Silver-assisted Gold-catalysed Synthesis of Glyco-Calix[4]arenes

A THESIS

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS OF THE DEGREE OF

Master of Science

by

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Under the Supervision of

Prof. Srinivas Hotha

2025

Certificate

This is to certify that this dissertation entitled **"Silver-assisted Gold-catalysed Synthesis of Glyco-Calix[4]arenes**" towards the partial fulfilment of the MS degree program at the Indian Institute of Science Education and Research, Pune represents study/work carried out by **"GEDE KAMDA"** under the supervision of "Prof. Srinivas Hotha, Department of Chemistry" during the academic year 2024-2025.

Date: 30 March 2025
Pune (MH), India

Srinivas Hotha

Declaration

I hereby declare that the matter embodied in the report entitled **"Silver-assisted Gold-catalysed Synthesis of Glyco-Calix[4]arenes "** are the results of the work carried out by me at the Department of Chemistry , IISER Pune, under the supervision of **Prof. Srinivas Hotha** and the same has not been submitted elsewhere for any other degree.

Date: 30 March 2025
Pune (MH), India

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This small piece of work is dedicated to them.

Gede Kamda

ABBREBIATION:

Å	Angstrom
Ag	Silver
AgOTf	Silver Triflate
Au	Gold
Ac	Acetate
AcCl	Acetyl chloride
AllOH	Allyl Alcohol
Bn	Benzyl
Bz	Benzoyl
BzCl	Benzoyl Chloride
BBN	9-Borabicyclo[3.3.1]nonane
$CDCl_3$	Deuterated Chloroform
CH_2Cl_2 / DCM	Dichloromethane
DEPT-135	Distortionless Enhancement by Polarization Transfer(135^0)
DMAP	N, N-Dimethyl aminopyridine
Eq.	Equivalents
EtOAc	Ethyl Acetate
h	Hour
Hz	Hertz
J	Coupling Constant
H_2O_2	Hydrogen Peroxide
mg	Milligram
Min	Minute
mL	Millilitre

MeOH	Methanol
MS	Molecular Sieve
NaOH	Sodium Hydroxide
Na_2SO_4	Sodium Sulfate
rt	Room Temperature
TLC	Thin Layer Chromatography
THF	Tetrahydrofuran
H_2O	Water

Abstract

In this study, glycosylation of calix[4]arenes was explored utilizing silver-assisted gold-catalyzed conditions. We have optimized reaction conditions for higher yields and selectivity. Alkynyl glycosyl carbonate donors were used due to their stability and efficiency. [Au]/[Ag]-catalysis enabled regio- and stereoselective glycosylation under mild conditions, avoiding the drawbacks of acid-based methods. Thus synthesized glycosylated calix[4]arenes would improve the solubility and bioactivity, making them promising candidates for further biomedical applications. These findings provide a sustainable and effective approach for carbohydrate-based molecular modifications.

Contents

Introduction

Carbohydrates:

Carbohydrates are among the most prevalent and widely researched organic molecules found on Earth's surface. These molecules are primarily comprised of carbon, hydrogen, and oxygen atoms, typically arranged in a 1:2:1 ratio. This composition aligns with the general molecular formula $(CH_2O)n$, here 'n' display the number of carbon atoms in the structure.[1] Carbohydrates are among the most prevalent biomolecules in Nature, performing essential functions in living organisms. They contribute to the structural framework of cells, play key roles in biological interactions such as cell adhesion, mediate host-pathogen recognition, and act as crucial reservoirs for energy production and storage. Their diverse roles make them indispensable for maintaining life and ensuring proper cellular function.[2]

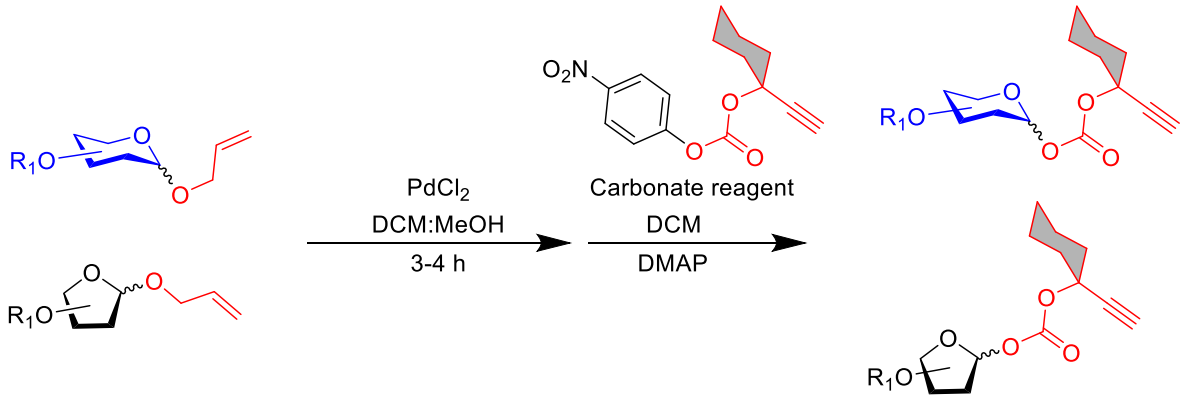
Glycosyl donors:

Glycosyl donors are fundamental building blocks in synthetic carbohydrate chemistry, enabling the formation of glycosidic bonds necessary for the construction of complex oligosaccharides and glycoconjugates. These specialized molecules act as reactive sugar intermediates, undergoing activation under specific conditions to transfer a glycosyl group to an acceptor molecule. The efficiency and selectivity of this transfer process depends largely on the nature of the glycosyl donor and its activation strategy. Over the years, a diverse array of glycosyl donors, such as glycosyl halides, trichloroacetimidates, and thioglycosides, have been widely used. However, these conventional donors often require harsh conditions, strong acids, or base catalysts, leading to side reactions, poor selectivity, or instability.

Hotha and his research team made a significant breakthrough in this field, introducing alkynyl glycosyl carbonate donors as an efficient alternative. These donors stand out due to their high stability, excellent regio- and stereoselectivity, and compatibility with catalytic activation methods. Unlike traditional glycosyl donors, alkynyl glycosyl carbonates are remarkably stable, allowing for easier storage and handling without the risk of decomposition.[3]

One of the most remarkable features of alkynyl glycosyl carbonates is their ability to be selectively activated using gold (Au) and silver (Ag) catalysts. The presence of an alkyne functionality within the glycosyl donor enhances its reactivity, allowing for precise catalytic

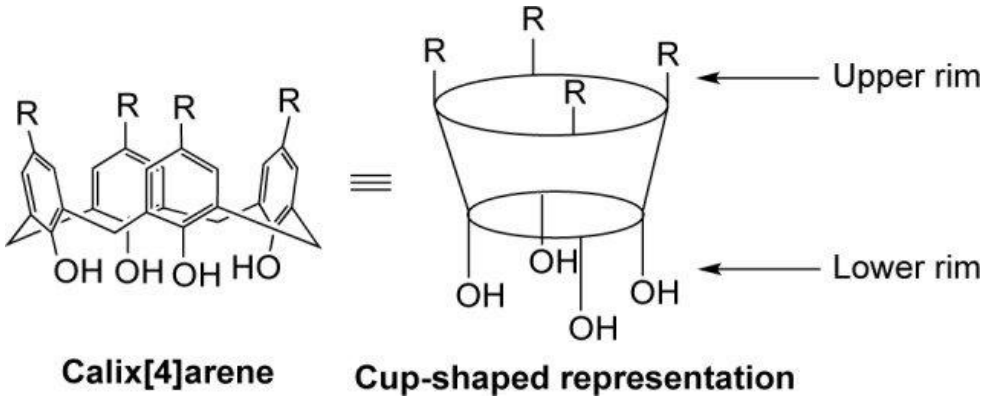
activation under mild reaction conditions. This strategic incorporation of an alkynyl group eliminates the need for strong acid-based promoters, making the glycosylation process more efficient and controlled. The carbonate donors could be efficiently activated at rt within a short reaction time (approximately 15 min), yielding highly selective and exceptional stability glycosylation products. They maintained their reactivity over extended periods, making them an ideal choice for glycosylation.



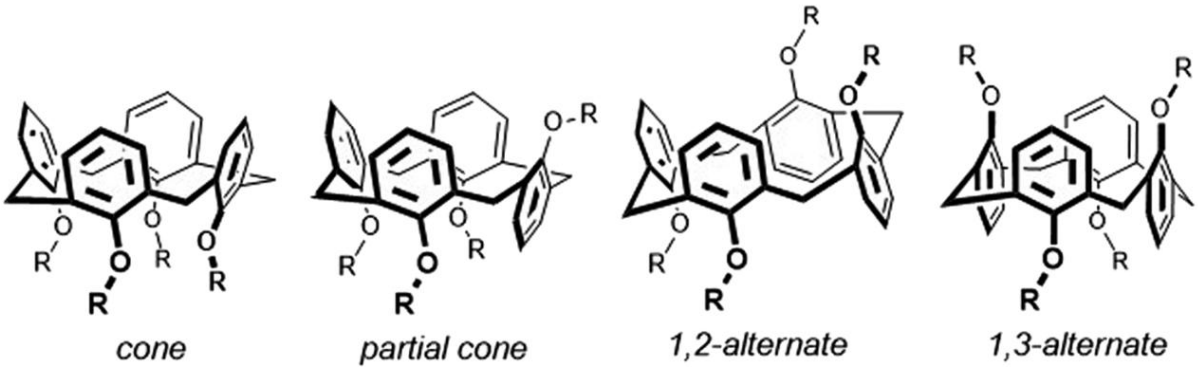
Scheme 1. *Synthesis of ethynylcyclohexyl glycosyl donors*

Calixarenes :

Calixarenes belong to a group of macrocyclic compounds which have attracted significant interest due to their versatility in supramolecular chemistry. These cyclic oligomers are synthesized through the condensation of phenols with formaldehyde, yielding a rigid structure with a well-defined cavity. The calixarene framework can be tailored by modifying the upper and lower rims, enabling a wide range of functionalization strategies.



The unique structural attributes of calixarenes allow them to act as molecular hosts. Their hydrophobic cavities provide a favorable environment for guest molecules, facilitating the development of molecular sensors, ion transport systems, and drug delivery platforms. The conformational flexibility of calixarenes, dictated by the number of repeating phenol units, further enhances their ability to accommodate different guest species. Depending on their functionalization, calixarenes can adopt various conformations, such as cone, partial cone, 1,2-alternate, and 1,3-alternate forms, each with distinct binding properties.



The functionalization of calixarenes has led to their application in diverse fields, ranging from environmental remediation to medicinal chemistry. In drug delivery, calixarenes have been explored as nanocarriers that improve the solubility and stability of therapeutic agents. Their capability to establish host-guest interactions with biomolecules has also made them useful in biosensing applications, where they serve as recognition elements for detecting toxins, viruses, and proteins. The introduction of glycosylation to calixarene chemistry further expands their potential by enhancing their H_2O solubility and bioactivity, making them particularly attractive for biomedical applications.[4,5]

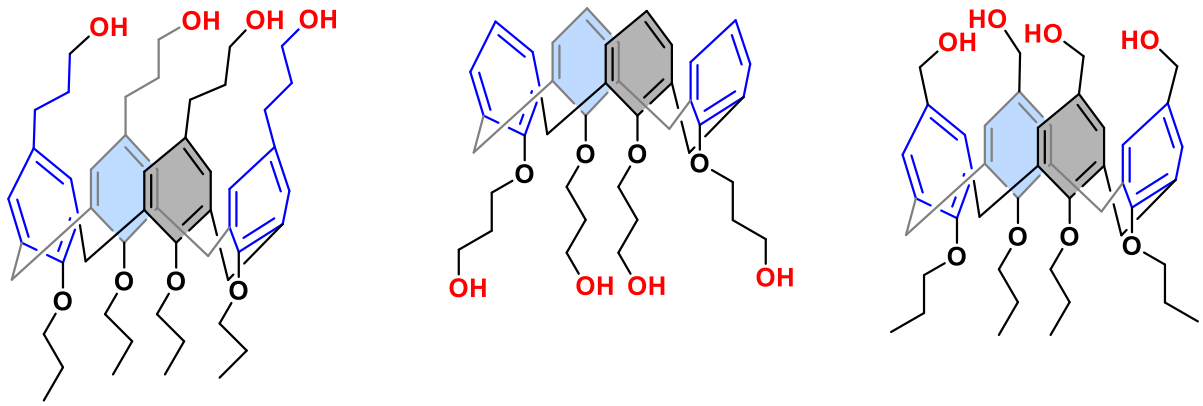
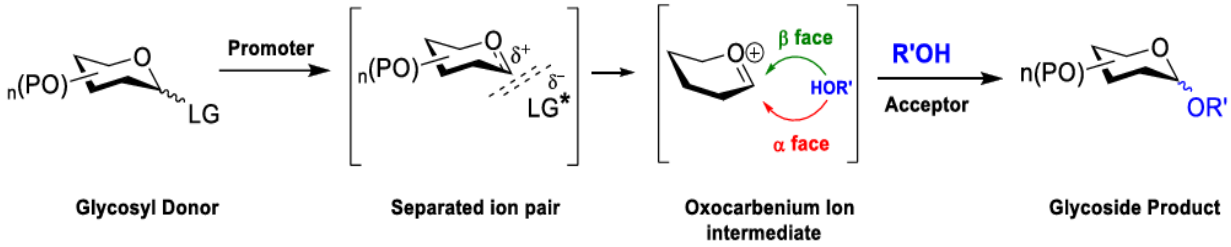


Figure 1. *Calixarene-tetrols*

Glycosylation:

The advancement of catalytic methodologies in organic synthesis has significantly enhanced the efficiency and selectivity of glycosylation reactions, which are essential for synthesizing oligosaccharides, glycoconjugates, and biologically relevant carbohydrates. Among the emerging catalytic strategies, [Au]/[Ag]-catalysis has proven to be a highly effective approach for promoting glycosidic bond formation under mild conditions. Hotha's group has extensively studied this dual-metal catalytic system and have demonstrated its remarkable potential in regio- and stereoselective glycosylation by synthesizing many giant oligosaccharides.[6]

The fundamental principle behind [Au]/[Ag]-catalyzed glycosylation lies in the synergistic activation of glycosyl donors by both the metals. Au(I) serves as a soft Lewis acid and alkyne activator, stabilizing the oxocarbenium ion intermediate—a highly reactive species that plays a crucial role in glycosylation. This stabilization minimizes undesired side reactions and enhances selectivity in the glycosidic bond formation. Silver triflate (AgOTf), on the other hand, scavenges the chloride ion and also perhaps facilitates the extrusion of the leaving group thereby increasing the electrophilic nature of the anomeric carbon and facilitating nucleophilic attack by the acceptor molecule. The combined action of Au and Ag catalysts ensures high reaction efficiency, faster reaction rates, and superior control over α- and β-anomeric selectivity.[7]



A key advantage of [Au]/[Ag]-catalysis over traditional acid-promoted glycosylation methods is the ability to perform glycosylation under neutral or near-neutral conditions, making it compatible with functionalized and sensitive carbohydrate substrates. Conventional glycosylation approaches often require strong acids or bases, leading to substrate degradation, side-product formation, and poor selectivity. In contrast, [Au]/[Ag]-catalysis provides a controlled and mild reaction environment, ensuring that even complex glycosyl donors, such

as carbonate-based donors, can undergo efficient glycosylation with minimal byproduct formation.[6]

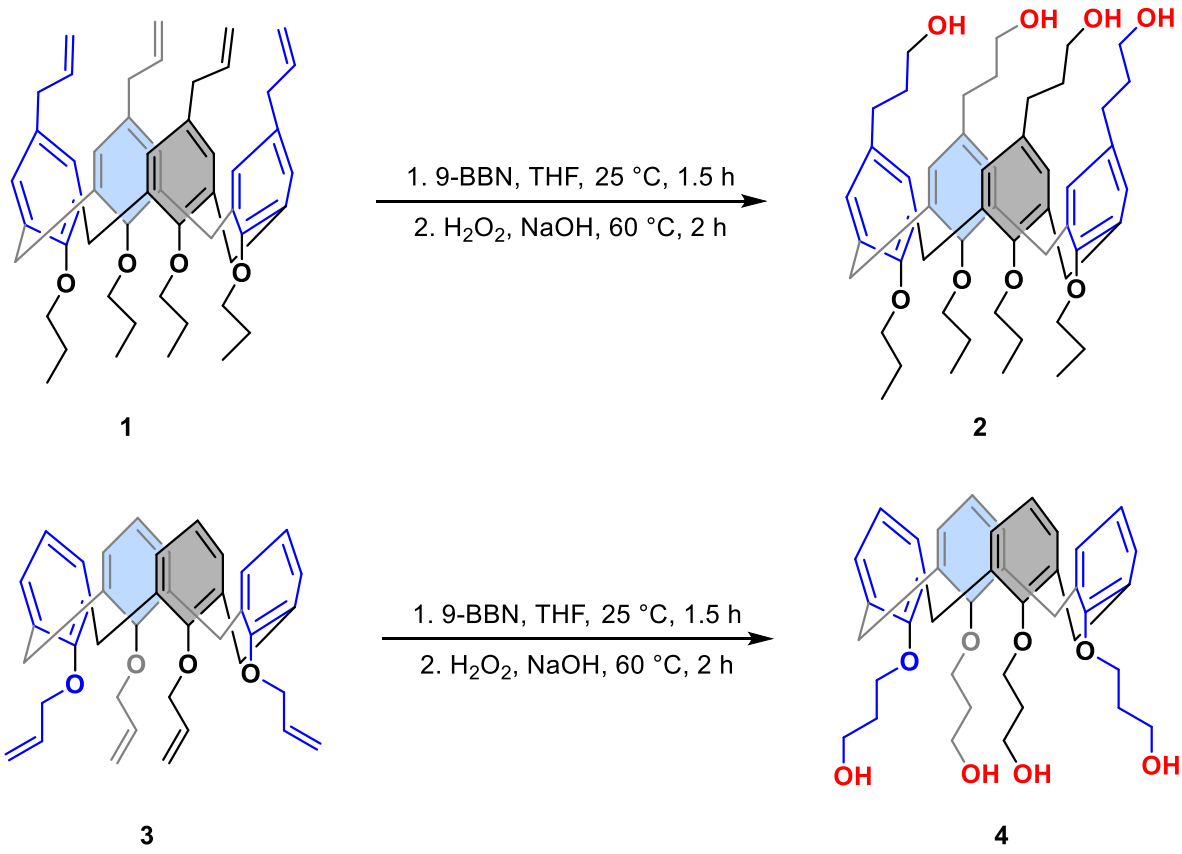
Beyond its applications in glycosylation, [Au]/[Ag]-catalysis is also an attractive green chemistry alternative due to its mild conditions, reduced energy requirements, and high atom efficiency. The recyclability of Au and Ag catalysts further contributes to the sustainability of this method. As research continues, refinements in [Au]/[Ag]-catalytic systems will likely lead to even greater efficiency, expanding their role in drug discovery, vaccine development, and biomedical research.

Statement of the goal of the project:

The goal of this project is to advance an efficient and selective method for the glycosylation of calix[4]arenes using silver-assisted gold catalysis. Traditional glycosylation methods often face challenges such as poor regio- and stereoselectivity, harsh reaction conditions, and limited functional group tolerance. To address these issues, this study focuses on utilizing alkynyl glycosyl carbonate donors, which provide enhanced stability and allow for catalytic activation under mild conditions. By optimizing reaction parameters, this research aims to establish a high-yielding and stereoselective glycosylation strategy while investigating the synergistic role of Au and Ag catalysts in promoting glycosidic bond formation. Additionally, functionalization through glycosylation is expected to improve the solubility and bioactivity of calixarenes, making them more suitable for applications of drug delivery and molecular recognition. The findings of this study will contribute to the advancement of carbohydrate-functionalized macrocycles and broaden their potential use in supramolecular chemistry and biomedical research.

Methodology:

Calix[4]arene were prepared by Alberto et. al. (Scheme 2)

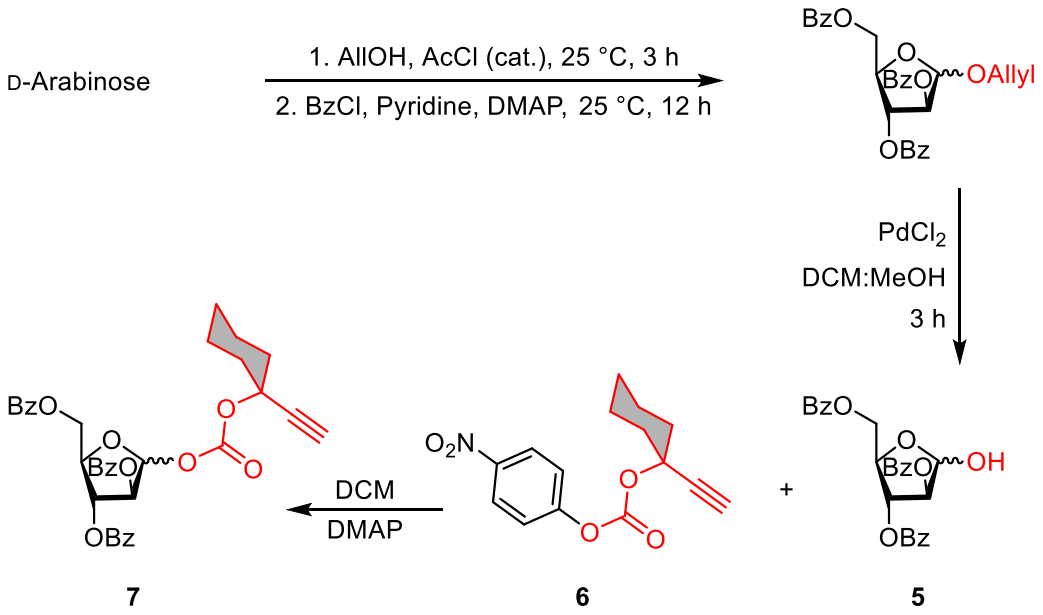


Scheme 2. *Synthesis for upper rim and lower rim calixarene-tetrols*

The tetraols present in the calix[4]arene are highly reactive and they can form ether bonds quite easily under acidic conditions as noticed by Marra et al. Attempted glycosylation using these tetraols resulted in the isolation of multimeric glycosides in very poor to moderate yields; the major product of the reaction being the cross reacted ethers. In this premise, we hypothesized that mild conditions offered by the [Au]/[Ag]-catalyzed glycosidations will be ideal for synthesizing glycosides of suitably substituted calix[4]arene derivatives. Accordingly, our synthesis efforts started with the preparation of glycosyl donors. We chose to work with furanosyl and pyranosyl glycosyl donors.

Results and Discussion:

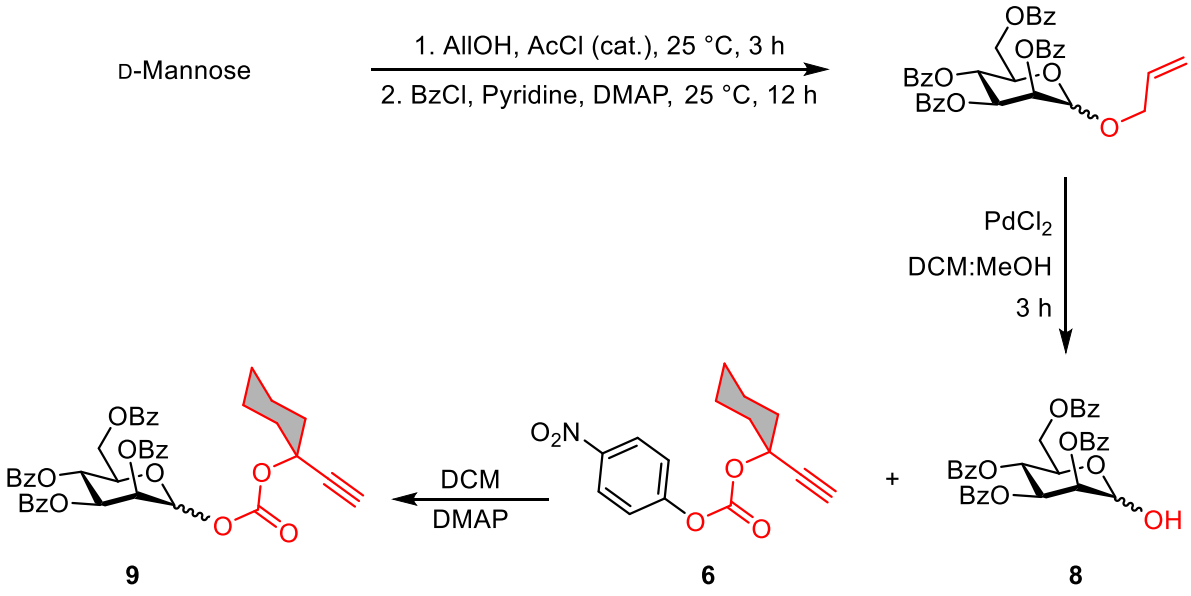
Synthesis of glycosyl donors



Scheme 3. *Synthesis of Arabinofuranosyl carbonate donor*

In a nitrogen atmosphere, a solution of readily available 2,3,5-tri-O-benzoyl arabinofuranose **5** (1.00 mmol) and p-nitrophenyl carbonate **6** (1.20 mmol) in anhydrous CH_2Cl_2 with DMAP at 25 °C was stirred for 12 h. Following completion, the rm was diluted with H_2O then subjected to extraction using EtOAc (3 × 50 mL). The combined organic layers were subsequently washed with a brine solution, separated, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure, yielding a yellow residue. This crude product was then purified through silica gel column chromatography, employing 30% EtOAc in hexane as the eluent, affording the arabinofuranosyl donor **7** in an 82% yield.

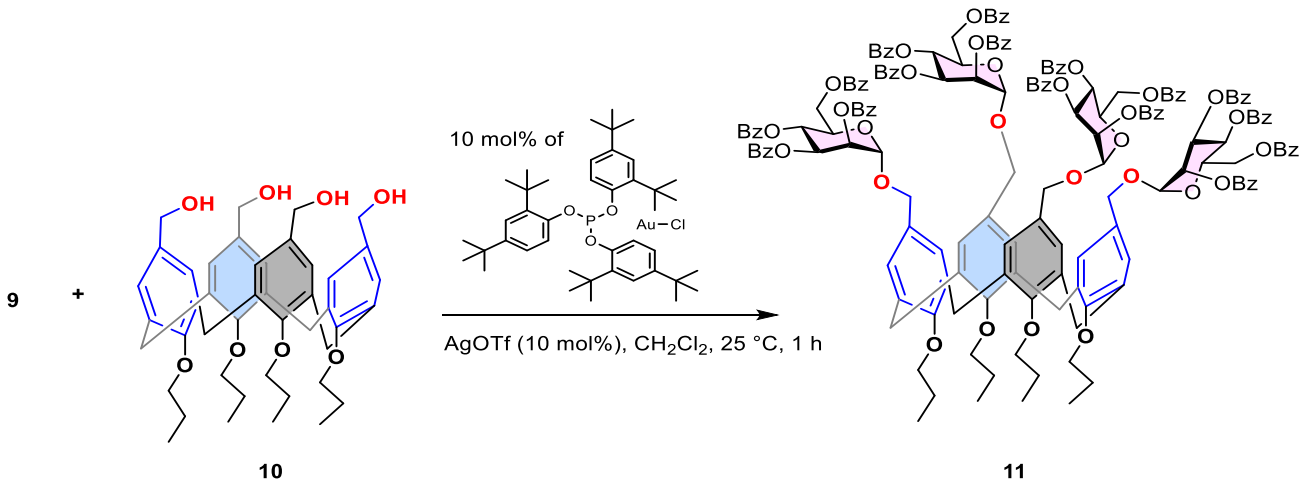
Characterization data of compound **7***:* ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 – 7.94 (m, 6H), 7.65 – 7.50 (m, 3H), 7.54 – 7.28 (m, 7H), 6.83 – 6.32 (m, 1H), 6.06 – 5.81 (m, 1H), 5.77 – 5.54 (m, 1H), 4.82 – 4.75 (m, 1H), 4.74 – 4.56 (m, 1H), 2.66 (s, 1H), 2.45 – 1.87 (m, 4H), 1.76 – 1.13 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.3, 166.3, 165.7, 165.2, 151.0, 133.9, 133.8, 133.8, 133.2, 133.2, 130.3, 130.2, 130.1, 130.1, 130.1, 130.0, 129.9, 129.7, 129.1, 128.8, 128.8, 128.7, 128.7, 128.6, 128.6, 128.6, 128.4, 102.4, 96.9, 83.4, 82.6, 81.3, 80.2, 78.7, 78.4, 77.5, 77.4, 76.8, 76.2, 75.5, 75.2, 75.1, 65.1, 63.6, 37.0, 36.8, 36.7, 36.6, 25.1, 25.0, 22.7, 22.5.



Scheme 4: *Synthesis of Mannopyranosyl carbonate donor*

In a nitrogen condition, a solution of readily available 2,3,4,6-tetra-O-benzoyl mannopyranose **8** (1.00 mmol) and p-nitrophenyl carbonate **6** (1.20 mmol) in anhydrous CH_2Cl_2, along with DMAP at 25 °C was stirred for 12 h. Following completion, the rm was diluted with H_2O then subjected to extraction using EtOAc (3 × 50 mL). The combined organic layers were subsequently washed with a brine solution, separated, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure, yielding a yellow residue. This crude product was then purified through silica gel column chromatography, utilizing 20% EtOAc in hexane as the eluent, affording the mannopyranosyl donor **9** in an 81%.

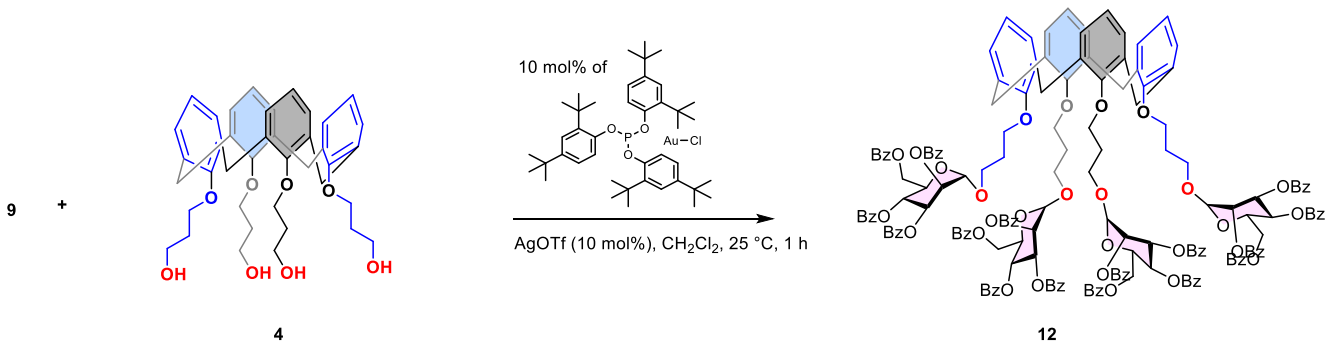
Characterization data of compound **9***:* ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 – 8.00 (m, 6H), 7.99 – 7.74 (m, 5H), 7.58 (ddt, *J* = 16.6, 10.7, 8.3 Hz, 2H), 7.52 – 7.21 (m, 16H), 6.15 – 5.68 (m, 4H), 4.80 – 4.62 (m, 1H), 4.62 – 4.44 (m, 2H), 2.62 (d, *J* = 13.8 Hz, 1H), 2.03 – 1.91 (m, 2H), 1.61 (s, 3H), 1.45 – 1.06 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.2, 165.6, 165. 5, 165.3, 165.2, 150.8, 150.2, 133.8, 133.7, 133.7, 133.6, 133.5, 133.4, 133.2, 130.2, 130.1, 130.1, 130.0, 130.0, 130.0, 129.9, 129.4, 129.1, 129.0, 128.9, 128.9, 128.8, 128.7, 128.6, 128.6, 128.5, 93.7, 93.5, 82.3, 79.4, 79.2, 75.8, 75.6, 73.4, 71.5, 71.0, 69.8, 69.3, 68.8, 66.5, 66.4, 62.8, 62.6, 36.9, 36.8, 36.7, 29.8, 25.0, 25.0, 22.8, 22.6, 20.8.



Scheme 4: *Mannose capping of the upper rim calix-tetrol*

Experimental procedure: A solution of mannopyranosyl donor **9** (1.0 mmol) and calix[4]arene acceptor **10** (0.16 mmol) in anhydrous CH_2Cl_2 (2 mL) was prepared and freshly activated 4Å MS were incorporated at 25 °C under a nitrogen condition. The rm was then stirred vigorously for 15 min at the same warmth before introducing chloro[tris(2,4-di-tert-butylphenyl)phosphite]gold(I) (10 mol%) and AgOTf (10 mol%) conjointly. The reaction was enabled to advance for 1 h, with its advancement tracked by TLC up till complete consumption of glycosyl acceptor **10** was confirmed. The rm was then filtered through a Celite® bed, and the resulting filtrate was concentrated under reduced pressure. The crude product was purified using silica gel column chromatography with 30% EtOAc in hexane as the eluent, yielding the mannopyranosyl-capped calixarene **11** in 81% yield. The reaction progress was tracked using TLC and MALDI-TOF analysis.

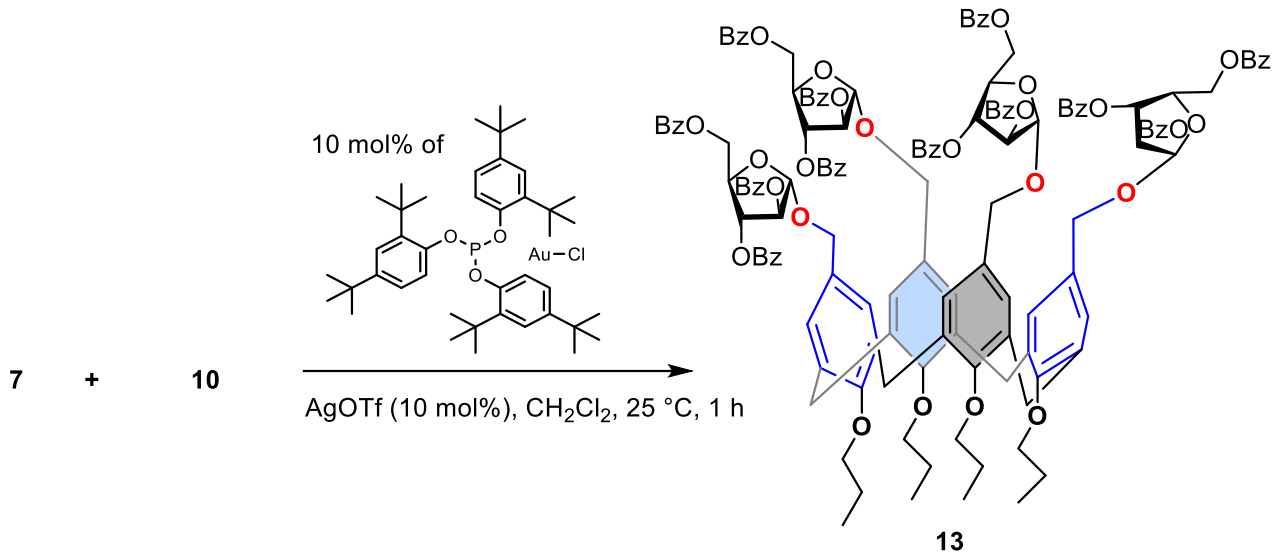
Characterization data of compound **11***:* ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 – 8.07 (m, 8H), 8.02 – 7.96 (m, 8H), 7.95 – 7.89 (m, 8H), 7.82 – 7.77 (m, 7H), 7.57 – 7.51 (m, 8H), 7.40 – 7.19 (m, 40H), 6.74 (m, 5H), 6.10 (t, *J* = 10.0 Hz, 2x2H), 5.89 (dd, *J* = 10.1, 3.2 Hz, 2x2H), 5.69 (q, *J* = 4.0, 2.6 Hz, 2x2H), 5.06 – 5.01 (m, 4H), 4.61 (dt, *J* = 12.1, 2.7 Hz, 2x2H), 4.51 (m, 8H), 4.47 – 4.26 (m, 14H), 3.91 (m, 8H), 3.25 (dd, *J* = 13.7, 5.7 Hz, 2x2H), 1.94 (m, 8H), 1.63 (m, 9H), 1.00-1.20 (m, 16H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.2, 165.6, 165.6, 165.4, 157.1, 133.5, 133.4, 133.2, 130.1, 130.0, 129.9, 129.9, 129.9, 129.7, 129.6, 129.3, 129.2, 128.8, 128.6, 128.6, 128.5, 128.4, 125.5, 124.3, 96.7, 70.7, 70.4, 70.3, 68.9, 67.1, 62.8, 35.2, 34.8, 34.0, 32.1, 31.6, 31.5, 31.2, 30.7, 30.3, 29.8, 29.8, 29.8, 29.7, 29.5, 23.4, 22.8, 14.3, 10.4. Maldi-TOF mass: 3050.7319



Scheme 5. *Glycosylation of lower rim calix-tetrol with mannosyl carbonate donor* **9**

Experimental procedure: A solution of mannopyranosyl donor **9** (1.0 mmol) and calix[4]arene acceptor **4** (0.16 mmol) in anhydrous CH_2Cl_2 (2 mL) was prepared, and freshly activated 4Å MS were incorporated at 25 °C under a nitrogen condition. The rm was then stirred vigorously for 15 min at the same warmth before introducing chloro[tris(2,4-di-tert-butylphenyl)phosphite]gold(I) (10 mol%) and AgOTf (10 mol%) conjointly. The reaction was enabled to advance for 1 h, with its advancement tracked by TLC up till complete consumption of glycosyl acceptor **4** was confirmed. The rm was then filtered through a Celite® bed, and the resulting filtrate was concentrated under reduced pressure. The crude product was purified using silica gel column chromatography with 30% EtOAc in hexane as the eluent, yielding the mannopyranosyl-capped calixarene **12** in 73% yield. The reaction progress was tracked using TLC and MALDI-TOF analysis.

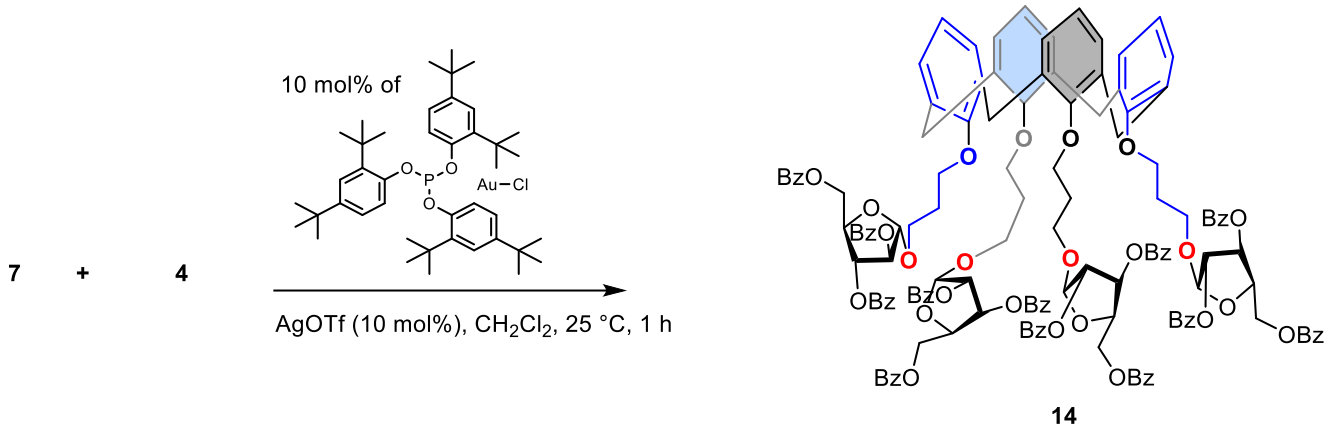
Characterization Data of Compound **12**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 – 8.03 (m, 8H), 7.96 – 7.91 (m, 8H), 7.87 – 7.75 (m, 8H), 7.52 (m, 9H), 7.43 – 7.20 (m, 40H), 6.69 – 6.59 (m, 8H), 6.10 (m, 3H), 5.92 – 5.83 (m, 4H), 5.74 – 5.65 (m, 4H), 5.09 – 4.99 (m, 4H), 4.62 – 4.57 (m, 4H), 4.33 (m, 8H), 4.26 – 3.96 (m, 14H), 3.86 – 3.72 (m, 4H), 3.38 (d, *J* = 13.3 Hz, 2x2H), 2.46 (m, 8H), 2.18 – 2.13 (m, 1H), 1.92 (bs, 2H), 1.62 (m, 8H), 0.92 – 0.84 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.2, 165.6 165.5, 165.3, 134.9, 133.5, 133.4, 133.1, 133.1, 130.1, 129.9, 129.9, 129.9, 129.8, 129.5, 129.3, 129.2, 128.6, 128.5, 128.5, 128.4, 122.4, 98.1, 72.0, 70.6, 70.3, 68.9, 66.9, 66.2, 62.8, 32.1, 31.4, 30.9, 29.8, 24.8, 22.8, 14.3. Maldi-TOF mass: 2994.7952



Scheme 6: *Glycosylation of upper rim calix-tetrol with furanoysl carbonate donor 7*

Experimental procedure: A solution of arabinofuranosyl donor **7** (1.0 mmol) and calix[4]arene acceptor **10** (0.16 mmol) in anhydrous CH_2Cl_2 (2 mL) was prepared, and freshly activated 4Å MS were incorporated at 25 °C under a nitrogen condition. The rm was then stirred vigorously for 15 min at the same warmth before intoducing chloro[tris(2,4-di-tert-butylphenyl)phosphite]gold(I) (10 mol%) and AgOTf (10 mol%) conjointly. The reaction was enabled to advanceo for 1 h, with its advancement monitored by TLC to track the complete consumption of glycosyl acceptor **10**. The rm was then filtered through a Celite® bed, and the filtrate was concentrated under reduced pressure. The crude product was purified using silica gel column chromatography, utilizing 20% EtOAc in hexane as the eluent, yielding the arabinofuranosyl-capped calixarene **13** with a 85% yield. TLC and MALDI-TOF analysis were employed to monitor the reaction progress.

Characterization Data of Compound **13**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 – 7.95 (m, 24H), 7.56 – 7.46 (m, 12H), 7.37 (m, 24H), 7.24 – 7.14 (m, 8H), 6.65 – 6.55 (m, 8H), 5.88 – 5.78 (m, 4H), 5.54 (m, 7H), 5.30 – 5.17 (m, 9H), 5.03 – 4.92 (m, 8H), 4.80 – 4.65 (m, 8H), 2.08 – 2.02 (m, 13H), 0.95 (m, 13H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.3, 165.9, 165.4, 156.5, 139.4, 133.5, 133.1, 131.0, 130.5, 130.1, 130.0, 130.0, 130.0, 129.3, 129.3, 129.0, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 124.6, 124.1, 124.1, 123.6, 122.2, 119.3, 116.0, 114.2, 104.6, 82.1, 81.3, 78.2, 77.5, 77.4, 76.8, 69.9, 68.9, 65.7, 63.9, 34.0, 32.1, 31.8, 31.6, 23.3, 22.8, 14.3, 10.4. Maldi-TOF mass: 2513.9827



Scheme 6: *Glycosylation of lower rim calix-tetrol* **4** *with furanoysl carbonate donor* **7**

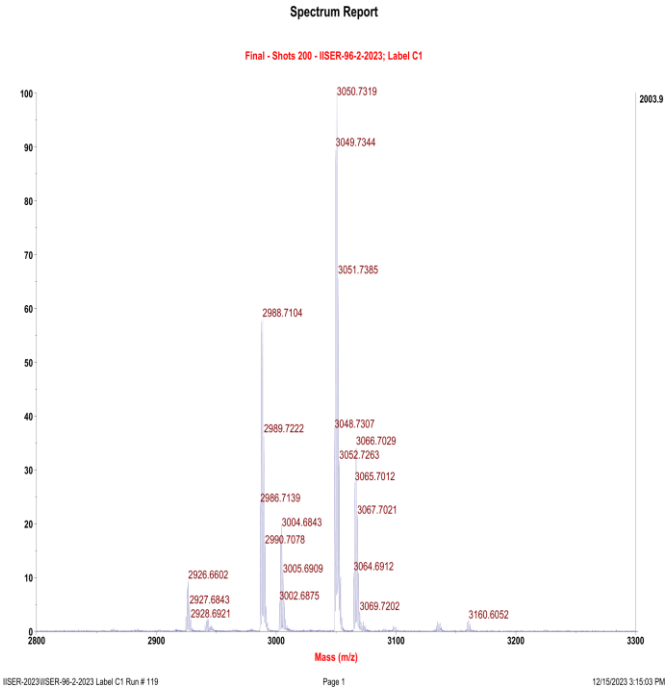
Experimental procedure: A solution of arabinofuranosyl donor **7** (1.0 mmol) and calix[4]arene acceptor **4** (0.16 mmol) in anhydrous CH_2Cl_2 (2 mL) was prepared, and freshly activated 4Å MS were incorporated at 25 °C under a nitrogen condition. The rm was then stirred vigorously for 15 min at the same warmth before introducing chloro[tris(2,4-di-tert-butylphenyl)phosphite]gold(I) (10 mol%) and AgOTf (10 mol%) conjointly. The reaction was enabled to advance for 1 h, with its advancement monitored by TLC to track the complete consumption of glycosyl acceptor **4**. The rm was then filtered through a Celite® bed, and the filtrate was concentrated under reduced pressure. The crude product was purified using silica gel column chromatography, utilizing 20% EtOAc in hexane as the eluent, yielding the arabinofuranosyl-capped calixarene **13** with a 87% yield. TLC and MALDI-TOF analysis were employed to monitor the reaction progress.

Characterization data of compound **14**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 – 7.92 (m, 24H), 7.55 – 7.49 (m, 11H), 7.40 – 7.33 (m, 12H), 7.21 – 7.14 (m, 7H), 5.49 (m, 7H), 5.19 (bs, 3H), 5.02 – 4.91 (m, 10H), 4.63 (m, 10H), 4.31 – 4.27 (m, 4H), 4.19 – 4.11 (m, 8H), 3.38 (m, 5H), 2.85 (m, 7H), 2.03 (m, 12H), 1.14 (m, 14H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.3, 165.9, 165.4, 156.5, 139.4, 133.5, 133.1, 131.0, 130.5, 130.1, 130.0, 130.0, 130.0, 129.3, 129.3, 129.0, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 124.6, 124.1, 124.1, 123.6, 122.2, 119.3, 116.0, 114.2, 104.6, 82.1, 81.3, 78.2, 77.5, 77.4, 76.8, 69.9, 68.9, 65.7, 63.9, 34.0, 32.1, 31.8, 31.6, 23.3, 22.8, 14.3, 10.4. Maldi-TOF mass: 2457.8179

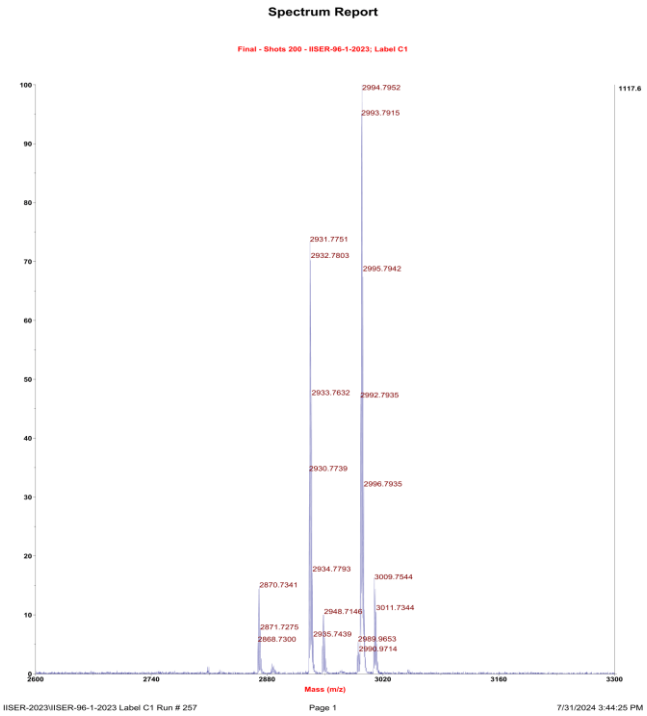
Conclusions:

In summary, [Au]/[Ag]-catalyzed glycosylation proved to be a highly efficient method for modifying calix[4]arenes, achieving excellent regio- and stereo- selectivity with high yields. The process overcame limitations of traditional methods by using alkynyl glycosyl carbonate donors, which offered superior stability and ease of handling. The resulting glycosylated calixarenes have potential applications in drug delivery and molecular recognition. This study contributes to advancing glycosylation methodologies, paving the way for future research into further functionalization and biomedical applications.

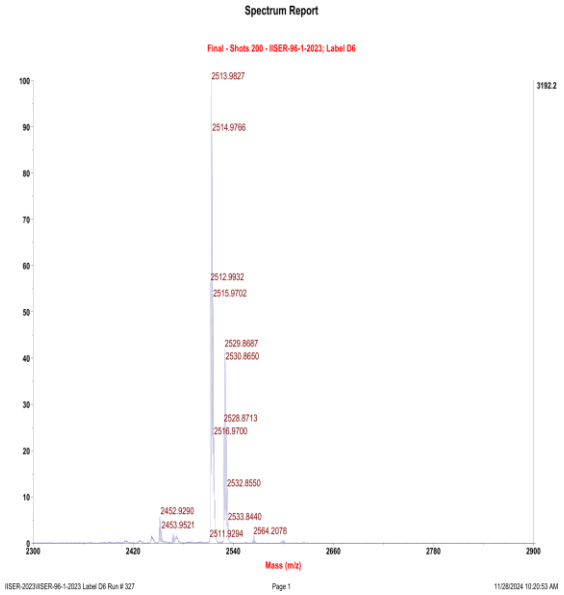
MALDI-TOF DATA CHART OF COMPOUND 11:



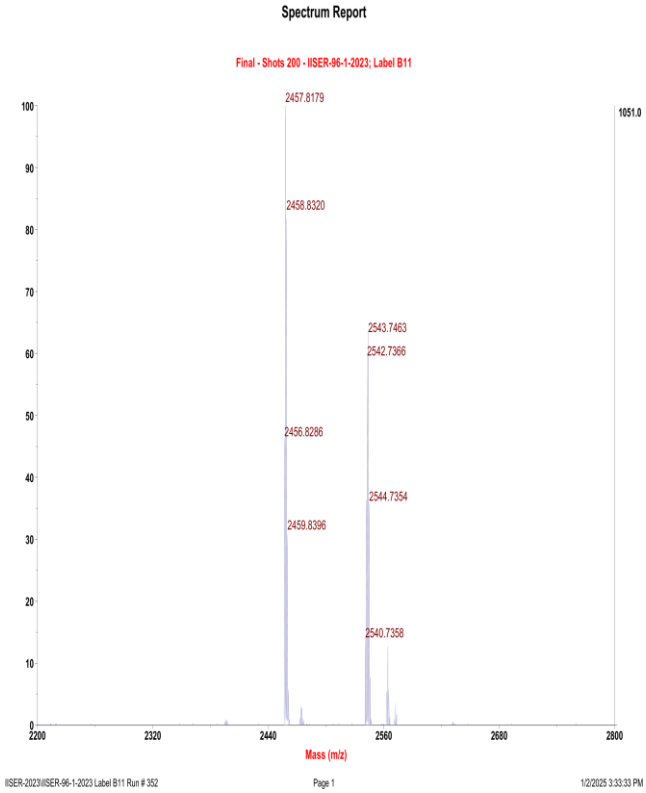
MALDI-TOF DATA CHART OF COMPOUND 12:



MALDI-TOF DATA CHART OF COMPOUND 13:

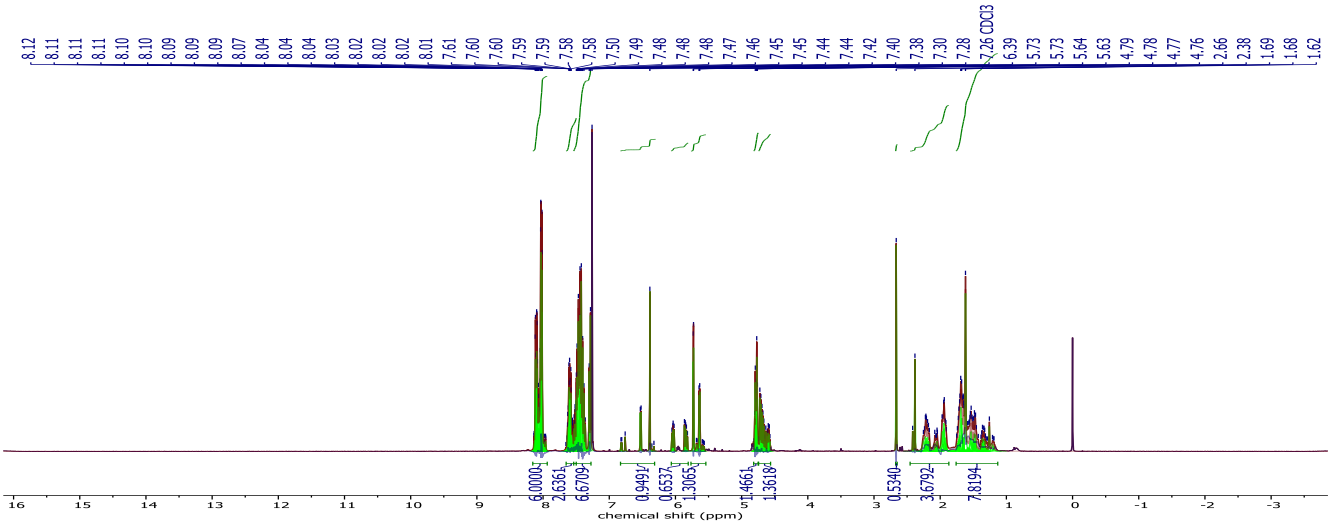


MALDI-TOF DATA CHART OF COMPOUND 14:

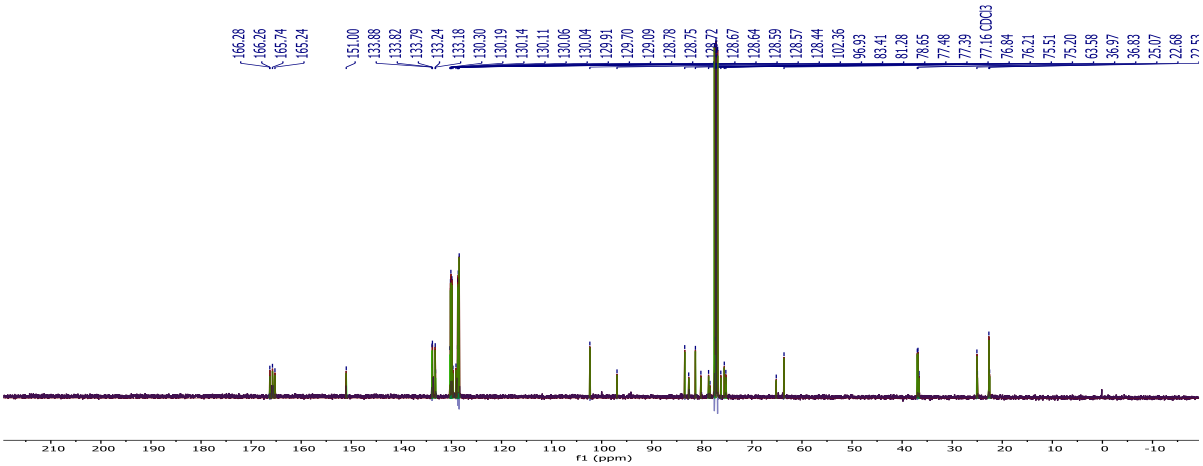


NMR Spectral Charts:

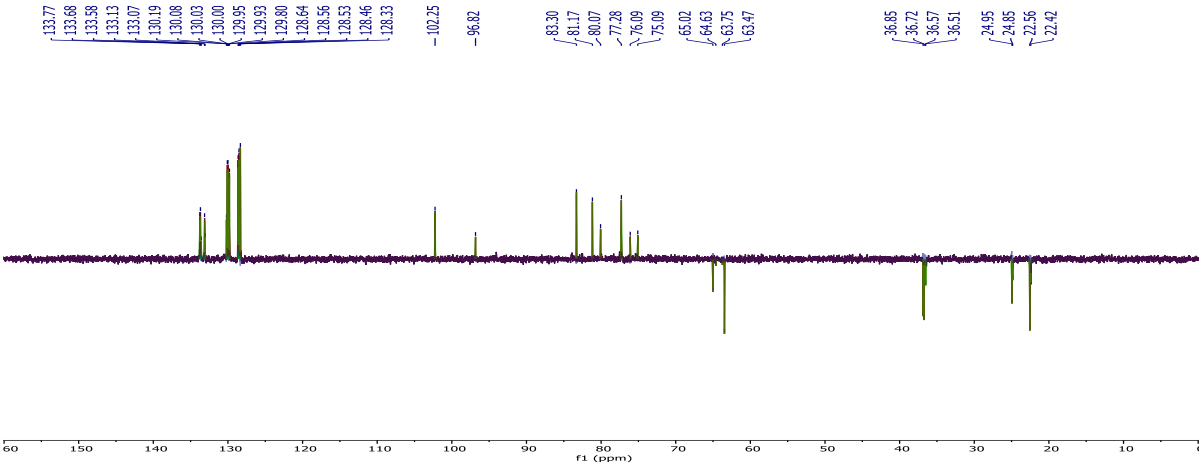
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound 7



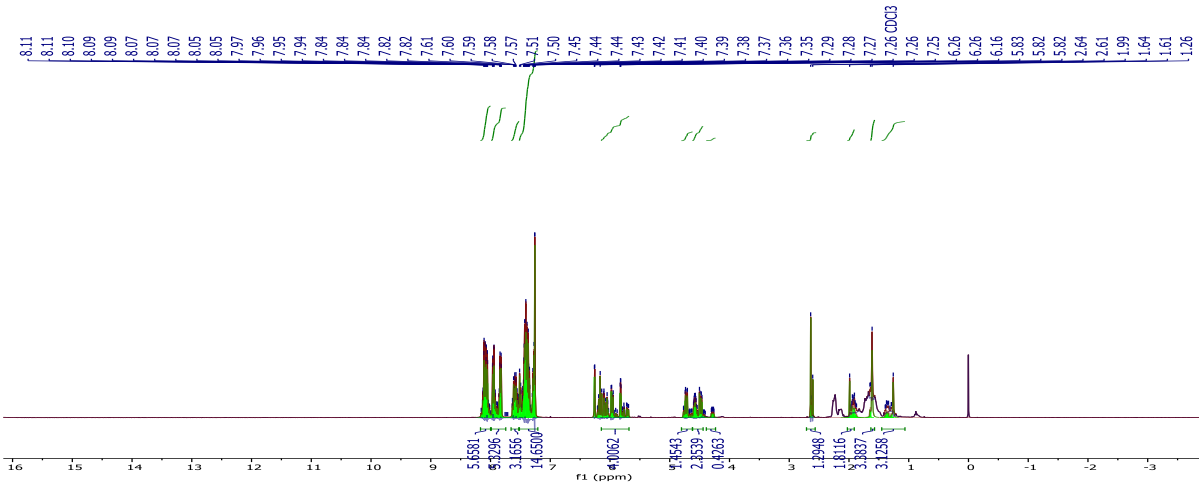
^{13}C NMR Spectrum (400 MHz, $CDCl_3$) of Compound 7



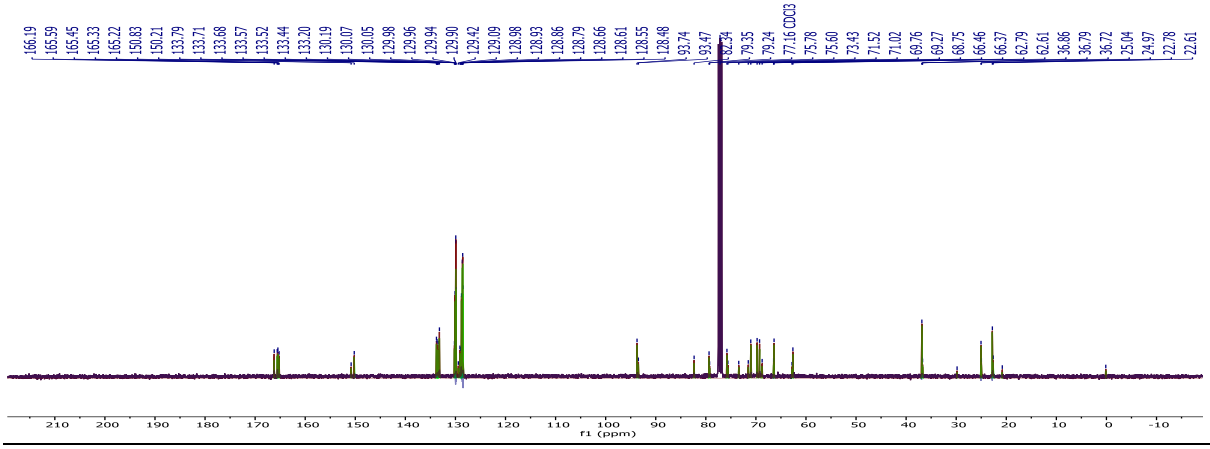
DEPT-135 NMR Spectrum (400 MHz, $CDCl_3$) of Compound 7



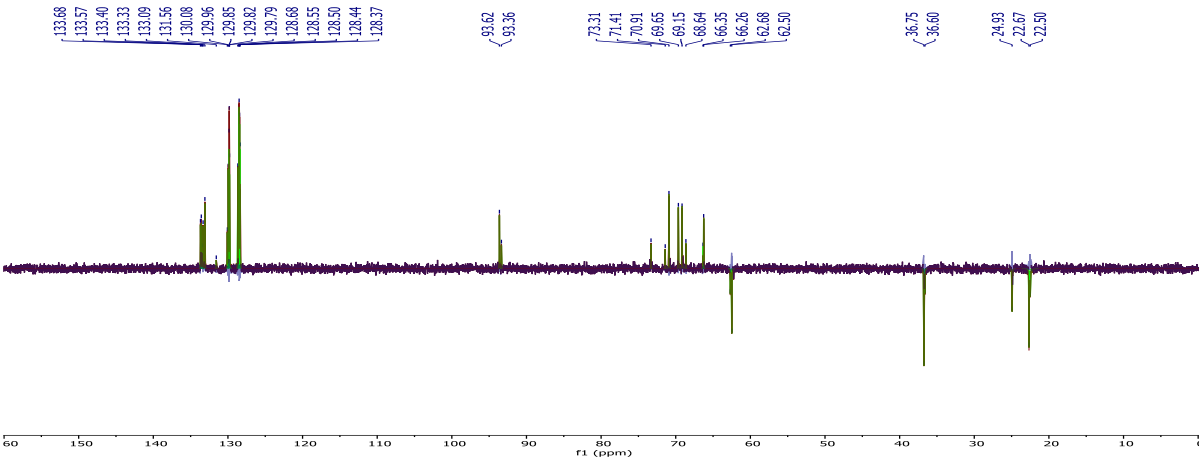
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound 9



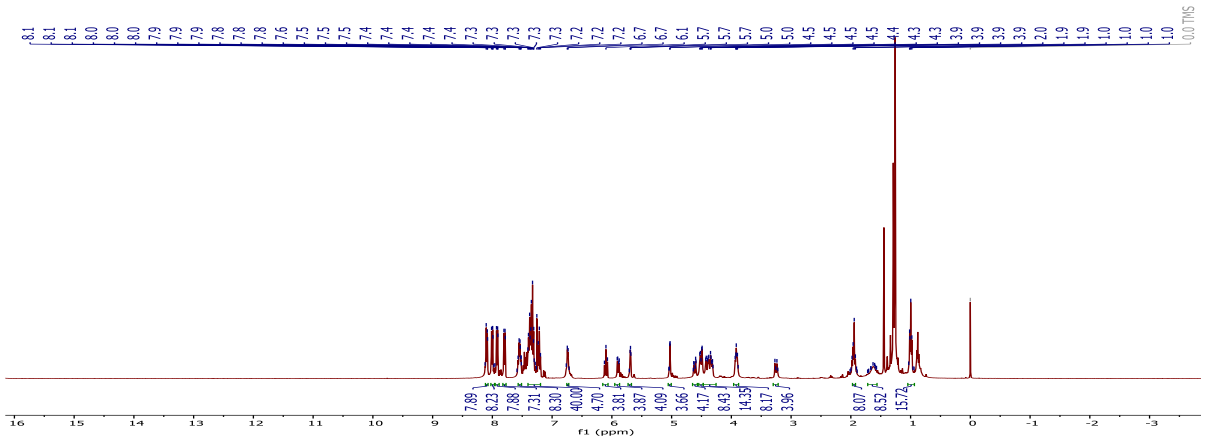
^{13}C NMR Spectrum (400 MHz, $CDCl_3$) of Compound 9



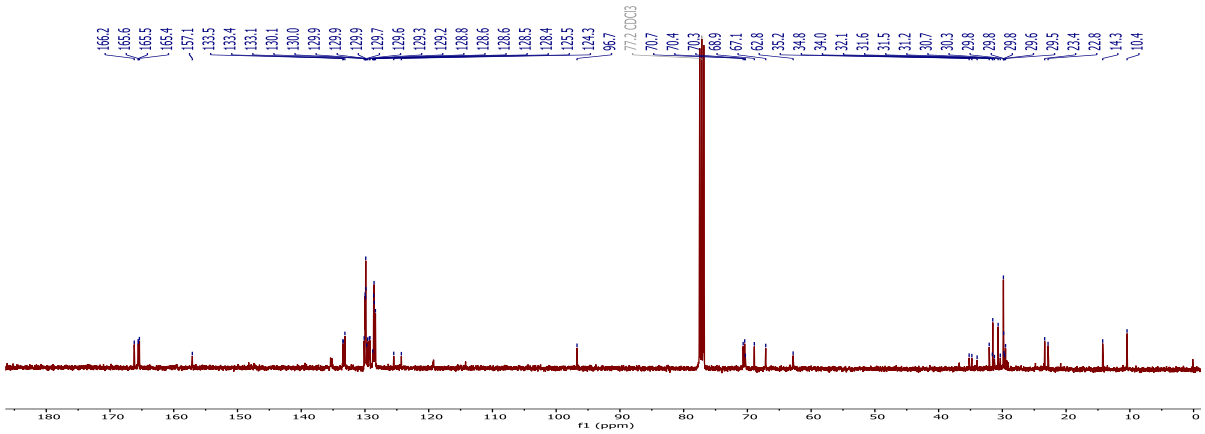
DEPT-135 NMR Spectrum (400 MHz, $CDCl_3$) of Compound 9



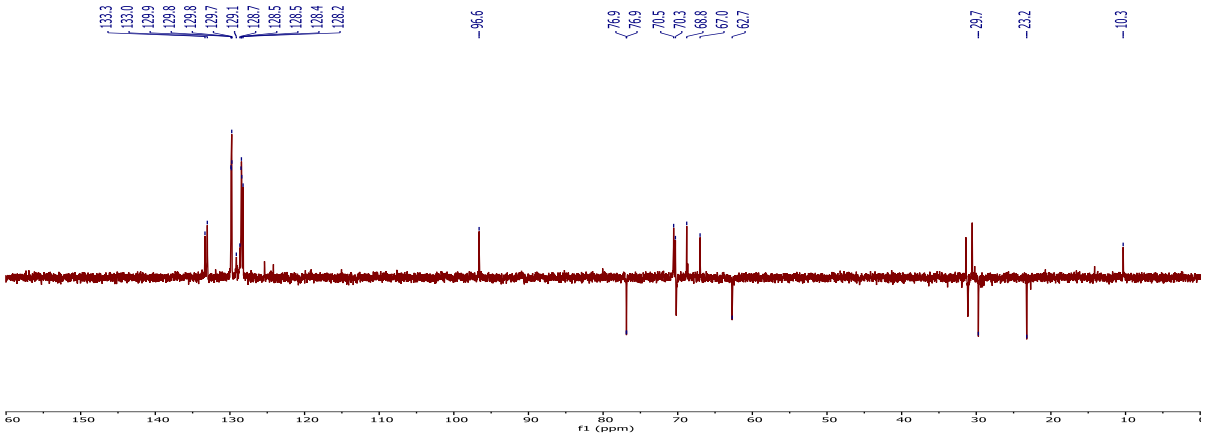
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound 11



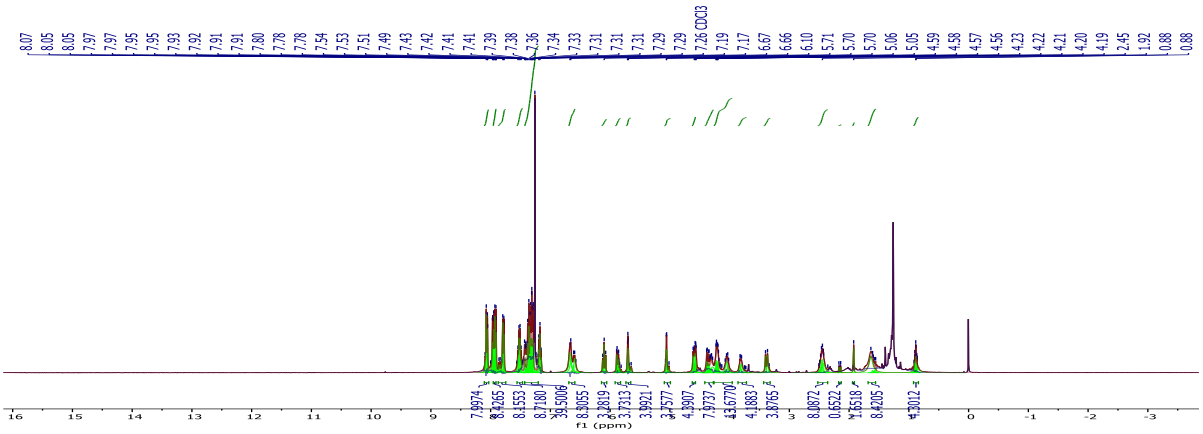
^{13}C NMR Spectrum (400 MHz, $CDCl_3$) of Compound 11



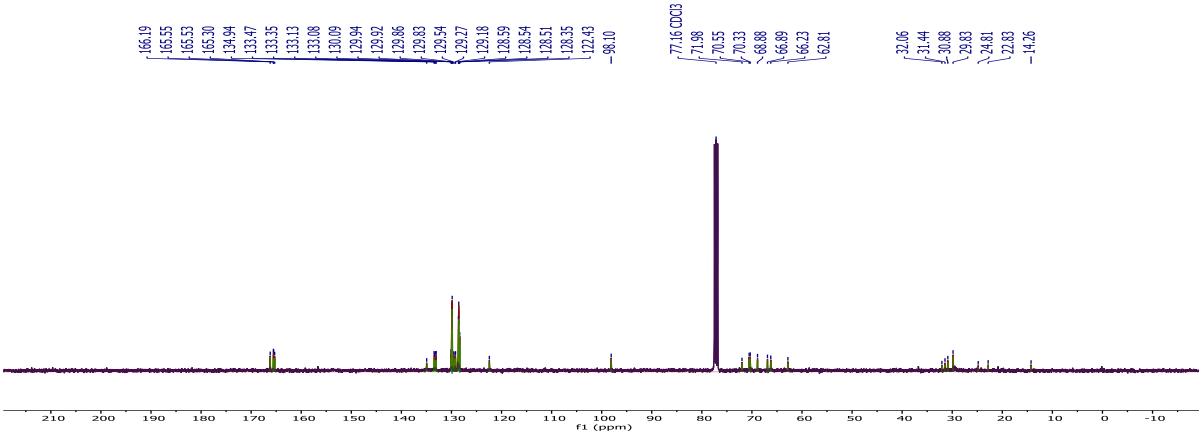
DEPT-135 NMR Spectrum (400 MHz, $CDCl_3$) of Compound 11



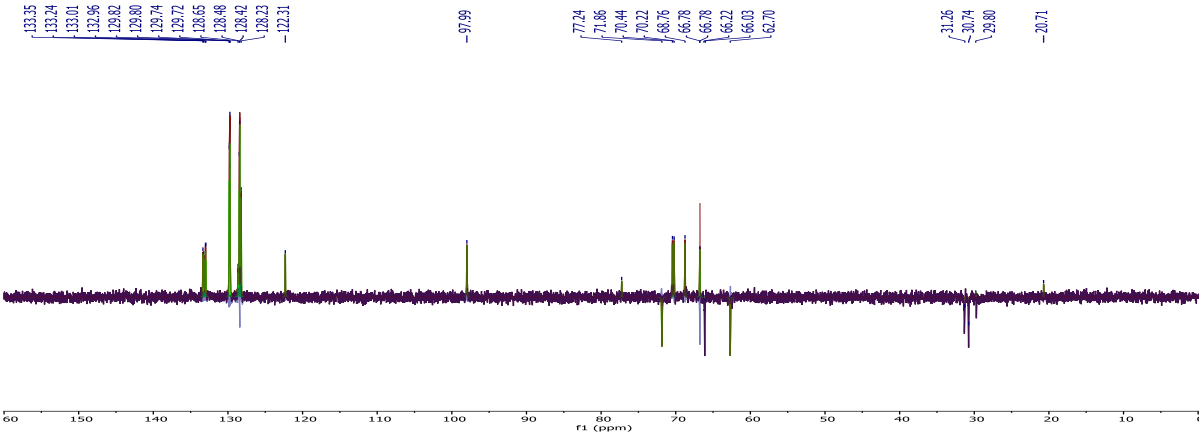
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound 12



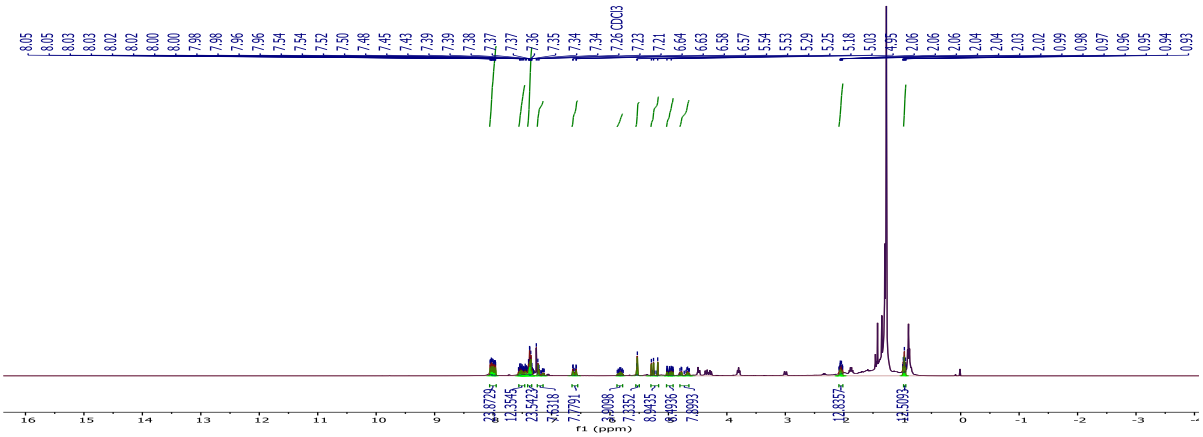
^{13}C NMR Spectrum (400 MHz, $CDCl_3$) of Compound 12



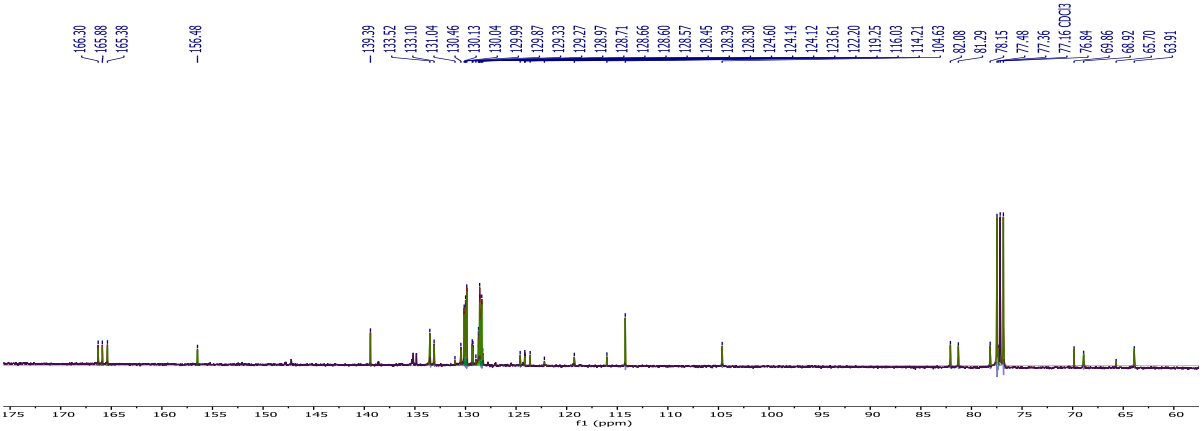
DEPT-135 NMR Spectrum (400 MHz, $CDCl_3$) of Compound 12



^{1}H NMR Spectrum (400 MHz, $CDCl_3$) OF COMPOUND 13



^{13}C NMR Spectrum (400 MHz, $CDCl_3$) of Compound 13



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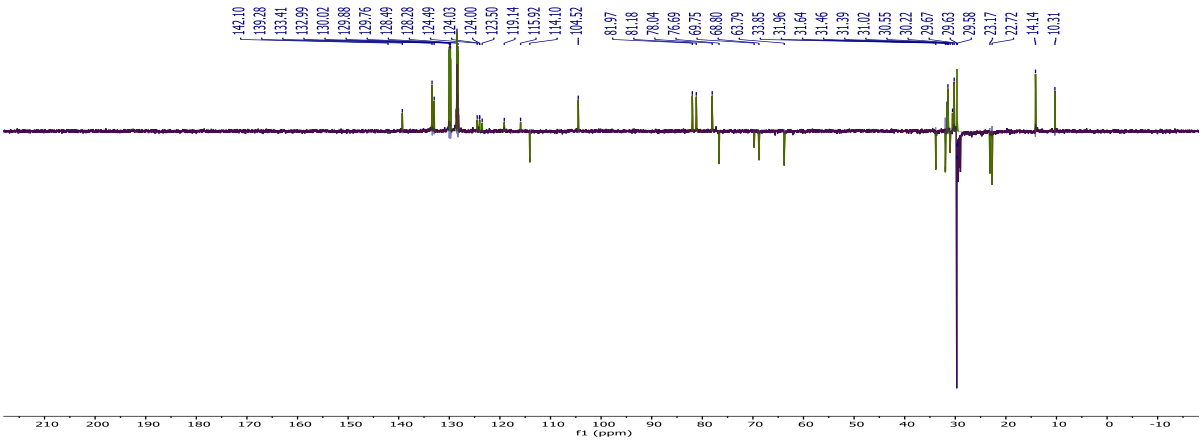
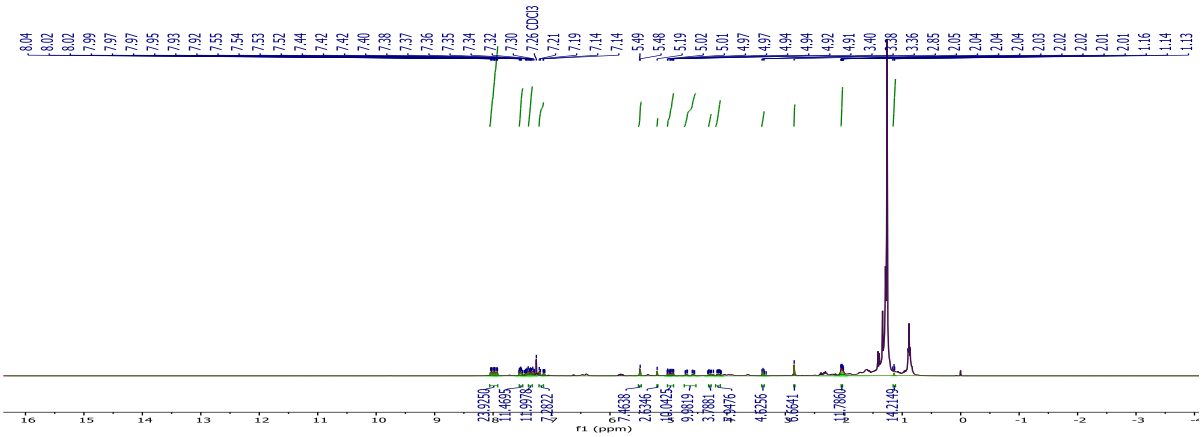
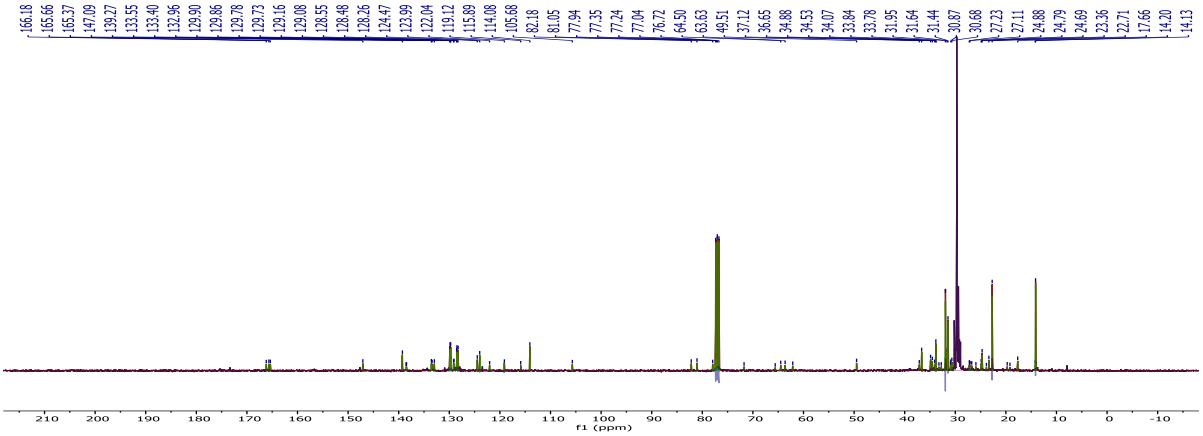


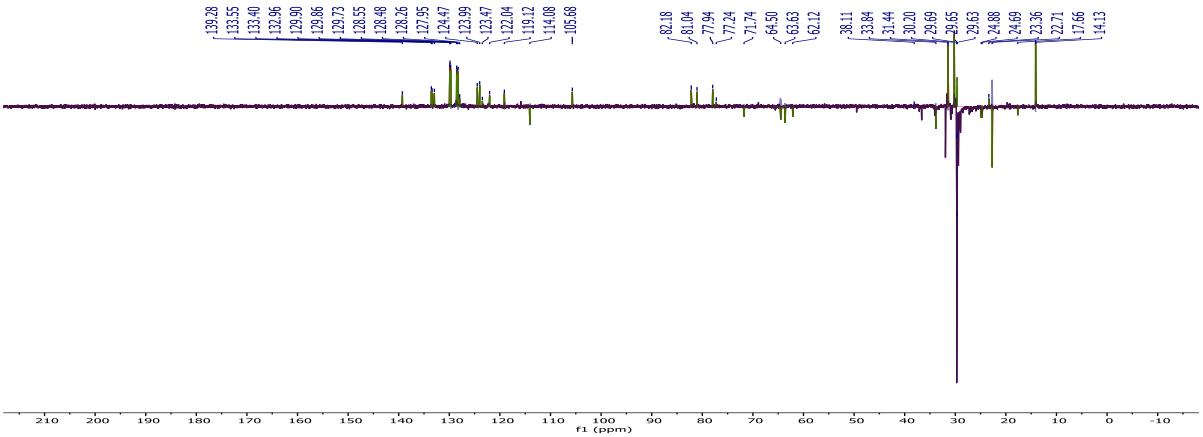
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound 14



^{13}C NMR Spectrum (400 MHz, $CDCl_3$) of Compound 14



DEPT-135 NMR Spectrum (400 MHz, $CDCl_3$) of Compound 14



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