Carbenoid Insertion Chemistry on Furanose Platforms as a Route to Natural Product Frameworks

By

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Thesis Abstract:

The following describes a successful synthetic pathway to create an analog of the natural product (+)-dihydrocanadensolide from the inexpensive and readily available D-xylose. The pathway will describe protecting group chemistry, an esterification, a diazo transfer reaction, and the key step being a metal-catalyzed intramolecular insertion reaction. The metal catalyst used in this step is rhodium(II) acetate and it will be shown to catalyze the decomposition of a diazoester, thus creating a new carbon-carbon bond by carbenoid insertion chemistry. The end result is a bicyclic compound with a fused furan ring system common to many important and useful natural products.

Acknowledgements

I would like to thank the Youngstown State University Department of Chemistry and the School of Graduate Studies for allowing me to pursue my Master's degree as well as Dr. John Jackson and Dr. Michael Serra for being members of my thesis committee and for giving their time and advice when I needed it. I would also like to say thank you to Dr. Matthias Zeller for all your help with my crystal structures, the glove box, and the NMR. Also, I'd like to thank the entire YSU Chemistry department for all your advice, time, assistance, and mentoring throughout the years. There are too many to thank by name, but I cannot express how grateful I am for all of your never-ending help.

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Introduction

Carbohydrate Background

Carbohydrates have been important to many civilizations, dating back to the ancient Egyptians and their use of grape sugars in the alcoholic fermentation process. The Chinese isolated sucrose from sugarcane and developed recipes for refining it. Carbohydrates have continued to be important through the generations and have remained vital to many aspects of modern life ranging from the food, textile, pharmaceutical and chemical industries.[1] Chemists began synthesizing carbohydrates as early as the 1800s. A German chemist by the name of Emil Fischer, was awarded the Nobel Prize in 1902 for his important work in sugar synthesis. His work, ranging from synthetic strategies of known carbohydrates to studies in fermentation and stereochemistry, enabled other scientists to see the biological importance of carbohydrates.[2]

Carbohydrates are called *saccharides* due to a derivation from the Latin word for sugar, sacchararum, and are classified in three main groups which are named according to the number of single sugar units linked together. The basic units of carbohydrates are *monosaccharides* which are simple sugars consisting of only one unit. *Oligosaccharides* are made up of 2-10 covalently linked monosaccharides, and *polysaccharides* are polymers of many monosaccharides.[3]

Monosaccharides are classified into two main groups according to the chemical nature of their carbonyl group, which can either be an aldehyde as in an aldose sugar such as glucose, or a ketone as in a ketose sugar such as fructose (Figure 1). They are further classified according to the number of carbon atoms in their chains, into three carbon units called trioses, four carbon units called tetroses, pentoses which have five carbons, hexoses which have six carbons, etc.[4]

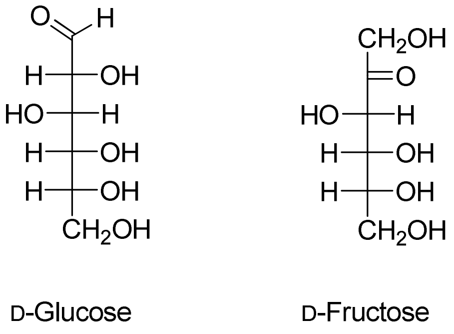


Figure 1: Fischer projections of two monosaccharides, D-glucose and D-fructose.

Figure 1 shows Fischer projections, which are one of three commonly used ways to draw monosaccharides. These projections were developed by Emil Fischer in the early 1900s, and are still used today to represent stereochemistry in chiral sugar molecules. The vertical lines on these figures represent groups pointing away from the viewer, while the horizontal lines point toward the viewer. The configuration about the highest numbered chiral carbon, which in the case of glucose and fructose would be C-5, describes the D and L notation of the sugar. When the hydroxyl is on the right hand side, the sugar is said to be D, while an L sugar has the hydroxyl on the left hand side.[4]

The other two common ways to depict carbohydrates are with Haworth projections, which show that carbohydrates actually exist as cyclic hemiacetals (or cyclic hemiketals in the case of ketoses), and with chair conformations which show the hydroxyl groups in the axial or equatorial positions (Figure 2).

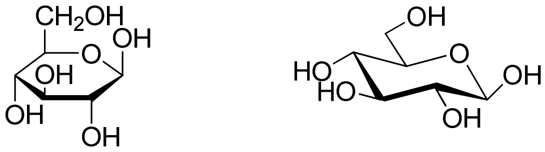


Figure 2: Haworth projection and chair conformation of β-D-glucopyranose.

The linear forms of monosaccharides are less energetically favorable than the cyclic hemiacetal form, and as a result these sugars are known to readily undergo cyclization (Figure 3). The cyclization may either result in a five-membered ring, a furanose, or a six-membered ring, a pyranose. The ring closure mechanism for glucose to form glucopyranose involves a nucleophilic attack of the oxygen atom at C-5 on the carbonyl carbon.[5] To form glucofuranose, the nucleophilic attack this time comes from the oxygen atom at C-4 on the carbonyl carbon. In the hemiacetal form C-1 is sp^2 hybridized and therefore can undergo attack from the top or bottom position to provide a mixture of alpha and beta anomers. The alpha configurations are given to sugars where the hydroxyl group at C-1, the anomeric carbon, is pointing below the plane of the molecule in the axial position. The beta configuration is specified when the hydroxyl group at the anomeric carbon is pointing above the plane in the equatorial position. Interconversion between the alpha and beta anomers (mutarotation) occurs quickly in the presence of an acid or base.[4]

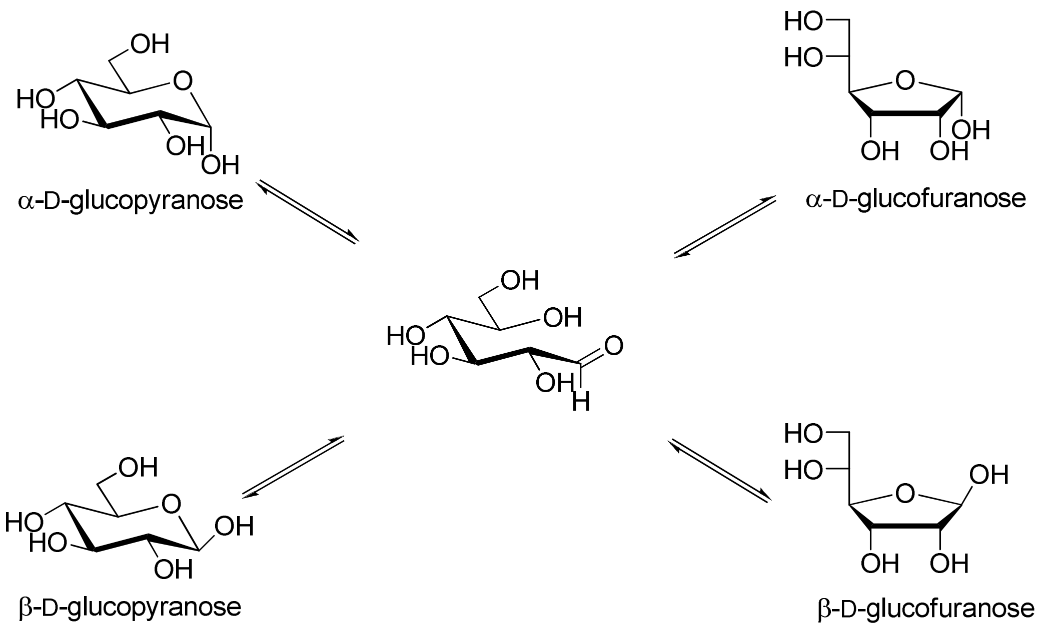
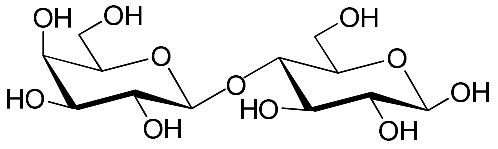


Figure 3: Ring closure of glucose to form the pyranose and furanose forms.

Monosaccharide units may be linked together through glycosidic bonds to form polymers. These bonds are formed when the anomeric hydroxyl group on one sugar condenses with a hydroxyl from another sugar, losing a molecule of water. When monosaccharide units come together in this way, they form oligosaccharides and polysaccharides.[6] Lactose (milk sugar) is an example of a disaccharide, or an oligosaccharide, which is comprised of a D-galactose and a D-glucose unit (Figure 4).



β-D-Galactopyranosyl-(1→ 4)-α-D-Glucopyranose

Figure 4: Lactose.

Oligosaccharides have been found to have a tremendous amount of biological importance, with roles ranging from cell differentiation to disease regulation.[7] Some other notable roles include hormonal activities, cell proliferation, cell-cell interactions and immune responses.[5,8] Due to the fact that carbohydrates have been found to be crucial to life processes and indispensible to many important industries, they have been extensively studied and recognized for their potential use in pharmaceuticals.

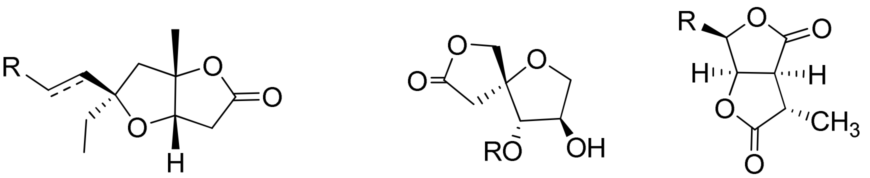
Natural Product Synthesis

Natural product synthesis involves reconstructing complex molecules normally found in biological systems, in a laboratory environment. Natural products have important biomedical and pharmacotherapeutic purposes and are used in antibacterial, antitumor, herbicidal and fungicidal agents, in addition to many others.[9] Because of the vast array of important uses, there is a desire to obtain relatively large quantities of these substances. The ability to synthesize these compounds in the laboratory enables large-scale production that may be cheaper and faster than isolating the product from its natural source. Another important reason to create natural products is that the type of chemistry required to create these large, stereo complex molecules requires a lot of careful retrosynthetic planning, for example, the order of reactions must be carefully planned as well as the use of appropriate protecting groups.[10] Often, these retrosynthetic analyses lead back to a simple chiral starting material. Carbohydrates, in addition to their well-documented usefulness in biological systems, are also an extremely important source of chiral carbon in natural product synthesis, and have been widely utilized due to the fact that they are commercially available and relatively inexpensive.[11]

The art of natural product synthesis involves using well-known chemistry as well as developing new techniques. Making molecules like these in the lab proves to be very challenging and pushes the limits of normal organic synthesis due to the required high level of regioselective and stereoselective control.[9] Because these molecules are so complex, new types of reactions and reaction sequences must be developed. Once successful syntheses are performed they may be expanded and tested on other systems. Eventually the emphasis shifts from synthesis with the sole intention of obtaining a target molecule, to focusing on particular transformation types, and this is where the most advances in synthetic organic chemistry occur.[12]

Another important result of natural product synthesis is it allows for studying places to introduce different functionalities and properties that may have enhanced biological activities. This is done by synthesizing analogs for *structure activity relationship* (SAR) studies. This type of relationship may be assessed by considering a series of molecules and making gradual changes to them, noting the effect upon their biological activity of each change. This technique is particularly useful to medicinal chemists who insert different functional groups in a target drug molecule and test what effect each modification has.

The structures of several useful natural products have two fused furan rings, which can be difficult to construct. The plakortones, the secosyrins and the canadensolides are three such families of compounds that have been heavily studied and synthesized in the laboratory using a multitude of chemical transformations (Figure 5). Each of these families of natural products belong to a furan-based system. The plakortones and canadensolides have fused rings and the secosyrins have a spiro furan system. Our group is interested in finding chemistry to create these ring backbones. Each of these natural products, although similar in structure have quite different properties. The plakortones have antimalarial properties, the secosyrins are plant pathogens and thus may be used as herbicidal agents, and the canadensolide family has antifungal properties.



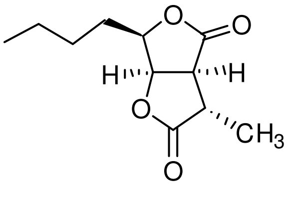
plakortone A, B, D

secosyrins 1, 2

canadensolides

Figure 5: Select natural products with furan-based ring systems.

Our group at Youngstown State University is focusing on the canadensolides, specifically (+)-dihydrocanadensolide (Figure 6), a naturally occurring compound originally isolated from the mold *Penicillium canadense*.[13] The interest in this bicyclic compound lies not only in its biomedical properties, but also in its stereochemical features. Developing a successful synthesis for this compound could potentially lead to important synthetic strategies and transformations, which eventually could be applied to more complex systems.

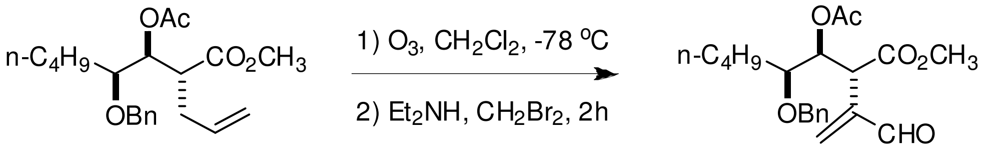


(+)-dihydrocanadensolide

Figure 6: Structure of (+)-dihydrocanadensolide.

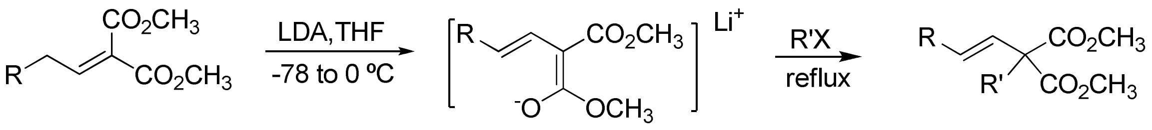
Several groups have successfully completed syntheses of this natural product, however, each of these syntheses have been lengthy and low yielding. Some of the main reaction types include, but are not limited to, α-methylenation, base-induced deconjugative alkylation, imino-Claisen reaction, copper-catalyzed intramolecular cyclopropanation of glycals, aldol-lactonization, and intramolecular radical cyclization.[13-20]

A group from Taiwan investigated the use of α-methylenation in natural product synthesis and completed a total synthesis of (±)-canadensolide using this chemistry as their key step. This involved introducing a methylene group by first completing an ozonolysis of a mono-substituted alkene, and subsequently treating the product with dibromomethane and diethylamine (Equation 1). To construct the two-ring system, the group first used an acid-catalyzed cyclization of the methyl acrylate in methanol to form the first furan ring, followed by a $SnCl_4$ debenzylation leading to the second ring.[13]



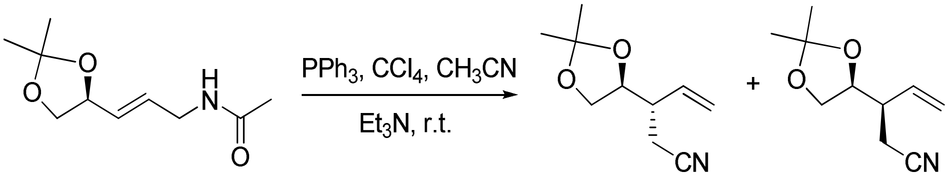
Equation 1: α-Methylenation.

Another group showed that conjugated olefinic esters may undergo stereospecific base-induced deconjugation and alkylation to form an alkenoate, which may then be converted into canadensolide. The mechanism has been proposed to go through a *trans* intermediate, even though the *cis* form is more stable, due to steric hindrance between the alkyl group and the methoxycarbonyl groups of the *cis* intermediate (Scheme 1). This product then went through hydrolysis, iodolactonization, and finally, introduction of the methylene and demethoxycarbonyl groups in the last step.[14]



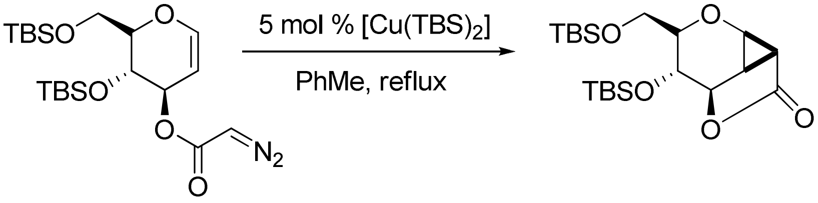
Scheme 1: Base-induced deconjugative alkylation.

The iminoketene-Claisen reaction was used by another group to form a crucial carbon-carbon bond in the asymmetric synthesis of (+)-canadensolide (Equation 2). The Claisen rearrangement has been used for 1,3 chirality transfer, and the imino-Claisen reaction uses mild reaction conditions that preserve the integrity of all the chiral centers in this natural product. This reaction involves an iminoketene intermediate which spontaneously rearranges and forms two diastereomeric nitriles in a 1:1 ratio (Equation 2). Following this reaction, base-catalyzed cyclization was used to form the first lactone ring. The second lactone ring was formed by ozonolysis followed by a reductive workup.[15]



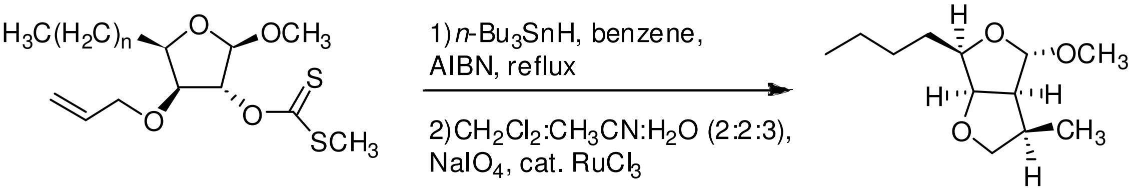
Equation 2: Iminoketene-Claisen reaction.

Another method of forming carbon-carbon bonds with the ultimate goal of forming bislactone rings was developed by a group at the University of Texas. The key step in their reaction sequence involved using glycal diazoesters in a copper-catalyzed intramolecular cyclopropanation reaction (Equation 3).[16]



Equation 3: Copper-catalyzed intramolecular cyclopropanation.

An intramolecular radical cyclization strategy was employed by another group. This group used D-xylose as a chiral starting material and built their structure on the furanose platform. The key carbon-carbon bond forming step used *n*-Bu_3SnH and AIBN in benzene, followed by oxidation to produce the lactone ring (Equation 4).[17]



Equation 4: Intramolecular radical cyclization.

Our group intends to create an analog of (+)-dihydrocanadensolide, beginning with D-xylose. The key step in our synthesis is regio-, and possibly stereoselective, C-C bond formation through intramolecular carbenoid insertion chemistry using rhodium(II) acetate as the catalyst. This method will be described in detail in the following sections.

Protecting Groups

The starting material in our synthesis, D-xylose, is a monosaccharide that is rich in both chirality and functionality. Due to the fact that even single-unit carbohydrates are so complex, a need arises to ensure that the chemistry that transforms one part of the molecule does not affect the rest of the structure. Protecting groups are introduced onto functional groups, thus hiding parts of the compound from the experimental conditions, and allowing access only to a specific area. There are many different types of protecting groups, each masking a certain functional group under specific reaction conditions.[21]

In our synthesis of (+)-dihydrocanadensolide, the starting material has numerous reactive hydroxyl groups which need to have their reactivities blocked. The lone electron pairs on oxygen make the groups nucleophilic and they will readily react with electrophilic reagents. Two different protecting groups will be used to protect the numerous hydroxyl groups on the starting material; the isopropylidene and the trityl group. The reasoning behind the choice of the isopropylidene protecting group was twofold; it protects both hydroxyl groups on the C-1 and C-2 carbons as well as locking D-xylose into its furanose form. The second protecting group, a trityl ether, will be used to protect the hydroxyl group at C-5 (Figure 7). With both of these protecting groups in place, the only hydroxyl group still remaining at C-3 can participate in the desired chemistry.

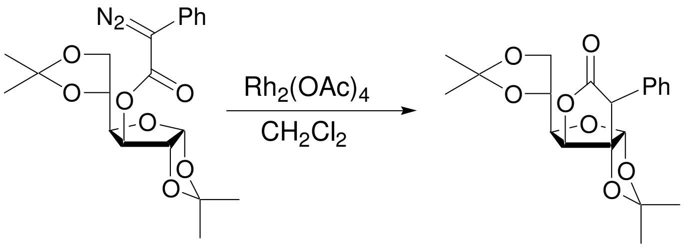
1,2-*O*-isopropylidene-D-xylofuranose 1,2-*O*-isopropylidene-5-*O*-trityl-D-xylofuranose

Figure 7: Use of various protecting groups on D-xylose.

Branched-Chain Carbohydrates

Branched-chain carbohydrates are sugars that have a carbon substituent directly attached to a non-terminal carbon.[22] They have been previously synthesized by a wide variety of procedures using, but not limited to, epoxides, 1,4-conjugate addition, Grignard reagents (1,2-addition), Wittig reagents and radical chemistry.[23]

Our group's focus is on a metal-catalyzed intramolecular insertion reaction. The goal is to create (+)-dihydrocanadensolide by C-C bond formation through intramolecular carbenoid insertion chemistry. This particular method seems to be underutilized, with the only reported success coming from our group.[24-26] The chemistry reported previously used the doubly protected diacetone-D-glucose, and demonstrated rhodium-catalyzed decomposition of a diazocarbonyl creating a carbenoid, which preferentially inserted at the C-H bond at the C-2 position creating two fused five-membered rings (Equation 5).[24]

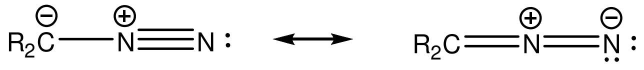


Equation 5: Rhodium(II) acetate-catalyzed insertion on a glucofuranose scaffold.

This project will utilize methods previously performed on the glucofuranose platform and apply them to the readily available, inexpensive monosaccharide, D-xylose.

Diazocarbonyl Compounds

Diazo compounds contain two nitrogen atoms joined together with the general formula $R_2C{=}N_2$, which is described as being a resonance hybrid of several linear forms, the most important being pictured below (Figure 8).[27]

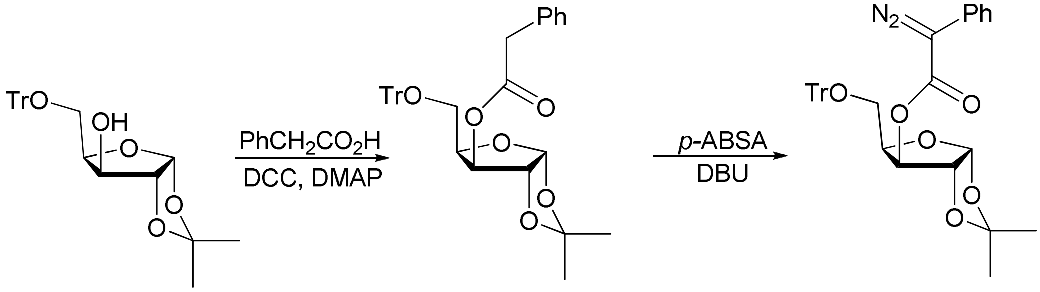


$$R_2\overset{\ominus}{C}-\overset{\oplus}{N}\equiv N: \longleftrightarrow R_2C=\overset{\oplus}{N}=\overset{\ominus}{\ddot{N}}:$$

Figure 8: Resonance forms of a diazo compound.

It is easily observed that the negative charge on the diazo compound is distributed between the carbon and terminal nitrogen. When the diazo compound is an α-diazoketone or α-diazoester, as in our synthesis, it is stabilized even further due to the delocalization of the negative charge into the neighboring carbonyl.

Diazo compounds have been synthesized by several methods, each focusing on the reactivity at the α-methylene position. If this position is sufficiently activated, for example having a carbonyl on either side, the diazo transfer can be carried out using a sulfonyl azide like tosyl azide and a base like triethylamine.[28] If it is only activated by one carbonyl, modifications such as using a stronger base or a different sulfonyl azide may be needed.[29-31] Our synthesis requires these modifications (Scheme 1). After a Steglich esterification on the hydroxyl group at C-3, the diazoester could be formed using *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) as the azide source and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the base (Scheme 2).



Scheme 2: Esterification and diazo transfer reaction.

Formation of the diazoester most likely occurs *via* the proposed mechanism in Figure 9, where -CH_2- is the carbon directly attached to the carbonyl on the ester.[32] R and R’ represent the phenyl group and the rest of the molecule, respectively. DBU first abstracts a proton, giving that carbon negative character, which then becomes associated with the terminal nitrogen on the azide group of *p*-ABSA (Figure 10). Then, because of the electronics of the azide, electrons are transferred through the system, creating the diazoester and releasing the byproduct, a sulfonyl amide.

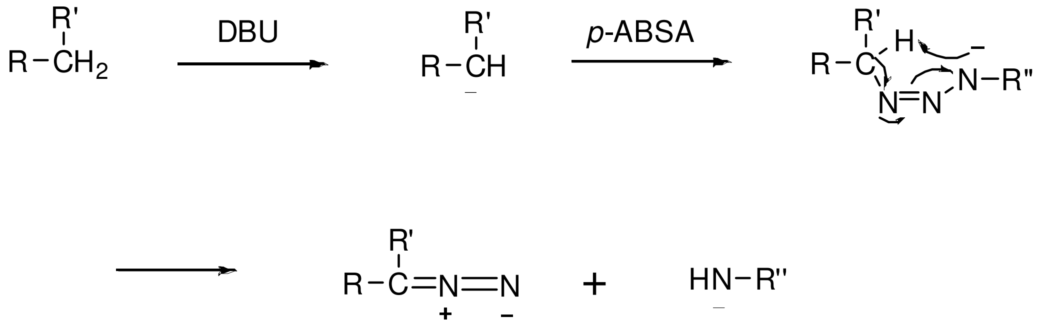
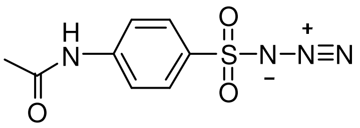


Figure 9: Proposed diazo transfer mechanism.



p-acetamidobenzenesulfonyl azide

Figure 10: Structure of *p*-ABSA.

Diazo carbonyl compounds have been used in many reactions involving metal catalysts and are useful for forming heterocyclic or carbocyclic rings, including cyclopropanation, ylide generation, aromatic cycloaddition and insertion into C-H, N-H, and S-H bonds.[31]

Many different metal catalysts have been used in the past, the most prominent being copper(II) and rhodium(II) used alone, as well as in complexes. Copper(II) was frequently used to facilitate diazo decomposition in many cyclopropanation and ylide formation reactions, and as a side product of these reactions, a C-H insertion would often occur. Rhodium(II) and rhodium(II) complexes have become important catalysts for α-diazo decomposition due to the reaction occurring under milder conditions as well as the preference for regioselective insertion rather than the cyclopropanation or ylide formation which occurred with copper catalysts.[31]

This synthesis will be utilizing rhodium(II) acetate to decompose a diazoester-modified sugar potentially yielding a branched chain sugar. A mechanistic cycle proposed by Doyle shows formation of a metallo-intermediate from an attack of the diazo functional group at the metal. This metal-stabilized carbene is formed by displacement of N_2. The resulting electrophilic carbene then reacts with a substrate that is present (S:); in our reaction the substrate is the C-H bond. This forms the product, concomitantly regenerating the catalyst. The structure of rhodium(II) acetate and the mechanistic cycle are shown below (Figure 11).[31]

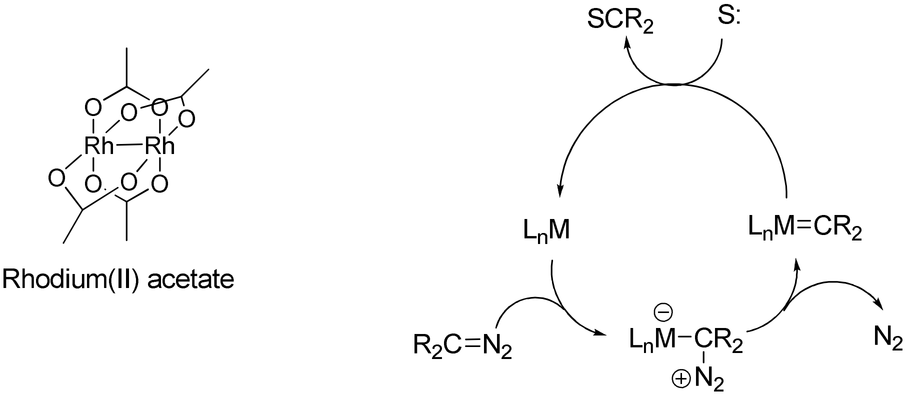
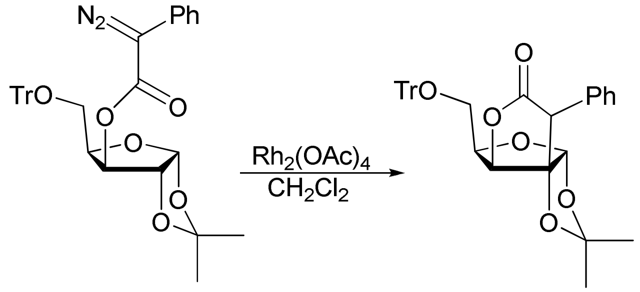
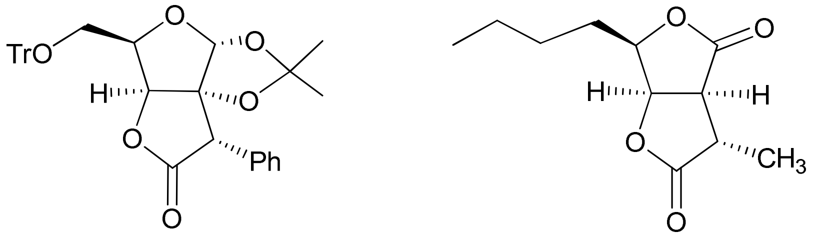


Figure 11: Rhodium(II) acetate and the metal-catalyzed diazo decomposition cycle.

When these reaction conditions are applied to the diazoester compound (Equation 6), the product should be a bicyclic system with fused five-membered lactone rings highly analogous to (+)-dihydrocanadensolide (Figure 12).



Equation 6: Rhodium(II) acetate-catalyzed insertion on a xylofuranose platform.



Insertion product

(+)-dihydrocanadensolide.

Figure 12: Comparison of bicyclic insertion analog to (+)-dihydrocanadensolide.

Comparison of these two compounds shows that the main stereochemical and structural features of the expected insertion product and the natural product are very closely related.

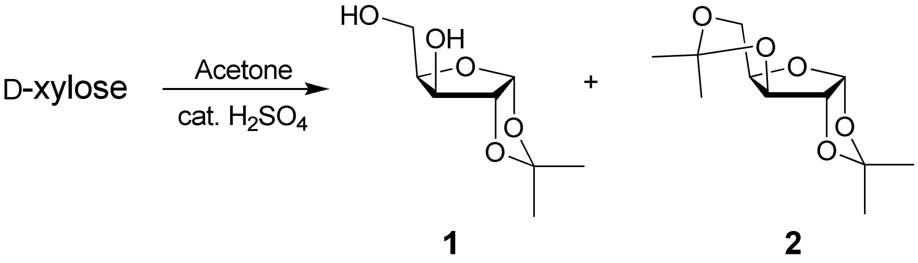
Statement of Problem:

Natural products play many important biomedical and pharmacotherapeutic roles and are used in a multitude of different applications ranging from anti-tumor agents to pesticides. Because they are so useful, there is a desire to obtain relatively large quantities of these substances without the tedious, expensive task of isolating them from their natural sources. Developing synthetic strategies to efficiently and inexpensively synthesize these large, often stereo complex molecules is a difficult but worthwhile task.

Our goal is to synthesize an analog of the natural product (+)-dihydrocanadensolide beginning with the readily available carbohydrate, D-xylose, an inexpensive source of chirality. The canadensolides are a family of compounds containing two lactone rings that have fungicidal properties and may be used in an array of applications. These fused rings could potentially be created by stereospecific C-C bond formation through intramolecular carbenoid insertion chemistry, resulting in two fused five-membered rings.

Results and Discussion

Carbohydrates are a readily available source of chirality and are able to serve as scaffolds for building larger, more stereo complex molecules such as natural products. Because of this, D-xylose was selected here as an inexpensive starting material. In this project, there was a desire to build a lactone ring onto the furanose form of D-xylose. To achieve this, the first step in the synthesis design called for an esterification of one of the hydroxyls. However, this sugar has several chiral centers each featuring a reactive hydroxyl group, so it was necessary to block the ones not planned to be involved in the desired reaction. The best way to control the reactivity of a carbohydrate is through the use of selective temporary protecting groups. Two different protecting groups were chosen to block the sugar and leave only one hydroxyl at C-3 open; these were the isopropylidene and the trityl group. The first of these was the isopropylidene protecting group which serves to protect the hydroxyls at C-1 and C-2 as well as locking the ring in its furanose form. It may be put in place by reacting the parent carbohydrate with acetone and a catalytic amount of sulfuric acid (Equation 7).



Equation 7: Protection of D-xylose with acetone.

When protecting D-xylose in this manner, two products are formed. The first, and desired product is the mono-protected isopropylidine D-xylofuranose (**1**), with the second product (**2**) containing two acetal groups. This reaction is well known, however the ratio of products obtained is dependent upon the workup. The first set of reaction conditions attempted involved dissolving D-xylose in acetone, adding a catalytic amount of sulfuric acid over one hour, and then allowing the reaction to stir for 12 hours before finally neutralizing with sodium hydroxide.[23] After attaining neutral pH, a study of the TLC plate (100% ethyl acetate) showed two non-UV-active spots (R_f = 0.35 and 0.64) that burned at a higher R_f than that of the starting material. The spot representing the starting material remained on the baseline, even after the reaction was allowed to run for 36 hours. After workup and purification by flash column chromatography (3:1 hexanes: ethyl acetate) the desired product (**1**) was isolated as a white solid in 5% yield and the second product (**2**) was obtained as a yellow syrup in 63% yield.

This reaction is in equilibrium and the desired product is thermodynamically favored; it was thought that a milder base would neutralize the reaction over 3 hours and possibly give the mono-protected product more time to form. The reaction was set up under the same conditions as before, except that the solution was neutralized with solid sodium bicarbonate, and allowed to stir for 3 hours. After neutralization, workup and purification as before, **1** was isolated in a 30% yield, **2** formed in a 35% yield, and the remainder was unreacted starting material.

Another reaction was attempted to drive the equilibrium in favor of the products, as the reaction never completely consumed the starting material. This reaction was run under the same conditions and $MgSO_4$ was added to absorb the water and hopefully drive the reaction to completion. As expected, TLC showed consumption of starting material, however it produced the desired product (**1**) in only 20% yield with the major product (**2**) in 76% yield.

The fourth and most successful set of reaction conditions used sodium carbonate as the base.[33] This involved dissolving D-xylose in a solution of acetone and sulfuric acid, partially neutralizing the reaction with a sodium carbonate solution, and allowing it to stir for 2.5 hours. The neutralization was then completed by adding solid sodium carbonate and allowing it to stir overnight. After workup and filtration over silica (30:1 chloroform: methanol), **1** was isolated as a colorless crystal in 79% yield, with **2** being formed as a yellow syrup in 14% yield.

A proton nuclear magnetic resonance spectrum (^{1}H NMR) was taken of the protected sugar, **1**, to prove it was produced. The appearance of two signals at 1.32 and 1.49 ppm are indicative of the methyl protons of the isopropylidene protecting group; moving downfield a broad singlet at 3.46 is the proton from the hydroxyl group at C-3. Next on the spectrum at 4.04 ppm is a multiplet for the two diastereotopic protons found at C-5. At 4.17 ppm a doublet of doublets signifies the proton at C-3 while at 4.32 ppm, an unresolved multiplet exists representing both H-4 and the proton on the remaining hydroxyl group at C-5. A doublet at 4.52 ppm corresponds to H-2 and it shares the same coupling constant of 3.68 Hz as the proton at C-3. Finally, a doublet at 5.98 ppm belongs to the proton at C-1. This shift is due to the proton being attached to the anomeric carbon which is itself attached to two electronegative oxygen atoms. A COSY NMR experiment ensured the proper assignment of protons in the ^{1}H NMR spectrum.

The ^{13}C spectrum of **1** shows two signals at 26.17 and 26.75 ppm for the methyl groups on the isopropylidene protecting groups, and peaks at 60.91, 76.61, 79.01, 85.59, and 104.83 ppm correlate to the carbons C-1 through C-5 on the sugar and at 104.83 ppm for the anomeric carbon. The remaining peak at 111.83 ppm corresponds to the quaternary carbon of the protecting group. Mass spectrometry shows a peak with an M^+ of 213.1, which is indicative of the addition of a sodium atom to the calculated molecular mass of 190.19. X-ray crystallography data supports the formation of the compound. (Figure 13).

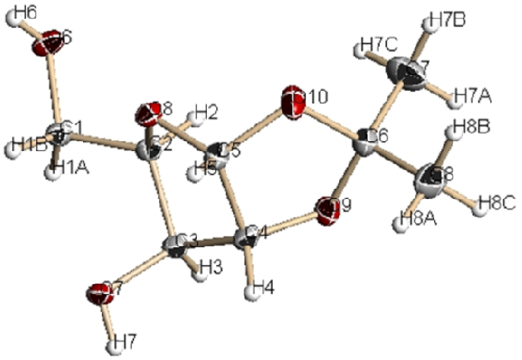
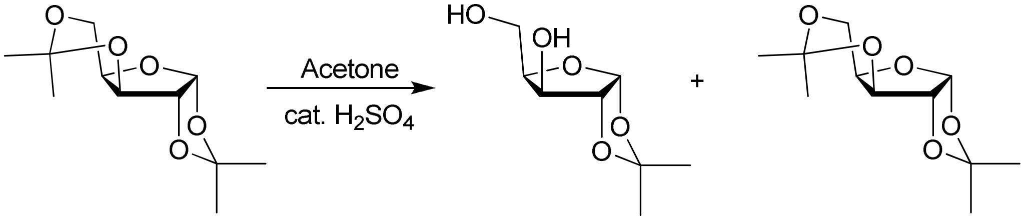


Figure 13: X-Ray crystal structure of 1,2-*O*-isopropylidene-α-D-xylofuranose **1**.

To prove that compound **2** was formed, NMR spectra of the yellow syrup were analyzed. Investigation of the ^{1}H NMR spectrum indicated the presence of two isopropylidene protecting groups by showing four peaks at 1.32, 1.38, 1.44, and 1.49 ppm. Analysis of the ^{13}C NMR spectrum also provided evidence for the formation of **2** by presenting four signals at 18.71, 26.18, 26.75 and 28.89 ppm for the methyl carbons on the two protecting groups, with two signals at 105.23 and 111.60 representing the quaternary carbons of the isopropylidene protecting groups. ESI mass spectrometric analysis provided an M^+ of 253.2, which corresponds to the calculated molecular mass of 230.12 with the addition of a sodium atom.

It was determined that **2** could be reacted under the same conditions to yield **1** in 83% yield, with the remainder of the yield being **2** (Equation 8). This resulted in **1** being isolated in an overall yield of 90% after both reactions.



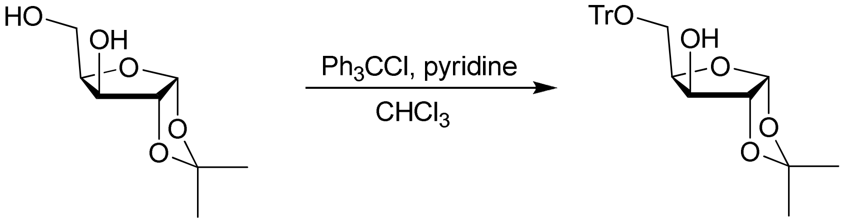
2 **1** **2**

Equation 8: Reaction of **2** to yield additional **1**.

Once the isopropylidene protecting group was successfully in place, two hydroxyl sites remained. One of these must be protected to prevent both nucleophilic oxygens from reacting with the electrophilic esterifying reagent that will be added in the next step. The primary hydroxyl at C-5 may be selectively protected which would deactivate this nucleophilic behavior. The protecting group chosen for this task was the trityl group, and it was selected because it rotates rapidly about the O-CPh_3 which sweeps out a large volume around the oxygen atom to prevent the approach of electrophiles.[21] Also, because triphenylmethyl chloride is hindered, it selectively reacts with primary alcohols resulting in the protection of only the hydroxyl at C-5.

To protect the hydroxyl at C-5, 1.0 eq. of triphenylmethyl chloride dissolved in chloroform was reacted with **1** in pyridine, at room temperature for 12 hours.[34]

Examination of the TLC plate (3:1 hexanes: ethyl acetate) after that time showed complete consumption of starting material and the presence of two less polar spots (R_f = 0.31 and 0.81). After workup and purification *via* flash column chromatography (3:1 hexanes: ethyl acetate), **3** was isolated as a white foam in 17% yield (Equation 9).



1 **3**

Equation 9: Trityl protection of 1,2-*O*-isopropylidene-α-D-xylofuranose.

NMR analysis showed the lower of the two spots on the TLC plate corresponded to the product (**3**) and the highest, most non-polar spot was triphenylmethanol. Excess alkylating reagents were needed because water in the reaction system hydrolyzed the triphenylmethyl chloride creating the alcohol byproduct. After increasing the equivalents of triphenylmethyl chloride incrementally to 1.1, 1.5, 2.2, and then 3.0, it was determined that using 3.0 eq. of this reagent produced the best yield of **3** at 91%.

The ^{1}H NMR spectrum showed the appearance of a 15 proton multiplet at 7.34 ppm representing the trityl group. This spectrum showed that the trityl group selectively protected the primary hydroxyl because the signal corresponding to the primary hydroxyl in the spectrum of **1** disappeared while the secondary hydroxyl remained as a broad singlet at 3.24 ppm. The isopropylidene protecting group remained intact throughout this reaction and appeared in the proton spectrum as two signals at 1.32 and 1.49 ppm. A

COSY experiment supported the proper assignment of the carbohydrate ring protons. The product was also confirmed by ^{13}C NMR with new signals appearing in the aromatic region 127.23, 128.01, 128.47, and 143.30 ppm corresponding to 18 carbons. These 4 signals show the symmetry of the phenyl rings of the trityl protecting group.

Mass spectrometry data supports the formation of product **3** due to an M^+ of 455.2, which corresponds to the calculated molecular mass of 432.51 and the presence of sodium. A single crystal was grown *via* vapor diffusion in hexanes and ethyl acetate and crystallography data supports the formation of the tritylated product (Figure 14).

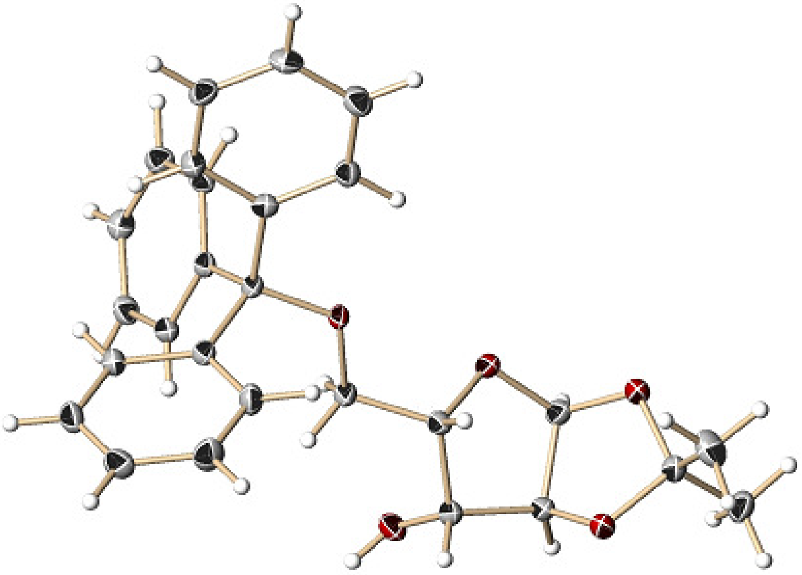
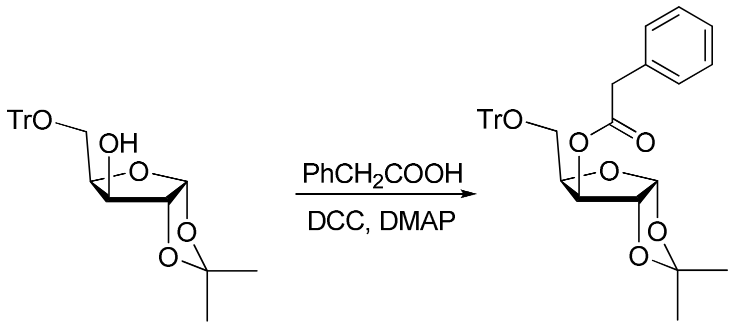


Figure 14: X-Ray crystal structure of trityl protected xylofuranose **3**.

Once the isopropylidene and trityl protecting groups were in place, an esterification could be completed on the only unprotected hydroxyl without interference from additional nucleophilic hydroxyl groups. A Steglich esterification reaction was performed starting from **3** (Equation 10), 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 the protected sugar with one free hydroxyl group and phenylacetic acid is the carboxylic acid.



3 **4**

Equation 10: Steglich esterification of protected xylofuranose **3**.

The purified protected sugar (**3**) was next reacted with phenylacetic acid, DMAP, and DCC under N_2 atmosphere.[26] After 12 hours, TLC (3:1 hexanes: ethyl acetate) showed complete consumption of starting material and the formation of a less polar spot (R_f = 0.55). Isolation of the product after workup and purification by flash column chromatography (3:1 hexanes: ethyl acetate) afforded **4** as a white foam (77%).

The structure of **4** was supported by the disappearance of the signal corresponding to the hydroxyl at C-3 at 3.24 ppm in the spectrum of the starting material **3** and the appearance of a signal at 3.36 ppm representing the -CH_2- group alpha to the carbonyl of the newly formed phenacyl ester **4**. The multiplet in the aromatic region which integrates to 20 protons is indicative of a fourth phenyl ring being added. The isopropylidene protecting group has again remained intact, as shown by two signals at 1.21 and 1.48 ppm. A COSY NMR experiment assured the proper assignment of protons in the ^{1}H NMR spectrum. ^{13}C NMR further supported product formation, with signals representing the 4 phenyl rings showing at 127.03, 127.11, 127.76, 128.48, 128.61, 129.06, 133.24, and 143.58 ppm. The number of carbons in these 8 signals totaled 24 which indicates the symmetry of the phenyl rings. There were two additional signals representing the carbons in the ester; the first of these appeared at 40.84 ppm and corresponded to the carbon alpha to the carbonyl and the second at 169.90 ppm representing the carbonyl carbon. Mass spectrometry shows a peak with an M^+ of 573.3, which is indicative of the addition of a sodium atom to the calculated molecular mass of 550.64. The product was crystallized using methanol and petroleum ether, and X-ray crystallography data served to absolutely confirm the structure (Figure 15).

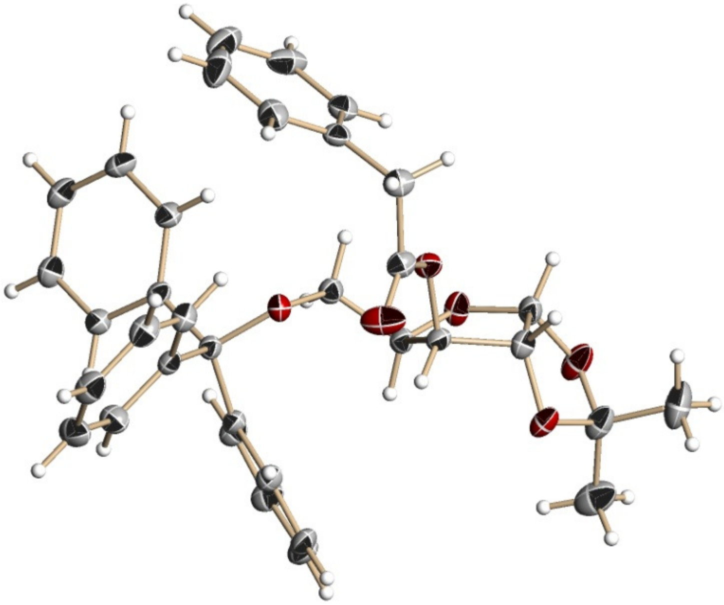
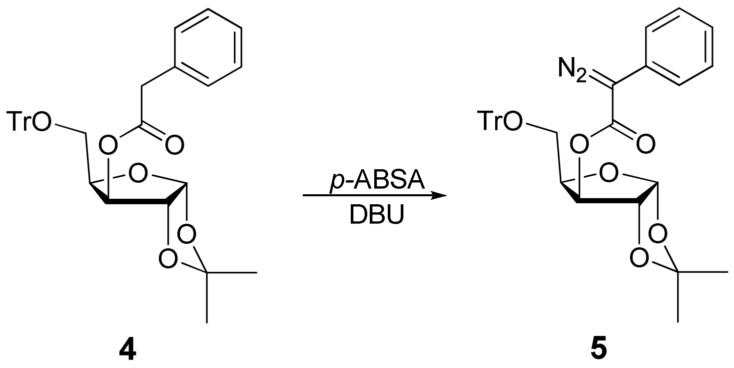


Figure 15: X-Ray structure of phenacyl ester **4**.

At this point a diazo transfer reaction was carried out on the newly formed phenyl ester (Equation 11).

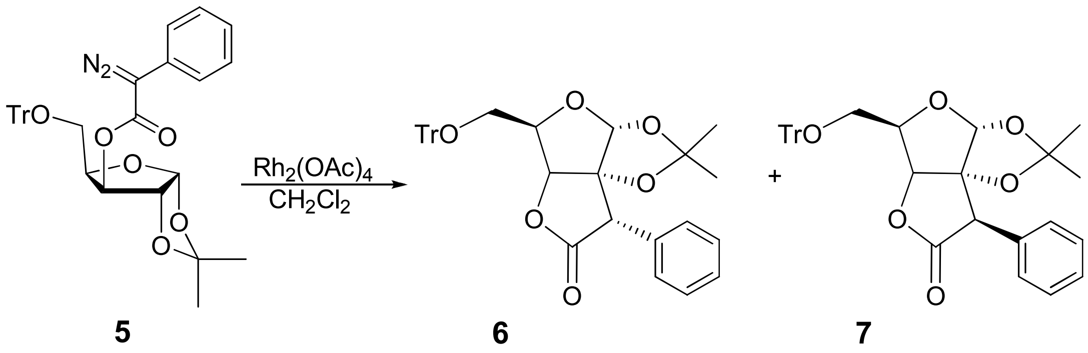


Equation 11: Formation of diazoester **5**.

Ester **4** was reacted with *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) and 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU).[26] After stirring overnight, TLC (3:1 hexanes: ethyl acetate) showed consumption of starting material and formation of a less polar spot having $R_f = 0.58$. After aqueous workup, the crude reaction mixture was purified using column chromatography (3:1 hexanes: ethyl acetate) to give **5** as a bright yellow foam in good yield (82%).

The ^1H NMR spectrum of **5** showed the disappearance of the signal at 3.36 ppm, indicative of the diazo group taking the place of the protons. The rest of the signals in this spectrum remained largely unchanged compared to that of **4**. This was further confirmed by infrared spectroscopy, which showed the characteristic diazo band at 2100 cm^{-1}. Analysis of the ^{13}C NMR spectrum of **5** showed the signal for the carbon alpha to the carbonyl on the phenyl ester had shifted downfield from 40.84 ppm to 124.89 ppm once the diazo group was attached. ESI mass spectrometric analysis provided an M^+ of 599.3, which corresponds to the calculated molecular mass of 576.64 with the addition of a sodium atom.

The diazoester readily decomposes and must be stored in the freezer or synthesized immediately prior to use. Once the diazoester was formed, a rhodium(II) acetate-catalyzed insertion reaction was attempted (Equation 12).



Equation 12: Formation of insertion products **6** and **7**.

This reaction is very air and water sensitive, so the newly synthesized diazoester was placed in a flame-dried round-bottomed flask and then dried using a vacuum pump. The rhodium(II) acetate catalyst was dried using a drying pistol and P_2O_5 as the dessicant. After drying for 3 days on the vacuum pump, the diazoester was then checked for purity and dissolved in anhydrous methylene chloride that had been degassed. This solution was added to a second flask containing 3% of the dried rhodium acetate in anhydrous degassed methylene chloride at 1mL/hour *via* syringe pump. An excess amount of solvent was used to dilute the reagents and encourage the intramolecular insertion reaction while attempting to reduce the possibility of dimer formation from intermolecular reactions.[26] After addition, the reaction was allowed to stir for 24 hours after which TLC showed a complex mixture of products. Careful column chromatography was used for the purification of this reaction, although this technique proved inadequate. Various solvent systems were studied using finer mesh silica gel, but each was unsuccessful.

Because this complex mixture was unable to be separated, it was not possible to determine if an insertion reaction had taken place, so an atmosphere controlled glove box was used. This was used to hopefully reduce the formation of byproducts and consequentially, the complexity of the mixture, thus allowing it to be separated by column chromatography. Another series of reactions were attempted in the glove box, which kept water at or below 300 ppm, and the oxygen levels at or below 10 ppm.

To a flame-dried round-bottom flask equipped with a magnetic stirring rod, the diazoester was added and placed on a vacuum pump for three days to dry. The flask was then placed in a glove box where anhydrous, degassed methylene chloride was added to dissolve the diazoester sugar. This bright yellow solution was drawn into a syringe, where it was added to a second solution containing 3% rhodium(II) acetate in anhydrous, degassed methylene chloride. The mixture was added *via* syringe pump at 1 mL/ hour for 20 hours. The reaction was allowed to stir for an additional 24 hours after which TLC (4:1 hexanes: ethyl acetate) showed consumption of starting material and the generation of a complex mixture of products. An attempt to purify this mixture was again made using flash column chromatography and a gradient solvent system starting with 9:1 hexanes: ethyl acetate and gradually changing to 1:3 hexanes: ethyl acetate. Each attempt to purify this mixture proved unsuccessful.

At this point it was thought that the catalyst was retaining moisture, so a fresh bottle of catalyst was used. The same reaction conditions as the previous glove box attempts were used. Again TLC analysis (4:1 hexanes: ethyl acetate) showed consumption of starting material and the generation of a complex mixture of products. Careful column chromatography with a gradient solvent system was again used in an attempt to resolve the mixture, and although some products coeluted, two products were able to be crystallized. The insertion products **6** and **7** showed on TLC at $R_f = 0.22$ and 0.37 respectively, with **6** as a colorless crystal (42%) and **7** as a white powder (23%).

After running several experiments under varying conditions, data was obtained that proved successful rhodium(II)-catalyzed insertion into the sugar framework. An analysis of the ^{1}H NMR of **6** showed that the phenyl rings and isopropylidene protecting group were still in place. In the ^{1}H NMR spectrum of the starting material, the signal for the proton on the anomeric carbon, C-1, showed as a doublet at 5.87 ppm because it was split by H-2. However in the NMR of **6**, this signal appears at 5.83 ppm as a singlet due to the fact that H-2 is no longer there and has been replaced by the new C-C bond. There is also a new signal at 3.94 ppm for the -CH- proton alpha to the ester, which was expected for the insertion onto the carbohydrate framework. COSY NMR experiments ensured proper assignment of the proton signals. The ^{13}C NMR spectrum of **6** shows a signal at 52.84 ppm representing the carbon that the phenyl ring is attached to on the newly formed lactone ring. This signal has shifted back upfield now that the electron-withdrawing diazo group is no longer attached.

Mass spectral data also helped to confirm the product was made, showing $M^+ = 571.3$ which is the formula weight plus sodium. An X-ray crystal structure was obtained and also helped to confirm the structure (Figure 16). The crystallographic data also shows that all of the protecting groups are still intact as well as the absolute stereochemistry of the newly formed lactone ring.

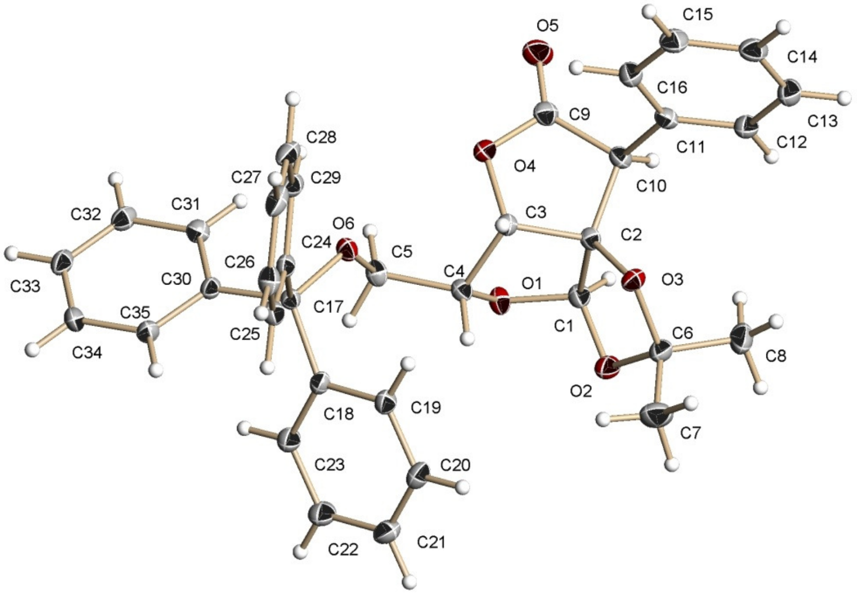


Figure 16: X-Ray crystal structure of **6**.

The structure of **7** was confirmed by the same methods as **6** and it was found to be structurally identical except for one chiral center. A study of ^{1}H NMR spectra of **7** showed all of the same peaks as **6**, however the peak for the carbon that the phenyl ring is attached to on the newly formed lactone ring, appeared slightly downfield at 4.34 ppm. Analysis of the ^{13}C NMR spectrum showed that the two had identical spectra. An X-ray crystal structure was also obtained for **7** and it was the most important piece of data that was used to confirm the stereochemistry (Figure 17). This structure not only confirms the C-H insertion, it clearly shows the different configuration of the new chiral center compared to **6**.

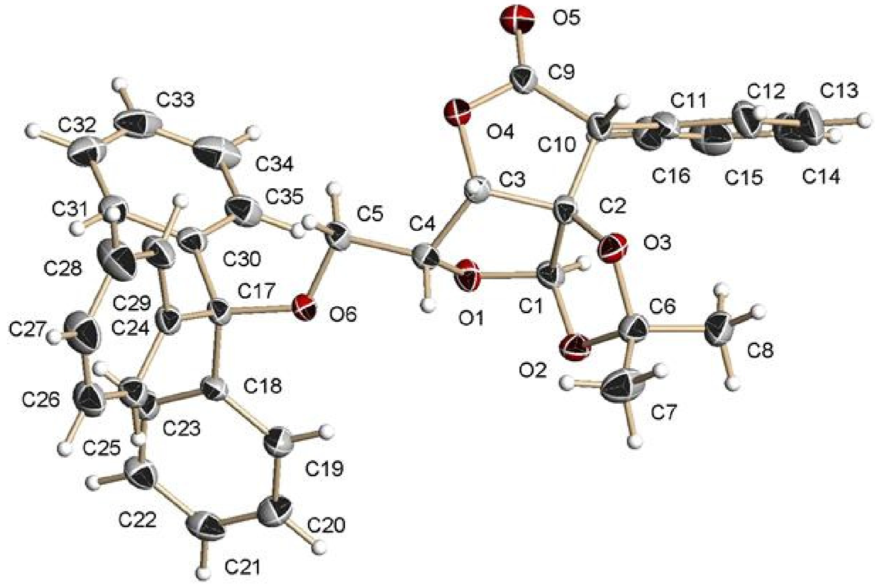


Figure 17: X-Ray crystal structure of **7**.

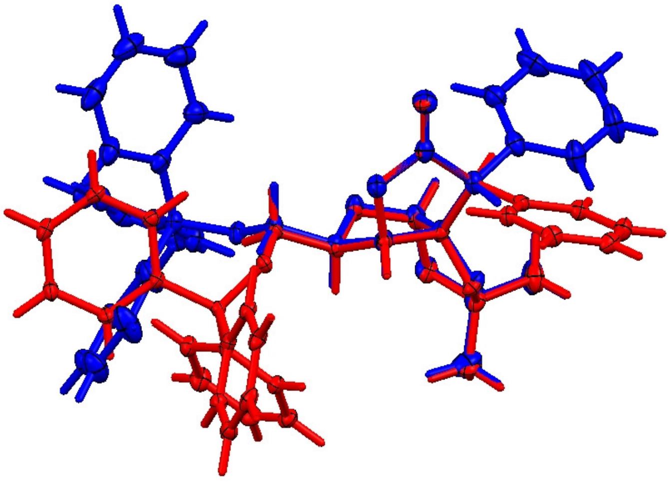


Figure 18: Overlay of **6** (red) and **7** (blue).

When the two crystal structures were overlaid (Figure 18), it can be observed that the fused lactone rings and the isopropylidene protecting groups in each of the two structures have essentially the same bond angles. Product **6** is in red while **7** is in blue. There are only two variations in these two structures. The first of these is the expected orientation about the new chiral center. In **6** the phenyl ring is *exo* relative to the furanose ring whereas in **7** the relationship is *endo*. The second variation is with the trityl group. Because this large group is flexible and rotates freely, it is not unexpected that it does not overlay exactly in the two structures.

Conclusion

Using rhodium(II) acetate to catalyze an insertion reaction in an attempt to create an analog to the natural product (+)-dihydrocanadensolide has shown significant success. The carbenoid insertion reaction produced two stereoisomers, both containing the bicyclic fused furan ring structure. This reaction sequence has shown success in the past on a glucofuranose platform and has now been applied to and shown to work on a xylofuranose platform. As both transformations create a complex and difficult to purify mixture of products, better separation methods must be employed.

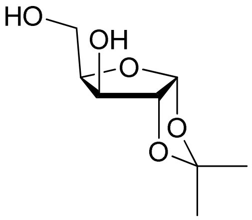
Future work in this project will involve application of this reaction sequence to synthesize the natural product, (+)-dihydrocanadensolide. This could be accomplished firstly by using propionic acid instead of phenylacetic acid in the Steglich esterification reaction. This would put a methyl group on the second lactone ring instead of a phenyl group. Once the insertion reaction was successful, the next steps would involve functional group transformations and an alkylation to obtain the final product. Also, further research may be done in testing this reaction sequence on other systems.

Experimental:

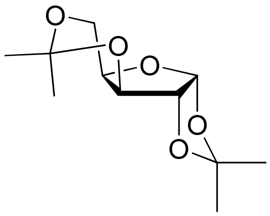
General Procedures

Reaction progress was monitored by thin layer chromatography (TLC) with UV light detection on Whatman 250 μm layer, aluminum-backed plates. The TLC plates were then treated with 5% sulfuric acid/methanol solution to burn the reaction material to provide indication of the carbohydrate product. Purification of products was achieved either by recrystallization or flash column chromatography, which was performed with 32-60 μm, 60-Å silica gel. Bruker Avance II and III 400 MHz NMR spectrometers and a Varian Gemini 2000 NMR spectrometer were used to obtain 400 MHz ^{1}H and 100 MHz ^{13}C spectra using $CDCl_3$ (0.1% w/v TMS) as the solvent. Chemical shifts (δ) are recorded in parts per million (ppm). Multiplicities for NMR spectra are listed as follows: s (singlet), d (doublet), dd (doublet of doublets), ddd (doublet of doublet of doublets), m (multiplet), and all coupling constants (*J*) are labeled in Hertz (Hz). A Bruker Esquire-HP 1100 LC/MS was used to obtain mass spectra. A Thermo Electron Corporation IR 200 infrared spectrometer was used to obtain the infrared data. A Perkin Elmer 323 automatic polarimeter was used to collect data on optical rotations. X-ray diffraction was used to determine the solid-state crystal structure of several of the compounds produced herein. For the samples, data was collected using a Bruker SMART APEX 4K CCD single crystal diffractometer at 100 K with Mo (K_α) radiation.

Acid-catalyzed reaction of D-xylose with acetone to form 1,2-*O*-isopropylidene-α-D-xylofuranose (1) and 1,2:3,5-di-*O*-isopropylidene-α-D-xylofuranose (2).



1



2

In a 500 mL round-bottom flask equipped with a magnetic stirring bar, finely ground D-xylose (10.0 g, 67.0 mmol) was added to a solution of acetone (260 mL) containing concentrated sulfuric acid (10 mL) and stirred at room temperature for 30 minutes until all of the solids had dissolved. The reaction flask was then placed in a 20 °C water bath while a 1.1 M solution of sodium carbonate (13.0 g, 123.0 mmol in 112 mL H_2O) was carefully added to partially neutralize the reaction. The water bath was removed and the reaction was allowed to stir at room temperature for 2.5 hours. TLC (100% ethyl acetate) showed formation of two new less polar spots (R_f = 0.35, 0.64) corresponding to **1** and **2** respectively. At this point 14 g of solid sodium carbonate was added to completely neutralize the reaction, which was allowed to stir until pH reached neutrality. The salts were filtered off, and the acetone/water solution was reduced on the rotary evaporator. The pale yellow residue was dissolved in chloroform and filtered over silica gel (30:1 chloroform: methanol) to remove any remaining salts and unreacted D-xylose. The eluent was then extracted with H_2O (3 x 50 mL), with **1** being in the aqueous layer and **2** in the organic layer. The aqueous layer was evaporated under reduced pressure and the resultant white powder was recrystallized with isopropanol to afford **1** as colorless crystals (79%). The organic layer was dried over $MgSO_4$ and reduced to yield **2** as a light yellow syrup (14%).

Product **1**

^{1}H NMR ($CDCl_3$): δ 1.32 (s, 1H, CH_3), 1.49 (s, 1H, CH_3), 3.46 (bs, 1H, OH), 4.04 (m, 2H, H-5, H-5'), 4.17 (dd, 1H, H-3, *J* = 3.68, 6.24 Hz), 4.32 (m, 2H, H-4 and OH), 4.52 (d, 1H, H-2, *J* = 3.68 Hz), 5.98 (d, 1H, H-1, *J* = 3.68 Hz).

^{13}C NMR ($CDCl_3$): δ 26.17, 26.75, 60.91, 76.61, 79.01, 85.59, 104.83, 111.83.

m/z calculated: 190.19 *m/z* found (ESI): 213.1 (+Na)

M.P. = 69-71 °C

R_f = 0.35 (ethyl acetate)

$[\alpha]_D$ = -6.4 (*c* = 1.0, CH_2Cl_2)

Product **2**

^{1}H NMR ($CDCl_3$): δ 1.32 (s, 1H, CH_3), 1.38 (s, 1H, CH_3), 1.44 (s, 1H, CH_3), 1.49 (s, 1H, CH_3), 4.04 (m, 2H, H-5, H-5'), 4.09 (m, 1H, H-3), 4.29 (m, 1H, H-4), 4.52 (d, 1H, H-2, *J* = 3.68 Hz), 6.00 (d, 1H, H-1, *J* =3.68 Hz).

^{13}C NMR ($CDCl_3$): δ 18.71, 26.18, 26.75, 28.89, 60.18, 71.64, 73.22, 84.69, 97.45, 105.23, 111.60.

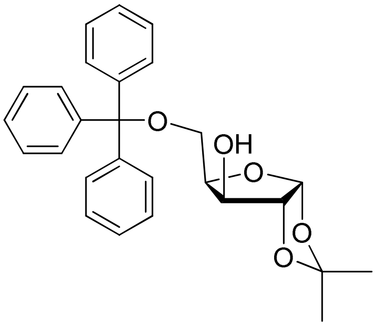
m/z calculated: 230.12 *m/z* found (ESI): 253.2 (+Na)

M.P. = N/A (syrup)

R_f = 0.64 (ethyl acetate)

$[\alpha]_D$ = +13.0 (c = 1.0, CH_2Cl_2)

Preparation of 1,2-*O*-isopropylidene-5-*O*-trityl-α-D-xylofuranose (3) from 1,2-*O*-isopropylidene-α-D-xylofuranose (2).



3

To a 100 mL round-bottom flask equipped with a magnetic stirring bar, **1** (1.0 g, 5.26 mmol) was dissolved in pyridine (10 mL), and the reaction was cooled on an ice bath. Next, 3.0 eq. of triphenylmethyl chloride (4.5 g, 16.14 mmol) was dissolved in chloroform (20 mL), and this solution was added dropwise over 60 minutes *via* an addition funnel. The reaction was allowed to stir for 12 hours after which TLC (3:1 hexanes: ethyl acetate) showed consumption of starting material and formation of a less polar spot (R_f = 0.31). De-ionized water (5 mL) was added to the reaction which was then stirred for an additional hour. The mixture was partitioned between de-ionized water (25 mL) and chloroform (25 mL). The combined organic layers were then washed with 5% sulfuric acid (3 x 40 mL) and de-ionized water (1 x 40 mL). The organics were then dried over $MgSO_4$, and evaporated under reduced pressure to afford a sticky yellow paste. The mixture was purified using flash column chromatography (3:1 hexanes: ethyl acetate) to yield **3** as a white foam (91%).

^{1}H NMR ($CDCl_3$): δ 1.32 (s, 1H, CH_3), 1.49 (s, 1H, CH_3), 3.24 (bs, 1H, OH), 3.46 (dd, 1H, H-5, *J* = 3.22, 10.27 Hz), 3.57 (dd, 1H, H-5', *J* = 5.21, 10.27 Hz), 4.27 (m, 2H, H-3, H-4), 4.53 (d, 1H, H-2, *J* = 3.72 Hz), 6.01 (d, 1H, H-1, *J* = 3.72 Hz), 7.34 (m, 15H, $OC\underline{Ph}_3$).

^{13}C NMR ($CDCl_3$): δ 26.14, 26.76, 61.75, 76.01, 78.59, 85.10, 87.41, 104.91, 111.46, 127.23 (3 x C), 128.01 (6 x C), 128.47 (6 x C), 143.30 (3 x C).

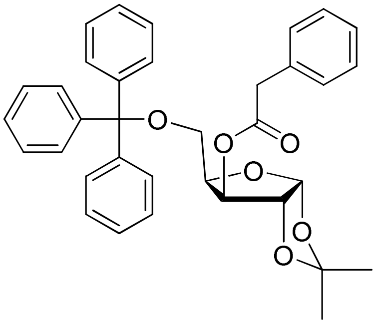
m/z calculated: 432.51 *m/z* found (ESI): 455.2 (+Na)

M.P. = 112-114 ^{o}C

R_f = 0.31 (3:1 hexanes: ethyl acetate)

$[\alpha]_D$ = -3.8 (*c* = 1.0, CH_2Cl_2)

Preparation of 1,2-*O*-isopropylidene-3-*O*-phenacyl-5-*O*-trityl-α-D-xylofuranose (4) from 1,2-*O*-isopropylidene-5-*O*-trityl-α-D-xylofuranose (3) *via* Steglich esterification.



4

A flame-dried 50 mL round-bottom flask was fitted with a septum and magnetic stirring bar and was then flushed with dry N_2 gas. Next, 1.0 eq. of **3** (0.433 g, 1 mmol), 1.1 eq. of phenylacetic acid (0.150 g, 1.1 mmol), and 0.16 eq. of 4-(dimethylamino) pyridine (DMAP) (0.020 g, 0.16 mmol) were added and dissolved in anhydrous methylene chloride (4.3 mL) and anhydrous acetonitrile (4.3 mL). While stirring under N_2 at room temperature, 1.1 eq. of a 1.0 M 1,3-dicyclohexylcarbodiimide (DCC) solution (1.1 mL, 1.1 mmol) was added dropwise over one hour, during which a white precipitate formed in the flask. After 12 hours, TLC (3:1 hexanes: ethyl acetate) showed the formation a less polar spot ($R_f = 0.55$). The reaction was cooled to 0 ^{o}C on an ice/water bath to precipitate out the DCC, which was then filtered off. The mixture was washed with 5% sulfuric acid (3 x 25 mL) and de-ionized water (2 x 25 mL). The organic layer was then dried over $MgSO_4$, reduced, and then purified by flash column chromatography (3:1 hexanes: ethyl acetate) to yield **4** as a white foam (77%).

^{1}H NMR ($CDCl_3$): δ 1.21 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 3.18 (dd, 1H, H-5, *J* = 6.71, 9.52 Hz), 3.36 (s, 2H, $\underline{CH_2}$Ph), 3.45 (dd, 1H, H-5’, *J* = 5.96, 9.52 Hz), 4.35 (d, 1H, H-2, *J* = 3.76 Hz), 4.40 (ddd, 1H, H-4, *J* = 3.00, 6.28, 6.28 Hz), 5.29 (d, 1H, H-3, *J* = 3.00 Hz), 5.79 (d, 1H, H-1, *J* = 3.76 Hz), 7.23 (m, 20H, OC$\underline{Ph_3}$, CH$\underline{Ph}$).

^{13}C NMR ($CDCl_3$): δ 26.13, 26.65, 40.84, 60.67, 76.30, 77.98, 83.14, 86.81, 104.70, 111.95, 127.03 (3 x C), 127.11, 127.76 (6 x C), 128.48 (2 x C), 128.61 (6 x C), 129.06 (2 x C), 133.24, 143.58 (3 x C), 169.90.

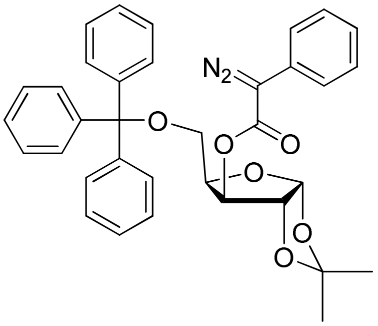
m/z calculated: 550.64 *m/z* found (ESI): 573.3 (+Na)

M.P. = 52-54 °C

R_f = 0.55 (3:1 hexanes: ethyl acetate)

$[\alpha]_D$ = -20.7 (*c* = 1.0, CH_2Cl_2)

Preparation of 3-*O*-(2-diazo-2-phenyacetyl)-1,2-*O*-isopropylidene-5-*O*-trityl-α-D-xylofuranose (5) from 1,2-*O*-isopropylidene-3-*O*-phenacyl-5-*O*-trityl-α-D-xylofuranose (4) *via* a diazo transfer reaction.



5

In a flame-dried 50 mL round-bottom flask equipped with a septum and magnetic stir bar, 1.0 eq. of **4** (1.0 g, 1.80 mmol) and 1.3 eq. of *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (0.562 g, 2.34 mmol) were added and the flask was purged with N_2. Next these solids were dissolved in anhydrous methylene chloride (10 mL) and anhydrous acetonitrile (10 mL). At this point, 1.3 eq. of 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) (0.36 mL, 2.34 mmol) was added *via* syringe over one hour during which time the reaction turned dark yellow. After stirring overnight, TLC (3:1 hexanes: ethyl acetate) showed consumption of starting material and formation of a less polar spot ($R_f = 0.58$). The reaction was washed with 5% sulfuric acid (3 x 40 mL) and de-ionized water (2 x 40 mL). The organics were dried over $MgSO_4$, evaporated under reduced pressure, and the resulting residue was purified using flash column chromatography (3:1 hexanes: ethyl acetate). The product, **5**, was afforded as a bright yellow foam (82%).

^{1}H NMR ($CDCl_3$): δ 1.29 (s, 3H, CH_3), 1.55 (s, 3H, CH_3), 3.23 (dd, 1H, H-5, *J* = 7.72, 9.16 Hz), 3.49 (dd, 1H, H-5', *J* = 5.36, 9.16 Hz), 4.56 (ddd, 1H, H-4, *J* = 3.04, 5.57, 5.57 Hz), 4.59 (d, 1H, H-2, *J* = 3.76 Hz), 5.54 (d, 1H, H-3, *J* = 3.04 Hz), 5.87 (d, 1H, H-1, *J* = 3.76 Hz), 7.25 (m, 20H, $OC\underline{Ph}_3$, $CH\underline{Ph}$).

^{13}C NMR ($CDCl_3$): δ 26.13, 26.68, 60.35, 76.30, 77.92, 83.35, 86.84, 104.70, 112.07, 123.68 (2 x C), 124.89, 125.92, 127.01 (3 x C), 127.74 (6 x C), 128.55 (6 x C), 128.92 (2 x C), 143.44 (3 x C), 163.30.

IR: 2093.42 cm^{-1}

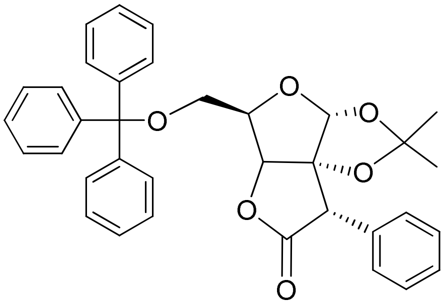
m/z calculated: 576.64 *m/z* found (ESI): 599.3 (+Na)

M.P. = 65-67 °C

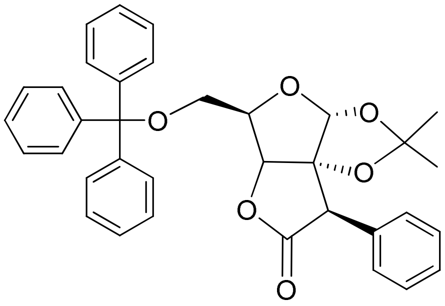
R_f = 0.58 (3:1 hexanes: ethyl acetate)

$[\alpha]_D$ = -165.2 (c = 1.0, CH_2Cl_2)

Rhodium (II) acetate-catalyzed decomposition of 3-*O*-(2-diazo-2-phenyacetyl)-1,2-*O*-isopropylidene-5-*O*-trityl-α-D-xylofuranose (4) to yield insertion products.



6



7

To a flame-dried 250 mL round-bottom flask equipped with a magnetic stirring rod, **5** (1.0 g, 1.735 mmol) was added and placed on a vacuum pump for three days to dry. The flask was then placed in a glove box (H_2O: 24.9 ppm, O_2: 78.1 ppm, 20 °C) where anhydrous, degassed methylene chloride (20 mL) was added to dissolve the diazoester sugar. This bright yellow solution was placed in a 20 mL syringe, where it was added to a second solution containing 0.4% rhodium (II) acetate (0.062 g, 0.140 mmol) in anhydrous, degassed methylene chloride (80 mL). The mixture was added *via* syringe pump at 1 mL/ hour for 20 hours. The reaction was allowed to stir for an additional 24 hours after which TLC (4:1 hexanes: ethyl acetate) showed consumption of starting material and the generation of a complex mixture of products. The insertion products **6** and **7** showed at $R_f = 0.22$ and 0.37 respectively. The reaction mixture was reduced and then purified by careful flash column chromatography followed by recrystallization to yield **6** as a colorless crystal (42%) and **7** as a white powder (23%).

Product **6**

^{1}H NMR ($CDCl_3$): δ 1.24 (s, 1H, CH_3), 1.42 (s, 1H, CH_3), 3.46 (dd, 1H, H-5, *J* = 5.84, 10.08 Hz), 3.57 (dd, 1H, H-5', *J* = 6.36, 10.08 Hz), 3.94 (s, 1H, $\underline{CH}Ph$), 4.43 (ddd, 1H, H-4, *J* = 2.89, 6.04, 6.04 Hz), 4.77 (d, 2H, H-2, H-3, *J* = 2.89 Hz), 5.83 (s, 1H, H-1), 7.28 (m, 20H, $OC\underline{Ph}_3$, $CH\underline{Ph}$).

^{13}C NMR ($CDCl_3$): δ 26.61, 27.54, 52.84, 61.30, 79.79, 85.50, 87.26, 93.28, 110.89, 113.18, 127.18 (3 x C), 127.92 (6 x C), 128.20, 128.71 (6 x C), 128.89 (2 x C), 129.00 (2 x C), 132.56, 143.65 (3 x C), 173.74.

m/z calculated: 548.62 *m/z* found (ESI): 571.3 (+Na)

M.P. = 184-186 °C

R_f = 0.22 (4:1 hexanes:ethyl acetate)

$[\alpha]_D = -80.9$ (*c* = 1.0, CH_2Cl_2)

Product **7**

^{1}H NMR (CDCl$_3$): δ 1.02 (s, 3H, CH$_3$), 1.46 (s, 3H, CH$_3$), 3.50 (dd, 1H, H-5, *J* = 6.00, 10.08 Hz), 3.57 (dd, 1H, H-5', *J* = 6.36, 10.08 Hz), 4.34 (s, 1H, $\underline{\text{CH}}$Ph), 4.44 (ddd, 1H, H-4, *J* = 3.08, 6.08, 6.08 Hz), 4.69 (d, 1H, H-3, *J* = 3.08 Hz), 5.42 (s, 1H, H-1), 7.24 (m, 20H, OC$\underline{\text{Ph}}_3$, CH$\underline{\text{Ph}}$).

^{13}C NMR (CDCl$_3$): δ 27.30, 28.71, 52.06, 61.09, 79.67, 84.37, 87.23, 95.84, 104.96, 112.23, 127.16 (3 x C), 127.89 (6 x C), 128.59, 128.70 (6 x C), 128.98 (2 x C), 130.03 (2 x C), 131.72, 143.68 (3 x C), 172.54.

m/z calculated: 548.62 *m/z* found (ESI): 571.3 (+Na)

M.P. = 184-186 °C

R$_f$ = 0.37 (4:1 hexanes: ethyl acetate)

$[\alpha]_D$ = -60.0 (*c* = 1.0, CH$_2$Cl$_2$)

References

1. El Khadem, H. S. *Carbohydrate Chemistry: Monosaccharides and Their Oligomers*, Academic Press: San Diego, 1988.
2. Guthrie, R. D., Honeyman, J. *An Introduction to the Chemistry of Carbohydrates*, Clarendon Press: Oxford, England, 1968.
3. Carey, F. A. *Organic Chemistry 5th Edition,* The McGraw-Hill Companies, Inc.: New York, 2003.
4. Voet, D., Voet, J. G. *Biochemistry 3rd Edition*, John Wiley & Sons, Inc.: New Jersey, 2004.
5. Boons, G.-J. *Carbohydrate Chemistry*, Thomson Science: London, 1998.
6. Stick, R. V. *Carbohydrates: The Sweet Molecules of Life*, Academic Press: San Diego, 2001.
7. Emil Fischer – Biography. 14 Apr. 2005. Nobelprize.org. 15 Nov. 2005. http://nobelprize.org/chemistry/laureates/1902/fischer-bio.html
8. Cell-Surface Receptors: A Biological Conduit for Information Transfer. 15 Nov. 2005. D.M. Secko. http://www.bioteach.ubc.ca/CellBiology/CellSurfaceReceptors
9. Nicolaou, K. C.; Snyder., "The essence of total synthesis," *PNAS* **2004**, *101*, 11929-11936.
10. Nicolaou, K. C., "The art and science of constructing the molecules of nature," *PNAS* **2004**, *101*, 119298.
11. Hanessian, S. "Approaches to the total synthesis of natural products using 'chiral templates' derived from carbohydrates," *Acc. Chem. Res.* **1979**, *12,* 159-165.

12. Kedling, S. J.; Danishefsky, S. J., “Prospects for total synthesis: A vision for a totally synthetic vaccine targeting epithelial tumors,” *PNAS* **2004**, *101,* 11937-11942.

13. Hon, Y.; Hsieh, C., “Dibromomethane as one-carbon source in organic synthesis: total synthesis of (+/-)-canadensolide,” *Tetrahedron* **2006**, *62,* 9713-9717.

14. Tsuboi, S.; Muranaka, K.; Sakai, T.; Takeda, A., “Highly stereo- and regioselective alkylation of alkylidenemalonates. Its application to the synthesis of (+/-)-canadensolide,” *J. Org. Chem.* **1986**, *51,* 4944-4946.

15. Nubbenmeyer, U., “Synthesis of (+)-canadensolide, (-)-santolinolide A and (+)-santolinolide B: The imino-Claisen reaction in natural product synthesis,” *Synthesis* **1993**, *11,* 1120-1128.

16. Yu, M.; Lynch, V.; Pagenkopf, B., “Intramolecular cyclopropanation of glycals: Studies toward the synthesis of canadensolide, sporothriolide, and xylobovide,” *Org. Lett.* **2001**, *3,* 2563-2566.

17. Sharma, G. V. M.; Gopinath, T., “Radical cyclisation approach for the synthesis of (+)-dihydrocanadensolide, (+)-dihydrosporothriolide and their C-3 epimers from D-xylose,” *Tetrahedron* **2003**, *59,* 6521-6530.

18. Anderson, R. C.; Fraser-Reid, B., “Synthesis of bis-γ-lactones from ‘diacetone glucose.’ 5. Optically active canadensolide,” *J. Org. Chem.* **1985**, *50,* 4786-4790.

19. Lertvorachon, J.; Thebtaranonth, Y.; Thongpanchang, T.; Thongyoo, P., “Stereoselective synthesis of naturally occurring α-methylenebis-γ-butyrolactones: An application of novel oxiranyl ‘remote’ anions,” *J. Org. Chem.* **2001**, *66,* 4692-4694.

20. Al-Abed, Y.; Naz, N.; Mootoo, D.; Voelter, W., "4-*O*-Tf-*O*-2,3-anhydro-β-L-ribopyranosides as chiron: A formal synthesis of canadensolide," *Tetrahedron Lett.* **1996**, *37,* 8641-8642.

21. Robertson, J. *Protecting Group Chemistry*, Oxford University Press Inc.: New York, 2000.

22. Collins, P. M.; Ferrier, R. J. *Monosaccharides: Their Chemistry and Their Roles in Natural Products*, John Wiley & Sons: Chichester, England, 1995, 208-289.

23. Hanessian, S. *Preparative Carbohydrate Chemistry,* Marcel Dekker Inc.: New York, 1997, 207-262.

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

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

26. Sacui, I. A., "Synthesis and decomposition of novel diazosugars," Youngstown State University MS Thesis, 2006.

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

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

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

30. 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.

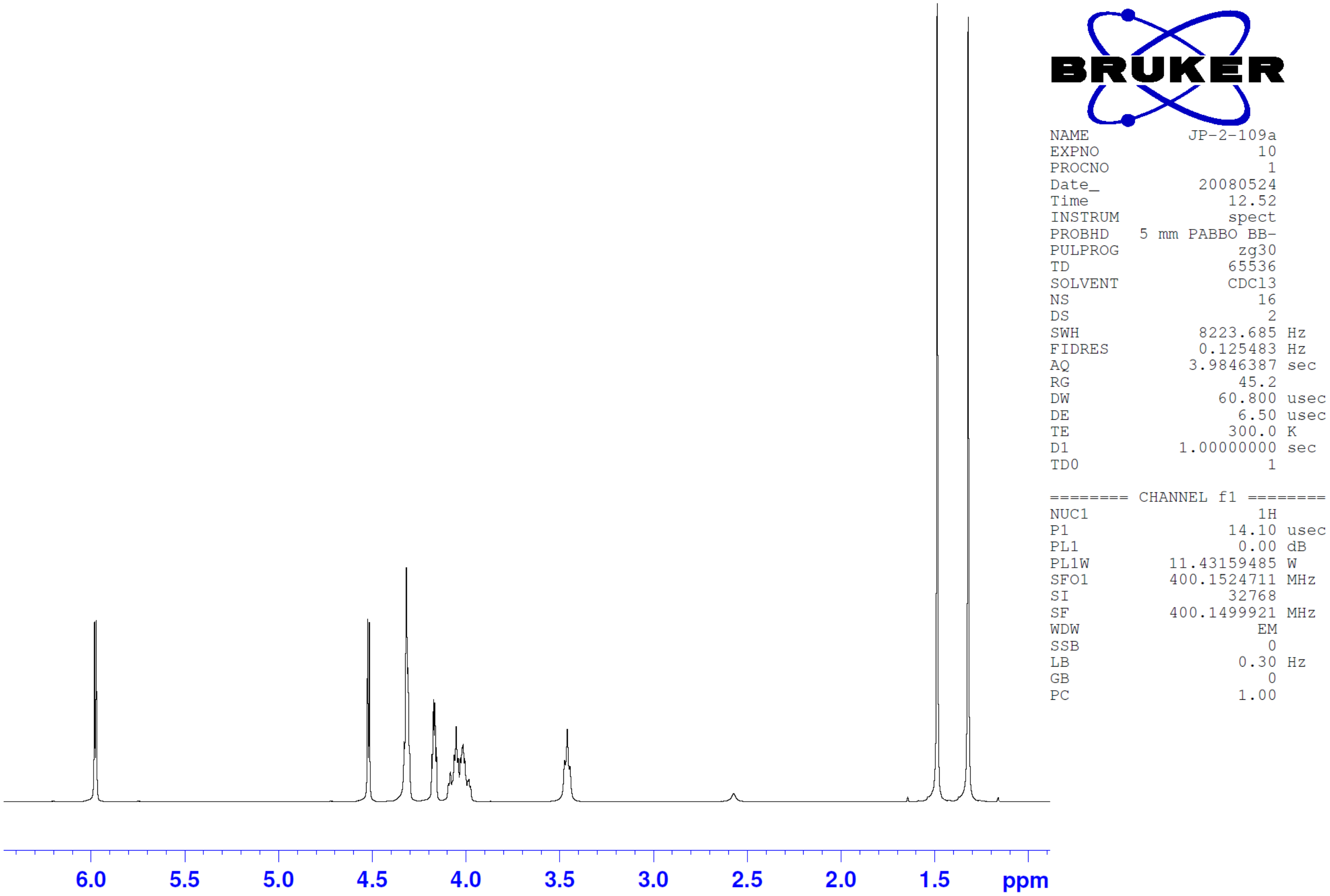
31. Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides,* John Wiley & Sons Inc.: New York, 1998.

32. Smith, M. B.; March, J. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, 6th Edition*, Wiley-Interscience, 2007.

33. Moravcová, J., Čapková, J., Staněk, J., "One-pot synthesis of 1,2-*O*-isopropylidene-α-D-xylofuranose," *Carbohydr. Res.* **1994**, *263*, 61-66.

34. Jones, G. B., Hynd, G., Wright, J. M., Sharma, A., "On the selective deprotection of trityl ethers," *J. Org. Chem.* **2000**, *65*, 263.

Appendix A



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TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
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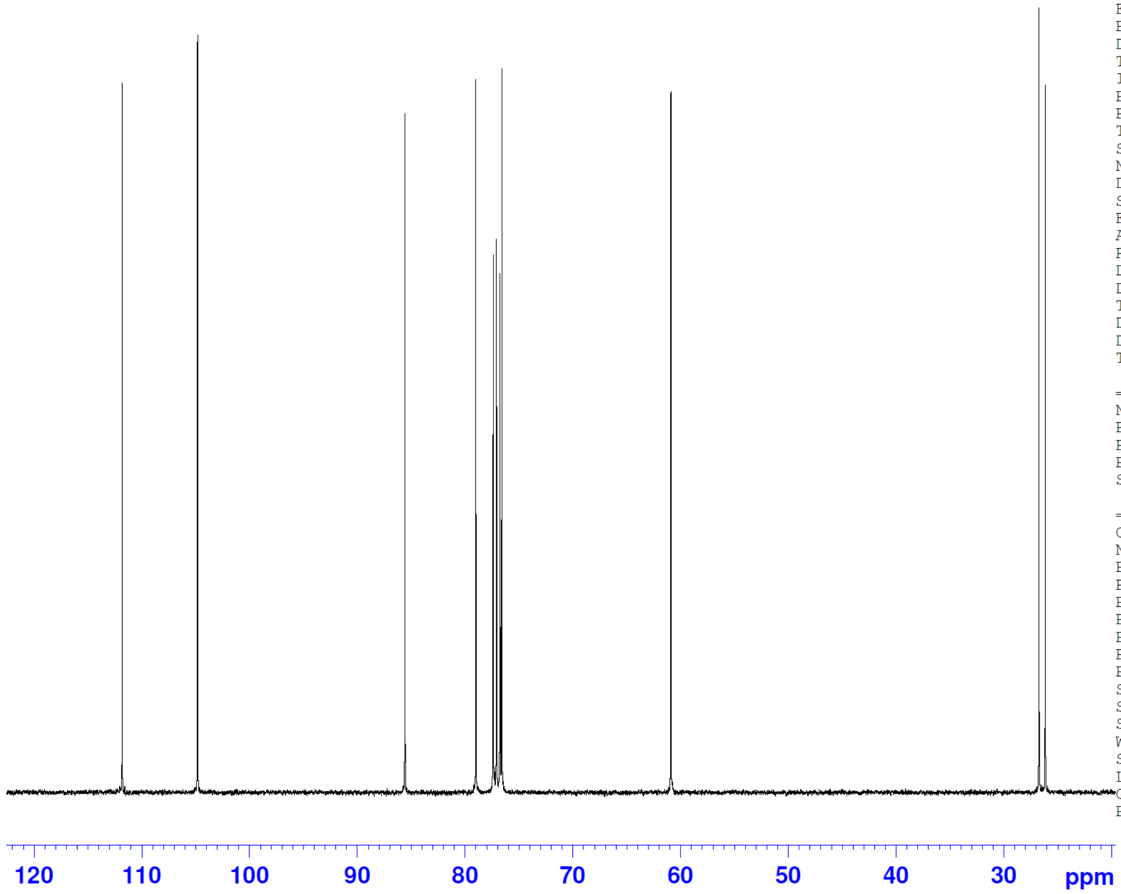
FIDRES             0.125483 Hz
AQ                3.9846387 sec
RG                     45.2
DW                   60.800 usec
DE                     6.50 usec
TE                    300.0 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    14.10 usec
PL1                    0.00 dB
PL1W            11.43159485 W
SFO1            400.1524711 MHz
SI                    32768
SF              400.1499921 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

Figure 19: 400 MHz ^{1}H spectrum of **1**.



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PROCNO                      1
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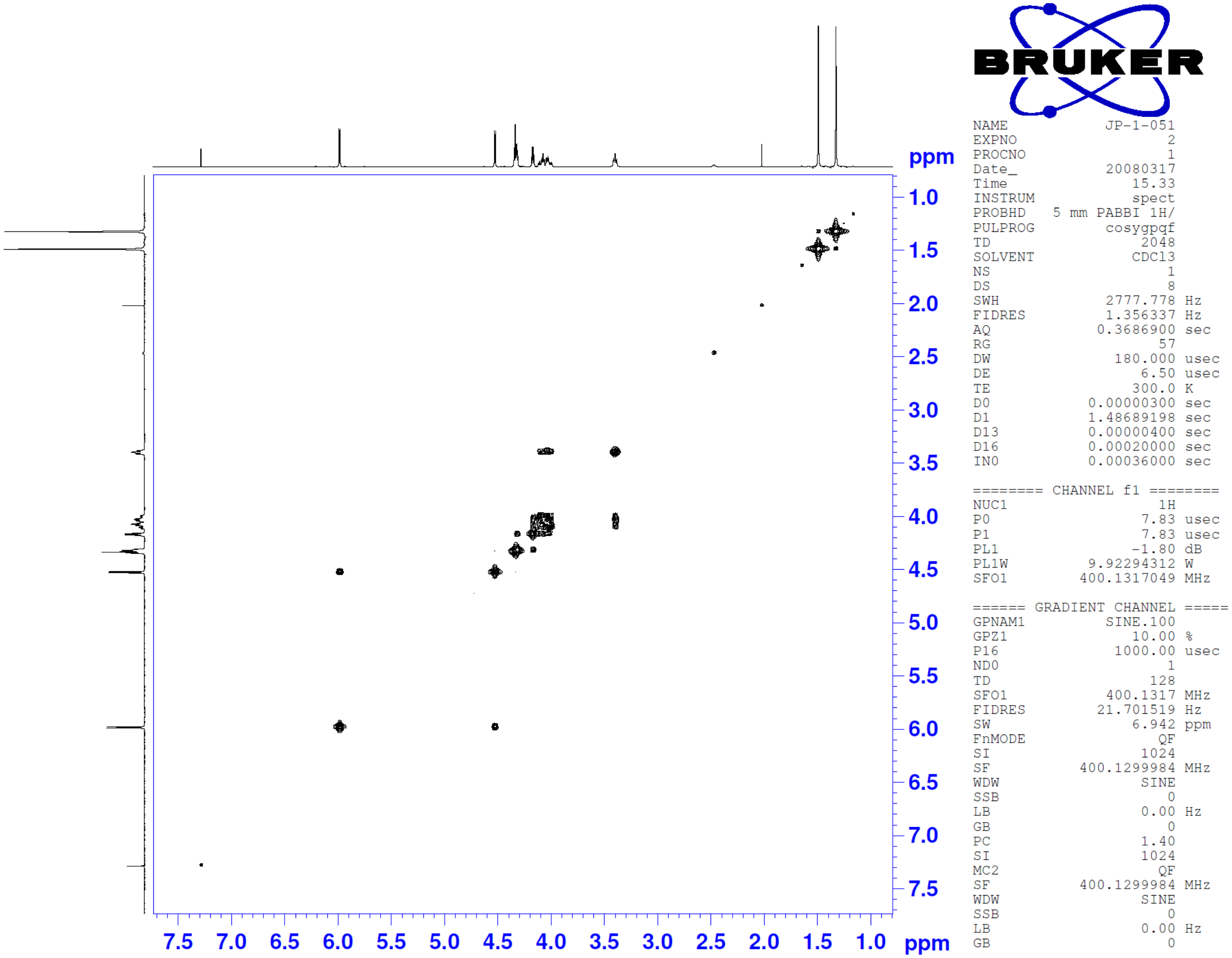
PULPROG               zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                       1024
DS                          4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                  1.3631988 sec
RG                       2050
DW                     20.800 usec
DE                       6.50 usec
TE                      300.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                       9.97 usec
PL1                     -1.00 dB
PL1W              50.97591400 W
SFO1              100.6278593 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    15.00 dB
PL13                    15.00 dB
PL2W              11.43159485 W
PL12W              0.36149877 W
PL13W              0.36149877 W
SFO2              400.1516006 MHz
SI                      32768
SF                100.6177936 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```

Figure 20: 100 MHz ^{13}C spectrum of **1**.



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PROCNO                    1
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PULPROG            cosygpqf
TD                     2048
SOLVENT               CDCl3
NS                        1
DS                        8
SWH                2777.778 Hz
FIDRES             1.356337 Hz
AQ                0.3686900 sec
RG                       57
DW                  180.000 usec
DE                     6.50 usec
TE                    300.0 K
D0               0.00000300 sec
D1               1.48689198 sec
D13              0.00000400 sec
D16              0.00020000 sec
IN0              0.00036000 sec

======== CHANNEL f1 ========
NUC1                     1H
P0                     7.83 usec
P1                     7.83 usec
PL1                   -1.80 dB
PL1W             9.92294312 W
SFO1            400.1317049 MHz

====== GRADIENT CHANNEL =====
GPNAM1             SINE.100
GPZ1                  10.00 %
P16                 1000.00 usec
ND0                       1
TD                      128
SFO1               400.1317 MHz
FIDRES            21.701519 Hz
SW                    6.942 ppm
FnMODE                   QF
SI                     1024
SF              400.1299984 MHz
WDW                    SINE
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.40
SI                     1024
MC2                      QF
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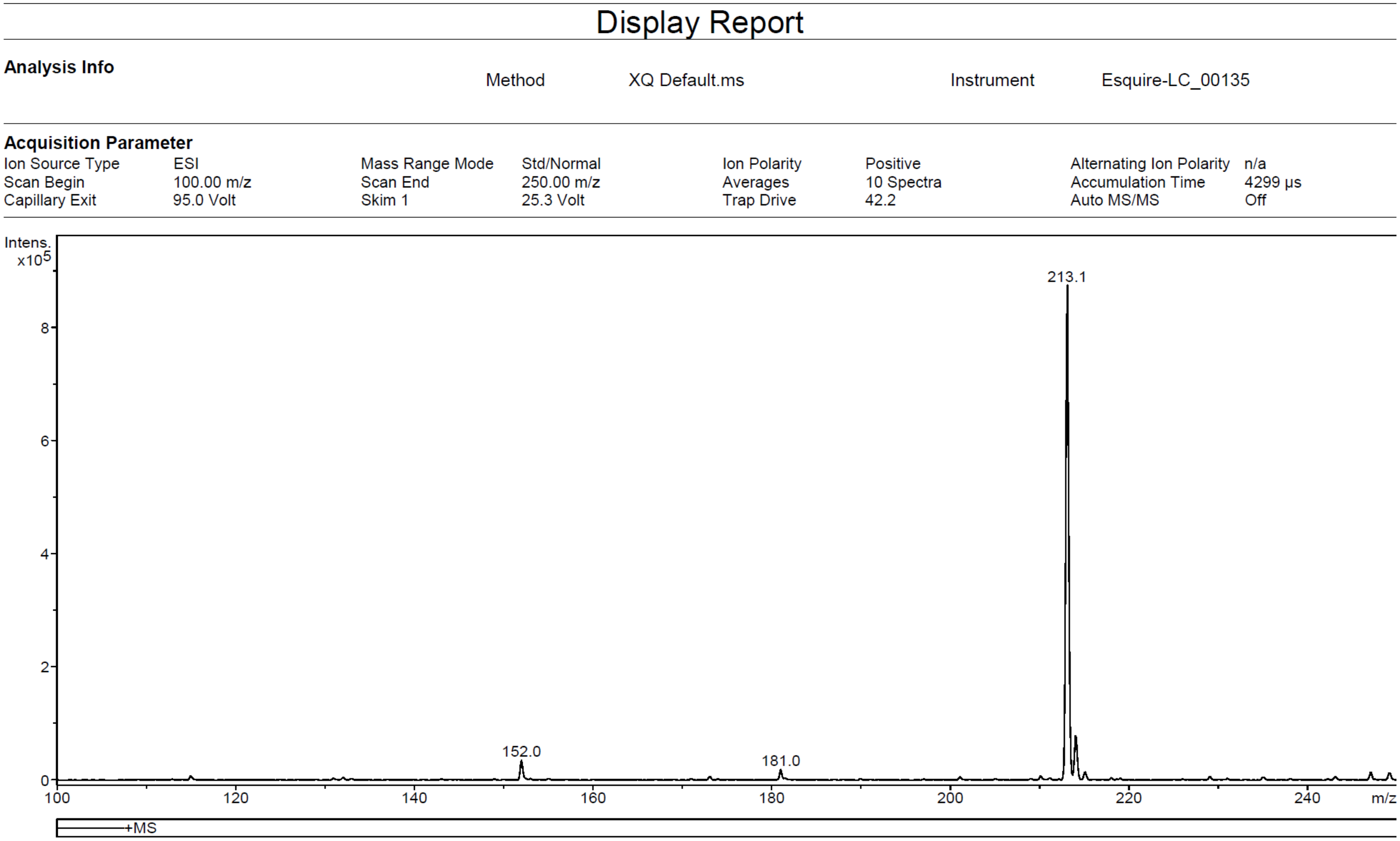
SSB                       0
LB                     0.00 Hz
GB                        0
```

Figure 21: 400 MHz ^{1}H-^{1}H COSY spectrum of **1.**



Display Report

Analysis Info

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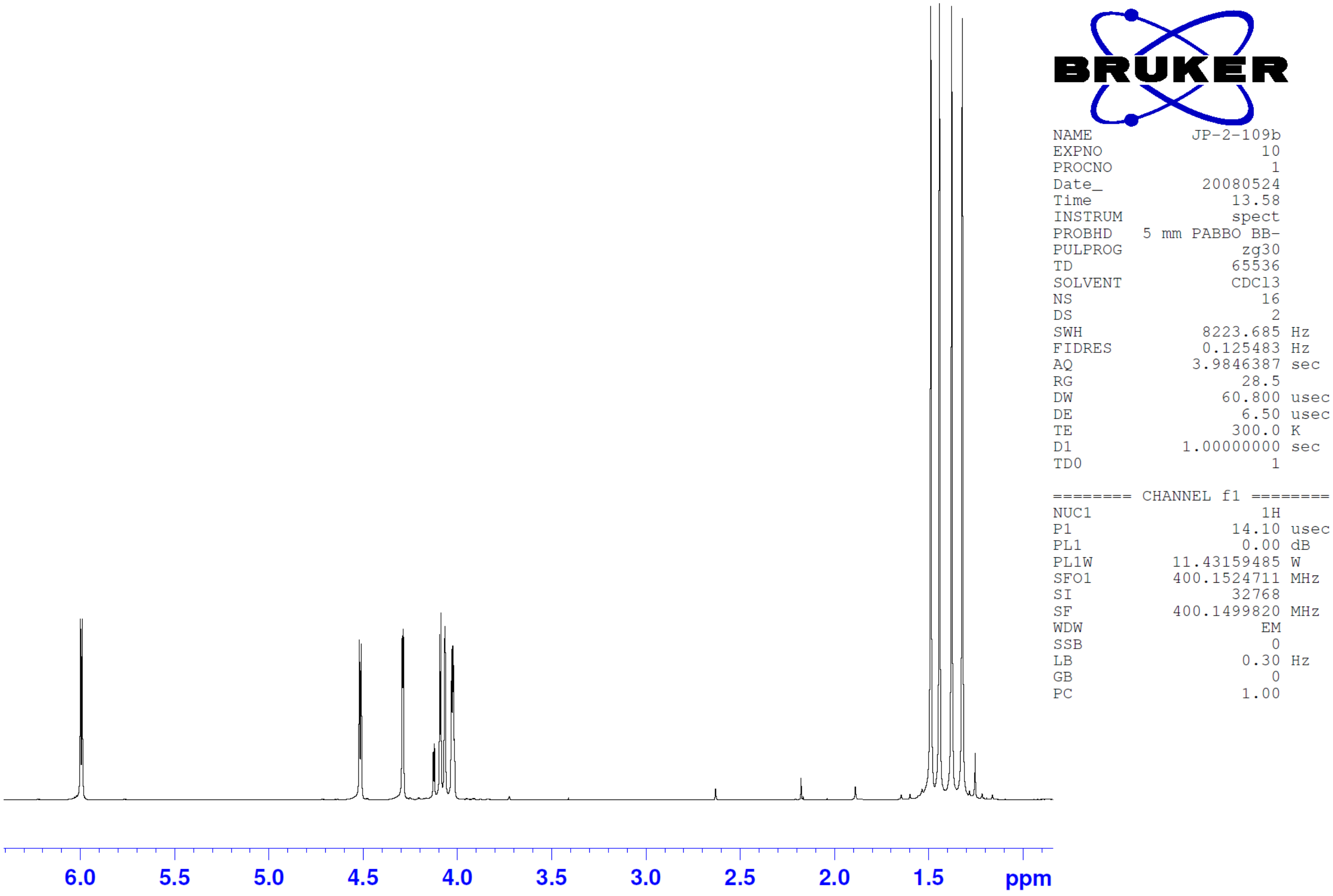
Acquisition Parameter

Ion Source Type	ESI	Mass Range Mode	Std/Normal	Ion Polarity	Positive	Alternating Ion Polarity	n/a
Scan Begin	100.00 m/z	Scan End	250.00 m/z	Averages	10 Spectra	Accumulation Time	4299 µs
Capillary Exit	95.0 Volt	Skim 1	25.3 Volt	Trap Drive	42.2	Auto MS/MS	Off

Figure 22: Mass spectrum of **1**.



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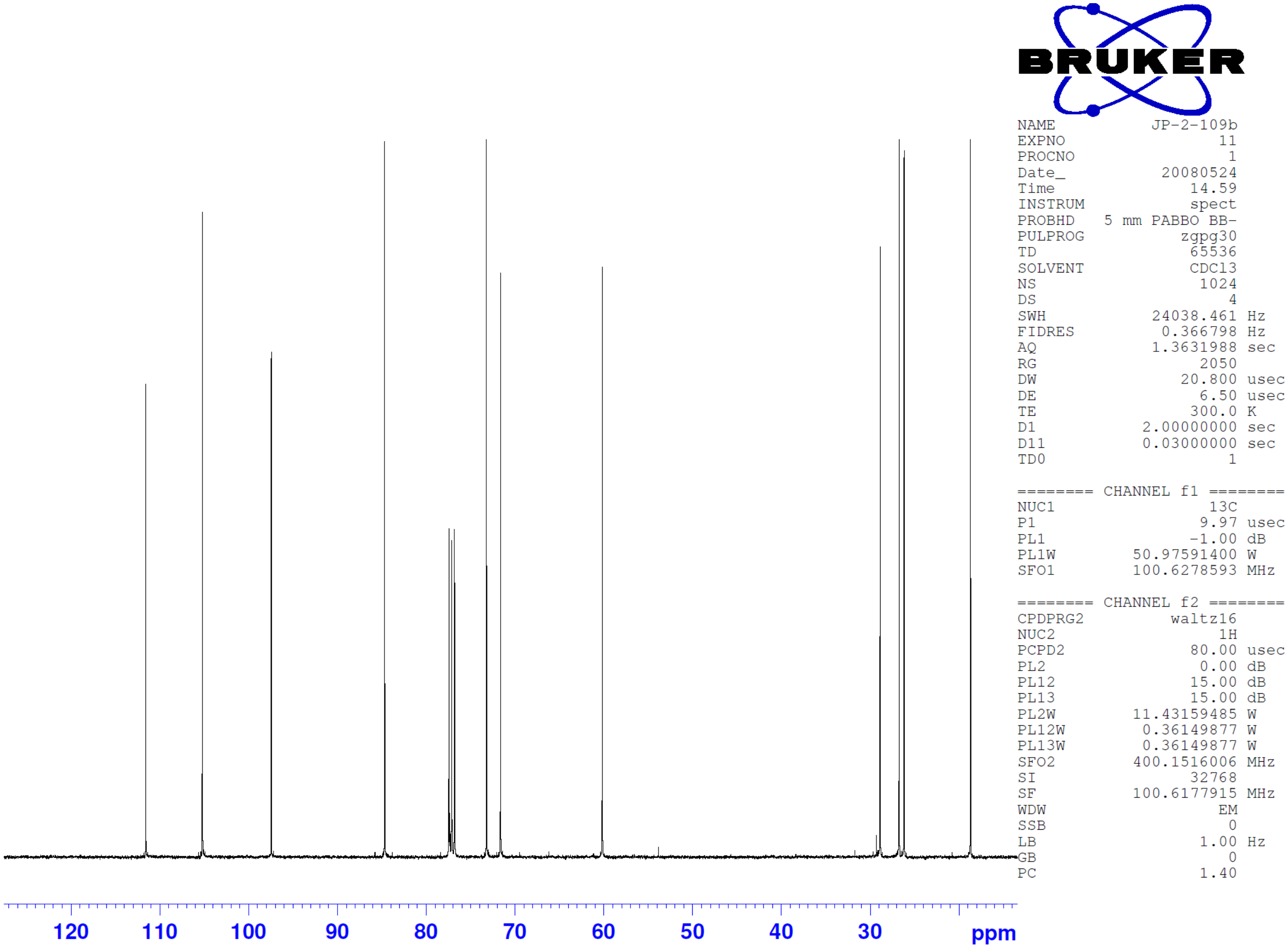
FIDRES             0.125483 Hz
AQ                3.9846387 sec
RG                     28.5
DW                   60.800 usec
DE                     6.50 usec
TE                    300.0 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    14.10 usec
PL1                    0.00 dB
PL1W            11.43159485 W
SFO1            400.1524711 MHz
SI                    32768
SF              400.1499820 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

Figure 23: 400 MHz ^{1}H spectrum of **2**.



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PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                  2050
DW                20.800 usec
DE                  6.50 usec
TE                 300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.97 usec
PL1                -1.00 dB
PL1W         50.97591400 W
SFO1         100.6278593 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               15.00 dB
PL2W         11.43159485 W
PL12W         0.36149877 W
PL13W         0.36149877 W
SFO2         400.1516006 MHz
SI                 32768
SF           100.6177915 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
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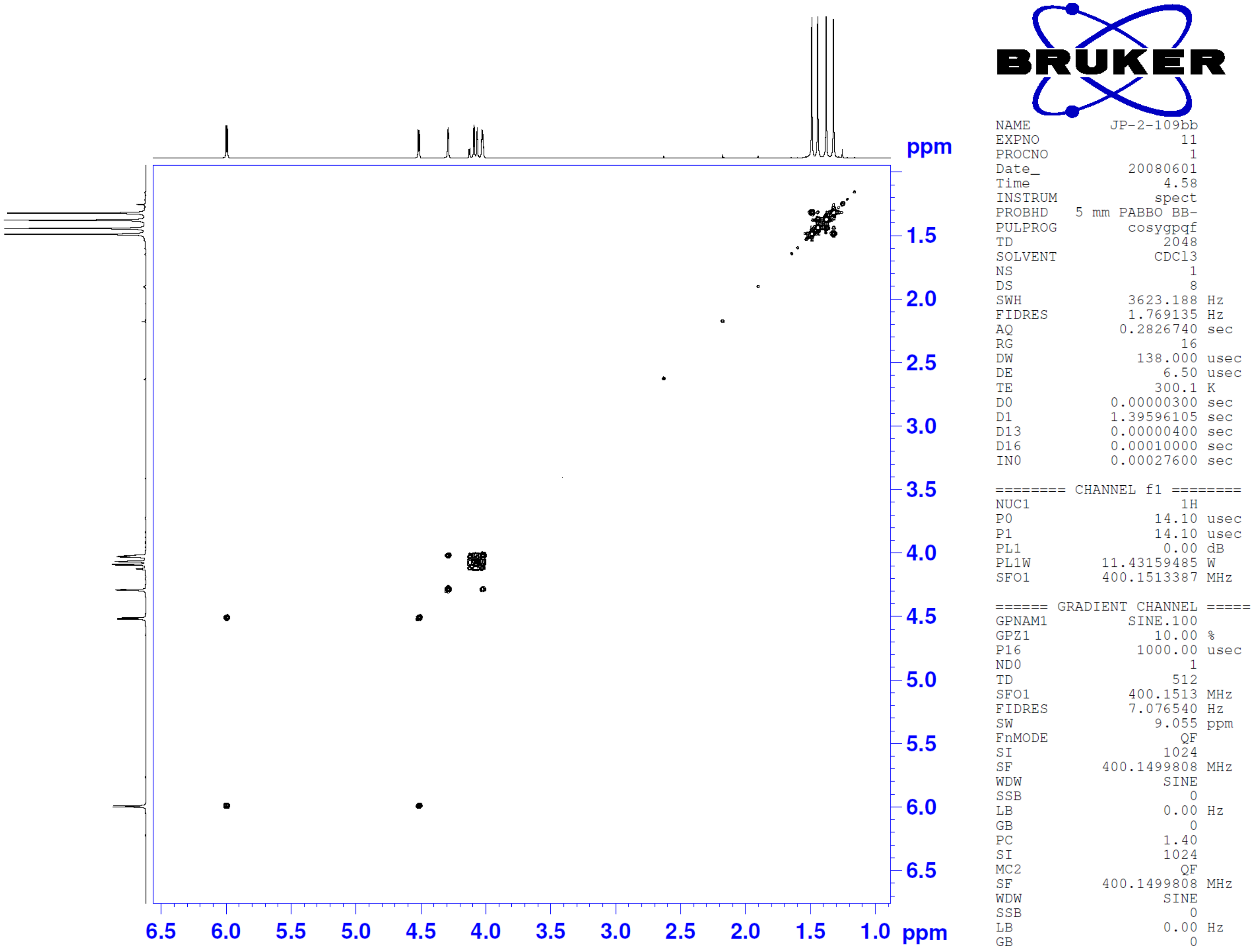
Figure 24: 100 MHz ^{13}C spectrum of **2**.



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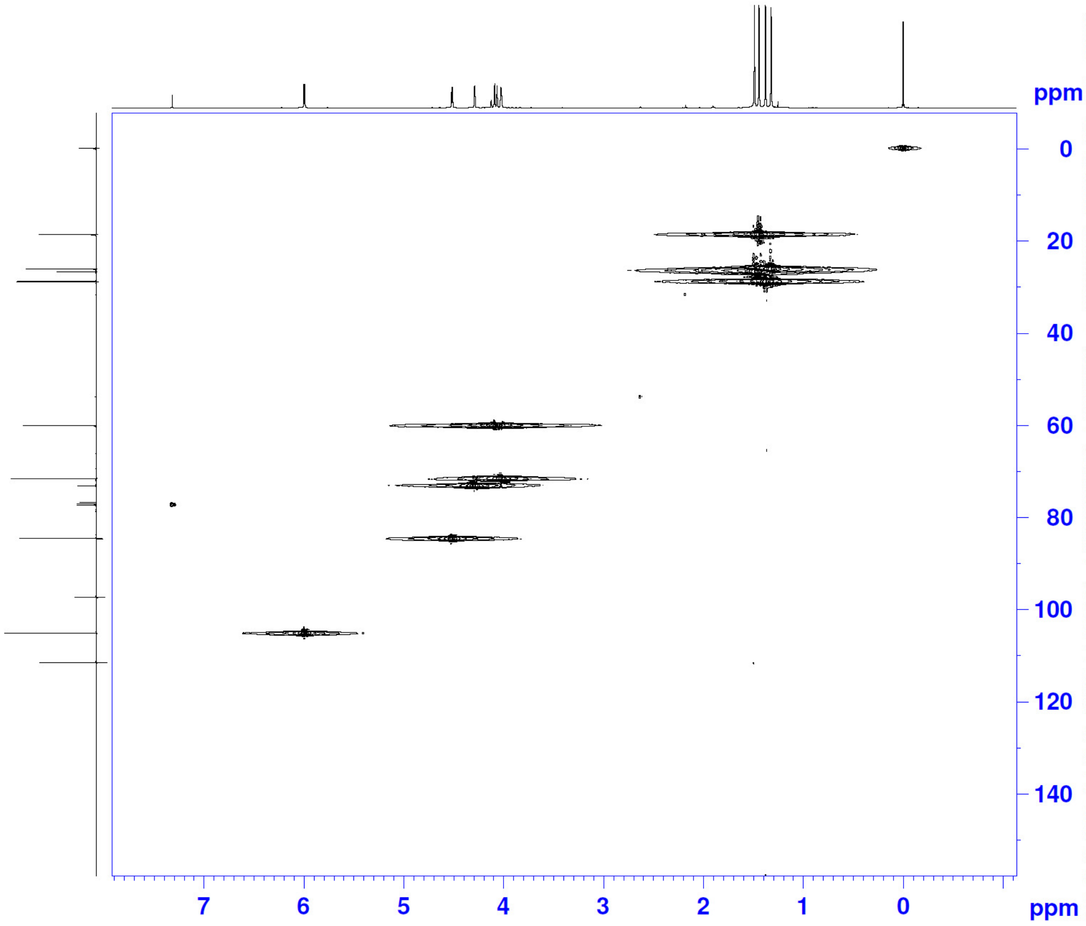
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                     8
SWH             3623.188 Hz
FIDRES          1.769135 Hz
AQ             0.2826740 sec
RG                    16
DW               138.000 usec
DE                  6.50 usec
TE                 300.1 K
D0            0.00000300 sec
D1            1.39596105 sec
D13           0.00000400 sec
D16           0.00010000 sec
IN0           0.00027600 sec

======== CHANNEL f1 ========
NUC1                  1H
P0                 14.10 usec
P1                 14.10 usec
PL1                 0.00 dB
PL1W         11.43159485 W
SFO1         400.1513387 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPZ1               10.00 %
P16              1000.00 usec
ND0                    1
TD                   512
SFO1            400.1513 MHz
FIDRES          7.076540 Hz
SW                 9.055 ppm
FnMODE                QF
SI                  1024
SF           400.1499808 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.40
SI                  1024
MC2                   QF
SF           400.1499808 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
```

Figure 25: 400 MHz ^{1}H-^{1}H COSY spectrum of **2**.



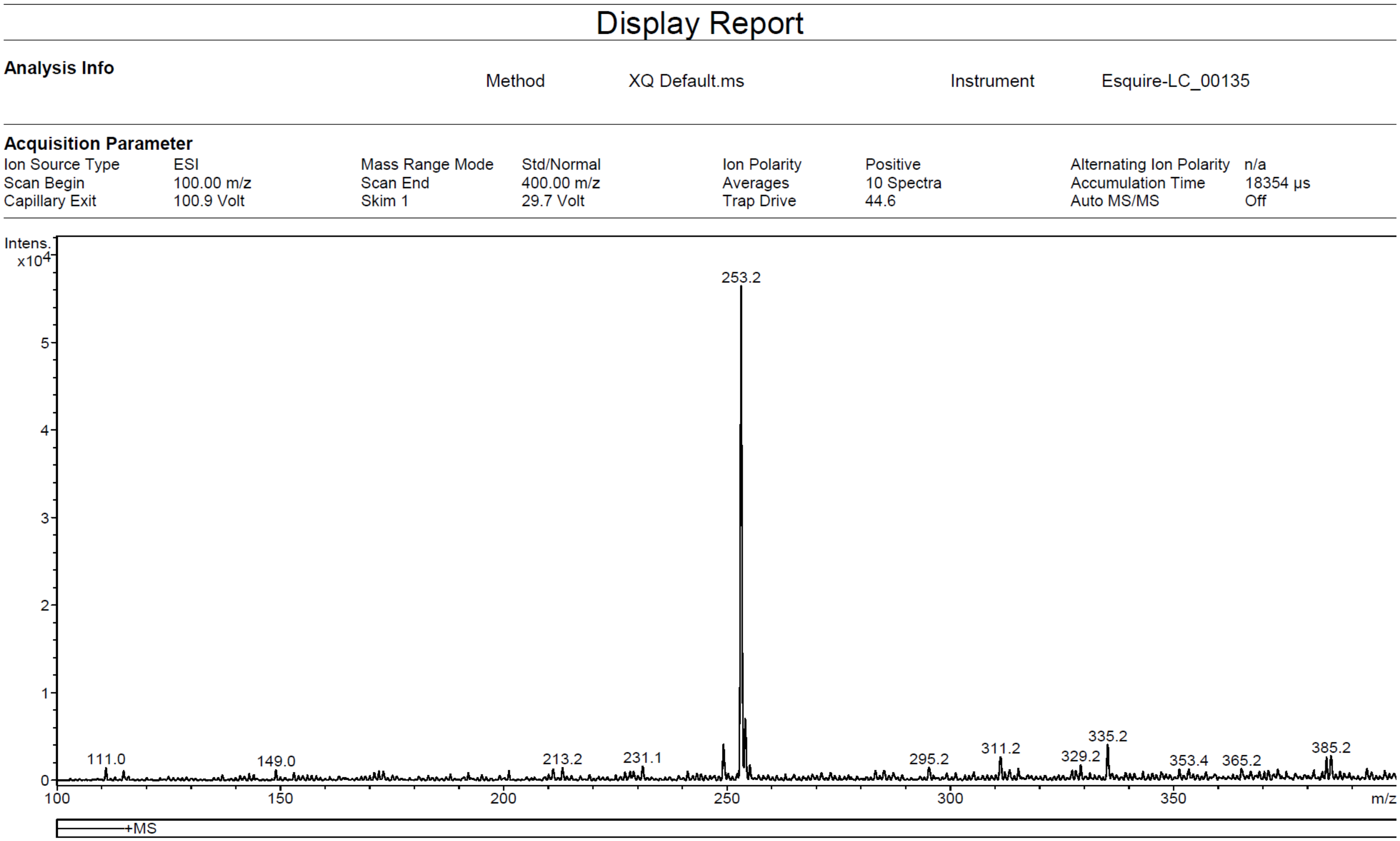
```
NAME            JP-2-109bb
EXPNO                   12
PROCNO                   1
Date_             20080601
Time                  5.15
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG         hsqcetgpsi2
TD                    1024
SOLVENT              CDCl3
NS                       2
DS                      16
SWH               3623.188 Hz
FIDRES            3.538270 Hz
AQ               0.1413620 sec
RG                    2050
DW                 138.000 usec
DE                    6.50 usec
TE                   300.1 K
CNST2          145.0000000
D0              0.00000300 sec
D1              1.45473897 sec
D4              0.00172414 sec
D11             0.03000000 sec
D13             0.00000400 sec
D16             0.00010000 sec
D24             0.00086207 sec
IN0             0.00003000 sec
ZGOPTNS

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.10 usec
P2                   28.20 usec
P28                2000.00 usec
PL1                   0.00 dB
PL1W           11.43159485 W
SFO1           400.1513387 MHz

======== CHANNEL f2 ========
CPDPRG2               garp
NUC2                   13C
P3                    9.50 usec
P4                   19.00 usec
PCPD2                70.00 usec
PL2                  -1.00 dB
PL12                 15.80 dB
PL2W           50.97591400 W
PL12W           1.06503785 W
SFO2           100.6253417 MHz

====== GRADIENT CHANNEL =====
GPNAM1            SINE.100
GPNAM2            SINE.100
GPNAM3            SINE.100
GPNAM4            SINE.100
GPZ1                 80.00 %
GPZ2                 20.10 %
GPZ3                 11.00 %
GPZ4                 -5.00 %
P16                1000.00 usec
P19                 600.00 usec
ND0                      2
TD                     256
SFO1              100.6253 MHz
FIDRES           65.111671 Hz
SW                 165.650 ppm
FnMODE      Echo-Antiecho
SI                    1024
SF             400.1499808 MHz
WDW                  QSINE
SSB                      2
LB                    0.00 Hz
GB                       0
PC                    1.40
SI                    1024
MC2         echo-antiecho
SF             100.6177980 MHz
WDW                  QSINE
SSB                      2
LB                    0.00 Hz
GB                       0
```

Figure 26: 400-100 MHz ^{1}H-^{13}C HSQC spectrum of **2**.



Display Report

Analysis Info

Method XQ Default.ms

Instrument Esquire-LC_00135

Acquisition Parameter

Ion Source Type	ESI	Mass Range Mode	Std/Normal	Ion Polarity	Positive	Alternating Ion Polarity	n/a
Scan Begin	100.00 m/z	Scan End	400.00 m/z	Averages	10 Spectra	Accumulation Time	18354 μs
Capillary Exit	100.9 Volt	Skim 1	29.7 Volt	Trap Drive	44.6	Auto MS/MS	Off

Figure 27: Mass spectrum of **2**.

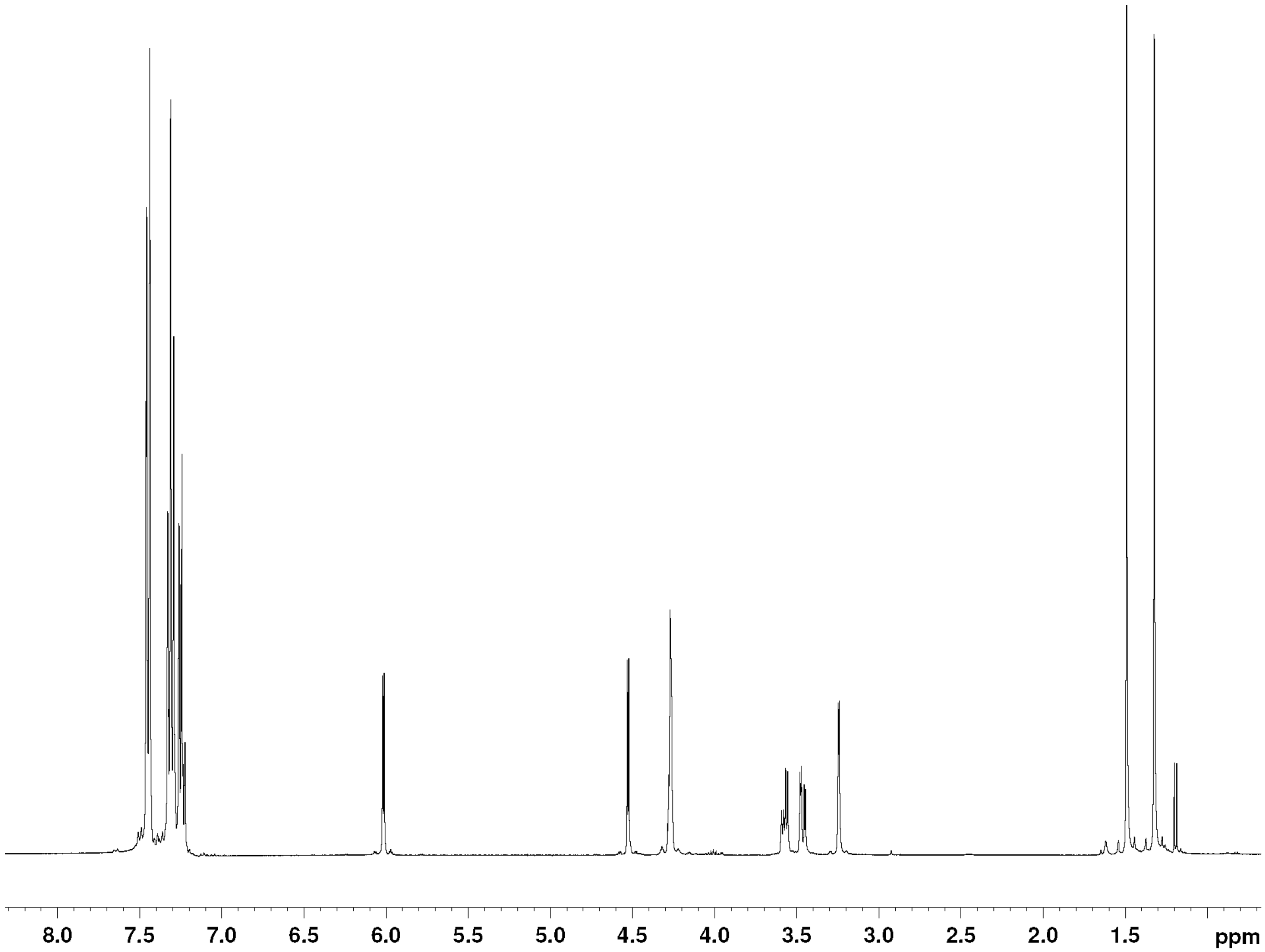
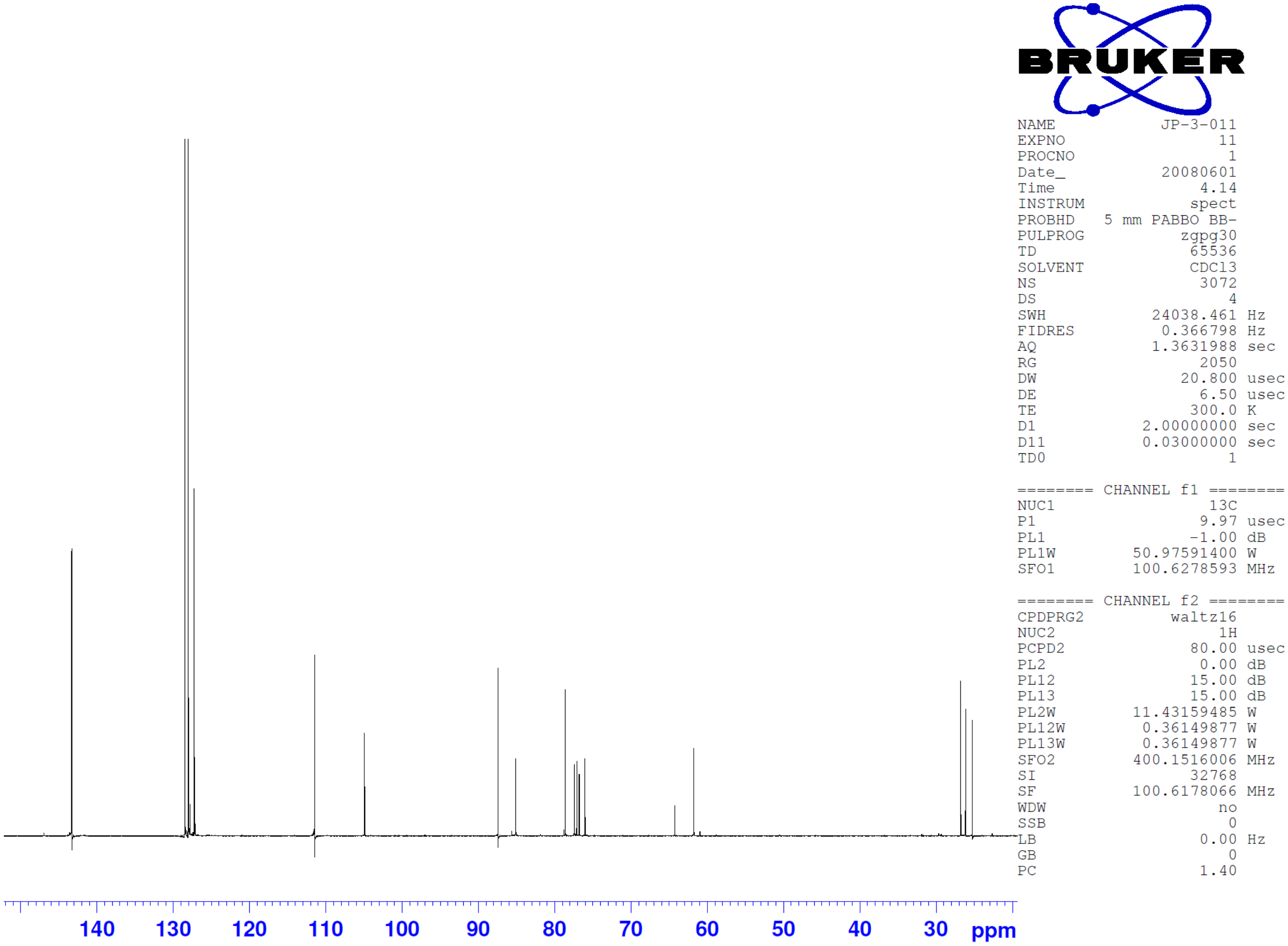


Figure 28: 400 MHz ^{1}H spectrum of **3**.

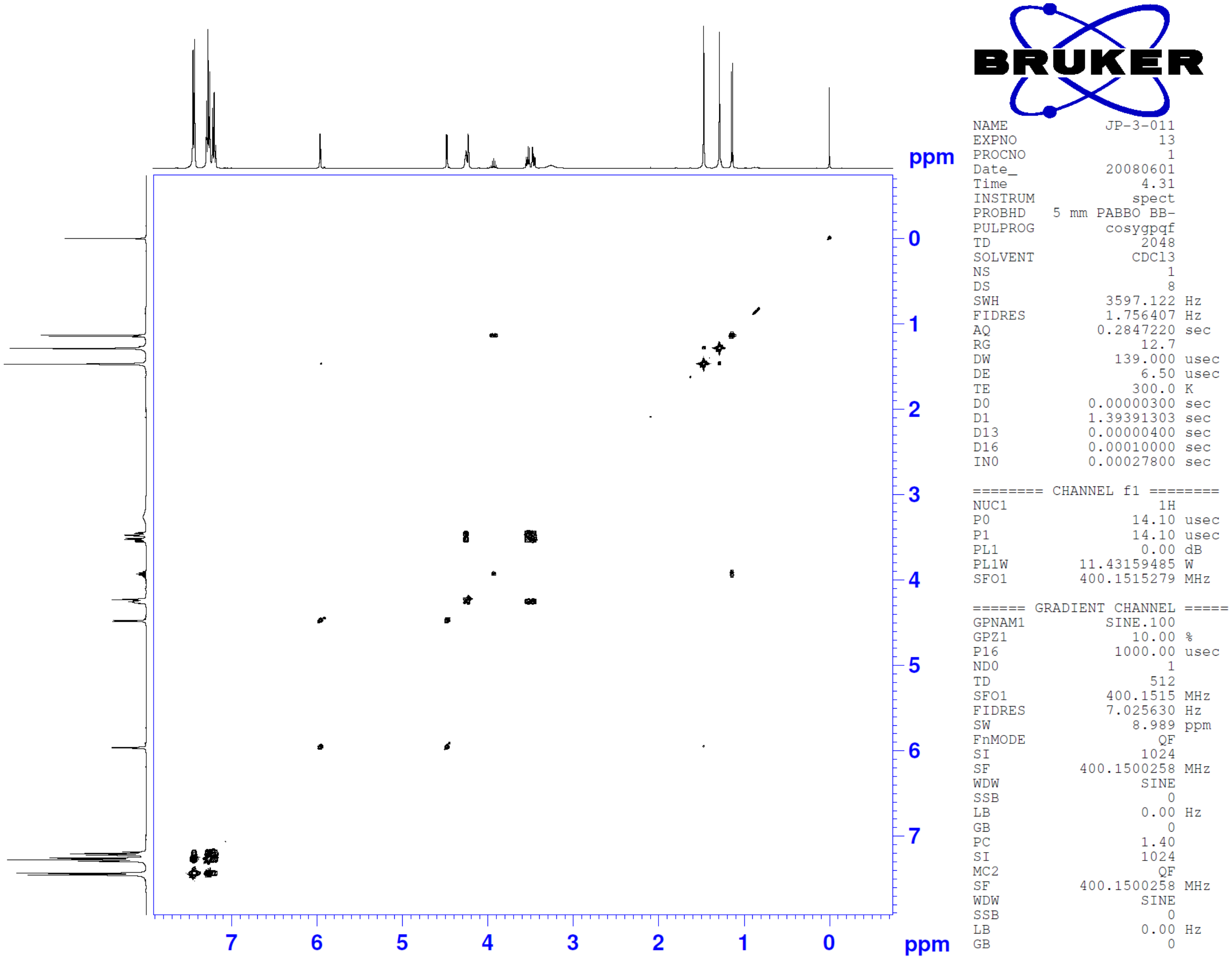


```
NAME            JP-3-011
EXPNO                 11
PROCNO                 1
Date_           20080601
Time                4.14
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 3072
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 2050
DW               20.800 usec
DE                 6.50 usec
TE                300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.97 usec
PL1               -1.00 dB
PL1W        50.97591400 W
SFO1        100.6278593 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W        11.43159485 W
PL12W        0.36149877 W
PL13W        0.36149877 W
SFO2        400.1516006 MHz
SI                32768
SF          100.6178066 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.40
```

Figure 29: 100 MHz ^{13}C spectrum of **3**.

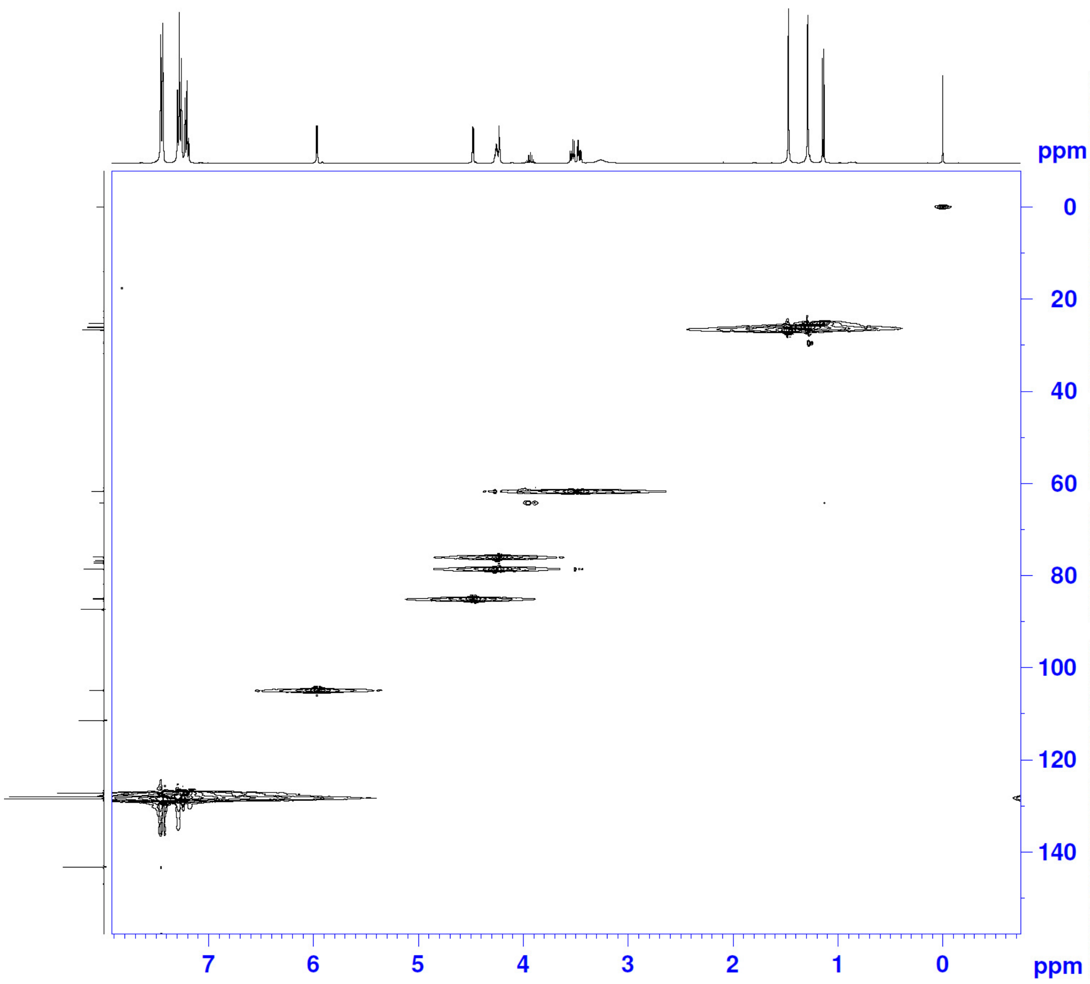


```
NAME             JP-3-011
EXPNO                  13
PROCNO                  1
Date_            20080601
Time                 4.31
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG          cosygpqf
TD                   2048
SOLVENT             CDCl3
NS                      1
DS                      8
SWH              3597.122 Hz
FIDRES           1.756407 Hz
AQ              0.2847220 sec
RG                   12.7
DW                139.000 usec
DE                   6.50 usec
TE                  300.0 K
D0             0.00000300 sec
D1             1.39391303 sec
D13            0.00000400 sec
D16            0.00010000 sec
IN0            0.00027800 sec

======== CHANNEL f1 ========
NUC1                   1H
P0                  14.10 usec
P1                  14.10 usec
PL1                  0.00 dB
PL1W          11.43159485 W
SFO1          400.1515279 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPZ1                10.00 %
P16               1000.00 usec
ND0                     1
TD                    512
SFO1             400.1515 MHz
FIDRES           7.025630 Hz
SW                  8.989 ppm
FnMODE                 QF
SI                   1024
SF            400.1500258 MHz
WDW                  SINE
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.40
SI                   1024
MC2                    QF
SF            400.1500258 MHz
WDW                  SINE
SSB                     0
LB                   0.00 Hz
GB                      0
```

Figure 30: 400 MHz ^{1}H-^{1}H COSY spectrum of **3**.



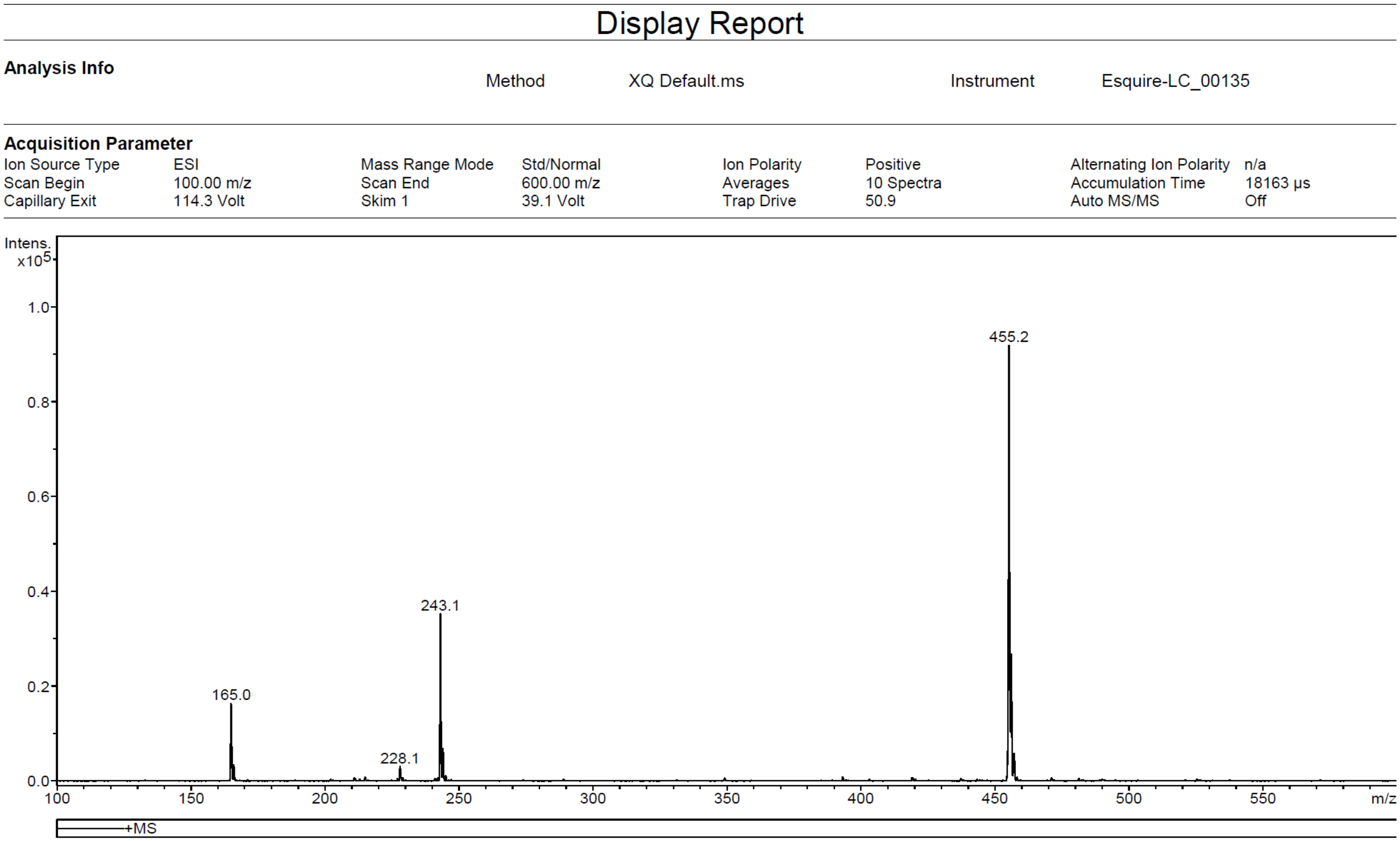
```
NAME                JP-3-011
EXPNO                     12
PROCNO                     1
Date_               20080601
Time                    4.16
INSTRUM                spect
PROBHD      5 mm PABBO BB-
PULPROG          hsqcetgpsi2
TD                      1024
SOLVENT                CDCl3
NS                         2
DS                        16
SWH                 3597.122 Hz
FIDRES              3.512815 Hz
AQ                 0.1423860 sec
RG                      2050
DW                   139.000 usec
DE                      6.50 usec
TE                     300.0 K
CNST2          145.0000000
D0                0.00000300 sec
D1                1.45371497 sec
D4                0.00172414 sec
D11               0.03000000 sec
D13               0.00000400 sec
D16               0.00010000 sec
D24               0.00086207 sec
IN0               0.00003000 sec
ZGOPTNS

======== CHANNEL f1 ========
NUC1                      1H
P1                     14.10 usec
P2                     28.20 usec
P28                  2000.00 usec
PL1                     0.00 dB
PL1W             11.43159485 W
SFO1             400.1515279 MHz

======== CHANNEL f2 ========
CPDPRG2                 garp
NUC2                     13C
P3                      9.50 usec
P4                     19.00 usec
PCPD2                  70.00 usec
PL2                    -1.00 dB
PL12                   15.80 dB
PL2W             50.97591400 W
PL12W             1.06503785 W
SFO2             100.6253417 MHz

====== GRADIENT CHANNEL =====
GPNAM1              SINE.100
GPNAM2              SINE.100
GPNAM3              SINE.100
GPNAM4              SINE.100
GPZ1                   80.00 %
GPZ2                   20.10 %
GPZ3                   11.00 %
GPZ4                   -5.00 %
P16                  1000.00 usec
P19                   600.00 usec
ND0                        2
TD                       256
SFO1                100.6253 MHz
FIDRES             65.111671 Hz
SW                   165.650 ppm
FnMODE         Echo-Antiecho
SI                      1024
SF               400.1500258 MHz
WDW                    QSINE
SSB                        2
LB                      0.00 Hz
GB                         0
PC                      1.40
SI                      1024
MC2           echo-antiecho
SF               100.6177980 MHz
WDW                    QSINE
SSB                        2
LB                      0.00 Hz
GB                         0
```

Figure 31: 400-100 MHz ^{1}H-^{13}C HSQC spectrum of **3**.



Display Report

Analysis Info

Method	XQ Default.ms	Instrument	Esquire-LC_00135

Acquisition Parameter

Ion Source Type	ESI	Mass Range Mode	Std/Normal	Ion Polarity	Positive	Alternating Ion Polarity	n/a
Scan Begin	100.00 m/z	Scan End	600.00 m/z	Averages	10 Spectra	Accumulation Time	18163 µs
Capillary Exit	114.3 Volt	Skim 1	39.1 Volt	Trap Drive	50.9	Auto MS/MS	Off

Figure 32: Mass spectrum of **3**.

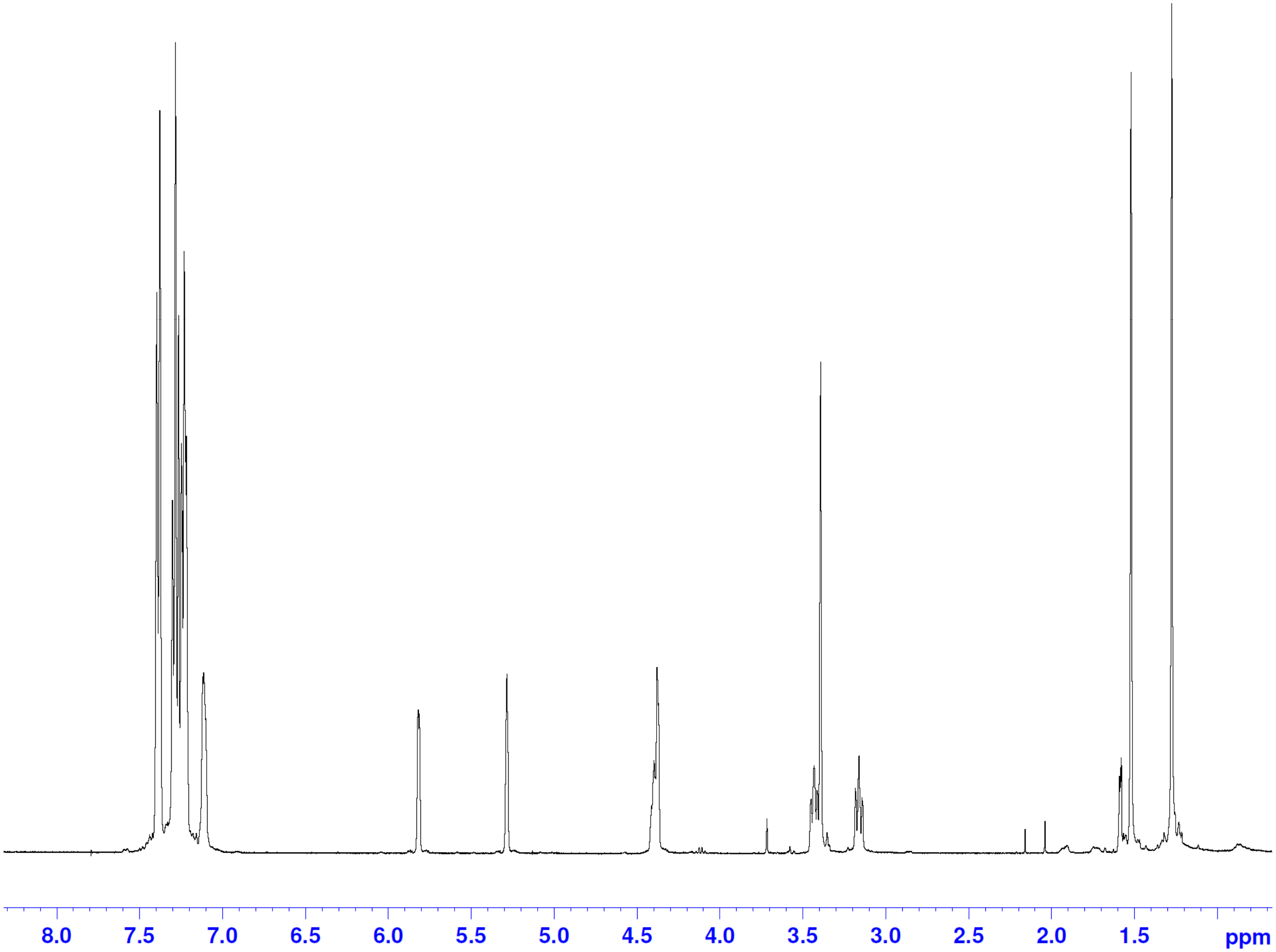
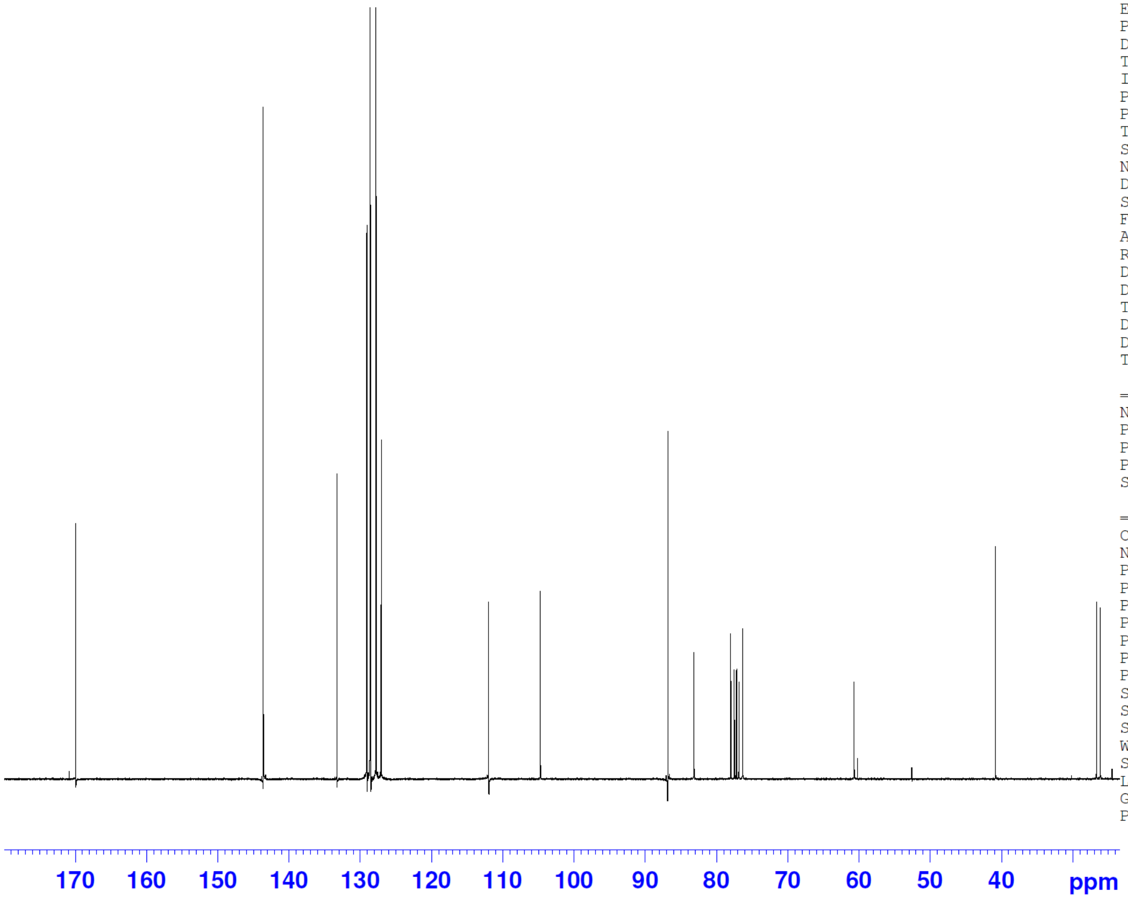


Figure 33: 400 MHz ^{1}H spectrum of **4**.

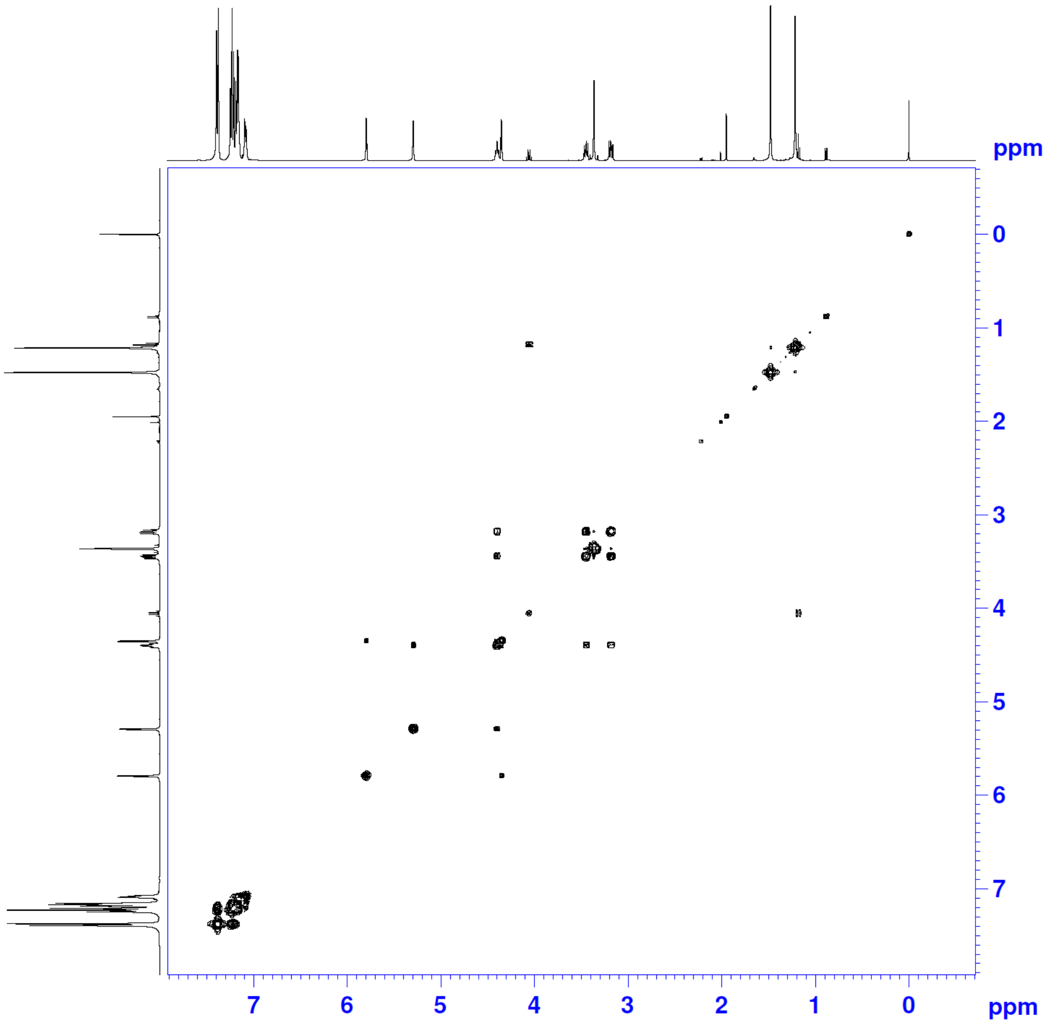


```
NAME           JP-2-087, T2
EXPNO                    11
PROCNO                    1
Date_              20080602
Time                  16.22
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631988 sec
RG                     2050
DW                   20.800 usec
DE                     6.50 usec
TE                    300.0 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                     9.97 usec
PL1                   -1.00 dB
PL1W            50.97591400 W
SFO1            100.6278593 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL2                    0.00 dB
PL12                  15.00 dB
PL13                  15.00 dB
PL2W            11.43159485 W
PL12W            0.36149877 W
PL13W            0.36149877 W
SFO2            400.1516006 MHz
SI                    32768
SF              100.6178196 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.40
```

Figure 34: 100 MHz ^{13}C spectrum of **4**.

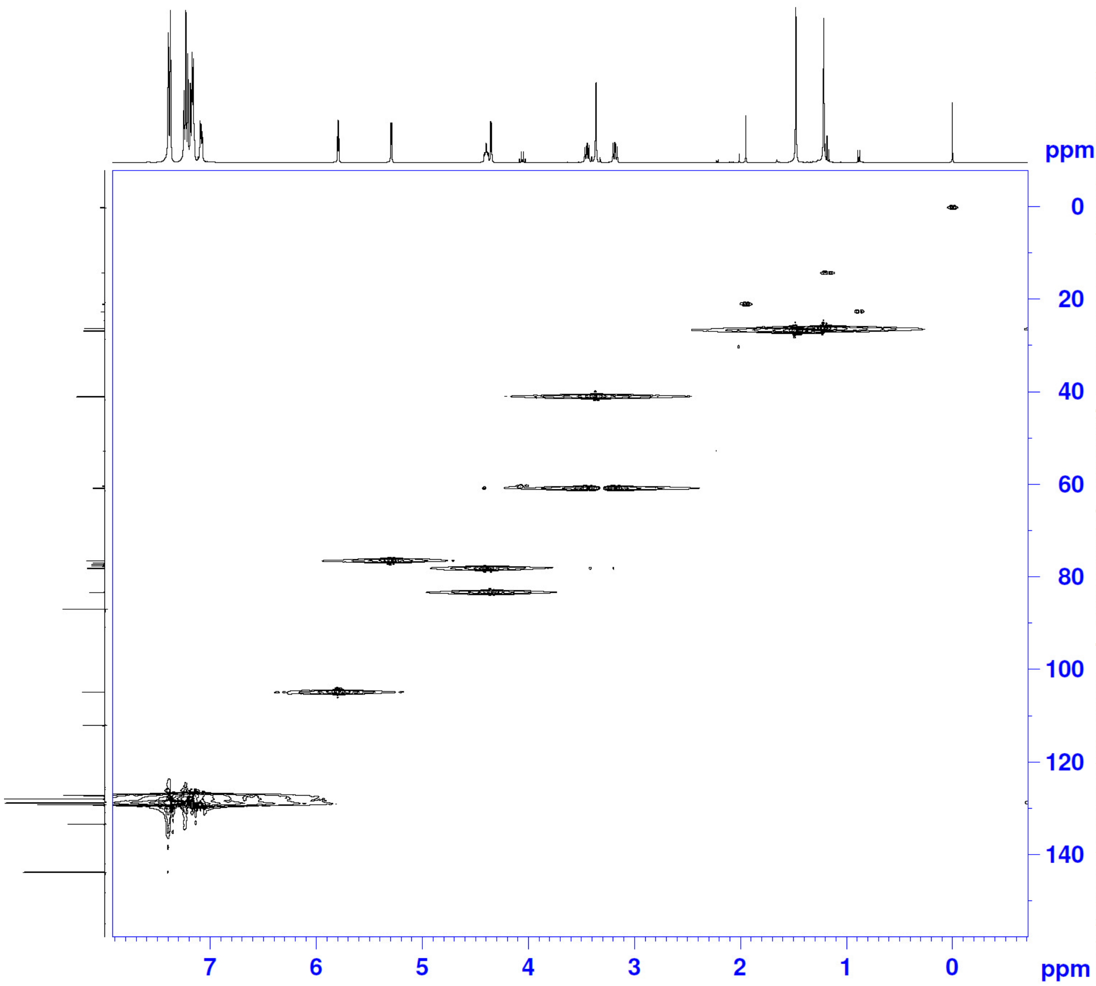


```
NAME         JP-2-087, T2
EXPNO                  12
PROCNO                  1
Date_            20080602
Time                16.23
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG          cosygpqf
TD                   2048
SOLVENT             CDCl3
NS                      1
DS                      8
SWH              3816.794 Hz
FIDRES           1.863669 Hz
AQ              0.2683380 sec
RG                      8
DW                131.000 usec
DE                   6.50 usec
TE                  299.9 K
D0             0.00000300 sec
D1             1.41029704 sec
D13            0.00000400 sec
D16            0.00010000 sec
IN0            0.00026200 sec

======== CHANNEL f1 ========
NUC1                   1H
P0                  14.10 usec
P1                  14.10 usec
PL1                  0.00 dB
PL1W          11.43159485 W
SFO1          400.1516847 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPZ1                10.00 %
P16               1000.00 usec
ND0                     1
TD                    128
SFO1             400.1517 MHz
FIDRES          29.818703 Hz
SW                  9.538 ppm
FnMODE                 QF
SI                   1024
SF            400.1500603 MHz
WDW                  SINE
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.40
SI                   1024
MC2                    QF
SF            400.1500603 MHz
WDW                  SINE
SSB                     0
LB                   0.00 Hz
GB                      0
```

Figure 35: 400 MHz ^{1}H-^{1}H COSY spectrum of **4**.



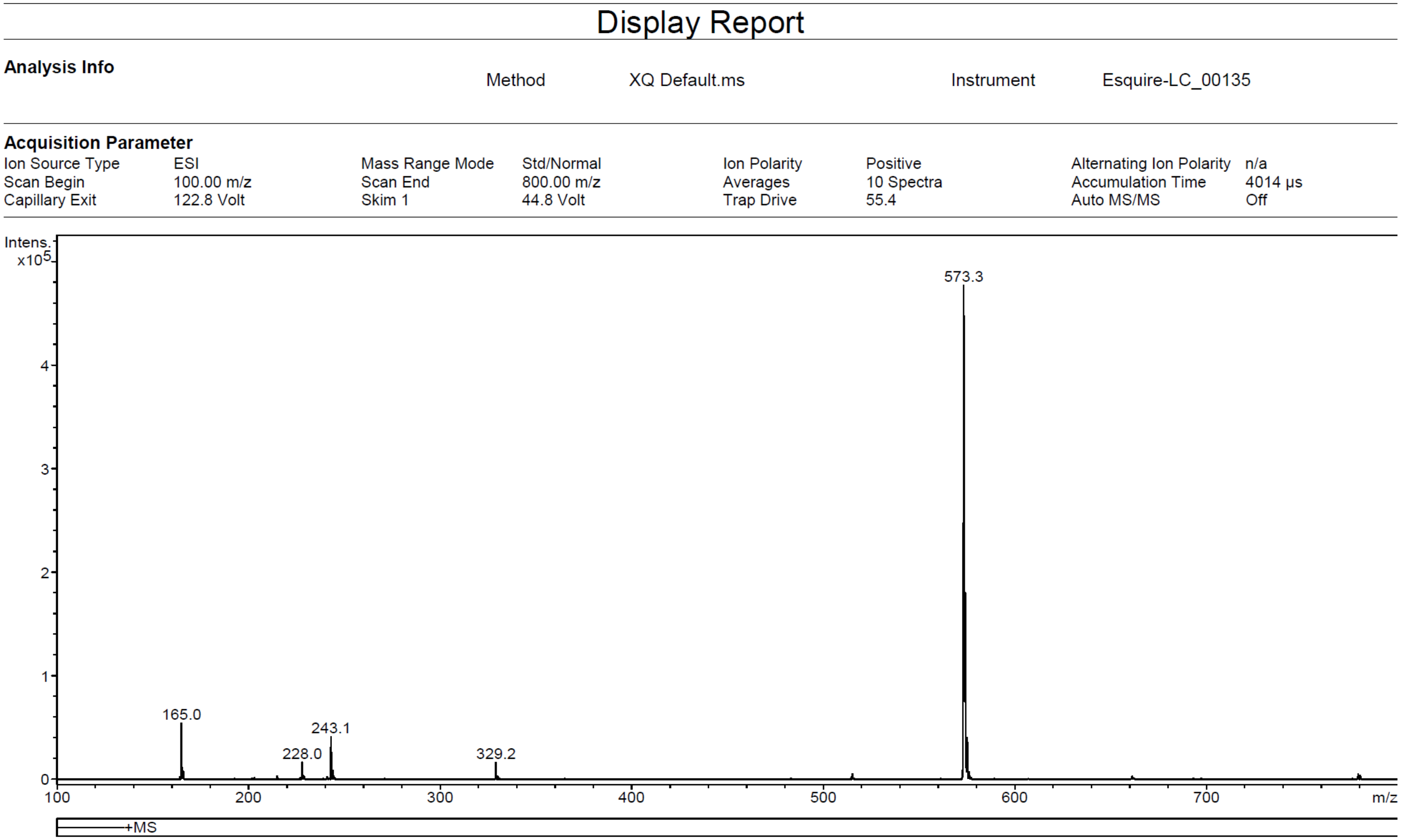
```
NAME         JP-2-087, T2
EXPNO                  13
PROCNO                  1
Date_            20080602
Time                16.29
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG       hsqcetgpsi2
TD                   1024
SOLVENT             CDCl3
NS                      2
DS                     16
SWH              3816.794 Hz
FIDRES           3.727338 Hz
AQ              0.1341940 sec
RG                   1620
DW                131.000 usec
DE                   6.50 usec
TE                  300.0 K
CNST2         145.0000000
D0             0.00000300 sec
D1             1.46190703 sec
D4             0.00172414 sec
D11            0.03000000 sec
D13            0.00000400 sec
D16            0.00010000 sec
D24            0.00086207 sec
IN0            0.00003000 sec
ZGOPTNS

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.10 usec
P2                  28.20 usec
P28               2000.00 usec
PL1                  0.00 dB
PL1W          11.43159485 W
SFO1          400.1516847 MHz

======== CHANNEL f2 ========
CPDPRG2              garp
NUC2                  13C
P3                   9.50 usec
P4                  19.00 usec
PCPD2               70.00 usec
PL2                 -1.00 dB
PL12                15.80 dB
PL2W          50.97591400 W
PL12W          1.06503785 W
SFO2          100.6253417 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPNAM3           SINE.100
GPNAM4           SINE.100
GPZ1                80.00 %
GPZ2                20.10 %
GPZ3                11.00 %
GPZ4                -5.00 %
P16               1000.00 usec
P19                600.00 usec
ND0                     2
TD                    256
SFO1             100.6253 MHz
FIDRES          65.111671 Hz
SW                165.650 ppm
FnMODE     Echo-Antiecho
SI                   1024
SF            400.1500603 MHz
WDW                 QSINE
SSB                     2
LB                   0.00 Hz
GB                      0
PC                   1.40
SI                   1024
MC2        echo-antiecho
SF            100.6177980 MHz
WDW                 QSINE
SSB                     2
LB                   0.00 Hz
GB                      0
```

Figure 36: 400-100 MHz ^1H-^{13}C HSQC spectrum of **4**.



Display Report

Analysis Info

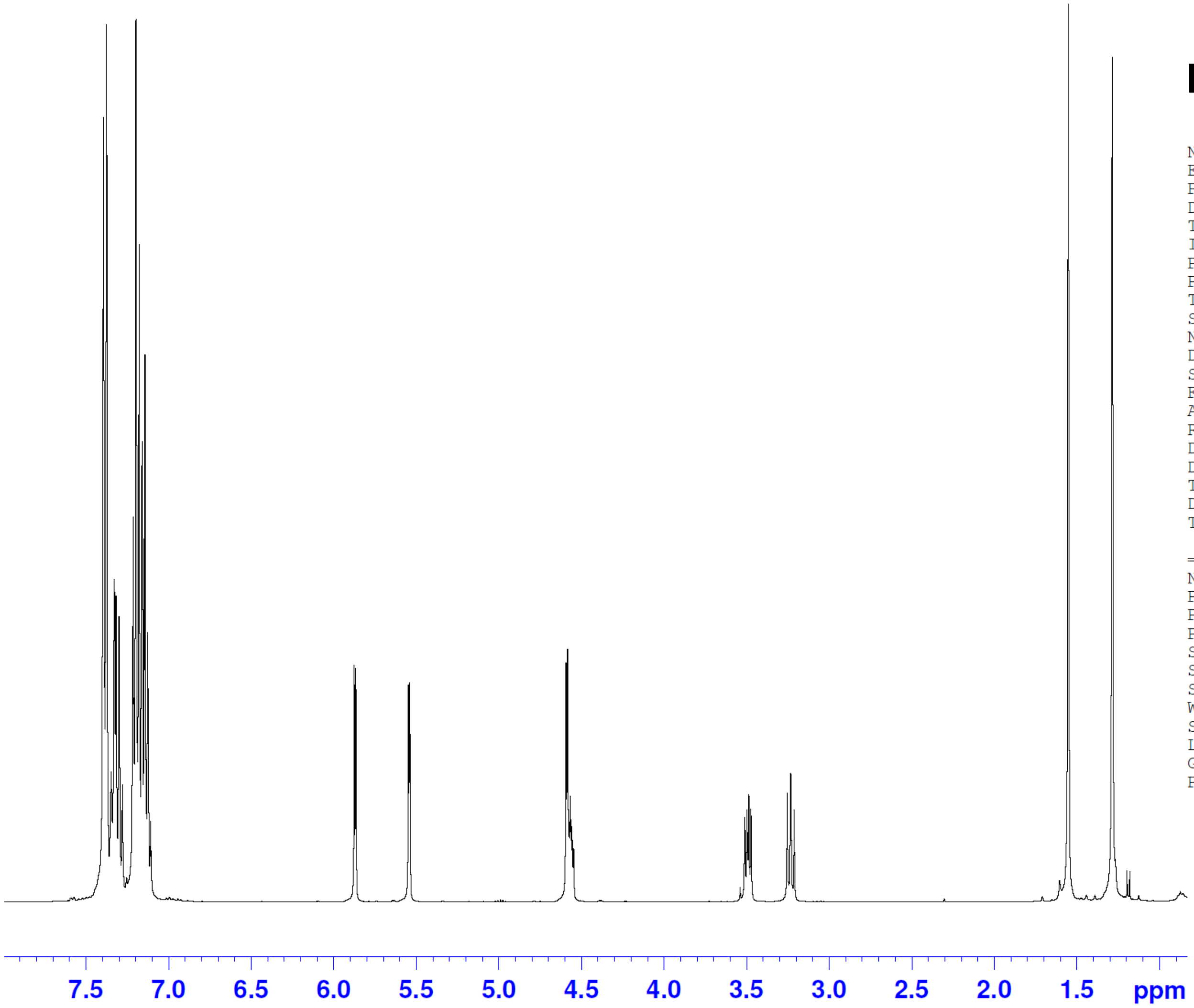
Method XQ Default.ms

Instrument Esquire-LC_00135

Acquisition Parameter

Ion Source Type	ESI	Mass Range Mode	Std/Normal	Ion Polarity	Positive	Alternating Ion Polarity	n/a
Scan Begin	100.00 m/z	Scan End	800.00 m/z	Averages	10 Spectra	Accumulation Time	4014 µs
Capillary Exit	122.8 Volt	Skim 1	44.8 Volt	Trap Drive	55.4	Auto MS/MS	Off

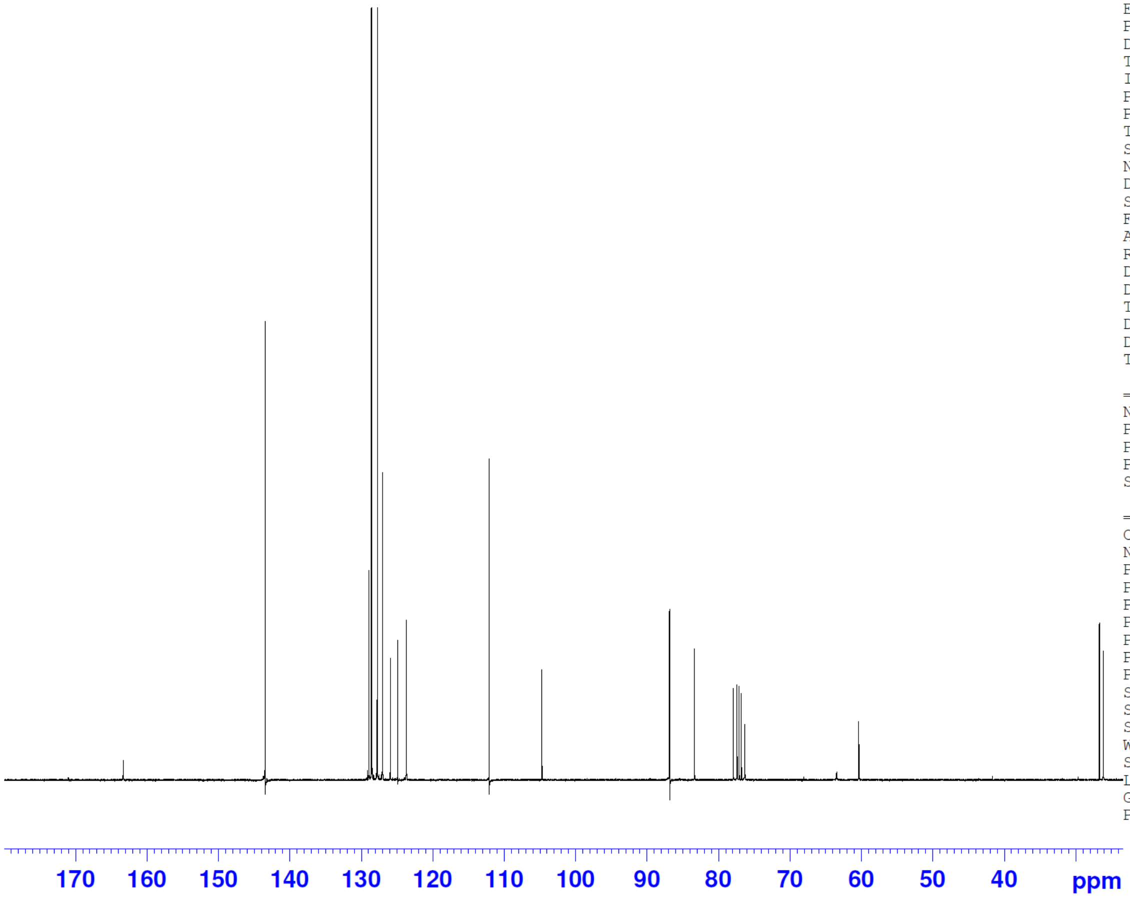
Figure 37: Mass spectrum of **4**.



```
NAME          JP-2-101, T2
EXPNO                   10
PROCNO                   1
Date_             20080602
TIme                 13.55
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ               3.9846387 sec
RG                    22.6
DW                  60.800 usec
DE                    6.50 usec
TE                   300.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.10 usec
PL1                   0.00 dB
PL1W           11.43159485 W
SFO1           400.1524711 MHz
SI                   32768
SF             400.1500480 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

Figure 38: 400 MHz ^{1}H spectrum of **5**.

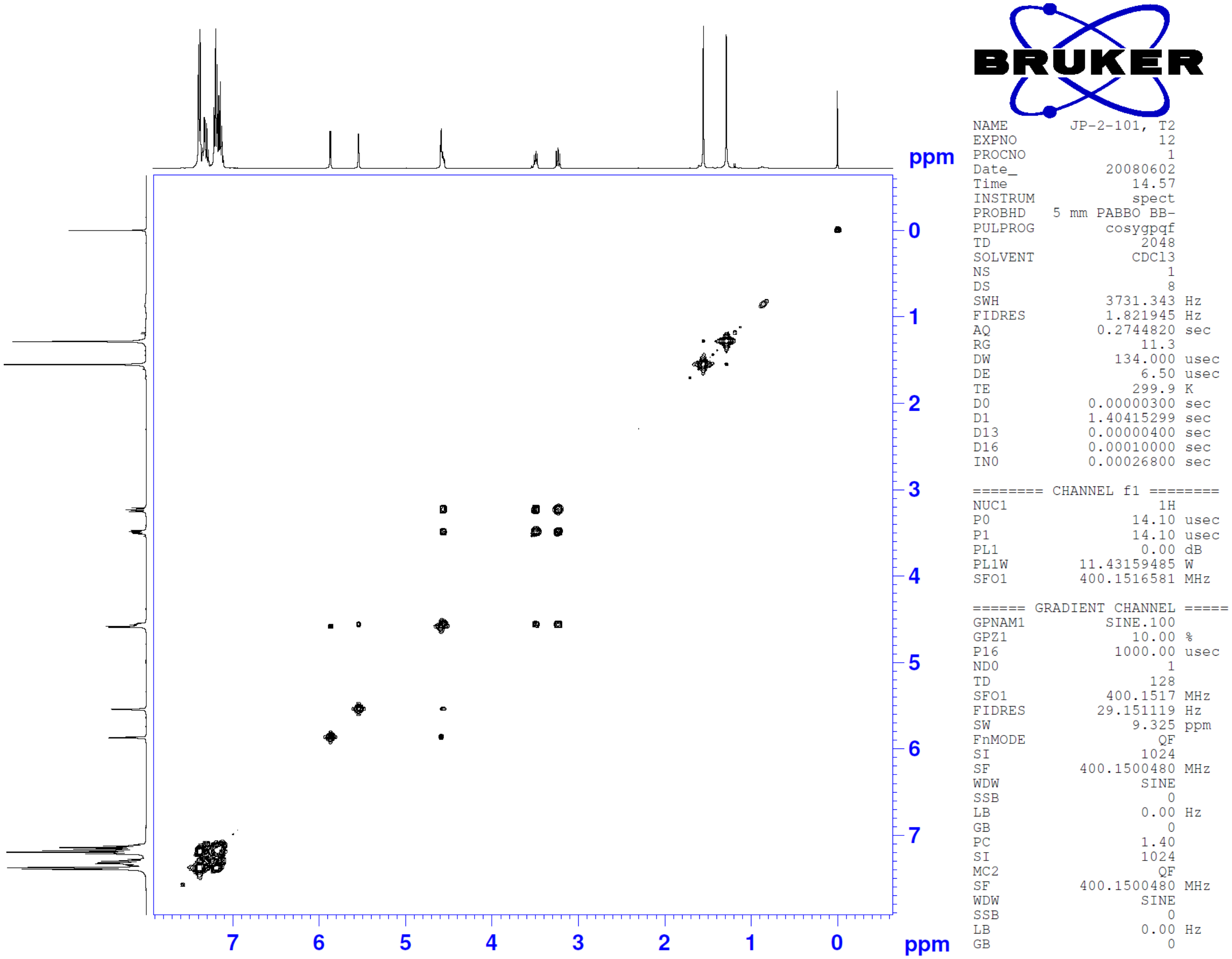


```
NAME          JP-2-101, T2
EXPNO                   11
PROCNO                   1
Date_             20080602
Time                 14.56
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                    2050
DW                  20.800 usec
DE                    6.50 usec
TE                   300.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.97 usec
PL1                  -1.00 dB
PL1W           50.97591400 W
SFO1           100.6278593 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 15.00 dB
PL13                 15.00 dB
PL2W           11.43159485 W
PL12W           0.36149877 W
PL13W           0.36149877 W
SFO2           400.1516006 MHz
SI                   32768
SF             100.6178139 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.40
```

Figure 39: 100 MHz ^{13}C spectrum of **5**.

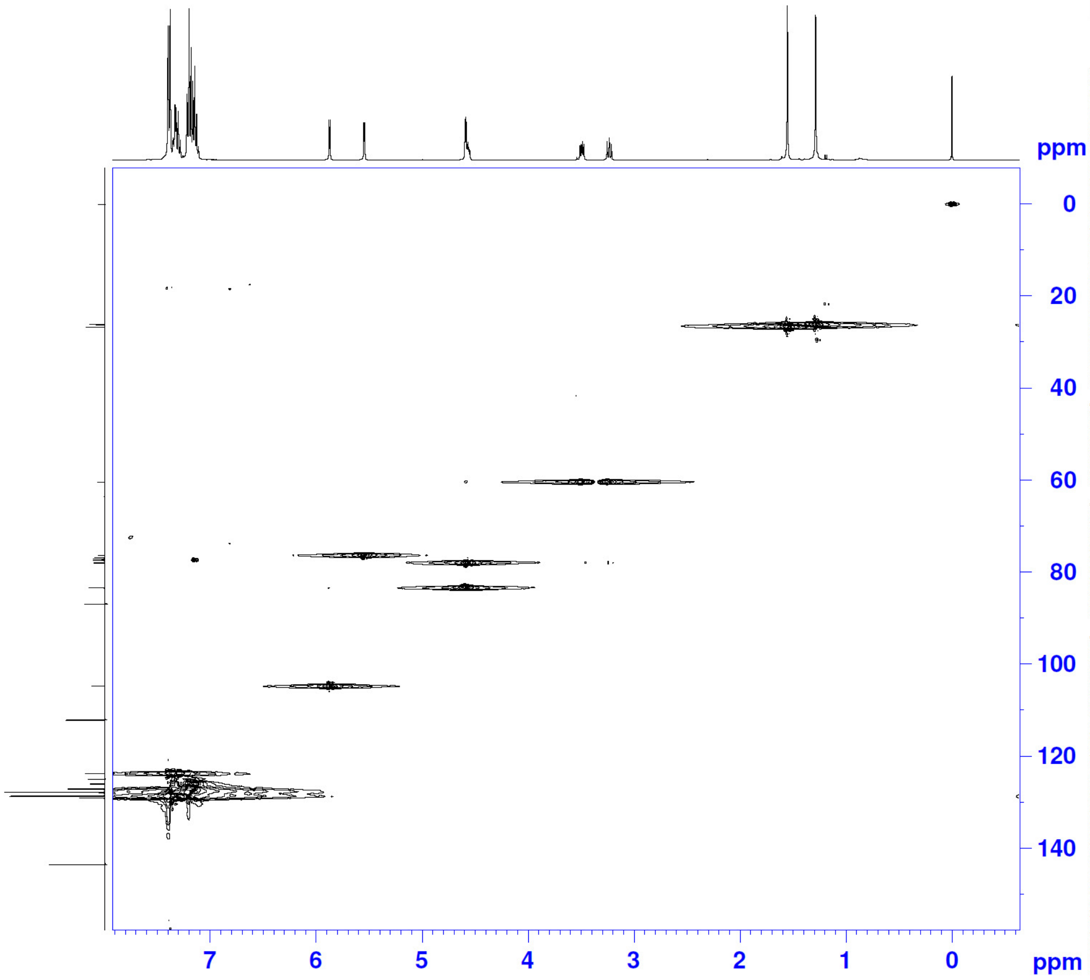


```
NAME          JP-2-101, T2
EXPNO                   12
PROCNO                   1
Date_             20080602
Time                 14.57
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG           cosygpqf
TD                    2048
SOLVENT              CDCl3
NS                       1
DS                       8
SWH               3731.343 Hz
FIDRES            1.821945 Hz
AQ               0.2744820 sec
RG                    11.3
DW                 134.000 usec
DE                    6.50 usec
TE                   299.9 K
D0              0.00000300 sec
D1              1.40415299 sec
D13             0.00000400 sec
D16             0.00010000 sec
IN0             0.00026800 sec

======== CHANNEL f1 ========
NUC1                    1H
P0                   14.10 usec
P1                   14.10 usec
PL1                   0.00 dB
PL1W           11.43159485 W
SFO1           400.1516581 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPZ1                10.00 %
P16               1000.00 usec
ND0                      1
TD                     128
SFO1              400.1517 MHz
FIDRES           29.151119 Hz
SW                   9.325 ppm
FnMODE                  QF
SI                    1024
SF             400.1500480 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.40
SI                    1024
MC2                     QF
SF             400.1500480 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0
```

Figure 40: 400 MHz ^{1}H-^{1}H COSY spectrum of **5**.



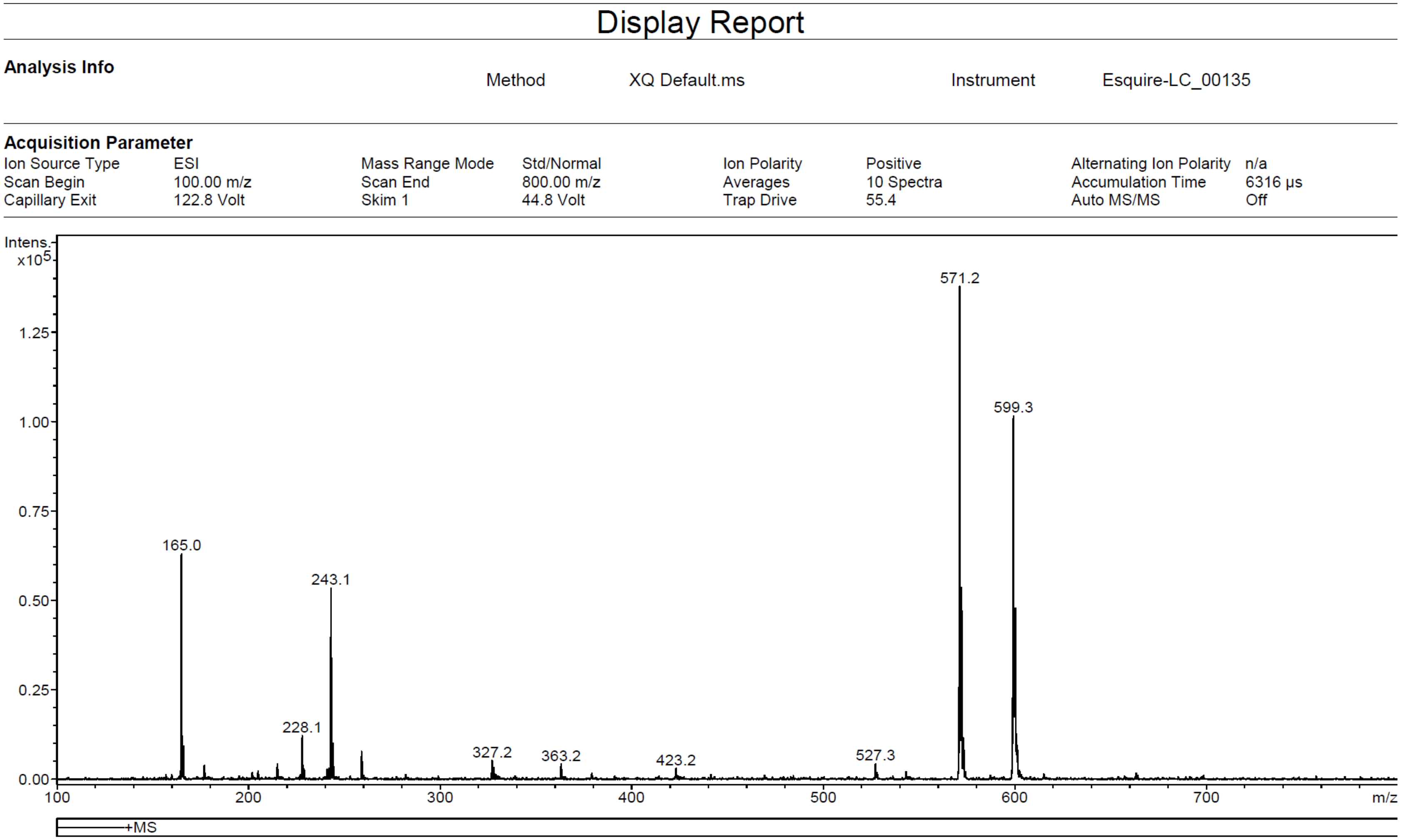
```
NAME          JP-2-101, T2
EXPNO                   13
PROCNO                   1
Date_             20080602
Time                 15.02
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG        hsqcetgpsi2
TD                    1024
SOLVENT              CDCl3
NS                       2
DS                      16
SWH               3731.343 Hz
FIDRES            3.643890 Hz
AQ               0.1372660 sec
RG                    2050
DW                 134.000 usec
DE                    6.50 usec
TE                   300.1 K
CNST2          145.0000000
D0              0.00000300 sec
D1              1.45883501 sec
D4              0.00172414 sec
D11             0.03000000 sec
D13             0.00000400 sec
D16             0.00010000 sec
D24             0.00086207 sec
IN0             0.00003000 sec
ZGOPTNS

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.10 usec
P2                   28.20 usec
P28                2000.00 usec
PL1                   0.00 dB
PL1W           11.43159485 W
SFO1           400.1516581 MHz

======== CHANNEL f2 ========
CPDPRG2               garp
NUC2                   13C
P3                    9.50 usec
P4                   19.00 usec
PCPD2                70.00 usec
PL2                  -1.00 dB
PL12                 15.80 dB
PL2W           50.97591400 W
PL12W           1.06503785 W
SFO2           100.6253417 MHz

====== GRADIENT CHANNEL =====
GPNAM1            SINE.100
GPNAM2            SINE.100
GPNAM3            SINE.100
GPNAM4            SINE.100
GPZ1                 80.00 %
GPZ2                 20.10 %
GPZ3                 11.00 %
GPZ4                 -5.00 %
P16                1000.00 usec
P19                 600.00 usec
ND0                      2
TD                     256
SFO1              100.6253 MHz
FIDRES           65.111671 Hz
SW                 165.650 ppm
FnMODE     Echo-Antiecho
SI                    1024
SF             400.1500480 MHz
WDW                  QSINE
SSB                      2
LB                    0.00 Hz
GB                       0
PC                    1.40
SI                    1024
MC2         echo-antiecho
SF             100.6177980 MHz
WDW                  QSINE
SSB                      2
LB                    0.00 Hz
GB                       0
```

Figure 41: 400-100 MHz ^{1}H-^{13}C HSQC spectrum of **5**.



Display Report

Analysis Info

Method	XQ Default.ms	Instrument	Esquire-LC_00135

Acquisition Parameter

Ion Source Type	ESI	Mass Range Mode	Std/Normal	Ion Polarity	Positive	Alternating Ion Polarity	n/a
Scan Begin	100.00 m/z	Scan End	800.00 m/z	Averages	10 Spectra	Accumulation Time	6316 µs
Capillary Exit	122.8 Volt	Skim 1	44.8 Volt	Trap Drive	55.4	Auto MS/MS	Off

Figure 42: Mass spectrum of **5**.

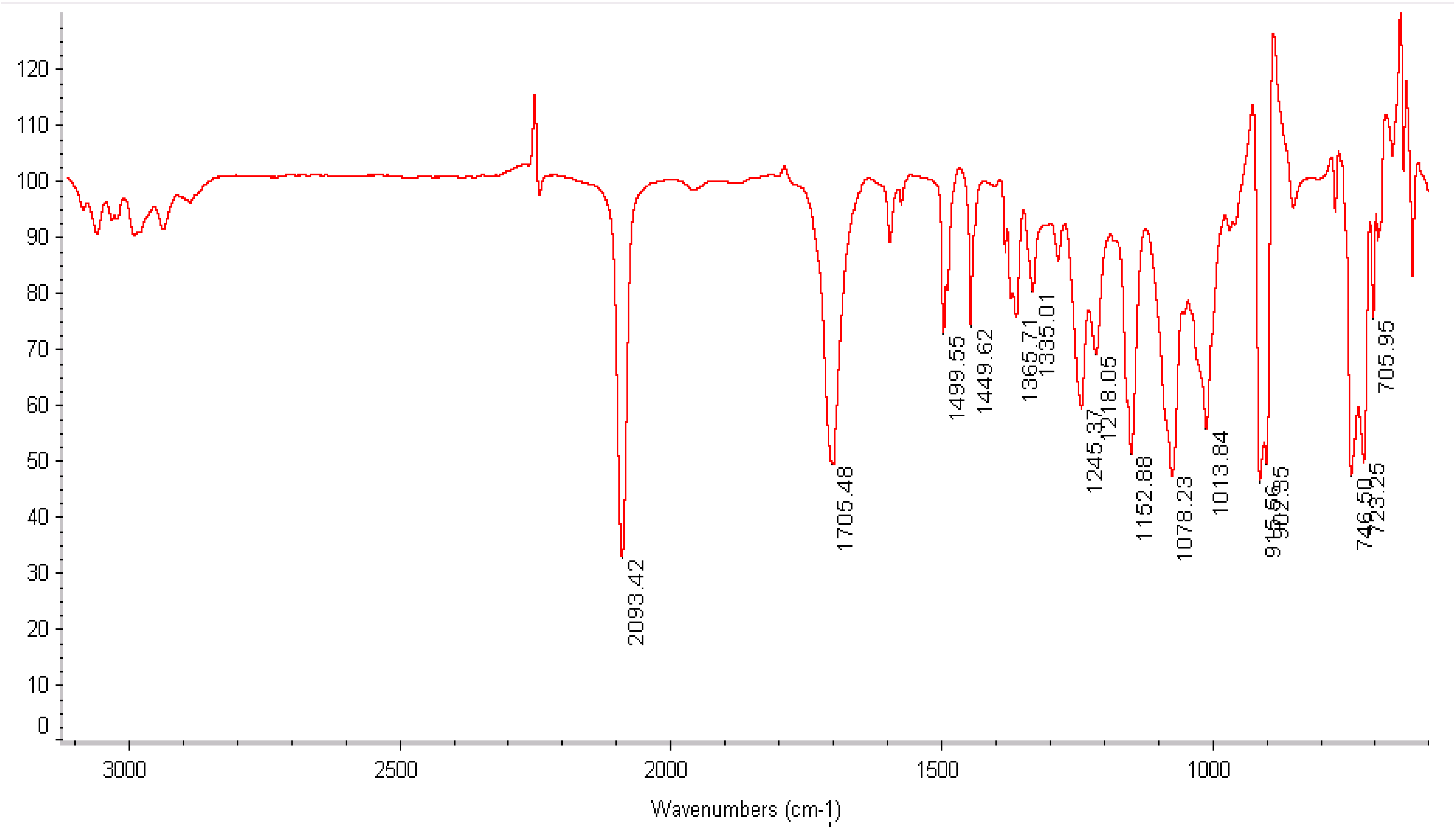
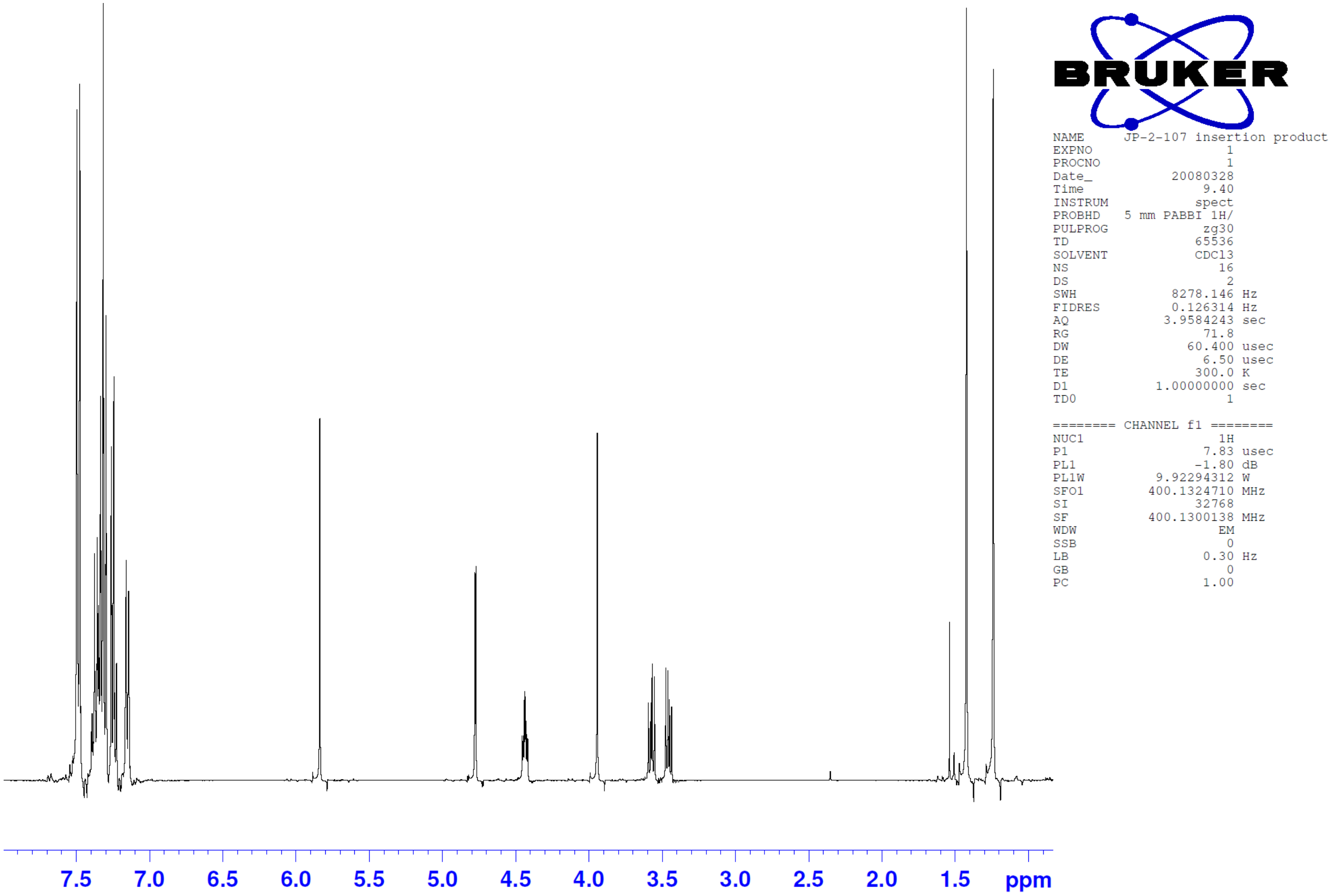


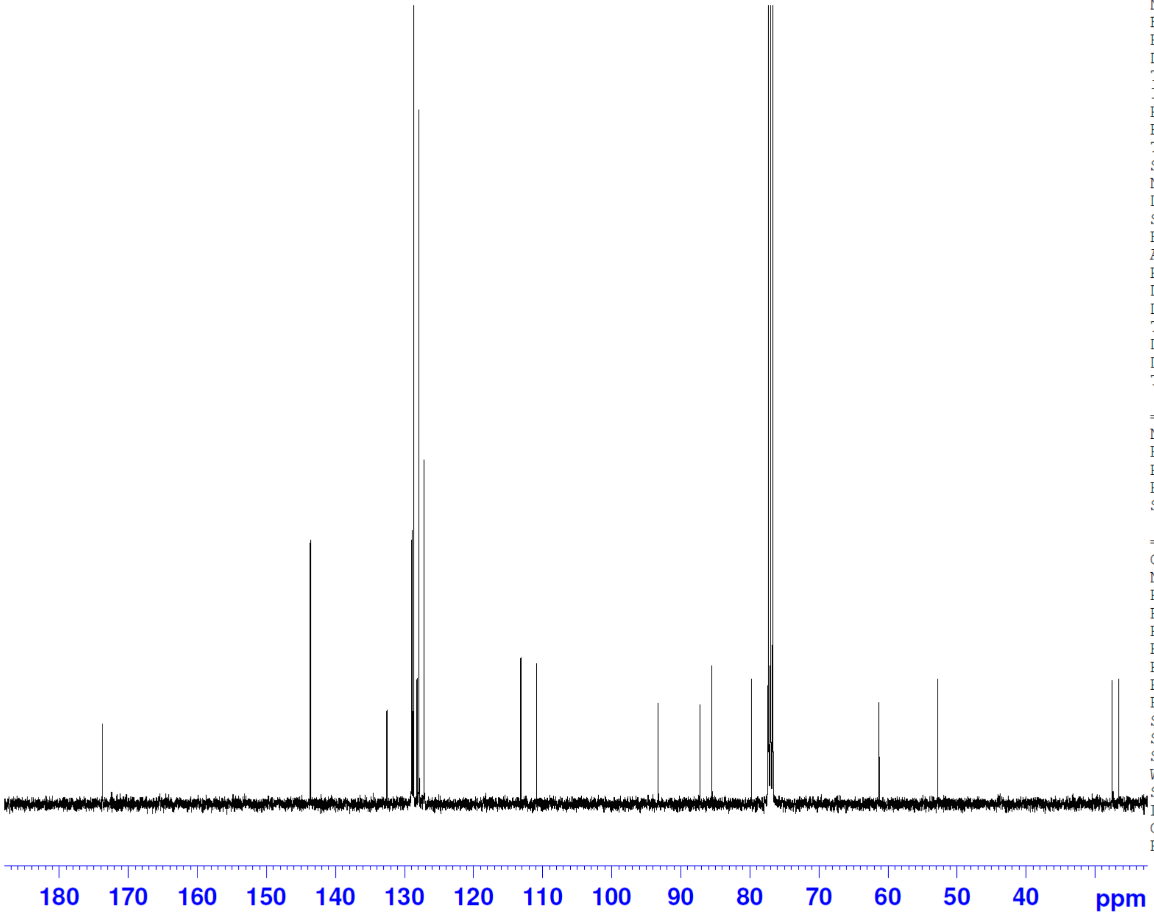
Figure 43: Infrared spectrum of **5**.



```
NAME      JP-2-107 insertion product
EXPNO                    1
PROCNO                   1
Date_             20080328
Time                  9.40
INSTRUM              spect
PROBHD   5 mm PABBI 1H/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ               3.9584243 sec
RG                    71.8
DW                  60.400 usec
DE                    6.50 usec
TE                   300.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.83 usec
PL1                  -1.80 dB
PL1W            9.92294312 W
SFO1           400.1324710 MHz
SI                   32768
SF             400.1300138 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

Figure 44: 400 MHz ^{1}H spectrum of **6**.

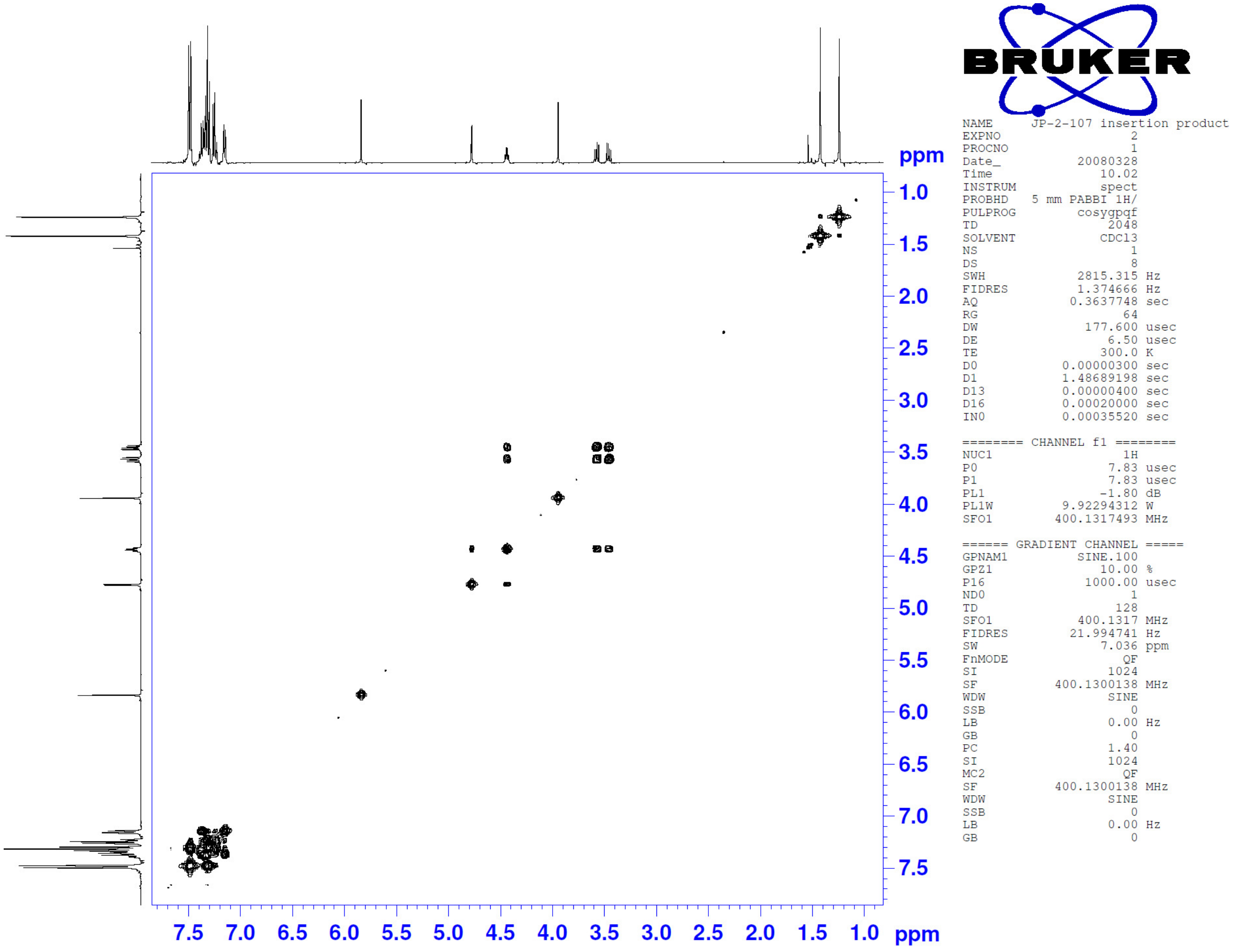


```
NAME      JP-2-107-Rhdecomp
EXPNO                   11
PROCNO                   1
Date_             20080524
Time                 12.47
INSTRUM              spect
PROBHD       5 mm PABBO BB-
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                    2050
DW                  20.800 usec
DE                    6.50 usec
TE                   300.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.97 usec
PL1                  -1.00 dB
PL1W           50.97591400 W
SFO1           100.6278593 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 15.00 dB
PL13                 15.00 dB
PL2W           11.43159485 W
PL12W           0.36149877 W
PL13W           0.36149877 W
SFO2           400.1516006 MHz
SI                   32768
SF             100.6177962 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

Figure 45: 100 MHz ^{13}C spectrum of **6**.

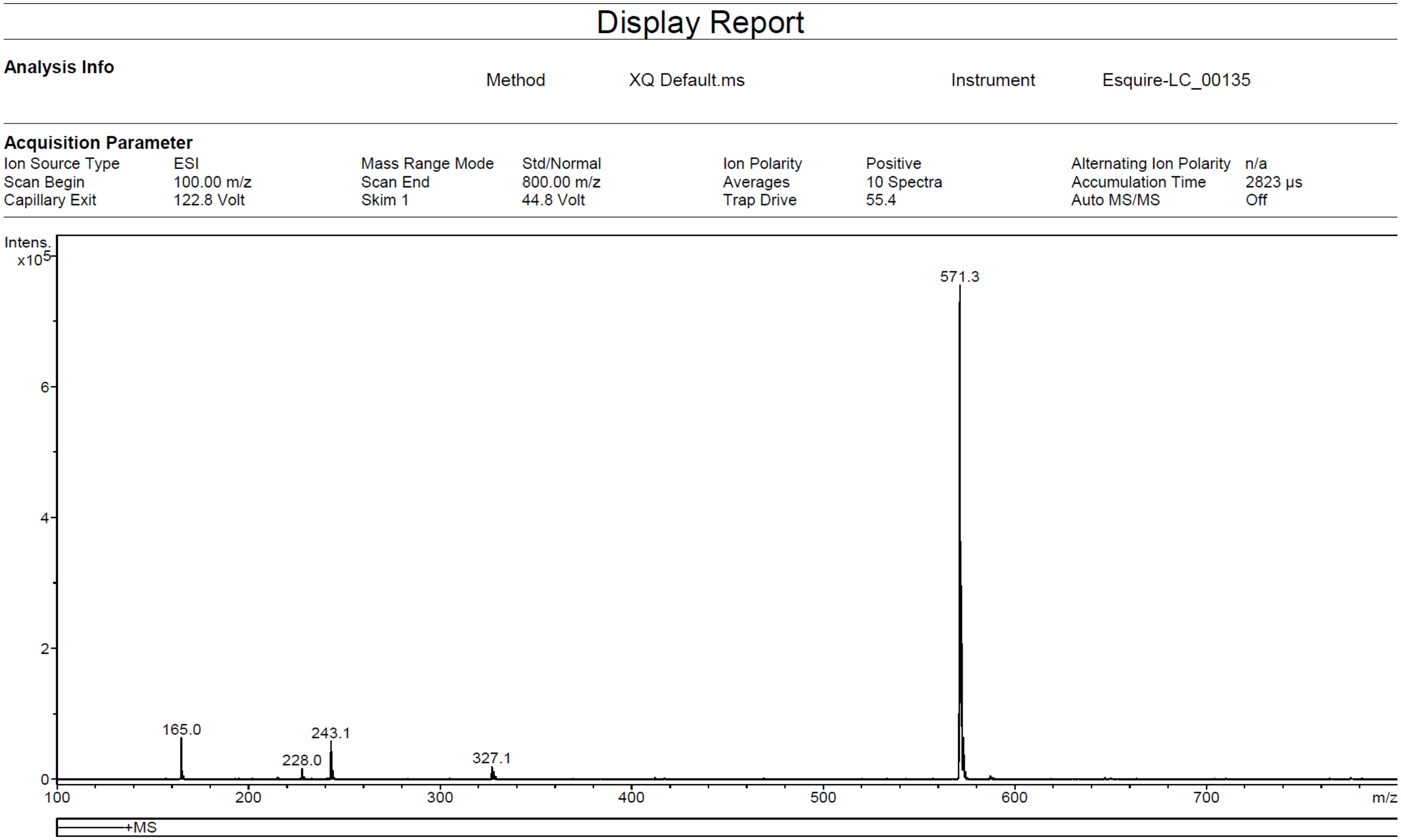


```
NAME       JP-2-107 insertion product
EXPNO                   2
PROCNO                  1
Date_            20080328
Time                10.02
INSTRUM             spect
PROBHD   5 mm PABBI 1H/
PULPROG          cosygpqf
TD                   2048
SOLVENT             CDCl3
NS                      1
DS                      8
SWH              2815.315 Hz
FIDRES           1.374666 Hz
AQ              0.3637748 sec
RG                     64
DW                177.600 usec
DE                   6.50 usec
TE                  300.0 K
D0             0.00000300 sec
D1             1.48689198 sec
D13            0.00000400 sec
D16            0.00020000 sec
IN0            0.00035520 sec

======== CHANNEL f1 ========
NUC1                   1H
P0                   7.83 usec
P1                   7.83 usec
PL1                 -1.80 dB
PL1W           9.92294312 W
SFO1          400.1317493 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPZ1                10.00 %
P16               1000.00 usec
ND0                     1
TD                    128
SFO1             400.1317 MHz
FIDRES          21.994741 Hz
SW                  7.036 ppm
FnMODE                 QF
SI                   1024
SF            400.1300138 MHz
WDW                  SINE
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.40
SI                   1024
MC2                    QF
SF            400.1300138 MHz
WDW                  SINE
SSB                     0
LB                   0.00 Hz
GB                      0
```

Figure 46: 400 MHz ^{1}H-^{1}H COSY spectrum of **6**.



Display Report

Analysis Info

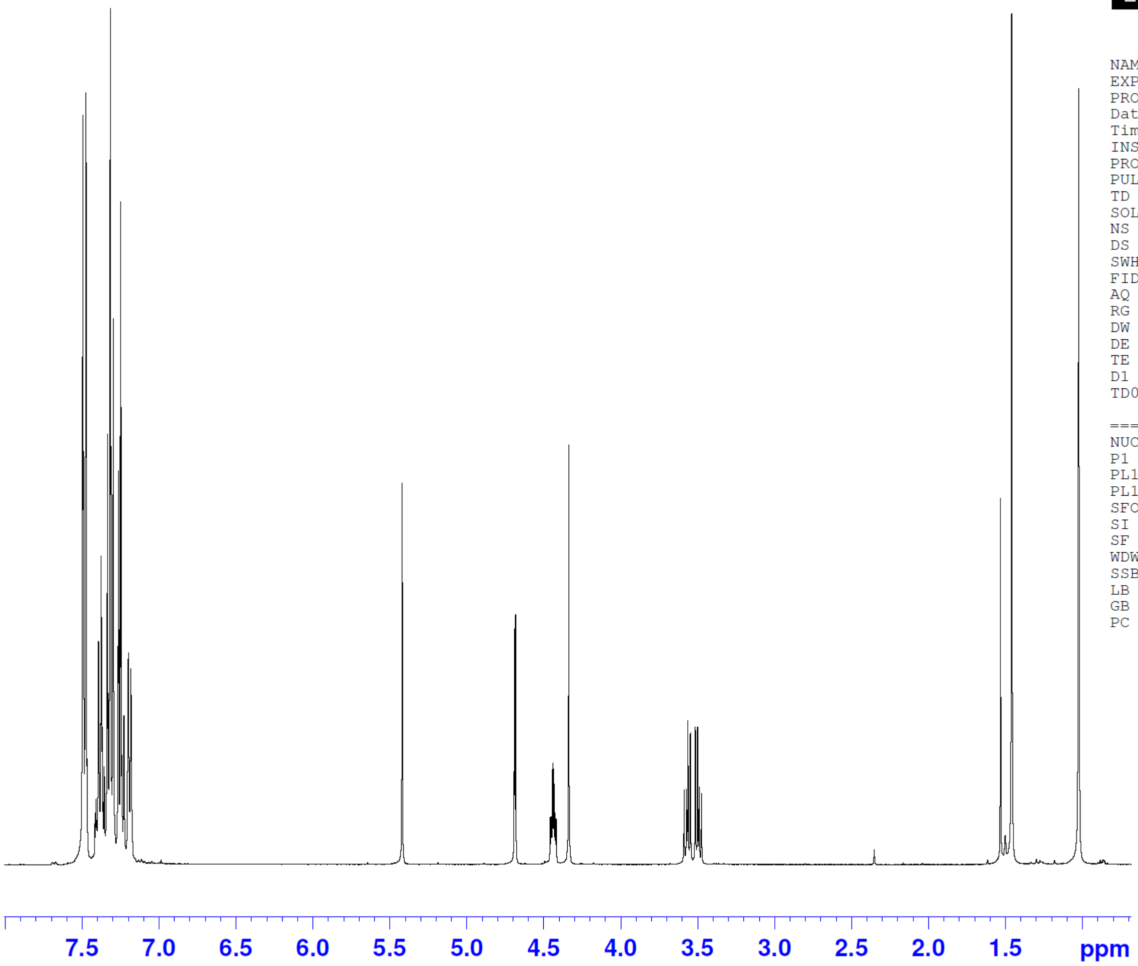
Method XQ Default.ms

Instrument Esquire-LC_00135

Acquisition Parameter

Ion Source Type	ESI	Mass Range Mode	Std/Normal	Ion Polarity	Positive	Alternating Ion Polarity	n/a
Scan Begin	100.00 m/z	Scan End	800.00 m/z	Averages	10 Spectra	Accumulation Time	2823 µs
Capillary Exit	122.8 Volt	Skim 1	44.8 Volt	Trap Drive	55.4	Auto MS/MS	Off

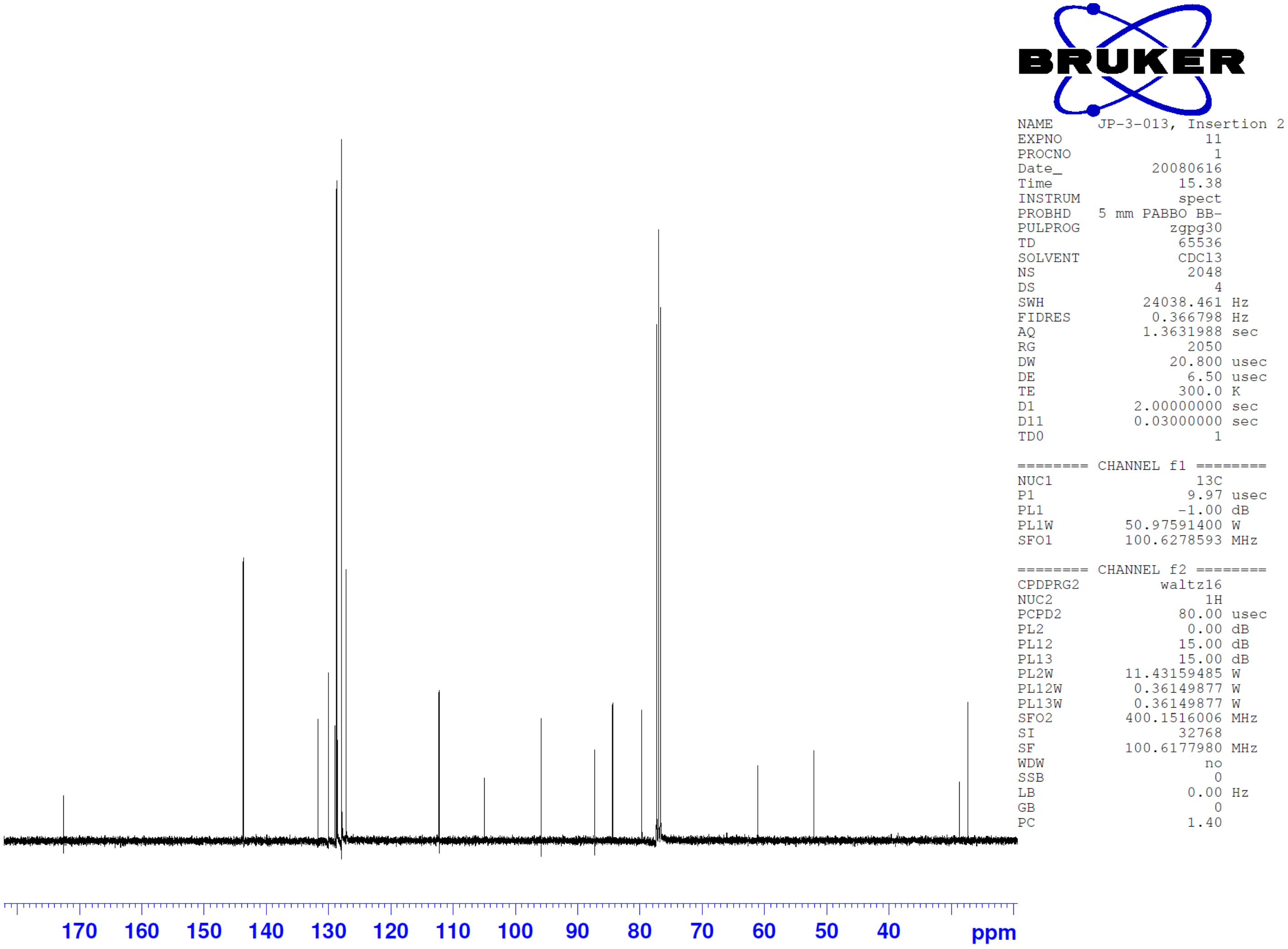
Figure 47: Mass spectrum of **6**.



```
NAME       JP-3-013, Insertion 2
EXPNO                 10
PROCNO                 1
Date_           20080616
Time               13.39
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ             3.9846387 sec
RG                   114
DW                60.800 usec
DE                  6.50 usec
TE                 300.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.10 usec
PL1                 0.00 dB
PL1W         11.43159485 W
SFO1         400.1524711 MHz
SI                 32768
SF           400.1500075 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

Figure 48: 400 MHz ^{1}H spectrum of **7**.

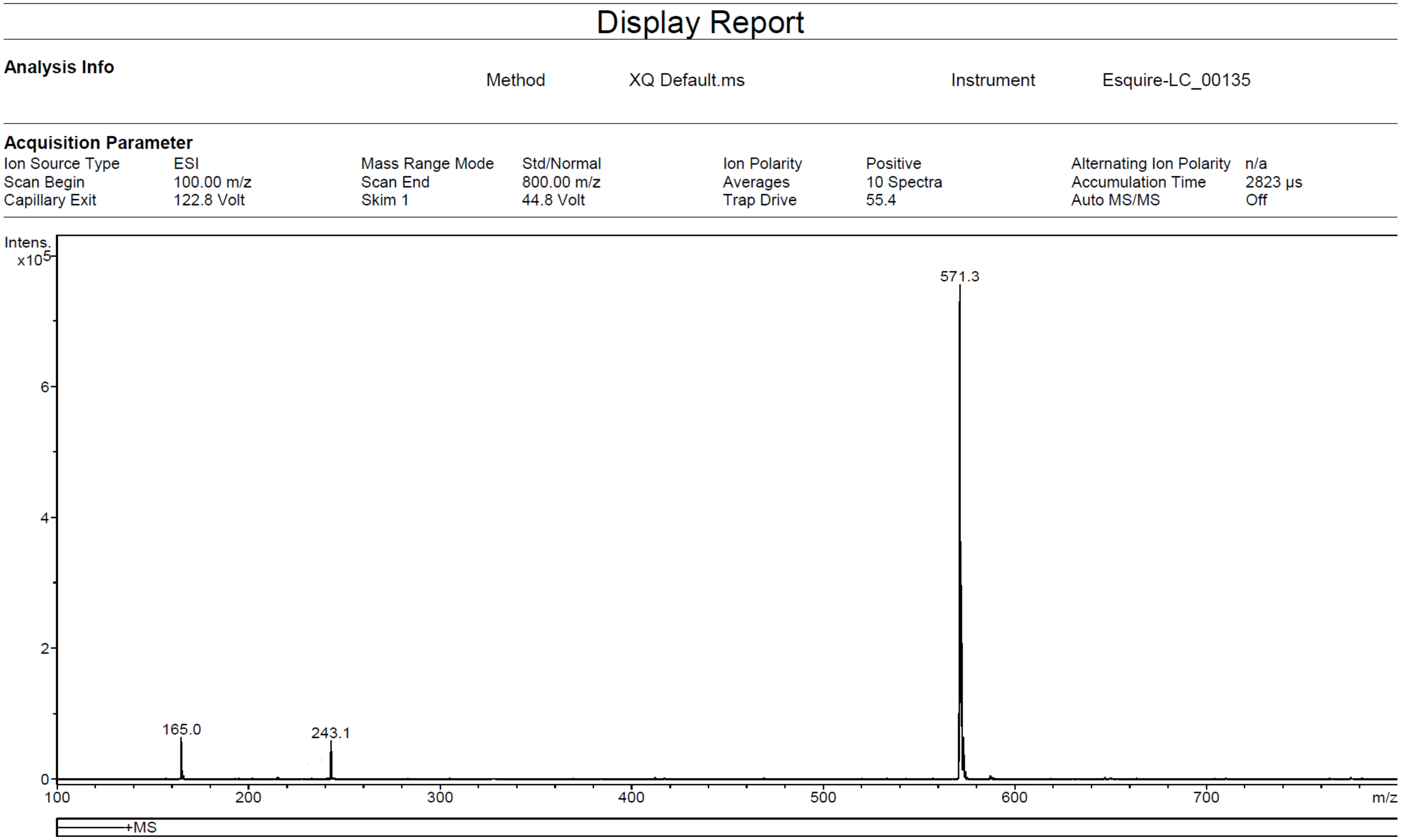


```
NAME      JP-3-013, Insertion 2
EXPNO                      11
PROCNO                      1
Date_                20080616
Time                    15.38
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG               zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                       2048
DS                          4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                  1.3631988 sec
RG                       2050
DW                     20.800 usec
DE                       6.50 usec
TE                      300.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                       9.97 usec
PL1                     -1.00 dB
PL1W              50.97591400 W
SFO1              100.6278593 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    15.00 dB
PL13                    15.00 dB
PL2W              11.43159485 W
PL12W              0.36149877 W
PL13W              0.36149877 W
SFO2              400.1516006 MHz
SI                      32768
SF                100.6177980 MHz
WDW                        no
SSB                         0
LB                       0.00 Hz
GB                          0
PC                       1.40
```

Figure 49: 100 MHz ^{13}C spectrum of **7**.



Display Report

Analysis Info

Method	XQ Default.ms	Instrument	Esquire-LC_00135

Acquisition Parameter

Ion Source Type	ESI	Mass Range Mode	Std/Normal	Ion Polarity	Positive	Alternating Ion Polarity	n/a
Scan Begin	100.00 m/z	Scan End	800.00 m/z	Averages	10 Spectra	Accumulation Time	2823 µs
Capillary Exit	122.8 Volt	Skim 1	44.8 Volt	Trap Drive	55.4	Auto MS/MS	Off

Figure 50: Mass spectrum of **7**.

Appendix B

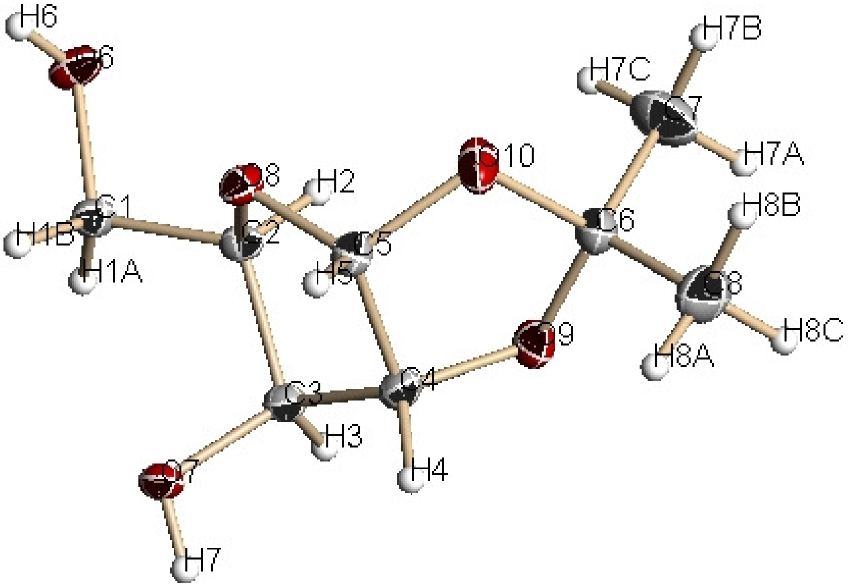


Figure 51: X-ray crystal structure of **1.**

Table 1: Crystal data and structure refinement for **1**.

Identification code: 07jp001m

Empirical formula: C20 H28 O5

Formula weight: 348.2

Temperature: 100(2) K

Wavelength: 0.71073 Å

Crystal system: Orthorhombic

Space group: $P2_12_12_1$

Unit cell dimensions

a = 8.5892(4) Å, $\alpha = 90^{o}$

b = 9.2786(4) Å, $\beta = 90^{o}$

c = 23.0353(11) Å, $\gamma = 90^{o}$

Volume, Z: 1835.82(15) Å^3, 4

Calculated density: 1.376 Mg/m^3

Absorption coefficient : 0.088 mm^{-1}

F(000): 720

Crystal size: 0.47 x 0.39 x 0.25 mm

θ range for data collection: 2.37 to 30.50^{o}

Limiting indices: $-12 \le h \le 12$, $-13 \le k \le 13$, $-32 \le l \le 32$

Reflections collected: 22130

Independent reflections: 5581 (R(int) = 0.0210)

Completeness to $\theta = 30.50^{o}$: 99.9 %

Absorption correction: Semi-empirical from equivalents

Max. and min. transmission: 0.978 and 0.960

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

Data / restraints / parameters: 5581 / 0 / 243

Goodness-of-fit on F^2: 1.045

Final R indices [I>2σ(I)] R1 = 0.0320, wR2 = 0.0829

R indices (all data): R1 = 0.0326, wR2 = 0.0835

Absolute structure parameter: -0.2(4)

Largest diff. peak and hole: 0.404 and -0.224 e x Å^3

Table 2: Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for **1.**

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	3803(1)	3884(1)	193(1)	17(1)
C(2)	4426(1)	3567(1)	791(1)	15(1)
C(3)	6004(1)	4237(1)	935(1)	16(1)
C(4)	6541(1)	3263(1)	1429(1)	17(1)
C(5)	5793(1)	1793(1)	1289(1)	17(1)
C(6)	5242(1)	2441(1)	2246(1)	20(1)
C(7)	3676(2)	2764(2)	2514(1)	37(1)
C(8)	6421(2)	1942(2)	2687(1)	35(1)
C(9)	-251(1)	6366(1)	-379(1)	18(1)
C(10)	-7(1)	7162(1)	186(1)	15(1)
C(11)	673(1)	6247(1)	675(1)	16(1)
C(12)	181(1)	7101(1)	1207(1)	17(1)
C(13)	-1337(1)	7863(1)	1018(1)	17(1)
C(14)	382(1)	9518(1)	1438(1)	19(1)
C(15)	1202(1)	10815(1)	1195(1)	25(1)
C(16)	167(2)	9574(1)	2093(1)	30(1)
O(1)	-597(1)	7357(1)	-837(1)	23(1)
O(2)	-1491(1)	7641(1)	415(1)	18(1)
O(3)	-20(1)	4849(1)	710(1)	18(1)
O(4)	-1095(1)	9338(1)	1155(1)	23(1)
O(5)	1254(1)	8259(1)	1282(1)	18(1)
O(6)	2204(1)	3469(1)	142(1)	20(1)
O(7)	7001(1)	4081(1)	443(1)	18(1)
O(8)	4697(1)	2037(1)	843(1)	17(1)
O(9)	5786(1)	3701(1)	1951(1)	21(1)
O(10)	5053(1)	1362(1)	1809(1)	26(1)

Table 3: Bond lengths [Å] and angles [deg] for **1.**

C(1)-O(6)	1.4314(11)
C(1)-C(2)	1.5057(12)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-O(8)	1.4433(11)
C(2)-C(3)	1.5276(12)
C(2)-H(2)	1.0000
C(3)-O(7)	1.4284(11)
C(3)-C(4)	1.5250(13)
C(3)-H(3)	1.0000
C(4)-O(9)	1.4241(11)
C(4)-C(5)	1.5421(13)
C(4)-H(4)	1.0000
C(5)-O(8)	1.4106(11)
C(5)-O(10)	1.4143(11)
C(5)-H(5)	1.0000
C(6)-O(10)	1.4299(12)
C(6)-O(9)	1.4312(12)
C(6)-C(8)	1.5058(15)
C(6)-C(7)	1.5101(15)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-O(1)	1.4311(11)
C(9)-C(10)	1.5096(12)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-O(2)	1.4496(10)
C(10)-C(11)	1.5265(12)
C(10)-H(10)	1.0000
C(11)-O(3)	1.4294(11)
C(11)-C(12)	1.5196(12)
C(11)-H(11)	1.0000
C(12)-O(5)	1.4262(11)
C(12)-C(13)	1.5456(13)
C(12)-H(12)	1.0000
C(13)-O(2)	1.4111(11)
C(13)-O(4)	1.4198(11)
C(13)-H(13)	1.0000
C(14)-O(5)	1.4327(11)

C(14)-O(4)	1.4359(12)
C(14)-C(15)	1.5028(14)
C(14)-C(16)	1.5206(14)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
O(1)-H(1)	0.8400
O(3)-H(3A)	0.8400
O(6)-H(6)	0.8400
O(7)-H(7)	0.8400

O(6)-C(1)-C(2)	111.38(8)
O(6)-C(1)-H(1A)	109.4
C(2)-C(1)-H(1A)	109.4
O(6)-C(1)-H(1B)	109.4
C(2)-C(1)-H(1B)	109.4
H(1A)-C(1)-H(1B)	108.0
O(8)-C(2)-C(1)	109.00(7)
O(8)-C(2)-C(3)	103.85(7)
C(1)-C(2)-C(3)	115.78(7)
O(8)-C(2)-H(2)	109.3
C(1)-C(2)-H(2)	109.3
C(3)-C(2)-H(2)	109.3
O(7)-C(3)-C(4)	110.56(7)
O(7)-C(3)-C(2)	108.53(7)
C(4)-C(3)-C(2)	100.91(7)
O(7)-C(3)-H(3)	112.1
C(4)-C(3)-H(3)	112.1
C(2)-C(3)-H(3)	112.1
O(9)-C(4)-C(3)	108.83(7)
O(9)-C(4)-C(5)	103.91(7)
C(3)-C(4)-C(5)	103.96(7)
O(9)-C(4)-H(4)	113.1
C(3)-C(4)-H(4)	113.1
C(5)-C(4)-H(4)	113.1
O(8)-C(5)-O(10)	111.27(8)
O(8)-C(5)-C(4)	106.81(7)
O(10)-C(5)-C(4)	105.01(7)
O(8)-C(5)-H(5)	111.2
O(10)-C(5)-H(5)	111.2
C(4)-C(5)-H(5)	111.2
O(10)-C(6)-O(9)	105.89(7)
O(10)-C(6)-C(8)	109.61(10)

O(9)-C(6)-C(8)	110.67(9)
O(10)-C(6)-C(7)	108.98(9)
O(9)-C(6)-C(7)	108.82(9)
C(8)-C(6)-C(7)	112.64(10)
C(6)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(6)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(6)-C(8)-H(8A)	109.5
C(6)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(6)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
O(1)-C(9)-C(10)	110.41(8)
O(1)-C(9)-H(9A)	109.6
C(10)-C(9)-H(9A)	109.6
O(1)-C(9)-H(9B)	109.6
C(10)-C(9)-H(9B)	109.6
H(9A)-C(9)-H(9B)	108.1
O(2)-C(10)-C(9)	109.96(7)
O(2)-C(10)-C(11)	103.78(7)
C(9)-C(10)-C(11)	114.56(7)
O(2)-C(10)-H(10)	109.4
C(9)-C(10)-H(10)	109.4
C(11)-C(10)-H(10)	109.4
O(3)-C(11)-C(12)	108.10(7)
O(3)-C(11)-C(10)	112.85(7)
C(12)-C(11)-C(10)	101.45(7)
O(3)-C(11)-H(11)	111.3
C(12)-C(11)-H(11)	111.3
C(10)-C(11)-H(11)	111.3
O(5)-C(12)-C(11)	108.17(7)
O(5)-C(12)-C(13)	103.58(7)
C(11)-C(12)-C(13)	104.27(7)
O(5)-C(12)-H(12)	113.3
C(11)-C(12)-H(12)	113.3
C(13)-C(12)-H(12)	113.3
O(2)-C(13)-O(4)	111.92(8)
O(2)-C(13)-C(12)	106.79(7)
O(4)-C(13)-C(12)	104.76(7)
O(2)-C(13)-H(13)	111.0
O(4)-C(13)-H(13)	111.0
C(12)-C(13)-H(13)	111.0

O(5)-C(14)-O(4)	104.68(7)
O(5)-C(14)-C(15)	108.34(8)
O(4)-C(14)-C(15)	109.74(8)
O(5)-C(14)-C(16)	109.88(9)
O(4)-C(14)-C(16)	110.35(8)
C(15)-C(14)-C(16)	113.47(9)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(14)-C(16)-H(16A)	109.5
C(14)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(9)-O(1)-H(1)	109.5
C(13)-O(2)-C(10)	108.72(7)
C(11)-O(3)-H(3A)	109.5
C(13)-O(4)-C(14)	110.00(7)
C(12)-O(5)-C(14)	107.87(7)
C(1)-O(6)-H(6)	109.5
C(3)-O(7)-H(7)	109.5
C(5)-O(8)-C(2)	109.01(7)
C(4)-O(9)-C(6)	108.45(7)
C(5)-O(10)-C(6)	110.38(8)

Table 4: Anisotropic displacement parameters [Å^2 x 10^3] for **1.**

The anisotropic displacement factor exponent takes the form: -2 π^2 [(h a*)^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	13(1)	19(1)	19(1)	0(1)	-1(1)	-1(1)
C(2)	12(1)	15(1)	18(1)	-1(1)	0(1)	0(1)
C(3)	14(1)	16(1)	18(1)	-2(1)	1(1)	-2(1)
C(4)	14(1)	19(1)	18(1)	-3(1)	-1(1)	-1(1)
C(5)	18(1)	17(1)	16(1)	-1(1)	-1(1)	1(1)
C(6)	22(1)	23(1)	16(1)	-2(1)	0(1)	-3(1)
C(7)	29(1)	38(1)	43(1)	-5(1)	16(1)	-3(1)
C(8)	34(1)	45(1)	26(1)	10(1)	-11(1)	-9(1)
C(9)	19(1)	18(1)	17(1)	-1(1)	-1(1)	-1(1)
C(10)	12(1)	16(1)	17(1)	-1(1)	0(1)	0(1)
C(11)	13(1)	14(1)	19(1)	-1(1)	0(1)	0(1)
C(12)	15(1)	18(1)	17(1)	-1(1)	0(1)	-1(1)
C(13)	14(1)	18(1)	20(1)	-3(1)	2(1)	-1(1)
C(14)	14(1)	20(1)	22(1)	-5(1)	1(1)	0(1)
C(15)	22(1)	21(1)	32(1)	-1(1)	-2(1)	-4(1)
C(16)	33(1)	35(1)	23(1)	-10(1)	6(1)	-1(1)
O(1)	23(1)	25(1)	20(1)	3(1)	-5(1)	-3(1)
O(2)	12(1)	22(1)	20(1)	-2(1)	0(1)	3(1)
O(3)	15(1)	14(1)	25(1)	-1(1)	1(1)	-1(1)
O(4)	15(1)	19(1)	37(1)	-8(1)	-4(1)	2(1)
O(5)	14(1)	19(1)	20(1)	-4(1)	-1(1)	0(1)
O(6)	13(1)	21(1)	27(1)	-6(1)	-3(1)	1(1)
O(7)	14(1)	21(1)	19(1)	-3(1)	3(1)	-4(1)
O(8)	17(1)	14(1)	19(1)	0(1)	-3(1)	-1(1)
O(9)	26(1)	20(1)	17(1)	-4(1)	2(1)	-2(1)
O(10)	43(1)	21(1)	15(1)	-1(1)	2(1)	-9(1)

Table 5: Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **1**.

	x	y	z	U(eq)
H(1A)	3904	4928	113	20
H(1B)	4429	3356	-99	20
H(2)	3644	3873	1088	18
H(3)	5905	5265	1060	19
H(4)	7699	3214	1467	20
H(5)	6596	1075	1166	20
H(7A)	3789	3532	2803	55
H(7B)	3271	1894	2702	55
H(7C)	2951	3077	2210	55
H(8A)	7415	1753	2493	53
H(8B)	6049	1056	2872	53
H(8C)	6564	2691	2982	53
H(9A)	701	5815	-477	21
H(9B)	-1120	5674	-335	21
H(10)	679	8016	117	18
H(11)	1832	6182	645	19
H(12)	54	6493	1562	20
H(13)	-2255	7469	1232	21
H(15A)	2228	10910	1378	38
H(15B)	584	11681	1275	38
H(15C)	1330	10701	775	38
H(16A)	-330	8682	2226	45
H(16B)	-491	10399	2194	45
H(16C)	1185	9677	2281	45
H(1)	-1397	7082	-1014	34
H(3A)	547	4248	539	27
H(6)	2139	2713	-58	30
H(7)	7882	4425	520	27

Table 6: Torsion angles [deg] for **1**.

O(6)-C(1)-C(2)-O(8)	75.44(9)
O(6)-C(1)-C(2)-C(3)	-167.97(7)
O(8)-C(2)-C(3)-O(7)	77.05(8)
C(1)-C(2)-C(3)-O(7)	-42.39(10)
O(8)-C(2)-C(3)-C(4)	-39.17(8)
C(1)-C(2)-C(3)-C(4)	-158.61(8)
O(7)-C(3)-C(4)-O(9)	165.50(7)
C(2)-C(3)-C(4)-O(9)	-79.79(8)
O(7)-C(3)-C(4)-C(5)	-84.24(8)
C(2)-C(3)-C(4)-C(5)	30.47(8)
O(9)-C(4)-C(5)-O(8)	102.12(8)
C(3)-C(4)-C(5)-O(8)	-11.72(9)
O(9)-C(4)-C(5)-O(10)	-16.13(9)
C(3)-C(4)-C(5)-O(10)	-129.98(8)
O(1)-C(9)-C(10)-O(2)	74.84(9)
O(1)-C(9)-C(10)-C(11)	-168.76(7)
O(2)-C(10)-C(11)-O(3)	76.95(8)
C(9)-C(10)-C(11)-O(3)	-42.95(10)
O(2)-C(10)-C(11)-C(12)	-38.47(8)
C(9)-C(10)-C(11)-C(12)	-158.37(7)
O(3)-C(11)-C(12)-O(5)	160.01(7)
C(10)-C(11)-C(12)-O(5)	-81.11(8)
O(3)-C(11)-C(12)-C(13)	-90.21(8)
C(10)-C(11)-C(12)-C(13)	28.67(8)
O(5)-C(12)-C(13)-O(2)	103.88(8)
C(11)-C(12)-C(13)-O(2)	-9.23(9)
O(5)-C(12)-C(13)-O(4)	-14.99(9)
C(11)-C(12)-C(13)-O(4)	-128.09(8)
O(4)-C(13)-O(2)-C(10)	98.32(9)
C(12)-C(13)-O(2)-C(10)	-15.78(9)
C(9)-C(10)-O(2)-C(13)	157.57(7)
C(11)-C(10)-O(2)-C(13)	34.58(9)
O(2)-C(13)-O(4)-C(14)	-118.77(8)
C(12)-C(13)-O(4)-C(14)	-3.42(10)
O(5)-C(14)-O(4)-C(13)	20.56(10)
C(15)-C(14)-O(4)-C(13)	136.64(9)
C(16)-C(14)-O(4)-C(13)	-97.60(10)
C(11)-C(12)-O(5)-C(14)	138.46(7)
C(13)-C(12)-O(5)-C(14)	28.21(9)
O(4)-C(14)-O(5)-C(12)	-30.77(9)
C(15)-C(14)-O(5)-C(12)	-147.81(8)
C(16)-C(14)-O(5)-C(12)	87.71(9)

O(10)-C(5)-O(8)-C(2)	100.35(8)
C(4)-C(5)-O(8)-C(2)	-13.73(9)
C(1)-C(2)-O(8)-C(5)	157.77(7)
C(3)-C(2)-O(8)-C(5)	33.81(9)
C(3)-C(4)-O(9)-C(6)	135.34(8)
C(5)-C(4)-O(9)-C(6)	25.04(9)
O(10)-C(6)-O(9)-C(4)	-24.65(10)
C(8)-C(6)-O(9)-C(4)	94.05(10)
C(7)-C(6)-O(9)-C(4)	-141.67(9)
O(8)-C(5)-O(10)-C(6)	-113.64(9)
C(4)-C(5)-O(10)-C(6)	1.56(10)
O(9)-C(6)-O(10)-C(5)	13.66(11)
C(8)-C(6)-O(10)-C(5)	-105.74(10)
C(7)-C(6)-O(10)-C(5)	130.57(10)

Table 7: Hydrogen bonds for **1** [Å and deg].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O1-H1	0.840	2.133	2.949	163.76
O3-H3A	0.840	1.840	2.647	160.78
O6-H6	0.840	1.891	2.728	174.85
O7-H7	0.840	1.895	2.726	169.67

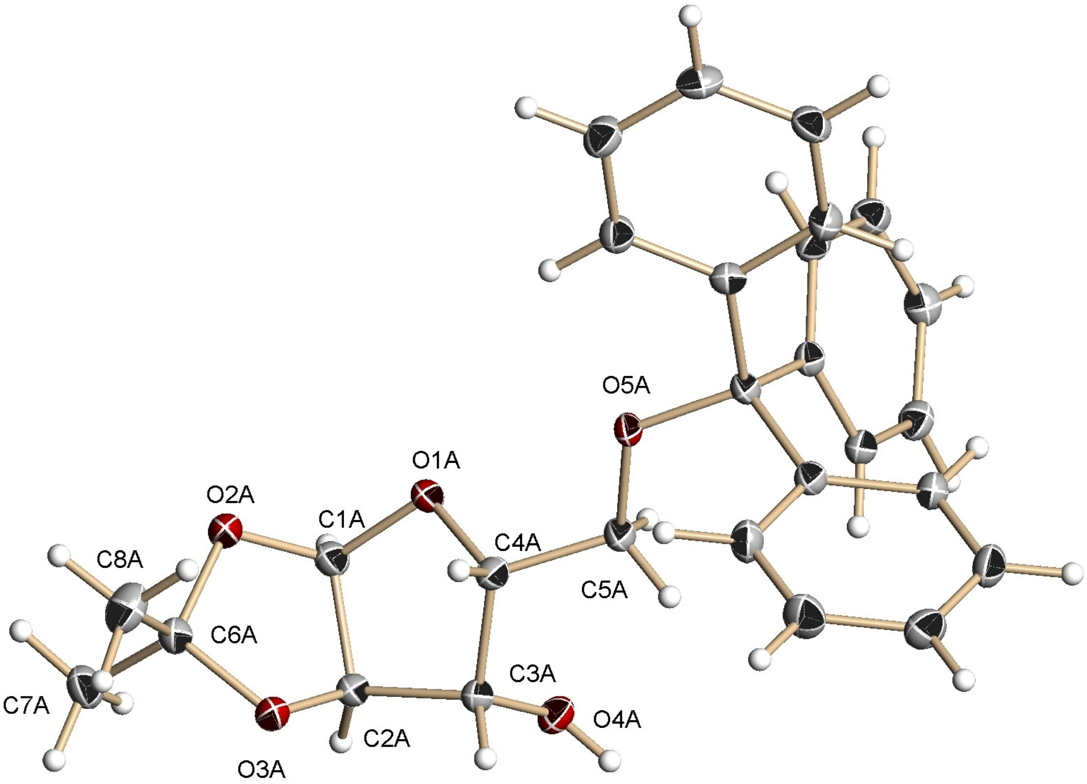


Figure 52: X-ray crystal structure of **3.**

Table 8. Crystal data and structure refinement for **3.**

Identification code: 07mz292m

Empirical formula: C27 H28 O5

Formula weight: 432.49

Temperature: 100(2) K

Wavelength: 0.71073 Å

Crystal system: Monoclinic

Space group: C2

Unit cell dimensions:

$a = 26.8285(18)$ Å, $\alpha = 90°$

$b = 10.5314(7)$ Å, $\beta = 111.3280(10)°$

$c = 16.9256(12)$ Å, $\gamma = 90°$

Volume, Z: 4454.7(5) Å^3, 8

Density (calculated): 1.290 Mg/m^3

Absorption coefficient: 0.088 mm^{-1}

$F(000)$: 1840

Crystal size: 0.55 × 0.43 × 0.23 mm

Crystal shape, colour: block, colourless

θ range for data collection: 1.29 to 28.28°

Limiting indices: $-32 \le h \le 35$, $-13 \le k \le 13$, $-22 \le l \le 22$

Reflections collected: 15504

Independent reflections: 5723 (R(int) = 0.0214)

Completeness to $\theta = 28.24°$: 98.1 %

Absorption correction: multi-scan

Max. and min. transmission: 0.980 and 0.883

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

Data / restraints / parameters: 5723 / 1 / 583

Goodness-of-fit on F^2: 1.066

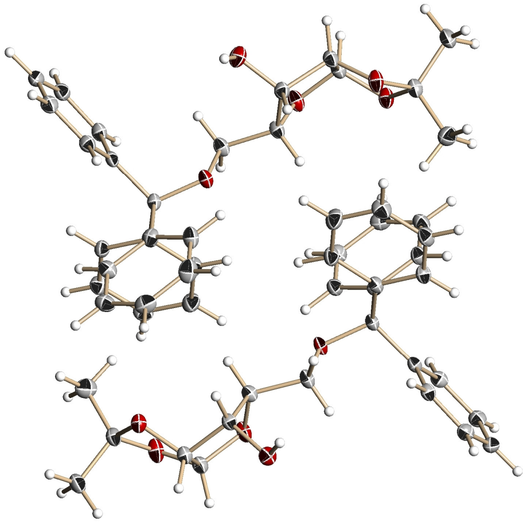
Final R indices [$I>2\sigma(I)$]: R1 = 0.0393, wR2 = 0.1060

R indices (all data): R1 = 0.0422, wR2 = 0.1086

Largest diff. peak and hole: 0.414 and -0.213 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.

Comments:



Two independent molecules are located in the asymmetric part of the unit cell (see figure to the right). They are related by a pseudo-inversion center. The observed pseudosymmetry applies to all but three atoms. Each a carbon atom is converted into an oxygen and vice versa, and a hydroxyl group would take the place of a hydrogen atom. The molecule is also chiral (not compatible with space group C2/c), and refinement in C2 resulted in well defined atom positions and ADPs.

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 or oxygen atom.

Table 9. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for **3**.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1A)	8182(1)	1377(2)	10908(1)	19(1)
C(2A)	8351(1)	-29(2)	10982(1)	18(1)
C(3A)	7896(1)	-708(2)	10294(1)	17(1)
C(4A)	7670(1)	351(2)	9642(1)	18(1)
C(5A)	7083(1)	160(2)	9120(1)	19(1)
C(6A)	9058(1)	1189(2)	10974(1)	20(1)
C(7A)	9439(1)	1199(2)	11889(1)	25(1)
C(8A)	9324(1)	1514(3)	10353(1)	30(1)
C(9A)	6401(1)	904(2)	7808(1)	16(1)
C(10A)	6364(1)	-368(2)	7338(1)	17(1)
C(11A)	6815(1)	-809(2)	7192(1)	22(1)
C(12A)	6785(1)	-1898(2)	6713(2)	27(1)
C(13A)	6308(1)	-2558(2)	6361(1)	26(1)
C(14A)	5858(1)	-2119(2)	6495(1)	23(1)
C(15A)	5885(1)	-1030(2)	6978(1)	20(1)
C(16A)	5977(1)	1059(2)	8214(1)	16(1)
C(17A)	5857(1)	52(2)	8660(1)	18(1)
C(18A)	5484(1)	212(2)	9050(1)	21(1)
C(19A)	5217(1)	1360(2)	8989(1)	21(1)
C(20A)	5340(1)	2365(2)	8564(1)	21(1)
C(21A)	5721(1)	2218(2)	8186(1)	19(1)
C(22A)	6353(1)	1955(2)	7156(1)	17(1)
C(23A)	5900(1)	2008(2)	6414(1)	21(1)

C(24A)	5857(1)	2926(2)	5805(1)	22(1)
C(25A)	6264(1)	3803(2)	5921(1)	23(1)
C(26A)	6711(1)	3766(2)	6663(1)	24(1)
C(27A)	6753(1)	2851(2)	7281(1)	20(1)
O(1A)	7728(1)	1499(1)	10147(1)	21(1)
O(2A)	8623(1)	2054(2)	10865(1)	25(1)
O(3A)	8811(1)	-25(1)	10750(1)	19(1)
O(4A)	7517(1)	-1117(1)	10646(1)	21(1)
O(5A)	6931(1)	1056(1)	8442(1)	18(1)
C(1B)	6676(1)	1235(2)	4073(1)	20(1)
C(2B)	6765(1)	-215(2)	4099(1)	20(1)
C(3B)	7274(1)	-439(2)	4879(1)	19(1)
C(4B)	7322(1)	791(2)	5384(1)	18(1)
C(5B)	7888(1)	1181(2)	5915(1)	20(1)
C(6B)	5911(1)	221(2)	4036(1)	19(1)
C(7B)	5564(1)	168(3)	3097(1)	27(1)
C(8B)	5595(1)	52(2)	4608(1)	28(1)
C(9B)	8594(1)	443(2)	7212(1)	16(1)
C(10B)	8645(1)	-606(2)	7871(1)	18(1)
C(11B)	9093(1)	-650(2)	8617(1)	22(1)
C(12B)	9137(1)	-1550(2)	9239(1)	24(1)
C(13B)	8734(1)	-2431(2)	9121(1)	26(1)
C(14B)	8292(1)	-2420(2)	8373(2)	29(1)
C(15B)	8247(1)	-1509(2)	7751(1)	24(1)
C(16B)	9014(1)	295(2)	6796(1)	16(1)
C(17B)	9271(1)	-865(2)	6814(1)	19(1)
C(18B)	9648(1)	-995(2)	6432(1)	22(1)
C(19B)	9767(1)	25(2)	6010(1)	22(1)
C(20B)	9497(1)	1165(2)	5956(1)	21(1)
C(21B)	9127(1)	1307(2)	6353(1)	20(1)
C(22B)	8636(1)	1715(2)	7678(1)	17(1)
C(23B)	9119(1)	2365(2)	8032(1)	19(1)
C(24B)	9151(1)	3473(2)	8499(1)	22(1)
C(25B)	8699(1)	3947(2)	8611(1)	25(1)
C(26B)	8217(1)	3304(2)	8268(1)	26(1)
C(27B)	8188(1)	2192(2)	7809(1)	22(1)
O(1B)	7111(1)	1764(2)	4738(1)	22(1)
O(2B)	6196(1)	1390(2)	4230(1)	21(1)
O(3B)	6316(1)	-736(1)	4241(1)	23(1)
O(4B)	7716(1)	-611(2)	4621(1)	25(1)
O(5B)	8064(1)	272(1)	6587(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 10. Bond lengths [Å] and angles [deg] for **3**.

C(1A)-O(2A)	1.405(2)
C(1A)-O(1A)	1.421(2)
C(1A)-C(2A)	1.540(3)
C(1A)-H(1A)	1.0000
C(2A)-O(3A)	1.423(2)
C(2A)-C(3A)	1.524(3)
C(2A)-H(2A)	1.0000
C(3A)-O(4A)	1.419(2)
C(3A)-C(4A)	1.530(3)
C(3A)-H(3A)	1.0000
C(4A)-O(1A)	1.456(2)
C(4A)-C(5A)	1.513(3)
C(4A)-H(4A)	1.0000
C(5A)-O(5A)	1.426(2)
C(5A)-H(5A1)	0.9900
C(5A)-H(5A2)	0.9900
C(6A)-O(3A)	1.426(3)
C(6A)-O(2A)	1.438(3)
C(6A)-C(8A)	1.510(3)
C(6A)-C(7A)	1.513(3)
C(7A)-H(7A1)	0.9800
C(7A)-H(7A2)	0.9800
C(7A)-H(7A3)	0.9800
C(8A)-H(8A1)	0.9800
C(8A)-H(8A2)	0.9800
C(8A)-H(8A3)	0.9800
C(9A)-O(5A)	1.444(2)
C(9A)-C(22A)	1.535(3)
C(9A)-C(16A)	1.537(2)
C(9A)-C(10A)	1.543(3)
C(10A)-C(15A)	1.393(3)
C(10A)-C(11A)	1.399(3)
C(11A)-C(12A)	1.390(3)

C(11A)-H(11A)	0.9500
C(12A)-C(13A)	1.385(3)
C(12A)-H(12A)	0.9500
C(13A)-C(14A)	1.386(3)
C(13A)-H(13A)	0.9500
C(14A)-C(15A)	1.395(3)
C(14A)-H(14A)	0.9500
C(15A)-H(15A)	0.9500
C(16A)-C(21A)	1.393(3)
C(16A)-C(17A)	1.405(3)
C(17A)-C(18A)	1.396(3)
C(17A)-H(17A)	0.9500
C(18A)-C(19A)	1.389(3)
C(18A)-H(18A)	0.9500
C(19A)-C(20A)	1.385(3)
C(19A)-H(19A)	0.9500
C(20A)-C(21A)	1.398(3)
C(20A)-H(20A)	0.9500
C(21A)-H(21A)	0.9500
C(22A)-C(27A)	1.388(3)
C(22A)-C(23A)	1.395(3)
C(23A)-C(24A)	1.387(3)
C(23A)-H(23A)	0.9500
C(24A)-C(25A)	1.389(3)
C(24A)-H(24A)	0.9500
C(25A)-C(26A)	1.386(3)
C(25A)-H(25A)	0.9500
C(26A)-C(27A)	1.396(3)
C(26A)-H(26A)	0.9500
C(27A)-H(27A)	0.9500
O(4A)-H(4A1)	0.8400
C(1B)-O(1B)	1.409(2)
C(1B)-O(2B)	1.417(2)
C(1B)-C(2B)	1.544(3)
C(1B)-H(1B)	1.0000
C(2B)-O(3B)	1.420(3)
C(2B)-C(3B)	1.533(3)
C(2B)-H(2B)	1.0000
C(3B)-O(4B)	1.417(2)
C(3B)-C(4B)	1.531(3)
C(3B)-H(3B)	1.0000
C(4B)-O(1B)	1.454(2)
C(4B)-C(5B)	1.513(3)
C(4B)-H(4B)	1.0000
C(5B)-O(5B)	1.430(2)
C(5B)-H(5B1)	0.9900

C(5B)-H(5B2)	0.9900
C(6B)-O(2B)	1.422(3)
C(6B)-O(3B)	1.429(2)
C(6B)-C(8B)	1.512(3)
C(6B)-C(7B)	1.523(3)
C(7B)-H(7B1)	0.9800
C(7B)-H(7B2)	0.9800
C(7B)-H(7B3)	0.9800
C(8B)-H(8B1)	0.9800
C(8B)-H(8B2)	0.9800
C(8B)-H(8B3)	0.9800
C(9B)-O(5B)	1.441(2)
C(9B)-C(22B)	1.537(3)
C(9B)-C(16B)	1.538(2)
C(9B)-C(10B)	1.540(3)
C(10B)-C(15B)	1.389(3)
C(10B)-C(11B)	1.392(3)
C(11B)-C(12B)	1.389(3)
C(11B)-H(11B)	0.9500
C(12B)-C(13B)	1.383(3)
C(12B)-H(12B)	0.9500
C(13B)-C(14B)	1.385(3)
C(13B)-H(13B)	0.9500
C(14B)-C(15B)	1.396(3)
C(14B)-H(14B)	0.9500
C(15B)-H(15B)	0.9500
C(16B)-C(17B)	1.398(3)
C(16B)-C(21B)	1.400(3)
C(17B)-C(18B)	1.391(3)
C(17B)-H(17B)	0.9500
C(18B)-C(19B)	1.389(3)
C(18B)-H(18B)	0.9500
C(19B)-C(20B)	1.387(3)
C(19B)-H(19B)	0.9500
C(20B)-C(21B)	1.394(3)
C(20B)-H(20B)	0.9500
C(21B)-H(21B)	0.9500
C(22B)-C(27B)	1.394(3)
C(22B)-C(23B)	1.394(3)
C(23B)-C(24B)	1.395(3)
C(23B)-H(23B)	0.9500
C(24B)-C(25B)	1.386(3)
C(24B)-H(24B)	0.9500
C(25B)-C(26B)	1.386(3)
C(25B)-H(25B)	0.9500
C(26B)-C(27B)	1.391(3)

C(26B)-H(26B)	0.9500
C(27B)-H(27B)	0.9500
O(4B)-H(4B1)	0.8400
O(2A)-C(1A)-O(1A)	111.51(16)
O(2A)-C(1A)-C(2A)	105.30(15)
O(1A)-C(1A)-C(2A)	106.87(16)
O(2A)-C(1A)-H(1A)	111.0
O(1A)-C(1A)-H(1A)	111.0
C(2A)-C(1A)-H(1A)	111.0
O(3A)-C(2A)-C(3A)	108.95(15)
O(3A)-C(2A)-C(1A)	103.52(15)
C(3A)-C(2A)-C(1A)	105.01(16)
O(3A)-C(2A)-H(2A)	112.9
C(3A)-C(2A)-H(2A)	112.9
C(1A)-C(2A)-H(2A)	112.9
O(4A)-C(3A)-C(2A)	108.55(15)
O(4A)-C(3A)-C(4A)	111.62(16)
C(2A)-C(3A)-C(4A)	101.90(16)
O(4A)-C(3A)-H(3A)	111.5
C(2A)-C(3A)-H(3A)	111.5
C(4A)-C(3A)-H(3A)	111.5
O(1A)-C(4A)-C(5A)	108.64(16)
O(1A)-C(4A)-C(3A)	104.61(14)
C(5A)-C(4A)-C(3A)	112.27(17)
O(1A)-C(4A)-H(4A)	110.4
C(5A)-C(4A)-H(4A)	110.4
C(3A)-C(4A)-H(4A)	110.4
O(5A)-C(5A)-C(4A)	108.36(16)
O(5A)-C(5A)-H(5A1)	110.0
C(4A)-C(5A)-H(5A1)	110.0
O(5A)-C(5A)-H(5A2)	110.0
C(4A)-C(5A)-H(5A2)	110.0
H(5A1)-C(5A)-H(5A2)	108.4
O(3A)-C(6A)-O(2A)	104.86(15)
O(3A)-C(6A)-C(8A)	108.13(17)
O(2A)-C(6A)-C(8A)	109.56(18)
O(3A)-C(6A)-C(7A)	110.72(17)
O(2A)-C(6A)-C(7A)	109.89(17)
C(8A)-C(6A)-C(7A)	113.32(18)
C(6A)-C(7A)-H(7A1)	109.5
C(6A)-C(7A)-H(7A2)	109.5
H(7A1)-C(7A)-H(7A2)	109.5
C(6A)-C(7A)-H(7A3)	109.5
H(7A1)-C(7A)-H(7A3)	109.5
H(7A2)-C(7A)-H(7A3)	109.5
C(6A)-C(8A)-H(8A1)	109.5

C(6A)-C(8A)-H(8A2)	109.5
H(8A1)-C(8A)-H(8A2)	109.5
C(6A)-C(8A)-H(8A3)	109.5
H(8A1)-C(8A)-H(8A3)	109.5
H(8A2)-C(8A)-H(8A3)	109.5
O(5A)-C(9A)-C(22A)	104.94(15)
O(5A)-C(9A)-C(16A)	110.16(14)
C(22A)-C(9A)-C(16A)	111.23(16)
O(5A)-C(9A)-C(10A)	109.87(15)
C(22A)-C(9A)-C(10A)	106.38(14)
C(16A)-C(9A)-C(10A)	113.83(16)
C(15A)-C(10A)-C(11A)	118.45(19)
C(15A)-C(10A)-C(9A)	122.38(17)
C(11A)-C(10A)-C(9A)	118.84(17)
C(12A)-C(11A)-C(10A)	120.4(2)
C(12A)-C(11A)-H(11A)	119.8
C(10A)-C(11A)-H(11A)	119.8
C(13A)-C(12A)-C(11A)	120.9(2)
C(13A)-C(12A)-H(12A)	119.6
C(11A)-C(12A)-H(12A)	119.6
C(12A)-C(13A)-C(14A)	119.0(2)
C(12A)-C(13A)-H(13A)	120.5
C(14A)-C(13A)-H(13A)	120.5
C(13A)-C(14A)-C(15A)	120.5(2)
C(13A)-C(14A)-H(14A)	119.7
C(15A)-C(14A)-H(14A)	119.7
C(10A)-C(15A)-C(14A)	120.66(19)
C(10A)-C(15A)-H(15A)	119.7
C(14A)-C(15A)-H(15A)	119.7
C(21A)-C(16A)-C(17A)	118.25(17)
C(21A)-C(16A)-C(9A)	120.93(17)
C(17A)-C(16A)-C(9A)	120.74(18)
C(18A)-C(17A)-C(16A)	120.46(19)
C(18A)-C(17A)-H(17A)	119.8
C(16A)-C(17A)-H(17A)	119.8
C(19A)-C(18A)-C(17A)	120.51(19)
C(19A)-C(18A)-H(18A)	119.7
C(17A)-C(18A)-H(18A)	119.7
C(20A)-C(19A)-C(18A)	119.40(18)
C(20A)-C(19A)-H(19A)	120.3
C(18A)-C(19A)-H(19A)	120.3
C(19A)-C(20A)-C(21A)	120.3(2)
C(19A)-C(20A)-H(20A)	119.8
C(21A)-C(20A)-H(20A)	119.8
C(16A)-C(21A)-C(20A)	121.00(19)
C(16A)-C(21A)-H(21A)	119.5

C(20A)-C(21A)-H(21A)	119.5
C(27A)-C(22A)-C(23A)	118.89(18)
C(27A)-C(22A)-C(9A)	21.47(17)
C(23A)-C(22A)-C(9A)	19.64(17)
C(24A)-C(23A)-C(22A)	120.43(19)
C(24A)-C(23A)-H(23A)	119.8
C(22A)-C(23A)-H(23A)	119.8
C(23A)-C(24A)-C(25A)	120.67(18)
C(23A)-C(24A)-H(24A)	119.7
C(25A)-C(24A)-H(24A)	119.7
C(26A)-C(25A)-C(24A)	119.06(19)
C(26A)-C(25A)-H(25A)	120.5
C(24A)-C(25A)-H(25A)	120.5
C(25A)-C(26A)-C(27A)	120.5(2)
C(25A)-C(26A)-H(26A)	119.8
C(27A)-C(26A)-H(26A)	119.8
C(22A)-C(27A)-C(26A)	120.46(19)
C(22A)-C(27A)-H(27A)	119.8
C(26A)-C(27A)-H(27A)	119.8
C(1A)-O(1A)-C(4A)	109.30(15)
C(1A)-O(2A)-C(6A)	109.31(16)
C(2A)-O(3A)-C(6A)	107.18(15)
C(3A)-O(4A)-H(4A1)	109.5
C(5A)-O(5A)-C(9A)	116.21(14)
O(1B)-C(1B)-O(2B)	110.50(16)
O(1B)-C(1B)-C(2B)	107.09(17)
O(2B)-C(1B)-C(2B)	104.49(17)
O(1B)-C(1B)-H(1B)	111.5
O(2B)-C(1B)-H(1B)	111.5
C(2B)-C(1B)-H(1B)	111.5
O(3B)-C(2B)-C(3B)	109.79(16)
O(3B)-C(2B)-C(1B)	104.78(16)
C(3B)-C(2B)-C(1B)	104.89(17)
O(3B)-C(2B)-H(2B)	112.3
C(3B)-C(2B)-H(2B)	112.3
C(1B)-C(2B)-H(2B)	112.3
O(4B)-C(3B)-C(4B)	111.70(17)
O(4B)-C(3B)-C(2B)	109.69(15)
C(4B)-C(3B)-C(2B)	102.60(16)
O(4B)-C(3B)-H(3B)	110.9
C(4B)-C(3B)-H(3B)	110.9
C(2B)-C(3B)-H(3B)	110.9
O(1B)-C(4B)-C(5B)	106.64(16)
O(1B)-C(4B)-C(3B)	104.25(14)
C(5B)-C(4B)-C(3B)	115.10(17)
O(1B)-C(4B)-H(4B)	110.2

C(5B)-C(4B)-H(4B)	110.2
C(3B)-C(4B)-H(4B)	110.2
O(5B)-C(5B)-C(4B)	105.13(16)
O(5B)-C(5B)-H(5B1)	110.7
C(4B)-C(5B)-H(5B1)	110.7
O(5B)-C(5B)-H(5B2)	110.7
C(4B)-C(5B)-H(5B2)	110.7
H(5B1)-C(5B)-H(5B2)	108.8
O(2B)-C(6B)-O(3B)	104.89(15)
O(2B)-C(6B)-C(8B)	109.41(17)
O(3B)-C(6B)-C(8B)	108.33(17)
O(2B)-C(6B)-C(7B)	110.29(18)
O(3B)-C(6B)-C(7B)	110.51(17)
C(8B)-C(6B)-C(7B)	113.06(17)
C(6B)-C(7B)-H(7B1)	109.5
C(6B)-C(7B)-H(7B2)	109.5
H(7B1)-C(7B)-H(7B2)	109.5
C(6B)-C(7B)-H(7B3)	109.5
H(7B1)-C(7B)-H(7B3)	109.5
H(7B2)-C(7B)-H(7B3)	109.5
C(6B)-C(8B)-H(8B1)	109.5
C(6B)-C(8B)-H(8B2)	109.5
H(8B1)-C(8B)-H(8B2)	109.5
C(6B)-C(8B)-H(8B3)	109.5
H(8B1)-C(8B)-H(8B3)	109.5
H(8B2)-C(8B)-H(8B3)	109.5
O(5B)-C(9B)-C(22B)	110.77(15)
O(5B)-C(9B)-C(16B)	109.98(14)
C(22B)-C(9B)-C(16B)	113.16(16)
O(5B)-C(9B)-C(10B)	104.28(15)
C(22B)-C(9B)-C(10B)	106.44(14)
C(16B)-C(9B)-C(10B)	111.80(16)
C(15B)-C(10B)-C(11B)	118.34(19)
C(15B)-C(10B)-C(9B)	121.58(18)
C(11B)-C(10B)-C(9B)	120.06(18)
C(12B)-C(11B)-C(10B)	121.1(2)
C(12B)-C(11B)-H(11B)	119.5
C(10B)-C(11B)-H(11B)	119.5
C(13B)-C(12B)-C(11B)	120.2(2)
C(13B)-C(12B)-H(12B)	119.9
C(11B)-C(12B)-H(12B)	119.9
C(12B)-C(13B)-C(14B)	119.4(2)
C(12B)-C(13B)-H(13B)	120.3
C(14B)-C(13B)-H(13B)	120.3
C(13B)-C(14B)-C(15B)	120.3(2)
C(13B)-C(14B)-H(14B)	119.8

C(15B)-C(14B)-H(14B)	119.8
C(10B)-C(15B)-C(14B)	120.6(2)
C(10B)-C(15B)-H(15B)	119.7
C(14B)-C(15B)-H(15B)	119.7
C(17B)-C(16B)-C(21B)	118.31(17)
C(17B)-C(16B)-C(9B)	121.14(18)
C(21B)-C(16B)-C(9B)	120.48(18)
C(18B)-C(17B)-C(16B)	120.89(19)
C(18B)-C(17B)-H(17B)	119.6
C(16B)-C(17B)-H(17B)	119.6
C(19B)-C(18B)-C(17B)	120.3(2)
C(19B)-C(18B)-H(18B)	119.9
C(17B)-C(18B)-H(18B)	119.9
C(20B)-C(19B)-C(18B)	119.45(18)
C(20B)-C(19B)-H(19B)	120.3
C(18B)-C(19B)-H(19B)	120.3
C(19B)-C(20B)-C(21B)	120.4(2)
C(19B)-C(20B)-H(20B)	119.8
C(21B)-C(20B)-H(20B)	119.8
C(20B)-C(21B)-C(16B)	120.6(2)
C(20B)-C(21B)-H(21B)	119.7
C(16B)-C(21B)-H(21B)	119.7
C(27B)-C(22B)-C(23B)	118.45(18)
C(27B)-C(22B)-C(9B)	119.26(18)
C(23B)-C(22B)-C(9B)	122.11(17)
C(22B)-C(23B)-C(24B)	120.65(19)
C(22B)-C(23B)-H(23B)	119.7
C(24B)-C(23B)-H(23B)	119.7
C(25B)-C(24B)-C(23B)	120.2(2)
C(25B)-C(24B)-H(24B)	119.9
C(23B)-C(24B)-H(24B)	119.9
C(24B)-C(25B)-C(26B)	119.7(2)
C(24B)-C(25B)-H(25B)	120.1
C(26B)-C(25B)-H(25B)	120.1
C(25B)-C(26B)-C(27B)	120.0(2)
C(25B)-C(26B)-H(26B)	120.0
C(27B)-C(26B)-H(26B)	120.0
C(26B)-C(27B)-C(22B)	121.0(2)
C(26B)-C(27B)-H(27B)	119.5
C(22B)-C(27B)-H(27B)	119.5
C(1B)-O(1B)-C(4B)	107.69(15)
C(1B)-O(2B)-C(6B)	107.73(16)
C(2B)-O(3B)-C(6B)	107.64(16)
C(3B)-O(4B)-H(4B1)	109.5
C(5B)-O(5B)-C(9B)	116.93(15)

Table 11. Anisotropic displacement parameters [Å^2 × 10^3] for **3**.

The anisotropic displacement factor exponent takes the form: -2 π2 [(h a*)^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1A)	18(1)	18(1)	19(1)	-1(1)	4(1)	1(1)
C(2A)	17(1)	15(1)	20(1)	0(1)	4(1)	0(1)
C(3A)	16(1)	15(1)	18(1)	0(1)	4(1)	0(1)
C(4A)	18(1)	15(1)	18(1)	0(1)	5(1)	-1(1)
C(5A)	16(1)	18(1)	19(1)	3(1)	1(1)	-2(1)
C(6A)	17(1)	18(1)	22(1)	-1(1)	4(1)	-1(1)
C(7A)	19(1)	27(1)	23(1)	-3(1)	2(1)	0(1)
C(8A)	34(1)	29(1)	29(1)	-3(1)	14(1)	-11(1)
C(9A)	13(1)	16(1)	16(1)	2(1)	2(1)	0(1)
C(10A)	16(1)	17(1)	17(1)	1(1)	3(1)	-1(1)
C(11A)	17(1)	23(1)	26(1)	-3(1)	6(1)	-4(1)
C(12A)	22(1)	27(1)	34(1)	-6(1)	11(1)	3(1)
C(13A)	29(1)	19(1)	27(1)	-5(1)	8(1)	-1(1)
C(14A)	21(1)	23(1)	24(1)	-3(1)	4(1)	-6(1)
C(15A)	16(1)	18(1)	23(1)	-1(1)	5(1)	-3(1)
C(16A)	15(1)	17(1)	15(1)	-1(1)	3(1)	-2(1)
C(17A)	16(1)	16(1)	20(1)	-1(1)	4(1)	-2(1)
C(18A)	21(1)	21(1)	19(1)	1(1)	7(1)	-4(1)
C(19A)	20(1)	25(1)	19(1)	-3(1)	8(1)	-1(1)
C(20A)	23(1)	19(1)	20(1)	-3(1)	7(1)	2(1)
C(21A)	22(1)	16(1)	18(1)	-2(1)	5(1)	-3(1)
C(22A)	18(1)	15(1)	17(1)	1(1)	7(1)	2(1)
C(23A)	19(1)	19(1)	22(1)	0(1)	5(1)	-3(1)
C(24A)	21(1)	22(1)	18(1)	1(1)	3(1)	3(1)
C(25A)	30(1)	17(1)	22(1)	4(1)	11(1)	2(1)
C(26A)	25(1)	22(1)	24(1)	2(1)	9(1)	-5(1)
C(27A)	19(1)	20(1)	19(1)	0(1)	5(1)	-2(1)
O(1A)	17(1)	16(1)	25(1)	-1(1)	0(1)	1(1)
O(2A)	18(1)	16(1)	36(1)	-1(1)	3(1)	-1(1)
O(3A)	17(1)	15(1)	24(1)	-1(1)	6(1)	0(1)
O(4A)	22(1)	17(1)	24(1)	1(1)	8(1)	-4(1)
O(5A)	14(1)	17(1)	18(1)	3(1)	0(1)	-3(1)
C(1B)	17(1)	21(1)	19(1)	1(1)	2(1)	-1(1)
C(2B)	17(1)	19(1)	20(1)	-2(1)	3(1)	2(1)
C(3B)	17(1)	19(1)	20(1)	0(1)	5(1)	2(1)
C(4B)	17(1)	15(1)	18(1)	1(1)	2(1)	1(1)
C(5B)	18(1)	17(1)	20(1)	3(1)	2(1)	-1(1)
C(6B)	17(1)	15(1)	23(1)	-2(1)	3(1)	1(1)

C(7B)	19(1)	35(1)	23(1)	-4(1)	2(1)	1(1)
C(8B)	26(1)	31(1)	28(1)	-2(1)	12(1)	-3(1)
C(9B)	13(1)	14(1)	19(1)	0(1)	4(1)	0(1)
C(10B)	19(1)	15(1)	22(1)	0(1)	8(1)	2(1)
C(11B)	23(1)	20(1)	21(1)	0(1)	5(1)	-1(1)
C(12B)	29(1)	22(1)	20(1)	0(1)	7(1)	4(1)
C(13B)	33(1)	21(1)	28(1)	6(1)	14(1)	6(1)
C(14B)	26(1)	24(1)	39(1)	6(1)	13(1)	-3(1)
C(15B)	18(1)	21(1)	29(1)	3(1)	5(1)	1(1)
C(16B)	12(1)	18(1)	16(1)	-2(1)	2(1)	-1(1)
C(17B)	19(1)	18(1)	19(1)	0(1)	5(1)	1(1)
C(18B)	22(1)	20(1)	22(1)	-4(1)	6(1)	1(1)
C(19B)	18(1)	28(1)	18(1)	-4(1)	6(1)	-2(1)
C(20B)	19(1)	22(1)	19(1)	0(1)	5(1)	-3(1)
C(21B)	17(1)	19(1)	21(1)	1(1)	3(1)	2(1)
C(22B)	17(1)	14(1)	17(1)	0(1)	4(1)	0(1)
C(23B)	16(1)	21(1)	21(1)	-2(1)	7(1)	-1(1)
C(24B)	22(1)	19(1)	25(1)	-3(1)	7(1)	-5(1)
C(25B)	29(1)	20(1)	25(1)	-5(1)	9(1)	0(1)
C(26B)	23(1)	26(1)	29(1)	-5(1)	11(1)	4(1)
C(27B)	18(1)	21(1)	26(1)	-2(1)	7(1)	-1(1)
O(1B)	19(1)	16(1)	25(1)	2(1)	0(1)	0(1)
O(2B)	17(1)	16(1)	28(1)	-2(1)	5(1)	0(1)
O(3B)	16(1)	16(1)	32(1)	-1(1)	4(1)	1(1)
O(4B)	21(1)	23(1)	34(1)	0(1)	12(1)	5(1)
O(5B)	15(1)	17(1)	20(1)	2(1)	1(1)	-1(1)

Table 12. Hydrogen coordinates (× 10^4) and isotropic displacement parameters ($Å^2$ × 10^3) for **3**.

	x	y	z	U(eq)
H(1A)	8096	1648	11411	23
H(2A)	8424	-388	11560	21
H(3A)	8031	-1434	10048	20
H(4A)	7881	423	9264	21
H(5A1)	7021	-715	8891	23
H(5A2)	6866	289	9479	23
H(7A1)	9243	976	12259	37
H(7A2)	9594	2049	12036	37
H(7A3)	9725	580	11964	37
H(8A1)	9590	862	10377	45
H(8A2)	9502	2340	10502	45

H(8A3)	9054	1553	9779	45
H(11A)	7144	-361	7421	27
H(12A)	7096	-2195	6627	33
H(13A)	6290	-3300	6033	31
H(14A)	5529	-2563	6256	28
H(15A)	5573	-737	7063	24
H(17A)	6031	-743	8697	22
H(18A)	5411	-470	9360	25
H(19A)	4953	1455	9236	25
H(20A)	5164	3158	8528	25
H(21A)	5807	2920	7906	23
H(23A)	5618	1412	6326	25
H(24A)	5546	2955	5304	26
H(25A)	6236	4419	5497	27
H(26A)	6990	4367	6752	29
H(27A)	7059	2841	7791	24
H(4A1)	7398	-1833	10448	32
H(1B)	6645	1599	3511	24
H(2B)	6799	-543	3566	24
H(3B)	7230	-1188	5212	22
H(4B)	7099	737	5745	21
H(5B1)	8119	1161	5573	24
H(5B2)	7894	2049	6143	24
H(7B1)	5289	828	2967	41
H(7B2)	5393	-667	2962	41
H(7B3)	5788	309	2758	41
H(8B1)	5841	46	5201	42
H(8B2)	5400	-755	4476	42
H(8B3)	5341	753	4518	42
H(11B)	9374	-54	8703	26
H(12B)	9444	-1559	9747	29
H(13B)	8761	-3039	9549	32
H(14B)	8017	-3035	8282	35
H(15B)	7941	-1506	7242	28
H(17B)	9187	-1574	7090	23
H(18B)	9825	-1784	6460	26
H(19B)	10030	-58	5761	26
H(20B)	9565	1852	5646	25
H(21B)	8951	2098	6322	24
H(23B)	9430	2050	7954	23
H(24B)	9483	3905	8741	27
H(25B)	8720	4710	8921	30
H(26B)	7907	3622	8347	31
H(27B)	7857	1752	7581	26
H(4B1)	7859	-1317	4795	38

Table 13. Torsion angles [deg] for **3**.

O(2A)-C(1A)-C(2A)-O(3A)	-14.69(19)
O(1A)-C(1A)-C(2A)-O(3A)	104.00(16)
O(2A)-C(1A)-C(2A)-C(3A)	-128.92(15)
O(1A)-C(1A)-C(2A)-C(3A)	-10.2(2)
O(3A)-C(2A)-C(3A)-O(4A)	159.06(15)
C(1A)-C(2A)-C(3A)-O(4A)	-90.58(18)
O(3A)-C(2A)-C(3A)-C(4A)	-83.05(18)
C(1A)-C(2A)-C(3A)-C(4A)	27.32(18)
O(4A)-C(3A)-C(4A)-O(1A)	80.59(18)
C(2A)-C(3A)-C(4A)-O(1A)	-35.09(18)
O(4A)-C(3A)-C(4A)-C(5A)	-37.0(2)
C(2A)-C(3A)-C(4A)-C(5A)	-152.71(16)
O(1A)-C(4A)-C(5A)-O(5A)	74.58(18)
C(3A)-C(4A)-C(5A)-O(5A)	-170.22(15)
O(5A)-C(9A)-C(10A)-C(15A)	151.83(17)
C(22A)-C(9A)-C(10A)-C(15A)	-95.1(2)
C(16A)-C(9A)-C(10A)-C(15A)	27.8(2)
O(5A)-C(9A)-C(10A)-C(11A)	-34.9(2)
C(22A)-C(9A)-C(10A)-C(11A)	78.2(2)
C(16A)-C(9A)-C(10A)-C(11A)	-158.94(17)
C(15A)-C(10A)-C(11A)-C(12A)	-1.4(3)
C(9A)-C(10A)-C(11A)-C(12A)	-174.95(19)
C(10A)-C(11A)-C(12A)-C(13A)	1.0(4)
C(11A)-C(12A)-C(13A)-C(14A)	-0.3(4)
C(12A)-C(13A)-C(14A)-C(15A)	-0.1(3)
C(11A)-C(10A)-C(15A)-C(14A)	1.0(3)
C(9A)-C(10A)-C(15A)-C(14A)	174.37(18)
C(13A)-C(14A)-C(15A)-C(10A)	-0.3(3)
O(5A)-C(9A)-C(16A)-C(21A)	96.5(2)
C(22A)-C(9A)-C(16A)-C(21A)	-19.5(2)
C(10A)-C(9A)-C(16A)-C(21A)	-139.60(18)
O(5A)-C(9A)-C(16A)-C(17A)	-80.3(2)
C(22A)-C(9A)-C(16A)-C(17A)	163.81(17)
C(10A)-C(9A)-C(16A)-C(17A)	43.7(2)
C(21A)-C(16A)-C(17A)-C(18A)	1.2(3)
C(9A)-C(16A)-C(17A)-C(18A)	177.97(17)
C(16A)-C(17A)-C(18A)-C(19A)	1.3(3)
C(17A)-C(18A)-C(19A)-C(20A)	-2.5(3)
C(18A)-C(19A)-C(20A)-C(21A)	1.2(3)
C(17A)-C(16A)-C(21A)-C(20A)	-2.4(3)
C(9A)-C(16A)-C(21A)-C(20A)	-179.24(17)
C(19A)-C(20A)-C(21A)-C(16A)	1.3(3)

O(5A)-C(9A)-C(22A)-C(27A)	-4.7(2)
C(16A)-C(9A)-C(22A)-C(27A)	114.4(2)
C(10A)-C(9A)-C(22A)-C(27A)	-121.1(2)
O(5A)-C(9A)-C(22A)-C(23A)	174.62(17)
C(16A)-C(9A)-C(22A)-C(23A)	-66.3(2)
C(10A)-C(9A)-C(22A)-C(23A)	58.2(2)
C(27A)-C(22A)-C(23A)-C(24A)	1.4(3)
C(9A)-C(22A)-C(23A)-C(24A)	-177.93(18)
C(22A)-C(23A)-C(24A)-C(25A)	0.2(3)
C(23A)-C(24A)-C(25A)-C(26A)	-1.3(3)
C(24A)-C(25A)-C(26A)-C(27A)	0.7(3)
C(23A)-C(22A)-C(27A)-C(26A)	-1.9(3)
C(9A)-C(22A)-C(27A)-C(26A)	177.35(18)
C(25A)-C(26A)-C(27A)-C(22A)	0.9(3)
O(2A)-C(1A)-O(1A)-C(4A)	101.98(19)
C(2A)-C(1A)-O(1A)-C(4A)	-12.6(2)
C(5A)-C(4A)-O(1A)-C(1A)	150.53(16)
C(3A)-C(4A)-O(1A)-C(1A)	30.45(19)
O(1A)-C(1A)-O(2A)-C(6A)	-120.08(17)
C(2A)-C(1A)-O(2A)-C(6A)	-4.5(2)
O(3A)-C(6A)-O(2A)-C(1A)	22.19(19)
C(8A)-C(6A)-O(2A)-C(1A)	138.05(17)
C(7A)-C(6A)-O(2A)-C(1A)	-96.84(19)
C(3A)-C(2A)-O(3A)-C(6A)	140.07(16)
C(1A)-C(2A)-O(3A)-C(6A)	28.71(18)
O(2A)-C(6A)-O(3A)-C(2A)	-32.06(18)
C(8A)-C(6A)-O(3A)-C(2A)	-148.90(17)
C(7A)-C(6A)-O(3A)-C(2A)	86.40(19)
C(4A)-C(5A)-O(5A)-C(9A)	171.90(15)
C(22A)-C(9A)-O(5A)-C(5A)	-178.49(15)
C(16A)-C(9A)-O(5A)-C(5A)	61.7(2)
C(10A)-C(9A)-O(5A)-C(5A)	-64.49(19)
O(1B)-C(1B)-C(2B)-O(3B)	119.11(16)
O(2B)-C(1B)-C(2B)-O(3B)	1.9(2)
O(1B)-C(1B)-C(2B)-C(3B)	3.5(2)
O(2B)-C(1B)-C(2B)-C(3B)	-113.76(16)
O(3B)-C(2B)-C(3B)-O(4B)	147.22(17)
C(1B)-C(2B)-C(3B)-O(4B)	-100.69(19)
O(3B)-C(2B)-C(3B)-C(4B)	-93.94(19)
C(1B)-C(2B)-C(3B)-C(4B)	18.1(2)
O(4B)-C(3B)-C(4B)-O(1B)	84.06(19)
C(2B)-C(3B)-C(4B)-O(1B)	-33.36(19)
O(4B)-C(3B)-C(4B)-C(5B)	-32.4(2)
C(2B)-C(3B)-C(4B)-C(5B)	-149.79(17)
O(1B)-C(4B)-C(5B)-O(5B)	174.81(14)
C(3B)-C(4B)-C(5B)-O(5B)	-70.13(19)

O(5B)-C(9B)-C(10B)-C(15B)	4.8(2)
C(22B)-C(9B)-C(10B)-C(15B)	121.9(2)
C(16B)-C(9B)-C(10B)-C(15B)	-114.0(2)
O(5B)-C(9B)-C(10B)-C(11B)	-173.82(17)
C(22B)-C(9B)-C(10B)-C(11B)	-56.6(2)
C(16B)-C(9B)-C(10B)-C(11B)	67.4(2)
C(15B)-C(10B)-C(11B)-C(12B)	-1.7(3)
C(9B)-C(10B)-C(11B)-C(12B)	176.89(18)
C(10B)-C(11B)-C(12B)-C(13B)	0.7(3)
C(11B)-C(12B)-C(13B)-C(14B)	1.0(3)
C(12B)-C(13B)-C(14B)-C(15B)	-1.4(3)
C(11B)-C(10B)-C(15B)-C(14B)	1.2(3)
C(9B)-C(10B)-C(15B)-C(14B)	-177.38(19)
C(13B)-C(14B)-C(15B)-C(10B)	0.3(4)
O(5B)-C(9B)-C(16B)-C(17B)	-95.5(2)
C(22B)-C(9B)-C(16B)-C(17B)	140.05(18)
C(10B)-C(9B)-C(16B)-C(17B)	19.9(2)
O(5B)-C(9B)-C(16B)-C(21B)	81.3(2)
C(22B)-C(9B)-C(16B)-C(21B)	-43.2(2)
C(10B)-C(9B)-C(16B)-C(21B)	-163.39(17)
C(21B)-C(16B)-C(17B)-C(18B)	2.8(3)
C(9B)-C(16B)-C(17B)-C(18B)	179.63(17)
C(16B)-C(17B)-C(18B)-C(19B)	-1.4(3)
C(17B)-C(18B)-C(19B)-C(20B)	-1.5(3)
C(18B)-C(19B)-C(20B)-C(21B)	2.9(3)
C(19B)-C(20B)-C(21B)-C(16B)	-1.4(3)
C(17B)-C(16B)-C(21B)-C(20B)	-1.4(3)
C(9B)-C(16B)-C(21B)-C(20B)	-178.26(17)
O(5B)-C(9B)-C(22B)-C(27B)	32.3(2)
C(16B)-C(9B)-C(22B)-C(27B)	156.39(18)
C(10B)-C(9B)-C(22B)-C(27B)	-80.4(2)
O(5B)-C(9B)-C(22B)-C(23B)	-152.53(17)
C(16B)-C(9B)-C(22B)-C(23B)	-28.5(2)
C(10B)-C(9B)-C(22B)-C(23B)	94.7(2)
C(27B)-C(22B)-C(23B)-C(24B)	-0.6(3)
C(9B)-C(22B)-C(23B)-C(24B)	-175.72(17)
C(22B)-C(23B)-C(24B)-C(25B)	-0.5(3)
C(23B)-C(24B)-C(25B)-C(26B)	1.0(3)
C(24B)-C(25B)-C(26B)-C(27B)	-0.5(3)
C(25B)-C(26B)-C(27B)-C(22B)	-0.6(3)
C(23B)-C(22B)-C(27B)-C(26B)	1.1(3)
C(9B)-C(22B)-C(27B)-C(26B)	176.42(19)
O(2B)-C(1B)-O(1B)-C(4B)	87.71(19)
C(2B)-C(1B)-O(1B)-C(4B)	-25.5(2)
C(5B)-C(4B)-O(1B)-C(1B)	159.69(16)
C(3B)-C(4B)-O(1B)-C(1B)	37.51(19)

O(1B)-C(1B)-O(2B)-C(6B)	-135.83(17)
C(2B)-C(1B)-O(2B)-C(6B)	-20.95(19)
O(3B)-C(6B)-O(2B)-C(1B)	32.43(18)
C(8B)-C(6B)-O(2B)-C(1B)	148.46(16)
C(7B)-C(6B)-O(2B)-C(1B)	-86.57(19)
C(3B)-C(2B)-O(3B)-C(6B)	129.93(17)
C(1B)-C(2B)-O(3B)-C(6B)	17.8(2)
O(2B)-C(6B)-O(3B)-C(2B)	-31.06(18)
C(8B)-C(6B)-O(3B)-C(2B)	-147.83(16)
C(7B)-C(6B)-O(3B)-C(2B)	87.8(2)
C(4B)-C(5B)-O(5B)-C(9B)	-178.17(15)
C(22B)-C(9B)-O(5B)-C(5B)	61.74(19)
C(16B)-C(9B)-O(5B)-C(5B)	-64.1(2)
C(10B)-C(9B)-O(5B)-C(5B)	175.88(15)

Table 14. Hydrogen bonds for **3** [Å and deg].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4B)-H(4B1)...O(1B)#1	0.84	2.16	2.944(2)	155.1
O(4A)-H(4A1)...O(1A)#2	0.84	1.99	2.810(2)	164.4

Symmetry transformations used to generate equivalent atoms:

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

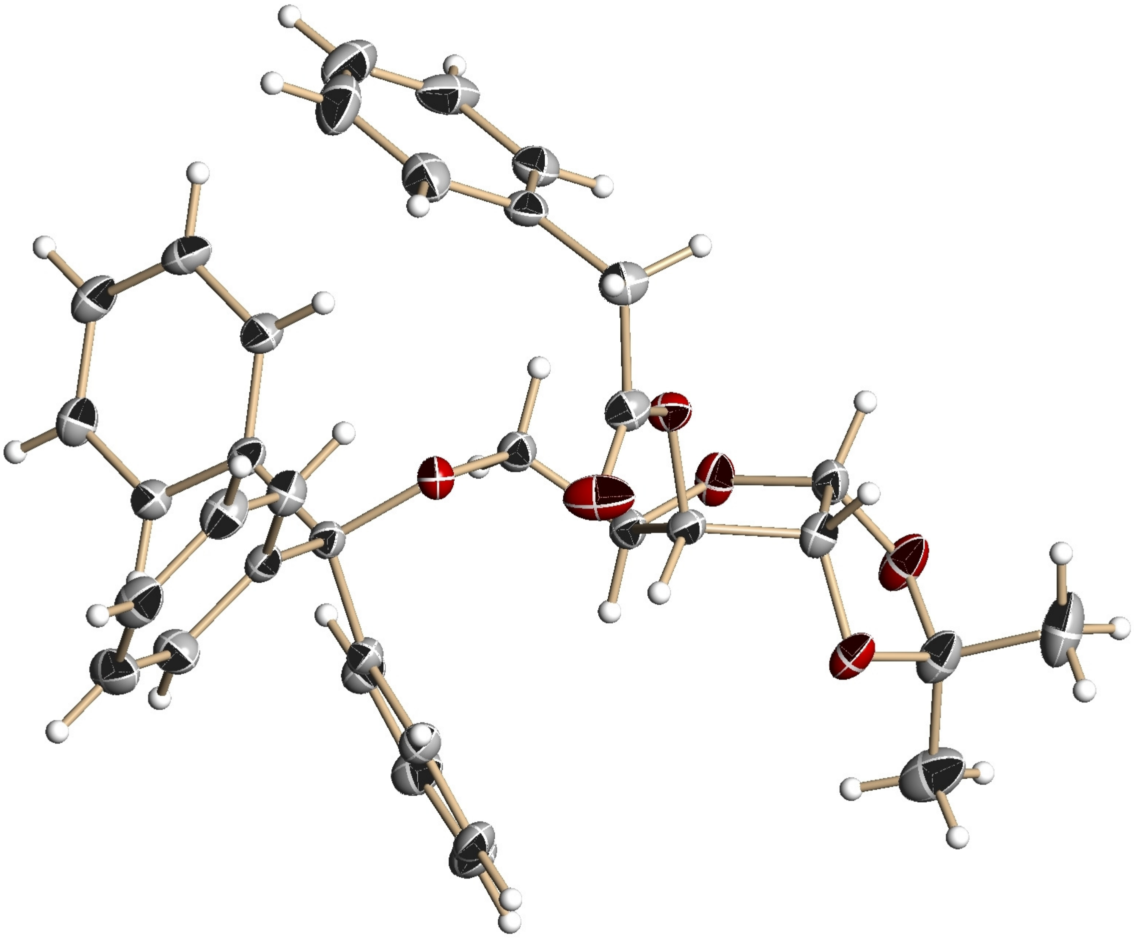


Figure 53: X-ray crystal structure of **4.**

Table 15: Crystal data and structure refinement for **4.**

Identification code: 08mz225_0m

Empirical formula: C35 H34 O6

Formula weight: 765.78

Temperature: 140(2) K

Wavelength: 0.71073 Å

Crystal system: Monoclinic

Space group: $P2_1$

Unit cell dimensions:

a = 9.7813(11) Å, $\alpha = 90°$

b = 12.0906(14) Å, $\beta = 98.872(2)°$

c = 12.2879(14) Å, $\gamma = 90°$

Volume, *Z*: 1435.8(3) Å^3, 2

Density (calculated): 1.274 Mg/m^3

Absorption coefficient: 0.086 mm^{-1}

F(000): 584

Crystal size: 0.48 × 0.36 × 0.34 mm

Crystal shape, colour: block, colourless

θ range for data collection: 2.11 to 28.28°

Limiting indices: $-13 \le h \le 129$, $0 \le k \le 16$, $0 \le l \le 16$

Reflections collected: 28895

Independent reflections: 3710 (*R*(int) = 0.0369)

Completeness to $\theta = 28.28°$: 99.6 %

Absorption correction: multi-scan

Max. and min. transmission: 0.971 and 0.906

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

Data / restraints / parameters: 3710 / 1 / 373

Goodness-of-fit on F^2: 1.023

Final R indices [$I>2\sigma(I)$]: R1 = 0.0342, wR2 = 0.0789

R indices (all data): R1 = 0.0372, wR2 = 0.0813

Largest diff. peak and hole: 0.215 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.

Comments:

The crystal under investigation was found to be non-merohedrally twinned. The orientation matrices for the two components were identified using the program Cell_Now, and the two components were integrated using Saint, resulting in a total of 28895 reflections. 11814 reflections (3471 unique ones) involved component 1 only (mean I/sigma = 8.9), 11652 reflections (3460 unique ones) involved component 2 only (mean I/sigma = 4.7), and 5429 reflections (1902 unique ones) involved both components (mean I/sigma = 8.9). The exact twin matrix identified by the integration program was found to be 0.99948 -0.00004 0.24562, -0.00006 -1.00005 -0.00001, 0.00041 0.00001 -1.00002.

The data were corrected for absorption using twinabs, and the structure was solved using direct methods with only the non-overlapping reflections of component 1. The structure was refined using the hklf 5 routine with all reflections of component 1 (including the overlapping ones) below a d-spacing threshold of 0.75, resulting in a BASF value of 0.226(1). Friedel pairs were merged.

The Rint value given is for all reflections before the cutoff at d = 0.75 and is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions (TWINABS (Sheldrick, 2007)).

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.

Table 16: Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{Å}^2 \times 10^3$] for **4**.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	1301(2)	8379(2)	12341(2)	25(1)
C(2)	1175(2)	7124(2)	12160(2)	25(1)
C(3)	1578(2)	6940(2)	11028(2)	21(1)
C(4)	2518(2)	7918(2)	10898(2)	21(1)
C(5)	2387(2)	8367(2)	9728(2)	22(1)
C(6)	2309(2)	7438(2)	13899(2)	32(1)
C(7)	3757(3)	7405(2)	14511(2)	46(1)
C(8)	1219(3)	7160(3)	14609(2)	50(1)
C(9)	-105(2)	6131(2)	9644(2)	25(1)
C(10)	-1491(2)	6349(2)	8952(2)	26(1)
C(11)	-1429(2)	7140(2)	8009(2)	24(1)
C(12)	-1250(2)	8271(2)	8200(2)	27(1)
C(13)	-1242(2)	8993(2)	7327(2)	38(1)
C(14)	-1411(2)	8593(3)	6262(2)	46(1)
C(15)	-1595(2)	7482(3)	6061(2)	45(1)
C(16)	-1597(2)	6748(2)	6932(2)	33(1)
C(17)	3755(2)	7463(2)	8479(2)	19(1)
C(18)	4972(2)	7421(2)	9429(2)	20(1)
C(19)	5146(2)	6450(2)	10053(2)	24(1)
C(20)	6072(2)	6407(2)	11028(2)	29(1)
C(21)	6847(2)	7328(2)	11390(2)	32(1)
C(22)	6710(2)	8294(2)	10774(2)	31(1)
C(23)	5770(2)	8334(2)	9797(2)	24(1)
C(24)	3756(2)	8440(2)	7681(2)	20(1)
C(25)	4959(2)	8790(2)	7302(2)	23(1)
C(26)	4919(2)	9647(2)	6546(2)	29(1)
C(27)	3671(2)	10148(2)	6132(2)	30(1)
C(28)	2465(2)	9789(2)	6479(2)	29(1)
C(29)	2510(2)	8939(2)	7246(2)	24(1)
C(30)	3643(2)	6405(2)	7782(2)	20(1)
C(31)	4828(2)	5942(2)	7473(2)	28(1)
C(32)	4744(2)	5001(2)	6812(2)	32(1)
C(33)	3471(3)	4522(2)	6448(2)	32(1)
C(34)	2290(2)	4984(2)	6744(2)	30(1)
C(35)	2368(2)	5923(2)	7408(2)	25(1)
O(1)	2077(2)	8790(1)	11560(1)	28(1)
O(2)	2022(2)	8509(1)	13416(1)	36(1)
O(3)	2219(2)	6697(1)	12984(1)	28(1)
O(4)	310(1)	7029(1)	10262(1)	23(1)

O(5)	2509(1)	7484(1)	8973(1)	22(1)
O(6)	546(2)	5292(1)	9660(2)	41(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 17: Bond lengths [Å] and angles [deg] for **4**.

C(1)-O(1)	1.403(3)
C(1)-O(2)	1.407(3)
C(1)-C(2)	1.536(3)
C(1)-H(1)	1.0000
C(2)-O(3)	1.420(2)
C(2)-C(3)	1.519(3)
C(2)-H(2)	1.0000
C(3)-O(4)	1.440(2)
C(3)-C(4)	1.522(3)
C(3)-H(3)	1.0000
C(4)-O(1)	1.437(2)
C(4)-C(5)	1.523(3)
C(4)-H(4)	1.0000
C(5)-O(5)	1.431(2)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-O(3)	1.430(3)
C(6)-O(2)	1.433(3)
C(6)-C(7)	1.498(3)
C(6)-C(8)	1.516(4)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800

C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-O(6)	1.196(3)
C(9)-O(4)	1.352(2)
C(9)-C(10)	1.509(3)
C(10)-C(11)	1.510(3)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-C(16)	1.391(3)
C(11)-C(12)	1.394(3)
C(12)-C(13)	1.384(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.382(4)
C(13)-H(13)	0.9500
C(14)-C(15)	1.372(5)
C(14)-H(14)	0.9500
C(15)-C(16)	1.391(4)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(17)-O(5)	1.444(2)
C(17)-C(18)	1.534(2)
C(17)-C(30)	1.534(3)
C(17)-C(24)	1.536(3)
C(18)-C(23)	1.387(3)
C(18)-C(19)	1.398(3)
C(19)-C(20)	1.387(3)
C(19)-H(19)	0.9500
C(20)-C(21)	1.381(3)
C(20)-H(20)	0.9500
C(21)-C(22)	1.387(3)
C(21)-H(21)	0.9500
C(22)-C(23)	1.395(3)
C(22)-H(22)	0.9500
C(23)-H(23)	0.9500
C(24)-C(29)	1.391(3)
C(24)-C(25)	1.396(3)
C(25)-C(26)	1.388(3)
C(25)-H(25)	0.9500
C(26)-C(27)	1.388(3)
C(26)-H(26)	0.9500
C(27)-C(28)	1.385(3)
C(27)-H(27)	0.9500
C(28)-C(29)	1.390(3)
C(28)-H(28)	0.9500
C(29)-H(29)	0.9500
C(30)-C(35)	1.389(3)

C(30)-C(31)	1.392(3)
C(31)-C(32)	1.393(3)
C(31)-H(31)	0.9500
C(32)-C(33)	1.382(3)
C(32)-H(32)	0.9500
C(33)-C(34)	1.382(3)
C(33)-H(33)	0.9500
C(34)-C(35)	1.394(3)
C(34)-H(34)	0.9500
C(35)-H(35)	0.9500

O(1)-C(1)-O(2)	110.92(18)
O(1)-C(1)-C(2)	106.86(17)
O(2)-C(1)-C(2)	105.29(17)
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(3)	109.88(16)
O(3)-C(2)-C(1)	102.90(16)
C(3)-C(2)-C(1)	104.59(17)
O(3)-C(2)-H(2)	112.9
C(3)-C(2)-H(2)	112.9
C(1)-C(2)-H(2)	112.9
O(4)-C(3)-C(2)	105.60(15)
O(4)-C(3)-C(4)	110.23(15)
C(2)-C(3)-C(4)	103.18(16)
O(4)-C(3)-H(3)	112.4
C(2)-C(3)-H(3)	112.4
C(4)-C(3)-H(3)	112.4
O(1)-C(4)-C(3)	105.77(15)
O(1)-C(4)-C(5)	106.52(15)
C(3)-C(4)-C(5)	114.32(16)
O(1)-C(4)-H(4)	110.0
C(3)-C(4)-H(4)	110.0
C(5)-C(4)-H(4)	110.0
O(5)-C(5)-C(4)	110.08(16)
O(5)-C(5)-H(5A)	109.6
C(4)-C(5)-H(5A)	109.6
O(5)-C(5)-H(5B)	109.6
C(4)-C(5)-H(5B)	109.6
H(5A)-C(5)-H(5B)	108.2
O(3)-C(6)-O(2)	104.82(15)
O(3)-C(6)-C(7)	108.43(19)
O(2)-C(6)-C(7)	110.0(2)
O(3)-C(6)-C(8)	110.5(2)
O(2)-C(6)-C(8)	109.2(2)

C(7)-C(6)-C(8)	113.6(2)
C(6)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(6)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(6)-C(8)-H(8A)	109.5
C(6)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(6)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
O(6)-C(9)-O(4)	124.01(18)
O(6)-C(9)-C(10)	126.0(2)
O(4)-C(9)-C(10)	109.99(17)
C(9)-C(10)-C(11)	113.85(17)
C(9)-C(10)-H(10A)	108.8
C(11)-C(10)-H(10A)	108.8
C(9)-C(10)-H(10B)	108.8
C(11)-C(10)-H(10B)	108.8
H(10A)-C(10)-H(10B)	107.7
C(16)-C(11)-C(12)	119.2(2)
C(16)-C(11)-C(10)	120.1(2)
C(12)-C(11)-C(10)	120.7(2)
C(13)-C(12)-C(11)	120.3(2)
C(13)-C(12)-H(12)	119.8
C(11)-C(12)-H(12)	119.8
C(14)-C(13)-C(12)	119.9(2)
C(14)-C(13)-H(13)	120.1
C(12)-C(13)-H(13)	120.1
C(15)-C(14)-C(13)	120.4(2)
C(15)-C(14)-H(14)	119.8
C(13)-C(14)-H(14)	119.8
C(14)-C(15)-C(16)	120.1(2)
C(14)-C(15)-H(15)	119.9
C(16)-C(15)-H(15)	119.9
C(11)-C(16)-C(15)	120.0(2)
C(11)-C(16)-H(16)	120.0
C(15)-C(16)-H(16)	120.0
O(5)-C(17)-C(18)	106.70(14)
O(5)-C(17)-C(30)	104.91(15)
C(18)-C(17)-C(30)	112.17(16)
O(5)-C(17)-C(24)	109.81(15)
C(18)-C(17)-C(24)	115.77(16)
C(30)-C(17)-C(24)	106.96(14)

C(23)-C(18)-C(19)	118.33(17)
C(23)-C(18)-C(17)	123.60(18)
C(19)-C(18)-C(17)	117.37(18)
C(20)-C(19)-C(18)	120.9(2)
C(20)-C(19)-H(19)	119.6
C(18)-C(19)-H(19)	119.6
C(21)-C(20)-C(19)	120.1(2)
C(21)-C(20)-H(20)	120.0
C(19)-C(20)-H(20)	120.0
C(20)-C(21)-C(22)	120.02(18)
C(20)-C(21)-H(21)	120.0
C(22)-C(21)-H(21)	120.0
C(21)-C(22)-C(23)	119.6(2)
C(21)-C(22)-H(22)	120.2
C(23)-C(22)-H(22)	120.2
C(18)-C(23)-C(22)	121.1(2)
C(18)-C(23)-H(23)	119.5
C(22)-C(23)-H(23)	119.5
C(29)-C(24)-C(25)	118.35(18)
C(29)-C(24)-C(17)	119.46(17)
C(25)-C(24)-C(17)	121.97(17)
C(26)-C(25)-C(24)	120.69(19)
C(26)-C(25)-H(25)	119.7
C(24)-C(25)-H(25)	119.7
C(27)-C(26)-C(25)	120.3(2)
C(27)-C(26)-H(26)	119.9
C(25)-C(26)-H(26)	119.9
C(28)-C(27)-C(26)	119.5(2)
C(28)-C(27)-H(27)	120.2
C(26)-C(27)-H(27)	120.2
C(27)-C(28)-C(29)	120.1(2)
C(27)-C(28)-H(28)	119.9
C(29)-C(28)-H(28)	119.9
C(28)-C(29)-C(24)	120.97(19)
C(28)-C(29)-H(29)	119.5
C(24)-C(29)-H(29)	119.5
C(35)-C(30)-C(31)	118.99(19)
C(35)-C(30)-C(17)	121.14(18)
C(31)-C(30)-C(17)	119.81(17)
C(30)-C(31)-C(32)	120.7(2)
C(30)-C(31)-H(31)	119.7
C(32)-C(31)-H(31)	119.7
C(33)-C(32)-C(31)	120.0(2)
C(33)-C(32)-H(32)	120.0
C(31)-C(32)-H(32)	120.0
C(34)-C(33)-C(32)	119.6(2)

C(34)-C(33)-H(33)	120.2
C(32)-C(33)-H(33)	120.2
C(33)-C(34)-C(35)	120.7(2)
C(33)-C(34)-H(34)	119.6
C(35)-C(34)-H(34)	119.6
C(30)-C(35)-C(34)	120.0(2)
C(30)-C(35)-H(35)	120.0
C(34)-C(35)-H(35)	120.0
C(1)-O(1)-C(4)	111.64(15)
C(1)-O(2)-C(6)	109.01(16)
C(2)-O(3)-C(6)	106.43(16)
C(9)-O(4)-C(3)	117.41(15)
C(5)-O(5)-C(17)	116.47(14)

Table 18: Anisotropic displacement parameters [Å^2 × 10^3] for **4**.

The anisotropic displacement factor exponent takes the form: -2 π2 [(h a*)^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	32(1)	26(1)	20(1)	-2(1)	8(1)	5(1)
C(2)	29(1)	25(1)	20(1)	2(1)	5(1)	-2(1)
C(3)	22(1)	21(1)	18(1)	2(1)	1(1)	3(1)
C(4)	25(1)	20(1)	18(1)	-2(1)	4(1)	2(1)
C(5)	25(1)	21(1)	21(1)	1(1)	4(1)	1(1)
C(6)	50(1)	24(1)	21(1)	-1(1)	4(1)	0(1)
C(7)	59(2)	38(1)	34(1)	-7(1)	-12(1)	3(1)
C(8)	75(2)	54(2)	26(1)	-2(1)	19(1)	-10(2)
C(9)	26(1)	21(1)	26(1)	3(1)	2(1)	-2(1)
C(10)	25(1)	20(1)	30(1)	1(1)	0(1)	-4(1)
C(11)	17(1)	27(1)	26(1)	2(1)	1(1)	2(1)
C(12)	22(1)	27(1)	32(1)	2(1)	3(1)	2(1)
C(13)	24(1)	32(1)	58(2)	18(1)	2(1)	1(1)
C(14)	31(1)	67(2)	39(1)	27(1)	0(1)	-5(1)
C(15)	37(1)	76(2)	23(1)	1(1)	3(1)	-10(1)
C(16)	27(1)	41(1)	31(1)	-7(1)	3(1)	-1(1)
C(17)	21(1)	19(1)	17(1)	0(1)	3(1)	1(1)
C(18)	23(1)	21(1)	17(1)	1(1)	3(1)	3(1)
C(19)	27(1)	23(1)	21(1)	0(1)	2(1)	1(1)
C(20)	36(1)	30(1)	19(1)	7(1)	4(1)	8(1)
C(21)	35(1)	38(1)	20(1)	-2(1)	-4(1)	5(1)
C(22)	35(1)	30(1)	25(1)	-6(1)	-4(1)	-2(1)
C(23)	30(1)	21(1)	21(1)	-1(1)	1(1)	-1(1)
C(24)	25(1)	19(1)	16(1)	-1(1)	1(1)	0(1)
C(25)	24(1)	25(1)	21(1)	1(1)	3(1)	1(1)
C(26)	33(1)	28(1)	25(1)	4(1)	7(1)	-3(1)
C(27)	40(1)	26(1)	23(1)	7(1)	3(1)	-1(1)
C(28)	31(1)	28(1)	24(1)	3(1)	-4(1)	4(1)
C(29)	24(1)	25(1)	21(1)	1(1)	0(1)	-1(1)
C(30)	25(1)	19(1)	16(1)	2(1)	2(1)	1(1)
C(31)	26(1)	31(1)	27(1)	-4(1)	2(1)	0(1)
C(32)	34(1)	31(1)	30(1)	-8(1)	3(1)	8(1)
C(33)	47(1)	24(1)	24(1)	-5(1)	1(1)	2(1)
C(34)	35(1)	29(1)	24(1)	-2(1)	-1(1)	-8(1)
C(35)	30(1)	26(1)	21(1)	1(1)	4(1)	-2(1)
O(1)	45(1)	18(1)	24(1)	-3(1)	12(1)	0(1)
O(2)	63(1)	25(1)	20(1)	-2(1)	3(1)	3(1)
O(3)	42(1)	22(1)	18(1)	1(1)	-1(1)	1(1)

O(4)	25(1)	21(1)	22(1)	-2(1)	0(1)	2(1)
O(5)	23(1)	22(1)	20(1)	-1(1)	6(1)	-1(1)
O(6)	42(1)	23(1)	51(1)	-7(1)	-11(1)	4(1)

Table 19: Hydrogen coordinates (× 10^4) and isotropic displacement parameters (Å^2 × 10^3) for **4.**

	x	y	z	U(eq)
H(1)	369	8737	12261	31
H(2)	233	6835	12221	30
H(3)	2051	6214	10971	25
H(4)	3502	7719	11174	25
H(5A)	1479	8736	9528	26
H(5B)	3121	8921	9684	26
H(7A)	3938	6676	14850	69
H(7B)	3868	7975	15085	69
H(7C)	4411	7542	13997	69
H(8A)	299	7198	14162	75
H(8B)	1272	7691	15217	75
H(8C)	1380	6412	14908	75
H(10A)	-2126	6655	9430	31
H(10B)	-1884	5638	8650	31
H(12)	-1134	8547	8932	32
H(13)	-1120	9764	7461	46
H(14)	-1399	9089	5664	55
H(15)	-1723	7214	5325	54
H(16)	-1712	5978	6792	40
H(19)	4623	5811	9806	29
H(20)	6173	5744	11448	34
H(21)	7474	7300	12062	38
H(22)	7253	8924	11014	37
H(23)	5675	8997	9378	29
H(25)	5815	8437	7564	28
H(26)	5749	9891	6311	34
H(27)	3644	10734	5614	36
H(28)	1606	10123	6192	34
H(29)	1676	8696	7477	28
H(31)	5704	6271	7716	34
H(32)	5560	4688	6610	39
H(33)	3410	3880	5998	38
H(34)	1415	4658	6493	36
H(35)	1549	6234	7606	30

Table 20: Torsion angles [deg] for **4**.

O(1)-C(1)-C(2)-O(3)	99.03(18)
O(2)-C(1)-C(2)-O(3)	-19.0(2)
O(1)-C(1)-C(2)-C(3)	-15.8(2)
O(2)-C(1)-C(2)-C(3)	-133.82(17)
O(3)-C(2)-C(3)-O(4)	160.50(15)
C(1)-C(2)-C(3)-O(4)	-89.66(18)
O(3)-C(2)-C(3)-C(4)	-83.77(18)
C(1)-C(2)-C(3)-C(4)	26.07(19)
O(4)-C(3)-C(4)-O(1)	84.78(18)
C(2)-C(3)-C(4)-O(1)	-27.59(19)
O(4)-C(3)-C(4)-C(5)	-32.1(2)
C(2)-C(3)-C(4)-C(5)	-144.44(16)
O(1)-C(4)-C(5)-O(5)	-167.24(14)
C(3)-C(4)-C(5)-O(5)	-50.8(2)
O(6)-C(9)-C(10)-C(11)	-107.9(3)
O(4)-C(9)-C(10)-C(11)	72.4(2)
C(9)-C(10)-C(11)-C(16)	107.5(2)
C(9)-C(10)-C(11)-C(12)	-74.7(2)
C(16)-C(11)-C(12)-C(13)	0.1(3)
C(10)-C(11)-C(12)-C(13)	-177.82(18)
C(11)-C(12)-C(13)-C(14)	0.0(3)
C(12)-C(13)-C(14)-C(15)	0.4(4)
C(13)-C(14)-C(15)-C(16)	-0.8(4)
C(12)-C(11)-C(16)-C(15)	-0.5(3)
C(10)-C(11)-C(16)-C(15)	177.41(19)
C(14)-C(15)-C(16)-C(11)	0.9(4)
O(5)-C(17)-C(18)-C(23)	-101.5(2)
C(30)-C(17)-C(18)-C(23)	144.15(19)
C(24)-C(17)-C(18)-C(23)	21.0(3)
O(5)-C(17)-C(18)-C(19)	68.7(2)
C(30)-C(17)-C(18)-C(19)	-45.6(2)
C(24)-C(17)-C(18)-C(19)	-168.77(18)
C(23)-C(18)-C(19)-C(20)	1.3(3)
C(17)-C(18)-C(19)-C(20)	-169.41(18)
C(18)-C(19)-C(20)-C(21)	-0.6(3)
C(19)-C(20)-C(21)-C(22)	-0.6(3)
C(20)-C(21)-C(22)-C(23)	1.1(3)
C(19)-C(18)-C(23)-C(22)	-0.9(3)
C(17)-C(18)-C(23)-C(22)	169.24(18)
C(21)-C(22)-C(23)-C(18)	-0.3(3)
O(5)-C(17)-C(24)-C(29)	-21.8(2)
C(18)-C(17)-C(24)-C(29)	-142.71(18)
C(30)-C(17)-C(24)-C(29)	91.5(2)
O(5)-C(17)-C(24)-C(25)	163.56(17)

C(18)-C(17)-C(24)-C(25)	42.7(3)
C(30)-C(17)-C(24)-C(25)	-83.1(2)
C(29)-C(24)-C(25)-C(26)	2.7(3)
C(17)-C(24)-C(25)-C(26)	177.39(19)
C(24)-C(25)-C(26)-C(27)	-1.8(3)
C(25)-C(26)-C(27)-C(28)	0.1(3)
C(26)-C(27)-C(28)-C(29)	0.7(3)
C(27)-C(28)-C(29)-C(24)	0.2(3)
C(25)-C(24)-C(29)-C(28)	-1.9(3)
C(17)-C(24)-C(29)-C(28)	-176.73(18)
O(5)-C(17)-C(30)-C(35)	23.1(2)
C(18)-C(17)-C(30)-C(35)	138.54(19)
C(24)-C(17)-C(30)-C(35)	-93.5(2)
O(5)-C(17)-C(30)-C(31)	-159.76(18)
C(18)-C(17)-C(30)-C(31)	-44.3(2)
C(24)-C(17)-C(30)-C(31)	83.6(2)
C(35)-C(30)-C(31)-C(32)	-0.8(3)
C(17)-C(30)-C(31)-C(32)	-178.0(2)
C(30)-C(31)-C(32)-C(33)	0.5(3)
C(31)-C(32)-C(33)-C(34)	0.1(4)
C(32)-C(33)-C(34)-C(35)	-0.3(3)
C(31)-C(30)-C(35)-C(34)	0.6(3)
C(17)-C(30)-C(35)-C(34)	177.77(18)
C(33)-C(34)-C(35)-C(30)	-0.1(3)
O(2)-C(1)-O(1)-C(4)	112.39(18)
C(2)-C(1)-O(1)-C(4)	-1.9(2)
C(3)-C(4)-O(1)-C(1)	18.8(2)
C(5)-C(4)-O(1)-C(1)	140.85(17)
O(1)-C(1)-O(2)-C(6)	-116.5(2)
C(2)-C(1)-O(2)-C(6)	-1.3(2)
O(3)-C(6)-O(2)-C(1)	21.1(2)
C(7)-C(6)-O(2)-C(1)	137.5(2)
C(8)-C(6)-O(2)-C(1)	-97.3(2)
C(3)-C(2)-O(3)-C(6)	143.26(17)
C(1)-C(2)-O(3)-C(6)	32.3(2)
O(2)-C(6)-O(3)-C(2)	-33.9(2)
C(7)-C(6)-O(3)-C(2)	-151.3(2)
C(8)-C(6)-O(3)-C(2)	83.6(2)
O(6)-C(9)-O(4)-C(3)	-3.6(3)
C(10)-C(9)-O(4)-C(3)	176.12(17)
C(2)-C(3)-O(4)-C(9)	-118.74(18)
C(4)-C(3)-O(4)-C(9)	130.45(18)
C(4)-C(5)-O(5)-C(17)	-109.74(17)
C(18)-C(17)-O(5)-C(5)	57.2(2)
C(30)-C(17)-O(5)-C(5)	176.39(14)
C(24)-C(17)-O(5)-C(5)	-68.98(18)

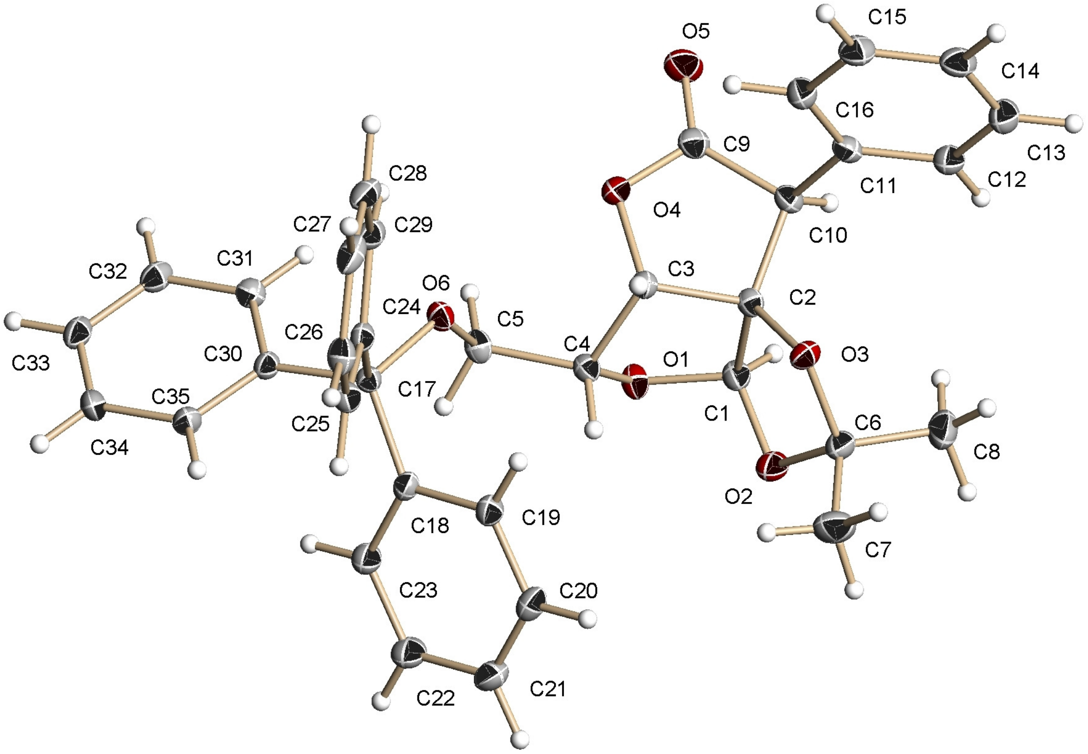


Figure 54: X-ray crystal structure of **6**.

Table 21: Crystal data and structure refinement for **6.**

Identification code: 08mz118_0m

Empirical formula: C35 H32 O6

Formula weight: 548.61

Temperature: 100(2) K

Wavelength: 0.71073 Å

Crystal system: Triclinic

Space group: P1

Unit cell dimensions:

a = 8.7096(6) Å, α = 101.4030(10)°

b = 9.1480(6) Å, β = 106.7210(10)°

c = 10.8575(12) Å, γ = 113.0710(10)°

Volume, *Z*: 713.35(10) Å^3, 1

Density (calculated): 1.277 Mg/m^3

Absorption coefficient: 0.087 mm^{-1}

F(000): 290

Crystal size: 0.60 × 0.48 × 0.44 mm

Crystal shape, colour: block, colourless

θ range for data collection: 2.09 to 28.28°

Limiting indices: $-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-14 \leq l \leq 14$

Reflections collected: 7235

Independent reflections: 3503 (R(int) = 0.0144)

Completeness to $\theta = 28.28°$: 98.9 %

Absorption correction: multi-scan

Max. and min. transmission: 0.962 and 0.866

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

Data / restraints / parameters: 3503 / 3 / 372

Goodness-of-fit on F^2: 1.045

Final R indices [$I > 2\sigma(I)$]: R1 = 0.0313, wR2 = 0.07983

R indices (all data): R1 = 0.0324, wR2 = 0.0808

Largest diff. peak and hole: 0.275 and -0.209 $e \times Å^{-3}$

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 refined with an isotropic displacement parameter 1.5 (methyl) or 1.2 times (all others) that of the adjacent carbon or nitrogen atom.

Table 22. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for **6.**

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	4248(2)	2538(2)	5341(2)	18(1)
C(2)	6045(2)	4206(2)	5765(2)	15(1)
C(3)	5858(2)	5505(2)	6770(2)	15(1)
C(4)	4344(2)	4410(2)	7128(2)	16(1)
C(5)	3310(2)	5259(2)	7578(2)	18(1)
C(6)	6712(3)	2120(2)	6248(2)	21(1)
C(7)	7642(3)	1926(3)	7564(3)	34(1)
C(8)	6883(3)	1192(3)	5015(2)	31(1)
C(9)	5339(2)	6052(2)	4734(2)	20(1)
C(10)	6219(2)	4917(2)	4612(2)	16(1)
C(11)	8178(2)	5936(2)	4794(2)	17(1)
C(12)	8973(2)	5130(2)	4185(2)	20(1)
C(13)	10769(3)	6025(3)	4351(2)	25(1)
C(14)	11804(3)	7736(2)	5144(2)	24(1)
C(15)	11032(3)	8562(2)	5759(2)	23(1)
C(16)	9223(2)	7667(2)	5579(2)	21(1)
C(17)	4690(2)	7038(2)	10035(2)	14(1)
C(18)	4603(2)	5465(2)	10370(2)	16(1)
C(19)	6086(2)	5153(2)	10529(2)	18(1)
C(20)	6023(3)	3681(2)	10724(2)	22(1)
C(21)	4462(3)	2469(2)	10750(2)	24(1)
C(22)	2976(3)	2756(2)	10588(2)	25(1)
C(23)	3050(2)	4248(2)	10404(2)	20(1)
C(24)	6512(2)	8648(2)	10961(2)	16(1)
C(25)	7545(2)	8854(2)	12290(2)	19(1)
C(26)	9193(2)	10331(2)	13097(2)	21(1)
C(27)	9811(2)	11620(2)	12584(2)	23(1)
C(28)	8770(2)	11438(2)	11271(2)	22(1)
C(29)	7127(2)	9966(2)	10459(2)	19(1)
C(30)	3171(2)	7437(2)	10155(2)	15(1)
C(31)	2106(2)	7711(2)	9090(2)	17(1)
C(32)	825(2)	8193(2)	9256(2)	20(1)
C(33)	584(2)	8394(2)	10473(2)	21(1)
C(34)	1639(3)	8120(2)	11541(2)	22(1)
C(35)	2936(2)	7658(2)	11388(2)	19(1)
O(1)	3128(2)	2970(2)	5868(1)	18(1)
O(2)	4841(2)	1559(2)	6008(1)	22(1)

O(3)	7465(2)	3901(2)	6449(1)	18(1)
O(4)	5249(2)	6419(2)	5974(1)	20(1)
O(5)	4812(2)	6635(2)	3912(2)	30(1)
O(6)	4662(2)	6825(2)	8669(1)	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 23. Bond lengths [Å] and angles [deg] for **6**.

C(1)-O(1)	1.403(2)
C(1)-O(2)	1.413(2)
C(1)-C(2)	1.557(2)
C(1)-H(1)	1.0000
C(2)-O(3)	1.408(2)
C(2)-C(10)	1.539(2)
C(2)-C(3)	1.540(2)
C(3)-O(4)	1.448(2)
C(3)-C(4)	1.518(2)
C(3)-H(3)	1.0000
C(4)-O(1)	1.445(2)
C(4)-C(5)	1.519(2)
C(4)-H(4)	1.0000
C(5)-O(6)	1.431(2)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-O(2)	1.426(2)
C(6)-O(3)	1.439(2)
C(6)-C(7)	1.508(3)
C(6)-C(8)	1.516(3)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800

C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-O(5)	1.198(2)
C(9)-O(4)	1.354(2)
C(9)-C(10)	1.520(3)
C(10)-C(11)	1.518(2)
C(10)-H(10)	1.0000
C(11)-C(12)	1.390(2)
C(11)-C(16)	1.398(2)
C(12)-C(13)	1.387(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.385(3)
C(13)-H(13)	0.9500
C(14)-C(15)	1.387(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.393(3)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(17)-O(6)	1.449(2)
C(17)-C(18)	1.532(2)
C(17)-C(30)	1.536(2)
C(17)-C(24)	1.537(2)
C(18)-C(23)	1.391(2)
C(18)-C(19)	1.400(2)
C(19)-C(20)	1.387(3)
C(19)-H(19)	0.9500
C(20)-C(21)	1.390(3)
C(20)-H(20)	0.9500
C(21)-C(22)	1.388(3)
C(21)-H(21)	0.9500
C(22)-C(23)	1.397(3)
C(22)-H(22)	0.9500
C(23)-H(23)	0.9500
C(24)-C(25)	1.393(2)
C(24)-C(29)	1.400(2)
C(25)-C(26)	1.394(3)
C(25)-H(25)	0.9500
C(26)-C(27)	1.387(3)
C(26)-H(26)	0.9500
C(27)-C(28)	1.387(3)
C(27)-H(27)	0.9500
C(28)-C(29)	1.390(3)
C(28)-H(28)	0.9500
C(29)-H(29)	0.9500

C(30)-C(31)	1.393(2)
C(30)-C(35)	1.399(2)
C(31)-C(32)	1.394(2)
C(31)-H(31)	0.9500
C(32)-C(33)	1.385(3)
C(32)-H(32)	0.9500
C(33)-C(34)	1.391(3)
C(33)-H(33)	0.9500
C(34)-C(35)	1.392(2)
C(34)-H(34)	0.9500
C(35)-H(35)	0.9500

O(1)-C(1)-O(2)	110.72(14)
O(1)-C(1)-C(2)	107.51(13)
O(2)-C(1)-C(2)	103.51(14)
O(1)-C(1)-H(1)	111.6
O(2)-C(1)-H(1)	111.6
C(2)-C(1)-H(1)	111.6
O(3)-C(2)-C(10)	116.69(14)
O(3)-C(2)-C(3)	111.24(13)
C(10)-C(2)-C(3)	104.63(13)
O(3)-C(2)-C(1)	105.56(14)
C(10)-C(2)-C(1)	115.33(14)
C(3)-C(2)-C(1)	102.57(13)
O(4)-C(3)-C(4)	110.06(14)
O(4)-C(3)-C(2)	105.27(13)
C(4)-C(3)-C(2)	103.70(13)
O(4)-C(3)-H(3)	112.4
C(4)-C(3)-H(3)	112.4
C(2)-C(3)-H(3)	112.4
O(1)-C(4)-C(3)	103.70(13)
O(1)-C(4)-C(5)	109.92(13)
C(3)-C(4)-C(5)	114.87(14)
O(1)-C(4)-H(4)	109.4
C(3)-C(4)-H(4)	109.4
C(5)-C(4)-H(4)	109.4
O(6)-C(5)-C(4)	106.00(13)
O(6)-C(5)-H(5A)	110.5
C(4)-C(5)-H(5A)	110.5
O(6)-C(5)-H(5B)	110.5
C(4)-C(5)-H(5B)	110.5
H(5A)-C(5)-H(5B)	108.7
O(2)-C(6)-O(3)	105.01(14)
O(2)-C(6)-C(7)	108.57(16)
O(3)-C(6)-C(7)	108.56(17)
O(2)-C(6)-C(8)	110.74(17)

O(3)-C(6)-C(8)	109.89(15)
C(7)-C(6)-C(8)	113.68(18)
C(6)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(6)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(6)-C(8)-H(8A)	109.5
C(6)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(6)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
O(5)-C(9)-O(4)	120.99(17)
O(5)-C(9)-C(10)	128.02(18)
O(4)-C(9)-C(10)	110.95(15)
C(11)-C(10)-C(9)	110.70(15)
C(11)-C(10)-C(2)	113.68(14)
C(9)-C(10)-C(2)	101.93(14)
C(11)-C(10)-H(10)	110.1
C(9)-C(10)-H(10)	110.1
C(2)-C(10)-H(10)	110.1
C(12)-C(11)-C(16)	118.73(16)
C(12)-C(11)-C(10)	119.51(16)
C(16)-C(11)-C(10)	121.76(16)
C(13)-C(12)-C(11)	120.70(17)
C(13)-C(12)-H(12)	119.7
C(11)-C(12)-H(12)	119.7
C(14)-C(13)-C(12)	120.27(18)
C(14)-C(13)-H(13)	119.9
C(12)-C(13)-H(13)	119.9
C(13)-C(14)-C(15)	119.82(17)
C(13)-C(14)-H(14)	120.1
C(15)-C(14)-H(14)	120.1
C(14)-C(15)-C(16)	119.88(18)
C(14)-C(15)-H(15)	120.1
C(16)-C(15)-H(15)	120.1
C(15)-C(16)-C(11)	120.59(17)
C(15)-C(16)-H(16)	119.7
C(11)-C(16)-H(16)	119.7
O(6)-C(17)-C(18)	108.78(13)
O(6)-C(17)-C(30)	110.54(13)
C(18)-C(17)-C(30)	114.12(13)
O(6)-C(17)-C(24)	103.67(13)
C(18)-C(17)-C(24)	112.45(13)

C(30)-C(17)-C(24)	106.78(13)
C(23)-C(18)-C(19)	118.10(16)
C(23)-C(18)-C(17)	122.84(15)
C(19)-C(18)-C(17)	118.81(15)
C(20)-C(19)-C(18)	121.24(16)
C(20)-C(19)-H(19)	119.4
C(18)-C(19)-H(19)	119.4
C(19)-C(20)-C(21)	120.18(17)
C(19)-C(20)-H(20)	119.9
C(21)-C(20)-H(20)	119.9
C(22)-C(21)-C(20)	119.28(17)
C(22)-C(21)-H(21)	120.4
C(20)-C(21)-H(21)	120.4
C(21)-C(22)-C(23)	120.38(17)
C(21)-C(22)-H(22)	119.8
C(23)-C(22)-H(22)	119.8
C(18)-C(23)-C(22)	120.81(17)
C(18)-C(23)-H(23)	119.6
C(22)-C(23)-H(23)	119.6
C(25)-C(24)-C(29)	119.06(16)
C(25)-C(24)-C(17)	122.27(15)
C(29)-C(24)-C(17)	118.65(15)
C(24)-C(25)-C(26)	120.53(17)
C(24)-C(25)-H(25)	119.7
C(26)-C(25)-H(25)	119.7
C(27)-C(26)-C(25)	120.09(17)
C(27)-C(26)-H(26)	120.0
C(25)-C(26)-H(26)	120.0
C(26)-C(27)-C(28)	119.68(17)
C(26)-C(27)-H(27)	120.2
C(28)-C(27)-H(27)	120.2
C(27)-C(28)-C(29)	120.54(18)
C(27)-C(28)-H(28)	119.7
C(29)-C(28)-H(28)	119.7
C(28)-C(29)-C(24)	120.07(17)
C(28)-C(29)-H(29)	120.0
C(24)-C(29)-H(29)	120.0
C(31)-C(30)-C(35)	119.06(16)
C(31)-C(30)-C(17)	120.98(15)
C(35)-C(30)-C(17)	119.78(15)
C(30)-C(31)-C(32)	120.13(16)
C(30)-C(31)-H(31)	119.9
C(32)-C(31)-H(31)	119.9
C(33)-C(32)-C(31)	120.65(16)
C(33)-C(32)-H(32)	119.7
C(31)-C(32)-H(32)	119.7

C(32)-C(33)-C(34)	119.58(17)
C(32)-C(33)-H(33)	120.2
C(34)-C(33)-H(33)	120.2
C(33)-C(34)-C(35)	120.08(17)
C(33)-C(34)-H(34)	120.0
C(35)-C(34)-H(34)	120.0
C(34)-C(35)-C(30)	120.49(16)
C(34)-C(35)-H(35)	119.8
C(30)-C(35)-H(35)	119.8
C(1)-O(1)-C(4)	106.10(12)
C(1)-O(2)-C(6)	108.32(13)
C(2)-O(3)-C(6)	108.54(13)
C(9)-O(4)-C(3)	111.67(13)
C(5)-O(6)-C(17)	118.34(13)

Table 24. Anisotropic displacement parameters [Å^2 × 10^3] for **6**.

The anisotropic displacement factor exponent takes the form: -2 π2 [(h a*)^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	17(1)	14(1)	19(1)	4(1)	8(1)	6(1)
C(2)	14(1)	15(1)	14(1)	4(1)	6(1)	6(1)
C(3)	16(1)	15(1)	15(1)	5(1)	7(1)	8(1)
C(4)	15(1)	15(1)	15(1)	4(1)	6(1)	6(1)
C(5)	15(1)	20(1)	15(1)	3(1)	6(1)	8(1)
C(6)	23(1)	18(1)	30(1)	12(1)	15(1)	12(1)
C(7)	39(1)	41(1)	40(1)	28(1)	20(1)	26(1)
C(8)	39(1)	23(1)	42(1)	10(1)	26(1)	17(1)
C(9)	17(1)	23(1)	25(1)	12(1)	11(1)	10(1)
C(10)	15(1)	19(1)	16(1)	8(1)	7(1)	8(1)
C(11)	17(1)	21(1)	17(1)	10(1)	8(1)	9(1)
C(12)	21(1)	18(1)	24(1)	9(1)	11(1)	9(1)
C(13)	23(1)	24(1)	33(1)	12(1)	16(1)	14(1)
C(14)	19(1)	24(1)	32(1)	16(1)	12(1)	9(1)
C(15)	21(1)	18(1)	27(1)	9(1)	10(1)	6(1)
C(16)	21(1)	20(1)	22(1)	8(1)	11(1)	10(1)
C(17)	14(1)	14(1)	13(1)	5(1)	6(1)	7(1)
C(18)	18(1)	16(1)	16(1)	5(1)	7(1)	10(1)

C(19)	18(1)	18(1)	20(1)	6(1)	8(1)	10(1)
C(20)	24(1)	22(1)	24(1)	7(1)	8(1)	15(1)
C(21)	31(1)	19(1)	27(1)	10(1)	13(1)	14(1)
C(22)	25(1)	18(1)	34(1)	12(1)	16(1)	9(1)
C(23)	20(1)	19(1)	25(1)	9(1)	11(1)	10(1)
C(24)	15(1)	15(1)	19(1)	4(1)	8(1)	8(1)
C(25)	19(1)	19(1)	19(1)	6(1)	9(1)	9(1)
C(26)	20(1)	23(1)	18(1)	2(1)	6(1)	11(1)
C(27)	16(1)	16(1)	32(1)	1(1)	8(1)	8(1)
C(28)	20(1)	17(1)	36(1)	11(1)	13(1)	11(1)
C(29)	18(1)	19(1)	23(1)	9(1)	9(1)	11(1)
C(30)	14(1)	15(1)	18(1)	6(1)	7(1)	8(1)
C(31)	15(1)	19(1)	17(1)	7(1)	6(1)	8(1)
C(32)	16(1)	19(1)	24(1)	9(1)	6(1)	10(1)
C(33)	17(1)	17(1)	32(1)	9(1)	13(1)	10(1)
C(34)	27(1)	24(1)	25(1)	12(1)	18(1)	16(1)
C(35)	22(1)	21(1)	19(1)	10(1)	10(1)	14(1)
O(1)	5(1)	17(1)	18(1)	1(1)	7(1)	5(1)
O(2)	22(1)	17(1)	33(1)	12(1)	15(1)	9(1)
O(3)	17(1)	16(1)	22(1)	8(1)	7(1)	9(1)
O(4)	24(1)	21(1)	25(1)	13(1)	14(1)	15(1)
O(5)	30(1)	42(1)	34(1)	25(1)	17(1)	24(1)
O(6)	18(1)	17(1)	14(1)	5(1)	8(1)	8(1)

Table 25. Hydrogen coordinates (× 10^4) and isotropic displacement parameters ($Å^2$ × 10^3) for **6**.

	x	y	z	U(eq)
H(1)	3627	1948	4321	21
H(3)	7023	6276	7599	18
H(4)	4862	4017	7861	19
H(5A)	2606	5472	6805	21
H(5B)	2453	4532	7904	21
H(7A)	7496	2568	8319	51
H(7B)	8944	2362	7767	51
H(7C)	7091	723	7461	51
H(8A)	6406	-12	4903	47
H(8B)	8170	1683	5157	47
H(8C)	6183	1306	4188	47
H(10)	5503	3975	3699	20

H(12)	8279	3953	3649	24
H(13)	11291	5462	3919	29
H(14)	13038	8342	5267	28
H(15)	11737	9736	6301	27
H(16)	8695	8239	5993	25
H(19)	7156	5965	10502	22
H(20)	7050	3500	10840	26
H(21)	4412	1456	10876	29
H(22)	1903	1934	10604	30
H(23)	2027	4432	10300	24
H(25)	7123	7980	12650	22
H(26)	9894	10457	13999	25
H(27)	10942	12621	13128	27
H(28)	9183	12328	10925	27
H(29)	6422	9854	9563	23
H(31)	2254	7569	8248	21
H(32)	109	8385	8527	23
H(33)	-296	8718	10577	25
H(34)	1473	8248	12375	26
H(35)	3668	7492	12126	22

Table 26: Torsion angles [deg] for **6**.

O(1)-C(1)-C(2)-O(3)	125.42(14)
O(2)-C(1)-C(2)-O(3)	8.20(17)
O(1)-C(1)-C(2)-C(10)	-104.23(16)
O(2)-C(1)-C(2)-C(10)	138.55(15)
O(1)-C(1)-C(2)-C(3)	8.83(17)
O(2)-C(1)-C(2)-C(3)	-108.38(14)
O(3)-C(2)-C(3)-O(4)	147.67(13)
C(10)-C(2)-C(3)-O(4)	20.84(16)
C(1)-C(2)-C(3)-O(4)	-99.90(14)
O(3)-C(2)-C(3)-C(4)	-96.70(15)
C(10)-C(2)-C(3)-C(4)	136.47(14)
C(1)-C(2)-C(3)-C(4)	15.73(16)
O(4)-C(3)-C(4)-O(1)	77.47(16)
C(2)-C(3)-C(4)-O(1)	-34.72(16)
O(4)-C(3)-C(4)-C(5)	-42.50(19)
C(2)-C(3)-C(4)-C(5)	-154.69(14)
O(1)-C(4)-C(5)-O(6)	-169.64(13)
C(3)-C(4)-C(5)-O(6)	-53.17(18)
O(5)-C(9)-C(10)-C(11)	74.7(2)

O(4)-C(9)-C(10)-C(11)	-103.15(16)
O(5)-C(9)-C(10)-C(2)	-164.0(2)
O(4)-C(9)-C(10)-C(2)	18.09(18)
O(3)-C(2)-C(10)-C(11)	-27.1(2)
C(3)-C(2)-C(10)-C(11)	96.28(17)
C(1)-C(2)-C(10)-C(11)	-151.85(15)
O(3)-C(2)-C(10)-C(9)	-146.25(14)
C(3)-C(2)-C(10)-C(9)	-22.87(16)
C(1)-C(2)-C(10)-C(9)	89.00(17)
C(9)-C(10)-C(11)-C(12)	-153.36(16)
C(2)-C(10)-C(11)-C(12)	92.63(19)
C(9)-C(10)-C(11)-C(16)	27.7(2)
C(2)-C(10)-C(11)-C(16)	-86.4(2)
C(16)-C(11)-C(12)-C(13)	0.0(3)
C(10)-C(11)-C(12)-C(13)	-179.05(17)
C(11)-C(12)-C(13)-C(14)	0.8(3)
C(12)-C(13)-C(14)-C(15)	-0.9(3)
C(13)-C(14)-C(15)-C(16)	0.2(3)
C(14)-C(15)-C(16)-C(11)	0.6(3)
C(12)-C(11)-C(16)-C(15)	-0.7(3)
C(10)-C(11)-C(16)-C(15)	178.31(16)
O(6)-C(17)-C(18)-C(23)	-106.99(18)
C(30)-C(17)-C(18)-C(23)	17.0(2)
C(24)-C(17)-C(18)-C(23)	138.77(17)
O(6)-C(17)-C(18)-C(19)	67.09(19)
C(30)-C(17)-C(18)-C(19)	-168.97(15)
C(24)-C(17)-C(18)-C(19)	-47.2(2)
C(23)-C(18)-C(19)-C(20)	-0.5(3)
C(17)-C(18)-C(19)-C(20)	-174.82(15)
C(18)-C(19)-C(20)-C(21)	0.7(3)
C(19)-C(20)-C(21)-C(22)	-0.5(3)
C(20)-C(21)-C(22)-C(23)	-0.1(3)
C(19)-C(18)-C(23)-C(22)	-0.1(3)
C(17)-C(18)-C(23)-C(22)	174.03(16)
C(21)-C(22)-C(23)-C(18)	0.4(3)
O(6)-C(17)-C(24)-C(25)	-145.64(16)
C(18)-C(17)-C(24)-C(25)	-28.3(2)
C(30)-C(17)-C(24)-C(25)	97.59(18)
O(6)-C(17)-C(24)-C(29)	35.92(18)
C(18)-C(17)-C(24)-C(29)	153.25(15)
C(30)-C(17)-C(24)-C(29)	-80.85(18)
C(29)-C(24)-C(25)-C(26)	-1.7(3)
C(17)-C(24)-C(25)-C(26)	179.85(15)
C(24)-C(25)-C(26)-C(27)	0.5(3)
C(25)-C(26)-C(27)-C(28)	0.8(3)
C(26)-C(27)-C(28)-C(29)	-1.0(3)

C(27)-C(28)-C(29)-C(24)	-0.2(3)
C(25)-C(24)-C(29)-C(28)	1.5(3)
C(17)-C(24)-C(29)-C(28)	-179.99(15)
O(6)-C(17)-C(30)-C(31)	-6.1(2)
C(18)-C(17)-C(30)-C(31)	-129.10(16)
C(24)-C(17)-C(30)-C(31)	106.02(17)
O(6)-C(17)-C(30)-C(35)	178.79(15)
C(18)-C(17)-C(30)-C(35)	55.8(2)
C(24)-C(17)-C(30)-C(35)	-69.09(19)
C(35)-C(30)-C(31)-C(32)	-0.2(2)
C(17)-C(30)-C(31)-C(32)	-175.33(16)
C(30)-C(31)-C(32)-C(33)	-0.4(3)
C(31)-C(32)-C(33)-C(34)	0.3(3)
C(32)-C(33)-C(34)-C(35)	0.5(3)
C(33)-C(34)-C(35)-C(30)	-1.1(3)
C(31)-C(30)-C(35)-C(34)	1.0(3)
C(17)-C(30)-C(35)-C(34)	176.15(16)
O(2)-C(1)-O(1)-C(4)	80.82(15)
C(2)-C(1)-O(1)-C(4)	-31.60(17)
C(3)-C(4)-O(1)-C(1)	41.79(16)
C(5)-C(4)-O(1)-C(1)	165.08(14)
O(1)-C(1)-O(2)-C(6)	-139.19(14)
C(2)-C(1)-O(2)-C(6)	-24.25(17)
O(3)-C(6)-O(2)-C(1)	31.43(18)
C(7)-C(6)-O(2)-C(1)	147.39(16)
C(8)-C(6)-O(2)-C(1)	-87.14(18)
C(10)-C(2)-O(3)-C(6)	-118.97(16)
C(3)-C(2)-O(3)-C(6)	121.13(15)
C(1)-C(2)-O(3)-C(6)	10.60(17)
O(2)-C(6)-O(3)-C(2)	-25.55(18)
C(7)-C(6)-O(3)-C(2)	-141.52(16)
C(8)-C(6)-O(3)-C(2)	93.59(18)
O(5)-C(9)-O(4)-C(3)	176.68(17)
C(10)-C(9)-O(4)-C(3)	-5.28(19)
C(4)-C(3)-O(4)-C(9)	-121.29(15)
C(2)-C(3)-O(4)-C(9)	-10.11(18)
C(4)-C(5)-O(6)-C(17)	-114.17(15)
C(18)-C(17)-O(6)-C(5)	48.42(18)
C(30)-C(17)-O(6)-C(5)	-77.62(17)
C(24)-C(17)-O(6)-C(5)	168.27(13)

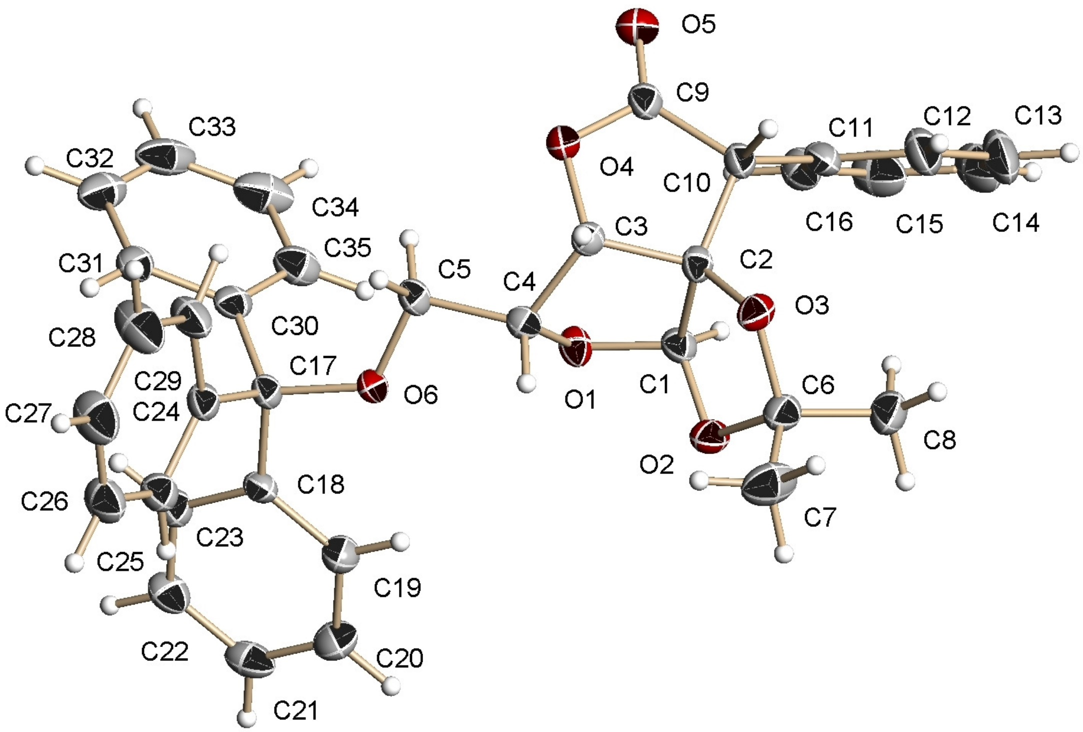


Figure 55: X-ray crystal structure of **7**.

Table 27. Crystal data and structure refinement for **7.**

Identification code: 08mz228_0m

Empirical formula: C35 H32 O6

Formula weight: 548.61

Temperature: 140(2) K

Wavelength: 0.71073 Å

Crystal system: Monoclinic

Space group: $P2_1$

Unit cell dimensions:

a = 10.5792(17) Å, $\alpha = 90°$

b = 8.6039(14) Å, $\beta = 102.063(3)°$

c = 15.509(3) Å, $\gamma = 90°$

Volume, *Z*: 1380.5(4) Å^3, 2

Density (calculated): 1.320 Mg/m^3

Absorption coefficient: 0.089 mm^{-1}

F(000): 580

Crystal size: 0.45 × 0.22 × 0.08 mm

Crystal shape, colour: plate, colourless

θ range for data collection: 1.34 to 28.28°

Limiting indices: $-14 \le h \le 12$, $-11 \le k \le 11$, $-19 \le l \le 20$

Reflections collected: 8771

Independent reflections: 3581 (*R*(int) = 0.0293)

Completeness to $\theta = 28.28°$: 98.4 %

Absorption correction: multi-scan

Max. and min. transmission: 0.993 and 0.869

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

Data / restraints / parameters: 3581 / 1 / 372

Goodness-of-fit on F^2: 1.152

Final R indices [$I>2\sigma(I)$]: R1 = 0.0430, wR2 = 0.1084

R indices (all data): R1 = 0.0554, wR2 = 0.1175

Largest diff. peak and hole: 0.303 and -0.331 $e \times Å^{-3}$

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 refined with an isotropic displacement parameter 1.5 (methyl) or 1.2 times (all others) that of the adjacent carbon atom.

Table 28. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [$Å^2$ × 10^3] for **7**.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	1808(3)	2434(3)	10107(2)	25(1)
C(2)	3168(2)	2688(3)	10697(2)	22(1)
C(3)	4079(2)	2225(3)	10077(2)	22(1)
C(4)	3194(2)	2140(3)	9171(2)	22(1)
C(5)	3606(3)	1065(3)	8517(2)	25(1)
C(6)	1997(3)	4988(4)	10574(2)	30(1)
C(7)	2226(3)	6519(4)	10176(3)	45(1)
C(8)	1226(3)	5108(5)	11294(2)	43(1)
C(9)	4183(3)	251(3)	11114(2)	26(1)
C(10)	3597(2)	1628(3)	11497(2)	23(1)
C(11)	2617(3)	1228(4)	12040(2)	29(1)
C(12)	2594(3)	2057(5)	12806(2)	40(1)
C(13)	1650(3)	1780(6)	13282(2)	52(1)
C(14)	728(4)	660(6)	13003(2)	52(1)
C(15)	747(3)	-197(5)	12251(2)	46(1)
C(16)	1688(3)	87(4)	11774(2)	33(1)
C(17)	2707(2)	344(3)	6953(2)	22(1)
C(18)	1332(2)	472(3)	6384(2)	22(1)
C(19)	447(3)	1493(4)	6609(2)	31(1)
C(20)	-801(3)	1596(4)	6098(2)	37(1)
C(21)	-1171(3)	677(4)	5363(2)	35(1)
C(22)	-290(3)	-350(4)	5132(2)	33(1)
C(23)	951(3)	-439(4)	5638(2)	28(1)
C(24)	3713(3)	1128(3)	6519(2)	25(1)
C(25)	3377(3)	2044(4)	5769(2)	29(1)
C(26)	4308(3)	2789(4)	5405(2)	37(1)
C(27)	5590(3)	2657(5)	5799(2)	45(1)
C(28)	5948(3)	1755(6)	6546(2)	52(1)
C(29)	5029(3)	972(5)	6898(2)	37(1)
C(30)	2980(3)	-1384(3)	7123(2)	27(1)
C(31)	3679(3)	-2248(4)	6628(2)	34(1)
C(32)	3778(4)	-3859(4)	6718(2)	46(1)
C(33)	3181(4)	-4625(4)	7292(2)	48(1)
C(34)	2490(4)	-3786(4)	7798(2)	45(1)
C(35)	2384(3)	-2180(4)	7712(2)	34(1)
O(1)	1975(2)	1640(2)	9356(1)	25(1)
O(2)	1363(2)	3967(2)	9892(1)	28(1)
O(3)	3230(2)	4276(2)	10915(1)	27(1)
O(4)	4536(2)	674(2)	10354(1)	26(1)

O(5)	4373(2)	-1032(3)	11401(1)	33(1)
O(6)	2612(2)	1174(2)	7743(1)	24(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 29. Bond lengths [Å] and angles [deg] for **7**.

C(1)-O(1)	1.393(3)
C(1)-O(2)	1.417(3)
C(1)-C(2)	1.550(3)
C(1)-H(1)	1.0000
C(2)-O(3)	1.406(3)
C(2)-C(10)	1.531(4)
C(2)-C(3)	1.549(4)
C(3)-O(4)	1.453(3)
C(3)-C(4)	1.519(3)
C(3)-H(3)	1.0000
C(4)-O(1)	1.443(3)
C(4)-C(5)	1.504(4)
C(4)-H(4)	1.0000
C(5)-O(6)	1.423(3)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-O(2)	1.429(3)
C(6)-O(3)	1.438(3)
C(6)-C(7)	1.496(5)
C(6)-C(8)	1.518(4)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800

C(9)-O(5)	1.192(4)
C(9)-O(4)	1.358(3)
C(9)-C(10)	1.515(4)
C(10)-C(11)	1.505(4)
C(10)-H(10)	1.0000
C(11)-C(12)	1.390(4)
C(11)-C(16)	1.390(4)
C(12)-C(13)	1.381(5)
C(12)-H(12)	0.9500
C(13)-C(14)	1.375(6)
C(13)-H(13)	0.9500
C(14)-C(15)	1.384(6)
C(14)-H(14)	0.9500
C(15)-C(16)	1.381(5)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(17)-O(6)	1.439(3)
C(17)-C(30)	1.527(4)
C(17)-C(24)	1.531(4)
C(17)-C(18)	1.539(3)
C(18)-C(19)	1.381(4)
C(18)-C(23)	1.386(4)
C(19)-C(20)	1.393(4)
C(19)-H(19)	0.9500
C(20)-C(21)	1.374(5)
C(20)-H(20)	0.9500
C(21)-C(22)	1.385(5)
C(21)-H(21)	0.9500
C(22)-C(23)	1.383(4)
C(22)-H(22)	0.9500
C(23)-H(23)	0.9500
C(24)-C(25)	1.388(4)
C(24)-C(29)	1.401(4)
C(25)-C(26)	1.390(4)
C(25)-H(25)	0.9500
C(26)-C(27)	1.371(4)
C(26)-H(26)	0.9500
C(27)-C(28)	1.380(5)
C(27)-H(27)	0.9500
C(28)-C(29)	1.386(5)
C(28)-H(28)	0.9500
C(29)-H(29)	0.9500
C(30)-C(31)	1.388(4)
C(30)-C(35)	1.393(5)
C(31)-C(32)	1.394(5)
C(31)-H(31)	0.9500

C(32)-C(33)	1.364(6)
C(32)-H(32)	0.9500
C(33)-C(34)	1.382(6)
C(33)-H(33)	0.9500
C(34)-C(35)	1.391(5)
C(34)-H(34)	0.9500
C(35)-H(35)	0.9500

O(1)-C(1)-O(2)	110.7(2)
O(1)-C(1)-C(2)	107.3(2)
O(2)-C(1)-C(2)	103.2(2)
O(1)-C(1)-H(1)	111.7
O(2)-C(1)-H(1)	111.7
C(2)-C(1)-H(1)	111.7
O(3)-C(2)-C(10)	113.1(2)
O(3)-C(2)-C(3)	113.3(2)
C(10)-C(2)-C(3)	103.4(2)
O(3)-C(2)-C(1)	105.7(2)
C(10)-C(2)-C(1)	118.4(2)
C(3)-C(2)-C(1)	102.7(2)
O(4)-C(3)-C(4)	109.4(2)
O(4)-C(3)-C(2)	105.4(2)
C(4)-C(3)-C(2)	104.0(2)
O(4)-C(3)-H(3)	112.5
C(4)-C(3)-H(3)	112.5
C(2)-C(3)-H(3)	112.5
O(1)-C(4)-C(5)	110.4(2)
O(1)-C(4)-C(3)	103.5(2)
C(5)-C(4)-C(3)	116.4(2)
O(1)-C(4)-H(4)	108.8
C(5)-C(4)-H(4)	108.8
C(3)-C(4)-H(4)	108.8
O(6)-C(5)-C(4)	105.1(2)
O(6)-C(5)-H(5A)	110.7
C(4)-C(5)-H(5A)	110.7
O(6)-C(5)-H(5B)	110.7
C(4)-C(5)-H(5B)	110.7
H(5A)-C(5)-H(5B)	108.8
O(2)-C(6)-O(3)	105.1(2)
O(2)-C(6)-C(7)	109.1(2)
O(3)-C(6)-C(7)	108.3(3)
O(2)-C(6)-C(8)	110.2(3)
O(3)-C(6)-C(8)	110.1(2)
C(7)-C(6)-C(8)	113.7(3)
C(6)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7B)	109.5

H(7A)-C(7)-H(7B)	109.5
C(6)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(6)-C(8)-H(8A)	109.5
C(6)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(6)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
O(5)-C(9)-O(4)	121.1(3)
O(5)-C(9)-C(10)	128.9(3)
O(4)-C(9)-C(10)	109.9(2)
C(11)-C(10)-C(9)	115.3(3)
C(11)-C(10)-C(2)	117.9(2)
C(9)-C(10)-C(2)	102.9(2)
C(11)-C(10)-H(10)	106.7
C(9)-C(10)-H(10)	106.7
C(2)-C(10)-H(10)	106.7
C(12)-C(11)-C(16)	118.6(3)
C(12)-C(11)-C(10)	119.9(3)
C(16)-C(11)-C(10)	121.5(3)
C(13)-C(12)-C(11)	120.9(3)
C(13)-C(12)-H(12)	119.6
C(11)-C(12)-H(12)	119.6
C(14)-C(13)-C(12)	119.8(3)
C(14)-C(13)-H(13)	120.1
C(12)-C(13)-H(13)	120.1
C(13)-C(14)-C(15)	120.3(3)
C(13)-C(14)-H(14)	119.9
C(15)-C(14)-H(14)	119.9
C(16)-C(15)-C(14)	119.8(4)
C(16)-C(15)-H(15)	120.1
C(14)-C(15)-H(15)	120.1
C(15)-C(16)-C(11)	120.6(3)
C(15)-C(16)-H(16)	119.7
C(11)-C(16)-H(16)	119.7
O(6)-C(17)-C(30)	112.3(2)
O(6)-C(17)-C(24)	109.6(2)
C(30)-C(17)-C(24)	112.4(2)
O(6)-C(17)-C(18)	103.2(2)
C(30)-C(17)-C(18)	106.9(2)
C(24)-C(17)-C(18)	112.1(2)
C(19)-C(18)-C(23)	118.4(2)
C(19)-C(18)-C(17)	120.7(2)
C(23)-C(18)-C(17)	120.9(2)

C(18)-C(19)-C(20)	120.6(3)
C(18)-C(19)-H(19)	119.7
C(20)-C(19)-H(19)	119.7
C(21)-C(20)-C(19)	120.4(3)
C(21)-C(20)-H(20)	119.8
C(19)-C(20)-H(20)	119.8
C(20)-C(21)-C(22)	119.4(3)
C(20)-C(21)-H(21)	120.3
C(22)-C(21)-H(21)	120.3
C(23)-C(22)-C(21)	119.9(3)
C(23)-C(22)-H(22)	120.0
C(21)-C(22)-H(22)	120.0
C(22)-C(23)-C(18)	121.2(3)
C(22)-C(23)-H(23)	119.4
C(18)-C(23)-H(23)	119.4
C(25)-C(24)-C(29)	117.7(3)
C(25)-C(24)-C(17)	122.6(2)
C(29)-C(24)-C(17)	119.6(3)
C(24)-C(25)-C(26)	121.5(3)
C(24)-C(25)-H(25)	119.2
C(26)-C(25)-H(25)	119.2
C(27)-C(26)-C(25)	119.9(3)
C(27)-C(26)-H(26)	120.0
C(25)-C(26)-H(26)	120.0
C(26)-C(27)-C(28)	119.6(3)
C(26)-C(27)-H(27)	120.2
C(28)-C(27)-H(27)	120.2
C(27)-C(28)-C(29)	120.8(3)
C(27)-C(28)-H(28)	119.6
C(29)-C(28)-H(28)	119.6
C(28)-C(29)-C(24)	120.3(3)
C(28)-C(29)-H(29)	119.8
C(24)-C(29)-H(29)	119.8
C(31)-C(30)-C(35)	117.8(3)
C(31)-C(30)-C(17)	122.0(3)
C(35)-C(30)-C(17)	119.7(3)
C(30)-C(31)-C(32)	121.0(4)
C(30)-C(31)-H(31)	119.5
C(32)-C(31)-H(31)	119.5
C(33)-C(32)-C(31)	120.7(4)
C(33)-C(32)-H(32)	119.7
C(31)-C(32)-H(32)	119.7
C(32)-C(33)-C(34)	119.3(3)
C(32)-C(33)-H(33)	120.3
C(34)-C(33)-H(33)	120.3
C(33)-C(34)-C(35)	120.5(4)

C(33)-C(34)-H(34)	119.8
C(35)-C(34)-H(34)	119.8
C(34)-C(35)-C(30)	120.8(4)
C(34)-C(35)-H(35)	119.6
C(30)-C(35)-H(35)	119.6
C(1)-O(1)-C(4)	107.1(2)
C(1)-O(2)-C(6)	108.5(2)
C(2)-O(3)-C(6)	109.4(2)
C(9)-O(4)-C(3)	111.6(2)
C(5)-O(6)-C(17)	121.0(2)

Table 30. Anisotropic displacement parameters [Å^2 × 10^3] for **7**.

The anisotropic displacement factor exponent takes the form: -2 π2 [(h a*)^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	22(1)	29(1)	21(1)	-1(1)	2(1)	0(1)
C(2)	21(1)	26(1)	20(1)	-5(1)	4(1)	-2(1)
C(3)	20(1)	23(1)	22(1)	-3(1)	3(1)	1(1)
C(4)	21(1)	23(1)	21(1)	0(1)	3(1)	-1(1)
C(5)	26(1)	30(1)	18(1)	-5(1)	1(1)	0(1)
C(6)	28(1)	33(2)	28(1)	-6(1)	0(1)	6(1)
C(7)	46(2)	28(2)	57(2)	-3(2)	0(2)	4(1)
C(8)	33(2)	62(2)	32(2)	-9(2)	5(1)	16(2)
C(9)	23(1)	32(2)	21(1)	-3(1)	2(1)	1(1)
C(10)	22(1)	30(1)	18(1)	-2(1)	4(1)	1(1)
C(11)	28(1)	38(2)	20(1)	5(1)	4(1)	6(1)
C(12)	37(2)	59(2)	24(1)	-6(2)	6(1)	1(2)
C(13)	46(2)	88(3)	25(2)	-3(2)	15(1)	8(2)
C(14)	43(2)	83(3)	36(2)	18(2)	20(2)	9(2)
C(15)	39(2)	55(2)	47(2)	21(2)	15(2)	-2(2)
C(16)	37(2)	33(2)	32(2)	4(1)	12(1)	0(1)
C(17)	23(1)	27(1)	17(1)	-3(1)	2(1)	1(1)
C(18)	24(1)	25(1)	18(1)	3(1)	3(1)	2(1)
C(19)	28(1)	36(2)	27(1)	-3(1)	3(1)	5(1)
C(20)	26(1)	45(2)	39(2)	1(2)	6(1)	8(1)
C(21)	24(1)	44(2)	33(2)	11(1)	-1(1)	-3(1)
C(22)	30(2)	40(2)	25(1)	-3(1)	-3(1)	-4(1)
C(23)	27(1)	34(2)	24(1)	-2(1)	4(1)	1(1)
C(24)	24(1)	32(2)	21(1)	-5(1)	4(1)	0(1)

C(25)	28(1)	34(2)	25(1)	-1(1)	4(1)	0(1)
C(26)	38(2)	44(2)	30(2)	5(1)	13(1)	-2(2)
C(27)	35(2)	66(2)	37(2)	3(2)	14(1)	-8(2)
C(28)	27(2)	96(3)	34(2)	8(2)	8(1)	-6(2)
C(29)	26(1)	62(2)	24(1)	7(2)	6(1)	3(1)
C(30)	29(1)	26(1)	22(1)	-4(1)	-5(1)	3(1)
C(31)	39(2)	36(2)	23(1)	-6(1)	-3(1)	11(1)
C(32)	51(2)	38(2)	38(2)	-15(2)	-16(2)	16(2)
C(33)	57(2)	27(2)	46(2)	-4(2)	-22(2)	5(2)
C(34)	50(2)	31(2)	44(2)	5(2)	-12(2)	-9(2)
C(35)	39(2)	29(2)	29(2)	2(1)	-2(1)	-4(1)
O(1)	22(1)	32(1)	21(1)	-5(1)	4(1)	-4(1)
O(2)	27(1)	28(1)	27(1)	-2(1)	-1(1)	4(1)
O(3)	25(1)	25(1)	29(1)	-8(1)	0(1)	2(1)
O(4)	26(1)	29(1)	21(1)	-1(1)	5(1)	5(1)
O(5)	35(1)	32(1)	32(1)	4(1)	4(1)	5(1)
O(6)	26(1)	27(1)	17(1)	-4(1)	1(1)	5(1)

Table 31. Hydrogen coordinates (× 10^4) and isotropic displacement parameters (Å^2 × 10^3) for **7**.

	x	y	z	U(eq)
H(1)	1225	1857	10427	29
H(3)	4803	2982	10099	26
H(4)	3086	3210	8914	27
H(5A)	4447	1395	8393	30
H(5B)	3687	-14	8742	30
H(7A)	1395	7001	9915	68
H(7B)	2724	6358	9717	68
H(7C)	2710	7201	10634	68
H(8A)	1100	4067	11518	64
H(8B)	383	5579	11053	64
H(8C)	1697	5754	11776	64
H(10)	4324	2172	11900	28
H(12)	3235	2823	13004	48
H(13)	1638	2361	13801	62
H(14)	75	474	13328	63
H(15)	114	-978	12064	55
H(16)	1700	-503	11258	40
H(19)	691	2131	7116	37
H(20)	-1401	2306	6258	44
H(21)	-2024	745	5018	41
H(22)	-537	-993	4627	39
H(23)	1553	-1137	5471	34
H(25)	2490	2164	5498	35
H(26)	4056	3390	4883	44
H(27)	6227	3183	5560	54
H(28)	6836	1670	6821	62
H(29)	5294	327	7401	45
H(31)	4095	-1735	6222	41
H(32)	4266	-4428	6376	55
H(33)	3239	-5724	7343	58
H(34)	2086	-4310	8207	53
H(35)	1898	-1618	8059	41

Table 32. Torsion angles [deg] for **7**.

O(1)-C(1)-C(2)-O(3)	129.9(2)
O(2)-C(1)-C(2)-O(3)	12.9(3)
O(1)-C(1)-C(2)-C(10)	-102.1(3)
O(2)-C(1)-C(2)-C(10)	140.9(2)
O(1)-C(1)-C(2)-C(3)	11.0(3)
O(2)-C(1)-C(2)-C(3)	-106.1(2)
O(3)-C(2)-C(3)-O(4)	144.4(2)
C(10)-C(2)-C(3)-O(4)	21.6(2)
C(1)-C(2)-C(3)-O(4)	-102.1(2)
O(3)-C(2)-C(3)-C(4)	-100.5(2)
C(10)-C(2)-C(3)-C(4)	136.7(2)
C(1)-C(2)-C(3)-C(4)	13.0(3)
O(4)-C(3)-C(4)-O(1)	80.3(2)
C(2)-C(3)-C(4)-O(1)	-31.9(3)
O(4)-C(3)-C(4)-C(5)	-40.9(3)
C(2)-C(3)-C(4)-C(5)	-153.1(2)
O(1)-C(4)-C(5)-O(6)	61.1(3)
C(3)-C(4)-C(5)-O(6)	178.7(2)
O(5)-C(9)-C(10)-C(11)	-30.4(4)
O(4)-C(9)-C(10)-C(11)	151.6(2)
O(5)-C(9)-C(10)-C(2)	-160.1(3)
O(4)-C(9)-C(10)-C(2)	21.9(3)
O(3)-C(2)-C(10)-C(11)	83.4(3)
C(3)-C(2)-C(10)-C(11)	-153.6(2)
C(1)-C(2)-C(10)-C(11)	-41.0(4)
O(3)-C(2)-C(10)-C(9)	-148.5(2)
C(3)-C(2)-C(10)-C(9)	-25.5(3)
C(1)-C(2)-C(10)-C(9)	87.1(3)
C(9)-C(10)-C(11)-C(12)	140.6(3)
C(2)-C(10)-C(11)-C(12)	-97.4(3)
C(9)-C(10)-C(11)-C(16)	-42.3(4)
C(2)-C(10)-C(11)-C(16)	79.6(4)
C(16)-C(11)-C(12)-C(13)	-1.5(5)
C(10)-C(11)-C(12)-C(13)	175.7(3)
C(11)-C(12)-C(13)-C(14)	0.7(6)
C(12)-C(13)-C(14)-C(15)	0.4(6)
C(13)-C(14)-C(15)-C(16)	-0.7(6)
C(14)-C(15)-C(16)-C(11)	-0.1(5)
C(12)-C(11)-C(16)-C(15)	1.2(5)
C(10)-C(11)-C(16)-C(15)	-175.9(3)
O(6)-C(17)-C(18)-C(19)	12.6(3)
C(30)-C(17)-C(18)-C(19)	131.2(3)
C(24)-C(17)-C(18)-C(19)	-105.2(3)
O(6)-C(17)-C(18)-C(23)	-167.1(3)

C(30)-C(17)-C(18)-C(23)	-48.5(3)
C(24)-C(17)-C(18)-C(23)	75.1(3)
C(23)-C(18)-C(19)-C(20)	0.3(5)
C(17)-C(18)-C(19)-C(20)	-179.4(3)
C(18)-C(19)-C(20)-C(21)	0.2(5)
C(19)-C(20)-C(21)-C(22)	-0.3(5)
C(20)-C(21)-C(22)-C(23)	-0.2(5)
C(21)-C(22)-C(23)-C(18)	0.8(5)
C(19)-C(18)-C(23)-C(22)	-0.8(4)
C(17)-C(18)-C(23)-C(22)	178.9(3)
O(6)-C(17)-C(24)-C(25)	-104.6(3)
C(30)-C(17)-C(24)-C(25)	129.7(3)
C(18)-C(17)-C(24)-C(25)	9.3(4)
O(6)-C(17)-C(24)-C(29)	73.2(3)
C(30)-C(17)-C(24)-C(29)	-52.4(3)
C(18)-C(17)-C(24)-C(29)	-172.9(3)
C(29)-C(24)-C(25)-C(26)	-0.2(5)
C(17)-C(24)-C(25)-C(26)	177.6(3)
C(24)-C(25)-C(26)-C(27)	-1.5(5)
C(25)-C(26)-C(27)-C(28)	1.4(6)
C(26)-C(27)-C(28)-C(29)	0.5(7)
C(27)-C(28)-C(29)-C(24)	-2.2(6)
C(25)-C(24)-C(29)-C(28)	2.1(5)
C(17)-C(24)-C(29)-C(28)	-175.9(3)
O(6)-C(17)-C(30)-C(31)	-149.4(2)
C(24)-C(17)-C(30)-C(31)	-25.2(3)
C(18)-C(17)-C(30)-C(31)	98.2(3)
O(6)-C(17)-C(30)-C(35)	39.0(3)
C(24)-C(17)-C(30)-C(35)	163.1(2)
C(18)-C(17)-C(30)-C(35)	-73.5(3)
C(35)-C(30)-C(31)-C(32)	0.0(4)
C(17)-C(30)-C(31)-C(32)	-171.8(3)
C(30)-C(31)-C(32)-C(33)	0.5(5)
C(31)-C(32)-C(33)-C(34)	-1.1(5)
C(32)-C(33)-C(34)-C(35)	1.2(5)
C(33)-C(34)-C(35)-C(30)	-0.7(5)
C(31)-C(30)-C(35)-C(34)	0.1(4)
C(17)-C(30)-C(35)-C(34)	172.1(3)
O(2)-C(1)-O(1)-C(4)	79.6(2)
C(2)-C(1)-O(1)-C(4)	-32.5(3)
C(5)-C(4)-O(1)-C(1)	165.9(2)
C(3)-C(4)-O(1)-C(1)	40.7(3)
O(1)-C(1)-O(2)-C(6)	-140.6(2)
C(2)-C(1)-O(2)-C(6)	-26.0(3)
O(3)-C(6)-O(2)-C(1)	29.6(3)
C(7)-C(6)-O(2)-C(1)	145.5(3)

C(8)-C(6)-O(2)-C(1)	-88.9(3)
C(10)-C(2)-O(3)-C(6)	-126.4(2)
C(3)-C(2)-O(3)-C(6)	116.3(2)
C(1)-C(2)-O(3)-C(6)	4.7(3)
O(2)-C(6)-O(3)-C(2)	-20.5(3)
C(7)-C(6)-O(3)-C(2)	-137.1(3)
C(8)-C(6)-O(3)-C(2)	98.1(3)
O(5)-C(9)-O(4)-C(3)	173.4(2)
C(10)-C(9)-O(4)-C(3)	-8.4(3)
C(4)-C(3)-O(4)-C(9)	-120.0(2)
C(2)-C(3)-O(4)-C(9)	-8.7(3)
C(4)-C(5)-O(6)-C(17)	177.2(2)
C(30)-C(17)-O(6)-C(5)	52.3(3)
C(24)-C(17)-O(6)-C(5)	-73.4(3)
C(18)-C(17)-O(6)-C(5)	167.1(2)