Synthesis of Oligomannuronates

A THESIS

SUBMITTED IN PARTIAL FULFIL THE REQUIREMENT OF

THE DEGREE OF

MASTER OF SCIENCE (MSc)

IN

CHEMISTRY

by

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Expert: Prof. S.G. Srivatsan

Dedicated to….
My Parents

Certificate

This is to certify that this dissertation entitled "**Scalable Synthesis of Oligomannuronates**" towards the partial fulfillment of the MSc degree program at the Indian Institute of Science Education and Research, Pune, represents study/work carried out by "Mayank Dahiya" under the supervision of "Prof. Srinivas Hotha, Department of Chemistry" during the academic year 2024-2026.

Date: 22 March 2026
Pune (MH), India

Srinivas Hotha

Declaration

I declare that this thesis submission reflects my original ideas, expressed in my own words. All external sources have been properly cited and referenced wherever other concepts or contributions are incorporated. I confirm my adherence to the highest standards of academic integrity and honesty, with no misrepresentation, fabrication, or falsification of any data, facts, ideas, or sources. I acknowledge that breaches of these principles could result in institutional disciplinary measures, including penalties for uncited seeds or materials lacking required permissions. I further declare that the content of this report, titled **"Scalable Synthesis of Oligomannuronates,"** is the result of my independent research conducted at the **Department of Chemistry, IISER Pune**, under the guidance of **Prof. Srinivas Hotha**. This work has not been presented for any other degree or qualification elsewhere.

Date: 6rd April 2026

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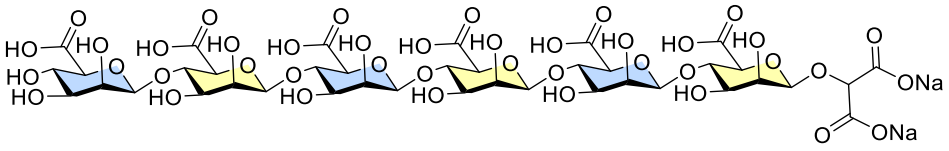
Contents

Abbreviations:

Å	Angstrom
Ac	Acetate
Ac_2O	Acetic anhydride
AcCl	Acetyl Chloride
AgOTf	Silver trifluoromethane sulphonate
$BF_3.OEt_2$	Boron trifluoride diethyl etherate
Bz	Benzoyl
Bn	Benzyl
$CDCl_3$	Chloroform-D
$CHCl_3$	Chloroform
D_20	Deutirium Oxide
DIC	*N,N'*-Diisopropylcarbodiimide
DMAP	*N,N'*-Dimethylaminopyridine
DMF	*N,N'*- Dimethylformamide
eq	equivalents
g	Gram
h	Hour
Hz	Hertz
Lev	Levulionate
MALDI-TOF	Matrix-Assisted Laser Desorption/Ionization-Time of Flight
MHz	Megahertz
mmol	Millimolar
rt	Room Temperature
TBAI	Tetra *n*-Butyl Ammonium Iodide
TBDPSCl	t-Butyldiphenylsilyl chloride

ABSTRACT

Alzheimer's is a devastating neurodegenerative disorder with limited effective treatment options. Sodium oligomannates are emerging as promising agents for targeting amyloid-beta and tau interactions in Alzheimer's therapy. As part of our continued interest in the synthesis of oligosaccharides of therapeutic significance, we chose to develop a streamlined, scalable synthesis of oliomannuronates by employing the Crich method for the *β*-mannosylation and, subsequently, in situ-generated RuO4-mediated reductive opening of the benzylidenes, and apart from this route, we have also tried different routes to reach the oligosaccharide



Sodium Oligomannuronate

We believe that the strategy will accelerate the development of next-generation therapeutics by making structurally defined oligomannuronates, including full-length and truncated forms, widely accessible. The results of this Project shown in this thesis.

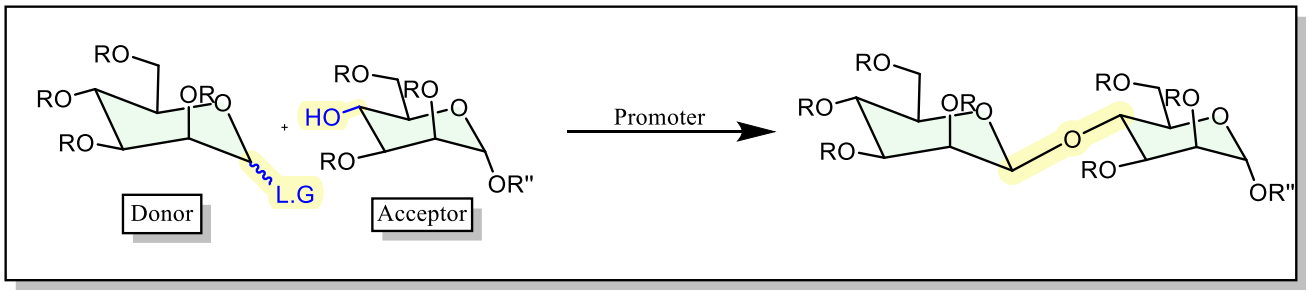
Introduction

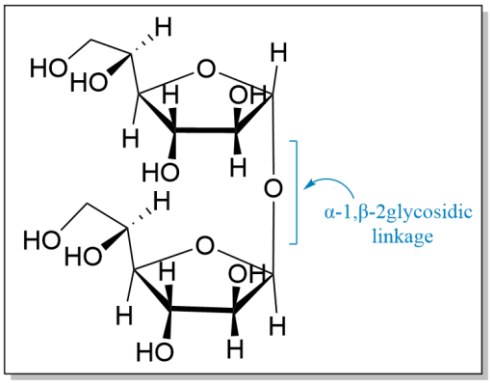
Carbohydrates are one of the most abundant and essential forms of biomolecules Present in nature. They play a crucial role in almost every living system by providing energy, forming structural components, and supporting numerous biological functions. From simple sugars that fuel our cells to complex polysaccharides that give strength to plants and animals, carbohydrates appear in many forms and perform diverse roles. They are also key players in processes like cell communication, growth, and immune responses. Due to their wide-ranging importance, carbohydrates remain a major focus of research in chemistry, biology, and medicine. Also, their chemical adaptability has made them key targets in understanding and treating complex diseases.

Glycosylation

Glycosylation is the main process that assembles carbohydrate monomer building blocks into oligo- and polysaccharides. These reactions pose challenges due to the multifunctionality of carbohydrates, and during the glycosylation process, hydroxyl groups on the sugar moiety that are not involved in glycosylation must be protected. Additionally, monosaccharide molecules.

Scheme-(1) Glycosylation Reaction



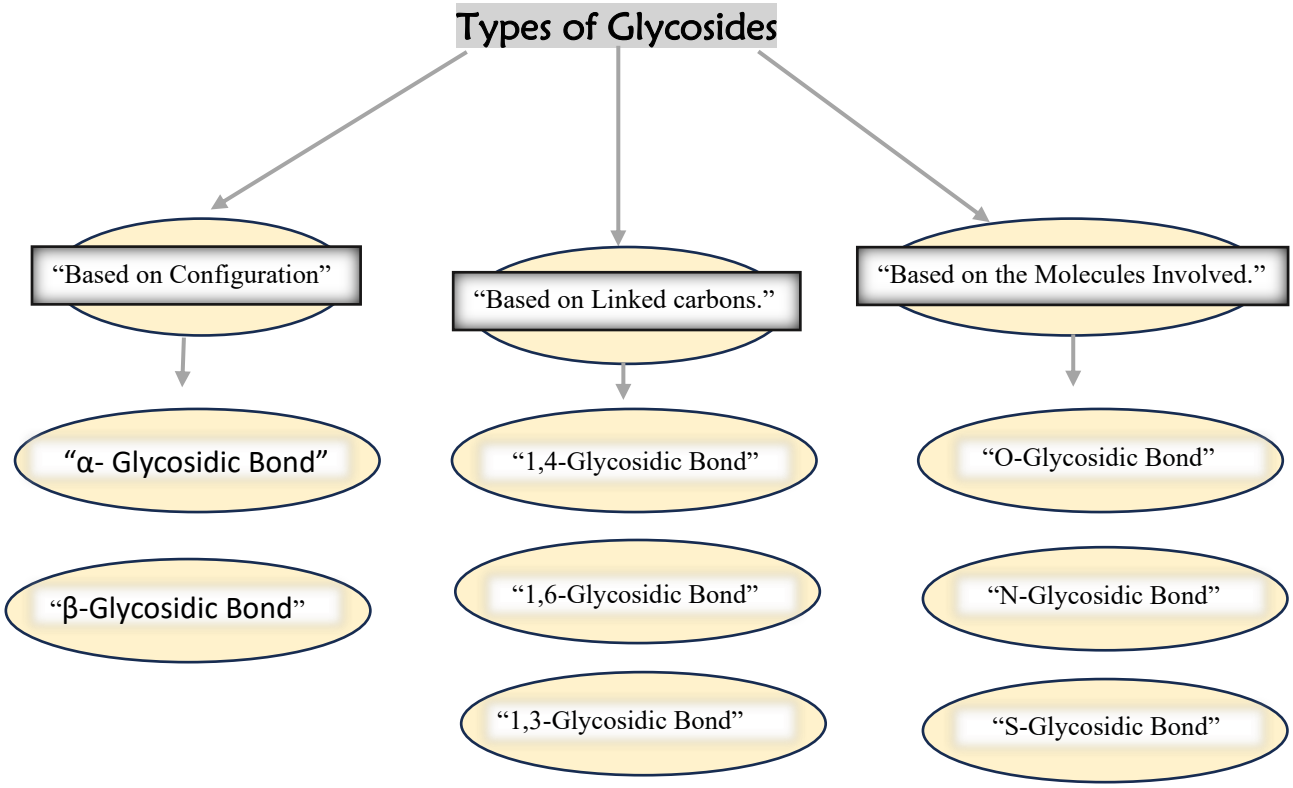


Glycosidic Bond:- A glycosidic bond is a covalent bond that connects a sugar molecule(or its derivative)to another molecule, which can be a sugar or a non sugar moeity such as alcohol or aglycone. This bond is formed between annomeric carbon of sugar and hydroxyl group(-OH)of the other molecule, typically through a condensation reaction that releases water.Glycosidic bonds are important for the formation of disaccharides,oligosaccharides and Polysaccharides. They also facilitate the attachment of sugars to protiens and lipids in glycoprotiens and glycolipids.

Fig-(1) Pictorial representation of a glycosidic bond

Formation of a glycosidic bond, known as glycosylation, is a crucial reaction in carbohydrate research. As shown in Scheme 1, glycosylation[2] involves the transformation of a hemiacetal (in which the leaving group, LG, is on the donor and the OH is on the acceptor), yielding an acetal. The strategic modification enhances the system's reactivity, significantly reducing reaction temperatures, and improves

selectivity. The compound that provides the anomeric carbon in the glycosidic linkage[3] is referred to as a glycosyl donor, and the other reaction partner that contributes an oxygen to the glycosidic linkage is termed a glycosyl acceptor, which can be a simple alcohol or another carbohydrate moiety with a free hydroxyl group. At the anomeric carbon, two stereoisomers known as anomers are formed during the glycosylation reaction, designated as α or β, which display a clear distereomeric relationship(1,2-cis or 1,2-trans). The "anomeric effect" dictates that an electronegative substituent attached to the anomeric carbon will favor an axial Position. Therefore, the α-isomer is formed as a thermodynamically favored product, and the β-isomer is formed as a kinetic product of D-sugars.



Also, carbohydrate synthesis plays[4] a crucial role in drug development, and the connection between carbohydrate chemistry and neurological disorders such as Alzheimer's disease[5] has gained increasing attention in recent years.

Alzheimer's Disease

Alzheimer's disease[6] is one of the most common neuroinflammatory diseases, as observed in people, affecting about 70% of all cases, which is a major health care challenge. Also, AD is detected by the extracellular deposition of misfolded and aggregated amyloid-β (Aβ)peptides, and also by the formation of intraneuronal neurofibrillary tangles made of (p-tau), as Alzheimer described histological

abnormalities in astroglia and microglia, and the recent studies have challenged and significantly changed this view, and immune-mediate disease mechanism have become a field of intense research and drug development in AD. So, for curing this disease, one must know or consider which immunological process and which time point should be tackled for therapeutic intervention, whereas immune modulation includes preventive, modifying-disease, or acute therapeutic strategies, and it is accepted that clinically silent or even inapparent disease stages may hold the greatest potential for such mediation. Studies show that, in humans, the inflammatory component in AD indicates that individual cellular compartments and specific immune mechanisms contribute to disease development. Whereas animal studies show that a specific pathology, for instance, tau deposition. Studies on brain pathology and microglial changes in AD state that the term 'plaques' was introduced in 1898. Alois Alzheimer described AD as the structure now known as Aβ plaques in the AD brain.

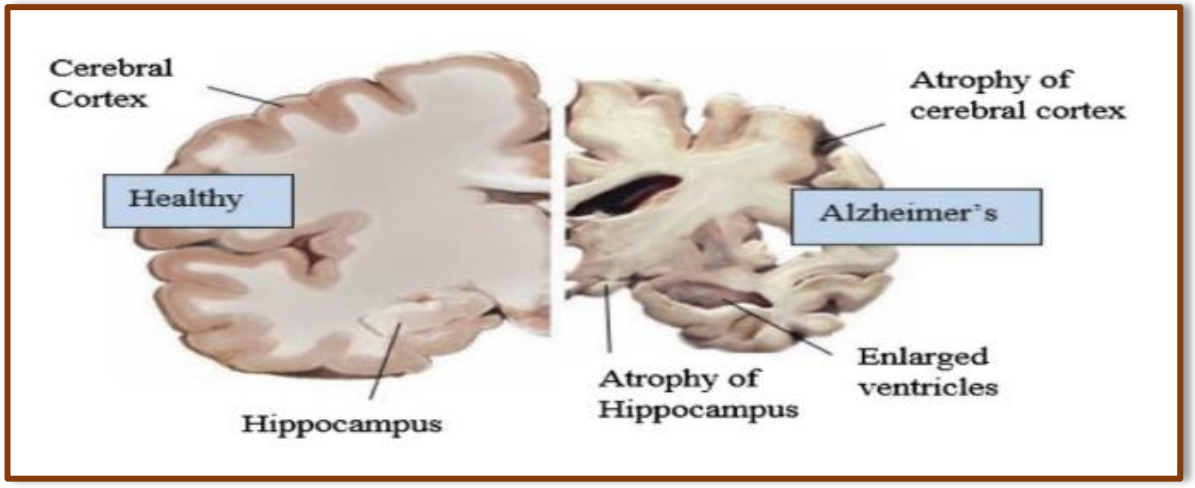


Fig- (2): Brain of a healthy patient versus that of an Alzheimer's patient[7]

Also, more recently, a novel mechanism involving the brain-gut axis has been proposed, and in the (Brain-Gut Axis), the Dysbiosis(imbalance) of the gut microbiota in people suffering from AD can lead to the Production of metabolites that drive peripheral immune cells to infiltrate the brain, causing neuroinflammation. Both N-linked glycosylation (N-glycosylation) and O-linked glycosylation (O-glycosylation) influence tau stability, Aβ processing, receptor signaling, synaptic integrity, and neuroinflammation. Dysregulated glycosylation patterns have been observed in the brains and cerebrospinal fluid of Alzheimer's patients, suggesting a potential, novel therapeutic target. Also, glycosyltransferases and glycosidases show altered expression in neurodegeneration, that linked to metabolic and inflammatory pathways.

Nowadays, people have a poor lifestyle and diet, which leads to several diseases and health-related issues, so a balanced diet with good nutrition and physical exercise confers beneficial effects on health and wellness in over 450million people worldwide, suffering from neurodegenerative disorders due to a poor lifestyle. Consuming non-digestible oligosaccharides (NDO_s)[8] from dietary sources can act as prebiotics,

supporting brain neuroprotection and other cognitive functions. Also, these NDO_s have a significant impact on oxidative stress by directly or indirectly neutralizing free radicals.

Treatments for Neurodegenerative Disorders

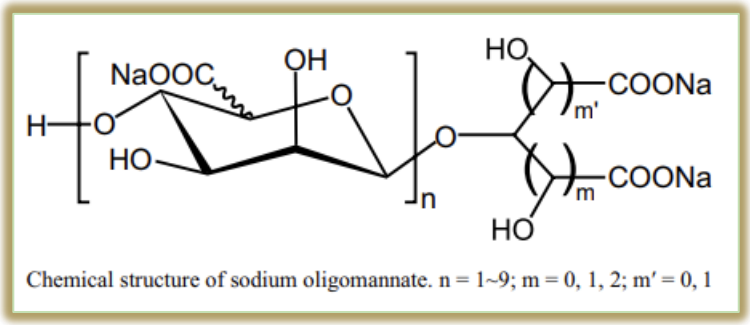
The neurodegenerative disorders, like Alzheimer's disease and Parkinson's disease, have different kinds of treatments; one is the **traditional symptomatic treatments** (which do not aim to stop the death of neurons, but are used for their chemical imbalances, causing memory loss and severe problems) and the other is **newer disease- modifying therapies** (they aim to change the biology of the disease)

Traditional Alzheimer's Treatments	New Standard Disease-Modifying Therapies.
Cholinesterase inhibitors (CHEIs)[1]: Donepezil, rivastigmine, and galantamine are recommended for daily function based on moderate evidence, as they inhibit the breakdown of acetylcholine, a neurotransmitter involved in learning and memory.	**Sodium oligomannate (GV-971)** is a marine-derived oligosaccharide that targets the gut axis and significantly improves cognition by reducing neuroinflammation and curing Alzheimer's patient.
NMDA Receptor Antagonists: Among all the possible targets involved in AD, acetylcholinesterase (AChE) and monoamine oxidase B (MAO-B) are well recognized because they control neurotransmitters responsible for memory Processes and regulate glutamate, which can overstimulate the brain cells.	**Lecanemab and Donanemab** are two new approved antiamyloid immunotherapies used to treat Alzheimer's disease and act as modifying agents: Lecanemab targets amyloid protofibrils, and Donanemab targets amyloid plaques.

"Sodium oligomannurunate (GV-971): A Novel Carbohydrate-Based Drug for Alzheimer's Therapy.":

- It is a marine algae-derived oral oligosaccharide developed by Shanghai Green Valley for the treatment of Alzheimer's disease (AD)[9]. As we know, in traditional medicine, drugs are only effective in the short term and do not reverse disease progression.

- It is a mixture of acidic linear oligosaccharides that is derived from marine brown algae. It is used to recondition the gut microbiota, thereby limiting its contribution to AD pathogenesis. It also penetrates the blood-brain barrier via transporters, including the glucose transporter, which binds to distinct regions of Aβ, thereby hindering Aβ fibril formation and destabilizing fibrils into non-toxic monomers.
- In its several trials on mice, it has been found that patients suffering from AD, so sodium oligomannate decreases cerebral glucose metabolic rate in various brain regions, and its treatment is related to an increase in $A\beta_{1\text{-}42}$ levels in the cerebrospinal fluid(CSF), which indicates the clearance of amyloid from the brain into CSF.
- Sodium oligomannate is formed via depolymerizing alginate, followed by oxidation to oligosaccharides. It has low oral bioavailability, and food does not significantly affect its absorption.



Chemical structure of sodium oligomannate. n = 1~9; m = 0, 1, 2; m′ = 0, 1

Fig- (3) Chemical structure of sodium oligomannate

- There are a few human trials still in progress, as the excretion route is not well established, and it has a half-life of only 10-20h.

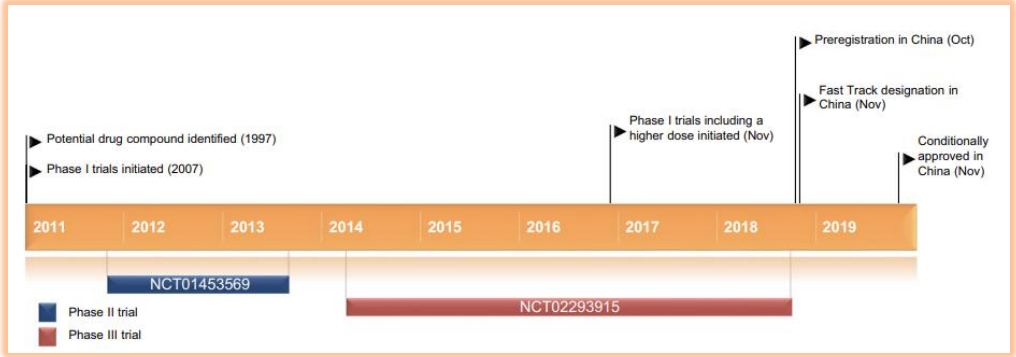


Fig 4: Depicting the development of sodium oligomannate and its trial

- Therefore, in conclusion, it suggests that it improves cognition in patients with mild to severe AD, exhibits a neuroprotective effect against Aβ toxicity in human neuroblastoma cells, and improves learning skills in mouse models of AD in several trials.

- In some trials, it is observed that it inhibits neuroinflammation by altering the different compositions of gut microbiota and controlling the amino acid metabolism, hence it disrupts the link between the brain and Th1 cells and changes in gut microbiota, leading to a decrease in neuroinflammation.

"Goal of the Project"

In this Project our goal is to establish synthesis of higher oligomannuronates following two methodologies David Crich's[10] method for *β*-mannosylation[11] and S Baskaran's procedure[12] to get a 3-in one approach apart from that we have tried several other methods to get the desired results. The scalable route is useful because the old, multi-step techniques can be eliminated.

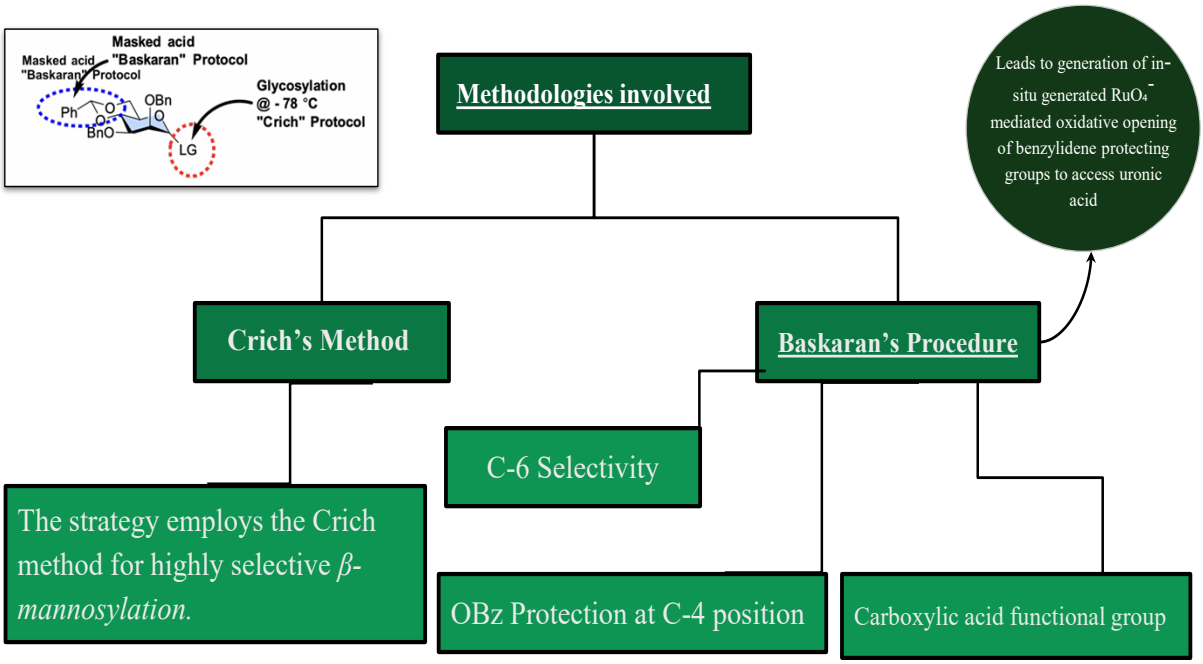
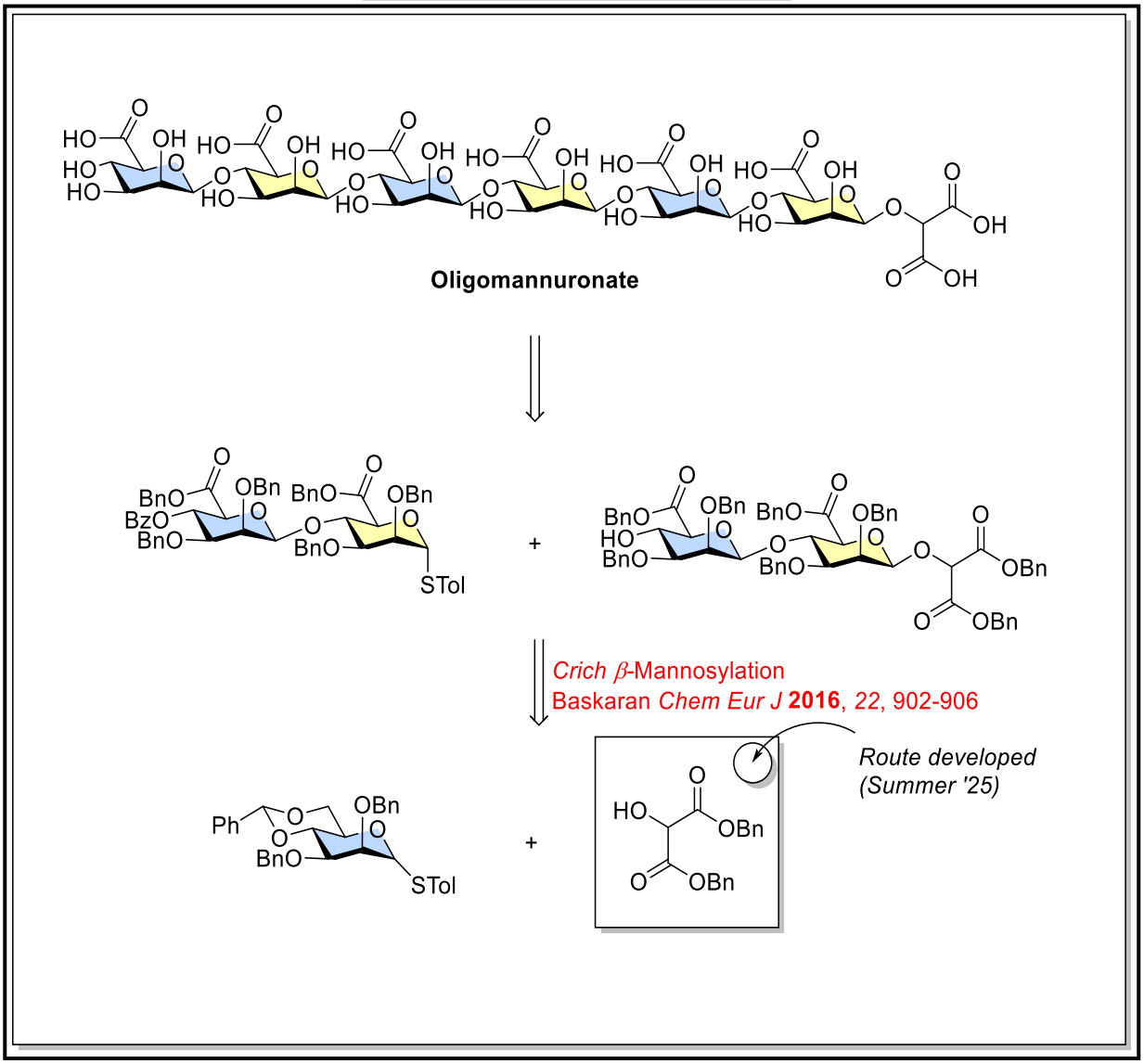
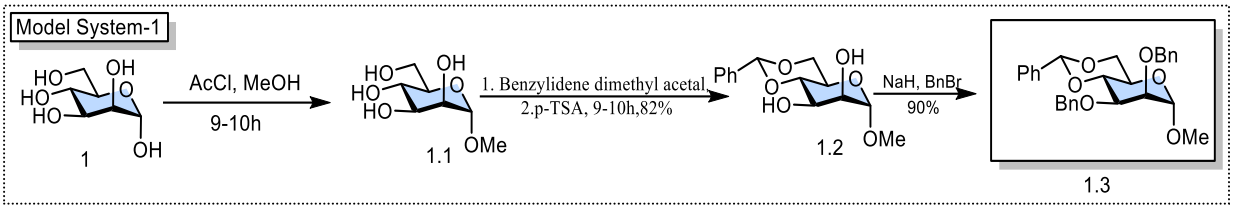


Fig. 5 Flow-chart of the methodologies involved

Retrosynthesis scheme



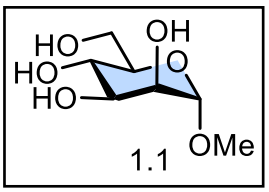
Results and Discussion:



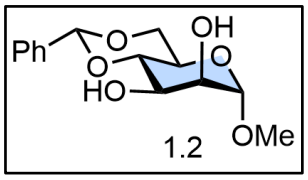
Scheme-2: Synthesis of Model System-1

Procedures:

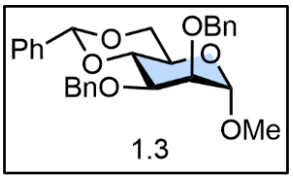
Synthesis of 1.1- For this, to get a methoxy group locked at the anomeric carbon (C-1) of D- mannose, firstly, we take a clean round-bottom flask and then add 10g(55.51mmol) of D-mannose into it, then dissolve it in methanol(56.14mL,1.39mol) for 15 minutes, and then add acetyl chloride(9.90 mL,138.77mmol) in 0°C and then reflux it at 65°C overnight. The reaction mixture was quenched with triethylamine, and the product was confirmed by TLC in 10% MeOH/DCM. The reaction mixture was concentrated in vacuo, and the crude product was purified by silica gel column chromatography to obtain a pure product.



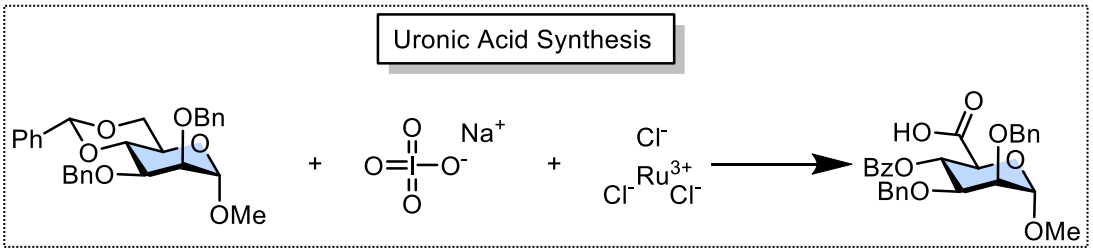
Synthesis of 1.2- To a solution of 1.1(5g,30.65mmol) in THF, Benzaldehyde-dimethyl acetal (11.50mL,76.62mmol) and para-toluene sulphonic acid (1.32g, 7.66mmol) were added at room temperature, and the reaction mixture was stirred for 5- 6 hours. Then, the product was confirmed through TLC in 30% EtOAc/Hexane, and the organic layer was washed with $NaHCO_3$ and extracted with ethyl acetate 2-3 times. The organic layer was concentrated under reduced pressure, purified by silica gel column chromatography, and the pure product was obtained at 17% ethyl acetate/hexane mixture.



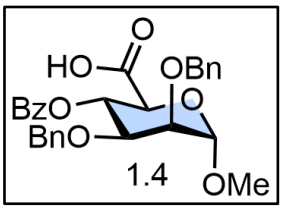
Synthesis of 1.3- To a solution of 1.2(4g,12.97mmol) in DMF, Sodium hydride (1.52g,46.21mmol) was added, and the mixture was stirred under an inert atmosphere. Tetrabutylammonium iodide (TBAI) (958.39mg, 2.59 mmol) was added, and then Benzyl Bromide (3.70mL, 31.14 mmol) was added dropwise at 0°C, and the reaction was stirred for 1 hour at room temperature. The Product was confirmed by TLC in 20% EtOAc/Hexane, and the organic layer was washed with chilled water several times, then with sodium bicarbonate, and finally extracted with ethyl acetate. The organic layer was concentrated under reduced pressure, purified by



silica gel column chromatography, and the pure Product was obtained at a 12% ethyl acetate mixture.

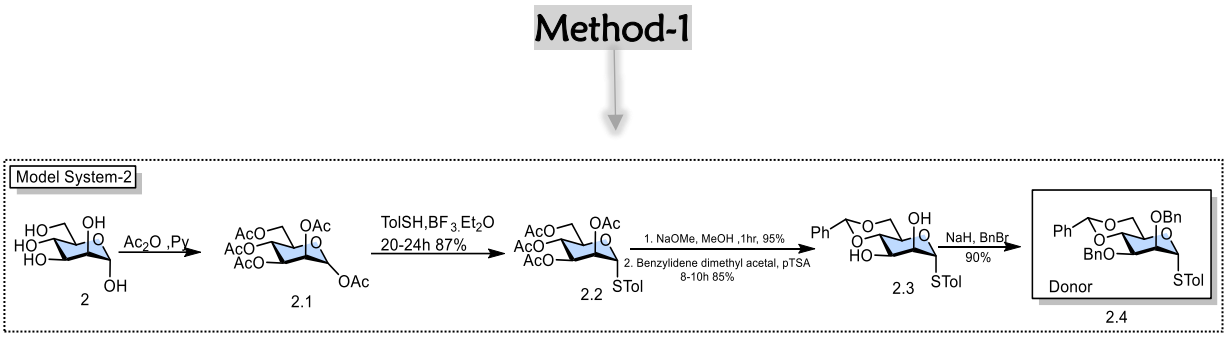


Scheme-3: Synthesis of Uronic Acid from model system-1 using Bhaskaran Protocol



Synthesis of 1.4- The compound 1.3(366mg,1mmol) was dissolved in CH_3CN: CCl_4: H_2O (2:2:0:1) (5.0mL) Solvent System and was continuously stirred, and then $NaIO_4$(2.14g,10mmol). After that, $RuCl_3 \cdot 3H_2O$ (40mg, 0.02 mmol) was added, and the mixture was stirred at room temperature for 2 h. After completion of the reaction, as indicated by TLC in 10% MeOH/DCM, the reaction was quenched with IPA (4mL), and the solid was filtered through a pad of celite and washed with ethyl acetate. The organic layer was collected, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the crude product was purified by silica gel column chromatography.

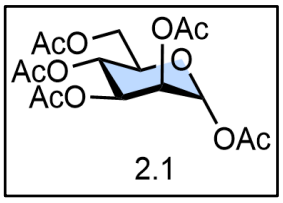
Results and Discussion: We have tried to reproduce the uronic acid[13] using the Bhaskaran's strategy it's a three way approach on model system 1.3 but every time after following all the protocols there is a sluggish behaviour which is observed its maybe due to the presence of bulky group protections like (OBn) to the mannose moiety, after a number of tries we are able to produce a crude product of the uronic acid not able to purify it. And the NMR of the crude sample is attached below.



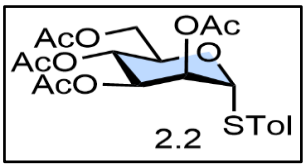
Scheme 4: Synthesis of Model System-2

Procedures

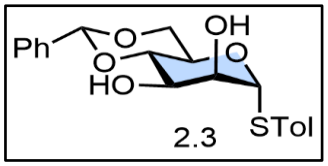
Synthesis of 2.1- To a Solution of 2(15g,83.26mmol) was dissolved in pyridine (150mL, 2.1mol), 4-Dimethylaminopyridine (DMAP)(508,61mg,4.61mmol), and acetic anhydride(94.4mL,999.19mmol) were added simultaneously one after other and the reaction mixture was stirred for 8-10h and then reaction was completed indicated by TLC in 20% EtOAc/Hexane and then the reaction mixture was washed several time with 1N HCl solution and with NaCl solution also and the organic layer was extracted using ethyl acetate. The Organic layer was dried over Na_2SO_4, concentrated under reduced pressure, and the crude product obtained was purified via silica gel column chromatography.



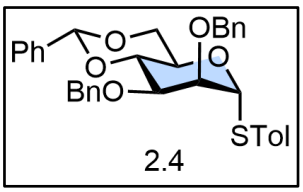
Synthesis of 2.2- The compound 2.1(13.50g, 34.59 mmol) was dissolved in CH_2Cl_2(80mL). Thio-cresol (10.74g, 86.46 mmol) was added, and the reaction mixture was cooled to 0°C and $BF_3.Et_2O$ (21.34mL, 172.93 mmol) was added to the reaction mixture dropwise, and the mixture was stirred overnight. The reaction was completed, as indicated by TLC in 20% EtOAc/ Hexane, and the reaction mixture was then washed with $NaHCO_3$ solution several times and then with NaCl solution, and the organic layer was extracted with ethyl acetate and dried over Na_2SO_4, concentrated under reduced pressure, and the crude product obtained was purified by silica gel column chromatography.

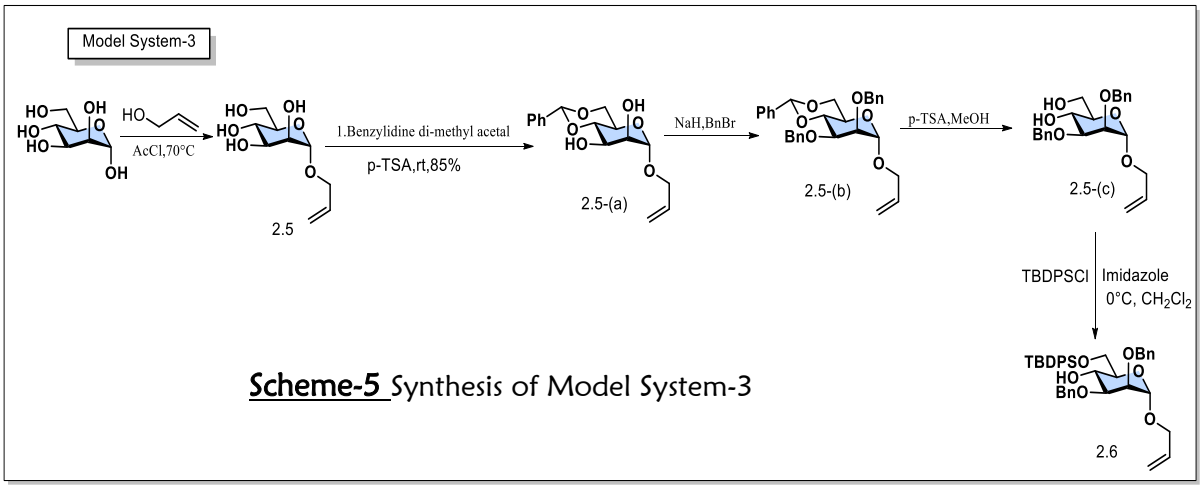


Synthesis of 2.3 - To a solution of 2.2(6g,36.78mmol) in THF, Benzaldehyde-dimethyl acetal (13.99mL,91.94mmol) and para-toluene sulphonic acid (1.58g, 9.19mmol) were added at room temperature, and the reaction mixture was stirred for 5-6 hours. Then, the product was confirmed through TLC in 30% EtOAc/Hexane, and the organic layer was washed with $NaHCO_3$ and extracted with ethyl acetate 2-3 times. The organic layer was dried over Na_2SO_4, concentrated under reduced pressure, purified by silica gel column chromatography, and the pure product was obtained as a 17% ethyl acetate/hexane mixture.



Synthesis of 2.4 - To a solution of 2.3(4g,15.92mmol) in DMF, Sodium hydride (1.74g,61.32mmol) was added, and the mixture was stirred under an inert atmosphere. Tetrabutylammonium iodide (TBAI) (1.18mg, 3.18 mmol) was added, and then Benzyl Bromide (4.54mL, 38.21mmol) was added dropwise at 0°C, and the reaction was stirred for 1 hour at room temperature. The Product was confirmed by TLC in 20% EtOAc/Hexane, and the organic layer was washed with chilled water several times, then with sodium bicarbonate, and finally extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, concentrated under reduced pressure, purified by silica gel column chromatography, and the pure Product was obtained from a 12% ethyl acetate mixture.

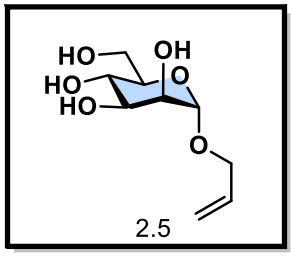




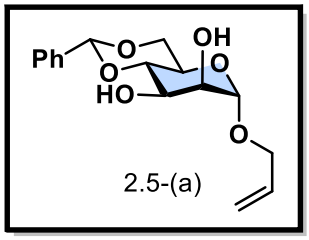
Scheme-5 Synthesis of Model System-3

Procedures

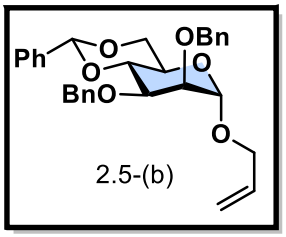
Synthesis of 2.5-The D-mannose(10g, 5.51mmol) was dissolved in allyl alcohol(113.25mL, 1.67mol) for 20 minutes with constant stirring at room temperature. Then acetyl chloride (9.87mL, 138.77 mmol) was slowly added to the reaction mixture, and the reaction was refluxed at 70 °C overnight. The reaction was monitored by thin-layer chromatography, and triethylamine was added to quench it. The crude product was obtained by concentrating the reaction mixture under reduced pressure, followed by a toluene wash to remove any remaining allyl alcohol. The yield obtained was around 11.56g (95%).



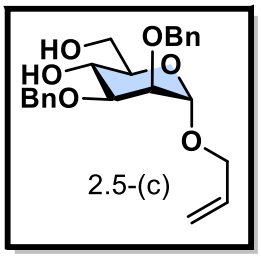
Synthesis of 2.5(a)- Compound 2.5 (11.56g,52.49mmol) was dissolved in THF, and benzaldehyde-dimethyl acetal (19.77mL,131.23mmol) and para-toluene sulphonic acid (2.26g, 13.12mmol) were added at room temperature, and the reaction mixture was stirred for 5- 6 hours. Then, the product was confirmed through TLC in 30% EtOAc/Hexane, and the organic layer was washed with $NaHCO_3$ and extracted with ethyl acetate 2-3 times. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Then the Crude compound was dissolved in ethanol solvent and kept at a low temperature in the refrigerator; after, a pure white solid was obtained, and a petroleum ether wash was applied, yielding a pure product. The yield of the product is 15.2g (96%).



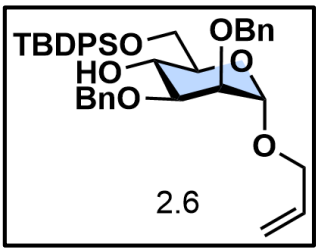
Synthesis of 2.5(b)- To a solution of 2.5(a)(15.23g,49.30mmol) in DMF, Sodium hydride (4.72g,172.54mmol) was added, and the mixture was stirred under an inert atmosphere. Tetrabutylammonium iodide (TBAI) (3.64g, 9.86 mmol) was added, and then Benzyl Bromide (4.54mL, 38.21mmol) was added dropwise at 0°C, and the reaction was stirred for 1 hour at room temperature. The Product was confirmed by TLC in 20% EtOAc/Hexane, and the organic layer was washed with chilled water several times, then with sodium bicarbonate, and finally extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, concentrated under reduced pressure, purified by silica gel column chromatography, and the pure Product was obtained at a 12% ethyl acetate mixture.



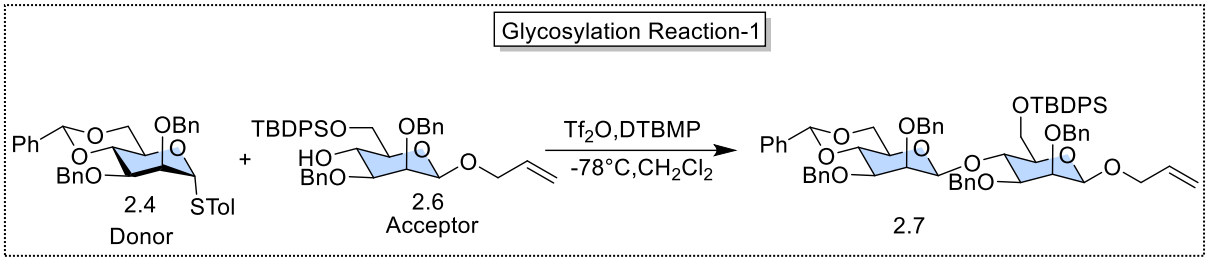
Synthesis of 2.5(C)- Compound 2.5(b)(22.12g,99.27mmol) was dissolved in CH_2Cl_2 (200mL), then methanol (600mL) was added, and then the mixture was stirred at room temperature. Later, p-TSA (2.78g, 16.78mmol) was added to the reaction mixture, which was stirred at room temperature for 1 h. The completion of the reaction was confirmed by thin-layer chromatography in 40% EtoAc/Hexane. The reaction mixture was then neutralized with triethylamine. After neutralization, the solvents were removed under reduced pressure. The crude sample was purified using silica gel column chromatography. The yield of the product is 17.37g (82%).



Synthesis of 2.6- Compound 2.5(c)(17.37g,42.68mmol) was dissolved in DMF (150mL), and imidazole (18.37g, 310.72mmol) was added at 25 °C. The mixture was cooled to 0°C, and *tert*-Butyl(chloro)diphenylsilane (TBDPSCl) (26.38mL, 112.71 mmol) was added slowly. The reaction mixture was then stirred at room temperature. After 1h, the reaction reaches completion, as indicated by thin-layer chromatography in 30% EtoAc/Hexane. The mixture was washed with chilled water, and the organic layer was



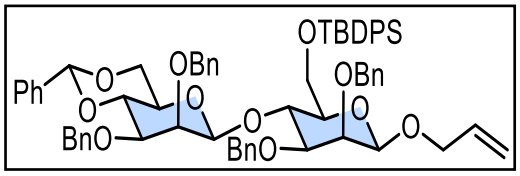
extracted with ethyl acetate. The ethyl acetate layers were washed with brine. The organic layer was dried over Na_2SO_4, and the filtrate was concentrated in vacuo. The crude was purified using silica gel column chromatography. The yield obtained is around 19.37g (86%).



Scheme-6: Synthesis of Disaccharide

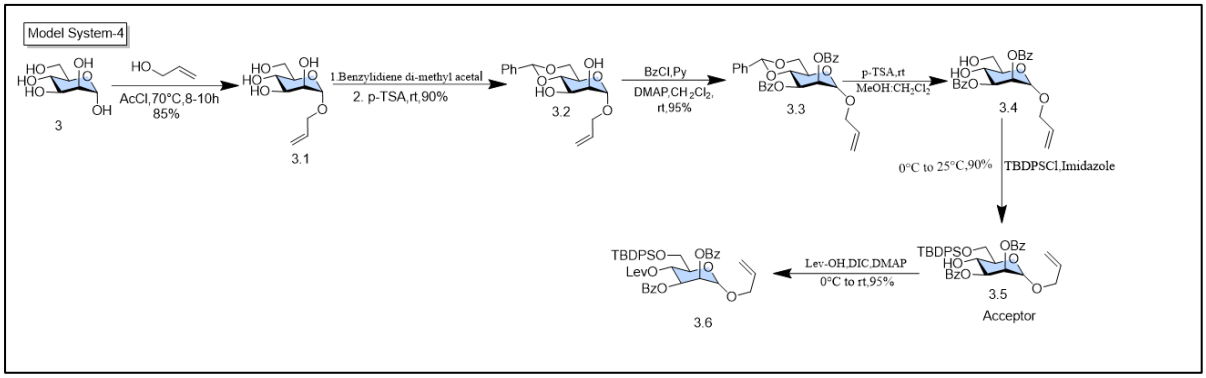
Procedure

Synthesis of 2.7: Compound 2.4(100mg,231.75mmol) was dissolved in CH_2Cl_2(2mL), and 2 spatulas of 4A° molecular sieves were also added. The reaction was started by stirring under an inert atmosphere, and then Triflic anhydride (0.0421mL, 254.92 mmol), 2,6-Di-tert-butyl-4-methylpyridine (45.83mg, 579.36mmol) was added to the reaction, and the reaction was cooled down to -78 °C (following David Crich's protocol)[14]Then, compound 2.6(177.67mg,278.09mmol) was added to the reaction mixture, and then the reaction was left on stirring till the donor, i.e., compound 2.4, got consumed, which is indicated by thin-layer chromatography in 30%EtOAc/Hexane, and the organic layer was washed with sodium bicarbonate, and finally extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, concentrated under reduced pressure, and purified by silica gel column chromatography.



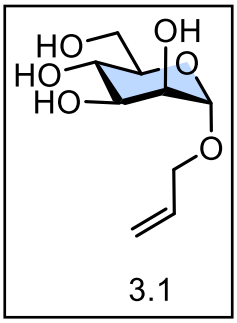
Results and Discussion: In this we have synthesized two model system (2.4) and (2.6) i.e donor and acceptor through different steps and then we have tried the glycosylation following the David crich's methodology that is at -78°C for the β-mannosylation but when we have tried this we found that the donor got completely consumed and it is indicated by thin layer chromatography also show some sluggish drag on the TLC on purification we are not able to get our desired moiety it's maybe due to the presence of such protecting groups[15] such as (OBn), (OTBDPS), which hinders the glycosylation process as the acceptor may not be sufficiently nucleophilic to react.

Method-2

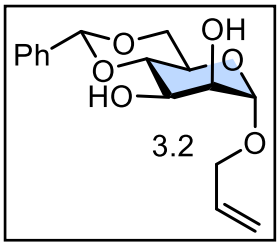


Scheme 7: Synthesis of Model System-4

Procedures

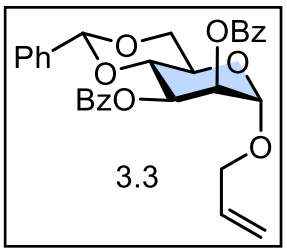


Synthesis of 3.1: D-mannose(40g,222.03mmol) was dissolved in allyl alcohol(453mL,6.66mol) for 20 minutes with constant stirring at room temperature. Then acetyl chloride (39.25mL, 555.07 mmol) was slowly added to the reaction mixture, and the reaction was refluxed at 70°C overnight. The reaction was monitored by thin-layer chromatography, and triethylamine was added to quench it. The crude product was obtained by concentrating the reaction mixture under reduced pressure, followed by a toluene wash to remove any remaining allyl alcohol. The yield obtained was around 46.4g (95%).

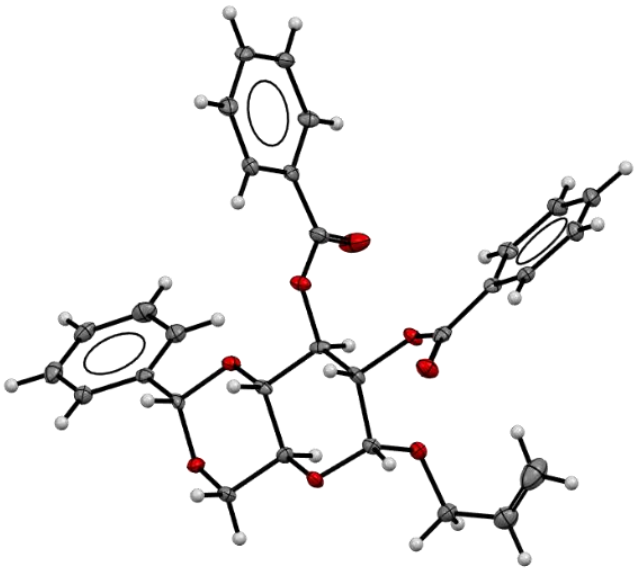


Synthesis of 3.2: Compound 3.1(46.4g,210.70mmol) was dissolved in THF, and benzaldehyde-dimethyl acetal (13.99mL,91.94mmol) and para-toluene sulphonic acid (1.58g, 9.19mmol) were added at room temperature, and the reaction mixture was stirred for 5- 6 hours. Then, the product was confirmed through TLC in 30% EtOAc/Hexane, and the organic layer was washed with $NaHCO_3$ and extracted with ethyl acetate 2-3 times. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Then the Crude compound was dissolved in ethanol solvent and kept at a low temperature in the refrigerator; after, a pure white solid was obtained, and a petroleum ether wash was applied, yielding a pure product. The yield of the product is 62.42g (96%).

Synthesis of 3.3: Compound 3.2(62.42g,320.47mmol) was dissolved in CH_2Cl_2, and pyridine(140mL,1.92mol) was added, and benzoyl chloride (80.77mL,1.8mol) was added dropwise at 0°C, and 4-Dimethylaminopyridine (DMAP)(420mg,4.21mmol) was added and left for stirring overnight. The reaction completion was indicated by thin-layer chromatography using 20% EtOAc/Hexane, and the organic layer was washed with $NaHCO_3$ and extracted with ethyl acetate 2-3 times. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Then the Crude compound was dissolved in ethanol solvent and kept at a low temperature in the refrigerator; after, a pure white Crystal was obtained, and a petroleum ether wash was applied, yielding a pure product. The yield of the product is 110.41g (92%). This was characterized by NMR and Single crystal-XRD. and crystallized in the $P2_1$ monoclinic space group.



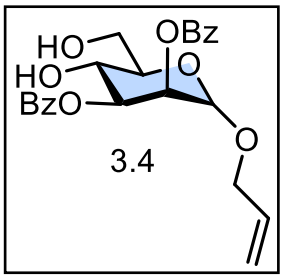
3.3



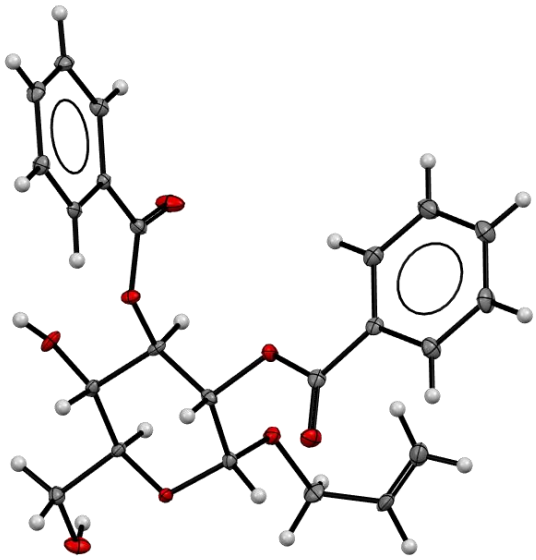
Crystal data and structure refinement table for structure-(**3.3**)

Identification code	TRY_a
Empirical formula	C30H28O8
Formula weight	516.52
Temperature/K	150(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	13.624(4)
b/Å	5.6354(14)
c/Å	16.604(5)
α/°	90
β/°	95.811(9)
γ/°	90
Volume/Å3	1268.3(6)

Z	2
ρcalcg/cm3	1.353
μ/mm-1	0.098
F(000)	544.0
Crystal size/mm3	0.32 × 0.23 × 0.21
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.688 to 57.22
Index ranges	-18 ≤ h ≤ 18, -7 ≤ k ≤ 7, -22 ≤ l ≤ 22
Reflections collected	28205
Independent reflections	5769 [Rint = 0.2267, Rsigma = 0.2254]
Data/restraints/parameters	5769/1/344
Goodness-of-fit on F2	1.113
Final R indexes [I>=2σ (I)]	R1 = 0.1004, wR2 = 0.1707
Final R indexes [all data]	R1 = 0.2223, wR2 = 0.2158
Largest diff. peak/hole / e Å-3	0.55/-0.49
Flack parameter	-1.6(9)



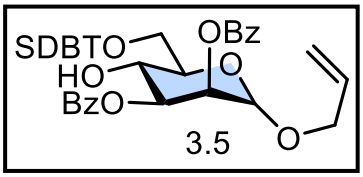
Synthesis of 3.4: Compound 3.3(20g,97.27mmol) was dissolved in CH_2Cl_2 (200mL), then methanol (600mL) was added, and then the mixture was stirred at room temperature. Later, p-TSA (2.52g, 15.63 mmol) was added to the reaction mixture, which was stirred at room temperature for 1 h. The completion of the reaction was confirmed by thin-layer chromatography in 40% EtoAc/Hexane. The reaction mixture was then neutralized with triethylamine. After neutralization, the solvents were removed under reduced pressure. The crude sample was divided into separate portions for recrystallization in the refrigerator, during which some product precipitated from ethyl acetate, the solvent. A pure white Crystal was obtained, and a petroleum ether wash was applied, yielding a pure product. The yield of the product is 11.42g(86%). This was characterized by NMR and single-crystal XRD, and crystallized in the $P2_12_12_1$ Orthorhombic space group.



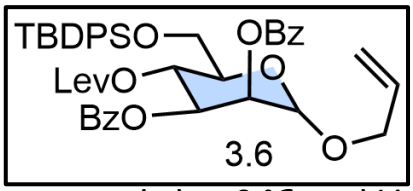
Crystal data and structure refinement table for Structure- (3.4)

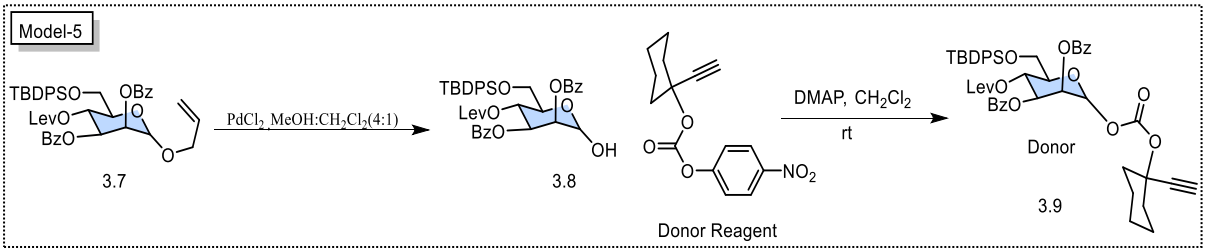
Identification code	TRY_a
Empirical formula	CHO
Formula weight	29.02
Temperature/K	150(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.6329(6)
b/Å	12.8468(17)
c/Å	28.728(4)
α/°	90
β/°	90
γ/°	90
Volume/Å3	2078.9(4)
Z	61
ρcalcg/cm3	1.414
μ/mm-1	0.131
F(000)	915.0
Crystal size/mm3	0.28 × 0.24 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.254 to 57.174
Index ranges	-7 ≤ h ≤ 6, -17 ≤ k ≤ 17, -38 ≤ l ≤ 38
Reflections collected	61749
Independent reflections	5276 [Rint = 0.2278, Rsigma = 0.1434]
Data/restraints/parameters	5276/0/283
Goodness-of-fit on F2	1.153
Final R indexes [I>=2σ (I)]	R1 = 0.0866, wR2 = 0.0980
Final R indexes [all data]	R1 = 0.1741, wR2 = 0.1172
Largest diff. peak/hole / e Å-3	0.43/-0.36
Flack parameter	0.5(7)

Synthesis of 3.5: Compound 3.4(11.42g,33.26mmol) was dissolved in DMF (110mL), and imidazole (12.27g, 180.25mmol) was added at 25 °C. The mixture was cooled to 0°C, and *tert*-Butyl(chloro)diphenylsilane (TBDPSCl) (18.77mL, 72.17 mmol) was added slowly. The reaction mixture was then stirred at room temperature. After 1h, the reaction reaches completion, as indicated by thin-layer chromatography in 30% EtoAc/Hexane. The mixture was washed with chilled water, and the organic layer was extracted with ethyl acetate. The ethyl acetate layers were washed with brine. The organic layer was dried over Na_2SO_4, and the filtrate was concentrated in vacuo. The oily residue was purified by silica gel column chromatography using ethyl acetate and Hexane. The yield obtained is around 14.42g (88%).



Synthesis of 3.6: Compound 3.5g(14.42g,30.34mmol) was dissolved in CH_2Cl_2 (140mL), and Levulinic acid (5.14g,44.29mmol),4-Dimethylaminopyridine (DMAP)(10.86g,88.89mmol) was added to the reaction mixture and stirred for 10 min. Then the reaction mixture was cooled to 0 °C, and N, N'-Diisopropylcarbodiimide (6.98 mmL, 44.60 mmol) was added dropwise, and the reaction was stirred for 3h at room temperature. The reaction goes to completion, indicated by thin-layer chromatography in 30% EtoAc/Hexane. The mixture was washed with chilled water, and the organic layer was extracted with ethyl acetate. The ethyl acetate layers were washed with brine. The organic layer was dried over Na_2SO_4, and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography using ethyl acetate and Hexane. The yield obtained is around 16.46g(81%). **Scheme-8** Synthesis of Model System-5

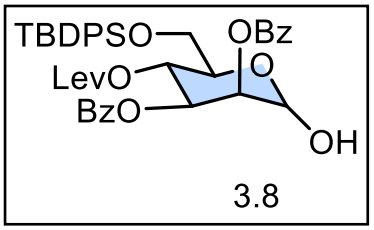




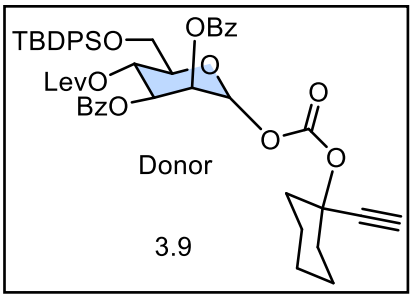
Scheme-8 Synthesis of Model System-5

Procedures

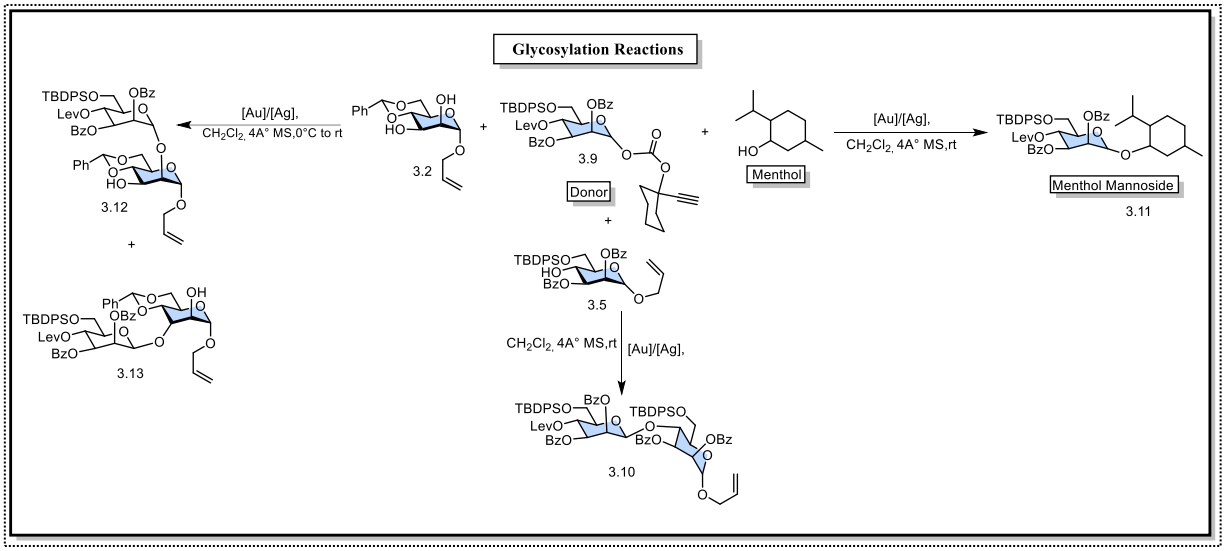
Synthesis of 3.8: The compound 3.7(4.0g,8.73mmol) will dissolve in a mixture of CH_2Cl_2: MeOH (1:3) (146mL:438mL), then $PdCl_2$ (464.27mg,2.62mmol) was added, and the reaction was stirred for 2-3h. The reaction was monitored by thin-layer chromatography; the reaction was then quenched with triethylamine, filtered through a sintered funnel, and the



filtrate was concentrated in vacuo. The residue product was purified by silica gel column chromatography using ethyl acetate and petroleum ether. The yield obtained was around 1.68g(81%

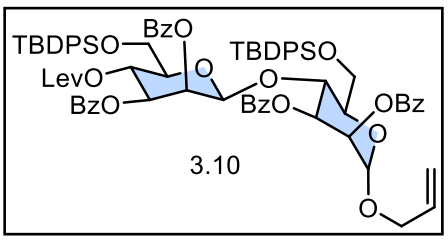


Synthesis of 3.9: The compound 3.8(1.68g,2.32mmol) was dissolved in CH_2Cl_2, then 4-dimethylaminopyridine (DMAP)(339.78mg,2.78mmol) was added to it, and the reaction was left stirring for 2-3h. The reaction goes to completion, indicated by thin-layer chromatography in 30% EtoAc/Hexane. The organic layer was washed with $NaHCO_3$ and extracted with ethyl acetate 2-3 times. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The yield obtained was around 1.86g(84%)



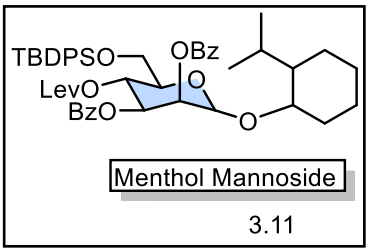
Scheme-9 Synthesis of Different Glycosylation Reactions

Procedures

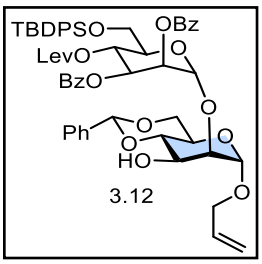


Synthesis of 3.10: The compound 3.9(300mg,342.84mmol) and compound 3.5(228.62mg,342.84mmol) were dissolved together and concentrated under controlled pressure, then kept for drying. After that, it was dissolved in CH2Cl2 (5mL), and 2 spatulas of 4A° molecular sieves were also added. And after vigorous stirring under an inert atmosphere at 25 °C for 10 minutes, simultaneously AgOTf(7.05mg,23.43mmol), Chloro[tris(2,4-di-tertbutylphenyl)phosphite]gold(I)[16](24.12mg,27.43mmol) was added to it and then left stirring for 1 hour. The reaction goes to completion, indicated by thin-layer chromatography in 30% EtoAc/Hexane. The reaction was then quenched

with triethylamine, filtered through a sintered funnel, and the filtrate was concentrated in vacuo. The residue product was purified by silica gel column chromatography using ethyl acetate and petroleum ether.



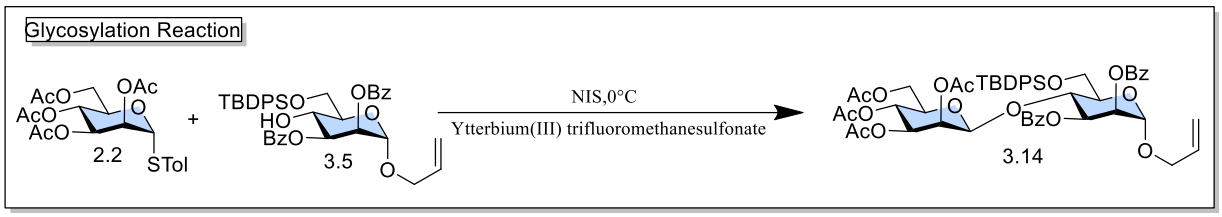
Synthesis of 3.11: The compound 3.9(220mg,251.41mmol) and menthol(39.29mg,251.41mmol) were dissolved together and concentrated under controlled pressure, then kept for drying. After that, it was dissolved in CH2Cl2 (4mL), and 2 spatulas of 4A° molecular sieves were also added. And after vigorous stirring under an inert atmosphere at 25°C for 10 minutes, AgOTf (5.17mg, 20.11 mmol) and Chloro[tris(2,4-di-tertbutylphenyl)phosphite]gold(I) (12.73mg, 20.11 mmol) were added simultaneously, and the mixture was stirred for 1 hour. The reaction goes to completion, indicated by thin-layer chromatography in 30% EtoAc/Hexane. The reaction was then quenched with triethylamine, filtered through a sintered funnel, and the filtrate was concentrated in vacuo. The residue product was purified by silica gel column chromatography using ethyl acetate and petroleum ether.



Synthesis of 3.12: The compound 3.9(200mg,228.56mmol) and compound 3.2(112.12mg,228.56mmol) were dissolved together and concentrated under controlled pressure, then kept for drying. After that, it was dissolved in CH_2Cl_2 (6mL), and 2 spatulas of 4A° molecular sieves were also added. And after vigorous stirring under an inert atmosphere at 0°C for 10 minutes, simultaneously AgOTf(4.70mg,18.28mmol), Chloro[tris(2,4-di-tertbutylphenyl)phosphite]gold(I)(16.08mg,18.28mmol) was added to it and then left stirring for 1 hour. The reaction goes to completion, indicated by thin-layer chromatography in 30% EtoAc/Hexane. The reaction was then quenched with triethylamine, filtered through a sintered funnel, and the filtrate was concentrated in vacuo. The residue product was purified by silica gel column chromatography using ethyl acetate and petroleum ether.

Results and Discussion: After the first unsuccessfull effort we have tried a different route through method-2 to achieve our desired moiety in which we have synthesized two different model system (3.9) and (3.5) and we have tried the glycosylation using AgOtf and Chloro[tris(2,4-di tertbutylphenyl)phosphite]gold(I) and the reaction was monitored through thin-layer chromatography and it was found that donor got completely consumed or 95%consumed but the acceptor will remain as it is so we have tried to recover the spots that formed on TLC but unfortunately its not the desired one because everytime a hemiacetal moiety is formed in the reaction,then we have tried a glycosylation between model system (3.9) and (3.2) but it shows some poor

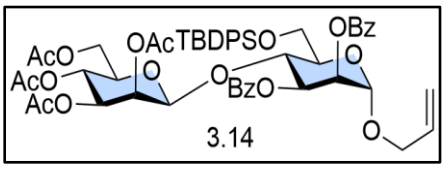
results again, so after every try we have tried the glycosylation of donor i.e (3.9) model system with menthol and in that we see that both the donor and acceptor got consumed and after recovering the product we have seen that menthol-mannoside is formed NMR of this is attached below but after this we can analyse that there is a problem with the acceptor earlier as due to the presence of such protecting groups[17] such as (OBz), (OTBDPS) Which hinders the glycosylation process as the acceptor maybe not enough nucleophilic to react.



Scheme-10 – Synthesis of Glycosylation Reaction

Procedure

Synthesis of 3.14: The compound 2.2(500mg,749.80mmol) and compound 3.5(248.41mg,749.80mmol) were dissolved together and concentrated under controlled pressure, then kept for drying. After that, it was dissolved in CH_2Cl_2 (4mL), and 2 spatulas of 4A° molecular sieves were also added. And after vigorous stirring under an inert atmosphere at 0°C for 20 minutes, *N,N*-Iodosuccinimide(185.56mg,824.78mmol), Ytterbium(III) trifluoromethanesulfonate(116.26mg,187.45mmol) was added simultaneously to the reaction mixture and then left stirring for 30 minutes. The reaction, indicated by thin-layer chromatography in 30% EtoAc/Hexane. The reaction was then quenched with triethylamine, filtered through a sintered funnel, and the filtrate was concentrated in vacuo. The residue product was purified by silica gel column chromatography using ethyl acetate and petroleum ether.

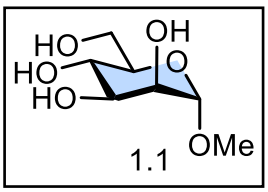


Results and Discussion: After all the failed attempts, we attempted another glycosylation reaction using two different model systems and different reagents, such as Ytterbium(III) trifluoromethanesulfonate and NIS, but the results were the same: the reactions failed at the C-4 position of mannose. Therefore, it's clear that the C-4 position is not very nucleophilic.

Conclusion: After trying every possible solution, we have come to the conclusion that the C-4 position of mannose in the acceptor is the least reactive and not very nucleophilic due to the presence of large nearby protecting groups, similar to the type of behavior we have observed in method-1, so the 1-4 glcosylation is not taking place, whereas with menthol its producing menthol-mannoside.

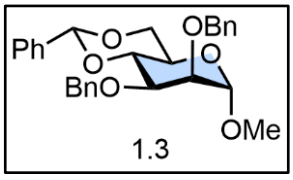
Spectral Data

For Model System (1.1) - ^{1}H NMR (401 MHz, D_2O): δ 3.90 (ddd, *J* = 22.4, 12.3, 2.3 Hz, 1H), 3.76 (dd, *J* = 12.4, 5.4 Hz, 1H), 3.73 – 3.62 (m, 2H), 3.59 – 3.54 (m, 1H), 3.42 (s, 3H), 3.21 (q, *J* = 7.3 Hz, 2H).**^{13}C NMR (101 MHz, Deuterium Oxide)** δ 103.22, 99.25, 75.90, 75.76, 73.10, 73.08, 71.56, 71.21, 69.65, 69.55, 60.75, 60.55, 57.18, 55.01, 46.67, 8.25.



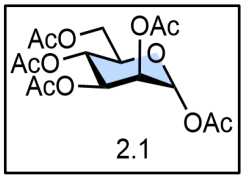
1.1

For Model System (1.3) - ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.46 (m, 2H), 7.42 – 7.27 (m, 13H), 5.58 (s, 1H), 4.94 – 4.72 (m, 4H), 4.43 (d, *J* = 7.7 Hz, 1H), 4.37 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.84 – 3.65 (m, 3H), 3.59 (s, 3H), 3.49 – 3.37 (m, 2H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.51, 138.42, 137.34, 128.96, 128.35, 128.31, 128.26, 128.08, 128.05, 127.71, 127.64, 126.02, 105.24, 101.15, 82.20, 81.53, 80.82, 77.24, 75.29, 75.13, 68.83, 65.99, 57.49, 30.95.



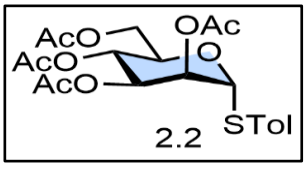
1.3

For Model System (2.1) - ^{1}H NMR (401 MHz, $CDCl_3$): δ 6.26 (d, *J* = 3.7 Hz, 1H), 5.41 (t, *J* = 9.9 Hz, 1H), 5.10 – 5.01 (m, 2H), 4.21 (ddd, *J* = 12.7, 8.6, 4.4 Hz, 1H), 4.08 – 4.00 (m, 2H), 2.06 – 2.01 (m, 4H), 2.00 – 1.92 (m, 11H).



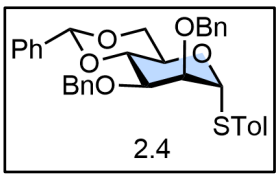
2.1

For Model System (2.2) - ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.34 (m, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 5.21 (t, *J* = 9.4 Hz, 1H), 4.98 (dt, *J* = 35.5, 9.7 Hz, 2H), 4.64 (d, *J* = 10.0 Hz, 1H), 4.27 – 4.12 (m, 2H), 3.70 (ddd, *J* = 10.0, 4.8, 2.7 Hz, 1H), 2.35 (s, 3H), 2.09 (d, *J* = 3.2 Hz, 6H), 2.02 (s, 3H), 1.99 (s, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.60, 170.21, 169.41, 169.26, 138.81, 133.84, 129.69, 127.54, 85.82, 77.26, 75.74, 74.02, 69.92, 68.20, 62.13, 29.69, 21.19, 20.77, 20.74, 20.60, 20.58.



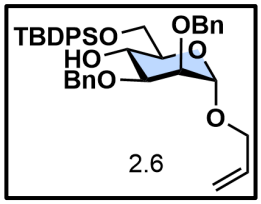
2.2

For Model System (2.4) - ^{1}H NMR (401 MHz, $CDCl_3$): δ 7.46 – 7.24 (m, 17H), 7.08 (d, *J* = 7.9 Hz, 2H), 5.55 (s, 1H), 4.92 – 4.71 (m, 4H), 4.66 (d, *J* = 9.7 Hz, 1H), 4.34 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.82 – 3.73 (m, 2H), 3.65 (t, *J* = 9.4 Hz, 1H), 3.48 – 3.38 (m, 2H), 2.31 (s, 3H).



2.4

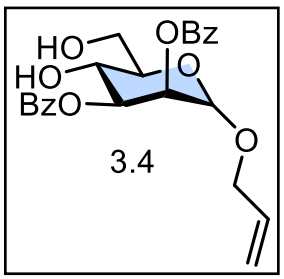
For Model System (2.6)- ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (dt, *J* = 8.0, 1.7 Hz, 4H), 7.47 – 7.27 (m, 15H), 5.88 (dddd, *J* = 16.7, 10.8, 6.1, 5.0 Hz, 1H), 5.23 – 5.16 (m, 1H), 4.92 (d, *J* = 1.7 Hz, 1H), 4.69 (s, 2H), 4.22 – 4.09 (m, 2H), 4.00 – 3.89 (m, 3H), 3.84 – 3.77 (m, 2H), 3.70 (dt, *J* = 9.4, 4.6 Hz, 1H), 1.07 (s, 9H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.76, 135.70, 133.87, 129.68, 129.67, 128.48,



2.6

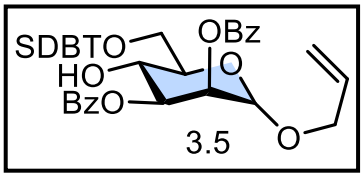
128.35, 127.81, 127.78, 127.76, 127.68, 127.61, 117.31, 97.05, 79.84, 74.30, 72.71, 72.63, 72.00, 68.19, 67.68, 64.69, 26.85, 19.30.

For Model System (3.4)- ^{1}**H NMR (400 MHz, $CDCl_3$):** δ 7.98 (dd, *J* = 8.2, 1.6 Hz, 4H), 7.55 – 7.48 (m, 2H), 7.37 (td, *J* = 7.7, 1.8 Hz, 4H), 5.85 (ddt, *J* = 15.8, 10.5, 5.5 Hz, 1H), 5.76 (ddd, *J* = 11.6, 7.5, 2.2 Hz, 1H), 5.33 (q, *J* = 1.7 Hz, 1H), 5.30 – 5.23 (m, 2H), 5.16 (dt, *J* = 10.3, 1.5 Hz, 1H), 4.85 – 4.65 (m, 1H), 4.25 (ddt, *J* = 13.1, 5.2, 1.6 Hz, 1H), 4.10 – 4.00 (m, 1H), 3.99 – 3.88 (m, 4H).



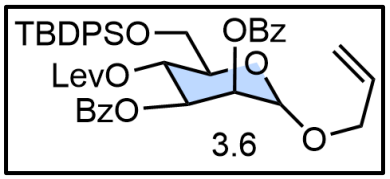
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.61, 165.99, 133.51, 133.41, 133.33, 129.89, 129.86, 129.16, 129.12, 128.46, 117.80, 95.26, 77.24, 74.41, 71.60, 71.31, 69.93, 68.68, 61.97.

For Model System (3.5)- ^{1}**H NMR (400 MHz, $CDCl_3$):** δ 7.99 (dt, *J* = 8.4, 1.4 Hz, 4H), 7.73 (dd, *J* = 7.6, 1.9 Hz, 4H), 7.50 – 7.31 (m, 12H), 5.82 (dddd, *J* = 15.4, 10.7, 7.1, 5.5 Hz, 2H), 5.31 – 5.21 (m, 3H), 5.12 (dq, *J* = 10.4, 1.5 Hz, 1H), 4.25 – 4.18 (m, 1H), 3.99 (dddt, *J* = 14.9, 11.8, 5.3, 2.5 Hz, 5H), 3.09 (s, 1H), 1.09 (s, 9H).



^{13}C NMR (101 MHz, $CDCl_3$) δ 167.24, 135.76, 135.71, 133.56, 133.36, 133.33, 133.09, 129.92, 129.51, 129.30, 128.46, 128.41, 127.86, 127.84, 117.61, 95.08, 74.17, 71.59, 71.57, 71.04, 68.39, 64.21, 26.94, 19.35.

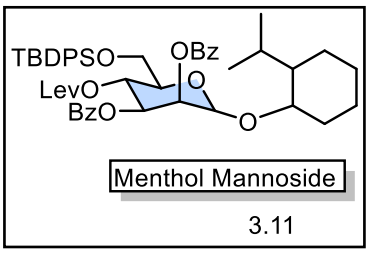
For Model System (3.6)- ^{1}**H NMR (400 MHz, $CDCl_3$):** δ 7.98 (ddt, *J* = 11.3, 7.0, 1.4 Hz, 4H), 7.76 (ddt, *J* = 13.2, 4.6, 2.9 Hz, 4H), 7.39 (d, *J* = 2.2 Hz, 8H), 7.30 (t, *J* = 7.6 Hz, 4H), 6.07 (t, *J* = 9.9 Hz, 1H), 5.89 – 5.75 (m, 1H), 5.47 (t, *J* = 9.9 Hz, 1H), 5.40 (d, *J* = 3.7 Hz, 1H), 5.32 – 5.23 (m, 2H), 5.11 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.26 (ddt, *J* = 13.3, 5.1, 1.6 Hz, 1H), 4.17 – 4.00 (m, 2H), 3.93 – 3.83 (m, 2H), 2.54 – 2.27 (m, 4H), 1.93 (s, 3H), 1.12 (s, 9H).



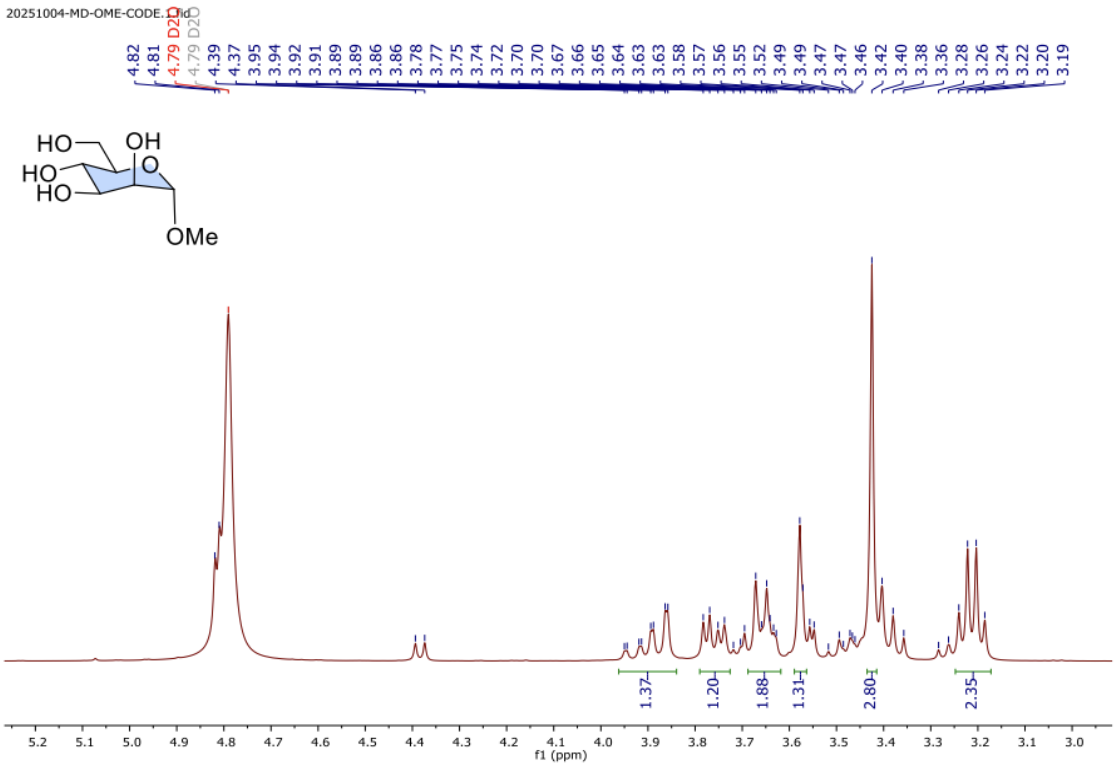
^{13}C NMR (101 MHz, $CDCl_3$) δ 205.42, 171.37, 135.85, 135.79, 133.48, 133.43, 133.35, 133.24, 129.94, 129.86, 129.83, 128.50, 128.45, 127.83, 127.80, 117.77, 94.95, 77.58, 72.14, 71.14, 70.62, 68.89, 68.48, 62.74, 37.84, 29.48, 27.97, 26.88, 19.39.

For Model System (3.9)- ^{1}H NMR (401 MHz, $CDCl_3$): δ 7.99 – 7.93 (m, 4H), 7.75 – 7.66 (m, 4H), 7.54 – 7.47 (m, 2H), 7.45 – 7.31 (m, 10H), 6.49 (d, *J* = 3.6 Hz, 1H), 6.02 (t, *J* = 10.0 Hz, 1H), 5.62 (t, *J* = 10.0 Hz, 1H), 5.46 (dd, *J* = 10.2, 3.7 Hz, 1H), 4.21 (ddd, *J* = 10.2, 3.8, 2.0 Hz, 1H), 3.89 – 3.78 (m, 2H), 2.54 (dd, *J* = 7.8, 6.6 Hz, 2H), 2.45 – 2.35 (m, 3H), 2.21 – 2.10 (m, 1H), 2.01 (s, 3H), 1.83 (dtd, *J* = 33.5, 13.2, 11.4, 6.3 Hz, 2H), 1.72 – 1.40 (m, 1H), 1.35 – 1.24 (m, 1H), 1.09 (s, 9H).

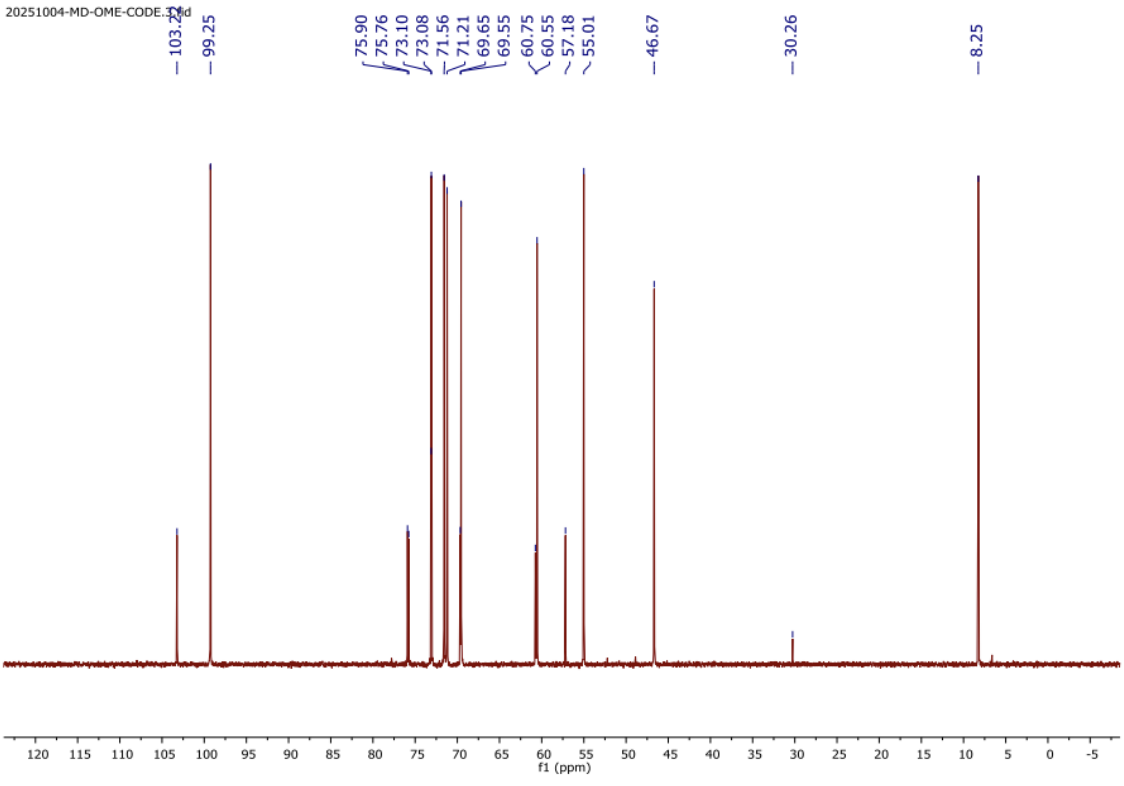
For Model System (3.11)- ^{1}H NMR (401 MHz, $CDCl_3$): δ 7.93 (ddt, *J* = 17.0, 7.1, 1.4 Hz, 4H), 7.68 (ddt, *J* = 16.0, 6.5, 1.6 Hz, 4H), 7.49 (tdd, *J* = 6.4, 4.6, 3.3 Hz, 2H), 7.45 – 7.33 (m, 10H), 5.62 (t, *J* = 9.7 Hz, 1H), 5.44 – 5.28 (m, 2H), 4.82 (d, *J* = 7.9 Hz, 1H), 3.86 – 3.67 (m, 3H), 3.51 (td, *J* = 10.7, 4.2 Hz, 1H), 2.42 (td, *J* = 6.9, 6.3, 1.9 Hz, 2H), 2.33 – 2.23 (m, 3H), 1.97 (s, 3H), 1.63 – 1.57 (m, 3H), 1.31 – 1.23 (m, 5H), 1.07 (s, 9H), 0.85 (d, *J* = 7.0 Hz, 3H), 0.75 (t, *J* = 6.5 Hz, 6H).



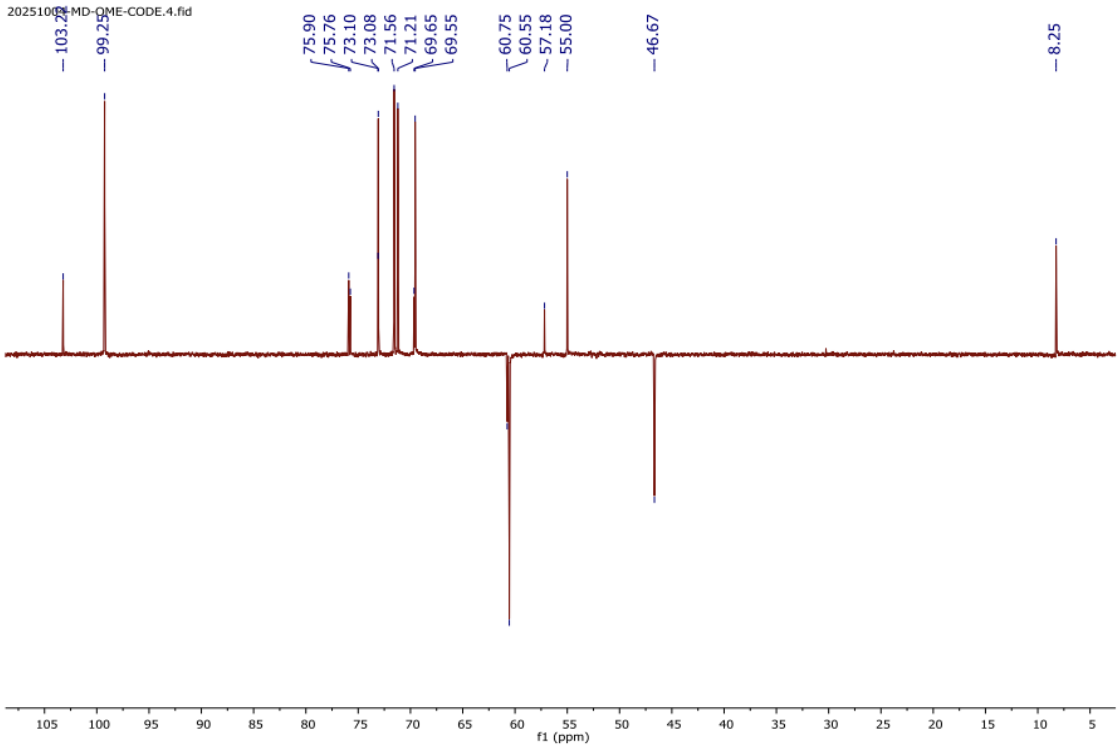
NMR spectra



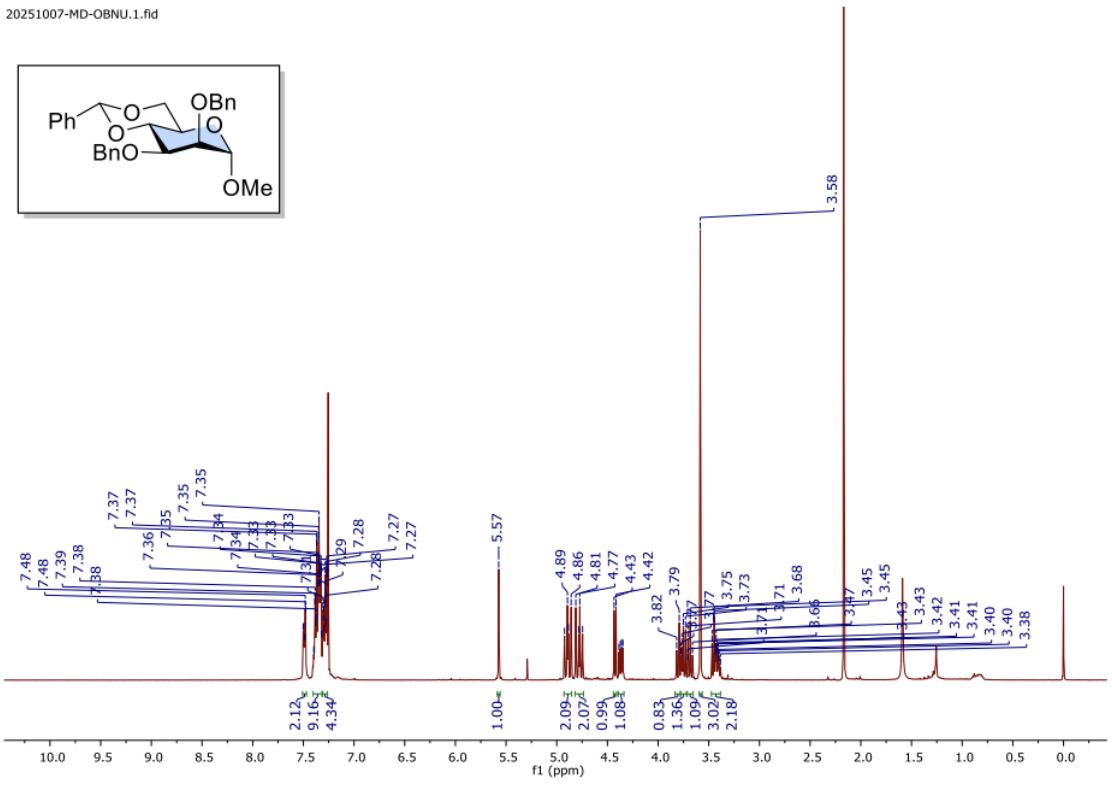
^{1}H-NMR (at 400 MHz) in $CDCl_3$ of Model System (1.1)



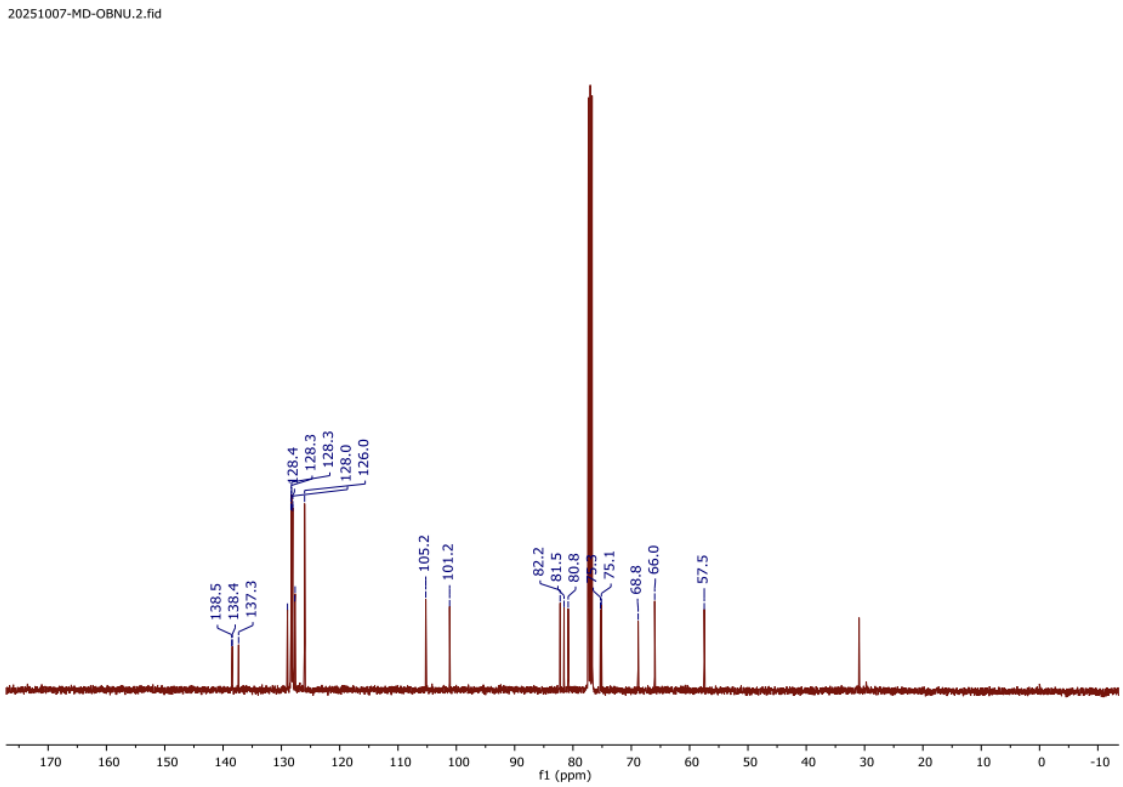
^{13}C-NMR (at 400 MHz) in $CDCl_3$ of Model System (1.1)



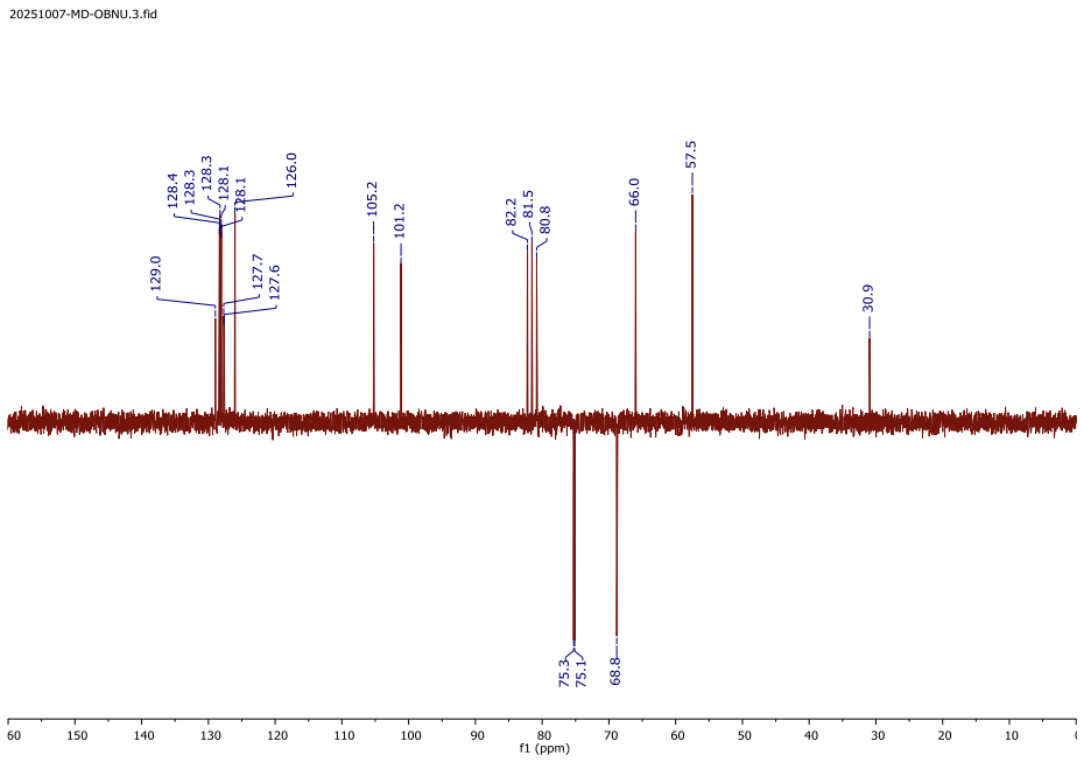
DEPT-135 NMR (at 400 MHz) in $CDCl_3$ of Model System (1.1)



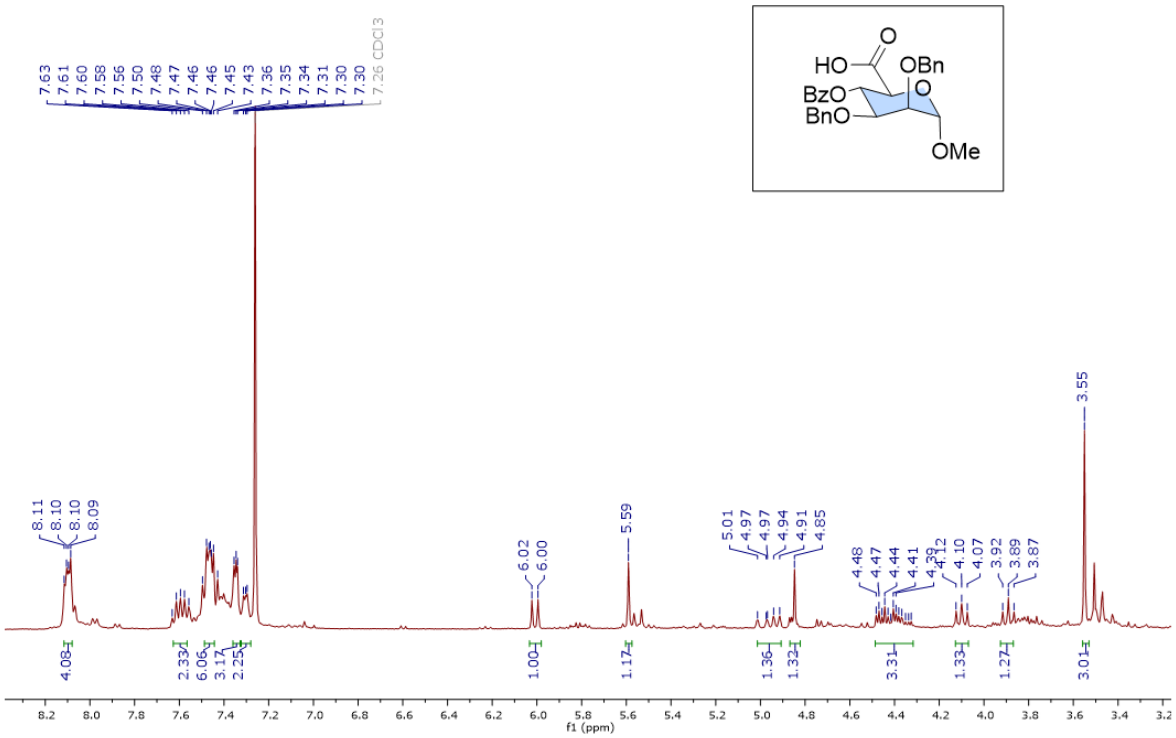
^{1}H-NMR (at 400 MHz) in $CDCl_3$ of Model System (1.3)



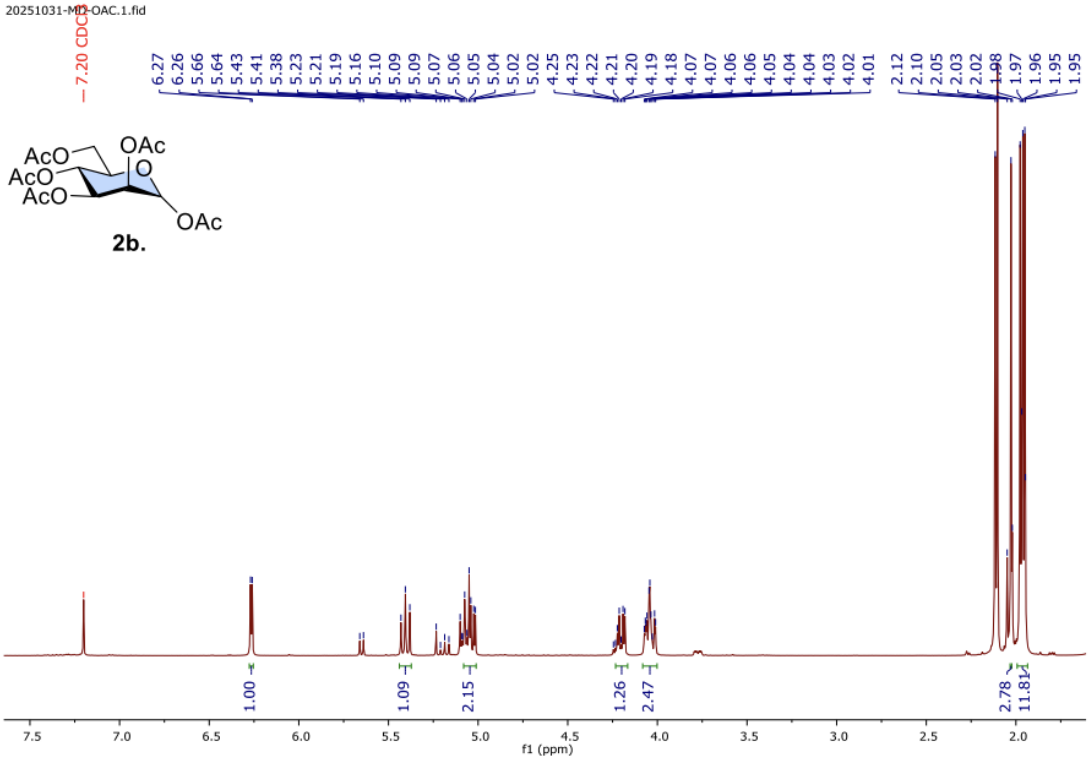
^{13}C-NMR (at 400 MHz) in $CDCl_3$ of Model System (1.3)



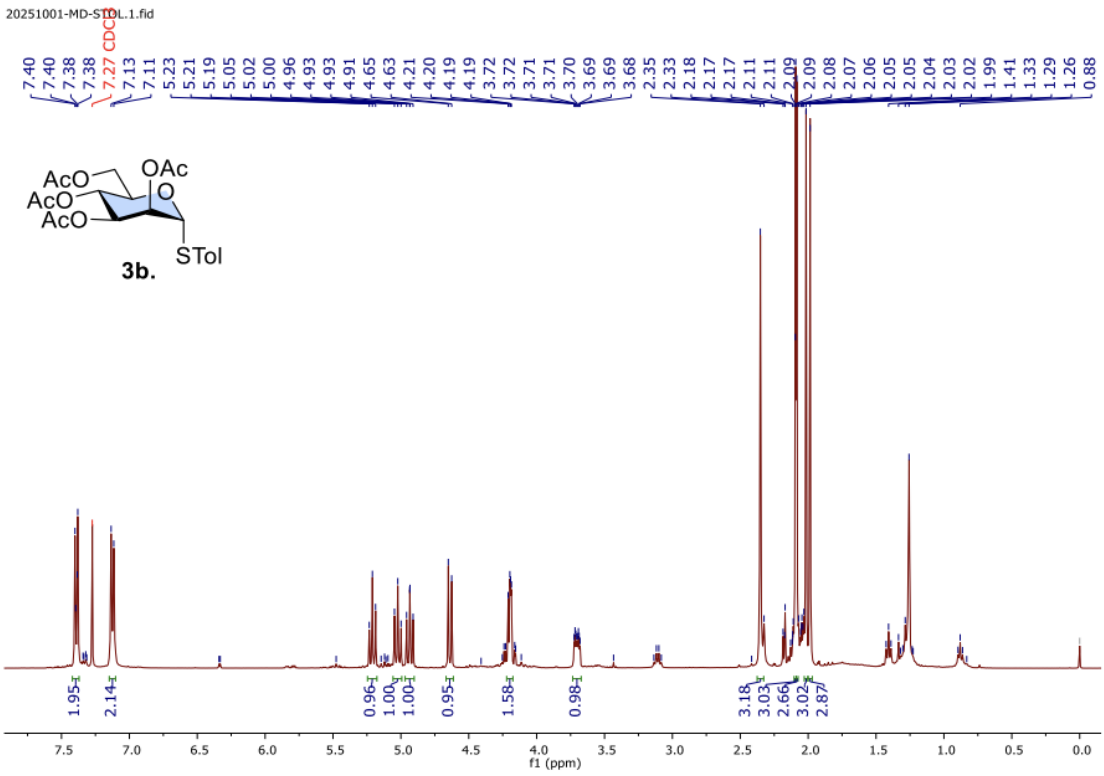
DEPT-135 NMR (at 400 MHz) in $CDCl_3$ of Model System (1.3)



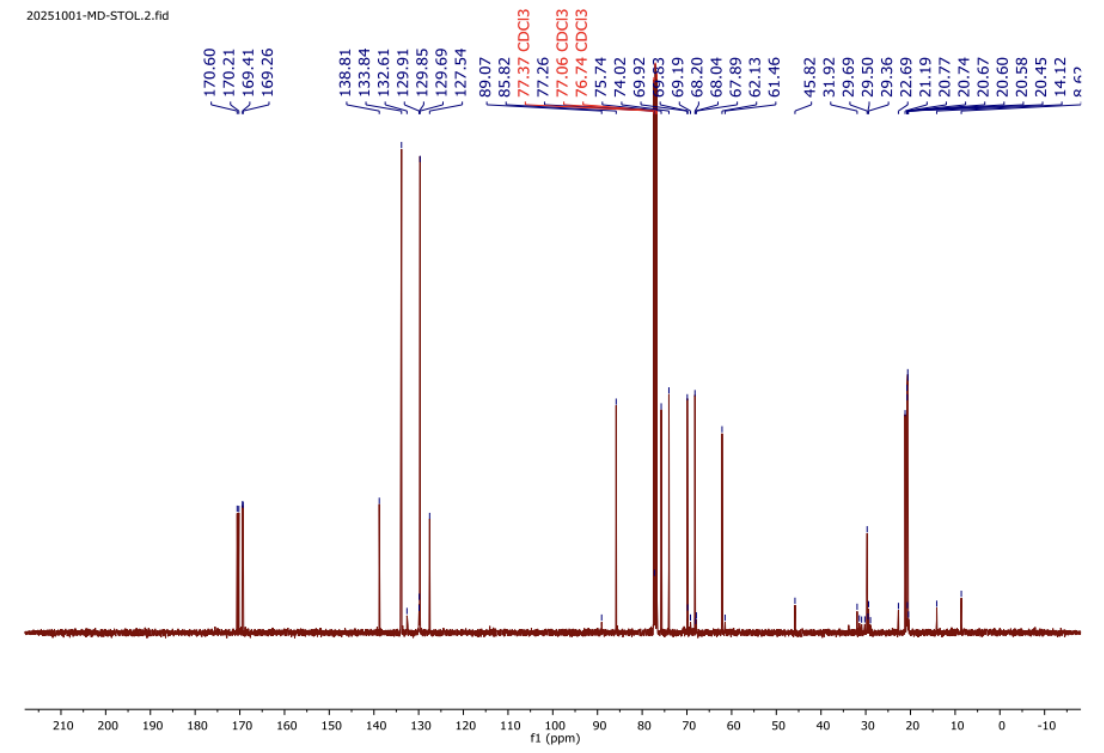
^{1}H-NMR (at 400 MHz) in $CDCl_3$ of Crude Uronic acid



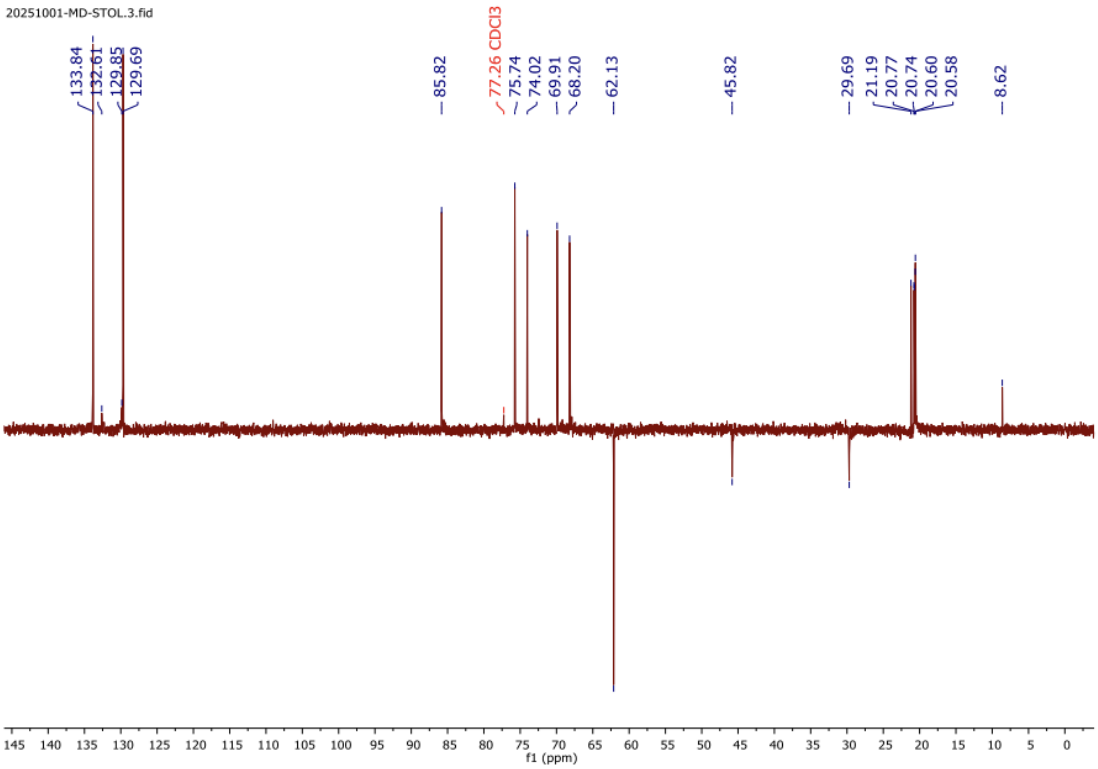
^{1}H-NMR (at 400 MHz) in $CDCl_3$ of Model System (2.1)



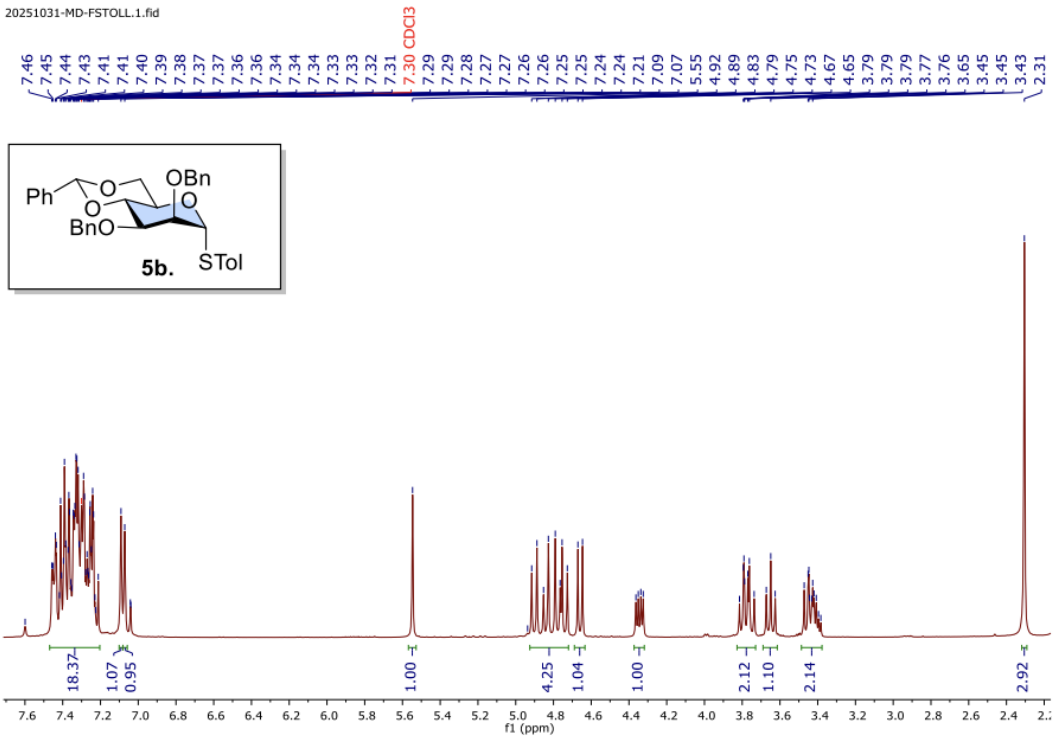
^{1}H-NMR (at 400 MHz) in $CDCl_3$ of Model System (2.2)



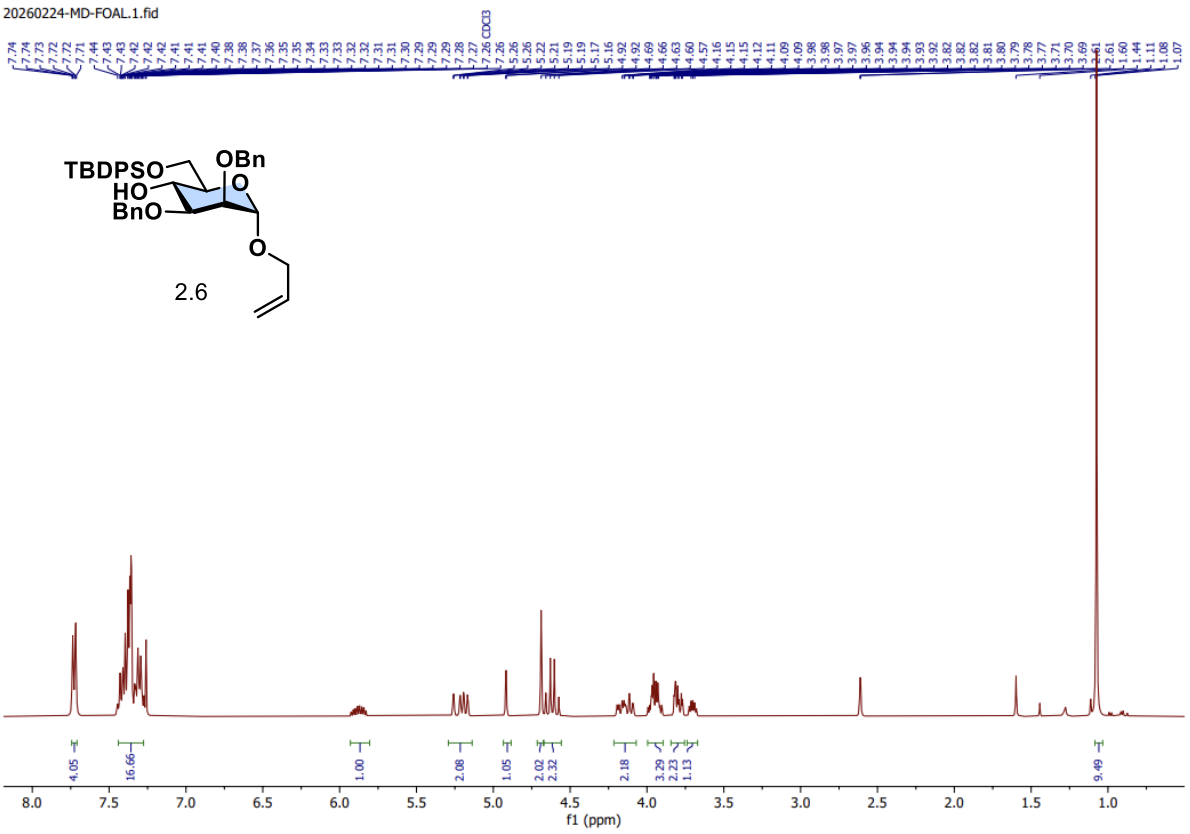
^{13}C-NMR (at 400 MHz) in $CDCl_3$ of Model System (2.2)



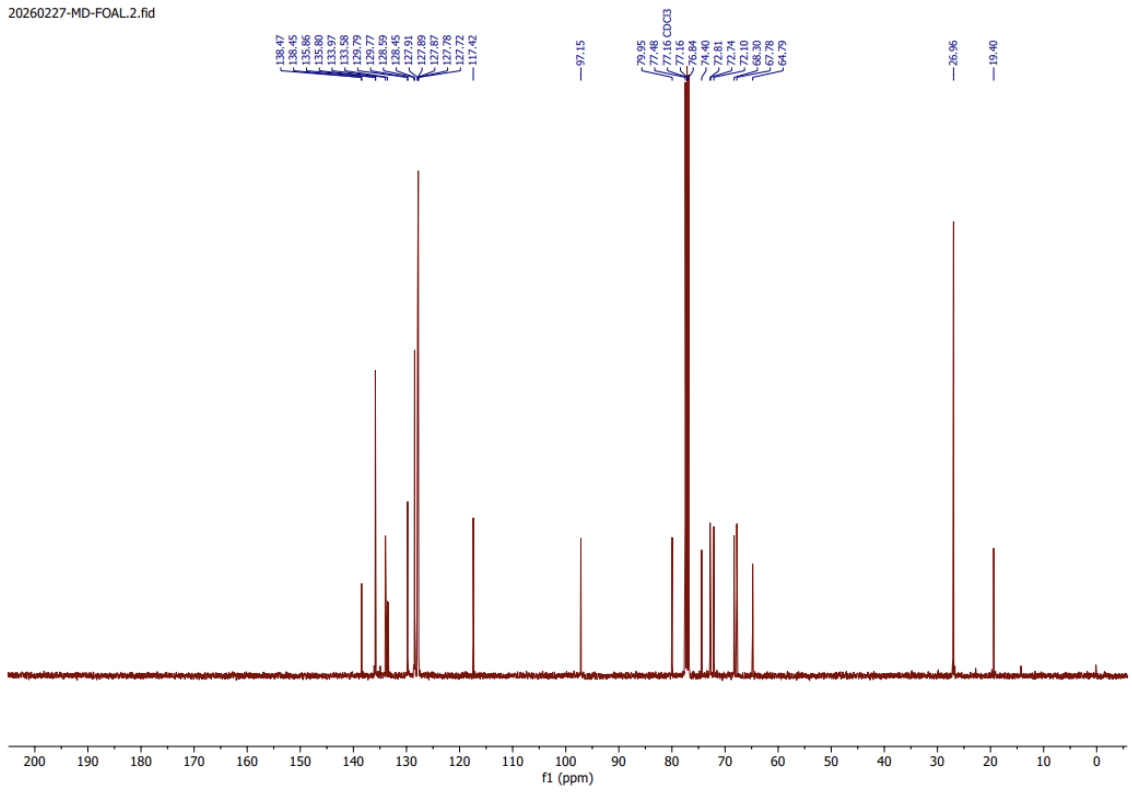
DEPT-135 NMR (at 400 MHz) in $CDCl_3$ of Model System (2.2)



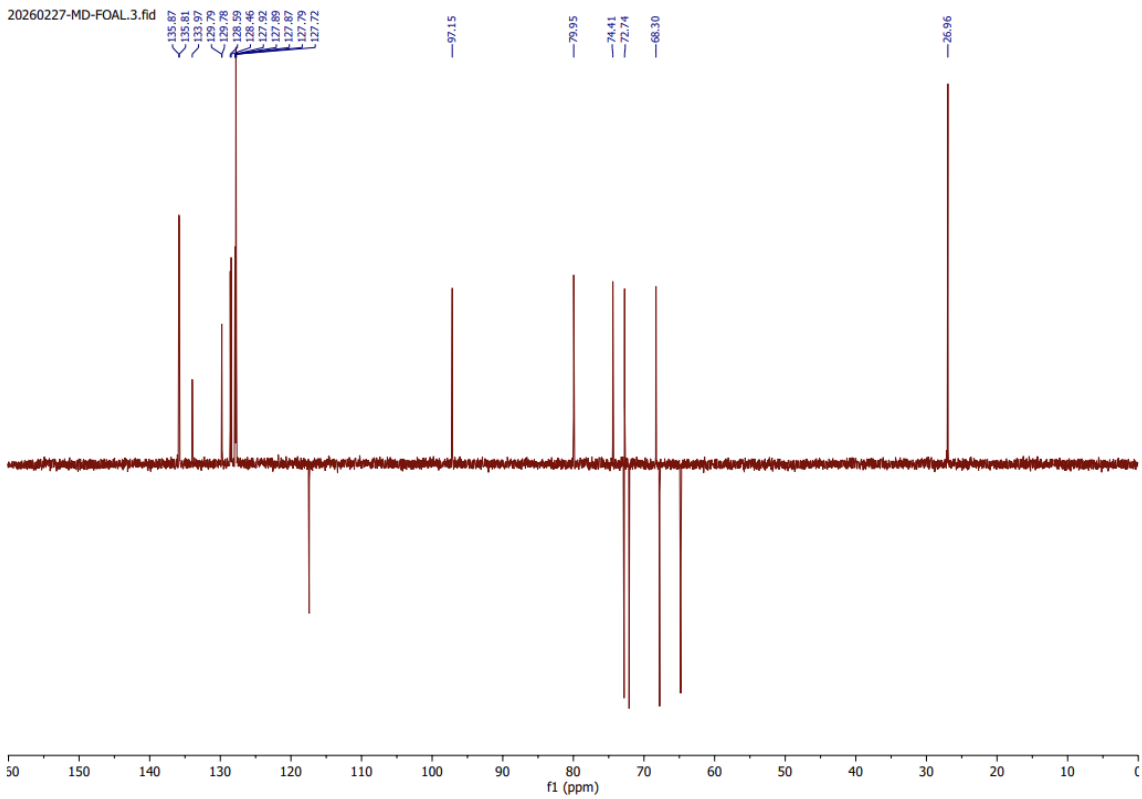
^{1}H-NMR (at 400 MHz) in $CDCl_3$ of Model System (2.4)



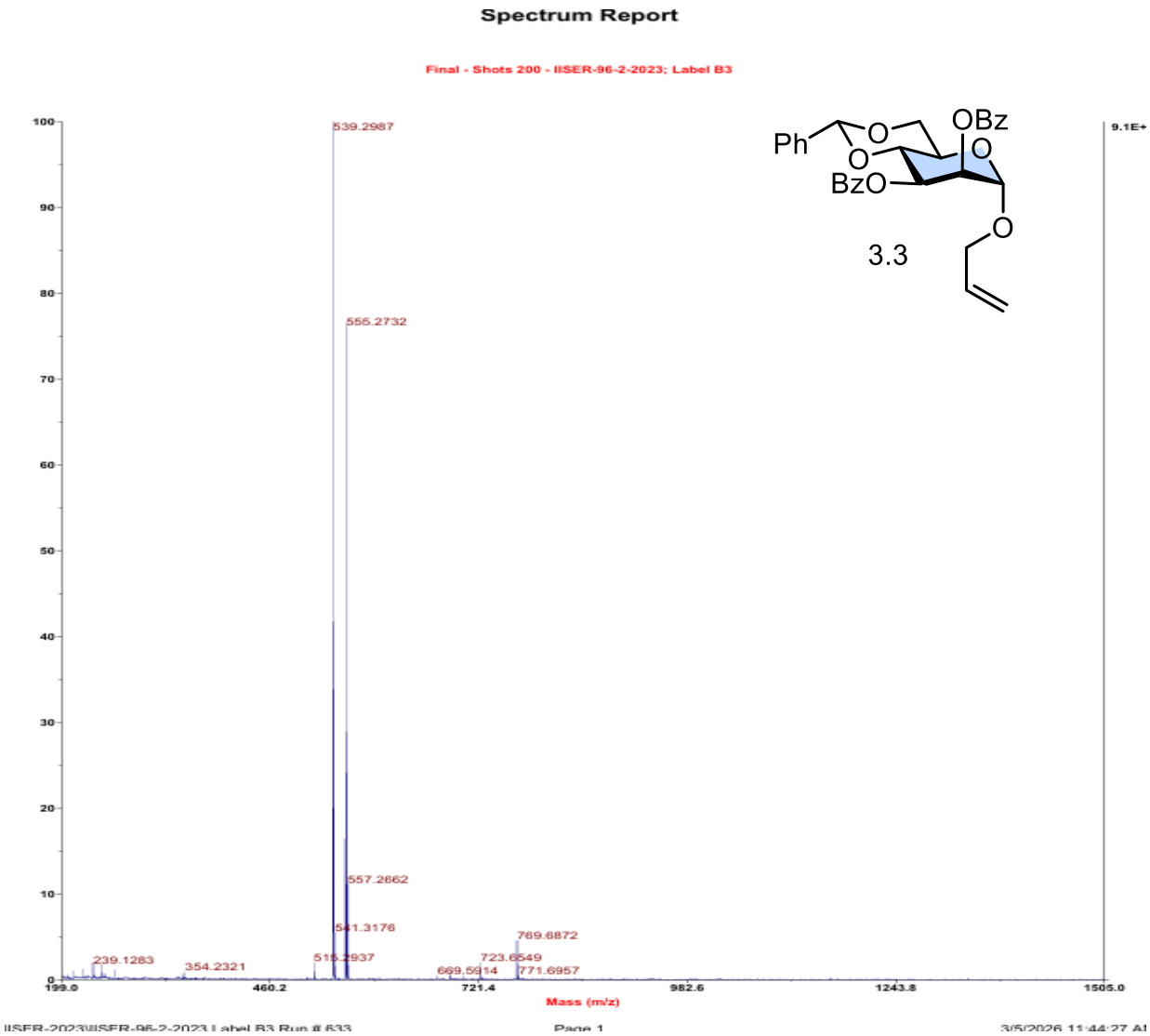
^{1}H-NMR (at 400 MHz) in $CDCl_3$ of Model System (2.6)



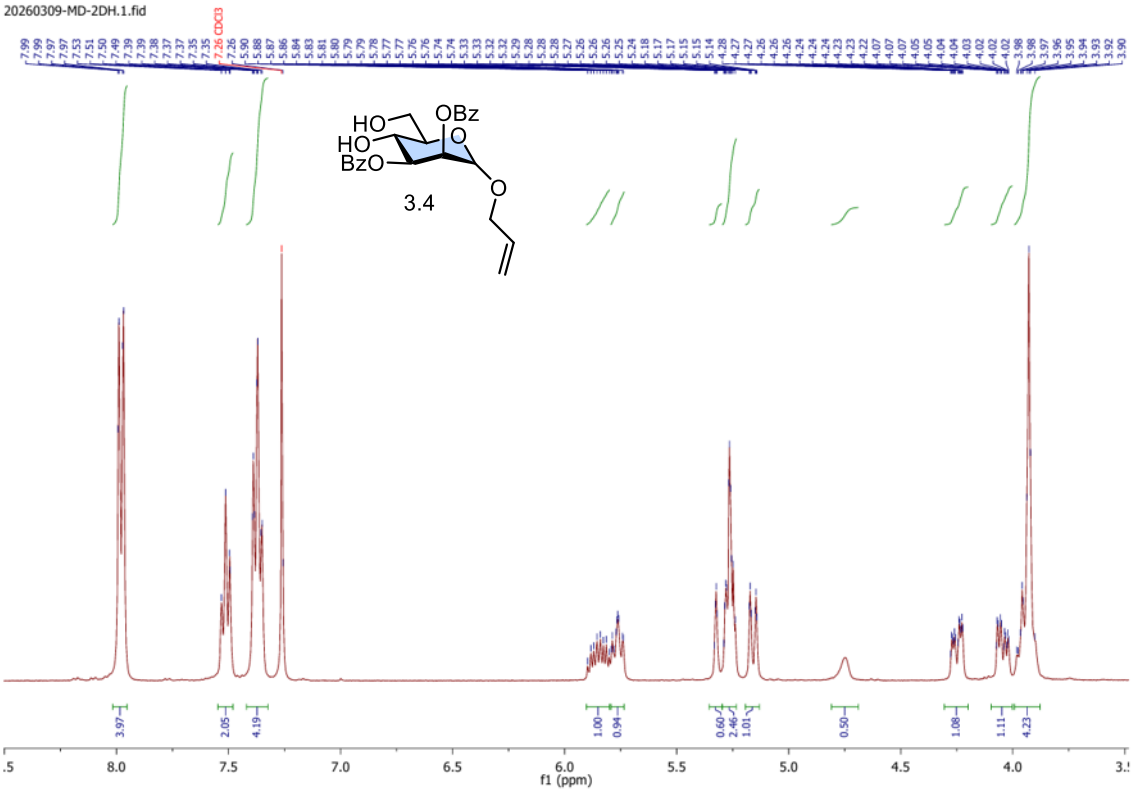
^{13}C-NMR (at 400 MHz) in $CDCl_3$ of Model System (2.6)



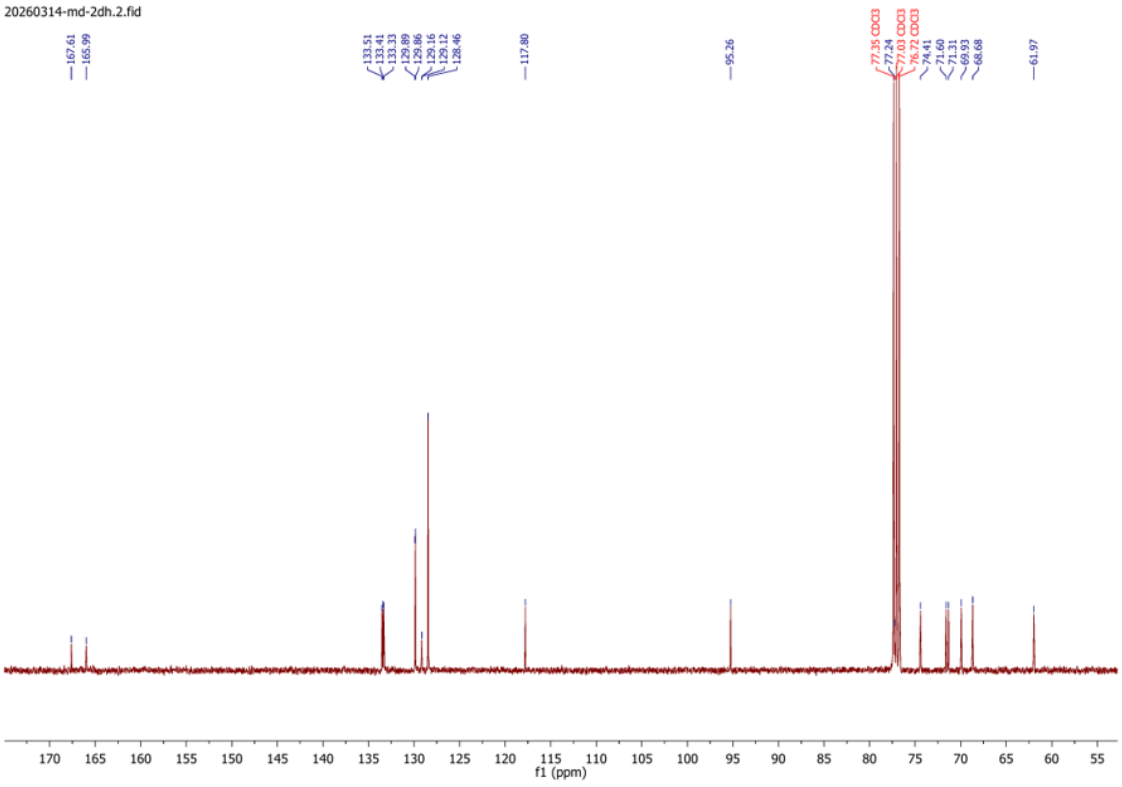
DEPT-135 NMR (at 400 MHz) in $CDCl_3$ of Model System (2.6)



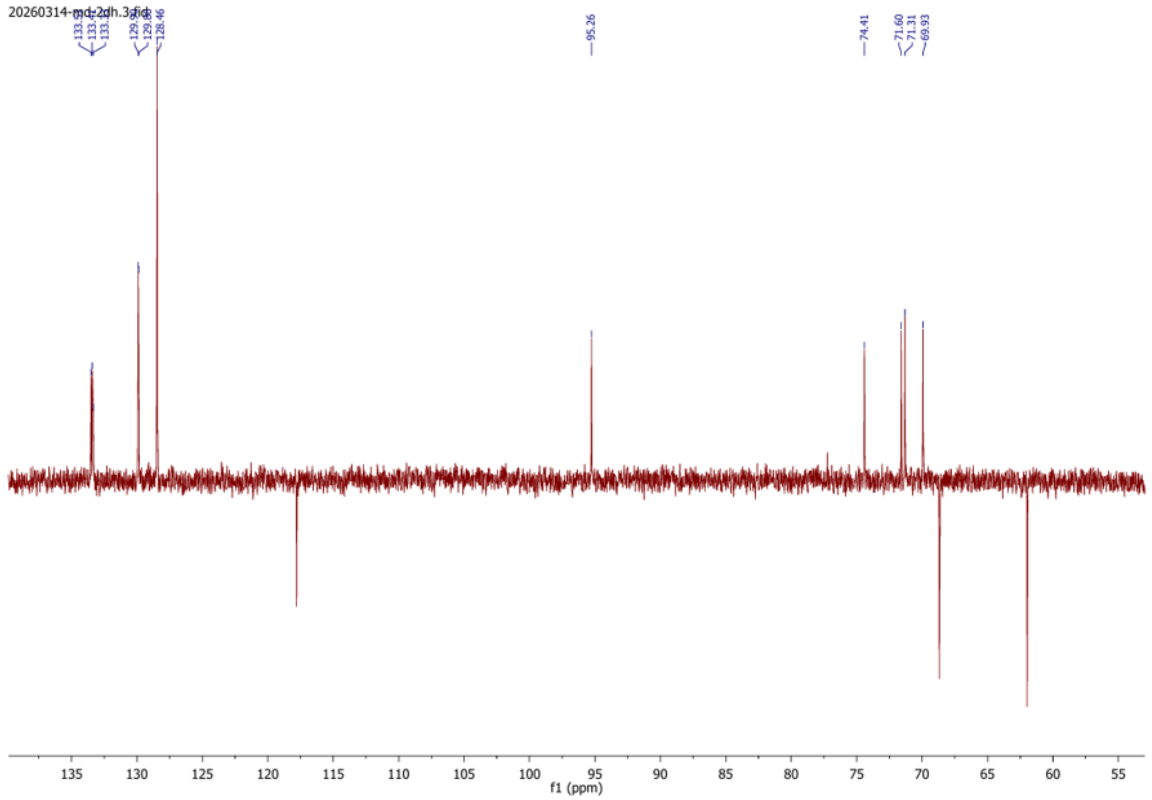
MALDI-TOF plot OF – 3.3 MODEL SYSTEM



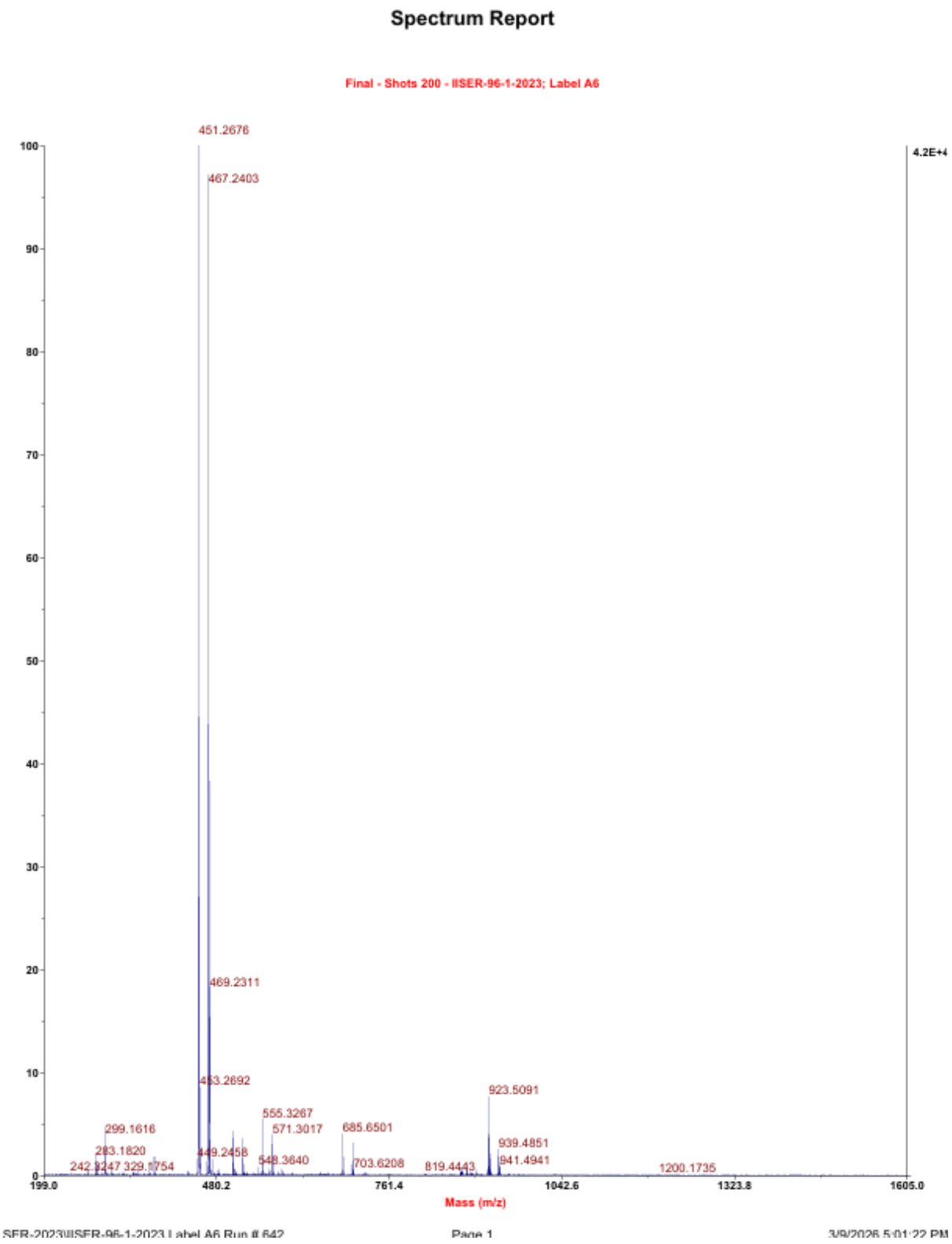
^{1}H-NMR (at 400 MHz) in $CDCl_3$ of Model System (3.4)



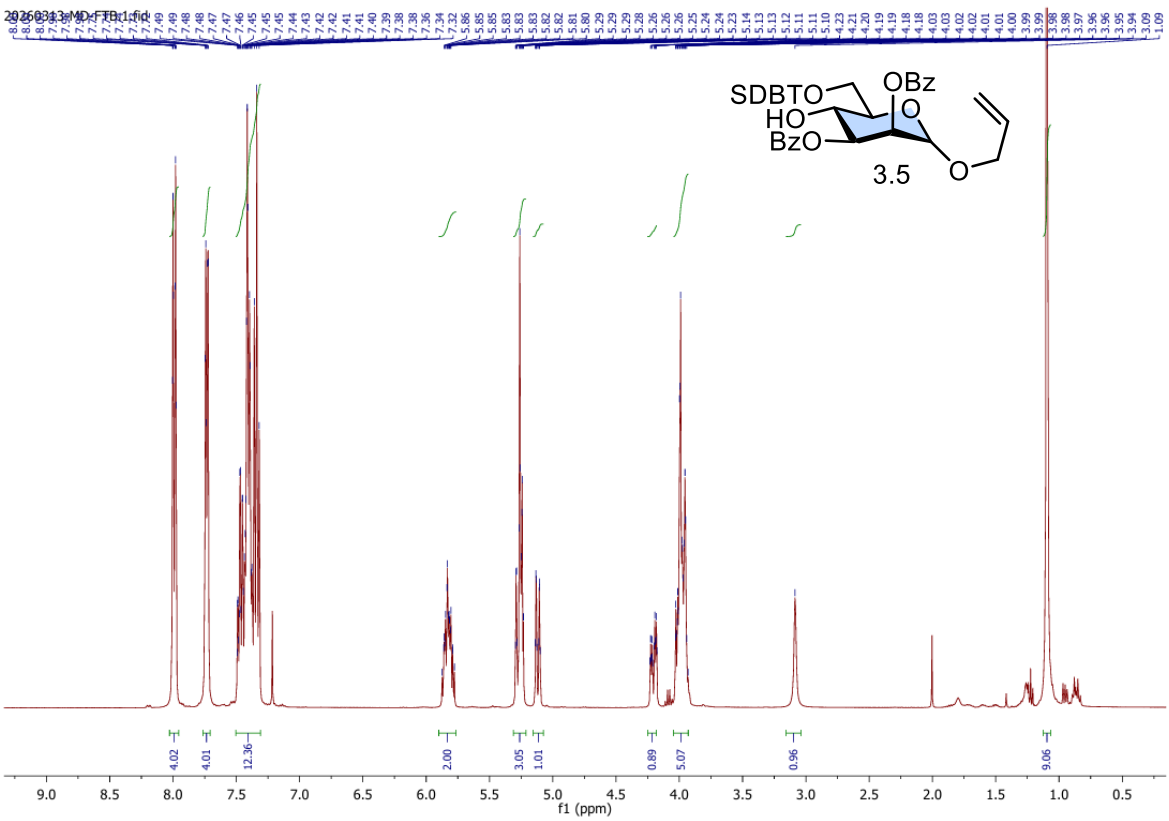
^{13}C-NMR (at 400 MHz) in $CDCl_3$ of Model System (3.4)



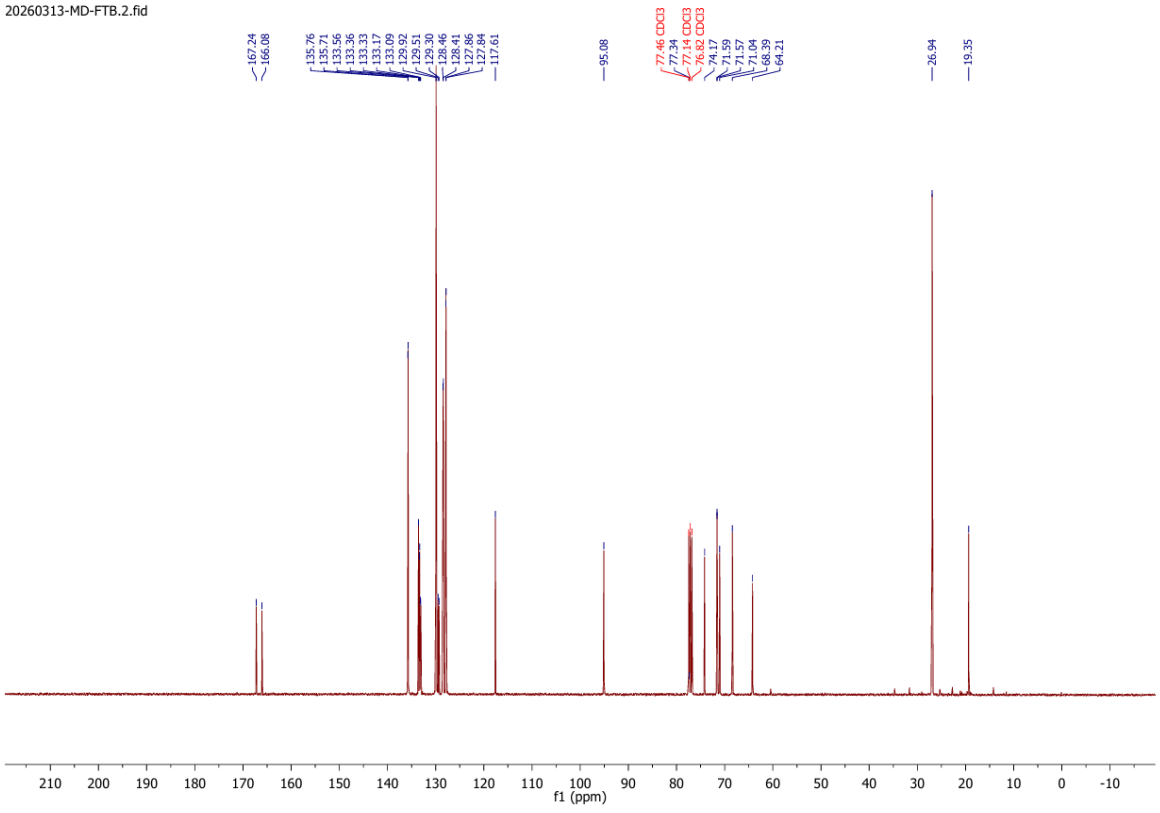
DEPT-135 NMR (at 400 MHz) in $CDCl_3$ of Model System (3.4)



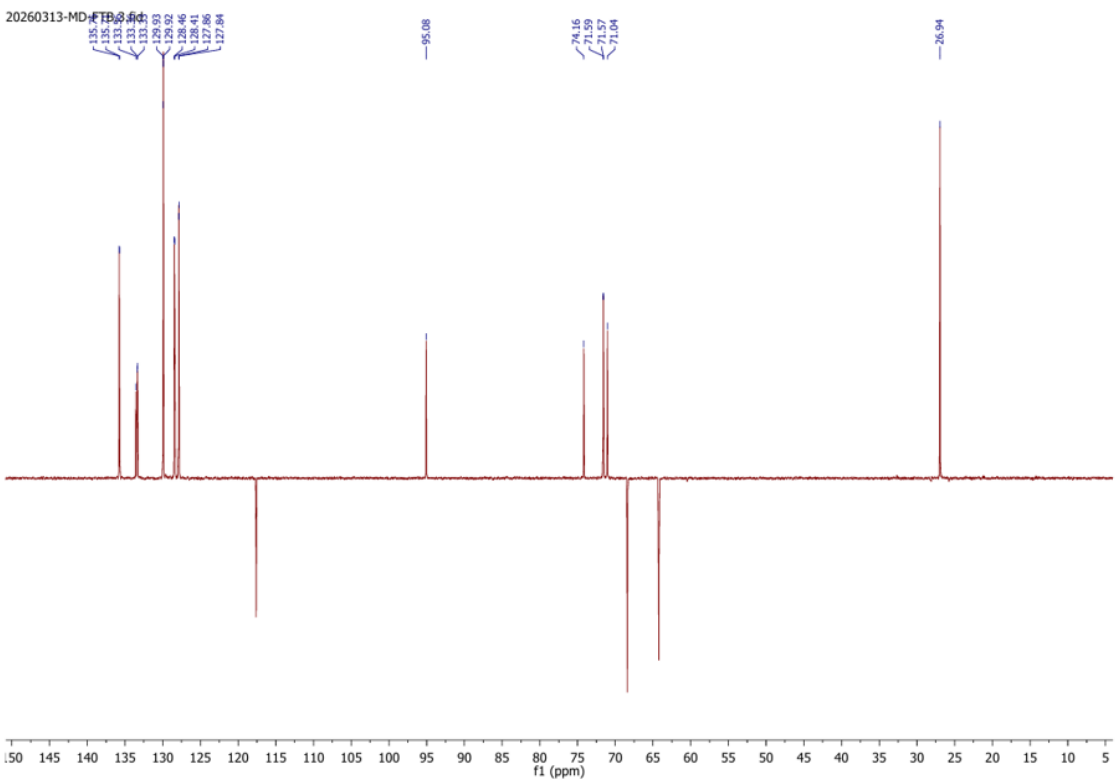
MALDI-TOF plot OF Moiety- 3.4



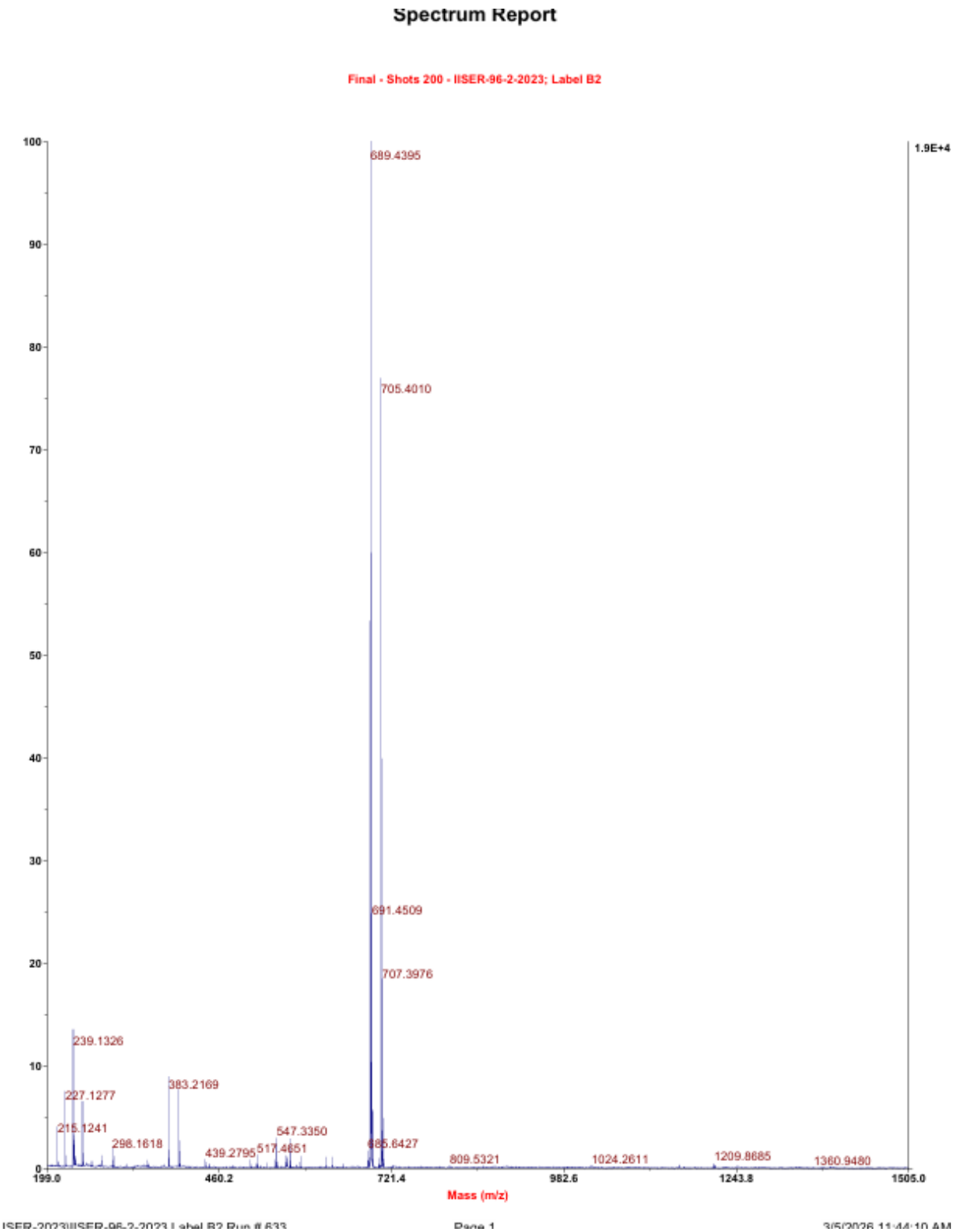
^{1}H-NMR (at 400 MHz) in $CDCl_3$ of Model System (3.5)



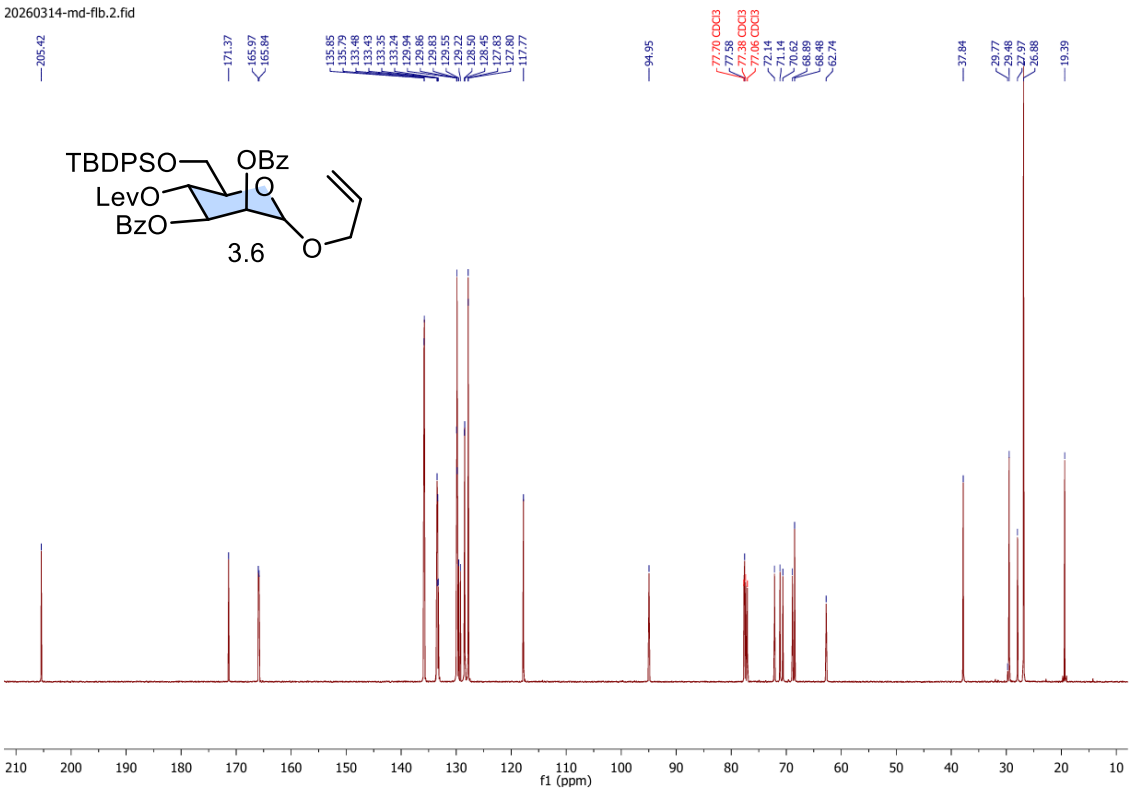
^{13}C-NMR (at 400 MHz) in $CDCl_3$ of Model System (3.5)



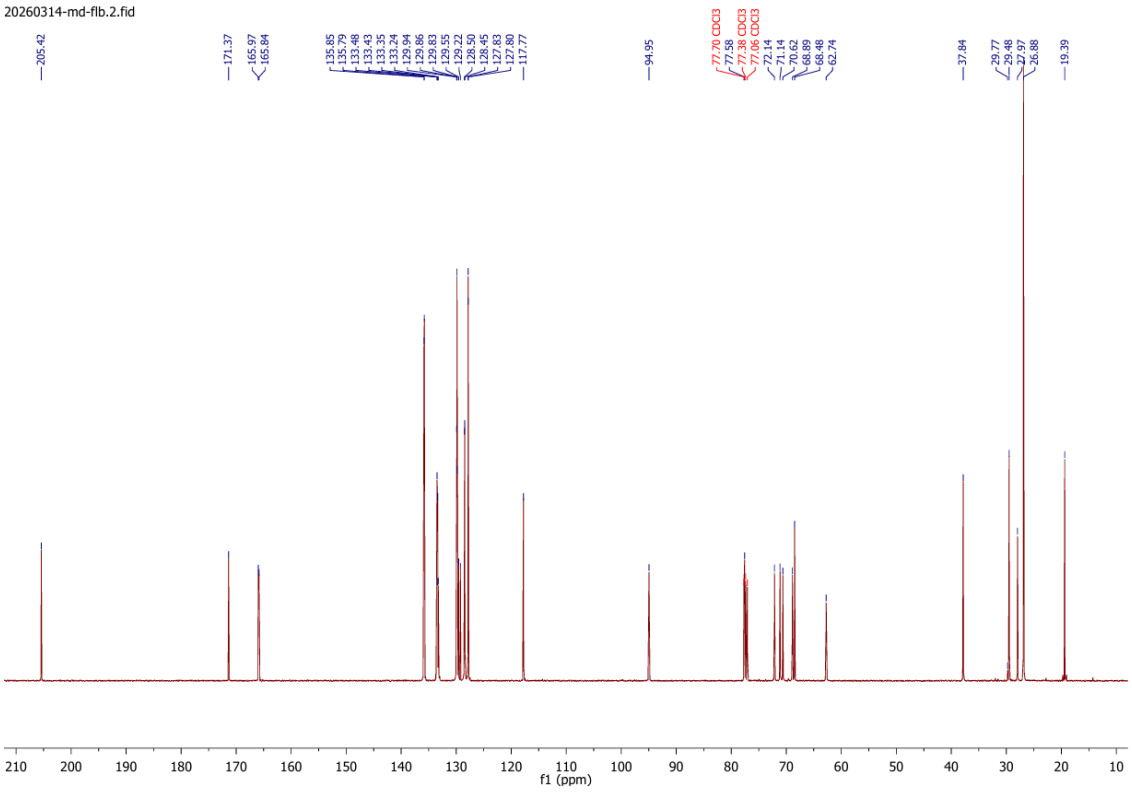
DEPT-135 NMR (at 400 MHz) in $CDCl_3$ of Model System (3.5)



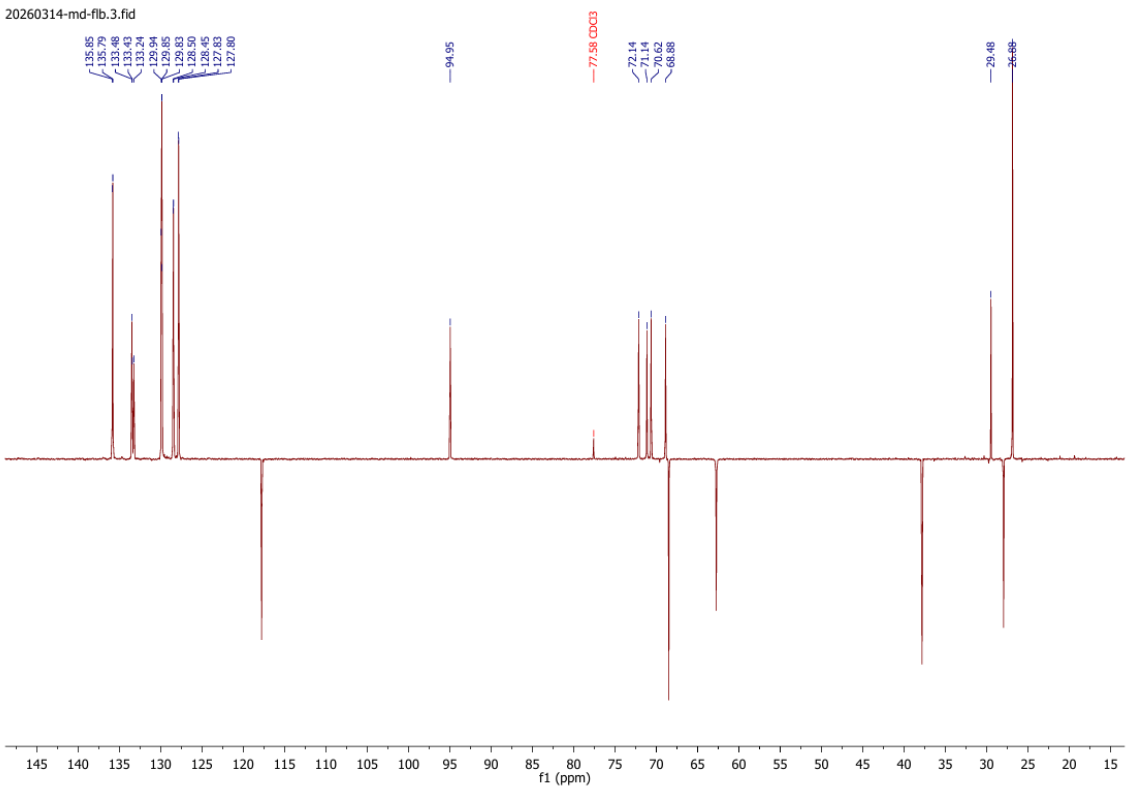
MALDI-TOF plot OF Moiety - 3.5



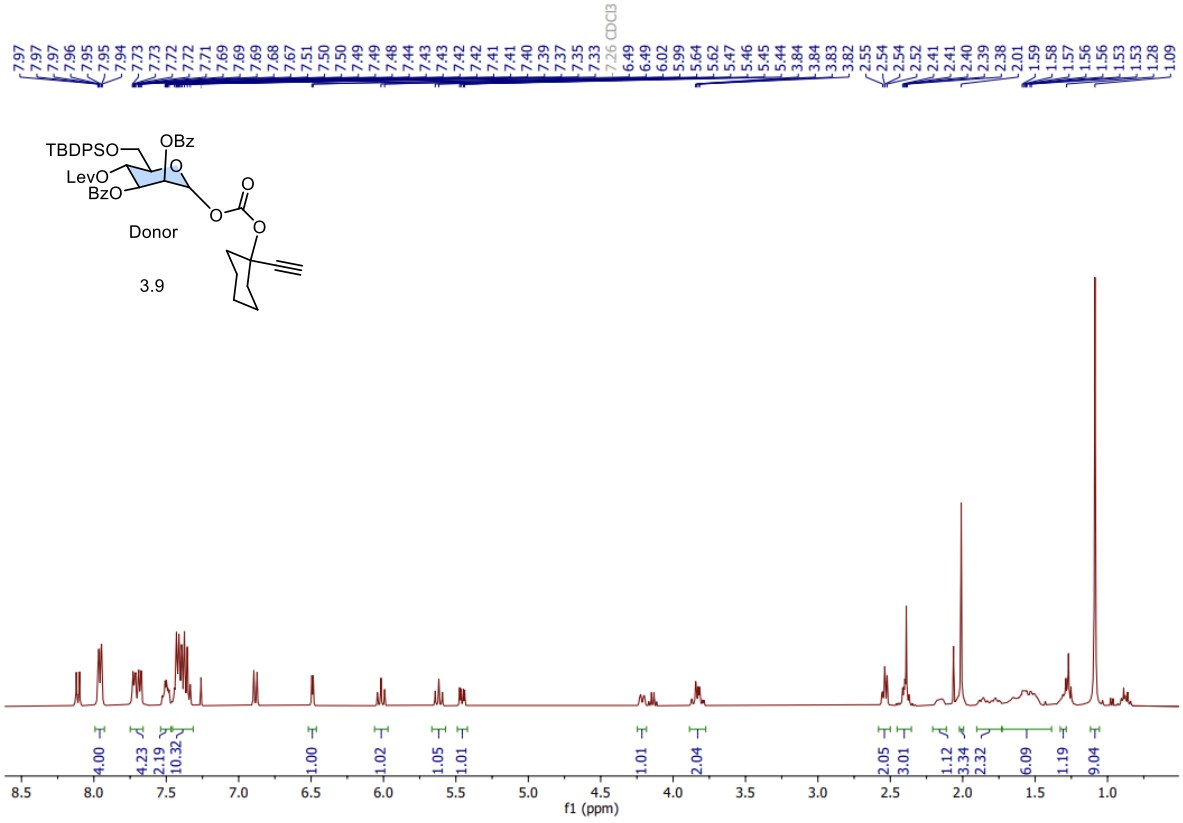
^{1}H-NMR (at 400 MHz) in $CDCl_3$ of Model System (3.6)



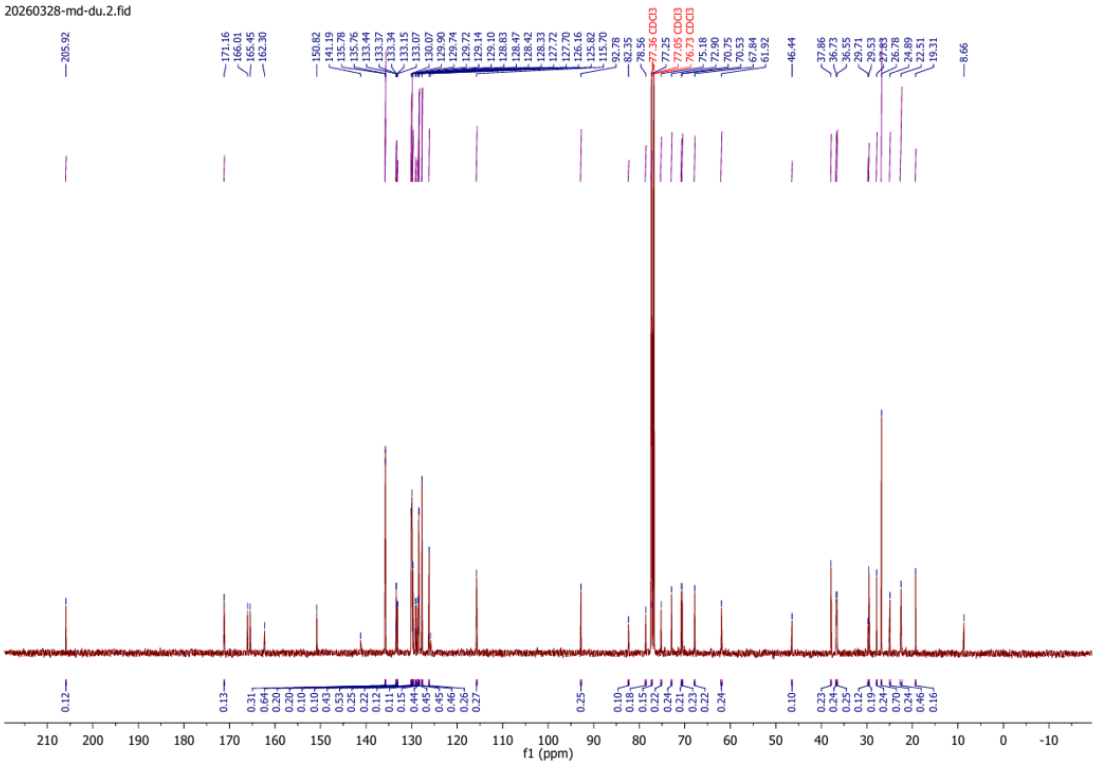
^{13}C-NMR (at 400 MHz) in $CDCl_3$ of Model System (3.6)



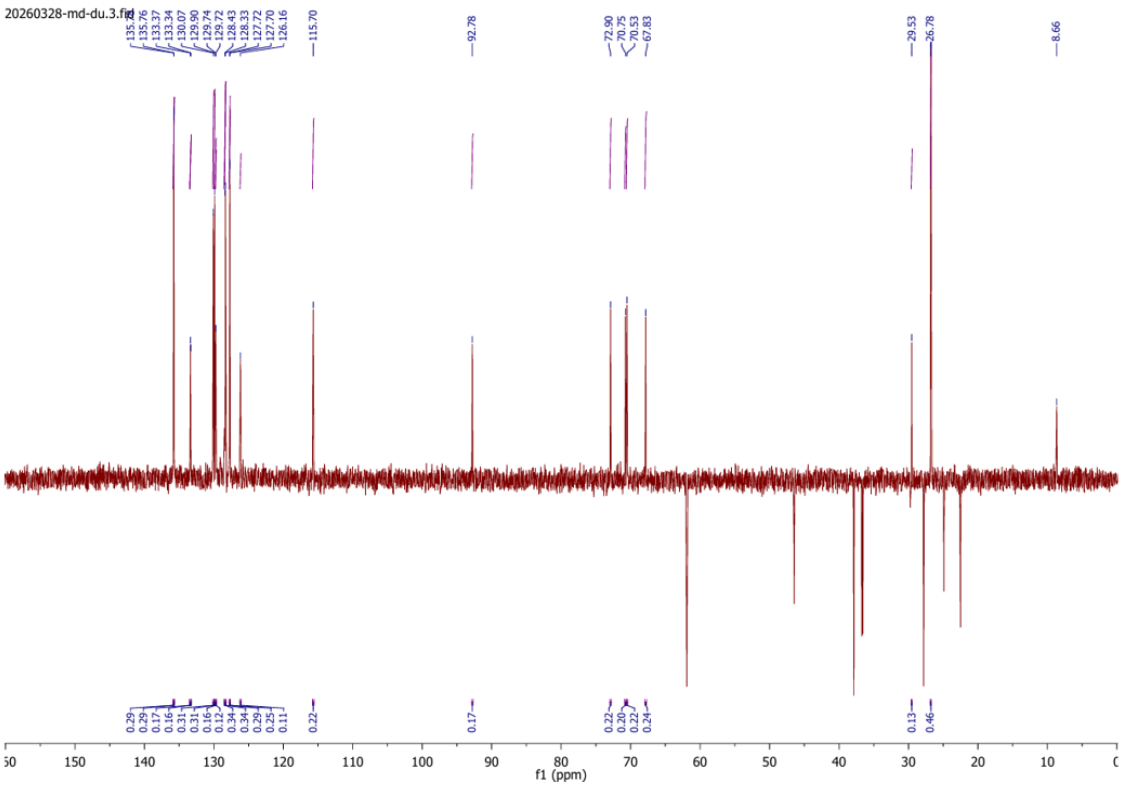
DEPT-135 NMR (at 400 MHz) in $CDCl_3$ of Model System (3.6)



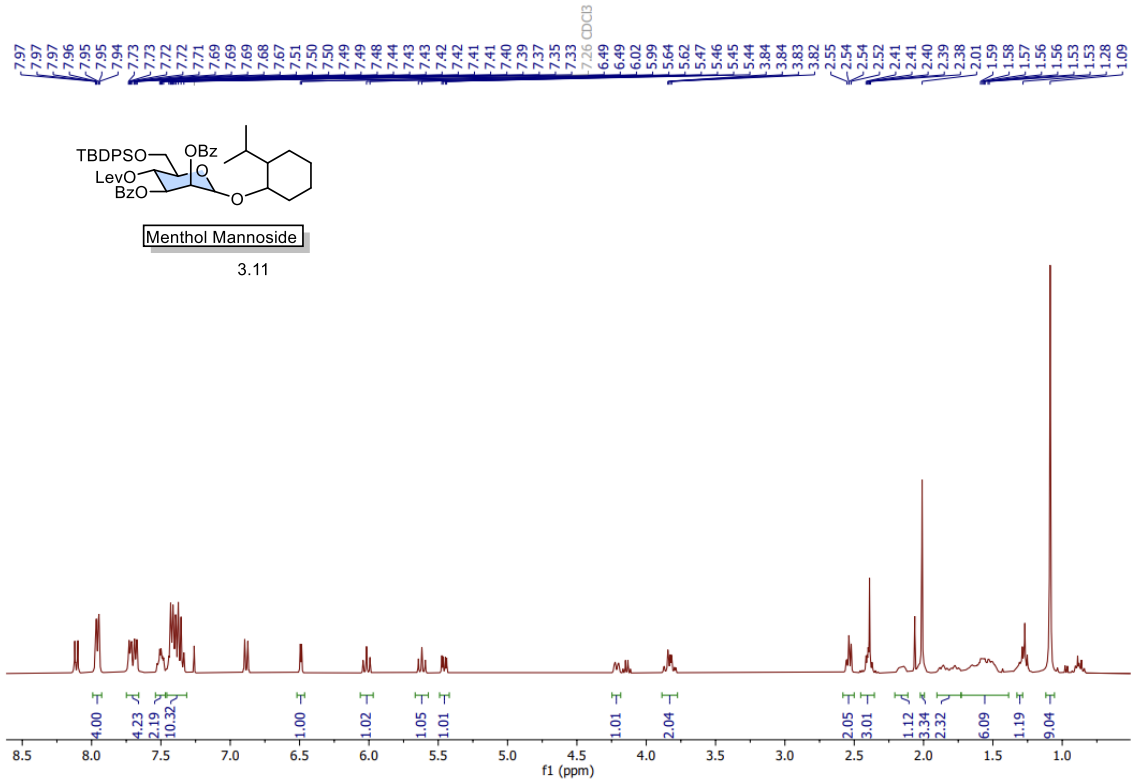
^{1}H-NMR (at 400 MHz) in $CDCl_3$ of Model System (3.9)



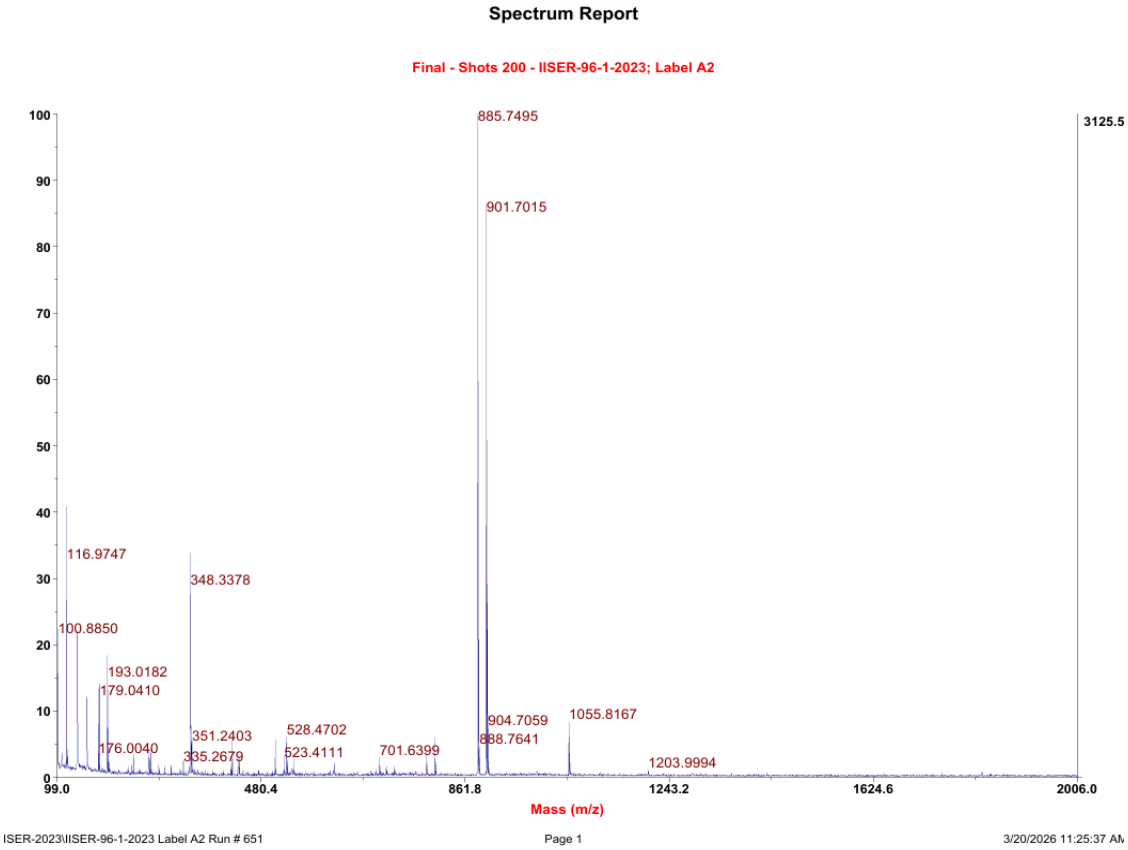
^{13}C-NMR (at 400 MHz) in $CDCl_3$ of Model System (3.9) MSc thesis



DEPT-135 NMR (at 400 MHz) in $CDCl_3$ of Model System (3.9)



^{1}H-NMR (at 400 MHz) in $CDCl_3$ of Model System (3.11)



MALDI-TOF plot of moiety- 3.11

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