (4).



38

Prepared from glucofuranose **4** (0.502 g, 1.9 mmol), *p*-ABSA (0.925 g, 3.8 mmol), and DBU (0.59 mL, 3.8 mmol) according to the general procedure described above. TLC showed the formation of product at $R_f = 0.15$ in 1:1 hexanes – ethyl acetate. The product was recrystalized from methanol to give 0.79 g of sulfonate ester **38** in 90% yield.

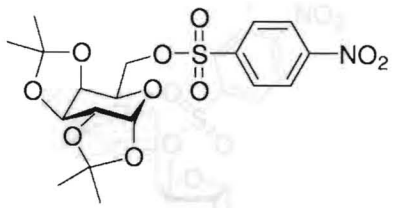
^{1}H NMR: δ 1.18 (s, 3H, -CH_3), 1.21 (s, 3H, -CH_3), 1.32 (s, 3H, -CH_3), 1.49 (s, 3H, -CH_3), 2.24 (s, 3H, -CH_3 α to C=O), 3.89-4.14 (m, 4H, H-4, H-5, H-6, H-6'), 4.77 (d, 1H, H-3, J = 1.8 Hz), 4.85 (d, 1H, H-2, J = 3.7 Hz), 5.92 (d, 1H, H-1, J = 3.7 Hz), 7.62 (s, H, N-H), 7.71 (d, 2H, Ar-H, J = 8.4 Hz), 7.88 (d, 2H, Ar-H, J = 8.1 Hz).

^{13}C NMR: δ26.1, 26.2, 27.5, 27.8, 27.9, 68.2, 72.9, 80.9, 83.3, 84.4, 106.2, 110.3, 113.6, 120.1, 130.8, 130.9, 144.3, 169.7.

MS: Calculated: 457.1 *m/z*, Found: (ESI pos) 480.2 *m/z* ($M+Na^+$).

Melting point: 98-102 °C

Synthesis of the 6-*O*-(*p*-nitro)benzenesulfonate ester of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (40) from 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (34).



40

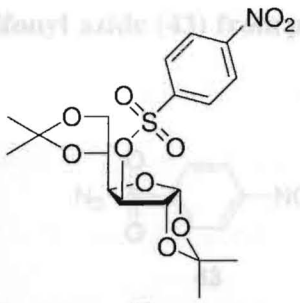
Prepared from galactopyranose **34** (0.43 g, 1.65 mmol), *p*-NBSA (0.765 g, 3.3 mmol), and DBU (0.51 mL, 3.3 mmol) according to the general procedure described above. TLC showed the formation of product at $R_f = 0.67$ in 1:1 hexanes – ethyl acetate. The product was purified by flash column, eluted with 10:1 hexanes – ethyl acetate, to give 0.45 g of sulfonate ester **40** in 61% yield.

^{1}H NMR: δ 1.26 (s, 3H, -CH_3), 1.29 (s, 3H, -CH_3), 1.32 (s, 6H, 2 x -CH_3), 4.15-4.32 (m, 5H, H-3, H-4, H-5, H-6, H-6'), 4.58 (dd, 1H, H-2, J = 2.5, 7.7 Hz), 5.37 (d, 1H, H-1, J = 5.1 Hz), 8.13 (d, 2H, Ar-H, J = 8.8 Hz), 8.37 (d, 2H, Ar-H, J = 8.8 Hz).

^{13}C NMR: δ 25.6, 26.1, 27.1, 27.2, 61.6, 67.1, 71.0, 71.3, 71.6, 97.1, 110.1, 110.8, 125.3, 130.5, 142.7, 151.7.

MS: Calculated: 445.1 *m/z*, Found: (ESI pos) 468.1 *m/z* ($M+Na^+$).

Synthesis of the 6-*O*-(*p*-nitro)benzenesulfonate ester of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (41) from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (4).



41

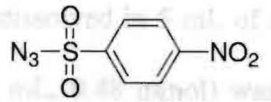
Prepared from glucofuranose **3** (0.51 g, 1.9 mmol), *p*-NBSA (0.901 g, 3.9 mmol), and DBU (0.60 mL, 3.9 mmol) according to the general procedure described above. TLC showed the formation of product at $R_f = 0.73$ in 1:1 hexanes – ethyl acetate. The product was purified by flash column, eluted with 4:1 hexanes – ethyl acetate, to give 0.22 g of sulfonate ester **41** in 25% yield.

^{1}H NMR: δ 1.09 (s, 3H, -CH_3), 1.16 (s, 3H, -CH_3), 1.21 (s, 3H, -CH_3), 1.33 (s, 3H, -CH_3), 3.88-4.11 (m, 4H, H-4, H-5, H-6, H-6'), 4.85 (d, 1H, H-3, J = 2.2 Hz), 4.88 (d, 1H, H-2, J = 3.7 Hz), 5.92 (d, 1H, H-1, J = 3.7 Hz), 8.14 (d, 2H, Ar-H, J = 8.8 Hz), 8.35 (d, 2H, Ar-H, J = 8.8 Hz).

^{13}C NMR: δ 26.2, 27.4, 27.8, 27.9, 61.6, 68.4, 72.7, 80.8, 84.5, 106.2, 110.3, 113.7, 125.2, 130.9, 142.3, 151.9.

MS: Calculated: 445.1 *m/z*, Found: (ESI pos) 464.1 *m/z* ($M+H_3O^+$).

Synthesis of *p*-nitrobenzenesulfonyl azide (43) from *p*-nitrobenzenesulfonyl chloride (42).



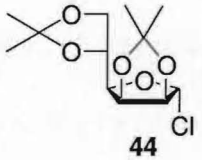
43

p-Nitrobenzenesulfonyl chloride (5.007 g, 22.26 mmol) and sodium azide (2.935 g, 45.12 mmol) were placed in a flame-dried round-bottom flask. Anhydrous methanol (50 mL) was added to dissolve the reagent. The mixture was let stir overnight, and then evaporated under reduced pressure at 40 °C or below. The residue was partitioned between CH_2Cl_2 (40 mL) and H_2O (40 mL). The organic layer was then dried over anhydrous $MgSO_4$, filtered, and evaporated to give 4.7 g of a yellow solid (91 % yield).

^{1}H NMR: δ 8.17 (d, 2H, Ar-H, J = 9.15 Hz), 8.17 (d, 2H, Ar-H, J = 9.15 Hz).

Melting point: 100-102 °C

Synthesis of 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranosyl chloride (44) from 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (1).



44

To a flame-dried 25 mL round-bottom flask, 1.0 equivalent of mannofuranose **1** (0.113 g, 0.43 mmol) and 1.0 equivalents of *p*-nitrobenzenesulfonyl chloride or *p*-tosyl chloride (0.099 g, 0.43 mmol) were dissolved in 5 mL of dry acetonitrile. While stirring at RT, 1.1 equivalents of DBU (1.1 mL, 0.48 mmol) was quickly added dropwise; the reaction changed from yellow to purple. The progress of the reaction was monitored by TLC (1:1 hexanes – ethyl acetate) for the disappearance of starting material and the appearance of a spot with a higher R_f value. The reaction was let run for 48 h before being evaporated. The residue was dissolved in CH_2Cl_2 (10 mL) and washed with 5% H_2SO_4 (3 x 10 mL) and H_2O (2 x 10 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The product was purified by flash column using 6:1 hexanes – ethyl acetate.[40]

^{1}H NMR: δ 1.34 (s, 3H, -CH_3), 1.39 (s, 3H, -CH_3), 1.47 (s, 6H, 2 x -CH_3), 4.02 (dd, 1H, H-6, J = 4.4, 8.8 Hz), 4.10 (dd, 1H, H-6', J = 6.0, 9.0 Hz), 4.21 (dd, 1H, H-4, J = 3.4, 7.9 Hz), 4.43 (ddd, 1H, H-5, J = 4.4, 6.2, 7.7 Hz), 4.88 (dd, 1H, H-3, J = 3.4, 5.6 Hz), 5.95 (d, 1H, H-2, J = 4.9 Hz), 6.08 (s, 1H, H-1).

References

1. Stick, R. V. *Carbohydrates: The Sweet Molecules of Life*, Academic Press: San Diego, 2001.
2. Davis, B. G., Fairbanks, J. F. *Carbohydrate Chemistry*, Oxford University Press: Oxford, 2002.
3. Guthrie, R. D., Honeyman, J. *Carbohydrates: An introduction to the Chemistry of Carbohydrates*, Clarendon Press: Oxford, 1968, 1-5.
4. Osburn, H. M. I. *Carbohydrates*, Academic Press: Amsterdam, 2003.
5. Collins, P. M.; Ferrier, R. J. *Monosacharides: Their Chemistry and Their Roles in Natural Products*, John Wiley & Sons: Chichester, England, 1995, 208-289.
6. Hanessian, S. *Preparative Carbohydrate Chemistry*, Marcel Dekker Inc.: New York, 1997, 207-262.
7. Lopez, J. C.; Lameignere, E.; Burnouf, C.; de Los Angeles Laborde, M.; Ghini, A. A.; Olesker, A.; Lukacs, G., "Efficient routes to pyranosidic homologated conjugated enals and dienes from monosaccharides," *Tetrahedron* **1993**, *49*, 7701-7722.
8. Loustau Cazalet, C., "Nouvelles voies de synthese de lactones bioactives," These, Universite de Nancy, France. 1994.
9. Plaumann, D. E.; Fitzsimmons, B. J.; Richie, B. M.; Fraser-Reid, B., "Synthetic route to 6,8-dioxabicyclo[3.2.1]octyl pheromones from D-glucose derivatives. 4. Synthesis of (-)-α-multistriatin," *J. Org. Chem.* **1982**, *47*, 941-946.

10. Moufid, N.; Chapleur, Y.; Mayon, P., "Radical cyclization of some unsaturated carbohydrate-derived propargyl derivatives," *J. Chem. Soc. Perkins Trans. 1* **1993**, 999.

11. Sarda, P.; Olesker, A.; Lukacs, G., "Synthesis of methyl 2-*C*-acetamidomethyl-2-deoxy-α-D-glucopyranoside and its *manno* isomer," *Carbohydr. Res.* **1992**, *229*, 161-165.

12. Berndt, D. F.; Norris, P., "Intramolecular carbene and nitrene insertion at C-2 of diacetone-D-glucose," *Tetrahedron Lett.* **2002**, *43*, 3961-3962.

13. Patai, S. *The Chemistry of Diazonium and Diazo Groups*, John Wiley & Sons: Chichester, England, 1978.

14. Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides*, John Wiley & Sons Inc.: New York, 1998.

15. Regitz, M.; Hocker, J.; Liedhegener, A., "*t*-Butyl diazoacetate." *Org. Synth. Coll. Vol. 5*, Baumgarten, H. E., Ed.; John Wiley & Sons: New York, 1973.

16. Regitz, M; Ruter, J.; Liedhegerner, A., "2-Diazocycloalkanones: 2-Diazocycloclohexanone," *Org. Synth.* **1971**, *51*, 86-89.

17. McClure, D. E.; Lumma, P. K.; Arison, B. H.; Jones, J. H.; Baldwin, J. J., "1,4-Oxazines *via* intramolecular ring closure of β-hydroxydiazoacetamides: Phenylalanine to tetrahydroindeno[1,2-*b*]-1,4-oxazin-3(2*H*)-ones," *J. Org. Chem.* **1983**, *48*, 2675-2679.

18. Sugihara, Y.; Yamamoto, H.; Mizoue, K.; Murata, I., "Cyclohepta[*a*]phenalene: A highly electron-donating nonalternant hydrocarbon," *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1247-1249.

19. Boyar, E. B.; Robinson, S. D., "Rhodium(II) carboxylates," *Coord. Chem. Rev.* **1983**, *50*, 109-208.

20. Felthouse, T. R., "The chemistry, structure, and metal-metal bonding in compounds of rhodium(II)," *Prog. Inorg. Chem.* **1982**, *29*, 73-166.

21. Wenkert, E.; Davis, L. L.; Mylari, B. L.; Solomon, M. F.; da Silva, R. R.; Shulman, S.; Warnet, R. J.; Ceccherelli, P.; Curini, M.; Pellicciari, R., "Cyclopentanone synthesis by intramolecular carbon-hydrogen insertion of diazoketones. A diterpene-to-steroid skeleton conversion," *J. Org. Chem.* **1982**, *47*, 3242-3247.

22. Ursini, A.; Pellicciari, R.; Tamburini, B.; Carlesso, R.; Gaviraghi, G., "A new synthesis of 6-oxopenicillanates by ozonolysis of 6-diazopenicillanates," *Synthesis* **1992**, 363-364.

23. Aller, E.; Brown, D. S.; Cox, G. G.; Miller, D. J.; Moody, C. J., "Diastereoselectivity in the O-H insertion reactions of rhodium carbenoids derived from phenyldiazoacetates of chiral alcohols. Preparation of α-hydroxy and α-alkoxy esters," *J. Org. Chem.* **1995**, *60*, 4449-4460.

24. Branderhorst, H. M.; Kemmink, J.; Liskamp, R. M. J.; Pieters, R. J., "Catalytic conversions of diazosugars," *Tetrahedron Lett.* **2002**, *43*, 9601-9603.

25. Patai, S. *The Chemistry of the Azido Group*, Interscience Publishers: London, 1971.

26. Brase, S.; Gil, C.; Knepper, K.; Zimmerman, V., "Organic azides: An exploding diversity of a unique class of compounds," *Angew. Chem. Int. Ed.* **2005**, *44*, 5188-5240.

27. Scriven, E. F. V. *Azides and Nitrenes: Reactivity and Utility*, Academic Press Inc.: Orlando, Florida, 1984.

28. Root, Y. Y., "Synthesis of Derivatives of D-ManAcA: Aminosugar component of *S. aureus* Capsular Polysaccharies," Youngstown State University MS Thesis, 2003.

29. Lee, S. H.; Yoon, J.; Chung, S. H.; Lee, Y. S. *Tetrahedron Lett.* **1993**, *34*, 6475-6478.

30. Thompson, A. S.; Humphrey, G. R.; DeMarco, A. M.; Mathre, D. J.; Grabowski, E. J. J., "Direct conversion of activated alcohols to azides using diphenyl phosphorazidate. A practical alternative to Mitsunobu conditions," *J. Org. Chem.* **1993**, *58*, 5886-5888.

31. De Belder, A. N., "Cyclic acetals of the aldoses and aldosides," *Adv. Carbohydr. Chem.* **1965**, *20*, 219-302.

32. De Belder, A. N., "Cyclic acetals of the aldoses and aldosides," *Adv. Carbohydr. Chem. Biochem.* **1977**, *34*, 179-241.

33. Leonard, N. J.; Carraway, K. L., "5-Amino-5-deoxyribose derivatives. Synthesis and use in the preparation of "reversed" nucleosides," *J. Heterocycl. Chem.* **1966**, *3*, 485-489.

34. Steglich, W.; Neises, B., "Simple method for the esterification of carboxylic acids," *Angew. Chem. Int. Ed.* **1978**, *17*, 522-524.

35. Berndt, D. F., "Synthesis and chemistry of new sugar-derived diazoesters and acyl azides," Youngstown State University MS Thesis, 2001.

36. Scoffier, G.; Gagnaire, D.; Utille, J. P., "Coupure selective par l'hydrazine des groupements acetyls anomers de residus glycosyles acetyls," *Carbohydr. Res.* **1975**, *39*,368-373.

37. Miner, P. L., "Synthesis of diverse compounds using mannofuranose as a chiral scaffold," Youngstown State University MS Thesis, 2004.

38. Stimac, A.; Kobe, J., "Stereoselective synthesis of 1,2-*cis*- and 2-deoxyglyco-furanosyl azides form glycosyl halides," *Carbohydr. Res.* **2000**, *329*, 317-324.

39. Brimacombe, J. S.; Minshall, J.; Tucker, L. C. N., "Nucleophilic displacements of methyl 2,3-*O*-isopropylidene-4-*O*-toluene-*p*-sulphonyl-α-D-*lyxo*- and -β-L-*ribo*-pyranosides, and deamination of the corresponding 4-amino sugars," *Carbohydr. Res.* **1976,** *52*, 31-47.

40. Cicchillo, R. M.; Norris, P., "A convenient synthesis of glycosyl chlorides from sugar hemiacetals using triphosgene as the chlorine source," *Carbohydr. Res.* **2000**, *328*, 431-434.

Appendix A

NMR, IR and Mass Spectra

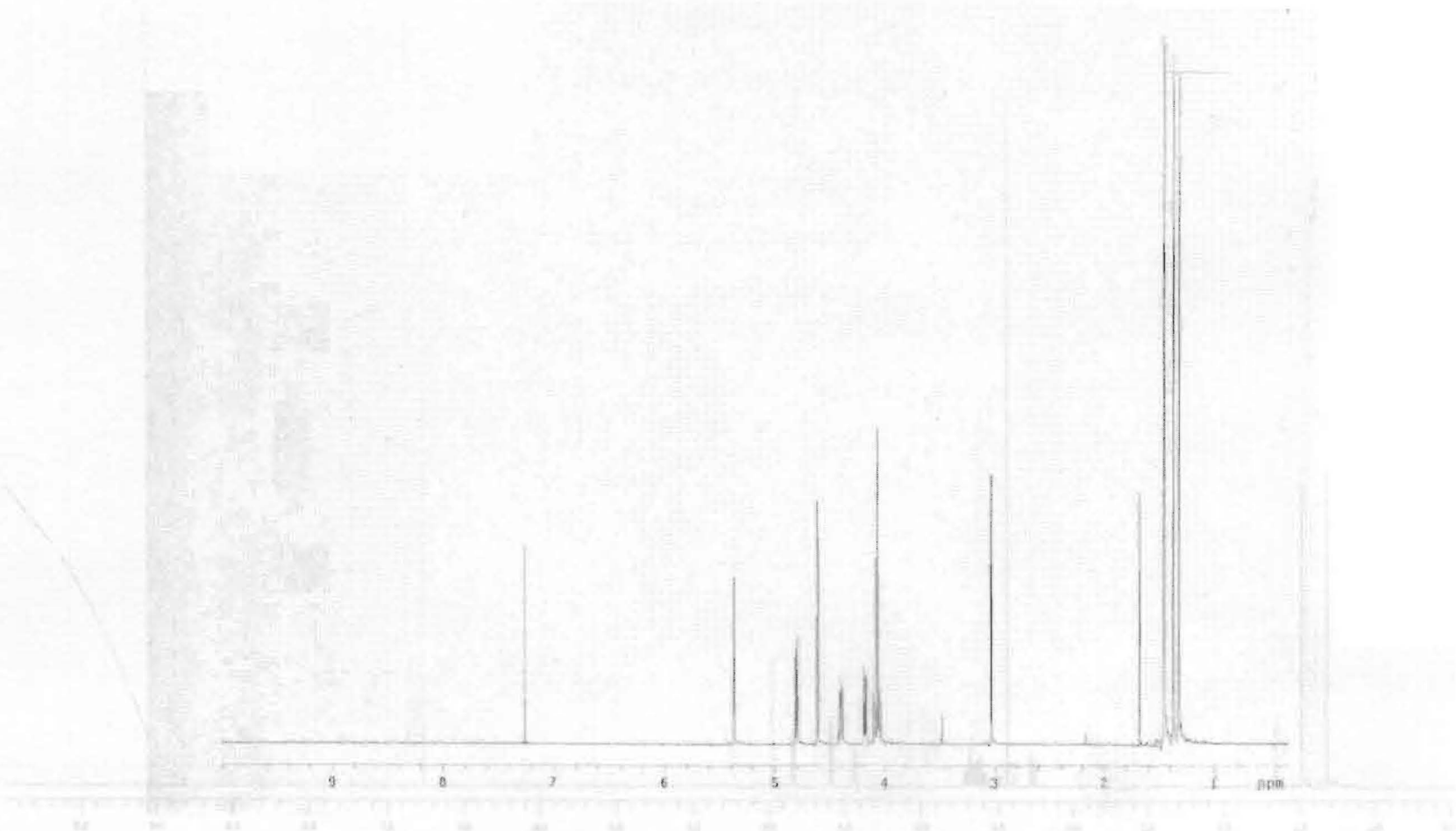


Figure 22: ^{1}H NMR spectrum of 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (**1**).

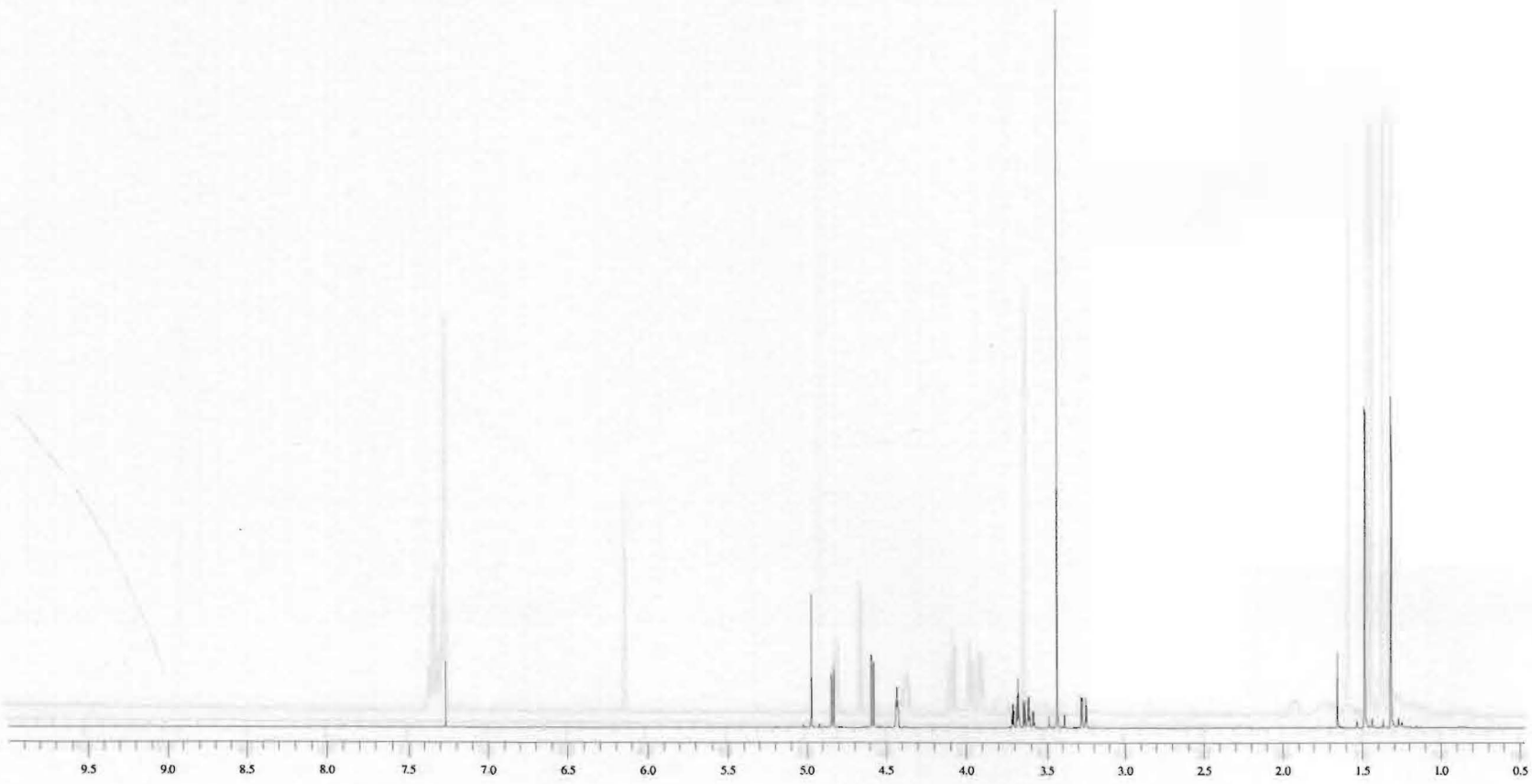


Figure 23: ^{1}H NMR spectrum of methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (**2**).

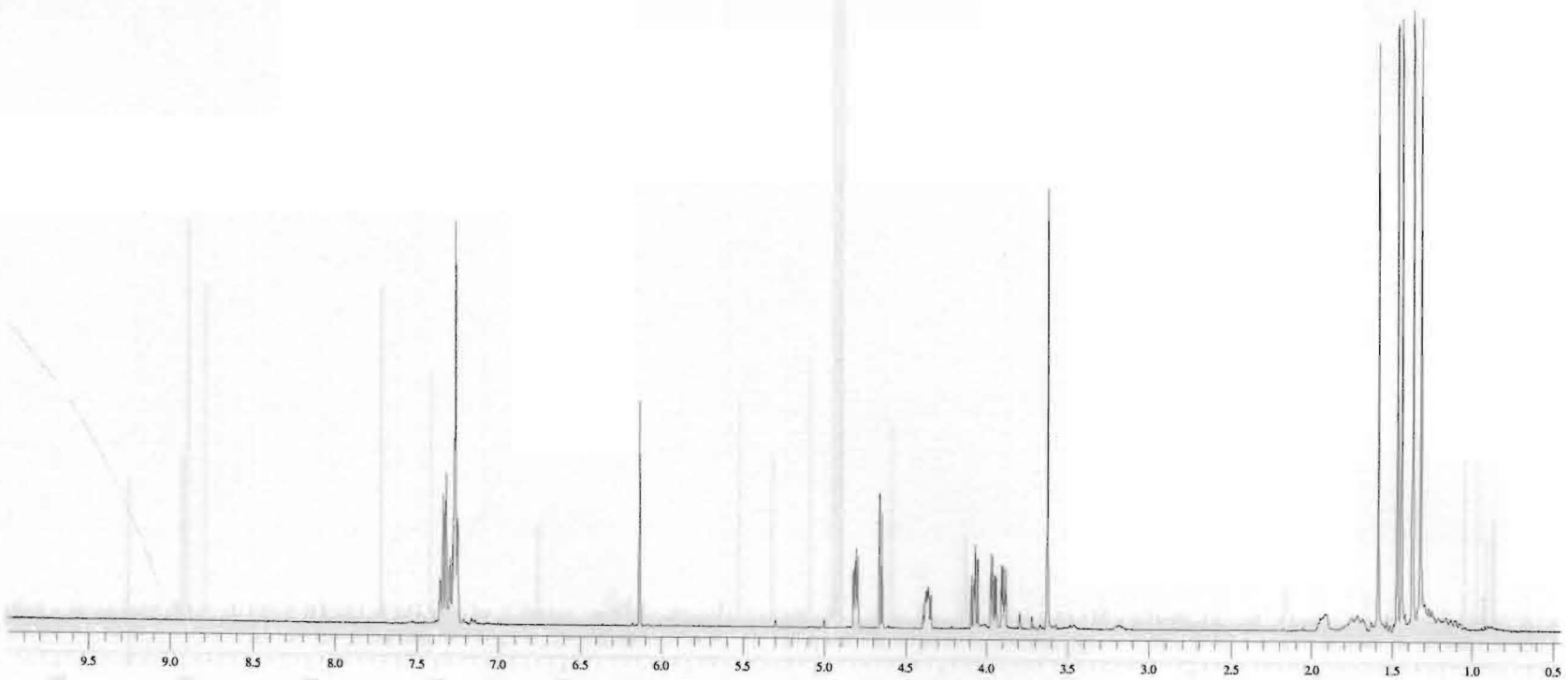


Figure 24: ^{1}H NMR spectrum of 2,3:5,6-di-*O*-isopropylidene-1-*O*-phenacyl-α-D-mannofuranose (**5**).

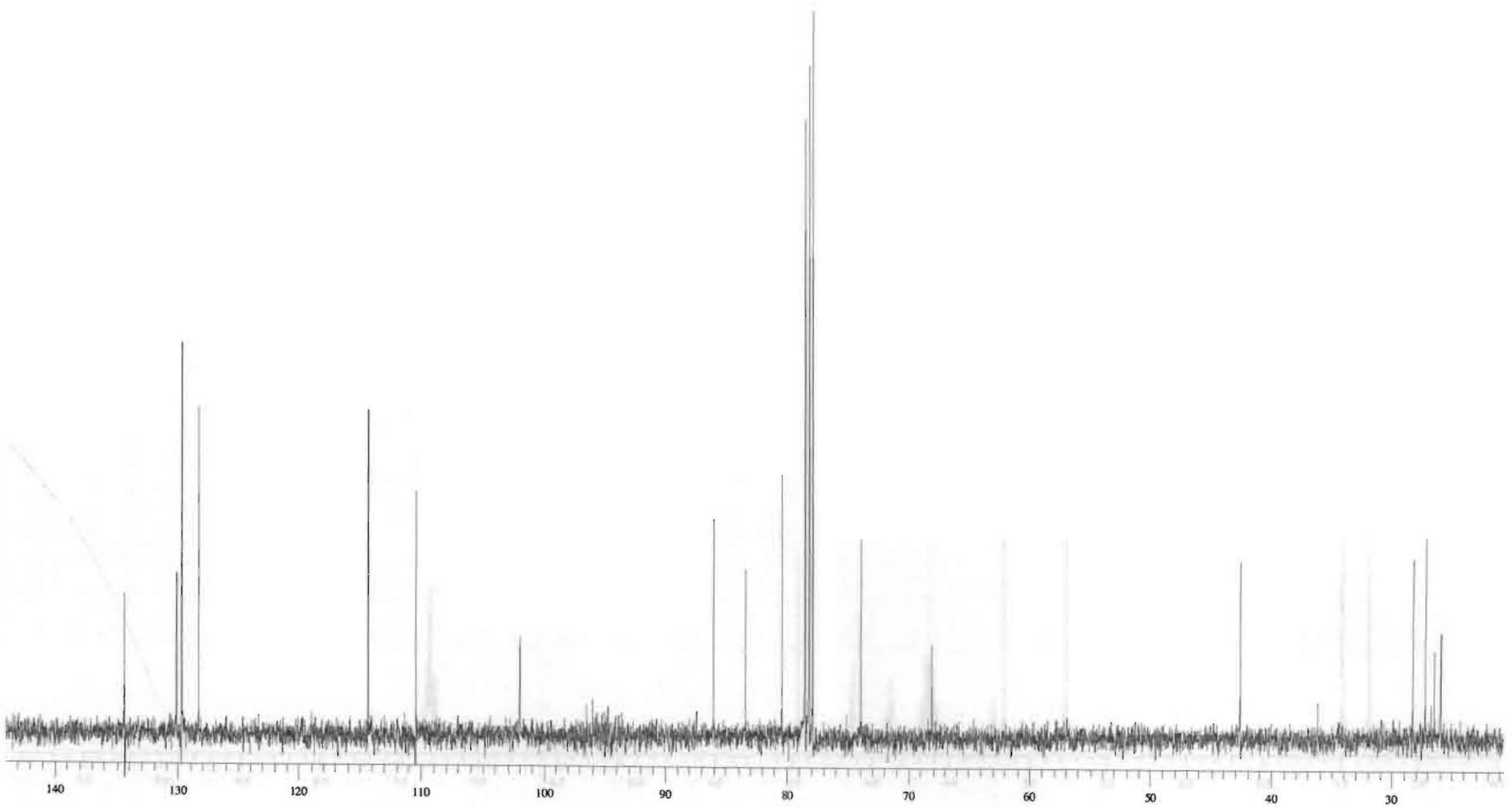


Figure 25: ^{13}C NMR spectrum of 2,3:5,6-di-*O*-isopropylidene-1-*O*-phenacyl-α-D-mannofuranose (**5**).

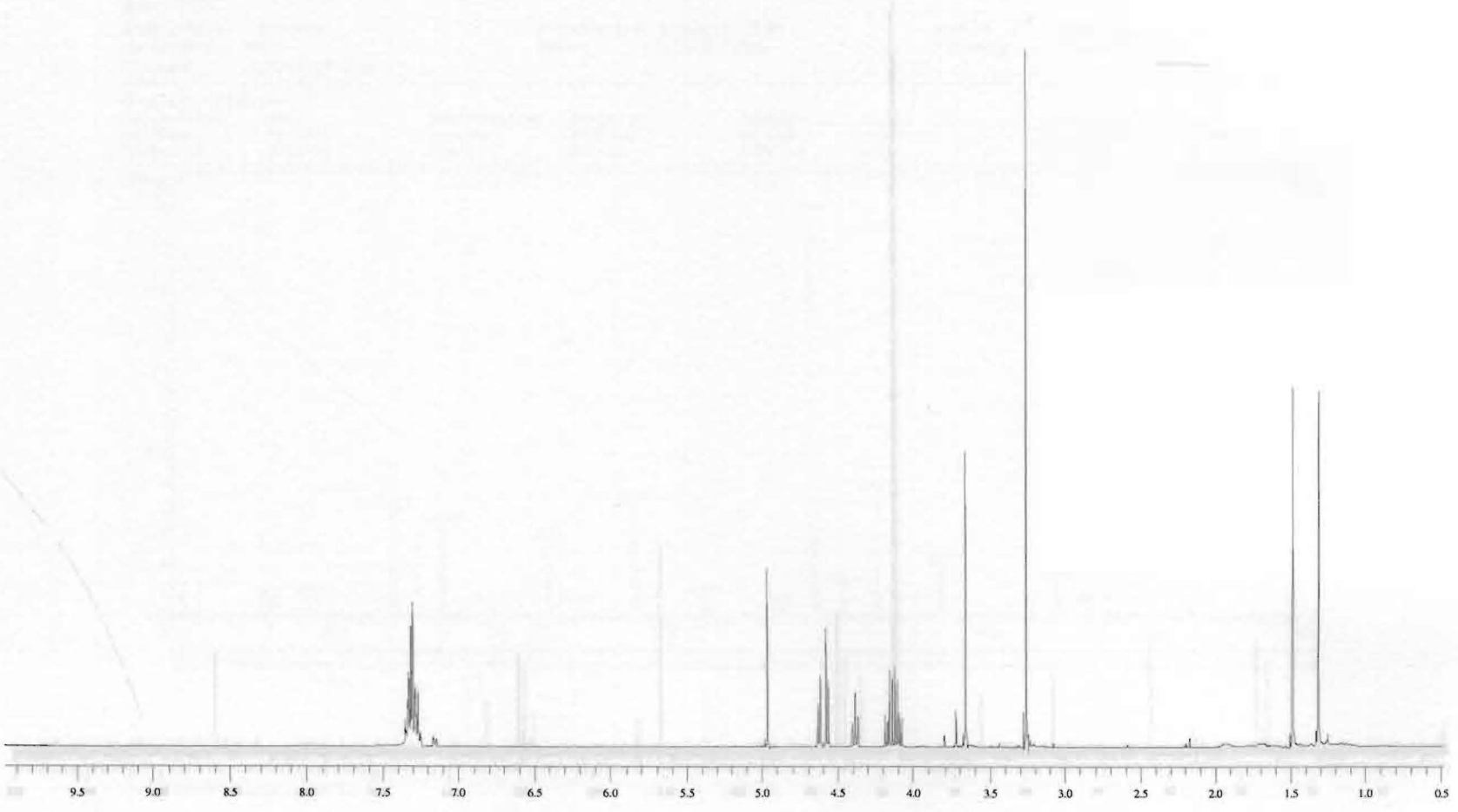


Figure 26: ^{1}H NMR spectrum of methyl 2,3-*O*-isopropylidene-5-*O*-phenacyl-β-D-ribofuranoside (**6**).

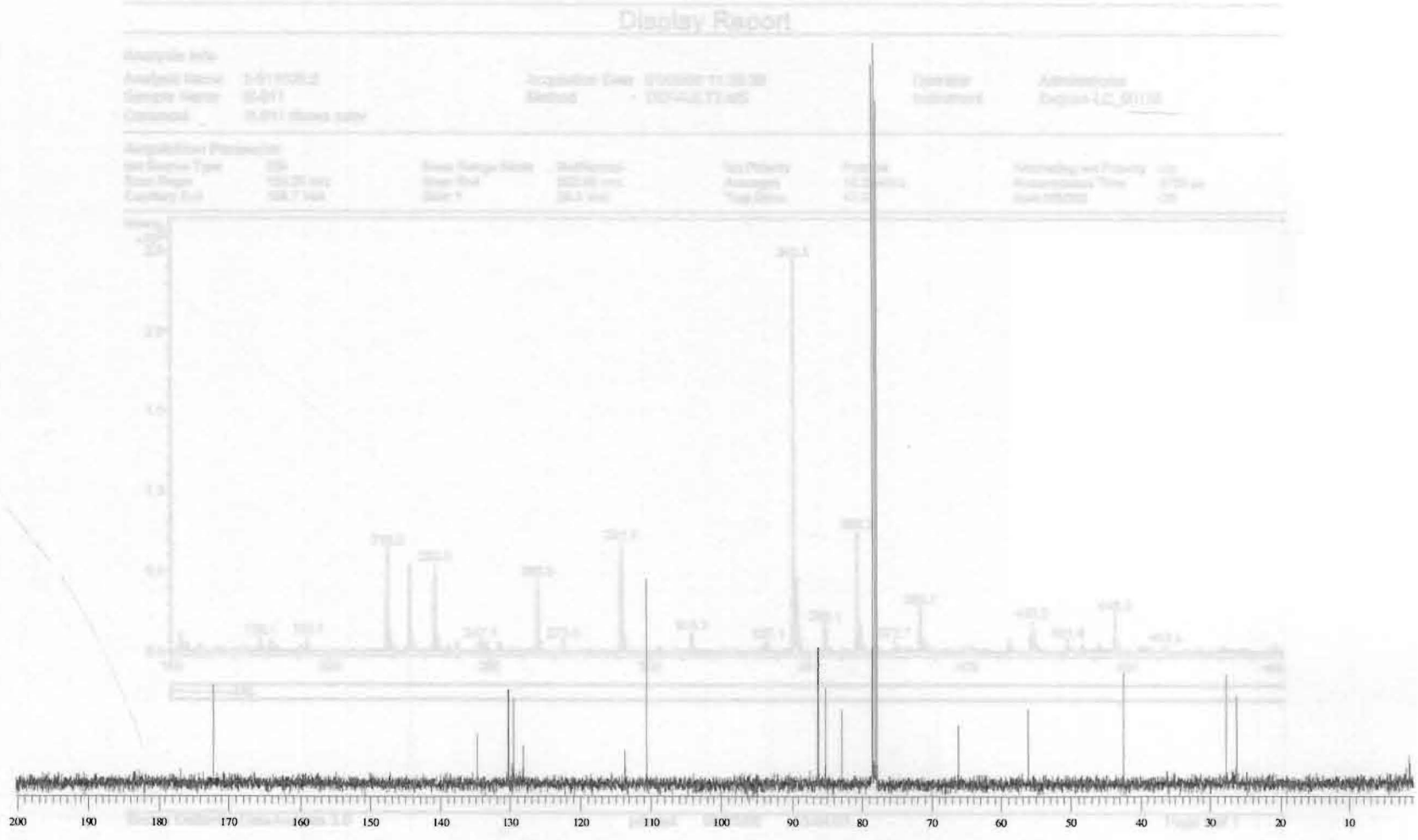


Figure 27: ^{13}C NMR spectrum of methyl 2,3-*O*-isopropylidene-5-*O*-phenacyl-β-D-ribofuranoside (**6**).

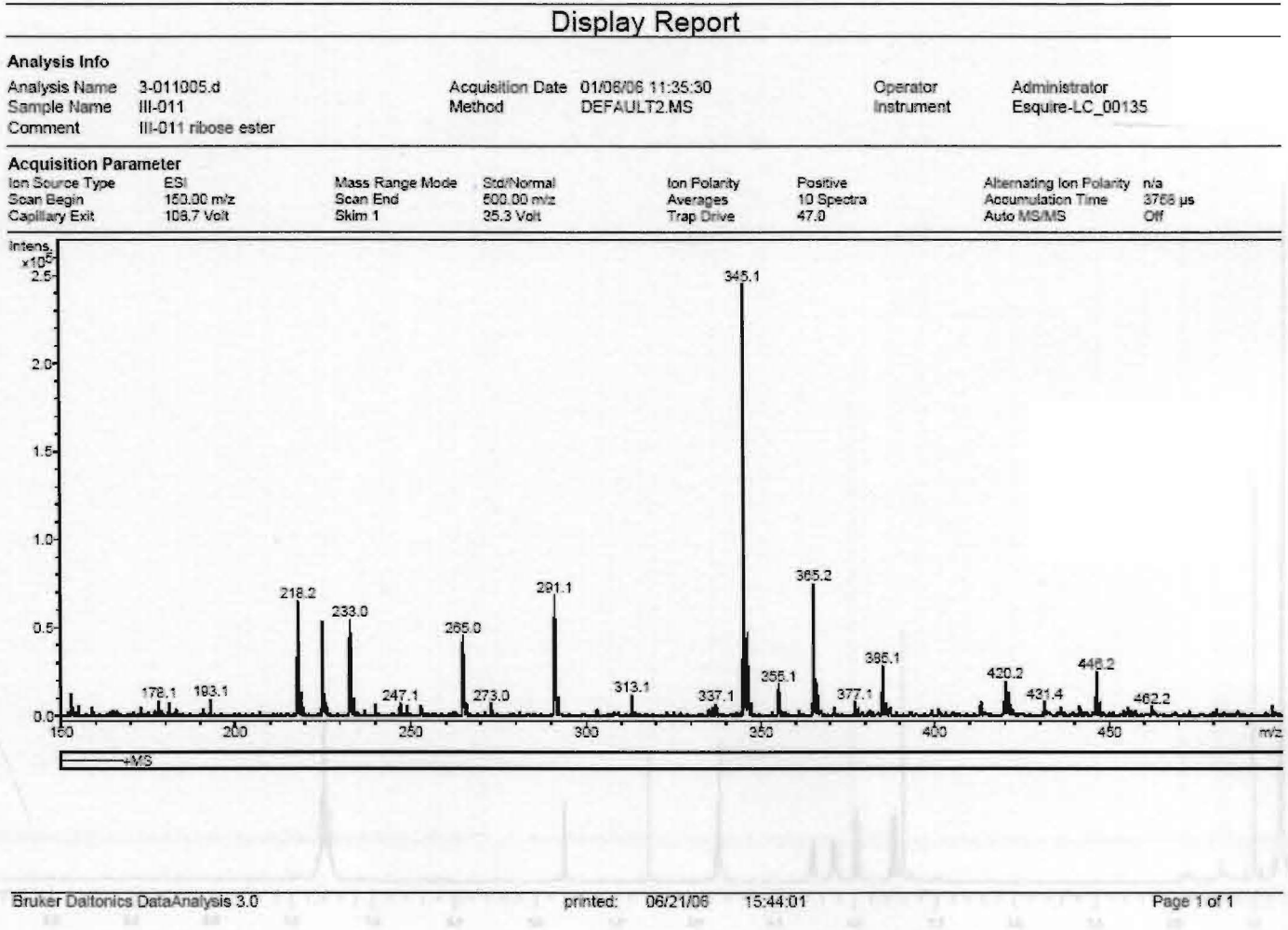


Figure 28: Mass spectrum of methyl 2,3-*O*-isopropylidene-5-*O*-phenacyl-β-D-ribofuranoside (**6**).

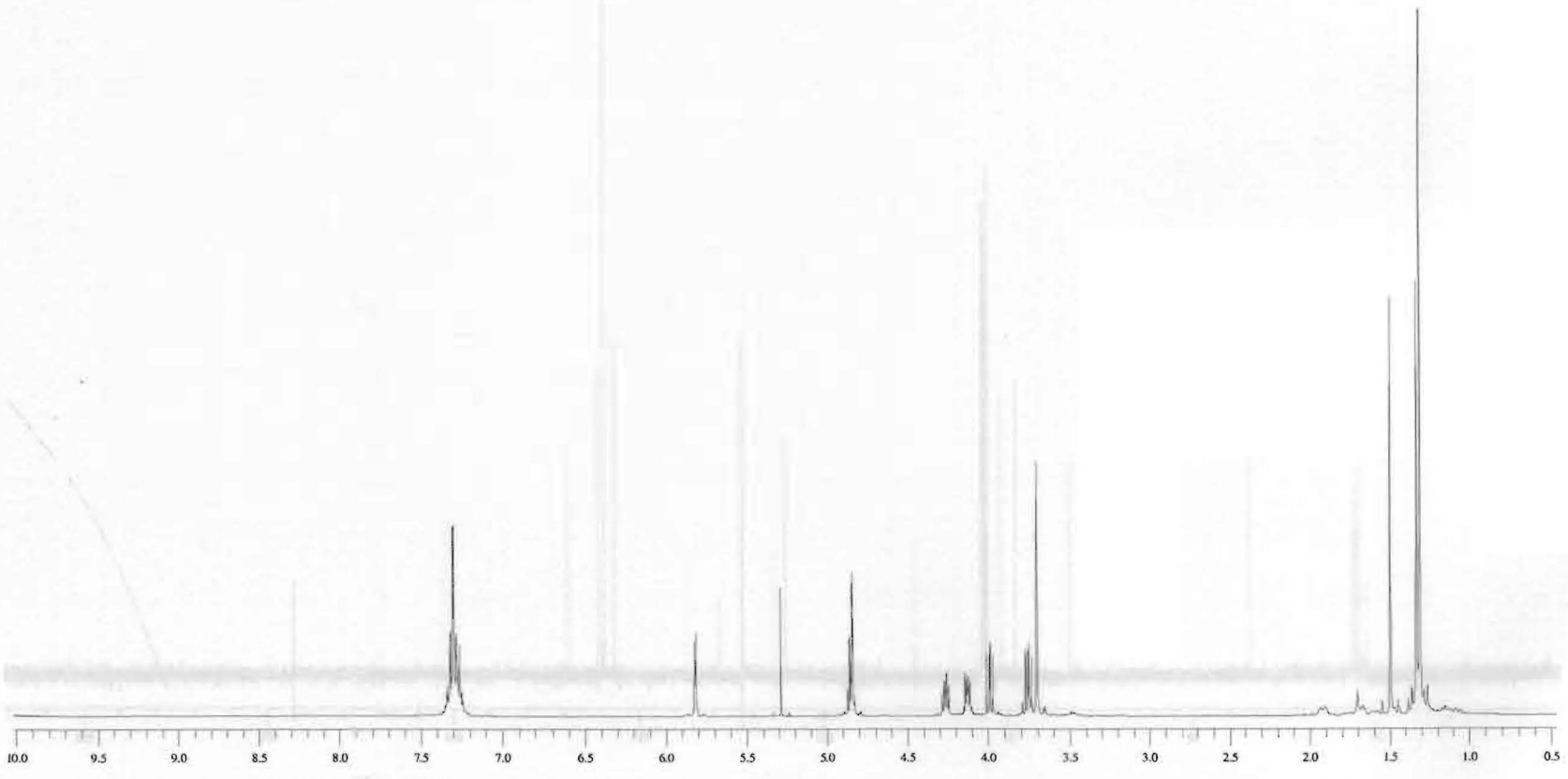


Figure 29: ^{1}H NMR spectrum of 1,2:5,6-di-*O*-isopropylidene-3-*O*-phenacyl-α-D-allofuranose (**7**).

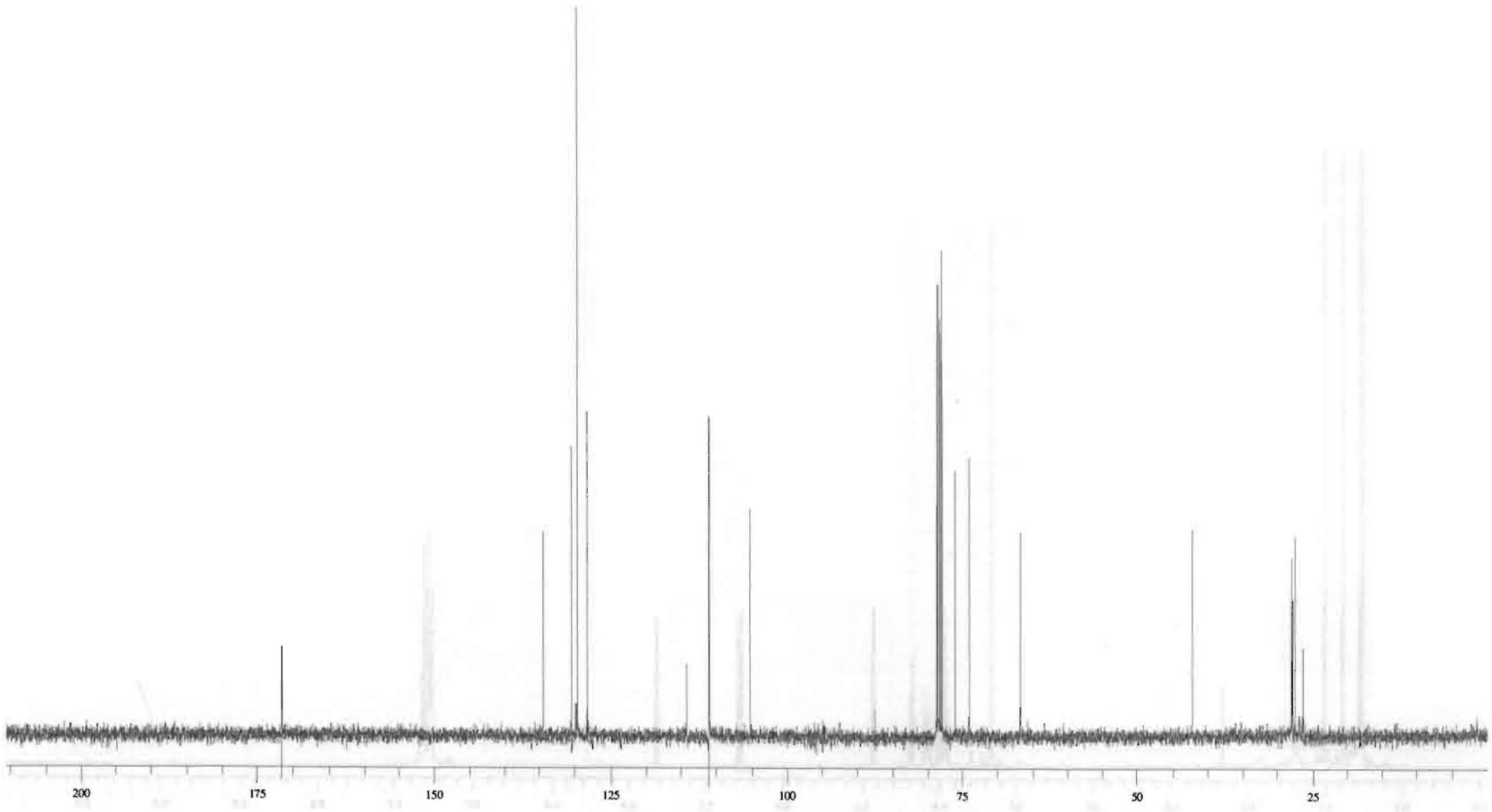


Figure 30: ^{13}C NMR spectrum of 1,2:5,6-di-*O*-isopropylidene-3-*O*-phenacyl-α-D-allofuranose (7).

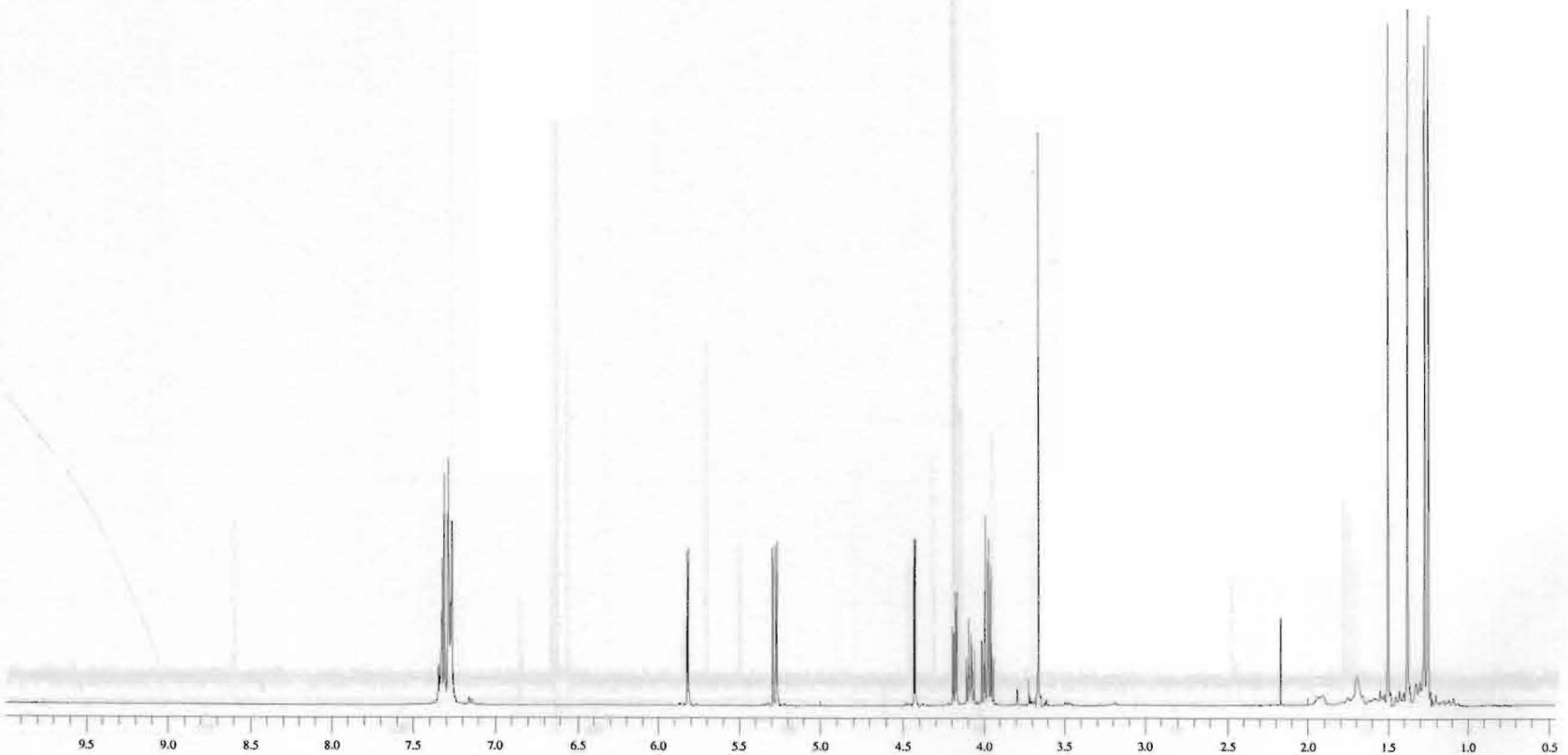


Figure 31: ^{1}H NMR spectrum of 1,2:5,6-di-*O*-isopropylidene-3-*O*-phenacyl-α-D-glucofuranose (**8**).

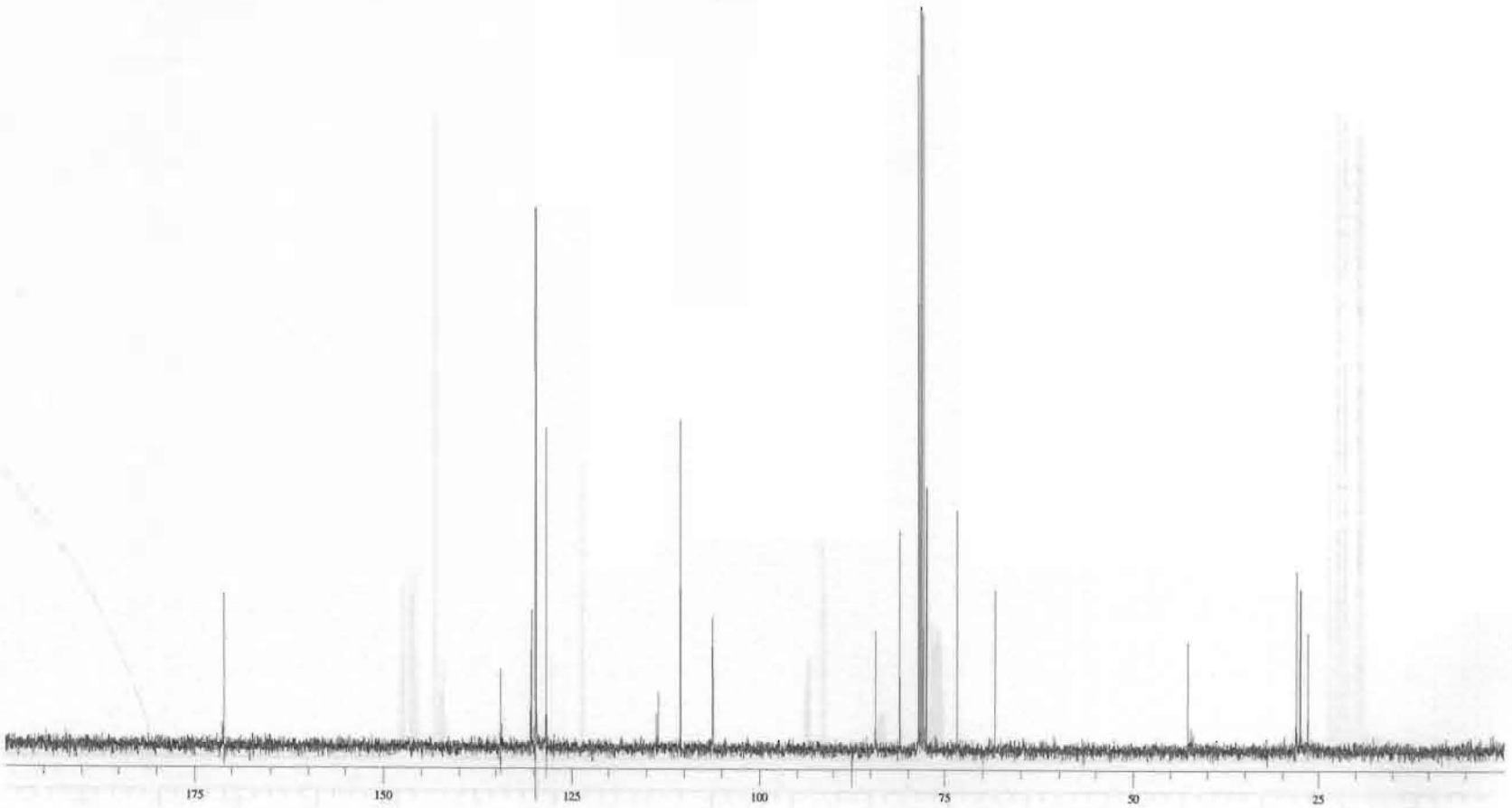


Figure 32: ^{13}C NMR spectrum of 1,2:5,6-di-*O*-isopropylidene-3-*O*-phenacyl-α-D-glucofuranose (**8**).

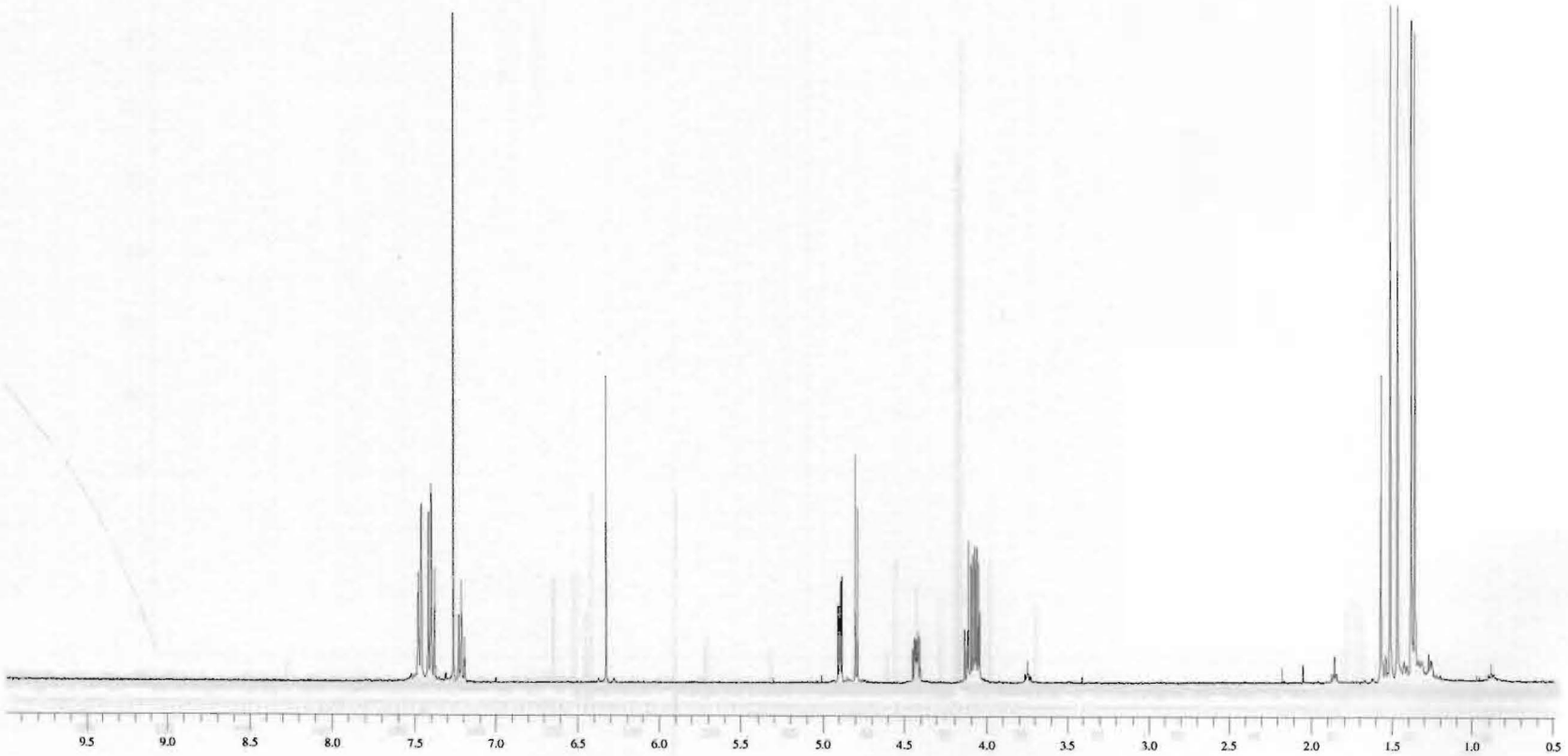


Figure 33: ^{1}H NMR spectrum of 2,3:5,6-di-*O*-isopropylidene-1-*O*-(phenacyldiazo)-α-D-mannofuranose (**9**).

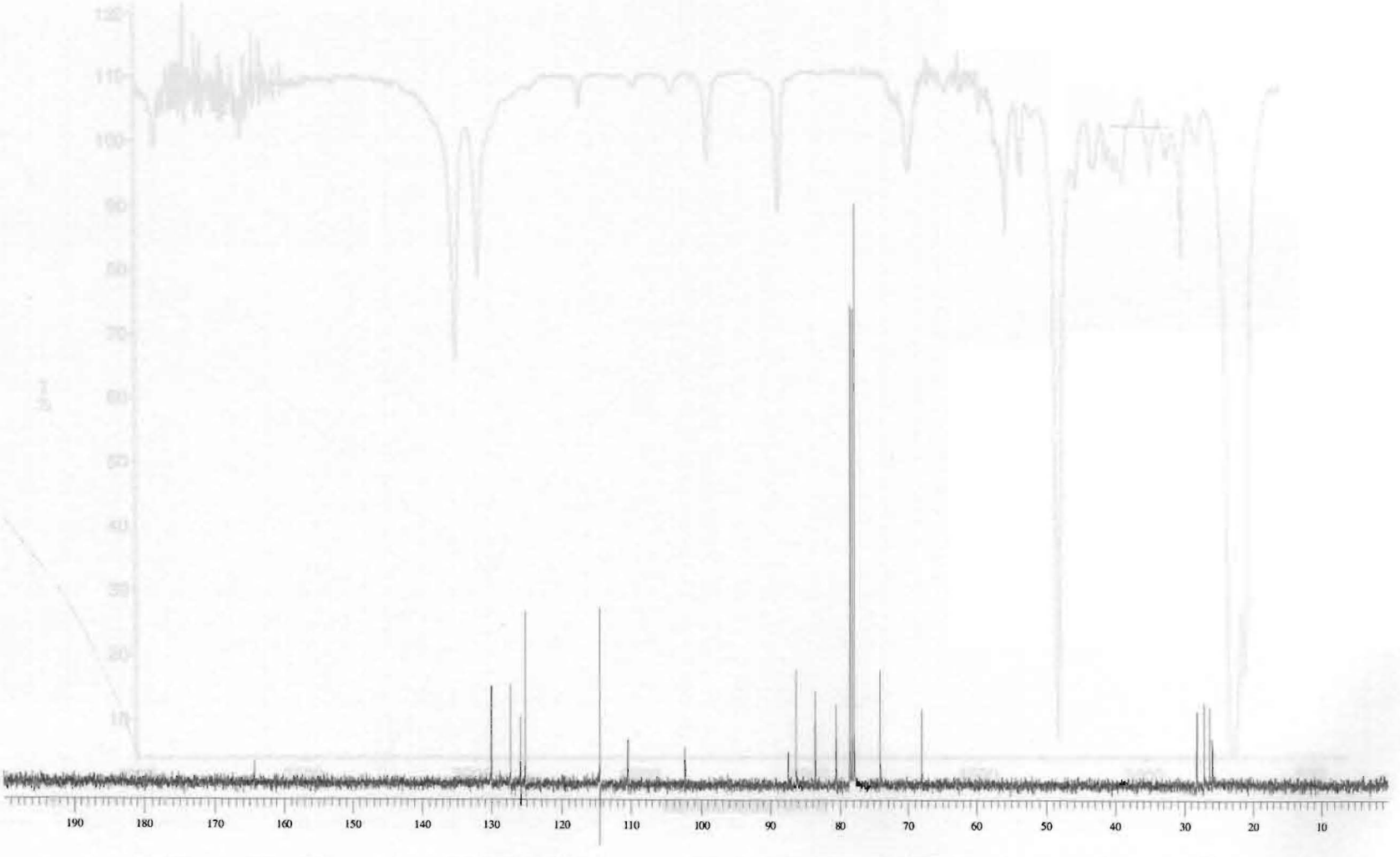


Figure 34: ^{13}C NMR spectrum of 2,3:5,6-di-*O*-isopropylidene-1-*O*-(phenacyldiazo)-α-D-mannofuranose (**9**).

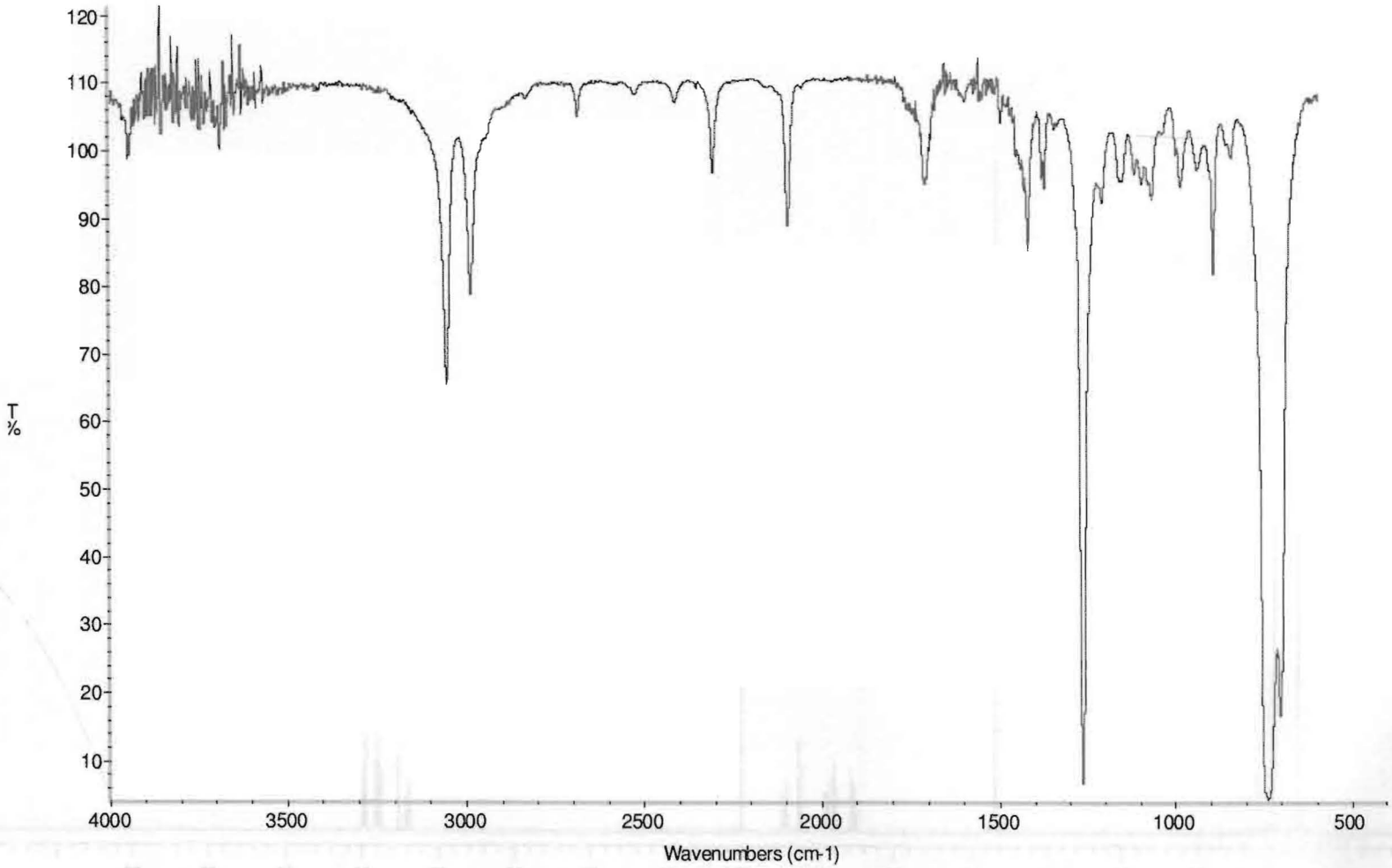


Figure 35: IR spectrum of 2,3:5,6-di-*O*-isopropylidene-1-*O*-(phenacyldiazo)-α-D-mannofuranose (**9**).

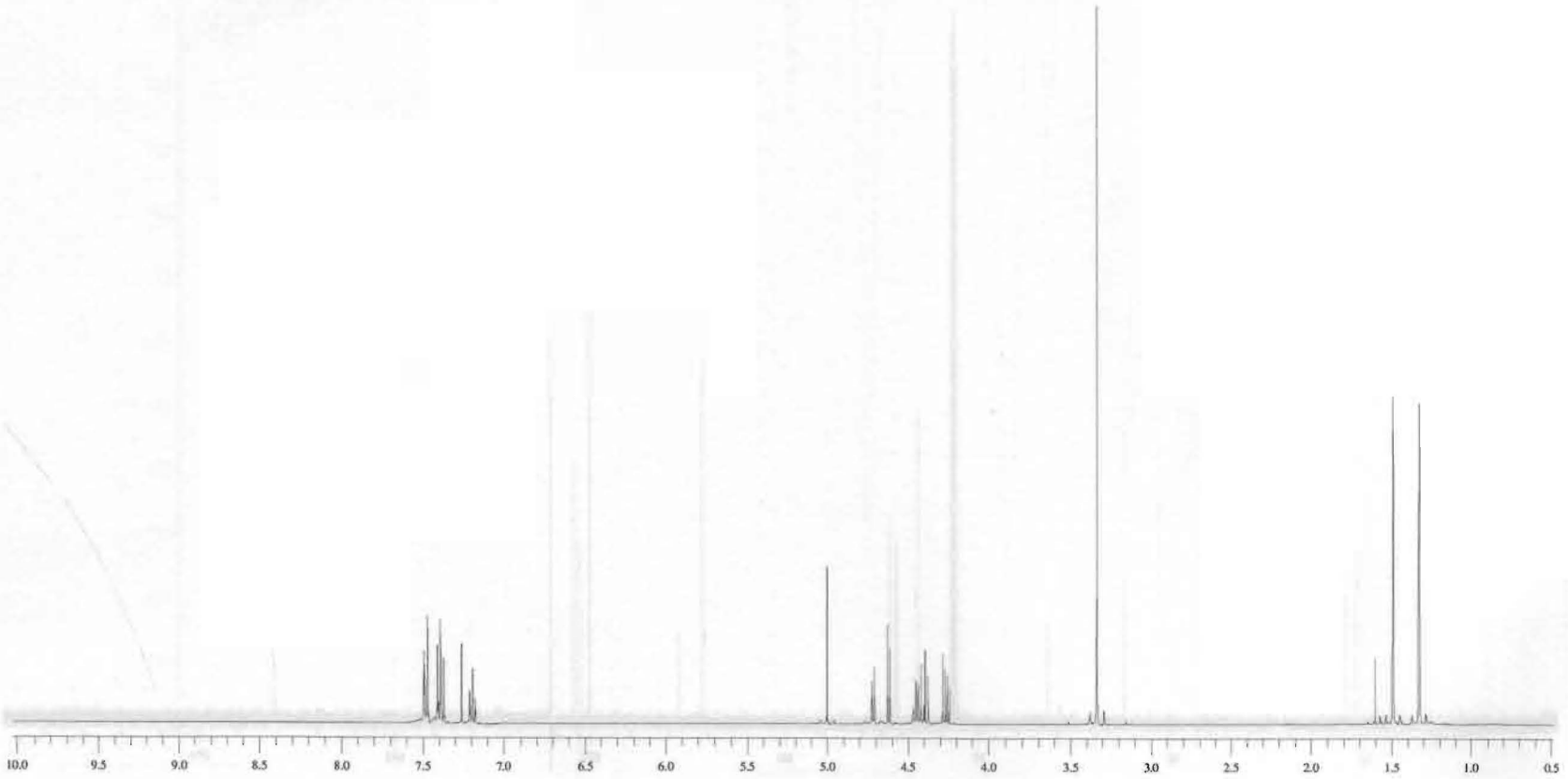


Figure 36: ^{1}H NMR spectrum of methyl 2,3-*O*-isopropylidene-5-*O*-(phenacyldiazo)-β-D-ribofuranoside (**10**).

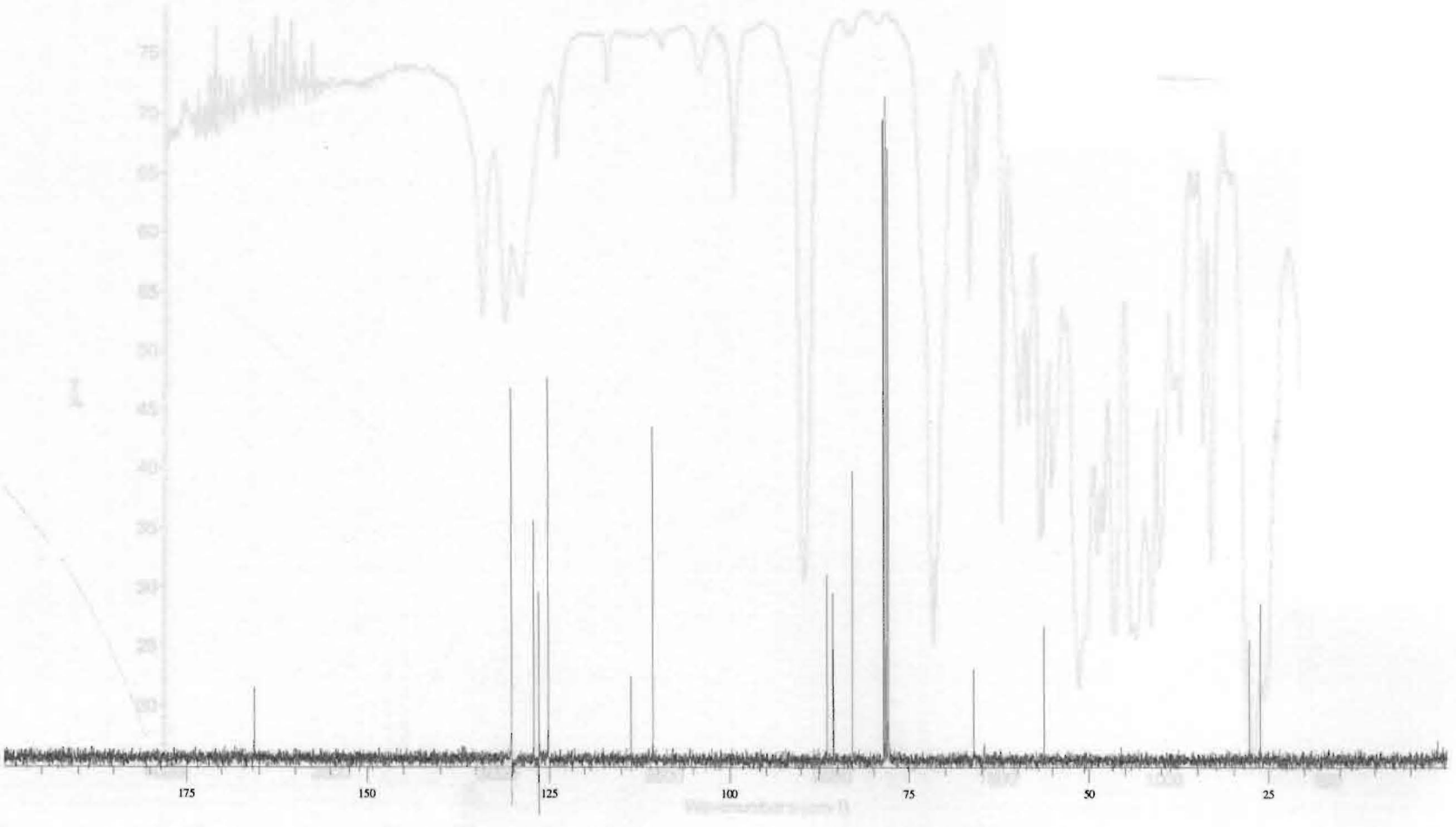


Figure 37: ^{13}C NMR spectrum of methyl 2,3-*O*-isopropylidene-5-*O*-(phenacyldiazo)-β-D-ribofuranoside (**10**).

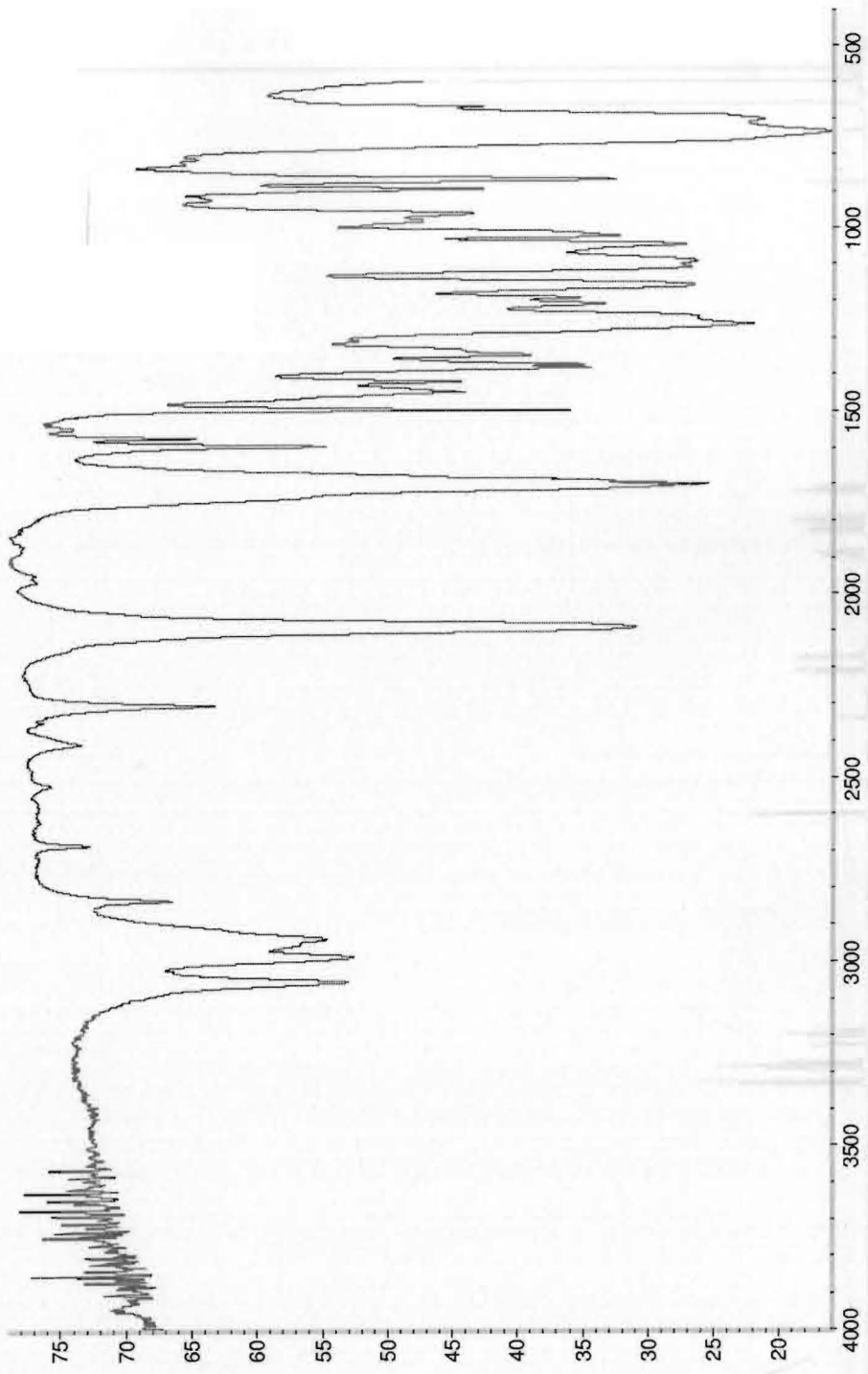


Figure 38: IR spectrum of methyl 2,3-*O*-isopropylidene-5-*O*-(phenacyldiazo)-β-D-ribofuranoside (**10**).

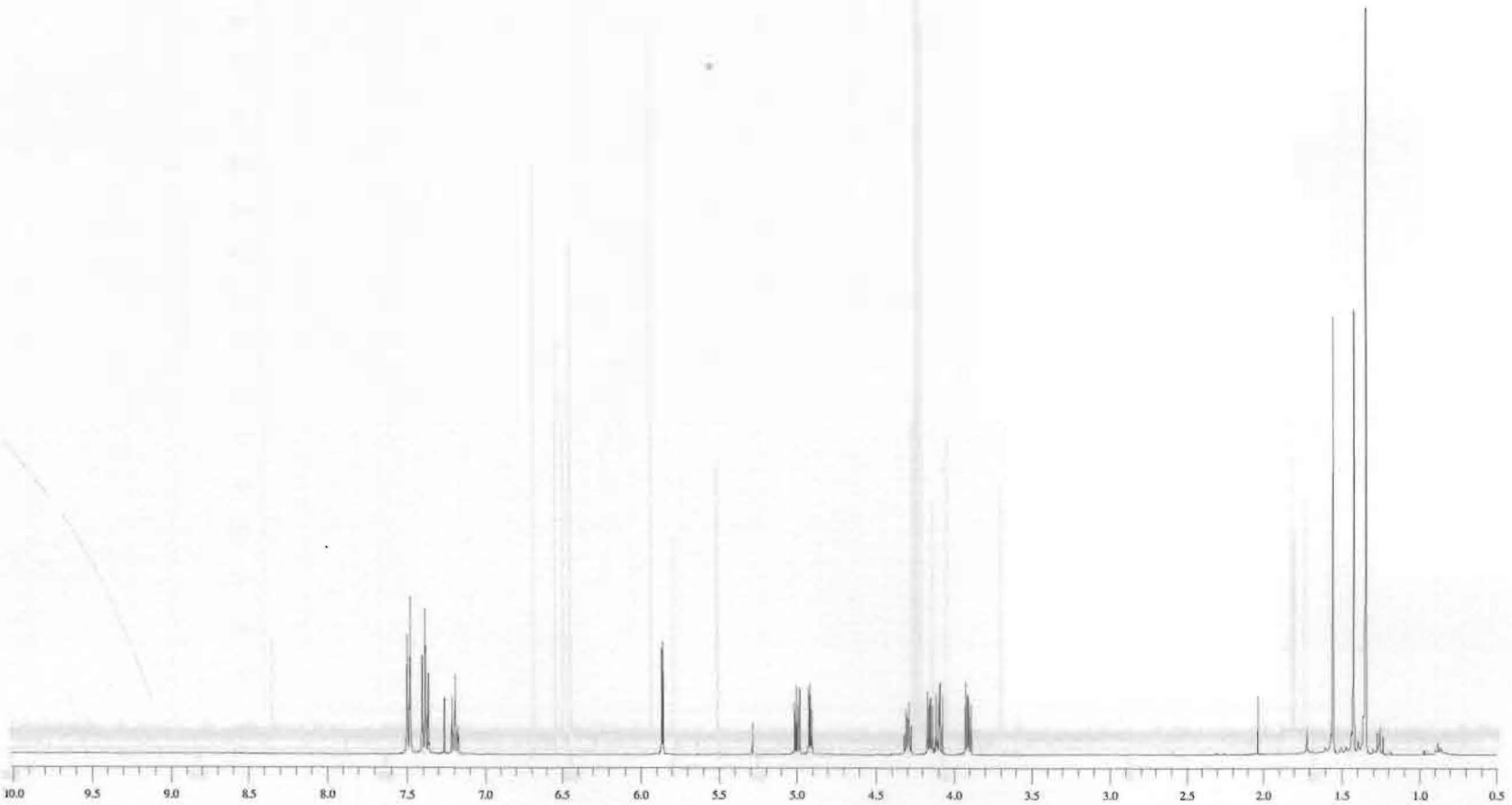


Figure 39: ^{1}H NMR spectrum of 1,2:5,6-di-*O*-isopropylidene-3-*O*-(phenacyldiazo)-α-D-allofuranose (**11**).

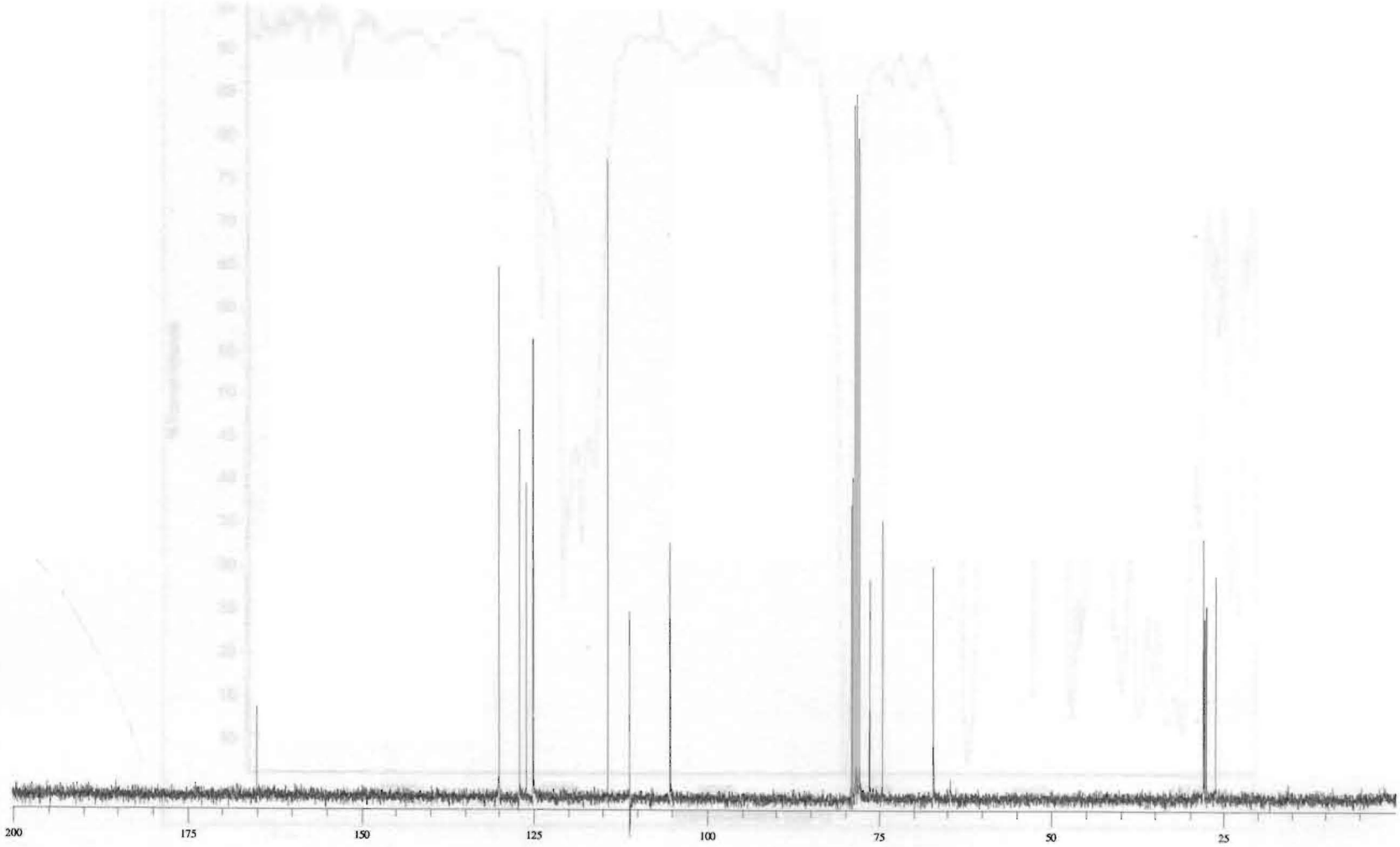


Figure 40: ^{13}C NMR spectrum of 1,2:5,6-di-*O*-isopropylidene-3-*O*-(phenacyldiazo)-α-D-allofuranose (**11**).

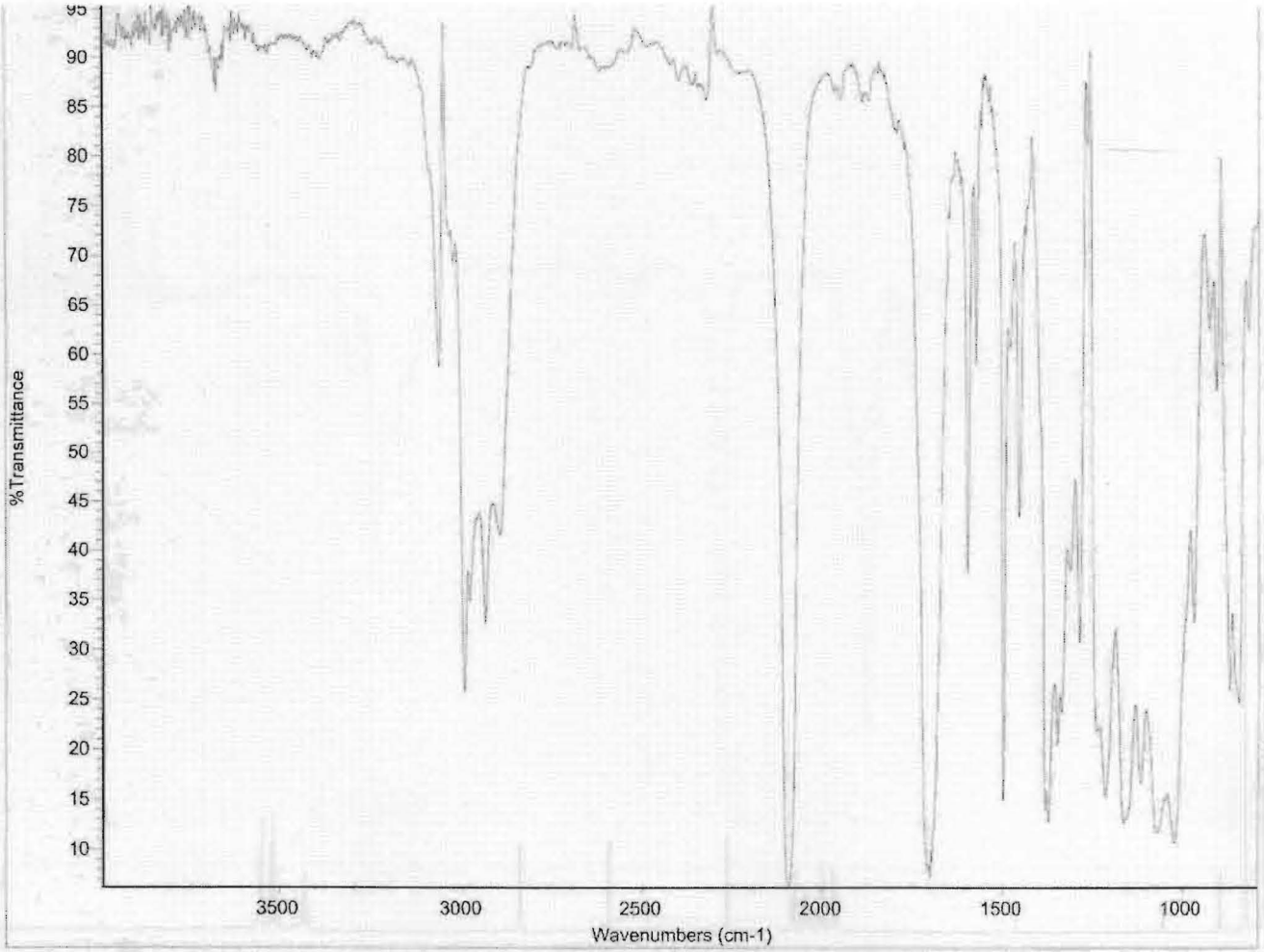


Figure 41: IR spectrum of 1,2:5,6-di-*O*-isopropylidene-3-*O*-(phenacyldiazo)-α-D-allofuranose (**11**).

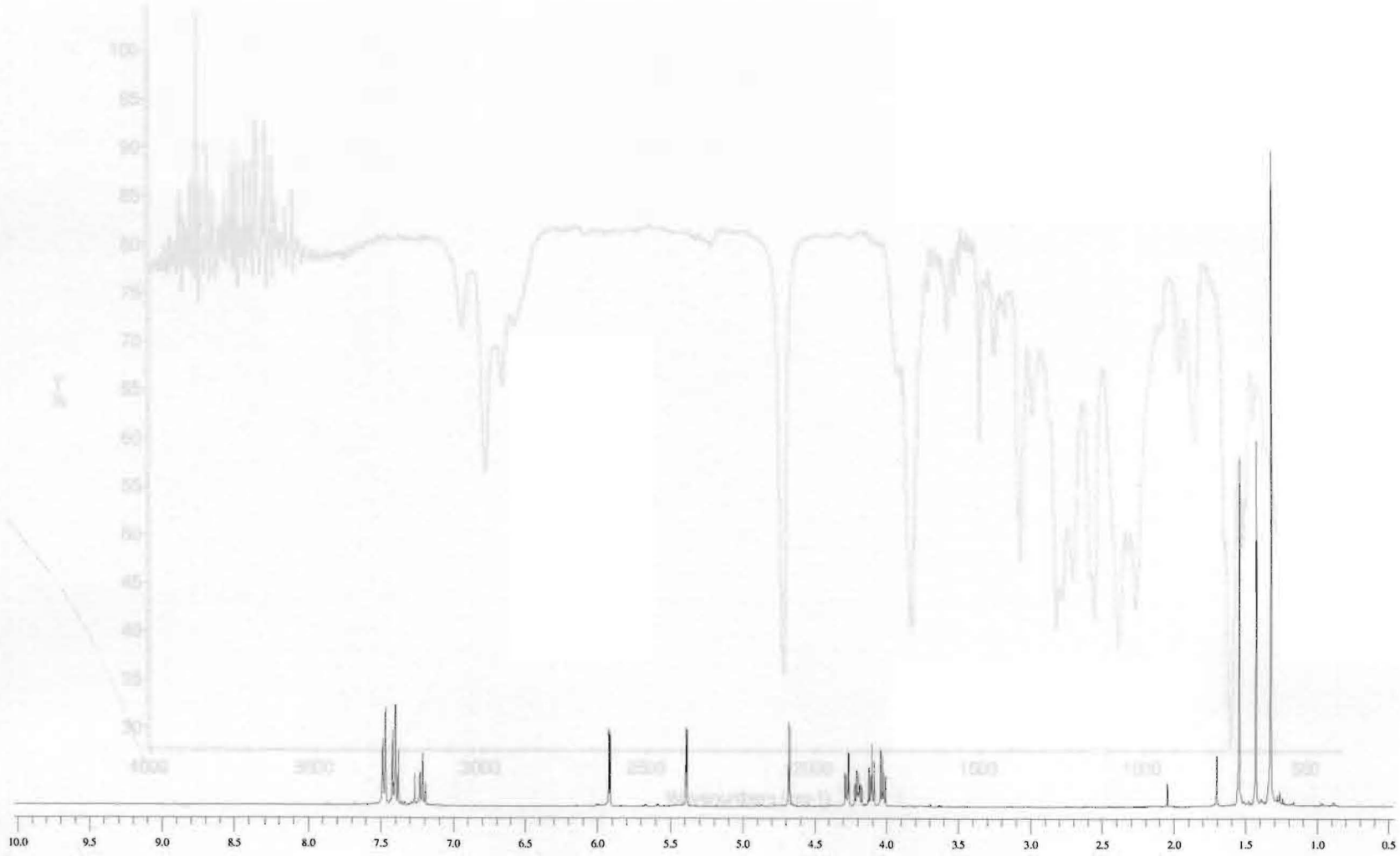


Figure 42: ^{1}H NMR spectrum of 1,2:5,6-di-*O*-isopropylidene-3-*O*-(phenacyldiazo)-α-D-glucofuranose (**12**).

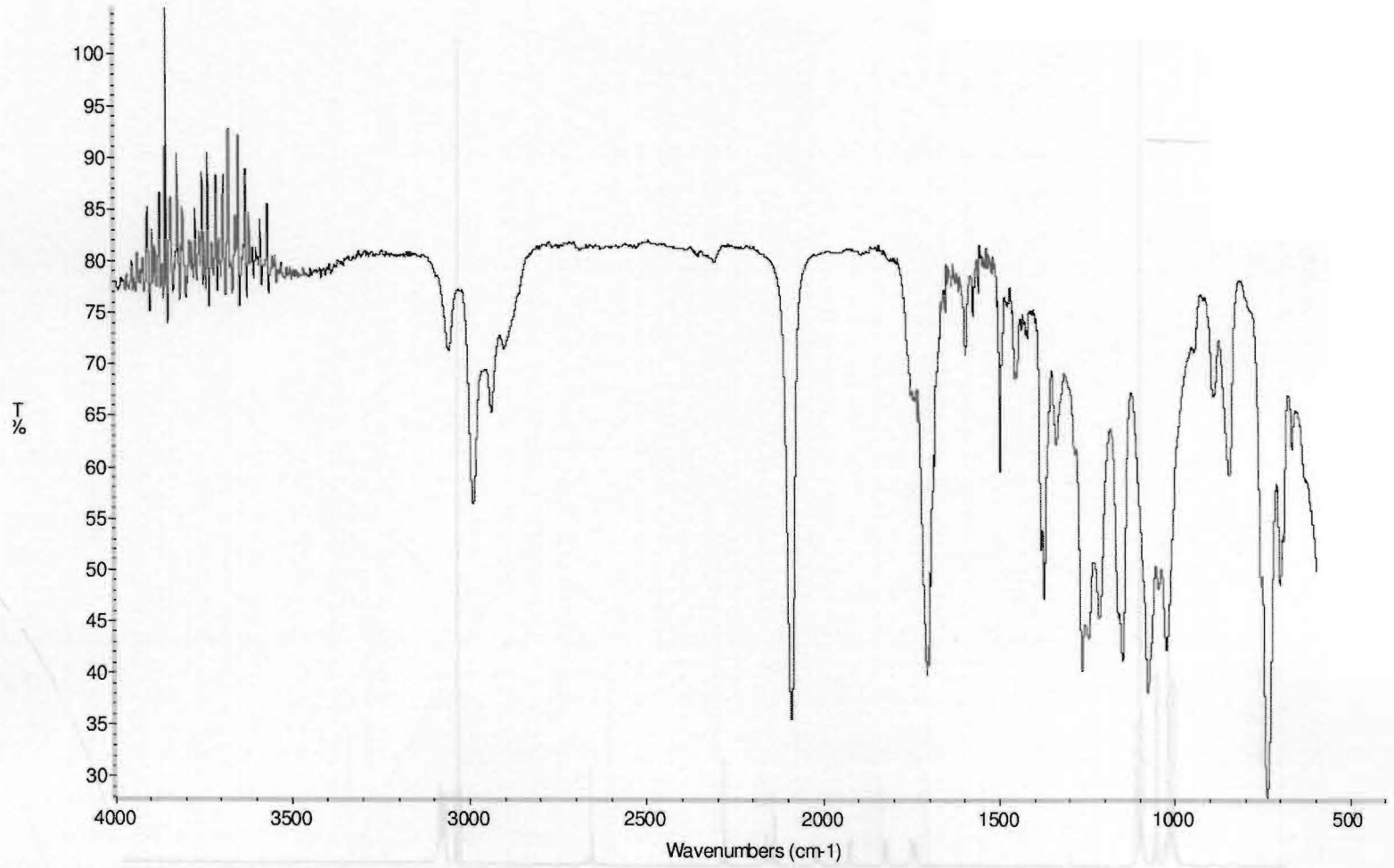


Figure 43: IR spectrum of 1,2:5,6-di-*O*-isopropylidene-3-*O*-(phenacyldiazo)-α-D-glucofuranose (**12**).

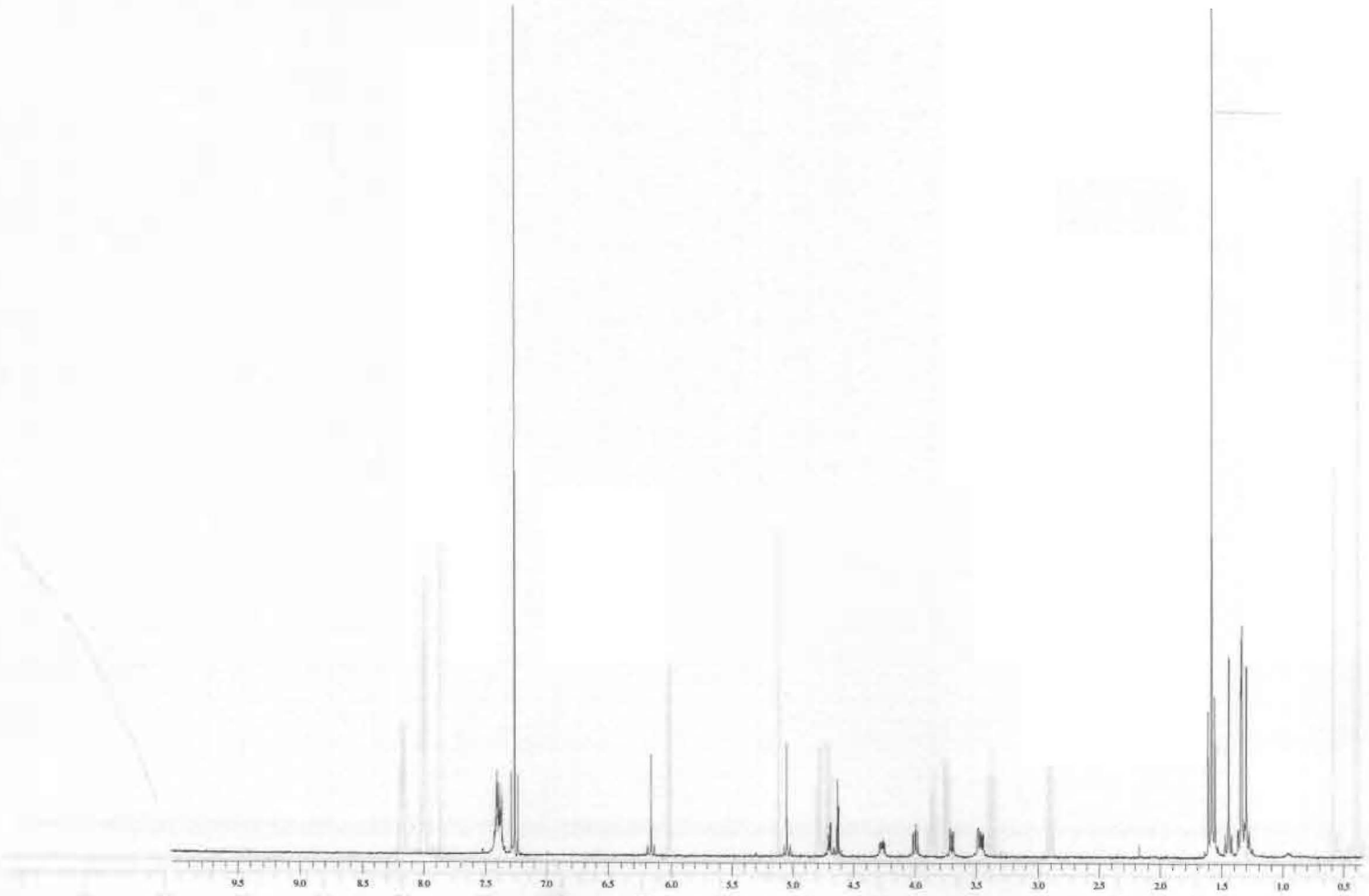


Figure 44: ^{1}H NMR spectrum of mannofuranose dimer **14**.

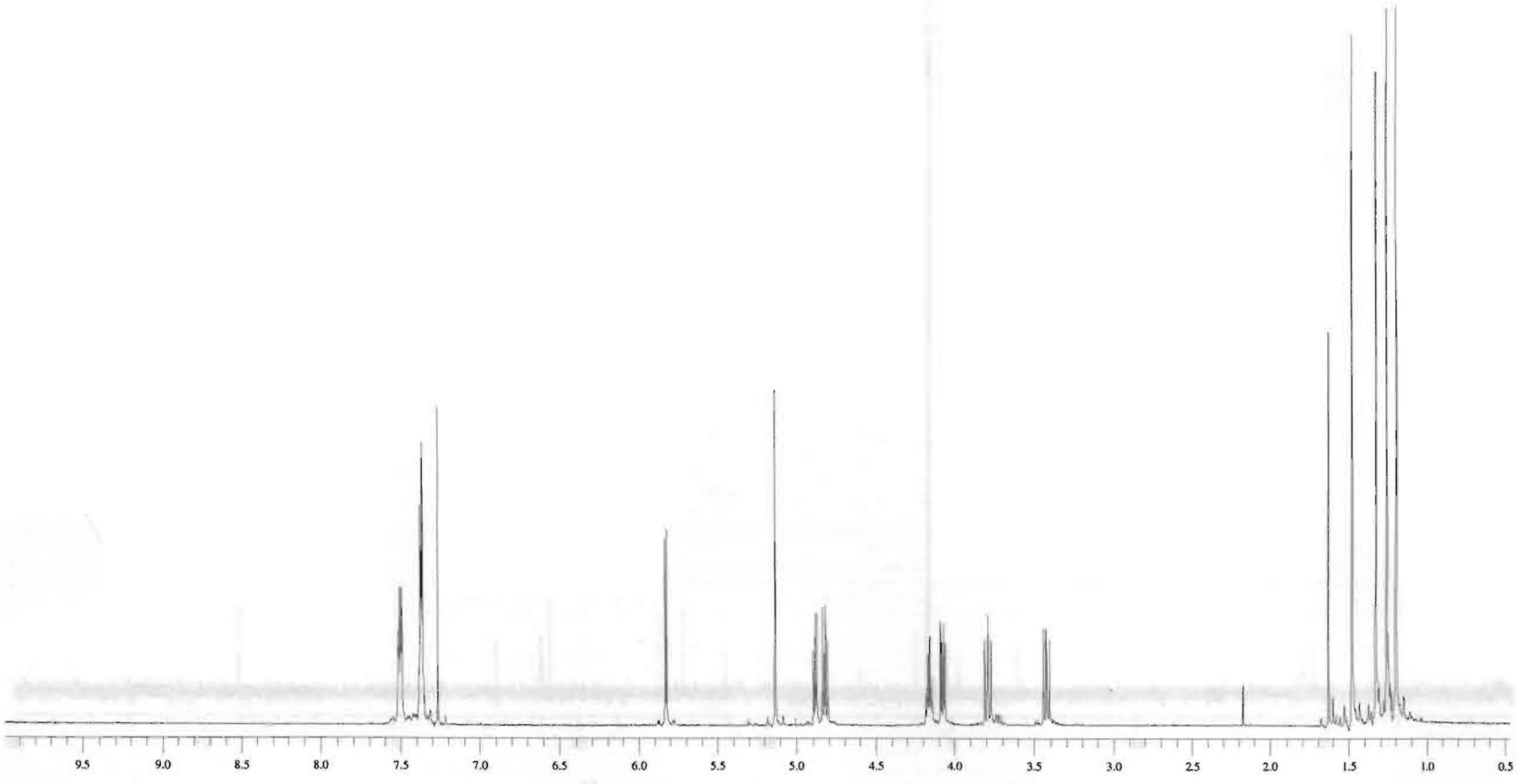


Figure 45: ^{1}H NMR spectrum of allofuranose dimer **15**.

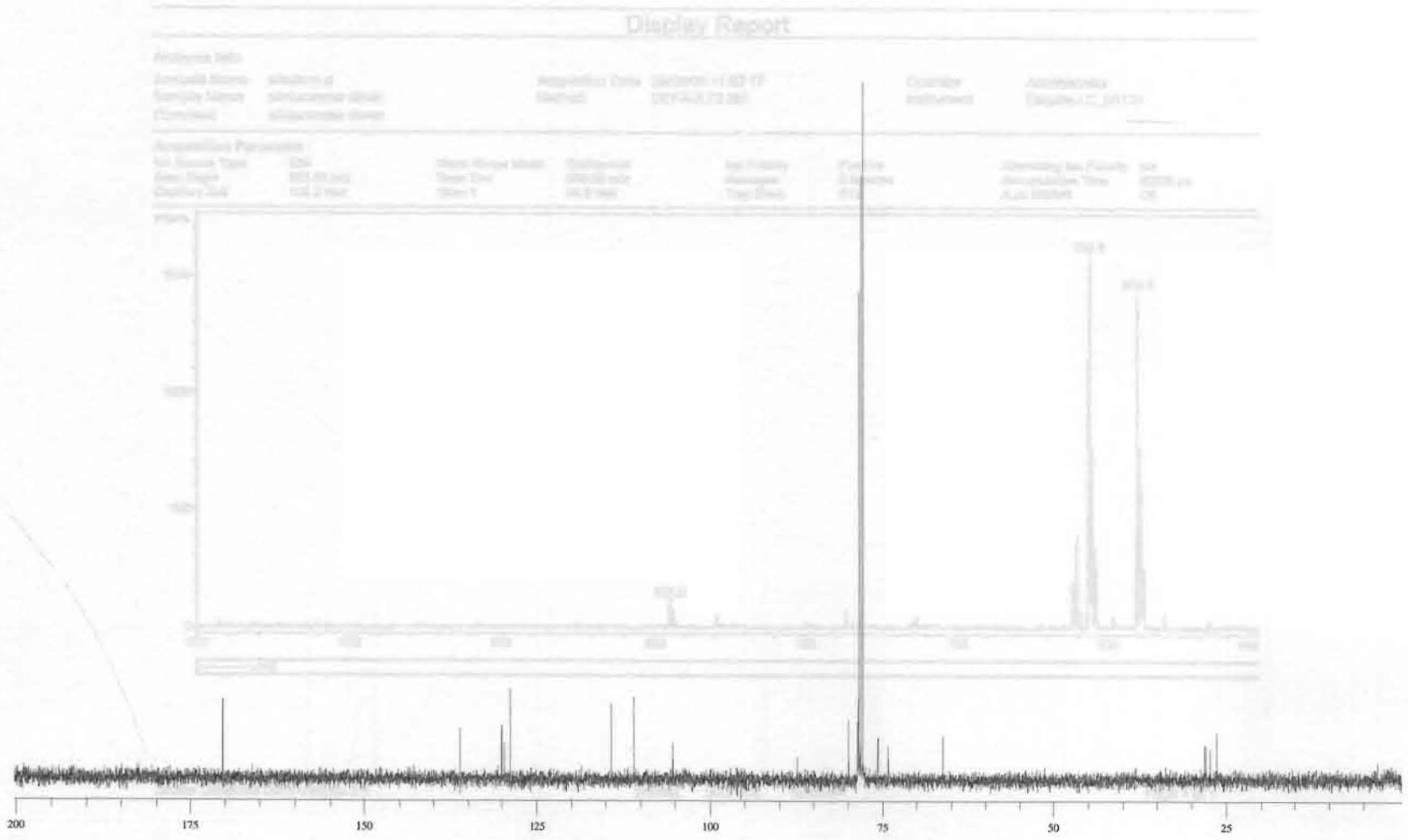


Figure 46: ^{13}C NMR spectrum of allofuranose dimer **15**.

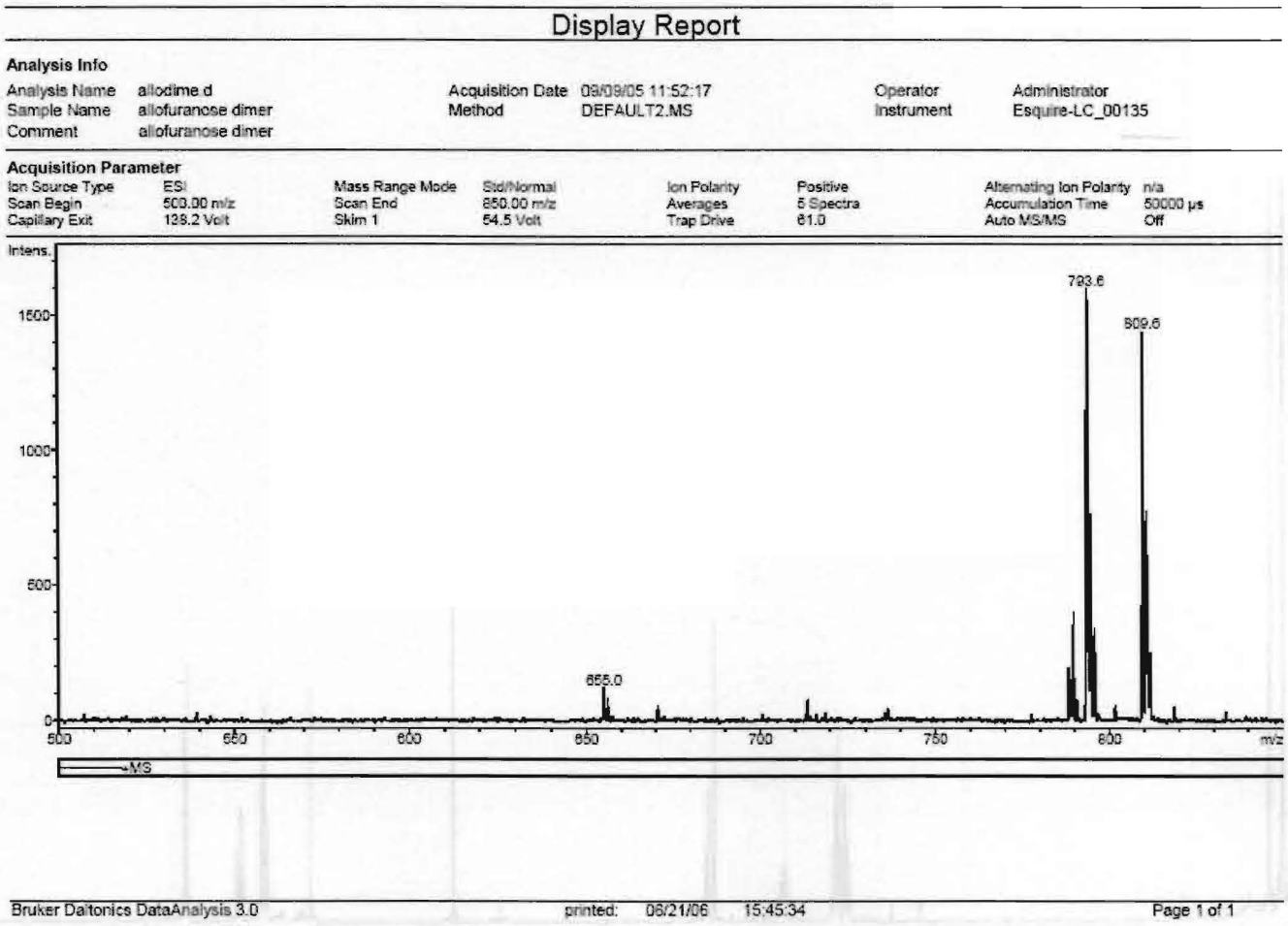


Figure 47: Mass spectrum of allofuranose dimer **15**.

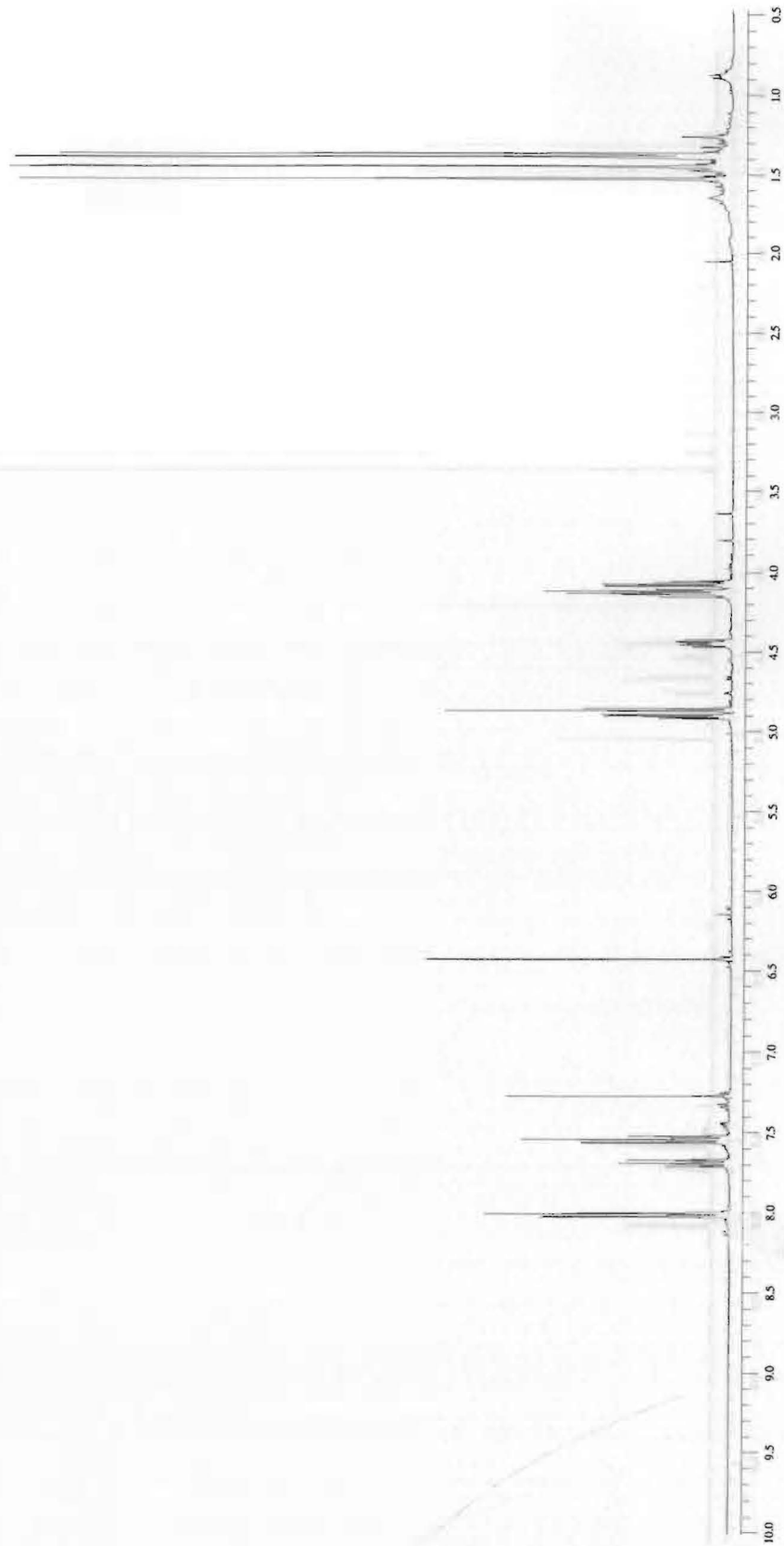


Figure 48: ^{1}H NMR spectrum of mannofuranose ketone **16**.

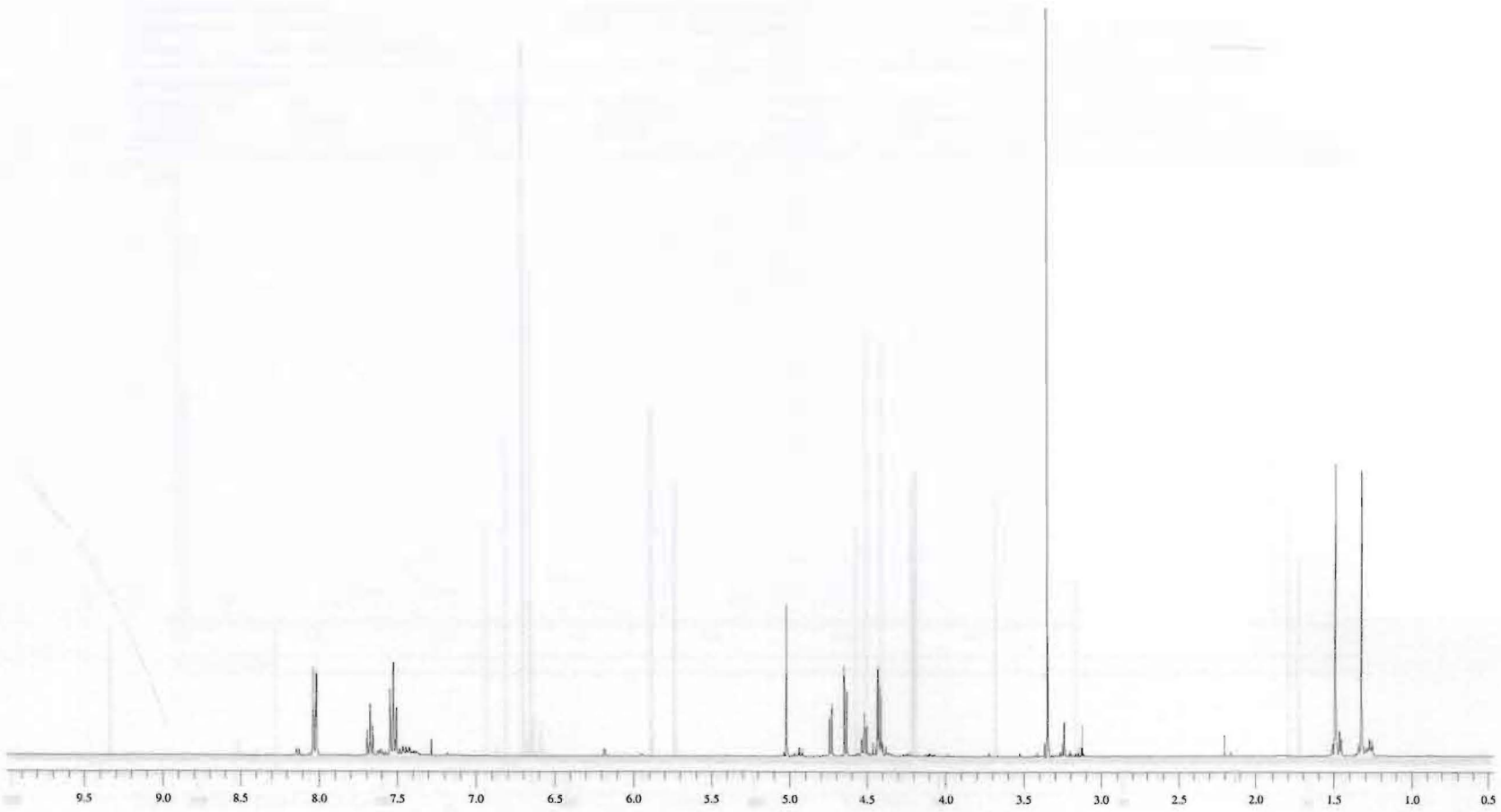


Figure 49: ^{1}H NMR spectrum of ribofuranose ketone **17**.

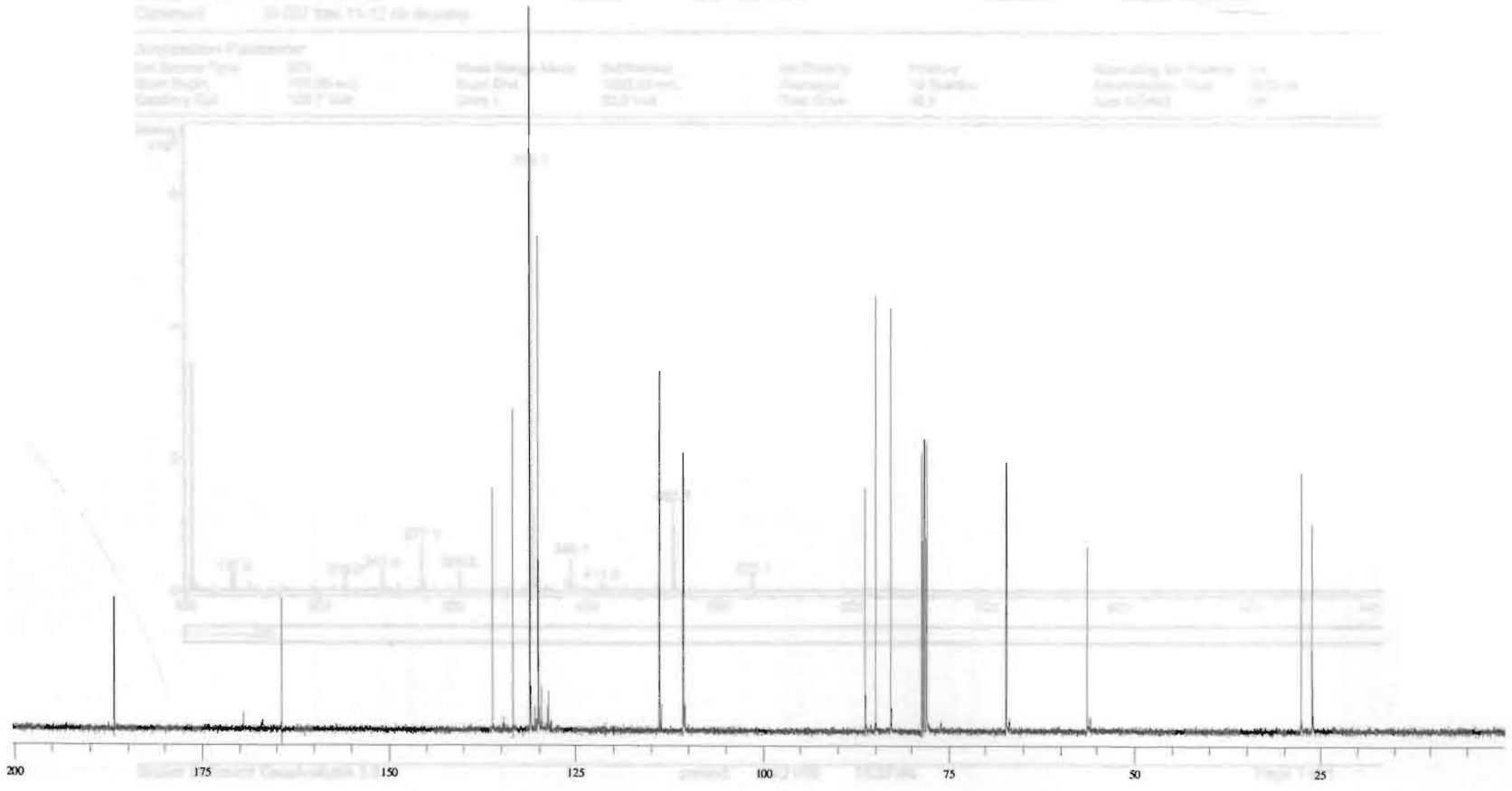


Figure 50: ^{13}C NMR spectrum of ribofuranose ketone **17**.

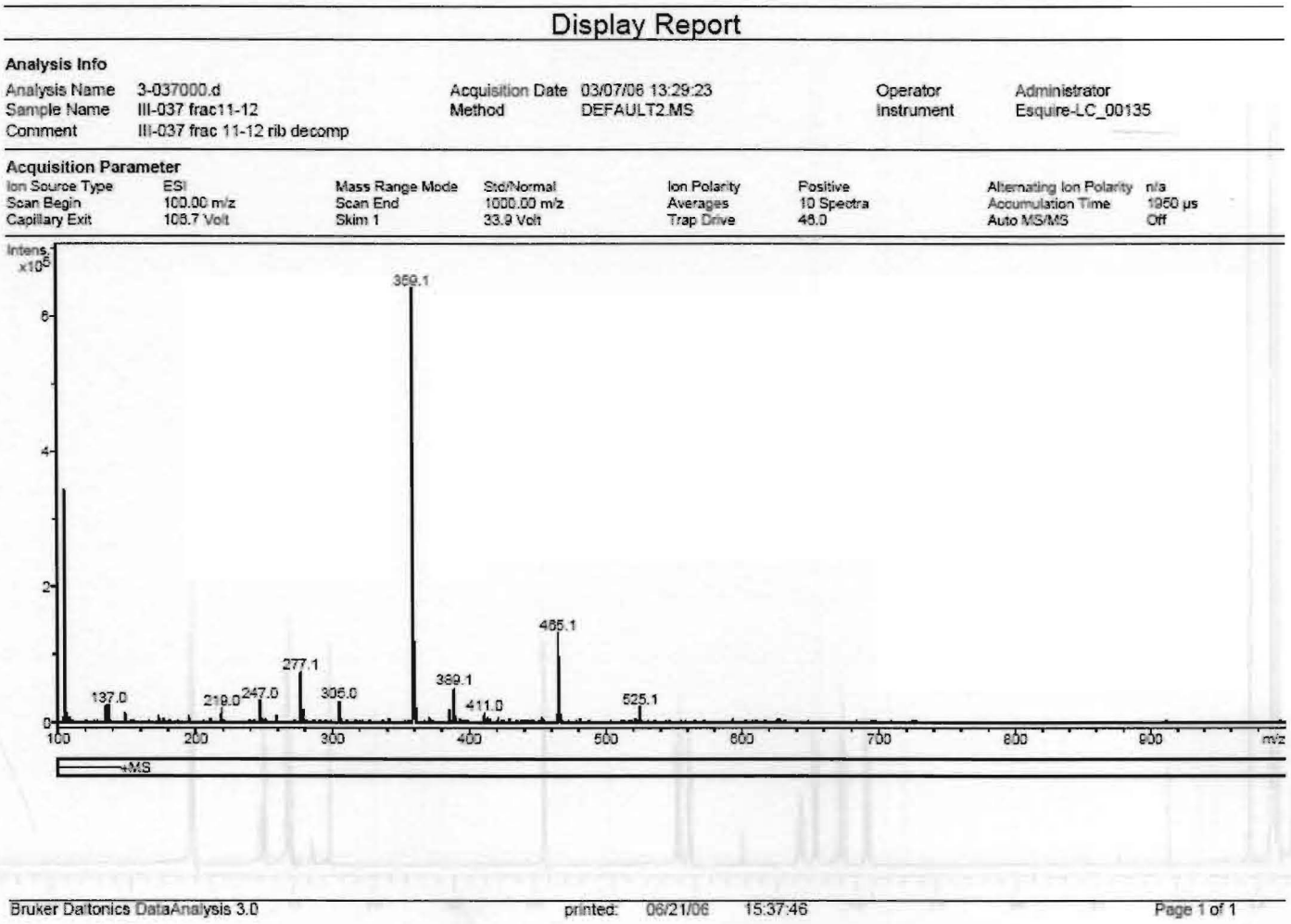


Figure 51: Mass spectrum of ribofuranose ketone **17**.

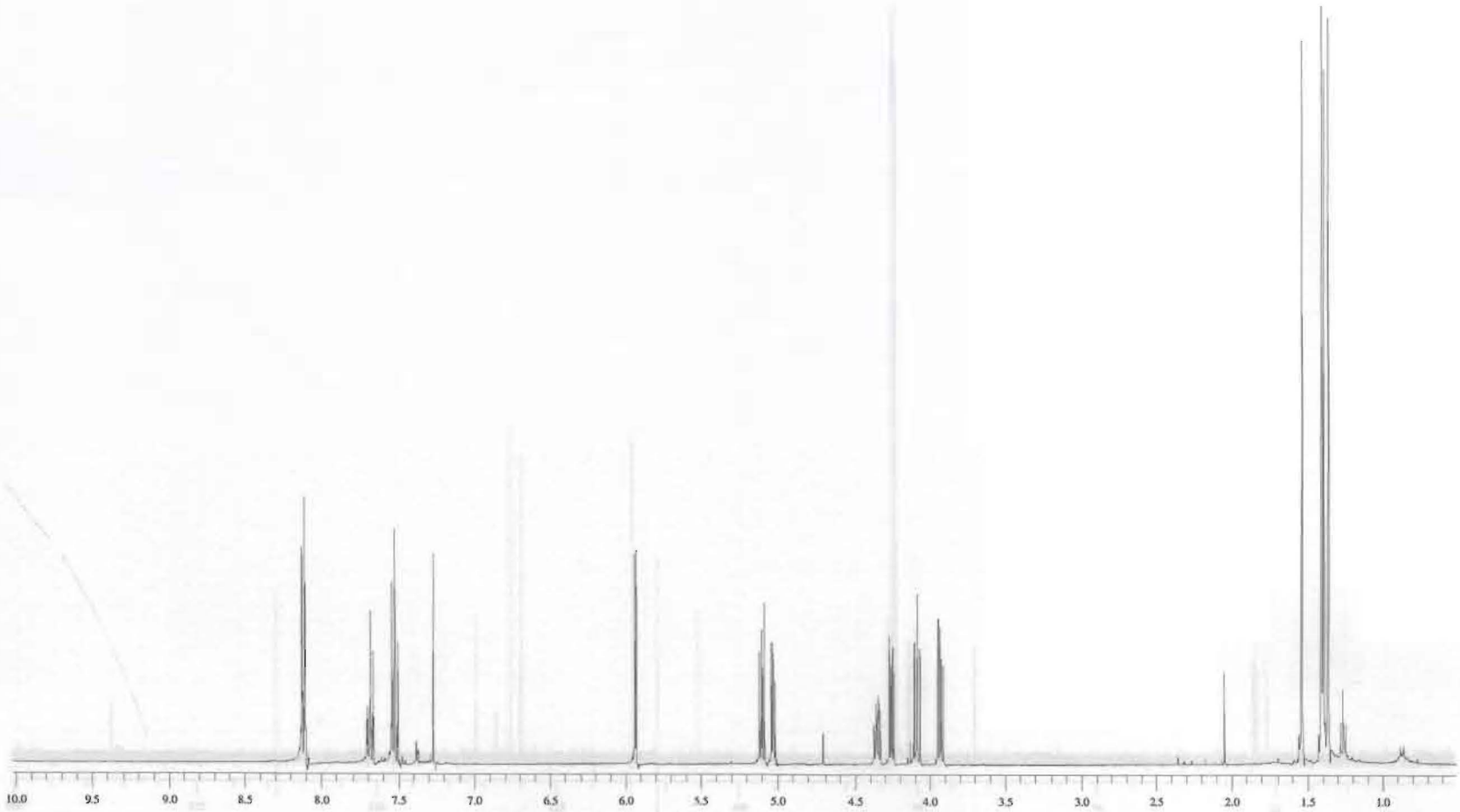


Figure 52: ^{1}H NMR spectrum of allofuranose ketone **18**.

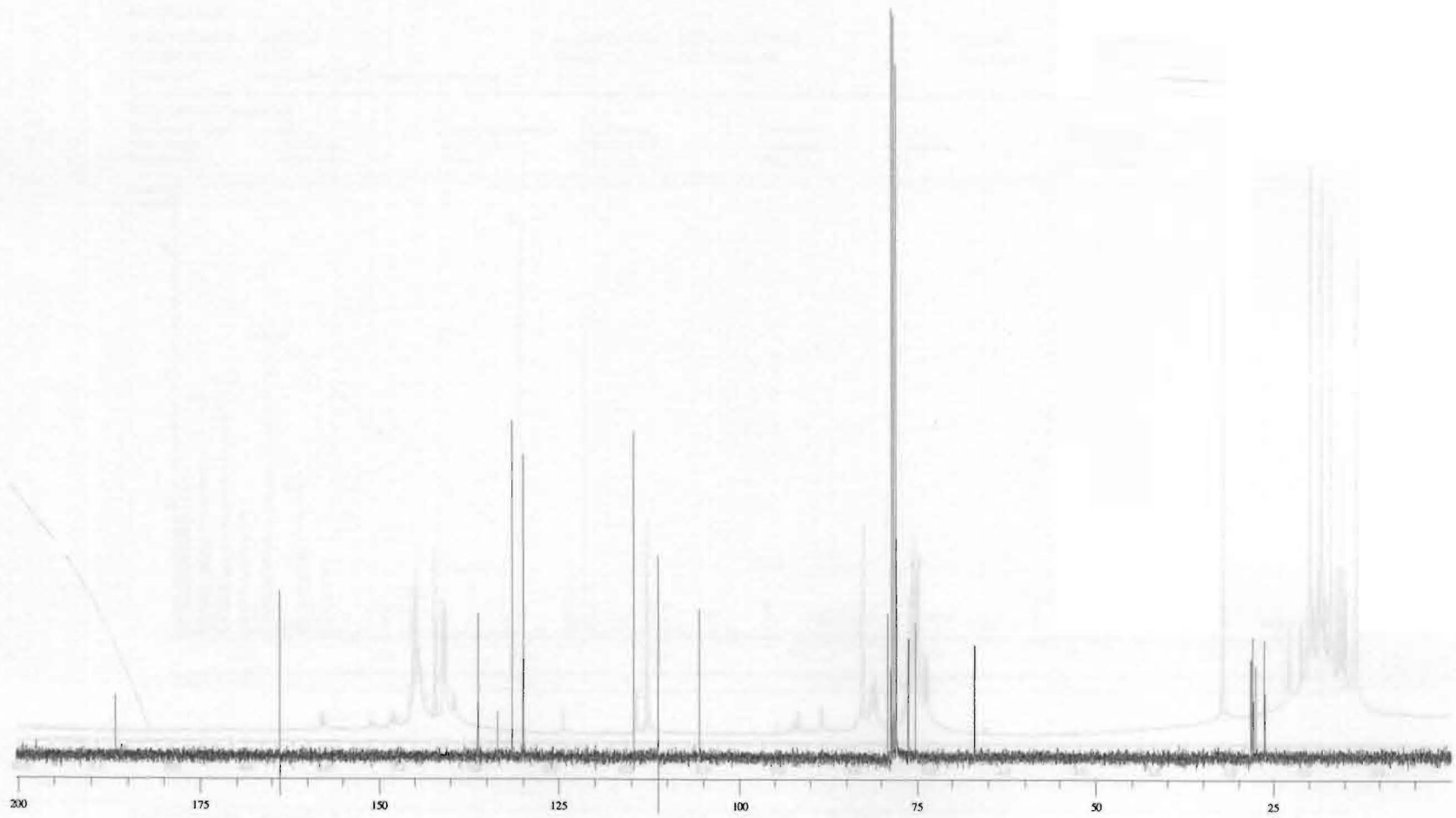


Figure 53: ^{13}C NMR spectrum of allofuranose ketone **18**.

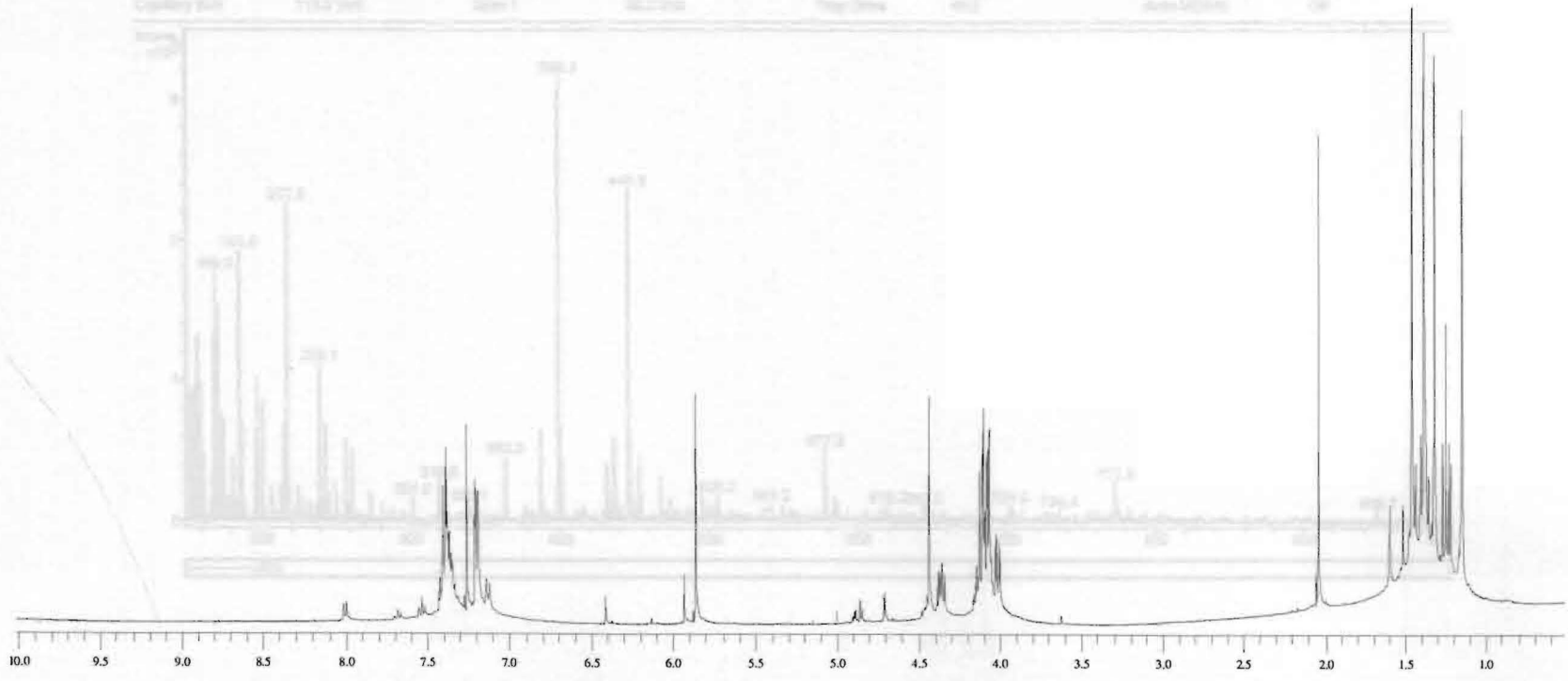


Figure 54: ^{1}H NMR spectrum of mannofuranose insertion product **19**.

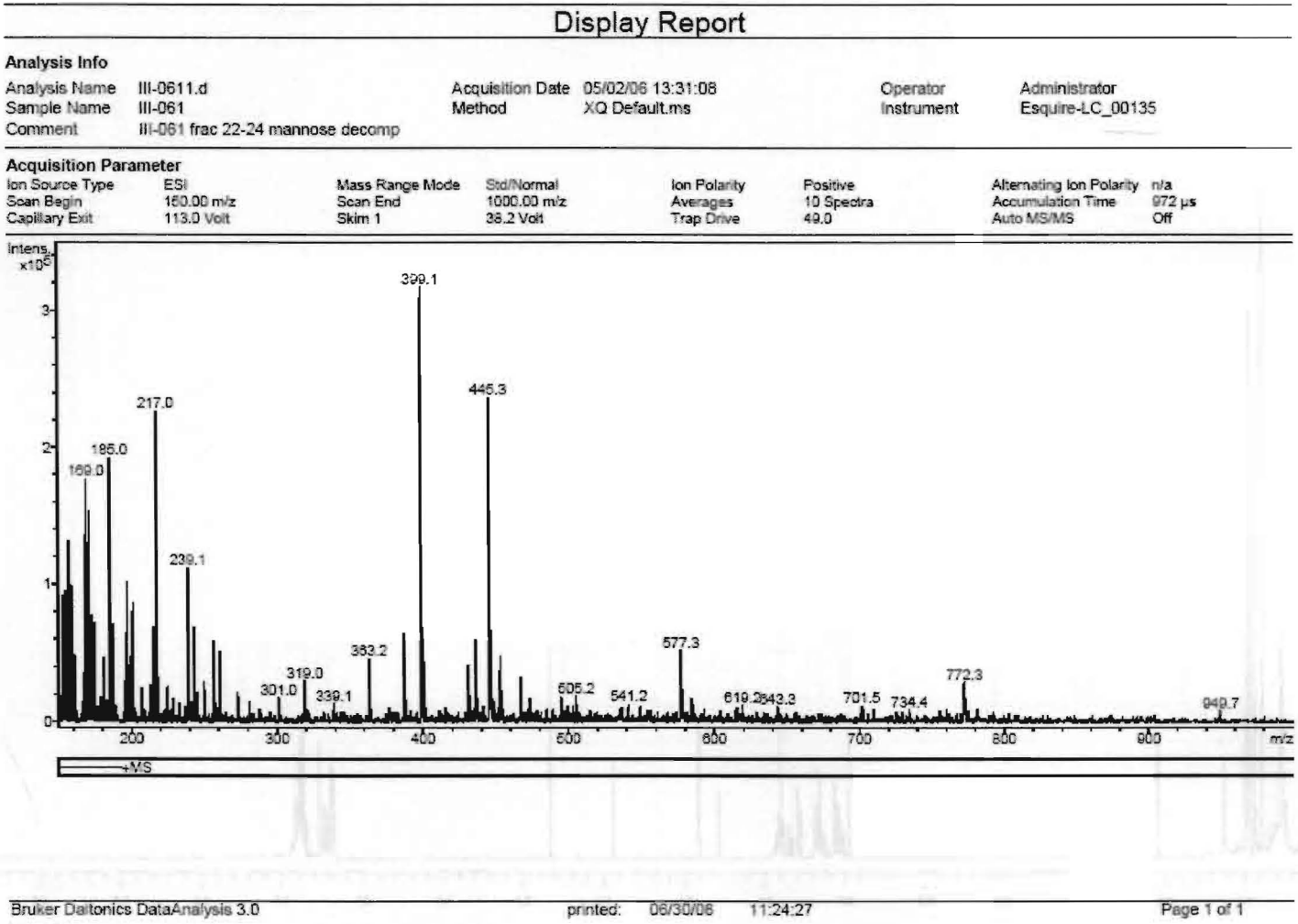


Figure 55: Mass spectrum of mannofuranose insertion product **19**.

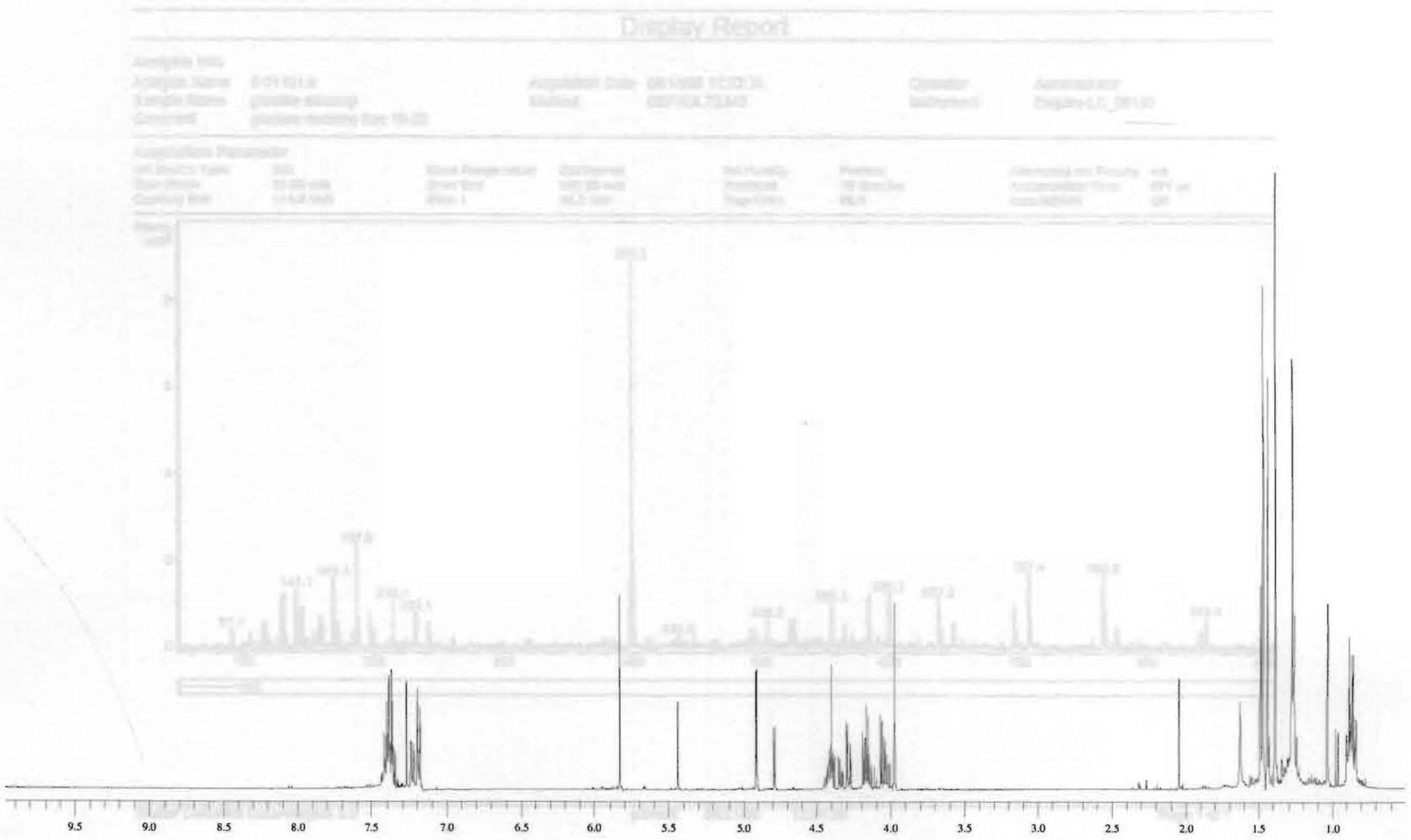


Figure 56: ^{1}H NMR spectrum of glucofuranose insertion product **20**.

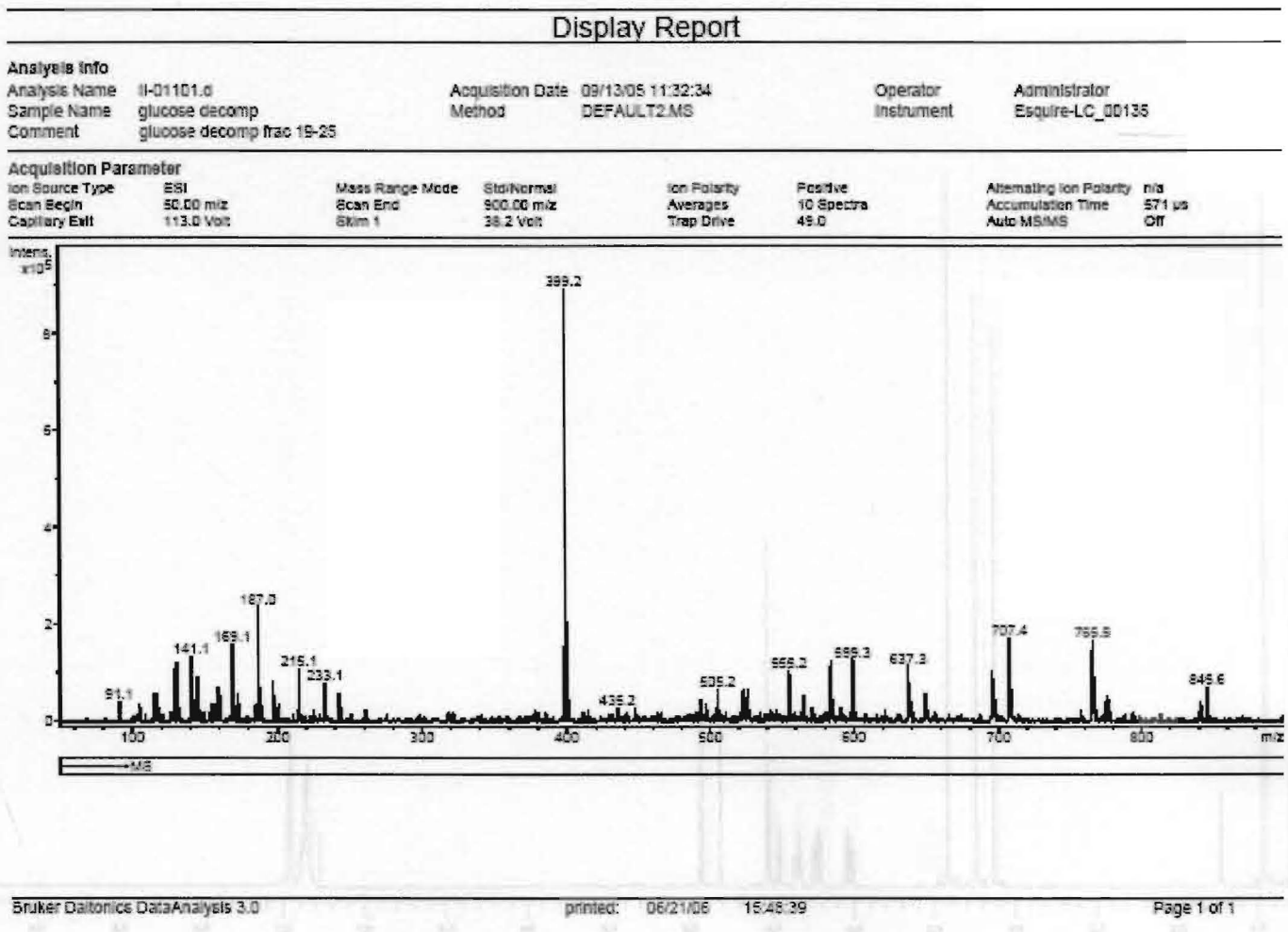


Figure 57: Mass spectrum of glucofuranose insertion product **20**.

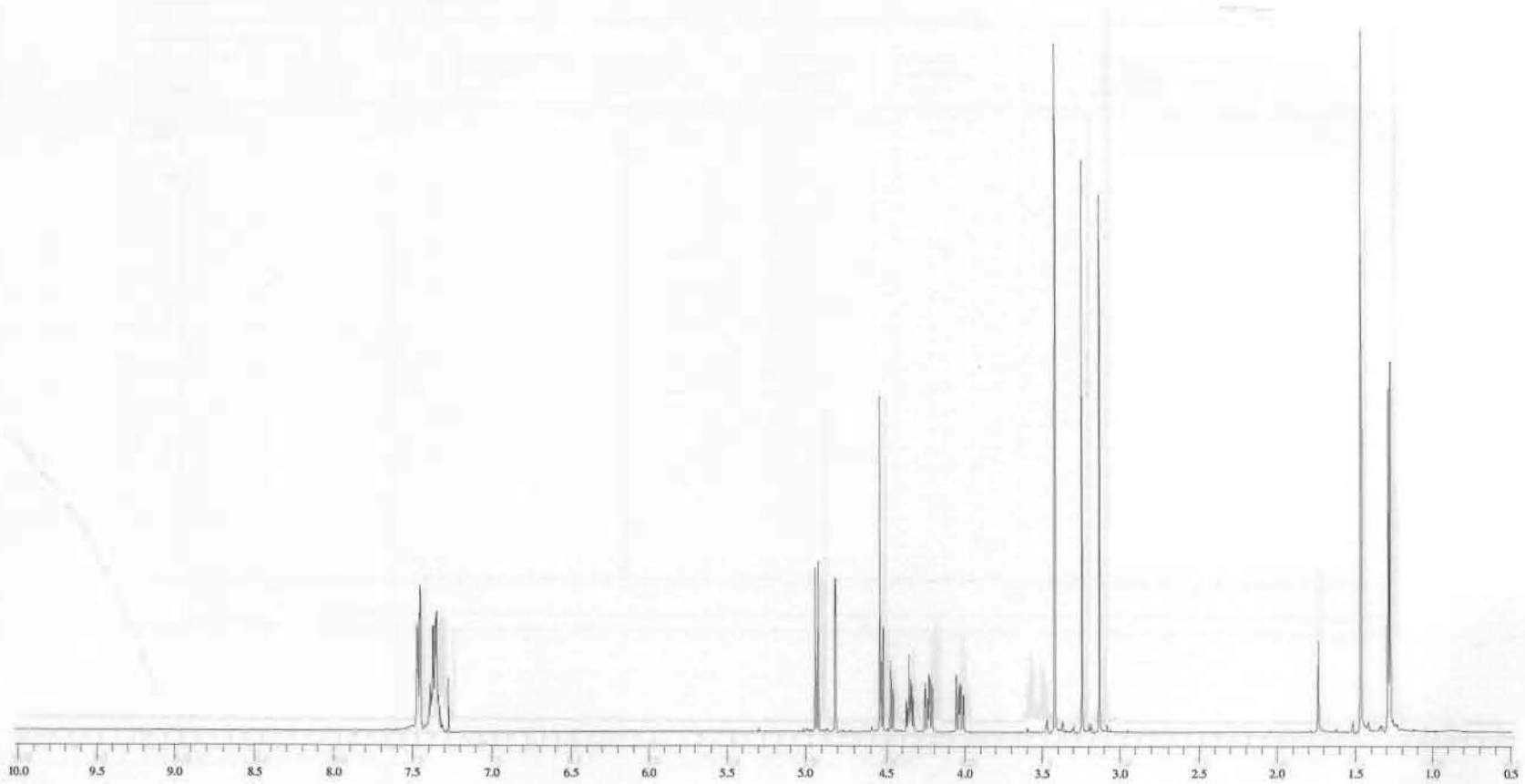


Figure 58: ^{1}H NMR specrum of methyl 2,3-*O*-isopropylidene-5-*O*-(2-methoxy-2-phenylacetyl)-β-D-ribofuranosides (**21**).

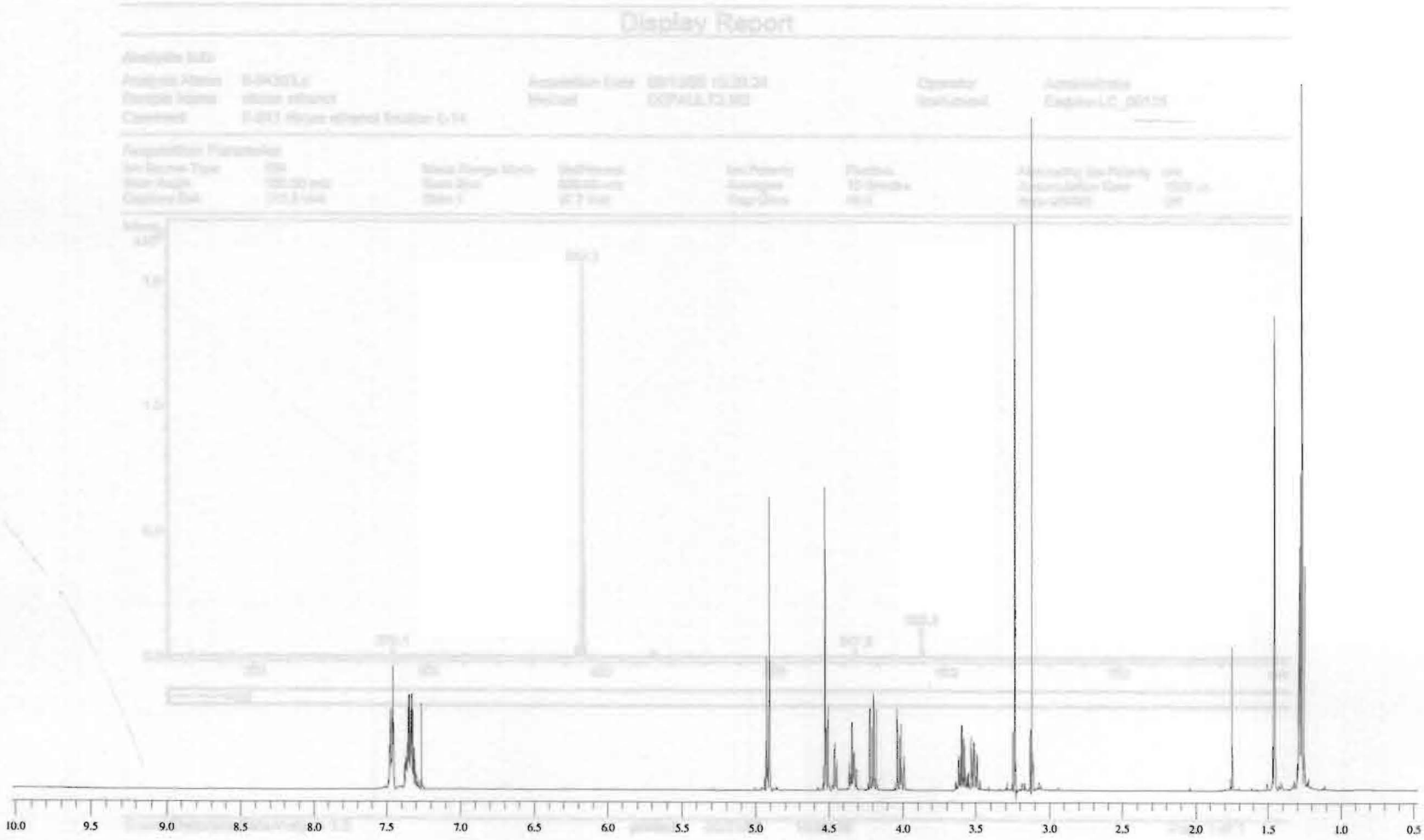


Figure 59: ^{1}H NMR spectrum of methyl 2,3-*O*-isopropylidene-5-*O*-(2-ethoxy-2-phenylacetyl)-β-D-ribofuranosides (**22**).

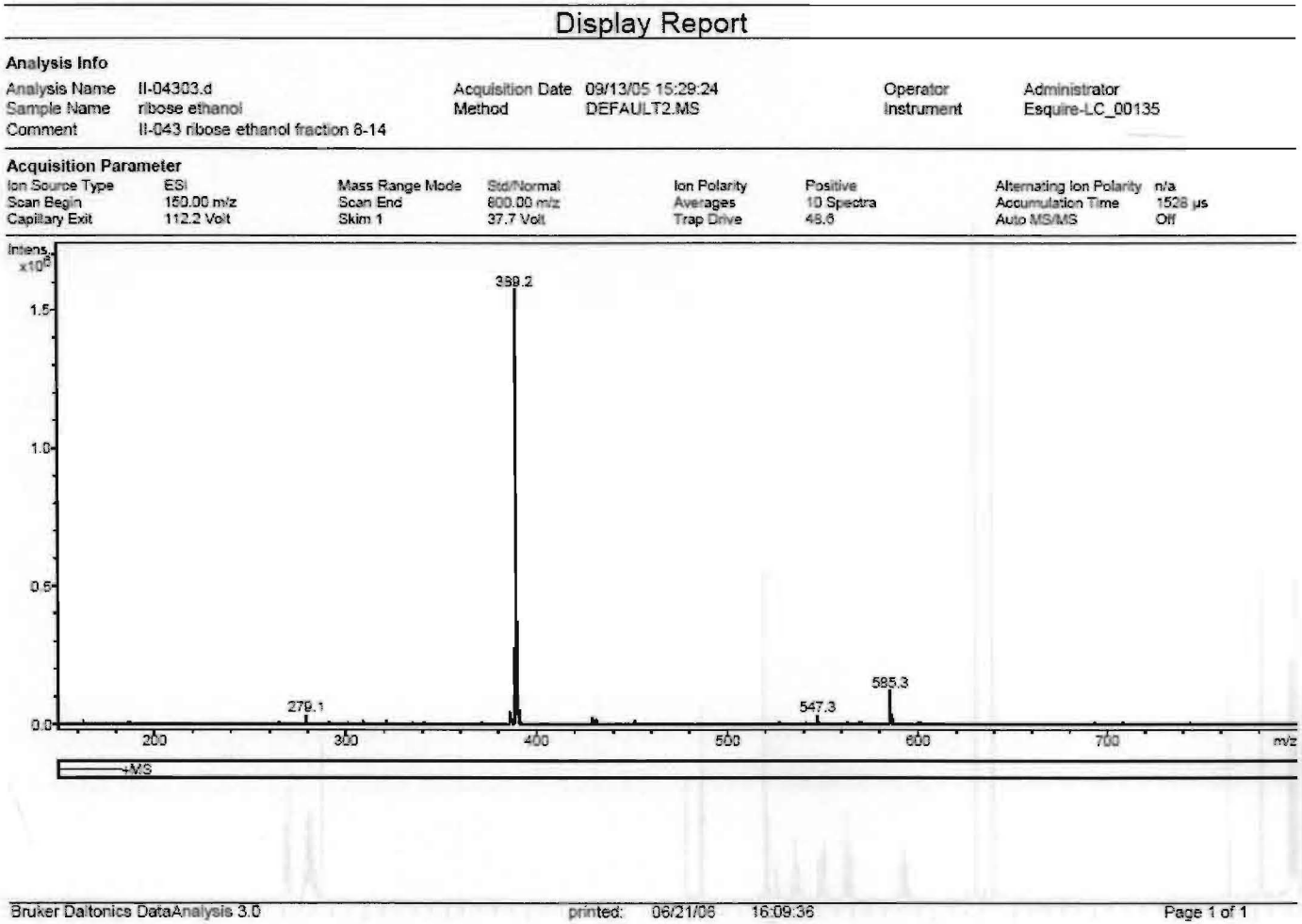


Figure 60: Mass spectrum of methyl 2,3-*O*-isopropylidene-5-*O*-(2-ethoxy-2-phenylacetyl)-β-D-ribofuranosides (**22**).

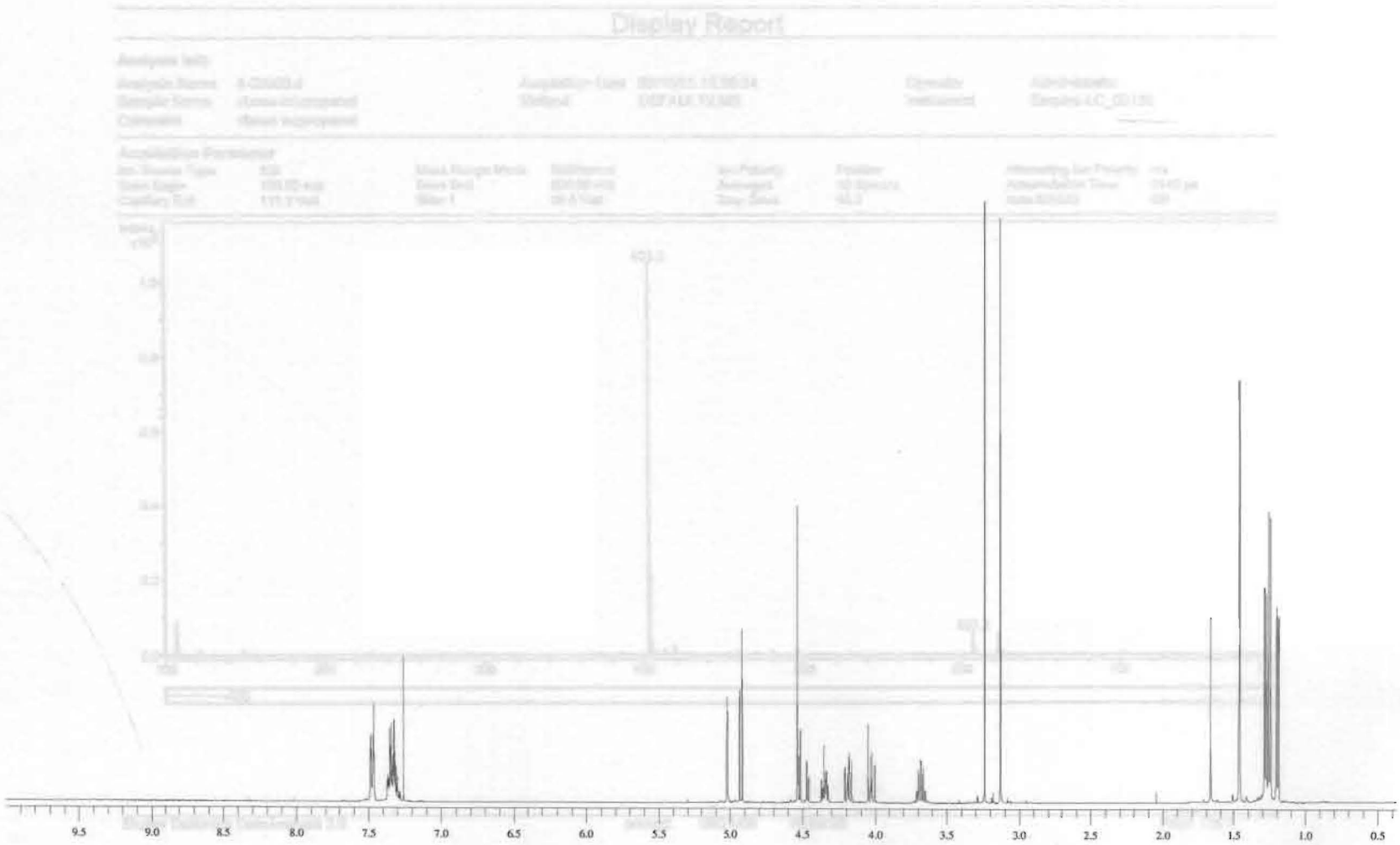


Figure 61: ^{1}H NMR spectrum of methyl 2,3-*O*-isopropylidene-5-*O*-(2-isopropoxy-2-phenylacetyl)-β-D-ribofuranosides (**23**).

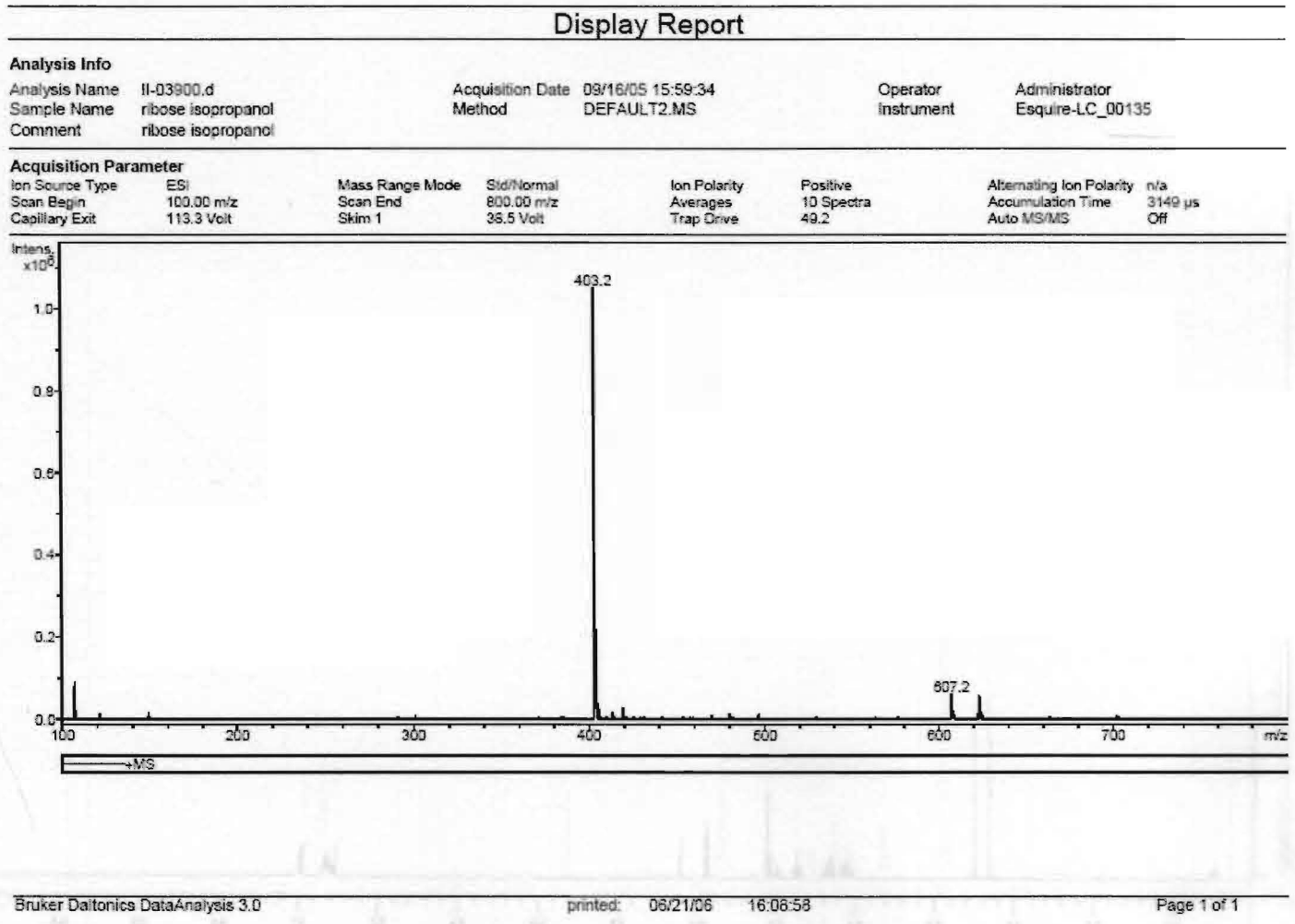


Figure 62: Mass spectrum of methyl 2,3-*O*-isopropylidene-5-*O*-(2-isopropoxy-2-phenylacetyl)-β-D-ribofuranose (**23**).

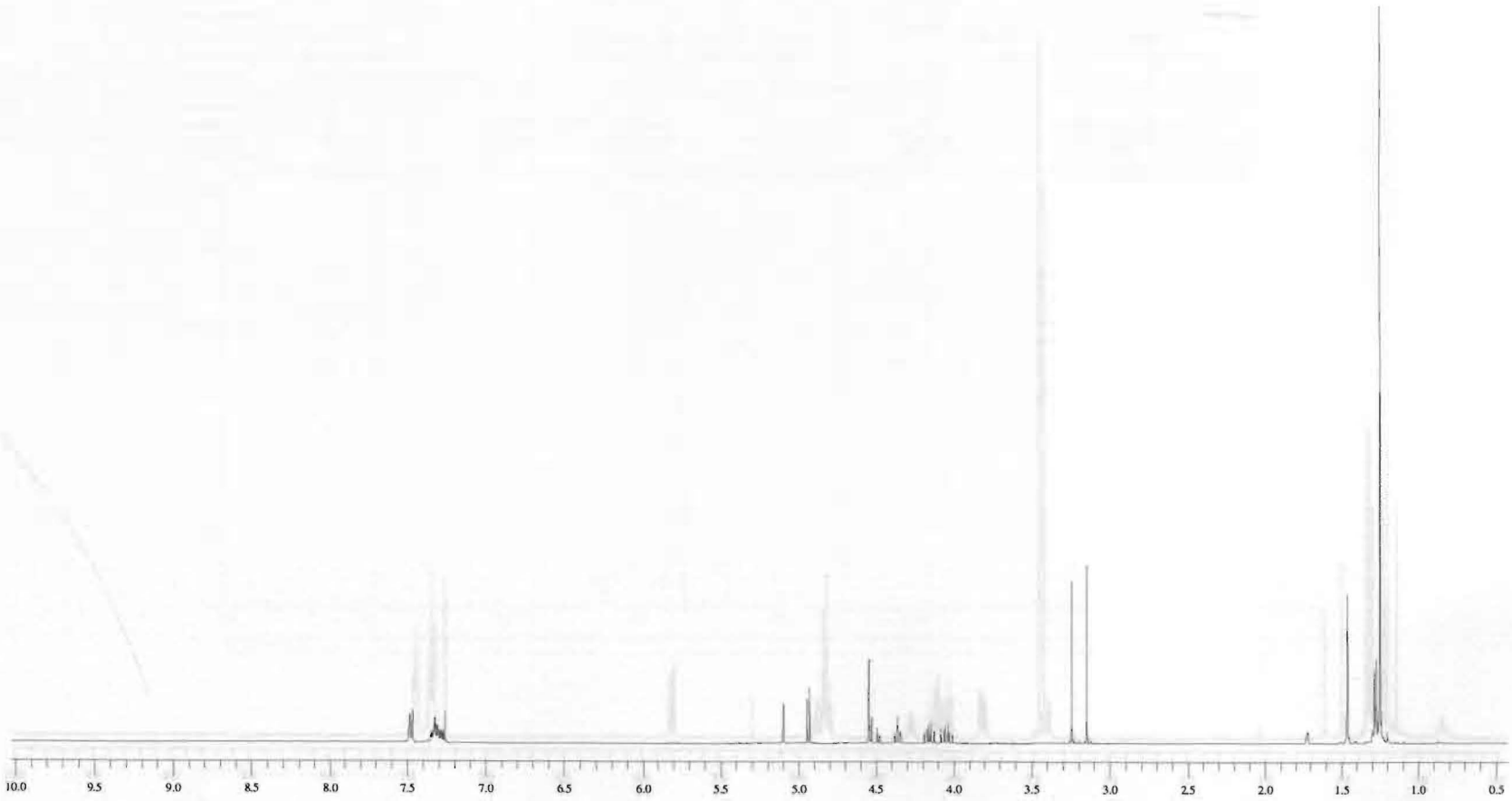


Figure 63: ^{1}H NMR spectrum of methyl 2,3-*O*-isopropylidene-5-*O*-(2-*t*-butoxy-2-phenylacetyl)-β-D-ribofuranosides (**24**).

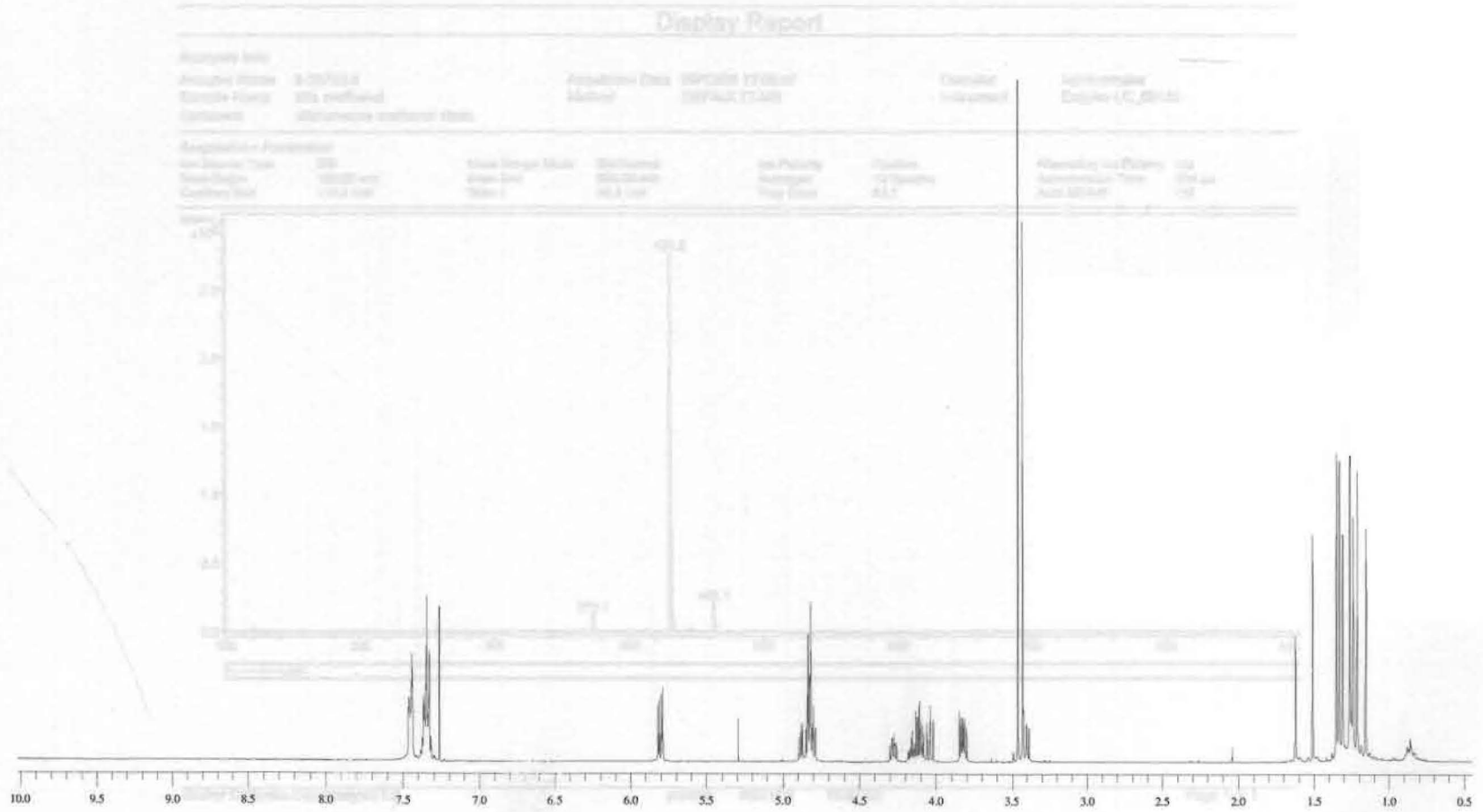


Figure 64: ^{1}H NMR spectrum of 1,2:5,6-di-*O*-isopropylidene-3-*O*-α-(2-methoxy-2-phenylacetyl)-α-D-allofuranose (**25**).

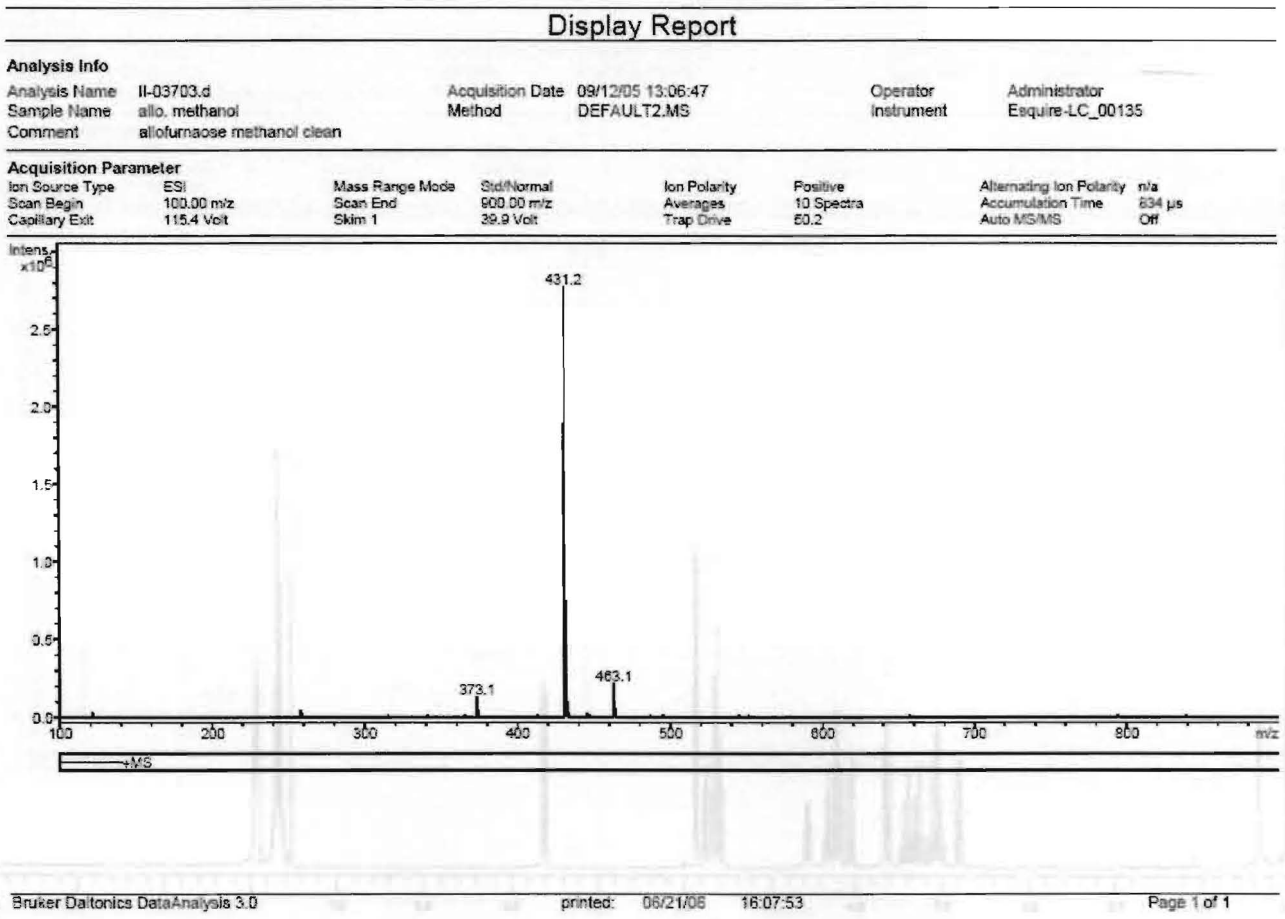


Figure 65: Mass spectrum of 1,2:5,6-di-*O*-isopropylidene-3-*O*-α-(2-methoxy-2-phenylacetyl)-α-D-allofuranose (**25**).

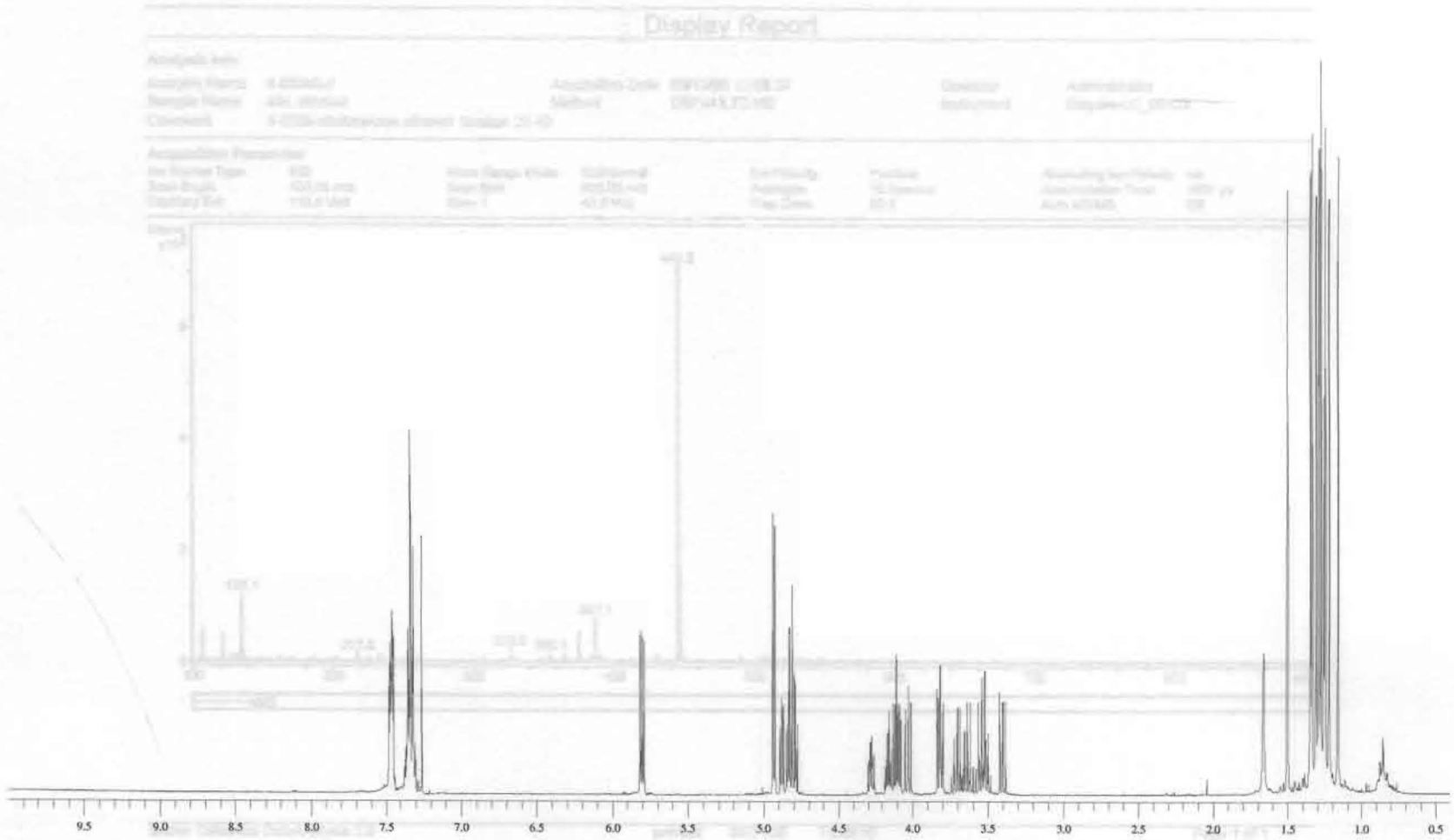


Figure 66: ^{1}H NMR spectrum of 1,2:5,6-di-*O*-isopropylidene-3-*O*-α-(2-ethoxy-2-phenylacetyl)-α-D-allofuranose (**26**).

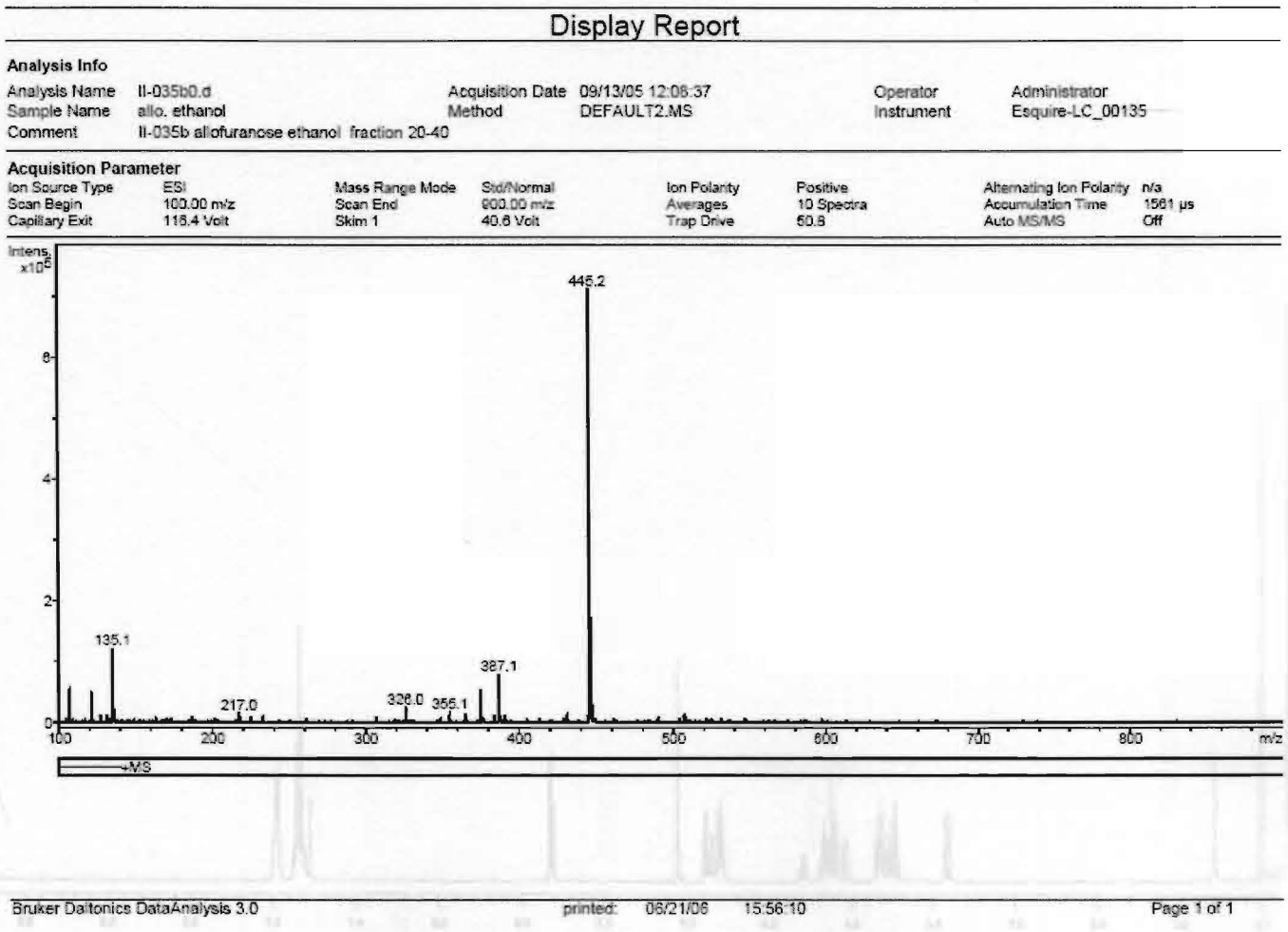


Figure 67: Mass spectrum of 1,2:5,6-di-*O*-isopropylidene-3-*O*-α-(2-ethoxy-2-phenylacetyl)-α-D-allofuranose (**26**).

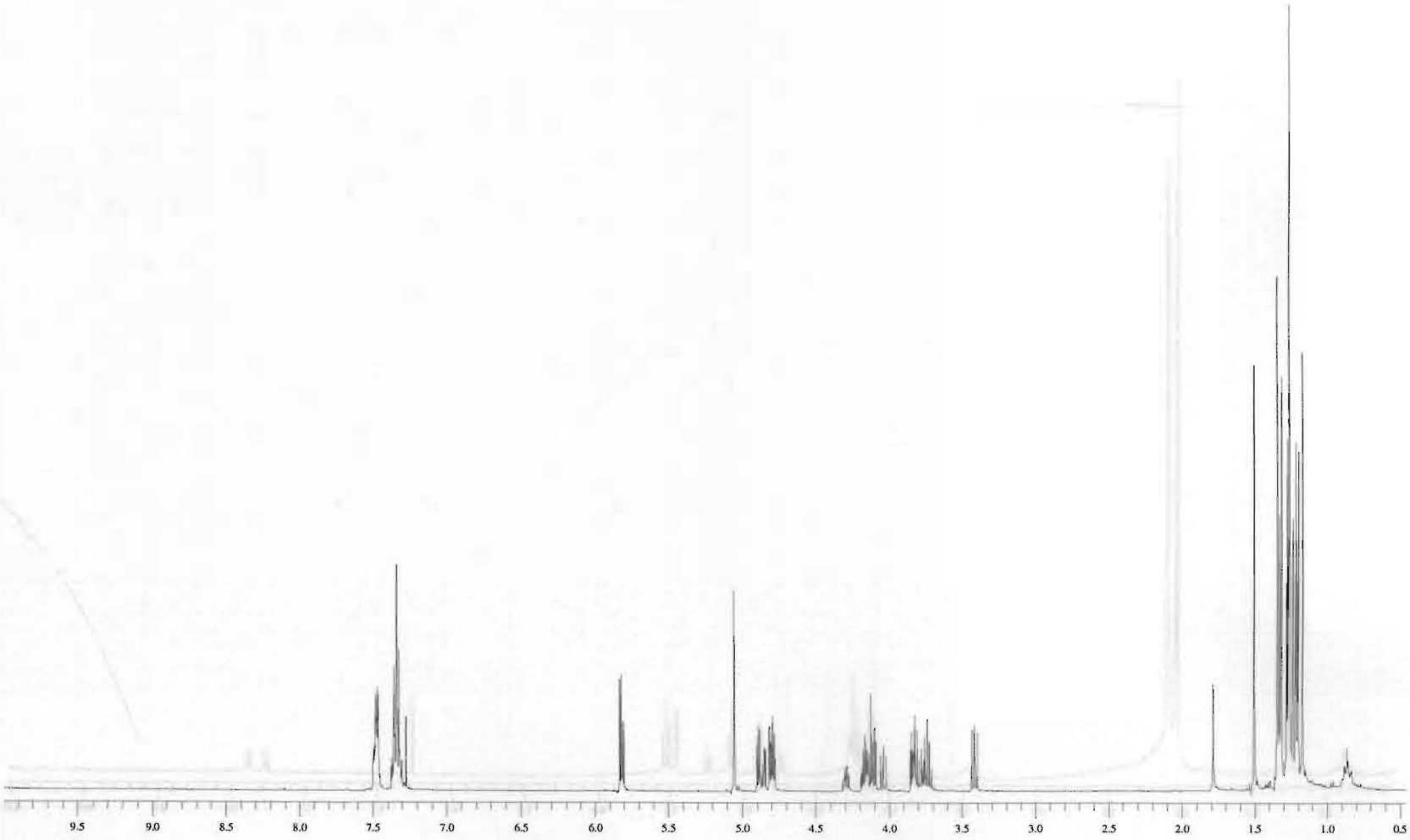


Figure 68: ^{1}H NMR spectrum of 1,2:5,6-di-*O*-isopropylidene-3-*O*-α-(2-isopropoxy-2-phenylacetyl)-α-D-allofuranose (**27**).

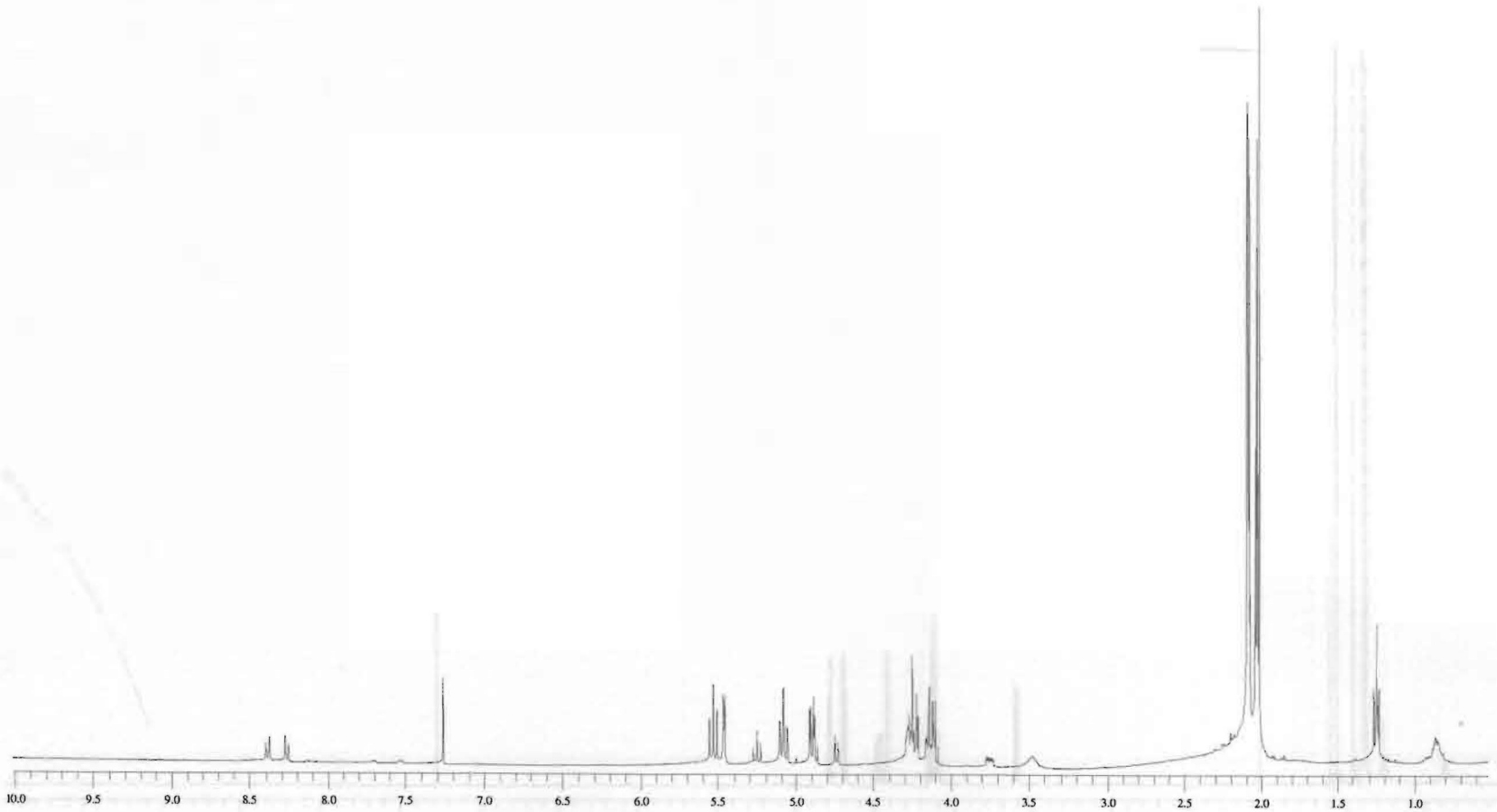


Figure 69: ^{1}H NMR spectrum of 2,3,4,6-tetra-*O*-acetyl-α/β-D-glucopyranose (**29**).

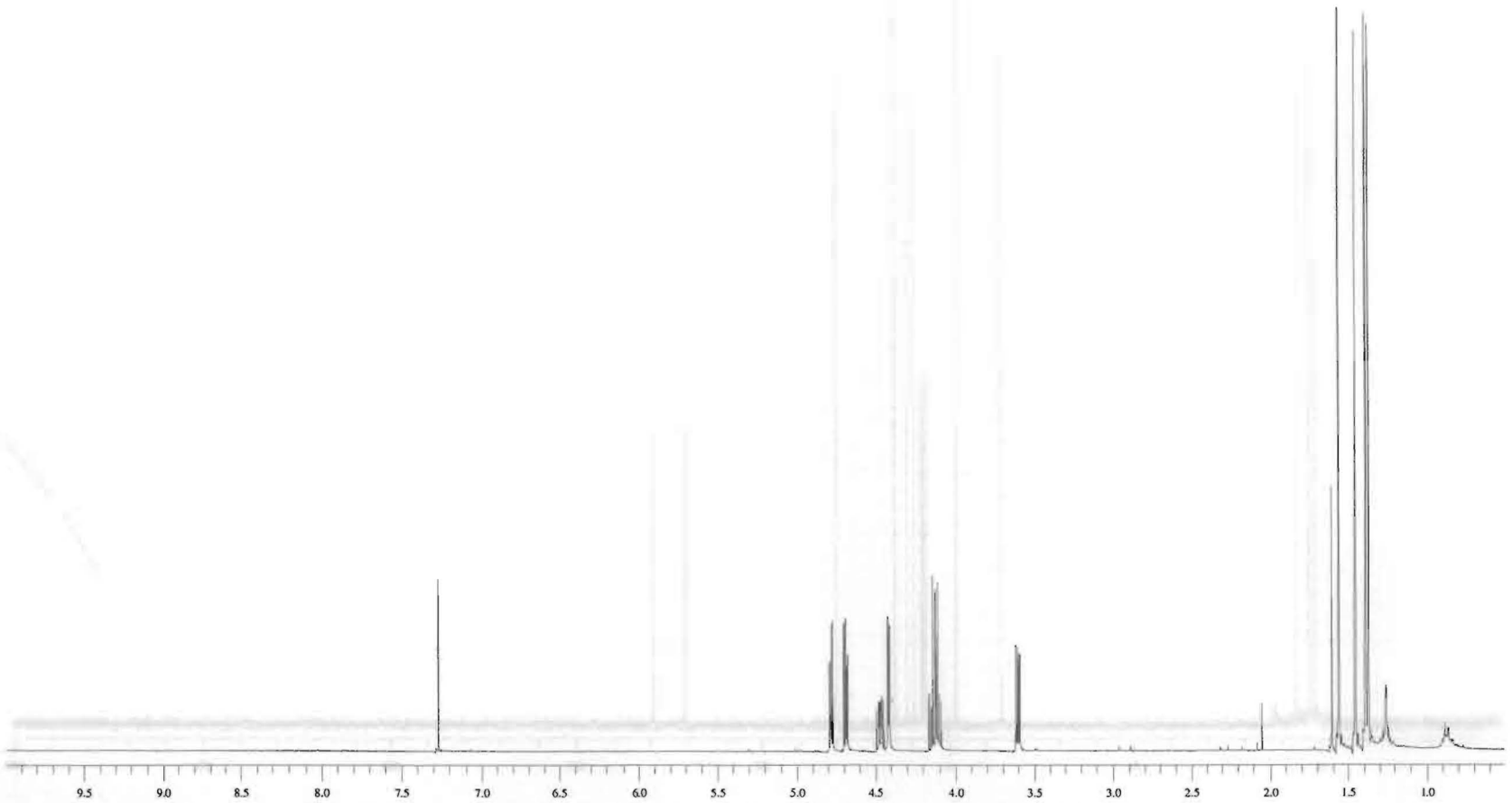


Figure 70: ^{1}H NMR spectrum of 1-azido-1-deoxy-2,3:5,6-di-*O*-isopropylidene-β-D-mannofuranose (**13**).

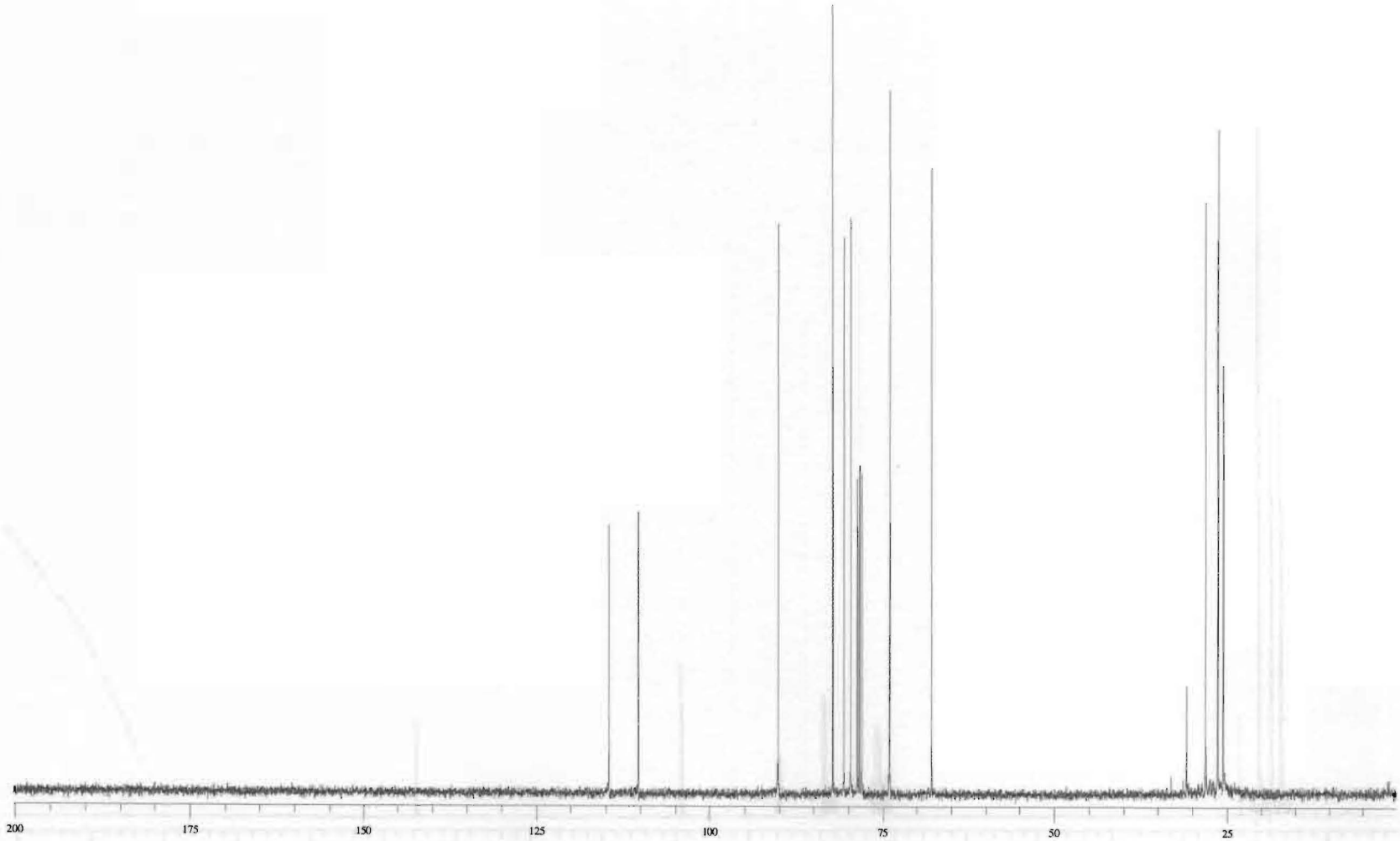


Figure 71: ^{13}C NMR spectrum of 1-azido-1-deoxy-2,3:5,6-di-*O*-isopropylidene-β-D-mannofuranose (**13**).

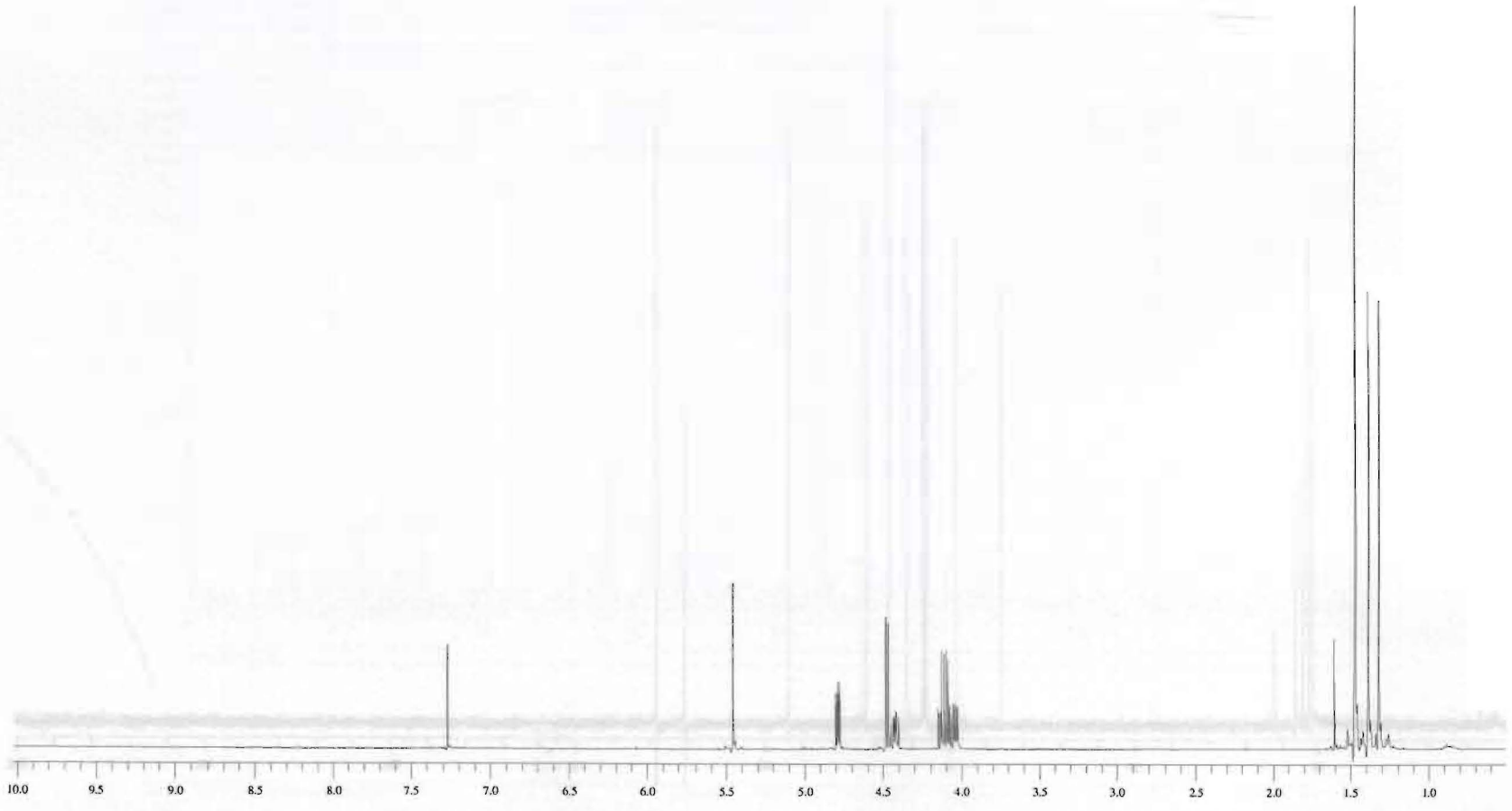


Figure 72: ^{1}H NMR spectrum of 1-azido-1-deoxy-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (**30**).

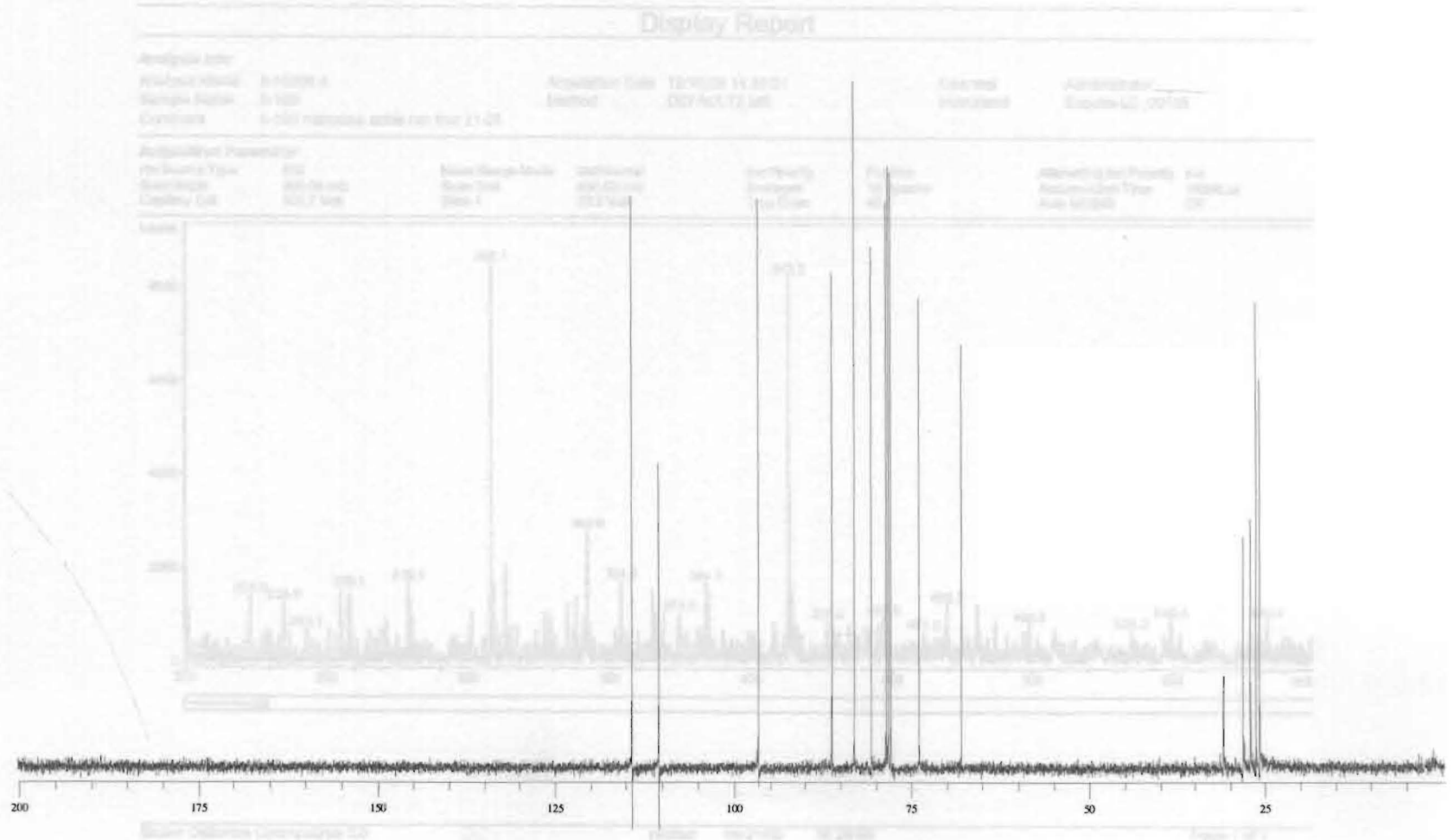


Figure73: ^{13}C NMR spectrum of 1-azido-1-deoxy-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (**30**).

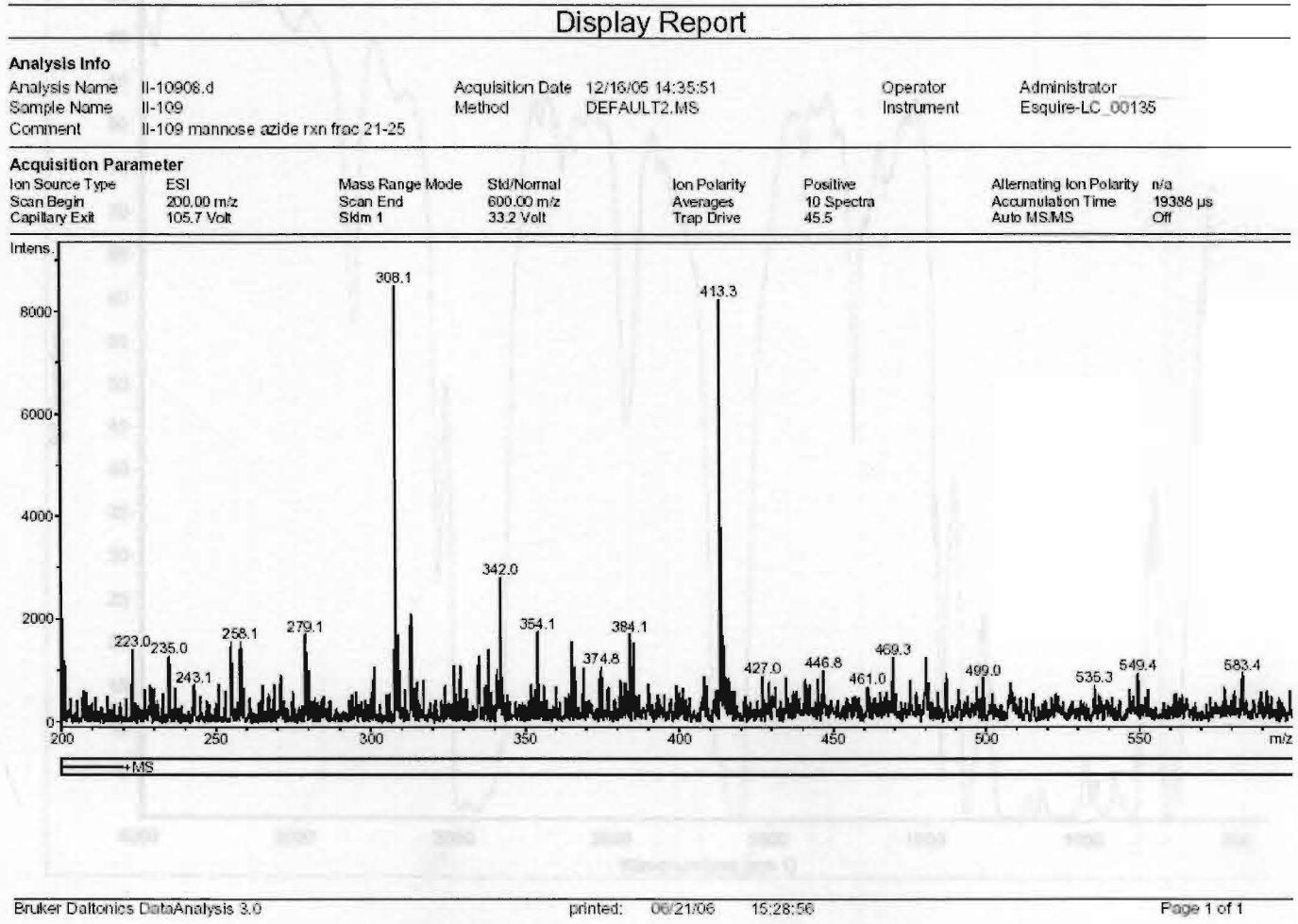


Figure74: Mass spectrum of 1-azido-1-deoxy-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (**30**).

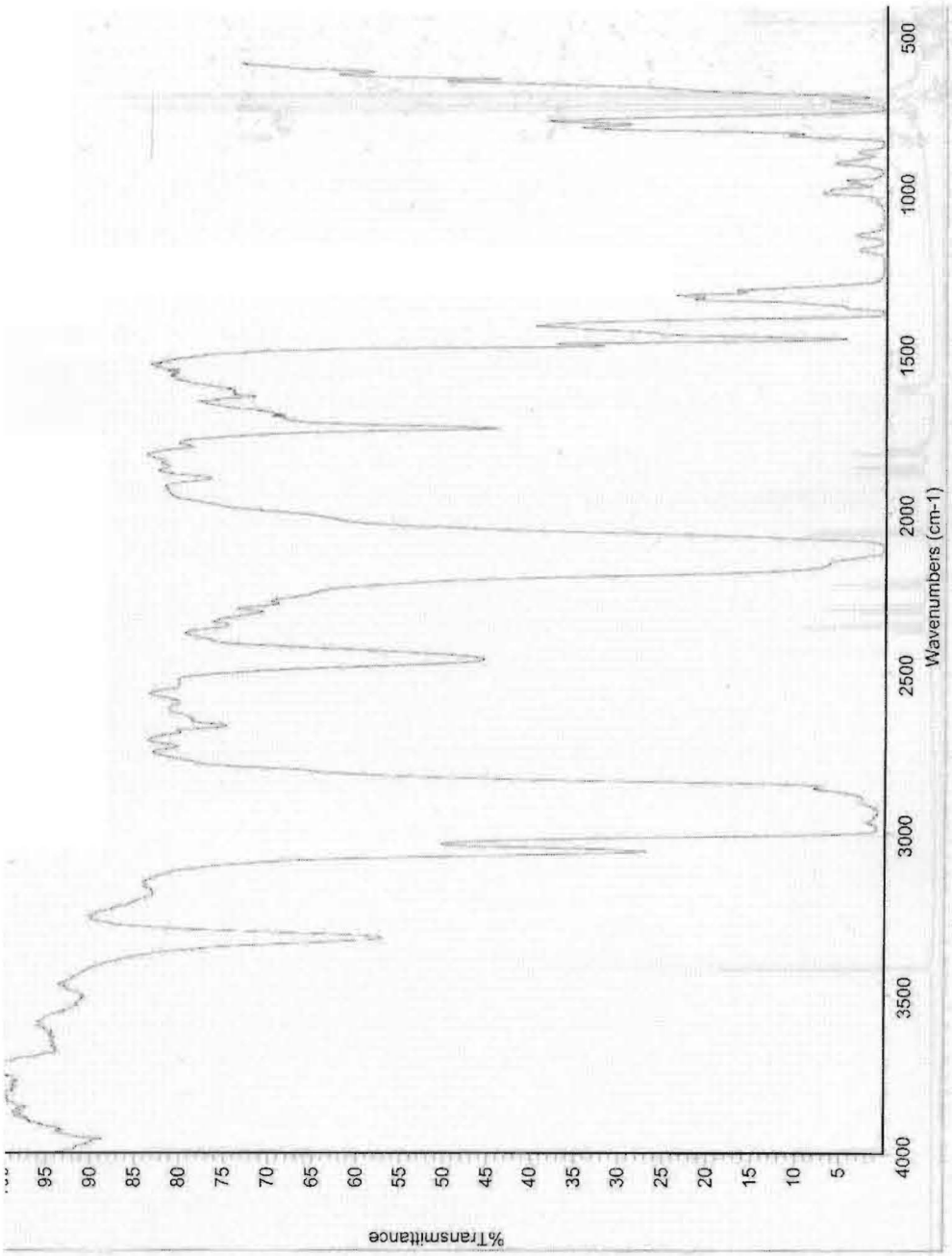


Figure75: IR spectrum of 1-azido-1-deoxy-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (**30**).

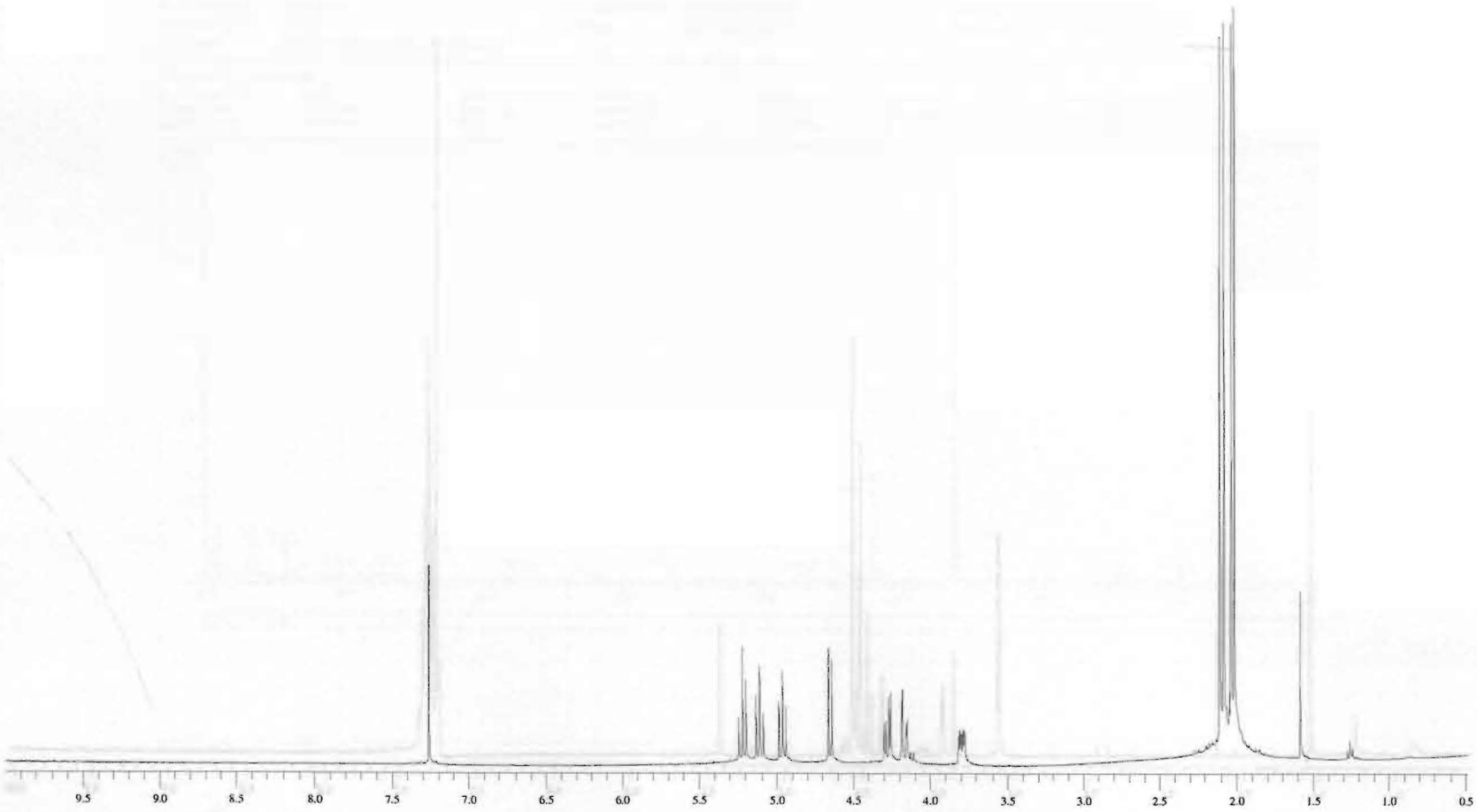


Figure 76: ^{1}H NMR spectrum of 1-azido-1-deoxy-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose (**32**).

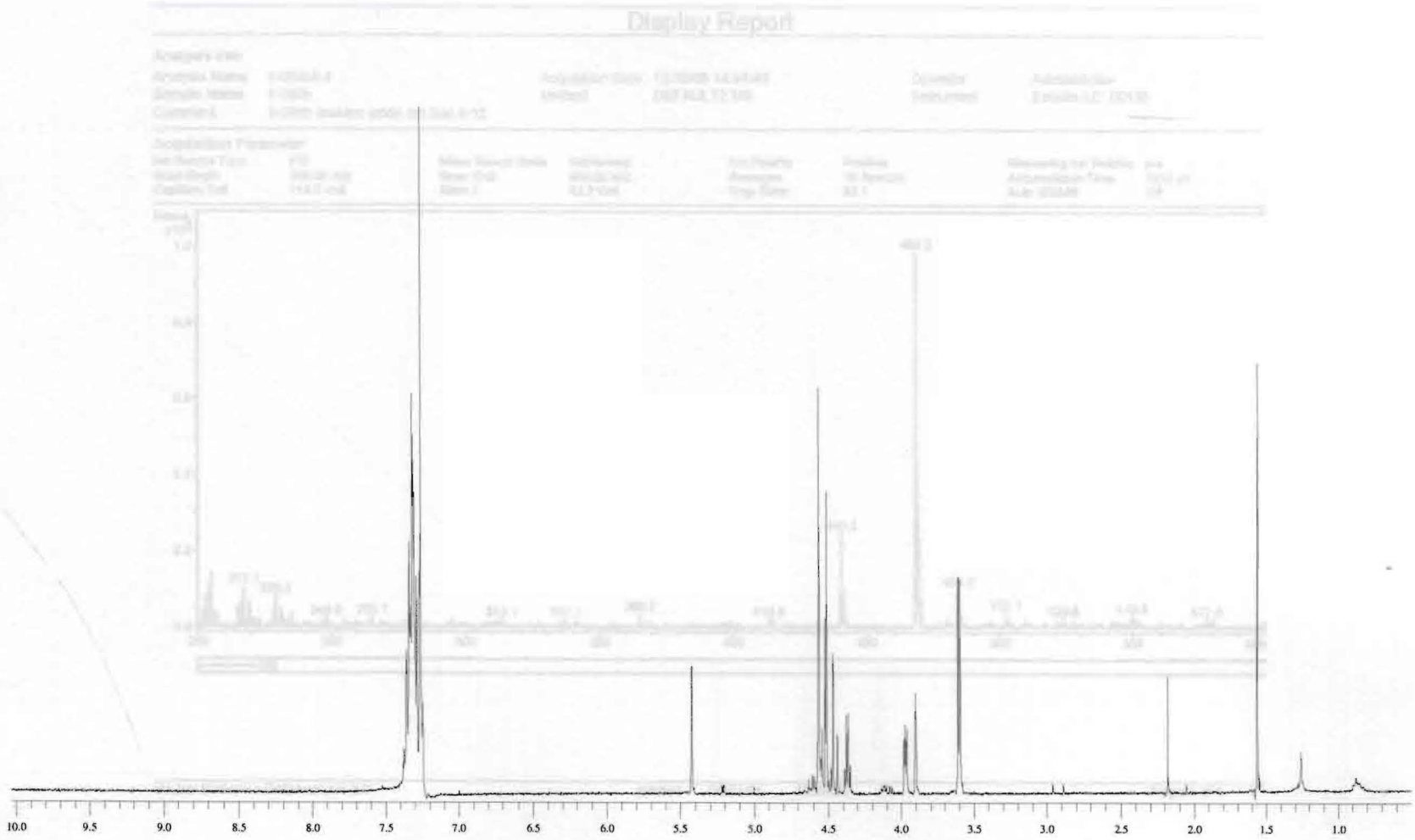


Figure 77: ^{1}H NMR spectrum of 2,3,5-tri-*O*-benzyl-α-D-arabinofuranosyl azide (**33α**).

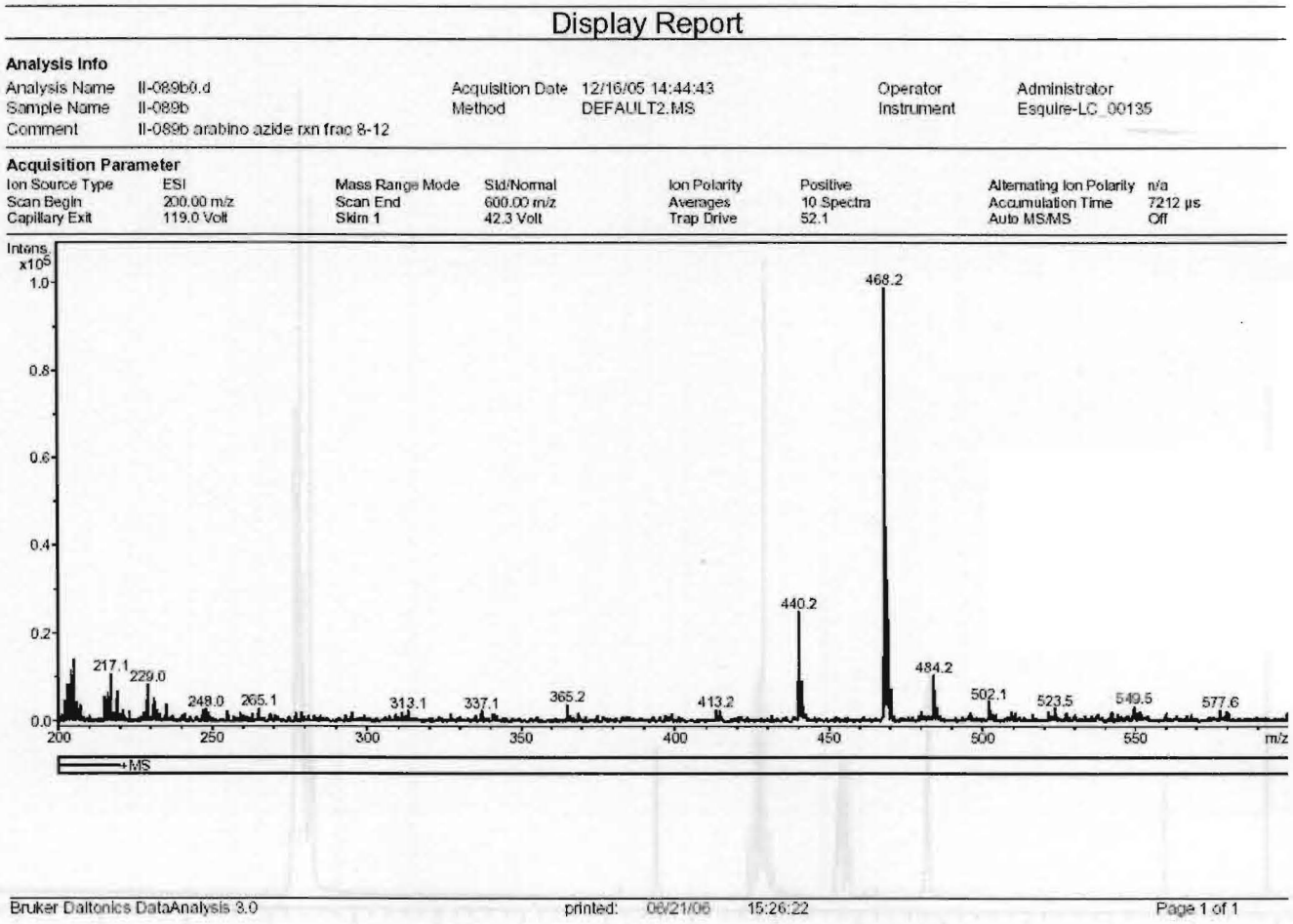


Figure 78: Mass spectrum of 2,3,5-tri-*O*-benzyl-α-D-arabinofuranosyl azide (**33α**).

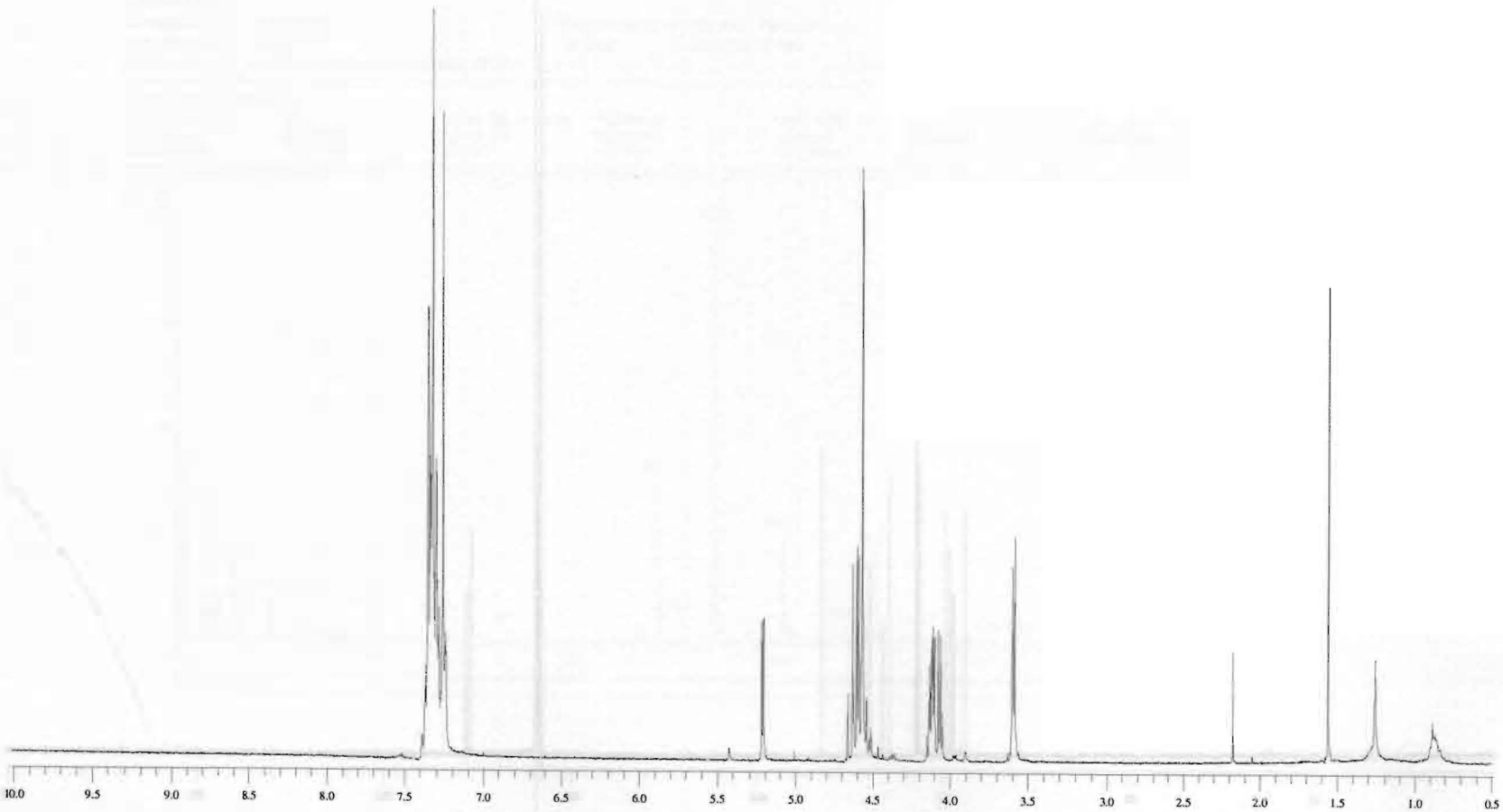


Figure 79: ^{1}H NMR spectrum of 2,3,5-tri-*O*-benzyl-β-D-arabinofuranosyl azide (**33β**).

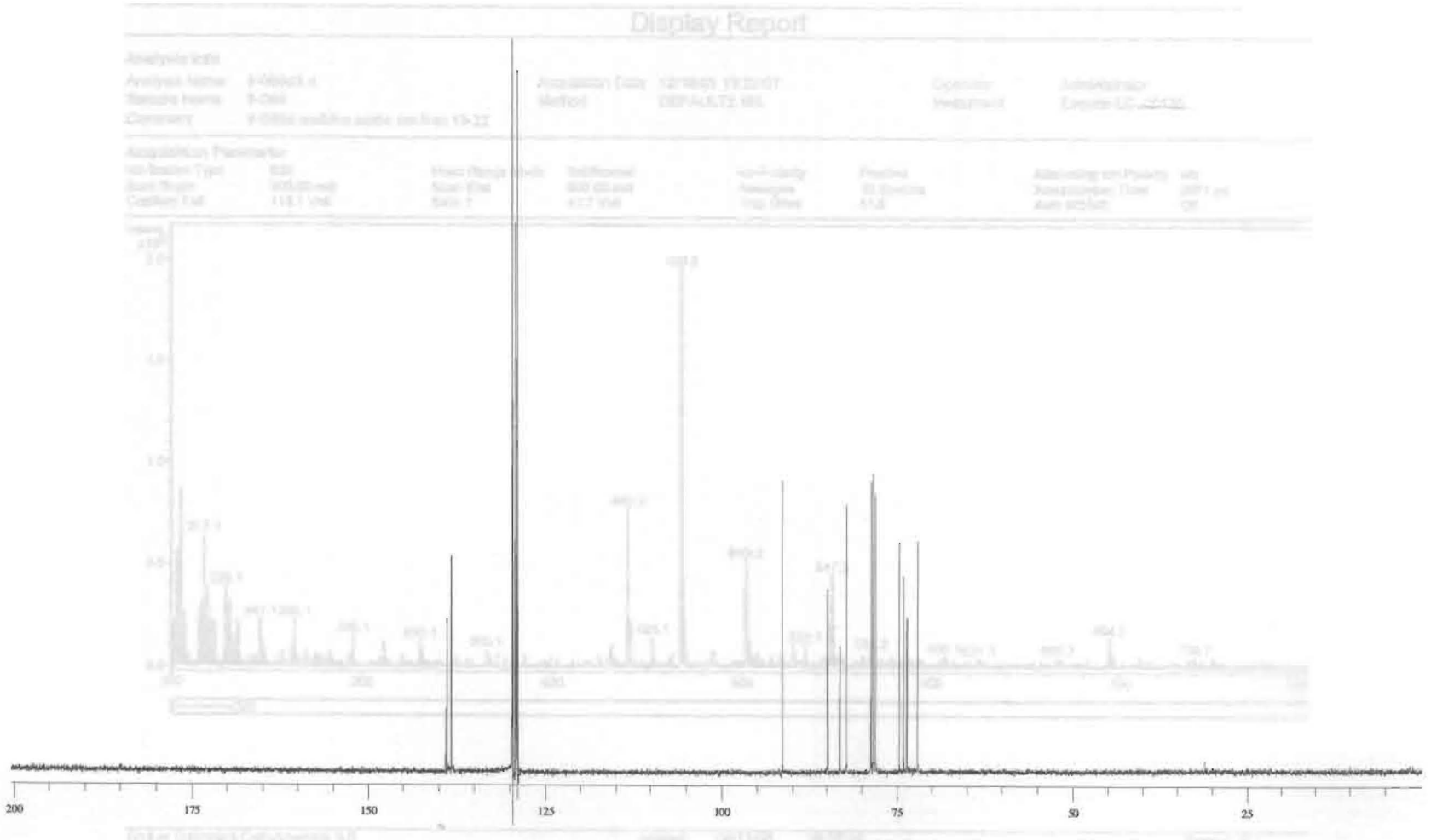


Figure 80: ^{13}C NMR spectrum of 2,3,5-tri-*O*-benzyl-β-D-arabinofuranosyl azide (**33β**).

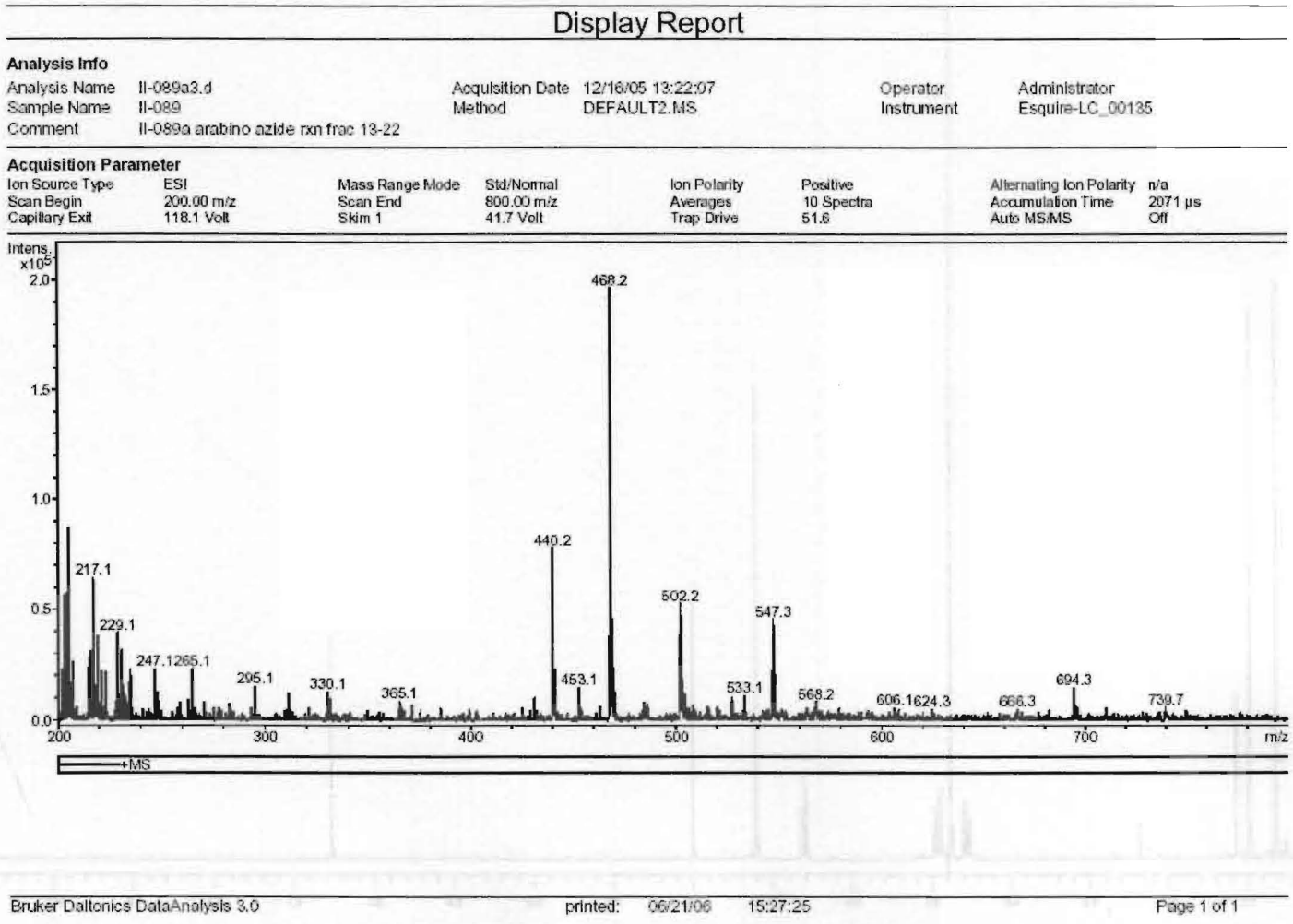


Figure 81: Mass spectrum of 2,3,5-tri-*O*-benzyl-β-D-arabinofuranosyl azide (**33β**).

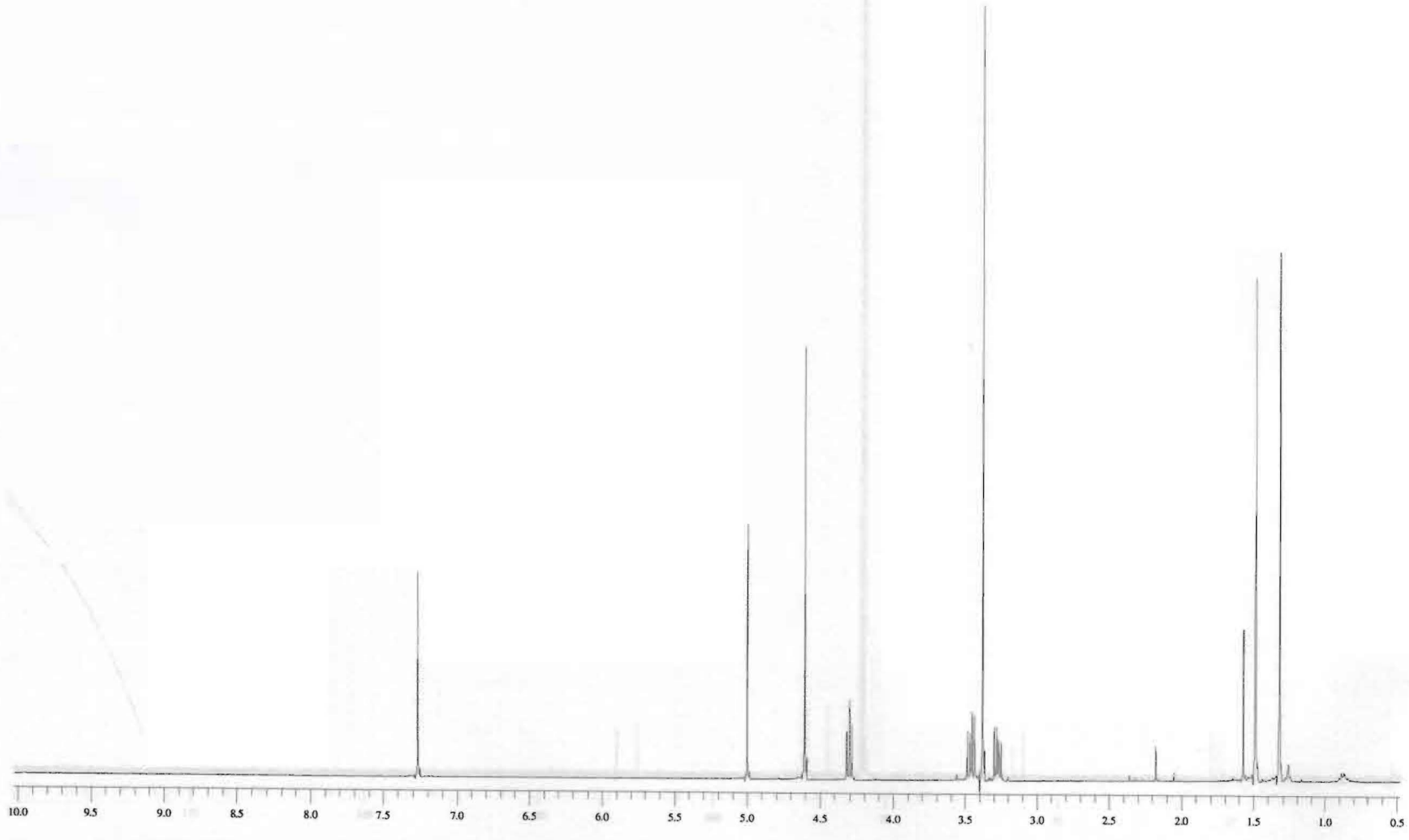


Figure 82: ^{1}H NMR spectrum of methyl 5-azido-5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranoside (**35**).

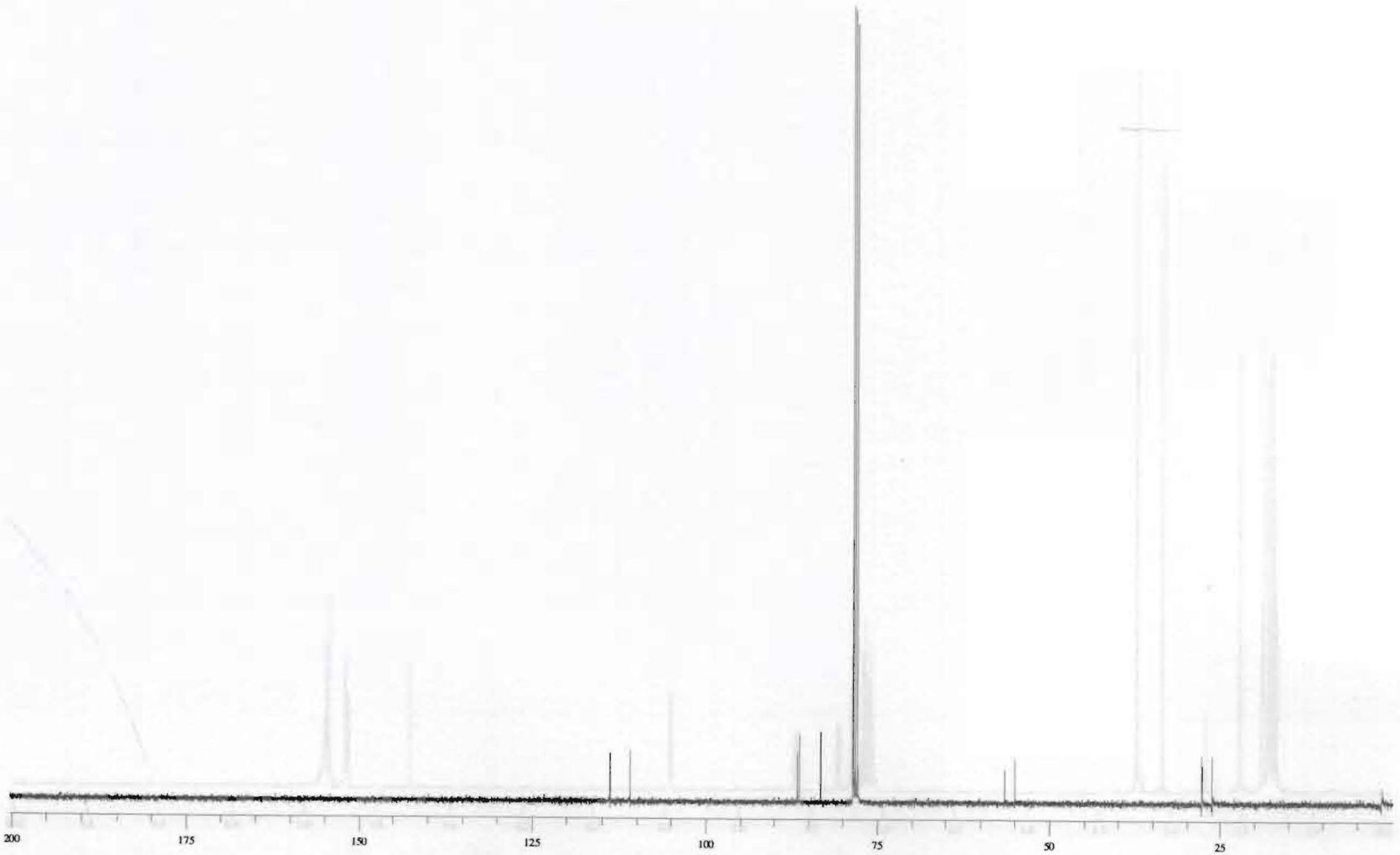


Figure 83: ^{13}C NMR spectrum of methyl 5-azido-5-deoxy-2,3-*O*-isopropylidene-β-D- ribofuranoside (**35**).

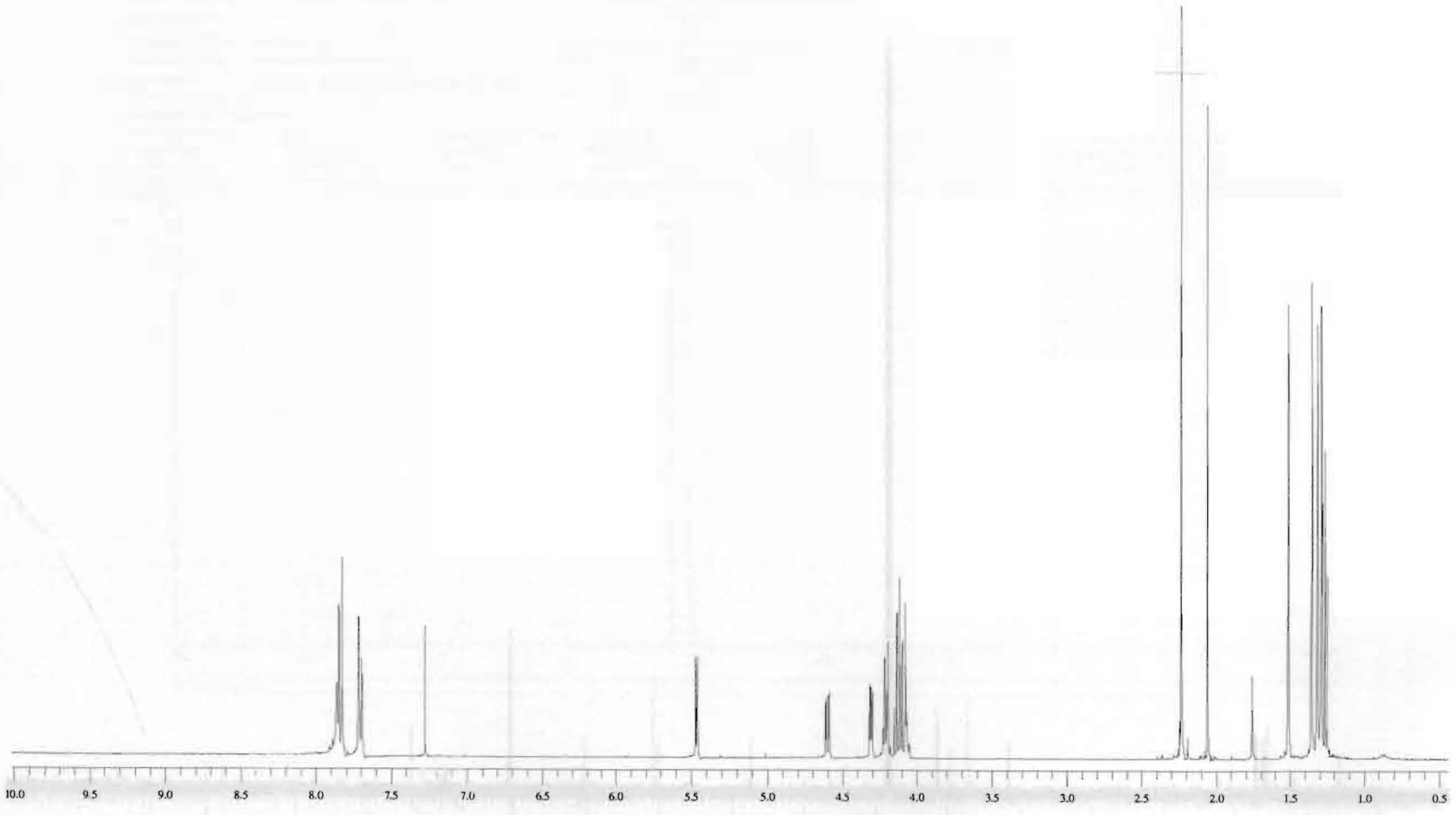


Figure 84: ^{1}H NMR spectrum of 6-*O*-(*p*-acetamido)benzenesulfonate ester of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**36**).

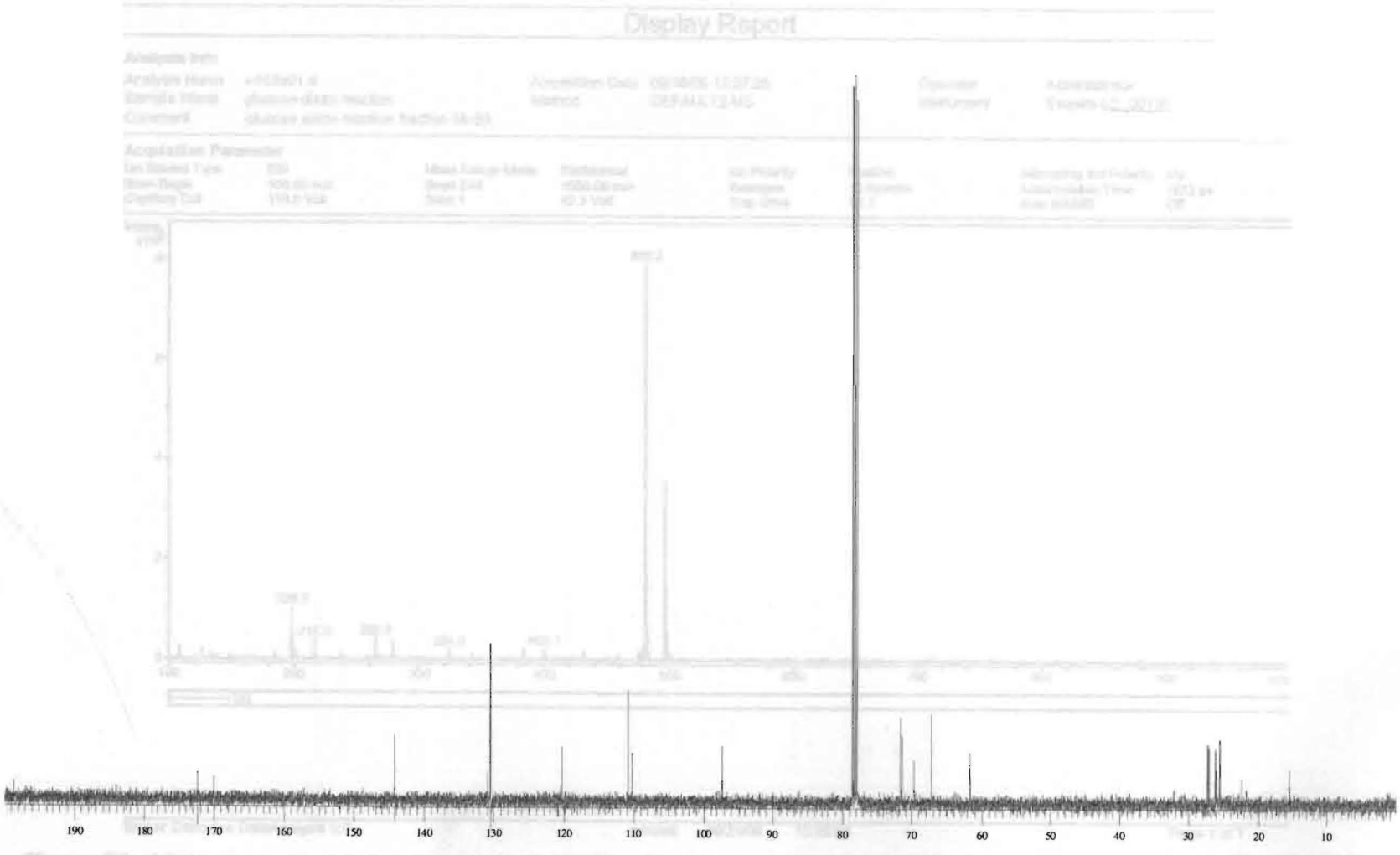


Figure 85: ^{13}C NMR spectrum of 6-*O*-(*p*-acetamido)benzenesulfonate ester of di-*O*-isopropylidene-α-D-galactopyranose (**36**).

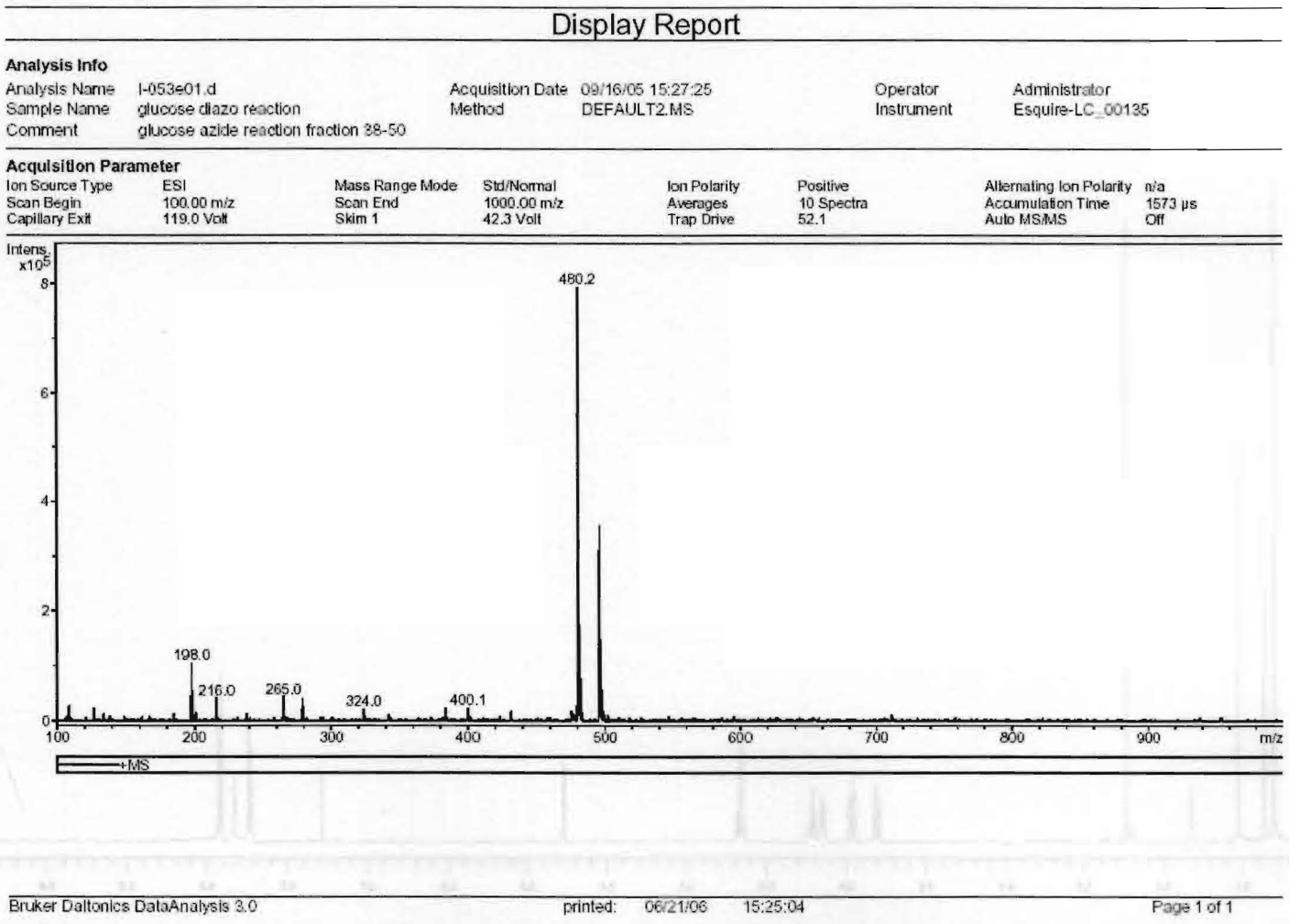


Figure 86: Mass spectrum of 6-*O*-(*p*-acetamido)benzenesulfonate ester of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**36**).

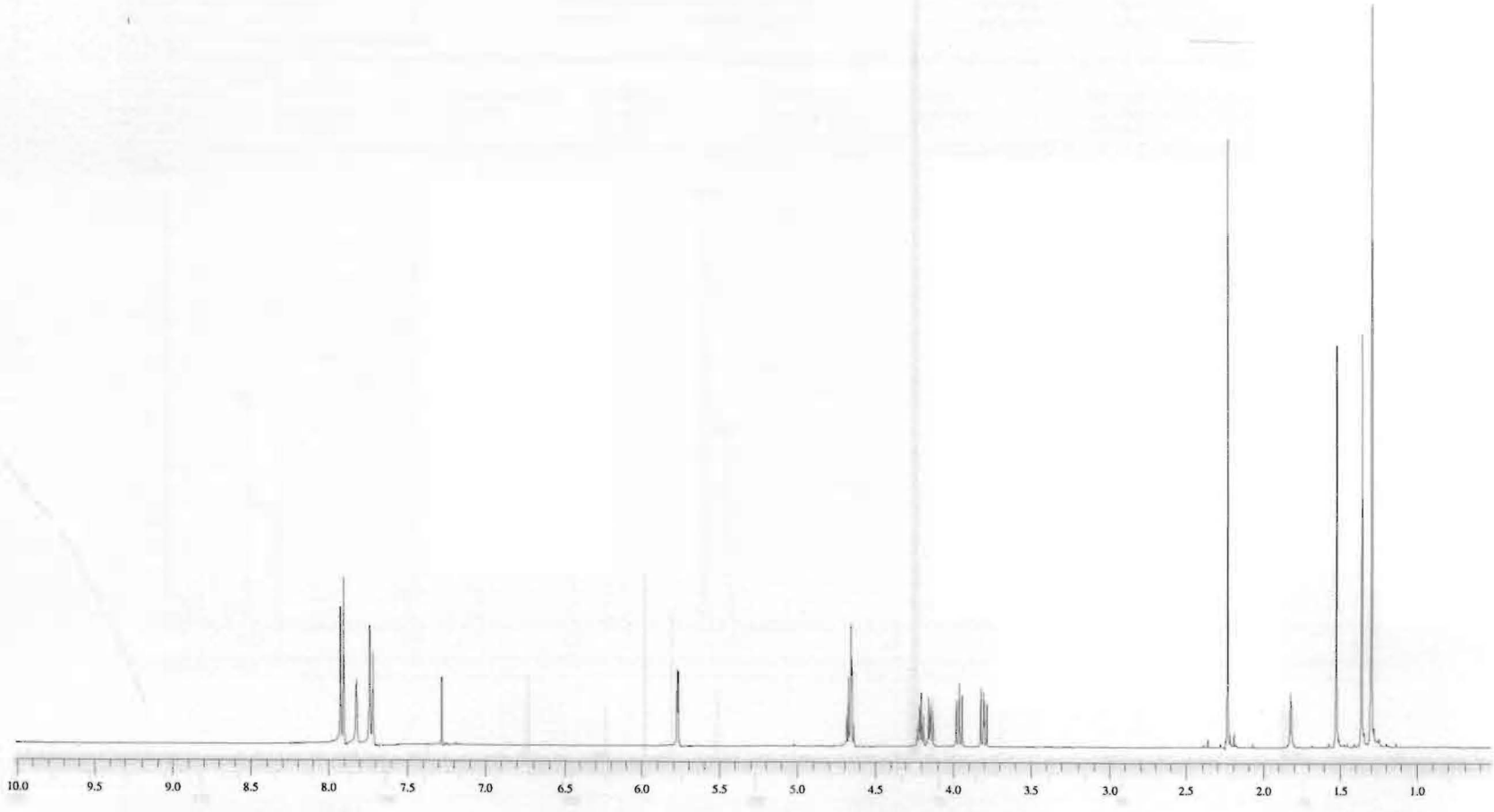


Figure 87: ^{1}H NMR spectrum of 3-*O*-(*p*-acetamido)benzenesulfonate ester of 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**37**).

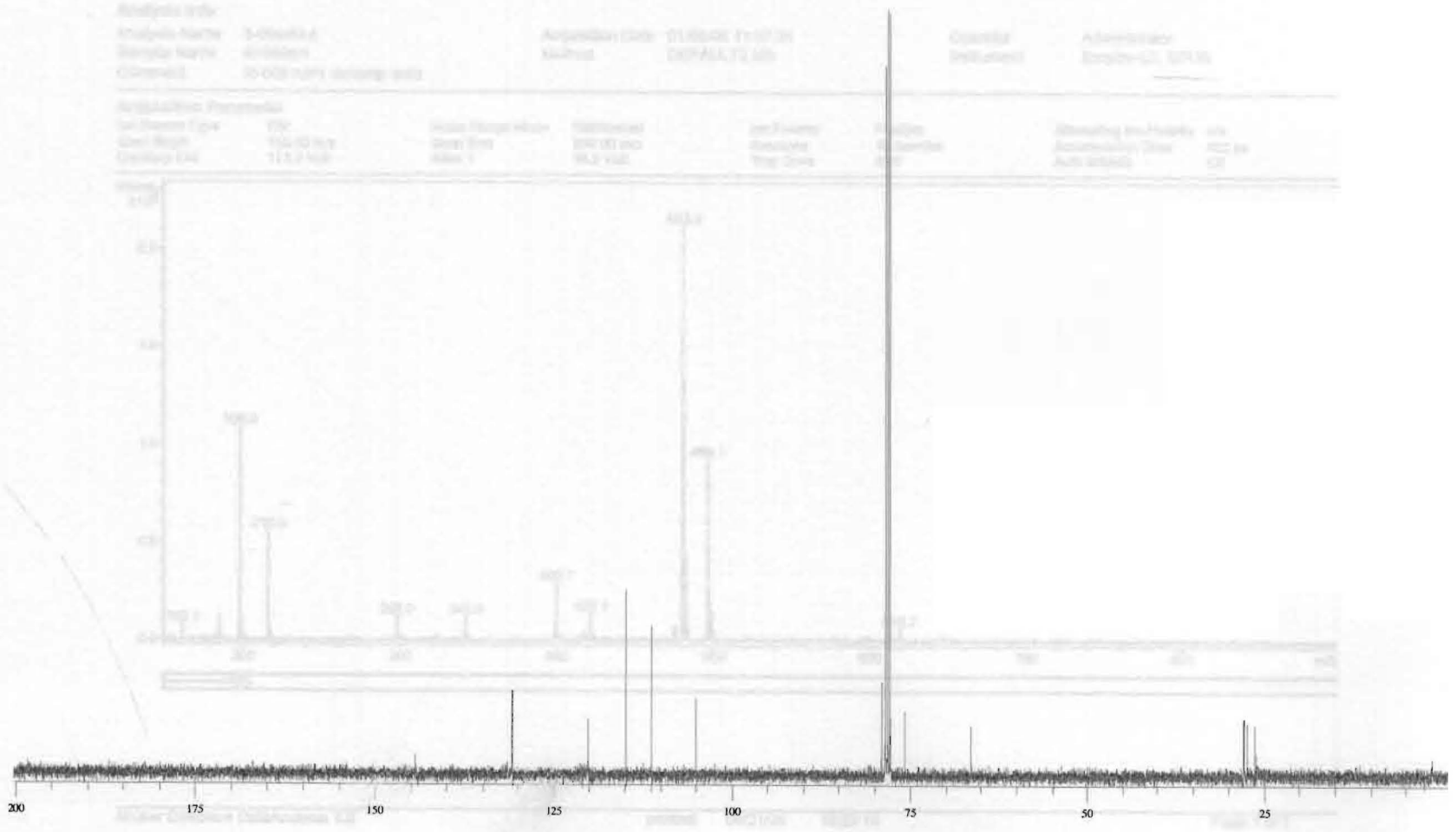


Figure 88: ^{13}C NMR spectrum of 3-*O*-(*p*-acetamido)benzenesulfonate ester of 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**37**).

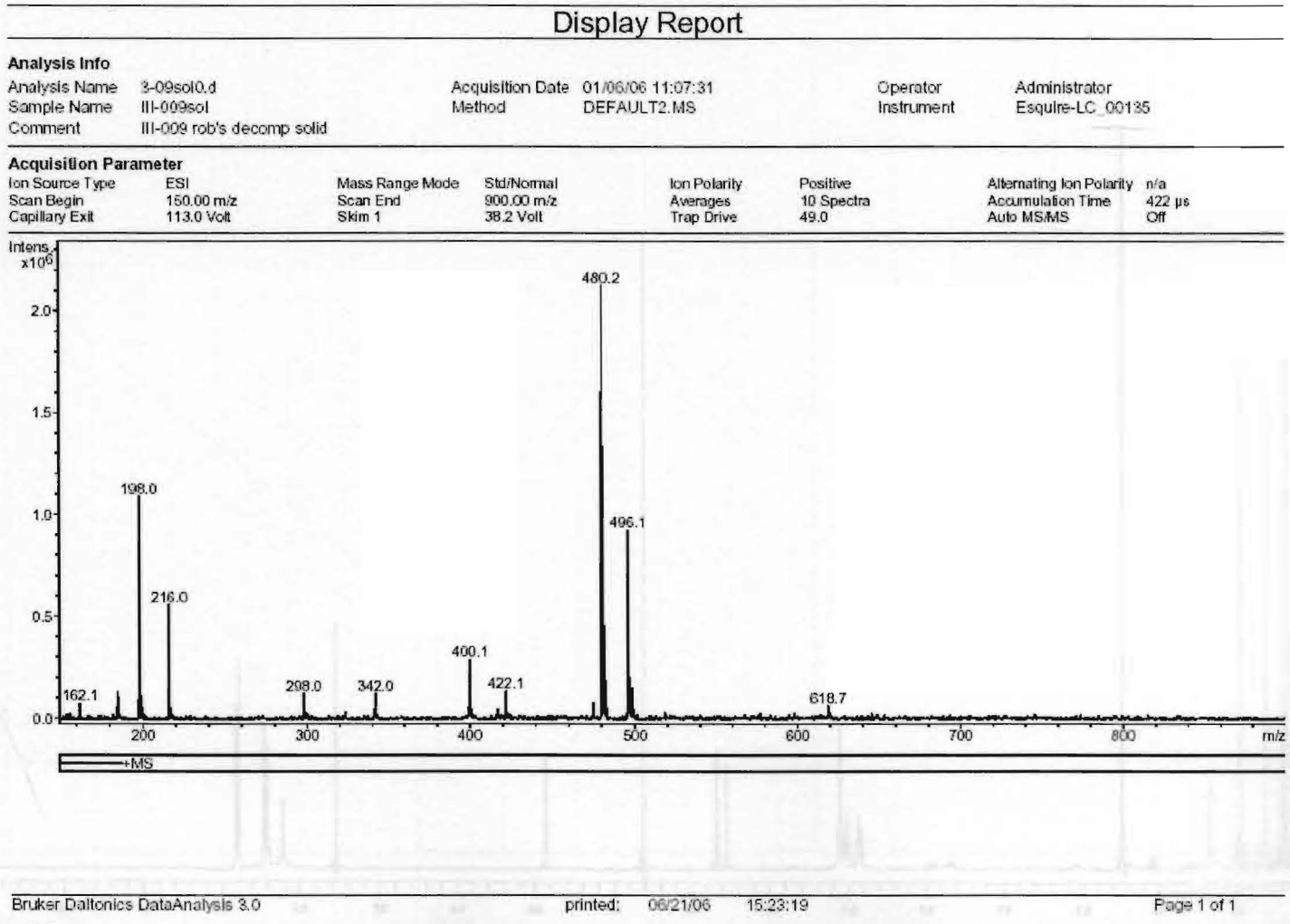


Figure 89: Mass spectrum of 3-*O*-(*p*-acetamido)benzenesulfonate ester of 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**37**).

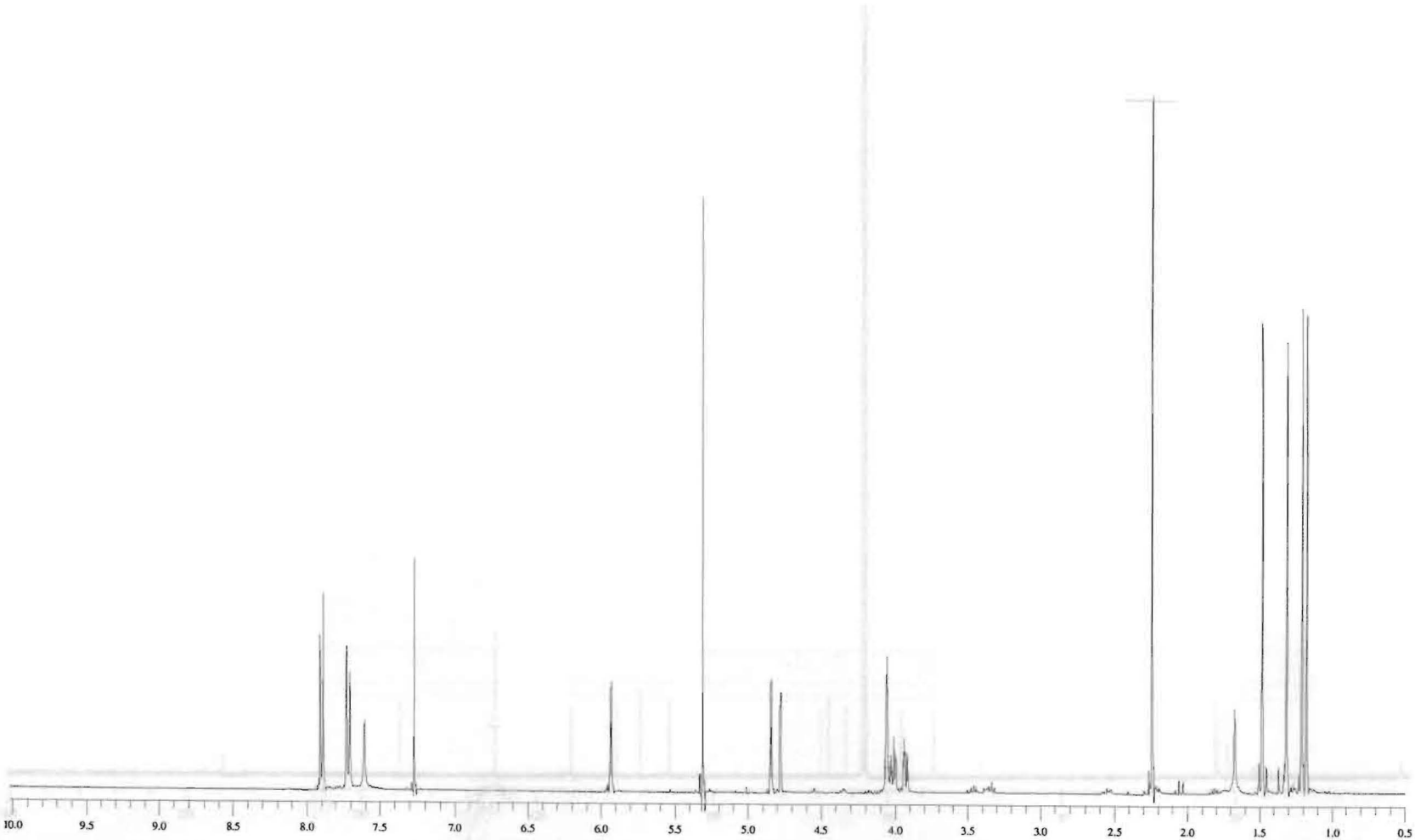


Figure 90: ^{1}H NMR spectrum of 6-*O*-(*p*-acetamido)benzenesulfonate ester of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**38**).

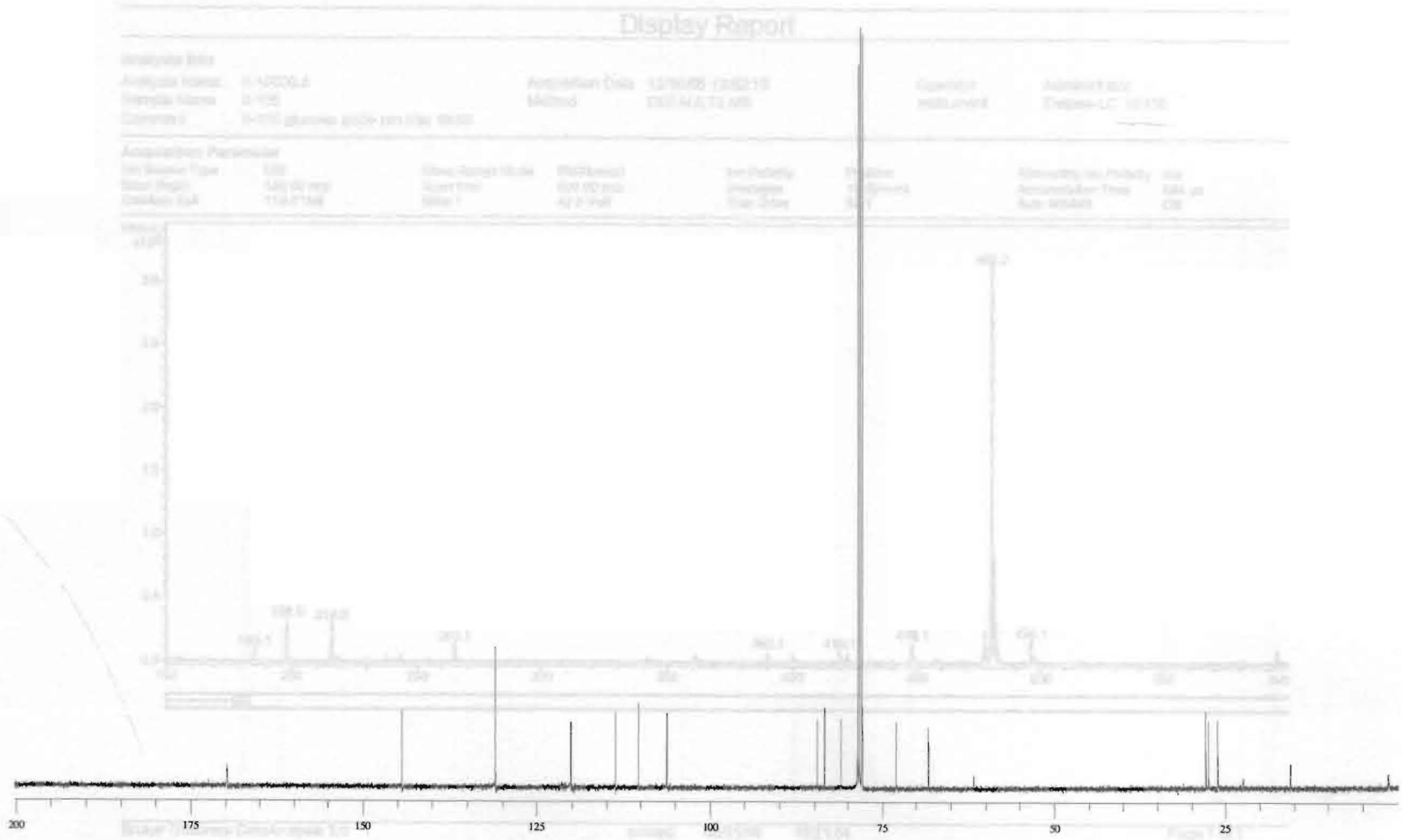


Figure 91: ^{13}C NMR spectrum of 6-*O*-(*p*-acetamido)benzenesulfonate ester of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**38**).

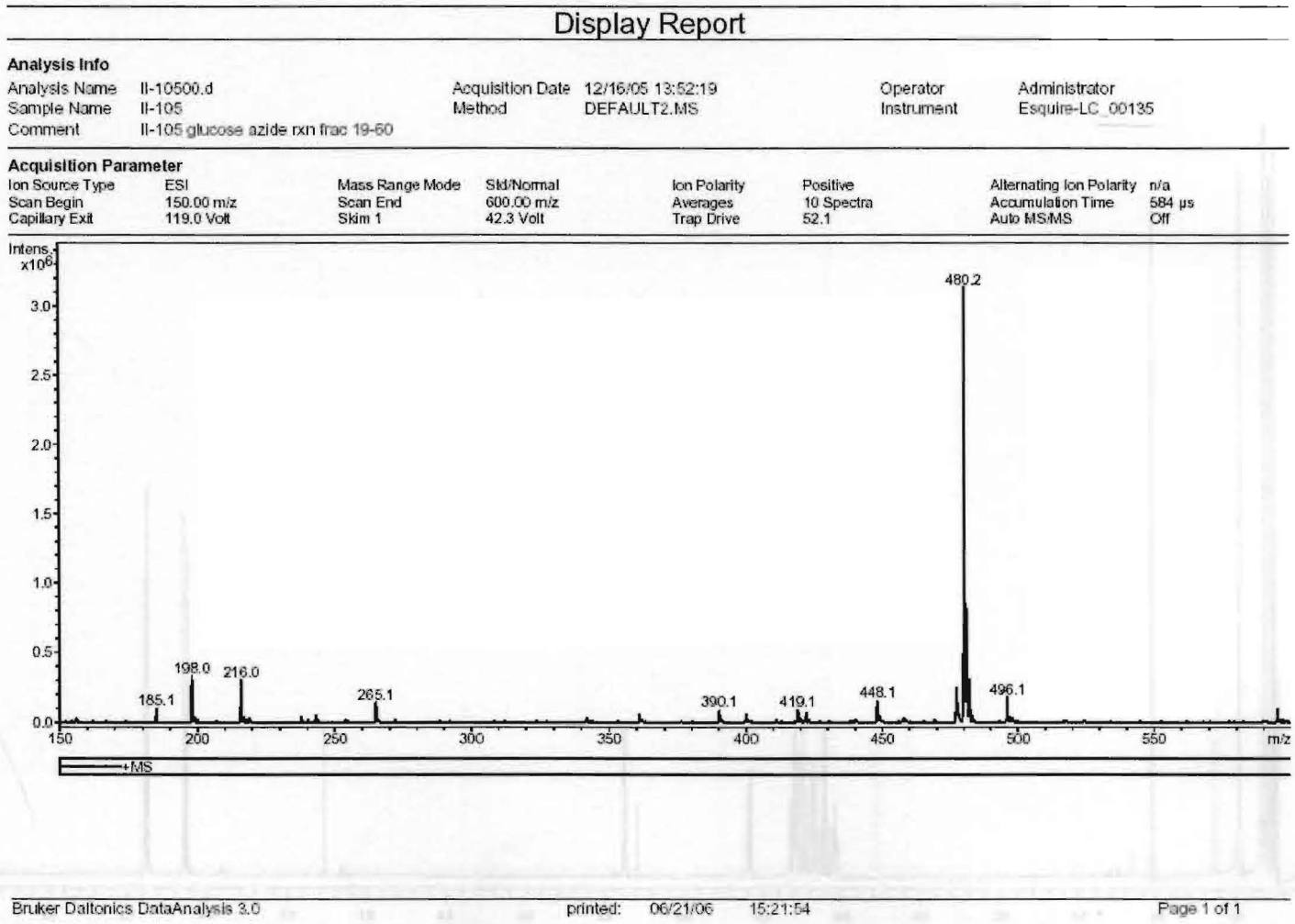


Figure 92: Mass spectrum of 6-*O*-(*p*-acetamido)benzenesulfonate ester of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**38**).

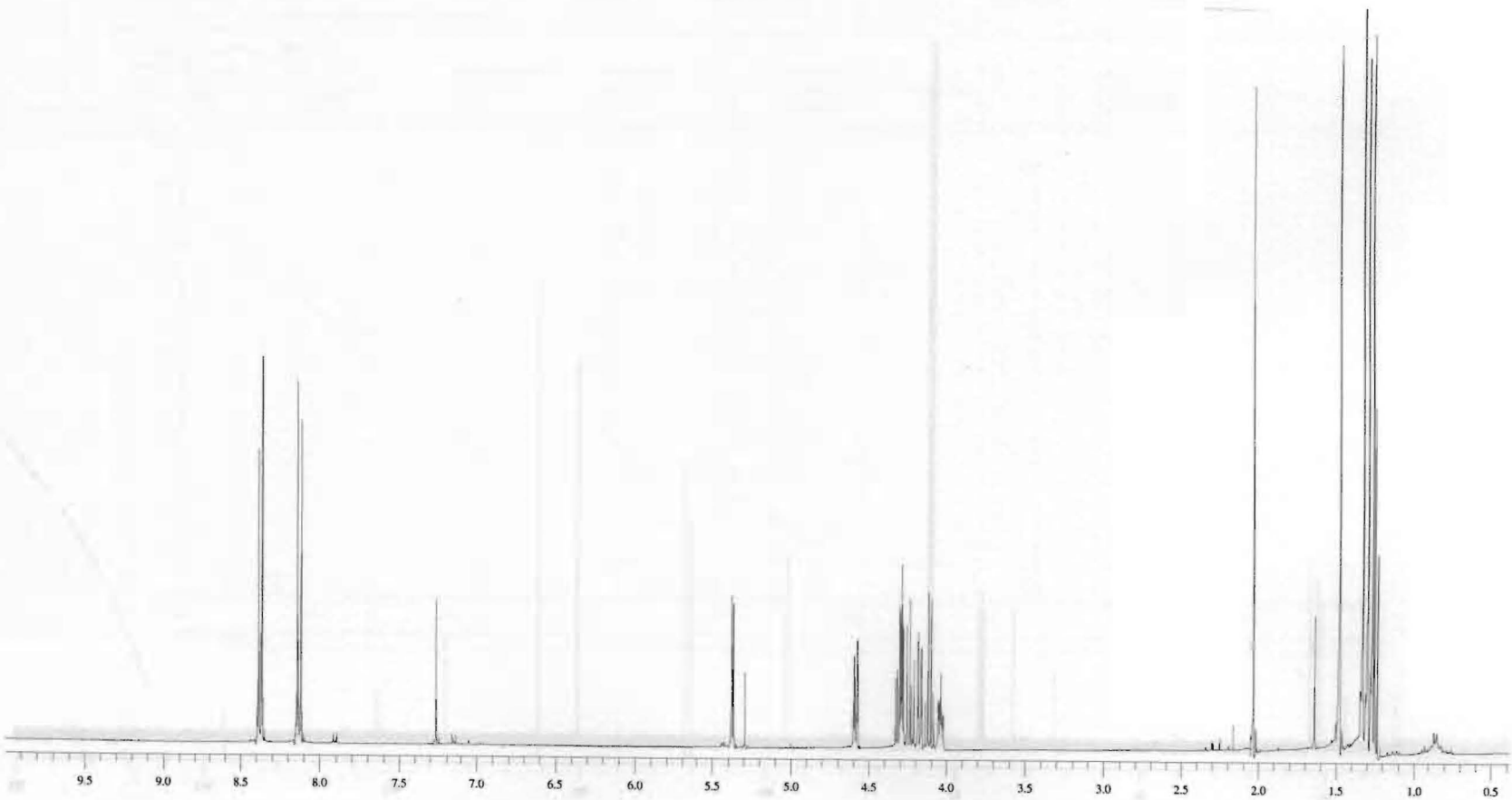


Figure 93: ^{1}H NMR spectrum of 6-*O*-(*p*-nitro)benzenesulfonate ester of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**40**).

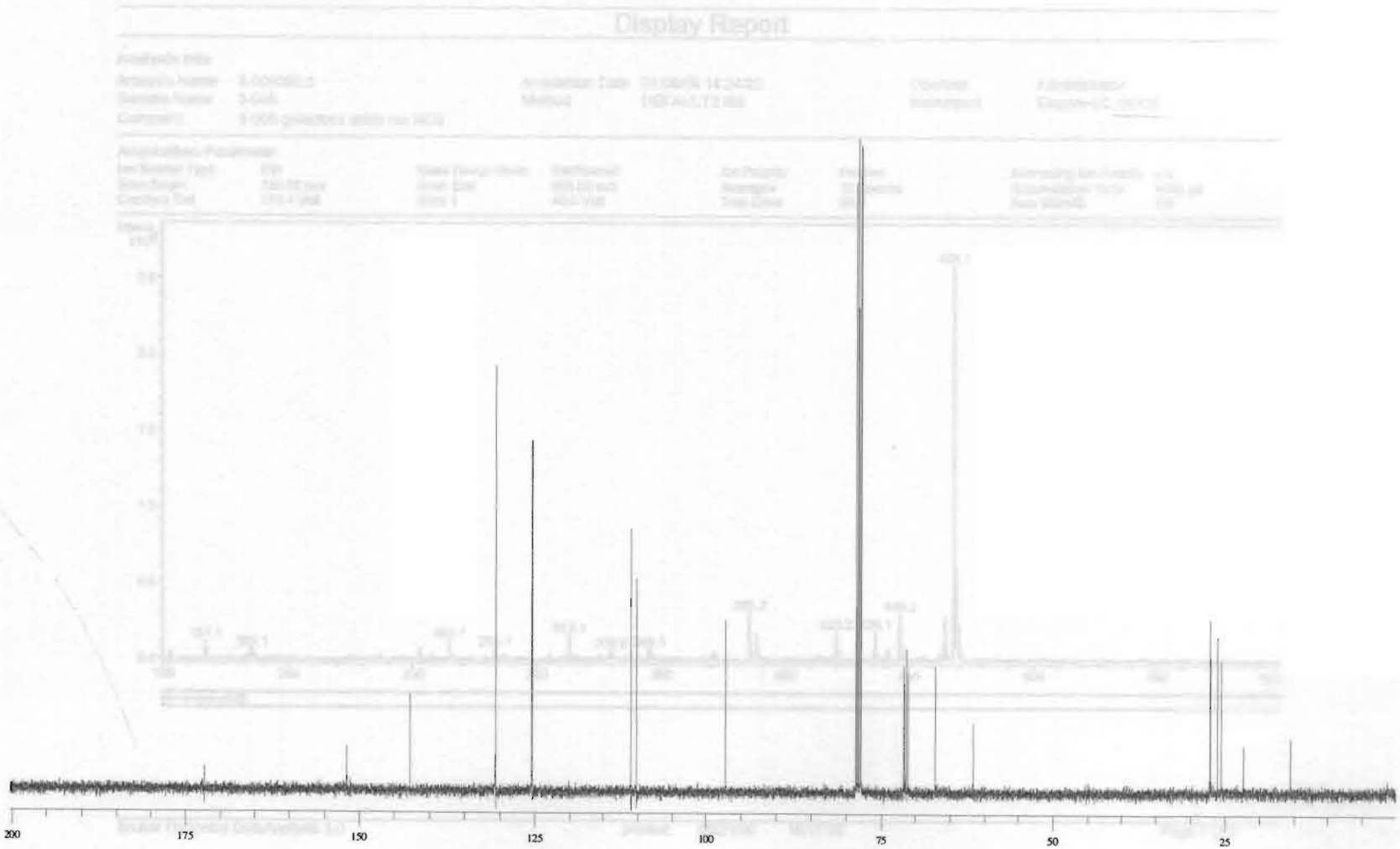


Figure 94: ^{13}C NMR spectrum of 6-*O*-(*p*-nitro)benzenesulfonate ester of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**40**).

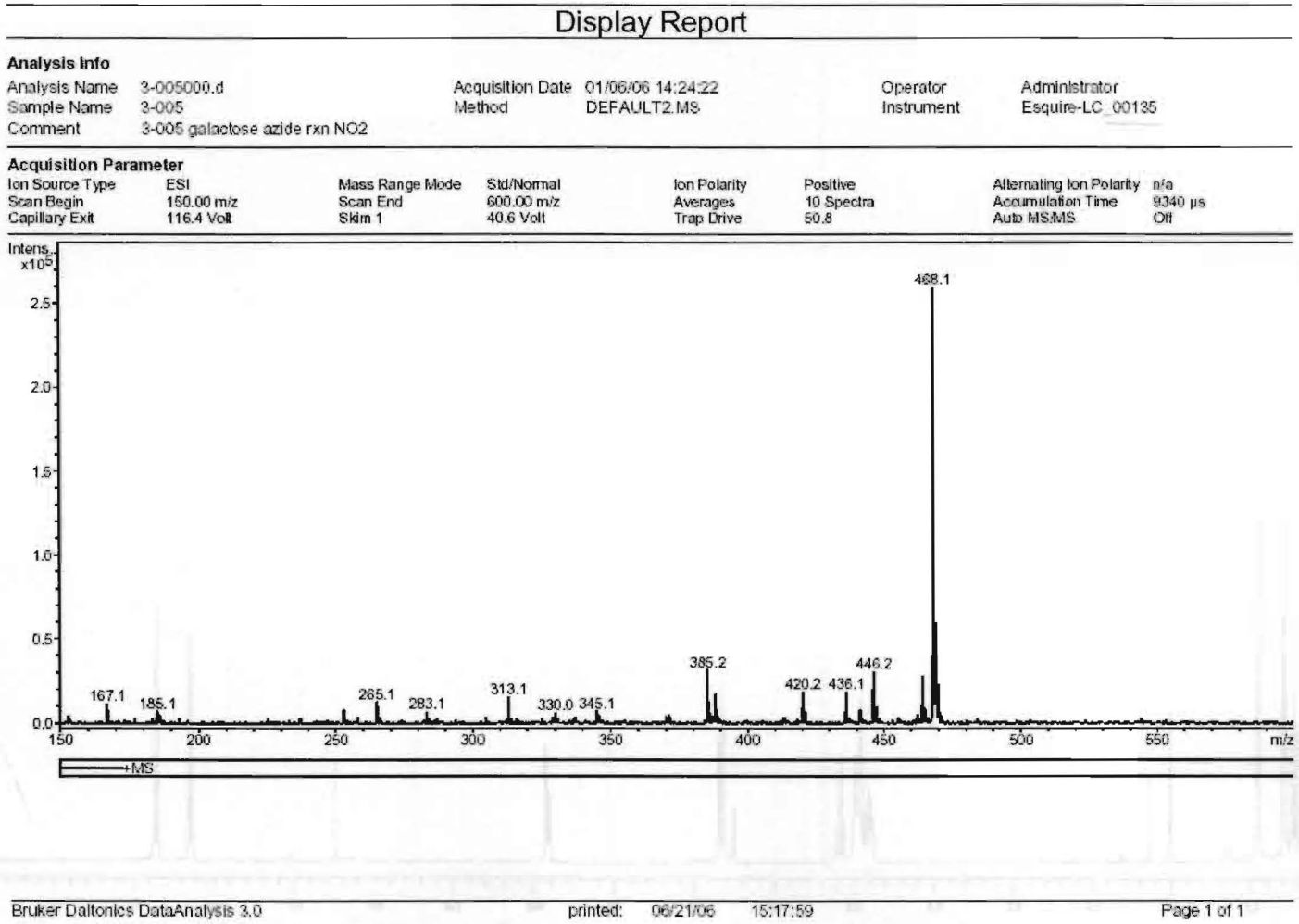


Figure 95: ^{13}C NMR spectrum of 6-*O*-(*p*-nitro)benzenesulfonate ester of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**40**).

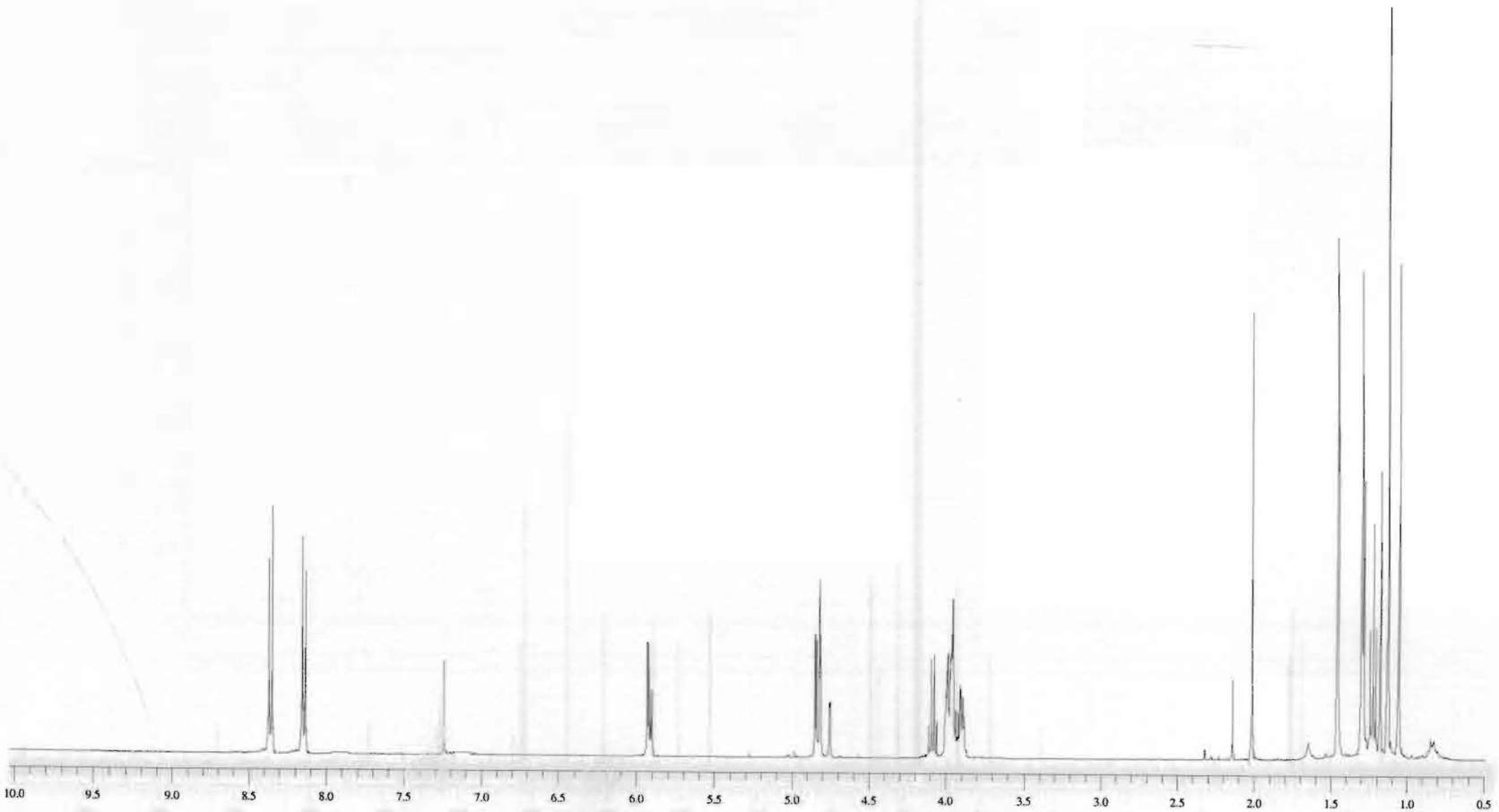


Figure 96: ^{1}H NMR spectrum of 6-*O*-(*p*-nitro)benzenesulfonate ester of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**41**).

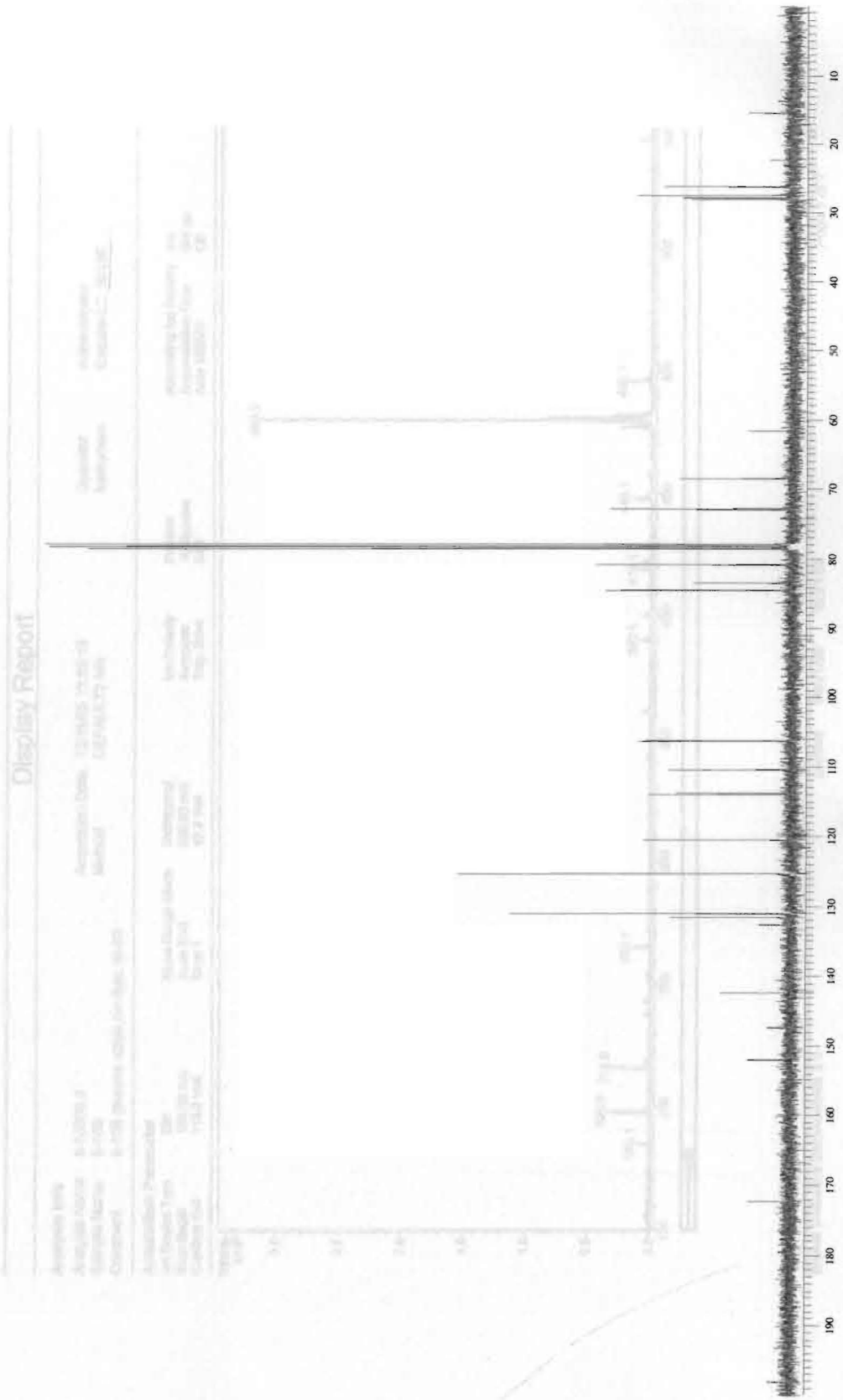


Figure 97: ^{13}C NMR spectrum of 6-*O*-(*p*-nitro)benzenesulfonate ester of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**41**).

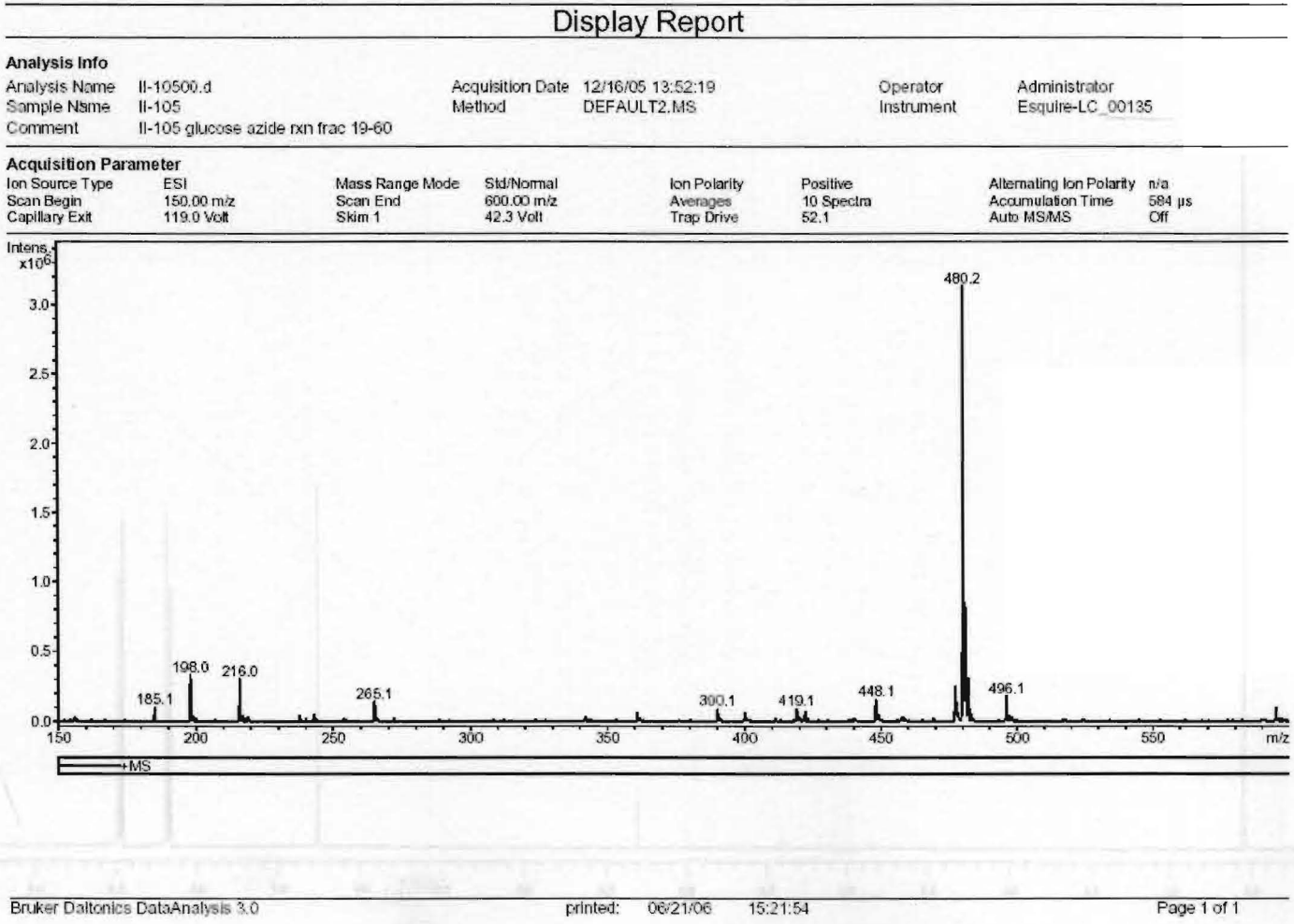


Figure 98: Mass spectrum of 6-*O*-(*p*-nitro)benzenesulfonate ester of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**41**).

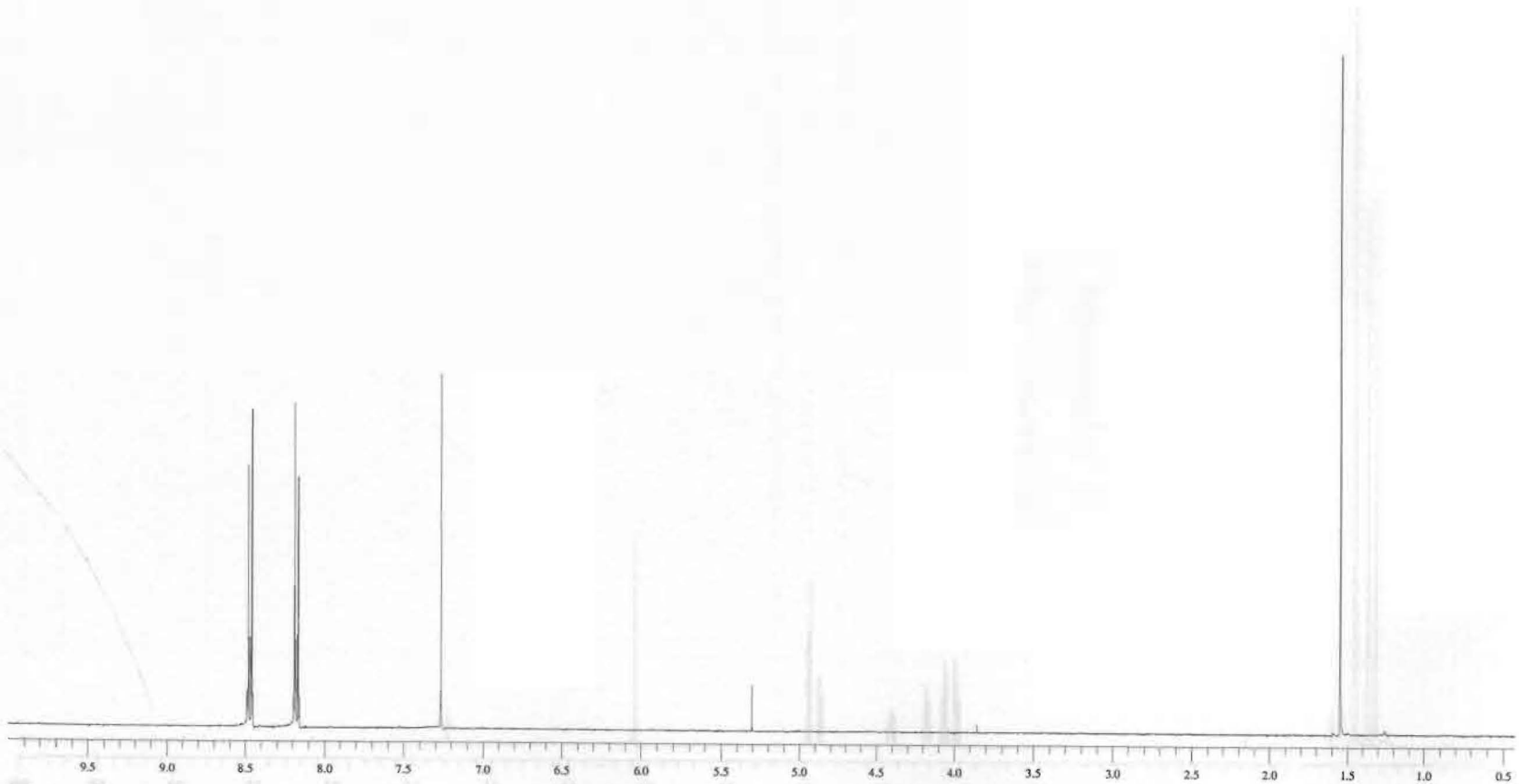


Figure 99: ^{1}H NMR spectrum of *p*-nitrobenzenesulfonyl azide (**43**).

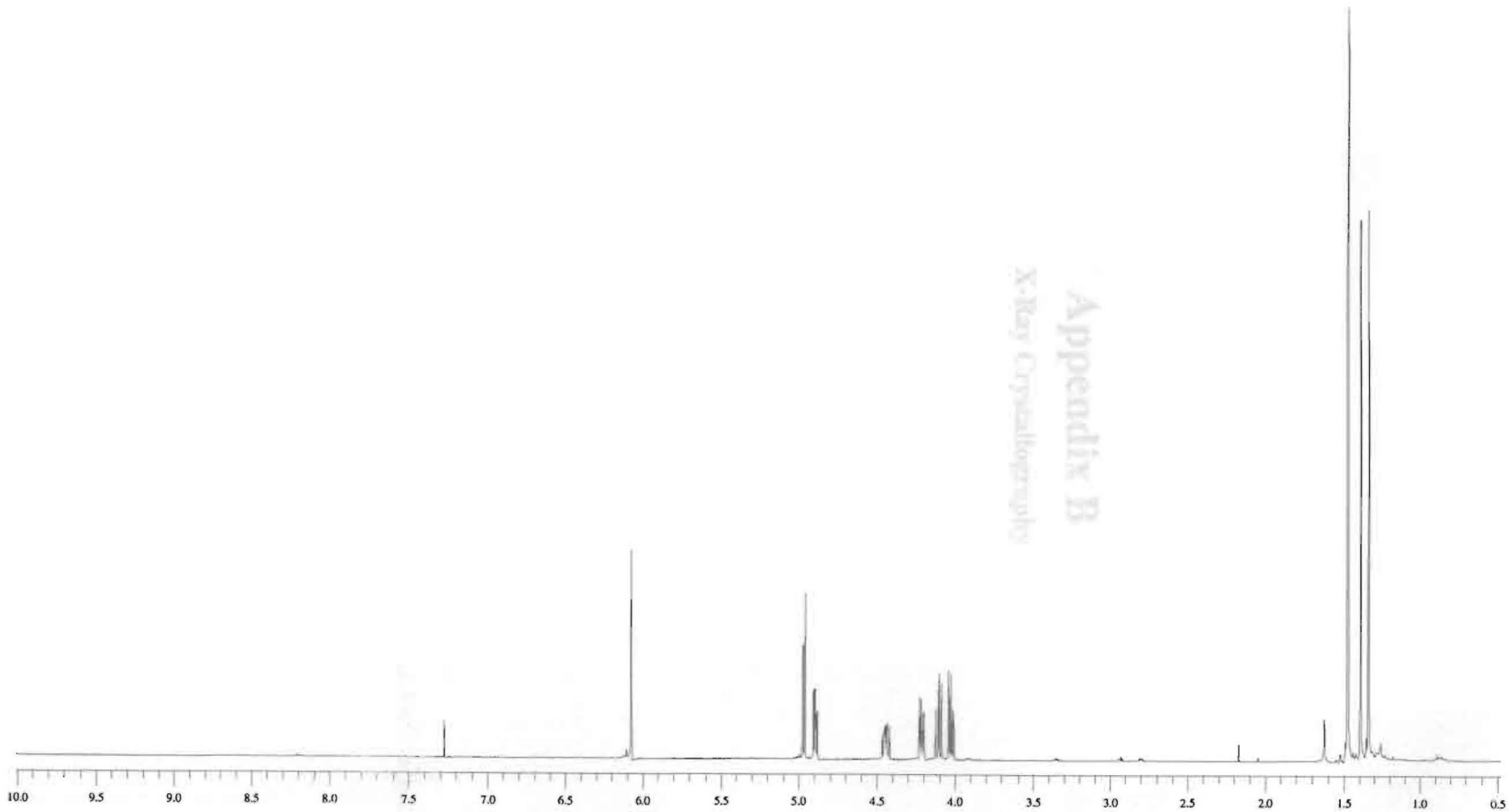
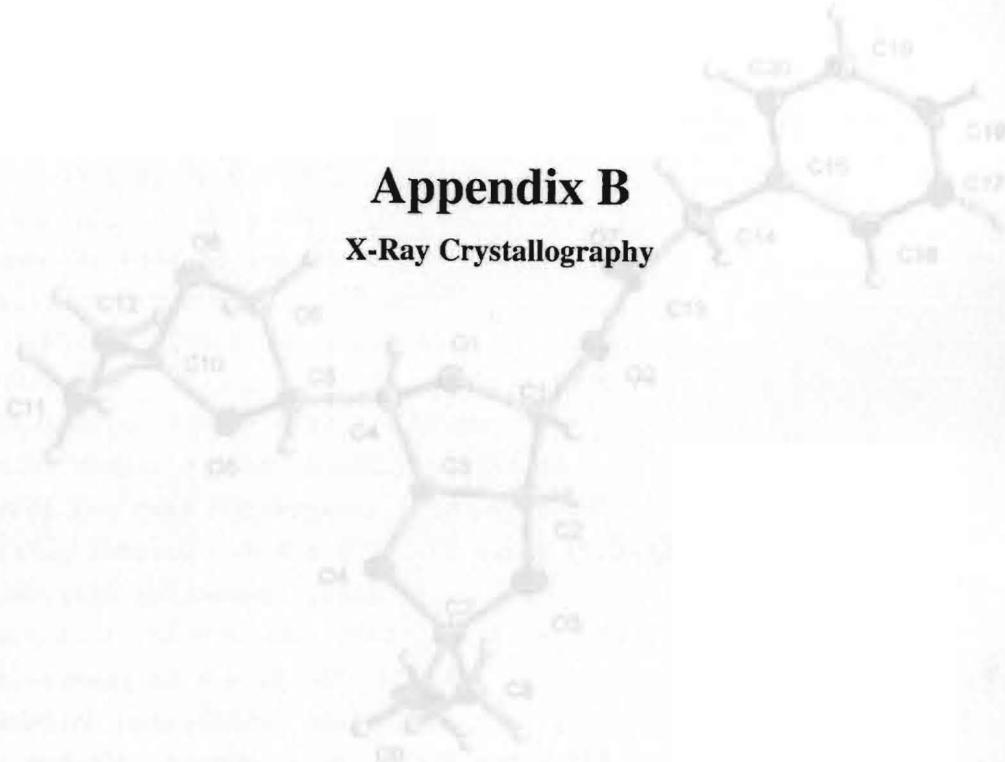


Figure 100: ^{1}H NMR spectrum of 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranosyl chloride (**44**).

Appendix B

X-Ray Crystallography



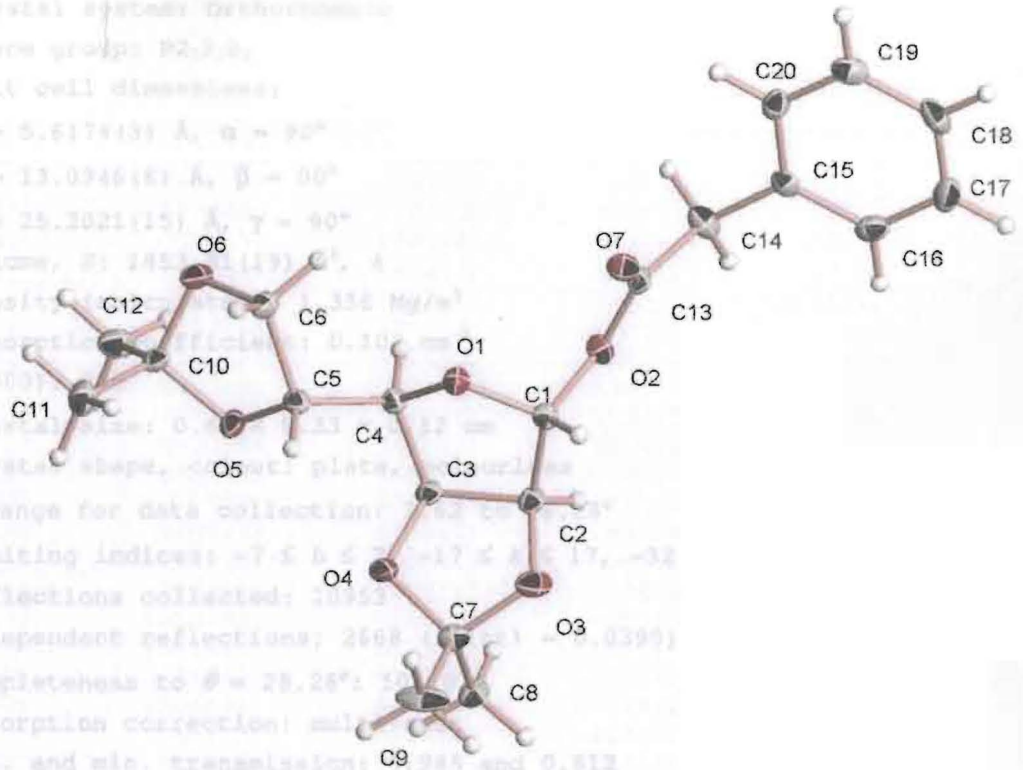


Figure 101: X-Ray crystal structure of 2,3:5,6-di-*O*-isopropylidene-1-*O*-phenacyl-α-D-mannofuranose (**5**).

Table 1. Crystal data and structure refinement for 06mz018m:

Identification code: 06mz018m
Empirical formula: C20 H26 O7
Formula weight: 378.41
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Orthorhombic
Space group: $P2_12_12_1$
Unit cell dimensions:
a = 5.6174(3) Å, α = 90°
b = 13.0946(8) Å, β = 90°
c = 25.2021(15) Å, γ = 90°
Volume, Z: 1853.81(19) $Å^3$, 4
Density (calculated): 1.356 Mg/m^3
Absorption coefficient: 0.102 mm^{-1}
F(000): 808
Crystal size: 0.60 × 0.33 × 0.12 mm
Crystal shape, colour: plate, colourless
θ range for data collection: 1.62 to 28.28°
Limiting indices: $-7 \leq h \leq 7$, $-17 \leq k \leq 17$, $-32 \leq l \leq 33$
Reflections collected: 18953
Independent reflections: 2668 (R(int) = 0.0399)
Completeness to θ = 28.28°: 100.0 %
Absorption correction: multi-scan
Max. and min. transmission: 0.988 and 0.812
Refinement method: Full-matrix least-squares on F^2
Data / restraints / parameters: 2668 / 0 / 248
Goodness-of-fit on F^2: 1.331
Final R indices [$I>2\sigma(I)$]: R1 = 0.0505, wR2 = 0.1171
R indices (all data): R1 = 0.0508, wR2 = 0.1173
Largest diff. peak and hole: 0.370 and -0.258 e × $Å^{-3}$

Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors

Treatment of hydrogen atoms:

All hydrogen atoms were placed in calculated positions and were isotropically refined with a displacement parameter 1.5 (methyl) or 1.2 times (all other) that of the adjacent carbon atom.

Table 2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for 06mz018m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	8021(4)	5064(2)	2149(1)	14(1)
C(2)	5653(5)	4707(2)	2383(1)	16(1)
C(3)	5230(5)	5420(2)	2861(1)	14(1)
C(4)	7276(5)	6186(2)	2840(1)	15(1)
C(5)	8432(5)	6452(2)	3362(1)	17(1)
C(6)	10386(5)	7277(2)	3312(1)	18(1)
C(7)	4927(5)	3763(2)	3128(1)	18(1)
C(8)	2243(5)	3600(2)	3108(1)	18(1)
C(9)	6133(5)	3004(3)	3485(1)	32(1)
C(10)	7721(5)	7797(2)	3933(1)	17(1)
C(11)	9020(6)	7498(2)	4439(1)	24(1)
C(12)	5801(6)	8580(2)	4028(1)	25(1)
C(13)	9301(5)	5799(2)	1341(1)	16(1)
C(14)	8400(5)	6279(2)	831(1)	22(1)
C(15)	9879(5)	5968(2)	360(1)	16(1)
C(16)	9133(5)	5172(2)	31(1)	21(1)
C(17)	10503(6)	4865(2)	-397(1)	26(1)
C(18)	12659(6)	5338(2)	-497(1)	25(1)
C(19)	13418(5)	6130(2)	-176(1)	23(1)
C(20)	12031(5)	6441(2)	249(1)	19(1)
O(1)	9107(3)	5693(1)	2528(1)	16(1)
O(2)	7450(3)	5629(1)	1676(1)	17(1)
O(3)	5940(4)	3720(1)	2611(1)	23(1)
O(4)	5450(4)	4766(1)	3309(1)	20(1)
O(5)	6671(3)	6912(1)	3696(1)	18(1)
O(6)	9344(4)	8164(1)	3544(1)	20(1)
O(7)	11329(3)	5606(2)	1443(1)	19(1)

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic)treatment of cell esds is used for estimating esds involving l.s. planes.

Table 3. Bond lengths [Å] and angles [deg] for 06mz018m.

C(1)-O(1)	1.400(3)
C(1)-O(2)	1.439(3)
C(1)-C(2)	1.528(3)
C(1)-H(1)	1.0000
C(2)-O(3)	1.424(3)
C(2)-C(3)	1.543(3)
C(2)-H(2)	1.0000
C(3)-O(4)	1.421(3)
C(3)-C(4)	1.527(4)
C(3)-H(3)	1.0000
C(4)-O(1)	1.447(3)
C(4)-C(5)	1.509(3)
C(4)-H(4)	1.0000
C(5)-O(5)	1.432(3)
C(5)-C(6)	1.545(4)
C(5)-H(5)	1.0000
C(6)-O(6)	1.427(3)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-O(4)	1.420(3)
C(7)-O(3)	1.423(3)
C(7)-C(9)	1.502(4)
C(7)-C(8)	1.523(4)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-O(6)	1.421(3)
C(10)-O(5)	1.431(3)
C(10)-C(12)	1.507(4)
C(10)-C(11)	1.520(4)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-O(7)	1.195(3)
C(13)-O(2)	1.358(3)
C(13)-C(14)	1.517(3)
C(14)-C(15)	1.506(4)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(20)	1.386(4)
C(15)-C(16)	1.395(4)
C(16)-C(17)	1.385(4)
C(16)-H(16)	0.9500
C(17)-C(18)	1.384(5)
C(17)-H(17)	0.9500
C(18)-C(19)	1.382(4)
C(18)-H(18)	0.9500
C(19)-C(20)	1.386(4)
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500

O(1)-C(1)-O(2)	111.1(2)
O(1)-C(1)-C(2)	107.23(19)
O(2)-C(1)-C(2)	106.4(2)
O(1)-C(1)-H(1)	110.6
O(2)-C(1)-H(1)	110.6
C(2)-C(1)-H(1)	110.6
O(3)-C(2)-C(1)	109.6(2)
O(3)-C(2)-C(3)	104.44(19)
C(1)-C(2)-C(3)	104.5(2)
O(3)-C(2)-H(2)	112.6
C(1)-C(2)-H(2)	112.6
C(3)-C(2)-H(2)	112.6
O(4)-C(3)-C(4)	111.0(2)
O(4)-C(3)-C(2)	104.03(19)
C(4)-C(3)-C(2)	104.7(2)
O(4)-C(3)-H(3)	112.2
C(4)-C(3)-H(3)	112.2
C(2)-C(3)-H(3)	112.2
O(1)-C(4)-C(5)	105.8(2)
O(1)-C(4)-C(3)	105.15(19)
C(5)-C(4)-C(3)	116.4(2)
O(1)-C(4)-H(4)	109.8
C(5)-C(4)-H(4)	109.8
C(3)-C(4)-H(4)	109.8
O(5)-C(5)-C(4)	108.2(2)
O(5)-C(5)-C(6)	104.2(2)
C(4)-C(5)-C(6)	113.3(2)
O(5)-C(5)-H(5)	110.3
C(4)-C(5)-H(5)	110.3
C(6)-C(5)-H(5)	110.3
O(6)-C(6)-C(5)	104.1(2)
O(6)-C(6)-H(6A)	110.9
C(5)-C(6)-H(6A)	110.9
O(6)-C(6)-H(6B)	110.9
C(5)-C(6)-H(6B)	110.9
H(6A)-C(6)-H(6B)	109.0
O(4)-C(7)-O(3)	104.2(2)
O(4)-C(7)-C(9)	109.1(2)
O(3)-C(7)-C(9)	110.0(2)
O(4)-C(7)-C(8)	110.2(2)
O(3)-C(7)-C(8)	111.0(2)
C(9)-C(7)-C(8)	112.0(2)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
O(6)-C(10)-O(5)	104.52(19)
O(6)-C(10)-C(12)	109.8(2)

O(5)-C(10)-C(12)	108.8(2)
O(6)-C(10)-C(11)	110.9(2)
O(5)-C(10)-C(11)	109.8(2)
C(12)-C(10)-C(11)	112.7(2)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
O(7)-C(13)-O(2)	124.2(2)
O(7)-C(13)-C(14)	126.0(2)
O(2)-C(13)-C(14)	109.8(2)
C(15)-C(14)-C(13)	111.8(2)
C(15)-C(14)-H(14A)	109.3
C(13)-C(14)-H(14A)	109.3
C(15)-C(14)-H(14B)	109.3
C(13)-C(14)-H(14B)	109.3
H(14A)-C(14)-H(14B)	107.9
C(20)-C(15)-C(16)	118.5(2)
C(20)-C(15)-C(14)	121.2(2)
C(16)-C(15)-C(14)	120.3(3)
C(17)-C(16)-C(15)	120.8(3)
C(17)-C(16)-H(16)	119.6
C(15)-C(16)-H(16)	119.6
C(18)-C(17)-C(16)	119.9(3)
C(18)-C(17)-H(17)	120.1
C(16)-C(17)-H(17)	120.1
C(19)-C(18)-C(17)	120.0(3)
C(19)-C(18)-H(18)	120.0
C(17)-C(18)-H(18)	120.0
C(18)-C(19)-C(20)	119.9(3)
C(18)-C(19)-H(19)	120.0
C(20)-C(19)-H(19)	120.0
C(19)-C(20)-C(15)	121.0(3)
C(19)-C(20)-H(20)	119.5
C(15)-C(20)-H(20)	119.5
C(1)-O(1)-C(4)	108.84(19)
C(13)-O(2)-C(1)	115.40(19)
C(7)-O(3)-C(2)	106.85(19)
C(7)-O(4)-C(3)	106.61(18)
C(10)-O(5)-C(5)	107.5(2)
C(10)-O(6)-C(6)	105.74(19)

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 06mz018m. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [(h a*)^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	12(1)	16(1)	16(1)	-1(1)	3(1)	2(1)
C(2)	14(1)	16(1)	18(1)	-2(1)	1(1)	-1(1)
C(3)	13(1)	14(1)	15(1)	0(1)	-1(1)	-1(1)
C(4)	15(1)	14(1)	15(1)	0(1)	0(1)	1(1)
C(5)	16(1)	18(1)	16(1)	1(1)	0(1)	-3(1)
C(6)	17(1)	17(1)	20(1)	-3(1)	2(1)	-2(1)
C(7)	13(1)	18(1)	22(1)	2(1)	0(1)	0(1)
C(8)	13(1)	18(1)	24(1)	-3(1)	1(1)	-1(1)
C(9)	13(1)	34(2)	50(2)	23(2)	0(1)	-3(1)
C(10)	17(1)	15(1)	19(1)	-2(1)	2(1)	-5(1)
C(11)	24(1)	28(1)	21(1)	-5(1)	-4(1)	-2(1)
C(12)	23(1)	21(1)	31(1)	2(1)	10(1)	2(1)
C(13)	19(1)	13(1)	15(1)	-3(1)	1(1)	2(1)
C(14)	21(1)	25(1)	18(1)	4(1)	3(1)	8(1)
C(15)	18(1)	17(1)	14(1)	5(1)	-1(1)	4(1)
C(16)	21(1)	18(1)	24(1)	5(1)	-4(1)	-3(1)
C(17)	38(2)	19(1)	20(1)	-3(1)	-6(1)	0(1)
C(18)	35(2)	26(1)	14(1)	3(1)	7(1)	10(1)
C(19)	19(1)	23(1)	26(1)	8(1)	3(1)	3(1)
C(20)	22(1)	16(1)	20(1)	-1(1)	-4(1)	2(1)
O(1)	13(1)	19(1)	17(1)	-2(1)	1(1)	0(1)
O(2)	15(1)	20(1)	14(1)	0(1)	1(1)	3(1)
O(3)	25(1)	14(1)	30(1)	1(1)	11(1)	2(1)
O(4)	23(1)	20(1)	17(1)	3(1)	-3(1)	-10(1)
O(5)	17(1)	20(1)	18(1)	-5(1)	3(1)	-6(1)
O(6)	19(1)	14(1)	26(1)	-1(1)	7(1)	-2(1)
O(7)	16(1)	21(1)	22(1)	3(1)	2(1)	-1(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for 06mz018m.

	x	y	z	U(eq)
H(1)	9061	4467	2063	17
H(2)	4323	4733	2119	19
H(3)	3639	5761	2846	17
H(4)	6738	6824	2657	18
H(5)	9090	5824	3534	20
H(6A)	11843	7072	3505	21
H(6B)	10795	7399	2935	21
H(8A)	1581	3657	3466	28
H(8B)	1902	2920	2964	28
H(8C)	1520	4120	2879	28
H(9A)	7855	3125	3482	49
H(9B)	5804	2310	3359	49
H(9C)	5528	3081	3848	49
H(11A)	10245	6989	4356	37
H(11B)	7882	7208	4692	37
H(11C)	9770	8104	4594	37
H(12A)	6512	9201	4176	37
H(12B)	4629	8305	4278	37
H(12C)	5013	8743	3692	37
H(14A)	6727	6071	772	26
H(14B)	8436	7032	866	26
H(16)	7668	4836	102	25
H(17)	9964	4330	-621	31
H(18)	13616	5120	-786	30
H(19)	14890	6461	-247	27
H(20)	12561	6986	468	23

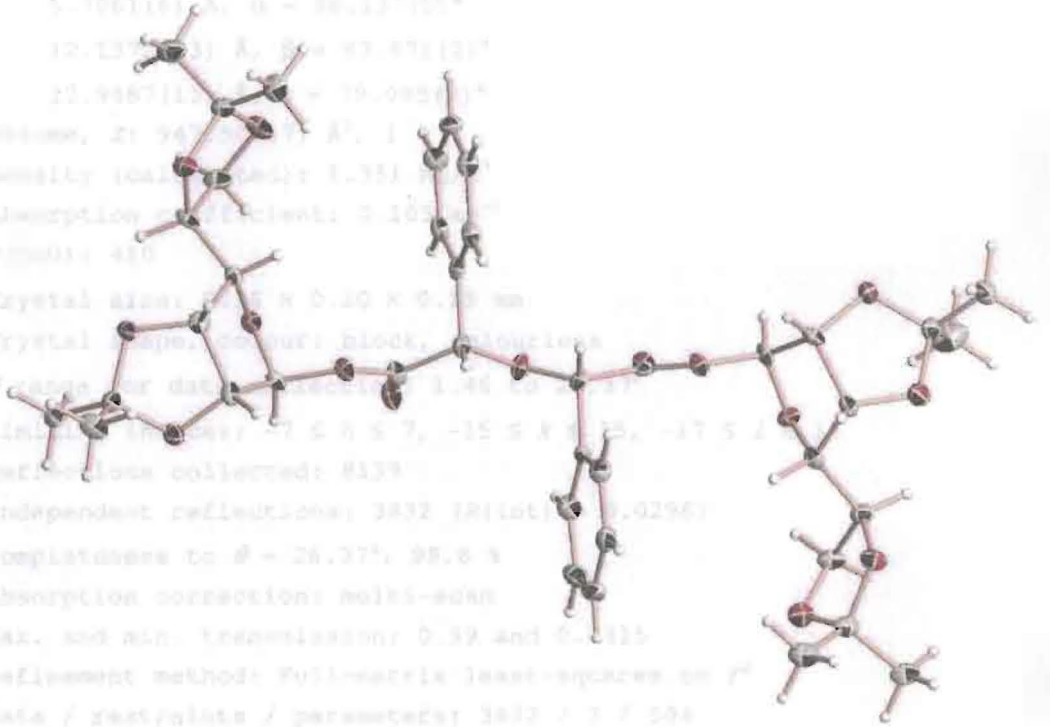


Figure 102: X-Ray crystal structure of mannofuranose dimeric ether **14**.

Table 1. Crystal data and structure refinement for 05mz046m:

Identification code: 05mz046m
Empirical formula: C40 H50 O15
Formula weight: 770.80
Temperature: 90(2) K
Wavelength: 0.71073 Å
Crystal system: Triclinic
Space group: P1
Unit cell dimensions:
a = 5.7061(6) Å, α = 88.137(2)°
b = 12.1372(13) Å, β = 87.671(2)°
c = 13.9487(15) Å, γ = 79.095(2)°
Volume, Z: 947.50(17) Å^3, 1
Density (calculated): 1.351 Mg/m^3
Absorption coefficient: 0.103 mm^{-1}
F(000): 410
Crystal size: 0.36 × 0.20 × 0.15 mm
Crystal shape, colour: block, colourless
θ range for data collection: 1.46 to 26.37°
Limiting indices: $-7 \leq h \leq 7$, $-15 \leq k \leq 15$, $-17 \leq l \leq 17$
Reflections collected: 8139
Independent reflections: 3832 (R(int) = 0.0296)
Completeness to θ = 26.37°: 98.8 %
Absorption correction: multi-scan
Max. and min. transmission: 0.99 and 0.7415
Refinement method: Full-matrix least-squares on F^2
Data / restraints / parameters: 3832 / 3 / 504
Goodness-of-fit on F^2: 1.289
Final R indices [$I>2\sigma(I)$]: R1 = 0.0664, wR2 = 0.1519
R indices (all data): R1 = 0.0664, wR2 = 0.1519
Largest diff. peak and hole: 0.388 and -0.290 e × Å^{-3}

Comments:
The molecule exhibits chemical two fold symmetry, but no crystallographical one. Treatment of hydrogen atoms: All hydrogen atoms were placed in calculated positions and were refined with an isotropic displacement parameter 1.5 (methyl) or 1.2 times (all others) that of the adjacent carbon atom.

Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors.

Table 2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for 05mz046m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	4169(6)	3518(3)	5342(3)	18(1)
O(2A)	2434(7)	5706(3)	4827(3)	23(1)
O(3A)	6223(6)	6012(3)	4605(3)	17(1)
O(4A)	4928(6)	7207(3)	3321(3)	16(1)
O(5A)	6429(7)	8926(3)	4547(3)	19(1)
O(6A)	8235(7)	8889(3)	3073(3)	19(1)
O(7A)	9266(7)	7005(3)	1295(3)	20(1)
O(8A)	6742(7)	5820(3)	934(3)	23(1)
C(1A)	5849(9)	4156(4)	4906(4)	16(1)
C(2A)	4532(10)	5375(4)	4783(4)	17(1)
C(3A)	5367(9)	7160(4)	4291(4)	13(1)
C(4A)	7435(9)	7783(4)	4410(4)	14(1)
C(5A)	8677(9)	7738(4)	3407(4)	16(1)
C(6A)	7233(9)	7054(4)	2826(4)	15(1)
C(7A)	6993(9)	7402(5)	1794(4)	18(1)
C(8A)	5252(10)	6850(5)	1246(4)	23(1)
C(9A)	7593(9)	9587(4)	3875(4)	18(1)
C(10A)	9814(10)	9857(5)	4323(5)	24(1)
C(11A)	5861(10)	10608(5)	3572(4)	22(1)
C(12A)	9036(9)	6098(5)	688(4)	19(1)
C(13A)	9136(12)	6529(6)	-338(5)	31(1)
C(14A)	10900(11)	5078(5)	912(5)	27(1)
C(15A)	6770(9)	3699(4)	3927(4)	17(1)
C(16A)	5255(9)	3827(4)	3158(4)	18(1)
C(17A)	6085(10)	3421(5)	2277(4)	22(1)
C(18A)	8452(10)	2860(5)	2139(4)	21(1)
C(19A)	9934(10)	2735(5)	2902(4)	20(1)
C(20A)	9144(10)	3156(5)	3795(4)	22(1)
O(2B)	1804(7)	1807(3)	5748(3)	20(1)
O(3B)	5113(6)	798(3)	6406(3)	18(1)
O(4B)	2454(6)	-61(3)	7348(3)	18(1)
O(5B)	5740(9)	-2180(3)	6443(3)	29(1)
O(6B)	5481(8)	-2321(4)	8069(3)	27(1)
O(7B)	3841(7)	-573(3)	9875(3)	21(1)
O(8B)	965(7)	1018(3)	9916(3)	24(1)
C(1B)	5285(9)	2655(4)	5959(4)	15(1)
C(2B)	3809(10)	1724(5)	6007(4)	17(1)
C(3B)	4008(10)	-184(4)	6534(4)	18(1)
C(4B)	6096(10)	-1131(5)	6762(4)	21(1)
C(5B)	5971(10)	-1242(5)	7873(4)	19(1)
C(6B)	3906(10)	-295(4)	8177(4)	19(1)

C(7B)	2444(10)	-582(5)	9053(4)	20(1)
C(8B)	187(10)	293(5)	9265(4)	20(1)
C(9B)	5049(10)	-2859(5)	7219(4)	21(1)
C(10B)	6707(11)	-3985(5)	7188(4)	24(1)
C(11B)	2448(12)	-2927(7)	7176(5)	36(2)
C(12B)	2639(10)	306(5)	10503(4)	20(1)
C(13B)	1406(10)	-201(5)	11335(4)	23(1)
C(14B)	4439(11)	984(6)	10812(5)	30(1)
C(15B)	5391(9)	3034(4)	6984(4)	16(1)
C(16B)	3356(10)	3670(5)	7417(4)	23(1)
C(17B)	3369(11)	3976(5)	8380(5)	28(1)
C(18B)	5420(12)	3675(5)	8891(4)	27(1)
C(19B)	7457(12)	3050(5)	8459(4)	26(1)
C(20B)	7466(11)	2734(5)	7514(4)	23(1)

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 3. Bond lengths [Å] and angles [deg] for 05mz046m.

O(1)-C(1B)	1.405(6)
O(1)-C(1A)	1.446(6)
O(2A)-C(2A)	1.188(7)
O(3A)-C(2A)	1.357(6)
O(3A)-C(3A)	1.447(6)
O(4A)-C(3A)	1.383(6)
O(4A)-C(6A)	1.443(6)
O(5A)-C(4A)	1.413(6)
O(5A)-C(9A)	1.437(6)
O(6A)-C(9A)	1.419(7)
O(6A)-C(5A)	1.437(6)
O(7A)-C(12A)	1.439(7)
O(7A)-C(7A)	1.452(6)
O(8A)-C(12A)	1.438(6)
O(8A)-C(8A)	1.442(7)
C(1A)-C(15A)	1.526(7)
C(1A)-C(2A)	1.535(7)
C(1A)-H(1A)	1.0000
C(3A)-C(4A)	1.534(6)
C(3A)-H(3A)	1.0000
C(4A)-C(5A)	1.540(7)
C(4A)-H(4A)	1.0000
C(5A)-C(6A)	1.543(7)
C(5A)-H(5A)	1.0000
C(6A)-C(7A)	1.493(8)
C(6A)-H(6A)	1.0000

C(7A)-C(8A)	1.538(7)
C(7A)-H(7A)	1.0000
C(8A)-H(8A1)	0.9900
C(8A)-H(8A2)	0.9900
C(9A)-C(11A)	1.493(8)
C(9A)-C(10A)	1.530(7)
C(10A)-H(10A)	0.9800
C(10A)-H(10B)	0.9800
C(10A)-H(10C)	0.9800
C(11A)-H(11A)	0.9800
C(11A)-H(11B)	0.9800
C(11A)-H(11C)	0.9800
C(12A)-C(14A)	1.505(8)
C(12A)-C(13A)	1.509(8)
C(13A)-H(13A)	0.9800
C(13A)-H(13B)	0.9800
C(13A)-H(13C)	0.9800
C(14A)-H(14A)	0.9800
C(14A)-H(14B)	0.9800
C(14A)-H(14C)	0.9800
C(15A)-C(16A)	1.392(7)
C(15A)-C(20A)	1.398(8)
C(16A)-C(17A)	1.372(8)
C(16A)-H(16A)	0.9500
C(17A)-C(18A)	1.402(8)
C(17A)-H(17A)	0.9500
C(18A)-C(19A)	1.373(8)
C(18A)-H(18A)	0.9500
C(19A)-C(20A)	1.387(8)
C(19A)-H(19A)	0.9500
C(20A)-H(20A)	0.9500
O(2B)-C(2B)	1.199(7)
O(3B)-C(2B)	1.343(7)
O(3B)-C(3B)	1.453(6)
O(4B)-C(3B)	1.406(7)
O(4B)-C(6B)	1.440(7)
O(5B)-C(4B)	1.414(7)
O(5B)-C(9B)	1.427(7)
O(6B)-C(5B)	1.406(7)
O(6B)-C(9B)	1.424(7)
O(7B)-C(7B)	1.425(7)
O(7B)-C(12B)	1.452(7)
O(8B)-C(8B)	1.424(7)
O(8B)-C(12B)	1.426(7)
C(1B)-C(15B)	1.523(7)
C(1B)-C(2B)	1.530(7)
C(1B)-H(1B)	1.0000
C(3B)-C(4B)	1.527(8)
C(3B)-H(3B)	1.0000
C(4B)-C(5B)	1.551(8)
C(4B)-H(4B)	1.0000
C(5B)-C(6B)	1.539(7)
C(5B)-H(5B)	1.0000
C(6B)-C(7B)	1.520(7)
C(6B)-H(6B)	1.0000
C(7B)-C(8B)	1.532(8)
C(7B)-H(7B)	1.0000

C(8B)-H(8B1)	0.9900
C(8B)-H(8B2)	0.9900
C(9B)-C(11B)	1.506(9)
C(9B)-C(10B)	1.509(8)
C(10B)-H(10D)	0.9800
C(10B)-H(10E)	0.9800
C(10B)-H(10F)	0.9800
C(11B)-H(11D)	0.9800
C(11B)-H(11E)	0.9800
C(11B)-H(11F)	0.9800
C(12B)-C(13B)	1.508(8)
C(12B)-C(14B)	1.515(8)
C(13B)-H(13D)	0.9800
C(13B)-H(13E)	0.9800
C(13B)-H(13F)	0.9800
C(14B)-H(14D)	0.9800
C(14B)-H(14E)	0.9800
C(14B)-H(14F)	0.9800
C(15B)-C(16B)	1.394(8)
C(15B)-C(20B)	1.404(8)
C(16B)-C(17B)	1.406(9)
C(16B)-H(16B)	0.9500
C(17B)-C(18B)	1.379(9)
C(17B)-H(17B)	0.9500
C(18B)-C(19B)	1.389(9)
C(18B)-H(18B)	0.9500
C(19B)-C(20B)	1.384(8)
C(19B)-H(19B)	0.9500
C(20B)-H(20B)	0.9500

C(1B)-O(1)-C(1A)	112.0(4)
C(2A)-O(3A)-C(3A)	116.1(4)
C(3A)-O(4A)-C(6A)	106.2(4)
C(4A)-O(5A)-C(9A)	108.0(4)
C(9A)-O(6A)-C(5A)	108.6(4)
C(12A)-O(7A)-C(7A)	109.2(4)
C(12A)-O(8A)-C(8A)	105.6(4)
O(1)-C(1A)-C(15A)	111.0(4)
O(1)-C(1A)-C(2A)	107.5(4)
C(15A)-C(1A)-C(2A)	109.4(4)
O(1)-C(1A)-H(1A)	109.6
C(15A)-C(1A)-H(1A)	109.6
C(2A)-C(1A)-H(1A)	109.6
O(2A)-C(2A)-O(3A)	126.1(5)
O(2A)-C(2A)-C(1A)	127.0(5)
O(3A)-C(2A)-C(1A)	106.9(4)
O(4A)-C(3A)-O(3A)	110.3(4)
O(4A)-C(3A)-C(4A)	106.4(4)
O(3A)-C(3A)-C(4A)	106.2(4)
O(4A)-C(3A)-H(3A)	111.3
O(3A)-C(3A)-H(3A)	111.3
C(4A)-C(3A)-H(3A)	111.3
O(5A)-C(4A)-C(3A)	107.4(4)
O(5A)-C(4A)-C(5A)	105.6(4)
C(3A)-C(4A)-C(5A)	103.6(4)
O(5A)-C(4A)-H(4A)	113.2
C(3A)-C(4A)-H(4A)	113.2

C(5A)-C(4A)-H(4A)	113.2
O(6A)-C(5A)-C(4A)	103.7(4)
O(6A)-C(5A)-C(6A)	109.9(4)
C(4A)-C(5A)-C(6A)	103.5(4)
O(6A)-C(5A)-H(5A)	113.0
C(4A)-C(5A)-H(5A)	113.0
C(6A)-C(5A)-H(5A)	113.0
O(4A)-C(6A)-C(7A)	111.0(4)
O(4A)-C(6A)-C(5A)	104.1(4)
C(7A)-C(6A)-C(5A)	114.8(4)
O(4A)-C(6A)-H(6A)	108.9
C(7A)-C(6A)-H(6A)	108.9
C(5A)-C(6A)-H(6A)	108.9
O(7A)-C(7A)-C(6A)	108.2(4)
O(7A)-C(7A)-C(8A)	102.8(4)
C(6A)-C(7A)-C(8A)	115.1(5)
O(7A)-C(7A)-H(7A)	110.2
C(6A)-C(7A)-H(7A)	110.2
C(8A)-C(7A)-H(7A)	110.2
O(8A)-C(8A)-C(7A)	102.6(4)
O(8A)-C(8A)-H(8A1)	111.2
C(7A)-C(8A)-H(8A1)	111.2
O(8A)-C(8A)-H(8A2)	111.2
C(7A)-C(8A)-H(8A2)	111.2
H(8A1)-C(8A)-H(8A2)	109.2
O(6A)-C(9A)-O(5A)	104.6(4)
O(6A)-C(9A)-C(11A)	109.0(5)
O(5A)-C(9A)-C(11A)	109.6(4)
O(6A)-C(9A)-C(10A)	110.8(4)
O(5A)-C(9A)-C(10A)	109.3(5)
C(11A)-C(9A)-C(10A)	113.2(5)
C(9A)-C(10A)-H(10A)	109.5
C(9A)-C(10A)-H(10B)	109.5
H(10A)-C(10A)-H(10B)	109.5
C(9A)-C(10A)-H(10C)	109.5
H(10A)-C(10A)-H(10C)	109.5
H(10B)-C(10A)-H(10C)	109.5
C(9A)-C(11A)-H(11A)	109.5
C(9A)-C(11A)-H(11B)	109.5
H(11A)-C(11A)-H(11B)	109.5
C(9A)-C(11A)-H(11C)	109.5
H(11A)-C(11A)-H(11C)	109.5
H(11B)-C(11A)-H(11C)	109.5
O(8A)-C(12A)-O(7A)	106.1(4)
O(8A)-C(12A)-C(14A)	107.4(5)
O(7A)-C(12A)-C(14A)	110.3(5)
O(8A)-C(12A)-C(13A)	111.0(5)
O(7A)-C(12A)-C(13A)	107.3(5)
C(14A)-C(12A)-C(13A)	114.5(5)
C(12A)-C(13A)-H(13A)	109.5
C(12A)-C(13A)-H(13B)	109.5
H(13A)-C(13A)-H(13B)	109.5
C(12A)-C(13A)-H(13C)	109.5
H(13A)-C(13A)-H(13C)	109.5
H(13B)-C(13A)-H(13C)	109.5
C(12A)-C(14A)-H(14A)	109.5
C(12A)-C(14A)-H(14B)	109.5

H(14A)-C(14A)-H(14B)	109.5
C(12A)-C(14A)-H(14C)	109.5
H(14A)-C(14A)-H(14C)	109.5
H(14B)-C(14A)-H(14C)	109.5
C(16A)-C(15A)-C(20A)	119.5(5)
C(16A)-C(15A)-C(1A)	120.2(5)
C(20A)-C(15A)-C(1A)	120.3(5)
C(17A)-C(16A)-C(15A)	120.2(5)
C(17A)-C(16A)-H(16A)	119.9
C(15A)-C(16A)-H(16A)	119.9
C(16A)-C(17A)-C(18A)	120.7(5)
C(16A)-C(17A)-H(17A)	119.6
C(18A)-C(17A)-H(17A)	119.6
C(19A)-C(18A)-C(17A)	118.7(5)
C(19A)-C(18A)-H(18A)	120.7
C(17A)-C(18A)-H(18A)	120.7
C(18A)-C(19A)-C(20A)	121.5(5)
C(18A)-C(19A)-H(19A)	119.2
C(20A)-C(19A)-H(19A)	119.2
C(19A)-C(20A)-C(15A)	119.3(5)
C(19A)-C(20A)-H(20A)	120.4
C(15A)-C(20A)-H(20A)	120.4
C(2B)-O(3B)-C(3B)	117.4(4)
C(3B)-O(4B)-C(6B)	107.2(4)
C(4B)-O(5B)-C(9B)	111.5(4)
C(5B)-O(6B)-C(9B)	112.0(4)
C(7B)-O(7B)-C(12B)	108.7(4)
C(8B)-O(8B)-C(12B)	105.5(4)
O(1)-C(1B)-C(15B)	113.0(4)
O(1)-C(1B)-C(2B)	108.3(4)
C(15B)-C(1B)-C(2B)	106.5(4)
O(1)-C(1B)-H(1B)	109.7
C(15B)-C(1B)-H(1B)	109.7
C(2B)-C(1B)-H(1B)	109.7
O(2B)-C(2B)-O(3B)	125.3(5)
O(2B)-C(2B)-C(1B)	125.9(5)
O(3B)-C(2B)-C(1B)	108.8(4)
O(4B)-C(3B)-O(3B)	109.7(4)
O(4B)-C(3B)-C(4B)	107.3(4)
O(3B)-C(3B)-C(4B)	103.7(4)
O(4B)-C(3B)-H(3B)	111.9
O(3B)-C(3B)-H(3B)	111.9
C(4B)-C(3B)-H(3B)	111.9
O(5B)-C(4B)-C(3B)	112.2(5)
O(5B)-C(4B)-C(5B)	104.7(5)
C(3B)-C(4B)-C(5B)	103.7(4)
O(5B)-C(4B)-H(4B)	111.9
C(3B)-C(4B)-H(4B)	111.9
C(5B)-C(4B)-H(4B)	111.9
O(6B)-C(5B)-C(6B)	113.2(5)
O(6B)-C(5B)-C(4B)	104.8(4)
C(6B)-C(5B)-C(4B)	104.1(4)
O(6B)-C(5B)-H(5B)	111.4
C(6B)-C(5B)-H(5B)	111.4
C(4B)-C(5B)-H(5B)	111.4
O(4B)-C(6B)-C(7B)	111.1(4)
O(4B)-C(6B)-C(5B)	104.9(4)

C(7B)-C(6B)-C(5B)	114.4(5)
O(4B)-C(6B)-H(6B)	108.8
C(7B)-C(6B)-H(6B)	108.8
C(5B)-C(6B)-H(6B)	108.8
O(7B)-C(7B)-C(6B)	107.9(4)
O(7B)-C(7B)-C(8B)	104.0(4)
C(6B)-C(7B)-C(8B)	114.0(5)
O(7B)-C(7B)-H(7B)	110.2
C(6B)-C(7B)-H(7B)	110.2
C(8B)-C(7B)-H(7B)	110.2
O(8B)-C(8B)-C(7B)	103.3(4)
O(8B)-C(8B)-H(8B1)	111.1
C(7B)-C(8B)-H(8B1)	111.1
O(8B)-C(8B)-H(8B2)	111.1
C(7B)-C(8B)-H(8B2)	111.1
H(8B1)-C(8B)-H(8B2)	109.1
O(6B)-C(9B)-O(5B)	105.5(4)
O(6B)-C(9B)-C(11B)	110.6(5)
O(5B)-C(9B)-C(11B)	110.7(5)
O(6B)-C(9B)-C(10B)	108.1(5)
O(5B)-C(9B)-C(10B)	107.7(5)
C(11B)-C(9B)-C(10B)	113.8(5)
C(9B)-C(10B)-H(10D)	109.5
C(9B)-C(10B)-H(10E)	109.5
H(10D)-C(10B)-H(10E)	109.5
C(9B)-C(10B)-H(10F)	109.5
H(10D)-C(10B)-H(10F)	109.5
H(10E)-C(10B)-H(10F)	109.5
C(9B)-C(11B)-H(11D)	109.5
C(9B)-C(11B)-H(11E)	109.5
H(11D)-C(11B)-H(11E)	109.5
C(9B)-C(11B)-H(11F)	109.5
H(11D)-C(11B)-H(11F)	109.5
H(11E)-C(11B)-H(11F)	109.5
O(8B)-C(12B)-O(7B)	105.1(4)
O(8B)-C(12B)-C(13B)	111.4(5)
O(7B)-C(12B)-C(13B)	109.9(5)
O(8B)-C(12B)-C(14B)	107.9(5)
O(7B)-C(12B)-C(14B)	108.9(5)
C(13B)-C(12B)-C(14B)	113.1(5)
C(12B)-C(13B)-H(13D)	109.5
C(12B)-C(13B)-H(13E)	109.5
H(13D)-C(13B)-H(13E)	109.5
C(12B)-C(13B)-H(13F)	109.5
H(13D)-C(13B)-H(13F)	109.5
H(13E)-C(13B)-H(13F)	109.5
C(12B)-C(14B)-H(14D)	109.5
C(12B)-C(14B)-H(14E)	109.5
H(14D)-C(14B)-H(14E)	109.5
C(12B)-C(14B)-H(14F)	109.5
H(14D)-C(14B)-H(14F)	109.5
H(14E)-C(14B)-H(14F)	109.5
C(16B)-C(15B)-C(20B)	119.1(5)
C(16B)-C(15B)-C(1B)	119.1(5)
C(20B)-C(15B)-C(1B)	121.7(5)
C(15B)-C(16B)-C(17B)	120.2(5)
C(15B)-C(16B)-H(16B)	119.9

C(17B)-C(16B)-H(16B)	119.9
C(18B)-C(17B)-C(16B)	120.0(6)
C(18B)-C(17B)-H(17B)	120.0
C(16B)-C(17B)-H(17B)	120.0
C(17B)-C(18B)-C(19B)	119.8(6)
C(17B)-C(18B)-H(18B)	120.1
C(19B)-C(18B)-H(18B)	120.1
C(20B)-C(19B)-C(18B)	120.8(6)
C(20B)-C(19B)-H(19B)	119.6
C(18B)-C(19B)-H(19B)	119.6
C(19B)-C(20B)-C(15B)	120.0(6)
C(19B)-C(20B)-H(20B)	120.0
C(15B)-C(20B)-H(20B)	120.0

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 05mz046m. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [(h a*)^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	13(2)	22(2)	22(2)	5(2)	-1(2)	-9(2)
O(2A)	13(2)	20(2)	38(2)	1(2)	3(2)	-7(2)
O(3A)	13(2)	17(2)	23(2)	-3(2)	0(2)	-7(2)
O(4A)	8(2)	17(2)	23(2)	0(2)	3(1)	-6(1)
O(5A)	21(2)	16(2)	22(2)	-3(2)	4(2)	-7(2)
O(6A)	19(2)	16(2)	24(2)	-6(2)	5(2)	-11(2)
O(7A)	14(2)	23(2)	24(2)	-5(2)	5(2)	-6(2)
O(8A)	14(2)	27(2)	30(2)	-6(2)	0(2)	-8(2)
C(1A)	11(2)	21(3)	19(3)	6(2)	0(2)	-9(2)
C(2A)	15(3)	15(3)	21(3)	0(2)	-4(2)	-6(2)
C(3A)	8(2)	10(2)	21(3)	-3(2)	3(2)	-4(2)
C(4A)	12(2)	14(2)	19(3)	-1(2)	-4(2)	-6(2)
C(5A)	7(2)	18(3)	25(3)	-3(2)	-1(2)	-4(2)
C(6A)	8(2)	16(2)	20(3)	-4(2)	4(2)	-3(2)
C(7A)	13(3)	21(3)	22(3)	-8(2)	-1(2)	-5(2)
C(8A)	20(3)	31(3)	20(3)	-8(2)	3(2)	-8(2)
C(9A)	18(3)	16(3)	22(3)	1(2)	2(2)	-12(2)
C(10A)	11(3)	25(3)	37(3)	-6(3)	-7(2)	-5(2)
C(11A)	22(3)	23(3)	23(3)	1(2)	3(2)	-9(2)
C(12A)	13(3)	24(3)	21(3)	-2(2)	1(2)	-7(2)
C(13A)	35(4)	32(3)	29(3)	-4(3)	-1(3)	-13(3)
C(14A)	23(3)	28(3)	30(3)	-1(3)	0(2)	-8(3)
C(15A)	15(3)	14(3)	25(3)	2(2)	2(2)	-8(2)
C(16A)	11(2)	17(3)	28(3)	2(2)	-9(2)	-5(2)
C(17A)	22(3)	24(3)	21(3)	-1(2)	-5(2)	-5(2)
C(18A)	25(3)	19(3)	19(3)	-3(2)	6(2)	-7(2)
C(19A)	13(3)	22(3)	26(3)	1(2)	1(2)	-7(2)
C(20A)	17(3)	21(3)	30(3)	8(2)	-8(2)	-8(2)
O(2B)	16(2)	25(2)	23(2)	-3(2)	0(2)	-8(2)
O(3B)	18(2)	14(2)	25(2)	1(2)	-2(2)	-8(2)
O(4B)	14(2)	25(2)	16(2)	1(2)	-2(1)	-8(2)
O(5B)	49(3)	17(2)	22(2)	-2(2)	4(2)	-9(2)

O(6B)	39(3)	22(2)	19(2)	1(2)	0(2)	-6(2)
O(7B)	16(2)	21(2)	24(2)	-1(2)	0(2)	1(2)
O(8B)	22(2)	26(2)	23(2)	0(2)	-2(2)	-5(2)
C(1B)	9(2)	18(3)	17(3)	3(2)	0(2)	-1(2)
C(2B)	17(3)	23(3)	10(2)	-6(2)	4(2)	-6(2)
C(3B)	22(3)	15(3)	21(3)	-2(2)	-1(2)	-13(2)
C(4B)	22(3)	16(3)	25(3)	-5(2)	-1(2)	-3(2)
C(5B)	21(3)	14(3)	24(3)	-3(2)	-1(2)	-4(2)
C(6B)	19(3)	14(3)	24(3)	-1(2)	-3(2)	-7(2)
C(7B)	20(3)	24(3)	18(3)	0(2)	2(2)	-8(2)
C(8B)	23(3)	27(3)	12(2)	-2(2)	0(2)	-6(2)
C(9B)	24(3)	20(3)	21(3)	2(2)	-1(2)	-7(2)
C(10B)	26(3)	25(3)	22(3)	-1(2)	-1(2)	-12(2)
C(11B)	28(3)	56(5)	24(3)	-1(3)	4(3)	-13(3)
C(12B)	19(3)	20(3)	19(3)	0(2)	-2(2)	-1(2)
C(13B)	19(3)	30(3)	19(3)	-6(2)	4(2)	0(2)
C(14B)	20(3)	39(4)	31(3)	-8(3)	3(3)	-9(3)
C(15B)	12(2)	20(3)	16(3)	3(2)	6(2)	-2(2)
C(16B)	15(3)	25(3)	31(3)	-3(2)	-3(2)	-7(2)
C(17B)	29(3)	22(3)	35(4)	-8(3)	7(3)	-6(3)
C(18B)	42(4)	27(3)	18(3)	-6(2)	3(3)	-19(3)
C(19B)	33(3)	25(3)	23(3)	6(2)	-5(2)	-11(3)
C(20B)	22(3)	24(3)	24(3)	2(2)	0(2)	-7(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for 05mz046m.

	x	y	z	U(eq)
H(1A)	7221	4126	5336	20
H(3A)	3915	7509	4676	15
H(4A)	8530	7449	4928	17
H(5A)	10415	7400	3418	20
H(6A)	7999	6243	2871	18
H(7A)	6550	8238	1729	22
H(8A1)	3911	6700	1672	28
H(8A2)	4604	7327	693	28
H(10A)	10927	9157	4468	36
H(10B)	9348	10264	4917	36
H(10C)	10591	10322	3872	36
H(11A)	6663	11063	3121	33
H(11B)	5259	11049	4137	33
H(11C)	4525	10382	3260	33
H(13A)	8953	5935	-772	47
H(13B)	10677	6756	-476	47
H(13C)	7843	7177	-430	47
H(14A)	10763	4872	1595	40
H(14B)	12492	5245	764	40
H(14C)	10658	4453	524	40
H(16A)	3641	4198	3243	22
H(17A)	5043	3521	1754	26
H(18A)	9020	2572	1530	25
H(19A)	11538	2350	2817	24
H(20A)	10206	3077	4311	26
H(1B)	6935	2352	5703	18
H(3B)	3181	-333	5947	22
H(4B)	7658	-954	6517	25
H(5B)	7506	-1153	8155	23
H(6B)	4576	386	8313	22
H(7B)	2025	-1339	8988	24
H(8B1)	-400	707	8672	24
H(8B2)	-1098	-63	9563	24
H(10D)	8364	-3877	7205	35
H(10E)	6483	-4358	6595	35
H(10F)	6351	-4450	7742	35
H(11D)	1976	-3343	7742	53
H(11E)	2192	-3315	6595	53
H(11F)	1484	-2168	7162	53
H(13D)	379	-684	11093	35
H(13E)	433	399	11710	35
H(13F)	2606	-649	11745	35
H(14D)	5668	500	11184	45
H(14E)	3626	1603	11209	45
H(14F)	5187	1287	10243	45
H(16B)	1955	3898	7060	28
H(17B)	1964	4389	8679	34
H(18B)	5440	3895	9538	33
H(19B)	8861	2838	8816	32
H(20B)	8876	2313	7224	28

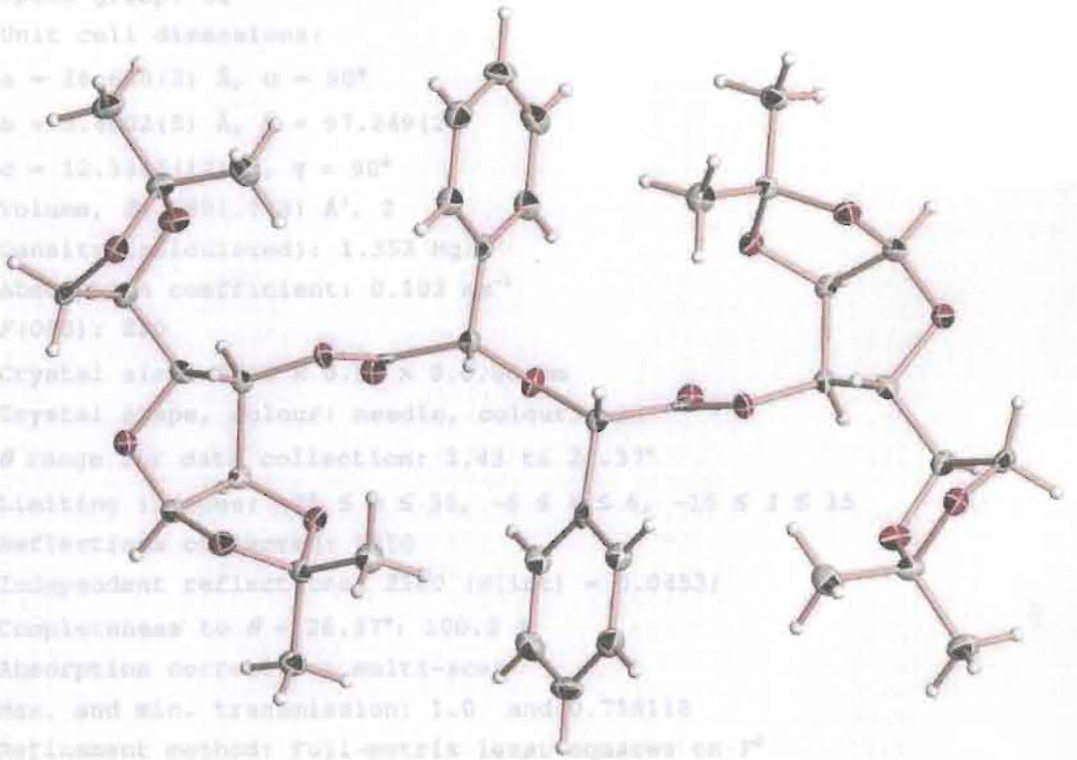


Figure 103: X-Ray crystal structure of allofuranose dimeric ether **15**.

Table 1. Crystal data and structure refinement for 05mz037m:

Identification code: 05mz037m
Empirical formula: C40 H50 O15
Formula weight: 770.80
Temperature: 90(2) K
Wavelength: 0.71073 Å
Crystal system: Monoclinic
Space group: C2
Unit cell dimensions:
a = 28.638(3) Å, α = 90°
b = 5.4002(5) Å, β = 97.249(2)°
c = 12.3306(12) Å, γ = 90°
Volume, *Z*: 1891.7(3) Å^3, 2
Density (calculated): 1.353 Mg/m^3
Absorption coefficient: 0.103 mm^{-1}
F(000): 820
Crystal size: 0.60 × 0.09 × 0.0.06 mm
Crystal shape, colour: needle, colourless
θ range for data collection: 1.43 to 26.37°
Limiting indices: $-35 \leq h \leq 35$, $-6 \leq k \leq 6$, $-15 \leq l \leq 15$
Reflections collected: 8530
Independent reflections: 2160 (*R*(int) = 0.0453)
Completeness to θ = 26.37°: 100.0 %
Absorption correction: multi-scan
Max. and min. transmission: 1.0 and 0.758118
Refinement method: Full-matrix least-squares on F^2
Data / restraints / parameters: 2160 / 1 / 253
Goodness-of-fit on F^2: 1.287
Final *R* indices [$I>2\sigma(I)$]: R1 = 0.0577, wR2 = 0.1150
R indices (all data): R1 = 0.0621, wR2 = 0.1167
Largest diff. peak and hole: 0.378 and -0.219 e × Å^{-3}

Comments:

The molecule has crystallographical two fold symmetry; the central ether oxygen atom is located on the two fold axis. Treatment of hydrogen atoms: All hydrogen atoms were placed in calculated positions and were refined with an isotropic displacement parameter 1.5 (methyl) or 1.2 times (all others) that of the adjacent carbon atom.

Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors.

Table 2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for 05mz037m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	5000	-748(7)	10000	16(1)
O(4)	2752(1)	2168(5)	8136(2)	17(1)
O(7)	3465(1)	2827(5)	5914(2)	19(1)
O(2)	4208(1)	-2765(5)	8845(2)	17(1)
O(3)	3967(1)	1126(5)	8388(2)	14(1)
O(5)	3039(1)	3255(5)	9905(2)	17(1)
O(8)	3090(1)	6551(5)	5909(2)	17(1)
O(6)	3586(1)	155(5)	10192(2)	16(1)
C(15)	5022(1)	907(7)	8165(3)	15(1)
C(20)	5341(1)	-909(8)	7948(3)	19(1)
C(4)	3190(1)	2473(7)	7686(3)	13(1)
C(10)	3392(1)	2243(8)	10708(3)	14(1)
C(3)	3492(1)	269(7)	8157(3)	12(1)
C(14)	4753(1)	707(7)	9153(3)	13(1)
C(8)	3350(2)	5116(9)	4219(3)	25(1)
C(13)	4285(1)	-585(7)	8798(3)	13(1)
C(1)	2859(1)	1280(8)	9202(3)	16(1)
C(18)	5466(1)	1193(9)	6287(3)	24(1)
C(2)	3284(1)	-449(7)	9230(3)	13(1)
C(12)	3770(1)	4157(8)	11002(3)	20(1)
C(9)	3918(1)	6568(8)	5827(3)	25(1)
C(19)	5561(1)	-763(9)	7015(3)	24(1)
C(6)	2750(1)	4712(8)	6082(3)	17(1)
C(17)	5155(1)	3024(9)	6516(3)	23(1)
C(16)	4933(1)	2893(7)	7444(3)	19(1)
C(5)	3058(1)	2491(7)	6458(3)	16(1)
C(11)	3166(1)	1314(8)	11692(3)	21(1)
C(7)	3458(1)	5291(7)	5452(3)	17(1)

All esds (except the esd in the dihedral angle between two l.s. planes)are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 3. Bond lengths [Å] and angles [deg] for 05mz037m.

O(1)-C(14)#1	1.422(4)
O(1)-C(14)	1.422(4)
O(4)-C(1)	1.396(4)
O(4)-C(4)	1.444(4)
O(7)-C(5)	1.427(4)
O(7)-C(7)	1.446(5)
O(2)-C(13)	1.200(5)
O(3)-C(13)	1.349(5)
O(3)-C(3)	1.432(4)
O(5)-C(1)	1.429(5)
O(5)-C(10)	1.431(4)
O(8)-C(6)	1.426(5)
O(8)-C(7)	1.427(4)
O(6)-C(2)	1.416(4)
O(6)-C(10)	1.440(4)
C(15)-C(20)	1.388(6)
C(15)-C(16)	1.396(5)
C(15)-C(14)	1.527(5)
C(20)-C(19)	1.382(6)
C(20)-H(20)	0.9500
C(4)-C(5)	1.514(5)
C(4)-C(3)	1.540(5)
C(4)-H(4)	1.0000
C(10)-C(12)	1.507(5)
C(10)-C(11)	1.529(5)
C(3)-C(2)	1.566(5)
C(3)-H(3)	1.0000
C(14)-C(13)	1.525(5)
C(14)-H(14)	1.0000
C(8)-C(7)	1.516(5)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(1)-C(2)	1.530(5)
C(1)-H(1)	1.0000
C(18)-C(17)	1.384(6)
C(18)-C(19)	1.391(6)
C(18)-H(18)	0.9500
C(2)-H(2)	1.0000
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(9)-C(7)	1.509(6)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(19)-H(19)	0.9500
C(6)-C(5)	1.526(5)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(17)-C(16)	1.380(5)
C(17)-H(17)	0.9500
C(16)-H(16)	0.9500
C(5)-H(5)	1.0000

C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800

C(14)#1-O(1)-C(14)	113.0(4)
C(1)-O(4)-C(4)	107.6(3)
C(5)-O(7)-C(7)	109.2(3)
C(13)-O(3)-C(3)	115.6(3)
C(1)-O(5)-C(10)	107.7(3)
C(6)-O(8)-C(7)	106.2(3)
C(2)-O(6)-C(10)	108.8(3)
C(20)-C(15)-C(16)	119.5(4)
C(20)-C(15)-C(14)	121.0(3)
C(16)-C(15)-C(14)	119.4(3)
C(19)-C(20)-C(15)	120.0(4)
C(19)-C(20)-H(20)	120.0
C(15)-C(20)-H(20)	120.0
O(4)-C(4)-C(5)	105.4(3)
O(4)-C(4)-C(3)	103.9(3)
C(5)-C(4)-C(3)	116.1(3)
O(4)-C(4)-H(4)	110.4
C(5)-C(4)-H(4)	110.4
C(3)-C(4)-H(4)	110.4
O(5)-C(10)-O(6)	105.7(3)
O(5)-C(10)-C(12)	109.1(3)
O(6)-C(10)-C(12)	109.8(3)
O(5)-C(10)-C(11)	110.0(3)
O(6)-C(10)-C(11)	108.6(3)
C(12)-C(10)-C(11)	113.4(3)
O(3)-C(3)-C(4)	107.4(3)
O(3)-C(3)-C(2)	111.4(3)
C(4)-C(3)-C(2)	104.8(3)
O(3)-C(3)-H(3)	111.0
C(4)-C(3)-H(3)	111.0
C(2)-C(3)-H(3)	111.0
O(1)-C(14)-C(13)	107.2(3)
O(1)-C(14)-C(15)	111.7(3)
C(13)-C(14)-C(15)	108.6(3)
O(1)-C(14)-H(14)	109.8
C(13)-C(14)-H(14)	109.8
C(15)-C(14)-H(14)	109.8
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
O(2)-C(13)-O(3)	124.8(3)
O(2)-C(13)-C(14)	126.5(4)
O(3)-C(13)-C(14)	108.7(3)
O(4)-C(1)-O(5)	109.5(3)
O(4)-C(1)-C(2)	108.1(3)
O(5)-C(1)-C(2)	102.6(3)
O(4)-C(1)-H(1)	112.1
O(5)-C(1)-H(1)	112.1
C(2)-C(1)-H(1)	112.1
C(17)-C(18)-C(19)	119.3(4)

C(17)-C(18)-H(18)	120.3
C(19)-C(18)-H(18)	120.3
O(6)-C(2)-C(1)	106.2(3)
O(6)-C(2)-C(3)	113.1(3)
C(1)-C(2)-C(3)	102.5(3)
O(6)-C(2)-H(2)	111.5
C(1)-C(2)-H(2)	111.5
C(3)-C(2)-H(2)	111.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(20)-C(19)-C(18)	120.5(4)
C(20)-C(19)-H(19)	119.8
C(18)-C(19)-H(19)	119.8
O(8)-C(6)-C(5)	102.2(3)
O(8)-C(6)-H(6A)	111.3
C(5)-C(6)-H(6A)	111.3
O(8)-C(6)-H(6B)	111.3
C(5)-C(6)-H(6B)	111.3
H(6A)-C(6)-H(6B)	109.2
C(16)-C(17)-C(18)	120.6(4)
C(16)-C(17)-H(17)	119.7
C(18)-C(17)-H(17)	119.7
C(17)-C(16)-C(15)	120.0(4)
C(17)-C(16)-H(16)	120.0
C(15)-C(16)-H(16)	120.0
O(7)-C(5)-C(4)	110.8(3)
O(7)-C(5)-C(6)	103.5(3)
C(4)-C(5)-C(6)	111.8(3)
O(7)-C(5)-H(5)	110.2
C(4)-C(5)-H(5)	110.2
C(6)-C(5)-H(5)	110.2
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
O(8)-C(7)-O(7)	104.9(3)
O(8)-C(7)-C(9)	108.7(3)
O(7)-C(7)-C(9)	109.3(3)
O(8)-C(7)-C(8)	111.1(3)
O(7)-C(7)-C(8)	109.2(3)
C(9)-C(7)-C(8)	113.3(3)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+2

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 05mz037m. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [(h a*)^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	19(2)	11(2)	17(2)	0	-4(2)	0
O(4)	15(1)	18(1)	16(1)	1(1)	1(1)	1(1)
O(7)	27(1)	14(2)	18(1)	3(1)	6(1)	8(1)
O(2)	19(1)	14(1)	20(1)	-1(1)	2(1)	1(1)
O(3)	11(1)	14(1)	18(1)	1(1)	0(1)	-2(1)
O(5)	20(1)	15(1)	16(1)	-1(1)	4(1)	2(1)
O(8)	19(1)	13(1)	18(1)	-1(1)	0(1)	3(1)
O(6)	18(1)	15(1)	14(1)	-1(1)	0(1)	4(1)
C(15)	12(2)	15(2)	16(2)	0(2)	-4(1)	-7(2)
C(20)	19(2)	15(2)	24(2)	0(2)	2(2)	4(2)
C(4)	14(2)	8(2)	17(2)	-2(2)	3(1)	0(2)
C(10)	14(2)	13(2)	17(2)	-1(2)	4(1)	4(2)
C(3)	12(2)	9(2)	16(2)	-3(2)	1(1)	2(2)
C(14)	14(2)	10(2)	15(2)	-2(2)	1(1)	-1(1)
C(8)	30(2)	28(2)	17(2)	3(2)	5(2)	6(2)
C(13)	16(2)	18(2)	6(2)	0(2)	6(1)	1(2)
C(1)	16(2)	16(2)	16(2)	-3(2)	3(1)	-4(2)
C(18)	26(2)	29(2)	19(2)	-4(2)	10(2)	-10(2)
C(2)	16(2)	9(2)	14(2)	2(2)	0(1)	-4(2)
C(12)	23(2)	13(2)	24(2)	3(2)	1(2)	-3(2)
C(9)	24(2)	22(2)	30(2)	-2(2)	6(2)	3(2)
C(19)	19(2)	21(2)	31(2)	-9(2)	6(2)	-2(2)
C(6)	20(2)	20(2)	11(2)	4(2)	-1(1)	0(2)
C(17)	24(2)	24(2)	20(2)	4(2)	1(2)	-5(2)
C(16)	20(2)	15(2)	21(2)	-1(2)	1(2)	2(2)
C(5)	18(2)	13(2)	16(2)	-4(2)	1(1)	3(2)
C(11)	20(2)	23(2)	20(2)	-2(2)	4(2)	-4(2)
C(7)	24(2)	13(2)	16(2)	2(2)	4(2)	5(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for 05mz037m.

	x	y	z	U(eq)
H(20)	5407	-2253	8440	23
H(4)	3343	4073	7937	16
H(3)	3469	-1147	7630	15
H(14)	4694	2399	9436	16
H(8A)	3344	6782	3902	37
H(8B)	3043	4326	4026	37
H(8C)	3594	4126	3931	37
H(1)	2584	446	9469	19
H(18)	5613	1272	5639	29
H(2)	3187	-2228	9224	16
H(12A)	3633	5612	11316	30
H(12B)	3906	4644	10344	30
H(12C)	4017	3459	11538	30
H(9A)	3986	6449	6625	37
H(9B)	3897	8315	5612	37
H(9C)	4171	5769	5490	37
H(19)	5780	-2008	6870	28
H(6A)	2541	4342	5399	21
H(6B)	2556	5234	6652	21
H(17)	5094	4384	6030	27
H(16)	4718	4154	7592	22
H(5)	2895	916	6212	19
H(11A)	2926	71	11449	31
H(11B)	3019	2706	12030	31
H(11C)	3408	570	12226	31

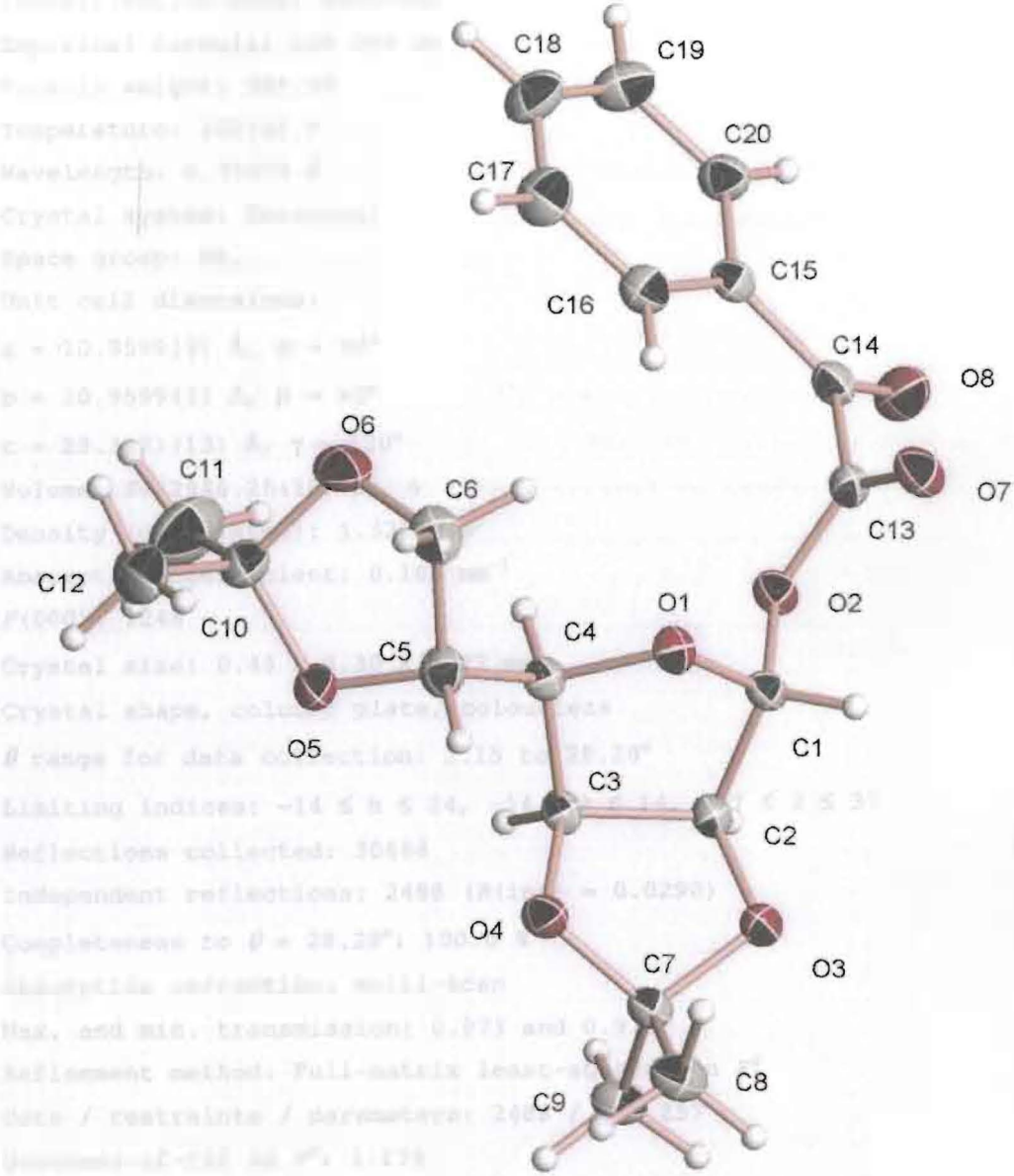


Figure 104: X-Ray crystal structure of mannofuranose ketone **16**.

Table 1. Crystal data and structure refinement for 06mz088m:

Identification code: 06mz088m

Empirical formula: C20 H24 O8

Formula weight: 392.39

Temperature: 100(2) K

Wavelength: 0.71073 Å

Crystal system: Hexagonal

Space group: $P6_1$

Unit cell dimensions:

a = 10.9599(3) Å, α = 90°

b = 10.9599(3) Å, β = 90°

c = 28.3221(13) Å, γ = 120°

Volume, Z: 2946.25(18) $Å^3$, 6

Density (calculated): 1.327 g/m^3

Absorption coefficient: 0.103 mm^{-1}

$F(000)$: 1248

Crystal size: 0.48 × 0.30 × 0.27 mm

Crystal shape, colour: plate, colourless

θ range for data collection: 2.15 to 28.28°

Limiting indices: $-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $-37 \leq l \leq 37$

Reflections collected: 30688

Independent reflections: 2488 (R(int) = 0.0290)

Completeness to θ = 28.28°: 100.0 %

Absorption correction: multi-scan

Max. and min. transmission: 0.973 and 0.916

Refinement method: Full-matrix least-squares on F^2

Data / restraints / parameters: 2488 / 1 / 257

Goodness-of-fit on F^2: 1.178

Final R indices [$I>2\sigma(I)$]: R1 = 0.0429, wR2 = 0.1048

R indices (all data): R1 = 0.0430, wR2 = 0.1049

Largest diff. peak and hole: 0.374 and -0.210 e × $Å^{-3}$

Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors

Treatment of hydrogen atoms:
All hydrogen atoms were placed in calculatedpositions and were refined with an isotropic displacement parameter 1.5 (methytl) or 1.2 timed that of the adjacent carbon atom.

Table 2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for 06mz088m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	386(2)	10854(2)	1408(1)	19(1)
C(2)	-766(2)	10140(2)	1780(1)	19(1)
C(3)	-803(2)	8728(2)	1878(1)	19(1)
C(4)	424(2)	8849(2)	1587(1)	20(1)
C(5)	236(2)	7501(2)	1371(1)	26(1)
C(6)	1508(3)	7742(3)	1075(1)	34(1)
C(7)	-3019(2)	8279(2)	1665(1)	22(1)
C(8)	-4048(3)	7620(3)	1264(1)	29(1)
C(9)	-3729(2)	8134(3)	2139(1)	27(1)
C(10)	1474(3)	6513(3)	1721(1)	32(1)
C(11)	2132(4)	6788(5)	2206(1)	60(1)
C(12)	1113(4)	5083(3)	1523(2)	52(1)
C(13)	2701(2)	12805(2)	1384(1)	21(1)
C(14)	4034(2)	13639(2)	1683(1)	23(1)
C(15)	5053(2)	13132(2)	1676(1)	22(1)
C(16)	4710(3)	11846(2)	1466(1)	26(1)
C(17)	5649(3)	11346(3)	1498(1)	36(1)
C(18)	6912(3)	12129(3)	1735(1)	38(1)
C(19)	7267(3)	13421(3)	1938(1)	36(1)
C(20)	6342(2)	13930(3)	1907(1)	27(1)
O(1)	587(2)	9809(2)	1205(1)	21(1)
O(2)	1657(2)	11849(2)	1657(1)	22(1)
O(3)	-2078(2)	9741(2)	1556(1)	24(1)
O(4)	-2115(2)	7692(2)	1681(1)	23(1)
O(5)	213(2)	6622(2)	1746(1)	29(1)
O(6)	2392(2)	7616(2)	1414(1)	34(1)
O(7)	2619(2)	13017(2)	974(1)	29(1)
O(8)	4158(2)	14629(2)	1909(1)	34(1)

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 3. Bond lengths [Å] and angles [deg] for 06mz088m.

C(1)-O(1)	1.394(2)
C(1)-O(2)	1.452(2)
C(1)-C(2)	1.525(3)
C(1)-H(1)	1.0000
C(2)-O(3)	1.425(3)
C(2)-C(3)	1.552(3)
C(2)-H(2)	1.0000
C(3)-O(4)	1.427(3)
C(3)-C(4)	1.525(3)
C(3)-H(3)	1.0000
C(4)-O(1)	1.457(2)
C(4)-C(5)	1.516(3)
C(4)-H(4)	1.0000
C(5)-O(5)	1.425(3)
C(5)-C(6)	1.531(3)
C(5)-H(5)	1.0000
C(6)-O(6)	1.419(4)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-O(4)	1.426(3)
C(7)-O(3)	1.439(3)
C(7)-C(8)	1.506(3)
C(7)-C(9)	1.521(3)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-O(6)	1.418(3)
C(10)-O(5)	1.448(3)
C(10)-C(11)	1.510(5)
C(10)-C(12)	1.519(4)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-O(7)	1.195(3)
C(13)-O(2)	1.345(3)
C(13)-C(14)	1.534(3)
C(14)-O(8)	1.206(3)

C(14)-C(15)	1.475(3)
C(15)-C(16)	1.398(3)
C(15)-C(20)	1.398(3)
C(16)-C(17)	1.390(4)
C(16)-H(16)	0.9500
C(17)-C(18)	1.384(4)
C(17)-H(17)	0.9500
C(18)-C(19)	1.391(4)
C(18)-H(18)	0.9500
C(19)-C(20)	1.382(4)
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500
O(1)-C(1)-O(2)	109.35(16)
O(1)-C(1)-C(2)	107.00(17)
O(2)-C(1)-C(2)	106.66(16)
O(1)-C(1)-H(1)	111.2
O(2)-C(1)-H(1)	111.2
C(2)-C(1)-H(1)	111.2
O(3)-C(2)-C(1)	107.52(16)
O(3)-C(2)-C(3)	104.76(16)
C(1)-C(2)-C(3)	103.82(17)
O(3)-C(2)-H(2)	113.3
C(1)-C(2)-H(2)	113.3
C(3)-C(2)-H(2)	113.3
O(4)-C(3)-C(4)	110.55(16)
O(4)-C(3)-C(2)	103.68(16)
C(4)-C(3)-C(2)	103.48(16)
O(4)-C(3)-H(3)	112.8
C(4)-C(3)-H(3)	112.8
C(2)-C(3)-H(3)	112.8
O(1)-C(4)-C(5)	108.14(17)
O(1)-C(4)-C(3)	104.43(16)
C(5)-C(4)-C(3)	116.74(18)
O(1)-C(4)-H(4)	109.1
C(5)-C(4)-H(4)	109.1
C(3)-C(4)-H(4)	109.1
O(5)-C(5)-C(4)	107.79(19)
O(5)-C(5)-C(6)	103.37(19)
C(4)-C(5)-C(6)	112.61(19)
O(5)-C(5)-H(5)	110.9
C(4)-C(5)-H(5)	110.9
C(6)-C(5)-H(5)	110.9
O(6)-C(6)-C(5)	102.7(2)
O(6)-C(6)-H(6A)	111.2
C(5)-C(6)-H(6A)	111.2
O(6)-C(6)-H(6B)	111.2
C(5)-C(6)-H(6B)	111.2
H(6A)-C(6)-H(6B)	109.1
O(4)-C(7)-O(3)	103.69(16)
O(4)-C(7)-C(8)	109.34(19)
O(3)-C(7)-C(8)	108.71(18)
O(4)-C(7)-C(9)	111.03(19)
O(3)-C(7)-C(9)	110.40(19)
C(8)-C(7)-C(9)	113.22(18)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5

C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
O(6)-C(10)-O(5)	105.03(19)
O(6)-C(10)-C(11)	108.8(3)
O(5)-C(10)-C(11)	108.6(2)
O(6)-C(10)-C(12)	111.2(2)
O(5)-C(10)-C(12)	109.7(2)
C(11)-C(10)-C(12)	113.1(3)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
O(7)-C(13)-O(2)	126.3(2)
O(7)-C(13)-C(14)	124.2(2)
O(2)-C(13)-C(14)	109.41(18)
O(8)-C(14)-C(15)	125.5(2)
O(8)-C(14)-C(13)	118.3(2)
C(15)-C(14)-C(13)	116.26(19)
C(16)-C(15)-C(20)	120.6(2)
C(16)-C(15)-C(14)	120.9(2)
C(20)-C(15)-C(14)	118.5(2)
C(17)-C(16)-C(15)	119.4(2)
C(17)-C(16)-H(16)	120.3
C(15)-C(16)-H(16)	120.3
C(18)-C(17)-C(16)	119.7(2)
C(18)-C(17)-H(17)	120.2
C(16)-C(17)-H(17)	120.2
C(17)-C(18)-C(19)	121.0(2)
C(17)-C(18)-H(18)	119.5
C(19)-C(18)-H(18)	119.5
C(20)-C(19)-C(18)	119.8(2)
C(20)-C(19)-H(19)	120.1
C(18)-C(19)-H(19)	120.1
C(19)-C(20)-C(15)	119.5(2)
C(19)-C(20)-H(20)	120.2
C(15)-C(20)-H(20)	120.2
C(1)-O(1)-C(4)	105.93(15)
C(13)-O(2)-C(1)	115.36(17)
C(2)-O(3)-C(7)	107.35(16)
C(7)-O(4)-C(3)	107.72(16)
C(5)-O(5)-C(10)	108.93(18)
C(10)-O(6)-C(6)	105.6(2)

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 06mz088m. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [(h a*)^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	17(1)	19(1)	17(1)	2(1)	-1(1)	6(1)
C(2)	21(1)	17(1)	18(1)	0(1)	0(1)	9(1)
C(3)	23(1)	18(1)	15(1)	1(1)	0(1)	9(1)
C(4)	22(1)	21(1)	17(1)	0(1)	0(1)	11(1)
C(5)	31(1)	24(1)	26(1)	-1(1)	1(1)	15(1)
C(6)	45(1)	33(1)	28(1)	2(1)	12(1)	23(1)
C(7)	20(1)	21(1)	21(1)	1(1)	1(1)	8(1)
C(8)	24(1)	33(1)	22(1)	-1(1)	-2(1)	9(1)
C(9)	23(1)	28(1)	24(1)	-2(1)	3(1)	9(1)
C(10)	31(1)	34(1)	40(1)	6(1)	9(1)	22(1)
C(11)	58(2)	95(3)	44(2)	12(2)	0(2)	52(2)
C(12)	53(2)	35(1)	80(3)	9(2)	26(2)	32(1)
C(13)	21(1)	17(1)	26(1)	1(1)	0(1)	9(1)
C(14)	21(1)	19(1)	24(1)	2(1)	-1(1)	7(1)
C(15)	22(1)	21(1)	19(1)	3(1)	2(1)	9(1)
C(16)	28(1)	24(1)	25(1)	-2(1)	0(1)	11(1)
C(17)	42(1)	33(1)	39(1)	-6(1)	4(1)	23(1)
C(18)	35(1)	44(1)	45(2)	-2(1)	3(1)	28(1)
C(19)	27(1)	42(1)	39(1)	-5(1)	-3(1)	18(1)
C(20)	24(1)	24(1)	31(1)	-2(1)	-1(1)	10(1)
O(1)	26(1)	22(1)	14(1)	2(1)	0(1)	12(1)
O(2)	21(1)	20(1)	20(1)	1(1)	-2(1)	7(1)
O(3)	20(1)	21(1)	29(1)	4(1)	-1(1)	9(1)
O(4)	20(1)	19(1)	26(1)	-2(1)	-1(1)	7(1)
O(5)	29(1)	27(1)	38(1)	9(1)	11(1)	19(1)
O(6)	29(1)	34(1)	41(1)	1(1)	11(1)	16(1)
O(7)	27(1)	28(1)	25(1)	6(1)	0(1)	8(1)
O(8)	30(1)	24(1)	49(1)	-11(1)	-7(1)	14(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for 06mz088m.

	x	y	z	U(eq)
H(1)	119	11340	1164	23
H(2)	-596	10726	2069	23
H(3)	-718	8573	2222	23
H(4)	1296	9288	1785	24
H(5)	-651	7016	1181	31
H(6A)	1228	7021	824	40
H(6B)	1979	8690	929	40
H(8A)	-3530	7771	968	44
H(8B)	-4641	8053	1243	44
H(8C)	-4642	6607	1321	44
H(9A)	-4381	7136	2205	41
H(9B)	-4252	8644	2131	41
H(9C)	-3012	8530	2388	41
H(11A)	2927	6617	2202	89
H(11B)	1428	6157	2435	89
H(11C)	2465	7769	2295	89
H(12A)	625	4933	1220	78
H(12B)	501	4344	1746	78
H(12C)	1982	5048	1476	78
H(16)	3842	11318	1302	32
H(17)	5425	10471	1358	43
H(18)	7547	11780	1759	46
H(19)	8141	13952	2097	43
H(20)	6582	14816	2041	33

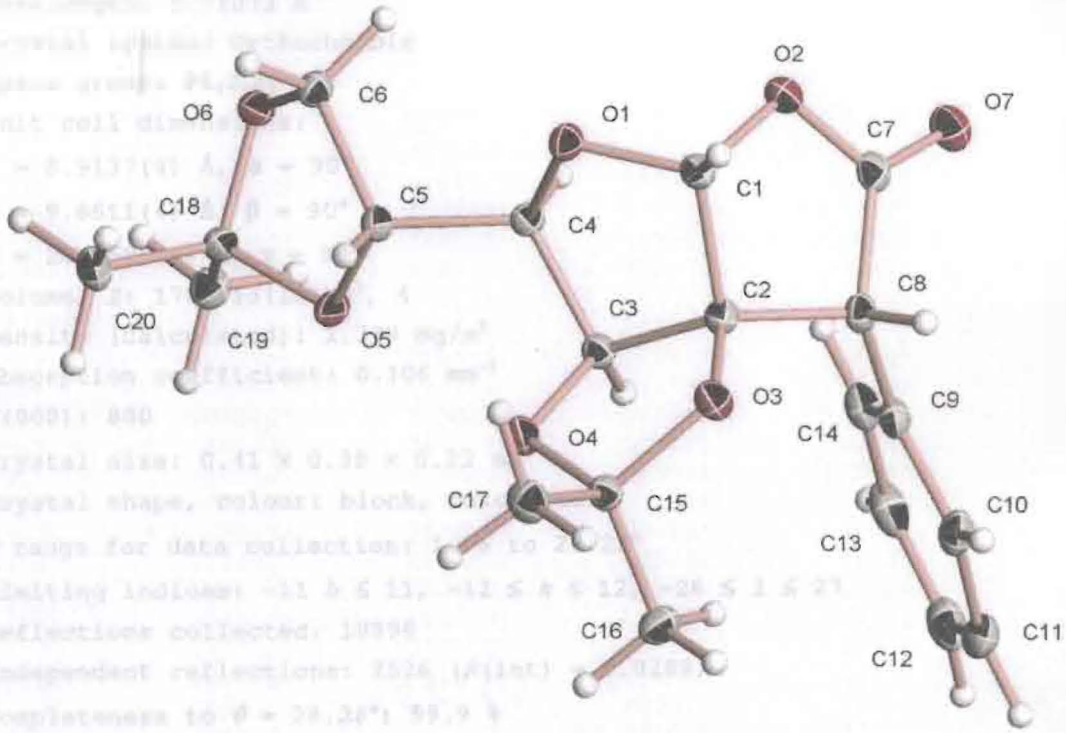


Figure 105: X-Ray crystal structure of mannofuranose insertion product **19**.

Table 1. Crystal data and structure refinement for 06mz136m:

Identification code: 06mz136m
Empirical formula: C20 H24 O7
Formula weight: 376.39
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Orthorhombic
Space group: $P2_12_12_1$
Unit cell dimensions:
a = 8.9137(4) Å, α = 90°
b = 9.6611(4) Å, β = 90°
c = 20.7525(9) Å, γ = 90°
Volume, Z: 1787.13(13) $Å^3$, 4
Density (calculated): 1.399 Mg/m^3
Absorption coefficient: 0.106 mm^{-1}
$F(000)$: 800
Crystal size: 0.41 × 0.38 × 0.22 mm
Crystal shape, colour: block, colourless
θ range for data collection: 1.96 to 28.28°
Limiting indices: $-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-26 \leq l \leq 27$
Reflections collected: 18596
Independent reflections: 2526 (R(int) = 0.0289)
Completeness to θ = 28.28°: 99.9 %
Absorption correction: multi-scan
Max. and min. transmission: 0.977 and 0.932
Refinement method: Full-matrix least-squares on F^2
Data / restraints / parameters: 2526 / 0 / 248
Goodness-of-fit on F^2: 1.117
Final R indices [$I>2\sigma(I)$]: R1 = 0.0371, wR2 = 0.0926
R indices (all data): R1 = 0.0375, wR2 = 0.0930
Largest diff. peak and hole: 0.405 and -0.185 e × $Å^{-3}$

Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors

Treatment of hydrogen atoms:

All hydrogen atoms were placed in calculated positions and were isotropically refined with a displacement parameter 1.5 (methyl) or 1.2 times (all others) that of the adjacent carbon atom.

Table 2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for 06mz136m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	4935(2)	5864(2)	6875(1)	15(1)
C(2)	3237(2)	6052(2)	6750(1)	14(1)
C(3)	2660(2)	6682(2)	7393(1)	14(1)
C(4)	4088(2)	6969(2)	7780(1)	13(1)
C(5)	4005(2)	6711(2)	8502(1)	14(1)
C(6)	5450(2)	7172(2)	8857(1)	15(1)
C(7)	4705(2)	7661(2)	6134(1)	16(1)
C(8)	3200(2)	6914(2)	6127(1)	14(1)
C(9)	1845(2)	7808(2)	6007(1)	16(1)
C(10)	653(2)	7275(2)	5652(1)	20(1)
C(11)	-662(2)	8034(3)	5570(1)	26(1)
C(12)	-771(3)	9352(3)	5829(1)	28(1)
C(13)	426(3)	9915(2)	6166(1)	25(1)
C(14)	1726(2)	9148(2)	6257(1)	20(1)
C(15)	1391(2)	4627(2)	7198(1)	15(1)
C(16)	-165(2)	4945(2)	6938(1)	19(1)
C(17)	1505(2)	3191(2)	7480(1)	20(1)
C(18)	3434(2)	8115(2)	9365(1)	15(1)
C(19)	2680(2)	9479(2)	9506(1)	19(1)
C(20)	3265(2)	7074(2)	9913(1)	20(1)
O(1)	5178(2)	5987(1)	7534(1)	16(1)
O(2)	5660(2)	6998(1)	6539(1)	17(1)
O(3)	2492(2)	4766(1)	6690(1)	17(1)
O(4)	1834(2)	5587(1)	7680(1)	17(1)
O(5)	2849(2)	7559(1)	8772(1)	17(1)
O(6)	4981(2)	8354(1)	9225(1)	16(1)
O(7)	5076(2)	8655(1)	5832(1)	21(1)

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 3. Bond lengths [Å] and angles [deg] for 06mz136m.

C(1)-O(1)	1.391(2)
C(1)-O(2)	1.451(2)
C(1)-C(2)	1.546(3)
C(1)-H(1)	1.0000
C(2)-O(3)	1.415(2)
C(2)-C(8)	1.538(2)
C(2)-C(3)	1.553(2)
C(3)-O(4)	1.420(2)
C(3)-C(4)	1.531(2)
C(3)-H(3)	1.0000
C(4)-O(1)	1.450(2)
C(4)-C(5)	1.519(2)
C(4)-H(4)	1.0000
C(5)-O(5)	1.431(2)
C(5)-C(6)	1.549(3)
C(5)-H(5)	1.0000
C(6)-O(6)	1.436(2)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-O(7)	1.195(2)
C(7)-O(2)	1.357(2)
C(7)-C(8)	1.523(3)
C(8)-C(9)	1.506(3)
C(8)-H(8)	1.0000
C(9)-C(10)	1.391(3)
C(9)-C(14)	1.399(3)
C(10)-C(11)	1.393(3)
C(10)-H(10)	0.9500
C(11)-C(12)	1.386(3)
C(11)-H(11)	0.9500
C(12)-C(13)	1.387(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.388(3)
C(13)-H(13)	0.9500
C(14)-H(14)	0.9500
C(15)-O(4)	1.420(2)
C(15)-O(3)	1.446(2)
C(15)-C(17)	1.508(3)
C(15)-C(16)	1.519(3)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800

C(18)-O(6)	1.428(2)
C(18)-O(5)	1.441(2)
C(18)-C(19)	1.508(3)
C(18)-C(20)	1.525(3)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800

O(1)-C(1)-O(2)	109.75(14)
O(1)-C(1)-C(2)	107.89(15)
O(2)-C(1)-C(2)	105.49(14)
O(1)-C(1)-H(1)	111.2
O(2)-C(1)-H(1)	111.2
C(2)-C(1)-H(1)	111.2
O(3)-C(2)-C(8)	113.07(14)
O(3)-C(2)-C(1)	111.75(15)
C(8)-C(2)-C(1)	103.02(14)
O(3)-C(2)-C(3)	105.31(14)
C(8)-C(2)-C(3)	120.17(15)
C(1)-C(2)-C(3)	103.09(14)
O(4)-C(3)-C(4)	110.22(14)
O(4)-C(3)-C(2)	103.90(14)
C(4)-C(3)-C(2)	104.27(14)
O(4)-C(3)-H(3)	112.6
C(4)-C(3)-H(3)	112.6
C(2)-C(3)-H(3)	112.6
O(1)-C(4)-C(5)	105.80(14)
O(1)-C(4)-C(3)	104.72(13)
C(5)-C(4)-C(3)	116.56(15)
O(1)-C(4)-H(4)	109.8
C(5)-C(4)-H(4)	109.8
C(3)-C(4)-H(4)	109.8
O(5)-C(5)-C(4)	109.11(14)
O(5)-C(5)-C(6)	104.35(13)
C(4)-C(5)-C(6)	112.40(15)
O(5)-C(5)-H(5)	110.3
C(4)-C(5)-H(5)	110.3
C(6)-C(5)-H(5)	110.3
O(6)-C(6)-C(5)	103.87(14)
O(6)-C(6)-H(6A)	111.0
C(5)-C(6)-H(6A)	111.0
O(6)-C(6)-H(6B)	111.0
C(5)-C(6)-H(6B)	111.0
H(6A)-C(6)-H(6B)	109.0

O(7)-C(7)-O(2)	122.08(18)
O(7)-C(7)-C(8)	128.30(18)
O(2)-C(7)-C(8)	109.60(15)
C(9)-C(8)-C(7)	115.90(15)
C(9)-C(8)-C(2)	117.86(15)
C(7)-C(8)-C(2)	103.28(14)
C(9)-C(8)-H(8)	106.3
C(7)-C(8)-H(8)	106.3
C(2)-C(8)-H(8)	106.3
C(10)-C(9)-C(14)	118.76(19)
C(10)-C(9)-C(8)	119.26(17)
C(14)-C(9)-C(8)	121.95(17)
C(9)-C(10)-C(11)	120.81(19)
C(9)-C(10)-H(10)	119.6
C(11)-C(10)-H(10)	119.6
C(12)-C(11)-C(10)	119.7(2)
C(12)-C(11)-H(11)	120.1
C(10)-C(11)-H(11)	120.1
C(11)-C(12)-C(13)	120.1(2)
C(11)-C(12)-H(12)	119.9
C(13)-C(12)-H(12)	119.9
C(12)-C(13)-C(14)	120.10(19)
C(12)-C(13)-H(13)	119.9
C(14)-C(13)-H(13)	119.9
C(13)-C(14)-C(9)	120.4(2)
C(13)-C(14)-H(14)	119.8
C(9)-C(14)-H(14)	119.8
O(4)-C(15)-O(3)	105.32(14)
O(4)-C(15)-C(17)	107.98(15)
O(3)-C(15)-C(17)	108.80(15)
O(4)-C(15)-C(16)	111.78(15)
O(3)-C(15)-C(16)	110.00(15)
C(17)-C(15)-C(16)	112.66(16)
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(15)-C(17)-H(17A)	109.5
C(15)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(15)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
O(6)-C(18)-O(5)	103.62(14)
O(6)-C(18)-C(19)	109.15(15)

O(5)-C(18)-C(19)	109.23(15)
O(6)-C(18)-C(20)	110.77(15)
O(5)-C(18)-C(20)	110.85(15)
C(19)-C(18)-C(20)	112.81(15)
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(18)-C(20)-H(20A)	109.5
C(18)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(1)-O(1)-C(4)	107.32(14)
C(7)-O(2)-C(1)	111.94(14)
C(2)-O(3)-C(15)	109.63(13)
C(3)-O(4)-C(15)	109.58(13)
C(5)-O(5)-C(18)	106.67(13)
C(18)-O(6)-C(6)	105.10(14)

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 06mz136m. The anisotropic displacement factor exponent takes the form: $-2\pi 2$ [(h a*)^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	15(1)	15(1)	14(1)	0(1)	1(1)	-1(1)
C(2)	15(1)	13(1)	13(1)	0(1)	-1(1)	0(1)
C(3)	15(1)	14(1)	13(1)	-1(1)	1(1)	-1(1)
C(4)	13(1)	13(1)	13(1)	-2(1)	0(1)	-2(1)
C(5)	14(1)	16(1)	12(1)	0(1)	1(1)	0(1)
C(6)	15(1)	16(1)	14(1)	-1(1)	-2(1)	1(1)
C(7)	19(1)	17(1)	12(1)	-5(1)	3(1)	-1(1)
C(8)	18(1)	14(1)	11(1)	-1(1)	0(1)	-1(1)
C(9)	19(1)	18(1)	12(1)	2(1)	2(1)	0(1)
C(10)	24(1)	21(1)	14(1)	3(1)	-2(1)	-1(1)
C(11)	22(1)	37(1)	18(1)	9(1)	-3(1)	0(1)
C(12)	27(1)	36(1)	21(1)	11(1)	7(1)	13(1)
C(13)	35(1)	21(1)	19(1)	4(1)	11(1)	6(1)
C(14)	26(1)	19(1)	15(1)	1(1)	5(1)	0(1)
C(15)	15(1)	16(1)	13(1)	-2(1)	1(1)	-2(1)
C(16)	17(1)	22(1)	19(1)	-2(1)	-3(1)	0(1)
C(17)	22(1)	17(1)	21(1)	5(1)	2(1)	0(1)
C(18)	14(1)	17(1)	14(1)	-1(1)	-1(1)	-2(1)
C(19)	20(1)	20(1)	17(1)	-3(1)	0(1)	2(1)
C(20)	23(1)	21(1)	14(1)	2(1)	3(1)	-2(1)
O(1)	16(1)	19(1)	12(1)	-2(1)	-1(1)	2(1)
O(2)	16(1)	19(1)	17(1)	1(1)	2(1)	-3(1)
O(3)	19(1)	16(1)	16(1)	-3(1)	3(1)	-5(1)
O(4)	20(1)	20(1)	13(1)	-2(1)	1(1)	-9(1)
O(5)	14(1)	24(1)	12(1)	-5(1)	-1(1)	1(1)
O(6)	14(1)	17(1)	15(1)	-2(1)	1(1)	-2(1)
O(7)	25(1)	19(1)	19(1)	1(1)	4(1)	-4(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for 06mz136m.

	x	y	z	U(eq)
H(1)	5294	4949	6711	17
H(3)	2040	7532	7325	16
H(4)	4440	7935	7697	16
H(5)	3795	5712	8589	17
H(6A)	5827	6428	9142	18
H(6B)	6247	7425	8546	18
H(8)	3245	6238	5763	17
H(10)	736	6382	5464	24
H(11)	-1480	7650	5338	31
H(12)	-1668	9871	5776	34
H(13)	358	10828	6334	30
H(14)	2539	9534	6492	24
H(16A)	-892	4923	7292	29
H(16B)	-440	4252	6614	29
H(16C)	-165	5867	6741	29
H(17A)	2539	3019	7619	30
H(17B)	1222	2508	7152	30
H(17C)	829	3113	7850	30
H(19A)	3158	9912	9881	29
H(19B)	1615	9321	9598	29
H(19C)	2778	10090	9132	29
H(20A)	3770	6208	9797	29
H(20B)	2198	6893	9989	29
H(20C)	3719	7451	10306	29

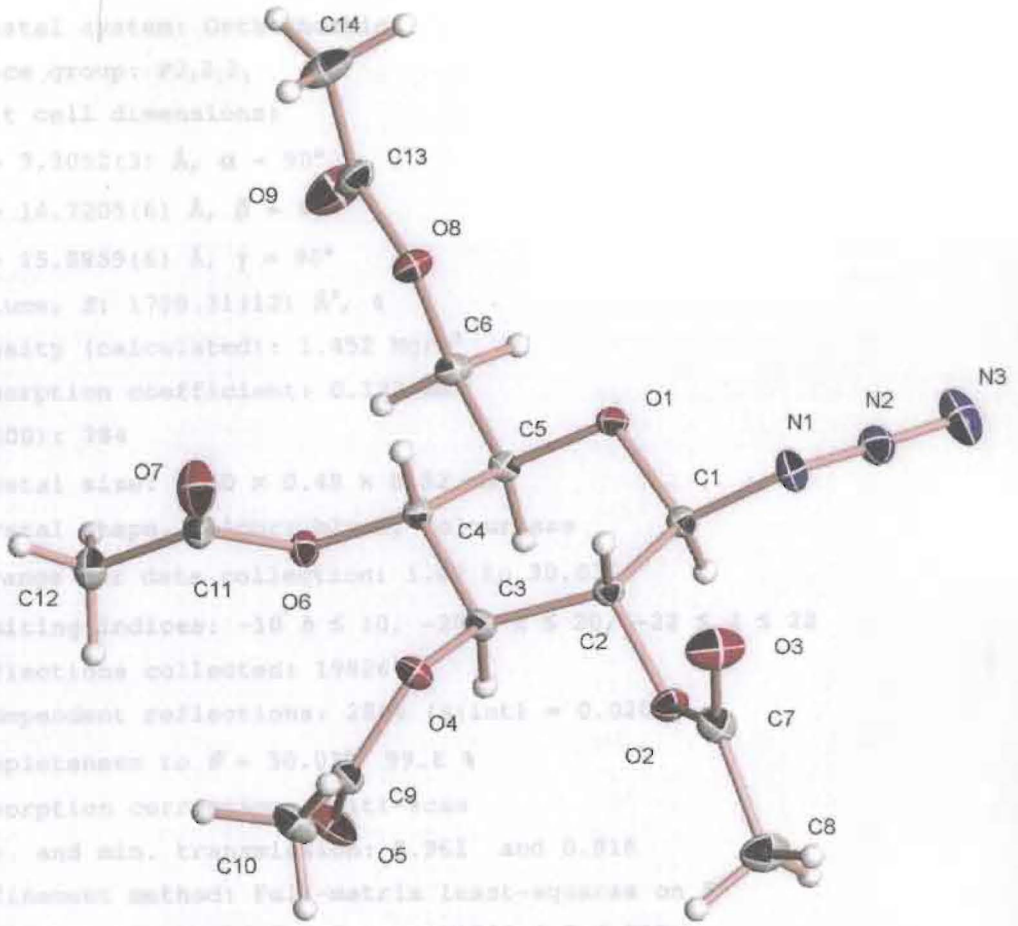


Figure 106: X-Ray crystal structure of 2,3,4,6-tetra-*O*-acetyl-1-azido-1-deoxy-β-D-glucopyranose (**32**).

Table 1. Crystal data and structure refinement for 06mz033m:

Identification code: 06mz033m

Empirical formula: C14 H19 N3 O9

Formula weight: 373.32

Temperature: 100(2) K

Wavelength: 0.71073 Å

Crystal system: Orthorhombic

Space group: $P2_12_12_1$

Unit cell dimensions:

a = 7.3052(3) Å, α = 90°

b = 14.7205(6) Å, β = 90°

c = 15.8859(6) Å, γ = 90°

Volume, *Z*: 1708.31(12) $Å^3$, 4

Density (calculated): 1.452 Mg/m^3

Absorption coefficient: 0.123 mm^{-1}

F(000): 784

Crystal size: 0.50 × 0.48 × 0.32 mm

Crystal shape, colour: block, colourless

θ range for data collection: 1.89 to 30.03°

Limiting indices: $-10 \le h \le 10$, $-20 \le k \le 20$, $-22 \le l \le 22$

Reflections collected: 19826

Independent reflections: 2844 (*R*(int) = 0.0200)

Completeness to θ = 30.03°: 99.8 %

Absorption correction: multi-scan

Max. and min. transmission: 0.961 and 0.916

Refinement method: Full-matrix least-squares on F^2

Data / restraints / parameters: 2844 / 0 / 299

Goodness-of-fit on F^2: 1.075

Final *R* indices [$I>2\sigma(I)$]: R1 = 0.0296, wR2 = 0.0767

R indices (all data): R1 = 0.0299, wR2 = 0.0769

Largest diff. peak and hole: 0.318 and -0.200 e × $Å^{-3}$

Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit are based on F^2, conventional R-factors R are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors

Treatment of hydrogen atoms:

All hydrogen atoms were located in the difference density Fourier map. Methyl hydrogen atoms were isotropically refined with a displacement parameter of 1.5 times that of the adjacent carbon or oxygen atom. All others were freely isotropically refined.

Table 2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for 06mz033m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	-1964(2)	492(1)	6468(1)	13(1)
C(2)	-214(2)	982(1)	6737(1)	12(1)
C(3)	941(2)	1242(1)	5973(1)	13(1)
C(4)	1200(2)	428(1)	5391(1)	12(1)
C(5)	-730(2)	109(1)	5158(1)	12(1)
C(6)	-846(2)	-588(1)	4469(1)	14(1)
C(7)	-301(2)	1937(1)	7969(1)	18(1)
C(8)	-784(2)	2884(1)	8235(1)	24(1)
C(9)	3340(2)	2346(1)	5961(1)	16(1)
C(10)	5002(2)	2661(1)	6425(1)	21(1)
C(11)	3932(2)	550(1)	4567(1)	16(1)
C(12)	4610(2)	855(1)	3727(1)	20(1)
C(13)	340(2)	-2005(1)	4071(1)	19(1)
C(14)	1317(2)	-2838(1)	4365(1)	29(1)
N(1)	-2797(1)	103(1)	7223(1)	17(1)
N(2)	-4457(2)	-68(1)	7146(1)	18(1)
N(3)	-5943(2)	-262(1)	7175(1)	30(1)
O(1)	-1524(1)	-238(1)	5917(1)	13(1)
O(2)	-723(1)	1821(1)	7139(1)	15(1)
O(3)	388(2)	1361(1)	8399(1)	29(1)
O(4)	2652(1)	1575(1)	6303(1)	15(1)
O(5)	2674(1)	2720(1)	5357(1)	24(1)
O(6)	2098(1)	706(1)	4629(1)	14(1)
O(7)	4828(1)	223(1)	5123(1)	26(1)
O(8)	234(1)	-1373(1)	4689(1)	16(1)
O(9)	-337(2)	-1895(1)	3390(1)	32(1)

All esds (except the esd in the dihedral angle between two l.s. planes)are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 3. Bond lengths [Å] and angles [deg] for 06mz033m.

C(1)-O(1)	1.4220(13)
C(1)-N(1)	1.4617(14)
C(1)-C(2)	1.5297(16)
C(1)-H(1)	0.932(18)
C(2)-O(2)	1.4384(13)
C(2)-C(3)	1.5262(15)
C(2)-H(2)	0.924(16)
C(3)-O(4)	1.4415(14)
C(3)-C(4)	1.5253(15)
C(3)-H(3)	0.961(18)
C(4)-O(6)	1.4358(13)
C(4)-C(5)	1.5319(15)
C(4)-H(4)	0.919(18)
C(5)-O(1)	1.4328(13)
C(5)-C(6)	1.5029(15)
C(5)-H(5)	1.002(17)
C(6)-O(8)	1.4416(14)
C(6)-H(6A)	0.987(19)
C(6)-H(6B)	0.97(2)
C(7)-O(3)	1.2000(17)
C(7)-O(2)	1.3644(14)
C(7)-C(8)	1.4978(18)
C(8)-H(8A)	0.95(2)
C(8)-H(8B)	0.97(2)
C(8)-H(8C)	0.97(2)
C(9)-O(5)	1.2089(15)
C(9)-O(4)	1.3548(14)
C(9)-C(10)	1.4936(17)
C(10)-H(10A)	1.01(2)
C(10)-H(10B)	0.92(2)
C(10)-H(10C)	0.93(2)
C(11)-O(7)	1.2005(16)
C(11)-O(6)	1.3626(14)
C(11)-C(12)	1.4930(17)
C(12)-H(12A)	0.94(2)
C(12)-H(12B)	0.96(2)
C(12)-H(12C)	0.92(2)
C(13)-O(9)	1.2007(17)
C(13)-O(8)	1.3539(14)
C(13)-C(14)	1.4938(19)
C(14)-H(14A)	0.99(3)
C(14)-H(14B)	0.95(3)
C(14)-H(14C)	0.89(3)
N(1)-N(2)	1.2447(15)
N(2)-N(3)	1.1228(18)
O(1)-C(1)-N(1)	107.64(9)
O(1)-C(1)-C(2)	109.82(9)
N(1)-C(1)-C(2)	107.67(9)
O(1)-C(1)-H(1)	109.5(11)
N(1)-C(1)-H(1)	110.1(11)
C(2)-C(1)-H(1)	112.0(11)
O(2)-C(2)-C(3)	106.33(8)

O(2)-C(2)-C(1)	108.22(9)
C(3)-C(2)-C(1)	110.98(9)
O(2)-C(2)-H(2)	110.3(10)
C(3)-C(2)-H(2)	111.1(10)
C(1)-C(2)-H(2)	109.8(10)
O(4)-C(3)-C(4)	112.34(9)
O(4)-C(3)-C(2)	105.95(8)
C(4)-C(3)-C(2)	110.71(9)
O(4)-C(3)-H(3)	109.3(12)
C(4)-C(3)-H(3)	107.2(11)
C(2)-C(3)-H(3)	111.4(11)
O(6)-C(4)-C(3)	110.12(9)
O(6)-C(4)-C(5)	107.69(8)
C(3)-C(4)-C(5)	105.83(9)
O(6)-C(4)-H(4)	108.5(11)
C(3)-C(4)-H(4)	113.2(11)
C(5)-C(4)-H(4)	111.3(11)
O(1)-C(5)-C(6)	110.29(9)
O(1)-C(5)-C(4)	106.12(8)
C(6)-C(5)-C(4)	115.90(10)
O(1)-C(5)-H(5)	111.2(10)
C(6)-C(5)-H(5)	108.0(9)
C(4)-C(5)-H(5)	105.2(10)
O(8)-C(6)-C(5)	109.92(9)
O(8)-C(6)-H(6A)	111.0(11)
C(5)-C(6)-H(6A)	108.5(11)
O(8)-C(6)-H(6B)	108.3(12)
C(5)-C(6)-H(6B)	107.6(12)
H(6A)-C(6)-H(6B)	111.5(16)
O(3)-C(7)-O(2)	123.76(12)
O(3)-C(7)-C(8)	126.53(12)
O(2)-C(7)-C(8)	109.69(11)
C(7)-C(8)-H(8A)	106.6(14)
C(7)-C(8)-H(8B)	110.9(14)
H(8A)-C(8)-H(8B)	115(2)
C(7)-C(8)-H(8C)	108.9(13)
H(8A)-C(8)-H(8C)	107(2)
H(8B)-C(8)-H(8C)	108.2(18)
O(5)-C(9)-O(4)	123.44(11)
O(5)-C(9)-C(10)	125.23(11)
O(4)-C(9)-C(10)	111.33(10)
C(9)-C(10)-H(10A)	104.1(12)
C(9)-C(10)-H(10B)	112.6(14)
H(10A)-C(10)-H(10B)	114.2(18)
C(9)-C(10)-H(10C)	108.2(13)
H(10A)-C(10)-H(10C)	104.1(17)
H(10B)-C(10)-H(10C)	112.9(18)
O(7)-C(11)-O(6)	123.37(11)
O(7)-C(11)-C(12)	126.72(12)
O(6)-C(11)-C(12)	109.90(10)
C(11)-C(12)-H(12A)	108.8(12)
C(11)-C(12)-H(12B)	113.3(12)
H(12A)-C(12)-H(12B)	106.0(18)
C(11)-C(12)-H(12C)	108.1(13)
H(12A)-C(12)-H(12C)	111.2(19)
H(12B)-C(12)-H(12C)	109.5(18)
O(9)-C(13)-O(8)	122.41(12)

O(9)-C(13)-C(14)	126.10(13)
O(8)-C(13)-C(14)	111.45(11)
C(13)-C(14)-H(14A)	109.4(15)
C(13)-C(14)-H(14B)	110.6(15)
H(14A)-C(14)-H(14B)	107.5(19)
C(13)-C(14)-H(14C)	109.6(16)
H(14A)-C(14)-H(14C)	111(2)
H(14B)-C(14)-H(14C)	109(2)
N(2)-N(1)-C(1)	113.81(10)
N(3)-N(2)-N(1)	171.44(14)
C(1)-O(1)-C(5)	109.87(8)
C(7)-O(2)-C(2)	118.61(9)
C(9)-O(4)-C(3)	117.41(9)
C(11)-O(6)-C(4)	117.56(9)
C(13)-O(8)-C(6)	114.01(9)

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 06mz033m. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [(h a^*)^2 U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
C(1)	14(1)	13(1)	13(1)	0(1)	1(1)	0(1)
C(2)	14(1)	11(1)	12(1)	-1(1)	0(1)	0(1)
C(3)	13(1)	13(1)	12(1)	0(1)	0(1)	-2(1)
C(4)	12(1)	13(1)	11(1)	0(1)	0(1)	0(1)
C(5)	12(1)	12(1)	12(1)	1(1)	-1(1)	-1(1)
C(6)	17(1)	13(1)	12(1)	-1(1)	-2(1)	1(1)
C(7)	24(1)	18(1)	14(1)	-2(1)	0(1)	-4(1)
C(8)	37(1)	19(1)	16(1)	-5(1)	-1(1)	0(1)
C(9)	17(1)	15(1)	15(1)	0(1)	2(1)	-3(1)
C(10)	21(1)	21(1)	21(1)	3(1)	-4(1)	-9(1)
C(11)	14(1)	18(1)	17(1)	-1(1)	2(1)	-1(1)
C(12)	18(1)	23(1)	17(1)	0(1)	4(1)	0(1)
C(13)	19(1)	19(1)	20(1)	-6(1)	1(1)	2(1)
C(14)	32(1)	21(1)	36(1)	-7(1)	-2(1)	11(1)
N(1)	15(1)	23(1)	14(1)	2(1)	1(1)	-4(1)
N(2)	19(1)	20(1)	16(1)	3(1)	1(1)	-1(1)
N(3)	20(1)	40(1)	31(1)	14(1)	1(1)	-6(1)
O(1)	16(1)	11(1)	13(1)	-1(1)	1(1)	-1(1)
O(2)	20(1)	14(1)	12(1)	-3(1)	-1(1)	1(1)
O(3)	48(1)	22(1)	17(1)	0(1)	-8(1)	3(1)
O(4)	15(1)	14(1)	15(1)	2(1)	-2(1)	-4(1)
O(5)	26(1)	23(1)	24(1)	10(1)	-6(1)	-8(1)
O(6)	13(1)	17(1)	12(1)	2(1)	1(1)	1(1)
O(7)	16(1)	41(1)	21(1)	7(1)	-2(1)	4(1)
O(8)	20(1)	14(1)	14(1)	-2(1)	-2(1)	4(1)
O(9)	41(1)	33(1)	22(1)	-13(1)	-10(1)	11(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for 06mz033m.

	x	y	z	U(eq)
H(1)	-2790(20)	882(12)	6202(11)	17(4)
H(2)	440(20)	621(11)	7104(9)	10(3)
H(3)	360(30)	1713(12)	5648(11)	21(4)
H(4)	1870(20)	-33(12)	5631(11)	16(4)
H(5)	-1390(20)	669(12)	4962(10)	14(4)
H(6A)	-2140(30)	-754(13)	4388(11)	20(4)
H(6B)	-330(30)	-319(13)	3962(12)	25(4)
H(8A)	-730(30)	2894(15)	8832(14)	36
H(8B)	-1960(30)	3068(16)	7998(13)	36
H(8C)	150(30)	3296(16)	8030(13)	36
H(10A)	6030(30)	2578(14)	6006(13)	32
H(10B)	5170(30)	2357(15)	6925(13)	32
H(10C)	4920(30)	3287(15)	6493(13)	32
H(12A)	4500(30)	1489(14)	3694(12)	29
H(12B)	3910(30)	618(14)	3266(12)	29
H(12C)	5810(30)	675(15)	3674(13)	29
H(14A)	550(40)	-3161(17)	4782(15)	44
H(14B)	2440(30)	-2681(16)	4637(14)	44
H(14C)	1560(30)	-3193(17)	3928(15)	44

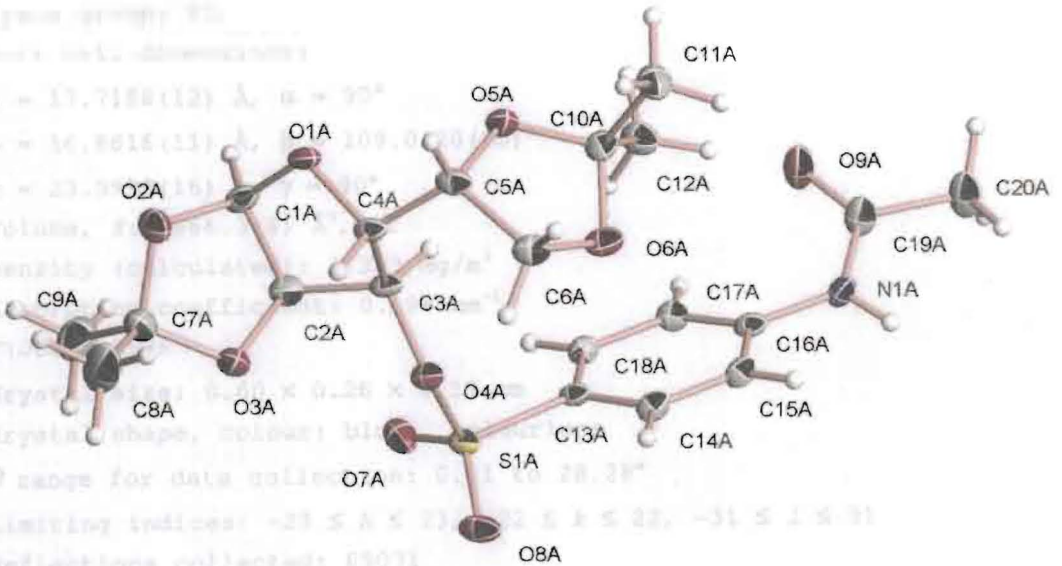


Figure 107: X-Ray crystal structure of 3-*O*-(*p*-acetamido)benzenesulfonate ester of 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**37**).

Table 1. Crystal data and structure refinement for 06mz009m:

Identification code: 06mz009m
Empirical formula: C20.333 H28.333 N O9.333 S
Moiety formula: C20 H27 N O9 S, 1/3(C H4 O)
Formula weight: 468.17
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Monoclinic
Space group: $P2_1$
Unit cell dimensions:
a = 17.7188(12) Å, α = 90°
b = 16.8616(11) Å, β = 109.0120(10)°
c = 23.5999(16) Å, γ = 90°
Volume, *Z*: 6666.3(8) $Å^3$, 12
Density (calculated): 1.399 Mg/m^3
Absorption coefficient: 0.199 mm^{-1}
F(000): 2976
Crystal size: 0.60 × 0.26 × 0.19 mm
Crystal shape, colour: block, colourless
θ range for data collection: 0.91 to 28.28°
Limiting indices: $-23 \leq h \leq 23$, $-22 \leq k \leq 22$, $-31 \leq l \leq 31$
Reflections collected: 69071
Independent reflections: 32664 (*R*(int) = 0.0284)
Completeness to θ = 28.28°: 99.9 %
Absorption correction: multi-scan
Max. and min. transmission: 0.963 and 0.814
Refinement method: Full-matrix least-squares on F^2
Data / restraints / parameters: 32664 / 1 / 1745
Goodness-of-fit on F^2: 1.044
Final *R* indices [$I>2\sigma(I)$]: R1 = 0.0602, wR2 = 0.1512
R indices (all data): R1 = 0.0657, wR2 = 0.1547
Largest diff. peak and hole: 1.774 and -0.670 e × $Å^{-3}$

Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit are based on F^2, conventional R-factors R are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors

Treatment of hydrogen atoms:

All hydrogen atoms were placed in calculated positions. All hydrogen atoms were isotropically refined with a displacement parameter 1.5 (methyl, methanol) or 1.2 times (all others) that of the adjacent carbon, oxygen or nitrogen atoms.

Table 2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for 06mz009m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(22)	9096(2)	6349(1)	7953(1)	30(1)
C(22)	8444(2)	6271(2)	7410(2)	29(1)
O(21)	3932(2)	5053(2)	3077(1)	32(1)
C(21)	3352(2)	4875(2)	2514(2)	32(1)
C(1A)	5583(2)	4008(2)	-939(2)	22(1)
C(2A)	6184(2)	3470(2)	-1092(1)	22(1)
C(3A)	6605(2)	3066(2)	-496(1)	19(1)
C(4A)	5946(2)	3035(2)	-205(1)	18(1)
C(5A)	6181(2)	2927(2)	464(1)	21(1)
C(5E)	6177(2)	6324(2)	10221(1)	20(1)
C(6A)	6593(2)	2130(2)	693(2)	24(1)
C(7A)	4957(2)	3301(2)	-1803(2)	29(1)
C(8A)	4299(3)	2689(3)	-1953(2)	54(1)
C(9A)	5012(3)	3766(3)	-2337(2)	49(1)
C(10A)	7422(2)	3114(2)	1181(1)	22(1)
C(11A)	7319(2)	3072(2)	1798(2)	29(1)
C(12A)	8178(2)	3534(2)	1196(2)	27(1)
C(13A)	8463(2)	2346(2)	-115(1)	16(1)
C(14A)	8682(2)	1802(2)	355(1)	20(1)
C(15A)	9342(2)	1943(2)	845(1)	20(1)
C(16A)	9796(2)	2640(2)	872(1)	18(1)
C(17A)	9587(2)	3164(2)	396(1)	19(1)
C(18A)	8913(2)	3025(2)	-101(1)	18(1)
C(19A)	10776(2)	3456(2)	1618(2)	25(1)
C(20A)	11496(2)	3411(2)	2179(2)	31(1)
O(1A)	5586(1)	3807(1)	-358(1)	22(1)
O(2A)	4836(1)	3841(2)	-1373(1)	26(1)
O(3A)	5692(1)	2910(1)	-1499(1)	26(1)
O(4A)	6877(1)	2268(1)	-545(1)	19(1)
O(5A)	6762(1)	3512(1)	763(1)	23(1)
O(6D)	7632(1)	9312(2)	4174(1)	28(1)
O(6A)	7415(1)	2340(1)	939(1)	25(1)
O(7A)	7622(1)	2703(2)	-1208(1)	27(1)
O(8D)	7548(2)	8359(2)	6104(1)	35(1)
O(8C)	7329(1)	5049(2)	5848(1)	29(1)
O(8A)	7624(1)	1329(1)	-872(1)	26(1)
O(9A)	10507(2)	4101(1)	1398(1)	34(1)
N(1A)	10465(2)	2749(2)	1388(1)	20(1)
S(1A)	7641(1)	2148(1)	-752(1)	18(1)

C(1B)	9487(2)	4496(2)	6024(1)	26(1)
C(2B)	8919(2)	4011(2)	6258(1)	25(1)
C(3B)	8442(2)	3528(2)	5709(1)	24(1)
C(4B)	9025(2)	3456(2)	5358(2)	26(1)
C(5B)	8696(2)	3297(2)	4693(2)	28(1)
C(6B)	8319(2)	2465(2)	4522(2)	34(1)
C(7B)	10196(2)	3847(2)	6906(2)	33(1)
C(8B)	10254(3)	4396(3)	7424(2)	49(1)
C(9B)	10813(3)	3201(3)	7044(2)	55(1)
C(10B)	7521(2)	3408(2)	3928(2)	29(1)
C(11B)	7789(2)	3432(3)	3381(2)	47(1)
C(12B)	6697(2)	3760(3)	3801(2)	36(1)
C(13B)	6681(2)	2650(2)	5450(1)	24(1)
C(14B)	6530(2)	1952(2)	5112(2)	29(1)
C(15B)	5874(2)	1922(2)	4597(2)	24(1)
C(16B)	5367(2)	2569(2)	4426(1)	21(1)
C(17B)	5525(2)	3274(2)	4763(1)	23(1)
C(18B)	6190(2)	3317(2)	5277(1)	23(1)
C(19B)	4193(2)	3020(2)	3586(2)	25(1)
C(20B)	3512(2)	2712(2)	3065(2)	30(1)
O(1B)	9386(1)	4233(2)	5437(1)	29(1)
O(2B)	10263(1)	4289(2)	6414(1)	30(1)
O(3B)	9424(1)	3485(2)	6687(1)	33(1)
O(4B)	8245(1)	2743(2)	5868(1)	25(1)
O(5B)	8056(2)	3829(2)	4413(1)	32(1)
O(6B)	7532(2)	2618(2)	4141(1)	41(1)
O(7B)	7468(1)	3354(2)	6455(1)	30(1)
O(8B)	7603(2)	1900(2)	6369(1)	38(1)
O(9B)	4278(2)	3726(2)	3710(1)	40(1)
N(1B)	4690(2)	2460(2)	3913(1)	21(1)
S(1B)	7505(1)	2675(1)	6108(1)	25(1)
C(1C)	9442(2)	7692(2)	5816(2)	28(1)
C(2C)	8884(2)	7134(2)	6020(1)	23(1)
C(3C)	8399(2)	6743(2)	5430(1)	22(1)
C(4C)	9020(2)	6682(2)	5104(1)	24(1)
C(5C)	8719(2)	6588(2)	4431(1)	27(1)
C(6C)	8300(2)	5783(2)	4220(2)	29(1)
C(7C)	10155(2)	6985(2)	6664(2)	29(1)
C(8C)	10828(2)	6400(3)	6760(2)	40(1)
C(9C)	10156(2)	7403(3)	7235(2)	40(1)
C(10C)	7502(2)	6782(2)	3714(1)	26(1)
C(11C)	7669(2)	6770(3)	3120(2)	37(1)
C(12C)	6734(2)	7208(3)	3667(2)	32(1)
C(13C)	6509(2)	6090(2)	5062(1)	21(1)
C(14C)	6097(2)	6800(2)	5028(1)	21(1)
C(15C)	5421(2)	6941(2)	4537(1)	20(1)
C(16C)	5169(2)	6372(2)	4081(1)	21(1)
C(17C)	5580(2)	5655(2)	4130(1)	22(1)
C(18C)	6257(2)	5513(2)	4619(1)	24(1)
C(19C)	4195(2)	7195(2)	3312(1)	23(1)
C(20C)	3508(2)	7135(2)	2735(2)	28(1)
O(1C)	9406(1)	7437(2)	5239(1)	29(1)
O(2C)	10204(1)	7557(2)	6235(1)	31(1)
O(3C)	9417(1)	6573(2)	6392(1)	25(1)
O(4C)	8106(1)	5957(1)	5499(1)	22(1)

O(5C)	8131(1)	7173(2)	4166(1)	30(1)
O(6C)	7482(1)	6008(2)	3934(1)	30(1)
O(7C)	7367(1)	6478(2)	6141(1)	26(1)
N(1C)	4494(2)	6494(2)	3569(1)	24(1)
S(1C)	7335(1)	5886(1)	5702(1)	21(1)
C(1D)	9501(2)	11055(2)	6037(2)	32(1)
C(2D)	8894(2)	10542(2)	6208(2)	27(1)
C(3D)	8463(2)	10110(2)	5621(1)	23(1)
C(4D)	9104(2)	10069(2)	5318(1)	25(1)
C(5D)	8849(2)	9956(2)	4645(1)	25(1)
C(6D)	8464(2)	9137(2)	4429(2)	28(1)
C(7D)	10129(2)	10350(3)	6905(2)	39(1)
C(8D)	10747(3)	9705(4)	7064(2)	59(1)
C(9D)	10123(3)	10871(4)	7430(2)	63(2)
C(10D)	7597(2)	10088(2)	3931(1)	25(1)
C(11D)	7700(2)	10060(2)	3317(1)	28(1)
C(12D)	6825(2)	10493(3)	3915(2)	33(1)
C(13D)	6650(2)	9320(2)	5309(2)	23(1)
C(14D)	6098(2)	9916(2)	5291(1)	23(1)
C(15D)	5420(2)	9981(2)	4790(1)	22(1)
C(16D)	5299(2)	9459(2)	4311(1)	22(1)
C(17D)	5859(2)	8866(2)	4339(2)	25(1)
C(18D)	6532(2)	8806(2)	4838(2)	25(1)
C(19D)	4252(2)	10153(2)	3519(2)	24(1)
C(20D)	3523(2)	10024(2)	2977(2)	31(1)
O(1D)	9456(1)	10847(2)	5448(1)	29(1)
O(2D)	10251(1)	10833(2)	6453(1)	33(1)
O(3D)	9367(1)	9989(2)	6630(1)	37(1)
O(4D)	8224(1)	9308(2)	5706(1)	24(1)
O(5D)	8244(1)	10510(2)	4348(1)	28(1)
O(7D)	7501(1)	9776(2)	6377(1)	32(1)
O(9D)	4494(2)	10814(1)	3691(1)	33(1)
O(10D)	4472(1)	7834(2)	3521(1)	30(1)
N(1D)	4610(2)	9482(2)	3799(1)	22(1)
S(1D)	7489(1)	9189(1)	5948(1)	25(1)
C(1E)	5481(2)	7427(2)	8823(2)	23(1)
C(2E)	6053(2)	6881(2)	8635(1)	22(1)
C(3E)	6518(2)	6480(2)	9227(1)	20(1)
C(4E)	5898(2)	6449(2)	9553(1)	19(1)
C(6E)	6509(2)	5494(2)	10434(2)	23(1)
C(7E)	4775(2)	6661(2)	8000(1)	25(1)
C(8E)	4153(2)	6029(2)	7945(2)	37(1)
C(9E)	4705(3)	7063(3)	7410(2)	44(1)
C(10E)	7383(2)	6427(2)	10976(1)	19(1)
C(11E)	7175(2)	6469(3)	11547(2)	40(1)
C(12E)	8202(2)	6743(2)	11054(2)	26(1)
C(13E)	8348(2)	5674(2)	9585(1)	18(1)
C(14E)	8887(2)	6291(2)	9644(1)	18(1)
C(15E)	9561(2)	6336(2)	10151(1)	18(1)
C(16E)	9688(2)	5751(2)	10594(1)	16(1)
C(17E)	9132(2)	5141(2)	10528(2)	21(1)
C(18E)	8470(2)	5095(2)	10026(2)	22(1)
C(19E)	10780(2)	6362(2)	11417(1)	20(1)
C(20E)	11499(2)	6156(2)	11944(2)	26(1)
O(1E)	5547(1)	7226(1)	9418(1)	23(1)

O(2E)	4716(1)	7247(2)	8422(1)	28(1)
O(3E)	5543(1)	6308(1)	8256(1)	25(1)
O(4E)	6775(1)	5682(1)	9155(1)	20(1)
O(5E)	6829(1)	6852(1)	10505(1)	26(1)
O(6E)	7330(1)	5634(1)	10761(1)	25(1)
O(7E)	7535(1)	6177(2)	8518(1)	25(1)
O(8E)	7461(1)	4758(1)	8753(1)	29(1)
O(9E)	10580(1)	7046(1)	11273(1)	29(1)
N(1E)	10374(1)	5728(2)	11107(1)	18(1)
S(1E)	7525(1)	5567(1)	8931(1)	19(1)
C(1F)	5479(2)	10771(2)	-967(1)	21(1)
C(2F)	6050(2)	10247(2)	-1164(1)	19(1)
C(3F)	6512(2)	9815(2)	-587(1)	18(1)
C(4F)	5880(2)	9757(2)	-274(2)	21(1)
C(5F)	6150(2)	9604(2)	391(2)	25(1)
C(6F)	6514(2)	8775(2)	570(2)	30(1)
C(7F)	4773(2)	10057(2)	-1813(2)	23(1)
C(8F)	4131(2)	9440(2)	-1888(2)	38(1)
C(9F)	4724(2)	10487(3)	-2391(2)	39(1)
C(10F)	7392(2)	9690(2)	1113(2)	28(1)
C(11F)	7250(2)	9650(3)	1715(2)	38(1)
C(12F)	8181(2)	10070(3)	1156(2)	36(1)
C(13F)	8350(2)	8950(2)	-258(1)	20(1)
C(14F)	8869(2)	9589(2)	-124(1)	19(1)
C(15F)	9559(2)	9550(2)	371(1)	20(1)
C(16F)	9721(2)	8863(2)	724(1)	19(1)
C(17F)	9186(2)	8232(2)	587(2)	24(1)
C(18F)	8499(2)	8274(2)	95(2)	24(1)
C(19F)	10912(2)	9309(2)	1549(1)	23(1)
C(20F)	11589(2)	8982(2)	2066(2)	30(1)
O(1F)	5529(1)	10538(1)	-381(1)	23(1)
O(2F)	4720(1)	10630(2)	-1380(1)	26(1)
O(3F)	5530(1)	9688(1)	-1559(1)	22(1)
O(4F)	6768(1)	9029(1)	-686(1)	22(1)
O(5F)	6774(1)	10142(1)	697(1)	28(1)
O(6F)	7345(2)	8927(2)	850(1)	31(1)
O(7F)	7572(1)	9598(1)	-1265(1)	25(1)
O(8F)	7430(1)	8156(1)	-1157(1)	27(1)
O(9F)	10794(2)	10013(2)	1436(1)	33(1)
N(1F)	10420(2)	8745(2)	1211(1)	20(1)
S(1F)	7523(1)	8936(1)	-909(1)	20(1)

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 3. Bond lengths [Å] and angles [deg] for 06mz009m.

O(22)-C(22)	1.425(4)
O(22)-H(22)	0.8400
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
O(21)-C(21)	1.421(4)
O(21)-H(21)	0.8400
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(1A)-O(1A)	1.410(4)
C(1A)-O(2A)	1.414(4)
C(1A)-C(2A)	1.529(4)
C(1A)-H(1A)	1.0000
C(2A)-O(3A)	1.426(4)
C(2A)-C(3A)	1.521(4)
C(2A)-H(2A)	1.0000
C(3A)-O(4A)	1.448(3)
C(3A)-C(4A)	1.536(4)
C(3A)-H(3A)	1.0000
C(4A)-O(1A)	1.443(4)
C(4A)-C(5A)	1.508(4)
C(4A)-H(4A)	1.0000
C(5A)-O(5A)	1.434(4)
C(5A)-C(6A)	1.541(4)
C(5A)-H(5A)	1.0000
C(5E)-O(5E)	1.439(4)
C(5E)-C(4E)	1.506(4)
C(5E)-C(6E)	1.537(4)
C(5E)-H(5E)	1.0000
C(6A)-O(6A)	1.425(4)
C(6A)-H(6A1)	0.9900
C(6A)-H(6A2)	0.9900
C(7A)-O(3A)	1.427(4)
C(7A)-O(2A)	1.430(4)
C(7A)-C(8A)	1.510(5)
C(7A)-C(9A)	1.513(5)
C(8A)-H(8A1)	0.9800
C(8A)-H(8A2)	0.9800
C(8A)-H(8A3)	0.9800
C(9A)-H(9A1)	0.9800
C(9A)-H(9A2)	0.9800
C(9A)-H(9A3)	0.9800
C(10A)-O(6A)	1.423(4)
C(10A)-O(5A)	1.429(4)

C(10A)-C(12A)	1.506(4)
C(10A)-C(11A)	1.526(4)
C(11A)-H(11A)	0.9800
C(11A)-H(11B)	0.9800
C(11A)-H(11C)	0.9800
C(12A)-H(12A)	0.9800
C(12A)-H(12B)	0.9800
C(12A)-H(12C)	0.9800
C(13A)-C(18A)	1.389(4)
C(13A)-C(14A)	1.394(4)
C(13A)-S(1A)	1.751(3)
C(14A)-C(15A)	1.371(4)
C(14A)-H(14A)	0.9500
C(15A)-C(16A)	1.414(4)
C(15A)-H(15A)	0.9500
C(16A)-C(17A)	1.380(4)
C(16A)-N(1A)	1.408(4)
C(17A)-C(18A)	1.394(4)
C(17A)-H(17A)	0.9500
C(18A)-H(18A)	0.9500
C(19A)-O(9A)	1.232(4)
C(19A)-N(1A)	1.352(4)
C(19A)-C(20A)	1.511(4)
C(20A)-H(20A)	0.9800
C(20A)-H(20B)	0.9800
C(20A)-H(20C)	0.9800
O(4A)-S(1A)	1.595(2)
O(6D)-C(10D)	1.422(4)
O(6D)-C(6D)	1.430(4)
O(7A)-S(1A)	1.418(3)
O(8D)-S(1D)	1.443(3)
O(8C)-S(1C)	1.454(3)
O(8A)-S(1A)	1.407(2)
N(1A)-H(1A1)	0.8800
C(1B)-O(1B)	1.410(4)
C(1B)-O(2B)	1.427(4)
C(1B)-C(2B)	1.533(4)
C(1B)-H(1B)	1.0000
C(2B)-O(3B)	1.423(4)
C(2B)-C(3B)	1.531(4)
C(2B)-H(2B)	1.0000
C(3B)-O(4B)	1.447(4)
C(3B)-C(4B)	1.525(4)
C(3B)-H(3B)	1.0000
C(4B)-O(1B)	1.443(4)
C(4B)-C(5B)	1.511(4)
C(4B)-H(4B)	1.0000
C(5B)-O(5B)	1.427(4)
C(5B)-C(6B)	1.549(5)
C(5B)-H(5B)	1.0000
C(6B)-O(6B)	1.415(5)
C(6B)-H(6B1)	0.9900
C(6B)-H(6B2)	0.9900
C(7B)-O(2B)	1.417(5)
C(7B)-O(3B)	1.431(4)
C(7B)-C(9B)	1.502(6)
C(7B)-C(8B)	1.510(6)

C(8B)-H(8B1)	0.9800
C(8B)-H(8B2)	0.9800
C(8B)-H(8B3)	0.9800
C(9B)-H(9B1)	0.9800
C(9B)-H(9B2)	0.9800
C(9B)-H(9B3)	0.9800
C(10B)-O(5B)	1.415(4)
C(10B)-O(6B)	1.422(5)
C(10B)-C(12B)	1.513(5)
C(10B)-C(11B)	1.515(5)
C(11B)-H(11D)	0.9800
C(11B)-H(11E)	0.9800
C(11B)-H(11F)	0.9800
C(12B)-H(12D)	0.9800
C(12B)-H(12E)	0.9800
C(12B)-H(12F)	0.9800
C(13B)-C(18B)	1.399(5)
C(13B)-C(14B)	1.399(5)
C(13B)-S(1B)	1.752(3)
C(14B)-C(15B)	1.381(5)
C(14B)-H(14B)	0.9500
C(15B)-C(16B)	1.387(5)
C(15B)-H(15B)	0.9500
C(16B)-C(17B)	1.406(5)
C(16B)-N(1B)	1.410(4)
C(17B)-C(18B)	1.391(4)
C(17B)-H(17B)	0.9500
C(18B)-H(18B)	0.9500
C(19B)-O(9B)	1.223(4)
C(19B)-N(1B)	1.351(4)
C(19B)-C(20B)	1.506(5)
C(20B)-H(20D)	0.9800
C(20B)-H(20E)	0.9800
C(20B)-H(20F)	0.9800
O(4B)-S(1B)	1.593(2)
O(7B)-S(1B)	1.421(3)
O(8B)-S(1B)	1.430(3)
N(1B)-H(1B1)	0.8800
C(1C)-O(2C)	1.408(4)
C(1C)-O(1C)	1.410(4)
C(1C)-C(2C)	1.550(5)
C(1C)-H(1C)	1.0000
C(2C)-O(3C)	1.420(4)
C(2C)-C(3C)	1.527(4)
C(2C)-H(2C)	1.0000
C(3C)-O(4C)	1.453(4)
C(3C)-C(4C)	1.537(4)
C(3C)-H(3C)	1.0000
C(4C)-O(1C)	1.431(4)
C(4C)-C(5C)	1.510(4)
C(4C)-H(4C)	1.0000
C(5C)-O(5C)	1.422(4)
C(5C)-C(6C)	1.550(5)
C(5C)-H(5C)	1.0000
C(6C)-O(6C)	1.436(4)
C(6C)-H(6C1)	0.9900
C(6C)-H(6C2)	0.9900

C(7C)-O(2C)	1.421(5)
C(7C)-O(3C)	1.434(4)
C(7C)-C(8C)	1.508(5)
C(7C)-C(9C)	1.520(5)
C(8C)-H(8C1)	0.9800
C(8C)-H(8C2)	0.9800
C(8C)-H(8C3)	0.9800
C(9C)-H(9C1)	0.9800
C(9C)-H(9C2)	0.9800
C(9C)-H(9C3)	0.9800
C(10C)-O(6C)	1.410(4)
C(10C)-O(5C)	1.427(4)
C(10C)-C(12C)	1.511(5)
C(10C)-C(11C)	1.524(4)
C(11C)-H(11G)	0.9800
C(11C)-H(11H)	0.9800
C(11C)-H(11I)	0.9800
C(12C)-H(12G)	0.9800
C(12C)-H(12H)	0.9800
C(12C)-H(12I)	0.9800
C(13C)-C(14C)	1.390(5)
C(13C)-C(18C)	1.392(5)
C(13C)-S(1C)	1.760(3)
C(14C)-C(15C)	1.389(4)
C(14C)-H(14C)	0.9500
C(15C)-C(16C)	1.401(4)
C(15C)-H(15C)	0.9500
C(16C)-C(17C)	1.396(4)
C(16C)-N(1C)	1.411(4)
C(17C)-C(18C)	1.388(4)
C(17C)-H(17C)	0.9500
C(18C)-H(18C)	0.9500
C(19C)-O(10D)	1.221(4)
C(19C)-N(1C)	1.355(4)
C(19C)-C(20C)	1.504(4)
C(20C)-H(20G)	0.9800
C(20C)-H(20H)	0.9800
C(20C)-H(20I)	0.9800
O(4C)-S(1C)	1.593(2)
O(7C)-S(1C)	1.426(2)
N(1C)-H(1C1)	0.8800
C(1D)-O(1D)	1.412(4)
C(1D)-O(2D)	1.422(4)
C(1D)-C(2D)	1.533(5)
C(1D)-H(1D)	1.0000
C(2D)-O(3D)	1.422(5)
C(2D)-C(3D)	1.531(4)
C(2D)-H(2D)	1.0000
C(3D)-O(4D)	1.450(4)
C(3D)-C(4D)	1.528(4)
C(3D)-H(3D)	1.0000
C(4D)-O(1D)	1.443(4)
C(4D)-C(5D)	1.515(4)
C(4D)-H(4D)	1.0000
C(5D)-O(5D)	1.423(4)
C(5D)-C(6D)	1.551(5)
C(5D)-H(5D)	1.0000

C(6D)-H(6D1)	0.9900
C(6D)-H(6D2)	0.9900
C(7D)-O(2D)	1.413(5)
C(7D)-O(3D)	1.429(4)
C(7D)-C(8D)	1.502(7)
C(7D)-C(9D)	1.524(6)
C(8D)-H(8D1)	0.9800
C(8D)-H(8D2)	0.9800
C(8D)-H(8D3)	0.9800
C(9D)-H(9D1)	0.9800
C(9D)-H(9D2)	0.9800
C(9D)-H(9D3)	0.9800
C(10D)-O(5D)	1.433(4)
C(10D)-C(12D)	1.519(4)
C(10D)-C(11D)	1.520(4)
C(11D)-H(11J)	0.9800
C(11D)-H(11K)	0.9800
C(11D)-H(11L)	0.9800
C(12D)-H(12J)	0.9800
C(12D)-H(12K)	0.9800
C(12D)-H(12L)	0.9800
C(13D)-C(18D)	1.371(5)
C(13D)-C(14D)	1.392(5)
C(13D)-S(1D)	1.754(3)
C(14D)-C(15D)	1.388(4)
C(14D)-H(14D)	0.9500
C(15D)-C(16D)	1.393(5)
C(15D)-H(15D)	0.9500
C(16D)-C(17D)	1.394(4)
C(16D)-N(1D)	1.412(4)
C(17D)-C(18D)	1.380(4)
C(17D)-H(17D)	0.9500
C(18D)-H(18D)	0.9500
C(19D)-O(9D)	1.214(4)
C(19D)-N(1D)	1.360(4)
C(19D)-C(20D)	1.509(4)
C(20D)-H(20J)	0.9800
C(20D)-H(20K)	0.9800
C(20D)-H(20L)	0.9800
O(4D)-S(1D)	1.596(2)
O(7D)-S(1D)	1.412(3)
N(1D)-H(1D1)	0.8800
C(1E)-O(2E)	1.411(4)
C(1E)-O(1E)	1.412(4)
C(1E)-C(2E)	1.540(4)
C(1E)-H(1E)	1.0000
C(2E)-O(3E)	1.423(4)
C(2E)-C(3E)	1.530(4)
C(2E)-H(2E)	1.0000
C(3E)-O(4E)	1.447(4)
C(3E)-C(4E)	1.532(4)
C(3E)-H(3E)	1.0000
C(4E)-O(1E)	1.440(4)
C(4E)-H(4E)	1.0000
C(6E)-O(6E)	1.427(4)
C(6E)-H(6E1)	0.9900
C(6E)-H(6E2)	0.9900

C(7E)-O(3E)	1.425(4)
C(7E)-O(2E)	1.430(4)
C(7E)-C(8E)	1.507(5)
C(7E)-C(9E)	1.519(5)
C(8E)-H(8E1)	0.9800
C(8E)-H(8E2)	0.9800
C(8E)-H(8E3)	0.9800
C(9E)-H(9E1)	0.9800
C(9E)-H(9E2)	0.9800
C(9E)-H(9E3)	0.9800
C(10E)-O(5E)	1.415(4)
C(10E)-O(6E)	1.421(4)
C(10E)-C(12E)	1.500(4)
C(10E)-C(11E)	1.512(4)
C(11E)-H(11M)	0.9800
C(11E)-H(11N)	0.9800
C(11E)-H(11O)	0.9800
C(12E)-H(12M)	0.9800
C(12E)-H(12N)	0.9800
C(12E)-H(12O)	0.9800
C(13E)-C(14E)	1.388(4)
C(13E)-C(18E)	1.391(4)
C(13E)-S(1E)	1.752(3)
C(14E)-C(15E)	1.392(4)
C(14E)-H(14E)	0.9500
C(15E)-C(16E)	1.401(4)
C(15E)-H(15E)	0.9500
C(16E)-C(17E)	1.396(4)
C(16E)-N(1E)	1.410(4)
C(17E)-C(18E)	1.372(4)
C(17E)-H(17E)	0.9500
C(18E)-H(18E)	0.9500
C(19E)-O(9E)	1.222(4)
C(19E)-N(1E)	1.361(4)
C(19E)-C(20E)	1.503(4)
C(20E)-H(20M)	0.9800
C(20E)-H(20N)	0.9800
C(20E)-H(20O)	0.9800
O(4E)-S(1E)	1.595(2)
O(7E)-S(1E)	1.420(3)
O(8E)-S(1E)	1.421(2)
N(1E)-H(1E1)	0.8800
C(1F)-O(2F)	1.402(4)
C(1F)-O(1F)	1.413(4)
C(1F)-C(2F)	1.525(4)
C(1F)-H(1F)	1.0000
C(2F)-O(3F)	1.432(4)
C(2F)-C(3F)	1.525(4)
C(2F)-H(2F)	1.0000
C(3F)-O(4F)	1.444(3)
C(3F)-C(4F)	1.534(4)
C(3F)-H(3F)	1.0000
C(4F)-O(1F)	1.443(4)
C(4F)-C(5F)	1.506(5)
C(4F)-H(4F)	1.0000
C(5F)-O(5F)	1.430(4)
C(5F)-C(6F)	1.541(5)

C(5F)-H(5F)	1.0000
C(6F)-O(6F)	1.427(4)
C(6F)-H(6F1)	0.9900
C(6F)-H(6F2)	0.9900
C(7F)-O(3F)	1.421(4)
C(7F)-O(2F)	1.433(4)
C(7F)-C(8F)	1.509(5)
C(7F)-C(9F)	1.521(5)
C(8F)-H(8F1)	0.9800
C(8F)-H(8F2)	0.9800
C(8F)-H(8F3)	0.9800
C(9F)-H(9F1)	0.9800
C(9F)-H(9F2)	0.9800
C(9F)-H(9F3)	0.9800
C(10F)-O(6F)	1.419(5)
C(10F)-O(5F)	1.429(4)
C(10F)-C(12F)	1.512(5)
C(10F)-C(11F)	1.522(5)
C(11F)-H(11P)	0.9800
C(11F)-H(11Q)	0.9800
C(11F)-H(11R)	0.9800
C(12F)-H(12P)	0.9800
C(12F)-H(12Q)	0.9800
C(12F)-H(12R)	0.9800
C(13F)-C(14F)	1.385(4)
C(13F)-C(18F)	1.386(4)
C(13F)-S(1F)	1.743(3)
C(14F)-C(15F)	1.390(4)
C(14F)-H(14F)	0.9500
C(15F)-C(16F)	1.402(4)
C(15F)-H(15F)	0.9500
C(16F)-C(17F)	1.392(4)
C(16F)-N(1F)	1.403(4)
C(17F)-C(18F)	1.382(4)
C(17F)-H(17F)	0.9500
C(18F)-H(18F)	0.9500
C(19F)-O(9F)	1.221(4)
C(19F)-N(1F)	1.358(4)
C(19F)-C(20F)	1.508(5)
C(20F)-H(20P)	0.9800
C(20F)-H(20Q)	0.9800
C(20F)-H(20R)	0.9800
O(4F)-S(1F)	1.596(2)
O(7F)-S(1F)	1.417(2)
O(8F)-S(1F)	1.427(2)
N(1F)-H(1F1)	0.8800

C(22)-O(22)-H(22)	109.5
O(22)-C(22)-H(22A)	109.5
O(22)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
O(22)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(21)-O(21)-H(21)	109.5
O(21)-C(21)-H(21A)	109.5
O(21)-C(21)-H(21B)	109.5

H(21A)-C(21)-H(21B)	109.5
O(21)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
O(1A)-C(1A)-O(2A)	111.4(2)
O(1A)-C(1A)-C(2A)	107.7(2)
O(2A)-C(1A)-C(2A)	105.7(2)
O(1A)-C(1A)-H(1A)	110.6
O(2A)-C(1A)-H(1A)	110.6
C(2A)-C(1A)-H(1A)	110.6
O(3A)-C(2A)-C(3A)	109.5(2)
O(3A)-C(2A)-C(1A)	103.4(2)
C(3A)-C(2A)-C(1A)	102.5(2)
O(3A)-C(2A)-H(2A)	113.5
C(3A)-C(2A)-H(2A)	113.5
C(1A)-C(2A)-H(2A)	113.5
O(4A)-C(3A)-C(2A)	114.7(2)
O(4A)-C(3A)-C(4A)	109.1(2)
C(2A)-C(3A)-C(4A)	102.3(2)
O(4A)-C(3A)-H(3A)	110.1
C(2A)-C(3A)-H(3A)	110.1
C(4A)-C(3A)-H(3A)	110.1
O(1A)-C(4A)-C(5A)	108.6(2)
O(1A)-C(4A)-C(3A)	101.3(2)
C(5A)-C(4A)-C(3A)	118.8(2)
O(1A)-C(4A)-H(4A)	109.2
C(5A)-C(4A)-H(4A)	109.2
C(3A)-C(4A)-H(4A)	109.2
O(5A)-C(5A)-C(4A)	109.9(2)
O(5A)-C(5A)-C(6A)	104.2(2)
C(4A)-C(5A)-C(6A)	114.2(3)
O(5A)-C(5A)-H(5A)	109.5
C(4A)-C(5A)-H(5A)	109.5
C(6A)-C(5A)-H(5A)	109.5
O(5E)-C(5E)-C(4E)	109.8(2)
O(5E)-C(5E)-C(6E)	104.3(2)
C(4E)-C(5E)-C(6E)	115.4(3)
O(5E)-C(5E)-H(5E)	109.0
C(4E)-C(5E)-H(5E)	109.0
C(6E)-C(5E)-H(5E)	109.0
O(6A)-C(6A)-C(5A)	103.4(2)
O(6A)-C(6A)-H(6A1)	111.1
C(5A)-C(6A)-H(6A1)	111.1
O(6A)-C(6A)-H(6A2)	111.1
C(5A)-C(6A)-H(6A2)	111.1
H(6A1)-C(6A)-H(6A2)	109.1
O(3A)-C(7A)-O(2A)	105.2(2)
O(3A)-C(7A)-C(8A)	108.1(3)
O(2A)-C(7A)-C(8A)	108.5(3)
O(3A)-C(7A)-C(9A)	111.2(3)
O(2A)-C(7A)-C(9A)	109.1(3)
C(8A)-C(7A)-C(9A)	114.4(4)
C(7A)-C(8A)-H(8A1)	109.5
C(7A)-C(8A)-H(8A2)	109.5
H(8A1)-C(8A)-H(8A2)	109.5
C(7A)-C(8A)-H(8A3)	109.5
H(8A1)-C(8A)-H(8A3)	109.5

H(8A2)-C(8A)-H(8A3)	109.5
C(7A)-C(9A)-H(9A1)	109.5
C(7A)-C(9A)-H(9A2)	109.5
H(9A1)-C(9A)-H(9A2)	109.5
C(7A)-C(9A)-H(9A3)	109.5
H(9A1)-C(9A)-H(9A3)	109.5
H(9A2)-C(9A)-H(9A3)	109.5
O(6A)-C(10A)-O(5A)	104.8(2)
O(6A)-C(10A)-C(12A)	109.4(2)
O(5A)-C(10A)-C(12A)	108.4(3)
O(6A)-C(10A)-C(11A)	110.7(3)
O(5A)-C(10A)-C(11A)	110.8(3)
C(12A)-C(10A)-C(11A)	112.4(3)
C(10A)-C(11A)-H(11A)	109.5
C(10A)-C(11A)-H(11B)	109.5
H(11A)-C(11A)-H(11B)	109.5
C(10A)-C(11A)-H(11C)	109.5
H(11A)-C(11A)-H(11C)	109.5
H(11B)-C(11A)-H(11C)	109.5
C(10A)-C(12A)-H(12A)	109.5
C(10A)-C(12A)-H(12B)	109.5
H(12A)-C(12A)-H(12B)	109.5
C(10A)-C(12A)-H(12C)	109.5
H(12A)-C(12A)-H(12C)	109.5
H(12B)-C(12A)-H(12C)	109.5
C(18A)-C(13A)-C(14A)	120.9(3)
C(18A)-C(13A)-S(1A)	119.2(2)
C(14A)-C(13A)-S(1A)	119.7(2)
C(15A)-C(14A)-C(13A)	119.8(3)
C(15A)-C(14A)-H(14A)	120.1
C(13A)-C(14A)-H(14A)	120.1
C(14A)-C(15A)-C(16A)	119.9(3)
C(14A)-C(15A)-H(15A)	120.1
C(16A)-C(15A)-H(15A)	120.1
C(17A)-C(16A)-N(1A)	123.3(3)
C(17A)-C(16A)-C(15A)	119.8(3)
N(1A)-C(16A)-C(15A)	116.9(3)
C(16A)-C(17A)-C(18A)	120.4(3)
C(16A)-C(17A)-H(17A)	119.8
C(18A)-C(17A)-H(17A)	119.8
C(13A)-C(18A)-C(17A)	119.1(3)
C(13A)-C(18A)-H(18A)	120.5
C(17A)-C(18A)-H(18A)	120.5
O(9A)-C(19A)-N(1A)	123.9(3)
O(9A)-C(19A)-C(20A)	121.0(3)
N(1A)-C(19A)-C(20A)	115.1(3)
C(19A)-C(20A)-H(20A)	109.5
C(19A)-C(20A)-H(20B)	109.5
H(20A)-C(20A)-H(20B)	109.5
C(19A)-C(20A)-H(20C)	109.5
H(20A)-C(20A)-H(20C)	109.5
H(20B)-C(20A)-H(20C)	109.5
C(1A)-O(1A)-C(4A)	108.7(2)
C(1A)-O(2A)-C(7A)	108.7(2)
C(2A)-O(3A)-C(7A)	106.9(2)
C(3A)-O(4A)-S(1A)	118.77(18)
C(10A)-O(5A)-C(5A)	108.2(2)

C(10D)-O(6D)-C(6D)	105.2(3)
C(10A)-O(6A)-C(6A)	105.4(2)
C(19A)-N(1A)-C(16A)	125.5(3)
C(19A)-N(1A)-H(1A1)	117.3
C(16A)-N(1A)-H(1A1)	117.3
O(8A)-S(1A)-O(7A)	120.11(15)
O(8A)-S(1A)-O(4A)	102.76(13)
O(7A)-S(1A)-O(4A)	109.55(13)
O(8A)-S(1A)-C(13A)	108.54(14)
O(7A)-S(1A)-C(13A)	109.46(14)
O(4A)-S(1A)-C(13A)	105.32(13)
O(1B)-C(1B)-O(2B)	110.1(3)
O(1B)-C(1B)-C(2B)	107.4(3)
O(2B)-C(1B)-C(2B)	104.2(3)
O(1B)-C(1B)-H(1B)	111.6
O(2B)-C(1B)-H(1B)	111.6
C(2B)-C(1B)-H(1B)	111.6
O(3B)-C(2B)-C(3B)	108.4(3)
O(3B)-C(2B)-C(1B)	104.7(3)
C(3B)-C(2B)-C(1B)	103.0(3)
O(3B)-C(2B)-H(2B)	113.3
C(3B)-C(2B)-H(2B)	113.3
C(1B)-C(2B)-H(2B)	113.3
O(4B)-C(3B)-C(4B)	109.3(3)
O(4B)-C(3B)-C(2B)	112.4(3)
C(4B)-C(3B)-C(2B)	102.5(2)
O(4B)-C(3B)-H(3B)	110.8
C(4B)-C(3B)-H(3B)	110.8
C(2B)-C(3B)-H(3B)	110.8
O(1B)-C(4B)-C(5B)	107.5(3)
O(1B)-C(4B)-C(3B)	102.1(3)
C(5B)-C(4B)-C(3B)	118.5(3)
O(1B)-C(4B)-H(4B)	109.4
C(5B)-C(4B)-H(4B)	109.4
C(3B)-C(4B)-H(4B)	109.4
O(5B)-C(5B)-C(4B)	110.4(3)
O(5B)-C(5B)-C(6B)	103.8(3)
C(4B)-C(5B)-C(6B)	114.8(3)
O(5B)-C(5B)-H(5B)	109.2
C(4B)-C(5B)-H(5B)	109.2
C(6B)-C(5B)-H(5B)	109.2
O(6B)-C(6B)-C(5B)	104.7(3)
O(6B)-C(6B)-H(6B1)	110.8
C(5B)-C(6B)-H(6B1)	110.8
O(6B)-C(6B)-H(6B2)	110.8
C(5B)-C(6B)-H(6B2)	110.8
H(6B1)-C(6B)-H(6B2)	108.9
O(2B)-C(7B)-O(3B)	104.7(3)
O(2B)-C(7B)-C(9B)	108.0(3)
O(3B)-C(7B)-C(9B)	108.1(3)
O(2B)-C(7B)-C(8B)	109.8(4)
O(3B)-C(7B)-C(8B)	111.1(3)
C(9B)-C(7B)-C(8B)	114.6(4)
C(7B)-C(8B)-H(8B1)	109.5
C(7B)-C(8B)-H(8B2)	109.5
H(8B1)-C(8B)-H(8B2)	109.5
C(7B)-C(8B)-H(8B3)	109.5

H(8B1)-C(8B)-H(8B3)	109.5
H(8B2)-C(8B)-H(8B3)	109.5
C(7B)-C(9B)-H(9B1)	109.5
C(7B)-C(9B)-H(9B2)	109.5
H(9B1)-C(9B)-H(9B2)	109.5
C(7B)-C(9B)-H(9B3)	109.5
H(9B1)-C(9B)-H(9B3)	109.5
H(9B2)-C(9B)-H(9B3)	109.5
O(5B)-C(10B)-O(6B)	104.8(3)
O(5B)-C(10B)-C(12B)	108.2(3)
O(6B)-C(10B)-C(12B)	109.8(3)
O(5B)-C(10B)-C(11B)	111.3(3)
O(6B)-C(10B)-C(11B)	110.7(3)
C(12B)-C(10B)-C(11B)	111.8(3)
C(10B)-C(11B)-H(11D)	109.5
C(10B)-C(11B)-H(11E)	109.5
H(11D)-C(11B)-H(11E)	109.5
C(10B)-C(11B)-H(11F)	109.5
H(11D)-C(11B)-H(11F)	109.5
H(11E)-C(11B)-H(11F)	109.5
C(10B)-C(12B)-H(12D)	109.5
C(10B)-C(12B)-H(12E)	109.5
H(12D)-C(12B)-H(12E)	109.5
C(10B)-C(12B)-H(12F)	109.5
H(12D)-C(12B)-H(12F)	109.5
H(12E)-C(12B)-H(12F)	109.5
C(18B)-C(13B)-C(14B)	121.6(3)
C(18B)-C(13B)-S(1B)	120.0(3)
C(14B)-C(13B)-S(1B)	118.4(3)
C(15B)-C(14B)-C(13B)	118.9(3)
C(15B)-C(14B)-H(14B)	120.6
C(13B)-C(14B)-H(14B)	120.6
C(14B)-C(15B)-C(16B)	120.5(3)
C(14B)-C(15B)-H(15B)	119.7
C(16B)-C(15B)-H(15B)	119.7
C(15B)-C(16B)-C(17B)	120.6(3)
C(15B)-C(16B)-N(1B)	115.9(3)
C(17B)-C(16B)-N(1B)	123.5(3)
C(18B)-C(17B)-C(16B)	119.6(3)
C(18B)-C(17B)-H(17B)	120.2
C(16B)-C(17B)-H(17B)	120.2
C(17B)-C(18B)-C(13B)	118.9(3)
C(17B)-C(18B)-H(18B)	120.6
C(13B)-C(18B)-H(18B)	120.6
O(9B)-C(19B)-N(1B)	122.5(3)
O(9B)-C(19B)-C(20B)	122.3(3)
N(1B)-C(19B)-C(20B)	115.2(3)
C(19B)-C(20B)-H(20D)	109.5
C(19B)-C(20B)-H(20E)	109.5
H(20D)-C(20B)-H(20E)	109.5
C(19B)-C(20B)-H(20F)	109.5
H(20D)-C(20B)-H(20F)	109.5
H(20E)-C(20B)-H(20F)	109.5
C(1B)-O(1B)-C(4B)	108.7(3)
C(7B)-O(2B)-C(1B)	109.6(2)
C(2B)-O(3B)-C(7B)	107.2(3)
C(3B)-O(4B)-S(1B)	117.0(2)

C(10B)-O(5B)-C(5B)	106.3(3)
C(6B)-O(6B)-C(10B)	106.9(3)
C(19B)-N(1B)-C(16B)	127.8(3)
C(19B)-N(1B)-H(1B1)	116.1
C(16B)-N(1B)-H(1B1)	116.1
O(7B)-S(1B)-O(8B)	120.64(16)
O(7B)-S(1B)-O(4B)	110.16(14)
O(8B)-S(1B)-O(4B)	102.85(15)
O(7B)-S(1B)-C(13B)	110.30(16)
O(8B)-S(1B)-C(13B)	108.03(17)
O(4B)-S(1B)-C(13B)	103.33(14)
O(2C)-C(1C)-O(1C)	111.2(3)
O(2C)-C(1C)-C(2C)	104.3(3)
O(1C)-C(1C)-C(2C)	106.3(3)
O(2C)-C(1C)-H(1C)	111.6
O(1C)-C(1C)-H(1C)	111.6
C(2C)-C(1C)-H(1C)	111.6
O(3C)-C(2C)-C(3C)	109.8(3)
O(3C)-C(2C)-C(1C)	103.4(2)
C(3C)-C(2C)-C(1C)	101.9(3)
O(3C)-C(2C)-H(2C)	113.5
C(3C)-C(2C)-H(2C)	113.5
C(1C)-C(2C)-H(2C)	113.5
O(4C)-C(3C)-C(2C)	114.0(3)
O(4C)-C(3C)-C(4C)	109.6(3)
C(2C)-C(3C)-C(4C)	101.7(2)
O(4C)-C(3C)-H(3C)	110.4
C(2C)-C(3C)-H(3C)	110.4
C(4C)-C(3C)-H(3C)	110.4
O(1C)-C(4C)-C(5C)	107.9(3)
O(1C)-C(4C)-C(3C)	101.4(2)
C(5C)-C(4C)-C(3C)	117.9(3)
O(1C)-C(4C)-H(4C)	109.7
C(5C)-C(4C)-H(4C)	109.7
C(3C)-C(4C)-H(4C)	109.7
O(5C)-C(5C)-C(4C)	110.4(3)
O(5C)-C(5C)-C(6C)	105.1(3)
C(4C)-C(5C)-C(6C)	113.5(3)
O(5C)-C(5C)-H(5C)	109.2
C(4C)-C(5C)-H(5C)	109.2
C(6C)-C(5C)-H(5C)	109.2
O(6C)-C(6C)-C(5C)	102.9(3)
O(6C)-C(6C)-H(6C1)	111.2
C(5C)-C(6C)-H(6C1)	111.2
O(6C)-C(6C)-H(6C2)	111.2
C(5C)-C(6C)-H(6C2)	111.2
H(6C1)-C(6C)-H(6C2)	109.1
O(2C)-C(7C)-O(3C)	105.6(3)
O(2C)-C(7C)-C(8C)	108.8(3)
O(3C)-C(7C)-C(8C)	108.2(3)
O(2C)-C(7C)-C(9C)	109.5(3)
O(3C)-C(7C)-C(9C)	111.0(3)
C(8C)-C(7C)-C(9C)	113.4(3)
C(7C)-C(8C)-H(8C1)	109.5
C(7C)-C(8C)-H(8C2)	109.5
H(8C1)-C(8C)-H(8C2)	109.5
C(7C)-C(8C)-H(8C3)	109.5

H(8C1)-C(8C)-H(8C3)	109.5
H(8C2)-C(8C)-H(8C3)	109.5
C(7C)-C(9C)-H(9C1)	109.5
C(7C)-C(9C)-H(9C2)	109.5
H(9C1)-C(9C)-H(9C2)	109.5
C(7C)-C(9C)-H(9C3)	109.5
H(9C1)-C(9C)-H(9C3)	109.5
H(9C2)-C(9C)-H(9C3)	109.5
O(6C)-C(10C)-O(5C)	105.0(3)
O(6C)-C(10C)-C(12C)	109.7(3)
O(5C)-C(10C)-C(12C)	107.5(3)
O(6C)-C(10C)-C(11C)	111.2(3)
O(5C)-C(10C)-C(11C)	110.7(3)
C(12C)-C(10C)-C(11C)	112.3(3)
C(10C)-C(11C)-H(11G)	109.5
C(10C)-C(11C)-H(11H)	109.5
H(11G)-C(11C)-H(11H)	109.5
C(10C)-C(11C)-H(11I)	109.5
H(11G)-C(11C)-H(11I)	109.5
H(11H)-C(11C)-H(11I)	109.5
C(10C)-C(12C)-H(12G)	109.5
C(10C)-C(12C)-H(12H)	109.5
H(12G)-C(12C)-H(12H)	109.5
C(10C)-C(12C)-H(12I)	109.5
H(12G)-C(12C)-H(12I)	109.5
H(12H)-C(12C)-H(12I)	109.5
C(14C)-C(13C)-C(18C)	121.6(3)
C(14C)-C(13C)-S(1C)	119.5(2)
C(18C)-C(13C)-S(1C)	118.8(3)
C(15C)-C(14C)-C(13C)	119.4(3)
C(15C)-C(14C)-H(14C)	120.3
C(13C)-C(14C)-H(14C)	120.3
C(14C)-C(15C)-C(16C)	119.7(3)
C(14C)-C(15C)-H(15C)	120.2
C(16C)-C(15C)-H(15C)	120.2
C(17C)-C(16C)-C(15C)	120.1(3)
C(17C)-C(16C)-N(1C)	118.0(3)
C(15C)-C(16C)-N(1C)	121.9(3)
C(18C)-C(17C)-C(16C)	120.3(3)
C(18C)-C(17C)-H(17C)	119.9
C(16C)-C(17C)-H(17C)	119.9
C(17C)-C(18C)-C(13C)	118.9(3)
C(17C)-C(18C)-H(18C)	120.5
C(13C)-C(18C)-H(18C)	120.5
O(10D)-C(19C)-N(1C)	122.9(3)
O(10D)-C(19C)-C(20C)	121.7(3)
N(1C)-C(19C)-C(20C)	115.4(3)
C(19C)-C(20C)-H(20G)	109.5
C(19C)-C(20C)-H(20H)	109.5
H(20G)-C(20C)-H(20H)	109.5
C(19C)-C(20C)-H(20I)	109.5
H(20G)-C(20C)-H(20I)	109.5
H(20H)-C(20C)-H(20I)	109.5
C(1C)-O(1C)-C(4C)	110.8(3)
C(1C)-O(2C)-C(7C)	110.0(3)
C(2C)-O(3C)-C(7C)	106.2(3)
C(3C)-O(4C)-S(1C)	118.32(19)

C(5C)-O(5C)-C(10C)	106.9(3)
C(10C)-O(6C)-C(6C)	106.0(3)
C(19C)-N(1C)-C(16C)	127.5(3)
C(19C)-N(1C)-H(1C1)	116.3
C(16C)-N(1C)-H(1C1)	116.3
O(7C)-S(1C)-O(8C)	120.56(15)
O(7C)-S(1C)-O(4C)	109.34(13)
O(8C)-S(1C)-O(4C)	102.48(14)
O(7C)-S(1C)-C(13C)	108.20(15)
O(8C)-S(1C)-C(13C)	108.94(15)
O(4C)-S(1C)-C(13C)	106.43(13)
O(1D)-C(1D)-O(2D)	110.7(3)
O(1D)-C(1D)-C(2D)	107.5(3)
O(2D)-C(1D)-C(2D)	104.4(3)
O(1D)-C(1D)-H(1D)	111.3
O(2D)-C(1D)-H(1D)	111.3
C(2D)-C(1D)-H(1D)	111.3
O(3D)-C(2D)-C(3D)	109.2(3)
O(3D)-C(2D)-C(1D)	104.5(3)
C(3D)-C(2D)-C(1D)	102.4(3)
O(3D)-C(2D)-H(2D)	113.3
C(3D)-C(2D)-H(2D)	113.3
C(1D)-C(2D)-H(2D)	113.3
O(4D)-C(3D)-C(4D)	108.5(3)
O(4D)-C(3D)-C(2D)	113.6(3)
C(4D)-C(3D)-C(2D)	102.7(2)
O(4D)-C(3D)-H(3D)	110.6
C(4D)-C(3D)-H(3D)	110.6
C(2D)-C(3D)-H(3D)	110.6
O(1D)-C(4D)-C(5D)	107.4(3)
O(1D)-C(4D)-C(3D)	101.2(3)
C(5D)-C(4D)-C(3D)	118.9(3)
O(1D)-C(4D)-H(4D)	109.6
C(5D)-C(4D)-H(4D)	109.6
C(3D)-C(4D)-H(4D)	109.6
O(5D)-C(5D)-C(4D)	110.7(3)
O(5D)-C(5D)-C(6D)	104.1(2)
C(4D)-C(5D)-C(6D)	113.9(3)
O(5D)-C(5D)-H(5D)	109.3
C(4D)-C(5D)-H(5D)	109.3
C(6D)-C(5D)-H(5D)	109.3
O(6D)-C(6D)-C(5D)	103.7(3)
O(6D)-C(6D)-H(6D1)	111.0
C(5D)-C(6D)-H(6D1)	111.0
O(6D)-C(6D)-H(6D2)	111.0
C(5D)-C(6D)-H(6D2)	111.0
H(6D1)-C(6D)-H(6D2)	109.0
O(2D)-C(7D)-O(3D)	105.0(3)
O(2D)-C(7D)-C(8D)	109.1(3)
O(3D)-C(7D)-C(8D)	108.0(4)
O(2D)-C(7D)-C(9D)	109.0(4)
O(3D)-C(7D)-C(9D)	111.0(3)
C(8D)-C(7D)-C(9D)	114.4(4)
C(7D)-C(8D)-H(8D1)	109.5
C(7D)-C(8D)-H(8D2)	109.5
H(8D1)-C(8D)-H(8D2)	109.5
C(7D)-C(8D)-H(8D3)	109.5

H(8D1)-C(8D)-H(8D3)	109.5
H(8D2)-C(8D)-H(8D3)	109.5
C(7D)-C(9D)-H(9D1)	109.5
C(7D)-C(9D)-H(9D2)	109.5
H(9D1)-C(9D)-H(9D2)	109.5
C(7D)-C(9D)-H(9D3)	109.5
H(9D1)-C(9D)-H(9D3)	109.5
H(9D2)-C(9D)-H(9D3)	109.5
O(6D)-C(10D)-O(5D)	105.1(3)
O(6D)-C(10D)-C(12D)	110.1(3)
O(5D)-C(10D)-C(12D)	107.8(3)
O(6D)-C(10D)-C(11D)	110.7(3)
O(5D)-C(10D)-C(11D)	110.6(3)
C(12D)-C(10D)-C(11D)	112.2(3)
C(10D)-C(11D)-H(11J)	109.5
C(10D)-C(11D)-H(11K)	109.5
H(11J)-C(11D)-H(11K)	109.5
C(10D)-C(11D)-H(11L)	109.5
H(11J)-C(11D)-H(11L)	109.5
H(11K)-C(11D)-H(11L)	109.5
C(10D)-C(12D)-H(12J)	109.5
C(10D)-C(12D)-H(12K)	109.5
H(12J)-C(12D)-H(12K)	109.5
C(10D)-C(12D)-H(12L)	109.5
H(12J)-C(12D)-H(12L)	109.5
H(12K)-C(12D)-H(12L)	109.5
C(18D)-C(13D)-C(14D)	120.8(3)
C(18D)-C(13D)-S(1D)	118.7(3)
C(14D)-C(13D)-S(1D)	120.5(3)
C(15D)-C(14D)-C(13D)	119.1(3)
C(15D)-C(14D)-H(14D)	120.4
C(13D)-C(14D)-H(14D)	120.4
C(14D)-C(15D)-C(16D)	120.1(3)
C(14D)-C(15D)-H(15D)	119.9
C(16D)-C(15D)-H(15D)	119.9
C(15D)-C(16D)-C(17D)	119.7(3)
C(15D)-C(16D)-N(1D)	122.6(3)
C(17D)-C(16D)-N(1D)	117.6(3)
C(18D)-C(17D)-C(16D)	119.8(3)
C(18D)-C(17D)-H(17D)	120.1
C(16D)-C(17D)-H(17D)	120.1
C(13D)-C(18D)-C(17D)	120.4(3)
C(13D)-C(18D)-H(18D)	119.8
C(17D)-C(18D)-H(18D)	119.8
O(9D)-C(19D)-N(1D)	123.0(3)
O(9D)-C(19D)-C(20D)	121.8(3)
N(1D)-C(19D)-C(20D)	115.2(3)
C(19D)-C(20D)-H(20J)	109.5
C(19D)-C(20D)-H(20K)	109.5
H(20J)-C(20D)-H(20K)	109.5
C(19D)-C(20D)-H(20L)	109.5
H(20J)-C(20D)-H(20L)	109.5
H(20K)-C(20D)-H(20L)	109.5
C(1D)-O(1D)-C(4D)	108.5(3)
C(7D)-O(2D)-C(1D)	109.5(3)
C(2D)-O(3D)-C(7D)	107.0(3)
C(3D)-O(4D)-S(1D)	118.45(19)

C(5D)-O(5D)-C(10D)	108.5(3)
C(19D)-N(1D)-C(16D)	125.1(3)
C(19D)-N(1D)-H(1D1)	117.4
C(16D)-N(1D)-H(1D1)	117.4
O(7D)-S(1D)-O(8D)	120.92(17)
O(7D)-S(1D)-O(4D)	110.19(14)
O(8D)-S(1D)-O(4D)	102.42(14)
O(7D)-S(1D)-C(13D)	109.86(16)
O(8D)-S(1D)-C(13D)	108.18(17)
O(4D)-S(1D)-C(13D)	103.79(13)
O(2E)-C(1E)-O(1E)	111.5(3)
O(2E)-C(1E)-C(2E)	104.9(3)
O(1E)-C(1E)-C(2E)	107.1(2)
O(2E)-C(1E)-H(1E)	111.0
O(1E)-C(1E)-H(1E)	111.0
C(2E)-C(1E)-H(1E)	111.0
O(3E)-C(2E)-C(3E)	108.5(3)
O(3E)-C(2E)-C(1E)	104.1(2)
C(3E)-C(2E)-C(1E)	102.1(2)
O(3E)-C(2E)-H(2E)	113.7
C(3E)-C(2E)-H(2E)	113.7
C(1E)-C(2E)-H(2E)	113.7
O(4E)-C(3E)-C(2E)	113.6(3)
O(4E)-C(3E)-C(4E)	109.4(2)
C(2E)-C(3E)-C(4E)	102.4(2)
O(4E)-C(3E)-H(3E)	110.4
C(2E)-C(3E)-H(3E)	110.4
C(4E)-C(3E)-H(3E)	110.4
O(1E)-C(4E)-C(5E)	109.2(2)
O(1E)-C(4E)-C(3E)	100.8(2)
C(5E)-C(4E)-C(3E)	119.1(2)
O(1E)-C(4E)-H(4E)	109.1
C(5E)-C(4E)-H(4E)	109.1
C(3E)-C(4E)-H(4E)	109.1
O(6E)-C(6E)-C(5E)	103.9(2)
O(6E)-C(6E)-H(6E1)	111.0
C(5E)-C(6E)-H(6E1)	111.0
O(6E)-C(6E)-H(6E2)	111.0
C(5E)-C(6E)-H(6E2)	111.0
H(6E1)-C(6E)-H(6E2)	109.0
O(3E)-C(7E)-O(2E)	105.7(2)
O(3E)-C(7E)-C(8E)	108.2(3)
O(2E)-C(7E)-C(8E)	109.3(3)
O(3E)-C(7E)-C(9E)	110.9(3)
O(2E)-C(7E)-C(9E)	109.1(3)
C(8E)-C(7E)-C(9E)	113.4(3)
C(7E)-C(8E)-H(8E1)	109.5
C(7E)-C(8E)-H(8E2)	109.5
H(8E1)-C(8E)-H(8E2)	109.5
C(7E)-C(8E)-H(8E3)	109.5
H(8E1)-C(8E)-H(8E3)	109.5
H(8E2)-C(8E)-H(8E3)	109.5
C(7E)-C(9E)-H(9E1)	109.5
C(7E)-C(9E)-H(9E2)	109.5
H(9E1)-C(9E)-H(9E2)	109.5
C(7E)-C(9E)-H(9E3)	109.5
H(9E1)-C(9E)-H(9E3)	109.5

H(9E2)-C(9E)-H(9E3)	109.5
O(5E)-C(10E)-O(6E)	104.4(2)
O(5E)-C(10E)-C(12E)	108.3(3)
O(6E)-C(10E)-C(12E)	109.1(2)
O(5E)-C(10E)-C(11E)	111.6(3)
O(6E)-C(10E)-C(11E)	110.8(3)
C(12E)-C(10E)-C(11E)	112.4(3)
C(10E)-C(11E)-H(11M)	109.5
C(10E)-C(11E)-H(11N)	109.5
H(11M)-C(11E)-H(11N)	109.5
C(10E)-C(11E)-H(11O)	109.5
H(11M)-C(11E)-H(11O)	109.5
H(11N)-C(11E)-H(11O)	109.5
C(10E)-C(12E)-H(12M)	109.5
C(10E)-C(12E)-H(12N)	109.5
H(12M)-C(12E)-H(12N)	109.5
C(10E)-C(12E)-H(12O)	109.5
H(12M)-C(12E)-H(12O)	109.5
H(12N)-C(12E)-H(12O)	109.5
C(14E)-C(13E)-C(18E)	121.1(3)
C(14E)-C(13E)-S(1E)	120.8(2)
C(18E)-C(13E)-S(1E)	118.0(2)
C(13E)-C(14E)-C(15E)	119.8(3)
C(13E)-C(14E)-H(14E)	120.1
C(15E)-C(14E)-H(14E)	120.1
C(14E)-C(15E)-C(16E)	119.2(3)
C(14E)-C(15E)-H(15E)	120.4
C(16E)-C(15E)-H(15E)	120.4
C(17E)-C(16E)-C(15E)	120.0(3)
C(17E)-C(16E)-N(1E)	117.0(3)
C(15E)-C(16E)-N(1E)	122.9(3)
C(18E)-C(17E)-C(16E)	120.7(3)
C(18E)-C(17E)-H(17E)	119.6
C(16E)-C(17E)-H(17E)	119.6
C(17E)-C(18E)-C(13E)	119.2(3)
C(17E)-C(18E)-H(18E)	120.4
C(13E)-C(18E)-H(18E)	120.4
O(9E)-C(19E)-N(1E)	122.5(3)
O(9E)-C(19E)-C(20E)	122.6(3)
N(1E)-C(19E)-C(20E)	114.9(3)
C(19E)-C(20E)-H(20M)	109.5
C(19E)-C(20E)-H(20N)	109.5
H(20M)-C(20E)-H(20N)	109.5
C(19E)-C(20E)-H(20O)	109.5
H(20M)-C(20E)-H(20O)	109.5
H(20N)-C(20E)-H(20O)	109.5
C(1E)-O(1E)-C(4E)	109.2(2)
C(1E)-O(2E)-C(7E)	110.1(2)
C(2E)-O(3E)-C(7E)	107.9(2)
C(3E)-O(4E)-S(1E)	118.72(18)
C(10E)-O(5E)-C(5E)	107.3(2)
C(10E)-O(6E)-C(6E)	106.7(2)
C(19E)-N(1E)-C(16E)	126.7(3)
C(19E)-N(1E)-H(1E1)	116.7
C(16E)-N(1E)-H(1E1)	116.7
O(7E)-S(1E)-O(8E)	120.64(15)
O(7E)-S(1E)-O(4E)	109.73(13)

O(8E)-S(1E)-O(4E)	102.70(13)
O(7E)-S(1E)-C(13E)	109.74(14)
O(8E)-S(1E)-C(13E)	108.79(15)
O(4E)-S(1E)-C(13E)	103.80(13)
O(2F)-C(1F)-O(1F)	111.9(2)
O(2F)-C(1F)-C(2F)	105.8(2)
O(1F)-C(1F)-C(2F)	107.5(2)
O(2F)-C(1F)-H(1F)	110.5
O(1F)-C(1F)-H(1F)	110.5
C(2F)-C(1F)-H(1F)	110.5
O(3F)-C(2F)-C(1F)	103.3(2)
O(3F)-C(2F)-C(3F)	108.1(2)
C(1F)-C(2F)-C(3F)	102.8(2)
O(3F)-C(2F)-H(2F)	113.8
C(1F)-C(2F)-H(2F)	113.8
C(3F)-C(2F)-H(2F)	113.8
O(4F)-C(3F)-C(2F)	113.6(2)
O(4F)-C(3F)-C(4F)	109.6(2)
C(2F)-C(3F)-C(4F)	101.4(2)
O(4F)-C(3F)-H(3F)	110.6
C(2F)-C(3F)-H(3F)	110.6
C(4F)-C(3F)-H(3F)	110.6
O(1F)-C(4F)-C(5F)	108.1(3)
O(1F)-C(4F)-C(3F)	101.4(2)
C(5F)-C(4F)-C(3F)	118.7(3)
O(1F)-C(4F)-H(4F)	109.4
C(5F)-C(4F)-H(4F)	109.4
C(3F)-C(4F)-H(4F)	109.4
O(5F)-C(5F)-C(4F)	110.4(3)
O(5F)-C(5F)-C(6F)	104.5(3)
C(4F)-C(5F)-C(6F)	113.7(3)
O(5F)-C(5F)-H(5F)	109.3
C(4F)-C(5F)-H(5F)	109.3
C(6F)-C(5F)-H(5F)	109.3
O(6F)-C(6F)-C(5F)	103.9(3)
O(6F)-C(6F)-H(6F1)	111.0
C(5F)-C(6F)-H(6F1)	111.0
O(6F)-C(6F)-H(6F2)	111.0
C(5F)-C(6F)-H(6F2)	111.0
H(6F1)-C(6F)-H(6F2)	109.0
O(3F)-C(7F)-O(2F)	105.5(2)
O(3F)-C(7F)-C(8F)	108.7(3)
O(2F)-C(7F)-C(8F)	109.0(3)
O(3F)-C(7F)-C(9F)	111.0(3)
O(2F)-C(7F)-C(9F)	108.6(3)
C(8F)-C(7F)-C(9F)	113.7(3)
C(7F)-C(8F)-H(8F1)	109.5
C(7F)-C(8F)-H(8F2)	109.5
H(8F1)-C(8F)-H(8F2)	109.5
C(7F)-C(8F)-H(8F3)	109.5
H(8F1)-C(8F)-H(8F3)	109.5
H(8F2)-C(8F)-H(8F3)	109.5
C(7F)-C(9F)-H(9F1)	109.5
C(7F)-C(9F)-H(9F2)	109.5
H(9F1)-C(9F)-H(9F2)	109.5
C(7F)-C(9F)-H(9F3)	109.5
H(9F1)-C(9F)-H(9F3)	109.5

H(9F2)-C(9F)-H(9F3)	109.5
O(6F)-C(10F)-O(5F)	105.1(3)
O(6F)-C(10F)-C(12F)	109.6(3)
O(5F)-C(10F)-C(12F)	107.7(3)
O(6F)-C(10F)-C(11F)	111.3(3)
O(5F)-C(10F)-C(11F)	110.0(3)
C(12F)-C(10F)-C(11F)	112.7(3)
C(10F)-C(11F)-H(11P)	109.5
C(10F)-C(11F)-H(11Q)	109.5
H(11P)-C(11F)-H(11Q)	109.5
C(10F)-C(11F)-H(11R)	109.5
H(11P)-C(11F)-H(11R)	109.5
H(11Q)-C(11F)-H(11R)	109.5
C(10F)-C(12F)-H(12P)	109.5
C(10F)-C(12F)-H(12Q)	109.5
H(12P)-C(12F)-H(12Q)	109.5
C(10F)-C(12F)-H(12R)	109.5
H(12P)-C(12F)-H(12R)	109.5
H(12Q)-C(12F)-H(12R)	109.5
C(14F)-C(13F)-C(18F)	121.3(3)
C(14F)-C(13F)-S(1F)	121.1(2)
C(18F)-C(13F)-S(1F)	117.4(2)
C(13F)-C(14F)-C(15F)	119.5(3)
C(13F)-C(14F)-H(14F)	120.3
C(15F)-C(14F)-H(14F)	120.3
C(14F)-C(15F)-C(16F)	119.5(3)
C(14F)-C(15F)-H(15F)	120.3
C(16F)-C(15F)-H(15F)	120.3
C(17F)-C(16F)-C(15F)	120.1(3)
C(17F)-C(16F)-N(1F)	115.8(3)
C(15F)-C(16F)-N(1F)	124.0(3)
C(18F)-C(17F)-C(16F)	120.2(3)
C(18F)-C(17F)-H(17F)	119.9
C(16F)-C(17F)-H(17F)	119.9
C(17F)-C(18F)-C(13F)	119.4(3)
C(17F)-C(18F)-H(18F)	120.3
C(13F)-C(18F)-H(18F)	120.3
O(9F)-C(19F)-N(1F)	121.4(3)
O(9F)-C(19F)-C(20F)	124.5(3)
N(1F)-C(19F)-C(20F)	114.1(3)
C(19F)-C(20F)-H(20P)	109.5
C(19F)-C(20F)-H(20Q)	109.5
H(20P)-C(20F)-H(20Q)	109.5
C(19F)-C(20F)-H(20R)	109.5
H(20P)-C(20F)-H(20R)	109.5
H(20Q)-C(20F)-H(20R)	109.5
C(1F)-O(1F)-C(4F)	108.2(2)
C(1F)-O(2F)-C(7F)	109.8(2)
C(7F)-O(3F)-C(2F)	107.8(2)
C(3F)-O(4F)-S(1F)	118.93(18)
C(10F)-O(5F)-C(5F)	107.6(3)
C(10F)-O(6F)-C(6F)	105.7(2)
C(19F)-N(1F)-C(16F)	127.5(3)
C(19F)-N(1F)-H(1F1)	116.2
C(16F)-N(1F)-H(1F1)	116.2
O(7F)-S(1F)-O(8F)	120.23(15)
O(7F)-S(1F)-O(4F)	109.76(13)

O(8F)-S(1F)-O(4F)	103.19(13)
O(7F)-S(1F)-C(13F)	108.44(15)
O(8F)-S(1F)-C(13F)	108.97(15)
O(4F)-S(1F)-C(13F)	105.21(14)

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 06mz009m. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [(h a*)^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(22)	36(1)	19(1)	28(1)	5(1)	0(1)	-8(1)
C(22)	28(2)	27(2)	26(2)	1(1)	3(1)	-6(1)
O(21)	35(1)	30(1)	25(1)	1(1)	3(1)	-11(1)
C(21)	30(2)	36(2)	25(2)	0(1)	2(1)	-10(2)
C(1A)	18(1)	14(1)	33(2)	-5(1)	7(1)	-1(1)
C(2A)	19(1)	21(2)	28(2)	-4(1)	10(1)	-4(1)
C(3A)	15(1)	17(1)	27(2)	-7(1)	9(1)	-1(1)
C(4A)	15(1)	14(1)	26(2)	-8(1)	8(1)	-4(1)
C(5A)	21(1)	18(1)	26(2)	-6(1)	11(1)	-4(1)
C(5E)	20(1)	16(1)	25(1)	-4(1)	7(1)	-4(1)
C(6A)	26(2)	22(2)	28(2)	-3(1)	13(1)	-3(1)
C(7A)	31(2)	26(2)	25(2)	-4(1)	3(1)	1(1)
C(8A)	39(2)	30(2)	67(3)	-10(2)	-18(2)	-4(2)
C(9A)	61(3)	57(3)	32(2)	12(2)	19(2)	28(2)
C(10A)	19(1)	26(2)	23(2)	-1(1)	9(1)	3(1)
C(11A)	25(2)	41(2)	23(2)	-3(1)	11(1)	4(1)
C(12A)	22(2)	29(2)	30(2)	-8(1)	10(1)	-6(1)
C(13A)	12(1)	13(1)	24(1)	-6(1)	6(1)	-3(1)
C(14A)	20(1)	14(1)	27(2)	2(1)	10(1)	-2(1)
C(15A)	19(1)	16(1)	25(1)	4(1)	8(1)	2(1)
C(16A)	14(1)	16(1)	25(1)	-4(1)	9(1)	-1(1)
C(17A)	16(1)	19(1)	23(1)	-1(1)	8(1)	-5(1)
C(18A)	17(1)	18(1)	21(1)	1(1)	9(1)	0(1)
C(19A)	19(1)	21(2)	31(2)	4(1)	3(1)	-6(1)
C(20A)	24(2)	26(2)	35(2)	6(1)	-3(1)	-10(1)
O(1A)	20(1)	20(1)	26(1)	-10(1)	6(1)	3(1)
O(2A)	18(1)	33(1)	25(1)	-6(1)	4(1)	-1(1)
O(3A)	26(1)	22(1)	25(1)	-7(1)	3(1)	1(1)
O(4A)	14(1)	19(1)	27(1)	-6(1)	9(1)	-3(1)
O(5A)	23(1)	17(1)	25(1)	-5(1)	4(1)	1(1)
O(6D)	19(1)	36(1)	29(1)	2(1)	10(1)	0(1)
O(6A)	23(1)	21(1)	33(1)	-5(1)	14(1)	-1(1)
O(7A)	16(1)	44(2)	22(1)	-7(1)	8(1)	0(1)
O(8D)	23(1)	39(2)	44(2)	19(1)	14(1)	9(1)
O(8C)	23(1)	35(1)	28(1)	-3(1)	8(1)	-11(1)
O(8A)	21(1)	25(1)	36(1)	-14(1)	13(1)	-7(1)
O(9A)	34(1)	17(1)	37(1)	3(1)	-10(1)	-5(1)
N(1A)	16(1)	15(1)	26(1)	2(1)	4(1)	1(1)
S(1A)	14(1)	20(1)	22(1)	-6(1)	7(1)	-3(1)

C(1B)	19(1)	36(2)	23(2)	-3(1)	6(1)	-6(1)
C(2B)	17(1)	35(2)	21(1)	-3(1)	5(1)	-6(1)
C(3B)	15(1)	34(2)	21(1)	1(1)	4(1)	-1(1)
C(4B)	18(1)	35(2)	24(2)	0(1)	7(1)	-5(1)
C(5B)	29(2)	36(2)	21(2)	-2(1)	11(1)	-8(1)
C(6B)	41(2)	38(2)	23(2)	-6(1)	10(2)	-11(2)
C(7B)	19(2)	45(2)	30(2)	0(2)	1(1)	-7(2)
C(8B)	33(2)	85(4)	28(2)	-12(2)	9(2)	-19(2)
C(9B)	28(2)	53(3)	65(3)	18(2)	-8(2)	-2(2)
C(10B)	25(2)	42(2)	20(2)	-7(1)	9(1)	-7(1)
C(11B)	31(2)	87(4)	26(2)	0(2)	12(2)	10(2)
C(12B)	27(2)	55(3)	30(2)	-10(2)	12(1)	-4(2)
C(13B)	14(1)	36(2)	23(2)	3(1)	7(1)	-4(1)
C(14B)	16(1)	33(2)	36(2)	6(2)	6(1)	2(1)
C(15B)	18(1)	22(2)	34(2)	-3(1)	10(1)	-2(1)
C(16B)	17(1)	30(2)	21(1)	4(1)	11(1)	1(1)
C(17B)	20(1)	27(2)	24(2)	-2(1)	9(1)	2(1)
C(18B)	22(2)	29(2)	22(1)	-1(1)	10(1)	-3(1)
C(19B)	21(2)	24(2)	28(2)	2(1)	7(1)	2(1)
C(20B)	22(2)	33(2)	32(2)	-4(2)	6(1)	2(1)
O(1B)	23(1)	42(2)	23(1)	-5(1)	8(1)	-11(1)
O(2B)	14(1)	47(2)	28(1)	-5(1)	5(1)	-7(1)
O(3B)	20(1)	46(2)	26(1)	7(1)	-1(1)	-11(1)
O(4B)	15(1)	36(1)	26(1)	3(1)	8(1)	-3(1)
O(5B)	33(1)	34(1)	21(1)	0(1)	-1(1)	-6(1)
O(6B)	33(1)	42(2)	47(2)	-2(1)	10(1)	-11(1)
O(7B)	24(1)	39(1)	27(1)	-4(1)	10(1)	-4(1)
O(8B)	27(1)	52(2)	35(1)	10(1)	11(1)	0(1)
O(9B)	45(2)	19(1)	42(2)	0(1)	-4(1)	5(1)
N(1B)	18(1)	21(1)	26(1)	-1(1)	8(1)	2(1)
S(1B)	17(1)	34(1)	25(1)	5(1)	7(1)	-2(1)
C(1C)	17(1)	34(2)	31(2)	-9(2)	5(1)	-1(1)
C(2C)	14(1)	28(2)	27(2)	-9(1)	8(1)	-1(1)
C(3C)	15(1)	28(2)	23(1)	-5(1)	5(1)	2(1)
C(4C)	14(1)	34(2)	24(2)	-9(1)	6(1)	-3(1)
C(5C)	21(2)	37(2)	24(2)	-2(1)	10(1)	-3(1)
C(6C)	28(2)	38(2)	24(2)	-9(1)	11(1)	-3(1)
C(7C)	14(1)	45(2)	26(2)	-12(2)	3(1)	-4(1)
C(8C)	19(2)	44(2)	51(2)	-3(2)	1(2)	3(2)
C(9C)	32(2)	60(3)	29(2)	-21(2)	10(2)	-16(2)
C(10C)	21(2)	40(2)	19(1)	-1(1)	8(1)	-4(1)
C(11C)	27(2)	63(3)	22(2)	-1(2)	11(1)	5(2)
C(12C)	21(2)	51(2)	26(2)	3(2)	9(1)	4(2)
C(13C)	12(1)	33(2)	17(1)	-1(1)	3(1)	-5(1)
C(14C)	19(1)	26(2)	18(1)	-3(1)	7(1)	-2(1)
C(15C)	17(1)	22(2)	23(1)	-2(1)	9(1)	1(1)
C(16C)	16(1)	29(2)	19(1)	-1(1)	6(1)	-3(1)
C(17C)	23(2)	24(2)	18(1)	-5(1)	5(1)	-1(1)
C(18C)	21(1)	31(2)	21(2)	1(1)	8(1)	0(1)
C(19C)	16(1)	33(2)	21(1)	-1(1)	5(1)	-4(1)
C(20C)	21(2)	30(2)	26(2)	-1(1)	-1(1)	1(1)
O(1C)	19(1)	39(1)	28(1)	-6(1)	7(1)	-5(1)
O(2C)	16(1)	46(2)	30(1)	-4(1)	5(1)	-7(1)
O(3C)	15(1)	33(1)	24(1)	-10(1)	3(1)	-2(1)
O(4C)	12(1)	29(1)	25(1)	-6(1)	7(1)	-5(1)
O(5C)	24(1)	35(1)	24(1)	-1(1)	-1(1)	-1(1)
O(6C)	26(1)	37(1)	29(1)	-5(1)	13(1)	-8(1)

O(7C)	17(1)	40(1)	19(1)	-7(1)	3(1)	-3(1)
N(1C)	17(1)	31(2)	19(1)	-4(1)	1(1)	-7(1)
S(1C)	14(1)	32(1)	18(1)	-3(1)	5(1)	-3(1)
C(1D)	19(2)	43(2)	32(2)	-16(2)	8(1)	-7(1)
C(2D)	18(1)	38(2)	26(2)	-8(1)	7(1)	-3(1)
C(3D)	16(1)	32(2)	22(1)	-3(1)	6(1)	1(1)
C(4D)	12(1)	41(2)	22(2)	-2(1)	6(1)	-1(1)
C(5D)	18(1)	37(2)	20(1)	1(1)	8(1)	2(1)
C(6D)	20(2)	39(2)	22(2)	-2(1)	6(1)	1(1)
C(7D)	20(2)	75(3)	22(2)	-5(2)	5(1)	-13(2)
C(8D)	28(2)	82(4)	53(3)	17(3)	-5(2)	3(2)
C(9D)	39(2)	120(5)	31(2)	-33(3)	13(2)	-20(3)
C(10D)	18(1)	36(2)	22(2)	2(1)	9(1)	4(1)
C(11D)	23(2)	41(2)	21(2)	1(1)	8(1)	2(1)
C(12D)	21(2)	46(2)	32(2)	9(2)	12(1)	6(2)
C(13D)	11(1)	34(2)	24(2)	6(1)	6(1)	-1(1)
C(14D)	17(1)	29(2)	24(2)	1(1)	8(1)	-2(1)
C(15D)	14(1)	22(2)	29(2)	5(1)	8(1)	3(1)
C(16D)	15(1)	25(2)	25(2)	5(1)	7(1)	0(1)
C(17D)	18(1)	29(2)	28(2)	0(1)	10(1)	2(1)
C(18D)	17(1)	28(2)	34(2)	8(1)	12(1)	6(1)
C(19D)	17(1)	27(2)	26(2)	2(1)	4(1)	2(1)
C(20D)	24(2)	23(2)	37(2)	-7(1)	-2(1)	5(1)
O(1D)	21(1)	41(1)	24(1)	-5(1)	7(1)	-5(1)
O(2D)	17(1)	54(2)	28(1)	-5(1)	6(1)	-5(1)
O(3D)	21(1)	62(2)	24(1)	0(1)	3(1)	-8(1)
O(4D)	13(1)	37(1)	25(1)	0(1)	9(1)	0(1)
O(5D)	23(1)	34(1)	22(1)	1(1)	3(1)	3(1)
O(7D)	18(1)	55(2)	23(1)	2(1)	7(1)	1(1)
O(9D)	31(1)	17(1)	39(1)	-1(1)	-4(1)	1(1)
O(10D)	26(1)	29(1)	31(1)	-4(1)	1(1)	-2(1)
N(1D)	16(1)	20(1)	30(1)	0(1)	6(1)	-3(1)
S(1D)	14(1)	38(1)	24(1)	5(1)	8(1)	3(1)
C(1E)	15(1)	21(2)	30(2)	-1(1)	5(1)	0(1)
C(2E)	16(1)	26(2)	27(2)	1(1)	9(1)	-2(1)
C(3E)	14(1)	18(1)	26(1)	-1(1)	4(1)	0(1)
C(4E)	14(1)	16(1)	25(1)	-1(1)	5(1)	0(1)
C(6E)	24(2)	18(1)	25(2)	0(1)	7(1)	-3(1)
C(7E)	20(2)	30(2)	23(2)	2(1)	3(1)	-2(1)
C(8E)	26(2)	35(2)	42(2)	-6(2)	2(2)	-9(2)
C(9E)	37(2)	64(3)	33(2)	20(2)	12(2)	11(2)
C(10E)	18(1)	20(1)	20(1)	1(1)	7(1)	4(1)
C(11E)	34(2)	63(3)	30(2)	-8(2)	19(2)	-14(2)
C(12E)	21(2)	26(2)	31(2)	0(1)	10(1)	-6(1)
C(13E)	11(1)	18(1)	24(1)	-3(1)	6(1)	0(1)
C(14E)	17(1)	14(1)	26(1)	2(1)	9(1)	-3(1)
C(15E)	14(1)	19(1)	24(1)	1(1)	8(1)	-3(1)
C(16E)	14(1)	12(1)	24(1)	-2(1)	8(1)	1(1)
C(17E)	18(1)	14(1)	33(2)	4(1)	10(1)	2(1)
C(18E)	15(1)	13(1)	38(2)	1(1)	10(1)	-1(1)
C(19E)	14(1)	20(1)	26(2)	0(1)	6(1)	3(1)
C(20E)	17(1)	27(2)	31(2)	2(1)	4(1)	1(1)
O(1E)	22(1)	19(1)	28(1)	0(1)	6(1)	7(1)
O(2E)	14(1)	36(1)	31(1)	-3(1)	3(1)	3(1)
O(3E)	18(1)	28(1)	25(1)	-4(1)	3(1)	2(1)
O(4E)	14(1)	17(1)	31(1)	-4(1)	8(1)	-3(1)
O(5E)	27(1)	13(1)	28(1)	0(1)	-3(1)	-1(1)

O(6E)	19(1)	17(1)	37(1)	2(1)	8(1)	1(1)
O(7E)	20(1)	30(1)	26(1)	-3(1)	7(1)	-2(1)
O(8E)	23(1)	24(1)	41(1)	-14(1)	12(1)	-5(1)
O(9E)	26(1)	14(1)	36(1)	-1(1)	-4(1)	-1(1)
N(1E)	17(1)	13(1)	25(1)	3(1)	6(1)	1(1)
S(1E)	14(1)	19(1)	25(1)	-5(1)	7(1)	-3(1)
C(1F)	14(1)	17(1)	31(2)	-1(1)	6(1)	2(1)
C(2F)	12(1)	17(1)	27(2)	1(1)	4(1)	0(1)
C(3F)	14(1)	10(1)	30(2)	0(1)	6(1)	5(1)
C(4F)	19(1)	14(1)	30(2)	-1(1)	8(1)	0(1)
C(5F)	24(2)	19(2)	33(2)	-1(1)	11(1)	1(1)
C(6F)	38(2)	22(2)	34(2)	4(1)	15(2)	5(1)
C(7F)	14(1)	25(2)	28(2)	2(1)	4(1)	3(1)
C(8F)	19(2)	39(2)	50(2)	-3(2)	2(2)	-9(2)
C(9F)	31(2)	51(2)	35(2)	12(2)	11(2)	17(2)
C(10F)	25(2)	36(2)	24(2)	5(1)	10(1)	7(1)
C(11F)	27(2)	61(3)	27(2)	6(2)	12(1)	9(2)
C(12F)	29(2)	49(2)	31(2)	4(2)	13(2)	0(2)
C(13F)	13(1)	18(1)	26(2)	1(1)	4(1)	3(1)
C(14F)	21(1)	12(1)	27(2)	2(1)	12(1)	0(1)
C(15F)	19(1)	14(1)	28(2)	-6(1)	10(1)	-2(1)
C(16F)	17(1)	15(1)	26(2)	-4(1)	9(1)	0(1)
C(17F)	19(1)	18(1)	33(2)	4(1)	6(1)	-1(1)
C(18F)	16(1)	16(1)	38(2)	-1(1)	4(1)	-1(1)
C(19F)	22(2)	22(2)	25(2)	-8(1)	10(1)	-7(1)
C(20F)	23(2)	39(2)	25(2)	-5(2)	4(1)	-3(1)
O(1F)	22(1)	17(1)	31(1)	-1(1)	9(1)	8(1)
O(2F)	13(1)	28(1)	34(1)	-3(1)	5(1)	4(1)
O(3F)	16(1)	20(1)	26(1)	0(1)	3(1)	3(1)
O(4F)	17(1)	14(1)	35(1)	2(1)	8(1)	1(1)
O(5F)	27(1)	20(1)	29(1)	1(1)	0(1)	4(1)
O(6F)	31(1)	27(1)	37(1)	7(1)	16(1)	12(1)
O(7F)	19(1)	25(1)	28(1)	1(1)	7(1)	5(1)
O(8F)	26(1)	10(1)	44(1)	-7(1)	9(1)	2(1)
O(9F)	36(1)	24(1)	32(1)	-1(1)	3(1)	-4(1)
N(1F)	19(1)	15(1)	27(1)	0(1)	7(1)	1(1)
S(1F)	16(1)	15(1)	28(1)	0(1)	6(1)	3(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for 06mz009m.

	x	y	z	U(eq)
H(22)	9094	5966	8180	46
H(22A)	7940	6315	7496	43
H(22B)	8471	5753	7229	43
H(22C)	8471	6693	7131	43
H(21)	4028	4644	3292	48
H(21A)	2841	4754	2571	48
H(21B)	3529	4415	2336	48
H(21C)	3287	5332	2246	48
H(1A)	5727	4578	-957	26
H(2A)	6555	3763	-1258	26
H(3A)	7059	3400	-249	23
H(4A)	5548	2619	-408	22
H(5A)	5698	2985	592	25
H(5E)	5726	6440	10376	24
H(6A1)	6394	1898	1003	29
H(6A2)	6506	1745	361	29
H(8A1)	4386	2302	-2235	81
H(8A2)	3783	2952	-2136	81
H(8A3)	4300	2418	-1585	81
H(9A1)	5448	4152	-2203	74
H(9A2)	4508	4045	-2527	74
H(9A3)	5117	3401	-2626	74
H(11A)	6805	2825	1762	44
H(11B)	7334	3610	1960	44
H(11C)	7752	2756	2068	44
H(12A)	8634	3288	1499	40
H(12B)	8143	4094	1295	40
H(12C)	8249	3493	802	40
H(14A)	8376	1334	336	24
H(15A)	9495	1573	1166	24
H(17A)	9904	3621	407	22
H(18A)	8764	3389	-426	22
H(20A)	11980	3517	2077	47
H(20B)	11529	2880	2354	47
H(20C)	11446	3806	2469	47
H(1A1)	10701	2320	1576	23
H(1B)	9384	5078	6036	31
H(2B)	8575	4346	6425	30
H(3B)	7949	3819	5471	29
H(4B)	9441	3051	5553	31
H(5B)	9130	3371	4513	34
H(6B1)	8618	2153	4311	41
H(6B2)	8313	2170	4883	41
H(8B1)	9819	4784	7303	73
H(8B2)	10768	4674	7541	73
H(8B3)	10213	4087	7765	73
H(9B1)	10754	2864	7365	82
H(9B2)	11347	3437	7171	82
H(9B3)	10740	2879	6684	82
H(11D)	7818	3984	3260	70

H(11E)	7406	3141	3052	70
H(11F)	8317	3186	3476	70
H(12D)	6529	3701	4156	55
H(12E)	6319	3484	3461	55
H(12F)	6710	4325	3705	55
H(14B)	6871	1506	5234	34
H(15B)	5770	1456	4359	29
H(17B)	5179	3717	4640	28
H(18B)	6308	3791	5506	28
H(20D)	3016	2736	3164	44
H(20E)	3619	2161	2983	44
H(20F)	3457	3038	2710	44
H(1B1)	4579	1967	3792	26
H(1C)	9279	8260	5815	33
H(2C)	8548	7417	6224	28
H(3C)	7947	7094	5202	26
H(4C)	9410	6251	5288	29
H(5C)	9175	6648	4273	32
H(6C1)	8520	5518	3933	35
H(6C2)	8355	5425	4563	35
H(8C1)	10801	6160	6376	61
H(8C2)	10781	5985	7038	61
H(8C3)	11339	6675	6930	61
H(9C1)	10659	7692	7406	61
H(9C2)	10101	7009	7525	61
H(9C3)	9708	7776	7143	61
H(11G)	8178	6501	3174	55
H(11H)	7697	7315	2985	55
H(11I)	7239	6485	2820	55
H(12G)	6286	6940	3371	48
H(12H)	6765	7758	3542	48
H(12I)	6652	7203	4058	48
H(14C)	6277	7185	5337	25
H(15C)	5131	7421	4510	24
H(17C)	5395	5263	3827	27
H(18C)	6543	5030	4650	29
H(20G)	3127	7562	2717	41
H(20H)	3243	6621	2717	41
H(20I)	3709	7182	2395	41
H(1C1)	4238	6065	3396	28
H(1D)	9393	11632	6069	38
H(2D)	8526	10857	6365	33
H(3D)	7994	10425	5372	28
H(4D)	9509	9658	5519	30
H(5D)	9320	10032	4506	30
H(6D1)	8676	8906	4125	33
H(6D2)	8564	8762	4768	33
H(8D1)	10729	9411	6701	89
H(8D2)	10639	9342	7352	89
H(8D3)	11278	9941	7241	89
H(9D1)	10642	11132	7599	95
H(9D2)	10017	10543	7739	95
H(9D3)	9704	11274	7291	95
H(11J)	8221	9829	3352	42
H(11K)	7670	10599	3155	42
H(11L)	7276	9735	3046	42
H(12J)	6374	10230	3619	49

H(12K)	6842	11051	3805	49
H(12L)	6761	10459	4312	49
H(14D)	6184	10273	5617	28
H(15D)	5038	10383	4774	26
H(17D)	5778	8506	4015	30
H(18D)	6916	8405	4855	30
H(20J)	3049	10220	3061	46
H(20K)	3461	9456	2884	46
H(20L)	3585	10312	2634	46
H(1D1)	4395	9025	3649	27
H(1E)	5616	7998	8793	27
H(2E)	6400	7168	8442	27
H(3E)	6984	6813	9456	24
H(4E)	5486	6040	9358	23
H(6E1)	6230	5255	10694	27
H(6E2)	6452	5138	10089	27
H(8E1)	4203	5619	7665	55
H(8E2)	3620	6268	7795	55
H(8E3)	4231	5791	8339	55
H(9E1)	5097	7493	7480	66
H(9E2)	4166	7282	7234	66
H(9E3)	4805	6675	7133	66
H(11M)	7158	7025	11664	60
H(11N)	7579	6185	11867	60
H(11O)	6651	6225	11482	60
H(12M)	8314	6695	10675	39
H(12N)	8598	6438	11366	39
H(12O)	8230	7302	11173	39
H(14E)	8795	6682	9339	22
H(15E)	9932	6758	10197	22
H(17E)	9214	4754	10835	25
H(18E)	8100	4673	9979	26
H(20M)	11968	6113	11813	39
H(20N)	11409	5649	12115	39
H(20O)	11589	6572	12249	39
H(1E1)	10559	5255	11241	22
H(1F)	5627	11343	-973	25
H(2F)	6397	10547	-1349	23
H(3F)	6977	10140	-344	22
H(4F)	5470	9353	-483	25
H(5F)	5688	9677	542	30
H(6F1)	6283	8515	852	36
H(6F2)	6422	8433	213	36
H(8F1)	4186	9026	-2164	57
H(8F2)	3605	9690	-2052	57
H(8F3)	4183	9203	-1498	57
H(9F1)	5126	10909	-2304	58
H(9F2)	4191	10720	-2565	58
H(9F3)	4822	10111	-2675	58
H(11P)	6717	9435	1658	56
H(11Q)	7290	10184	1886	56
H(11R)	7652	9307	1988	56
H(12P)	8619	9749	1415	54
H(12Q)	8205	10604	1324	54
H(12R)	8232	10104	755	54
H(14F)	8754	10051	-368	23
H(15F)	9918	9986	469	24

H(17F)	9292	7771	832	28
H(18F)	8133	7844	1	29
H(20P)	11962	8697	1910	45
H(20Q)	11377	8618	2300	45
H(20R)	11869	9420	2322	45
H(1F1)	10556	8249	1309	24

Table 6. Hydrogen bonds for 06mz009m [Å and deg].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(22)-H(22)...O(9F)#1	0.84	1.82	2.647(3)	166.5
O(21)-H(21)...O(9B)	0.84	1.81	2.650(4)	174.8
N(1A)-H(1A1)...O(22)#1	0.88	1.94	2.793(4)	161.7
N(1B)-H(1B1)...O(9D)#2	0.88	1.96	2.825(4)	167.8
N(1C)-H(1C1)...O(21)	0.88	1.87	2.736(4)	166.8
N(1D)-H(1D1)...O(10D)	0.88	2.04	2.846(4)	151.5
N(1E)-H(1E1)...O(9A)#3	0.88	1.99	2.819(3)	156.7
N(1F)-H(1F1)...O(9E)#4	0.88	2.03	2.879(3)	161.0

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y-1/2,-z+1 #2 x,y-1,z #3 x,y,z+1 #4 x,y,z-1