Towards mimics of UDP-*N*-acetyl-L-fucosamine (UDP-L-FucNAc) as potential inhibitors of *Staphylococcus aureus* capsular polysaccharide biosynthesis

by

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Thesis Abstract

The following is an account of attempted syntheses toward novel mimics of UDP-*N*-acetyl-L-fucosamine (UDP-L-FucNAc) to serve as inhibitors of or substrates for bacterial glycosyltransferases responsible for the biosynthesis of the capsular polysaccharide of *Staphylococcus aureus*.

Acknowledgements

I would like to dedicate this thesis to my grandfather, George Rehtorik. Your constant encouragement and support continues to sustain my quest for knowledge. I also must thank my mother. Without your benevolent altruism I would not be here. I owe everything I am to you and I cannot thank you enough. I owe a special thanks to Dr. Peter Norris, whose role as an advisor has shown me a path. Without the time spent in your lab I would be still be lost, wandering blindly in the dark. I also must thank Dr. Serra and Dr. Jackson, not only for there involvement on my thesis committee but for their instruction in and out of class. Dr. Zeller and Ray Hoff have been extremely helpful in the instruction and maintenance of our instrumentation. Dr. Zeller always spared time from his busy schedule for any and every question; thank you for your help. The education I received from Youngstown State University has been an invaluable experience which has prepared me for the rest of my career.

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Introduction

Staphylococcus aureus: Pathogenesis

Staphylococcus aureus (*Staph*) is a Gram-positive opportunistic bacterium responsible for a wide array of infectious diseases in both human and other animal systems. There are 32 different species of *Staphylococci*; *S. aureus*, associated with the asymptomatic colonization of skin and mucosa as well as major wound infections, is of the utmost concern.[1] If unchallenged, *S. aureus* infection may lead to several serious conditions such as osteomyelitis, endocarditis, septic arthritis, and bacteremia causing secondary infections of vital organs.[2,3] *S. aureus* also secretes multiple virulence factors, known as *exotoxins*, that are responsible for toxic shock syndrome, food poisoning, and scalded skin syndrome.[3,4] Individuals with the highest risk of infection include surgical outpatients and the immuno-compromised. However, cases of community-acquired *S. aureus* infection in otherwise healthy persons are increasing rapidly.[2] Due to the aggressive pathogenic nature of *S. aureus* the bacterium is considered a notorious nosocomial agent, responsible for over 1 million serious hospital-acquired infections each year.[4] Thirty percent of the population, including hospital staff and long-term care givers, act as vectors spreading infection due to the innocent colonization of their nasal mucosa.[5] In order to prevent pandemics, extreme care is taken to sequester patients with serious infection in dedicated wards. Choosing effective therapies is becoming increasingly difficult, and an understanding of bacterial acquired resistance, as well as mechanism of antibiotic action, is fundamental to development of novel bactericidal compounds.

Antibiotic Resistance: β-Lactams

S. aureus resistance to general antibiotics has emerged swiftly due to their extensive and inappropriate use. Several different classes of antibiotics are employed to combat *Staph* infections with some of the more prominent antibiotics including: β-lactams, tetracyclines, aminoglycosides, quinolones, and glycopeptides. Alexander Fleming's discovery of the β-lactam penicillin in 1928 was a monumental scientific finding. The drug found widespread use as an antibacterial agent by the 1940s. The cyclic amide at the core of the antibiotic mimics a bacterial enzyme's natural substrate, D-alanyl-D-alanine (Figure 1).[6]

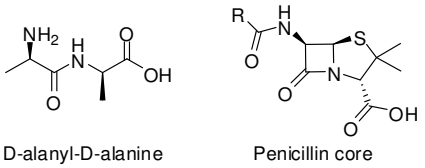


Figure 1: D-Alanyl-D-alanine structural analog

D-Alanyl-D-alanine is used by penicillin-binding proteins (PBPs) in the synthesis of the peptidoglycan cell wall. The β-lactam antibiotic non-covalently associates with the PBP and undergoes an irreversible acylation, simultaneously cleaving the cyclic amide and covalently inactivating the enzyme.[5-7] Once inactivated, the PBP is unable to synthesize peptidoglycan and is opsonized for phagocytotsis. However, by 1948 more than 50% of *S. aureus* clinical isolates were found to exhibit resistance to the β-lactam penicillin. The percentage of penicillin-resistance in *S. aureus* isolates has steadily increased since the 1940s to about 90% as of 2000. This resistance was attributed to the penicillin-mediated selection of *S.aureus* strains that possessed PBPs capable of catalyzing multiple reactions. β-Lactamase confers the ability to deacylate the inactivating amide of

the β-lactam from the catalytic serine residue responsible for cell wall synthesis.[5-7] In order to deal with the rapidly developing resistance new antibiotics had to be developed.

In the early 1960s many new antibiotics were realized, most with the β-lactam moiety at their core. Penicillin G was the progenitor of a series of bulky derivatives that were effective bactericidal agents against strains exhibiting β-lactamase activity (Figure 2).

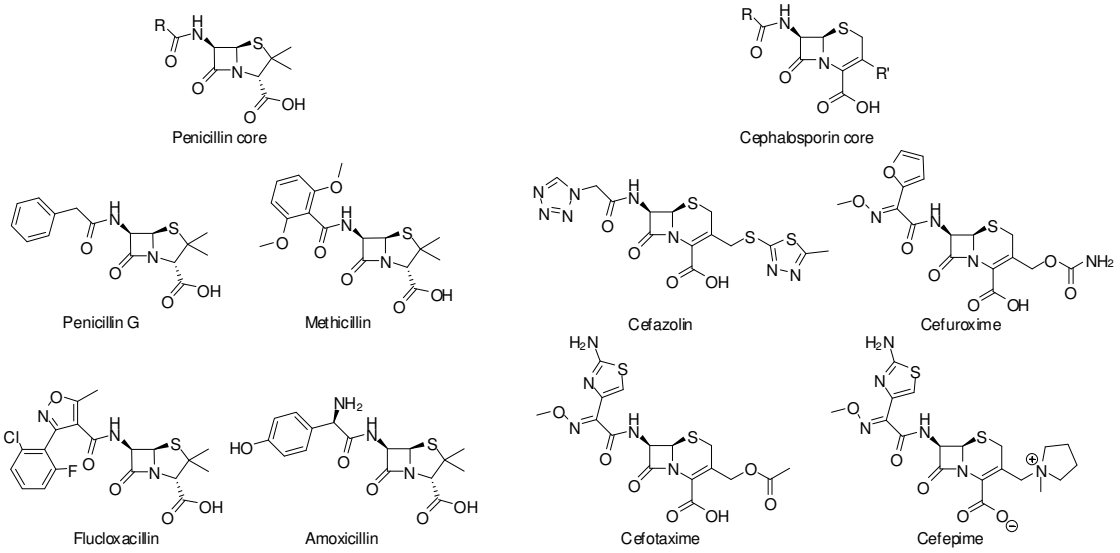


Figure 2: Penicillin G and penicillinase-stable derivatives

The cephalosporins were suggested as a penicillin surrogate and it was found that replacement of the 6' acyl group of penicillin G with a bulkier moiety significantly hindered β-lactamase attack. Similarly to penicillin G, both the cephalosporins and bulky penicillin derivatives like methicillin derive their bactericidal effect from disrupting cell wall formation through the inactivation of PBPs. Unfortunately, shortly after their conception, resistance was observed in 1961. As with β-lactamase-borne penicillin resistance, the PBP family of proteins was determined to be the source of methicillin

resistance. Normal *S. aureus* produces three PBPs; methicillin resistant *S. aureus* (MRSA) produces a fourth, PBP 2a. PBP 2a is encoded by the m*ecA* gene and is capable of cell wall production in the presence of methicillin-like antibiotics. It has been suggested that *S. aureus* strains obtained the *mecA* DNA from transduction via bacteriophages. Regardless of origin, PBP 2a has a reduced binding affinity for all β-lactam based antibiotics. This is a result of changes in structure in and around the active site. The groove where the initial non-covalent interaction between antibiotic and catalytic serine residue takes place is narrowed, resulting in an energetically disfavored enzyme-deactivating acylation.[5-7] The future of penicillin-based antibiotics lies with medicinal chemists who are currently working on a new generation of antibiotics that maximizes active site interactions while preserving the β-lactam ring.

Antibiotic Resistance: Tetracyclines

Tetracyclines, discovered in the late 1940s, were natural products isolated from several species of *Streptomyces*. Tetracycline antibiotics are used to control a wide array of microbes, including the protozoan parasites *Plasmodium falciparum* and *Leishmania major*, as well as both Gram-positive and -negative bacteria. The original compounds were found to inhibit bacterial protein synthesis, but their inherent insolubility limited their therapeutic use. Due to the relative ease of their synthesis and absence of deleterious side effects, multiple derivatives have been synthesized. The anti-bacterial nature of tetracycline molecules does not tolerate much structural deviation. The fused ringed core along with the extended phenolic keto-enol system, 4-dimethylamino group, and

stereochemical configuration of carbons 4a and 12a are paramount for bactericidal activity of this class of compounds (Figure 3).[7,8]

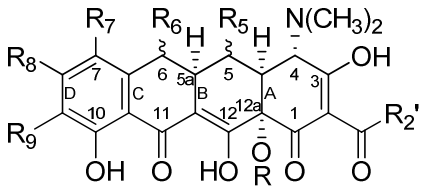


Figure 3: conserved motif of tetracycline antibiotics

Tetracyclines halt bacterial translation by blocking the association of amino-acyl tRNA with the ribosome acceptor site.[9] In order to find the ribosome, the neutral lipophilic tetracycline must first traverse the cell membrane aided by the pH-dependent proton motve force. In the cytoplasm the tetracycline phenolic keto-enol system coordinates with divalent metal ions such as magnesium. This activated complex is then able to bind to the bacterial 30S ribosomal subunit causing drastic changes in tertiary structure, in turn suspending translation.[7-9]

Global overuse of many tetracyclines has contributed to extensive resistance in both Gram-positive and Gram-negative bacteria. The first (1948-1963) and second (1965-1972) generation of tetracyclines (Figure 4) were used liberally in both the hospital and the veterinary settings, as well as agriculturally as growth enhancers added to livestock feed. As a result, resistant strains were isolated in the mid-1950s and were commonplace by the 1970s.[5] Tetracycline resistance is accredited to the chromosomal integration of transmissible plasmids containing the *tet* family of genes. In Gram-positive *staphylococci*, *tet* genes code for two disparate modes of resistance. The *tetK* and *tetL* genes are found to encode an efflux protein responsible for the export of tetracycline from the cytoplasm

while *tetM* codes for a protein that hinders the antibiotic's ability to bind bacterial ribosomes.[8,9] In an attempt to overcome the efflux and ribosomal protection conferred by the *tet* genes, a third generation of tetracyclines were developed in the early 1990s. These compounds, referred to as *glycylcyclines*, are derivatives of minocycline which had previously been the most efficacious agent of its class. All of the glycylcyclines possess a substituted glycylamido group at the C-9 position (Figure 4).[9]

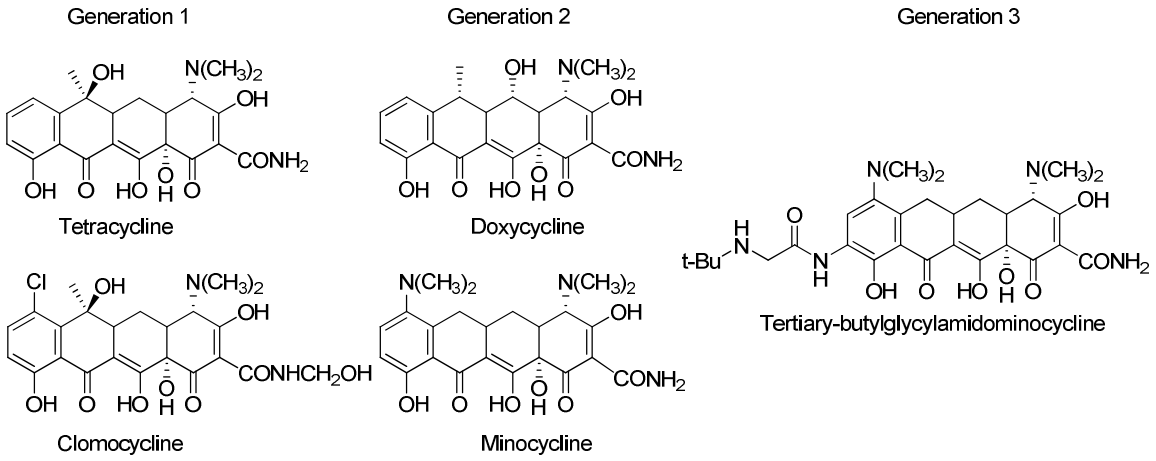


Figure 4: Representative tetracyclines

The glycylcycline modifications have sensitized once resistant *tet*-containing bacteria. An increased ribosomal binding affinity is responsible for disrupting the ribosomal protection conferred by TetM proteins while the distal alkylamine moiety of the glycylamido group is poorly recognized by the efflux proteins TetK and TetL, maintaining intracellular concentration of antibiotics. The practice of infusing livestock feed with tetracyclines has been banned by the European Union (EU) but is still prevalent in many other countries.[7-9] This lavish application could result in zoonotic bacteria rapidly acquiring resistance to glycylcyclines and must be curtailed.

Antibiotic Resistance: Aminoglycosides

Streptomycin, isolated in 1943, was the first of a class of antibiotics known as aminoglycosides. As the name implies, members belonging to this class share amino hexose moieties within their superstructure (Figure 5).

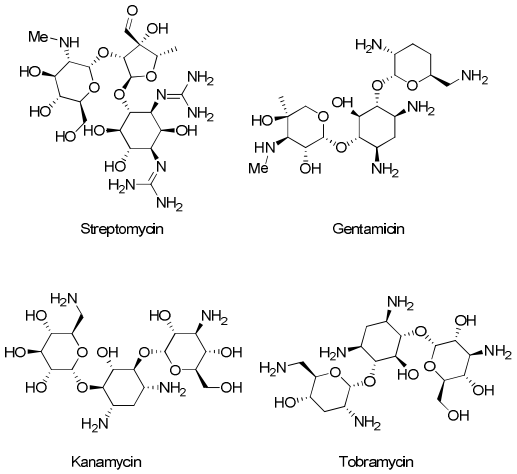


Figure 5: Aminoglycoside antibiotics

Much like tetracyclins, aminoglycosides are bactericidal inhibitors of translation. The initial association of the small molecule with the 30S ribosomal subunit interferes with protein synthesis in multiple ways. Translation is impeded by the antibiotic's ability to block the formation of the ribosomal initiation complex, cause problems in the decoding of mRNA transcript, and inhibit ribosomal translocation. Aminoglycosides alone are not a particularly effective treatment against Gram-positive cocci such as *S. aureus*. Most often in a clinical setting a cell wall inhibiting antibiotic, such as a β-lactam or glycopeptide, is combined with an aminoglycoside to maximize the therapeutic impact. The increased intracellular transport of aminoglycoside, due to cell wall inhibition, is suggested to be the source of the synergy.[7,9,10]

Staphylococcal resistance to aminoglycosides was first observed in the early 1960s and increased steadily. Multi-drug resistance (MDR) became of major concern in the latter part of the 1970s as strains of MRSA were isolated that had intermediate resistance to gentamycin, a potent aminoglycoside. Strains of bacteria were found expressing genes that encoded enzymes capable of inactivating the aminoglycosides, simply referred to as *aminoglycoside modifying enzymes* (AMEs). The amino and hydroxy functionality of aminoglycosides are susceptible to modification by three different AMEs: aminoglycoside-3'-*O*-phosphoryltransferase-III [*aph*(3')-*III*], aminoglycoside-4'-*O*-phosphoryltransferase-I [*ant*(4')-*I*], and the bifunctional enzyme aminoglycoside-6'-*N*-acetyltransferase/2"-*O*-phosphoryltransferase [*aac*(6')-*aph*(2")].[5,9-11] All of the AMEs share the ability to decrease the aminoglycoside's ability to associate with the 30S ribosomal subunit. The enzymes encoded by [*aph*(3')-*III*] and [*ant*(4')-*I*] confer low level resistance and are less frequently found in clinical isolates. The [*aac*(6')-*aph*(2")] encoded enzyme capable of acetyltransferase and phosphotransferase activity is the most clinically prevalent source of Gram-positive aminoglycoside inactivation (tobramycin, kentamycin, gentamycin).[10,11]

Antibiotic Resistance: Quinolones

The quinolone class of compounds includes several small biologically active molecules that block bacterial replication (Figure 6). In order to exhibit their bactericidal effect, the antibiotics bind enzymes associated with the processing of DNA. Specifically, the topoisomerase IV and DNA-gyrase are both topoisomerases; together, they are responsible for the majority of bacterial DNA processing. The primary function of DNA-

gyrase is to maintain the level of DNA supercoiling, therby, facilitating the progression through replication. Topoisomerase IV is involved in a process called *decatenation* which is the separation of daughter chromosomes after a round of replication. Quinolone antibiotics bind near a conserved topoisomerase tyrosine residue which is transiently bound to the phosphate backbone of DNA during catalysis. The antibiotic must bind the enzyme in complex with DNA where it causes large scale conformational changes, ostensibly trapping the catalytic intermediate. The quinolone-enzyme-DNA complex contains DNA with double stranded breaks (DSBs). Once released from the complex it is the cleaved DSB-DNA, not the quinolone-directed inhibition of replication, which is responsible for bacterial death. Low levels of quinolone are found to be bacteriostatic, reversibly pausing replication without formation of DSBs, while higher levels promote cell death.[12]

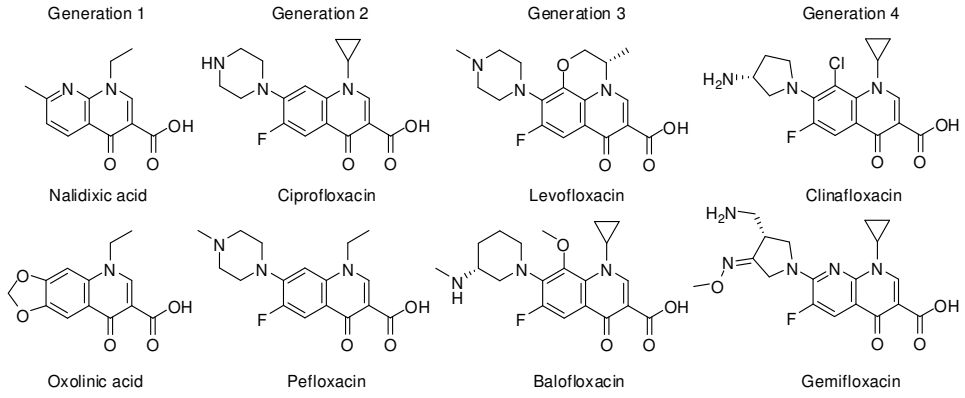


Figure 6: Quinolone antibiotic evolution

Resistance to quinolone antibiotics is efflux-mediated, as well as the result of a series of mutational events in and around the antibiotic binding site. In *S. aureus*, topoisomerase IV is the primary target of quinolone antibiotics while concomitantly the

origin of their resistance. Mutations within the quinolone resistance-determining region (QRDR) increase the antibiotic's rate of disassociation, thereby allowing replication to proceed unabated. Mutations in the *grl*A gene of topoisomerase IV lead to Ser80-Phe/Tyr and Glu84-Lys amino acid replacements, conferring low-level resistance. However, mutations in both the GrlA subunit of topoisomerase IV and a Ser84-Leu mutation in the GyrA subunit of DNA-gyrase lead to much higher antibiotic minimum inhibitory concentrations (100 to >800 mg/L). Efflux-mediated resistance is a result of inducible over-expression of the multi-drug transporter encoding *norA* gene. In an attempt of overcome the resistance due to antibiotic efflux newer quinolones, such as clinaflozacin, are modified at C-7 and C-8 as well as being fluorinated in order to hinder their recognition by efflux pumps. The newer generations of quinolones are also more potent, having been synthetically tailored to exploit both topoisomerase IV and DNA-gyrase targets.[12]

Antibiotic Resistance: Glycopeptides

Glycopeptide antibiotics, for example vancomycin, are the preferred therapy for multi-drug resistant infections such as methicillin-resistant *Staphylococcus aureus*. Vancomycin was first isolated in the mid-1950s by the Eli Lilly pharmaceutical company from the bacterium *Amycolatopsis orientalis*. Early on the compound found limited use due to toxicity stemming from its difficult purification. However, due to improvements vancomycin, along with teicoplanin and gentamycin, find use as drugs of last resort. Antibiotics in the vancomycin glycopeptide family are large macromolecules composed of

a common heptapeptide backbone with a diverse array of sugar moieties appended through chlorinated aromatic side chains (Figure 7).[13,14]

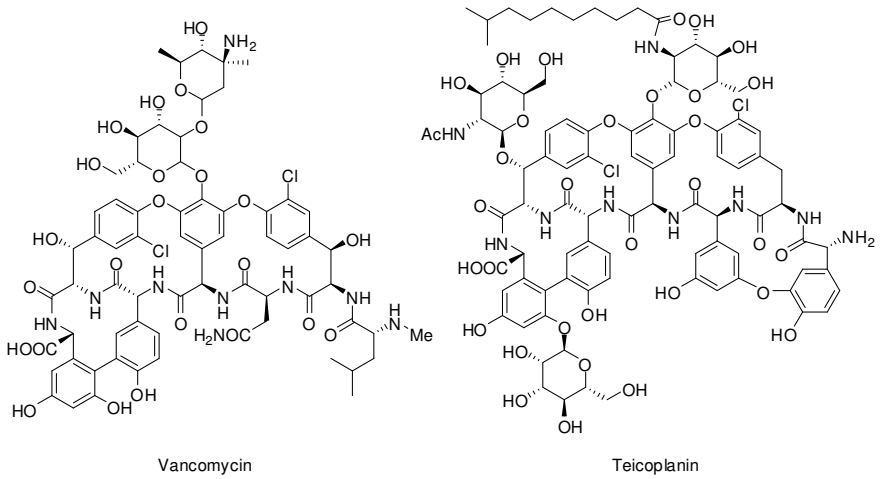


Figure 7: Vancomycin and related glycopeptide antibiotics

Much like β-lactam antibiotics, vancomycin interferes with the biosynthesis of the peptidoglycan cell wall. Glycopeptide antibiotics like vancomycin recognize bacterial cell wall precursors known as *mucopeptides* and associate with their terminal (*N*-acetyl-L-lysyl)-D-alanyl-D-alanine residue through a series of five hydrogen bonds (Figure 8). The highly conserved stereochemistry of the glycopeptide amino acid backbone, α-Cs 1-7 (*R,R,S,R,R,S,S)*, creates a binding pocket which is imperative for bactericidal activity. The antibiotic shields nascent peptidoglycan strands from strengthening trans-peptidase-catalyzed cross-linking, as well as protective transglycosylation. Without these modifications the bacterium has an increased susceptibility to both autolysis and phagocytosis.[13-14]

Since 1959, vancomycin has been used in the clinic without significant bacterial resistance, until recently. The late 1980s bore witness to multiple strains of VRE (vancomycin resistant enterococci). Genetic analysis of VRE strains revealed five genes

that were responsible for the resistant phenotype. These *van* genes encode enzymes that alter the composition of the terminal (*N*-acetyl-L-lysyl)-D-alanyl-D-alanine mucopeptide residue. The terminal alanine amino acid is replaced by a lactate residue converting the mucopeptide precusor to (*N*-acetyl-L-lysyl)-D-alanyl-D-lactate. The *van* genes lie dormant until the bacterium detects the presence of vancomycin which triggers their expression. The replacement of the terminal alanine residue's NH with an O abolishes a hydrogen bond and introduces a repulsive interaction (Figure 8).

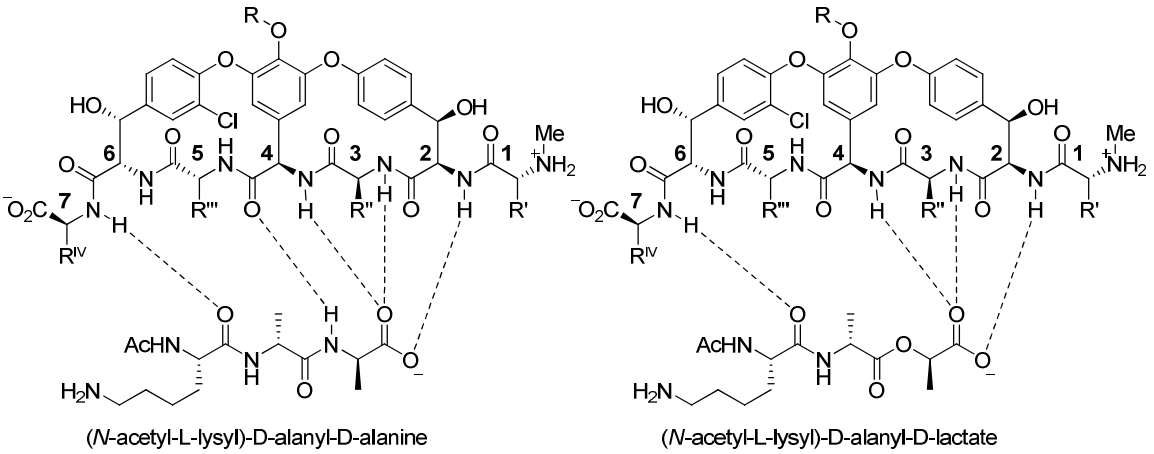


Figure 8: Glycopeptide mucopeptide binding

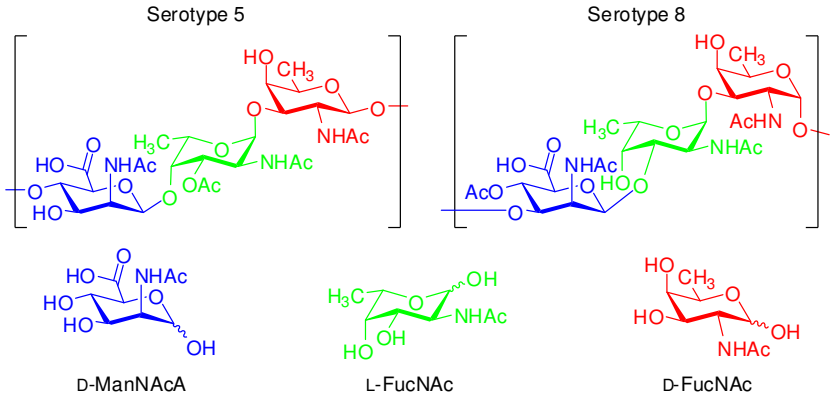
This lowers the binding affinity of the antibiotic by about 1000 fold. Enterococci are not known as serious pathogens; however, while this type of resistance has yet to be observed in *Staphylococci*, the horizontal transfer of genetic material through bacterial conjugation is well documented.[11,13,14] The mechanism of glycopeptide resistance in *Staphylococcus aureus* is not entirely clear. As of 1997, strains of *Staphylococcus aureus* that had intermediate resistance to vancomycin were isolated within the United States. Studies have suggested these vancomycin-intermediate *Staphylococcus aureus* (VISA) strains overproduce peptidoglycan cell wall with decreased amounts of cross-linking as well as

free D-alanyl-D-alanine.[15-20] These are, in essence, false targets binding the glycopeptide drugs and keeping them from their lethal targets. With the numerous ways that bacteria acquire resistance; modification of target site, enzymatic inactivation, and ability to alter intracellular concentrations of antibiotics, vancomycin-resistant *Staphylococcus aureus* threatens to outpace efforts to destroy it.

Staphylococcus aureus: Capsular Polysaccharide

Staphylococcus aureus derives its resilience and pathogenic nature from its extracellular capsule. Serotyping studies, conducted in 1982 by Karakawa and Vann, documented that the majority of *S. aureus* strains are encapsulated. Later, according to Vann's method, Sampolinsky *et al.* were able to identify 11 distinct serotypes. Highly encapsulated serotypes were found to conceal bacterial cell wall immunoglobulin from their cognate receptors on human polymorphonuclear leukocytes, thus enabling the bacterium to evade phagocytosis.[2] Non-mucoid strains that form a capsule, such as serotypes 5 and 8, are referred to as *micro-encapsulated* in order to differentiate them from other non-mucoid strains that lack a capsule. Serotypes 5 and 8 predominate as infectious agents, manifesting themselves in nearly 25 and 50 percent of all human clinical isolates respectively, representative strains include Reynolds and Becker.[2,21,22] The capsule has been shown to greatly enhance the virulence of the bacterium by facilitating resistance to serum-mediated killing, evasion of phagocytic uptake, as well as mediating adherence to eukaryotic cells. *S. aureus* mutants devoid of a capsule are found to be approximately one thousand times less virulent.[21] Both capsules of serotype 5 and 8 are composed of a polymer of repeating trisaccharides that consist of *N*-acetyl-D-fucosamine

(D-FucNAc), *N*-acetyl-L-fucosamine (L-FucNAc), and *N*-acetyl-D-mannosamine uronic acid (D-ManAcA). The varying arrangement of glycosidic bonds and position of *O*-acetylation are the discerning factors between serotypes 5 and 8 (Figure 9).[2,21,22]



Type 5 →4)-β-D-ManNAcA-(1→4)-α-L-FucNAc(3OAc)-(1→3)-β-D-FucNAc-(1→

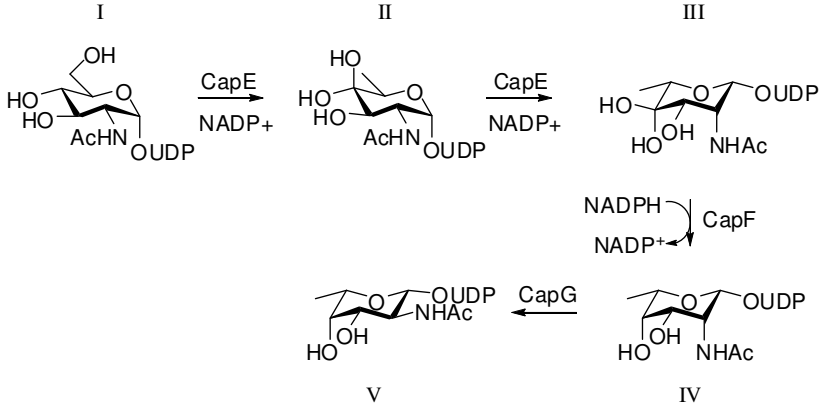
Type 8 →3)-β-D-ManNAcA(4OAc)-(1→3)-α-L-FucNAc-(1→3)-α-D-FucNAc-(1→

Figure 9: Capsular polysaccharides of serotypes 5 and 8

Staphylococcus aureus: Serotype 5 Biosynthesis of UDP-L-FucNAc

UDP-L-fucosamine is an integral building block in the synthesis of the polysaccharide capsule of both serotypes 5 and 8. This residue is also found in other harmful bacteria, such as the O-antigen of *Pseudomonas aeruginosa*, and therefore an understanding of its biosynthesis is a prerequisite for the development of novel bactericidal agents. In *Staphylococci*, the *cap* family of genes is responsible for the synthesis of the three capsular monosaccharides from a common precursor, UDP-*N*-acetylglucosamine (UDP-GlcNAc). As of 2004, the functionality of six of the sixteen *cap*5 genes has been elucidated within the laboratory of J. C Lee.[2,21] Nucleotide sequencing of *cap*5 and *cap*8 gene clusters have determined that twelve of the sixteen *cap*

genes are nearly identical; *cap*H through K are found to be type-specific. Therefore, it is not hard to imagine that between serotypes 5 and 8 most of the enzymes involved in capsular biosynthesis share a common functionality. The fact that L-FucNAc is seldom found elsewhere in nature, other than incorporated into bacterial polysaccharides, makes the residue of particular scientific interest as a template for the development of therapeutic agents. The enzymes that are responsible for the synthesis of UDP-L-FucNAc are Cap5E, Cap5F, and Cap5G. The commonly accepted biosynthetic pathway is presented in Scheme 1.



Scheme 1: Serotype 5 biosynthesis of UDP-L-FucNAc

The bifunctional enzyme Cap5E possesses 4,6-dehydratase and 3,5-epimerase activity. UDP-GlcNAc (**I**) is first converted to UDP-2-acetamido-2,6-dideoxy-α-D-*xylo*-4-hexulose (**II**) by Cap5E then epimerized at C-3 and C-5 to provide UDP-2-acetamido-2,6-dideoxy-β-L-*lyxo*-4-hexulose (**III**). The reductase, Cap5F, is responsible for a NADPH-driven C-4 reduction of the *lyxo*-keto-intermediate to form UDP-2-acetamido-2,6-dideoxy-β-L-talose (**IV**) (UDP-2,6-dideoxy-TalNAc). UDP-2,6-dideoxy-TalNAc is then epimerized at C-2 by Cap5G yielding UDP-L-FucNAc (**V**). Finally, the glycosyl transferase Cap5L incorporates UDP-L-FucNAc into the polysaccharide capsule through a

condensation reaction with the C-3 hydroxyl of the preceding D-FucNAc residue. Elimination of the bacterium's protective capsule may sensitize a once resistant strain to traditional antibiotics or possibly permit the immune system to clear the exposed bacterium. A thorough understanding of *Staphylococcal* capsular biosynthesis is imperative in order for the development of subsequent antibiotics conceived for its disruption.[2,21-23]

Carbohydrates and their Classification

Carbohydrates are among the most prevalent biological molecules found on earth. They are involved in vital processes such as glycolysis, where they are metabolized to produce ATP and acetyl coenzyme A, as well as photosynthesis. Carbohydrates also provide structural rigidity in plants and chitinous animals as polymers of β-D-glucose and *N*-acetyl-D-glucosamine, respectively. These macromolecules may also be found positioned on the surface of organisms for identification purposes such as recognition of self from non-self in an immune response. Many pharmaceuticals, including the aforementioned aminoglycoside and glycopeptide antibiotics, owe their therapeutic activity to carbohydrate moieties. The elements found most commonly incorporated into these ubiquitous compounds are carbon, hydrogen, oxygen, and nitrogen.

Carbohydrates are grouped into two types which are known as polyhydroxy ketones (ketoses) and polyhydroxy aldehydes (aldoses) of the form H-$[CHOH]_n$-CO-$[CHOH]_m$-H and H-$[CHOH]_n$-CHO, respectively.[24] Monosaccharides are the simplest form of carbohydrates; linked together they form oligosaccharides (2-10 monomers) and polysaccharides (>10 monomers). However, the distinction between an oligosaccharide

and polysaccharide is somewhat vague. The term oligosaccharide is generally used when referring to a molecule of known structure rather than a polymer of indeterminate length known as a polysaccharide or glycan. Polysaccharides composed of the same repeating monosaccharide are known as *homopolysaccharides* (homoglycans) while those with two or more unique repeating units are named *heteropolysaccharides* (heteroglycans). Despite the variations in terminology, polymers of monosaccharides are formed by condensation reactions producing a glycosidic linkage. For example, in β-D-lactose (milk sugar) loss of water between β-D-galactose and D-glucose forms a β-glycosidic bond (Figure 10).

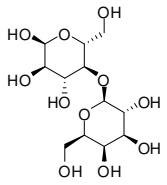


Figure 10: β-D-Lactose

Monosaccharides can take four distinct configurational forms: α-D, β-D, α-L, and β-L. The D or L configuration is assigned upon examination of the highest numbered chiral carbon in a Fisher projection (Figure 11). If the hydroxyl projects to the right the molecule is assigned the D-configuration, if to the left then the L-configuration.

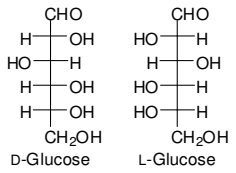


Figure 11: Fisher projection D / L convention

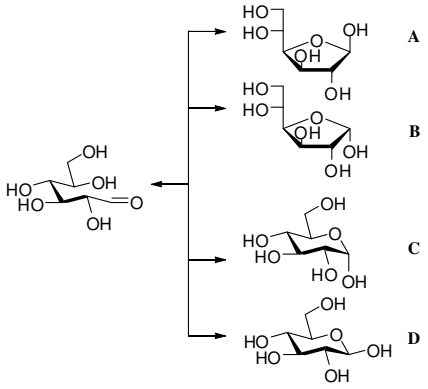


Figure 12: Configurations of D-glucose

In the solid state monosaccharides adopt the more favorable cyclic structure but in solution the hemiacetal ring is able to transiently open and close generating four distinct isomers. For example, in D-glucose there is an equilibrium between β-D-glucofuranose (**A**), α-D-glucofuranose (**B**), α-D-glucopyranose (**C**), and β-D-glucopyranose (**D**) forms (Figure 12). This occurs upon attack at the carbonyl carbon by the hydroxyl on C-5 which results in the pyranose forms whereas attack by the C-4 hydroxyl yields the furanose form.[24]

Azidodeoxy Sugar Chemistry

Azides are common precursors of many nitrogenous carbohydrates containing amines, ureas, carbodiimides and amides. The azide functionality is immensely important to carbohydrate chemistry due to its versatile nature as both electrophile and nucleophile (Figure 13).

Figure 13: Azide resonance

N-Glycosylation is an important post-translational modification of proteins while deoxy-aminosugars are a common component of glycosidic antibiotics. The hydrophilicity the glycoside moiety imparts alters the pharmacokinetics of circulation, elimination, and concentration of its accompanying aglycone. Due to the prominence in biologically active molecules, it is necessary to have facile synthetic routes towards *N*-glycosides. There are many well documented reactions of azides to afford amides. The most straight forward means involves the metal-catalyzed reduction of the glycosyl azide to the corresponding amine followed by subsequent acylation to yield the glycosyl amide. Despite the apparent ease of this route it has several complicating factors including poor anomeric control and potential hydrolysis of the anomeric amine.[25,26] Better anomeric control may be achieved through use of the Staudinger reaction.

The Staudinger reaction is a well known technique for synthesizing a variety of glycosyl amides, including complex glycopeptides, from a reaction between an azide, phosphine, and anhydride or acid chloride acylating agent. The reaction proceeds through a phospho-aza ylide which is susceptible to anomerization, the degree of which is dependent on the reactivity of the acylating agent. There have been several documented cases of a marked solvent effect on yield as well as anomeric ratio of the glycosyl amide product.[26-28] This effect is amplified in glycosyl azides that are electron-deficient.[29] The use of alkyl or aryl phosphines as reducing agents leads to the generation of problematic phosphine oxides. Due to the amphoteric character of the phosphine oxide its chromatographic separation from product proves difficult. This synthetic complication may be avoided by the use of bis(diphenylphosphino)ethane (DPPE).[30,31] The increased polarity of the DPPE oxide allows for clean separation of unwanted reagent from amide

product. Various modifications of the original three component Staudinger reaction have been devised in order to optimize rate of reaction and anomeric control. One such modification is the traceless ligation process.[32-34] The central deviation from the original Staudinger is the use of functionalized phosphines intended to prevent anomerization by increasing the rate of acylation (Figure 14).

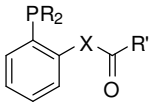


Figure 14: Representative functionalized phosphine; X = O or S

The non-carbonyl oxygen or sulfur acts as a cleavable linkage between the phosphine and the acyl group. The acylation step is facilitated by the coordination of reacting species, bringing them in close proximity. The participating functional groups are mutually reactive and tolerant of numerous coexisting functional groups, which eliminates the need for distal protecting groups. Through use of the Staudinger reaction and its modifications one may synthesize a large library of glycosyl amides from a myriad of sugar-derived azides with a good degree of anomeric control and accompanying high yields.[32-34]

Statement of Problem:

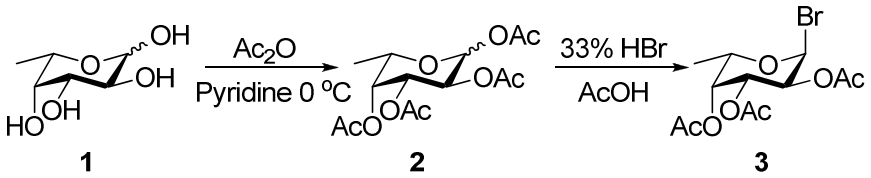
The lavish and improper use of antibiotics throughout time has systematically selected for strains of bacteria that have a decreased sensitivity to agents including, β-lactams, aminoglycosides, tetracyclines, and quinolone antibiotics. Recently, methicillin-resistant *Staphylococcus aureus*, an extremely dangerous human pathogen, has attained the level of a so called "super-bug" by acquisition of resistance to drugs of last resort (vancomycin, teicoplanin, gentamicin).

The following research describes an attempt towards the synthesis of bacterial polysaccharide capsule precursor, uridine-diphospho-*N*-acetyl-L-fucosamine (UDP-L-FucNAc), mimics. Deriving analogs by alteration of the L-FucNAc *N*-acetyl moiety will enable our group to develop novel compounds that may act as competitive inhibitors of or substrates for bacterial glycosyl transferases responsible for L-FucNAc incorporation and capsule elongation. The terminal methyl group of the *N*-acetyl moiety will be replaced with a tri-fluoro or tri-deutero group as a means of detecting capsular incorporation, quantified by NMR for further study. If successful in impeding capsular biosynthesis, our compounds may be employed in the fight against multi-drug resistant strains of *Staphylococcus aureus*.

Results and Discussion:

1. Synthesis of protected 2-azidodeoxy sugar azides

This thesis documents an attempt toward the synthesis of UDP-*N*-acetyl-L-fucosamine as well as a facile high yielding reaction for the synthesis of sugar-derived ureas.



Scheme 2: Synthesis of 1-bromo-2,3,4-tri-*O*-acetyl-α-L-fucose (**3**) from L-fucose (**1**).

The formation of α-fucosyl bromide **3** was a high yielding two-step synthesis from the commercially available L-fucose (Scheme 2). Firstly, L-fucose was dissolved in pyridine and chilled to 0 °C while acetic anhydride was slowly added. The resultant reaction provided 1,2,3,4-tetra-*O*-acetyl-L-fucose (**2**) as an anomeric mix with an R*f* of 0.39 in a solution of 1:1 hexanes-ethyl acetate. Analysis of the proton NMR spectrum revealed two series of four singlets between 1.99 to 2.19 ppm corresponding to the distal methyl moieties on the acetyl protecting groups. The 3:1 anomeric ratio, favoring the α-anomer, was determined by integration of the deshielded H-1 protons. Proton assignment was achieved through calculation of coupling constants as well as 2-dimensional COSY experiments, provided in appendix A. Eight peaks ranging from 169 to 171 ppm in the ^{13}C NMR spectrum lent credence to the formation of the tetraacetate products and were attributed to the four carbonyl carbons of each anomer. The rest of the carbon signals were assigned by heteronuclear single quantum coherence (HSQC) NMR experiments.

Electro-spray ionization of the transparent syrup for mass spectral analysis yielded a parent ion of 355.1, which is indicative of the mass of the tetraacetate plus an atom of sodium. Final confirmation of tetraacetate formation was achieved by structural refinement of a crystal formed by vapor diffusion of hexanes into a solution of product and ethyl acetate (Figure 15).

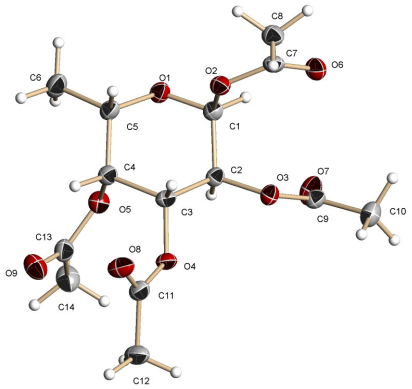
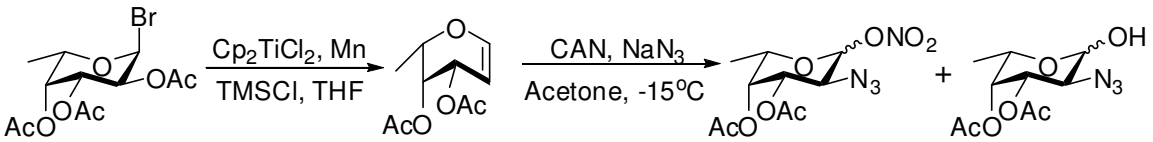


Figure 15: Structural refinement of 1,2,3,4-tetra-*O*-acetyl-α-L-fucose (**2**)

Formation of α-1-bromo-2,3,4-tri-*O*-acetyl-L-fucose (**3**) proceeds through an S_N1 mechanism initiated by the addition of 33% hydrobromic acid in glacial acetic acid to the tetraacetate (**2**). The reaction was closely monitored over four hours by TLC (1:1 hexanes-ethyl acetate) until the starting material was consumed and a new spot with an R*f* of approximately 0.52 was visualized. Analysis of the ^{1}H-NMR spectrum revealed one anomer with the three singlets between 2.01 and 2.18 ppm corresponding to the loss of an acetyl protecting group and a deshielded doublet with a small coupling constant, 3.97 ppm, indicative of the α-bromide. The ^{13}C NMR spectrum confirmed the loss of an acetyl protecting group as there were only three signals between 169.74 to 170.23 ppm.

Figure 16: The stereo-electronic anomeric effect

All other peaks in the ^{1}H and ^{13}C spectra were assigned by a calculation of coupling constants and analysis of 2-dimensional COSY and HSQC spectra, respectively. The inherent instability of compound **3** inhibited its characterization by mass spectrometry. The alpha bromide is thermodynamically favored due to a stereo-electronic effect known as the *anomeric effect* (Figure 16). The antiperiplaner orientation of the oxygen's axial lone-pair with the bromide allows for donation of electron density to the antibonding (σ*) orbital, making the α bond-forming transition state more thermodynamically stable and thus the only isomer observed. It is imperative to keep the bromination reaction as dry as possible. The slightest amount of moisture in the reaction vessel causes varying degrees of α-fucosyl bromide hydrolysis resulting in an anomeric mix of 2,3,4-tri-*O*-acetyl-L-fucose (R*f* = 0.18 in 1:1 hexanes-ethyl acetate).



3 **4** **6** **7**

Scheme 3:
Synthesis of 3,4-di-*O*-acetyl-2-azidodeoxy-1-nitro-α,β-L-fucose (**6**) and 3,4-di-*O*-acetyl-2-azidodeoxy-α,β-L-fucose (**7**)

Glycals are important precursors in the synthesis of functionalized polysaccharides as well as *O*- and *C*-glycosides. Thus, dry fucosyl bromide (**3**) dissolved in anhydrous THF was added dropwise to a solution as titanocene(III) chloride (Cp_2TiCl), powdered manganese, and TMSCl in anhydrous THF. The reaction was monitored by TLC (3:1 hexanes-ethyl acetate) and left to stir overnight. Upon completion, the reaction mixture was a shade of blue-green which upon contact with oxygen turned a bright yellow-orange. The fucal product was observed to have a lower R*f* (0.36) than the bromide starting material. Analysis of the proton NMR spectrum showed the loss of a 3H singlet, leaving two acetyl peaks between 2.02 and 2.16 ppm. The hydrogen of C-3 (4.64 ppm) showed an interesting multiplicity; the signal was manifested as ddd instead of the expected dd. This was attributed to H-3's coupling to H-2, H-4, and the additional allylic coupling to H-1. The solid state structure of **4** was determined through refinement of a crystal obtained from refrigeration of the product oil (Figure 17).

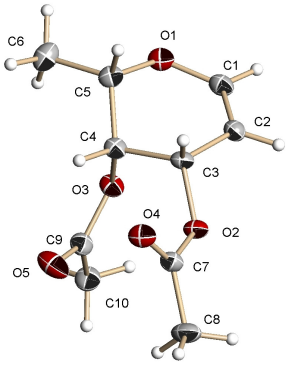
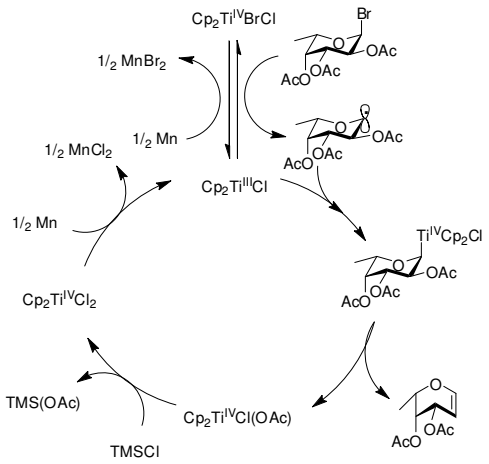


Figure 17: Structural refinement of 3,4-di-*O*-acetyl-L-fucal (**4**)

The proposed mechanism of the titanium(IV)-catalyzed reduction of glycosyl bromides to 1,2-unsaturated sugars provides insight on how the reaction may be optimized

for maximum yield (Scheme 4). The Mn metal initiates the reaction by reducing Cp_2TiCl_2 into Cp_2TiCl which transfers an electron to the glycosyl halide. This anomeric radical is then trapped by an additional molecule of Cp_2TiCl generating a glycosyl titanium complex. It is important to note that at this point there are two fates of the complex, reductive loss of the C-2 protecting group to afford the glycal (**4**) or abstraction of a hydrogen radical from solvent or other proton donor. If the concentration of Cp_2TiCl in solution is low there is a higher probability of proton abstraction yielding the anhydroalditol byproduct (**5**). In order to maximize the yield the fucosyl bromide concentration must be kept low in comparison to the free Cp_2TiCl reducing agent. The use of less or poor hydrogen-donating solvents, like benzene, have been suggested to increase the glycal production.[35-37]



Scheme 4: Mechanism of titanocene(III) chloride catalyzed glycal synthesis [37]

Once purified, fucal **4** was dissolved in dry acetone, cooled to -15 °C, and transferred *via* cannula to a reaction vessel containing CAN [$Ce(NH_4)_2(NO_3)_6$] and NaN_3. The reaction was cooled to -15 °C and allowed to stir overnight while being monitored by TLC (2:1 hexanes-ethyl acetate). Upon completion, TLC showed two sets of compounds,

the azidonitrates (**6**), R*f* = 0.45, and the di-protected fucosyl azides (**7**) with an R*f* of 0.18. A preliminary flash column using 2:1 hexanes-ethyl acetate was sufficient to separate compounds **6** and **7** from one another. However, purification of the anomers by chromatography proved difficult. ^{1}H NMR of the crude azidonitrate mixture showed trace amounts of another compound which had a similar R*f* and could not be resolved by flash chromatography. The proton NMR spectrum of the azidonitrate anomeric mixture (1:3, α:β) revealed four singlets between 2.06 and 2.19 ppm which are indicative of the two acetyl groups on either anomer. The characterization of the azidonitrate product by mass spectrometry proved elusive and was determined to be a result of premature loss of the nitro group upon electrospray ionization.

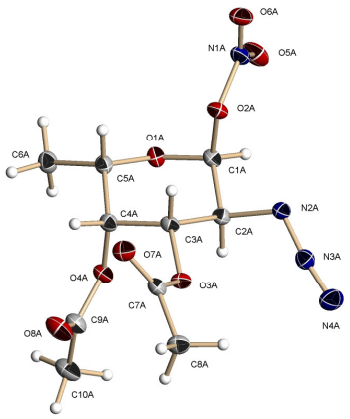
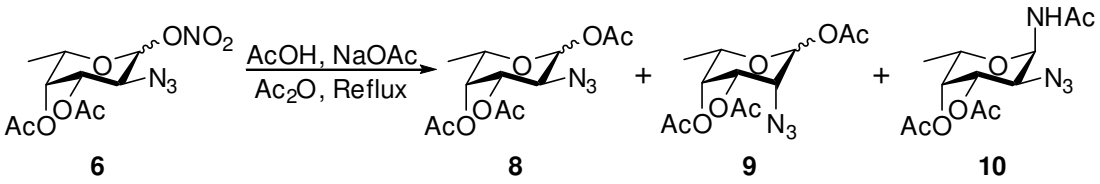


Figure 18: Structural refinement of 3,4-di-*O*-acetyl-2-azidodeoxy-1-nitro-α-L-fucose (**6**)

The equatorial oreintation of the C-2 azido group was confirmed by X-ray crystallography where there was a gauche alignment between H-1 and H-2 (Figure 18). The azidonitration is suggested to be initiated by the a regioselective anti-Markovnikov addition of azide radicals. The quasiaxial orientation of the fucal's C-4 acetyl protecting group hinders

radical attack from beneath, impeding the formation of the epimeric talose azidonitrate form.[38-40]

The formation of the di-protected fucose-derived azide is suggested to occur through H_2O solvolysis of the anomeric nitro group. The proton NMR spectrum of carbohydrate **7** revealed an anomeric mixture with a total of four acetyl protecting group peaks between 2.06 and 2.19 ppm along with two broad singlets, 4.31 and 4.99 ppm, corresponding to the exchangeable hydrogen of the hydroxyl moieties. This was later confirmed by doping the NMR sample with D_2O. Both carbohydrate **6** and **7** were characterized by 2-D COSY and HSQC NMR experiments.



Equation 1: Synthesis of 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α,β-L-fucose (**8**), 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α,β-L-fucose (**9**), and 3,4-di-*O*-acetyl-1-*N*-acetyl-2-azidodeoxy-α-L-fucose (**10**)

In order to replace the anomeric nitro group with an acetate the crude anomeric mix of carbohydrate **6** was refluxed in glacial acetic acid combined with sodium acetate and acetic anhydride. The reaction was permitted to reflux for 5 hours, monitored by TLC (3:1 petroleum ether-ethyl acetate). Utilizing the same solvent system, flash column chromatography afforded two compounds of interest; the fucose (**8**, R*f* 0.35) and talose (**9**, R*f* 0.16) azidoacetates. An anomeric mix of 1,3,4-tri-*O*-acetyl-2-azidodeoxy-L-fucose (**8**) was also obtained by conventional acetylation of compound **7** using pyridine and acetic anhydride. ^{1}H-NMR experiments aided in the determination of the conformation of the C-

2 azide. The beta-anomer of compound **8** had a deshielded doublet (5.56 ppm) that represented H-1 with a coupling constant of 8.49 Hz, indicative of it's antiperiplaner coupling with an axial H-2 which is present in the fucose azido-β-acetate. The alpha-anomer of compound **9** had a 6.11 ppm doublet corresponding to it's equatorial H-1; the doublet possessed a very small coupling (1.52 Hz) to it's neighbor, H-2. This small coupling constant was evidence of a *gauche* relationship, found only if the hydrogen of C-2 was also equatorial as in the α-anomer of the talose azidoacetate. Two-dimensional COSY and HSQC experiments enabled the further characterization of the configuration of the C-2 azido group.

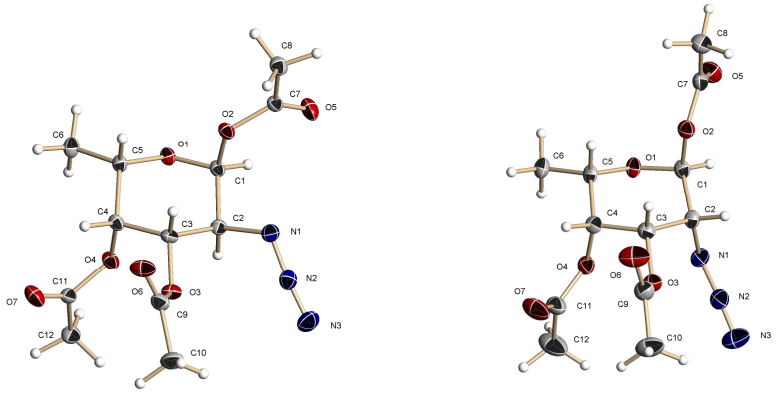


Figure 19: Structural refinement of 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α-L-fucose (**8**) and 1,3,4-tri-*O*-acetyl-2-azido-2,6-dideoxy-α-L-talose (**9**).

These data were confirmed upon the structural refinement of talose and fucose azidoacetate α-anomer crystals (Figure 19).

The 6-deoxy-L-talose configuration is introduced in the previous azidonitration reaction, converting 3,4-di-*O*-acetyl-L-fucal (**4**) into the 6-deoxytalosyl azidonitrate, and characterized after its acetolysis as the 6-deoxytalosyl azidoacetate. The regioselectivity of glycal azidonitration is dependant on steric bulk of the surrounding protecting groups, especially at C-4 in the case of fucal **4**, and reaction temperature.[21-23] According to

literature protocol the azidonitration reaction was cooled to -15 °C with an ethylene glycol/dry ice slurry and stirred overnight. As the reaction was left overnight the dry ice sublimed, allowing the temperature to reach ambient levels. The increase in temperature conferred enough energy to promote azide radical attack from the hindered *re*-face of the fucal's C-2. The uncontrolled rate of warming is suggested as the reason for the inconsistent yields of the 6-deoxy-L-talose epimer. The versatile CAN azidonitration reaction is worthy of additional research. By varying the reaction temperature and utilizing different protection strategies, the reaction may be optimized to provide the 6-deoxy-L-talosyl azidonitrate epimer as the major product. This could have a profound effect on the development of molecules meant to inhibit the biosynthesis of *Staphylococcal* capsular polysaccharides. The last step of UDP-L-FucNAc biosynthesis, before incorporation, is the enzymatic C-2 epimerization of UDP-6-deoxy-L-TalNAc (Scheme 1). By synthesizing derivatives meant to inactivate the enzymes responsible for UDP-6-deoxy-L-TalNAc epimerization (Cap5G) and the UDP-L-FucNAc incorporation (glycosyltransferases) one has an increased chance of disabling the protection conferred by the bacterium's capsule.[21-23]

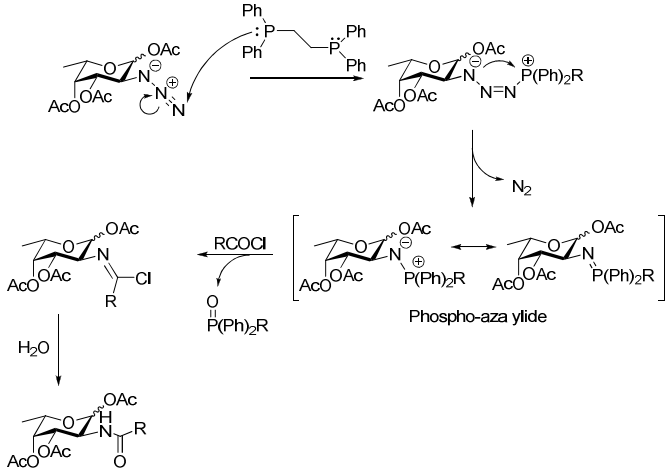
The solvent used in azidonitration reactions has ramifications on the subsequent acetolysis of their azidonitrate products. The *N*-glycoside (α-3,4-di-*O*-acetyl-1-*N*-acetyl-2-azidodeoxy-L-fucose) **10** was isolated, in variable yields, from the acetolysis reaction shown in Scheme 5. The formation of the azidoamide carbohydrate was attributed to the spontaneous solvolysis of the transient carbocation generated upon loss of the azidonitrate's (**6**) anomeric nitro group. Yields of such solvolysis products were found to be dependent on the concentration and nucleophilicity of the solvent present.[41,42] In the

case of azidoamide (**10**) formation, the azidonitration solvent employed was acetonitrile instead of acetone. After its isolation, the crude azidonitrate product was submitted to acetolysis; the presence of extraneous acetonitrile most likely trapped the glycosyl carbocation intermediate. The acetonitrile-fucosyl intermediate, upon hydrolysis in the acidic medium, provided the acetamido *N*-glycoside.

3,4-Di-*O*-acetyl-1-*N*-acetyl-2-azidodeoxy-α-L-fucose was characterized by NMR, mass spectrometry, and X-ray diffraction. The ^{1}H-NMR spectrum showed a total of six ^{1}H signals including a double of doublets (5.86 ppm) representing H-1 that was coupled not only to H-2 but also to a highly deshielded doublet (7.38 ppm) corresponding to the anomeric amide proton. The three signals between 170.73 and 171.64 representing three carbonyl carbons in the ^{13}C NMR spectrum added further proof of azidoamide formation. Mass spectral analysis of carbohydrate **10** provided a parent ion of 337.1 which is the molecular weight of the azidoamide plus an atom of sodium. The alpha configuration was confirmed upon crystallographic refinement of a crystal obtained by vapor diffusion of hexanes into a dilute solution of azidoamide in ethyl acetate.

2. Conversion of azides to amides *via* modified Staudinger reaction

The following amides were obtained *via* a modified Staudinger reaction utilizing the bis phosphine DPPE and various acid chlorides as acylating agents. The mechanism proceeds *via* a triazophosphadiene, which after release of nitrogen gas, yields a phosphoaza ylide (Figure 19). This aza-Wittig reagent then attacks the electrophilic carbonyl of the acid chloride generating an imidoyl chloride. The amide product is formed upon hydrolysis of the imidoyl chloride intermediate.

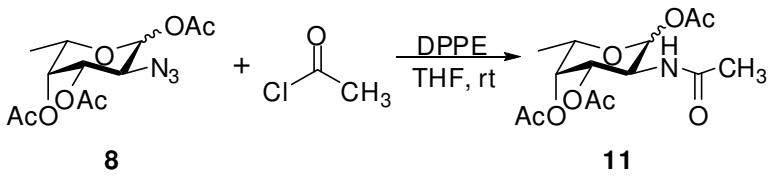


Scheme 5: Modified Staudinger reaction mechanism

Table 1: Synthesis of protected L-FucNAc and derivatives.

Starting Material	Acid Chloride	Product	% Yield
8	Acetyl chloride	**11**	82
	(Trideutero)acetyl chloride	**12**	68
	(Trifluoro)acetyl chloride	**13**	37
	(Trimethyl)acetyl chloride	**14**	63*

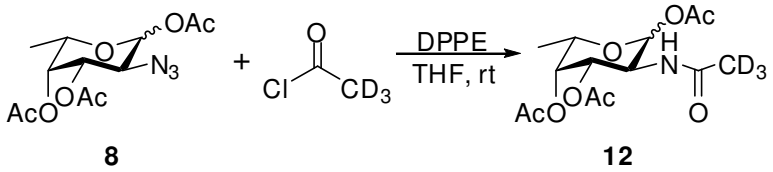
* 5 equivalents of acid chloride were used in order to obtain yield.



8 **11**

Equation 2: Synthesis of 1,3,4-tri-*O*-acetyl-2-*N*-acetyl-α,β-L-fucose (**11**)

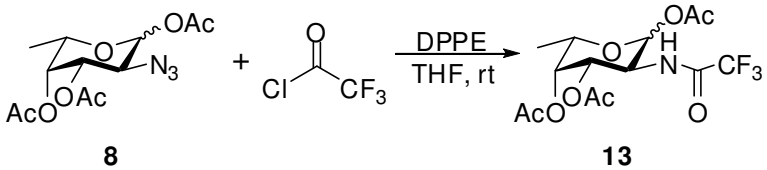
The modified Staudinger reaction of 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α-L-fucose (**8**) with acetyl chloride provided the amide product **11** in good yield, 82%, as a clear syrup. The coupling consistent for the α-anomeric H-1 doublet of the azidoacetate was 3.68 Hz and the amide product's (**11**) was 3.64 Hz, suggesting little to no anomerization took place during the course of the reaction. The reaction was monitored by TLC (R*f* = 0.27 in 6:1 ethyl acetate-hexanes) and upon completion was purified *via* flash column using the same solvent system. Investigation of the proton NMR spectrum showed a change in shift, downfield, of approximately 0.5 ppm for the signals corresponding to H-2 in both anomers. This shift was attributed to the deshielding nature of the C-2 amide. The multiplicity of the H-2 signal was a doublet of doubled doublets, characteristic of a proton that is coupled to three protons with different electronic environments. The position of the amide was confirmed by comparison of the coupling constants between the deshielded amide proton (6.61 ppm, 8.88 Hz) and the proton of C-2 (4.64 ppm, 8.91 Hz). In the azidoacetate ^{13}C NMR spectrum the three downfield signals representing the carbonyls of the acetyl protecting groups were joined by a fourth in the product's spectrum, confirming the addition of the *N*-acetyl functionality. Mass spectrometry of amide **11** provided a parent ion of 354.3 which is the calculated molecular weight, 331.1 amu, plus an atom of sodium.



8 **12**

Equation 3: Synthesis of 1,3,4-tri-*O*-acetyl-2-*N*-(trideutero)acetyl-α,β-L-fucose (**12**)

The reaction between the β-azide **8**, DPPE, and (trideutero)acetyl chloride provided the beta anomer of **12** as a white solid (Equation 3). The reaction was monitored by TLC (8:1 ethyl acetate-hexanes) and showed the formation of a new compound with a much lower R*f*, 0.14, than the azidoacetate starting material. The crude reaction mixture was purified by column chromatography and provided the product in a 68 % yield. The proton NMR spectrum was relied upon heavily for the characterization of carbohydrate **12**. The appearance of a deshielded doublet (5.75 ppm) with a large coupling constant of 9.52 Hz, also found in the H-2 doublet of doubled doublets (9.48 Hz), was indicative of the amide proton located next to C-2. The H-N doublet was the only evidence of amide addition in the ^{1}H-NMR spectrum as there were only three peaks, between 2.02 and 2.20 ppm, corresponding to the acetyl protecting groups. This was to be expected as the fourth amide acetyl group contained deuterium. The ^{13}C NMR spectrum showed evidence of four carbonyl carbons, three of which belonged to the ester protecting groups. The fourth was assigned to the carbonyl within the amide functional group. The product of the Staudinger reaction in Equation 3 was analyzed by ESI mass spectrometry. The parent ion isolated was 357.2 which, minus sodium, was 3 amu more than that found for the non-deuterated *N*-acetyl variant (**11**). These data combined confirmed the formation of 1,3,4-tri-*O*-acetyl-2-*N*-(trideutero)acetyl-L-fucose.



8 **13**

Equation 4: Synthesis of 1,3,4-tri-*O*-acetyl-2-*N*-(trifluoro)acetyl-α,β-L-fucose (**13**)

Preparation of the amide **13** from 2-azidodeoxy sugar azide **8**, DPPE, and (trifluoro)acetyl chloride provided the product in poor yield. The low and inconsistent yields were attributed to the problematic formation of the phospho-aza ylide prior to acylation. The gaseous fluorinated acid chloride was bubbled through a solution of azidoacetate **8** in THF before addition of the DPPE solution. The presence of acylating agent before phosphine addition has been documented to produce higher yields in Staudinger reactions.[29] The majority of the azidoacetate starting material (R*f* = 0.49, 2:1 hexanes-ethyl acetate) was found unreacted, even after a 24 hour period. The phospho-aza ylide was not formed properly upon the addition of 0.65 equivalents of DPPE, as judged by TLC and nitrogen evolution. In order to consume the starting material, a reaction was conducted where a solution of DPPE was added to the azidoacetate in THF. The reaction went as expected, forming the phospho-aza ylide (R*f* = 0.43, 2:1 hexanes-ethyl acetate) with the concomitant release of nitrogen. (Trifluoro)acetyl chloride was then bubbled through the solution and permitted to stir overnight. This sequence of reactant addition provided the amide **13** in similarly low yields to the general procedure. The highest yield of amide **13**, 37%, was achieved by bubbling acid chloride continuously before and during DPPE addition. The reaction was then permitted to stir for four hours after which an additional 0.25 mmol of DPPE was added dropwise. The acylating agent is suspected of prohibiting proper ylide formation. (Trifluoro)acetic anhydride was used as an alternative acylating agent for the formation of **13**. This variation of the reaction yielded no product over a 24 hour period. There was also no evidence of phospho-aza ylide formation; nitrogen evolution during phosphine addition was not observed.

Characterization of the fluorinated compound was achieved through NMR, mass spectrometry, and X-ray crystallography. On interpretation of the ^{1}H-NMR spectrum six 1H signals were observed, the most downfield of which was determined to belong to the proton on the amide (6.56 ppm). The amide doublet had a coupling constant of 9.44 Hz, which was similar to a coupling constant found the H-2 doublet of doublets (9.22 Hz).

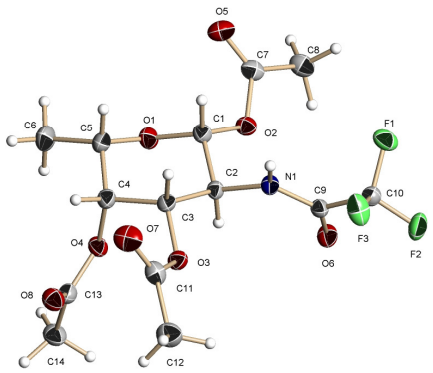
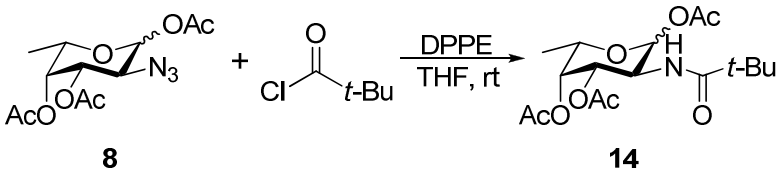


Figure 20: Structural refinement of 1,3,4-tri-*O*-acetyl-2-*N*-(trifluoro)acetyl-β-L-fucose

This is indicative of an amide nitrogen appended to C-2. The two signals in the ^{13}C NMR spectrum (~150 ppm) represent the carbonyl and the distal fluorinated methyl carbon of the amide moiety. Mass spectral analysis of compound **13** provide a parent ion peak of 408.2 which, minus sodium, is the approximate calculated molecular mass of the fluorinated carbohydrate. The formation of the desired product was confirmed upon structural refinement of a crystal obtained from vapor diffusion of hexanes into a dilute solution of 1,3,4-tri-*O*-acetyl-2-*N*-(trifluoro)acetyl-β-L-fucose in ethyl acetate (Figure 20).



Equation 5: Synthesis of 1,3,4-tri-*O*-acetyl-2-*N*-(trimethyl)acetyl-β-L-fucose

The reaction of azido sugar **8** with DPPE and (trimethyl)acetyl chloride in THF provided the amide **14** (R*f* = 0.26, 1:1 hexanes-ethyl acetate) in a 63% yield. In order to attain this level of product formation the general procedure for the synthesis of glycosyl amides from 2-azidodeoxy sugar azides was deviated from. Due to the acid chloride's bulky steric environment, nucleophilic attack of the phospho-aza ylide is probably impeded. The use of 5 equivalents of acylating agent instead of 2 provided carbohydrate **14** in reasonable yield. A compound with a much lower R*f* (0.13, 2:1 ethyl acetate-hexanes) than the azidoacetate **8** or amide product **14** was observed upon using the 2 equivalents of the bulky acid chloride. Under the general conditions for the synthesis of amides from azides byproduct **15**, a bis(1,3,4-tri-*O*-acetyl-L-fucos-2-yl)urea, was isolated. The slow acylation step between the aza-Wittig reagent and bulky acid chloride increased the longevity of the phospo-aza ylide. As a result CO_2 trapped the ylide as the reaction was quenched with a solution of saturated $NaHCO_3$ (Scheme 6).

Confirmation of 1,3,4-tri-*O*-acetyl-2-*N*-(trimethyl)acetyl-β-L-fucose (**14**) formation was obtained through 1- and 2-dimensional NMR spectroscopy, mass spectrometry, and X-ray crystallography. The 9H singlet at 1.12 ppm in the proton NMR spectrum provided strong evidence for product formation. This peak represented the *tert*-butyl group appended to the carbonyl of the amide. The location of the amide, on C-2, was determined by the comparison of coupling constants as well as interpretation of the COSY spectrum. The signal for H-2 superficially appears to be a quartet but upon closer investigation the signal was determined to be a doublet of doubled doublets where the *J*-values between H-2, H-1, H-3, and H-N are extremely similar. The ^{13}C NMR spectrum revealed a highly deshielded signal (178 ppm) which corresponds to the carbonyl of the

tert-butyl amide. The ^{13}C signal at 38.91 ppm represents the tertiary carbon of the *tert*-butyl group. Mass spectrometry conducted on purified carbohydrate **14** provided a parent ion of 396.2 which is the calculated molecular weight of the *tert*-butyl amide product (373.2) plus an atom of sodium. X-ray diffraction data obtained from a β-anomer crystal of **14** confirmed the addition of the C-2 *tert*-butyl amide (Figure 21).

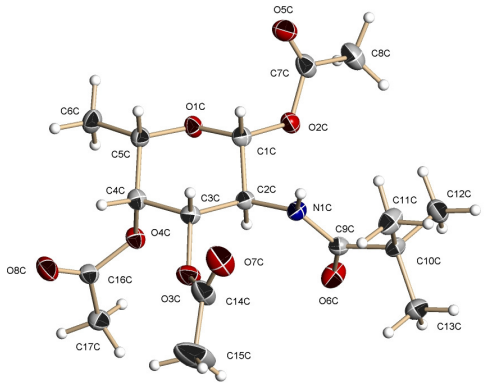
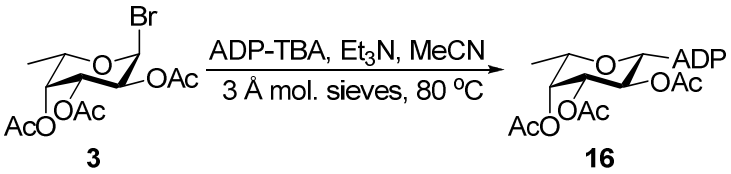


Figure 21: Structural refinement of 1,3,4-tri-*O*-acetyl-2-*N*-(trimethyl)acetyl-β-L-fucose

3. Formation of *O*-acetyl protected glycosyl nucleotides

Glycosyl nucleotides are primary building blocks of complex carbohydrate-containing natural products. Glycotransferases use the energy stored in the phosphodiester bond to glycosylate free hydroxyls of proteins, oligo- and polysaccharides as well as myriad other aglycones. The enzymatic synthesis of glycosyl nucleotides using glycosyltransferases has been well documented. Unfortunately, this method is characterized by laborious purification, problematic scale-up, and poor availability of proper enzymes.[43] Due to these drawbacks, total organic synthesis presents a reliable and versatile alternative for the preparation of glycosyl nucleotides. The two most common

synthetic routes to glycosyl nucleotides are condensation of a sugar with a nucleotide diphosphate or the phosphomorpholidate coupling of an activated nucleotide monophosphate to a sugar monophosphate.[44-47] Recently, glycosyl nucleotides have been synthesized by the direct displacement of acylated glycosyl bromides with high stereoselectivity.[48]



3 **16**

Equation 6:
Synthesis of Adenosine 5-(2',3',4'-tri-*O*-acetyl-β-L-fucopyranosyl)-diphosphate (**17**)

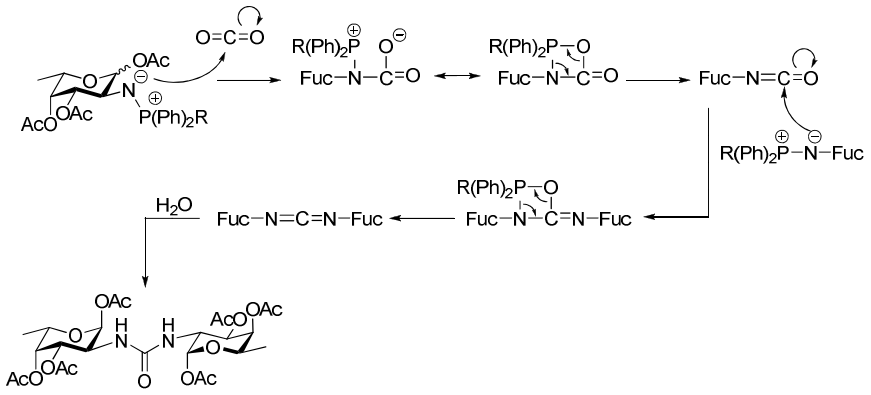
The glycosyl nucleotide synthesis *via* the direct displacement of glycosyl bromides requires organic-soluble nucleotides. In order to mask the hydrophilic nucleotide phoshoryl groups, available nucleotide sodium salts had to be converted to tetrabutyl ammonium salts followed by subsequent freeze drying.[44,49] A combination of 1:1:1 fucosyl bromide:ADP-TBA:Et_3N in anhydrous MeCN was reacted at 80 °C for 30 minutes while being monitored by TLC (160:70:5:0.25 $CHCl_3$-MeOH-dH_2O-NH_4OH). In order to determine the necessary mass of ADP-TBA salt required, an average molecular mass was obtained upon analysis of the ^{1}H-NMR spectrum. As the reaction came to completion a preliminary flash column was run, using the aforementioned TLC solvent. The fractions that eluted contained degraded fucosyl bromide and tetrabutyl-ammonium salts. A substantial amount of white precipitate, caught in the bed of the column, was eluted with MeOH doped with NH_4OH. The recovered precipitate was purified *via* MPLC (35:35:5:0.15 $CHCl_3$-MeOH-dH_2O-NH_4OH). A UV-active compound that migrated with

an R*f* of 0.46, in the more polar MPLC solvent system, was isolated and characterized as the glycosyl nucleotide product, adenosine 5-(2',3',4'-tri-*O*-acetyl-β-L-fucopyranosyl)-diphosphate (**17**). The 29% yield was similar to yields found in current literature.[48] Analysis of the proton NMR spectrum revealed three 3H singlets (1.97-2.18 ppm) which were the acetyl groups on the sugar moiety. A ratio of 3:1 was observed between the integration of each acetyl peak to a doublet at 6.11 ppm which corresponded to the anomeric carbon of the nucleotide's ribose sugar. Two singlets at 8.18 and 8.47 ppm were indicative of the hydrogens on C-2" and C-8" of the nitrogenous base. These peaks were found to have a 1:1 integration ratio with the H-5' of the acetylated fucose, indicative of all three hydrogens located on the same molecule. A ^{31}P-NMR experiment confirmed that the product isolated contained two coupled atoms of phosphorus. The chemical shift of the two phosphorus doublets had moved upfield by approximately 6 ppm due to fucose attachment. The signals in the ^{13}C NMR spectrum were identified by HSQC experiments. Three of the carbons of the adenine base are not present in the spectrum do to variations in the relaxation time of this type of carbons. One of the tertiary carbons within the adenine ring (139.89 ppm) was detected by HSQC experiments, although not visualized in the carbon spectrum. COSY NMR experiments were indispensible during the assignment of hydrogen signals.

Formation of protected sugar-derived ureas

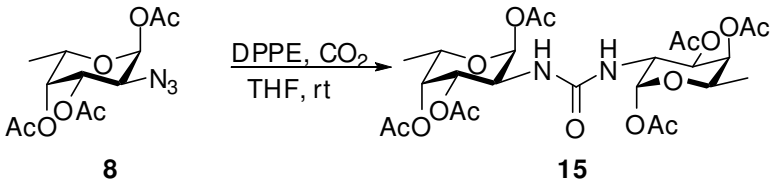
Sugar-derived ureas may be prepared from an aza-Wittig reaction involving the *in situ* generation of isocyanate functionality. Some glycosyl ureas have been reported to possess interesting biological properties; the disaccharides linked through a ureido bridge

exhibit antibiotic, anti-tumorigenic, and anti-trypanosomal activities. Some ureido glucouronate derivatives are potent inhibitors of the glycogen phosphorylase and α-glucosidases which pay a role in diabetes. Recently, multiple syntheses have been proposed, the majority of which require an isocyanate intermediate or starting material. Several of these syntheses involve toxic reagents such as triphosgene for isocyanate formation.[50-53]



Scheme 6: Mechanism of azidodeoxy sugar derived urea formation

The optimized synthesis used here involves reagents that are relatively mild and readily available (Scheme 6). The phospho-aza ylide, generated from a reaction between an azide and DPPE, attacks electrophilic CO_2 producing an intermediate isocyanate. The isocyanate is subsequently attacked by another ylide molecule and converted to the diimide. Hydrolysis of the diimide affords the glycosyl urea in good yield after chromatographic purification.[50-53]



8 **15**

Equation 7: Synthesis of bis(1,3,4-tri-*O*-acetyl-α-L-fucos-2-yl) urea (**15**)

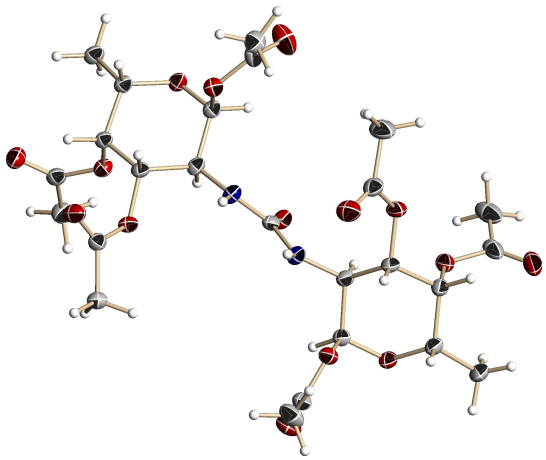
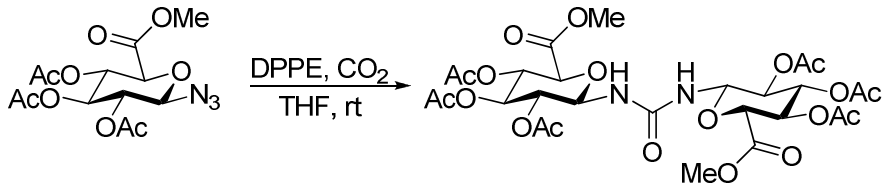


Figure 22: Structural refinement of bis(1,3,4-tri-*O*-acetyl-α-L-fucos-2-yl) urea (**15**)

Formation of the glycosyl urea **15** was achieved by bubbling CO_2, from the sublimation of dry ice, through a solution of azide **8** and DPPE in THF. The reaction was then left to stir overnight and monitored by TLC (2:1 ethyl acetate-hexanes). Completion of the reaction was judged by the appearance of a compound with an R*f* of 0.13. After column chromatography in a 4:1 ethyl acetate-hexanes mixture, bis(1,3,4-tri-*O*-acetyl-L-fucos-2-yl) urea was isolated in 78% yield. The ureido sugar was extensively characterized by 1- and 2-dimensional NMR, mass spectrometry, and X-ray crystallography. The proton NMR spectrum showed six 1H peaks. Comparison with the HSQC spectrum revealed that one of the hydrogens, a multiplet (4.44 - 4.55 ppm) was that of an amide nitrogen. The ^{13}C NMR spectrum had a peak at 155.97 ppm which corresponded to the carbonyl of the central urea. Analysis by mass spectrometry provided

a parent ion peak of 627.3, which is approximately the weight of compound **15** plus an atom of sodium. X-ray diffraction data was obtain from a crystal formed by vapor diffusion of carbon tetrachloride into a dilute solution of **15** and ethyl acetate. These data together confirmed proper product formation.



18

Equation 8: Synthesis of bis(2,3,4-tri-*O*-acetyl-glucouronosyl) urea (**18**)

Preparation of the urea **18** was carried out in similar fashion as the synthesis of the fucose derived urea, according to the general procedure for preparation of sugar derived ureas from azidodeoxy sugars. Carbon dioxide, from the sublimation of dry ice in toluene, was bubbled through a solution of glucouronosyl azide in THF. As the azide solution was infused with CO_2, a solution of DPPE in THF was added dropwise to the reaction vessel. The reaction was permitted to stir overnight while monitored by TLC (2:1 ethyl acetate-hexanes). The consumption of azide starting material revealed two products. The less polar of which migrated with an R*f* of 0.37 and the second compound trailed with an R*f* of 0.23. Multiple recrystallization with isopropanol provided a mixture of the two compounds which were subsequently separated by flash column chromatography in a solution of ethyl acetate and hexanes (2:1). Both compounds were isolated as white solids readily crystallized for X-ray diffractometry by vapor diffusion of hexanes into ethyl acetate. The major product of this reaction was determined to be the more polar bis

(2,3,4-tri-*O*-acetyl-glucouronosyl) (**18**) urea while bis (2,3,4-tri-*O*-acetyl-glucouronosyl) diimide (**19**) was isolated in trace amounts. The compounds were characterized with NMR spectrometry, mass spectrometry, and X-ray crystallography. The proton spectrum of symmetric urea **18** revealed four double doublets between 4.90-5.45 ppm, all of which have J_1 and J_2 coupling constants of similar size. The signal at 5.10 ppm corresponding to H-1, determined by COSY and HSQC experiments, was manifested as a double of doublets. This is indicative of a hydrogen located on an atom between two atoms with protons in different electronic environments, the protons of C-2 and the nitrogen. The deshielded doublet at 6.30 ppm represents the protons of the urea nitrogen. The ^{13}C-NMR spectrum revealed a total of 14 carbon signals. The signal at 150.32 ppm, representing the central carbonyl of the urea moiety, was half the intensity of the other peaks. The deshielded double intensity signals between 170.81-169.63 ppm represent the six carbonyl carbons of the acetyl protecting groups. The presence of 14 signals of the carbon NMR in conjunction with the mass spectrum (292.2 amu) confirmed the symmetrical nature of glycosyl urea **18**.

Isolation of glucouronosyl diimide (**19**) was confirmed by X-ray crystallography (Figure 23). Through the analysis of the X-ray data and NMR spectroscopy it was determined that the β-configuration of the azide was retained in the urea product. The 4.81 ppm doublet in the proton spectrum of diimide **19** corresponds to the hydrogen of the anomeric carbon. The H-1 doublet's coupling constant (8.78 Hz), indicative of an antiperiplaner arrangement of the two hydrogen atoms, was also observed in the 5.00 ppm multiplet representing of the axial H-2.

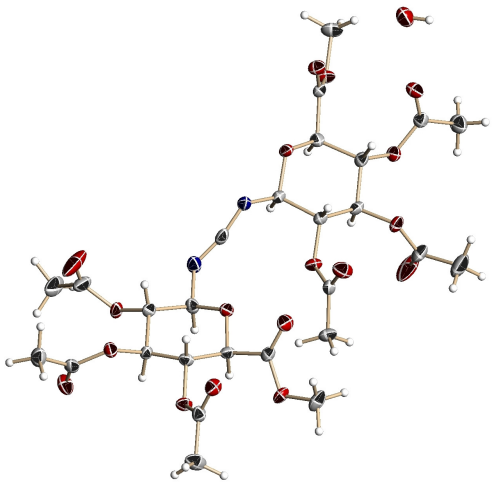


Figure 23: Structural refinement of bis(2,3,4-tri-*O*-acetyl-β-glucouronosyl) diimide

The signals of H-2, H-3, H-4, and H-5 were observed to have unexpected multiplicity. Through the comparison of the proton spectrum to literature sources the observed multiplicity was attributed to second-order NMR effects of the form ABXY.[54-55] The H-3 and H-4 signals (5.21-5.28 ppm) are overlapping and coupled to one another. This effects the multiplicity of hydrogen nuclei coupled to the atoms involved, (H-2 and H-5). The ^{13}C-NMR spectrum of the diimide **19** revealed 14 signals which provided further evidence of the bis glycosyl diimide's symmetrical nature. The signal at 137.25 ppm corresponding to the axis of symmetry, the carbon of the diimide, was observed to have a fraction of the intensity of the other signals.

Conclusions:

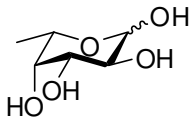
The total synthesis of UDP-L-FucNAc derivatives by the direct displacement of glycosyl bromides was not achieved due to complications in the bromination of L-FucNAc derivatives. However, the synthesis of adenosine-5-(2',3',4'-tri-*O*-acetyl-β-L-fucopyranosyl)-diphosphate was accomplished in yields comparable to literature values.[48] The glycosyl nucleotide synthesis *via* direct displacement of glycosyl bromides remains a viable synthetic route. Other glycosyl nucleotide syntheses show promise, including the phosphomorpholidate coupling, and may be a way to obviate the bromination of the L-FucNAc derivatives.

Experimental:

General Procedures

Reactions performed were monitored by thin layer chromotography (TLC) on Whatman silica gel aluminum-backed plates. In order to visualize the compounds after TLC the following agents were employed: UV light, 5% H_2SO_4 in EtOH, *p*-anisaldehyde in EtOH, and a $KMnO_4$ solution in EtOH. The crude reaction mixtures were purified *via* flash column chromatography with 60 Å silica or medium rressure liquid chromatography (MPLC) with 0-60 Å silica in the cases where recrystallization failed to produce purity. Compound characterization was achieved by several means including 1- and 2-dimensional NMR (Bruker Avance at 400 MHz and 100 MHz for ^{1}H and ^{13}C, respectively), mass spectrometry (Bruker Daltonics Esquire), X-ray crystallography (Bruker-Nonius SMART APEX CCD Diffractometer), infra-red spectrometry (Thermo Electron Corporation Nicolet Nexus 670 FT-IR), and melting point. The abbreviations pertaining to the multiplicity observed in the NMR experiments are as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doubled doublets (ddd), triplet (t), quartet (q), broad singlet (bs), multiplet (m).

L-fucose (1) purchased from Sigma-Aldrich.



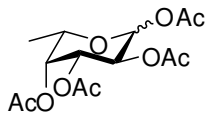
1

α-Anomer

^{1}H NMR (DMSO) : δ 1.07 (d, 3H, H-6, *J* = 6.56 Hz); 3.45-3.52 (m, 2H, H-2, H-4); 3.58 (ddd, 1H, H-3, *J* = 3.52, 6.04, 9.95 Hz); 3.98 (q, 1H, H-5, *J* = 6.55 Hz); 4.26 (d, 1H, H-O, *J* = 7.00 Hz); 4.32 (d, 1H, H-O, *J* = 4.48 Hz); 4.43 (d, 1H, H-O, *J* = 5.92 Hz); 4.90 (dd, 1H, H-1, *J* = 4.06, 4.06 Hz); 6.05 (d, 1H, H-O, *J* = 4.20 Hz).

^{13}C NMR ($CDCl_3$) : δ 16.74 (C-6); 65.21 (C-5); 68.55 (C-2); 69.63 (C-3); 71.94 (C-4); 92.67 (C-1).

Formation of 1,2,3,4-tetra-*O*-acetyl-α,β-L-fucose (2) from α,β-L-fucose.



2

L-Fucose (20.0 g, 0.12 mol), purchased from Sigma-Aldrich, was placed into a flame-dried round-bottom of suitable size. The reaction vessel was outfitted with a

magnetic stir bar and rubber septum then placed under a nitrogen atmosphere. The solid was dissolved in pyridine (65 mL) and cooled with an ice bath. Once cooled, acetic anhydride (65 mL) was added at a medium rate to the solution. Upon completion, 3 hours as judged by TLC in a 1:1 hexanes-ethyl acetate solution, the reaction was poured over ice in an Erlenmeyer flask. After the ice had mostly melted the product was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were then sequentially washed with 5% H_2SO_4 (3 x 50 mL) and distilled water (1 x 50 mL) in order to remove the pyridine. The organic phase was then dried with $MgSO_4$, filtered, and concentrated *in vacuo* to provide 39.84 g of α,β-1,2,3,4-tetra-*O*-acetyl-L-fucose as an extremely thick colorless syrup (98%). Crystals of the α-anomer, sufficient for X-ray diffractometry, were obtained from the anomeric mix by vapor diffusion with ethyl acetate and hexanes.

α-Anomer

^{1}H NMR ($CDCl_3$) : δ 1.16 (d, 3H, H-6, *J* = 6.52 Hz); 2.01 (s, 3H, CO$\underline{CH_3}$); 2.02 (s, 3H, CO$\underline{CH_3}$); 2.16 (s, 3H, CO$\underline{CH_3}$); 2.19 (s, 3H, CO$\underline{CH_3}$); 4.30 (q, 1H, H-5, *J* = 6.48 Hz); 5.32 (m, 3H, H-2, H-3, H-4); 6.33 (d, 1H, H-1, *J* = 3.24 Hz).

^{13}C NMR ($CDCl_3$) : δ 15.92 (C-6); 20.57 (CO$\underline{CH_3}$); 20.61 (CO$\underline{CH_3}$); 20.67 (CO$\underline{CH_3}$); 20.91 (CO$\underline{CH_3}$); 66.47 (C-2); 67.25 (C-5); 67.80 (C-3); 70.55 (C-4); 89.88 (C-1); 169.15 ($\underline{C}OCH_3$); 169.94 ($\underline{C}OCH_3$); 170.13 ($\underline{C}OCH_3$); 170.51 ($\underline{C}OCH_3$).

m/z calculated: 332.3 *m/z* found (ESI): 355.2 ($+Na^+$)

R*f* = 0.39 (1:1 hexanes: ethyl acetate).

β-Anomer:

^{1}H NMR ($CDCl_3$) : δ 1.23 (d, 3H, H-6, *J* = 6.50 Hz); 1.99 (s, 3H, CO$\underline{CH_3}$); 2.05 (s, 3H, CO$\underline{CH_3}$); 2.12 (s, 3H, CO$\underline{CH_3}$); 2.19 (s, 3H, CO$\underline{CH_3}$); 4.00 (q, 1H, H-5, *J* = 6.46 Hz); 5.10 (dd, 1H, H-3, *J* = 3.39 10.41 Hz); 5.26-5.37 (m, 2H, H-2, H-4); 5.70 (d, 1H, H-1, *J* = 8.28 Hz).

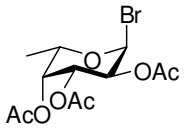
^{13}C NMR ($CDCl_3$) : δ 15.92 (C-6); 20.55 (CO$\underline{CH_3}$); 20.59 (CO$\underline{CH_3}$); 20.63 (CO$\underline{CH_3}$); 20.81 (CO$\underline{CH_3}$); 67.94 (C-2); 69.98 (C-3); 70.20 (C-5); 71.21 (C-4); 92.15 (C-1); 169.11 ($\underline{C}OCH_3$); 169.44 ($\underline{C}OCH_3$); 169.94 ($\underline{C}OCH_3$); 170.48 ($\underline{C}OCH_3$).

m/z calculated: 332.3 *m/z* found (ESI): 355.1 (+Na)

M.P (°C) = N/A (syrup)

R*f* = 0.39 (1:1 hexanes : ethyl acetate).

Formation of 1-bromo-2,3,4-tri-*O*-acetyl-α-L-fucose (3) from 1,2,3,4-tetra-*O*-acetyl-α,β-L-fucose.



3

1,2,3,4-Tetra-*O*-acetyl-α,β-L-fucose (**2**, 5.02 g, 15.11 mmol) was placed in a suitably sized flame-dried round-bottom flask and permitted to dry under vacuum for at least 24 hours. The reaction vessel was outfitted with a magnetic stir bar and rubber

septum then placed under a nitrogen atmosphere. The tetra-*O*-acetyl-L-fucose was dissolved in a solution of 33% HBr in glacial acetic acid (22 mL) and cooled with an ice bath. The reaction was allowed to stir until consumption of the starting material, 5-6 hours, was observed visually and judged by TLC (1:1 hexanes-ethyl acetate). The reaction mixture was then diluted with CH_2Cl_2 (30 mL) and transferred to a 500 mL Erlenmeyer flask containing a stir bar and ice. The Erlenmeyer was placed in an ice bath on top of a stir plate while chilled 10% NaOH (~150 mL) was added slowly until the solution tested slightly acidic on pH paper. The organic phase was then separated and stirred with saturated $NaHCO_3$ until neutral, after which the product was extracted with CH_2Cl_2 (3 x 30 mL) and kept in an ice bath. The combined organic extracts were then washed with distilled water (2 x 40 mL). The organic phase was then dried with $MgSO_4$, filtered, and concentrated *in vacuo* to provide 4.90 g of 1-bromo-2,3,4-tri-*O*-acetyl-α-L-fucose as a pale yellow syrup (91%).

^{1}H NMR ($CDCl_3$) : δ 1.22 (d, 3H, H-6, *J* = 6.56 Hz); 2.01 (s, 3H, CO$\underline{CH_3}$); 2.11 (s, 3H, CO$\underline{CH_3}$); 2.18 (s, 3H, CO$\underline{CH_3}$); 4.42 (q, 1H, H-5, *J* = 6.56 Hz); 5.02 (dd, 1H, H-2, *J* = 3.94, 10.50 Hz); 5.36 (dd, 1H, H-4, *J* = 1.22, 3.38 Hz); 5.40 (dd, 1H, H-3, *J* = 3.32, 10.56 Hz); 6.70 (d, 1H, H-1, *J* = 3.97 Hz).

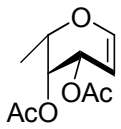
^{13}C NMR ($CDCl_3$) : δ 15.54 (C-6); 20.55 (CO$\underline{CH_3}$); 20.61 (CO$\underline{CH_3}$); 20.76 (CO$\underline{CH_3}$); 67.81 (C-2); 68.37 (C-3); 69.82 (C-5); 69.94 (C-4); 89.39 (C-1); 169.74 ($\underline{C}OCH_3$); 170.06 ($\underline{C}OCH_3$); 170.23 ($\underline{C}OCH_3$).

m/z calculated: 353.18 *m/z* found (ESI): N/A

M.P (°C) = N/A (syrup)

R*f* = 0.52 (1:1 hexanes : ethyl acetate).

Formation of 3,4-di-*O*-acetyl-L-fucal (4) and anhydroalditol byproduct (5) from 1-bromo-2,3,4-tri-*O*-acetyl-α-L-fucose.



4

Fucosyl bromide **3** (13.28 g, 37.60 mmol) was placed in a flame-dried round-bottom flask of suitable size and thoroughly dried under vacuum overnight. The morning after, Cp_2TiCl_2 (6.08 g, 24.43 mmol) and powdered Mn (3.97 g, 72.31 mmol) were added to a flame-dried reaction vessel containing a magnetic stir bar then sealed with a rubber septum and placed under a nitrogen atmosphere. The dry fucosyl bromide (**3**) was dissolved with THF (150 mL) and transferred *via* cannula to the reaction vessel. While stirring at room temperature a catalytic amount of TMSCl (1.3 mL) was added to the mixture. The reaction was then permitted to stir overnight and monitored by TLC (3:1 hexanes-ethyl acetate). When complete, if kept under inert conditions, the reaction turned from a dark red to a blue-green color. Upon consumption of starting material the solution was diluted with CH_2Cl_2 and quickly passed through a filter column of silica gel to remove inorganic material. The pooled organic phase was concentrated *in vacuo* then purified by 3:1 hexane-ethyl acetate flash chromatography to provide 5.19 g of 3,4-di-*O*-

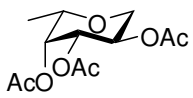
acetyl-L-fucal (64%) as a light-yellow oil and 2.43 g of the anhydroalditol byproduct **5** (24%). Crystals of both **4** and **5**, sufficient for X-ray diffractometry, were obtained from concentrated solutions kept at length at -4 °C.

^{1}H NMR ($CDCl_3$) : δ 1.28 (d, 3H, H-6, J = 6.60 Hz); 2.02 (s, 3H, CO$\underline{CH_3}$); 2.16 (s, 3H, CO$\underline{CH_3}$); 4.23 (q, 1H, H-5, J = 6.57 Hz); 4.64 (ddd, 1H, H-3, J = 1.96, 1.96, 6.33 Hz); 5.29 (m, 1H, H-2); 5.58 (m, 1H, H-4); 6.47 (dd, 1H, H-1, J = 1.92, 6.33 Hz).

^{13}C NMR ($CDCl_3$) : δ 16.51 (C-6); 20.68 (CO$\underline{CH_3}$); 20.83 (CO$\underline{CH_3}$); 64.92 (C-4); 66.10 (C-2); 71.37 (C-5); 98.09 (C-3); 145.85 (C-1); 170.09 ($\underline{C}OCH_3$); 170.40 ($\underline{C}OCH_3$).

m/z calculated: 214.2 *m/z* found (ESI): 215.1 ($+H^+$)

R*f* = 0.36 (3:1 hexanes-ethyl acetate).



5

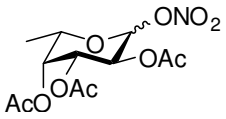
^{1}H NMR ($CDCl_3$) : δ 1.17 (d, 3H, H-6, *J* = 6.48 Hz); 2.01 (s, 3H, CO$\underline{CH_3}$); 2.05 (s, 3H, CO$\underline{CH_3}$); 2.18 (s, 3H, CO$\underline{CH_3}$); 3.28 (dd, 1H, H-1a, *J* = 10.52, 10.98 Hz); 3.73 (dq, 1H, H-5, *J* = 6.46, 0.92 Hz); 4.13 (dd, 1H, H-1b, *J* = 5.62, 11.22 Hz); 5.03 (dd, 1H, H-3, *J* = 3.42, 10.26 Hz); 5.21 (ddd, 1H, H-2, *J* = 5.52, 10.31, 10.31 Hz); 5.29 (dd, 1H, H-4, *J* = 0.96, 3.44 Hz).

^{13}C NMR ($CDCl_3$) : δ 16.42 (C-6); 20.68 (CO$\underline{CH_3}$); 20.73 (CO$\underline{CH_3}$); 20.82 (CO$\underline{CH_3}$); 66.51 (C-2); 67.06 (C-1); 70.80 (C-4); 71.97 (C-3); 73.38 (C-5); 170.04 ($\underline{C}OCH_3$); 170.24 ($\underline{C}OCH_3$); 170.63 ($\underline{C}OCH_3$).

m/z calculated: 274.3 *m/z* found (ESI): 297.1 ($+Na^+$)

R*f* = 0.22 (3:1 hexanes : ethyl acetate).

Formation of 3,4-di-*O*-acetyl-2-azidodeoxy-1-nitrodeoxy-α,β-L-fucose (6) and 3,4-di-*O*-acetyl-2-azidodeoxy-α,β-L-fucose (7) from 3,4-di-*O*-acetyl-L-fucal.



6

3,4-Di-*O*-acetyl-L-fucal (**4**, 2.13 g, 9.94 mmol) was placed in a flame-dried round-bottom flask of suitable size and thoroughly dried under vacuum overnight. CAN (10.84 g, 19.77 mmol) and NaN_3 (1.35 g, 20.76 mmol) were added to a flame-dried reaction vessel containing a magnetic stir bar, then sealed with a rubber septum and placed under a

nitrogen atmosphere. The dry fucal was dissolved in anhydrous acetone and subsequently cooled to -15 °C using a dry ice-ethylene glycol bath. The reaction vessel was place in a dry ice-ethylene glycol slurry (-15 °C) while the fucal solution was transferred *via* cannula at a slow rate. The reaction was then permitted to stir overnight and monitored by TLC (2:1 hexanes-ethyl acetate). Upon consumption of starting material the solution was diluted with diethyl ether (50 mL) and washed with dH_2O (4 x 20 mL). The organic phase was dried with $MgSO_4$, filtered, and concentrated *in vacuo,* after which the crude product was purified *via* flash chromatography using (2:1 hexanes-ethyl acetate) to provide 1.74 g (64%) of 3,4-di-*O*-acetyl-2-azidodeoxy-L-fucose (**6**) as a pale yellow-brown syrup and 1.01 g (32%) of 3,4-di-*O*-acetyl-2-azidodeoxy-1-nitrodeoxy-L-fucose (**7**) as a yellow syrup. Crystals of 3,4-di-*O*-acetyl-2-azidodeoxy-1-nitrodeoxy-α-L-fucose, sufficient for X-ray diffractometry, were obtained from the anomeric mix by vapor diffusion with ethyl acetate and hexanes.

α-Anomer:

^{1}H NMR ($CDCl_3$) : δ 1.18 (d, 3H, H-6, *J* = 6.48 Hz); 2.07 (s, 3H, CO$\underline{CH_3}$); 2.19 (s, 3H, CO$\underline{CH_3}$); 4.10 (dd, 1H, H-2, *J* = 4.18, 11.30 Hz); 4.31 (q, 1H, H-5, *J* = 6.44 Hz); 5.26 (dd, 1H, H-3, *J* = 3.30, 11.46 Hz); 5.35 (dd, 1H, H-4, *J* = 1.13, 3.23 Hz); 6.32 (d, 1H, H-1 *J* = 4.12 Hz).

^{13}C NMR ($CDCl_3$) : δ 15.71 (C-6); 20.39 (CO$\underline{CH_3}$); 20.44 (CO$\underline{CH_3}$); 55.72 (C-2); 67.94 (C-5); 68.84 (C-3); 69.55 (C-4); 97.33 (C-1); 169.40 ($\underline{C}OCH_3$); 170.00 ($\underline{C}OCH_3$).

m/z calculated: 318.2 *m/z* found (ESI): N/A

R*f* = 0.61 (3:1 petroleum ether : ethyl acetate).

β-Anomer:

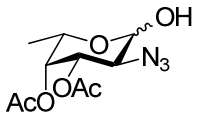
^{1}H NMR ($CDCl_3$) : δ 1.24 (d, 3H, H-6, *J* = 6.44 Hz); 2.06 (s, 3H, CO$\underline{CH_3}$); 2.19 (s, 3H, CO$\underline{CH_3}$); 3.56 (dd, 1H, H-2, *J* = 8.94, 10.62); 3.87 (dq, 1H, H-5, *J* = 6.41, 0.95 Hz); 4.60 (d, 1H, H-1, *J* = 8.88 Hz); 4.85 (dd, 1H, H-3, *J* = 3.32, 10.64 Hz); 5.22 (dd, 1H, H-4 *J* = 0.80, 3.28 Hz).

^{13}C NMR ($CDCl_3$) : δ 15.93 (C-6); 20.46 (2 x CO$\underline{CH_3}$, double intensity); 60.30 (C-2); 69.11 (C-4); 71.23 (C-5); 71.80 (C-3); 89.12 (C-1); 169.62 ($\underline{C}OCH_3$); 170.23 ($\underline{C}OCH_3$).

m/z calculated: 318.2 *m/z* found (ESI): N/A

M.P (°C) = N/A (syrup)

R*f* = 0.61 (3:1 petroleum ether : ethyl acetate).



7

α-Anomer :

^{1}H NMR ($CDCl_3$) : δ 1.15 (d, 3H, H-6, *J* = 6.52 Hz); 2.18 (s, 3H, CO$\underline{CH_3}$); 2.19 (s, 3H, CO$\underline{CH_3}$); 3.71 (dd, 1H, H-2, *J* = 3.46, 11.02 Hz); 4.31 (bs, 1H, H-O); 4.42 (q, 1H, H-5, *J* = 6.63 Hz); 5.30 (dd, 1H, H-4, *J* = 1.06, 3.19 Hz); 5.40 (m, 2H, H-1, H-3).

^{13}C NMR ($CDCl_3$) : δ 15.97 (C-6); 20.60 (CO<u>C</u>H$_3$); 20.64 (CO<u>C</u>H$_3$); 58.06 (C-2); 64.65 (C-5); 68.90 (C-3); 70.92 (C-4); 92.25 (C-1); 170.83 (2 x <u>C</u>OCH$_3$, double intensity).

m/z calculated: 273.2 *m/z* found (ESI): 296.1 (+Na^+)

M.P (°C) = N/A (syrup)

R*f* = 0.23 (2:1 hexanes : ethyl acetate).

β-Anomer :

^{1}H NMR ($CDCl_3$) : δ 1.21 (d, 3H, H-6, *J* = 6.44 Hz); 2.06 (s, 3H, CO<u>C</u>H$_3$); 2.07 (s, 3H, CO<u>C</u>H$_3$); 3.64 (dd, 1H, H-2, *J* = 7.94, 10.86 Hz); 3.84 (dq, 1H, H-5, *J* = 6.45, 0.92 Hz); 4.68 (d, 1H, H-1, *J* = 7.96 Hz); 4.82 (dd, 1H, H-3, *J* = 3.36, 10.84 Hz); 4.99 (bs, 1H, H-O); 5.30 (dd, 1H, H-4, *J* = 0.72, 3.28 Hz).

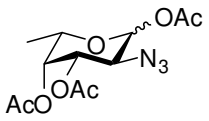
^{13}C NMR ($CDCl_3$) : δ 16.14 (C-6); 20.66 (CO<u>C</u>H$_3$); 20.72 (CO<u>C</u>H$_3$); 62.04 (C-2); 69.31 (C-5); 69.72 (C-4); 71.76 (C-3); 96.20 (C-1); 170.31 (2 x <u>C</u>OCH$_3$, double intensity).

m/z calculated: 273.2 *m/z* found (ESI): 296.1 (+Na^+)

M.P (°C) = N/A (syrup)

R*f* = 0.18 (2:1 hexanes : ethyl acetate).

Formation of 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α,β-L-fucose (8), 1,3,4-tri-*O*-acetyl-2-azido-2,6-dideoxy-α,β-L-talose (9), and 3,4-di-*O*-acetyl-1-*N*-acetyl-2-azidodeoxy-α-L-fucose (10) from 3,4-di-*O*-acetyl-2-azidodeoxy-1-nitro-α,β-L-fucose.



8

3,4-Di-*O*-acetyl-2-azidodeoxy-1-nitro-α,β-L-fucose (**7**, 2.94 g, 9.24 mmol) was placed into a flame-dried round-bottom of suitable size, equipped with a magnetic stir bar and condenser, and dissolved in glacial acetic acid (90 mL, 1.55 mol). NaOAc (5.48 g, 66.78 mmol) and Ac_2O (3.90 mL, 40.91 mmol) were combined with the solution of **7** in the reaction vessel. The reaction was allowed to reflux for 5 hours then poured over ice and allowed to cool. The products were extracted with CH_2Cl_2 (4 x 30 mL). The combined organic extracts were then carefully poured into a suitable sized Erlenmeyer with a stir bar and saturated $NaHCO_3$ (50 mL) for neutralization. Once neutralized the organic phase was washed with dH_2O**.**

α-Isomer:

^{1}H NMR ($CDCl_3$) : δ 1.15 (d, 3H, H-6, *J* = 6.52 Hz); 2.08 (s, 3H, CO$\underline{CH_3}$); 2.17 (s, 3H, CO$\underline{CH_3}$); 2.19 (s, 3H, CO$\underline{CH_3}$); 3.91 (m, 1H, H-2); 4.21 (q, 1H, H-5, *J* = 6.55 Hz); 5.36 (m, 2H, H-3, H-4); 6.29 (d, 1H, H-1, *J* = 3.68 Hz).

^{13}C NMR ($CDCl_3$) : δ 15.96 (C-6); 20.63 (CO$\underline{CH_3}$); 20.70 (CO$\underline{CH_3}$); 21.00 (CO$\underline{CH_3}$); 56.72 (C-2); 67.20 (C-5); 69.14 (C-3); 70.03 (C-4); 90.67 (C-1); 168.98 ($\underline{C}OCH_3$); 169.94 ($\underline{C}OCH_3$); 170.37 ($\underline{C}OCH_3$).

m/z calculated: 315.3 *m/z* found (ESI): 338.2 ($+Na^+$)

M.P (°C) = 155-157

R*f* = 0.46 (1:1 hexanes : ethyl acetate).

β-Isomer:

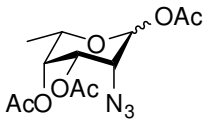
^{1}H NMR ($CDCl_3$) : δ 1.21 (d, 3H, H-6, *J* = 6.52 Hz); 2.07 (s, 3H, CO$\underline{CH_3}$); 2.19 (s, 3H, CO$\underline{CH_3}$); 2.20 (s, 3H, CO$\underline{CH_3}$); 3.82 (dd, 1H, H-2, *J* = 10.82, 8.54 Hz); 3.94 (dq, 1H, H-5, *J* = 6.46, 0.82 Hz); 4.91 (dd, 1H, H-3, *J* = 3.36, 10.80 Hz); 5.23 (dd, 1H, H-4, *J* = 0.80, 3.32 Hz); 5.56 (d, 1H, H-1, *J* = 8.49 Hz).

^{13}C NMR ($CDCl_3$) : δ 15.95 (C-6), 20.62 (2 x CO$\underline{CH_3}$, double intensity); 20.93 (CO$\underline{CH_3}$); 59.63, 69.33, 70.21, 71.66, 92.86, 168.78 ($\underline{C}OCH_3$); 169.69 ($\underline{C}OCH_3$); 170.34 ($\underline{C}OCH_3$).

m/z calculated: 315.3 *m/z* found (ESI): 338.2 (+Na^+)

M.P (°C) = N/A (syrup)

R*f* = 0.35 (3:1 petroleum ether : ethyl acetate).



9

α-Anomer :

^{1}H NMR ($CDCl_3$) : δ 1.22 (d, 3H, H-6, *J* = 6.52 Hz); 2.10 (s, 3H, CO$\underline{CH_3}$); 2.14 (s, 3H, CO$\underline{CH_3}$); 2.24 (s, 3H, CO$\underline{CH_3}$); 3.80 (m, 1H, H-2); 4.21 (dq, 1H, H-5, *J* = 6.49, 1.44 Hz);

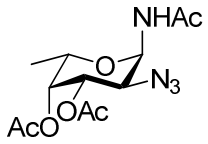
5.28 (m, 1H, H-4); 5.39(dd, 1H, H-3, *J* = 3.80, 3.80 Hz); 6.11 (d, 1H, H-1, *J* = 1.52 Hz).

^{13}C NMR ($CDCl_3$) : δ 16.05 (C-6); 20.52 (CO$\underline{C}H_3$); 20.66 (CO$\underline{C}H_3$); 20.94 (CO$\underline{C}H_3$); 56.65 (C-2); 67.45 (C-5); 67.81 (C-3); 68.24 (C-4); 92.28 (C-1); 168.36 ($\underline{C}OCH_3$); 169.62 ($\underline{C}OCH_3$); 170.80 ($\underline{C}OCH_3$).

m/z calculated: 315.3 *m/z* found (ESI): 338.1 ($+Na^+$)

M.P (°C) = 106-109

R*f* = 0.16 (petroleum ether : ethyl acetate).



10

α-Anomer:

^{1}H NMR ($CDCl_3$) : δ 1.13 (d, 3H, H-6, *J* = 6.44 Hz); 2.10 (s, 3H, CO$\underline{C}H_3$); 2.11 (s, 3H, CO$\underline{C}H_3$); 2.20 (s, 3H, CO$\underline{C}H_3$); 4.01 (q, 1H, H-5, *J* = 6.39 Hz); 4.16 (dd, 1H, H-2, *J* = 5.53, 11.08 Hz); 5.22 (d, 1H, H-4, *J* = 2.68 Hz); 5.27 (dd, 1H, H-3, *J* = 3.34, 11.10 Hz);

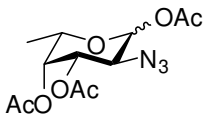
5.86 (dd, 1H, H-1, *J* = 5.58, 8.06 Hz); 7.38 (d, 1H, H-N, *J* = 8.08 Hz).

^{13}C NMR ($CDCl_3$) : δ 16.21 (C-6); 20.69 (CO$\underline{C}H_3$); 20.83 (CO$\underline{C}H_3$); 23.26 (CO$\underline{C}H_3$); 56.65 (C-2); 65.38 (C-5); 70.09 (C-4); 70.21 (C-3); 75.43 (C-1); 170.73 ($\underline{C}OCH_3$); 170.84 ($\underline{C}OCH_3$); 171.64 ($\underline{C}OCH_3$).

m/z calculated: 314.3 *m/z* found (ESI): 337.1 ($+Na^+$)

R*f* = 0.04 (petroleum ether : ethyl acetate).

Formation of 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α,β-L-fucose (8) from 3,4-di-*O*-acetyl-2-azidodeoxy-α,β-L-fucose.



8

3,4-Di-*O*-acetyl-2-azidodeoxy-α,β-L-fucose (**7**, 4.75 g, 17.38 mmol) was placed into a flame-dried round-bottom of suitable size. The reaction vessel was outfitted with a magnetic stir bar and rubber septum then placed under a nitrogen atmosphere. The solid was dissolved in pyridine (10 mL, 124.13 mmol) and cooled with an ice bath. Once cooled, acetic anhydride (10 mL 105.98 mmol) was added at a medium rate to the solution. Upon completion, 3 hours as judged by TLC in a 1:1 hexanes-ethyl acetate solution, the reaction was poured over ice in an Erlenmeyer flask. After the ice mostly melted the product was extracted with CH_2Cl_2 (3 x 20 mL). The combine organic extracts were then sequentially washed with 5% H_2SO_4 (3 x 20 mL) and distilled water (1 x 20 mL) in order to remove the pyridine. The organic phase was then dried with $MgSO_4$, filtered, and concentrated *in vacuo* to provide 4.75 g of α,β-1,3,4-tri-O-acetyl-2-azidodeoxy-L-fucose as a light yellow syrup (89%). Crystals of the α-anomer, sufficient

for X-ray diffractometry, were obtained from the anomeric mix by vapor diffusion with ethyl acetate and hexanes.

m/z calculated: 315.3 *m/z* found (ESI): 338.2 ($+Na^+$)

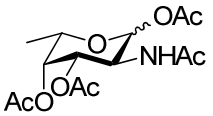
M.P (°C) = 155

R*f* = 0.46 (1:1 hexanes : ethyl acetate)

General procedure for the synthesis of amides from azides employing the modified Staudinger reaction.

One equivalent of azide was placed into a flame-dried round-bottom of suitable size outfitted with a magnetic stir bar and rubber septum then placed under a nitrogen atmosphere. The sugar was dissolved in anhydrous THF (0.1g/mL) then 2 equivalents of acylating agent (acid chloride or anhydride) was added. A solution of bis(diphenylphosphino)ethane (DPPE, 0.65 eq) in anhydrous THF (0.1 g/mL) was added dropwise to the room temperature reaction vessel. The mixture was allowed to stir for 2 hours and monitored by TLC. After the TLC showed consumption of the phospho-aza ylide, saturated $NaHCO_3$ was added and the reaction was permitted to stir overnight. The THF was taken off *in vacuo* and the remaining aqueous phase was extracted three times with $CHCl_3$. The combined organic extracts where then washed with dH_2O. The organic phase was then dried with $MgSO_4$, filtered, concentrated, and purified by flash column chromatography and/or recrystallization.

Formation of 1,3,4-tri-*O*-acetyl-2-*N*-acetyl-α,β-L-fucose (11) from 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α,β-L-fucose.



11

Prepared from 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α,β-L-fucose **8** (0.32 g, 1.00 mmol), acetyl chloride (0.14 mL, 2.00 mmol), DPPE (0.26 g, 0.65 mmol), and 7.3 mL of anhydrous THF total according to the aforementioned general procedure for synthesizing amides. Purification preformed by flash chromatography (7:1 ethyl acetate-hexanes) provided 0.27g (82%) of 1,3,4-tri-*O*-acetyl-2-*N*-acetyl-α,β-L-fucose which could be recrystallized with isopropanol to give the β-anomer as a white solid.

α-Anomer:

^{1}H NMR ($CDCl_3$) : δ 1.15 (d, 3H, H-6, *J* = 6.49 Hz); 1.95 (s, 3H, CO$\underline{CH_3}$); 2.01 (s, 3H, CO$\underline{CH_3}$); 2.17 (s, 3H, CO$\underline{CH_3}$); 2.19 (s, 3H, CO$\underline{CH_3}$); 4.22 (q, 1H, H-5, *J* = 6.44 Hz); 4.64 (ddd, 1H, H-2, *J* = 3.56, 8.91, 11.76 Hz); 5.21 (dd, 1H, H-3, *J* = 3.14, 11.62 Hz); 5.26 (d, 1H, H-4, *J* = 2.52 Hz); 6.19 (d, 1H, H-1, *J* = 3.64 Hz); 6.61 (d, 1H, N-H, *J* = 8.88 Hz).

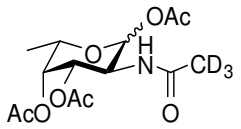
^{13}C NMR ($CDCl_3$) : δ 16.09 (C-6); 20.65 (CO$\underline{CH_3}$); 20.72 (CO$\underline{CH_3}$); 20.93 (CO$\underline{CH_3}$); 20.90 (CO$\underline{CH_3}$); 46.65 (C-2); 66.99 (C-5); 68.12 (C-3); 69.95 (C-4); 91.41 (C-1); 169.53 ($\underline{C}OCH_3$); 170.64 ($\underline{C}OCH_3$); 170.73 ($\underline{C}OCH_3$); 170.75 ($\underline{C}OCH_3$).

m/z calculated: 331.1 *m/z* found (ESI): 354.3 ($+Na^+$)

M.P (°C) = N/A (syrup)

R*f* = 0.27 (6:1 ethyl acetate-hexanes).

Formation of 1,3,4-tri-*O*-acetyl-2-*N*-(trideutero)acetyl-α,β-L-fucose (12) from 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α,β-L-fucose.



12

Prepared from 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α,β-L-fucose **8** (0.47 g, 1.48 mmol), acetyl-(D_3) chloride (0.22 mL, 3.12 mmol), DPPE (0.42 g, 0.99 mmol), and 11.1 mL of anhydrous THF total according to the aforementioned general procedure for synthesizing amides. Purification preformed by flash chromatography (8:1 ethyl acetate-hexanes) provided 0.34 g (68%) of 1,3,4-tri-*O*-acetyl-2-*N*-(D_3)-acetyl-α,β-L-fucose which could be recrystallized with isopropanol to give the β-anomer as a white solid.

α-Anomer:

^{1}H NMR ($CDCl_3$) : δ 1.15 (d, 3H, H-6, *J* = 6.48 Hz); 2.02 (s, 3H, CO$\underline{CH_3}$); 2.16 (s, 3H, CO$\underline{CH_3}$); 2.19 (s, 3H, CO$\underline{CH_3}$); 4.17 (q, 1H, H-5, *J* = 6.56 Hz); 4.68 (ddd, 1H, H-2, *J* = 3.65, 6.86, 11.42 Hz); 5.22 (dd, 1H, H-3, *J* = 3.24, 11.44 Hz); 5.26 (dd, 1H, H-4, *J* = 1.10, 3.22 Hz); 5.84 (d, 1H, H-N, *J* = 9.12 Hz); 6.18 (d, 1H, H-1, *J* = 3.68 Hz).

^{13}C NMR ($CDCl_3$) : δ 16.10 (C-6); 20.68 (CO<u>C</u>H$_3$); 20.78 (CO<u>C</u>H$_3$); 20.99 (CO<u>C</u>H$_3$); 46.82 (C-2); 67.14 (C-5); 68.26 (C-3); 69.98 (C-4); 91.62 (C-1); 169.25 (<u>C</u>OCH$_3$); 170.39 (<u>C</u>OCH$_3$); 170.68 (<u>C</u>OCH$_3$); 171.18 (<u>C</u>OCH$_3$).

m/z calculated: 334.1 *m/z* found (ESI): 357.2 (+Na^+)

M.P (°C) = N/A (syrup)

R*f* = 0.14 (8:1 ethyl acetate : hexanes).

β-Anomer:

^{1}H NMR ($CDCl_3$) : δ 1.23 (d, 3H, H-6, *J* = 6.44 Hz); 2.02 (s, 3H, CO<u>C</u>H$_3$); 2.13 (s, 3H, CO<u>C</u>H$_3$); 2.20 (s, 3H, CO<u>C</u>H$_3$); 3.95 (dq, 1H, H-5, *J* = 0.78, 6.50 Hz); 4.42 (ddd, 1H, H-2, *J* = 9.11, 9.48, 11.27 Hz); 5.11 (dd, 1H, H-3, *J* = 3.36, 11.28 Hz); 5.22 (dd, 1H, H-4, *J* = 0.73, 3.32 Hz); 5.71 (d, 1H, H-1, *J* = 8.76 Hz); 5.75 (d, 1H, H-N, *J* = 9.52 Hz).

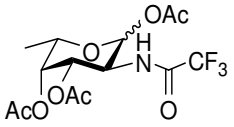
^{13}C NMR ($CDCl_3$) : δ 16.11 (C-6); 20.74 (2 x CO<u>C</u>H$_3$, double intensity); 20.98(CO<u>C</u>H$_3$); 20.93 (CO<u>C</u>H$_3$); 45.58 (C-2); 69.45 (C-4); 70.30 (C-5); 70.75 (C-3); 92.99 (C-1); 169.81 (<u>C</u>OCH$_3$); 170.43 (<u>C</u>OCH$_3$); 170.70 (<u>C</u>OCH$_3$); 170.87 (<u>C</u>OCH$_3$).

m/z calculated: 334.1 *m/z* found (ESI): 357.2 (+Na^+)

M.P (°C) = 156-159

R*f* = 0.13 (8:1 ethyl acetate : hexanes).

Formation of 1,3,4-tri-*O*-acetyl-2-*N*-(trifluoro)-acetyl-α,β-L-fucose (13) from 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α,β-L-fucose.



13

1,3,4-Tri-*O*-acetyl-2-azidodeoxy-α,β-L-fucose (**8**, 0.37 g, 1.18 mmol) was placed into a flame-dried round-bottom of suitable size which was outfitted with a magnetic stir bar and rubber septum then placed under a nitrogen atmosphere. The solid was dissolved in THF (4.0 mL) and cooled with an ice bath. The (trifluoro)acetyl chloride was bubbled into solution for 1 minute prior to, as well as throughout, the first DPPE addition. As the reaction was allowed to approach room temperature, a solution of DPPE (0.30 g, 0.77 mmol) in anhydrous THF (3 mL) was added in a dropwise fashion. Four hours later, additional DPPE (0.10 g, 0.25 mmol) in THF (1 mL) was added dropwise and permitted to stir at room temperature overnight. After consumption of starting material **8**, judged by TLC (2:1 hexanes-ethyl acetate), saturated $NaHCO_3$ was added slowly to the reaction. The neutralization was accompanied by excessive evolution of CO_2 and a color change ranging from brownish yellow through dark olive green back to brown. The reaction mixture was worked up according to the aforementioned general procedure for synthesizing amides. Purification performed using flash chromatography (2:1 hexanes-ethyl acetate) provided 0.17 g (37%) of 1,3,4-tri-*O*-acetyl-2-*N*-(trifluoro)-acetyl-α,β-L-fucose. Crystals of the β-anomer, sufficient for X-ray diffractometry, were obtained from the anomeric mix by vapor diffusion with ethyl acetate and hexanes.

β-Anomer:

^{1}H NMR ($CDCl_3$) : δ 1.25 (d, 3H, H-6, *J* = 6.40 Hz); 2.02 (s, 3H, CO$\underline{CH_3}$); 2.12 (s, 3H, CO$\underline{CH_3}$); 2.21 (s, 3H, CO$\underline{CH_3}$); 3.94 (dq, 1H, H-5, *J* = 0.96, 6.44 Hz); 4.47 (ddd, 1H, H-2, *J* = 9.28, 9.28, 11.12 Hz); 5.14 (dd, 1H, H-3, *J* = 3.28, 11.28 Hz); 5.25 (dd, 1H, H-4, *J* = 0.78, 3.30 Hz); 5.74 (d, 1H, H-1, *J* = 8.76 Hz); 6.56 (d, 1H, N-H, *J* = 9.44 Hz).

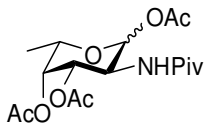
^{13}C NMR ($CDCl_3$) : δ 16.03 (C-6); 20.45 (CO$\underline{CH_3}$); 20.63 (CO$\underline{CH_3}$); 20.68 (CO$\underline{CH_3}$); 50.48 (C-2); 69.18 (C-4); 70.28 (C-3); 70.75 (C-5); 92.40 (C-1); 157.44 (CO$\underline{CF_3}$); 157.81 ($\underline{C}OCF_3$); 169.64 ($\underline{C}OCH_3$); 170.43 ($\underline{C}OCH_3$); 170.90 ($\underline{C}OCH_3$).

m/z calculated: 385.1 *m/z* found (ESI): 408.2 ($+Na^+$)

M.P (°C) = 157-159

R*f* = 0.20 (2:1 hexanes : ethyl acetate).

Formation of 1,3,4-tri-*O*-acetyl-2-*N*-(trimethyl)-acetyl-α,β-L-fucose 12 and byproduct bis(1,3,4-tri-*O*-α-fucos-2-yl) urea 15 from 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α,β-L-fucose.



14

Prepared from 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α,β-L-fucose **8** (0.17 g, 0.55 mmol), trimethyl acetyl chloride (0.34 mL, 2.76 mmol), DPPE (0.14 g, 0.36 mmol), and

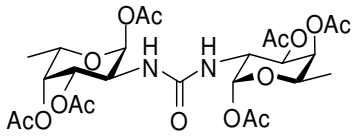
6.00 mL of anhydrous THF total according to the aforementioned general procedure for synthesizing amides, with the exception of a total of 5 equivalents of acylating agent used. Purification preformed by flash chromatography (2:1 ethyl acetate-hexanes) provided 0.13 g (63%) of 1,3,4-tri-*O*-acetyl-2-*N*-(trimethyl)-acetyl-α,β-L-fucose and trace amounts of the bis(1,3,4-tri-*O*-α-fucos-2-yl) urea byproduct. Crystals of the β-anomer of **14**, sufficient for X-ray diffractometry, were obtained from the anomeric mix by vapor diffusion with ethyl acetate and hexanes.

^{1}H NMR ($CDCl_3$) : δ 1.12 (s, 9H, CO($\underline{CH}_3$)$_3$) 1.25 (d, 3H, H-6, *J* = 6.36 Hz); 2.00 (s, 3H, CO$\underline{CH}_3$); 2.10 (s, 3H, CO$\underline{CH}_3$); 2.20 (s, 3H, CO$\underline{CH}_3$); 3.91 (q, 1H, H-5, *J* = 6.38 Hz); 4.50 (ddd, 1H, H-2, *J* = 9.26, 9.26, 11.13 Hz); 5.12 (dd, 1H, H-3, *J* = 3.22, 11.30 Hz); 5.21 (d, 1H, H-4, *J* = 3.08 Hz); 5.58 (d, 1H, H-N, *J* = 9.48 Hz); 5.72 (d, 1H, H-1, *J* = 8.80 Hz).

^{13}C NMR ($CDCl_3$) : δ 16.25 (C-6); 20.60 (CO$\underline{CH}_3$); 20.69 (CO$\underline{CH}_3$); 20.81 (CO$\underline{CH}_3$); 27.29 [C($\underline{CH}_3$)$_3$]; 38.88 ($\underline{C}$(CH$_3$)$_3$); 49.61 (C-2); 69.55 (C-4); 70.62 (C-3); 70.66 (C-5); 93.30 (C-1); 169.68 ($\underline{C}$OCH$_3$); 170.60 ($\underline{C}$OCH$_3$); 170.86 ($\underline{C}$OCH$_3$); 178.57 [$\underline{C}$OC(CH$_3$)$_3$].

m/z calculated: 373.2 *m/z* found (ESI): 396.2 (+Na$^+$)

R*f* = 0.26 (1:1 hexanes : ethyl acetate).



15

^{1}H NMR ($CDCl_3$) : δ 1.34 (d, 6H, H-6, H-6' *J* = 6.48 Hz); 2.02 (s, 6H, 2 x CO$\underline{CH_3}$); 2.15 (s, 6H, 2 x CO$\underline{CH_3}$); 2.02 (s, 6H, 2 xCO$\underline{CH_3}$); 4.13 (q, 2H, H-5, H-5', *J* = 6.49 Hz); 4.50 (m, 4H, H-2, H-2', H-N, H-N'); 5.15 (dd, 2H, H-3, H-3', *J* = 2.70, 10.83 Hz); 5.23 (d, 2H, H-4, H-4', *J* = 2.88 Hz); 6.13 (d, 2H, H-1, H-1', *J* = 2.93 Hz).

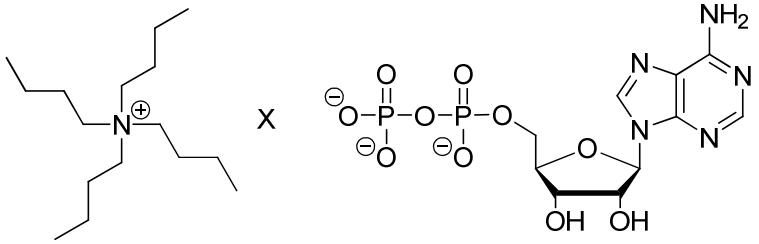
^{13}C NMR ($CDCl_3$) : δ 16.10 (C-6, C-6'); 20.73 (2 x CO$\underline{CH_3}$); 20.84 (2 x CO$\underline{CH_3}$); 20.96 (2 x CO$\underline{CH_3}$); 47.85 (C-2, C-2'); 67.25 (C-5, C-5'); 68.47 (C-3, C-3'); 70.07 (C-4, C-4'); 92.17 (C-1, C-1'); 155.97 [$\underline{C}O(NH)_2$]; 169.13 (2 x $\underline{C}OCH_3$); 170.69 (2 x $\underline{C}OCH_3$); 171.61 (2 x $\underline{C}OCH_3$).

m/z calculated: 604.6 *m/z* found(ESI): 627.3 ($+Na^+$)

M.P (°C) = 247-251 (decomposes)

R*f* = 0.13 (2:1 ethyl acetate : hexanes).

Formation of Adenosine diphosphate-tetrabutyl ammonium salt (16) from Adenosine diphosphate-sodium salt.



16

Adenosine diphosphate-tetrabutyl ammonium salt (ADP-TBA) was prepared from the commercially available sodium salt purchased from Sigma-Aldrich. ADP-Na salt

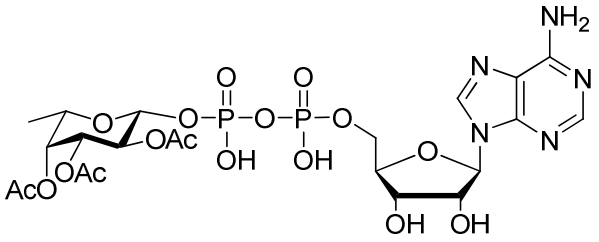
(0.56 g, 1.32 mmol) was dissolved in distilled H_2O (7 mL) and stirred with Amberlite IR-120*H* ion-exchange resin (0.8 g) for 2 hours. The ion-exchange resin was then filtered off and the filtrate's pH adjusted to 6 with an aqueous 40% weight solution of $(Bu)_4NOH$. Extreme care was taken in maintaining a pH due to the deleterious effects of pH's above or below 6. A 15 mL aliquot of the ADP-TBA solution were placed in 50 mL conical tubes and spun in a dry ice acetone bath, thus freezing the material in a thin film around the inner tube. The frozen solution was either kept in a -80 °C freezer or lyophilized over 72 hours to desiccate the ADP-TBA. The solid ADP-TBA salt was stored in a dry vessel at -4 °C until needed. An average molecular weight was obtained by the integration of ^{1}H-NMR signals.

^{1}H NMR ($CDCl_3$) : δ 0.90 (t, 12H, H-4', *J* = 7.32 Hz); 1.33-1.44 (m, 8H, H-3'); 1.56-1.68 (m, 8H, H-2'); 3.30 (t, 8H, H-1', *J* = 7.70 Hz); 4.13-4.21 (m, 0.84H, H-5); 4.22-4.30 (m, 0.45H, H-2); 4.67 (dd, 0.39H, H-3, *J* = 11.37, 11.37 Hz); 4.84 (dd, 0.39H, H-4, *J* = 4.67, 7.96 Hz); 6.20 (s, 0.41H, H-1); 8.21 (s, 0.48H, H-Ar); 8.91 (s, 0.39H, H-Ar).

^{13}P NMR ($CDCl_3$) : δ -3.75 (d, 1P, *J* = 20.75 Hz); -4.75 (d, 1P, *J* = 20.75 Hz).

m/z calculated from integration of proton NMR spectrum: 1048.9

Formation of Adenosine 5-(2',3',4'-tri-*O*-acetyl-β-L-fucopyranosyl)-diphosphate (17) from 1-bromo-2,3,4-tri-O-acetyl-α-L-fucose.



17

Fucosyl bromide **3** (0.20 g, 0.55 mmol) was place in a flame-dried round-bottom flask of suitable size and thoroughly dried under vacuum overnight. Lyophilized adenosine diphosphate tetrabutyl ammonium salt (0.58 g, 0.55 mmol) and several 3 Å molecular sieves were placed in a flame-dried three-neck round-bottom outfitted with a condenser, thermometer, magnetic stir bar, and rubber septa. The apparatus was then evacuated with nitrogen. Anhydrous Et_3N (0.73 mL, 0.55 mmol) and MeCN (17 mL) were added to the reaction vessel and allow to stir at room temperature for 15 minutes. A solution of dry fucosyl bromide **3** in MeCN (11 mL) was added *via* syringe to the reaction vessel and the mixture was permitted to reflux at 75 °C for 30 minutes, monitored by TLC (160:70:5:0.25 $CHCl_3$-MeOH-dH_2O-NH_4OH). After 30 minutes the mixture was filtered to remove the molecular sieves. The products were purified by flash column using 160:70:5:0.25 $CHCl_3$-MeOH-dH_2O-NH_4OH as the eluent. The precipitate that had gathered in the bed of the flash column was then flushed with MeOH doped with a small amount of NH_4OH. MPLC (Medium Pressure Liquid Chromatography 35:35:5:0.15

$CHCl_3$-MeOH-dH_2O-NH_4OH) was used to isolate 0.11 g of 2,3,4-di-*O*-acetyl-1-(adenosine diphospho)-β-L-fucose (29%) as an off-white solid.

^{1}H NMR (D_2O) : δ 1.14 (d, 1H, H-6' *J* = 6.26 Hz); 1.97 (s, 3H, CO$\underline{CH_3}$); 2.12 (s, 3H, CO$\underline{CH_3}$); 2.18 (s, 3H, CO$\underline{CH_3}$); 4.04 (q, 1H, H-5', *J* = 6.23 Hz); 4.22 (s, 2H, H-5); 4.38 (s, 1H, H-4); 4.51 (dd, 1H, H-3, *J* = 4.10, 4.15 Hz); 4.75 (dd, 1H, H-2, *J* = 5.34, 5.38 Hz). 5.04-5.12 (m, 2H, H-2', H-3'); 5.22-5.28 (m, 2H, H-1', H-4'); 6.11 (d, 1H, H-1, *J* = 5.67 Hz); 8.18 (s, 1H, H-Ar); 8.47 (s, 1H, H-Ar).

^{13}C NMR (D_2O) : δ 14.92 (C-6'); 19.88 (CO$\underline{CH_3}$); 19.94 (CO$\underline{CH_3}$); 20.36 (CO$\underline{CH_3}$); 65.26 (C-5); 69.86 (C-3'); 69.99 (C-5'); 70.30 (C-3); 70.68 (C-4'); 71.38 (C-2'); 74.21 (C-2); 83.75 (C-4); 86.82 (C-1); 95.35 (C-1') 139.89 (C-Ar); 152.80 (C-Ar); 155.48 (C-Ar); 172.67, ($\underline{C}OCH_3$); 173.17 ($\underline{C}OCH_3$); 173.61 ($\underline{C}OCH_3$).

^{31}P NMR (D_2O) : δ -9.96 (d, 1P, *J* = 20.73 Hz); -11.29 (d, 1P, *J* = 20.29 Hz)

m/z calculated: 699.4 *m/z* found(ESI): N/A

R*f* = 0.46 (35 : 35 : 5 : 0.15 $CHCl_3$: MeOH : dH_2O : NH_4OH).

Bromination of α-1,3,4-tri-*O*-acetyl-2-*N*-(D_3)-acetyl-L-fucose (12).

1,3,4-Tri-*O*-acetyl-2-*N*-(D_3)-acetyl-α-L-fucose (**12**, 0.93 g, 2.81 mmol) was placed in a suitable size flame-dried round-bottom flask and permitted to dry under vacuum for at least 24 hours. The reaction vessel was outfitted with a magnetic stir bar and rubber septum then placed under a nitrogen atmosphere. The tetra-*O*-acetyl-L-fucose was

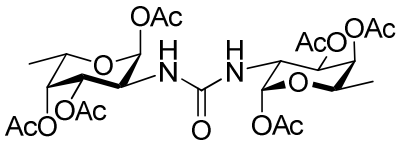
dissolved in a solution of 33% HBr in glacial acetic acid (4 mL) and cooled with an ice bath. The reaction was allowed to stir until consumption of the starting material, 5-6 hours, was observed visually and judged by TLC (20:1 $CHCl_3$-MeOH). The reaction mixture was then diluted with CH_2Cl_2 (30 mL) and transferred to a suitable size Erlenmeyer flask containing a stir bar and ice. The Erlenmeyer was placed in an ice bath on top of a stir plate while chilled saturated $NaHCO_3$ was added until neutral, after which the product was extracted with CH_2Cl_2 (3 x 30 mL) and kept in an ice bath. The combined organic extracts were then washed with distilled water (2 x 40 mL). The organic phase was then dried with $MgSO_4$, filtered, and concentrated *in vacuo* to provide a complex mixture of two anomeric compounds.

General procedure for the synthesis of bis-sugar-derived ureas from sugar azides employing the aza-Wittg reaction.

One equivalent of sugar azide was placed into a flame-dried round-bottom of suitable size outfitted with a magnetic stir bar and rubber septum with pressure outlet. The sugar was dissolved in anhydrous THF (0.1g/mL). Carbon dioxide was then bubbled through the sugar solution by cannula from another vessel containing dry ice submerged in toluene. A solution of bis(diphenylphosphino) ethane (DPPE, 0.65 eq) in anhydrous THF (0.1 g/mL) was added dropwise to the reaction vessel, at room temperature, while continuing to bubble CO_2. The mixture was allowed to stir for 2 hours and monitored by TLC. After the TLC showed consumption of the phospho-aza ylide, saturated $NaHCO_3$ was added and the reaction was permitted to stir overnight. The THF was taken off *in vacuo* and the remaining aqueous phase was extracted three times with $CHCl_3$. The

combined organic extracts were then washed with dH_2O. The organic phase was then dried with $MgSO_4$, filtered, concentrated, and purified by flash column chromatography and/or recrystallization.

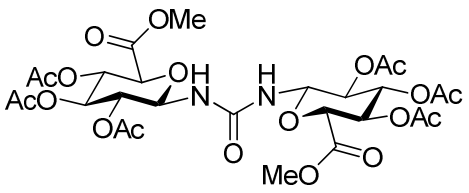
Formation of bis(1,3,4-tri-*O*-acetyl-α-L-fucos-2-yl) urea 15 from 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α-L-fucose (8).



15

bis(1,3,4-tri-*O*-acetyl-α-L-fucos-2-yl) Urea **15** was prepared from azidoacetyl-L-fucose **8** (0.32 g, 1.03 mmol), DPPE (0.27 g, 0.67 mmol) and an excess of CO_2 according to the protocol previously mentioned for the synthesis of bis-glycosyl ureas from glycosyl azides. Purification of the crude material was performed by flash column in a solution of ethyl acetate and hexanes (2:1). The compound of readily recrystallized in isopropanol for further purification. A compound migrating with an R*f* = 0.13 was isolated (0.27 g, 87%) as a white solid and confirmed by NMR spectroscopy, mass spectrometry as glycosyl urea **15**. Vapor diffusion of carbon tetrachloride into a solution of **15** and ethyl acetate provided a crystal sufficient for X-ray diffractometry.

Formation of bis(2,3,4-tri-*O*-acetyl-β-glucouronosyl) urea 18 from 2,3,4-tri-*O*-acetyl-β-glucouronosyl azide.



18

bis(2,3,4-tri-*O*-acetyl-β-glucouronsyl) Urea **18** was prepared from 2,3,4-tri-*O*-acetyl-glucouronosyl azide (0.36 g, 1.00 mmol), DPPE (0.27 g, 0.67 mmol) and an excess of CO_2 according to the protocol previously mentioned for the synthesis of bis-glycosyl ureas from sugar azides. The crude reaction mixture was purified by flash column chromatography (2:1 ethyl acetate-hexanes); two compounds were isolated. The first compound, with an R*f* of 0.37, was the minor product. The second compound had an R*f* of 0.23 and was determined to be the more polar glycosyl urea. The small amount of the less polar byproduct was crystallized for X-ray diffractometry by the diffusion of hexanes into a solution of toluene and byproduct **19**.

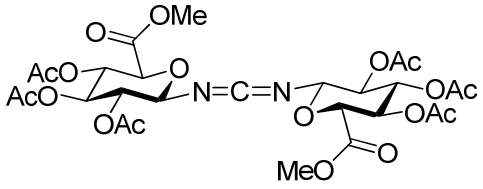
^{1}H NMR ($CDCl_3$) : δ 2.03 (s, 6H, 2 x CO$\underline{CH_3}$); 2.04 (s, 6H, 2 x CO$\underline{CH_3}$); 2.08 (s, 6H, 2 x CO$\underline{CH_3}$); 3.74 (s, 6H, 2 x OMe); 4.15 (d, 2H, H-5, H-5', *J* = 10.03 Hz); 4.93 (dd, 2H, H-2, H-2', *J* = 9.54, 9.54 Hz); 5.10 (dd, 2H, H-1, H-1', *J* = 9.41, 9.41 Hz); 5.23 (dd, 2H, H-4, H-4', *J* = 9.89, 9.89 Hz); 5.36 (dd, 2H, H-3, H-3', *J* = 9.54, 9.54 Hz); 6.30 (d, 2H, H-N, H-N', *J* = 9.28 Hz).

^{13}C NMR ($CDCl_3$) : δ 20.47 (2 x CO$\underline{CH_3}$); 20.60 (2 x CO$\underline{CH_3}$); 20.65 (2 x CO$\underline{CH_3}$); 53.06 (2 x O$\underline{CH_3}$); 69.40 (C-2, C-2'); 69.62 (C-4, C-4'); 72.12 (C-3, C-3'); 73.54 (C-5, C-

5'); 79.88 (C-1, C-1'); 155.32 [$\underline{C}O(NH)_2$]; 167.95 [2 x ($\underline{C}O$)OCH_3]; 169.63 (2 x $\underline{C}OCH_3$); 169.75 (2 x $\underline{C}OCH_3$); 170.81 (2 x $\underline{C}OCH_3$).

m/z calculated: 692.6 *m/z* found (ESI): 692.2

R*f* = 0.23 (2:1 ethyl acetate : hexanes)



19

^{1}H NMR ($CDCl_3$) : δ 2.02 (s, 6H, 2 x $CO\underline{CH_3}$); 2.03 (s, 6H, 2 x $CO\underline{CH_3}$); 2.06 (s, 6H, 2 x $CO\underline{CH_3}$); 3.78 (s, 6H, 2 x OMe); 4.06-4.16 (m, 2H, H-5, H-5'); 4.81 (d, 2H, H-1, H-1', *J* = 8.53 Hz); 4.90-5.05 (m, 2H, H-2, H-2'); 5.12-5.39 (m, 4H, H-3, H-3', H-4, H-4').

^{13}C NMR ($CDCl_3$) : δ 20.44 (2 x $CO\underline{CH_3}$); 20.51 (2 x $CO\underline{CH_3}$); 20.55 (2 x $CO\underline{CH_3}$); 52.99 (2 x $O\underline{CH_3}$); 69.06 (C-4, C-4'); 72.06 (C-3, C-3'); 72.08 (C-2, C-2'); 74.25 (C-5, C-5'); 84.06 (C-1, C-1'); 137.25 ($\underline{C}N_2$); 166.51 [2 x ($\underline{C}O$)OCH_3]; 169.14 (2 x $\underline{C}OCH_3$); 169.29 (2 x $\underline{C}OCH_3$); 170.03 (2 x $\underline{C}OCH_3$).

R*f* = 0.37 (2:1 ethyl acetate : hexanes)

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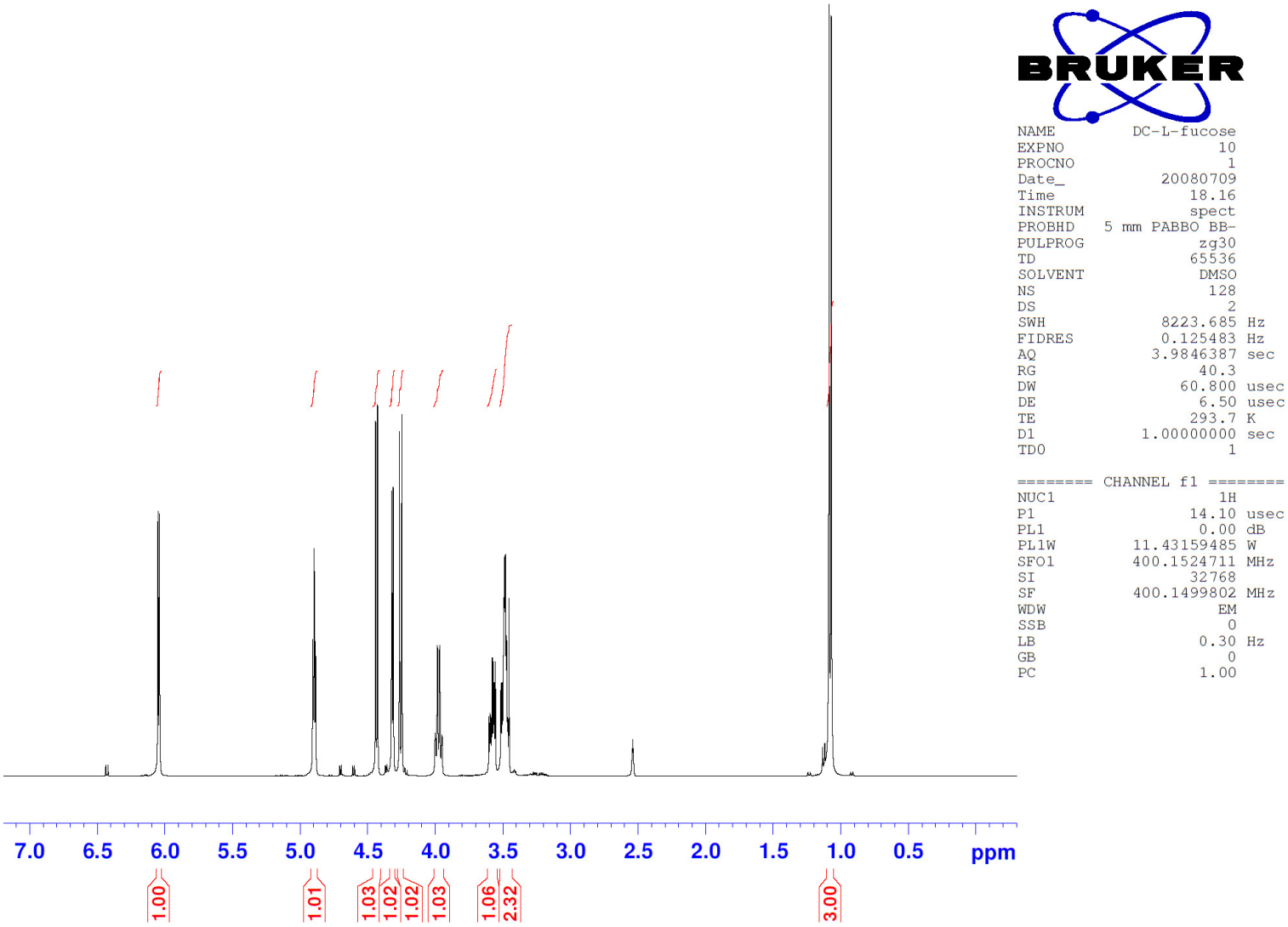
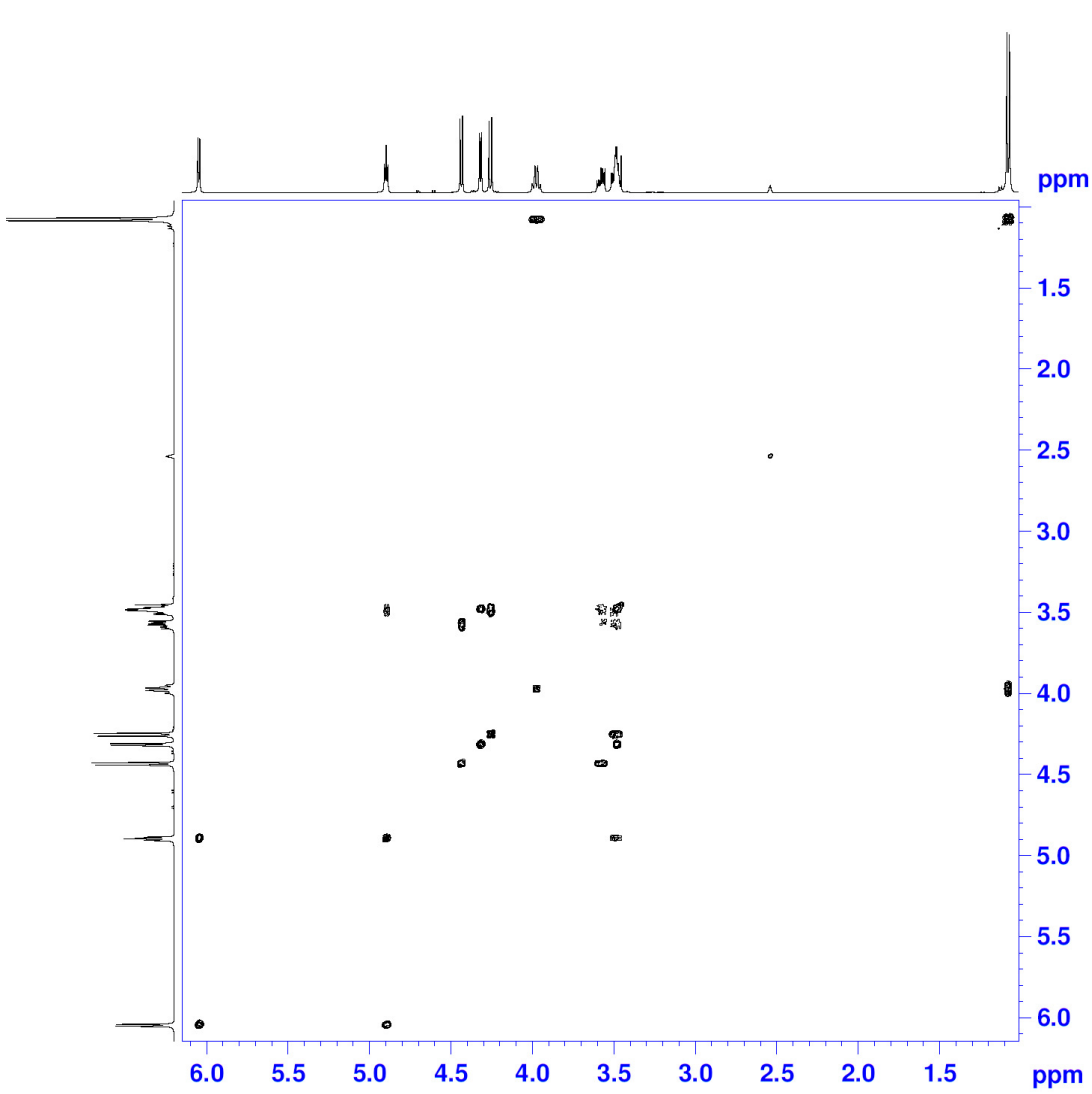
Appendix A

NMR and Mass Spectra



NAME	DC-L-fucose
EXPNO	10
PROCNO	1
Date_	20080709
Time	18.16
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	DMSO
NS	128
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	40.3
DW	60.800 usec
DE	6.50 usec
TE	293.7 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	400.1499802 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Figure 24 : ^{1}H NMR spectrum of α-L-fucose (**1**)



BRUKER

NAME	DC-L-fucose
EXPNO	11
PROCNO	1
Date_	20080709
Time	18.17
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	cosygpqf
TD	2048
SOLVENT	DMSO
NS	1
DS	8
SWH	2890.173 Hz
FIDRES	1.411217 Hz
AQ	0.3543540 sec
RG	18
DW	173.000 usec
DE	6.50 usec
TE	293.6 K
D0	0.00000300 sec
D1	1.32428098 sec
D13	0.00000400 sec
D16	0.00010000 sec
IN0	0.00034600 sec
======== CHANNEL f1 ========	
NUC1	1H
P0	14.10 usec
P1	14.10 usec
PL1	0.00 dB
PL1W	11.43159485 W
SFO1	400.1511918 MHz
====== GRADIENT CHANNEL =====	
GPNAM1	SINE.100
GPZ1	10.00 %
P16	1000.00 usec
ND0	1
TD	256
SFO1	400.1512 MHz
FIDRES	11.289740 Hz
SW	7.223 ppm
FnMODE	QF
SI	1024
SF	400.1499802 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.40
SI	1024
MC2	QF
SF	400.1499802 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

Figure 25 : COSY NMR spectrum of α -L-fucose (**1**)

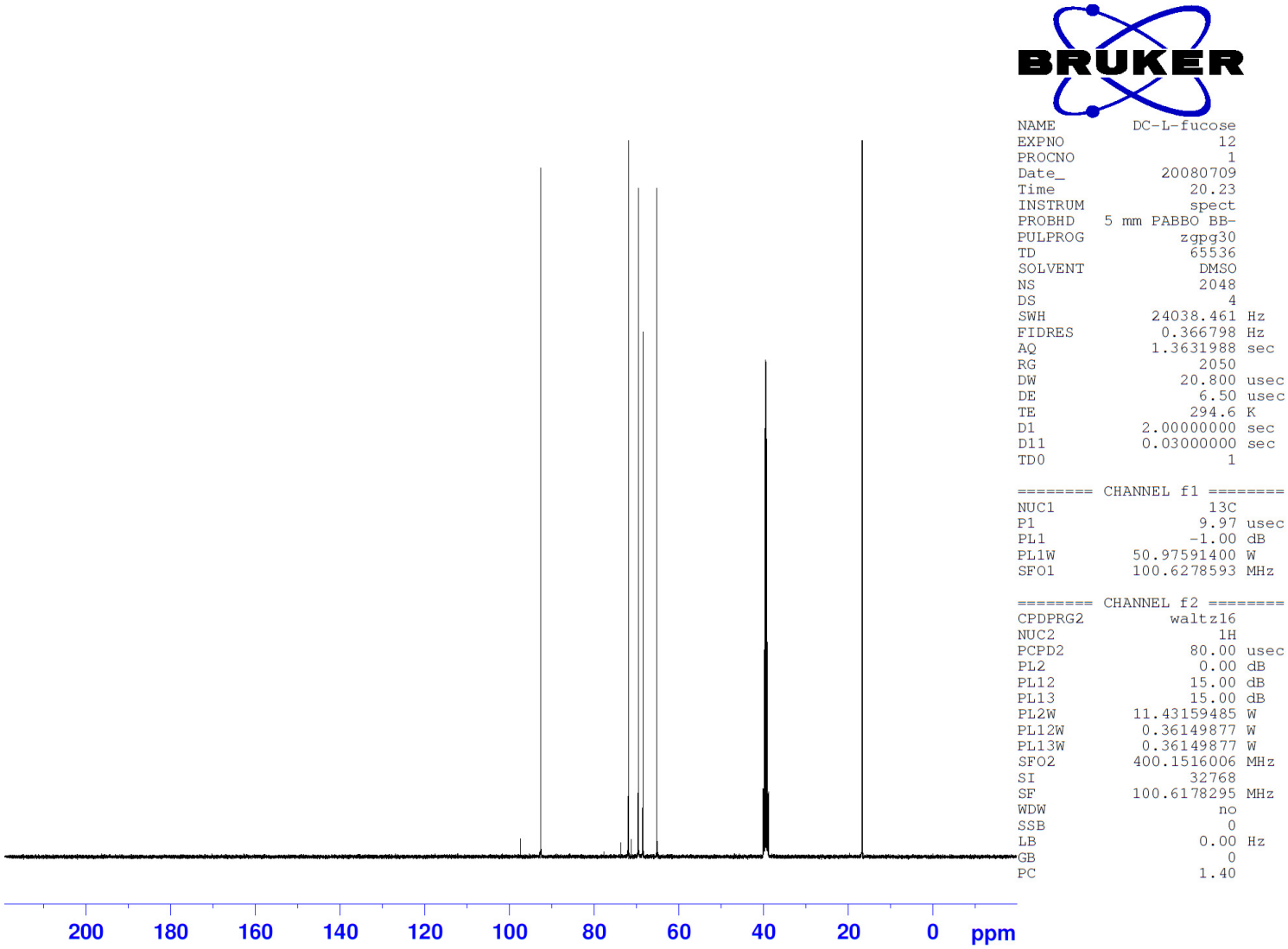
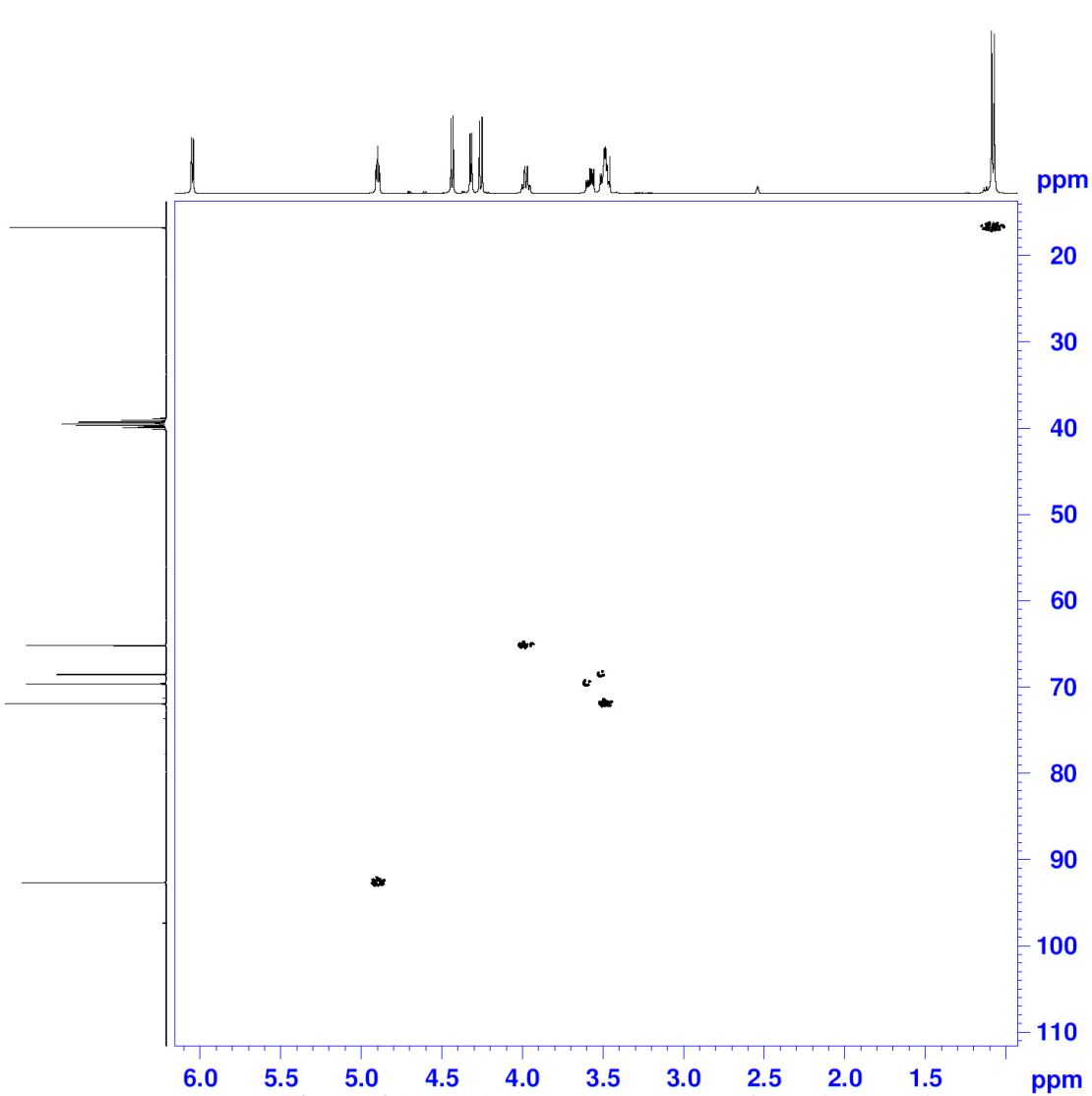


Figure 26 : ^{13}C NMR spectrum of α -L-fucose (**1**)




```
NAME                DC-L-fucose
EXPNO                        13
PROCNO                        1
Date_                  20080709
Time                      20.25
INSTRUM                   spect
PROBHD    5 mm PABBO BB-
PULPROG          hsqcetgpsi2
TD                         1024
SOLVENT                  DMSO
NS                            2
DS                           16
SWH                   2890.173 Hz
FIDRES                2.822435 Hz
AQ                    0.1772020 sec
RG                         2050
DW                     173.000 usec
DE                       6.50 usec
TE                      294.1 K
CNST2                145.0000000
D0                    0.00000300 sec
D1                    1.41889906 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                400.1511918 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                  400.1499802 MHz
WDW                       QSINE
SSB                           2
LB                         0.00 Hz
GB                            0
PC                         1.40
SI                         1024
MC2              echo-antiecho
SF                  100.6178295 MHz
WDW                       QSINE
SSB                           2
LB                         0.00 Hz
GB                            0
```

Figure 27 : HSQC NMR spectrum of α-L-fucose (**1**)

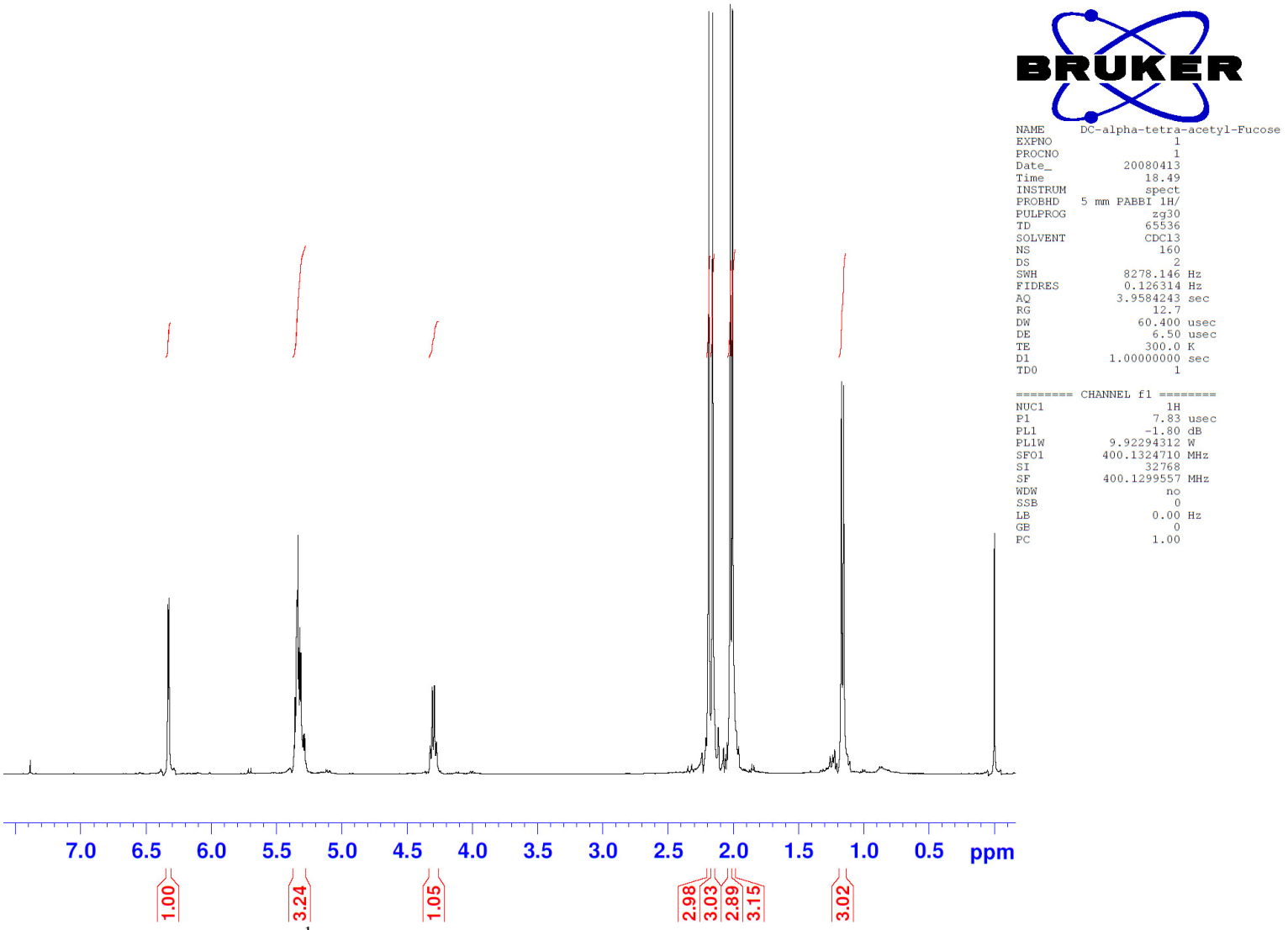


Figure 28 : ^{1}H NMR spectrum of 1,2,3,4-tetra-*O*-acetyl-α-L-fucose (**2**)

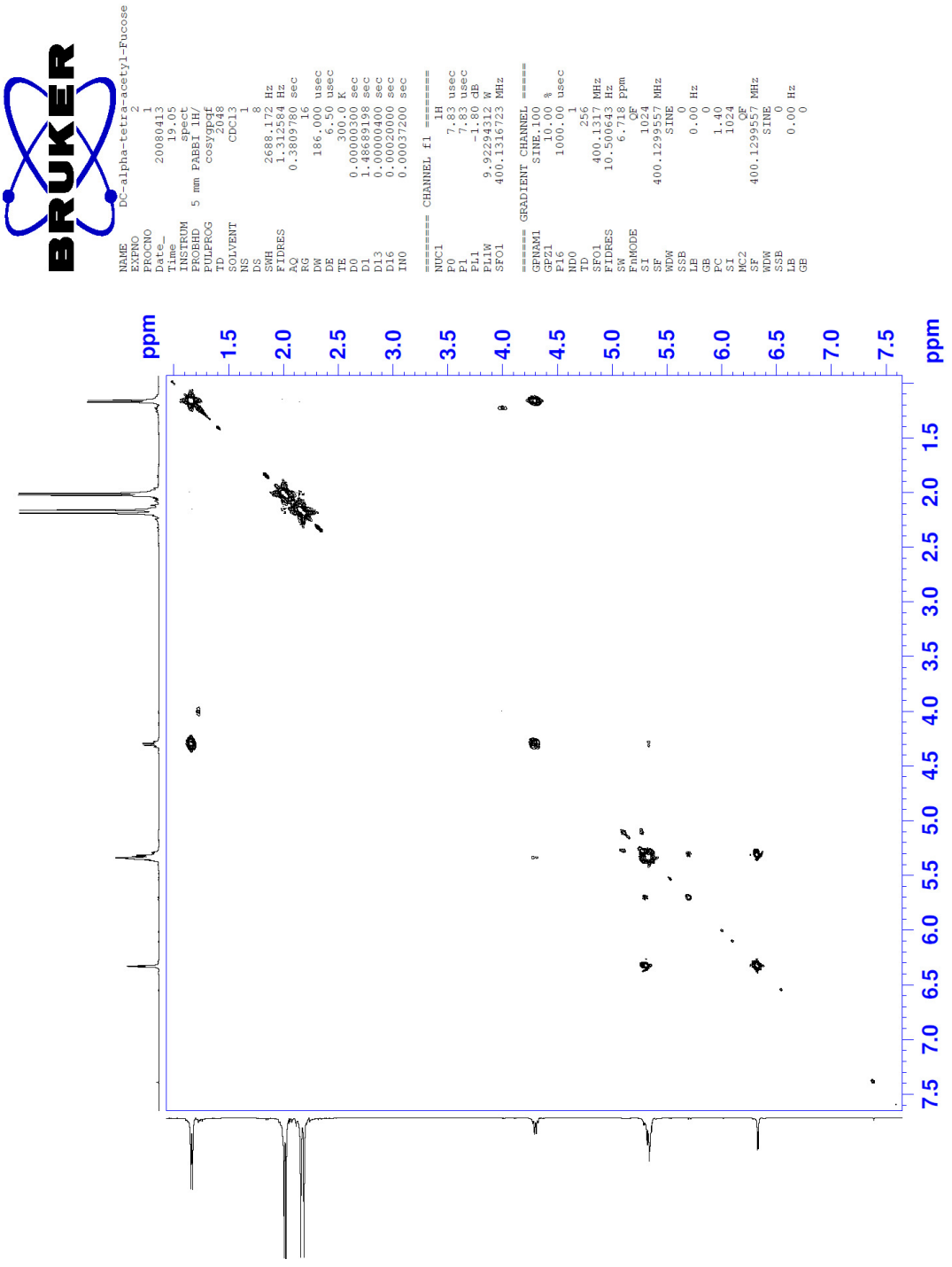
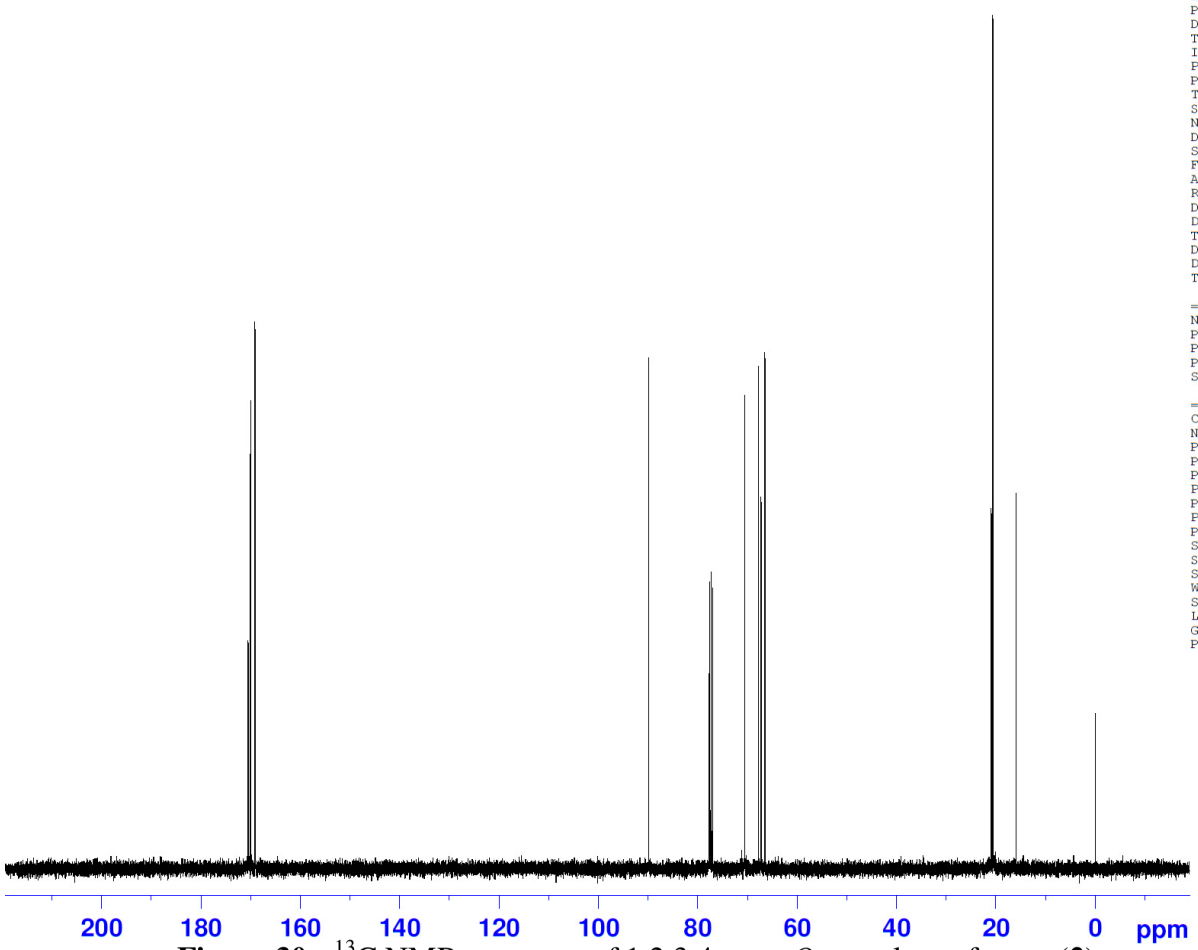


Figure 29 : COSY NMR spectrum of 1,2,3,4-tetra-*O*-acetyl-α-L-fucose (**2**)




```
NAME        DC-alpha-tetra-acetyl-Fucose
EXPNO                                  3
PROCNO                                 1
Date_                           20080413
Time                               19.37
INSTRUM                            spect
PROBHD     5 mm PABBI 1H/
PULPROG                         zgpg30
TD                                 65536
SOLVENT                         CDCl3
NS                                   557
DS                                     4
SWH                          23980.814 Hz
FIDRES                        0.365918 Hz
AQ                           1.3664756 sec
RG                                   128
DW                              20.850 usec
DE                               6.50 usec
TE                              300.0 K
D1                          2.00000000 sec
D11                         0.03000000 sec
TD0                                    1

======== CHANNEL f1 ========
NUC1                               13C
P1                              14.90 usec
PL1                             -3.78 dB
PL1W                       69.57576752 W
SFO1                      100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                    waltz16
NUC2                               1H
PCPD2                           75.00 usec
PL2                             -1.80 dB
PL12                            17.72 dB
PL13                           120.00 dB
PL2W                       9.92294312 W
PL12W                      0.11082572 W
PL13W                      0.00000000 W
SFO2                      400.1316005 MHz
SI                                32768
SF                        100.6127565 MHz
WDW                                   no
SSB                                    0
LB                               0.00 Hz
GB                                     0
PC                               1.40
```

Figure 30 : ^{13}C NMR spectrum of 1,2,3,4-tetra-*O*-acetyl-α-L-fucose (**2**)

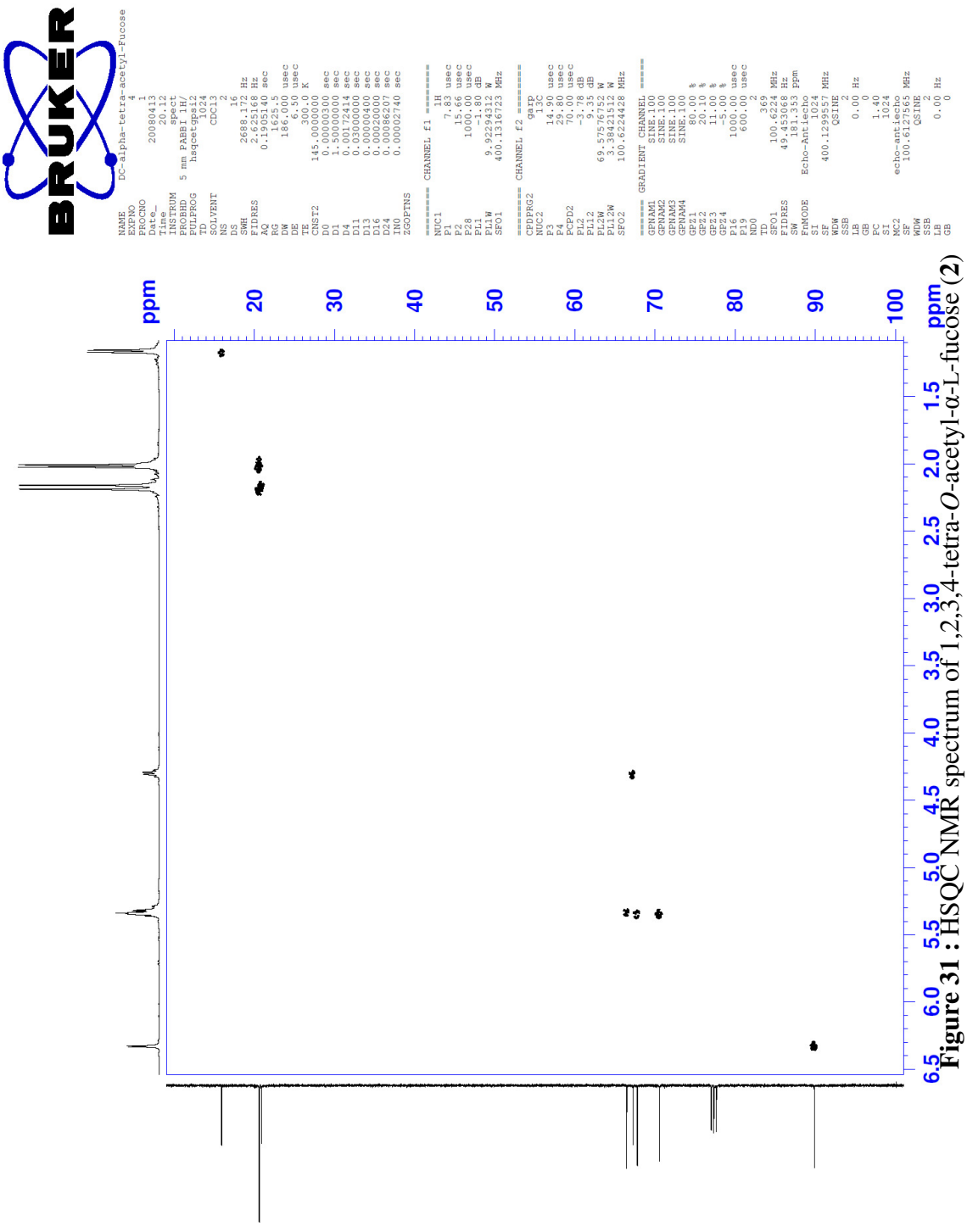


Figure 31 : HSQC NMR spectrum of 1,2,3,4-tetra-*O*-acetyl-α-L-fucose (**2**)

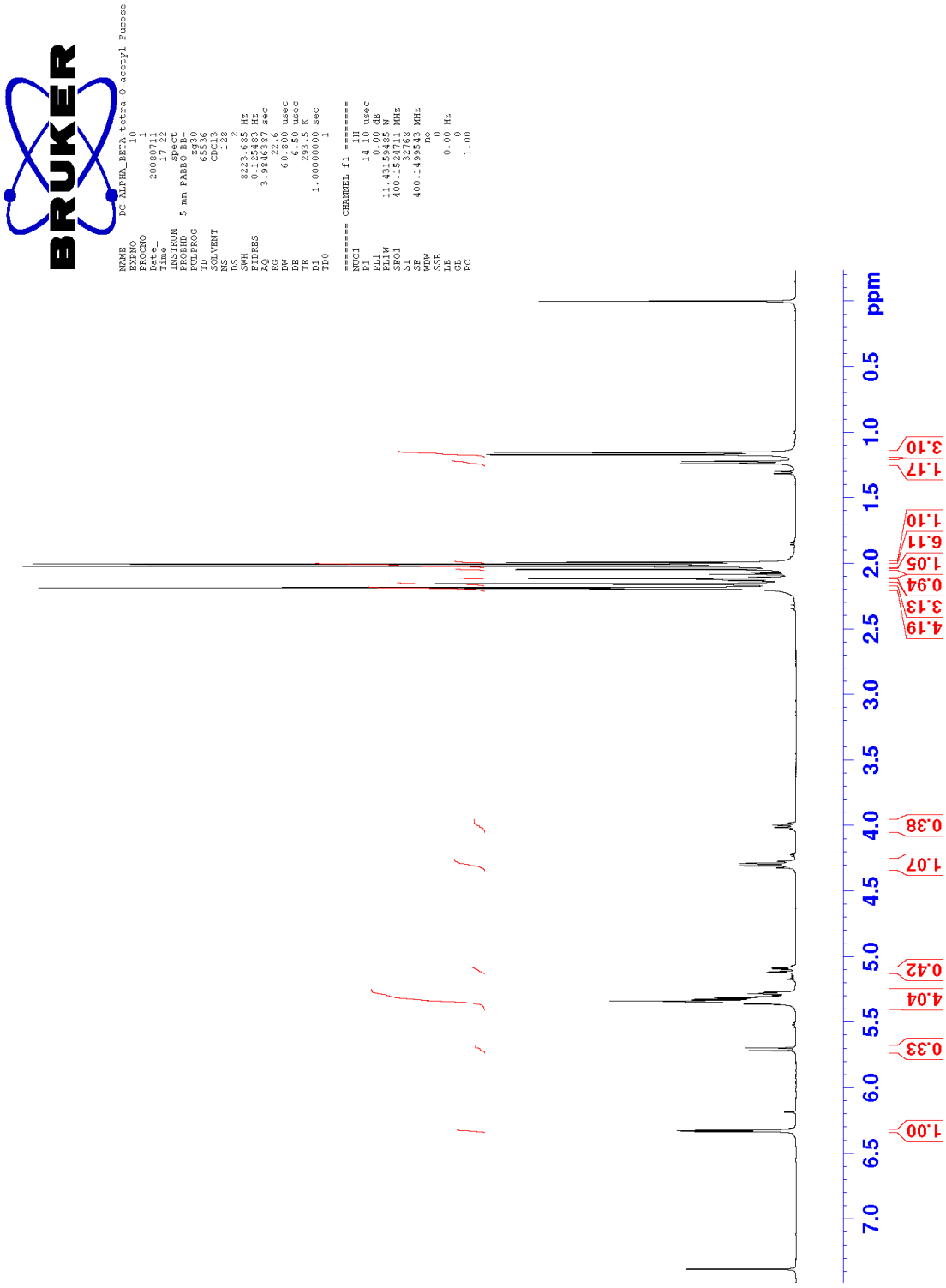


Figure 32 : ^{1}H NMR spectrum of 1,2,3,4-tetra-*O*-acetyl-α,β-L-fucose (**2**)

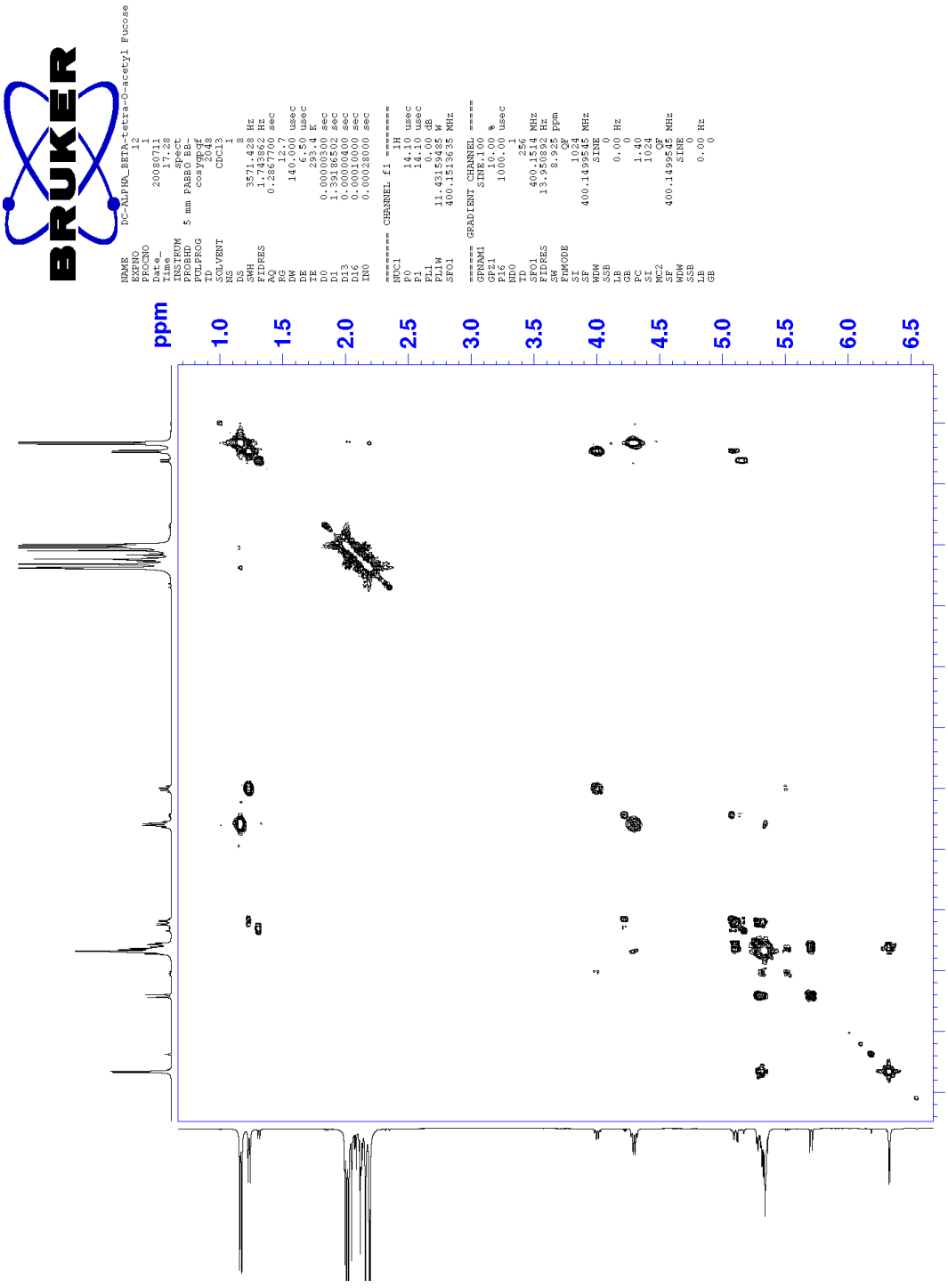
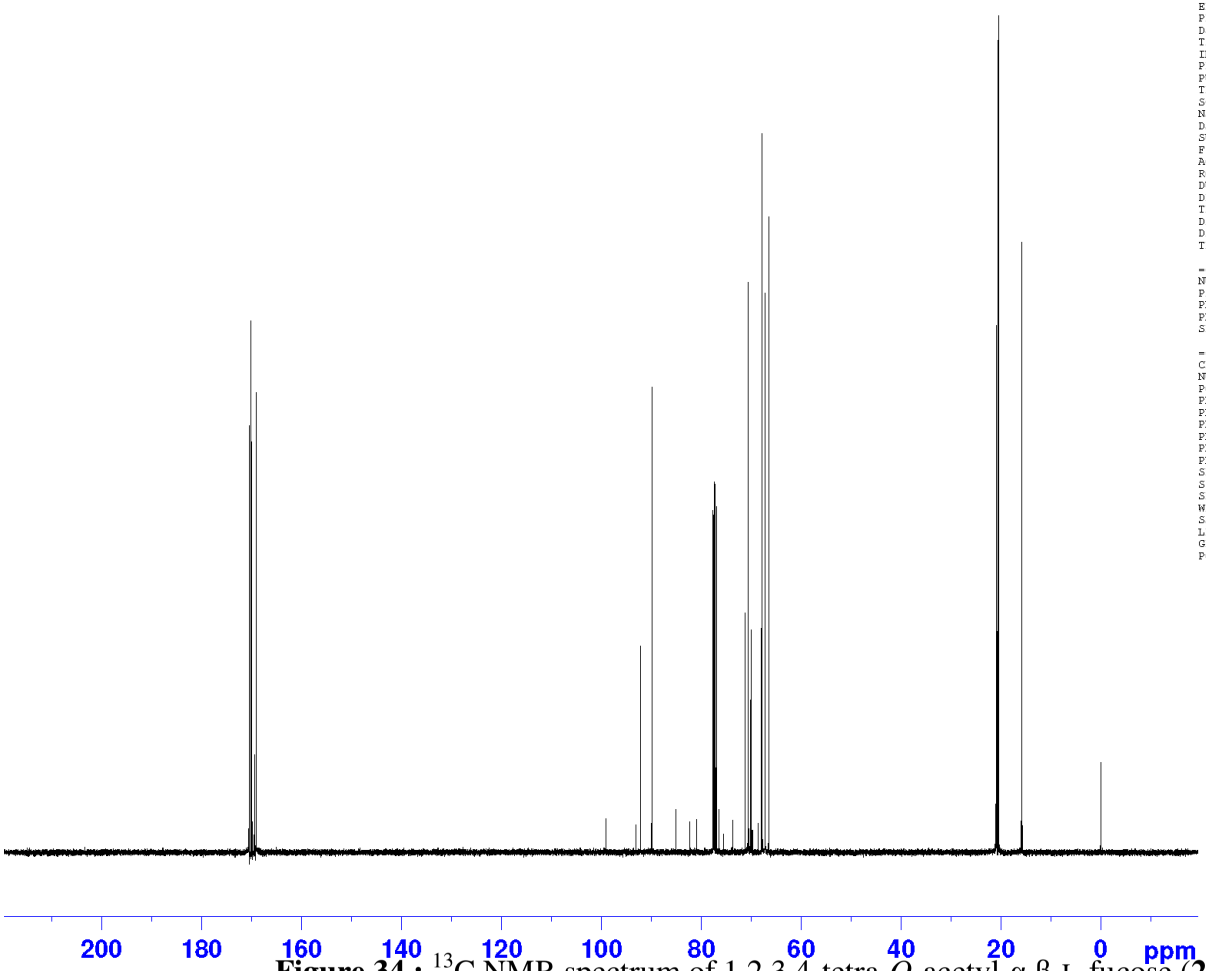


Figure 33 : COSY NMR spectrum of 1,2,3,4-tetra-*O*-acetyl-α,β-L-fucose (**2**)

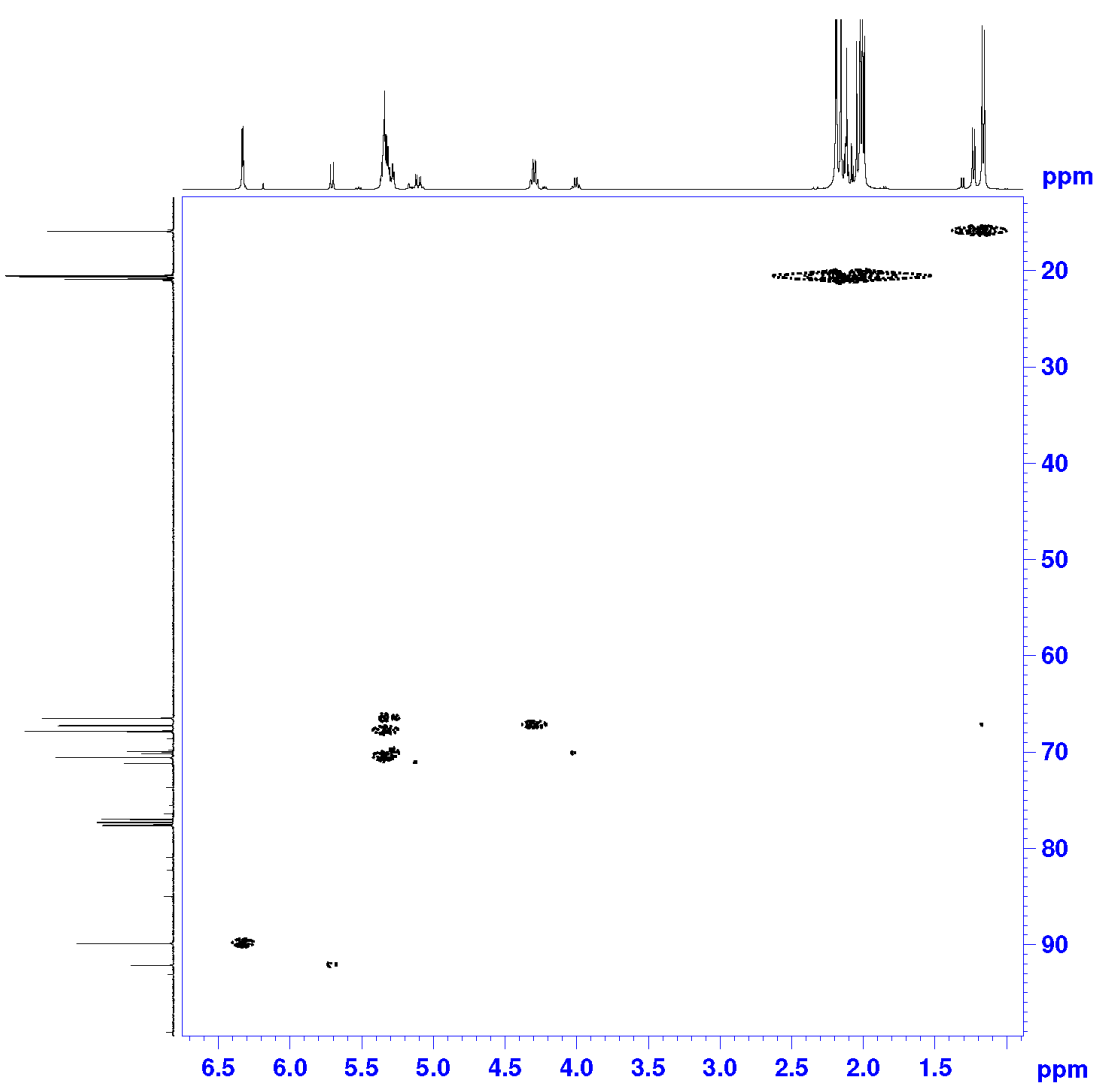



```
NAME      DC-ALPHA_BETA-tetra-O-acetyl Fucose
EXPNO                 13
PROCNO                 1
Date_           20080711
Time               18.36
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 2050
DW               20.800 usec
DE                6.50 usec
TE               294.6 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         100.6177845 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.40
```

Figure 34 : ^{13}C NMR spectrum of 1,2,3,4-tetra-*O*-acetyl-α,β-L-fucose (**2**)



BRUKER

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PROCNO                      1
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INSTRUM                 spect
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PULPROG       hsqcetgpsi2
TD                       1024
SOLVENT                 CDCl3
NS                          2
DS                         16
SWH                  3571.428 Hz
FIDRES               3.487723 Hz
AQ                  0.1434100 sec
RG                       2050
DW                    140.000 usec
DE                      6.50 usec
TE                     294.0 K
CNST2               145.0000000
D0                   0.00000300 sec
D1                   1.45269096 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
2GOPTNS

======== 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               400.1513635 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                400.1499545 MHz
WDW                     QSINE
SSB                         2
LB                       0.00 Hz
GB                          0
PC                       1.40
SI                       1024
MC2            echo-antiecho
SF                100.6177845 MHz
WDW                     QSINE
SSB                         2
LB                       0.00 Hz
GB                          0
```

Figure 35 : HSQC NMR spectrum of 1,2,3,4-tetra-*O*-acetyl-α,β-L-fucose (**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
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Capillary Exit	84.8 Volt	Skim 1	17.4 Volt	Trap Drive	37.5	Auto MS/MS	Off

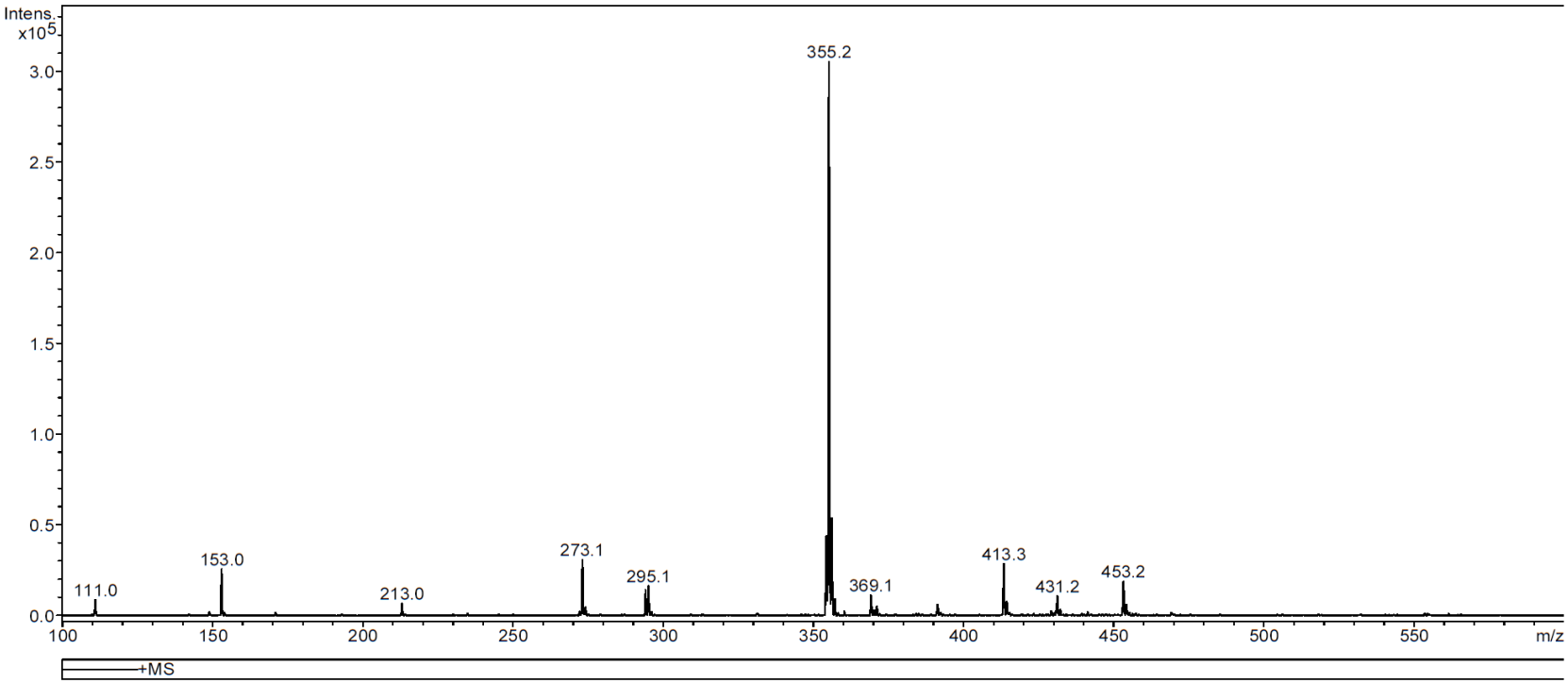


Figure 36 : Mass spectrum of 1,2,3,4-tetra-*O*-acetyl-L-fucose (**2**)

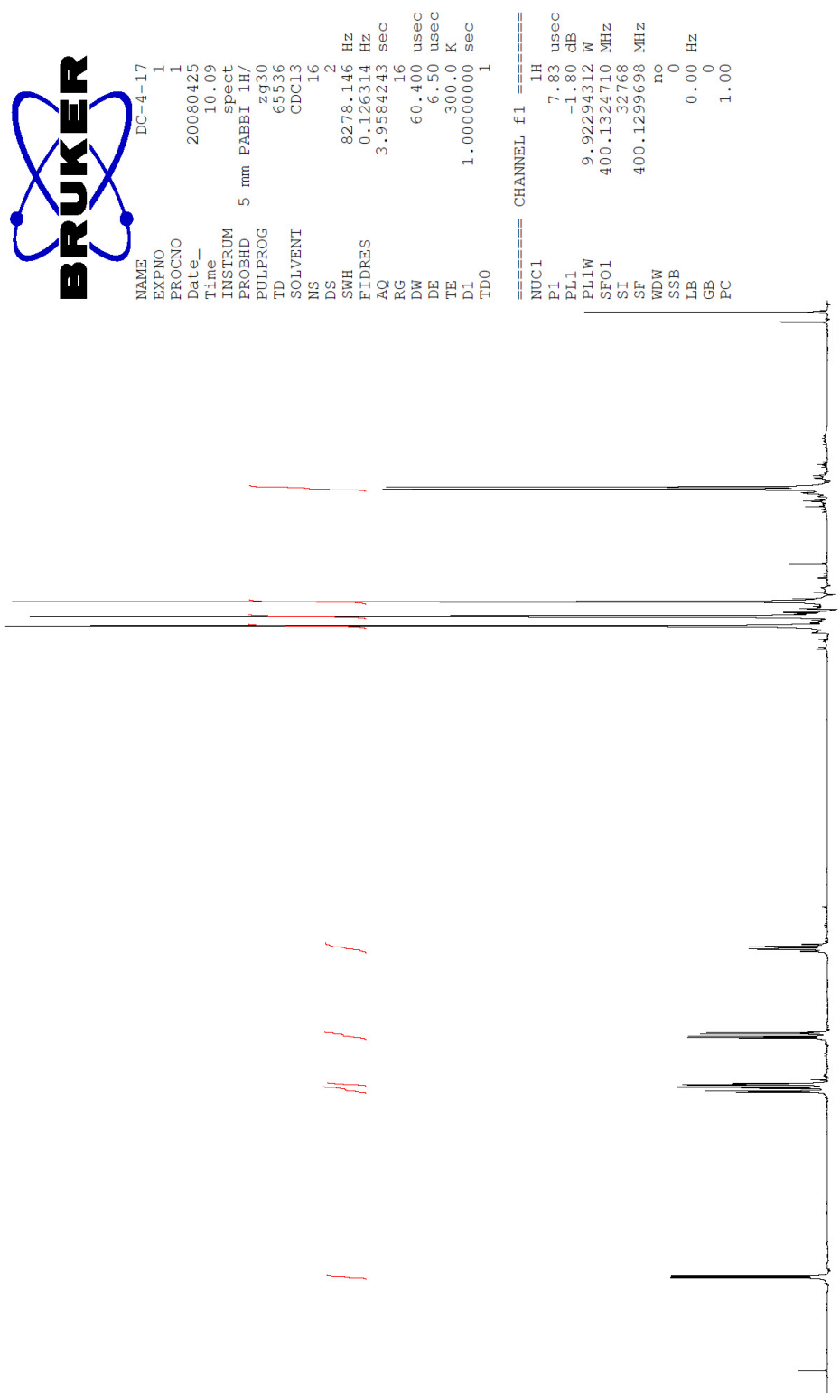


Figure 37 : ^{1}H NMR spectrum of 1-bromo-2,3,4-tri-*O*-acetyl-α-L-fucose (**3**)

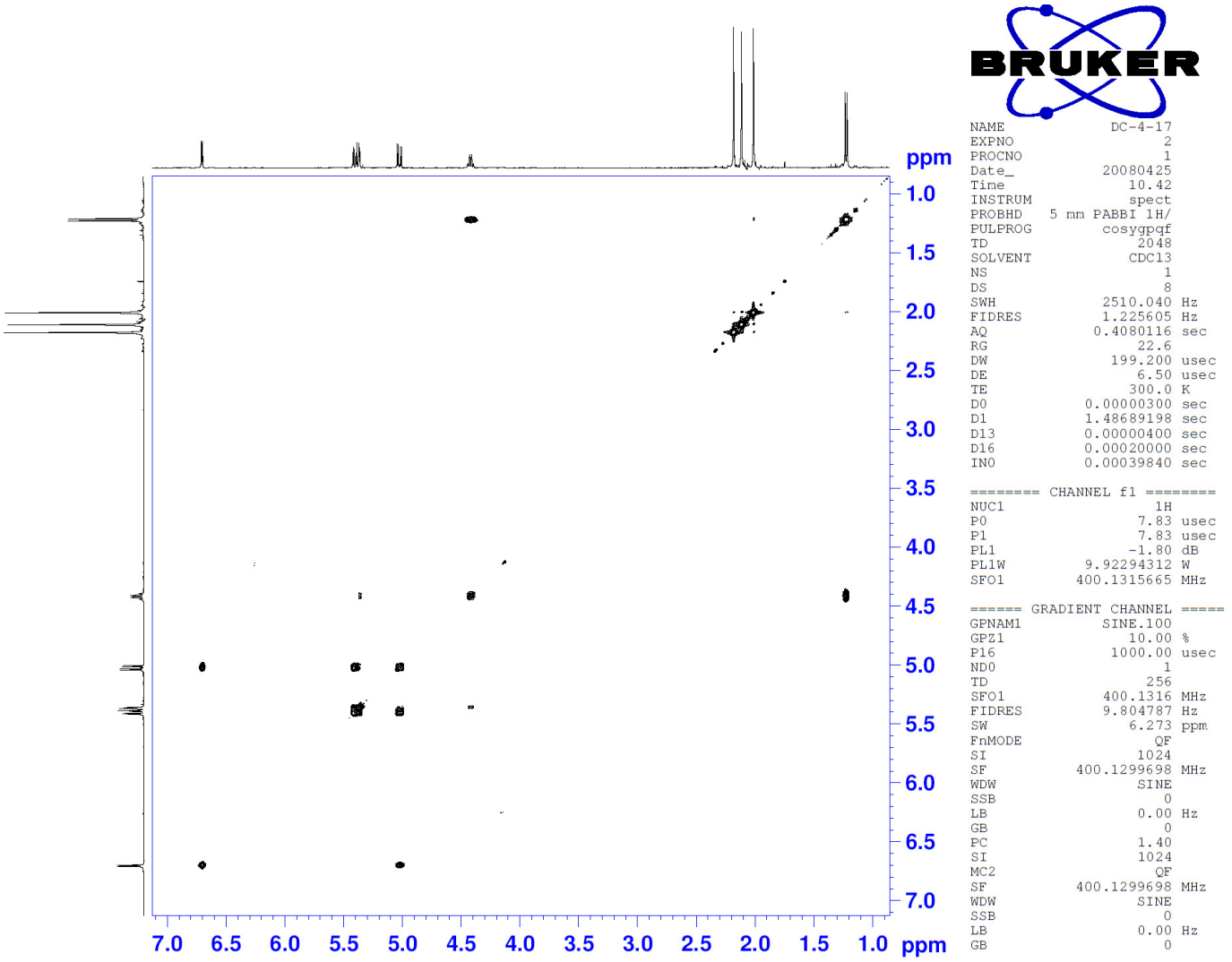


Figure 38 : COSY NMR spectrum of 1-bromo-2,3,4-tri-*O*-acetyl-α-L-fucose (**3**)

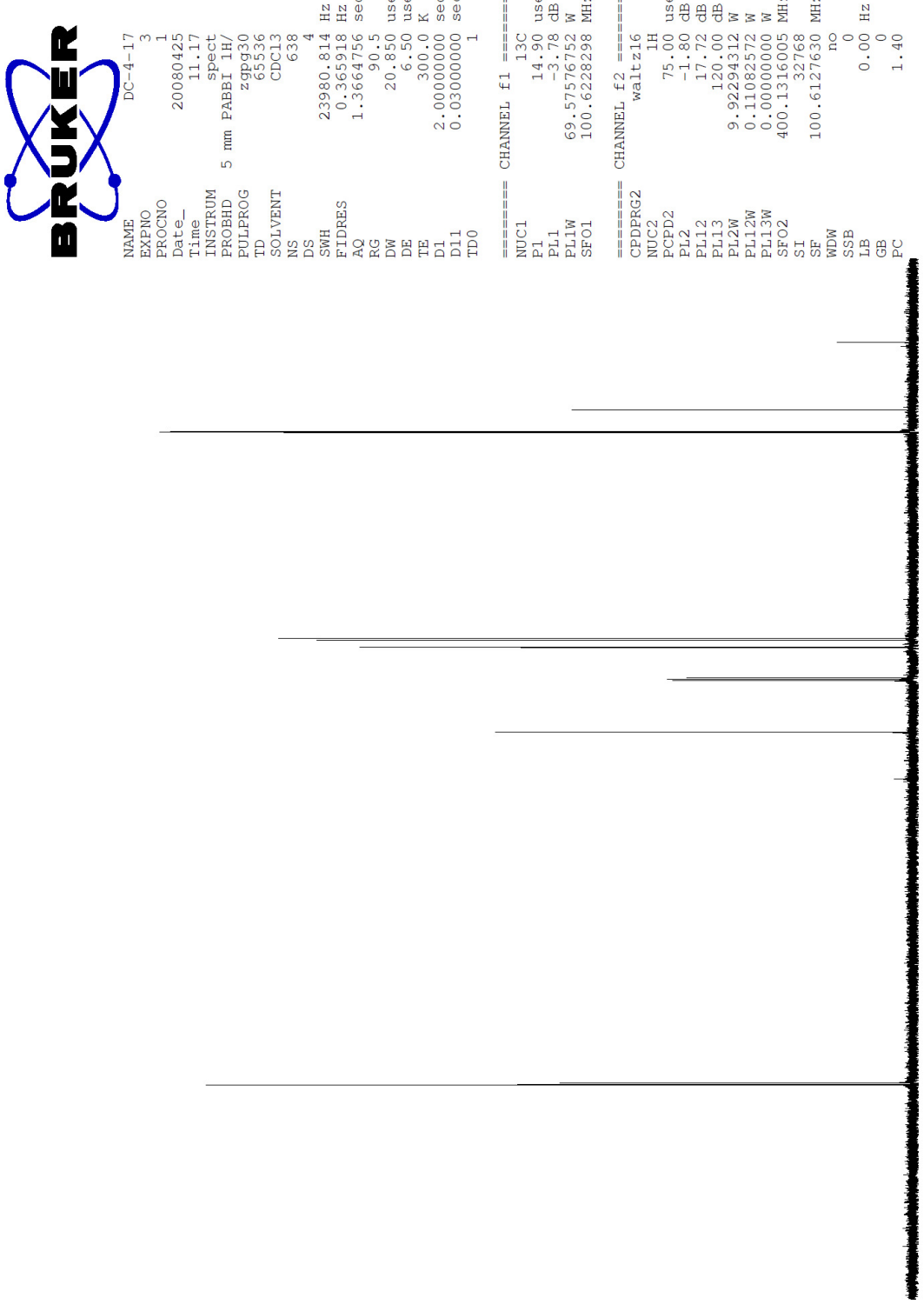


Figure 39 : ^{13}C NMR spectrum of 1-bromo-2,3,4-tri-*O*-acetyl-α-L-fucose (**3**)

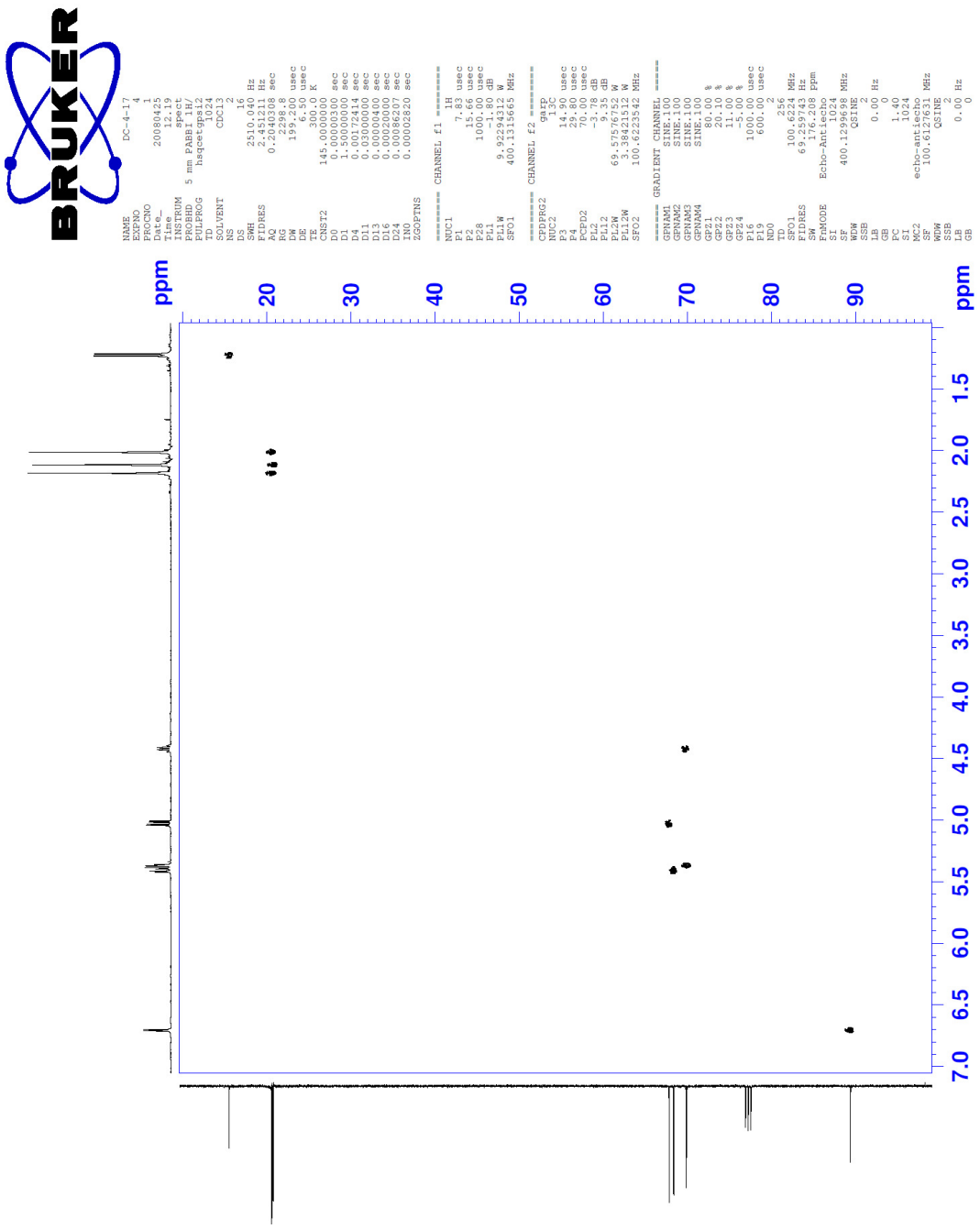


Figure 40 : HSQC NMR spectrum of 1-bromo-2,3,4-tri-*O*-acetyl-α-L-fucose (**3**)

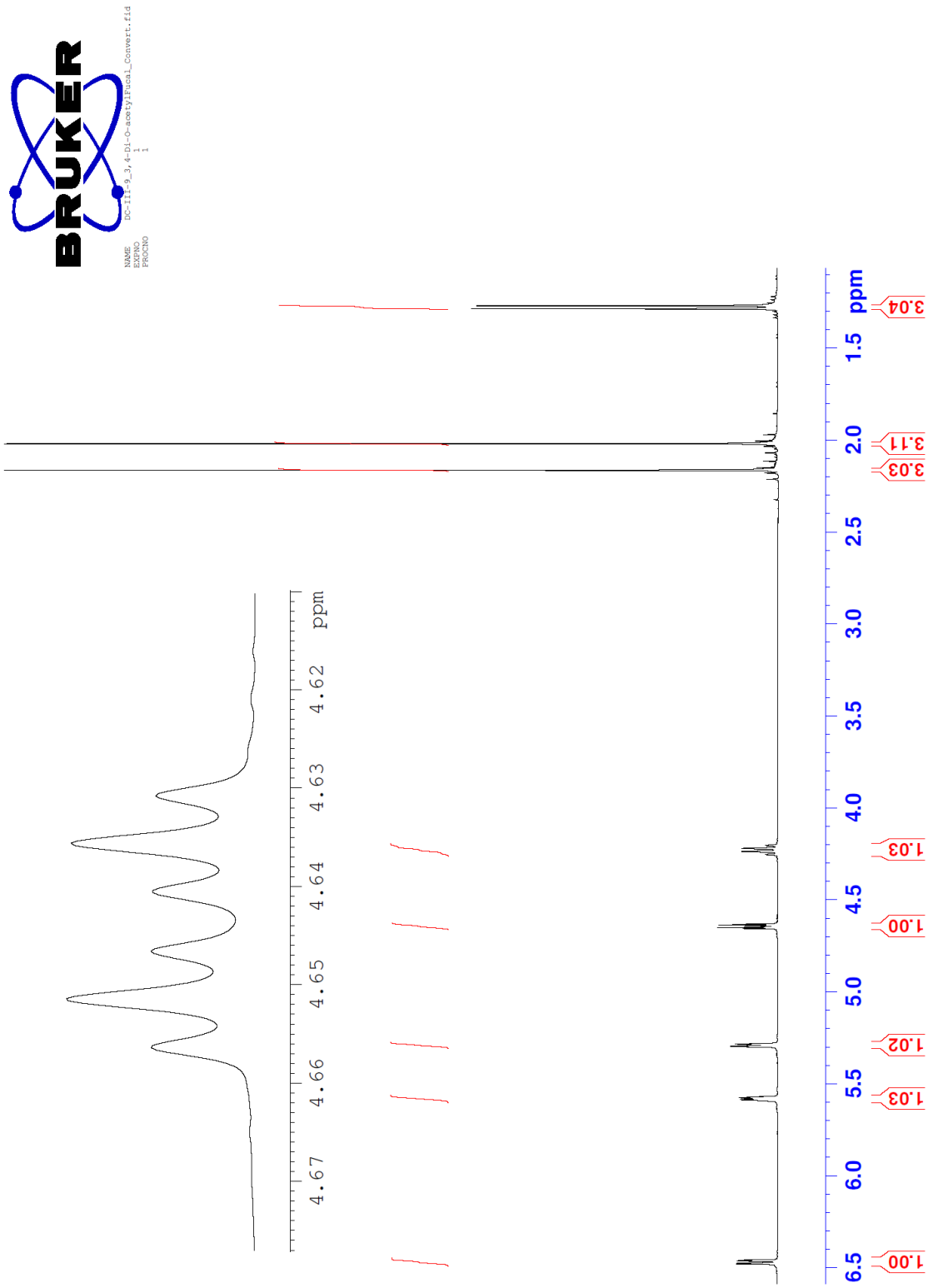
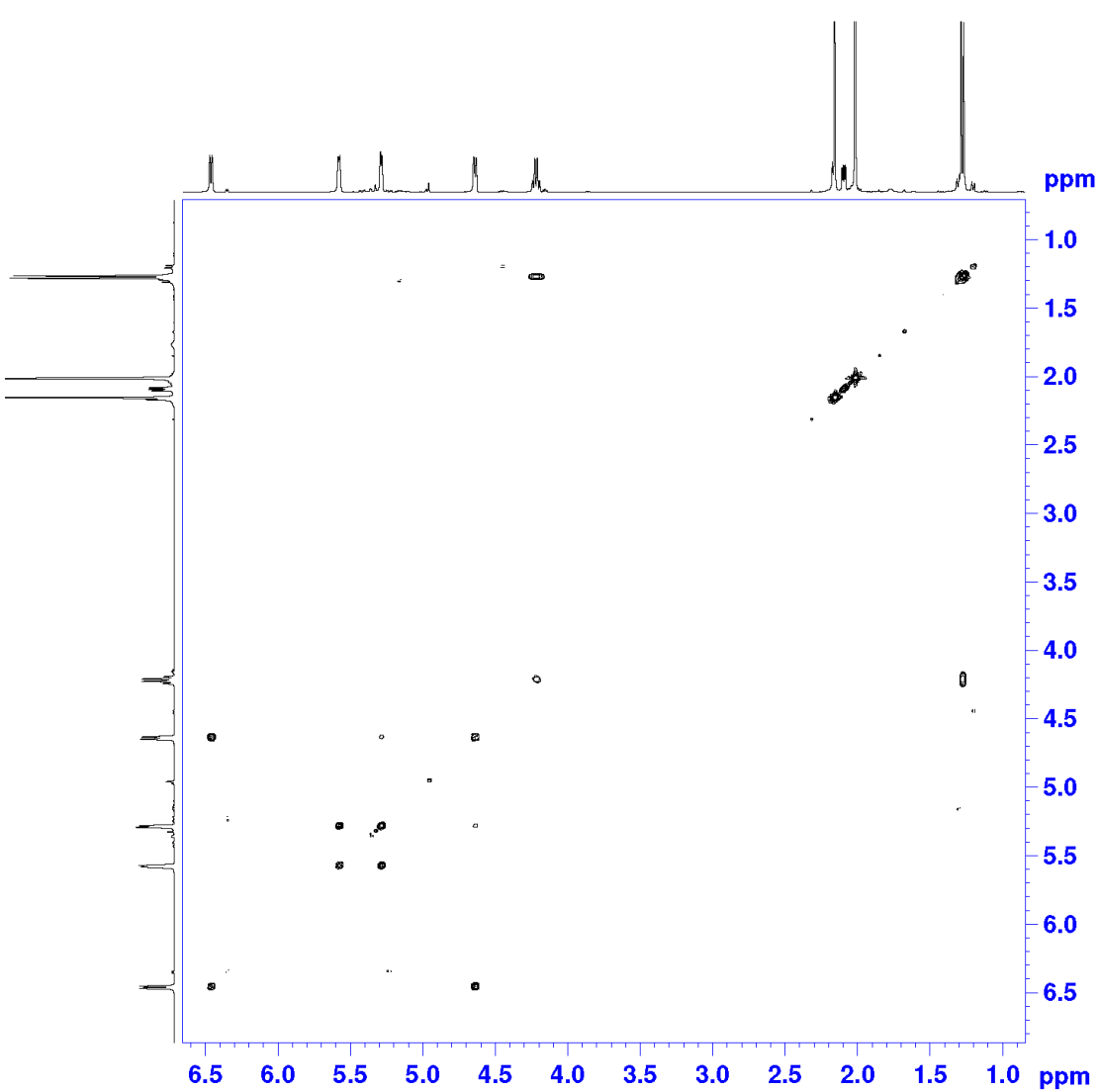


Figure 41 : ^{1}H NMR spectrum of 3,4-di-*O*-acetyl-L-fucal (**4**)



BRUKER

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PULPROG	cosygpqf	
TD	2048	
SOLVENT	CDCl3	
NS	1	
DS	8	
SWH	3267.974	Hz
FIDRES	1.595690	Hz
AQ	0.3133940	sec
RG	50.8	
DW	153.000	usec
DE	6.50	usec
TE	300.0	K
D0	0.00000300	sec
D1	1.36524105	sec
D13	0.00000400	sec
D16	0.00010000	sec
IN0	0.00030600	sec
======== CHANNEL f1 ========		
NUC1	1H	
P0	14.10	usec
P1	14.10	usec
PL1	0.00	dB
PL1W	11.43159485	W
SFO1	400.1512576	MHz
====== GRADIENT CHANNEL =====		
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GPZ1	10.00	%
P16	1000.00	usec
ND0	1	
TD	256	
SFO1	400.1513	MHz
FIDRES	12.765523	Hz
SW	8.167	ppm
FnMODE	QF	
SI	1024	
SF	400.1499926	MHz
WDW	SINE	
SSB	0	
LB	0.00	Hz
GB	0	
PC	1.40	
SI	1024	
MC2	QF	
SF	400.1499926	MHz
WDW	SINE	
SSB	0	
LB	0.00	Hz
GB	0	

Figure 42 : COSY NMR spectrum of 3,4-di-*O*-acetyl-L-fucal (**4**)

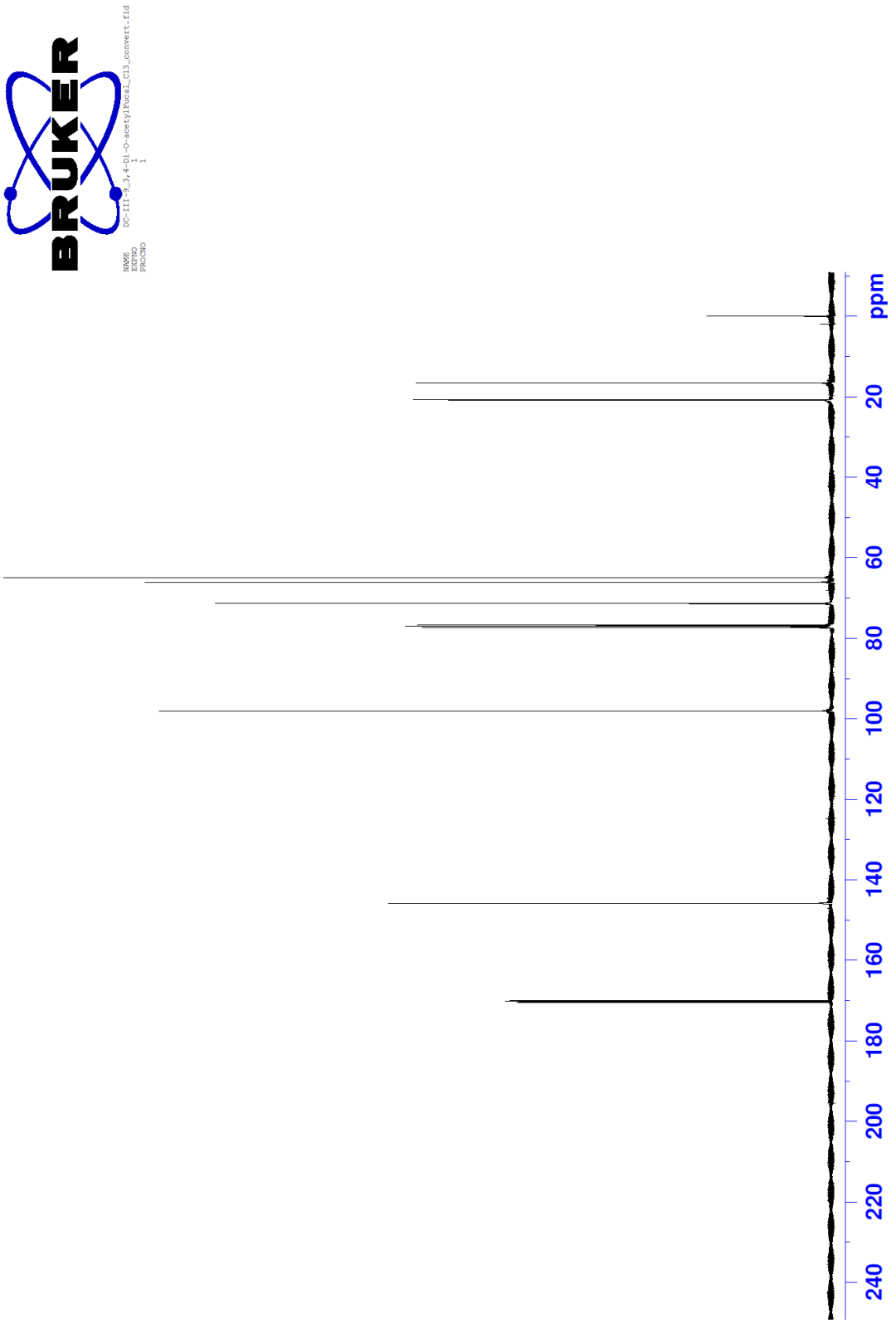


Figure 43 : ^{13}C NMR spectrum of 3,4-di-*O*-acetyl-L-fucal (**4**)

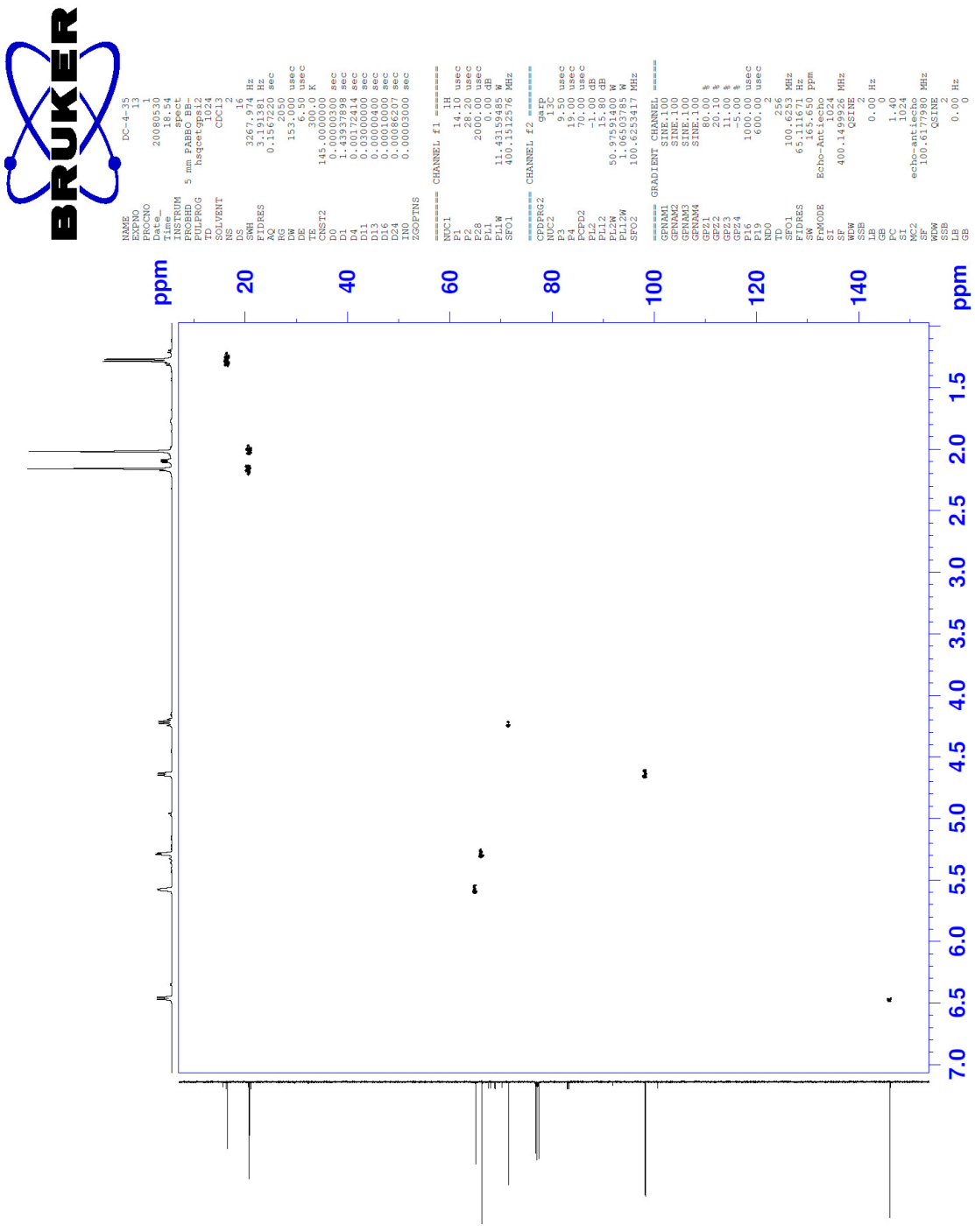


Figure 44 : HSQC NMR spectrum of 3,4-di-*O*-acetyl-L-fucal (**4**)

Display Report

Analysis Info

Method XQ Default.ms Instrument Esquire-LC_00135

Acquisition Parameter

Ion Source Type	APCI	Mass Range Mode	Std/Normal	Ion Polarity	Positive	Alternating Ion Polarity	n/a
Scan Begin	50.00 m/z	Scan End	1000.00 m/z	Averages	5 Spectra	Accumulation Time	749 µs
Capillary Exit	83.2 Volt	Skim 1	16.0 Volt	Trap Drive	46.1	Auto MS/MS	Off

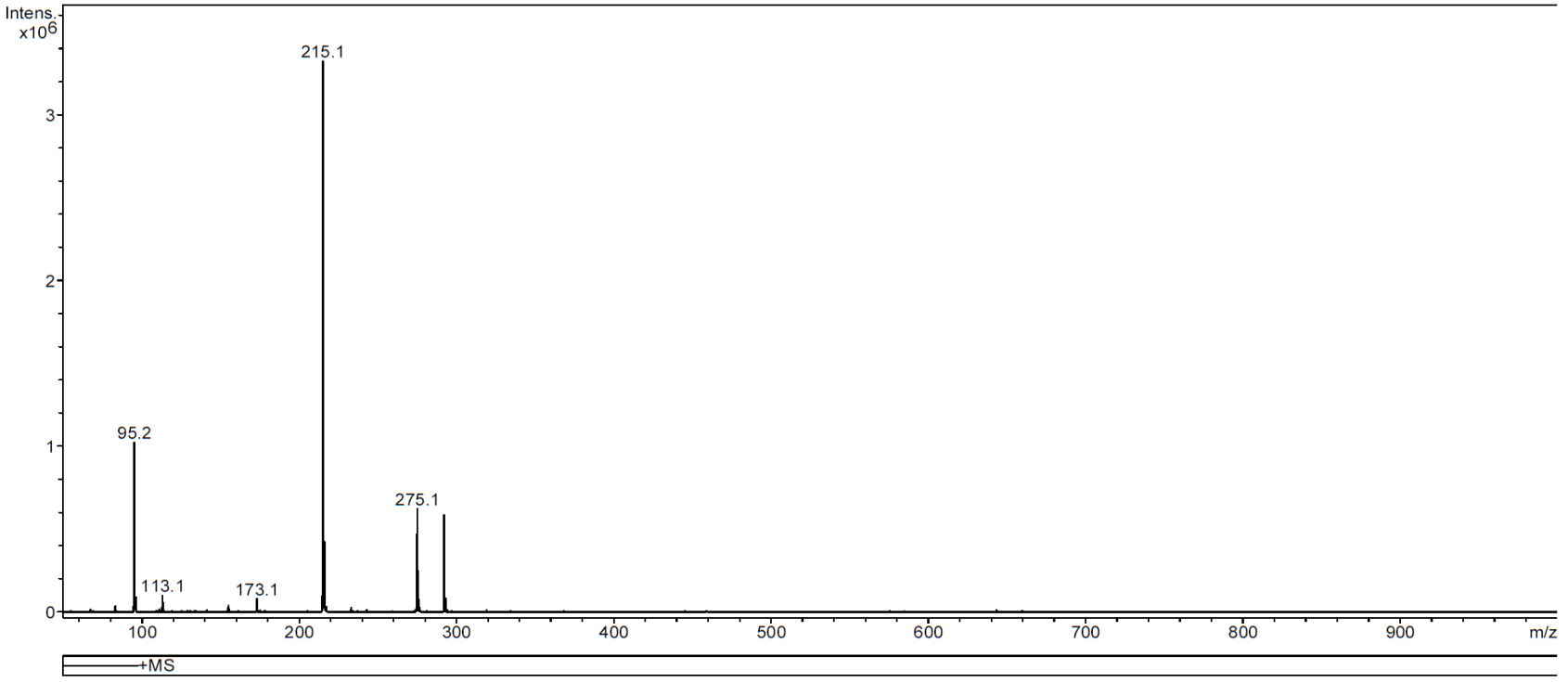


Figure 45 : Mass spectrum of 3,4-di-*O*-acetyl-L-fucal (**4**)

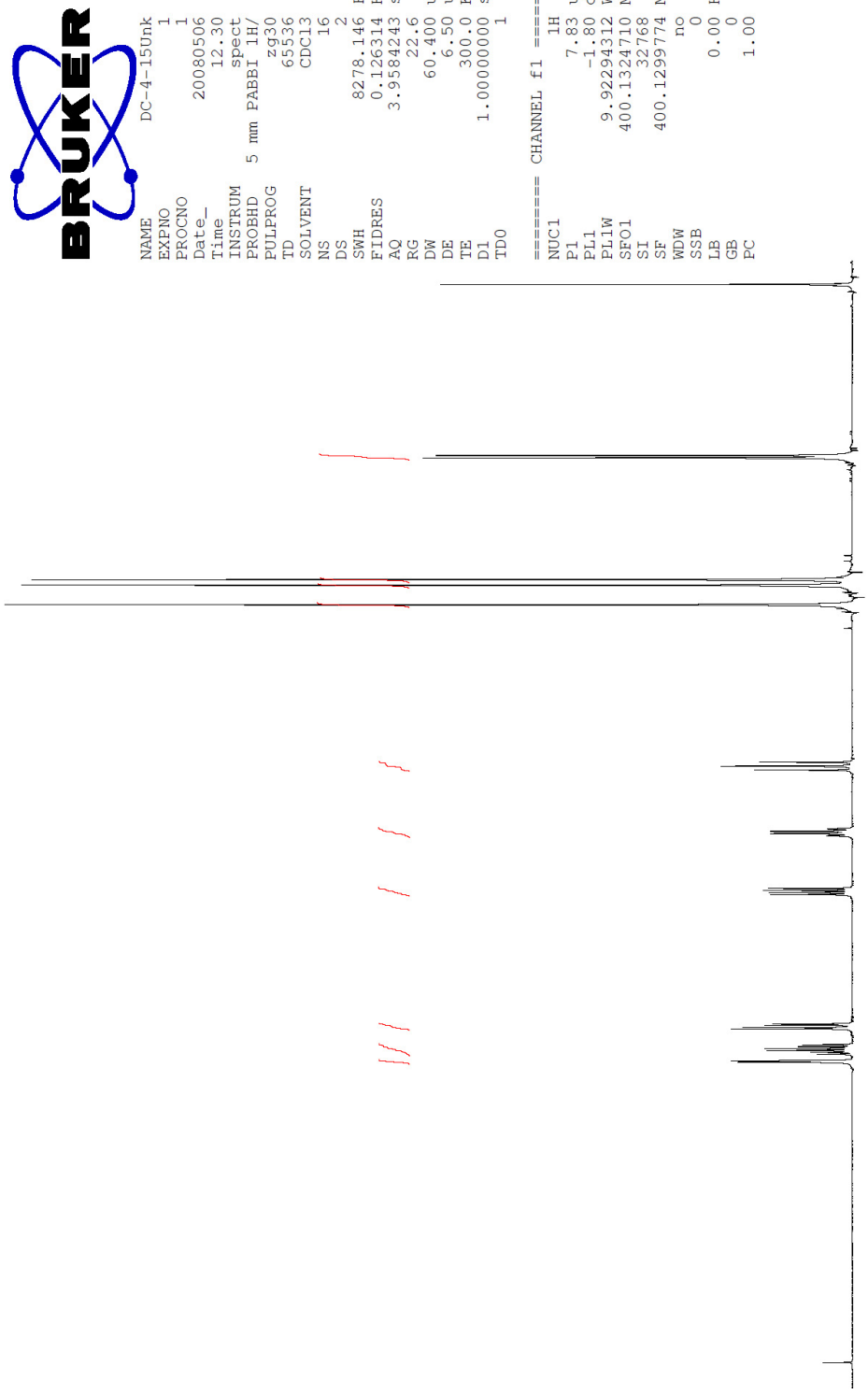


Figure 46 : ^{1}H NMR spectrum of 2,3,4-tri-*O*-acetyl-1-deoxy-L-fucose (**5**)

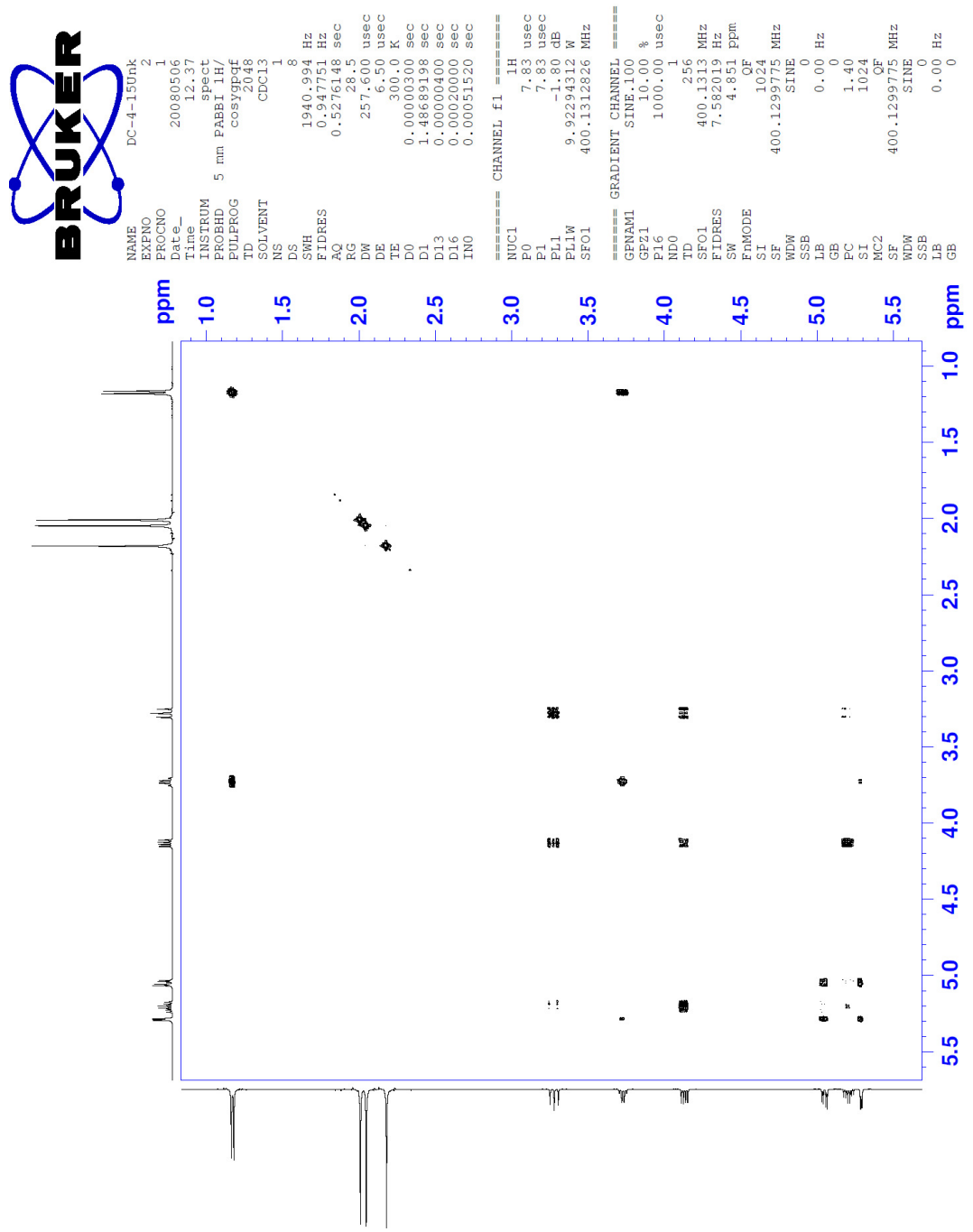


Figure 47 : COSY NMR spectrum of 2,3,4-tri-*O*-acetyl-1-deoxy-L-fucose (**5**)

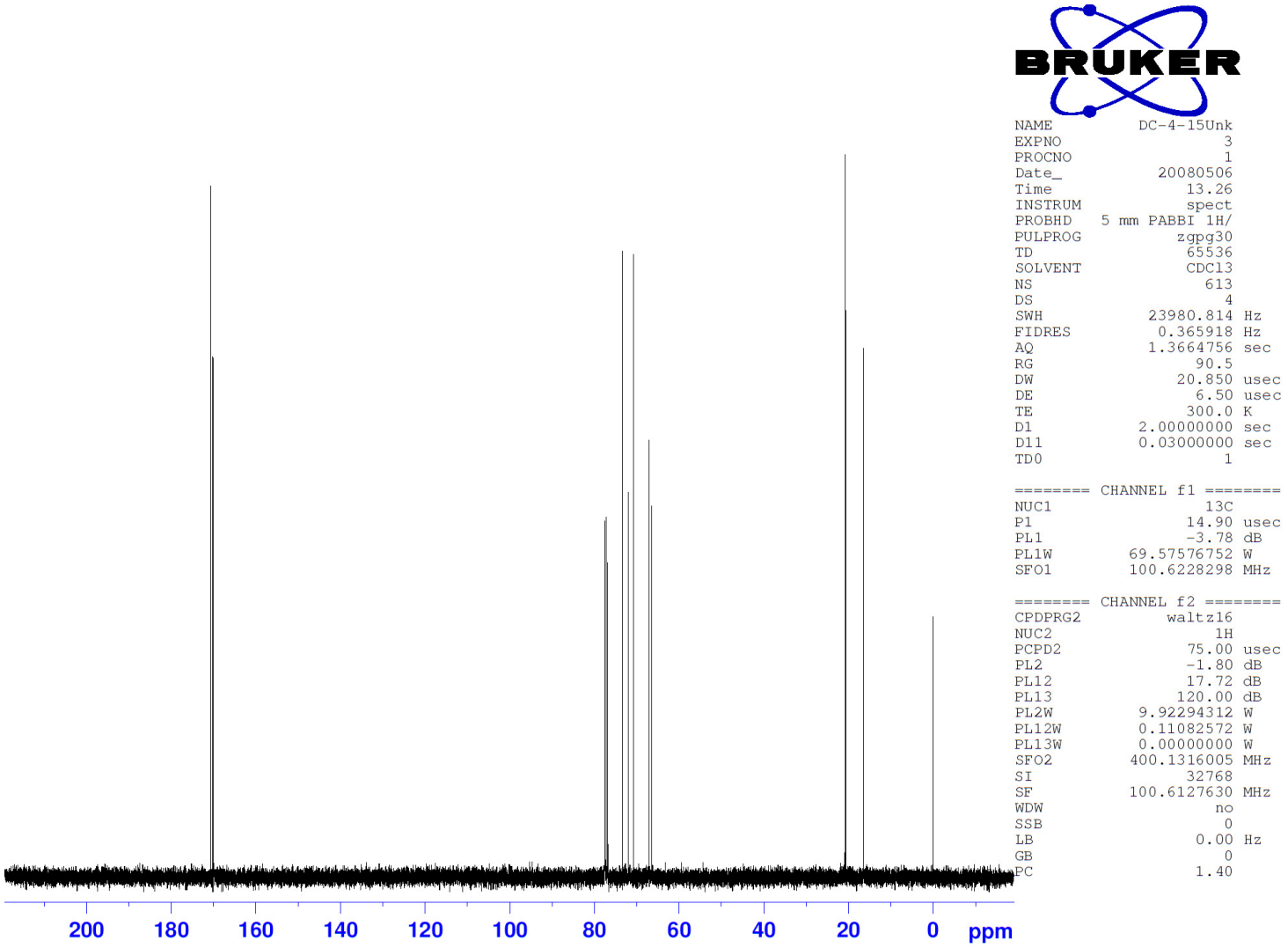


Figure 48 : ^{13}C NMR spectrum of 2,3,4-tri-*O*-acetyl-1-deoxy-L-fucose (**5**)

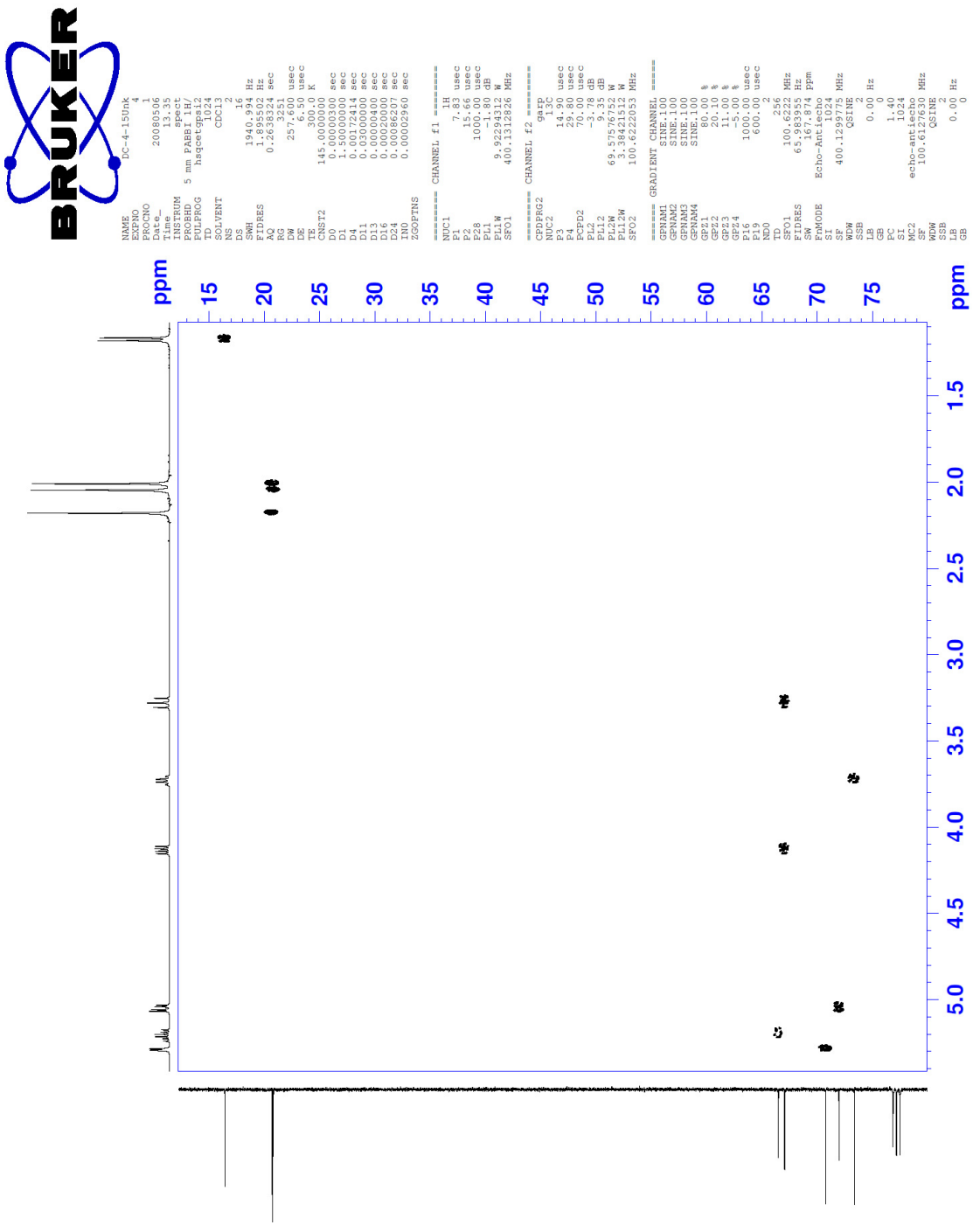


Figure 49 : HSQC NMR spectrum of 2,3,4-tri-*O*-acetyl-1-deoxy-L-fucose (**5**)

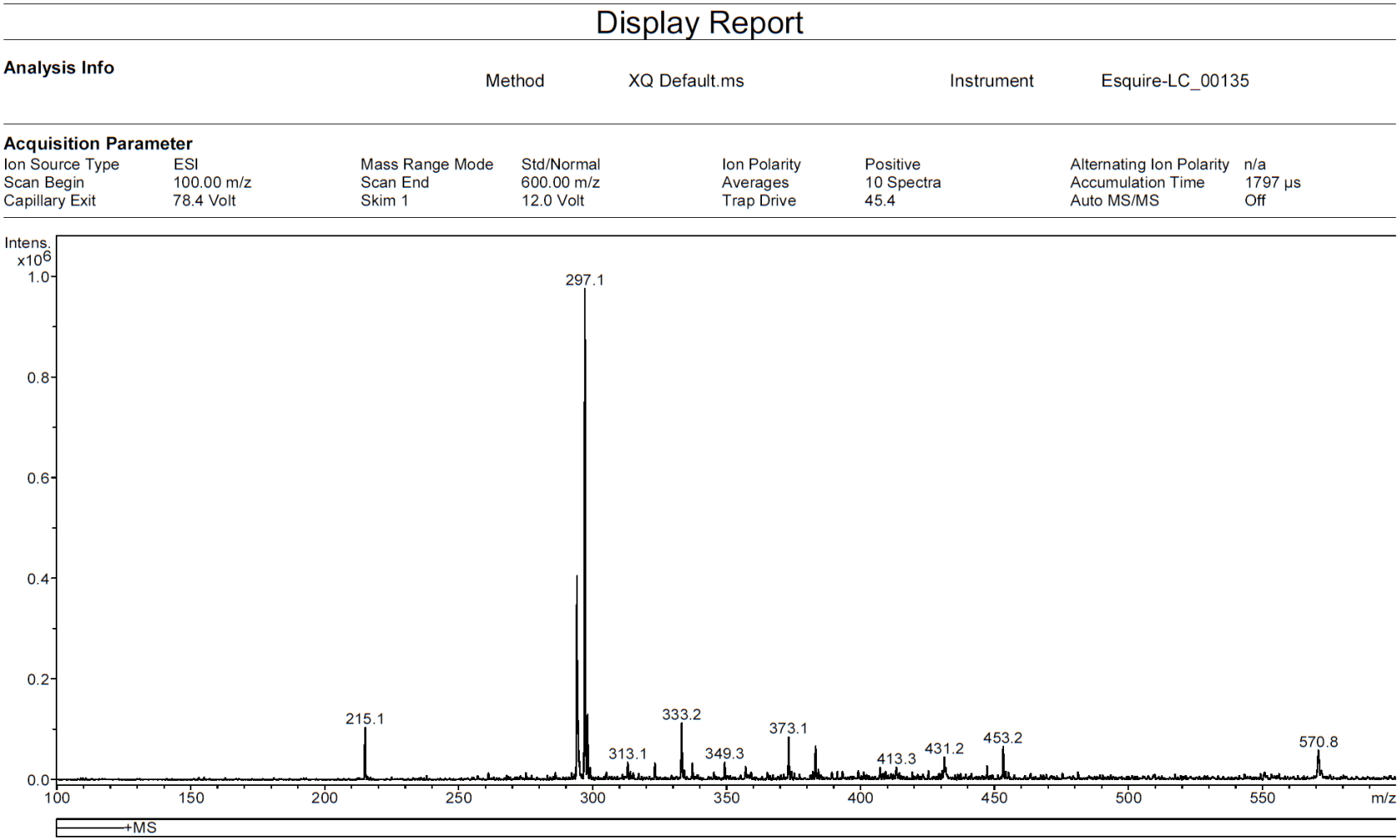


Figure 50 : Mass spectrum of 2,3,4-tri-*O*-acetyl-1-deoxy-L-fucose (**5**)

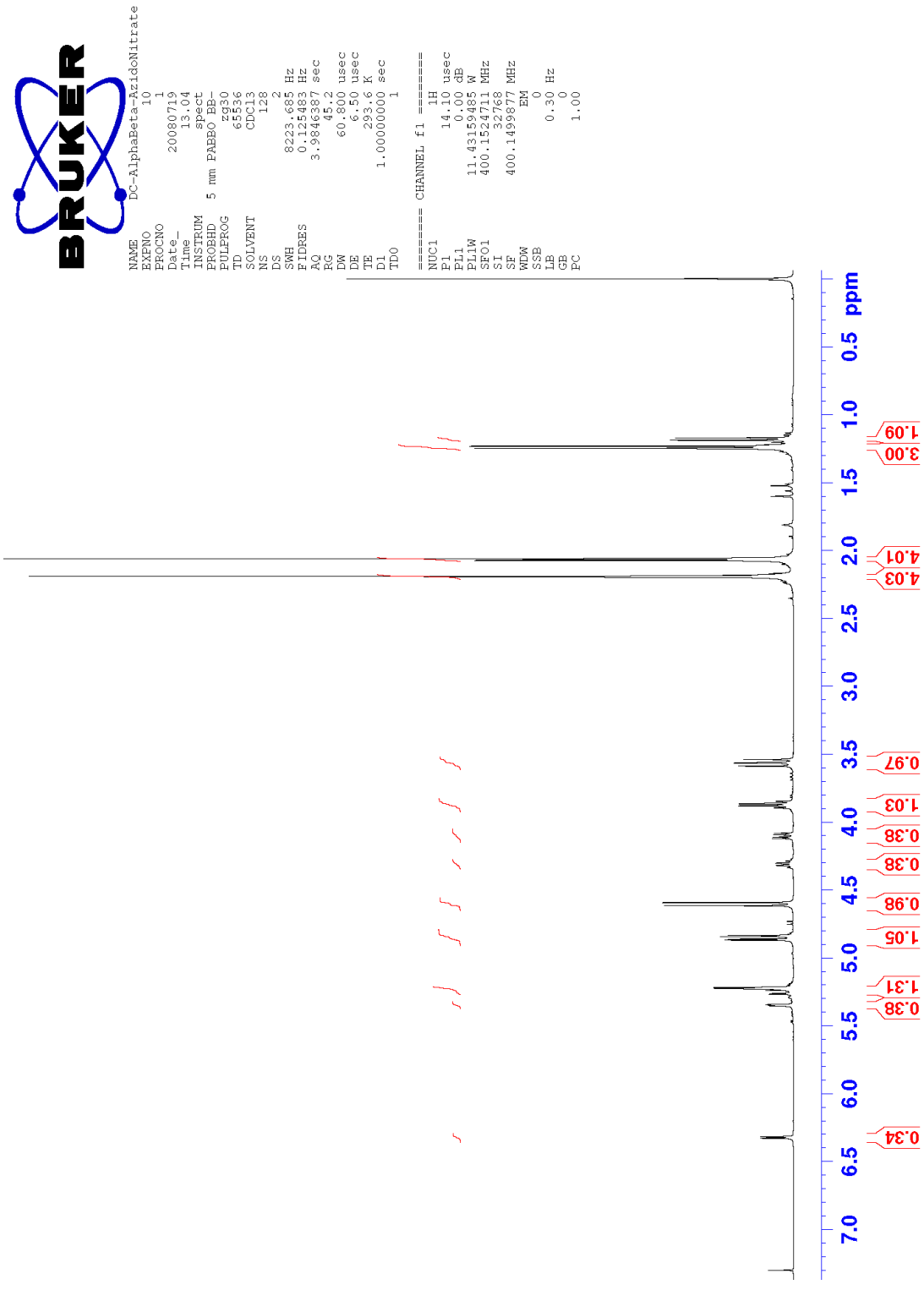


Figure 51 : ^{1}H NMR spectrum of 3,4-di-*O*-acetyl-2-azidodeoxy-1-nitro-α,β-L-fucose (**6**)

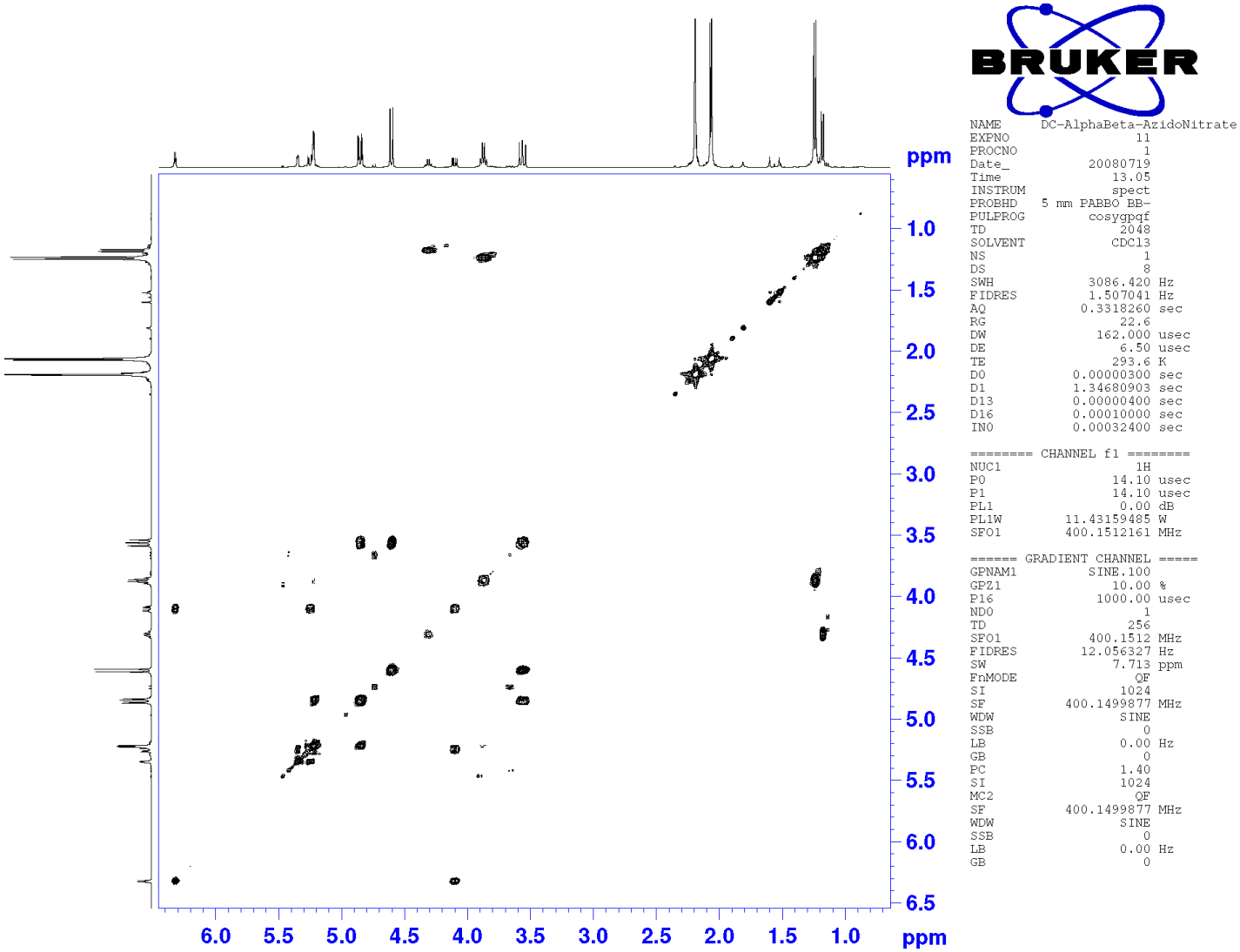
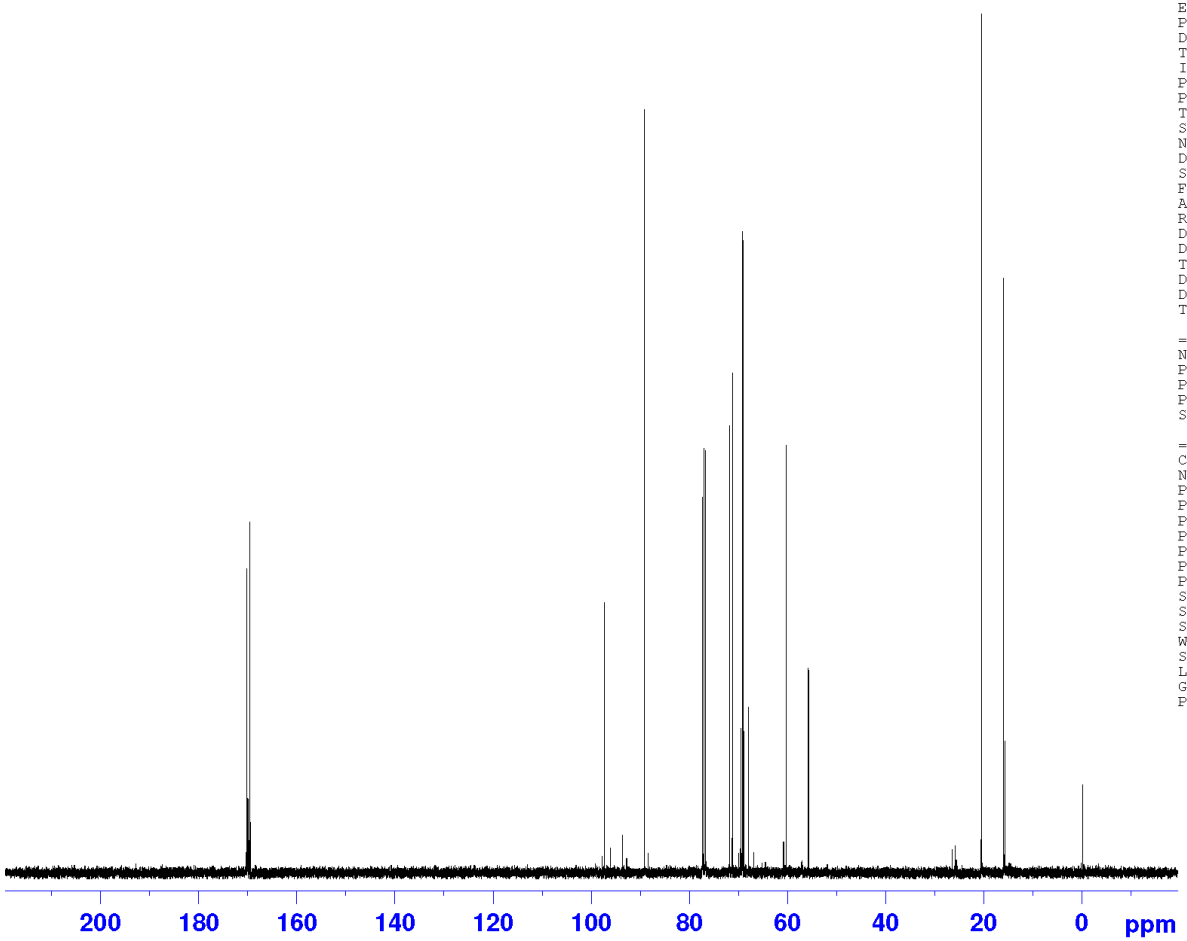


Figure 52 : COSY NMR spectrum of 3,4-di-*O*-acetyl-2-azidodeoxy-1-nitrodeoxy-α,β-L-fucose (**6**)

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PROCNO                  1
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PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   518
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                294.6 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          100.6178071 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.40
```

Figure 53 : ^{13}C NMR spectrum of 3,4-di-*O*-acetyl-2-azidodeoxy-1-nitrodeoxy-α,β-L-fucose (**6**)

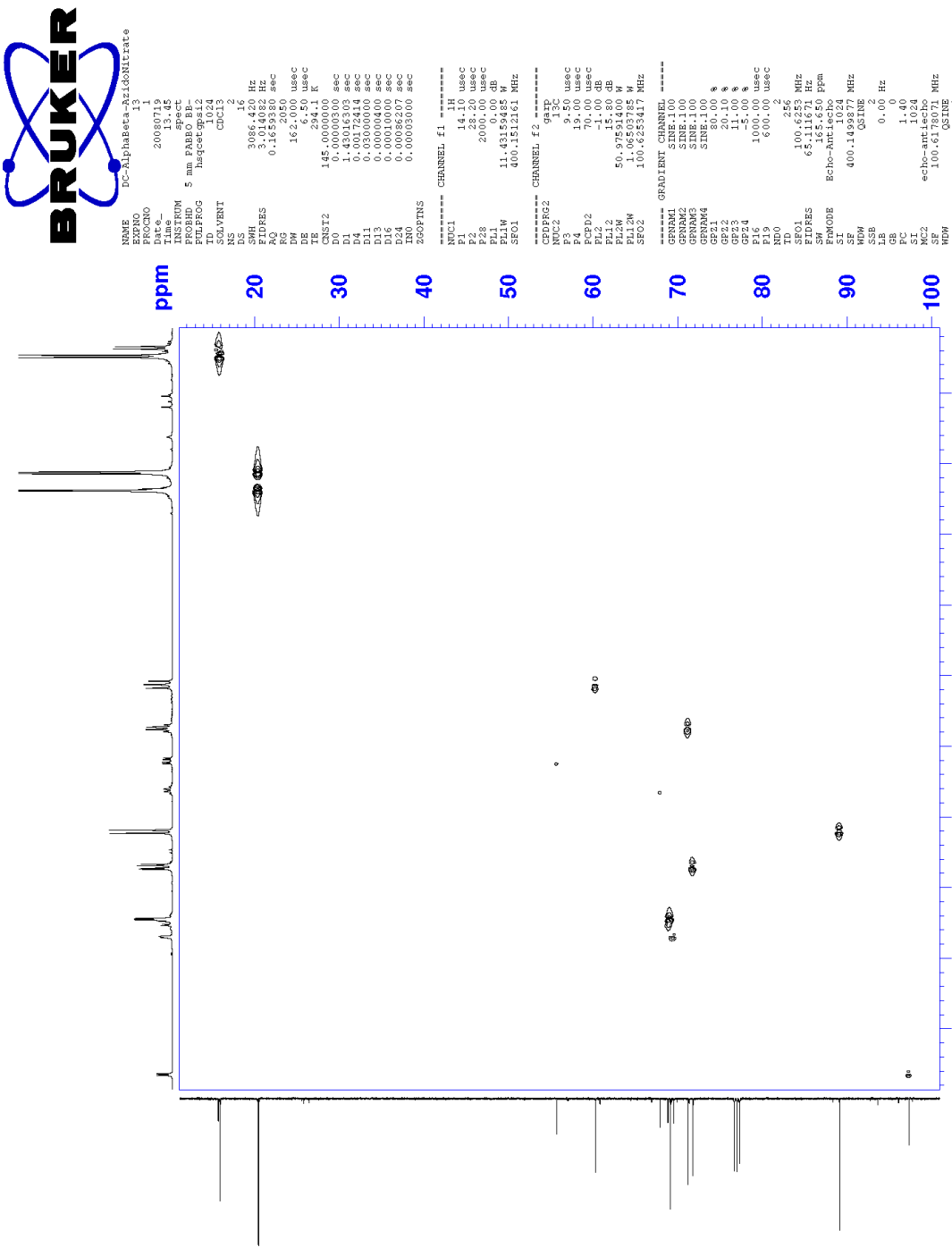


Figure 54 : HSQC NMR spectrum of 3,4-di-*O*-acetyl-2-azidodeoxy-1-nitrodeoxy-α,β-L-fucose (**6**)

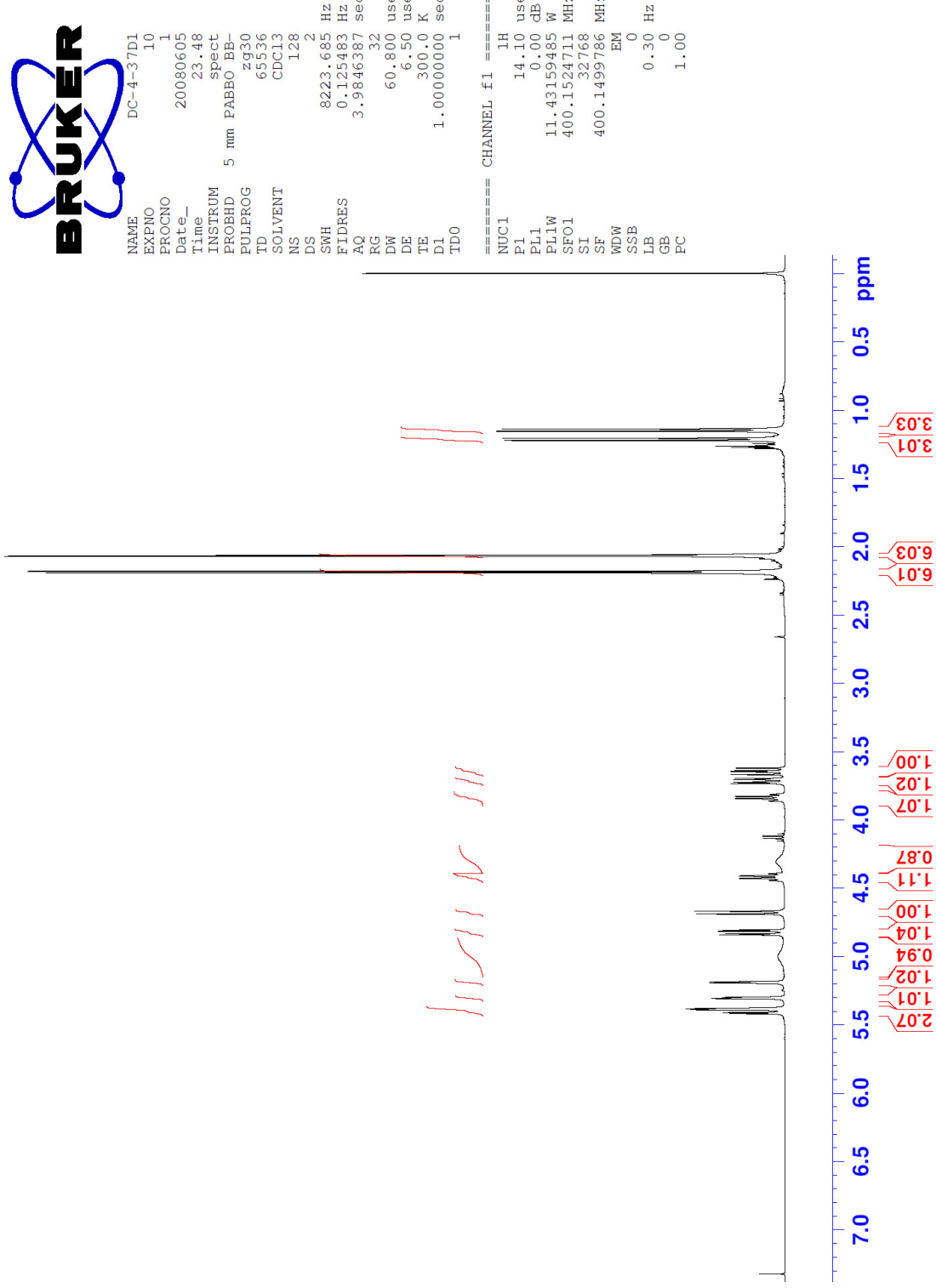


Figure 55 : ^{1}H NMR spectrum of α,β-3,4-di-*O*-acetyl-2-azidodeoxy-L-fucose (**7**)

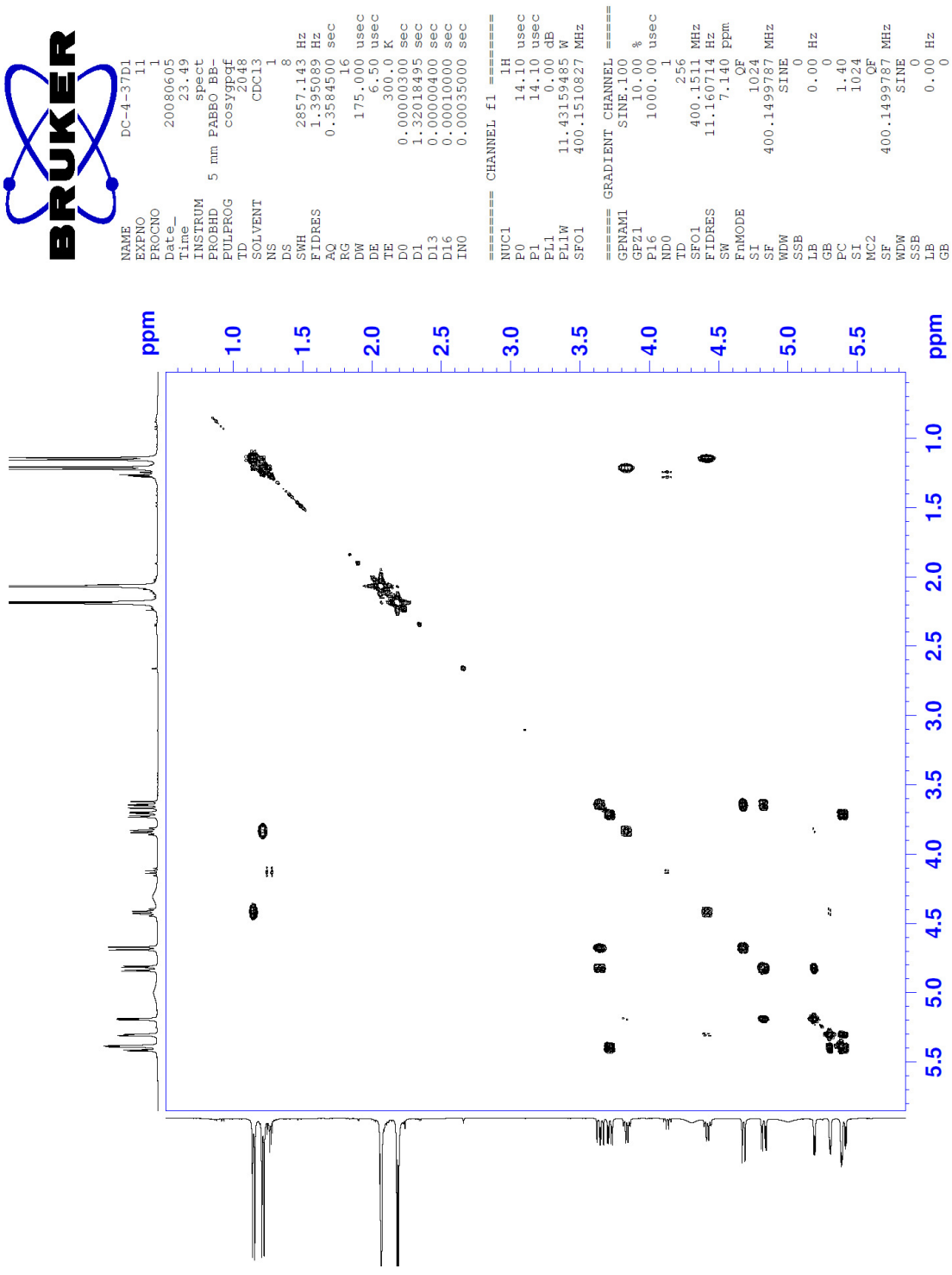
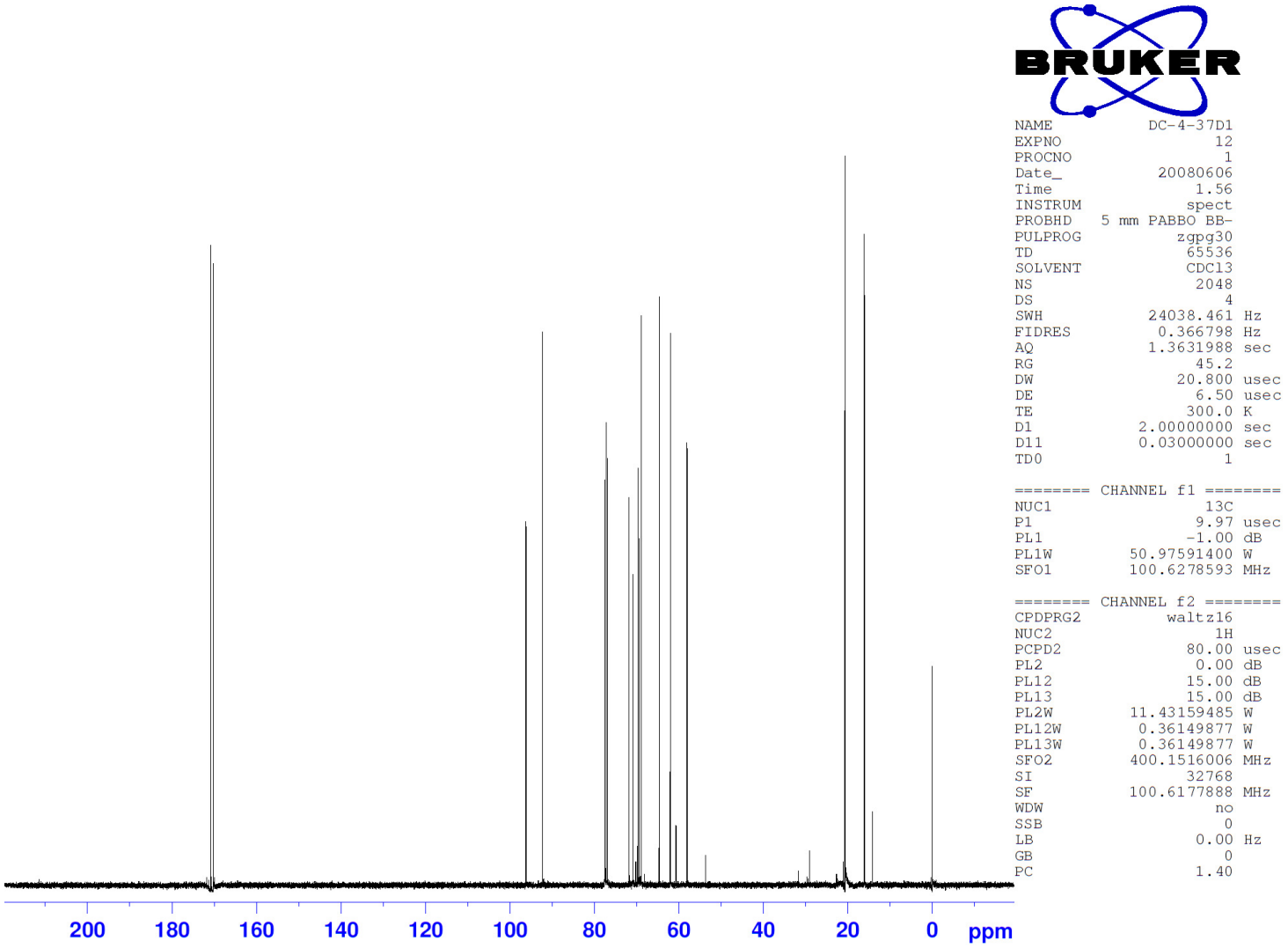


Figure 56 : COSY NMR spectrum of 3,4-di-*O*-acetyl-2-azidodeoxyα,β-L-fucose (**7**)



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PROCNO	1
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PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	2048
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	45.2
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	100.6177888 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.40

Figure 57 : ^{13}C NMR spectrum of 3,4-di-*O*-acetyl-2-azidodeoxy-α,β-L-fucose (**7**)

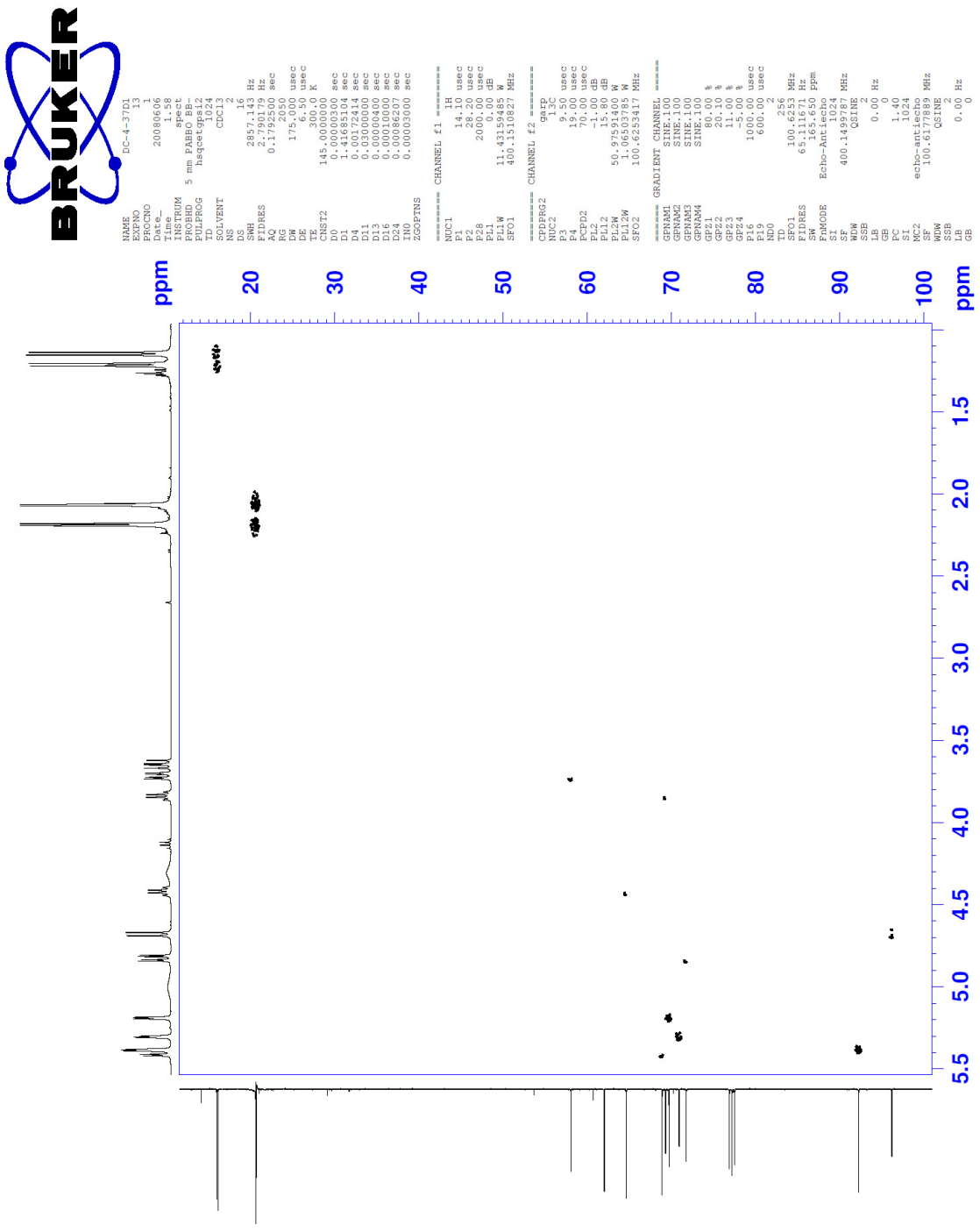


Figure 58 : HSQC NMR spectrum of 3,4-di-*O*-acetyl-2-azidodeoxy-α,β-L-fucose (**7**)

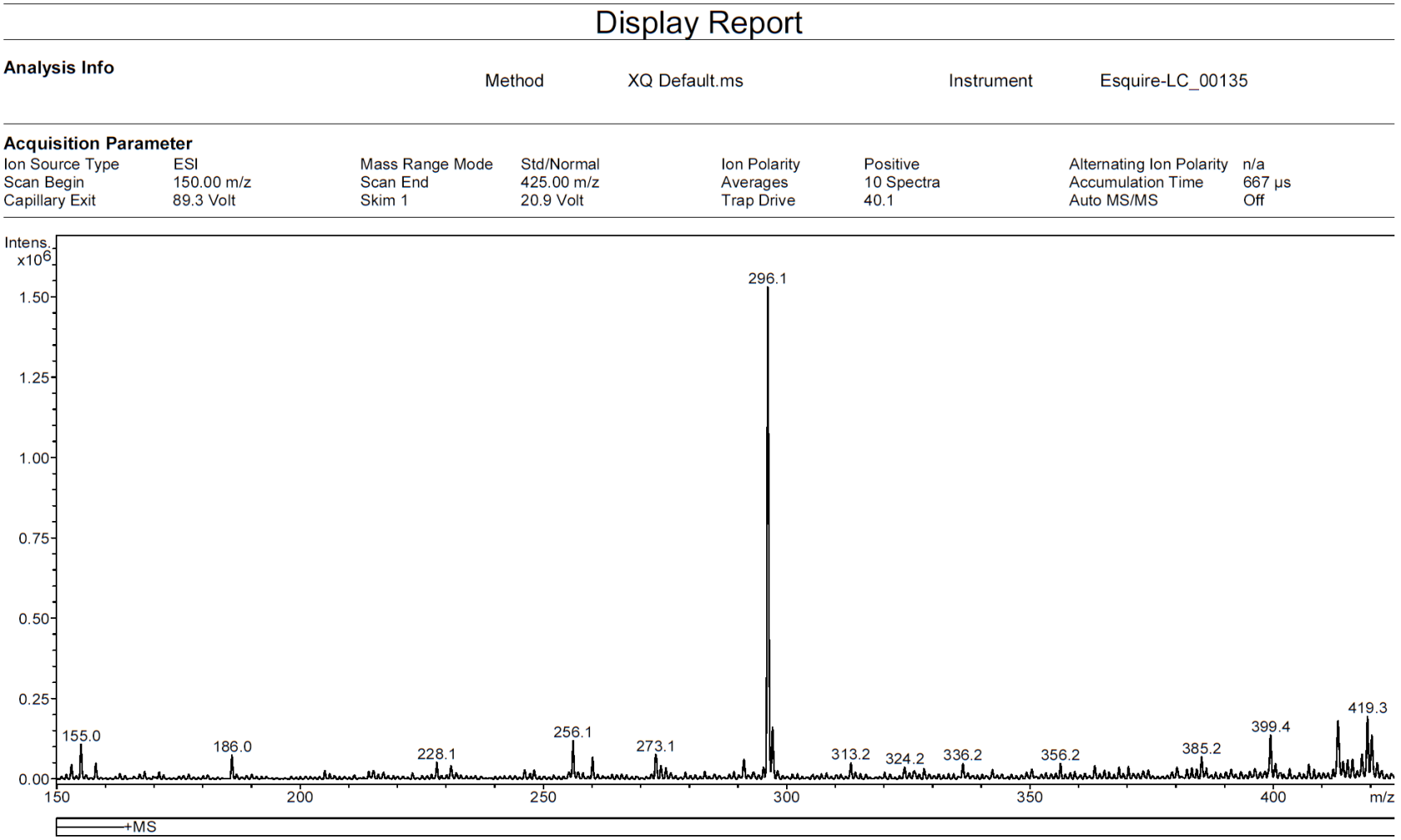


Figure 59 : Mass spectrum of 3,4-di-*O*-acetyl-2-azidodeoxy-α,β-L-fucose (**7**)

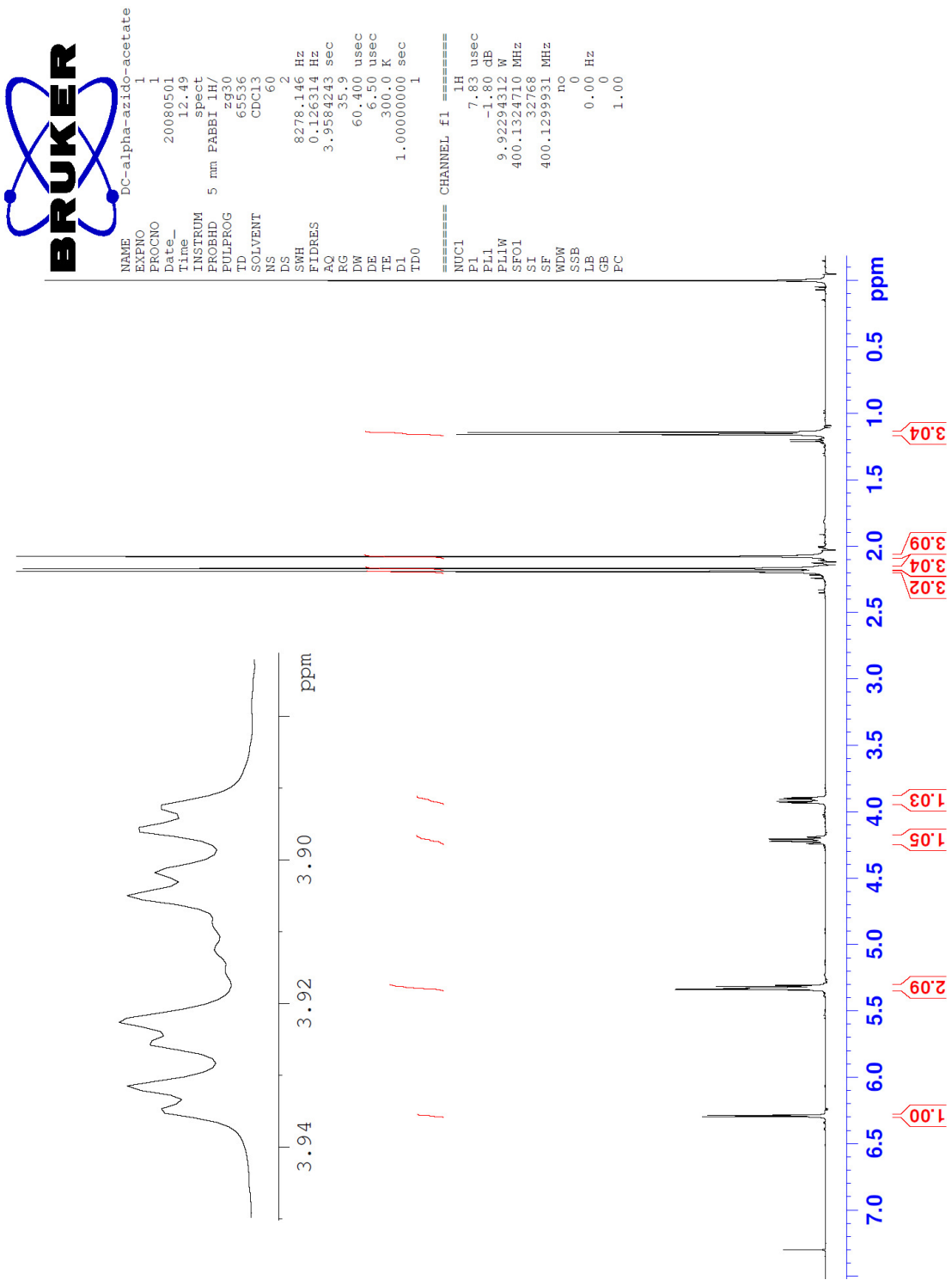


Figure 60 : ^{1}H NMR spectrum of 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α-L-fucose (**8**)

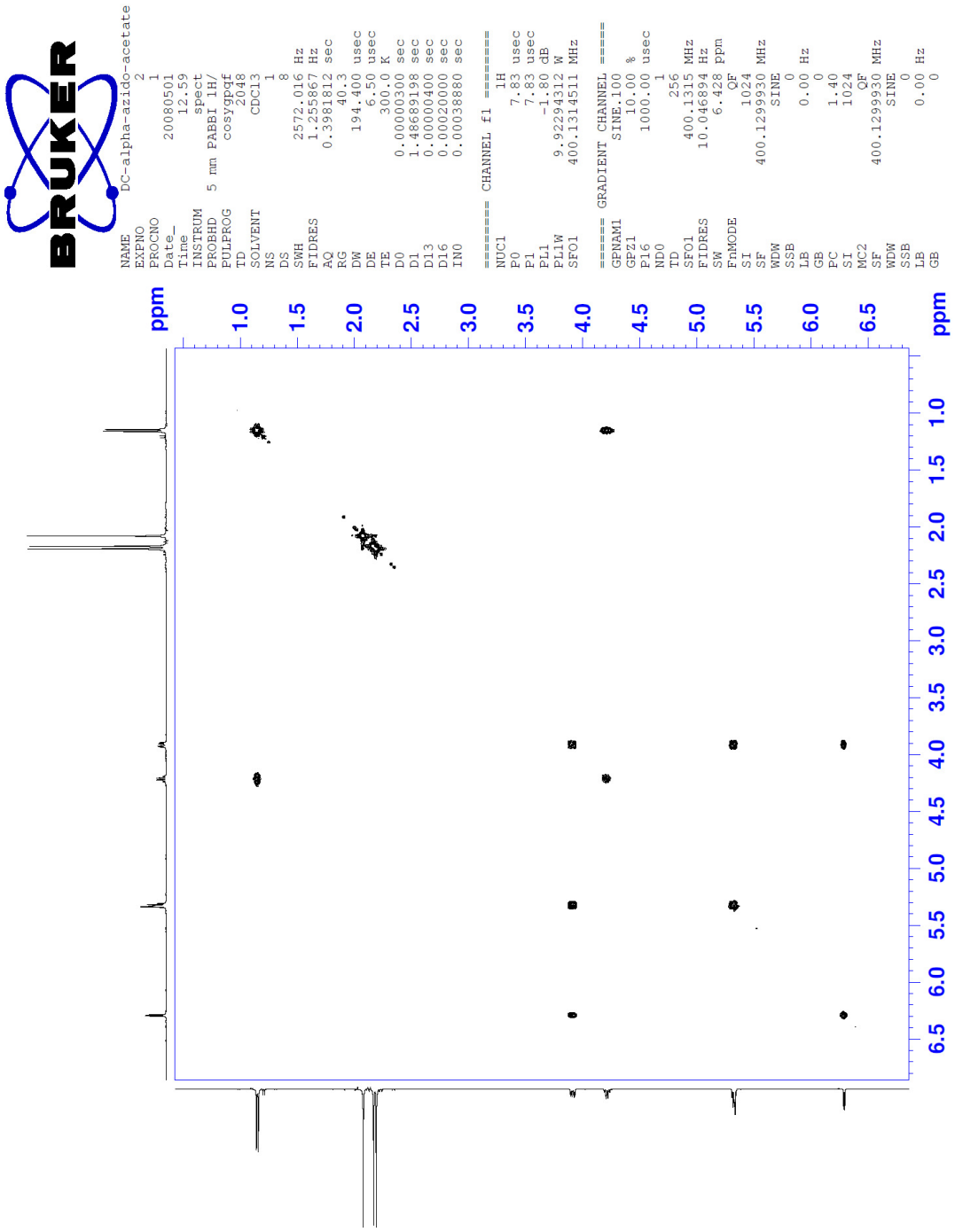


Figure 61 : COSY NMR spectrum of 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α-L-fucose (**8**)

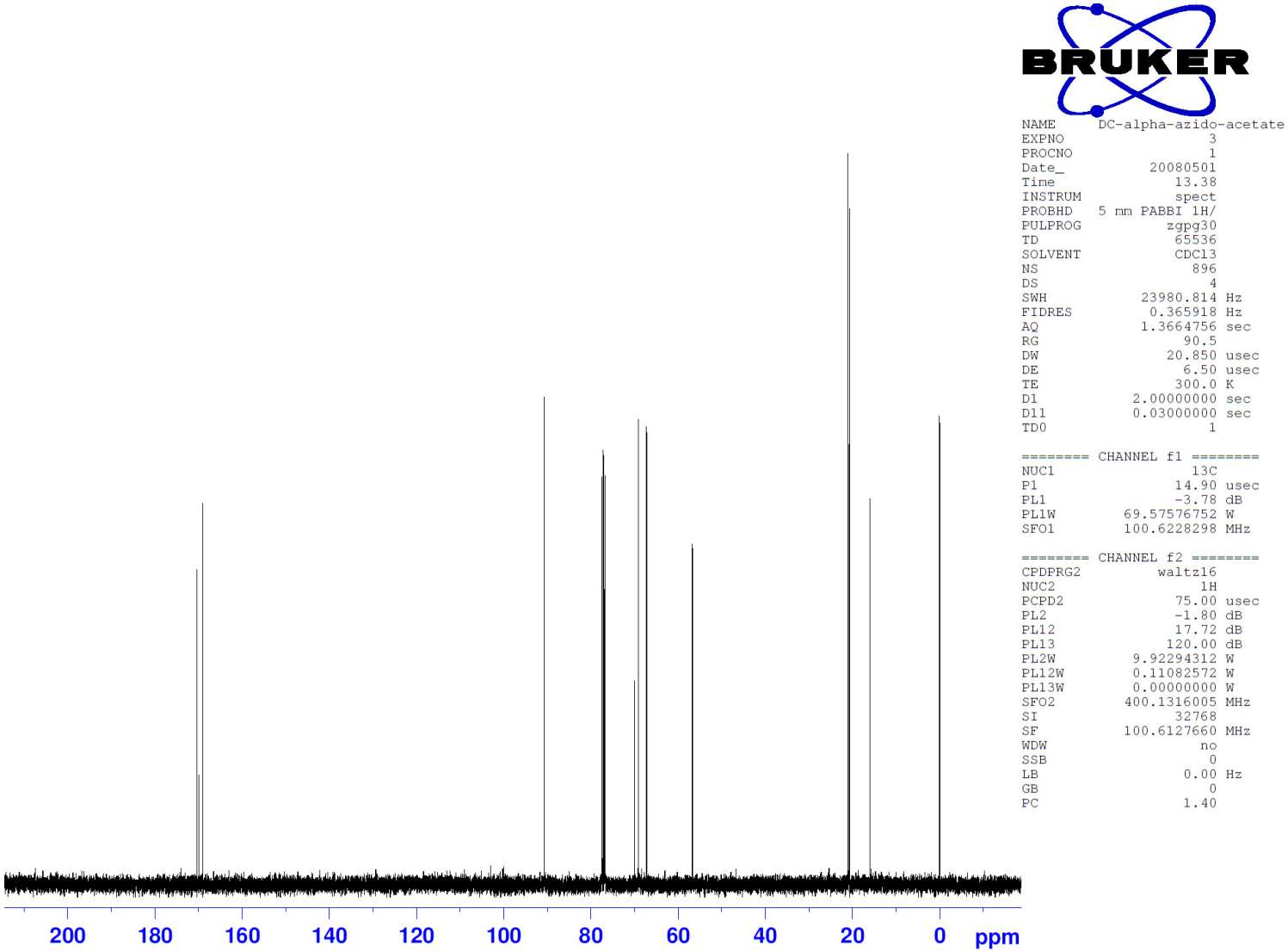


Figure 62 : ^{13}C NMR Spectrum of α-1,3,4-Tri-*O*-acetyl-2-azidodeoxy-L-fucose **(8)**

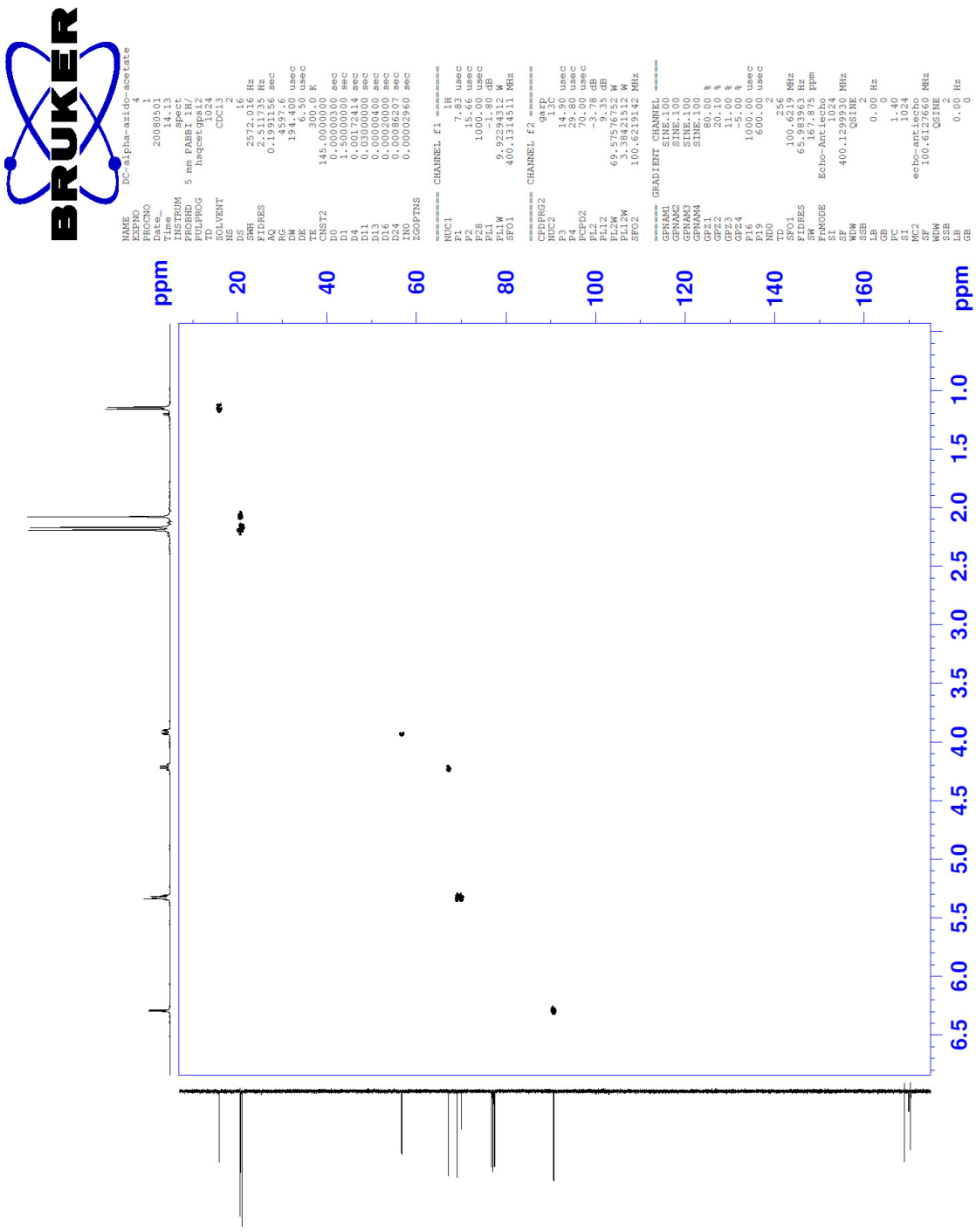


Figure 63 : HSQC NMR spectrum of 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α-L-fucose (**8**)

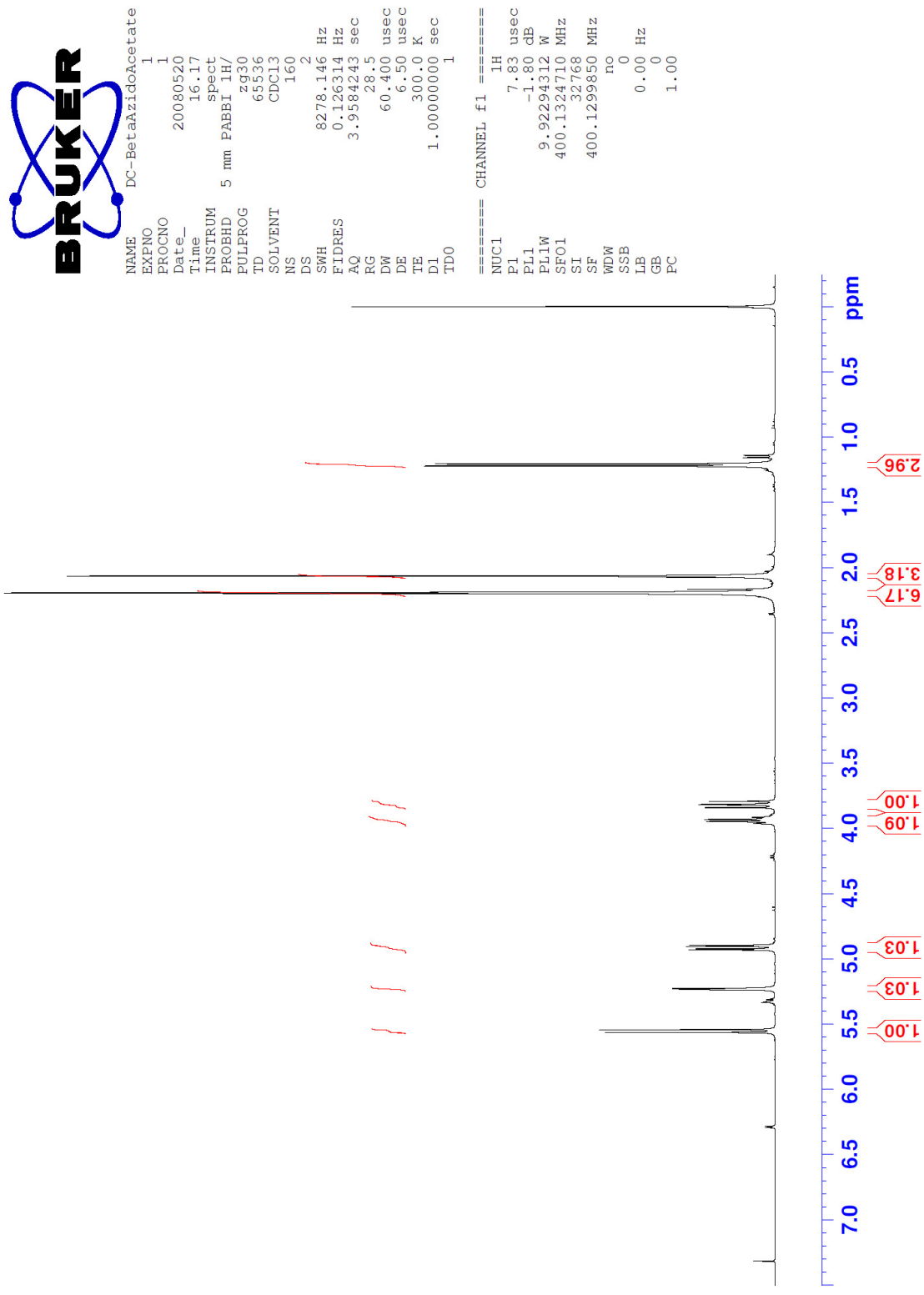


Figure 64 : ^{1}H NMR spectrum of 1,3,4-tri-*O*-acetyl-2-azidodeoxy-β-L-fucose (**8**)

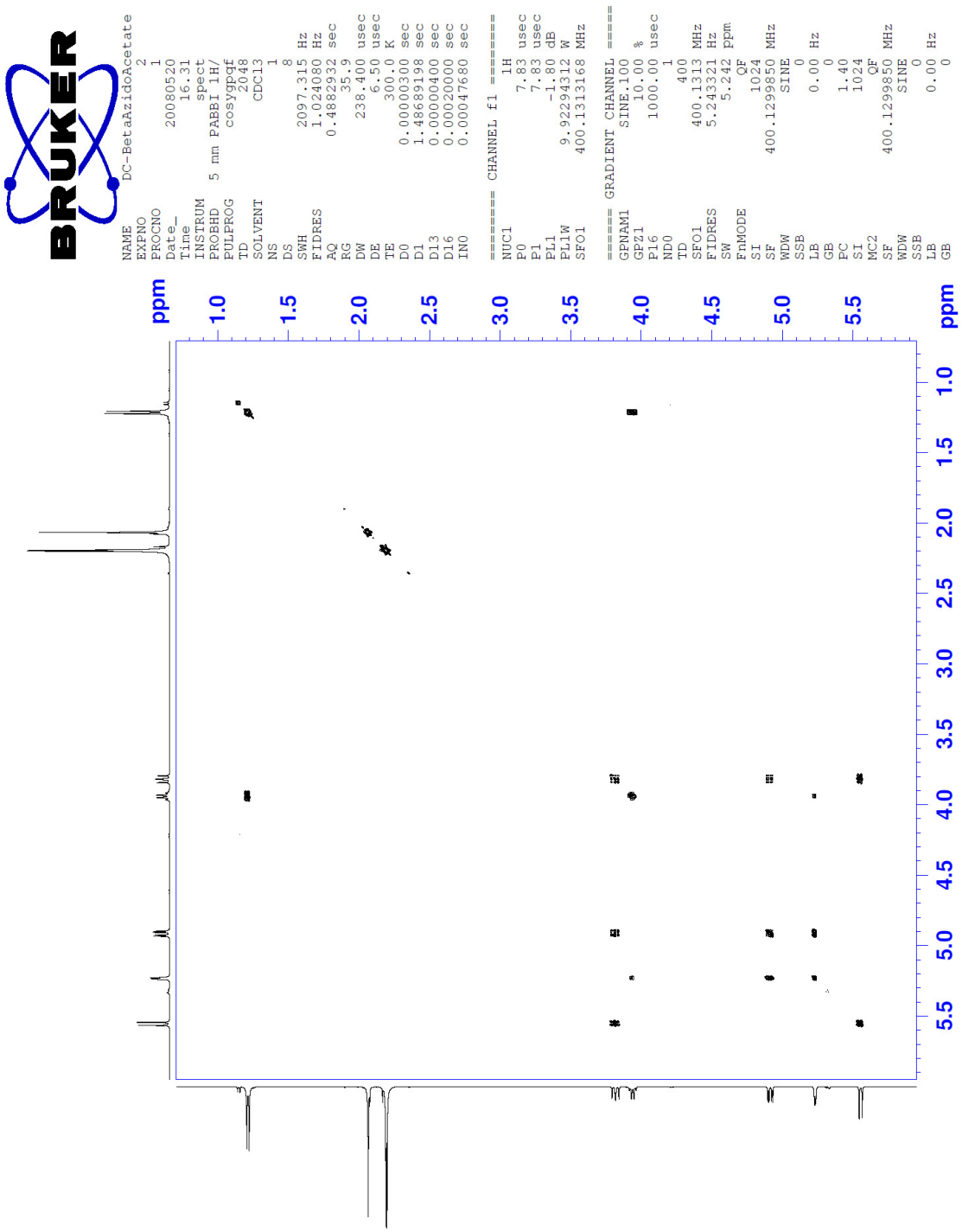


Figure 65 : COSY NMR spectrum of 1,3,4-tri-*O*-acetyl-2-azidodeoxy-β-L-fucose (**8**)

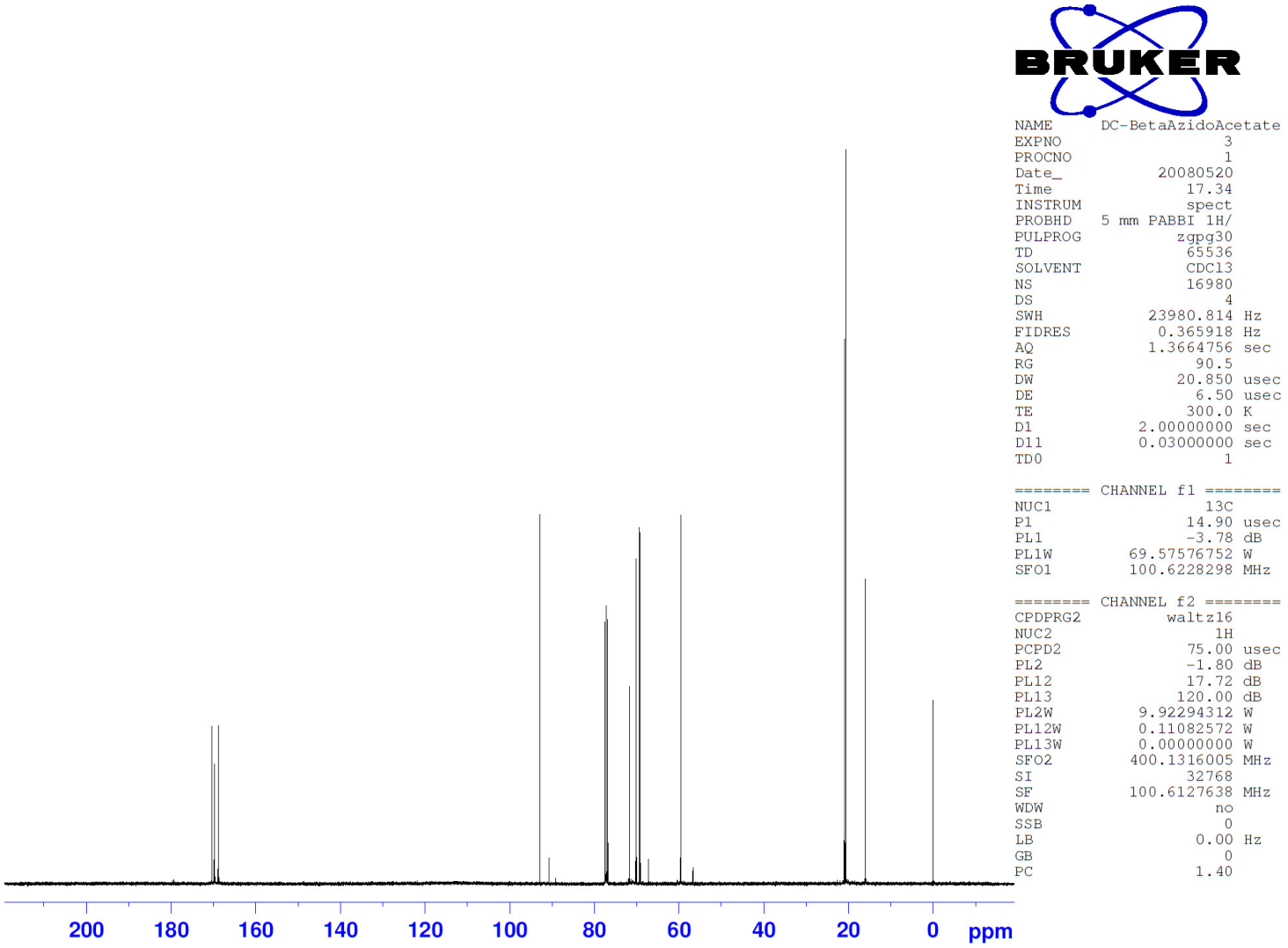


Figure 66 : ^{13}C NMR spectrum of 1,3,4-tri-*O*-acetyl-2-azidodeoxy-β-L-fucose (**8**)

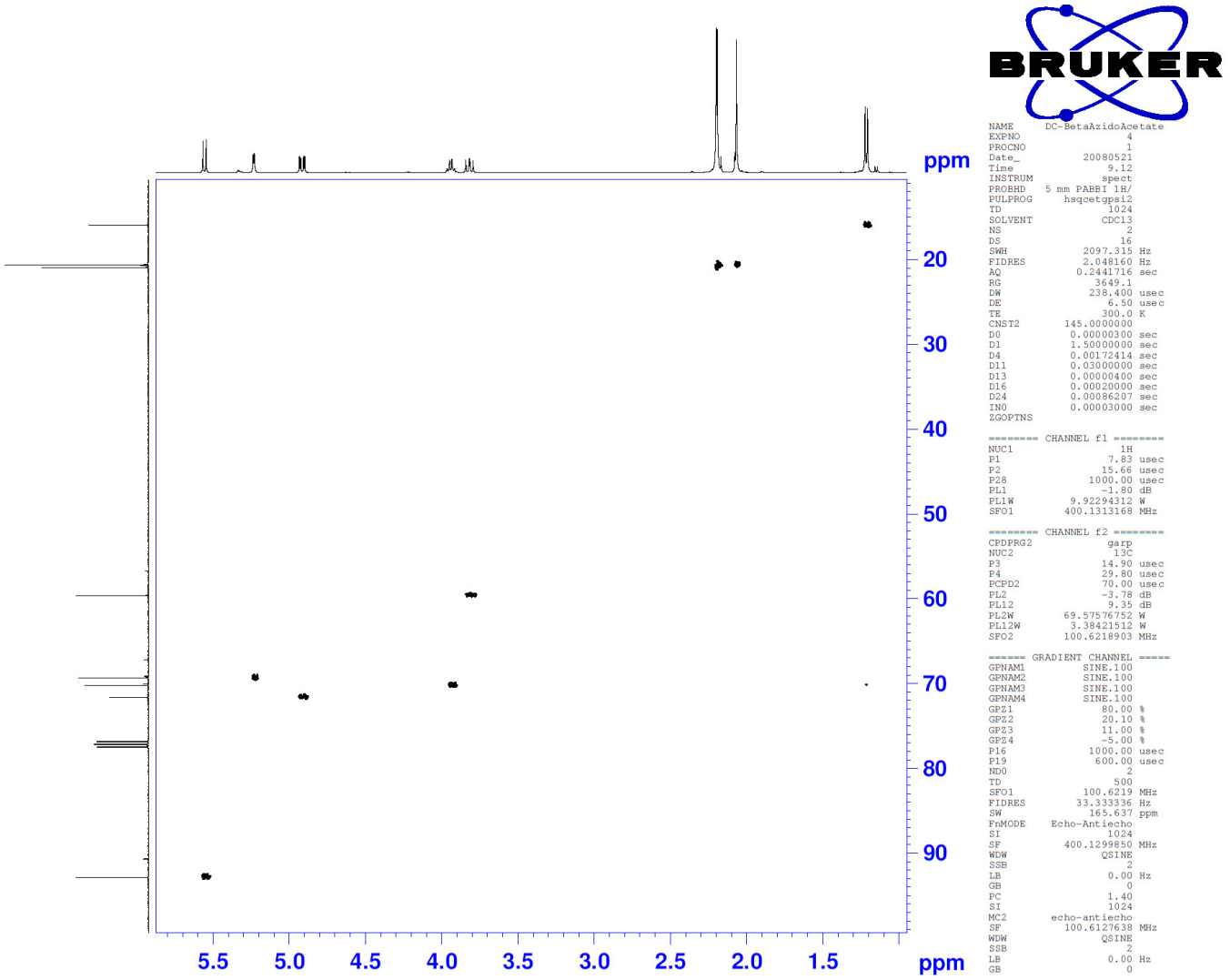


Figure 67 : HSQC NMR spectrum of 1,3,4-tri-*O*-acetyl-2-azidodeoxy-β-L-fucose (**8**)

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	120.00 m/z	Scan End	600.00 m/z	Averages	10 Spectra	Accumulation Time	1363 µs
Capillary Exit	99.4 Volt	Skim 1	28.6 Volt	Trap Drive	40.1	Auto MS/MS	Off

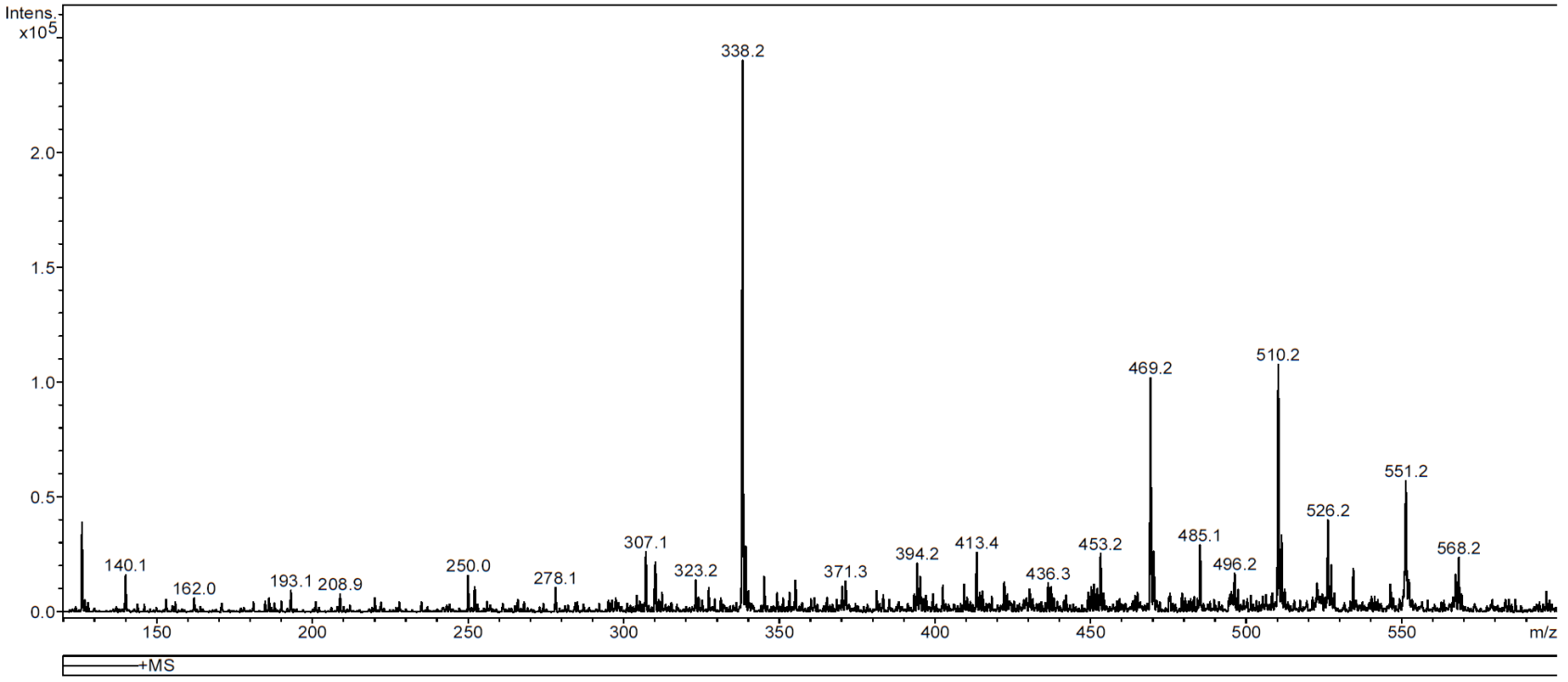


Figure 68 : Mass spectrum of 1,3,4-tri-*O*-acetyl-2-azidodeoxy-L-fucose (**8**)

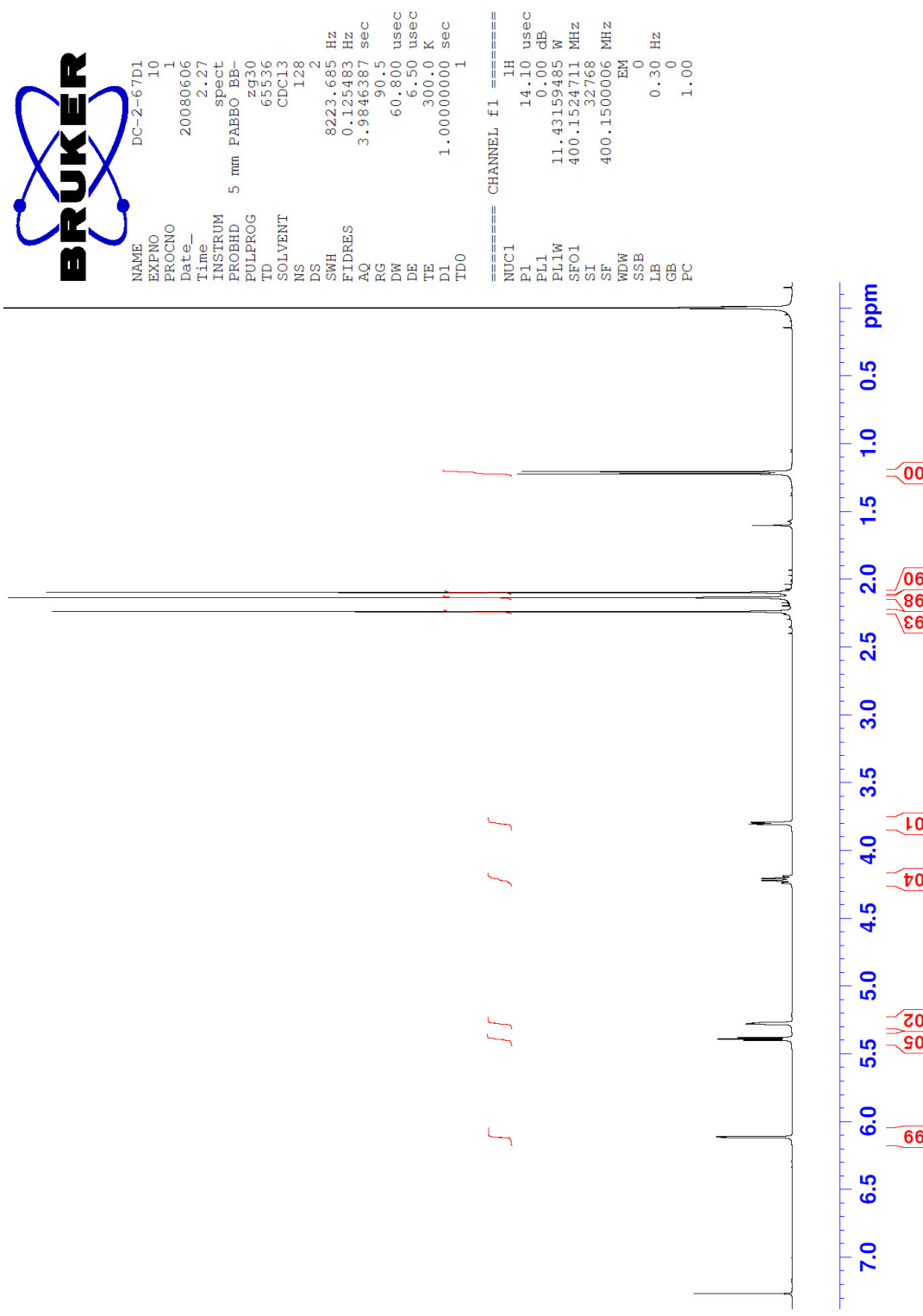


Figure 69 : ^{1}H NMR spectrum of 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α-L-talose (**9**)

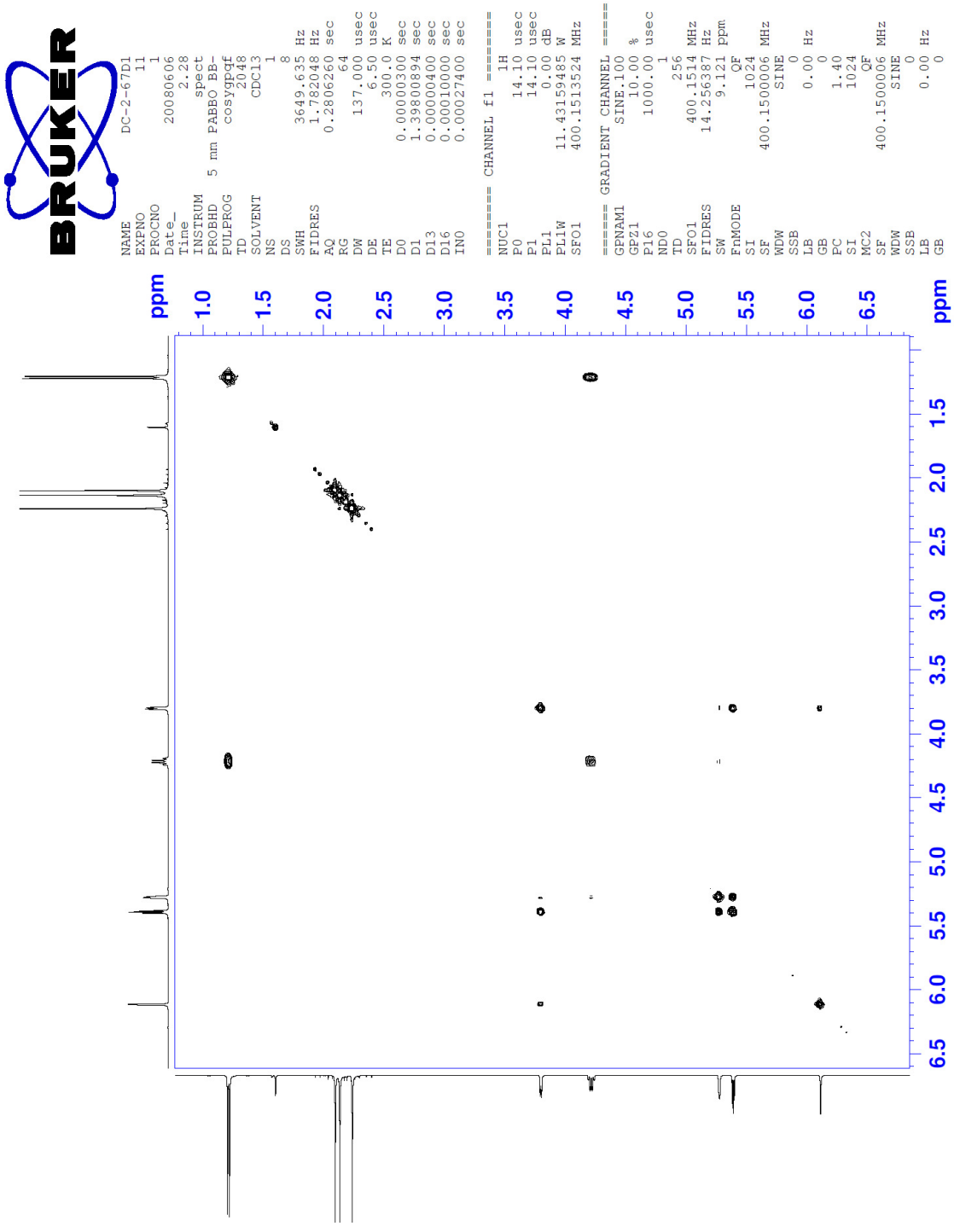


Figure 70 : COSY NMR spectrum of 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α-L-talose (**9**)

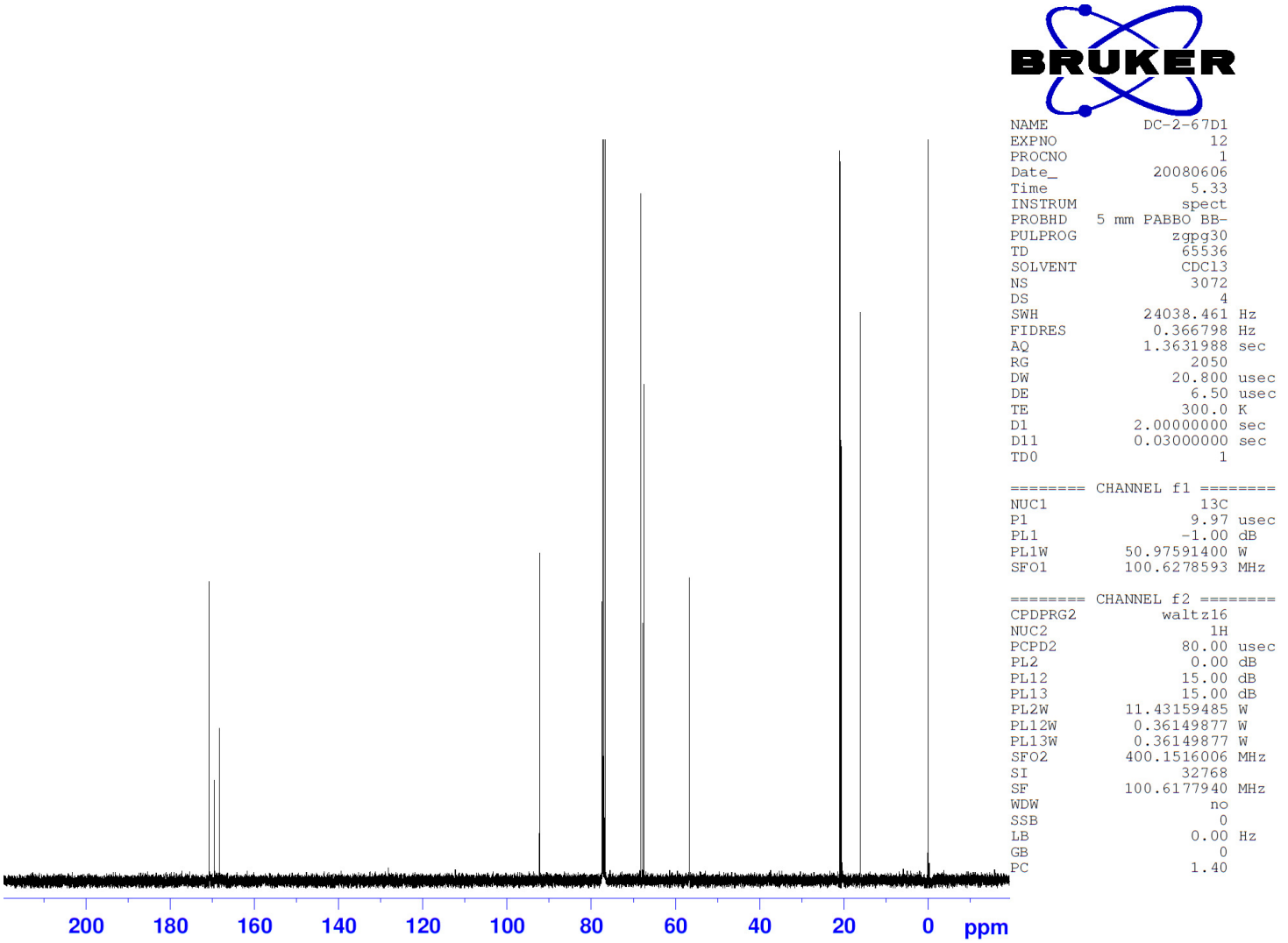


Figure 71 : ^{13}C NMR spectrum of 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α-L-talose (**9**)

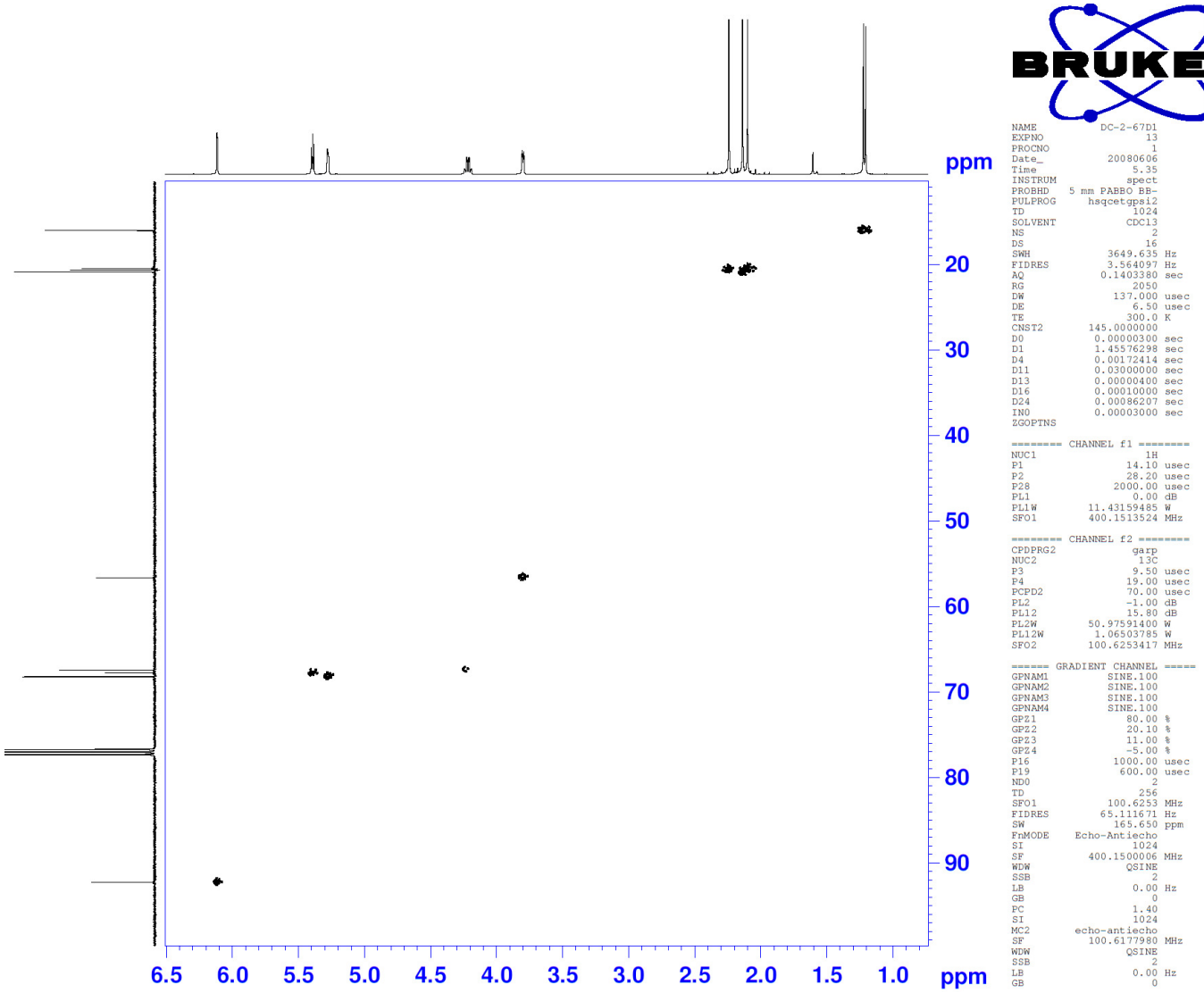


Figure 72 : HSQC NMR spectrum of 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α-L-talose (**9**)

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	9706 µs
Capillary Exit	84.2 Volt	Skim 1	16.8 Volt	Trap Drive	42.2	Auto MS/MS	Off

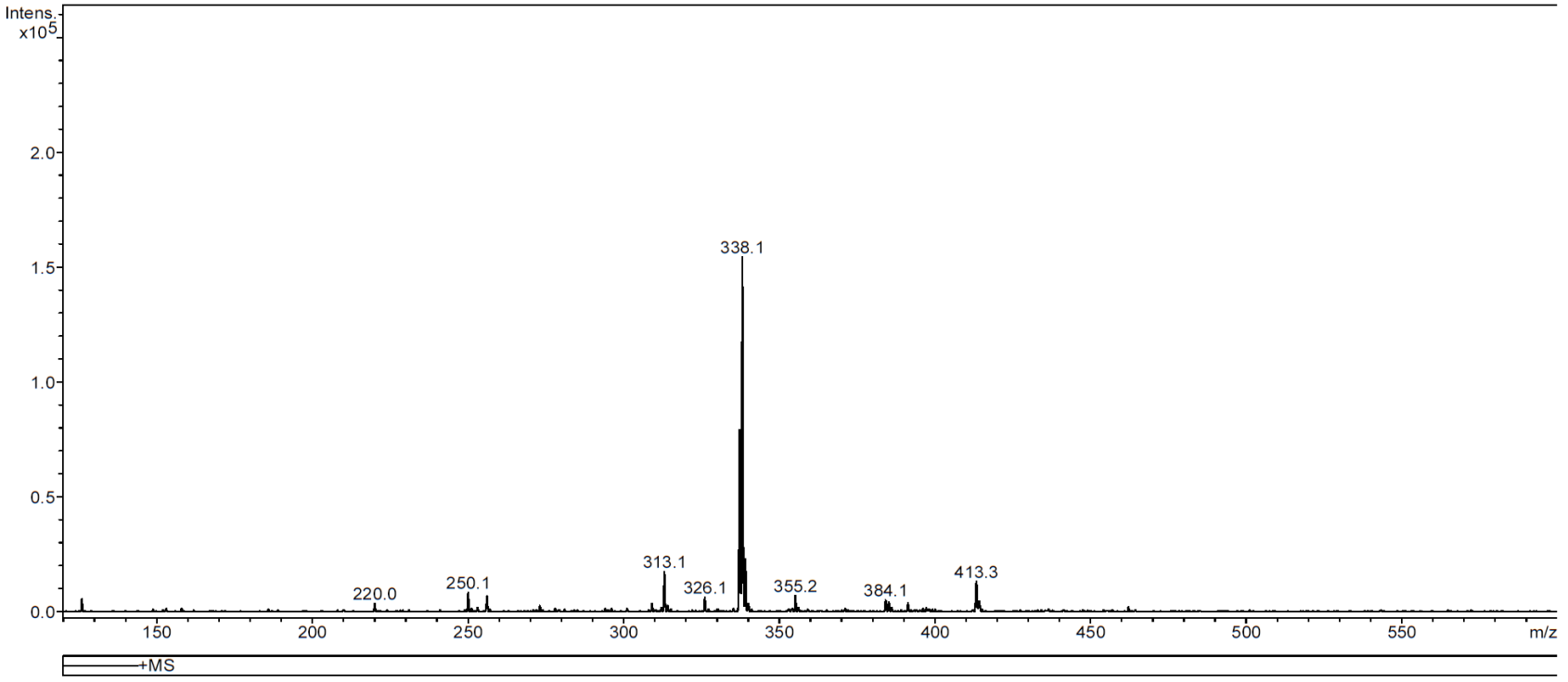


Figure 73 : Mass spectrum of 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α-L-talose (**9**)

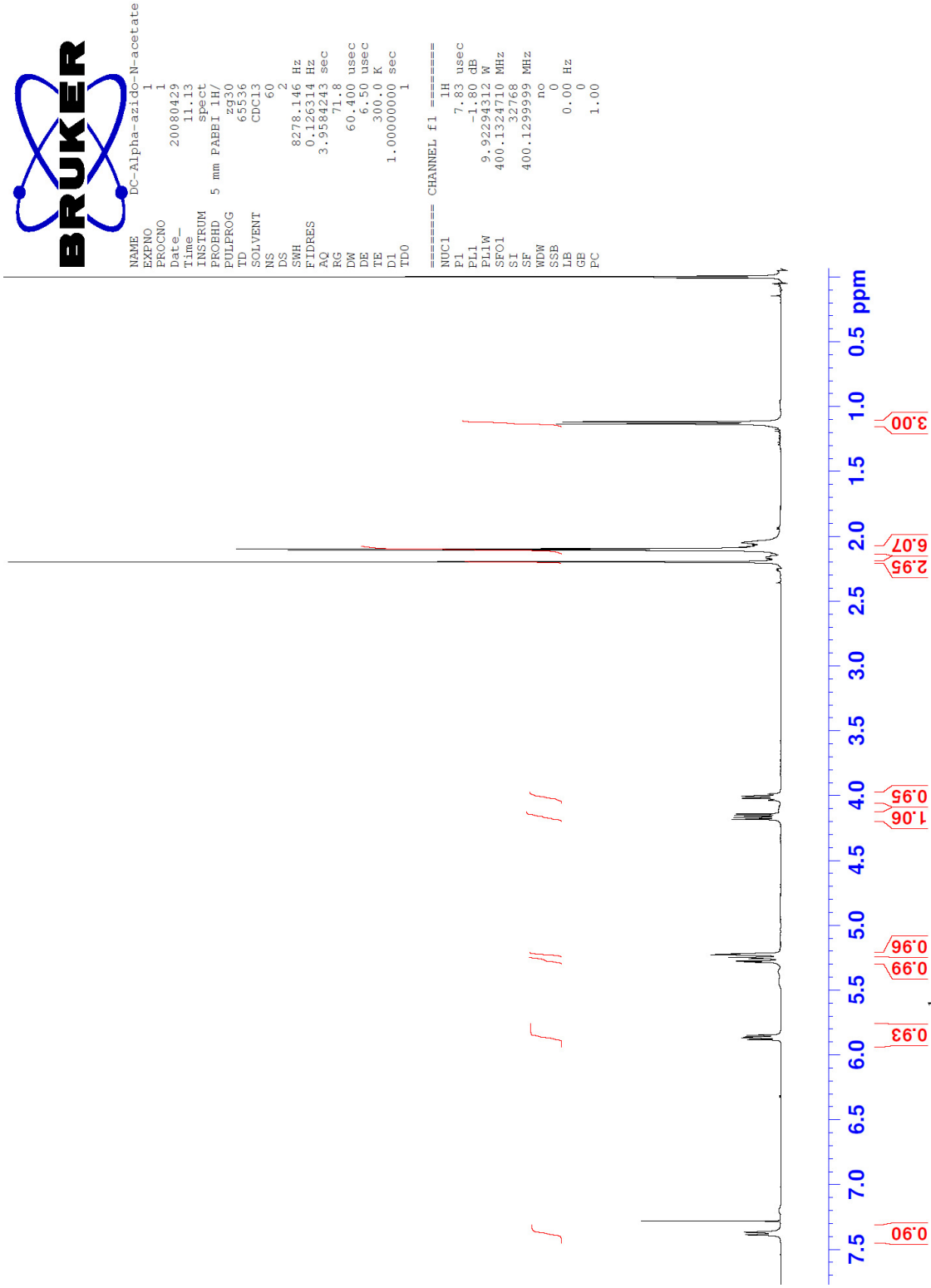


Figure 74 : ^{1}H NMR spectrum of 3,4-di-*O*-acetyl-1-*N*-acetyl-2-azidodeoxy-α-L-fucose (**10**)

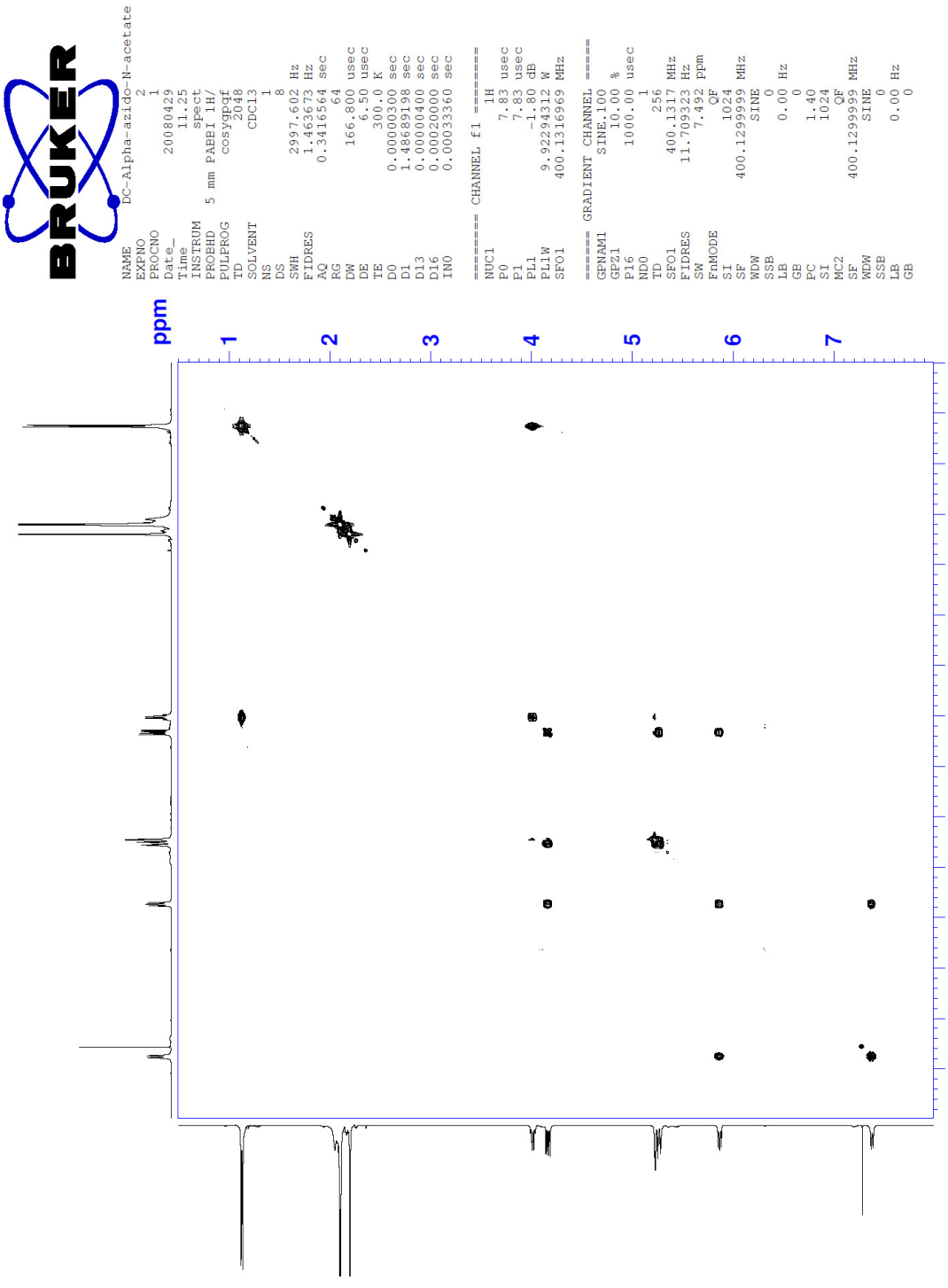


Figure 75 : COSY NMR spectrum of 3,4-di-*O*-acetyl-1-*N*-acetyl-2-azidodeoxy-α-L-fucose (**10**)

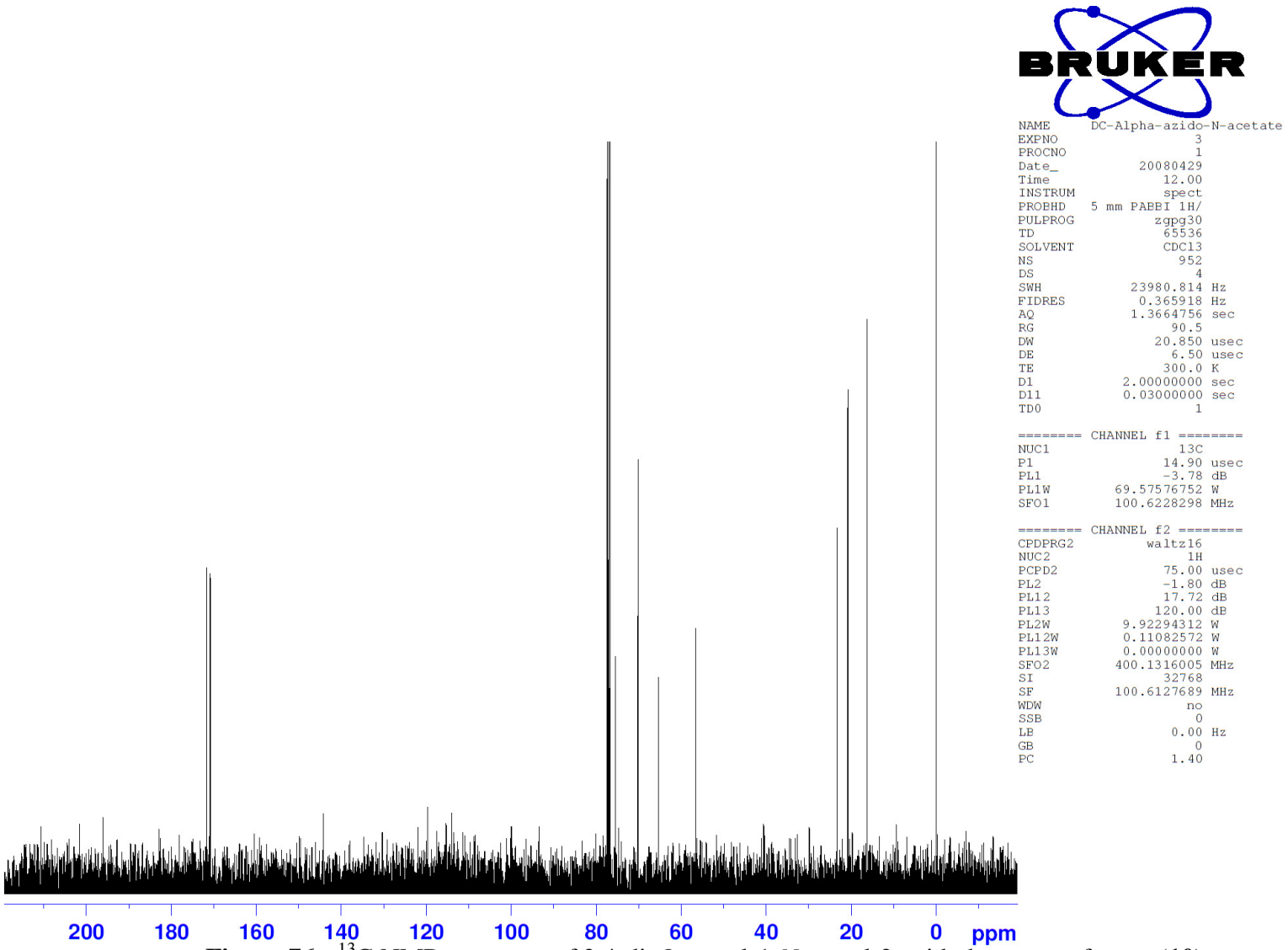


Figure 76 : ^{13}C NMR spectrum of 3,4-di-*O*-acetyl-1-*N*-acetyl-2-azidodeoxy-α-L-fucose (**10**)

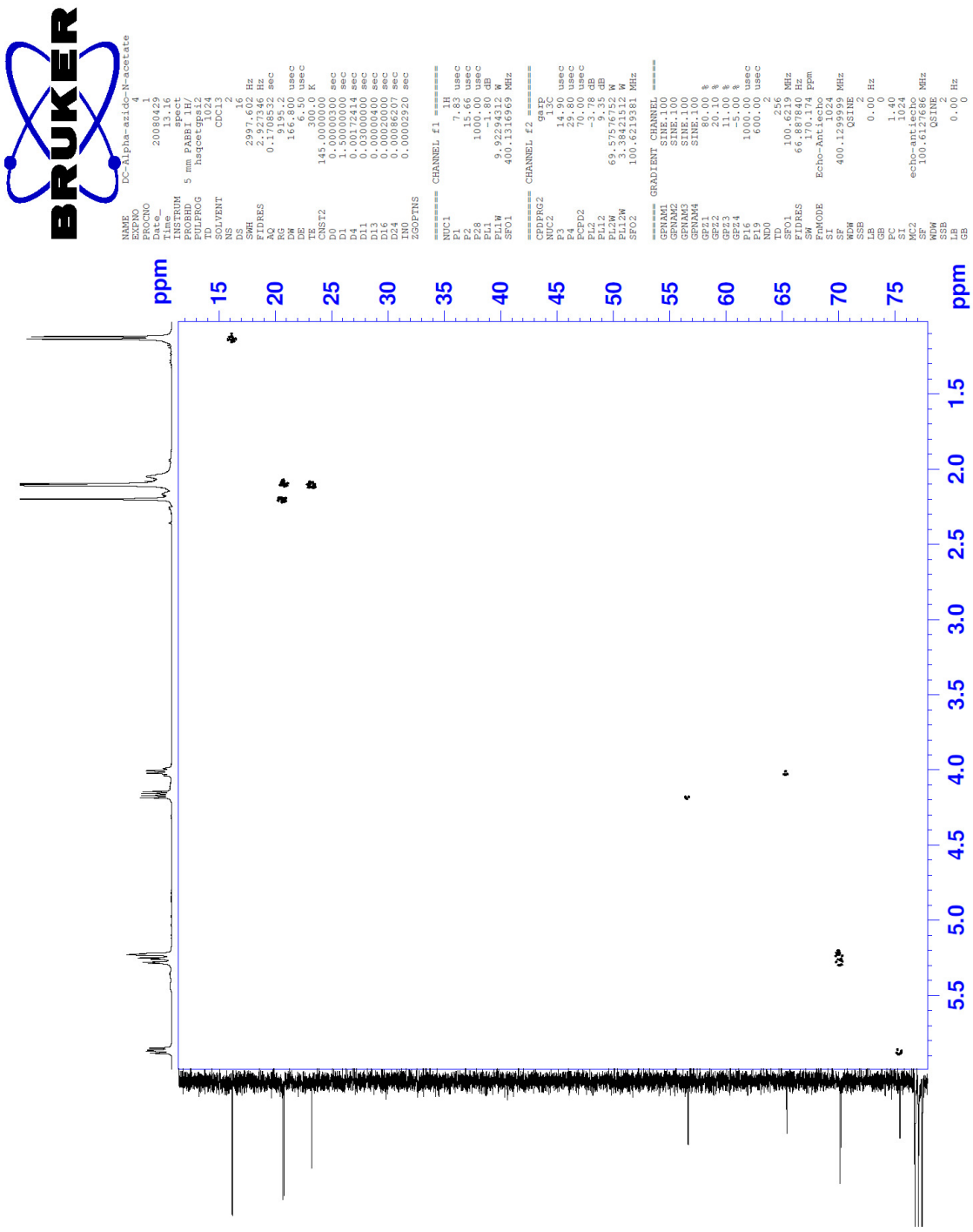


Figure 77 : HSQC NMR spectrum of 3,4-di-*O*-acetyl-1-*N*-acetyl-2-azidodeoxy-α-L-fucose (**10**)

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	939 µs
Capillary Exit	100.8 Volt	Skim 1	29.6 Volt	Trap Drive	47.0	Auto MS/MS	Off

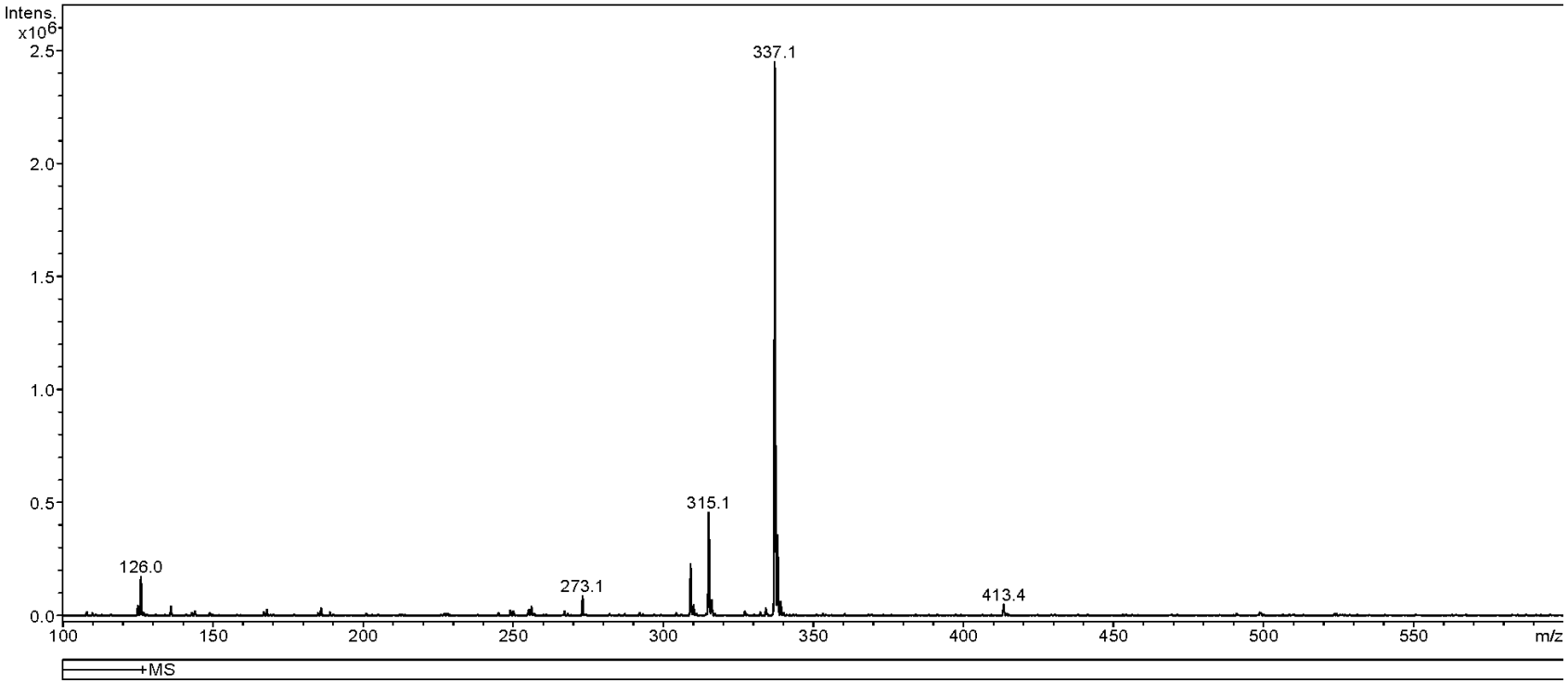


Figure 78 : Mass spectrum of 3,4-di-*O*-acetyl-1-*N*-acetyl-2-azidodeoxy-α-L-fucose (**10**)

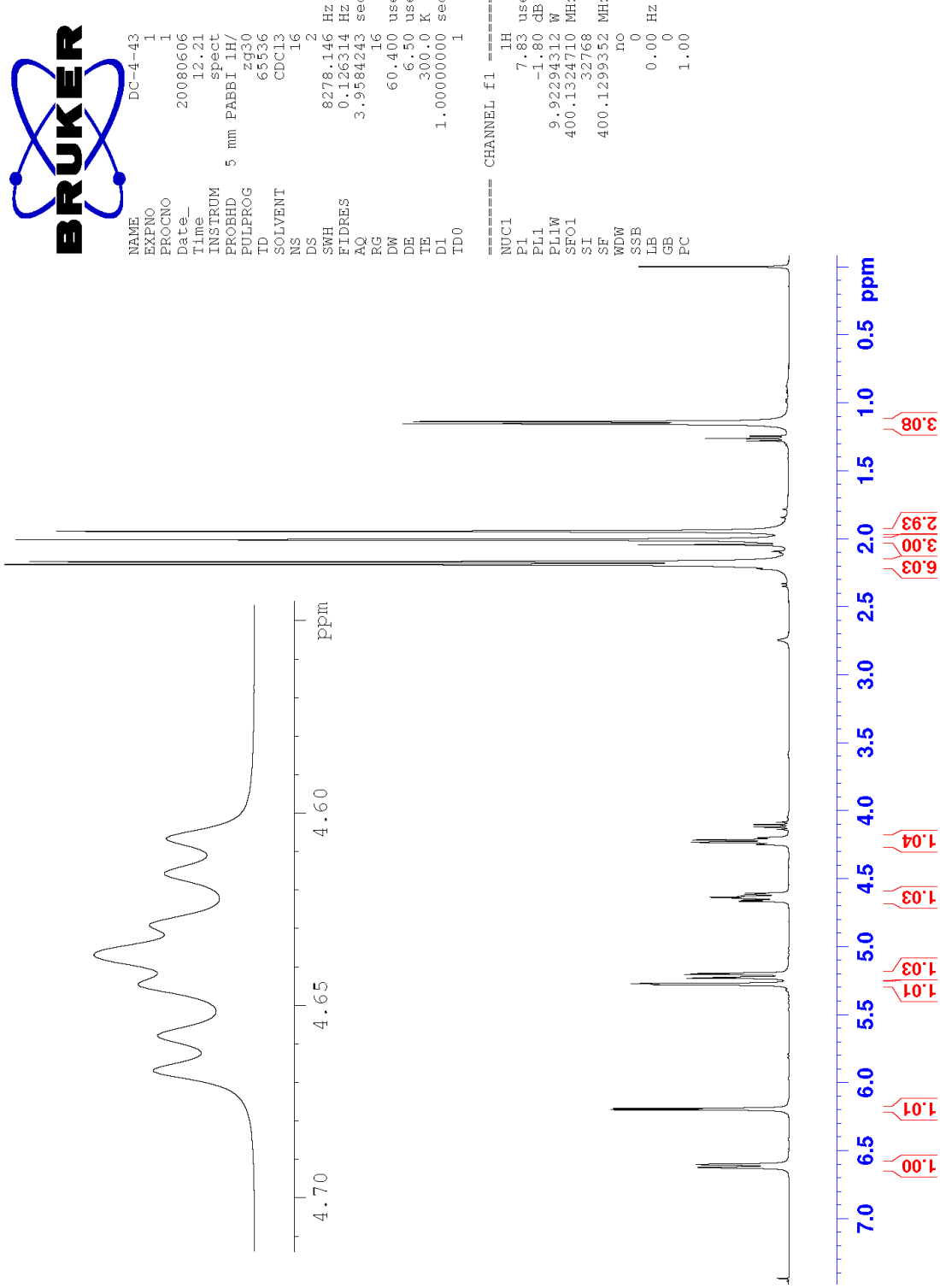


Figure 79 : ^{1}H NMR spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-acetyl-α-L-fucose (**11**)

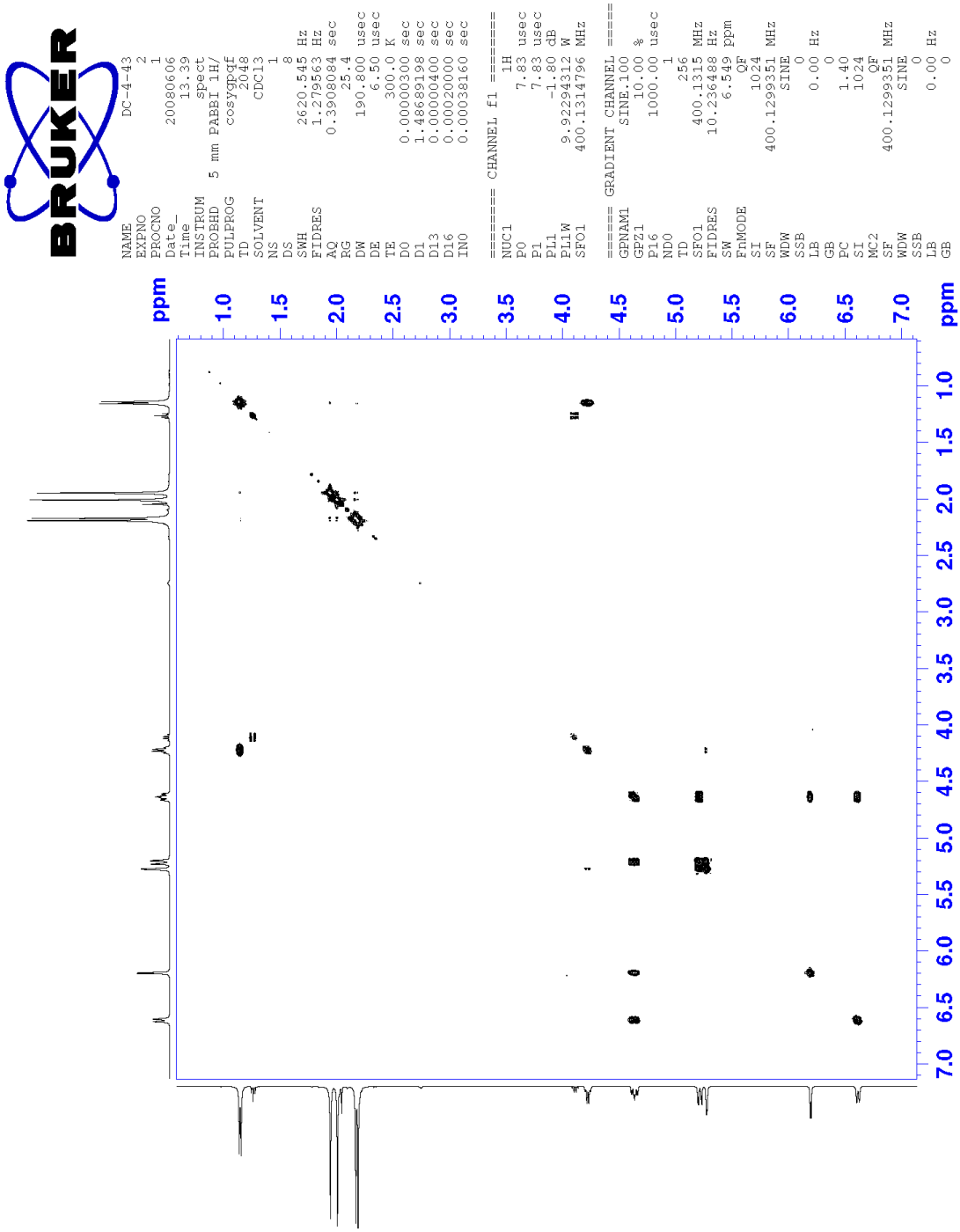


Figure 80 : COSY spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-acetyl-α-L-fucose (**11**)

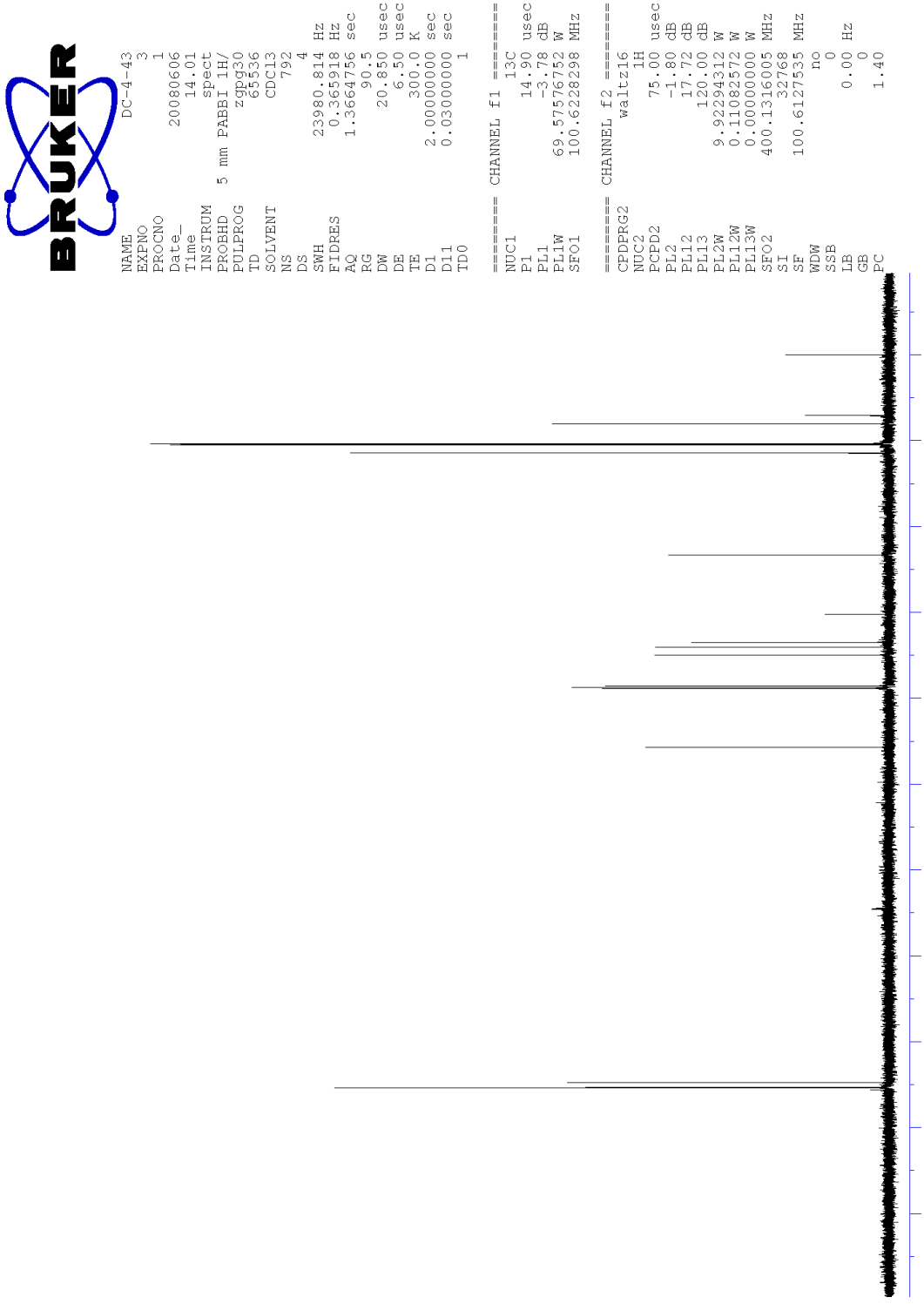


Figure 81 : ^{13}C spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-acetyl-α-L-fucose (**11**)

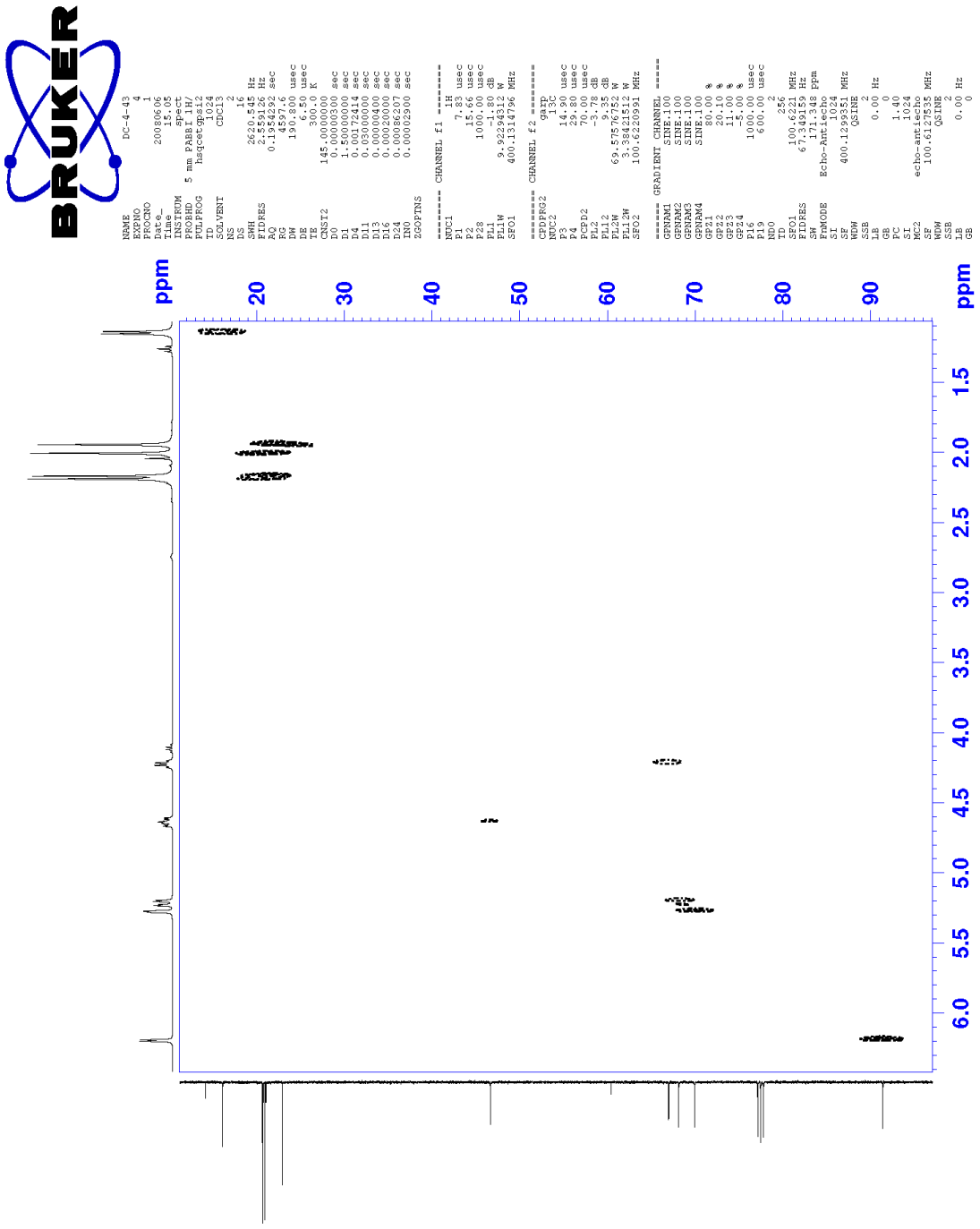


Figure 82 : HSQC spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-acetyl-α-L-fucose (**11**)

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	3936 µs
Capillary Exit	97.2 Volt	Skim 1	27.0 Volt	Trap Drive	37.6	Auto MS/MS	Off

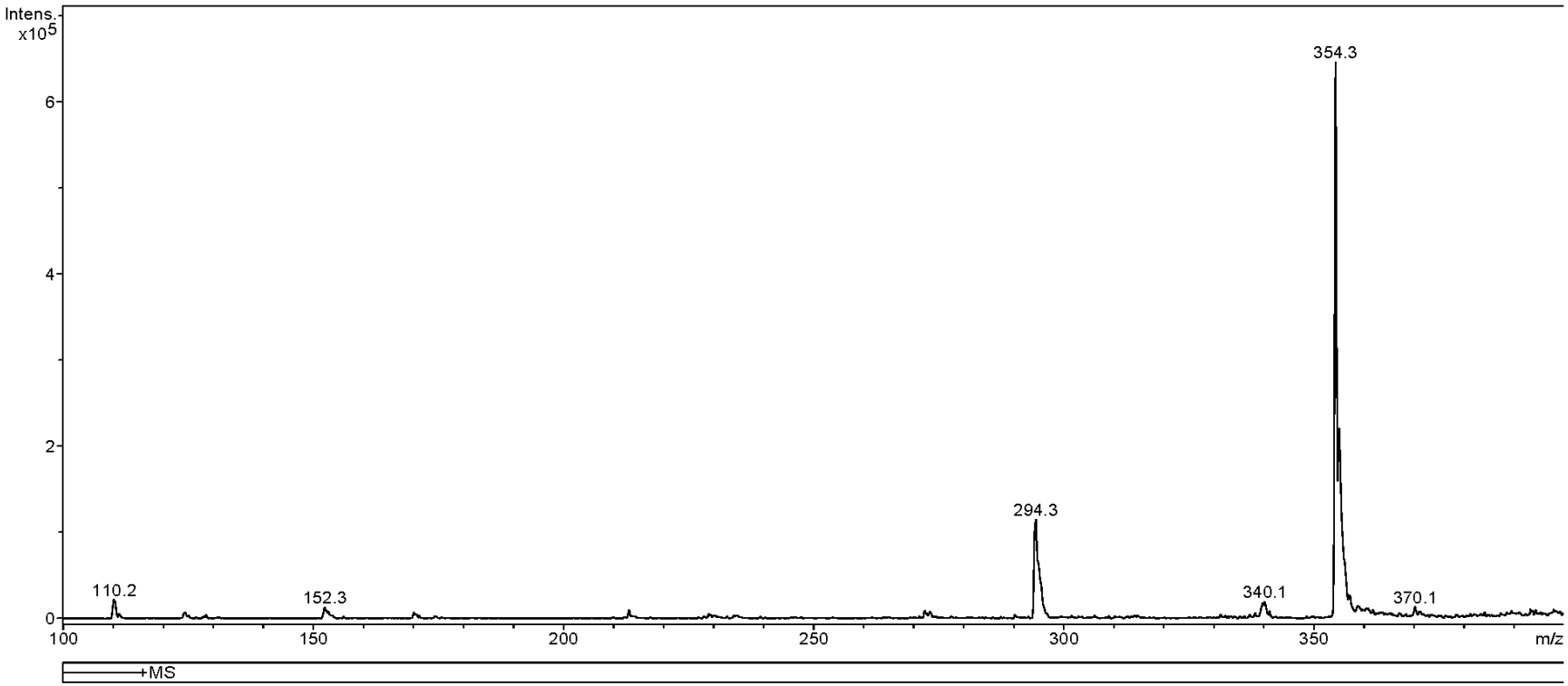


Figure 83 : Mass spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-acetyl-α-L-fucose (**11**)

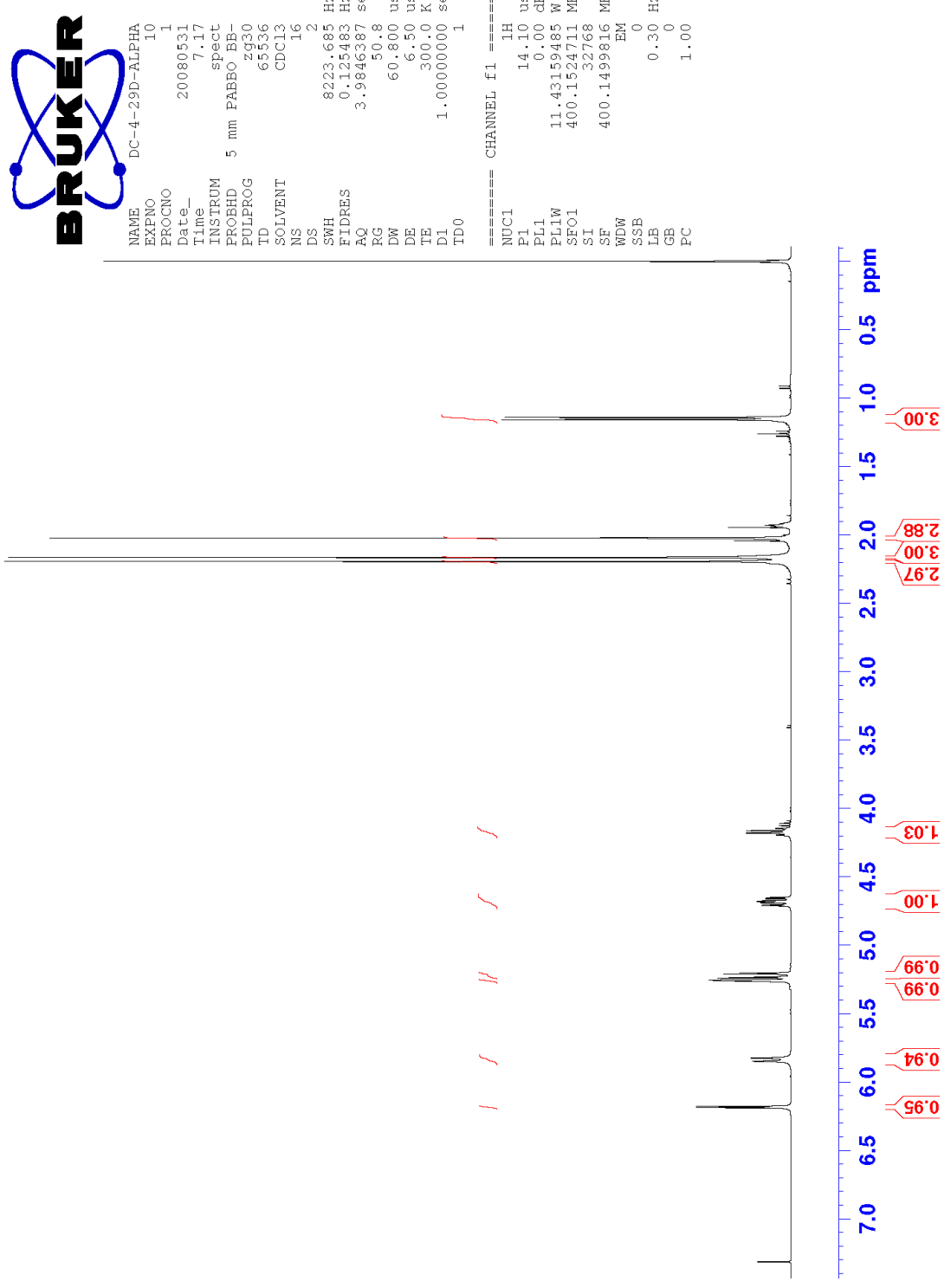


Figure 84 : ^{1}H spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-(trideutero)acetyl-α-L-fucose (**12**)

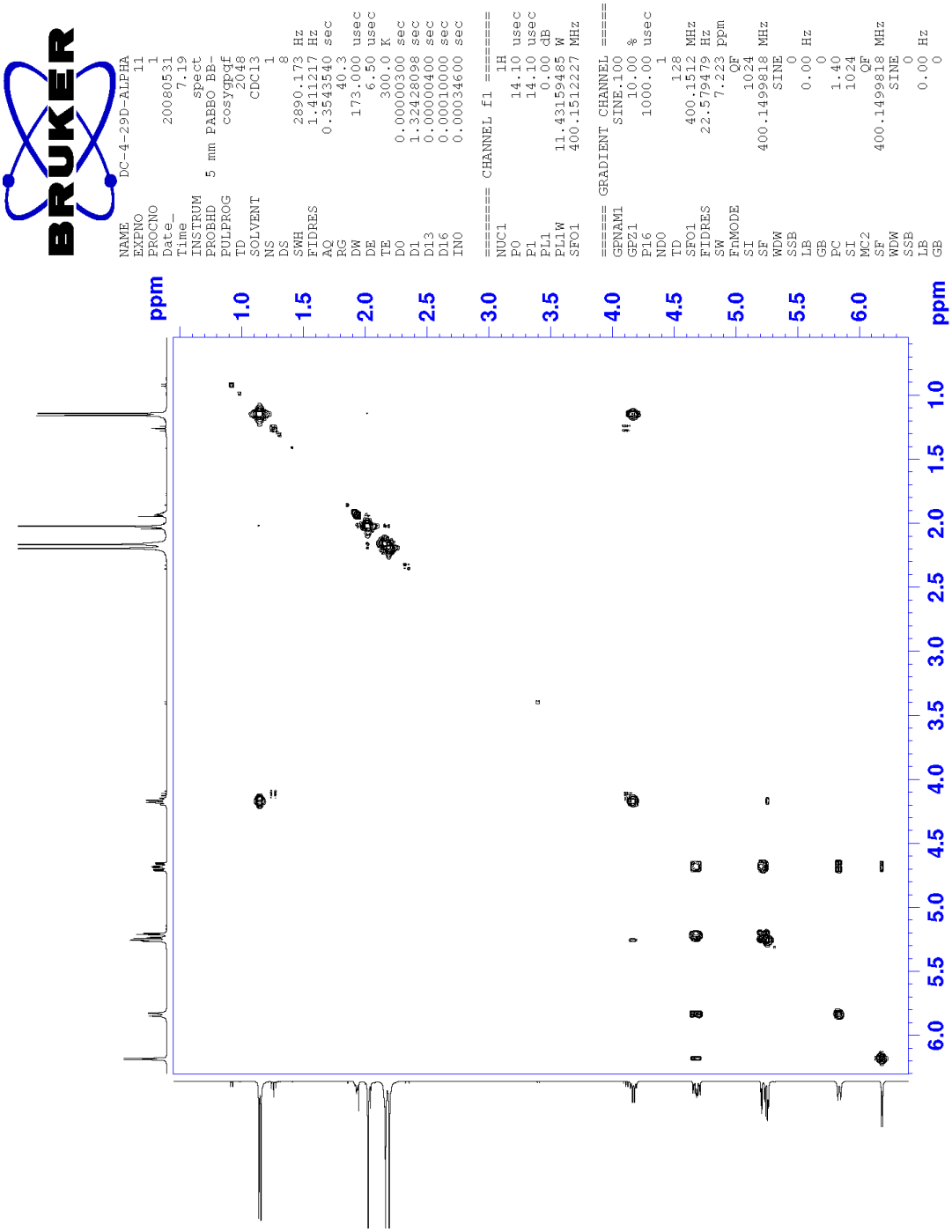


Figure 85 : COSY spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-(trideutero)acetyl-α-L-fucose (**12**)

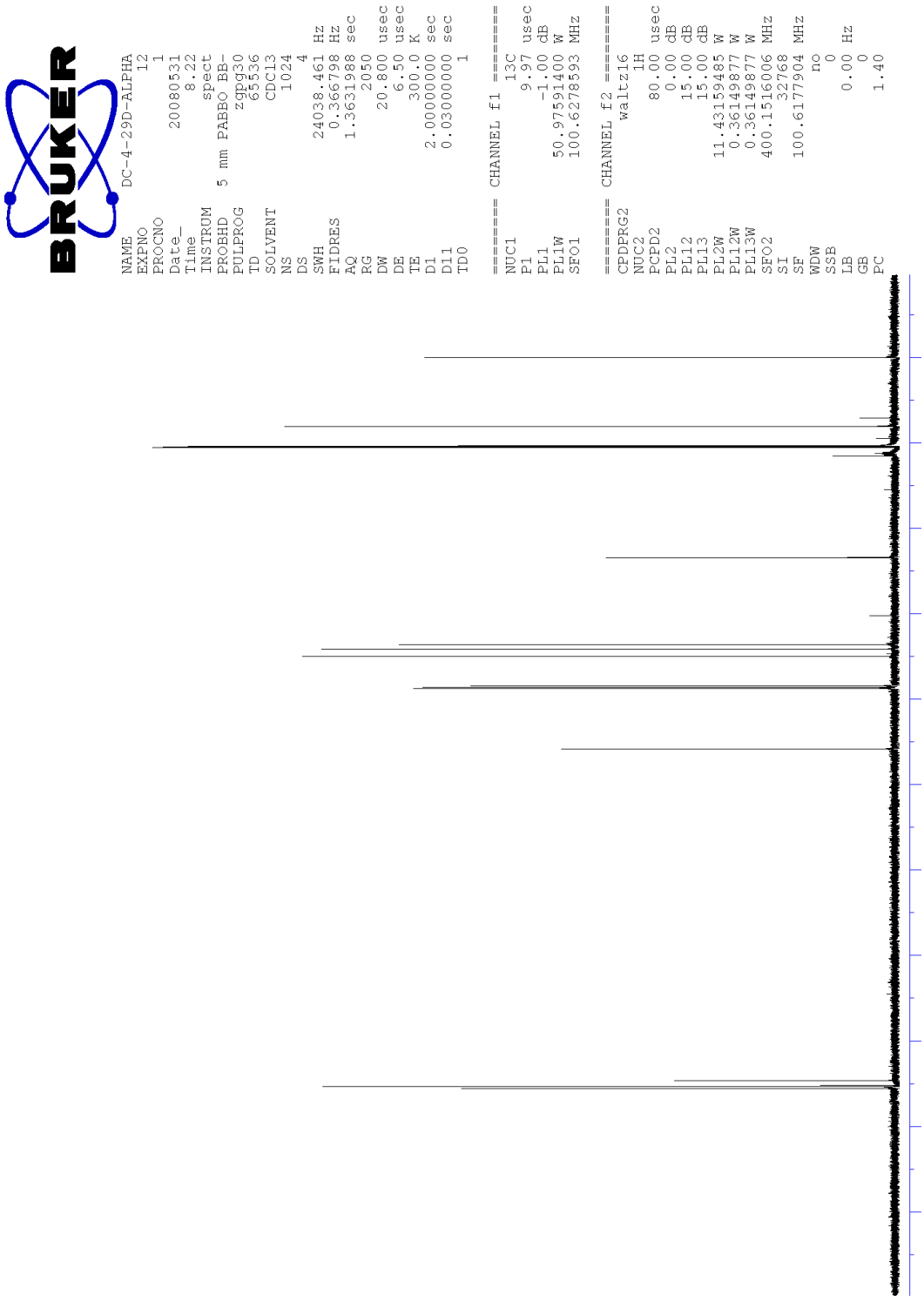


Figure 86 : ^{13}C spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-(trideutero)acetyl-α-L-fucose (**12**)

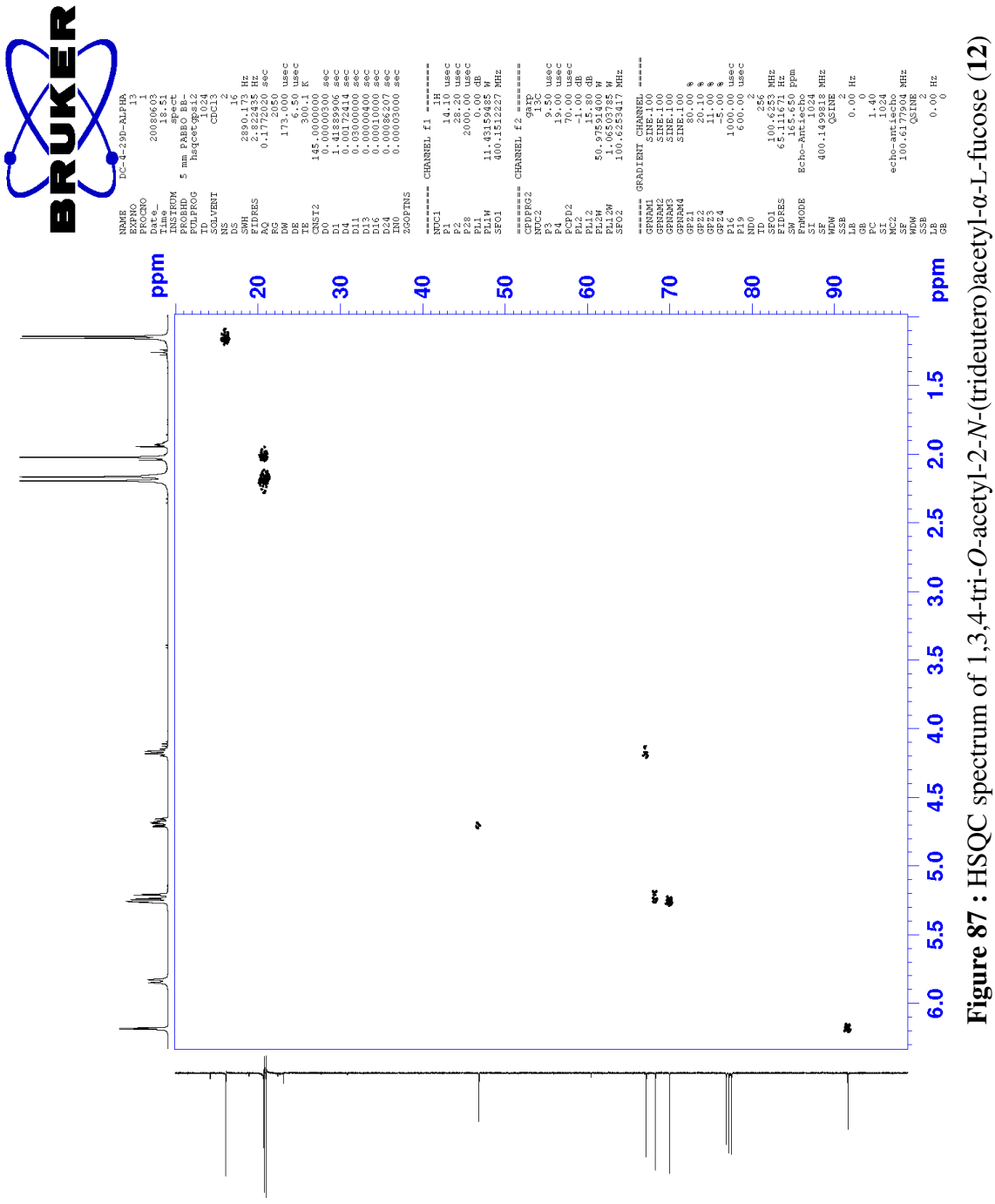


Figure 87 : HSQC spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-(trideutero)acetyl-α-L-fucose (**12**)

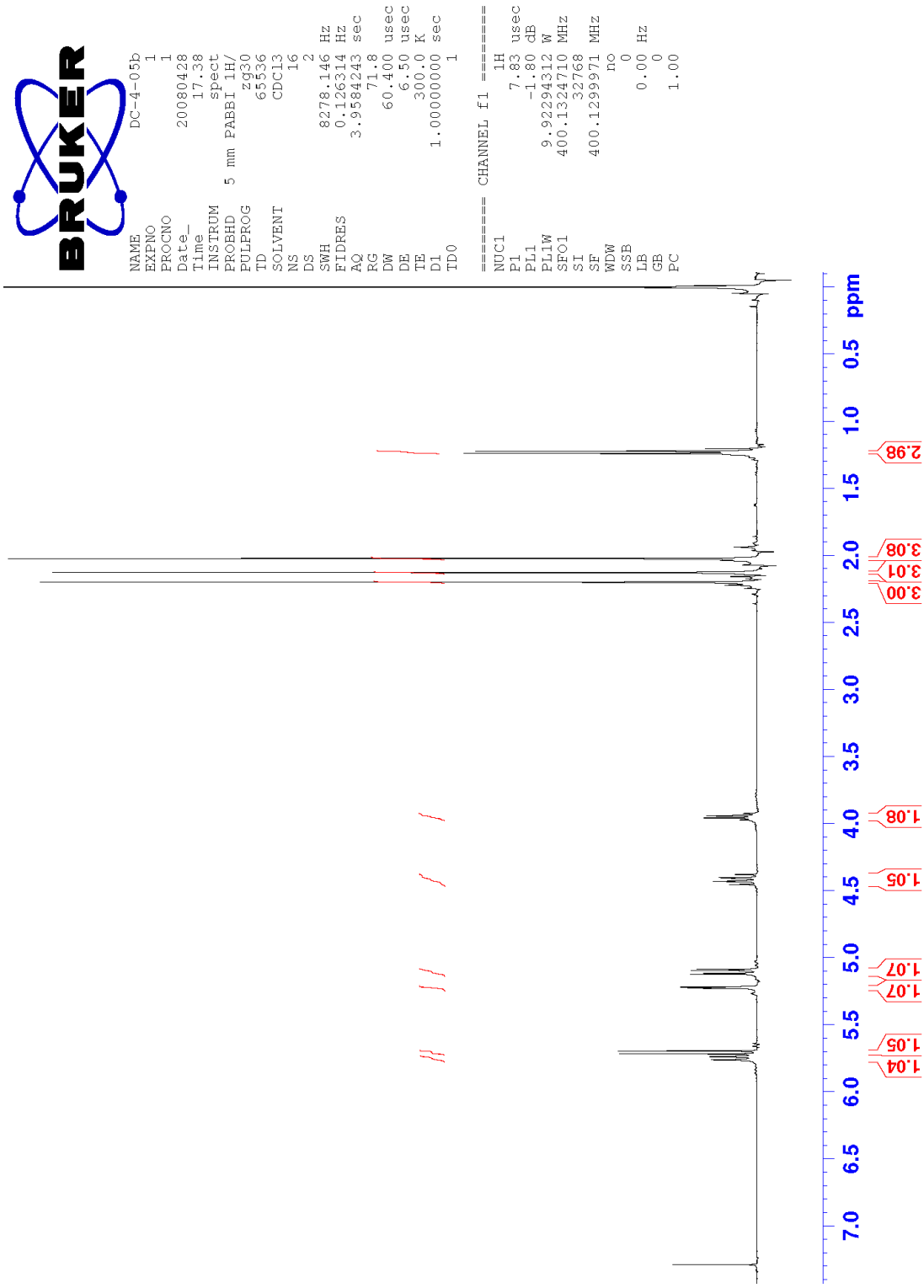


Figure 88 : ^{1}H spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-(trideutero)acetyl-β-L-fucose (**12**)

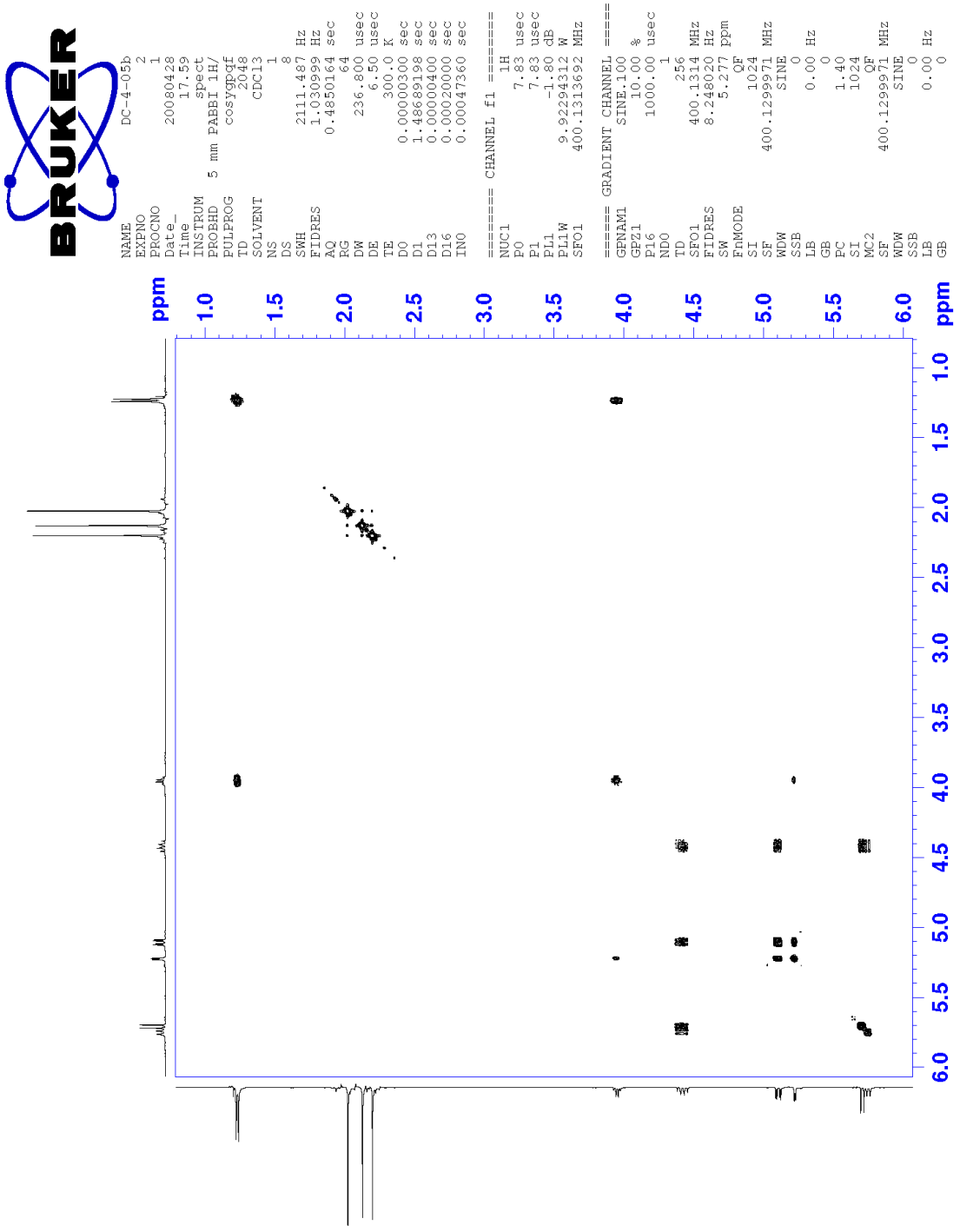


Figure 89 : COSY spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-(trideutero)acetyl-β-L-fucose (**12**)

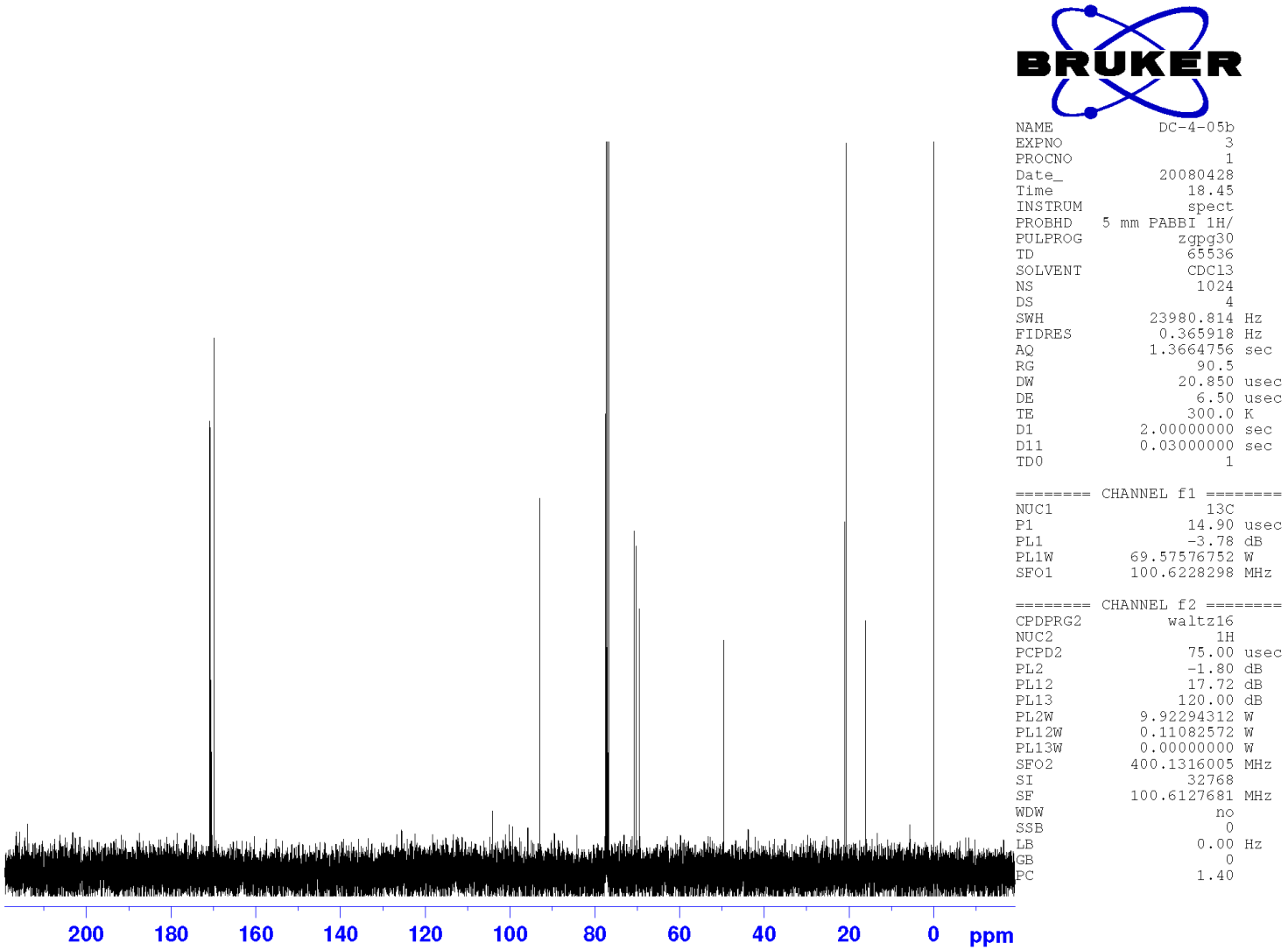


Figure 90 : ^{13}C spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-(trideutero)acetyl-β-L-fucose (**12**)

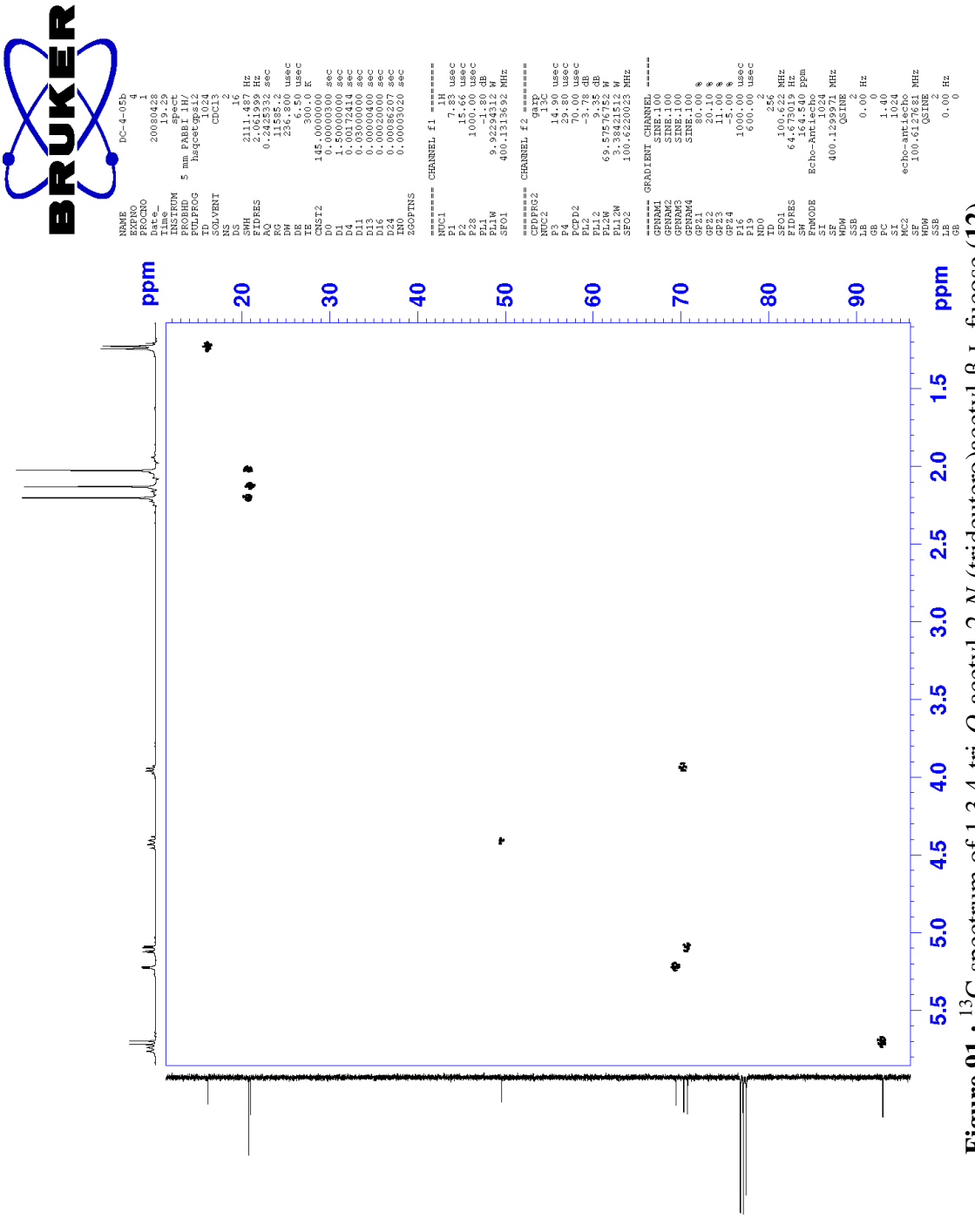


Figure 91 : ^{13}C spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-(trideutero)acetyl-β-L-fucose (**12**)

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	5607 µs
Capillary Exit	83.5 Volt	Skim 1	16.2 Volt	Trap Drive	36.3	Auto MS/MS	Off

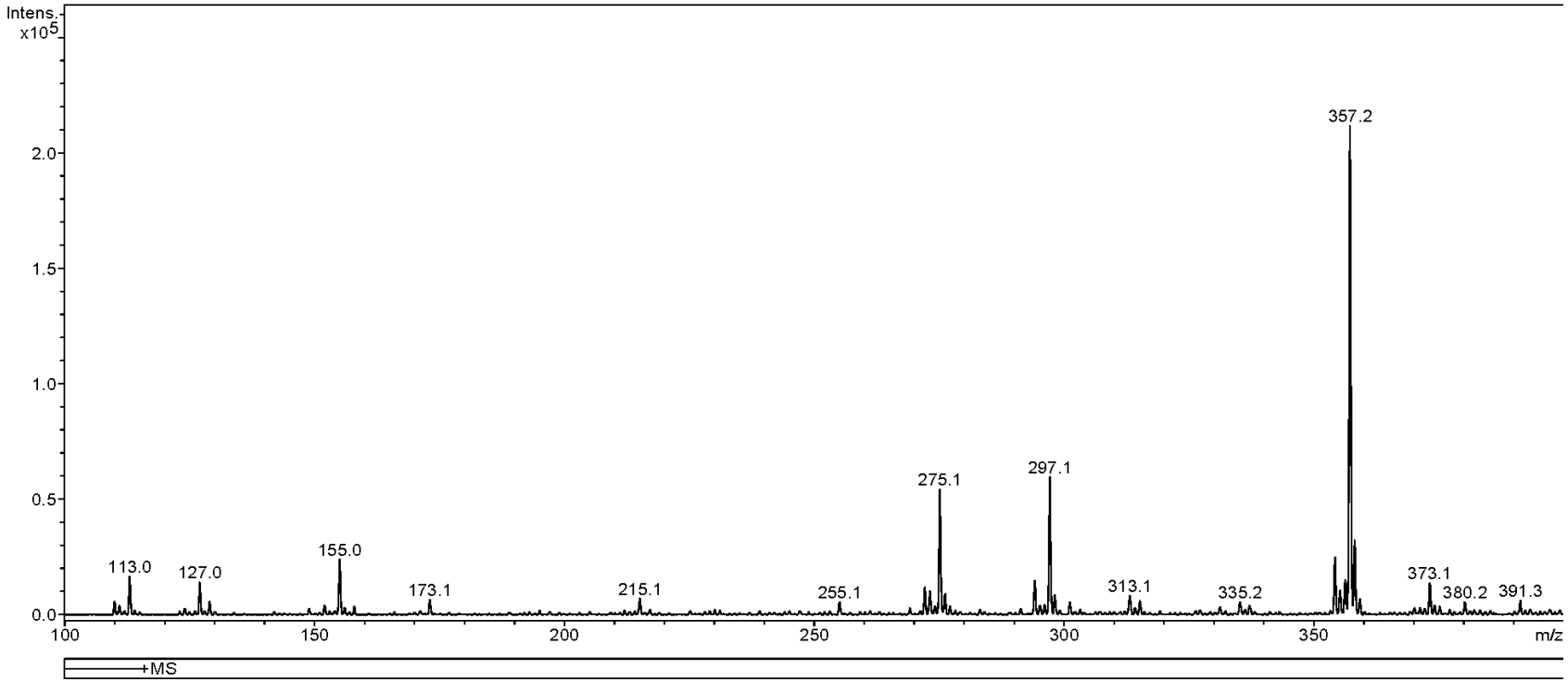


Figure 92 **:** Mass spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-(trideutero)acetyl-L-fucose (**12**)

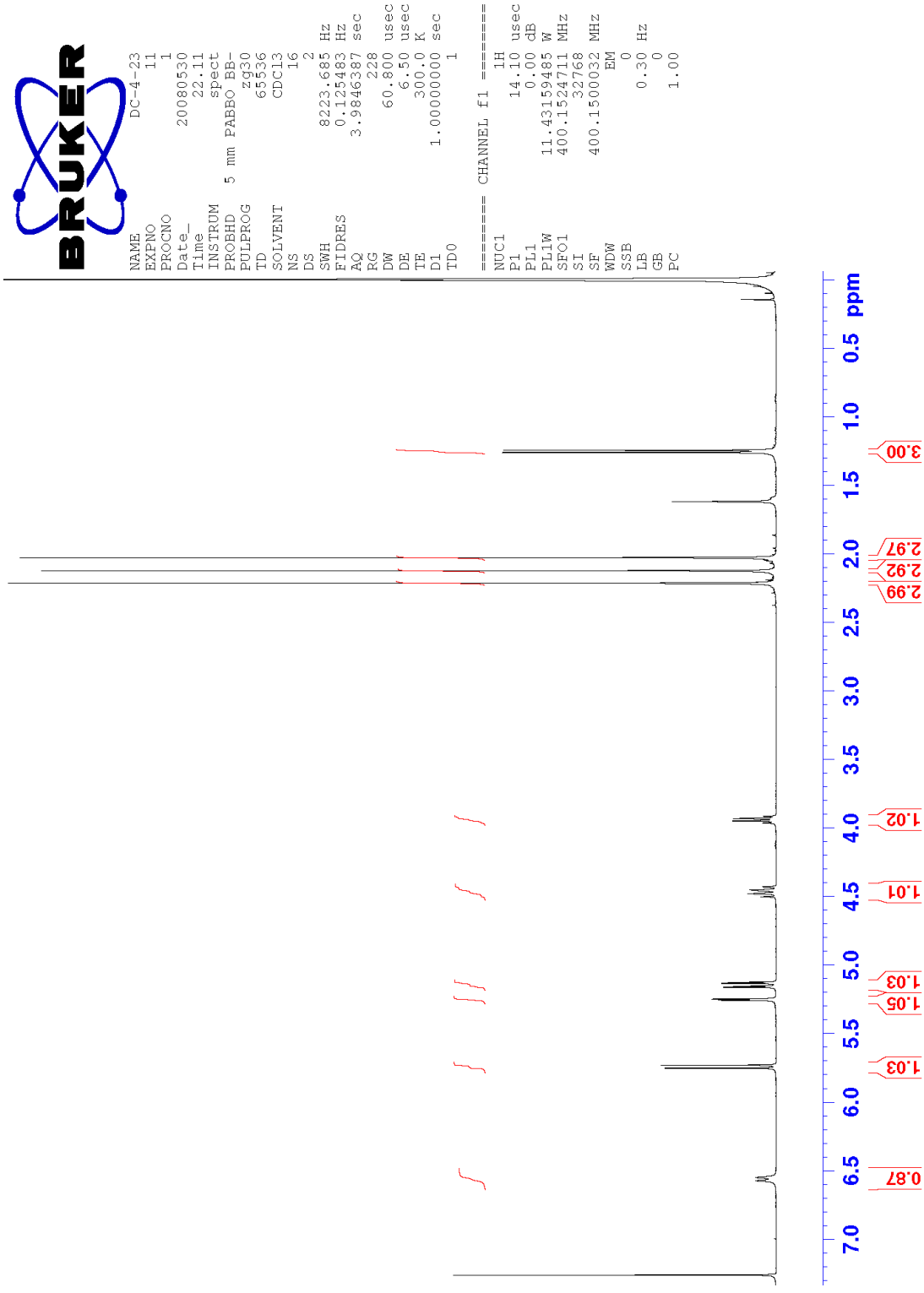


Figure 93 **:** ^{1}H NMR spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-(trifluoro)acetyl-β-L-fucose (**13**)

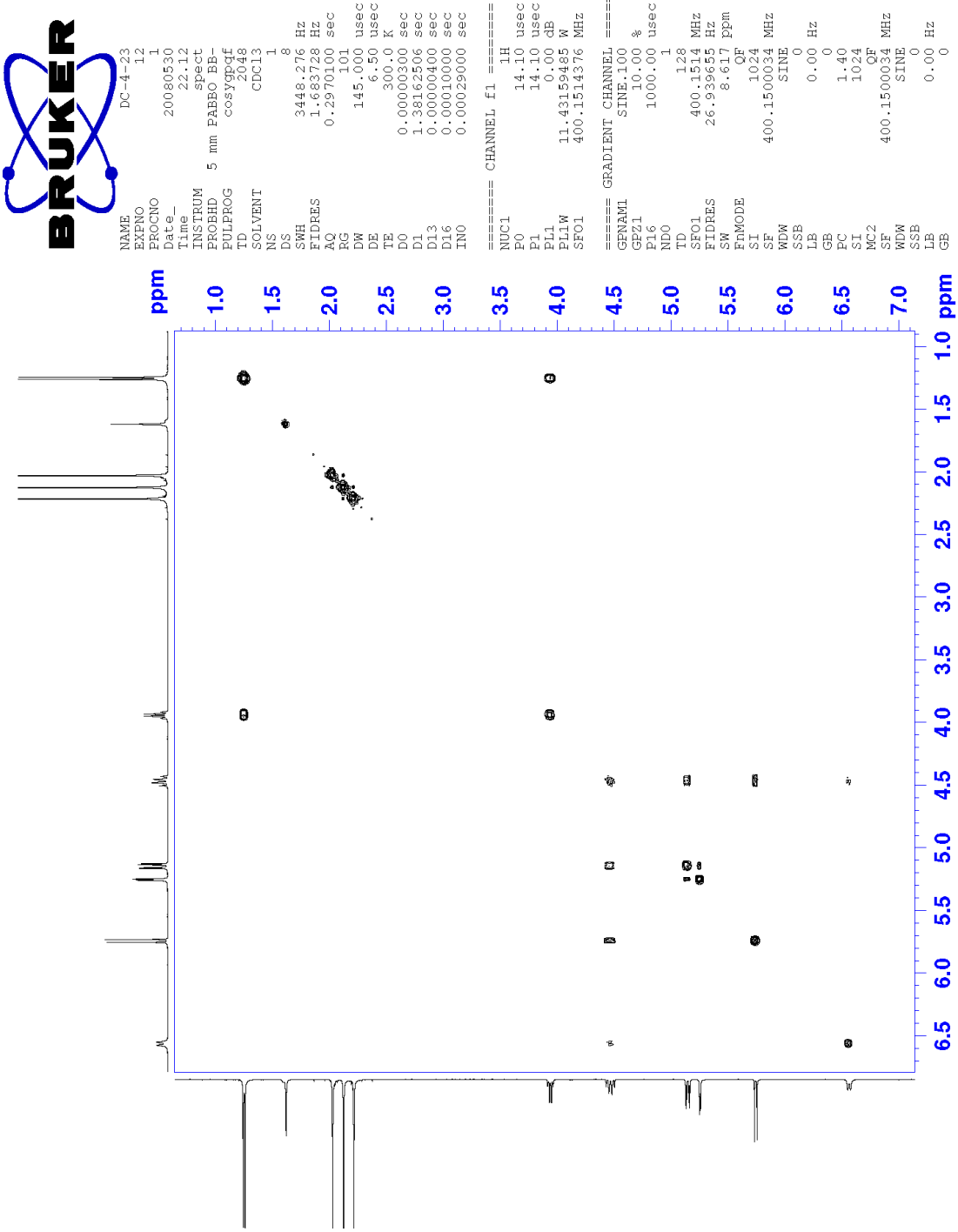


Figure 94 **:** COSY NMR spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-(trifluoro)acetyl-β-L-fucose (**13**)

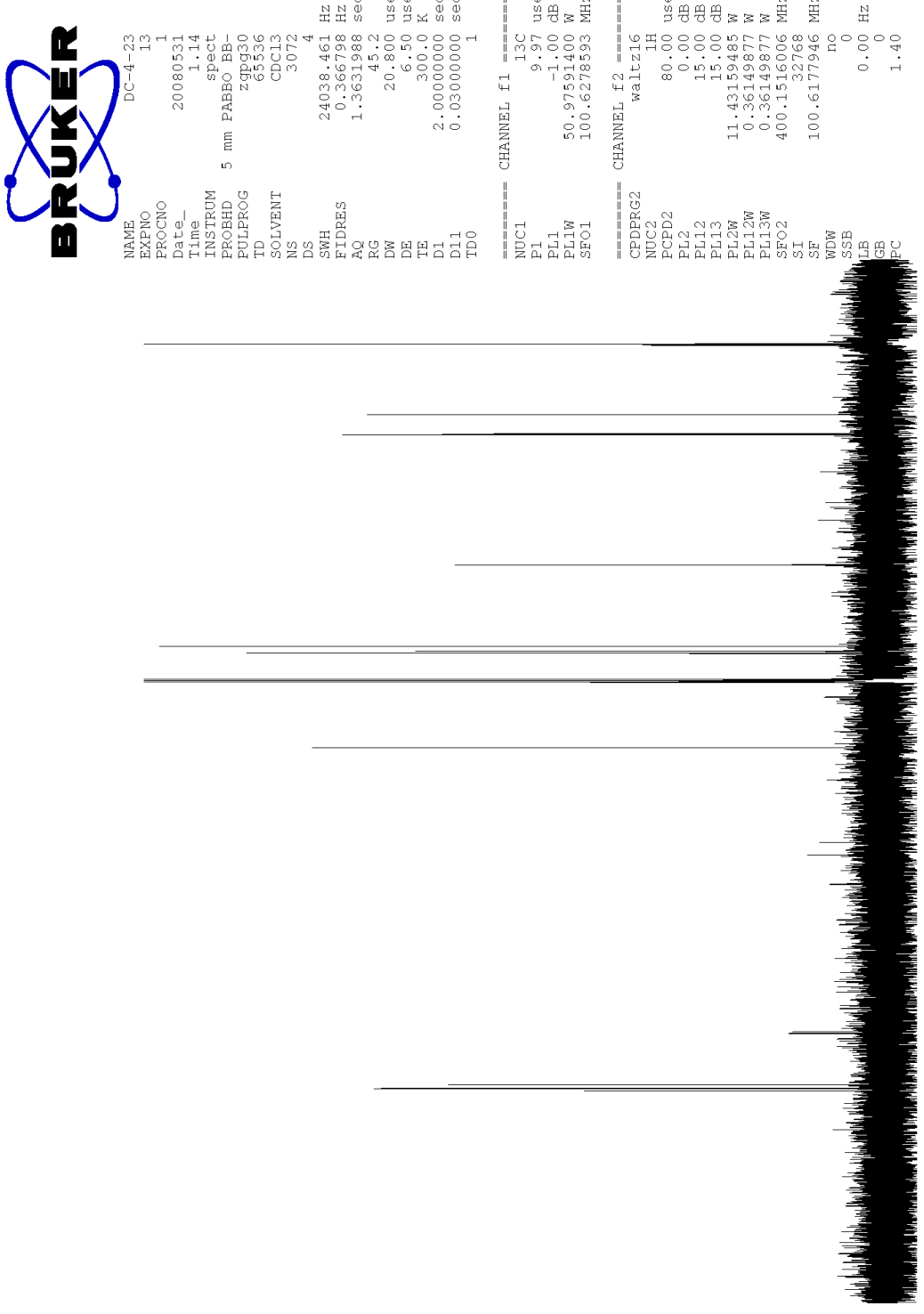


Figure 95 : ^{13}C NMR spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-(trifluoro)acetyl-β-L-fucose (**13**)

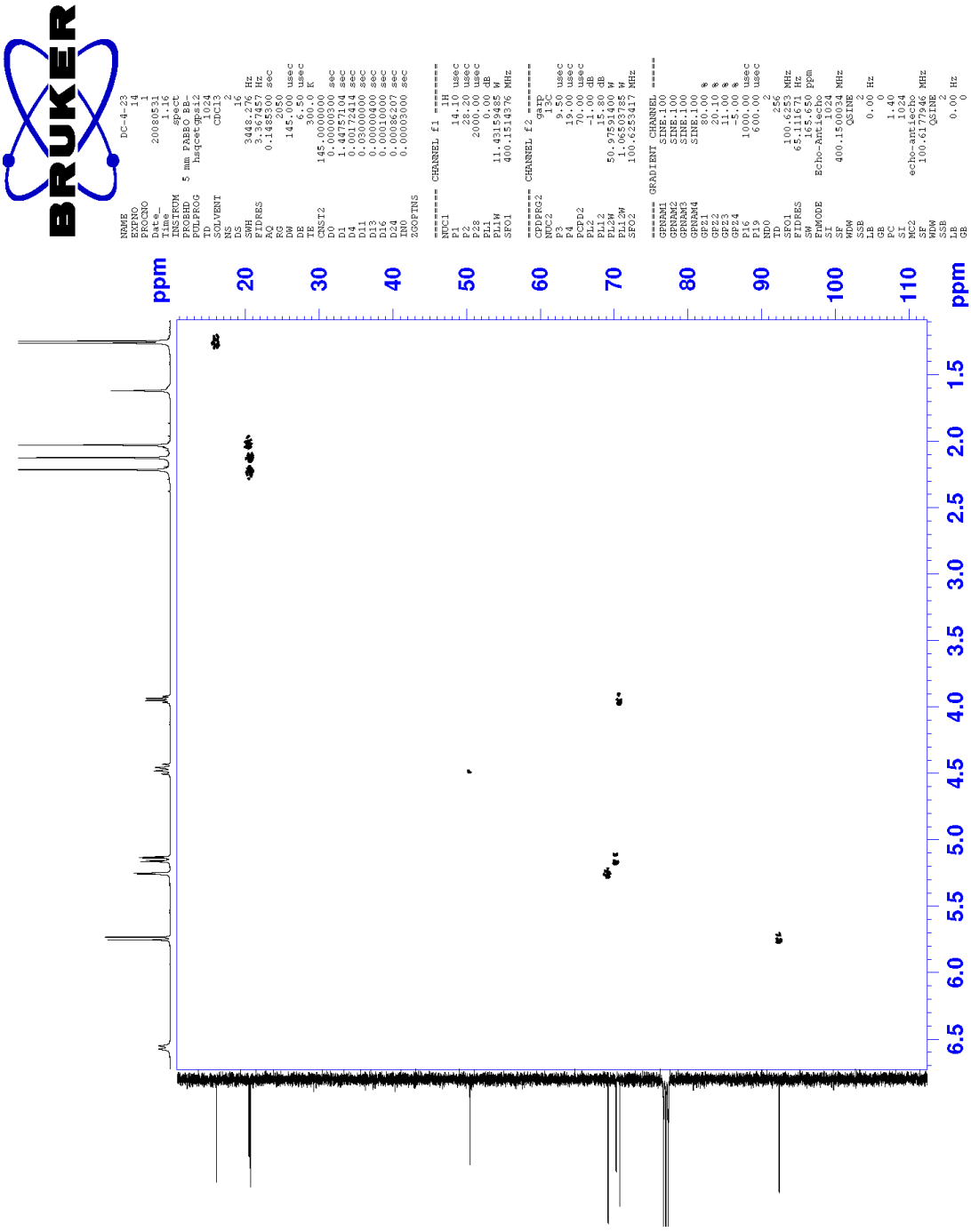


Figure 96 **:** HSQC NMR spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-(trifluoro)acetyl-β-L-fucose (**13**)

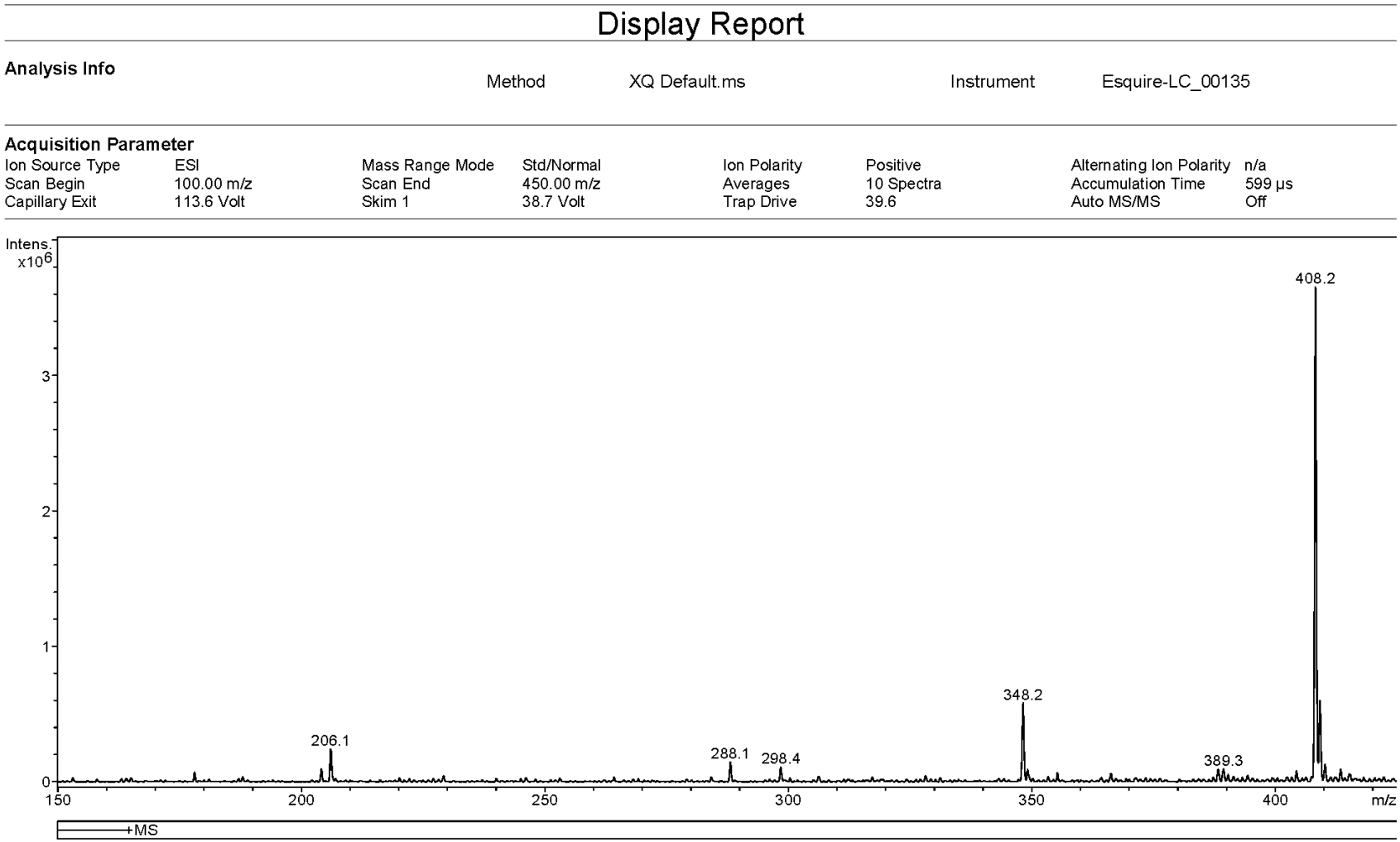


Figure 97**:** Mass spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-(trifluoro)acetyl-L-fucose (**13**)

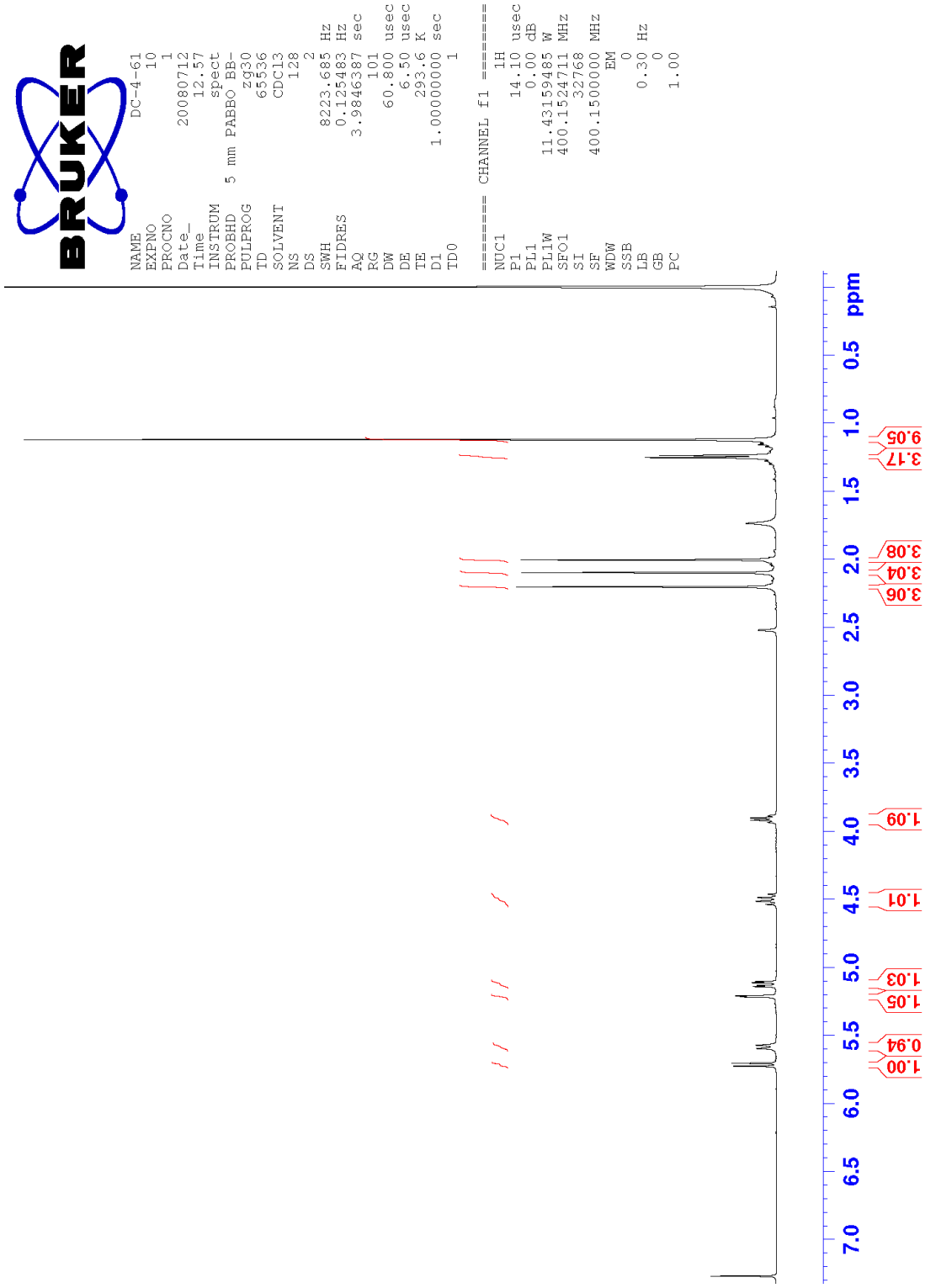


Figure 98 : ^{1}H NMR spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-(trimethyl)acetyl-β-L-fucose (**14**)

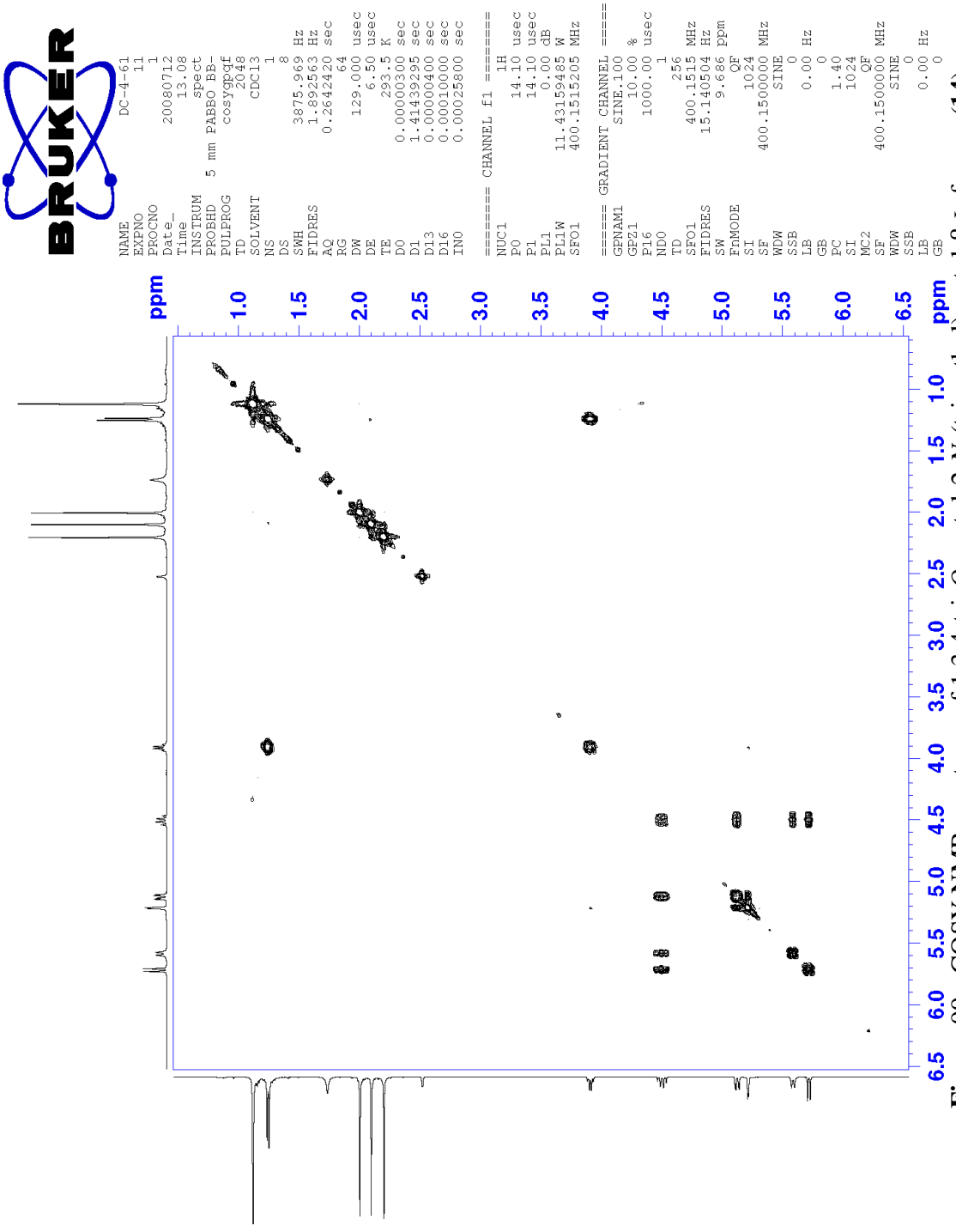


Figure 99 **:** COSY NMR spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-(trimethyl)acetyl-β-L-fucose (**14**)

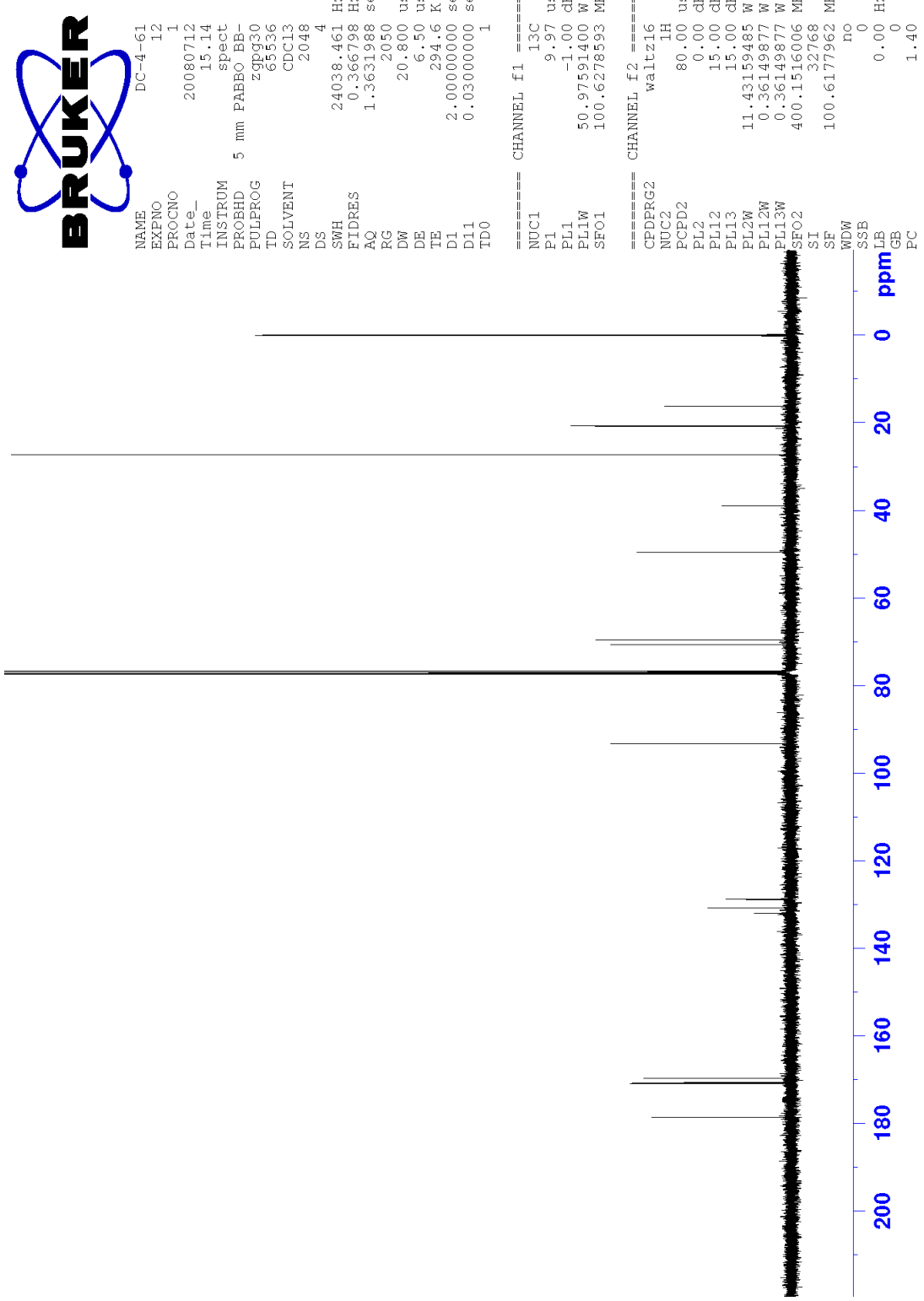


Figure 100 **:** ^{13}C NMR spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-(trimethyl)acetyl-β-L-fucose (**14**)

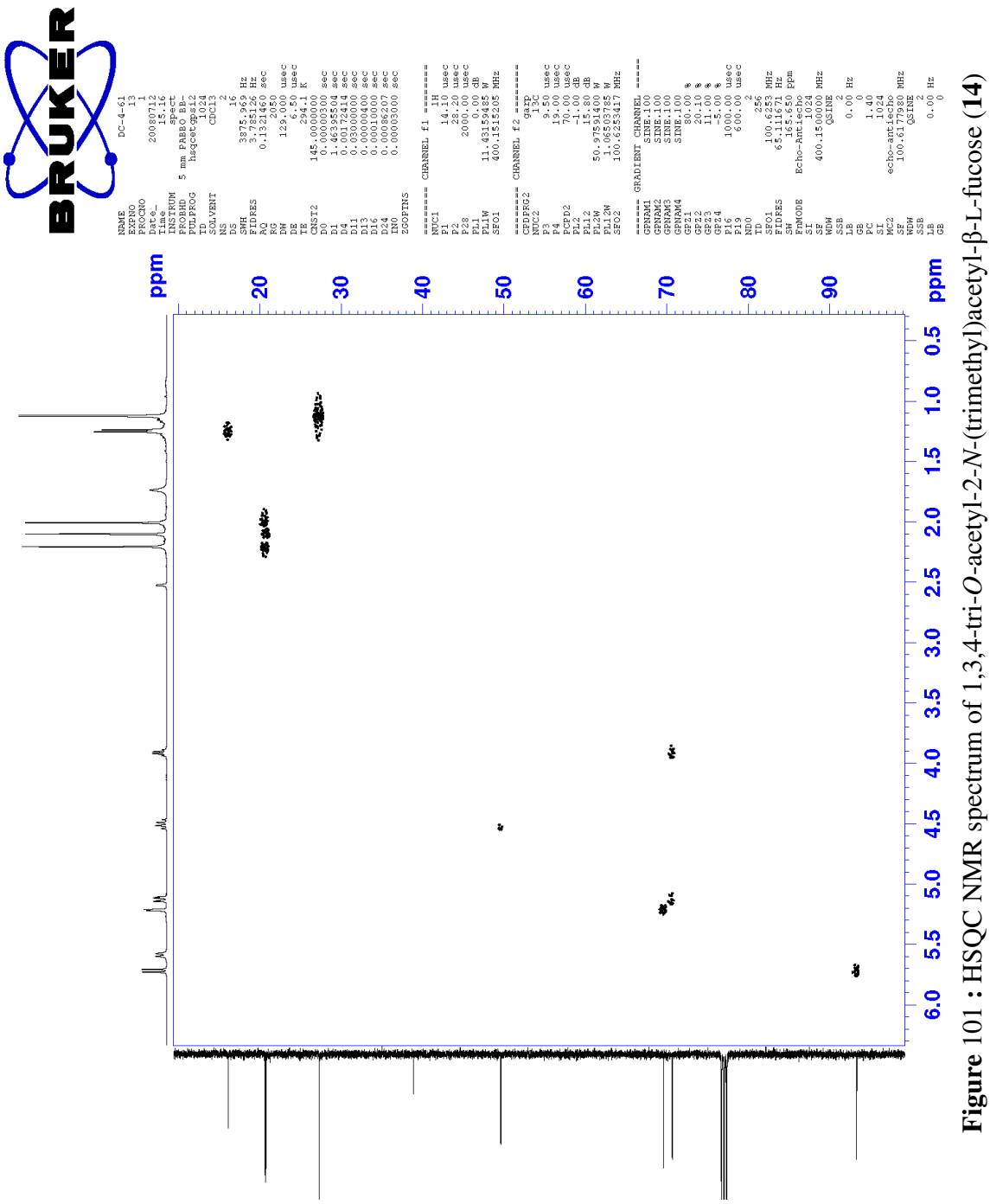


Figure 101 **:** HSQC NMR spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-(trimethyl)acetyl-β-L-fucose (**14**)

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	150.00 m/z	Scan End	600.00 m/z	Averages	10 Spectra	Accumulation Time	527 µs
Capillary Exit	103.1 Volt	Skim 1	31.3 Volt	Trap Drive	41.0	Auto MS/MS	Off

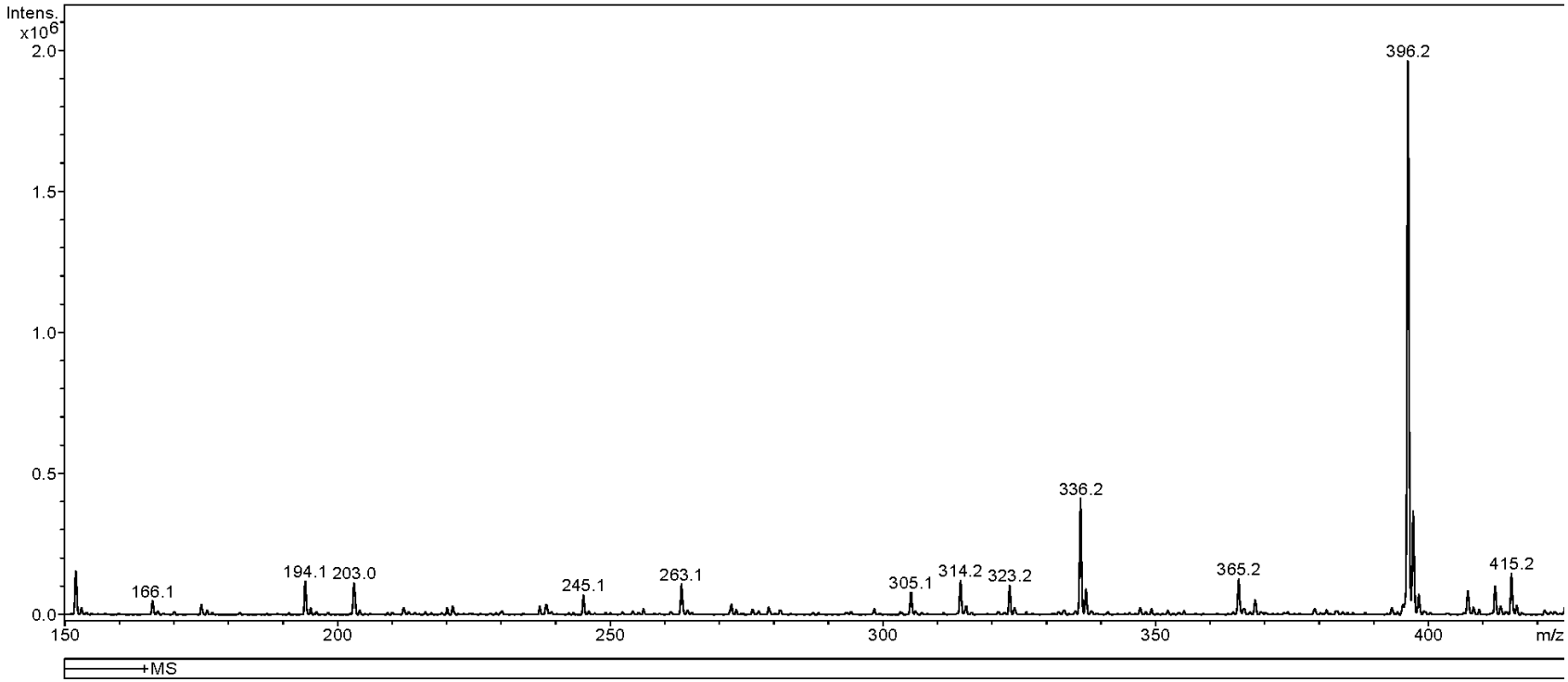


Figure 102 **:** Mass spectrum of 1,3,4-tri-*O*-acetyl-2-*N*-(trimethyl)acetyl-L-fucose (**14**)

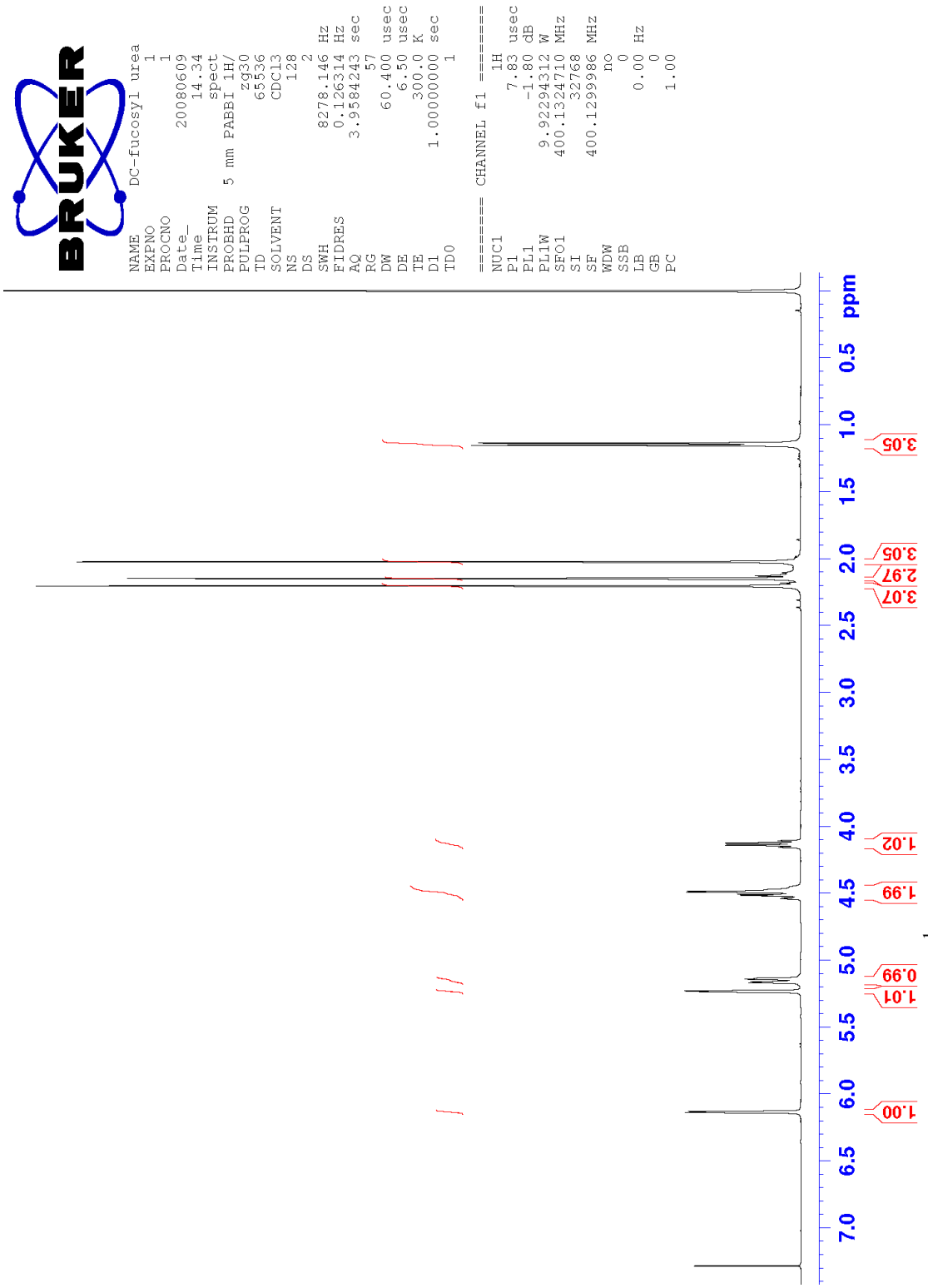


Figure 103 **:** ^{1}H NMR spectrum of bis(1,3,4-tri-*O*-acetyl-α-L-fucos-2-yl) urea (**15**)

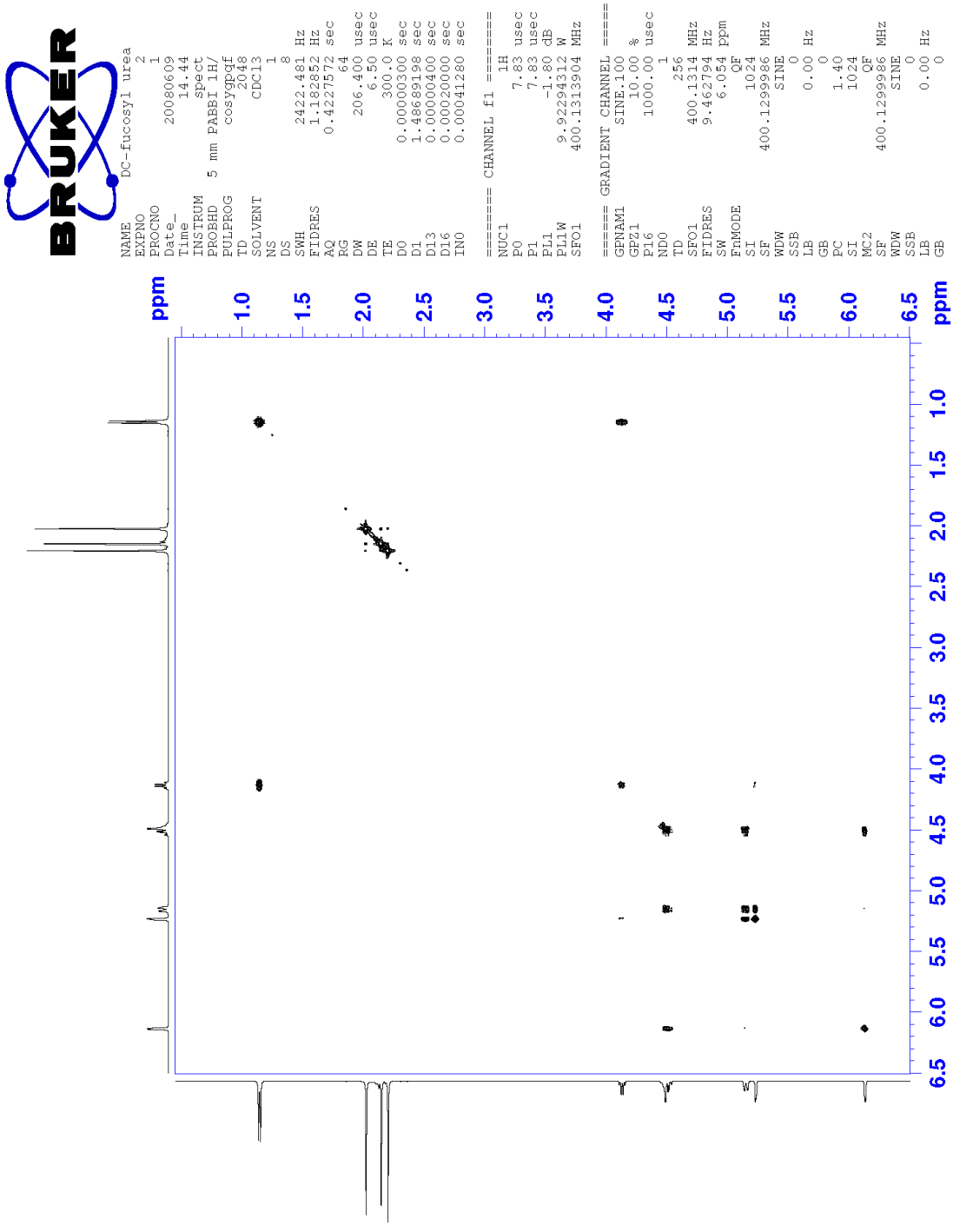


Figure 104 **:** COSY NMR spectrum of bis(1,3,4-tri-*O*-acetyl-α-L-fucos-2-yl) urea (**15**)

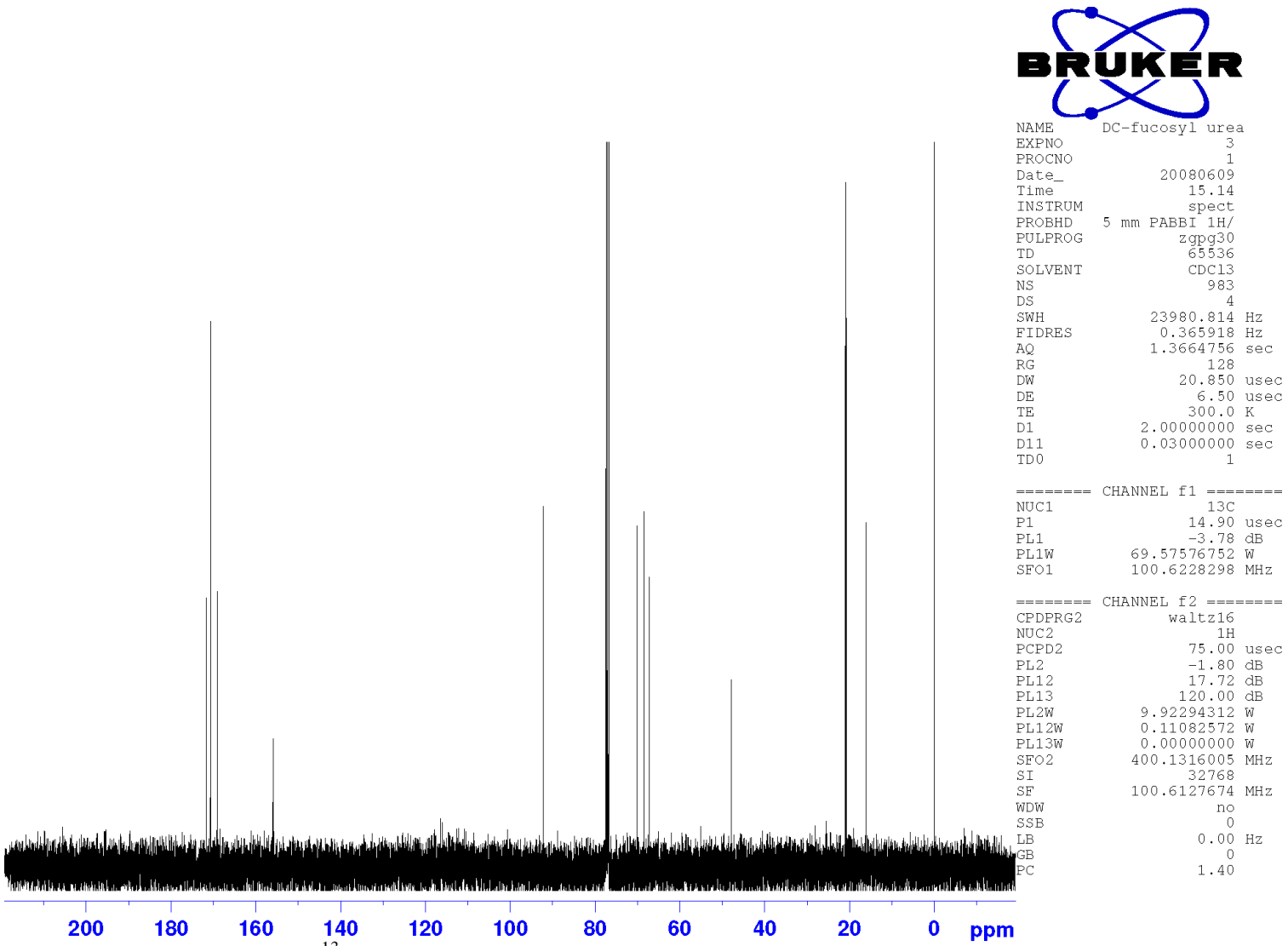


Figure 105 **:** ^{13}C NMR spectrum of bis(1,3,4-tri-*O*-acetyl-α-L-fucos-2-yl) urea (**15**)

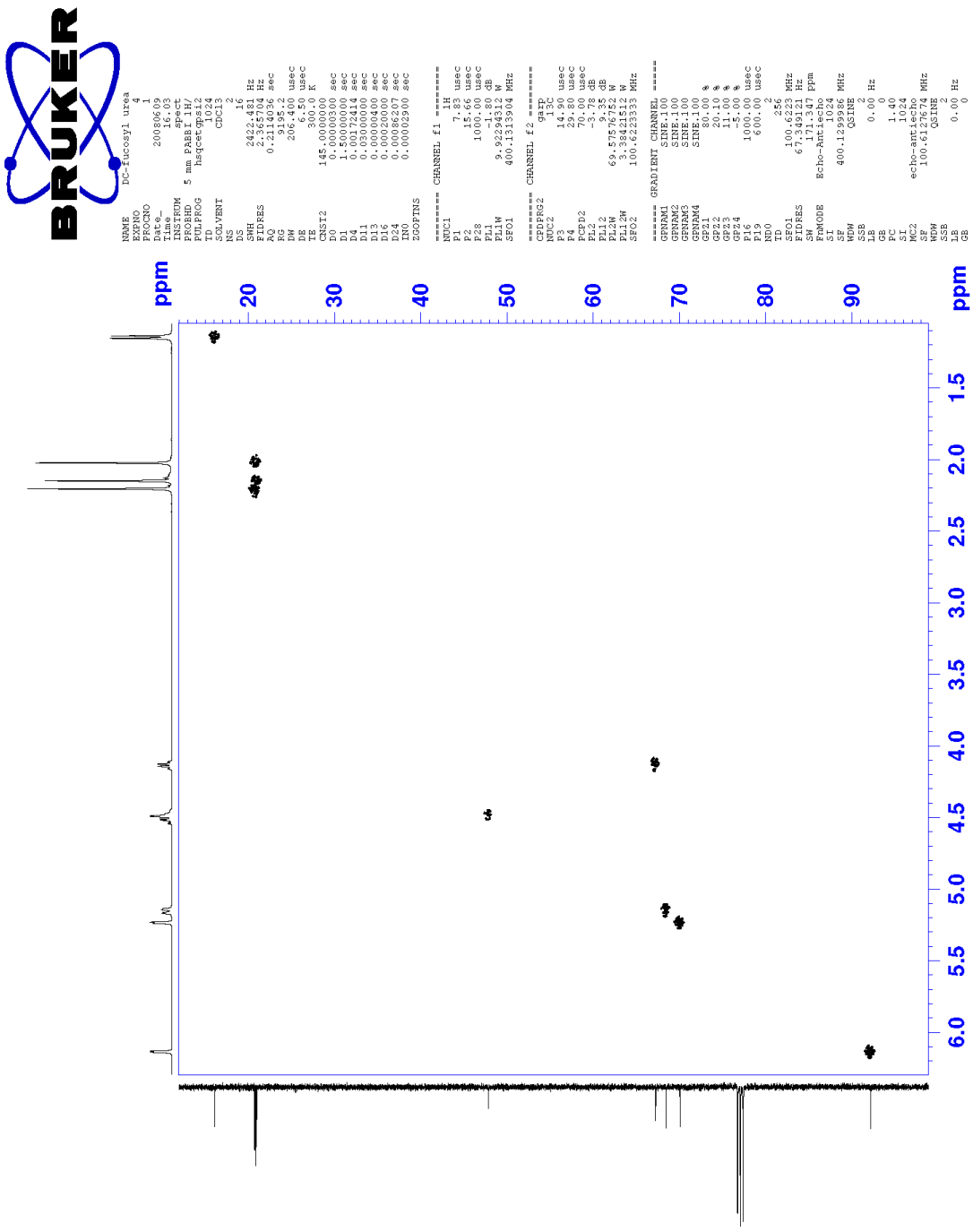


Figure 106 **:** HSQC NMR spectrum of bis(1,3,4-tri-*O*-acetyl-α-L-fucos-2-yl) urea (**15**)

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	7846 µs
Capillary Exit	88.0 Volt	Skim 1	19.9 Volt	Trap Drive	59.0	Auto MS/MS	Off

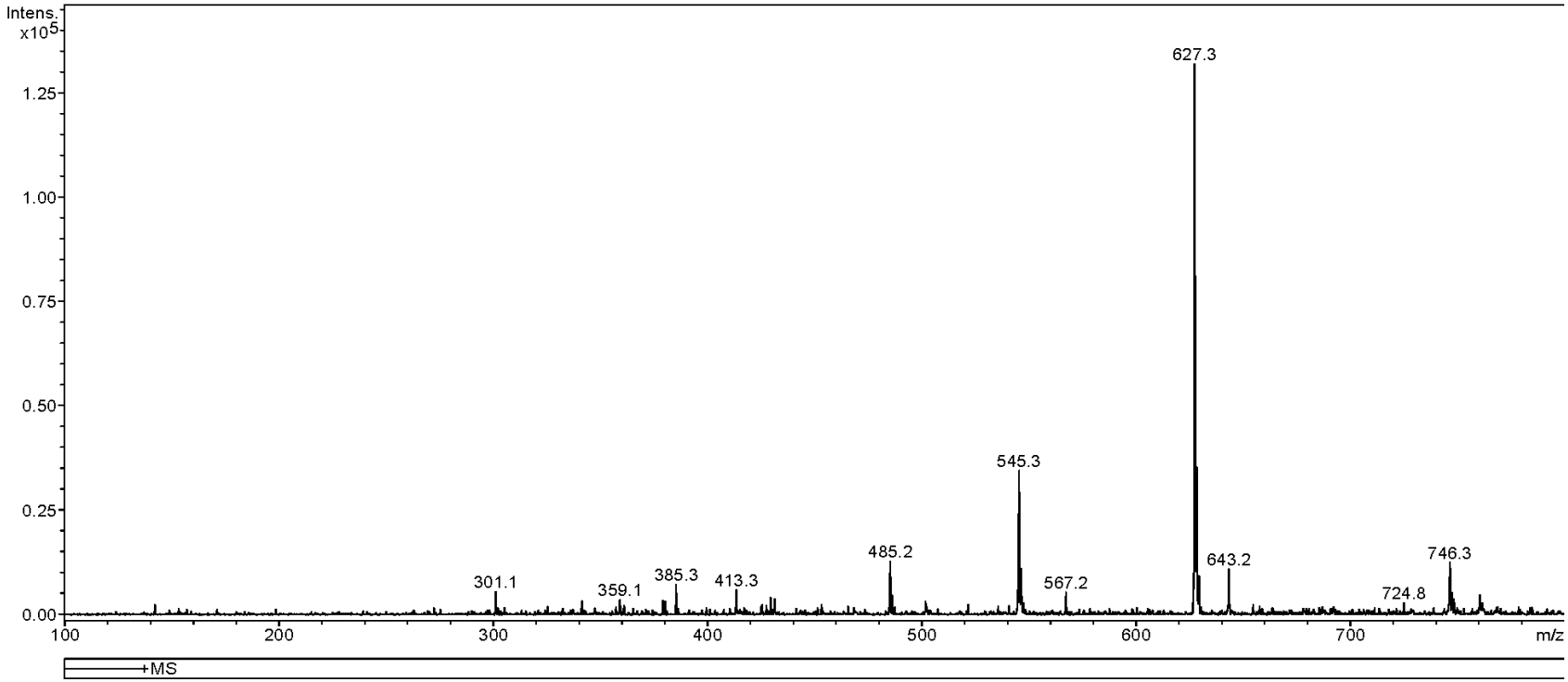


Figure 107 **:Mass** spectrum of bis(1,3,4-tri-*O*-acetyl-α-L-fucos-2-yl) urea (**15**)

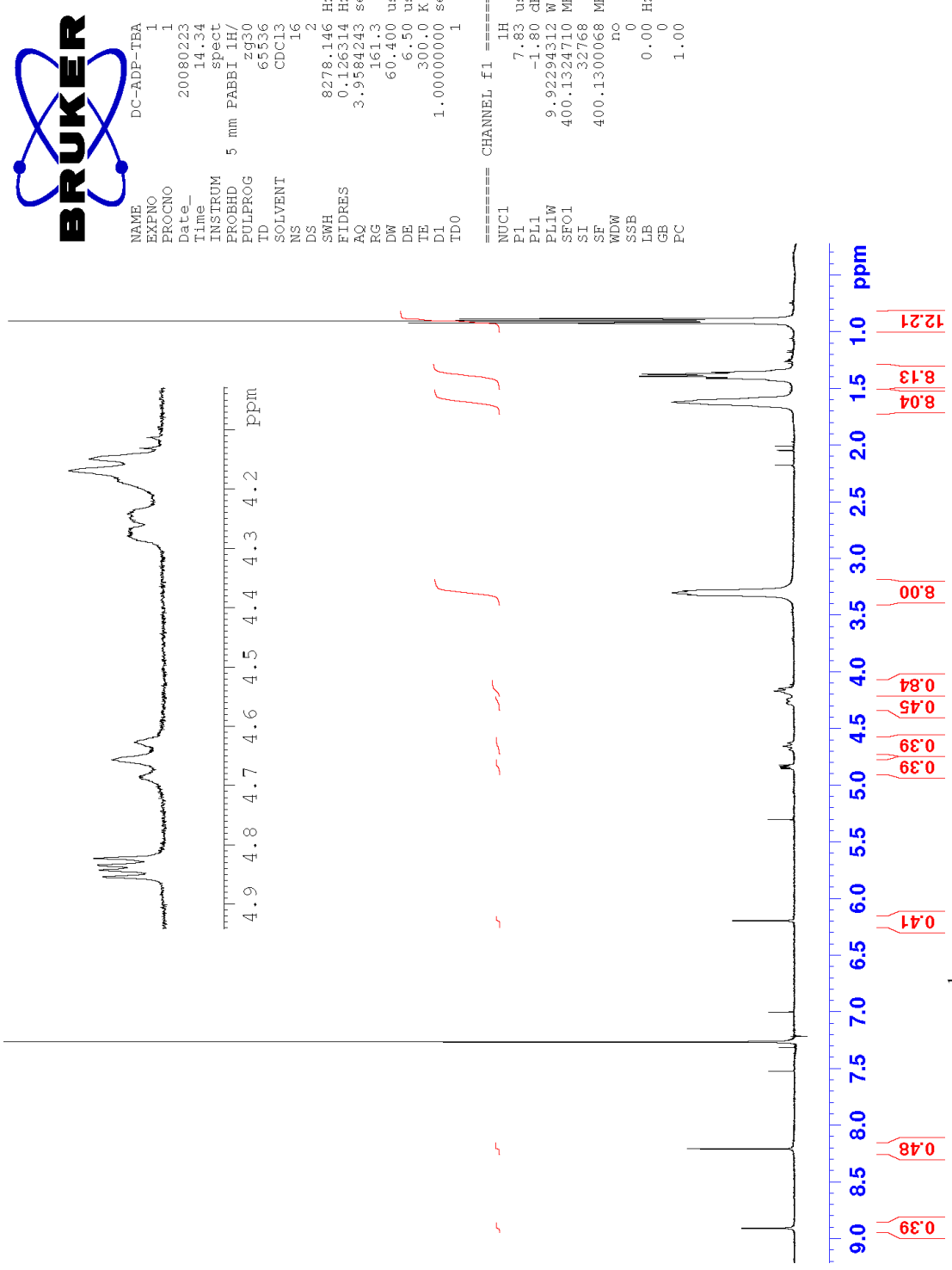


Figure 108 **:** ^{1}H NMR spectrum of adenosine diphosphate-tetrabutyl ammonium salt **(16)**

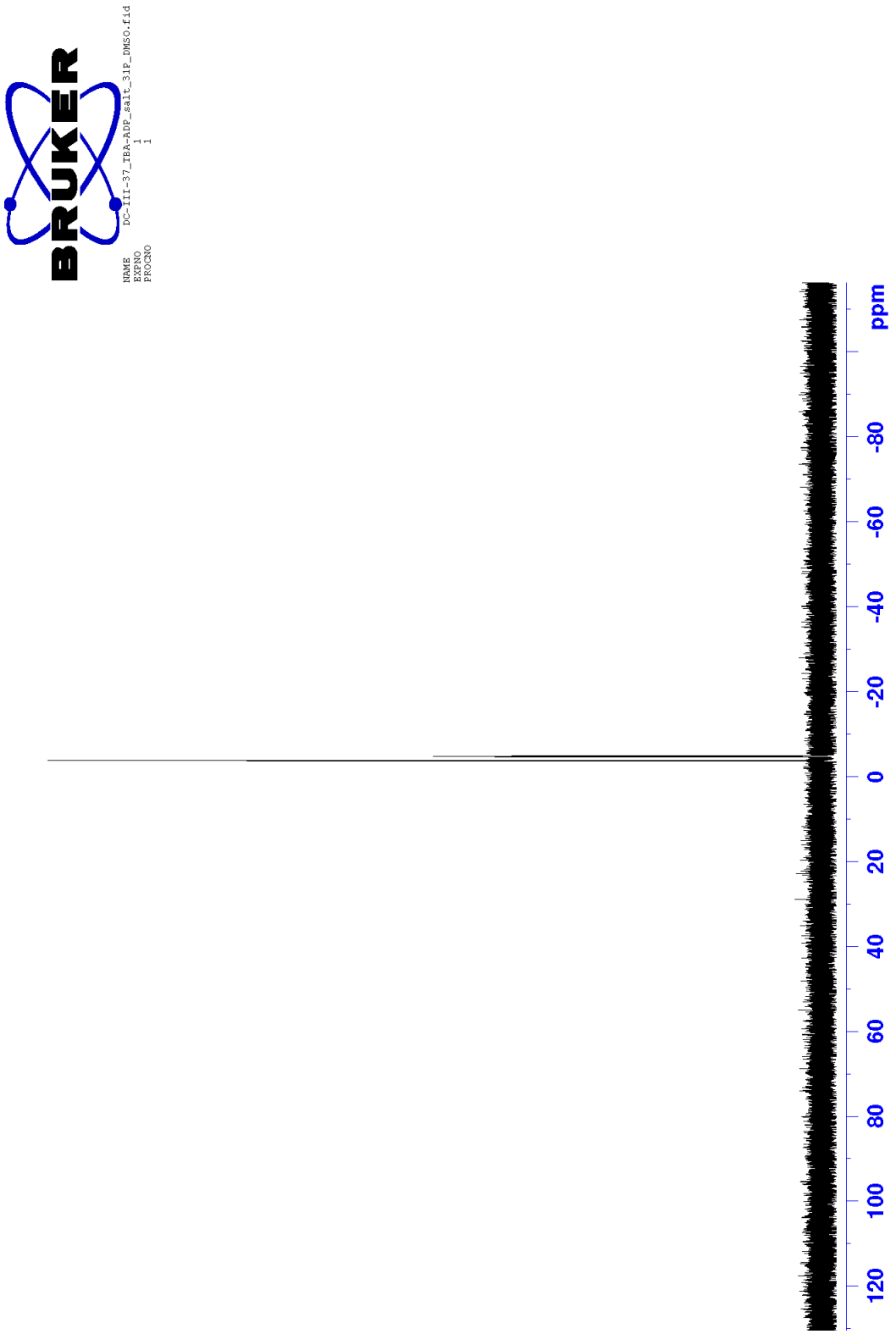


Figure 109 **:** ^{31}P NMR spectrum of adenosine diphosphate-tetrabutyl ammonium salt (**16**)

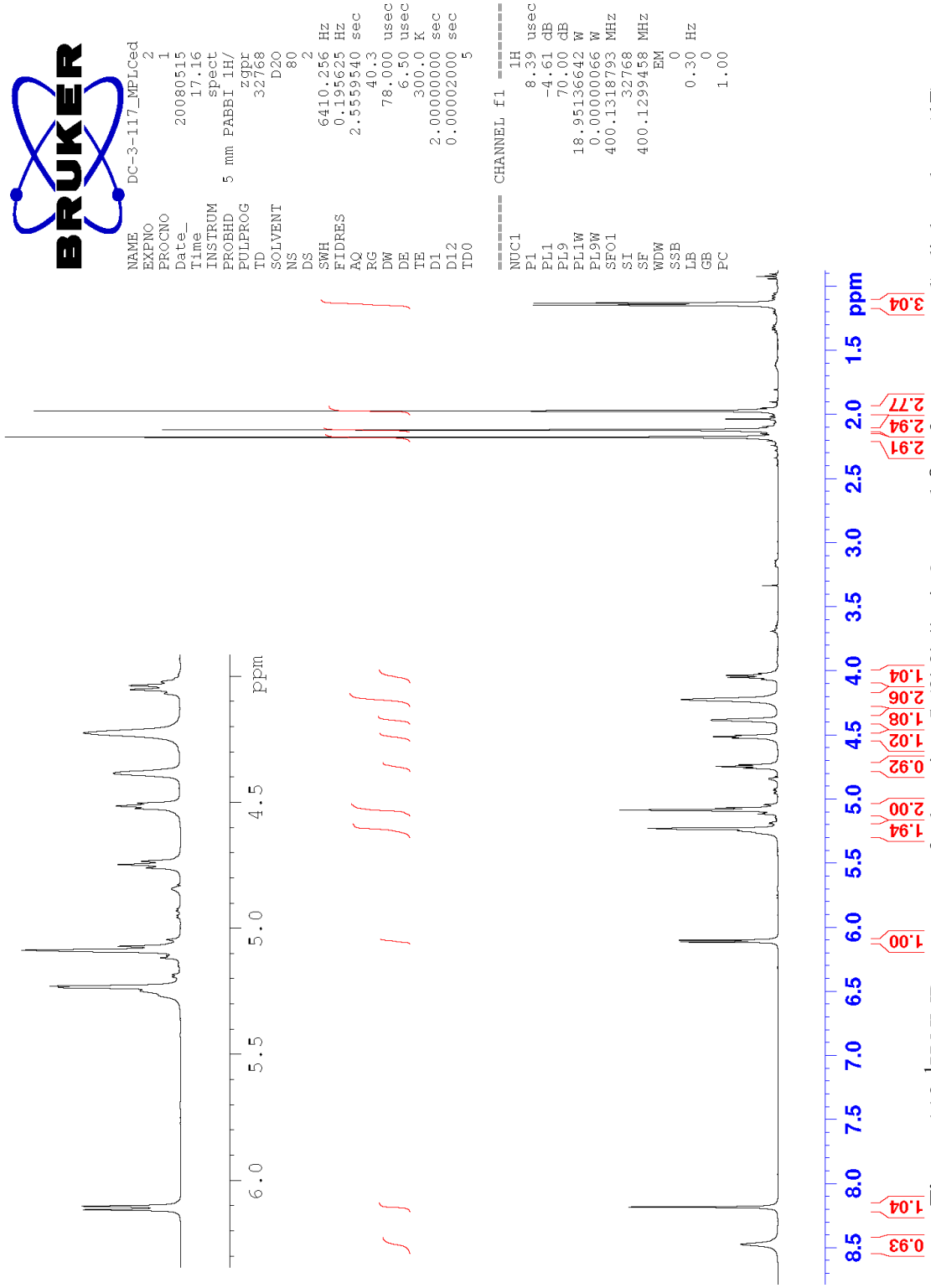


Figure 110: ^{1}H NMR spectrum of adenosine-5-(2',3',4'-tri-*O*-acetyl-β-L-fucopyranosyl)-diphosphate (**17**)

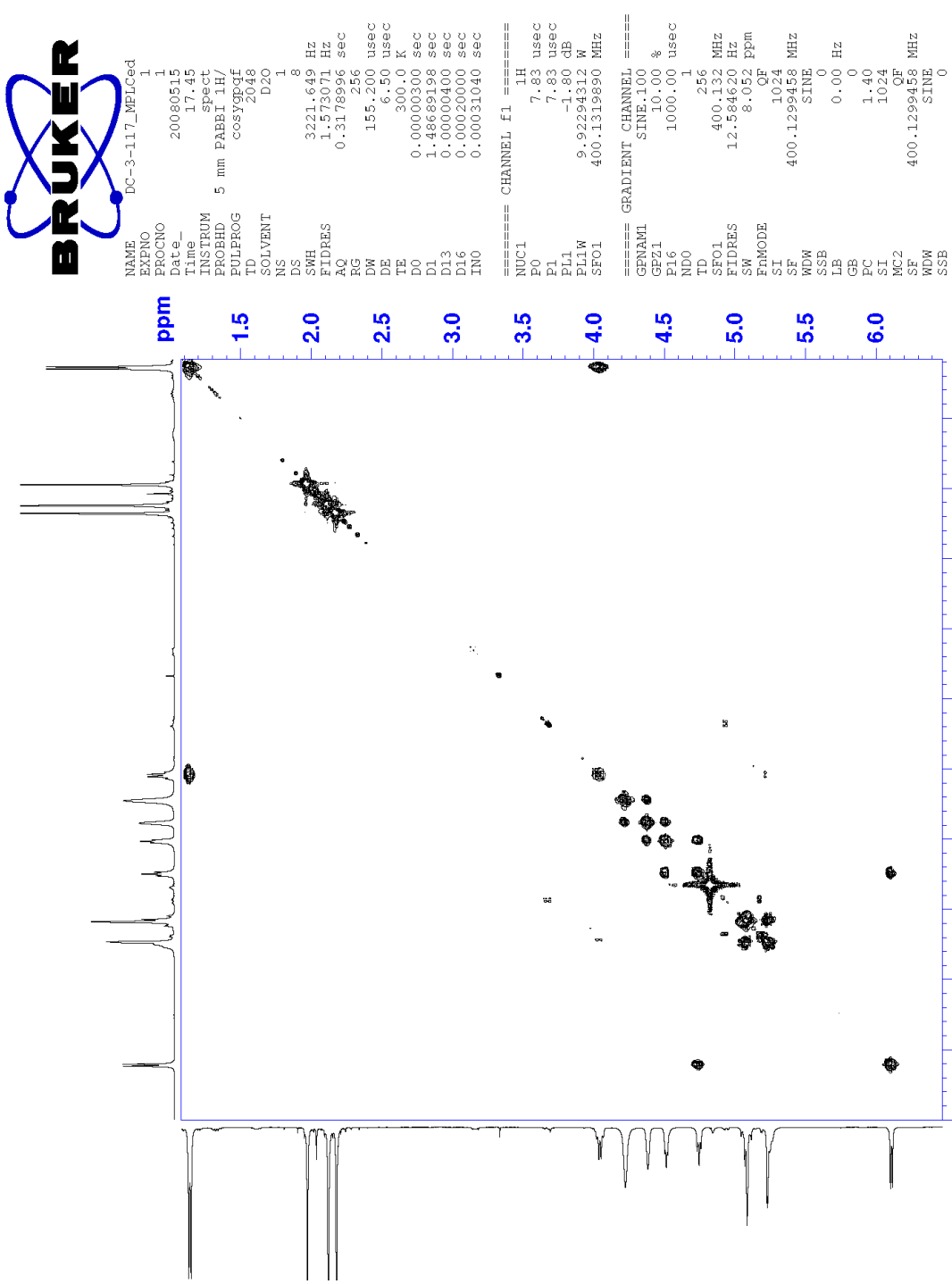


Figure 111:COSY NMR spectrum of adenosine-5-(2',3',4'-tri-*O*-acetyl-β-L-fucopyranosyl)-diphosphate (**17**)

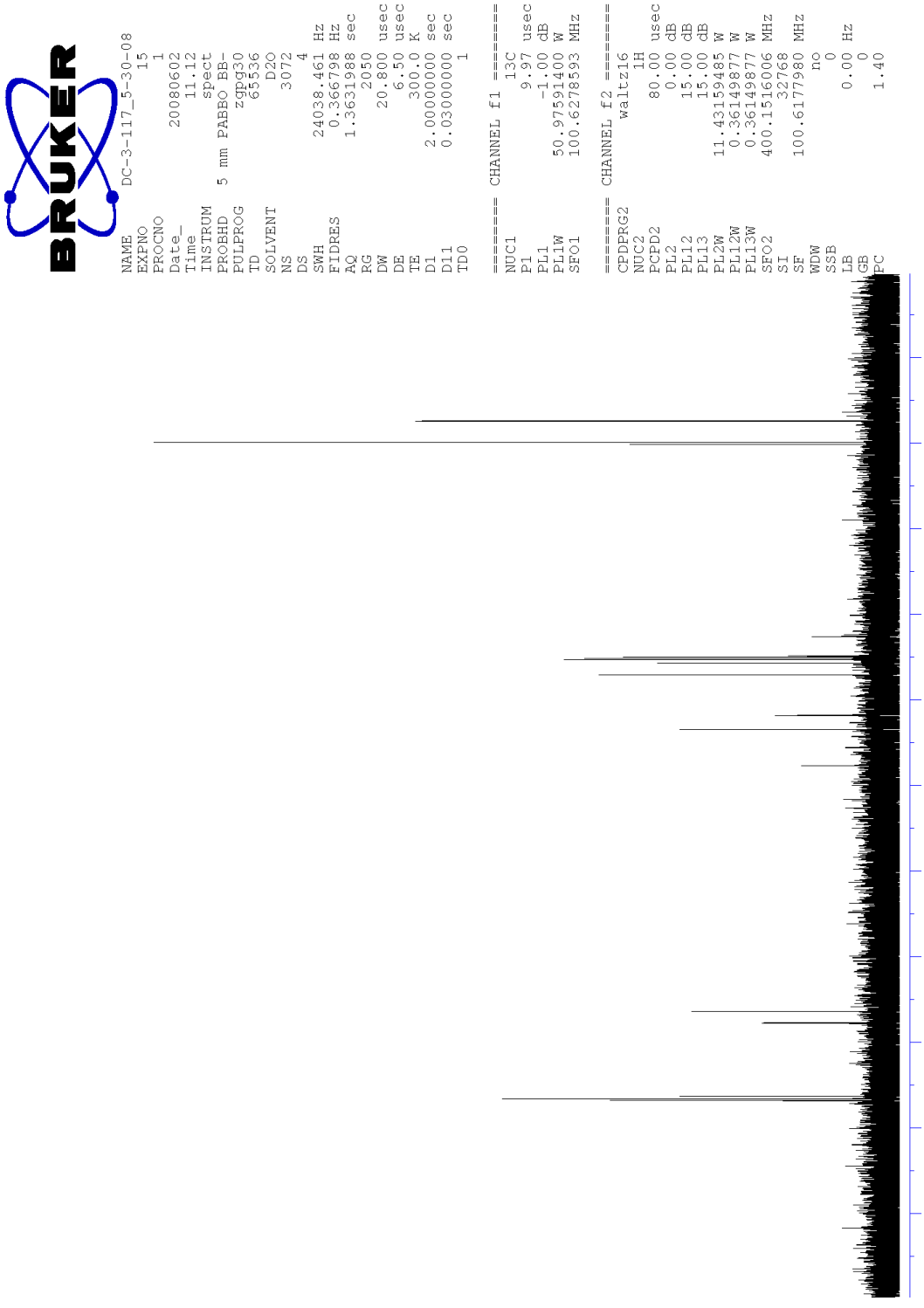


Figure 112: ^{13}C NMR spectrum of adenosine-5-(2',3',4'-tri-*O*-acetyl-β-L-fucopyranosyl)-diphosphate (**17**)

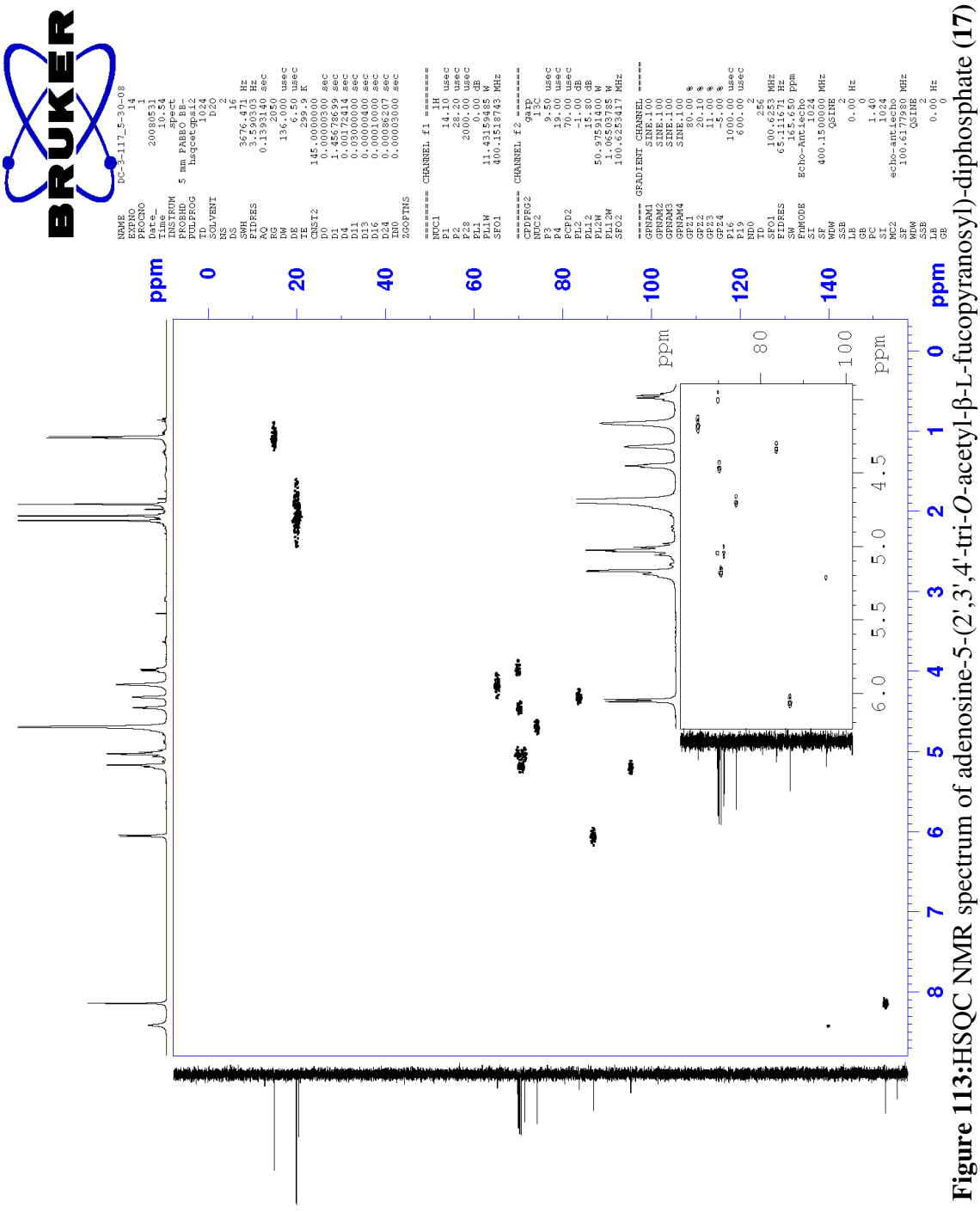


Figure 113:HSQC NMR spectrum of adenosine-5-(2',3',4'-tri-*O*-acetyl-β-L-fucopyranosyl)-diphosphate (**17**)

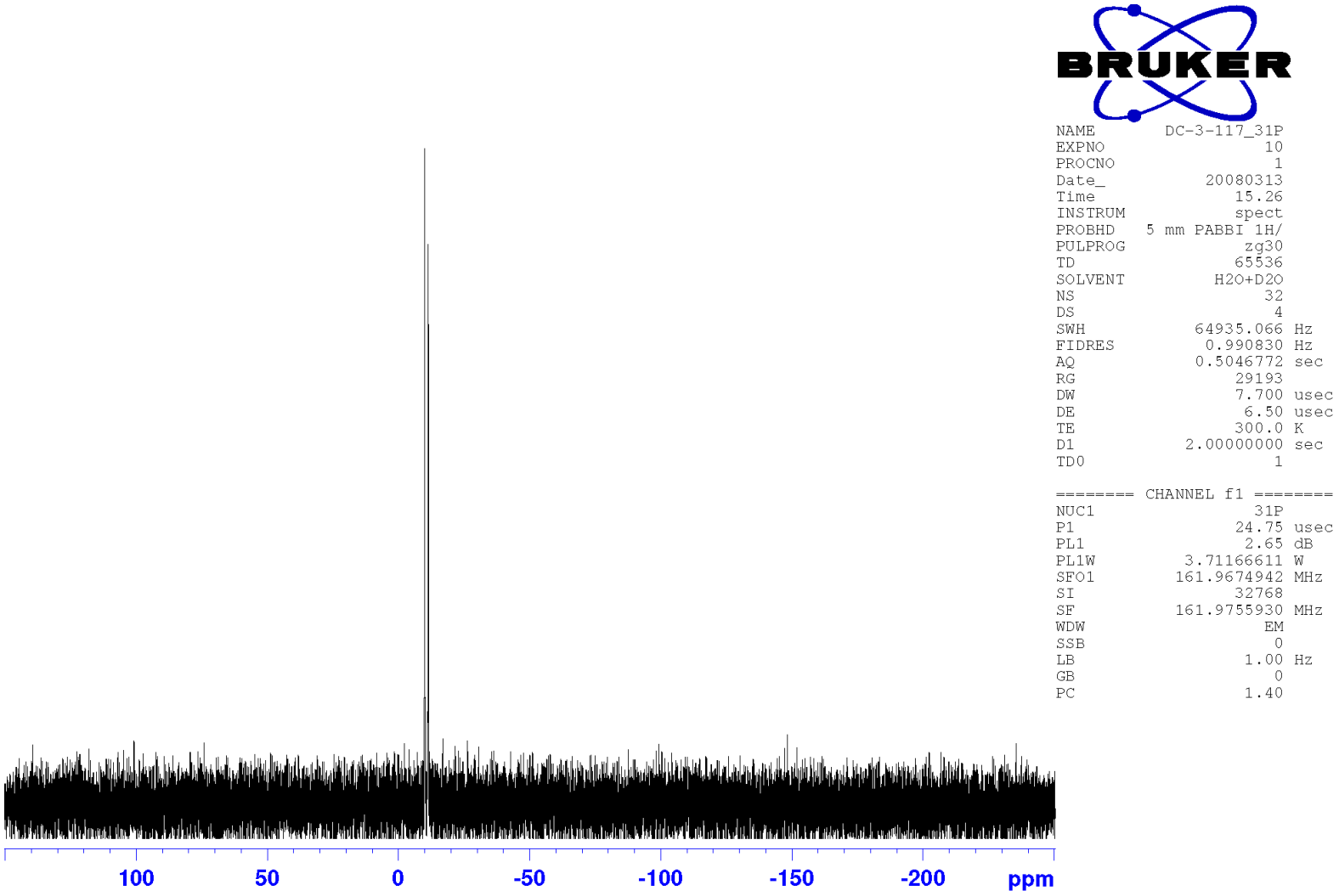


Figure 114: ^{31}P NMR spectrum of adenosine-5-(2',3',4'-tri-*O*-acetyl-β-L-fucopyranosyl)-diphosphate **(17)**

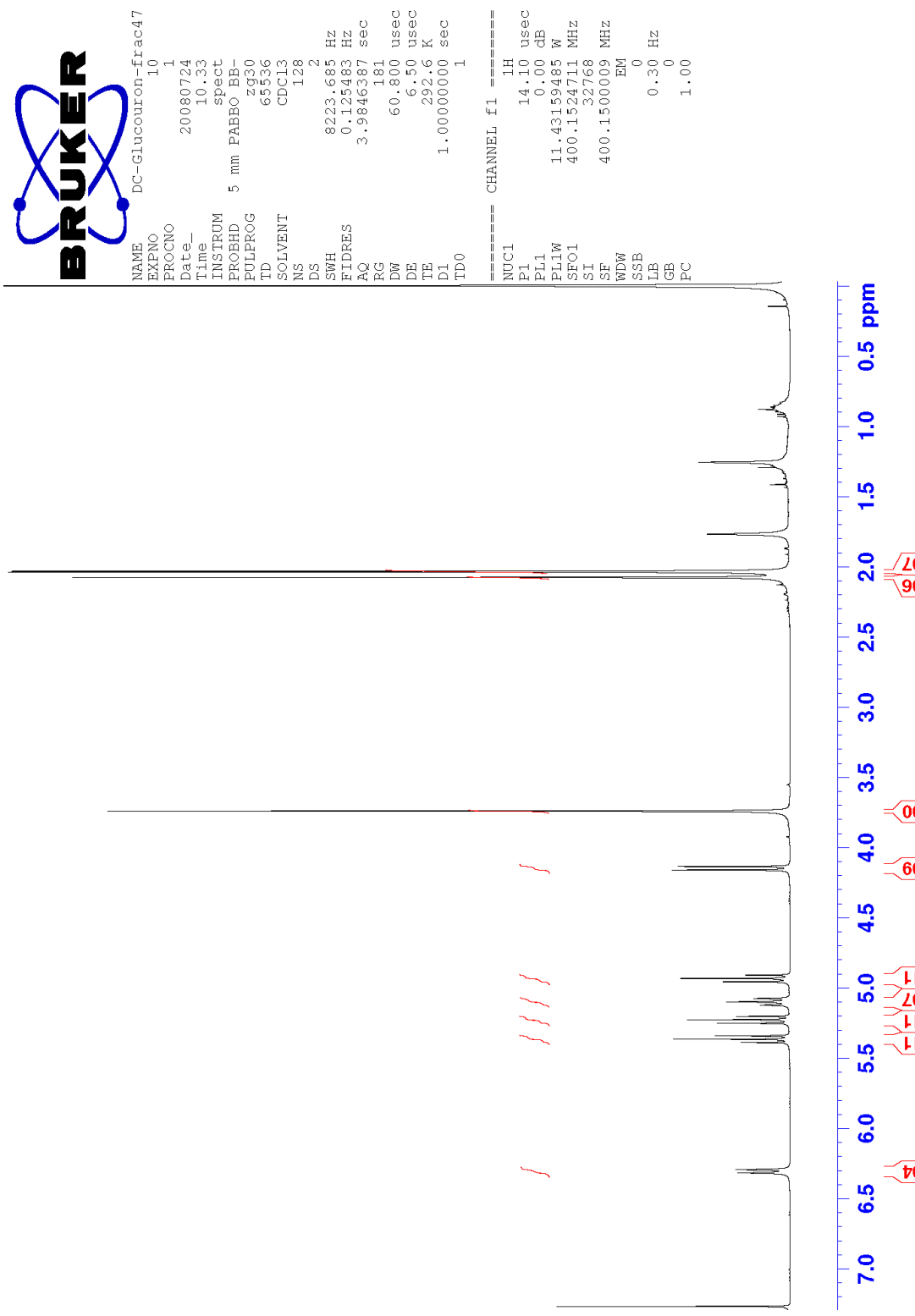
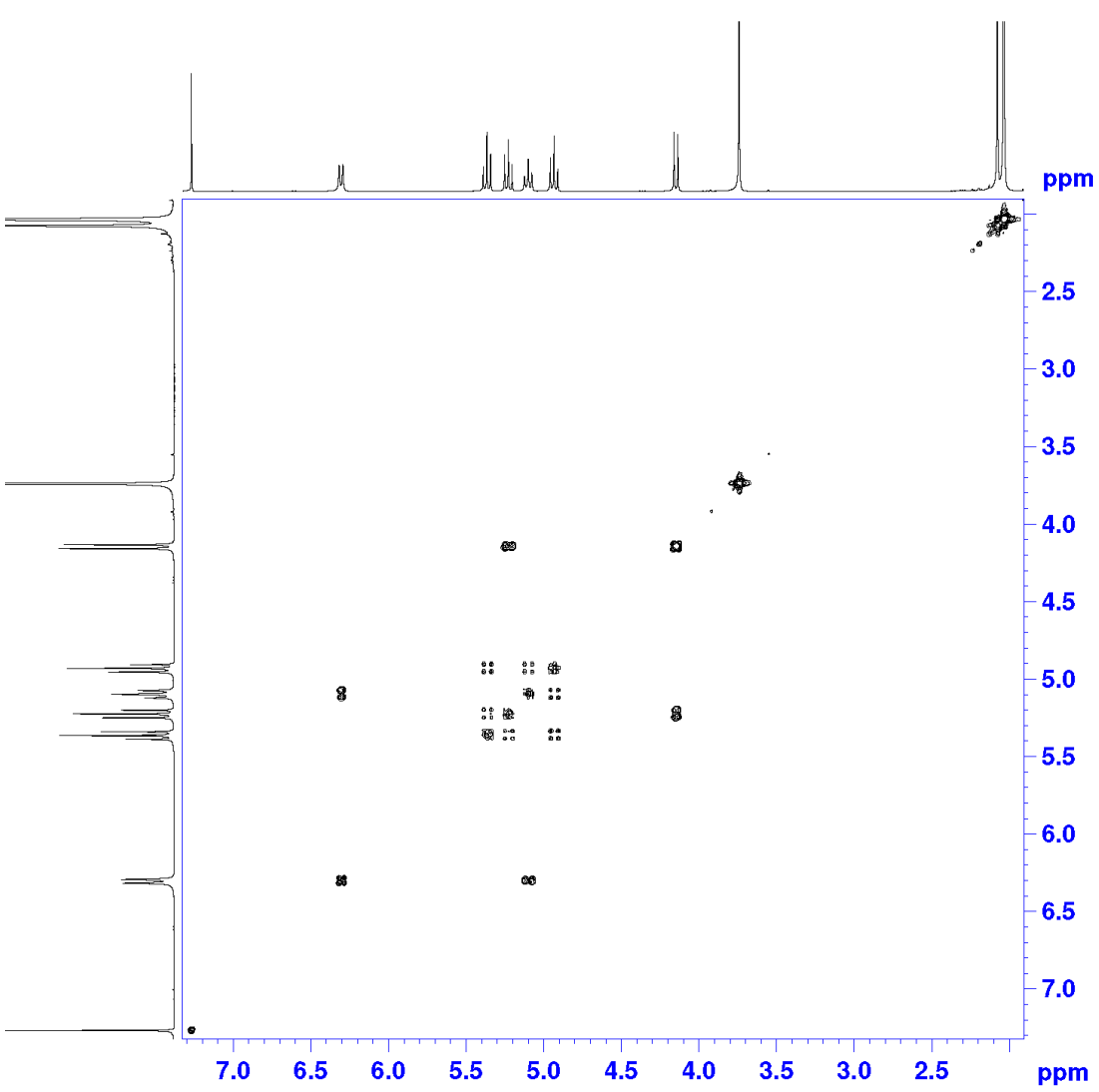


Figure 115: H NMR spectrum of bis(2,3,4-tri-*O*-acetyl-β-glucouronosyl) urea (**18**)



BRUKER

```
NAME          DC-Glucouron-frac47
EXPNO                          11
PROCNO                          1
Date_                    20080724
Time                        10.45
INSTRUM                     spect
PROBHD    5 mm PABBO BB-
PULPROG                 cosygpqf
TD                          2048
SOLVENT                     CDCl3
NS                              1
DS                              8
SWH                      3968.254 Hz
FIDRES                   1.937624 Hz
AQ                       0.2580980 sec
RG                             64
DW                        126.000 usec
DE                          6.50 usec
TE                         292.6 K
D0                    0.00000300 sec
D1                    1.42053699 sec
D13                   0.00000400 sec
D16                   0.00010000 sec
IN0                   0.00025200 sec

======== CHANNEL f1 ========
NUC1                           1H
P0                          14.10 usec
P1                          14.10 usec
PL1                          0.00 dB
PL1W                11.43159485 W
SFO1                400.1513141 MHz

====== GRADIENT CHANNEL =====
GPNAM1                  SINE.100
GPZ1                        10.00 %
P16                       1000.00 usec
ND0                             1
TD                            256
SFO1                    400.1513 MHz
FIDRES                 15.500992 Hz
SW                         9.917 ppm
FnMODE                        QF
SI                          1024
SF                  400.1500010 MHz
WDW                         SINE
SSB                            0
LB                          0.00 Hz
GB                             0
PC                          1.40
SI                          1024
MC2                           QF
SF                  400.1500010 MHz
WDW                         SINE
SSB                            0
LB                          0.00 Hz
GB                             0
```

Figure 116:COSY NMR spectrum of bis(2,3,4-tri-*O*-acetyl-β-glucouronosyl) urea **(18)**

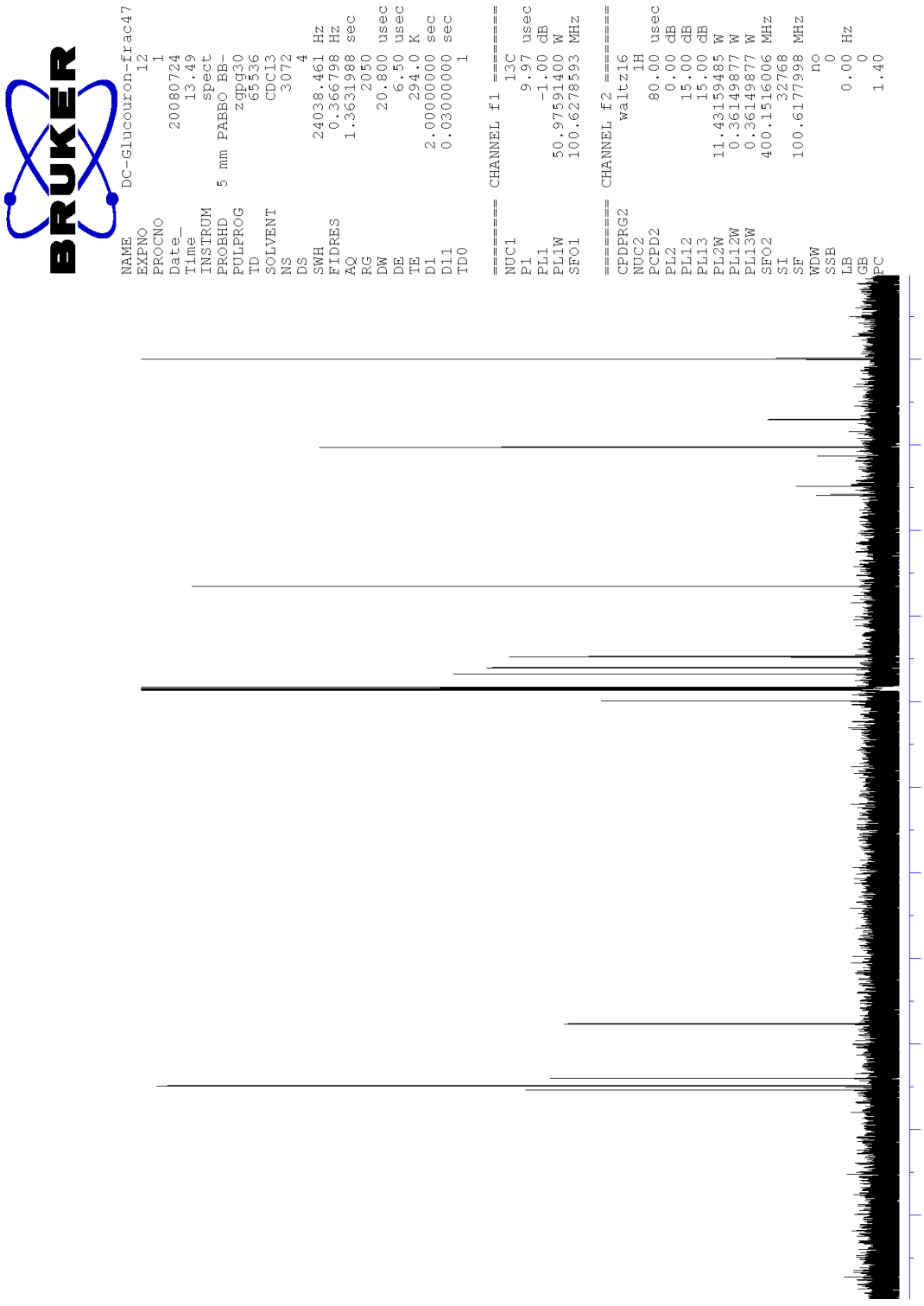


Figure 117: ^{13}C NMR spectrum of bis(2,3,4-tri-*O*-acetyl-β-glucuronosyl) urea **(18)**

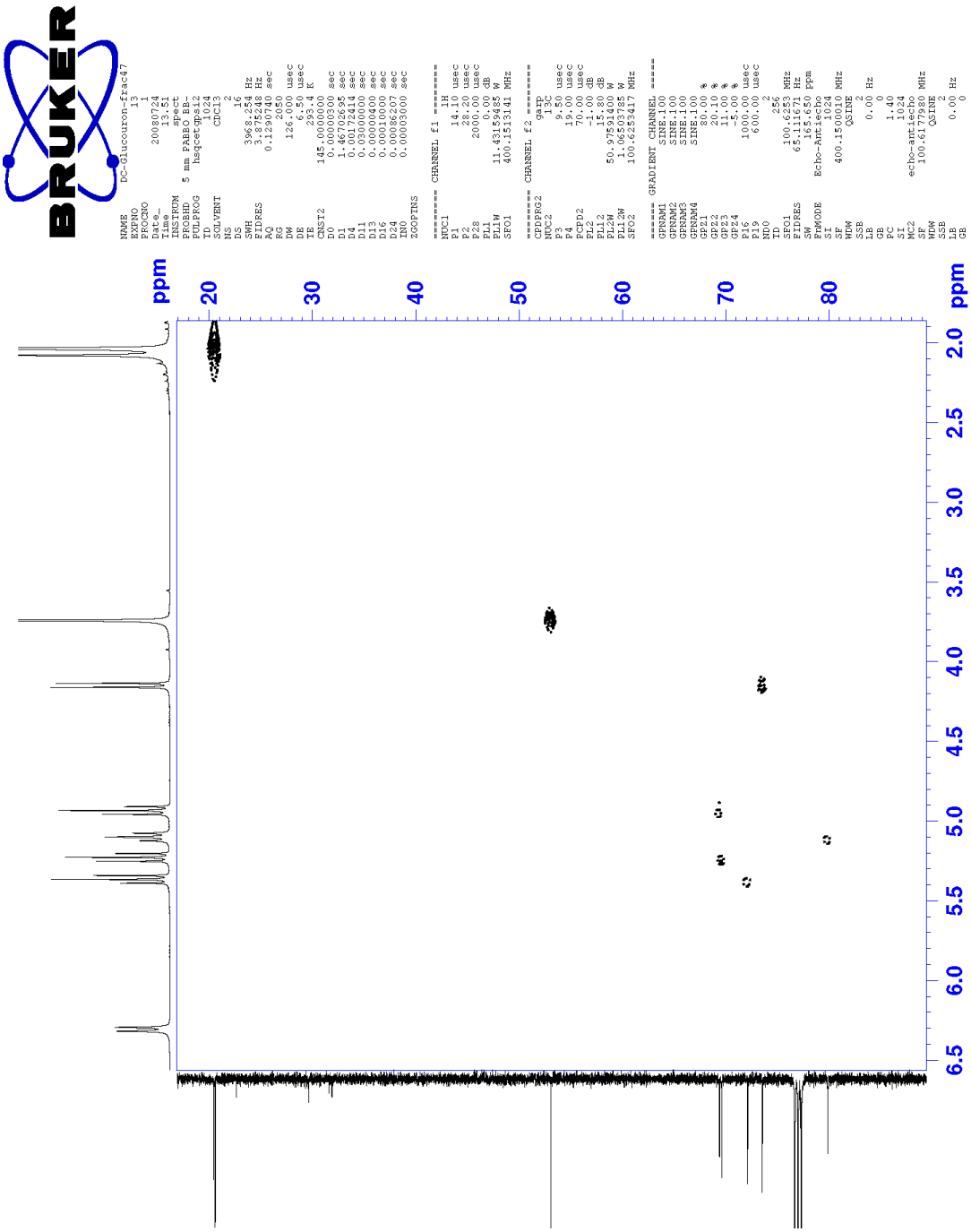


Figure 118:HSQC NMR spectrum of bis(2,3,4-tri-*O*-acetyl-β-glucouronosyl) urea (**18**)

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	3905 µs
Capillary Exit	80.6 Volt	Skim 1	13.9 Volt	Trap Drive	61.5	Auto MS/MS	Off

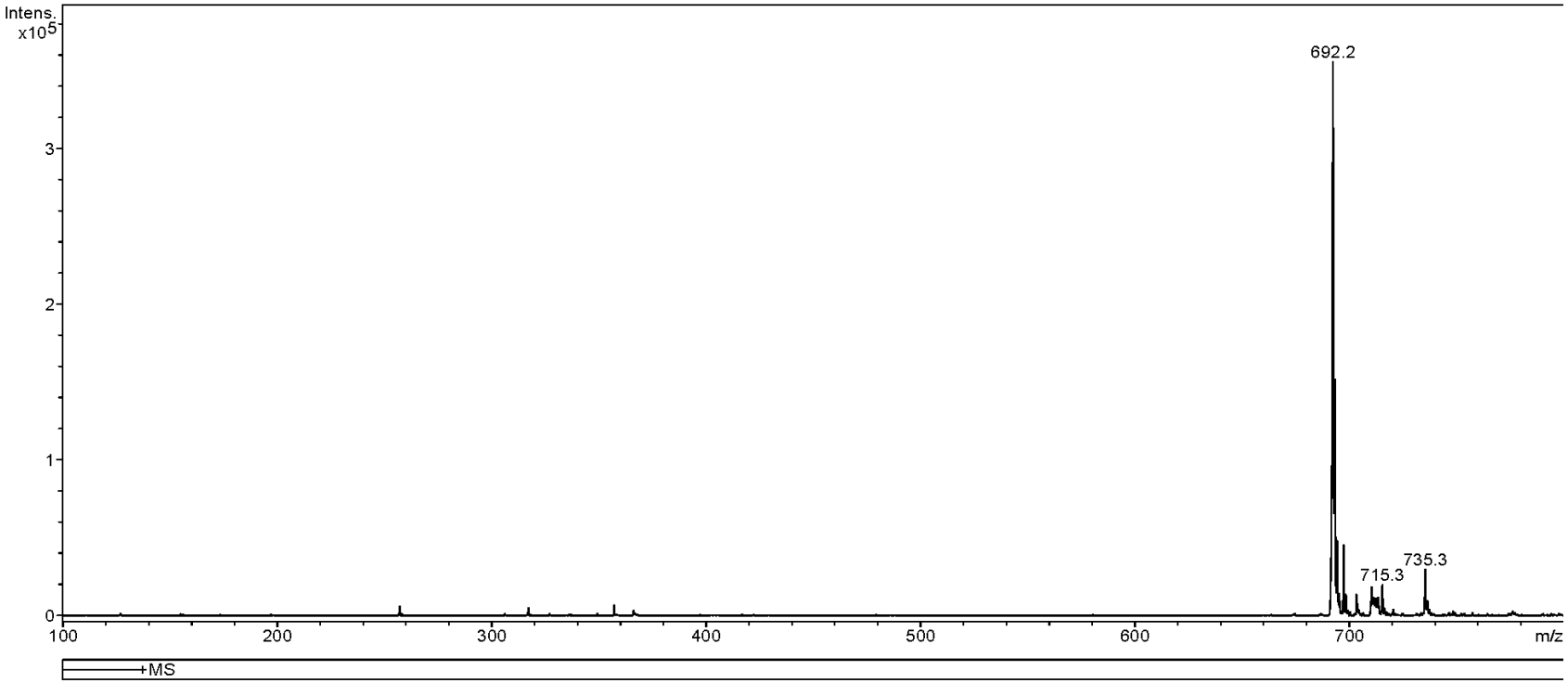


Figure 119 : Mass spectrum of bis(2,3,4-tri-*O*-acetyl-β-glucouronosyl) urea **(18)**

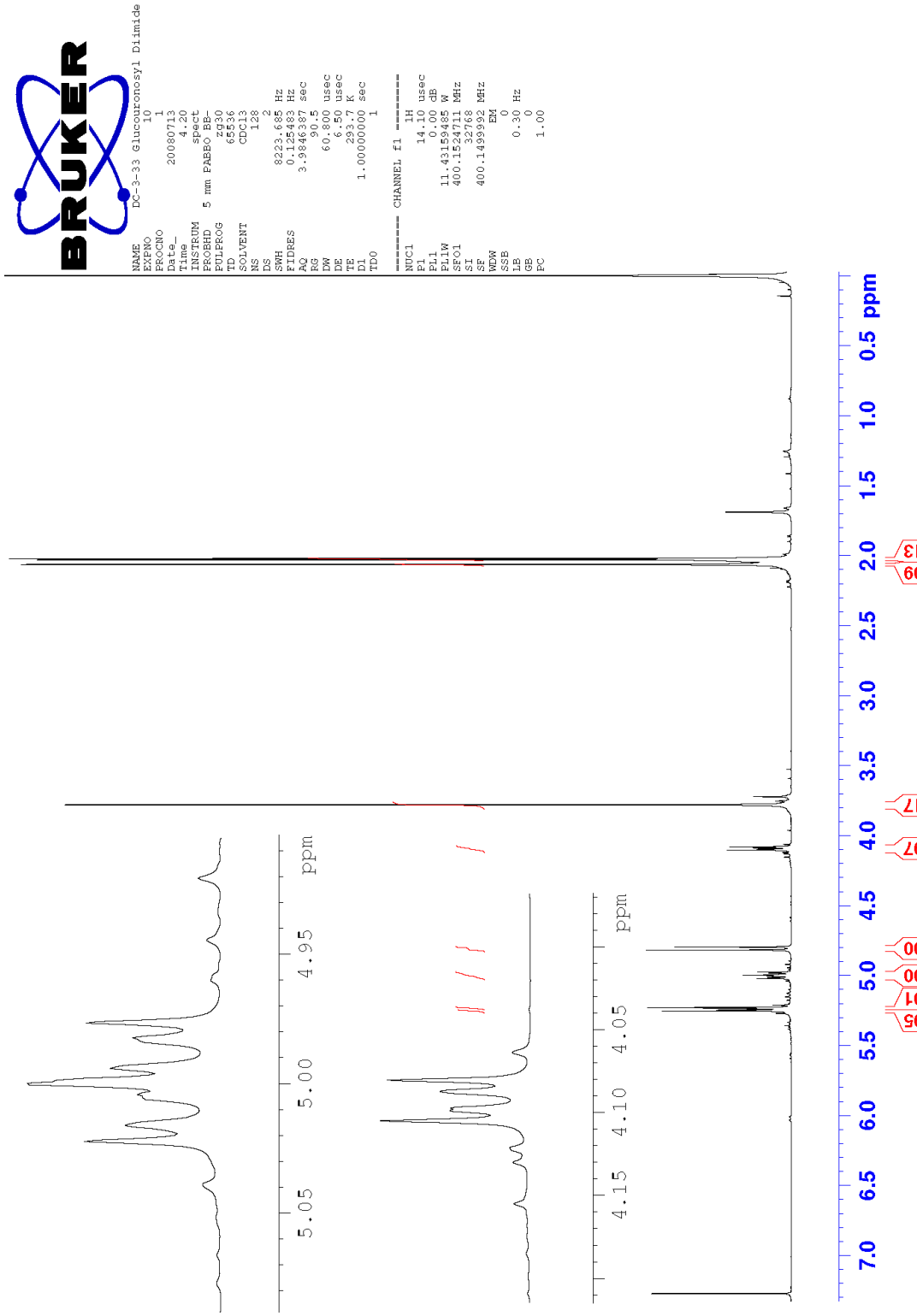


Figure 120 : ^{1}H NMR spectrum of bis(2,3,4-tri-*O*-acetyl-β-glucouronosyl) diimide (**19**)

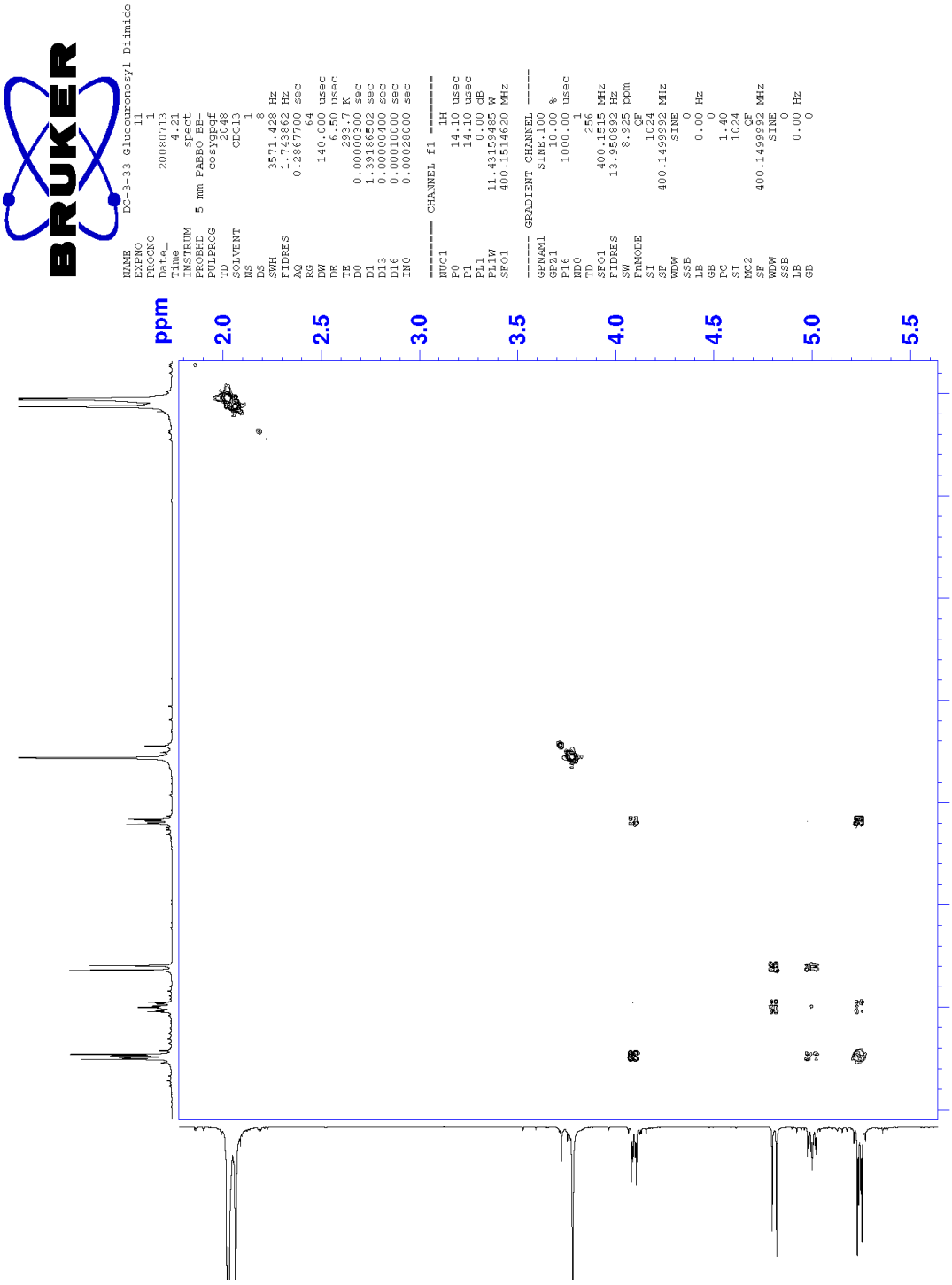


Figure 121 : COSY **NMR** spectrum of bis(2,3,4-tri-*O*-acetyl-β-glucouronosyl) diimide (**19**)

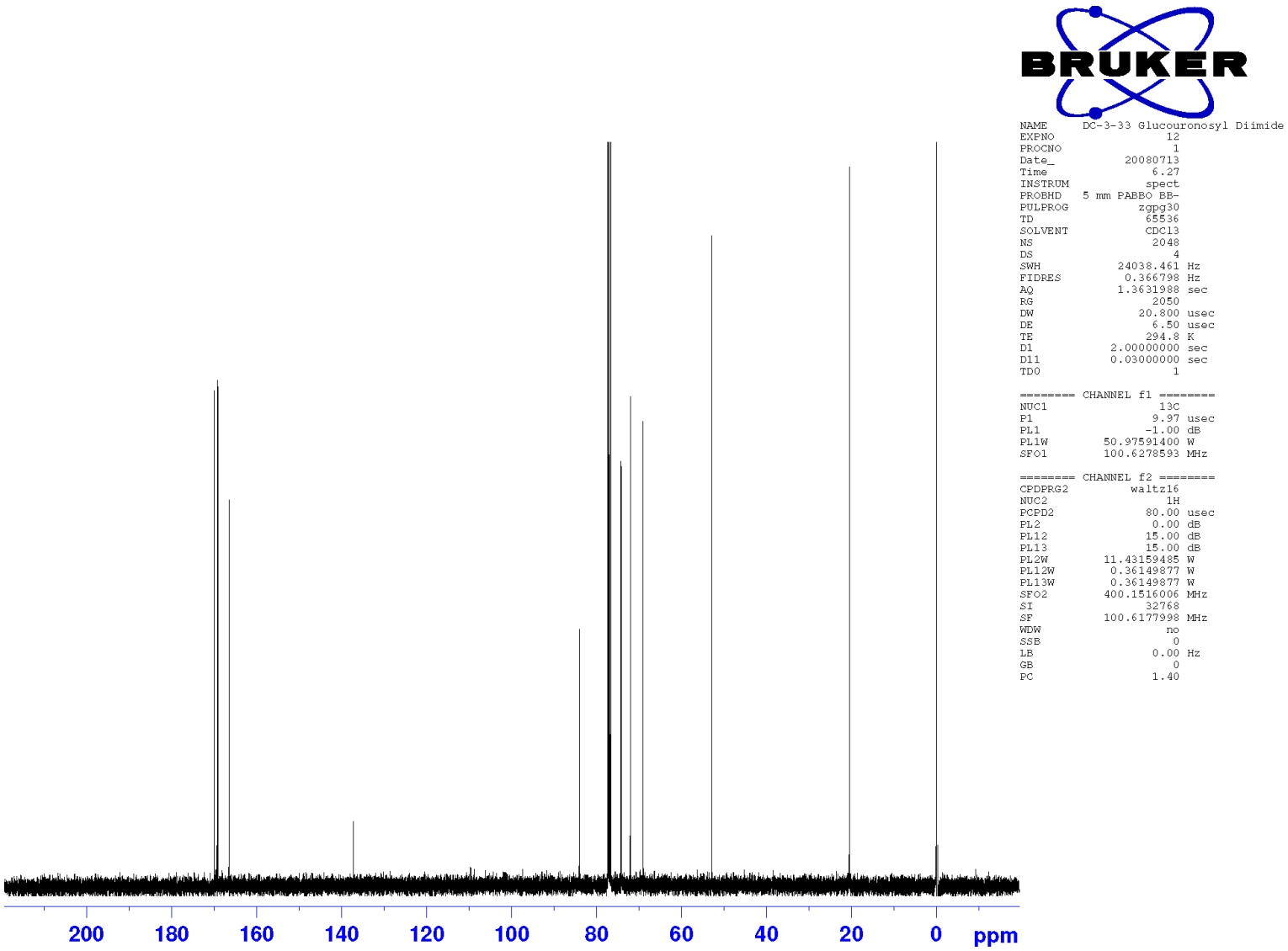


Figure 122 : ^{13}C **NMR** spectrum of bis(2,3,4-tri-*O*-acetyl-β-glucouronosyl) diimide **(19)**

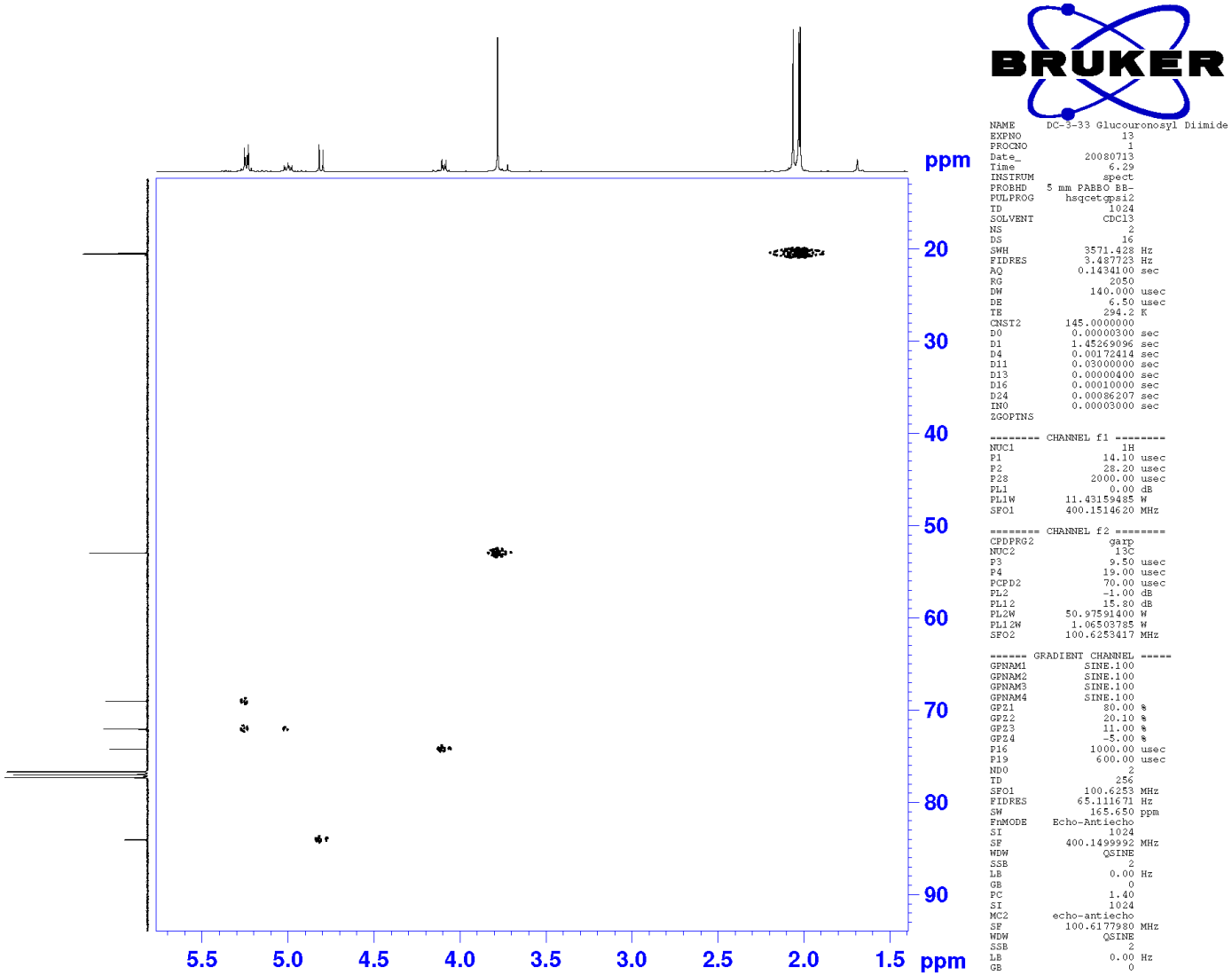


Figure 123 : HSQC **NMR** spectrum of bis(2,3,4-tri-*O*-acetyl-β-glucouronosyl) diimide **(19)**

Appendix B

X-ray Crystallography Data

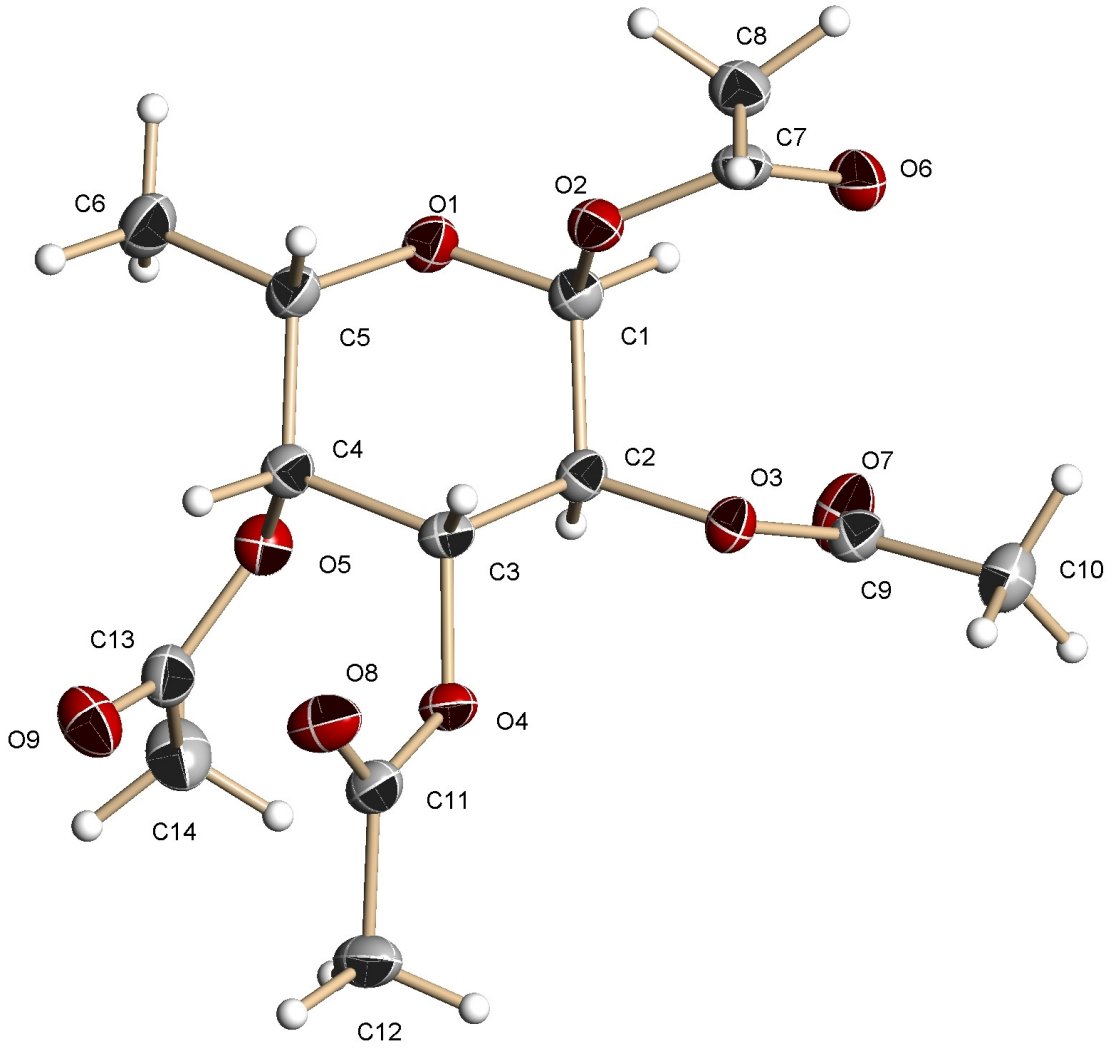


Figure 124 : Crystallographic refinement of 1,2,3,4-tetra-*O*-acetyl-α-L-fucose (**2**)

Table 1. Crystal data and structure refinement for 07mz243m:

Identification code: 07mz243m
Empirical formula: C14 H20 O9
Formula weight: 332.30
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Orthorhombic
Space group: $P2_12_12_1$
Unit cell dimensions:
a = 10.0028(6) Å, α = 90°
b = 10.3743(6) Å, β = 90°
c = 15.8334(9) Å, γ = 90°
Volume, Z: 1643.06(17) $Å^3$, 4
Density (calculated): 1.343 Mg/m^3
Absorption coefficient: 0.113 mm^{-1}
F(000): 704
Crystal size: 0.48 × 0.48 × 0.30 mm
Crystal shape, colour: block, colourless
θ range for data collection: 2.35 to 28.28°
Limiting indices: $-13 \le h \le 12$, $-13 \le k \le 13$, $-20 \le l \le 19$
Reflections collected: 10636
Independent reflections: 2308 (R(int) = 0.0230)
Completeness to θ = 28.28°: 99.2 %
Absorption correction: multi-scan
Max. and min. transmission: 0.967 and 0.822
Refinement method: Full-matrix least-squares on F^2
Data / restraints / parameters: 2308 / 0 / 213
Goodness-of-fit on F^2: 1.088
Final R indices [$I>2\sigma(I)$]: R1 = 0.0343, wR2 = 0.0866
R indices (all data): R1 = 0.0373, wR2 = 0.0881
Largest diff. peak and hole: 0.289 and −0.165 e × $Å^{-3}$

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

Treatment of hydrogen atoms:
All hydrogen atoms were placed in calculated positions and were refined with an isotropic displacement parameter 1.5 (methyl) or 1.2 times (all others) that of

the adjacent carbon atom.

Table 2. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [Å^2 × 10^3] for 07mz243m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	8271(2)	1695(2)	229(1)	21(1)
C(2)	7882(2)	1235(2)	1113(1)	20(1)
C(3)	6486(2)	668(2)	1102(1)	20(1)
C(4)	6427(2)	-400(2)	430(1)	21(1)
C(5)	6906(2)	95(2)	-419(1)	23(1)
C(6)	7038(2)	-966(2)	-1076(1)	32(1)
C(7)	7775(2)	3930(2)	18(1)	23(1)
C(8)	6753(2)	4832(2)	-339(1)	27(1)
C(9)	9114(2)	2607(2)	2016(1)	23(1)
C(10)	9049(2)	3776(2)	2568(1)	29(1)
C(11)	4975(2)	-76(2)	2158(1)	25(1)
C(12)	4914(2)	-806(2)	2972(1)	32(1)
C(13)	6717(2)	-2425(2)	1118(1)	27(1)
C(14)	7766(2)	-3278(2)	1500(1)	34(1)
O(1)	8216(1)	685(1)	-348(1)	24(1)
O(2)	7351(1)	2691(1)	-38(1)	23(1)
O(3)	7898(1)	2305(1)	1692(1)	21(1)
O(4)	6270(1)	113(1)	1926(1)	23(1)
O(5)	7304(1)	-1425(1)	707(1)	25(1)
O(6)	8826(1)	4234(1)	333(1)	28(1)
O(7)	10108(1)	2004(1)	1862(1)	33(1)
O(8)	4041(1)	309(2)	1755(1)	32(1)
O(9)	5534(1)	-2581(1)	1174(1)	34(1)

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

Table 3. Bond lengths [Å] and angles [deg] for 07mz243m.

C(1)-O(1)	1.3917(19)
C(1)-O(2)	1.447(2)
C(1)-C(2)	1.529(2)
C(1)-H(1)	1.0000
C(2)-O(3)	1.4407(18)
C(2)-C(3)	1.515(2)
C(2)-H(2)	1.0000
C(3)-O(4)	1.442(2)
C(3)-C(4)	1.537(2)
C(3)-H(3)	1.0000
C(4)-O(5)	1.446(2)

C(4)-C(5)	1.516(2)
C(4)-H(4)	1.0000
C(5)-O(1)	1.452(2)
C(5)-C(6)	1.519(2)
C(5)-H(5)	1.0000
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-O(6)	1.206(2)
C(7)-O(2)	1.357(2)
C(7)-C(8)	1.496(2)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-O(7)	1.199(2)
C(9)-O(3)	1.357(2)
C(9)-C(10)	1.497(2)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-O(8)	1.200(2)
C(11)-O(4)	1.361(2)
C(11)-C(12)	1.495(2)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-O(9)	1.198(2)
C(13)-O(5)	1.359(2)
C(13)-C(14)	1.500(3)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800

O(1)-C(1)-O(2)	108.64(13)
O(1)-C(1)-C(2)	110.86(13)
O(2)-C(1)-C(2)	109.18(13)
O(1)-C(1)-H(1)	109.4
O(2)-C(1)-H(1)	109.4
C(2)-C(1)-H(1)	109.4
O(3)-C(2)-C(3)	108.51(13)
O(3)-C(2)-C(1)	109.82(12)
C(3)-C(2)-C(1)	110.21(14)
O(3)-C(2)-H(2)	109.4
C(3)-C(2)-H(2)	109.4
C(1)-C(2)-H(2)	109.4
O(4)-C(3)-C(2)	106.41(13)
O(4)-C(3)-C(4)	109.46(13)
C(2)-C(3)-C(4)	108.89(13)
O(4)-C(3)-H(3)	110.7
C(2)-C(3)-H(3)	110.7
C(4)-C(3)-H(3)	110.7
O(5)-C(4)-C(5)	109.03(13)
O(5)-C(4)-C(3)	107.24(13)
C(5)-C(4)-C(3)	110.96(13)
O(5)-C(4)-H(4)	109.9
C(5)-C(4)-H(4)	109.9
C(3)-C(4)-H(4)	109.9
O(1)-C(5)-C(4)	111.05(14)
O(1)-C(5)-C(6)	106.28(14)
C(4)-C(5)-C(6)	112.91(14)
O(1)-C(5)-H(5)	108.8
C(4)-C(5)-H(5)	108.8
C(6)-C(5)-H(5)	108.8

C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
O(6)-C(7)-O(2)	123.21(16)
O(6)-C(7)-C(8)	126.00(16)
O(2)-C(7)-C(8)	110.77(14)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
O(7)-C(9)-O(3)	123.18(15)
O(7)-C(9)-C(10)	125.23(16)
O(3)-C(9)-C(10)	111.58(15)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
O(8)-C(11)-O(4)	123.25(16)
O(8)-C(11)-C(12)	126.58(16)
O(4)-C(11)-C(12)	110.17(15)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
O(9)-C(13)-O(5)	124.46(17)
O(9)-C(13)-C(14)	125.55(18)
O(5)-C(13)-C(14)	109.98(16)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(1)-O(1)-C(5)	113.87(12)
C(7)-O(2)-C(1)	117.29(13)
C(9)-O(3)-C(2)	115.33(12)
C(11)-O(4)-C(3)	116.46(13)
C(13)-O(5)-C(4)	116.40(13)

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 07mz243m. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [(h\ a^*)^2\ U11 + ... + 2\ h\ k\ a^*\ b^*\ U12]$

	U11	U22	U33	U23	U13	U12
C(1)	18(1)	25(1)	21(1)	0(1)	0(1)	0(1)
C(2)	18(1)	23(1)	19(1)	-2(1)	-1(1)	1(1)
C(3)	20(1)	25(1)	17(1)	2(1)	1(1)	1(1)
C(4)	18(1)	24(1)	21(1)	-1(1)	-1(1)	0(1)

C(5)	20(1)	29(1)	20(1)	-2(1)	0(1)	-2(1)
C(6)	31(1)	38(1)	26(1)	-9(1)	3(1)	-5(1)
C(7)	23(1)	28(1)	18(1)	3(1)	4(1)	-2(1)
C(8)	25(1)	28(1)	26(1)	3(1)	-2(1)	0(1)
C(9)	22(1)	26(1)	19(1)	0(1)	-2(1)	1(1)
C(10)	29(1)	29(1)	29(1)	-6(1)	-6(1)	3(1)
C(11)	22(1)	32(1)	20(1)	-1(1)	0(1)	-3(1)
C(12)	28(1)	45(1)	24(1)	8(1)	-1(1)	-8(1)
C(13)	30(1)	23(1)	27(1)	-3(1)	-4(1)	-1(1)
C(14)	32(1)	28(1)	42(1)	4(1)	-8(1)	2(1)
O(1)	20(1)	30(1)	22(1)	-4(1)	3(1)	-2(1)
O(2)	21(1)	25(1)	22(1)	2(1)	-2(1)	-1(1)
O(3)	19(1)	23(1)	21(1)	-3(1)	-1(1)	1(1)
O(4)	20(1)	29(1)	18(1)	2(1)	1(1)	-2(1)
O(5)	22(1)	25(1)	27(1)	-1(1)	-1(1)	3(1)
O(6)	22(1)	31(1)	29(1)	2(1)	-2(1)	-5(1)
O(7)	22(1)	40(1)	36(1)	-11(1)	-7(1)	5(1)
O(8)	20(1)	51(1)	25(1)	4(1)	0(1)	0(1)
O(9)	27(1)	31(1)	45(1)	5(1)	-3(1)	-4(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for 07mz243m.

	x	y	z	U(eq)
H(1)	9199	2054	244	26
H(2)	8531	565	1307	24
H(3)	5807	1351	981	24
H(4)	5492	-731	378	25
H(5)	6257	754	-630	28
H(6A)	7278	-585	-1622	47
H(6B)	6185	-1423	-1129	47
H(6C)	7736	-1572	-901	47
H(8A)	6018	4934	65	40
H(8B)	6405	4480	-870	40
H(8C)	7167	5672	-446	40
H(10A)	9672	3677	3041	44
H(10B)	8138	3877	2786	44
H(10C)	9293	4540	2238	44
H(12A)	5162	-234	3439	48
H(12B)	5537	-1534	2949	48
H(12C)	4004	-1128	3060	48
H(14A)	8108	-2881	2018	51
H(14B)	8500	-3392	1097	51
H(14C)	7374	-4120	1634	51

Table 6. Torsion angles [deg] for 07mz242m.

O(1)-C(1)-C(2)-O(3)	-177.86(12)
O(2)-C(1)-C(2)-O(3)	-58.21(16)
O(1)-C(1)-C(2)-C(3)	-58.37(17)
O(2)-C(1)-C(2)-C(3)	61.28(16)
O(3)-C(2)-C(3)-O(4)	-66.90(15)
C(1)-C(2)-C(3)-O(4)	172.82(13)
O(3)-C(2)-C(3)-C(4)	175.20(12)
C(1)-C(2)-C(3)-C(4)	54.92(16)
O(4)-C(3)-C(4)-O(5)	-50.32(17)

C(2)-C(3)-C(4)-O(5)	65.63(16)
O(4)-C(3)-C(4)-C(5)	-169.30(13)
C(2)-C(3)-C(4)-C(5)	-53.35(17)
O(5)-C(4)-C(5)-O(1)	-64.63(16)
C(3)-C(4)-C(5)-O(1)	53.27(18)
O(5)-C(4)-C(5)-C(6)	54.62(18)
C(3)-C(4)-C(5)-C(6)	172.52(15)
O(2)-C(1)-O(1)-C(5)	-60.61(17)
C(2)-C(1)-O(1)-C(5)	59.37(17)
C(4)-C(5)-O(1)-C(1)	-57.33(17)
C(6)-C(5)-O(1)-C(1)	179.53(14)
O(6)-C(7)-O(2)-C(1)	-5.6(2)
C(8)-C(7)-O(2)-C(1)	175.89(13)
O(1)-C(1)-O(2)-C(7)	-137.64(15)
C(2)-C(1)-O(2)-C(7)	101.35(16)
O(7)-C(9)-O(3)-C(2)	-2.8(2)
C(10)-C(9)-O(3)-C(2)	176.54(14)
C(3)-C(2)-O(3)-C(9)	156.28(14)
C(1)-C(2)-O(3)-C(9)	-83.19(16)
O(8)-C(11)-O(4)-C(3)	-7.7(2)
C(12)-C(11)-O(4)-C(3)	172.72(14)
C(2)-C(3)-O(4)-C(11)	159.42(14)
C(4)-C(3)-O(4)-C(11)	-83.06(17)
O(9)-C(13)-O(5)-C(4)	9.2(3)
C(14)-C(13)-O(5)-C(4)	-169.72(15)
C(5)-C(4)-O(5)-C(13)	-142.83(14)
C(3)-C(4)-O(5)-C(13)	96.95(16)

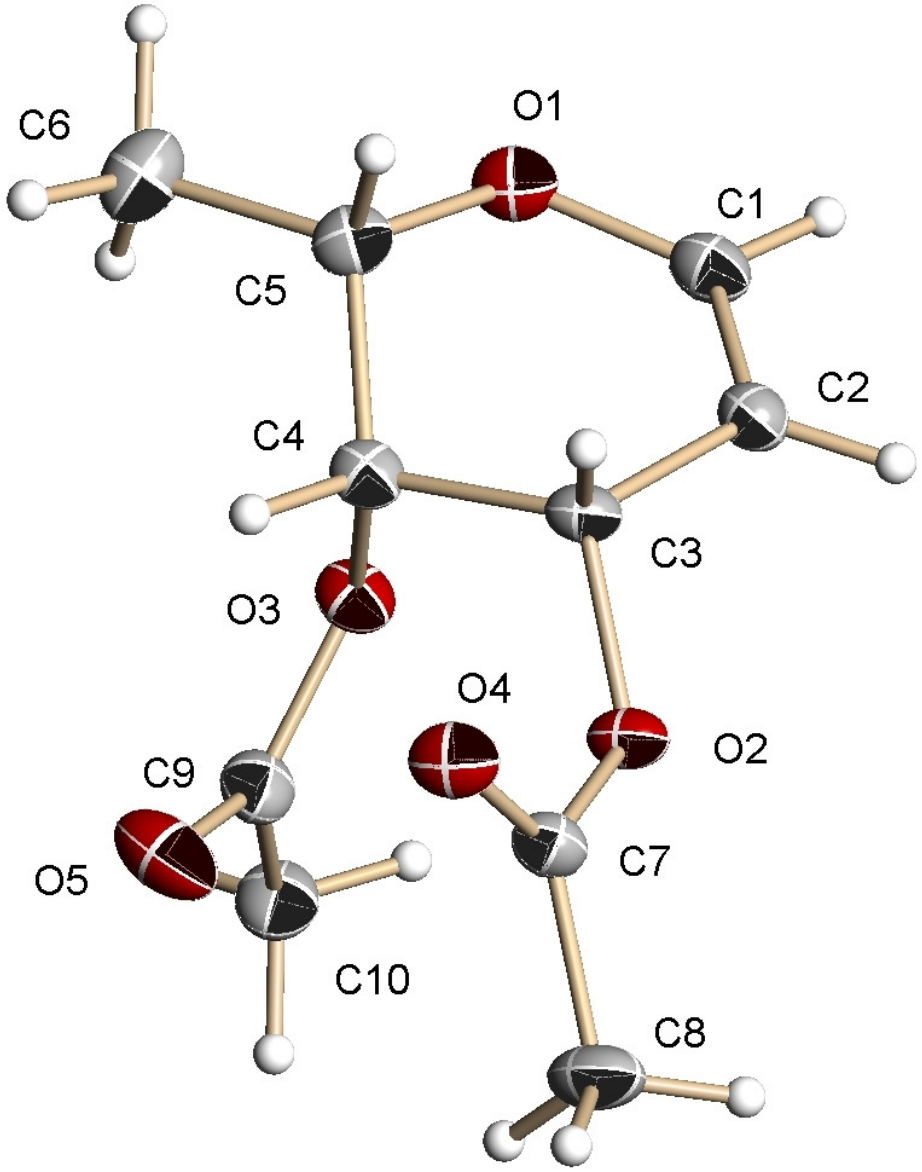


Figure 125 : Crystallographic refinement of 3,4-di-O-acetyl-L-fucal (**4**)

Table 1. Crystal data and structure refinement for 07mz180m:

Identification code: 07mz180m
Empirical formula: C10 H14 O5
Formula weight: 214.21
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Monoclinic
Space group: $P2_1$
Unit cell dimensions:
a = 6.7675(6) Å, α = 90°
b = 8.2966(7) Å, β = 98.7560(10)°
c = 9.8898(8) Å, γ = 90°
Volume, Z: 548.81(8) $Å^3$, 2
Density (calculated): 1.296 Mg/m^3
Absorption coefficient: 0.104 mm^{-1}
F(000): 228
Crystal size: 0.60 × 0.49 × 0.38 mm
Crystal shape, colour: block, colourless
θ range for data collection: 2.08 to 28.28°
Limiting indices: $-81 \le h \le 9$, $-11 \le k \le 8$, $-13 \le l \le 13$
Reflections collected: 4227
Independent reflections: 1449 (R(int) = 0.0193)
Completeness to θ = 28.26°: 100.0 %
Absorption correction: multi-scan
Max. and min. transmission: 0.961 and 0.862
Refinement method: Full-matrix least-squares on F^2
Data / restraints / parameters: 1449 / 1 / 139
Goodness-of-fit on F^2: 1.122
Final R indices [$I>2\sigma(I)$]: R1 = 0.0310, wR2 = 0.0813
R indices (all data): R1 = 0.0319, wR2 = 0.0827
Largest diff. peak and hole: 0.200 and -0.217 e × $Å^{-3}$

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

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

Table 2. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [$Å^2$ × 10^3] for 07mz180m. U(eq) is defined as one third of the trace

of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	502(2)	6696(2)	1061(2)	24(1)
C(2)	-460(2)	7943(2)	1501(2)	22(1)
C(3)	423(2)	8907(2)	2721(2)	20(1)
C(4)	2683(2)	8626(2)	3007(2)	21(1)
C(5)	3065(2)	6820(2)	2994(2)	23(1)
C(6)	5249(2)	6348(3)	3318(2)	31(1)
C(7)	-51(2)	11612(2)	3452(2)	21(1)
C(8)	-389(3)	13308(2)	2947(2)	32(1)
C(9)	4363(2)	10830(2)	2105(2)	24(1)
C(10)	5050(2)	11437(3)	825(2)	28(1)
O(1)	2320(2)	6132(2)	1659(1)	25(1)
O(2)	-13(2)	10584(2)	2384(1)	22(1)
O(3)	3577(2)	9337(2)	1906(1)	23(1)
O(4)	179(2)	11189(2)	4627(1)	27(1)
O(5)	4504(2)	11557(2)	3168(1)	37(1)

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

Table 3. Bond lengths [Å] and angles [deg] for 07mz180m.

C(1)-C(2)	1.330(2)
C(1)-O(1)	1.364(2)
C(1)-H(1)	0.9500
C(2)-C(3)	1.495(2)
C(2)-H(2)	0.9500
C(3)-O(2)	1.451(2)
C(3)-C(4)	1.530(2)
C(3)-H(3)	1.0000
C(4)-O(3)	1.4490(17)
C(4)-C(5)	1.521(2)
C(4)-H(4)	1.0000
C(5)-O(1)	1.4561(19)
C(5)-C(6)	1.515(2)
C(5)-H(5)	1.0000
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-O(4)	1.2017(19)
C(7)-O(2)	1.3610(19)
C(7)-C(8)	1.499(3)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-O(5)	1.203(2)
C(9)-O(3)	1.351(2)
C(9)-C(10)	1.500(2)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800

C(2)-C(1)-O(1)	125.40(15)

C(2)-C(1)-H(1)	117.3
O(1)-C(1)-H(1)	117.3
C(1)-C(2)-C(3)	121.64(15)
C(1)-C(2)-H(2)	119.2
C(3)-C(2)-H(2)	119.2
O(2)-C(3)-C(2)	106.56(12)
O(2)-C(3)-C(4)	110.58(13)
C(2)-C(3)-C(4)	109.46(13)
O(2)-C(3)-H(3)	110.1
C(2)-C(3)-H(3)	110.1
C(4)-C(3)-H(3)	110.1
O(3)-C(4)-C(5)	107.67(13)
O(3)-C(4)-C(3)	108.63(12)
C(5)-C(4)-C(3)	108.37(13)
O(3)-C(4)-H(4)	110.7
C(5)-C(4)-H(4)	110.7
C(3)-C(4)-H(4)	110.7
O(1)-C(5)-C(6)	106.43(13)
O(1)-C(5)-C(4)	110.97(13)
C(6)-C(5)-C(4)	114.46(15)
O(1)-C(5)-H(5)	108.3
C(6)-C(5)-H(5)	108.3
C(4)-C(5)-H(5)	108.3
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
O(4)-C(7)-O(2)	123.54(16)
O(4)-C(7)-C(8)	125.98(16)
O(2)-C(7)-C(8)	110.47(13)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
O(5)-C(9)-O(3)	124.37(16)
O(5)-C(9)-C(10)	125.12(17)
O(3)-C(9)-C(10)	110.50(15)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(1)-O(1)-C(5)	115.06(12)
C(7)-O(2)-C(3)	116.72(12)
C(9)-O(3)-C(4)	117.63(13)

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 07mz180m. The anisotropic displacement factor exponent takes the form: $-2\ \pi 2\ [(h\ a^*)^2\ U11 + ... + 2\ h\ k\ a^*\ b^*\ U12]$

	U11	U22	U33	U23	U13	U12
C(1)	29(1)	21(1)	21(1)	-2(1)	6(1)	-4(1)
C(2)	23(1)	21(1)	22(1)	-1(1)	3(1)	-3(1)
C(3)	25(1)	15(1)	20(1)	0(1)	5(1)	-1(1)
C(4)	24(1)	22(1)	17(1)	1(1)	6(1)	-3(1)

C(5)	26(1)	23(1)	19(1)	2(1)	7(1)	1(1)
C(6)	29(1)	39(1)	26(1)	4(1)	6(1)	8(1)
C(7)	23(1)	18(1)	23(1)	-2(1)	6(1)	-1(1)
C(8)	47(1)	18(1)	31(1)	-1(1)	3(1)	1(1)
C(9)	22(1)	25(1)	25(1)	4(1)	5(1)	-4(1)
C(10)	27(1)	31(1)	28(1)	9(1)	7(1)	-3(1)
O(1)	30(1)	24(1)	22(1)	-2(1)	8(1)	1(1)
O(2)	31(1)	16(1)	19(1)	0(1)	5(1)	0(1)
O(3)	26(1)	24(1)	20(1)	2(1)	8(1)	-5(1)
O(4)	36(1)	24(1)	21(1)	-2(1)	8(1)	1(1)
O(5)	49(1)	34(1)	30(1)	-5(1)	11(1)	-17(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for 07mz180m.

	x	y	z	U(eq)
H(1)	-128	6155	264	28
H(2)	-1741	8227	1028	26
H(3)	-199	8588	3536	24
H(4)	3268	9104	3907	25
H(5)	2333	6304	3685	27
H(6A)	5372	5174	3263	47
H(6B)	5791	6709	4244	47
H(6C)	5996	6856	2658	47
H(8A)	-744	13986	3685	48
H(8B)	-1479	13326	2172	48
H(8C)	836	13720	2655	48
H(10A)	4972	12616	801	42
H(10B)	4191	10992	25	42
H(10C)	6435	11099	814	42

Table 6. Torsion angles [deg] for 07mz180m.

O(1)-C(1)-C(2)-C(3)	1.7(3)
C(1)-C(2)-C(3)-O(2)	138.74(16)
C(1)-C(2)-C(3)-C(4)	19.1(2)
O(2)-C(3)-C(4)-O(3)	-49.02(16)
C(2)-C(3)-C(4)-O(3)	68.08(16)
O(2)-C(3)-C(4)-C(5)	-165.73(12)
C(2)-C(3)-C(4)-C(5)	-48.64(17)
O(3)-C(4)-C(5)-O(1)	-55.51(15)
C(3)-C(4)-C(5)-O(1)	61.81(16)
O(3)-C(4)-C(5)-C(6)	64.96(16)
C(3)-C(4)-C(5)-C(6)	-177.72(12)
C(2)-C(1)-O(1)-C(5)	9.9(2)
C(6)-C(5)-O(1)-C(1)	-167.05(15)
C(4)-C(5)-O(1)-C(1)	-41.92(18)
O(4)-C(7)-O(2)-C(3)	-2.9(2)
C(8)-C(7)-O(2)-C(3)	176.38(14)
C(2)-C(3)-O(2)-C(7)	155.87(13)
C(4)-C(3)-O(2)-C(7)	-85.26(16)
O(5)-C(9)-O(3)-C(4)	5.9(2)
C(10)-C(9)-O(3)-C(4)	-174.81(13)
C(5)-C(4)-O(3)-C(9)	-146.07(13)
C(3)-C(4)-O(3)-C(9)	96.77(15)

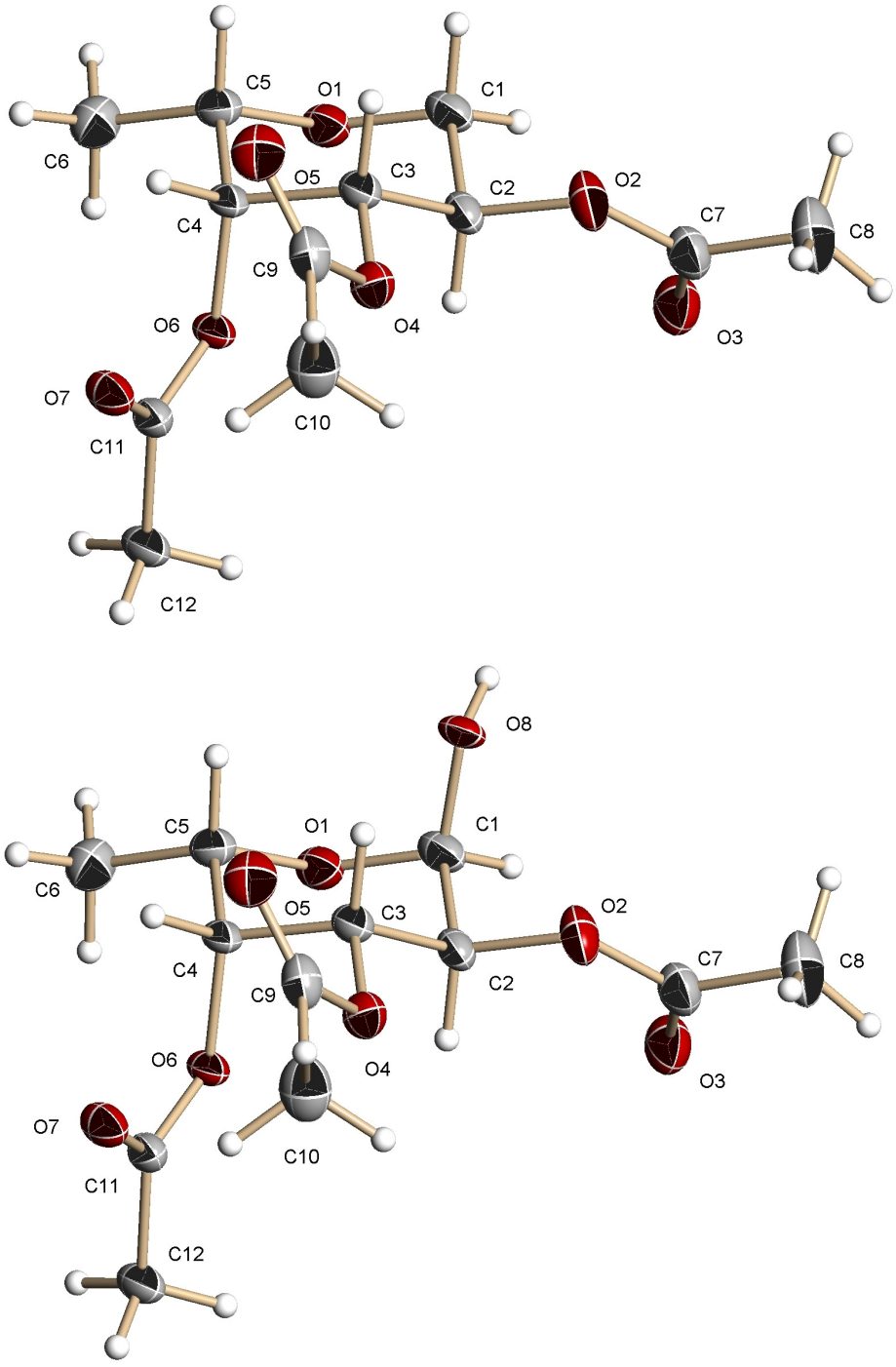


Figure 126 :

Crystallographic refinement of 2,3,4-tri-*O*-acetyl-1-deoxy-L-fucose (**5**) co-crystallized with hydrolysis product of 1-bromo-2,3,4-tri-*O*-acetyl-L-fucose.

Table 1. Crystal data and structure refinement for 08mz001_0m:

Identification code: 08mz001_0m
Empirical formula: C12 H18 O7.63
Moiety formula: 0.367(C12 H18 O7), 0.633(C12 H18 O8)
Formula weight: 284.39
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Monoclinic
Space group: $P2_1$
Unit cell dimensions:
a = 8.7602(15) Å, α = 90°
b = 7.9774(13) Å, β = 93.453(2)°
c = 10.0502(17) Å, γ = 90°
Volume, Z: 701.1(2) $Å^3$, 2
Density (calculated): 1.347 Mg/m^3
Absorption coefficient: 0.113 mm^{-1}
F(000): 302.1
Crystal size: 0.65 × 0.41 × 0.12 mm
Crystal shape, colour: plate, colourless
θ range for data collection: 2.03 to 28.26°
Limiting indices: $-11 \le h \le 11$, $-10 \le k \le 10$, $-13 \le l \le 13$
Reflections collected: 7099
Independent reflections: 1864 (R(int) = 0.0242)
Completeness to θ = 28.26°: 99.8 %
Absorption correction: multi-scan
Max. and min. transmission: 0.987 and 0.828
Refinement method: Full-matrix least-squares on F^2
Data / restraints / parameters: 1864 / 1 / 187
Goodness-of-fit on F^2: 1.043
Final R indices [$I>2\sigma(I)$]: R1 = 0.0319, wR2 = 0.0822
R indices (all data): R1 = 0.0354, wR2 = 0.0846
Largest diff. peak and hole: 0.279 and −0.159 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 substitution pattern at carbon atom C1 was tentatively refined as being partially C(H)OH, partially CH2. The occupancy ratio refined to 0.633(6) to 0.367(6).

Treatment of hydrogen atoms:
All hydrogen atoms were placed in calculated positions and were refined with an

isotropic displacement parameter 1.5 (methyl, hydroxyl) or 1.2 times (all others) that of the adjacent carbon or oxygen atom.

Table 2. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [$Å^2$ × 10^3] for 08mz001_0m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	991(2)	-124(2)	9760(2)	26(1)
C(2)	2200(2)	914(2)	9108(2)	23(1)
C(3)	2013(2)	645(2)	7615(2)	22(1)
C(4)	404(2)	1196(2)	7129(2)	21(1)
C(5)	-799(2)	267(2)	7874(2)	25(1)
C(6)	-2406(2)	873(3)	7528(2)	33(1)
C(7)	4212(2)	946(3)	10791(2)	30(1)
C(8)	5785(3)	307(4)	11178(2)	46(1)
C(9)	3382(2)	1148(3)	5700(2)	28(1)
C(10)	4421(3)	2349(3)	5060(2)	39(1)
C(11)	533(2)	4057(2)	6405(2)	23(1)
C(12)	322(2)	5835(2)	6841(2)	29(1)
O(1)	-497(2)	443(2)	9301(1)	26(1)
O(2)	3715(2)	369(2)	9571(1)	32(1)
O(3)	3463(2)	1840(2)	11455(1)	36(1)
O(4)	3145(2)	1621(2)	6979(1)	25(1)
O(5)	2793(2)	-69(2)	5187(1)	33(1)
O(6)	243(1)	2977(2)	7401(1)	21(1)
O(7)	907(2)	3626(2)	5317(1)	27(1)
O(8)	1346(2)	-1795(2)	9432(2)	23(1)

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

Table 3. Bond lengths [Å] and angles [deg] for 08mz001_0m.

C(1)-O(8)	1.412(3)
C(1)-O(1)	1.430(2)
C(1)-C(2)	1.523(3)
C(1)-H(1B)	0.9900
C(1)-H(1C)	0.9900
C(1)-H(1)	1.0000
C(2)-O(2)	1.446(2)
C(2)-C(3)	1.515(2)
C(2)-H(2)	1.0000
C(3)-O(4)	1.441(2)
C(3)-C(4)	1.528(2)
C(3)-H(3)	1.0000
C(4)-O(6)	1.455(2)
C(4)-C(5)	1.522(3)
C(4)-H(4)	1.0000
C(5)-O(1)	1.449(2)
C(5)-C(6)	1.509(3)
C(5)-H(5)	1.0000

C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-O(3)	1.199(3)
C(7)-O(2)	1.357(2)
C(7)-C(8)	1.498(3)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-O(5)	1.201(3)
C(9)-O(4)	1.367(2)
C(9)-C(10)	1.493(3)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-O(7)	1.210(2)
C(11)-O(6)	1.356(2)
C(11)-C(12)	1.499(3)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
O(8)-H(8)	0.8400

O(8)-C(1)-O(1)	115.66(17)
O(8)-C(1)-C(2)	104.13(16)
O(1)-C(1)-C(2)	109.44(14)
O(1)-C(1)-H(1B)	109.8
C(2)-C(1)-H(1B)	109.8
O(8)-C(1)-H(1C)	107.8
O(1)-C(1)-H(1C)	109.8
C(2)-C(1)-H(1C)	109.8
H(1B)-C(1)-H(1C)	108.2
O(8)-C(1)-H(1)	109.1
O(1)-C(1)-H(1)	109.1
C(2)-C(1)-H(1)	109.1
H(1B)-C(1)-H(1)	109.6
O(2)-C(2)-C(3)	108.57(14)
O(2)-C(2)-C(1)	110.28(15)
C(3)-C(2)-C(1)	108.20(15)
O(2)-C(2)-H(2)	109.9
C(3)-C(2)-H(2)	109.9
C(1)-C(2)-H(2)	109.9
O(4)-C(3)-C(2)	109.06(14)
O(4)-C(3)-C(4)	110.45(14)
C(2)-C(3)-C(4)	108.58(14)
O(4)-C(3)-H(3)	109.6
C(2)-C(3)-H(3)	109.6
C(4)-C(3)-H(3)	109.6
O(6)-C(4)-C(5)	107.78(14)
O(6)-C(4)-C(3)	108.60(14)
C(5)-C(4)-C(3)	110.83(14)
O(6)-C(4)-H(4)	109.9
C(5)-C(4)-H(4)	109.9
C(3)-C(4)-H(4)	109.9
O(1)-C(5)-C(6)	108.03(15)
O(1)-C(5)-C(4)	110.39(15)
C(6)-C(5)-C(4)	113.23(16)
O(1)-C(5)-H(5)	108.4
C(6)-C(5)-H(5)	108.4
C(4)-C(5)-H(5)	108.4
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5

C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
O(3)-C(7)-O(2)	123.24(18)
O(3)-C(7)-C(8)	125.70(19)
O(2)-C(7)-C(8)	111.05(18)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
O(5)-C(9)-O(4)	122.72(18)
O(5)-C(9)-C(10)	126.26(19)
O(4)-C(9)-C(10)	111.02(18)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
O(7)-C(11)-O(6)	124.02(17)
O(7)-C(11)-C(12)	125.25(17)
O(6)-C(11)-C(12)	110.72(15)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(1)-O(1)-C(5)	113.41(14)
C(7)-O(2)-C(2)	115.28(15)
C(9)-O(4)-C(3)	114.56(15)
C(11)-O(6)-C(4)	117.22(13)
C(1)-O(8)-H(8)	109.5

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 08mz001_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [(h a*)^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	38(1)	19(1)	21(1)	3(1)	0(1)	3(1)
C(2)	29(1)	19(1)	20(1)	2(1)	-4(1)	5(1)
C(3)	28(1)	17(1)	21(1)	1(1)	-1(1)	1(1)
C(4)	29(1)	12(1)	21(1)	-2(1)	-3(1)	1(1)
C(5)	32(1)	19(1)	24(1)	0(1)	-2(1)	-3(1)
C(6)	30(1)	34(1)	34(1)	0(1)	-1(1)	-2(1)
C(7)	33(1)	32(1)	24(1)	5(1)	-3(1)	4(1)
C(8)	38(1)	62(2)	36(1)	3(1)	-11(1)	15(1)
C(9)	26(1)	35(1)	23(1)	2(1)	-2(1)	7(1)
C(10)	34(1)	52(1)	30(1)	7(1)	3(1)	-1(1)
C(11)	29(1)	18(1)	20(1)	1(1)	-4(1)	1(1)
C(12)	45(1)	17(1)	24(1)	1(1)	-4(1)	2(1)
O(1)	33(1)	22(1)	22(1)	1(1)	1(1)	-2(1)
O(2)	34(1)	36(1)	23(1)	-2(1)	-7(1)	14(1)
O(3)	40(1)	39(1)	28(1)	-4(1)	-7(1)	6(1)
O(4)	28(1)	26(1)	20(1)	2(1)	0(1)	-2(1)
O(5)	34(1)	35(1)	29(1)	-7(1)	3(1)	5(1)

O(6)	31(1)	13(1)	18(1)	0(1)	-2(1)	2(1)
O(7)	39(1)	22(1)	20(1)	2(1)	0(1)	2(1)
O(8)	32(1)	12(1)	23(1)	4(1)	2(1)	-1(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for 08mz001_0m.

	x	y	z	U(eq)
H(1B)	1111	-1322	9531	31
H(1C)	1119	-10	10741	31
H(1)	1116	19	10749	31
H(2)	2065	2128	9320	27
H(3)	2153	-570	7409	27
H(4)	241	984	6150	25
H(5)	-744	-951	7644	30
H(6A)	-3133	168	7976	49
H(6B)	-2622	807	6561	49
H(6C)	-2506	2037	7821	49
H(8A)	6215	939	11948	68
H(8B)	6439	447	10428	68
H(8C)	5730	-884	11410	68
H(10A)	5009	1751	4409	58
H(10B)	5124	2850	5744	58
H(10C)	3812	3233	4606	58
H(12A)	776	6594	6208	43
H(12B)	823	5995	7730	43
H(12C)	-773	6077	6869	43
H(8)	1007	-2446	10001	34

Table 6. Torsion angles [deg] for 07mz075m.

O(8)-C(1)-C(2)-O(2)	-56.36(19)
O(1)-C(1)-C(2)-O(2)	179.42(14)
O(8)-C(1)-C(2)-C(3)	62.26(19)
O(1)-C(1)-C(2)-C(3)	-61.96(18)
O(2)-C(2)-C(3)-O(4)	-60.44(19)
C(1)-C(2)-C(3)-O(4)	179.86(14)
O(2)-C(2)-C(3)-C(4)	179.15(14)
C(1)-C(2)-C(3)-C(4)	59.46(18)
O(4)-C(3)-C(4)-O(6)	-57.39(18)
C(2)-C(3)-C(4)-O(6)	62.15(18)
O(4)-C(3)-C(4)-C(5)	-175.60(14)
C(2)-C(3)-C(4)-C(5)	-56.06(18)
O(6)-C(4)-C(5)-O(1)	-65.30(18)
C(3)-C(4)-C(5)-O(1)	53.41(19)
O(6)-C(4)-C(5)-C(6)	55.96(19)
C(3)-C(4)-C(5)-C(6)	174.67(16)
O(8)-C(1)-O(1)-C(5)	-55.8(2)
C(2)-C(1)-O(1)-C(5)	61.40(19)
C(6)-C(5)-O(1)-C(1)	178.83(16)
C(4)-C(5)-O(1)-C(1)	-56.9(2)
O(3)-C(7)-O(2)-C(2)	0.2(3)
C(8)-C(7)-O(2)-C(2)	179.83(18)
C(3)-C(2)-O(2)-C(7)	162.41(17)
C(1)-C(2)-O(2)-C(7)	-79.2(2)
O(5)-C(9)-O(4)-C(3)	-6.1(3)
C(10)-C(9)-O(4)-C(3)	172.92(16)
C(2)-C(3)-O(4)-C(9)	162.75(15)

C(4)-C(3)-O(4)-C(9)	-78.00(18)
O(7)-C(11)-O(6)-C(4)	0.3(3)
C(12)-C(11)-O(6)-C(4)	-179.83(15)
C(5)-C(4)-O(6)-C(11)	-145.64(15)
C(3)-C(4)-O(6)-C(11)	94.24(17)

Table 7. Hydrogen bonds for 08mz001_0m [Å and deg].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(8)-H(8)...O(1)#1	0.84	1.89	2.673(2)	155.0

Symmetry transformations used to generate equivalent atoms:

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

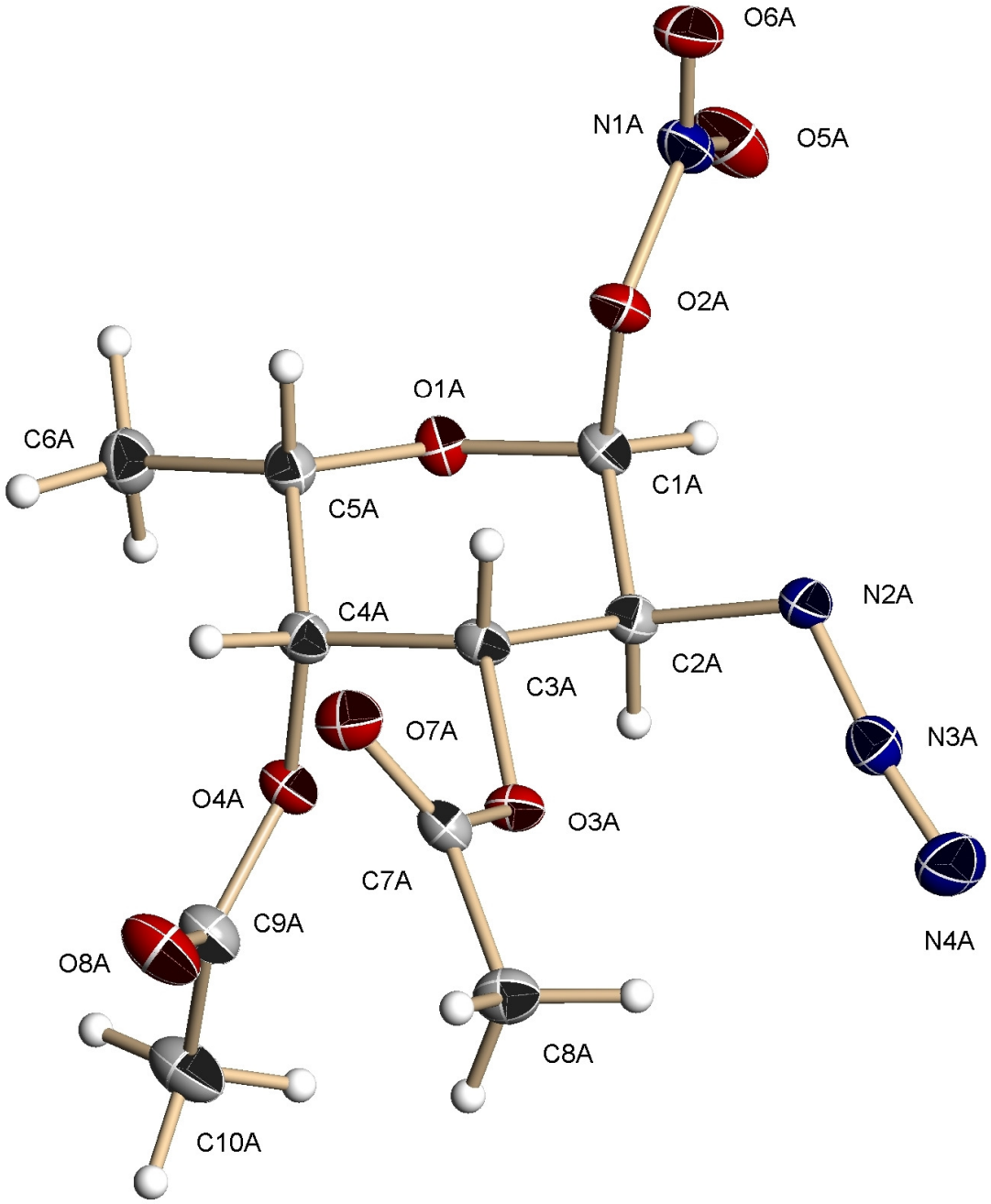


Figure 127 :

Crystallographic refinement of 3,4-di-*O*-acetyl-2-azidodeoxy-1-nitro-α-L-fucose (**6**)

Table 1. Crystal data and structure refinement for 07mz158m:

Identification code: 07mz158m
Empirical formula: C10 H14 N4 O8
Formula weight: 650.19
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Orthorhombic
Space group: $P2_12_12_1$
Unit cell dimensions:
a = 8.2169(6) Å, α = 90°
b = 15.8825(12) Å, β = 90°
c = 21.7738(16) Å, γ = 90°
Volume, *Z*: 2841.6(4) $Å^3$, 8
Density (calculated): 1.488 Mg/m^3
Absorption coefficient: 0.130 mm^{-1}
F(000): 1328
Crystal size: 0.52 × 0.50 × 0.36 mm
Crystal shape, colour: block, colourless
θ range for data collection: 1.59 to 28.28°
Limiting indices: $-10 \le h \le 10$, $21 \le k \le 21$, $28 \le l \le 28$
Reflections collected: 25826
Independent reflections: 3960 (*R*(int) = 0.0568)
Completeness to θ = 28.28°: 100.0 %
Absorption correction: multi-scan
Max. and min. transmission: 0.954 and 0.783
Refinement method: Full-matrix least-squares on F^2
Data / restraints / parameters: 3960 / 0 / 403
Goodness-of-fit on F^2: 1.047
Final *R* indices [$I>2\sigma(I)$]: R1 = 0.0330, wR2 = 0.0825
R indices (all data): R1 = 0.0348, wR2 = 0.0840
Largest diff. peak and hole: 0.273 and -0.183 e × $Å^{-3}$

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

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

Table 2. Atomic coordinates [× 10^4] and equivalent isotropic

displacement parameters [$Å^2 \times 10^3$] for 07mz158m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1A)	1519(2)	6893(1)	9607(1)	17(1)
C(2A)	3138(2)	7005(1)	9282(1)	17(1)
C(3A)	2871(2)	7019(1)	8590(1)	16(1)
C(4A)	1645(2)	7707(1)	8425(1)	17(1)
C(5A)	83(2)	7579(1)	8792(1)	18(1)
C(6A)	-1136(2)	8286(1)	8717(1)	23(1)
C(7A)	4653(2)	6882(1)	7737(1)	18(1)
C(8A)	6392(2)	6982(1)	7548(1)	23(1)
C(9A)	3093(3)	8946(1)	8120(1)	23(1)
C(10A)	3549(3)	9813(1)	8318(1)	30(1)
C(1B)	2547(2)	4348(1)	7901(1)	18(1)
C(2B)	3935(2)	4333(1)	8373(1)	18(1)
C(3B)	3204(2)	4270(1)	9016(1)	16(1)
C(4B)	2164(2)	3471(1)	9048(1)	18(1)
C(5B)	837(2)	3517(1)	8560(1)	18(1)
C(6B)	-187(3)	2726(1)	8511(1)	25(1)
C(7B)	4189(2)	4434(1)	10031(1)	20(1)
C(8B)	5676(3)	4376(2)	10424(1)	30(1)
C(9B)	3866(2)	2355(1)	9418(1)	20(1)
C(10B)	5124(3)	1726(1)	9220(1)	27(1)
N(1A)	-35(2)	5652(1)	9875(1)	22(1)
N(2A)	4178(2)	6288(1)	9469(1)	18(1)
N(3A)	5655(2)	6412(1)	9413(1)	21(1)
N(4A)	7021(2)	6443(1)	9386(1)	31(1)
N(1B)	763(2)	5434(1)	7517(1)	23(1)
N(2B)	4937(2)	5095(1)	8292(1)	21(1)
N(3B)	6420(2)	4970(1)	8344(1)	23(1)
N(4B)	7785(2)	4943(1)	8373(1)	37(1)
O(1A)	410(2)	7514(1)	9446(1)	18(1)
O(2A)	942(2)	6061(1)	9430(1)	19(1)
O(3A)	4447(2)	7162(1)	8323(1)	18(1)
O(4A)	2296(2)	8531(1)	8574(1)	19(1)
O(5A)	-240(2)	5997(1)	10360(1)	31(1)
O(6A)	-535(2)	4987(1)	9695(1)	28(1)
O(7A)	3575(2)	6594(1)	7431(1)	24(1)
O(8A)	3355(2)	8647(1)	7618(1)	31(1)
O(1B)	1531(2)	3658(1)	7952(1)	19(1)
O(2B)	1680(2)	5131(1)	8021(1)	19(1)
O(3B)	4553(2)	4230(1)	9437(1)	19(1)
O(4B)	3205(2)	2758(1)	8924(1)	18(1)
O(5B)	821(2)	5058(1)	7041(1)	37(1)
O(6B)	13(2)	6063(1)	7642(1)	26(1)
O(7B)	2855(2)	4629(1)	10199(1)	23(1)
O(8B)	3492(2)	2502(1)	9939(1)	29(1)

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

Table 3. Bond lengths [Å] and angles [deg] for 07mz158m.

C(1A)-O(1A)	1.388(2)
C(1A)-O(2A)	1.456(2)
C(1A)-C(2A)	1.518(2)
C(1A)-H(1A)	1.0000
C(2A)-N(2A)	1.480(2)
C(2A)-C(3A)	1.523(2)
C(2A)-H(2A)	1.0000
C(3A)-O(3A)	1.438(2)
C(3A)-C(4A)	1.529(2)
C(3A)-H(3A)	1.0000
C(4A)-O(4A)	1.450(2)
C(4A)-C(5A)	1.526(2)
C(4A)-H(4A)	1.0000
C(5A)-O(1A)	1.453(2)
C(5A)-C(6A)	1.513(3)
C(5A)-H(5A)	1.0000
C(6A)-H(6A1)	0.9800
C(6A)-H(6A2)	0.9800
C(6A)-H(6A3)	0.9800
C(7A)-O(7A)	1.199(2)
C(7A)-O(3A)	1.362(2)
C(7A)-C(8A)	1.495(3)
C(8A)-H(8A1)	0.9800
C(8A)-H(8A2)	0.9800
C(8A)-H(8A3)	0.9800
C(9A)-O(8A)	1.210(2)
C(9A)-O(4A)	1.357(2)
C(9A)-C(10A)	1.491(3)
C(10A)-H(10A)	0.9800
C(10A)-H(10B)	0.9800
C(10A)-H(10C)	0.9800
C(1B)-O(1B)	1.383(2)
C(1B)-O(2B)	1.456(2)
C(1B)-C(2B)	1.536(2)
C(1B)-H(1B)	1.0000
C(2B)-N(2B)	1.474(2)
C(2B)-C(3B)	1.527(2)
C(2B)-H(2B)	1.0000
C(3B)-O(3B)	1.440(2)
C(3B)-C(4B)	1.532(2)
C(3B)-H(3B)	1.0000
C(4B)-O(4B)	1.445(2)
C(4B)-C(5B)	1.524(2)
C(4B)-H(4B)	1.0000
C(5B)-O(1B)	1.459(2)
C(5B)-C(6B)	1.516(3)
C(5B)-H(5B)	1.0000
C(6B)-H(6B1)	0.9800
C(6B)-H(6B2)	0.9800
C(6B)-H(6B3)	0.9800
C(7B)-O(7B)	1.197(2)
C(7B)-O(3B)	1.366(2)
C(7B)-C(8B)	1.495(3)
C(8B)-H(8B1)	0.9800
C(8B)-H(8B2)	0.9800
C(8B)-H(8B3)	0.9800
C(9B)-O(8B)	1.197(2)

C(9B)-O(4B)	1.365(2)
C(9B)-C(10B)	1.502(3)
C(10B)-H(10D)	0.9800
C(10B)-H(10E)	0.9800
C(10B)-H(10F)	0.9800
N(1A)-O(6A)	1.199(2)
N(1A)-O(5A)	1.202(2)
N(1A)-O(2A)	1.4158(19)
N(2A)-N(3A)	1.236(2)
N(3A)-N(4A)	1.125(2)
N(1B)-O(5B)	1.198(2)
N(1B)-O(6B)	1.204(2)
N(1B)-O(2B)	1.4156(19)
N(2B)-N(3B)	1.240(2)
N(3B)-N(4B)	1.124(3)

O(1A)-C(1A)-O(2A)	111.38(14)
O(1A)-C(1A)-C(2A)	112.01(14)
O(2A)-C(1A)-C(2A)	105.52(14)
O(1A)-C(1A)-H(1A)	109.3
O(2A)-C(1A)-H(1A)	109.3
C(2A)-C(1A)-H(1A)	109.3
N(2A)-C(2A)-C(1A)	106.74(14)
N(2A)-C(2A)-C(3A)	111.55(14)
C(1A)-C(2A)-C(3A)	109.69(15)
N(2A)-C(2A)-H(2A)	109.6
C(1A)-C(2A)-H(2A)	109.6
C(3A)-C(2A)-H(2A)	109.6
O(3A)-C(3A)-C(2A)	105.84(14)
O(3A)-C(3A)-C(4A)	112.72(13)
C(2A)-C(3A)-C(4A)	109.80(14)
O(3A)-C(3A)-H(3A)	109.5
C(2A)-C(3A)-H(3A)	109.5
C(4A)-C(3A)-H(3A)	109.5
O(4A)-C(4A)-C(5A)	108.24(14)
O(4A)-C(4A)-C(3A)	110.41(14)
C(5A)-C(4A)-C(3A)	109.66(14)
O(4A)-C(4A)-H(4A)	109.5
C(5A)-C(4A)-H(4A)	109.5
C(3A)-C(4A)-H(4A)	109.5
O(1A)-C(5A)-C(6A)	106.39(14)
O(1A)-C(5A)-C(4A)	111.57(14)
C(6A)-C(5A)-C(4A)	113.64(15)
O(1A)-C(5A)-H(5A)	108.4
C(6A)-C(5A)-H(5A)	108.4
C(4A)-C(5A)-H(5A)	108.4
C(5A)-C(6A)-H(6A1)	109.5
C(5A)-C(6A)-H(6A2)	109.5
H(6A1)-C(6A)-H(6A2)	109.5
C(5A)-C(6A)-H(6A3)	109.5
H(6A1)-C(6A)-H(6A3)	109.5
H(6A2)-C(6A)-H(6A3)	109.5
O(7A)-C(7A)-O(3A)	123.58(17)
O(7A)-C(7A)-C(8A)	126.49(17)
O(3A)-C(7A)-C(8A)	109.92(16)
C(7A)-C(8A)-H(8A1)	109.5
C(7A)-C(8A)-H(8A2)	109.5
H(8A1)-C(8A)-H(8A2)	109.5
C(7A)-C(8A)-H(8A3)	109.5
H(8A1)-C(8A)-H(8A3)	109.5
H(8A2)-C(8A)-H(8A3)	109.5
O(8A)-C(9A)-O(4A)	123.53(18)
O(8A)-C(9A)-C(10A)	125.42(18)

O(4A)-C(9A)-C(10A)	111.03(16)
C(9A)-C(10A)-H(10A)	109.5
C(9A)-C(10A)-H(10B)	109.5
H(10A)-C(10A)-H(10B)	109.5
C(9A)-C(10A)-H(10C)	109.5
H(10A)-C(10A)-H(10C)	109.5
H(10B)-C(10A)-H(10C)	109.5
O(1B)-C(1B)-O(2B)	111.51(14)
O(1B)-C(1B)-C(2B)	112.43(14)
O(2B)-C(1B)-C(2B)	104.85(14)
O(1B)-C(1B)-H(1B)	109.3
O(2B)-C(1B)-H(1B)	109.3
C(2B)-C(1B)-H(1B)	109.3
N(2B)-C(2B)-C(3B)	112.53(15)
N(2B)-C(2B)-C(1B)	108.72(14)
C(3B)-C(2B)-C(1B)	108.86(15)
N(2B)-C(2B)-H(2B)	108.9
C(3B)-C(2B)-H(2B)	108.9
C(1B)-C(2B)-H(2B)	108.9
O(3B)-C(3B)-C(2B)	106.45(14)
O(3B)-C(3B)-C(4B)	111.37(14)
C(2B)-C(3B)-C(4B)	108.34(14)
O(3B)-C(3B)-H(3B)	110.2
C(2B)-C(3B)-H(3B)	110.2
C(4B)-C(3B)-H(3B)	110.2
O(4B)-C(4B)-C(5B)	109.31(14)
O(4B)-C(4B)-C(3B)	108.11(14)
C(5B)-C(4B)-C(3B)	109.14(14)
O(4B)-C(4B)-H(4B)	110.1
C(5B)-C(4B)-H(4B)	110.1
C(3B)-C(4B)-H(4B)	110.1
O(1B)-C(5B)-C(6B)	106.25(14)
O(1B)-C(5B)-C(4B)	111.12(14)
C(6B)-C(5B)-C(4B)	113.97(15)
O(1B)-C(5B)-H(5B)	108.5
C(6B)-C(5B)-H(5B)	108.5
C(4B)-C(5B)-H(5B)	108.5
C(5B)-C(6B)-H(6B1)	109.5
C(5B)-C(6B)-H(6B2)	109.5
H(6B1)-C(6B)-H(6B2)	109.5
C(5B)-C(6B)-H(6B3)	109.5
H(6B1)-C(6B)-H(6B3)	109.5
H(6B2)-C(6B)-H(6B3)	109.5
O(7B)-C(7B)-O(3B)	123.52(17)
O(7B)-C(7B)-C(8B)	126.08(18)
O(3B)-C(7B)-C(8B)	110.40(16)
C(7B)-C(8B)-H(8B1)	109.5
C(7B)-C(8B)-H(8B2)	109.5
H(8B1)-C(8B)-H(8B2)	109.5
C(7B)-C(8B)-H(8B3)	109.5
H(8B1)-C(8B)-H(8B3)	109.5
H(8B2)-C(8B)-H(8B3)	109.5
O(8B)-C(9B)-O(4B)	123.61(18)
O(8B)-C(9B)-C(10B)	125.35(18)
O(4B)-C(9B)-C(10B)	111.03(16)
C(9B)-C(10B)-H(10D)	109.5
C(9B)-C(10B)-H(10E)	109.5
H(10D)-C(10B)-H(10E)	109.5
C(9B)-C(10B)-H(10F)	109.5
H(10D)-C(10B)-H(10F)	109.5
H(10E)-C(10B)-H(10F)	109.5
O(6A)-N(1A)-O(5A)	129.84(17)
O(6A)-N(1A)-O(2A)	112.01(15)

O(5A)-N(1A)-O(2A)	118.14(16)
N(3A)-N(2A)-C(2A)	114.70(15)
N(4A)-N(3A)-N(2A)	172.9(2)
O(5B)-N(1B)-O(6B)	129.07(17)
O(5B)-N(1B)-O(2B)	118.64(15)
O(6B)-N(1B)-O(2B)	112.29(15)
N(3B)-N(2B)-C(2B)	113.95(16)
N(4B)-N(3B)-N(2B)	172.6(2)
C(1A)-O(1A)-C(5A)	114.81(13)
N(1A)-O(2A)-C(1A)	114.81(13)
C(7A)-O(3A)-C(3A)	116.11(14)
C(9A)-O(4A)-C(4A)	117.02(14)
C(1B)-O(1B)-C(5B)	115.50(13)
N(1B)-O(2B)-C(1B)	114.29(13)
C(7B)-O(3B)-C(3B)	115.02(14)
C(9B)-O(4B)-C(4B)	117.08(14)

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 07mz158m. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [(h a*)^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1A)	21(1)	15(1)	16(1)	1(1)	1(1)	0(1)
C(2A)	17(1)	15(1)	17(1)	0(1)	1(1)	-1(1)
C(3A)	18(1)	16(1)	14(1)	0(1)	3(1)	-2(1)
C(4A)	19(1)	17(1)	15(1)	0(1)	1(1)	-1(1)
C(5A)	18(1)	19(1)	16(1)	1(1)	0(1)	1(1)
C(6A)	23(1)	23(1)	24(1)	3(1)	1(1)	5(1)
C(7A)	22(1)	15(1)	17(1)	2(1)	2(1)	0(1)
C(8A)	21(1)	26(1)	23(1)	0(1)	4(1)	-2(1)
C(9A)	28(1)	20(1)	22(1)	4(1)	2(1)	-1(1)
C(10A)	43(1)	22(1)	25(1)	2(1)	3(1)	-7(1)
C(1B)	21(1)	16(1)	18(1)	0(1)	-1(1)	2(1)
C(2B)	19(1)	15(1)	20(1)	1(1)	-1(1)	0(1)
C(3B)	16(1)	16(1)	17(1)	0(1)	-2(1)	1(1)
C(4B)	18(1)	18(1)	16(1)	-2(1)	-1(1)	1(1)
C(5B)	18(1)	20(1)	16(1)	0(1)	0(1)	0(1)
C(6B)	26(1)	26(1)	24(1)	1(1)	-1(1)	-7(1)
C(7B)	24(1)	17(1)	19(1)	1(1)	-3(1)	-4(1)
C(8B)	26(1)	43(1)	22(1)	-1(1)	-7(1)	-1(1)
C(9B)	22(1)	17(1)	22(1)	3(1)	-4(1)	-2(1)
C(10B)	31(1)	23(1)	28(1)	1(1)	-6(1)	8(1)
N(1A)	19(1)	21(1)	26(1)	8(1)	5(1)	2(1)
N(2A)	17(1)	17(1)	22(1)	3(1)	0(1)	-1(1)
N(3A)	23(1)	18(1)	22(1)	1(1)	1(1)	2(1)
N(4A)	21(1)	28(1)	46(1)	4(1)	2(1)	2(1)
N(1B)	25(1)	21(1)	23(1)	2(1)	-6(1)	1(1)
N(2B)	19(1)	18(1)	26(1)	2(1)	1(1)	0(1)
N(3B)	23(1)	20(1)	26(1)	1(1)	-1(1)	-2(1)
N(4B)	22(1)	30(1)	60(1)	2(1)	-6(1)	-2(1)
O(1A)	21(1)	18(1)	16(1)	0(1)	1(1)	3(1)
O(2A)	20(1)	17(1)	20(1)	2(1)	5(1)	-2(1)
O(3A)	17(1)	19(1)	18(1)	0(1)	3(1)	-3(1)
O(4A)	24(1)	16(1)	17(1)	1(1)	2(1)	-2(1)
O(5A)	38(1)	29(1)	26(1)	6(1)	15(1)	4(1)
O(6A)	23(1)	21(1)	40(1)	6(1)	2(1)	-5(1)
O(7A)	25(1)	26(1)	21(1)	-2(1)	2(1)	-3(1)
O(8A)	46(1)	24(1)	23(1)	3(1)	9(1)	-3(1)
O(1B)	23(1)	17(1)	16(1)	0(1)	1(1)	-1(1)

O(2B)	23(1)	17(1)	18(1)	1(1)	-3(1)	3(1)
O(3B)	18(1)	21(1)	18(1)	-1(1)	-3(1)	1(1)
O(4B)	21(1)	15(1)	18(1)	0(1)	-2(1)	2(1)
O(5B)	55(1)	32(1)	24(1)	-6(1)	-15(1)	10(1)
O(6B)	24(1)	22(1)	34(1)	2(1)	-2(1)	5(1)
O(7B)	24(1)	24(1)	20(1)	0(1)	1(1)	-1(1)
O(8B)	38(1)	29(1)	20(1)	4(1)	-2(1)	5(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for 07mz158m.

	x	y	z	U(eq)
H(1A)	1697	6907	10062	21
H(2A)	3653	7545	9416	20
H(3A)	2445	6460	8452	19
H(4A)	1394	7679	7976	21
H(5A)	-439	7043	8654	21
H(6A1)	-730	8792	8924	35
H(6A2)	-2178	8119	8898	35
H(6A3)	-1288	8405	8279	35
H(8A1)	6533	6775	7128	35
H(8A2)	7089	6659	7827	35
H(8A3)	6694	7579	7567	35
H(10A)	2568	10161	8347	45
H(10B)	4297	10060	8018	45
H(10C)	4082	9787	8720	45
H(1B)	3018	4367	7477	22
H(2B)	4627	3826	8297	21
H(3B)	2521	4777	9105	20
H(4B)	1664	3415	9465	21
H(5B)	102	4000	8660	21
H(6B1)	490	2262	8361	38
H(6B2)	-1086	2823	8224	38
H(6B3)	-624	2582	8916	38
H(8B1)	5360	4401	10858	46
H(8B2)	6407	4845	10329	46
H(8B3)	6234	3842	10343	46
H(10D)	4929	1189	9428	41
H(10E)	6210	1934	9326	41
H(10F)	5054	1644	8774	41

Table 6. Torsion angles [deg] for 07mz158m.

O(1A)-C(1A)-C(2A)-N(2A)	-177.50(14)
O(2A)-C(1A)-C(2A)-N(2A)	-56.15(17)
O(1A)-C(1A)-C(2A)-C(3A)	-56.49(19)
O(2A)-C(1A)-C(2A)-C(3A)	64.86(16)
N(2A)-C(2A)-C(3A)-O(3A)	-64.30(17)
C(1A)-C(2A)-C(3A)-O(3A)	177.64(13)
N(2A)-C(2A)-C(3A)-C(4A)	173.77(14)
C(1A)-C(2A)-C(3A)-C(4A)	55.71(18)
O(3A)-C(3A)-C(4A)-O(4A)	-53.14(18)
C(2A)-C(3A)-C(4A)-O(4A)	64.59(18)
O(3A)-C(3A)-C(4A)-C(5A)	-172.32(14)
C(2A)-C(3A)-C(4A)-C(5A)	-54.59(19)
O(4A)-C(4A)-C(5A)-O(1A)	-67.51(17)
C(3A)-C(4A)-C(5A)-O(1A)	53.00(19)

O(4A)-C(4A)-C(5A)-C(6A)	52.77(19)
C(3A)-C(4A)-C(5A)-C(6A)	173.28(15)
O(1B)-C(1B)-C(2B)-N(2B)	-179.13(14)
O(2B)-C(1B)-C(2B)-N(2B)	-57.80(17)
O(1B)-C(1B)-C(2B)-C(3B)	-56.22(19)
O(2B)-C(1B)-C(2B)-C(3B)	65.10(17)
N(2B)-C(2B)-C(3B)-O(3B)	-61.27(18)
C(1B)-C(2B)-C(3B)-O(3B)	178.14(13)
N(2B)-C(2B)-C(3B)-C(4B)	178.85(14)
C(1B)-C(2B)-C(3B)-C(4B)	58.26(18)
O(3B)-C(3B)-C(4B)-O(4B)	-56.78(17)
C(2B)-C(3B)-C(4B)-O(4B)	59.97(17)
O(3B)-C(3B)-C(4B)-C(5B)	-175.58(14)
C(2B)-C(3B)-C(4B)-C(5B)	-58.83(18)
O(4B)-C(4B)-C(5B)-O(1B)	-62.93(18)
C(3B)-C(4B)-C(5B)-O(1B)	55.12(18)
O(4B)-C(4B)-C(5B)-C(6B)	57.07(19)
C(3B)-C(4B)-C(5B)-C(6B)	175.12(15)
C(1A)-C(2A)-N(2A)-N(3A)	-157.79(16)
C(3A)-C(2A)-N(2A)-N(3A)	82.4(2)
C(3B)-C(2B)-N(2B)-N(3B)	99.33(19)
C(1B)-C(2B)-N(2B)-N(3B)	-140.00(17)
O(2A)-C(1A)-O(1A)-C(5A)	-61.11(19)
C(2A)-C(1A)-O(1A)-C(5A)	56.80(19)
C(6A)-C(5A)-O(1A)-C(1A)	-179.81(14)
C(4A)-C(5A)-O(1A)-C(1A)	-55.36(19)
O(6A)-N(1A)-O(2A)-C(1A)	176.94(15)
O(5A)-N(1A)-O(2A)-C(1A)	-3.3(2)
O(1A)-C(1A)-O(2A)-N(1A)	-88.22(17)
C(2A)-C(1A)-O(2A)-N(1A)	150.01(14)
O(7A)-C(7A)-O(3A)-C(3A)	5.9(2)
C(8A)-C(7A)-O(3A)-C(3A)	-173.41(14)
C(2A)-C(3A)-O(3A)-C(7A)	155.22(14)
C(4A)-C(3A)-O(3A)-C(7A)	-84.75(18)
O(8A)-C(9A)-O(4A)-C(4A)	-4.0(3)
C(10A)-C(9A)-O(4A)-C(4A)	174.42(16)
C(5A)-C(4A)-O(4A)-C(9A)	-147.08(16)
C(3A)-C(4A)-O(4A)-C(9A)	92.88(18)
O(2B)-C(1B)-O(1B)-C(5B)	-62.93(18)
C(2B)-C(1B)-O(1B)-C(5B)	54.51(19)
C(6B)-C(5B)-O(1B)-C(1B)	-178.66(15)
C(4B)-C(5B)-O(1B)-C(1B)	-54.18(19)
O(5B)-N(1B)-O(2B)-C(1B)	-2.9(2)
O(6B)-N(1B)-O(2B)-C(1B)	177.26(15)
O(1B)-C(1B)-O(2B)-N(1B)	-80.51(17)
C(2B)-C(1B)-O(2B)-N(1B)	157.57(14)
O(7B)-C(7B)-O(3B)-C(3B)	0.4(3)
C(8B)-C(7B)-O(3B)-C(3B)	-179.70(15)
C(2B)-C(3B)-O(3B)-C(7B)	160.42(14)
C(4B)-C(3B)-O(3B)-C(7B)	-81.68(18)
O(8B)-C(9B)-O(4B)-C(4B)	8.5(3)
C(10B)-C(9B)-O(4B)-C(4B)	-170.63(15)
C(5B)-C(4B)-O(4B)-C(9B)	-147.23(15)
C(3B)-C(4B)-O(4B)-C(9B)	94.07(17)

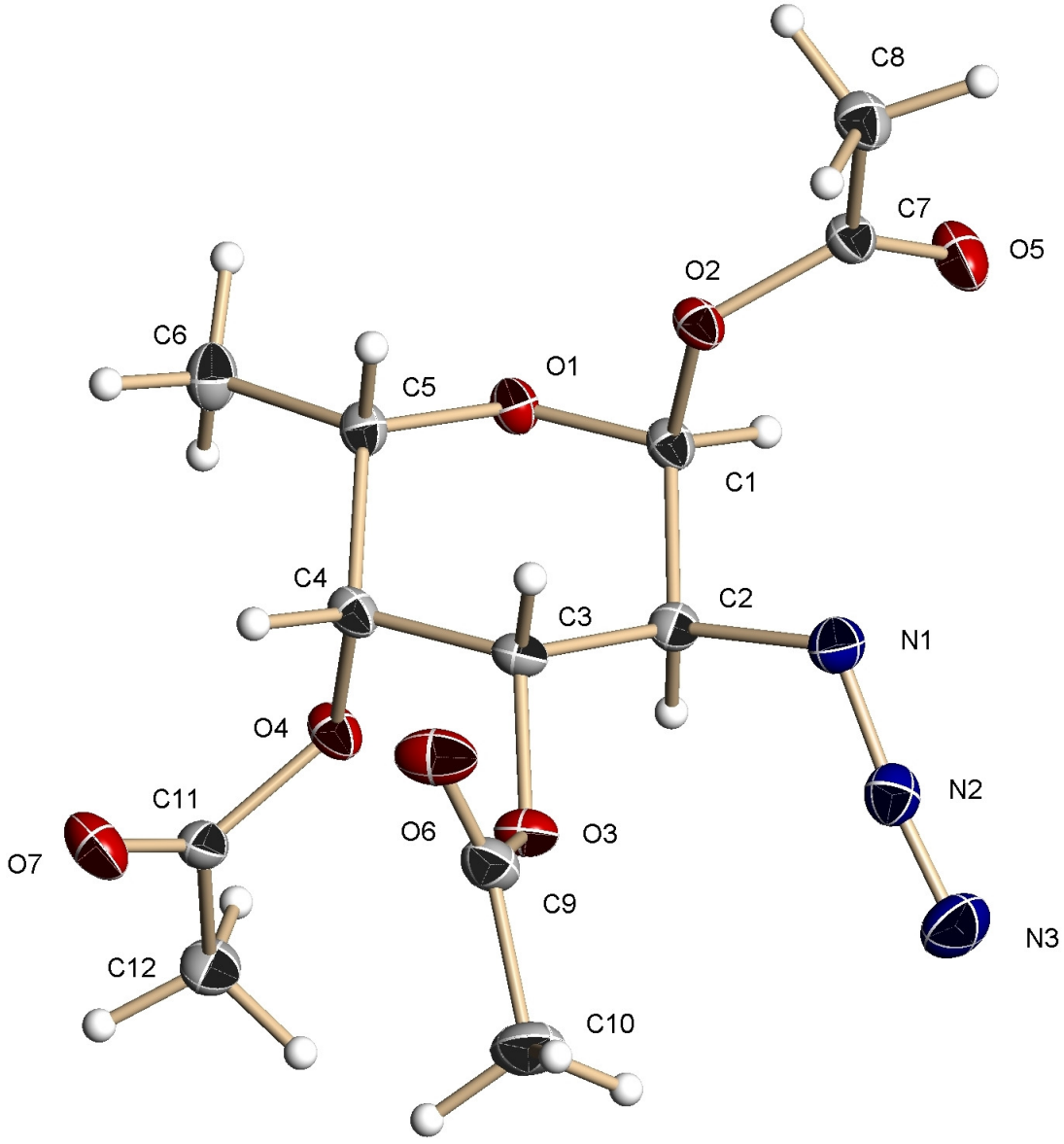


Figure 128:

Crystallographic refinement of 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α-L-fucose **(8)**

Table 1. Crystal data and structure refinement for 07mz170m:

Identification code: 07mz170m
Empirical formula: C12 H17 N3 O7
Formula weight: 315.29
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Monoclinic
Space group: $P2_1$
Unit cell dimensions:
a = 8.6518(9) Å, α = 90°
b = 7.0538(7) Å, β = 98.026(2)°
c = 12.2094(13) Å, γ = 90°
Volume, *Z*: 737.82(13) $Å^3$, 2
Density (calculated): 1.419 Mg/m^3
Absorption coefficient: 0.118 mm^{-1}
F(000): 332
Crystal size: 0.55 × 0.38 × 0.26 mm
Crystal shape, colour: block, colourless
θ range for data collection: 1.68 to 28.28°
Limiting indices: $-11 \le h \le 11$, $-9 \le k \le 9$, $-16 \le l \le 16$
Reflections collected: 7147
Independent reflections: 1978 (*R*(int) = 0.0456)
Completeness to θ = 28.28°: 99.9 %
Absorption correction: multi-scan
Max. and min. transmission: 0.970 and 0.836
Refinement method: Full-matrix least-squares on F^2
Data / restraints / parameters: 1978 / 1 / 203
Goodness-of-fit on F^2: 1.066
Final *R* indices [$I>2\sigma(I)$]: R1 = 0.0327, wR2 = 0.0892
R indices (all data): R1 = 0.0332, wR2 = 0.0902
Largest diff. peak and hole: 0.337 and −0.223 e × $Å^{-3}$

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

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

Table 2. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [Å^2 × 10^3] for 07mz170m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	4382(2)	2412(2)	2846(1)	16(1)
C(2)	2629(2)	2027(2)	2660(1)	16(1)
C(3)	2321(2)	-14(2)	2289(1)	17(1)
C(4)	3229(2)	-1384(2)	3096(1)	16(1)
C(5)	4954(2)	-871(2)	3227(1)	16(1)
C(6)	5964(2)	-2029(3)	4093(1)	23(1)
C(7)	5406(2)	3994(2)	1368(1)	18(1)
C(8)	5939(2)	3701(3)	263(1)	22(1)
C(9)	-31(2)	-1284(3)	1309(1)	22(1)
C(10)	-1775(2)	-1217(3)	1229(2)	30(1)
C(11)	1912(2)	-2704(2)	4519(1)	19(1)
C(12)	1299(2)	-2221(3)	5576(1)	25(1)
N(1)	1920(2)	3369(2)	1805(1)	22(1)
N(2)	558(2)	3801(2)	1898(1)	22(1)
N(3)	-681(2)	4303(3)	1908(1)	31(1)
O(1)	5194(1)	1094(2)	3554(1)	17(1)
O(2)	4950(1)	2334(2)	1785(1)	18(1)
O(3)	658(1)	-295(2)	2206(1)	21(1)
O(4)	2667(1)	-1195(2)	4155(1)	20(1)
O(5)	5376(2)	5487(2)	1832(1)	27(1)
O(6)	692(1)	-2082(2)	681(1)	29(1)
O(7)	1765(2)	-4201(2)	4049(1)	28(1)

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

Table 3. Bond lengths [Å] and angles [deg] for 07mz170m.

C(1)-O(1)	1.3913(18)	C(7)-C(8)	1.4994(19)
C(1)-O(2)	1.4492(16)	C(8)-H(8A)	0.9800
C(1)-C(2)	1.526(2)	C(8)-H(8B)	0.9800
C(1)-H(1)	1.0000	C(8)-H(8C)	0.9800
C(2)-N(1)	1.4772(19)	C(9)-O(6)	1.196(2)
C(2)-C(3)	1.522(2)	C(9)-O(3)	1.3638(19)
C(2)-H(2)	1.0000	C(9)-C(10)	1.500(2)
C(3)-O(3)	1.4422(17)	C(10)-H(10A)	0.9800
C(3)-C(4)	1.519(2)	C(10)-H(10B)	0.9800
C(3)-H(3)	1.0000	C(10)-H(10C)	0.9800
C(4)-O(4)	1.4497(15)	C(11)-O(7)	1.200(2)
C(4)-C(5)	1.523(2)	C(11)-O(4)	1.3556(19)
C(4)-H(4)	1.0000	C(11)-C(12)	1.501(2)
C(5)-O(1)	1.4492(19)	C(12)-H(12A)	0.9800
C(5)-C(6)	1.513(2)	C(12)-H(12B)	0.9800
C(5)-H(5)	1.0000	C(12)-H(12C)	0.9800
C(6)-H(6A)	0.9800	N(1)-N(2)	1.237(2)
C(6)-H(6B)	0.9800	N(2)-N(3)	1.131(2)
C(6)-H(6C)	0.9800		
C(7)-O(5)	1.198(2)	O(1)-C(1)-O(2)	108.98(12)
C(7)-O(2)	1.3569(18)	O(1)-C(1)-C(2)	112.25(12)

O(2)-C(1)-C(2)		O(3)-C(9)-C(10)	111.01(14)
108.30(11)		C(9)-C(10)-H(10A)	109.5
O(1)-C(1)-H(1)	109.1	C(9)-C(10)-H(10B)	109.5
O(2)-C(1)-H(1)	109.1	H(10A)-C(10)-H(10B)	109.5
C(2)-C(1)-H(1)	109.1	C(9)-C(10)-H(10C)	109.5
N(1)-C(2)-C(3)		H(10A)-C(10)-H(10C)	109.5
110.95(11)		H(10B)-C(10)-H(10C)	109.5
N(1)-C(2)-C(1)		O(7)-C(11)-O(4)	123.83(13)
107.29(12)		O(7)-C(11)-C(12)	125.77(15)
C(3)-C(2)-C(1)		O(4)-C(11)-C(12)	110.39(14)
110.01(12)		C(11)-C(12)-H(12A)	109.5
N(1)-C(2)-H(2)	109.5	C(11)-C(12)-H(12B)	109.5
C(3)-C(2)-H(2)	109.5	H(12A)-C(12)-H(12B)	109.5
C(1)-C(2)-H(2)	109.5	C(11)-C(12)-H(12C)	109.5
O(3)-C(3)-C(4)		H(12A)-C(12)-H(12C)	109.5
112.24(12)		H(12B)-C(12)-H(12C)	109.5
O(3)-C(3)-C(2)		N(2)-N(1)-C(2)	113.62(13)
106.40(12)		N(3)-N(2)-N(1)	174.04(17)
C(4)-C(3)-C(2)		C(1)-O(1)-C(5)	115.30(11)
110.82(11)		C(7)-O(2)-C(1)	117.11(11)
O(3)-C(3)-H(3)	109.1	C(9)-O(3)-C(3)	116.46(11)
C(4)-C(3)-H(3)	109.1	C(11)-O(4)-C(4)	117.24(12)
C(2)-C(3)-H(3)	109.1		
O(4)-C(4)-C(3)			
108.21(12)			
O(4)-C(4)-C(5)			
109.31(11)			
C(3)-C(4)-C(5)			
109.11(12)			
O(4)-C(4)-H(4)	110.1		
C(3)-C(4)-H(4)	110.1		
C(5)-C(4)-H(4)	110.1		
O(1)-C(5)-C(6)			
106.09(11)			
O(1)-C(5)-C(4)			
110.90(12)			
C(6)-C(5)-C(4)			
113.99(13)			
O(1)-C(5)-H(5)	108.6		
C(6)-C(5)-H(5)	108.6		
C(4)-C(5)-H(5)	108.6		
C(5)-C(6)-H(6A)	109.5		
C(5)-C(6)-H(6B)	109.5		
H(6A)-C(6)-H(6B)	109.5		
C(5)-C(6)-H(6C)	109.5		
H(6A)-C(6)-H(6C)	109.5		
H(6B)-C(6)-H(6C)	109.5		
O(5)-C(7)-O(2)			
123.67(12)			
O(5)-C(7)-C(8)			
125.17(15)			
O(2)-C(7)-C(8)			
111.16(13)			
C(7)-C(8)-H(8A)	109.5		
C(7)-C(8)-H(8B)	109.5		
H(8A)-C(8)-H(8B)	109.5		
C(7)-C(8)-H(8C)	109.5		
H(8A)-C(8)-H(8C)	109.5		
H(8B)-C(8)-H(8C)	109.5		
O(6)-C(9)-O(3)			
123.17(14)			
O(6)-C(9)-C(10)			
125.82(15)			

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 07mz170m. The anisotropic displacement factor exponent takes the form: $-2\pi 2$ [(h a*)^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	20(1)	15(1)	14(1)	0(1)	4(1)	-1(1)
C(2)	18(1)	18(1)	14(1)	1(1)	5(1)	1(1)
C(3)	14(1)	19(1)	17(1)	-1(1)	4(1)	-3(1)
C(4)	20(1)	15(1)	15(1)	-1(1)	6(1)	-3(1)
C(5)	19(1)	14(1)	16(1)	-1(1)	2(1)	0(1)
C(6)	27(1)	19(1)	20(1)	3(1)	-1(1)	2(1)
C(7)	17(1)	18(1)	18(1)	3(1)	3(1)	-1(1)
C(8)	26(1)	21(1)	19(1)	1(1)	7(1)	-1(1)
C(9)	19(1)	23(1)	23(1)	2(1)	2(1)	-4(1)
C(10)	17(1)	34(1)	41(1)	-3(1)	4(1)	-3(1)
C(11)	16(1)	20(1)	20(1)	4(1)	4(1)	1(1)
C(12)	27(1)	28(1)	23(1)	6(1)	12(1)	4(1)
N(1)	21(1)	25(1)	21(1)	6(1)	4(1)	3(1)
N(2)	25(1)	22(1)	19(1)	3(1)	2(1)	2(1)
N(3)	24(1)	38(1)	31(1)	6(1)	2(1)	8(1)
O(1)	20(1)	15(1)	16(1)	-1(1)	1(1)	-2(1)
O(2)	22(1)	16(1)	17(1)	-1(1)	7(1)	-2(1)
O(3)	16(1)	25(1)	23(1)	-3(1)	5(1)	-3(1)
O(4)	27(1)	17(1)	17(1)	-1(1)	10(1)	-3(1)
O(5)	40(1)	18(1)	25(1)	-1(1)	13(1)	-4(1)
O(6)	22(1)	37(1)	28(1)	-11(1)	5(1)	-7(1)
O(7)	36(1)	22(1)	28(1)	-1(1)	10(1)	-10(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for 07mz170m.

	x	y	z	U(eq)
H(1)	4572	3709	3167	19
H(2)	2188	2252	3363	20
H(3)	2649	-188	1541	20
H(4)	3073	-2714	2817	20
H(5)	5339	-1057	2499	20
H(6A)	7052	-1614	4136	34
H(6B)	5887	-3373	3889	34
H(6C)	5606	-1849	4812	34
H(8A)	6029	4931	-95	33
H(8B)	5179	2911	-202	33
H(8C)	6957	3068	364	33
H(10A)	-2241	-1362	455	45
H(10B)	-2092	3	1512	45
H(10C)	-2133	-2248	1670	45
H(12A)	365	-1429	5411	38
H(12B)	2099	-1528	6066	38
H(12C)	1032	-3390	5940	38

Table 6. Torsion angles [deg] for 07mz170m.

O(1)-C(1)-C(2)-N(1)	-173.71(11)
O(2)-C(1)-C(2)-N(1)	-53.35(15)
O(1)-C(1)-C(2)-C(3)	-52.92(14)
O(2)-C(1)-C(2)-C(3)	67.44(14)
N(1)-C(2)-C(3)-O(3)	-65.32(14)
C(1)-C(2)-C(3)-O(3)	176.12(11)
N(1)-C(2)-C(3)-C(4)	172.40(11)
C(1)-C(2)-C(3)-C(4)	53.84(14)
O(3)-C(3)-C(4)-O(4)	-55.37(15)
C(2)-C(3)-C(4)-O(4)	63.43(15)
O(3)-C(3)-C(4)-C(5)	-174.22(11)
C(2)-C(3)-C(4)-C(5)	-55.41(15)
O(4)-C(4)-C(5)-O(1)	-63.08(15)
C(3)-C(4)-C(5)-O(1)	55.07(14)
O(4)-C(4)-C(5)-C(6)	56.57(17)
C(3)-C(4)-C(5)-C(6)	174.73(12)
C(3)-C(2)-N(1)-N(2)	89.18(16)
C(1)-C(2)-N(1)-N(2)	-150.63(14)
O(2)-C(1)-O(1)-C(5)	-64.47(15)
C(2)-C(1)-O(1)-C(5)	55.49(15)
C(6)-C(5)-O(1)-C(1)	178.84(12)
C(4)-C(5)-O(1)-C(1)	-56.89(14)
O(5)-C(7)-O(2)-C(1)	0.8(2)
C(8)-C(7)-O(2)-C(1)	-179.10(12)
O(1)-C(1)-O(2)-C(7)	-127.58(13)
C(2)-C(1)-O(2)-C(7)	110.04(14)
O(6)-C(9)-O(3)-C(3)	8.6(2)
C(10)-C(9)-O(3)-C(3)	-171.24(14)
C(4)-C(3)-O(3)-C(9)	-100.82(15)
C(2)-C(3)-O(3)-C(9)	137.80(13)
O(7)-C(11)-O(4)-C(4)	4.3(2)
C(12)-C(11)-O(4)-C(4)	-175.49(12)
C(3)-C(4)-O(4)-C(11)	113.78(14)
C(5)-C(4)-O(4)-C(11)	-127.50(14)

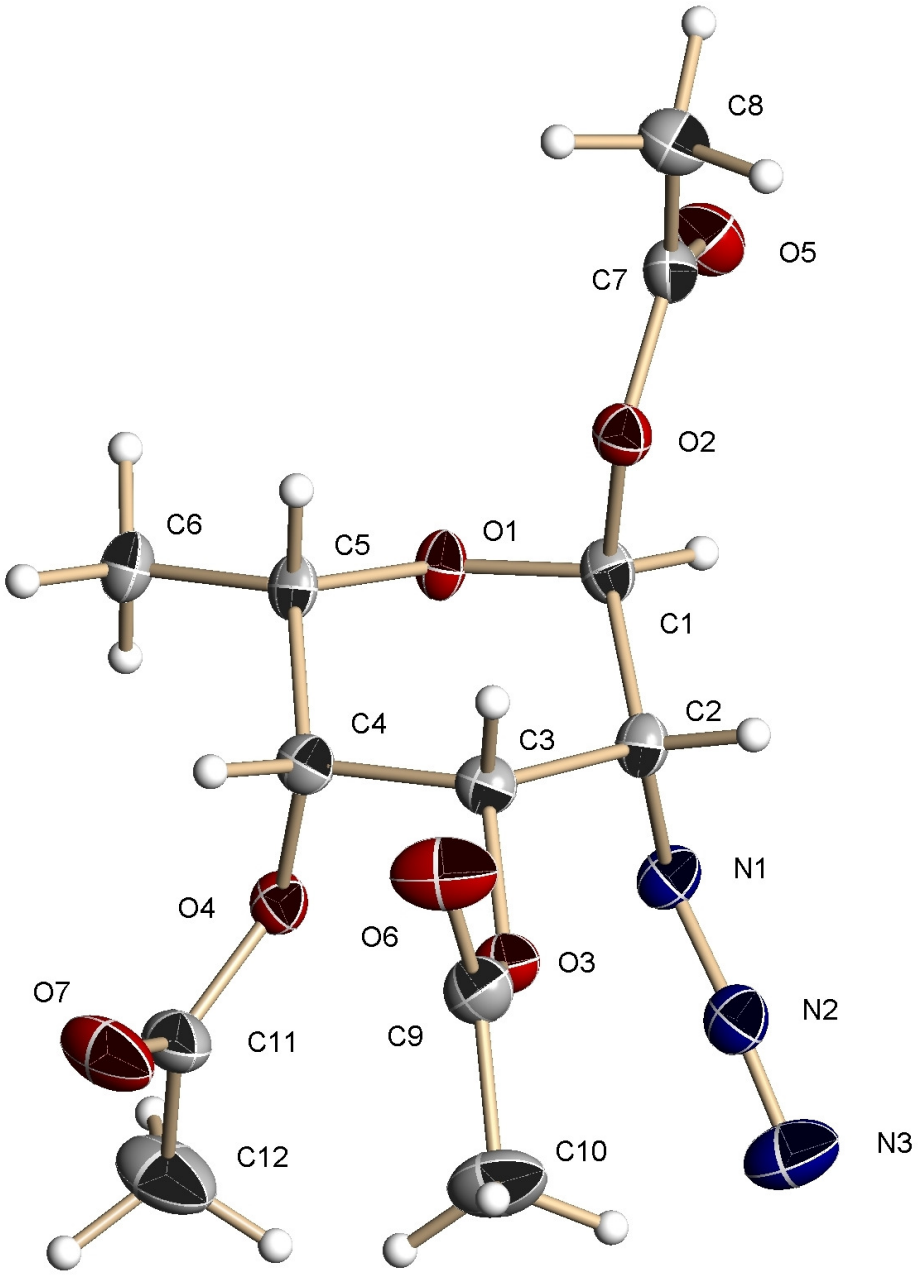


Figure 129 :

Crystallographic refinement of 1,3,4-tri-*O*-acetyl-2-azidodeoxy-α-L-talose (**9**)

Table 1. Crystal data and structure refinement for 07mz224m:

Identification code: 07mz224m
Empirical formula: C12 H17 N3 O7
Formula weight: 315.29
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Orthorhombic
Space group: $P2_12_12_1$
Unit cell dimensions:
a = 7.0940(8) Å, α = 90°
b = 8.9030(10) Å, β = 90°
c = 24.354(3) Å, γ = 90°
Volume, *Z*: 1538.2(3) $Å^3$, 4
Density (calculated): 1.361 g/m^3
Absorption coefficient: 0.113 mm^{-1}
F(000): 664
Crystal size: 0.43 × 0.40 × 0.32
Crystal shape, colour: block, colourless
θ range for data collection: 1.67 to 28.28°
Limiting indices: $-8 \le h \le 9$, $-11 \le k \le 11$, $-20 \le l \le 32$
Reflections collected: 7029
Independent reflections: 2200 (*R*(int) = 0.0365)
Completeness to θ = 28.28°: 99.3 %
Absorption correction: multi-scan
Max. and min. transmission: 0.964 and 0.709
Refinement method: Full-matrix least-squares on F^2
Data / restraints / parameters: 2200 / 0 / 203
Goodness-of-fit on F^2: 1.114
Final *R* indices [$I>2\sigma(I)$]: R1 = 0.0625, wR2 = 0.1741
R indices (all data): R1 = 0.0643, wR2 = 0.1755
Largest diff. peak and hole: 0.524 and −0.285 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

Part of the indene ring is disordered over two positions with an occupancy ratio of 0.712(6) to 0.288(6). Equivalent bonds within the disordered moieties were restrained to be each the same within a standard deviation of 0.02 Å, and equivalent atoms were set to have identical ADPs.

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

Table 2. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [Å^2 × 10^3] for 07mz224m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	4602(5)	5909(4)	2398(1)	21(1)
C(2)	4414(4)	4898(4)	1893(1)	20(1)
C(3)	2344(5)	4820(4)	1723(1)	21(1)
C(4)	1375(4)	6338(4)	1693(1)	20(1)
C(5)	1733(4)	7226(4)	2217(1)	20(1)
C(6)	1037(5)	8819(4)	2190(1)	25(1)
C(7)	4378(5)	5410(4)	3357(1)	25(1)
C(8)	3327(6)	4532(4)	3777(1)	32(1)
C(9)	910(5)	3038(4)	1130(1)	28(1)
C(10)	945(7)	2438(5)	554(2)	42(1)
C(11)	1055(6)	7226(5)	777(1)	31(1)
C(12)	2028(7)	8113(7)	341(2)	50(1)
N(1)	5678(4)	5579(3)	1478(1)	24(1)
N(2)	6026(4)	4737(4)	1081(1)	27(1)
N(3)	6427(6)	4127(5)	697(1)	42(1)
O(1)	3725(3)	7301(3)	2331(1)	21(1)
O(2)	3739(3)	5086(3)	2844(1)	23(1)
O(3)	2256(4)	4099(3)	1196(1)	24(1)
O(4)	2114(3)	7191(3)	1237(1)	22(1)
O(5)	5635(4)	6280(3)	3445(1)	33(1)
O(6)	-155(5)	2643(4)	1487(1)	42(1)
O(7)	-430(4)	6613(4)	732(1)	44(1)

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

Table 3. Bond lengths [Å] and angles [deg] for 07mz224m.

C(1)-O(1)	1.396(4)
C(1)-O(2)	1.447(4)
C(1)-C(2)	1.529(4)
C(1)-H(1)	1.0000
C(2)-N(1)	1.481(4)
C(2)-C(3)	1.527(4)
C(2)-H(2)	1.0000

C(3)-O(3)	1.437(4)
C(3)-C(4)	1.518(4)
C(3)-H(3)	1.0000
C(4)-O(4)	1.444(4)
C(4)-C(5)	1.522(4)
C(4)-H(4)	1.0000
C(5)-O(1)	1.441(4)
C(5)-C(6)	1.503(5)
C(5)-H(5)	1.0000
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-O(5)	1.201(5)
C(7)-O(2)	1.360(4)
C(7)-C(8)	1.488(5)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-O(6)	1.203(5)
C(9)-O(3)	1.353(4)
C(9)-C(10)	1.502(5)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-O(7)	1.191(5)
C(11)-O(4)	1.351(4)
C(11)-C(12)	1.491(6)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
N(1)-N(2)	1.248(4)
N(2)-N(3)	1.119(5)

O(1)-C(1)-O(2)	110.4(3)
O(1)-C(1)-C(2)	113.0(2)
O(2)-C(1)-C(2)	105.6(2)
O(1)-C(1)-H(1)	109.3
O(2)-C(1)-H(1)	109.3
C(2)-C(1)-H(1)	109.3
N(1)-C(2)-C(3)	114.6(3)
N(1)-C(2)-C(1)	104.7(3)
C(3)-C(2)-C(1)	109.2(3)
N(1)-C(2)-H(2)	109.4
C(3)-C(2)-H(2)	109.4
C(1)-C(2)-H(2)	109.4
O(3)-C(3)-C(4)	109.6(3)
O(3)-C(3)-C(2)	107.7(3)
C(4)-C(3)-C(2)	114.1(3)
O(3)-C(3)-H(3)	108.4
C(4)-C(3)-H(3)	108.4
C(2)-C(3)-H(3)	108.4
O(4)-C(4)-C(3)	109.9(2)
O(4)-C(4)-C(5)	108.1(2)
C(3)-C(4)-C(5)	110.3(3)
O(4)-C(4)-H(4)	109.5
C(3)-C(4)-H(4)	109.5
C(5)-C(4)-H(4)	109.5
O(1)-C(5)-C(6)	106.7(3)
O(1)-C(5)-C(4)	110.4(3)
C(6)-C(5)-C(4)	113.4(3)
O(1)-C(5)-H(5)	108.7
C(6)-C(5)-H(5)	108.7
C(4)-C(5)-H(5)	108.7

C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
O(5)-C(7)-O(2)	123.2(3)
O(5)-C(7)-C(8)	126.1(3)
O(2)-C(7)-C(8)	110.7(3)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
O(6)-C(9)-O(3)	124.2(3)
O(6)-C(9)-C(10)	125.5(4)
O(3)-C(9)-C(10)	110.3(3)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
O(7)-C(11)-O(4)	123.9(3)
O(7)-C(11)-C(12)	125.9(4)
O(4)-C(11)-C(12)	110.2(3)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
N(2)-N(1)-C(2)	113.7(3)
N(3)-N(2)-N(1)	171.8(4)
C(1)-O(1)-C(5)	114.7(3)
C(7)-O(2)-C(1)	116.2(3)
C(9)-O(3)-C(3)	116.6(3)
C(11)-O(4)-C(4)	116.7(3)

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 07mz224m. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [(h a^*)^2 U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
C(1)	14(1)	23(1)	25(1)	2(1)	-2(1)	-2(1)
C(2)	15(1)	20(1)	25(1)	0(1)	0(1)	-1(1)
C(3)	18(1)	24(1)	22(1)	1(1)	0(1)	-3(1)
C(4)	14(1)	26(1)	22(1)	2(1)	1(1)	-3(1)
C(5)	11(1)	21(1)	26(1)	0(1)	0(1)	0(1)
C(6)	18(1)	26(2)	31(2)	-1(1)	1(1)	4(1)
C(7)	25(2)	26(2)	25(1)	-1(1)	-3(1)	8(1)
C(8)	34(2)	34(2)	26(2)	2(1)	-1(2)	2(2)
C(9)	25(2)	31(2)	29(2)	-3(1)	-2(1)	-3(2)
C(10)	43(2)	51(3)	32(2)	-16(2)	1(2)	-11(2)
C(11)	26(2)	43(2)	23(2)	4(2)	1(1)	2(2)
C(12)	40(2)	77(4)	32(2)	20(2)	1(2)	-11(3)

N(1)	21(1)	25(1)	26(1)	-2(1)	4(1)	-2(1)
N(2)	19(1)	33(2)	30(1)	2(1)	2(1)	-2(1)
N(3)	40(2)	52(2)	34(2)	-9(2)	11(2)	-7(2)
O(1)	13(1)	20(1)	30(1)	-2(1)	-2(1)	-1(1)
O(2)	20(1)	25(1)	23(1)	1(1)	-1(1)	0(1)
O(3)	22(1)	26(1)	23(1)	-2(1)	1(1)	-3(1)
O(4)	17(1)	25(1)	24(1)	2(1)	2(1)	0(1)
O(5)	32(1)	33(1)	32(1)	-3(1)	-8(1)	-5(1)
O(6)	40(2)	52(2)	34(1)	-8(1)	3(1)	-24(2)
O(7)	27(1)	75(2)	31(1)	10(1)	-7(1)	-13(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for 07mz224m.

	x	y	z	U(eq)
H(1)	5968	6068	2480	25
H(2)	4873	3866	1985	24
H(3)	1655	4182	1995	26
H(4)	-12	6190	1644	25
H(5)	1092	6706	2529	23
H(6A)	1272	9319	2542	38
H(6B)	-319	8822	2113	38
H(6C)	1703	9356	1897	38
H(8A)	3734	4839	4144	47
H(8B)	3581	3459	3726	47
H(8C)	1973	4719	3736	47
H(10A)	85	1581	525	63
H(10B)	2228	2115	462	63
H(10C)	547	3228	299	63
H(12A)	1112	8413	61	75
H(12B)	3015	7496	172	75
H(12C)	2596	9011	505	75

Table 6. Torsion angles [deg] for 07mz224m.

O(1)-C(1)-C(2)-N(1)	72.2(3)
O(2)-C(1)-C(2)-N(1)	-167.1(2)
O(1)-C(1)-C(2)-C(3)	-50.9(3)
O(2)-C(1)-C(2)-C(3)	69.8(3)
N(1)-C(2)-C(3)-O(3)	52.5(4)
C(1)-C(2)-C(3)-O(3)	169.6(2)
N(1)-C(2)-C(3)-C(4)	-69.4(3)
C(1)-C(2)-C(3)-C(4)	47.7(3)
O(3)-C(3)-C(4)-O(4)	-51.5(3)
C(2)-C(3)-C(4)-O(4)	69.3(3)
O(3)-C(3)-C(4)-C(5)	-170.6(2)
C(2)-C(3)-C(4)-C(5)	-49.8(3)
O(4)-C(4)-C(5)-O(1)	-67.5(3)
C(3)-C(4)-C(5)-O(1)	52.7(3)
O(4)-C(4)-C(5)-C(6)	52.2(3)
C(3)-C(4)-C(5)-C(6)	172.4(2)
C(3)-C(2)-N(1)-N(2)	-75.0(4)
C(1)-C(2)-N(1)-N(2)	165.4(3)
O(2)-C(1)-O(1)-C(5)	-59.0(3)
C(2)-C(1)-O(1)-C(5)	59.0(3)
C(6)-C(5)-O(1)-C(1)	177.1(2)

C(4)-C(5)-O(1)-C(1)	-59.2(3)
O(5)-C(7)-O(2)-C(1)	-2.9(5)
C(8)-C(7)-O(2)-C(1)	177.9(3)
O(1)-C(1)-O(2)-C(7)	-84.1(3)
C(2)-C(1)-O(2)-C(7)	153.5(3)
O(6)-C(9)-O(3)-C(3)	-2.3(5)
C(10)-C(9)-O(3)-C(3)	177.6(3)
C(4)-C(3)-O(3)-C(9)	-100.0(3)
C(2)-C(3)-O(3)-C(9)	135.4(3)
O(7)-C(11)-O(4)-C(4)	0.7(6)
C(12)-C(11)-O(4)-C(4)	-178.5(3)
C(3)-C(4)-O(4)-C(11)	100.9(3)
C(5)-C(4)-O(4)-C(11)	-138.6(3)

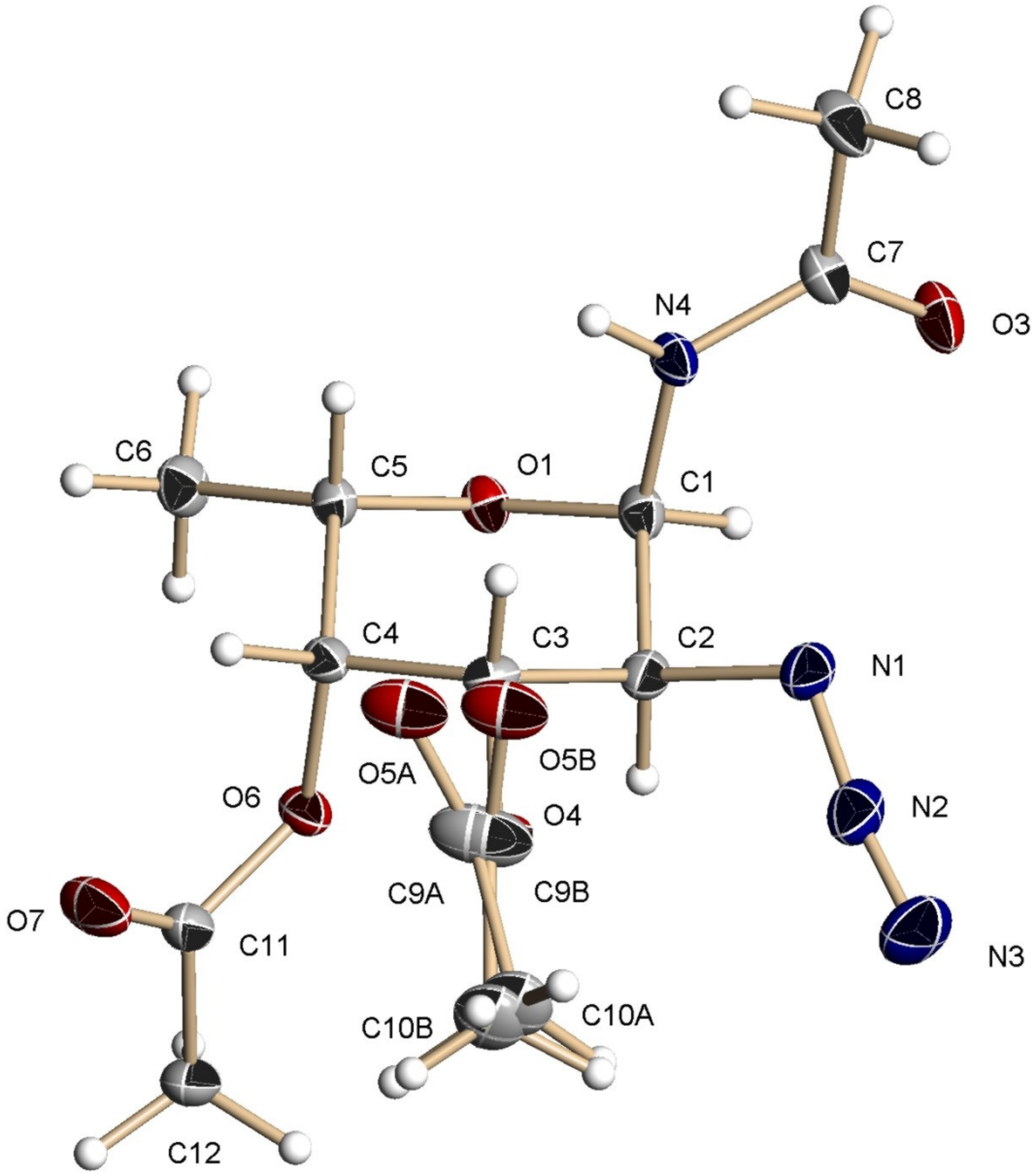


Figure 130 :

Crystallographic refinement of 3,4-di-*O*-aceyl-1-*N*-acetyl-2-azidodeoxy-α-L-fucose (**10**)

Table 1. Crystal data and structure refinement for 06mz005m:

Identification code: 06mz005m
Empirical formula: C12 H20 N4 O7
Moiety formula: C12 H18 N4 O6, H2 O
Formula weight: 332.32
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Monoclinic
Space group: C2
Unit cell dimensions:
a = 26.4805(13) Å, α = 90°
b = 6.9125(3) Å, β = 95.4210(10)°
c = 8.8419(4) Å, γ = 90°
Volume, *Z*: 1611.24(13) Å^3, 4
Density (calculated): 1.370 Mg/m^3
Absorption coefficient: 0.113 mm^{-1}
F(000): 704
Crystal size: 0.39 × 0.21 × 0.18 mm
Crystal shape, colour: block, colourless
θ range for data collection: 1.54 to 28.27°
Limiting indices: −34 ≤ *h* ≤ 35, −9 ≤ *k* ≤ 9, −11 ≤ *l* ≤ 11
Reflections collected: 8386
Independent reflections: 2157 (*R*(int) = 0.0205)
Completeness to θ = 28.27°: 100.0 %
Absorption correction: multi-scan
Max. and min. transmission: 0.980 and 0.919
Refinement method: Full-matrix least-squares on F^2
Data / restraints / parameters: 2157 / 50 / 226
Goodness-of-fit on F^2: 1.068
Final *R* indices [$I>2\sigma(I)$]: R1 = 0.0338, wR2 = 0.0876
R indices (all data): R1 = 0.0347, wR2 = 0.0884
Largest diff. peak and hole: 0.381 and −0.185 e × Å^{-3}

Comments:
One molecule of solvate water is located in the asymmetric part of the unit cell. One of the acetyl substituents is disordered over two positions. One of these positions is hydrogen bonded to the water molecule, the other one not. The disorder of the acetyl group was thus refined together with a disorder of one of the two water hydrogen atoms. The occupancy ratio refined to 0.515(4) to 0.485(4). The anisotropic displacement parameters for the acetyl methyl groups were kept identical, as were those of all the disordered keto carbon and oxygen atoms, and all anisotropic displacement parameters in each disordered moiety were restraint to be similar within a standard deviation of 0.04. The distances O4–C9a and O4–C9b were restraint to be identical within a standard deviation of

0.02, as were the distances C9a–C10a and C9b and C10b. The disordered moieties were further restraint to be flat within a standard deviation of 0.1.

Treatment of hydrogen atoms:
The solvate water hydrogen atoms were located in the difference density Fourier map and their O–H distance was restraint to be identical within a standard deviation of 0.02. All other hydrogen atoms were placed in calculated positions and all hydrogen atoms were refined with an isotropic displacement parameter 1.5 (methyl, water) or 1.2 times (all others) that of the adjacent carbon atom or oxygen atom.

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

Table 2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for 06mz005m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	3534(1)	11141(3)	10104(2)	17(1)
C(2)	3572(1)	10740(3)	8413(2)	17(1)
C(3)	3717(1)	8632(3)	8191(2)	17(1)
C(4)	3344(1)	7287(3)	8869(2)	16(1)
C(5)	3301(1)	7832(3)	10523(2)	16(1)
C(6)	2893(1)	6714(3)	11236(2)	22(1)
C(7)	4259(1)	12708(3)	11523(2)	20(1)
C(8)	4782(1)	12432(3)	12331(2)	27(1)
C(11)	2704(1)	6050(3)	7042(2)	21(1)
C(12)	2210(1)	6547(3)	6156(2)	25(1)
C(9A)	4101(5)	7391(16)	6079(19)	31(1)
O(5A)	4379(1)	6395(6)	6955(3)	31(1)
C(10A)	4087(10)	7530(40)	4380(20)	32(2)
C(9B)	4115(5)	7560(17)	6020(20)	31(1)
O(5B)	4523(1)	7368(6)	6750(4)	31(1)
C(10B)	4036(11)	7290(50)	4320(20)	32(2)
N(1)	3963(1)	12064(3)	7921(2)	24(1)
N(2)	3938(1)	12356(3)	6533(2)	27(1)
N(3)	3963(1)	12758(4)	5307(2)	39(1)
O(1)	3181(1)	9857(2)	10670(1)	17(1)
N(4)	4026(1)	11073(2)	10981(2)	18(1)
O(3)	4064(1)	14319(2)	11363(2)	26(1)
O(4)	3708(1)	8324(2)	6574(1)	24(1)
O(6)	2853(1)	7498(2)	8014(1)	19(1)
O(7)	2939(1)	4590(2)	6921(2)	32(1)
O(8)	5373(1)	7592(2)	8941(2)	23(1)

All esds (except the esd in the dihedral angle between two l.s. planes)

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

Table 3. Bond lengths [Å] and angles [deg] for 06mz005m.

C(1)-O(1)	1.414(2)		
C(1)-N(4)		1.452(2)	
C(1)-C(2)		1.533(2)	
C(1)-H(1)		1.0000	
C(2)-N(1)		1.477(2)	
C(2)-C(3)		1.524(2)	
C(2)-H(2)		1.0000	
C(3)-O(4)		1.444(2)	
C(3)-C(4)		1.520(2)	
C(3)-H(3)		1.0000	
C(4)-O(6)		1.4476(19)	
C(4)-C(5)		1.525(2)	
C(4)-H(4)		1.0000	
C(5)-O(1)		1.444(2)	
C(5)-C(6)		1.514(2)	
C(5)-H(5)		1.0000	
C(6)-H(6A)		0.9800	
C(6)-H(6B)		0.9800	
C(6)-H(6C)		0.9800	
C(7)-O(3)		1.231(2)	
C(7)-N(4)		1.354(2)	
C(7)-C(8)		1.508(2)	
C(8)-H(8A)		0.9800	
C(8)-H(8B)		0.9800	
C(8)-H(8C)		0.9800	
C(11)-O(7)		1.196(3)	
C(11)-O(6)		1.354(2)	
C(11)-C(12)		1.500(3)	
C(12)-H(12A)		0.9800	
C(12)-H(12B)		0.9800	
C(12)-H(12C)		0.9800	
C(9A)-O(5A)		1.227(15)	
C(9A)-O(4)		1.332(10)	
C(9A)-C(10A)		1.501(11)	
C(10A)-H(10A)		0.9800	
C(10A)-H(10B)		0.9800	
C(10A)-H(10C)		0.9800	
C(9B)-O(5B)		1.212(16)	
C(9B)-O(4)		1.333(10)	
C(9B)-C(10B)		1.511(11)	
C(10B)-H(10D)		0.9800	
C(10B)-H(10E)		0.9800	
C(10B)-H(10F)		0.9800	
N(1)-N(2)		1.240(2)	
N(2)-N(3)		1.127(3)	
N(4)-H(4A)		0.8800	
O(8)-H(8D)		0.84(2)	
O(8)-H(8E)		0.85(3)	
O(8)-H(8F)		0.84(3)	
O(1)-C(1)-N(4)			112.36(14)
O(1)-C(1)-C(2)			109.77(13)
N(4)-C(1)-C(2)			112.12(13)
O(1)-C(1)-H(1)			107.4

N(4)-C(1)-H(1)	107.4
C(2)-C(1)-H(1)	107.4
N(1)-C(2)-C(3)	111.28(14)
N(1)-C(2)-C(1)	106.72(14)
C(3)-C(2)-C(1)	109.83(14)
N(1)-C(2)-H(2)	109.7
C(3)-C(2)-H(2)	109.7
C(1)-C(2)-H(2)	109.7
O(4)-C(3)-C(4)	110.51(14)
O(4)-C(3)-C(2)	106.74(14)
C(4)-C(3)-C(2)	110.70(13)
O(4)-C(3)-H(3)	109.6
C(4)-C(3)-H(3)	109.6
C(2)-C(3)-H(3)	109.6
O(6)-C(4)-C(3)	108.51(13)
O(6)-C(4)-C(5)	109.34(12)
C(3)-C(4)-C(5)	109.71(14)
O(6)-C(4)-H(4)	109.8
C(3)-C(4)-H(4)	109.8
C(5)-C(4)-H(4)	109.8
O(1)-C(5)-C(6)	106.57(14)
O(1)-C(5)-C(4)	111.27(14)
C(6)-C(5)-C(4)	113.23(14)
O(1)-C(5)-H(5)	108.6
C(6)-C(5)-H(5)	108.6
C(4)-C(5)-H(5)	108.6
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
O(3)-C(7)-N(4)	122.82(15)
O(3)-C(7)-C(8)	121.72(17)
N(4)-C(7)-C(8)	115.45(17)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
O(7)-C(11)-O(6)	123.80(16)
O(7)-C(11)-C(12)	125.68(17)
O(6)-C(11)-C(12)	110.52(16)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
O(5A)-C(9A)-O(4)	120.3(11)
O(5A)-C(9A)-C(10A)	128.6(14)
O(4)-C(9A)-C(10A)	110.5(15)
O(5B)-C(9B)-O(4)	123.9(13)
O(5B)-C(9B)-C(10B)	123.4(14)
O(4)-C(9B)-C(10B)	112.0(16)
C(9B)-C(10B)-H(10D)	109.5
C(9B)-C(10B)-H(10E)	109.5
H(10D)-C(10B)-H(10E)	109.5
C(9B)-C(10B)-H(10F)	109.5
H(10D)-C(10B)-H(10F)	109.5
H(10E)-C(10B)-H(10F)	109.5
N(2)-N(1)-C(2)	114.81(15)

N(3)-N(2)-N(1)	171.9(2)
C(1)-O(1)-C(5)	114.67(12)
C(7)-N(4)-C(1)	121.22(15)
C(7)-N(4)-H(4A)	119.4
C(1)-N(4)-H(4A)	119.4
C(9A)-O(4)-C(3)	117.2(8)
C(9B)-O(4)-C(3)	119.0(8)
C(11)-O(6)-C(4)	116.84(14)
H(8D)-O(8)-H(8E)	97(5)
H(8D)-O(8)-H(8F)	110(5)
H(8E)-O(8)-H(8F)	
69(4)	

Table 4. Anisotropic displacement parameters [Å^2 × 10^3] for 06mz005m. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [(h a*)^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	16(1)	13(1)	22(1)	0(1)	1(1)	1(1)
C(2)	15(1)	18(1)	19(1)	3(1)	-1(1)	-1(1)
C(3)	16(1)	21(1)	13(1)	1(1)	0(1)	2(1)
C(4)	16(1)	15(1)	16(1)	0(1)	-1(1)	1(1)
C(5)	17(1)	13(1)	17(1)	-1(1)	2(1)	0(1)
C(6)	20(1)	24(1)	23(1)	1(1)	6(1)	-6(1)
C(7)	19(1)	17(1)	24(1)	-3(1)	2(1)	-3(1)
C(8)	19(1)	22(1)	39(1)	-5(1)	-5(1)	-2(1)
C(11)	24(1)	21(1)	16(1)	1(1)	-1(1)	-5(1)
C(12)	26(1)	28(1)	20(1)	3(1)	-6(1)	-5(1)
C(9A)	28(1)	42(1)	24(1)	-10(1)	0(1)	8(1)
O(5A)	28(1)	42(1)	24(1)	-10(1)	0(1)	8(1)
C(10A)	44(4)	32(6)	21(1)	-8(2)	7(2)	1(4)
C(9B)	28(1)	42(1)	24(1)	-10(1)	0(1)	8(1)
O(5B)	28(1)	42(1)	24(1)	-10(1)	0(1)	8(1)
C(10B)	44(4)	32(6)	21(1)	-8(2)	7(2)	1(4)
N(1)	21(1)	26(1)	25(1)	8(1)	-1(1)	-6(1)
N(2)	19(1)	28(1)	32(1)	9(1)	1(1)	-5(1)
N(3)	40(1)	49(1)	29(1)	16(1)	3(1)	-13(1)
O(1)	16(1)	14(1)	21(1)	-3(1)	3(1)	1(1)
N(4)	17(1)	13(1)	22(1)	-2(1)	-1(1)	1(1)
O(3)	23(1)	14(1)	40(1)	-3(1)	-1(1)	0(1)
O(4)	24(1)	33(1)	14(1)	2(1)	2(1)	6(1)
O(6)	17(1)	17(1)	20(1)	-2(1)	-3(1)	0(1)
O(7)	38(1)	25(1)	30(1)	-10(1)	-8(1)	5(1)
O(8)	22(1)	20(1)	26(1)	-2(1)	2(1)	1(1)

Table 5. Hydrogen coordinates (× 10^4) and isotropic displacement parameters (Å^2 × 10^3) for 06mz005m.

	x	y	z	U(eq)
H(1)	3398	12482	10191	21
H(2)	3239	11017	7825	21
H(3)	4067	8392	8685	20
H(4)	3463	5919	8807	19
H(5)	3635	7572	11118	19
H(6A)	2887	7112	12298	33

H(6B)	2966	5326	11193	33
H(6C)	2563	6980	10680	33
H(8A)	5034	13035	11737	41
H(8B)	4854	11046	12443	41
H(8C)	4797	13036	13337	41
H(12A)	2265	7565	5419	38
H(12B)	1969	7006	6853	38
H(12C)	2072	5395	5619	38
H(10A)	4434	7562	4085	48
H(10B)	3909	8717	4034	48
H(10C)	3908	6406	3917	48
H(10D)	3983	8550	3824	48
H(10E)	3738	6469	4063	48
H(10F)	4336	6667	3962	48
H(4A)	4175	9948	11164	21
H(8D)	5512(9)	6510(40)	8830(30)	34
H(8E)	5123(14)	7420(90)	8270(50)	34
H(8F)	5101(14)	7440(100)	9340(60)	34

Table 6. Hydrogen bonds for 06mz005m [Å and deg].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(4)-H(4A)...O(8)#1	0.88	2.03	2.883(2)	163.2
O(8)-H(8D)...O(3)#2	0.84(2)	1.90(2)	2.737(2)	170(3)
O(8)-H(8F)...O(8)#1	0.84(3)	2.06(3)	2.846(3)	156(5)
O(8)-H(8E)...O(5A)	0.85(3)	2.30(3)	3.135(3)	164(5)

Symmetry transformations used to generate equivalent atoms:

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

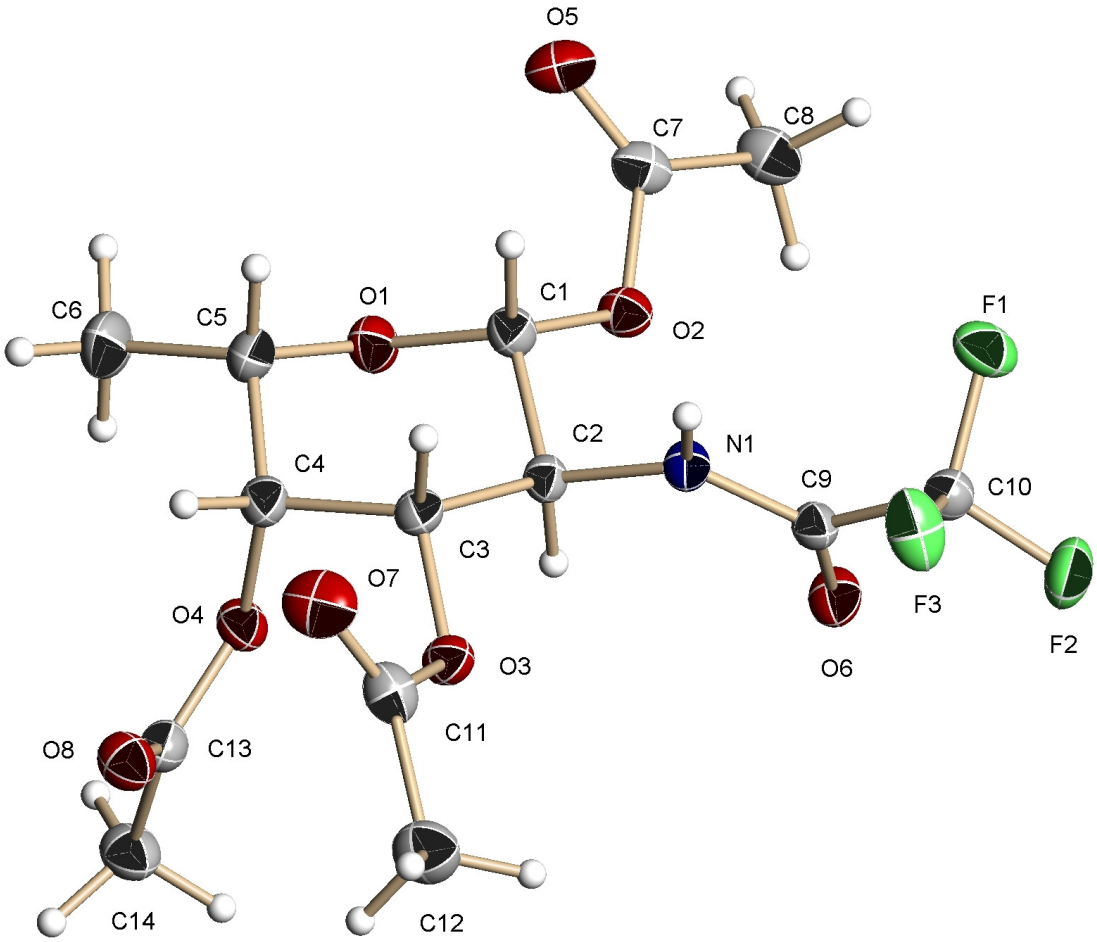


Figure 131 :
Crystallographic refinement of 1,3,4-tri-*O*-acetyl-2-*N*-(trifluoro)acetyl-β-L-fucose (**13**)

Table 1. Crystal data and structure refinement for 07mz409m:

Identification code: 07mz409m
Empirical formula: C14 H18 F3 N O8
Formula weight: 385.29
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Orthorhombic
Space group: $P2_12_12_1$
Unit cell dimensions:
a = 5.1818(10) Å, α = 90°
b = 16.968(3) Å, β = 90°
c = 19.484(4) Å, γ = 90°
Volume, Z: 1713.1(6) $Å^3$, 4
Density (calculated): 1.494 Mg/m^3
Absorption coefficient: 0.142 mm^{-1}
F(000): 800
Crystal size: 0.48 × 0.31 × 0.30 mm
Crystal shape, colour: block, colourless
θ range for data collection: 1.59 to 28.28°
Limiting indices: $-6 \le h \le 6$, $-22 \le k \le 21$, $-22 \le l \le 25$
Reflections collected: 11396
Independent reflections: 2463 (R(int) = 0.0317)
Completeness to θ = 28.28°: 99.9 %
Absorption correction: multi-scan
Max. and min. transmission: 0.958 and 0.839
Refinement method: Full-matrix least-squares on F^2
Data / restraints / parameters: 2463 / 0 / 239
Goodness-of-fit on F^2: 1.081
Final R indices [$I>2\sigma(I)$]: R1 = 0.0348, wR2 = 0.0837
R indices (all data): R1 = 0.0384, wR2 = 0.0860
Largest diff. peak and hole: 0.320 and −0.174 e × $Å^{-3}$

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

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

Table 2. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [Å^2 × 10^3] for 07mz409m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	3284(4)	4309(1)	6585(1)	22(1)
C(2)	3853(4)	5095(1)	6940(1)	19(1)
C(3)	1888(4)	5231(1)	7508(1)	21(1)
C(4)	1620(4)	4514(1)	7978(1)	23(1)
C(5)	1276(4)	3767(1)	7553(1)	28(1)
C(6)	1281(6)	3021(1)	7984(1)	41(1)
C(7)	4717(4)	3639(1)	5595(1)	25(1)
C(8)	6855(5)	3572(1)	5091(1)	30(1)
C(9)	5799(4)	6076(1)	6178(1)	20(1)
C(10)	5122(4)	6737(1)	5663(1)	23(1)
C(11)	943(4)	6336(1)	8214(1)	27(1)
C(12)	2161(5)	7012(1)	8586(1)	36(1)
C(13)	3851(4)	4711(1)	9041(1)	24(1)
C(14)	6171(4)	4456(1)	9435(1)	30(1)
F(1)	4052(3)	6437(1)	5099(1)	34(1)
F(2)	7208(3)	7132(1)	5479(1)	37(1)
F(3)	3429(3)	7249(1)	5928(1)	37(1)
N(1)	3700(3)	5741(1)	6448(1)	20(1)
O(1)	3363(3)	3694(1)	7070(1)	27(1)
O(2)	5283(3)	4173(1)	6106(1)	23(1)
O(3)	2777(3)	5912(1)	7873(1)	23(1)
O(4)	3917(3)	4416(1)	8393(1)	24(1)
O(5)	2690(3)	3290(1)	5579(1)	33(1)
O(6)	8048(3)	5908(1)	6287(1)	27(1)
O(7)	-1313(3)	6167(1)	8207(1)	38(1)
O(8)	2109(3)	5113(1)	9256(1)	29(1)

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

Table 3. Bond lengths [Å] and angles [deg] for 07mz409m.

C(1)-O(1)	1.409(2)
C(1)-O(2)	1.414(2)
C(1)-C(2)	1.530(2)
C(1)-H(1)	1.0000
C(2)-N(1)	1.459(2)
C(2)-C(3)	1.521(3)
C(2)-H(2)	1.0000
C(3)-O(3)	1.433(2)
C(3)-C(4)	1.530(2)

C(3)-H(3)	1.0000
C(4)-O(4)	1.448(2)
C(4)-C(5)	1.524(3)
C(4)-H(4)	1.0000
C(5)-O(1)	1.438(3)
C(5)-C(6)	1.520(3)
C(5)-H(5)	1.0000
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-O(5)	1.206(3)
C(7)-O(2)	1.377(2)
C(7)-C(8)	1.485(3)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-O(6)	1.218(2)
C(9)-N(1)	1.336(2)
C(9)-C(10)	1.546(3)
C(10)-F(2)	1.321(2)
C(10)-F(1)	1.332(2)
C(10)-F(3)	1.338(2)
C(11)-O(7)	1.203(3)
C(11)-O(3)	1.364(2)
C(11)-C(12)	1.497(3)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-O(8)	1.206(2)
C(13)-O(4)	1.359(2)
C(13)-C(14)	1.490(3)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
N(1)-H(1A)	0.8800

O(1)-C(1)-O(2)	107.51(15)
O(1)-C(1)-C(2)	109.69(14)
O(2)-C(1)-C(2)	107.44(15)
O(1)-C(1)-H(1)	110.7
O(2)-C(1)-H(1)	110.7
C(2)-C(1)-H(1)	110.7
N(1)-C(2)-C(3)	109.06(15)
N(1)-C(2)-C(1)	110.33(14)
C(3)-C(2)-C(1)	109.38(15)
N(1)-C(2)-H(2)	109.4
C(3)-C(2)-H(2)	109.4
C(1)-C(2)-H(2)	109.4
O(3)-C(3)-C(2)	105.59(15)
O(3)-C(3)-C(4)	111.86(14)
C(2)-C(3)-C(4)	112.04(15)
O(3)-C(3)-H(3)	109.1
C(2)-C(3)-H(3)	109.1
C(4)-C(3)-H(3)	109.1
O(4)-C(4)-C(5)	107.69(16)
O(4)-C(4)-C(3)	110.55(16)
C(5)-C(4)-C(3)	110.28(15)
O(4)-C(4)-H(4)	109.4
C(5)-C(4)-H(4)	109.4
C(3)-C(4)-H(4)	109.4
O(1)-C(5)-C(6)	106.77(18)
O(1)-C(5)-C(4)	109.80(16)
C(6)-C(5)-C(4)	113.10(16)

O(1)-C(5)-H(5)	109.0
C(6)-C(5)-H(5)	109.0
C(4)-C(5)-H(5)	109.0
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
O(5)-C(7)-O(2)	121.82(19)
O(5)-C(7)-C(8)	126.48(19)
O(2)-C(7)-C(8)	111.70(18)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
O(6)-C(9)-N(1)	127.64(18)
O(6)-C(9)-C(10)	120.02(17)
N(1)-C(9)-C(10)	112.33(16)
F(2)-C(10)-F(1)	108.13(16)
F(2)-C(10)-F(3)	108.16(15)
F(1)-C(10)-F(3)	107.12(17)
F(2)-C(10)-C(9)	110.98(16)
F(1)-C(10)-C(9)	110.62(15)
F(3)-C(10)-C(9)	111.67(15)
O(7)-C(11)-O(3)	123.1(2)
O(7)-C(11)-C(12)	126.7(2)
O(3)-C(11)-C(12)	110.24(19)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
O(8)-C(13)-O(4)	123.33(19)
O(8)-C(13)-C(14)	126.13(18)
O(4)-C(13)-C(14)	110.53(17)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(9)-N(1)-C(2)	122.31(16)
C(9)-N(1)-H(1A)	118.8
C(2)-N(1)-H(1A)	118.8
C(1)-O(1)-C(5)	110.66(15)
C(7)-O(2)-C(1)	115.40(15)
C(11)-O(3)-C(3)	116.27(16)
C(13)-O(4)-C(4)	117.10(16)

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 07mz409m. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [(h\ a^*)^2\ U11 + ... + 2\ h\ k\ a^*\ b^*\ U12]$

	U11	U22	U33	U23	U13	U12

C(1)	23(1)	23(1)	21(1)	2(1)	-1(1)	0(1)
C(2)	17(1)	21(1)	18(1)	3(1)	-1(1)	0(1)
C(3)	17(1)	23(1)	21(1)	1(1)	-1(1)	-2(1)
C(4)	20(1)	28(1)	23(1)	3(1)	-1(1)	-4(1)
C(5)	31(1)	27(1)	26(1)	4(1)	0(1)	-9(1)
C(6)	60(2)	30(1)	34(1)	8(1)	2(1)	-15(1)
C(7)	29(1)	21(1)	25(1)	0(1)	-6(1)	6(1)
C(8)	31(1)	33(1)	27(1)	-5(1)	-1(1)	6(1)
C(9)	19(1)	23(1)	18(1)	0(1)	1(1)	-1(1)
C(10)	23(1)	22(1)	23(1)	0(1)	1(1)	-1(1)
C(11)	28(1)	29(1)	24(1)	2(1)	2(1)	6(1)
C(12)	41(1)	32(1)	34(1)	-6(1)	2(1)	2(1)
C(13)	23(1)	27(1)	23(1)	3(1)	-1(1)	-4(1)
C(14)	25(1)	38(1)	27(1)	1(1)	-3(1)	0(1)
F(1)	46(1)	31(1)	25(1)	2(1)	-11(1)	1(1)
F(2)	35(1)	38(1)	38(1)	13(1)	4(1)	-10(1)
F(3)	48(1)	29(1)	34(1)	6(1)	12(1)	16(1)
N(1)	15(1)	23(1)	21(1)	4(1)	-1(1)	1(1)
O(1)	33(1)	23(1)	24(1)	4(1)	-1(1)	-1(1)
O(2)	22(1)	26(1)	23(1)	-2(1)	0(1)	0(1)
O(3)	21(1)	24(1)	24(1)	-2(1)	2(1)	-2(1)
O(4)	23(1)	28(1)	20(1)	3(1)	-2(1)	0(1)
O(5)	31(1)	31(1)	38(1)	-8(1)	-4(1)	-4(1)
O(6)	18(1)	35(1)	28(1)	6(1)	0(1)	0(1)
O(7)	23(1)	47(1)	43(1)	-7(1)	2(1)	9(1)
O(8)	26(1)	34(1)	26(1)	0(1)	1(1)	2(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for 07mz409m.

	x	y	z	U(eq)
H(1)	1569	4326	6351	27
H(2)	5625	5078	7143	22
H(3)	173	5350	7296	25
H(4)	89	4585	8284	28
H(5)	-390	3800	7296	34
H(6A)	1030	2562	7686	62
H(6B)	-121	3045	8321	62
H(6C)	2937	2973	8224	62
H(8A)	7100	3017	4967	45
H(8B)	8448	3778	5294	45
H(8C)	6428	3875	4678	45
H(12A)	825	7392	8718	54
H(12B)	3422	7269	8286	54
H(12C)	3032	6817	8999	54
H(14A)	7672	4763	9285	45
H(14B)	6490	3895	9352	45
H(14C)	5878	4543	9926	45
H(1A)	2170	5917	6325	24

Table 6. Torsion angles [deg] for 07mz409m

O(1)-C(1)-C(2)-N(1)	-178.24(16)
O(2)-C(1)-C(2)-N(1)	65.18(18)
O(1)-C(1)-C(2)-C(3)	-58.3(2)
O(2)-C(1)-C(2)-C(3)	-174.85(14)

N(1)-C(2)-C(3)-O(3)	-67.42(17)
C(1)-C(2)-C(3)-O(3)	171.83(14)
N(1)-C(2)-C(3)-C(4)	170.57(15)
C(1)-C(2)-C(3)-C(4)	49.8(2)
O(3)-C(3)-C(4)-O(4)	-48.1(2)
C(2)-C(3)-C(4)-O(4)	70.21(19)
O(3)-C(3)-C(4)-C(5)	-167.11(16)
C(2)-C(3)-C(4)-C(5)	-48.8(2)
O(4)-C(4)-C(5)-O(1)	-65.92(18)
C(3)-C(4)-C(5)-O(1)	54.8(2)
O(4)-C(4)-C(5)-C(6)	53.2(2)
C(3)-C(4)-C(5)-C(6)	173.9(2)
O(6)-C(9)-C(10)-F(2)	-10.0(3)
N(1)-C(9)-C(10)-F(2)	170.95(16)
O(6)-C(9)-C(10)-F(1)	110.0(2)
N(1)-C(9)-C(10)-F(1)	-69.0(2)
O(6)-C(9)-C(10)-F(3)	-130.8(2)
N(1)-C(9)-C(10)-F(3)	50.2(2)
O(6)-C(9)-N(1)-C(2)	0.2(3)
C(10)-C(9)-N(1)-C(2)	179.09(14)
C(3)-C(2)-N(1)-C(9)	137.93(18)
C(1)-C(2)-N(1)-C(9)	-101.9(2)
O(2)-C(1)-O(1)-C(5)	-176.48(14)
C(2)-C(1)-O(1)-C(5)	67.0(2)
C(6)-C(5)-O(1)-C(1)	171.77(17)
C(4)-C(5)-O(1)-C(1)	-65.27(19)
O(5)-C(7)-O(2)-C(1)	-3.0(3)
C(8)-C(7)-O(2)-C(1)	176.33(15)
O(1)-C(1)-O(2)-C(7)	81.58(18)
C(2)-C(1)-O(2)-C(7)	-160.43(14)
O(7)-C(11)-O(3)-C(3)	-1.1(3)
C(12)-C(11)-O(3)-C(3)	178.37(15)
C(2)-C(3)-O(3)-C(11)	154.77(15)
C(4)-C(3)-O(3)-C(11)	-83.1(2)
O(8)-C(13)-O(4)-C(4)	-7.9(3)
C(14)-C(13)-O(4)-C(4)	171.16(16)
C(5)-C(4)-O(4)-C(13)	-142.17(16)
C(3)-C(4)-O(4)-C(13)	97.29(18)

Table 7. Hydrogen bonds for 07mz409m [Å and deg].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(6)#1	0.88	2.14	2.959(2)	155.2

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z

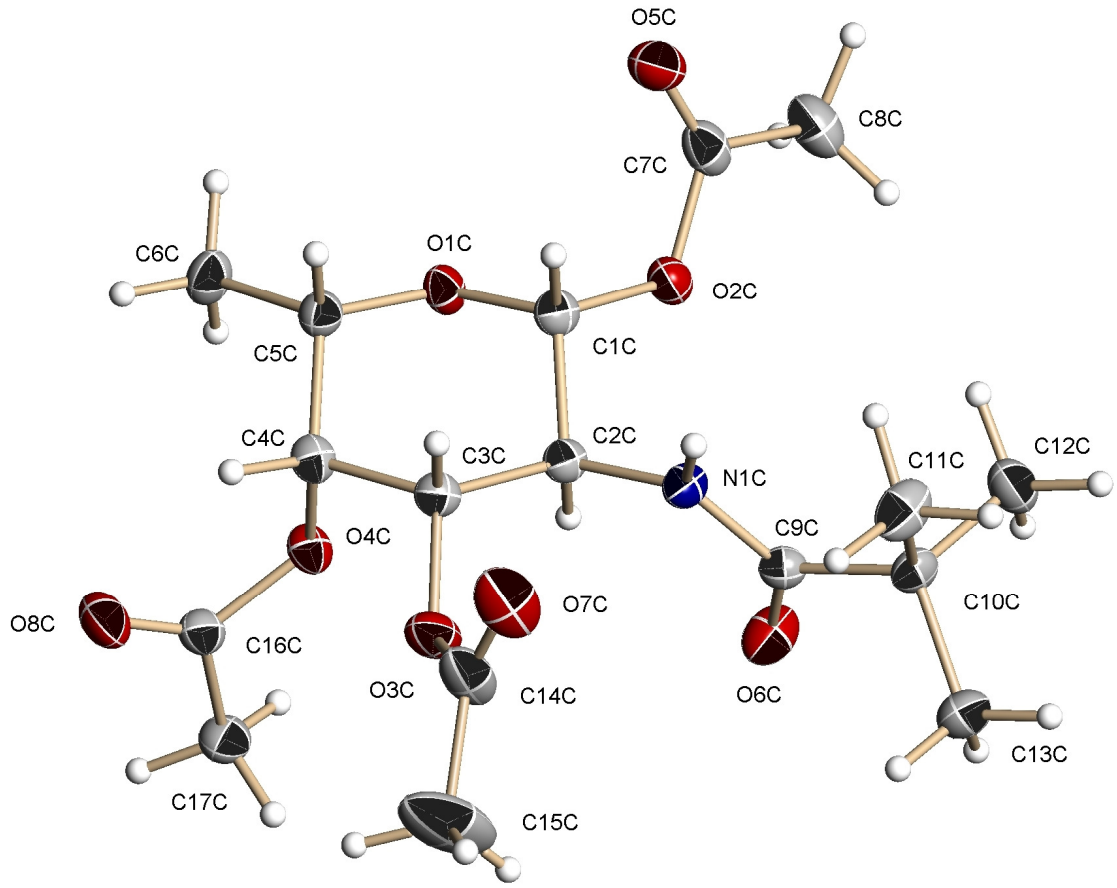


Figure 132 :

Crystallographic refinement of 1,3,4-di-*O*-acetyl-2-*N*-(trimethyl)acetyl-β-L-fucose (**14**)

Table 1. Crystal data and structure refinement for 07mz349m:

Identification code: 07mz349m
Empirical formula: C68 H108.732 N4 O32.366
Moiety formula: 4(C17 H27 N O8), 0.366(H2 O)
Formula weight: 1500.16
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Monoclinic
Space group: $P2_1$
Unit cell dimensions:
a = 10.7017(12) Å, α = 90°
b = 19.136(2) Å, β = 90.596(2)°
c = 19.912(2) Å, γ = 90°
Volume, *Z*: 4077.6(8) $Å^3$, 2
Density (calculated): 1.223 Mg/m^3
Absorption coefficient: 0.097 mm^{-1}
F(000): 1607.3
Crystal size: 0.49 × 0.30 × 0.18 mm
Crystal shape, colour: block, colourless
θ range for data collection: 1.02 to 28.28°
Limiting indices: $-14 \le h \le 14$, $-25 \le k \le 16$, $-26 \le l \le 25$
Reflections collected: 21605
Independent reflections: 10227 (*R*(int) = 0.0347)
Completeness to θ = 28.28°: 98.2 %
Absorption correction: multi-scan
Max. and min. transmission: 0.983 and 0.887
Refinement method: Full-matrix least-squares on F^2
Data / restraints / parameters: 10227 / 4 / 982
Goodness-of-fit on F^2: 1.072
Final *R* indices [$I>2\sigma(I)$]: R1 = 0.0562, wR2 = 0.1503
R indices (all data): R1 = 0.0620, wR2 = 0.1595
Largest diff. peak and hole: 0.384 and −0.294 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 monoclinic compound crystallizes in a metrically orthorhombic setting with four crystallographically independent molecules in the asymmetric part of the unit cell. Solving the structure by simple direct methods proofed to be difficult and the program ShelxD was used to identify the initial model for

refinement (Usón, I. & Sheldrick, G. M. (1999). *Curr. Opin. Struct. Biol.* **9**, 643-648. Schneider, T. R. & Sheldrick, G. M. (2002). *Acta Cryst.* **D58**, 1772-1779). The crystal under investigation was also found to be pseudo-merohedrally twinned. Introduction of the twin operation reduced the R values by about a factor of two. The twin matrix used was 1 0 0, 0 -1 0, 0 0 -1 and the twin ratio refined to 92.0(1) to 8.0(1)%.

A solvate water molecule present in the unit cell is only partially occupied with an occupancy rate of 36.6(11)%. Also apparently unoccupied voids of 42.00 cubic Angstrom are present in the structure. No significant residual electron density is localized in the voids.

Carbon atom C15c of one of the acetate groups and the attached hydrogen atoms show relatively large isotropic displacement parameters, but it is in the normal range when compared to its neighboring atoms. The large ADPs of this acetate group can also be rationalized by its proximity to the partially occupied water solvate molecule and one of the unoccupied voids present in the structure.

Treatment of hydrogen atoms:
The water hydrogen atoms were located in difference density Fourier maps and the O-H distances were restrained to be 0.84(2) Å. The H...H distance in the water molecule was restrained to be 1.4(2) Å. All other hydrogen atoms were placed in calculated positions and all H atoms were refined with an isotropic displacement parameter 1.5 (methyl, water) or 1.2 times (all others) that of the adjacent carbon, oxygen or nitrogen atom. Methyl H atoms were allowed to rotate to best fit the experimental electron density.

Table 2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for 07mz349m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1A)	599(4)	5250(2)	4568(2)	24(1)
C(2A)	907(4)	4526(2)	4298(2)	22(1)
C(3A)	-162(4)	4320(2)	3820(2)	23(1)
C(4A)	-372(4)	4868(2)	3271(2)	23(1)
C(5A)	-504(4)	5591(2)	3590(2)	24(1)
C(6A)	-517(5)	6180(2)	3074(2)	31(1)
C(7A)	1322(4)	5961(2)	5465(2)	29(1)
C(8A)	2488(5)	6216(3)	5812(2)	35(1)
C(9A)	2071(4)	3616(2)	4920(2)	23(1)
C(10A)	2052(4)	3095(2)	5507(2)	27(1)
C(11A)	1469(5)	3407(3)	6139(2)	35(1)
C(12A)	3406(5)	2880(3)	5664(3)	41(1)
C(13A)	1290(5)	2452(2)	5275(2)	38(1)

C(14A)	-390(4)	3080(2)	3702(2)	25(1)
C(15A)	140(5)	2467(2)	3324(2)	38(1)
C(16A)	494(4)	4606(2)	2205(2)	24(1)
C(17A)	1708(4)	4465(2)	1861(2)	28(1)
C(1B)	5391(4)	5643(2)	4430(2)	23(1)
C(2B)	5305(3)	4879(2)	4668(2)	21(1)
C(3B)	6493(4)	4733(2)	5080(2)	22(1)
C(4B)	6589(4)	5248(2)	5667(2)	24(1)
C(5B)	6527(4)	5995(2)	5397(2)	27(1)
C(6B)	6494(5)	6532(3)	5954(2)	36(1)
C(7B)	4386(4)	6261(2)	3540(2)	30(1)
C(8B)	3150(5)	6333(3)	3193(2)	39(1)
C(9B)	5955(4)	4258(2)	3644(2)	21(1)
C(10B)	5637(4)	3641(2)	3175(2)	25(1)
C(11B)	6606(4)	3608(2)	2622(2)	29(1)
C(12B)	4325(4)	3743(2)	2872(2)	31(1)
C(13B)	5696(5)	2965(2)	3593(2)	33(1)
C(14B)	7530(4)	3722(2)	5479(2)	29(1)
C(15B)	7341(5)	2975(3)	5687(3)	43(1)
C(16B)	5724(4)	4738(3)	6659(2)	31(1)
C(17B)	4531(5)	4659(3)	7036(2)	41(1)
C(1C)	5618(4)	4701(2)	9399(2)	23(1)
C(2C)	5883(4)	5445(2)	9643(2)	21(1)
C(3C)	4807(4)	5660(2)	10095(2)	22(1)
C(4C)	4628(4)	5132(2)	10661(2)	22(1)
C(5C)	4514(4)	4395(2)	10376(2)	24(1)
C(6C)	4496(4)	3836(2)	10913(2)	29(1)
C(7C)	6378(4)	3952(2)	8552(2)	30(1)
C(8C)	7569(5)	3700(3)	8242(2)	40(1)
C(9C)	7093(3)	6252(2)	8951(2)	21(1)
C(10C)	7212(4)	6642(2)	8283(2)	24(1)
C(11C)	5951(4)	6783(3)	7930(2)	34(1)
C(12C)	8010(5)	6166(2)	7839(2)	34(1)
C(13C)	7894(4)	7331(2)	8408(2)	32(1)
C(14C)	4489(6)	6899(2)	10123(2)	42(1)
C(15C)	4805(11)	7525(3)	10532(3)	87(3)
C(16C)	5514(4)	5382(2)	11740(2)	25(1)
C(17C)	6722(4)	5564(2)	12087(2)	31(1)
C(1D)	417(4)	4204(2)	9591(2)	25(1)
C(2D)	325(3)	4933(2)	9279(2)	22(1)
C(3D)	1509(4)	5044(2)	8872(2)	21(1)
C(4D)	1655(4)	4474(2)	8346(2)	25(1)
C(5D)	1623(4)	3764(2)	8691(2)	29(1)
C(6D)	1686(6)	3157(2)	8210(3)	43(1)
C(7D)	-632(4)	3642(2)	10481(2)	24(1)
C(8D)	-1879(4)	3558(2)	10799(2)	32(1)
C(9D)	965(4)	5656(2)	10259(2)	22(1)
C(10D)	623(4)	6294(2)	10687(2)	25(1)
C(11D)	1610(5)	6388(2)	11243(2)	35(1)
C(12D)	-668(4)	6179(3)	11007(2)	32(1)
C(13D)	590(5)	6950(2)	10237(2)	34(1)
C(14D)	2516(4)	6015(2)	8386(2)	26(1)
C(15D)	2327(5)	6733(3)	8091(3)	41(1)
C(16D)	795(4)	4888(2)	7300(2)	28(1)
C(17D)	-352(4)	4865(3)	6857(2)	36(1)
N(1A)	1036(3)	4021(2)	4843(2)	24(1)
N(1B)	5116(3)	4381(2)	4130(2)	24(1)
N(1C)	6018(3)	5916(2)	9074(2)	21(1)
N(1D)	127(3)	5485(2)	9773(2)	24(1)
O(1A)	518(3)	5739(2)	4042(1)	25(1)
O(2A)	1615(3)	5474(2)	4982(1)	26(1)
O(3A)	174(3)	3673(2)	3492(1)	25(1)
O(4A)	704(3)	4854(2)	2842(1)	23(1)

O(5A)	276(3)	6131(2)	5583(2)	37(1)
O(6A)	2943(3)	3646(2)	4534(2)	35(1)
O(7A)	-1180(3)	3053(2)	4122(2)	33(1)
O(8A)	-522(3)	4521(2)	1971(2)	39(1)
O(1B)	5427(3)	6093(2)	4993(1)	27(1)
O(2B)	4288(3)	5796(2)	4067(1)	28(1)
O(3B)	6424(3)	4022(2)	5313(1)	26(1)
O(4B)	5532(3)	5137(2)	6100(1)	27(1)
O(5B)	5343(3)	6530(2)	3391(2)	39(1)
O(6B)	6909(3)	4606(2)	3589(1)	25(1)
O(7B)	8513(3)	4018(2)	5449(1)	29(1)
O(8B)	6709(3)	4499(3)	6808(2)	49(1)
O(1C)	5545(3)	4238(2)	9944(1)	24(1)
O(2C)	6637(3)	4472(2)	9009(1)	25(1)
O(3C)	5070(3)	6326(2)	10397(2)	32(1)
O(4C)	5721(3)	5179(2)	11093(1)	23(1)
O(5C)	5351(3)	3753(2)	8429(2)	35(1)
O(6C)	7981(3)	6230(2)	9346(2)	33(1)
O(7C)	3838(4)	6881(2)	9636(2)	47(1)
O(8C)	4506(3)	5412(2)	11981(2)	37(1)
O(1D)	500(3)	3692(2)	9073(1)	29(1)
O(2D)	-704(3)	4070(2)	9931(1)	26(1)
O(3D)	1423(3)	5730(2)	8575(1)	24(1)
O(4D)	616(3)	4508(2)	7872(1)	27(1)
O(5D)	326(3)	3377(2)	10668(2)	35(1)
O(6D)	1929(3)	5319(2)	10347(1)	26(1)
O(7D)	3511(3)	5727(2)	8453(1)	28(1)
O(8D)	1743(3)	5187(2)	7175(2)	36(1)
O(1)	2419(8)	2685(5)	9923(5)	35(3)

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

Table 3. Bond lengths [Å] and angles [deg] for 07mz349m.

C(1A)-O(1A)	1.406(5)
C(1A)-O(2A)	1.423(5)
C(1A)-C(2A)	1.525(6)
C(1A)-H(1A)	1.0000
C(2A)-N(1A)	1.458(5)
C(2A)-C(3A)	1.533(5)
C(2A)-H(2A)	1.0000
C(3A)-O(3A)	1.446(5)
C(3A)-C(4A)	1.529(5)
C(3A)-H(3A)	1.0000
C(4A)-O(4A)	1.442(5)
C(4A)-C(5A)	1.531(5)
C(4A)-H(4A)	1.0000
C(5A)-O(1A)	1.437(5)
C(5A)-C(6A)	1.525(6)
C(5A)-H(5A)	1.0000
C(6A)-H(6A1)	0.9800
C(6A)-H(6A2)	0.9800

C(6A)-H(6A3)	0.9800
C(7A)-O(5A)	1.190(6)
C(7A)-O(2A)	1.378(5)
C(7A)-C(8A)	1.501(6)
C(8A)-H(8A1)	0.9800
C(8A)-H(8A2)	0.9800
C(8A)-H(8A3)	0.9800
C(9A)-O(6A)	1.216(5)
C(9A)-N(1A)	1.359(5)
C(9A)-C(10A)	1.538(6)
C(10A)-C(11A)	1.531(6)
C(10A)-C(12A)	1.536(6)
C(10A)-C(13A)	1.544(6)
C(11A)-H(11A)	0.9800
C(11A)-H(11B)	0.9800
C(11A)-H(11C)	0.9800
C(12A)-H(12A)	0.9800
C(12A)-H(12B)	0.9800
C(12A)-H(12C)	0.9800
C(13A)-H(13A)	0.9800
C(13A)-H(13B)	0.9800
C(13A)-H(13C)	0.9800
C(14A)-O(7A)	1.197(5)
C(14A)-O(3A)	1.354(5)
C(14A)-C(15A)	1.506(6)
C(15A)-H(15A)	0.9800
C(15A)-H(15B)	0.9800
C(15A)-H(15C)	0.9800
C(16A)-O(8A)	1.189(5)
C(16A)-O(4A)	1.369(4)
C(16A)-C(17A)	1.500(5)
C(17A)-H(17A)	0.9800
C(17A)-H(17B)	0.9800
C(17A)-H(17C)	0.9800
C(1B)-O(2B)	1.408(5)
C(1B)-O(1B)	1.414(5)
C(1B)-C(2B)	1.540(5)
C(1B)-H(1B)	1.0000
C(2B)-N(1B)	1.447(5)
C(2B)-C(3B)	1.532(5)
C(2B)-H(2B)	1.0000
C(3B)-O(3B)	1.440(5)
C(3B)-C(4B)	1.532(5)
C(3B)-H(3B)	1.0000
C(4B)-O(4B)	1.445(5)
C(4B)-C(5B)	1.529(6)
C(4B)-H(4B)	1.0000
C(5B)-O(1B)	1.431(5)
C(5B)-C(6B)	1.512(6)
C(5B)-H(5B)	1.0000
C(6B)-H(6B1)	0.9800
C(6B)-H(6B2)	0.9800
C(6B)-H(6B3)	0.9800
C(7B)-O(5B)	1.186(6)
C(7B)-O(2B)	1.381(5)
C(7B)-C(8B)	1.491(6)
C(8B)-H(8B1)	0.9800
C(8B)-H(8B2)	0.9800
C(8B)-H(8B3)	0.9800
C(9B)-O(6B)	1.224(5)
C(9B)-N(1B)	1.347(5)
C(9B)-C(10B)	1.541(5)
C(10B)-C(11B)	1.523(6)

C(10B)-C(12B)	1.535(6)
C(10B)-C(13B)	1.540(6)
C(11B)-H(11D)	0.9800
C(11B)-H(11E)	0.9800
C(11B)-H(11F)	0.9800
C(12B)-H(12D)	0.9800
C(12B)-H(12E)	0.9800
C(12B)-H(12F)	0.9800
C(13B)-H(13D)	0.9800
C(13B)-H(13E)	0.9800
C(13B)-H(13F)	0.9800
C(14B)-O(7B)	1.196(5)
C(14B)-O(3B)	1.353(5)
C(14B)-C(15B)	1.503(7)
C(15B)-H(15D)	0.9800
C(15B)-H(15E)	0.9800
C(15B)-H(15F)	0.9800
C(16B)-O(8B)	1.183(6)
C(16B)-O(4B)	1.365(5)
C(16B)-C(17B)	1.495(6)
C(17B)-H(17D)	0.9800
C(17B)-H(17E)	0.9800
C(17B)-H(17F)	0.9800
C(1C)-O(1C)	1.404(4)
C(1C)-O(2C)	1.414(5)
C(1C)-C(2C)	1.530(5)
C(1C)-H(1C)	1.0000
C(2C)-N(1C)	1.456(5)
C(2C)-C(3C)	1.526(5)
C(2C)-H(2C)	1.0000
C(3C)-O(3C)	1.436(5)
C(3C)-C(4C)	1.526(5)
C(3C)-H(3C)	1.0000
C(4C)-O(4C)	1.447(4)
C(4C)-C(5C)	1.524(6)
C(4C)-H(4C)	1.0000
C(5C)-O(1C)	1.438(5)
C(5C)-C(6C)	1.513(5)
C(5C)-H(5C)	1.0000
C(6C)-H(6C1)	0.9800
C(6C)-H(6C2)	0.9800
C(6C)-H(6C3)	0.9800
C(7C)-O(5C)	1.186(6)
C(7C)-O(2C)	1.375(5)
C(7C)-C(8C)	1.502(7)
C(8C)-H(8C1)	0.9800
C(8C)-H(8C2)	0.9800
C(8C)-H(8C3)	0.9800
C(9C)-O(6C)	1.228(5)
C(9C)-N(1C)	1.343(5)
C(9C)-C(10C)	1.530(5)
C(10C)-C(13C)	1.526(6)
C(10C)-C(12C)	1.535(6)
C(10C)-C(11C)	1.540(6)
C(11C)-H(11G)	0.9800
C(11C)-H(11H)	0.9800
C(11C)-H(11I)	0.9800
C(12C)-H(12G)	0.9800
C(12C)-H(12H)	0.9800
C(12C)-H(12I)	0.9800
C(13C)-H(13G)	0.9800
C(13C)-H(13H)	0.9800
C(13C)-H(13I)	0.9800

C(14C)-O(7C)	1.188(7)
C(14C)-O(3C)	1.372(6)
C(14C)-C(15C)	1.485(8)
C(15C)-H(15G)	0.9800
C(15C)-H(15H)	0.9800
C(15C)-H(15I)	0.9800
C(16C)-O(8C)	1.186(5)
C(16C)-O(4C)	1.366(4)
C(16C)-C(17C)	1.500(6)
C(17C)-H(17G)	0.9800
C(17C)-H(17H)	0.9800
C(17C)-H(17I)	0.9800
C(1D)-O(2D)	1.407(5)
C(1D)-O(1D)	1.426(5)
C(1D)-C(2D)	1.531(5)
C(1D)-H(1D)	1.0000
C(2D)-N(1D)	1.460(5)
C(2D)-C(3D)	1.526(5)
C(2D)-H(2D)	1.0000
C(3D)-O(3D)	1.443(5)
C(3D)-C(4D)	1.522(5)
C(3D)-H(3D)	1.0000
C(4D)-O(4D)	1.453(5)
C(4D)-C(5D)	1.523(6)
C(4D)-H(4D)	1.0000
C(5D)-O(1D)	1.435(5)
C(5D)-C(6D)	1.509(6)
C(5D)-H(5D)	1.0000
C(6D)-H(6D1)	0.9800
C(6D)-H(6D2)	0.9800
C(6D)-H(6D3)	0.9800
C(7D)-O(5D)	1.199(5)
C(7D)-O(2D)	1.368(5)
C(7D)-C(8D)	1.492(6)
C(8D)-H(8D1)	0.9800
C(8D)-H(8D2)	0.9800
C(8D)-H(8D3)	0.9800
C(9D)-O(6D)	1.228(5)
C(9D)-N(1D)	1.352(5)
C(9D)-C(10D)	1.537(6)
C(10D)-C(11D)	1.531(6)
C(10D)-C(13D)	1.543(6)
C(10D)-C(12D)	1.543(6)
C(11D)-H(11J)	0.9800
C(11D)-H(11K)	0.9800
C(11D)-H(11L)	0.9800
C(12D)-H(12J)	0.9800
C(12D)-H(12K)	0.9800
C(12D)-H(12L)	0.9800
C(13D)-H(13J)	0.9800
C(13D)-H(13K)	0.9800
C(13D)-H(13L)	0.9800
C(14D)-O(7D)	1.205(5)
C(14D)-O(3D)	1.348(5)
C(14D)-C(15D)	1.507(6)
C(15D)-H(15J)	0.9800
C(15D)-H(15K)	0.9800
C(15D)-H(15L)	0.9800
C(16D)-O(8D)	1.194(5)
C(16D)-O(4D)	1.366(5)
C(16D)-C(17D)	1.504(6)
C(17D)-H(17J)	0.9800
C(17D)-H(17K)	0.9800

C(17D)-H(17L)	0.9800
N(1A)-H(1A1)	0.8800
N(1B)-H(1B1)	0.8800
N(1C)-H(1C1)	0.8800
N(1D)-H(1D1)	0.8800
O(1)-H(1E)	0.84(2)
O(1)-H(1F)	0.84(2)

O(1A)-C(1A)-O(2A)	105.8(3)
O(1A)-C(1A)-C(2A)	110.8(3)
O(2A)-C(1A)-C(2A)	108.1(3)
O(1A)-C(1A)-H(1A)	110.7
O(2A)-C(1A)-H(1A)	110.7
C(2A)-C(1A)-H(1A)	110.7
N(1A)-C(2A)-C(1A)	111.1(3)
N(1A)-C(2A)-C(3A)	110.9(3)
C(1A)-C(2A)-C(3A)	106.8(3)
N(1A)-C(2A)-H(2A)	109.3
C(1A)-C(2A)-H(2A)	109.3
C(3A)-C(2A)-H(2A)	109.3
O(3A)-C(3A)-C(4A)	107.5(3)
O(3A)-C(3A)-C(2A)	108.2(3)
C(4A)-C(3A)-C(2A)	111.8(3)
O(3A)-C(3A)-H(3A)	109.8
C(4A)-C(3A)-H(3A)	109.8
C(2A)-C(3A)-H(3A)	109.8
O(4A)-C(4A)-C(3A)	107.4(3)
O(4A)-C(4A)-C(5A)	109.9(3)
C(3A)-C(4A)-C(5A)	109.7(3)
O(4A)-C(4A)-H(4A)	109.9
C(3A)-C(4A)-H(4A)	109.9
C(5A)-C(4A)-H(4A)	109.9
O(1A)-C(5A)-C(6A)	106.1(3)
O(1A)-C(5A)-C(4A)	111.4(3)
C(6A)-C(5A)-C(4A)	112.9(3)
O(1A)-C(5A)-H(5A)	108.8
C(6A)-C(5A)-H(5A)	108.8
C(4A)-C(5A)-H(5A)	108.8
C(5A)-C(6A)-H(6A1)	109.5
C(5A)-C(6A)-H(6A2)	109.5
H(6A1)-C(6A)-H(6A2)	109.5
C(5A)-C(6A)-H(6A3)	109.5
H(6A1)-C(6A)-H(6A3)	109.5
H(6A2)-C(6A)-H(6A3)	109.5
O(5A)-C(7A)-O(2A)	122.9(4)
O(5A)-C(7A)-C(8A)	126.9(4)
O(2A)-C(7A)-C(8A)	110.3(4)
C(7A)-C(8A)-H(8A1)	109.5
C(7A)-C(8A)-H(8A2)	109.5
H(8A1)-C(8A)-H(8A2)	109.5
C(7A)-C(8A)-H(8A3)	109.5
H(8A1)-C(8A)-H(8A3)	109.5
H(8A2)-C(8A)-H(8A3)	109.5
O(6A)-C(9A)-N(1A)	122.1(4)
O(6A)-C(9A)-C(10A)	121.8(4)
N(1A)-C(9A)-C(10A)	116.0(3)
C(11A)-C(10A)-C(12A)	109.3(4)
C(11A)-C(10A)-C(9A)	112.4(4)
C(12A)-C(10A)-C(9A)	108.0(4)
C(11A)-C(10A)-C(13A)	109.8(4)
C(12A)-C(10A)-C(13A)	110.0(4)
C(9A)-C(10A)-C(13A)	107.4(3)
C(10A)-C(11A)-H(11A)	109.5

C(10A)-C(11A)-H(11B)	109.5
H(11A)-C(11A)-H(11B)	109.5
C(10A)-C(11A)-H(11C)	109.5
H(11A)-C(11A)-H(11C)	109.5
H(11B)-C(11A)-H(11C)	109.5
C(10A)-C(12A)-H(12A)	109.5
C(10A)-C(12A)-H(12B)	109.5
H(12A)-C(12A)-H(12B)	109.5
C(10A)-C(12A)-H(12C)	109.5
H(12A)-C(12A)-H(12C)	109.5
H(12B)-C(12A)-H(12C)	109.5
C(10A)-C(13A)-H(13A)	109.5
C(10A)-C(13A)-H(13B)	109.5
H(13A)-C(13A)-H(13B)	109.5
C(10A)-C(13A)-H(13C)	109.5
H(13A)-C(13A)-H(13C)	109.5
H(13B)-C(13A)-H(13C)	109.5
O(7A)-C(14A)-O(3A)	124.8(4)
O(7A)-C(14A)-C(15A)	126.0(4)
O(3A)-C(14A)-C(15A)	109.2(4)
C(14A)-C(15A)-H(15A)	109.5
C(14A)-C(15A)-H(15B)	109.5
H(15A)-C(15A)-H(15B)	109.5
C(14A)-C(15A)-H(15C)	109.5
H(15A)-C(15A)-H(15C)	109.5
H(15B)-C(15A)-H(15C)	109.5
O(8A)-C(16A)-O(4A)	123.5(4)
O(8A)-C(16A)-C(17A)	126.0(4)
O(4A)-C(16A)-C(17A)	110.5(3)
C(16A)-C(17A)-H(17A)	109.5
C(16A)-C(17A)-H(17B)	109.5
H(17A)-C(17A)-H(17B)	109.5
C(16A)-C(17A)-H(17C)	109.5
H(17A)-C(17A)-H(17C)	109.5
H(17B)-C(17A)-H(17C)	109.5
O(2B)-C(1B)-O(1B)	107.2(3)
O(2B)-C(1B)-C(2B)	107.6(3)
O(1B)-C(1B)-C(2B)	109.6(3)
O(2B)-C(1B)-H(1B)	110.8
O(1B)-C(1B)-H(1B)	110.8
C(2B)-C(1B)-H(1B)	110.8
N(1B)-C(2B)-C(3B)	112.6(3)
N(1B)-C(2B)-C(1B)	113.9(3)
C(3B)-C(2B)-C(1B)	106.6(3)
N(1B)-C(2B)-H(2B)	107.8
C(3B)-C(2B)-H(2B)	107.8
C(1B)-C(2B)-H(2B)	107.8
O(3B)-C(3B)-C(4B)	111.4(3)
O(3B)-C(3B)-C(2B)	107.5(3)
C(4B)-C(3B)-C(2B)	109.8(3)
O(3B)-C(3B)-H(3B)	109.4
C(4B)-C(3B)-H(3B)	109.4
C(2B)-C(3B)-H(3B)	109.4
O(4B)-C(4B)-C(5B)	108.4(3)
O(4B)-C(4B)-C(3B)	108.3(3)
C(5B)-C(4B)-C(3B)	109.4(3)
O(4B)-C(4B)-H(4B)	110.2
C(5B)-C(4B)-H(4B)	110.2
C(3B)-C(4B)-H(4B)	110.2
O(1B)-C(5B)-C(6B)	107.4(3)
O(1B)-C(5B)-C(4B)	110.6(3)
C(6B)-C(5B)-C(4B)	112.3(3)
O(1B)-C(5B)-H(5B)	108.8

C(6B)-C(5B)-H(5B)	108.8
C(4B)-C(5B)-H(5B)	108.8
C(5B)-C(6B)-H(6B1)	109.5
C(5B)-C(6B)-H(6B2)	109.5
H(6B1)-C(6B)-H(6B2)	109.5
C(5B)-C(6B)-H(6B3)	109.5
H(6B1)-C(6B)-H(6B3)	109.5
H(6B2)-C(6B)-H(6B3)	109.5
O(5B)-C(7B)-O(2B)	122.8(4)
O(5B)-C(7B)-C(8B)	127.5(4)
O(2B)-C(7B)-C(8B)	109.7(4)
C(7B)-C(8B)-H(8B1)	109.5
C(7B)-C(8B)-H(8B2)	109.5
H(8B1)-C(8B)-H(8B2)	109.5
C(7B)-C(8B)-H(8B3)	109.5
H(8B1)-C(8B)-H(8B3)	109.5
H(8B2)-C(8B)-H(8B3)	109.5
O(6B)-C(9B)-N(1B)	122.1(3)
O(6B)-C(9B)-C(10B)	122.8(3)
N(1B)-C(9B)-C(10B)	115.1(3)
C(11B)-C(10B)-C(12B)	110.4(3)
C(11B)-C(10B)-C(13B)	109.4(4)
C(12B)-C(10B)-C(13B)	110.6(4)
C(11B)-C(10B)-C(9B)	108.8(3)
C(12B)-C(10B)-C(9B)	109.7(3)
C(13B)-C(10B)-C(9B)	107.9(3)
C(10B)-C(11B)-H(11D)	109.5
C(10B)-C(11B)-H(11E)	109.5
H(11D)-C(11B)-H(11E)	109.5
C(10B)-C(11B)-H(11F)	109.5
H(11D)-C(11B)-H(11F)	109.5
H(11E)-C(11B)-H(11F)	109.5
C(10B)-C(12B)-H(12D)	109.5
C(10B)-C(12B)-H(12E)	109.5
H(12D)-C(12B)-H(12E)	109.5
C(10B)-C(12B)-H(12F)	109.5
H(12D)-C(12B)-H(12F)	109.5
H(12E)-C(12B)-H(12F)	109.5
C(10B)-C(13B)-H(13D)	109.5
C(10B)-C(13B)-H(13E)	109.5
H(13D)-C(13B)-H(13E)	109.5
C(10B)-C(13B)-H(13F)	109.5
H(13D)-C(13B)-H(13F)	109.5
H(13E)-C(13B)-H(13F)	109.5
O(7B)-C(14B)-O(3B)	123.7(4)
O(7B)-C(14B)-C(15B)	125.8(4)
O(3B)-C(14B)-C(15B)	110.5(4)
C(14B)-C(15B)-H(15D)	109.5
C(14B)-C(15B)-H(15E)	109.5
H(15D)-C(15B)-H(15E)	109.5
C(14B)-C(15B)-H(15F)	109.5
H(15D)-C(15B)-H(15F)	109.5
H(15E)-C(15B)-H(15F)	109.5
O(8B)-C(16B)-O(4B)	123.1(4)
O(8B)-C(16B)-C(17B)	126.8(4)
O(4B)-C(16B)-C(17B)	110.1(4)
C(16B)-C(17B)-H(17D)	109.5
C(16B)-C(17B)-H(17E)	109.5
H(17D)-C(17B)-H(17E)	109.5
C(16B)-C(17B)-H(17F)	109.5
H(17D)-C(17B)-H(17F)	109.5
H(17E)-C(17B)-H(17F)	109.5
O(1C)-C(1C)-O(2C)	106.1(3)

O(1C)-C(1C)-C(2C)	110.6(3)
O(2C)-C(1C)-C(2C)	108.8(3)
O(1C)-C(1C)-H(1C)	110.4
O(2C)-C(1C)-H(1C)	110.4
C(2C)-C(1C)-H(1C)	110.4
N(1C)-C(2C)-C(3C)	112.0(3)
N(1C)-C(2C)-C(1C)	110.4(3)
C(3C)-C(2C)-C(1C)	107.4(3)
N(1C)-C(2C)-H(2C)	109.0
C(3C)-C(2C)-H(2C)	109.0
C(1C)-C(2C)-H(2C)	109.0
O(3C)-C(3C)-C(2C)	109.9(3)
O(3C)-C(3C)-C(4C)	107.7(3)
C(2C)-C(3C)-C(4C)	111.0(3)
O(3C)-C(3C)-H(3C)	109.4
C(2C)-C(3C)-H(3C)	109.4
C(4C)-C(3C)-H(3C)	109.4
O(4C)-C(4C)-C(5C)	109.9(3)
O(4C)-C(4C)-C(3C)	106.9(3)
C(5C)-C(4C)-C(3C)	110.4(3)
O(4C)-C(4C)-H(4C)	109.9
C(5C)-C(4C)-H(4C)	109.9
C(3C)-C(4C)-H(4C)	109.9
O(1C)-C(5C)-C(6C)	106.9(3)
O(1C)-C(5C)-C(4C)	110.8(3)
C(6C)-C(5C)-C(4C)	113.2(3)
O(1C)-C(5C)-H(5C)	108.6
C(6C)-C(5C)-H(5C)	108.6
C(4C)-C(5C)-H(5C)	108.6
C(5C)-C(6C)-H(6C1)	109.5
C(5C)-C(6C)-H(6C2)	109.5
H(6C1)-C(6C)-H(6C2)	109.5
C(5C)-C(6C)-H(6C3)	109.5
H(6C1)-C(6C)-H(6C3)	109.5
H(6C2)-C(6C)-H(6C3)	109.5
O(5C)-C(7C)-O(2C)	123.3(4)
O(5C)-C(7C)-C(8C)	126.9(4)
O(2C)-C(7C)-C(8C)	109.8(4)
C(7C)-C(8C)-H(8C1)	109.5
C(7C)-C(8C)-H(8C2)	109.5
H(8C1)-C(8C)-H(8C2)	109.5
C(7C)-C(8C)-H(8C3)	109.5
H(8C1)-C(8C)-H(8C3)	109.5
H(8C2)-C(8C)-H(8C3)	109.5
O(6C)-C(9C)-N(1C)	121.7(3)
O(6C)-C(9C)-C(10C)	120.1(4)
N(1C)-C(9C)-C(10C)	118.1(3)
C(13C)-C(10C)-C(9C)	108.9(3)
C(13C)-C(10C)-C(12C)	109.8(4)
C(9C)-C(10C)-C(12C)	105.3(3)
C(13C)-C(10C)-C(11C)	109.7(3)
C(9C)-C(10C)-C(11C)	113.7(3)
C(12C)-C(10C)-C(11C)	109.3(4)
C(10C)-C(11C)-H(11G)	109.5
C(10C)-C(11C)-H(11H)	109.5
H(11G)-C(11C)-H(11H)	109.5
C(10C)-C(11C)-H(11I)	109.5
H(11G)-C(11C)-H(11I)	109.5
H(11H)-C(11C)-H(11I)	109.5
C(10C)-C(12C)-H(12G)	109.5
C(10C)-C(12C)-H(12H)	109.5
H(12G)-C(12C)-H(12H)	109.5
C(10C)-C(12C)-H(12I)	109.5

H(12G)-C(12C)-H(12I)	109.5
H(12H)-C(12C)-H(12I)	109.5
C(10C)-C(13C)-H(13G)	109.5
C(10C)-C(13C)-H(13H)	109.5
H(13G)-C(13C)-H(13H)	109.5
C(10C)-C(13C)-H(13I)	109.5
H(13G)-C(13C)-H(13I)	109.5
H(13H)-C(13C)-H(13I)	109.5
O(7C)-C(14C)-O(3C)	124.1(4)
O(7C)-C(14C)-C(15C)	126.8(5)
O(3C)-C(14C)-C(15C)	109.1(5)
C(14C)-C(15C)-H(15G)	109.5
C(14C)-C(15C)-H(15H)	109.5
H(15G)-C(15C)-H(15H)	109.5
C(14C)-C(15C)-H(15I)	109.5
H(15G)-C(15C)-H(15I)	109.5
H(15H)-C(15C)-H(15I)	109.5
O(8C)-C(16C)-O(4C)	123.5(4)
O(8C)-C(16C)-C(17C)	125.8(4)
O(4C)-C(16C)-C(17C)	110.7(3)
C(16C)-C(17C)-H(17G)	109.5
C(16C)-C(17C)-H(17H)	109.5
H(17G)-C(17C)-H(17H)	109.5
C(16C)-C(17C)-H(17I)	109.5
H(17G)-C(17C)-H(17I)	109.5
H(17H)-C(17C)-H(17I)	109.5
O(2D)-C(1D)-O(1D)	106.4(3)
O(2D)-C(1D)-C(2D)	108.0(3)
O(1D)-C(1D)-C(2D)	109.7(3)
O(2D)-C(1D)-H(1D)	110.9
O(1D)-C(1D)-H(1D)	110.9
C(2D)-C(1D)-H(1D)	110.9
N(1D)-C(2D)-C(3D)	112.6(3)
N(1D)-C(2D)-C(1D)	113.3(3)
C(3D)-C(2D)-C(1D)	106.9(3)
N(1D)-C(2D)-H(2D)	107.9
C(3D)-C(2D)-H(2D)	107.9
C(1D)-C(2D)-H(2D)	107.9
O(3D)-C(3D)-C(4D)	112.1(3)
O(3D)-C(3D)-C(2D)	107.1(3)
C(4D)-C(3D)-C(2D)	111.0(3)
O(3D)-C(3D)-H(3D)	108.9
C(4D)-C(3D)-H(3D)	108.9
C(2D)-C(3D)-H(3D)	108.9
O(4D)-C(4D)-C(3D)	109.4(3)
O(4D)-C(4D)-C(5D)	108.3(3)
C(3D)-C(4D)-C(5D)	108.9(3)
O(4D)-C(4D)-H(4D)	110.1
C(3D)-C(4D)-H(4D)	110.1
C(5D)-C(4D)-H(4D)	110.1
O(1D)-C(5D)-C(6D)	107.7(4)
O(1D)-C(5D)-C(4D)	110.4(3)
C(6D)-C(5D)-C(4D)	113.5(3)
O(1D)-C(5D)-H(5D)	108.4
C(6D)-C(5D)-H(5D)	108.4
C(4D)-C(5D)-H(5D)	108.4
C(5D)-C(6D)-H(6D1)	109.5
C(5D)-C(6D)-H(6D2)	109.5
H(6D1)-C(6D)-H(6D2)	109.5
C(5D)-C(6D)-H(6D3)	109.5
H(6D1)-C(6D)-H(6D3)	109.5
H(6D2)-C(6D)-H(6D3)	109.5
O(5D)-C(7D)-O(2D)	122.8(4)

O(5D)-C(7D)-C(8D)	126.1(4)
O(2D)-C(7D)-C(8D)	111.1(3)
C(7D)-C(8D)-H(8D1)	109.5
C(7D)-C(8D)-H(8D2)	109.5
H(8D1)-C(8D)-H(8D2)	109.5
C(7D)-C(8D)-H(8D3)	109.5
H(8D1)-C(8D)-H(8D3)	109.5
H(8D2)-C(8D)-H(8D3)	109.5
O(6D)-C(9D)-N(1D)	121.7(4)
O(6D)-C(9D)-C(10D)	122.9(4)
N(1D)-C(9D)-C(10D)	115.5(3)
C(11D)-C(10D)-C(9D)	109.1(3)
C(11D)-C(10D)-C(13D)	109.6(4)
C(9D)-C(10D)-C(13D)	109.1(3)
C(11D)-C(10D)-C(12D)	109.4(3)
C(9D)-C(10D)-C(12D)	109.6(3)
C(13D)-C(10D)-C(12D)	109.9(4)
C(10D)-C(11D)-H(11J)	109.5
C(10D)-C(11D)-H(11K)	109.5
H(11J)-C(11D)-H(11K)	109.5
C(10D)-C(11D)-H(11L)	109.5
H(11J)-C(11D)-H(11L)	109.5
H(11K)-C(11D)-H(11L)	109.5
C(10D)-C(12D)-H(12J)	109.5
C(10D)-C(12D)-H(12K)	109.5
H(12J)-C(12D)-H(12K)	109.5
C(10D)-C(12D)-H(12L)	109.5
H(12J)-C(12D)-H(12L)	109.5
H(12K)-C(12D)-H(12L)	109.5
C(10D)-C(13D)-H(13J)	109.5
C(10D)-C(13D)-H(13K)	109.5
H(13J)-C(13D)-H(13K)	109.5
C(10D)-C(13D)-H(13L)	109.5
H(13J)-C(13D)-H(13L)	109.5
H(13K)-C(13D)-H(13L)	109.5
O(7D)-C(14D)-O(3D)	123.6(4)
O(7D)-C(14D)-C(15D)	125.1(4)
O(3D)-C(14D)-C(15D)	111.3(4)
C(14D)-C(15D)-H(15J)	109.5
C(14D)-C(15D)-H(15K)	109.5
H(15J)-C(15D)-H(15K)	109.5
C(14D)-C(15D)-H(15L)	109.5
H(15J)-C(15D)-H(15L)	109.5
H(15K)-C(15D)-H(15L)	109.5
O(8D)-C(16D)-O(4D)	123.7(4)
O(8D)-C(16D)-C(17D)	125.6(4)
O(4D)-C(16D)-C(17D)	110.6(4)
C(16D)-C(17D)-H(17J)	109.5
C(16D)-C(17D)-H(17K)	109.5
H(17J)-C(17D)-H(17K)	109.5
C(16D)-C(17D)-H(17L)	109.5
H(17J)-C(17D)-H(17L)	109.5
H(17K)-C(17D)-H(17L)	109.5
C(9A)-N(1A)-C(2A)	122.2(3)
C(9A)-N(1A)-H(1A1)	118.9
C(2A)-N(1A)-H(1A1)	118.9
C(9B)-N(1B)-C(2B)	123.9(3)
C(9B)-N(1B)-H(1B1)	118.0
C(2B)-N(1B)-H(1B1)	118.0
C(9C)-N(1C)-C(2C)	122.1(3)
C(9C)-N(1C)-H(1C1)	119.0
C(2C)-N(1C)-H(1C1)	119.0
C(9D)-N(1D)-C(2D)	123.9(3)

C(9D)-N(1D)-H(1D1)	118.1
C(2D)-N(1D)-H(1D1)	118.1
C(1A)-O(1A)-C(5A)	112.1(3)
C(7A)-O(2A)-C(1A)	115.5(3)
C(14A)-O(3A)-C(3A)	117.7(3)
C(16A)-O(4A)-C(4A)	115.5(3)
C(1B)-O(1B)-C(5B)	112.4(3)
C(7B)-O(2B)-C(1B)	117.0(3)
C(14B)-O(3B)-C(3B)	115.6(3)
C(16B)-O(4B)-C(4B)	117.2(3)
C(1C)-O(1C)-C(5C)	112.4(3)
C(7C)-O(2C)-C(1C)	115.9(3)
C(14C)-O(3C)-C(3C)	117.2(3)
C(16C)-O(4C)-C(4C)	116.2(3)
C(1D)-O(1D)-C(5D)	112.1(3)
C(7D)-O(2D)-C(1D)	116.9(3)
C(14D)-O(3D)-C(3D)	115.5(3)
C(16D)-O(4D)-C(4D)	116.9(3)
H(1E)-O(1)-H(1F)	114(4)

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 07mz349m. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [(h a*)^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1A)	25(2)	27(2)	18(2)	0(1)	1(1)	-2(2)
C(2A)	24(2)	23(2)	19(2)	3(1)	1(1)	-1(1)
C(3A)	27(2)	21(2)	21(2)	-1(1)	4(1)	-1(1)
C(4A)	23(2)	26(2)	20(2)	1(1)	-1(1)	-2(2)
C(5A)	31(2)	21(2)	22(2)	-1(1)	1(1)	1(2)
C(6A)	41(2)	23(2)	29(2)	2(2)	-6(2)	1(2)
C(7A)	42(2)	22(2)	21(2)	1(2)	-2(2)	-2(2)
C(8A)	45(3)	31(2)	28(2)	-2(2)	-6(2)	-5(2)
C(9A)	22(2)	24(2)	23(2)	-4(2)	-1(1)	0(1)
C(10A)	29(2)	25(2)	27(2)	4(2)	-3(2)	3(2)
C(11A)	41(2)	42(2)	21(2)	2(2)	-3(2)	11(2)
C(12A)	37(2)	48(3)	37(2)	2(2)	-7(2)	16(2)
C(13A)	53(3)	24(2)	37(2)	3(2)	1(2)	-3(2)
C(14A)	27(2)	25(2)	24(2)	0(2)	-6(1)	-2(2)
C(15A)	59(3)	25(2)	31(2)	-5(2)	2(2)	1(2)
C(16A)	27(2)	24(2)	21(2)	-1(1)	-2(1)	2(2)
C(17A)	30(2)	30(2)	23(2)	0(2)	3(2)	1(2)
C(1B)	24(2)	26(2)	21(2)	2(1)	-1(1)	0(2)
C(2B)	21(2)	24(2)	19(2)	-1(1)	0(1)	-1(1)
C(3B)	24(2)	22(2)	19(2)	-2(1)	3(1)	1(1)
C(4B)	24(2)	29(2)	18(2)	-2(1)	-1(1)	1(2)
C(5B)	30(2)	26(2)	25(2)	-4(2)	1(2)	1(2)
C(6B)	46(3)	35(2)	26(2)	-10(2)	-1(2)	3(2)
C(7B)	42(2)	27(2)	22(2)	-2(2)	-4(2)	0(2)
C(8B)	49(3)	39(3)	28(2)	2(2)	-8(2)	7(2)
C(9B)	25(2)	22(2)	16(2)	1(1)	-3(1)	2(1)
C(10B)	31(2)	21(2)	24(2)	-2(1)	-1(2)	-4(2)
C(11B)	36(2)	25(2)	26(2)	-5(2)	2(2)	1(2)
C(12B)	34(2)	32(2)	26(2)	-5(2)	-6(2)	0(2)
C(13B)	41(2)	24(2)	32(2)	3(2)	-3(2)	-3(2)
C(14B)	28(2)	33(2)	25(2)	1(2)	4(2)	5(2)
C(15B)	45(3)	33(2)	52(3)	13(2)	2(2)	8(2)

C(16B)	30(2)	41(2)	21(2)	2(2)	0(2)	-2(2)
C(17B)	36(2)	59(3)	28(2)	11(2)	4(2)	1(2)
C(1C)	27(2)	23(2)	19(2)	4(1)	-3(1)	-1(1)
C(2C)	23(2)	21(2)	19(2)	3(1)	-3(1)	-1(1)
C(3C)	25(2)	21(2)	21(2)	1(1)	-2(1)	1(1)
C(4C)	21(2)	26(2)	20(2)	2(1)	-2(1)	2(1)
C(5C)	24(2)	25(2)	21(2)	2(1)	1(1)	-3(2)
C(6C)	33(2)	24(2)	30(2)	7(2)	6(2)	-1(2)
C(7C)	42(2)	28(2)	20(2)	3(2)	2(2)	5(2)
C(8C)	48(3)	43(3)	27(2)	-5(2)	5(2)	8(2)
C(9C)	22(2)	18(2)	23(2)	0(1)	-2(1)	1(1)
C(10C)	29(2)	16(2)	26(2)	3(1)	2(2)	-1(1)
C(11C)	32(2)	34(2)	34(2)	16(2)	-8(2)	-3(2)
C(12C)	45(3)	30(2)	25(2)	-2(2)	6(2)	1(2)
C(13C)	37(2)	25(2)	35(2)	0(2)	2(2)	-6(2)
C(14C)	80(4)	17(2)	29(2)	1(2)	12(2)	7(2)
C(15C)	191(10)	21(3)	49(3)	-4(2)	-9(5)	-1(4)
C(16C)	31(2)	23(2)	20(2)	1(1)	-1(1)	-2(2)
C(17C)	33(2)	35(2)	24(2)	-1(2)	-4(2)	-8(2)
C(1D)	26(2)	25(2)	23(2)	3(2)	-2(1)	0(2)
C(2D)	20(2)	23(2)	22(2)	2(1)	-1(1)	-3(1)
C(3D)	23(2)	20(2)	20(2)	2(1)	-1(1)	0(1)
C(4D)	25(2)	24(2)	25(2)	0(2)	1(1)	1(2)
C(5D)	37(2)	23(2)	26(2)	-1(2)	2(2)	1(2)
C(6D)	68(3)	21(2)	42(2)	-6(2)	14(2)	2(2)
C(7D)	32(2)	17(2)	23(2)	1(1)	2(2)	-3(2)
C(8D)	35(2)	32(2)	29(2)	4(2)	3(2)	-2(2)
C(9D)	21(2)	22(2)	22(2)	4(1)	3(1)	-1(1)
C(10D)	33(2)	20(2)	22(2)	4(1)	0(2)	3(2)
C(11D)	47(3)	28(2)	31(2)	-6(2)	-7(2)	3(2)
C(12D)	32(2)	35(2)	30(2)	-1(2)	6(2)	4(2)
C(13D)	46(3)	23(2)	33(2)	3(2)	-1(2)	3(2)
C(14D)	33(2)	24(2)	21(2)	3(1)	-5(2)	-5(2)
C(15D)	42(3)	29(2)	52(3)	18(2)	-3(2)	-2(2)
C(16D)	29(2)	35(2)	20(2)	-3(2)	0(1)	2(2)
C(17D)	30(2)	54(3)	23(2)	-9(2)	-3(2)	1(2)
N(1A)	22(2)	26(2)	23(1)	5(1)	2(1)	2(1)
N(1B)	24(2)	26(2)	22(1)	-2(1)	-2(1)	-5(1)
N(1C)	23(2)	23(2)	18(1)	4(1)	-5(1)	-2(1)
N(1D)	24(2)	25(2)	22(1)	0(1)	-3(1)	3(1)
O(1A)	32(1)	22(1)	21(1)	1(1)	-3(1)	-2(1)
O(2A)	28(1)	26(1)	23(1)	-2(1)	-1(1)	-2(1)
O(3A)	29(1)	22(1)	22(1)	-2(1)	4(1)	-3(1)
O(4A)	24(1)	28(1)	19(1)	1(1)	-2(1)	-2(1)
O(5A)	39(2)	36(2)	37(2)	-11(1)	-2(1)	4(1)
O(6A)	25(1)	35(2)	44(2)	7(1)	8(1)	3(1)
O(7A)	35(2)	31(2)	33(2)	3(1)	4(1)	-5(1)
O(8A)	29(2)	59(2)	29(1)	-14(2)	-4(1)	6(2)
O(1B)	33(2)	25(1)	24(1)	-3(1)	-2(1)	5(1)
O(2B)	26(1)	33(2)	25(1)	4(1)	-1(1)	1(1)
O(3B)	27(1)	24(1)	26(1)	0(1)	-1(1)	0(1)
O(4B)	30(1)	33(2)	20(1)	1(1)	3(1)	3(1)
O(5B)	48(2)	35(2)	34(2)	8(1)	-8(1)	-8(2)
O(6B)	26(1)	27(1)	21(1)	-2(1)	0(1)	-4(1)
O(7B)	24(1)	37(2)	27(1)	-2(1)	2(1)	6(1)
O(8B)	33(2)	75(3)	40(2)	24(2)	-2(1)	2(2)
O(1C)	31(1)	22(1)	18(1)	4(1)	3(1)	3(1)
O(2C)	30(1)	25(1)	22(1)	-1(1)	3(1)	1(1)
O(3C)	49(2)	21(1)	27(1)	-2(1)	-1(1)	-1(1)
O(4C)	23(1)	29(1)	17(1)	1(1)	-3(1)	2(1)
O(5C)	48(2)	29(2)	29(1)	-2(1)	-2(1)	-4(1)
O(6C)	27(2)	37(2)	35(2)	12(1)	-8(1)	-5(1)
O(7C)	74(3)	29(2)	38(2)	8(2)	4(2)	20(2)

O(8C)	31(2)	55(2)	25(1)	-10(1)	2(1)	-6(2)
O(1D)	37(2)	23(1)	27(1)	-2(1)	3(1)	-5(1)
O(2D)	25(1)	30(2)	24(1)	8(1)	1(1)	0(1)
O(3D)	25(1)	23(1)	25(1)	5(1)	-3(1)	1(1)
O(4D)	31(1)	32(2)	20(1)	-3(1)	-2(1)	-5(1)
O(5D)	39(2)	33(2)	33(2)	12(1)	3(1)	9(1)
O(6D)	24(1)	29(2)	25(1)	-1(1)	-3(1)	4(1)
O(7D)	26(1)	30(2)	28(1)	3(1)	-5(1)	-5(1)
O(8D)	30(2)	50(2)	28(1)	7(1)	0(1)	-4(1)
O(1)	32(5)	37(5)	36(5)	6(4)	2(4)	3(4)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for 07mz349m.

	x	y	z	U(eq)
H(1A)	-194	5240	4828	28
H(2A)	1706	4547	4043	26
H(3A)	-949	4253	4079	28
H(4A)	-1143	4752	3005	28
H(5A)	-1301	5607	3848	29
H(6A1)	-618	6629	3304	47
H(6A2)	-1213	6110	2758	47
H(6A3)	272	6180	2829	47
H(8A1)	2383	6707	5939	52
H(8A2)	3197	6172	5507	52
H(8A3)	2645	5934	6215	52
H(11A)	1601	3088	6518	52
H(11B)	571	3475	6064	52
H(11C)	1863	3858	6240	52
H(12A)	3414	2522	6017	61
H(12B)	3880	3289	5817	61
H(12C)	3789	2690	5258	61
H(13A)	1629	2276	4852	57
H(13B)	415	2587	5206	57
H(13C)	1343	2086	5618	57
H(15A)	-230	2033	3493	57
H(15B)	1048	2452	3390	57
H(15C)	-54	2517	2845	57
H(17A)	1592	4517	1374	41
H(17B)	1984	3988	1963	41
H(17C)	2340	4798	2020	41
H(1B)	6143	5714	4144	28
H(2B)	4577	4842	4977	25
H(3B)	7239	4787	4786	26
H(4B)	7387	5174	5922	28
H(5B)	7277	6083	5114	32
H(6B1)	6510	7002	5760	54
H(6B2)	7223	6469	6250	54
H(6B3)	5729	6472	6214	54
H(8B1)	3143	6760	2922	58
H(8B2)	2488	6358	3529	58
H(8B3)	3008	5927	2902	58
H(11D)	6407	3221	2317	44
H(11E)	7437	3535	2822	44
H(11F)	6600	4048	2370	44
H(12D)	4151	3369	2547	46
H(12E)	4281	4196	2644	46
H(12F)	3705	3727	3230	46

H(13D)	5040	2974	3933	49
H(13E)	6515	2930	3815	49
H(13F)	5571	2561	3298	49
H(15D)	7892	2672	5426	65
H(15E)	6469	2841	5604	65
H(15F)	7537	2925	6166	65
H(17D)	4598	4260	7342	62
H(17E)	3841	4580	6717	62
H(17F)	4372	5085	7294	62
H(1C)	4827	4688	9127	27
H(2C)	6677	5446	9912	25
H(3C)	4020	5693	9822	27
H(4C)	3862	5251	10920	27
H(5C)	3721	4364	10107	28
H(6C1)	4374	3377	10703	43
H(6C2)	3811	3928	11223	43
H(6C3)	5292	3840	11161	43
H(8C1)	7372	3396	7859	59
H(8C2)	8056	3437	8576	59
H(8C3)	8057	4101	8088	59
H(11G)	6094	7037	7510	50
H(11H)	5421	7065	8223	50
H(11I)	5535	6339	7830	50
H(12G)	7586	5716	7778	50
H(12H)	8826	6090	8055	50
H(12I)	8126	6388	7401	50
H(13G)	8717	7236	8608	48
H(13H)	7406	7620	8715	48
H(13I)	7996	7578	7981	48
H(15G)	4343	7929	10359	131
H(15H)	5704	7616	10507	131
H(15I)	4576	7441	11001	131
H(17G)	6931	6053	11995	46
H(17H)	7388	5260	11920	46
H(17I)	6635	5496	12572	46
H(1D)	1151	4172	9905	29
H(2D)	-403	4935	8960	26
H(3D)	2248	5031	9184	25
H(4D)	2463	4534	8105	30
H(5D)	2354	3734	9007	34
H(6D1)	1688	2718	8464	65
H(6D2)	2451	3190	7947	65
H(6D3)	958	3168	7908	65
H(8D1)	-2234	3104	10674	48
H(8D2)	-2438	3932	10643	48
H(8D3)	-1785	3585	11288	48
H(11J)	1595	5982	11543	53
H(11K)	1428	6812	11499	53
H(11L)	2438	6428	11041	53
H(12J)	-1313	6172	10654	48
H(12K)	-841	6560	11322	48
H(12L)	-671	5733	11248	48
H(13J)	1418	7025	10043	51
H(13K)	359	7358	10506	51
H(13L)	-26	6884	9875	51
H(15J)	2852	7070	8335	61
H(15K)	1447	6867	8131	61
H(15L)	2558	6728	7616	61
H(17J)	-769	5321	6865	53
H(17K)	-923	4505	7022	53
H(17L)	-109	4754	6396	53
H(1A1)	424	3978	5132	28
H(1B1)	4411	4144	4119	29

H(1C1)	5375	5982	8803	26
H(1D1)	-579	5720	9754	28
H(1E)	1750(70)	2890(60)	10000(90)	53
H(1F)	2320(130)	2260(30)	9840(90)	53

Table 6. Torsion angles [deg] for 07mz349m

O(1A)-C(1A)-C(2A)-N(1A)	178.0(3)
O(2A)-C(1A)-C(2A)-N(1A)	62.5(4)
O(1A)-C(1A)-C(2A)-C(3A)	-60.9(4)
O(2A)-C(1A)-C(2A)-C(3A)	-176.5(3)
N(1A)-C(2A)-C(3A)-O(3A)	-65.8(4)
C(1A)-C(2A)-C(3A)-O(3A)	173.1(3)
N(1A)-C(2A)-C(3A)-C(4A)	176.1(3)
C(1A)-C(2A)-C(3A)-C(4A)	54.9(4)
O(3A)-C(3A)-C(4A)-O(4A)	-50.6(4)
C(2A)-C(3A)-C(4A)-O(4A)	67.9(4)
O(3A)-C(3A)-C(4A)-C(5A)	-170.0(3)
C(2A)-C(3A)-C(4A)-C(5A)	-51.5(4)
O(4A)-C(4A)-C(5A)-O(1A)	-65.9(4)
C(3A)-C(4A)-C(5A)-O(1A)	51.9(4)
O(4A)-C(4A)-C(5A)-C(6A)	53.4(4)
C(3A)-C(4A)-C(5A)-C(6A)	171.2(3)
O(6A)-C(9A)-C(10A)-C(11A)	142.3(4)
N(1A)-C(9A)-C(10A)-C(11A)	-40.1(5)
O(6A)-C(9A)-C(10A)-C(12A)	21.7(5)
N(1A)-C(9A)-C(10A)-C(12A)	-160.7(4)
O(6A)-C(9A)-C(10A)-C(13A)	-96.9(5)
N(1A)-C(9A)-C(10A)-C(13A)	80.8(4)
O(2B)-C(1B)-C(2B)-N(1B)	56.9(4)
O(1B)-C(1B)-C(2B)-N(1B)	173.2(3)
O(2B)-C(1B)-C(2B)-C(3B)	-178.2(3)
O(1B)-C(1B)-C(2B)-C(3B)	-61.9(4)
N(1B)-C(2B)-C(3B)-O(3B)	-54.9(4)
C(1B)-C(2B)-C(3B)-O(3B)	179.4(3)
N(1B)-C(2B)-C(3B)-C(4B)	-176.3(3)
C(1B)-C(2B)-C(3B)-C(4B)	58.0(4)
O(3B)-C(3B)-C(4B)-O(4B)	-56.4(4)
C(2B)-C(3B)-C(4B)-O(4B)	62.6(4)
O(3B)-C(3B)-C(4B)-C(5B)	-174.3(3)
C(2B)-C(3B)-C(4B)-C(5B)	-55.4(4)
O(4B)-C(4B)-C(5B)-O(1B)	-63.2(4)
C(3B)-C(4B)-C(5B)-O(1B)	54.8(4)
O(4B)-C(4B)-C(5B)-C(6B)	56.7(4)
C(3B)-C(4B)-C(5B)-C(6B)	174.7(4)
O(6B)-C(9B)-C(10B)-C(11B)	-5.9(5)
N(1B)-C(9B)-C(10B)-C(11B)	175.2(3)
O(6B)-C(9B)-C(10B)-C(12B)	-126.7(4)
N(1B)-C(9B)-C(10B)-C(12B)	54.3(4)
O(6B)-C(9B)-C(10B)-C(13B)	112.7(4)
N(1B)-C(9B)-C(10B)-C(13B)	-66.2(4)
O(1C)-C(1C)-C(2C)-N(1C)	177.3(3)
O(2C)-C(1C)-C(2C)-N(1C)	61.1(4)
O(1C)-C(1C)-C(2C)-C(3C)	-60.4(4)
O(2C)-C(1C)-C(2C)-C(3C)	-176.6(3)
N(1C)-C(2C)-C(3C)-O(3C)	-64.8(4)
C(1C)-C(2C)-C(3C)-O(3C)	173.9(3)
N(1C)-C(2C)-C(3C)-C(4C)	176.2(3)
C(1C)-C(2C)-C(3C)-C(4C)	54.9(4)
O(3C)-C(3C)-C(4C)-O(4C)	-53.1(4)
C(2C)-C(3C)-C(4C)-O(4C)	67.2(4)

O(3C)-C(3C)-C(4C)-C(5C)	-172.7(3)
C(2C)-C(3C)-C(4C)-C(5C)	-52.3(4)
O(4C)-C(4C)-C(5C)-O(1C)	-64.9(4)
C(3C)-C(4C)-C(5C)-O(1C)	52.7(4)
O(4C)-C(4C)-C(5C)-C(6C)	55.1(4)
C(3C)-C(4C)-C(5C)-C(6C)	172.8(3)
O(6C)-C(9C)-C(10C)-C(13C)	-42.5(5)
N(1C)-C(9C)-C(10C)-C(13C)	140.1(4)
O(6C)-C(9C)-C(10C)-C(12C)	75.1(5)
N(1C)-C(9C)-C(10C)-C(12C)	-102.3(4)
O(6C)-C(9C)-C(10C)-C(11C)	-165.2(4)
N(1C)-C(9C)-C(10C)-C(11C)	17.4(5)
O(2D)-C(1D)-C(2D)-N(1D)	59.4(4)
O(1D)-C(1D)-C(2D)-N(1D)	175.0(3)
O(2D)-C(1D)-C(2D)-C(3D)	-175.9(3)
O(1D)-C(1D)-C(2D)-C(3D)	-60.3(4)
N(1D)-C(2D)-C(3D)-O(3D)	-55.2(4)
C(1D)-C(2D)-C(3D)-O(3D)	179.7(3)
N(1D)-C(2D)-C(3D)-C(4D)	-177.8(3)
C(1D)-C(2D)-C(3D)-C(4D)	57.1(4)
O(3D)-C(3D)-C(4D)-O(4D)	-56.9(4)
C(2D)-C(3D)-C(4D)-O(4D)	62.8(4)
O(3D)-C(3D)-C(4D)-C(5D)	-175.1(3)
C(2D)-C(3D)-C(4D)-C(5D)	-55.3(4)
O(4D)-C(4D)-C(5D)-O(1D)	-63.3(4)
C(3D)-C(4D)-C(5D)-O(1D)	55.6(4)
O(4D)-C(4D)-C(5D)-C(6D)	57.8(5)
C(3D)-C(4D)-C(5D)-C(6D)	176.6(4)
O(6D)-C(9D)-C(10D)-C(11D)	-3.9(5)
N(1D)-C(9D)-C(10D)-C(11D)	176.0(3)
O(6D)-C(9D)-C(10D)-C(13D)	115.9(4)
N(1D)-C(9D)-C(10D)-C(13D)	-64.2(5)
O(6D)-C(9D)-C(10D)-C(12D)	-123.7(4)
N(1D)-C(9D)-C(10D)-C(12D)	56.2(4)
O(6A)-C(9A)-N(1A)-C(2A)	-0.7(6)
C(10A)-C(9A)-N(1A)-C(2A)	-178.4(3)
C(1A)-C(2A)-N(1A)-C(9A)	-126.2(4)
C(3A)-C(2A)-N(1A)-C(9A)	115.1(4)
O(6B)-C(9B)-N(1B)-C(2B)	-6.4(6)
C(10B)-C(9B)-N(1B)-C(2B)	172.5(3)
C(3B)-C(2B)-N(1B)-C(9B)	-56.9(5)
C(1B)-C(2B)-N(1B)-C(9B)	64.8(5)
O(6C)-C(9C)-N(1C)-C(2C)	-6.9(6)
C(10C)-C(9C)-N(1C)-C(2C)	170.4(3)
C(3C)-C(2C)-N(1C)-C(9C)	123.5(4)
C(1C)-C(2C)-N(1C)-C(9C)	-116.8(4)
O(6D)-C(9D)-N(1D)-C(2D)	-5.2(6)
C(10D)-C(9D)-N(1D)-C(2D)	174.8(3)
C(3D)-C(2D)-N(1D)-C(9D)	-57.1(5)
C(1D)-C(2D)-N(1D)-C(9D)	64.4(5)
O(2A)-C(1A)-O(1A)-C(5A)	-178.1(3)
C(2A)-C(1A)-O(1A)-C(5A)	65.0(4)
C(6A)-C(5A)-O(1A)-C(1A)	177.0(3)
C(4A)-C(5A)-O(1A)-C(1A)	-59.7(4)
O(5A)-C(7A)-O(2A)-C(1A)	8.0(6)
C(8A)-C(7A)-O(2A)-C(1A)	-173.3(3)
O(1A)-C(1A)-O(2A)-C(7A)	86.0(4)
C(2A)-C(1A)-O(2A)-C(7A)	-155.2(3)
O(7A)-C(14A)-O(3A)-C(3A)	2.8(6)
C(15A)-C(14A)-O(3A)-C(3A)	-177.0(3)
C(4A)-C(3A)-O(3A)-C(14A)	-134.6(3)
C(2A)-C(3A)-O(3A)-C(14A)	104.6(4)
O(8A)-C(16A)-O(4A)-C(4A)	12.9(6)

C(17A)-C(16A)-O(4A)-C(4A)	-167.3(3)
C(3A)-C(4A)-O(4A)-C(16A)	111.6(3)
C(5A)-C(4A)-O(4A)-C(16A)	-129.1(3)
O(2B)-C(1B)-O(1B)-C(5B)	-178.9(3)
C(2B)-C(1B)-O(1B)-C(5B)	64.6(4)
C(6B)-C(5B)-O(1B)-C(1B)	176.6(3)
C(4B)-C(5B)-O(1B)-C(1B)	-60.6(4)
O(5B)-C(7B)-O(2B)-C(1B)	-0.4(6)
C(8B)-C(7B)-O(2B)-C(1B)	177.1(4)
O(1B)-C(1B)-O(2B)-C(7B)	95.0(4)
C(2B)-C(1B)-O(2B)-C(7B)	-147.2(3)
O(7B)-C(14B)-O(3B)-C(3B)	1.2(5)
C(15B)-C(14B)-O(3B)-C(3B)	-177.7(3)
C(4B)-C(3B)-O(3B)-C(14B)	-81.6(4)
C(2B)-C(3B)-O(3B)-C(14B)	158.0(3)
O(8B)-C(16B)-O(4B)-C(4B)	2.0(7)
C(17B)-C(16B)-O(4B)-C(4B)	-178.2(4)
C(5B)-C(4B)-O(4B)-C(16B)	-142.8(4)
C(3B)-C(4B)-O(4B)-C(16B)	98.6(4)
O(2C)-C(1C)-O(1C)-C(5C)	-178.0(3)
C(2C)-C(1C)-O(1C)-C(5C)	64.1(4)
C(6C)-C(5C)-O(1C)-C(1C)	176.6(3)
C(4C)-C(5C)-O(1C)-C(1C)	-59.7(4)
O(5C)-C(7C)-O(2C)-C(1C)	7.9(6)
C(8C)-C(7C)-O(2C)-C(1C)	-172.7(3)
O(1C)-C(1C)-O(2C)-C(7C)	84.9(4)
C(2C)-C(1C)-O(2C)-C(7C)	-156.1(3)
O(7C)-C(14C)-O(3C)-C(3C)	-3.8(7)
C(15C)-C(14C)-O(3C)-C(3C)	175.9(5)
C(2C)-C(3C)-O(3C)-C(14C)	101.5(4)
C(4C)-C(3C)-O(3C)-C(14C)	-137.5(4)
O(8C)-C(16C)-O(4C)-C(4C)	12.0(6)
C(17C)-C(16C)-O(4C)-C(4C)	-167.4(3)
C(5C)-C(4C)-O(4C)-C(16C)	-122.2(3)
C(3C)-C(4C)-O(4C)-C(16C)	118.0(3)
O(2D)-C(1D)-O(1D)-C(5D)	-179.1(3)
C(2D)-C(1D)-O(1D)-C(5D)	64.3(4)
C(6D)-C(5D)-O(1D)-C(1D)	174.0(4)
C(4D)-C(5D)-O(1D)-C(1D)	-61.6(4)
O(5D)-C(7D)-O(2D)-C(1D)	-1.3(6)
C(8D)-C(7D)-O(2D)-C(1D)	178.8(3)
O(1D)-C(1D)-O(2D)-C(7D)	92.5(4)
C(2D)-C(1D)-O(2D)-C(7D)	-149.8(3)
O(7D)-C(14D)-O(3D)-C(3D)	0.2(5)
C(15D)-C(14D)-O(3D)-C(3D)	-179.2(3)
C(4D)-C(3D)-O(3D)-C(14D)	-78.9(4)
C(2D)-C(3D)-O(3D)-C(14D)	159.1(3)
O(8D)-C(16D)-O(4D)-C(4D)	0.0(6)
C(17D)-C(16D)-O(4D)-C(4D)	179.2(3)
C(3D)-C(4D)-O(4D)-C(16D)	94.0(4)
C(5D)-C(4D)-O(4D)-C(16D)	-147.5(3)

Table 7. Hydrogen bonds for 07mz349m [Å and deg].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1F)...O(6C)#1	0.84(2)	2.58(15)	3.174(10)	129(15)
O(1)-H(1E)...O(5D)	0.84(2)	2.23(8)	3.006(10)	155(17)
N(1D)-H(1D1)...O(6C)#2	0.88	1.99	2.827(5)	158.4
N(1C)-H(1C1)...O(7D)	0.88	2.16	2.965(4)	151.5
N(1B)-H(1B1)...O(6A)	0.88	2.02	2.842(5)	154.4

N(1A)-H(1A1)...O(7B)#2	0.88	2.15	2.970(4)	155.0

Symmetry transformations used to generate equivalent atoms:

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

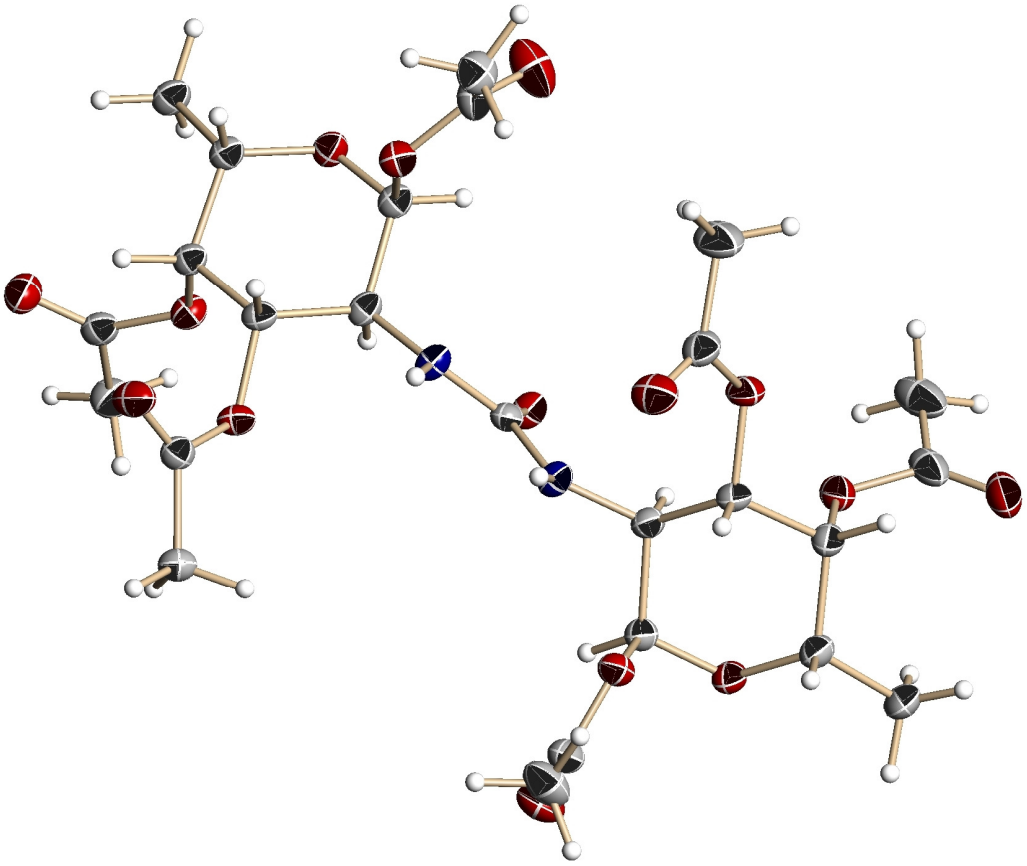


Figure 133 :
Crystallographic refinement of bis(1,3,4-tri-*O*-acetyl-α-L-fucos-2-yl) urea (**15**)

Table 1. Crystal data and structure refinement for 07mz346m:

Identification code: 07mz346m
Empirical formula: C75 H112.70 N6 O47.35
Moiety formula: 3(C25 H36 N2 O15), 2.35(H2 O)
Formula weight: 1856.01
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Monoclinic
Space group: C2
Unit cell dimensions:
a = 29.0725(19) Å, α = 90°
b = 7.5580(5) Å, β = 102.6650(10)°
c = 21.3782(14) Å, γ = 90°
Volume, Z: 4583.1(5) Å^3, 2
Density (calculated): 1.345 Mg/m^3
Absorption coefficient: 0.113 mm^{-1}
F(000): 1967
Crystal size: 0.60 × 0.40 × 0.28 mm
Crystal shape, colour: block, colourless
θ range for data collection: 1.44 to 28.28°
Limiting indices: −38 ≤ h ≤ 37, −10 ≤ k ≤ 7, −23 ≤ l ≤ 28
Reflections collected: 13831
Independent reflections: 6084 (R(int) = 0.0196)
Completeness to θ = 28.28°: 99.8 %
Absorption correction: multi-scan
Max. and min. transmission: 0.969 and 0.900
Refinement method: Full-matrix least-squares on F^2
Data / restraints / parameters: 6084 / 13 / 631
Goodness-of-fit on F^2: 1.057
Final R indices [I>2σ(I)]: R1 = 0.0404, wR2 = 0.0977
R indices (all data): R1 = 0.0447, wR2 = 0.1016
Largest diff. peak and hole: 0.555 and −0.225 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 > 2σ(F^2) is used only for calculating R-factors

Comments:
One of the two independent molecules is located on a two fold axis. The urea group of this molecule is also disordered over two positions by a slight shift along the C=O bond axis. This disorder is induced by a disorder of solvate

water molecules neighboring the urea group with either two or three water molecules filling the void between the sugar molecules. The occupancy ratio is 0.65(1) to 0.35(1) in favor of the site with only two water molecules. Equivalent bond distances within the disordered urea moieties were restrained to be the same within a standard deviation of 0.02 Å, and the ADPs of equivalent atoms were set to be identical.

Treatment of hydrogen atoms:
Water and not disordered urea hydrogen atoms were located in difference density Fourier maps and the O–H and N–H distances were restrained to be 0.84(2) and 0.88(2) Å, respectively. H...H distances in the water molecules were restrained to be 1.45(2) Å. All other hydrogen atoms were placed in calculated positions and all H atoms were refined with an isotropic displacement parameter 1.5 (methyl, water) or 1.2 times (all others) that of the adjacent carbon, oxygen or nitrogen atom. Methyl H atoms were allowed to rotate to best fit the experimental electron density.

Table 2. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [$Å^2$ × 10^3] for 07mz346m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	7095(1)	1126(3)	5989(1)	22(1)
C(2)	7446(1)	2149(3)	6493(1)	22(1)
C(3)	7181(1)	3638(3)	6749(1)	23(1)
C(4)	6803(1)	2790(3)	7042(1)	25(1)
C(5)	6466(1)	1741(3)	6524(1)	26(1)
C(6)	6098(1)	709(4)	6771(1)	33(1)
C(7)	6780(1)	1698(4)	4873(1)	28(1)
C(8)	6612(1)	3118(4)	4388(1)	41(1)
C(9)	8286(1)	2112(3)	6517(1)	21(1)
C(10)	7672(1)	6152(4)	7042(1)	30(1)
C(11)	7990(1)	7058(4)	7594(1)	43(1)
C(12)	6901(1)	1538(4)	8101(1)	36(1)
C(13)	7273(1)	706(4)	8609(1)	45(1)
C(14)	9406(1)	3061(3)	7136(1)	23(1)
C(15)	9115(1)	2322(3)	6509(1)	22(1)
C(16)	9369(1)	2653(3)	5967(1)	21(1)
C(17)	9863(1)	1866(3)	6140(1)	21(1)
C(18)	10129(1)	2550(3)	6792(1)	23(1)
C(19)	10590(1)	1589(4)	7045(1)	27(1)
C(20)	9357(1)	5966(4)	7572(1)	32(1)
C(21)	9298(1)	7877(4)	7401(1)	33(1)
C(22)	9057(1)	2623(3)	4837(1)	23(1)
C(23)	8678(1)	1756(3)	4339(1)	25(1)
C(24)	10075(1)	−1034(3)	5850(1)	25(1)
C(25)	9915(1)	−2921(4)	5820(1)	31(1)
O(1)	6718(1)	471(2)	6224(1)	25(1)
O(2)	6927(1)	2377(2)	5467(1)	25(1)
O(4)	7494(1)	4633(2)	7239(1)	27(1)
O(5)	7054(1)	1650(3)	7545(1)	28(1)
O(6)	6788(1)	140(3)	4760(1)	38(1)

O(7)	8352(1)	816(2)	6868(1)	25(1)
O(8)	7583(1)	6655(3)	6495(1)	37(1)
O(9)	6529(1)	2086(3)	8161(1)	45(1)
O(10)	9859(1)	2352(2)	7283(1)	24(1)
O(11)	9414(1)	4969(2)	7065(1)	25(1)
N(1)	7844(1)	2758(3)	6251(1)	23(1)
N(2)	8644(1)	3055(3)	6359(1)	23(1)
O(13)	9083(1)	1821(2)	5411(1)	23(1)
O(14)	9804(1)	-29(2)	6150(1)	23(1)
O(15)	9358(1)	5337(3)	8092(1)	49(1)
O(16)	9304(1)	3838(3)	4759(1)	32(1)
O(17)	10396(1)	-466(3)	5637(1)	32(1)
C(26)	5678(1)	5110(4)	8821(1)	32(1)
C(27)	5673(1)	5860(5)	9484(1)	38(1)
C(28)	6152(1)	5528(4)	9931(1)	33(1)
C(29)	6550(1)	6228(3)	9640(1)	27(1)
C(30)	6510(1)	5450(3)	8976(1)	25(1)
C(31A)	6860(1)	6204(4)	8620(1)	36(1)
C(32)	5536(1)	2190(4)	8371(1)	33(1)
C(33)	5575(1)	278(4)	8540(1)	41(1)
C(35)	6411(1)	5790(5)	11060(1)	46(1)
C(36)	6432(2)	7021(7)	11613(1)	67(1)
C(37)	6808(1)	9121(4)	10031(1)	41(1)
C(38)	6658(1)	11015(4)	10005(1)	46(1)
O(18)	6051(1)	5776(3)	8577(1)	29(1)
O(19)	5709(1)	3213(3)	8897(1)	34(1)
O(21)	6152(1)	6481(3)	10517(1)	43(1)
O(22)	6506(1)	8136(2)	9595(1)	31(1)
O(23)	5369(1)	2804(3)	7850(1)	40(1)
O(25)	6621(1)	4422(4)	11071(1)	61(1)
O(26)	7144(1)	8515(3)	10395(1)	78(1)
N(3)	5293(6)	4961(18)	9700(9)	48(2)
C(34)	5000	5924(16)	10000	41(3)
O(24)	5000	7563(17)	10000	46(3)
O(29)	4478(2)	1193(8)	9543(2)	63(2)
N(3B)	5302(11)	5250(40)	9795(18)	48(2)
C(34B)	5000	6410(50)	10000	41(3)
O(24B)	5000	8030(50)	10000	46(3)
O(27)	5000	1984(18)	10000	86(6)
O(28)	4353(4)	-38(18)	9370(5)	81(4)

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

Table 3. Bond lengths [Å] and angles [deg] for 07mz346m.

C(1)-O(1)	1.393(3)
C(1)-O(2)	1.461(3)
C(1)-C(2)	1.524(3)
C(1)-H(1)	1.0000
C(2)-N(1)	1.441(3)
C(2)-C(3)	1.531(3)

C(2)-H(2)	1.0000
C(3)-O(4)	1.439(3)
C(3)-C(4)	1.521(3)
C(3)-H(3)	1.0000
C(4)-O(5)	1.445(3)
C(4)-C(5)	1.529(3)
C(4)-H(4)	1.0000
C(5)-O(1)	1.440(3)
C(5)-C(6)	1.510(3)
C(5)-H(5)	1.0000
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-O(6)	1.203(3)
C(7)-O(2)	1.350(3)
C(7)-C(8)	1.497(4)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-O(7)	1.223(3)
C(9)-N(2)	1.364(3)
C(9)-N(1)	1.375(3)
C(10)-O(8)	1.204(3)
C(10)-O(4)	1.363(3)
C(10)-C(11)	1.495(4)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-O(9)	1.191(4)
C(12)-O(5)	1.360(3)
C(12)-C(13)	1.494(4)
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-O(10)	1.394(3)
C(14)-O(11)	1.451(3)
C(14)-C(15)	1.526(3)
C(14)-H(14)	1.0000
C(15)-N(2)	1.449(3)
C(15)-C(16)	1.524(3)
C(15)-H(15)	1.0000
C(16)-O(13)	1.438(2)
C(16)-C(17)	1.523(3)
C(16)-H(16)	1.0000
C(17)-O(14)	1.444(3)
C(17)-C(18)	1.527(3)
C(17)-H(17)	1.0000
C(18)-O(10)	1.450(2)
C(18)-C(19)	1.516(3)
C(18)-H(18)	1.0000
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-O(15)	1.209(3)
C(20)-O(11)	1.360(3)
C(20)-C(21)	1.491(4)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-O(16)	1.199(3)
C(22)-O(13)	1.355(3)
C(22)-C(23)	1.505(3)
C(23)-H(23A)	0.9800

C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-O(17)	1.206(3)
C(24)-O(14)	1.352(3)
C(24)-C(25)	1.497(4)
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
N(1)-H(1A)	0.868(18)
N(2)-H(2A)	0.856(18)
C(26)-O(18)	1.395(3)
C(26)-O(19)	1.444(4)
C(26)-C(27)	1.529(4)
C(26)-H(26)	1.0000
C(27)-N(3)	1.456(8)
C(27)-N(3B)	1.460(14)
C(27)-C(28)	1.528(4)
C(27)-H(27)	1.0000
C(28)-O(21)	1.445(3)
C(28)-C(29)	1.524(3)
C(28)-H(28)	1.0000
C(29)-O(22)	1.449(3)
C(29)-C(30)	1.518(3)
C(29)-H(29)	1.0000
C(30)-O(18)	1.439(3)
C(30)-C(31A)	1.509(3)
C(30)-H(30)	1.0000
C(31A)-H(31A)	0.9800
C(31A)-H(31B)	0.9800
C(31A)-H(31C)	0.9800
C(32)-O(23)	1.205(3)
C(32)-O(19)	1.367(3)
C(32)-C(33)	1.487(5)
C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800
C(35)-O(25)	1.198(4)
C(35)-O(21)	1.344(3)
C(35)-C(36)	1.494(5)
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800
C(37)-O(26)	1.199(4)
C(37)-O(22)	1.354(3)
C(37)-C(38)	1.493(4)
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800
N(3)-C(34)	1.382(8)
N(3)-H(3A)	0.8800
C(34)-O(24)	1.238(10)
C(34)-N(3)#1	1.382(8)
O(29)-H(29A)	0.83(2)
O(29)-H(29B)	0.86(2)
N(3B)-C(34B)	1.377(16)
N(3B)-H(3B)	0.8800
C(34B)-O(24B)	1.226(16)
C(34B)-N(3B)#1	1.377(17)
O(27)-H(27A)	0.85(2)
O(28)-H(28A)	0.86(2)
O(28)-H(28B)	0.86(2)

O(1)-C(1)-O(2)	110.36(17)

O(1)-C(1)-C(2)	112.53(17)
O(2)-C(1)-C(2)	105.77(18)
O(1)-C(1)-H(1)	109.4
O(2)-C(1)-H(1)	109.4
C(2)-C(1)-H(1)	109.4
N(1)-C(2)-C(1)	111.95(17)
N(1)-C(2)-C(3)	113.51(19)
C(1)-C(2)-C(3)	108.32(17)
N(1)-C(2)-H(2)	107.6
C(1)-C(2)-H(2)	107.6
C(3)-C(2)-H(2)	107.6
O(4)-C(3)-C(4)	108.59(17)
O(4)-C(3)-C(2)	110.91(17)
C(4)-C(3)-C(2)	107.62(19)
O(4)-C(3)-H(3)	109.9
C(4)-C(3)-H(3)	109.9
C(2)-C(3)-H(3)	109.9
O(5)-C(4)-C(3)	105.39(17)
O(5)-C(4)-C(5)	111.6(2)
C(3)-C(4)-C(5)	109.05(17)
O(5)-C(4)-H(4)	110.2
C(3)-C(4)-H(4)	110.2
C(5)-C(4)-H(4)	110.2
O(1)-C(5)-C(6)	106.2(2)
O(1)-C(5)-C(4)	111.19(17)
C(6)-C(5)-C(4)	113.92(19)
O(1)-C(5)-H(5)	108.4
C(6)-C(5)-H(5)	108.4
C(4)-C(5)-H(5)	108.4
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
O(6)-C(7)-O(2)	123.0(2)
O(6)-C(7)-C(8)	125.5(2)
O(2)-C(7)-C(8)	111.5(2)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
O(7)-C(9)-N(2)	122.99(19)
O(7)-C(9)-N(1)	123.0(2)
N(2)-C(9)-N(1)	114.0(2)
O(8)-C(10)-O(4)	123.4(2)
O(8)-C(10)-C(11)	125.9(2)
O(4)-C(10)-C(11)	110.7(2)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
O(9)-C(12)-O(5)	123.6(3)
O(9)-C(12)-C(13)	126.6(2)
O(5)-C(12)-C(13)	109.8(2)
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5

H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
O(10)-C(14)-O(11)	111.64(18)
O(10)-C(14)-C(15)	111.75(18)
O(11)-C(14)-C(15)	106.89(18)
O(10)-C(14)-H(14)	108.8
O(11)-C(14)-H(14)	108.8
C(15)-C(14)-H(14)	108.8
N(2)-C(15)-C(16)	111.22(17)
N(2)-C(15)-C(14)	111.63(18)
C(16)-C(15)-C(14)	109.97(17)
N(2)-C(15)-H(15)	108.0
C(16)-C(15)-H(15)	108.0
C(14)-C(15)-H(15)	108.0
O(13)-C(16)-C(17)	111.95(18)
O(13)-C(16)-C(15)	105.56(16)
C(17)-C(16)-C(15)	109.81(17)
O(13)-C(16)-H(16)	109.8
C(17)-C(16)-H(16)	109.8
C(15)-C(16)-H(16)	109.8
O(14)-C(17)-C(16)	106.35(17)
O(14)-C(17)-C(18)	111.14(18)
C(16)-C(17)-C(18)	110.55(18)
O(14)-C(17)-H(17)	109.6
C(16)-C(17)-H(17)	109.6
C(18)-C(17)-H(17)	109.6
O(10)-C(18)-C(19)	105.56(17)
O(10)-C(18)-C(17)	112.36(17)
C(19)-C(18)-C(17)	113.21(19)
O(10)-C(18)-H(18)	108.5
C(19)-C(18)-H(18)	108.5
C(17)-C(18)-H(18)	108.5
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
O(15)-C(20)-O(11)	122.6(3)
O(15)-C(20)-C(21)	125.7(3)
O(11)-C(20)-C(21)	111.6(2)
C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
O(16)-C(22)-O(13)	123.5(2)
O(16)-C(22)-C(23)	127.1(2)
O(13)-C(22)-C(23)	109.42(19)
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
O(17)-C(24)-O(14)	124.0(2)
O(17)-C(24)-C(25)	125.6(2)
O(14)-C(24)-C(25)	110.34(19)
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5

H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(1)-O(1)-C(5)	116.12(18)
C(7)-O(2)-C(1)	117.13(19)
C(10)-O(4)-C(3)	115.94(18)
C(12)-O(5)-C(4)	118.6(2)
C(14)-O(10)-C(18)	115.61(16)
C(20)-O(11)-C(14)	117.31(19)
C(9)-N(1)-C(2)	119.22(18)
C(9)-N(1)-H(1A)	118.1(19)
C(2)-N(1)-H(1A)	120.0(19)
C(9)-N(2)-C(15)	118.85(19)
C(9)-N(2)-H(2A)	118.4(19)
C(15)-N(2)-H(2A)	119.4(19)
C(22)-O(13)-C(16)	117.40(17)
C(24)-O(14)-C(17)	117.82(18)
O(18)-C(26)-O(19)	111.5(2)
O(18)-C(26)-C(27)	112.2(2)
O(19)-C(26)-C(27)	106.0(2)
O(18)-C(26)-H(26)	109.0
O(19)-C(26)-H(26)	109.0
C(27)-C(26)-H(26)	109.0
N(3)-C(27)-C(28)	112.0(9)
N(3B)-C(27)-C(28)	109.0(18)
N(3)-C(27)-C(26)	106.5(6)
N(3B)-C(27)-C(26)	117.6(13)
C(28)-C(27)-C(26)	109.1(2)
N(3)-C(27)-H(27)	109.7
N(3B)-C(27)-H(27)	101.3
C(28)-C(27)-H(27)	109.7
C(26)-C(27)-H(27)	109.7
O(21)-C(28)-C(29)	109.1(2)
O(21)-C(28)-C(27)	106.7(2)
C(29)-C(28)-C(27)	110.9(2)
O(21)-C(28)-H(28)	110.1
C(29)-C(28)-H(28)	110.1
C(27)-C(28)-H(28)	110.1
O(22)-C(29)-C(30)	109.6(2)
O(22)-C(29)-C(28)	108.0(2)
C(30)-C(29)-C(28)	109.8(2)
O(22)-C(29)-H(29)	109.8
C(30)-C(29)-H(29)	109.8
C(28)-C(29)-H(29)	109.8
O(18)-C(30)-C(31A)	106.11(19)
O(18)-C(30)-C(29)	111.01(19)
C(31A)-C(30)-C(29)	113.8(2)
O(18)-C(30)-H(30)	108.6
C(31A)-C(30)-H(30)	108.6
C(29)-C(30)-H(30)	108.6
C(30)-C(31A)-H(31A)	109.5
C(30)-C(31A)-H(31B)	109.5
H(31A)-C(31A)-H(31B)	109.5
C(30)-C(31A)-H(31C)	109.5
H(31A)-C(31A)-H(31C)	109.5
H(31B)-C(31A)-H(31C)	109.5
O(23)-C(32)-O(19)	122.8(3)
O(23)-C(32)-C(33)	126.3(3)
O(19)-C(32)-C(33)	110.8(2)
C(32)-C(33)-H(33A)	109.5
C(32)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
C(32)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5

H(33B)-C(33)-H(33C)	109.5
O(25)-C(35)-O(21)	122.6(3)
O(25)-C(35)-C(36)	126.2(3)
O(21)-C(35)-C(36)	111.0(3)
C(35)-C(36)-H(36A)	109.5
C(35)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(35)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
O(26)-C(37)-O(22)	123.3(3)
O(26)-C(37)-C(38)	125.4(3)
O(22)-C(37)-C(38)	111.3(2)
C(37)-C(38)-H(38A)	109.5
C(37)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
C(37)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(26)-O(18)-C(30)	114.41(18)
C(32)-O(19)-C(26)	117.8(2)
C(35)-O(21)-C(28)	116.6(2)
C(37)-O(22)-C(29)	117.8(2)
C(34)-N(3)-C(27)	119.3(7)
C(34)-N(3)-H(3A)	120.3
C(27)-N(3)-H(3A)	120.3
O(24)-C(34)-N(3)#1	121.8(5)
O(24)-C(34)-N(3)	121.8(5)
N(3)#1-C(34)-N(3)	116.4(10)
H(29A)-O(29)-H(29B)	120(4)
C(34B)-N(3B)-C(27)	122.2(15)
C(34B)-N(3B)-H(3B)	118.9
C(27)-N(3B)-H(3B)	118.9
O(24B)-C(34B)-N(3B)	129.3(12)
O(24B)-C(34B)-N(3B)#1	129.3(12)
N(3B)-C(34B)-N(3B)#1	101(2)
H(28A)-O(28)-H(28B)	113(4)

Symmetry transformations used to generate equivalent atoms:

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

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 07mz346m. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [(h a*)^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	21(1)	22(1)	23(1)	-2(1)	4(1)	0(1)
C(2)	19(1)	24(1)	22(1)	0(1)	2(1)	-2(1)
C(3)	21(1)	23(1)	24(1)	-4(1)	3(1)	-5(1)
C(4)	23(1)	24(1)	28(1)	-6(1)	8(1)	-4(1)
C(5)	20(1)	27(1)	31(1)	-3(1)	6(1)	-3(1)
C(6)	25(1)	39(2)	36(1)	-7(1)	11(1)	-12(1)
C(7)	26(1)	33(1)	25(1)	-5(1)	3(1)	0(1)
C(8)	50(2)	45(2)	24(1)	-1(1)	3(1)	11(1)
C(9)	20(1)	22(1)	19(1)	-3(1)	2(1)	-1(1)
C(10)	27(1)	26(1)	38(1)	-5(1)	9(1)	-6(1)

C(11)	48(2)	39(2)	41(1)	-9(1)	7(1)	-20(1)
C(12)	49(2)	33(1)	28(1)	-10(1)	16(1)	-19(1)
C(13)	67(2)	40(2)	28(1)	-1(1)	9(1)	-20(2)
C(14)	21(1)	22(1)	24(1)	3(1)	5(1)	-1(1)
C(15)	18(1)	22(1)	25(1)	5(1)	4(1)	1(1)
C(16)	20(1)	20(1)	21(1)	1(1)	2(1)	-3(1)
C(17)	20(1)	21(1)	22(1)	3(1)	3(1)	-2(1)
C(18)	20(1)	25(1)	23(1)	3(1)	3(1)	-1(1)
C(19)	20(1)	30(1)	28(1)	3(1)	1(1)	2(1)
C(20)	33(1)	33(1)	35(1)	1(1)	14(1)	3(1)
C(21)	33(1)	28(1)	38(1)	0(1)	9(1)	6(1)
C(22)	20(1)	25(1)	24(1)	-1(1)	3(1)	3(1)
C(23)	24(1)	24(1)	25(1)	-1(1)	1(1)	-1(1)
C(24)	22(1)	28(1)	24(1)	1(1)	1(1)	1(1)
C(25)	33(1)	25(1)	36(1)	-1(1)	8(1)	-1(1)
O(1)	23(1)	24(1)	30(1)	-5(1)	7(1)	-5(1)
O(2)	25(1)	25(1)	22(1)	-2(1)	2(1)	1(1)
O(4)	27(1)	27(1)	26(1)	-5(1)	4(1)	-10(1)
O(5)	30(1)	32(1)	24(1)	-2(1)	8(1)	-7(1)
O(6)	48(1)	36(1)	28(1)	-9(1)	2(1)	-2(1)
O(7)	21(1)	26(1)	28(1)	6(1)	5(1)	0(1)
O(8)	42(1)	33(1)	34(1)	4(1)	6(1)	-11(1)
O(9)	51(1)	48(1)	44(1)	-17(1)	28(1)	-16(1)
O(10)	21(1)	29(1)	21(1)	6(1)	3(1)	1(1)
O(11)	26(1)	23(1)	26(1)	2(1)	5(1)	0(1)
N(1)	20(1)	25(1)	24(1)	7(1)	4(1)	0(1)
N(2)	19(1)	21(1)	28(1)	7(1)	4(1)	1(1)
O(13)	23(1)	23(1)	22(1)	2(1)	0(1)	-3(1)
O(14)	22(1)	20(1)	28(1)	3(1)	5(1)	-1(1)
O(15)	78(2)	39(1)	37(1)	3(1)	25(1)	7(1)
O(16)	34(1)	35(1)	25(1)	4(1)	3(1)	-11(1)
O(17)	29(1)	31(1)	39(1)	-3(1)	12(1)	-2(1)
C(26)	30(1)	38(2)	29(1)	5(1)	6(1)	0(1)
C(27)	35(1)	49(2)	32(1)	0(1)	12(1)	1(1)
C(28)	40(1)	37(1)	22(1)	1(1)	8(1)	4(1)
C(29)	33(1)	26(1)	22(1)	1(1)	3(1)	3(1)
C(30)	28(1)	26(1)	22(1)	0(1)	3(1)	1(1)
C(31A)	38(1)	38(2)	33(1)	-5(1)	12(1)	-9(1)
C(32)	23(1)	43(2)	32(1)	3(1)	1(1)	-6(1)
C(33)	37(1)	41(2)	40(1)	6(1)	-3(1)	-7(1)
C(35)	59(2)	53(2)	25(1)	4(1)	6(1)	11(2)
C(36)	98(3)	74(3)	27(1)	-4(2)	11(2)	27(2)
C(37)	60(2)	28(1)	28(1)	-1(1)	-5(1)	2(1)
C(38)	70(2)	27(1)	36(1)	-3(1)	0(1)	7(1)
O(18)	30(1)	32(1)	23(1)	3(1)	3(1)	0(1)
O(19)	32(1)	40(1)	28(1)	4(1)	3(1)	-5(1)
O(21)	60(1)	50(1)	21(1)	0(1)	12(1)	15(1)
O(22)	40(1)	26(1)	25(1)	-1(1)	0(1)	6(1)
O(23)	37(1)	46(1)	32(1)	6(1)	-5(1)	-6(1)
O(25)	92(2)	51(2)	32(1)	1(1)	-6(1)	16(2)
O(26)	93(2)	32(1)	77(2)	-1(1)	-51(2)	5(1)
N(3)	46(2)	68(5)	39(6)	-14(3)	26(3)	-8(3)
C(34)	33(2)	57(9)	33(2)	0	10(2)	0
O(24)	37(2)	57(11)	47(2)	0	17(1)	0
O(29)	87(3)	52(3)	41(2)	2(2)	-1(2)	12(3)
N(3B)	46(2)	68(5)	39(6)	-14(3)	26(3)	-8(3)
C(34B)	33(2)	57(9)	33(2)	0	10(2)	0
O(24B)	37(2)	57(11)	47(2)	0	17(1)	0
O(27)	109(12)	40(7)	131(15)	0	77(11)	0
O(28)	108(8)	70(8)	71(6)	19(6)	31(5)	2(6)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for 07mz346m.

	x	y	z	U(eq)
H(1)	7260	123	5826	27
H(2)	7568	1323	6857	26
H(3)	7032	4442	6390	28
H(4)	6626	3720	7225	30
H(5)	6302	2586	6189	31
H(6A)	6254	-129	7100	49
H(6B)	5899	58	6416	49
H(6C)	5903	1527	6957	49
H(8A)	6291	2846	4154	61
H(8B)	6821	3180	4087	61
H(8C)	6613	4258	4607	61
H(11A)	8094	8191	7451	64
H(11B)	8265	6309	7759	64
H(11C)	7819	7267	7934	64
H(13A)	7124	102	8920	67
H(13B)	7487	1623	8829	67
H(13C)	7451	-152	8413	67
H(14)	9244	2767	7490	27
H(15)	9088	1013	6560	26
H(16)	9389	3954	5891	25
H(17)	10040	2190	5805	25
H(18)	10198	3835	6749	28
H(19A)	10525	353	7134	40
H(19B)	10759	2160	7440	40
H(19C)	10784	1632	6724	40
H(21A)	9352	8589	7793	49
H(21B)	8977	8084	7151	49
H(21C)	9525	8215	7145	49
H(23A)	8665	2316	3922	38
H(23B)	8373	1893	4458	38
H(23C)	8750	495	4312	38
H(25A)	10160	-3681	5713	47
H(25B)	9623	-3046	5491	47
H(25C)	9856	-3273	6237	47
H(1A)	7823(10)	3730(30)	6031(12)	28
H(2A)	8574(10)	3850(30)	6069(11)	27
H(26)	5374	5415	8519	39
H(27)	5608	7160	9450	45
H(28)	6196	4234	10023	39
H(29)	6862	5904	9920	33
H(30)	6560	4142	9018	31
H(31A)	6800	7471	8547	54
H(31B)	6827	5599	8207	54
H(31C)	7181	6031	8875	54
H(33A)	5905	-93	8604	61
H(33B)	5382	-414	8191	61
H(33C)	5464	83	8935	61
H(36A)	6709	7789	11656	100
H(36B)	6455	6334	12007	100
H(36C)	6146	7748	11537	100
H(38A)	6922	11747	10229	70
H(38B)	6392	11147	10213	70
H(38C)	6564	11395	9557	70
H(3A)	5251	3815	9640	58
H(29A)	4620(30)	250(80)	9660(30)	94

H(29B)	4440(30)	1510(100)	9150(16)	94
H(3B)	5271	4110	9853	58
H(27A)	4820(60)	1600(300)	9670(70)	129
H(28A)	4530(50)	-780(170)	9230(80)	122
H(28B)	4300(60)	910(150)	9150(80)	122

Table 6. Torsion angles [deg] for 07mz346m

O(1)-C(1)-C(2)-N(1)	177.65(19)
O(2)-C(1)-C(2)-N(1)	-61.8(2)
O(1)-C(1)-C(2)-C(3)	-56.4(2)
O(2)-C(1)-C(2)-C(3)	64.1(2)
N(1)-C(2)-C(3)-O(4)	-56.2(2)
C(1)-C(2)-C(3)-O(4)	178.79(17)
N(1)-C(2)-C(3)-C(4)	-174.87(17)
C(1)-C(2)-C(3)-C(4)	60.1(2)
O(4)-C(3)-C(4)-O(5)	-60.5(2)
C(2)-C(3)-C(4)-O(5)	59.7(2)
O(4)-C(3)-C(4)-C(5)	179.60(19)
C(2)-C(3)-C(4)-C(5)	-60.3(2)
O(5)-C(4)-C(5)-O(1)	-60.9(2)
C(3)-C(4)-C(5)-O(1)	55.1(3)
O(5)-C(4)-C(5)-C(6)	59.1(3)
C(3)-C(4)-C(5)-C(6)	175.1(2)
O(10)-C(14)-C(15)-N(2)	179.72(17)
O(11)-C(14)-C(15)-N(2)	-57.9(2)
O(10)-C(14)-C(15)-C(16)	-56.3(2)
O(11)-C(14)-C(15)-C(16)	66.1(2)
N(2)-C(15)-C(16)-O(13)	-59.2(2)
C(14)-C(15)-C(16)-O(13)	176.67(17)
N(2)-C(15)-C(16)-C(17)	180.00(19)
C(14)-C(15)-C(16)-C(17)	55.8(2)
O(13)-C(16)-C(17)-O(14)	-49.6(2)
C(15)-C(16)-C(17)-O(14)	67.3(2)
O(13)-C(16)-C(17)-C(18)	-170.39(17)
C(15)-C(16)-C(17)-C(18)	-53.5(2)
O(14)-C(17)-C(18)-O(10)	-67.1(2)
C(16)-C(17)-C(18)-O(10)	50.7(2)
O(14)-C(17)-C(18)-C(19)	52.3(2)
C(16)-C(17)-C(18)-C(19)	170.21(18)
O(2)-C(1)-O(1)-C(5)	-64.6(2)
C(2)-C(1)-O(1)-C(5)	53.3(2)
C(6)-C(5)-O(1)-C(1)	-176.78(18)
C(4)-C(5)-O(1)-C(1)	-52.3(3)
O(6)-C(7)-O(2)-C(1)	-1.0(3)
C(8)-C(7)-O(2)-C(1)	179.21(19)
O(1)-C(1)-O(2)-C(7)	-85.5(2)
C(2)-C(1)-O(2)-C(7)	152.55(18)
O(8)-C(10)-O(4)-C(3)	-0.7(3)
C(11)-C(10)-O(4)-C(3)	179.9(2)
C(4)-C(3)-O(4)-C(10)	-145.2(2)
C(2)-C(3)-O(4)-C(10)	96.8(2)
O(9)-C(12)-O(5)-C(4)	13.0(4)
C(13)-C(12)-O(5)-C(4)	-164.9(2)
C(3)-C(4)-O(5)-C(12)	141.6(2)
C(5)-C(4)-O(5)-C(12)	-100.1(2)
O(11)-C(14)-O(10)-C(18)	-64.4(2)
C(15)-C(14)-O(10)-C(18)	55.3(2)
C(19)-C(18)-O(10)-C(14)	-176.66(19)
C(17)-C(18)-O(10)-C(14)	-52.8(3)
O(15)-C(20)-O(11)-C(14)	9.2(4)

C(21)-C(20)-O(11)-C(14)	-171.0(2)
O(10)-C(14)-O(11)-C(20)	-99.7(2)
C(15)-C(14)-O(11)-C(20)	137.81(19)
O(7)-C(9)-N(1)-C(2)	13.7(3)
N(2)-C(9)-N(1)-C(2)	-165.80(19)
C(1)-C(2)-N(1)-C(9)	-115.7(2)
C(3)-C(2)-N(1)-C(9)	121.3(2)
O(7)-C(9)-N(2)-C(15)	11.9(3)
N(1)-C(9)-N(2)-C(15)	-168.59(19)
C(16)-C(15)-N(2)-C(9)	139.7(2)
C(14)-C(15)-N(2)-C(9)	-97.1(2)
O(16)-C(22)-O(13)-C(16)	10.1(3)
C(23)-C(22)-O(13)-C(16)	-169.75(17)
C(17)-C(16)-O(13)-C(22)	-95.9(2)
C(15)-C(16)-O(13)-C(22)	144.61(18)
O(17)-C(24)-O(14)-C(17)	8.4(3)
C(25)-C(24)-O(14)-C(17)	-171.19(19)
C(16)-C(17)-O(14)-C(24)	133.90(18)
C(18)-C(17)-O(14)-C(24)	-105.7(2)
O(18)-C(26)-C(27)-N(3)	-175.7(9)
O(19)-C(26)-C(27)-N(3)	-53.7(9)
O(18)-C(26)-C(27)-N(3B)	-179.4(18)
O(19)-C(26)-C(27)-N(3B)	-57.4(18)
O(18)-C(26)-C(27)-C(28)	-54.6(3)
O(19)-C(26)-C(27)-C(28)	67.4(3)
N(3)-C(27)-C(28)-O(21)	-70.6(5)
N(3B)-C(27)-C(28)-O(21)	-58.5(10)
C(26)-C(27)-C(28)-O(21)	171.8(2)
N(3)-C(27)-C(28)-C(29)	170.8(5)
N(3B)-C(27)-C(28)-C(29)	-177.2(10)
C(26)-C(27)-C(28)-C(29)	53.2(3)
O(21)-C(28)-C(29)-O(22)	-51.8(3)
C(27)-C(28)-C(29)-O(22)	65.4(3)
O(21)-C(28)-C(29)-C(30)	-171.2(2)
C(27)-C(28)-C(29)-C(30)	-54.1(3)
O(22)-C(29)-C(30)-O(18)	-63.9(3)
C(28)-C(29)-C(30)-O(18)	54.6(3)
O(22)-C(29)-C(30)-C(31A)	55.8(3)
C(28)-C(29)-C(30)-C(31A)	174.2(2)
O(19)-C(26)-O(18)-C(30)	-60.7(3)
C(27)-C(26)-O(18)-C(30)	58.1(3)
C(31A)-C(30)-O(18)-C(26)	178.0(2)
C(29)-C(30)-O(18)-C(26)	-57.9(3)
O(23)-C(32)-O(19)-C(26)	1.5(4)
C(33)-C(32)-O(19)-C(26)	-177.4(2)
O(18)-C(26)-O(19)-C(32)	-83.1(3)
C(27)-C(26)-O(19)-C(32)	154.5(2)
O(25)-C(35)-O(21)-C(28)	-2.7(5)
C(36)-C(35)-O(21)-C(28)	172.3(3)
C(29)-C(28)-O(21)-C(35)	-90.6(3)
C(27)-C(28)-O(21)-C(35)	149.6(3)
O(26)-C(37)-O(22)-C(29)	10.0(5)
C(38)-C(37)-O(22)-C(29)	-168.6(3)
C(30)-C(29)-O(22)-C(37)	-136.6(2)
C(28)-C(29)-O(22)-C(37)	103.8(3)
N(3B)-C(27)-N(3)-C(34)	26(11)
C(28)-C(27)-N(3)-C(34)	103.1(15)
C(26)-C(27)-N(3)-C(34)	-137.7(13)
C(27)-N(3)-C(34)-O(24)	12(2)
C(27)-N(3)-C(34)-N(3)#1	-168(2)
N(3)-C(27)-N(3B)-C(34B)	-142(16)
C(28)-C(27)-N(3B)-C(34B)	111(3)
C(26)-C(27)-N(3B)-C(34B)	-124(3)

C(27)-N(3B)-C(34B)-O(24B)	-5(5)
C(27)-N(3B)-C(34B)-N(3B)#1	175(5)

Table 7. Hydrogen bonds for 07mz346m [Å and deg].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(6)#2	0.868(18)	2.47(2)	3.174(3)	139(2)
N(1)-H(1A)...O(8)	0.868(18)	2.58(3)	3.113(3)	121(2)
N(2)-H(2A)...O(6)#2	0.856(18)	2.092(19)	2.909(3)	159(3)
N(3)-H(3A)...O(29)#1	0.88	2.64	3.271(19)	129.0
O(29)-H(29A)...O(24)#3	0.83(2)	2.35(2)	3.185(12)	179(9)
O(29)-H(29B)...O(15)#4	0.86(2)	2.39(6)	3.112(5)	142(7)
N(3)-H(3A)...O(27)	0.88	1.81	2.538(17)	138.3
O(27)-H(27A)...O(28)	0.85(2)	1.82(14)	2.564(17)	145(24)
O(28)-H(28A)...O(24)#3	0.86(2)	2.27(15)	2.744(15)	115(13)

Symmetry transformations used to generate equivalent atoms:

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

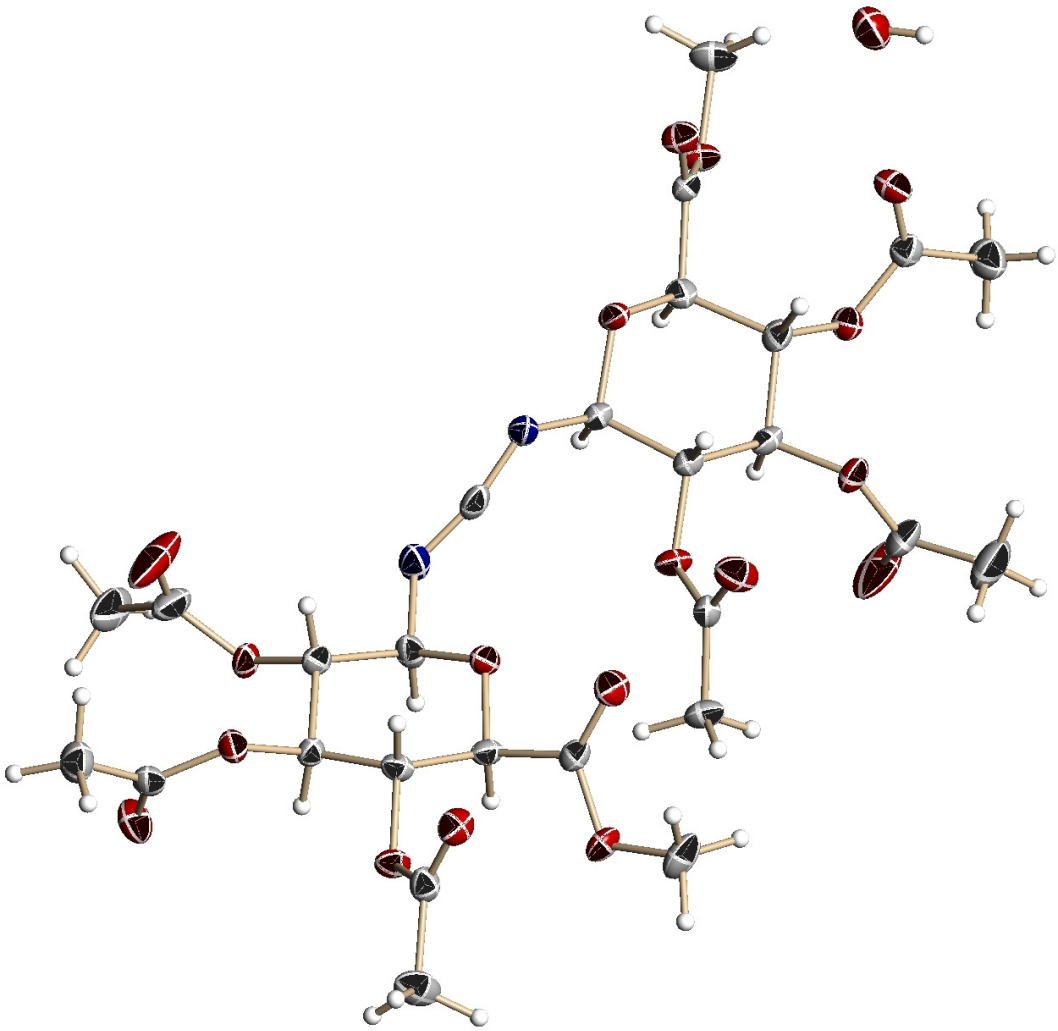


Figure 134 :
Crystallographic refinement of
bis(2,3,4-tri-*O*-acetyl-β-glucouronoayl) diimide (**15**)

Table 1. Crystal data and structure refinement for 07mz524m:

Identification code: 07mz524m
Empirical formula: C27 H34.58 N2 O18.29
Moiety formula: C27 H34 N2 O18, 0.288(H2 O)
Formula weight: 679.75
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Monoclinic
Space group: $P2_1$
Unit cell dimensions:
a = 5.3913(6) Å, α = 90°
b = 19.343(2) Å, β = 90.548(2)°
c = 15.2139(17) Å, γ = 90°
Volume, Z: 1586.5(3) $Å^3$, 2
Density (calculated): 1.423 Mg/m^3
Absorption coefficient: 0.123 mm^{-1}
F(000): 713.8
Crystal size: 0.46 × 0.30 × 0.10 mm
Crystal shape, colour: block, yellow
θ range for data collection: 1.34 to 28.28°
Limiting indices: $-7 \le h \le 6$, $-21 \le k \le 25$, $-20 \le l \le 13$
Reflections collected: 9614
Independent reflections: 4012 (R(int) = 0.0495)
Completeness to θ = 28.28°: 98.9 %
Absorption correction: multi-scan
Max. and min. transmission: 0.988 and 0.794
Refinement method: Full-matrix least-squares on F^2
Data / restraints / parameters: 4012 / 5 / 448
Goodness-of-fit on F^2: 1.077
Final R indices [$I>2\sigma(I)$]: R1 = 0.0486, wR2 = 0.1055
R indices (all data): R1 = 0.0693, wR2 = 0.1295
Largest diff. peak and hole: 0.458 and −0.299 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 solvate water molecule is only 29(1)% occupied.

Treatment of hydrogen atoms:
The water O-H bonds and O...H hydrogen bonds were restrained to be 0.84(2) and 1.7(1) and 1.9(1) Å, respectively. All other hydrogen atoms were placed in calculated positions and all H atoms were refined with an isotropic displacement parameter 1.5 (methyl, hydroxyl) or 1.2 times (all others) that of the adjacent carbon or oxygen atom.

Table 2. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [Å^2 × 10^3] for 07mz524m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	1022(8)	3952(2)	823(3)	26(1)
C(1A)	3398(7)	4023(2)	2116(3)	20(1)
C(2A)	4286(7)	4770(2)	2177(3)	20(1)
C(3A)	4876(8)	4946(2)	3125(3)	22(1)
C(4A)	6736(8)	4438(2)	3505(3)	22(1)
C(5A)	5769(7)	3695(2)	3357(3)	22(1)
C(6A)	7702(7)	3171(2)	3643(3)	20(1)
C(7A)	2879(8)	5749(2)	1356(3)	23(1)
C(8A)	725(8)	6229(2)	1272(3)	31(1)
C(9A)	4882(10)	6116(2)	3630(4)	40(1)
C(10A)	6362(12)	6774(3)	3577(5)	59(2)
C(11A)	9210(8)	4549(2)	4804(3)	24(1)
C(12A)	9338(9)	4900(3)	5667(3)	36(1)
C(13A)	9125(9)	2480(2)	4814(3)	34(1)
C(1B)	-1939(8)	4468(2)	-176(3)	24(1)
C(2B)	-2714(7)	4124(2)	-1041(3)	22(1)
C(3B)	-3719(7)	4652(2)	-1691(2)	19(1)
C(4B)	-1977(7)	5262(2)	-1778(3)	20(1)
C(5B)	-1256(7)	5539(2)	-857(3)	20(1)
C(6B)	747(8)	6095(2)	-922(3)	22(1)
C(7B)	-4590(9)	3003(2)	-1114(4)	39(1)
C(8B)	-6685(10)	2590(2)	-745(4)	49(1)
C(9B)	-5970(8)	4049(2)	-2830(3)	25(1)
C(10B)	-5642(9)	3708(2)	-3707(3)	34(1)
C(11B)	-2103(8)	6192(2)	-2829(3)	24(1)
C(12B)	-3835(9)	6713(2)	-3230(3)	37(1)
C(13B)	1454(10)	7271(2)	-1228(3)	38(1)
N(1A)	2984(6)	3829(2)	1209(2)	24(1)
N(1B)	-888(7)	3958(2)	398(2)	30(1)
O(1)	9430(20)	2843(7)	7030(8)	42(4)
O(1A)	5371(5)	3589(1)	2438(2)	22(1)
O(2A)	2270(5)	5206(1)	1896(2)	23(1)
O(3A)	4887(6)	5816(2)	1039(2)	35(1)
O(4A)	6003(5)	5621(1)	3147(2)	27(1)
O(5A)	2980(8)	6028(2)	4015(3)	68(1)
O(6A)	6965(5)	4614(1)	4417(2)	24(1)
O(7A)	10899(5)	4239(2)	4462(2)	28(1)
O(8A)	7250(5)	2948(1)	4456(2)	26(1)
O(9A)	9428(5)	2993(1)	3199(2)	27(1)
O(1B)	-162(5)	4994(1)	-357(2)	24(1)
O(2B)	-4686(5)	3653(1)	-810(2)	24(1)
O(3B)	-3090(8)	2806(2)	-1644(4)	75(2)
O(4B)	-3828(5)	4336(1)	-2555(2)	23(1)
O(5B)	-7865(6)	4068(2)	-2423(2)	35(1)
O(6B)	-3355(5)	5781(1)	-2255(2)	23(1)

O(7B)	77(5)	6136(2)	-2962(2)	27(1)
O(8B)	-296(5)	6713(1)	-1078(2)	26(1)
O(9B)	2911(5)	5991(2)	-853(2)	31(1)

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

Table 3. Bond lengths [Å] and angles [deg] for 07mz524m.

C(1)-N(1B)	1.210(5)
C(1)-N(1A)	1.228(5)
C(1A)-O(1A)	1.438(4)
C(1A)-N(1A)	1.445(5)
C(1A)-C(2A)	1.524(5)
C(1A)-H(1A)	1.0000
C(2A)-O(2A)	1.438(4)
C(2A)-C(3A)	1.512(5)
C(2A)-H(2A)	1.0000
C(3A)-O(4A)	1.440(5)
C(3A)-C(4A)	1.515(5)
C(3A)-H(3A)	1.0000
C(4A)-O(6A)	1.433(5)
C(4A)-C(5A)	1.545(5)
C(4A)-H(4A)	1.0000
C(5A)-O(1A)	1.428(5)
C(5A)-C(6A)	1.516(5)
C(5A)-H(5A)	1.0000
C(6A)-O(9A)	1.205(5)
C(6A)-O(8A)	1.334(5)
C(7A)-O(3A)	1.196(5)
C(7A)-O(2A)	1.376(5)
C(7A)-C(8A)	1.491(6)
C(8A)-H(8A1)	0.9800
C(8A)-H(8A2)	0.9800
C(8A)-H(8A3)	0.9800
C(9A)-O(5A)	1.199(6)
C(9A)-O(4A)	1.354(5)
C(9A)-C(10A)	1.505(7)
C(10A)-H(10A)	0.9800
C(10A)-H(10B)	0.9800
C(10A)-H(10C)	0.9800
C(11A)-O(7A)	1.212(5)
C(11A)-O(6A)	1.347(5)
C(11A)-C(12A)	1.479(6)
C(12A)-H(12A)	0.9800
C(12A)-H(12B)	0.9800
C(12A)-H(12C)	0.9800
C(13A)-O(8A)	1.458(5)
C(13A)-H(13A)	0.9800
C(13A)-H(13B)	0.9800
C(13A)-H(13C)	0.9800
C(1B)-O(1B)	1.426(5)
C(1B)-N(1B)	1.431(5)
C(1B)-C(2B)	1.529(5)

C(1B)-H(1B)	1.0000
C(2B)-O(2B)	1.447(4)
C(2B)-C(3B)	1.519(5)
C(2B)-H(2B)	1.0000
C(3B)-O(4B)	1.451(5)
C(3B)-C(4B)	1.514(5)
C(3B)-H(3B)	1.0000
C(4B)-O(6B)	1.441(4)
C(4B)-C(5B)	1.546(5)
C(4B)-H(4B)	1.0000
C(5B)-O(1B)	1.425(4)
C(5B)-C(6B)	1.528(5)
C(5B)-H(5B)	1.0000
C(6B)-O(9B)	1.188(5)
C(6B)-O(8B)	1.341(5)
C(7B)-O(3B)	1.210(6)
C(7B)-O(2B)	1.339(5)
C(7B)-C(8B)	1.498(7)
C(8B)-H(8B1)	0.9800
C(8B)-H(8B2)	0.9800
C(8B)-H(8B3)	0.9800
C(9B)-O(5B)	1.201(5)
C(9B)-O(4B)	1.344(5)
C(9B)-C(10B)	1.500(6)
C(10B)-H(10D)	0.9800
C(10B)-H(10E)	0.9800
C(10B)-H(10F)	0.9800
C(11B)-O(7B)	1.199(5)
C(11B)-O(6B)	1.364(5)
C(11B)-C(12B)	1.500(6)
C(12B)-H(12D)	0.9800
C(12B)-H(12E)	0.9800
C(12B)-H(12F)	0.9800
C(13B)-O(8B)	1.454(5)
C(13B)-H(13D)	0.9800
C(13B)-H(13E)	0.9800
C(13B)-H(13F)	0.9800
O(1)-H(1C)	0.85(2)
O(1)-H(1D)	0.84(2)

N(1B)-C(1)-N(1A)	169.0(4)
O(1A)-C(1A)-N(1A)	106.3(3)
O(1A)-C(1A)-C(2A)	107.5(3)
N(1A)-C(1A)-C(2A)	110.5(3)
O(1A)-C(1A)-H(1A)	110.8
N(1A)-C(1A)-H(1A)	110.8
C(2A)-C(1A)-H(1A)	110.8
O(2A)-C(2A)-C(3A)	107.6(3)
O(2A)-C(2A)-C(1A)	107.6(3)
C(3A)-C(2A)-C(1A)	109.6(3)
O(2A)-C(2A)-H(2A)	110.7
C(3A)-C(2A)-H(2A)	110.7
C(1A)-C(2A)-H(2A)	110.7
O(4A)-C(3A)-C(2A)	108.1(3)
O(4A)-C(3A)-C(4A)	107.5(3)
C(2A)-C(3A)-C(4A)	110.5(3)
O(4A)-C(3A)-H(3A)	110.2
C(2A)-C(3A)-H(3A)	110.2
C(4A)-C(3A)-H(3A)	110.2
O(6A)-C(4A)-C(3A)	105.5(3)
O(6A)-C(4A)-C(5A)	112.9(3)
C(3A)-C(4A)-C(5A)	109.0(3)
O(6A)-C(4A)-H(4A)	109.8

C(3A)-C(4A)-H(4A)	109.8
C(5A)-C(4A)-H(4A)	109.8
O(1A)-C(5A)-C(6A)	106.3(3)
O(1A)-C(5A)-C(4A)	108.9(3)
C(6A)-C(5A)-C(4A)	110.5(3)
O(1A)-C(5A)-H(5A)	110.3
C(6A)-C(5A)-H(5A)	110.3
C(4A)-C(5A)-H(5A)	110.3
O(9A)-C(6A)-O(8A)	125.2(4)
O(9A)-C(6A)-C(5A)	124.2(4)
O(8A)-C(6A)-C(5A)	110.6(3)
O(3A)-C(7A)-O(2A)	123.0(4)
O(3A)-C(7A)-C(8A)	127.3(4)
O(2A)-C(7A)-C(8A)	109.7(4)
C(7A)-C(8A)-H(8A1)	109.5
C(7A)-C(8A)-H(8A2)	109.5
H(8A1)-C(8A)-H(8A2)	109.5
C(7A)-C(8A)-H(8A3)	109.5
H(8A1)-C(8A)-H(8A3)	109.5
H(8A2)-C(8A)-H(8A3)	109.5
O(5A)-C(9A)-O(4A)	123.6(4)
O(5A)-C(9A)-C(10A)	127.1(5)
O(4A)-C(9A)-C(10A)	109.3(5)
C(9A)-C(10A)-H(10A)	109.5
C(9A)-C(10A)-H(10B)	109.5
H(10A)-C(10A)-H(10B)	109.5
C(9A)-C(10A)-H(10C)	109.5
H(10A)-C(10A)-H(10C)	109.5
H(10B)-C(10A)-H(10C)	109.5
O(7A)-C(11A)-O(6A)	122.3(4)
O(7A)-C(11A)-C(12A)	125.4(4)
O(6A)-C(11A)-C(12A)	112.3(4)
C(11A)-C(12A)-H(12A)	109.5
C(11A)-C(12A)-H(12B)	109.5
H(12A)-C(12A)-H(12B)	109.5
C(11A)-C(12A)-H(12C)	109.5
H(12A)-C(12A)-H(12C)	109.5
H(12B)-C(12A)-H(12C)	109.5
O(8A)-C(13A)-H(13A)	109.5
O(8A)-C(13A)-H(13B)	109.5
H(13A)-C(13A)-H(13B)	109.5
O(8A)-C(13A)-H(13C)	109.5
H(13A)-C(13A)-H(13C)	109.5
H(13B)-C(13A)-H(13C)	109.5
O(1B)-C(1B)-N(1B)	110.3(3)
O(1B)-C(1B)-C(2B)	108.8(3)
N(1B)-C(1B)-C(2B)	109.2(3)
O(1B)-C(1B)-H(1B)	109.5
N(1B)-C(1B)-H(1B)	109.5
C(2B)-C(1B)-H(1B)	109.5
O(2B)-C(2B)-C(3B)	108.9(3)
O(2B)-C(2B)-C(1B)	105.1(3)
C(3B)-C(2B)-C(1B)	111.1(3)
O(2B)-C(2B)-H(2B)	110.5
C(3B)-C(2B)-H(2B)	110.5
C(1B)-C(2B)-H(2B)	110.5
O(4B)-C(3B)-C(4B)	105.6(3)
O(4B)-C(3B)-C(2B)	108.5(3)
C(4B)-C(3B)-C(2B)	111.3(3)
O(4B)-C(3B)-H(3B)	110.4
C(4B)-C(3B)-H(3B)	110.4
C(2B)-C(3B)-H(3B)	110.4
O(6B)-C(4B)-C(3B)	105.7(3)

O(6B)-C(4B)-C(5B)	109.7(3)
C(3B)-C(4B)-C(5B)	110.0(3)
O(6B)-C(4B)-H(4B)	110.4
C(3B)-C(4B)-H(4B)	110.4
C(5B)-C(4B)-H(4B)	110.4
O(1B)-C(5B)-C(6B)	105.4(3)
O(1B)-C(5B)-C(4B)	109.0(3)
C(6B)-C(5B)-C(4B)	110.9(3)
O(1B)-C(5B)-H(5B)	110.4
C(6B)-C(5B)-H(5B)	110.4
C(4B)-C(5B)-H(5B)	110.4
O(9B)-C(6B)-O(8B)	125.2(4)
O(9B)-C(6B)-C(5B)	124.7(4)
O(8B)-C(6B)-C(5B)	110.1(3)
O(3B)-C(7B)-O(2B)	123.7(4)
O(3B)-C(7B)-C(8B)	126.3(4)
O(2B)-C(7B)-C(8B)	109.9(4)
C(7B)-C(8B)-H(8B1)	109.5
C(7B)-C(8B)-H(8B2)	109.5
H(8B1)-C(8B)-H(8B2)	109.5
C(7B)-C(8B)-H(8B3)	109.5
H(8B1)-C(8B)-H(8B3)	109.5
H(8B2)-C(8B)-H(8B3)	109.5
O(5B)-C(9B)-O(4B)	124.0(4)
O(5B)-C(9B)-C(10B)	125.5(4)
O(4B)-C(9B)-C(10B)	110.5(4)
C(9B)-C(10B)-H(10D)	109.5
C(9B)-C(10B)-H(10E)	109.5
H(10D)-C(10B)-H(10E)	109.5
C(9B)-C(10B)-H(10F)	109.5
H(10D)-C(10B)-H(10F)	109.5
H(10E)-C(10B)-H(10F)	109.5
O(7B)-C(11B)-O(6B)	123.2(4)
O(7B)-C(11B)-C(12B)	126.8(4)
O(6B)-C(11B)-C(12B)	110.0(4)
C(11B)-C(12B)-H(12D)	109.5
C(11B)-C(12B)-H(12E)	109.5
H(12D)-C(12B)-H(12E)	109.5
C(11B)-C(12B)-H(12F)	109.5
H(12D)-C(12B)-H(12F)	109.5
H(12E)-C(12B)-H(12F)	109.5
O(8B)-C(13B)-H(13D)	109.5
O(8B)-C(13B)-H(13E)	109.5
H(13D)-C(13B)-H(13E)	109.5
O(8B)-C(13B)-H(13F)	109.5
H(13D)-C(13B)-H(13F)	109.5
H(13E)-C(13B)-H(13F)	109.5
C(1)-N(1A)-C(1A)	122.0(4)
C(1)-N(1B)-C(1B)	131.5(4)
H(1C)-O(1)-H(1D)	116(10)
C(5A)-O(1A)-C(1A)	110.7(3)
C(7A)-O(2A)-C(2A)	116.2(3)
C(9A)-O(4A)-C(3A)	117.6(4)
C(11A)-O(6A)-C(4A)	118.0(3)
C(6A)-O(8A)-C(13A)	114.5(3)
C(5B)-O(1B)-C(1B)	110.8(3)
C(7B)-O(2B)-C(2B)	118.4(3)
C(9B)-O(4B)-C(3B)	118.9(3)
C(11B)-O(6B)-C(4B)	118.2(3)
C(6B)-O(8B)-C(13B)	114.7(3)

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 07mz524m. The

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

	U11	U22	U33	U23	U13	U12
C(1)	37(2)	13(2)	27(2)	1(2)	-3(2)	-3(2)
C(1A)	22(2)	15(2)	23(2)	0(1)	-2(2)	2(1)
C(2A)	21(2)	17(2)	23(2)	0(1)	0(2)	2(1)
C(3A)	24(2)	14(2)	27(2)	-2(1)	3(2)	2(1)
C(4A)	27(2)	20(2)	19(2)	-4(2)	2(2)	2(2)
C(5A)	22(2)	22(2)	23(2)	-1(2)	0(2)	2(2)
C(6A)	22(2)	14(2)	25(2)	0(1)	-2(2)	0(1)
C(7A)	25(2)	19(2)	26(2)	-2(2)	-6(2)	-2(2)
C(8A)	34(2)	21(2)	38(3)	5(2)	-3(2)	7(2)
C(9A)	45(3)	22(2)	52(3)	-15(2)	-3(2)	6(2)
C(10A)	65(4)	26(3)	86(5)	-16(3)	-1(3)	-5(3)
C(11A)	29(2)	21(2)	21(2)	2(2)	0(2)	0(2)
C(12A)	36(3)	41(3)	31(3)	-8(2)	-3(2)	3(2)
C(13A)	37(3)	34(2)	32(3)	11(2)	-1(2)	11(2)
C(1B)	28(2)	22(2)	23(2)	6(2)	-8(2)	-5(2)
C(2B)	22(2)	15(2)	30(2)	4(2)	-3(2)	-3(1)
C(3B)	21(2)	16(2)	20(2)	0(1)	-1(2)	-1(1)
C(4B)	18(2)	21(2)	23(2)	5(1)	-1(2)	1(1)
C(5B)	19(2)	16(2)	25(2)	4(1)	0(2)	2(1)
C(6B)	26(2)	19(2)	21(2)	-3(1)	2(2)	1(2)
C(7B)	30(2)	18(2)	68(4)	-1(2)	0(2)	3(2)
C(8B)	38(3)	21(2)	88(4)	4(2)	2(3)	-11(2)
C(9B)	28(2)	20(2)	26(2)	5(2)	-8(2)	0(2)
C(10B)	39(3)	32(2)	29(2)	-6(2)	-4(2)	-3(2)
C(11B)	26(2)	22(2)	25(2)	2(2)	-2(2)	-6(2)
C(12B)	31(2)	34(2)	48(3)	21(2)	-2(2)	-2(2)
C(13B)	54(3)	17(2)	41(3)	0(2)	5(2)	-7(2)
N(1A)	29(2)	19(2)	23(2)	-1(1)	-7(1)	2(1)
N(1B)	37(2)	22(2)	31(2)	5(1)	-11(2)	-6(2)
O(1)	40(8)	42(8)	43(8)	1(6)	-12(6)	-4(5)
O(1A)	28(2)	18(1)	21(1)	-3(1)	-4(1)	6(1)
O(2A)	22(1)	18(1)	28(2)	5(1)	3(1)	4(1)
O(3A)	28(2)	34(2)	43(2)	14(1)	-1(1)	-2(1)
O(4A)	31(2)	15(1)	34(2)	-3(1)	0(1)	-3(1)
O(5A)	58(3)	40(2)	106(4)	-38(2)	32(3)	1(2)
O(6A)	26(2)	25(1)	21(1)	-4(1)	-1(1)	2(1)
O(7A)	24(2)	35(2)	26(2)	0(1)	-2(1)	4(1)
O(8A)	28(2)	22(1)	26(2)	7(1)	1(1)	7(1)
O(9A)	29(2)	25(2)	27(2)	-1(1)	2(1)	6(1)
O(1B)	21(1)	17(1)	35(2)	5(1)	-6(1)	-3(1)
O(2B)	29(2)	16(1)	27(2)	2(1)	-4(1)	-7(1)
O(3B)	54(3)	27(2)	144(5)	-29(2)	36(3)	-5(2)
O(4B)	21(1)	25(1)	25(2)	-4(1)	-2(1)	-1(1)
O(5B)	24(2)	44(2)	36(2)	-5(1)	-1(1)	-8(1)
O(6B)	21(1)	20(1)	29(2)	8(1)	1(1)	1(1)
O(7B)	25(2)	25(1)	31(2)	1(1)	8(1)	-3(1)
O(8B)	33(2)	14(1)	30(2)	1(1)	4(1)	-1(1)
O(9B)	21(2)	27(2)	45(2)	-1(1)	2(1)	-3(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for 07mz524m.

	x	y	z	U(eq)
H(1A)	1859	3954	2467	24

H(2A)	5772	4843	1800	24
H(3A)	3325	4944	3480	26
H(4A)	8373	4497	3211	26
H(5A)	4191	3622	3685	27
H(8A1)	1056	6570	812	46
H(8A2)	469	6466	1833	46
H(8A3)	-767	5965	1116	46
H(10A)	6017	7062	4092	88
H(10B)	5897	7026	3041	88
H(10C)	8135	6663	3564	88
H(12A)	10713	5232	5669	54
H(12B)	9609	4557	6131	54
H(12C)	7778	5146	5771	54
H(13A)	10772	2687	4746	51
H(13B)	9056	2039	4497	51
H(13C)	8808	2400	5439	51
H(1B)	-3425	4680	106	29
H(2B)	-1288	3866	-1299	27
H(3B)	-5404	4812	-1511	23
H(4B)	-462	5125	-2110	25
H(5B)	-2748	5725	-552	24
H(8B1)	-6321	2096	-806	74
H(8B2)	-8220	2700	-1065	74
H(8B3)	-6883	2702	-121	74
H(10D)	-5511	4063	-4165	50
H(10E)	-7074	3411	-3834	50
H(10F)	-4128	3428	-3697	50
H(12D)	-3471	6764	-3857	56
H(12E)	-3615	7159	-2935	56
H(12F)	-5551	6556	-3161	56
H(13D)	2789	7107	-1608	56
H(13E)	2159	7424	-665	56
H(13F)	596	7659	-1513	56
H(1C)	10400(300)	3190(70)	7060(120)	62
H(1D)	8800(300)	2710(90)	7510(80)	62

Table 6. Torsion angles [deg] for 07mz075m.

O(1A)-C(1A)-C(2A)-O(2A)	-177.2(3)
N(1A)-C(1A)-C(2A)-O(2A)	67.2(4)
O(1A)-C(1A)-C(2A)-C(3A)	-60.5(4)
N(1A)-C(1A)-C(2A)-C(3A)	-176.1(3)
O(2A)-C(2A)-C(3A)-O(4A)	-70.5(4)
C(1A)-C(2A)-C(3A)-O(4A)	172.8(3)
O(2A)-C(2A)-C(3A)-C(4A)	172.0(3)
C(1A)-C(2A)-C(3A)-C(4A)	55.3(4)
O(4A)-C(3A)-C(4A)-O(6A)	67.6(4)
C(2A)-C(3A)-C(4A)-O(6A)	-174.6(3)
O(4A)-C(3A)-C(4A)-C(5A)	-171.0(3)
C(2A)-C(3A)-C(4A)-C(5A)	-53.2(4)
O(6A)-C(4A)-C(5A)-O(1A)	174.4(3)
C(3A)-C(4A)-C(5A)-O(1A)	57.6(4)
O(6A)-C(4A)-C(5A)-C(6A)	-69.1(4)
C(3A)-C(4A)-C(5A)-C(6A)	174.1(3)
O(1A)-C(5A)-C(6A)-O(9A)	36.4(5)
C(4A)-C(5A)-C(6A)-O(9A)	-81.7(5)
O(1A)-C(5A)-C(6A)-O(8A)	-144.9(3)
C(4A)-C(5A)-C(6A)-O(8A)	97.0(4)
O(1B)-C(1B)-C(2B)-O(2B)	-174.3(3)
N(1B)-C(1B)-C(2B)-O(2B)	65.3(4)
O(1B)-C(1B)-C(2B)-C(3B)	-56.6(4)

N(1B)-C(1B)-C(2B)-C(3B)	-177.0(3)
O(2B)-C(2B)-C(3B)-O(4B)	-78.9(4)
C(1B)-C(2B)-C(3B)-O(4B)	165.7(3)
O(2B)-C(2B)-C(3B)-C(4B)	165.3(3)
C(1B)-C(2B)-C(3B)-C(4B)	50.0(4)
O(4B)-C(3B)-C(4B)-O(6B)	74.4(4)
C(2B)-C(3B)-C(4B)-O(6B)	-168.1(3)
O(4B)-C(3B)-C(4B)-C(5B)	-167.3(3)
C(2B)-C(3B)-C(4B)-C(5B)	-49.8(4)
O(6B)-C(4B)-C(5B)-O(1B)	173.1(3)
C(3B)-C(4B)-C(5B)-O(1B)	57.2(4)
O(6B)-C(4B)-C(5B)-C(6B)	-71.2(4)
C(3B)-C(4B)-C(5B)-C(6B)	172.9(3)
O(1B)-C(5B)-C(6B)-O(9B)	23.7(5)
C(4B)-C(5B)-C(6B)-O(9B)	-94.2(5)
O(1B)-C(5B)-C(6B)-O(8B)	-156.9(3)
C(4B)-C(5B)-C(6B)-O(8B)	85.1(4)
N(1B)-C(1)-N(1A)-C(1A)	-132(2)
O(1A)-C(1A)-N(1A)-C(1)	158.7(4)
C(2A)-C(1A)-N(1A)-C(1)	-84.9(5)
N(1A)-C(1)-N(1B)-C(1B)	-139(2)
O(1B)-C(1B)-N(1B)-C(1)	11.2(7)
C(2B)-C(1B)-N(1B)-C(1)	130.7(5)
C(6A)-C(5A)-O(1A)-C(1A)	174.9(3)
C(4A)-C(5A)-O(1A)-C(1A)	-65.9(4)
N(1A)-C(1A)-O(1A)-C(5A)	-174.6(3)
C(2A)-C(1A)-O(1A)-C(5A)	67.1(4)
O(3A)-C(7A)-O(2A)-C(2A)	9.2(6)
C(8A)-C(7A)-O(2A)-C(2A)	-168.6(3)
C(3A)-C(2A)-O(2A)-C(7A)	104.5(4)
C(1A)-C(2A)-O(2A)-C(7A)	-137.5(3)
O(5A)-C(9A)-O(4A)-C(3A)	-2.3(7)
C(10A)-C(9A)-O(4A)-C(3A)	179.2(4)
C(2A)-C(3A)-O(4A)-C(9A)	121.7(4)
C(4A)-C(3A)-O(4A)-C(9A)	-118.9(4)
O(7A)-C(11A)-O(6A)-C(4A)	-13.1(6)
C(12A)-C(11A)-O(6A)-C(4A)	166.2(3)
C(3A)-C(4A)-O(6A)-C(11A)	-144.4(3)
C(5A)-C(4A)-O(6A)-C(11A)	96.7(4)
O(9A)-C(6A)-O(8A)-C(13A)	3.2(6)
C(5A)-C(6A)-O(8A)-C(13A)	-175.5(3)
C(6B)-C(5B)-O(1B)-C(1B)	174.3(3)
C(4B)-C(5B)-O(1B)-C(1B)	-66.5(4)
N(1B)-C(1B)-O(1B)-C(5B)	-174.3(3)
C(2B)-C(1B)-O(1B)-C(5B)	66.0(4)
O(3B)-C(7B)-O(2B)-C(2B)	-7.9(7)
C(8B)-C(7B)-O(2B)-C(2B)	175.7(4)
C(3B)-C(2B)-O(2B)-C(7B)	108.7(4)
C(1B)-C(2B)-O(2B)-C(7B)	-132.2(4)
O(5B)-C(9B)-O(4B)-C(3B)	4.0(6)
C(10B)-C(9B)-O(4B)-C(3B)	-176.0(3)
C(4B)-C(3B)-O(4B)-C(9B)	-145.6(3)
C(2B)-C(3B)-O(4B)-C(9B)	95.0(4)
O(7B)-C(11B)-O(6B)-C(4B)	0.7(6)
C(12B)-C(11B)-O(6B)-C(4B)	-177.9(3)
C(3B)-C(4B)-O(6B)-C(11B)	-144.7(3)
C(5B)-C(4B)-O(6B)-C(11B)	96.8(4)
O(9B)-C(6B)-O(8B)-C(13B)	4.4(6)
C(5B)-C(6B)-O(8B)-C(13B)	-174.9(3)

Table 7. Hydrogen bonds for 07mz524m [Å and deg].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1C)...O(5B)#1	0.85(2)	2.10(7)	2.901(13)	158(17)
O(1)-H(1D)...O(3B)#2	0.84(2)	1.67(8)	2.444(14)	152(16)

Symmetry transformations used to generate equivalent atoms:

#1 x+2,y,z+1 #2 x+1,y,z+1