STEREOSELECTIVE GLYCOSIDATIONS AND APPLICATION TO THE MYCOBACTERIAL ARABINOGALACTAN BY GOLD(III) CATALYSIS

A THESIS

SUBMITTED IN PARTIAL FULFILMENT OF THE

REQUIREMENTS

OF THE DEGREE OF

DOCTOR OF PHILOSOPHY

BY

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Dedicated to…

My Parents

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CERTIFICATE

Certified that, the work incorporated in the thesis entitled, "***Stereoselective Glycosidations and Application to the Mycobacterial Arabinogalactan by Gold(III) Catalysis***" submitted by ***Shivaji Ashokrao Thadke*** was carried out by the candidate, under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other University or institution.

Date: 29th April 2014 **Dr. Srinivas Hotha**
Pune (MH), India.

DECLARATION

I declare that this written submission represents my ideas in my own words and where others' ideas have been included; I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that violation of the above will be cause for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

Date: 29th April 2014 **Shivaji Ashokrao Thadke**

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Acknowledgements

Words are not enough to express feelings*…*

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Lastly, I would like express my deep feelings about Lord SriKrishna who always see mine up & downs and show me a right path to reach the destiny.

Shivaji Ashokrao Thadke

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Contents…

General remarks

- ^{1}H NMR spectra were recorded on AV 200, AV 400, DRX-500 MHz, JEOL ECX 400 or Bruker Avance 500 MHz spectrometer using tetramethylsilane (TMS) as an internal standard. Chemical shifts are expressed in ppm units downfield to TMS.
- ^{13}C NMR spectra were recorded on AV 50, AV 100, DRX-125 MHz, JEOL ECX 100 or Bruker Avance 125 MHz spectrometer.
- High resolution mass spectroscopy (HRMS) was performed on Waters Synapt G2 and Maldi-TOF.
- Low resolution mass spectroscopy (LRMS) was performed on Waters Acquity UPLC-MS (H Class).
- IR spectra were recorded on Perkin-Elmer 1310 and Perkin-Elmer 1600 FT-IR spectrometers with sodium chloride optics and are measured in cm^{-1}.
- Specific rotations were measured on a JASCO P-1020 or Rudolph polarimeter and measured in degree.
- All reactions were monitored by Thin-Layer Chromatography carried out on precoated Merck silica plates (F254, 0.25 mm thickness); compounds were visualized by UV light or by staining with anisaldehyde spray.
- All reactions were carried out under nitrogen or argon atmosphere with dry freshly prepared solvents under anhydrous conditions and yields refer to chromatographically homogenous materials unless otherwise stated.
- All evaporators were carried out under reduced pressure on Büchi and Heildoph rotary evaporator below 45 °C unless otherwise specified.
- Silica gel (100-200) and (230-400) mesh were used for column chromatography.
- All gold and transition metal salts were purchased from multinational commercial vendors.
- Materials were obtained from commercial suppliers and were used without further purification.
- Scheme, Figure and Compound numbers in abstract and individual chapters are different.

Abbreviations

Å – Angstrom

Ac – Acetate

AcBr – Acetyl bromide

AcCl – Acetyl chloride

AcOH – Acetic acid

Ac_2O – Acetic anhydride

AG – Arabinogalactan

AIBN – Azobisisobutyronitrile

ara*f* – arabinofuranosyl / arabinofuranoside

Bn – Benzyl

BnBr – Benzyl bromide

Boc – *t*-butylcarbonyl

Bz – Benzoyl

BzCl – Benzoyl chloride

Calcd – Calculated

CAN – Cerric ammonium nitrate

cat. – catalytic

$CDCl_3$ – Chloroform-D

$CHCl_3$ – Chloroform

Con A – Concanavalin A

COSY – Correlation Spectroscopy

CTA – Chain transfer agent

d – days

Da – Dalton

DBU – 1,8-Diazabicycloundec-7-ene

DEPT – Distortionless Enhancement by Polarization Transfer

DIPEA – *N*,*N*-Diisopropylethylamine

DMAP – *N*,*N*-Dimethylaminopyridine

DMF – *N*,*N*'-Dimethyl formamide

D_2O – Deuterium oxide

δ – delta (in PPM)

eq. – equivalents

Et_3N – Triethyl amine

EtOH – Ethanol

EtOAc – Ethyl acetate

Et_2O – Diethyl ether

g – gram

gal*f* – galactofuranosyl / galactofuranoside

GDA – Diacetonideglucofuranoside

GPC – Gel Permeation Chromatography

h – hour

HRMS – High-Resolution Mass Spectrometry

HSQC – Heteronuclear Single Quantum Coherence

Hz – Hertz

Im. – Imidazole

IR – Infrared

J – coupling constant

Kg – Kilogram

LAH – Lithium aluminium hydride

LAM – Lipoarabinomannan.

LCMS – Liquid-chromatography Mass spectrometry

lyx*f* – lyxofuranoside / lyxofuranosyl

man*p* – mannopyranosyl / mannopyranoside

MeOD – Methanol-D_4

mg – milligram

min. – minutes

MHz – Megahertz

mL – millilitre

mmol – millimolar

Mn – Number average molecular weight

MS – Molecular sieves

Mtb – *Mycobacterium tuberculosis*

NGP – Neighbouring group participation

NHPth – *N*-Hydroxy pthalimide

NHS – *N*-Hydroxy succinimide

NIS – *N*-Iodo succinimide

NMR – Nuclear Magnetic Resonances

NNGP – Non-neighbouring group participation

NPG – *n*-Pentenyl glycoside

PDI – Polydispersity index

PMB – *p*-Methoxy benzyl

PMBCl – *p*-Methoxy benzyl chloride

Py – Pyridine

PTSA, TsOH – *p*-Toluene sulfonic acid

ppm – parts per million

rha*p* – Rhamnopyranosyl / rhamnopyranoside

rib*f* – ribofuranoside / ribofuranosyl

rt – room temperature

sat – saturated

Tb – *tuberculosis*

TBAF – tetra-*n*-Butyl ammonium fluoride

TBAI – tetra-*n*-Butyl ammonium iodide

TBDPS – *t*-Butyldiphenylsilyl

TBDPSCl – *t*-Butyldiphenylsilylchloride

TCA – trichloroacetimidate

TfOH – Triflouromethanesulfonic acid

THF – Tetrahydrofuran

TLC – Thin Layer Chromatography

TMSOTf – Trimethylsilyltrifluoromethanesulfonate

µg – microgram

µmol – micromolar

µL – microliter

UP-LCMS – Ultra-Violet Performance Liquid-chromatography Mass spectrometry

xyl*f* – xylofuranosyl / xylofuranoside

Abstract

The thesis entitled, "***Stereoselective Glycosidations and Application to the Mycobacterial Arabinogalactan by Gold(III) Catalysis***" is divided into two chapters. Chapter one describes stereoselective synthesis of glycoconjugates using propargyl/methyl glycosides and propargyl 1,2-*O*-orthoesters as glycosyl donors under gold (III) catalysis. Chapter one is further divided into three sections. Section A describes the synthesis of 1,6-anhydro sugars from propargyl and methyl glycosides. Section B gives information about the synthesis and utility of glycoacrylates/acrylamides using pyranosyl propargyl 1,2-orthoesters. Section C shows identification of a new methodology for the stereoselective synthesis of aminooxy glycosides using pyranosyl/furanosyl propargyl 1,2-*O*-orthobenzoates. In chapter two, the facile synthesis of 1,2-*O*-orthoesters and activation of furanosyl propargyl 1,2-*O*-orthobenzoates as glycosyl donors in the presence of gold (III) catalysis to give 1,2-*trans* glycoconjugates is delineated. Bio-inspired epimerisation of 1,2-*trans* glycoconjugates to 1,2-*cis* glycoconjugates and application of these protocols for the synthesis of Mycobacterial pentadodecameric arabinogalactan is also delineated in chapter two.

Chapter 1: Stereoselective Glycoconjugates by Gold Catalysis

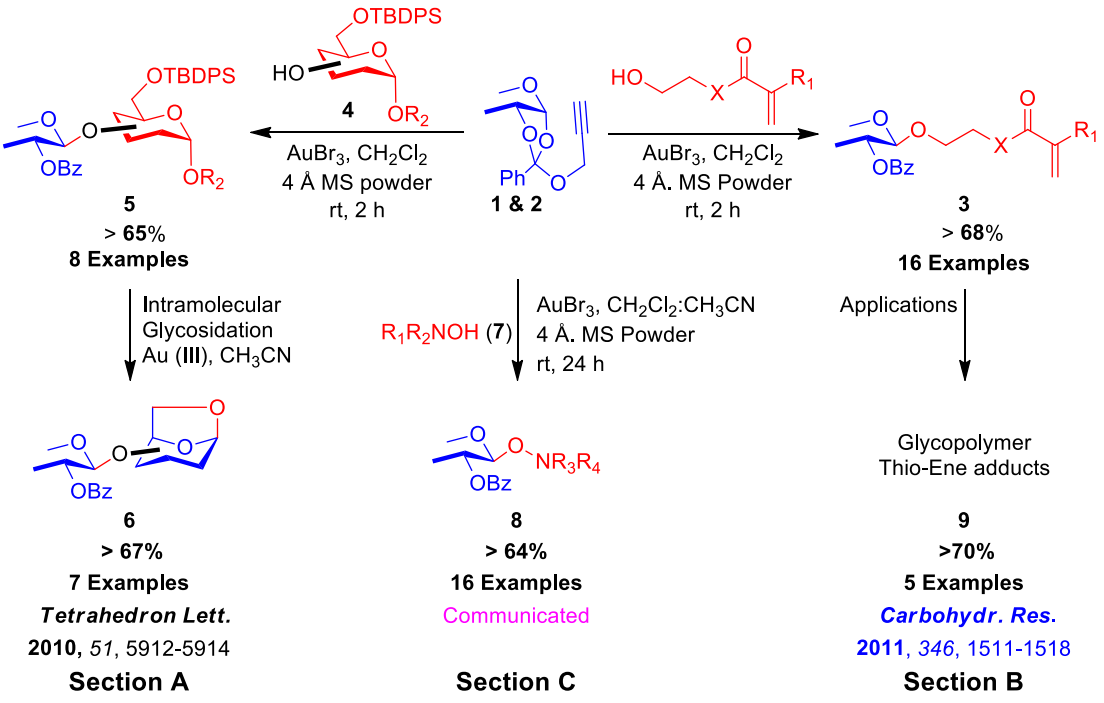
Glycoconjugates are essential for all living organisms. They regulate cell/cell and cell/invader interactions such as inflammation, tissue engineering, viral and bacterial infections, cell-growth control, wound healing, blood coagulation, tumour metastasis, and disease of nervous system; and many carbohydrates analogues have now been identified and entered into the clinical trials. For example, glycopolymer based drugs are used to locate certain lectins which are present on the malignant cells in chemotherapy of cancer to avoid unwanted damage during therapy. Syntheses of stereoselective glycoconjugates are difficult and access to stereoselective glycoconjugates is recommended tool for the glycochemistry world. In this premise, recently identified propargyl 1,2-*O*-orthoesters are interesting for the synthesis of stereoselective glycomonomers which can be subsequently polymerised. The salient feature of gold catalyzed activation of 1,2-*O*-orthoesters procedure are, (i) catalytic activation; (ii) stable glycosyl donor; (iii) easily accessible; (iv) high yielding; (v)

orthogonal to other glycosyl donors; and (vi) leaving group traceless after the glycosidation.

Section A: **Synthesis of 1,6-Anhydro Sugars**

1,6-Anhydro sugars (**6**) are intramolecular cyclic glycosides and are known to be useful synthons for the preparation of various glycosyl compounds such as *S*-glycosides, *N*-glycosides, glycosyl halides, *C*-glycosides, proteo-glycans and can act also as glycomonomers for the synthesis of stereoregular glycopolymer. In this regard, we utilized propargyl/methyl glycosides (**5**) for the synthesis of 1,6-anhydro sugars (**6**) in the presence of gold tribromide. Seven representative 1,6-anhydro saccharides were synthesized which are derived from mono-, di-, and trisaccharides.

Scheme 1:



Section B: **Synthesis of Glycoacrylates/acrylamides and their Applications**

Glycoacrylate/acrylamides (**3**) are very good for the glycopolymer synthesis and 1,4-Michael addition products. In section B, 1,2-*O*-orthoesters (**1**) were utilized for the synthesis of 1,2-*trans* glycoacrylates/acrylamides (**3**). These glycomonomers

were further utilized for the synthesis of glycopolymer and thio-ene reactions. The protocol was demonstrated by the use of 16 examples of glycomonomers, and one example for the demonstration of glycopolymer synthesis and three examples of thio-ene reactions.

Section C: **Synthesis of Aminooxy Glycosides**

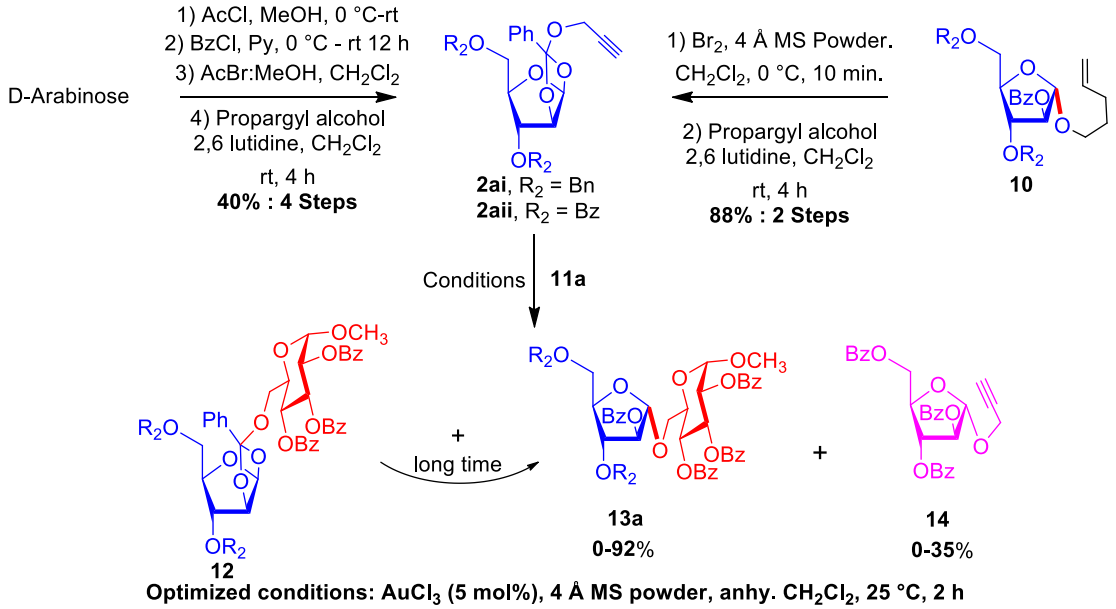
Chemo/regioselective attachment of sugar moiety to peptide, proteins, functionalised polymers and natural products is a difficult task in carbohydrate chemistry. Generally orthogonal coupling between acid-alcohol, azido-alkyne, amine-acid are useful techniques for the installation of sugar to any conjugates. The formation of imine bond is much more easily compared to the above mention orthogonal couplings. However, introduction of amine to sugar or conjugates is tough to acquire aminoglycosides or aminoconjugates in one step. Hence, in a separate endeavour propargyl 1,2-*O*-orthoester (**1** & **2**) strategy was exploited to install protected aminooxy (**8**) moiety at the anomeric carbon of sugar residue in 1,2-*trans* fashion and followed by saponification with methyl amine to afford free amino group at the reducing end. The protocol was gauged through a panel of substrates which are mono- di-, trisaccharides and oligosaccharides.

Chapter 2: Single Donor Chemistry for *Mycobacterial* Arabinogalactan by Gold Catalysis

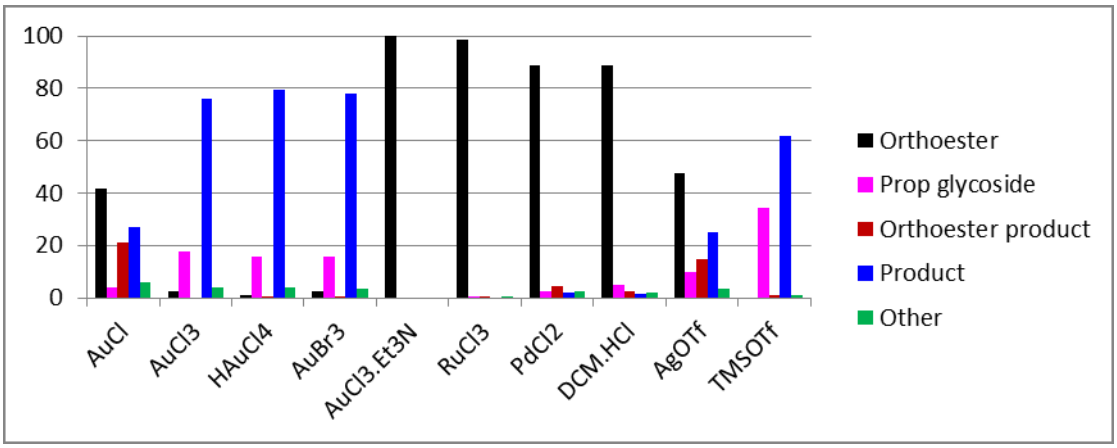
Tuberculosis (Tb) kills more than three millions lives every year globally (WHO 2011) and the causative agent is *Mycobacterium Tuberculosis (*Mtb*)*. Brennan *et al*. unravelled the fine structure of the cell wall of Mtb which mainly consists of two major interconnected oligosaccharides (AG & LAM) as well as non-oligosaccharides parts (mycolic acids). Arabinogalactan (AG) consists of tridodecameric arabinan which is attached to the galactan. In AG, there are mainly four 1,2-*cis* and nineteen 1,2-*trans* interglycosidic linkages present which is required for the survival of Mtb. The synthesis of arabinogalactan is challenging and hence, there were many synthetic efforts in the literature regarding major motifs and dodecasaccharide in arabinogalactan. Challenges in synthesis coupled with enticing biological significance encouraged us to synthesize pentadodecameric arabinogalactan using gold catalysis. Our laboratory was working on propargyl glycosides as stable glycosyl donors to obtain glycosides as well as oligosaccharides

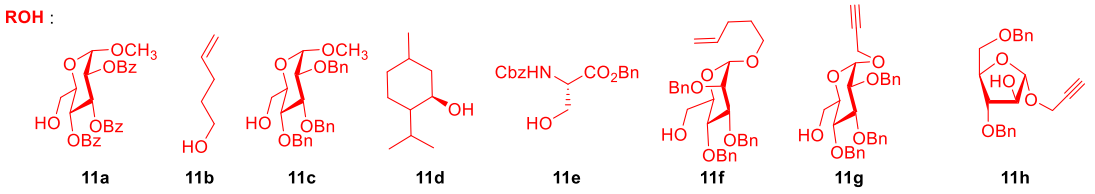
in good yield. In AG and LAM both arabinose and galactose in furanosides form. The chemistry of furanosides and pyranosides is not similar. Earlier studies from our group suggested that, propargyl arabinofuranosides are not suitable for

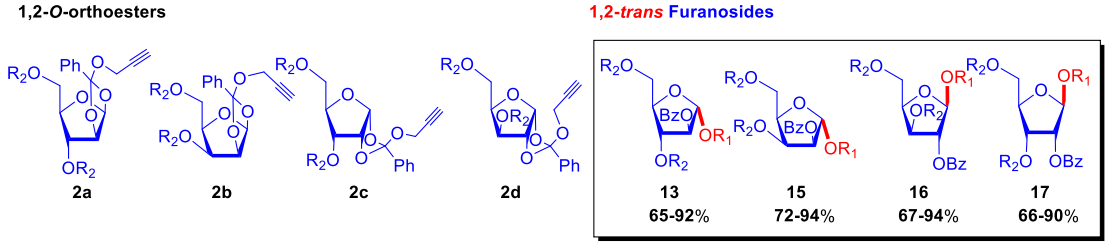
Scheme 1:



Optimized conditions: $AuCl_3$ (5 mol%), 4 Å MS powder, anhy. CH_2Cl_2, 25 °C, 2 h







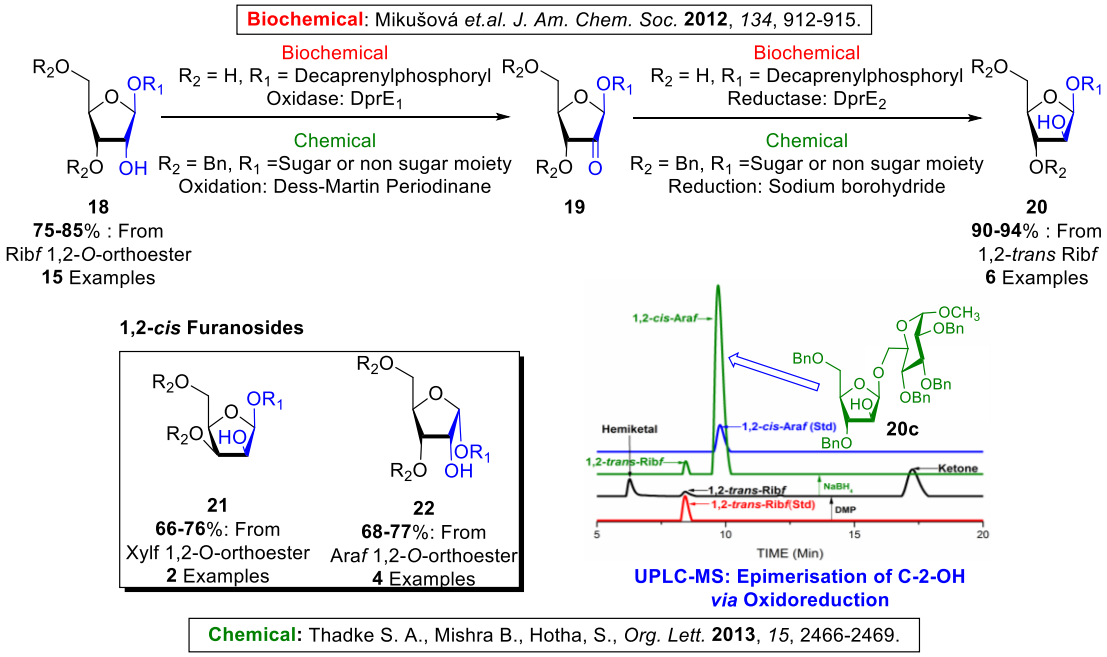
oligosaccharides as they give α/β mixture of products. Therefore, first we studied the furanosyl propargyl 1,2-orthobenzoates (**2**) as glycosyl donors with catalytic amount of gold salts or any other. Simply, arabinofuranosyl propargyl 1,2-orthobenzoate (**2a**) was obtained from D-arabinose in four steps i.e. Fischer glycosidation, benzoylation, bromination and further reaction with propargyl alcohol and 2,6-lutidine. However, this approach for the synthesis of 1,2-*O*-orthoester is restricted to the monosaccharides level (**2**) and not applicable for oligosaccharyl 1,2-*O*-orthoester synthesis (For example, **27**). The use of acetyl bromide in methanol and dichloromethane for bromination was restricted due to the possible hydrolysis of interglycosidic bond in case of higher oligosaccharides. Thus, we modified the bromination step with pentenyl glycoside and molecular bromine followed by propargyl alcohol, 2,6-lutidine treatment in dichloromethane to give oligosaccharyl propargyl 1,2-*O*-orthoester (**27**) in very good yield. Orthoester (**2a**) and glycosyl acceptor (**11a**) were dissolved in anhydrous dichloromethane and added freshly activated 4 Å Molecular sieves (MS) powder. The reaction mixture was stirred at room temperature (rt) for 10 min and catalytic amount of gold (III) chloride was added. The progress of the reaction was judged with TLC as well as UPLC-MS. 1,2-*O*-orthoester (**2a**) has disappeared within 1 h and two new compounds were observed. Major compound was the required 1,2-*trans* glycoside (**13a**) which is more than 80% in yield and minor compound was the direct glycosidation product (**14**) is less than 15%. We used several alkynophilic, non-alkynophilic Lewis and, Brønsted acids for the activation of 1,2-*O*-orthoester (**2a**) without any surprising results were obtained. After several experiments, the gold (III) chloride (7 mol%), 4 Å MS powder in anhydrous CH_2Cl_2 was found to be the best condition for the synthesis of glycoconjugates.

As discussed earlier, there are mainly two types of linkages in arabinogalactan i.e. 1,2-*trans* and 1,2-*cis* out of which 1,2-*trans* linkages can be easily obtained by *C*-2-benzoyl/acetate protecting group in glycosyl donor and from 1,2-*O*-orthoesters as glycosyl donors. Synthesis of 1,2-*cis* glycosides is much more difficult. Although, there are few reports on stereoselective synthesis of 1,2-*cis* glycosides, a mixture of α- and β-isomers are often observe in the reaction with α-isomer(1,2-cis glycoside) being the major product. Meanwhile, Mikušová and Besra independently disclosed

the biochemical epimerization of β-decaprenylphosphoryl ribofuranoside *C*-2-OH (**18**) to β-decaprenylphosphoryl arabinofuranoside (**20**).

Similar strategy can be envisaged for the epimerization of *C*-2 alcohol in 1,2-*trans* glycosides to afford 1,2-*cis* glycosides in a chemical manner. 1,2-*trans* Glycosides could be easily obtained by employing 1,2-*O*-orthoester strategy can be saponified into *C*-2-OH (**18**) which can be oxidized with Dess-Martin Periodinane (DMP) in CH_2Cl_2 to form 2-ulose (**19**) derivative. 2-Ulose derivative (19) was reduced with $NaBH_4$ in methanol to generate furanosyl 1,2-*cis* alcohol (**20**) in a fully

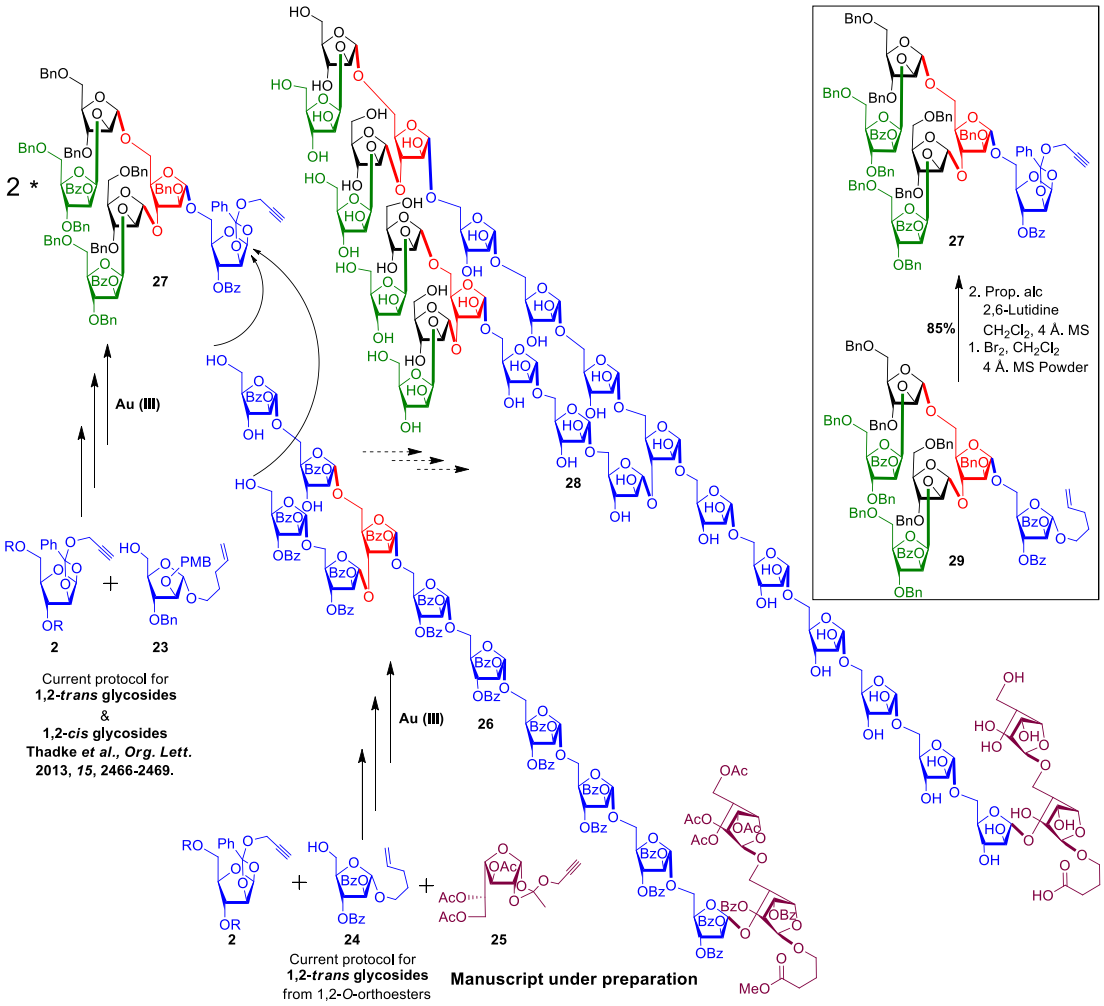
Scheme 2:



distereoselective fashion. Further, same reaction was monitored through UPLC-MS to prove the clean epimerization of β-ribofuranoside to β-arabinofuranoside. First we injected standards of β-rib*f* (t_R = 8.48 min.) and β-ara*f* (t_R = 9.93 min.) to define the individual retention times on UPLC-MS platform. β-Rib*f* (**18**) was oxidised with Dess-Martin Periodinane in CH_2Cl_2 to form 2-ulose (**19**) derivative which was observed at t_R 17.45 min. along with hemiketal at t_R 6.30 min. in UPLC-MS chromatogram. 2-Ulose derivative of ribofuranosides was reduced with $NaBH_4$ in methanol to give 1,2-*cis* (β)-araf (**20**) in highly distereoselective fashion. Later, we utilised similar protocol for the synthesis of several 1,2-*cis* (β)-ara*f* (**20**), 1,2-*cis* (β)-lyx*f* (**21**) and 1,2-*cis* (α)-rib*f* (**22**) in fully distereoselective fashion. Stereochemical outcome can be explained by closely looking at the C-2-ulose derivatives of all the four furanosides which reveals the differential steric crowding around the ketone that

is undergoing the reduction. The ring oxygen, C-5-OBn and C-1 glycoside prevent the hydride to attack from the *exo*-attack in the case of β-ribf→β-araf conversion; and hence, hydride prefers the *endo*-attack on the ketone to give β-araf only. Similarly, *endo*-attack in the α-araf→α-ribf conversion is sterically not favourable and hence, the *exo*-attack product was observed. Also, in case of β-xylf→β-lyxf conversion, the *endo*-attack is sterically demanding which results into *exo*-isomer. The ring oxygen, C-3-OBn, and the C-5-OBn make the *exo*-attack complete unavailable for the hydride to attack on the ketone giving back the starting material in case of α-lyxf→α-xylf.

Scheme 3:



Protocols identified vide supra were effectively utilized for the convergent synthesis of pentadodecameric arabinogalactan (**28**) of Mtb cell wall. Synthetic endeavour started from the arabinofuranosyl propargyl 1,2-*O*-orthoester (**2a**) to give required 1,2-*O*-orthoesters, and pent-4-enyl arabinofuranosides (**23** & **24**) as glycosyl acceptors. Iterative glycosidations followed by deprotection gave tridodecamer (**26**, 350 mg). Synthesis of hexasaccharyl 1,2-*O*-orthoester **27** and final glycosylation and

subsequent deprotection steps are under progress. Oligosaccharyl 1,2-*O*-orthoester was obtained from pent-4-enyl oligosaccharide which was treated with Br_2 followed by treatment of propargyl alcohol in CH_2Cl_2. All glycosidations were carried out using gold (III) catalysis in anhydrous CH_2Cl_2, deprotection of OTBDPS bond by HF.Py in THF:Py(5:1) and -OBz group by NaOMe in methanol. Full experimental details and characterization data are described in chapter two.

In summary, gold (III) catalysis was efficiently exploited for the stereoselective synthesis of glycoconjugates and for the mycobacterial arabinogalactan for the first time using single donor chemistry. The salient feature of this endeavour are, (i) single donor chemistry; (ii) high yielding convergent synthesis; (iii) efficient; (iv) modular and finally it enables synthesis of various "Chemical" mutants of arabinogalactan. In future, methods developed in this exemplary endeavour facilitate synthesis of variety of furanosides and pyranosides in a facile manner.

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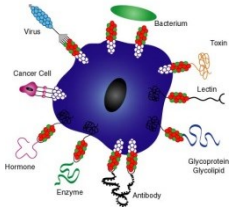
Stereoselective Glycosidations by Gold(III) Catalysis

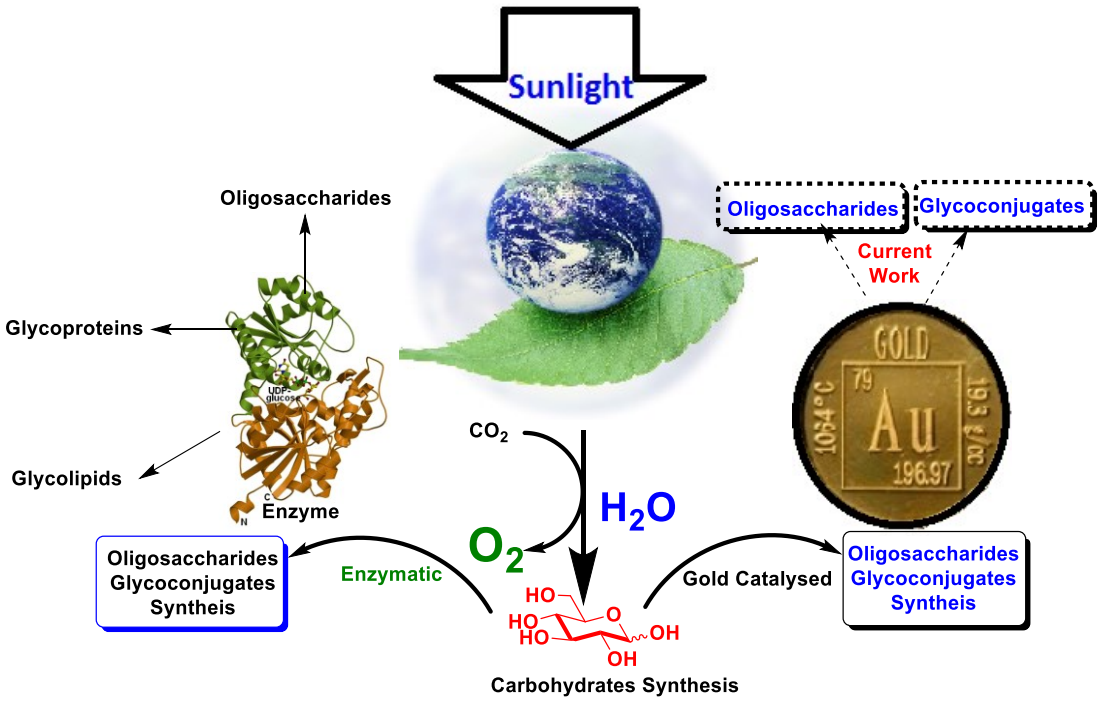
Carbohydrates 



1.1 – Introduction

Plant tissues (biomass) are the major proportion of organic matter on earth and are composed of carbohydrates. The photosynthetic apparatus in the green plants utilises solar energy to effect the reduction of atmospheric CO_2 and in a complex sequence of reactions produces glucose (carbohydrate) reported by Dumans in 1838. Carbohydrates enter into the living organism through food as a form of glycoconjugates. These glycoconjugates are essential source of all living organisms. They regulate cell/cell[1] and cell/invader[2] interactions which play a significant role in the construction of energy to build the organs as well as organisms. Carbohydrates also play important innings in disorders such as inflammation, viral and bacterial infections, cell-growth control, wound healing, blood coagulation, tumour metastasis, and disease of nervous system,[3a,b] numerous carbohydrates analogues have now been identified and entered into the clinical trials.[3c] For example, glycopolymer based or surrounded drugs are used to locate certain lectins which present on the malignant cells in chemotherapy of cancer to avoid unwanted damage during therapy (**Figure 1.1**).[1,2]

Figure 1.1: Carbohydrates and cell surface



Glycoconjugates are present as micro and heterogeneous form as well as in very low concentration. Isolation of such species from food or any other natural

sources is very difficult to study their original role in living organism. Therefore, chemical or enzymatic synthesis can be employed to obtain good quantity of glycoconjugates.

1.2 – Early life of sugar[4]

In the late of 19th century, after the satisfactory results of Le Bel and van't Hoff for the tetrahedron structure of carbon; Emil Fischer in 1884 identified the structure of glucose (First carbohydrate). Meanwhile, Heinz and Heidi proposed the cyclic structure of glucose in aqueous solution with two different optical rotations (α and β) which was earlier suggested by von Bayer in 1870 and again by Tollens in 1883. In 1926, W. N. Haworth suggested that, cyclic six membered rings with a hexagon can have several conformations. After the successful story of Fischer and Haworth on glucose, Odd Hassel and Richard Barton showed that the pyranose ring is of non-planar shape. Glucose is present in chair form with axial and equatorial hydrogen atoms and useful for the prediction of glucopyranoside in chair form which is in rapid equilibrium with boat conformation. From the conformational study of glucose molecule, Edward observed that the energy difference between two conformations is to about 1.5 KJmol^{-1} in favour of β-isomer which has three times lesser value (3.5 KJmole^{-1}) for an equatorial over an axial hydroxyl group which favours the formation of α-isomer. This phenomenon was named as "anomeric effect" (explained in **1.4.3**) by Lemieux.

1.3 – Glycobiology and Glycoconjugates[5]

The term glycobiology was first coined by Dwek in 1988 to recognise carbohydrate chemistry and biochemistry to understand the cellular and molecular biology of glycans or glycoconjugates. Glycoconjugates are defined as 'carbohydrates covalently linked to the other chemical substances such as proteins, lipids, organic molecules, natural products, other sugar residues, and peptides. These are further classified as glycolipids, glycoproteins, glycolipids, oligosaccharides, polysaccharides, glycopeptides, etc. As discussed earlier, glycoconjugates play important role in various biological processes such as drug delivery systems, tissue engineering, energy creation in living organism, and cell-cell interactions due to the presence of various glycan binding receptors. For example, Antigens: Landsteiner and co-workers showed that, the human blood can be classified on the basis of its

ability to clump together agglutinative of red blood cells. The cause of agglutination is due to the oligosaccharides' displayed on surface of red blood cells which differentiate the blood group which inturn arises from differences in a series of genetically encoded glycosyltransferases. These glycoconjugates (oligosaccharides) were built from glucose, galactose, fucose, *N*-acetyl galactosamine with a lipid.[5a] In addition, glycoconjugates are also useful in chemical processes such as column chromatography, sensor, polymer chemistry, etc.[1,2]

1.4 – Synthesis of glycoconjugates[6-15]

In glycoconjugates, carbohydrates are attached to one another or to other moiety through different linkages such as *Sugar-O-*, *Sugar-S-*, *Sugar-N-*, *Sugar-C-* and some binary linkages such as *Sugar*-carbamate-, *Sugar-O-N*-linkages between two sugar molecules or sugar molecule and any glycosyl acceptors or hydroxy groups. There are several terms involved in the synthesis of glycoconjugates or glycosides. Understanding these factors is of paramount importance for appreciating the glycoside synthesis and hence explained below.

1.4.1 – Glycosidation[6]

Glycosidation can be defined as, 'nucleophilic displacement of leaving group attached to anomeric carbon of sugar residue'. The nucleophile may be alcohol, thio, amino, carbon nucleophile, and some binary linked nucleophile such as *-O-N-*, *-OCOO-*. Glycosidation reaction occurs between a glycosyl donor that donates glycosyl moiety and glycosyl acceptor which accepts glycosyl moiety. Generally, there are two types of glycosidation, i.e. enzymatic glycosidation and chemical glycosidation.

1.4.1.1 – Enzymatic glycosidation[6b,c]

In human body, glycoconjugates are synthesized by the help of several enzymes. The selectivity and regiospecificity for the complex oligosaccharides and glycoconjugates depends upon the specificity of enzymes (glycosyltransferases, glycosidases, and glycosynthases) present in the cell. From this, concept of formation of stereoselctive and regioselective glycoconjugates, Leloir identified enzymes for the biosynthesis of oligosaccharides and further named as 'Leloir enzymes'. According to Leloir pathway, enzyme requires sugar nucleotides as glycosylation donors and with specific hydroxy group of the acceptor sugar (**Figure 1.2**).

Figure 1.2: Enzymatic synthesis of oligosaccharides

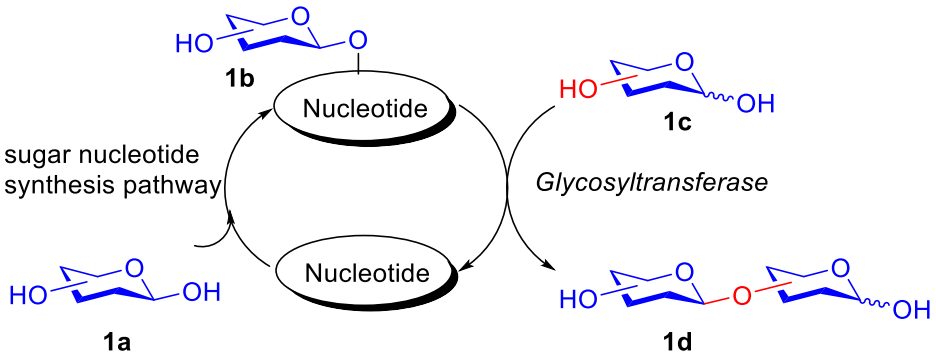


Table 1.1: Few enzymes in glycosidation

Donor + Acceptor $\xrightarrow{\text{Enzymes}}$ Glycoconjugates

Enzymes	Glycosyl donor	Advantages	Disadvantages
Glycosidase	Nitrophenyl glycoside	• Easy to perform • Low cost	• Low yield • Low regioselctivity
Glycosynthase	Glycosyl fluoride	• High yield	• Low avilability • Unpredictable regioselctivity
Leloir glycosyltransferase	Sugar necleotide	• High yield • High stereo & regioselctivity • Essential for important sugar sequences	• High cost
Non-Leloir glycosyltransferase	Sugar phosphate	• High yield • High stereo & regioselctivity	• Not essential for important sugar sequences

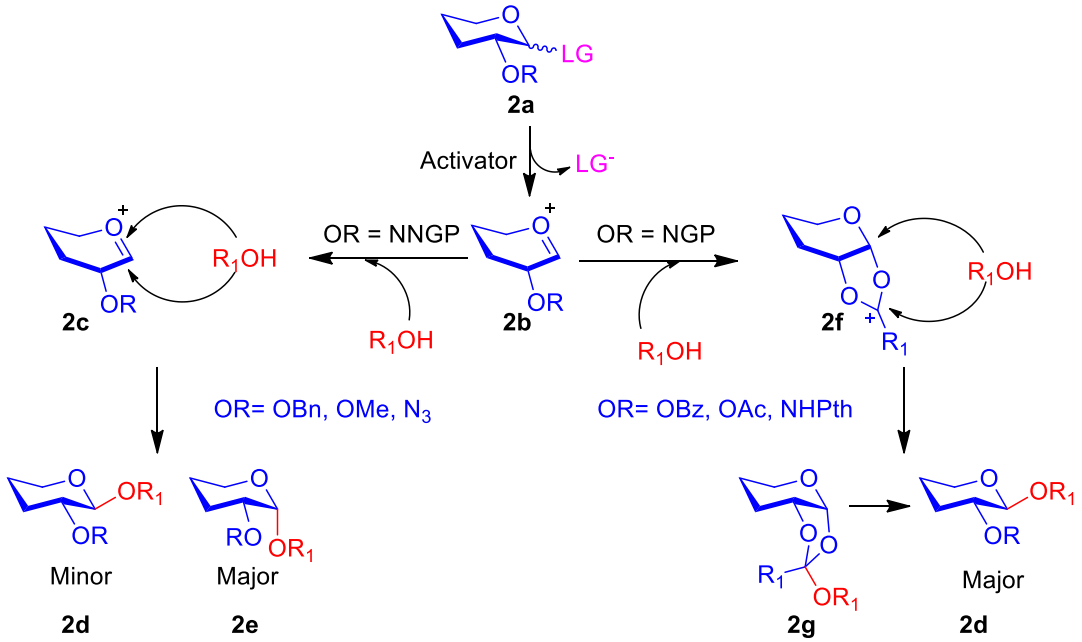
Some other enzymes are useful for the formation of glycosidic bond such as glycosidase, glycosynthase, and non-Leloir glycosyltransferase described in **Table 1.1.** The enzymatic glycosidation gives only recommended stereoselective and regioselective glycoconjugates but accesses to such kind of enzymes or their synthesis is a herculean task. Since specific enzymes are used for each transformation, several enzymes would be required for the synthesis of complex oligosaccharides. To avoid these drawbacks, chemical glycosidation is more suitable.

1.4.1.2 – Chemical glycosidation and importance of glycosyl donor[6a]

In chemical glycosidation, leaving group is displaced from glycosyl donor using a chemical reagent called as an activator (Lewis acid, Brønsted acid, Neutral

reagents, inorganic salts) to form oxacarbenium ion intermediate (**2b**). The oxacarbenium ion is subjected to stabilise/destabilise such short-lived, high energy species and further attack by any nucleophile to form glycoconjugate in α:β fashion (**Scheme 1.1**).

Scheme 1.1: General route for glycosidation

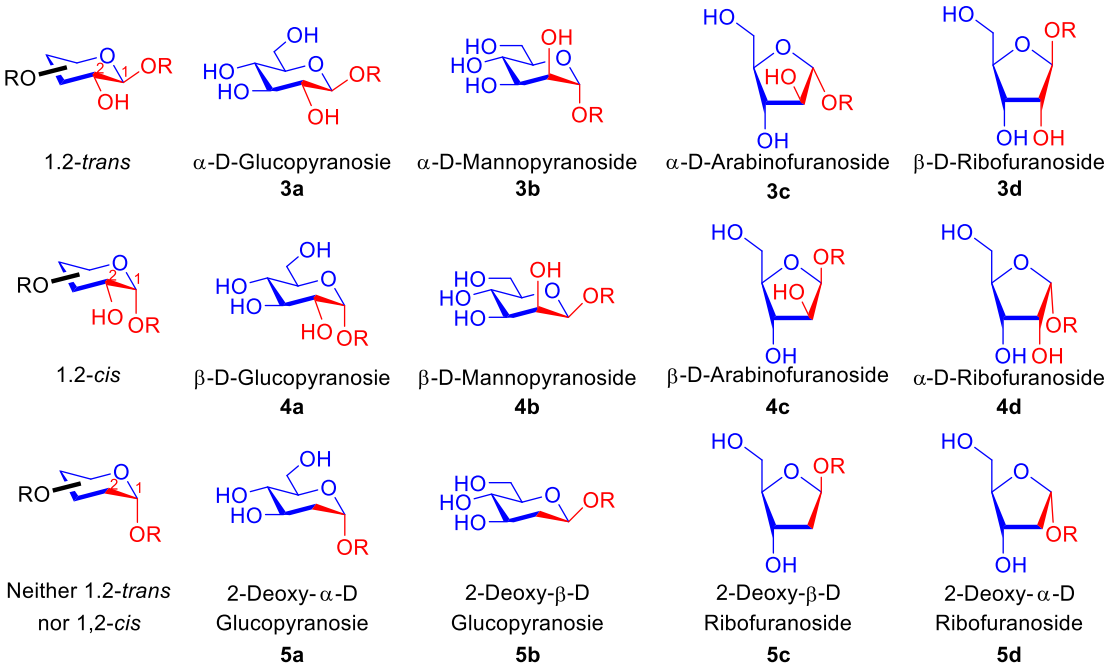


The formation of 1,2-*cis* and 1,2-*trans* glycoconjugates largely depends on the functionality on *C*-2 position of glycosyl donor. The substituent at *C*-2 is a functionalised with ether linkage such as benzyl, methyl, 4-methoxybenzyl, azide, etc. then resultant glycoside will be in 1,2-*cis* and 1,2- *trans* mixture. This occurs because nucleophile can attack either from the β-side or α-side. Same glycosidation reaction gives pure 1,2-*trans* glycoside when *C*-2 is functionalised as an ester such as acetate, benzoate. This is due to the neighbouring group participation of an ester group at *C*-2 position in glycosyl donor which forms corresponding stable acycloxonium ion **2f** to avoid attack from the other side to form pure 1,2-*trans* glycoside. The α-product is more thermodynamically favoured because of the anomeric effect. A substantial amount of the kinetically derived β-linked product is often obtained owing to the equilibrium character of glycosylation. Various factors such as temperature, protecting groups, conformation, solvent, promoter, steric hindrance or leaving groups influence outcome of the glycosylation reaction.

1.4.2 – Types of glycosidic linkages

There are two major types of glycosidic linkages based on orientation of two groups present in saccharide at position *C*-1 and *C*-2 respectively. If both groups at

Figure 1.4: Types of 1,2-linkages



C-1 and *C*-2 are co-planar then it is called as 1,2-*cis* linkages and if both groups at *C*-1 and *C*-2 positions are non-coplanar then it is called as 1,2-*trans* linkages. In some cases, *C*-2 position is substituted with hydrogen instead of hydroxy group then it is known as *deoxy* but still named as 1,2-*cis* and 1,2-*trans* based on the orientation of group present at *C*-1 position.

1.4.2.1 – 1,2-*trans* glycosides

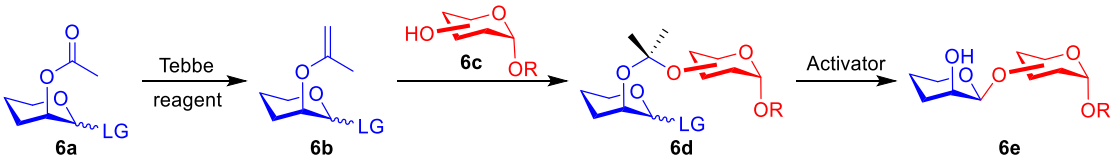
Synthesis of 1,2-*trans* glycosides is relatively straightforward and can be accessible by using neighbouring group participation group at *C*-2 position of the glycosyl donor (**Scheme 1.1**).

1.4.2.2 – 1,2-*cis* glycosides

Synthesis of 1,2-*cis* glycosides are difficult compared to 1,2-*trans* glycoside but not impossible. Non participation group at *C*-2 position in most of the glycosyl donors gives the major portion as 1,2-*cis* glycoside. 1,2-*cis* Glycosides can be synthesized from the intramolecular glycosyl acceptor delivery (IAD) between

glycosyl donor and glycosyl acceptor which is introduced by Hindsgaul.[6o] For example, synthesis of β-mannoside can be obtained by using acetal linkage as an IAD between glycosyl acceptor and glycosyl donor with suitable leaving group (**Scheme 1.2**).

Scheme 1.2: **Intramolecular glycosidation for 1,2-*cis* mannosides**

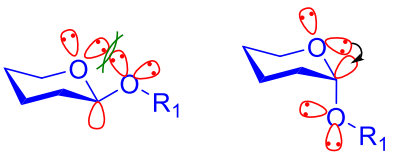


Indirect methods such as epimerisation at *C*-2 position using oxidation reduction strategy and nucleophilic displacement are important techniques for the synthesis of 1,2-*cis* glycoside.

1.4.3 – Anomeric effect[6d,e]

The most stable form of cyclohexane is chair conformation with all substituents in the equatorial positions. This criterion is applicable to 1-hydroxy derivative of sugar which is more stable in β-conformation via intramolecular hydrogen-bond formation with sugar *O*-5 (endocyclic oxygen in sugar). Replacement of -*OH* with other substitutes such as, -*OR*, -*SR*, -halide or any other polar group would make the sugar prefer axial conformation at the anomeric carbon. This phenomenon was first observed by Edward[6d] and later named as 'anomeric effect' by Lemieux.[6e]

Figure 1.4: Anomeric effect

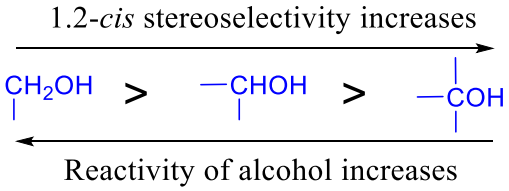


The anomeric effect is explained by means of two main factors namely, 1) the dipole-dipole interaction and 2) the stereoelectronic effect. The two non-bonding electron pairs on the ring oxygen and other polarised bond between the anomeric carbon and exocyclic heteroatom shows the two dipoles in same direction which can cause repulsion that allows α-conformation instead of β-conformation. According to

the stereoelectronic interpretation, the non-bonding electrons of the endocyclic oxygen atom (the p-orbital of which is axially oriented) are syn-periplanar to the anti-bonding orbital of the anomeric substituent when it is at α-position. As a result, the two orbitals can mix, establishing an $n \rightarrow \sigma^*$ sp interaction, which stabilises the α-anomer.

1.4.4 – Glycosyl acceptors[6f,g,h,i,j]

The formation of 1,2-*cis* stereoselectivity not only depends upon the glycosyl donor but also on glycosyl acceptors. The most reactive hydroxyl groups give less 1,2-*cis* stereoselectivity and vice versa.[6f] Regarding the sugar or aliphatic glycosyl acceptors, the primary alcohol give less 1,2-*cis* selectivity than the secondary alcohol. The same strategy also applies for the glycopeptides synthesis. For example, glycosylation between secondary hydroxyl groups of threonine generally gives more 1,2-*cis* selectivity with 2-NNGP group in glucosyl bromide or trichloroacetimidates.[6g]

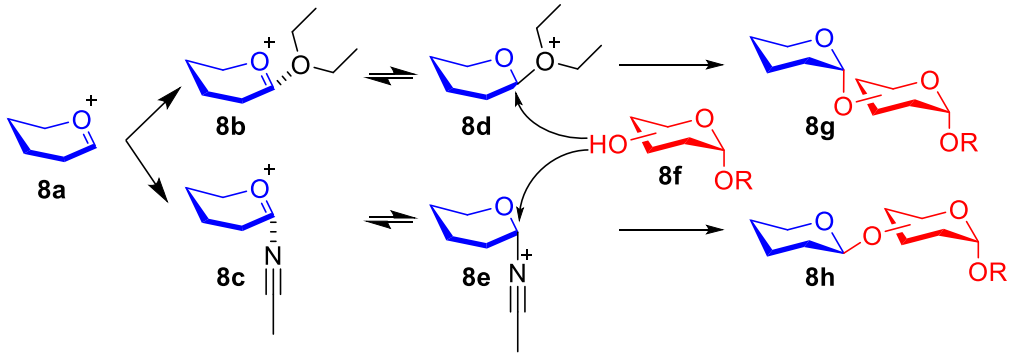


Only in few cases, primary alcohols were found to give more 1,2-*cis* selectivity than secondary alcohols. The electron withdrawing groups such as -OAc, -OBz in glycosyl acceptors (protection of other hydroxyl group in sugar) decreases the reactivity of alcohol which results in the 1,2-*cis* selectivity and vice-versa.[6h] The protection of alcohol with trityl,[6i] silyl[6j] group increases the reactivity of alcohol to form corresponding 1,2-*trans* glycosides.

1.4.5 – Reaction conditions (solvents, promoters, temperature and pressure)[6k,l,m,n]

1.4.5.1 – Effect of solvents[6k]:- Polar solvents such as acetonitrile, DMF, etc. favour formation of 1,2-*trans* glycosides *via* charge separation between *O*-5 and β-*O*-1 and 1,2-*cis* glycosides are observed with the non-polar solvents like dichloromethane, 1,2-dichloroethane, nitroethane, or toluene. However, some solvents such as, CH_3CN, $C_2H_5OC_2H_5$ interact with the oxacarbenium ion and lead to preferential formation of 1,2-*trans* or 1,2-*cis* glycosides in *C*-2 non-participation protected glycosyl donors (**Scheme 1.3**).

Scheme 1.3: Solvent effects on glycosidation



1.4.5.2 – Promoters[6l]:- Milder motivating conditions are usually favourable for 1,2-*cis* glycosylation. For example, halide-ion-catalyzed reactions give the best outcomes for the glycosylation with glycosyl halides; thioglycosides perform better when triggered through a mild agent, such as iodonium dicollidine perchlorate (IDCP); however trichloroacetimidates are best initiated by the Lewis as well as Brønsted acids, such as trimethylsilyl trifluoromethanesulfonate (TMS-triflate, TMSOTf) or triflouromethanesulfonic acid (triflic acid, TfOH).

1.4.5.3 – Temperature and pressure[6m,n]:- No change in the selectivity occurs in the *C*-2 non-participating glycosyl donors but remarkable increase in the reaction yield was noted after applying high pressure to the reaction. Generally, 1,2-*trans* selectivity favours with kinetically controlled reaction in *C*-2 non-participating glycosyl donors.

1.4.6 – Accounts of glycosyl donors[7-16]

As discussed earlier in glycosidation, glycosyl donor is donating glycosyl moiety to acceptor in the presence of activator to form corresponding glycoconjugates. The story of glycosyl donor begins with Fischer glycosidation[7a] with reactive acceptors such as methanol in the presence of Brønsted acid. Further, hemiacetals was used in the alkylation with suitable strong base and alkyl halide to get glycoconjugates. Even hemiacetals can be activated with Lewis/Brønsted acid and desiccant with excess of glycosyl acceptor.[7b,c] Later several glycosyl donors came into the race for glycoconjugates synthesis with pertinent conditions. Some of the routinely used methods are explained below.

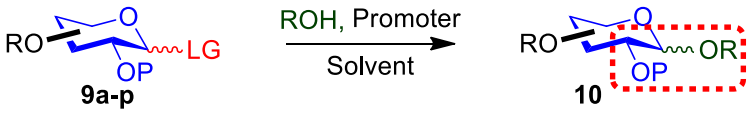
1.4.6.1 – Koenings-Knorr glycosidation[8]: Koenings-Knorr[8a] used glycosyl halide (chloride/bromide) as a glycosyl donor which plays a historical role in the

development of the glycosidic linkages (α:β-linkages based on *C*-2 protecting group) in the presence of silver salts (Ag_2O, AgOTf, and Ag_2CO_3). Helferich modified this methodology with solvent soluble heavy metals salts ($HgBr_2$, HgCN, and HgO). Glycosyl iodides bearing with the instability were generated *in situ* from other glycosyl halide. Mukaiyama[8b] identified the first successful activation of glycosyl fluorides which are too unreactive and stable compared to other glycosyl halide in the presence of combination of $SnCl_2$ and $AgClO_4$ to afford oligosaccharides. The use glycosyl chloride/bromide for the large scale preparation of glycosides was not recommended, owing to the accumulation of light- and moisture sensitive toxic, heavy metal wastes. Even the stability of glycosyl halide was based on protecting groups which greatly limits the formation of glycosides.

1.4.6.2 – Glycosyl esters[9] and 1,2-Orthoesters[10]: The readily available per acetate derivative of sugar can also act as a glycosyl donor using stoichiometric or more than stoichiometric Lewis/Brønsted acid and excess of acceptor. The selectivity of resultant glycosides depends upon the promoter and solvent system. For example, formation of α-glucosides was reported with the $SnCl_4$-$AgClO_4$ system in ether, whereas the β-glucosides were reported with same catalyst in acetonitrile (see **1.4.5.1**). The acyloxy group is not as good leaving group as others and requires strong acidic conditions which are suitable for acid stable glycosyl acceptor and donor. Under strongly acidic conditions, anomerization of β-glycoside to the thermodynamically more stable α-glycoside occurs. The ester group is further converted into halide in the presence of acid-halide and the resultant glycosyl halide under basic condition gives 1,2-orthoester in the presence of a nucleophile. This was discovered by Kochetkov.[10] In his life time, several 1,2-orthoesters were made and successfully activated them under acidic conditions into 1,2-*trans* glycosides.

1.4.6.3 – Glycosyl trichloroacetimidate[11]: The imidate was used firstly by Sinaÿ for the synthesis of glycoside but Schmidt extended this methodology with trichloroacetimidates (TCA) as a better glycosyl donor comparative to the other glycosyl donors. The TCA can be obtained by a reaction of lactol with trichloroacetonitrile in the presence of base and further activation could be done using catalytic amount of Lewis/Brønsted acids. Stronger Lewis/Brønsted acids give thermodynamically more stable products i.e. 1,2-*cis* glycoside and vice versa.

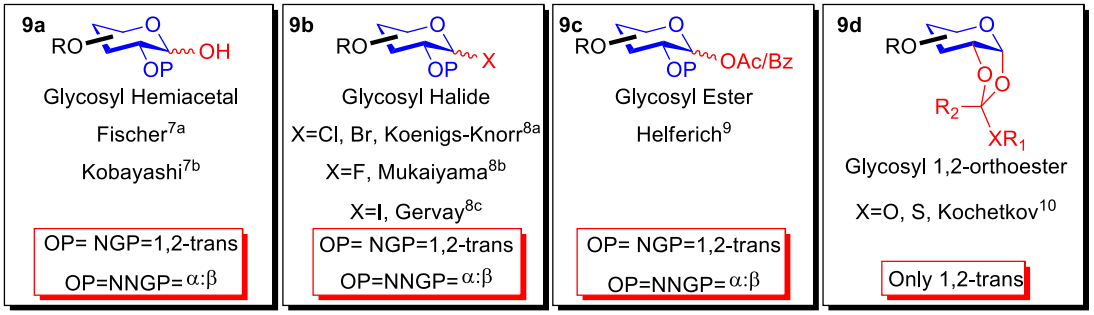
Scheme 1.4: Different types of glycosyl donor for glycoconjugates



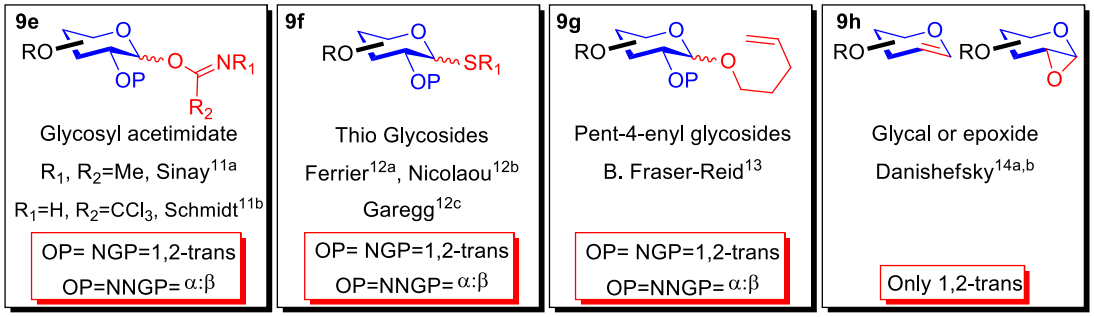
OP = NGP = Neighbouring group participation = OAc, OBz, NHAc, etc

OP = NNGP = Non neighbouring group participation = OMe, OBn, N_3, etc

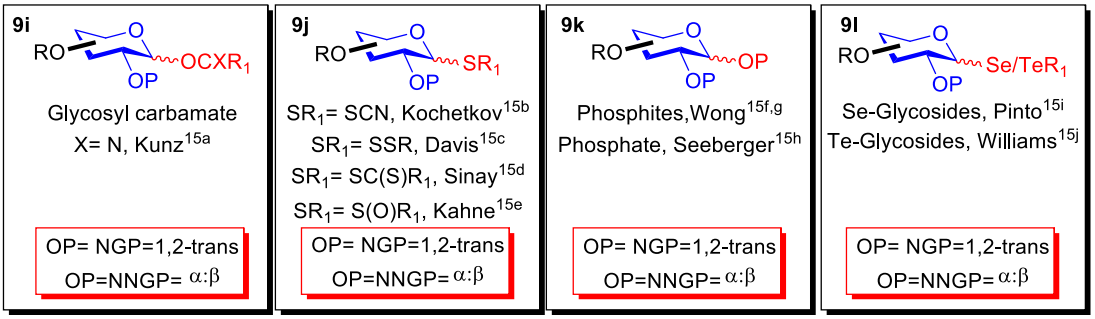
Earlier approches for glycoconjugates synthesis:- First generation of glycosyl donor



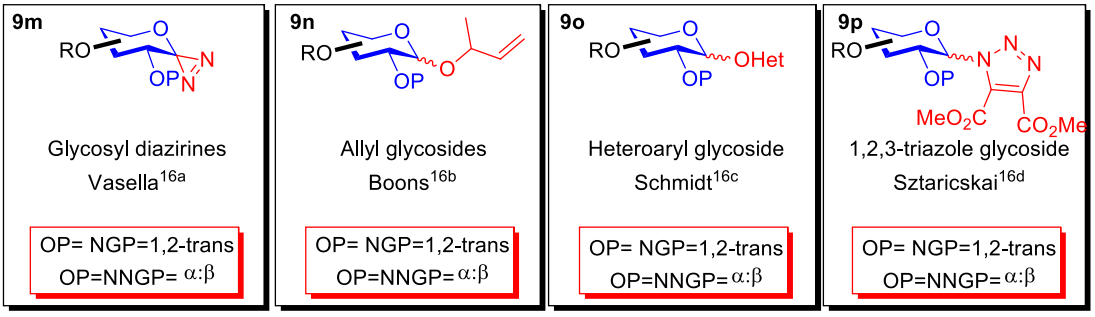
Second generation of glycosyl donor



Third generation: Modified glycosyl donors



Other glycosyl donors



1.4.6.4 – Thio glycosides[12]: The thioglycosides are readily prepared from per-acetate sugar and thiols in the presence of Lewis acids ($BF_3.Et_2O$, TMSOTf, and $SnCl_4$) and also from glycosyl halide/trichloroacetimidates and thiols. Stable thio glycosides tolerate diverse range of chemical manipulations and are inert under several glycosidation conditions. Thio glycosides can be activated in the presence of any soft electrophilic reagents under mild conditions to form corresponding sulfonium ion and further are attacked by alcohol to form corresponding glycoconjugates.

1.4.6.5 – *n*-Pentenyl glycosides[13]: Bert Fraser-Reid introduced the *n*-pentenyl glycoside (NPG) in late 1980s. NPG can be activated by halogenation (with NBS, NIS, I_2, IDCP) of double bond which results in cyclisation to release glycosyl acceptor to form active oxacarbenium species and further attack of nucleophile gives resultant glycosides. The reactivity differences caused by the nature of protecting groups or torsional effects are not specific to *n*-pentenyl glycosides, but turned out to be a fairly general in nature. Armed–disarmed type glycosylations could be performed on other types of glycosyl donors, including thioglycosides and glycosyl fluorides.

1.4.6.6 – Glycals or 1,2-Anhydro sugars[14]: 1,2-Anhydro sugars were firstly used for the synthesis of sucrose by Lemieux and recently came into the limelight because of the work by Danishefsky and co-workers. They developed a highly efficient procedure for 1,2-anhydro sugars preparation via oxidation of glycals with dimethyldioxirane (DMDO) and further activated with $ZnCl_2$ to generate 1,2-*trans* glycosides.

1.4.6.7 – Other glycosyl donors[15-19]: Though there are several other glycosyl donors came in glycochemistry but very few of them are useful for the synthesis of glycoconjugates. Others were synthesized for specific applications or not studied well.

1.5 – Requires another glycosyl donor for glycoconjugates?

All the known glycosyl donors require different conditions for glycosidations. Each glycosyl donor has its own advantage/disadvantageous over the other glycosyl donor. For example, if we select Fisher type glycosidation, then it is difficult to synthesize oligosaccharides as glycosyl acceptors are required as solvents. In Koneing-Knorr halide type glycosidation, the synthesis and storage of glycosyl

Table 1.2: Accounts of glycosyl donors

Glycosyl donor	Synthesis from	Activator (S/C)	Advantages	Disadvantages
Hemiacetal	→ sugar → Perester sugar	L/B (S/C)	→ Making of building blocks	→ Excess acceptor & activator requires → Not suitable for oligosacc. → Anomerisation → Harsh cond.
G. ester	→ sugar → Hemiacetal	L/B (S)	→ Easy avilable → Lost cost for disacc. syn.	→ Selectivity depends upon promoter and solvents → Not suitable for oligosacc. → Anomerisation
G. halide	→ Perester sugar → Hemiacetal	Heavy Metal salts (S/C)	→ Oligosacc. syn. → syn.of other G.D.	→ Toxic metals as an activator → Purification problem → Unstable
1,2-Orthoester	→ G.halide	L/B (C)	→ Oligosacc. syn. → Stereoselectivity	→ Unwanted orthoester product with alglycone → Rearranges acyl/benzoyl group
G. TCA	→ Hemiacetal	L/B (C)	→ Oligosacc. syn.	→ Unstable → Two steps for syn. of G. D. → High cost
Thio G.	→ G.halide → Hemiacetal → Perester sugar	L/B (S/C) NIS, I_2, Br_2 (S)	→ Nautral products syn, → G.halide, NPG syn. → Oligosacc syn	→ Health effect → Unpleasant odour
NPG	→ Fischer glycosidation	Various Tfs (C) NIS, I_2, Br_2 ((S)	→ Nautral products syn, → G.halide syn. → Oligosacc syn	→ High cost of 4-pentenol → Removal of side product is difficult → Selection of catalyst is vary from alcohol to alcohol → Restricted for Orthogonality
Glycal or 1,2-anhydro sugar	→ G.halide, → C_2-hydroxy G.D. → G. halide	DMDO then $ZnCl_2$	→ Latent-active donor → Free C_2 hydroxyl will get after glycosidation	→ Only DMDO requirs for epoxidation → Restricted for Orthogonality → Yiled loss for glycosidation due to two steps

Oligosacc. = oligosacchride, G. = Glycosyl/glycoside, syn. = synthesis, G. D. = Glycosyl donor, C = Catalyst, L =Lewis acids, B = Bronsted acids, TCA =Trichloroactimidate, S = Stiochiometric NPG = n-pentenyl glycosides

Table 1.3: Accounts of glycosyl donors

Glycosyl donor	Synthesis from	Activator (S/C)	Advantages	Disadvantages
Allyl G.	→ sugar → Perester sugar	Stron bases then L (C)	→ Latent active donor	→ Not liable for base sensitive compounds → Two step requires for activation → Restricted for orthogonality
Se/Te G.	→ G. halide → Perester sugar	L/B (S) NIS, K_2CO_3	→ Can be activated in the presence thio G. → Mild promoters requires	→ Metal salts as a side products
G. Phosphate /Phosphite	→ G. halide → Hemiacetal	L/B (S) NIS, I_2	→ Mostly used for sialylations	→ Very unstable and reaction at low temp.
G. carbamate	→ Hemiacetal	L/B (C)	→ Stereoselectivity → Leaving group based IAD	→ High temp. requires for decarboxylation → CO_2 generated
1,2,3-Triazole G.	→ G. azide	TMSOTf	→ Natural products syn.	→ Side product is 1,2,3-triazole → Not good leaving group
Heteroaryl G.	→ G.halide → Hemiacetal → Perester sugar	L/B (S/C)	→ Can be activated in absence of protecting group in G.D. → In Natural products syn.	→ Pyridine analogues are health effective → Unpleasant odour → Excess glycosyl acceptor requires
Diazaridine G.	→ carbene intermediate	Various Tfs (C) NIS, I_2, Br_2 ((S)	→ No aglycone in reaction mix. → N_2- generated	→ Highly unstable

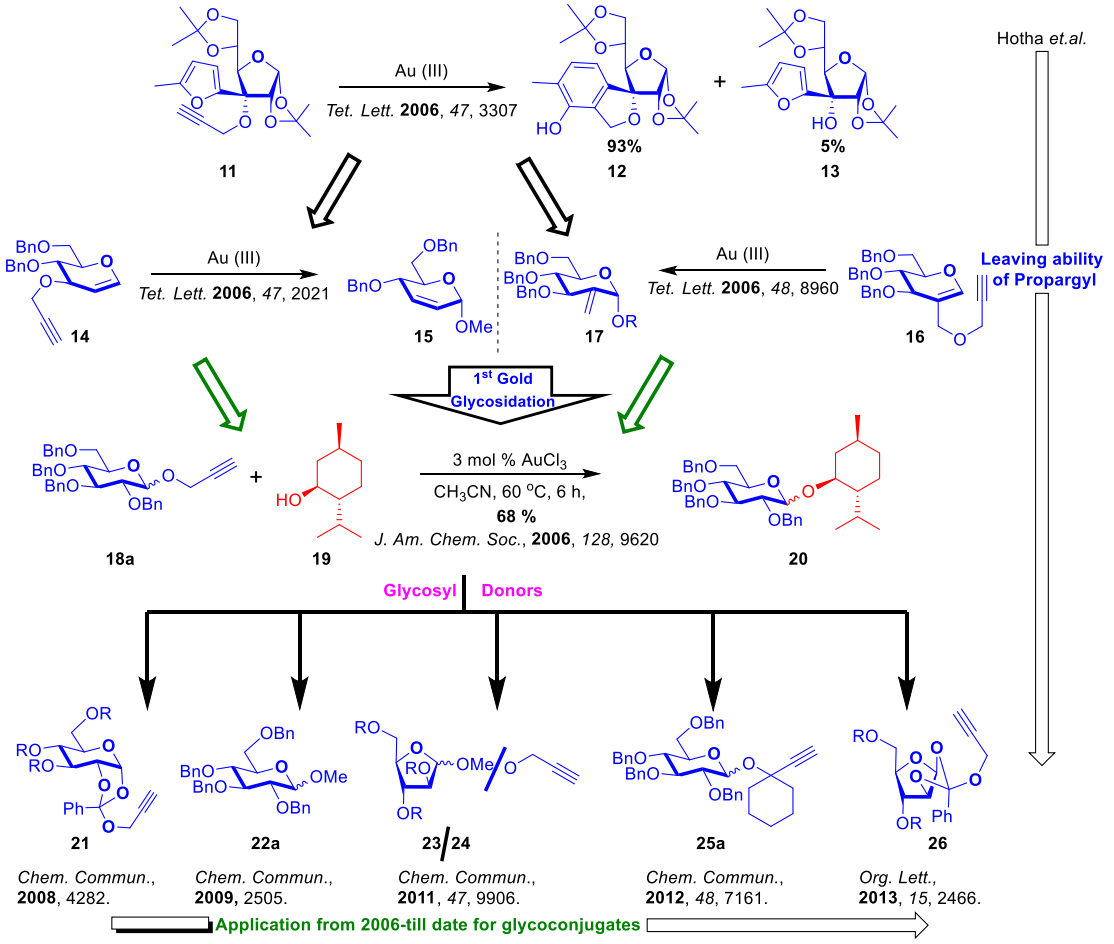
Oligosacc. = oligosacchride, G. = Glycosyl/glycoside, syn. = synthesis, G. D. = Glycosyl donor, C = Catalyst, L =Lewis acids, B = Bronsted acids, Se/Te = Seleno/Telluro, S = Stiochiometric

donors were little bit difficult due to instability of anomeric halide except glycosyl fluoride and use of toxic heavy metal salts. If we move to stable glycosyl donors such as thio-, pentenyl-, and acetate-, carbamate-, modified thio glycosides- then stoichiometric reagents are required and removal of side products becomes difficult from the expected product. Thio- and pentenyl- have unpleasant odour and health issues which also limits the use of these glycosyl donors. The investigation of stable 1,2-*O*-orthoesters were not much utilised for the synthesis of glycoconjugates because of its high reactivity to form direct glycosidation product which decreases the overall yield of expected product. Further with latent-active donors or two step activation donors such as glycal and allyl glycoside which required two step activation causes overall yield loss and specific reagents are required for the activation of the latent-active donors. The glycosyl donors such as pentenyl-, thio-, modified thio-, glycal, and allyl- were restricted for the orthogonal activation because of reagents (like as NIS) used in this process also react with other double bonds in reactants. Other glycosyl donors, such as diaziridines-, triazole-, and phosphate/phosphite are not utilised much for glycoconjugates synthesis due to instability, interglycosidic bond cleavage, and some other reasons. For most of the glycosyl donors, there are no unique reagents which can activate the donor with all types of aglycons. For different aglycons, different activators are needed. Thus, there is some confusion to select activator among the all. Upto now, only trichloroacetimidates are the best option for the different kinds of oligosaccharides/glycoconjugates synthesis but not all glycosyl trichloroacetimidates cannot be stored for long time. Therefore, there is no universal glycosyl donor for glycoconjugates and still modification/investigation is necessary in glycosyl donor chemistry for the synthesis of glycoconjugates. The desirable features of a universal glycosyl donor shall be:

1) Easy synthesis/less number of steps
2) Stable and long shelf-life
3) Needs catalytic amount of activator/promoter and unique catalyst
4) Minimum or no side products
5) Orthogonal activation
6) No cleavage of interglycosidic bond in oligosaccharide synthesis.
7) Lesser reaction time
8) Compatible for all types aglycons

In this regard, while doing Hashmi reaction on propargyl substituted sugars in diversity oriented synthesis (DOS) Hotha and Kashyap identified the 3-*O*-propargyloxy group was liberating from propargyl glycosides (**11**) in the presence of gold(III) chloride to form (**13**) along with required product (**12**). With these surprising results, several attempts on propargyl sugar showed propargyloxy group is behaving as a leaving group. Propargyl glycosides (**18a** and **25a**) can fulfil some of the conditions of ideal glycosyl donor enlisted above.

Scheme 1.5: Identification of propargyl moiety as a leaving group



Propargyl glycosides opened a new and interesting area in glycochemistry. Further, this story is extended with propargyl 1,2-orthoester (**21** and **26**) for the synthesis of 1,2-*trans* glycosides. Methyl glycosides (**22a** and **23**) and propargyl furanosides (**24**) are also found to act as glycosyl donors for the synthesis of glycoconjugates under same gold catalysis conditions (**Scheme 1.5**). In chapter one, the utility of propargyl glycosides and 1,2-orthoeseter to several stereoselective glycoconjugates is discussed.

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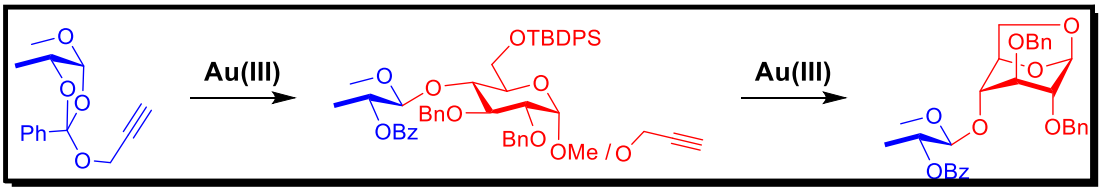
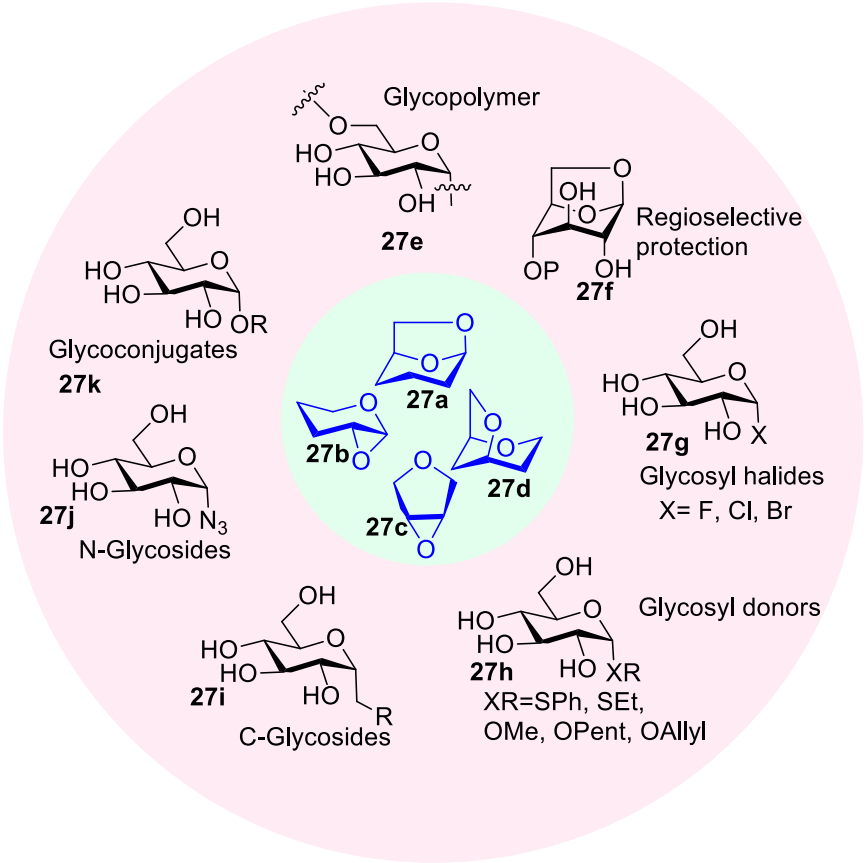
Section A: Synthesis of 1,6-Anhydro Sugars



1A.1 – Introduction

Anhydro sugars[1] are also called as intramolecular anhydrides which are heteromorphic sugar derivatives that arise from the elimination of water molecule from two vicinal hydroxyl groups of the corresponding aldoses/ketoses. Anhydro sugars and their derivatives are known to be useful synthons for the preparation of various glycosyl compounds such as *S*-glycosides,[2a,b,c] *N*-glycosides,[2d] glycosyl halides,[2e,f] *C*-glycosides,[2g,h] and proteo-glycans[2i] (**Figure 1A.1**). Anhydro sugars bearing a bicyclic/tricyclic skeleton composed of oxiranes, oxetane, oxalone (tetrahydrofuran form) and oxane (tetrahydropyran form) which affords regioselective reactions at particular hydroxyl groups in those sugars. Regioselective protection of single hydroxyl group in monosaccharides in the presence of others is a difficult task.

Figure 1A.1: Application of anhydro sugars in various fields of carbohydrates



The reactivity of primary hydroxyl group and anomeric hydroxyl group is almost similar; followed by the reactivity of hydroxyl group at *C*-2, *C*-3 and *C*-4. Hence, protection of *C*-1 and *C*-6 is first carried out in order to protect either *C*-2 or *C*-3 or *C*-4 hydroxyl groups in monosaccharides; therefore, 1,6-anhydro sugars are relatively

easier to synthesize. Anhydro sugars act as monomers for cationic ring opening polymerization which gives stereoregular linear polysaccharide derivatives[2j] or hyper-branched polysaccharide[2k] derivatives respectively.

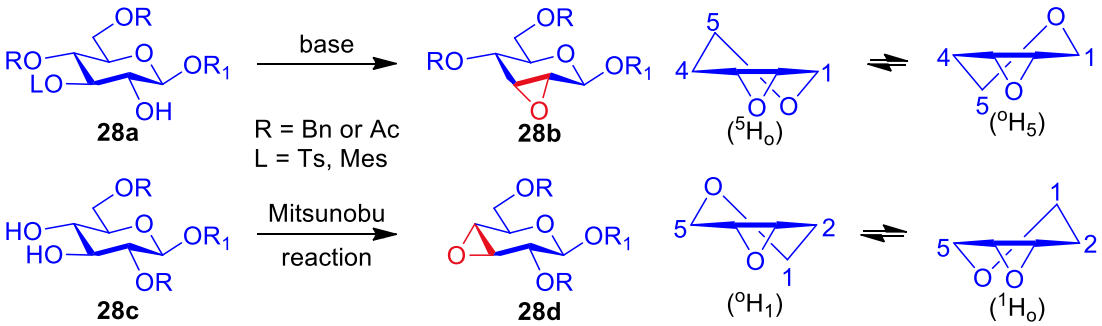
1.A.2 – Classification of Anhydro sugars

Anhydro sugars are classified into three main categories i.e. anomeric anhydro sugars, non anomeric anhydro sugars and di-anhydro sugars.

1A.2.1 – Non-anomeric anhydro sugars: This type of anhydro sugars having an oxiranes/oxalone ring fused with a either pyranose or furanose and classified into five main categories' i.e. endo-cyclic anhydro sugars, exo-cyclic anhydro sugars, oxetanes, oxolane, and oxanes.

1A.2.1.1 – Endo-cyclic/oxirane anhydro sugars[3]: Oxirane types of sugars generally adopt $^{5}H_{0}$ (half chair confirmation) or $^{0}H_{5}$ for 2,3-anhydropyranose (**28b**) and $^{1}H_{0}$ or $^{0}H_{1}$ for 3,4-anhydropyranose (**28d**) respectively. These sugars with epoxy rings generally used for starting materials for the synthesis of tosyloxy (**7**), halo,

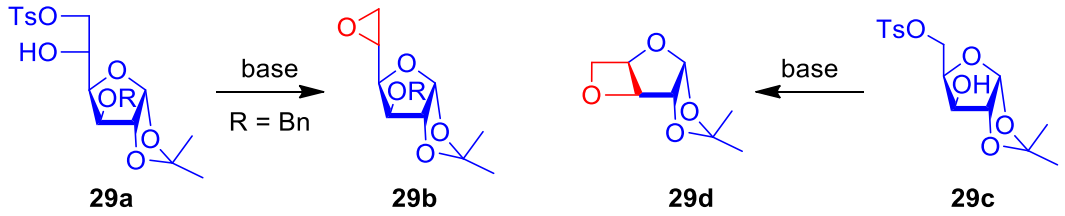
Scheme 1A.1: Synthesis of 2,3-anhydro and 3,4-anhydro sugars.



amino, azido, thio, deoxy, and branched chain derivatives. The oxirane ring is more reactive than oxetane or oxalone ring and opened with nucleophiles under basic or acidic conditions (**Scheme 1A.1**). These kinds of anhydro sugars (**28b**, **28d**) are prepared by S_N2 nucleophilic substitution with base or epoxidation of double bond or by a Mitsunobu reaction (**28c**), or deamination of vicinal *trans*-amino alcohols.

1A.2.1.2 – Exo-cyclic anhydro sugars[4]: This is similar to steric arrangement of oxolane ring of furanose derivatives (**29b)** and can be synthesized by using selective alkylation between *C*-5 and *C*-6 hydroxyl group or selective tosylation at *C*-6 (**29a**) position followed by treatment with a base (**Scheme 1A.2**). Anhydro sugars of gluco-, manno-, ido-, allo- and galacto- are useful in the regioselective S_N2 reactions.

Scheme 1A.2: Synthesis of 5,6-anhydrofuranose and 3,5-anhydrofuranose derivative

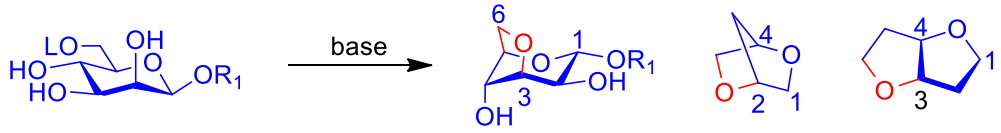


29a **29b** **29d** **29c**

1A.2.1.3 – Oxetanes[5]: Four membered epoxide is named as oxetanes (**29d**) are prepared from the selective alkylation between *C*-3 and *C*-6 hydroxyl group bearing a suitable leaving group (**29c**).

1A.2.1.4 – Oxolane[6]: 3,6-Anhydropyranoses (**30b**) or 2,5-Anhydrofuranoses (**30c**) are known as oxolane derivatives of anhydro sugars which show $^{1}C_{4}$ or $^{2,4}B$ conformation respectively (**Scheme 1A.3**).

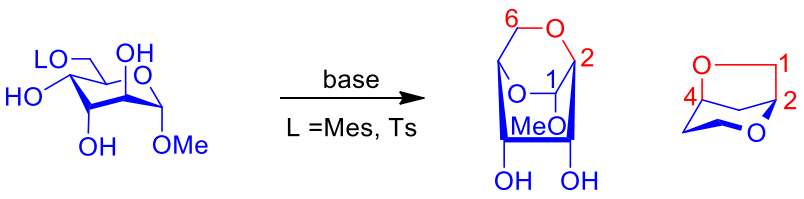
Scheme 1A.3: Synthesis of 3,6-anhydro sugar.



30a **30b** ($^{1}C_{4}$) **30c** ($^{2,4}B$) **30d**

These rings are relatively stable towards acidic and basic conditions. Reactivity of these sugars is predominant in the presence of free or potential functional group. 2,5-anhydrofuranoses are possible for all kind of sugars such as L-arabino, D-xylo-, D-lyxo-, D-ribo-, manno-, altro-, gluco-, D-allose-, L-idose- and L-talose-.

Scheme 1A.4: Synthesis of 2,6-anhydropyranose

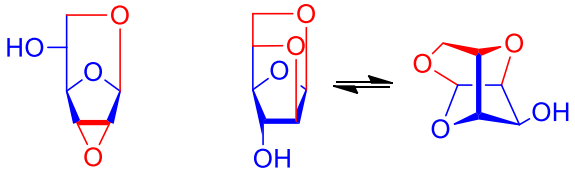


22b **31** ($^{2,5}B$) **31c** ($^{4}C_{o}$)

1A.2.1.5 – Oxane[7]: Oxane derivatives (**31**) of anhydro sugars both present in pyranose as well as furanose form exhibit in $^{2,5}B$ or $B_{2,5}$ or $^{1}C_{O}$ conformation (**Scheme 1A.4**). Altro-, ido-, manno-, and talo- derivatives of anhydro sugars are present in

pyranoside form. Up to now only mannofuranose derivatives are known among this class of anhydro sugars.

1A.2.2 – Dianhydro sugars[8]: Oxirane, oxetane and oxolane derivative of 1,6-anhydro sugars are known in literature which can be obtained from corresponding tosylates between any two hydroxyl group of 1,6 anhydro sugars. Dianhydro derivatives of allofuranose (**32a**), gulofuranose (**32b**), idofuranose, gulopyranose and glucopyranose are known.



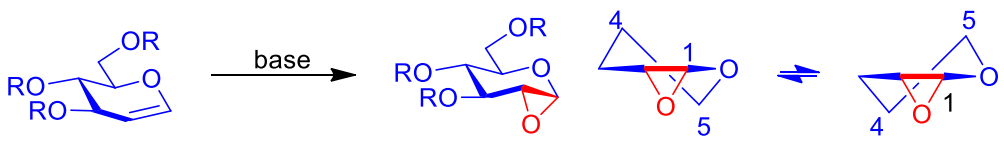
32a **32b**

1A.2.3 – Anomeric anhydro sugars

Anomeric carbon atom contributing in an acetal linkage with two of the hydroxyl groups from corresponding sugar can form respective anhydro sugar. These are the products of intramolecular glycosidation of sugar; their bicyclic nature shows suitable conformations which are useful for a number of regioselective reactions. Usually anomeric anhydro sugars containing oxirane, oxetane, or oxolane ring are further classified as 1,2-anhydro sugars, 1,6-anhydro sugars and miscellaneous anhydro sugars (1,3-anhydro, 1,4-anhydro sugars and 1,5 anhydro sugars)

1A.2.3.1 – 1,2-Anhydro sugars[9]: 1,2-Anhydro sugar (**33b**) is an epoxide which adopts $^{4}H_{5}$ or $^{5}H_{4}$ conformation and also known as Brigl's anhydride named after his discovery. Basically, 1,2-anhydro sugars have proven to be versatile glycosyl donors for the preparation of several glycoconjugates. Danishefsky *et al.*[9b] (**Scheme 1.A.5**)

Scheme 1A.5: Synthesis of 1,2-anhydro sugars

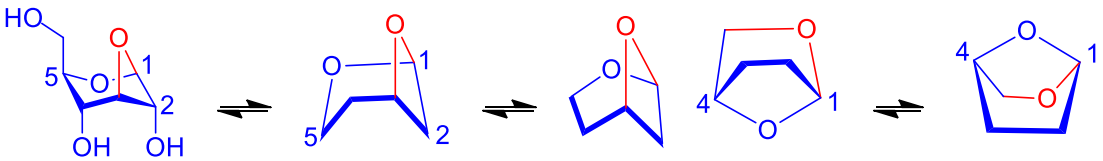


33a **33b** ($^{4}H_{5}$) ($^{5}H_{4}$)

showed an efficient synthesis of 1,2-anhydro sugars (**33b**) by epoxidation of glycals (**33a**) with 3,3-dimethyldioxirane. Also, several complex oligosaccharides in which glycosidation steps were carried out using 1,2-anhydro sugars as a glycosyl donors

were performed. 1,2-Anhydro sugars are useful for the synthesis of other glycosyl donors such as fluro, thiophenyl, *n*-pentenyl glycosides. It acts as a valuable synthon for the synthesis of oligosaccharides, *C*-glycosides, aminoglycosides and natural products.

1A.2.3.2 – Miscellaneous anhydro sugars (1,3-anhydro , 1,4-anhydro and 1,5-anhydro sugars)[10]: 1,3-Anhydro sugars (**34a**) are highly useful for the synthesis of thromboxane like blood platelet aggregation factors and also polymeric glycoforms of this type which are commonly found in plants, bacteria, yeast and fungi.

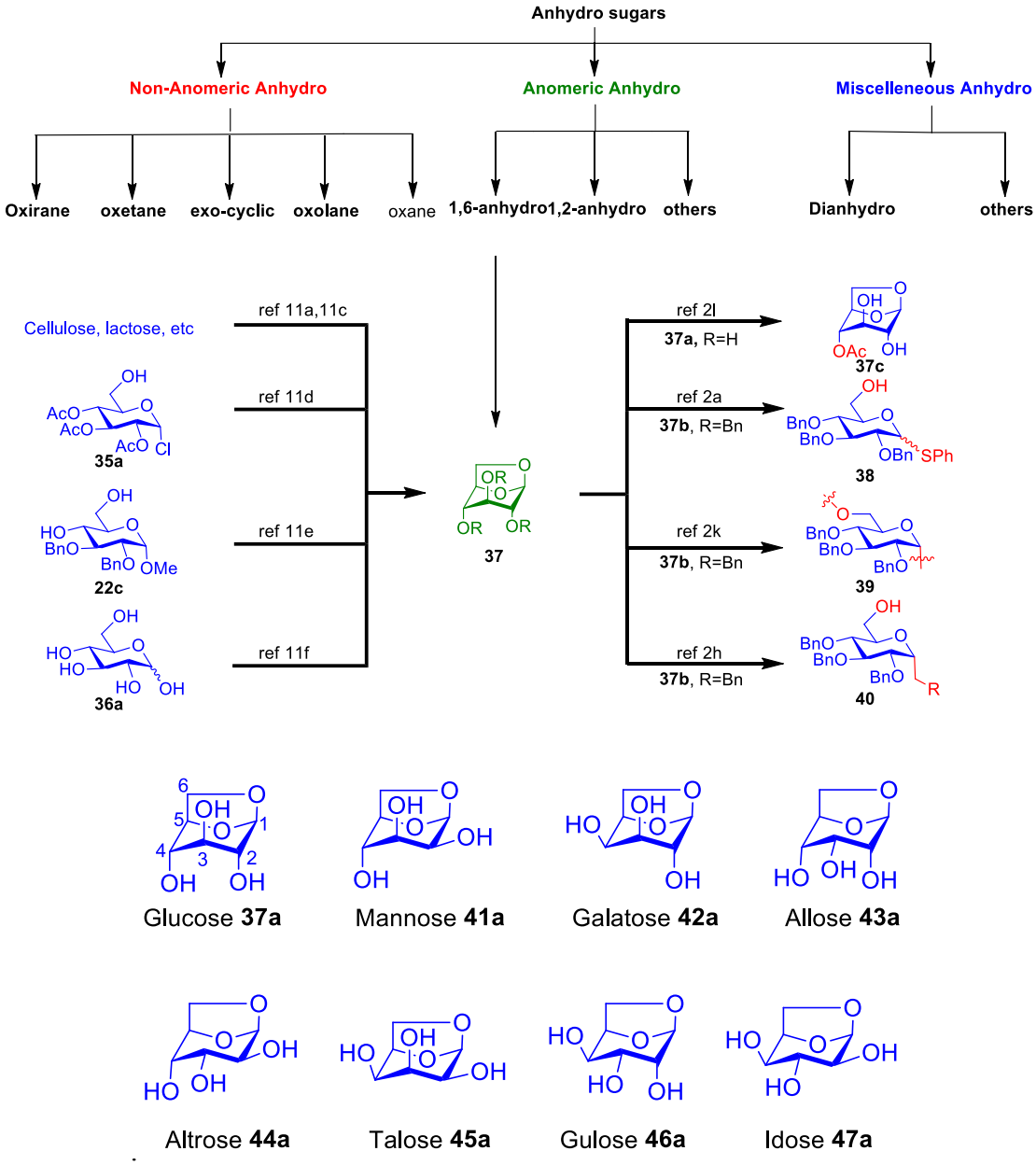


34a ($^{5}C_{2}$) ($B_{2,5}$) (E_{2}) **34b** ($B_{1,4}$) ($^{1,4}B$)

1,3-Anhydro sugars are present in $^{5}C_{2}$, $B_{2,5}$, or E_{2} conformation and obtained from Mitsunobu reaction between *C*-1 and *C*-3 hydroxyl groups. 1,4 Anhydro sugars (**34b**) are also referred as 1,5-anhydrofuranoses having $B_{1,4}$ or $^{1,4}B$ conformation. It was prepared from glycosyl fluorides and unprotected *C*-4 hydroxyl group with Lewis acid. 1,6-Anhydrohexofuranoses have been isolated from the pyrolysis distillates of 1,6-anhydro-β-D-glucofuranose and 1,6-α-D-galactofuranose.

1A.2.3.3 – 1,6-Anhydro sugars[11,2]: 1,6-Anhydro sugars (**37**) also known as 'glucosans' (glucose anhydrides) or 'levoglucosan' (negative optical rotation) was first isolated by Tanret in 1894.[13a] Levoglucosan shows $^{1}C_{4}$ confirmation in which all hydroxyl groups are located axially which is opposite to normal $^{4}C_{1}$ conformation of glucopyranoside (**Figure 1A.2**). Of all anhydro sugars, 1,6-anhydro sugars widely studied due to their bicyclic and rigid nature for the synthesis of glycoconjugates, regioselective protection, stereoregular polymerization, hyperbranched polymerization, *S*-glycosides, *N*-glycosides, *O*-glycosides, *C*-glycosides, and etc. There are eight possible isomers of 1,6-anhydro hexopyranoses (**37a** and **41a** to **47a**) which have dissimilar reactivity pattern. In earlier days, 1,6-anhydro sugars were synthesized from the pyrolysis of cellulose[11a], starch[11b], and lactose[11c] and further purified by the protection of every compound into the corresponding

Figure 1A.2: Classification of anhydro sugars and synthesis and application of 1,6 anhydro sugars



isopropylidene acetal. The crude isopropylidene acetal was extracted with suitable organic solvent and removal of acetonide group to obtain parental glycosans. However, pyrolysis and subsequent purification leads to poor yields. Later 1,6-anhydro sugars were also obtained from the selective alkylation between *C*-1 and *C*-6 hydroxyl group using halides at the anomeric centre (**35**) or protection of any one hydroxyl group with leaving group.[11d] Yields obtained in this process were good but reagents are used in stoichiometric amounts and strongly basic conditions required for alkylation or nucleophilic displacement. 1,6 Anhydro sugar yielded along with the by-

product while employing a suitable leaving group (**22c**) at anomeric centre in the presence of Lewis acid or Brønsted acid under harsh conditions.[11e] In strongly acidic media, an anhydro sugar undergoes polymerization in protic solvent to give glycopolymer which is not always useful. Shoda *et al.*[11f] reported the effective synthesis of 1,6-anhydro glucopyranose using ionic liquid and glucose (**36**) and also this methodology was further applied on higher oligosaccharides as well. Nevertheless, this methodology is not successfully shown for 1,6-anhydr sugars of manno- or galacto- or other hexopyranoses. Therefore, chemical synthesis of 1,6 anhydro sugars is desirable in such a way that it can be obtained in simple steps, with suitable glycosyl donors, using catalytic amount of activator, and should be easy to purify.

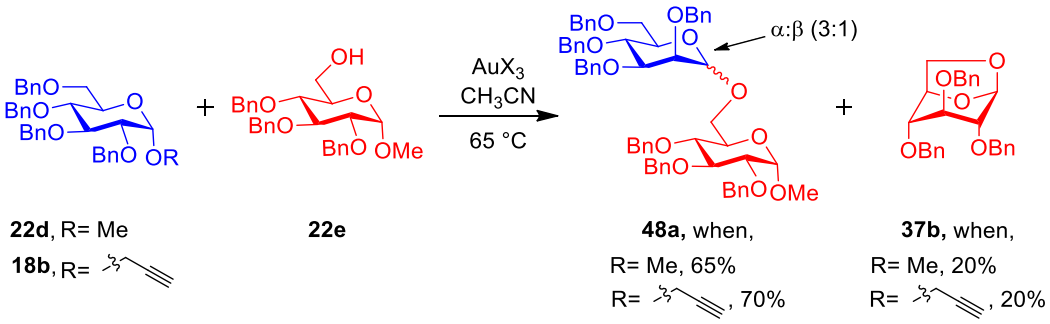
1A.3 – Present work

The D- and L- anhydro sugars have immense importance as valuable synthons for the synthesis of biologically potent active compounds in the field of glycobiology.[12] For example, Bleomycin A2, a glycopeptide antibiotic with significant antitumor activity, contains a carbohydrate moiety consisting of a α-1-2 linked 3-*O*-carbamoyl-D-mannopyranose with L-gulopyranose. Adenomycin, a nucleoside antibiotic showed antibacterial activity contains L-gulosamine as an important L-form sugar. L-Altrose is a potent constituent of extracellular polysaccharides from *Butyrivbrio fibrisolvens* strain CF_3.[12b] Synthesis of such D- and L-sugars analogues and its role in glycobiology which can be obtained from the L-sugars only is a subject of interest. 1,6-Anhydro hexopyranoses in both D- and L- form are valuable synthons for carbohydrate-based synthesis of oligosaccharides, biologically active molecules and natural products.

1A.3.1 – Synthesis of Glu-, Gal- and Man- 1,6-anhydro Sugars

Alkyl glycosides (**18b**[13a] and **22d**[13c]) were identified as glycosyl donors under the activation of catalytic amount of AuX_3/CH_3CN at 65 °C. In the case of glucose and galactose, Hotha and Kashyap obtained a mixture of α:β glycosides **48a**. In these endeavours, a minor amount of side product was noticed which was later identified as 1,6-anhydro compound (**Scheme 1A.6**).

Scheme 1A.6: Propargyl / Methyl glycoside act as a glycosyl donor in oligosaccharide synthesis

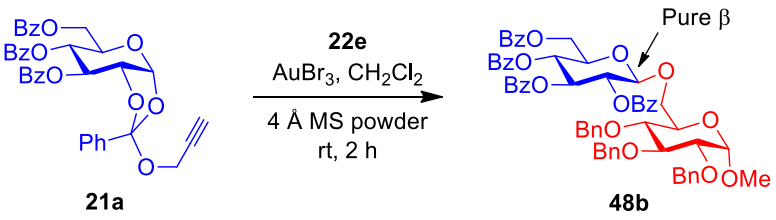


Initially formation of 1,6-anhydro sugar was highlighted due to cleavage of primary benzyl group in **18b** followed by intramolecular glycosidation to give 1,6 anhydro

sugar. After careful investigation it is observed that methyl glycoside (**22e**) can also be activated in the presence of gold (III) salts. Further, screening with the several alkyl glycosyl donors with several Lewis acids along under gold catalysis then finally confirmed that methyl glycosides can also behave as glycosyl donors in the presence of gold (III) bromide at 70 ^{o}C.[13c]

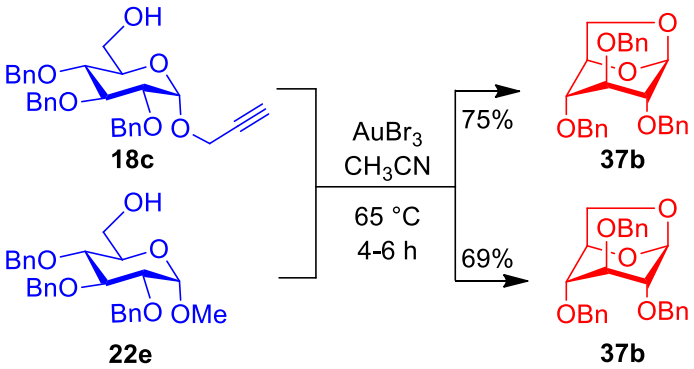
Modification of propargyl glycosides to propargyl 1,2-*O*-orthoester (**21a**) in the presence of catalytic amount of $AuBr_3/CH_2Cl_2$/4 Å MS powder at room temperature resulted into 1,2-*trans* disaccharides (**48b**) in good yield (**Scheme 1A.7**).[13b] In this glycosidation, formation of 1,6-anhydro sugar was restricted due to the decrease in temperature.

Scheme 1A.7: Synthesis of 1,2-*trans* glycosides using 1,2-*O*-propargyl orthoester



The aforementioned discussion ensued us to investigate synthesis of 1,6-anhydro sugars using gold (III) catalysis on alkyl glycosides. To begin our investigation, compounds **18c** and **22e** were separately heated to 65 °C in CH_3CN in the presence of 5 mol% of $AuBr_3$ for 6 h to observe formation of 1,6-anhydro sugar (**37b**) in very good yields. The structural homogeneity was confirmed by the NMR correlations and other spectroscopic analyses (**Scheme 1A.8**).

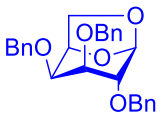
Scheme 1A.8: Glycopolymer synthesis by using propargyl/methyl glycosides



In the ^{1}H NMR spectrum of **37b,** the *H*-1 proton was observed as a singlet at δ 5.46 ppm confirming as the β-conformation of glucopyranoside along with other

pyranoside ring protons (*H*-2,3,4,5, and 6) between δ 3.34-4.41 ppm and benzylic protons around δ 4.54-4.65 ppm. The aromatic protons were noticed as multiplet in the aromatic region with 15 protons. In the ^{13}C NMR spectrum, the *C*-1 carbon was observed at δ 100.5 ppm and rest of the pyranoside ring carbons along with benzylic carbons were noticed between δ 65.3 and 77.6 ppm. Three quaternary carbons were noticed at δ 137.7, 137.7, 137.7 ppm in the aromatic region indicating the presence of three substituted aromatic rings and set of 15 carbons found around δ 128.0 ppm confirmed the presence of three benzyl groups. This data perfectly matched with that of literature values[1,2] and confirmed the formation of 1,6-anhydro sugar. Similarly, this methodology was investigated for the synthesis of 1,6 anhydro sugars of mannose (**41b)** in 71% from propargyl mannopyranoside and 62% from methyl mannopyranoside and galactose (**42b**) in 76% from propargyl galactopyranoside and 65% from methyl galactopyranosides.[14]

41b



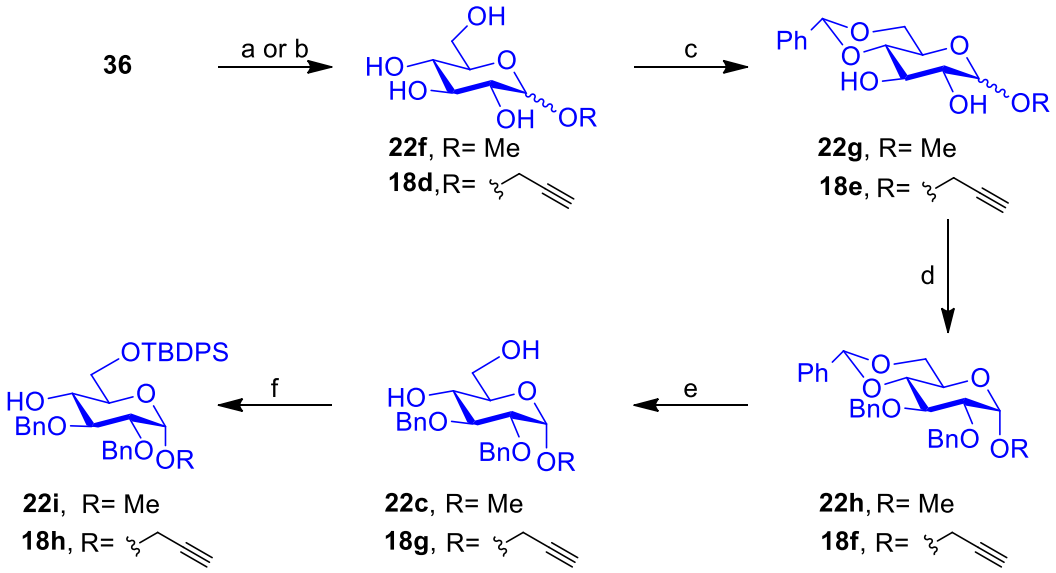
42b

1A.3.2 – Synthesis of glycosyl acceptor

For the synthesis of 1,6-anhydro sugars of higher oligosaccharides, we required glycosyl acceptors which can assemble into the glycosyl donor/acceptor. Therefore, first synthesis of glycosyl acceptors which were required for the synthesis of higher oligosaccharides glycosyl donor/acceptor was performed (**Scheme 1A.9**). Glucose was refluxed with methanolic hydrochloric acid (for methyl glycoside preparation) and propargyl alcohol and silica:H_2SO_4 (for propargyl glycoside synthesis) in separate flasks at 75 °C under inert atmosphere afforded corresponding methyl/propargyl glucopyranoside (**22f/18d**) in good yield. Methyl or propargyl glucoside (**22f** or **18d**) was stirred with benzilidinedimethylacetal in the presence of PTSA on rotary evaporator at 60 °C for 2 h to yield **22g/18e**. Subsequently, glycosyl acceptor (**22i** or **18h**) was obtained from compound **22g** or **18e** in three straightforward steps *viz.* benzylation with sodium hydride and benzyl bromide in DMF, deprotection of benzylidine group by using PTSA in methanol and protection of selective primary hydroxyl group with TBDPSCl/Im. The formation of **22i** and **18h** were further confirmed by the NMR and Mass spectroscopic techniques. In the

^{1}H NMR spectrum of **22i**, the singlet was noticed at δ 1.06 (9H) ppm and in the aromatic region ten protons rather than two benzylic aromatic protons indicated the presence of *t*-butyldiphenylsilyl group.

Scheme 1A.9: Synthesis of methyl or propargyl 6-*O*-(*t*-butyldiphenylsilyl) 2,3-di-*O*-benzyl-α-D-glucopyranoside

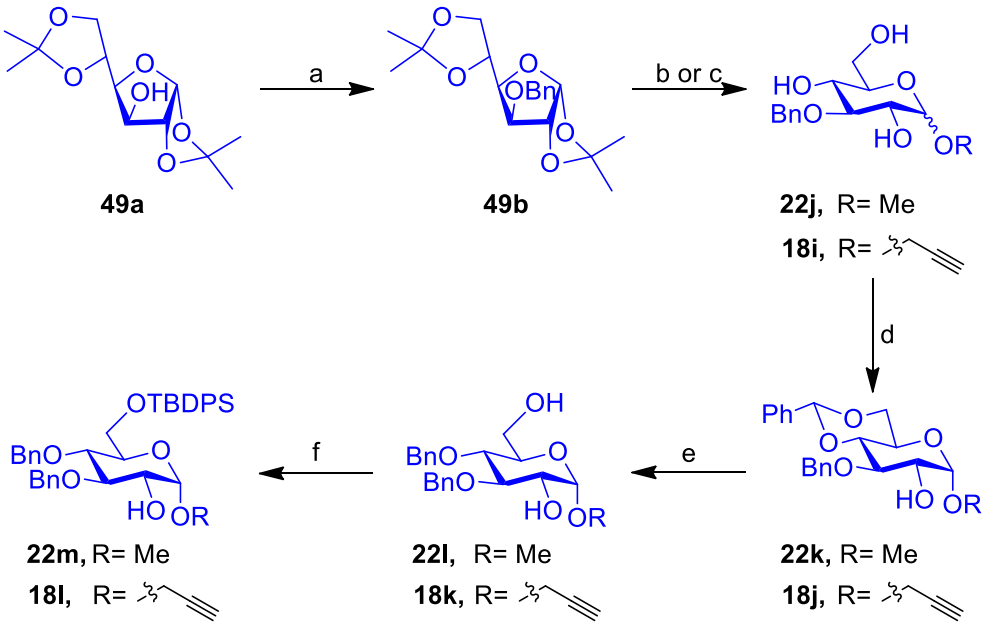


Reagents: a) HCl(dry), MeOH (for methylation), reflux, 24 h, 82%, b) Propargyl alcohol, Silica:H_2SO_4 (cat), 70 °C, 4 h, 75%, c) Benzaldehyde dimethylacetal, PTSA (cat), DMF, rota vapour, 60 °C, 2 h, d) Separation, NaH, BnBr, TBAI (cat), DMF, 0 °C, 2.5 h, 50% for **22h** from **22f**, 48% for **18f** from **18d**, e) Separation, PTSA (cat.) methanol, overnight, rt, f) TBDPSCl, Im., DMF, rt, 2 h, 64% for **22i** from **22h**, 60% for **18h** from **18f**.

A singlet for three protons at δ 3.33 ppm confirmed the presence of *O*-methyl glucoside. Doublet (J = 4.3 Hz) was observed at δ 4.68 ppm which confirmed the formation of pure α-isomer at *C*-1 and other pyranoside ring protons along with benzylic protons were noticed between δ 3.37 and 4.93 ppm. In the ^{13}C NMR spectrum of **22i**, resonances were observed at δ 26.7 (3C) and 19.1 ppm (disappeared in DEPT) indicated the presence of *t*-butyl group and δ 97.7 ppm for an α-isomer. Similarly, in the ^{1}H and ^{13}C NMR spectrum of **18h,** the new resonances appeared at δ 2.50 ppm (t, J = 2.3Hz, 1H), δ 4.26 ppm (d, J = 2.4Hz, 2H) and δ 79.0, 78.8 and 51.0 ppm for propargyloxy moiety and rest of the resonances in accordance with the glycosyl acceptor **22i**. Simultaneously, synthesis of methyl/propargyl 6-O-(*t*-butyldiphenylsilyl)-3,4-di-*O*-benzyl-α-D-glucopyranoside (**22m**/**18l**) was achieved

from 1,2:5,6-diacetonide glucofuranoside (**49a**) which was benzylated under standard benzylation conditions to afford 3-*O*-benzyl 1,2:5,6-diacetonide glucofuranoside (**49b**) in

Scheme 1A.10: Synthesis of methyl or propargyl 3,4-di-*O*-benzyl-*O*-(*t*-butyldiphenylsilyl)-α-D-glucopyranoside



Reagents: a) NaH, BnBr, TBAI(cat.), DMF, 0 °C, 2.5 h, b) HCl(dry), MeOH (for methylation), reflux, 24 h, 73% for **22j** from **49a**, c) Propargyl alcohol, HCl (dry), 1,4-dioxane, 70 °C, overnight, 70% for **18i** from **49a,** d) Benzaldehyde dimethylacetal, PTSA (cat), DMF, rota vapour, 60 °C, 2 h, 82% for **22k**, 85% for **18j**, e) Separation, LAH, $AlCl_3$, CH_2Cl_2:Et_2O (1:3), 0 °C to rt to reflux, 30 min, 57% for **22l** from **22k,** 55% for **18k** from **18j**, f) TBDPSCl, Im., DMF, rt, 2 h, 61% for **22m,** 65% for **18l**.

quantitative yield. Compound **49b** was refluxed with methanolic hydrochloric acid solution followed by the treatment with benzylidinedimethylacetal in the presence of catalytic amount of PTSA in DMF at 60 °C for 2 h to obtain methyl 3-*O*-benzyl 4,6-*O*-benzilidine-α-D-glucopyranoside (**22j**) in 70% yield. The selective reduction/cleavage of 4,6-*O*-benzylidine (**22k)** was carried out by the treatment of LAH:$AlCl_3$ in CH_2Cl_2:Et_2O mixture to afford **22l** that was subsequently treated with TBDPSCl/Im. in DMF afforded required glycosyl acceptor (**22m**) in good yield (**Scheme 1A.10**). The formation of **22m** was confirmed on the basis of NMR spectroscopy. In the ^{1}H NMR spectrum of **22m**, the characteristic resonances presented at δ 1.07 ppm (*t*-butyl), 3.38 ppm (OMe) and 4.77 ppm (d, *J*=3.3Hz) (*H*-1)

confirmed the presence of *t*-butyl group in TBDPS and pure α-isomer with methoxy group at reducing end. In the ^{13}C NMR spectrum of **22m**, the resonances were noticed at δ 19.2, 26.7, and 99.1 ppm indicated that the presence of *t*-butyl group in TBDPS and anomeric carbon with α-isomer respectively.

Scheme 1A.11: Synthesis of higher linear oligosaccharides 1,6-anhydro sugars.

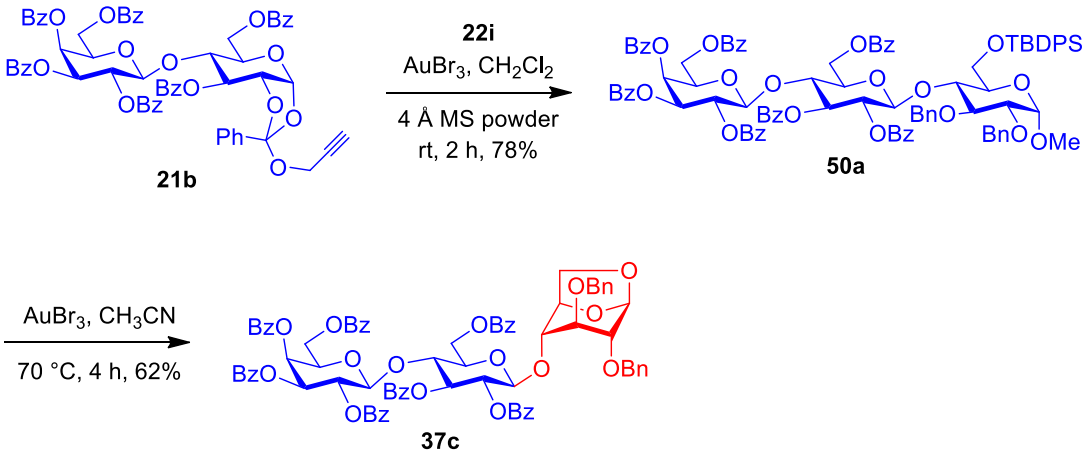


Table 1A.1: Synthesis of di/tri-saccharides 1,6-anhydro sugars

Donor	Aglycon	6-O-TBDPS di/tri-saccharide Time (h) / Yield (%) (from orthoester)	1,6-Anhydro di/tri-saccharide Time (h) / Yield (%) (from 6-O-TBDPS di/tri-saccharide)
21a	**22i**	**50b**	**37d**
		4/75	18/68
21a	**22m**	**50c**	**37e**
		8/67	24/64
21a	**18h**	**50d**	**37d**
		8/69	18/72
21a	**18l**	**50e**	**37e**
		4/73	18/71
21b	**22m**	**50f**	**37h**
		4/72	10/64
21b	**18h**	**50g**	**37c**
		8/68	18/65
21b	**18l**	**50h**	**37h**
		8/69	10/67

Similar set of reactions was applied for the synthesis of **18l** but instead of methanolic hydrochloric acid; the reaction was carried out in propargyl alcohol and dioxane-HCl.

1A.3.3 – Synthesis of oligosaccharides 1,6-anhydro sugars

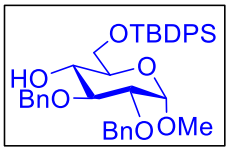
A CH_2Cl_2 solution of lactose propargyl orthoester **21b** and glycosyl acceptor **22i** under argon atmosphere was stirred for 30 min in the presence of freshly activated 4 Å MS powder at room temperature. Catalytic amount of gold(III) bromide was added to the reaction mixture and continued stirring for another 2 h at room temperature to form trisaccharides **50a**. In the ^{1}H NMR spectrum of **50a**, the characteristic resonances corresponding to -OMe and 6-*O*-Si-C$(CH_3)_3$ were observed as individual singlets at δ 3.21 and 0.98 ppm respectively. Three anomers were identified at δ 4.97 (d, *J* = 7.9 Hz), 4.71 (d, *J* = 7.4 Hz) and 4.57 (d, *J* = 3.8 Hz) ppm. The resonances at δ 100.7, 100.0, and 98.2 ppm found in the ^{13}C NMR spectrum indicated the presence of two-β- and one-α-linkage in the trisaccharide **50a**. Seven carbonyl groups (disappear in DEPT spectrum) observed in the ester region indicated the presence of seven benzoate groups. The *t*-butyl group at δ 26.7, 19.4 ppm and methyl group at δ 55.1 ppm represented the presence of TBDPS group and methoxy group in trisaccharides **50a**. Having obtained the required glycosyl acceptor for the preparation of 1,6-anhydro sugar, the intramolecular glycosidation reaction between **50a** was performed in the presence of gold tribromide in acetonitrile at 70 °C to obtain 1,6-anhydro sugar (**37c**). Interesting to note that one pot cleavage of -OTBDPS bond followed by intramolecular glycosidation was accomplished by single gold tribromide reagent (**Scheme 1A.11**) in a domino fashion. In the ^{1}H NMR spectrum of **37c**, the characteristic three anomeric protons were observed at δ 4.83 (d, *J* = 7.9 Hz), 4.95 (d, *J* = 8.0 Hz) and 5.34 (d, *J* = 0.9 Hz) ppm. Resonances observed at δ 5.34 ppm with 0.9 Hz coupling constant was due to 1,6-anhydro linkage at the reducing end. Three anomers at δ 101.0, 100.5 and 100.4 ppm in the ^{13}C NMR spectrum represented the presence of three-β-isomer in compound **37c**. Encouraged with this, this methodology was also explored with glucosyl (**21a**) and lactosyl propargyl orthoester (**21b**) and glycosyl acceptor (**22i**, **22m**, **18h** and **18l**) under the same conditions to afford higher oligosaccharide 1,6-anhydro sugars (**37d** to **37j**) in good yields (**Table 1A.1**).[14]

1A.4 – Conclusion

In conclusion, we identified a new and versatile method for the synthesis of 1,6-anhydro sugars by using propargyl or methyl glycosides in the presence of $AuBr_3$ as a catalyst. The methodology was also applied for the synthesis of higher oligosaccharides 1,6-anhydro sugars (di/tri-saccharides). Interestingly, cleavage of silyl ether under $AuBr_3$ at 70 ºC followed by intramolecular glycosidation happened in a domino fashion resulting into the 1,6-anhydro sugar formation. Easy synthesis of 1,6-anhydro sugars would facilitate the synthesis of glycopolymers in future.

1A.5– Experimental and Characterization Data

Methyl 2,3-di-*O*-benzyl-6-*O*-(*t*-butyldiphenylsilyl)-α-D-glucopyranoside (**22i**): Glucose (15 g, 83.26 mmol) was refluxed for 24 h in 1M methanolic hydrochloric acid solution (100 mL) (for propargylation: dioxane:HCl solution and proaprgyl alcohol) and on next day the reaction mixture was neutralised with Et_3N and concentrated on rotary evaporator. The resultant crude residue was purified by silica gel column chromatography (10:90 methanol:DCM) to obtain **22f** as (13.2 g, 82%) as a gum.



To a solution of methyl α-D-glucopyranoside **22f** (13.0 g, 66.95 mmol) (propargyl-α-D-glucopyranoside) prepared *vide supra* in anhydrous DMF (15 mL) was added benzaldehyde dimethyl acetal (11.60 mL, 76.99 mmol) followed by the addition of catalytic amount of PTSA (1.15 g, 6.69 mmol). The resultant reaction mixture was concentrated on a rotary evaporator at 60 °C for 2 h. The progress of the reaction was monitor through TLC and after completion of the reaction, the reaction mixture was neutralised with Et_3N (4 mL) and DMF was concentrated on rota evaporator at 75 °C. The obtained crude mixture was diluted with ice-water and washed with pet ether (to remove excess benzaldehyde dimethyl acetal) and dried overnight in dark. The resultant residue was redissolved in dry DMF (20 mL) and cooled to 0 °C in an ice bath. Sodium hydride (60% dispersion in mineral oil) (6.18 g, 257.49 mmol) was added slowly portion-wise and the reaction mixture became a cake like solid. Benzyl bromide (16.82 mL, 141.62 mmol) was added dropwise slowly. After 2 h at room temperature, MeOH (2 mL) and water (100 mL) were added to reaction mixture and the compound was extracted out from water with EtOAc (2x100 mL). The organic layer was washed with saturated sodium chloride solution, dried over sodium sulphate and concentrated. The concentrated crude residue was purified by silica gel column chromatography (EtOAc:pet ether, 15:85) to get pure α-isomer **22h** (15.0 g, 50% over two steps) as a colourless solid.

To a solution of **22h** (10.0 g,21.62 mmol) in MeOH (60 mL) was added the catalytic amount of PTSA (0.41 g, 2.16 mmol) monohydrate and the reaction mixture was stirred at room temperature for 15 h, the reaction mixture was quenched with Et_3N (1 mL) and concentrated. The resultant residue was washed with water, extracted with EtOAc, dried over sodium sulphate and concentrated on a rota

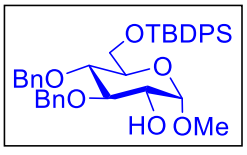
evaporator to obtain pure diol **22c** which was used for next step without any additional purification.

A mixture of TBDPSCl (5.9 g, 21.62 mmol) and imidazole (2.94 g, 43.24 mmol) in anhydrous DMF (60 mL) was added to a stirring solution of diol **22c** in DMF (40 mL). The progress of reaction was monitored by TLC-MS and after completion of the reaction, the reaction mixture was poured into a cold 1M HCl solution (100 mL) and extracted with the EtOAc (2x50 mL). Thus collected EtOAc layers were washed with water, sat. aq. solution of sodium bicarbonate, dried over sodium sulphate and concentrated under diminished pressure. The resultant crude residue was purified by silica gel column chromatography (EtOAc:pet ether, 20:80) to get **22i** (8.50 g, 64% over two steps) as a pale yellow coloured thick syrup.

$[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +57.1°; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.06 (s, 9H), 2.72 (s, 1H), 3.33 (s, 3H), 3.40 (dd, *J* = 9.5, 2.4 Hz, 1H), 3.54 (t, *J* = 9.1 Hz, 1H), 3.69 (d, *J* = 9.8 Hz, 1H), 3.89 (s, 2H), 4.13 (t, *J* = 9.0 Hz, 1H), 4.62 (d, *J* = 11.2 Hz, 1H), 4.67 (d, *J* = 3.4 Hz, 1H), 4.70 (s, 2H), 4.90 (d, *J* = 11.2 Hz, 1H), 7.00 – 7.56 (m, 16H), 7.59 – 7.86 (m, 4H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 19.1, 26.7, 26.7, 26.7, 54.8, 63.9, 70.9, 71.1, 72.9, 75.3, 79.5, 81.4, 97.7, 127.5, 127.5, 127.5, 127.5, 127.5, 127.6, 127.7, 127.8, 127.8, 127.8, 127.8, 127.9, 128.3, 128.3, 128.3, 128.3, 129.5, 129.5, 133.0, 133.1, 135.5, 135.5, 137.9, 138.6; HRMS (MALDI-TOF): m/z calcd for $[C_{37}H_{44}O_6Si+Na]^+$: 635.2805; Found, 635.2800.

Similar procedure was applied for the synthesis of Prop-2-ynyl-2,3-di-*O*-benzyl-6-*O*-(*t*-butyldiphenylsilyl)-α-D-glucopyranoside (**18h**).

Methyl 3,4-di-*O*-benzyl-6-*O*-(*t*-butyldiphenylsilyl)-α-D-glucopyranoside (**22m**): To a solution of diacetone glucose (**49a**) (10.0 g, 38.42 mmol) in dry DMF (20 mL) was added sodium hydride (60% dispersion in mineral oil) (1.8 g, 76.84 mmol) in portion-wise and the reaction mixture became a cake-like solid. Benzyl bromide (5.02 mL, 7.23 g) was added slowly. After 2 h at room temperature, MeOH (2 mL) and water (100 mL) were added to reaction mixture and the compound was extracted with EtOAc (2x100 mL). The organic layer was washed with brine solution, dried over anhydrous sodium sulphate and concentrated *in vacuo*. The crude residue was redissolved in 1N methanolic hydrochloric acid solution (for propargylation:- propargyl alcohol:dioxane:HCl (dry) solution) and refluxed for 24 h under inert atmosphere.



The progress of reaction was monitored by TLC analysis and after the complete disappearance of starting material, the reaction mixture was quenched with Et_3N (10 mL), concentrated and purified by silica gel column chromatography to achieve triol **22j** (EtOAc:Pet ether, 60:40) (8.0 g, 73% over two steps) as a clear pale brown coloured gum.

To a anhydrous DMF (15 mL) solution of triol **22j** (8.0 g, 28.14 mmol) was added benzaldehydedimethylacetal (4.28 mL, 30.95 mmol) followed by the addition of catalytic amount of PTSA (0.5 g, 2.81 mmol). The resultant solution was rotated on a rotary evaporator at 60 °C for 2 h. The progress of the reaction was monitored TLC-MS and after completion of the reaction, neutralised with Et_3N (4 mL) and DMF was concentrated under diminished pressure below 75 °C. The obtained crude mixture purified by flash silica gel column chromatography to afford pure α-isomer **22k** (EtOAc:Pet ether, 25:75) (6.0 g, 57% over two steps) as a white solid.

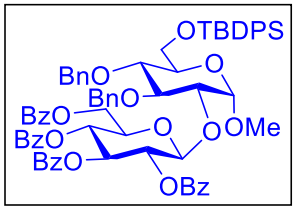
To a solution of alcohol **22k** (6.0 g, 16.11 mmol) in mixture of DCM:Et_2O (3:1, 15 mL) was added LAH (1.2 g, 32.22 mmol) portion wise under argon atmosphere at 0 °C. A pale yellow coloured solution of aluminium chloride (6.4 g, 48.33 mmol) in ether was added slowly at 0 °C and warmed the reaction to room temperature. After that ice bath was exchanged with oil bath and round bottom flask was fitted with a reflux condenser. The reaction mixture was refluxed at 40 °C for 30 min. The progress of reaction mixture was judged by TLC analysis. Excess LAH was quenched by adding excess of EtOAc and 10N NaOH, solid material was filtered through celite, organic layer was concentrated and used for next step without any additional purification.

A mixture of TBDPSCl (4.4 g, 16.11 mmol) and imidazole (2.2 g, 32.22 mmol) in anhydrous DMF (40 mL) was added to a stirring solution of diol **22l** in DMF (30 mL). The reaction mixture was judged with TLC and after completion of the reaction; the reaction mixture was poured into a 1M HCl solution and extracted with the EtOAc (2x50 mL). The collected EtOAc layer was washed with water, sat. aq. solution of sodium bicarbonate, dried over anhydrous sodium sulphate and concentrated *in vacuo*. The resultant crude residue was purified by silica gel column chromatography (EtOAc:pet ether, 20:80) to acquire **22m** (6.0 g, 61% over two steps) as a thick syrup.

$[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +52.9º; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.07 (s, 9H), 2.32 (d, *J* = 6.4 Hz, 1H), 3.38 (s, 3H), 3.73 (dt, *J* = 12.5, 7.4 Hz, 2H), 3.69 (s, 2H), 3.91 (s, 2H), 4.64 (d, *J* = 10.8 Hz, 1H), 4.77 (d, *J* = 3.3 Hz, 1H), 4.85 (t, *J* = 5.8 Hz, 1H), 4.90 (d, *J* = 3.1 Hz, 2H), 7.06 – 7.46 (m, 16H), 7.62 – 7.80 (m, 4H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 19.2, 26.7, 26.7, 26.7, 54.8, 62.7, 71.6, 73.0, 74.9, 75.4, 77.6, 83.3, 99.1, 127.5, 127.6, 127.6, 127.6, 127.6, 127.7, 127.7, 127.9, 127.9, 128.3, 128.3, 128.4, 128.4, 129.5, 129.5, 133.1, 133.5, 134.7, 135.5, 135.5, 135.7, 135.8, 138.1, 138.5; HRMS (MALDI-TOF): m/z calcd for $[C_{37}H_{44}O_6Si+Na]^+$: 635.2805; Found, 635.2819.

Similar procedure was applied for the synthesis of Prop-2-ynyl-3,4-di-*O*-benzyl-6-*O*-(*t*-butyldiphenylsilyl)-α-D-glucopyranoside (**18l**).

Methyl-2-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-3,4-di-*O*-benzyl-6-*O*-(*t*-butyldiphenylsilyl)-α-D-glucopyranoside (**50c**): To a CH_2Cl_2 (8 mL) solution of propargyl 1,2 orthobenzoate **21a** (0.1 g, 0.16 mmol) and glycosyl acceptor **22m** (97 mg, 0.16 mmol) was added 4 Å MS powder. After 10 min stirring at room temprature, gold tribromide (6.9 mg, 15.76 µmol) was added to the reaction mixture under argon atmoshpere. The reaction mixture was stirred for another 2 h at room temperture and progress of the reaction was monitored through TLC-MS analysis. The reaction mixture was quenched with Et_3N (2 mL) and filtered through a bed of celite. The collected filtrate was concentrated and purified by flash silica gel column chromatography to form (**50c**) (0.125 g, 67.0%) as a fluffy solid.

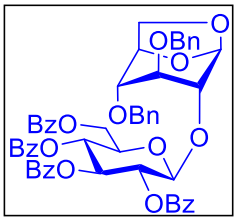


$[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.6) +17.3º; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.04 (s, 9H), 3.35 (s, 3H), 3.39 (s, 1H), 3.50 – 4.03 (m, 5H), 4.22 (ddd, *J* = 9.2, 4.6, 2.8 Hz, 1H), 4.48 (dt, *J* = 10.6, 3.7 Hz, 2H), 4.60 (d, *J* = 12.3 Hz, 1H), 4.68 (d, *J* = 3.2 Hz, 1H), 4.77 (dd, *J* = 11.0, 2.8 Hz, 1H), 4.89 – 4.92 (m, 1H), 5.03 (d, *J* = 3.3 Hz, 1H), 5.22 (d, *J* = 7.8 Hz, 1H), 5.72 (dd, *J* = 9.5, 4.3 Hz, 1H), 5.79 (dd, *J* = 9.4, 2.4 Hz, 1H), 5.92 (d, *J* = 9.5 Hz, 1H), 6.86 – 7.60 (m, 30H), 7.61 – 8.14 (m, 10H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 19.2, 26.8, 26.8, 26.8, 54.8, 62.9, 69.4, 71.1, 72.0, 72.3, 73.2, 74.8, 75.3, 77.8, 81.0, 82.0, 83.4, 99.1, 102.2, 127.1, 127.3, 127.3, 127.4, 127.5, 127.6, 127.6, 127.6, 127.6, 127.7, 127.7, 127.8, 128.0, 128.0, 128.1, 128.1, 128.1, 128.2, 128.2, 128.2, 128.2, 128.3, 128.4, 128.4, 128.4, 128.7, 128.7, 128.8, 129.3, 129.6, 129.6, 129.7, 129.7,

129.7, 129.7, 129.8, 133.0, 133.2, 133.2, 133.4, 133.5, 135.6, 135.6, 135.7, 135.7, 135.8, 138.0, 138.4, 165.0, 165.2, 165.8, 166.1; HRMS (MALDI-TOF): m/z calcd for $[C_{71}H_{70}O_{15}Si+Na]^+$: 1213.4382; Found, 1213.4380.

Similar procedure was adopted for the synthesis of disaccharides (**50b**, **50d** and **50e**) and trisaccharides (**50a**, **50f, 50g, and 50h**)

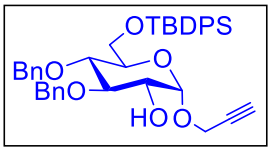
1,6-Anhydro-2-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-3,4-tri-*O*-benzyl-β-D-gluco pyranoside (**37e**): To a solution of **50c** (0.1 g, 83.94 µmol) in anhydrous acetonitrile (4 mL) was added gold bromide (2.6 mg, 5.88 µmol) under argon atmoshpere. The resulting mixture was stirred for another 2 h at 70 °C and progress of the reaction was monitored through TLC-MS. The reaction mixture was quenched with Et_3N (1 mL), concentrated *in vacuo* and purified by flash silica gel column chromatography to obtain **37e** (0.06 g, 77.6%) as a fluffy solid.



$[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +16.2°; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.07 (s, 1H), 3.42 (s, 1H), 3.49 (dd, *J* = 7.3, 6.0 Hz, 1H), 3.77 (d, *J* = 7.9 Hz, 1H), 3.80 – 3.94 (m, 2H), 4.34 (d, *J* = 7.9 Hz, 1H), 4.34 – 4.48 (m, 2H), 4.43 (d, *J* = 6.6 Hz, 2H), 4.56 (d, *J* = 10.3 Hz, 1H), 4.62 (ABq, *J* = 12.5 Hz, 2H), 5.21 (s, 1H), 5.39 (dd, *J* = 9.7, 8.0 Hz, 1H), 5.58 (t, *J* = 9.7 Hz, 1H), 5.75 (t, *J* = 9.6 Hz, 1H), 7.16 – 7.67 (m, 22H), 7.74 – 8.15 (m, 8H); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 62.8, 64.8, 69.5, 71.2, 71.4, 72.2, 72.2, 72.5, 74.2, 75.2, 75.7, 76.0, 99.8, 100.2, 127.8, 127.9, 127.9, 128.2, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.5, 128.6, 128.7, 128.7, 129.3, 129.4, 129.6, 129.6, 129.6, 129.6, 129.7, 129.7, 129.8, 129.8, 133.2, 133.3, 133.3, 133.5, 137.7, 137.9, 164.9, 165.2, 165.7, 166.0; HRMS (MALDI-TOF): m/z calcd for $[C_{54}H_{48}O_{14}+Na]^+$: 943.2942; Found, 943.2949.

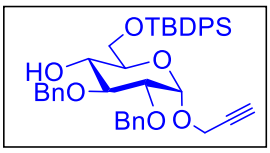
Similar procedure was applied for the synthesis of monosaccharides (**37b, 41b,** and **42b**), disaccharides (**37e**) and trisaccharides (**37c** and **37h**).

Prop-2-ynyl-3,4-di-*O*-benzyl-6-*O*-(*t*-butyldiphenylsilyl)-α-D-glucopyranoside (**18l**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +31.7°; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.06 (s, 9H), 2.41 (t, *J* = 2.4 Hz, 1H), 2.68 (s, 1H), 3.45 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.55 (d, *J* = 9.8 Hz, 1H), 3.64 (d, *J* = 9.1 Hz, 1H), 3.88 (d, *J* = 2.9 Hz, 2H), 4.12 (t, *J* = 9.0 Hz, 1H), 4.22 (d, *J* = 2.3 Hz, 2H),

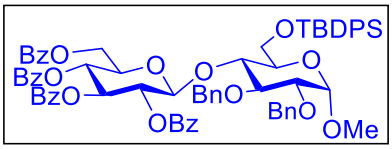


4.62 (d, *J* = 11.1 Hz, 1H), 4.76 (ABq, *J* = 11.8 Hz, 2H), 4.91 (d, *J* = 11.1 Hz, 1H), 5.15 (d, *J* = 3.6 Hz, 1H), 7.14 – 7.50 (m, 16H), 7.69 (ddt, *J* = 6.4, 4.2, 1.8 Hz, 4H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 19.2, 26.7, 26.7, 26.7, 53.9, 62.8, 71.6, 72.4, 73.4, 74.7, 77.2, 77.3, 78.8, 79.1, 93.9, 127.5, 127.5, 127.6, 127.6, 127.8, 127.8, 128.0, 128.0, 128.1, 128.1, 128.3, 128.3, 128.5, 129.5, 129.6, 133.2, 133.4, 134.7, 134.7, 135.5, 135.5, 135.7, 137.7, 138.3; HRMS (MALDI-TOF) m/z calcd for $[C_{39}H_{44}O_6Si+Na]^+$: 659.2805; Found, 659.2800.

Prop-2-ynyl-2,3-di-*O*-benzyl-6-*O*-(*t*-butyldiphenylsilyl)-α-D-glucopyranoside (**18h**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.6) +37.7°;^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.05 (s, 9H), 2.41 (t, *J* = 2.3 Hz, 1H), 2.45 (d, *J* = 1.8 Hz, 1H), 3.56 (dd, *J* = 9.5, 3.6 Hz, 1H), 3.60 – 3.68 (m, 2H), 3.74 – 3.89 (m, 3H), 4.26 (d, *J* = 2.4 Hz, 2H), 4.73 (s, 2H), 4.75 (d, *J* = 10.3 Hz, 1H), 5.00 (d, *J* = 11.3 Hz, 1H), 5.11 (d, *J* = 3.6 Hz, 1H), 7.12 – 7.62 (m, 16H), 7.48 – 7.88 (m, 4H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 19.1, 26.7, 26.7, 26.7, 53.9, 63.7, 70.8, 71.5, 72.5, 74.7, 75.3, 78.8, 79.0, 81.2, 94.5, 127.5, 127.6, 127.6, 127.6, 127.6, 127.7, 127.9, 127.9, 128.0, 128.0, 128.3, 128.3, 128.4, 128.4, 129.6, 129.6, 133.0, 133.1, 135.5, 135.5, 135.5, 135.5, 137.8, 138.6; HRMS (MALDI-TOF): m/z calcd for $[C_{39}H_{44}O_6Si+Na]^+$: 659.2805; Found, 659.2815.

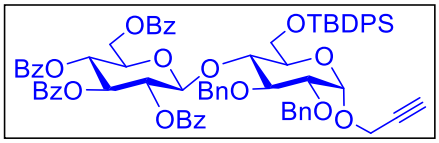


Methyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,3-di-*O*-benzyl-6-*O*-(*t*-butyldiphenylsilyl)-α-D-glucopyranoside (**50b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) +17.7°; ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 1.07 (s, 9H), 3.23 (s, 3H), 3.31 – 3.42 (m, 1H), 3.48 (dd, *J* = 9.6, 3.7 Hz, 1H), 3.73 (d, *J* = 11.6 Hz, 1H), 3.81 – 4.00 (m, 2H), 4.21 (t, *J* = 9.4 Hz, 1H), 4.30 (dd, *J* = 12.1, 5.2 Hz, 1H), 4.43 (dd, *J* = 5.5, 2.4 Hz, 1H), 4.56 (dd, *J* = 8.5, 3.2 Hz, 1H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.79 (d, *J* = 12.1 Hz, 2H), 5.15 (d, *J* = 11.1 Hz, 1H), 5.28 (d, *J* = 8.0 Hz, 1H), 5.52 – 5.72 (m, 2H), 5.83 (ABq, *J* = 9.5 Hz, 2H), 7.02 – 8.34 (m, 40H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 19.5, 26.8, 26.8, 26.8, 55.1, 61.4, 63.1, 69.9, 70.5, 72.0, 72.2, 73.2, 73.6, 75.5, 76.7, 79.3, 79.9, 98.2, 100.3, 127.2, 127.6, 127.6, 127.7, 127.8, 128.0, 128.1, 128.2, 128.2, 128.2, 128.2, 128.2, 128.2, 128.2, 128.2, 128.2, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.7, 128.8, 129.6, 129.7, 129.7, 129.7, 129.8, 129.8, 130.2, 132.5, 132.9, 133.1, 133.3, 133.7, 135.4, 135.9,



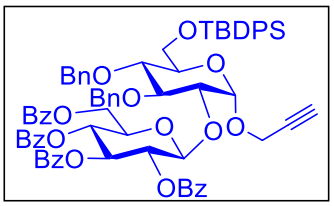
138.4, 139.2, 164.7, 165.1, 165.6, 166.0; HRMS (MALDI-TOF): m/z calcd for $[C_{71}H_{70}O_{15}Si+Na]^+$: 1213.4382; Found, 1213.4376.

Prop-2-ynyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,3-di-*O*-benzyl-6-*O*-(*t*-butyldiphenylsilyl)-α-D-glucopyranoside (**50d**):



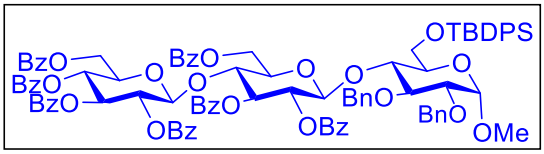
$[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +26.5°; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.07 (s, 9H), 2.26 (t, *J* = 2.3 Hz, 1H), 3.43 (d, *J* = 9.8 Hz, 1H), 3.53 (dd, *J* = 9.6, 3.8 Hz, 1H), 3.72 (d, *J* = 11.1 Hz, 1H), 3.83 – 4.02 (m, 3H), 4.11 (d, *J* = 2.2 Hz, 2H), 4.22 (t, *J* = 9.4 Hz, 1H), 4.32 (dd, *J* = 13.4, 3.9 Hz, 1H), 4.53 (dd, *J* = 12.1, 3.1 Hz, 2H), 4.72 (d, *J* = 6.0 Hz, 1H), 4.75 – 4.83 (m, 1H), 5.07 (d, *J* = 3.8 Hz, 1H), 5.13 (d, *J* = 11.0 Hz, 1H), 5.27 (d, *J* = 8.0 Hz, 1H), 5.61 (ABq, *J* = 9.6 Hz, 2H), 5.78 (d, *J* = 9.6 Hz, 1H), 7.19 – 7.93 (m, 40H); ^{13}C NMR (50.13 MHz, $CDCl_3$): δ 19.4, 26.8, 26.8, 26.8, 54.4, 61.2, 63.1, 69.9, 71.1, 72.1, 72.2, 73.2, 73.2, 74.5, 75.6, 76.6, 78.8, 79.0, 79.7, 95.3, 100.3, 127.2, 127.6, 127.7, 127.7, 127.7, 127.9, 127.9, 128.0, 128.0, 128.1, 128.1, 128.2, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.8, 128.8, 128.8, 129.6, 129.6, 129.7, 129.7, 129.8, 129.8, 129.8, 129.8, 129.8, 130.2, 132.5, 132.9, 133.1, 133.3, 133.7, 135.4, 135.4, 135.9, 135.9, 138.3, 139.1, 164.7, 165.1, 165.6, 166.0; HRMS (MALDI-TOF): m/z calcd for $[C_{73}H_{70}O_{15}Si+Na]^+$: 1237.4382; Found, 1213.4389.

Prop-2-ynyl-2-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-3,4-di-*O*-benzyl-6-*O*-(*t*-butyldiphenyl-silyl)-α-D-glucopyranoside (**50e**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.4) +19.4°; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.03 (s, 9H), 2.40 (t, *J* = 2.2 Hz, 1H), 3.37 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.48 (t, *J* = 9.3 Hz, 1H), 3.59 – 3.95 (m, 2H), 4.04 – 4.19 (m, 1H), 4.18 (d, *J* = 2.1 Hz, 2H), 4.24 (d, *J* = 2.0 Hz, 1H), 4.34 (d, *J* = 12.1 Hz, 1H), 4.44 (d, *J* = 9.5 Hz, 1H), 4.35- 4.46 (m, 2H), 4.57 (dd, *J* = 11.6, 4.9 Hz, 2H), 4.88 (d, *J* = 3.6 Hz, 1H), 5.12 (d, *J* = 11.1 Hz, 1H), 5.54 (d, *J* = 7.9 Hz, 1H), 5.65 (d, *J* = 9.7 Hz, 1H), 5.75 (d, *J* = 9.6 Hz, 1H), 5.93 (d, *J* = 9.5 Hz, 1H), 7.05 – 7.57 (m, 28H), 7.63 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.80 – 8.07 (m, 10H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 19.2, 26.7, 26.7, 26.7, 53.5, 63.0, 63.2, 69.8, 71.8, 72.5, 73.1, 73.1, 74.7, 74.8, 75.4, 78.6, 78.8, 79.2, 80.1, 93.8, 100.9, 127.3, 127.5, 127.5, 127.5, 127.5, 127.5, 127.6, 127.8, 127.8, 127.9, 128.0, 128.0, 128.0, 128.0, 128.1, 128.1, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.4, 128.7,

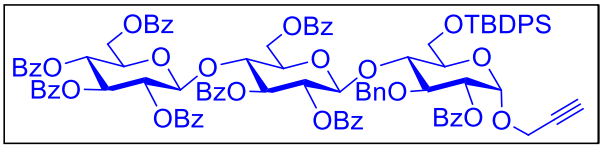


128.7, 129.4, 129.5, 129.5, 129.6, 129.6, 129.6, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 132.8, 133.1, 133.2, 133.3, 133.4, 135.5, 135.5, 135.6, 135.6, 137.6, 138.3, 165.1, 165.2, 165.8, 166.0; HRMS (MALDI-TOF): m/z calcd for $[C_{73}H_{70}O_{15}Si+Na]^+$: 1237.4382; Found, 1213.4391.

Methyl-4-*O*-(2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-2,3-di-*O*-benzyl-6-*O*-(*t*-butyldiphenylsilyl)-α-D-gluco-pyranoside (**50a**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +38.5°; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 0.98 (s, 9H), 3.21 (s, 3H), 3.34 (s, 1H), 3.40 (dd, *J* = 9.7, 3.6 Hz, 1H), 3.39 – 3.48 (m, 1H), 3.60 (dd, *J* = 11.2, 6.8 Hz, 1H), 3.68 (dt, *J* = 11.5, 4.5 Hz, 1H), 3.72 – 3.80 (m, 2H), 3.83 (d, *J* = 10.0 Hz, 1H), 3.88 (t, *J* = 9.4 Hz, 1H), 4.11 (t, *J* = 9.4 Hz, 1H), 4.20 (t, *J* = 9.3 Hz, 1H), 4.30 (dd, *J* = 12.3, 4.1 Hz, 2H), 4.43 (d, *J* = 11.8 Hz, 1H), 4.56 (dd, *J* = 7.7, 4.2 Hz, 2H), 4.70 (dd, *J* = 10.8, 6.0 Hz, 2H), 4.98 (d, *J* = 7.9 Hz, 1H), 5.06 (d, *J* = 11.2 Hz, 1H), 5.30 (dd, *J* = 10.3, 3.2 Hz, 1H), 5.47 (t, *J* = 8.0 Hz, 1H), 5.54 (t, *J* = 9.3 Hz, 1H), 5.62 – 5.82 (m, 2H), 6.90 – 7.69 (m, 39H), 7.66 – 7.79 (m, 6H), 7.85 – 8.11 (m, 10H); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 19.3, 26.7, 26.7, 26.7, 55.1, 60.9, 61.4, 62.7, 67.4, 69.7, 70.5, 71.2, 71.7, 72.1, 72.7, 73.2, 73.5, 75.3, 75.6, 76.4, 77.2, 77.2, 79.0, 80.0, 98.2, 100.0, 100.7, 126.9, 127.3, 127.5, 127.6, 127.6, 127.8, 127.9, 128.1, 128.1, 128.2, 128.2, 128.2, 128.2, 129.2, 129.2, 128.3, 128.4, 128.5, 128.5, 128.5, 128.5, 128.6, 128.6, 128.6, 129.6, 129.6, 129.6, 129.6, 128.6, 128.8, 128.9, 129.4, 129.5, 129.5, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.7, 129.7, 129.8, 129.8, 130.0, 130.4, 132.7, 133.0, 133.1, 133.2, 133.3, 133.3, 133.4, 133.4, 133.5, 135.4, 135.4, 135.9, 135.9, 138.4, 139.1, 164.7, 164.8, 165.1, 165.2, 165.3, 165.5, 165.8; HRMS (MALDI-TOF): m/z calcd for $[C_{98}H_{92}O_{23}Si+Na]^+$: 1687.5696; Found, 1687.5690.

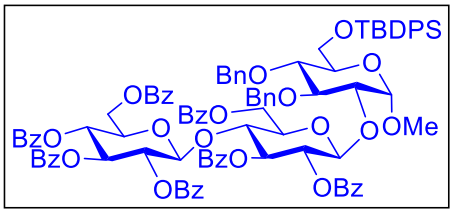


Prop-2-ynyl-4-*O*-(2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-2,3-di-*O*-benzyl-6-*O*-(*t*-butyldiphenylsilyl)-α-D-glucopyranoside (**50g**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) +45.2°; ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 0.98 (s, 9H), 2.24 (t, *J* = 1.5 Hz, 1H), 3.40 (d, *J* = 8.7 Hz, 1H), 3.44 – 3.51 (m, 2H), 3.62 (dd, *J* = 11.1, 6.5 Hz, 1H), 3.73 (ddd, *J* = 37.7, 15.6, 6.3 Hz, 2H), 3.82 – 3.92 (m, 2H), 4.10 (s, 2H), 4.13 (d,



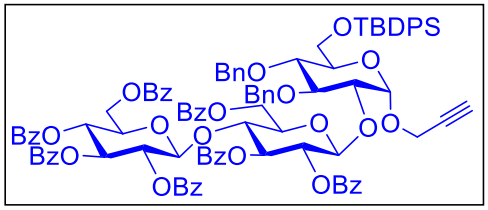
J = 9.4 Hz, 1H), 4.22 (t, *J* = 9.3 Hz, 1H), 4.29 – 4.39 (m, 2H), 4.45 (d, *J* = 11.4 Hz, 1H), 4.56 – 4.64 (m, 2H), 4.69 (d, *J* = 11.8 Hz, 2H), 4.74 (d, *J* = 7.7 Hz, 1H), 5.00 (dd, *J* = 12.1, 5.7 Hz, 2H), 5.06 (d, *J* = 11.1 Hz, 1H), 5.24 – 5.39 (m, 1H), 5.39 – 5.60 (m, 1H), 5.66 – 5.82 (m, 2H), 6.89 – 8.14 (m, 55H); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 19.3, 26.8, 26.8, 26.8, 54.4, 60.9, 61.2, 62.6, 67.5, 69.8, 71.1, 71.3, 71.7, 72.1, 72.7, 73.2, 73.2, 74.5, 75.4, 75.6, 76.3, 78.8, 78.8, 78.9, 79.8, 95.3, 100.0, 100.7, 127.0, 127.4, 127.4, 127.6, 127.7, 127.9, 127.9, 127.9, 128.2, 128.2, 128.2, 128.2, 128.2, 128.3, 128.5, 128.5, 128.6, 128.6, 128.6, 128.6, 128.6, 128.6, 128.6, 128.6, 128.6, 128.6, 128.7, 128.8, 128.9, 129.4, 129.5, 129.5, 129.5, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.7, 129.7, 129.7, 129.7, 129.8, 129.9, 130.0, 130.0, 130.1, 130.4, 132.7, 133.0, 133.0, 133.2, 133.3, 133.3, 133.4, 133.4, 133.5, 135.4, 135.4, 135.9, 135.9, 138.3, 139.1, 164.7, 164.8, 165.1, 165.2, 165.4, 165.5, 165.8; HRMS (MALDI-TOF): m/z calcd for $[C_{100}H_{92}O_{23}Si+Na]^+$: 1711.5696; Found, 1711.5691.

Methyl-2-*O*-(2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-3,4-di-*O*-benzyl-6-*O*-(*t*-butyldiphenylsilyl)-α-D-glucopyra-noside

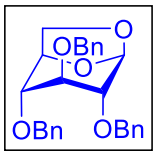


(**50f**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.7) +38.9°; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.02 (s, 9H), 3.23 (s, 3H), 3.55 (t, *J* = 9.3 Hz, 1H), 3.68 (td, *J* = 17.6, 11.9 Hz, 4H), 3.82 (s, 2H), 3.93 (dt, *J* = 17.5, 7.8 Hz, 3H), 4.28 (t, *J* = 9.4 Hz, 1H), 4.45 (d, *J* = 11.4 Hz, 1H), 4.50 (dd, *J* = 11.6, 3.7 Hz, 1H), 4.56 (d, *J* = 11.4 Hz, 1H), 4.64 (d, *J* = 10.7 Hz, 1H), 4.72 (d, *J* = 11.8 Hz, 1H), 4.86 – 4.98 (m, 3H), 5.07 (d, *J* = 7.8 Hz, 1H), 5.44 (d, *J* = 10.1 Hz, 1H), 5.71 (t, *J* = 8.4 Hz, 1H), 5.74 – 5.80 (m, 2H), 5.84 (t, *J* = 9.4 Hz, 1H), 6.88 – 8.07 (m, 55H); ^{13}C NMR (100.25 MHz, $CDCl_3$): δ 19.2, 26.7, 26.7, 26.7, 54.7, 61.0, 62.2, 62.7, 67.5, 69.8, 70.9, 71.3, 71.7, 71.7, 72.9, 73.2, 74.8, 75.3, 76.0, 77.2, 77.6, 80.9, 82.2, 99.0, 101.0, 102.2, 127.1, 127.2, 127.2, 127.4, 127.5, 127.5, 127.6, 127.6, 127.6, 127.6, 127.8, 128.0, 128.0, 128.0, 128.1, 128.2, 128.2, 128.2, 128.3, 128.4, 128.5, 128.5, 128.5, 128.6, 128.6, 128.6, 128.6, 128.6, 128.6, 128.6, 128.7, 128.8, 129.2, 129.3, 129.4, 129.5, 129.5, 129.5, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.7, 129.7, 129.8, 129.9, 129.9, 130.0, 132.9, 133.1, 133.1, 133.2, 133.4, 133.4, 133.5, 135.5, 135.5, 135.7, 135.8, 137.9, 138.3, 164.7, 165.1, 165.2, 165.4, 165.4, 165.5, 165.8; HRMS (MALDI-TOF): m/z calcd for $[C_{98}H_{92}O_{23}Si+Na]^+$: 1687.5696; Found, 1687.5699.

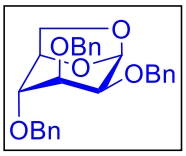
Prop-2-ynyl-2-*O*-(2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-3,4-di-*O*-benzyl-6-*O*-(*t*-butyldiphenylsilyl)-α-D-glucopyranoside (**50h**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +37.6°; ^1H NMR (500.13 MHz, $CDCl_3$): δ 0.99 (s, 9H), 2.36 (t, *J* = 2.4 Hz, 1H), 3.30 (dd, *J* = 9.6, 3.7 Hz, 1H), 3.36 – 3.43 (m, 1H), 3.57 (t, *J* = 4.1 Hz, 1H), 3.60 (d, *J* = 8.6 Hz, 1H), 3.63 (t, *J* = 5.5 Hz, 1H), 3.67 – 3.71 (m, 2H), 3.72 – 3.77 (m, 1H), 3.78 (t, *J* = 6.8 Hz, 1H), 4.13 (dABq, *J* = 15.8, 2.4 Hz, 2H), 4.26 (t, *J* = 9.4 Hz, 1H), 4.31 (t, *J* = 11.3 Hz, 1H), 4.38 (dd, *J* = 12.1, 4.3 Hz, 1H), 4.43 – 4.48 (m, 2H), 4.50 (dd, *J* = 15.1, 11.3 Hz, 2H), 4.77 (d, *J* = 7.9 Hz, 1H), 4.82 (d, *J* = 3.7 Hz, 1H), 5.01 (d, *J* = 11.0 Hz, 1H), 5.31 (dd, *J* = 10.3, 3.4 Hz, 1H), 5.40 (d, *J* = 8.1 Hz, 1H), 5.56 (dd, *J* = 10.0, 8.1 Hz, 1H), 5.66 – 5.72 (m, 2H), 5.81 (t, *J* = 9.2 Hz, 1H), 6.87 – 7.54 (m, 37H), 7.58 (dd, *J* = 8.0, 1.3 Hz, 4H), 7.69 – 7.78 (m, 2H), 7.85 – 7.90 (m, 2H), 7.95 – 8.05 (m, 10H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 19.2, 26.8, 26.8, 26.8, 53.6, 61.0, 62.7, 63.1, 67.5, 69.8, 71.3, 71.8, 71.8, 72.5, 72.7, 72.9, 73.2, 74.6, 74.6, 75.5, 76.0, 78.8, 78.9, 80.1, 93.9, 100.7, 100.9, 127.2, 127.5, 127.5, 127.5, 127.5, 127.5, 127.5, 127.7, 127.8, 127.8, 127.9, 127.9, 128.0, 128.0, 128.0, 128.2, 128.2, 128.2, 128.2, 128.3, 128.4, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.6, 128.6, 128.6, 128.6, 128.7, 128.7, 128.9, 129.5, 129.5, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.7, 129.7, 129.7, 129.8, 129.8, 129.8, 129.8, 130.0, 130.0, 133.1, 133.1, 133.2, 133.2, 133.3, 133.4, 133.4, 133.5, 133.5, 135.6, 135.6, 135.7, 135.7, 137.7, 138.4, 164.9, 165.2, 165.4, 165.4, 165.4, 165.5, 165.8; HRMS (MALDI-TOF): m/z calcd for $[C_{100}H_{92}O_{23}Si+Na]^+$: 1711.5696; Found, 1711.5693.



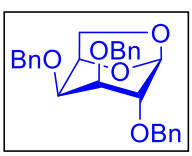
1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (**37b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) –26.0°; ^1H NMR (200.13 MHz, $CDCl_3$): δ 3.29 – 3.38 (m, 2H), 3.58 (s, 1H), 3.67 (dd, *J* = 7.0, 6.0 Hz, 1H), 3.84 – 3.97 (m, 1H), 4.41 (ABq, *J* = 12.6 Hz, 2H), 4.54 (d, *J* = 2.0 Hz, 2H), 4.58 (ABq, *J* = 12.6 Hz, 2H), 4.48 – 4.67 (m, 1H), 5.46 (s, 1H), 6.81 – 7.71 (m, 15H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 65.3, 71.1, 71.7, 71.9, 74.2, 75.8, 75.9, 76.6, 100.5, 127.6, 127.7, 127.7, 127.7, 127.8, 127.8, 127.9, 127.9, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 137.7, 137.7, 137.8; HRMS (MALDI-TOF): m/z calcd for $[C_{27}H_{28}O_5+Na]^+$: 455.1834; Found, 455.1840.



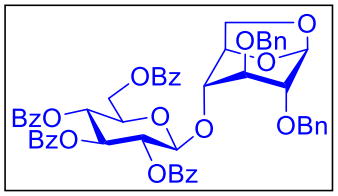
1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-mannopyranoside (**41b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) –16.0; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.47 (t, *J* = 1.6 Hz, 1H), 3.58 (dd, *J* = 5.3, 1.7 Hz, 1H), 3.73 (dd, *J* = 6.9, 6.1 Hz, 1H), 3.82 (dq, *J* = 4.9, 1.6 Hz, 1H), 4.24 (dd, *J* = 7.2, 0.8 Hz, 1H), 4.44 (ABq, *J* = 12.2 Hz, 2H), 4.46 – 4.53 (m, 2H), 4.55 (d, *J* = 1.0 Hz, 2H), 4.59 (ABq, *J* = 12.5 Hz, 2H), 7.02 – 7.51 (m, 15H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 64.9, 71.3, 71.4, 73.3, 74.1, 74.3, 74.4, 76.3, 100.1, 127.7, 127.7, 127.8, 127.8, 127.9, 128.0, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 137.6, 137.9, 137.9; HRMS (MALDI-TOF): m/z calcd for $[C_{27}H_{28}O_5+Na$, 455.1834; Found, 455.1830.



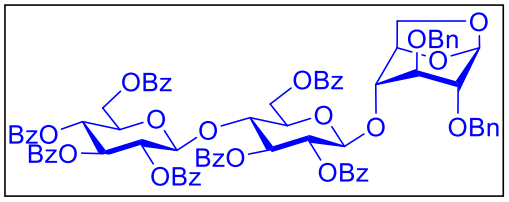
1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-galactopyranoside (**42b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) –34.9°; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.52 (s, 1H), 3.63 (t, *J* = 5.9 Hz, 1H), 3.80 (dd, *J* = 5.1, 1.4 Hz, 1H), 3.88 (t, *J* = 4.3 Hz, 1H), 4.44 (ABq, *J* = 12.9 Hz, 2H), 4.35 – 4.65 (m, 2H), 4.55 (s, 2H), 4.56 (ABq, *J* = 11.9 Hz, 2H), 5.36 (s, 1H), 7.16 – 7.47 (m, 15H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 64.3, 71.1, 72.1, 72.7, 73.0, 73.1, 74.1, 76.3, 100.2, 127.6, 127.6, 127.6, 127.8, 127.8, 127.8, 127.9, 127.9, 128.0, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 137.5, 137.9, 138.2; HRMS (MALDI-TOF): m/z calcd for $[C_{27}H_{28}O_5+Na]^+$: 455.1834; Found, 455.1836.



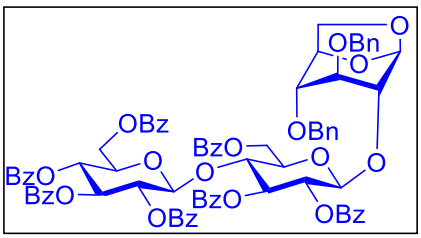
1,6-Anhydro-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,3-tri-*O*-benzyl-β-D-glucopyranoside (**37e**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.9) –13.4; ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 3.27 (s, 1H), 3.55 (dd, *J* = 7.1, 6.1 Hz, 1H), 3.65 (s, 1H), 3.80 (s, 1H), 3.84 (d, *J* = 7.1 Hz, 1H), 4.10 (dq, *J* = 8.5, 2.7 Hz, 1H), 4.34 (d, *J* = 12.3 Hz, 1H), 4.38 (d, *J* = 12.0 Hz, 1H), 4.43 (dd, *J* = 17.9, 5.8 Hz, 1H), 4.43 (s, 1H), 4.48 (d, *J* = 12.3 Hz, 1H), 4.56 (dd, *J* = 12.2, 2.9 Hz, 1H), 4.64 (d, *J* = 5.1 Hz, 1H), 5.25 (d, *J* = 8.0 Hz, 1H), 5.37 (s, 1H), 5.56 (dd, *J* = 9.8, 8.0 Hz, 1H), 5.66 (t, *J* = 9.7 Hz, 1H), 5.89 (t, *J* = 9.6 Hz, 1H), 7.05 – 7.62 (m, 22H), 7.80 – 8.05 (m, 8H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 63.0, 65.4, 69.6, 71.2, 72.0, 72.1, 72.4, 73.0, 74.2, 75.3, 77.7, 99.7, 100.4, 120.0, 127.6, 127.6, 127.7, 127.7, 127.7, 127.8, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.7, 128.8, 129.2, 129.5, 129.7, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 130.1, 133.2, 133.2, 133.3, 133.5, 137.6, 137.8, 165.0, 165.2, 165.8, 166.1; HRMS (MALDI-TOF): m/z calcd for $[C_{54}H_{48}O_{14}+Na]^+$: 943.2942; Found, 943.2950.



1,6-Anhydro-4-*O*-(2,3,6-tri-*O*-benzoyl-β-D-glucopyranosyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl))-2,3-tri-*O*-benzyl-β-D-glucopyranoside (**37c**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) +28.2°; ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 3.23 (s, 1H), 3.54 (dd, *J* = 7.1, 6.2 Hz, 1H), 3.58 (dt, *J* = 9.9, 2.9 Hz, 1H), 3.63 (dd, *J* = 11.4, 6.8 Hz, 1H), 3.65 – 3.68 (m, 3H), 3.73 (dd, *J* = 11.4, 6.6 Hz, 1H), 3.81 (d, *J* = 6.9 Hz, 1H), 3.86 (t, *J* = 6.8 Hz, 1H), 4.22 (t, *J* = 9.5 Hz, 1H), 4.27 (d, *J* = 12.5 Hz, 1H), 4.34 – 4.35 (m, 2H), 4.37 (s, 1H), 4.44 (d, *J* = 12.4 Hz, 1H), 4.49 (d, *J* = 5.8 Hz, 1H), 4.83 (d, *J* = 7.9 Hz, 1H), 4.95 (d, *J* = 8.0 Hz, 1H), 5.33 – 5.35 (m, 2H), 5.37 (d, *J* = 3.4 Hz, 1H), 5.69 – 5.79 (m, 3H), 6.94 – 7.68 (m, 31H), 7.71 – 8.17 (m, 14H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 61.1, 62.2, 65.3, 67.5, 69.9, 71.0, 71.4, 71.8, 71.8, 71.9, 73.0, 73.1, 74.3, 75.0, 75.8, 76.0, 78.7, 100.4, 100.5, 101.0, 127.5, 127.5, 127.7, 127.7, 127.7, 127.8, 128.2, 128.2, 128.2, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.5, 128.6, 128.6, 128.6, 128.6, 128.7, 128.9, 129.4, 129.4, 129.4, 129.4, 129.5, 129.5, 129.6, 129.6, 129.6, 129.6, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 129.9, 130.0, 130.0, 133.1, 133.2, 133.2, 133.4, 133.4, 133.4, 133.5, 137.6, 137.9, 164.7, 165.0, 165.2, 165.4, 165.4, 165.6, 165.8; HRMS (MALDI-TOF): m/z calcd for $[C_{81}H_{70}O_{22}+Na]^+$: 1417.4256; Found, 1417.4251.



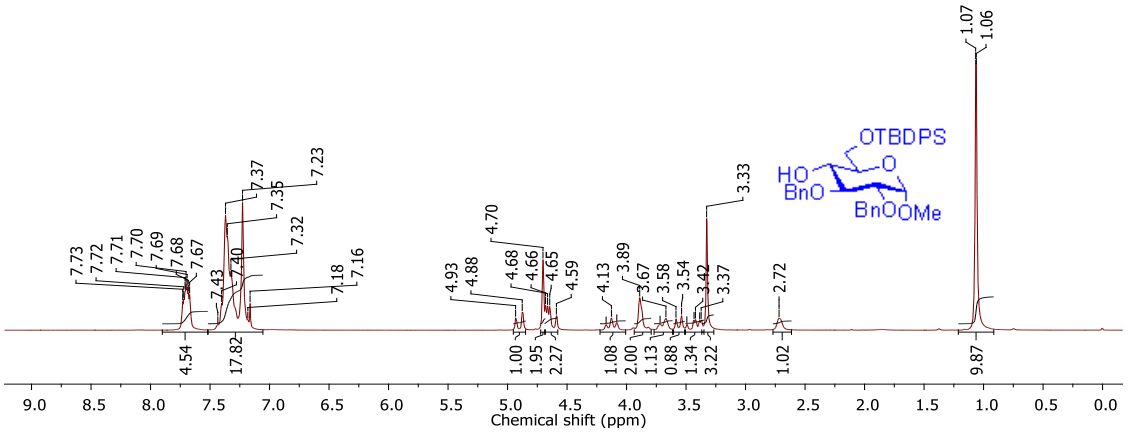
1,6-Anhydro-2-*O*-(2,3,6-tri-*O*-benzoyl-β-D-glucopyranosyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl))-2,3-tri-*O*-benzyl-β-D-glucopyranoside (**37h**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.3) +47.4°; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 3.02 (s, 1H), 3.24 – 3.36 (m, 1H), 3.35 (s, 1H), 3.46 (t, *J* = 6.6 Hz, 1H), 3.68 (dd, *J* = 6.5, 3.9 Hz, 2H), 3.72 (d, *J* = 7.4 Hz, 1H), 3.76 (s, 1H), 3.91 (t, *J* = 6.7 Hz, 1H), 4.07 – 4.13 (m, 1H), 4.12 (d, *J* = 8.1 Hz, 1H), 4.33 (d, *J* = 12.5 Hz, 1H), 4.37 (d, *J* = 2.5 Hz, 2H), 4.42 (d, *J* = 5.3 Hz, 1H), 4.48 (d, *J* = 12.7 Hz, 1H), 4.54 (d, *J* = 10.2 Hz, 1H), 4.69 (d, *J* = 4.7 Hz, 1H), 4.83 (d, *J* = 7.9 Hz, 1H), 5.19 (s, 1H), 5.28 (dd, *J* = 9.9, 8.1 Hz, 1H), 5.41 (dd, *J* = 10.4, 3.3 Hz, 1H), 5.61 (t, *J* = 9.5 Hz, 1H), 5.70 – 5.80 (m, 2H), 6.96 – 7.68 (m, 31H), 7.71 – 8.14 (m, 14H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 61.0, 61.9, 64.6, 67.4, 69.9, 70.9, 71.2, 71.3, 71.6, 72.3, 72.5, 72.8, 73.8, 74.9, 75.0, 75.7, 76.2, 99.7, 100.2, 101.0, 127.7, 127.7, 127.8, 128.2, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.4, 128.5,



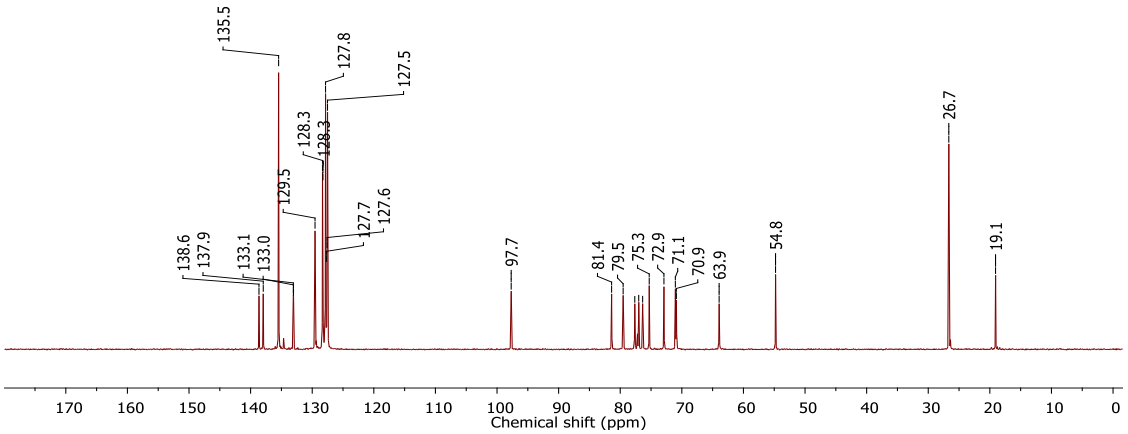
128.5, 128.6, 128.6, 128.6, 128.6, 128.6, 128.6, 128.6, 128.6, 128.6, 128.7, 128.8, 129.3, 129.3, 129.4, 129.5, 129.5, 129.5, 129.5, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.7, 129.7, 129.8, 129.9, 129.9, 129.9, 133.1, 133.2, 133.3, 133.4, 133.5, 133.5, 133.6, 137.6, 137.9, 164.7, 165.0, 165.2, 165.3, 165.4, 165.5, 165.7; HRMS (MALDI-TOF): m/z calcd for $[C_{81}H_{70}O_{22}+Na]^+$: 1417.4256; Found, 1417.4251.

1A.6 – Spectral Charts

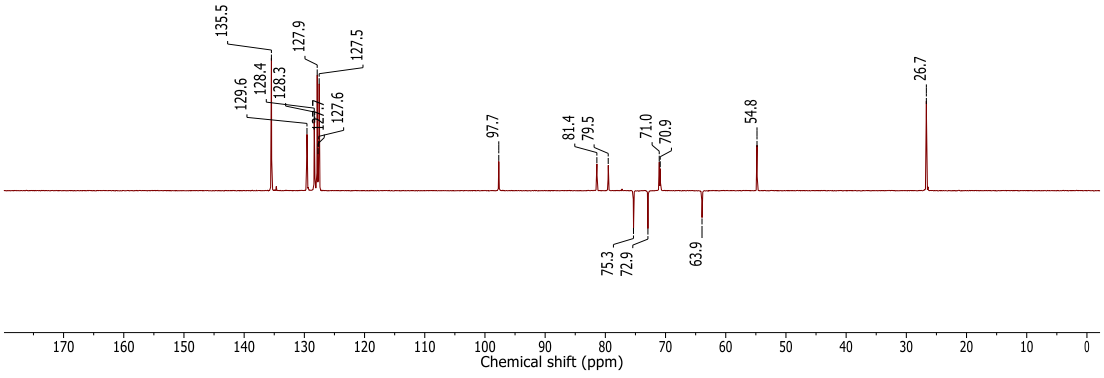
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **22i**



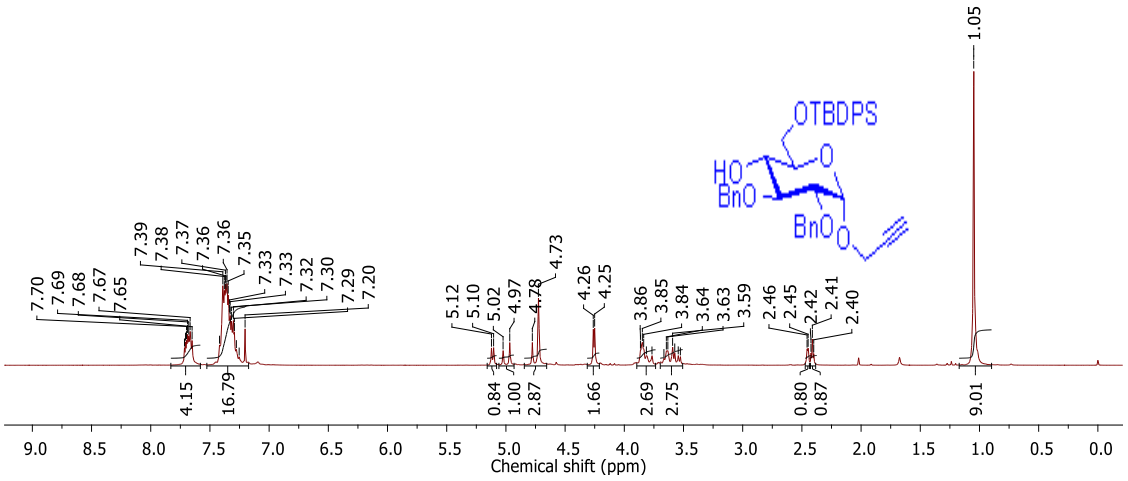
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **22i**



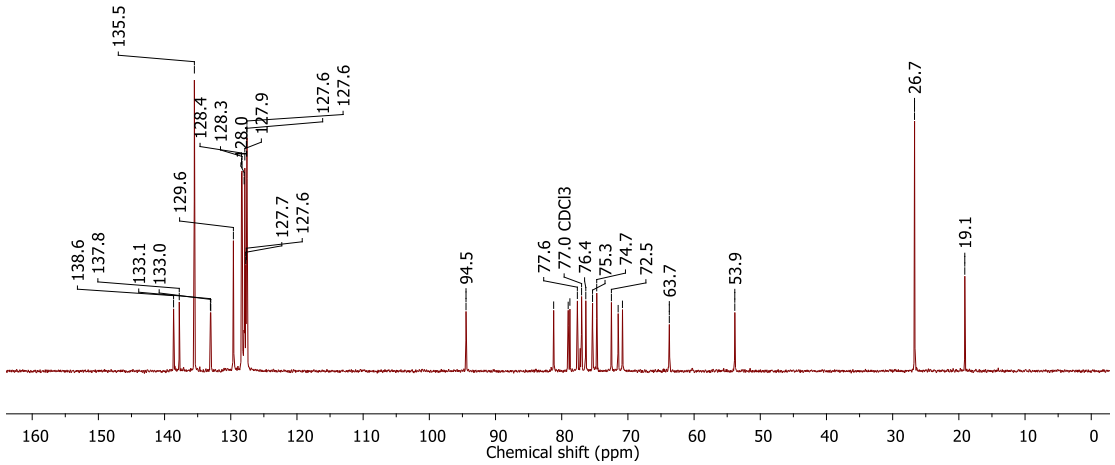
DEPT Spectrum (50.32 MHz, $CDCl_3$) of Compound **22i**



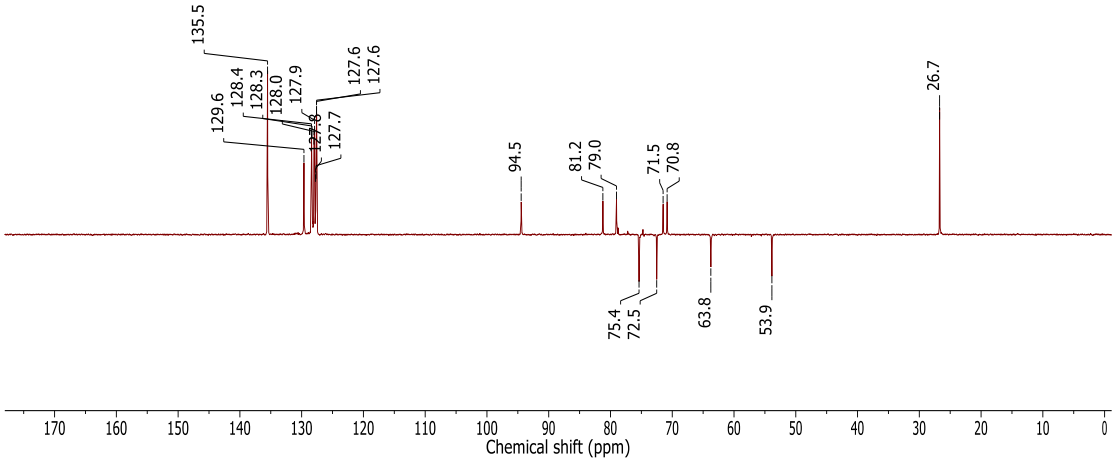
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **18h**



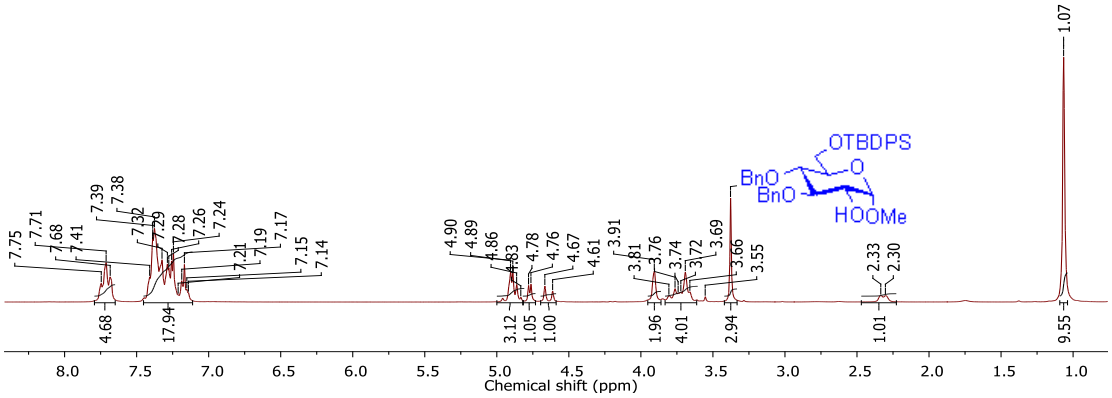
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **18h**



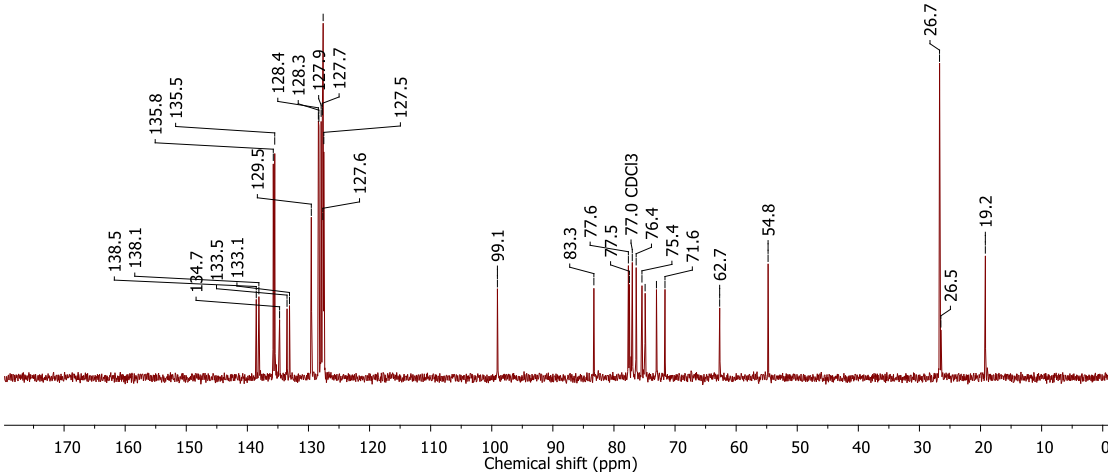
DEPT Spectrum (50.32 MHz, $CDCl_3$) of Compound **18h**



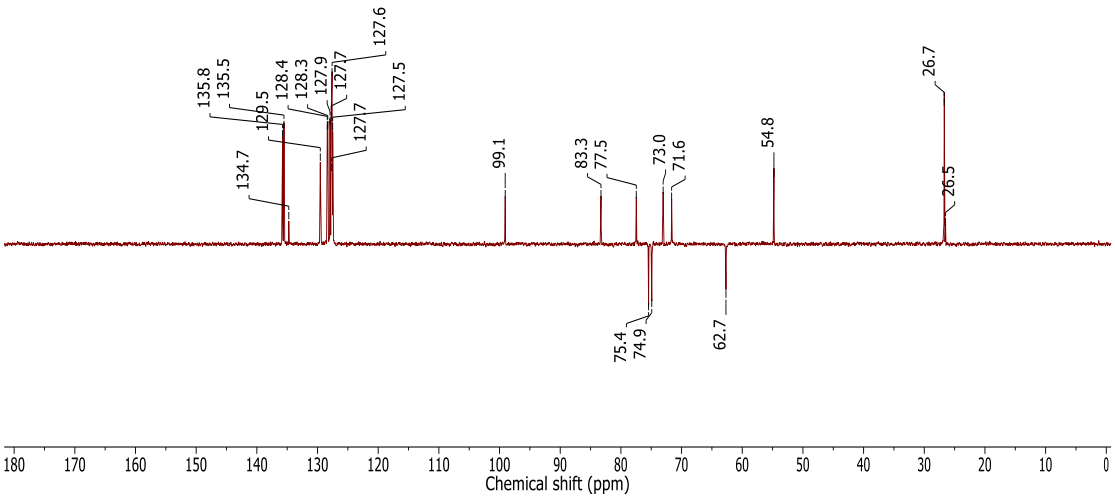
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **22m**



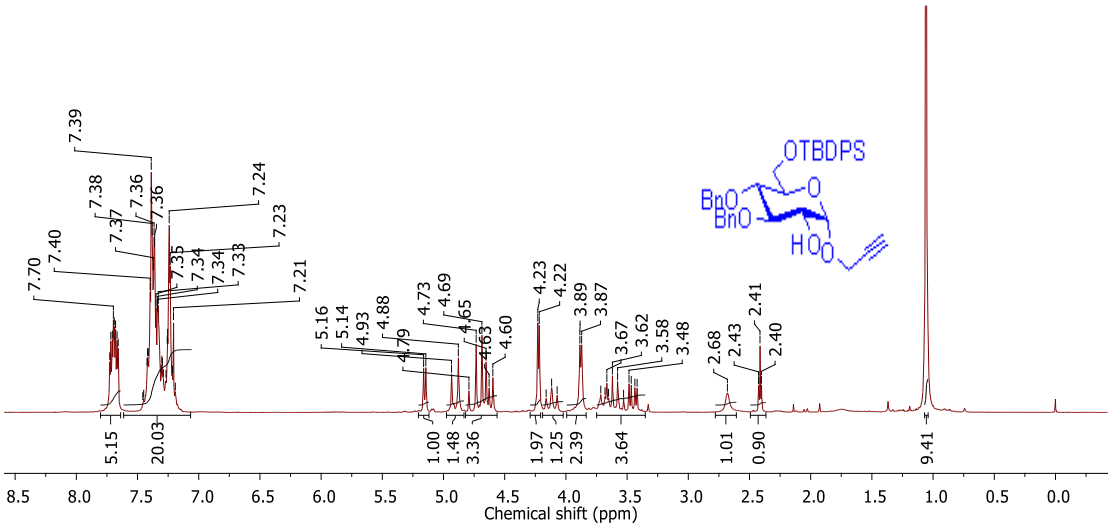
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **22m**



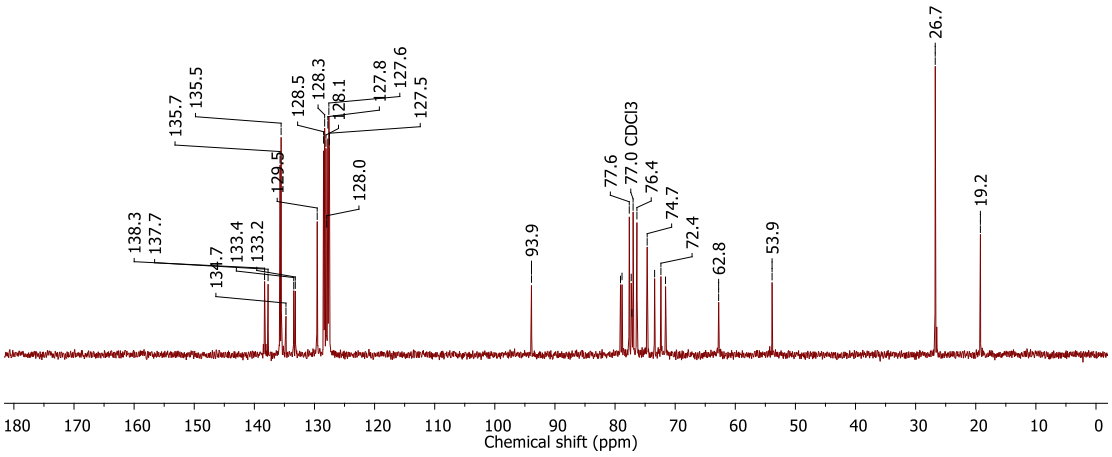
DEPT Spectrum (50.32 MHz, $CDCl_3$) of Compound **22m**



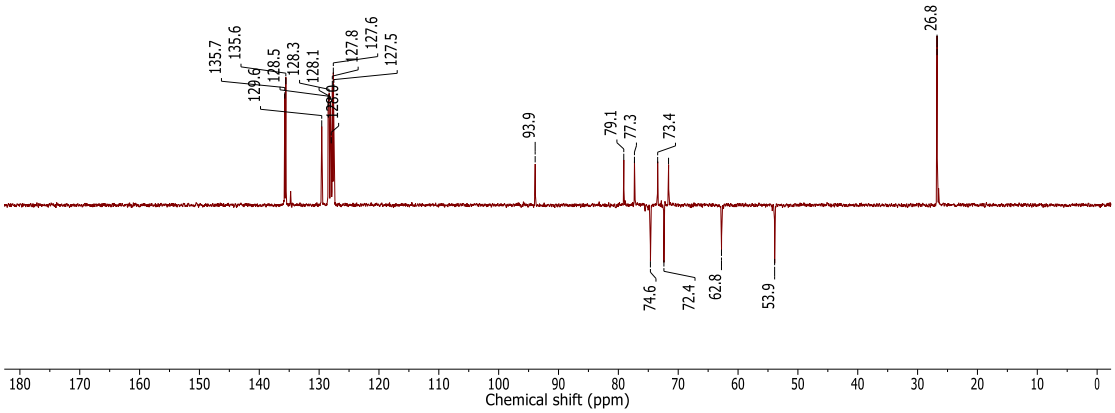
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **18l**



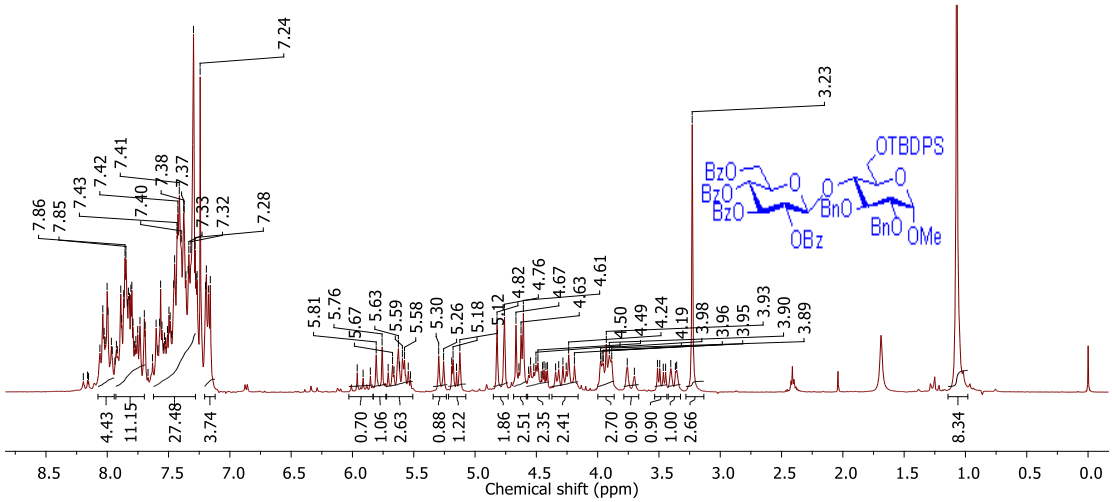
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **18l**



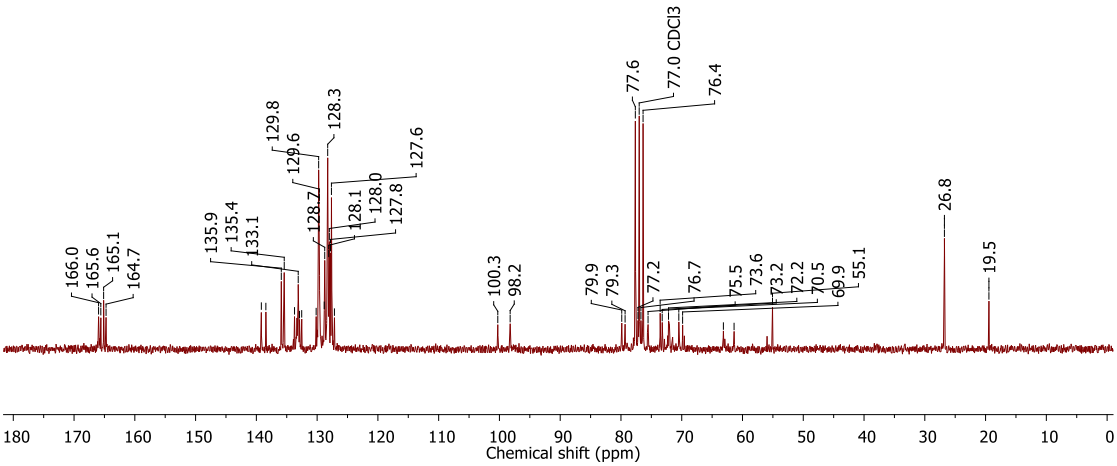
DEPT Spectrum (50.32 MHz, $CDCl_3$) of Compound **18l**



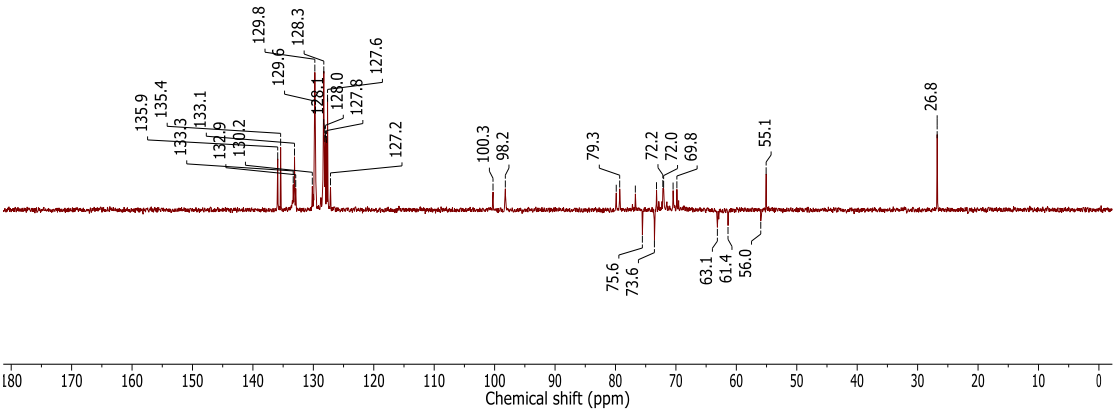
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **50b**



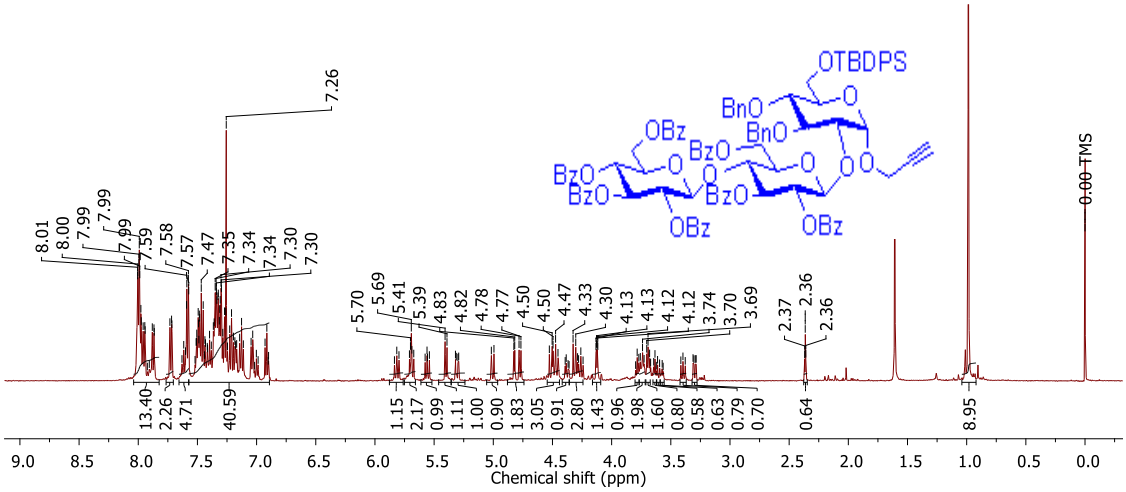
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **50b**



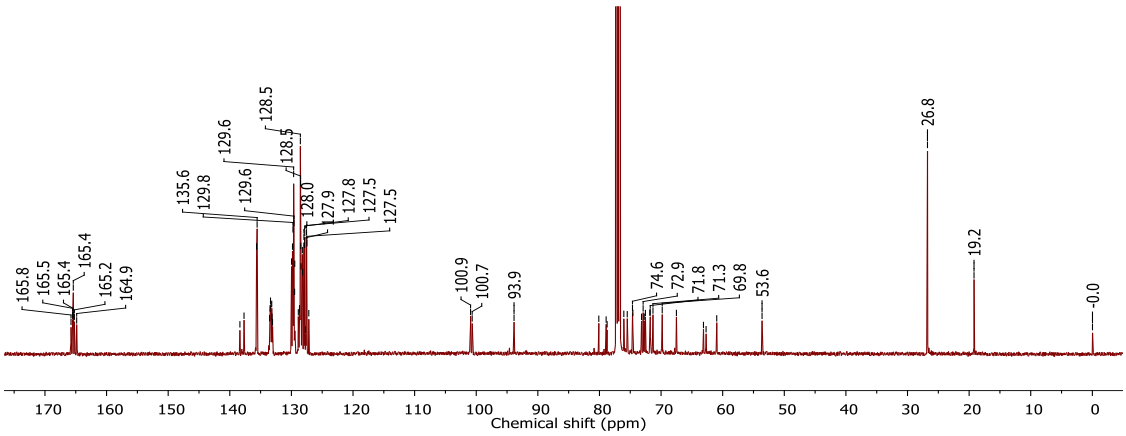
DEPT Spectrum (50.32 MHz, $CDCl_3$) of Compound **50b**



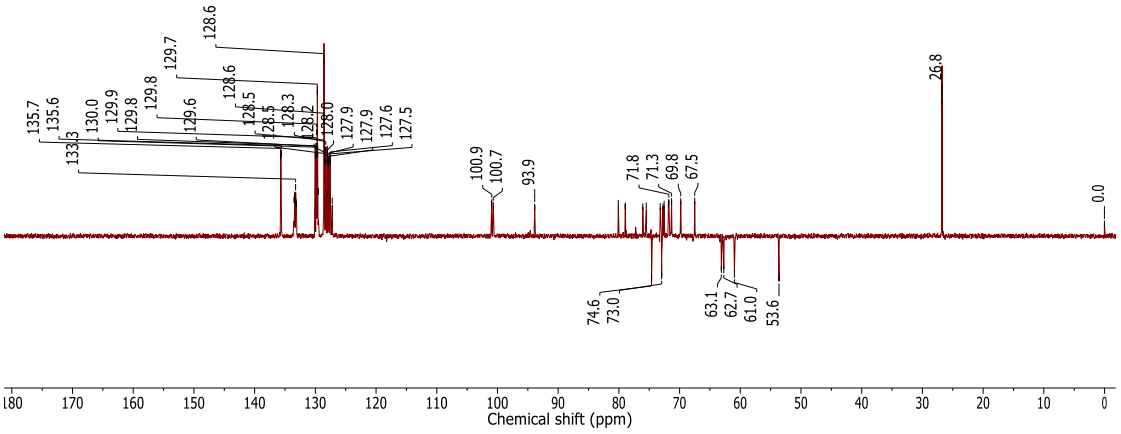
^{1}H NMR Spectrum (500.13 MHz, $CDCl_3$) of Compound **50h**



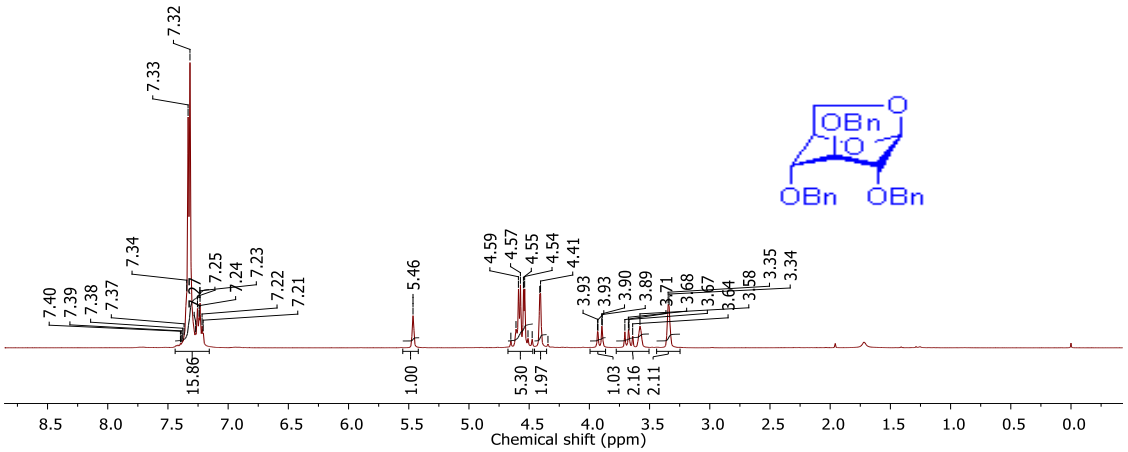
^{13}C NMR Spectrum (125.76 MHz, $CDCl_3$) of Compound **50h**



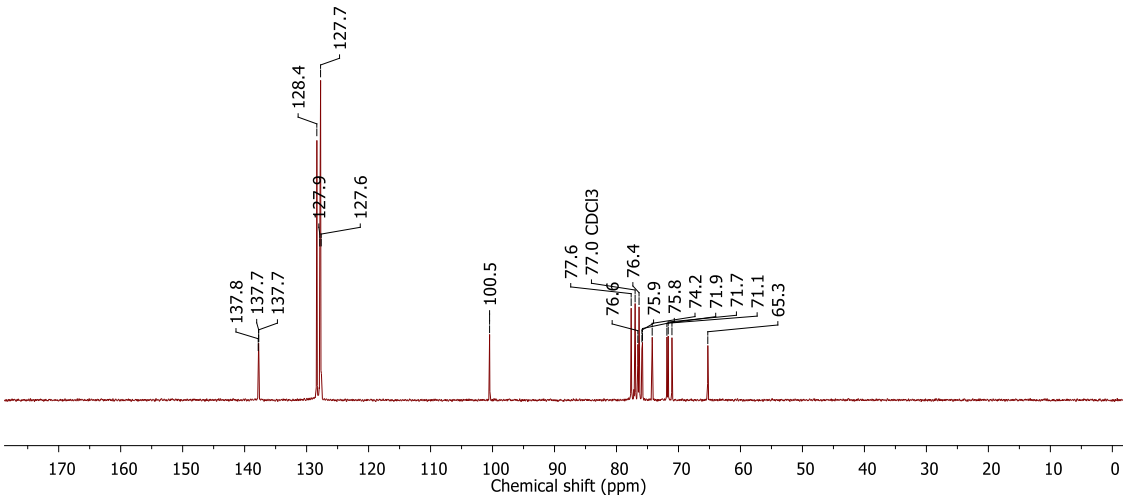
DEPT Spectrum (125.76 MHz, $CDCl_3$) of Compound **50h**



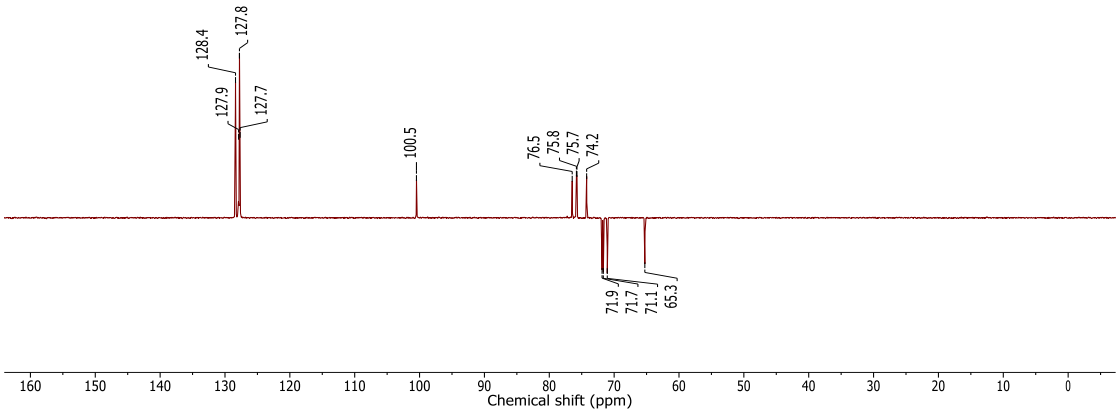
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **37b**



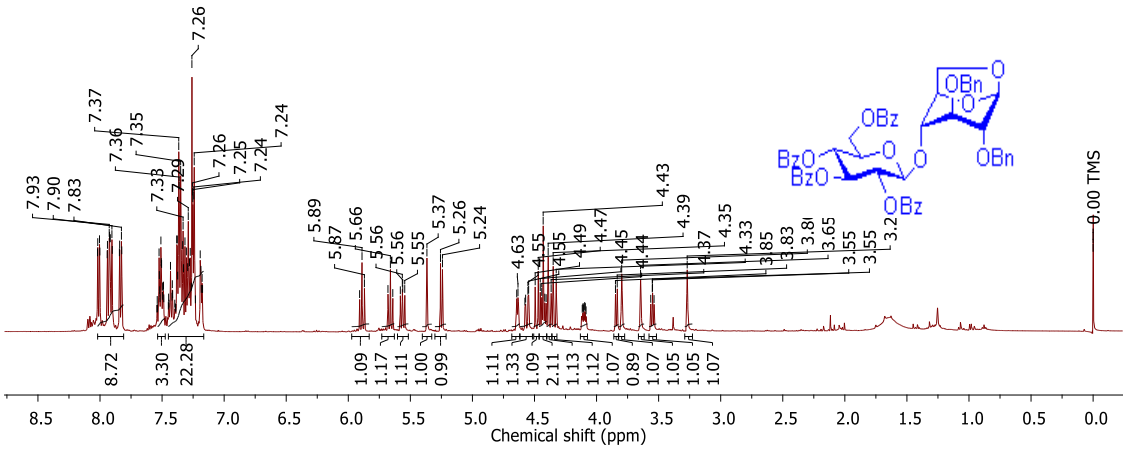
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **37b**



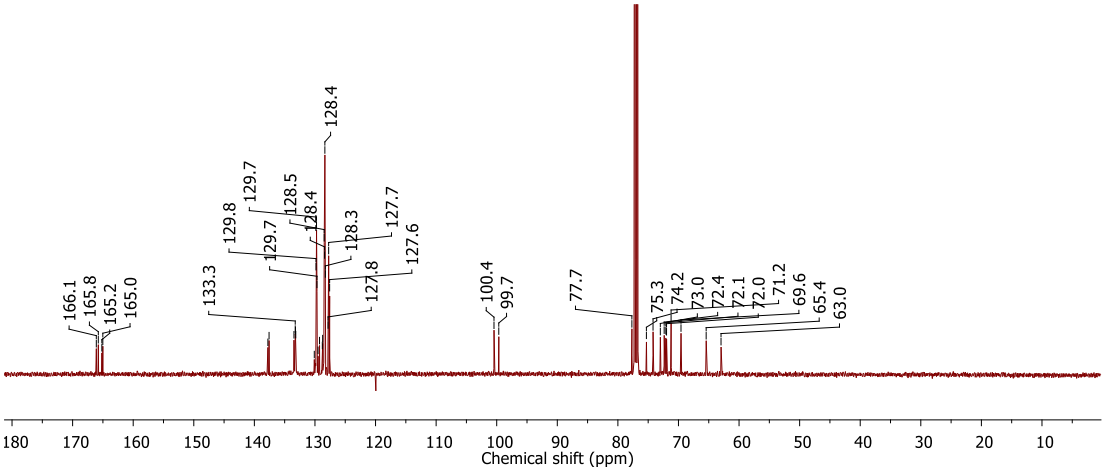
DEPT Spectrum (50.32 MHz, $CDCl_3$) of Compound **37b**



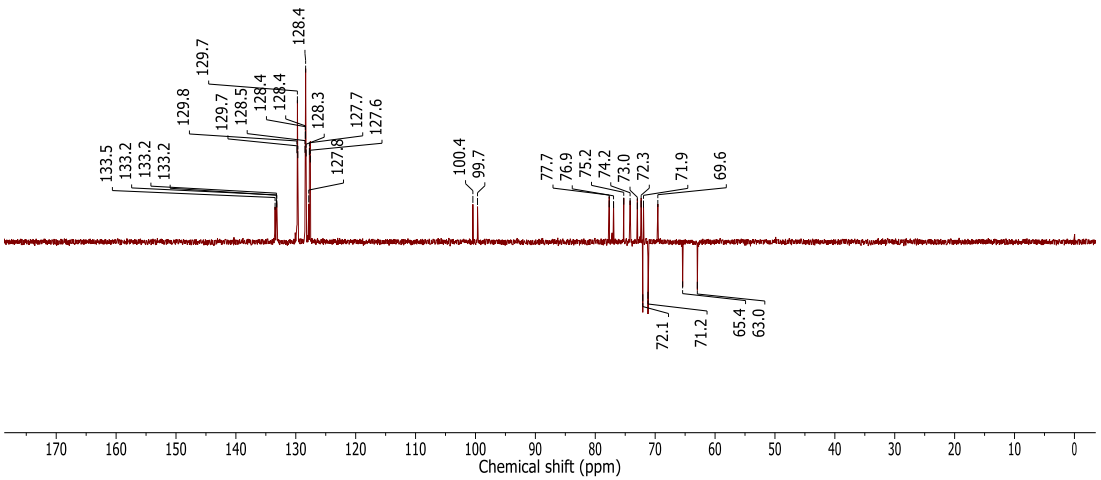
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **37d**



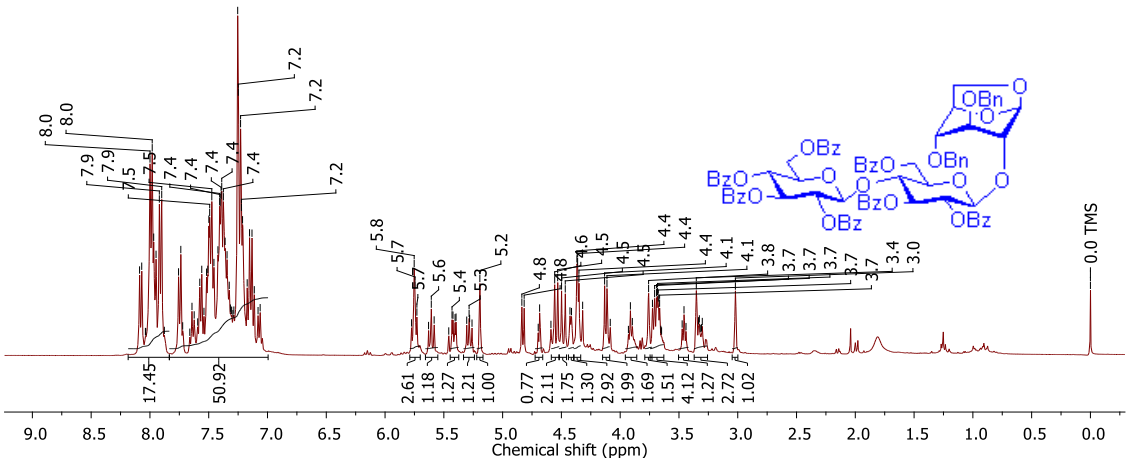
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **37d**



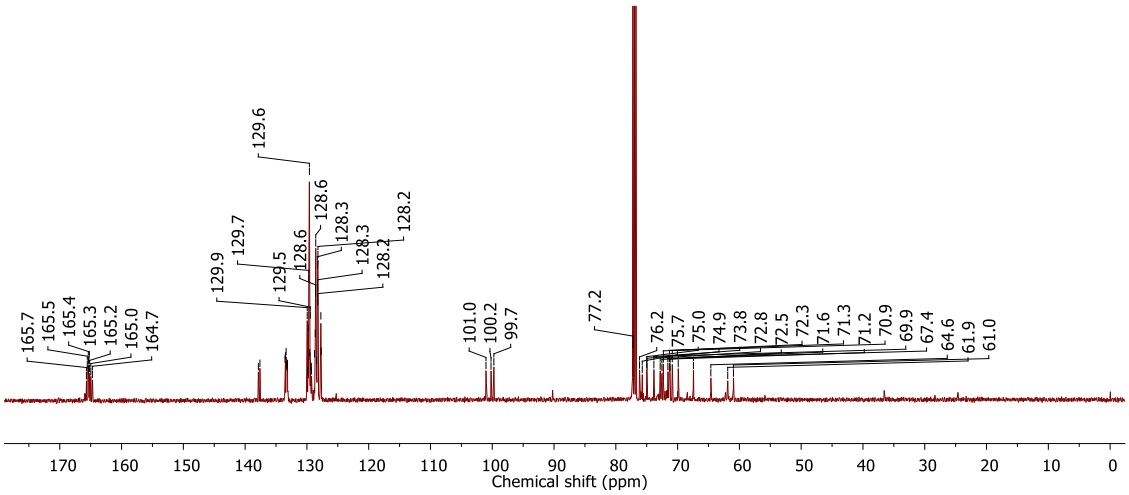
DEPT Spectrum (50.32 MHz, $CDCl_3$) of Compound **37d**



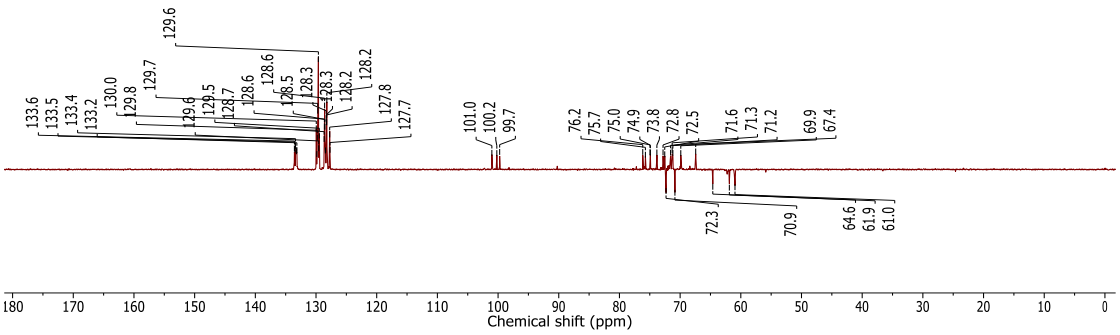
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **37h**



^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **37h**



DEPT Spectrum (50.32 MHz, $CDCl_3$) of Compound **37h**



Details of experimental procedures, characterization data and spectral charts for some of the compounds in this endeavour are also given in the supporting information of *Tetrahedron Lett.*, **2010**, *51*, 5912-5914.

1A.7 – References

1. (a) Peat, S. *Adv. Carbohydr. Chem*., **1946**, *2*, 37-77; (b) Williams, N. R. *Adv. Carbohydr. Chem. Biochem.,* **1971**, *25*, 109-179; (c) Černý, M. *Adv. Carbohydr. Chem. Biochem.,* **2003**, *58*, 121-198.
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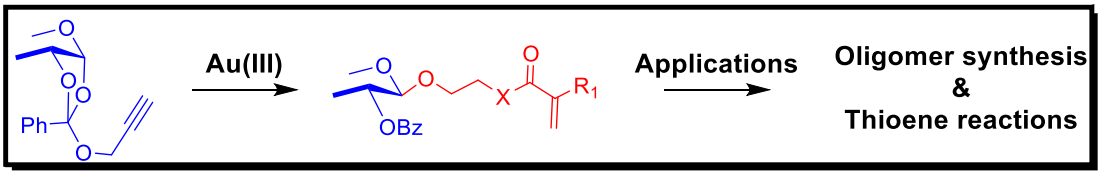
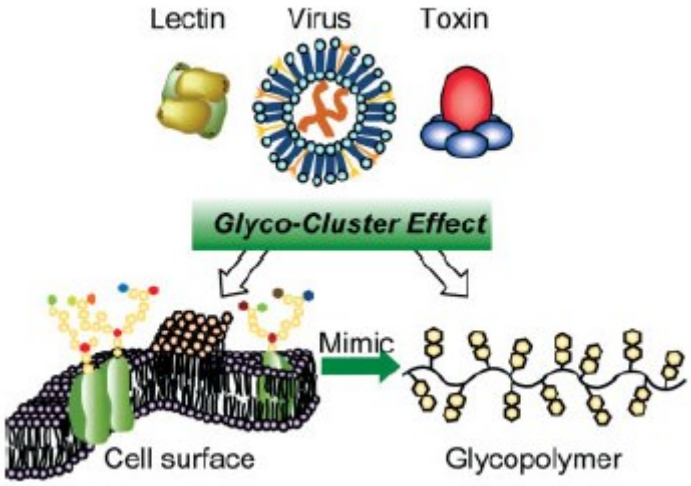
Section B: Synthesis of Glycoacrylates/acrylamides and Their Applications



1B.1 – Introduction

The understanding of biological role that carbohydrates play has considerably increased over the last 30-40 years after the identification of myriad of biological processes such as inflammation, cell-cell contacts, signal transmission, drug delivery, and fertilisation.[1] Lack of knowledge could be attributed to the complexity of glycoconjugates which makes them much more difficult to study compared to nucleic acids and proteins. Glycoconjugates participation in numerous biological processes is mediated through protein-saccharide interactions.[1] The protein-saccharide interactions are weak but are amplified by the multivalent effect of clustered saccharides and such an effect as called as "glyco-cluster effect" (**Figure 1B.1**).[2]

Figure 1B.1: Systematic representation of glycopolymer and its interaction

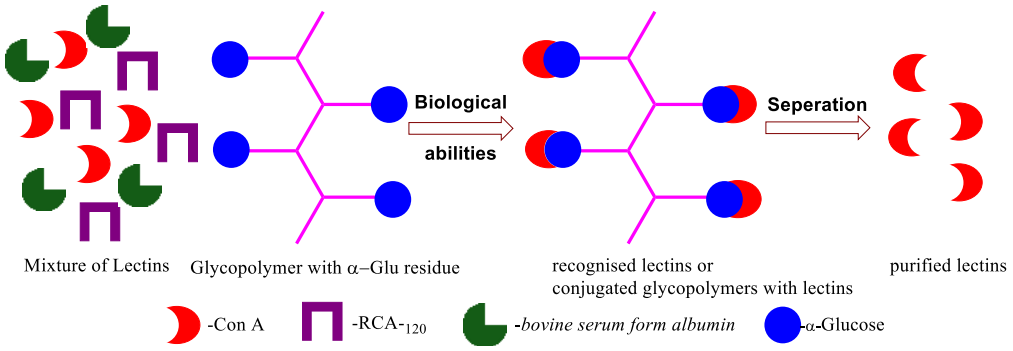


For example, natural glycolipid on the cell surfaces forms a densely packed saccharide domain such as raft[3a] and caveolae[3b], and interacts with protein effectively. Similarly some synthetic glycoclusters/glycopolymers[3c,d,e] have been reported to strengthen the signal as compared to monosaccharide due to the dendritic effect. Generally, in these processes, synthetic as well as natural glycopolymers with pendant saccharides have received more attention by synthetic glycochemists. Glycopolymers exhibit large multivalent effect of densely packed saccharides with polymer backbone and are applicable for biomaterials.[3f,g] In this regard, glycopolymers have been investigated in diverse applications such as macromolecular drug as well as drug delivery system,[4] bio-catalytic and bio-sensitive hydrogels,[5] lectins recognition,[6] matrices for controlled cell culture,[7] stationary phases for chromatography,[8] surface modifiers.[9]

1B.1.1 – Biological abilities of glycopolymer and application in separation[6,7, 8, 9]

Glycopolymers strongly interact with lectins by the multivalent effect and are measured by using fluorescent-labelled lectins. For example, the α-D-glucose containing glycopolymers show strong recognition abilities of concanavain A (α-man*p* and α-glu*p* recognition lectin). Several lectins are present on the cell surface such as Con A, *Ricinus communis agglutinin* 120 (RCA120) and *bovine serum form albumin* (protein without recognition ability). The α-glucose containing glycopolymer specifically recognises only Con A from rest of the lectins on cell surface. The binding constant of α-glucose containing glycopolymer with Con A is 10 times more than that of monomeric α-glucose. After the recognition of the lectin Con A which can be easily separated from the other lectins using proper separation techniques (**Figure 1B.2**).

Figure 1B.2: Cartoon representation of biological abilities and separation



Not only cell adhesions are related to the protein-saccharide interactions but also saccharides have affinities with protein toxins, bacterial and viral pathogens. The interaction between hepatocyte and β-gal *via* asialoglycoprotein receptor is an example of cell adhesion and *N*-acetyl neuraminic acid interaction with influenza viruses *via* hemagglutinin and neuraminidase.

1B.1.2 – Drug delivery system using glycopolymer[4]

As discussed earlier, carbohydrates/glycopolymers have been hailed as vital molecules in the human body and responsible for various biological functions. The last few decades, glycopolymer technology is opening up a myriad of new chances for disease therapy.[4e] For example; chemotherapy is the treatment of cancer and hence is not site specific. To improve the location and finding ability of drugs to avoid

unwanted damage during chemotherapy, glycopolymer based or glycopolymer surrounded drugs are used to locate certain lectins which are present on the malignant cells.[4a,b]

In another example, asialoglycoprotein receptors (ASGP-R) on the surface of hepatocytes have been proposed as target permitting organ-specific therapy for various diseases, including viral, parasitic and malignant disorders.[4c,d]

1B.1.3 – Self-assembling properties of glycopolymer[10]

The glycopolymers with hydrophobic unit as well as hydrophilic unit show amphiphilic properties which facilitate them to have self-assembling properties. Glycopolymers can form nano- and micro- structures based on its amphiphilicity. For example, the gold, glass and silicon like substrate were hydrophobized and immersed in the aqueous solution of glycopolymer to generate ultrathin-layer of about 10 Å of gold. In this, only hydrophobic unit was selectively adsorbed on the hydrophobic part of glycopolymer. Further this can be selectively applied to get micro-fabrication of saccharides.

1B.1.4 – Synthesis of glycopolymers[11,12,13]

Glycopolymers can be synthesized mainly in two ways:

1B.1.4.1 – Polymerization of glycomonomers

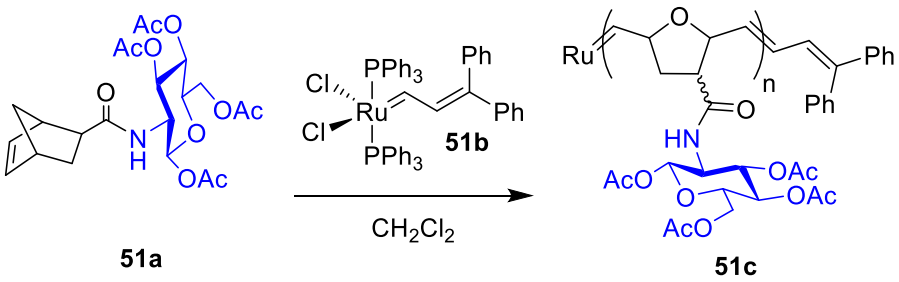
1B.1.4.2 – Post-polymerization grafting of saccharides

1B.1.4.1 – Polymerization of glycomonomers [11,12]

1B.1.4.1.1 – Ring opening metathesis polymerization (ROMP)[11]

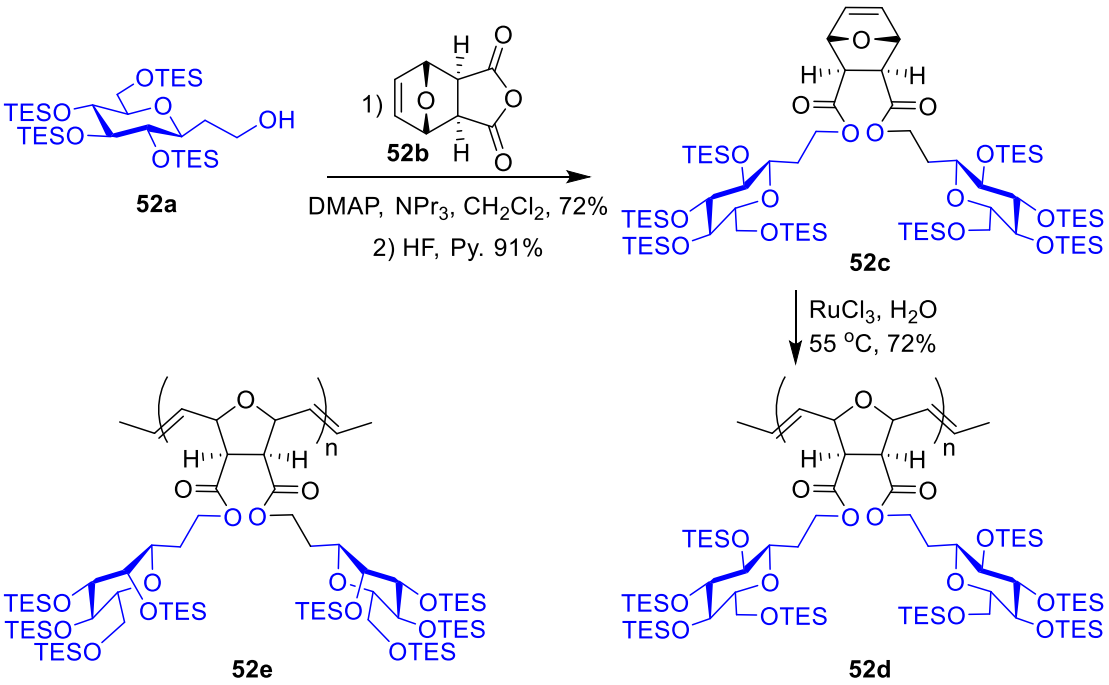
ROMP firstly coined by Robert Grubbs with strained cyclic olefins **51a** to produce stereoregular and monodisperse glycopolymers[11a] **51c** and co-polymers (**Scheme 1B.1**).

Scheme 1B.1: Synthesis of glycopolymer by ROMP



Following the work of Grubbs, several glycochemists used this methodology to make metathesis products in sugar analogues. For example, Kiessling *et al.*[11b] used ROMP strategy to make glycopolymers using ruthenium catalysts. The monomer **52c** prepared from fully silyl protected *C*-glycoside **52a** (2- hydroxy ethyl) and anhydride **52b.** Monomer **52c** further underwent metathesis reaction with ruthenium chloride in water to give glycopolymer **52d** (**Scheme 1B.2**). The lectin binding ability of resultant multivalent glycopolymers was tested with Con A. To assess the activity of multivalent glycopolymer **52d (**or **52e)** vs. divalent **52c** and monovalent **52a** to inhibit erythrocyte agglutination by Con A was studied to find the concentration of glucose moieties in solution required for each substrate. A 2-fold dilution but its glycopolymer prevented erythrocyte agglutination at a glucose residue concentration at least 2000-fold lower than that required of the monomeric methyl α-D-glucopyranoside and 7-oxanorbornene **52c.**

Scheme 1B.2: Synthesis of glycopolymer by ROMP



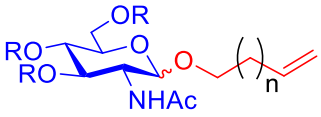
1B.1.4.1.2 – Controlled radical polymerization (CRP)[12]

ROMP polymerizations are highly sensitive to monomer functionality and impurities. In ROMP, monomer is required with full or partially protection and stringent control over the polymerization conditions. It also necessitates the post

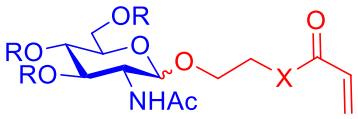
polymerization removal of the residual heavy metal catalyst for further biological applications.

1B.1.4.1.2.1 – Stable free radical polymerization (SFRP)

SFRP is a useful technique for the synthesis of linear and branched polymers with a reactive end group on each polymeric chain. Nitroxide mediated polymerization[12a] (NMP) for the synthesis of glycopolymer demands all hydroxyl groups in glycomonomers to be fully protected. Chaikof *et al.*[12b] used cyanoxyl-mediated radical polymerization (CMRP) as a controlled radical polymerization to produce several with or without end-functionalised biomimetic glycopolymers from alkenyl (**53a** and **53b**), acryloyl (**54a**), and acrylamidyl (**55a**) glycomonomers at ambient temperature.



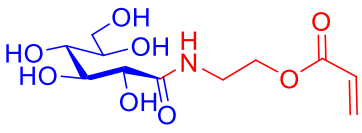
53a, n=0
53b, n=2



54a, X=O
55a, X=NH

1B.1.4.1.2.2 – Atom transfer radical polymerization (ATRP)

ATRP is based on the formation of C-C bond by atom transfer radical addition and needs reversible activation of an inactive species and a catalytic amount of transition metal halides.



56a

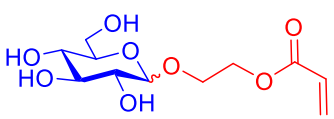
56b

Narain and Armes successfully applied this methodology for the synthesis of protected glycopolymers from fully protected glycomonomers (**56a**, **56b**) at ambient temperature.[12c]

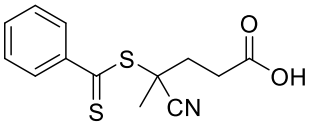
1B.1.4.1.2.3 – Reversible addition-fragmentation chain transfer polymerization (RAFT)

RAFT is an advantageous CRP technique that is widely used for the synthesis of glycopolymers owing to its tolerance to a wide range of reaction conditions and functionalities on glycomonomers. Lowe *et al.*[12d] first showed that glucosyl methacrylate (**54a**) can be polymerized under basic aqueous conditions with (4-

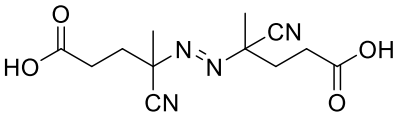
cyanopentanoic acid)-4-dithiobenzoate (CPADB, **57a**) as the chain transfer agent (CTA) and 4,4'-azobis(4-cyanopentanoic acid) (ACPA, **57b**) as the radical initiator. Polymerizations proceeded under controlled manner, displaying *pseudo* first order kinetics and the PDI remained below 1.07 throughout the polymerization.



54b



57a

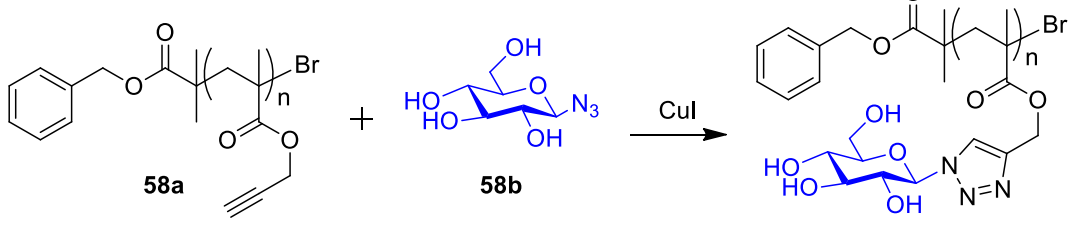


57b

1B.1.4.2 – Post-polymerization grafting of saccharides[13]

Nature produces peptides first and then attaches sugar residue to form glycopeptides in a post translational manner. Post-polymerization glycosidation methods are useful to reduce the complex reactions and purification procedures which are often associated with the synthesis of glycomonomers. Synthetic glycochemists mostly accept the method earlier described (see **1B.1.4.1**) for the syntheses of glycopolymers because of functionalised monomers can get converted into functionalised glycopolymers. But sometimes complete functionalization is not necessary in the resultant glycopolymers then in those cases, this method is most suitable for the synthesis of glycopolymers. For example, click reaction: The idea of click reaction was first disclosed by Sharpless and co-workers in 2001.[13a] The click reaction or Huisgen dipolar cycloaddition[13b] between terminal alkyne and azide in the presence of Cu(I) catalyst generates the quantitative yield of stable triazole ring (**Scheme 1B.3**). Pioneering from this work, Haddleton and co-workers synthesized well-defined glycopolymers (**58c**) containing galactosyl, mannosyl chain functionality from the corresponding alkyne polymer (**58a**) and protected or unprotected sugar azides (**58b**).[13c]

Scheme 1B.3: Synthesis of glycopolymer by post-polymerization glycosidation

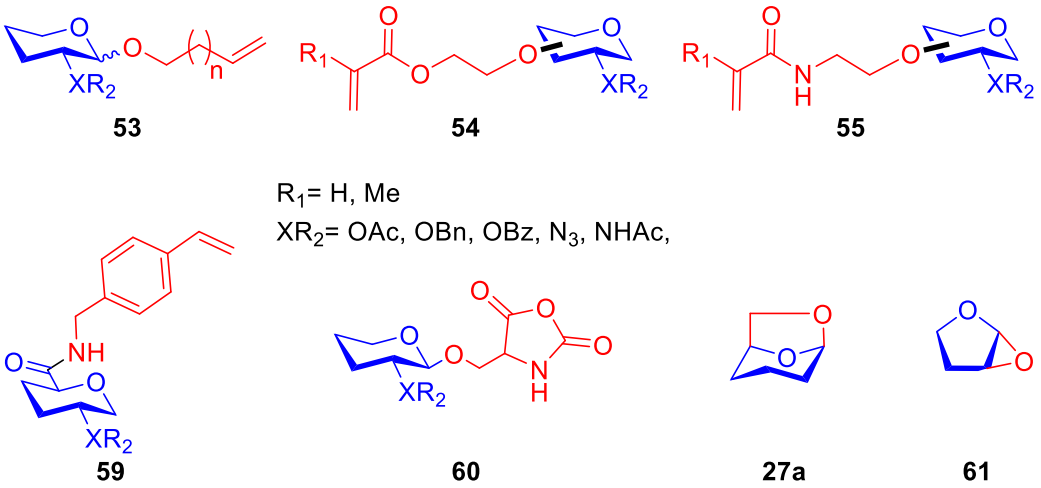


Polymerisation from glycomonomers is more advantageous to form stereoregular glycopolymers with good periodicity whereas, post-polymer grafting may result into the uncapped functionalities thereby regular periodicity can be envisaged easily.

1B.1.5 – Introduction to glycomonomers:[11, 12, 14]

Glycomonomers are the sugar residues that are attached to polymerizable functional group and it acts as precursor of random glycopolymers, neo-glycopeptides/proteins and as well as for the synthesis of natural product analogues.

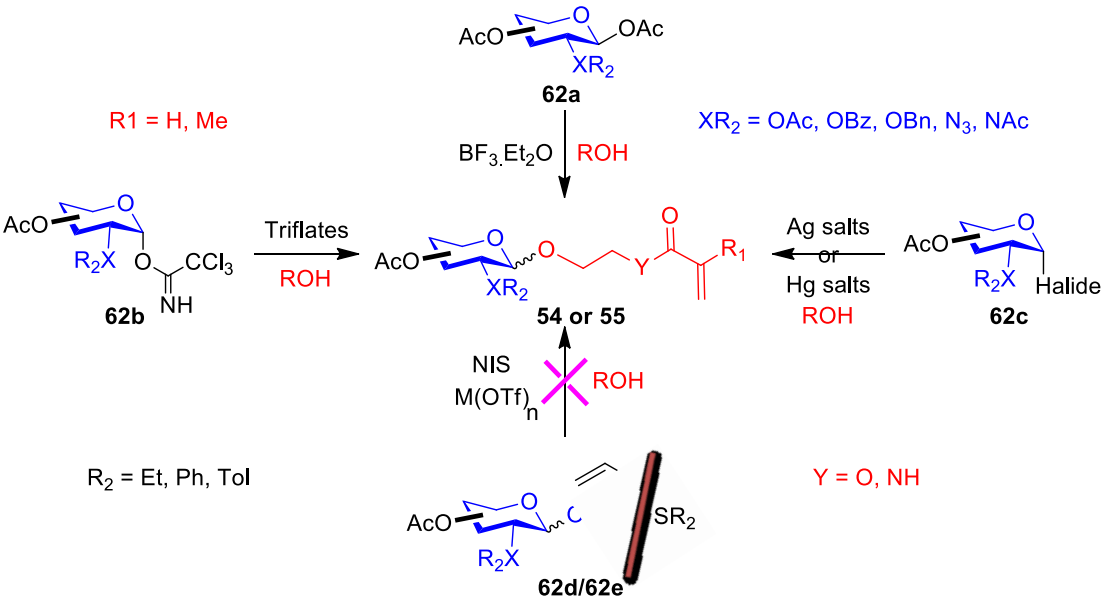
Figure 1B.3: Different glycomonomers



Some of the polymerizable functional groups are vinyl, styrene, acrylate/acrylamide, *N*-carboxyanhydrides (NCA), allyl, etc. Glycomonomers such as (2-hydroxyethyl) metha/acryloxy sugar (**54**), (2-hydroxyethyl) metha/acrylamidoxy sugar (**55**), vinyl sugar (**53**), styrene sugar (**59**), NCA sugar (**60**) [14a], anhydro sugar (**27a** and **61**),[14b] are some of the widely used monomers to obtain glycopolymers (**Figure 1B.3**). General methods are used for the synthesis of glycomonomers resulting in α,β–mixture of glycosides from glycosyl halide, trichloroacetimidate, per-*O*-acetylated sugars using $BF_3.Et_2O$ as a reagent (**Scheme 1B.4**). Isolation of glycomonomers from these methods [per-*O*-acetyl glycoside (**62a**), glycosyl halide (**62c**)] is quite cumbersome because of the tedious acid-base work-up, removal of side products, anomerization, column purification, etc. Trichloroacetimidate (**62b**) is a good option for the synthesis of these kinds of glycomonomers but synthesis and storage of trichloroacetimidate is quite difficult because of its instability. From the second generation methods, *n*-pentenyl glycosides (**62d**) or thio-glycosides (**62e**) are not

useful for the synthesis above mentioned glycomonomers as NIS used for the activation of *n*-pentenyl group will react with the olefin in acrylate (**54**)/acrylamide (**55**)/vinyl resulting into a mixture of products.

Scheme 1B.4: Synthesis of glycomonomers by various glycosidation



Propargyl 1,2-*O*-orthoesters as a glycosyl donor in the presence of gold tribromide at ambient temperature are the better option for the synthesis of glycomonomers with minimal side products (**Scheme 1B.4**).[15]

1B.2 – Present work

Glycopolymers are studied for a variety of applications such as drug delivery agents, hydrogels, extracellular matrices for controlled cell culture, supports for chromatography, and sometimes as multivalent biological probes. In addition, the multivalent display of pendant glycans is understood to be beneficial in mimicking natural cell surface oligosaccharides. Nature uses glycolipids and glycoproteins effectively in cell signalling, cell–cell differentiation, and communication.[1] This happens as a result of very specific interactions that takes place between the glycans of the glycoproteins and corresponding receptors at the cell surface. Isolation of naturally occurring glycopolymers from the natural sources is difficult as they exist in the micro-heterogeneous forms. To investigate the basic roles of carbohydrate moieties in glycoconjugates interactions on cell surface, simple model polymers with excellent solubility in aqueous medium needs to be synthesized from polymerizable glycomonomers.[4,6,7,8,9]

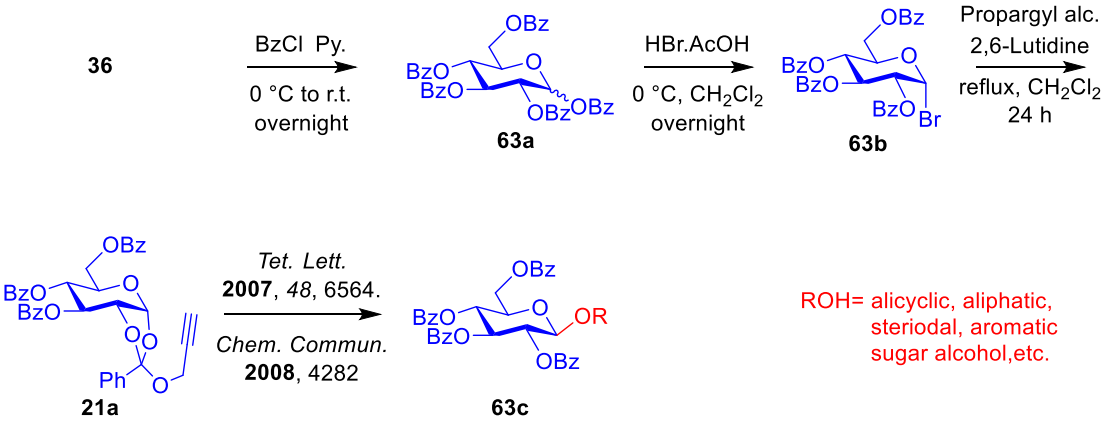
1B.2.1 – Synthesis of glycomonomers

The most commonly used glycomonomer for such polymerization reactions are acryloyl and acrylamido glycosides bearing a linker of various lengths. The resulting glycopolymers formed, such as polyacrylamide glycoside, could be non-toxic and water soluble. Further, the degree of incorporation of the oligosaccharide can be varied by copolymerization with another acrylamide monomer. Similarly, neoglycoproteins can be synthesized from glyco *N*-carboxyanhydrides which in turn can be obtained from amino acid glycoconjugates.

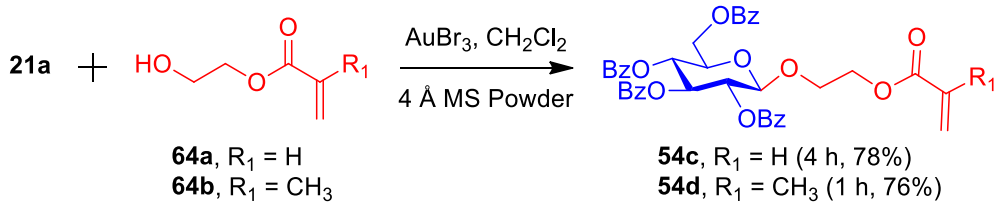
Recently identified glucosyl propargyl 1,2-*O*-orthoester[15] (**21a**) (**Scheme 1B.5**) was treated with commercially available 2-hydroxyethyl acrylate (**64a**) in the presence of catalytic amount of gold(III) bromide in CH_2Cl_2/4 Å MS powder at room temperature for 8 h to give corresponding 1,2-*trans* glucosyl acrylate (**54c**) (**Scheme 1B.6**). In the ^{1}H NMR spectrum of **54c**, characteristic anomeric (*H*-1) resonances were observed as doublet (J = 7.8 Hz) at δ 4.92 ppm for β-D-glycopyranoside. Terminal olefinic methylene protons appeared at δ 6.20 ppm as a doublet of doublet (J = 17.1, 1.7 Hz, 1H) and olefinic methine proton at δ 5.57 ppm as a mulitplet. Sugar *H*-2, *H*-3, *H*-4 protons were observed between δ 5.62 and δ 5.96 ppm. Diastereotopic

H-6 protons were identified at δ 4.49 (dd, *J* = 12.2, 5.1 Hz) and δ 4.65 (dd, *J* = 12.2, 3.2 Hz) ppm.

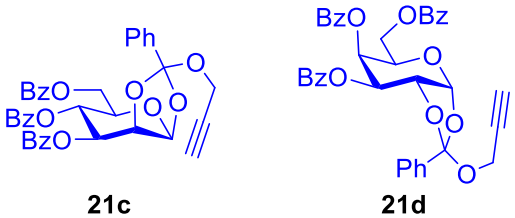
Scheme 1B.5: Synthesis of glycoconjugates using propargyl 1,2-*O*-orthoester and Au (III) salts[15b]



Scheme 1B.6: Synthesis of glycoacrylate/methacrylates using propargyl 1,2-*O*-orthoester[16]



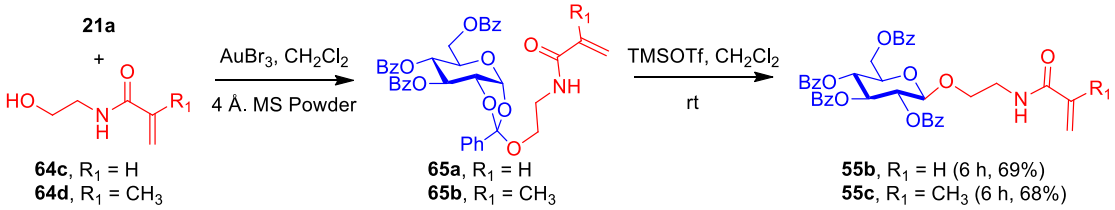
In the ^{13}C NMR spectrum of **54c**, resonances at δ 101.1 ppm were noticed for *C*-1 with 1,2-*trans* geometry or β–configuration. The carbohydrate *C*-2, *C*-3, *C*-4, *C*-5 carbons appeared at δ 72.7, 71.6, 72.3 and 69.6 ppm. The five carbonyl peaks presented in ester region were identified between δ 165.0-166.1 ppm which confirmed the presence of five ester groups in compound **54c**. Resonances at δ 127.7 ppm indicated the presence of olefin methine group in compound **54c**. From DEPT spectrum, it was confirmed that there were four methylene resonances observed at δ 63.0, 67.5, and 130.9 ppm. Four quaternary carbons presented at 128.8, 128.8, 129.2 and 129.5 ppm proved the presence of four mono-substituted phenyl groups.



A similar reaction was carried out between orthoester **21a** and 2-hydroxy ethyl methacrylate (**64b**) to obtain respective glucosyl methacrylate (**54d**). The ^{1}H NMR spectrum of **54d** was similar to that of **54c** with only difference that additional resonances around δ 1.75 ppm for the methyl group are noticed and resonances due to olefinic methine in the olefinic region was disappeared. The olefinic methylene was found as a multiplet between δ 5.86 to 5.96 ppm. Similarly, in the ^{13}C NMR spectrum, additional resonances at δ 18.0 ppm (for –CH_3) and disappearance of quaternary carbon at 135.7 ppm in DEPT spectrum confirmed the formation of **54d**.

Encouraged with this, we explored the utility of the current protocol to the other glycosyl 1,2-orthoesters, such as mannosyl (**21c**), galactosyl (**21d**) and lactosyl (**21b**) 1,2-orthoesters to obtain corresponding glycoacrylates/methacrylates **54e** to **54j** from glycosyl acceptors **64a** and **64b** in good yields.

Scheme 1B.7: Synthesis of glycoacrylamide/methacrylamide using propargyl 1,2-*O*-orthoester[16]

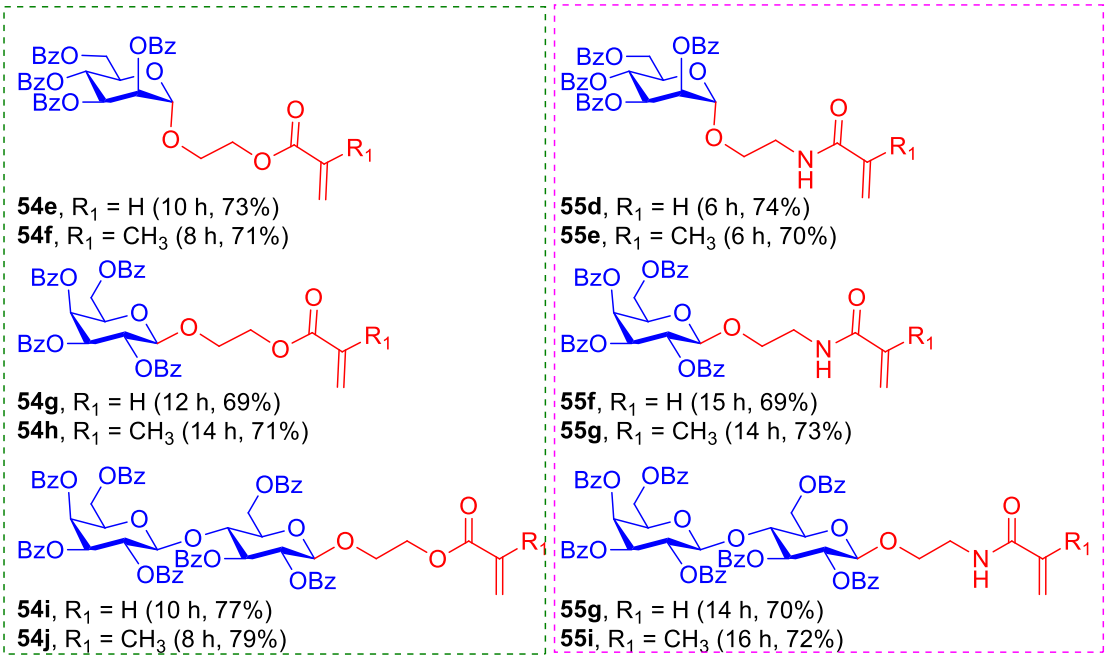


Oligomers can be obtained from these glycomonomers (acrylates/methacrylates) easily by free radical oligomerization and further saponification of all benzoyl groups would be necessary in order to get the polyhydroxy oligomers. However, orthogonal deprotection of benzoates in the presence of acrylate esters could pose a difficult task. Thus, hydroxylethyl acrylamides were considered to be superior as they would enable preparation of glycopolymers with acrylamide backbone and later facilitate saponification of benzoates to achieve water soluble polyacrylamides.

Accordingly, per-*O*-benzoylated glucose 1,2-orthoester (**21a**) was allowed to react with commercially available 2-hydroxyethyl acrylamide **64c** and 2-hydroxyethyl methacrylamide **64d** in the presence of 7 mol % of $AuBr_3$. Surprisingly, a single product identified as per-*O*-benzoylated hydroxyethyl acrylamide 1,2-orthoester (**65a**) was isolated which was subsequently converted to the required glucose-hydroxyethyl

acrylamide conjugate **55b** by reacting with TMSOTf in CH_2Cl_2 at room temperature in 69% over two steps (**Scheme 1B.7**). In the ^{1}H NMR spectrum of **65a**, the anomeric *H*-1 seemed to at δ 6.05 ppm (*J* = *6.0* Hz) which indicated the *H*-1 is in α-fashion. The multiplet obtained from three protons i.e. *H*-3, *H*-2 and olefinic –CH=CH_2 in acrylamide were observed between δ 5.99 to 6.28 ppm. Broad singlet was noticed at δ 5.74 ppm for amide group in compound **65a**. The doublet of doublet around δ 5.55 ppm pointed out the presence of –CH=CH_2. H-4 and H-5 exhibited triplet and multiplet around δ 4.78 ppm and 4.09 ppm respectively.

Table 1B.1: Different glycomonomers (glycoacrylate/acrylamide) using propargyl 1,2-*O*-orthoesters[16]



In the ^{13}C NMR spectrum, the anomeric carbon appeared at δ 97.5 ppm which confirmed α-configuration. Four carbonyls instead of five around δ 165.0 ppm and one quaternary carbon at δ 121.2 ppm (disappeared in DEPT spectrum) for 1,2-*O*-orthoester product were noticed. The rest of the carbons were found in carbohydrate region, aromatic and olefinic region. Subsequently, conversion from **65a** to **55b** was proved on the basis of NMR study. In the ^{1}H NMR spectrum of **55b**, resonances at δ 4.87 ppm observed as doublet with a coupling constant of 7.9 Hz specified that the anomeric proton was in β-orientation. Terminal olefinic =CH_2 of acrylamide showed the two doublet of doublets at δ 6.14 (*J* = 9.8, 7.9 Hz, 1H) ppm and δ 5.43 (*J* = 10.2,

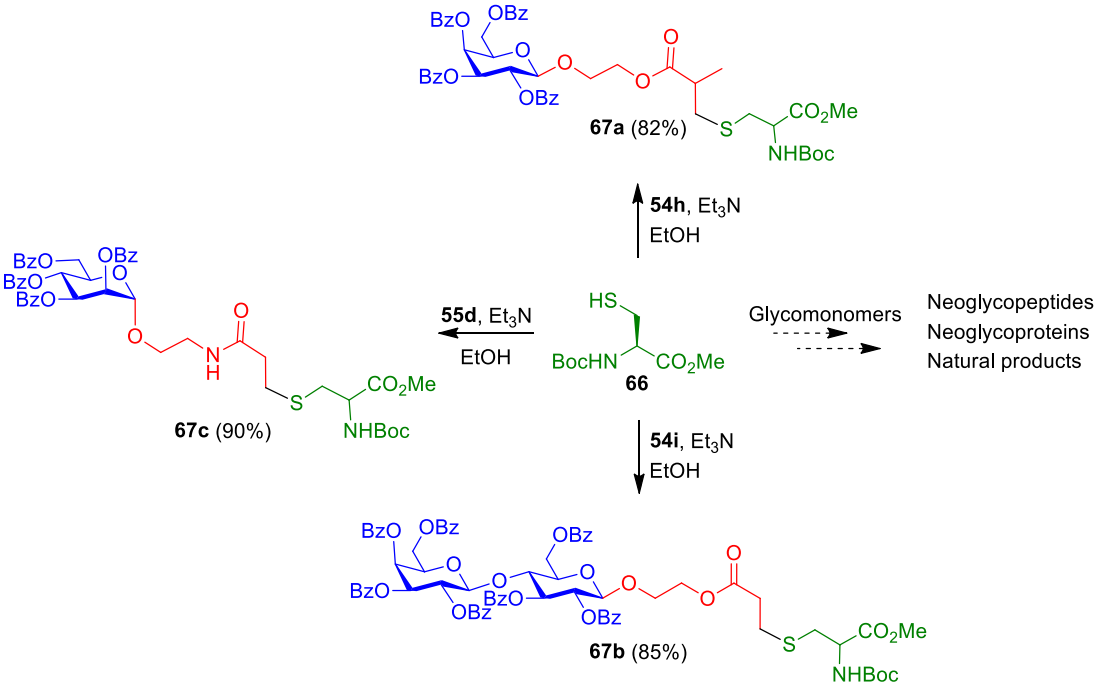
1.6 Hz, 1H) ppm due to its diastereotopic nature. Olefinic methine appeared as a doublet of doublet (J = 9.8, 7.9 Hz) at δ 5.53 ppm. Rest of the protons appeared as similar to that of **65a**. A similar attempt with the hydroxyethyl methacrylamide **64d** also gave first orthoester product **65b** which could then successfully be converted to the glucomethacrylamide **55c** with an overall yield of 68%.

The general applicability of this methodology has been gauged with the other orthoesters **21b**, **21d**, and **21b** to acquire corresponding acrylamides **55d** to **55i** in very good yields (**Table 1B.1**). A single step conversion of orthoester **21a** to **55b**, **55c** in the presence of TMSOTf was found to give only a small quantity of desired product (10%) and the major product was observed to be the propargyl 2,3,4,6-tetra-*O*-benzoyl β-D-glucopyanoside (70%) may be because of the strong Lewis and Brønsted acid character of TMSOTf.

1B.2.2 – 'Thio-ene' click reactions on glycomonomers

Glycomonomers with α,β-unsaturated double bond are well suited for the synthesis of thio-derivatives using free radical or thio-ene click reaction which are highly useful for the synthesis of neoglycoproteins, peptide, and natural products. Glycosides of acrylate/acrylamide (**54** and **55**) are excellent scaffolds for attaching cysteine or any other thiolate *per se*.

Scheme 1B.8: 'Thio-ene' clicks reaction on glycomonomers with cysteine-SH[16]

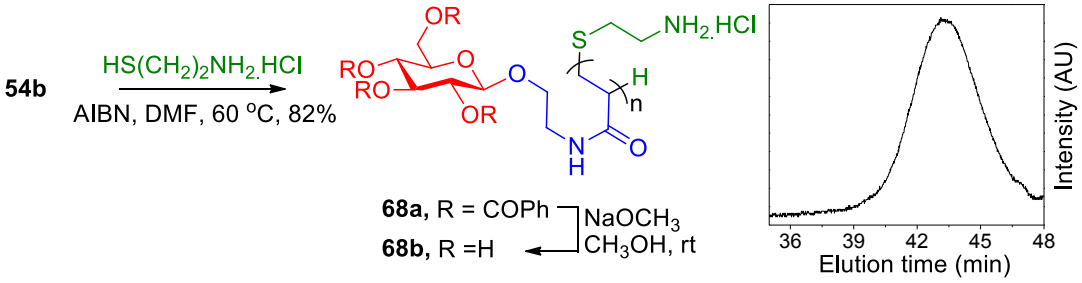


BocCys(SH)OMe (**66**) was considered as a model substrate for the 'thiol-ene click' reaction as cysteine residues are frequently noticed in proteins which would ensue to extend the current procedure to synthesize glycoproteins in future. For example, cysteine residue **66** smoothly reacted with acrylate (**54h** and **54i**) or acrylamide (**55d**) in the presence of Et_3N in EtOH at room temperature to give Michael addition products **67a**, **67b**, and **67c** respectively. Similarly, lactose derived acrylate **54i** also gave the corresponding 'thio-click' product in 85% yield whereas galactose-methacrylate **54h** resulted in the isolation of thiolate addition product as a 1:1 diastereomeric mixture at the newly generated chiral centre. The formation of compounds **67b** to **67c** was confirmed on the basis of NMR study. In the ^{1}H NMR spectrum of **67b**, olefinic resonances disappeared and two new singlets at δ 3.74 ppm for three protons and at δ 1.44 ppm for nine protons for *N*-Boc and methyl ester confirmed the assigned structure. Similarly, in the ^{13}C NMR spectrum, loss of two resonances approximately at δ 126.0 and 130.8 ppm confirmed the reduction of double bond in compound **54i**. Additional resonances observed in the carbonyl region at δ 171.4 ppm and in the carbamate region at δ 155.1 ppm confirmed the presence of methyl ester and carbamate in compound **67b**.

1B.2.3 – Oligomer synthesis (In collaboration with Dr. Sayam Sen Gupta and Dr. M. Kar, NCL, Pune)

With these monomers in hand, oligomerization was attempted with AIBN of per-*O*-benzoylated glucose acrylamide monomer **55b** using AIBN as an initiator and 2-aminoethanethiol hydrochloride as the Chain Terminating Agent (CTA) in DMF. The resulting oligomer **68a** was characterized by both NMR and GPC spectroscopic analysis.

Scheme 1B.9: Oligomerization of glycomonomer and GPC chromatogram[16]



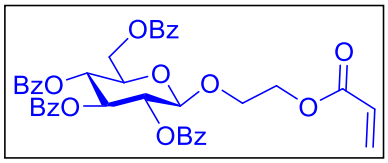
The ^{1}H spectrum of **68a** was found to be similar to that of monomer **54b** but the absence of resonances in the olefinic region and new resonances found in the aliphatic region between δ 2.00 to 3.50 ppm indicated the formation of oligomer (**68a**). From the ^{13}C and DEPT spectrum, no olefinic –CH and $–CH_2$ resonances in olefinic region were noticed. From the MALDI-TOF/spectrum, the M_n was determined to be 5600 Da and from both MALDI-TOF/GPC the PDI was found to be 1.08. Since, 2-aminoethanethiol hydrochloride was used as the CTA, the polymer chains had an amino- end group which can be further modified using amine reactive compounds. Later per-*O*-benzoate groups of the resulting oligomer **68a** were removed under Zemplén debenzoylation conditions to afford the oligomer **68b** containing free hydroxyl groups of the carbohydrate. To be able to prove that the biological abilities of the glucose moieties is still active and not lost during the oligomerization process, the resulting glycopolymer **68b** was tested by using Con-A lectin interaction with β-D-glucose moieties.[11b,c] It is observed that, the rate of agglutination of the polymer **68b** with Con-A was monitored at 490 nm. The turbidity assay measures the changes in absorbance at a wavelength of 490 nm using UV-Vis spectroscopy. The binding of the multivalent polymer to Con-A forms a gel network with concomitant increase in size that causes significant scattering, thus leading to a turbid solution. The turbidity increases with conjugation time and reached plateaus after three min. Similar, multivalent characteristics showed by the polyvalent glycopolymers were also observed earlier by Kiessling and co-workers.[11d]

1B.3 – Summary

In summary, a new high yielding synthetic methodology was identified for the facile synthesis of sugar-acrylate/acrylamide from stable glycosyl 1,2-*O*-orthoesters in the presence of gold(III) bromide. Thiolate Michael addition onto sugar-acrylate/acrylamide was also studied that would serve as an alternate synthesis for amino acid glycoconjugates as well as a strategy for the glycosylation of cysteine containing proteins. Furthermore, the sugar monomers were explored for the synthesis of oligomers and its activity through lectin-binding with Con-A. In future, the resultant glycopolymer and thio-ene adduct will be evaluated for biological activities.

1B.4 – Experimental and characterization data

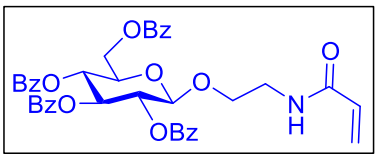
(2-Acryloyloxyethyl)-2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (**54c**): To a solution of glycosyl donor **21a** (0.635 g, 1.0 mmol), glycosyl acceptor **64a** (0.143 g, 1.1 mmol) and 4 Å molecular sieves powder (100 mg) in anhydrous CH_2Cl_2 (10 mL) was added $AuBr_3$ (0.031 g, 0.07 mmol) under argon atmosphere at room temperature. The reaction mixture was stirred at room temperature for the specified time and the completion of the reaction was judged by TLC analysis. The reaction mixture was filtered through celite and the filtrate was concentrated *in vacuo* to obtain a crude residue which was purified by conventional silica gel column chromatography using ethyl acetate-petroleum ether as mobile phase.



$[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) +18.8°; IR (cm^{-1}, $CHCl_3$): 3064, 2974, 1732, 1602, 1248, 1215, 1105, 758; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.77 – 3.94 (m, 1H), 4.03 – 4.33 (m, 4H), 4.49 (dd, *J* = 12.2, 5.1 Hz, 1H), 4.65 (dd, *J* = 12.2, 3.2 Hz, 1H), 4.92 (d, *J* = 7.8 Hz, 1H), 5.48 – 5.67 (m, 2H), 5.72 (d, *J* = 10.9 Hz, 1H), 5.83 (t, *J* = 7.0 Hz, 1H), 5.88 – 5.98 (m, 1H), 6.20 (dd, *J* = 17.1, 1.7 Hz, 1H), 6.98 – 7.68 (m, 12H), 7.68 – 8.31 (m, 8H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 63.0, 63.0, 67.5, 69.6, 71.6, 72.3, 72.7, 101.1, 127.7, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.7, 128.7, 129.2, 129.5, 129.7, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 129.8, 130.9, 133.1, 133.2, 133.2, 133.4, 165.0, 165.1, 165.7, 165.8, 166.1; HRMS (MALDI-TOF): *m/z* calcd for $[C_{39}H_{34}O_{12}+Na]^+$: 717.1948, Found: 717.1981.

Similar procedure was applied for the synthesis of glycomonomers (**54d** to **54j**).

(2-Acrylamidoethyl)-2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (**55b**): To a solution of glycosyl donor **21a** (0.635 g, 1 mmol), glycosyl acceptor **64c** (0.142 g 1.1 mmol) and 4 Å molecular sieves powder (100 mg) in anhydrous CH_2Cl_2 (10 mL) was added $AuBr_3$ (0.031 g, 0.07 mmol) under argon atmosphere at room temperature. The reaction mixture was stirred at room temperature for the specified time and the completion of the reaction was judged by TLC analysis. The reaction mixture was filtered through a bed of celite and the filtrate was concentrated *in vacuo* to obtain a crude residue which was purified by conventional silica gel column chromatography using ethyl acetate-petroleum ether as mobile phase to obtain

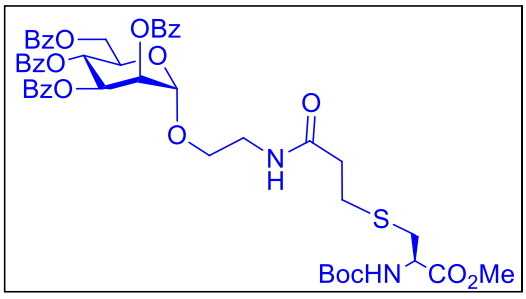


compound **65a**. Further, compound **65a** was redissolved in dry dichloromethane (10 mL) and trifluoromethanesulphonate (5 µL) was added and the reaction mixture was stirred for 5 min at room temperature and diluted with dichloromethane (10 mL) and sat. aq. solution of sodium bicarbonate (10 mL). The organic layer was separated and concentrated *in vacuo* to obtain a crude residue which was purified by conventional silica gel column chromatography using ethyl acetate-petroleum ether as mobile phase.

$[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.5) +29.1°; IR (cm^{-1}, $CHCl_3$): 3391, 3310, 3064, 2957, 1732, 1669, 1452, 1269, 1177, 1109, 709; ^1H NMR (200.13 MHz, $CDCl_3$): δ 3.31 – 3.72 (m, 2H), 3.77 (ddd, *J* = 10.2, 7.4, 3.2 Hz, 1H), 3.96 (ddd, *J* = 9.4, 5.5, 3.6 Hz, 1H), 4.19 (ddd, *J* = 9.6, 4.9, 3.0 Hz, 1H), 4.48 (dd, *J* = 12.3, 5.0 Hz, 1H), 4.71 (dd, *J* = 12.2, 2.9 Hz, 1H), 4.87 (d, *J* = 7.9 Hz, 1H), 5.43 (dd, *J* = 10.2, 1.6 Hz, 1H), 5.53 (dd, *J* = 9.8, 7.9 Hz, 1H), 5.71 (t, *J* = 9.7 Hz, 1H), 5.84 (d, *J* = 10.2 Hz, 1H), 5.94 (t, *J* = 9.7 Hz, 1H), 6.03 – 6.16 (m, 1H) , 6.14 (dd, *J* = 16.9, 1.5 Hz, 1H), 7.14 – 7.69 (m, 12H), 7.76 – 8.16 (m, 8H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 39.1, 62.7, 69.3, 69.3, 71.9, 72.4, 72.6, 101.4, 126.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.6, 128.6, 128.9, 129.4, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 130.4, 130.4, 133.2, 133.3, 133.5, 133.5, 165.1, 165.2, 165.5, 165.7, 166.1; HRMS (MALDI-TOF): *m/z* calcd for $[C_{39}H_{35}NO_{11}+Na]^+$: 716.2108, Found: 716.2194.

Similar procedure was applied for the synthesis of glycomonomers (**55c** to **55i**).

Procedure for the thiolate addition (**67c**): Acrylate monomer **54e** (0.200 g, 0.29 mmol) and cysteine derivative **66** (0.166 g, 0.72 mmol) were dissolved in EtOH (1 mL) and Et_3N (0.5 mL) was added under argon atmosphere at room temperature. The reaction mixture was stirred at room temperature for the specified time and the completion of the reaction was judged by the TLC analysis. The reaction mixture was concentrated *in vacuo* to obtain a crude residue which was purified by conventional silica gel column chromatography using ethyl acetate-petroleum ether as mobile phase to obtain thiolate addition product **67c** (0.21 g, 82%).



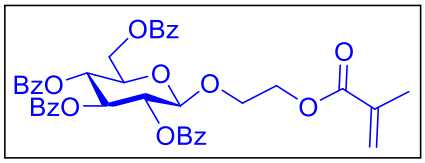
$[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +61.3°; IR (cm^{-1}, $CHCl_3$):3420, 3371, 3065, 2978, 1732, 1662, 1452, 1267, 1167, 1097, 756, 712; ^1H NMR (400.13 MHz, $CDCl_3$): δ 1.44 (s, 9H),

2.05 (s, 1H), 2.55 (t, *J* = 6.9 Hz, 2H), 2.89 (t, *J* = 7.0 Hz, 2H), 3.01 (d, *J* = 5.2 Hz, 2H), 3.53 (d, *J* = 5.4 Hz, 1H), 3.69 (d, *J* = 9.9 Hz, 1H), 3.72 (s, 3H), 3.94 (dd, *J* = 8.9, 4.7 Hz, 1H), 4.37 – 4.58 (m, 3H), 4.71 (dd, *J* = 11.9, 2.2 Hz, 1H), 5.14 (s, 1H), 5.54 (d, *J* = 7.7 Hz, 1H), 5.74 (s, 1H), 5.91 (dd, *J* = 10.1, 3.2 Hz, 1H), 6.11 (t, *J* = 10.0 Hz, 1H), 6.53 (s, 1H), 7.20 – 7.63 (m, 12H), 7.84 (d, *J* = 7.3 Hz, 2H), 7.90 – 8.12 (m, 6H); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 28.2, 28.2, 28.2, 28.4, 34.7, 36.5, 39.1, 52.5, 53.4, 62.8, 66.8, 67.7, 69.0, 70.0, 70.2, 80.1, 97.8, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.6, 128.6, 128.8, 128.8, 129.0, 129.6, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 133.1, 133.3, 133.5, 133.5, 155.2, 165.4, 165.4, 165.6, 166.1, 171.1, 171.5; HRMS (MALDI-TOF): *m/z* calcd for $[C_{48}H_{52}N_2O_{15}SN+Na]^+$: 951.2986, Found: 951.2981.

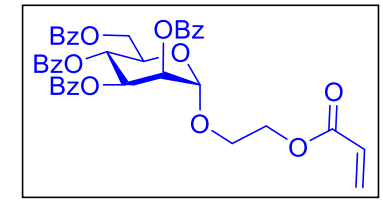
Similar procedure was applied for the synthesis of cysteine adduct of glycoacrylate/acrylamide (**67a**, and **67b**).

Procedure for the synthesis of oligomer (**68b**): The per-*O*-benzoylated monomer (**55b**) (400 mg, 641.3 µmol), 2-aminoethanethiol hydrochloride (3.64 mg, 32.06 µmol) and AIBN (4 % by weight of the monomer) were dissolved under N_2 in anhydrous DMF (0.4 mL) in a Schlenk tube with side arm, subjected to three freeze-pump-thaw cycles, cannulated into the polymerization flask and magnetically stirred at 60 ºC for 72 h. The reaction mixture was cooled, concentrated under diminished pressure and poured into a large excess of Et_2O (100 mL/g of oligomer). The oligomer **68a** was filtered and further purified through two dissolution (in tetrahydrofuran)/precipitation cycles (in Et_2O) until the disappearance of the residual monomers (**55b**) as monitored by TLC. The polymer **68a** was characterized by GPC in chloroform and by NMR spectral analysis. A very narrow molecular weight distribution (MWD) was obtained from Gel Permeation Chromatography (M_w/M_n = 1.08). Yield: 72%. Subsequently, oligomer **68a** was re-dissolved in 10 mL of anhydrous methanol and freshly prepared sodium methoxide (1 mL) was added to the reaction mixture and stirred for 4 h at room temperature. After 4 h the reaction mixture was quenched with Amberlite IR-120 resin, filtered and concentrated *in vacuo* to obtain the crude glycopolymer **68b**. Crude glycopolymer again dissolved in water (10 mL) and extracted with ethyl acetate. Aqueous layer was collected and lyophilized to obtain pure oligomer in good yield.

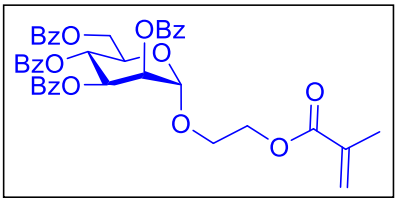
(2-Methacryloyloxyethyl)-2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (**54d**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) +27.8°; IR (cm^{-1}, $CHCl_3$): 3069, 2976, 1730, 1603, 1265, 1215, 1106, 769; ^1H NMR (200.32 MHz, $CDCl_3$): δ 1.51 – 2.08 (m, 3H), 3.89 (dd, *J* = 6.9, 4.0 Hz, 1H), 3.98 – 4.36 (m, 4H), 4.43 – 4.55 (m, 1H), 4.65 (dd, *J* = 12.2, 3.1 Hz, 1H), 4.92 (d, *J* = 7.8 Hz, 1H), 5.26 – 5.39 (m, 1H), 5.55 (dd, *J* = 9.7, 7.9 Hz, 1H), 5.69 (t, *J* = 9.7 Hz, 1H), 5.83 – 5.97 (m, 2H), 7.17 – 7.65 (m, 12H), 7.76 – 8.13 (m, 8H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 18.0, 63.0, 63.2, 67.4, 69.6, 71.6, 72.3, 72.8, 101.0, 125.8, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.7, 128.7, 129.1, 129.5, 129.7, 129.7, 129.7, 129.8, 129.8, 129.8, 129.8, 129.9, 133.2, 133.2, 133.3, 133.4, 135.6, 165.0, 165.2, 165.8, 166.1, 167.1; HRMS (MALDI-TOF): *m/z* calcd for $[C_{40}H_{36}O_{12}+Na]^+$: 731.2104, Found: 731.2171.



(2-Acryloyloxyethyl)-2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranoside (**54e**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.4) –52.5°; IR (cm^{-1}, $CHCl_3$): 3057, 2976, 1726, 1603, 1264, 1215, 1109, 771; ^1H NMR (200.13 MHz, $CDCl_3$): δ 3.80 – 4.16 (m, 2H), 4.40 – 4.57 (m, 4H), 4.62 – 4.77 (m, 1H), 5.17 (d, *J* = 1.8 Hz, 1H), 5.75 (dd, *J* = 3.2, 1.8 Hz, 1H), 5.88 (dd, *J* = 10.3, 1.6 Hz, 1H), 5.96 (dd, *J* = 10.1, 3.3 Hz, 1H), 6.14 (t, *J* = 10.0 Hz, 1H), 6.25 (d, *J* = 10.3 Hz, 1H), 6.50 (dd, *J* = 17.3, 1.6 Hz, 1H), 7.06 – 7.73 (m, 12H), 7.73 – 8.22 (m, 8H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 62.8, 63.0, 66.1, 66.8, 68.9, 69.9, 70.2, 97.6, 126.6, 128.0, 128.2, 128.2, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.9, 129.0, 129.2, 129.6, 129.6, 129.7, 129.7, 129.7, 129.8, 129.9, 131.4, 133.0, 133.1, 133.4, 133.4, 165.3, 165.4, 165.4, 165.9, 166.1; HRMS (MALDI-TOF): *m/z* calcd for $[C_{39}H_{34}O_{12}+Na]^+$: 717.1948, Found: 717.1938.

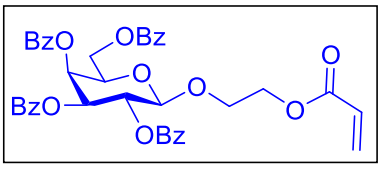


(2-Methacryloyloxyethyl)-2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranoside (**54f**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.3) –54.1°; IR (cm^{-1}, $CHCl_3$): 3064, 2976, 1728, 1603, 1265, 1215, 1109, 770; ^1H NMR (200.13 MHz, $CDCl_3$): δ 1.88 – 2.04 (m, 3H), 3.78 – 4.18 (m, 2H), 4.46 (dd, *J* = 9.6, 5.9 Hz, 4H), 4.61 – 4.75 (m, 1H), 5.17 (d, *J* = 1.8 Hz, 1H), 5.62 (quintet, *J* = 1.5 Hz, 1H), 5.73 (dd, *J* = 3.2, 1.8 Hz, 1H) , 5.93 (dd, *J* = 10.1, 3.3 Hz, 1H), 6.10 (t, *J* = 9.4 Hz, 1H), 6.15 – 6.26 (m, 1H), 6.96 – 7.73 (m, 12H), 7.73 – 8.20 (m, 8H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ

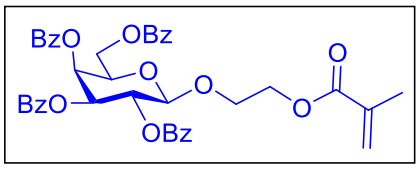


18.2, 62.6, 63.1, 65.9, 66.7, 68.8, 69.8, 70.1, 97.4, 126.0, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.4, 128.5, 128.5, 128.8, 128.9, 129.1, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.7, 129.7, 133.0, 133.1, 133.4, 133.4, 135.9, 165.2, 165.3, 165.3, 166.0, 167.0; HRMS (MALDI-TOF): *m/z* calcd for $[C_{40}H_{36}O_{12}+Na]^+$: 731.2104, Found: 731.2135.

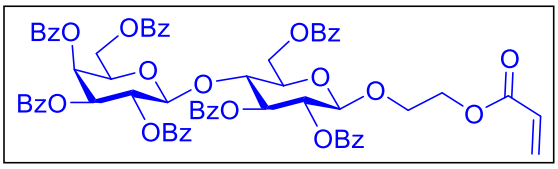
(2-Acryloyloxyethyl)-2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside (**54g**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +76.0°; IR (cm^{-1}, $CHCl_3$): 3072, 1726, 1603, 1267, 1111, 765; ^1H NMR (200.13 MHz, $CDCl_3$): δ 3.81 – 3.90 (m, 1H), 3.94 (dd, *J* = 6.5, 4.5 Hz, 1H), 4.19 (dq, *J* = 11.4, 4.6, 3.8 Hz, 1H), 4.25 – 4.35 (m, 2H), 4.37 – 4.51 (m, 2H), 4.70 (dd, *J* = 10.1, 5.4 Hz, 1H), 4.94 (d, *J* = 7.8 Hz, 1H), 5.58 (dd, *J* = 10.4, 1.7 Hz, 1H), 5.63 – 5.70 (m, 1H), 5.83 (d, *J* = 10.4 Hz, 1H), 6.04 (d, *J* = 3.3 Hz, 1H), 6.19 (dd, *J* = 17.1, 1.7 Hz, 1H), 7.12 – 7.71 (m, 12H), 7.74 – 8.16 (m, 8H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 61.9, 63.0, 67.5, 67.9, 69.4, 71.3, 71.5, 101.4, 127.5, 127.9, 128.2, 128.2, 128.2, 128.3, 128.4, 128.4, 128.5, 128.5, 128.6, 128.8, 129.1, 129.2, 129.6, 129.6, 129.6, 129.6, 129.9, 129.9, 130.8, 131.2, 133.1, 133.2, 133.2, 133.5, 165.1, 165.4, 165.4, 165.7, 165.9; HRMS (MALDI-TOF): m/z Calcd for $[C_{39}H_{34}O_{12}+Na]^+$: 717.1948; Found, 717.1883.



(2-methacryloyloxyethyl)-2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside (**54h**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +78.5°; IR (cm^{-1}, $CHCl_3$): 3065, 2976, 1728, 1602, 1267, 1215, 756; ^1H NMR (200.13 MHz, $CDCl_3$): δ 1.75 (s, 3H), 3.92 (ddd, *J* = 11.1, 6.9, 3.9 Hz, 1H), 4.17 (ddd, *J* = 11.3, 4.6, 2.8 Hz, 1H), 4.25 – 4.35 (m, 2H), 4.40 (s, 1H), 4.47 (d, *J* = 6.5 Hz, 1H), 4.69 (dd, *J* = 10.5, 5.9 Hz, 1H), 4.93 (d, *J* = 7.9 Hz, 1H), 5.33 (quintet, *J* = 1.5 Hz, 1H), 5.63 (dd, *J* = 10.4, 3.4 Hz, 1H), 5.81 (d, *J* = 7.8 Hz, 1H), 5.89 (s, 1H), 6.02 (d, *J* = 3.1 Hz, 1H), 7.06 – 7.73 (m, 12H), 7.72 – 8.15 (m, 8H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 18.0, 61.9, 63.2, 67.4, 68.0, 69.5, 71.3, 71.6, 101.3, 125.7, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.5, 128.6, 128.6, 128.9, 129.1, 129.2, 129.6, 129.6, 129.7, 129.7, 129.7, 129.7, 129.9, 129.9, 133.1, 133.2, 133.2, 133.5, 135.6, 165.1, 165.4, 165.5, 165.9, 167.0; HRMS (MALDI-TOF): *m/z* calcd for $[C_{40}H_{36}O_{12}+Na]^+$: 731.2104, Found: 731.2230.

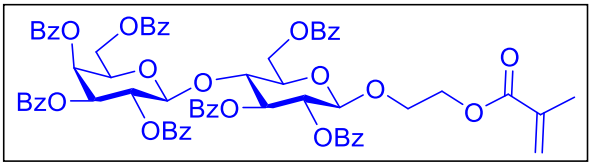


(2-Acryloyloxyethyl)-2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galacto-pyranosyl)-β-D-glucopyranoside (**54i**):



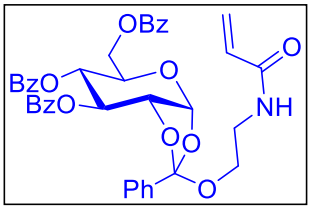
$[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +48.4°; IR (cm^{-1}, $CHCl_3$): 3064, 2976, 1730, 1603, 1215, 1095, 769; ^1H NMR (200.13 MHz, $CDCl_3$): δ 3.50 – 3.99 (m, 6H), 4.04 – 4.27 (m, 3H), 4.34 – 4.58 (m, 2H), 4.68 (d, *J* = 7.9 Hz, 1H), 4.80 (d, *J* = 7.9 Hz, 1H), 5.30 (dd, *J* = 10.3, 3.3 Hz, 1H), 5.40 (dd, *J* = 9.8, 7.9 Hz, 1H), 5.45 (dd, *J* = 10.4, 1.6 Hz, 1H), 5.62 (d, *J* = 8.7 Hz, 1H), 5.57 – 5.83 (m, 3H), 6.06 (dd, *J* = 17.1, 1.6 Hz, 1H), 6.98 – 7.56 (m, 21H), 7.61 – 7.69 (m, 2H), 7.73 – 8.04 (m, 12H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 61.0, 62.2, 63.0, 67.4, 67.4, 69.8, 71.3, 71.5, 71.7, 72.7, 73.0, 75.8, 100.9, 101.0, 127.6, 128.1, 128.2, 128.2, 128.2, 128.2, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.6, 128.7, 129.2, 129.3, 129.4, 129.5, 129.5, 129.5, 129.5, 129.6, 129.6, 129.6, 129.6, 129.7, 129.7, 129.8, 129.9, 129.9, 130.8, 133.1, 133.2, 133.3, 133.3, 133.3, 133.4, 133.5, 164.7, 165.0, 165.1, 165.3, 165.3, 165.5, 165.7, 165.8; HRMS (MALDI-TOF): *m/z* calcd for $[C_{66}H_{56}O_{20}+Na]^+$: 1191.3263, Found: 1191.3123.

(2-Methacryloyloxyethyl)-2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-gal-actopyranosyl)-β-D-glucopyra-noside (**54j**):

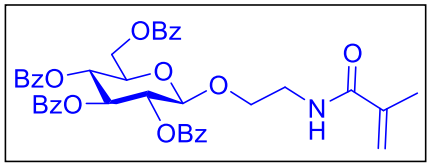


$[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.3) +49.2°; IR (cm^{-1}, $CHCl_3$): 3064, 2976, 1730, 1603, 1452, 1269, 1215, 1096, 758; ^1H NMR (200.13 MHz, $CDCl_3$): δ 1.47 – 1.88 (m, 3H), 3.63 – 3.93 (m, 5H), 3.94 – 4.07 (m, 1H), 4.09 – 4.36 (m, 3H), 4.48 (dd, *J* = 12.4, 3.9 Hz, 1H), 4.52 – 4.68 (m, 1H), 4.77 (d, *J* = 7.9 Hz, 1H), 4.87 (d, *J* = 7.9 Hz, 1H), 5.25 – 5.30 (m, 1H), 5.37 (dd, *J* = 10.3, 3.3 Hz, 1H), 5.48 (dd, *J* = 9.8, 7.9 Hz, 1H), 5.65 – 5.87 (m, 4H), 7.03 – 7.68 (m, 21H), 7.68 – 7.77 (m, 2H), 7.82 – 8.10 (m, 12H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 18.0, 61.0, 62.2, 63.2, 67.4, 67.5, 69.8, 71.4, 71.5, 71.7, 72.8, 73.0, 75.9, 100.9, 101.0, 125.7, 128.2, 128.2, 128.2, 128.2, 128.3, 128.3, 128.3, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.6, 128.6, 128.6, 128.6, 128.6, 128.8, 129.2, 129.4, 129.4, 129.5, 129.6, 129.6, 129.6, 129.6, 129.6, 129.7, 129.7, 129.7, 129.8, 129.8, 129.9, 130.0, 133.2, 133.2, 133.4, 133.4, 133.4, 133.4, 133.5, 135.6, 164.8, 165.1, 165.2, 165.4, 165.4, 165.5, 165.8, 167.0; HRMS (MALDI-TOF): *m/z* calcd for $[C_{67}H_{58}O_{20}+Na]^+$: 1205.3419, Found: 1205.3211.

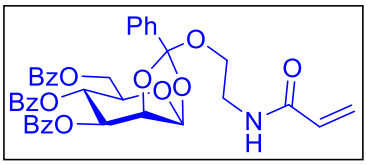
Characterization data for compound (**65a**): IR (cm^{-1}, $CHCl_3$): 3440, 3395, 3320, 3069, 2965, 1726, 1665, 1534, 1455, 1270, 1078, 760; ^1H NMR (200.13 MHz, $CDCl_3$): δ 3.45 (s, 4H), 3.99 – 4.20 (m, 1H), 4.25 – 4.61 (m, 2H), 4.78 (s, 1H), 5.55 (dd, *J* = 21.9, 9.3 Hz, 2H), 5.74 (s, 1H), 5.93 – 6.17 (m, 3H), 6.24 (d, *J* = 15.5 Hz, 1H), 7.13 – 7.84 (m, 14H), 7.83 – 8.29 (m, 6H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 39.0, 62.8, 63.8, 67.5, 68.3, 69.1, 72.2, 97.5, 121.2, 126.0, 126.5, 128.1, 128.1, 128.3, 128.3, 128.4, 128.4, 128.4, 128.5, 128.5, 128.8, 128.9, 129.4, 129.5, 129.5, 129.7, 129.7, 129.8, 129.9, 129.9, 130.5, 133.0, 133.5, 133.6, 135.0, 164.5, 165.1, 165.4, 165.9; HRMS (MALDI-TOF): *m/z* calcd for $[C_{39}H_{35}NO_{11}+Na]^+$: 716.2108, Found: 716.2120.



(2-Methacrylamidoethyl)-2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (**55c**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +29.1°; IR (cm^{-1}, $CHCl_3$): 3391, 3310, 3064, 2957, 1728, 1603, 1451, 1215, 1113, 1026, 756; ^1H NMR (200.13 MHz, $CDCl_3$): δ 1.61 – 1.82 (m, 3H), 3.32 – 3.68 (m, 2H), 3.77 (ddd, *J* = 10.2, 7.5, 3.3 Hz, 1H), 3.97 (ddd, *J* = 9.5, 5.5, 3.6 Hz, 1H), 4.19 (ddd, *J* = 9.6, 5.1, 3.0 Hz, 1H), 4.49 (dd, *J* = 12.2, 5.2 Hz, 1H), 4.66 (dd, *J* = 12.2, 3.0 Hz, 1H), 4.88 (d, *J* = 7.9 Hz, 1H), 5.09 (quintet, *J* = 1.3 Hz, 1H), 5.50 (s, 1H), 5.57 (d, *J* = 7.9 Hz, 1H), 5.70 (t, *J* = 9.7 Hz, 1H), 5.94 (t, *J* = 9.7 Hz, 1H), 6.20 (dd, *J* = 9.8, 5.3 Hz, 1H), 7.15 – 7.65 (m, 12H), 7.78 – 8.13 (m, 8H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 18.2, 39.1, 62.9, 69.0, 69.4, 71.8, 72.3, 72.6, 101.2, 119.5, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.6, 128.6, 128.8, 129.4, 129.6, 129.6, 129.6, 129.6, 129.7, 129.7, 129.7, 133.2, 133.2, 133.4, 133.4, 139.5, 165.1, 165.1, 165.7, 166.0, 168.2; HRMS (MALDI-TOF): *m/z* calcd for $[C_{40}H_{37}NO_{11}+Na]^+$: 730.2264, Found:730.2349.

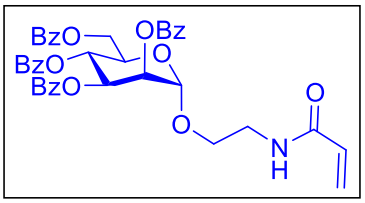


Characterization data for compound: $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) –73.2°; IR (cm^{-1}, $CHCl_3$):3439, 3393, 3323, 3065, 2955, 1724, 1664, 1524, 1450, 1269, 1076, 761; ^1H NMR (200.13 MHz, $CDCl_3$): δ 3.37 – 3.68 (m, 4H), 3.98 – 4.17 (m, 1H), 4.33 (dd, *J* = 12.1, 4.5 Hz, 1H), 4.52 (dd, *J* = 12.1, 3.2 Hz, 1H), 5.09 (dd, *J* = 3.9, 2.9 Hz, 1H), 5.59 (dd, *J* = 8.2, 1.8 Hz, 1H), 5.66 (dd, *J* = 10.0, 4.0 Hz, 1H), 5.81 (d, *J* = 2.8 Hz, 1H), 5.87 (t, *J* = 9.5 Hz, 1H), 5.89 – 6.04 (m, 1H), 6.08 (d, *J* = 10.0 Hz, 1H), 6.24 (dd, *J* = 16.9, 1.8 Hz, 1H), 7.19 – 7.60 (m, 12H), 7.60 – 7.76 (m, 2H), 7.80 –

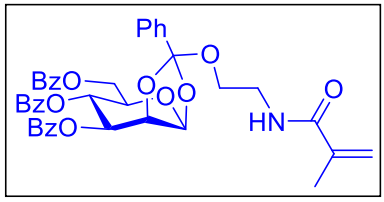


8.10 (m, 6H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 39.0, 62.8, 62.8, 66.2, 71.1, 71.8, 76.4, 97.7, 122.9, 126.1, 126.2, 126.5, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.7, 128.8, 129.4, 129.4, 129.6, 129.6, 129.6, 129.6, 129.7, 129.9, 129.9, 130.5, 130.5, 132.9, 133.4, 133.5, 136.3, 165.1, 165.4, 165.9, 165.9; HRMS (MALDI-TOF): *m/z* calcd for $[C_{39}H_{35}NO_{11}+Na]^+$: 716.2108, Found: 716.2220.

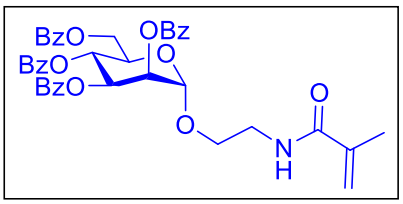
(2-Acrylamidoethyl)-2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranoside (**55d**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) −58.0°; IR (cm^{-1}, $CHCl_3$): 3393, 3308, 3064, 2932, 1732, 1628, 1452, 1267, 1109, 1070, 756; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.49 – 3.90 (m, 3H), 3.94 – 4.03 (m, 1H), 4.36 – 4.58 (m, 2H), 4.62 – 4.78 (m, 1H), 5.12 (d, *J* = 1.7 Hz, 1H), 5.69 (dd, *J* = 9.4, 2.4 Hz, 1H), 5.74 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.09 (t, *J* = 9.9 Hz, 1H), 6.28 (d, *J* = 9.4 Hz, 1H), 6.33 (d, *J* = 2.4 Hz, 1H), 6.42 (d, *J* = 2.4 Hz, 1H), 6.44 (bs, 1H), 7.16 – 7.69 (m, 12H), 7.80 – 8.15 (m, 8H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 39.2, 62.8, 66.8, 67.6, 69.0, 70.0, 70.2, 97.8, 126.8, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.8, 128.8, 129.0, 129.6, 129.6, 129.6, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 130.6, 133.1, 133.3, 133.4, 133.5, 165.4, 165.4, 165.6, 165.7, 166.1; HRMS (MALDI-TOF): *m/z* calcd for $[C_{39}H_{35}NO_{11}+Na]^+$: 716.2108, Found:716.2220.



Characterization data for compound: $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) −77.2°; IR (cm^{-1}, $CHCl_3$): 3443, 3412, 3065, 2928, 1728, 1672, 1518, 1452, 1269, 1093, 758; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.94 (s, 3H), 2.97 – 3.51 (m, 2H), 3.90 – 4.32 (m, 3H), 4.40 – 4.61 (m, 2H), 4.77 (dd, *J* = 12.3, 2.7 Hz, 1H), 5.19 – 5.28 (m, 1H), 5.57 (d, *J* = 2.5 Hz, 1H), 5.62 (dd, *J* = 10.0, 4.2 Hz, 1H), 5.72 (s, 1H), 6.11 (t, *J* = 9.9 Hz, 1H), 6.35 (bs, 1H), 7.08 – 7.69 (m, 14H), 7.83 – 8.18 (m, 6H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 18.6, 39.3, 62.2, 62.3, 66.1, 71.2, 71.8, 75.7, 95.7, 119.3, 123.5, 125.5, 125.5, 128.3, 128.3, 128.4, 128.4, 128.4, 128.5, 128.5, 128.6, 128.7, 129.3, 129.4, 129.6, 129.6, 129.7, 129.7, 129.9, 129.9, 130.0, 133.4, 133.5, 133.6, 137.8, 139.9, 165.1, 165.8, 166.0, 168.3; HRMS (MALDI-TOF): *m/z* calcd for $[C_{40}H_{37}NO_{11}+Na]^+$: 730.2264, Found: 730.2245.

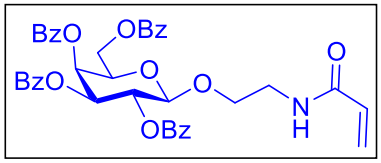


(2-Methacrylamidoethyl)-2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranoside (**55e**): $[\alpha]_D^{25}$ ($CHCl_3$, *c*0.9) −53.5°; IR (cm^{-1}, $CHCl_3$): 3480, 3439, 3086, 2930, 1730, 1662, 1452, 1267, 1109, 1068,

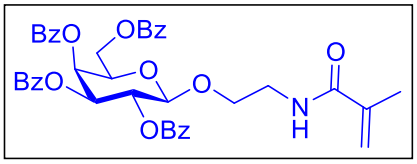


758; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.04 (s, 3H), 3.53 – 3.68 (m, 1H), 3.69 – 3.81 (m, 2H), 3.97 – 4.05 (m, 1H), 4.44 (ddd, *J* = 9.9, 4.2, 2.6 Hz, 1H), 4.52 (dd, *J* = 12.2, 4.6 Hz, 1H), 4.70 (dd, *J* = 12.2, 2.5 Hz, 1H), 5.15 (d, *J* = 1.3 Hz, 1H), 5.41 (s, 1H), 5.74 (dd, *J* = 3.2, 1.8 Hz, 1H), 5.81 (s, 1H), 5.93 (dd, *J* = 10.1, 3.3 Hz, 1H), 6.12 (t, *J* = 10.1 Hz, 1H), 6.41 (bs, 1H), 7.13 – 7.69 (m, 12H), 7.81 – 7.89 (m, 2H), 7.94 – 8.01 (m, 2H), 8.03 – 8.13 (m, 4H); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 18.7, 39.3, 62.8, 66.8, 67.4, 69.1, 69.9, 70.2, 97.7, 120.0, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.6, 128.6, 128.8, 128.9, 129.1, 129.6, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 129.8, 129.8, 133.1, 133.3, 133.5, 133.6, 139.8, 165.4, 165.4, 165.6, 166.1, 168.5; HRMS (MALDI-TOF): *m/z* calcd for $[C_{40}H_{37}NO_{11}+Na]^+$: 730.2264, Found:730.2245.

(2-Acrylamidoethyl)-2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside (**55f**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +79.7°; IR (cm^{-1}, $CHCl_3$): 3481, 3434, 3070, 2927, 1731, 1661, 1454, 1268, 1110, 1068, 754; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.33 – 3.70 (m, 2H), 3.67 – 3.87 (m, 1H), 3.94 – 4.15 (m, 1H), 4.42 (tt, *J* = 12.5, 6.0 Hz, 2H), 4.68 (dd, *J* = 10.8, 6.3 Hz, 1H), 4.86 (d, *J* = 7.7 Hz, 1H), 5.42 (dd, *J* = 10.3, 1.4 Hz, 1H), 5.57 – 5.81 (m, 2H), 5.78 – 5.86 (m, 1H), 5.97 – 6.20 (m, 3H), 7.16 – 7.70 (m, 12H), 7.75 – 8.18 (m, 8H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 38.9, 62.0, 68.0, 69.1, 69.8, 71.3, 71.4, 101.6, 126.2, 128.2, 128.2, 128.4, 128.4, 128.5, 128.5, 128.5, 128.6, 128.6, 128.8, 128.9, 129.1, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.9, 129.9, 130.3, 133.3, 133.3, 133.5, 133.6, 165.4, 165.4, 165.4, 166.0; HRMS(MALDI-TOF): m/z calcd for $[C_{39}H_{35}O_{11}N+Na]^+$: 716.2108; Found, 716.2123.

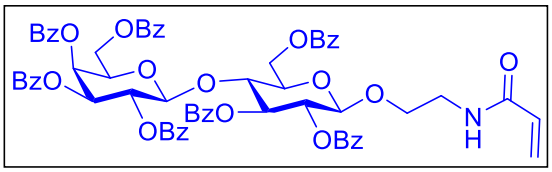


(2-Methacryloyloxyethyl)-2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside (**55g**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +78.5°; IR (cm^{-1}, $CHCl_3$): 3482, 3431, 3065, 2923, 1727, 1661, 1455, 1269, 1110, 1068, 758; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.75 (s, 3H), 3.32 – 3.61 (m, 1H), 3.53 – 3.76 (m, 1H), 3.78 (td, *J* = 7.7, 3.8 Hz, 1H), 4.04 (ddd, *J* = 9.4, 5.5, 3.6 Hz, 1H), 4.44 (d, *J* = 10.6 Hz, 1H), 4.67 (dd, *J* = 10.4, 6.0 Hz, 1H), 4.88 (d, *J* = 7.7 Hz, 1H), 5.05 – 5.17 (m, 1H), 5.51 (s, 1H), 5.66 (dd, *J* = 10.4, 3.3 Hz, 1H), 5.81 (dd, *J* = 10.4, 7.7 Hz, 1H), 6.02 (d, *J* = 3.2 Hz, 1H), 6.25 (t, *J* = 5.2 Hz, 1H), 7.15 – 7.71 (m, 12H), 7.71 – 8.18 (m, 8H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 18.2, 39.1, 62.0, 68.0, 68.8, 69.8, 71.4, 71.4, 101.4, 119.5, 128.2, 128.2, 128.4,



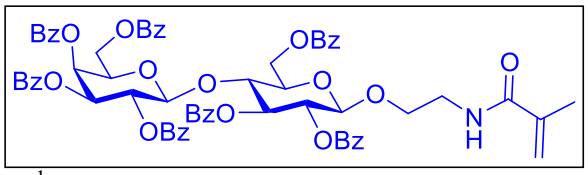
128.4, 128.4, 128.4, 128.4, 128.5, 128.6, 128.8, 128.8, 129.2, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.9, 129.9, 133.3, 133.3, 133.4, 133.6, 139.5, 165.3, 165.4, 165.4, 165.9, 168.2; HRMS (MALDI-TOF): m/z calcd for $[C_{40}H_{36}O_{12}+Na]^+$: 731.2104; Found, 731.2230.

(2-Acrylamidoethyl)-2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-β-D-glucopyranoside (**55h**):



$[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +46.2°; IR (cm^{-1}, $CHCl_3$): 3390, 3315, 3066, 2976, 1730, 1603, 1452, 1269, 1215, 756; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.13 – 3.58 (m, 2H), 3.58 – 4.01 (m, 6H), 4.27 (t, *J* = 9.4 Hz, 1H), 4.49 (dd, *J* = 12.2, 3.9 Hz, 1H), 4.64 (d, *J* = 10.0 Hz, 1H), 4.71 (d, *J* = 10.0 Hz, 1H), 4.93 (d, *J* = 7.8 Hz, 1H), 5.31 – 5.57 (m, 3H), 5.63 – 5.91 (m, 4H), 6.03 (bs, 1H), 6.10 (dd, *J* = 16.9, 1.6 Hz, 1H), 7.08 – 7.64 (m, 21H), 7.71 – 7.76 (m, 2H), 7.86 – 8.09 (m, 12H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 38.9, 60.9, 62.0, 67.4, 69.2, 69.8, 71.3, 71.6, 71.7, 72.5, 73.1, 75.7, 100.9, 101.2, 126.1, 128.1, 128.2, 128.2, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.7, 128.8, 129.2, 129.2, 129.3, 129.4, 129.4, 129.5, 129.5, 129.5, 129.6, 129.6, 129.6, 129.6, 129.7, 129.7, 129.8, 129.9, 130.3, 133.2, 133.2, 133.3, 133.4, 133.4, 133.4, 133.5, 164.7, 165.1, 165.2, 165.3, 165.3, 165.3, 165.4, 165.8; HRMS (MALDI-TOF): *m/z* calcd for $[C_{66}H_{57}NO_{19}+Na]^+$: 1190.3423, Found: 1190.3345.

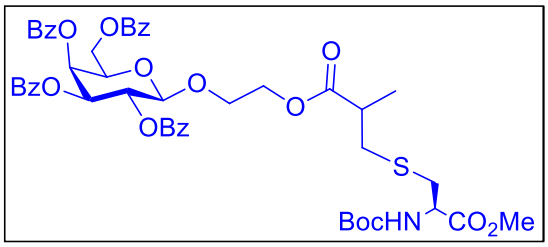
(2-Methacrylamidoethyl)-2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-β-D-glucopyranoside (**55i**):



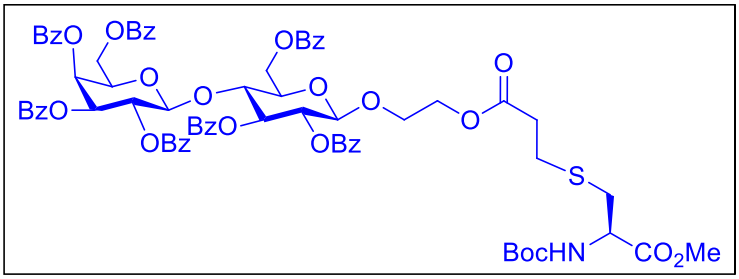
$[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) +46.0°; IR (cm^{-1}, $CHCl_3$):3456, 3310, 3086, 2883, 1734, 1603, 1452, 1269, 1095, 756; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 1.69 (s, 3H), 3.22 – 3.57 (m, 2H), 3.62 – 3.76 (m, 3H), 3.88 (dt, *J* = 10.1, 4.9 Hz, 3H), 4.25 (t, *J* = 9.5 Hz, 1H), 4.48 (dd, *J* = 12.3, 4.2 Hz, 1H), 4.56 – 4.67 (m, 1H), 4.70 (d, *J* = 7.9 Hz, 1H), 4.88 (d, *J* = 7.9 Hz, 1H), 5.00 – 5.08 (m, 1H), 5.32 – 5.53 (m, 3H), 5.63 – 5.91 (m, 3H), 6.10 (bs, 1H), 6.99 – 7.66 (m, 21H), 7.69 – 7.78 (m, 2H), 7.86 – 8.10 (m, 12H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 18.2, 39.1, 61.0, 62.2, 67.4, 69.0, 69.8, 71.3, 71.7, 71.8, 72.6, 73.1, 75.9, 100.9, 101.1, 119.4, 128.2, 128.2, 128.2, 128.2, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.6, 128.6, 128.6, 128.6, 128.6, 128.8, 128.9, 129.3, 129.3, 129.5, 129.5, 129.5, 129.5, 129.6, 129.6, 129.6, 129.6, 129.6,

129.7, 129.7, 129.7, 129.7, 129.8, 129.9, 129.9, 133.2, 133.2, 133.4, 133.4, 133.4, 133.4, 133.5, 139.6, 164.7, 165.2, 165.2, 165.3, 165.4, 165.5, 165.8, 168.2; HRMS (MALDI-TOF): *m/z* calcd for $[C_{67}H_{59}NO_{19}+Na]^+$: 1204.3579, Found:1204.3570.

Characterization data for compound **67a**: $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +61.3°; IR (cm^{-1}, $CHCl_3$): 3432, 3374, 3064, 2980, 1730, 1603, 1501, 1267, 1215, 1096, 769; ^1H NMR (200.13 MHz, $CDCl_3$): δ 1.01 (d, *J* = 6.5 Hz, 3H), 1.45 (s, 9H), 2.18 – 2.76 (m, 3H), 2.91 (d, *J* = 5.2 Hz, 2H), 3.74 (s, 3H), 3.76 – 3.98 (m, 1H), 4.08 – 4.58 (m, 6H), 4.70 (dd, *J* = 9.7, 5.0 Hz, 1H), 4.92 (dd, *J* = 7.8, 2.0 Hz, 1H), 5.41 (d, *J* = 8.0 Hz, 1H), 5.64 (dd, *J* = 10.4, 3.3 Hz, 1H), 5.82 (dd, *J* = 10.4, 7.8 Hz, 1H), 6.02 (d, *J* = 3.2 Hz, 1H), 7.04 – 7.72 (m, 12H), 7.69 – 7.89 (m, 2H), 7.84 – 8.29 (m, 6H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 16.4, 16.5, 28.2, 28.2, 28.2, 28.2, 28.2, 28.2, 34.9, 35.0, 35.6, 35.6, 39.8, 39.8, 52.5, 52.5, 53.2, 61.9, 61.9, 63.2, 63.3, 67.4, 67.4, 68.0, 68.0, 69.5, 69.5, 71.3, 71.3, 71.5, 71.5, 77.2, 80.1, 80.1, 101.2, 101.4, 128.2-129.9(40C), 133.2, 133.2, 133.2, 133.3, 133.3, 133.3, 133.5, 133.5, 155.0, 155.1, 165.1, 165.1, 165.4, 165.4, 165.4, 165.5, 165.9, 166.0, 171.3, 171.3, 174.4, 174.5; HRMS (MALDI-TOF): *m/z* calcd for $[C_{49}H_{53}NO_{16}S+Na]^+$: 966.2983, Found: 966.3002.



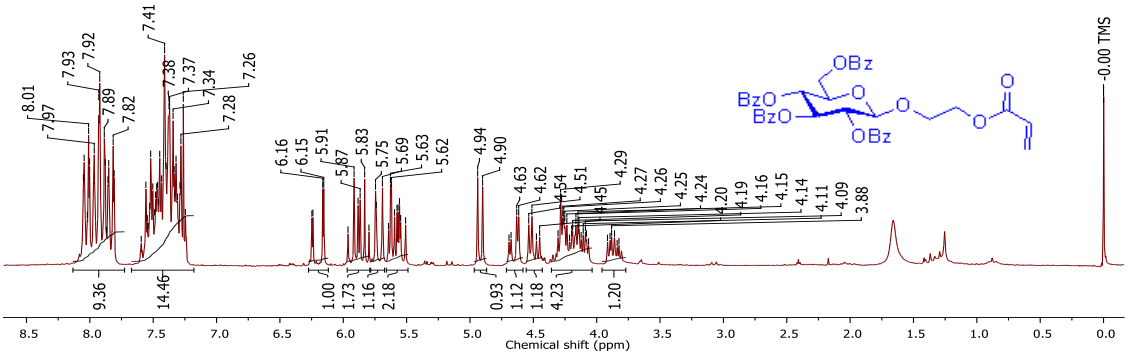
Characterization data for compound **67b**: $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +61.3°; IR (cm^{-1}, $CHCl_3$): 3433, 3373, 3070, 2980, 1728, 1603, 1452, 1269, 1176, 1071, 758, 710; ^1H NMR (200.13 MHz, $CDCl_3$): δ 1.44 (s, 9H), 2.22 (t, *J* = 7.3 Hz, 2H), 2.55 (t, *J* = 7.0 Hz, 2H), 2.89 (d, *J* = 5.1 Hz, 2H), 3.69-3.74 (m, 3H), 3.74 (s, 3H), 3.77 – 4.08 (m, 3H), 4.15 (t, *J* = 4.6 Hz, 2H), 4.27 (t, *J* = 9.5 Hz, 1H), 4.39 – 4.69 (m, 3H), 4.75 (d, *J* = 7.8 Hz, 1H), 4.88 (d, *J* = 7.9 Hz, 1H), 5.35 (d, *J* = 3.2 Hz, 1H), 5.40 (d, *J* = 3.3 Hz, 1H), 5.47 (dd, *J* = 9.8, 7.9 Hz, 1H), 5.67 – 5.77 (m, 2H), 5.84 (t, *J* = 9.5 Hz, 1H), 7.05 – 7.67 (m, 21H), 7.68 – 7.75 (m, 2H), 7.82 – 8.09 (m, 12H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 27.2, 28.2, 28.2, 28.2, 34.0, 34.5, 52.5, 53.1, 55.5, 61.0, 62.2, 63.1, 67.4, 69.8, 71.3, 71.5, 71.7, 72.7, 73.0, 75.9, 80.1, 100.9, 101.0, 128.2, 128.2, 128.2, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5,



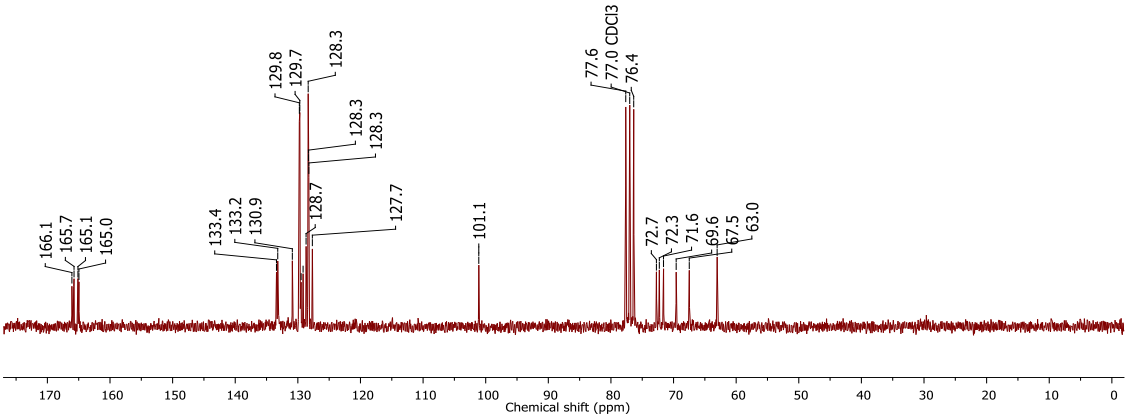
128.6, 128.6, 128.6, 128.7, 129.2, 129.3, 129.4, 129.5, 129.5, 129.5, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 129.9, 133.1, 133.2, 133.3, 133.4, 133.4, 133.4, 133.5, 155.5, 164.7, 165.0, 165.1, 165.3, 165.3, 165.5, 165.8, 171.3, 171.4; HRMS (MALDI-TOF): *m/z* calcd for $[C_{75}H_{73}NO_{24}S+Na]^+$: 1426.4141, Found: 1426.3896.

1B.5 – Spectral Charts

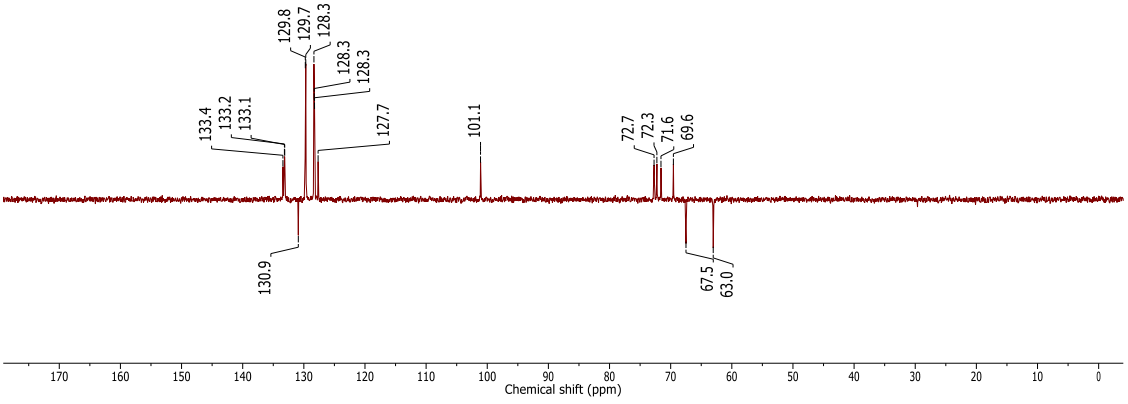
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **54c**



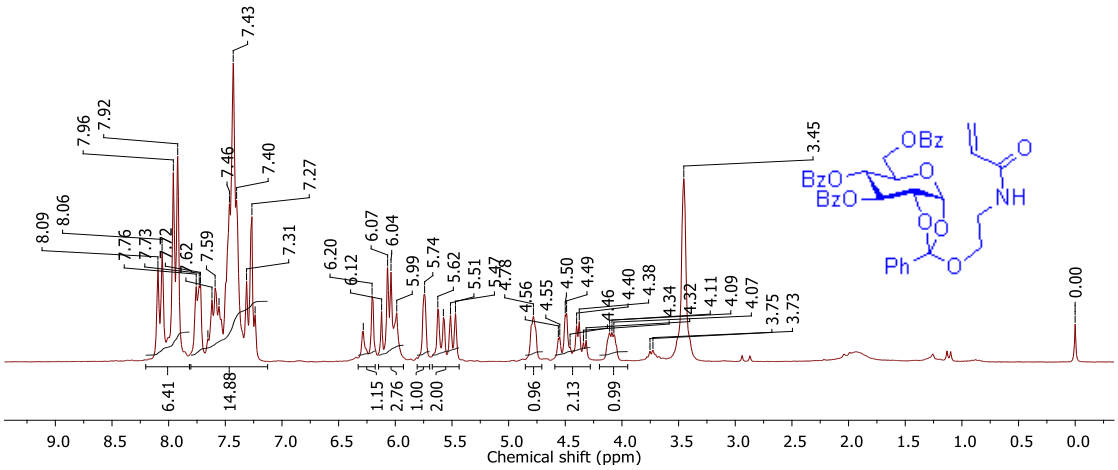
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **54c**



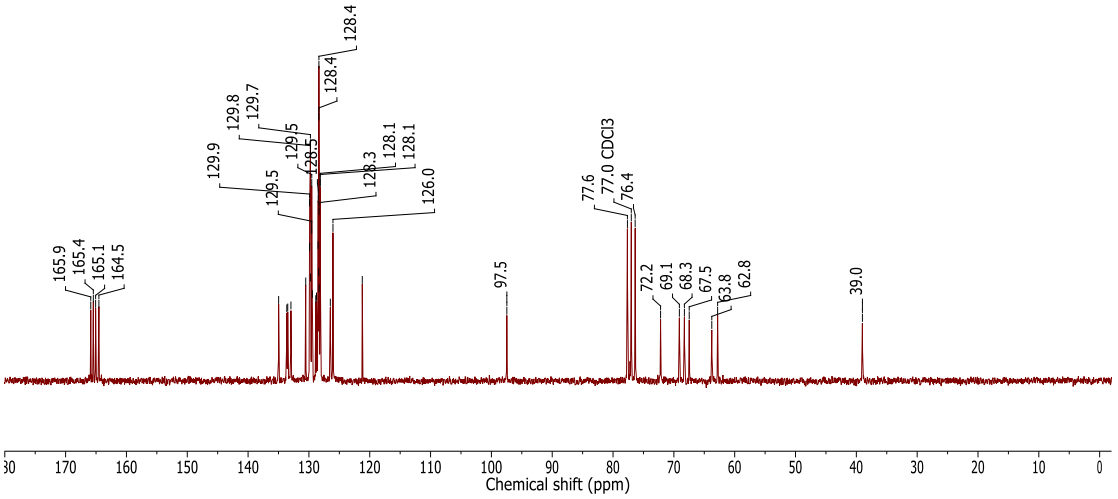
DEPT Spectrum (50.32 MHz, $CDCl_3$) of Compound **54c**



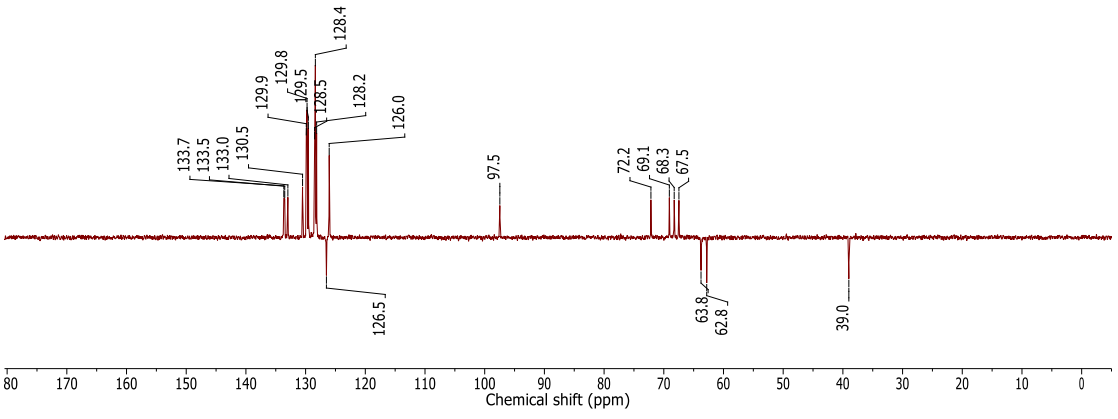
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **65a**



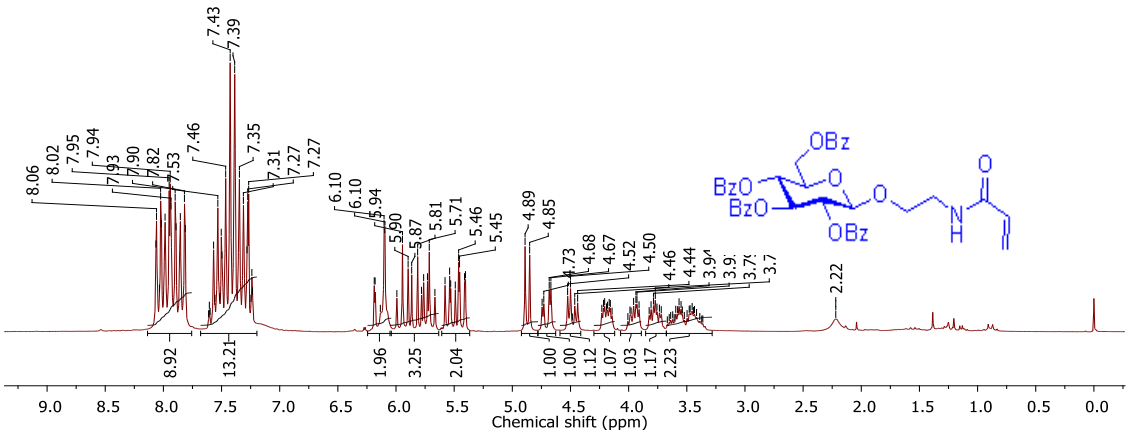
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **65a**



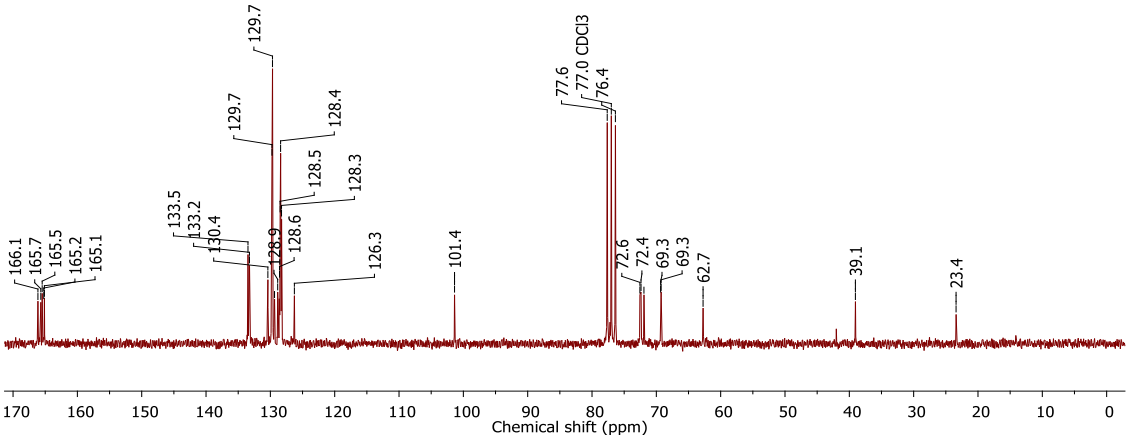
DEPT Spectrum (50.32 MHz, $CDCl_3$) of Compound **65a**



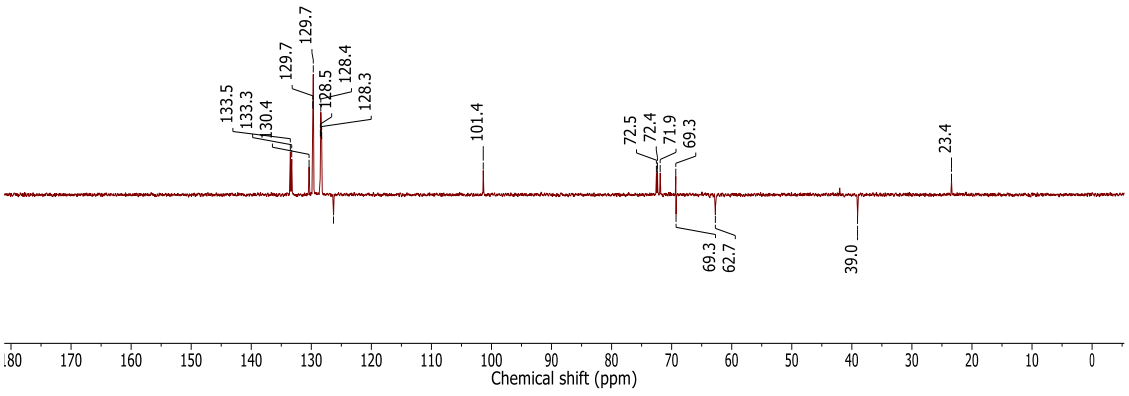
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **55b**



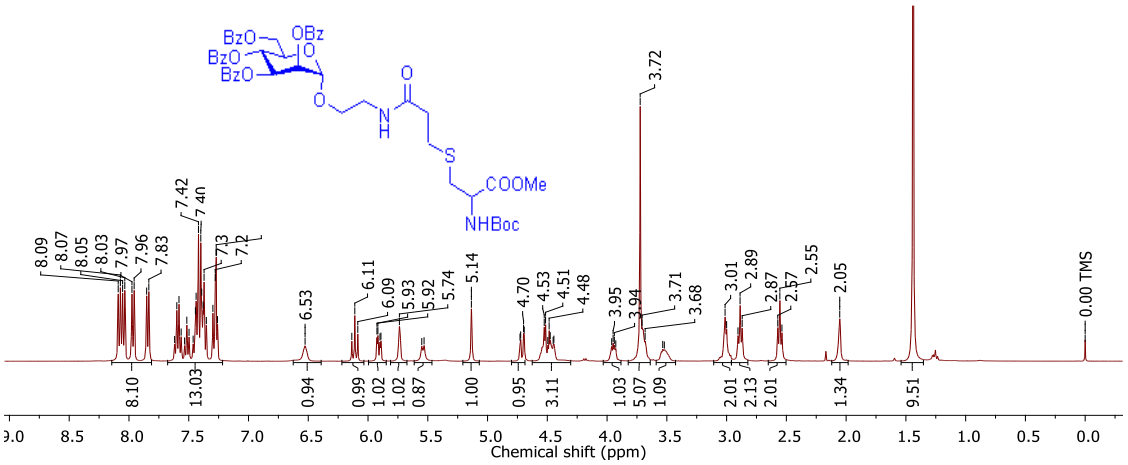
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **55b**



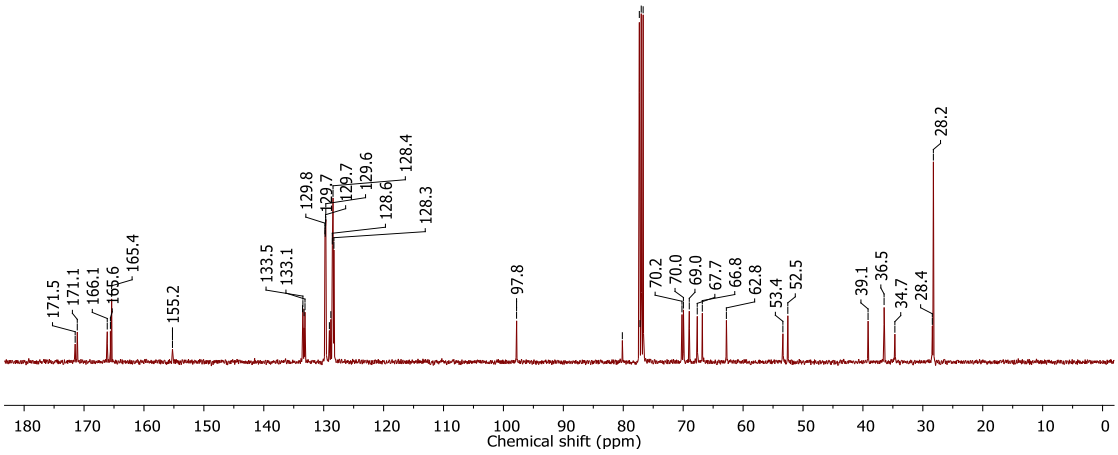
DEPT Spectrum (50.32 MHz, $CDCl_3$) of Compound **55b**



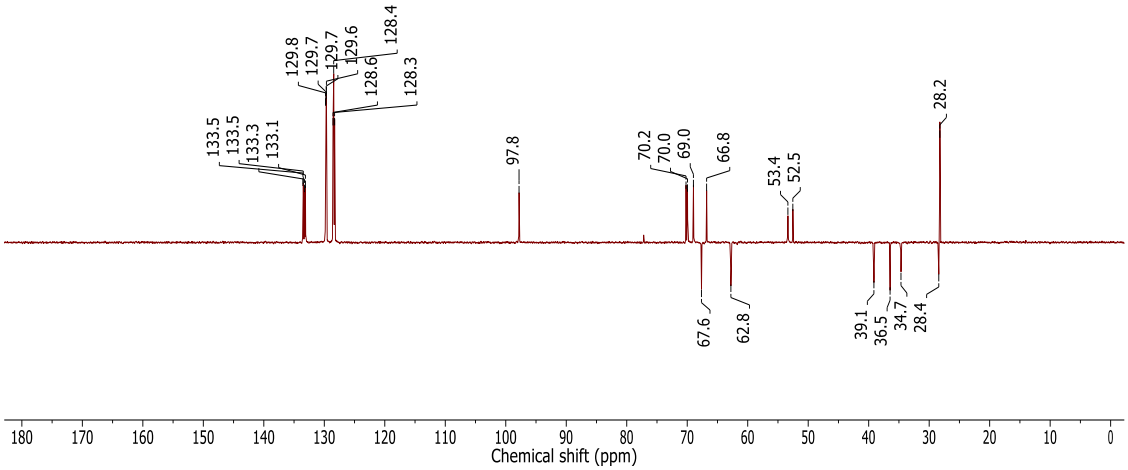
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **67c**



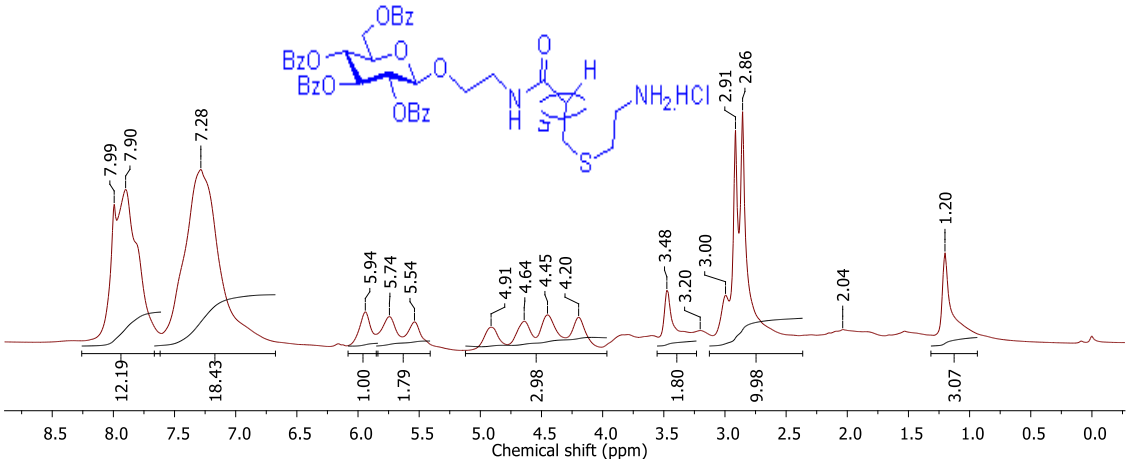
^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **67c**



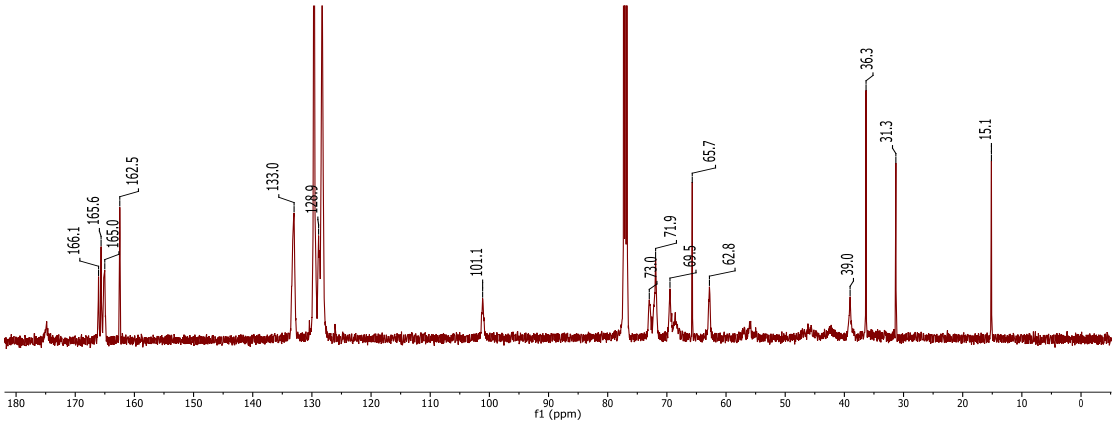
DEPT Spectrum (50.32 MHz, $CDCl_3$) of Compound **67c**



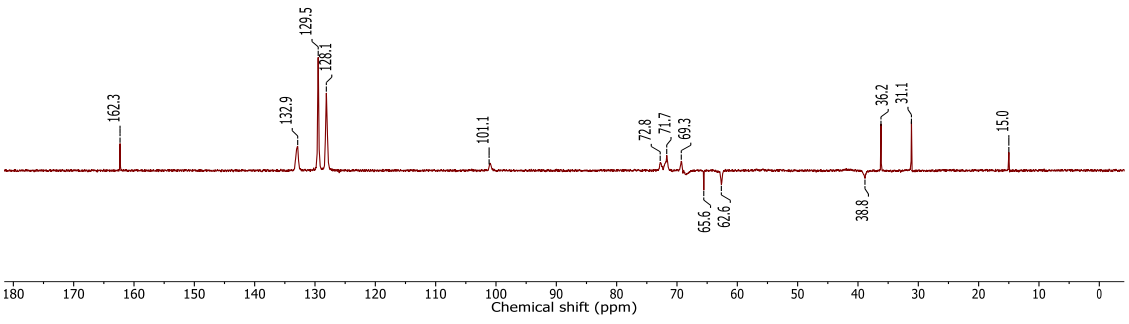
^{1}H NMR Spectrum (200.13 MHz, $CDCl_3$) of Compound **68a**



^{13}C NMR Spectrum (50.32 MHz, $CDCl_3$) of Compound **68a**



DEPT Spectrum (50.32 MHz, $CDCl_3$) of Compound **68a**



Details of experimental procedures, characterization data and spectral charts for some of the compounds in this endeavour are also given in the supporting information of *Carbohydr. Res.* **2011**, *346*, 1511-1518.

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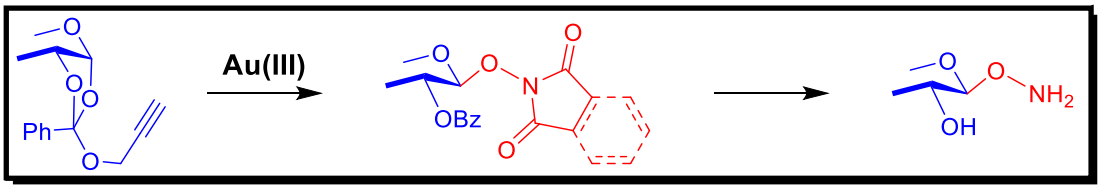
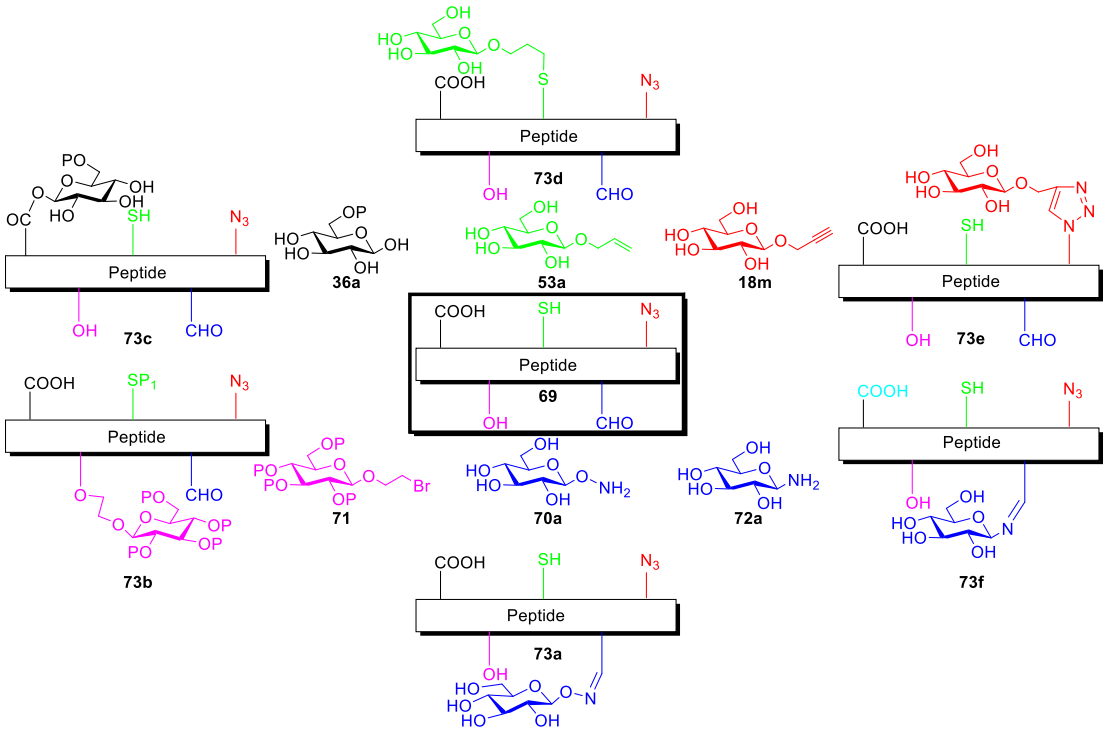
Section C: Synthesis of 1,2-trans Aminooxy Glycosides



1C.1 – Introduction

Neoglycoproteins synthesis by ligating carbohydrate molecules to the proteins is interesting.[1] The chemospecific/regiospecific chemical synthesis of glycopeptides remains a difficult task due to the presence of several functional groups present in the glycan as well as the protein. The recently developed chemoselective/regioselective ligation of oligosaccharides by reaction of nucleophilic or electrophilic sugar analogues with orthogonal functional group is advantageous.[2] Chemo-/regio- selective formation of imines (**73f** and **73a**) by the use of amino (**72a**) or aminooxy (**70a**) sugars and peptides containing aldehyde bond is a good example.

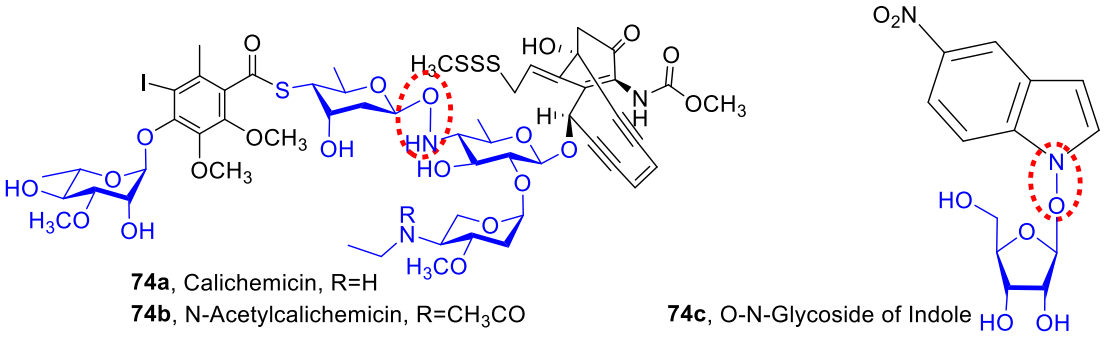
Figure 1C.1: Orthogonal ligation



In the recent past, 1,3-dipolar cycloaddition reaction between azide and alkyne (**18m**) resulting in the formation of triazole ring (**73e**) is widely investigated. Similarly, other orthogonal functional groups such as thio-click (**53a**), esterification (**36a**), and alkylation (**71**) are also used for the synthesis of glycoproteins (**Figure 1C.1**).[3] However, amine and oxygen linkages are routinely found in glycoproteins which are be considered as natural linkages.

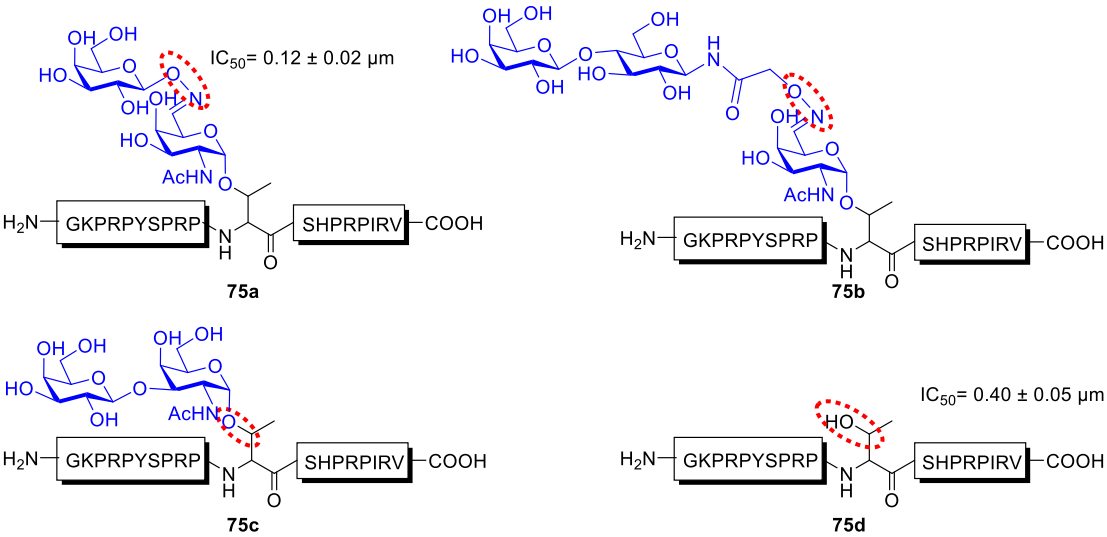
In addition, unusual glycosidic linkage found in the natural product Calichemicin (**74a**)[4] illustrated the importance of aminooxy glycosides.

Figure 1C.2: *O*-*N*-Linkages - Calichemicins and *N*-hydroxyindole sugar



Calichemicins (also known as the LL-E33288 antibiotics) were obtained from *Micromonispora echinospora ssp.* in the microbial fermentation. Calichemicins showed extraordinary potency against the murine tumours and are approximately 4000-fold more active than Adriamycin with optimal dose at 0.5-1.5 µg/kg (**Figure 1C.2**).[2] Calichemicins showed conformational control [partly due to the aminooxy linkage] which allowed selective binding of the antibiotics to specific DNA sequences. Recently, aminooxy linkages reported as synthetic linkages for the study of glycoproteins by orthogonal synthesis of imine bond between glycoside and proteins.[5] In the nucleic acid biochemistry, *N*-hydroxyindole/1-hydroxybenzotriazole (**74c**) and its analogues were widely used.[6]

Figure 1C.3: Aminooxy glycosides – Enhanced biological activity

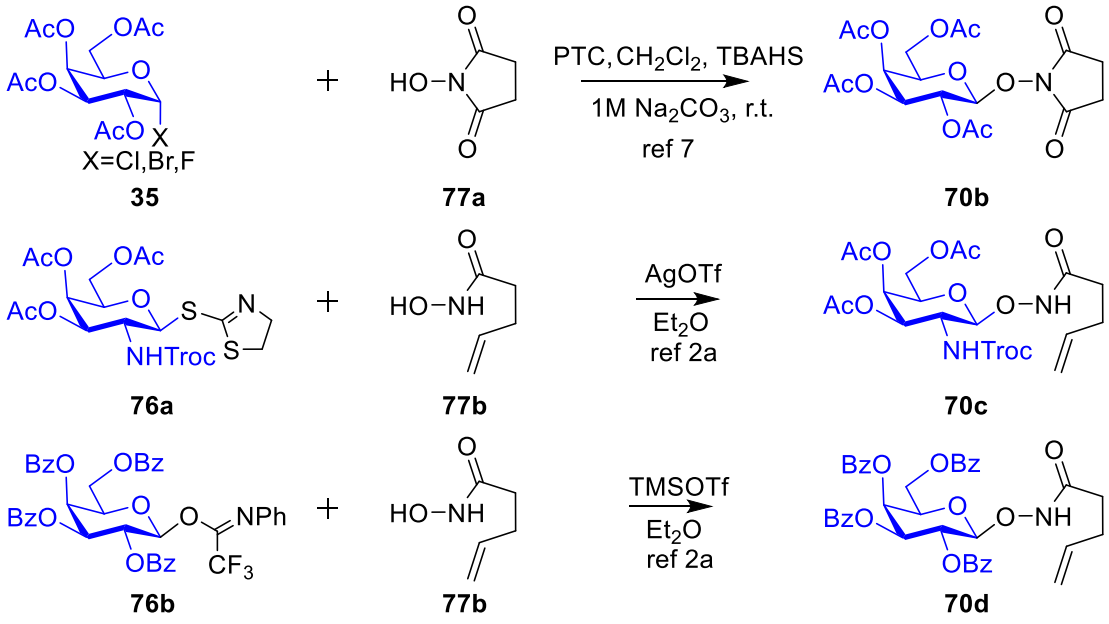


For example, Bertozzi group[5a] showed the chemoselective ligation for an insect derived, antibacterial 19-amino acid glycopeptide Drosocin and showed its biological activity varied on the glycosidation. Drosocin's potency in blocking

bacterial growth was improved by 2- to 8- fold due to a single *O*-linked disaccharide **75c** (Gal→GalNAc) at Thr11. Threonine derivative was incorporated into the Drosocin **75d** with the use of Fmoc-based solid phase methods to give GalNAc Drosocin followed by oxidation to the corresponding *C*-6 aldehyde. Resulting aldehyde was further ligated with aminooxy glycosides of galactose, aminooxy glucosamine and lactosamine to obtain corresponding ligated Drosocin (**75a** and **75b**). Furthermore, efficacies of unglycosylated **75d** vs. glycosylated Drosocin **75a-c** were determined after chemoselectively ligating to Drosocin **75d** (**Figure 1C.3**). Ligated Drosocin **75a** was found to be 3- to 4- fold more potent in blocking bacterial growth (IC_{50} =0.12±0.02 μm) than corresponding unglycosylated Drosocin **75d** (IC_{50} =0.40±0.05 μm).

The above delineated example shows that aminooxy glycosides are useful for the study of protein and carbohydrate interactions as well as in the total synthesis of natural products and analogues of biologically active molecules.

Scheme 1C.1: Synthesis of aminooxy glycosides



Encouraging biological features prompted us to develop a method for the synthesis of aminooxy saccharides by the treatment of catalytic amount of gold(III) salts with propargyl 1,2-*O*-orthoesters in presence of *N*-hydroxy containing glycosyl acceptors (**Scheme 1C.1**).[2,7,8]

1C.2 – Present work

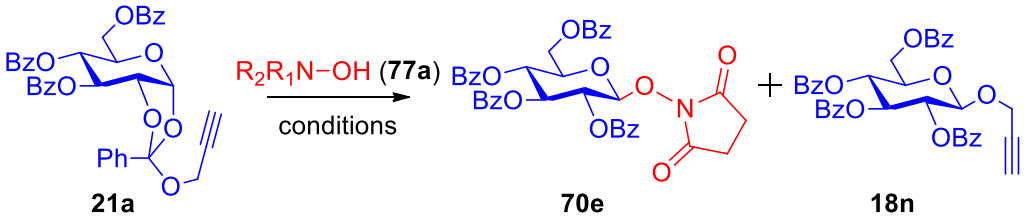
The importance of protein–bound oligosaccharides in cell-cell recognition events and in modifying protein folding and stability were highlighted in a number of recent studies. These studies motivated the development of new synthetic methods for the synthesis of glycoproteins with well-defined glycoforms. Many of the difficulties inherent to the synthesis of such complex molecules including the requirement of extensive protecting group manipulations and the chemical sensitivity of glycosidic bond have been investigated by several groups.[2,5,6]

1C.2.1 – Synthesis of aminooxy pyranosides using gold (III) catalysis

Glycopeptides with aminooxy linkages are important for studying protein-carbohydrate interactions as aminooxy linkages is one of the best mimics of the natural *O*-glycosidic bond. Recently from our group, pyranosyl[8a,b] and furanosyl[8e] propargyl 1,2-orthobenzoates were identified as novel glycosyl donors for the stereoselective synthesis of glycoconjugates. In this premise, propargyl 1,2-*O*-orthoesters can be hypothesized to realize the synthesis of aminooxy glycosides in a stereoselective manner by using catalytic amount of AuX_3 (X = Cl, Br) in CH_2Cl_2. Accordingly, propargyl 3,4,6-tri-*O*-benzoyl glucopyranoside 1,2-orthobenzoate (**21a)** was treated with *N*-hydroxy succinimide (**77a**) and freshly activated 4 Å MS powder in the presence of 7 mol% $AuBr_3$ in anhydrous CH_2Cl_2:CH_3CN (4:1) at room temperature afforded **70e** in good yield (**Scheme 1C.2**). Compound **70e** was confirmed by the ^1H and ^{13}C spectral data to have β-configuration at the anomeric position. Anomeric proton was noticed at δ 5.47 ppm (d, J = 7.5 Hz) and anomeric carbon was identified at δ 103.2 ppm. The appearance of new multiplet around δ 2.58 ppm confirmed the presence of two methylenes of succinimide present in compound **70e**. In the ^{13}C NMR spectrum, four benzoyl carbonyls were noticed between δ 165.1-165.9 ppm and two amide carbonyls were identified at δ 169.9 ppm of compound **70e**. In the DEPT spectrum, two CH_2s of succinimide moiety were present at δ 25.2 ppm of compound **70e**. Similarly, **21a** was treated with *N*-hydoxypthalimide (**77b**) under above mentioned conditions to give **70f** in 67% yield. In case of CH_2Cl_2 solvent, the time required to complete the reaction was quite longer because of poor solubility of glycosyl acceptor in CH_2Cl_2; however, the rate of glycosidation reaction was slow in

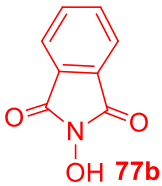
CH_3CN. Hence, after several combinations CH_2Cl_2:CH_3CN (4:1) system was found to be best for the reaction to give good yields in reasonable time.

Scheme 1C.2: Synthesis of aminooxy pyranosides



Catalyst	solvent	time (h)	70e (%)	18n (%)
$AuBr_3$	CH_2Cl_2	48	10	70
$AuBr_3$	CH_2Cl_2:CH_3CN	24	72	15
$AuBr_3$	CH_3CN	24	20	60
$AuBr_3$	CH_2Cl_2:THF	24	10	20
$AuBr_3$	THF	24	00	40
$AuBr_3$	CH_2Cl_2:DMF	24	55	24
$AuBr_3$:HCl	CH_2Cl_2:CH_3CN	24	45	38
$AuBr_3$:TMSOTf	CH_2Cl_2:CH_3CN	24	40	32
AuCl	CH_2Cl_2:CH_3CN	24	10	10
HAuCl4	CH_2Cl_2:CH_3CN	24	65	20

Optimized condition: $AuBr_3$ / CH_2Cl_2:THF / 4 Å M.S. powder / rt / 24 h

Glycosyl donor / Aglycone	21a	21b	21c	21d
77a	**70e** 70%	**70g** 73%	**70i** 69%	**70k** 72%
 OH **77b**	**70f** 67%	**70h** 70%	**70j** 64%	**70l** 65%

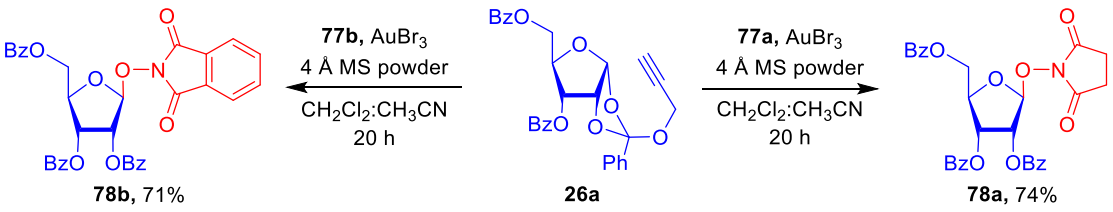
The reaction conducted in CH_2Cl_2:THF (4:1) did not complete even after 24 h. Furthermore, increasing the acidity of gold salts using dry HCl:CH_2Cl_2 and TMSOTf

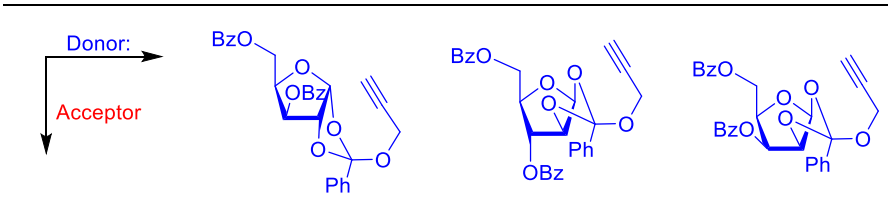
caused increase in the rearrgened glycosidation product formation. The reaction was found to be very slow when the catalyst was changed from $AuBr_3$ to AuCl. $HAuCl_4$ works well but being hygroscopic is a bit of problem for handling. Further, applicability of this method was gauged by CH_3CN:CH_2Cl_2 (1:4), 7mol% $AuBr_3$, 4 Å MS powder at room temperature. Accordingly, galactosyl (**21d**), mannosyl (**21c**) and lactosyl (**21b**) propargyl 1,2-orthoesters were treated with glycosyl acceptors **77a** and **77b**. The glycosylation reaction proceeded smoothly and gave the corresponding protected aminooxy glycosides (**70g** to **70l**) in good yields (**Scheme 1C.2**).

1C.2.2 – Synthesis of aminooxy furanosides

Above delineated methodology could be suitable for the synthesis of pyranoside and furanosides. Interesting to note that there were very few reports on the synthesis of furanosides with aminooxy glycosidic linkages. Furanosides in greater abundance were found in mycobacterial cell wall (see chapter 2) and hence, access to aminooxy arbino- and other furanosides should be enticing. Initial studies were carried out with model ribofuranosyl propargyl 1,2-*O*-orthoesters (**26a**). Accordingly, ribofuranosyl propargyl orthoester (**26a**) was treated with glycosyl acceptor **77a** under standard gold-catalyzed glycosidation conditions to obtain desired product **78a** in 74% yield after 20 h (**Scheme 1C.3**).

Scheme 1C.3: Synthesis of aminooxy furanosides using 1,2-orthoester strategy





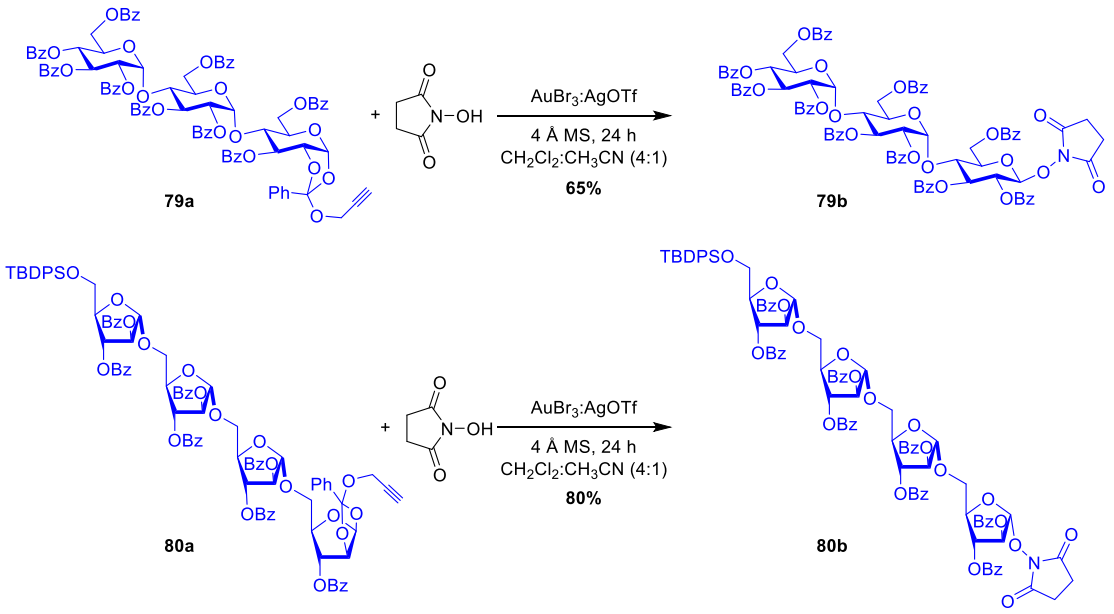
77a	**78c** 76%	**78e** 80%	**78g** 71%
77b	**78d** 72%	**78f** 75%	**78h** 70%

Analytical data of **78a** confirmed the formation of required product. In the ^{1}H NMR spectrum of **78a,** resonances of *H*-1 were observed at δ 5.10 ppm as a singlet and in the ^{13}C NMR spectrum, *C*-1 resonances were noticed at δ 109.9 ppm which confirmed the formation of 1,2-*trans* ribofuranoside. The singlet observed at δ 2.69 in the ^{1}H NMR and CH_2- resonances presented at δ 50.0 ppm (–ve phase in DEPT) and amide resonances at δ 158.0 ppm in the ^{13}C NMR indicated the presence of succinimidyl group of aminooxy ribofuranoside **78a**. The applicability of the methodology was judged with other furanosyl propargyl donors such as arabinosyl (**26c**), xylosyl (**26b**), lyxosyl (**26d**) and glycosyl acceptor (**77a** and **77b**) to form respective 1,2-*trans* glycosides (**78c** to **78h**) in good yield (**Scheme 1C.3**).

1C.2.3 – Synthesis of oligosaccahryl 1,2-*trans* aminooxy glycosides

Monosaccahryl and disaccharyl aminooxy glycosides were synthesized from different glycosyl donors and activators by different glycochemists. Stereoselective syntheses of oligosaccahryl aminooxy glycosides are difficult due to anomerization and interglycosidic bond cleavage in acidic media, low yield, acid-base sensitive functional groups in oligosaccharides which results into low yield, more side products, etc.

Scheme 1C.3: Oligosaccahryl 1,2-*trans* aminooxy glycosides

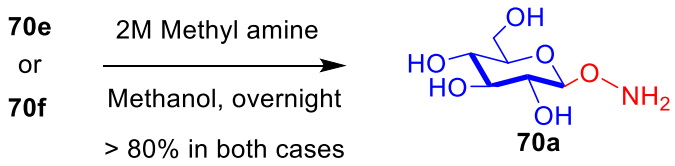


In this regard, a recent observation that 1,2-orthoesters of oligosaccharides (see chapter 2) from *n*-pentenyl glycosides in two steps will be of immense importance. Accordingly, propargyl 1,2-*O*-orthoester (**79a** and **80a**) was treated with *N*-hydroxy succinimide and 4 Å MS powder in the presence of catalytic amount of gold bromide and silver triflate as an additive in dichloromethane at room temperature to acquire oligosaccahryl 1,2-*trans* aminooxy glycosides (**79b** and **80b**) in very good yield. The use of the silver triflate as an additive is advantageous for the following reasons: 1) number of disarmed sugar residues and sterics decrease the reactivity of 1,2-*O*-orthoester, and 2) the combination of gold (III) and silver (I) catalyst increases the binding affinity towards the alkyne moiety to hold the alkyne in complex form and further increase the acidity resulting into the 1,2-*trans* product. Both of the aminooxy oligosaccharides were confirmed on the basis of NMR and mass spectrometric tools. In the ^{1}H NMR spectrum of **80b**, the four anomeric proton resonances were noticed as individual singlets at δ 5.28, 5.29, 5.50, and 5.79 ppm. The succinimidyl methylenes were noticed as singlets at δ 2.65 ppm. In the ^{13}C NMR spectrum of **80b**, the anomeric carbons were noticed at δ 105.7, 105.8, 105.9, and 108.2 ppm. Two methylenes and two amido groups of succinimidyl group were noticed at δ 25.4 (2C) and 171.0 (2C) ppm which confirmed the formation of compound **80b**.

1C.2.4 – Deprotection of benzoate and succinimide group

Ligation to other biomolecules requires free amino group at the reducing end. Deprotection of the succinimidyl moiety and benzoate groups present in the glycosides **70e** and **70f** can be affected by standard procedure using 2M methyl amine in methanol.[9] Accordingly, the aminooxy glycoside **70e**/**70f** was treated with 2M methyl amine in methanol at room temperature for 2 h and then the reaction mixture was refluxed for 24 h. The reaction proceeded well and gave aminooxy glucopyranoside (**70a**) in 85% yield from succinimidate and 80% from pthalimidate.

Scheme 1C.4: Global deprotection of aminooxy glucopyranoside



Complete deprotection of imido group on amine and benzoyl group was achieved in one step by using an excess of 2M methyl amine in methanol (**Scheme 1C.4**). The free amine could be useful for the synthesis of oxime-based glycoproteins, dendrimers, and fluorescent sugar molecule.

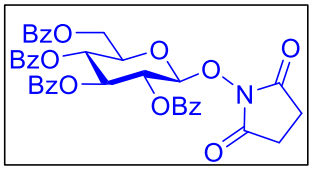
1C.5 – Conclusion

In summary, an efficient gold(III) catalyzed synthesis of 1,2-*trans* aminooxy pyranosides and furanosides was identified from easily accessible propargyl 1,2-orthoesters of pyranosides and furanosides which are otherwise difficult to syntheize. Utility of developed protocol was also applicable for the synthesis of aminooxyoligosaccharides. The key glycosidation reaction is catalytic, high yielding, mild and is found to give 1,2-*trans* diastereoselectivity. In future, synthesis of calichemicin and other analogues can be prepared by the use of gold-catalysis.

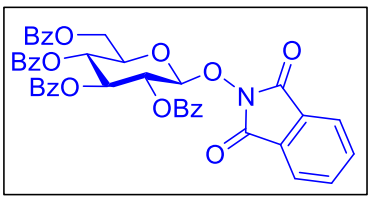
1C.6 – Experimental and characterization data

General procedure for 1,2-*trans*-glycosylation: To a CH_2Cl_2 solution (5 mL) containing glycosyl donor **21a** (0.2 mmol) and glycosyl acceptor **77a** (0.3 mmol)) with 4 Å MS powder (100 mg) was added a catalytic amount of $AuBr_3$ (14 µmol) (Silver triflate (7 mol%) as an additive for oligosaccharides) and stirred at room temperature. After 24 h, the reaction mixture was neutralized by the addition of Et_3N (1 mL) and filtered through a bed of celite and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography using ethyl acetate-petroleum ether to obtain **70e** (70%).

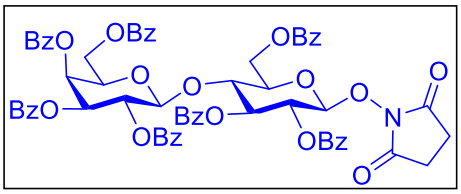
Succinimidyl-2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (**70e**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.6): –35.4º; IR (cm^{-1}, $CHCl_3$): 3067, 2947, 1733, 1596, 1454, 1276, 1102, 710; ^1H NMR (399.78 MHz, $CDCl_3$): δ 2.51 – 2.68 (m, 4H), 4.23 (d, *J* = 3.8 Hz, 1H), 4.53 – 4.70 (m, 2H), 5.48 (d, *J* = 7.5 Hz, 1H), 5.78 (t, *J* = 8.9 Hz, 2H), 5.93 (t, *J* = 9.2 Hz, 1H), 7.15 – 7.61 (m, 12H), 7.86 (d, *J* = 7.5 Hz, 2H), 7.90 (d, *J* = 7.6 Hz, 2H), 7.97 (d, *J* = 7.6 Hz, 2H), 8.04 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 25.2, 25.2, 63.1, 69.6, 70.3, 72.4, 72.7, 103.2, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.5, 128.9, 129.4, 129.7, 129.7, 129.8, 128.8, 129.8, 129.8, 130.0, 130.0, 133.2, 133.4, 133.4, 133.5, 165.1, 165.1, 165.6, 165.9, 169.9, 169.9; HRMS (Waters Synapt G2): m/z calcd for $[C_{38}H_{31}NO_{12}+Na]^+$: 716.1744; Found: 716.1736.



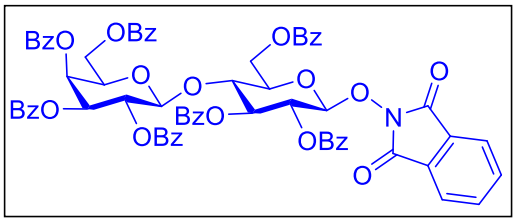
Phthalimidyl-2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (**70f**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) –21.4º; IR (cm^{-1}, $CHCl_3$): 3065, 2926, 1725, 1591, 1454, 1267, 1110, 714; ^1H NMR (399.78 MHz, $CDCl_3$): δ 4.23 (dt, *J* = 9.5, 4.7 Hz, 1H), 4.62 (d, *J* = 4.0 Hz, 2H), 5.81 (t, *J* = 9.6 Hz, 1H), 5.86 (t, 1H), 5.97 (t, *J* = 9.3 Hz, 1H), 7.20 – 7.59 (m, 13H), 7.69 – 7.94 (m, 10H), 8.04 – 8.14 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 63.2, 69.6, 70.2, 72.6, 72.8, 104.5, 123.8, 123.8, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.6, 128.6, 129.0, 129.4, 129.6, 129.6, 129.8, 129.8, 129.8, 129.8, 130.0, 130.0, 132.9, 133.4, 133.4, 133.5, 134.6, 134.6, 162.5, 162.5, 165.1, 165.1, 165.6, 165.9; HRMS (Waters Synapt G2): m/z calcd for $[C_{42}H_{31}O_{12}N+Na]^+$: 764.1744; Found: 764.1731



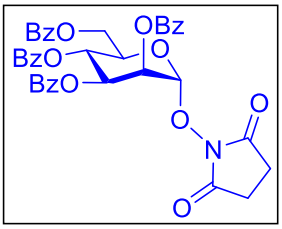
Succinimidyl-4-O-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-benzoyl-β-D-glucopyranoside (**70g**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.4) +3.6°; IR (cm^{-1}, $CHCl_3$): 3069, 2919, 1731, 1591, 1451, 1268, 1102, 711; ^1H NMR (399.78 MHz, $CDCl_3$): δ 2.54 (s, 4H), 3.68 (dd, *J* = 11.4, 6.8 Hz, 1H), 3.86 (dd, *J* = 11.3, 6.3 Hz, 1H), 3.93 – 4.04 (m, 2H), 4.48 – 4.67 (m, 3H), 4.93 (d, *J* = 8.0 Hz, 1H), 5.39 – 5.44 (m, 2H), 5.67 – 5.83 (m, 4H), 7.12 – 7.66 (m, 21H), 7.73 (d, *J* = 7.1 Hz, 2H), 7.88 – 8.07 (m, 12H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 25.2, 25.2, 61.3, 62.3, 67.6, 69.8, 70.4, 71.5, 71.7, 72.9, 73.5, 75.5, 101.1, 102.4, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.6, 128.8, 128.9, 129.3, 129.4, 129.5, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 130.0, 130.0, 130.0, 130.0, 133.2, 133.3, 133.3, 133.4, 133.5, 164.8, 165.0, 165.2, 165.2, 165.4, 165.5, 165.7, 170.0, 170.0; HRMS (Waters Synapt G2): m/z calcd for $[C_{65}H_{53}NO_{20}+Na]^+$: 1190.3059; Found: 1190.3059.



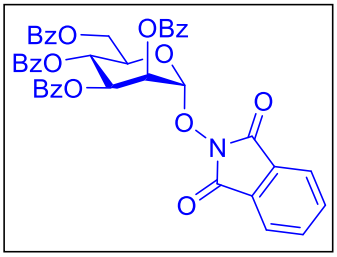
Phthalimidyl-4-O-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-benzoyl-β-D-glucopyranoside (**70h**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.4) +13.7°; IR (cm^{-1}, $CHCl_3$): 3065, 2962, 1790, 1732, 1596, 1453, 1268, 1103, 709; ^1H NMR (399.78 MHz, $CDCl_3$): δ 3.66 (dd, *J* = 11.4, 6.9 Hz, 1H), 3.83 (dd, *J* = 11.4, 6.2 Hz, 1H), 3.91 – 4.05 (m, 1H), 4.50 – 4.61 (m, 3H), 4.93 (d, *J* = 7.9 Hz, 1H), 5.38 – 5.43 (m, 1H), 5.43 (d, *J* = 7.0 Hz, 2H), 5.70 – 5.81 (m, 3H), 5.85 (t, *J* = 8.5 Hz, 1H), 7.12 – 7.77 (m, 25H), 7.88 – 8.12 (m, 14H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 61.3, 62.5, 67.6, 69.8, 70.3, 71.5, 71.7, 72.9, 73.5, 75.6, 101.0, 104.1, 123.7, 123.7, 128.2, 128.2, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.8, 129.0, 129.3, 129.4, 129.4, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 130.0, 130.0, 130.0, 130.0, 133.1, 133.2, 133.3, 133.5, 134.5, 162.4, 162.4, 164.7, 165.1, 165.2, 165.2, 165.4, 165.6, 165.7; HRMS (Waters Synapt G2): m/z calcd for $[C_{69}H_{53}NO_{20}+Na]^+$: 1238.3059; Found: 1238.3059.



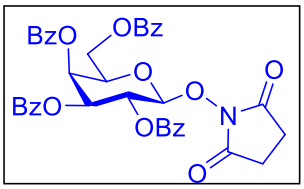
Succinimidyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranoside (**70i**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.5) –6.4°; IR (cm-1, $CHCl_3$): 3072, 2923, 1730, 1593, 1451, 1268, 1103, 710; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 2.75 (s, 4H), 4.45 (dd, *J* = 12.5, 3.6 Hz, 1H), 4.75 (dd, *J* = 12.5, 2.2 Hz, 1H), 5.27 (dt, *J* = 10.3, 2.9 Hz, 1H), 5.62 (d, *J* = 1.6 Hz, 1H), 5.95 (dd, *J* = 10.1, 3.4 Hz, 1H), 6.09 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.21 (t, *J* = 10.3 Hz, 1H), 7.24 – 7.65 (m, 12H), 7.78 – 7.89 (m, 2H), 7.95 – 8.03 (m, 4H), 8.11 – 8.19 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 25.4, 25.4, 62.0, 65.7, 68.0, 69.5, 71.2, 101.5, 128.3, 128.3, 128.5, 128.5, 128.5, 128.5, 128.6, 128.6, 128.7, 129.8, 129.7, 129.7, 129.7, 129.8, 129.8, 129.8, 129.9, 129.9, 129.9, 129.9, 133.1, 133.2, 133.5, 133.6, 164.7, 165.3, 165.3, 166.0, 170.4, 170.4; HRMS (Waters Synapt G2): m/z calcd for $[C_{38}H_{31}O_{12}N+Na]^+$: 716.1744; Found: 716.1727.



Phthalimidyl-2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranoside (**70j**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 2.3) –8.4°; IR (cm^{-1}, $CHCl_3$): 3068, 2925, 1729, 1594, 1450, 1268, 1107, 715; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 4.50 (dd, *J* = 12.5, 3.9 Hz, 1H), 4.83 (d, *J* = 12.3 Hz, 1H), 5.43 (d, *J* = 10.3 Hz, 1H), 5.72 (s, 1H), 6.04 (dd, *J* = 10.1, 3.1 Hz, 1H), 6.16 – 6.22 (m, 1H), 6.26 (t, *J* = 10.3 Hz, 1H), 7.22 – 7.63 (m, 12H), 7.67 – 7.90 (m, 6H), 8.03 (d, *J* = 7.3 Hz, 4H), 8.12 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 62.2, 65.8, 68.0, 69.6, 71.1, 102.4, 123.7, 128.2, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.5, 128.7, 128.8, 129.6, 129.7, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 129.8, 132.9, 133.0, 133.2, 133.3, 133.5, 133.6, 134.7, 134.7, 162.8, 162.9, 164.7, 165.3, 165.3, 166.0; HRMS (Waters Synapt G2): m/z calcd for $[C_{42}H_{31}O_{12}N+Na]^+$: 764.1744; Found: 764.1740.

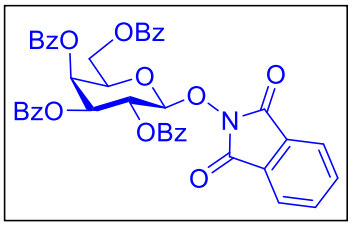


Succinimidyl-2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside (**70k**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.4) +6.2°; IR (cm^{-1}, $CHCl_3$): 3065, 2928, 1731, 1594, 1452, 1270, 1103, 711; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 2.56 – 2.74 (m, 4H), 4.33 (t, *J* = 7.3 Hz, 1H), 4.41 (dd, *J* = 11.2, 7.2 Hz, 1H), 4.73 (dd, *J* = 11.2, 6.3 Hz, 1H), 5.37 (d, *J* = 8.3 Hz, 1H), 5.62 (dd, *J* = 10.3, 3.5 Hz, 1H), 5.95 – 6.04 (m, 2H), 7.17 – 7.68 (m, 12H), 7.76 – 7.81 (m, 2H), 7.95 – 8.16 (m, 6H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 25.3, 25.3, 61.2, 67.3, 67.8, 71.4, 71.9, 104.4, 128.3, 128.3, 128.3, 128.3, 128.5, 128.5,

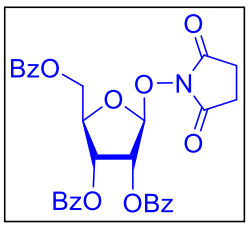


128.5, 128.6, 128.6, 129.1, 129.2, 129.8, 129.8, 129.8, 129.8, 129.8, 130.0, 130.0, 130.1, 130.1, 133.3, 133.4, 133.4, 133.7, 165.3, 165.4, 165.6, 165.9, 169.9, 169.9; HRMS (Waters Synapt G2): m/z calcd for $[C_{38}H_{31}O_{12}N+Na]^+$: 716.1744; Found: 716.1737.

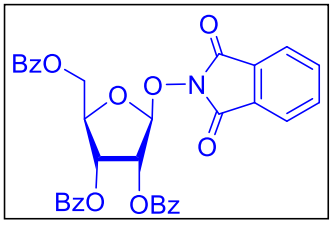
Phthalimidyl-2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside (**70l**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +10.0º; IR (cm^{-1}, $CHCl_3$): 3068, 2925, 1729, 1594, 1450, 1268, 1107, 715; ^1H NMR (399.78 MHz, $CDCl_3$): δ 4.34 (t, *J* = 6.7 Hz, 1H), 4.45 (dd, *J* = 11.2, 7.0 Hz, 1H), 4.70 (dd, *J* = 11.3, 6.5 Hz, 1H), 5.45 (d, *J* = 8.3 Hz, 1H), 5.65 (dd, *J* = 10.3, 3.5 Hz, 1H), 6.02 (d, *J* = 3.4 Hz, 1H), 6.06 (dd, *J* = 10.3, 8.3 Hz, 1H), 7.22 – 7.29 (m, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.37 – 7.56 (m, 7H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.74 (dd, *J* = 5.3, 3.2 Hz, 2H), 7.81 (td, *J* = 5.5, 2.2 Hz, 4H), 7.90 – 7.94 (m, 2H), 8.07 – 8.16 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 61.4, 67.4, 67.9, 71.6, 72.0, 105.4, 123.8, 123.8, 128.3, 123.3, 123.3, 128.3, 128.4, 128.4, 128.5, 128.6, 128.6, 128.7, 128.7, 128.7, 129.2, 129.2, 129.7, 129.7, 129.8, 129.8, 130.0, 130.0, 130.2, 130.2, 133.2, 133.3, 133.4, 133.7, 134.7, 134.7, 162.5, 162.5, 165.4, 165.4, 165.6, 165.9; HRMS (Waters Synapt G2): m/z calcd for $[C_{42}H_{31}O_{12}N+Na]^+$: 764.1744; Found: 764.1740.



Succinimidyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranoside (**78a**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2): –27.8º; IR (cm^{-1}, $CHCl_3$): 3076, 2943, 1730, 1592, 1449, 1271, 1107, 711; ^1H NMR (399.78 MHz, $CDCl_3$): δ 2.74 (s, 4H), 4.66 – 4.79 (m, 1H), 4.83 (d, *J* = 8.5 Hz, 1H), 4.88 (dd, *J* = 11.0, 4.2 Hz, 1H), 5.90 (s, 1H), 5.91 – 5.97 (m, 2H), 7.20 – 7.61 (m, 9H), 7.84 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.95 (dd, *J* = 8.2, 1.1 Hz, 2H), 8.00 (dd, *J* = 8.1, 1.1 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 25.5, 25.5, 65.1, 72.1, 73.8, 81.0, 107.7, 128.2, 128.2, 128.3, 128.3, 128.5, 128.5, 128.6, 128.6, 129.6, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 133.0, 133.4, 133.6, 164.8, 165.0, 166.0, 170.8, 170.8; HRMS (Waters Synapt G2): m/z calcd for $[C_{30}H_{25}O_{10}N+Na]^+$: 582.1376; Found: 582.1379.

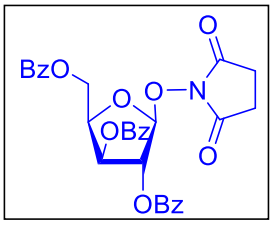


Phthalimidyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranoside (**78b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) –20.6º; IR (cm^{-1}, $CHCl_3$): 3072, 2955, 1791, 1733, 1596, 1455, 1272, 1109, 707; ^1H NMR (399.78 MHz, $CDCl_3$): δ 4.88 (s, 1H), 4.83 – 4.97 (m, 2H), 5.97 (s, 1H), 6.04 (t, *J* = 6.0 Hz, 1H), 6.08 (d, *J* = 5.0 Hz, 1H), 7.27 – 7.64 (m, 9H),

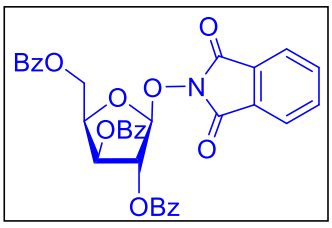


7.75 (dd, *J* = 5.5, 3.2 Hz, 2H), 7.81 – 7.91 (m, 4H), 7.97 – 8.05 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 65.2, 72.4, 73.9, 80.9, 109.1, 123.7, 128.2, 128.2, 128.3, 128.3, 128.5, 128.5, 128.6, 128.7, 128.8, 128.8, 129.6, 129.7, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 132.9, 133.4, 133.6, 134.6, 134.6, 163.1, 163.2, 164.8, 165.1, 166.1; HRMS (Waters Synapt G2): m/z calcd for $[C_{34}H_{25}O_{10}N+Na]^+$: 607.1478; Found: 630.1375

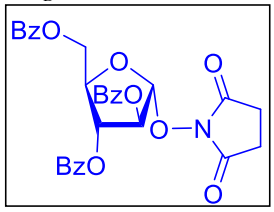
Succinimidyl-2,3,5-tri-*O*-benzoyl-β-D-xylofuranoside (**78c**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.6) –49.8°; IR (cm^{-1}, $CHCl_3$): 3071, 2956, 1791, 1732, 1596, 1455, 1272, 1109, 707; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 2.78 (s, 4H), 4.76 (dd, *J* = 11.7, 5.2 Hz, 1H), 4.94 (dd, *J* = 11.7, 7.2 Hz, 1H), 5.08 (t, *J* = 7.0, 5.2 Hz, 1H), 5.80 (s, 1H), 5.90 (s, 1H), 5.92 (d, *J* = 5.2 Hz, 1H), 7.35 – 7.67 (m, 9H), 7.95 – 8.08 (m, 4H), 8.23 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 25.5, 25.5, 62.9, 73.9, 79.1, 81.9, 108.1, 128.3, 128.3, 128.4, 128.5, 128.5, 128.6, 128.6, 128.8, 129.6, 129.7, 129.7, 130.0, 130.0, 130.3, 130.3, 133.1, 133.6, 133.9, 164.7, 165.2, 166.1, 170.9, 170.9; HRMS (Waters Synapt G2): m/z calcd for $[C_{30}H_{25}O_{10}N+Na]^+$: 582.1376; Found: 582.1374.



Phthalimidyl-2,3,5-tri-*O*-benzoyl-β-D-xylofuranoside (**78d**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.3) –77.1°; IR (cm^{-1}, $CHCl_3$): 3076, 2928, 1728, 1591, 1452, 1265, 1105, 712 ; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 4.84 (dd, *J* = 11.6, 5.5 Hz, 1H), 4.94 (dd, *J* = 11.6, 7.0 Hz, 1H), 5.02 – 5.11 (m, 1H), 5.87 (s, 1H), 5.91 (s, 2H), 7.09 – 7.63 (m, 11H), 7.63 – 8.32 (m, 8H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 63.0, 74.0, 79.1, 81.9, 109.4, 123.8, 123.8, 128.4, 128.4, 128.4, 128.6, 128.6, 128.6, 128.7, 128.9, 129.1, 129.1, 129.7, 129.8, 129.8, 130.1, 130.1, 130.3, 130.4, 133.1, 133.7, 133.9, 134.6, 134.6, 163.3, 163.4, 164.6, 165.3, 166.2; HRMS (Waters Synapt G2): m/z calcd for $[C_{34}H_{25}O_{10}N+Na]^+$: 630.1376; Found: 630.1370.

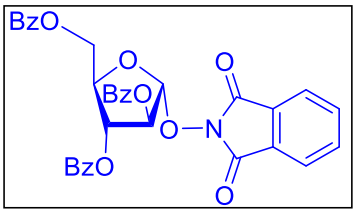


Succinimidyl 2,3,5-tri-*O*-benzoyl-α-D-arabinofuranoside (**78e**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.3) +34.0°; IR (cm^{-1}, $CHCl_3$): 3065, 2933, 1790, 1728, 1597, 1450, 1270, 1108, 713; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 2.73 (s, 4H), 4.66 (dd, *J* = 12.3, 4.3 Hz, 1H), 4.83 (dd, *J* = 12.3, 3.1 Hz, 1H), 5.14 (q, *J* = 4.4 Hz, 1H), 5.66 (d, *J* = 5.0 Hz, 1H), 5.81 (d, *J* = 1.2 Hz, 1H), 5.88 (s, 1H), 7.22 (t, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.45 (q, *J* = 7.5 Hz, 3H), 7.56 (q, *J* = 7.6 Hz, 2H), 7.91 – 7.96 (m, 2H), 7.96 – 8.00 (m,

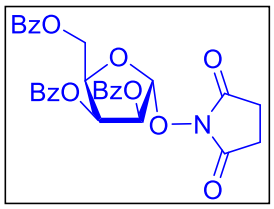


2H), 8.07 – 8.13 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 25.5, 25.2, 62.9, 77.1, 80.3, 83.6, 108.2, 128.2, 128.2, 128.4, 128.4, 128.5, 128.5, 128.5, 128.9, 129.5, 129.7, 129.7, 129.9, 129.9, 130.0, 130.0, 133.0, 133.6, 133.6, 165.0, 165.8, 166.0, 170.9, 170.9; HRMS (Waters Synapt G2): m/z calcd for $[C_{30}H_{25}O_{10}N+Na]^+$: 582.1376; Found: 582.1383

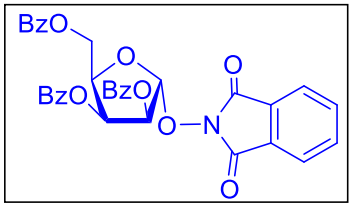
Phthalimidyl-2,3,5-tri-*O*-benzoyl-α-D-arabinofuranoside (**78f**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.6) +36.6°; IR (cm^{-1}, $CHCl_3$): 3056, 2986, 1788, 1730, 1592, 1453, 1270, 1109, 708; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 4.68 (dd, *J* = 12.3, 4.5 Hz, 1H), 4.85 (dd, *J* = 12.3, 3.2 Hz, 1H), 5.25 (q, *J* = 4.5 Hz, 1H), 5.69 (dd, *J* = 5.0, 0.7 Hz, 1H), 5.90 (d, *J* = 1.2 Hz, 1H), 5.94 (s, 1H), 7.21 (t, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 3H), 7.57 (q, *J* = 7.6 Hz, 2H), 7.74 (dq, *J* = 6.7, 3.8 Hz, 2H), 7.82 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.94 – 8.01 (m, 4H), 8.09 – 8.16 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 63.0, 77.2, 80.3, 83.5, 109.1, 123.6, 123.6, 128.2, 128.2, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.9, 128.9, 129.5, 129.7, 128.7, 129.9, 129.9, 130.0, 130.0, 133.0, 133.6, 133.6, 134.5, 134.5, 163.3, 163.3, 165.0, 165.8, 166.1; HRMS (Waters Synapt G2): m/z calcd for $[C_{34}H_{25}O_{10}N+Na]^+$: 630.1376; Found: 630.1368.



Succinimidyl 2,3,5-tri-*O*-benzoyl-α-D-lyxofuranoside (**78g**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) +70.5°; IR (cm^{-1}, $CHCl_3$): 3066, 2953, 1729, 1592, 1451, 1270, 1107, 711; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 2.54 – 2.96 (m, 4H), 4.65 (dABq, *J* = 18.9, 11.7, 7.0 Hz, 2H), 5.27 (dt, *J* = 6.7, 5.0 Hz, 1H), 5.94 (dd, *J* = 5.7, 0.9 Hz, 1H), 5.97 (s, 1H), 6.19 (t, *J* = 5.5 Hz, 1H), 7.18 – 7.59 (m, 9H), 7.81 – 7.93 (m, 4H), 8.00 (dd, *J* = 8.3, 1.2 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 25.4, 25.4, 62.3, 71.5, 75.0, 78.7, 107.5, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 129.5, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 133.1, 133.5, 133.5, 164.7, 165.0, 166.0, 170.9, 170.9; HRMS (Waters Synapt G2): m/z calcd for $[C_{30}H_{25}O_{10}N+Na]^+$: 582.1376; Found: 582.1386.

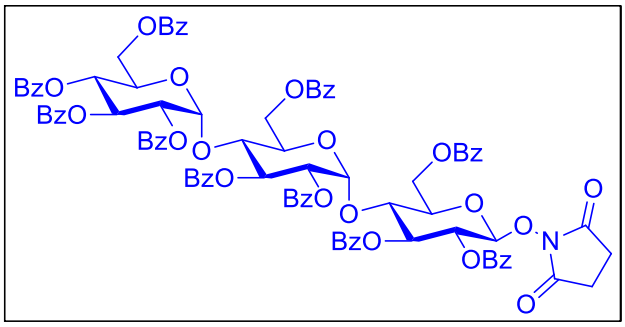


Phthalimidyl-2,3,5-tri-*O*-benzoyl-α-D-lyxofuranoside (**78h**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +54.9°; IR (cm^{-1}, $CHCl_3$): 3066, 2956, 1732, 1592, 1453, 1270, 1118, 707; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 4.64 (d, *J* = 1.9 Hz, 1H), 4.66 (s, 1H), 5.36 (d, *J* = 6.2 Hz, 1H), 5.99 (s, 1H), 6.01 (dd, *J* = 5.3, 1.1 Hz, 1H), 6.22 (t,

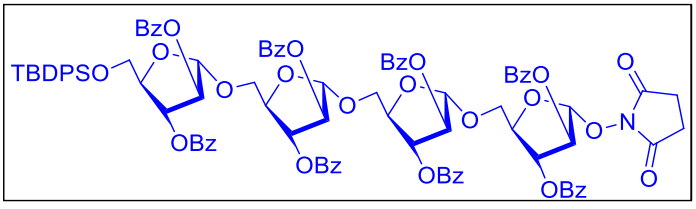


J = 5.4 Hz, 1H), 7.20 – 7.39 (m, 6H), 7.49 (dt, *J* = 14.2, 7.3 Hz, 3H), 7.71 – 7.81 (m, 4H), 7.85 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.90 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.98 (dd, *J* = 8.2, 1.1 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 62.4, 71.6, 75.1, 78.6, 108.6, 123.6, 123.6, 128.2, 128.2, 128.4, 128.4, 128.4, 128.4, 128.5, 128.6, 128.9, 129.6, 129.7, 129.7, 129.8, 129.8, 129.8, 129.8, 133.0, 133.5, 133.6, 134.3, 134.5, 134.5, 163.2, 163.2, 164.7, 165.1, 166.1; HRMS (Waters Synapt G2): m/z calcd for $[C_{34}H_{25}O_{10}N+Na]^+$: 630.1376; Found: 630.1381.

Succinimidyl-2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl)-α-D-glucopyranosyl)-β-D-glucopyranoside (**79b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +44.1°; IR (cm^{-1}, $CHCl_3$): 3070, 2927, 1729, 1591, 1450, 1268, 1109, 715; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 2.48 – 2.69 (m, 4H), 4.15 – 4.32 (m, 3H), 4.35 – 4.47 (m, 2H), 4.49 (s, 1H), 4.73 (dd, *J* = 12.4, 3.5 Hz, 1H), 4.76 – 4.98 (m, 4H), 5.11 (dd, *J* = 10.1, 3.8 Hz, 1H), 5.26 (dd, *J* = 10.5, 3.9 Hz, 1H), 5.43 – 5.56 (m, 3H), 5.62 (d, *J* = 3.9 Hz, 1H), 5.67 (t, *J* = 9.8 Hz, 1H), 5.76 (d, *J* = 4.0 Hz, 1H), 5.96 (dd, *J* = 10.0, 8.7 Hz, 1H), 6.04 – 6.15 (m, 1H), 6.94 – 8.28 (m, 50H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 25.3, 25.3, 62.3, 63.2, 63.3, 69.1, 69.9, 70.0, 70.6, 70.8, 70.9, 71.7, 73.1, 73.6, 73.9, 74.9, 77.2, 96.8, 96.8, 101.5, 127.9, 128.0, 128.0, 128.1, 128.1, 128.1, 128.2, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.6, 128.6, 128.6, 128.7, 128.8, 128.9, 129.2, 129.5, 129.5, 129.5, 129.5, 129.5, 129.7, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 129.8, 129.8, 129.9, 129.9, 129.9, 129.9, 129.9, 129.9, 130.0, 130.0, 130.0, 130.0, 130.0, 130.0, 133.0, 133.0, 133.0, 133.1, 133.2, 133.2, 133.2, 133.3, 133.3, 133.4, 164.8, 164.8, 164.8, 165.0, 165.3, 165.5, 165.6, 165.8, 165.9, 166.0, 170.3, 170.3; HRMS (Waters Synapt G2) : m/z calcd for $[C_{92}H_{75}O_{28}+Na]^+$: 1664.4373; Found: 1664.4370.

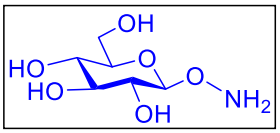


Succinimidyl-2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-O-(*t*-butyldi-phenylsilyl)-α-D-arabinofuranosyl)-α-D-



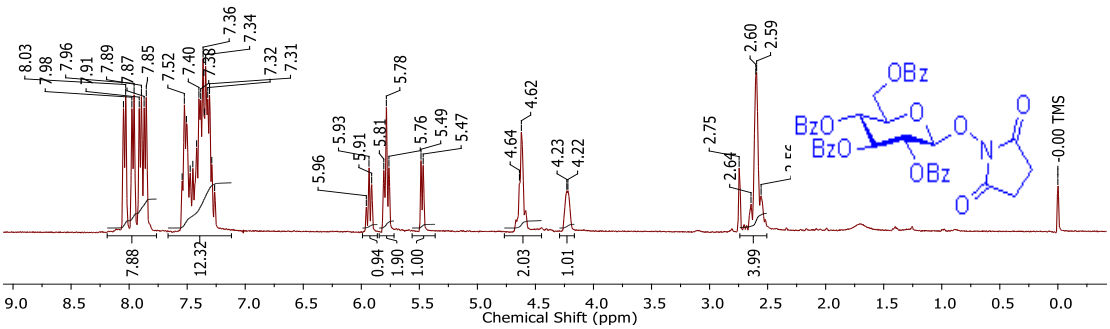
arabinofuranosyl)-α-D-arabino-furanosyl)-α-D-arabinofuranoside (**80b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +13.2º; IR (cm^{-1}, $CHCl_3$): 3068, 2931, 1727, 1596, 1456, 1265, 1109, 713; ^1H NMR (399.78 MHz, $CDCl_3$): δ 0.92 (s, 9H), 2.65 (s, 4H), 3.78 – 3.86 (m, 3H), 3.88 (d, *J* = 4.5 Hz, 2H), 4.07 (ddd, *J* = 16.5, 9.6, 5.6 Hz, 3H), 4.40 (q, *J* = 4.5 Hz, 1H), 4.51 (quintet, *J* = 3.9 Hz, 2H), 4.93 (q, *J* = 3.3 Hz, 1H), 5.28 (s, 1H), 5.29 (s, 1H), 5.31 (s, 1H), 5.48 (s, 1H), 5.50 (s, 1H), 5.52 – 5.57 (m, 4H), 5.65 (d, *J* = 5.1 Hz, 1H), 5.75 (s, 1H), 5.79 (s, 1H), 7.08 – 7.50 (m, 30H), 7.56 – 7.65 (m, 4H), 7.74 – 8.13 (m, 16H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 19.2, 25.4, 25.4, 26.7, 26.7, 26.7, 63.3, 65.0, 65.7, 65.7, 76.5, 77.1, 77.1, 77.2, 80.0, 81.4, 81.4, 82.0, 82.0, 82.0, 83.1, 84.1, 105.7, 105.8, 105.9, 108.2, 127.6, 127.6, 127.6, 127.6, 128.1, 128.1, 128.2, 128.2, 128.2, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.9, 128.9, 129.0, 129.0, 129.0, 129.1, 129.2, 129.6, 129.6, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 129.8, 129.8, 129.9, 129.9, 130.0, 130.0, 130.0, 130.0, 133.0, 133.1, 133.1, 133.2, 133.2, 133.2, 133.3, 133.3, 133.4, 133.5, 135.6, 135.6, 135.6, 135.6, 164.9, 165.1, 165.1, 165.1, 165.4, 165.5, 165.5, 165.6, 171.0, 171.0; HRMS (Waters Synapt G2) : m/z calcd for $[C_{96}H_{87}O_{27}N+Na]^+$: 1736.5132; Found: 1736.5130.

Aminooxy-β-D-glucopyranoside (**4**): $[\alpha]_D^{25}$ (H_2O, *c* 1.7) –5.9º; IR (cm^{-1}, KBr): 3345, 2931, 1265, 1109, 713; ^1H NMR (399.78 MHz, D_2O): δ 3.08 – 3.02 (m, 1H), 3.16 – 3.10 (m, 1H), 3.25 – 3.19 (m, 1H), 3.25 (t, *J* = 9.1 Hz, 1H), 3.48 (dd, *J* = 12.3, 5.9 Hz, 1H), 3.68 (dd, *J* = 12.3, 2.1 Hz, 1H), 4.32 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (100.53 MHz, D_2O): δ 60.6, 69.4, 71.6, 75.7, 75.7, 104.9; HRMS (Waters Synapt G2): m/z calcd for $[C_6H_{13}NO_6+Na]^+$: 218.0641; Found: 218.0641.

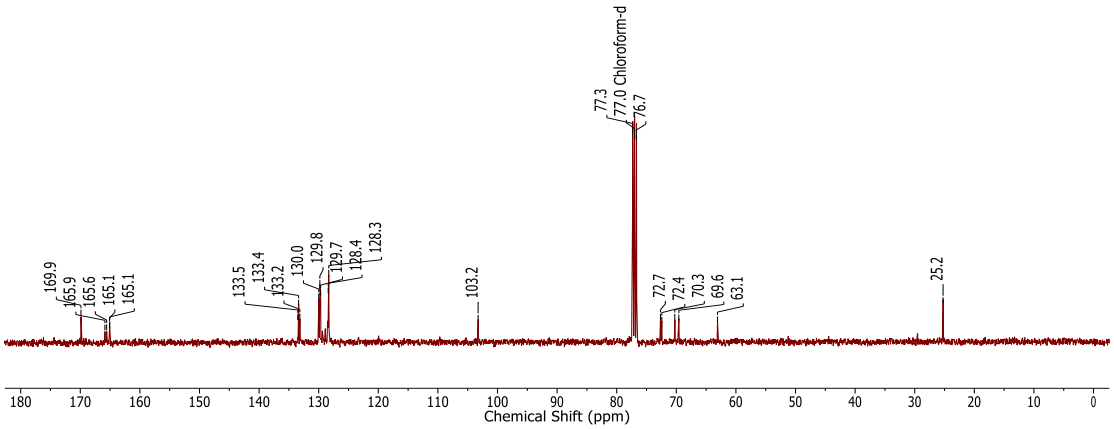


1C.7 – Spectral Charts

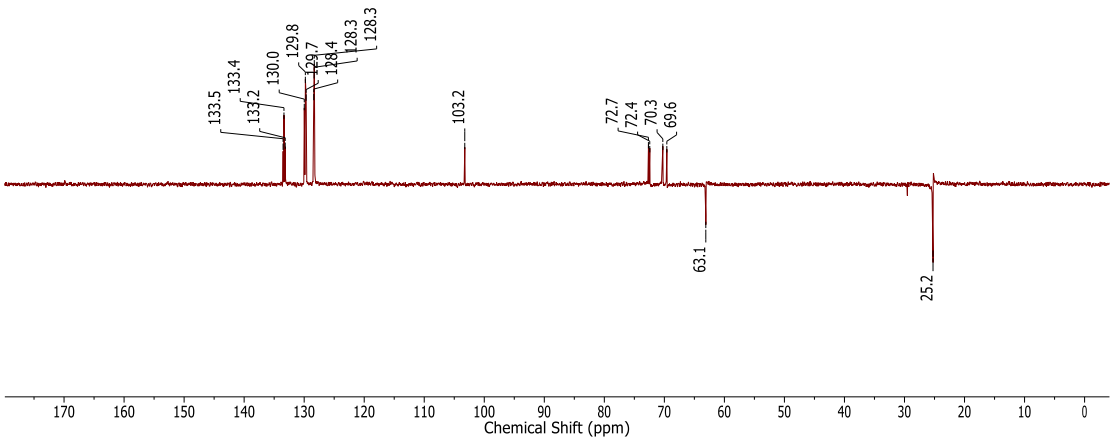
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **70e**



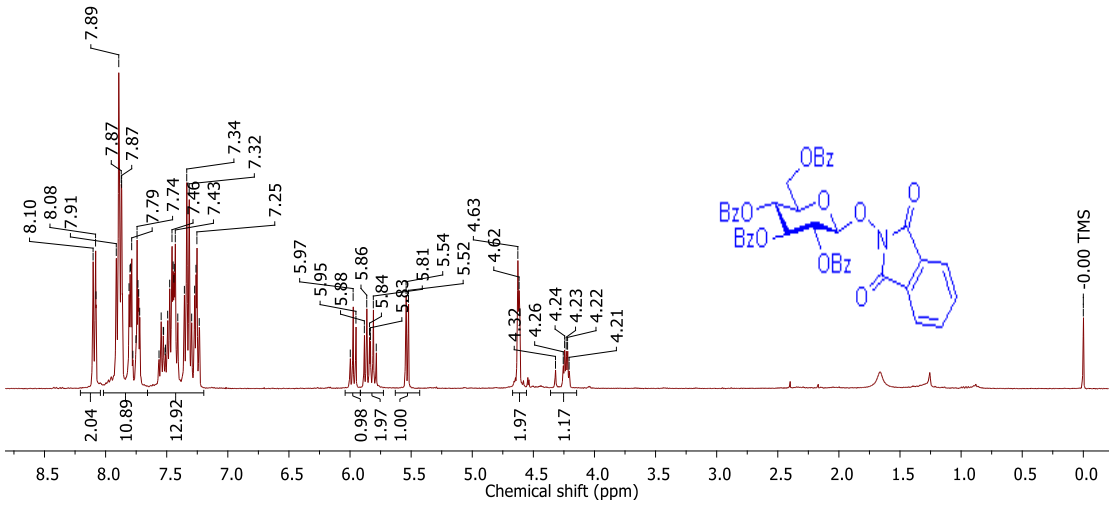
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **70e**



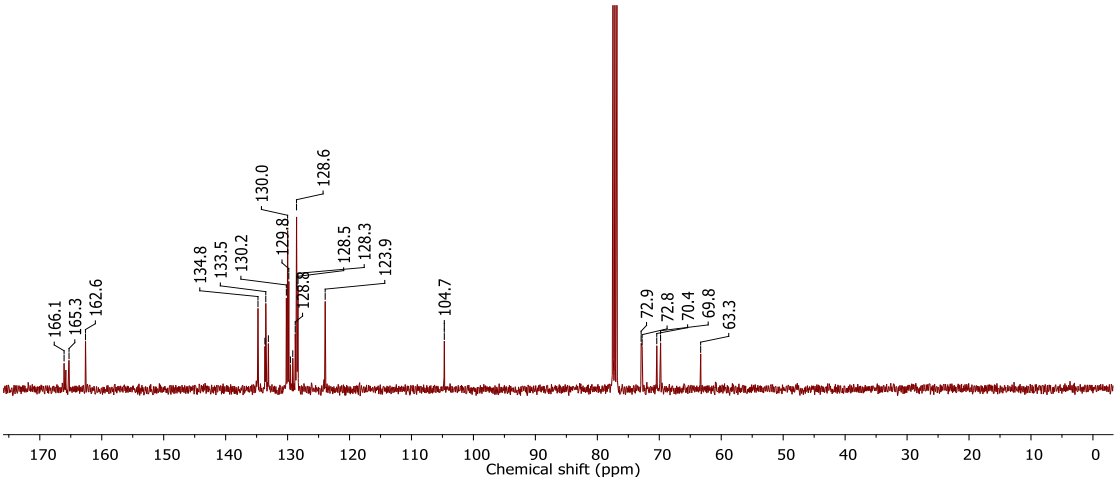
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **70e**



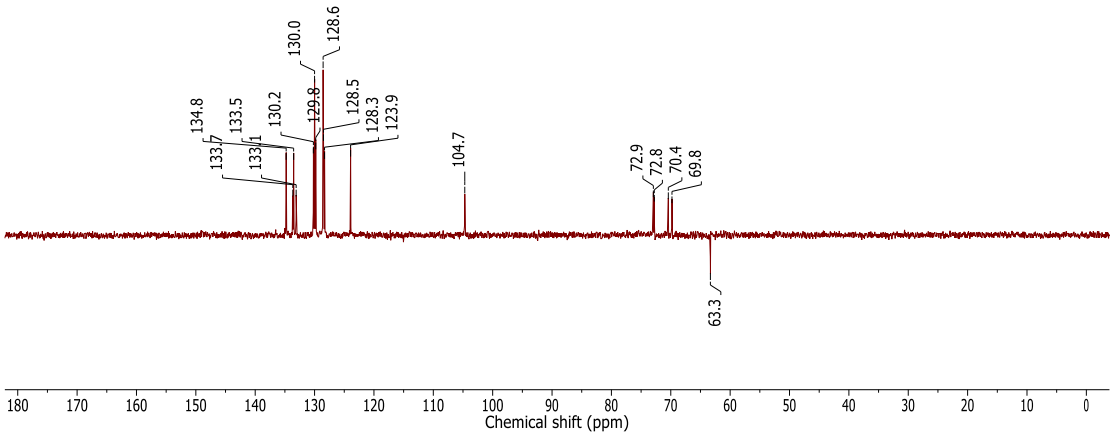
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **70f**



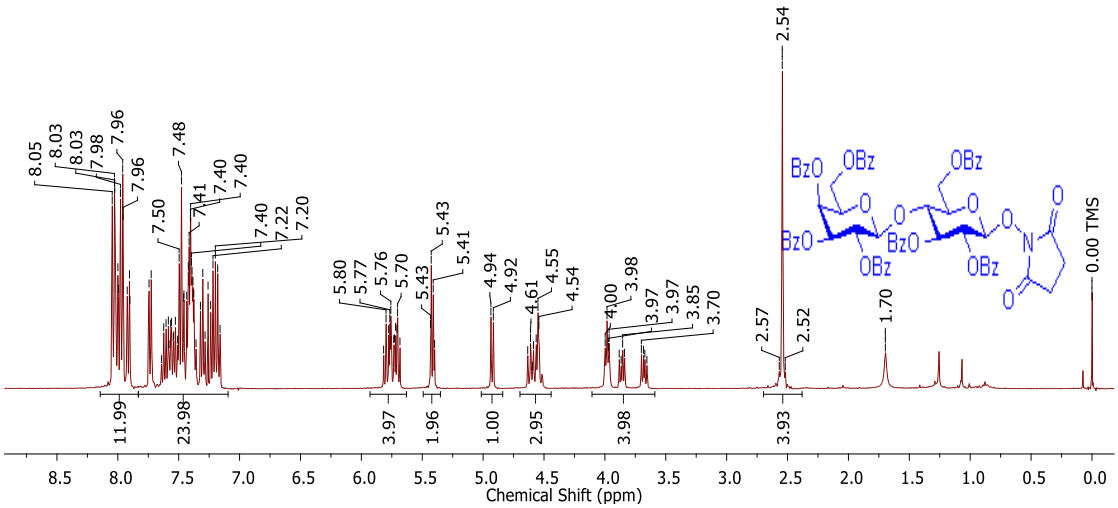
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **70f**



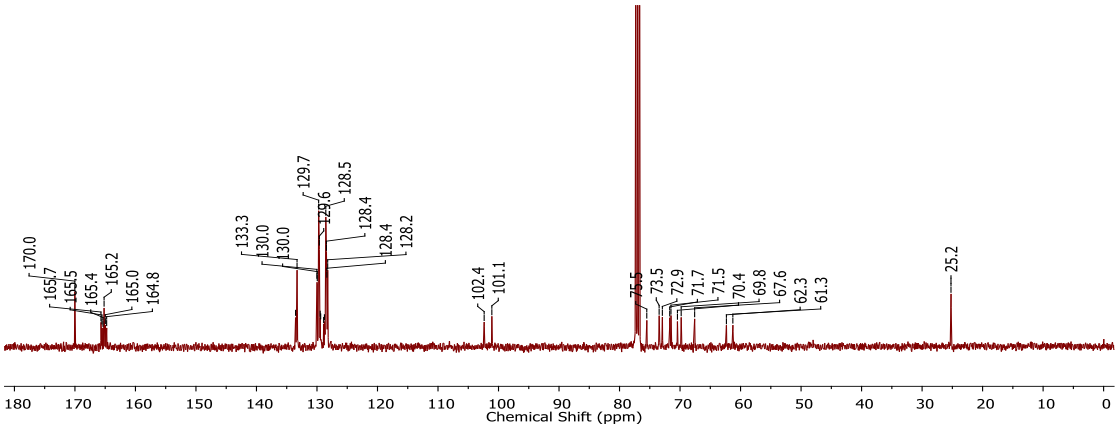
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **70f**



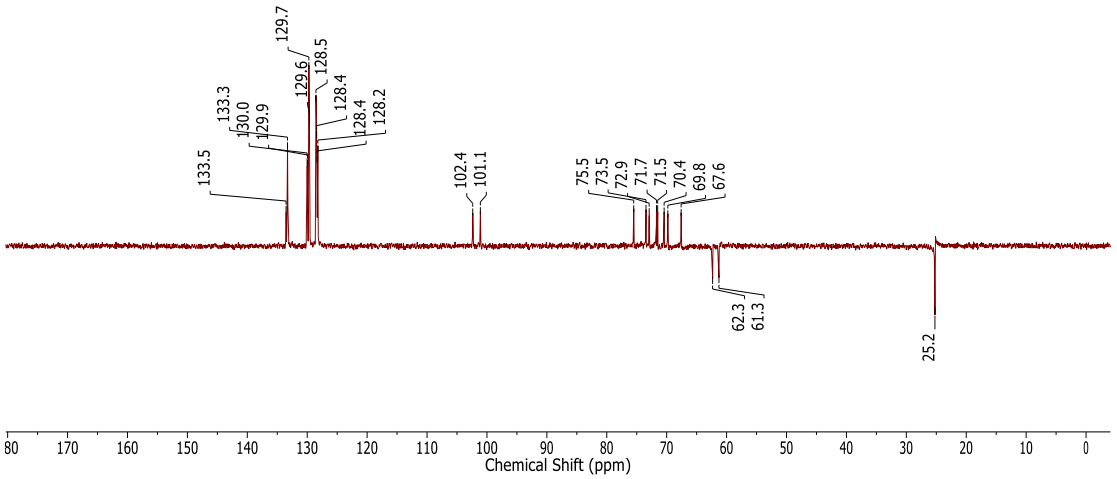
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **70g**



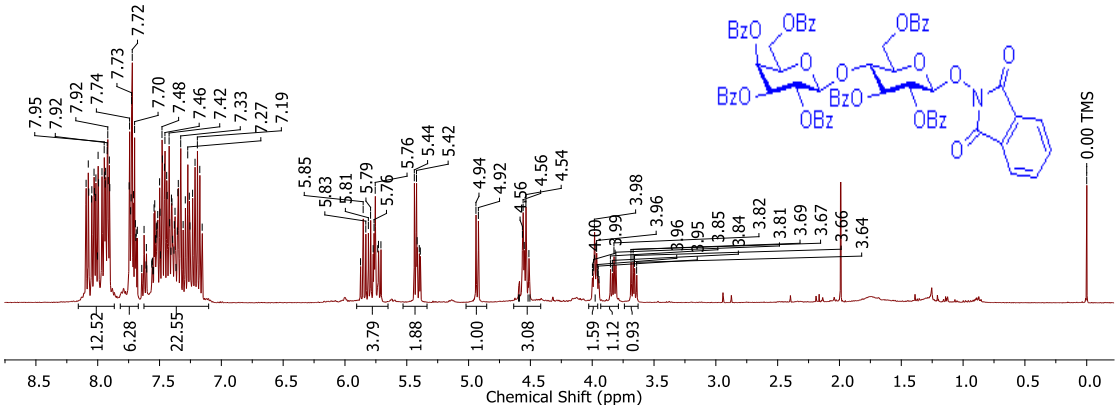
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **70g**



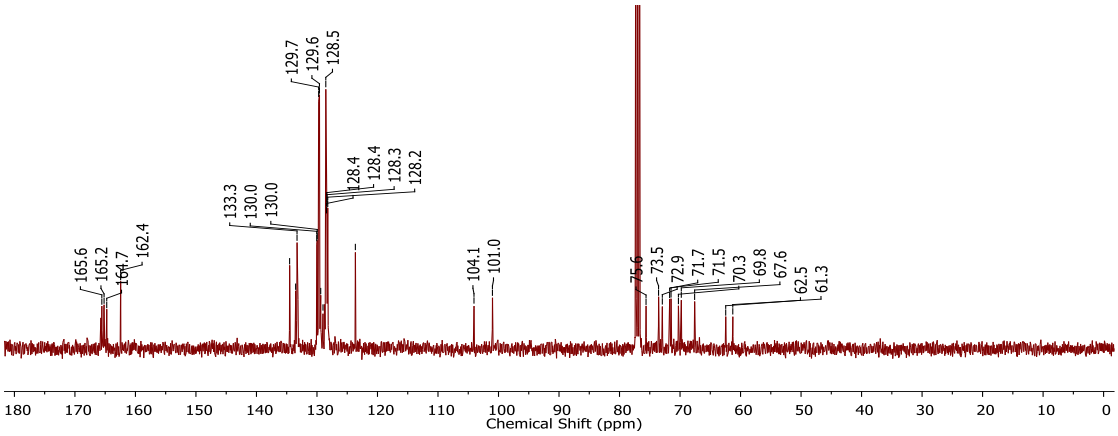
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **70g**



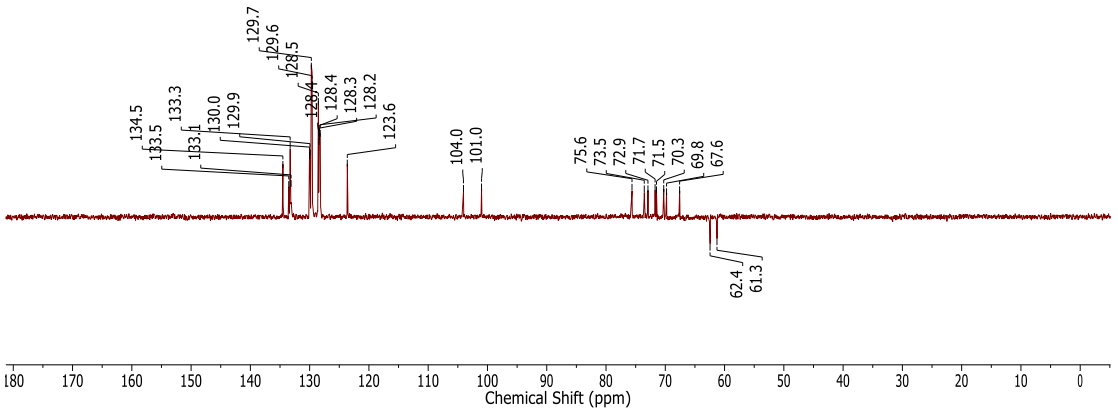
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **70h**



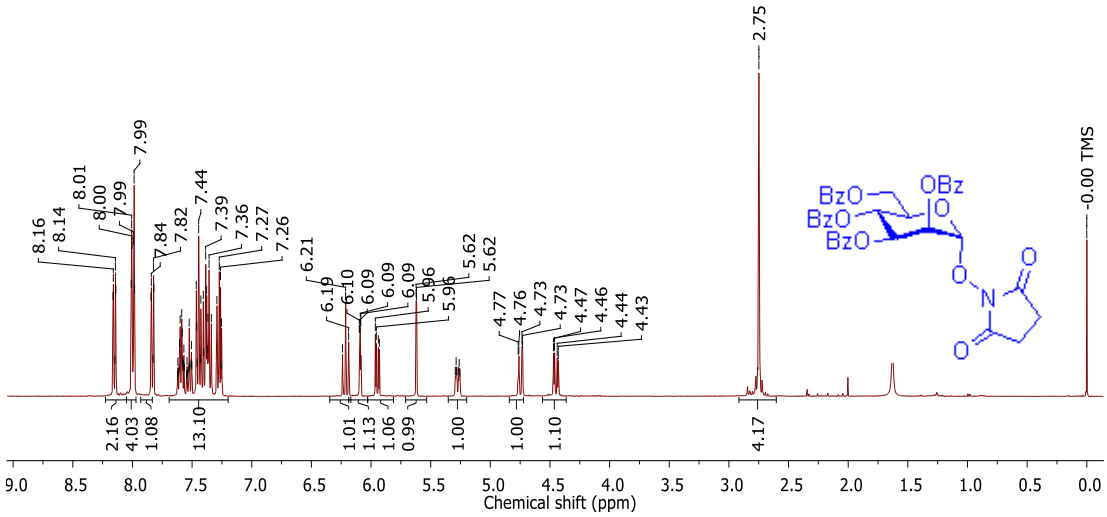
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **70h**



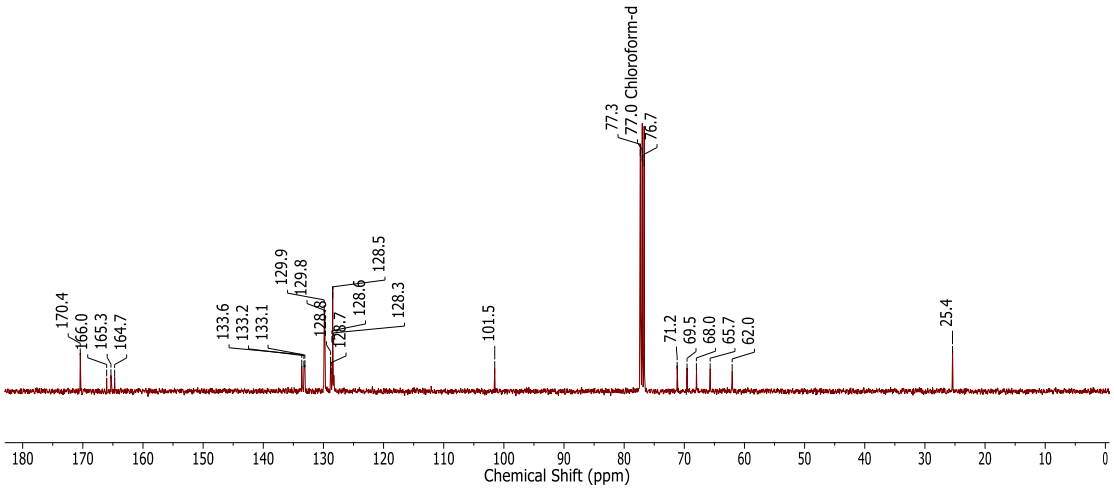
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **70h**



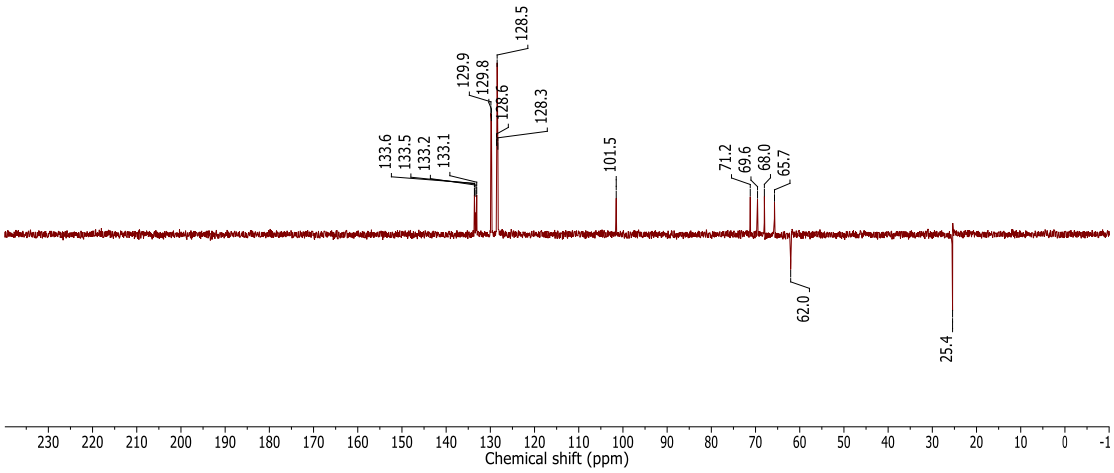
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **70i**



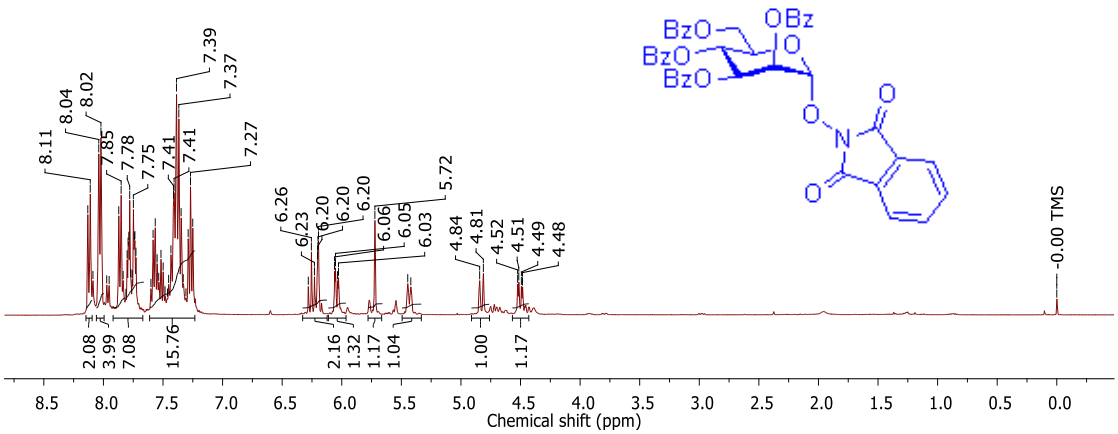
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **70i**



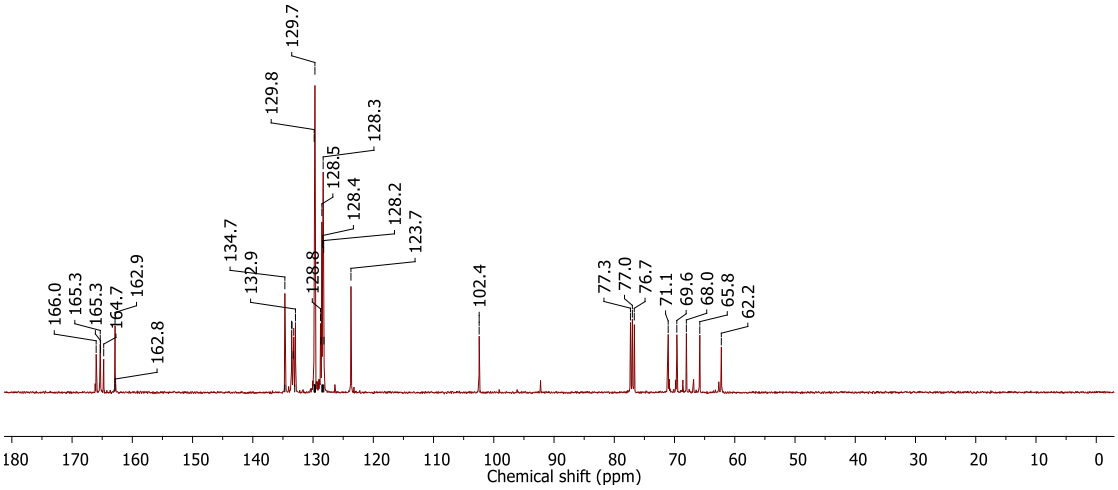
NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **70i**



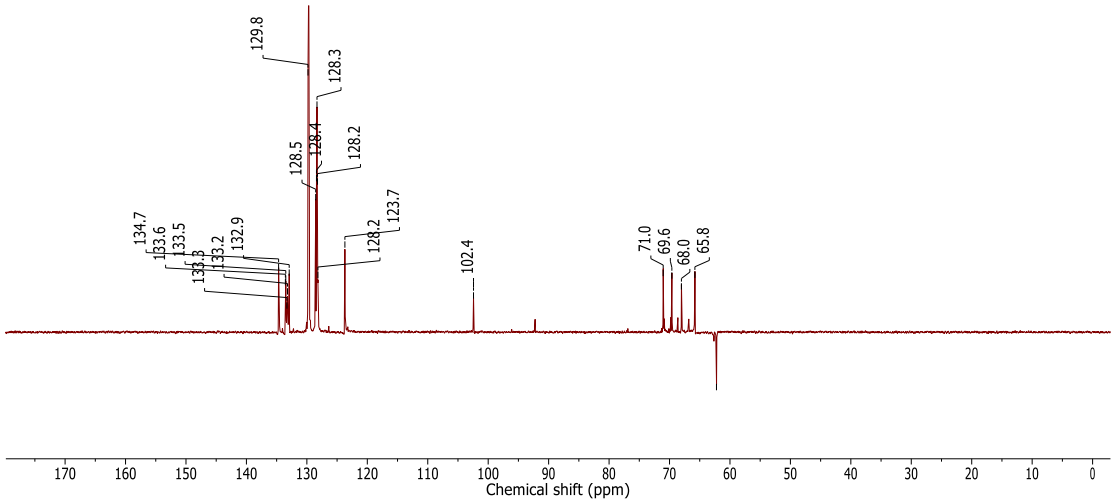
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **70j**



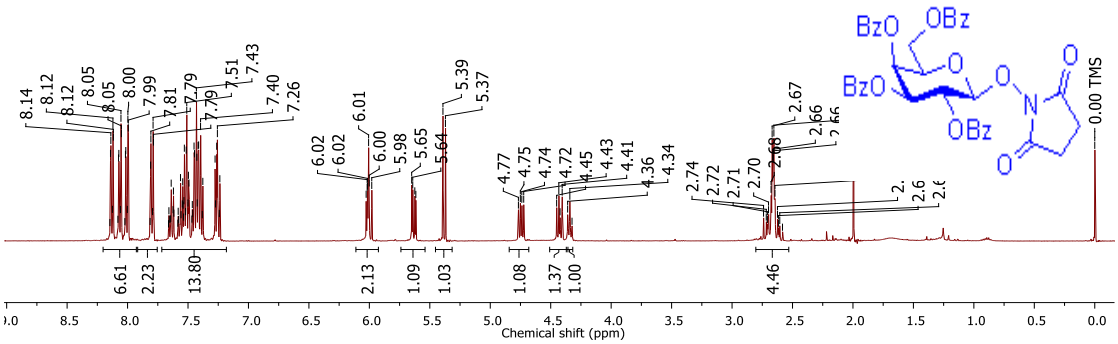
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **70j**



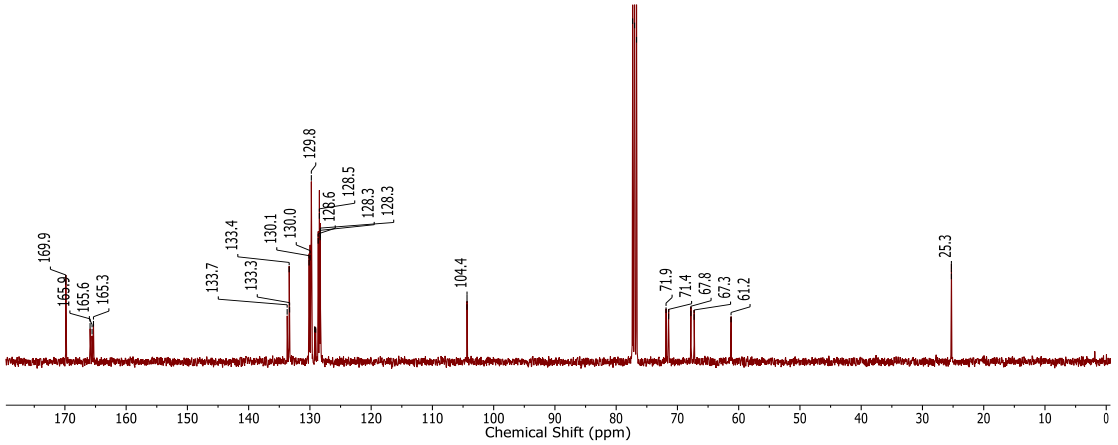
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **70j**



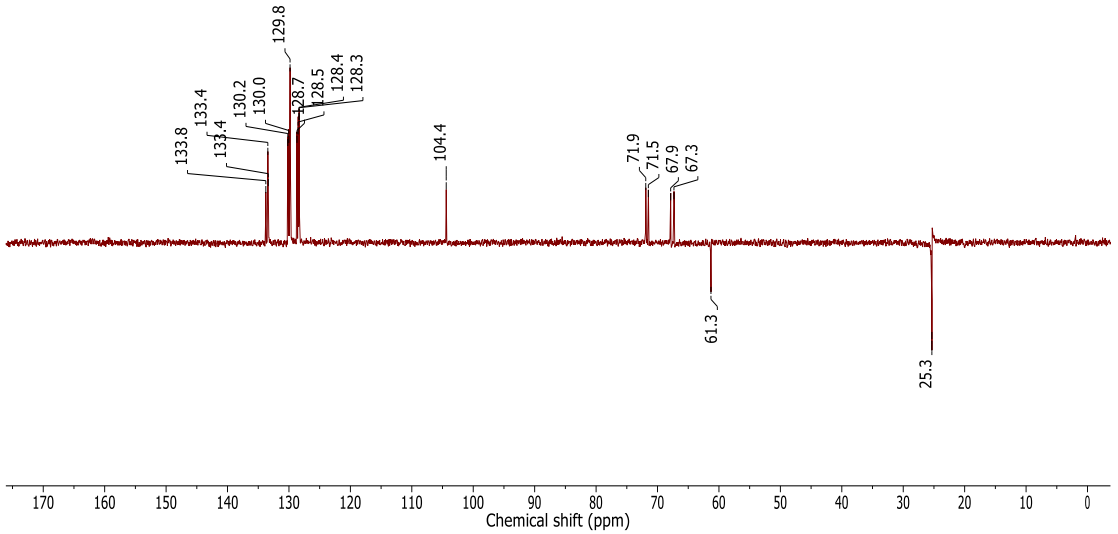
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **70k**



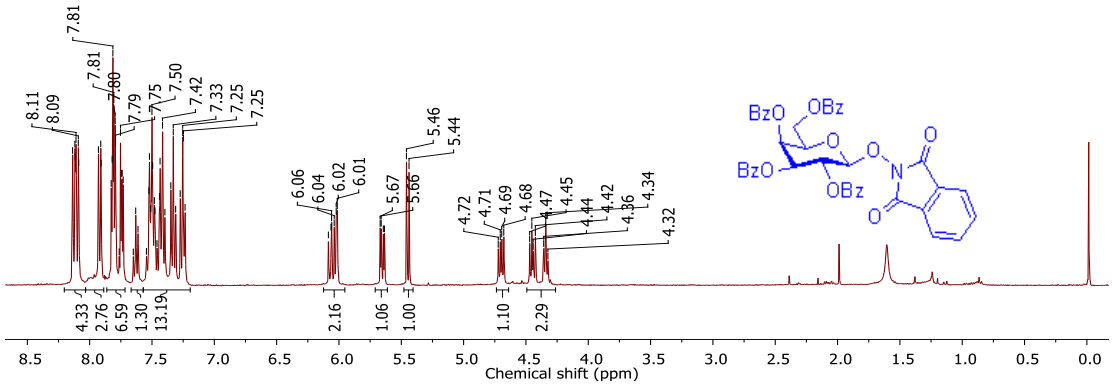
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **70k**



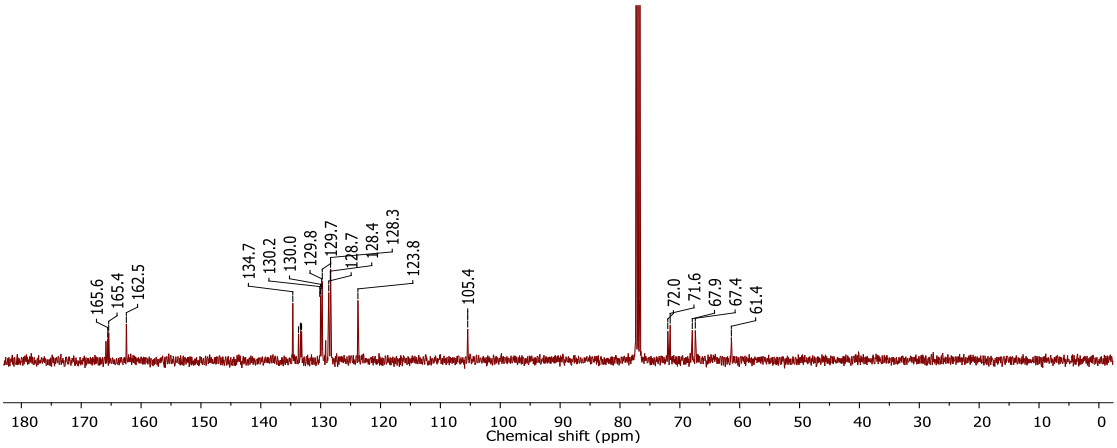
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **70k**



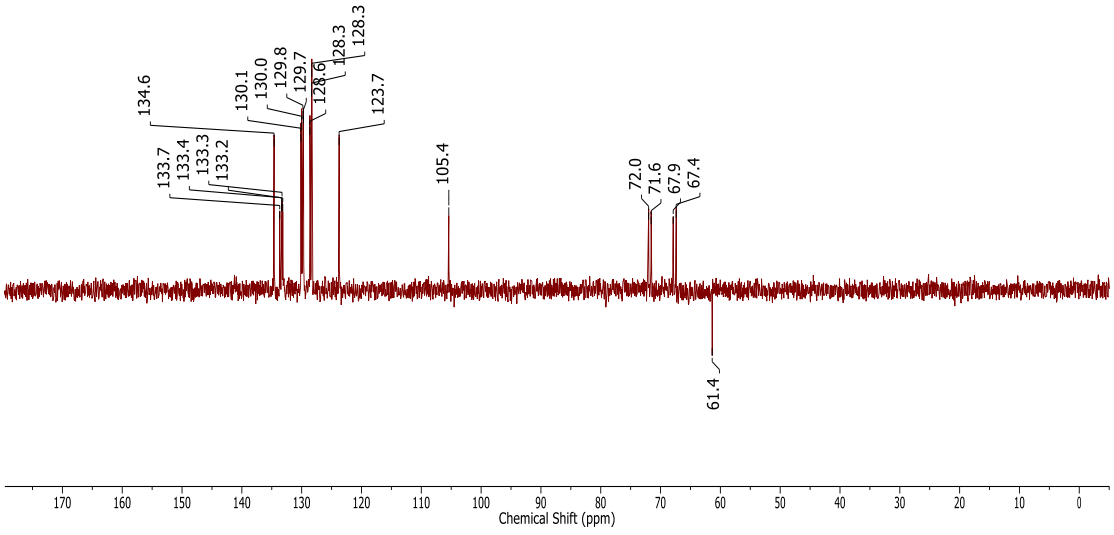
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **70l**



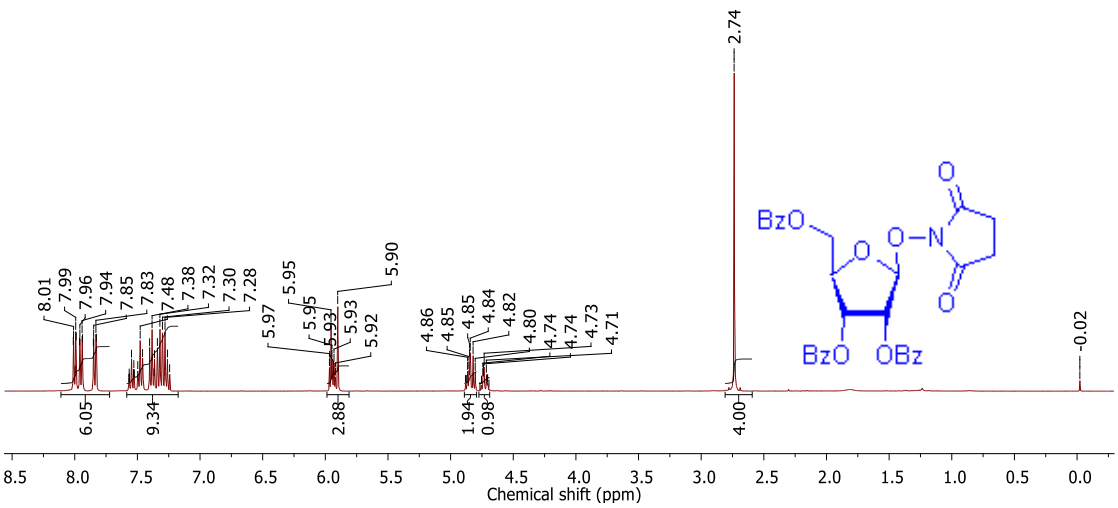
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **70l**



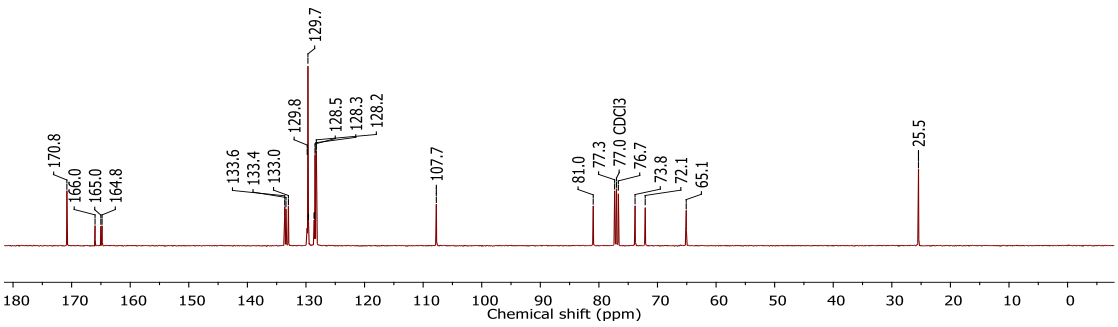
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **70l**



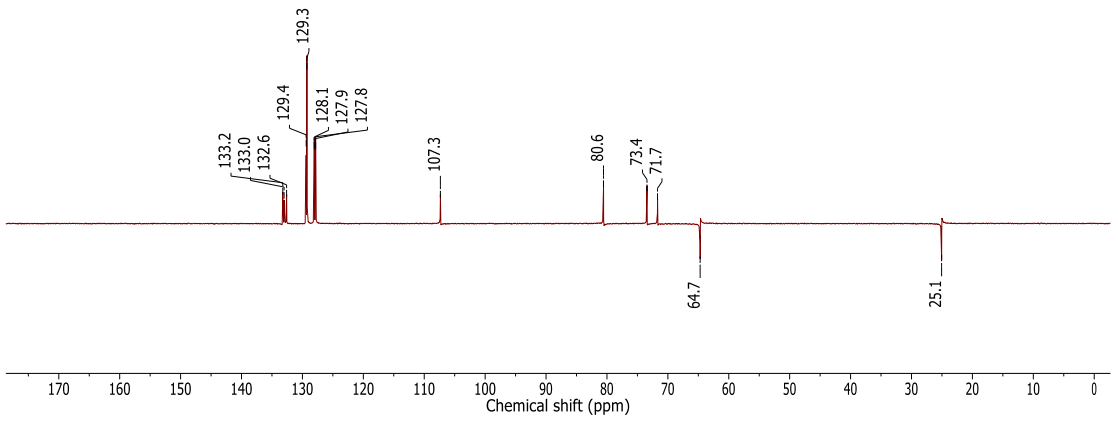
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **78a**



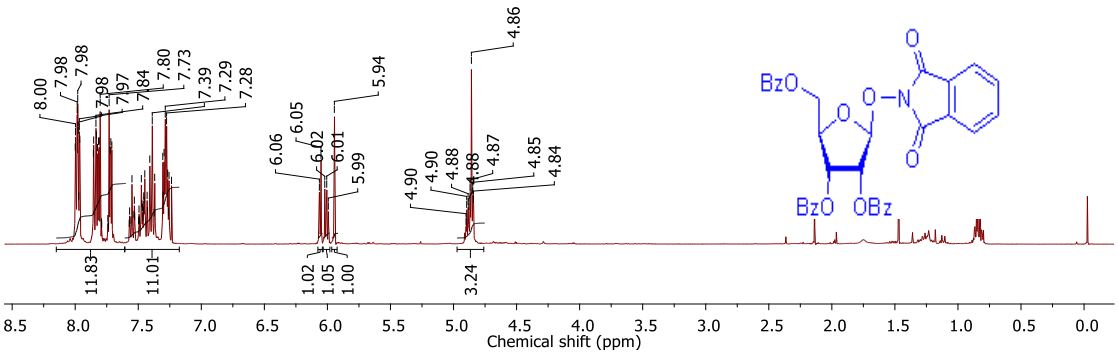
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **78a**



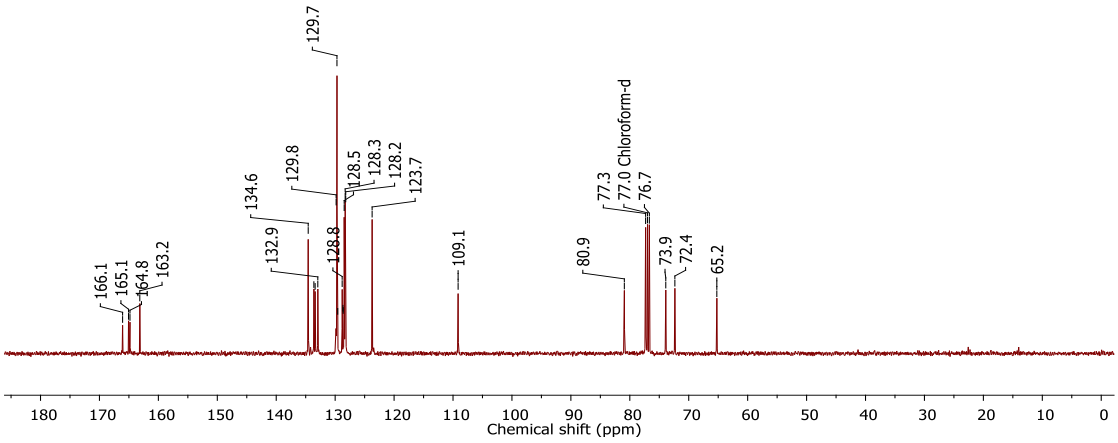
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **78a**



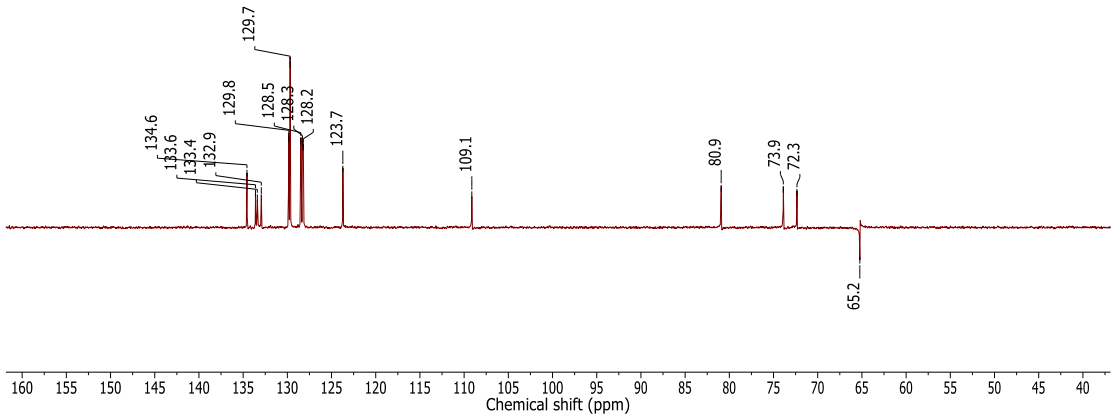
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **78b**



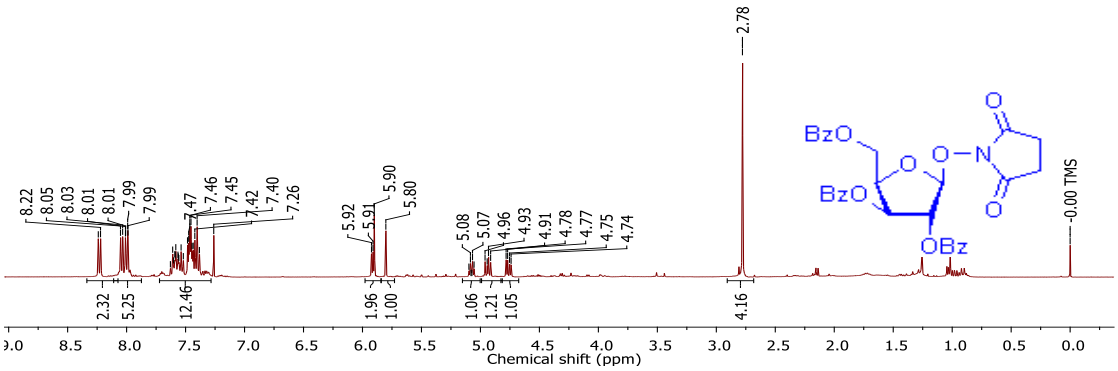
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **78b**



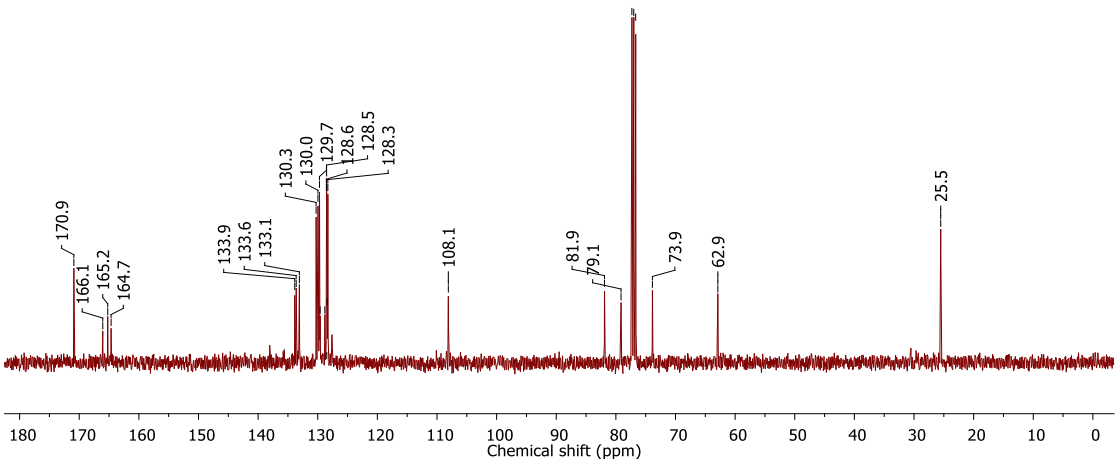
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **78b**



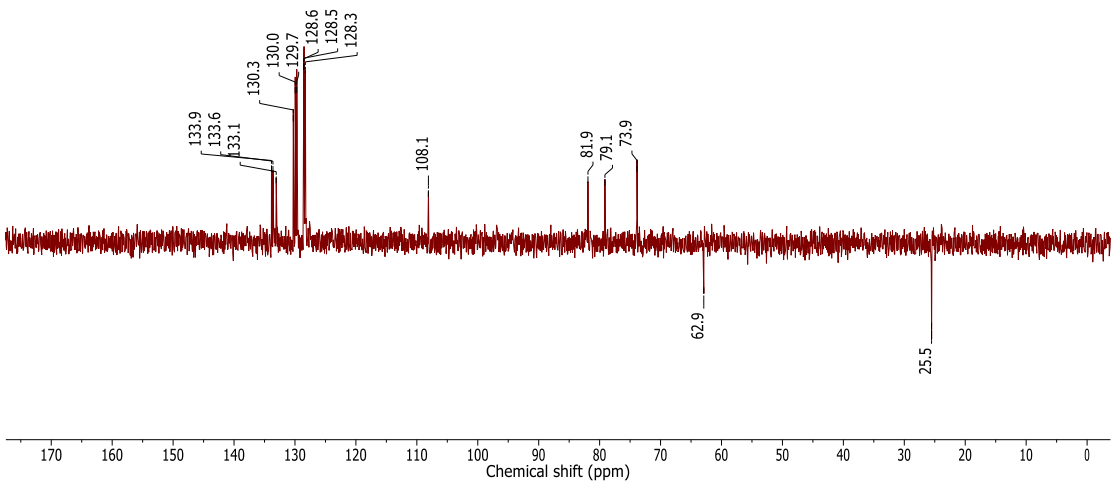
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **78c**



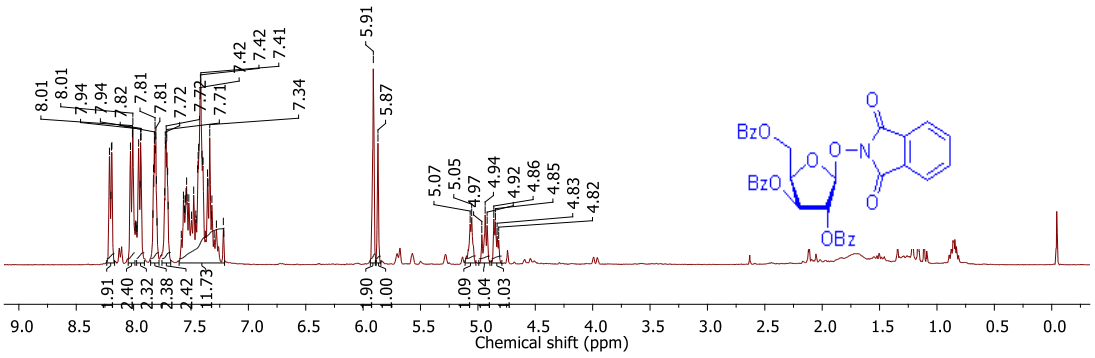
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **78c**



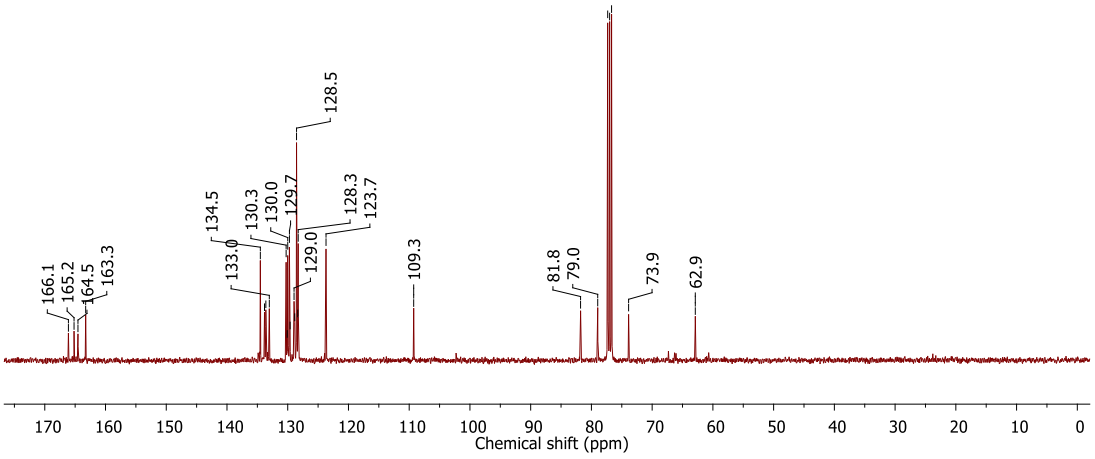
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **78c**



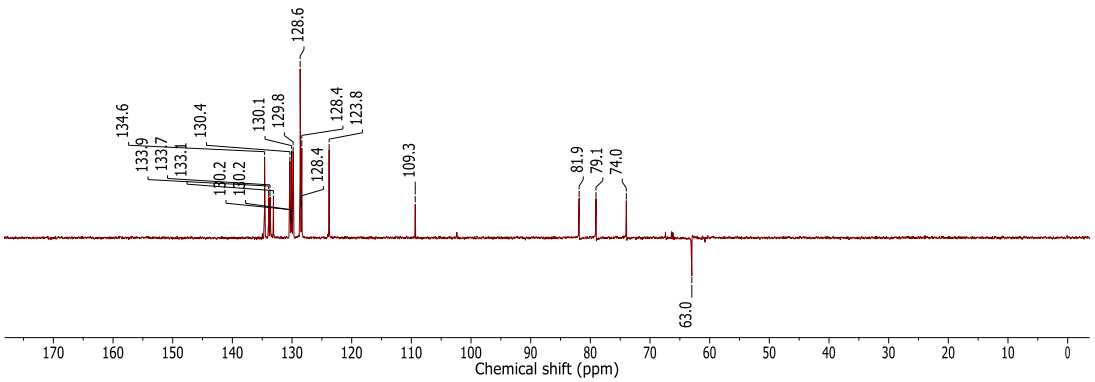
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **78d**



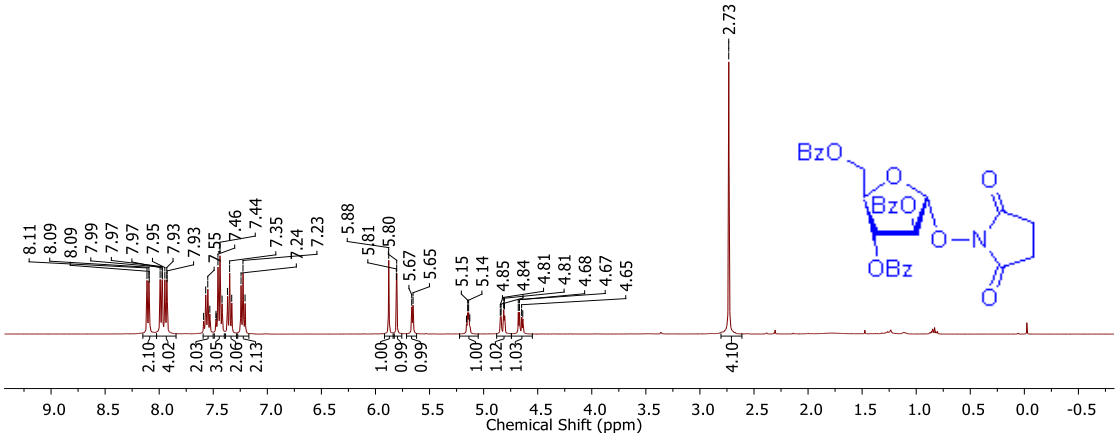
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **78d**



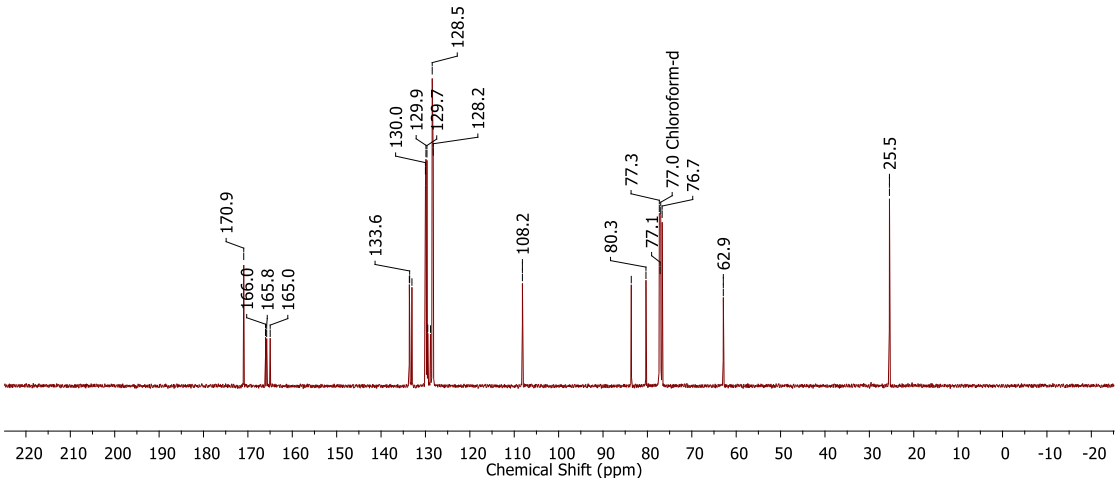
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **78d**



^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **78e**



^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **78e**



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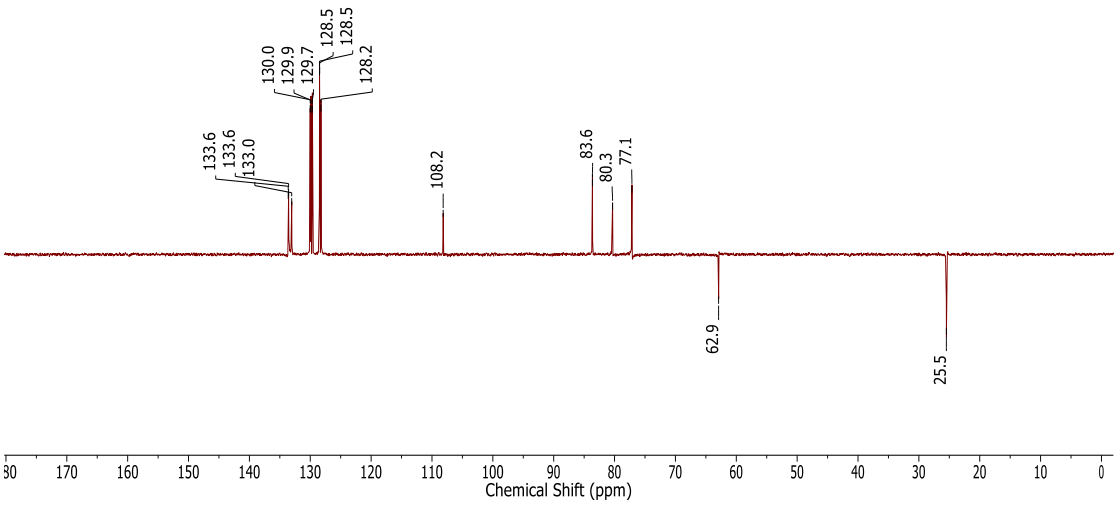

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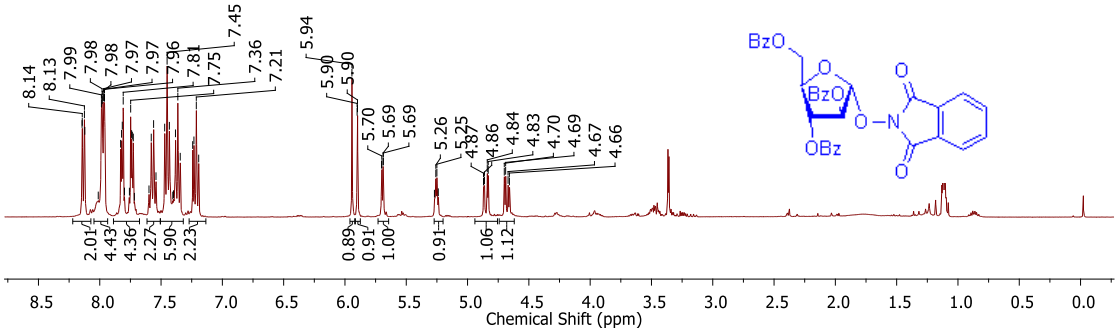
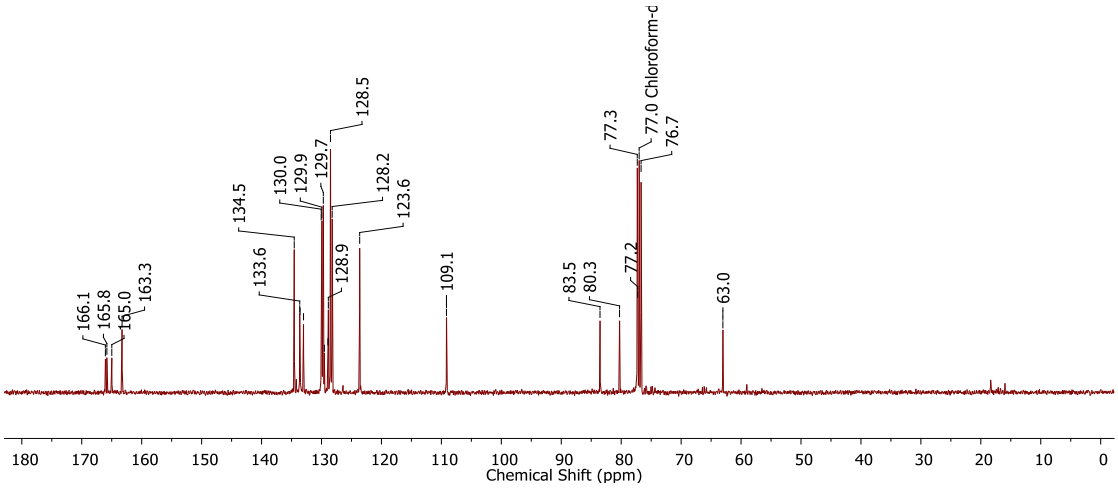


^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **78f**



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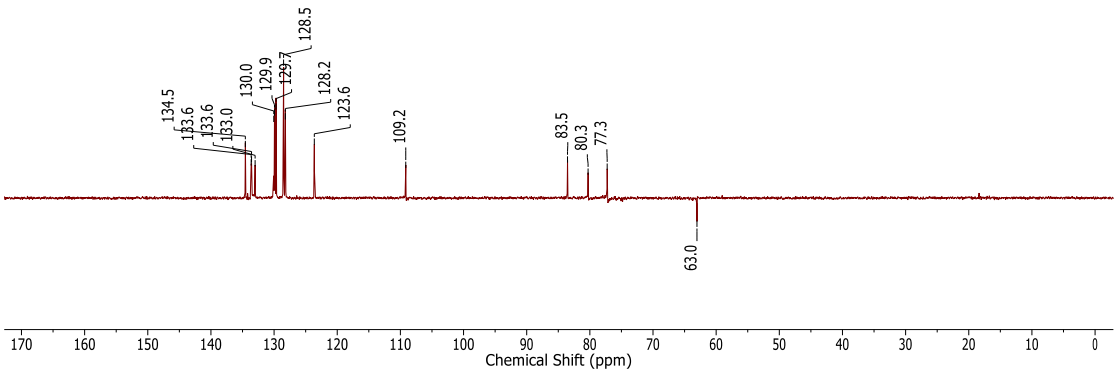

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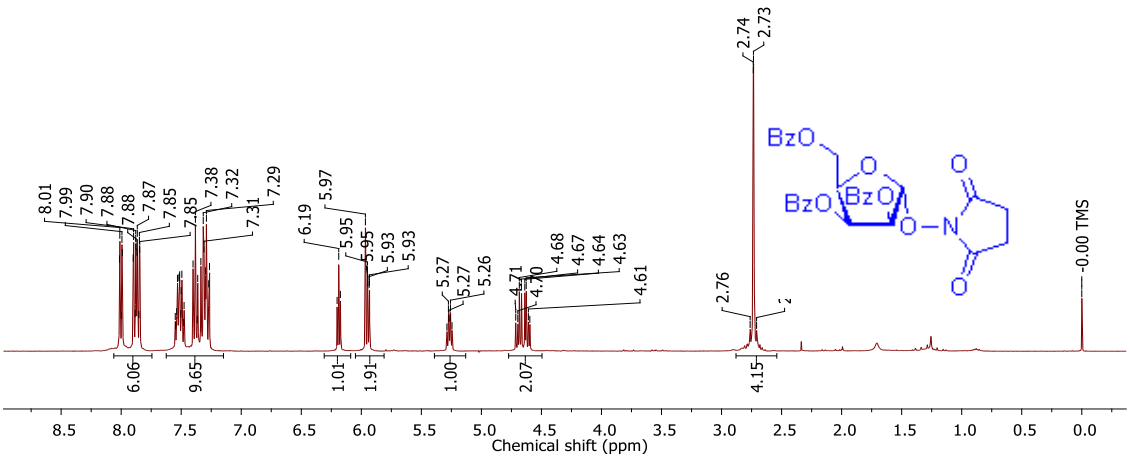

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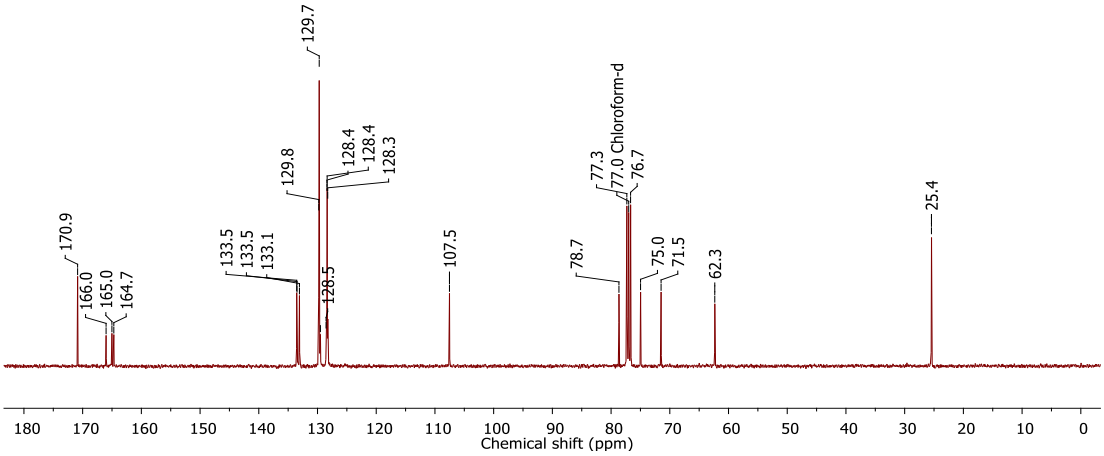

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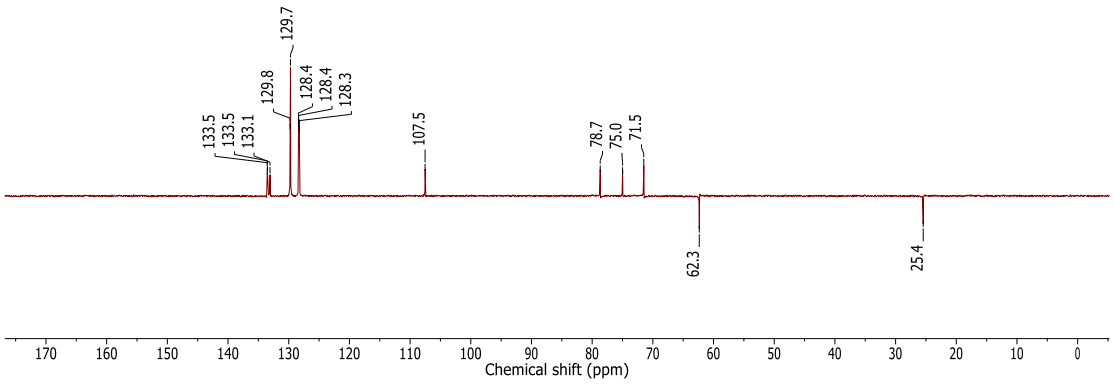
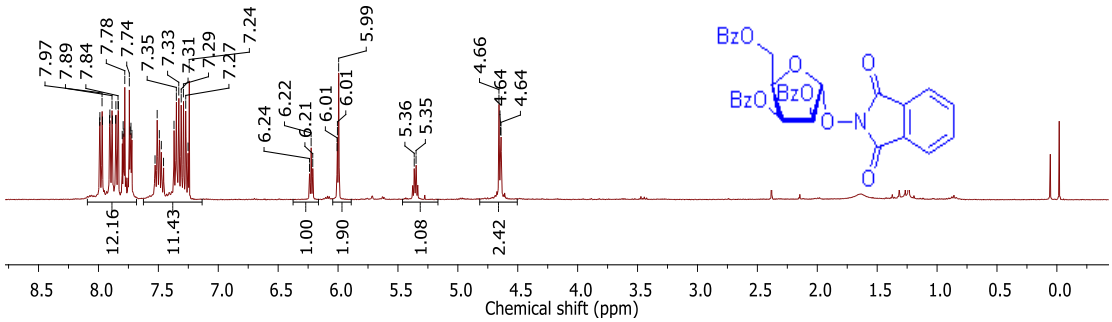


^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **78h**



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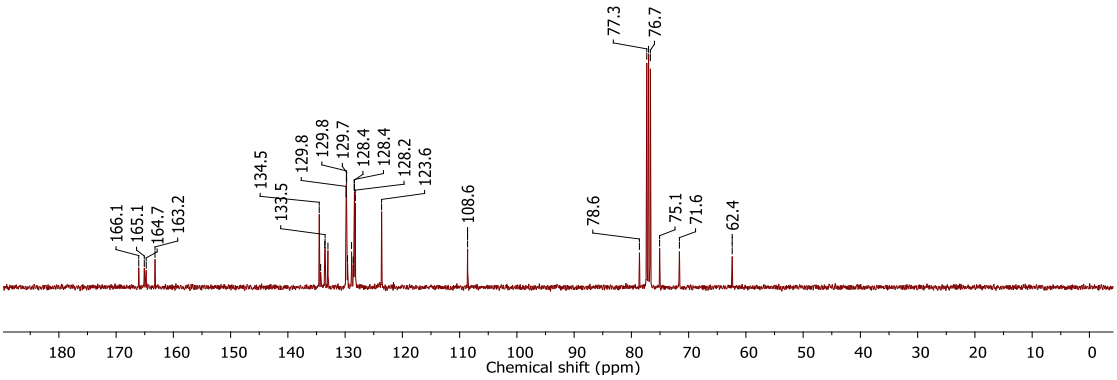

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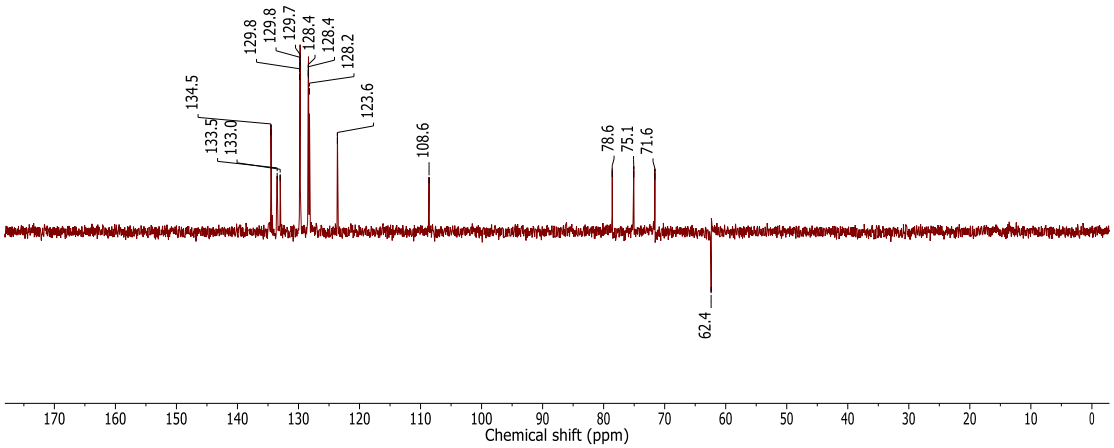
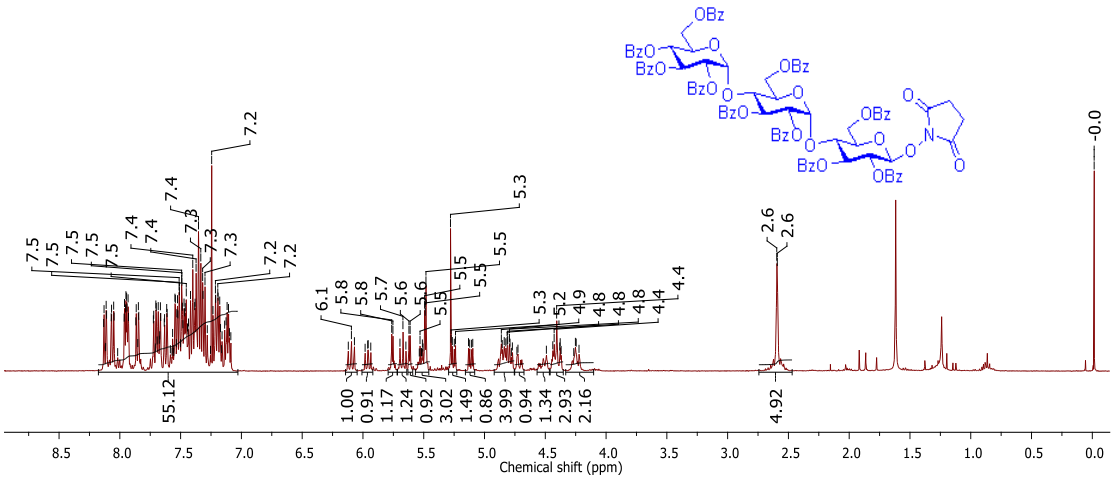


^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **79b**



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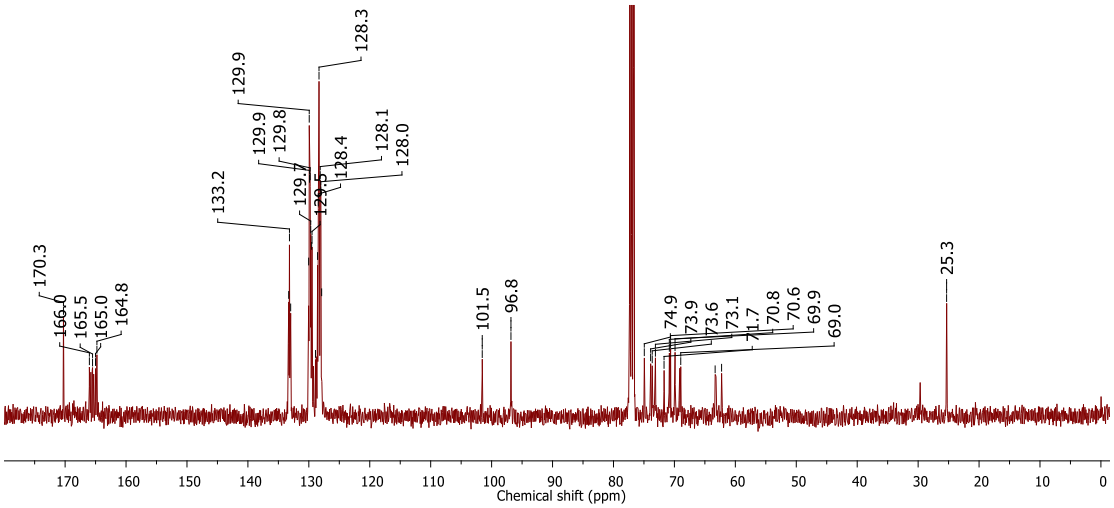

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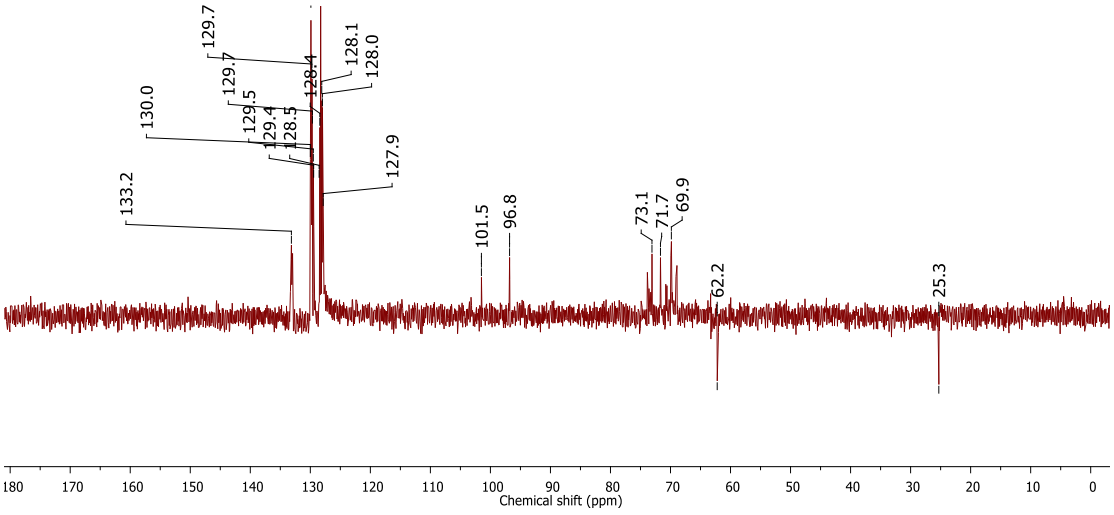

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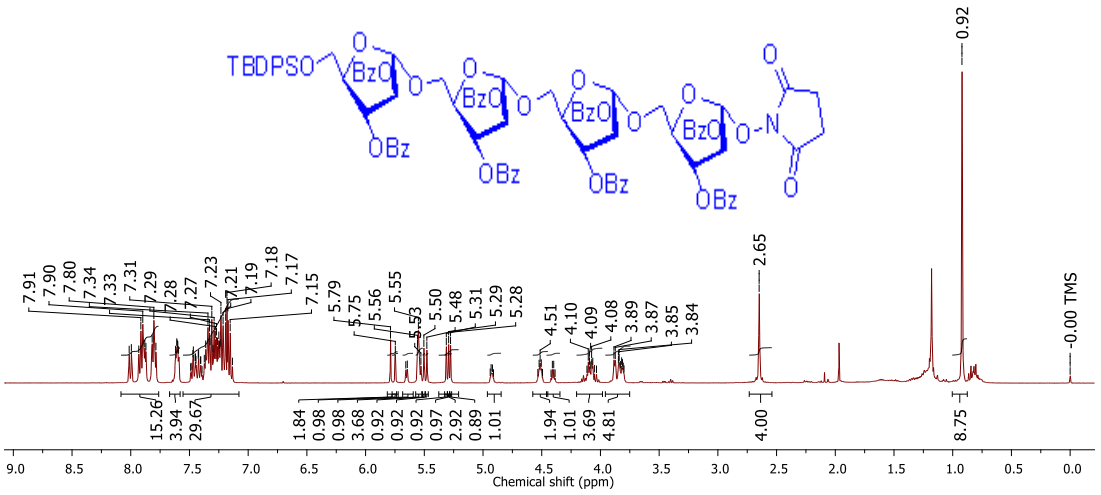

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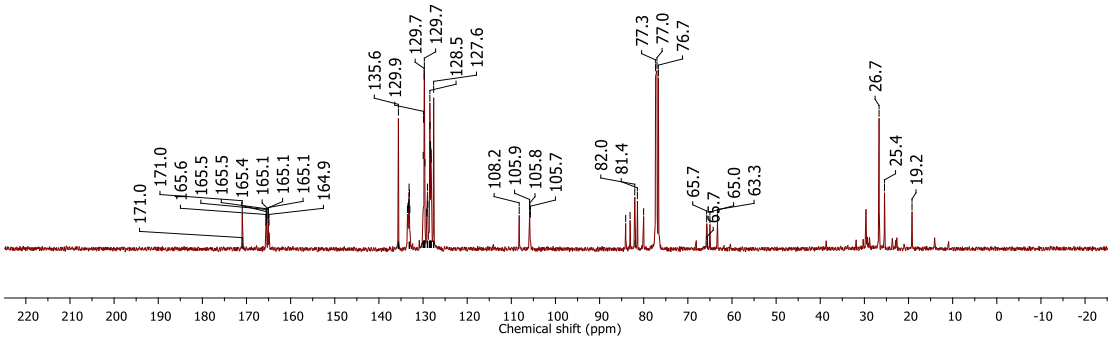

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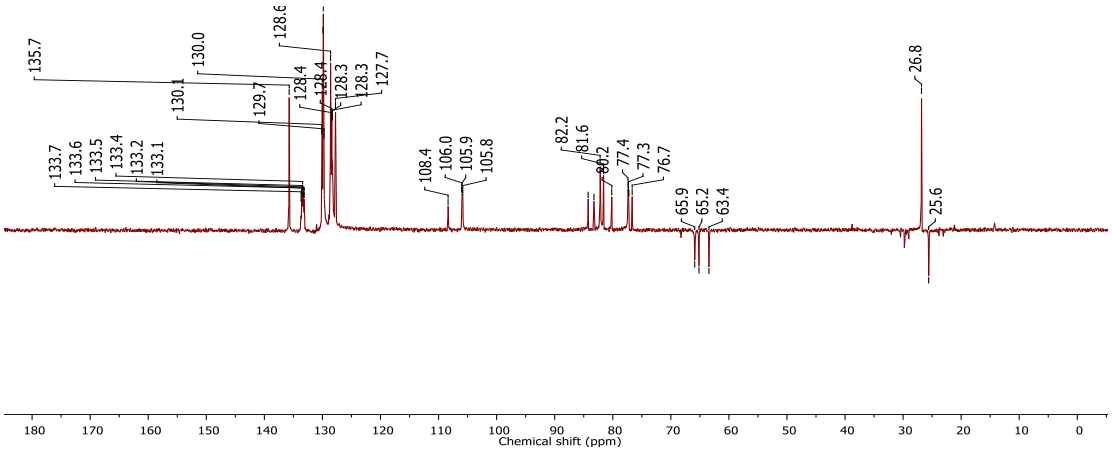

Details of experimental procedures, characterization data and spectral charts for some of the compounds will also be given in the supporting information of *(Manuscript communicated)*.

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R.; Thadke, S. A.; Hotha, S. *J. Org. Chem*., **2009**, *74*, 9233-9236; (d) Shaikh, A. Y.; Sureshkumar, G.; Pati, D.; Gupta, S. S.; Hotha, S. *Org. Biomol. Chem*., **2011**, *9*, 5951-5959; (e) Thadke, S. A.; Mishra, B.; Hotha, S. *Org. Lett*., **2013**, *15*, 2466-2469.

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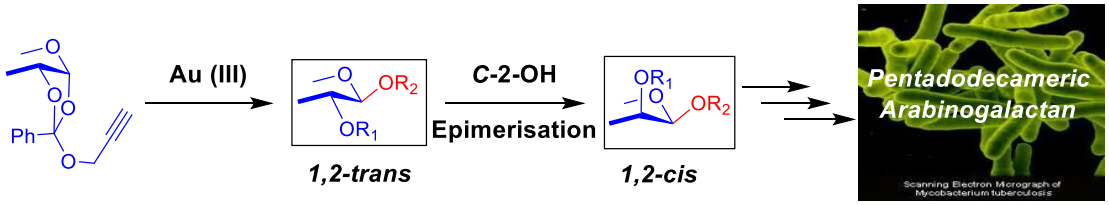
Single Donor Chemistry for Mycobacterial Cell Surface Molecule Arabinogalactan by Gold(III) Catalysis



2.1–*Tuberculosis*: Introduction

Tuberculosis (TB) is one of the deadliest diseases killing more than 1.3 million lives every year globally (WHO 2012).[1a] One/third of World's population is infected with this infectious disease caused by the various stains of *Mycobacterium tuberculosis (*Mtb*).*[1b] Tuberculosis fit into second biggest killer disease amongst bacterial pathogens. It is the main cause of mortality in HIV coinfected individuals.[1c] This combined with emergence of multiple and an extensively drug resistant strain (MDR and XDR) has led to an escalation in number of infected cases worldwide. Therefore, there is an urgent need to understand chemical mycobacteriology in order to improve existing intervention strategies. Usually Mtb attacks the lungs of human beings but can also affect the central nervous system, lymphnodes, bones and skin.[1d]

The classic symptoms of TB are chronic cough with blood-stained sputum, fever, night sweats and weight loss. Diagnosis of TB is done through radiology microscopic examination, microbiological culture of body fluids and also skin tuberculin test. Tuberculosis prevention and control efforts primarily rely on the vaccination of infants. The first milestone in the intervention against TB was the development of Bacillus-Clamette-Guerin (BCG) vaccine by Albert Calmette and Camille Guerin in 1920s. This is effective against disseminated disease in childhood, confers inconsistent protection against contracting pulmonary TB.[2a] Treatment of TB based on killing of mycobacteria using antibiotics such as combination of streptomycin, rifampicin, isoniazid, pyrazinamide and ethambutol for first two months, and only rifampicin and isoniazid for the next four months. Further, the World Health Organization (WHO) has achieved some success with improved treatment regimens which decrease in case numbers and also declared as a "Global Health Emergency" in 1993.[2b] BCG vaccine and the drugs currently in use have their own limitations and needs researchers to develop new TB vaccines as well as drugs to combat TB. Though several molecules are in phase I and II clinical trials,[2c] still more achievements are required for managing the tuberculosis effectively. One of the characteristics of Mtb is its unique cell wall. Importantly, mammalian cells do not have any cell wall thereby making cell wall biosynthesis a rewarding alternative for drug development (**Figure 2.2**).[2]

2.2– Introduction: *Mycobacterium tuberculosis*

Mtb is a pathogenic bacterial species which was identified by Robert Koch in late 1800s. Koch also found that Mtb has a thick and waxy cell wall cultures.[3]

2.2.1– Phylogeny of Mtb[4]

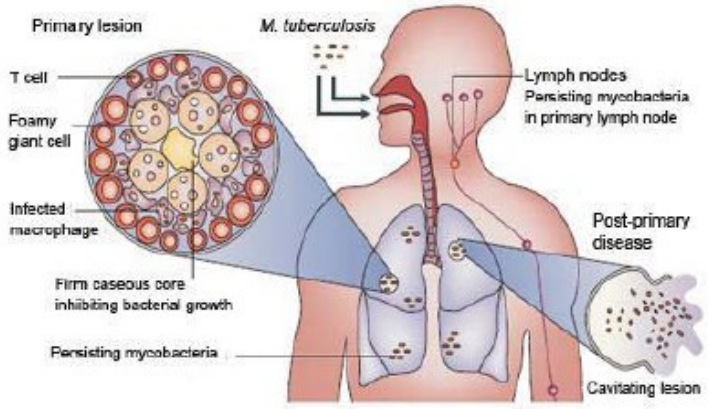
This is the largest taxonomic unit present in the bacterial domain and belongs to phylum actinobacteria. Mtb belong to a genera *Corynebacterium, Mycobacterium* and *Nocardia* form a monophyletic taxon called CMN group. The unusual waxy cell wall envelope mainly composed of unique long chain fatty acids called as mycolic acids. Presence of 85 different species proves its high diversity in mycobacterial species. Out of this, non-pathogenic bacterial species are related to soil growing *Streptomyces* or *actinomyces* and Mtb and M. leprae like bacterial species are the slow growing pathogens. Major part of the *Mycobacteria* complex consist of Mtb, M. africanum, M. Canettii, M. Bovis and M. Microti. Genome sequencing of Mtb and M. leprae gave the information about the evolutionary relationship between members of Mtb complex. Several studies also disclosed that Mtb isolates demonstrated a clear phylogeographic distribution i.e. different families were associated with specific geographical regions. The data arises from the high TB burden areas like east and south-east Asia, Indian sub-continent and Africa to completely define the phylogeny of Mtb. These data have huge information in development of better and more reliable diagnostic tools, drugs, vaccines and biomarkers.

2.2.2– Pathogenesis of Mtb[5]

Once Mtb enters through aerosol and is taken up by alveolar macrophages finally reaches to lungs. Macrophages play the contradictory roles of being the initial soldiers against Mtb which stands the antimicrobial weapons of macrophages and found itself in the phagosome by blocking its fusion with acidic lysosome. Meanwhile, activation of macrophages and dendritic cells induces an elaborate immune response initiated by secretion of cytokines like Interleukin-12 (IL-12) and Tumour necrosis factor-α (TNF-α) and chemokines like (C-C) Ligand 5 (CCL5) and macrophage inflammatory protein-1α (MIP-1α) finally leading to organized cellular structures called granulomas, hallmark of chronic infections. These are organized collections of differentiated macrophages mainly but other cells like T-cells, some B-cells, neutrophils, dendritic cells and fibroblasts are also found in Mtb granulomas,

though, and Mtb is primarily found inside macrophages adaptive response facilitated by T cells is also crucial for the completion and maintenance of these structures wherein Mtb is walled off from host tissue. (**Figure 2.1**)

Figure 2.1: Pathogenesis of Mtb (Adopted from Stewart G. R. *et al*. *Nature Reviews microbiology*, **2003**, *1*, 97-105)



Mtb infections can have multiple outcomes including an early clearance which does not leave any sign or direct progress to lively disease also called primary disease or a subclinical asymptomatic infection named as latent TB which can reboot at a later time of point. The last is the most likely scenario with about two billion individuals, almost a third of the world's population, harbouring dormant Mtb with a 10% risk of reactivation while 90% of individuals remain protected. In these individuals, Mtb is never completely eliminated and likely to switch into an alternate metabolic state which is considered almost dormant or non-replicating. These dormant bacteria which are refractive to current anti-TB drugs are also found to co-exist with actively dividing bacteria in diseased individuals leading to prolonged therapy. This results in frequent patient non-compliance and thus emergence of resistance. Reactivation leading to post primary disease is mostly a consequence of immune suppression either due to a disease like AIDS or diabetes or even therapies like anti-TNF antibody treatment. Persistence, reactivation and drug resistance in the context of the pathogen as well as the host are the primary areas of research in TB.

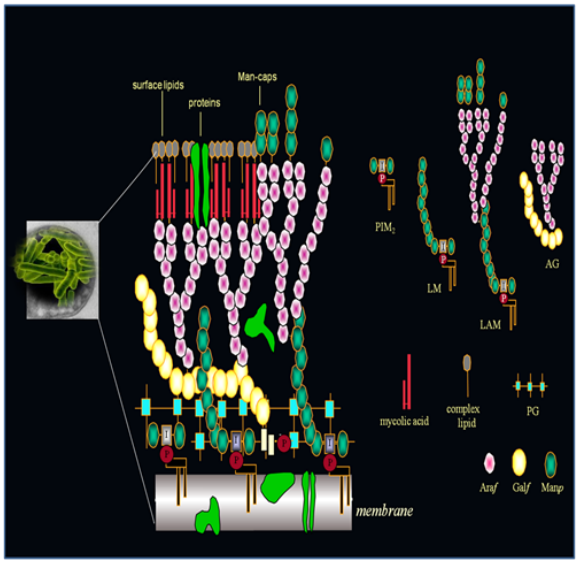
2.2.3–Characteristics of Mtb[6]

Mtb is an aerobic, rod like shaped with 0.3-0.5µm in diameter and of variable length. It is slow growing bacteria compared to other bacterial species with an average replication time of 22-24 hours. In an artificial culture media it arranges into cluttered colonies reflecting the distinctive composition of its lipid rich cell wall (**Figure 2.2**).

2.2.4–Structure of Mtb[7]

Brennan *et al.*[7a] had completely unravelled the fine structure of the cell wall of Mtb. It had been hypothesized that, the Mtb mainly consists of three major interconnected oligosaccharides as well as non-oligosaccharides parts. Oligosaccharides parts termed as Arabinogalactan (AG), Lipoglycans: lipoarabinomannan (LAM) and lipomannan (LM) and non-sugar part i.e. mycolic acid (**Figure 2.2**).

Figure 2.2: Mtb cell wall envelope



AG and **LAM** are the major constituents:

AG:
Arabinose and Galactose in Furanosyl form which is not present in humans

LAM:
Arabinose in furanosyl form and Mannose in pyranosyl form

AG and **LAM** have octadecamer of Arabinofuranose with two types of linkages (α or 1,2-*trans* and or *1,2-cis*)

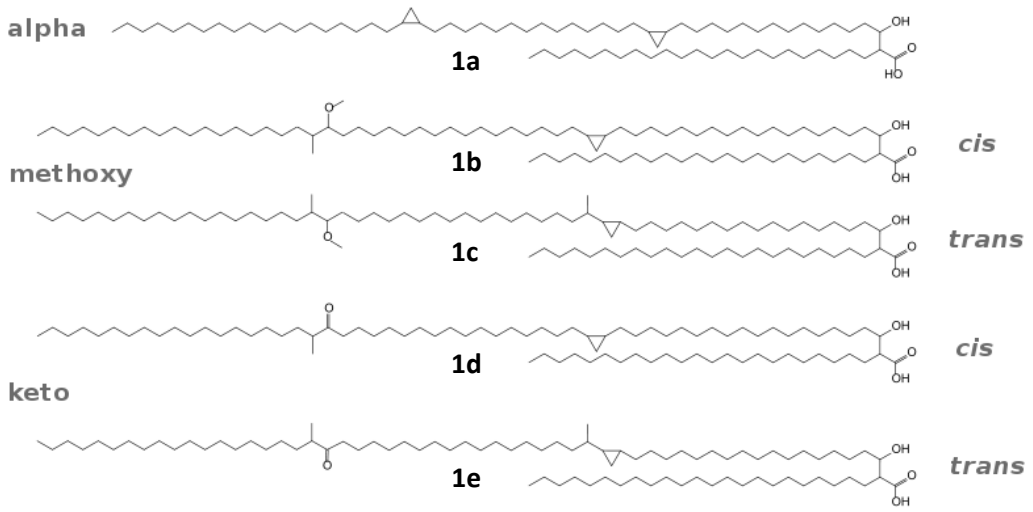
Additionally **AG** is capped with unique **Mycolic acids** having cyclopropane

2.2.4.1–Mycolic acid[7,8]

On non-reducing terminal end of arabinogalactan, it has branched arabinofuranosides with decoration of mycolic acid esters (MA). Mycolic acids are long chain fatty acids which were first isolated by Stodola *et al.*[8a] in 1938 from an extract of Mtb. Later Asselineau and Lederer[8b] stated that mycolic acid contains β-hydroxycarboxylic acid with a long α-alkyl side chain (**Figure 2.3**). Mtb is mainly characterized by very hydrophobic (C_{54} to C_{63}) fatty acids with linear saturated α-alkyl (C_{22} or C_{24}) chain. These chains are functionalised with α-, methoxy and keto mycolic acid which is also known for major classification of M. *tuberculosis*. The α-mycolic acid is the most abundant form (>70%), whereas methoxy- and keto- mycolic acid are the minor components (10 to 15%). The role of mycolic acids are still undefined as it resides at the outer region of the cell wall and therefore likely to be important for the initial contact with receptors. The mycolic acids are responsible for

the growth of bacteria inside the macrophages effectively hiding from the host immune system.

Figure 2.3: Structure of Mycolic acids



Deletion of any merogroup such as cyclopropane ring of the α-mycolic acid, or methoxy- or keto mycolates in Mtb had a profound effect on the growth of these bacteria in different phases. For example, deletion of keto mycolates leads to restricted growth of Mtb in macrophages.

2.2.4.2–Lipoglycans (Lipoarabinomannan (LAM) and Lipomannan (LM))[7,9]

LAM is a glycolipid, consists of 120 carbohydrate residues, out of which 71 are arabinose in furanosyl form and 49 are mannose in pyranosyl form. LAM is responsible for survival of the bacteria after the inactivation of macrophages and hunts the oxidative radicals which are liable to avoid infection in human body from these bacteria. Some of the important features of LAM are:

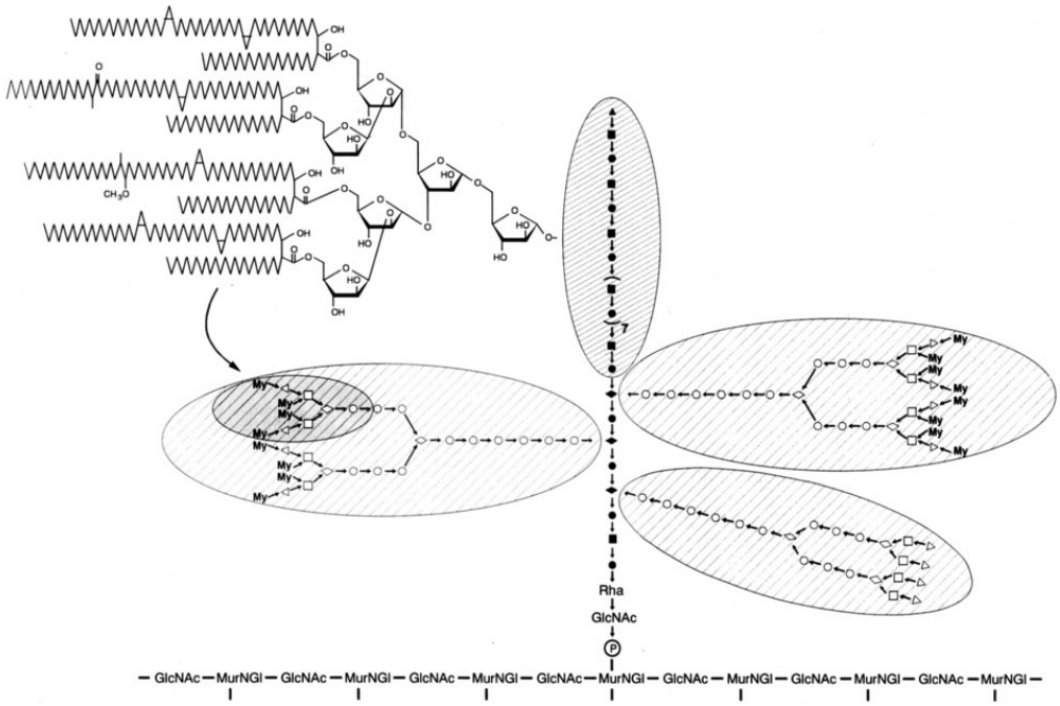
1. Non-reducing end of LAM is attached to hexa-arabinofuranosides similar to AG and reducing end attached to Lipomannan
2. Ara*f* termini are extensively capped with man*p* residues
3. Mycolic acids are not present in LAM

2.2.4.3–Arabinogalactan (AG)[7,8,10]

The fine structure of arabinogalactan (**Figure 2.4**) was observed after the partial depolymerization of the per-*O*-alkylated polysaccharides and generated oligomers by GC-MS, NMR and FABMS analysis.[8] Arabinogalactan consists of furanose form of D-galactose (Gal*f*) and D-Arabinose (Ara*f*) and terminal

arabinofuranosides are esterified with mycolic acids, which are potentially immunogenic to mammals. Both LAM and AG share arabinan as a common oligosaccharide of 18 units. The entire arabinan is attached to the galactan which runs across the cell wall in arabinogalactan.[2] Arabinogalactan consist of 23-arabinofuranosides which is attached to the galactan chain through 1→5 position of galactofuranosides. In arabinan, there are mainly four 1,2-*cis* and nineteen 1,2-*trans* internal linkages present which are highly required for the survival Mtb. From the careful analysis of GC-MS and FABMS of AG, the following generalization can be envisioned:

Figure 2.4: Structure of Arabinogalactan (A**G)**



1. AG polymer contains approximately 100 sugar residues, 69 of which are arabinose and 31 of which are galactose.
2. Within AG, all arabinose and galactose residues are in the furanose form[10a]
3. The non-reducing termini of arabinan consist of a branched penta arabinofuranosyl structure [β-D-ara*f*-(1→-α-D-ara*f*]$_2$-3,-5-α-D-ara*f*(1→5)-…
4. Mainly three types of linkages based on position of hydroxyl group i.e. Major 1→5, four 1→2, and two 1→3 linkages are present
5. The arabinan chains are attached to the alternating 5-β-D-gal*f* moieties at 8, 10 and 12 positions.[10c]

6. The galactan portion of AG is linked to the C-6 of muramyl residues of peptidoglycan *via* the glycophosphoryl bridge L-Rha*p*-(1→3)-D-GlcNAc-(1→PO_3)
7. Primary hydroxyl group in terminal non-reducing pentaarabinofuranoside are capped with mycolic acids.[8]

The major degradation products were the pentaarabinofuranosides, branched tetrasaccharides, and linear disaccharides. Mild acid hydrolysis of per-*O*-methylated AG gave major structural motifs which were named as motifs A-E. Terminal structural motif A is the highly significant due to the presence of 1,2-*cis* linkages. Motif B and C are the major constituents of entire AG. Motif D composed of alternating 6-linked and 5-linked galactofuranosyl disaccharide's residues. In motif E, ara*f* is alternatively attached to gal*f* *via* 1→5 linkage.

2.2.5– Drug development and importance of AG and LAM[11]

Some of the basic reasons to target AG are: 1) it is essential for viability and 2) three of the four sugars of which it is composed; D-ara*f*, D-gal*f*, and L-Rha*p* are not found in humans. Enzymes involved in the formation of sugar donor and their polymerization could be potential drug targets. The isolation and expression of the genes for these enzymes is a high research priority. Inhibitors of the resultant enzymes can be obtained by using high-throughput screens and by enzyme characterization and the subsequent design for rational inhibitors. The non-reducing ends in both AG and LAM are capped with branched arabinofuranosides known as motif A with α-1→5 linked to the remaining polymer. In, LAM both primary hydroxyl groups are substituted with mannopyranosyl residues. The mannopyranosyl residues on arabinan moiety in the initially infected stage are bound to the mannose biniding proteins. Similarly, hydroxyl groups in AG are substituted with mycolic acid. The major degradation products of AG such as motif A-E are important for the drug development. These motifs are responsible for the antigenicity of AG and that serological activity resides largely in fraction containing 2-linked arabinofuranosyl residues i.e. motif A. Structural motif A is the major humeral immunological epitope of AG. Monoclonal antibodies raised against LAM also react with purified cell wall, suggesting an arabinose containing epitope common to LAM and AG. The motif A both in LAM and AG plays important role both in infection and survival of the organism in human being. Some of the currently used drugs to treat TB such as

Ethambutol, rifampicin, isoniazid, streptomycin are recently shown to be arabinosyltransferase inhibitors.

2.2.6– Biosynthesis of LAM and AG[12]

Although both LAM and AG contain an arabinan domain of similar structure and increasing evidence for AG confirms the well-defined structure of arabinan domain is correct. The LAM is more heterogeneous. The biosynthesis of mycobacterial arabinan is still not clearly understood. In AG and LAM, the majority of Ara*f* residues are installed by a family of arabinotransferases (AraTs), EmbA, EmbB, and EmbC. In all processes, the biochemical reactions were carried out by decaprenylphosphorylarabinose (DPA). The *m*AG[12a] biosynthesis is achieved by EmbA and EmbB enzymes and LAM[12b] is achieved by EmbC. These enzymes could not be isolated and purified in pure form yet; but it is possible to check their activity in mycobacterial membrane. Besra and co-workers have reported a distinct AraT, designated AftA[12c] which installed the first Ara*f* residue to the galactan. Similarly, AftB[12d] is involved in arabinan biosynthesis and installed terminal β-(1→2) araf in AG. Recently from Chatterjee and co-workers[12e] reported biosynthesis of terminal arabinan domain containing α-(1→5) and α-(1→3) linkages in AG was achieved.

2.2.7– Chemical synthetic approaches towards Mtb major fragments[13,14]

Few milligram quantities of standard samples are required for checking these hypotheses which can be easily obtained by chemical synthesis. As explained in chapter 1, there are several glycosyl donors for the synthesis of pyranosidic glycoconjugates and the same is not true for furanosides. The chemistry of furanosides and pyranosides is not similar. The furanosides are more reactive than pyranosides and not similar in several factors. For example, anomeric effect found in pyranosides but same is not really useful in furanosides. The first arabinosyl donor **2a**[13a] was stated by Mukaiyama and Kawabata (later **2b**[13b] and **2c**[13c]) for the synthesis of glycoconjugates. In 1996, 1,2-anhydro sugars **2d**[13d] by Kong group were utilised for stereoselective α-arabinofuranosylations. Mereyala *et al.* introduced *n*-pentenyl arabinofuranoside (**2i**)[13e] and thiopyridyl arabinofuranosides (**2j**)[13f] and completed the first total synthesis of pentaarabinofuranosyl motif A. Later, introduction of various arabinofuranosyl donors **2e**,[13g] **2f**,[13h] **2g**,[13i] and **2h**[13j] for the synthesis of glycoconjugates were studied (**Table 2.1**).

Major and selected efforts for the synthesis of oligosaccharides of mycobacterial cell wall are described below.

2.2.7.1– Mereyala *et al*.[14a]

First total synthesis of arabinofuranosyl motif A in Mtb Cell wall was achieved using pent-4-enyl arabinofuranoside and thiopyridyl arabinofuranoside as glycosyl donors. The key glycosidation step was the formation of β-arabinofuranoside using armed thiopyridyl glycosyl donor **2j**.

2.2.7.2– A. Hölemann *et al*. [14b]

A dodecasaccharide fragment containing six α-Ara*f* and six α-Man*p* residues was obtained *via* a [6+6] strategy. The key glycosylations step for the synthesis of dodecasaccharide was coupling between mannan and arabinan domains.

2.2.7.3– B. -F. Reid *et al*. [14c]

The B. -F. Reid group has synthesized 28-mer fragment containing the inositol of Mtb. The 28-mer containing fifteen α-Man*p*, and twelve α-Ara*f* residues was synthesized using key glycosylation step with [12+16] coupling between arabinomannan trichloroacetimidate donor and mannosylated inositol acceptor. In this synthetic strategy, lack of β-Ara*f* was observed on non-reducing side of both AG and LAM in Mtb.

2.2.7.4– M Joe *et al*. [14d]

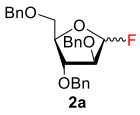
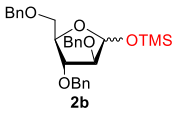
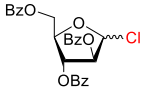
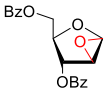
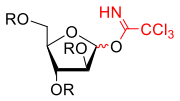
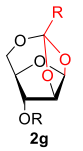
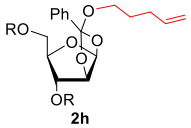
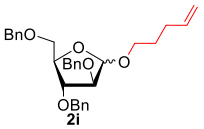
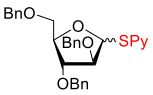
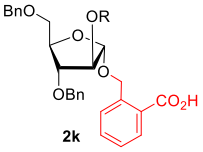
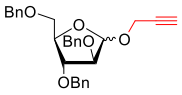
First total synthesis of 22-mer containing β-Ara*f* present in both LAM and AG was achieved by Lowary group. The key glycosylation step was involved for the synthesis of 22-mer is [(2X5)+7+5] strategy. The 12-mer was achieved with the coupling between pentaarabinofuranoside acceptor and branched trichloroacetimidate heptaarabinofuranoside donor. 22-Mer was achieved with the glycosylation reaction between 12-mer arabinan diol acceptor and non-reducing branched pentaarabinofuranoside trichloroacetimidate containing β-Ara*f* as a donor.

2.2.7.1– A. Ishiwata *et al*. [14e]

Followed by Lowary group, Ishiwata *et al*. synthesized the 22-mer containing β-Ara*f*. Synthetic strategy for 22-mer was totally different from the Lowary group and installation of β-Araf was carried out by double intramolecular glycosyl acceptor delivery using *O*-NAP ethers. The key glycosylation step involved for the synthesis of 22-mer is [(2X7)+8] strategy. The 22-mer was obtained with the glycosylation

reaction between two units of thio-toluyl heptamer containing β-Ara*f* as a donor and octaarabinofuranoside diol as an acceptor.

Table 2.1: Accounts of arabinofuranosyl donors

 **2a** Mukaiyama Teruaki *Chem. Lett.* **1983**, 935 α/β–Mixture	 **2b** Mukaiyama Teruaki *Chem. Lett.* **1992**, 1401 α/β–Mixture	 **2c** Yasuyuki Kawabata *Carbohydr. Res.* **1995**, *267*, 39 α–or 1,2-*trans* only	 **2d** Fanzuo Kong *Carbohydr. Res.* **1996**, *286*, 161 α– or 1,2-*trans* only
 **2e** Fanzuo Kong *Synlett.* **1999**, 1648 R = Bz α only or predominant Bn α/β Mixture; β-major	 **2f** Todd L. Lowary *Tetrahedron* **1999**, 55, 5965 Org. Lett. **2000**, *2*, 1493 J. Am. Chem. Soc. **2000**, *122*, 1251 α/β–Mixture	 **2g** Jacques Prandi *Chem Commun.* **2000**, 659 α–or 1,2-*trans* only	 **2h** Fraser-Reid Bert *Org. Lett.* **2004**, *6*, 3051 α– or 1,2-*trans* only
 **2i** Mukund K Gurjar *Chem. Commun.* **1998**, 985 α/β– Mixture	 **2j** Mukund K Gurjar *Chem. Commun.* **1998**, 985 α/β– Mixture	 **2k** Kwan Soo Kim *Org. Lett.* **2005**, *7*, 3263 R = Bz α only or predominant Bn α/β Mixture	 **2l** Srinivas Hotha *Chem. Commun.* **2011**, *47*, 9906 α/β– Mixture

In all synthetic strategies, there was no installation of gal*f* and to load one sugar residue after these many steps is a great difficulty. Even, all strategies used different glycosyl donors for attaching sugars at various positions. Trichloroacetimidate donor was found to suitable for the higher oligoarabinofuranosides synthesis. Installation of β–ara*f* in Lowary method required fully armed or *C*-2 benzyl protected glycosyl donor. With all this, glycosidation between *C*-2 benzyl protected glycosyl donor and branched arabinan acceptor gave major β-isomer but not in a fully distereoselective fashion. Therefore, many modifications are required in chemistry for facile synthesis of arabinan portion. In addition, the challenge of gal*f* installation is not yet addressed by any synthesis thus far. Performing all key furanosylations by single donor chemistry would be highly useful since the number of building blocks required for the synthesis will reduce

significantly. In the chapter 2, a new method for the 1,2-*trans* and 1,2-*cis* furanosylations from propargyl 1,2-*O*-orthoesters is described and in addition investigation was further extended for the synthesis of pentadodecameric arabinogalactan to prove robustness of our identified methods and importantly gold-catalyzed glycosidations.

2.3– Present work

Arabinogalactan (AG) is the major component of Mtb cell wall which could facilitate development of new therapeutic agents against Mtb and also to develop a single dose drug for dreadful tuberculosis, in a much broader prospective. Many glycosyl transferases with mycolic acids, arabinose, galactose and mannose are involved in the formation of structural complexity of cell surface of Mtb which causes difficulty in understanding the cell biology of Mtb. Importantly, major motifs found in AG are named as motifs A to E which are repeating units in AG. This chapter deals with the identification of new methodologies for the synthesis of AG.

2.3.1– Retrosynthetic analysis

Arabinose is mostly found in plant kingdom and very rarely in living organisms. Arabinogalactan consists of both 1,2-*trans* as well as 1,2-*cis* interglycosidic linkages. 1,2-*trans* Linkages can be easily achieved by using the neighbouring group participation in the glycosyl donor. 1,2-*cis* Linkages are relatively difficult to synthesize in pure distereospecific form. Several attempts were attempted to achieve major 1,2-*cis* linkages but yet no method to acquire fully 1,2-*cis* furanosidic linkage with all kinds of acceptors. Herein, a strategy for the diastereoselective synthesis of 1,2-*cis* and *trans* arabinofuranosidic linkages was investigated and further showed that the developed methods are excellent for the synthesis of pentadodesaccharide AG using propargyl glycosides as glycosyl donors .

Retrosynthetic analysis of the pentadodecasaccharyl arabinogalactan was carried out keeping in view of the salient features of gold(III) catalysis for glycosidation chemistry that our laboratory has developed over the last several years. Terminal portion of the AG is conserved and thus the first disconnection was envisioned to install terminal hexasaccharide onto a tridecasaccharyl arabinogalactan **4b**. The tridecasaccharyl arabinogalactan (**4b**) can be realized through a glycosidation reaction between middle hexasaccharide and a heptasaccharide which in turn can be obtained from a tetrasaccharide and trisaccharide. Hence, successful synthesis of pentadodesaccharide arabinogalactan requires:

(a) Robust and reliable method for 1,2-*trans* arabinofuranosylations

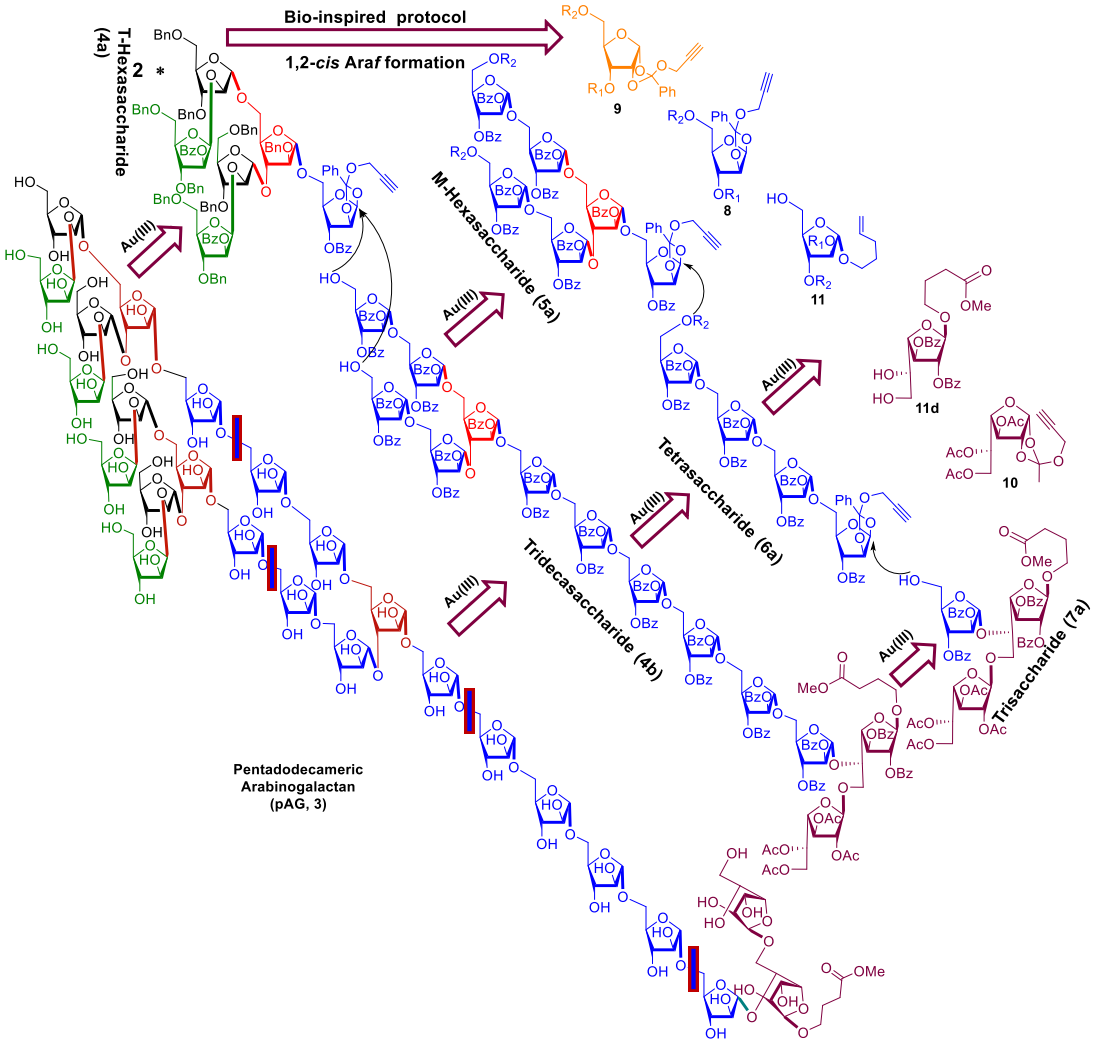
(b) Robust and reliable method for 1,2-*cis* arabinofuranosylation

(c) A readily convertible but stable protecting group at the reducing end of all identified major motifs

(d) A robust method to convert alkyl glycosides to 1,2-*O*-orthoesters, if required

(e) Easily accessible building blocks in large quantities

Scheme 2.1: Retrosynthetic analysis of AG



In this direction, *n*-pentenyl glycosides were checked towards the third objective as *n*-pentenyl glycosides can be easily activated in the presence of propargyl orthoesters orthogonally.[15b] In addition, *n*-pentenyl glycosides are known to get converted to corresponding bromoaldoses easily.[16a] Earlier studies from our group[15c] showed that bromoaldoses can be converted into the propargyl 1,2-orthoesters under Kochetkov[16b] conditions. After the identification of methods for the last two objectives, synthesis of building blocks in large quantities from respective pentoses/hexoses became straight forward. Hence, identification of methods for 1,2-*trans* (objective 'a') and 1,2-*cis* (object 'b') under gold catalysis was first investigated.

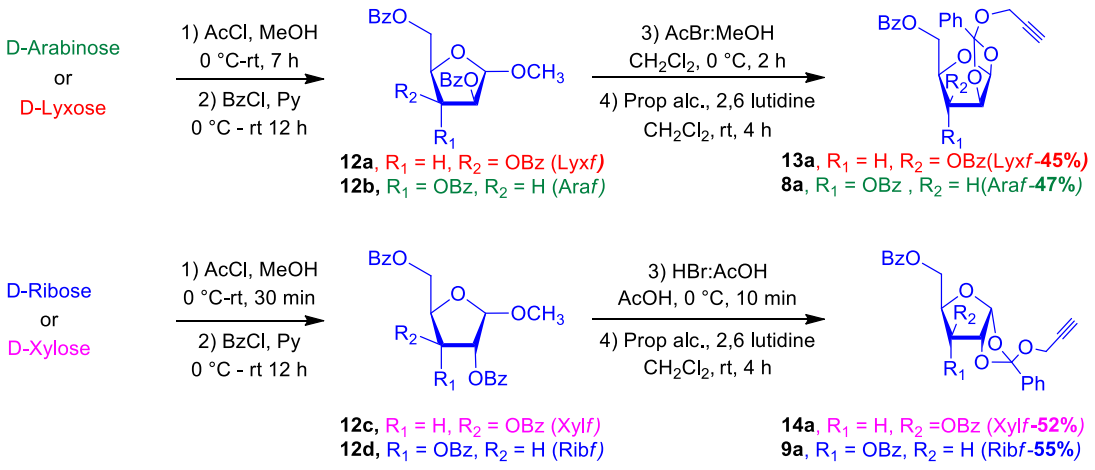
2.3.2– Method development for 1,2-*trans* furanosides

Hotha *et al.*[15a,c] identified propargyloxy pyranosides as glycosyl donors in the presence of catalytic amount of gold (III) salts (see Chapter 1). Later investigation by Vidadala *et al.*[13l] proved that dichotomy in propargyl furanosides. Rib*f* and lyx*f* gave 1,2-*trans* furanosides exclusively whereas xyl*f* and ara*f* resulted into a diastereomeric mixture. Hence, propargyl arabinofuranosides are not really suitable for oligoarabinofuranosides synthesis.

Earlier investigations by Sureshkumar[15c] on pyranosides demonstrated that propargyl 1,2-orthoesters enable synthesis of 1,2-*trans* pyranosides in a highly diastereoselective manner. However, propargyl 1,2-*O*-orthoesters of furanosides were never investigated for 1,2-*trans* furanosylations. 1,2-*O*-orthoesters would be excellent as they are stable and conformationally locked to give 1,2-*trans* furanosides diastereoselectively. Hence, before venturing into the actual arabinan synthesis, applicability of propargyl 1,2-orthoesters for the 1,2-*trans* furanosylations was investigated.

Propargyl 1,2-*O*-orthoesters can be synthesized from corresponding bromoaldoses in the presence of strong organic base and propargyl alcohol. Bromoaldoses can be obtained from methyl/alkyl furanosides. Accordingly, methyl furanosides were synthesized by reported procedures[16c,d] and then per-*O*-benzoylation using BzCl and pyridine to obtain methyl furanosides of all four pentoses **12a-d** in good yields. Reaction with HBr/AcOH at 0 °C for 10 min gave bromoaldoses from **12c** and **12d** whereas, **12a**,**b** required indirect generation of HBr from AcBr/MeOH at 0 °C for 2 h.

Scheme 2.2: Synthesis of furanosyl 1,2-*O*-orthoesters

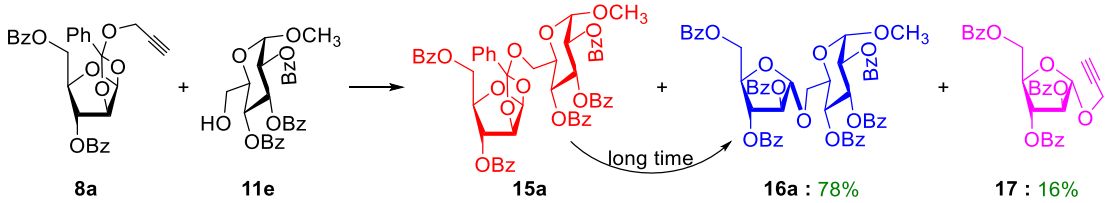


Resulting furanosyl bromides were treated with propargyl alcohol and 2,6-lutidine to afford desired propargyl 1,2-orthoesters (**8a**, **9a**, **13a**, and **14a**) in good yields (**Scheme 2.2**). In the ^{1}H NMR spectrum of **8a**, characteristic anomeric (*H*-1) proton was observed at δ 6.41 (d, *J* = 4.2 Hz) ppm for β-D-arabinofuranoside. Sugar *H*-2, *H*-3, *H*-4 protons were identified at δ 5.20, 5.55 and 4.67 ppm as doublet, singlet and triplet respectively. Two *H*-5 protons were observed at δ 4.30 (d, *J* = 7.2 Hz). The propargyl methylene and methine were noticed at δ 3.98 (d, *J* = 2.3 Hz) and at δ 2.41 (t, *J* = 2.3 Hz) ppm due to the long range couplings. Four sets of aromatic protons in aromatic region also showed the presence of three different phenyl ring environments. Set of four protons at δ 8.04 ppm with doublet multiplicity indicated the presence of two benzoyl group. Shielding of two protons from benzoyl region to δ 7.70 ppm indicated that the one of the three benzoyl groups got converted into 1,2-*O*-orthobenzoate form. The remaining nine protons were observed between δ 7.59 and 7.37 ppm. In the ^{13}C NMR spectrum of **8a**, the characteristic resonances observed at δ 105.4 (*C*-1), 123.6 ppm (quaternary carbon in 1,2-*O*-orthobenzoate - disappeared in DEPT spectrum) and presence of two carbonyls at δ 165.4 and 165.9 ppm instead of three indicated the successful formation of 1,2-*O*-orthoester. Resonances found at δ 79.2, 73.8 (disappeared in DEPT) and 51.9 ppm indicated the propargyloxy moiety in compound **8a**. The rest of the sugar carbons appeared at δ 78.4, 78.0, 71.8 and 63.6 ppm. Similarly, propargyl 1,2-*O*-orthoesters of lyx*f* (**13a**), rib*f* (**9a**), and xyl*f* (**14a**) were synthesized and characterized thoroughly by using NMR and Mass spectroscopic techniques (**Scheme 2.2**). With these orthoesters in our hand, now the next challenge is that how to activate these orthoesters?

To begin our investigation, arabinofuranoside propargyl 1,2-*O*-orthoester **8a** was treated with model glycosyl acceptor **11e** and 4 Å MS powder in the presence of gold(III) tribromide in dichloromethane (standard condition for propargyl 1,2-*O*-orthoesters in pyranosides case[15c]). Surprisingly, complete consumption of 1,2-*O*-orthoester was observed within 2 h and formation of two new compounds (**16a** & **17**) on TLC indicated the activation of 1,2-*O*-orthoester in the presence of gold (III) bromide (**Scheme 2.3**). In the ^{1}H NMR spectrum of **16a**, the characteristic anomeric resonances for α-arabinofuranoside found as a singlet at δ 5.35 ppm. A doublet (*J* = 3.6 Hz) at δ 5.25 ppm which was characteristic for α-glucopyranoside also was noticed. *H*-2 proton in arabinofuranoside showed singlet due to vicinal-trans coupling

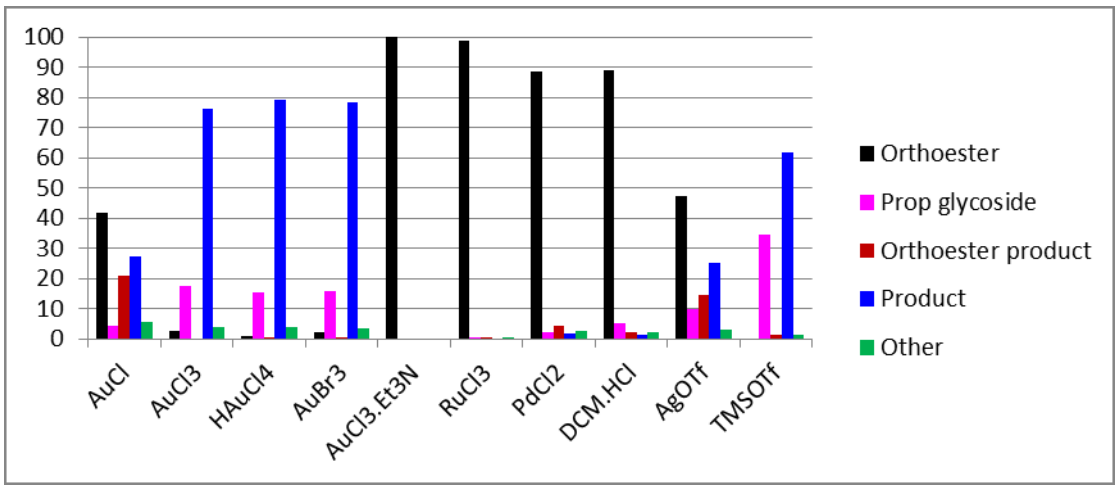
with *H*-1 and *H*-3. The *H*-3 proton in arabinofuranoside was identified at δ 5.53 ppm as a doublet. The resonances observed at δ 6.14 and δ 5.73 ppm as triplets with same coupling constants for *H*-3 and *H*-4 in glucopyranoside. The doublet of doublet at δ 5.30 ppm (*J* = 10.1, 3.6 Hz) was assigned for the *H*-2 proton of glucopyranoside which is *cis* to *H*-1 and *trans* to *H*-3. Diastereotopic *H*-6 protons in glycopyranoside were identified at δ 4.05 and δ 3.78 ppm as doublet of doublets. A multiplet around δ 4.29 ppm was observed due to *H*-5 protons in glucopyranoside. In the ^{13}C NMR spectrum, individual anomeric resonances for α-arabinofuranoside and α-glucopyranoside were observed at δ 105.4 and 97.0 ppm respectively. Methoxy group at the reducing end was identified at δ 55.5 ppm. Rest of the carbons in arabinofuranoside and glucopyranoside appeared between δ 63.7 and 81.9 ppm. Six carbonyl groups were displayed in the carbonyl region and thirty carbons in aromatic region indicated the presence of six benzoyl group as in compound **16a.**

Scheme 2.3: Catalyst screening through UP-LCMS



Optimized conditions: $AuCl_3$ (5 mol%), 4 Å MS powder, anhy. CH_2Cl_2, 25 °C, 2 h

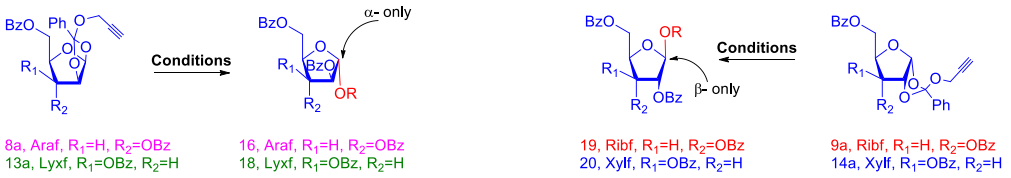
Chart 2.1: Catalyst screening through UPLC-MS



Further, the furanosylation reaction shown in Scheme 2.3 was monitored by the UPLC-MS to understand the diastereoselectivity and percentage of conversion. Initially, standards of all starting materials and products along with side products were

injected into UPLC-MS to obtain the corresponding individual retention times. Gratifying to find that similar of yield was noticed in UPLC-MS chromatogram compare to what was obtained after column chromatography purification. Further, the furanosylation was optimised with other gold and alkynophilic salts in search of better, mild and reliable reaction conditions. Similar reactivity was noticed in $AuCl_3$ and $HAuCl_4$. Decreased Lewis acidity in AuCl was not found to be beneficial whereas other alkynophilic reagents ($PdCl_2$, $RuCl_3$, and AgOTf) did not give any desirable yields (Chart 2.1). In TMSOTf, the reaction completed in two hour but the percentage of product (**17**) was more compared to gold(III) reaction. Controlled experiment with $AuCl_3$:Et_3N did not show any product which meant that there is formation of Brønsted acid in the reaction. There was no considerable progress after two hours in catalytic amount of 1M DCM:HCl (dry) which again indicated that gold(III) salts are required along with the Brønsted acid. Gold(III) salts are effective over other metal salts,

Table 2.2: Substrate scope



Conditions: ROH, $AuCl_3$, CH_2Cl_2, 4 Å Molecular Sieves Powder, rt, 2 h

Aglycon → / Donor ↓	**11e**	**11f**	**11g**	**11h**	**11i**	**11j**	**11k**	**11l**	**11m**	**11n**
8a	16a:78%	16b:92%	16c:83%	16d:82%	16e:90%	16f:82%	16g:80%	16h:77%	16i:81%	16j:72%
13a	18a:75%	18b:94%	18c:ND	18d:81%	18e:78%	18f:72%	18g:72%	18h:73%	18i:75%	18j:ND
9a	19a:79%	19b:90%	19c:85%	19d:82%	19e:88%	19f:89%	19g:75%	19h:75%	19i:86%	19j:66%
15b	20a:80%	20b:94%	20c:85%	20d:78%	20e:88%	20f:88%	20g:77%	20h:78%	20i:86%	20j:67%

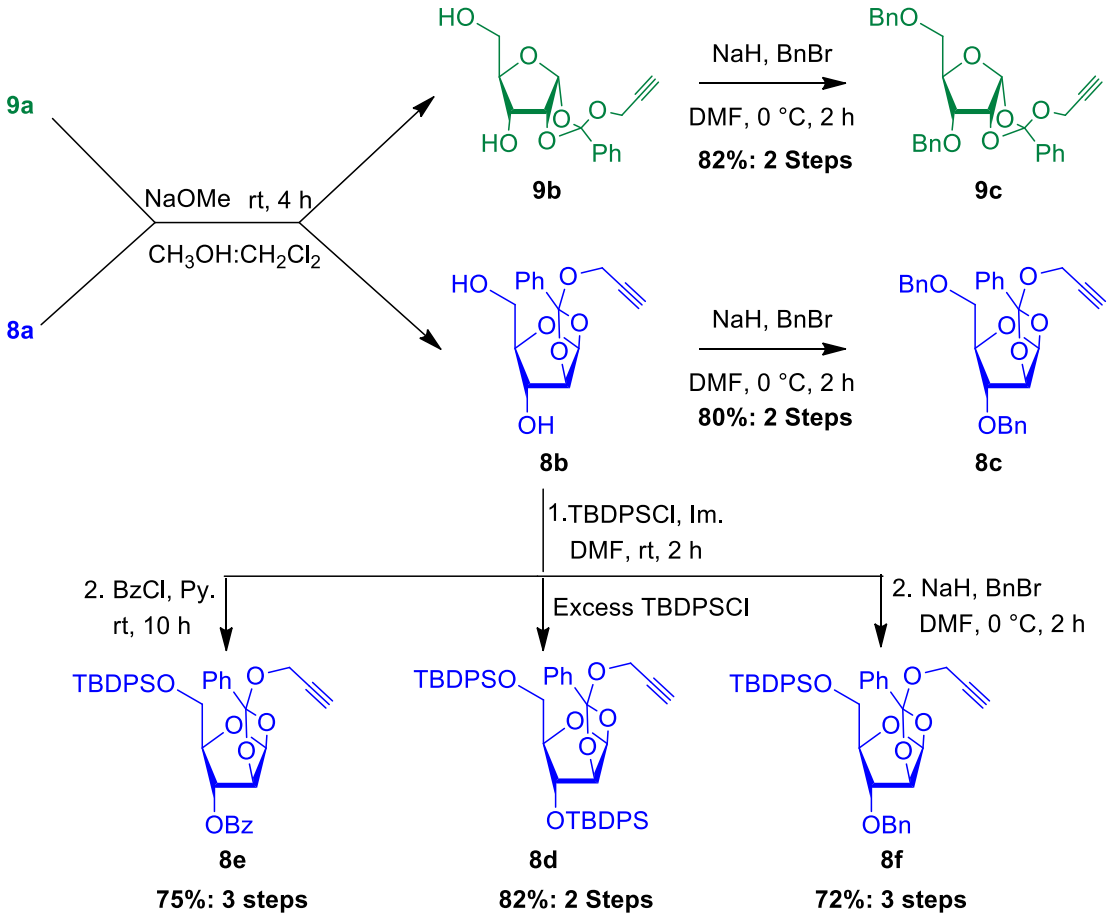
Lewis acids and Brønsted acid for the activation of 1,2-*O*-orthoester. Due to the cost effectiveness and high moisture sensitivity of $AuBr_3$ and $HAuCl_4$ respectively, $AuCl_3$ was found to be ideal for this reaction (**Chart 2.1**). The same reaction conditions were established with other furanosyl 1,2-*O*-orthoester (**9a**, **13a**, and **14b**) to obtain 1,2-*trans* furanosides in very good yield. Further, the first gold-catalyzed furanosidation was found to be suitable even for other acceptors such as alcohols with olefin (**11f**), aromatic alcohol (**11g**), steroidal alcohol (**11h**), amino acid alcohol (**11i**), and partially protected sugar alcohols (**16j** to **16n**) to achieve corresponding furanosylconjugates.

Interestingly, propargyl 1,2-*O*-orthoester was also orthogonally activated in the presence of methyl (**11j and 11k**), pentenyl (**11l**), and propargyl glycosides (**11m** and **11n**) to form corresponding glycoside with leaving group at the reducing end for further glycosidations (**Table 2.2**).

2.3.3– Construction of building blocks

Main aim for our on-going research is to study the Mtb cell wall structure, conformation, and its role.

Scheme 2.4: Synthesis of basic building blocks



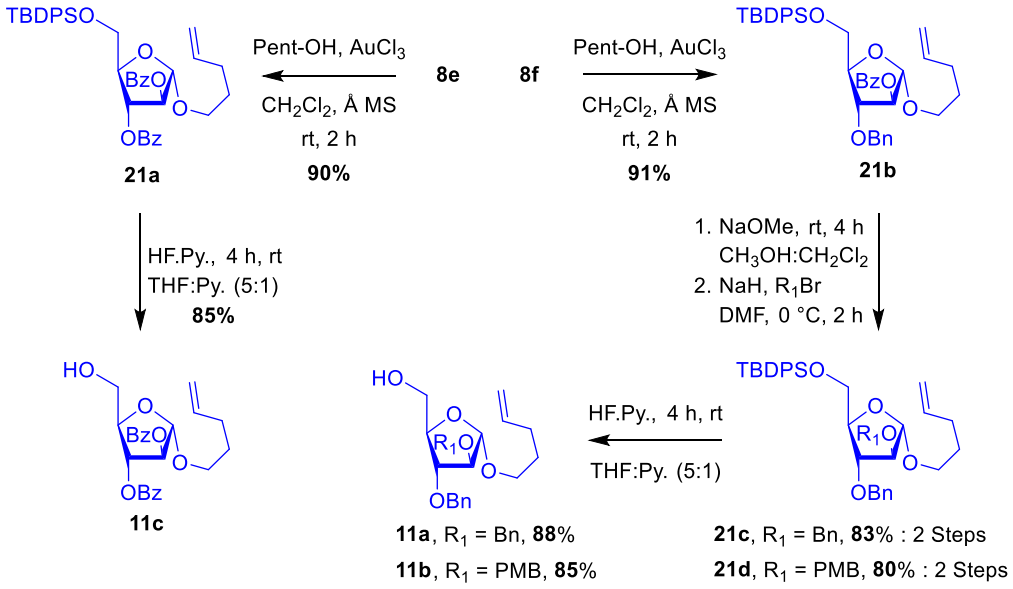
As per a general strategy identified by retrosynthetic analysis, the synthesis of the building blocks in large quantities has been first dealt with. The major units (**4** to **7**) can be obtained from general building blocks (**8** to **11**) which inturn can be easily obtained from our standard 1,2-*O*-orthoester protocol. Accordingly, propargyl 2,3-di-*O*-benzoyl arabinofuranoside 1,2-*O*-orthobenzoate (**8a**) was saponified under Zemplén conditions to obtain diol (**8b**) in excellent yields (**Scheme 2.4**). The crude

diol **8b** without any further purification was treated with excess of TBDPSCl/Im. to generate **8d** in 82% yield (**Scheme 2.4**). The ^{1}H NMR spectrum of **8d** was similar to that of compound **8a** only difference was the presence of two different *t*-butyl groups at δ 1.09 ppm and 0.84 ppm indicated the presence of two TBDPS groups instead of benzoyl groups. In the ^{13}C NMR spectrum of **8d**, the presence of resonances at δ 26.8, 26.7, 19.1 and 19.0 ppm indicated the presence of *t*-butyl group in TBDPS moiety. Absence of carbonyl groups from carbonyl region indicated the compound **8d** devoid of benzoyl groups. Rest of the ^{13}C NMR spectrum of **8d** was similar to that of **8a**. The selective protection of crude diol **8b** was achieved by using one equivalent of TBDPSCl/Im. in DMF followed by treatment with NaH/BnBr/DMF and BzCl/Py in separate flasks to acquire corresponding benzylated (**8e**) and benzoylated (**8f**) orthoester (**Scheme 2.4**). In the ^{1}H NMR spectrum of **8e**, appearance of *H*-1 at δ 6.22 (d, *J* = 4.4 Hz) ppm, *t*-butyl group at δ 0.94 ppm as a singlet and benzylic methylene at δ 5.29 ppm as a singlet confirmed the compound **8e**. In addition, the ^{13}C NMR spectrum of **8e** revealed, *C*-1 at δ 106.7 ppm, *t*-butyl group at δ 26.9 and 19.3 ppm and characteristic resonances for quaternary carbon present in 1,2-*O*-orthobenozte at δ 122.5 ppm. Similarly, NMR spectrum of **8f** showed the presence of *t*-butyl group (at δ 0.99 ppm in the ^{1}H NMR and at δ 26.1, 19.1 ppm in the ^{13}C NMR in TBDPS moiety and aromatic benzoylic ortho protons (at δ 8.09 ppm in the ^{1}H NMR) as well as carbonyl group (at δ 165.1 ppm in the ^{13}C NMR) indicated the presence of TBDPS moiety and benzoyl groups. Propargyl 2,3-di-*O*-benzyl arabinofuranoside 1,2-*O*-orthobenzoate (**8c**) was obtained from crude diol **8b** by treatment with excess of NaH/BnBr in DMF (**Scheme 2.4**). In the NMR spectrum of **8c**, only deviation from **8a** was the absence of two benzoyl groups (absence of carbonyl group near δ 165.1 ppm in the ^{13}C NMR) and presence of two benzylic methylenic protons (4 extra protons around δ 4.58 ppm) in the ^{1}H NMR and two CH_2 at δ 73.3 and 71.6 ppm in the ^{13}C/DEPT NMR confirmed the successful synthesis of compound **8c** (**Scheme 2.4**).

Further, **8e** was utilised for the synthesis of pent-4-enyl 2,3-di-*O*-benzoyl α-D-arabinofuranoside **11c** in two steps. In the arabinogalactan, first gold-catalyzed glycosidation was done between orthoester **8e** and pent-4-en-1-ol in the presence of 4 Å MS in CH_2Cl_2 to afford **21a**. The deprotection of 5-*O*-TBDPS group in **21a** was achieved using HF.Py in THF to generate alcohol **11c** in 77% yield over two steps. In

the ^{1}H NMR spectrum of **11c**, the anomeric proton was observed at δ 5.23 ppm and in the ^{13}C NMR spectrum the anomeric carbon was noticed at δ 105.5 ppm indicated the compound in 1,2-*trans* fashion. Similarly, pent-4-enyl 2,3-di-*O*-benzyl α-D-arabinofuranoside **11a** and pent-4-enyl 2-*O*-(*p*-methoxybenzyl)-3-*O*-benzyl-α-D-arabinofuranoside **11b** were prepared from orthoester **8f** in four steps i.e. 1.

Scheme 2.5: Synthesis of basic building blocks



glycosidation reaction between the orthoester **8f** and pent-4-en-1-ol in the presence of gold trichloride, 2. Saponification, 3. benzylation of **21b** under aforementioned conditions, and 4. deprotection of silyl ether using HF.Py (**Scheme 2.4**). In the ^{1}H NMR spectrum of **11a**, resonances for anomeric proton were noticed at δ 5.01 ppm as singlet and terminal olefinic -C<u>H</u>=CH$_2$ protons in pentenyl moiety displayed at δ 5.82 ppm as a ddt multiplicity and two vinylic protons [-CH=C<u>H</u>$_2$] as a multiplet between δ 4.95 and 5.05 ppm. *H*-2 and *H*-3 protons appeared as individual multiplets around δ 3.81 and 3.64 ppm respectively. Two doublets of triplets showed at δ 3.71 and 3.40 ppm were characteristic for the presence of -OCH$_2$ group in pentenyl moiety. Two internal CH$_2$ groups from pentenyl moiety were observed as individual quartet and quintet at δ 2.12 and δ 1.69 ppm respectively. Free hydroxyl group (D$_2$O exchangeable) in compound **11a** was appeared as a broad singlet at δ 2.05 ppm. In the ^{13}C NMR spectrum of **11a**, the resonances for anomeric carbon were noticed at δ 106 ppm. Terminal olefinic -<u>C</u>H=<u>C</u>H$_2$ carbons in pentenyl moiety displayed at δ 138.1 and 114.8 ppm respectively. Two carbons from benzylic <u>C</u>H$_2$ were appeared at δ 4.49 and

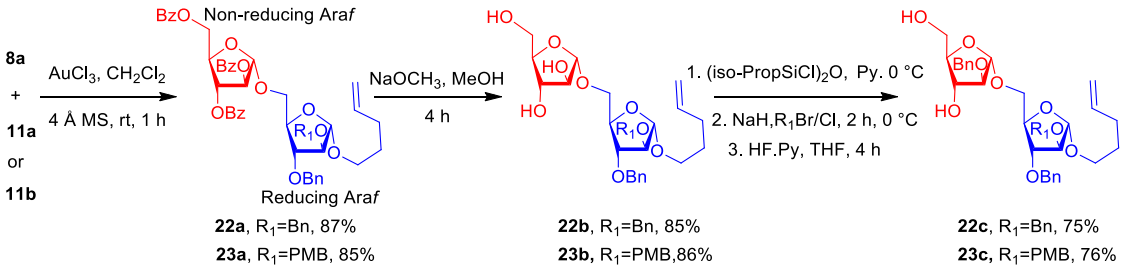
4.60 ppm in the ^{1}H NMR spectrum. Arabinofuranosidic *C*-2, *C*-3, *C*-4 and *C*-5 carbons were noticed at δ 81.8, 82.6, 88.0 and δ 66.8 ppm. Three individual CH_2s from pentenyl moiety were observed at δ 62.1, 30.2 and 28.2 ppm respectively. Aromatic protons showed two sets of carbons in the aromatic region, i.e. around δ 127.9 ppm for ten carbons and around δ 137.0 ppm for two quaternary substituted phenyl carbons.

With these different monomers in our hand, simultaneously we started the synthesis of Terminal-hexasaccharide (or T-Hexasaccharide), Middle-hexasaccharide (or M-hexasaccharide), tetrasaccharide and trisaccharide portions of AG.

2.3.4– Synthesis of T-hexasaccharide 1,2-*O*-orthoester

The main synthetic endeavour started with the reaction between orthoester (**8a**) and glycosyl acceptor **11a** (and **11b**) in the presence of catalytic amount of gold trichloride and 4 Å

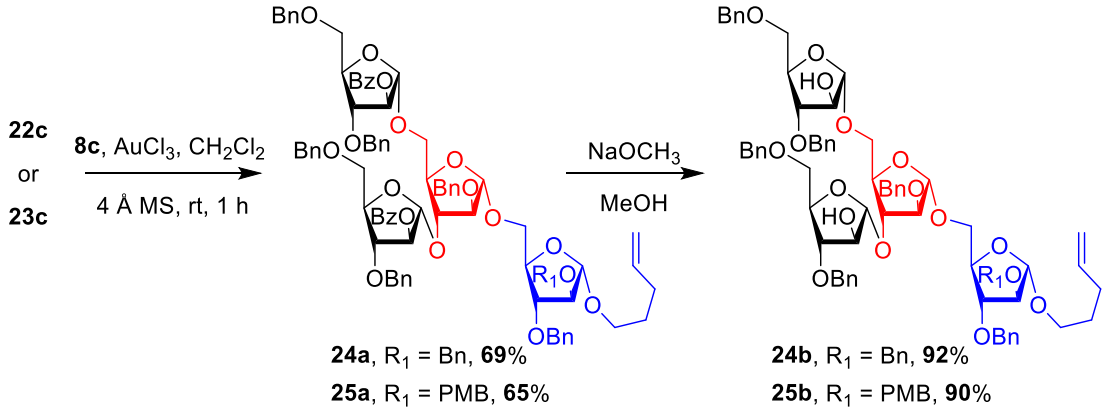
Scheme 2.6: Gold (III) for disaccharide of AG



MS powder in dichloromethane to obtain disaccharide **22a** (and **23a**) in 87% yield. In the ^{1}H NMR spectrum of **22a**, the anomeric protons were noticed as a two singlets at δ 5.36 and 5.04 ppm. Resonances at δ 5.82 ppm displayed as ddt for one proton and the resonances between δ 4.93 and 5.04 ppm displayed multiplets for two protons indicated the presence of -CH=CH_2 group in compound **22a**. Two doublet of triplet at δ 3.71 and 3.39 (J = 9.6, 6.5 Hz) ppm were showed for two protons with adjacent -CH_2 group in the pentenyl moiety. Quartet and quintet were observed at δ 2.10 and 1.66 ppm respectively which are characteristic for methylene of pentenyl moiety. In the aromatic region, a set of six protons were observed around δ 7.99 ppm and another set of nineteen protons around δ 7.39 ppm indicated the presence of five aromatic protons out of which three were from benzoates and two were from benzyl

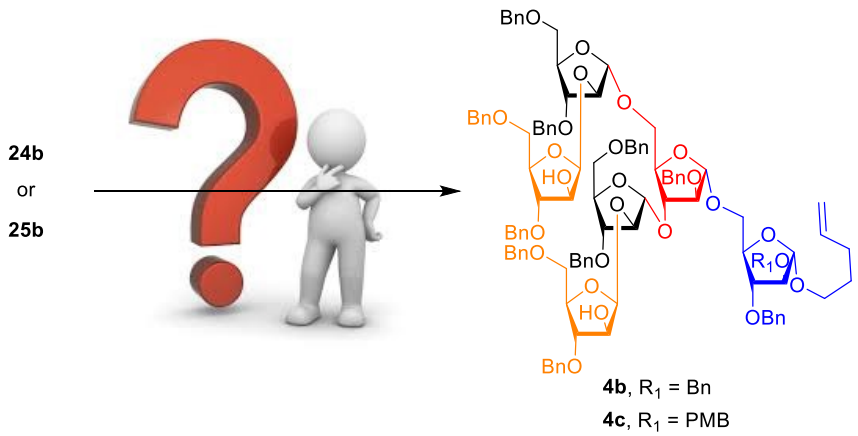
moiety. In the ^{13}C NMR spectrum of **22a**, two anomeric carbons of non-reducing and reducing arabinofuranosides were identified at δ 106.0 and 105.6 ppm. Olefinic methine and methylene in the pentenyl moiety were identified at δ 138.1 and 114.8 ppm. Rest of the carbohydrate carbons present in the disaccharide were displayed between δ 63.7 and 88.5 ppm. The resonances found at δ 30.3 and 28.7 ppm were characteristics for the presence of two -CH_2's in the pentenyl moiety. From the DEPT spectrum, it is evident that there were eight methylenes present in the compound **22a**. Three carbonyl carbons found around δ 165.7 ppm confirmed the presence of three benzoate groups in compound **22a**. Thirty carbons were found between δ 127.6 and 137.8 ppm and out of which five disappeared in DEPT spectrum which concluded the presence of five aromatic rings. Benzoyl groups in the compound **22a** were deprotected in the presence of sodium methoxide and methanol to form triol **22b (**and **23b)** in good yield. Triol **22b** (and **23b**) was first reacted with 1,1,2,2-tetraisopropyldichlorodisiloxane in pyridine to block *O*-3 and *O*-5 hydroxyl groups; further, treated with sodium hydride and benzyl bromide (and *p*-methoxy benzyl chloride) and followed by the treatment of TBAF in THF to acquire diol **22c** (and **23c**) in 90% over three steps. In the ^{1}H NMR spectrum of **22c**, only difference from the **22a** was that there were no benzoylic ortho protons in the aromatic region and additional five extra protons present in the aromatic region confirmed the absence of benzoyl group and presence of three benzyl group. In the ^{13}C NMR spectrum of **22c** which was similar to that of **22a** with difference that there were no resonances due to carbonyls in the ester region. Extra methylene resonances were observed in the ^{13}C and DEPT NMR indicating one more benzylic methylene. Rest of the protons and carbons of **22c** were looking similar to that of **22a**. Similar set of reactions were performed for the synthesis of **23c** and data of **23c** was also similar to that of **22c**. In the ^{1}H NMR of **23c** additional resonances were noticed at δ 3.79 ppm as a singlet for methoxy group of PMB moiety and two protons were shielded from δ 7.28 to 6.87 ppm due to one of the di-substituted phenyl ring of PMB group (**Scheme 2.6**). In the ^{13}C NMR spectrum, the resonances presented at δ 159.5, 113.9, and 62.6 ppm (from DEPT) indicated the presence of PMB group in compound **23c**. The corresponding diol **22c** (and **23c)** was converted into tetrasaccharide in 69% yield by treating with excess of orthoester (2.5 eq.) **8c** in the presence of catalytic amount of gold trichloride in CH_2Cl_2 (**Scheme 2.7**).

Scheme 2.7: Gold (III) for tetrasaccharide diol of AG



In the ^{1}H NMR of **24a**, characteristic additional anomeric resonances were observed in the region of anomeric protons i.e. around δ 5.30 ppm with two protons in **24a** and indicated the presence of two more sugar residues from **22c**. Even increase in the number of protons in sugar region as well as aromatic region indicated the presence of two extra arabinose residues in **24a**. Protons with singlet multiplicity at δ 5.34 and 5.45 ppm indicated the presence of two electron withdrawing substitutions at the respective alcohols in compound **24a** i.e. benzoate groups. This was again confirmed by the deshileding of four protons in aromatic region from δ 7.29 to 7.95 ppm. In the ^{13}C NMR of **24a**, four anomers were observed at δ 105.4, 106.0, 106.2 and 106.3 ppm indicating the presence of four arabinofuranosides in 1,2-*trans* fashion. Tetrasaccharide **24a** gave good matching in the HRMS viz. calcd m/z for $[C_{88}H_{92}O_{19}+Na]^{+}$: 1475.6131; Found: 1475.6117.

Scheme 2.8: How to convert diRib*f*tetAra*f* diol to hexaAra*f*?



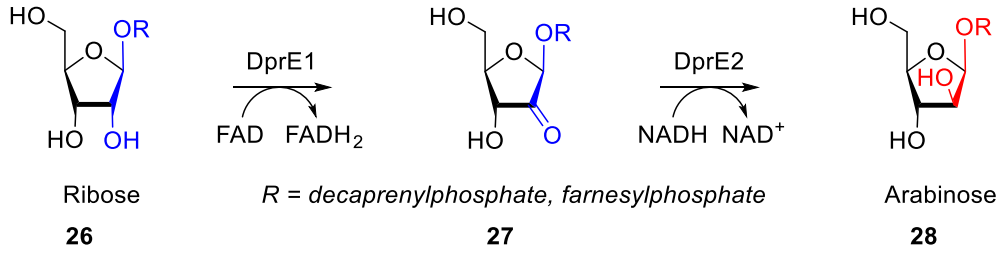
Tetrasaccharide diol **24b** (and **25b**) was obtained in good yield from di-*O*-benzoyl tetrasaccharide **24a** (and **25b**) and sodium methoxide in methanol. The absence of

characteristic two sets of protons at δ 7.29 and 7.95 ppm for 10 protons in aromatic region of the ^{1}H NMR spectrum and carbonyl carbons at δ 165.2 ppm, 12 aromatic carbons in the ^{13}C NMR spectrum indicated the formation of diol **24b**. Tetrasaccharide **24a** gave good matching in the HRMS *viz*. calcd m/z for $[C_{74}H_{84}O_{17}+Na]^{+}$: 1267.5606; Found: 1267.5649. Now, the next step towards the synthesis of T-hexasaccharide is to install two β-arabinofuranosides onto the tetrasaccharide diol (**24b** and **25b**). Next challenge is how to install them in a distereoselective fashion (**Scheme 2.8**). Current protocol enables only 1,2-*trans* and 1,2-*cis* furanosides are renowned for their synthetic difficulty.

2.3.4.1– Biochemical[17a] and chemical[17b] epimerisation of β-Rib*f* to β-Ara*f*

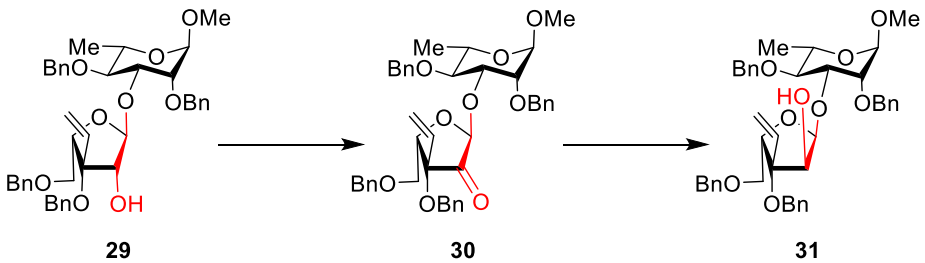
For a long time, biochemists thought that β-arabinofuranosides **28** are obtained from β-ribofuranosides **26** by epimerization at the *C*-2 position (**Scheme 2.9**).[17a] In

Scheme 2.9: Biochemically interconversion of β-Rib*f* to β-Ara*f*



addition, chemistry of pyranosides has a long precedence of oxido-reduction strategy for the conversion of 1,2-*trans* to 1,2-*cis* pyranosides;[17c] however, a parallel approach

Scheme 2.10: Chemical transformation of β-Rib*f* to β-Ara*f*

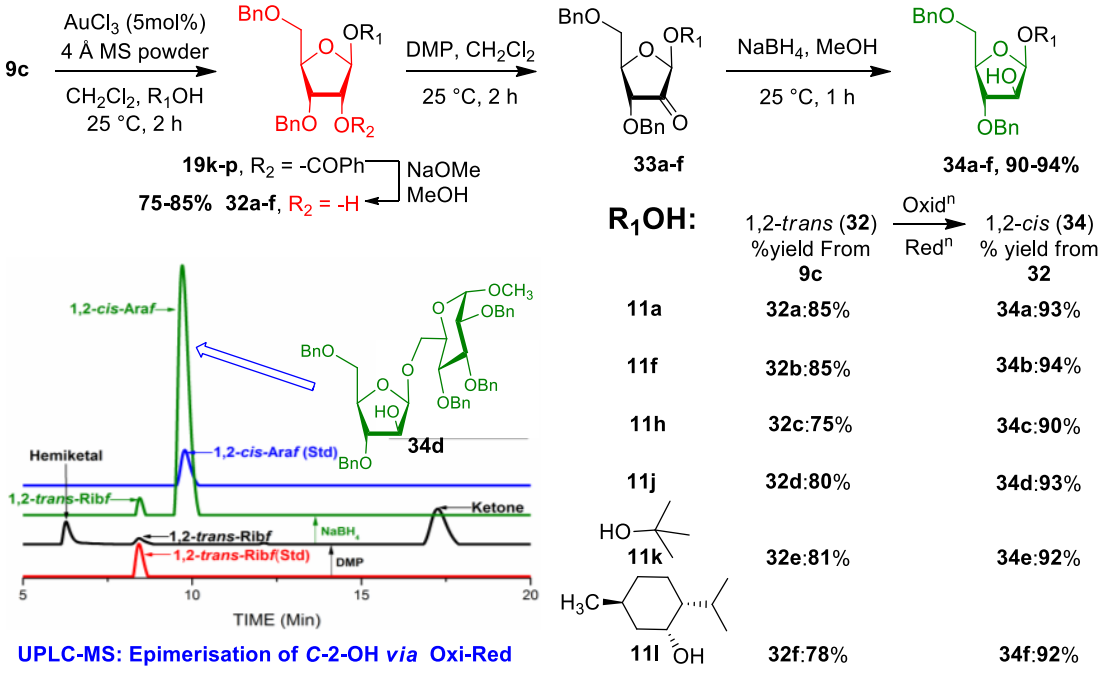


in furanosides is rare except for a report of oxido-reduction strategy on a highly substituted L-arabinofuranosyl **29** system by de Oliviera *et al.* (**Scheme 2.10**).[17b]

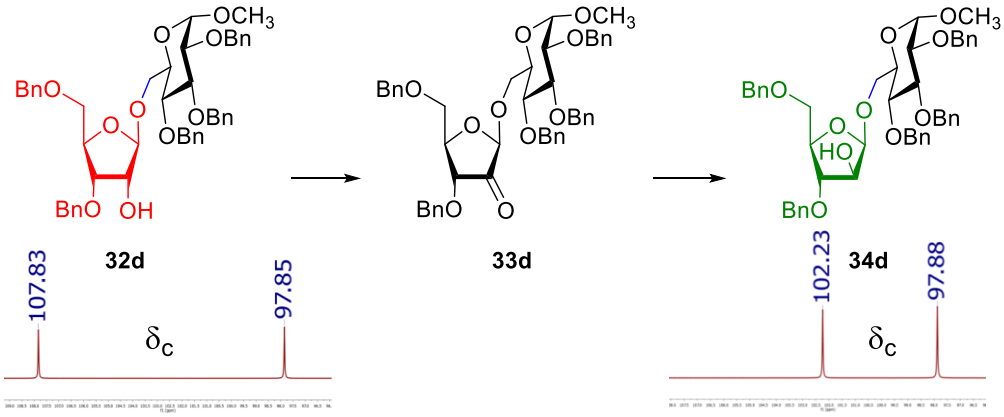
2.3.4.2– Chemical conversion of 1,2-*trans* to 1,2-*cis* furanosides[18]

The biochemical approach of Mtb and many examples in pyranosides had encouraged us to investigate the chemical conversion of 1,2-*trans* (or β-) ribofuranosides to 1,2-*cis* (or β-) arabinofuranosides. To evaluate, a suitably protected propargyl 1,2-orthoester of ribofuranose was required. Accordingly, ribofuranosyl donor **10c** was synthesized from D-ribose and subjected to the aforementioned gold (III) catalyzed glycosidation with a panel of glycosyl acceptors (**11b, 111, 11h, 11j, 11k & 11l**) to obtain corresponding β-ribofuranosides (**19k-p**) in very good yields.

Scheme 2.11: Gold (III) repotire for β-ribofuranoside to β-arabinofuranoside

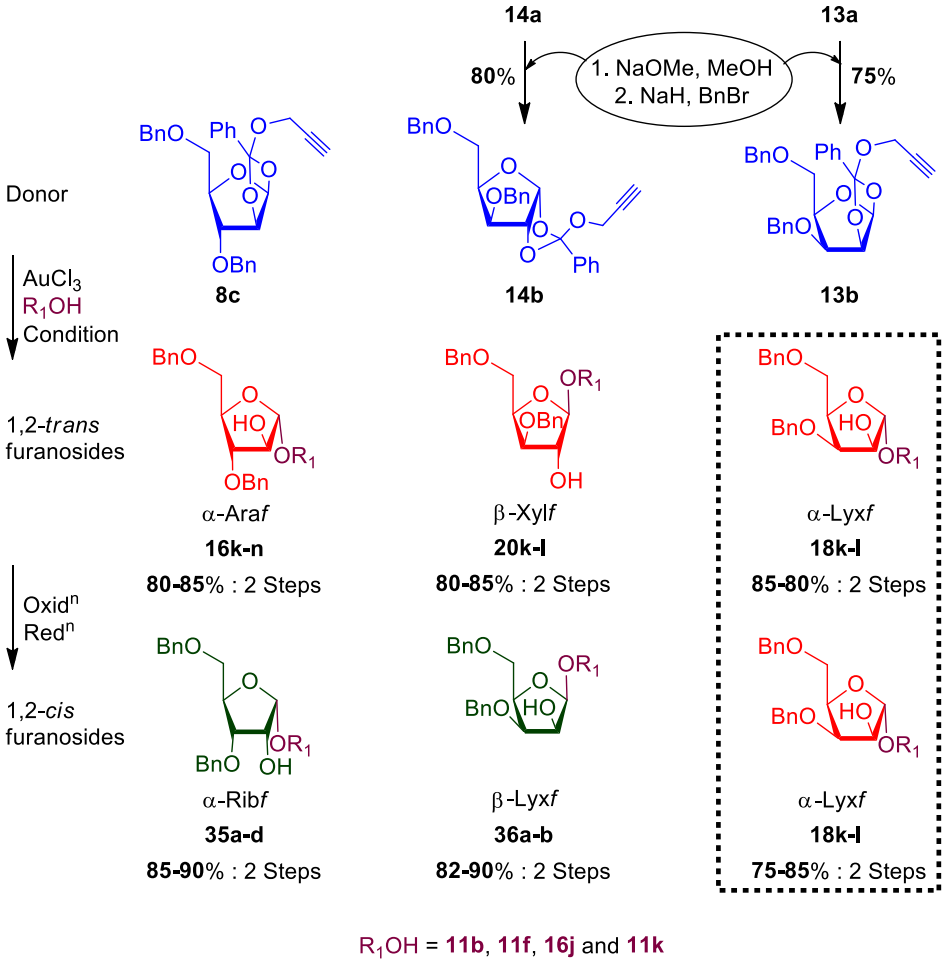


Scheme 2.12: Partial ^{13}C: Anomers for β-ribofuranoside to β-arabinofuranoside



Subsequently, all ribofuranosides **19k-p** in parallel were saponified under Zemplén conditions (NaOMe, MeOH) to **32a-f** and oxidized with Dess-Martin periodinane in CH_2Cl_2 at 25 °C to the respective 2-ribulofuranoses (**33a-f**) in greater than 90% yields. Crude residue of oxidation reaction was noticed to contain ribulofuranoses **33a-f** were subsequently subjected to $NaBH_4$ reduction in CH_3OH to observe complete conversion to 1,2-*cis*-arabinofuranosides **34a-f** (**Scheme 2.11**). Conversion of β-ribofuranoside to β-arabinofuranoside was monitored by UPLC-MS using a model β-ribofuranoside **32d**. Initially, pure samples of β-ribofuranoside **32d** & β-arabinofuranoside **34d** were injected into a UPLC-MS to find two well separated peaks at t_R 8.48 min for β-rib*f* and t_R 9.93 min for β-ara*f*. Then, the reaction mixture of DMP oxidation after completion of the reaction as adjudged by the TLC-MS was injected to find hydrated gem-diol (t_R = 6.30 min) in addition to the required ketone (**38c**) (t_R = 17.45 min) and the remaining starting material (8%).

Scheme 2.13: Gold (III) repotire for 1,2–*trans* furanosides to 1,2–*cis* furanosides



R_1OH = **11b**, **11f**, **16j** and **11k**

Subsequently, the reaction mixture of the $NaBH_4$ reaction was injected to find a 8:92 ratio of **33d:34d** which clearly showed that the reduction took place in a highly distereoselective manner. The diastereoselective conversion was confirmed by means of NMR spectral analysis. Anomeric carbons of ribofuranoside **32d** were noticed at δ 97.9, 107.8 ppm whereas those of arabinofuranoside **34d** were found at δ 98.0 and 102.4 ppm. In addition, $^1J_{C\text{-}H}$ values of rib*f* **32d** were found to be 171 and 176 Hz whereas $^1J_{C\text{-}H}$ values of ara*f* **34d** were noticed to be 174 and 183 Hz. Subsequently, 1,2-*cis* rib*f* which are also equally challenging were envisioned from 1,2-*trans* araf. Accordingly, orthoester **8b** was converted into orthoester **8c** under aforementioned conditions in two steps. Gold-catalyzed furanosylation with **11e**, **11f**, **11j**, and **11l** afforded easily 1,2-*trans* arabinofuranosides **16k-n**. Oxidation by Dess-Martin periodinane and subsequent reduction with $NaBH_4$ gave 1,2-*cis* ribofuranosides **35a-d** in a fully diastereoselective manner.

In continuation, 1,2-*cis* lyxofuranosides **36a**,**b** were found to be resulting by similar set of reactions from 1,2-*trans* xylofuranosides **20k**,**l**. Similarly, 1,2-*cis* xylofuranosides are envisaged from 1,2-*trans* lyxofuranosides **18k**,**l** which can be conveniently synthesized from orthoester **13b**. However, the oxidation with Dess-Martin periodinane followed by the reduction using $NaBH_4$ resulted into the starting 1,2-*trans* lyxofuranosides **18k**,**l** but not required 1,2-*cis* xylofuranoside.

Stereochemical outcome can be explained by closely looking at the *C*-2-ulose derivatives of all the four furanosides reveals the differential steric crowding around the ketone that is undergoing the reduction. The ring oxygen, *C*-5-OBn and *C*-1 glycoside prevent the hydride to attack from the *exo*-face in the case of β-rib*f*→β-ara*f* conversion; and hence, hydride prefers the *endo*-attack on the ketone to give β-ara*f* only. Similarly, *endo*-face in the α-araf→α-ribf conversion is sterically not favourable and hence, the *exo*-attack product was observed. Also, in case of β-xyl*f*→β-lyx*f* conversion, the *exo*-face is sterically demanding which results into *endo*-facial attack of the *C*-2 ulose derivative. The ring oxygen, C-3-OBn, and the *C*-5-OBn make the *exo*-face complete unavailable for the hydride to attack on the ketone giving back the starting material in case of α-lyx*f*→α-xyl*f* (**Scheme 2.13**). Identification of facile protocols for 1,2-*cis* and 1,2-*trans* arabinofuranosides inspired to synthesize T-hexasaccharide en-route pentadodecameric arabinogalactan of Mtb. Accordingly, the gold-catalyzed furanosylation between glycosyl acceptor **24b** (and

25b) and two molar equivalents of ribofuranosyl donor **9c** followed by saponification under Zemplén conditions resulted into hexafuranosyl glycosyl acceptor **4b** (and **4c**) in 56% yield over two steps (**Scheme 2.14**).

Scheme 2.14: Bio-inspired gold (III) repotire for T-hexafuranoside synthesis

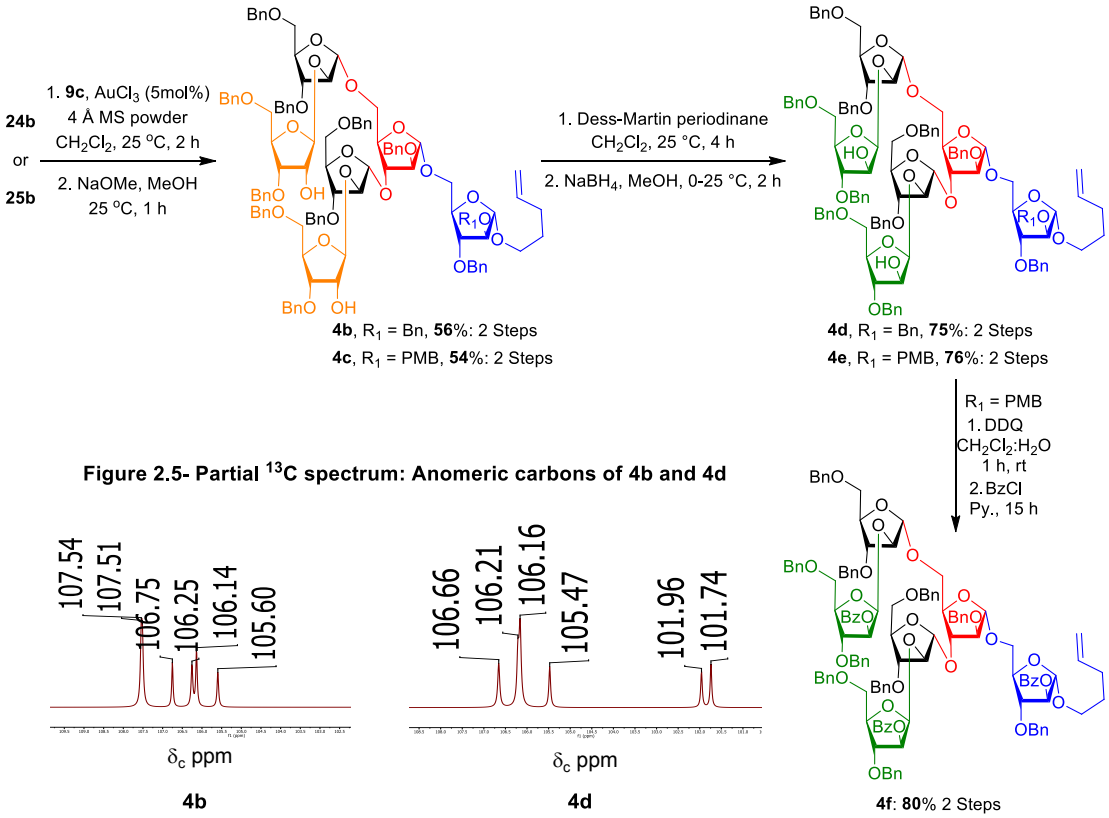


Figure 2.5- Partial ^{13}C spectrum: Anomeric carbons of 4b and 4d

Glycosyl acceptor **4b** (and **4c**) was oxidized with Dess-Martin periodinane to give the 2-ulose derivative. $NaBH_4$-mediated distereoselective reduction of the 2-ulose derivative gave the hexaarabinofuranoside **4d** (and **4e**) with two 1,2-*cis* and four 1,2-*trans* linkages (**Scheme 2.14**).

Conversion of rib*f* hexasaccharide (**4b**) to ara*f* hexasaccharide was confirmed by its anomeric ^{13}C NMR spectral signatures (**Figure 2.5**). The six anomeric carbons of compound **4b** were observed as a single set between δ 105.6-107.5 ppm, whereas those of compound **4d** were noticed as two sets. The two carbons linked in 1,2-*cis* fashion were identified at δ 101.7 and 102.0 ppm, and the remaining four 1,2-*trans* anomeric protons observed around δ 106 ppm. $^{1}J_{C\text{-}H}$ values for four 1,2-*trans* linkages were noticed to be 173-177 Hz, and that of the other two 1,2-*cis* linkages were found to be around 183 Hz of hexasaccharide **4d**, whereas all $^{1}J_{C\text{-}H}$ values of compound **4b** were noticed between 173 and 176 Hz only. Similarly, more versatile 2-*O*-PMB

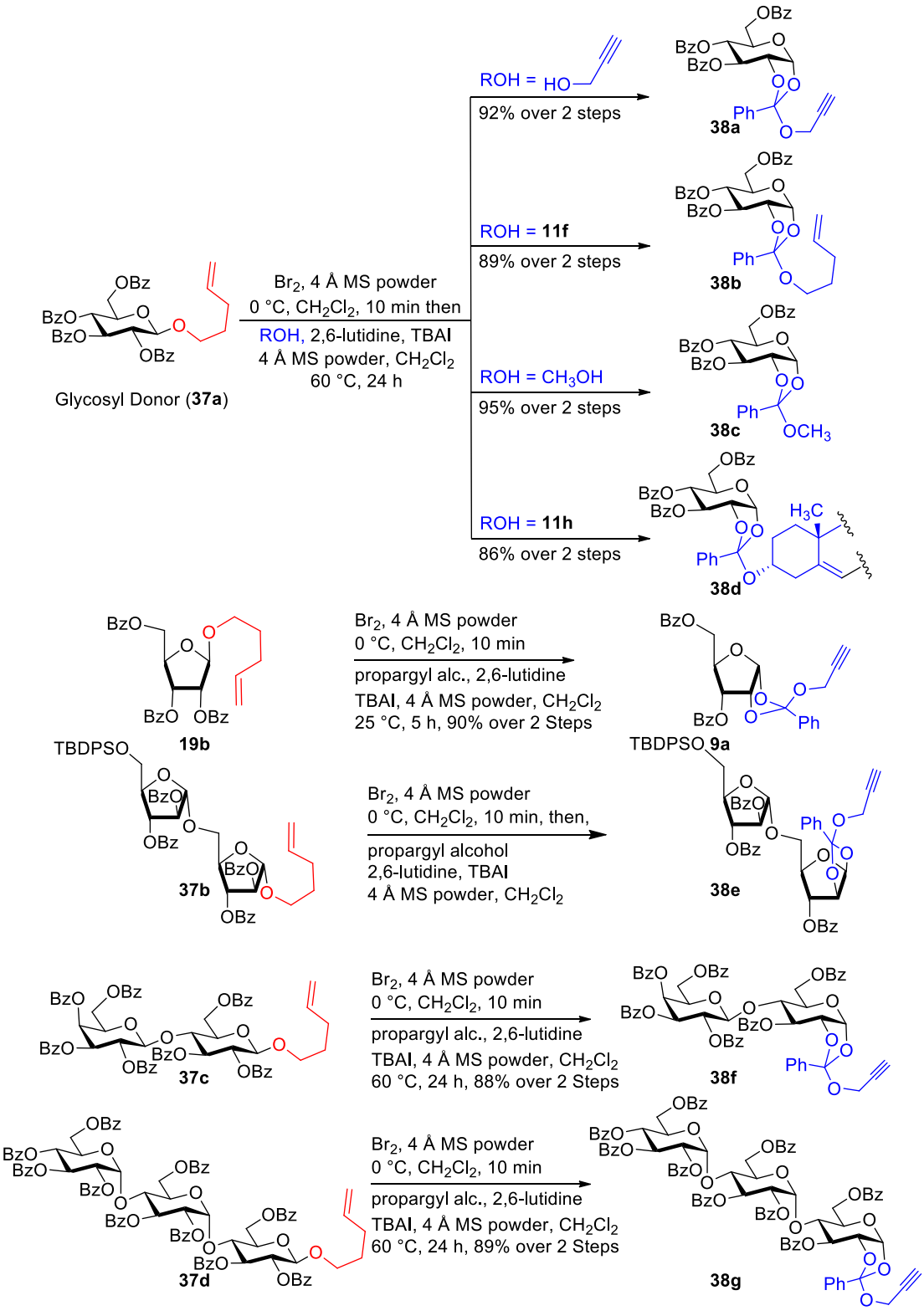
containing rib*f*-hexasaccharide **4c** was synthesized and further converted successfully into T-hexasaccharide **4e**. In continuation, hexasaccharide **4e** was converted into the pent-4-enyl tri-*O*-benzoyl hexasaccharide **4f** in two steps. First diol **4e** was converted into the triol using DDQ in CH_2Cl_2 and water followed by treated with benzoyl chloride in pyridine for overnight to get pent-4-enyl tri-*O*-benzoyl hexasaccharides **4f** in 80% over two steps.

2.3.4.3– Conversion of *n*-pentenyl glycosides to glycosyl propargyl 1,2-orthoester

Synthesis of oligosaccharides requires more than one building block and often, more than one glycosyl donor as well. Also, alkyl (e.g. pentenyl and propargyl) glycosides are not very reactive compared to the trichloroacetamidates. As a result, it would be ideal if the strategy that we develop can compare the relative reactivity's of T-hexasaccharide by synthesizing the *n*-pentenyl glycosides, propargyl 1,2-orthoesters and the trichloroacetamidate as the donor. Conversion of *n*-pentenyl glycosides into 1,2-orthoesters is hitherto unknown in the literature. However, *n*-pentenyl containing monosaccharides were converted to bromoaldoses by Fraser-Reid group earlier. But, there were no reports on the conversion of *n*-pentenyl containing oligosaccharides into bromoaldoses thus far. Gratifying to note that propargyl 1,2-orthoesters can be synthesized if bromoaldoses are available for the oligosaccharides. In this premise, we thought of exploring these conversions before proceeding further. Hence, conversion[19a] of *n*-pentenyl glycosides into the corresponding glycosyl bromide which could eventually be transformed into 1,2-orthoesters under mild conditions would be highly rewarding. Switching of *n*-pentenyl glycosides to propargyl 1,2-orthoesters would be beneficial: (i) for increased reactivity and yield; (ii) as the glycosidation becomes catalytic; (iii) since the leaving group becomes traceless; (iv) affords 1,2-*trans* stereoselectivity; (v) for facilitated purification; (vi) as the glycan synthesis need not be restarted; (vii) for orthogonal activation, and (viii) for the convergent synthesis of glycans.

Mindful of these advantages, we considered conversion of *n*-pentenyl glycosides into propargyl 1,2-orthoesters. Easily accessible *n*-pentenyl 2,3,4,6-tetra-*O*-benzoyl β-D-glucopyranoside (**37a**)[19b] was treated with molecular bromine in the presence of 4 Å molecular sieves at 0 ºC in CH_2Cl_2 for 10 min to observe complete conversion of compound **37a** into anomeric bromide. The glucosyl bromide was

Scheme 2.15: Conversion *n*-pentenyl glycoside into glycosyl 1,2-orthoesters



quickly concentrated in *vacuo* and redissolved in CH_2Cl_2, treated with propargyl alcohol, 2,6-lutidine, TBAI in the presence of 4 Å MS powder at 60 ºC for 24 h to obtain propargyl 1,2-orthoester **38a** in 92% yield over two steps (**Scheme 2.15**).[15c] Similarly, *n*-pentenyl orthoester **38b** was obtained in 89% yield under aforementioned

conditions from the glucosyl bromide synthesized *vide supra*. In this endeavour, less reactive *n*-pentenyl glycoside was converted into more reactive and stable *n*-pentenyl or propargyl 1,2-orthoesters in very high yields. In addition, the methodology has been checked by preparing methyl and cholesterol glucosides **38c** and **38d** in 95% and 86% yields respectively.[19c]

The protocol was not only applicable for pyranosides but also for furanosides. For example, the *n*-pentenyl 2,3,5-tri-*O*-benzoyl β-D-ribofuranoside **19b** was successfully converted into propargyl 1,2-orthobenzoate **9a** at room temperature in 90% yield over two steps. Similarly, per-*O*-benzoyl derivatives of *n*-pentenyl lactoside **37c** and maltotrioside **37d** were subjected to the above delineated reaction conditions to obtain corresponding propargyl 1,2-orthobenzoates **38e** and **38f** in 88% and 89% yield respectively (**Scheme 2.15**).

2.3.5– Synthesis of 1,2-*O*-orthoester of middle hexasaccharide (Scheme 2.16)

Simultaneously, 1,2-*O*-orthoester **8d** was treated with glycosyl acceptor **11c** under gold(III) catalyzed glycosidation conditions to give disaccharide **22e** in 81% yield. Subsequently, disaccharide **22e** on treatment with HF.Py in THF gave disaccharide diol **22f** in 90% yield. In the ^{1}H NMR spectrum of **22f**, two arabinosyl *1,2-trans* anomeric protons were observed as individual singlets at δ 5.39 and 5.26 ppm. Olefinic methine and methylenes appeared as ddt and multiplet around δ 5.83 and 5.00 ppm respectively and two double triplets were noticed at δ 3.79 and 3.55 ppm and two multiplets around δ 2.18 and 1.76 ppm indicated the presence of pentenyloxy group at the reducing end. 15-Aromatic protons in aromatic region in ^{1}H NMR and 18-carbons in aromatic region ^{13}C along with 3-carbonyl at δ 165.4, 165.9 and 166.5 ppm disclosed the attendance of three benzoyl rings. Pent di-*O*TBDPS tetraarabinofuranoside **24c** was obtained by using gold-catalyzed glycosidation between disaccharide diol **22f** and orthoester **8e**. In the ^{1}H NMR spectrum of **24c**, four anomeric protons were observed at δ 5.18, 5.30, 5.37 and 5.56 ppm as individual singlets. Rest of protons residue as well as aromatic protons were identified in a sugar region and aromatic region respectively. Two additional resonances were located at δ 0.97 and 0.92 ppm for *t*-butyl group of TBDPS moiety. In the ^{13}C NMR spectrum of **24c**, four anomeric carbons were located at δ 105.5, 105.5, 105.8 and 106.1 ppm. New resonances identified around δ 26 and 19 ppm for *t*-butyl group in TBDPS moiety. Additionally, confirmed by mass spectroscopy wherein the molecular ion was

identified at 2492.7968 Daltons (calcd for $[C_{19}H_{28}O_{12}+Na]^+$: 2492.7968). Further, deprotection of silyl ether of tetrasaccharide **24c** was achieved by using HF.Py in THF:Py and resulting diol was treated with orthoester **8e** in the presence of gold trichloride and 4 Å MS powder in anhydrous dichloromethane to give pent-4-enyl di-*O*-TBDPS hexasaccharide **5b** in 78% over two steps. In the ^{1}H NMR spectrum, all protons and carbons were similar to that of di-OTBDPS tetrasaccharide **24c**. The difference between tetrasaccharide **24c** and hexasaccharide **5b** was that the integration of protons and increase in the number of carbons in respective regions. Hexasaccharyl 1,2-*O*-orthoester **5a** was achieved in 81% from pent-4-enyl hexasaccharide **5b** by adopting the aforementioned reaction conditions (**Scheme 2.16**). The formation of 1,2-*O*-orthoester was confirmed by the NMR and Mass spectroscopic techniques. In the ^{1}H NMR spectrum of **5a**, five 1,2-*trans* anomeric protons were noticed as individual singlets at δ 4.99, 5.23, 5.26, 5.38, and 5.60 ppm and 1,2-*cis* anomeric proton present in 1,2-*O*-orthobenzoates was noticed as a doublet at δ 6.28 (J = 4.3 Hz) ppm.

Scheme 2.16: Gold (III) for middle hexamer 1,2-*O*-orthoester of AG

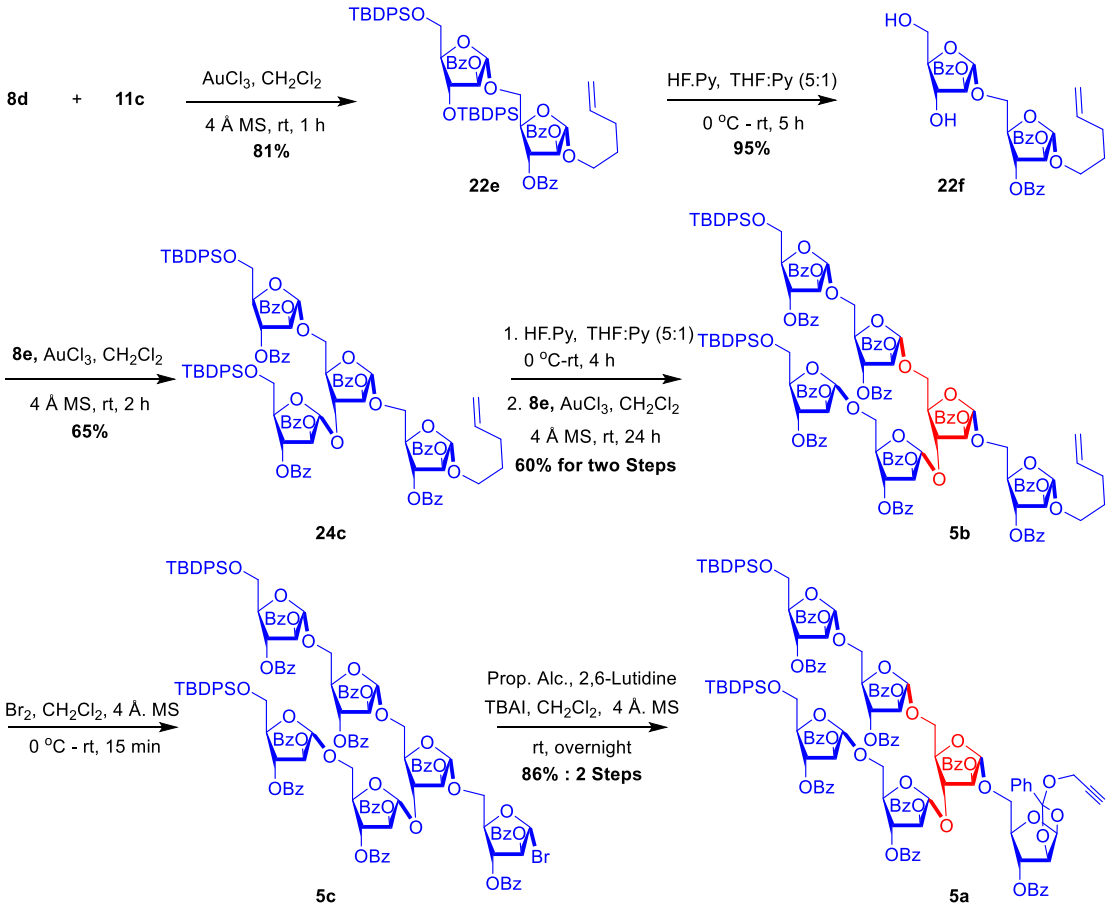
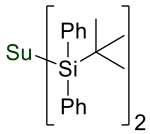
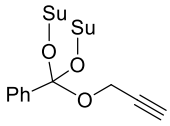


Table 2.3: ^{1}H NMR and ^{13}C NMR for **5a**

Nos.	**^{1}H** **δ (m, *J*= XX Hz, XX H) (note)**	**^{13}C** **δ**
***H*-1/*C*-1**	4.99 (s, 1H), 5.23 (s, 1H), 5.26 (s, 1H) 5.38 (s, 1H), 5.60 (s, 1H) 6.28 (d, *J* = 4.3 Hz, 1H) (for orthoester)	105.3, 105.5, 105.8, 105.9, 106.1, 106.6
***H*-2/*C*-2**	5.06 (d, *J* = 4.3 Hz, 1H) 5.67 (d, J = 4.5 Hz, 1H), 5.62 (s, 1H), 5.61 (s, 1H), 5.59 (s, 1H), 5.54 (s, 1H)	76.8, 77.0, 77.2 (3C), 82.0
***H*-3/*C*-3**	5.52 (s, 1H), 5.50 (s, 2H), 5.45 (s, 1H), 5.44 (s, 1H), 5.35 (s, 1H)	77.7, 81.2, 81.4, 81.5, 82.0, 82.5
***H*-4/*C*-4**	4.30-4.32 (m, 1H), 4.41-4.50 (m, 2H), 4.46-4.50 (m, 3H)	82.6, 82.8, 83.1 (2C), 84.8, 85.3
***H*-5/*C*5**	4.19 (dd, *J* = 11.3, 3.4 Hz, 1H), 4.15 (dd, *J* = 11.1, 4.1 Hz, 2H)	65.4 (2C), 65.6 (2C), 66.6 (2C)
	0.99 (s, 9H), 0.99 (s, 9H) 7.21-7.69 (m, 20H)	26.7 (6C), 19.2 (2C), 127.6-135.6 (24C)
	2.36 (t, *J* = 2.3 Hz, 1H) 4.48 (d, J = 4.2 Hz, 2H) 7.21-7.53 (m, 5H)	52.0, 76.8, 79.3, 122.5 (orthoester C), 126.4, 127.7-135.6 (4C)
Ph-COO-	7.21-8.02 (m, 50H)	127.6- 135.6 (60C), 164.9, 165.0 (2C), 165.1, 165.2, 165.4 (3C), 165.5, 165.6

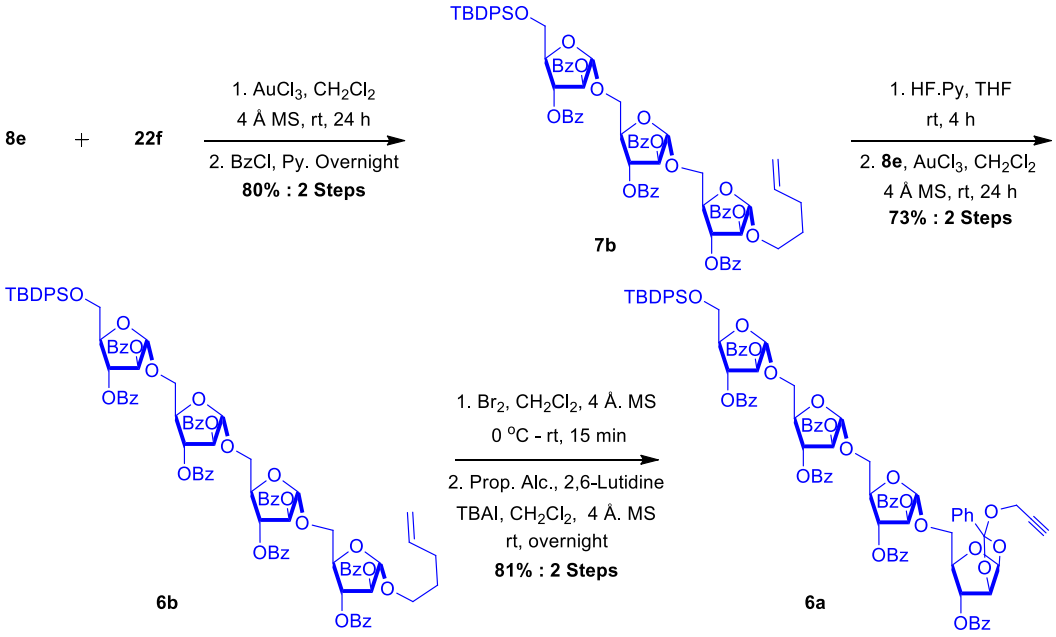
The presence of triplet at δ 2.36 (*J* = 2.3 Hz) ppm and doublet at δ 4.48 ppm indicated the presence of propargyloxy moiety in compound **5a**. In the ^{13}C spectrum of **5a**, the six anomeric carbon resonances were noticed at δ 105.3, 105.5, 105.8,

105.9, 106.1, 106.6 ppm. Resonances present at δ 122.5 ppm for the quaternary carbon in 1,2-*O*-orthobenzoate of middle hexasaccharide **5a**.

2.3.6– Synthesis of tetrasaccharide of AG (Scheme 2.17)

Regioselective gold-catalyzed glycosidation between orthoester **8e** and diol **22f** in anhydrous dichloromethane and 4 Å MS powder followed by benzoylation using BzCl/Py for overnight to generate triarabinofuranoside **7b** in 80% over two steps. In the ^{1}H NMR spectrum of **7b**, three anomers (*H*-1) observed for linear arabinofuranosides as individual singlets at δ 5.20, 5.38 and 5.38 ppm. In the ^{13}C NMR spectrum of **7b**, three distinguishable anomers appeared at δ 105.6, 105.8 and 105.9 ppm confirming the triarabinofuranoside **7b**. The selective deprotection of OTBDPS group in trisaccharide **7b** was achieved by using HF.Py in THF:Py to give trisaccharide glycosyl acceptor which was further treated with orthoester **8e** under standard gold (III) conditions to obtain pent-4-enyl tetrasaccharide **6b** in 73% yield.

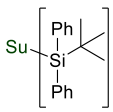
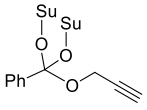
Scheme 2.17: Gold (III) catalysis for tetrasaccharide of AG



The ^{1}H NMR spectrum of **6b** was found to be similar to that of **7b**. Only difference was found to be that four anomeric protons were observed in **6b** instead of three anomeric protons in anomeric region of **7b**. In the ^{13}C NMR spectrum of **6b**, four anomeric carbons were found in the anomeric region and rest of the ring carbons were identified in appropriate regions which was similar to compound **7b**. Pent-4-enyl tetrasaccharide **6b** was treated with molecular bromine and 4 Å MS powder in

dichloromethane followed by propargyl alcohol, 2,6-lutidine, catalytic amount of TBAI and Å MS powder in anhydrous dichloromethane to generate tetrasaccharide propargyl 1,2-*O*-orthobenzoate **6a** in 81% yield. Formation of compound **6a** was confirmed on the basis of NMR techniques. The four resonances were noticed as individual singlets at 5.06 (s), 5.38 (s), 5.60 (s), 6.35 (d, J = 4.3 Hz) ppm in ^{1}H NMR and at 105.4, 105.8, 105.9, and 106.7 ppm along with quaternary carbon at 122.5 ppm in ^{13}C NMR spectrum for four anomeric proton and carbons respectively confirmed the successful synthesis of tetrasaccharide 1,2-orthoester **6a**.

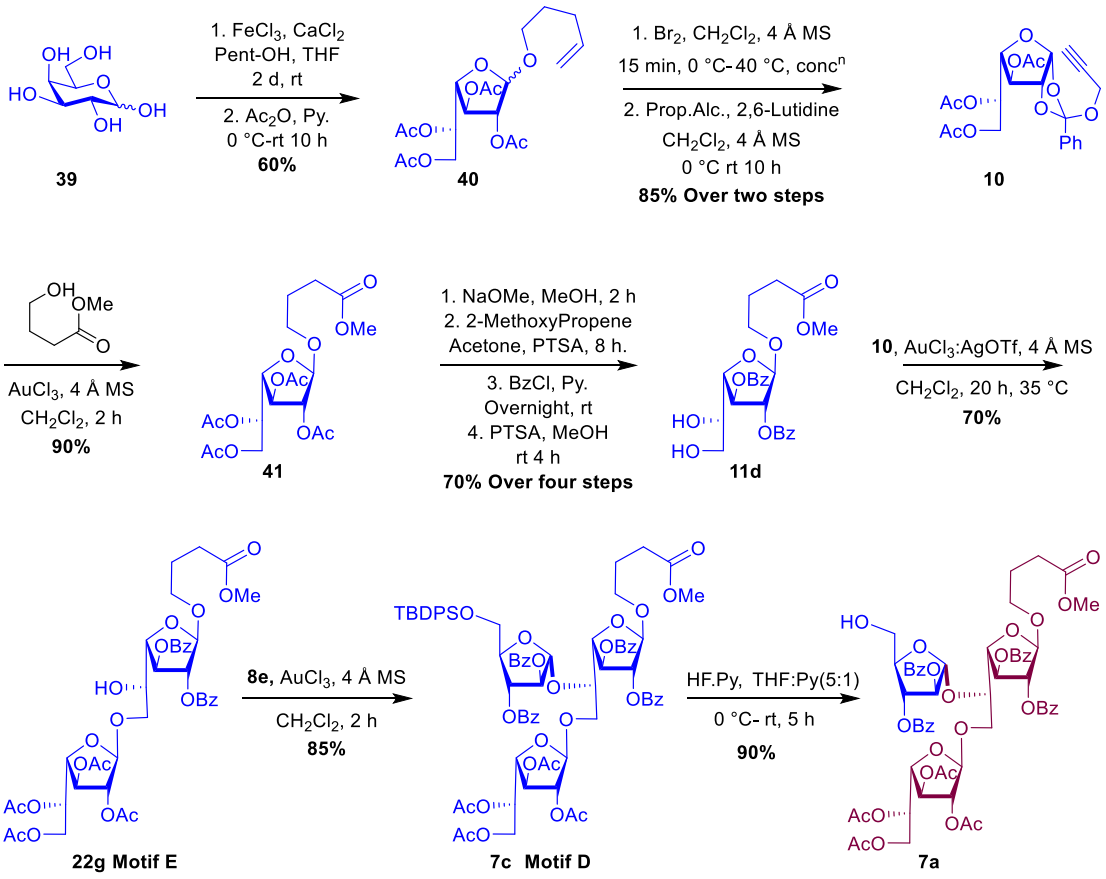
Table 2.4: ^{1}H NMR and ^{13}C NMR for **6a**

Nos.	**^{1}H** **δ (m, *J* = value Hz, number H) (ppm)**	**^{13}C** **δ (ppm)**
***H*-1/*C*-1**	5.06 (s, 1H), 5.38 (s, 1H), 5.60 (s, 1H) 6.35 (d, J = 4.3 Hz, 1H) (for orthoester)	105.4, 105.8, 105.9, 106.7
***H*-2/*C*-2**	5.11 (d, J = 4.3 Hz, 1H), 5.30 (s, 1H) 5.45 (J = 1.2 Hz, 1H), 5.52 (s, 1H)	77.3, 76.7, 77.2, 82.1
***H*-3/*C*-3**	5.56 (d, J = 1.3 Hz, 1H), 5.61-5.63 (m, 3H)	81.4, 81.5, 82.0, 82.1
***H*-4/*C*-4**	4.28 (dd, J = 7.4, 3.9 Hz, 1H), 4.49 (q, J = 4.6 Hz, 1H), 4.58-4.62 (m, 2H)	82.1, 83.1, 84.8, 85,3
***H*-5/*C*-5**	3.51 (dd, J = 10.3, 7.2 Hz, 1H), 3.67 (dd, J = 11.2, 2.7 Hz, 1H), 3.78 (dd, J = 10.3, 7.7 Hz, 1H), 3.88 (dd, J = 9.5, 2.5 Hz, 1H), 3.92 (dd, J = 5.2, 2.4 Hz, 2H), 4.07 (dd, J = 11.2, 4.0 Hz, 1H), 4.17 (dd, J = 11.3, 4.1 Hz, 1H)	63.3, 65.5, 65.7, 66.4
	1.00 (s, 9H), 7.21-7.69 (m, 10H)	26.7 (9C), 19.2 (2C), 127.6-135.6 (12C)
	2.36 (t, J = 2.5 Hz, 1H), 3.96 (d, J = 4.5 Hz, 2H), 7.21-7.53 (m, 5H)	52.0, 77.7, 79.3 122.5 (orthoester C), 126.4, 127.7-135.6 (5C)
Ph-COO-	7.21-7.70 (m, 21H), 7.87-8.05 (m, 14H)	127.6- 135.6 (42C), 165.0, 165.1, 165.2 (2C), 165.4, 165.6 (2C),

2.3.7– Synthesis of terminal trisaccharide AG (Scheme 2.18)

Synthesis of α- and β-arabinofuranosides and major fragments of AG was done by exploiting propargyl 1,2-*O*-orthoester strategy. Now the challenge is that how to achieve galactofuranoside in stereoselctive manner? We thought that, we can use similar 1,2-*O*-orthoester strategy for the synthesis of trisaccharide containing galactofuranoside of AG. Thus, commercially available D-galactose **39** was treated with $FeCl_3/CaCl_2$/Pent-4-en-1-ol[20] in dry THF at room temperature for two days followed by acetylation using Ac_2O/Py to form pent-4-enyl per-*O*-acetylated galactofuranoside (**40**). Propargyl galactofuranoside 1,2-*O*-orthoacetate (**10**) was obtained from pent-4-enyl galactose **40** under aforementioned protocol through the intermediary of bromoaldoses.

Scheme 2.18: Gold (III) for trimer of AG



In the ^{1}H NMR spectrum of orthoacetate **10**, the anomeric (*H*-1) resonances were found at δ 5.99 (d, *J* = 4.0 Hz) ppm, *H*-2 proton was identified at δ 4.77 (d, *J* = 4.0 Hz) ppm whereas *H*-3 proton appeared at δ 5.11 (d, *J* = 2.5 Hz) ppm and *H*-4 proton showed as a dd (*J* = 7.8, 2.5 Hz) at δ 4.19 ppm. *H*-5 proton showed ddd (*J* = 7.8, 6.0,

4.0 Hz) multiplicity at δ 5.27 ppm due to the adjacent diastereotopic -CH_2 and -CH protons. Diastereotopic *H*-6 protons in galactofuranoside appeared as two different dds' at δ 4.41 (*J* = 12.2, 3.9 Hz) and at δ 4.15 (*J* = 9.6, 6.1 Hz) ppm. Propargylic methylene group appeared as a doublet (*J* = 2.5 Hz) at δ 4.14 ppm and terminal methine as a triplet (*J* = 2.4 Hz) at δ 2.42 ppm. Three methyl groups from acetate moiety were noticed as individual singlets at δ 2.11, 2.10, and 2.06 ppm. One more methyl group from 1,2-*O*-orthoacetate displayed as a singlet at 1.75 ppm. In the ^{13}C NMR spectrum of **10**, anomeric carbon (*C*-1) appeared at δ 105.3 ppm. Galactofuranoside *C*-2, *C*-3, *C*-4, *C*-5 and *C*-6 were observed at δ 83.6, 76.3, 84.5, 69.7 and 62.8 ppm. Propargylic methine, methylene and quaternary carbon were displayed at δ 73.7, 51.0 and 79.5 ppm respectively. Three -$\underline{C}O\underline{C}H_3$ were found at δ 170.5/20.8, 169.9/20.6 and 169.6/20.6 ppm. The characteristic 1,2-*O*-orthoacetate resonances were found at δ 124.1 ppm and corresponding methyl resonances in orthoacetate at δ 21.8 ppm which proved the formation of propargyl 1,2-*O*-orthoacetate. In addition, the orthoacetate was further confirmed by Mass spectroscopic analysis. Further, galactofuranosyl 1,2-*O*-orthoester **10** was treated with 4-hydroxy methyl butanoate in the presence of 10 mol% of gold trichloride to form **41** in 90% yield. In the ^{1}H NMR of **41** spectrum, methoxy resonances were observed as a singlet at δ 3.58 ppm which was characteristic of methyl ester presence in the gal*f* **41**. Similarly, in the ^{13}C NMR spectrum of **41**, methyl resonances observed at δ 51.4 ppm and one more carbonyl was found in the carbonyl region at δ 173.5 ppm which was from the methyl ester present in the compound **41**. Diol **11d** was obtained from **41** in 75% over four steps; *viz.* saponification of **41** under Zemplén conditions, 5,6-isopropylidine protection by using 2-methoxypropene in the presence of PTSA in dry acetone, benzoylation of diol with BzCl/Py, and deprotection of 5,6-acetonide with PTSA in methanol. In the ^{1}H NMR spectrum of **11d**, all galactofuranoside ring protons, *H*-5, *H*-6 and reducing end methyl ester chain protons were found similar to **41**. All methyl resonances in acetate groups were disappeared and two new benzoate proton resonances appeared in aromatic region which confirmed the formation of product **11d**. In the ^{13}C NMR spectrum of **11d**, all methyl resonances and carbonyl resonances in acetate groups disappeared and new two carbonyl resonances found around δ 165 ppm and twelve carbons in the aromatic region indicated the presence of two benzoate groups. Regioselective gold trichloride and silver triflate catalyzed glycosidation between diol **11d** and 1,2-*O*-orthoester **10** at 35 °C in anhydrous

dichloromethane resulted in the disaccharide alcohol **22g** in 70 % yield. In the ^{1}H NMR spectrum of **22g**, two galactofuranoside anomers found as singlets at δ 5.11 and 5.26 ppm respectively. Methyl resonances in the methyl ester were observed as a singlet at δ 3.67 ppm. Four methyl resonances of four acetate groups were noticed as individual singlets at δ 2.05, 2.05, 2.08 and 2.13 ppm respectively. In the ^{13}C NMR spectrum of **22g**, two anomeric carbons were noticed at δ 105.9 and 105 ppm. Rest of the galactofuranoside carbons were displayed between δ 66.3 and 83.1 ppm. Three different sets in the carbonyl region at δ 173.6, 170.0 (4C) and 165.5 (2C) ppm were indicated the presence of methyl ester, four acetate groups and two benzoyl groups. Three carbons of the reducing end were observed at δ 62.6, 30.6 and 24.8 ppm. Glycosidation reaction between disaccharide alcohol **22g** and propargyl orthoester **8e** in the presence of gold trichloride in anhydrous dichloromethane followed by treatment with HF.Py in THF:Py resulted in trisaccharide **7a** in 77% over two steps. The additional resonances both in the ^{1}H and ^{13}C NMR at anomeric, aliphatic, aromatic region indicated the formation of product **7a**. In the ^{1}H NMR spectrum of **7a**, three anomers found accordingly at δ 5.72, 5.24 and 5.02 ppm as singlets and ^{13}C NMR spectrum of **7a** showed three anomeric carbons at δ 106.6, 105.7 and 105.3 ppm.

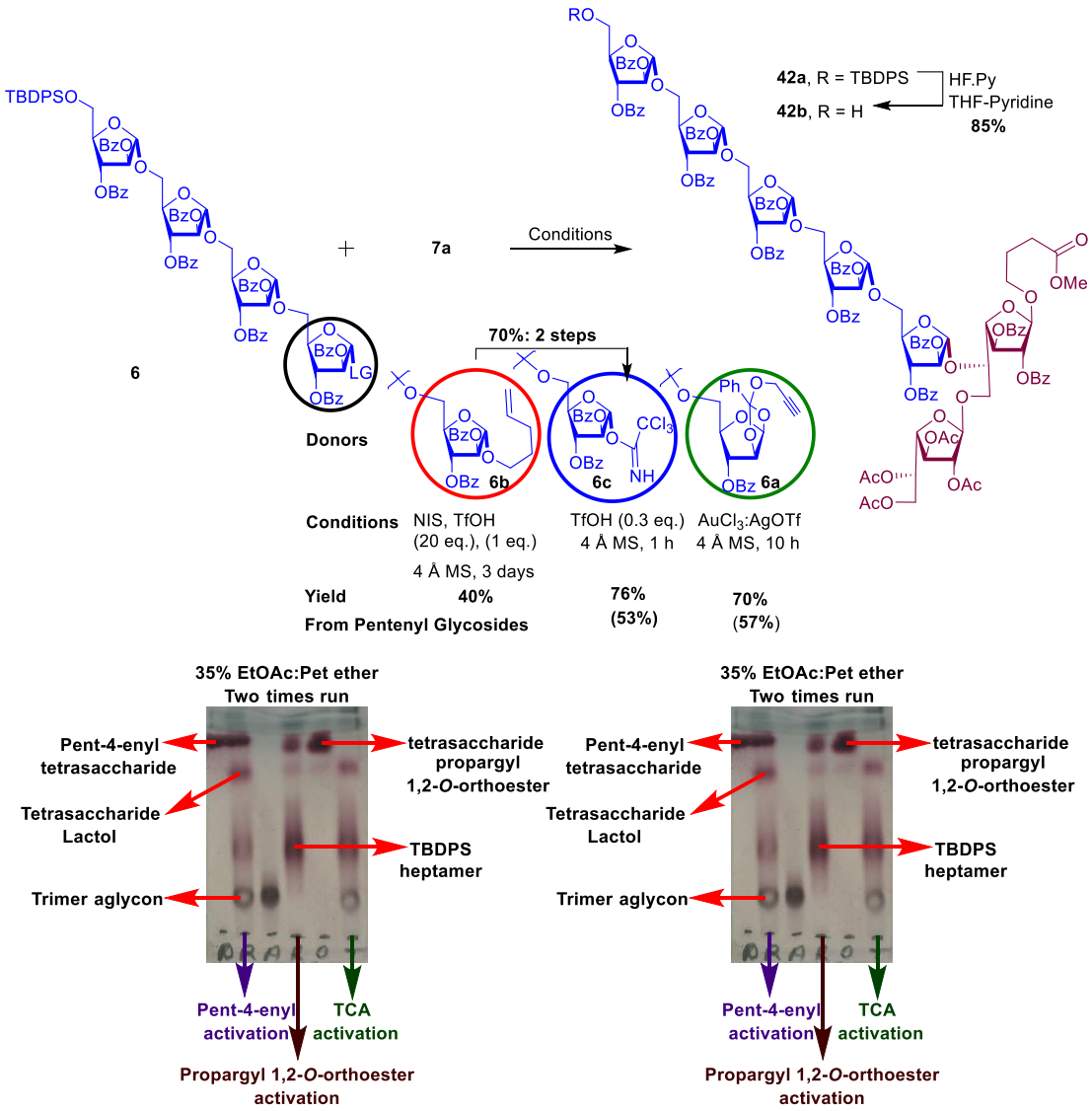
Having synthesized all major fragments, the synthesis of heptaarabinofuranoside, tridecasaccharide, and pentadodecasaccharyl arabinogalactan in a facile manner was attempted.

2.3.8– Synthesis of heptamer in AG

Terminal heptasaccharide was obtained in good yield from building blocks **6** and **7a** as illustrated in **Scheme 2.19**. The comparative study between glycosyl donors showed that the utility of three glycosyl donors and efficiency towards glycosidation reaction for higher oligosaccharides. Heptasaccharide **42a** was achieved from glycosyl donor **6b** and trimer **7a** using NIS/TfOH in anhydrous dichloromethane in 50 % yield. In this glycosylation process, 10 eq. of NIS and 0.6 eq. of TfOH were used in three different portions over three days. Purification of heptamer **42a** posed a big challenge due to succinimide and side product. Glycosyl donor **6b** was converted into the glycosyl bromide which was unstable and was converted into propargyl 1,2-orthoester **6a**. To improve the yield of gold catalyzed glycosidation reaction, dichloromethane solution of 1,2-*O*-orthoester **6a** was added drop-wise to the solution

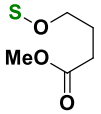
of glycosyl acceptor **7a**, catalytic amount of gold trichloride, silver triflate and 4 Å MS powder in anhydrous dichloromethane to afford the required heptasaccharide **42a** in 70 % yield in 15h. The overall yield was obtained 57% (70% for glycosidation) from the pent-4-enyl tetrasaccharide **6b** after three steps. Further, this yield was compared with unstable trichloroacetimidate (used routine steps for its synthesis) reaction between **7a** and **6c**; surprisingly, we observed similar yield for glycosidation in both cases. Although, the yield loss (51% over three steps) in the synthesizing of trichloroacetimidate glycosyl donor from pent-4-enyl tetrasaccharide **6b** for heptasaccharide **42a** was

Scheme 2.19: Gold (III) for Heptamer of AG



found. The formation of TBDPS heptasaccharide was initially compared by TLC. On the TLC plate, the starting glycosyl acceptor **7a** was completely consumed in 1,2-*O*-orthoester

Table 2.5: ^{1}H NMR and ^{13}C NMR for **42b**

Nos.	**^{1}H** **δ (m, *J*= XX Hz, XX H) (ppm)**	**^{13}C** **δ (ppm)**
H*-1/*C*-1** **5-ara*f* & 2-gal*f	5.05 (s, 1H), 5.24 (s, 1H), 5.40 (s, 3H), 5.48 (d, *J* = 1.4 Hz, 1H), 5.74 (s, 1H)	105.3, 105.5, 105.7 (3C), 105.8, 106.7
H*-2/*C*-2** **5-ara*f* & 2-gal*f	4.95 (dd, *J* = 5.9, 2.0 Hz, 1H), 5.00 (d, *J* = 2.2 Hz, 1H), 5.60-5.65 (m, 4H), 5.69 (d, *J* = 4.9 Hz, 1H)	75.2, 76.2, 76.6, 77.0, 77.1 (2C), 77.2
H*-3/*C*-3** **5-ara*f* & 2-gal*f	5.40 (s, 2H), 5.60-5.76 (m, 5H)	77.6, 81.0, 81.4, 81.5 (3C), 81.6
H*-4/*C*-4** **5-ara*f* & 2-gal*f	4.12-4.62 (m, 7H)	81.9, 82.2 (2C), 82.2 (2C), 82.3, 83.5
H*-5/*C*-5** **5-ara*f	3.89-4.62 (m, 10H)	66.5, 65.6, 65.7, 66.0, 66.6
H*-5/*C*-5** **2-gal*f	5.35 (dt, *J* = 7.6, 3.9 Hz, 1H) 3.89-4.00 (m, 1H)	69.1, 79.9
H*-6/*C*-6** **2-gal*f	3.75-3.94 (m, 2H), 4.15-4/29 (m, 2H)	62.2, 66.3
	1.95-2.01 (m, 2H), 2.49 (t, *J* = 7.5 Hz, 2H) 3.56 (dt, *J* = 9.8, 6.1 Hz, 1H), 3.75-3.83 (m, 1H), 3.66 (s, 3H)	30.6, 24.8, 51.5, 62.6, 173.6 (CO)
4 × $COCH_3$	1.91 (s, 3H), 1.96 (s, 3H), 2.00 (s, 3H), 2.07 (s, 3H)	20.4 (2C), 20.6, 20.7, 169.3, 169.9 (2C), 170.4
12 × Ph-COO-	7.21-7.59 (m, 36H), 7.84-8.07 (m, 24H)	128.2- 133.4 (60C), 165.0 (4C), 165.2,

		165.4, 165.5 (3C), 165.6, (2C), 166.0

reaction conditions. However, in pent-4-enyl as well as trichloracetimidate glycosidation case, starting glycosyl acceptor **7a** remained even after prolonged periods of time. More equivalents of glycosyl donor were required; complete consumption of starting glycosyl acceptor **7a**, however, with more equivalents of glycosyl donor, the formation of side products got increased. Purification of the heptasaccharyl **42b** became a herculean when the glycosidation was conducted with *n*-pentenyl or trichloroacetimidate donor due to the side products. However, gold(III) catalyzed reaction gave clean conversion without or minimum side products and hence purification became easier. Heptasaccharide glycosyl acceptor **42b** in 85% was obtained from **42a** by treatment with HF.Py in THF:Py for 4 h at room temperature. Heptasaccharide alcohol **42b** was confirmed thoroughly based on exhaustive NMR and Mass spectral analysis (**Table 2.7**). In the ^{1}H NMR spectrum, the seven anomers were noticed at δ 5.05, 5.24, 5.40 (3H), 5.48, 5.74 ppm. In the ^{13}C NMR spectrum, seven anomeric resonances were noticed at δ 105.3, 105.5, 105.7 (3C), 105.8, 106.7 ppm. In the carbonyl region, distinguishable carbonyl carbons were observed at δ 173.6 ppm for methyl ester, at δ 169.3, 169.9 (2C), 170.4 ppm for acetate, and around δ 165.0 ppm (13C) for benzoates. The observed m/z value for heptasaccharide glycosyl acceptor (2542.6235) was found to be in good agreement with the calculated value.

2.3.9– Synthesis of tridecasaccharide of AG

In continuation, heptasaccharide alcohol **42b** was treated with two equivalents of hexafuranosyl donor **5** in the presence of activator to achieve tridodecamer in moderate yield. Comparative studies between glycosyl donors showed that, the propargyl 1,2-*O*-orthoester glycosyl donor **5a** and trichloracetimidate glycosyl donor **5e** were superior compared to *n*-pentenyl glycosyl donor (**5b**) with glycosyl acceptor **42b** to obtain the tridecasaccharide **43a** in 65% and 68% yield over three steps respectively. Formation of tridecasaccharide was fully confirmed by the NMR spectroscopy and Mass analysis (**Table 2.8** and **Table 2.9**). In the ^{1}H NMR spectrum of **43**, 13-anomeric protons were noticed as individual singlets at δ 5.05, 5.21, 5.24, 5.29, 5.30, 5.36, 5.37, 5.38, 5.38, 5.49, 5.51, 5.52, 5.73 ppm. In the ^{13}C NMR spectrum of **43**, resonances for 13- anomeric carbons were noticed at δ 105.2, 105.4,

105.6, 105.9 (8C), 106.1, 106.7 ppm. The m/z for tridecasaccharide **43** was found in the MALDI-TOF spectrum at 4956.7632 Daltons (Calculated m/z for $[C_{273}H_{254}O_{84}Si_2+Na]$: 4956.5107). Deprotection of di-*O*-TBDPS in **43** was successfully achieved by using HF.Py in THF:Py to give tridecamer **4b** in 83% yield. The m/z for tridecasaccharide **4b** was found in the MALDI-TOF spectrum at 4480.2752 Dalton (calculated m/z for $[C_{241}H_{218}NaO_{84}+Na]$: 4480.3862).

Scheme 2.20- Gold (III) catalysis for tridecamer of AG

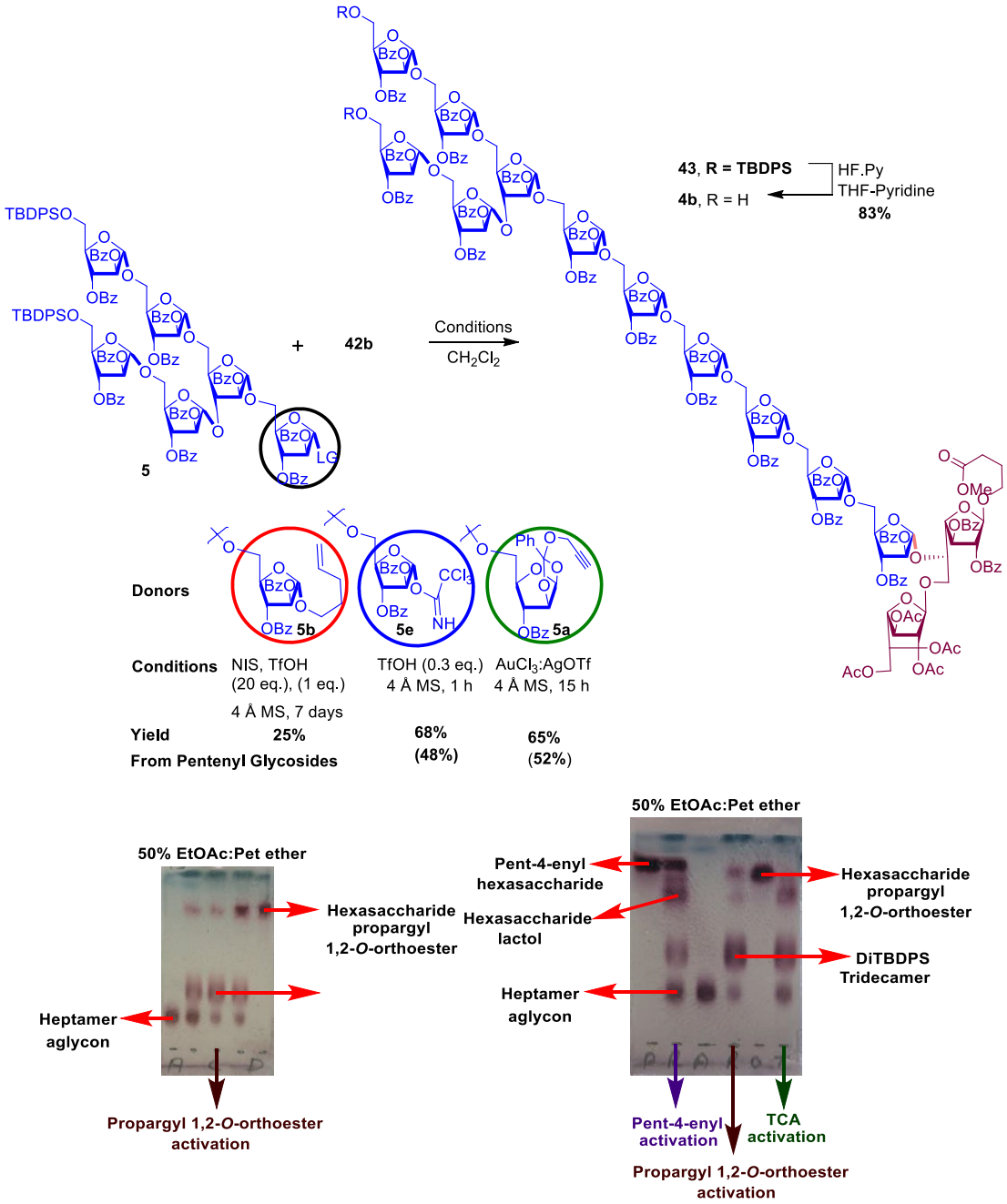


Table 2.6: ^{1}H NMR (*H*-1 to *H*-5/6) and ^{13}C NMR (*C*-1 to *C*-5/6) for **43**

^{1}H's	**13×*H*-1**	**13×*H*-2**	**13×*H*-3**	**13×*H*-4**	**11× *H*-5/*H*-5' 2×*H*-5 from gal*f*#**	**2× *H*-6/*H*-6' from gal*f*#**
δ	5.05 (s, 1H) 5.21 (s, 1H) 5.24 (s, 1H) 5.29 (s, 1H) 5.30 (s, 1H) 5.36 (s, 1H) 5.37 (s, 1H) 5.38 (s, 2H) 5.49 (s, 1H) 5.51 (d, 1H) (*1.3 Hz*) 5.52(d, 1H) (*1.1 Hz*) 5.73 (s, 1H)	5.50 (d, 1H) (1.5 *Hz*) 5.54 (d, 1H) (0.9 *Hz*) 5.58-5.64 (m, 8H) 5.68 (d, 1H) (*4.8 Hz*) 5.72-5.75 (m, 2H)	4.94 (dd, 1H) (*5.9, 2.0 Hz*) 4.99 (d, 1H) (*2.1 Hz*) 5.32-5.35 (m, 1H) 5.44 (d, 1H) (*1.0 Hz*) 5.47 (d, 1H) (*1.1 Hz*) 5.49 (s, 1H) 5.58-5.64 (m, 7H)	4.37-4.61 (m, 13H)	3.72-4.03 (m, 15H) 4.09-4.20 (m, 7H) 4.38-4.61# (m, 2H)	4.10-4.20 (m, 2H) 4.26-4.31 (m, 2H)
^{13}C's	**13×*C*-1**	**13×*C*-2**	**13×*C*-3**	**13×*C*-4**	**11× *C*-5 from Ara*f* 2×*C*-5 from gal*f*#**	**2× *C*-6 from gal*f***
δ	105.2 105.4 105.6 105.9 (8C) 106.1 106.7	75.2 76.3 76.7 77.0 (4C) 77.1 (2C) 77.2 (4C)	80.0 80.3 81.0 81.4 (4C) 81.5 81.6 (3C) 82.0 (2C)	82.0 (4C) 82.1 82.2 82.3 (2C) 82.5 82.6 (2C) 82.9 83.1	62.7 63.1 65.4 (2C) 65.5 65.6 (2C) 65.7 (3C) 66.4 69.1# 81.2#	63.2 66.6

Table 2.7: ^{1}H NMR (side chain, TBDPS group, acetate and aromatic) and ^{13}C NMR (side chain, TBDPS group, acetate and aromatic) for 43

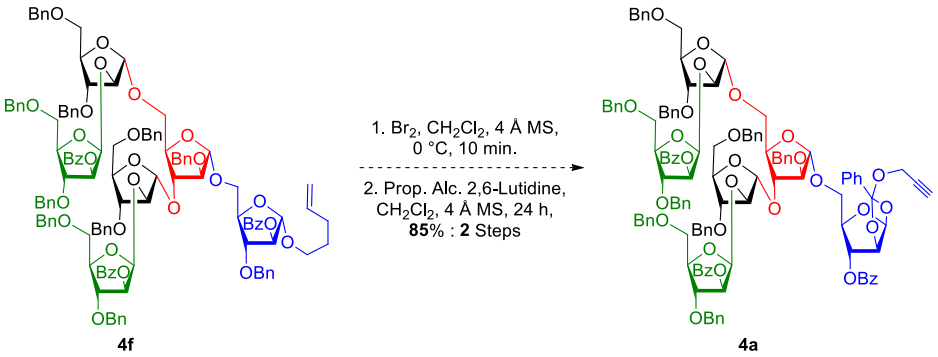
^{1}H's	***T*-butyl protons in TBDPS**	***S*OCH$_2$CH$_2$CH$_2$COOMe**	***S*OCH$_2$CH$_2$CH$_2$COOMe**	***S*OCH$_2$CH$_2$CH$_2$COOMe**	***S*OCH$_2$CH$_2$CH$_2$COOMe**	**4× OCOCH$_3$**	**23× PhCOO- & 2× Ph$_2$Si(*t*-butyl)**
δ	0.97 (s) 0.99 (s)	3.55 (dt, 1H) (*9.8, 6.1 Hz*) 3.78 (dt, 1H) (*9.9, 5.8 Hz*)	1.95-2.01 (m, 2H)	2.49 (dd, 2H) (7.9, 7.1 Hz)	3.66 (s)	1.90 (s) 1.96 (s) 1.99 (s) 2.07 (s)	7.15-8.8.07 (m, 135H)
^{13}C's	***T*-butyl carbons in TBDPS**	***S*OCH$_2$CH$_2$CH$_2$COOMe**	***S*OCH$_2$CH$_2$CH$_2$COOMe**	***S*OCH$_2$CH$_2$CH$_2$COOMe**	***S*OCH$_2$CH$_2$CH$_2$COOMe**	**4× OCOCH$_3$**	**23× PhCOO- & 2× Ph$_2$Si(*t*-butyl)**
δ	26.7 (6C) 19.2 (2C)	65.8	29.7	30.6	51.5 173.7	20.5 (2C) 20.6 20.8 169.3 170.0 170.0 170.4	127.6-135.6 (162C) 164.7 164.9 165.0 (4C) 165.1 (2C) 165.2 (3C) 165.3 165.4 (2C) 165.5 (6C) 165.6 (3C)

S: Sugar # - Indicated the protons and carbons from galactofuranoside *C/H*-5 and *C/H*-6 positions

2.3.10– Synthesis of hexasaccharide propargyl 1,2-*O*-orthoester

Successful identification of conditions for the conversion of *n*-pentenyl glycosides to 1,2-*O*-orthoesters, the attention was focussed on the conversion of pentenyl glycoside **4f** to the orthoester donor **4a**. Accordingly, the formation of T-hexasaccharyl 1,2-orthoester under above delineated conditions is under progress.

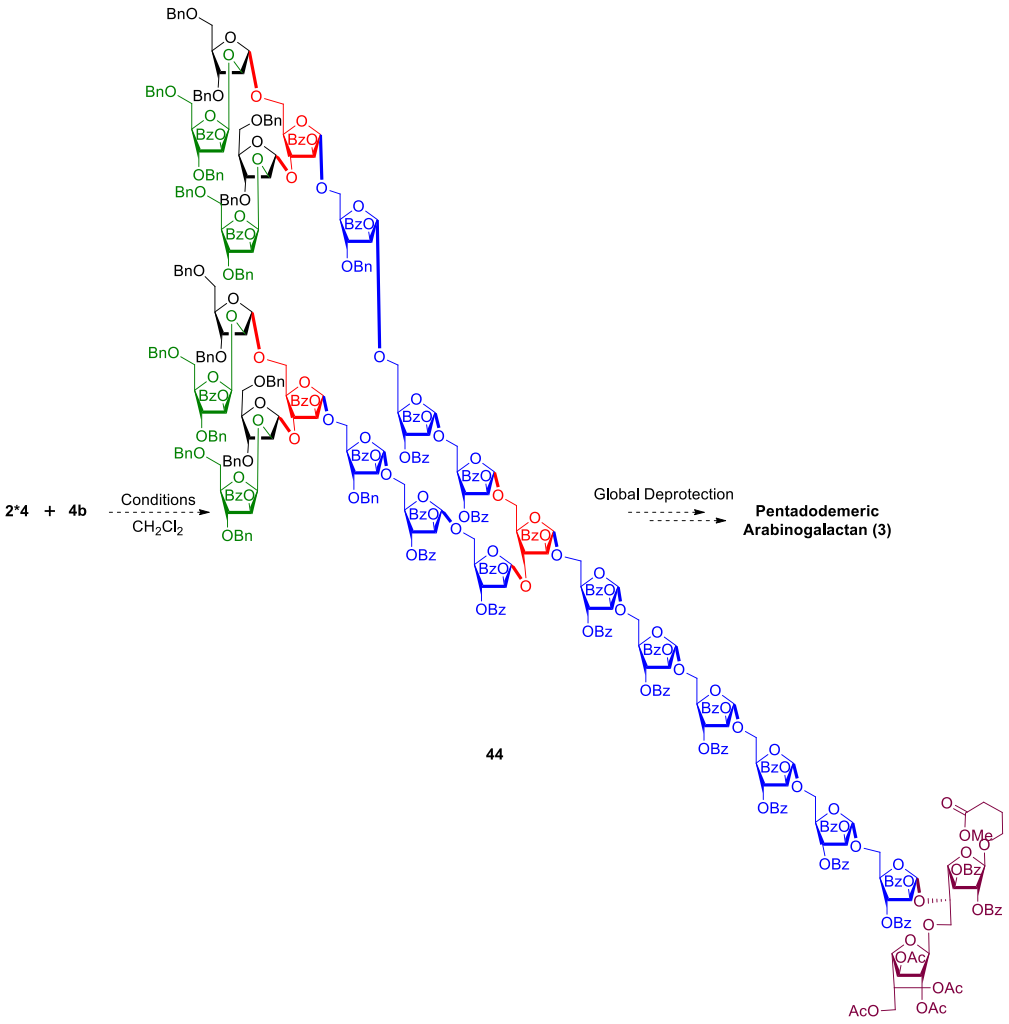
Scheme 2.21: Conversion of pent-4-enyl hexaara*f* to hexaara*f* 1,2-*O*-orthoester



2.3.11– Synthesis of AG

The final glycosidation reaction was carried out between glycosyl acceptor **4b** and glycosyl donor **4** to afford arabinogalactan **44**. However, the NPG-based glycosidation reaction between **4f** and **44** gave very poor yield and removal of other products from expected product has become quite a challenge.

Scheme 2.22- Gold (III) catalysis for AG



Hence, total synthesis of arabinogalactan by using gold-catalyzed glycosidation might be more suitable for this conversion as it yields lesser side products and the purification might become easier. However, T-hexasaccharyl 1,2-orthoester (**4a**) is required in order to perform this important final glycosidation. Synthesis of 1,2-orthoester and the final glycosidation steps are currently under investigation. The partially purified pentadodecameryl arabinogalactan gave reasonably good ^{1}H NMR spectrum. Furthermore quantity of the material is required for recording the ^{13}C NMR spectrum. These studies are currently in progress.

2.4– Conclusion

In summary, methodologies for the facile synthesis of monosaccahryl as well as oligosaccharyl 1,2-*O*-orthoesters were successfully developed. Monosaccahryl as well as oligosaccharyl 1,2-*O*-orthoesters were orthogonally activated in the presence of gold(III) catalysts to give 1,2-*trans* glycoconjugates. Further, gold catalyzed glycosidation repertoire was extended for the synthesis of 1,2-*trans* glycoconjugates and converted into 1,2-*cis* glycoconjugates in a bio-inspired manner. The utility of identified methodologies for the synthesis of 1,2-*O*-orthoesters, 1,2-*trans* and 1,2-*cis* furanosides were successfully utilised for the synthesis of terminal hexaarabinofuranoside diol (1.53% from 30 convergent steps) and tridecasaccharyl arabinogalactan (0.91% over 31 convergent synthesis). Single donor chemistry is required for the synthesis of tridecamer and hexarabinofuranoside diol. Catalytic activation, easy purification, high yielding steps, less reaction time, and minimal side products are the major advantageous factor for this methodology. Total synthesis of pentadodecasaccharyl arabinogalactan was achieved and confirmed by means of ^{1}H NMR and mass spectroscopic means. Unambiguous characterization by ^{13}C NMR spectral studies is still pending for which more quantity of pentadodecasaccharide was required. These studies are currently under progress in our group. In future, after completion of total synthesis of pentadodecasaccharide, the biological and physical property of these saccharides (mono, di, tri, and oligosaccharides) will be the focus in our research group.

2.5– Experimental and Characterization data

3,5-Di-*O*-benzoyl-β-D-arabinofuranoside-prop-2-ynyl-1,2-orthobenzoate (**8a**): Acetyl chloride (12 mL, 0.17 mol) was treated with methanol (10 mL) at 0 ^{o}C for 30 min to form methanol:hydrochloric acid solution. Further, this solution was added to the solution of arabinose (20 g, 0.13 mol) in methanol (125 mL) at 0 $^{\circ}$C and allowed to warm upto 25 ºC. Progress of reaction was monitored by the TLC (EtOAc:MeOH:*n*BuOH) until disappearance of starting material. After completion of the reaction (6.5 h), the reaction mixture was quenched with excess pyridine (40 mL) and concentrated *in vacuo*, and obtained a crude residue of α:β methyl arabinofuranoside along with some amount of pyranoside (less than 5%) which was redissolved in anhydrous pyridine (200 mL) and cooled to 0 ^{o}C, and slowly treated with benzoyl chloride (60 mL, 0.53 mol). The reaction mixture was stirred for overnight at room temperature and few ice pieces were added to the reaction mixture; stirred for another 30 min at room temperature and then extracted with dichloromethane (2x150 mL). The extract was washed with 3N H_2SO_4, sat. aq. sodium bicarbonate solution and organic layer was collected and dried over sodium sulphate, concentrated *in vacuo* to yield α:β methyl 2,3,5-tri-*O*-benzoyl arabinofuranosides. Resulting α,β mixture of arabinofuranosides crystallized in hot ethanol (5%) and resulting crystals were collected by filtration to give pure methyl α-D-2,3,5-tri-*O*-benzoyl arabinofuranoside as white solid (31 g, 48.8%, m.p. 100 ^{o}C).

Methyl 2,3,5-tri-*O*-benzoyl-α-D-arabinofuranoside (31 g, 0.065 mol) prepared *vide supra* was redissolved in dry CH_2Cl_2 (150 mL) and cooled to 0 ^{o}C. Acetyl bromide (26.7 mL, 0.36 mol) was added to the reaction mixture followed by the drop wise addition of methanol (11.85 mL, 0.29 mol) with constant stirring at 0 ^{o}C. Additionally, the reaction mixture was stirred for 2 h at 0 ^{o}C before dilution with CH_2Cl_2 (500 mL). The reaction mixture was poured into the ice-water mixture and aqueous layer was extracted with CH_2Cl_2 (2x250 mL) and organic layer was washed with cold saturated sodium bicarbonate solution, dried over sodium sulphate and concentrated under reduced pressure to give 2,3,5-tri-*O*-benzoyl arabinofuranosyl bromide as white foam which was immediately used in the next step without additional purification.

The crude arabinofuranosyl bromide was dissolved in 200 mL of anhydrous CH_2Cl_2, propargyl alcohol (5.6 mL, 0.10 mol) and 2,6-lutidine (15.1 mL, 0.13mol).

Tetra *n*-butyl ammonium iodide (1.44 g, 3.9 mmol) was added to the reaction and stirred for 4 h at room temperature. The reaction mixture was diluted with CH_2Cl_2 (250 mL) and water (500 mL) and the aqueous layer was extracted with CH_2Cl_2 (2 x 100 mL) and the organic extract was washed with saturated oxalic acid solution, saturated sodium bicarbonate solution. The organic phase was collected, dried over sodium sulphate and concentrated *in vacuo*. The crude residue of orthoester was purified by silica gel column chromatography (EtOAc: Petroleum ether 20:80) to obtain **1a** (25 g, 76.8% over two steps) as white solid.

Similar procedure was applied for the synthesis of 3,5-di-*O*-benzoyl-α-D-lyxofuranoside-prop-2-ynyl-1,2-orthobenzoate **(13a)** (7.5 g, 45% over four steps) as thick syrup

In ribofuranoside and xylofuranoside case, instead of acetyl bromide and methanol we used HBr:AcOH in acetic acid for 10 and 30 min. at 0 °C to get ribosyl bromide and xylosyl bromide. Rest of the procedure was similar to above mentioned in **1c** to form 2,5-di-*O*-benzoyl-α-D-ribofuranoside-prop-2-ynyl-1,2-orthobenzoate **(9a**, 18.3 g, 55% over four steps) as thick syrup and 3,5-di-*O*-benzoyl-α-D-xylofuranoside-prop-2-ynyl-1,2-orthobenzoate **(14a**, 17.34 g, 52% over four steps) as a thick yellow syrup.

β-D-Arabinofuranoside-prop-2-ynyl-1,2-orthobenzoate (**8b**): Propargyl 1,2-*O*-orthoester **8a** (50 g, 100 mmol) and sodium methoxide (1.34 g, 25.0 mmol) was stirred in anhydrous CH_2Cl_2:methanol for 2 h at room temperature. After completion of the reaction, the reaction mixture was concentrated *in vacuo* and redissolved in water and EtOAc, extracted with EtOAc (2x50 mL). The collected extract was dried over sodium sulphate and concentrated *in vacuo*. The resultant crude residue was stirred in presence of pet ether (for removal of methyl benzoate) for 10 min. and the pet ether was decanted to afford pure diol orthoester **8b** (28 g) in quantitative yield and further used without any purification and analytical characterizations.

Similar procedure was applied for the synthesis of **9b**.

3,5-Di-*O*-benzyl-β-D-arabinofuranoside-prop-2-ynyl-1,2-orthobenzoate (**8c**): Diol orthoester **8b** (5 g, 17.2 mmol) was dissolved in dry dimethylformamide (DMF) (40 mL) and cooled to 0 ^{o}C in ice bath. Sodium hydride (60% dispersion in mineral oil) (1.5 eq. per OH) was added portion-wise and the reaction mixture became cake like solid. Benzyl bromide (1.1 eq per OH) was added slowly. After 2 h at 0 ^{o}C, MeOH (1

mL) and water (100 mL) were added to reaction mixture and the compound was taken out from water with EtOAc (2x100 mL). The organic layer was washed with saturated sodium chloride solution, dried over sodium sulphate and concentrated. The concentrated crude was purified by silica gel column chromatography (EtOAc:pet ether, 15:85) to give **8c** (6.5 g, 80% over two steps) as a thick syrup.

Similar procedure was applied for the formation of **9c** (82%: 2 steps), **13b** (75% : 2 steps), and **14b** (80% : 2 steps) as a thick syrup.

3,5-Di-*O*-(*t*-butyldiphenyl)silyl-β-D-arabinofuranoside-prop-2-ynyl-1,2-*O*-orthobenzoate (**8d**): Crude diol orthoester **8b** (2.9 g, 10 mmol) was dissolved in dry dimethylformamide (DMF) (40 mL) and cooled to 0 ^{o}C in ice bath. Solution of TBDPSCl (2.5 eq.) / Im (5 eq.) in DMF was added drop-wise at 0 ^{o}C over 10 min. After 2 h at room temperature, water (100 mL) were added to reaction mixture and the compound was taken out from water with EtOAc (2x100 mL). The organic layer was washed with saturated sodium chloride solution, dried over sodium sulphate and concentrated. The concentrated crude was purified by silica gel column chromatography (EtOAc:pet ether, 5:95) to give **8d** (6.3 g, 82%) as a thick syrup.

3-*O*-Benzoyl 5-*O*-(*t*-butyldiphenyl)silyl-β-D-arabinofuranosyl-prop-2-ynyl-1,2-*O*-orthobenzoate (**8e**): Crude diol orthoester **8b** (7.0 g, 24 mmol) was dissolved in dry dimethylformamide (DMF, 80 mL) and cooled to 0 ^{o}C in ice bath. Solution of TBDPSCl (1 eq.) / Im (2 eq.) in DMF was added drop-wise at 0 ^{o}C over 10 min. After 2 h at room temperature, water (100 mL) were added to reaction mixture and the compound was taken out from water with EtOAc (2x100 mL). The organic layer was washed with saturated sodium chloride solution, dried over sodium sulphate and concentrated. The concentrated crude was redissolved in Py (50 mL) and added benzoyl chloride at 0 ^{o}C over 10 min. the reaction mixture was left for overnight and next day morning excess of benzoyl chloride was quenched with ice-chips. After several washing the organic layer was dried and concentrated on rota vapour. The resultant crude was purified by silica gel column chromatography (EtOAc:pet ether, 8:92) to give **8e** (11.4 g, 75% over three steps) as a thick syrup.

3-*O*-Benzyl 5-*O*-(*t*-butyldiphenyl)silyl-β-D-arabinofuranosyl-prop-2-ynyl-1,2-*O*-orthobenzoate (**8f**): The obtained diol orthoester **8b** (5.0 g, 17.2 mmol) was dissolved in dry dimethylformamide (DMF) (60 mL) and cooled to 0 ^{o}C in ice bath.

Solution of TBDPSCl (1 eq.) / Im (2 eq.) in DMF was added drop-wise at 0 ^{o}C over 10 min. After 2 h at room temperature, water (100 mL) were added to reaction mixture and the compound was taken out from water with EtOAc (2x100 mL). The organic layer was washed with saturated sodium chloride solution, dried over sodium sulphate and concentrated. The concentrated crude was redissolved in DMF (50 mL) and added sodium hydride (2 eq.) at 0 ^{o}C. Benzyl bromide was added to the same over 10 min at 0 ^{o}C. After 2 h at 0 ^{o}C, excess of benzyl bromide and sodium hydride was quenched with addition of methanol and ice-chips. After proper extraction from water layer, the organic layer was dried and concentrated on rota vapour. The resultant crude was purified by silica gel column chromatography (EtOAc:pet ether, 6:94) to give **8f** (7.8 g, 72% over three steps) as a thick syrup

General procedure for gold (III) catalyzed 1,2-*trans* furanosylation: To a CH_2Cl_2 solution (5 mL) containing glycosyl donor (**8a**, 0.1 mmol) and glycosyl acceptor (**11e**, 0.1 mmol)) with 4 Å molecular sieves powder (100 mg) was added a catalytic amount of $AuCl_3$ (7 μmol) (Silver triflate as an additive for oligosaccharides) and stirred at room temperature. After 2 h at room temperature, the reaction mixture was neutralized by the addition of Et_3N and filtered through celite and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography using ethyl acetate-petroleum ether to obtain 1,2-trans glycosides as a flappy solid (**16a**, 0.74 mg, 78%).

With this general procedure the yields were obtained for gold catalyzed glycosidations: **16a-j** (65-92%), **18a-l** (72-94%), **19a-p** (66-90%), **20a-l** (67-94%), **21a** (90%), **21b** (91%), **22a** (87%), **23a** (85%), **24a** (69%), **25a** (65%), **4b** (62%), **4c** (61%), **22d** (80%), **37a-c** (76-80%), **22e** (81%), **24c** (65%), **5b** (64%), **7b** (84%), **6b** (78%), **41** (90%), **22g** (70%), **7c** (85%), **6a** (70%), and **5a** (65%).

General procedure for pentenyl glycosidation for 1,2-*trans* furanosylation: To a CH_2Cl_2 solution (5 mL) containing glycosyl donor (**6b**, 0.06 mmol) and glycosyl acceptor (**7a**, 0.04 mmol)) with 4 Å molecular sieves powder (100 mg) was added 3 molar eq. of NIS at 0 ^{o}C in ice bath and stirred for 10 min. After 10 min. catalytic amount of TfOH (0.3 eq.) was added to the reaction mixture at 0 ^{o}C. The progress of reaction was monitored through TLC. After completion of reaction, the reaction mixture was neutralized by the addition of Et_3N and filtered through celite. The

filtrate was washed with sat solution of sodium bicarbonate and sodium thiosulphate. The collected organic layer was dried over sodium sulphate and concentrated *in vacuo*. The resulting residue was purified by silica gel / flash silica gel column chromatography using ethyl acetate-petroleum ether to obtain **42a** (65 mg, 40%).

General procedure applied for the synthesis of 1,2-*trans* tridecamer (**43a**, 25%) as a fluppy solid.

General procedure for the synthesis of trichloroacetimidate donors: To a CH_3CN:H_2O solution (10:1 mL) containing glycosyl donor (**6b**, 0.1 mmol) was added 3 molar eq. of NIS at room temperature and stirred for another 4 h. After completion of reaction, the reaction mixture was concentrated and diluted with dichloromethane. Compound in dichloromethane was washed with sat solution of sodium bicarbonate and sodium thiosulphate. The collected organic layer was dried over sodium sulphate and concentrated *in vacuo*. The resulting residue was purified by silica gel / flash silica gel column chromatography using ethyl acetate-petroleum ether to give corresponding α:β mixture of lactol.

To an anhydrous CH_2Cl_2 solution (10 mL) containing lactol was added catalytic amount of DBU at room temperature and stirred for 5 min. After 5 min, 4 molar eq. of trichloroacetonitrile was dropwise added to the reaction mixture and left the reaction mixture for another 4 h at room temperature. After completion of reaction, the reaction mixture was concentrated and purified by neutral silica gel column chromatography using ethyl acetate-petroleum ether to achieve trichloroacetimidate glycosyl donor **6c (1**48 mg, 70% over two steps).

Similar procedure was applied for the synthesis of **5e** (69%: 2 steps) as a fluppy solid from **5b**.

General procedure for trichloroacetimidate glycosidation for 1,2-*trans* furanosylation: To a CH_2Cl_2 solution (5 mL) containing glycosyl donor (**6c**, 0.06 mmol) and glycosyl acceptor (**7a**, 0.035 mmol)) with 4 Å molecular sieves powder (100 mg) was added catalytic amount of TfOH (0.3 eq.) at –20 ^{o}C. After 15 min. the reaction mixture was quenched by the addition of Et_3N and filtered through celite and concentrated *in vacuo.* The resulting residue was purified by flash silica gel column chromatography using ethyl acetate-petroleum ether to obtain **42a** (76%) as fluppy solid.

Similar procedure was applied for the synthesis of **43a** (68%) as a fluppy solid from **5e**.

General procedure for 1,2-*cis*-furanosylation: To a CH_2Cl_2 solution (5 mL) containing orthoester donor **9c** (0.2 mmol) and glycosyl acceptor **11j** (0.2 mmol)) with 4 Å molecular sieves powder (100 mg) was added a catalytic amount of $AuCl_3$ (14 µmol) and stirred at room temperature. After 2 h, the reaction mixture was neutralized by the addition of Et_3N and filtered through celite and concentrated *in vacuo* to obtain a reddish brown residue which was redissolved in CH_3OH (5 mL) and added $NaOCH_3$ (20 µmol) and stirred at 25 ºC for 2 h and concentrated *in vacuo*. The crude residue was purified by silica gel column chromatography using ethyl acetate-petroleum ether to obtain compound **32d** in 80% over two steps.

General procedure was applied for the formation of **32a-f** (75-85%), **4b** (56%) and **4c** (54%).

Alcohol **32d** (0.2 mmol) was redissolved in CH_2Cl_2, added Dess-Martin periodinane (0.3 mmol) and stirred at 25 ºC for 2 h. The reaction mixture was diluted CH_2Cl_2 and washed with sodium thiosulfate and sodium bicarbonate solutions. Combined organic layers was washed with brine solution, dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to 2-ribuloside **33d** which was subsequently redissolved in CH_3OH (5 mL) and treated with $NaBH_4$ (0.2 mmol) in three portions at 0 ºC. After 30 min, the reaction mixture was poured over ice and extracted with ethyl acetate, washed with brine, and dried over anhydrous Na_2SO_4. The solution was decanted and concentrated *in vacuo* to obtain a pale yellow residue which upon purification by silica gel column chromatography gave colour less thick syrup **34d** in 93% yield over two steps.

General procedure was applied for the formation of **34a-f** (90-95%), **4d** (75%), and **4e** (76%).

Pent-4-enyl 2-O-(*p*-methoxybenzyl)-3-*O*-benzyl-α-D-arabinofuranoside (**11b**): To a solution of orthoester **3b** (5.0 g, 9.4 mmol) and pent-4-en-1-ol in anhydrous CH_2Cl_2 (100 mL) was added 4 Å MS powder and the reaction mixture was stirred under inert atmosphere for 10 min. Catalytic amount of gold (III) chloride (0.2 g, 3.3 mmol), was added to the reaction and further reaction mixture stirred for another 2 h at room

temperature. After completion of reaction, the reaction mixture was quenched with Et_3N, filtered the solution through cotton-celite and concentrated the filtrate on rota vapour. Thus, obtained crude residue was suspended in methanol and CH_2Cl_2 mixture and added NaOMe (cat). The progress of reaction was monitored through TLC and neutralised with careful addition of Amberlite IR-120 resin, filtered the solution through cotton and concentrated the filtrate rota vapour. The obtained crude was purified through silica gel column chromatography to form pure alcohol.

To this pure alcohol without any additional analytical characterization was dissolved in DMF (25 mL) and added sodium hydride in portion-wise at 0 °C in ice-water bath to afford cake like reaction mixture. 4-Methoxy benzyl bromide was dropwise added to the same cake like reaction mixture at 0 °C and continued stirring for another 2 h at 0 °C. After 2 h reaction mixture was quenched with cold water and extracted compound with ethyl acetate. The organic layer was washed with brine solution and dried over sodium sulphate, concentrated in rota vapour to give crude 2-PMB alkylated product in good yield.

To a solution of crude PMB alkylated product in THF was added HF:Py (5 mL) in THF:Py (50:10 mL) and the reaction mixture was left for another 4h on stirrer. The reaction mixture was neutralised with sat solution of sodium bicarbonate and concentrated at 35 ^oC. The resultant crude was dissolved in EtOAc and washed with water. The organic layer was taken out from water layer, dried and concentrated in rota vapour to give crude **11b** which was further purified by column chromatography (EtOAc:pet ether, 25:75) to obtained pure **11b** (2.6g, 83.5 % over two steps)..

Similar procedure was applied for the synthesis of **11a** (66.5% over four steps)

Synthesis of pentenyl galactofuranoside (**40**): To a solution of D-galactose (20 g, 111 mmol) and pent-4-enyl in (16.4 mL, 166 mmol) anhydrous THF (60 mL for 20 g) was portion-wise added $FeCl_3$ (54g, 333mmol) at 0 ^oC with magnetically constant stirring. After 5 min. $CaCl_2$ (12.3 g, 111 mmol) was added to the same reaction at 0 ^oC and left the reaction mixture for 48 h at room temperature. After completion of reaction, the reaction mixture was concentrated on rota vapour and further applied high *vacuo* generate dried pentenyl galactofuranoside along with minor amount of pentenyl galactopyranoside. To this crude, excess of Py was added carefully at 0 ^oC and stirred for another 10 min in ice-water bath. Excess of acetic anhydride (10 eq.) was dropwise added to the reaction mixture at 0 ^oC and left the reaction mixture for

overnight at room temperature. Next day morning, reaction mixture was diluted with EtOAc and 4N solution of hydrochloric acid. The reaction mixture was transferred into separating funnel and organic layer was separated. Several washing with sat solution of sodium bicarbonate and water was given to the organic layer. The collected organic layer was dried over sodium sulphate, concentrated and purified in silica gel column chromatography to afford pure α:β pentenyl galactofuranoside (**40**, 27.7 g, 60% over two steps) as thick syrup.

Synthesis of galactofuranoside diol (**11d**): To a solution of **41** (5 g, 11.2 mmol) in anhydrous methanol was added freshly prepared catalytic amount of sodium methoxide at room temperature. After 2 h at room temperature, the reaction mixture was quenched with Amberlite IR-120 resin and filtered through cotton. The filtrate was concentrated and used in next step without any additional purification. The obtained crude was dissolved in acetone (50 mL) and 2-methoxy propene (1.6 mL, 16.7 mmol) and added catalytic amount of PTSA (192 mg, 1.1 mmol). The progress of reaction mixture was judged with TLC and neutralised with Et_3N (4 mL). The reaction mixture was concentrated and redissolved in excess pyridine. 4 Eq. of benzoyl chloride was added to the reaction at 0 ^oC and the reaction mixture was left with constant stirring for overnight at room temperature. Next day morning, the acid-base work-up was done (as usual for Py reaction) and after concentration to give crude 5,6-acetonide 2,3-di-*O*-benzoyl galactofuranoside. The obtained crude was dissolved in methanol and added catalytic amount of PTSA. The slightly acidic reaction mixture was stirred for another 4 h at room temperature to get crude required diol. The crude diol was further purified using flash silica gel column chromatography to give pure diol (3.8 g) in **70** % over four steps.

Formation of orthoester using bromine and pent-4-enyl glycosides: Pent-4-enyl 2,3,5-tri-*O*-benzoyl-α-D-arabinofuranoside (1 g, 1.9 mmol) prepared vide supra was redissolved in dry CH_2Cl_2 (10 mL) and cooled to 0 ^oC. Bromine:CH_2Cl_2 (0.21 mL, 2.8 mmol) was dropwise added to the reaction mixture with constant stirring at 0 ^oC. Additionally, the reaction mixture was stirred for 10 min. at 0 ^oC. The reaction mixture was concentrated under reduced pressure to give 2,3,5-tri-*O*-benzoyl arabinofuranosyl bromide as white foam which was immediately used in the next step without any additional purification.[2]

The crude arabinofuranosyl bromide was dissolved in 10 mL anhydrous CH_2Cl_2, propargyl alcohol (0.22 mL, 3.9 mmol) and 2, 6-lutidine (0.88 mL, 7.54 mmol). Catalytic amount of tetra *n*-butyl ammonium iodide was added to the reaction and stirred for 4h at room temperature. The reaction mixture was diluted with CH_2Cl_2 (250 mL) and water (500 mL) and the aqueous layer was extracted with CH_2Cl_2 (2x) and the organic extract was washed with saturated oxalic acid solution, saturated sodium bicarbonate solution. The organic phase was collected, dried over sodium sulphate and concentrated *in vacuo*. The crude residue of orthoester was purified by silica gel column chromatography (EtOAc:Petroleum ether 20:80) to obtain **1a** (0.8 g, 85% over two steps) as a white solid.

Similar procedure were applied for the synthesis of **13a** (80%), **9a** (89%), **14a** (87%), **22e** (81%), **38a-c** (74-84%) and **10** (85%).

General procedure for deprotection *O*-silyl bond in di/tri/oligo/polysaccharide: To a solution of *O*-TBDPS protected saccharide (**22e**, 4.6 g, 4.1 mmol) in THF:Py (10:2) was added HF.Py (9.58 mL) and the reaction mixture was left for another 4 h on stirrer. The reaction mixture was quenched with sat solution of sodium-bicarbonate and compound was extracted with EtOAc from aqueous layer. The EtOAc layer was dried over sodium sulphate and concentrated on rota vapour at 35 ^{o}C. The crude was purified by flash column chromatography (EtOAc:pet ether, 25:75) to give hydroxyl saccharide (**22f**, 2.55 g, 95 % over two steps) as a yellow gummy residue.

General procedure was applied for the deprotection of **24c** (94%), **7b** (94%), **7c** (90%), **42a** (85%), **43a** (83%).

General procedure for the deprotection of benzoate groups in di/tetrasaccharide: To a solution of benzoyl protected saccharide (**23a**, 5.0 g, 5.7 mmol) in anhydrous MeOH:CH_2Cl_2 (25 mL:15 mL) was added NaOMe (0.1 g, 2.0 mmol), and the reaction mixture was stirred under inert atmosphere for 2 h. The reaction mixture was carefully quenched with Amberlite IR-120 resin; the solution was filtered through celite pad and concentrated *in vacuo* to obtain a residue. The obtained crude residue was purified by silica gel column chromatography (pet ether: EtOAc, 50:50) to give corresponding triol (**23b**, 2.8, 86%) as thick syrup.

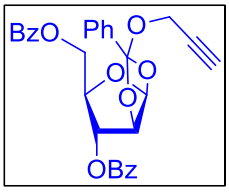
General procedure was applied for the deprotection of **22a** (85%), **24a** (92%), and **25b** (90%).

Pent-4-enyl-2,3-di-*O*-benzyl-5-*O*-(2-*O*-(*p*-methoxybenzyl)-α-D-arabinofuranosyl)-α-D-arabinofu-ranoside (**23c**): To triol **23b** in pyridine (15mL) at 0 ^{o}C was added 1,3-dichloro 1,1,3,3-tetraisopropyldisiloxane (1.1 eq.), and the resulting mixture was warmed to room temperature. The reaction mixture was quenched with methanol (0.5 mL) and poured into 100 mL of 10% hydrochloric acid solution and EtOAc (1:1) and the aqueous phase was extracted with EtOAc (2x25mL). The EtOAc layer was washed with sodium bicarbonate solution, brine solution, dried (sodium sulphate) and concentrated. The resultant crude residue was redissolved in dry DMF (15mL) and cooled to 0 ^{o}C. Sodium hydride in dispersion oil (2 eq.) was added followed by the addition of benzyl bromide (1.15 eq.) at 0 ^{o}C and warmed to room temperature for 2 h. Excess benzyl bromide and sodium hydride were quenched with methanol (0.5mL) and reaction mixture was poured into the ice cold water and EtOAc solution. The organic phase was separated from the aqueous phase and washed with brine, dried and concentrated *in vacuo*. The crude residue in THF at 0 ^{o}C was added HF:Py solution (10.2 mL), and reaction mixture was stirred at room temperature for 4h. The reaction mixture was concentrated, and purified by flash silica gel chromatography (EtOAc:pet ether, 35:65) to obtain **16** (76% over three steps) as a syrup.

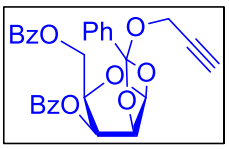
Similar procedure was applied for the synthesis of **22c** (75% over three steps)

Characterization data

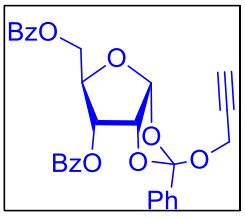
3, 5-Di-O-benzoyl-β-D-arabinofuranoside (prop-2-yn-1-yl)-1,2-orthobenzoate (**8a**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.5) –15.3°; IR (cm^{-1}, $CHCl_3$): 3293, 3071, 2974, 1723, 1594, 1450, 1268, 1107, 717; ^1H NMR (399.78 MHz, $CDCl_3$): δ 2.41 (t, *J* = 2.3 Hz, 1H), 3.98 (d, *J* = 2.3 Hz, 2H), 4.30 (d, *J* = 7.2 Hz, 2H), 4.67 (t, *J* = 7.2 Hz, 1H), 5.20 (d, *J* = 4.2 Hz, 1H), 5.55 (s, 1H), 6.41 (d, *J* = 4.2 Hz, 1H), 7.33 – 7.46 (m, 7H), 7.54 (dt, *J* = 21.2, 7.3 Hz, 2H), 7.70 (dd, *J* = 6.5, 2.9 Hz, 2H), 8.03 (d, *J* = 7.7 Hz, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 51.9, 63.6, 73.8, 77.5, 79.2, 84.3, 84.7, 106.5, 122.7, 126.3, 126.3, 128.2, 128.2, 128.4, 128.4, 128.4, 128.4, 128.8, 129.5, 129.6, 129.6, 129.7, 129.7, 130.0, 132.9, 133.5, 134.0, 165.1, 165.7; HRMS (Waters Synapt G2) : m/z calcd for $[C_{29}H_{24}O_8+Na]^+$: 523.1369; Found: 523.1379.



3,5-Di-*O*-benzyl-β-D-lyxofuranoside (prop-2-yn-1-yl)-1,2-orthobenzoate (**13a**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) –44.7°; IR (cm^{-1}, $CHCl_3$): 3290, 3065, 2918, 1723, 1591, 1445, 1269, 1099, 713; ^1H NMR (399.78 MHz, $CDCl_3$): δ 2.38 (t, *J* = 2.5 Hz, 1H), 3.97 (d, *J* = 2.5 Hz, 2H), 4.33 (dd, *J* = 11.9, 7.7 Hz, 1H), 4.56 (dd, *J* = 11.9, 5.3 Hz, 1H), 4.77 (td, *J* = 7.5, 5.3 Hz, 1H), 5.31 (dd, *J* = 5.7, 4.3 Hz, 1H), 5.51 (dd, *J* = 7.4, 5.8 Hz, 1H), 6.26 (d, *J* = 4.2 Hz, 1H), 7.29 – 7.73 (m, 11H), 7.84 – 8.04 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 51.9, 63.6, 71.8, 73.8, 78.0, 78.4, 79.2, 105.4, 123.6, 126.4, 126.4, 128.2, 128.2, 128.4, 128.4, 128.5, 128.5, 128.7, 129.6, 129.6, 129.6, 129.9, 129.9, 129.9, 133.0, 133.5, 134.5, 165.4, 165.9; HRMS (Waters Synapt G2) : m/z calcd for $[C_{29}H_{24}O_8+Na]^+$: 523.1369; Found: 523.1377.

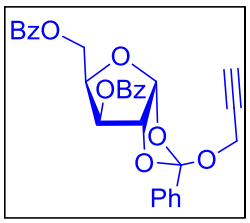


3,5-Di-*O*-benzoyl-α-D-ribofuranoside (prop-2-yn-1-yl)-1,2-orthobenzoate (**9a**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 2.6) +123.1°; IR (cm^{-1}, $CHCl_3$): 3291, 3066, 2930, 1725, 1602, 1451, 1271, 1099, 710; ^1H NMR (399.78 MHz, $CDCl_3$): δ 2.40 (t, *J* = 2.4 Hz, 1H), 4.07 (dABq, *J* = 15.2, 2.4 Hz, 2H), 4.17 – 4.29 (m, 1H), 4.39 (dd, *J* = 12.3, 4.8 Hz, 1H), 4.62 (dd, *J* = 12.3, 3.3 Hz, 1H), 5.07 (dd, *J* = 9.3, 5.3 Hz, 1H), 5.33 (dd, *J* = 5.1, 4.3 Hz, 1H), 6.25 (d, *J* = 4.2 Hz, 1H), 7.24 – 7.81 (m, 11H), 7.89 – 8.10 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 51.5, 62.4, 72.8, 73.8, 76.2, 77.7, 79.1, 104.7, 123.5, 126.3, 126.3, 128.3, 128.3, 128.3, 128.3, 128.5, 128.5, 128.8, 129.4, 129.6, 129.7, 129.7,



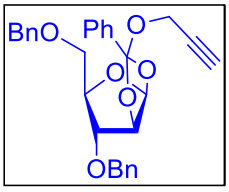
129.9, 129.9, 133.2, 133.6, 135.8, 165.5, 166.0; HRMS (Waters Synapt G2) : m/z calcd for $[C_{29}H_{24}O_8+Na]^+$: 523.1369; Found: 523.1364.

3,5-Di-*O*-benzoyl-α-D-xylofuranoside (prop-2-yn-1-yl)-1,2-orthobenzoate (**14a**):



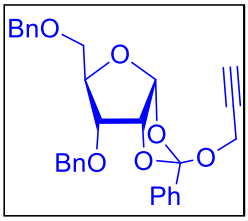
$[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) –4.2°; IR (cm^{-1}, $CHCl_3$): 3290, 3068, 2930, 1725, 1591, 1447, 1268, 1105, 706; ^1H NMR (399.78 MHz, $CDCl_3$): δ 2.40 (t, J = 2.4 Hz, 1H), 4.12 – 3.93 (m, 2H), 4.64 – 4.43 (m, 1H), 4.56 (dd, J = 7.1, 5.9 Hz, 2H), 5.04 (d, J = 4.1 Hz, 1H), 5.66 (d, J = 3.1 Hz, 1H), 6.37 (d, J = 4.1 Hz, 1H), 7.79 – 7.32 (m, 11H), 8.16 – 7.88 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 51.8, 61.5, 73.8, 76.0, 77.8, 79.2, 84.0, 105.2, 122.8, 126.2, 126.2, 128.3, 128.3, 128.4, 128.4, 128.6, 128.6, 128.7, 129.3, 129.6, 129.6, 129.7, 129.8, 129.9, 133.1, 133.7, 134.9, 165.0, 165.9; HRMS (Waters Synapt G2) : m/z calcd for $[C_{29}H_{24}O_8+Na]^+$: 523.1369; Found: 523.1395.

3,5–Di–*O*-benzyl-β-D-arabinofuranoside (prop-2-yn-1-yl)-1,2-orthobenzoate (**8c**):



$[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) –16.0°; IR (cm^{-1}, $CHCl_3$): 3291, 3033, 2928, 2867, 1721, 1592, 1453, 1275, 1111, 701; ^1H NMR (399.78 MHz, $CDCl_3$): δ 2.38 (t, *J* = 2.3 Hz, 1H), 3.20 (dd, *J* = 9.8, 7.9 Hz, 1H), 3.33 (dd, *J* = 9.8, 6.4 Hz, 1H), 3.97 (dd, *J* = 9.9, 2.4 Hz, 1H), 4.02 (s, 1H), 4.23 (d, *J* = 12.0 Hz, 1H), 4.35 (d, *J* = 12.3 Hz, 1H), 4.40 (t, *J* = 7.3 Hz, 1H), 4.55-4.66 (m, 1H), 4.58 (d, *J* = 2.6 Hz, 2H), 5.02 (d, *J* = 4.5 Hz, 1H), 6.25 (d, *J* = 4.4 Hz, 1H), 7.11 – 7.17 (m, 2H), 7.31 (m, 11H), 7.54 – 7.59 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 51.7, 69.8, 71.5, 73.2, 73.6, 79.4, 82.6, 85.1, 85.1, 106.5, 122.4, 122.4, 126.4, 122.4, 127.6, 127.6, 127.8, 128.0, 128.0, 128.3, 128.3, 128.3, 128.3, 128.5, 128.5, 129.7, 135.2, 137.0, 137.8; HRMS (Waters Synapt G2) : m/z calcd for $[C_{29}H_{28}O_6+Na]^+$: 495.1784; Found: 495.1787.

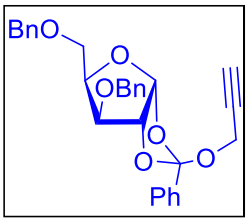
3,5-Di-*O*-benzyl-α-D-ribofuranoside (prop-2-yn-1-yl)-1,2-orthobenzoate (**9c**): $[\alpha]_D^{25}$



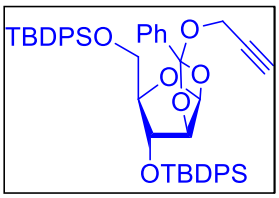
($CHCl_3$, *c* 0.7) +21.3°; IR (cm^{-1}, $CHCl_3$): 3290, 3060, 2928, 1722, 1590, 1450, 1262, 1110, 707; ^1H NMR (399.78 MHz, $CDCl_3$): δ 2.40 (t, *J* = 2.1 Hz, 1H), 3.46 – 3.58 (m, 1H), 3.69 (d, *J* = 11.3 Hz, 1H), 3.84 – 3.98 (m, 2H), 4.01 – 4.08 (m, 2H), 4.45 (d, *J* = 12.2 Hz, 1H), 4.54 (d, *J* = 13.4 Hz, 2H), 4.76 (d, *J* = 11.5 Hz, 1H), 4.90 (t, *J* = 4.1 Hz, 1H), 6.09 (dd, *J* = 4.1, 1.4 Hz, 1H), 7.11 – 7.46 (m, 13H), 7.62 – 7.84 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 51.6, 67.3, 72.1, 73.3, 73.5, 76.9, 77.4, 78.3, 79.6, 104.7, 123.2, 126.4, 126.4, 127.6, 127.6, 127.6, 128.0, 128.0,

128.0, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 129.5, 135.3, 137.3, 137.8; HRMS (Waters Synapt G2) : m/z calcd for $[C_{29}H_{28}O_6+Na]^+$: 495.1784; Found: 495.1789.

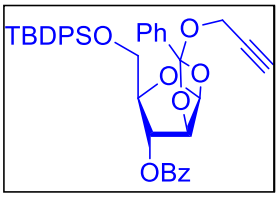
3,5-Di-*O*-benzyl-α-D-xylofuranoside (prop-2-yn-1-yl)-1,2-orthobenzoate (**14c**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.3) –9.4°; IR (cm^{-1}, $CHCl_3$): 3293, 3070, 2925, 1594, 1450, 1270, 1103, 710; ^1H NMR (399.78 MHz, $CDCl_3$): δ 2.39 (t, *J* = 2.5 Hz, 1H), 3.72 (d, *J* = 6.1 Hz, 2H), 4.00 (d, *J* = 3.3 Hz, 1H), 4.02 (dABq, *J* = 15.5, 2.5 Hz, 2H), 4.13 – 4.23 (m, 1H), 4.46 (d, *J* = 11.9 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 11.9 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.95 (d, *J* = 4.1 Hz, 1H), 6.23 (d, *J* = 4.1 Hz, 1H), 7.15 – 7.50 (m, 13H), 7.54 – 7.75 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 51.8, 67.2, 72.0, 73.4, 73.6, 79.5, 79.9, 81.1, 82.9, 105.4, 122.4, 126.2, 126.2, 127.6, 127.6, 127.6, 127.7, 127.7, 128.0, 128.3, 128.3, 128.3, 128.4, 128.4, 128.5, 129.7, 135.1, 137.2, 137.8; HRMS (Waters Synapt G2) : m/z calcd for $[C_{29}H_{28}O_6+Na]^+$: 495.1784; Found: 495.1780.



3,5-Di-*O*-(*t*-butyldiphenylsilyl)-α-D-arabinofuranoside (prop-2-yn-1-yl)-1,2-ortho-benzoate (**8d**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) –3.0°; IR (cm^{-1}, $CHCl_3$): 3298, 3065, 2936, 2114, 1594, 1466, 1272, 1110, 701; ^1H NMR (399.78 MHz, $CDCl_3$): δ 0.84 (s, 9H), 1.09 (s, 9H), 2.27 (t, *J* = 2.4 Hz, 1H), 3.17 (dd, *J* = 10.4, 8.5 Hz, 1H), 3.34 (dd, *J* = 10.3, 6.4 Hz, 1H), 3.79 (dABq, *J* = 15.5, 2.4 Hz, 2H), 3.92 (s, 1H), 4.42 (s, 1H), 4.83 (d, *J* = 4.2 Hz, 1H), 6.26 (d, *J* = 4.2 Hz, 1H), 6.99 – 7.52 (m, 21H), 7.59 – 7.75 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 19.0, 19.1, 26.7, 26.7, 26.7, 26.8, 26.8, 26.9, 51.7, 63.6, 73.5, 77.1, 79.5, 87.1, 90.2, 106.6, 122.0, 126.3, 126.3, 127.4, 127.5, 127.5, 127.5, 127.8, 127.8, 127.8, 128.1, 128.1, 129.3, 129.4, 129.5, 129.5, 129.9, 130.0, 132.8, 133.0, 133.2, 133.3, 134.5, 135.4, 135.4, 135.4, 135.4, 135.7, 135.7, 135.7, 135.7; HRMS (Waters Synapt G2) : m/z calcd for $[C_{47}H_{52}O_6Si_2+Na]^+$: 768.3302; Found: 768.3300.

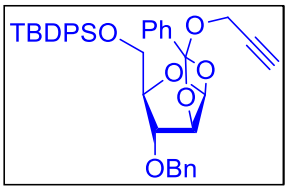


3-*O*-Benzoyl-5-*O*-(*t*-butyldiphenylsilyl)-α-D-arabinofuranoside (prop-2-yn-1-yl)-1,2-*O*-orthobenzoate (**8e**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) –20.0°; IR (cm^{-1}, $CHCl_3$): 3293, 3066, 2939, 1727, 1595, 1453, 1266, 1106, 704; ^1H NMR (399.78 MHz, $CDCl_3$): δ 0.99 (s, 9H), 2.37 (t, *J* = 2.2 Hz, 1H), 3.63 (dd, *J* = 7.5, 4.1 Hz, 2H), 3.84 – 4.02 (m, 2H), 4.46 (t, *J* = 7.5 Hz, 1H), 5.09 (d, *J* = 4.3 Hz, 1H), 5.67 (s, 1H), 6.33 (d, *J* = 4.3

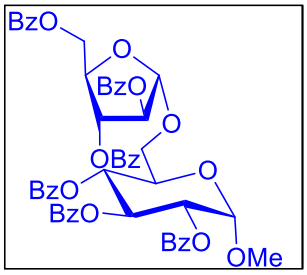


Hz, 1H), 6.97 – 7.86 (m, 18H), 8.09 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 19.1, 26.7, 26.7, 26.7, 51.9, 63.4, 73.7, 77.5, 79.3, 85.0, 87.2, 106.5, 122.4, 126.3, 126.3, 127.5, 127.6, 127.6, 127.6, 128.2, 128.3, 128.4, 128.4, 129.2, 129.6, 129.6, 129.6, 129.8, 129.8, 133.1, 133.1, 133.4, 134.2, 135.3, 135.4, 135.4, 135.4, 165.1; HRMS (Waters Synapt G2) : m/z calcd for $[C_{38}H_{38}O_7Si+Na]^+$: 657.2284; Found: 657.2281.

3-*O*-Benzyl-5-*O*-(*t*-butyldiphenylsilyl)-α-D-arabinofuranoside (prop-2-yn-1-yl)-1,2 -orthobenzoate (**8f**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.3) –18.9°; IR (cm^{-1}, $CHCl_3$): 3294, 3062, 2935, 2123, 1590, 1458, 1317, 1107, 700; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 0.94 (s, 9H), 2.37 (t, *J* = 2.4 Hz, 1H), 3.43 (d, *J* = 9.9 Hz, 1H), 3.56 (dd, *J* = 10.2, 5.4 Hz, 1H), 3.93 (dABq, *J* = 15.5, 2.6 Hz, 2H), 4.20 (s, 1H), 4.33 (dd, *J* = 9.6, 5.4 Hz, 1H), 4.60 (s, 1H), 5.03 (d, *J* = 4.3 Hz, 1H), 5.29 (s, 1H), 6.22 (d, *J* = 4.4 Hz, 1H), 7.04 – 7.61 (m, 20H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 19.1, 26.7, 26.7, 26.8, 51.8, 63.4, 71.5, 73.6, 79.5, 82.5, 85.1, 86.9, 106.5, 122.3, 126.3, 126.3, 127.6, 127.6, 127.6, 127.6, 127.7, 127.7, 127.9, 128.2, 128.2, 128.5, 128.5, 129.6, 129.6, 129.7, 133.1, 133.2, 134.7, 135.3, 135.3, 135.4, 135.4, 137.2; HRMS (Waters Synapt G2) : m/z calcd for $[C_{38}H_{40}O_6Si+Na]^+$: 643.2492; Found: 643.2490.

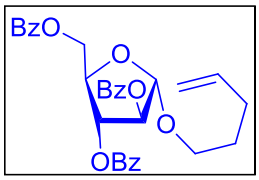


Methyl-2,3,4-tri–*O*–benzoyl-6–*O*-(2,3,5–tri–*O*-benzoyl–α-D-arabinofuranosyl)-α-D–glucopyranoside (**16a**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +28.5°; IR (cm^{-1}, $CHCl_3$): 3062, 2928, 1727, 1596, 1453, 1269, 1104, 710; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 3.44 (s, 3H), 3.79 (d, *J* = 11.0 Hz, 1H), 4.05 (dd, *J* = 11.0, 4.1 Hz, 1H), 4.29 (d, *J* = 8.6 Hz, 1H), 4.61 (dd, *J* = 11.6, 4.9 Hz, 1H), 4.66 – 4.70 (m, 1H), 4.74 (dd, *J* = 11.5, 2.8 Hz, 1H), 5.25 (d, *J* = 3.5 Hz, 1H), 5.30 (dd, *J* = 10.1, 3.6 Hz, 1H), 5.35 (s, 1H), 5.54 (d, *J* = 4.3 Hz, 1H), 5.61 (s, 1H), 5.73 (t, *J* = 9.9 Hz, 1H), 6.14 (t, *J* = 9.8 Hz, 1H), 7.14 – 7.67 (m, 18H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.93 (dd, *J* = 17.2, 8.0 Hz, 4H), 7.97 – 8.01 (m, 4H), 8.22 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 55.5, 63.7, 65.0, 68.4, 68.9, 70.6, 72.0, 77.7, 81.3, 81.9, 97.0, 105.4, 128.2, 128.2, 128.2, 128.2, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.9, 129.0, 129.1, 129.1, 129.3, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 129.9, 129.9, 129.9, 129.9, 130.0, 130.0, 132.9, 133.0, 133.3, 133.3, 133.5, 133.5,

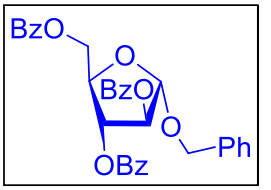


165.0, 165.3, 165.8, 165.8, 165.9, 166.2; HRMS (Waters Synapt G2) : m/z calcd for $[C_{54}H_{46}O_{16}+Na]^+$: 973.2684; Found: 973.2706.

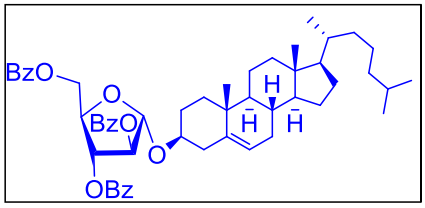
(Pent-4-enyl) 2,3,5-tri-*O*-benzoyl-α-D-arabinofuranoside (**16b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) –4.6°; IR (cm^{-1}, $CHCl_3$): 3068, 2929, 1725, 1593, 1266, 1109, 700; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.76 (quintet, *J* = 6.7 Hz, 2H), 2.19 (q, *J* = 4.4 Hz, 2H), 3.56 (dt, *J* = 9.5, 6.2 Hz, 1H), 3.82 (dt, *J* = 9.5, 6.6 Hz, 1H), 4.58 (q, *J* = 4.8 Hz, 1H), 4.68 (dd, *J* = 11.9, 5.0 Hz, 1H), 4.83 (dd, *J* = 11.9, 3.5 Hz, 1H), 4.96 (dq, *J* = 10.0, 1.4 Hz, 1H), 5.02 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.28 (s, 1H), 5.52 (d, *J* = 1.0 Hz, 1H), 5.58 (d, *J* = 4.7 Hz, 1H), 5.83 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.49 – 7.54 (m, 1H), 7.55 – 7.64 (m, 2H), 8.00 (dd, *J* = 8.1, 1.1 Hz, 2H), 8.05 (dd, *J* = 8.0, 1.0 Hz, 2H), 8.09 (dd, *J* = 8.3, 1.0 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.7, 30.3, 63.8, 66.8, 77.0, 77.9, 81.0, 82.0, 105.7, 115.0, 128.3, 128.3, 128.5, 128.5, 128.5, 129.0, 129.1, 129.7, 129.7, 129.7, 129.8, 129.8, 129.9, 129.9, 133.0, 133.5, 133.5, 138.0, 165.5, 165.8, 166.2; HRMS (Waters Synapt G2) : m/z calcd for $[C_{31}H_{30}O_8+Na]^+$: 553.1838, Found: 553.1844.



Benzyl 2,3,5-tri-*O*-benzoyl-α -D-arabinofuranoside (**16c**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.5) +5.8°; IR (cm^{-1}, $CHCl_3$): 3066, 2928, 1724, 1596, 1452, 1266, 1108, 708; ^1H NMR (399.78 MHz, $CDCl_3$): δ 4.61 (q, *J* = 4.6 Hz, 1H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.69 (dd, , *J* = 12.7, 5.0 Hz, 1H), 4.84 (dd, *J* = 11.9, 3.5 Hz, 1H), 4.88 (d, *J* = 12.0 Hz, 1H), 5.40 (s, 1H), 5.60(d, *J* = 5.2 Hz, 1H), 5.61 (s, 1H), 7.26 – 7.70 (m, 14H), 7.98 – 8.08 (m, 6H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 63.8, 68.8, 77.8, 81.3, 81.9, 104.9, 127.7, 127.7, 127.8, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 129.0, 129.1, 129.7, 129.8, 129.8, 129.9, 129.9, 130.0, 130.0, 133.1, 133.5, 133.5, 137.3, 165.4, 165.8, 166.2; HRMS (Waters Synapt G2) : m/z calcd for $[C_{33}H_{28}O_8+Na]^+$: 575.1682; Found: 575.1681.

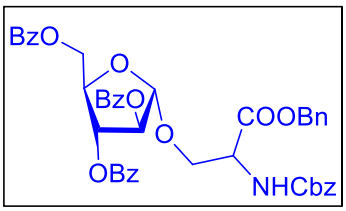


Cholesteryl 2,3,5-tri-*O*-benzoyl-α-D-arabinofuranoside (**16d**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1) +3.7°; IR (cm^{-1}, $CHCl_3$): 3034, 2940, 1726, 1596, 1455, 1267, 1108, 709; ^1H NMR (399.78 MHz, $CDCl_3$): δ 0.68 (s, 3H), 0.86 (d, *J* = 1.7 Hz, 3H), 0.87 (d, *J* = 1.7 Hz, 3H), 0.92 (d, *J* = 6.5 Hz, 3H),

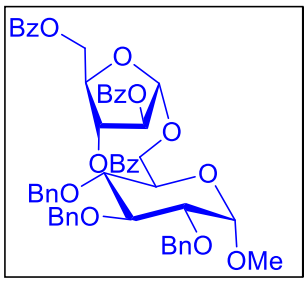


0.93 – 1.71 (m, 24H), 1.78 – 1.85 (m, 1H), 1.88 (dt, *J* = 12.8, 3.0 Hz, 1H), 1.99 (td, *J* = 11.8, 11.2, 4.8 Hz, 3H), 2.41 (d, *J* = 7.3 Hz, 2H), 3.63 (dtd, *J* = 11.2, 7.2, 6.5, 4.3 Hz, 1H), 4.62 (q, *J* = 4.8 Hz, 1H), 4.68 (dd, *J* = 11.8, 5.0 Hz, 1H), 4.82 (dd, *J* = 11.8, 3.4 Hz, 1H), 5.35 (d, *J* = 4.6 Hz, 1H), 5.45 (s, 1H), 5.49 (s, 1H), 5.57 (d, *J* = 5.0 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.49 – 7.68 (m, 3H), 8.01 (d, *J* = 7.4 Hz, 2H), 8.05 (d, *J* = 7.2 Hz, 2H), 8.09 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 11.8, 18.7, 19.4, 21.0, 22.6, 22.8, 23.8, 24.3, 27.7, 28.0, 28.2, 31.8, 31.9, 35.8, 36.1, 36.7, 37.0, 39.5, 39.7, 40.0, 42.3, 50.0, 56.1, 56.7, 63.8, 76.6, 77.9, 80.7, 82.5, 103.8, 121.9, 128.3, 128.3, 128.5, 128.5, 128.5, 128.5, 129.1, 129.2, 129.7, 129.8, 129.8, 129.8, 129.8, 129.9, 129.9, 133.0, 133.4 133.5, 140.6, 165.5, 165.8, 166.2; HRMS (Waters Synapt G2) m/z calcd for $[C_{53}H_{66}O_8+Na]^+$: 853.4655; Found: 853.4664

Benzyl-*N*-(benzyloxycarbonyl)-*O*-(2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl)-L-serinate (**16e**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.3) –5.3°; IR (cm^{-1}, $CHCl_3$): 3064, 2926, 1723, 1594, 1450, 1261, 1120, 703; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 4.09 (qd, *J* = 10.2, 2.8 Hz, 2H), 4.50 (q, *J* = 4.4 Hz, 1H), 4.61 (dd, *J* = 12.0, 5.3 Hz, 1H), 4.65 (dt, *J* = 2.6, 8.9 Hz, 1H), 4.76 (dd, *J* = 11.9, 3.5 Hz, 1H), 5.04 (ABq, *J* = 12.3 Hz, 2H), 5.20 (ABq, *J* = 12.3 Hz, 2H), 5.22 (s, 1H), 5.42 (s, 1H), 5.53 (d, *J* = 4.3 Hz, 1H), 5.80 (d, *J* = 8.7 Hz, 1H), 7.20 – 7.43 (m, 16H), 7.50 (q, *J* = 7.5 Hz, 2H), 7.57 (tt, *J* = 15.0, 7.3, 1.3 Hz,1H), 7.98 (d, *J* = 7.3 Hz, 2H), 8.03 (d, *J* = 7.6 Hz, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 54.3, 63.6, 66.9, 67.4, 67.4, 68.0, 81.4, 81.8, 105.8, 128.0, 128.0, 128.1, 128.2, 128.2, 128.2, 128.2, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.7, 128.8, 129.5, 129.7, 129.7, 129.8, 129.8, 129.8, 133.0, 133.5, 133.5, 135.1, 136.0, 155.8, 165.2, 165.5, 166.1, 169.7. ; HRMS (Waters Synapt G2) : m/z calcd for $[C_{44}H_{39}O_{12}+Na]^+$: 796.2370; Found: 796.2372.

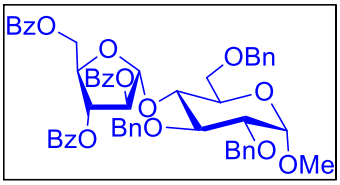


Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl)-α-D-glucopyranoside (**16f**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +17.7°; IR (cm^{-1}, $CHCl_3$): 3038, 2924, 1724, 1591, 1450, 1266, 1104, 706; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 3.33 (s, 3H), 3.58 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.67 (t, *J* = 9.3 Hz, 1H), 3.73 – 3.85 (m, 2H), 3.99 (t, *J* = 9.2 Hz, 1H), 4.10 (dd, *J* = 11.0, 3.5 Hz, 1H), 4.47 (q, *J* = 4.5 Hz, 1H), 4.57 (dd, *J* =12.0, 5.0 Hz,

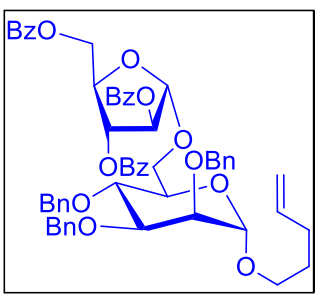


1H), 4.60 (s, 1H), 4.62 (d, *J* = 6.6 Hz, 1H), 4.67 (d, *J* = 12.1 Hz, 1H), 4.73 (dd, *J* = 12.0, 3.3 Hz, 1H), 4.77 (d, *J* = 1.8 Hz, 1H), 4.80 (s, 1H), 4.82 (d, *J* = 11.0 Hz, 1H), 4.98 (d, *J* = 10.9 Hz, 1H), 5.41 (s, 1H), 5.52 (d, *J* = 4.4 Hz, 1H), 5.59 (s, 1H), 7.14 – 7.44 (m, 21H), 7.45 – 7.51 (m, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.97 (d, *J* = 5.3 Hz, 2H), 7.99 (d, *J* = 5.1 Hz, 2H), 8.04 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 55.1, 63.7, 66.0, 69.8, 73.4, 75.0, 75.6, 77.8, 77.8, 80.0, 81.7, 81.8, 81.9, 98.0, 106.1, 127.4, 127.4, 127.5, 127.7, 127.9, 127.9, 127.9, 128.1, 128.1, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.9, 129.0, 129.6, 129.7, 129.7, 129.8, 129.8, 129.8, 129.8, 133.0, 133.5, 133.5, 138.1, 138.2, 138.8, 165.2, 165.6, 166.2; HRMS (Waters Synapt G2) : m/z calcd for $[C_{54}H_{52}O_{13}+Na]^+$: 931.3306; Found: 931.3332.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl)-α-D-glucopyranoside (**16g**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.5) +2.4°; IR (cm^{-1}, $CHCl_3$): 3020, 2925, 1725, 1596, 1453, 1268, 1105, 758; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 3.43 (s, 3H), 3.56 (dd, *J* = 9.6, 3.4 Hz, 1H), 3.66 (dd, *J* = 9.1, 3.0 Hz, 1H), 3.70 (t, *J* = 8.3 Hz, 1H), 3.84 (s, 1H), 3.85 (d, *J* = 4.9 Hz, 1H), 4.06 (t, *J* = 9.1 Hz, 1H), 4.27 (q, *J* = 4.4 Hz, 1H), 4.40 (d, *J* = 12.1 Hz, 1H), 4.48 (dd, *J* = 18.7, 6.9 Hz, 1H), 4.49 (s, 1H), 4.57 (dd, *J* = 11.8, 3.8 Hz, 1H), 4.63 (dd, *J* = 7.8, 4.3 Hz, 2H), 4.76 (d, *J* = 7.3 Hz, 1H), 4.79 (d, *J* = 6.1 Hz, 1H), 5.00 (d, *J* = 10.9 Hz, 1H), 5.47 (d, *J* = 4.4 Hz, 1H), 5.55 (s, 1H), 5.82 (s, 1H), 6.93 – 7.71 (m, 24H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.97 (d, *J* = 7.4 Hz, 2H), 8.05 – 8.10 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 55.3, 63.7, 69.0, 69.5, 73.3, 73.4, 73.9, 75.4, 77.9, 79.9, 81.7, 81.7, 81.9, 97.9, 106.7, 127.2, 127.5, 127.5, 127.5, 127.5, 127.5, 127.9, 128.1, 128.1, 128.1, 128.1, 128.2, 128.2, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.8, 129.1, 129.6, 129.6, 129.6, 129.8, 129.8, 129.8, 129.8, 132.9, 133.4, 133.5, 137.8, 137.9, 138.2, 165.0, 165.5, 166.1; HRMS (Waters Synapt G2) : m/z calcd for $[C_{54}H_{52}O_{13}+Na]^+$: 931.3306; Found: 931.3328.

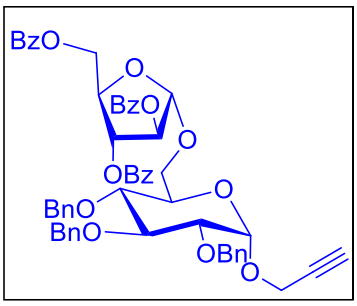


(Pent-4-enyl) 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl)-α-D-mannopyranoside (**16h**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.3) +3.0°; IR (cm^{-1}, $CHCl_3$): 3070, 2926, 1725, 1595, 1440, 1267, 1107, 707; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.58 (quintet, *J* = 6.9 Hz, 2H), 2.02 (q, *J* = 13.4, 5.7 Hz, 2H), 3.32 (dt, *J* =

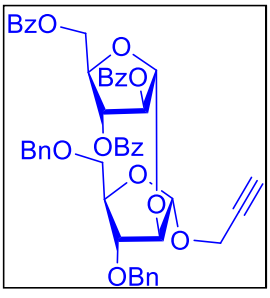


9.6, 6.3 Hz, 1H), 3.66 (dt, *J* = 9.6, 6.5 Hz, 1H), 3.75 – 3.85 (m, 3H), 3.93 (dd, *J* = 9.4, 3.0 Hz, 1H), 4.11 (t, *J* = 9.7 Hz, 1H), 4.17 (dd, *J* = 11.3, 4.5 Hz, 1H), 4.48 (q, *J* = 7.9, 4.4 Hz, 1H), 4.59 (dd, *J* = 11.4, 4.6 Hz, 2H), 4.63 (s, 2H), 4.73 (s, 2H), 4.76 (dd, *J* = 12.1, 3.3 Hz, 1H), 4.83 – 4.87 (m, 2H), 4.91 – 5.01 (m, 2H), 5.48 (s, 1H), 5.51 (d, *J* = 4.4 Hz, 1H), 5.69 (s, 1H), 5.70 – 5.81 (m, 1H), 7.07 – 7.71 (m, 24H), 7.93 – 8.12 (m, 6H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.5, 30.2, 63.8, 66.5, 66.8, 71.1, 72.0, 72.5, 74.6, 74.8, 75.1, 77.9, 80.2, 81.8, 81.9, 97.9, 106.0, 114.9, 127.5, 127.5, 127.5, 127.5, 127.5, 127.5, 127.6, 127.6, 127.6, 127.7, 127.7, 128.2, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.5, 128.5, 128.5, 129.0, 129.1, 129.7, 129.7, 129.7, 129.8, 129.8, 130.0, 130.0, 132.9, 133.3, 138.0, 138.3, 138.3, 138.4, 138.5, 165.1, 165.8, 166.2; HRMS (Waters Synapt G2) : m/z calcd for $[C_{58}H_{58}O_{13}+Na]^+$: 985.3775; Found: 985.3784.

Propargyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl)-α-D-glucopyranoside (**16i**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +24.9°; IR (cm^{-1}, $CHCl_3$): 3293, 3031, 2925, 1724, 1595, 1446, 1266, 1104, 706; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 2.42 (t, *J* = 2.4 Hz, 1H), 3.64 (dd, *J* = 9.7, 3.7 Hz, 1H), 3.70 (t, *J* = 9.0 Hz, 1H), 3.79 (dd, *J* = 11.3, 1.6 Hz, 1H), 3.86 (qd, *J* = 10.0, 3.4, 1.9 Hz, 1H), 4.01 (t, *J* = 9.3 Hz, 1H), 4.10 (dd, *J* = 11.3, 3.7 Hz, 1H), 4.27 (ddd, *J* = 18.3, 15.9, 2.3 Hz, 2H), 4.48 (q, *J* = 4.7 Hz, 1H), 4.61 (d, *J* = 4.8 Hz, 1H), 4.62 (d, *J* = 10.9 Hz, 1H), 4.53 – 4.71 (m, 1H), 4.74 (d, *J* = 5.3 Hz, 1H), 4.72 – 4.77 (m, 1H), 4.79 (d, *J* = 10.9 Hz, 1H), 4.84 (d, *J* = 10.9 Hz, 1H), 5.00 (d, *J* = 10.8 Hz, 1H), 5.08 (d, *J* = 3.6 Hz, 1H), 5.41 (s, 1H), 5.54 (d, *J* = 4.5 Hz, 1H), 5.60 (d, *J* = 0.9 Hz, 1H), 7.10 – 7.69 (m, 24H), 7.91 – 8.13 (m, 6H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 54.4, 63.7, 65.8, 70.4, 73.0, 74.8, 74.9, 75.0, 75.6, 77.5, 77.8, 78.8, 79.5, 81.7, 81.8, 95.0, 106.1, 127.4, 127.4, 127.5, 127.7, 127.8, 127.9, 127.9, 128.1, 128.1, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.9, 128.9, 129.6, 129.7, 129.7, 129.8, 129.8, 129.8, 133.0, 133.5, 133.5, 137.9, 138.1, 138.7, 165.2, 165.6, 166.1; HRMS (Waters Synapt G2) : m/z calcd for $[C_{56}H_{52}O_{13}+Na]^+$: 955.3306; Found: 955.3319.

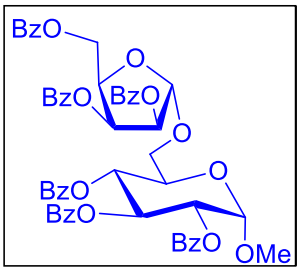


Propargyl 3,5-di-*O*-benzyl-2-*O*-(2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl)-α-D arabinofuranoside (**16j**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +22.3°; IR (cm^{-1}, $CHCl_3$): 3297, 3067, 2927, 1724, 1593, 1453, 1267, 1108, 706;

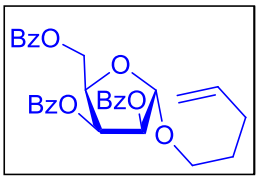


^{1}H NMR (399.78 MHz, $CDCl_3$): δ 2.32 (t, *J* = 2.4 Hz, 1H), 3.66 (dABq, *J* = 14.0, 10.7 Hz, 2H), 3.97 (dd, *J* = 6.4, 2.7 Hz, 1H), 4.20 – 4.26 (m, 1H), 4.28 (d, *J* = 2.4 Hz, 2H), 4.28 – 4.30 (m, 1H), 4.56 (ABq, *J* = 15.7 Hz, 2H), 4.58 – 4.65 (m, 1H), 4.62 (d, *J* = 13.3 Hz, 1H), 4.69 (dd, *J* = 11.7, 4.7 Hz, 2H), 4.78 (dd, *J* = 11.9, 3.8 Hz, 1H), 5.22 (s, 1H), 5.37 (s, 1H), 5.46 (d, *J* = 1.3 Hz, 1H), 5.59 (d, *J* = 4.0 Hz, 1H), 7.09 – 7.35 (m, 10H), 7.38 – 7.67 (m, 9H), 7.94 – 8.16 (m, 6H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 54.0, 63.6, 69.5, 72.4, 73.4, 74.5, 77.5, 79.0, 81.00, 81.4, 82.2, 83.2, 86.5, 104.7, 105.5, 127.6, 127.7, 127.7, 127.7, 127.9, 127.9, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.5, 128.5, 128.5, 128.5, 128.9, 129.0, 129.6, 129.7, 129.7, 129.9, 129.9, 129.9, 129.9, 133.1, 133.5, 133.6, 137.6, 137.9, 165.3, 165.6, 166.1; HRMS (Waters Synapt G2) : m/z calcd for $[C_{48}H_{44}O_{12}+Na]^+$: 835.2730; Found: 835.2722.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,5-tri-*O*-benzoyl-α-D-lyxofuranosyl)-α-D-gluco-pyranoside (**18a**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) +57.5°; IR (cm^{-1}, $CHCl_3$): 3073, 2927, 1729, 1594, 1453, 1271, 1104, 709; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 3.49 (s, 3H), 3.76 (dd, *J* = 11.1, 2.5 Hz, 1H), 4.03 (dd, *J* = 11.1, 4.3 Hz, 1H), 4.27 (ddd, *J* = 10.2, 4.1, 2.5 Hz, 1H), 4.54 (d, *J* = 6.1 Hz, 2H), 4.79 (q, *J* = 6.1 Hz, 1H), 5.27 (d, *J* = 3.7 Hz, 1H), 5.31 (dd, *J* = 9.9, 3.7 Hz, 1H), 5.37 (d, *J* = 0.3 Hz, 1H), 5.71 (dd, *J* = 5.4, 1.0 Hz, 1H), 5.74 (t, *J* = 10.0 Hz, 1H), 6.11 (t, *J* = 5.7 Hz, 1H), 6.16 (t, *J* = 9.8 Hz, 1H), 7.14 – 7.63 (m, 18H), 7.81 – 8.03 (m, 12H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 55.7, 63.2, 65.8, 68.3, 69.0, 70.6, 71.8, 72.1, 75.8, 76.1, 97.1, 104.5, 128.2, 128.2, 128.2, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.9, 129.0, 129.0, 129.1, 129.2, 129.6, 129.6, 129.6, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 129.9, 129.9, 133.0, 133.0, 133.3, 133.3, 133.3, 133.3, 165.0, 165.2, 165.2, 165.7, 165.8, 166.1; HRMS (Waters Synapt G2): m/z calcd for $[C_{54}H_{46}O_{16}+Na]^+$: 973.2684; Found: 973.2680.

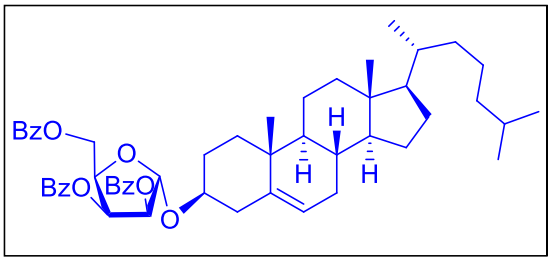


Pent-4-enyl 2,3,5–tri–*O*-benzoyl α-D-lyxofuranoside (**18b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 2.4) +11.9°; IR (cm^{-1}, $CHCl_3$): 3076, 2929, 1729, 1592, 1449, 1269, 1112, 707; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.72 (quintet, *J* = 6.7 Hz, 2H), 2.15 (q, *J* = 6.9 Hz, 2H), 3.53 (dt, *J* = 9.5, 6.4 Hz, 1H), 3.80 (dt, *J* = 9.5, 6.5 Hz, 1H), 4.58 – 4.69 (m, 2H), 4.82 (q, *J* = 6.2 Hz, 1H), 4.97 (dq, *J* = 10.1, 1.4 Hz, 1H), 5.04 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.31 (d, *J* = 1.0 Hz, 1H), 5.62 (dd, *J* = 5.2, 1.2 Hz, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz,

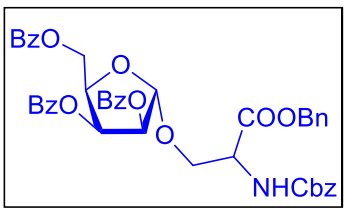


1H), 6.05 (t, *J* = 5.8 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 4H), 7.44 – 7.57 (m, 3H), 7.86 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.92 – 7.97 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.6, 30.2, 63.4, 67.6, 71.9, 75.5, 76.1, 104.7, 115.0, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.8, 129.0, 129.6, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 133.1, 133.4, 133.4, 137.9, 165.2, 165.3, 166.2; HRMS (Waters Synapt G2): m/z calcd for $[C_{31}H_{30}O_8+Na]^+$: 553.1838; Found: 553.1854.

Cholesteryl 2,3,5-tri-*O*-benzoyl-α-D-lyxofuranoside (**18d**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.4) +10.3°; IR (cm^{-1}, $CHCl_3$): 3072, 2938, 1730, 1599, 1460, 1263, 1103, 710; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 0.67 (s, 3H), 0.84 (d, *J* = 1.8 Hz, 3H), 0.86 (d, *J* = 1.8 Hz, 3H), 0.90 (d, *J* = 6.5 Hz, 3H), 1.01 (s, 3H), 0.97 – 2.10 (m, 26H), 2.30 – 2.44 (m, 2H), 3.57 (dt, *J* = 11.1, 6.2 Hz, 1H), 4.61 (dd, *J* = 11.3, 5.5 Hz, 1H), 4.65 (dd, *J* = 11.2, 6.2 Hz, 1H), 4.85 (q, *J* = 6.2 Hz, 1H), 5.34 (d, *J* = 5.2 Hz, 1H), 5.46 (d, *J* = 0.7 Hz, 1H), 5.59 (dd, *J* = 5.2, 1.1 Hz, 1H), 6.06 (t, *J* = 6.0 Hz, 1H), 7.25 – 7.39 (m, 6H), 7.42 – 7.58 (m, 3H), 7.86 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.95 (ddd, *J* = 8.0, 6.4, 1.3 Hz, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 11.8, 18.7, 19.4, 21.0, 22.6, 22.8, 23.8, 24.3, 27.9, 28.0, 28.2, 31.8, 31.9, 35.8, 36.1, 36.7, 37.0, 39.5, 39.7, 40.1, 42.3, 50.1, 56.1, 56.7, 63.4, 71.9, 75.3, 76.4, 77.7, 103.0, 121.9, 128.3, 128.3, 128.3, 128.3, 128.5, 128.5, 128.8, 129.1, 129.6, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 133.0, 133.4, 133.4, 140.5, 165.3, 165.3, 166.2; HRMS (Waters Synapt G2): m/z calcd for $[C_{53}H_{66}O_8+Na]^+$: 853.4655; Found: 853.4664.

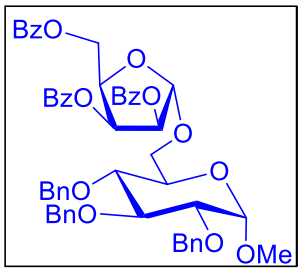


Benzyl-*N*-(benzyloxycarbonyl)-*O*-(2,3,5-tri-*O*-benzoyl-α-D-lyxofuranosyl)-L-serinate (**18e**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.4) +1.9°; IR (cm^{-1}, $CHCl_3$): 3434, 3368, 3067, 2924, 1727, 1594, 1454, 1267, 1111, 707; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 3.99 (d, *J* = 8.9 Hz, 1H), 4.15 (dd, *J* = 10.5, 2.8 Hz, 1H), 4.52 – 4.65 (m, 3H), 4.70 (q, *J* = 5.7 Hz, 1H), 5.03 (d, *J* = 12.3 Hz, 1H), 5.10 (d, *J* = 12.1 Hz, 1H), 5.20 (s, 2H), 5.25 (q, *J* = 12.1 Hz, 1H), 5.49 (d, *J* = 5.2 Hz, 1H), 5.87 (t, *J* = 5.5 Hz, 1H), 5.97 (d, *J* = 8.7 Hz, 1H), 7.21 – 7.39 (m, 17H), 7.51 (dt, *J* = 13.6, 7.4 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.98 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 54.5, 63.1, 67.0, 67.5, 69.6, 71.5, 75.9, 76.1, 105.5, 128.0,

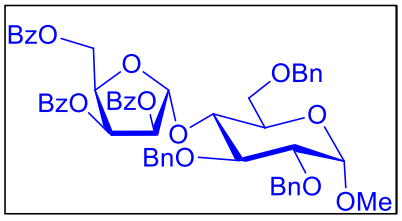


128.0, 128.1, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.6, 128.6, 128.7, 128.8, 129.5, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 133.1, 133.5, 133.5, 135.2, 136.2, 156.0, 165.0, 165.1, 166.1, 169.7; HRMS (Waters Synapt G2): m/z calcd for $[C_{44}H_{39}O_{12}+Na]^+$: 796.2370; Found: 796.2372.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-α-D-lyxofuranosyl)-α-D-gluco-pyranoside (**18f**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) +33.3°; IR (cm^{-1}, $CHCl_3$): 3072, 2924, 1729, 1595, 1456, 1268, 1100, 709; ^1H NMR (399.78 MHz, $CDCl_3$): δ 3.37 (s, 3H), 3.57 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.61 (d, *J* = 9.5 Hz, 1H), 3.72 – 3.85 (m, 2H), 4.01 (t, *J* = 9.3 Hz, 1H), 4.06 (dd, *J* = 11.3, 3.9 Hz, 1H), 4.53 – 4.70 (m, 5H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.79 (q, *J* = 6.0 Hz, 1H), 4.83 (d, *J* = 10.9 Hz, 1H), 4.94 (d, *J* = 10.8 Hz, 1H), 5.00 (d, *J* = 10.9 Hz, 1H), 5.43 (s, 1H), 5.69 (dd, *J* = 5.2, 1.3 Hz, 1H), 6.03 (t, *J* = 5.8 Hz, 1H), 7.19 – 7.43 (m, 21H), 7.44 – 7.61 (m, 3H), 7.82 – 7.88 (m, 2H), 7.89 – 7.92 (m, 2H), 7.93 – 7.98 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 55.2, 63.4, 66.5, 69.8, 71.7, 73.4, 75.1, 75.7, 75.9, 77.5, 75.7, 80.0, 82.0, 98.0, 105.0, 127.5, 127.7, 127.8. 127.8, 127.9, 127.9, 127.9, 128.1, 128.1, 128.2, 128.2, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.7, 129.0, 129.5, 129.6, 129.6, 129.7, 129.7, 129.7, 129.7, 133.0, 133.4, 133.4, 138.1, 138.1, 138.7, 165.0, 165.2, 166.1; HRMS (Waters Synapt G2): m/z calcd for $[C_{54}H_{52}O_{13}+Na]^+$: 931.3306; Found: 931.3314.

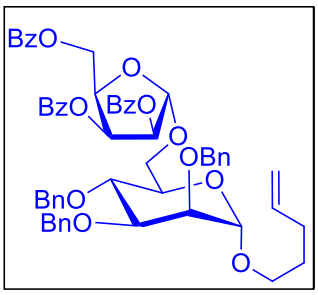


Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,5-tri-*O*-benzoyl-α-D-lyxofuranosyl)-α-D-gluco-pyranoside (**18g**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) +24.0°; IR (cm^{-1}, $CHCl_3$): 3065, 2923, 1729, 1595, 1454, 1269, 1104, 706; ^1H NMR (399.78 MHz, $CDCl_3$): δ 3.41 (s, 3H), 3.52 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.58 – 3.68 (m, 1H), 3.73 (d, *J* = 10.8 Hz, 1H), 3.78 (d, *J* = 5.4 Hz, 2H), 3.79 (s, 1H), 3.94 – 4.00 (m, 1H), 4.44 – 4.51 (m, 4H), 4.61 (d, *J* = 3.5 Hz, 1H), 4.62 (t, *J* = 12.5 Hz, 1H), 4.70 (d, *J* = 11.0 Hz, 1H), 4.73 (d, *J* = 12.1 Hz, 1H), 4.94 (d, *J* = 10.9 Hz, 1H), 5.60 (dd, *J* = 5.1, 1.5 Hz, 1H), 5.79 (d, *J* = 1.4 Hz, 1H), 5.87 (t, *J* = 5.2 Hz, 1H), 7.03 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.14 – 7.39 (m, 18H), 7.41 – 7.59 (m, 3H), 7.73 – 7.84 (m, 4H), 7.87 – 7.95 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 55.3, 63.3, 68.9, 69.4, 71.7, 73.2, 73.3, 75.1, 75.5, 75.7, 76.1, 79.8, 81.5, 97.8, 105.6, 127.3, 127.5, 127.6, 127.7, 127.7, 127.9, 128.1, 128.1, 128.1, 128.1, 128.1, 128.2, 128.3, 128.3, 128.3, 128.3, 128.3,

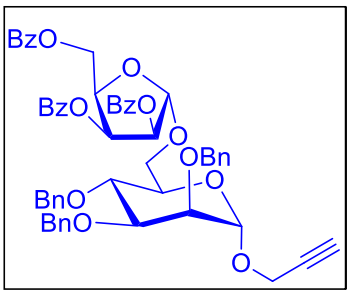


128.4, 128.4, 128.4, 128.4, 128.7, 128.8, 129.5, 129.6, 129.6, 129.7, 129.7, 129.7, 129.7, 133.0, 133.3, 133.4, 137.9, 138.0, 138.3, 165.0, 165.1, 166.0; HRMS (Waters Synapt G2): m/z calcd for $[C_{54}H_{52}O_{13}+Na]^+$: 931.3306; Found: 931.3315.

Pent-4-enyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-α-D-lyxofuranosyl)-α-D-mannopyranoside (**18h**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) +23.6°; IR (cm^{-1}, $CHCl_3$): 3079, 2925, 1728, 1592, 1456, 1263, 1103, 714; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.61 (quintet, *J* = 7.9 Hz, 2H), 2.05 (q, *J* = 7.6 Hz, 2H), 3.35 (dt, *J* = 9.7, 6.4 Hz, 1H), 3.66 (dt, *J* = 9.7, 6.6 Hz, 1H), 3.72 – 3.79 (m, 2H), 3.85 (dd, *J* = 11.1, 1.7 Hz, 1H), 3.91 (dd, *J* = 9.3, 2.9 Hz, 1H), 3.98 (t, *J* = 9.4 Hz, 1H), 4.09 (dd, *J* = 11.1, 5.0 Hz, 1H), 4.55 (dd, *J* = 11.6, 5.4 Hz, 1H), 4.60 (d, *J* = 6.7 Hz, 1H), 4.63 (s, 2H), 4.67 (d, *J* = 10.8 Hz, 1H), 4.71 (d, *J* = 3.8 Hz, 2H), 4.77 – 4.85 (m, 2H), 4.91 – 5.01 (m, 3H), 5.48 (s, 1H), 5.69 – 5.82 (m, 2H), 6.04 (t, *J* = 6.1 Hz, 1H), 7.20 – 7.41 (m, 20H), 7.42 – 7.59 (m, 4H), 7.80 – 7.87 (m, 2H), 7.93 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.96 (dd, *J* = 8.2, 1.2 Hz, 2H): ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.5, 30.2, 63.5, 67.0, 67.0, 71.3, 71.8, 72.0, 72.5, 74.5, 74.8, 75.2, 75.6, 76.0, 80.2, 97.8, 104.7, 114.9, 127.5, 127.6, 127.6, 127.6, 127.7, 127.8, 127.8, 128.0, 128.0, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.8, 129.1, 129.6, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 133.0, 133.3, 133.3, 138.0, 138.3, 138.4, 138.5, 165.1, 165.2, 166.2; HRMS (Waters Synapt G2): m/z calcd for $[C_{58}H_{58}O_{13}+Na]^+$: 985.3775; Found: 985.3776.

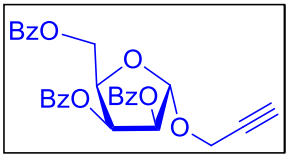


Prop-2-ynyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-α-D-lyxofuranosyl)-α-D-glucopyranoside (**18i**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.9) +41.4°; IR (cm^{-1}, $CHCl_3$): 3293, 3062, 2925, 1728, 1595, 1453, 1268, 1102, 705; ^1H NMR (399.78 MHz, $CDCl_3$): δ 2.42 (t, *J* = 2.3 Hz, 1H), 3.54 – 3.69 (m, 2H), 3.74 – 3.85 (m, 2H), 4.00 (t, *J* = 9.3 Hz, 1H), 4.05 (dd, *J* = 11.2, 3.6 Hz, 1H), 4.26 (ddd, *J* = 18.5, 15.9, 2.3 Hz, 2H), 4.56 (dd, *J* = 11.5, 5.5 Hz, 1H), 4.61 (dd, *J* = 11.6, 6.7 Hz, 1H), 4.66 (d, *J* = 10.7 Hz, 1H), 4.71 (d, *J* = 10.0 Hz, 2H), 4.77 (dd, *J* = 12.0, 6.2 Hz, 1H), 4.82 (d, *J* = 10.9 Hz, 1H), 4.93 (d, *J* = 10.7 Hz, 1H), 5.00 (d, *J* = 10.9 Hz, 1H), 5.04 (d, *J* = 3.6 Hz, 1H), 5.41 (d, *J* = 0.9 Hz, 1H), 5.67 (dd, *J* = 5.3, 1.1 Hz, 1H), 6.02 (t, *J* = 5.6 Hz, 1H), 7.19 – 7.42 (m, 21H), 7.43 – 7.58 (m, 3H), 7.84 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.90 (dd, *J* = 8.3, 1.1 Hz,

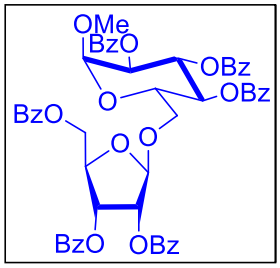


2H), 7.94 (dd, *J* = 8.0, 1.0 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 54.5, 63.4, 70.5, 71.7, 73.1, 74.8, 74.8, 75.2, 75.7, 75.8, 75.9, 78.9, 79.5, 81.8, 95.2, 105.0, 127.6, 127.8, 127.8, 127.9, 127.9, 127.9, 127.9, 128.2, 128.2, 128.2, 128.2, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.7, 129.0, 129.5, 129.6, 129.6, 129.7, 129.7, 129.7, 129.7, 133.0, 133.4, 133.4, 137.9, 138.1, 138.7, 165.1, 165.2, 166.1; HRMS (Waters Synapt G2): m/z calcd for $[C_{56}H_{52}O_{13}+Na]^+$: 955.3306; Found: 955.3326.

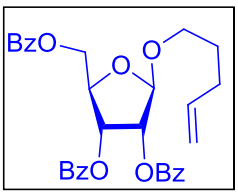
Prop-2-ynyl 2,3,5-tri-*O*-benzoyl-α-D-lyxofuranoside: $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +16.7°; IR (cm^{-1}, $CHCl_3$): 3294, 2925, 1726, 1595, 1453, 1268, 1112, 700; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 2.46 (t, *J* = 2.4 Hz, 1H), 4.35 (t, *J* = 2.3 Hz, 2H), δ 4.61 (dd, *J* = 11.6, 5.6 Hz, 1H), 4.67 (dd, *J* = 11.6, 6.6 Hz, 1H), 4.84 (q, *J* = 6.2 Hz, 1H), 5.53 (d, *J* = 1.1 Hz, 1H), 5.68 (dd, *J* = 5.4, 1.2 Hz, 1H), 6.06 (t, *J* = 5.7 Hz, 1H), 7.25 – 7.62 (m, 9H), 7.85 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.91 – 8.02 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 54.8, 63.2, 71.7, 75.1, 76.1, 76.1, 78.5, 103.0, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.7, 128.9, 129.5, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 133.1, 133.5, 133.5, 165.2, 166.2, 169.2; HRMS (Waters Synapt G2): m/z calcd for $[C_{29}H_{24}O_8+Na]^+$: 523.1369; Found: 523.1371.



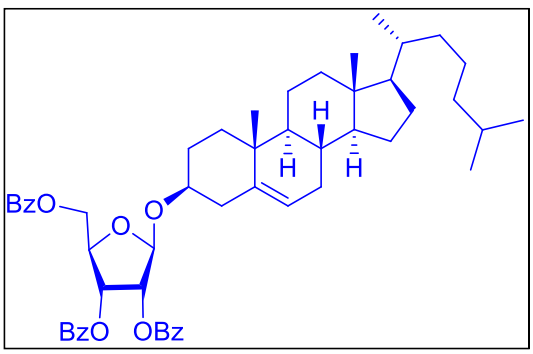
Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-α-D-glucopyra-noside (**19a**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.9): +52.8°; IR (cm^{-1}, $CHCl_3$): 3062, 2944, 1727, 1588, 1449, 1274, 1103, 710; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 3.47 (s, 3H), 3.74 (dd, *J* = 11.6, 6.7 Hz, 1H), 3.96 (dd, *J* = 11.5, 2.2 Hz, 1H), 4.24 (ddd, *J* = 9.2, 6.6, 2.0 Hz, 1H), 4.46 – 4.57 (m, 1H), 4.65 – 4.72 (m, 2H), 5.22 (t, *J* = 3.9 Hz, 1H), 5.25 (dd, *J* = 9.9, 3.6 Hz, 1H), 5.36 (s, 1H), 5.50 (t, *J* = 9.9 Hz, 1H), 5.75 (d, *J* = 4.9 Hz, 1H), 5.86 (dd, *J* = 6.9, 4.9 Hz, 1H), 6.12 (t, *J* = 9.7 Hz, 1H), 7.22 – 7.64 (m, 18H), 7.87 (ddd, *J* = 8.6, 7.4, 1.2 Hz, 6H), 7.96 – 8.04 (m, 6H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 55.6, 64.7, 66.9, 68.9, 69.5, 70.4, 72.1, 72.2, 75.4, 79.1, 96.7, 106.1, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.8, 128.9, 129.0, 129.2, 129.6, 129.6, 129.6, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 129.8, 129.8, 129.9, 129.9, 133.0, 133.1, 133.3, 133.3, 133.3, 133.4, 165.1, 165.3, 165.3, 165.7, 165.7, 166.1; HRMS (Waters Synapt G2): m/z calcd for $[C_{54}H_{46}O_{16}+Na]^+$: 973.2684; Found: 973.2690.



(Pent-4-enyl) 2,3,5-tri-*O*-benzoyl-β-D-ribofuranoside (**19b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1): +41.0°; IR (cm^{-1}, $CHCl_3$): 3070, 2927, 1728, 1596, 1450, 1269, 1113, 709; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.63 (tq, *J* = 13.8, 6.9, 6.3 Hz, 2H), 2.08 (q, *J* = 7.1 Hz, 2H), 3.45 (dt, *J* = 9.4, 6.8 Hz, 1H), 3.78 (dt, *J* = 9.3, 6.5 Hz, 1H), 4.51 (dd, *J* = 12.9, 6.6 Hz, 1H), 4.69-4.74 (m, 2H), 4.91 – 4.97 (m, 1H), 4.97 – 5.04 (m, 1H), 5.24 (s, 1H), 5.68 (d, *J* = 4.7 Hz, 1H), 5.75 (ddt, *J* = 16.8, 10.3, 6.6 Hz, 1H), 5.87 (dd, *J* = 6.4, 5.0 Hz, 1H), 7.29 – 7.43 (m, 6H), 7.48 – 7.58 (m, 3H), 7.87 – 7.89 (m, 2H), 8.00-8.07 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.5, 30.1, 64.9, 67.8, 72.5, 75.5, 78.7, 105.5, 115.0, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.9, 129.2, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 133.1, 133.3, 133.4, 137.8, 165.2, 165.4, 166.1; HRMS (Waters Synapt G2): m/z calcd for $[C_{31}H_{30}O_8+Na]^+$: 553.1838; Found: 553.1836.



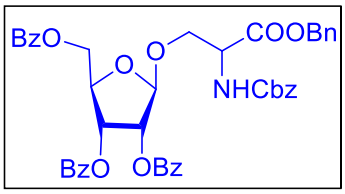
Benzyl 2,3,5-tri-*O*-benzoyl-β-D-ribofuranoside (**19c**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0): +12.1°; IR (cm^{-1}, $CHCl_3$):): 3068, 2930, 1727, 1595, 1453, 1268, 1112, 706; ^1H NMR (399.78 MHz, $CDCl_3$): δ 4.53 – 4.59 (m, 1H), 4.59 (d, *J* = 11.8 Hz, 1H), 4.74 (dd, *J* = 15.3, 3.5 Hz 1H), 4.75-4.78(m, 1H), 4.82 (d, *J* = 11.8 Hz, 1H), 5.35 (s, 1H), 5.78 (d, *J* = 4.8 Hz, 1H), 5.94 (dd, *J* = 7.0, 4.8 Hz, 1H), 7.26 – 7.35 (m, 10H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.88 (d, *J* = 7.3 Hz, 2H), 8.03 (dd, *J* = 12.3, 7.3 Hz, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 64.6, 69.6, 72.3, 75.6, 79.0, 104.4, 127.8, 127.9, 127.9, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.8, 129.1, 129.5, 129.6, 129.7, 129.7, 129.7, 129.7, 129.7, 133.0, 133.3, 133.4, 136.7, 165.2, 165.3, 166.2; HRMS (Waters Synapt G2): m/z calcd for $[C_{33}H_{28}O_8+Na]^+$: 575.1682; Found: 575.1697.



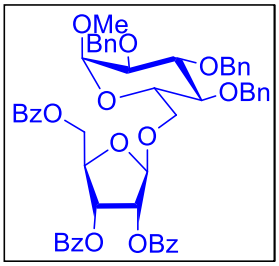
Cholesteryl 2,3,5-tri-*O*-benzoyl-β-D-ribofuranoside (**19d**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.3): –1.5°; IR (cm^{-1}, $CHCl_3$): 3071, 2942, 1729, 1591, 1455, 1269, 1111, 709; ^1H NMR (399.78 MHz, $CDCl_3$): δ 0.66 (s, 3H), 0.85 (dd, *J* = 6.6, 1.5 Hz, 6H), 0.88 – 1.66 (m, 25H), 1.73 – 2.03 (m, 6H), 2.21 (t, *J* = 11.1 Hz, 1H), 2.38 (ddd, *J* = 13.0, 4.5, 1.9 Hz, 1H), 3.55 (dq, *J* = 11.1, 5.6, 4.4 Hz, 2H), 4.52 (q, *J* = 13, 6.8 Hz 1H), 4.64 – 4.74 (m, 2H), 5.33 (d, *J* = 5.1 Hz, 1H), 5.41 (s, 1H), 5.63 (d, *J* = 4.8 Hz, 1H), 5.88

(dd, *J* = 6.4, 4.9 Hz, 1H), 7.27 – 7.45 (m, 6H), 7.45 – 7.61 (m, 3H), 7.88 (d, *J* = 7.6 Hz, 2H), 8.03 (dd, *J* = 15.8, 7.5 Hz, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 12.0, 18.8, 19.4, 21.1, 22.7, 22.9, 23.9, 24.4, 28.1, 28.3, 29.6, 31.9, 32.0, 35.9, 36.3, 36.8, 37.2, 38.6, 39.6, 39.9, 42.4, 50.2, 56.2, 56.8, 65.2, 72.8, 76.2, 78.1, 78.6, 103.9, 122.1, 128.4, 128.4, 128.4, 128.4, 128.6, 128.6, 129.1, 129.4, 129.8, 129.8, 129.8, 129.9, 129.9, 129.9, 129.9, 133.2, 133.4, 133.5, 140.4, 165.4, 165.5, 166.3; HRMS (Waters Synapt G2): m/z calcd for $[C_{53}H_{66}O_8+Na]^+$: 853.4655; Found: 853.4664.

Benzyl-*N*-(benzyloxycarbonyl)-*O*-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-L-serinate (**19e**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.3): +12.1°; IR (cm^{-1}, $CHCl_3$): 3371, 3061, 2947, 1725, 1596, 1504, 1453, 1267, 1114, 703; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 3.82 (dd, *J* = 10.1, 3.2 Hz, 1H), 4.30 (dd, *J* = 10.1, 3.2 Hz, 1H), 4.44 (qd, *J* = 11.6, 5.7 Hz, 2H), 4.57 – 4.73 (m, 2H), 5.12 (s, 2H), 5.23 (ABq, *J* = 12.23 Hz, 2H), 5.25 (s, 1H), 5.59 (t, *J* = 5.20 Hz, 1H), 5.64 (d, *J* = 5.0 Hz, 1H), 5.79 (d, *J* = 8.6 Hz, 1H), 7.23 – 7.43 (m, 16H), 7.46 – 7.53 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.88 (d, *J* = 7.3 Hz, 2H), 7.97 (d, *J* = 7.5 Hz, 2H), 8.01 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 54.2, 65.5, 67.1, 67.6, 68.4, 72.7, 75.3, 79.3, 106.0, 128.0, 128.0, 128.1, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.6, 128.6, 128.8, 129.0, 129.5, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 133.1, 133.4, 133.5, 135.1, 136.1, 155.9, 165.1, 165.2, 166.0, 169.6; HRMS (Waters Synapt G2): m/z calcd for $[C_{44}H_{39}O_{12}N+Na]^+$: 796.2370; Found: 796.2360.

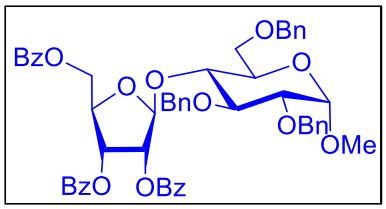


Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-α-D-gluco-pyranoside (**19f**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.9): +50.5°; IR (cm^{-1}, $CHCl_3$): 3022, 2940, 1728, 1602, 1453, 1270, 1106, 761; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 3.32 (s, 3H), 3.51 (t, *J* = 9.3 Hz, 1H), 3.56 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.61 (dd, *J* = 10.8, 4.7 Hz, 1H), 3.72 (dd, *J* = 10.0, 4.2 Hz, 1H), 3.97 (t, *J* = 11.0 Hz, 2H), 4.54 (dd, *J* = 11.5, 6.0 Hz, 1H), 4.58 (s, 1H), 4.60 (d, *J* = 7.3 Hz, 1H), 4.62 – 4.72 (m, 3H), 4.80 (dd, *J* = 11.3, 9.3 Hz, 2H), 4.87 (d, *J* = 11.2 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 5.14 (s, 1H), 5.63 (d, *J* = 4.9 Hz, 1H), 5.82 (t, *J* = 5.6 Hz, 1H), 7.15 – 7.60 (m, 24H), 7.82 – 7.89 (m, 2H), 7.96 – 8.05 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 55.3, 65.4, 66.7, 69.8, 72.8, 73.5, 75.0, 75.5, 75.8, 77.4, 79.1, 80.2, 82.2, 97.9, 105.9, 127.6, 127.8, 128.0, 128.0, 128.0, 128.0, 128.0, 128.2, 128.2, 128.4,

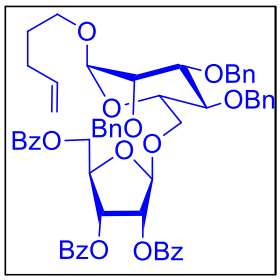


128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.6, 128.6, 128.6, 128.6, 129.0, 129.1, 129.3, 129.8, 129.8, 129.8, 129.9, 129.9, 129.9, 133.2, 133.5, 133.6, 138.3, 138.4, 138.9, 165.2, 165.4, 166.3; HRMS (Waters Synapt G2): m/z calcd for $[C_{54}H_{52}O_{13}+Na]^+$: 931.3306; Found: 931.3313.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-α-D-gluco-pyranoside (**19g**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1): +34.2°; IR (cm^{-1}, $CHCl_3$): 3072, 2923, 1728, 1602, 1453, 1268, 1106, 700; ^1H NMR (399.78 MHz, $CDCl_3$): δ 3.35 (s, 3H), 3.52 (dd, *J* = 9.2, 3.5 Hz, 1H), 3.62 – 3.71 (m, 2H), 3.79 (dd, *J* = 10.9, 3.6 Hz, 1H), 3.85 – 3.99 (m, 2H), 4.43 – 4.52 (m, 1H), 4.55 (d, *J* = 5.9 Hz, 2H), 4.57 (d, *J* = 5.4 Hz, 1H), 4.60 (d, *J* = 6.2 Hz, 2H), 4.56 – 4.64 (m, 1H), 4.75 (d, *J* = 12.2 Hz, 1H), 4.88 (d, *J* = 10.5 Hz, 1H), 5.00 (d, *J* = 10.5 Hz, 1H), 5.59 (dd, *J* = 4.8, 1.9 Hz, 1H), 5.64 (d, *J* = 1.9 Hz, 1H), 5.75 (t, *J* = 5.4 Hz, 1H), 7.09 – 7.45 (m, 21H), 7.47 – 7.62 (m, 3H), 7.87 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.93 (dd, *J* = 8.2, 1.1 Hz, 2H), 8.02 (dd, *J* = 8.2, 1.2 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 55.3, 64.6, 68.4, 69.4, 72.0, 73.3, 73.4, 75.3, 75.4, 77.2, 78.6, 79.7, 80.6, 98.1, 106.7, 127.3, 127.4, 127.5, 127.5, 127.9, 127.9, 127.9, 128.1, 128.1, 128.2, 128.2, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.9, 129.1, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7. 129.7. 133.0, 133.4, 133.4, 137.9, 138.0, 138.8, 165.1, 165.3, 166.0; HRMS (Waters Synapt G2): m/z calcd for $[C_{54}H_{52}O_{13}+Na]^+$: 931.3306; Found: 931.3286.

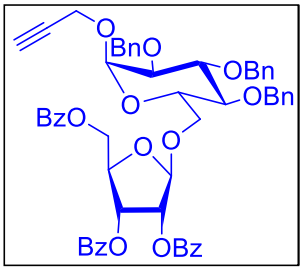


(Pent-4-enyl) 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-α-D-manno-pyranoside (**19h**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.3): +35.2°; IR (cm^{-1}, $CHCl_3$): 3072, 2926, 1728, 1599, 1453, 1268, 1109, 705; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.59 (quintet, *J* = 6.9 Hz, 2H), 2.04 (q, *J* = 7.0 Hz, 2H), 3.31 (dt, *J* = 9.7, 6.4 Hz, 1H), 3.62 (dt, *J* = 9.7, 6.6 Hz, 1H), 3.68 – 3.79 (m, 3H), 3.82 – 3.93 (m, 2H), 4.03 (d, *J* = 9.1 Hz, 1H), 4.62 (s, 2H), 4.57 – 4.72 (m, 5H), 4.74 (s, 1H), 4.81 (d, *J* = 1.5 Hz, 1H), 4.91 (s, 1H), 4.92 – 5.01 (m, 2H), 5.32 (s, 1H), 5.70 (d, *J* = 4.9 Hz, 1H), 5.72 – 5.84 (m, 2H), 7.09 – 7.67 (m, 24H), 7.86 (d, *J* = 7.4 Hz, 2H), 7.97 – 8.09 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.5, 30.2, 65.7, 66.9, 67.1, 71.5, 72.0, 72.4, 72.9, 74.5, 74.7, 75.0, 75.4, 79.0, 80.2, 97.6, 105.7, 114.8, 127.5, 127.5, 127.6, 127.6, 127.6, 127.8, 127.8, 128.0, 128.0, 128.3, 128.3, 128.3,

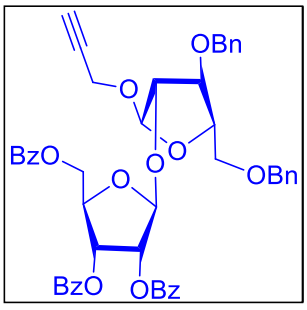


128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 129.0, 129.3, 129.7, 129.7, 129.8, 129.8, 132.9, 132.9, 133.2, 133.4, 138.1, 138.3, 138.4, 138.5, 165.1, 165.2, 166.2; HRMS (Waters Synapt G2): m/z calcd for $[C_{58}H_{58}O_{13}+Na]^+$: 985.3775; Found: 985.3776.

(Prop-2-ynyl) 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-α-D-glucopyranoside (**19i**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1): +70.0°; IR (cm^{-1}, $CHCl_3$): 3293, 3072, 2927, 1727, 1595, 1453, 1268, 1107, 706; ^1H NMR (399.78 MHz, $CDCl_3$): δ 2.42 (t, *J* = 2.1 Hz, 1H), 3.55 (t, *J* = 9.5 Hz, 1H), 3.62 (td, *J* = 10.1, 9.3, 4.1 Hz, 2H), 3.80 (dd, *J* = 10.2, 3.5 Hz, 1H), 3.95 (d, *J* = 9.4 Hz, 1H), 4.00 (t, *J* = 9.3 Hz, 1H), 4.24 (d, *J* = 2.0 Hz, 2H), 4.55 (dd, *J* = 11.6, 5.9 Hz, 1H), 4.61 (d, *J* = 11.3 Hz, 1H), 4.63 – 4.73 (m, 2H), 4.75 (d, *J* = 3.2 Hz, 2H), 4.81 (d, *J* = 10.9 Hz, 1H), 4.89 (d, *J* = 11.2 Hz, 1H), 5.01 (d, *J* = 10.9 Hz, 1H), 5.04 (d, *J* = 3.6 Hz, 1H), 5.15 (s, 1H), 5.64 (d, *J* = 4.9 Hz, 1H), 5.82 (t, *J* = 5.5 Hz, 1H), 7.14 – 7.46 (m, 20H), 7.44 – 7.54 (m, 3H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 2H), 8.00 (d, *J* = 7.8 Hz, 2H), 8.04 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 54.6, 65.2, 66.3, 70.4, 72.6, 73.0, 74.7, 74.9, 75.3, 75.6, 77.2, 79.0, 79.0, 79.6, 81.9, 95.1, 105.7, 127.5, 127.6, 127.8, 127.9, 127.9, 127.9, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.9, 129.1, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 133.0, 133.3, 133.4, 137.9, 138.2, 138.7, 165.1, 165.3, 166.1; HRMS (Waters Synapt G2): m/z calcd for $[C_{56}H_{52}O_{13}+Na]^+$: 955.3306; Found: 955.3303.

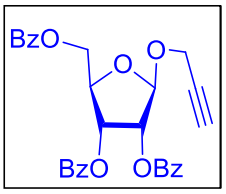


(Prop-2-ynyl) 3,5-di-*O*-benzyl-2-*O*-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-α-D-arabinofuranoside (**19j**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.8): +31.7°; IR (cm^{-1}, $CHCl_3$): ^1H NMR (399.78 MHz, $CDCl_3$): δ 2.30 (t, *J* = 2.3 Hz, 1H), 3.54 (dd, *J* = 10.7, 5.6 Hz, 1H), 3.57 (dd, *J* = 10.8, 4.0 Hz, 1H), 4.07 (dd, *J* = 6.4, 2.7 Hz, 1H), 4.22 – 4.27 (m, 1H), 4.28 (dd, *J* = 2.3, 1.4 Hz, 2H), 4.49 (s, 2H), 4.53 (ABq, *J* = 11.8 Hz, 2H), 4.62 (dd, *J* = 6.1, 4.1 Hz, 2H), 4.78 (d, *J* = 11.8 Hz, 1H), 4.96 (q, *J* = 5.5 Hz, 1H), 5.38 (d, *J* = 17.6 Hz, 2H), 5.57 (s, 1H), 5.83 (dd, *J* = 5.4, 1.7 Hz, 1H), 7.16 – 7.72 (m, 19H), 7.98 (ddd, *J* = 8.3, 2.8, 1.2 Hz, 4H), 8.06 (dd, *J* = 8.3, 1.3 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 54.1, 69.5, 72.4, 72.5, 73.4, 74.7, 75.6, 76.9, 77.1, 79.2, 81.7, 83.8, 86.9, 104.2, 105.4, 127.7,

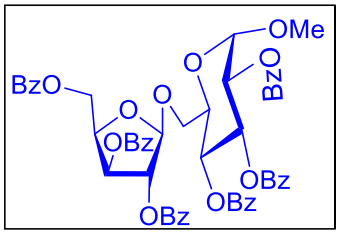


127.7, 127.7, 127.7, 127.7, 127.8, 127.8, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, , 129.7, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 133.2, 133.4, 133.5, 137.6, 137.9, 138.1, 165.1, 165.3, 166.0; HRMS (Waters Synapt G2): m/z calcd for $[C_{48}H_{44}O_{12}+Na]^+$: 835.2730; Found: 835.2735.

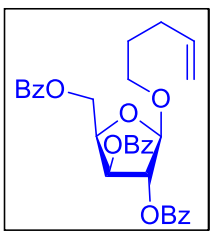
(Prop-2-ynyl) 2,3,5-tri-*O*-benzoyl-β-D-ribofuranoside: $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0): +82.9°; IR (cm^{-1}, $CHCl_3$): 3392, 3065, 2924, 1722, 1595, 1453, 1270, 1117, 703; ^1H NMR (399.78 MHz, $CDCl_3$): δ 2.45 (t, *J* = 2.4 Hz, 1H), 4.40 (dABq, *J* = 16.1, 2.2 Hz, 2H), 4.58 (dd, *J* = 11.6, 5.6 Hz, 1H), 4.67 (dd, *J* = 11.6, 6.9 Hz, 1H), 5.00 (q, *J* = 6.1 Hz, 1H), 5.46 (s, 1H), 5.9 (d, *J* = 0.7 Hz 1H), 5.87 (dd, *J* = 5.9, 1.2 Hz, 1H), 7.37-7.48 (m, 6H), 7.48 – 7.65 (m, 3H), 7.97-7.99 (m, 2H), 8.02 – 8.07 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 54.5, 64.4, 72.0, 75.3, 75.5, 78.2, 79.3, 103.3, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.8, 129.1, 129.6, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 133.2, 133.4, 133.5, 165.1, 165.3, 166.2; HRMS (Waters Synapt G2): m/z calcd for $[C_{29}H_{24}O_8+Na]^+$: 523.1369; Found: 523.1365.



Methyl 2,3,4–tri–*O*-benzoyl–6–*O*-(2,3,5-tri–*O*-benzoyl-β-D-xylofuranosyl)-α-D-glucopyranoside (**20a**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.3) +33.3°; IR (cm^{-1}, $CHCl_3$): 3074, 2929, 1727, 1596, 1457, 1268, 1105, 709; ^1H NMR (399.78 MHz, $CDCl_3$): δ 3.39 (s, 3H), 3.79 (dd, *J* = 11.0, 5.6 Hz, 1H), 4.07 (d, *J* = 11.3 Hz, 1H), 4.25-4.32 (m, 1H), 4.55 – 4.71 (m, 2H), 4.95 (q, *J* = 5.4 Hz, 1H), 5.22 (d, *J* = 9.5 Hz, 1H), 5.25 (s, 1H), 5.32 (s, 1H), 5.60 (d, *J* = 10.0 Hz, 1H), 5.63 (s, 1H), 5.87 (d, *J* = 5.2 Hz, 1H), 6.16 (t, *J* = 9.4 Hz, 1H), 7.18 – 7.68 (m, 18H), 7.85 (d, *J* = 7.5 Hz, 2H), 7.93 (t, *J* = 7.5 Hz, 4H), 7.99 (d, *J* = 7.5 Hz, 2H), 8.04 (d, *J* = 7.5 Hz, 2H), 8.11 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 55.5, 63.5, 66.6, 68.9, 69.3, 70.5, 72.2, 75.2, 79.0, 81.0, 96.8, 106.5, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.6, 128.6, 128.9, 129.0, 129.1, 129.2, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.8, 129.8, 129.9, 129.9, 129.9, 129.9, 130.0, 130.0, 133.0, 133.0, 133.3, 133.3, 133.5, 133.6, 164.8, 165.2, 165.3, 165.7, 165.8, 166.0; HRMS (Waters Synapt G2): m/z calcd for $[C_{54}H_{46}O_{16}+Na]^+$: 973.2684; Found: 973.2707.

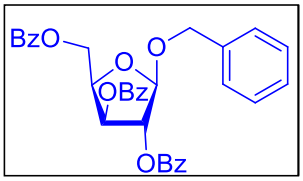


Pent-4-enyl 2,3,5-tri-*O*-benzoyl-β-D-xylofuranoside (**20b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +14.2°; IR (cm^{-1}, $CHCl_3$): 3074, 2927, 1725, 1594, 1453, 1262, 1108, 706; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.75 (quitent, *J* = 6.7

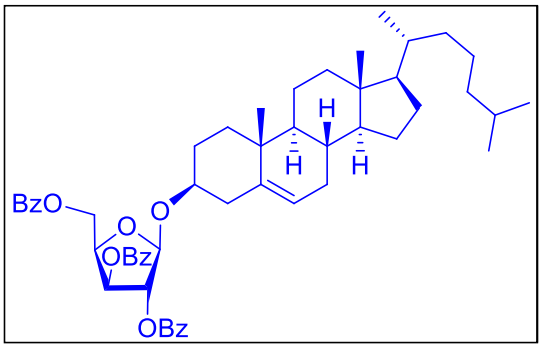


Hz, 2H), 2.18 (q, *J* = 7.1 Hz, 2H), 3.54 (dt, *J* = 9.3, 6.4 Hz, 1H), 3.87 (dt, *J* = 9.3, 6.5 Hz, 1H), 4.64 (dABq, *J* = 11.4, 6.3 Hz, 2H), 4.93 – 4.99 (m, 2H), 4.97 (s, 1H), 5.24 (s, 1H), 5.64 (d, *J* = 0.8 Hz, 1H), 5.81 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 5.87 (dd, *J* = 5.8, 1.4 Hz, 1H), 7.34 – 7.69 (m, 9H), 7.96 – 8.02 (m, 2H), 8.03 – 8.09 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.7, 30.2, 63.6, 67.6, 75.3, 78.6, 81.1, 106.1, 114.9, 128.3, 128.3, 128.5, 128.5, 128.5, 128.5, 128.5, 129.0, 129.6, 129.7, 129.7, 129.9, 129.9, 129.9, 129.9, 133.0, 133.5, 133.6, 138.0, 165.1, 165.3, 166.1; HRMS (Waters Synapt G2): m/z calcd for $[C_{31}H_{30}O_8+Na]^+$: 553.1838; Found: 553.1837.

Benzyl 2,3,5-tri-*O*-benzoyl-β-D-xylofuranoside (**20c**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.7) +6.7°; IR (cm^{-1}, $CHCl_3$): 3067, 2923, 1725, 1595, 1450, 1262, 1106, 700; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 4.57 – 4.66 (m, 2H), 4.67 – 4.74 (m, 1H), 4.93 (d, *J* = 11.5 Hz, 1H), 5.01 (q, *J* = 5.8 Hz, 1H), 5.37 (s, 1H), 5.61 (s, 1H), 5.90 (d, *J* = 5.6 Hz, 1H), 7.40 (m, 12H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.98 (t, *J* = 7.6 Hz, 4H), 8.06 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 63.6, 69.5, 75.1, 79.1, 81.0, 105.2, 127.8, 128.0, 128.0, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.9, 129.6, 129.7, 129.7, 129.9, 129.9, 129.9, 129.9, 133.1, 133.5, 133.6, 137.1, 165.0, 165.2, 166.1; HRMS (Waters Synapt G2): m/z calcd for $[C_{33}H_{28}O_8+Na]^+$: 575.1682; Found: 575.1693.

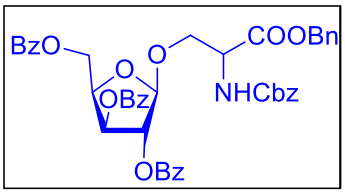


Cholesteryl 2,3,5-tri-O-benzoyl-β-D-xylofuranoside (**20d**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.6) –25.5°; IR (cm^{-1}, $CHCl_3$): 2940, 1728, 1601, 1453, 1263, 1107, 708; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 0.68 (s, 3H), 0.86 (d, *J* = 1.7 Hz, 3H), 0.87 (d, *J* = 1.7 Hz, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 1.01 (s, 3H), 1.06 – 2.09 (m, 26H), 2.28 (ddd, *J* = 13.3, 4.5, 1.7 Hz, 1H), 2.43 (ddd, *J* = 13.2, 4.3, 1.7 Hz, 1H), 3.65 (tt, *J* = 11.1, 4.5 Hz, 1H), 4.64 (qd, *J* = 11.4, 6.4 Hz, 2H), 4.95 (q, *J* = 6.2 Hz, 1H), 5.34 (d, *J* = 4.9 Hz, 1H), 5.42 (s, 1H), 5.52 (d, *J* = 1.1 Hz, 1H), 5.88 (dd, *J* = 5.9, 1.5 Hz, 1H), 7.32 – 7.64 (m, 9H), 7.96 – 8.00 (m, 2H), 8.07 (d, *J* = 8.2 Hz, 4H): ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 11.8, 18.6, 19.3, 21.0, 22.5, 22.8, 23.7, 24.2, 27.9, 28.2, 29.5, 31.8, 31.9, 35.7, 36.1, 36.7, 37.2, 38.3, 39.4, 39.7, 42.2, 50.0, 56.0, 56.7, 63.7, 75.3, 77.0, 78.4, 81.5, 103.9, 121.9, 128.2, 128.2, 128.4, 128.4,

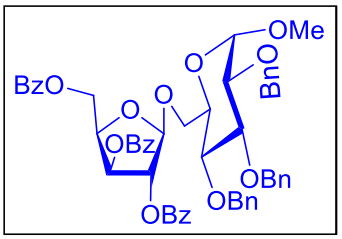


128.4, 128.4, 129.0, 129.0, 129.5, 129.6, 129.6, 129.8, 129.8, 129.9, 129.9, 133.0, 133.4, 133.5, 140.2, 165.1, 165.2, 166.1; HRMS (Waters Synapt G2): m/z calcd for $[C_{53}H_{66}O_8+Na]^+$: 853.4655; Found: 853.4667.

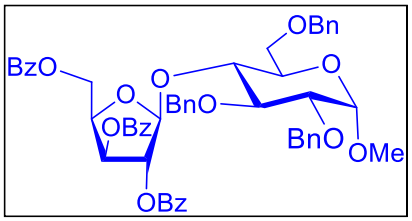
Benzyl *N*-(benzyloxycarbonyl)-*O*-(2,3,5-tri-*O*-benzoyl-β-D-xylofuranosyl)-L-serinate (**20e**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +23.7°; IR (cm^{-1}, $CHCl_3$): 3431, 3365, 3030, 2933, 1724, 1591, 1447, 1262, 1107, 706; ^1H NMR (399.78 MHz, $CDCl_3$): δ 3.85 (dd, *J* = 10.0, 3.3 Hz, 1H), 4.40 (dd, *J* = 10.0, 2.8 Hz, 1H), 4.51 (ddd, *J* = 16.8, 11.4, 6.6 Hz, 2H), 4.66 (dt, *J* = 8.7, 3.0 Hz, 1H), 4.94 (q, *J* = 6.1 Hz, 1H), 5.10 (d, *J* = 4.3 Hz, 2H), 5.13 (d, *J* = 11.0 Hz, 1H), 5.21 (s, 1H), 5.25 (d, *J* = 12.2 Hz, 1H), 5.51 (d, *J* = 1.5 Hz, 1H), 5.70 – 6.09 (m, 2H), 7.16 – 7.72 (m, 19H), 7.95 (dd, *J* = 8.2, 1.2 Hz, 2H), 8.00 – 8.06 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 54.2, 63.3, 67.3, 67.4, 68.0, 74.3, 79.1, 81.1, 106.8, 128.0, 128.0, 128.2, 128.2, 128.3, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.6, 128.6, 128.6, 128.7, 129.4, 129.6, 129.6, 129.6, 129.9, 129.9, 129.9, 129.9, 133.1, 133.7, 133.7, 135.1, 136.1, 156.0, 165.1, 165.2, 165.9, 169.7; HRMS (Waters Synapt G2): m/z calcd for $[C_{44}H_{39}O_{12}N+Na]^+$: 796.2370; Found: 796.2371.



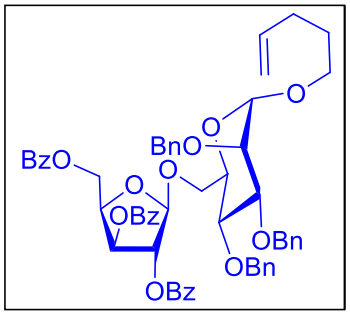
Methyl-2,3,4–tri–*O*-benzyl–6–*O*-(2,3,5-tri–*O*-benzoyl-β-D-xylofuranosyl)-α-D-glucopyranoside (**20f**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.9) +35.7°; IR (cm^{-1}, $CHCl_3$): 3068, 2925, 1725, 1594, 1457, 1263, 1103, 706; ^1H NMR (399.78 MHz, $CDCl_3$): δ 3.27 (s, 3H), 3.51 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.63 (t, *J* = 9.4 Hz, 1H), 3.71 (dd, *J* = 10.5, 4.2 Hz, 1H), 3.77 (dd, *J* = 10.0, 2.9 Hz, 1H), 3.98 (t, *J* = 9.2 Hz, 1H), 4.03 (dd, *J* = 9.7, 0.9 Hz, 1H), 4.56 (dd, *J* = 11.5, 5.8 Hz, 1H), 4.65 (d, *J* = 6.3 Hz, 2H), 4.67 (s, 2H), 4.75 (d, *J* = 12.1 Hz, 1H), 4.85 (ABq, *J* = 11.0 Hz, 2H), 4.91 – 5.04 (m, 2H), 5.17 (s, 1H), 5.50 (d, *J* = 1.2 Hz, 1H), 5.85 (dd, *J* = 6.0, 1.4 Hz, 1H), 7.11 – 7.74 (m, 24H), 7.95 (dd, *J* = 8.1, 1.1 Hz, 2H), 8.00 – 8.06 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 55.0, 63.8, 66.4, 69.7, 73.2, 75.0, 75.2, 75.7, 77.4, 78.8, 80.2, 81.2, 82.1, 97.8, 106.0, 127.5, 127.6, 127.8, 127.9, 127.9, 127.9, 127.9, 128.0, 128.0, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.9, 128.9, 129.6, 129.6, 129.7, 129.9, 129.9, 129.9, 129.9, 133.0, 133.5, 133.6, 138.2, 138.3, 138.7, 165.0, 165.2, 166.1; HRMS (Waters Synapt G2): m/z calcd for $[C_{54}H_{52}O_{13}+Na]^+$: 931.3306; Found: 931.3309.



Methyl2,3,6–tri–*O*-benzyl–4–*O*-(2,3,5-tri–*O*-benzoyl-β-D-xylofuranosyl)-α-D-glucopyranoside (**20g**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.6) +29.0°; IR (cm^{-1}, $CHCl_3$): 3071, 2924, 1725, 1595, 1443, 1262, 1105, 706; ^1H NMR (399.78 MHz, $CDCl_3$): δ 3.36 (s, 3H), 3.53 (dd, *J* = 9.4, 3.6 Hz, 1H), 3.59 (d, *J* = 9.2 Hz, 1H), 3.65 – 3.77 (m, 2H), 3.91 (t, *J* = 9.2 Hz, 1H), 3.99 (t, *J* = 9.1 Hz, 1H), 4.38 (s, 2H), 4.52 (dd, *J* = 11.6, 6.4 Hz, 1H), 4.56 (s, 1H), 4.58 (d, *J* = 7.4 Hz, 1H), 4.63 (dd, *J* = 11.5, 5.3 Hz, 1H), 4.73 (d, *J* = 12.1 Hz, 1H), 4.81 (q, *J* = 5.6 Hz, 1H), 4.91 (d, *J* = 10.5 Hz, 1H), 5.10 (d, *J* = 10.5 Hz, 1H), 5.51 (s, 1H), 5.57 (s, 1H), 5.76 (dd, *J* = 5.1, 1.8 Hz, 1H), 7.06 – 7.68 (m, 24H), 7.95 (d, *J* = 7.4 Hz, 2H), 7.98 (d, *J* = 7.4 Hz, 2H), 8.02 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 55.3, 63.0, 68.4, 69.5, 73.2, 73.5, 74.9, 75.2, 77.7, 78.4, 79.7, 80.7, 80.8, 98.1, 107.9, 127.3, 127.3, 127.4, 127.4, 127.7, 127.7, 127.8, 128.1, 128.1, 128.1, 128.1, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.8, 128.9, 129.5, 129.7, 129.7, 129.9, 129.9, 129.9, 129.9, 133.0, 133.6, 133.6, 137.8, 138.1, 138.9, 164.9, 165.2, 166.0; HRMS (Waters Synapt G2): m/z calcd for $[C_{54}H_{52}O_{13}+Na]^+$: 931.3306; Found: 931.3311.

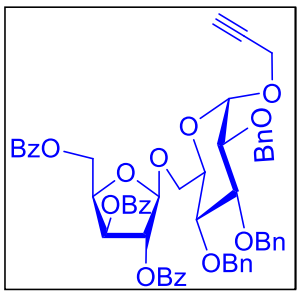


Pent-4-enyl 2,3,4–tri–*O*-benzyl–6–*O*-(2,3,5-tri–*O*-benzoyl-β-D-xylofuranosyl)-α-D-mannopyranoside (**20h**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +26.3°; IR (cm^{-1}, $CHCl_3$): 3074, 2926, 1726, 1595, 1450, 1264, 1108, 710; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.49 (quintet, *J* = 6.9 Hz, 2H), 1.89 – 1.99 (m, 2H), 3.22 (dt, *J* = 9.8, 6.4 Hz, 1H), 3.54 (dt, *J* = 9.7, 6.5 Hz, 1H), 3.73 – 3.79 (m, 2H), 3.84 (dd, *J* = 10.8, 5.8 Hz, 1H), 3.90 (dd, *J* = 9.3, 3.0 Hz, 1H), 3.97 (t, *J* = 9.4 Hz, 1H), 4.08 (dd, *J* = 10.8, 1.2 Hz, 1H), 4.58 – 4.62 (m, 1H), 4.62 (s, 2H), 4.64 (d, *J* = 2.6 Hz, 1H), 4.67 (d, *J* = 2.3 Hz, 2H), 4.73 (dd, *J* = 11.5, 7.1 Hz, 1H), 4.79 (d, *J* = 1.6 Hz, 1H), 4.88 (s, 1H), 4.91 (s, 1H), 4.89 – 4.99 (m, 2H), 5.32 (s, 1H), 5.57 (d, *J* = 1.2 Hz, 1H), 5.69 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.85 (dd, *J* = 6.2, 1.5 Hz, 1H), 7.10 – 7.69 (m, 24H), 7.97 (dd, *J* = 8.0, 1.0 Hz, 2H), 8.02 – 8.15 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.5, 30.1, 63.8, 66.8, 67.5, 71.5, 72.1, 72.3, 74.5, 74.8, 75.1, 75.5, 78.7, 80.2, 81.3, 97.6, 106.4, 114.7, 127.5, 127.5, 127.6, 127.6, 127.6, 127.8, 127.8, 128.0, 128.0, 128.2, 128.2, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.5, 128.5, 128.5, 128.5, 128.9, 129.1,

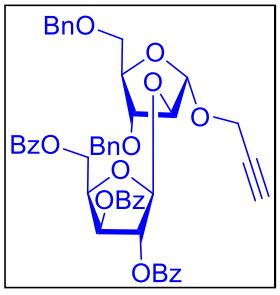


129.7, 129.7, 129.8, 129.9, 129.9, 130.0, 130.0, 132.9, 133.4, 133.5, 138.0, 138.2, 138.4, 138.5, 164.9, 165.4, 166.1.; HRMS (Waters Synapt G2): m/z calcd for $[C_{58}H_{58}O_{13}+Na]^+$: 985.3775; Found: 985.3779.

(Prop-2-ynyl) 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-β-D-xylofuranosyl)-α-D-glucopyranoside (**20i**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +38.0°; IR (cm^{-1}, $CHCl_3$): 3293, 3065, 3034, 2926, 1726, 1596, 1453, 1264, 1105, 706; ^1H NMR (399.78 MHz, $CDCl_3$): δ 2.38 (t, *J* = 2.3 Hz, 1H), 3.56 (dd, *J* = 9.6, 3.7 Hz, 1H), 3.66 (t, *J* = 9.2 Hz, 1H), 3.74 (dd, *J* = 10.7, 4.0 Hz, 1H), 3.83 (dd, *J* = 10.0, 2.6 Hz, 1H), 4.01 (t, *J* = 9.4 Hz, 2H), 4.19 (dABq, *J* = 16.0, 2.4 Hz, 2H), 4.58 (dd, *J* = 11.5, 5.7 Hz, 1H), 4.63 – 4.69 (m, 2H), 4.72 (s, 2H), 4.86 (ABq, *J* = 11.0 Hz, 2H), 4.93 – 5.03 (m, 2H), 5.12 (d, *J* = 3.6 Hz, 1H), 5.18 (s, 1H), 5.51 (d, *J* = 1.1 Hz, 1H), 5.86 (dd, *J* = 6.0, 1.4 Hz, 1H), 7.06 – 7.71 (m, 24H), 7.98 (dd, *J* = 8.2, 1.0 Hz, 2H), 8.01 – 8.08 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 54.3, 63.8, 66.2, 70.3, 72.8, 74.7, 75.0, 75.2, 75.7, 78.8, 79.0, 79.7, 81.1, 81.1, 81.9, 95.0, 105.9, 127.5, 127.6, 127.8, 127.9, 127.9, 128.0, 128.0, 128.0, 128.0, 128.0, 128.0, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.9, 129.6, 129.6, 129.9, 129.9, 129.9, 129.9, 133.0, 133.5, 133.6, 138.0, 138.2, 138.7, 165.0, 165.2, 166.0; HRMS (Waters Synapt G2): m/z calcd for $[C_{56}H_{52}O_{13}+Na]^+$: 955.3306; Found: 955.3308.

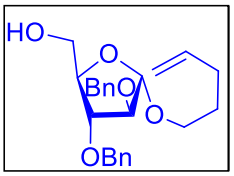


(Prop-2-ynyl) 3,5–di–*O*-benzyl–2–*O*-(2,3,5-tri–*O*-benzoyl-β-D-xylofuranosyl)-α-D-arabinofuranoside (**20j**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.9) +38.8°; IR (cm^{-1}, $CHCl_3$): 3074, 2929, 1727, 1596, 1457, 1268, 1105, 709;^1H NMR (399.78 MHz, $CDCl_3$): δ 2.30 (t, *J* = 2.3 Hz, 1H), 3.53 – 3.61 (m, 2H), 4.07 (dd, *J* = 6.4, 2.7 Hz, 1H), 4.22 – 4.27 (m, 1H), 4.28 (dd, *J* = 2.3, 1.4 Hz, 2H), 4.49 (s, 2H), 4.53 (d, *J* = 11.8 Hz, 1H), 4.62 (dd, *J* = 6.1, 4.1 Hz, 2H), 4.78 (d, *J* = 11.8 Hz, 1H), 4.96 (q, *J* = 5.5 Hz, 1H), 5.36 (s, 1H), 5.40 (s, 1H), 5.57 (d, *J* = 1.5 Hz, 2H), 5.83 (dd, *J* = 5.4, 1.7 Hz, 1H), 7.03 – 7.77 (m, 19H), 7.79 – 8.32 (m, 6H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 54.1, 63.3, 69.7, 72.3, 73.3, 74.6, 74.9, 79.0, 79.1, 80.9, 81.6, 83.9, 86.5, 104.3, 105.9, 127.6, 127.7, 127.7, 127.7, 127.7, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.8, 129.4, 129.7, 129.7, 129.8, 129.9, 129.9, 129.9, 133.2, 133.6, 133.7, 137.6, 137.9, 164.9, 165.2,

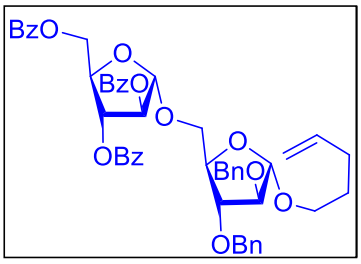


166.0, HRMS (Waters Synapt G2): m/z calcd for $[C_{48}H_{44}O_{12}+Na]^+$: 812.2833; Found: 812.2830.

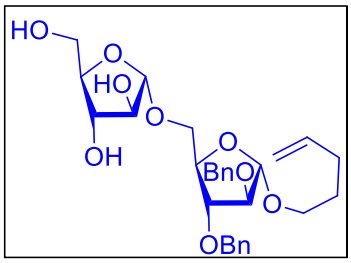
Pent-4-enyl 2,3-di-*O*-benzyl-α-D-arabinofuranoside (**11a**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.4) +72.6°; IR (cm^{-1}, $CHCl_3$): 3439, 3065, 3044, 2924, 2865, 1591, 1455, 1105, 740, 698; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.69 (quintet, *J* = 6.7 Hz, 2H), 2.05 (s, 1H), 2.13 (q, *J* = 6.9 Hz, 2H), 3.40 (dt, *J* = 9.6, 6.5 Hz, 1H), 3.59 – 3.69 (m, 1H), 3.71 (dt, *J* = 9.6, 6.6 Hz, 1H), 3.78 – 3.88 (m, 1H), 3.98 (dd, *J* = 6.5, 3.0 Hz, 1H), 4.03 (dd, *J* = 3.0, 1.1 Hz, 1H), 4.12 (ddd, *J* = 6.7, 3.9, 2.9 Hz, 1H), 4.51 (dd, *J* = 11.8, 4.4 Hz, 2H), 4.57 (dd, *J* = 14.7, 11.9 Hz, 2H), 4.97 (ddt, *J* = 9.9, 2.2, 1.3 Hz, 1H), 5.01 (s, 1H), 5.02 (dt, *J* = 17.2, 1.7 Hz, 1H), 5.82 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 7.12 – 7.51 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.6, 30.2, 62.1, 66.8, 71.9, 72.2, 81.8, 82.6, 88.0, 106.2, 114.8, 127.7, 127.7, 127.8, 127.9, 127.9, 127.9, 128.4, 128.4, 128.4, 128.4, 137.3, 137.7, 138.1; HRMS (Waters Synapt G2): m/z calcd for $[C_{24}H_{30}O_5+Na]^+$: 421.1991; Found: 421.1995.



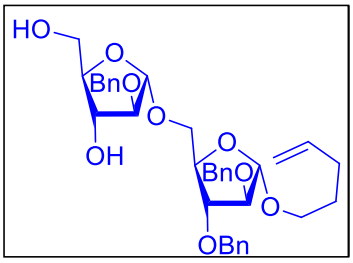
Pent-4-enyl 2,3-di-*O*-benzyl-5-*O*-(2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl)-α-D-arabinofuranoside (**22a**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +2.0°; IR (cm^{-1}, $CHCl_3$): 3079, 3026, 2927, 1724, 1594, 1452, 1266, 1106, 707; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.66 (quintet, *J* = 6.9 Hz, 2H), 2.11 (q, *J* = 7.0 Hz, 2H), 3.39 (dt, *J* = 9.6, 6.5 Hz, 1H), 3.70 (dt, *J* = 6.6 Hz, 1H), 3.75 (dd, *J* = 11.0, 3.5 Hz, 1H), 3.94 (dd, *J* = 11.0, 4.5 Hz, 1H), 4.04 (d, *J* = 4.8 Hz, 2H), 4.18 – 4.27 (m, 1H), 4.39 (q, *J* = 4.3 Hz, 1H), 4.43 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 11.8 Hz, 1H), 4.55 (d, *J* = 13.5 Hz, 1H), 4.57 (s, 1H), 4.61 (dd, 1H), 4.79 (dd, *J* = 12.0, 3.1 Hz, 1H), 4.93 – 4.97 (m, 1H), 4.97 – 5.03 (m, 1H), 5.04 (s, 1H), 5.36 (s, 1H), 5.53 (d, *J* = 4.9 Hz, 1H), 5.59 (s, 1H), 5.80 (ddt, *J* = 16.9, 10.0, 6.8 Hz, 1H), 7.15 – 7.66 (m, 19H), 7.94 – 8.03 (m, 4H), 8.06 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.7, 30.3, 63.7, 66.2, 66.9, 72.1, 72.1, 77.8, 79.6, 81.4, 81.9, 83.0, 88.5, 105.6, 106.0, 114.8, 127.6, 127.6, 127.7, 127.9, 128.0, 128.0, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 129.0, 129.0, 129.6, 129.7, 129.7, 129.8, 129.8, 129.9, 129.9, 133.0, 133.4, 133.4, 137.5, 137.8, 138.1, 165.2, 165.7, 166.2; HRMS (Waters Synapt G2): m/z calcd for $[C_{50}H_{50}O_{12}+Na]^+$: 865.3200; Found: 865.3188.



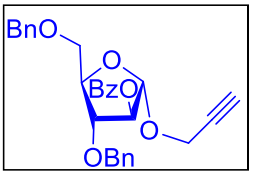
Pent-4-enyl 2,3-di-*O*-benzyl-5-*O*-(α-D-arabinofuranosyl)-α-D-arabinofuranoside (**22b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.5) +92.6°; IR (cm^{-1}, $CHCl_3$): 3402, 3069, 3037, 2927, 1591, 1363, 1103, 742, 697; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.67 (quintet, *J* = 6.7 Hz, 2H), 2.08 – 2.15 (m, 2H), 2.27 (bs, 1H), 3.38 (dt, *J* = 9.7, 6.5 Hz, 2H), 3.48 (bs, 1H), 3.62 – 3.71 (m, 3H), 3.73 – 3.83 (m, 4H), 3.90 (q, *J* = 2.3 Hz, 1H), 3.93 (bs, 1H), 3.98 (dd, *J* = 2.4, 0.8 Hz, 1H), 4.01 (bs, 1H), 4.16 (dq, *J* = 5.3, 3.1 Hz, 1H), 4.41 (d, *J* = 12.2 Hz, 1H), 4.47 (d, *J* = 12.1 Hz, 1H), 4.56 (dd, *J* = 12.1, 9.0 Hz, 1H), 4.94 – 4.99 (m, 1H), 4.99 (s, 2H), 5.00 – 5.05 (m, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 7.16 – 7.51 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.6, 30.2, 61.7, 65.9, 66.8, 71.9, 72.0, 77.7, 78.9, 80.4, 83.6, 86.8, 87.3, 105.9, 107.5, 114.8, 127.8, 127.8, 127.8, 128.0, 128.1, 128.1, 128.4, 128.4, 128.5, 128.5, 137.1, 137.5, 138.1; HRMS (Waters Synapt G2): m/z calcd for $[C_{29}H_{38}O_9+Na]^+$: 553.2414; Found: 553.2410.



Pent-4-enyl 2,3-di-*O*-benzyl-5-*O*-(2-*O*-benzyl-α-D-arabinofuranosyl)-α-D-arabinofuranoside (**22c**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +78.2°; IR (cm^{-1}, $CHCl_3$): 3425, 3069, 3026, 2925, 2876, 1592, 1455, 1104, 742, 697; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.67 (quintet, *J* = 6.9 Hz, 2H), 2.11 (q, *J* = 6.9 Hz, 2H), 2.16 – 2.25 (m, 1H), 3.07 (d, *J* = 11.1 Hz, 1H), 3.39 (dt, *J* = 9.8, 6.5 Hz, 1H), 3.59 – 3.77 (m, 4H), 3.77 – 3.84 (m, 2H), 3.89 (q, *J* = 3.2 Hz, 1H), 3.92 (s, 1H), 3.96 – 4.00 (m, 1H), 4.04 – 4.11 (m, 1H), 4.13 – 4.19 (m, 1H), 4.39 (d, *J* = 12.2 Hz, 1H), 4.47 (d, *J* = 12.1 Hz, 1H), 4.52 (d, *J* = 11.7 Hz, 1H), 4.53 – 4.64 (m, 3H), 4.91 – 5.08 (m, 1H), 5.00 (s, 1H), 4.99 – 5.08 (m, 1H), 5.12 (s, 1H), 5.81 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 7.05 – 7.60 (m, 15H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.6, 30.3, 62.6, 65.7, 66.8, 71.6, 71.9, 72.1, 75.1, 80.5, 83.6, 86.6, 87.1, 87.1, 105.0, 106.0, 114.9, 127.8, 127.8, 127.9, 127.9, 127.9, 128.0, 128.1, 128.2, 128.2, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 137.0, 137.2, 137.5, 138.1; HRMS (Waters Synapt G2): m/z calcd for $[C_{36}H_{44}O_9+Na]^+$: 643.2883; Found: 643.2883.

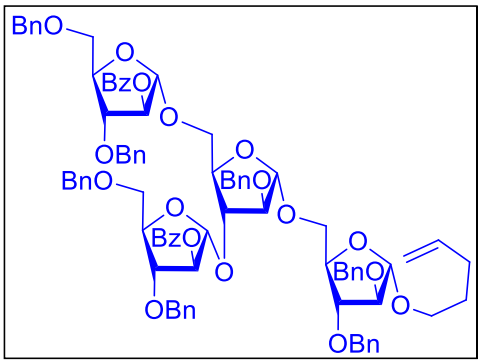


Propargyl-2-*O*-benzoyl-3,5-di-*O*-benzyl-α-D-arabinofuranoside: $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.8) +57.4°; IR (cm^{-1}, $CHCl_3$): 3292, 3067, 2924, 1722, 1591, 1452, 1262, 1107, 704; ^1H NMR (399.78 MHz, $CDCl_3$): δ 2.42 (t, *J* = 2.4 Hz, 1H), 3.58 (dd, *J* = 10.8, 5.2 Hz, 1H), 3.64 (dd, *J* = 10.8,



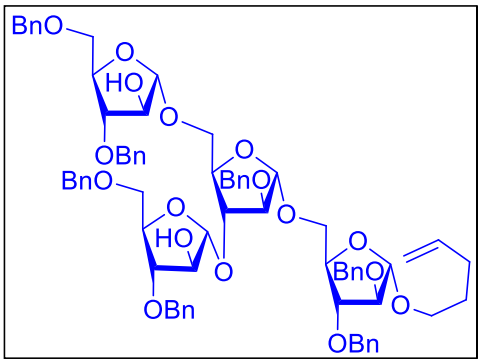
3.7 Hz, 1H), 4.00 (d, *J* = 5.4 Hz, 1H), 4.31 – 4.34 (m, 1H), 4.34 (d, *J* = 2.4 Hz, 2H), 4.55 (ABq, *J* = 12.1 Hz, 2H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.82 (d, *J* = 12.1 Hz, 1H), 5.42 (d, *J* = 1.1 Hz, 1H), 5.44 (s, 1H), 7.07 – 7.64 (m, 13H), 7.83 – 8.16 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 53.9, 69.3, 72.3, 73.4, 74.8, 78.8, 81.7, 82.7, 83.3, 104.2, 127.6, 127.6, 127.6, 127.8, 128.0, 128.0, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 129.4, 129.8, 129.8, 133.4, 137.5, 137.8, 165.3; HRMS (Waters Synapt G2): m/z calcd for $[C_{29}H_{28}O_6+Na]^+$: 495.1784; Found: 495.1780.

Pent-4-enyl-2,3-di-*O*-benzyl-5-*O*-(2-*O*-benzyl-3-*O*-(2-*O*-benzoyl-3,5-di-*O*-benzyl-α-D-arabinofuranosyl)-5-*O*-(2-*O*-benzoyl-3,5-di-*O*-benzyl-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofuranoside

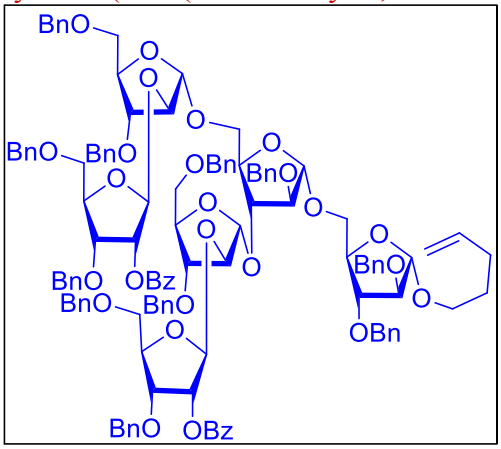


(**24a**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +78.8°; IR (cm^{-1}, $CHCl_3$): 3267, 3030, 2924, 1723, 1592, 1455, 1263, 1108, 704; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.66 (quintet, *J* = 6.8, 6.2 Hz, 2H), 2.11 (q, *J* = 7.2 Hz, 2H), 3.37 (dt, *J* = 9.5, 6.5 Hz, 1H), 3.51 - 3.54 (m, 1H), 3.55 (dd, *J* = 8.5, 4.3 Hz, 1H), 3.58 (d, *J* = 3.4 Hz, 1H), 3.61 (d, *J* = 3.4 Hz, 1H), 3.65 (dd, *J* = 7.6, 3.3 Hz, 1H), 3.65 – 3.76 (m, 2H), 3.77 (d, *J* = 11.5 Hz, 1H), 3.87 (dd, *J* = 11.6, 4.2 Hz, 1H), 3.97- 4.06 (m, 5H), 4.11 – 4.18 (m, 2H), 4.16 – 4.26 (m, 1H), 4.26 – 4.33 (m, 1H), 4.33 – 4.45 (m, 4H), 4.47 – 4.59 (m, 10H), 4.75 (dd, *J* = 21.3, 12.2 Hz, 2H), 4.92 – 5.05 (m, 3H), 5.13 (s, 1H), 5.30 (s, 1H), 5.34 (s, 1H), 5.45 (s, 1H), 5.80 (ddt, *J* = 13.2, 10.0, 6.4 Hz, 1H), 7.09 – 7.34 (m, 35H), 7.38 (t, *J* = 7.7 Hz, 4H), 7.50 – 7.63 (m, 2H), 7.91 – 8.02 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.7, 30.3, 65.6, 66.2, 66.9, 69.0, 69.2, 71.9, 71.9, 72.0, 72.0, 72.3, 73.3, 73.3, 79.8, 80.1, 80.1, 81.6, 82.1, 82.2, 82.4, 83.1, 83.1, 83.5, 88.1, 88.6, 105.4, 106.0, 106.2, 106.3, 114.8, 120.0, 127.4, 127.5, 127.5, 127.5, 127.6, 127.6, 127.6, 127.6, 127.7, 127.8, 127.8, 127.8, 127.8, 127.8, 127.8, 127.8, 127.9, 128.2, 128.2, 128.2, 128.2, 128.2, 128.2, 128.2, 128.2, 128.2, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 129.5, 129.6, 129.8, 129.8, 129.8, 129.8, 133.2, 133.2, 137.6, 137.7, 137.7, 137.8, 138.0, 138.0, 138.1, 138.2, 165.2, 165.2; HRMS (Waters Synapt G2): m/z calcd for $[C_{88}H_{92}O_{19}+Na]^+$: 1475.6131; Found: 1475.6117.

Pent-4-enyl-2,3-di-*O*-benzyl-5-*O*-(2-*O*-benzyl-3-*O*-(3,5-di-*O*-benzyl-α-D-arabino-furanosyl)-5-*O*-(3,5-di-*O*-benzyl-α-D-arabino-furanosyl)-α-D-arabinofuranosyl)-α-D-arab-inofuranoside (**24b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) +107.5°; IR (cm^{-1}, $CHCl_3$): 3432, 3260, 3040, 2922, 2879, 1590, 1455, 1106, 742, 698; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.67 (quintet, *J* = 6.7 Hz, 2H), 2.11 (q, *J* = 7.4 Hz, 2H), 3.37 (dt, *J* = 9.7, 6.6 Hz, 1H), 3.43 (ddd, *J* = 10.5, 4.4, 3.1 Hz, 2H), 3.56 (ddd, *J* = 10.5, 4.0, 2.5 Hz, 2H), 3.65 (ddd, *J* = 16.3, 11.5, 3.2 Hz, 2H), 3.71 (dt, *J* = 9.8, 6.7 Hz, 1H), 3.82 (td, *J* = 3.7, 1.6 Hz, 2H), 3.87 (dd, *J* = 11.5, 4.2 Hz, 1H), 3.94 (dd, *J* = 11.7, 3.8 Hz, 1H), 4.01- 4.03 (m, 1H), 4.05 (d, *J* = 3.6 Hz, 1H), 4.07 (dd, *J* = 3.4, 1.3 Hz, 1H), 4.08 – 4.17 (m, 3H), 4.13 (d, *J* = 3.5 Hz, 1H), 4.22 (dt, *J* = 3.6, 2.8 Hz, 1H), 4.27 (dt, *J* = 4.2, 2.8 Hz, 1H), 4.32 (dd, *J* = 6.8, 3.4 Hz, 1H), 4.40 (dd, *J* = 12.0, 8.7 Hz, 2H), 4.46 (d, *J* = 11.5 Hz, 1H), 4.48 (d, *J* = 13.3 Hz, 2H), 4.52 – 4.56 (m, 6H), 4.56 – 4.62 (m, 3H), 4.98 (s, 1H), 4.94 – 5.05 (m, 2H), 5.05 (s, 1H), 5.08 (s, 1H), 5.13 (d, *J* = 0.8 Hz, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 7.04 – 7.66 (m, 35H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.7, 30.3, 65.6, 65.8, 66.9, 69.6, 69.7, 71.7, 71.8, 71.8 72.1, 72.3, 73.6, 73.6 78.3, 78.4, 79.0, 79.9, 80.8, 82.3, 83.0, 83.1, 84.5, 84.8, 87.6, 88.6, 106.0, 106.1, 107.6, 109.1, 114.8, 127.6, 127.6, 127.6, 127.6, 127.7, 127.7, 127.7, 127.7, 127.7, 127.7, 127.7, 127.8, 127.8, 127.8, 127.9, 127.9, 127.9, 127.9, 127.9, 128.0, 128.0, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.5, 137.2, 137.3, 137.4, 137.5, 137.8, 137.9, 137.9, 138.1; HRMS (Waters Synapt G2): m/z calcd for $[C_{74}H_{84}O_{17}+Na]^+$: 1267.5606; Found: 1267.5649.

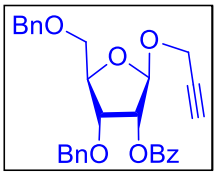


Pent-4-enyl 2,3-di-*O*-benzyl-5-*O*-(2-*O*-benzyl-3-*O*-(2-*O*-(2-*O*-benzoyl-3,5-di-*O*-benzyl-β-D-ribofuranosyl)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl)-5-*O*-(2-*O*-(2-*O*-benzoyl-3,5-di-*O*-benzyl-β-D-ribofuranosyl)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl)-α-D-arabinofuranoside: $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.8) +49.0°; IR (cm^{-1}, $CHCl_3$): 3033, 2924, 1724, 1591, 1455, 1268, 1101,



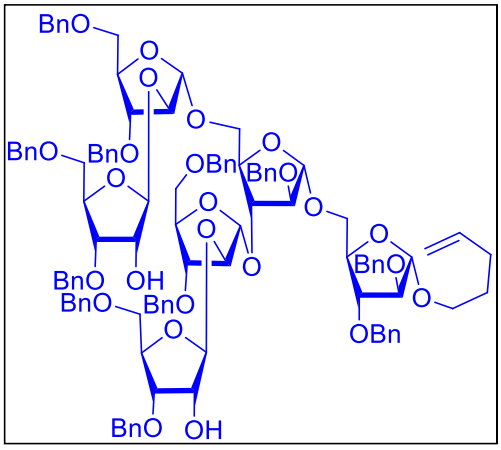
698; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.65 (quintet, *J* = 6.7 Hz, 2H), 2.10 (q, *J* = 7.0 Hz, 2H), 3.34 (dt, *J* = 9.7, 6.5 Hz, 1H), 3.48 – 3.57 (m, 6H), 3.60 (dt, *J* = 10.1, 3.7 Hz, 2H), 3.63 (dd, *J* = 10.3, 3.3 Hz, 1H), 3.69 (dt, *J* = 9.7, 6.6 Hz, 1H), 3.75 (dd, *J* = 11.7, 2.0 Hz, 1H), 3.82 (dd, *J* = 11.6, 4.4 Hz, 1H), 3.95 (dd, *J* = 11.9, 4.5 Hz, 1H), 3.99 (s, 1H), 4.00 (d, *J* = 5.2 Hz, 2H), 4.03 (dd, *J* = 6.3, 2.3 Hz, 1H), 4.05 – 4.07 (m, 1H), 4.07 – 4.18 (m, 3H), 4.21 (td, *J* = 7.7, 7.1, 4.5 Hz, 3H), 4.28 (dd, *J* = 5.7, 4.1 Hz, 1H), 4.32 (dt, *J* = 11.0, 3.1 Hz, 5H), 4.39 (d, *J* = 7.1 Hz, 5H), 4.36 – 4.44 (m, 2H), 4.45 (dd, *J* = 13.1, 2.8 Hz, 2H), 4.49 (d, *J* = 13.1 Hz, 1H), 4.51 (d, *J* = 3.6 Hz, 2H), 4.52 (s, 4H), 4.55 (d, *J* = 3.7 Hz, 1H), 4.59 – 4.65 (m, 3H), 4.66 (d, *J* = 12.4 Hz, 1H), 4.96 (s, 1H), 4.93 – 5.05 (m, 2H), 5.10 (d, *J* = 0.4 Hz, 1H), 5.17 (s, 2H), 5.22 (s, 1H), 5.32 (s, 1H), 5.47 (t, *J* = 4.0 Hz, 2H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 7.14 – 7.33 (m, 55H), 7.41 (td, *J* = 7.8, 2.3 Hz, 4H), 7.55 (q, *J* = 7.4 Hz, 2H), 8.03 – 8.09 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.7, 30.2, 65.5, 66.0, 66.8, 69.4, 69.7, 70.7, 70.8, 71.6, 71.8, 71.9, 71.9, 72.2, 72.9, 73.0, 73.0, 73.0, 73.0, 73.2, 73.2 74.6, 74.7, 77.7, 77.7, 79.7, 80.0, 80.4, 80.4, 81.2, 81.6, 83.1, 83.9, 84.0, 86.0, 86.0, 88.1, 88.4, 105.0, 105.1, 105.2, 106.0, 106.2, 106.5, 114.7, 127.3-129.8(65), 133.2, 133.2, 137.4, 137.4, 137.6, 137.6, 137.9, 138.0, 138.0, 138.2, 138.2, 138.2, 138.3, 138.3, 165.4, 165.4. HRMS (Waters Synapt G2): m/z calcd for $[C_{126}H_{132}O_{27}+Na]^+$: 2100.8887; Found: 2100.8669.

Propargyl-2-benzoyl-3,5-di-*O*-benzyl-β-D-ribofuranoside: $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) +75°; IR (cm^{-1}, $CHCl_3$): 3290, 3074, 3036, 2928, 2867, 1720, 1595, 1455, 1278, 1110, 700; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 2.39 (t, *J* = 1.8 Hz, 1H), 3.46 – 3.56 (m, 1H), 3.69 (d, *J* = 11.3 Hz, 1H), 3.84 – 3.98 (m, 2H), 4.01 – 4.08 (m, 2H), 4.45 (d, *J* = 12.2 Hz, 1H), 4.54 (d, *J* = 13.4 Hz, 2H), 4.76 (m, 1H), 4.90 (m, 1H), 6.09 (dd, *J* = 4.1, 1.4 Hz, 1H), 7.07 – 7.46 (m, 13H), 7.55 – 7.86 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 53.9, 70.5, 72.9, 73.1, 74.2, 74.8, 77.5, 78.6, 80.7, 103.1, 127.5, 127.5, 127.5, 127.7, 127.9, 127.9, 128.2, 128.2, 128.2, 128.2, 128.3, 128.3, 129.4, 129.8, 129.8, 133.2, 137.3, 138.0, 165.3; HRMS (Waters Synapt G2): m/z calcd for $[C_{29}H_{28}O_6+Na]^+$: 495.1784; Found: 495.1780.

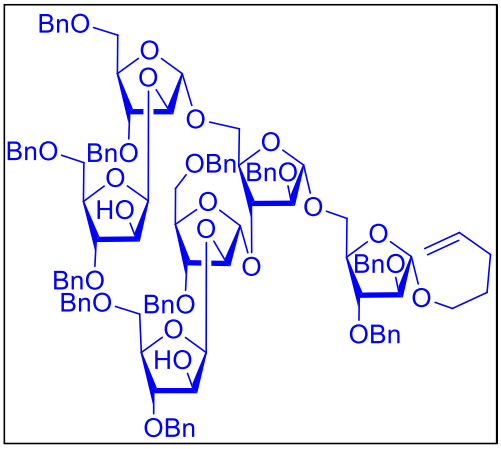


Pent-4-enyl-2,3-di-*O*-benzyl-5-*O*-(2-*O*-benzyl-3-*O*-(2-*O*-(3,5-di-*O*-benzyl-β-D-ribo-furanosyl)-3,5-di-*O*-benzyl-α-D-arabino-furanosyl)-5-*O*-(2-*O*-(3,5-di-*O*-benzyl-β-D-ribofuranosyl)-3,5-di-*O*-benzyl-α-D-ara-binofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofuranoside (**4b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +32.6°; IR (cm^{-1}, $CHCl_3$): 3458, 3063, 3032, 2925, 2869, 1590, 1454, 1106, 740, 697; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ

1.66 (t, *J* = 6.7 Hz, 2H), 2.11 (q, *J* = 7.4 Hz, 2H), 2.58 (bs, 2H), 3.36 (dt, *J* = 9.7, 6.5 Hz, 1H), 3.49 (dd, *J* = 5.2, 1.1 Hz, 4H), 3.51 (dd, *J* = 4.9, 2.7 Hz, 2H), 3.54 (d, *J* = 3.2, 1.3 Hz, 1H), 3.53 – 3.63 (m, 1H), 3.66 (dd, *J* = 11.4, 3.2 Hz, 1H), 3.71 (dt, *J* = 9.4, 6.5 Hz, 2H), 3.75 (dd, *J* = 11.2, 2.5 Hz, 1H), 3.92 (dd, *J* = 10.5, 3.4 Hz, 1H), 3.96 (dd, *J* = 8.7, 2.9 Hz, 1H), 3.99 (dd, *J* = 3.8, 2.8 Hz, 1H), 4.00 – 4.02 (m, 4H), 4.03 (t, *J* = 4.1 Hz, 1H), 4.06 (dd, *J* = 3.8, 1.5 Hz, 1H), 4.10 – 4.17 (m, 3H), 4.17 – 4.25 (m, 3H), 4.25 – 4.29 (m, 2H), 4.32 – 4.35 (m, 1H), 4.37 (dd, *J* = 3.5, 1.6 Hz, 4H), 4.39 (d, *J* = 2.0 Hz, 1H), 4.43 (t, *J* = 4.8 Hz, 2H), 4.43 (t, *J* = 10.2 Hz, 1H), 4.47 (d, *J* = 4.1 Hz, 2H), 4.49 – 4.50 (m, 2H), 4.51 – 4.60 (m, 9H), 4.63 (t, *J* = 12.2 Hz, 1H), 4.98 (s, 1H), 4.93 – 5.05 (m, 2H), 5.06 (s, 1H), 5.11 (s, 2H), 5.12 (s, 1H), 5.15 (d, *J* = 1.3 Hz, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 7.04 – 7.52 (m, 55H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.7, 30.3, 65.7, 66.0, 66.9, 69.4, 69.5, 71.2, 71.2, 71.2, 71.7, 71.8, 71.8, 71.9, 72.3, 72.5, 72.6, 73.0, 73.0, 73.2, 73.2, 73.6, 73.6, 79.2, 79.2, 79.9, 80.0, 80.3, 80.4, 80.8, 81.4, 83.1, 83.5, 83.5, 86.0, 86.0, 88.0, 88.5, 105.4, 106.0, 106.1, 106.6, 107.4, 107.4, 114.7, 127.4-128.5(55C), 137.1, 137.2, 137.5, 137.7, 138.0, 138.0, 138.0, 138.1, 138.2, 138.2, 138.2, 138.2; 2D HSQC NMR ($^1J_{C\text{-}H}$, Hz): 175.0, 173.0, 176.1, 175.8, 176.2, 175.6; HRMS (Waters Synapt G2): m/z calcd for $[C_{112}H_{124}O_{25}+Na]^+$: 1892.8363; Found: 1892.7896.

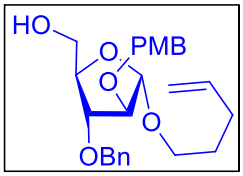


Pent-4-enyl-2,3-di-*O*-benzyl-5-*O*-(2-*O*-benzyl-3-*O*-(2-*O*-(3,5-di-*O*-benzyl-β-D-arabinofuranosyl)-3,5-di-O-benzyl-α-D-arabinofuranosyl)-5-*O*-(2-*O*-(3,5-di-*O*-benzyl-β-D-arabinofuranosyl)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofuranoside (**4d**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +24.2°; IR (cm^{-1}, $CHCl_3$): 3423, 3080, 3030, 2925, 2869, 1592, 1456, 1109, 742, 695; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.66 (quintet, *J* = 6.7 Hz, 2H), 2.11 (q, *J* = 7.3 Hz, 2H), 2.66 (s, 1H), 3.36 (dt, *J* = 9.6, 6.5 Hz, 1H), 3.50 (dt, *J* = 10.9, 4.6 Hz, 5H), 3.52 – 3.59 (m, 3H), 3.69 (dtd, *J* = 17.1, 6.4, 3.2 Hz,

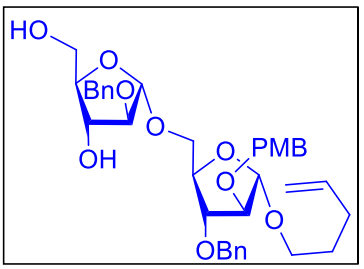


4H), 3.76 – 3.86 (m, 3H), 3.93 (dd, *J* = 11.8, 3.7 Hz, 1H), 3.97 – 4.05 (m, 5H), 4.07 (dd, *J* = 5.7, 1.6 Hz, 1H), 4.05 – 4.20 (m, 5H), 4.19 – 4.24 (m, 2H), 4.28 (q, *J* = 4.1 Hz, 2H), 4.40 (dt, *J* = 12.0, 3.4 Hz, 8H), 4.48 (dd, *J* = 12.0, 5.9 Hz, 4H), 4.50 – 4.69 (m, 10H), 4.72 (d, *J* = 11.9 Hz, 2H), 4.88 (d, *J* = 4.8 Hz, 1H), 4.98 (s, 1H), 4.92 – 5.07 (m, 2H), 5.05 (s, 1H), 5.08 (d, *J* = 4.7 Hz, 1H), 5.11 (s, 1H), 5.80 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 7.13 – 7.38 (m, 55H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.8, 30.4, 66.1, 67.0, 69.4, 69.5, 71.8, 71.9, 71.9, 72.0, 72.1, 72.4, 73.2, 73.4, 73.4, 73.4, 80.0, 80.1, 80.1, 80.2, 80.5, 80.6, 80.9, 81.4, 81.7, 81.7, 83.3, 83.6, 83.8, 84.2, 84.3, 86.2, 86.3, 86.4, 86.4, 86.5, 88.0, 88.6, 101.7, 102.0, 105.5, 106.2, 106.2, 106.7, 114.9, 127.7-130.3 (55C), 137.6, 137.6, 138.0, 138.1, 138.1, 138.1, 138.1, 138.1, 138.2, 138.2, 138.3, 138.3; 2D HSQC NMR ($^1J_{C\text{-}H}$, Hz): 183.1, 183.0, 174.9, 175.0, 175.7, 176.2; HRMS (Waters Synapt G2): m/z calcd for $[C_{112}H_{124}O_{25}+Na]^+$: 1892.8363; Found: 1892.7859.

(Pent-4-enyl) 2-*O*-(4-methoxybenzyl)-3-*O*-benzyl-α-D-arabinofuranside (**11b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.4) +68.7°; IR (cm^{-1}, $CHCl_3$): 3440, 2924, 1610, 1510, 1455, 1249, 1171, 742; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.69 (quintet, *J* = 6.8 Hz, 2H), 2.14 (q, *J* = 7.0 Hz, 2H), 2.19 (s, 1H), 3.40 (dt, *J* = 9.6, 6.5 Hz, 1H), 3.64 (d, *J* = 11.6 Hz, 1H), 3.71 (dt, *J* = 9.5, 6.6 Hz, 1H), 3.79 (s, 3H), 3.80 (d, *J* = 31.5 Hz, 1H), 3.97 (dd, *J* = 6.5, 2.9 Hz, 1H), 4.02 (d, *J* = 2.5 Hz, 1H), 4.12 (dt, *J* = 6.5, 3.4 Hz, 1H), 4.44 (ABq, *J* = 11.4 Hz, 2H), 4.39 – 4.62 (m, 1H), 4.58 (ABq, *J* = 11.9 Hz, 2H), 5.00 (s, 1H), 4.95 – 5.07 (m, 1H), 5.82 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 2H), 7.18 – 7.42 (m, 7H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.6, 30.2, 55.2, 62.1, 66.8, 71.5, 72.1, 81.7, 82.6, 87.6, 106.2, 113.8, 114.8, 127.6, 127.7, 128.3, 128.3, 128.5, 129.3, 129.6, 129.6, 137.8, 138.0, 138.1, 159.3; HRMS (Waters Synapt G2): m/z calcd for $[C_{25}H_{32}O_6+Na]^+$: 451.2097; Found: 451.2101.

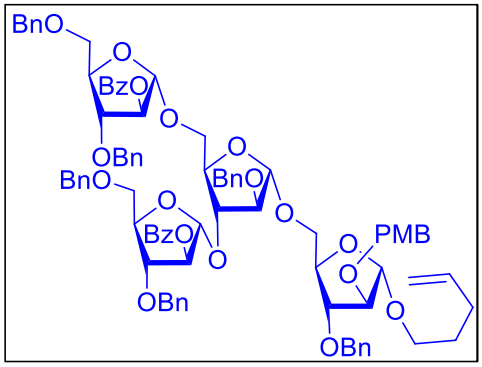


(Pent-4-enyl)-2-*O*-(4-methoxybenzyl)-3-*O*-benzyl-5-*O*-(2-*O*-benzyl-α-D-arabinofuranosyl)-α-D-arabinofuranoside (**23c**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.6) +82.4°; IR (cm^{-1}, $CHCl_3$): 3420, 2924, 1604, 1509, 1453, 1250, 1098, 769; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.65 (quintet, *J* = 6.7 Hz, 2H), 2.10 (q, *J* = 6.6 Hz, 2H), 3.37 (dt, *J* = 9.8, 6.5 Hz, 1H), 3.60 – 3.72 (m, 4H), 3.73 – 3.77 (m, 2H), 3.79 (s, 3H), 3.80 (d, *J* = 5.0 Hz, 1H), 3.88 (q, *J* = 3.2 Hz, 1H),



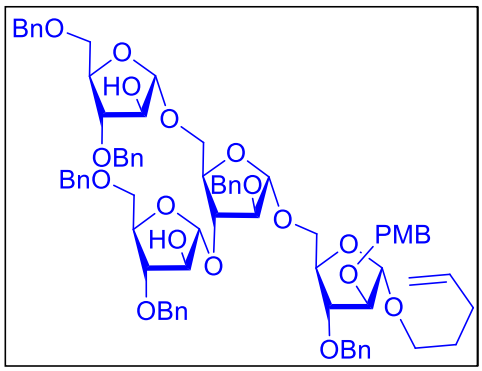
3.90 (s, 1H), 3.95 (dd, *J* = 2.2, 0.7 Hz, 1H), 4.05 (d, *J* = 2.2 Hz, 1H), 4.10 – 4.17 (m, 2H), 4.36 (d, *J* = 10.3 Hz, 1H), 4.39 (d, *J* = 9.8 Hz, 1H), 4.48 (s, 1H), 4.51 (s, 2H), 4.58 (d, *J* = 11.6 Hz, 1H), 4.96 (s, 1H), 4.92 – 5.04 (m, 2H), 5.10 (s, 1H), 5.80 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 6.84 – 6.90 (m, 2H), 7.19 – 7.39 (m, 12H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.6, 30.3, 55.3, 62.6, 65.7, 66.8, 71.6, 71.7, 71.9, 75.2, 80.5, 83.7, 86.7, 86.8, 87.1, 105.0, 106.0, 113.9, 114.8, 127.8, 127.8, 127.8, 127.8, 127.9, 128.0, 128.4, 128.4, 128.4, 128.5, 128.5, 129.2, 129.8, 129.8, 137.0, 137.6, 138.1, 159.5; HRMS (Waters Synapt G2): m/z calcd for $[C_{37}H_{46}O_{10}+Na]^+$: 673.2989; Found: 673.2988.

(Pent-4-enyl)-2-*O*-(4-methoxybenzyl)-3-*O*-benzyl-5-*O*-(2-*O*-benzyl-3-*O*-(2-*O*-benzoyl-3,5-di-*O*-benzyl-α-D-arabinofuranosyl)-5-*O*-(2-*O*-benzoyl-3,5-di-*O*-benzyl-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofuranoside (**25a**):



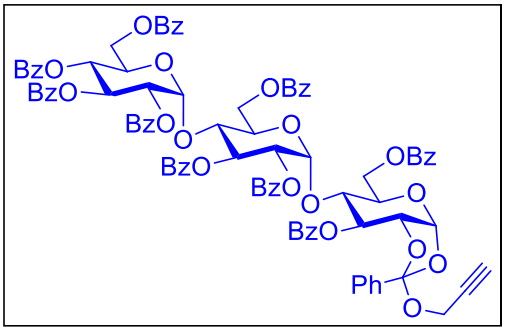
$[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.5) +60.5°; IR (cm^{-1}, $CHCl_3$): 3032, 2924, 1724, 1599, 1453, 1306, 1260, 1106, 705; ^{1}H NMR 399.78 MHz, $CDCl_3$): δ 1.69 (d, *J* = 7.6 Hz, 2H), 2.13 (q, *J* = 6.9 Hz, 2H), 3.52 – 3.75 (m, 8H), 3.76 (s, 3H), 3.77 – 3.83 (m, 1H), 3.85 – 3.93 (m, 1H), 3.98 – 4.09 (m, 6H), 4.12 – 4.21 (m, 1H), 4.23 (dt, *J* = 7.2, 4.1 Hz, 1H), 4.32 (q, *J* = 4.2 Hz, 1H), 4.35 – 4.62 (m, 13H), 4.60 – 4.72 (m, 1H), 4.73 – 4.77 (m, 1H), 4.80 (d, *J* = 12.2 Hz, 1H), 4.99 (s, 1H), 4.94 – 5.07 (m, 2H), 5.16 (d, *J* = 1.3 Hz, 1H), 5.32 (s, 1H), 5.37 (s, 1H), 5.47 (s, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 6.83 (d, *J* = 8.6 Hz, 2H), 7.05 – 7.50 (m, 36H), 7.57 (q, *J* = 7.3 Hz, 2H), 7.91 – 8.04 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.7, 30.3, 55.1, 65.6, 66.0, 66.8, 68.9, 69.2, 71.5, 71.8, 71.9, 72.0, 72.2, 73.2, 73.2, 79.8, 80.0, 80.0, 81.5, 82.0, 82.1, 82.3, 83.1, 83.1, 83.4, 88.1, 88.2, 105.4, 106.1, 106.1, 106.2, 113.7, 113.7, 114.7, 127.4, 127.4, 127.4, 127.4, 127.4, 127.5, 127.5, 127.5, 127.5, 127.7, 127.7, 127.7, 127.8, 127.8, 127.8, 127.8, 127.9, 128.0, 128.1, 128.1, 128.2, 128.2, 128.2, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 129.5, 129.5, 129.6, 129.6, 129.6, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 133.1, 133.2, 137.7, 137.7, 137.8, 137.9, 138.0, 138.0, 138.2, 159.2, 165.1, 165.2; HRMS (Waters Synapt G2): m/z calcd for $[C_{89}H_{94}O_{20}+Na]^+$: 1482.6338; Found: 1482.6330.

(Pent-4-enyl)-2-*O*-(4-methoxybenzyl)-3-*O*-benzyl-5-*O*-(2-*O*-benzyl-3-*O*-(3,5-di-*O*-benzyl-α-D-arabinofuranosyl)-5-*O*-(3,5-di-*O*-benzyl-α-D-arabinofuranosyl)-α-D-arabino-furanosyl)-α-D-arabinofuranoside (**25b**):



$[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.3) +107.4°; IR (cm^{-1}, $CHCl_3$): 3441, 3032, 2922, 1604, 1507, 1454, 1250, 1101, 742; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.67 (quintet, *J* = 6.8 Hz, 2H), 2.12 (q, *J* = 7.0 Hz, 2H), 3.33 (bs, 1H), 3.38 (dt, *J* = 9.6, 6.6 Hz, 2H), 3.44 (dt, *J* = 10.4, 3.0 Hz, 2H), 3.51 – 3.62 (m, 2H), 3.63 – 3.75 (m, 3H), 3.77 (s, 3H), 3.81 – 3.88 (m, 3H), 3.94 (dd, *J* = 11.7, 3.7 Hz, 1H), 3.99 – 4.08 (m, 3H), 4.09 – 4.18 (m, 5H), 4.20 – 4.30 (m, 2H), 4.33 (dd, *J* = 6.6, 3.2 Hz, 1H), 4.43 (s, 2H), 4.46 (s, 1H), 4.37 – 4.63 (m, 6H), 4.51 (s, 2H), 4.54 (d, *J* = 2.3 Hz, 2H), 4.97 (s, 1H), 4.91 – 5.05 (m, 2H), 5.06 (s, 1H), 5.08 (s, 1H), 5.14 (s, 1H), 5.81 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 6.84 (d, *J* = 8.6 Hz, 2H), 7.07 – 7.83 (m, 32H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.7, 30.2, 55.2, 65.5, 65.8, 66.8, 69.6, 69.7, 71.7, 71.7, 71.8, 71.8, 72.2, 73.5, 73.5, 78.3, 78.4, 79.0, 79.8, 80.8, 82.3, 82.9, 83.1, 84.5, 84.8, 87.5, 88.2, 106.0, 106.0, 107.5, 109.1, 113.8, 114.8, 127.5, 127.6, 127.6, 127.6, 127.7, 127.7, 127.7, 127.7, 127.7, 127.7, 127.7, 127.7, 127.8, 127.9, 127.9, 127.9, 127.9, 128.2, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 129.4, 129.7, 129.7, 137.2, 137.3, 137.5, 137.8, 137.8, 137.9, 138.1, 159.3; HRMS (Waters Synapt G2): m/z calcd for $[C_{75}H_{86}O_{18}+Na]^+$: 1297.5712; Found: 1297.5710.

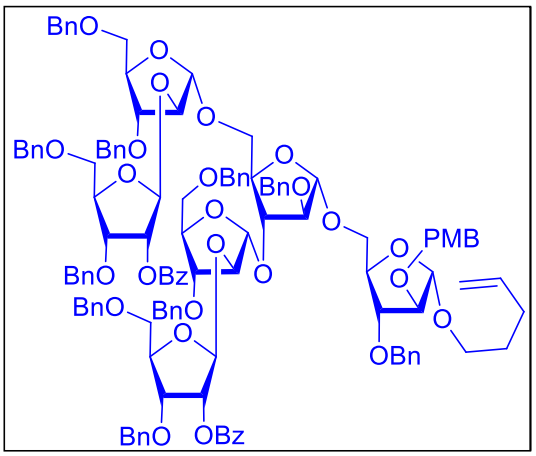
3,6-Di-*O*-benzoyl-4-*O*-(2,3,6-tri-O-benzoyl-4-O-(2,3,4,6-tetra-O-benzoyl-α-D-glucopyranosyl)-α-D-glucopyranosyl)-β-D-(prop-2-yn-1-yl)-1,2-orthobenzoate (**38g**):



$[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) +89.0°; IR (cm^{-1}, $CHCl_3$): 3301, 3065, 2970, 2114, 1728, 1640, 1451, 1267, 1101, 707; ^1H NMR (399.78 MHz, $CDCl_3$): δ 2.18 (d, *J* = 1.9 Hz, 1H), 2.91 – 3.01 (m, 1H), 3.11 – 3.19 (m, 1H), 3.89 (d, *J* = 7.8 Hz, 1H), 4.09 – 4.17 (m, 2H), 4.22 – 4.59 (m, 7H), 4.78 (q, *J* = 8.4 Hz, 2H), 5.07 (dd, *J* = 10.3, 3.9 Hz, 1H), 5.22 (dd, *J* = 10.6, 3.9 Hz, 1H), 5.32 – 5.39 (m, 1H), 5.65 (t, *J* = 9.8 Hz, 1H), 5.83 (d, *J* = 3.7 Hz, 1H), 5.94 (d, *J* = 5.2 Hz, 1H), 6.01 – 6.19 (m, 3H), 6.79 – 7.57

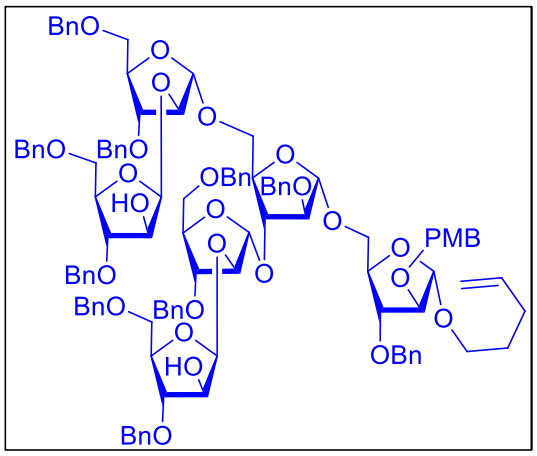
(m, 32H), 7.55 – 8.11 (m, 18H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 51.8, 62.3, 63.3, 63.6, 67.5, 67.9, 68.9, 69.1, 69.2, 69.8, 70.8, 71.0, 71.7, 72.4, 72.9, 73.0, 73.7, 78.9, 94.0, 97.0, 97.6, 121.3, 126.7-130.2 (50C), 132.8, 133.0, 133.0, 133.1, 133.2, 133.2, 133.3, 133.3, 133.6, 133.6, 164.7, 164.8, 165.0, 165.5, 165.7, 165.7, 165.9, 166.0, 166.1; HRMS (Waters Synapt G2) : m/z calcd for $[C_{91}H_{74}O_{26}+Na]^+$: 1605.4366; Found: 1605.4385.

(Pent-4-enyl)-2-*O*-(4-methoxybenzyl)-3-*O*-benzyl-5-*O*-(2-*O*-benzyl-3-*O*-(2-*O*-(2-*O*-Pent-4-enyl-2-*O*-(4-methoxybenzyl)-3-*O*-benzyl-5-*O*-(2-*O*-benzyl-3-*O*-(2-*O*-(3,5-di-*O*-benzyl-β-D-ribo-furanosyl)-3,5-di-*O*-benzyl-α-D-arabino-furanosyl)-5-*O*-(2-*O*-(3,5-di-*O*-benzyl-β-D-ribofuranosyl)-3,5-di-*O*-benzyl-α-D-ara-binofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofura-noside: $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.4) +58.3°; IR



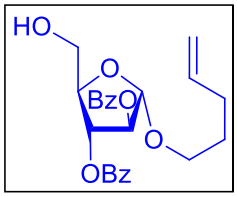
(cm^{-1}, $CHCl_3$): 3030, 2923, 1726, 1591, 1453, 1268, 1106, 771; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.65 (quintet, *J* = 6.7 Hz, 2H), 2.10 (q, *J* = 7.0 Hz, 2H), 3.28 – 3.42 (m, 1H), 3.46 – 3.64 (m, 10H), 3.65 – 3.85 (m, 4H), 3.75 (s, 3H), 3.91 – 4.09 (m, 5H), 4.07 – 4.26 (m, 5H), 4.31 – 4.37 (m, 5H), 4.38 – 4.44 (m, 9H), 4.44 – 4.55 (m, 10H), 4.61 (d, *J* = 2.7 Hz, 2H), 4.64 (d, *J* = 2.5 Hz, 2H), 4.59 – 4.75 (m, 1H), 4.93 (s, 1H), 4.94 – 5.05 (m, 2H), 5.10 (s, 1H), 5.17 (s, 1H), 5.23 (s, 1H), 5.32 (s, 1H), 5.47 (t, *J* = 4.5 Hz, 2H), 5.81 (ddt, *J* = 12.4, 8.9, 3.2 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 2H), 7.13 – 7.34 (m, 52H), 7.37 – 7.47 (m, 4H), 7.55 (q, *J* = 7.2 Hz, 2H), 7.99 – 8.12 (m, 4H); 13C NMR (100.53 MHz, $CDCl_3$): δ 28.7, 30.2, 55.1, 65.8, 66.8, 69.4, 69.4, 69.6, 70.6, 70.7, 71.5, 71.5, 71.7, 71.8, 72.1, 72.9, 72.9, 72.9, 72.9, 72.9, 73.2, 73.2, 73.2, 74.6, 74.6, 76.7, 76.9, 77.3, 77.7, 80.4, 80.4, 81.2, 81.6, 83.1, 83.8, 83.9, 86.0, 86.0, 88.0, 105.0, 105.0, 105.2, 106.0, 106.1, 106.5, 113.7, 113.7, 114.7, 127.5-138.2 (76C), 159.2, 165.3, 165.4; HRMS (Waters Synapt G2): m/z calcd for $[C_{127}H_{134}O_{28}+Na]^+$: 2130.8993; Found: 2130.8545.

Pent-4-enyl-2-*O*-(4-methoxybenzyl)-3-*O*-benzyl-5-*O*-(2-*O*-benzyl-3-*O*-(2-*O*-(3,5-di-*O*-benzyl-β-D-arab-inofuranosyl)-3,5-di-O-benzyl-α-D-arabinofuranosyl)-5-*O*-(2-*O*-(3,5-di-*O*-benzyl-β-D-arabinofuranosyl)-3,5-di-*O*-benzyl-α-D-ara-binofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofuranoside (**4e**): IR (cm^{-1}, $CHCl_3$): 3425, 3070,

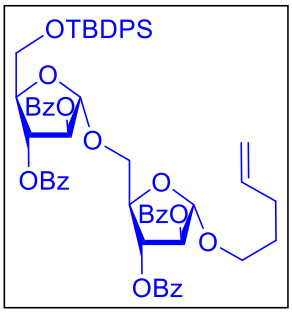


3027, 2927, 2869, 1591, 1452, 1109, 742, 695; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.59 – 1.74 (m, 2H), 2.11 (q, *J* = 7.0 Hz, 2H), 3.21 – 3.62 (m, 9H), 3.63 – 3.88 (m, 9H), 3.76 (s, 3H), 3.88 – 4.28 (m, 14H), 4.26 – 4.69 (m, 23H), 4.73 (d, *J* = 11.9 Hz, 1H), 4.83 – 4.95 (m, 1H), 4.95 (s, 1H), 4.97 (s, 1H), 5.00 (d, *J* = 2.0 Hz, 1H), 5.04 (d, *J* = 1.7 Hz, 1H), 5.07 (s, 1H), 4.99 – 5.21 (m, 1H), 5.12 (s, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 6.79 – 6.88 (m, 2H), 7.16 – 7.43 (m, 52H); ^{13}C NMR (100.53, $CDCl_3$): δ 28.9, 30.4, 55.4, 67.0, 67.0, 69.3, 69.6, 69.9, 71.8, 72.0, 72.1, 72.4, 72.7, 73.2, 73.2, 73.3, 73.4, 73.5, 77.6, 78.1, 78.3, 79.9, 80.0, 80.1, 80.5, 80.6, 81.3, 81.4, 81.7, 82.4, 83.3, 83.5, 83.6, 83.8, 84.2, 86.3, 86.5, 87.9, 88.3, 101.8, 102.0, 105.5, 106.2, 106.2, 106.7, 113.9, 113.9, 114.9, 126.4-138.2 (63C), 138.3, 159.4; HRMS (Waters Synapt G2): m/z calcd for $[C_{113}H_{126}O_{26}+Na]^+$: 1922.8469; Found: 1922.8315.:

(Pent-4-enyl) 2,3-di-*O*-benzoyl-α-D-arabinofuranoside (**11c**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) –32.8°; IR(cm^{-1}, $CHCl_3$): 3512, 3071, 2931, 1723, 1601, 1451, 1265, 1176, 710; ^{1}H NMR (399.78, $CDCl_3$): δ 1.60 – 1.94 (m, 2H), 2.08 – 2.31 (m, 2H), 2.43 (bs, 1H), 3.54 (dt, *J* = 9.5, 6.2 Hz, 1H), 3.79 (dt, *J* = 9.5, 6.6 Hz, 1H), 3.99 (d, *J* = 11.7 Hz, 2H), 4.32 (q, *J* = 4.1 Hz, 1H), 4.89 – 5.08 (m, 2H), 5.23 (s, 1H), 5.40 – 5.48 (m, 1H), 5.53 (d, *J* = 1.3 Hz, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 7.24 – 7.77 (m, 6H), 7.79 – 8.35 (m, 4H); ^{13}C NMR (100.53, $CDCl_3$): δ 28.7, 30.2, 62.3, 66.7, 77.8, 81.7, 83.6, 105.5, 114.9, 128.4, 128.4, 128.5, 128.5, 129.0, 129.1, 129.7, 129.8, 129.9, 129.9, 133.5, 133.5, 138.0, 165.3, 166.1; HRMS (Waters Synapt G2) : m/z calcd for $[C_{24}H_{26}O_7+Na]^+$: 449.1576; Found: 449.1573.

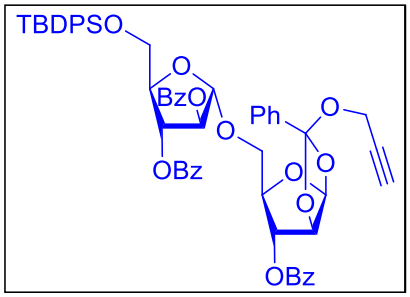


(Pent-4-enyl)-2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benozyl-5-*O*-(*t*-butyldiphenylsilyl)-α-D-arabinofuranosyl)-α-D-arabinofuranoside (**37b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) –12.4°; IR(cm^{-1}, $CHCl_3$): 3070, 2927, 1727, 1594, 1451, 1268, 1115, 715; ^{1}H NMR (399.78, $CDCl_3$): 1.02 (s, 9H), 1.68 – 1.80 (m, 2H), 2.12 – 2.23 (m, 2H), 3.52 (dt, *J* = 9.0, 5.9 Hz, 1H), 3.79 (dt, *J* = 9.2, 6.5 Hz, 1H), 3.93

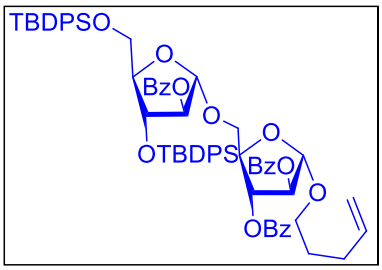


(dd, *J* = 11.2, 2.5 Hz, 1H), 3.99 (d, *J* = 4.4 Hz, 1H), 4.20 (dt, *J* = 11.1, 6.5 Hz, 1H), 4.33 (d, *J* = 2.3 Hz, 1H), 4.48 (d, *J* = 3.9 Hz, 1H), 4.51 (dd, *J* = 10.5, 5.9 Hz, 1H), 4.92 – 5.06 (m, 2H), 5.22 (s, 1H), 5.38 (s, 1H), 5.51 (s, 1H), 5.58 (s, 1H), 5.63 (s, 1H), 5.64 (s, 1H), 5.81 (ddt, *J* = 16.8, 10.1, 6.5 Hz, 1H), 7.14 – 7.80 (m, 22H), 7.87 – 8.19 (m, 8H); 19.2, 26.7, 26.7, 26.7, 28.7, 30.3, 63.3, 66.1, 66.6, 72.4, 77.5, 81.7, 81.8, 82.1, 83.2, 105.6, 105.9, 114.9, 127.5-133.3 (30C) , 135.6, 135.6, 135.6, 135.7, 135.9, 135.9, 138.1, 165.2, 165.4, 165.5, 165.6; HRMS (Waters Synapt G2) : m/z calcd for $[C_{59}H_{60}O_{31}Si+Na]^+$: 1027.3701; Found: 1027.3711.

3-*O*-Benzoyl-5-*O*-(2,3-di-*O*-benozyl-5-*O*-(*t*-butyldiphenylsilyl)-α-D-arabinofuranosyl)-α-D-arabinofuranoside (prop-2-yn-1-yl)-1,2-*O*-orthobenzoate (**38b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) −18.9°; IR(cm^{-1}, $CHCl_3$): 3434, 3070, 2931, 1721, 1588, 1264, 1107, 706; ^1H NMR (399.78, $CDCl_3$): δ 1.01 (s, 9H), 2.37 (t, *J* = 2.5 Hz, 1H), 3.51 (dd, *J* = 10.4, 7.5 Hz, 1H), 3.72 – 3.80 (m, 1H), 3.90 – 3.96 (m, 1H), 3.96 – 4.02 (m, 1H), 4.26 (q, *J* = 4.4 Hz, 1H), 4.34 (d, *J* = 2.2 Hz, 1H), 4.44 – 4.56 (m, 1H), 4.61 (t, *J* = 7.4 Hz, 1H), 5.05 (s, 1H), 5.12 (d, *J* = 4.3 Hz, 1H), 5.34 – 5.45 (m, 1H), 5.50 – 5.68 (m, 2H), 6.36 (d, *J* = 4.3 Hz, 1H), 7.10 – 7.75 (m, 24H), 7.86 – 8.22 (m, 6H); ^{13}C NMR (100.53, $CDCl_3$): δ 19.3, 26.8, 26.8, 26.8, 52.0, 63.2, 66.8, 73.8, 77.2, 77.9, 79.4, 82.2, 83.2, 85.0, 85.4, 105.9, 106.8, 122.6, 126.5, 126.5, 127.7, 127.7, 127.7, 127.7, 127.8, 128.0, 128.0, 128.3, 128.4, 128.4, 128.5, 128.5, 128.5, 128.6, 128.6, 129.7, 129.7, 129.9, 129.9, 130.0, 130.0, 130.0, 130.0, 130.0, 133.2, 133.3, 133.5, 133.6, 135.6, 135.7, 135.7, 135.7, 135.7, 136.0, 165.3, 165.4, 165.7; HRMS (Waters Synapt G2) : m/z calcd for $[C_{57}H_{54}O_{13}Si+Na]^+$: 997.3231; Found: 997.3238.

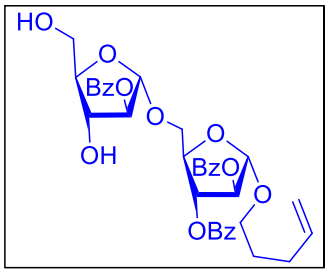


Pent-4-enyl 2,3-di-*O*-benzoyl-5-*O*-(2-*O*-benzoyl-3,5-di-*O*-((*t*-butyldiphenyl)silyl)-α-D-arabinofuranosyl)-α-D-arabinofuranoside (**22e**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) 27.8°; IR (cm^{-1}, $CHCl_3$): 3067, 2932, 2114, 1726, 1642, 1454, 1264, 1109, 705; ^1H NMR (399.78 MHz, $CDCl_3$): δ 0.93 (s, 9H), 0.98 (s, 9H), 1.68 – 1.83 (m, 2H), 2.10 – 2.28 (m, 2H), 3.52 (dt, *J* = 9.6, 6.5 Hz, 1H), 3.59 (dd, *J* = 11.6, 4.6 Hz, 1H), 3.69 (dd, *J* = 11.5, 2.6 Hz, 1H), 3.83 (dt, *J* = 9.5, 6.6 Hz, 1H), 3.93 (dd, *J* = 11.0, 4.1 Hz, 1H), 4.10 (dd, *J* = 11.1,



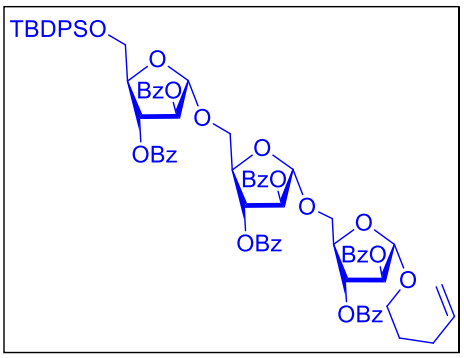
6.1 Hz, 1H), 4.36 (dq, *J* = 6.0, 2.7 Hz, 1H), 4.50 (dd, *J* = 5.9, 2.0 Hz, 1H), 4.56 (q, *J* = 5.1, 4.6 Hz, 1H), 4.90 – 5.07 (m, 2H), 5.10 (s, 1H), 5.23 (s, 1H), 5.32 (d, *J* = 2.0 Hz, 1H), 5.51 (d, *J* = 1.4 Hz, 1H), 5.51 – 5.59 (m, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 7.10 – 7.22 (m, 4H), 7.23 – 7.47 (m, 14H), 7.53 – 7.63 (m, 11H), 7.68 – 7.75 (m, 2H), 8.03 – 8.12 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 19.1, 19.2, 26.7, 26.7, 26.7, 26.7, 26.7, 26.8, 26.8, 28.8, 30.3, 62.7, 66.7, 66.9, 76.9, 77.8, 81.4, 81.9, 84.8, 85.0, 105.7, 106.1, 114.8, 127.5, 127.5, 127.5, 127.6, 127.6, 127.6, 127.6, 127.6, 127.6, 128.0, 128.0, 128.4, 128.4, 128.4, 128.5, 129.3, 129.4, 129.4, 129.5, 129.7, 129.7, 129.7, 129.7, 129.9, 129.9, 129.9, 130.0, 132.7, 132.9, 133.2, 133.2, 133.3, 133.3, 133.5, 135.6, 135.6, 135.7, 135.7, 135.7, 135.7, 135.8, 135.8, 138.2, 165.1, 165.5, 165.6; HRMS (Waters Synapt G2): m/z calcd for $[C_{68}H_{74}O_{12}Si_2+Na]^+$: 1161.4617; Found: 1161.4610.

Pent-4-enyl-2,3-di-*O*-benzoyl-5-*O*-(2-*O*-benzoyl-α-D-arabinofuranosyl)-α-D-arabinofuranoside (**22f**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) 24.4°; IR (cm^{-1}, $CHCl_3$): 3506, 3069, 2930, 1721, 1600, 1451, 1267, 1111, 863; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.68 – 1.80 (m, 2H), 2.12 – 2.23 (m, 2H), 2.21 (bs, 1H), 3.53 (dt, *J* = 9.5, 6.2 Hz, 1H), 3.72 – 3.84 (m, 3H), 3.93 (ddd, *J* = 12.0, 6.4, 3.1 Hz, 2H), 4.14 (d, *J* = 5.0 Hz, 1H), 4.17 (dd, *J* = 10.9, 4.9 Hz, 1H), 4.27 – 4.33 (m, 1H), 4.40 (q, *J* = 4.8 Hz, 1H), 4.92 – 5.04 (m, 2H), 5.15 (d, *J* = 2.4 Hz, 1H), 5.24 (s, 1H), 5.38 (s, 1H), 5.50 (d, *J* = 1.4 Hz, 1H), 5.54 (d, *J* = 5.0 Hz, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 7.36 – 7.49 (m, 5H), 7.50 – 7.72 (m, 4H), 7.98 (dd, *J* = 8.2, 1.2 Hz, 2H), 8.06 (d, *J* = 7.8 Hz, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.7, 30.2, 62.0, 65.8, 66.8, 76.5, 77.3, 81.6, 81.9, 84.4, 86.0, 105.1, 105.6, 114.9, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.9, 129.0, 129.1, 129.7, 129.7, 129.8, 129.8, 129.9, 129.9, 133.5, 133.5, 133.6, 138.0, 165.4, 165.9, 166.5; HRMS (Waters Synapt G2): m/z calcd for $[C_{36}H_{38}O_{12}+Na]^+$: 685.2261; Found: 685.2255.

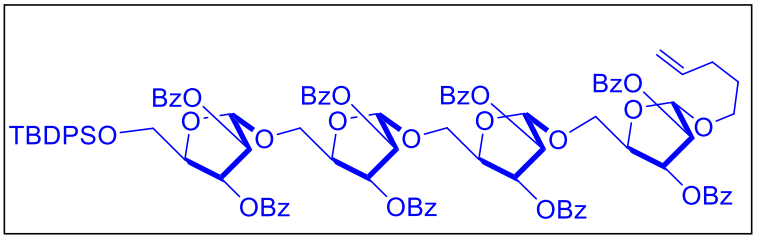


Pent-4-enyl-2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-((*t*-butyl-diphenyl)silyl)-α-D-arabinofurano-syl)-α-D-arabinofuranosyl)-α-D-arabinofuranoside (**7b**) : $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +5.0°; IR (cm^{-1}, $CHCl_3$): 3030, 2928, 1725, 1455, 1268, 1030; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.00 (s, 9H), 1.62 – 1.80 (m, 2H), 2.07 – 2.25 (m, 2H), 3.38 (d, *J* = 2.9 Hz, 1H), 3.49 (dt, *J* = 9.6, 6.2 Hz, 1H), 3.76

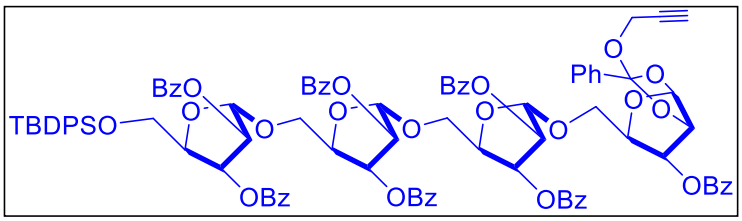
(dt, *J* = 9.5, 6.6 Hz, 1H), 3.91 (dt, *J* = 11.2, 2.4 Hz, 2H), 3.96 (d, *J* = 4.6 Hz, 2H), 4.18 (dt, *J* = 10.6, 5.0 Hz, 2H), 4.42 (q, *J* = 4.6 Hz, 1H), 4.48 (q, *J* = 4.6 Hz, 1H), 4.62 (q, *J* = 4.1 Hz, 1H), 4.88 – 5.13 (m, 2H), 5.20 (s, 1H), 5.38 (d, *J* = 3.5 Hz, 2H), 5.49 (d, *J* = 1.1 Hz, 1H), 5.55 (d, *J* = 1.1 Hz, 1H), 5.57 – 5.68 (m, 3H), 5.80 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 7.18 – 7.60 (m, 24H), 7.64 – 7.72 (m, 4H), 7.85 – 8.05 (m, 12H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 19.2, 26.7, 26.7, 26.7, 28.7, 30.3, 63.3, 65.8, 66.0, 66.6, 66.6, 77.3, 81.5, 81.8, 81.8, 82.1, 82.1, 82.1, 83.1, 105.6, 105.8, 105.9, 114.9, 127.6, 127.6, 127.6, 127.6, 127.6, 127.6, 128.2, 128.2, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 129.0, 129.0, 129.1, 129.2, 129.2, 129.3, 129.6, 129.6, 129.7, 129.7, 129.8, 129.8, 129.8, 129.8, 129.8, 129.9, 129.9, 129.9, 130.1, 133.0, 133.1, 133.2, 133.3, 133.3, 133.4, 135.6, 135.6, 135.6, 135.6, 138.1, 165.1, 165.2, 165.4, 165.4, 165.6, 165.6; HRMS (Waters Synapt G2): m/z calcd for $[C_{78}H_{76}O_{19}Si+Na]^+$: 1367.4648; Found: 1367.4634.



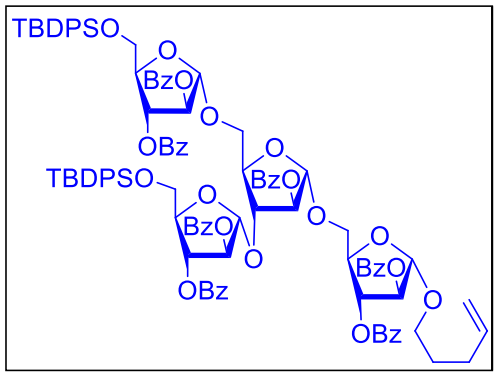
Pent-4-enyl-2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(*t*-butyldiphenylsilyl)-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofuranoside (**6b**) : $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) +2.4°; IR (cm^{-1}, $CHCl_3$): 3068, 2933, 1724, 1599, 1452, 1266, 1109, 708; ^{1}H NMR (399.78 MHz, $CDCl_3$): 0.99 (s, 9H), 1.79 – 1.65 (m, 2H), 2.21 – 2.09 (m, 2H), 3.50 (dt, *J* = 9.5, 6.2 Hz, 1H),3.76 (dt, *J* = 9.5, 6.6 Hz, 1H), 3.98 – 3.85 (m, 6H), 4.17 (ddd, *J* = 14.7, 7.9, 3.2 Hz, 3H), 4.42 (dd, *J* = 7.6, 4.5 Hz, 1H), 4.47 (q, *J* = 4.5 Hz, 1H), 4.64 – 4.56 (m, 2H), 5.04 – 4.90 (m, 2H), 5.21 (s, 1H), 5.35 (s, 1H), 5.39 (s, 1H), 5.40 (s, 1H), 5.48 (t, *J* = 2.1 Hz, 1H), 5.53 (t, *J* = 4.0 Hz, 1H), 5.65 – 5.59 (m, 5H), 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 7.59 – 7.19 (m, 30H), 7.67 (m, 4H), δ 8.06 – 7.86 (m, 16H); ^{13}C NMR (100.53 MHz, $CDCl_3$): 19.4, 26.9, 26.9, 26.9, 28.9, 30.4, 60.6, 63.4, 65.8, 65.9, 66.0, 66.8, 66.8, 77.3, 77.4, 81.7, 81.7, 81.9, 81.9, 82.1, 82.1, 82.3, 83.2, 105.7, 105.9, 106.0, 106.0, 115.0, 127.8–130.1 (50C), 133.2, 133.3, 133.3, 133.3, 133.5, 133.5, 133.5, 133.5, 135.8, 135.8, 138.2, 165.3, 165.3, 165.4, 165.6, 165.6,



165.7, 165.7, 165.8; HRMS (Waters Synapt G2): m/z calcd for $[C_{97}H_{92}O_{25}Si+Na]^+$: 1708.5628; Found: 1708.5620.

3-*O*-Benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(*t*-butyldiphenylsilyl)-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofuranoside prop-2-ynyl 1,2-O-orthobenzoate (**6a**) : 

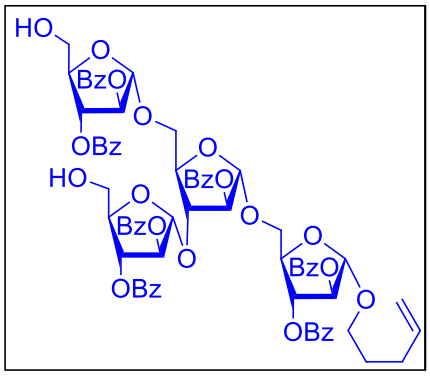
$[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) –2.1°; IR (cm^{-1}, $CHCl_3$): 3302, 3071, 2927, 2105, 1725, 1596, 1454, 1265, 1107, 708; ^1H NMR (399.78 MHz, $CDCl_3$): HRMS (Waters Synapt G2): m/z calcd for $[C_{78}H_{76}O_{19}Si+Na]^+$: 1678.5158; Found: 1678.5206.

Pent-4-enyl-2,3-di-*O*-benzoyl-5-*O*-(2-*O*-benzoyl-3-*O*-(2,3-di-*O*-benzoyl-5-*O*-((*t*-butyldiphenyl)silyl)-α-D-arabinofurano-syl)-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-((*t*-butyl-diphenyl)silyl)-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofura-noside (**24c**): 

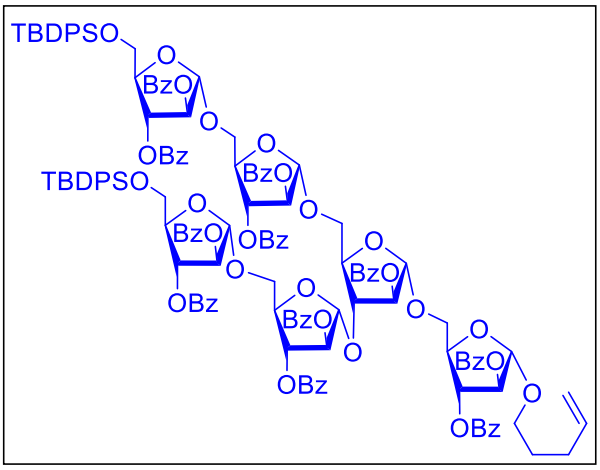
$[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +11.7; IR (cm^{-1}, $CHCl_3$): 3293, 3071, 2974, 1723, 1594, 1450, 1268, 1107, 717; ^1H NMR (399.78 MHz, $CDCl_3$): δ 0.92 (s, 9H), 0.97 (s, 9H), 1.64 – 1.77 (m, 2H), 2.15 (dd, *J* = 8.9, 4.7 Hz, 2H), 3.48 (dt, *J* = 9.5, 6.2 Hz, 1H), 3.76 (dt, *J* = 9.6, 6.6 Hz, 1H), 3.86-3.90 (m, 6H), 4.05 (dd, *J* = 11.5, 4.6 Hz, 1H), 4.16 (dd, *J* = 11.2, 4.7 Hz, 1H), 4.31 – 4.40 (m, 2H), 4.40 (q, *J* = 4.6 Hz, 1H), 4.46 (d, *J* = 6.1 Hz, 1H), 4.51-4.54 (m, 1H), 4.85 – 5.05 (m, 2H), 5.18 (s, 1H), 5.30 (s, 1H), 5.37 (s, 1H), 5.42 (d, *J* = 1.2 Hz, 1H), 5.47 (dd, *J* = 4.2, 1.3 Hz, 2H), 5.52 (d, *J* = 1.2 Hz, 1H), 5.57 (td, *J* = 11.2, 10.2, 5.3 Hz, 4H), 5.79 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 7.11 – 7.57 (m, 34H), 7.56 – 7.73 (m, 7H), 7.75 – 8.08 (m, 14H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 19.2, 19.2, 26.6, 26.6, 26.7, 26.7, 26.7, 26.7, 28.7, 30.3, 63.2, 63.2, 65.8, 65.8, 66.7, 77.1, 77.1, 80.9, 81.8, 81.9, 81.9, 81.9, 82.0, 82.2, 82.6, 83.4, 83.7, 105.5, 105.5, 105.8, 106.1, 114.8, 127.6, 127.6, 127.6, 127.6, 127.6, 127.6, 127.6, 127.6, 127.6, 128.2, 128.2, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 129.0, 129.2, 129.2, 129.2, 129.3, 129.3, 129.5, 129.6, 129.6, 129.6, 129.7, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 129.8, 129.8, 129.9, 129.9, 130.0, 130.0, 133.0, 133.1, 133.1, 133.2, 133.2,

133.2, 133.4, 135.5, 135.5, 135.5, 135.6, 135.6, 135.6, 135.6, 135.6, 135.6, 135.6, 135.6, 138.1, 164.9, 165.1, 165.3, 165.3, 165.4, 165.5, 165.5; HRMS (Waters Synapt G2): m/z calcd for $[C_{106}H_{106}O_{24}Si_2+Na]^+$: 1841.6510; Found: 1841.6533.

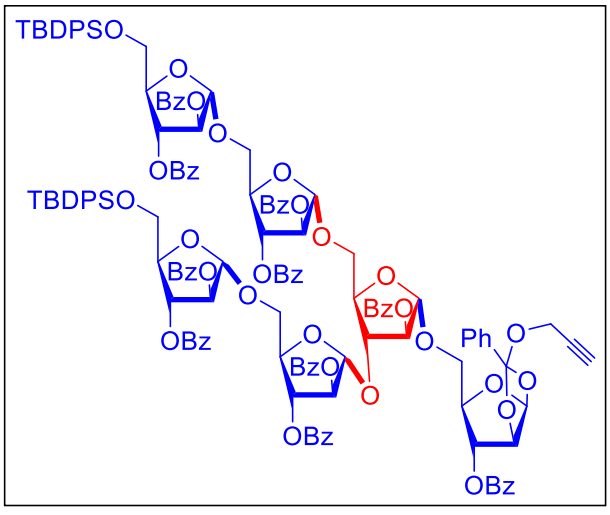
Pent-4-enyl-2,3-di-*O*-benzoyl-5-*O*-(2-*O*-benzoyl-3-*O*-(2,3-di-*O*-benzoyl-α-D-arabinofuranosyl)-5-*O*-(2,3-di-*O*-benzoyl-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofuranoside: $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.5) −15.3°; IR (cm^{-1}, $CHCl_3$): 3293, 3071, 2974, 1723, 1594, 1450, 1268, 1107, 717; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.63 – 1.79 (m, 2H), 2.07 – 2.22 (m, 2H), 2.72 (s, 2H), 3.37 (d, *J* = 3.0 Hz, 1H), 3.46 – 3.55 (m, 1H), 3.73 – 3.85 (m, 2H), 3.85 – 3.93 (m, 3H), 3.99 (ddd, *J* = 11.4, 7.2, 3.6 Hz, 2H), 4.17 (dd, *J* = 11.2, 4.5 Hz, 1H), 4.30 (q, *J* = 5.0 Hz, 1H), 4.38 (dq, *J* = 13.5, 4.7 Hz, 2H), 4.46 – 4.56 (m, 2H), 4.86 – 5.06 (m, 2H), 5.18 (dd, *J* = 5.0, 1.5 Hz, 1H), 5.21 (s, 1H), 5.25 (d, *J* = 4.5 Hz, 1H), 5.31 (s, 1H), 5.35 (s, 1H), 5.37 (s, 1H), 5.43 (d, *J* = 1.7 Hz, 1H), 5.45 (d, *J* = 1.2 Hz, 1H), 5.51 (d, *J* = 1.4 Hz, 1H), 5.57 (d, *J* = 1.2 Hz, 1H), 5.62 (d, *J* = 5.0 Hz, 1H), 5.80 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 7.14 – 7.65 (m, 21H), 7.82 – 8.11 (m, 14H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.7, 30.3, 62.6, 62.7, 64.9, 65.7, 66.7, 77.1, 77.9, 78.0, 80.7, 81.0, 81.5, 81.5, 81.8, 81.9, 82.7, 84.0, 84.1, 105.1, 105.3, 105.5, 105.6, 114.9, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.5, 128.9, 128.9, 129.0, 129.0, 129.1, 129.2, 129.3, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 129.8, 129.8, 129.8, 129.8, 129.8, 129.8, 129.9, 133.3, 133.4, 133.4, 133.4, 133.4, 133.4, 133.5, 138.1, 164.7, 165.1, 165.4, 165.5, 165.6, 166.1, 166.1; HRMS (Waters Synapt G2): m/z calcd for $[C_{74}H_{70}O_{24}+Na]^+$: 1365.4155; Found: 1365.4120.



Pent-4-enyl 2,3-di-*O*-benzoyl-5-*O*-(2-*O*-benzoyl-3-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-((*t*-butyldiphenyl)-silyl)-α-D-arabinofurano-syl)-α-D-arabinofuranosyl)-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-((*t*-butyldiphenyl)-silyl)-α-D-arabinofuranosyl)-α-D-ara-binofura-nosyl)-α-D-arabinofurano-syl)-α-D-ara-binofuranoside (**5b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.7) +10.2°; IR (cm^{-1}, $CHCl_3$): 3071, 2928, 1726, 1591, 1454, 1265, 1108, 708; ^1H NMR (399.78 MHz, $CDCl_3$): δ 0.96 (s, 9H), 0.98 (s, 9H), 1.63 – 1.77 (m, 2H), 2.06 – 2.22 (m, 2H), 3.21 – 3.37 (m, 1H), 3.36 – 3.39 (m, 2H), 3.42 – 3.55 (m, 3H), 3.68 – 4.07 (m, 9H), 4.13 (dt, *J* = 10.6, 5.2 Hz, 3H), 4.30 – 4.58 (m, 4H), 4.84 – 5.07 (m, 2H), 5.19 (s, 1H), 5.22 (s, 1H), 5.31 (d, *J* = 3.4 Hz, 2H), 5.36 (s, 1H), 5.43 (d, *J* = 1.3 Hz, 1H), 5.46 (d, *J* = 1.2 Hz, 1H), 5.51 (d, *J* = 1.5 Hz, 2H), 5.52 (d, *J* = 1.3 Hz, 1H), 5.54 (d, *J* = 0.9 Hz, 1H), 5.55 – 5.63 (m, 3H), 5.79 (ddt, *J* = 16.9, 10.3, 6.7 Hz, 1H), 7.15 – 7.61 (m, 45H), 7.60 – 7.73 (m, 6H), 7.79 – 8.09 (m, 24H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 19.2, 19.2, 26.7, 26.7, 26.7, 26.7, 26.7, 26.7, 28.7, 30.3, 63.1, 63.3, 65.6, 65.7, 65.8, 66.7, 66.7, 74.9, 75.1, 77.2, 81.3, 81.5, 81.7, 81.8, 81.9, 81.9, 82.0, 82.1, 82.4, 82.4, 82.5, 82.6, 82.6, 83.0, 83.1, 105.3, 105.5, 105.8, 105.9, 105.9, 106.0, 114.8, 127.6-129.9 (75C), 133.0, 133.1, 133.1, 133.2, 133.2, 133.2, 133.2, 133.2, 133.2, 133.2, 133.4, 135.6 (4C), 138.1, 164.8, 165.0, 165.0, 165.1, 165.3, 165.4, 165.4, 165.5, 165.5, 165.5, 165.5; HRMS (Waters Synapt G2): m/z calcd for $[C_{144}H_{136}O_{36}Si_2+Na]^+$: 2522.8438; Found: 2522.8486.

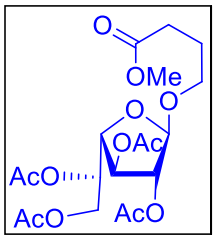


Propargyl 1,2-*O*-orthobenozoate 3-*O*-benzoyl-5-*O*-(2-*O*-benzoyl-3-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-O-benzoyl-5-O-((*t*-butyldiphenyl)-silyl)-α-D-ara-binofurano-syl)-α-D-arabinofurano-syl)-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-((*t*-butyldi-phenyl)-silyl)-α-D-

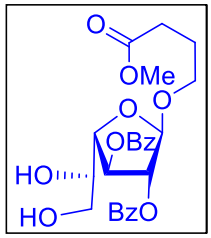


arabinofurano-syl)-α-D-arabinofurano-syl)-α-D-arabinofura-nosyl)-α-D-arabino-furanoside (**5b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) –31.8°; IR (cm^{-1}, $CHCl_3$): 3297, 3067, 2926, 1726, 1596, 1456, 1265, 1107, 707; HRMS (Waters Synapt G2): m/z calcd for $[C_{19}H_{28}O_{12}+Na]^+$: 2492.7968; Found: 2492.7959.

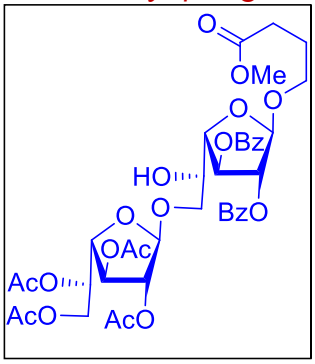
(3-(Methoxycarbonyl)propyl)-2,3,5,6-tetra-*O*-acetyl-β-L-galactofuranoside (**41**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) –31.8; IR (cm^{-1}, $CHCl_3$): 2945, 1742, 1229, 1050, 754; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.81 (q, *J* = 6.6, 6.0 Hz, 2H), 1.97 (s, 3H), 2.00 (s, 3H), 2.01 (s, 3H), 2.04 (s, 3H), 2.32 (t, *J* = 7.3 Hz, 2H), 3.39 (dt, *J* = 9.8, 5.9 Hz, 1H), 3.58 (s, 3H), 3.59 – 3.64 (m, 1H), 4.06 – 4.17 (m, 2H), 4.24 (dd, *J* = 11.8, 4.4 Hz, 1H), 4.85 – 4.94 (m, 3H), 5.19 – 5.43 (m, 1H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 20.5, 20.6, 20.6, 20.7, 24.6, 30.4, 51.4, 62.5, 66.2, 69.1, 76.4, 79.8, 81.2, 105.2, 169.5, 169.9, 169.9, 170.4, 173.5; HRMS (Waters Synapt G2): m/z calcd for $[C_{19}H_{28}O_{12}+Na]^+$: 471.1478; Found: 471.1478.



(3-(Methoxycarbonyl)-propyl)-2,3,-di-*O*-benzoyl-β-L-galactofuranoside (**11d**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.7) +28.9°; IR (cm^{-1}, $CHCl_3$): 3116, 2938, 1721, 1591, 1448, 1265, 1112, 712; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.88 (quintet, *J* = 6.8 Hz, 2H), 2.37 (t, *J* = 7.4 Hz, 2H), 2.54 (bs, 1H), 2.85 (d, *J* = 7.1 Hz, 1H), 3.42 – 3.55 (m, 1H), 3.56 (s, 3H), 3.64 – 3.82 (m, 3H), 4.03 (bs, 1H), 4.19 – 4.29 (m, 1H), 5.15 (s, 1H), 5.39 (s, 1H), 5.51 (d, *J* = 4.7 Hz, 1H), 7.30 – 7.42 (m, 4H), 7.44 – 7.59 (m, 2H), 7.90 – 8.04 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 24.9, 30.5, 51.6, 64.0, 66.2, 70.7, 77.8, 81.4, 83.7, 105.6, 128.5, 128.5, 128.5, 128.5, 129.0, 129.0, 129.8, 129.8, 129.8, 129.9, 133.5, 133.5, 165.3, 166.0, 173.8; HRMS (Waters Synapt G2): m/z calcd for $[C_{25}H_{28}O_{10}+Na]^+$: 511.1580; Found: 511.1579.

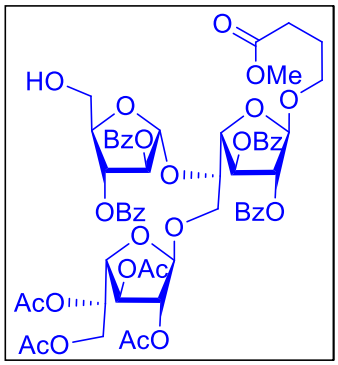


(3-(Methoxycarbonyl)-propyl)2,3-di-*O*-benzoyl-6-*O*-(2,3,5,6-tetra-*O*-acetyl-β-L-gal-actofuranosyl)-β-L-galactofuranoside (**22g**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) –8.6°; IR (cm^{-1}, $CHCl_3$): 3478, 3070, 2927, 1737, 1591, 1447, 1231, 1110, 715; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.95 – 2.02 (m, 2H), 2.05 (s, 7H), 2.08 (s, 3H), 2.13 (s, 3H), 2.48 (t, *J* = 7.4 Hz, 2H), 3.58 (dt, *J* = 9.6, 6.0 Hz, 1H), 3.67 (s, 3H), 3.70 (dd, *J* = 10.5, 7.2 Hz, 1H), 3.81 (dt, *J* = 9.6, 6.3

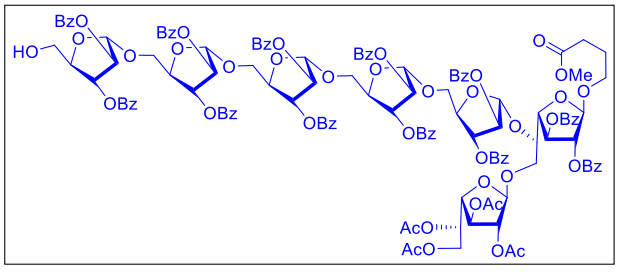


Hz, 1H), 3.86 (dd, *J* = 10.4, 4.5 Hz, 1H), 4.20 (dd, *J* = 11.9, 7.2 Hz, 1H), 4.26 – 4.33 (m, 3H), 4.36 (dd, *J* = 11.9, 4.2 Hz, 1H), 5.02 (dd, *J* = 5.7, 1.8 Hz, 1H), 5.07 (d, *J* = 1.7 Hz, 1H), 5.11 (s, 1H), 5.26 (s, 1H), 5.39 (dt, *J* = 7.6, 4.0 Hz, 1H), 5.48 – 5.49 (m, 1H), 5.66 (d, *J* = 4.1 Hz, 1H), 7.42 – 7.54 (m, 4H), 7.54 – 7.65 (m, 2H), 8.01 – 8.13 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 20.6, 20.7, 20.7, 20.8, 24.9, 30.6, 51.6, 62.7, 66.3, 69.0, 69.3, 69.5, 76.3, 77.8, 80.2, 81.3, 81.5, 83.2, 105.7, 106.0, 128.5, 128.5, 128.5, 128.5, 129.1, 129.2, 129.9, 129.9, 129.9, 129.9, 133.6, 133.6, 165.4, 165.9, 169.7, 170.0, 170.1, 170.6, 173.7; HRMS (Waters Synapt G2): m/z calcd for $[C_{39}H_{46}O_{29}+Na]^+$: 841.2531; Found: 841.2533.

(3-(Methoxycarbonyl)-propyl)2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-α-D-arabino-furanosyl)-6-*O*-(2,3,5,6-tetra-*O*-acetyl-β-L-galactofura-noside: $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) –9.7°; IR (cm^{-1}, $CHCl_3$): 3393, 2924, 1727, 1591, 1449, 1261, 1107, 715; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.94 (s, 3H), 1.97 (s, 3H), 1.99 (s, 3H), 1.99 (m, 2H), 2.07 (s, 3H), 2.40 – 2.53 (m, 3H), 3.55 (dt, *J* = 9.8, 6.0 Hz, 1H), 3.64 (s, 3H), 3.71 – 3.85 (m, 2H), 3.88-3.99 (m, 3H), 4.13 (dd, *J* = 11.9, 7.5 Hz, 1H), 4.26 – 4.33 (m, 2H), 4.40 (m, 2H), 4.42 – 4.48 (m, 1H), 4.94 (dd, *J* = 6.1, 2.2 Hz, 1H), 5.01 (d, *J* = 2.1 Hz, 1H), 5.02 (s, 1H), 5.24 (s, 1H), 5.33 (dt, *J* = 7.5, 3.8 Hz, 1H), 5.46 (dd, *J* = 5.6, 2.1 Hz, 1H), 5.48 (d, *J* = 1.8 Hz, 1H), 5.55 (d, *J* = 2.0 Hz, 1H), 5.70 (dd, *J* = 5.2, 1.6 Hz, 1H), 5.72 (s, 1H), 7.28 – 7.60 (m, 10H), 7.68 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.90 – 8.10 (m, 8H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 20.5, 20.5, 20.6, 20.8, 24.8, 30.6, 51.5, 62.2, 62.7, 66.3, 67.2, 69.1, 75.4, 76.3, 77.0, 77.2, 77.3, 79.8, 81.2, 82.3, 82.3, 83.0, 105.3, 105.7, 106.6, 127.8, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 129.1, 129.1, 129.1, 129.1, 129.2, 129.8, 129.8, 129.8, 129.9, 129.9, 129.9, 129.9, 129.9, 133.3, 133.3, 133.4, 133.4, 165.2, 165.6, 165.7, 165.9, 169.6, 170.0, 170.0, 170.5, 173.7; HRMS (Waters Synapt G2): m/z calcd for $[C_{58}H_{62}O_{25}+Na]^+$: 1181.3478; Found: 1181.4769.

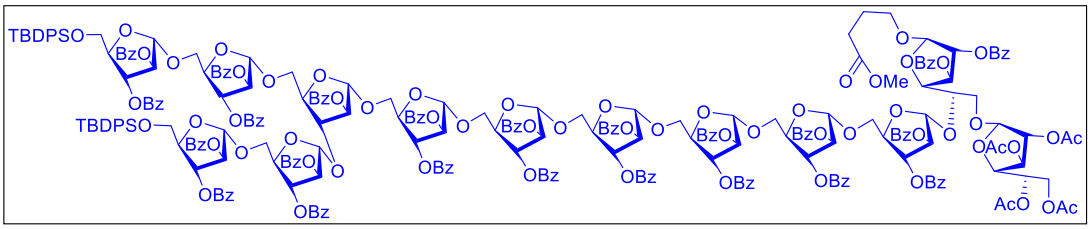


(3-(Methoxycarbonyl)-propyl) 2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*- (2,3-di-*O*-benzoyl-α-D-arabinofurano-syl)-α-D-arabinofuranosyl)-α-D-



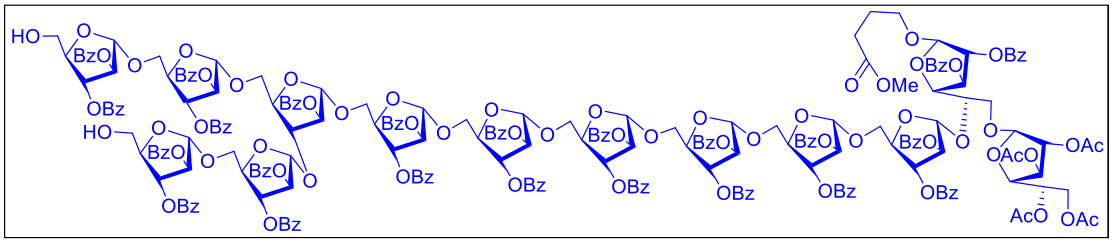
arabinofurano-syl)-α-D-ara-binofuranosyl)-α-D-ara-binofuranosyl)-6-*O*-(2,3,5,6-tetra-*O*-acetyl-β-D-galactofuranosyl)-β-D-galactofuranoside (**42b**) $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +3.9°; IR (cm^{-1}, $CHCl_3$): 3333, 2925, 1725, 1591, 1451, 1263, 1108, 711; HRMS (Waters Synapt G2) : m/z calcd for $[C_{50}H_{54}O_{10}+Na]^+$: 2542.7298; Found: 2542.7332.

(3-(Methoxycarbonyl)-propyl) 2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2-*O*-benzoyl-3-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-



benzoyl-5-*O*-(*t*-butyldiphenylsilyl)-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(*t*-butyldiphenylsilyl)-α-D-ara-binofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofurano-syl)-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)a-D-arabinofuranosyl)-α-D-ara-binofuranosyl)-α-D-arabinofuranosyl)-6-*O*-(2,3,5,6-tetra-*O*-acetyl-β-D-galactofura-nosyl)-β-D-galactofuranoside (**42b**) $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.8) +12.9°; IR (cm^{-1}, $CHCl_3$): 3060, 2927, 1726, 1591, 1452, 1269, 1108, 710; HRMS (Waters Synapt G2) : m/z calcd for $[C_{273}H_{254}O_{84}Si_2+Na]^+$: 4956.5107; Found: 4956.5207.

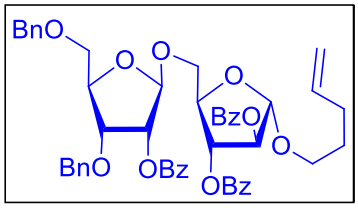
(3-(Methoxycarbonyl)-propyl) 2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-



O-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2-*O*-benzoyl-3-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-5-*O*-(2,3-di-*O*-benzoyl-5-*O*-(2,3-di-*O*-benzoyl-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofura-nosyl)-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-α-D-arabinofurano-syl)-α-D-arabinofuranosyl)-α-D-arabinofuranosyl)-6-*O*-(2,3,5,6-tetra-*O*-acetyl-β-D-galactofuranosyl)-β-D-galactofuranoside (**42b**) $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.8) +12.9°; IR (cm^{-1},

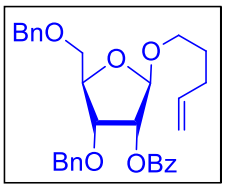
$CHCl_3$): 3060, 2927, 1726, 1591, 1452, 1269, 1108, 710; 3420, 3029, 2925, 1600, 1454, 1361, 1065, 741; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.89 (s, 3H), 1.95 (s, 3H), 1.90 – 2.04 (m, 2H), 1.98 (s, 3H), 2.06 (s, 3H), 2.48 (t, J = 7.5 Hz, 2H), 3.54 (dt, J = 9.8, 6.2 Hz, 2H), 3.64 (s, 3H), 3.68 – 4.07 (m, 18H), 4.06 – 4.21 (m, 7H), 4.24 – 4.32 (m, 2H), 4.32 – 4.37 (m, 2H), 4.38 – 4.54 (m, 7H), 4.52 – 4.65 (m, 6H), 4.94 (dd, J = 5.9, 2.0 Hz, 1H), 4.98 (d, J = 2.2 Hz, 1H), 5.04 (s, 1H), 5.23 (s, 1H), 5.27 (s, 1H), 5.33 (s, 1H), 5.35 (s, 2H), 5.37 (s, 2H), 5.37 – 5.39 (m, 5H), 5.42 (d, J = 1.4 Hz, 1H), 5.45 (d, J = 1.2 Hz, 1H), 5.48 (d, J = 1.5 Hz, 1H), 5.50 (d, J = 1.4 Hz, 1H), 5.52 (s, 1H), 5.53 (s, 1H), 5.55 – 5.57 (m, 3H), 5.58 (s, 1H), 5.60 – 5.64 (m, 3H), 5.62 (s, 8H), 5.67 (d, J = 4.9 Hz, 1H), 5.69 – 5.77 (m, 3H), 7.08 – 7.67 (m, 69H), 7.73 – 8.17 (m, 46H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 20.5, 20.5, 20.6, 20.7, 30.6, 31.9, 51.5, 62.1, 62.2, 62.7, 64.8, 65.4, 65.5, 65.6, 65.6, 65.6, 65.7, 66.3, 66.6, 69.1, 69.1, 75.2, 75.2, 76.3, 76.3, 77.0, 77.0, 77.1, 77.1, 77.1, 77.2, 77.2, 77.2, 77.4, 77.5, 79.9, 80.5, 81.0, 81.1, 81.2, 81.4, 81.4, 81.4, 81.4, 81.4, 81.5, 81.5, 81.5, 81.5, 81.6, 81.9, 82.0, 82.0, 82.2, 82.2, 82.3, 82.4, 82.8, 83.7, 83.8, 83.8, 83.8, 105.3, 105.4, 105.5, 105.5, 105.5, 105.6, 105.7, 105.8, 105.8, 105.8, 105.8, 105.9, 106.7, 128.2-133.5 (138C), 164.7, 164.9, 165.0, 165.0, 165.0, 165.0, 165.0, 165.0, 165.1, 165.2, 165.2, 165.2, 165.4, 165.5, 165.5, 165.5, 165.5, 165.5, 165.6, 165.6, 165.6, 165.8, 165.9, 169.3, 169.9, 170.0, 170.4, 173.7; HRMS (Waters Synapt G2) : m/z calcd for $[C_{241}H_{218}O_{84}+Na]^+$: 4480.2752; Found: 4480.3862 and 2251.6384 (half mass).

(Pent-4-enyl) 2,3-di-*O*-benzyl-5-*O*-(2-*O*-benzoyl 3,5-di-*O*-benzyl β-D-ribofuranosyl)-α-D-arabinofuranoside (**19k**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +46.6°; IR (cm^{-1}, $CHCl_3$): 3069, 3040, 2924, 1725, 1594, 1454, 1268, 1108, 702; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.68 (quintet, *J* = 6.8 Hz, 2H), 2.13 (q, *J* = 7.3 Hz, 2H), 3.39 (dt, *J* = 9.7, 6.5 Hz, 1H), 3.53 (dt, *J* = 10.6, 6.3 Hz, 2H), 3.63 (dd, *J* = 10.5, 3.4 Hz, 1H), 3.72 (dt, *J* = 9.7, 6.6 Hz, 1H), 3.81 (dd, *J* = 7.1, 3.3 Hz, 1H), 3.91 (dd, *J* = 11.1, 3.2 Hz, 1H), 4.01 (dd, *J* = 3.3, 1.3 Hz, 1H), 4.16 (td, *J* = 6.5, 3.2 Hz, 1H), 4.20 (dd, *J* = 7.7, 4.4 Hz, 1H), 4.29 – 4.36 (m, 1H), 4.38 (d, *J* = 11.5 Hz, 1H), 4.49 (dd, *J* = 11.9, 3.5 Hz, 2H), 4.53 (s, 2H), 4.56 (dd, *J* = 11.9, 2.8 Hz, 2H), 4.60 (d, *J* = 11.5 Hz, 1H), 4.92 – 5.07 (m, 2H), 5.00 (s, 1H), 5.12 (s, 1H), 5.51 (d, *J* = 4.4 Hz, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 7.11 – 7.41 (m, 20H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.52 – 7.66 (m, 1H), 8.08 (dd, *J* = 8.3, 1.2 Hz, 2H); ^{13}C NMR (100.53 MHz,

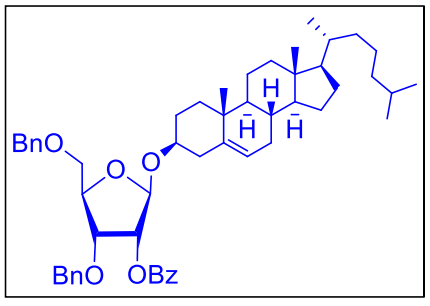


$CDCl_3$): δ 28.7, 30.3, 66.9, 67.5, 71.4, 72.1, 72.1, 73.0, 73.2, 74.3, 78.2, 80.1, 80.6, 83.4, 88.3, 105.5, 106.1, 114.8, 127.5, 127.6, 127.6, 127.7, 127.7, 127.8, 127.8, 127.9, 127.9, 127.9, 127.9, 127.9, 127.9, 127.9, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 129.7, 129.9, 129.9, 133.2, 137.5, 137.8, 138.2, 165.5; HRMS (Waters Synapt G2) : m/z calcd for $[C_{50}H_{54}O_{10}+Na]^+$: 837.3615; Found: 837.3619.

(Pent-4-enyl) 2-*O*-benzoyl 3,5-di-*O*-benzyl-β-D-ribofuranoside (**19l**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +33.3°; IR (cm^{-1}, $CHCl_3$): 3071, 3026, 2925, 2869, 1725, 1592, 1452, 1268, 1113, 702; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.62 (quintet, *J* = 6.9 Hz, 2H), 2.06 (q, *J* = 6.4 Hz, 2H), 3.41 (dt, *J* = 9.5, 6.6 Hz, 1H), 3.54 (dd, *J* = 10.5, 6.3 Hz, 1H), 3.67 (dd, *J* = 10.4, 3.3 Hz, 1H), 3.73 (dt, *J* = 9.4, 6.6 Hz, 1H), 4.24 (dd, *J* = 7.7, 4.4 Hz, 1H), 4.35 (td, *J* = 7.0, 6.3, 3.4 Hz, 1H), 4.45 (d, *J* = 11.5 Hz, 1H), 4.58 (d, *J* = 12.1 Hz, 2H), 4.64 (d, *J* = 11.5 Hz, 1H), 4.90 – 5.07 (m, 2H), 5.12 (s, 1H), 5.46 (d, *J* = 4.4 Hz, 1H), 5.78 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 7.12 – 7.27 (m, 5H), 7.25 – 7.40 (m, 5H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.51 – 7.62 (m, 1H), 8.09 (dd, *J* = 8.1, 1.2 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.6, 30.1, 67.2, 71.3, 73.0, 73.2, 74.4, 78.2, 80.4, 105.2, 114.8, 127.5, 127.6, 127.6, 127.8, 127.9, 127.9, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 129.6, 129.8, 129.8, 133.2, 137.4, 138.0, 138.1, 165.6; HRMS (Waters Synapt G2) : m/z calcd for $[C_{31}H_{34}O_6+Na]^+$: 525.2252; Found: 525.2250.

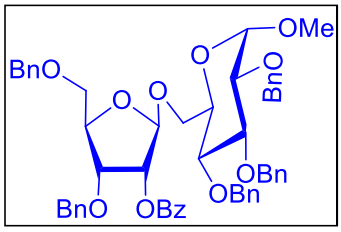


Cholesteryl 2-*O*-benzoyl 3,5-di-*O*-benzyl β-D-ribofuranoside (**19m**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) –8.0°; IR (cm^{-1}, $CHCl_3$): 3070, 3036, 2937, 2852, 1726, 1593, 1457, 1270, 1113, 702; ^1H NMR (399.78 MHz, $CDCl_3$): δ 0.66 (s, 3H), 0.85 (d, *J* = 1.8 Hz, 3H), 0.86 (d, *J* = 1.8 Hz, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.96 (s, 3H), 0.90 – 1.19 (m, 9H), 1.28 – 1.37 (m, 4H), 1.39 – 1.57 (m, 7H), 1.68 – 1.87 (m, 4H), 1.89 – 2.06 (m, 2H), 2.10 – 2.20 (m, 1H), 2.34 (ddd, *J* = 13.2, 4.9, 1.9 Hz, 1H), 3.47 – 3.54 (m, 1H), 3.55 (dd, *J* = 10.4, 6.3 Hz, 1H), 3.65 (dd, *J* = 10.4, 3.4 Hz, 1H), 4.22 (dd, *J* = 7.7, 4.3 Hz, 1H), 4.27 – 4.35 (m, 1H), 4.44 (d, *J* = 11.5 Hz, 1H), 4.56 (ABq, *J*=12.2 Hz, 2H), 4.63 (d, *J* = 11.5 Hz, 1H), 5.28 (s, 1H), 5.30 – 5.34 (m, 1H), 5.42 (d, *J* = 4.3 Hz, 1H), 7.20 (m, 5H), 7.24 – 7.35 (m, 5H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.46 – 7.62 (m, 1H), 8.07 (dd, *J* = 8.2, 1.3 Hz, 2H); ^{13}C NMR

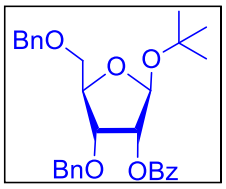


(100.53 MHz, $CDCl_3$): δ 11.8, 18.7, 19.3, 21.0, 22.6, 22.6, 22.8, 22.8, 23.8, 24.3, 28.0, 28.2, 29.5, 31.9, 31.9, 35.8, 36.2, 36.7, 37.2, 38.4, 39.5, 39.8, 42.3, 50.1, 56.1, 56.7, 71.6, 73.0, 73.2, 74.9, 78.3, 80.2, 103.4, 121.9, 127.5, 127.7, 127.7, 127.7, 127.9, 127.9, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 129.9, 129.9, 133.2, 137.5, 138.2, 140.3, 165.7. HRMS (Waters Synapt G2) : m/z calcd for $[C_{53}H_{70}O_6+Na]^+$: 825.5070; Found: 825.5073.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2-*O*-benzoyl 3,5-di-*O*-benzyl β-D-ribofuranosyl) α-D-glucopyranoside (**19n**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +39.3°; IR (cm^{-1}, $CHCl_3$): 3063, 3031, 2922, 2873, 1724, 1596, 1455, 1268, 1083, 702; ^1H NMR (399.78, MHz, $CDCl_3$): δ 3.34 (s, 3H), 3.49 (dd, *J* = 9.4, 8.8 Hz, 1H), 3.52 (d, *J* = 3.2 Hz, 1H), 3.56 (t, *J* = 6.7 Hz, 1H), 3.60 (dd, *J* = 11.0, 5.1 Hz, 1H), 3.64 (dd, *J* = 10.5, 3.6 Hz, 1H), 3.73 (ddd, *J* = 10.0, 4.9, 1.6 Hz, 1H), 3.95 (dd, *J* = 11.0, 1.8 Hz, 1H), 3.99 (t, *J* = 9.2 Hz, 1H), 4.22 (dd, *J* = 7.5, 4.5 Hz, 1H), 4.33 (ddd, *J* = 7.3, 6.2, 3.5 Hz, 1H), 4.42 (d, *J* = 11.5 Hz, 1H), 4.53 (s, 2H), 4.57 (s, 1H), 4.59 (d, *J* = 5.0 Hz, 1H), 4.61 (d, *J* = 9.2 Hz, 1H), 4.67 (d, *J* = 12.1 Hz, 1H), 4.79 (d, *J* = 12.3 Hz, 1H), 4.82 (d, *J* = 10.9 Hz, 1H), 4.89 (d, *J* = 11.1 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 5.06 (s, 1H), 5.44 (d, *J* = 4.5 Hz, 1H), 7.13 – 7.49 (m, 27H), 7.57 (tt, *J* = 7.1, 1.2 Hz, 1H), 8.06 (dd, *J* = 8.3, 1.2 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 55.1, 66.5, 69.9, 71.3, 72.9, 73.2, 73.3, 74.3, 74.9, 75.7, 77.6, 78.0, 79.8, 80.6, 82.1, 97.9, 105.7, 127.5, 127.6, 127.6, 127.6, 127.7, 127.8, 127.8, 127.9, 127.9, 127.9, 127.9, 127.9, 127.9, 128.0, 128.0 , 128.2, 128.0, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 129.6, 129.8, 129.8, 133.2, 137.4, 138.1, 138.2, 138.2, 138.7, 165.5; HRMS (Waters Synapt G2) : m/z calcd for $[C_{54}H_{56}O_{11}+Na]^+$: 903.3720; Found: 903.3729.

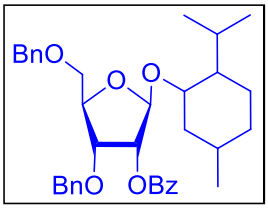


t-Butyl 2-*O*-benzoyl 3,5-di-O-benzyl-β-D-ribofuranoside (**19o**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.7) +30.3°; IR (cm^{-1}, $CHCl_3$): 2975, 2927, 2892, 1723, 1592, 1456, 1269, 1113, 703; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.23 (s, 9H), 3.60 (dd, *J* = 10.4, 6.2 Hz, 1H), 3.67 (dd, *J* = 10.4, 3.8 Hz, 1H), 4.22 (dd, *J* = 7.3, 4.4 Hz, 1H), 4.29 (td, *J* = 6.7, 3.8 Hz, 1H), 4.46 (d, *J* = 11.5 Hz, 1H), 4.56 (ABq, *J* = 12.1 Hz, 2H), 4.61 (d, *J* = 11.8 Hz, 1H), 5.30 (d, *J* = 4.3 Hz, 1H), 5.38 (s, 1H), 7.05 – 7.39 (m, 10H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 8.01 – 8.12 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.7, 28.7,

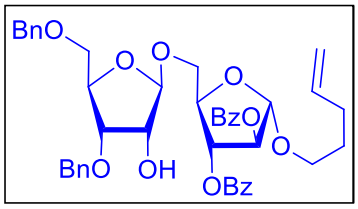


28.7, 71.9, 72.9, 73.2, 75.4, 75.8, 78.5, 80.1, 100.4, 127.5, 127.7, 127.7, 127.7, 127.8, 127.9, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 129.8, 129.9, 129.9, 133.2, 137.6, 138.3, 165.8; HRMS (Waters Synapt G2) : m/z calcd for $[C_{30}H_{34}O_6+Na]^+$: 513.2253; Found: 513.2249.

Menthyl 2-*O*-benzoyl 3,5-di-*O*-benzyl β-D-ribofuranoside (**19p**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) −13.1°; IR (cm^{-1}, $CHCl_3$): 3073, 3036, 2923, 2862, 1725, 1592, 1455, 1268, 1109, 705; ^1H NMR (399.78 MHz, $CDCl_3$): δ 0.72 (d, *J* = 12.1 Hz, 3H), 0.75 - 0.90(m, 2H), 0.85 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.94 (dd, *J* = 13.0, 3.2 Hz, 1H), 0.99 (dd, *J* = 13.4, 3.7 Hz, 1H), 1.14 – 1.23 (m, 1H), 1.26 – 1.40 (m, 2H), 1.58 – 1.68 (m, 2H), 2.06 – 2.14 (m, 2H), 3.47 (dd, *J* = 10.6, 4.1 Hz, 1H), 3.53 (dd, *J* = 10.2, 7.2 Hz, 1H), 3.65 (dd, *J* = 10.2, 3.4 Hz, 1H), 4.12 (dd, *J* = 8.2, 4.2 Hz, 1H), 4.36 (td, *J* = 7.6, 3.3 Hz, 1H), 4.45 (d, *J* = 11.4 Hz, 1H), 4.64 (d, *J* = 11.3 Hz, 1H), 5.33 (s, 1H), 5.41 (d, *J* = 4.2 Hz, 1H), 7.15 – 7.37 (m, 10H), 7.38 – 7.48 (m, 2H), 7.52 – 7.60 (m, 1H), 8.05 – 8.10 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 16.0, 21.1, 22.3, 23.0, 25.2, 31.3, 34.4, 39.8, 47.8, 72.0, 73.0, 73.3, 75.1, 75.6, 78.5, 79.8, 101.7, 127.6, 127.7, 127.7, 127.8, 128.0, 128.0, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 129.7, 129.9, 129.9, 133.2, 137.5, 138.1, 165.7; HRMS (Waters Synapt G2) : m/z calcd for $[C_{36}H_{44}O_6+Na]^+$: 595.3036; Found: 595.3036.

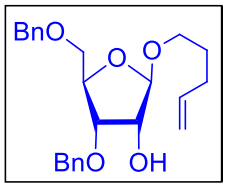


Pent-4-enyl 2,3-di-*O*-benzyl 5-*O*-(3,5-di-*O*-benzyl β-D-ribofuranosyl) α-D-arabinofuranoside (**32a**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +10.5°; IR (cm^{-1}, $CHCl_3$): 3432, 3071, 3030, , 2923, 2860, 1591, 1455, 1105, 698; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.68 (quintet, *J* = 6.6 Hz, 2H), 2.12 (q, *J* = 6.9 Hz, 2H), 2.68 (d, *J* = 2.6 Hz, 1H), 3.39 (dt, *J* = 9.7, 6.5 Hz, 1H), 3.50 (dd, *J* = 11.0, 6.4 Hz, 1H), 3.53 (d, *J* = 5.6 Hz, 2H), 3.71 (dt, *J* = 9.7, 6.6 Hz, 1H), 3.78 (dd, *J* = 7.1, 3.4 Hz, 1H), 3.86 (dd, *J* = 11.0, 3.2 Hz, 1H), 4.00 (dd, *J* = 3.4, 1.3 Hz, 1H), 4.05 (t, *J* = 4.9 Hz, 1H), 4.07 (s, 1H), 4.07 – 4.10 (m, 1H), 4.12 (td, *J* = 6.6, 3.2 Hz, 1H), 4.22 (q, *J* = 5.6 Hz, 1H), 4.48 (dd, *J* = 11.8, 2.0 Hz, 2H), 4.51 (d, *J* = 4.8 Hz, 2H), 4.54 (s, 2H), 4.57 (dd, *J* = 8.6, 3.5 Hz, 1H), 4.98 (s, 1H), 4.99 (d, *J* = 0.9 Hz, 1H), 4.93 – 5.06 (m, 2H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 7.08 – 7.57 (m, 20H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.7, 30.3, 66.9, 67.5, 71.8, 72.1, 72.1, 72.7, 73.2, 73.3, 79.8, 80.1, 80.7, 83.5, 88.3, 106.1, 107.7, 114.8, 127.6, 127.6, 127.6, 127.7,

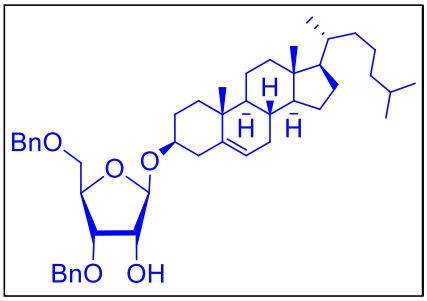


127.7, 127.7, 127.9, 127.9, 127.9, 127.9, 127.9, 128.2, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.6, 128.6 , 137.1, 137.5, 137.8, 138.1, 138.2; HRMS (Waters Synapt G2) : m/z calcd for $[C_{43}H_{50}O_9+Na]^+$: 733.3352; Found: 733.3350.

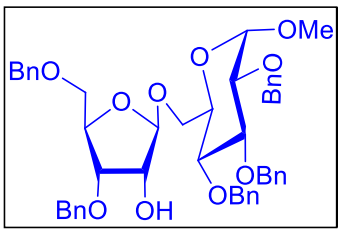
(Pent-4-enyl) 3,5-di-*O*-benzyl β-D-ribofuranoside (**32b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) –24.9°; IR (cm^{-1}, $CHCl_3$): 3437, 3072, 3030, 2925, 2862, 1591, 1453, 1111, 705; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.59 (d, *J* = 7.0 Hz, 2H), 1.96 – 2.12 (m, 2H), 2.72 (d, *J* = 3.1 Hz, 1H), 3.36 (dt, *J* = 9.6, 6.6 Hz, 1H), 3.52 – 3.54 (m, 1H), 3.55 (s, 1H), 3.66 (dt, *J* = 9.6, 6.6 Hz, 1H), 4.03 – 4.10 (m, 2H), 4.22 (q, *J* = 5.6 Hz, 1H), 4.57 (d, *J* = 7.9 Hz, 4H), 4.95 (s, 1H), 4.92 – 5.03 (m, 2H), 5.77 (ddt, *J* = 16.9, 10.2, 6.5 Hz, 1H), 7.07 – 7.51 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.6, 30.2, 67.2, 71.7, 72.7, 73.3, 73.4, 79.8, 80.4, 107.5, 114.8, 127.6, 127.7, 127.7, 127.9, 127.9, 128.2, 128.3, 128.3, 128.6, 128.6, 137.1, 138.1, 138.1; HRMS (Waters Synapt G2) : m/z calcd for $[C_{24}H_{30}O_5+Na]^+$: 421.1991; Found: 421.1990.



Cholesteryl 3,5-di-*O*-benzyl β-D-ribofuranoside (**32c**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) –59.9°; IR (cm^{-1}, $CHCl_3$): 3414, 3033, 2935, 2856, 1592, 1457, 1105, 698; ^1H NMR (399.78 MHz, $CDCl_3$): δ 0.66 (s, 3H), 0.86 (dd, *J* = 6.6, 1.7 Hz, 6H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.96 (s, 3H), 0.92 – 1.59 (m, 20H), 1.68 – 1.88 (m, 3H), 1.90 – 2.05 (m, 3H), 2.05 – 2.19 (m, 1H), 2.34 (ddd, *J* = 13.2, 4.6, 1.9 Hz, 1H), 2.71 (d, *J* = 3.2 Hz, 1H), 3.46 (tt, *J* = 11.0, 4.4 Hz, 1H), 3.54 (d, *J* = 5.6 Hz, 2H), 4.02 (dd, *J* = 4.4, 3.2 Hz, 1H), 4.07 (t, *J* = 5.1 Hz, 1H), 4.20 (q, *J* = 5.7 Hz, 1H), 4.56 (d, *J* = 9.1 Hz, 4H), 5.11 (s, 1H), 5.32 (d, *J* = 5.2 Hz, 1H), 7.12 – 7.51 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 11.8, 18.7, 19.3, 21.0, 22.6, 22.8, 23.8, 24.3, 28.0, 28.2, 29.6, 31.9, 31.9, 35.8, 36.2, 36.7, 37.3, 38.4, 39.5, 39.8, 42.3, 50.1, 56.1, 56.7, 71.9, 72.7, 73.3, 73.3, 73.8, 77.2, 79.9, 80.3, 105.5, 121.9, 127.6, 127.7, 127.9, 127.9, 128.2, 128.3, 128.3, 128.6, 128.6, 137.2, 138.1, 140.4; HRMS (Waters Synapt G2) : m/z calcd for $[C_{46}H_{66}O_5+Na]^+$: 721.4808; Found: 721.4797.

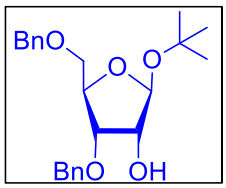


Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,5-di-*O*-benzyl β-D-ribofuranosyl) α-D-glucopyranoside (**32d**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) –1.5°; IR (cm^{-1}, $CHCl_3$): 3456, 3073, 3031, 2923, 2862, 1594, 1455, 1059, 740; ^1H NMR (399.78 MHz, $CDCl_3$): δ 2.71

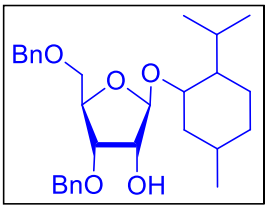


(d, *J* = 2.7 Hz, 1H), 3.33 (s, 3H), 3.46 (t, *J* = 9.2 Hz, 1H), 3.51 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.55 (d, *J* = 5.6 Hz, 2H), 3.55 (dd, *J* = 10.9, 5.0 Hz, 1H), 3.70 (ddd, *J* = 10.0, 4.8, 1.5 Hz, 1H), 3.89 (dd, *J* = 10.9, 1.7 Hz, 1H), 3.98 (t, *J* = 9.2 Hz, 1H), 4.00 – 4.12 (m, 2H), 4.22 (q, *J* = 5.5 Hz, 1H), 4.50 (ABq, *J* = 12.0 Hz, 2H), 4.56 (s, 3H), 4.57 (d, *J* = 9.8 Hz, 1H), 4.67 (d, *J* = 12.2 Hz, 1H), 4.80 (t, *J* = 10.8 Hz, 2H), 4.88 (d, *J* = 11.0 Hz, 1H), 4.95 (s, 1H), 4.99 (d, *J* = 10.8 Hz, 1H), 7.19 – 7.43 (m, 25H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 55.0, 66.3, 69.9, 71.6, 72.7, 73.2, 73.3, 73.3, 74.9, 75.7, 77.6, 79.6, 79.9, 80.7, 82.1, 97.9, 107.8, 127.5, 127.6, 127.6, 127.6, 127.7, 127.8, 127.8, 127.8, 127.8, 127.8, 127.9, 127.9, 128.1, 128.1, 128.1, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 137.1, 138.1, 138.1, 138.1, 138.6; HRMS (Waters Synapt G2) : m/z calcd for $[C_{47}H_{52}O_{10}+Na]^+$: 799.3458; Found: 799.3470.

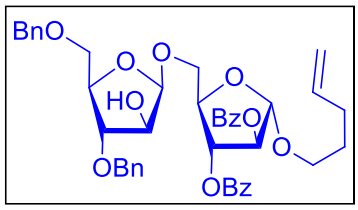
t-Butyl 3,5-di-O-benzyl-β-D-ribofuranoside (**32e**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) –35.4°; IR (cm^{-1}, $CHCl_3$): 3439, 3090, 2972, 2929, 2869, 1591, 1458, 1097, 740, 697; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.20 (s, 9H), 2.74 (d, *J* = 3.7 Hz, 1H), 3.58 (dABq, *J* = 10.1, 5.2 Hz, 2H), 3.95 (t, *J* = 3.4 Hz, 1H), 4.05 (t, *J* = 5.3 Hz, 1H), 4.16 (q, *J* = 5.7 Hz, 1H), 4.57 (s, 2H), 4.58 (ABq, *J* = 11.6 Hz, 2H), 5.20 (d, *J* = 1.1 Hz, 1H), 7.23 – 7.43 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.8, 28.8, 28.8, 72.1, 72.1, 73.3, 74.5, 74.8, 80.0, 80.0, 102.5, 127.6, 127.7, 127.7, 127.9, 127.9, 128.1, 128.3, 128.3, 128.5, 128.5, 137.3, 138.2; HRMS (Waters Synapt G2) : m/z calcd for $[C_{23}H_{30}O_5+Na]^+$: 409.1991; Found: 409.1990.



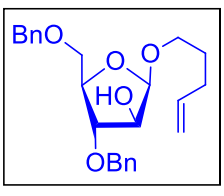
Menthyl 3,5-di-*O*-benzyl β-D-ribofuranoside (**32f**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) –73.8°; IR (cm^{-1}, $CHCl_3$): 3414, 3043, 2924, 2861, 1591, 1457, 1111, 691; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 0.70 (d, *J* = 6.9 Hz, 3H), 0.83 (d, *J* = 7.2 Hz, 3H), 0.70 – 1.05 (m, 2H), 0.89 (d, *J* = 6.5 Hz, 3H), 1.08 – 1.21 (m, 1H), 1.21 – 1.44 (m, 2H), 1.60 (d, *J* = 14.7 Hz, 2H), 1.96 – 2.26 (m, 2H), 2.64 (d, *J* = 2.7 Hz, 1H), 3.42 (td, *J* = 10.6, 4.2 Hz, 1H), 3.55 (d, *J* = 5.7 Hz, 2H), 3.90 – 4.05 (m, 2H), 4.22 (q, *J* = 5.6 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.54 – 4.64 (m, 3H), 5.16 (s, 1H), 6.90 – 7.67 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 16.0, 21.1, 22.3, 23.0, 25.1, 31.3, 34.4, 39.9, 47.9, 72.0, 72.7, 73.0, 74.1, 75.4, 79.7, 80.2, 103.8, 127.6, 127.7, 127.7, 127.9, 127.9, 128.2, 128.4, 128.4, 128.6, 128.6, 137.2, 138.1; HRMS (Waters Synapt G2) : m/z calcd for $[C_{29}H_{40}O_5+Na]^+$: 491.2773; Found: 491.2775.



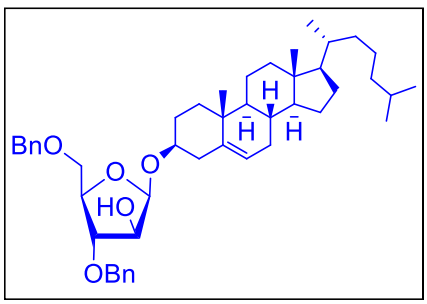
(Pent-4-enyl) 2,3-di-*O*-benzyl 5-*O*-(3,5-di-*O*-benzyl β-D-arabinofuranosyl)-α-D-arabinofuranoside (**34a**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.8) +15.5°; IR (cm^{-1}, $CHCl_3$): 3443, 3077, 3032, 2926, 2866, 1594, 1453, 1109, 741, 697; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.67 (quintet, *J* = 7.1 Hz, 2H), 2.12 (q, *J* = 6.9 Hz, 2H), 2.97 (s, 1H), 3.38 (dt, *J* = 9.6, 6.5 Hz, 1H), 3.48 (dd, *J* = 11.1, 5.4 Hz, 1H), 3.53 (d, *J* = 5.9 Hz, 2H), 3.69 (dt, *J* = 9.7, 6.6 Hz, 1H), 3.77 – 3.82 (m, 2H), 3.96 (dd, *J* = 11.1, 2.9 Hz, 1H), 3.99 (dd, *J* = 2.5, 1.0 Hz, 1H), 4.12 (q, *J* = 5.8 Hz, 1H), 4.16 (td, *J* = 5.7, 2.9 Hz, 1H), 4.20 (s, 1H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 11.9 Hz, 1H), 4.51 – 4.59 (m, 5H), 4.72 (d, *J* = 11.9 Hz, 1H), 4.87 (d, *J* = 4.7 Hz, 1H), 4.99 (s, 1H), 4.93 – 5.06 (m, 2H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 7.10 – 7.56 (m, 20H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.7, 30.3, 66.9, 68.3, 71.8, 72.1, 72.2, 72.2, 73.2, 78.3, 80.8, 80.9, 83.8, 84.7, 87.8, 102.3, 106.3, 114.9, 127.6, 127.6, 127.6, 127.6, 127.7, 127.7, 127.8, 127.8, 127.8, 128.0, 128.1, 128.1, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 137.2, 137.6, 138.0, 138.1, 138.1; HRMS (Waters Synapt G2) : m/z calcd for $[C_{43}H_{50}O_9+Na]^+$: 733.3353; Found: 733.3351.



(Pent-4-enyl) 3,5-di-*O*-benzyl β-D-arabinofuranoside (**34b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) –38.7°; IR (cm^{-1}, $CHCl_3$): 3441, 3072, 3033, 2929, 2866, 1592, 1444, 1118, 1042, 732, 698; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.64 (quintet, *J* = 6.9 Hz, 2H), 2.01 – 2.11 (m, 2H), 2.60 (d, *J* = 9.6 Hz, 1H), 3.43 (dt, *J* = 9.6, 6.6 Hz, 1H), 3.52 (d, *J* = 5.8 Hz, 2H), 3.76 (dt, *J* = 9.6, 6.5 Hz, 1H), 3.83 (t, *J* = 5.8 Hz, 1H), 4.13 (q, *J* = 5.6 Hz, 1H), 4.21 – 4.27 (m, 1H), 4.55 (s, 2H), 4.61 (d, *J* = 11.9 Hz, 1H), 4.75 (d, *J* = 11.9 Hz, 1H), 4.94 (d, *J* = 4.7 Hz, 1H), 4.93 – 5.05 (m, 2H), 5.77 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 6.97 – 7.59 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.6, 30.2, 67.8, 71.8, 72.1, 73.3, 77.9, 80.7, 84.8, 101.6, 115.0, 127.6, 127.6, 127.7, 127.7, 127.7, 127.7, 128.3, 128.3, 128.3, 128.3, 137.9, 137.9, 138.0; HRMS (Waters Synapt G2) : m/z calcd for $[C_{24}H_{30}O_5+Na]^+$: 421.1991; Found: 421.1990.

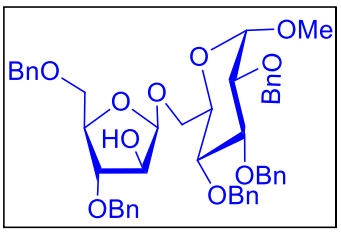


Cholesteryl 3,5-di-*O*-benzyl β-D-arabinofuranoside (**34c**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.7) –49.3°; IR (cm^{-1}, $CHCl_3$): 3418, 3033, 2939, 2866, 1591, 1451, 1110, 1034, 731, 692; ^1H NMR (399.78 MHz, $CDCl_3$): δ 0.67 (s, 3H), 0.86 (d, *J* = 1.8 Hz, 3H), 0.87 (d, *J* = 1.8 Hz, 3H), 0.91 (d, *J* =

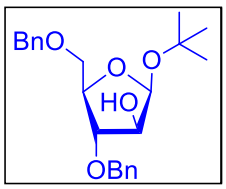


6.5 Hz, 3H), 0.98 (s, 3H), 0.94 – 1.19 (m, 6H), 1.21 – 1.38 (m, 6H), 1.40 – 1.67 (m, 9H), 1.75 – 1.90 (m, 3H), 1.90 – 2.08 (m, 1H), 2.10 – 2.25 (m, 1H), 2.32 (ddd, J = 13.0, 4.8, 1.9 Hz, 2H), 2.62 (d, J = 9.4 Hz, 1H), 3.49 – 3.57 (m, 3H), 3.82 (t, J = 5.7 Hz, 1H), 4.12 (q, J = 5.7 Hz, 1H), 4.16 – 4.31 (m, 1H), 4.55 (s, 2H), 4.62 (d, J = 11.9 Hz, 1H), 4.76 (d, J = 11.9 Hz, 1H), 5.13 (d, J = 4.8 Hz, 1H), 5.33 (d, J = 5.2 Hz, 1H), 7.00 – 7.59 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 11.8, 18.7, 19.3, 21.0, 22.6, 22.8, 23.8, 24.3, 28.0, 28.2, 29.7, 31.8, 31.9, 35.8, 36.2, 36.7, 37.2, 38.8, 39.5, 39.7, 42.3, 50.1, 56.1, 56.7, 71.8, 72.2, 73.3, 77.6, 78.2, 80.6, 85.0, 100.3, 122.1, 127.6, 127.6, 127.7, 127.7, 127.8, 127.8, 128.3, 128.3, 128.3, 128.3, 138.0, 140.1, 140.1; HRMS (Waters Synapt G2) : m/z calcd for $[C_{46}H_{66}O_5+Na]^+$: 721.4808; Found: 721.4799.

Methyl 2,3,4-tri-*O*-benzyl 6-*O*-(3,5-di-*O*-benzyl β-D-arabinofuranosyl)-α-D-glucopyranoside (**34d**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +2.0°; IR (cm^{-1}, $CHCl_3$): 3421, 3063, 3033, 2926, 2866, 1588, 1454, 1106, 1063, 735, 692; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 2.59 (s, 1H), 3.31 (s, 3H), 3.33 – 3.40 (m, 2H), 3.49 (dd, J = 9.7, 3.5 Hz, 1H), 3.50 (d, J = 5.9 Hz, 2H), 3.54 (dd, J = 11.1, 5.8 Hz, 1H), 3.74 (ddd, J = 10.1, 5.8, 1.9 Hz, 1H), 3.80 (t, J = 5.8 Hz, 1H), 3.94 (d, J = 2.1 Hz, 1H), 3.97 (t, J = 9.3 Hz, 1H), 4.09 (q, J = 5.7 Hz, 1H), 4.15 – 4.24 (m, 1H), 4.48 (ABq, J = 12.0 Hz, 2H), 4.53 (dd, J = 7.3, 3.8 Hz, 1H), 4.58 (d, J = 11.9 Hz, 1H), 4.65 (d, J = 12.2 Hz, 1H), 4.72 (d, J = 11.9 Hz, 1H), 4.77 (d, J = 7.3 Hz, 1H), 4.80 (d, J = 6.0 Hz, 1H), 4.87 (dd, J = 7.9, 3.2 Hz, 2H), 4.98 (d, J = 10.7 Hz, 1H), 7.02 – 7.65 (m, 25H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 55.2, 67.3, 69.9, 71.8, 72.0, 73.2, 73.4, 75.0, 75.8, 77.9, 78.2, 79.9, 80.8, 82.0, 84.6, 97.9, 102.2, 127.6, 127.6, 127.6, 127.6, 127.7, 127.7, 127.7, 127.8, 127.8, 127.8, 128.0, 128.0, 128.0, 128.1, 128.1, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 137.9, 138.0, 138.0, 138.0, 138.5; HRMS (Waters Synapt G2) : m/z calcd for $[C_{47}H_{52}O_{10}+Na]^+$: 799.3458; Found: 799.3438.

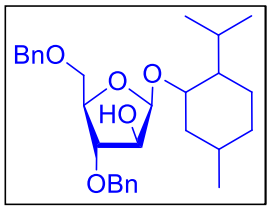


t-Butyl 3,5-di-*O*-benzyl β-D-arabinofuranoside (**34e**)**:** $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.2) –7.8°; IR (cm^{-1}, $CHCl_3$): 3391, 2933, 2862, 1585, 1467, 1127; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.24 (s, 9H), 2.64 (d, J = 9.1 Hz, 1H), 3.58 (dABq, J = 10.0, 6.4 Hz, 2H), 3.81 (t, J = 5.4 Hz, 1H), 4.09 (q, J = 5.6 Hz, 1H), 4.18 (dt, J = 9.1, 5.3 Hz, 1H), 4.56 (s, 2H),

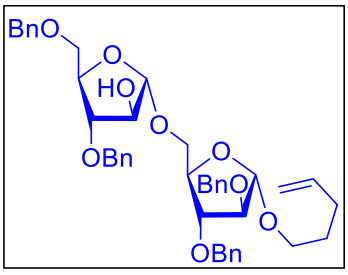


4.63 (d, *J* = 11.9 Hz, 1H), 4.75 (d, *J* = 11.9 Hz, 1H), 5.26 (d, *J* = 4.9 Hz, 1H), 6.80 – 7.63 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.8, 28.8, 28.8, 71.7, 72.3, 73.3, 75.7, 77.3, 80.5, 85.3, 96.4, 127.6, 127.6, 127.7, 127.7, 127.8, 127.8, 128.3, 128.3, 128.3, 128.3, 138.1, 138.1; HRMS (Waters Synapt G2) : m/z calcd for $[C_{23}H_{30}O_5+Na]^+$: 409.1991; Found: 409.1984.

Menthyl 3,5-di-*O*-benzyl β-D-arabinofuranoside (**34f**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) –89.3°; IR (cm^{-1}, $CHCl_3$): 3529, 3083, 3036, 2926, 2864, 1591, 1456, 1117, 1029, 732, 685; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 0.74 (d, *J* = 6.9 Hz, 3H), 0.86 (d, *J* = 7.0 Hz, 3H), 0.69 – 1.11 (m, 2H), 0.90 (d, *J* = 6.5 Hz, 3H), 1.15 – 1.28 (m, 1H), 1.28 – 1.42 (m, 2H), 1.58 – 1.73 (m, 2H), 2.01 – 2.25 (m, 2H), 2.70 (d, *J* = 8.8 Hz, 1H), 3.48 – 3.61 (m, 3H), 3.80 (t, *J* = 5.9 Hz, 1H), 4.09 (q, *J* = 5.9 Hz, 1H), 4.21 (dt, *J* = 8.8, 5.4 Hz, 1H), 4.53 (ABq, *J* = 12.0 Hz, 2H), 4.62 (d, *J* = 11.9 Hz, 1H), 4.78 (d, *J* = 11.9 Hz, 1H), 5.20 (d, *J* = 5.0 Hz, 1H), 7.06 – 7.55 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 15.8, 21.0, 22.2, 22.9, 25.2, 31.4, 34.3, 40.4, 47.8, 71.9, 72.2, 73.3, 76.8, 77.1, 79.9, 84.9, 98.2, 127.6, 127.6, 127.7, 127.7, 127.7, 127.7, 128.3, 128.3, 128.3, 128.3, 138.0, 138.0; HRMS (Waters Synapt G2) : m/z calcd for $[C_{29}H_{40}O_5+Na]^+$: 491.2773; Found: 491.2773.

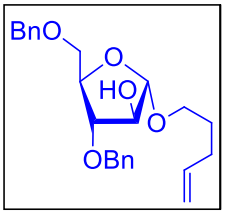


(Pent-4-enyl) 2,3-di-*O*-benzyl-5-*O*-(3,5-di-*O*-benzyl-α-D-arabinofuranosyl)-α-D-arabinofuranoside (**16k**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.9) +62.3°; IR (cm^{-1}, $CHCl_3$): 3387, 3079, 3032, 2923, 1591, 1453, 1314, 1047, 769; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.67 (quintet, *J* = 6.9 Hz, 2H), 2.11 (q, *J* = 6.9 Hz, 2H), 3.35 – 3.43 (m, 1H), 3.48 (dd, *J* = 10.3, 2.5 Hz, 1H), 3.63 (dd, *J* = 10.3, 2.2 Hz, 1H), 3.67 – 3.74 (m, 2H), 3.85 – 3.86 (m, 1H), 3.90 (dd, *J* = 11.6, 3.6 Hz, 1H), 3.98 – 4.01 (m, 1H), 4.09 (dd, *J* = 6.9, 3.3 Hz, 1H), 4.15 (dd, *J* = 6.8, 3.4 Hz, 1H), 4.19 (s, 2H), 4.26 – 4.30 (m, 1H), 4.43 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 3.2 Hz, 1H), 4.48 (s, 2H), 4.49 (s, 1H), 4.52 (s, 1H), 4.60 (d, *J* = 8.3 Hz, 1H), 4.63 (d, *J* = 8.3 Hz, 1H), 4.92 – 5.05 (m, 2H), 5.01 (s, 1H), 5.09 (s, 1H), 5.81 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 7.13 – 7.55 (m, 20H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.7, 30.3, 65.8, 66.9, 69.6, 71.9, 71.9, 72.2, 73.7, 77.9, 80.3, 82.9, 83.1, 84.8, 88.5, 106.0, 109.2, 114.8, 127.5, 127.6, 127.6, 127.7, 127.8, 127.8, 127.8, 127.9, 127.9, 128.0, 128.1, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.6, 137.1,

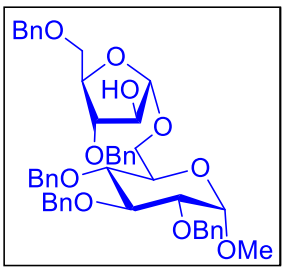


137.5, 137.8, 138.1, 138.2; HRMS (Waters Synapt G2): m/z calcd for $[C_{43}H_{50}O_9+Na]^+$: 733.3353; Found: 733.3350.

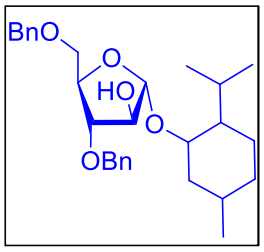
(Pent-4-enyl) 3,5-di-O-benzyl-α-D-arabinofuranside (**16l**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.7) +119.4°; IR (cm^{-1}, $CHCl_3$): 3441, 3072, 3033, 2929, 2866, 1592, 1444, 1118, 1042, 732, 698; ^1H NMR (399.78 MHz, $CDCl_3$): δ 1.64 – 1.67 (m, 2H), 1.92-2.09 (m, 2H), 3.32 – 3.47 (m, 2H), 3.60 – 3.69 (m, 3H), 3.87 (s, 1H), 4.01 (s, 1H), 4.21 (s, 1H), 4.42 – 4.48 (m, 2H), 4.56 (dd, *J* = 23.8, 11.9 Hz, 2H), 4.63 (dd, *J* = 26.0, 10.6 Hz, 3H), 5.73-5.81 (m, 1H), 7.21 – 7.31 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.7, 30.2, 66.9, 69.7, 71.9, 73.7, 77.8, 83.2, 85.2, 109.0, 114.7, 127.7, 127.7, 127.8, 127.8, 128.0, 128.0, 128.3, 128.4, 128.5, 128.5, 137.0, 137.8, 138.2; HRMS (Waters Synapt G2): m/z calcd for $[C_{24}H_{30}O_5+Na]^+$: 421.1991; Found: 421.1990.



Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,5-di-*O*-benzyl-α-D-arabinofuranosyl)-α-D-gluco-pyranoside (**16m**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +47.1°; IR (cm^{-1}, $CHCl_3$): 3425, 3070, 2927, 2866, 1591, 1451, 1106, 1063, 735; ^1H NMR (399.78 MHz, $CDCl_3$): δ 3.35 (s, 3H), 3.45 (dd, *J* = 10.4, 2.1 Hz, 1H), 3.51 (dd, *J* = 9.8, 3.7 Hz, 2H), 3.58 (ddd, *J* = 10.9, 4.9, 2.0 Hz, 2H), 3.60 – 3.71 (m, 1H), 3.74 (dd, *J* = 9.9, 2.3 Hz, 2H), 3.86 (d, *J* = 2.4 Hz, 1H), 3.95 (t, *J* = 9.3 Hz, 1H), 4.16 (dd, *J* = 7.8, 2.6 Hz, 2H), 4.18 (d, *J* = 2.6 Hz, 1H), 4.26 (d, *J* = 10.7 Hz, 1H), 4.42 (d, *J* = 11.7 Hz, 1H), 4.46 (d, *J* = 11.8 Hz, 1H), 4.60 (t, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 3.7 Hz, 1H), 4.68 (s, 2H), 4.79 (d, *J* = 11.4 Hz, 2H), 4.95 (d, *J* = 10.9 Hz, 1H), 5.10 (s, 1H), 7.10 – 7.44 (m, 25H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 55.1, 65.5, 69.7, 69.7, 72.0, 73.3, 73.7, 74.8, 75.6, 77.2, 77.4, 79.7, 82.0, 84.0, 85.4, 98.2, 109.5, 127.4, 127.4, 127.6, 127.6, 127.7, 127.7, 127.8, 127.8, 127.8, 127.9, 127.9, 128.0, 128.1, 128.1, 128.2, 128.2, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 136.8, 137.6, 138.1, 138.6, 138.9; HRMS (Waters Synapt G2): m/z calcd for $[C_{47}H_{52}O_{10}+Na]^+$: 799.3458; Found: 799.3451.

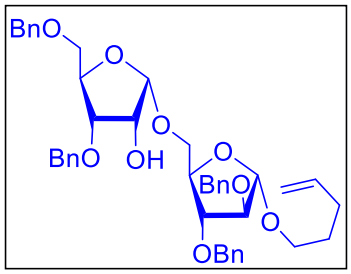


Menthyl 3,5-di-O-benzyl-α-D-arabinofuranside (**16n**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +62.3°; IR (cm^{-1}, $CHCl_3$): 3357, 3071, 2970, 1591, 1453, 1368, 1105, 741; ^1H NMR (399.78 MHz, $CDCl_3$): δ 0.76 (d, *J* = 7.0 Hz, 3H), 0.87 (d, *J* = 4.3 Hz, 3H), 0.89 (d, *J* = 3.7 Hz, 3H), 0.96 (dd, *J* = 12.7, 3.1 Hz, 1H), 1.00 – 1.08 (m, 1H),

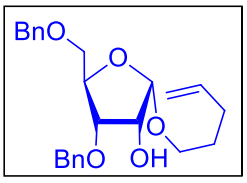


1.08 – 1.16 (m, 1H), 1.22 – 1.32 (m, 1H), 1.38 (ddq, *J* = 11.9, 6.4, 3.3 Hz, 1H), 1.55 – 1.67 (m, 2H), 2.08 – 2.20 (m, 2H), 3.22 – 3.40 (m, 2H), 3.49 (dd, *J* = 10.4, 2.3 Hz, 1H), 3.66 (dd, *J* = 10.4, 2.3 Hz, 1H), 3.85 (d, *J* = 3.1 Hz, 1H), 4.12 (d, *J* = 10.4 Hz, 1H), 4.30 (q, *J* = 2.4 Hz, 1H), 4.49 (t, *J* = 12.4 Hz, 2H), 4.61 (d, *J* = 11.8 Hz, 1H), 4.67 (d, *J* = 12.2 Hz, 1H), 5.08 (s, 1H), 7.04 – 7.53 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 16.2, 21.1, 22.3, 23.2, 25.3, 31.6, 34.3, 42.9, 48.3, 69.8, 71.8, 73.7, 77.9, 79.1, 83.0, 85.3, 110.2, 127.6, 127.6, 127.8, 127.8, 128.0, 128.0, 128.3, 128.3, 128.5, 128.5, 137.0, 138.0; HRMS (Waters Synapt G2): m/z calcd for $[C_{29}H_{40}O_5+Na]^+$: 491.2773; Found: 491.2776.

(Pent-4-enyl) 2,3-di-*O*-benzyl-5-*O*-(3,5-di-*O*-benzyl-α-D-arabinofuranosyl)-α-D-arabinofuranoside (**35a**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.9) +62.7°; IR (cm^{-1}, $CHCl_3$): 3315, 3070, 3031, 2927, 1594, 1454, 1314, 1047, 770; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.67 (quintet, *J* = 6.8 Hz, 2H), 2.11 (q, *J* = 6.9 Hz, 2H), 3.34 – 3.49 (m, 3H), 3.65 – 3.74 (m, 3H), 3.76 (dd, *J* = 6.9, 3.2 Hz, 1H), 3.95 (dd, *J* = 11.3, 3.8 Hz, 1H), 3.97 – 4.00 (m, 1H), 4.05 (dd, *J* = 6.1, 2.7 Hz, 1H), 4.09 – 4.28 (m, 3H), 4.40 – 4.58 (m, 7H), 4.65 (d, *J* = 12.3 Hz, 1H), 4.92 – 5.05 (m, 2H), 5.02 (s, 1H), 5.06 (d, *J* = 4.5 Hz, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 7.00 – 7.71 (m, 20H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.7, 30.3, 66.8, 67.2, 70.0, 71.9, 72.1, 72.7, 73.4, 76.5, 80.9, 82.0, 83.5, 87.9, 102.2, 106.1, 114.8, 127.6, 127.6, 127.6, 127.6, 127.6, 127.7, 127.7, 127.7, 127.8, 127.9, 128.0, 128.0, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 137.5, 137.9, 138.0, 138.1, 138.2; HRMS (Waters Synapt G2): m/z calcd for $[C_{43}H_{50}O_9+Na]^+$: 733.3353; Found: 733.3350.

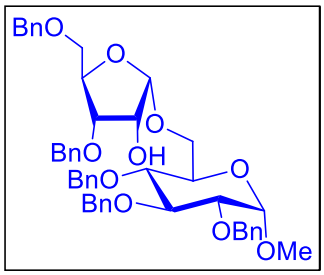


(Pent-4-enyl) 3,5-di-O-benzyl-α-D-ribofuranside (**35b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.4) +38.7°; IR (cm^{-1}, $CHCl_3$): 3430, 3071, 3032, 2929, 1594, 1454, 1118, 1042, 731, 698; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 1.71 (quintet, *J* = 6.9 Hz, 2H), 2.08 – 2.17 (m, 2H), 2.96 (s, 1H), 3.40 (dd, *J* = 10.4, 4.3 Hz, 1H), 3.46 (dd, *J* = 10.1, 3.6 Hz, 1H), 3.50 (dt, *J* = 9.1, 6.1 Hz, 1H), 3.79 (tdd, *J* = 6.6, 5.9, 5.2, 2.1 Hz, 2H), 4.11 (s, 1H), 4.16 (q, *J* = 3.9 Hz, 1H), 4.48 (ABq, *J* = 12.2 Hz, 2H), 4.55 (d, *J* = 12.2 Hz, 1H), 4.70 (d, *J* = 12.3 Hz, 1H), 4.92 – 5.05 (m, 2H), 4.99 (s, 1H), 5.81 (ddt, *J* = 16.9, 10.3, 6.6 Hz, 1H), 6.51 – 7.74 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 28.8, 30.2, 67.5, 70.0, 71.7,

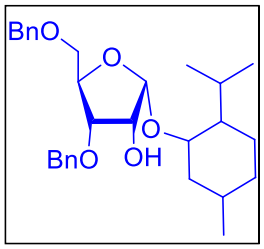


72.7, 73.4, 76.5, 81.7, 101.5, 114.7, 127.6, 127.6, 127.6, 127.7, 127.7, 127.7, 128.3, 128.3, 128.3, 128.4, 137.8, 138.0, 138.2; HRMS (Waters Synapt G2): m/z calcd for $[C_{24}H_{30}O_5+Na]^+$: 421.1991; Found: 421.1990.

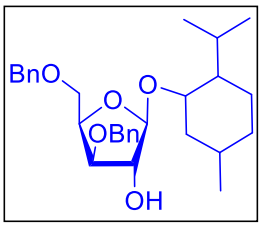
Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,5-di-*O*-benzyl-α-D-ribofuranosyl)-α-D-glucopyranoside (**35c**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.6) +23.7°; IR (cm^{-1}, $CHCl_3$): 3435, 3070, 2921, 1600, 1452, 1362, 1067, 740; ^1H NMR (399.78 MHz, $CDCl_3$): ^1H NMR (399.78 MHz, $CDCl_3$): δ 3.32 (s, 3H), 3.33 – 3.44 (m, 3H), 3.48 – 3.53 (m, 1H), 3.61 (t, *J* = 9.3 Hz, 1H), 3.66 (dd, *J* = 11.0, 1.7 Hz, 1H), 3.71 – 3.77 (m, 1H), 3.79 (dd, *J* = 6.9, 2.8 Hz, 1H), 3.96 (t, *J* = 9.3 Hz, 1H), 4.12 (d, *J* = 3.7 Hz, 1H), 4.10 – 4.21 (m, 2H), 4.38 – 4.52 (m, 3H), 4.58 – 4.70 (m, 4H), 4.75 – 4.84 (m, 3H), 4.96 (d, *J* = 10.9 Hz, 1H), 5.06 (d, *J* = 4.7 Hz, 1H), 7.00 – 7.63 (m, 25H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 55.1, 66.2, 69.8, 70.0, 72.0, 72.9, 73.4, 75.0, 75.8, 76.9, 77.2, 77.7, 80.0, 82.0, 82.2, 98.0, 101.8, 127.6, 127.6, 127.7, 127.7, 127.7, 127.7, 127.9, 127.9, 127.9, 128.0, 128.0, 128.0, 128.0, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 137.8, 137.8, 138.2, 138.4, 138.8; HRMS (Waters Synapt G2): m/z calcd for $[C_{47}H_{52}O_{10}+Na]^+$: 799.3458; Found: 799.3454.



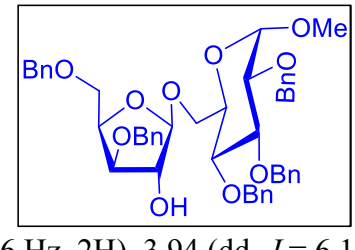
Menthyl 3,5-di-*O*-benzyl-α-D-ribofuranside (**35d**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.9) +48.2°; IR (cm^{-1}, $CHCl_3$): 3554, 3030, 2930, 1643, 1454, 1264, 1097, 764; ^1H NMR (399.78 MHz, $CDCl_3$): δ 0.77 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 4.3 Hz, 2H), 0.79 – 1.03 (m, 3H), 0.91 (d, *J* = 3.8 Hz, 2H), 1.03 – 1.20 (m, 1H), 1.27 – 1.50 (m, 2H), 1.55 – 1.70 (m, 3H), 2.10 – 2.28 (m, 2H), 2.94 (d, *J* = 10.2 Hz, 1H), 3.37 (dd, *J* = 10.6, 4.4 Hz, 1H), 3.48 (dABq, *J* = 10.4, 4.0 Hz, 2H), 3.78 (dd, *J* = 7.0, 3.5 Hz, 1H), 4.10 (bs, 1H), 4.19 (q, *J* = 4.0 Hz, 1H), 4.52 (ABq, *J* = 12.1 Hz, 2H), 4.56 (d, *J* = 12.3 Hz, 1H), 4.73 (d, *J* = 12.3 Hz, 1H), 5.09 (d, *J* = 4.7 Hz, 1H), 7.12 – 7.42 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 15.9, 21.2, 22.3, 23.0, 25.3, 31.6, 34.3, 43.2, 48.5, 70.1, 72.0, 72.5, 73.4, 76.5, 80.0, 81.3, 102.7, 127.6, 127.6, 127.6, 127.6, 127.6, 127.6, 128.3, 128.3, 128.3, 128.3, 137.9, 138.2; HRMS (Waters Synapt G2): m/z calcd for $[C_{29}H_{40}O_5+Na]^+$: 491.2773; Found: 491.2769.



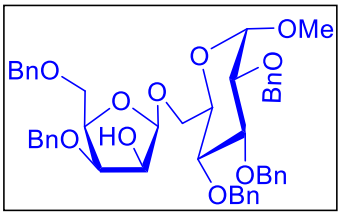
Menthyl 3,5-di-O-benzyl-β-D-xylofuranside (**35d**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.5) –15.1°; IR (cm^{-1}, $CHCl_3$): 3554, 3030, 2930, 1643, 1454, 1264, 1097, 764; ^1H NMR (399.78 MHz, $CDCl_3$): δ 0.70 (d, *J* = 6.9 Hz, 3H), 0.80 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.62 – 1.07 (m, 3H), 1.09 – 1.48 (m, 2H), 1.55 – 1.72 (m, 2H), 2.08 – 2.17 (m, 2H), 2.21 – 2.34 (m, 1H), 3.48 (td, *J* = 10.6, 4.1 Hz, 1H), 3.68 (dd, *J* = 10.0, 6.6 Hz, 1H), 3.79 (dd, *J* = 10.1, 4.9 Hz, 1H), 3.95 (dd, *J* = 5.5, 3.1 Hz, 1H), 4.24 (s, 1H), 4.40 – 4.50 (m, 1H), 4.50 (dd, *J* = 11.9, 1.8 Hz, 2H), 4.59 (d, *J* = 12.1 Hz, 1H), 4.63 (d, *J* = 11.8 Hz, 1H), 5.12 (d, *J* = 1.7 Hz, 1H), 6.74 – 7.79 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 15.9, 21.0, 22.3, 23.0, 24.8, 31.3, 34.5, 39.6, 48.0, 69.5, 72.1, 73.4, 74.7, 79.1, 79.9, 83.1, 104.0, 127.4, 127.4, 127.5, 127.5, 127.7, 127.7, 128.2, 128.3, 128.3, 128.3, 138.0, 138.3; HRMS (Waters Synapt G2): m/z calcd for $[C_{29}H_{40}O_5+Na]^+$: 491.2773; Found: 491.2770.



Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,5-di-*O*-benzyl-β-D-xylofuranosyl)-α-D-glucopyranoside (**20k**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) –6.1°; IR (cm^{-1}, $CHCl_3$): 3420, 3029, 2925, 1600, 1454, 1361, 1065, 741; ^1H NMR (399.78 MHz, $CDCl_3$): δ 2.15 (bs, 1H), 3.28 (s, 3H), 3.43 – 3.54 (m, 2H), 3.58 (dd, *J* = 10.8, 5.5 Hz, 1H), 3.68 (dd, *J* = 10.3, 7.1 Hz, 1H), 3.76 (dd, *J* = 10.4, 4.6 Hz, 2H), 3.94 (dd, *J* = 6.1, 3.1 Hz, 1H), 3.96 – 4.02 (m, 2H), 4.14 – 4.26 (m, 1H), 4.41 – 4.49 (m, 2H), 4.49 (d, *J* = 15.4 Hz, 1H), 4.53 – 4.61 (m, 4H), 4.63 (d, *J* = 12.1 Hz, 1H), 4.76 (d, *J* = 12.1 Hz, 1H), 4.81 (d, *J* = 10.9 Hz, 1H), 4.85 (dd, *J* = 6.4, 4.6 Hz, 2H), 4.97 (d, *J* = 10.9 Hz, 1H), 6.80 – 7.70 (m, 25H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 55.0, 66.9, 69.7, 69.9, 72.1, 73.3, 73.3, 74.8, 75.7, 77.8, 79.3, 79.8, 79.9, 82.0, 83.5, 97.8, 108.5, 127.4, 127.4, 127.5, 127.6, 127.6, 127.6, 127.7, 127.8, 127.8, 127.8, 127.9, 127.9, 128.0, 128.0, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 131.5, 137.8, 138.1, 138.2, 138.3, 138.7; HRMS (Waters Synapt G2): m/z calcd for $[C_{47}H_{52}O_{10}+Na]^+$: 799.3458; Found: 799.3450.

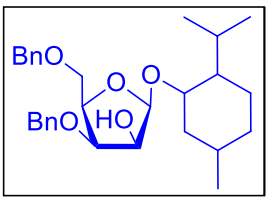


Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,5-di-*O*-benzyl-β-D-lyxofuranosyl)-α-D-glucopyranoside (**36a**): $[\alpha]^{25}{}_D$ ($CHCl_3$, *c* 1.0) –16.7°; IR (cm^{-1}, $CHCl_3$): 3425, 3067, 2927, 1600, 1451, 1362, 1068, 745; ^1H NMR (399.78 MHz, $CDCl_3$): δ 3.24 (s, 3H), 3.40 – 3.47 (m, 1H), 3.49 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.58 (dd, *J* =

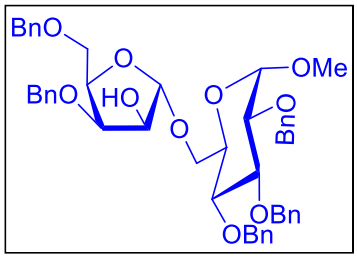


10.9, 6.1 Hz, 1H), 3.64 (dd, *J* = 9.8, 6.3 Hz, 1H), 3.73 – 3.82 (m, 2H), 3.94 – 4.04 (m, 3H), 4.13 (t, *J* = 5.3 Hz, 1H), 4.19 – 4.30 (m, 1H), 4.48 (ABq, *J* = 11.8 Hz, 2H), 4.56 (dd, *J* = 10.6, 4.1 Hz, 2H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.68 (d, *J* = 11.8 Hz, 2H), 4.75 (s, 1H), 4.79 (d, *J* = 5.3 Hz, 1H), 4.83 (d, *J* = 3.1 Hz, 1H), 4.82 – 4.91 (m, 1H), 4.97 (ABq, *J* = 10.8 Hz, 2H), 6.72 – 7.72 (m, 25H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 54.9, 67.6, 69.8, 70.1, 73.0, 73.3, 73.5, 74.4, 75.0, 75.7, 78.2, 79.3, 80.0, 82.1, 97.7, 101.4, 127.3, 127.3, 127.6, 127.6, 127.6, 127.6, 127.7, 127.7, 127.8, 127.8, 127.8, 128.0, 128.0, 128.0, 128.0, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 138.0, 138.1, 138.1, 138.2, 138.7; HRMS (Waters Synapt G2) : m/z calcd for $[C_{47}H_{52}O_{10}+Na]^+$: 799.3458; Found: 799.3457.

Menthyl 3,5-di-O-benzyl-β-D-lyxofuranside (**36b**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.5) −138.1°; IR (cm^{-1}, $CHCl_3$): 3427, 2939, 1584, 1454, 1148, 1027, 740; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 0.70 (d, *J* = 6.9 Hz, 3H), 0.80 (d, *J* = 7.2 Hz, 3H), 0.75 – 0.96 (m, 2H), 0.90 (d, *J* = 6.5 Hz, 3H), 1.07 – 1.44 (m, 2H), 1.54 – 1.73 (m, 3H), 2.07 (dd, *J* = 12.1, 4.0 Hz, 1H), 2.22 – 2.43 (m, 1H), 3.02 (d, *J* = 11.4 Hz, 1H), 3.47 (td, *J* = 10.6, 4.2 Hz, 1H), 3.63 (dd, *J* = 9.4, 6.2 Hz, 1H), 3.79 (dd, *J* = 9.4, 6.5 Hz, 1H), 3.94 – 4.05 (m, 1H), 4.08 – 4.27 (m, 2H), 4.47 (d, *J* = 11.8 Hz, 1H), 4.56 (d, *J* = 11.8 Hz, 1H), 4.63 (d, *J* = 11.6 Hz, 1H), 4.75 (d, *J* = 11.7 Hz, 1H), 5.13 (d, *J* = 5.2 Hz, 1H), 7.10 – 7.73 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 15.9, 21.1, 22.3, 22.8, 24.7, 31.3, 34.4, 39.9, 48.0, 69.4, 73.0, 73.5, 74.4, 75.1, 77.7, 78.8, 96.5, 127.0, 127.0, 127.3, 127.6, 127.9, 127.9, 128.2, 128.2, 128.3, 128.3, 138.0, 138.5; HRMS (Waters Synapt G2): m/z calcd for $[C_{29}H_{40}O_5+Na]^+$: 491.2773; Found: 491.2773.

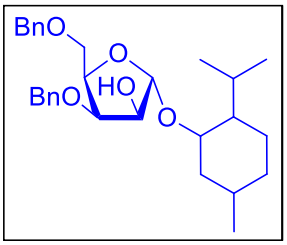


Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,5-di-*O*-benzyl-α-D-lyxofuranosyl)-α-D-glucopyranoside (**18k**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.7) +48.1°; IR (cm^{-1}, $CHCl_3$): 3386, 3032, 2923, 1597, 1454, 1271, 1057, 703; ^{1}H NMR (399.78 MHz, $CDCl_3$): δ 3.34 (s, 3H), 3.64 – 3.45 (m, 5H), 3.75 – 3.68 (m, 1H), 3.96 (t, *J* = 9.2 Hz, 1H), 4.01 (dd, *J* = 11.1, 3.3 Hz, 1H), 4.13 (dd, *J* = 10.2, 4.9 Hz, 1H), 4.22 – 4.17 (m, 1H), 4.64 – 4.36 (m, 7H), 4.69 (t, *J* = 12.4 Hz, 2H), 4.86 – 4.77 (m, 3H), 4.98 (d, *J* = 10.8 Hz, 1H), 5.04 (s, 1H), 7.49 – 7.02 (m, 25H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 55.2, 65.8, 67.7, 69.7, 71.9, 72.4, 73.3, 73.8, 75.0, 75.8, 77.2, 77.5, 77.6, 79.8, 82.0, 98.1, 107.5, 127.7, 127.7, 127.7, 127.8, 127.8,



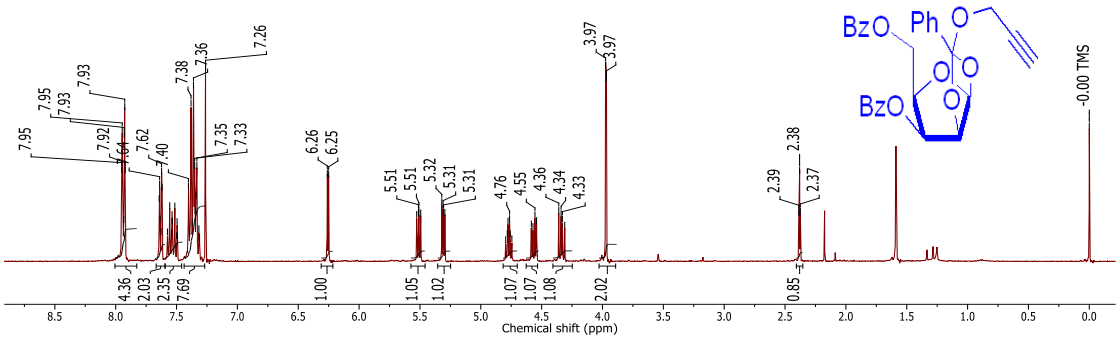
127.8, 127.8, 127.8, 127.9, 127.9, 127.9, 128.0, 128.0, 128.1, 128.1, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128. 4, 137.0, 137.7, 138.1, 138.2, 138.7; HRMS (Waters Synapt G2): m/z calcd for $[C_{47}H_{52}O_{10}+Na]^+$: 799.3458; Found: 799.3450.

Menthyl 3,5-di-O-benzyl-α-D-lyxofuranside (**18l**): $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +58.1°; IR (cm^{-1}, $CHCl_3$): 3429, 2927, 1594, 1455, 1150, 1028, 741; ^1H NMR (399.78 MHz, $CDCl_3$): δ 0.77 (d, *J* = 6.9 Hz, 3H), 0.82 (dd, *J* = 12.3, 3.2 Hz, 1H), 0.87 (d, *J* = 5.3 Hz, 3H), 0.89 (d, *J* = 5.7 Hz, 3H), 0.89 – 1.00 (m, 1H), 1.08 – 1.21 (m, 1H), 1.30 – 1.46 (m, 1H), 1.52 – 1.72 (m, 3H), 1.96 – 2.15 (m, 2H), 3.29 (td, *J* = 10.6, 4.4 Hz, 1H), 3.61 (dd, *J* = 10.5, 2.1 Hz, 1H), 3.66 (dd, *J* = 10.5, 3.2 Hz, 1H), 4.08 (dd, *J* = 9.9, 4.7 Hz, 1H), 4.29 – 4.42 (m, 2H), 4.45 (d, *J* = 4.8 Hz, 1H), 4.48 (d, *J* = 11.4 Hz, 1H), 4.54 (d, *J* = 11.8 Hz, 1H), 4.64 (d, *J* = 11.8 Hz, 1H), 4.72 (d, *J* = 11.3 Hz, 1H), 5.04 (s, 1H), 7.03 – 7.67 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$): δ 16.2, 21.1, 22.2, 23.2, 25.5, 31.6, 34.3, 43.2, 48.7, 67.9, 72.0, 72.4, 73.9, 77.0, 78.0, 79.1, 108.5, 127.7, 127.7, 127.7, 127.8, 127.9, 127.9, 128.4, 128.4, 128.4, 128.4, 137.2, 137.9; HRMS (Waters Synapt G2): m/z calcd for $[C_{29}H_{40}O_5+Na]^+$: 491.2773; Found: 491.2767.

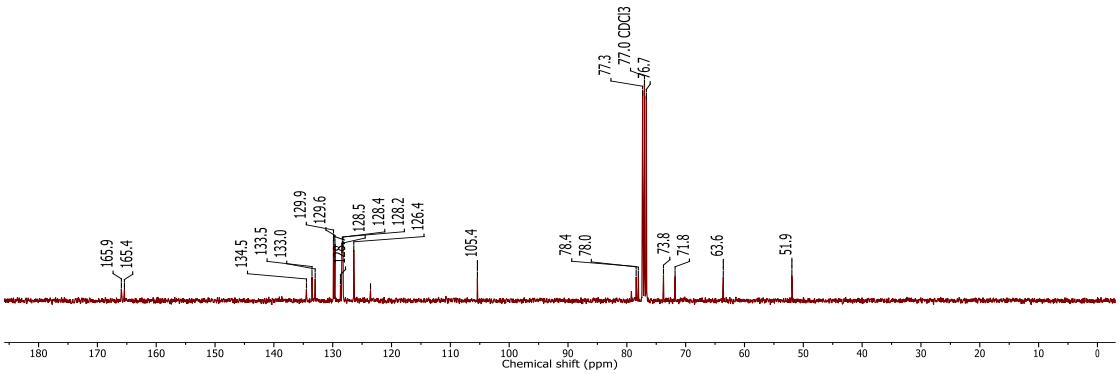


2.6– Spectral charts

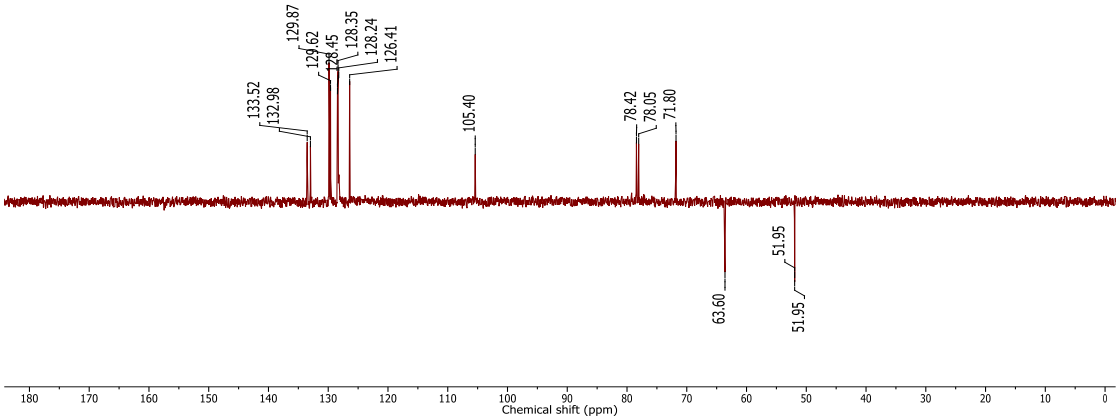
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) Of Compound **13a**



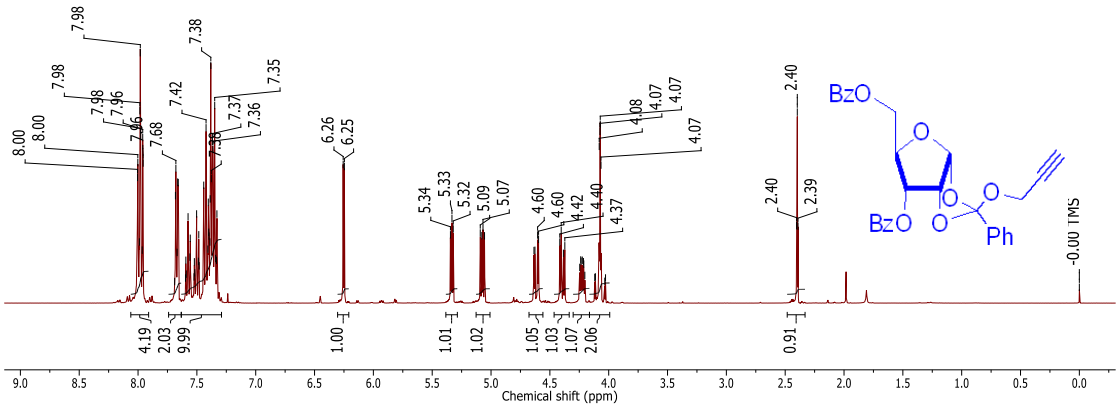
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **13a**



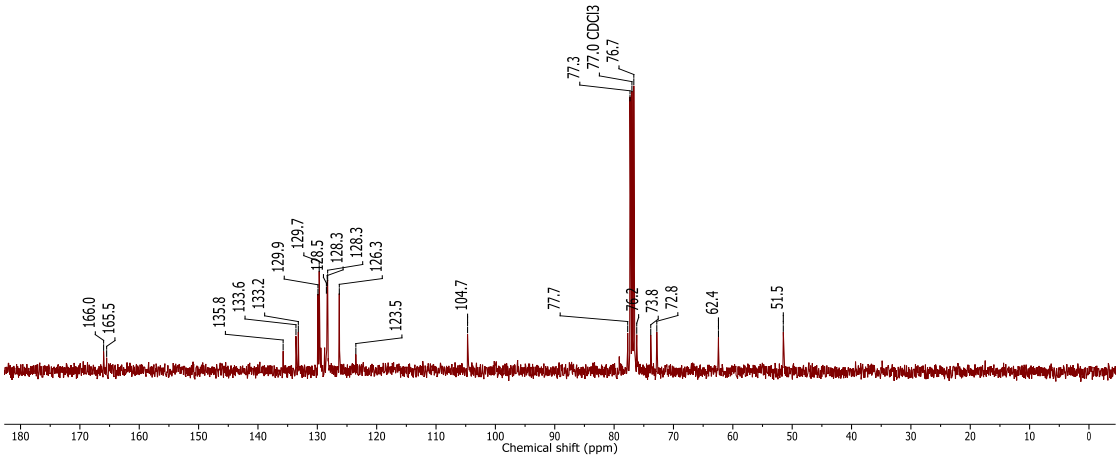
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **13a**



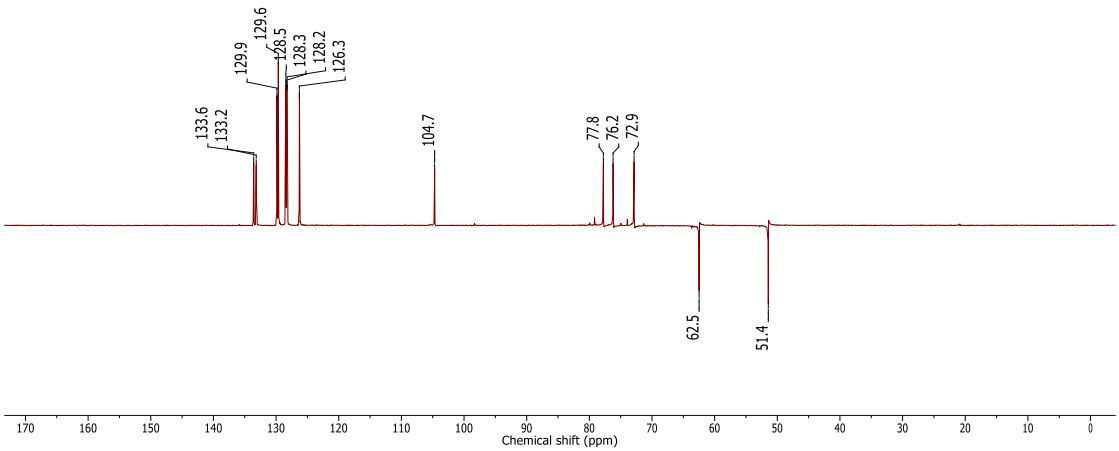
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **9a**



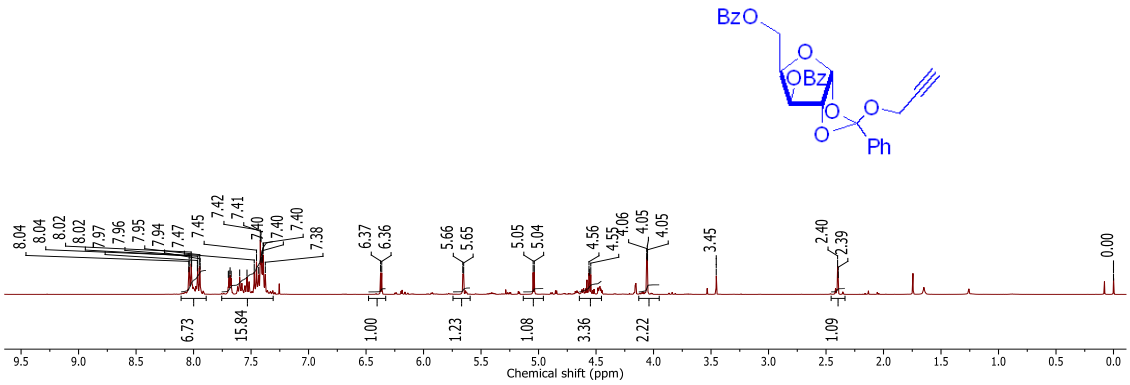
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **9a**



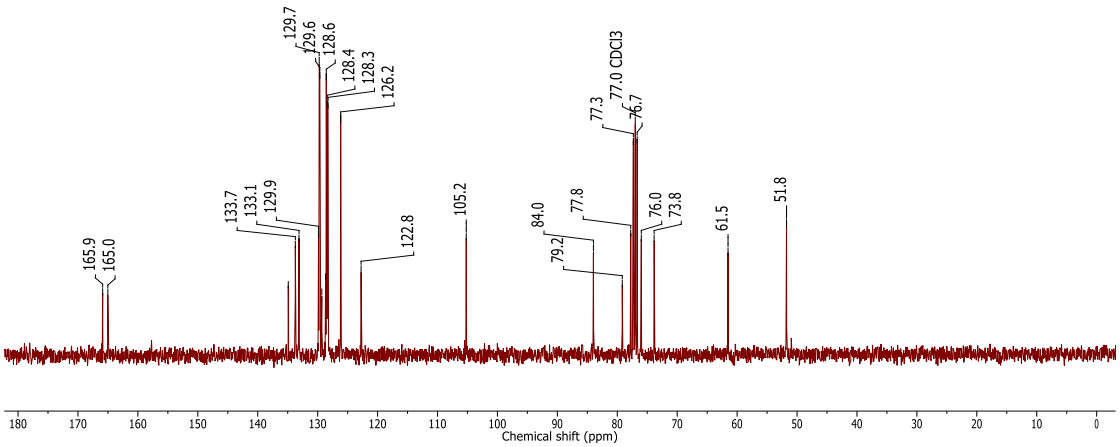
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **9a**



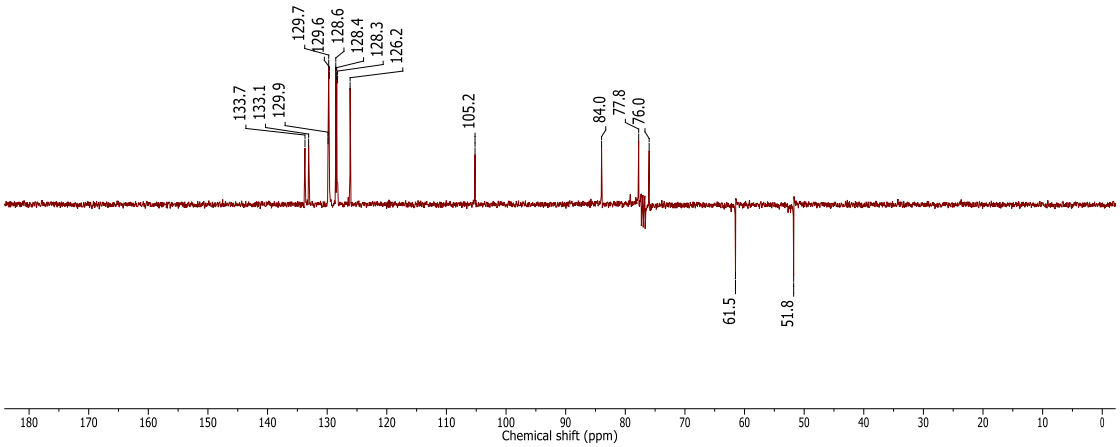
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **14a**



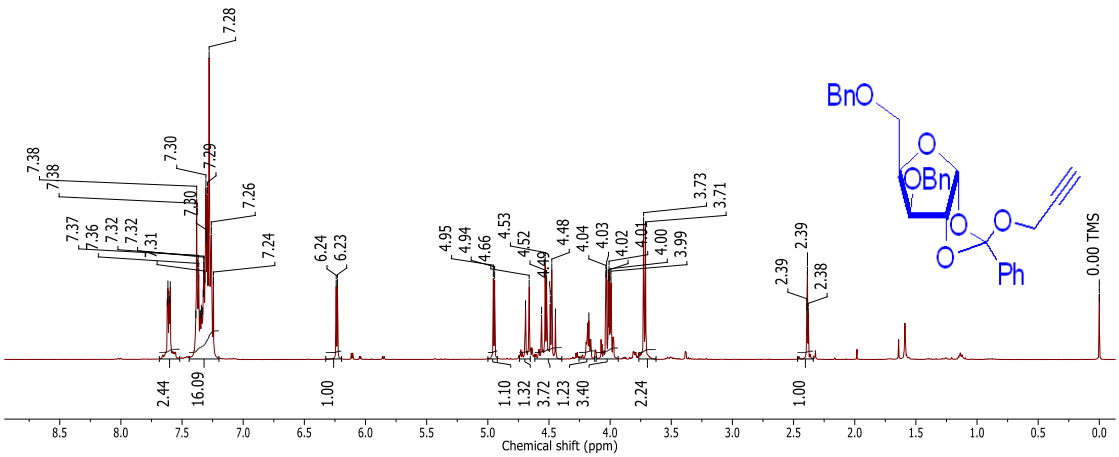
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **14a**



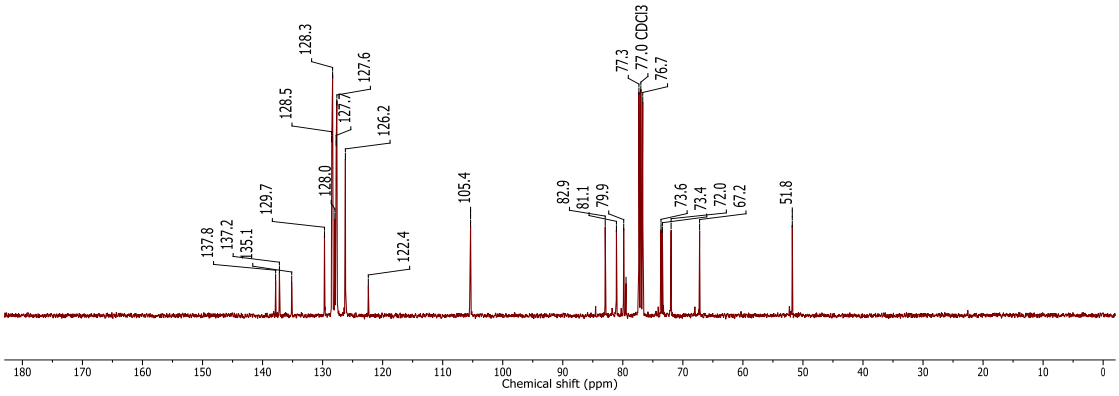
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **14a**



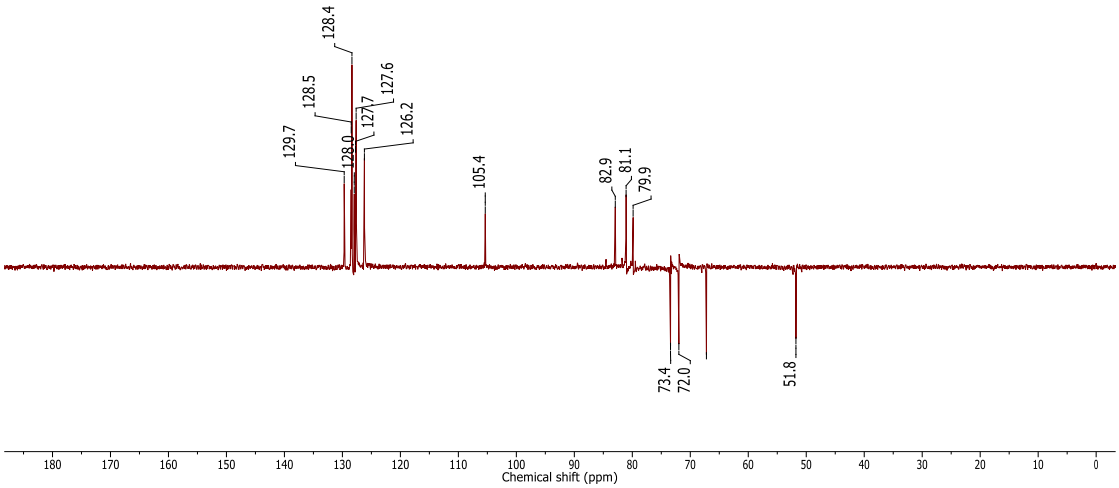
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **14c**



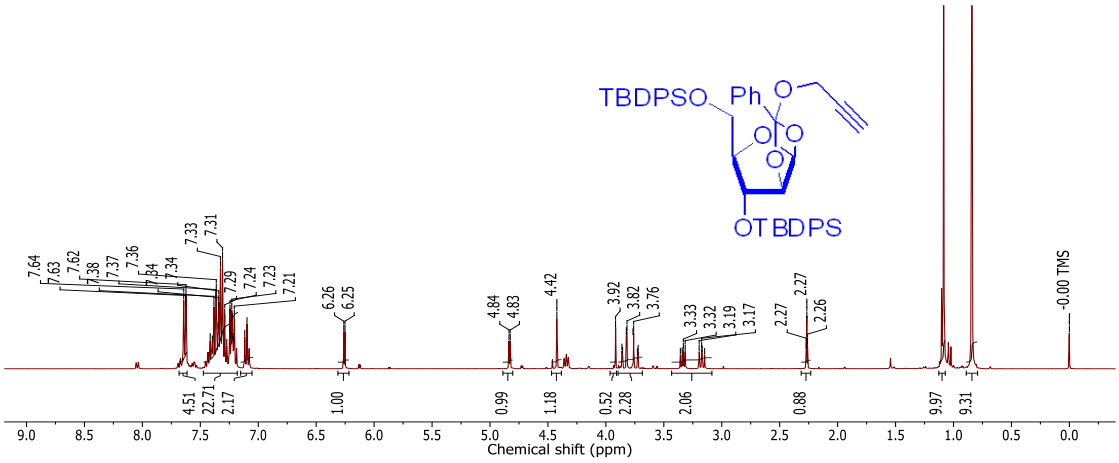
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **14c**



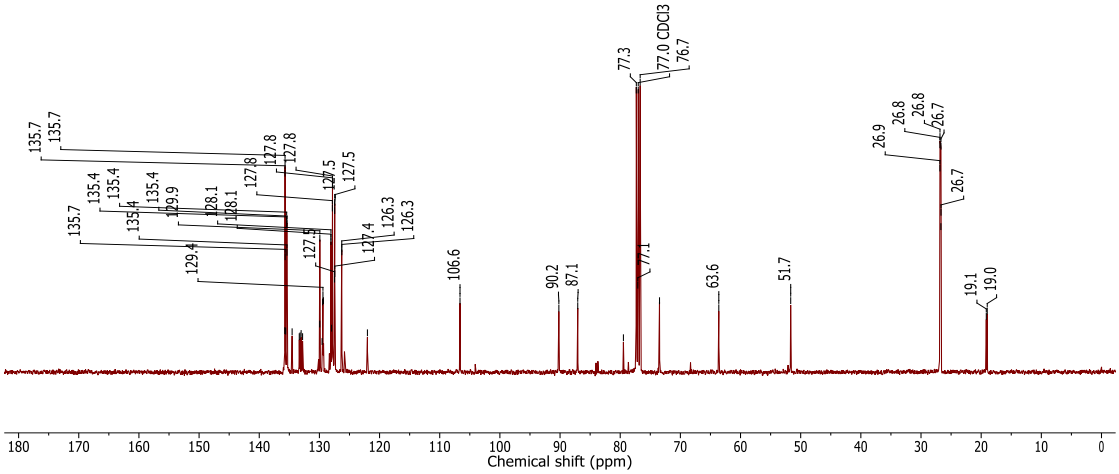
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **14c**



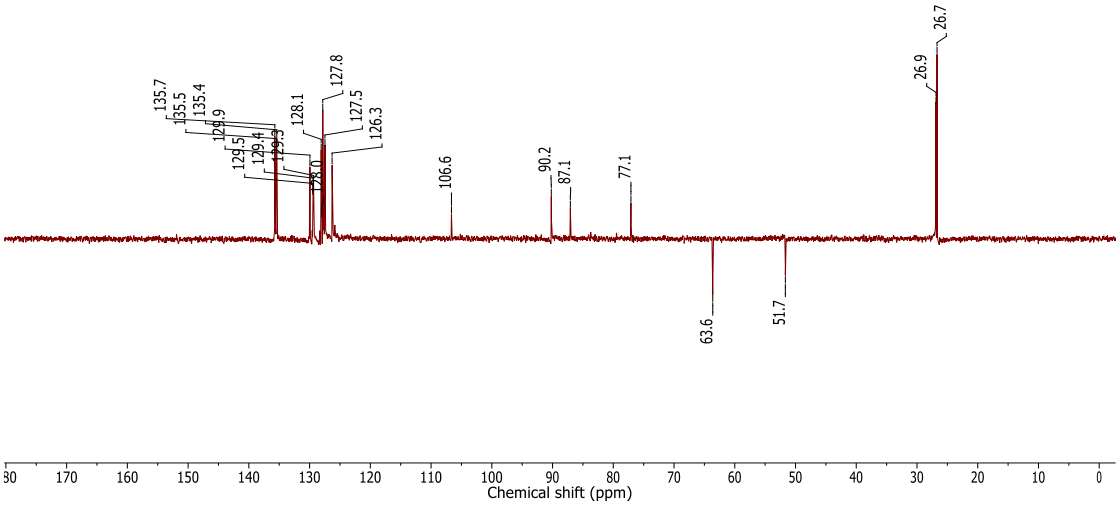
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **8d**



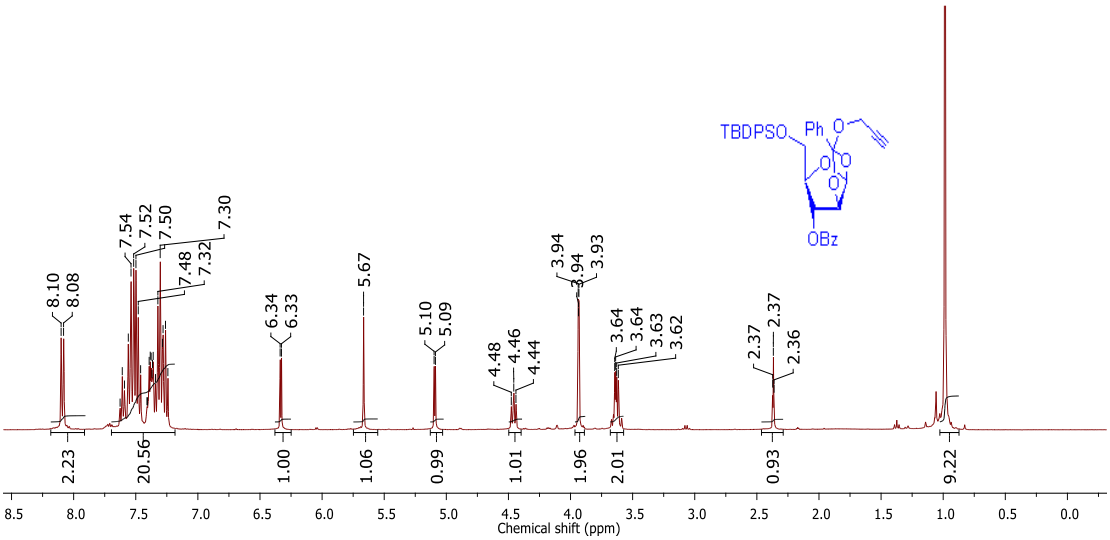
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **8d**



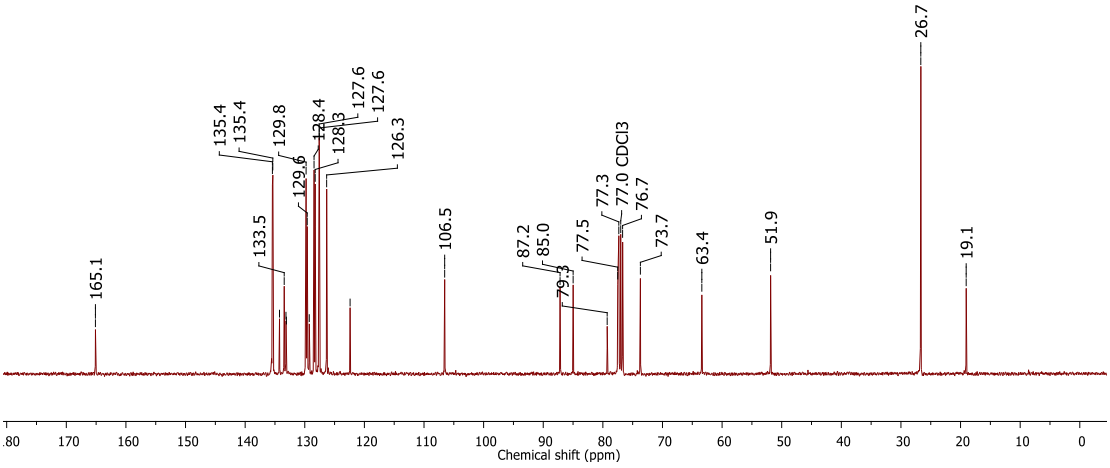
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **8d**



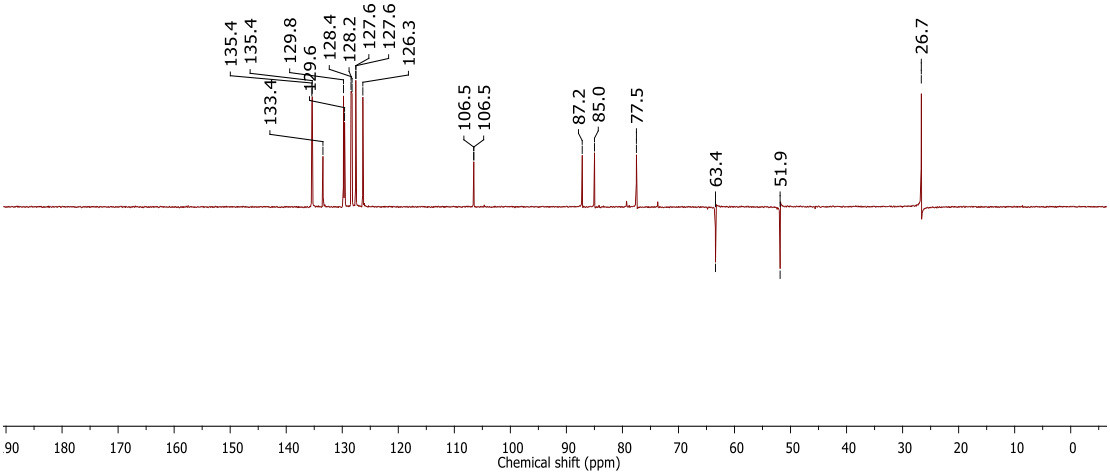
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **8e**



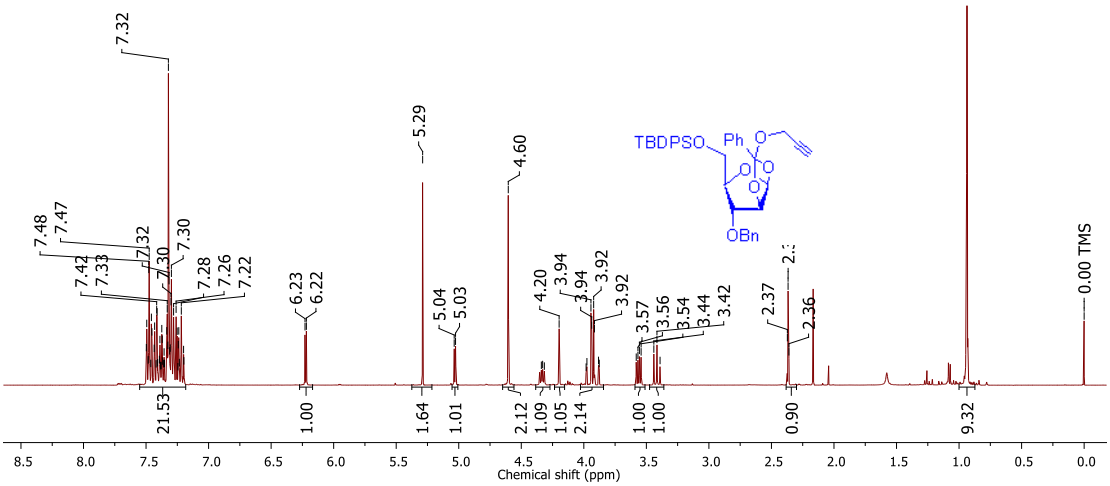
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **8e**



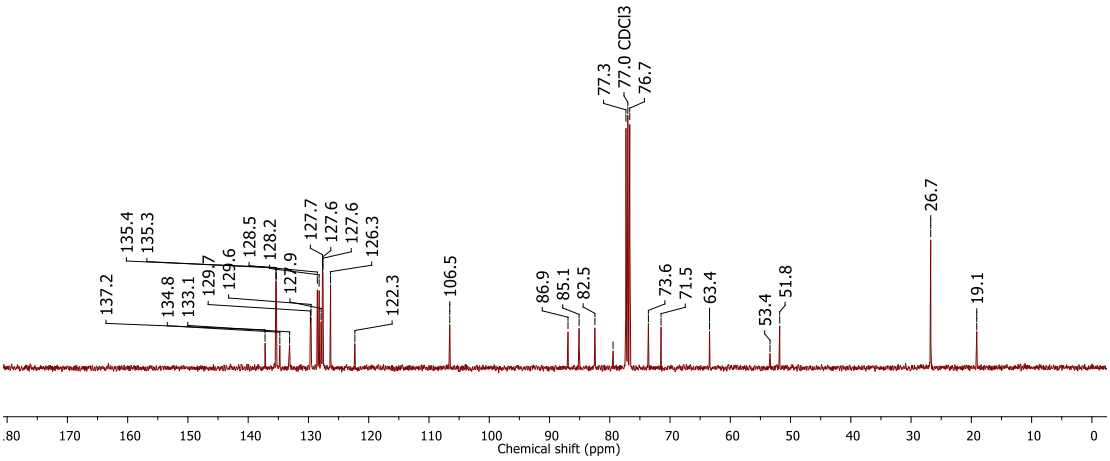
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **8e**



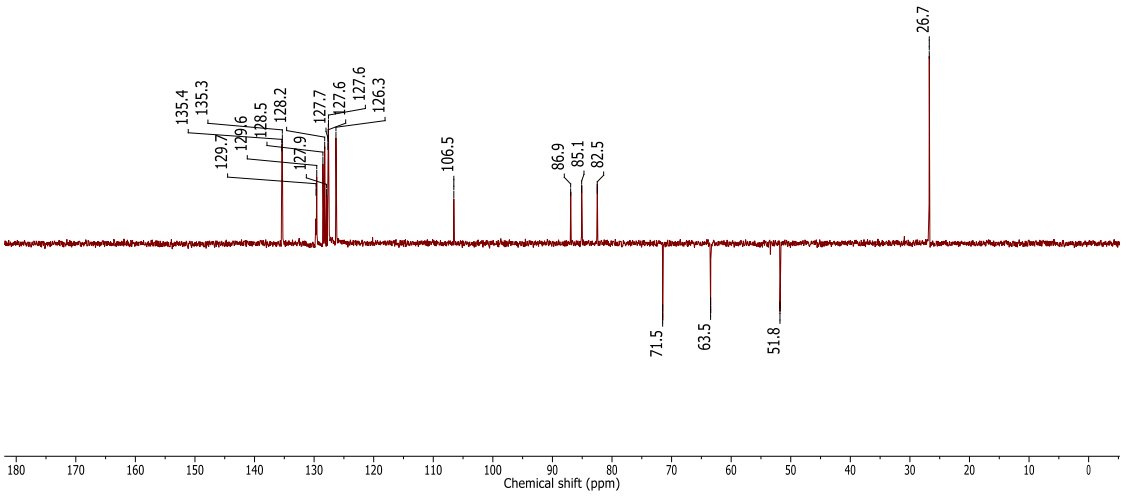
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **8f**



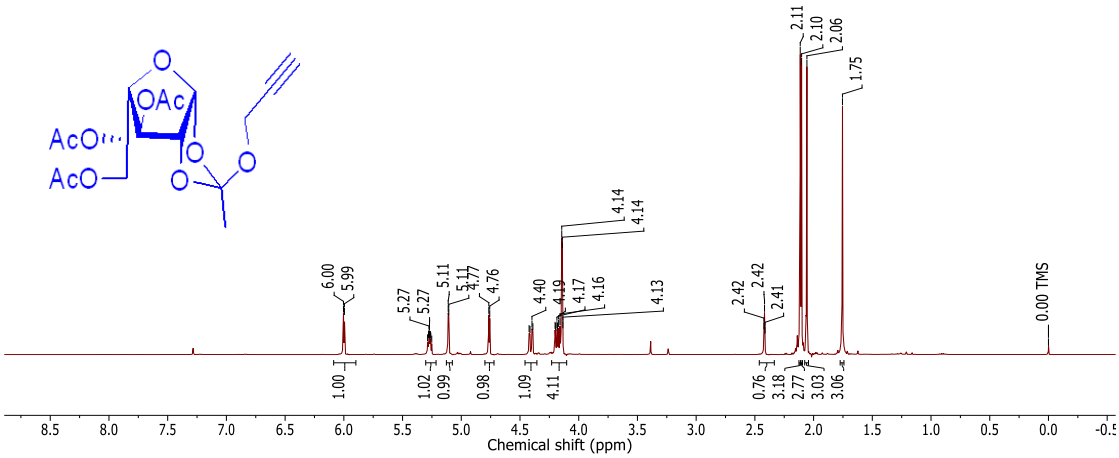
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **8f**



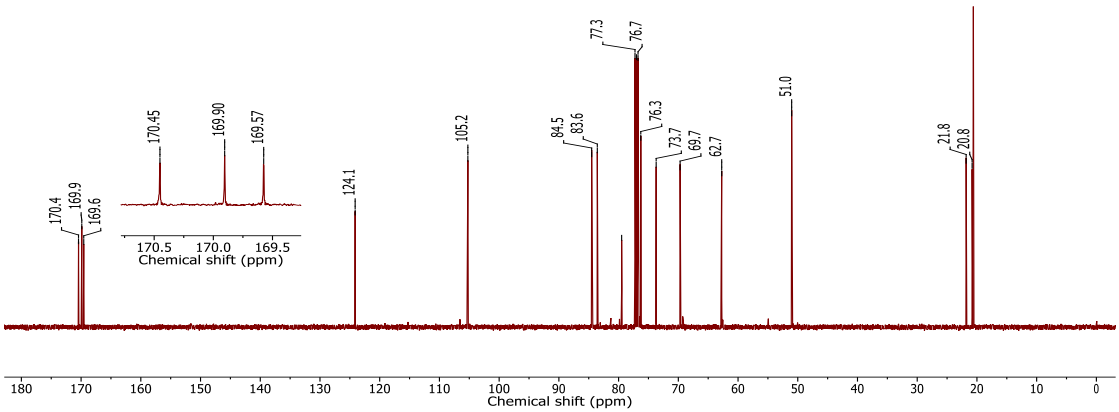
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **8f**



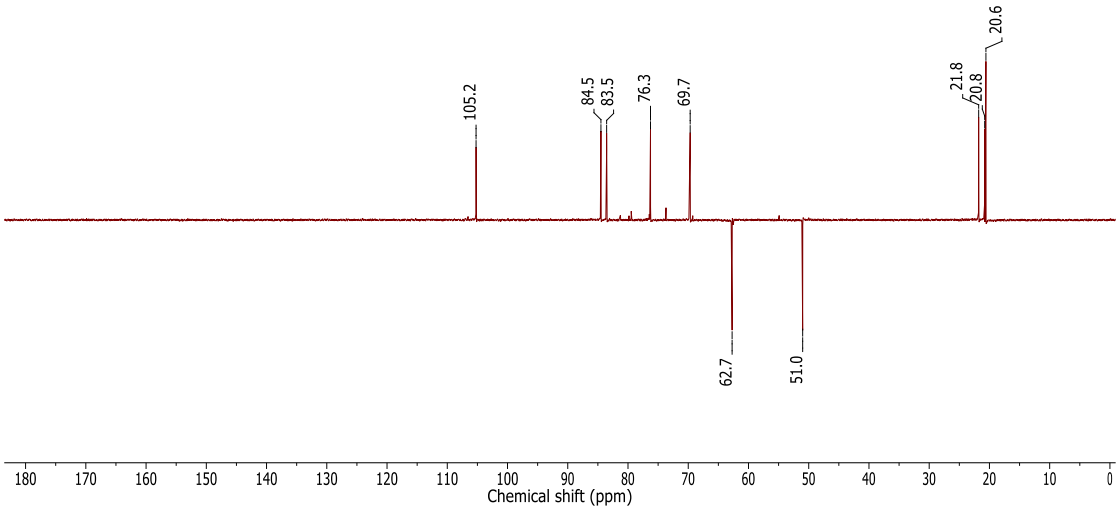
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **10**



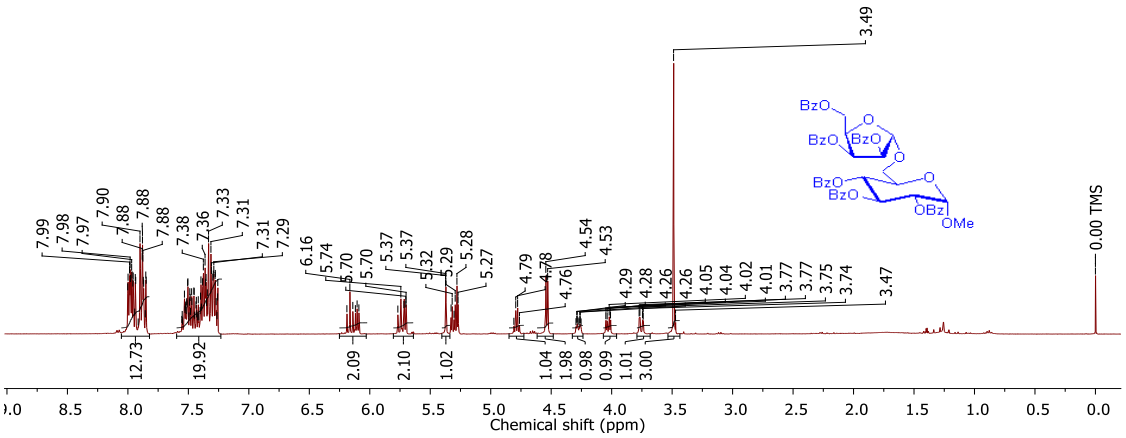
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **10**



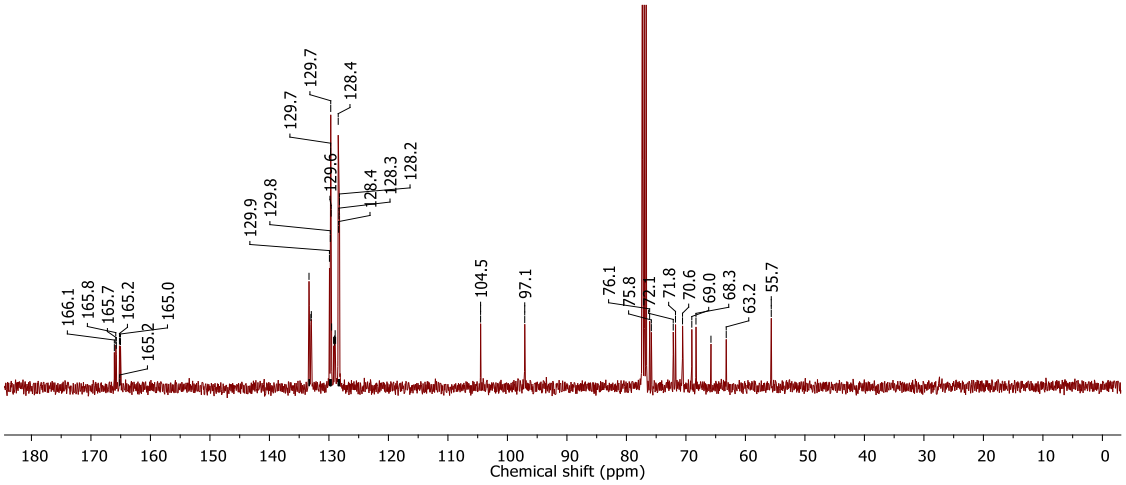
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **10**



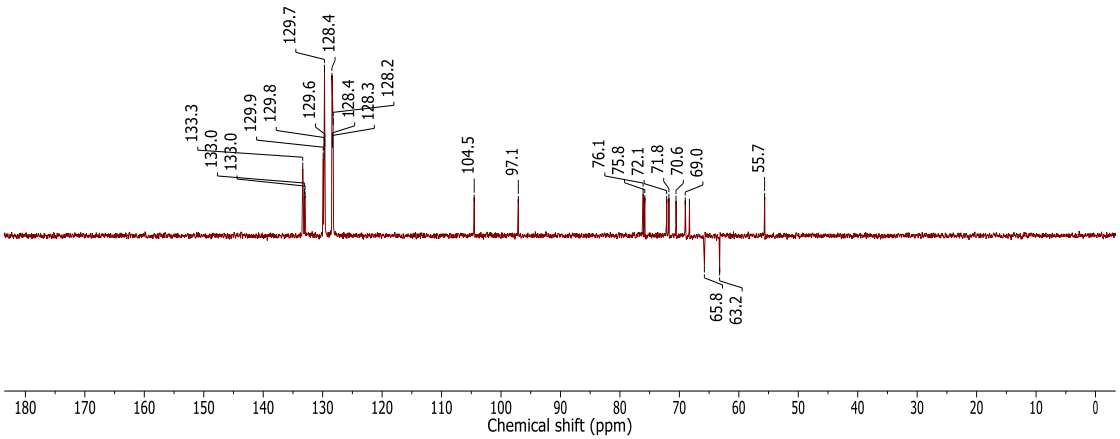
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **18a**



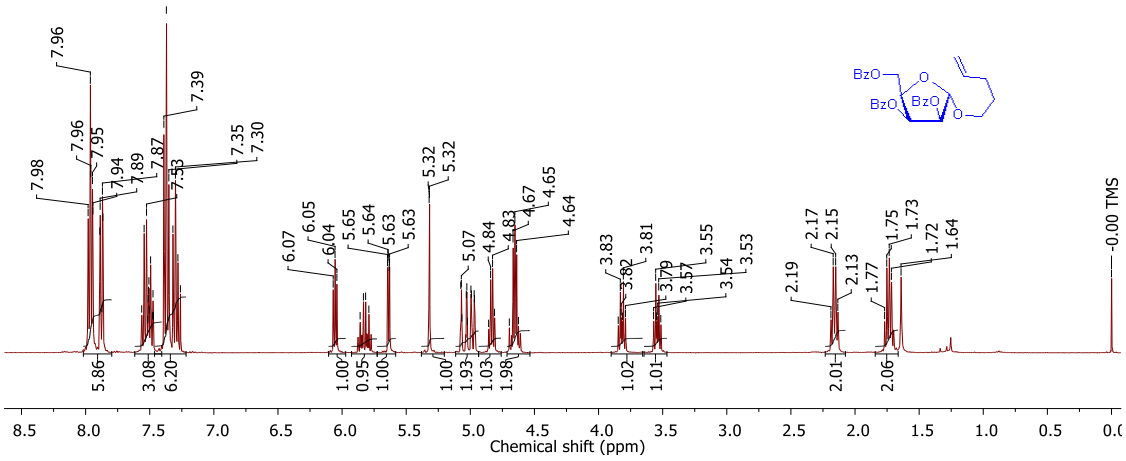
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **18a**



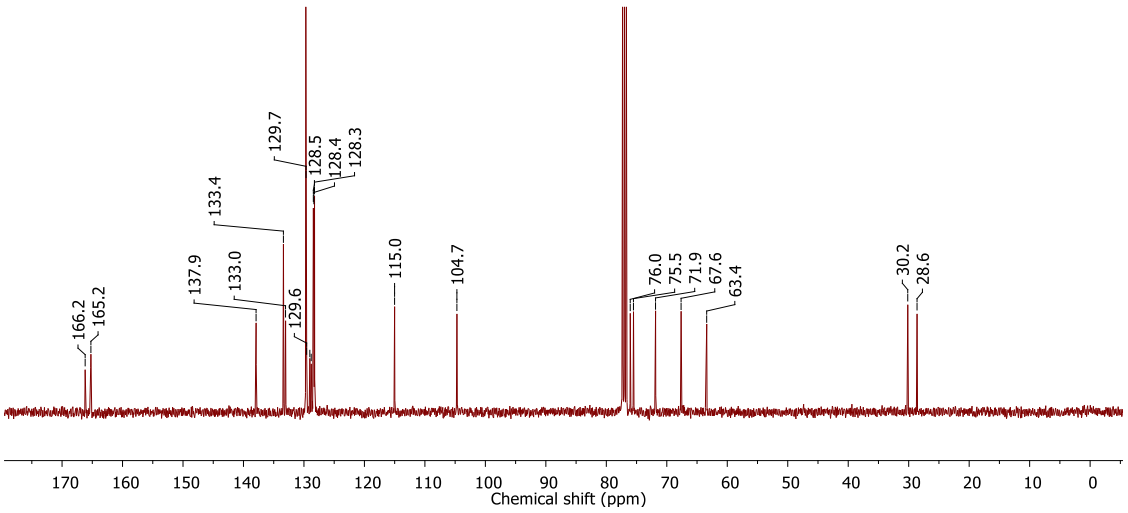
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **18a**



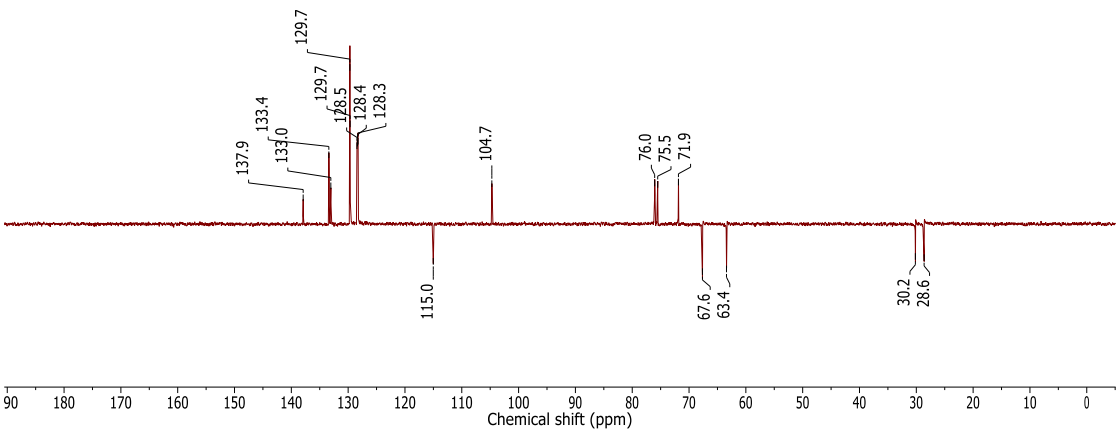
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **18b**



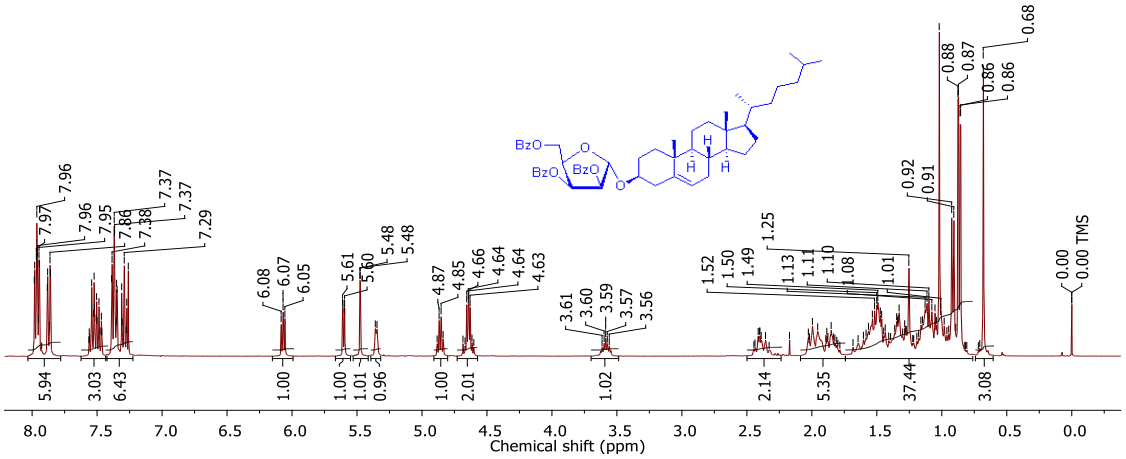
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **18b**



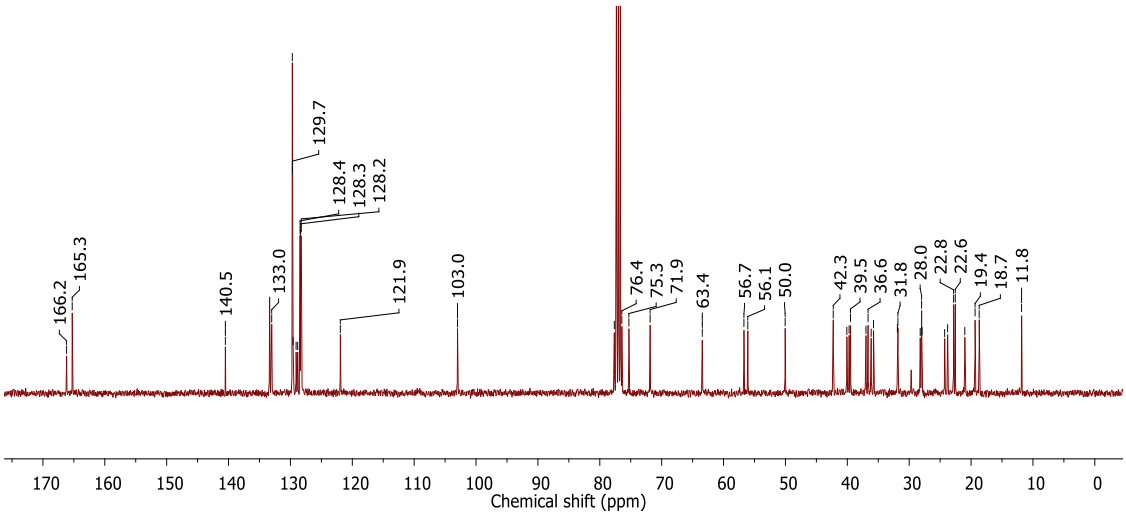
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **18b**



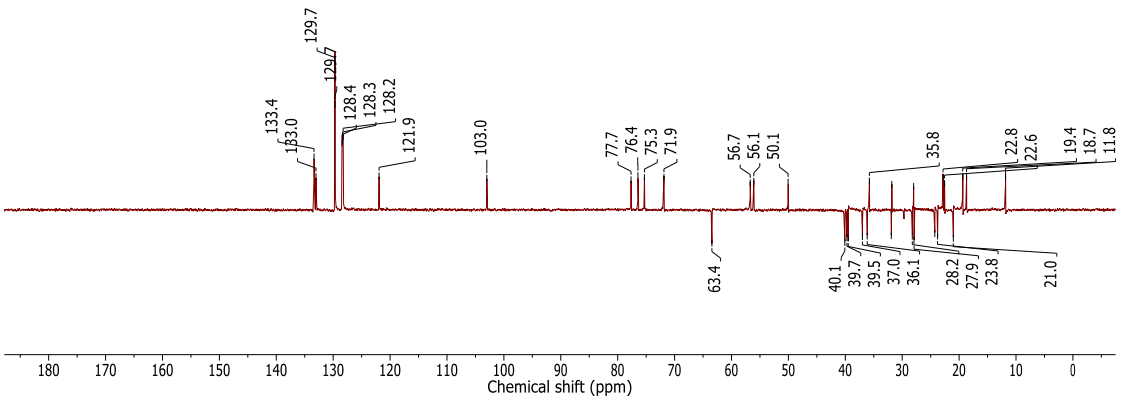
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **18d**



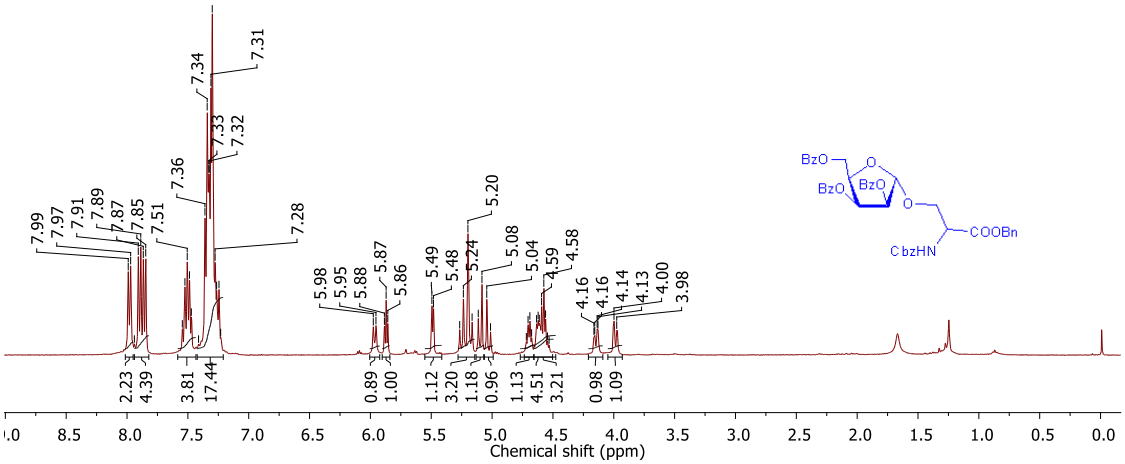
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **18d**



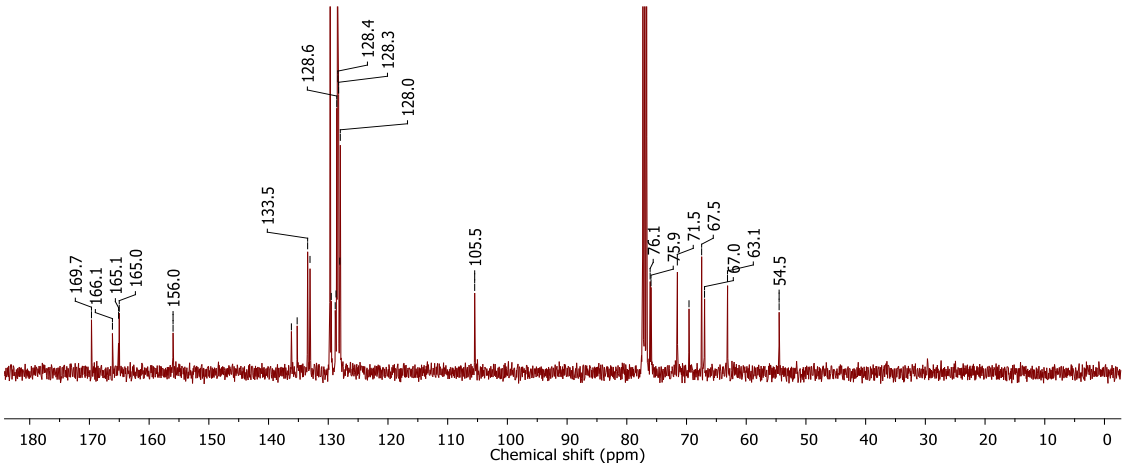
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **18d**



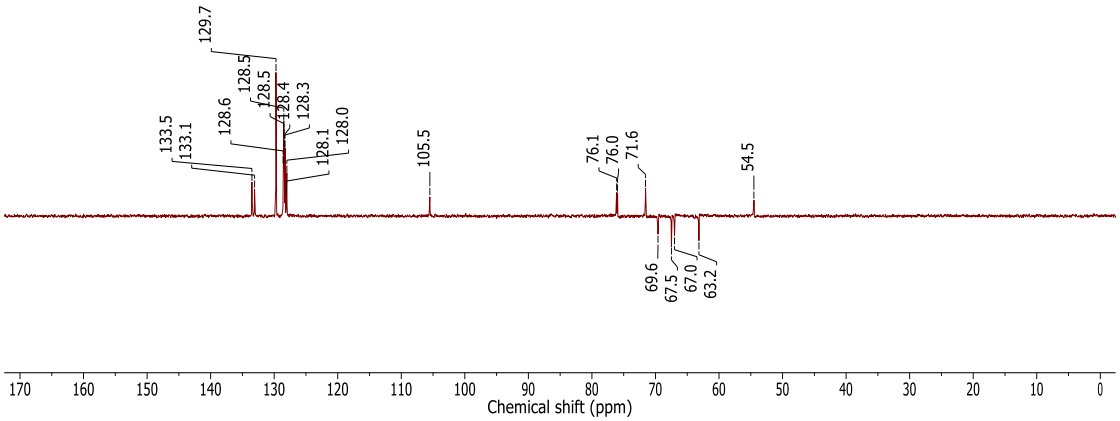
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **18e**



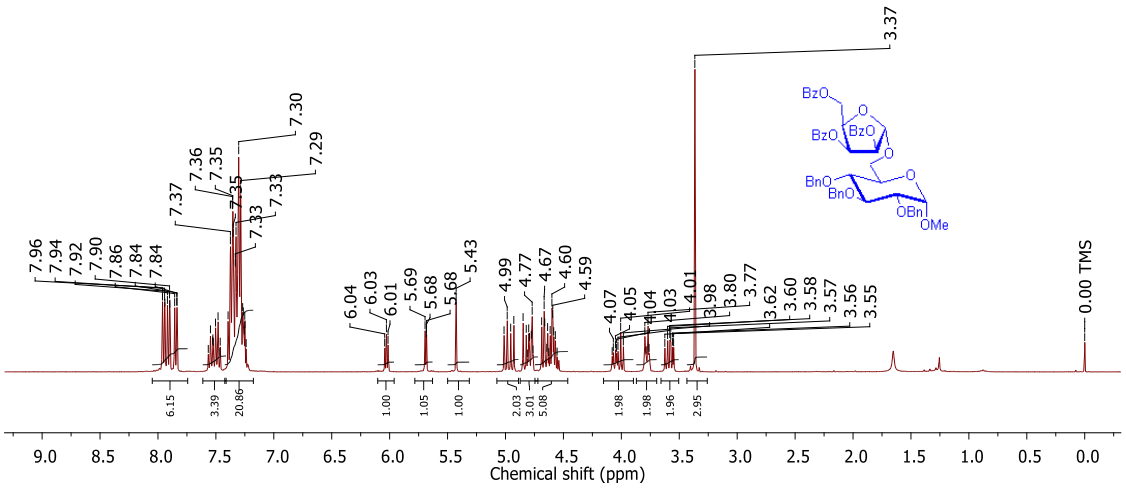
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **18e**



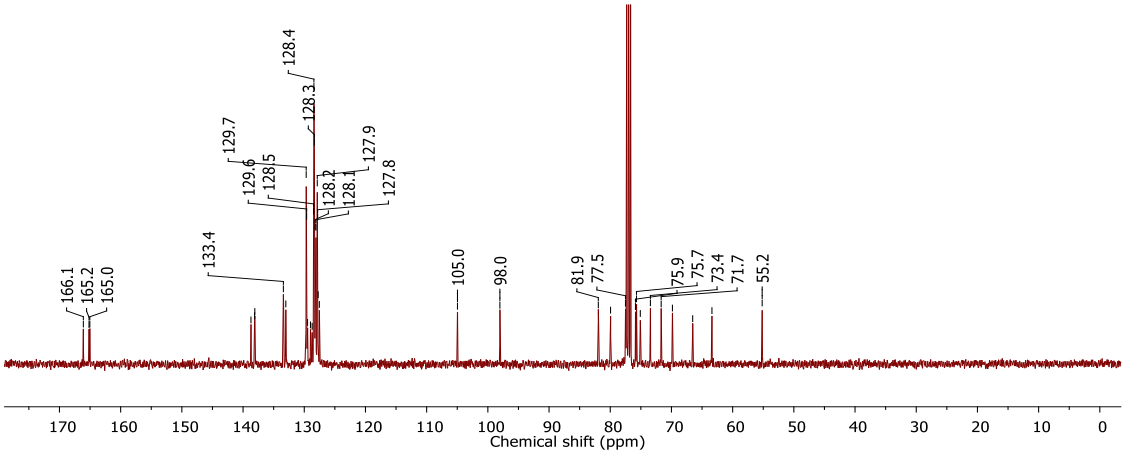
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **18e**



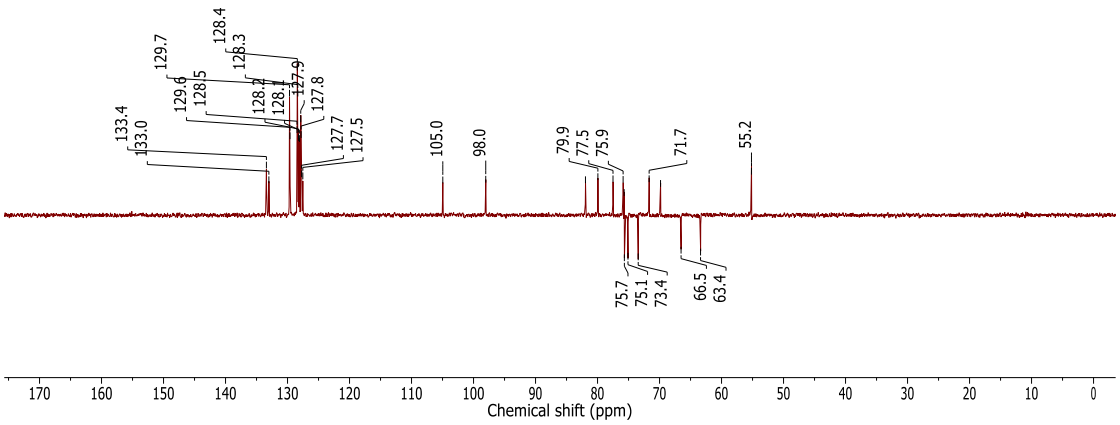
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **18f**



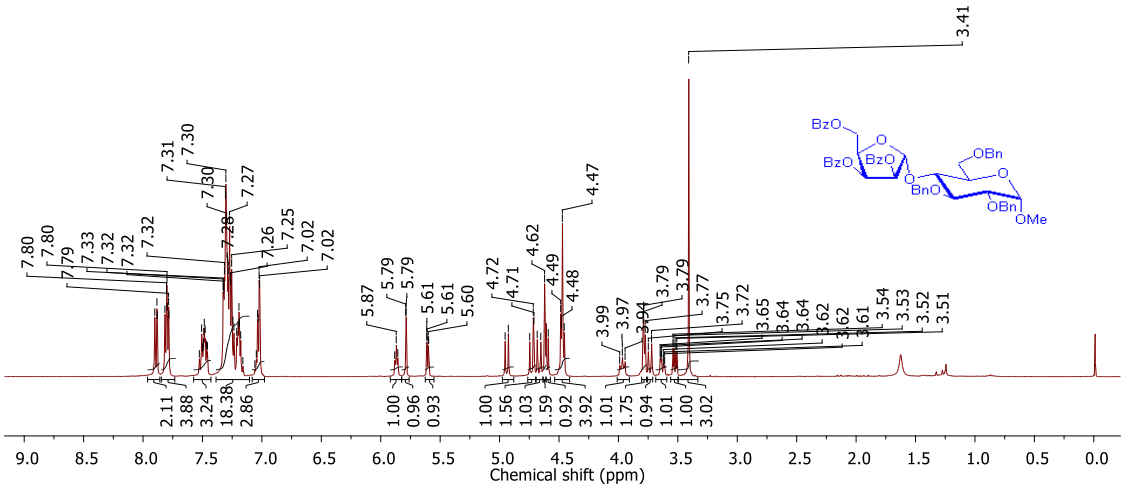
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **18f**



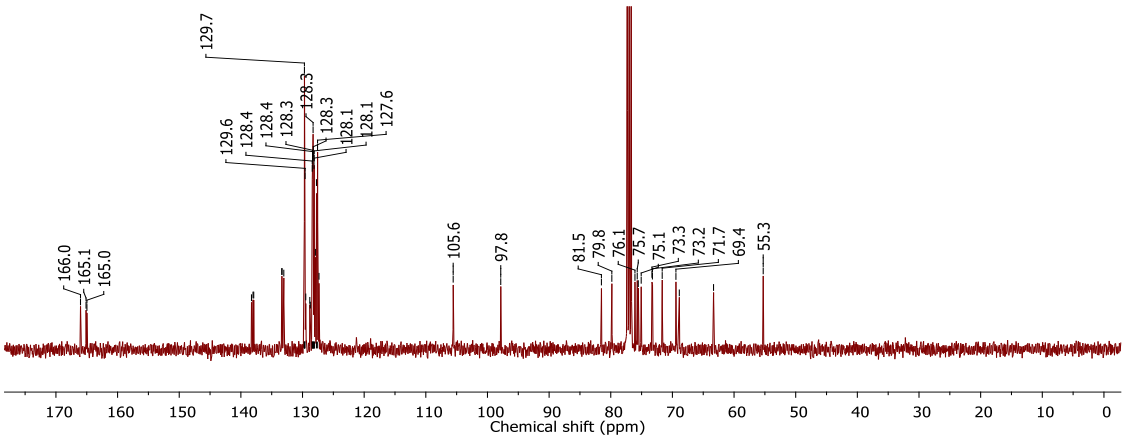
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **18f**



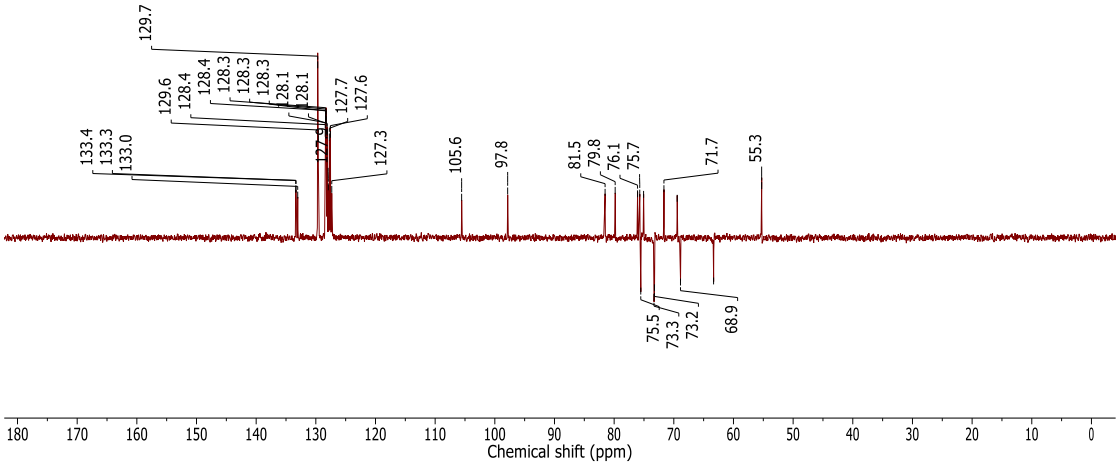
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **18g**



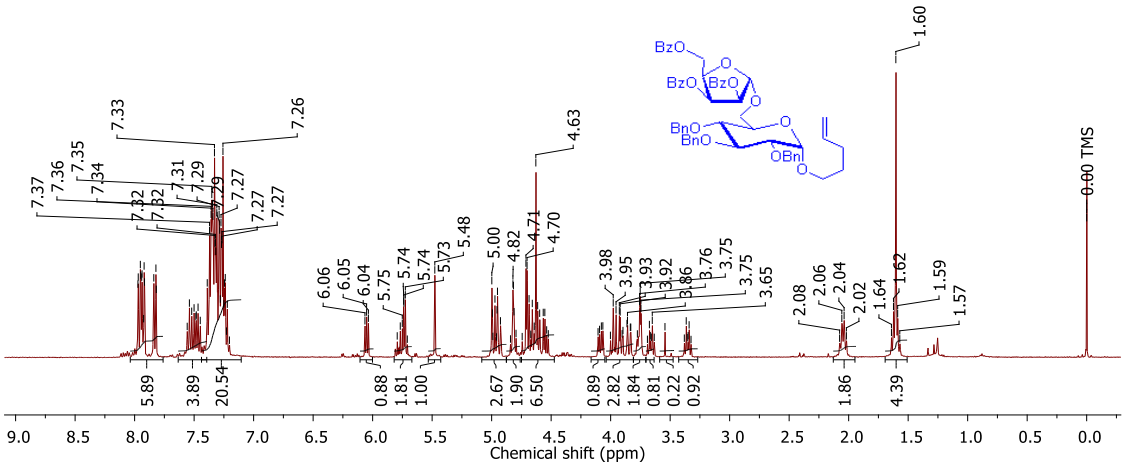
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **18g**



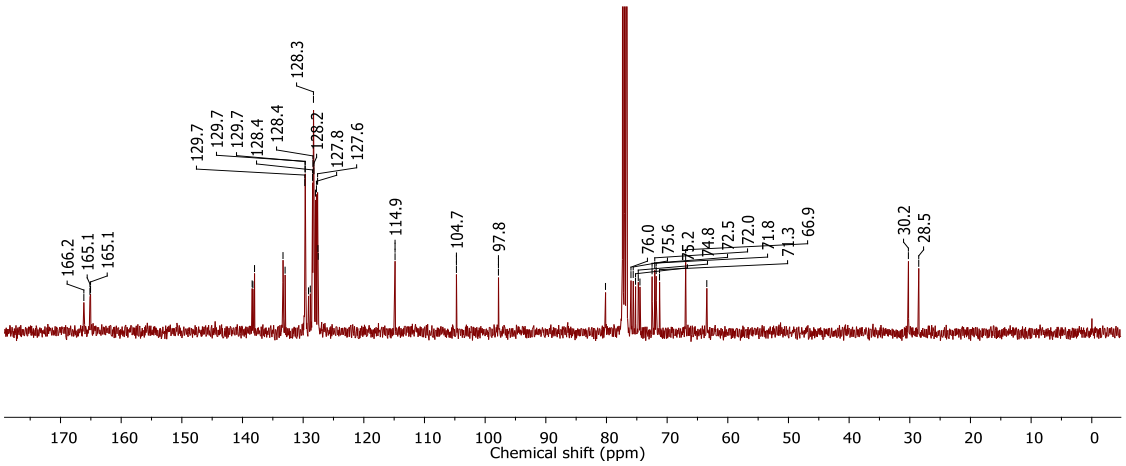
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **18g**



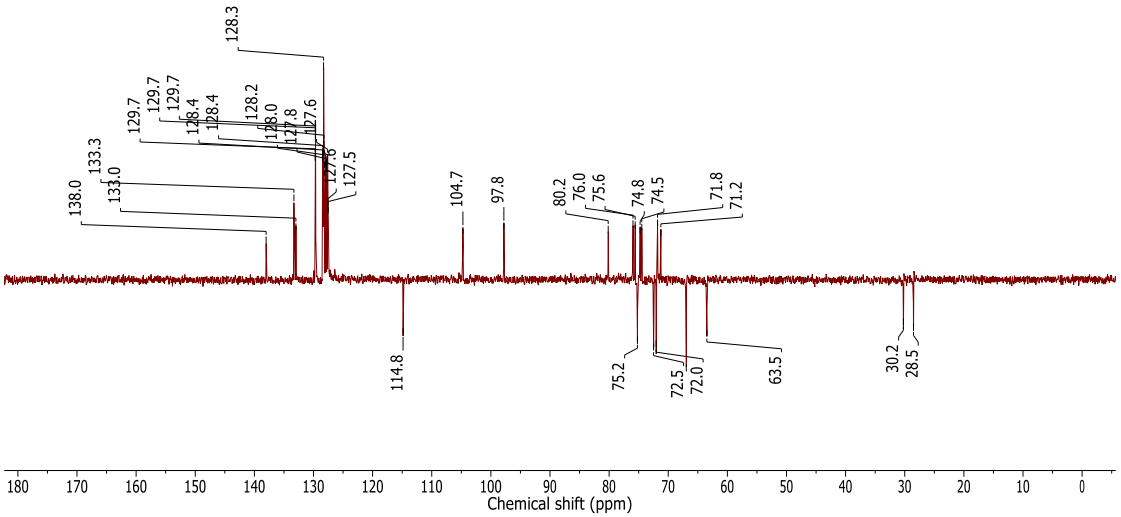
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **18h**



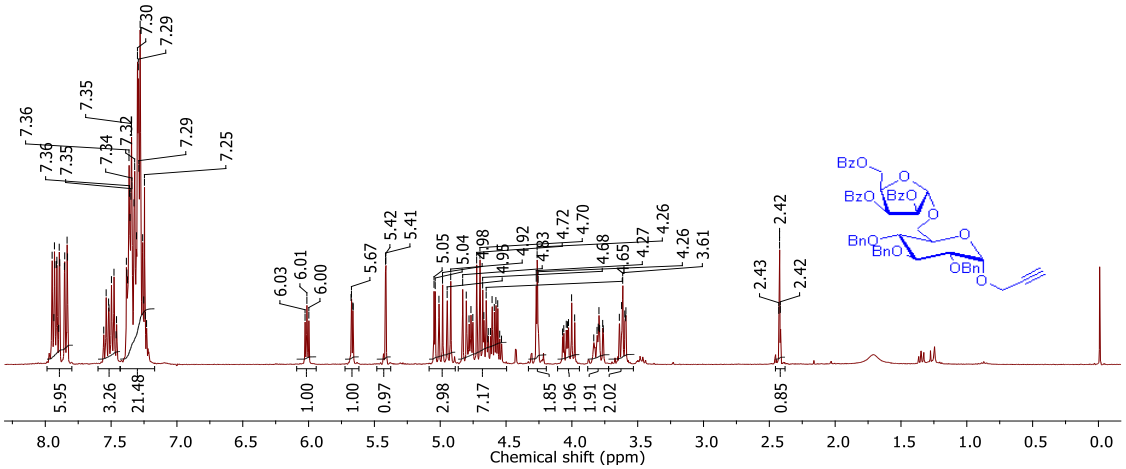
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **18h**



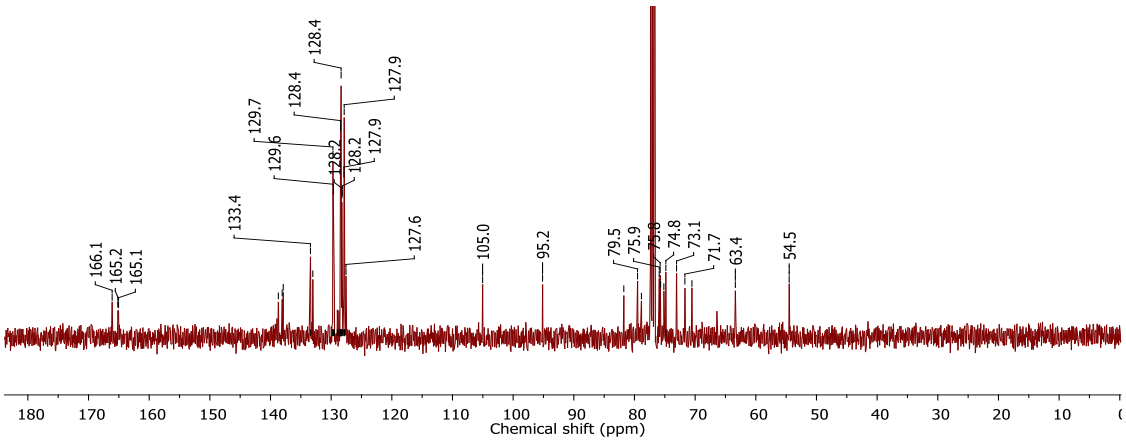
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **18h**



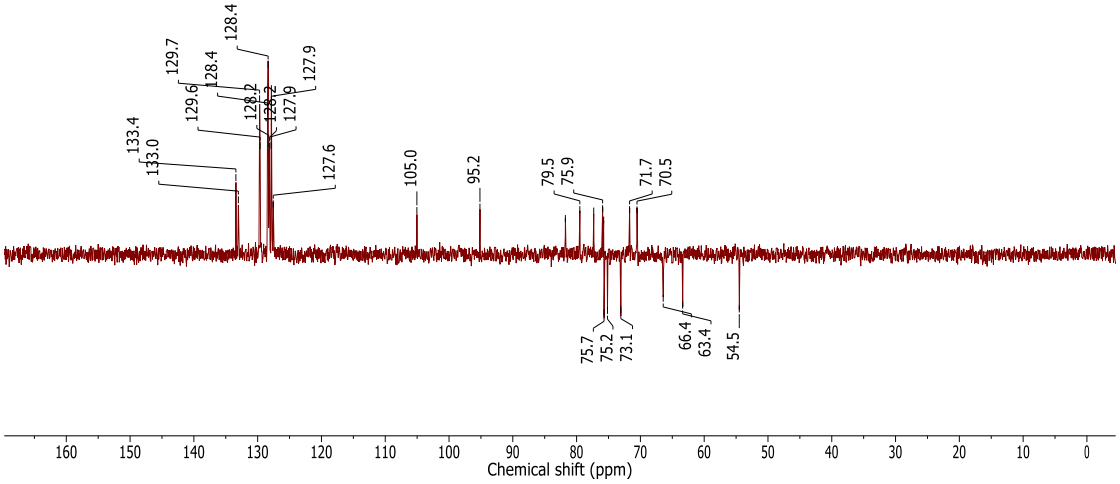
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **18i**



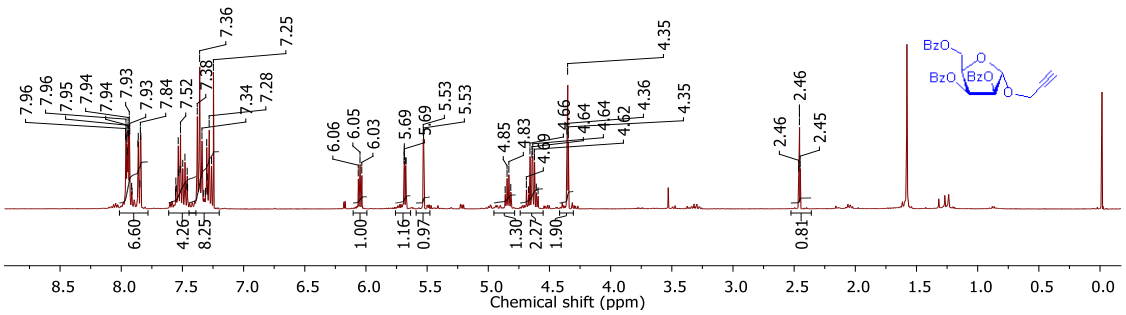
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **18i**



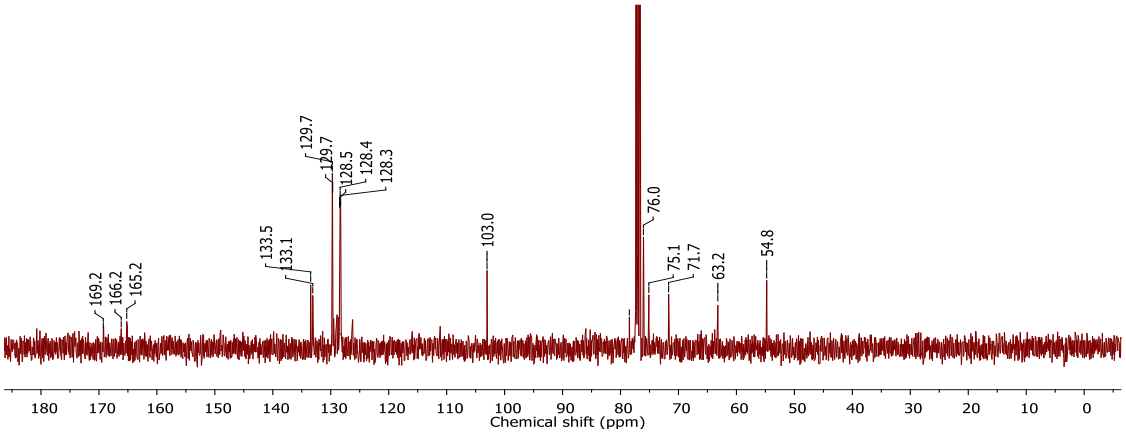
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **18i**



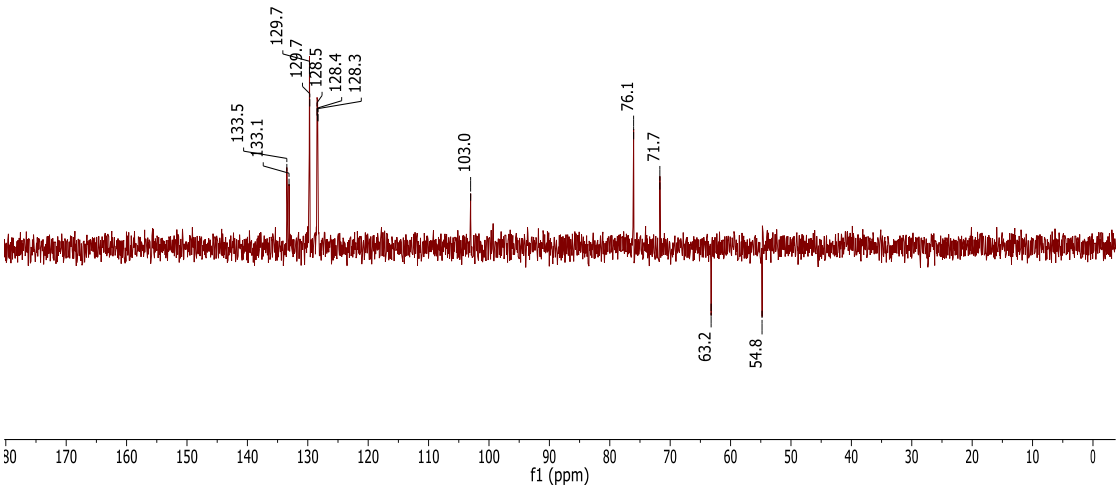
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound



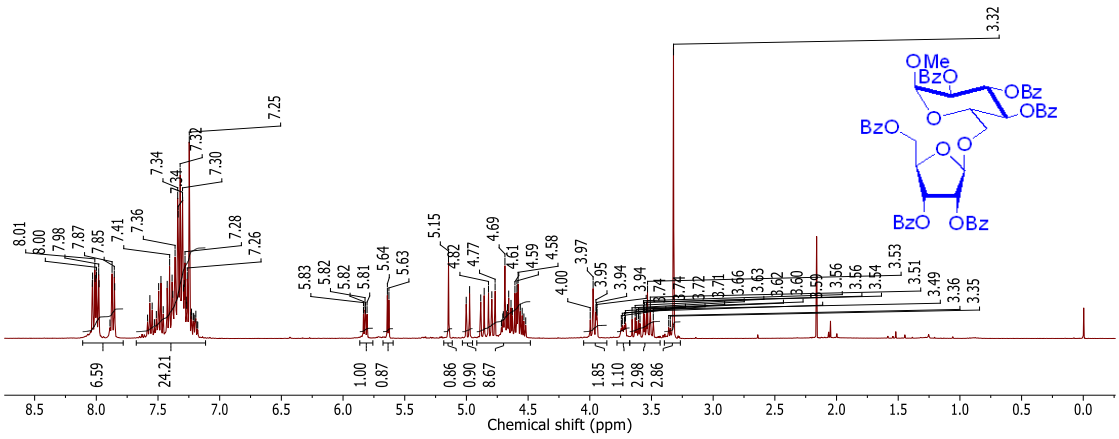
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound



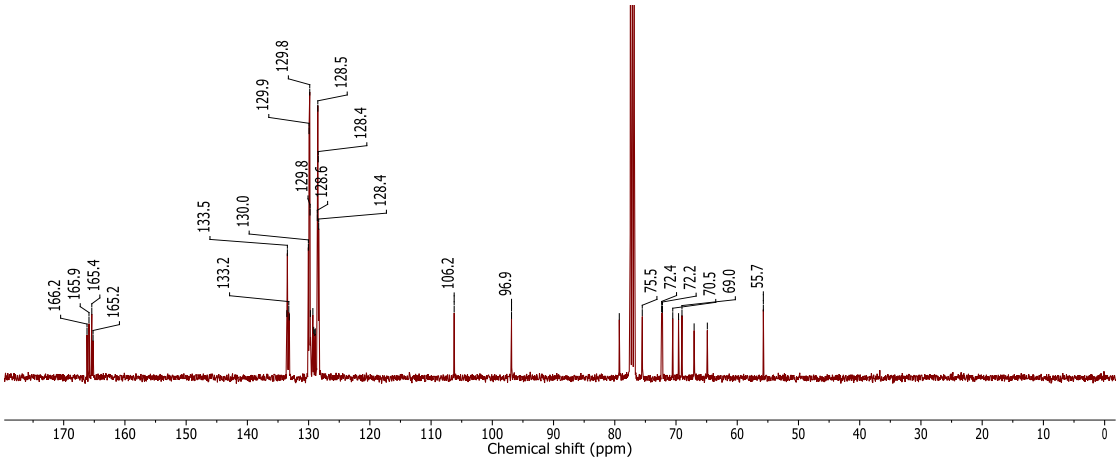
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound



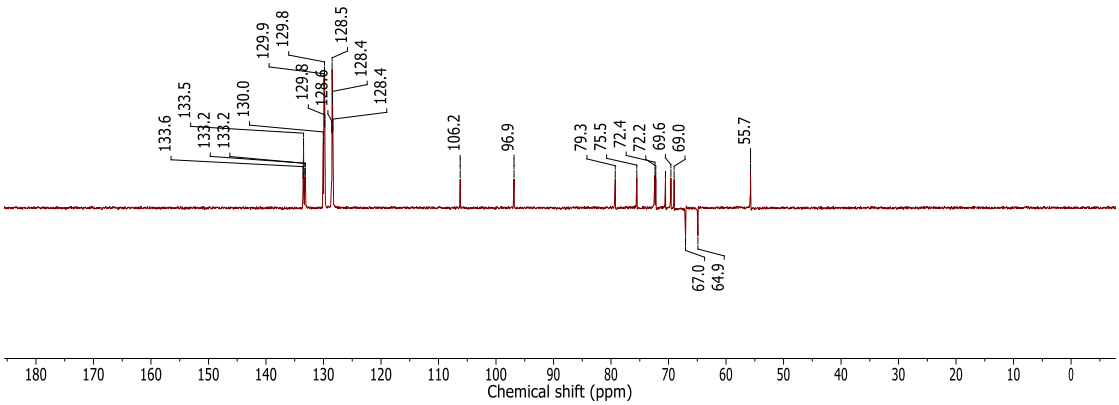
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) Of Compound **19a**



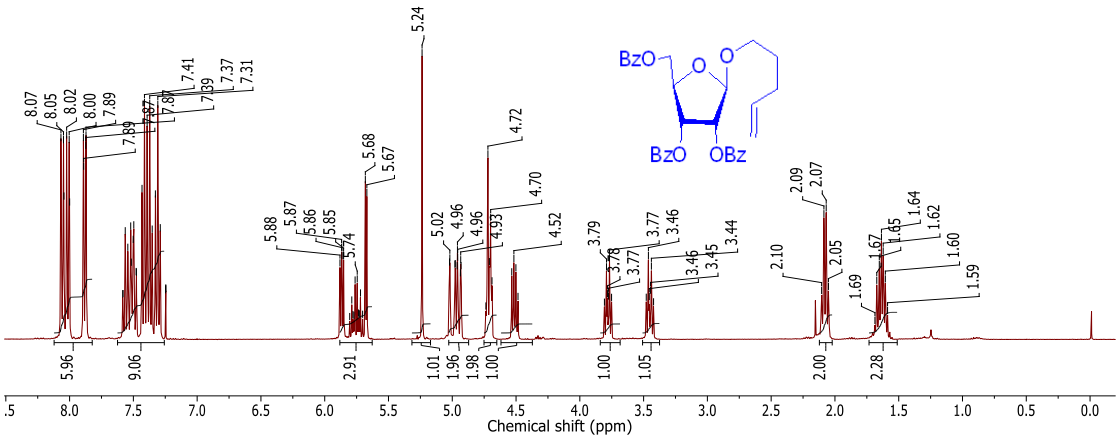
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **19a**



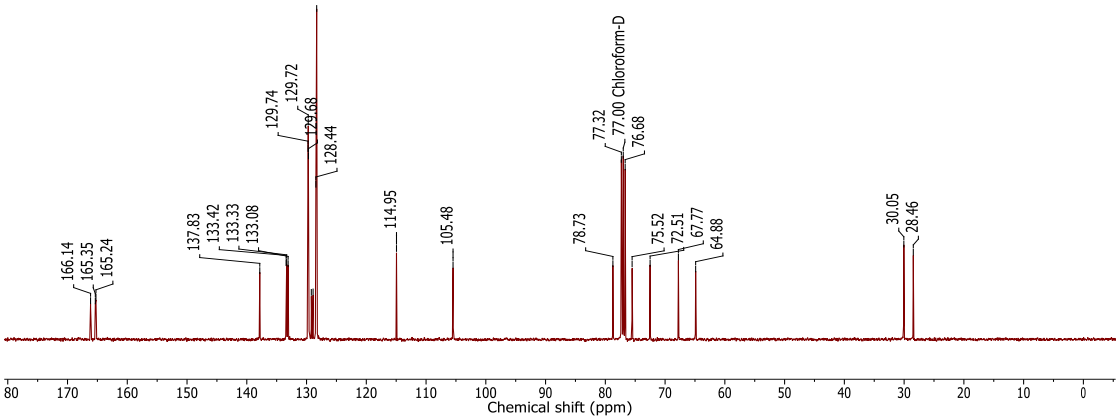
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **19a**



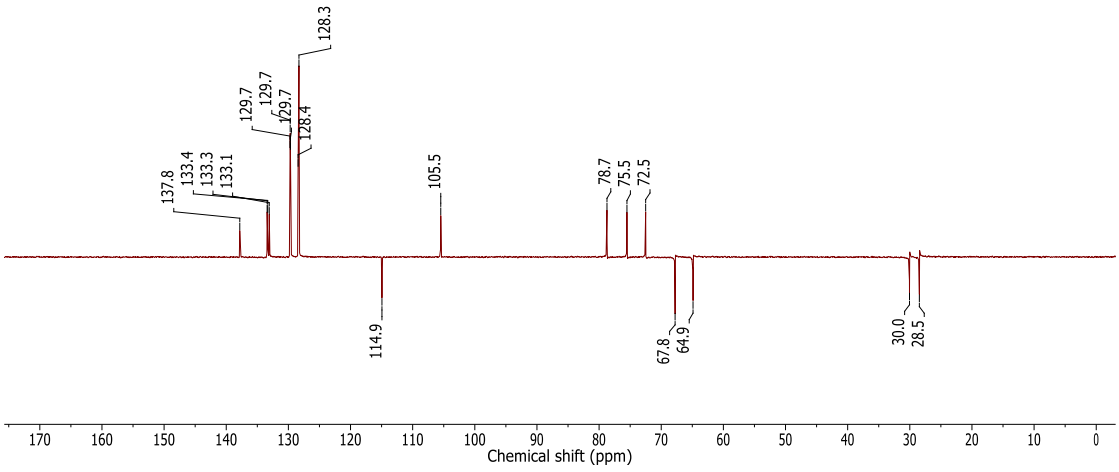
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) Of Compound **19b**



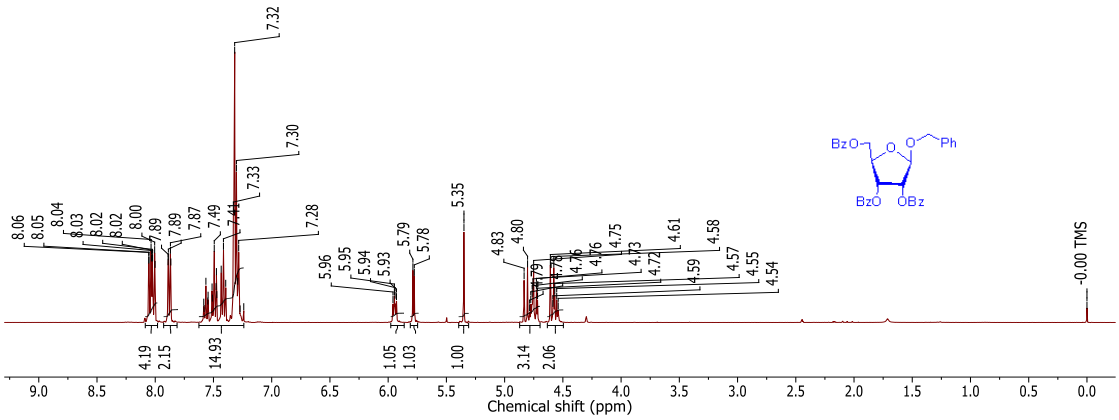
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **19b**



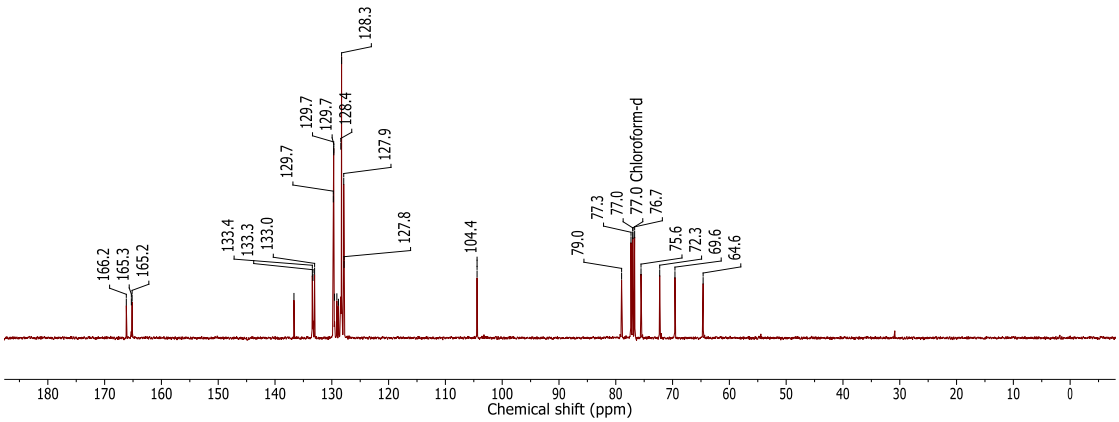
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **19b**



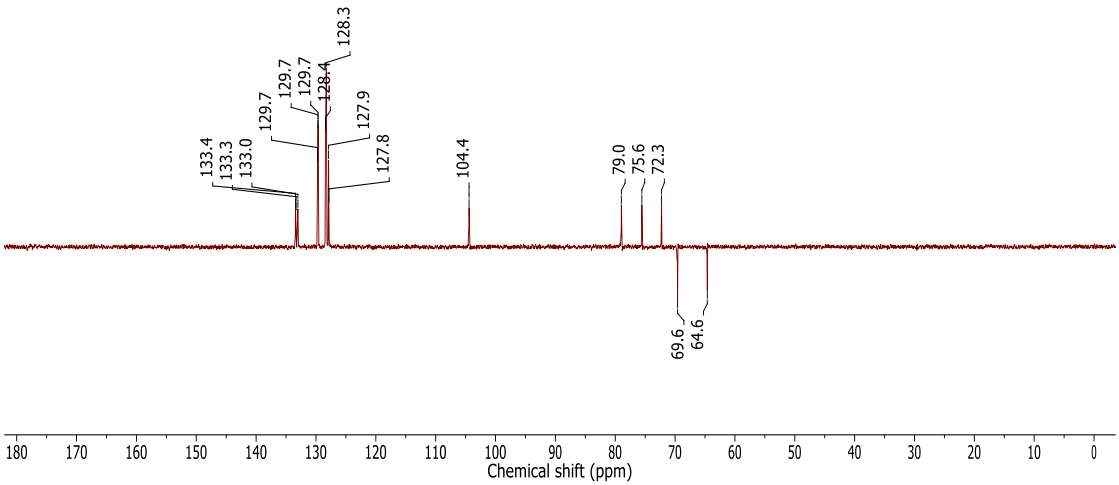
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) Of Compound **19c**



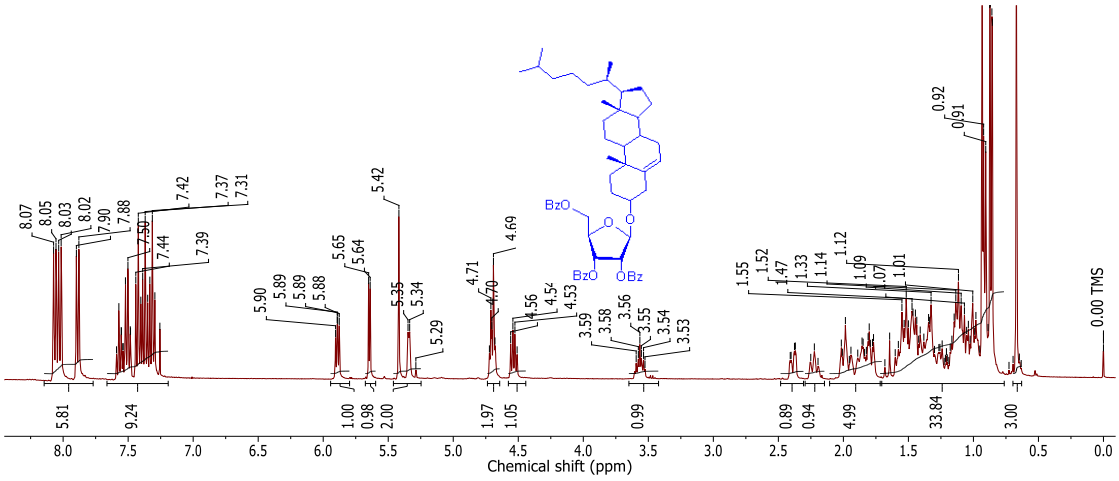
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **19c**



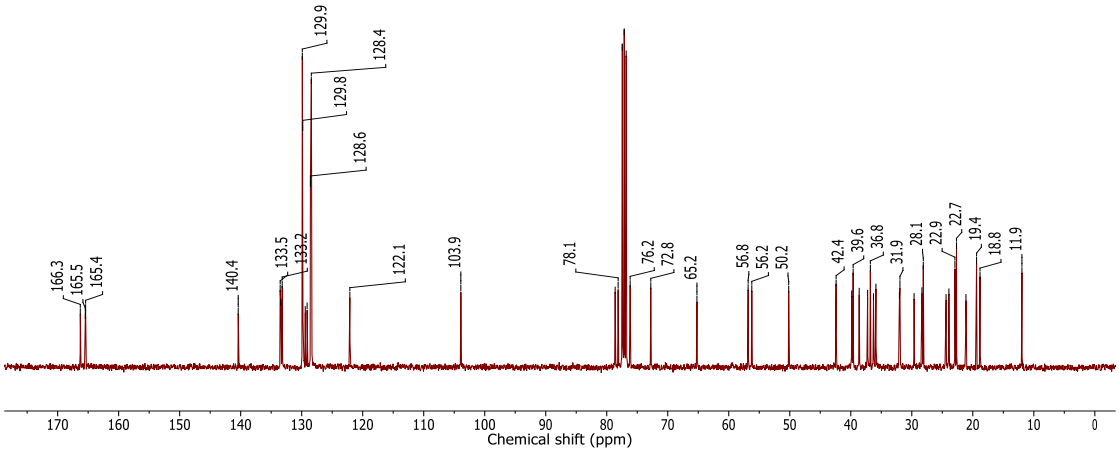
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **19c**



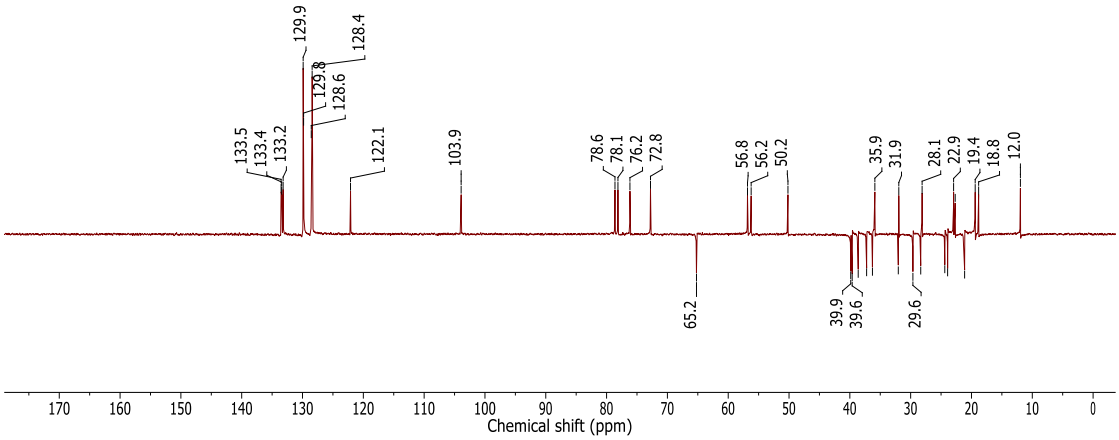
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) Of Compound **19d**



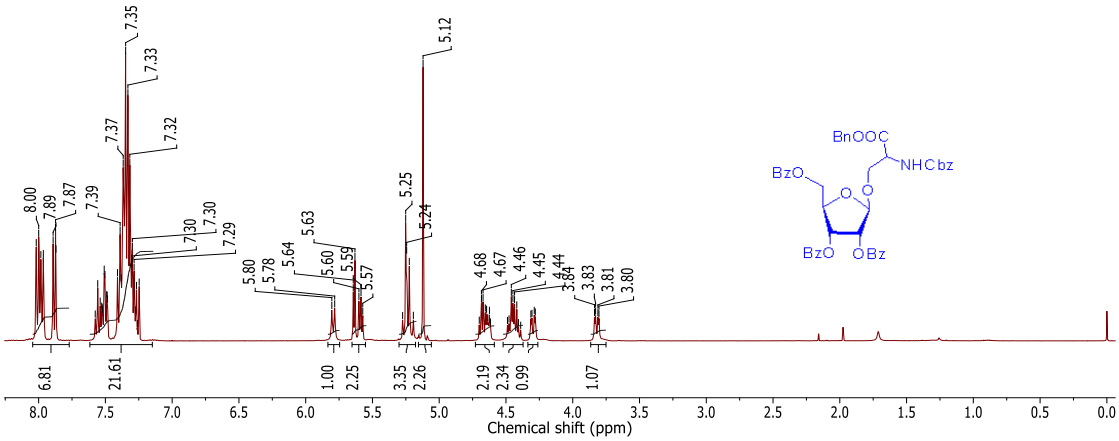
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **19d**



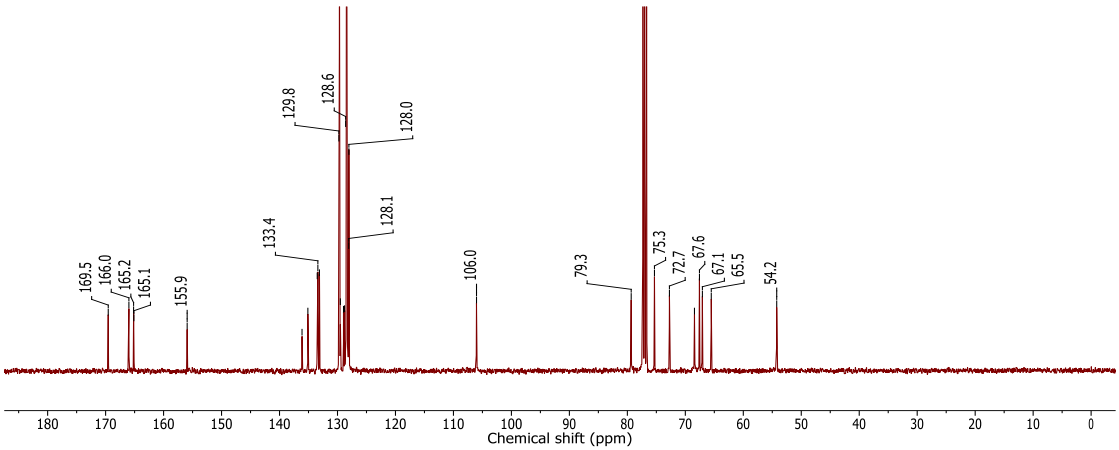
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **19d**



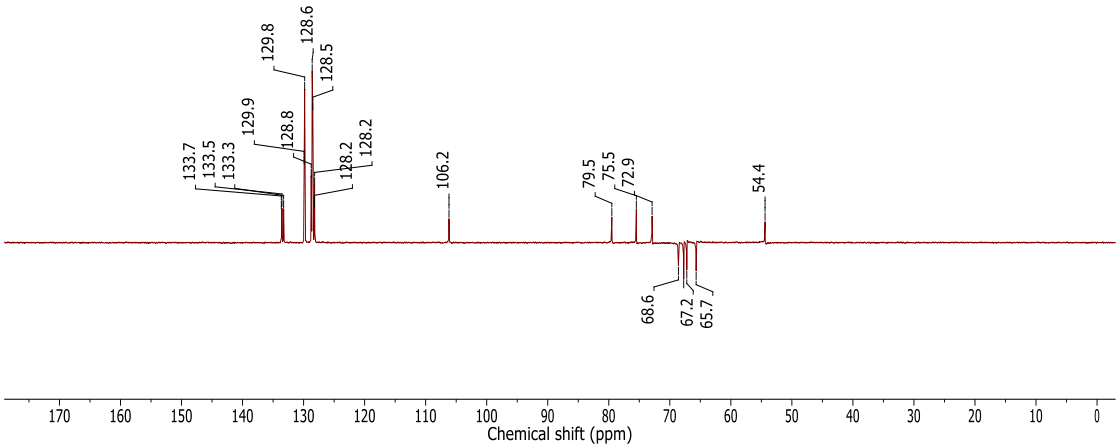
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) Of Compound **19e**



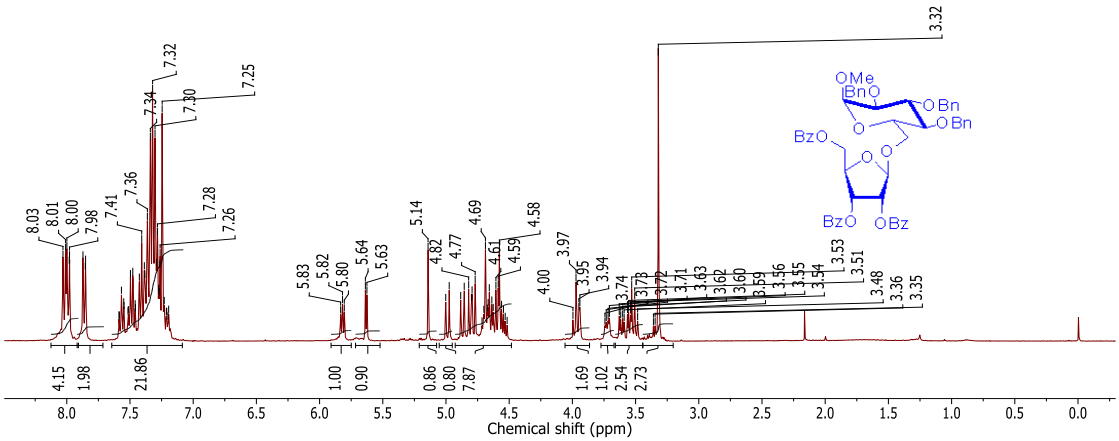
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **19e**



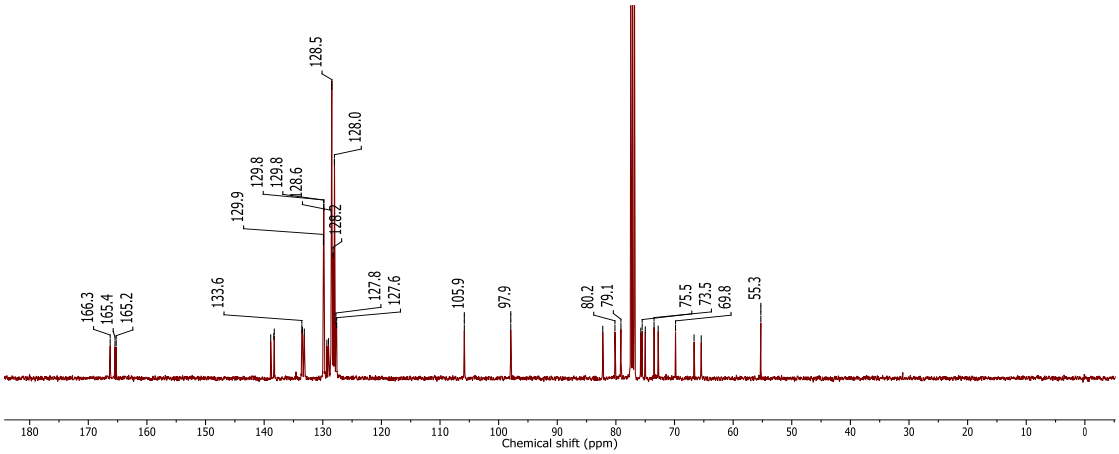
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **19e**



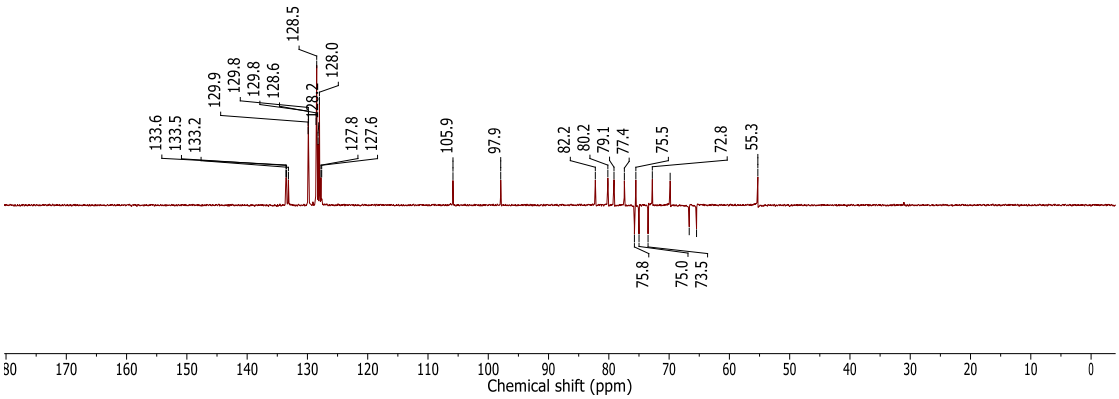
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) Of Compound **19f**



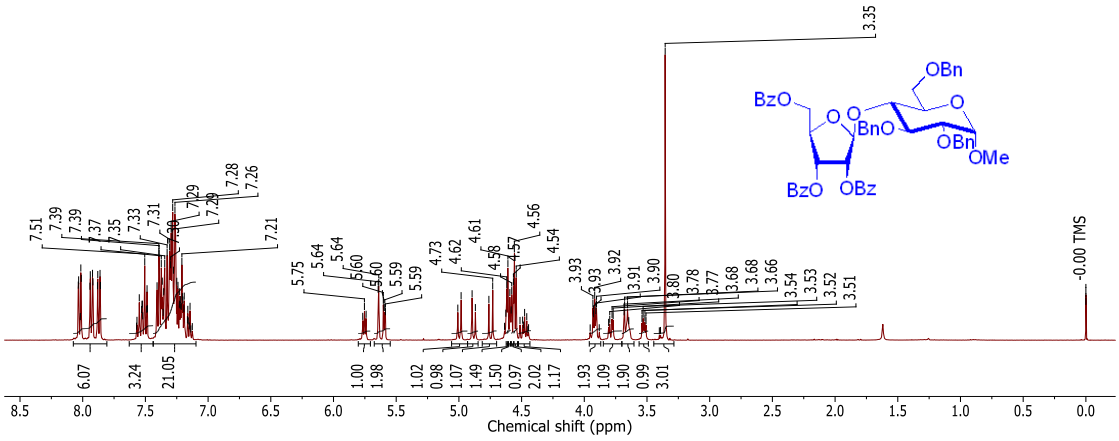
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **19f**



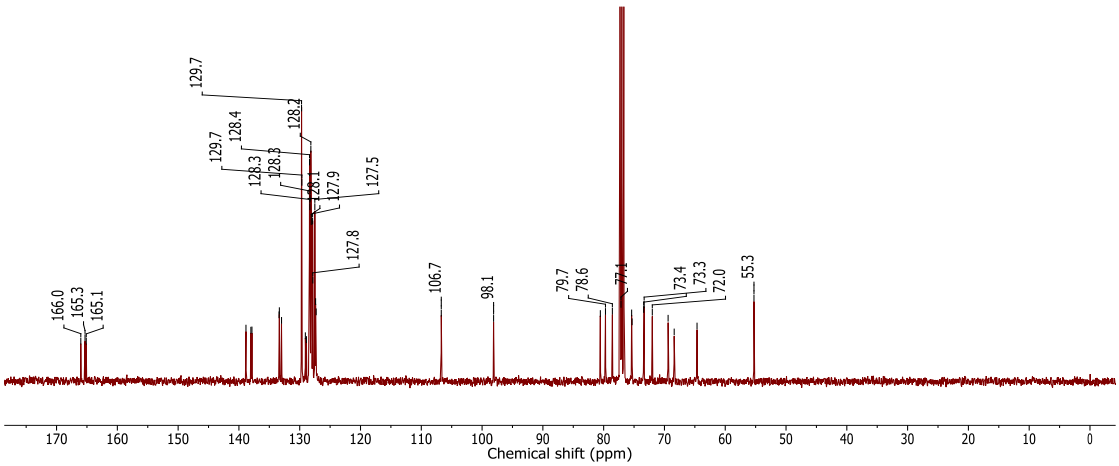
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **19f**



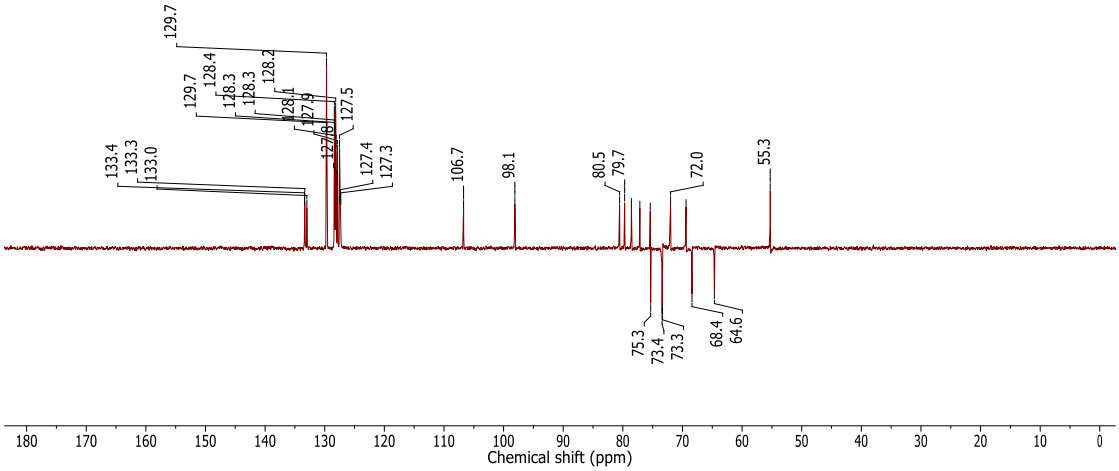
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) Of Compound **19g**



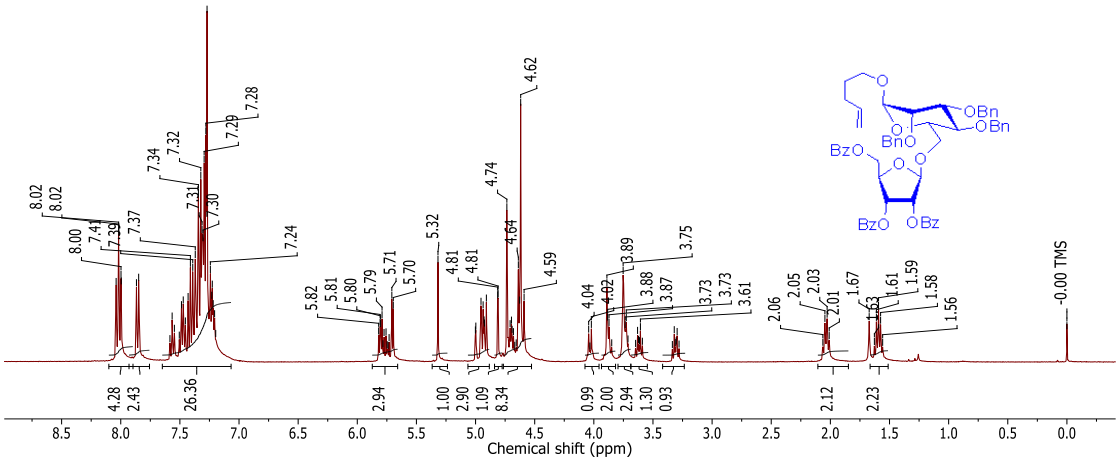
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **19g**



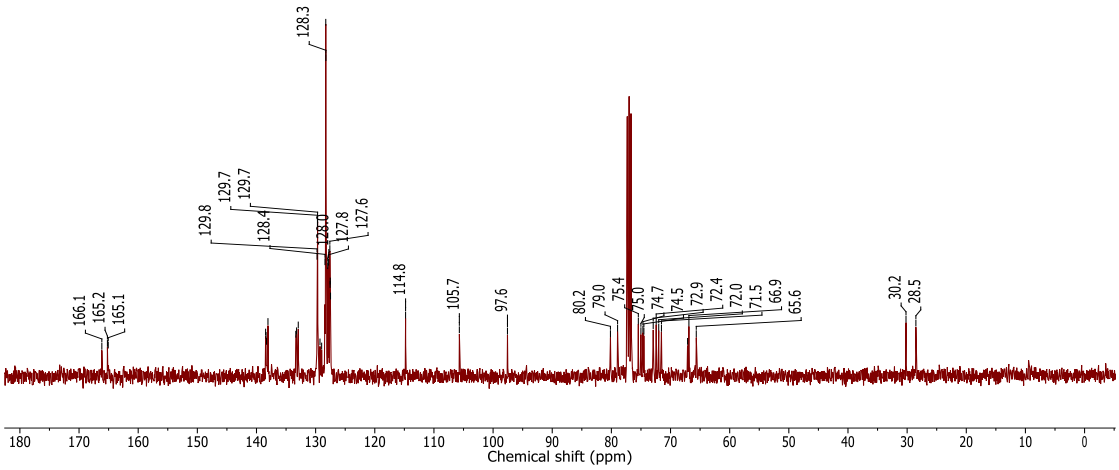
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **19g**



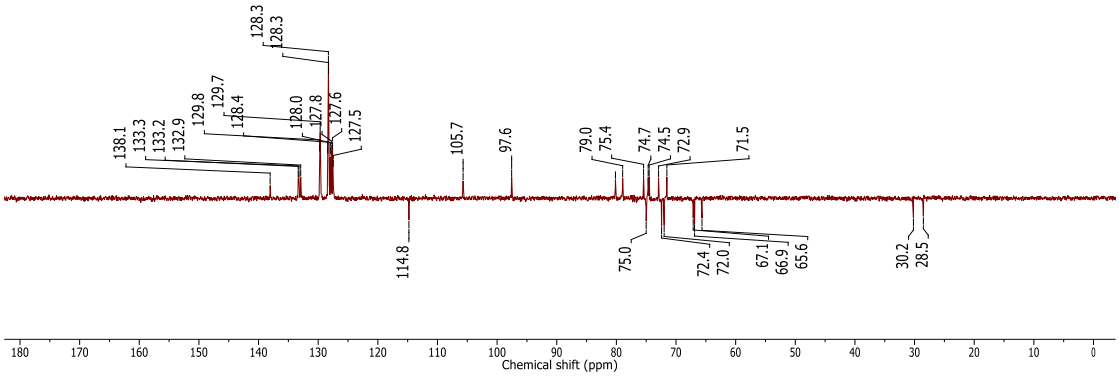
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) Of Compound **19h**



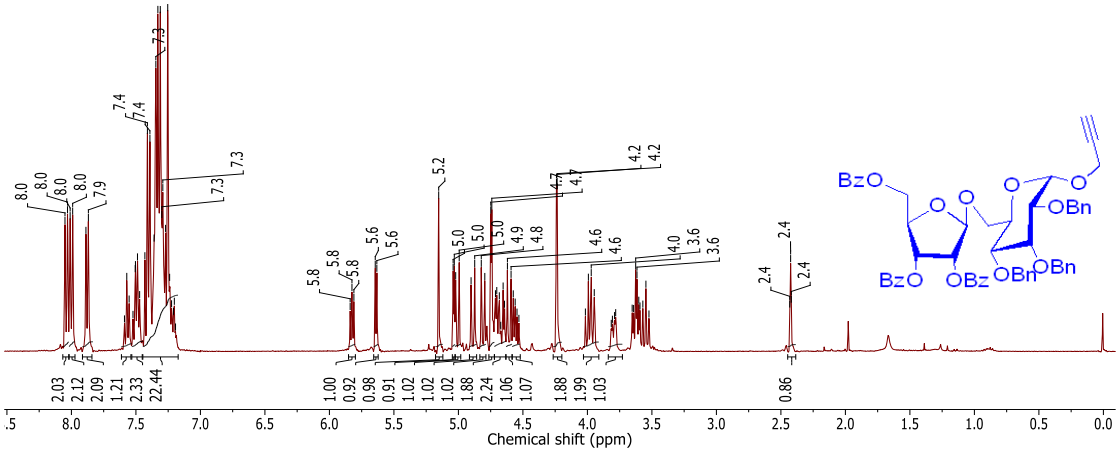
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **19h**



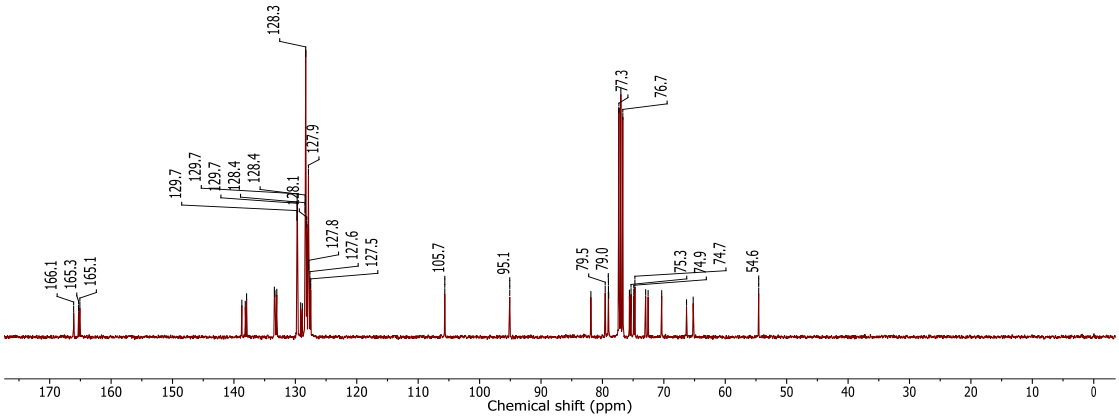
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **19h**



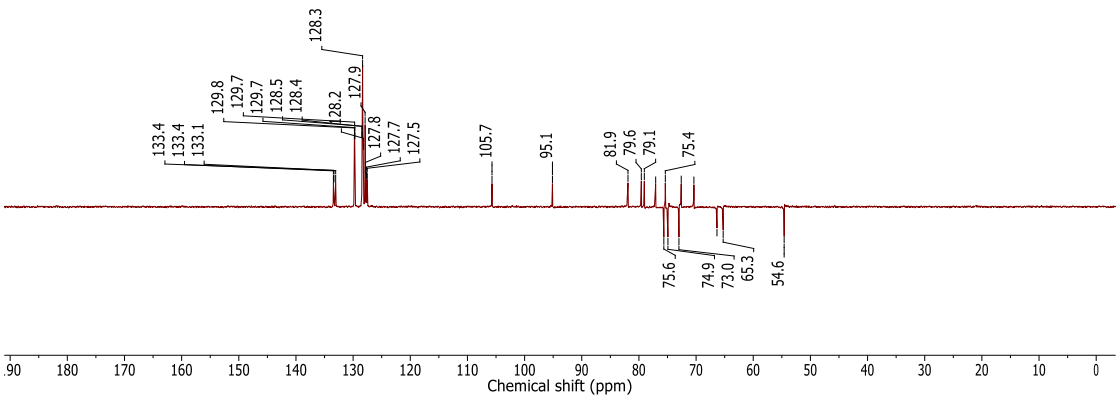
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) Of Compound **19i**



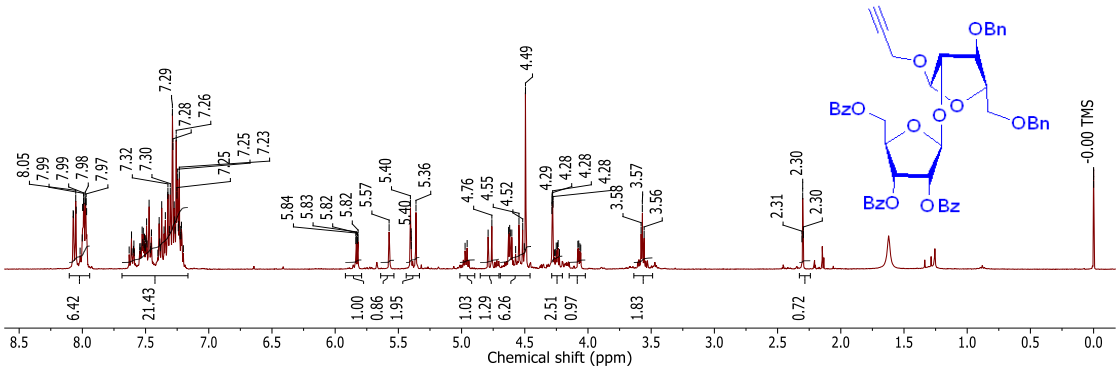
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **19i**



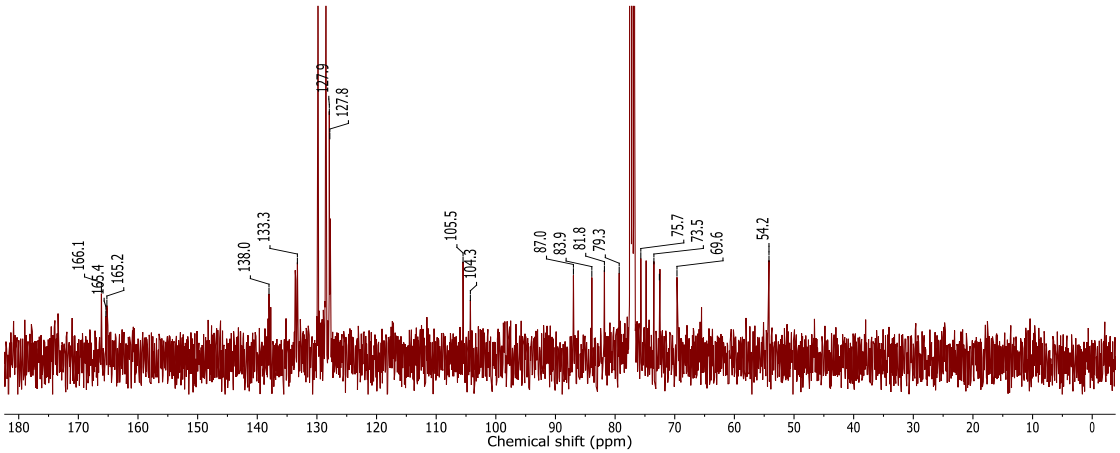
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **19i**



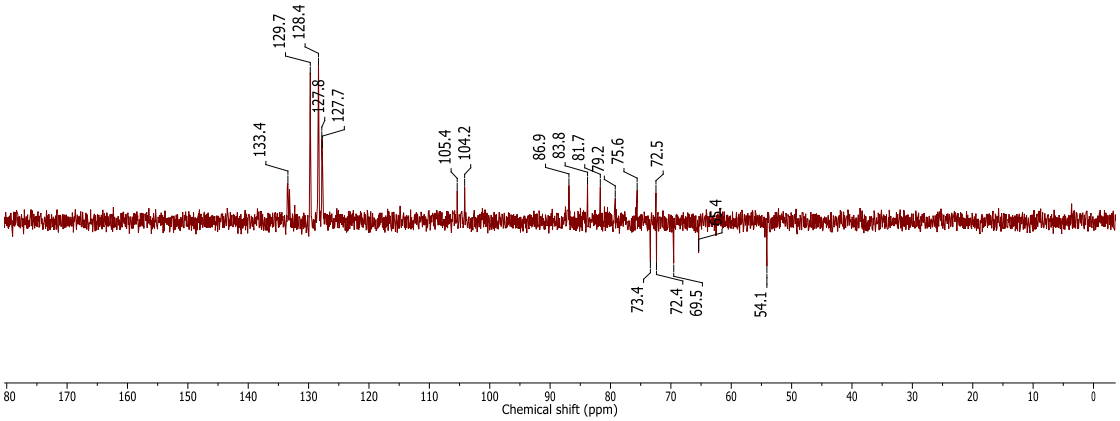
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) Of Compound **19j**



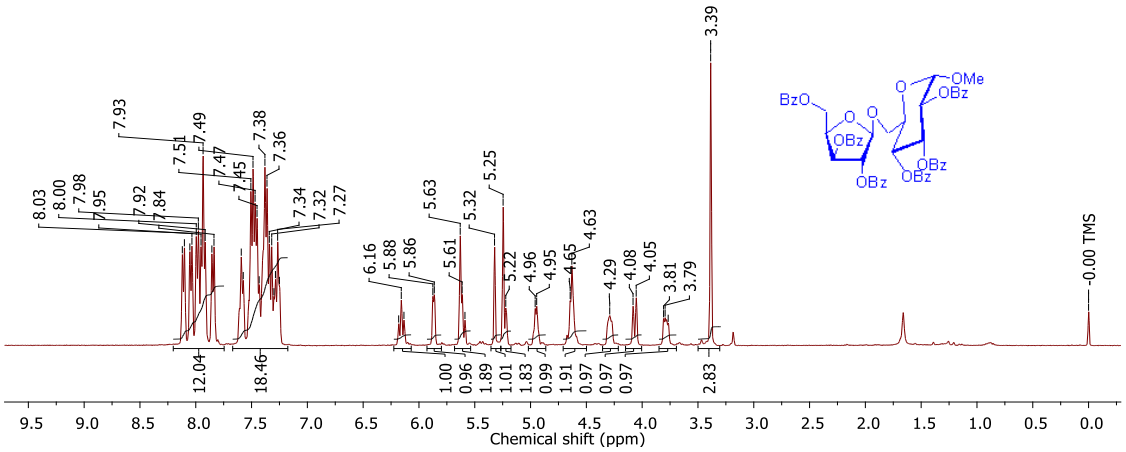
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **19j**



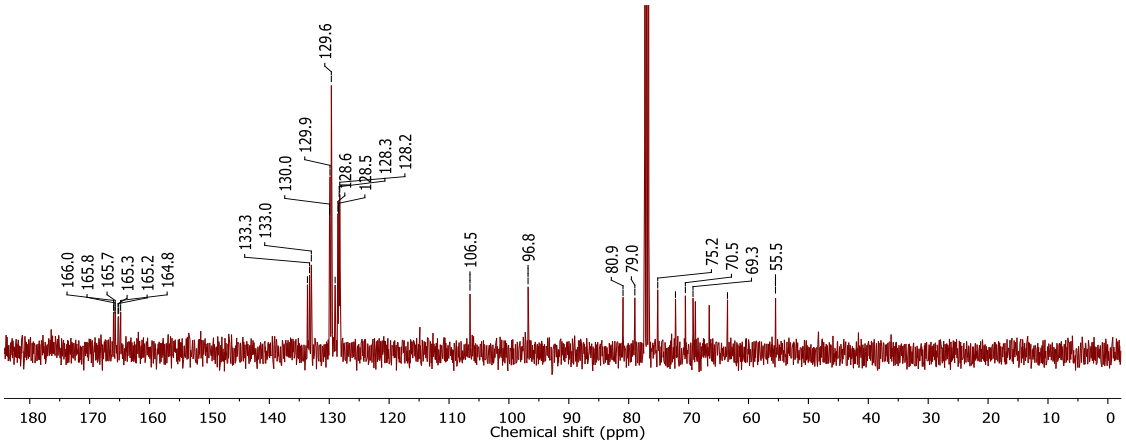
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **19j**



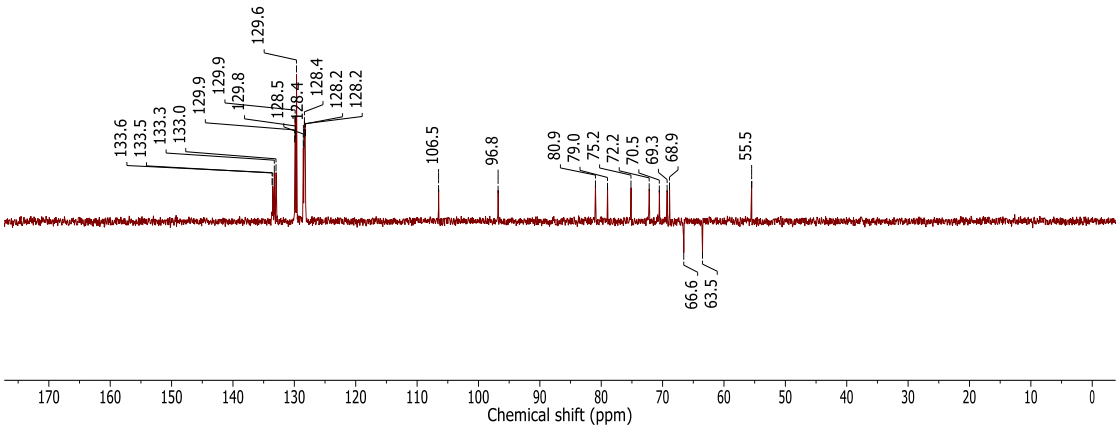
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **20a**



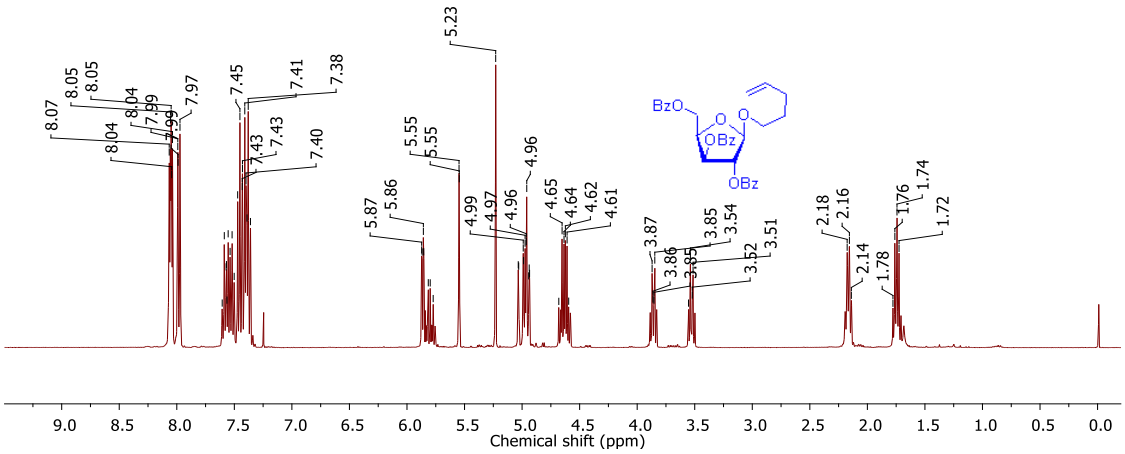
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20a**



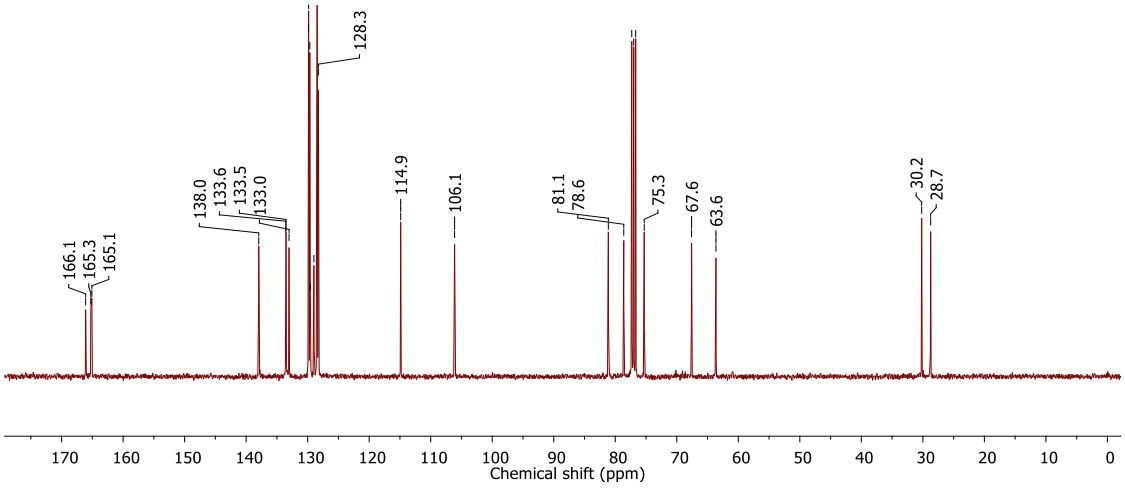
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20a**



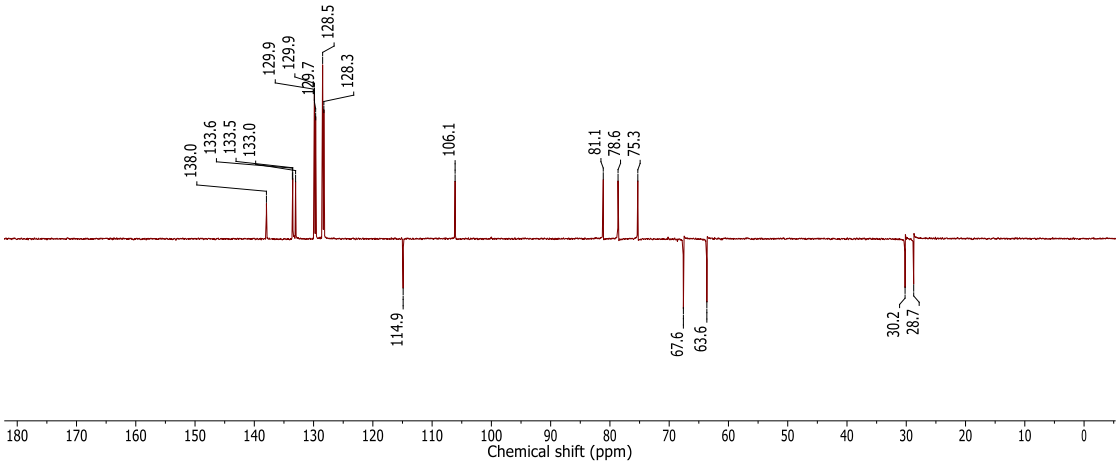
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **20b**



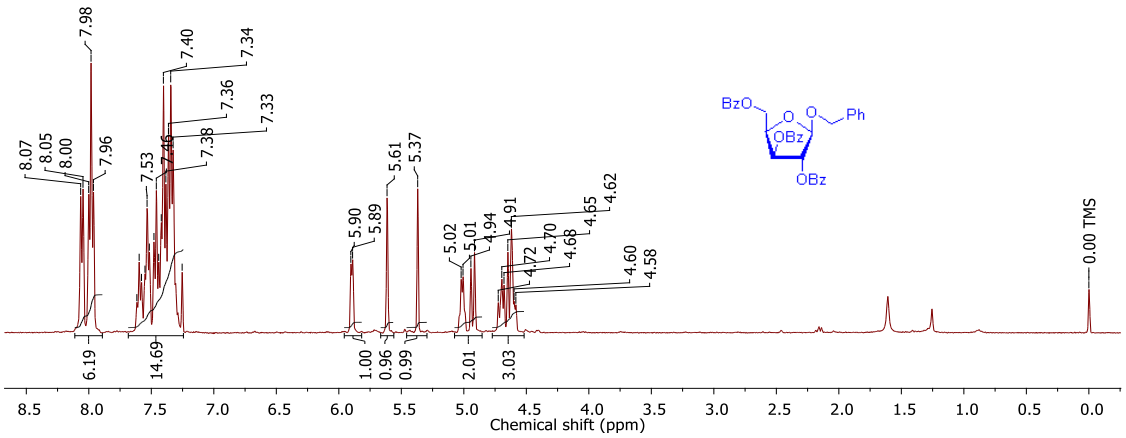
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20b**



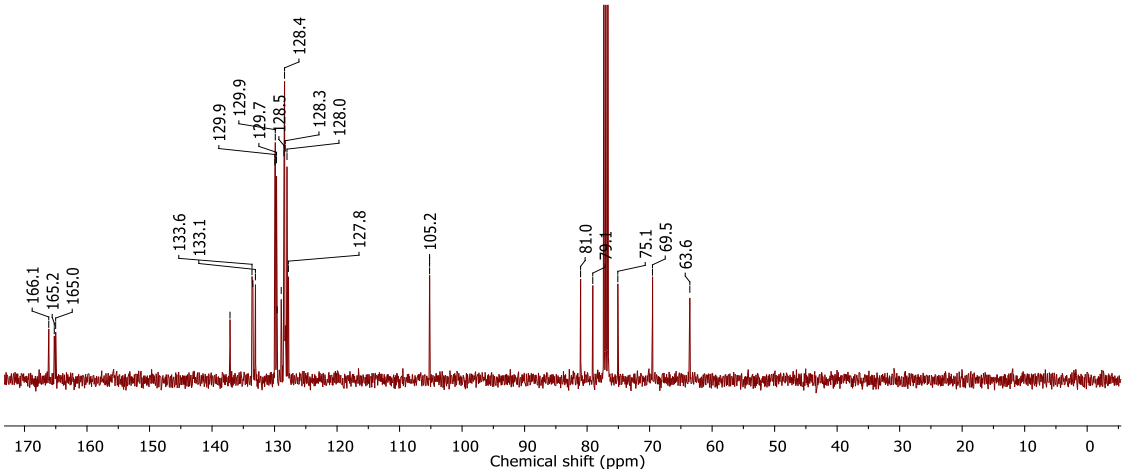
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20b**



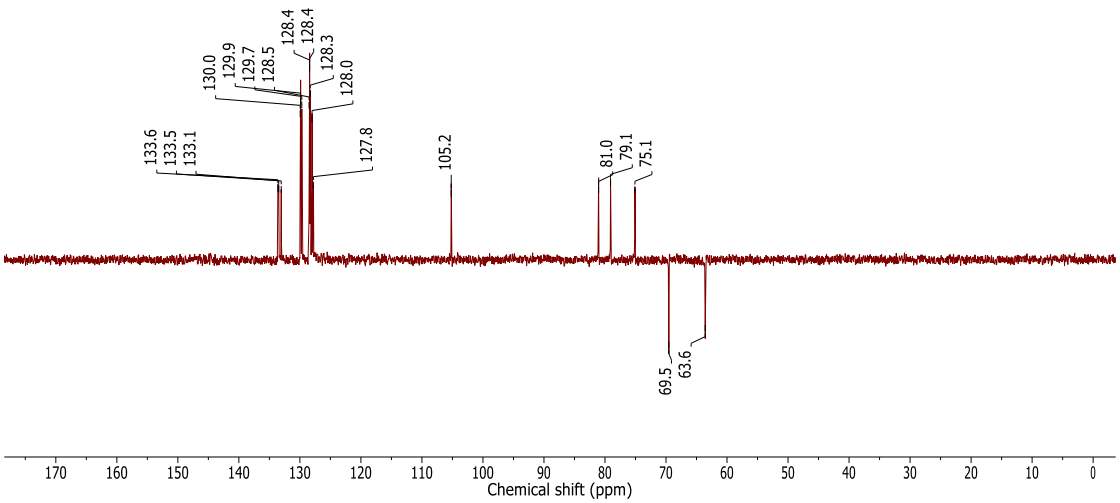
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **20c**



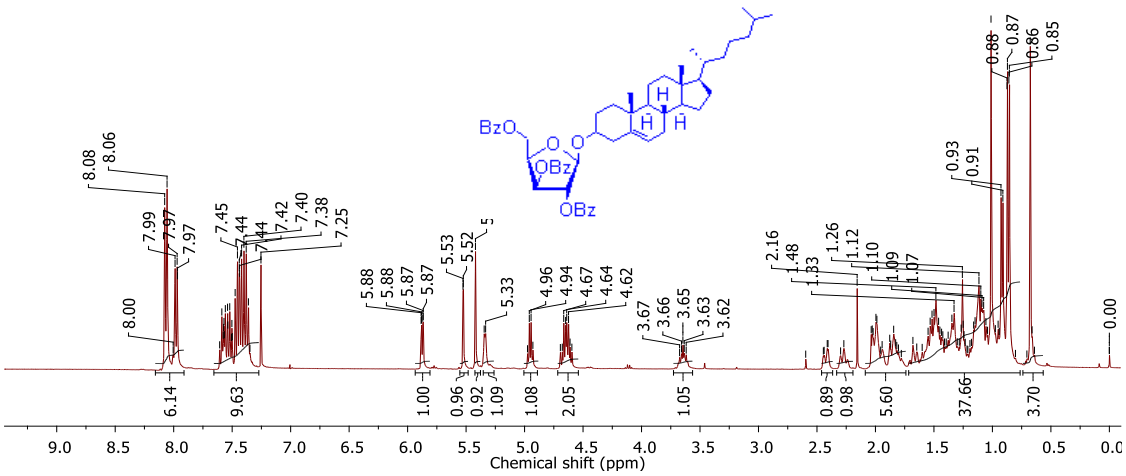
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20c**



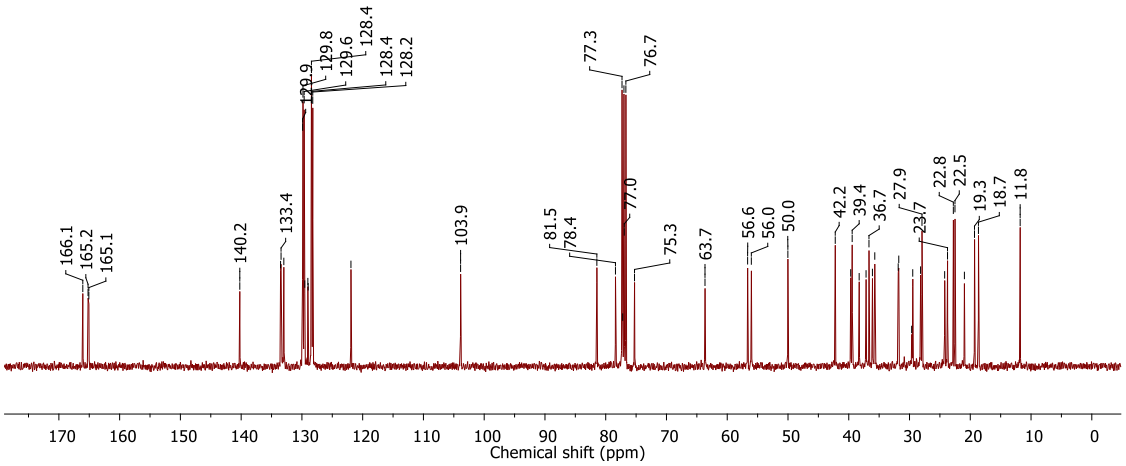
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20c**



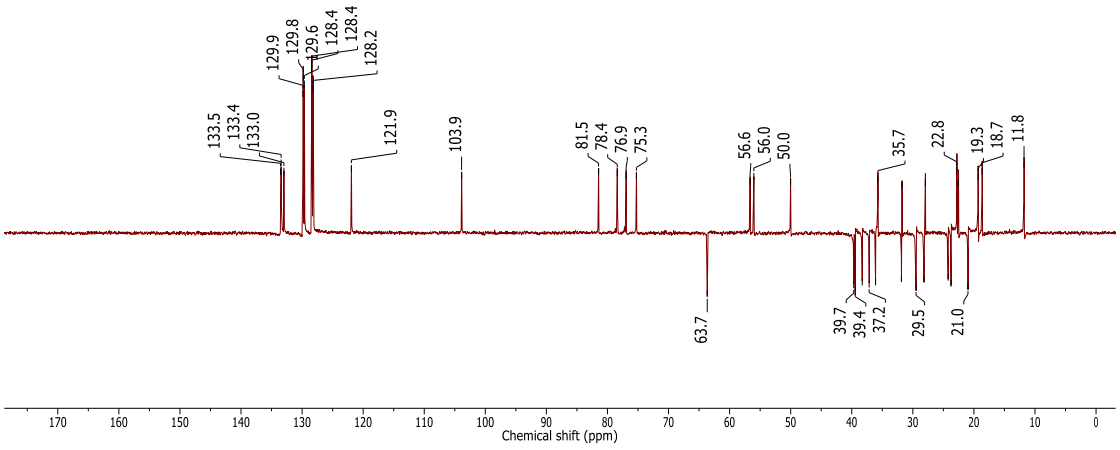
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **20d**



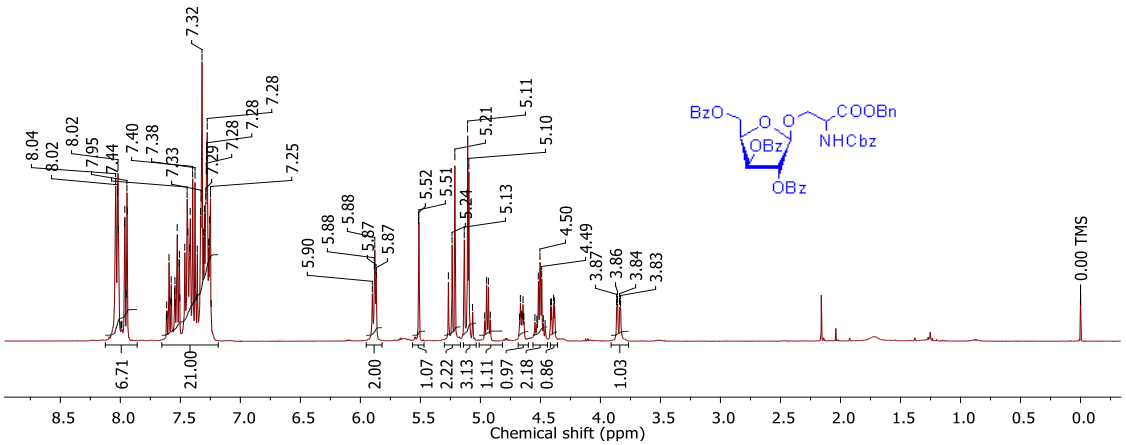
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20d**



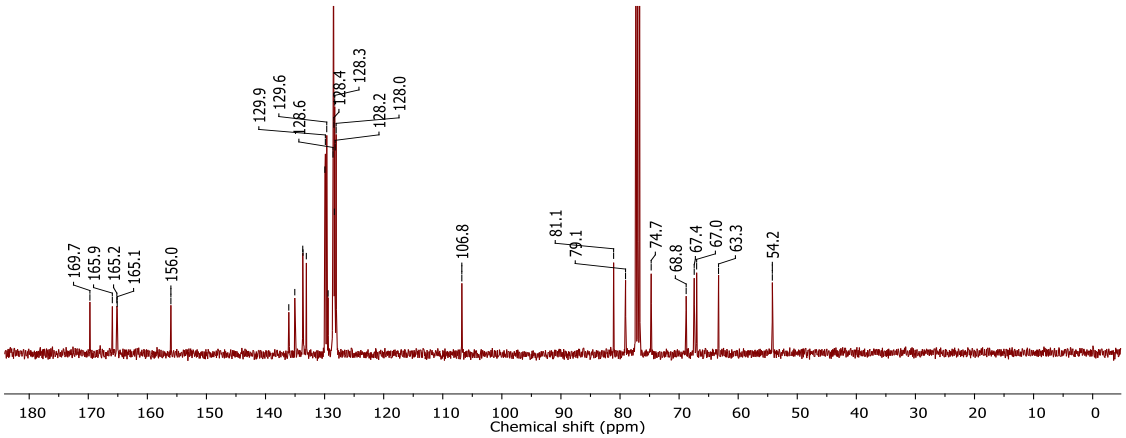
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20d**



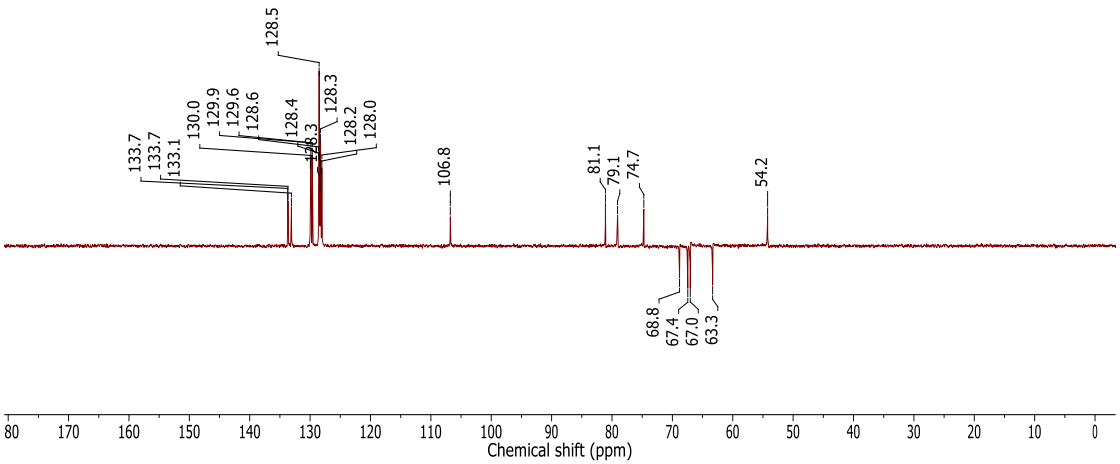
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **20e**



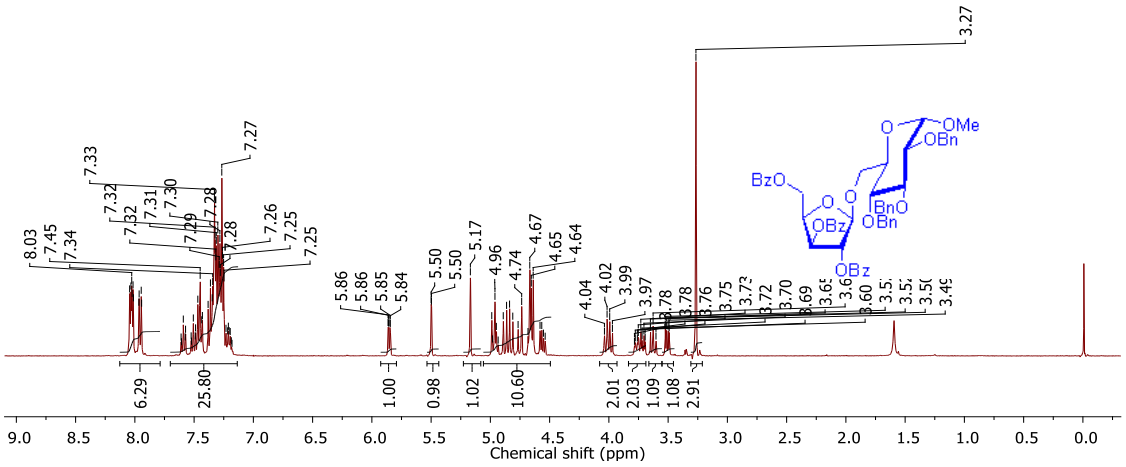
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20e**



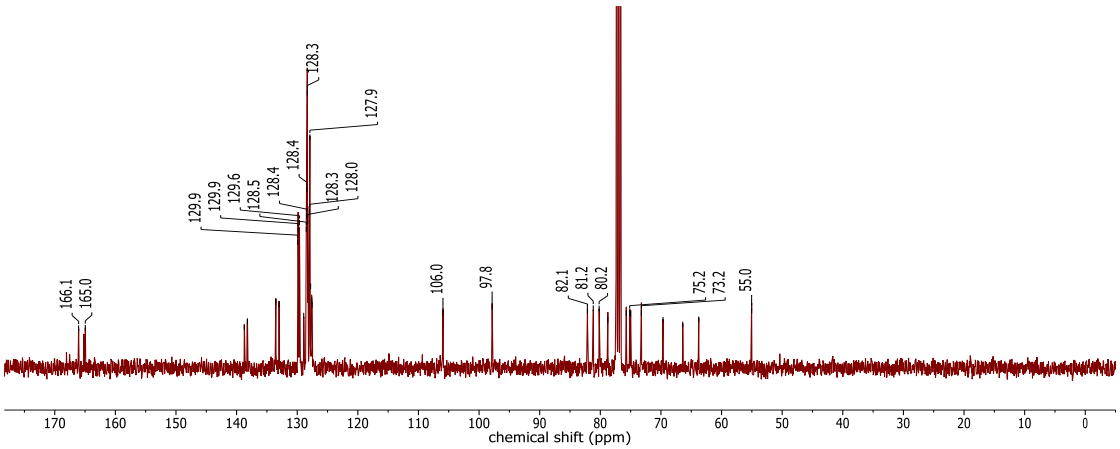
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20e**



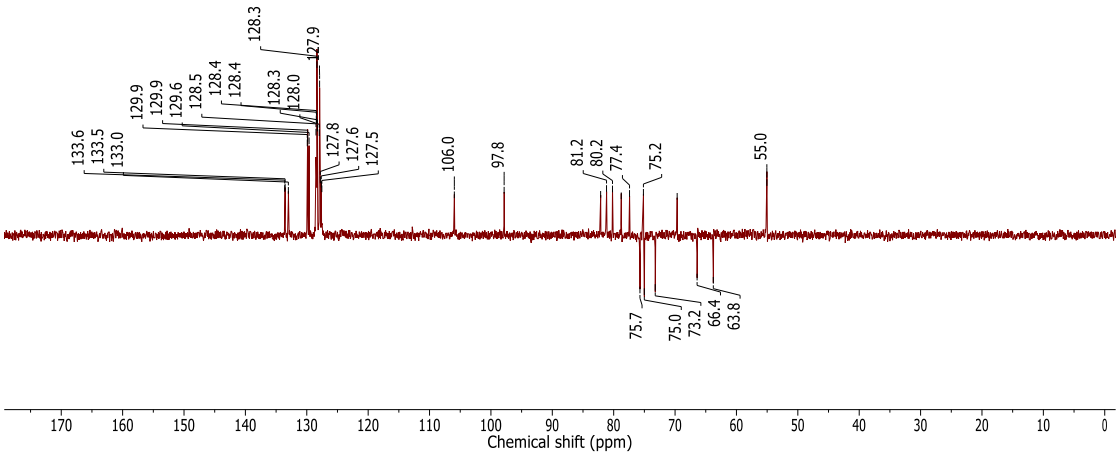
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **20f**



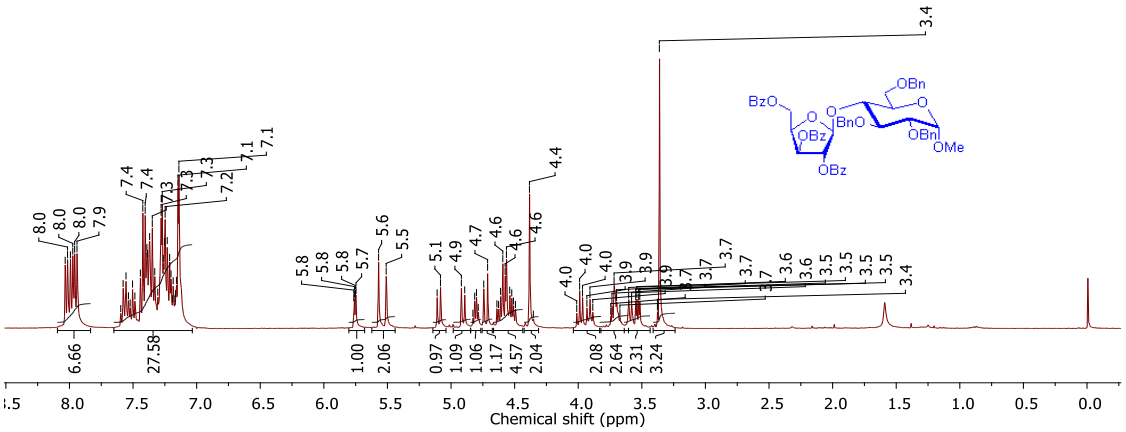
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20f**



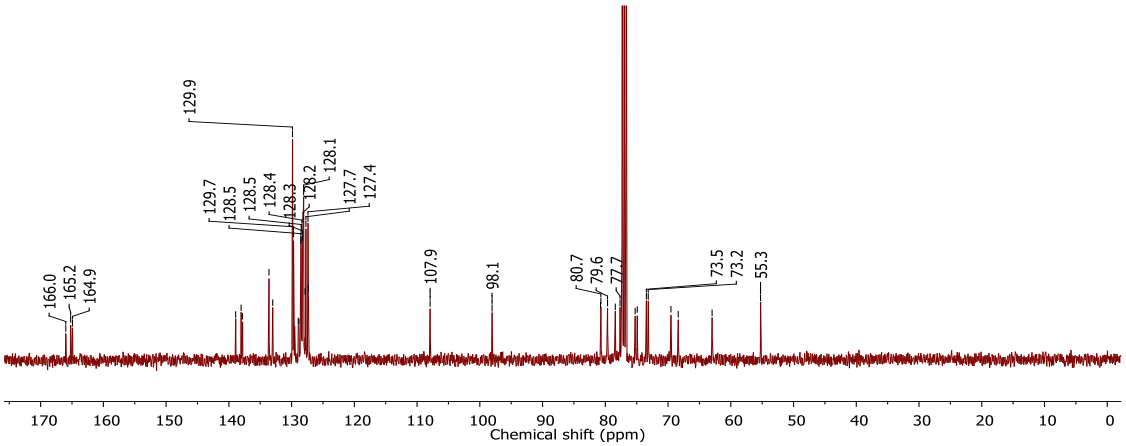
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20f**



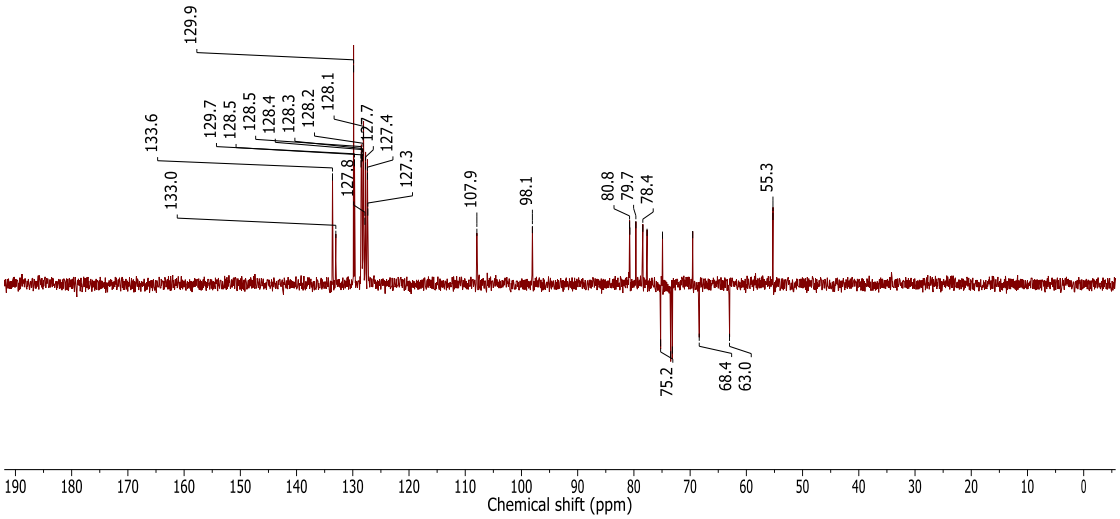
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **20g**



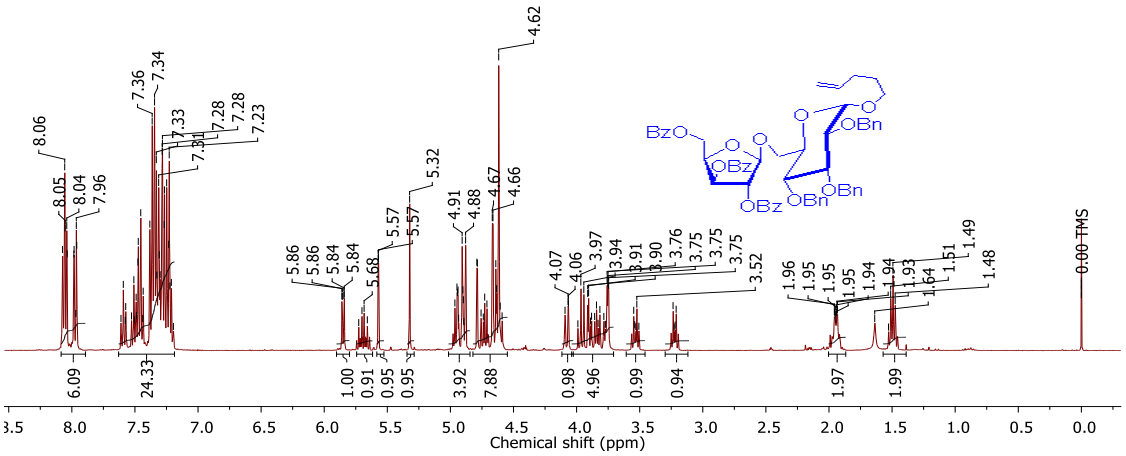
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20g**



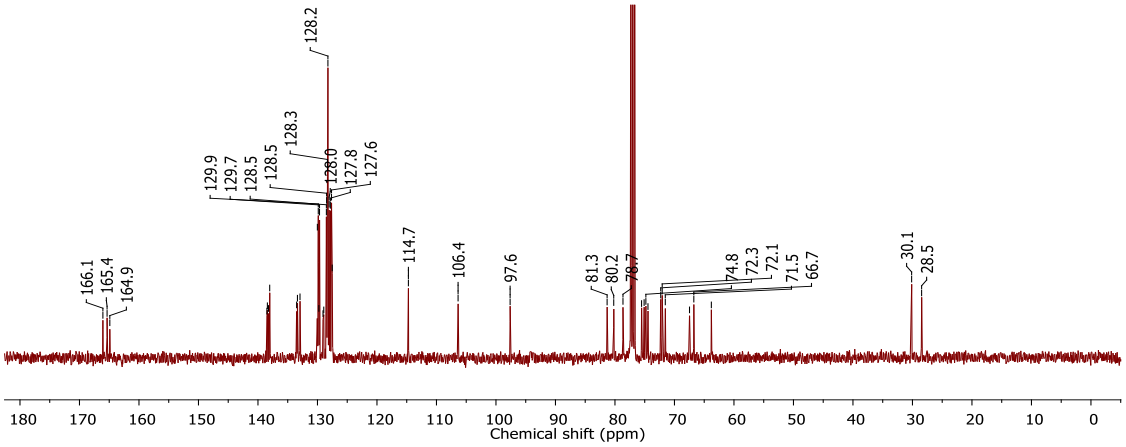
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20g**



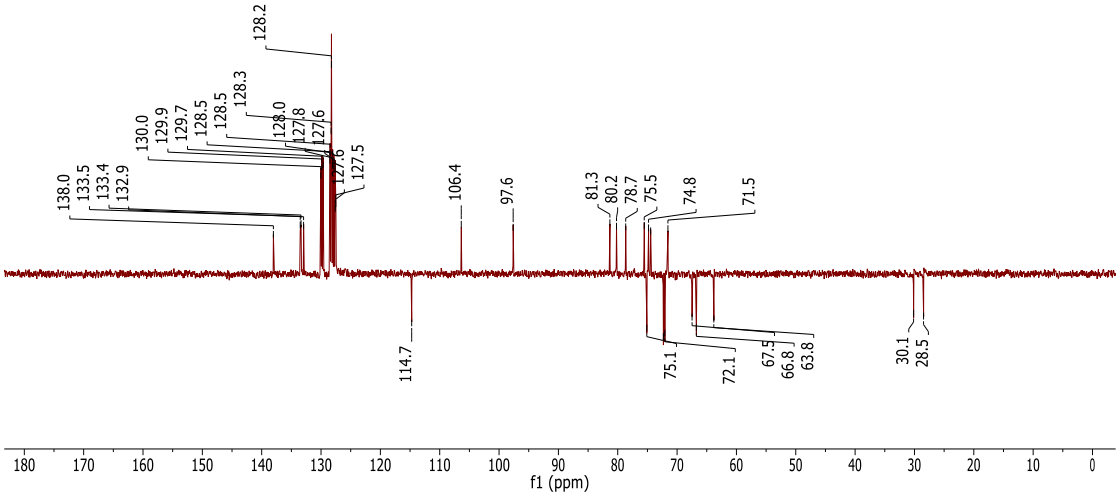
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **20h**



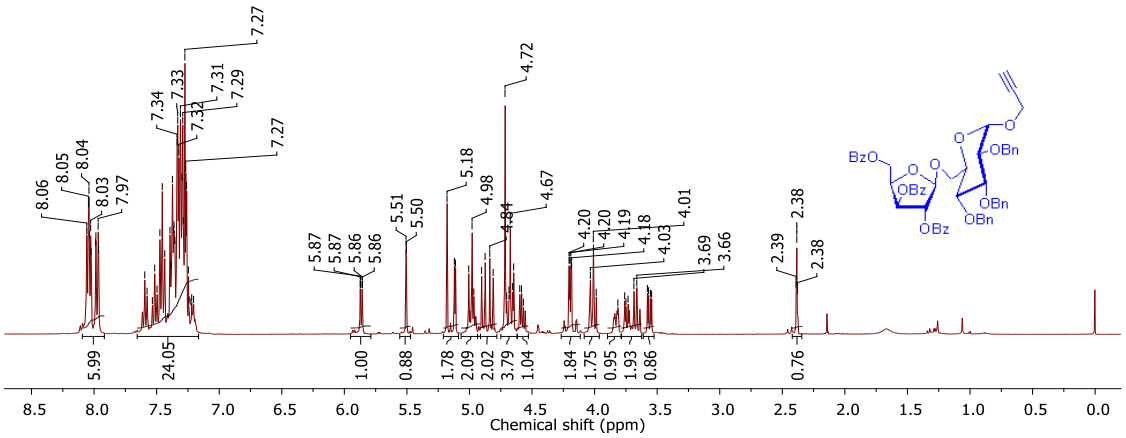
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20h**



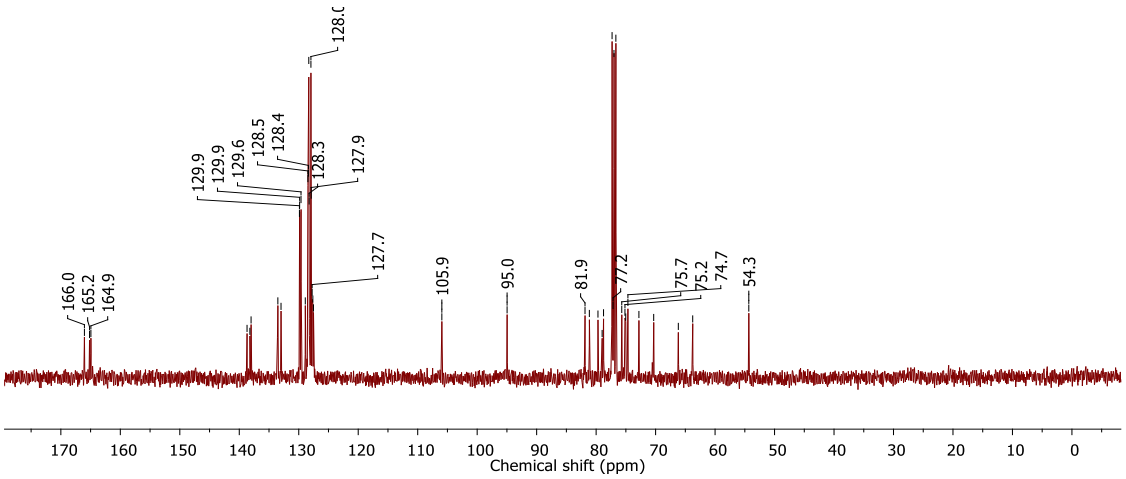
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20h**



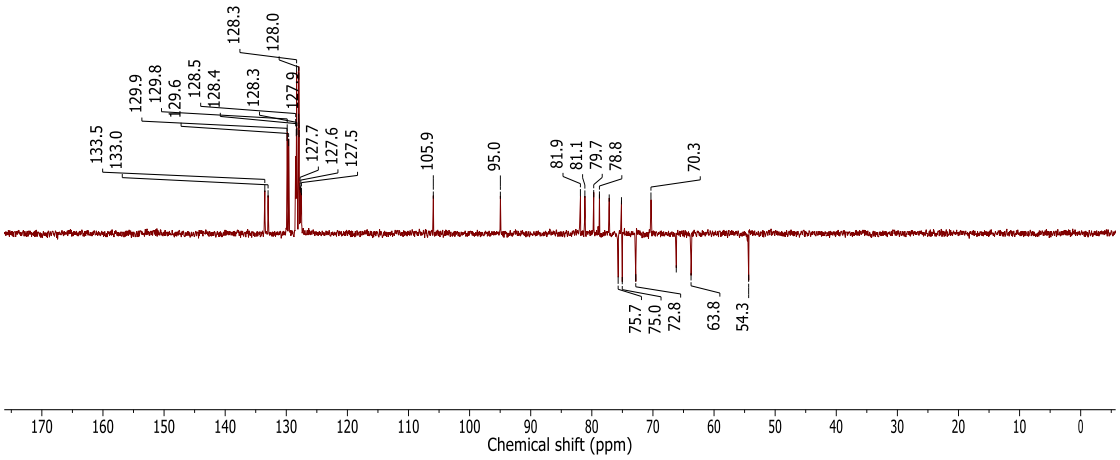
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **20i**



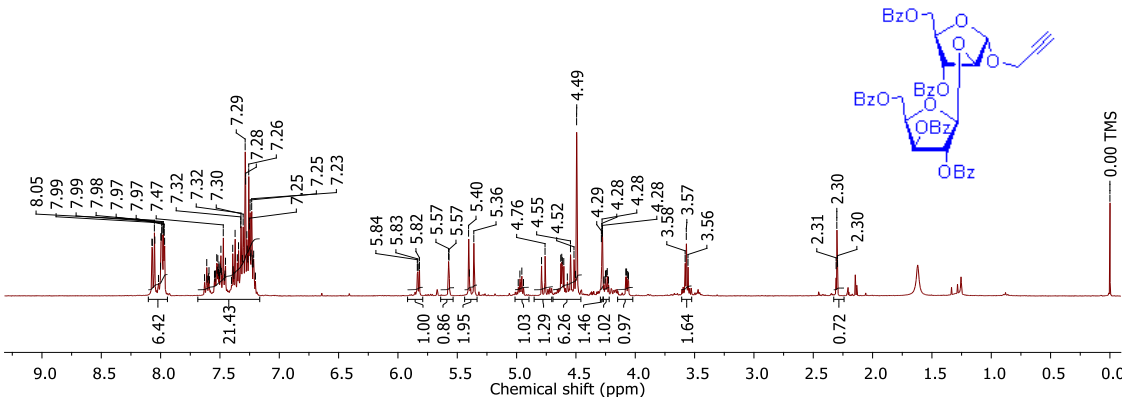
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20i**



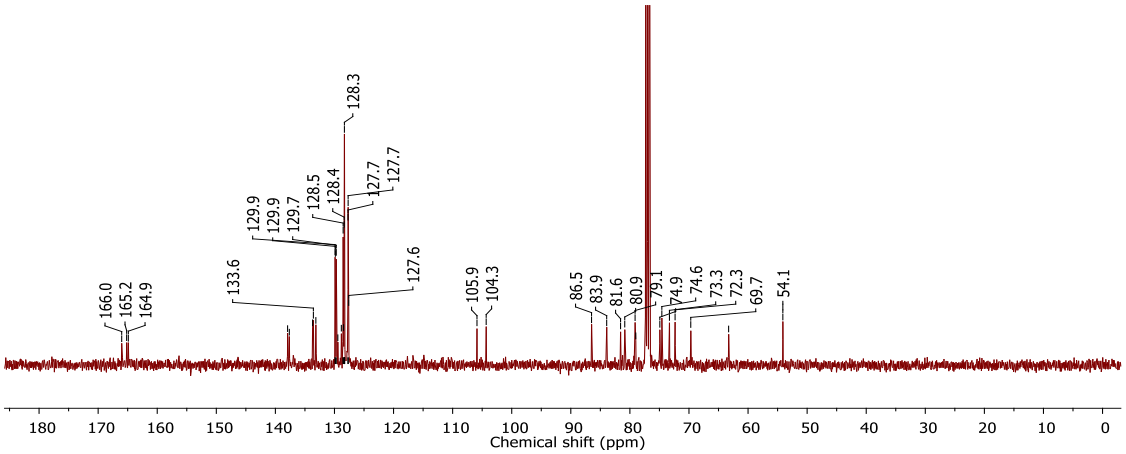
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20i**



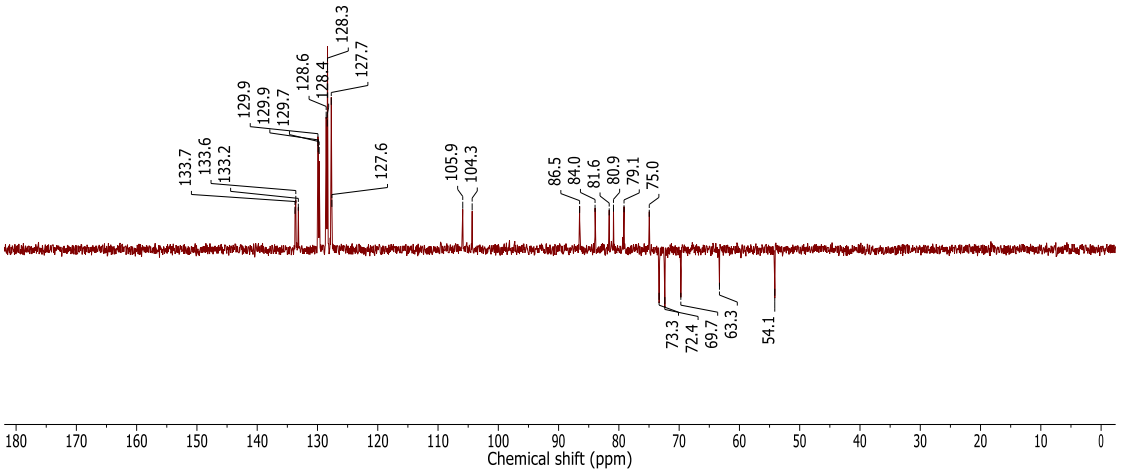
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **20j**



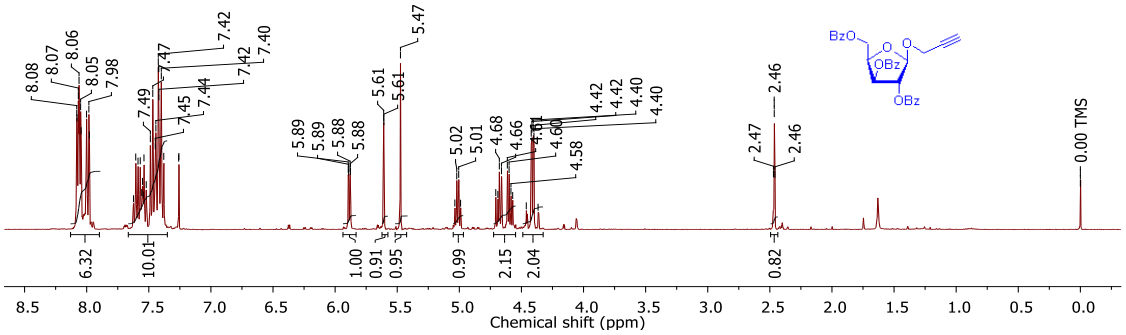
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20j**



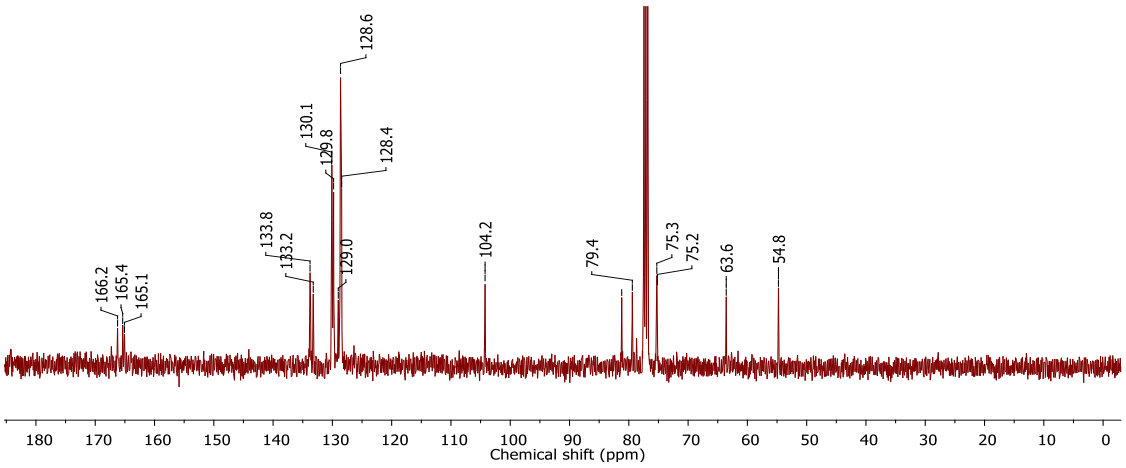
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20j**



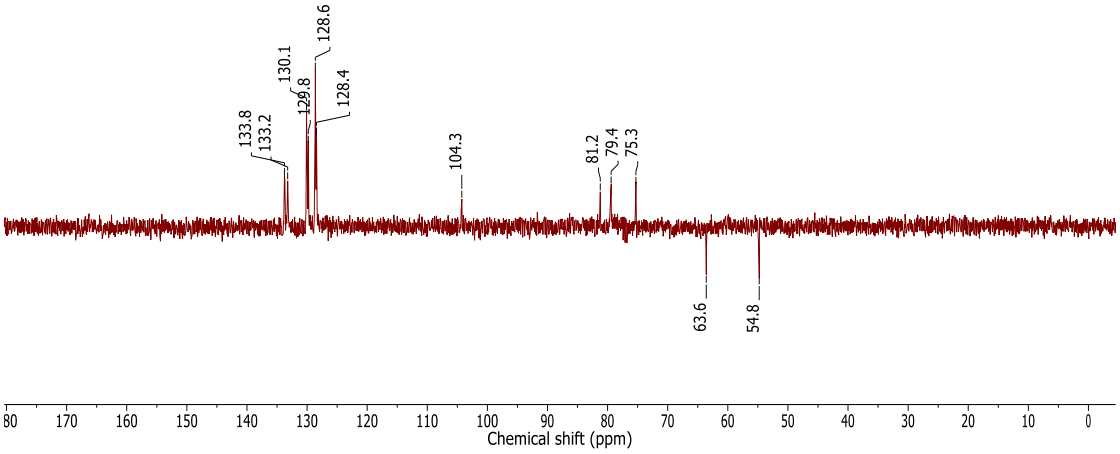
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound



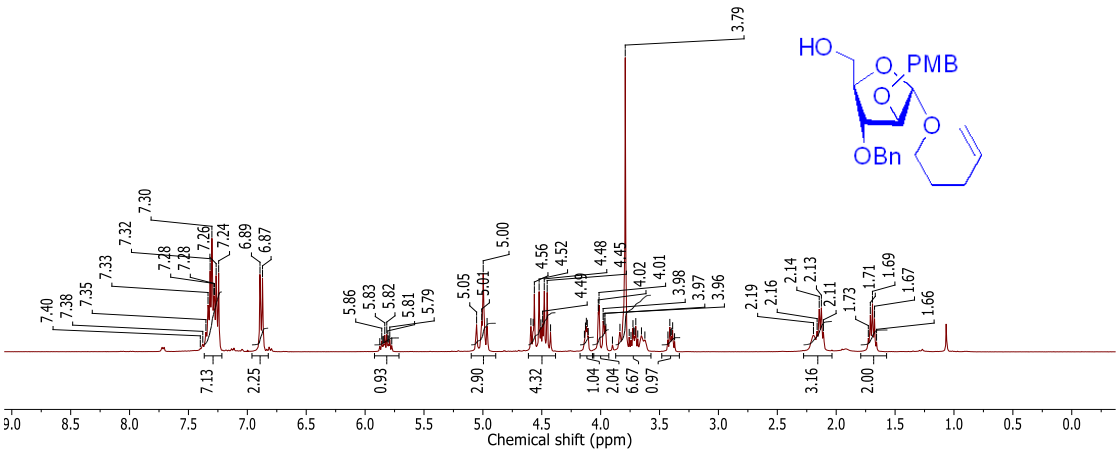
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound



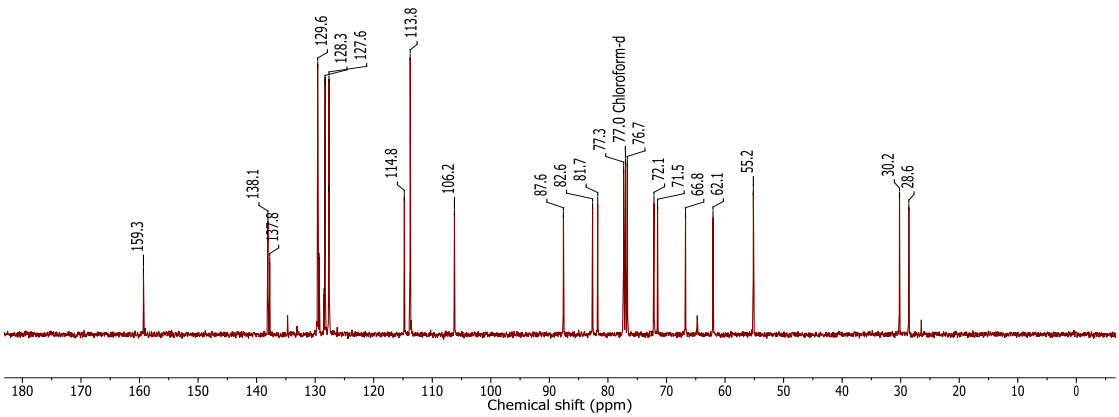
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound



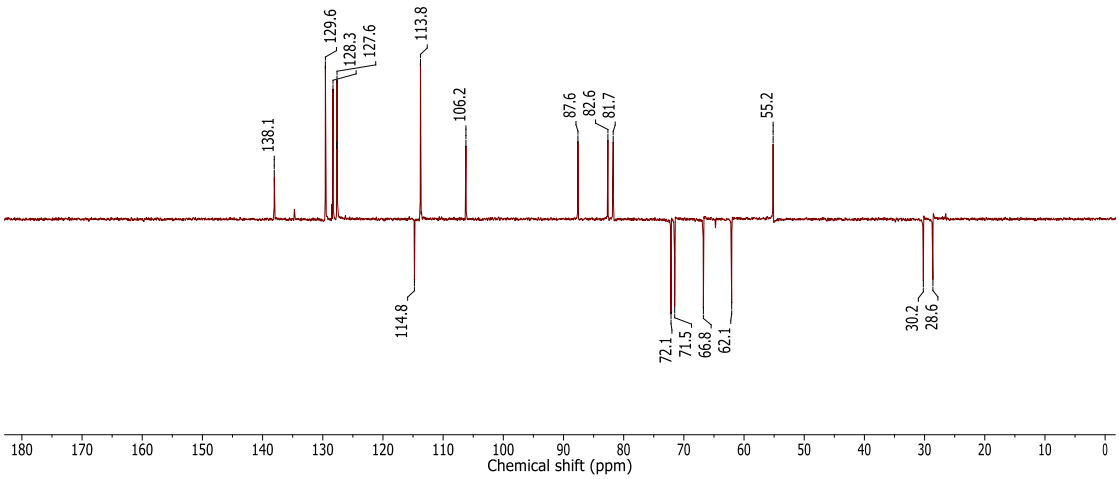
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) Of Compound **11b**



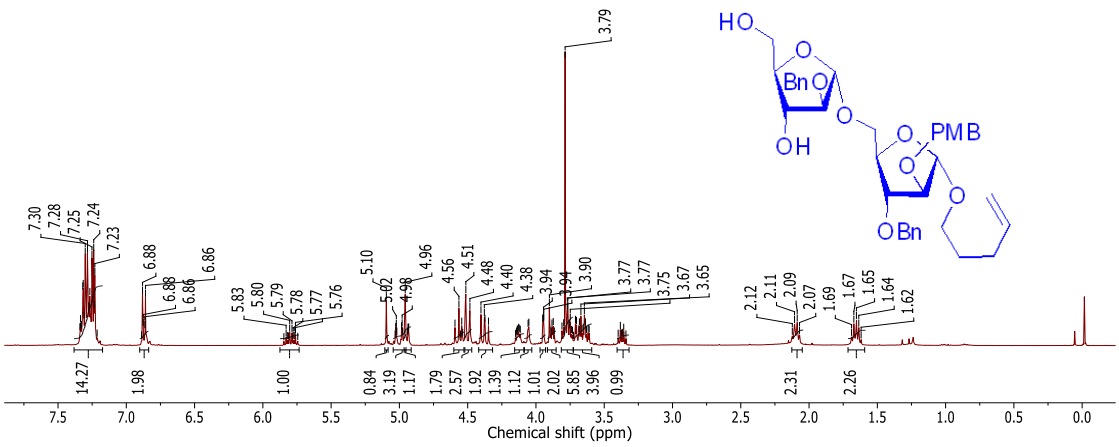
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **11b**



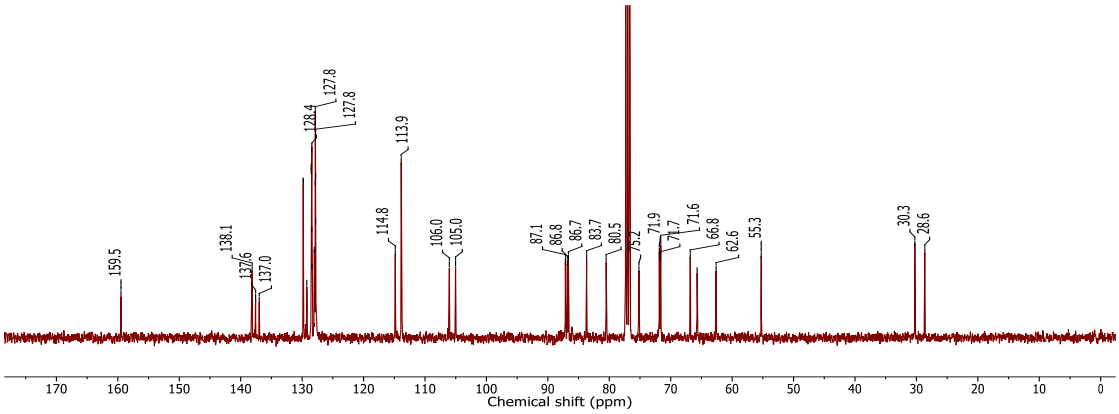
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **11b**



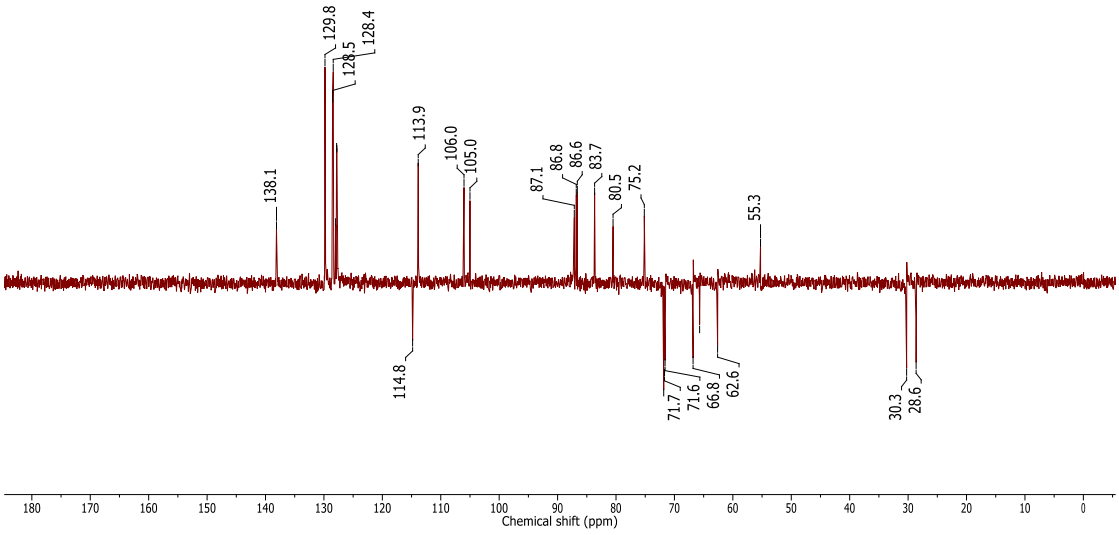
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) Of Compound **23c**



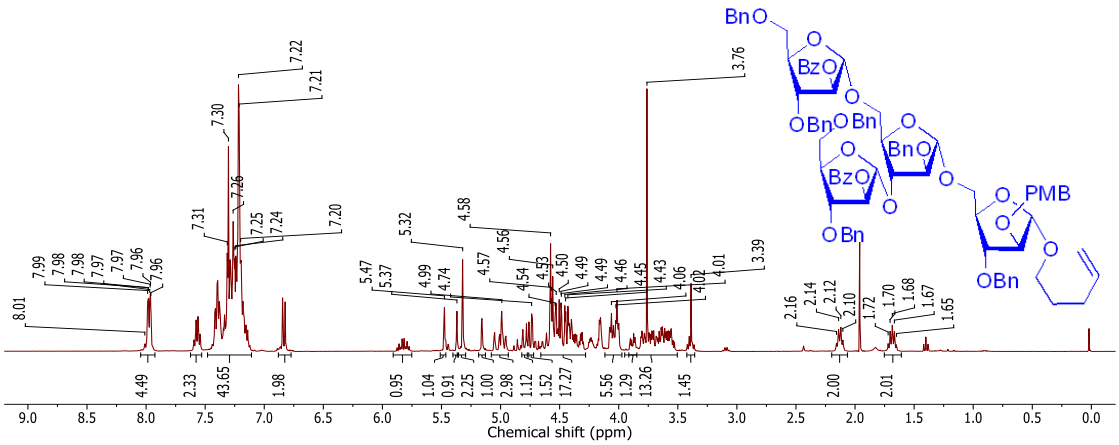
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **23c**



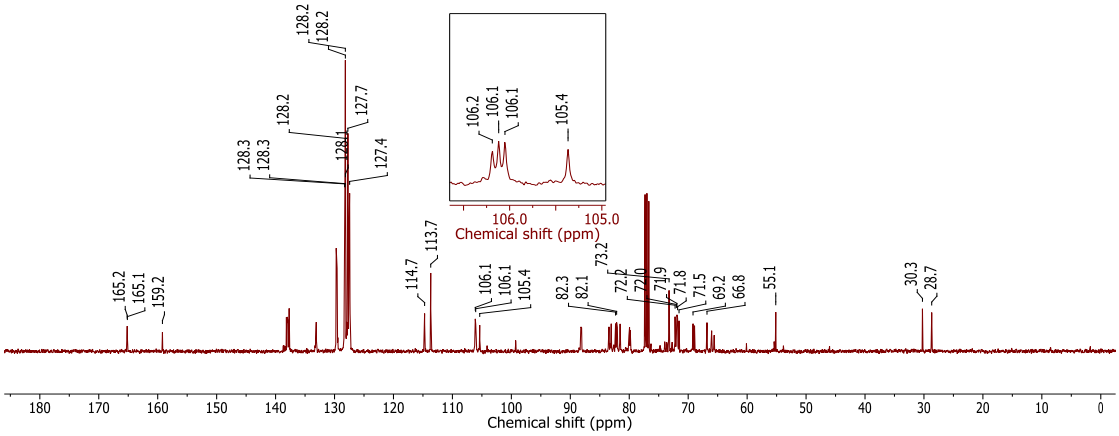
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **23c**



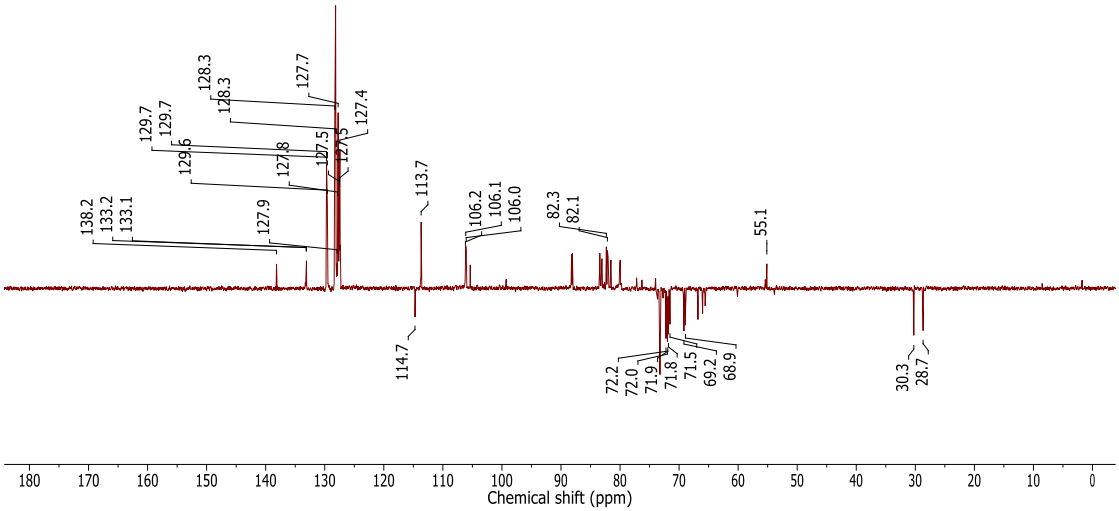
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) Of Compound **25a**



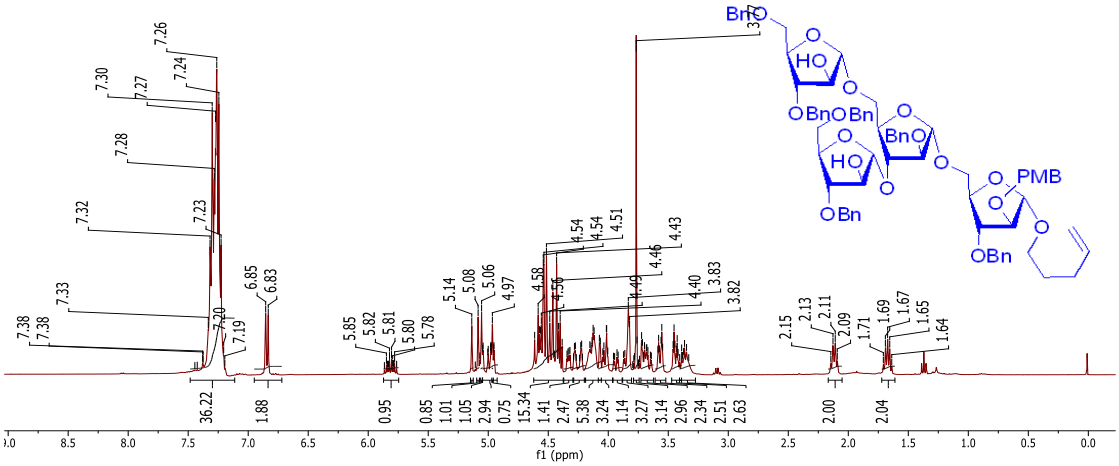
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **25a**



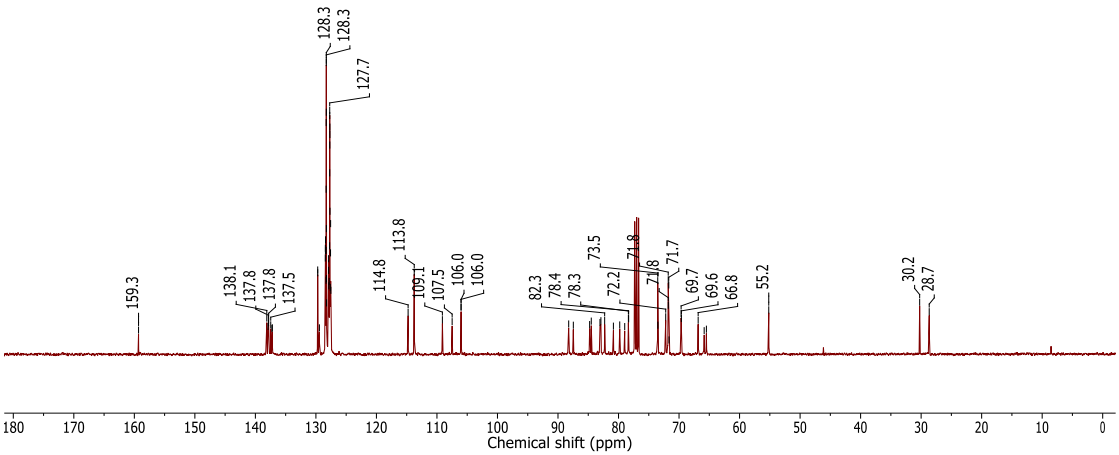
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **25a**



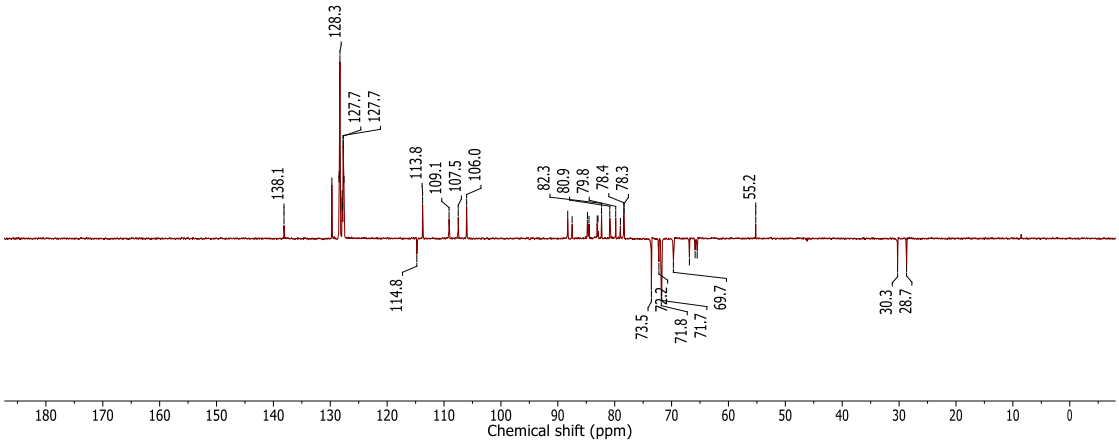
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) Of Compound **25b**



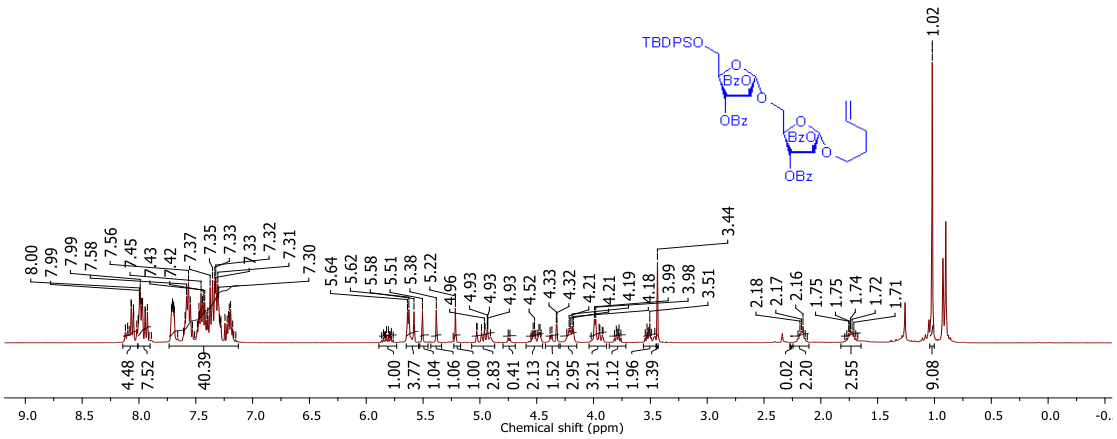
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **25b**



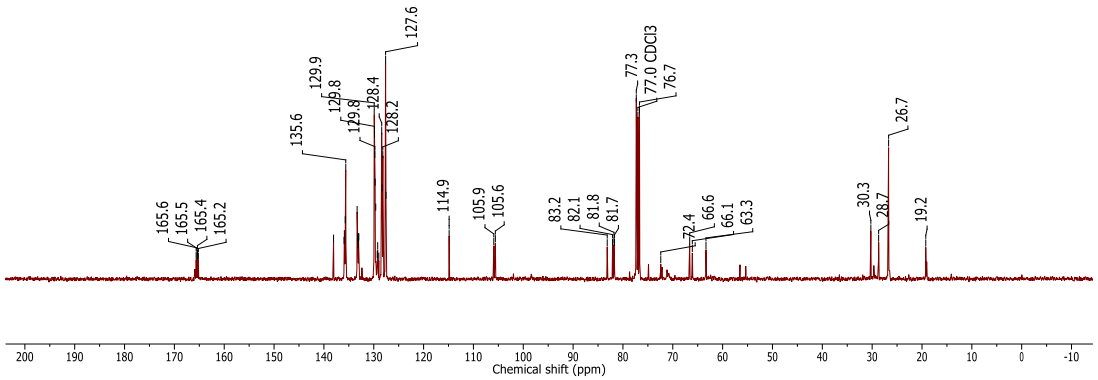
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **25b**



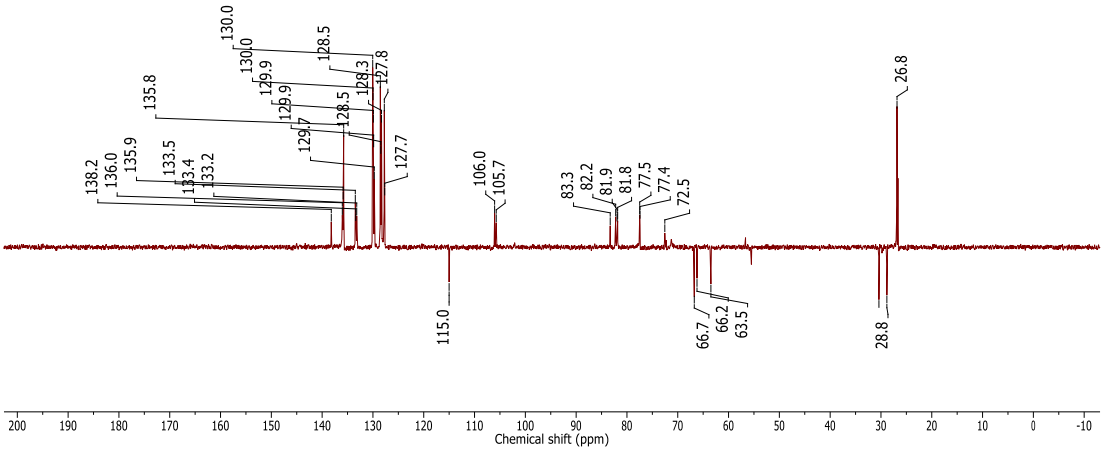
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **37b**



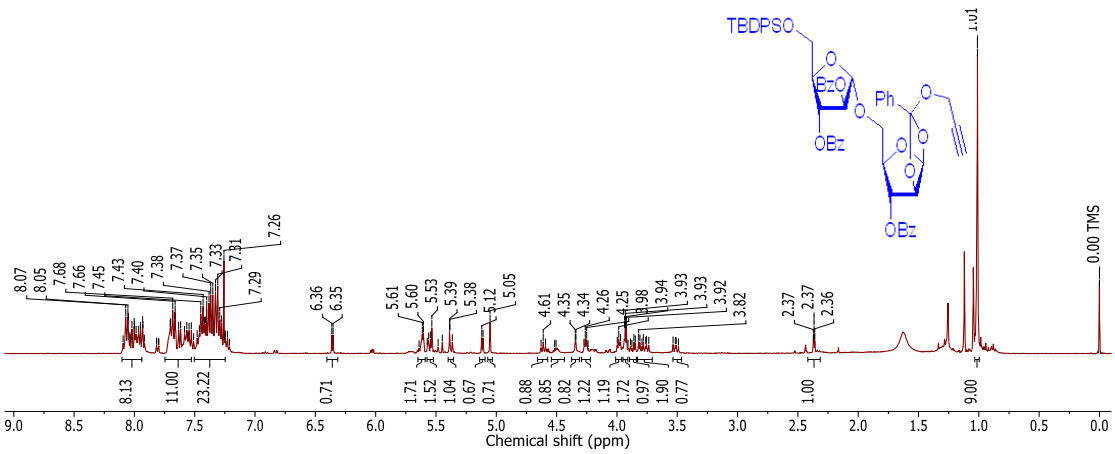
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **37b**



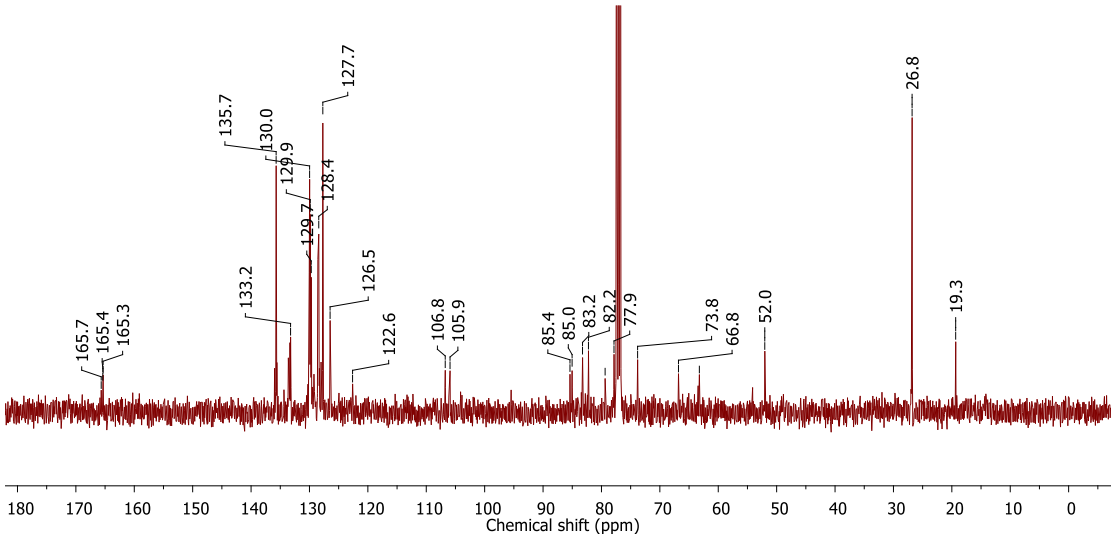
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **37b**



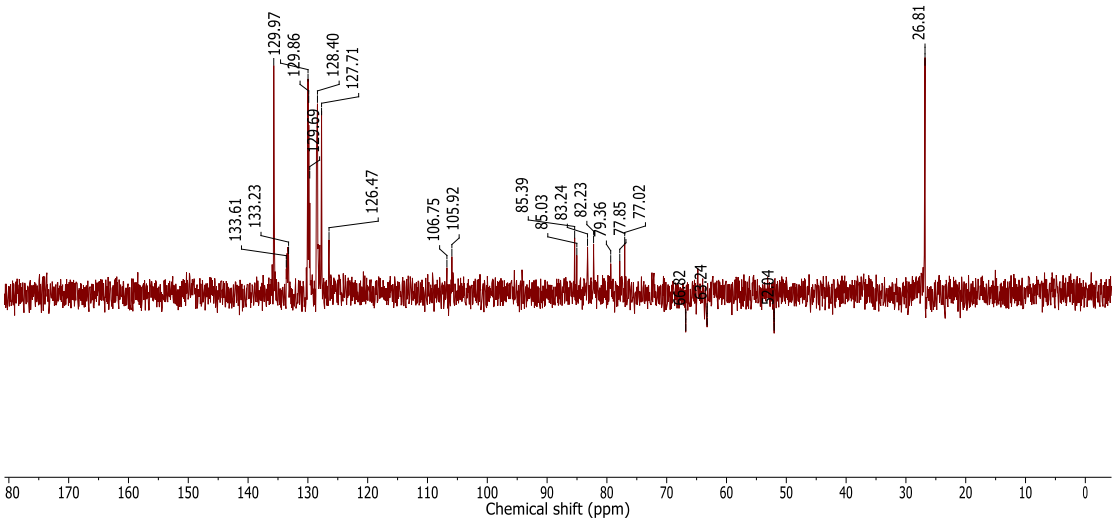
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **38e**



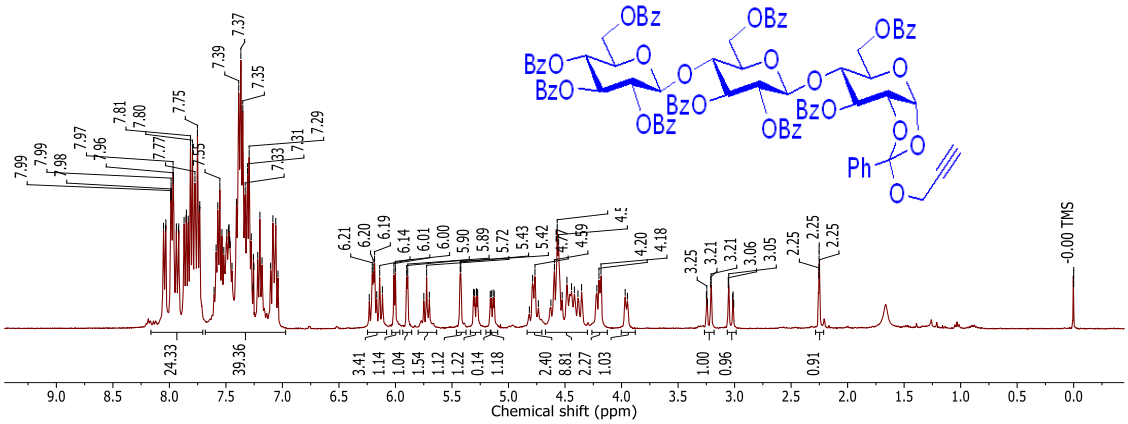
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **38e**



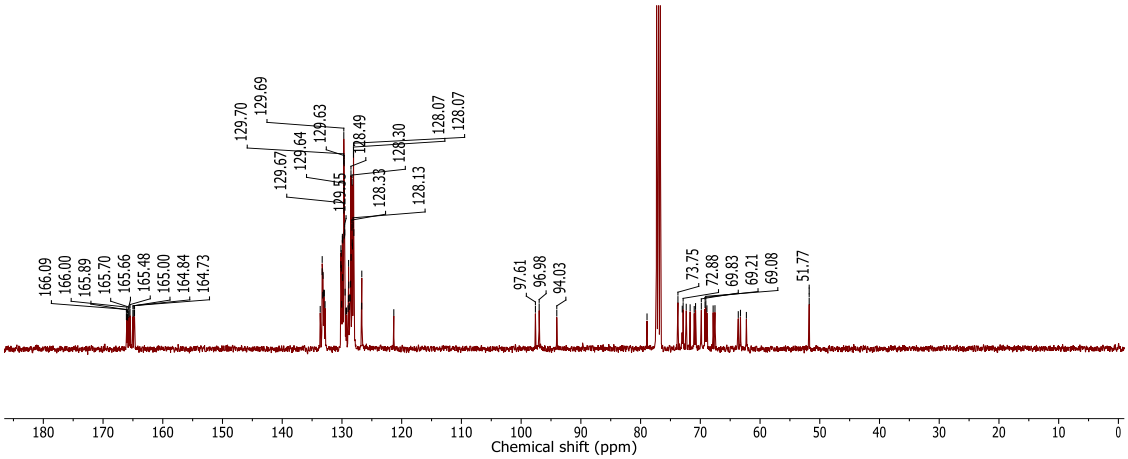
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **38e**



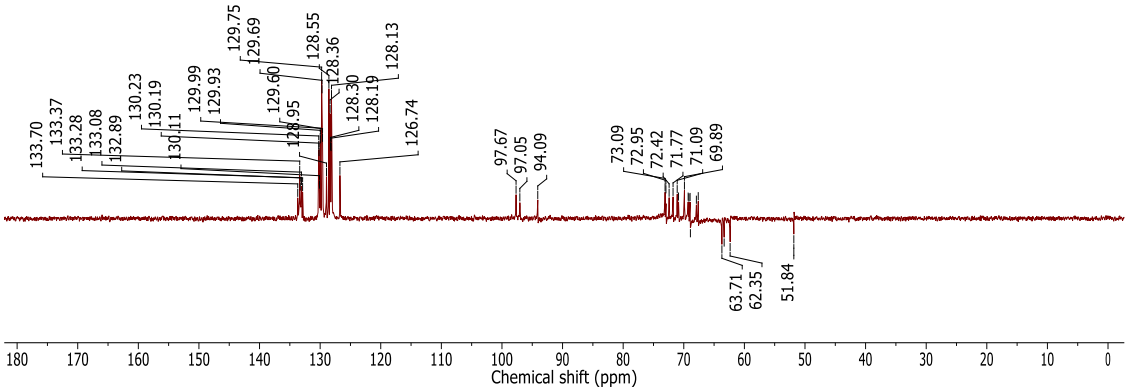
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) Of Compound **38g**



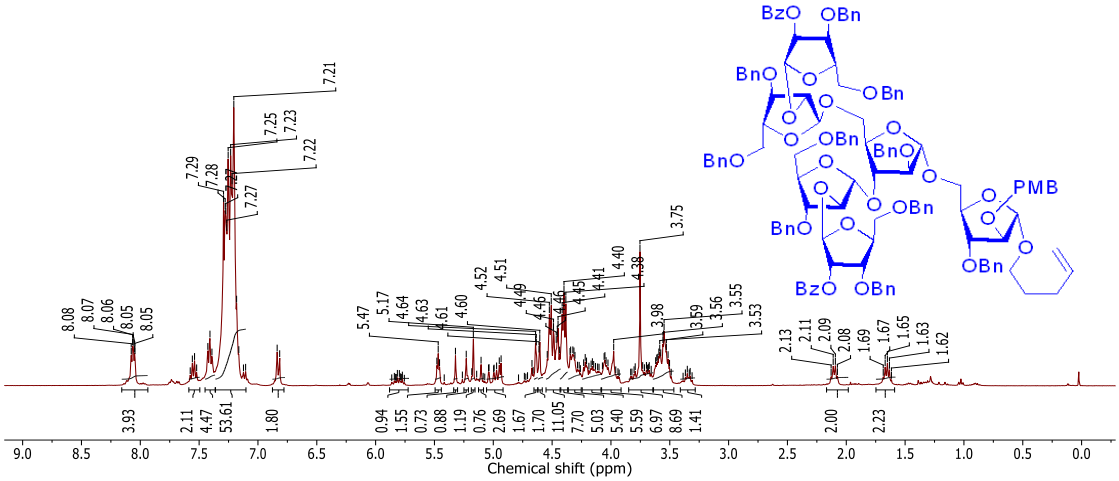
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **38g**



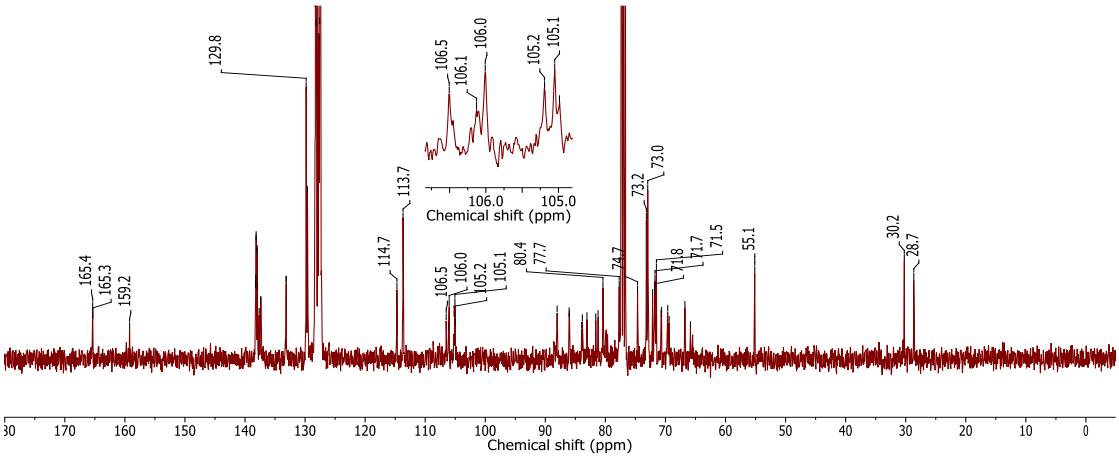
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **38g**



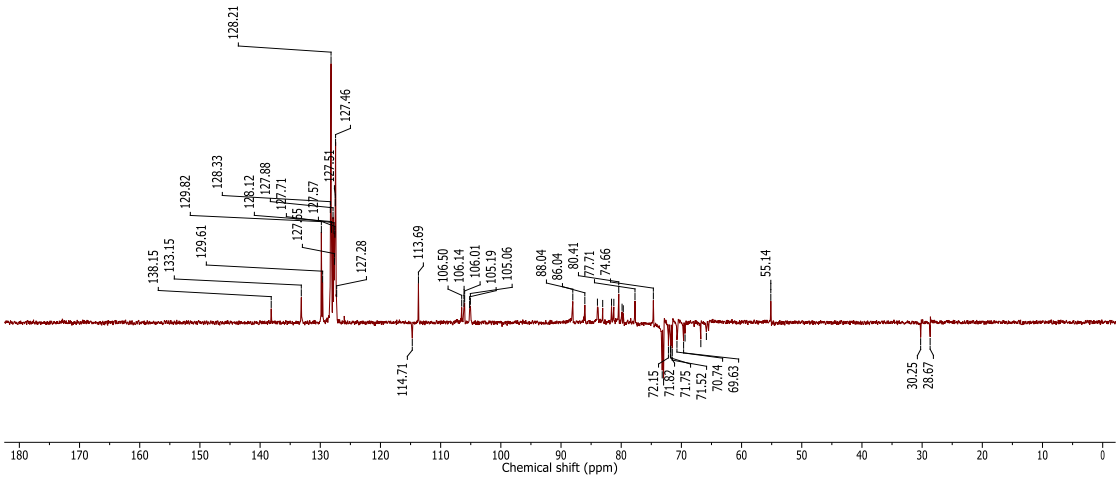
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) Of Compound



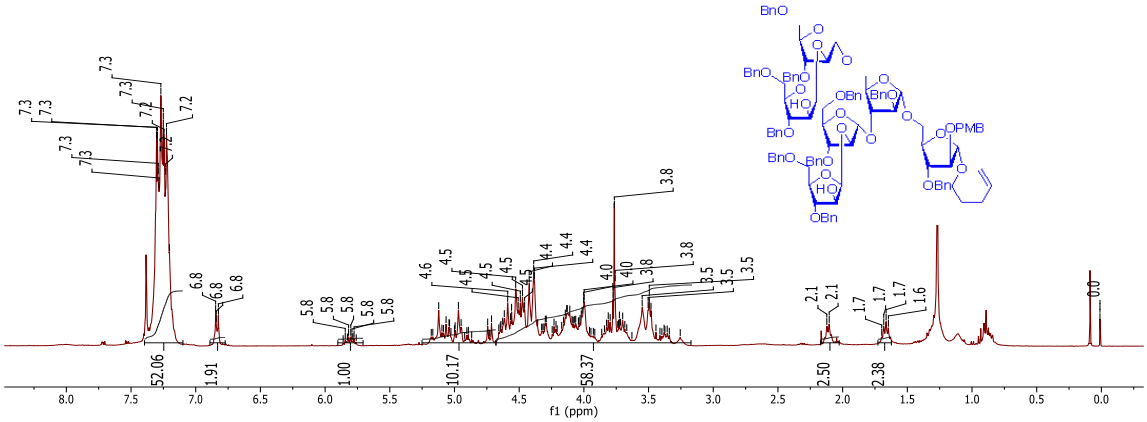
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound



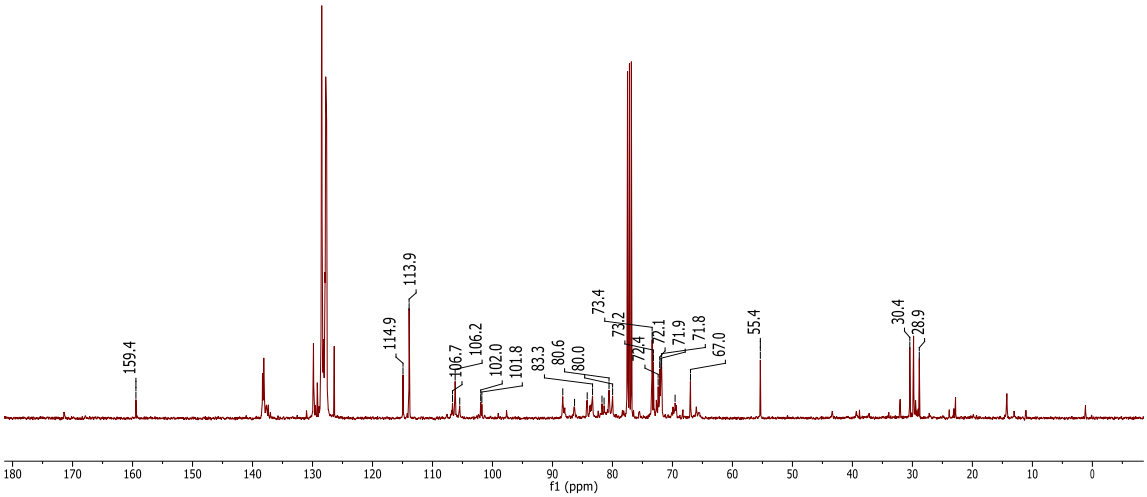
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound



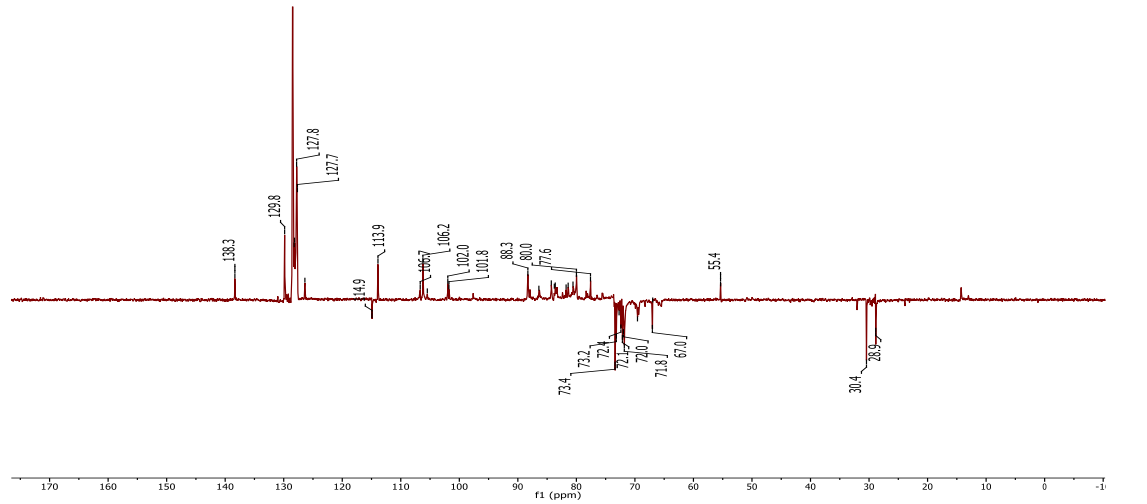
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) Of Compound **4e**



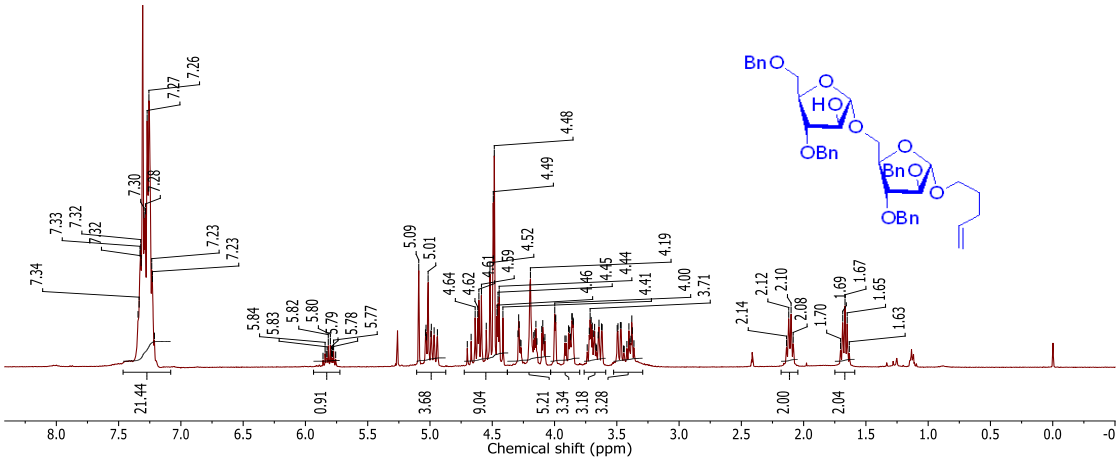
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **4e**



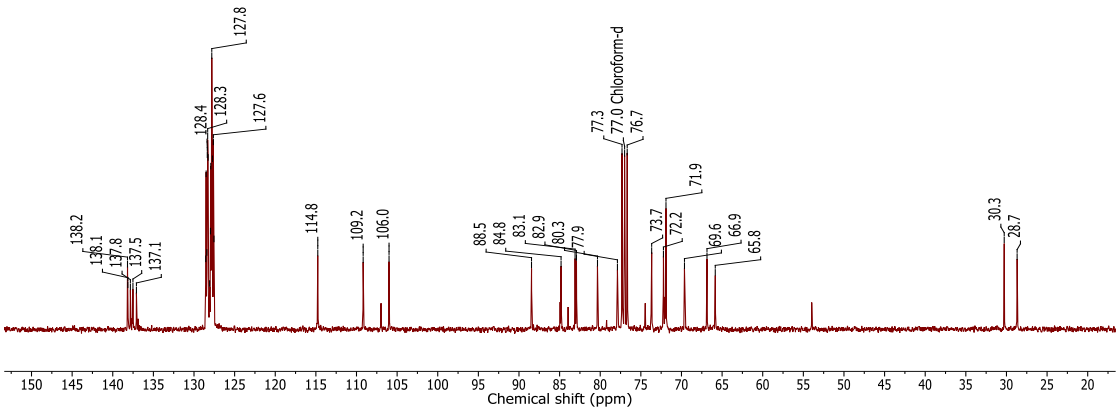
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) Of Compound **4e**



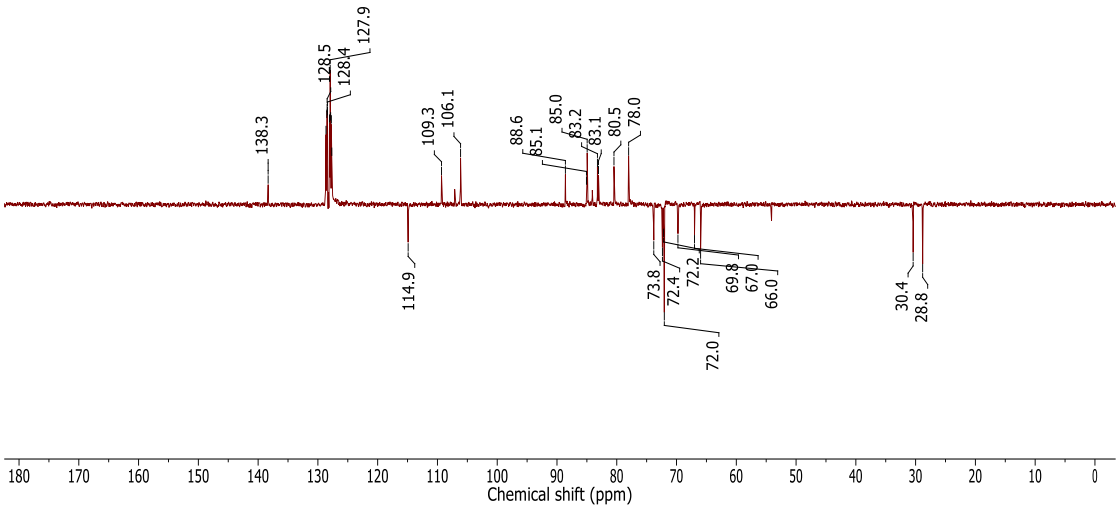
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **16k**



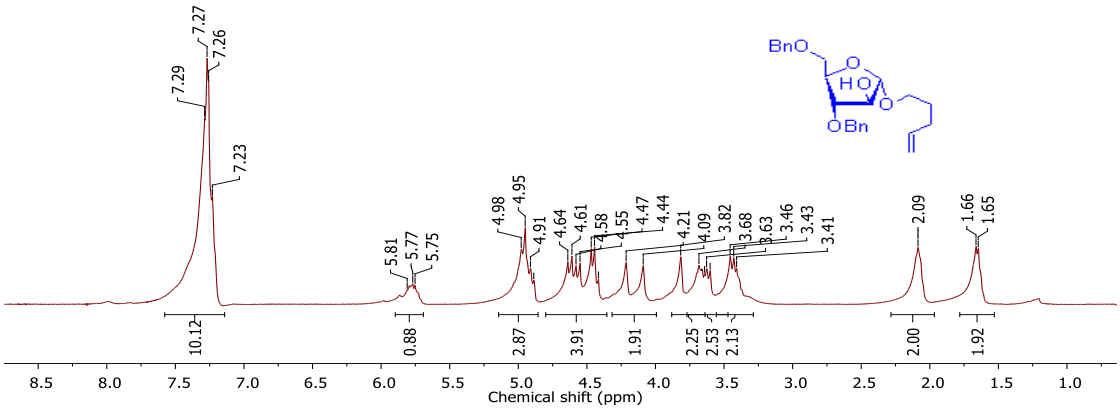
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **16k**



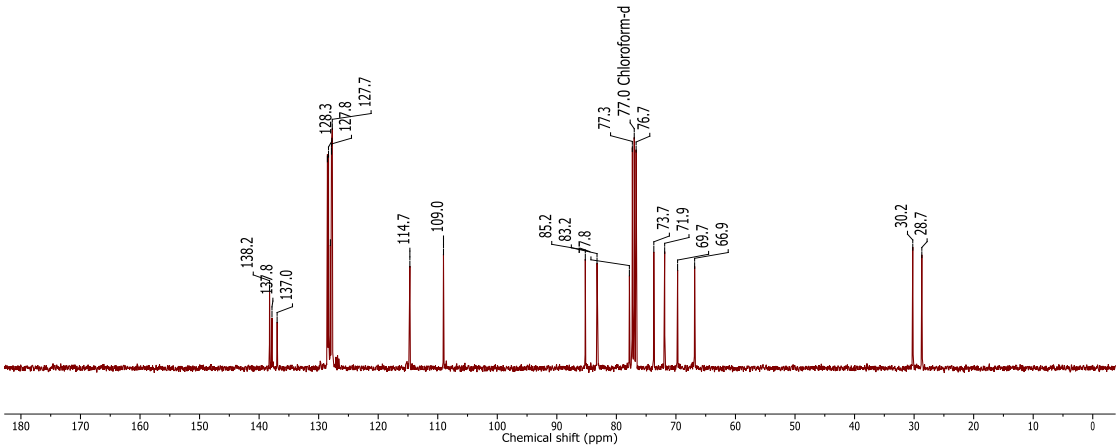
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **16k**



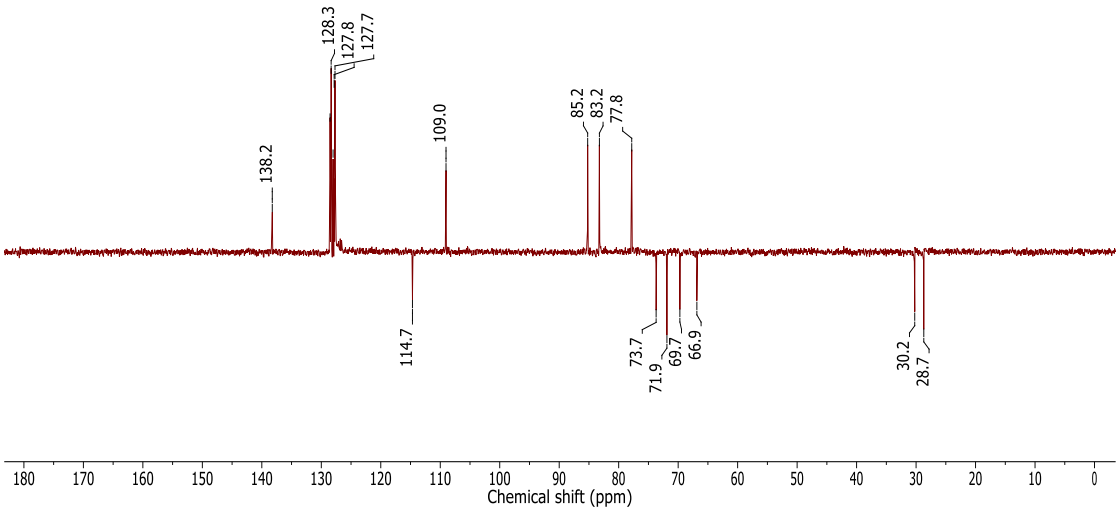
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **16l**



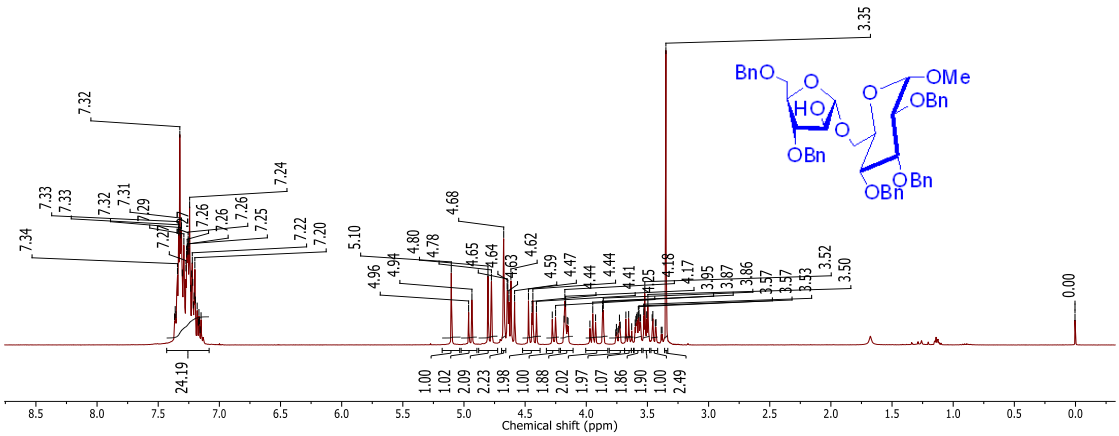
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **16l**



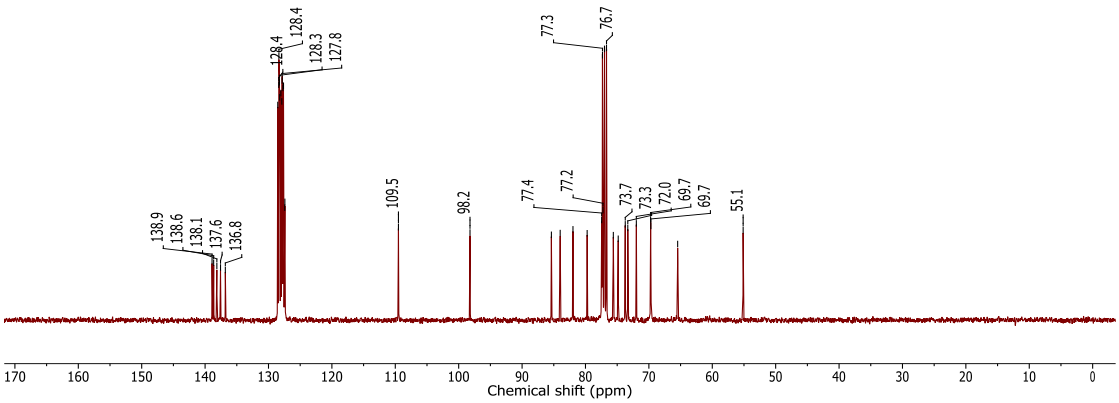
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **16l**



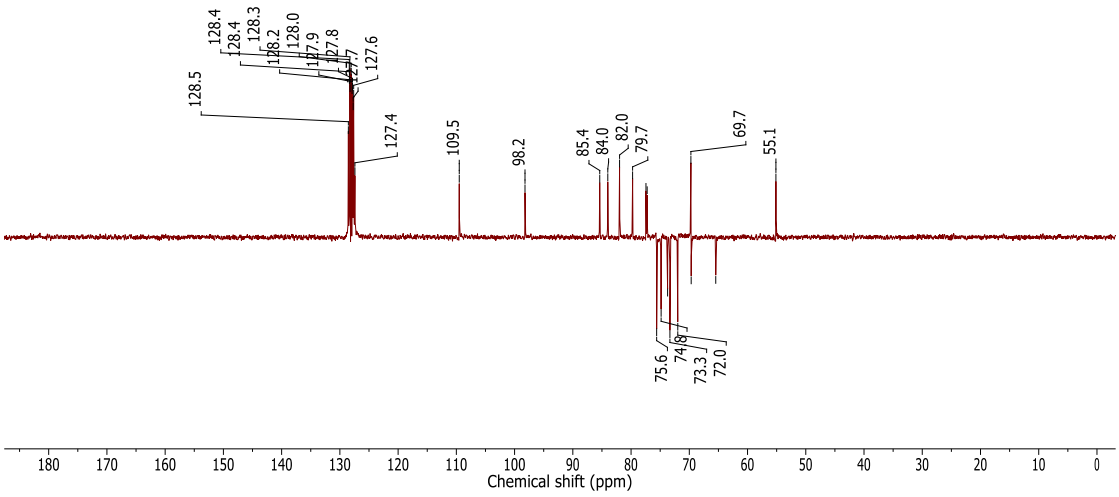
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **16m**



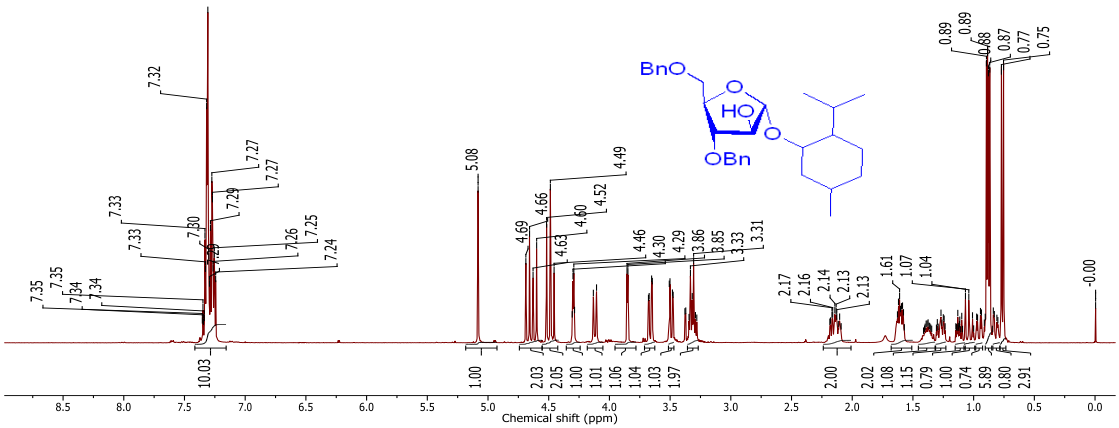
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **16m**



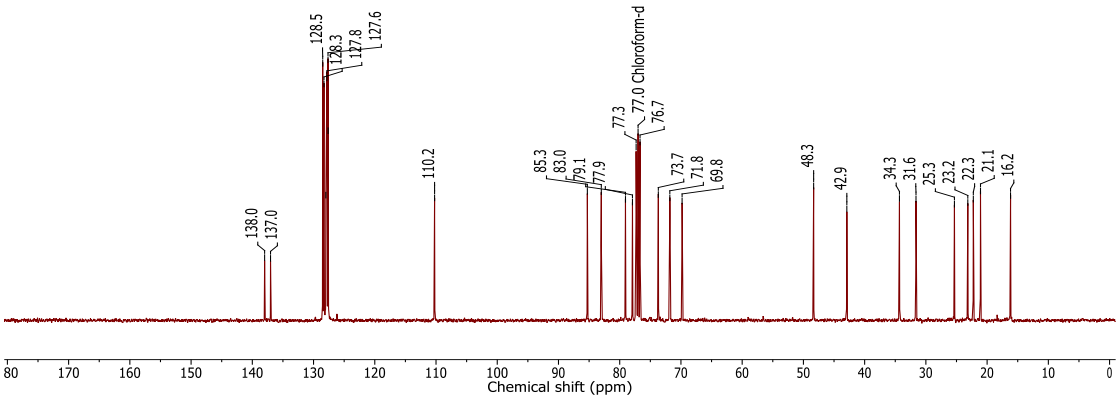
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **16m**



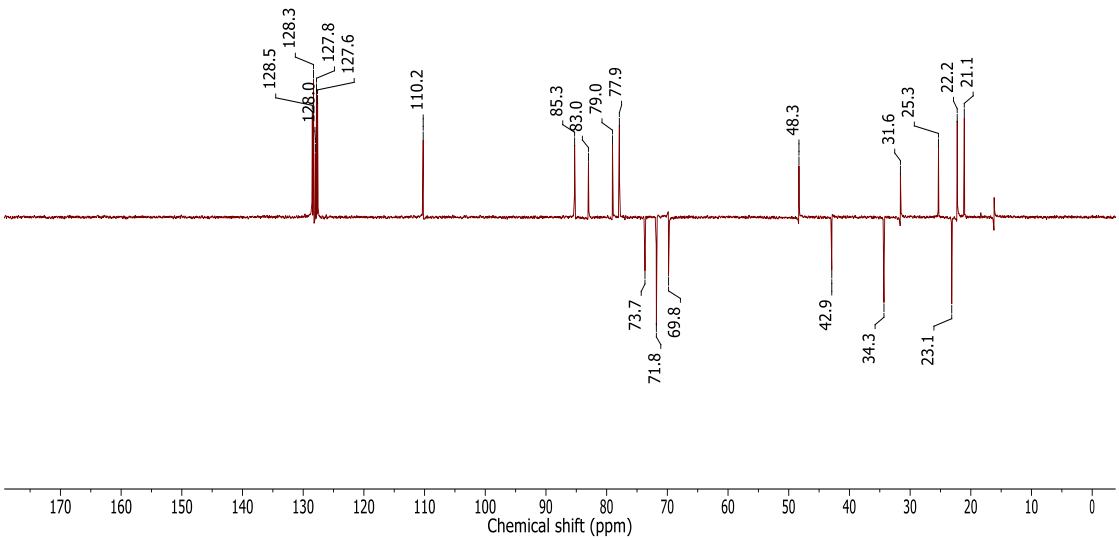
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **16n**



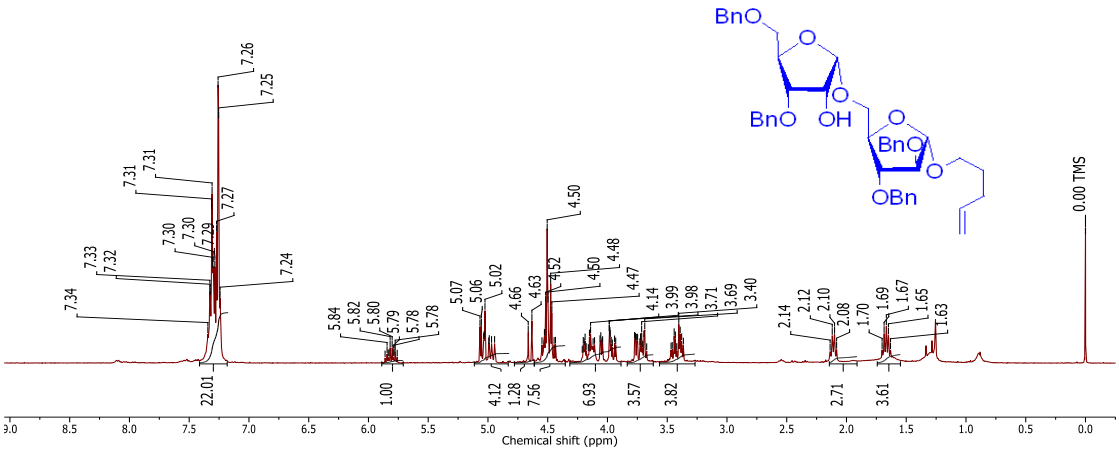
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **16n**



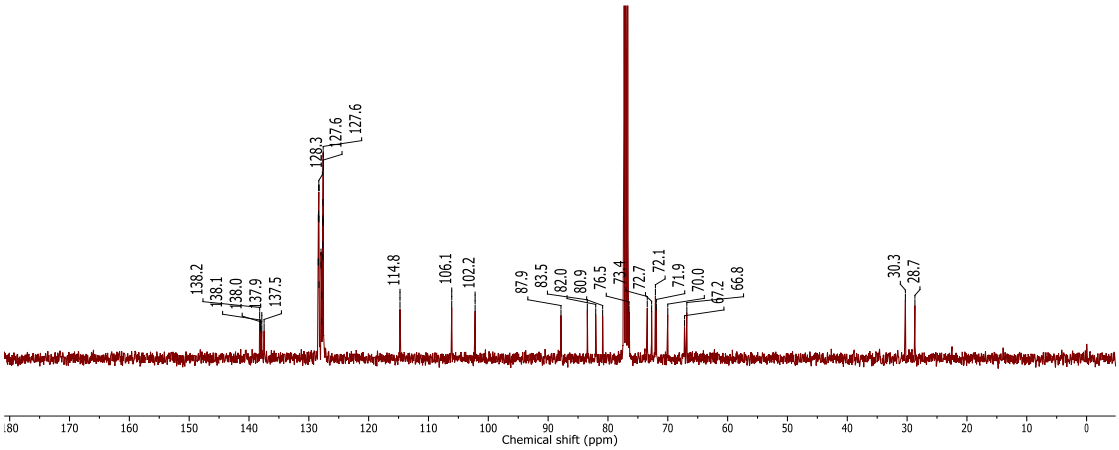
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **16n**



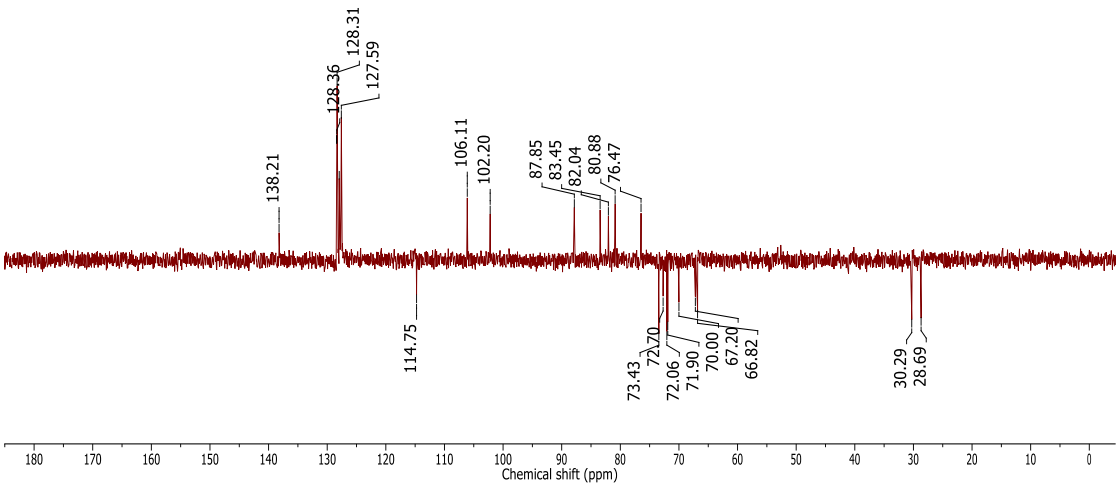
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **35a**



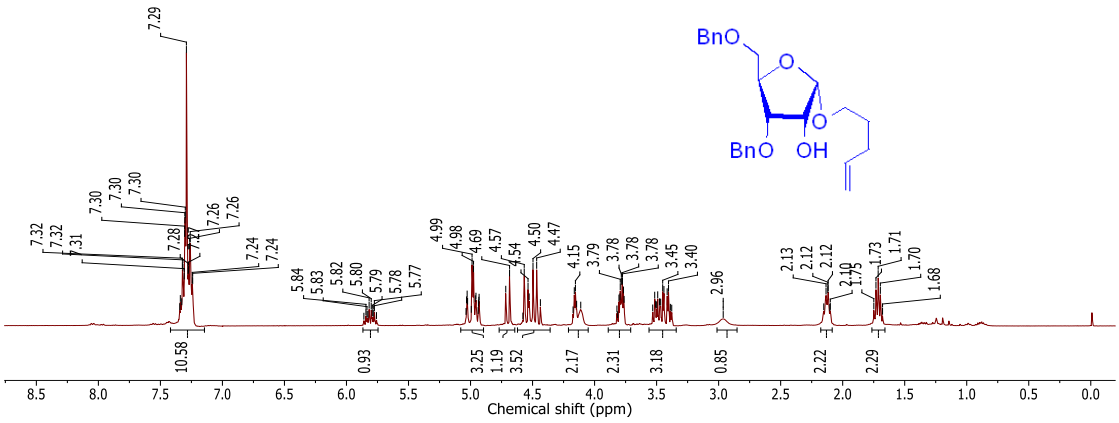
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **35a**



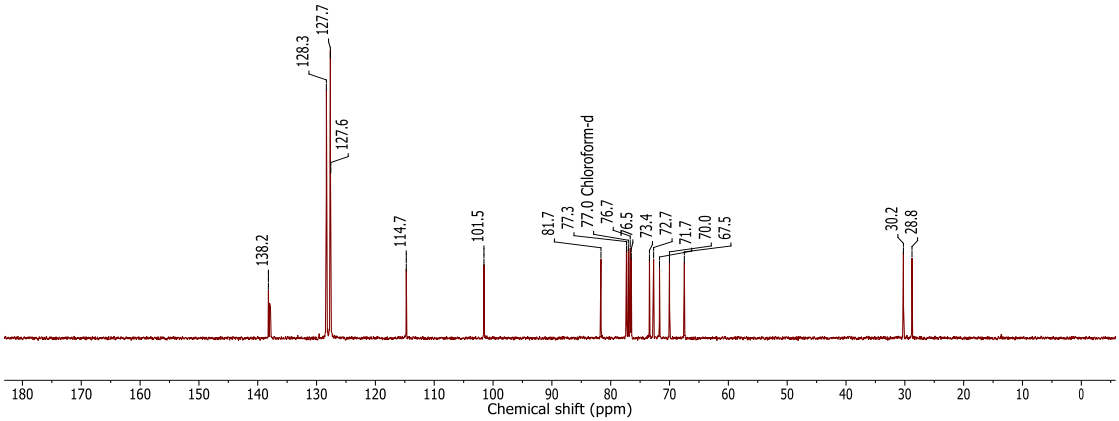
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **35a**



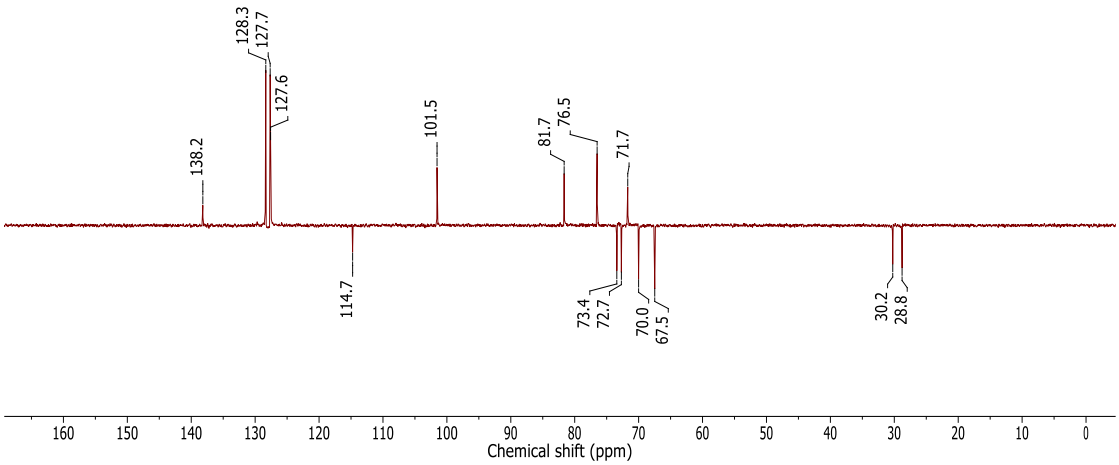
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **35b**



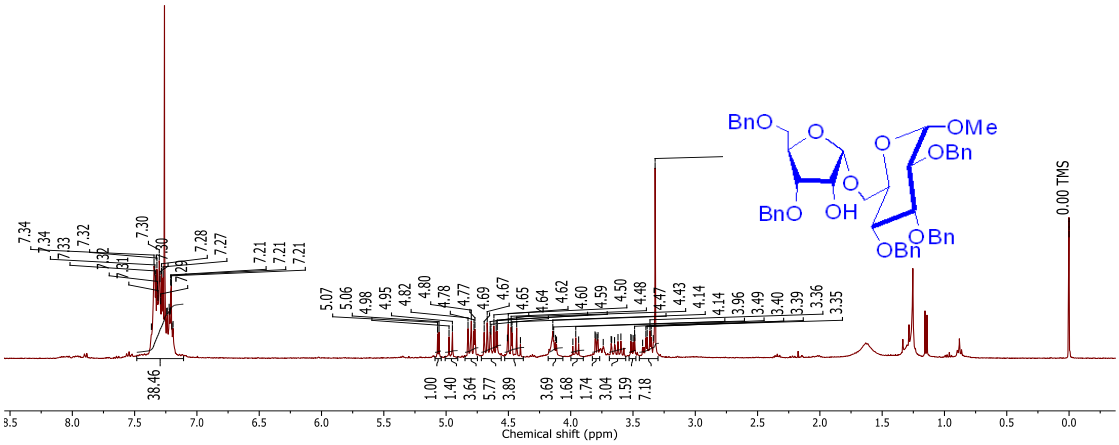
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **35b**



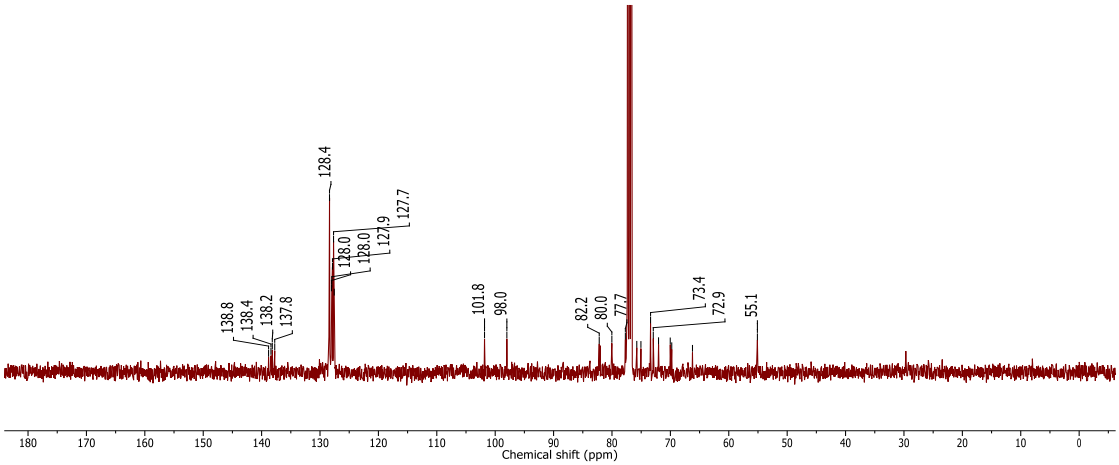
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **35b**



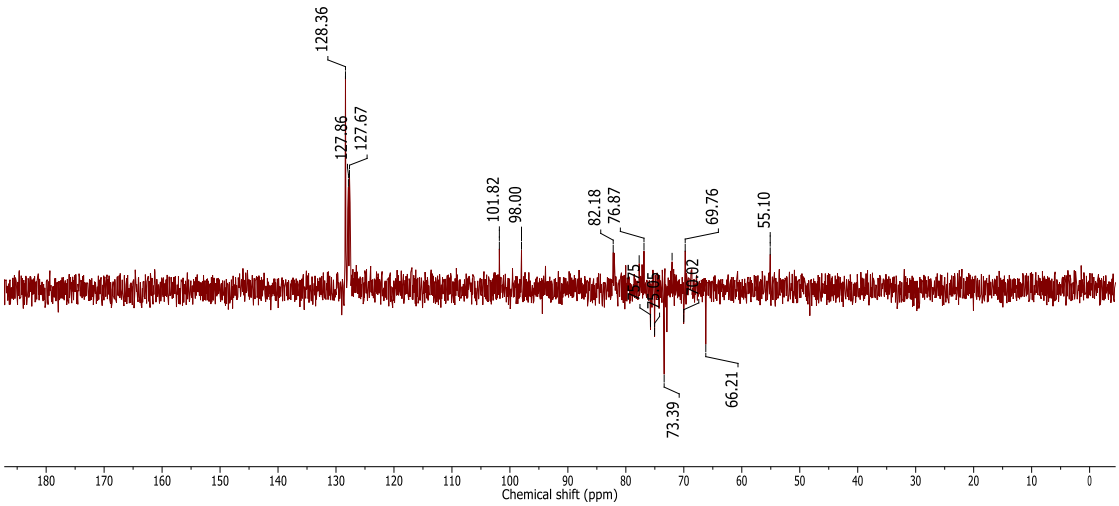
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **35c**



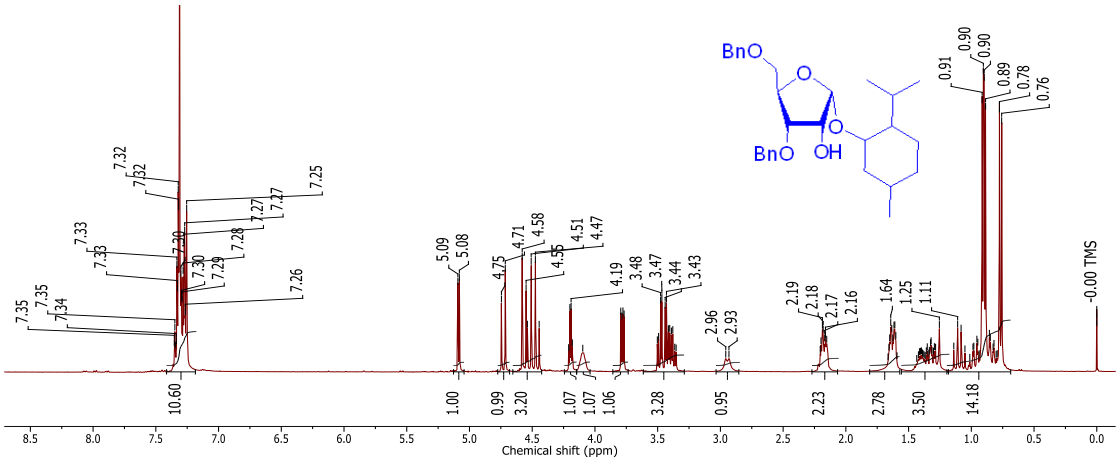
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **35c**



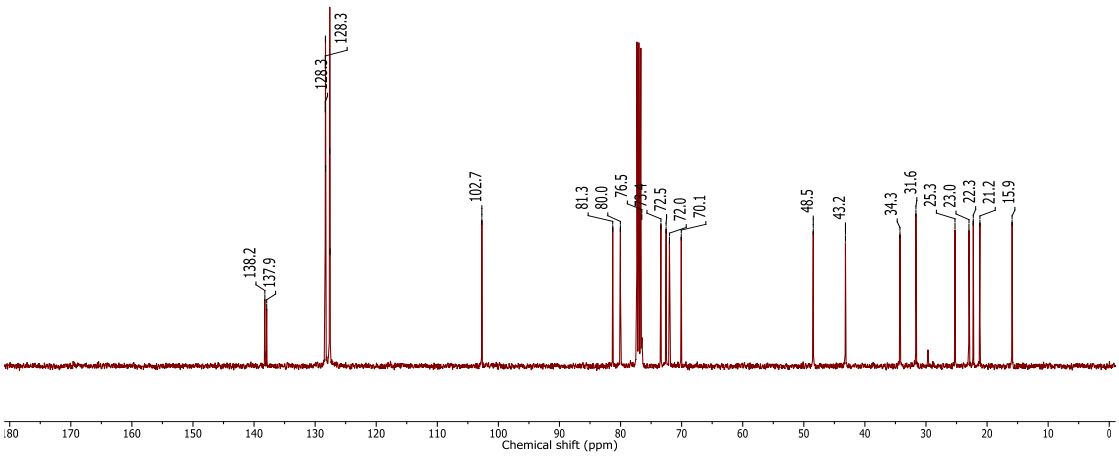
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **35c**



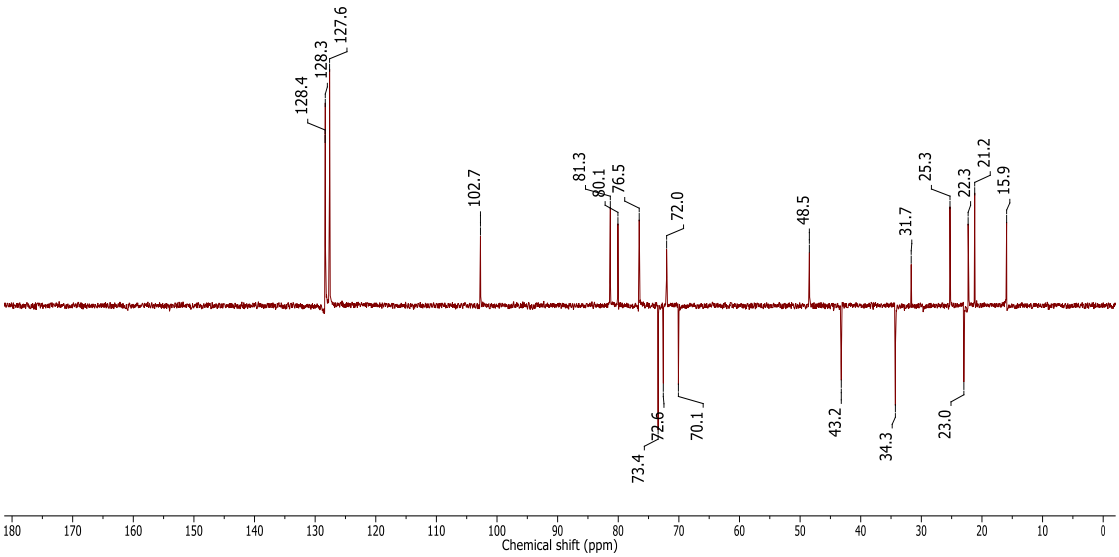
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **35d**



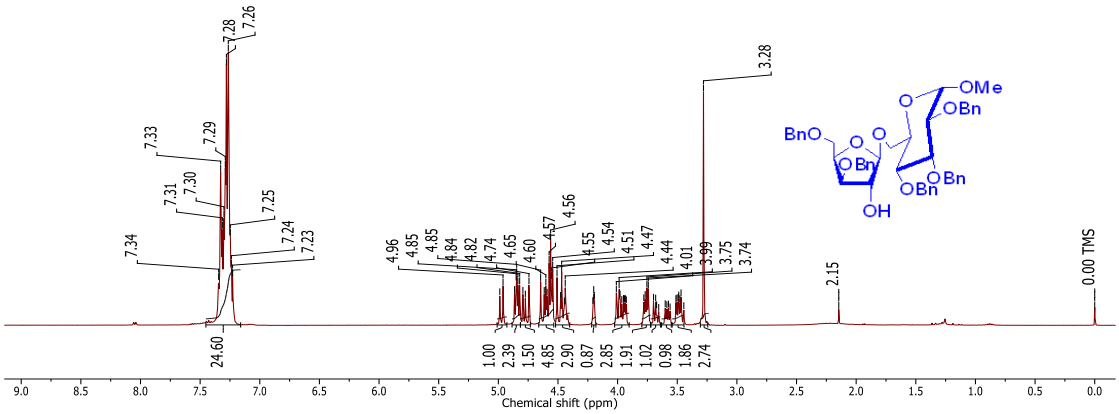
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **35d**



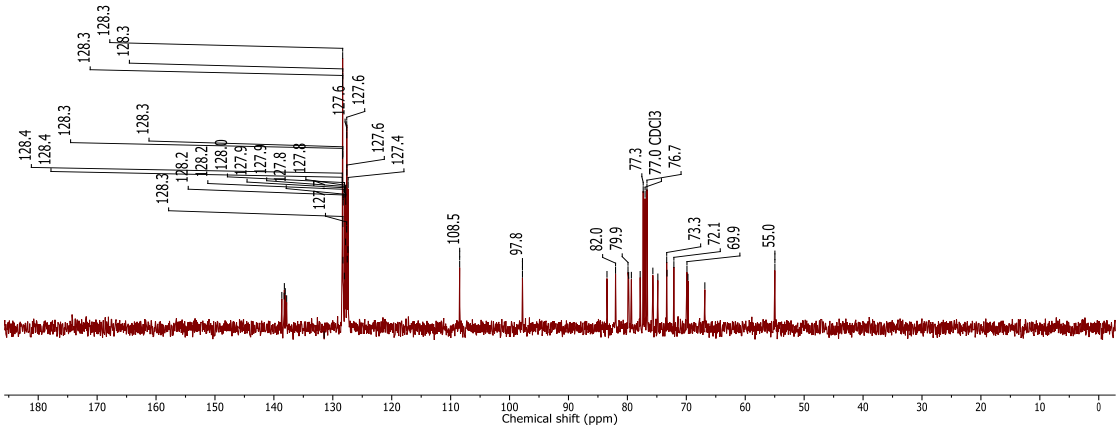
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **35d**



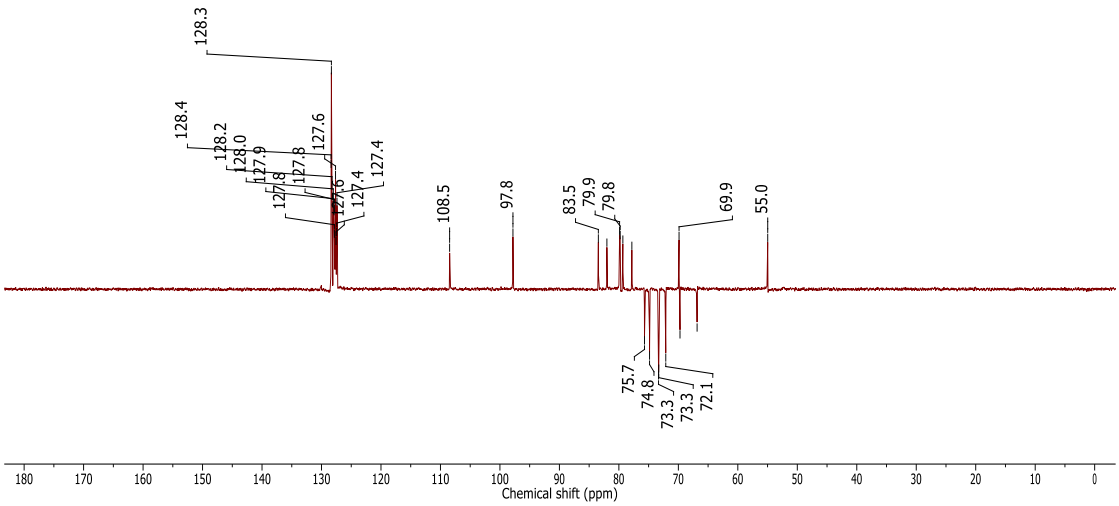
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **20k**



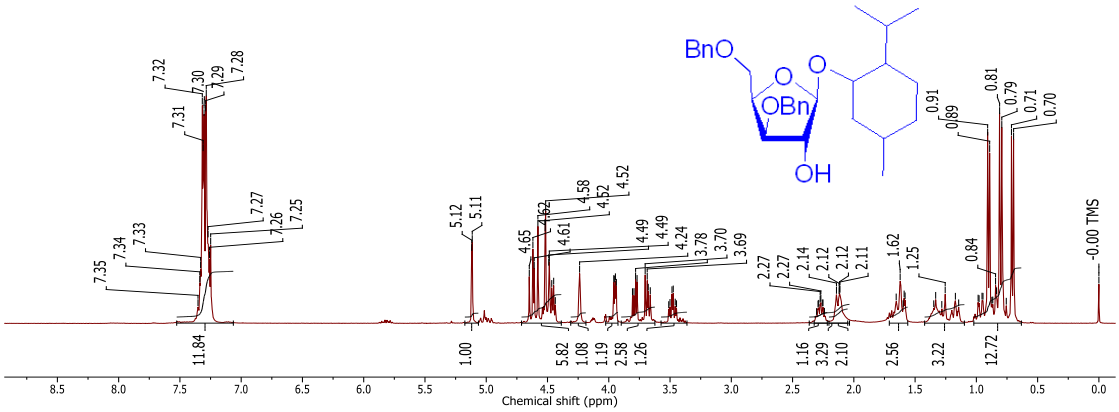
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20k**



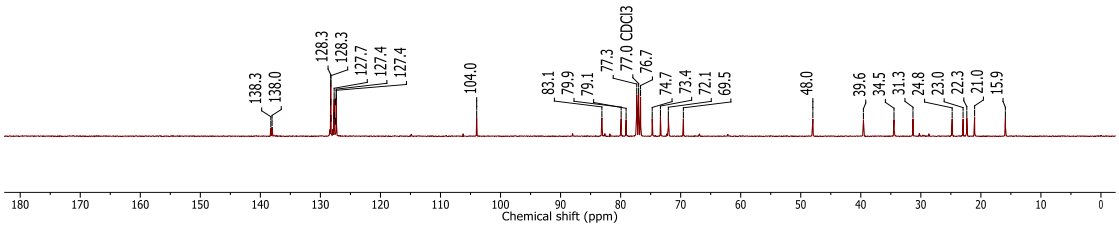
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20k**



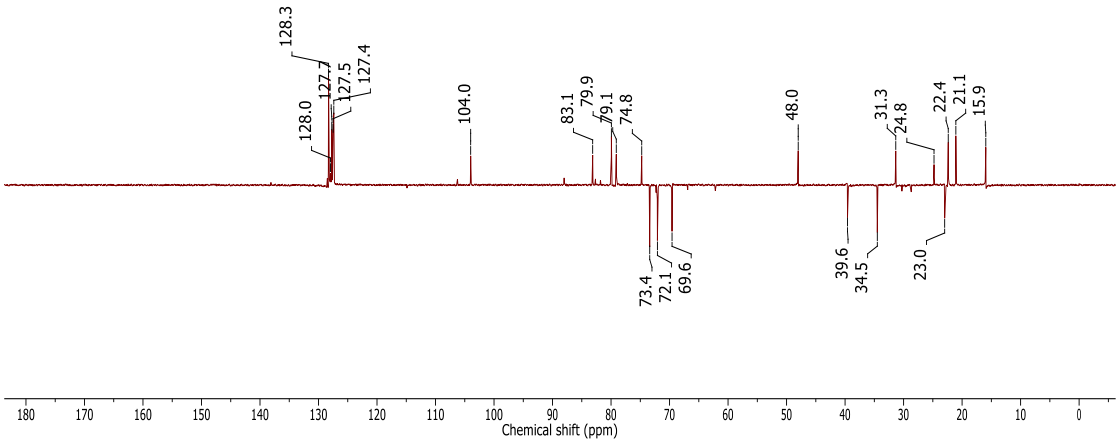
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **20l**



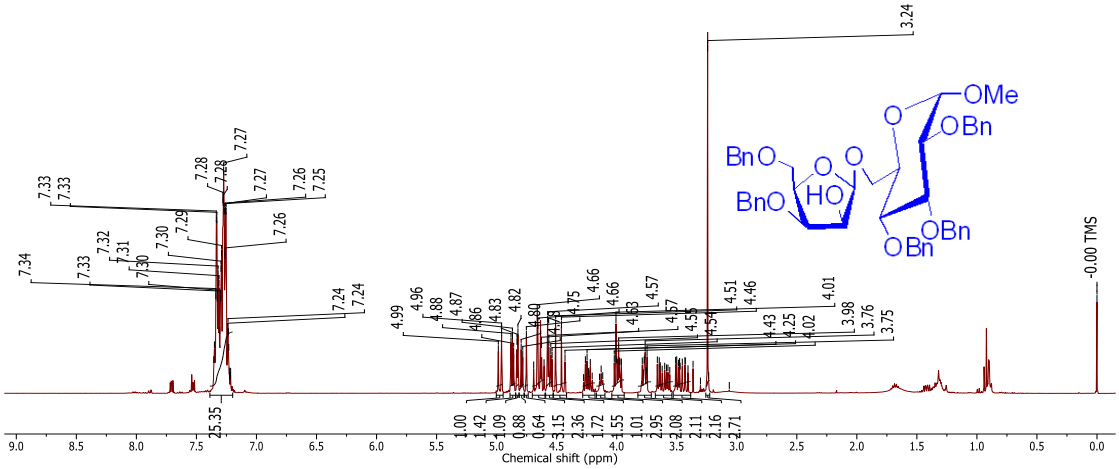
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20l**



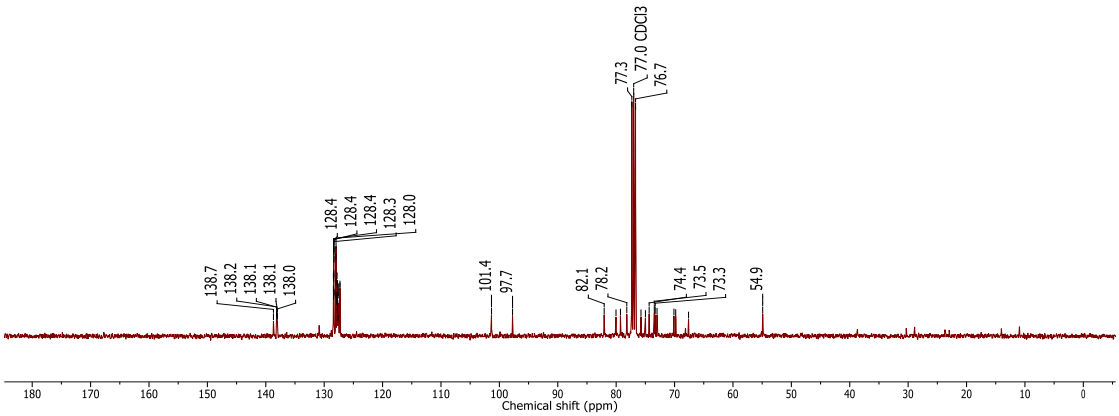
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **20l**



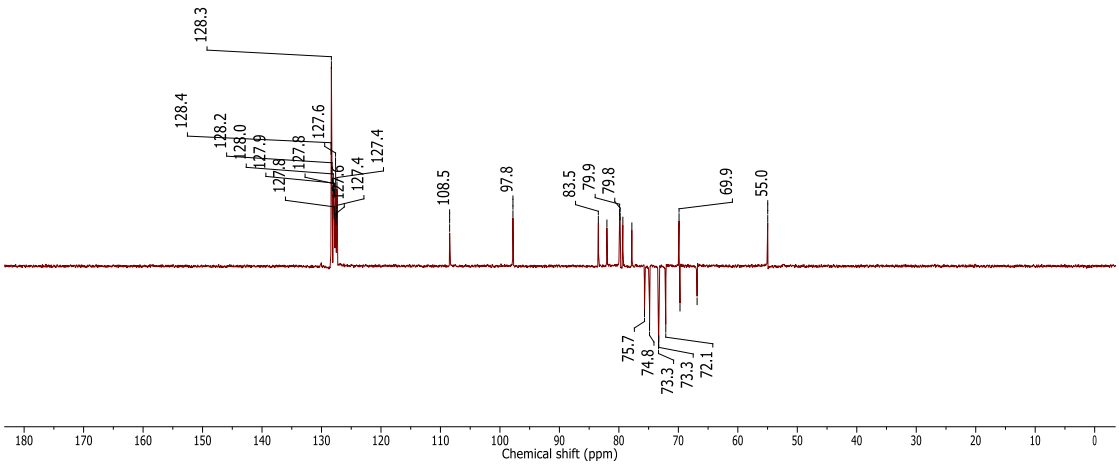
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **36a**



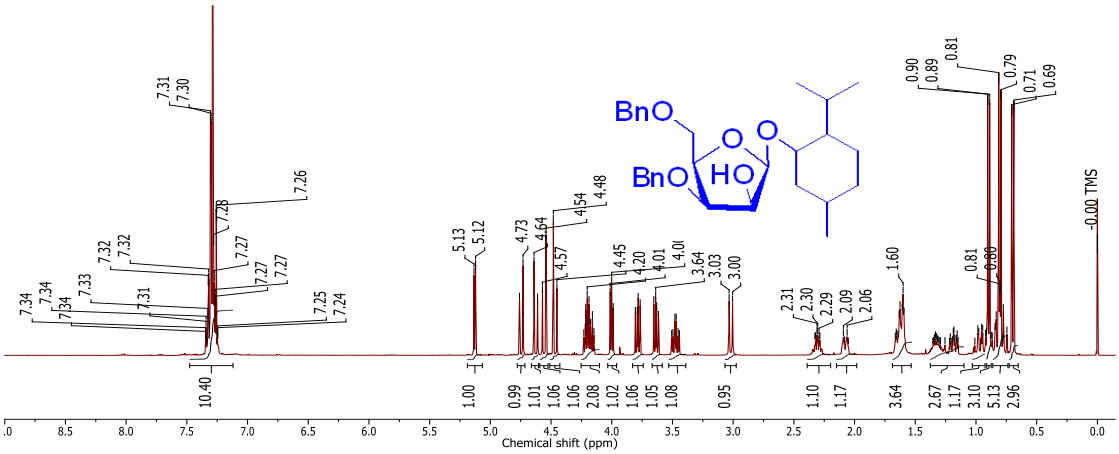
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **36a**



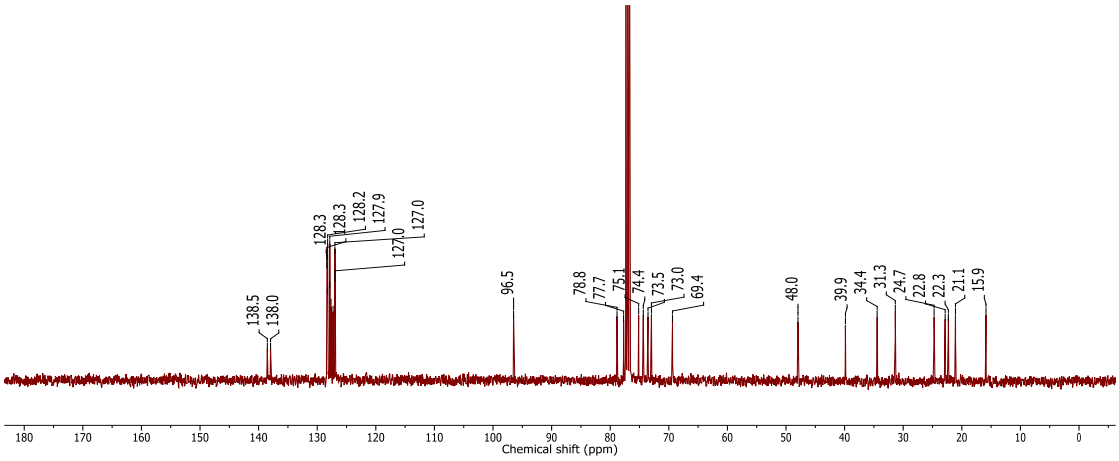
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **36a**



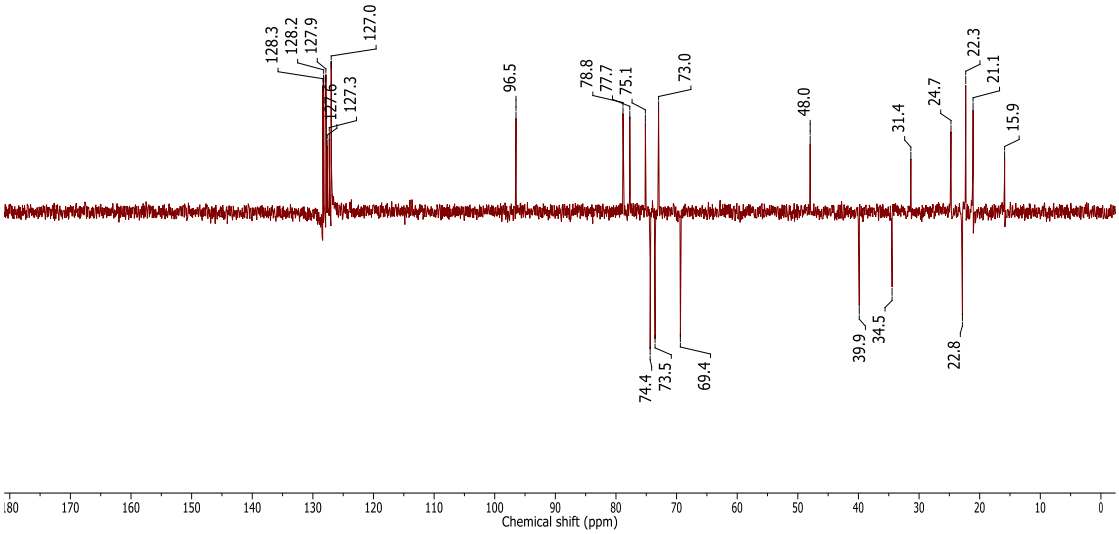
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **36b**



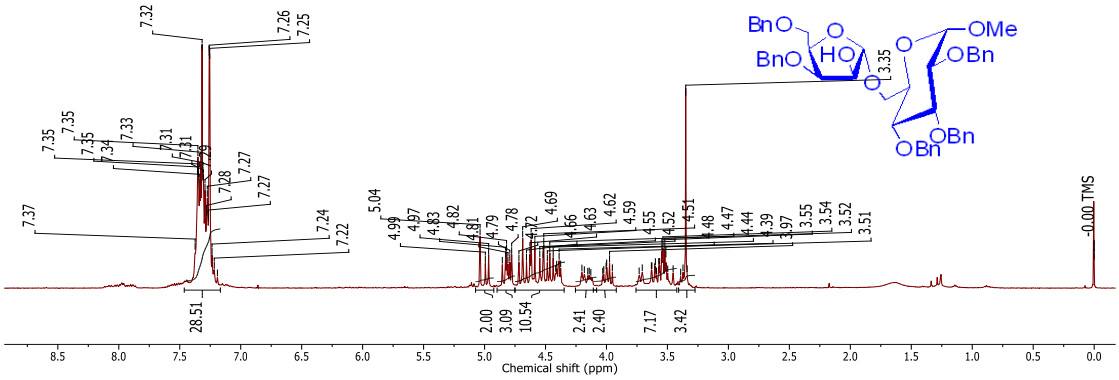
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **36b**



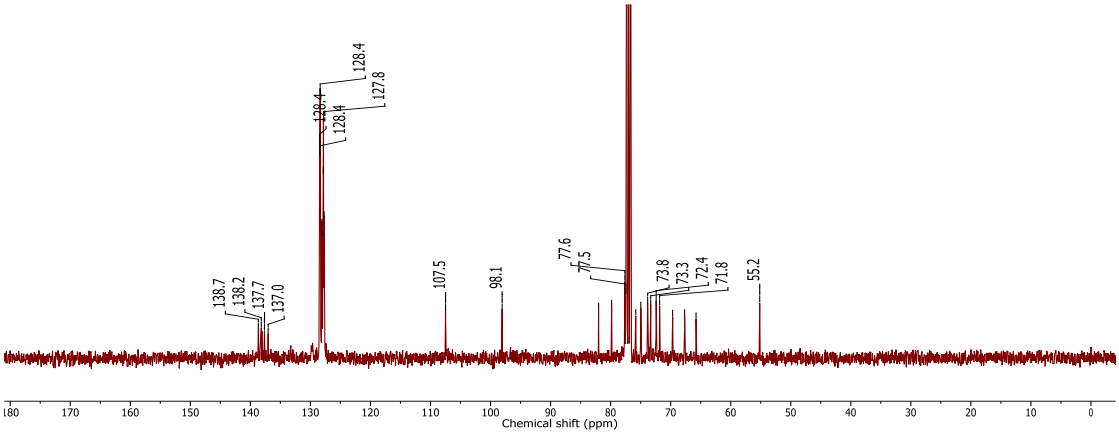
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **36b**



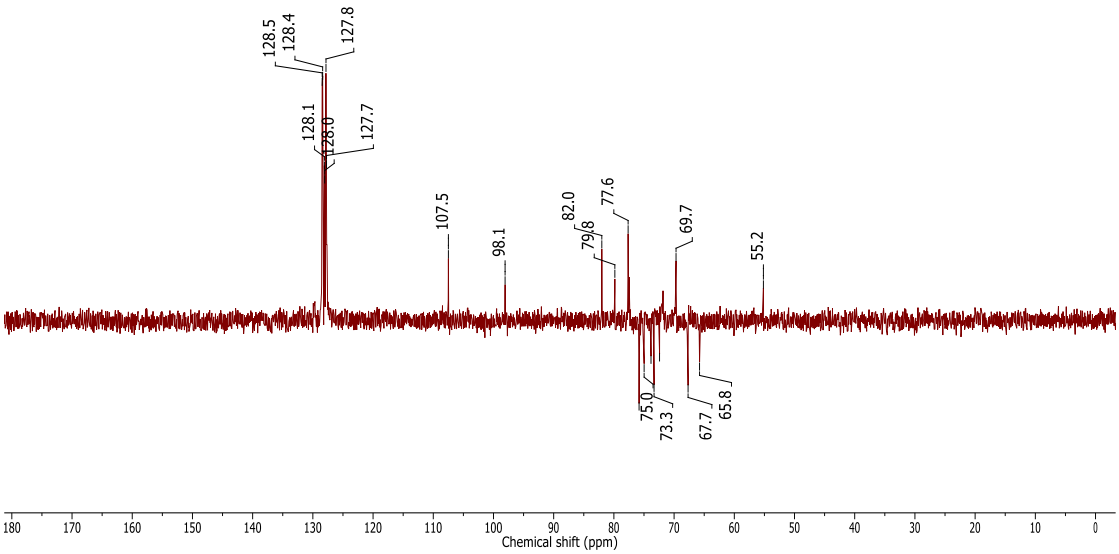
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **18k**



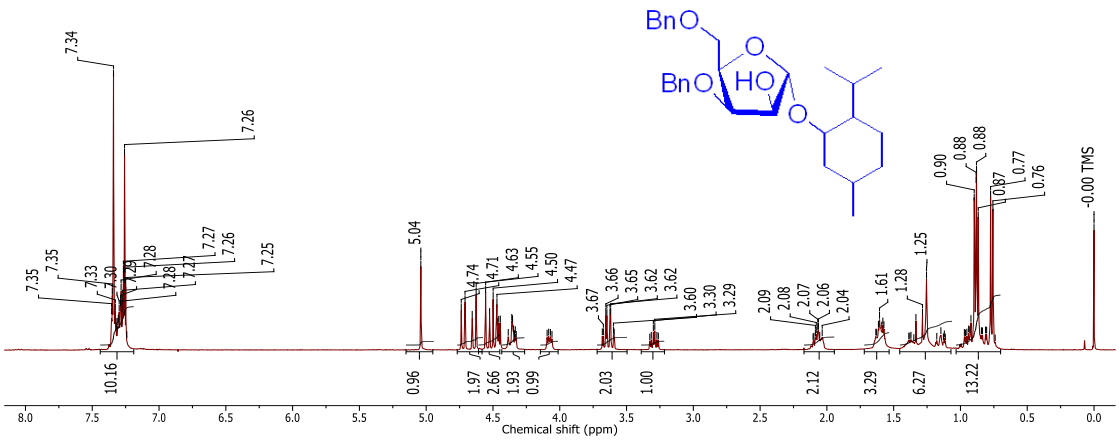
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **18k**



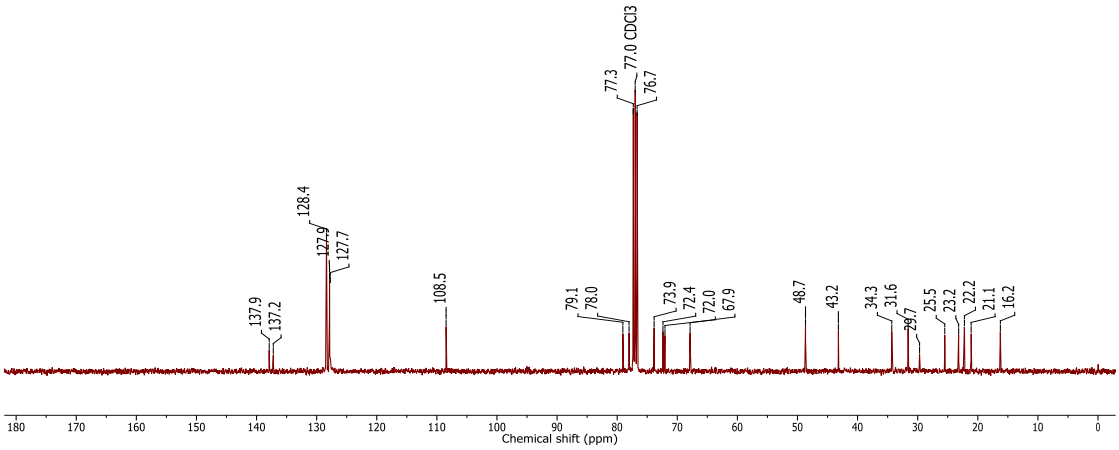
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **18k**



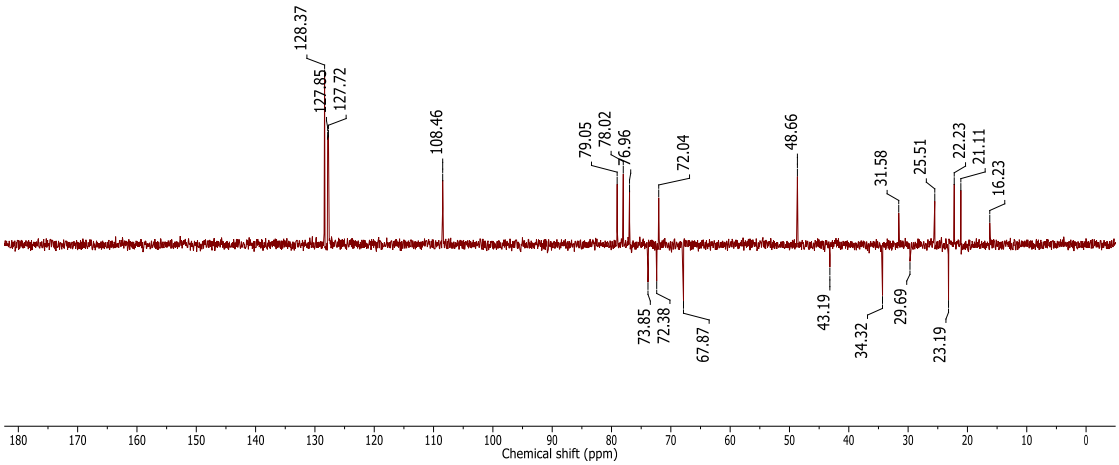
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **18l**



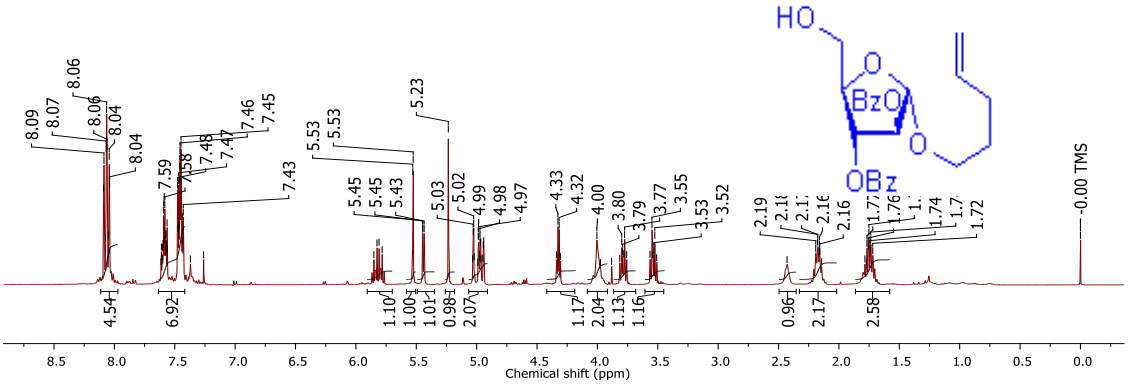
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **18l**



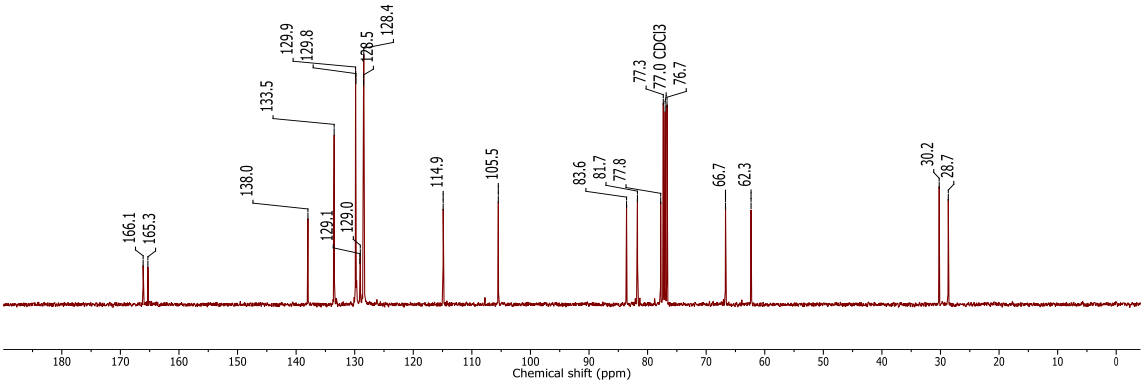
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **18l**



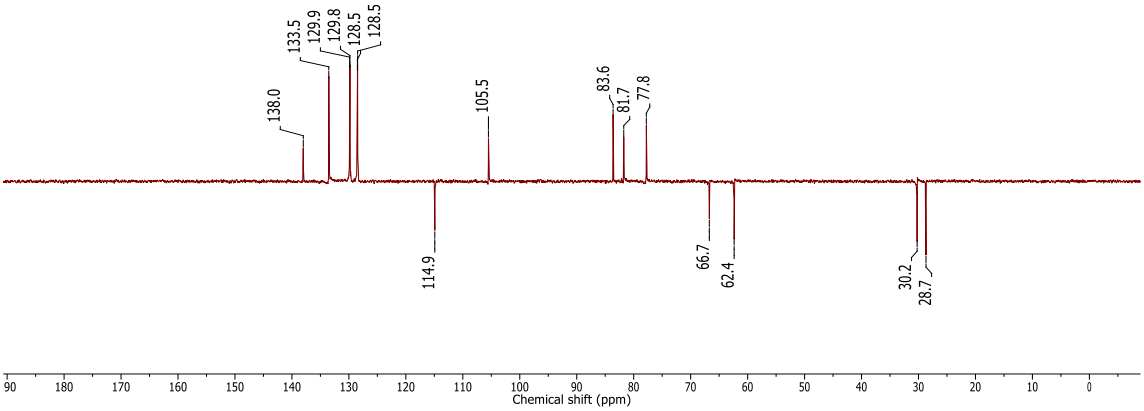
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **11c**



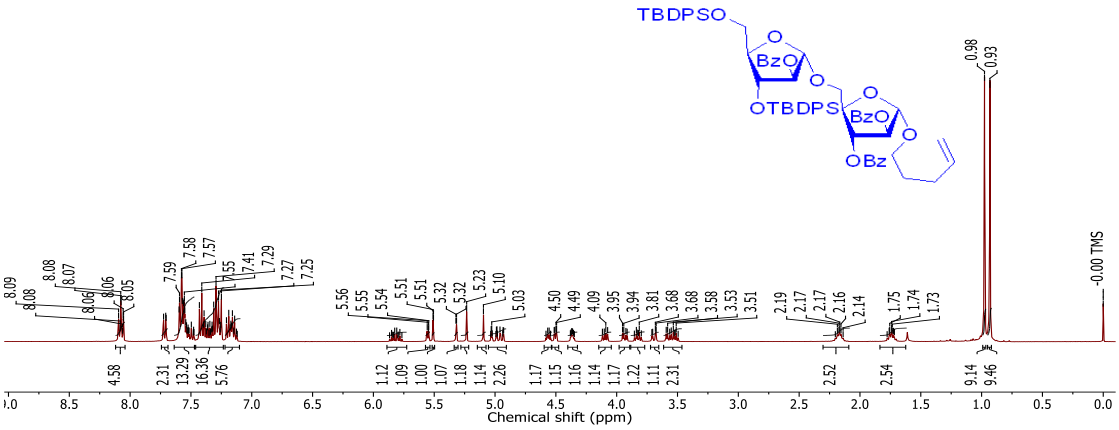
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **11c**



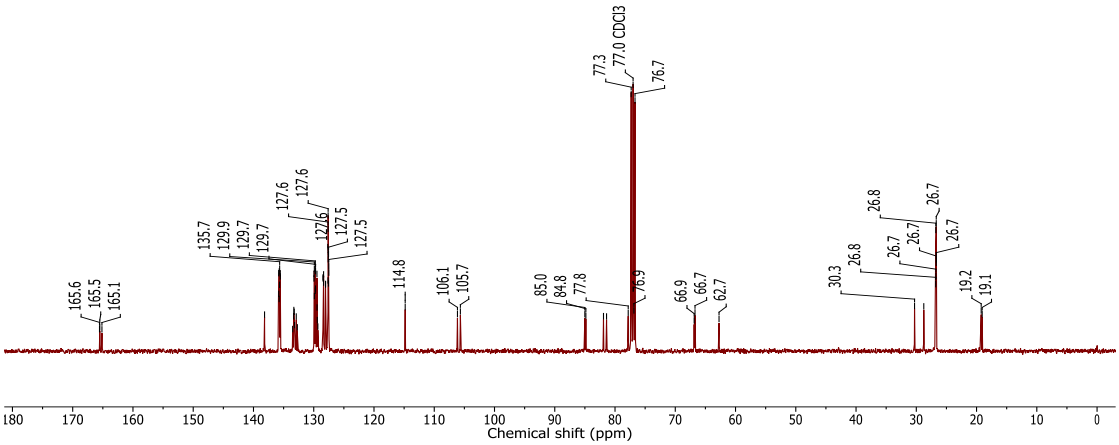
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **11c**



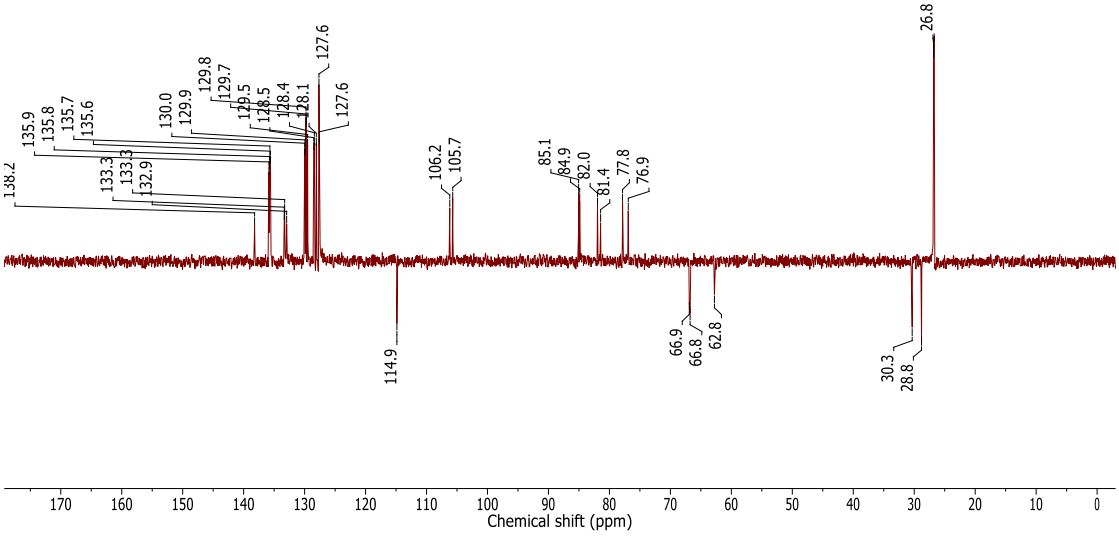
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **22e**



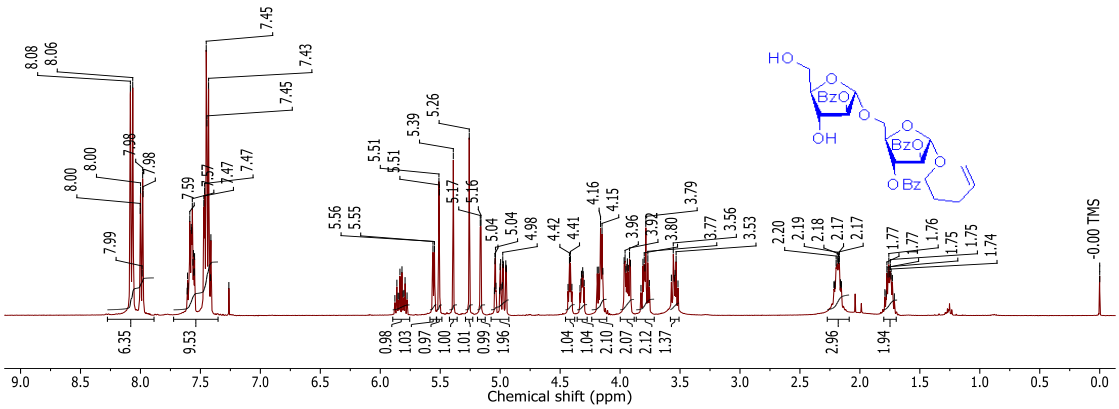
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **22e**



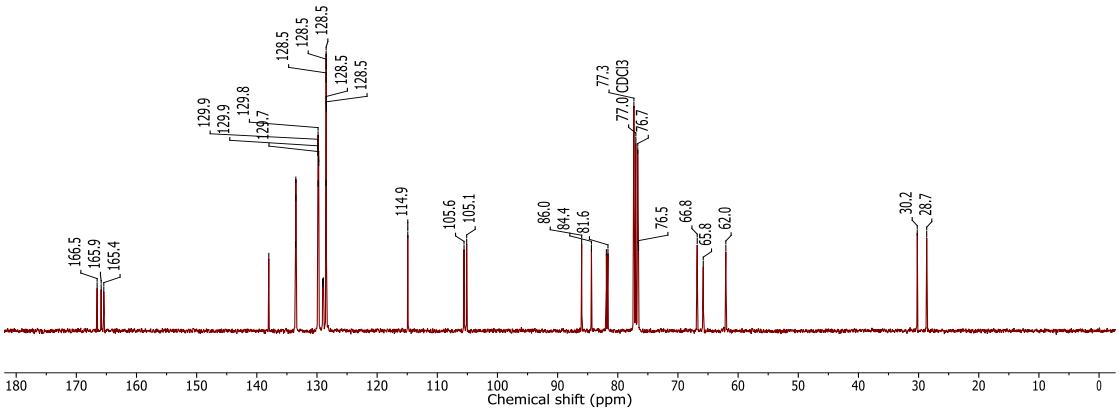
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **22e**



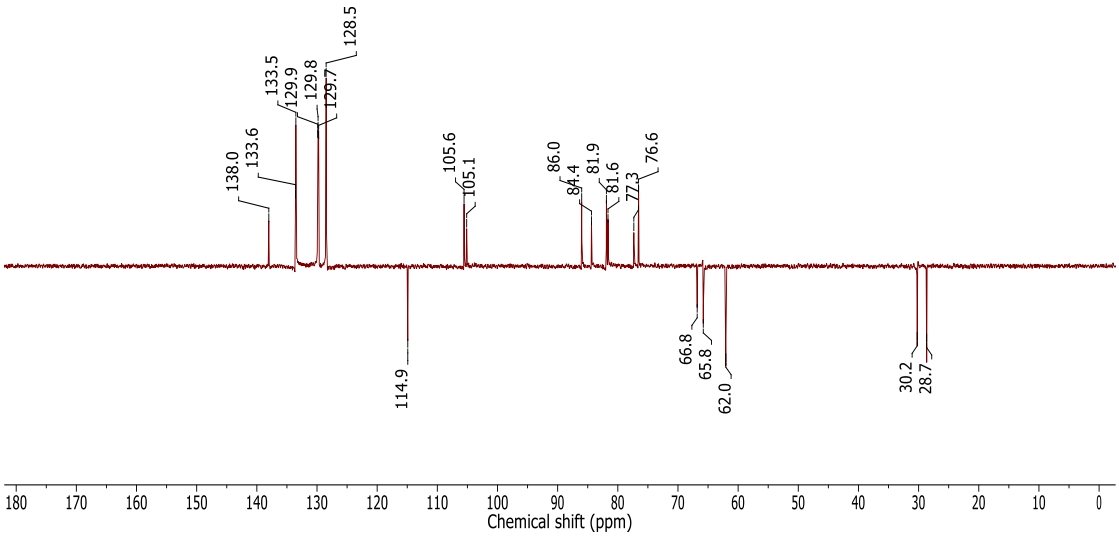
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **22f**



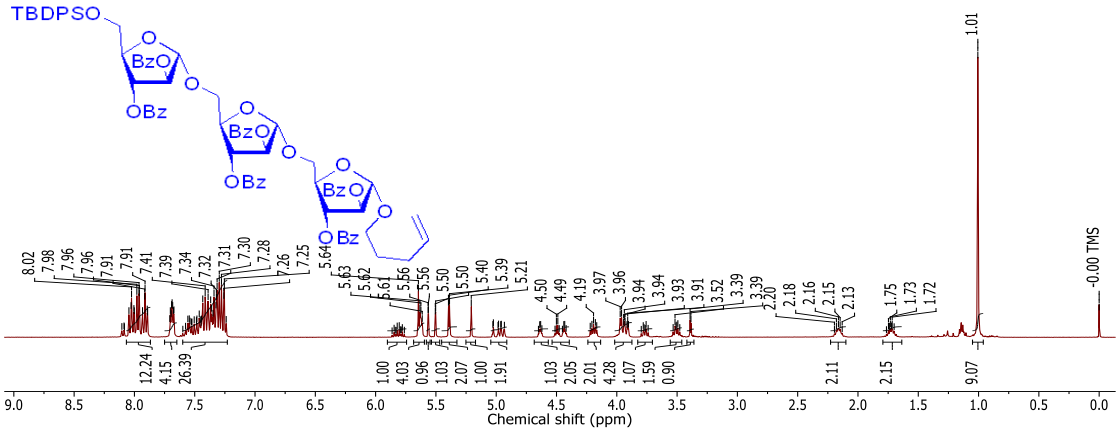
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **22f**



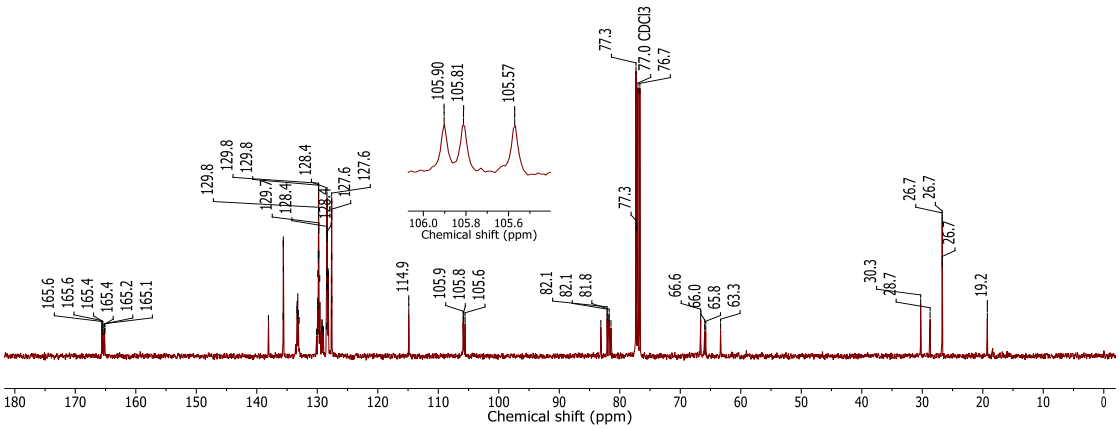
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **22f**



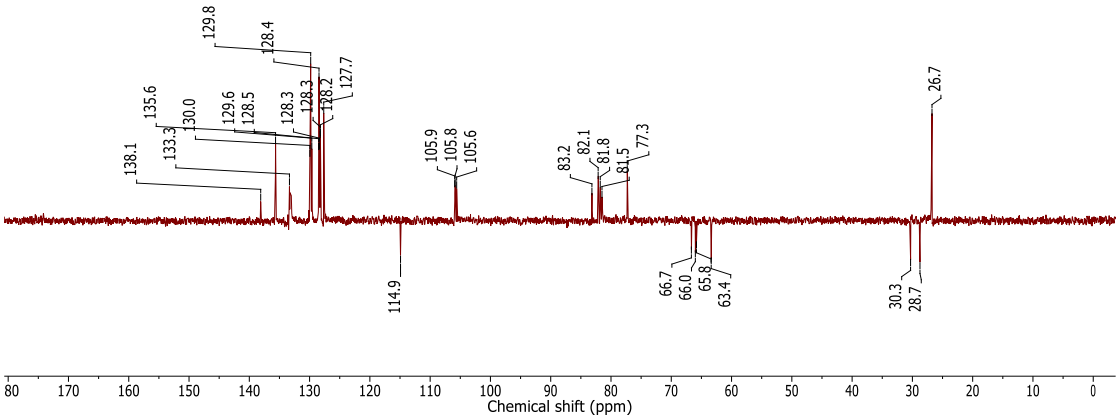
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **6b**



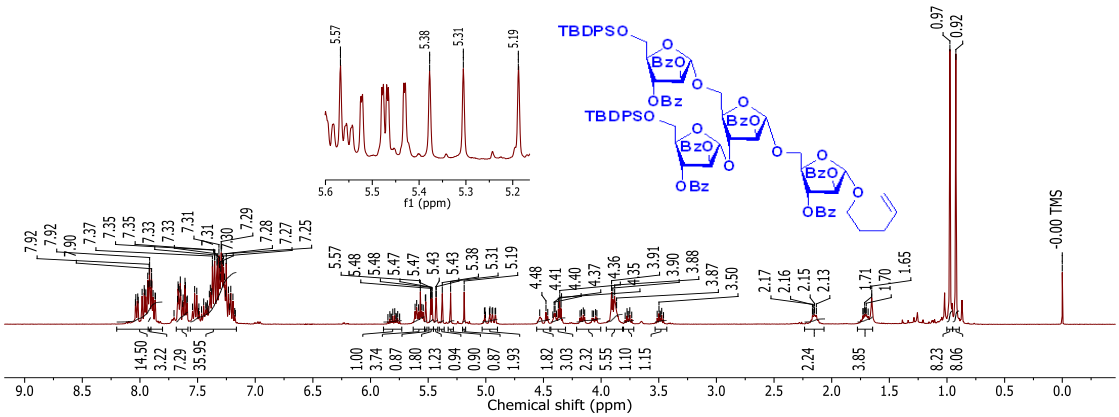
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **6b**



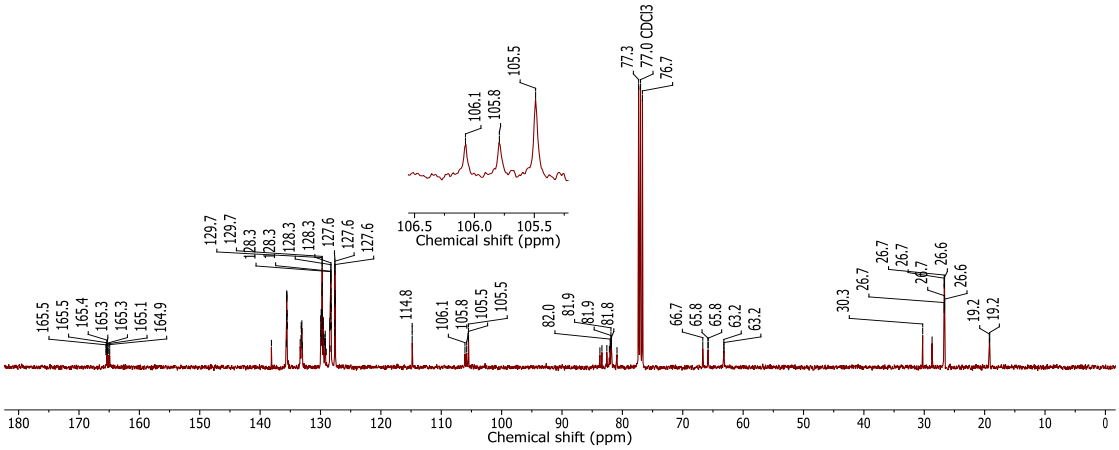
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **6b**



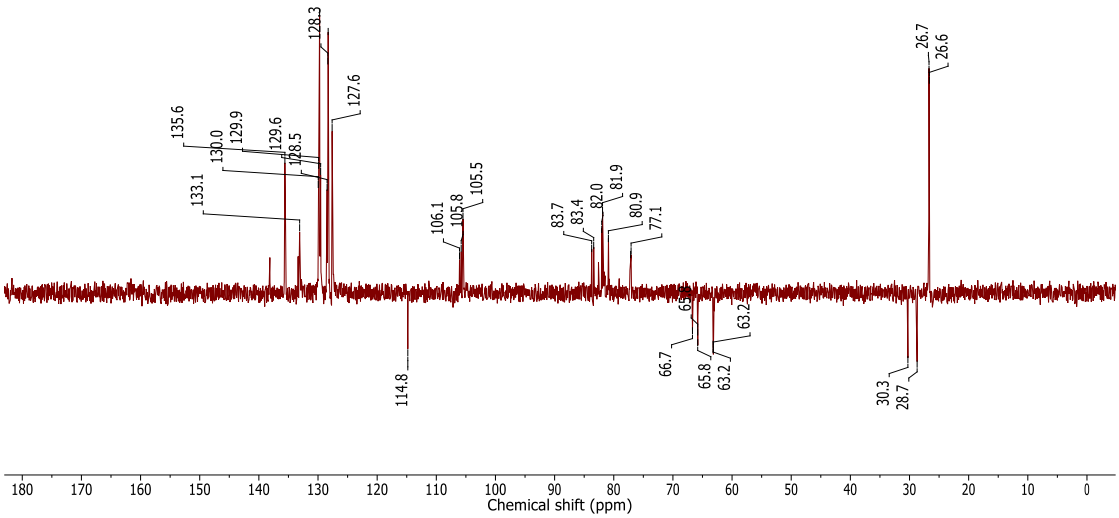
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **24c**



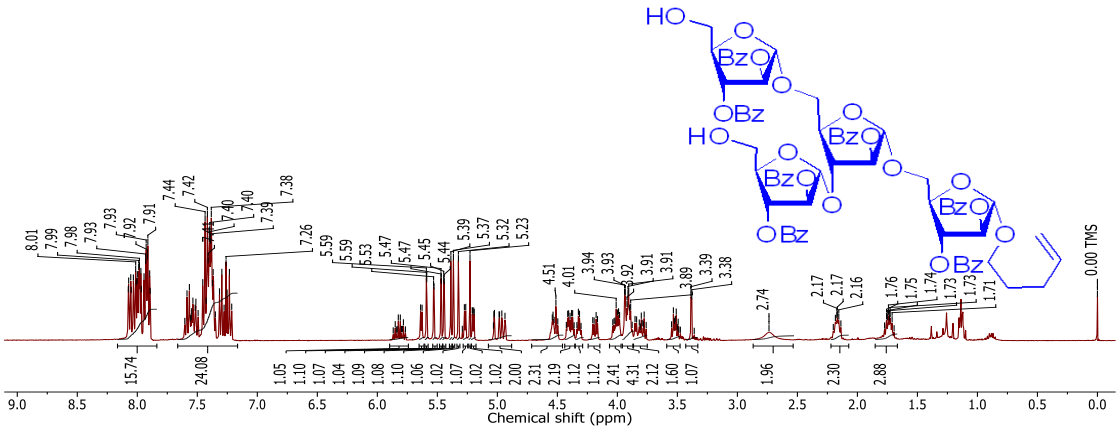
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **24c**



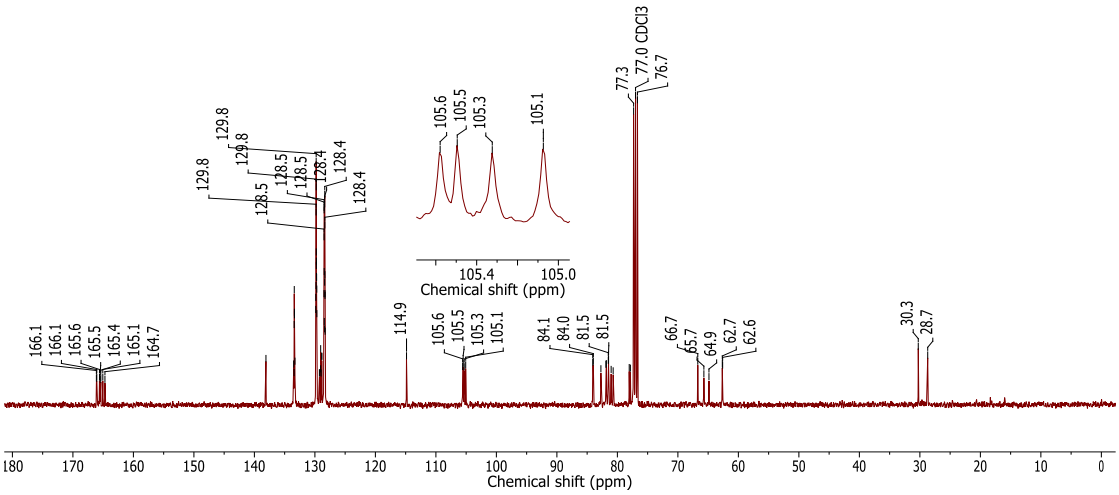
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **24c**



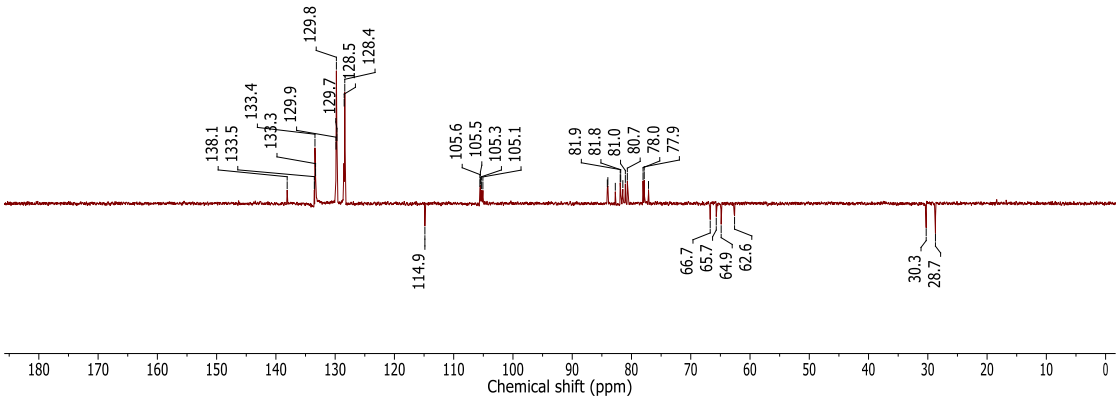
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound



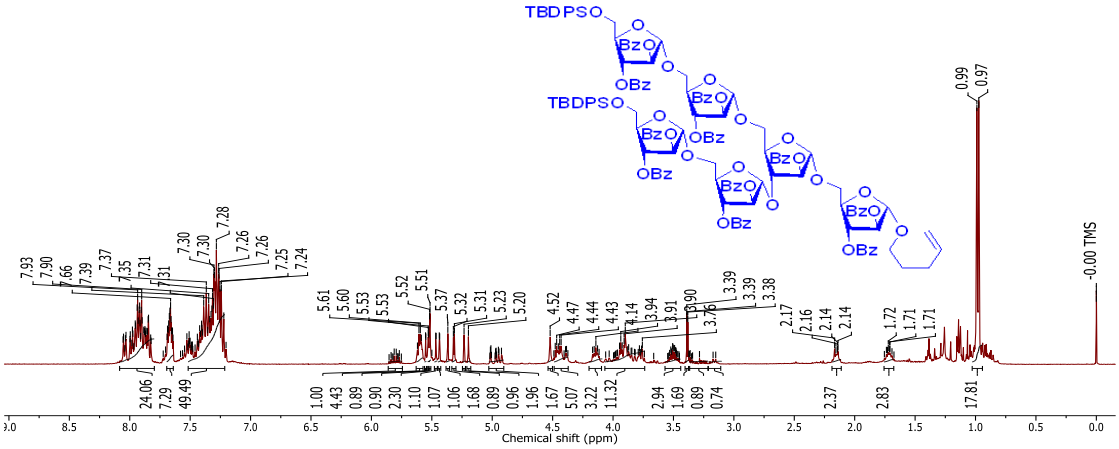
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound



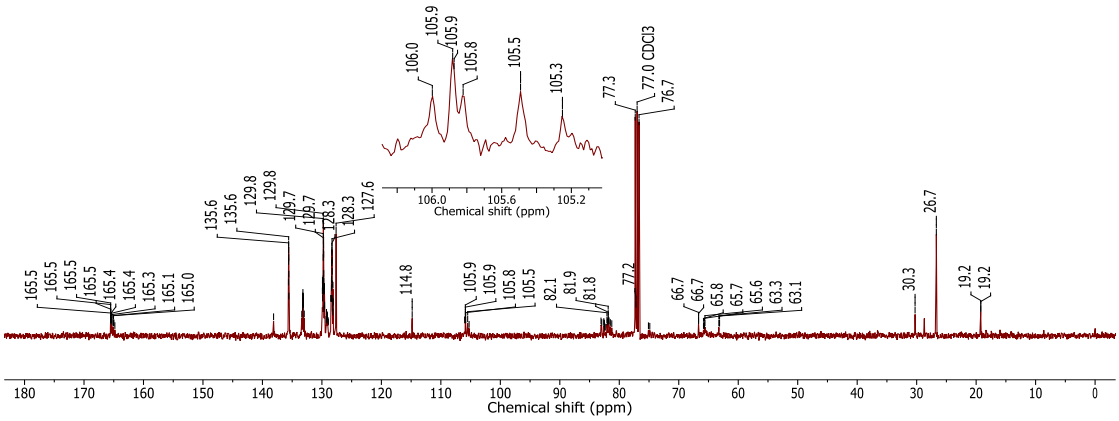
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound



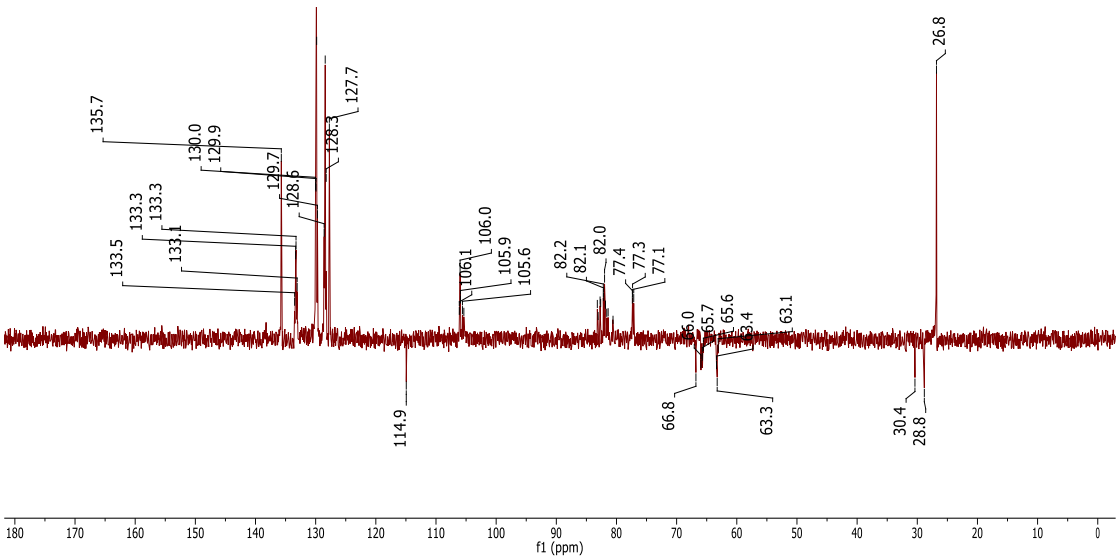
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **5b**



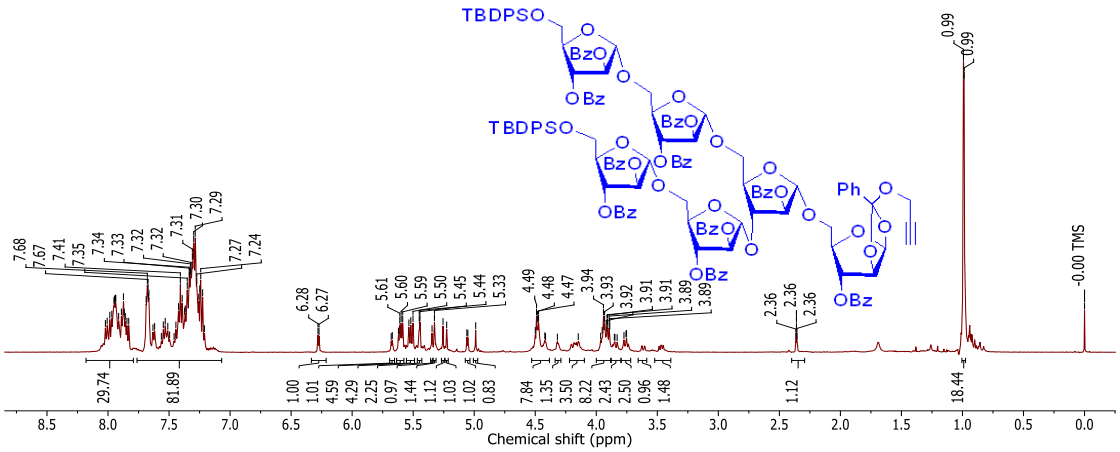
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **5b**



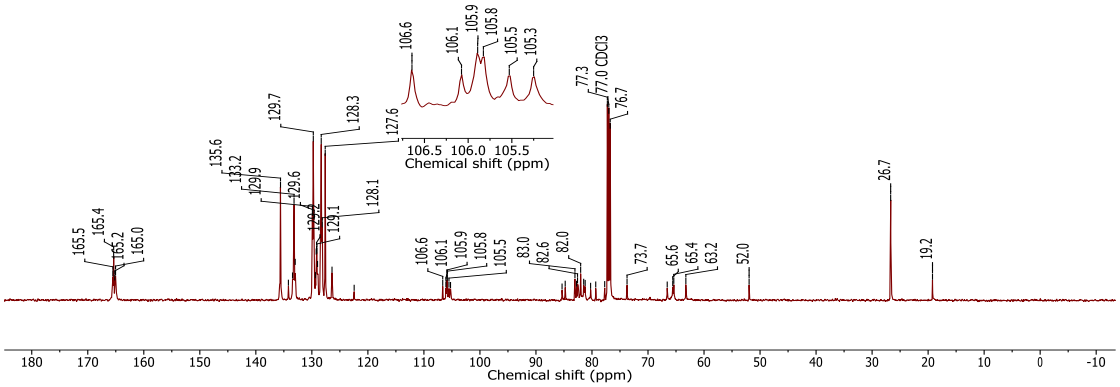
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **5b**



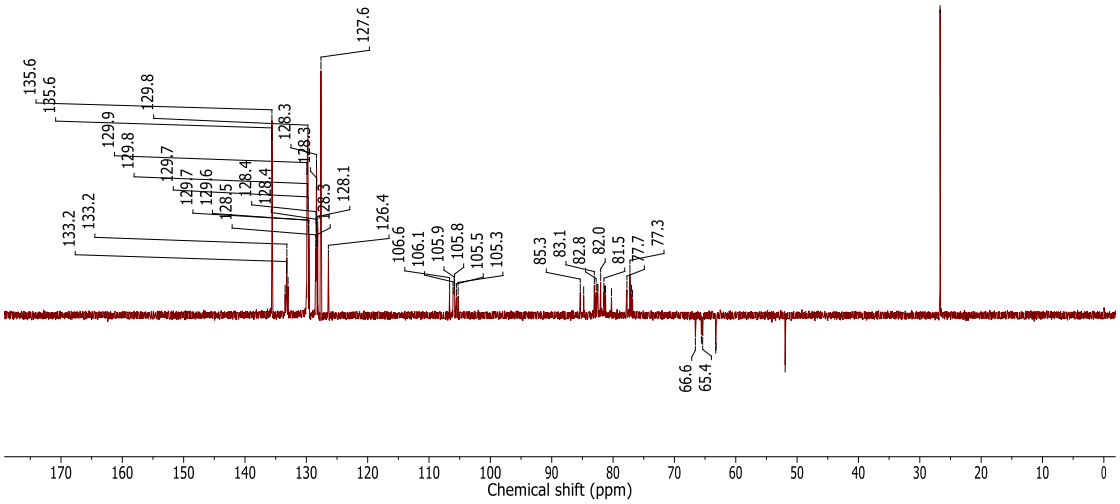
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **5a**



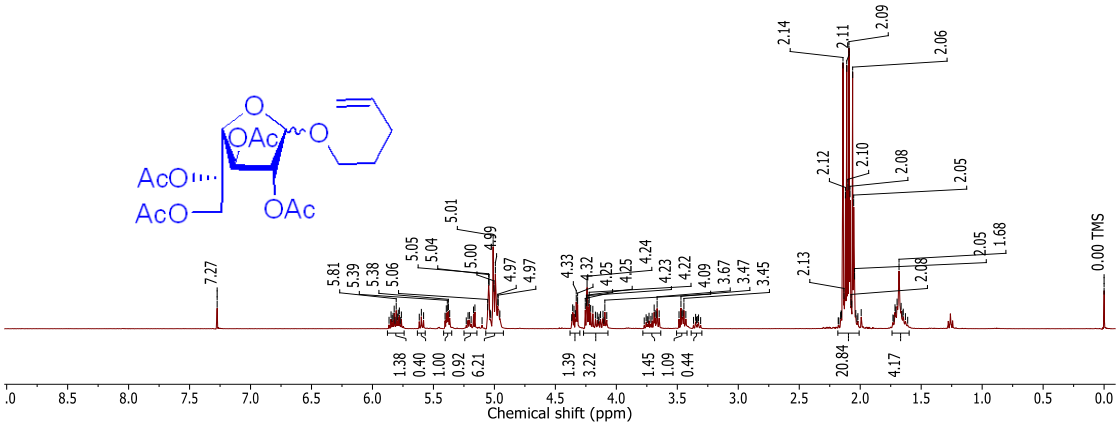
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **5a**



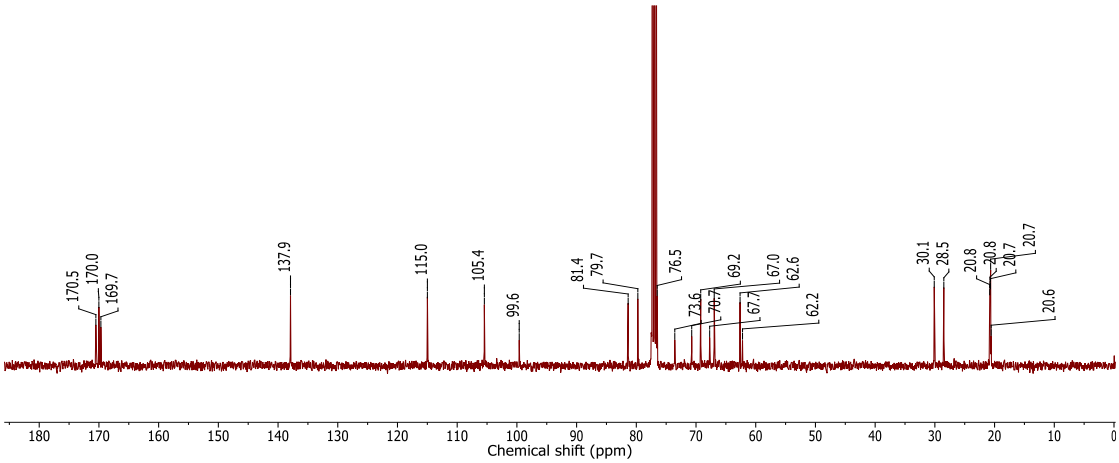
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **5a**



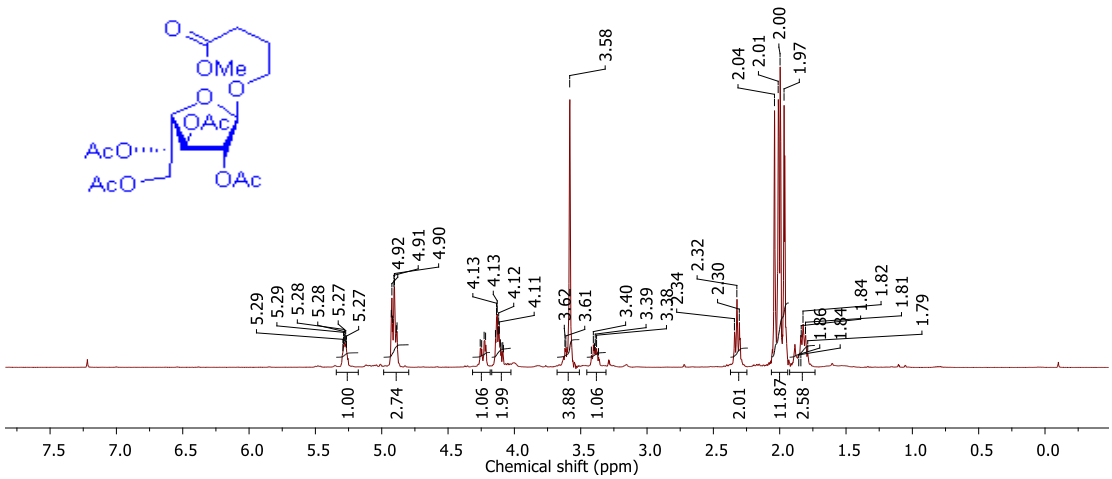
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **40**



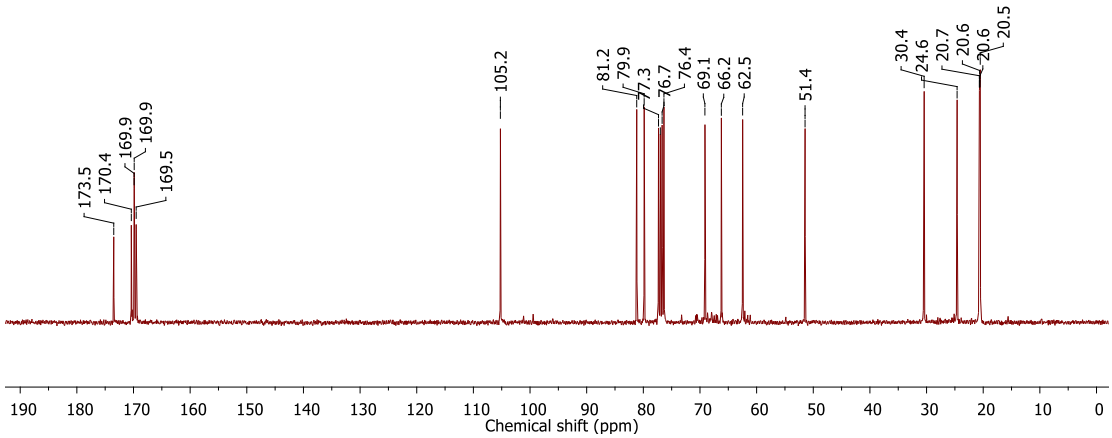
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **40**



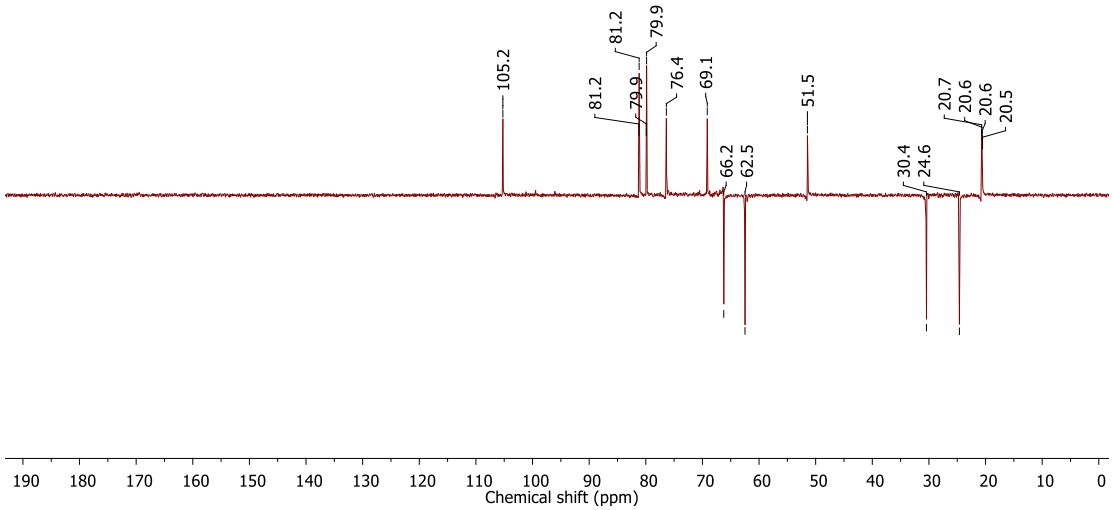
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **41**



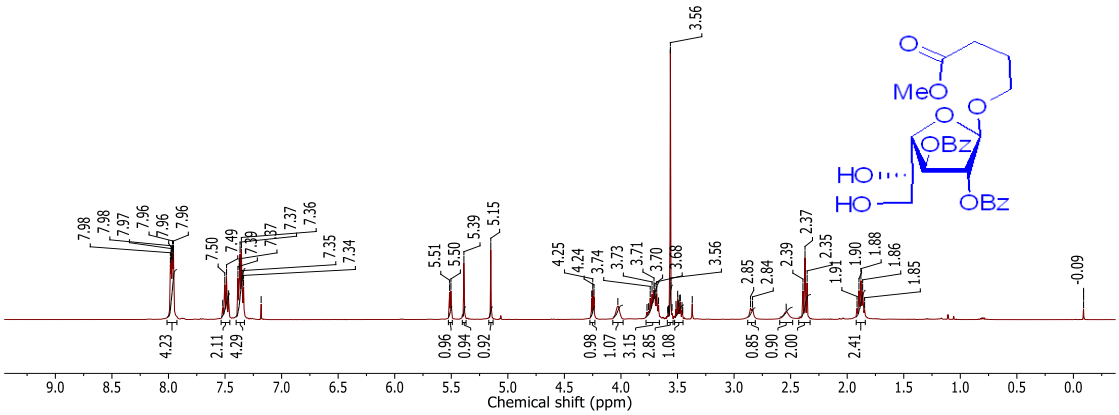
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **41**



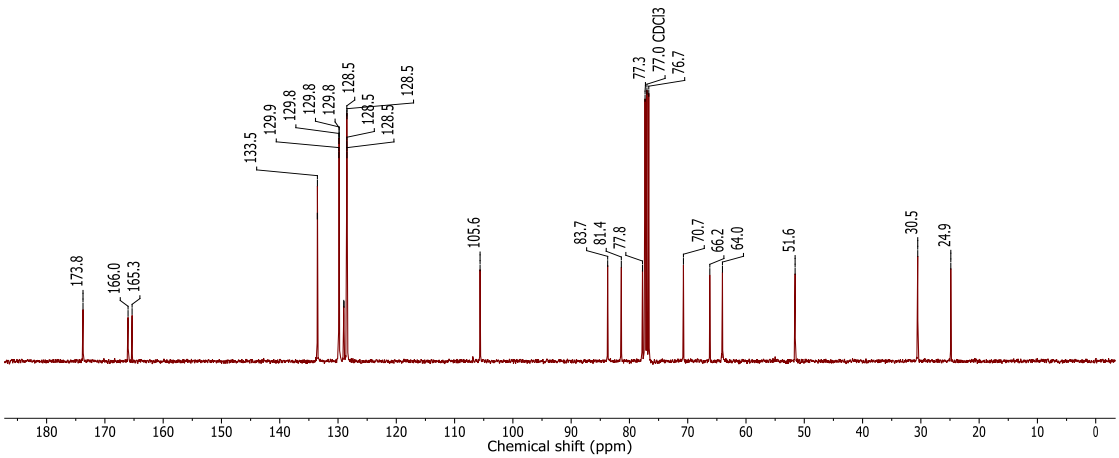
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **41**



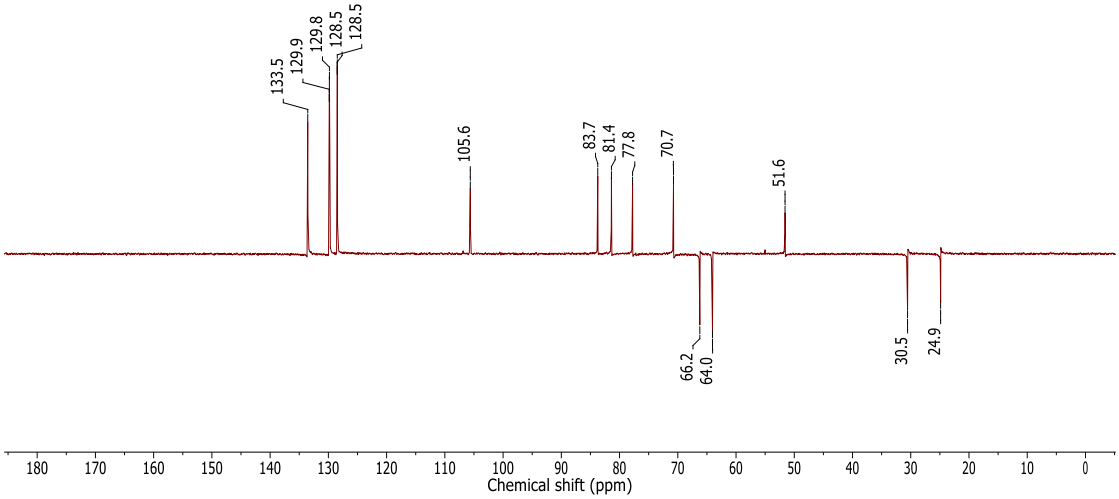
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **11d**



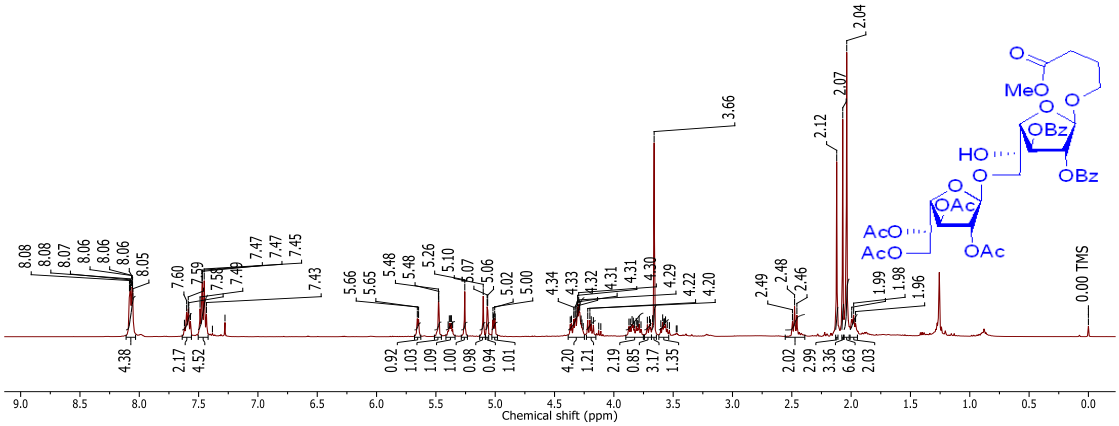
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **11d**



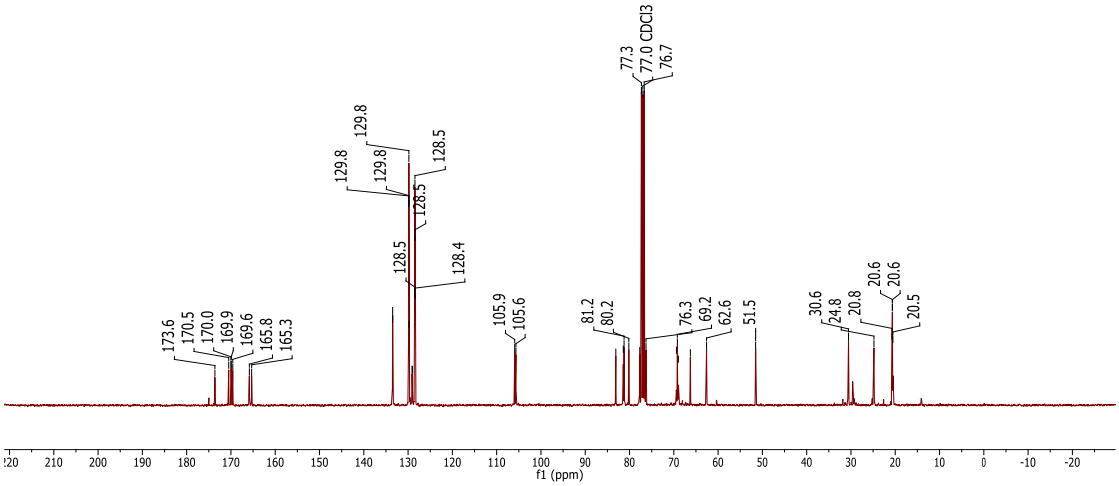
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **11d**



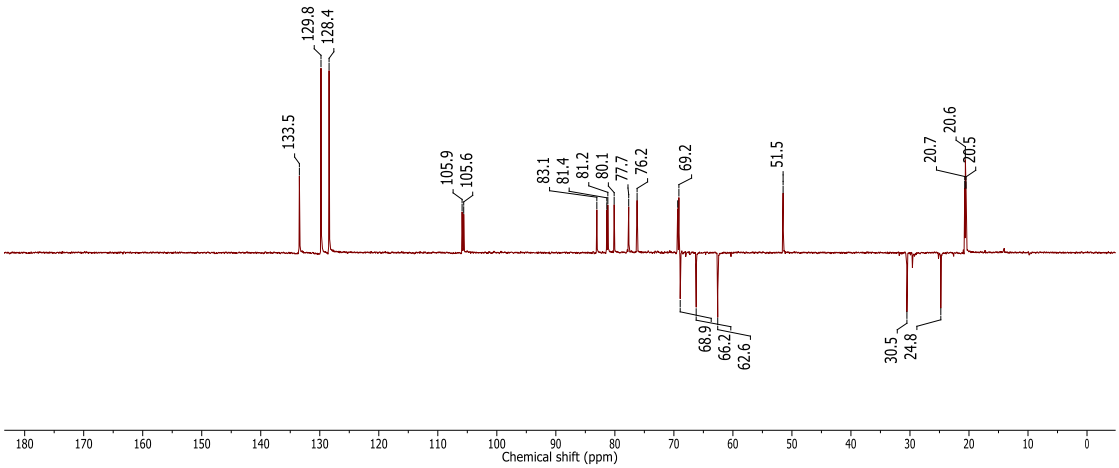
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **22g**



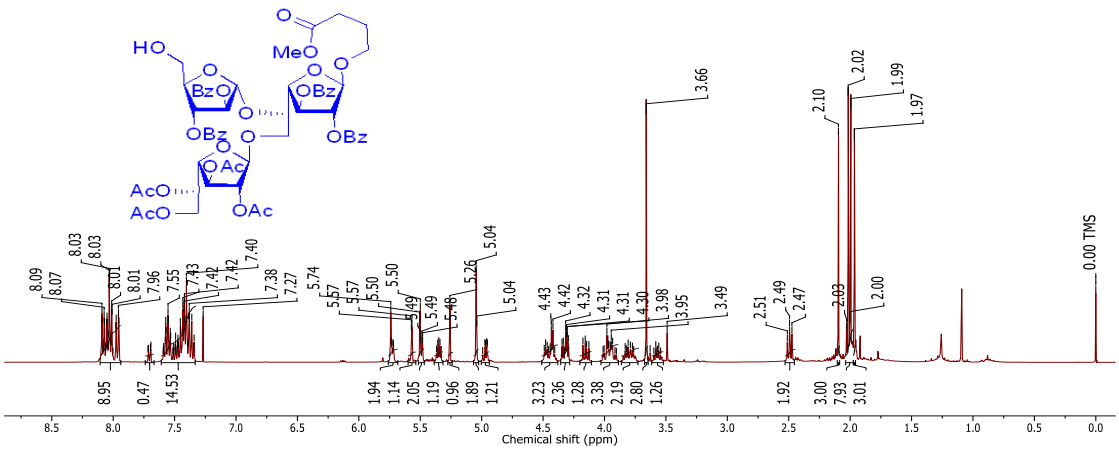
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **22g**



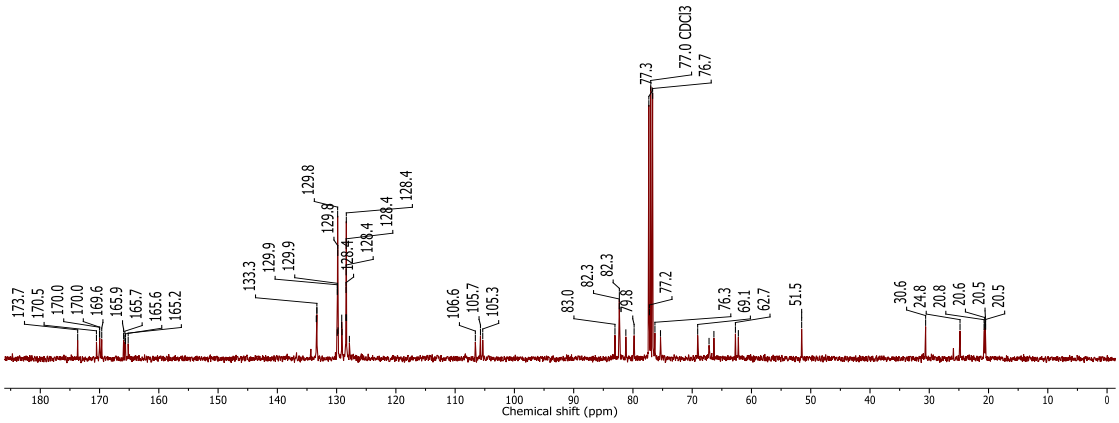
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **22g**



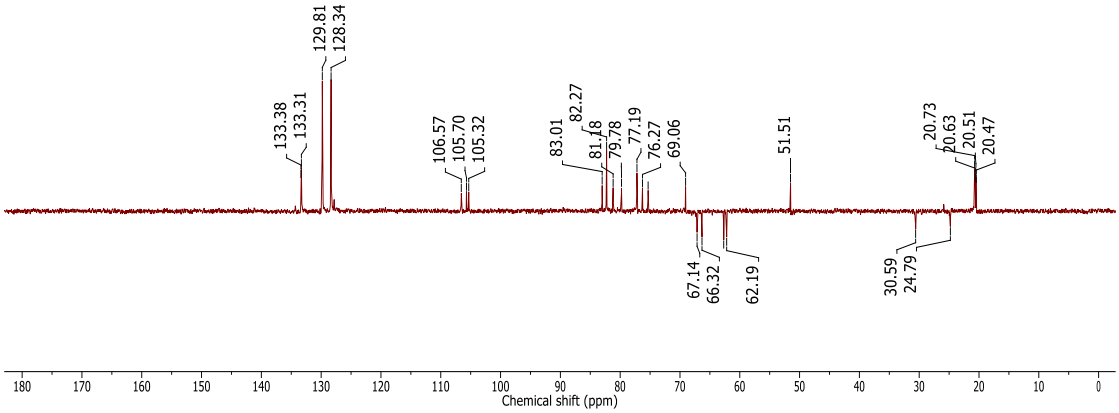
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **7a**



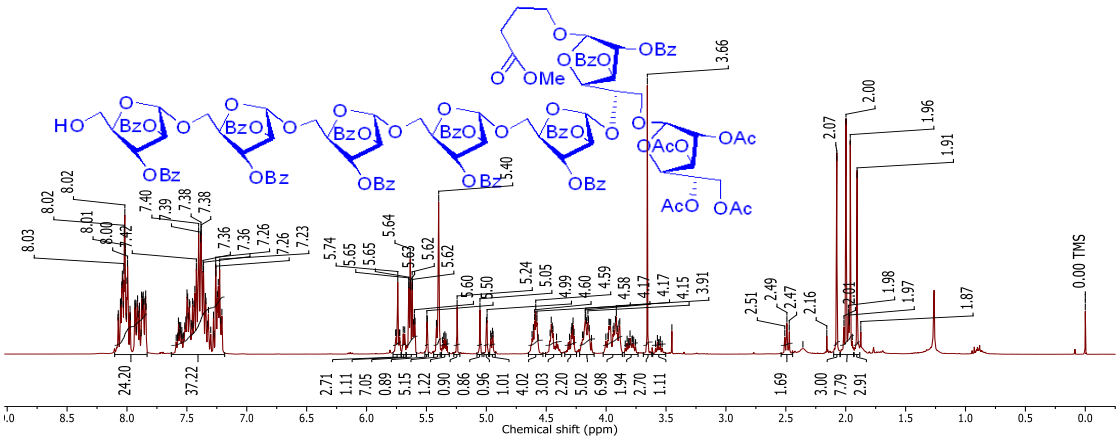
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **7a**



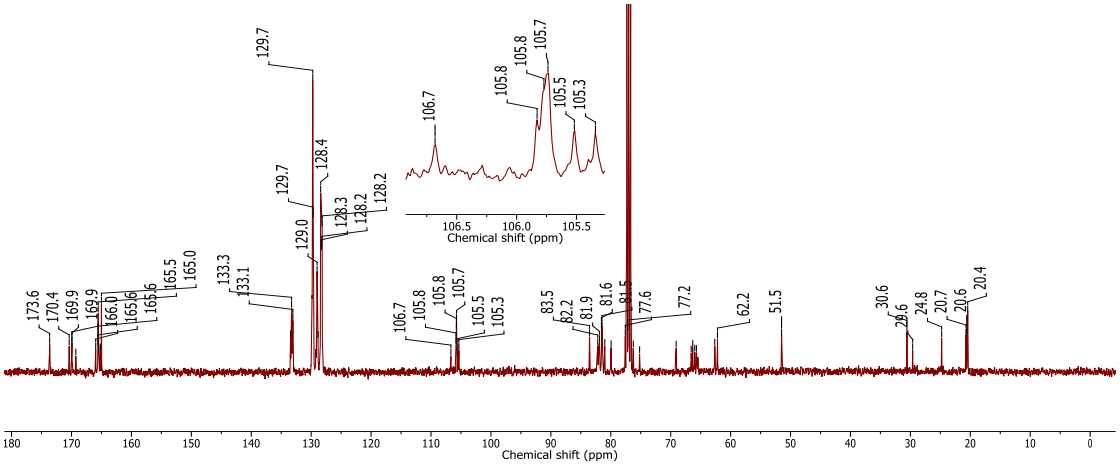
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **7a**



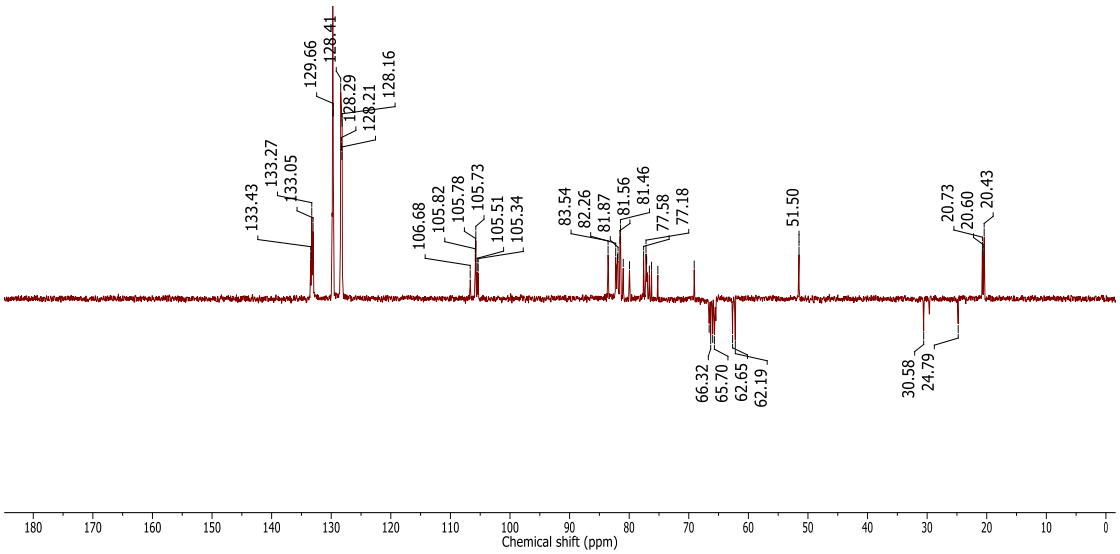
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **42b**



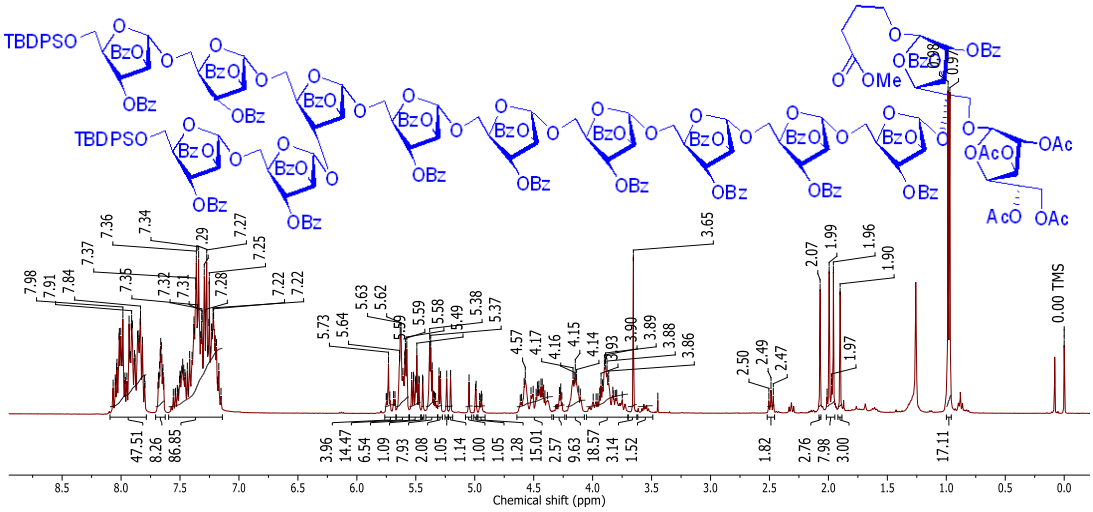
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **42b**



DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **42b**



^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **43a**



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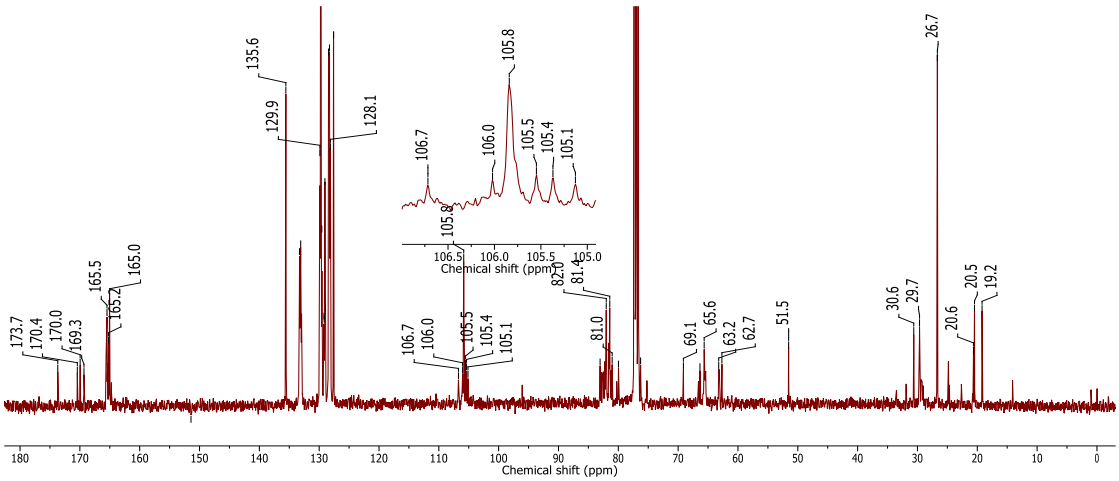
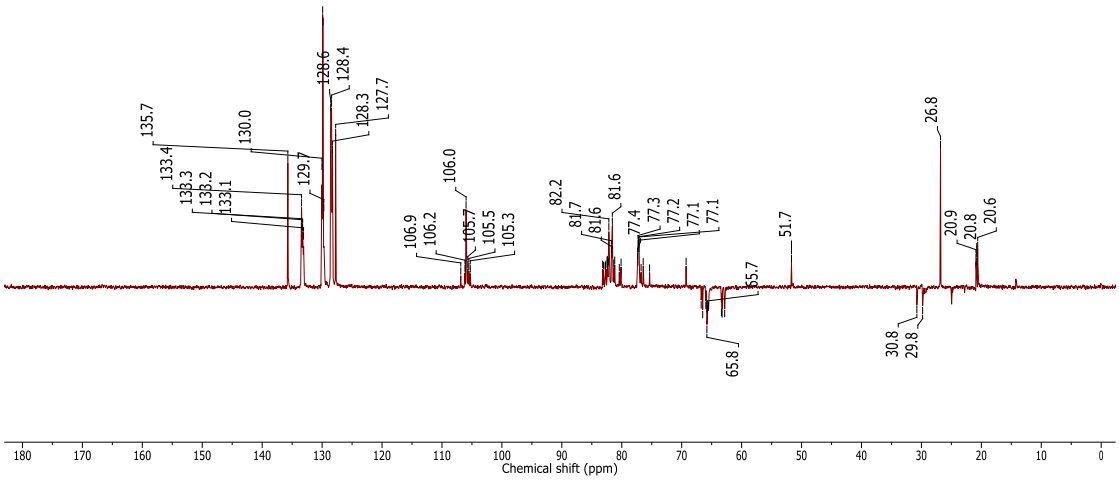
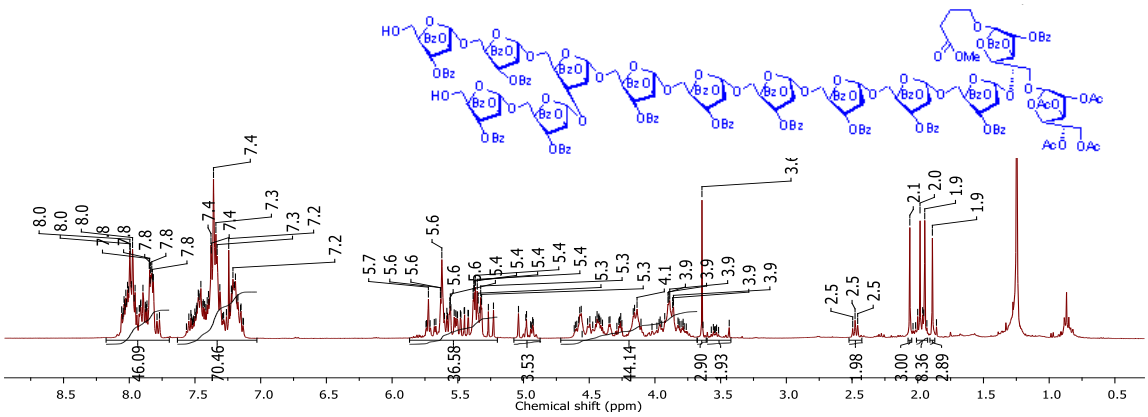


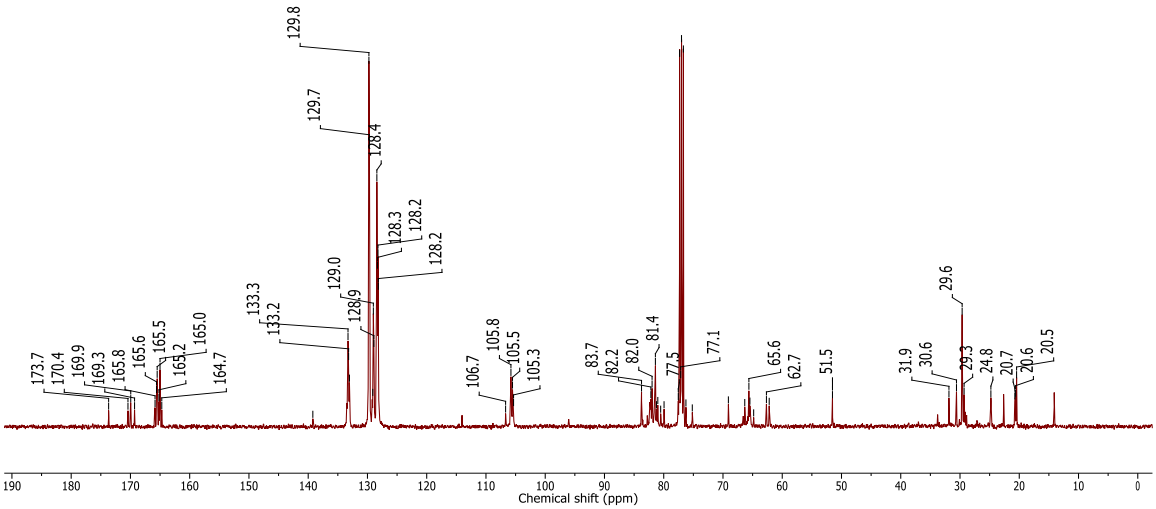
DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **43a**



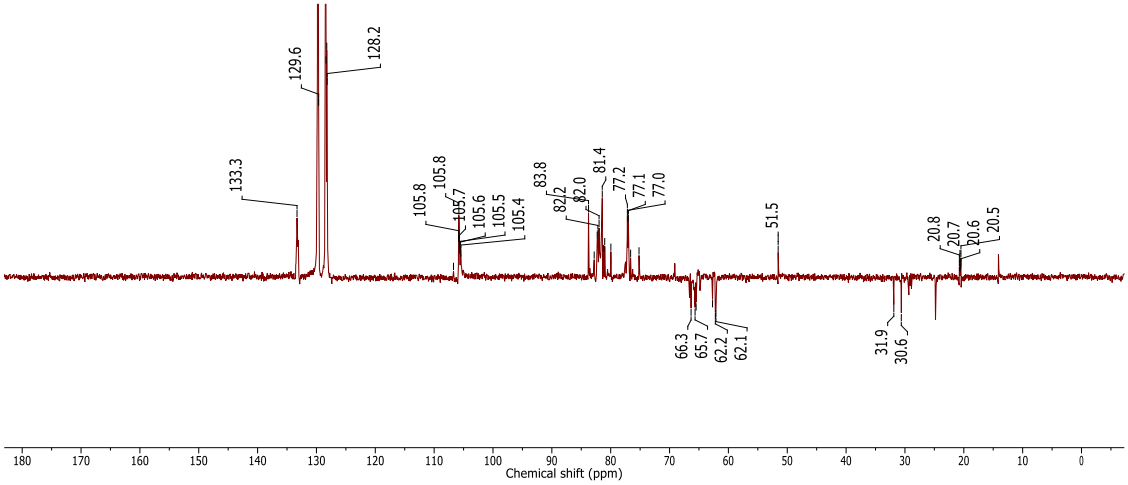
^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **43a**



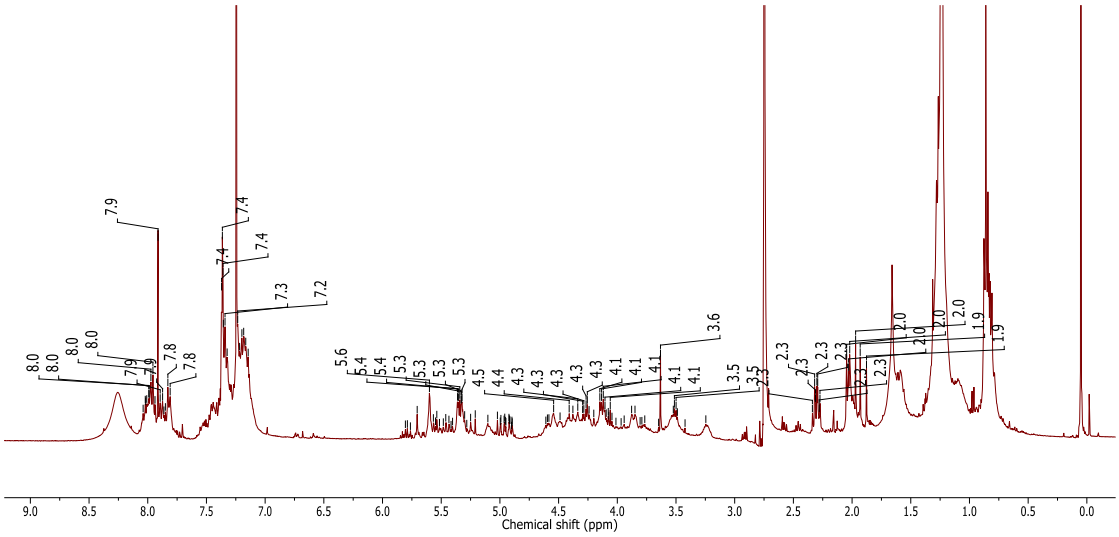
^{13}C NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **43a**



DEPT NMR Spectrum (100.53 MHz, $CDCl_3$) of Compound **43a**



^{1}H NMR Spectrum (399.78 MHz, $CDCl_3$) of Compound **44**



Details of experimental procedures, characterization data and spectral charts for some of the compounds in this endeavour are also given in the supporting information of *Organic Letters*, **2013**, *15*, 2466-2469.

2.7– References

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Publications

1. Orthogonal Activation of Propargyl and *n*-Pentenyl Glycosides and 1, 2-Orthoesters. Srinivasa Rao Vidadala, **Shivaji A. Thadke** and Srinivas Hotha. *J. Org. Chem.,* **2009,** *74,* 9233-9236.

2. Gold catalyzed Glycosidations: Synthesis of 1,6-Anhydro Saccharides. **Shivaji A. Thadke** and Srinivas Hotha. *Tetrahedron. Lett.,* **2010**, *51,* 5912–5914.

3. Gold Catalyzed Glycosidations for the Synthesis of Sugar Acrylate/Acrylamide Hybrids and Their Utility. **Shivaji A. Thadke**, Mritunjoy Kar, Sayam Sen Gupta, and Srinivas Hotha. *Carbohydr. Res.,* **2011**, *346,* 1511–1518.

4. Synthesis of Thioglycosides from Propargyl Glycosides Exploiting Alkynophilic Gold Catalyst. Srinivasa Rao Vidadala, **Shivaji A. Thadke**, Srinivas Hotha, and Sudhir Kashyap. *J. Carbohydr. Chem.,* **2012***, 31,* 241–251.

5. Facile synthesis of β- and α- Arabinofuranosides and Application to Cell Wall Motifs of *M. tuberculosis*. **Shivaji A. Thadke**, Biojoynanda Mishra, and Srinivas Hotha. *Org. Lett.*, **2013**, *15* (10), 2466–2469.

6. Efficient synthesis of aminooxy glycosides by gold catalysis. **Shivaji A. Thadke** and Srinivas Hotha.

7. Gold(III) catalysed glycosidations for α- and β- furanosides. **Shivaji A. Thadke**, Bijoyananda Mishra, and Srinivas Hotha.

8. Conversion of pent-4-enyl glycosides to glycosyl 1,2-*O*-orthoester and synthesis of mycobacterial arabinan. **Shivaji A. Thadke** and Srinivas Hotha.

9. Single donor chemistry for mycobacterial arabinogalactan. **Shivaji A. Thadke**, Biojoynanda Mishra, B. V. Rao, Maidul Islam, and Srinivas Hotha.

10. Aldol Reaction Catalyzed by Site Isolated Proline Anchored on MCM-41. Bharmana Malvi, **Shivaji A. Thadke**, Rajeesh P., Srinivas Hotha, Sayam Sen Gupta.