Republic of Iraq
Ministry of Higher Education
& Scientific Research
University of Kerbala/College of Science
Department of Chemistry

Synthesis of New Perfluoroethyl Triazoles Derived from α-D-Galactose sugar *Via* Click Chemistry and Study Some of their Thermodynamic Functions

A Thesis

Submitted to the Council of the College of Science University of Kerbala as a Partial Fulfillment of the Requirements for MSc. degree in Chemistry

By

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بسم الله الرحمن الرحيم

﴿يَرْفَعِ اللَّهُ الَّذِينَ آمَنُوا مِنْكُمْ وَالَّذِينَ أُوتُوا الْعِلْمَ دَرَجَاتٍ وَاللَّهُ بِمَا تَعْمَلُونَ خَبِيرٌ﴾

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(سورة المجادلة/ الآية ١١)

Dedication

To my dear parents , brother and sister with faithfulness

Ahmed

Acknowledgment

Thanks to Allah the one the single for this entire blessing during the pursuit of my academic and career goals.

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Last, I would like to express my thanks to all individuals who helped me in one way or another in the fulfillment of this work.

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Summary

This work includes synthesis of new perfluoro triazole starting from D-galactose. Firstly, 1,2:3,4-di-O-isopropylidene-α-D-galactose **(66)** was synthesized by the reaction of D- galactose, acetone and sulfuric acid in presence $ZnCl_2$ then the work was been divided into two lines.

The first line describes: Williamson etherfication of compound **(66)** with propargyl bromide in basic media gave the terminal alkyne derivative 6-O-prop-2-ynyl-1,2:3,4-di-O-isopropylidene-α-D-galactose **(67)**.

While the second one describes the synthesis of 1,2:3,4-di-O-isopropylidene-α-D-galactose-6-O-triflate **(68)** with good leaving group from the esterfication of compound **(66)** by trifluoromethanesulfonic anhydride in dry pyridine. The treatment of derivative **(68)** with sodium azide afforded 6-azido-6-deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactose **(69)** in good yield.

The derivatives **(67)** and **(69)** have been utilized to synthesize of the targeted perfluoro triazoles *via* Cu (I) catalyst 1,3-dipolarcycloaddition: the reaction of derivative **(67)** with azides as active group and ethyl spacer with different perfluoro chain, afforded triazole derivatives **(74-76)**.

While the reaction of compound **(69)** with perfluoroethyl propargyl ethers **(71-73)** using the same Cu (I) catalyst conditions yielded the perfluorotriazoles **(77-79)**.

All the synthesized compounds have been characterized by spectroscopic methods [FT-IR; ^{1}H and ^{13}C NMR], while the targeted compounds **(74-79)** have been characterized by [FT-IR; ^{1}H, ^{13}C NMR, HSQC, COSY and Mass] spectroscopic methods. The thermodynamic functions (ΔH, ΔG and ΔS) of compounds **(74-79)** have been studied using DSC instrument, thermodynamics calculations showed increasing the enthalpy values corresponding with increasing the perfluoro chain which caused by the rigidity of perfluoro chain reason the helical shape.

Abbreviations

Symbol	Definition
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
$Pd_2(dba)_3$	Tris(dibenzylideneacetone)dipalladium
MW	Microwave
DIPEA	N,N-Diisopropylethylamine
THF	Tetrahydrofuran
DMSO	Dimethyl sulfoxide
DMF	Dimethylformamide
DCM	Dichloro methane
EtOAc	Ethyl acetate
ΔE	Change of Energy
W	Work
ΔH	Change of Enthalpy
ΔS	Change of Entropy
ΔG	Change of Gibbs free energy
DSC	Differential Scanning Calorimetry
υ	Stretching
δ	Bending in IR and chemical shift in NMR
ppm	part per million
R_f	factor of retention
^{1}H NMR	Proton Nuclear Magnetic Resonance
^{13}C NMR	Carbon–13– Nuclear Magnetic Resonance
FT-IR	Fourier Transform Infrared
COSY	Correlation Spectroscopy
HSQC	Heteronuclear Single Quantum Coherence
HR-MS	High resolution mass spectrum
LC-MS	Liquid chromatography-mass spectrometry
Hz	Hertz
J	Coupling constant
s	singlet
d	doublet
dd	doublet of doublet
ddd	doublet of doublet of doublet
t	triplet

tt	triplet of triplet
ttt	triplet of triplet of triplet
m	multiplet
t-Bu	tertiary butanol
$TMSN_3$	Trimethylsilyl azide
ICTA	International Center for Technology Assessment
h	hour
rt	room temperature
Et_2O	diethyl ether

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Chapter One

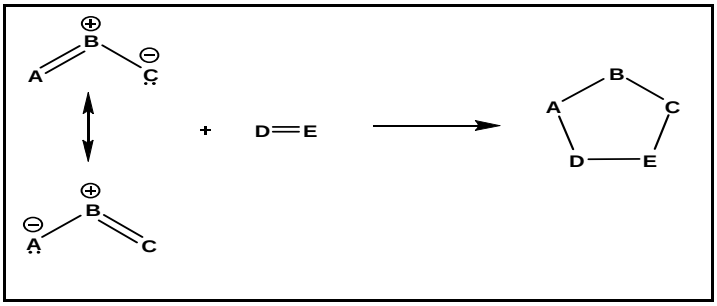
INTRODUCTION

Introduction

The chemistry of heterocyclic compounds continuous to be an explore field in the organic chemistry, heterocycles can be synthesized either by ring synthesis or by transformation of an existing ring, the relative importance of ring synthesis to preparation by substitution increases as the number of heteroatoms in the ring increases, an importance of triazoles derivative lies in the field that these have occupied an unique position in heterocyclic chemistry[1]. Nitrogen heterocyclic compounds are broadly distributed in medical chemistry [2] and in nature include amino acids, purines, and many other natural products[3]. The chemistry of triazoles has received much attention because of their used in pharmaceuticals[4], biologically active agents[5], and used as fungicides[6]. 1,2,3-Triazoles have been widely used in synthetic intermediate and industrial applications such as dyes and anticorrosive agents[7].

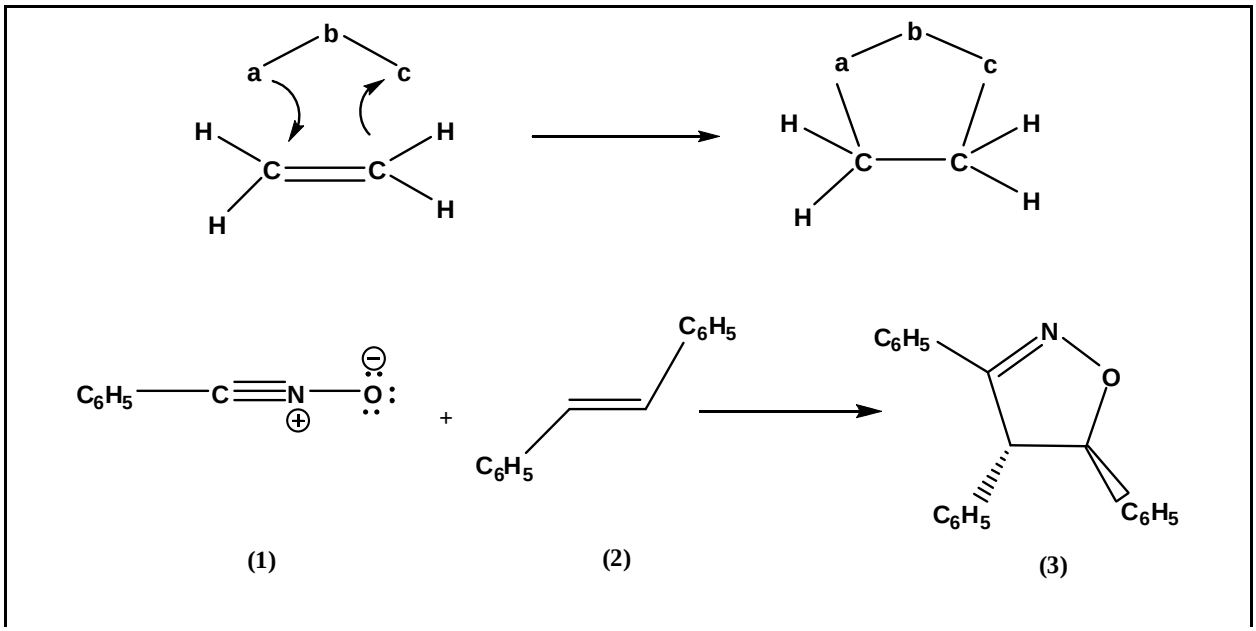
(1.1) 1,3-Dipolar cycloaddition:

The dipolar compounds have a sequence of three atoms a-b-c, of which (a) has a sextet electrons in the outer shell and (c) an octet with at least one unshared pair an atom with six electrons in the outer shell which is usually instable and compounds will delocalize the change to alleviate this electronic arrangement[8]. The 1,3-dipolar is a spaces which can be represented by zwitterionic resonance structures, these zwitterions undergo 1,3-dipolar cycloaddition to multiple bond systems, referred to “dipolarophiles”[9].

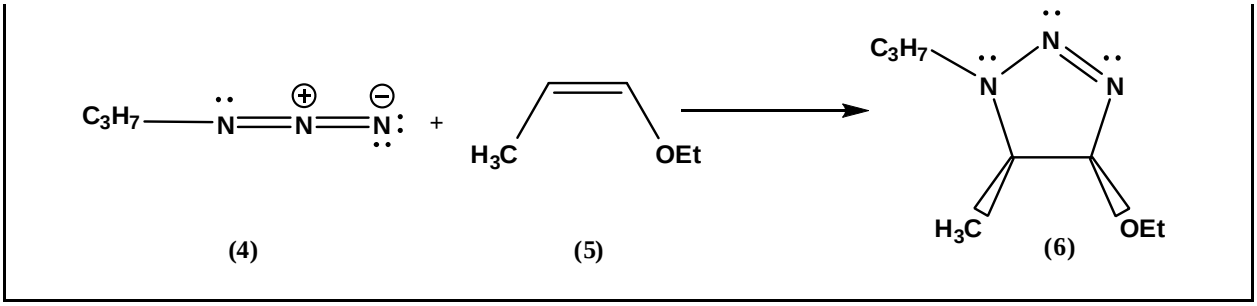


Cycloaddition reactions are one of the most important class of reactions in synthetic chemistry, the class 1,3-dipolar cycloaddition reaction has found extensive use as a high yield and stereocontrolled method for the synthesis of many different heterocyclic five-membered ring compounds[10].

The 1,3-dipolar cycloaddition process has emerged as the method of choice to effect the requirements of connecting two molecules in a general, fast, and efficient process. 1,3-Dipolar cycloaddition have been used to make a large number of heterocyclic compounds the reaction is stereospecific and the geometry of the olefin is maintained in the cyclic product[11] Scheme (1-1).



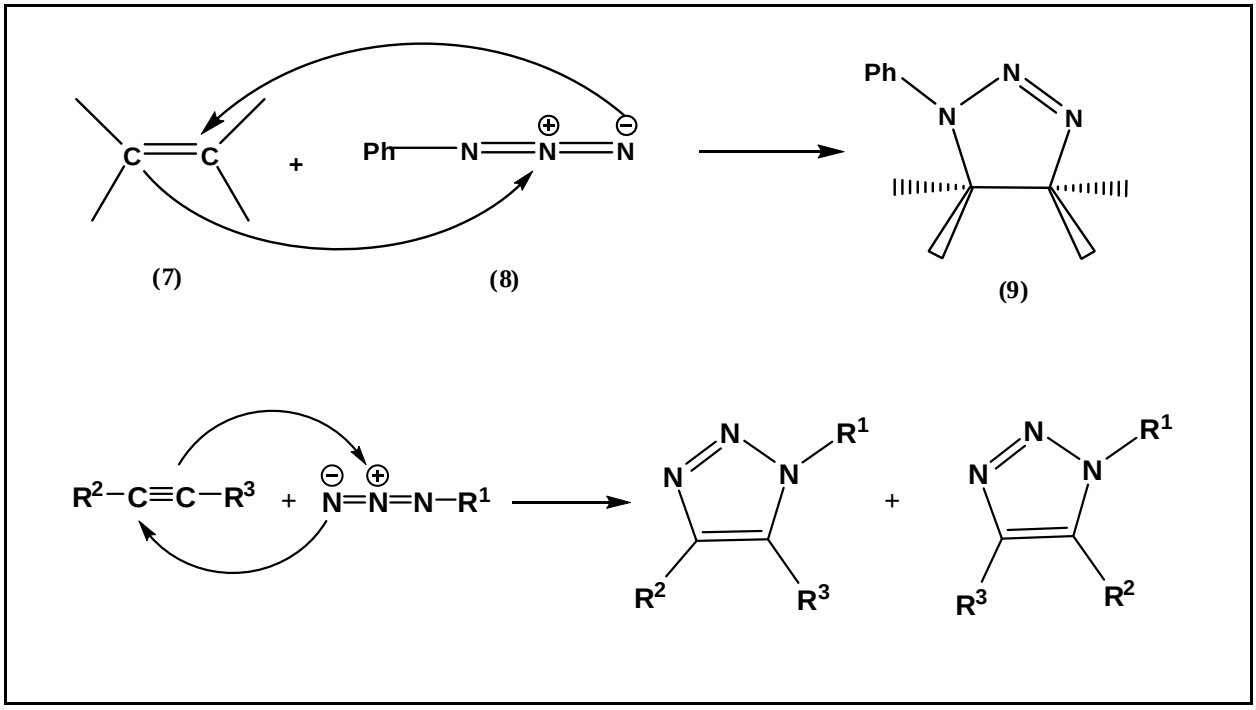
(1) (2) (3)



(4) (5) (6)

Scheme (1-1) 1,3-Dipolar cycloaddition

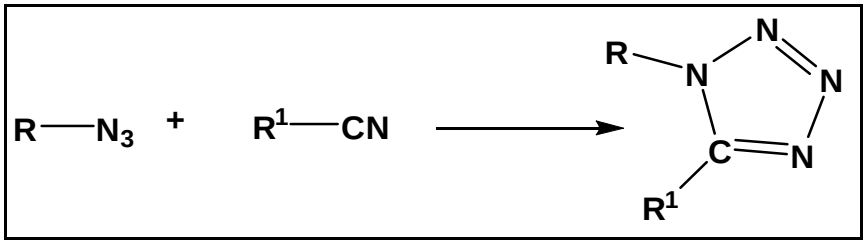
Azides add to carbon-carbon double and triple bonds with 1,3-dipolar cycloaddition to give triazoline and triazoles[12] respectively. Scheme (1-2).



(7) (8) (9)

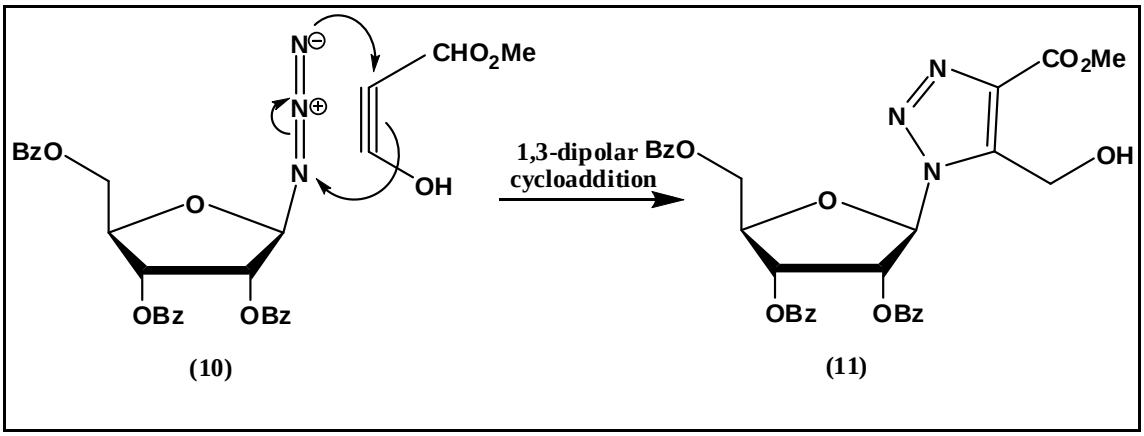
Scheme (1-2) Formation of traizoline (9) and triazole by 1,3-dipolar cycloaddition

The reaction between azides and nitriles *via* 1,3-dipolar cycloaddition gives tetrazoles[13]. Scheme (1-3).



Scheme (1-3) Formation tetrazoles by 1,3-dipolar cycloaddition

The difficulty in trying to forecast which way round a 1,3-dipolar cycloaddition will go is well illustrated when a substituted azide adds to an alkyne in the synthesis of 1,2,3-triazoles. Reaction of an alkyl azide with an asymmetrical alkyne, having an electron-withdrawing group at one end and an alkyl group at the other, gives mostly a single triazole. It looks as if the more nucleophilic end of the azide has attacked the wrong end of the alkyne, but remember that: (1) it is very difficult to predict which is the more nucleophilic end of a 1,3-dipole and (2) it may be either HOMO (dipole) and LUMO (alkyne) or LUMO (dipole) and HOMO (alkyne) that dominate the reaction, the reason for doing the reaction was to make analogues of natural nucleosides[14]. Scheme (1-4).



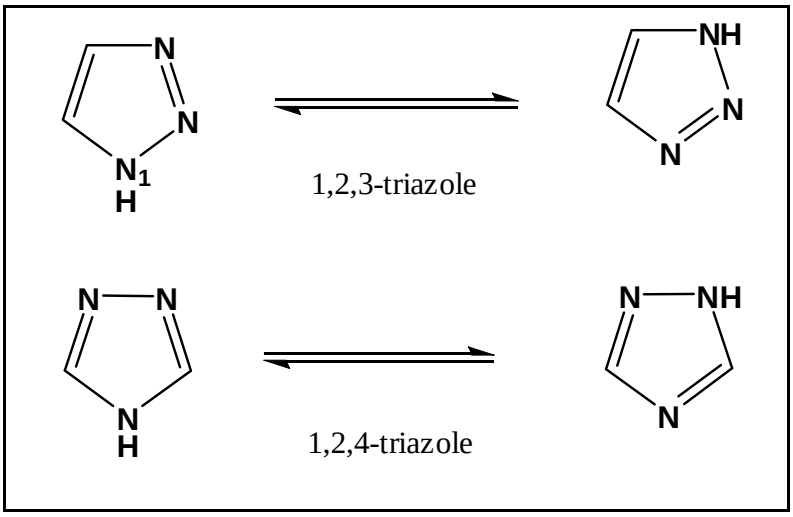
Scheme (1-4) Effect of electron withdrawing group on 1,3-dipolar cycloaddition

(1.2)Triazoles:

Triazoles are five-membered heterocycle contains three nitrogen atoms, there are two types of triazoles 1,2,3-triazoles and 1,2,4-triazoles[15]. Scheme (1-5).

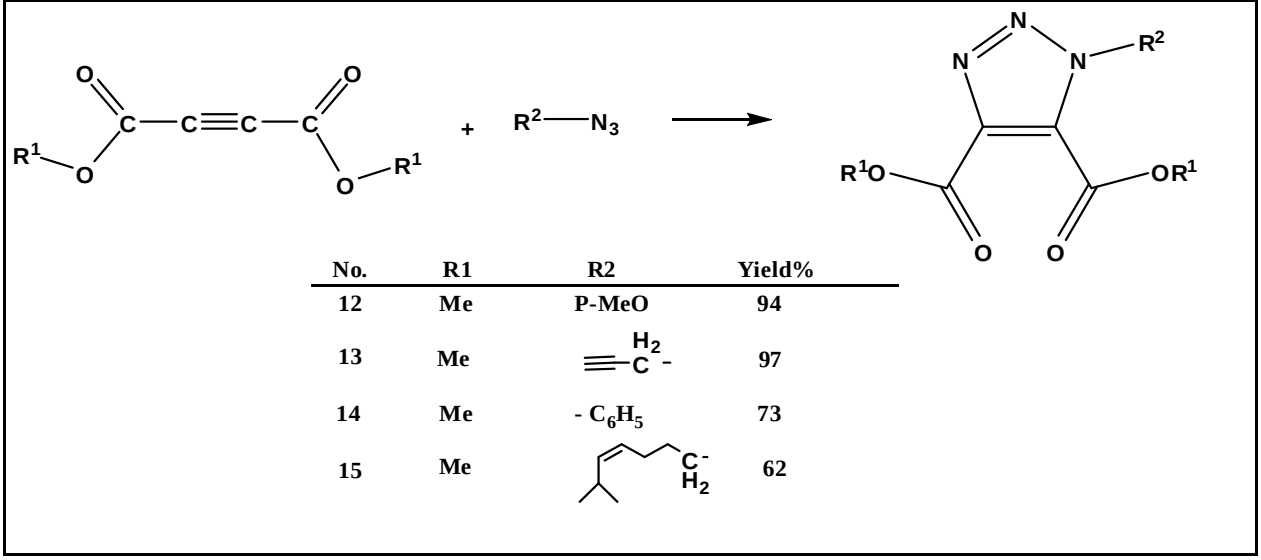
Scheme (1-5) 1,2,3- and 1,2,4-Triazoles structures

Each triazole has one pyrrole-like nitrogen and two pyridine-like nitrogens, both triazoles have tautomerized [16] shown in scheme (1-6).



Scheme (1-6) Triazoles tautomeric forms

Many 1,2,3-triazoles have been prepared by 1,3-dipolar cycloadditions of acetylenes with azides. Generally, the more electron-withdawing the substituents on the acetylene, the easier the cycloaddition reactions electron-withdawing substituents on azides have the opposite effect, bulky substituents hinder the reaction rate, but lead to better selectivity[17] scheme (1-7).

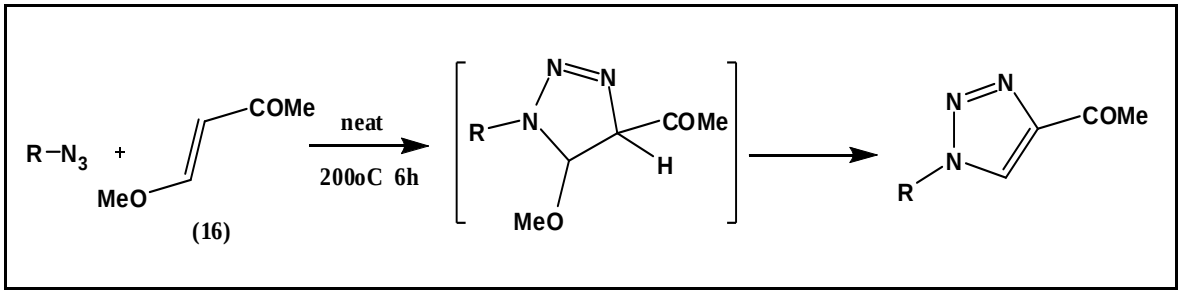


No.	R1	R2	Yield%
12	Me	P-MeO	94
13	Me	H_2C-	97
14	Me	- C_6H_5	73
15	Me	C^-H_2	62

Scheme (1-7) Effect of substituents on triazole formation

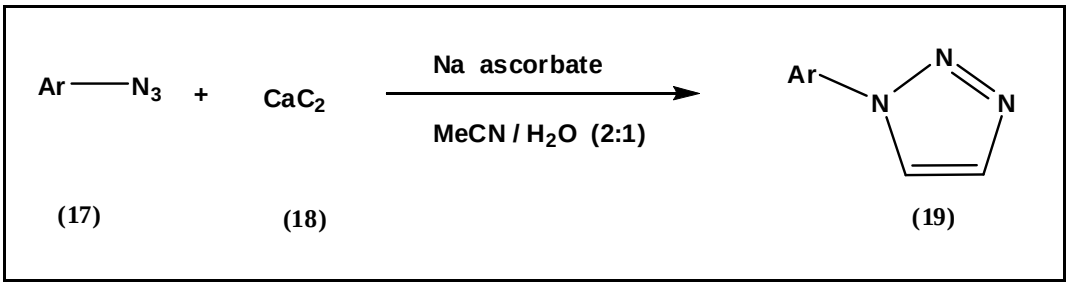
(1.2.1) 1,2,3-Triazoles:

Five-membered heterocycle contain three N-atoms in the 1,2,3 positions,it was known as *V*-triazole (*V* meanings Vicinal) [18] . All ring atoms in 1,2,3-triazoles are sp^2-hybridized, the six available electrons are in delocalization, in the other hand its aromatic[19], azides have been add to acetylenic compounds to give 1,2,3-triazoles. 1,2,3-Triazoles were prepared in good to modest yields by cycloaddition of alkyl azides onto enol ethers under solvent free conditions. The reaction can access ring-fused triazoles that are unavailable by azide-alkyne cycloadditions and is easily scalable. The 1,2,3-triazole products bear functionality that may be readily derivatized[20] scheme (1-8).



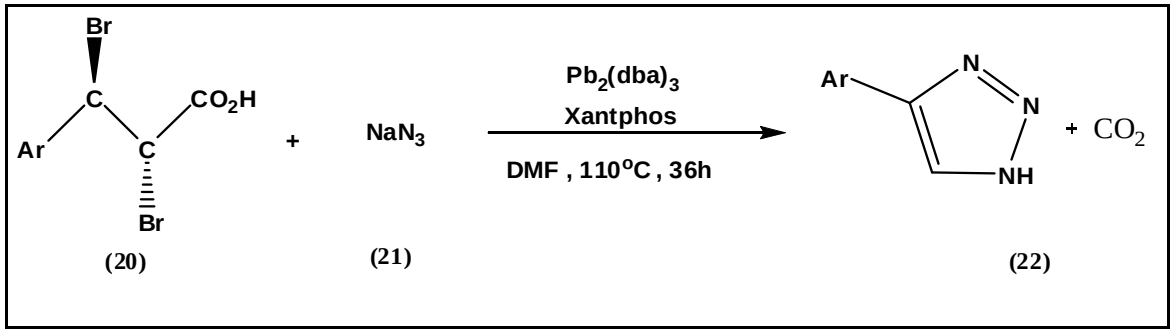
Scheme (1-8) Triazole formation

Q. Yang[21] *et. al* synthesized the 1-monosubstituted aryl 1,2,3-triazoles in good yields using calcium carbide (18) as a source of acetylene to produce N-monosubstituted 1,2,3-triazole (19). Scheme (1-9).



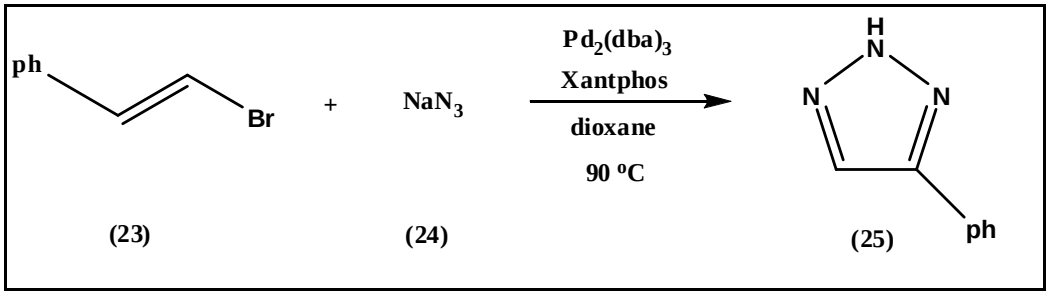
Scheme (1-9) Formation of compound[22] (19)

4-Aryl-1,2,3-triazoles, C-monosubstituted triazole, were synthesized from anti-3-aryl-2,3-dibromopropanoic acid and sodium azide by a one-pot method using N,N-dimethyl formamide as a solvent in presence of $Pd_2(dba)_3$ and xantphos[23] scheme (1-10).



Scheme (1-10) Formation of compound (22)

The coupling of an azide with an alkenyl halide under palladium catalysis conditions led to the formation of 1,2,3-triazoles[24]. Scheme (1-11).



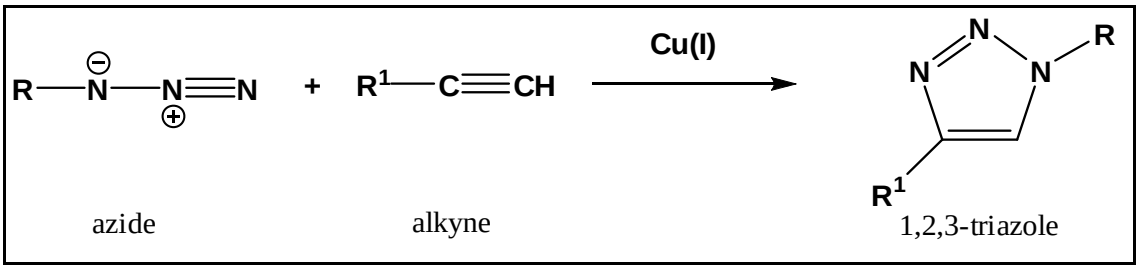
Scheme (1-11) Formation of compound (25)

(1.3) Click Chemistry:

(1.3.1) Discovery of Click:

The click chemistry concept was introduced by K. B. Sharpless [25] *et al.* in 2001 to describe reaction that are high yielding[26] , stereospecific[27], and used under mild conditions, moreover, the copper-catalyzed azide–alkyne cycloaddition click reaction can be performed in various solvents including water and in the presence of numerous other functional groups [28].

Click reaction involves a copper-catalyzed triazole formation from additional an azide to an terminal alkyne[29] scheme (1-11).



Scheme (1-12) Formation of triazole *via* click chemistry

The azide/alkyne click reaction which is an appealing concept proposed by Sharpless and co-workers is not a scientific discipline but rather a synthetic philosophy inspired by the simplicity and efficiency of the chemistry that takes place in nature[30]. The general strategy for click chemistry was defined as an

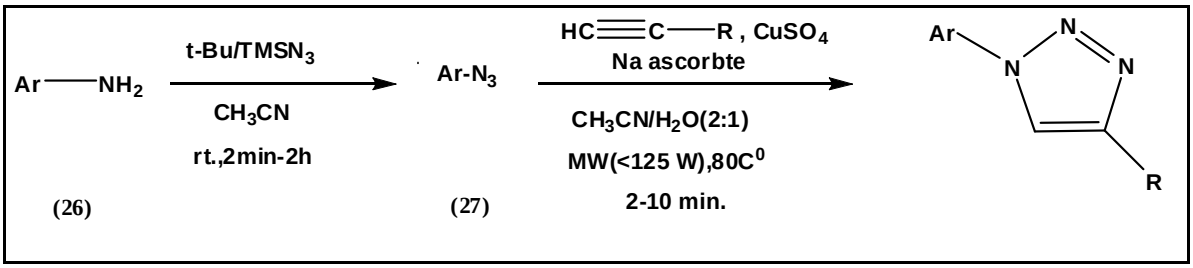
approach which is essentially modular, and employs small molecules that can be quickly stitched together to form complex functional compounds, such as in nature proteins and complex carbohydrates are formed by joining smaller modular units. Click chemistry presented as a set of reactions that can be envisioned for single trajectory, as these reactions are driven by a high thermodynamic driving force, usually greater than 20 kcal/mol, and so complete rapidly and selectively to produce a single product. Three classes of reactions were singled out as ideal candidates for click chemistry, that include:

1) nucleophilic opening of electrophiles, like epoxides, and aziridines.

2) mild condensation reactions of carbonyl compounds for example hydrazones and oximes from aldehydes.

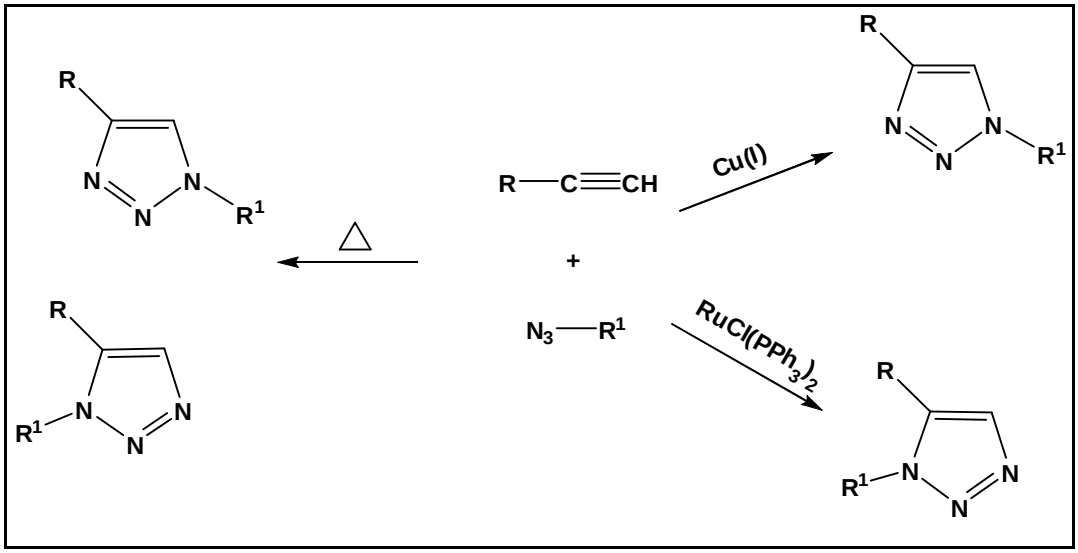
3) cycloaddition reactions[31].

Microwave irradiation significantly enhances the rate of formation of 1,4- derived from an efficient one-pot azidation of anilines with the reagent combination t-Bu and $TMSN_3$[32]. Scheme (1-13).



Scheme (1-13) Microwave formation of 1,2,3-triazole

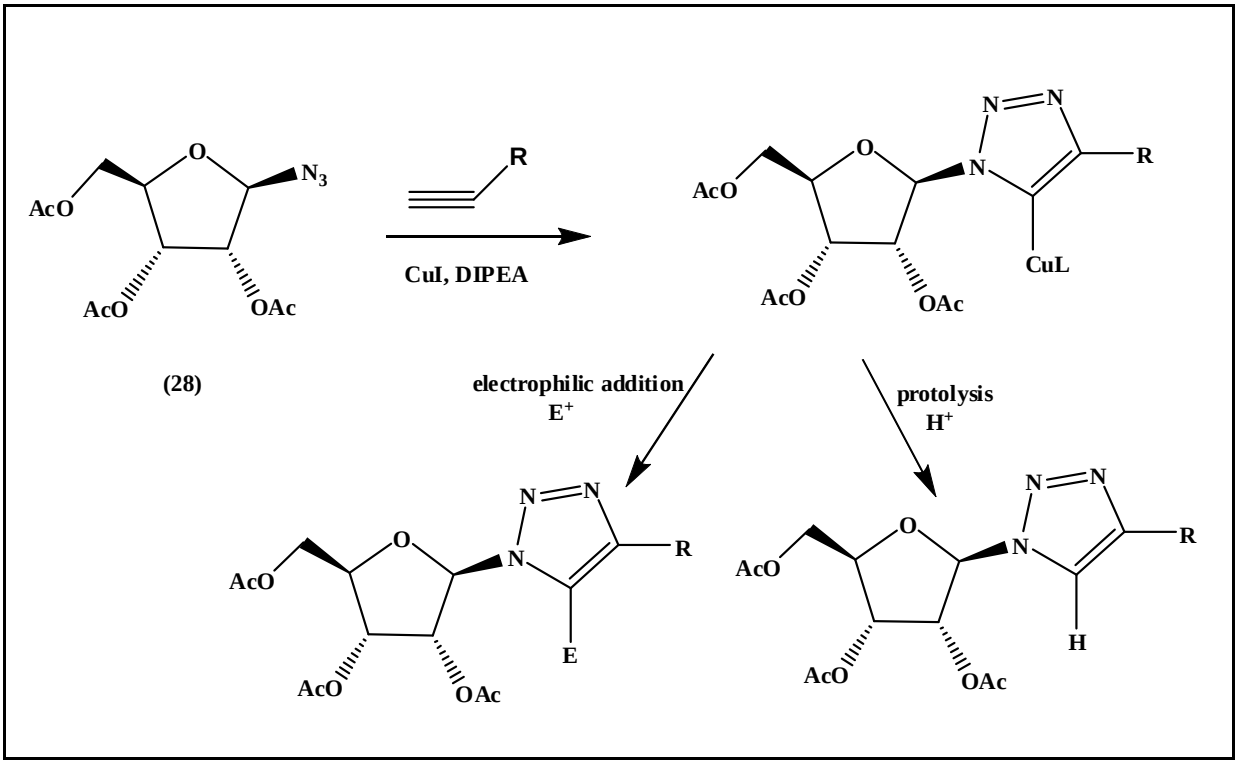
The [3+2] cycloaddition reaction between azides and alkynes was described by L. Zhang[33] and co-workers they are used ruthenium complexes instead of copper(I) for the cycloaddition reaction, which led exclusively to the formation of the 1,5-disubstituted triazoles. Scheme(1-14).



Scheme (1-14) Description 1,4- and 1,5-triazoles[34]

The objective of click chemistry is to establish an ideal set of straightforward and highly selective reactions. Click reaction of azide/alkyne is a recent re-discovery of a reaction fulfilling many requirements which include often quantitative yields, a high tolerance of functional groups, an insensitivity of the reaction to solvents, irrespective of their polar/non-polar character, and reactions at various types of interfaces, such as solid/liquid, liquid/liquid, or even solid/solid interfaces[30].

Based on the discovery of copper-catalyzed azide-alkyne 1,3-dipolar cycloaddition, that the 4,5-disubstituted triazole could be obtained through trapping cupper-triazole intermediate by electophiles during the reaction [35]. Scheme (1-15).



Scheme (1-15) Electrophilic addition *vs* protolysis of Cu(I)-Catalyzed

(1.3.2) Classification of click reactions:

Click chemistry encompasses a group of powerful linking reactions that are simple to perform, have high yields, require no or minimal purification, and are versatile in joining diverse structures without the prerequisite of protection steps. There are four major classes of click reactions cycloadditions these primarily refer to 1,3-dipolar cycloadditions, but also include hetero-Diels-Alder cycloadditions & nucleophilic ring-openings these refer to the openings of strained heterocyclic electrophiles, such as aziridines, epoxides, cyclic sulfates, aziridinium ions, episulfonium ions, etc. & carbonyl chemistry of the non-aldol type examples include the formations of ureas, thioureas, hydrazones, oxime, ethers, amides, aromatic heterocycles, etc. carbonyl reactions of the aldol type generally have low thermodynamic driving forces, hence they have longer reaction times and give side products, and therefore cannot be considered click reactions & additions to carbon-

carbon multiple bonds examples include epoxidations, aziridinations, dihydroxylations, sulfenyl halide additions, nitrosyl halide additions, and certain Michael additions. Among the four major classes, cycloadditions, particularly the CuI-catalyzed Huisgen 1,3-dipolar cycloaddition of azides and terminal alkynes to form 1,2,3-triazoles, are the most widely used[36].

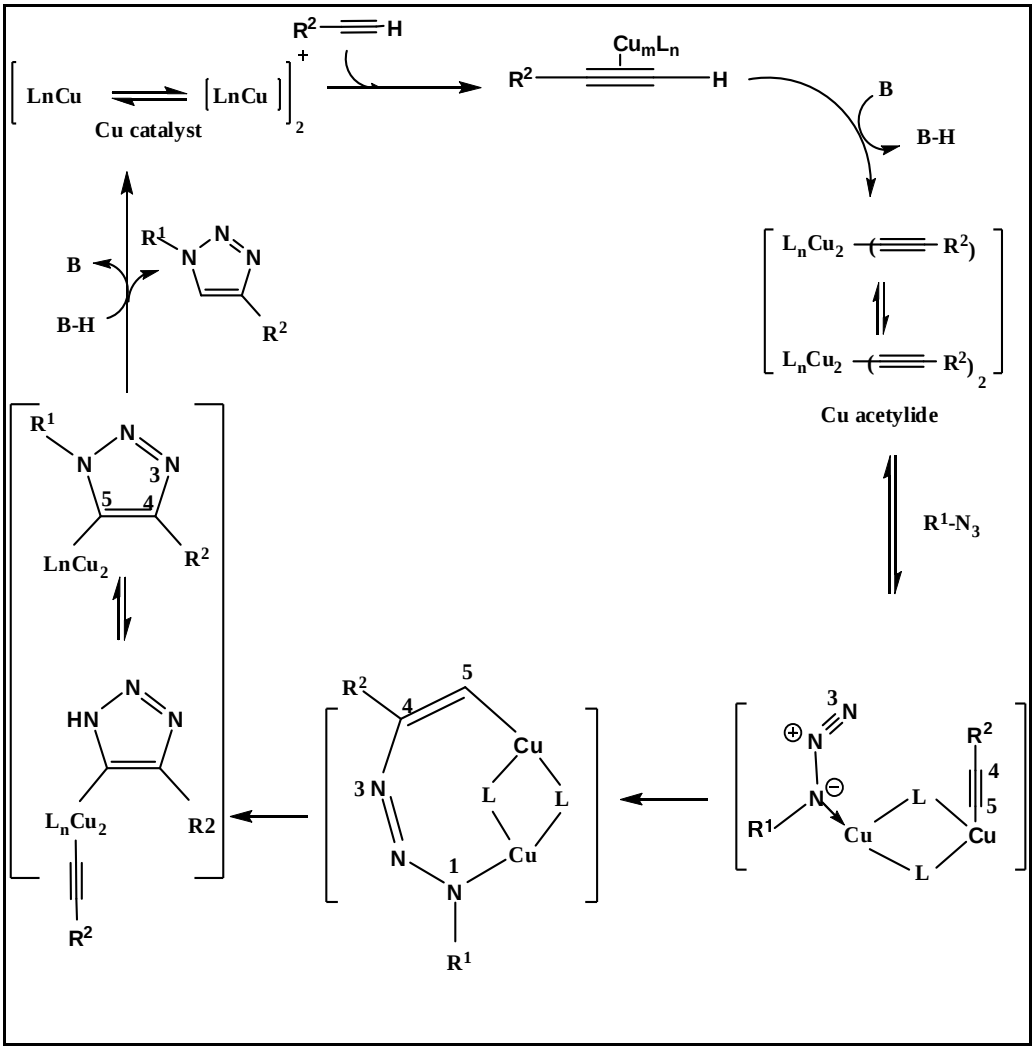
(1.3.3) Metal strategies in click chemistry:

Cycloaddition reactions, the metal catalyzed azide/alkyne click reaction which is a variation of the Huisgen 1,3-dipolar cycloaddition reaction between terminal acetylenes and azides were shown to be the most effective and versatile and thus became the prime example of click chemistry. However, in some particular cases, the presence of transition metal catalysts may be a problem. Additionally, the use of copper(I) catalyzed azide–alkyne cycloaddition for in *vivo* applications is limited by the fact that, if present in more than trace quantities, copper ions are potentially toxic for living organisms, the development of metal free click strategies is particularly relevant. In recent years, metal free [3+2] cycloaddition reactions, Diels–Alder reactions, and thiol alkene radical addition reactions have come to the fore as click reactions because of their simple synthetic procedures and high yields, alternative click reactions to expand the range of opportunities for new applications[37].

(1.3.4) Mechanism of Click reaction:

The 1,3-dipolar addition reaction of alkyne and azide under thermal condition affords both 1,4- and 1,5- regioisomers because the activation energies for the concerted process leading to both isomers are very close. Two groups have independently discovered that a catalytic amount of Cu(I) not only significantly accelerates the reaction rate, but also gives exclusive 1,4-disubstituted 1,2,3-

triazole in a regiospecific[38]. Click reaction catalyzed with Cu(I) as the following mechanism[39] shows in scheme(1-16).



Scheme (1-16) Mechanism of click reaction using Cu(I)

Click chemistry is widely recognized with cupper-catalyzed, Huisgen 1,3-dipolar cycloaddition of azides and terminal alkynes, this reaction is usually quite slow in the absence of an appropriate catalyst for alkynes are poor 1,3-dipole acceptors but in the presence of cupper(I), which can bind to terminal alkynes, cycloaddition reactions are quite accelerated and regioselective. The incorporation of copper to acetylide to form copper acetylide complex, azide activated copper acetylide

complex to generate a copper acetylide-azide complex it is toward nucleophilic attack of acetylide carbon C(4) at N(3) of the azide generating metallocycle[40].

This metallocycle positions the bound azide properly for subsequent ring contraction by a transnnular association of the N(1) lone pair of electron with the C(5)-Cu π*orbital[41].

The difference in ring size for dimeric complexes may change the kinetic slightly, but most likely the transformation from metallocycle into triazole-copper derivative, protonation of triazole-copper derivative followed by dissociation of the product ends the reaction and regenerates the catalyst[42].

The unhindered terminal coordination of the two reactants to the catalytic Cu(I) cluster as a starting point for the reaction provides for catalysis of triazole formation almost independently of the substitutions. The most significant are the electronic effects that influence the formation of the Cu(I) acetylides and the establishment of the transition state of the reaction[43].

(1.3.5) Applications of click chemistry:

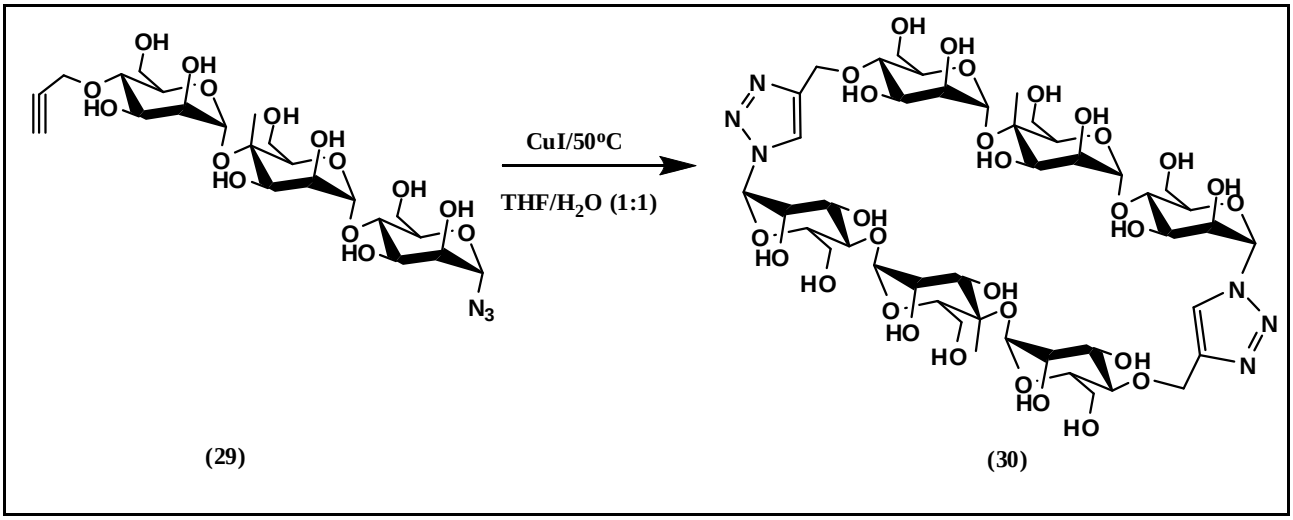
Application of click chemistry based reactions leads to the formation of carbon-heteroatom bonds by using molecules possessing high intrinsic reactivity. Click chemistry has wide spread applications, some of them are preparative organic synthesis of 1,4-substituted triazoles[44], modification of peptide function with triazoles[45], modification of natural products and pharmaceuticals[46], modification of DNA and nucleotides[47], carbohydrate clusters and carbohydrate conjugation by Cu(I) catalyzed[48] and nanotechnology[49].

Click chemistry is not a strategy only for organic synthesis, today it has an enormous potential in materials science, polymer chemistry, biological applications comprising and drug discovery, the development of the copper (I)-

catalyzed cycloaddition reaction between azides and terminal alkynes has led to many interesting applications of click reactions including the synthesis of natural product derivatives[50]. Although azides and alkynes display high mutual reactivity, individually these functional groups are two of the least reactive in organic synthesis, a new approach in organic synthesis with click chemistry that involves the successful achievement of a polymerization process represents an important task in macromolecular science. That have been termed bioorthogonal because of their stability and inertness towards the functional groups typically found in biologymolecules[51]. This bioorthogonality has allowed the use of the azide-alkyne [3+2] cycloaddition in various biological applications including target guided synthesis[52] and activity-based protein profiling[53].

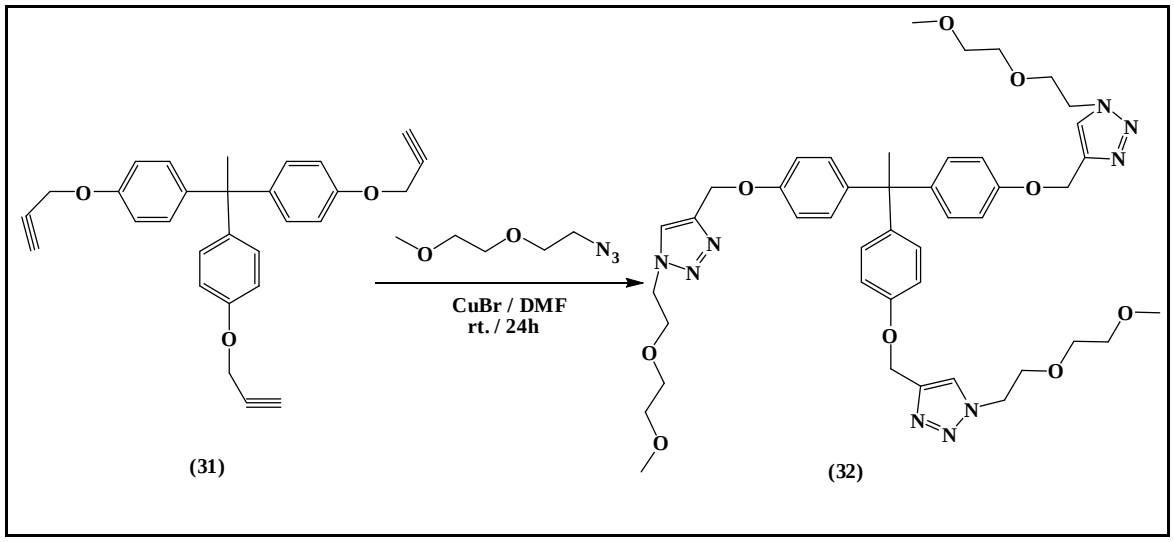
Also click chemistry has widespread applications in organic synthesis of 1,4-substituted triazoles[54], modification of peptide function with trizoles[55], pharmacenticals as a drugs modification[56].

Click reaction can be utilized to construct building blocks for the rapid synthesis of molecules with diverse structure and function. The synthesis of macrocycles is the most striking example of the synthetic application of this click process the synthesis of cyclodextrin analogs *via* regioselective Cu(I)-catalyzed cyclodimerization of an alkynyl –azido trisaccharide [57]. Scheme (1-17).



Scheme (1-17) Synthesis of cyclodextrin (30) *via* click reaction

Click chemistry strategy was successfully applied to macromolecular chemistry, affording polymeric materials varying from block copolymer to complex macromolecular structures, O. ALtintas [58] *et al.* applied a click chemistry strategy to the formation of star polymers (nonlinear polymer) were recovered in yields as high as 87% because of the highly efficient click reaction. Scheme (1-18).



Scheme (1-18) Synthesis polymer (32) *via* click reaction

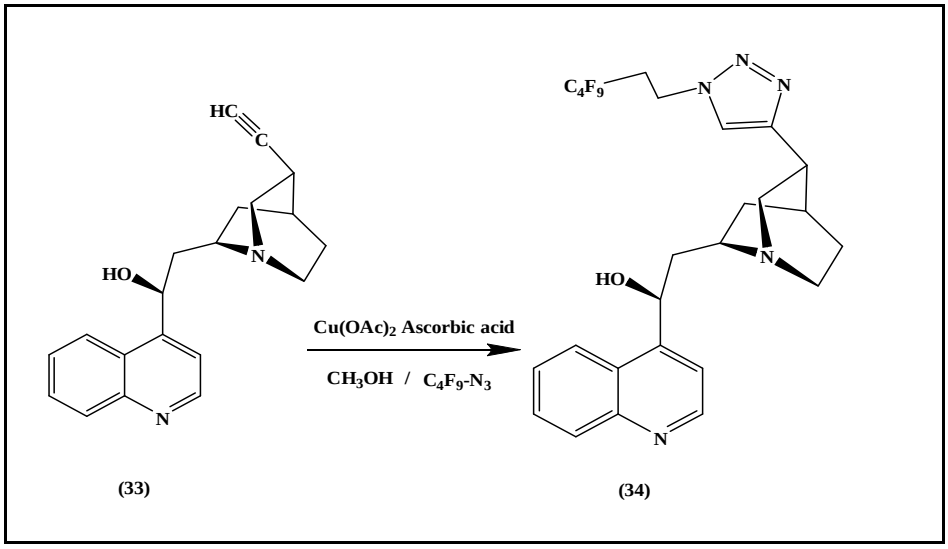
K. B. Sharpless [59] and Co-workers demonstrated the power of nucleophilic ring opening and 1,3-dipolar cycloaddition click reactions in the construction of steroid-like skeletons from diepoxides.

(1.4) Fluorinated Compounds:

Fluorinated compounds are synthetic organo fluorine chemical compounds that have multiple fluorine atoms they can be polyfluorinated or fluoro carbon-based (perfluorinated)[60] , perfluoro- / perfluorinated describes specifically a substance where all hydrogen atoms attached to carbon atoms are replaced with fluorine atoms. This compounds have a wide range of function and can serve as refrigerants[61], pharmaceuticals[62][66], and surfactants[63].

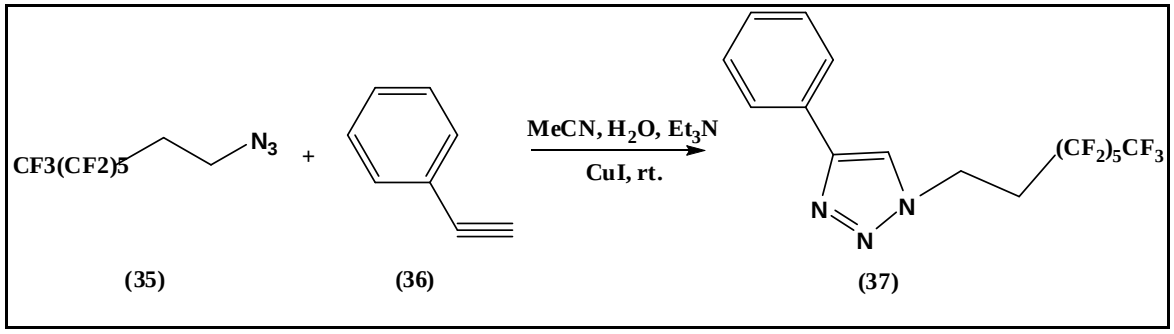
The carbon-fluorine bond is referred to the strongest in organic chemistry because of stability added by its partial ionic character, the ionic character is a result from the electronegativity of fluorine, it induces partial charges on the carbon and fluorine atoms,leading to electrostatic attraction making the bond short and strong [64]. Perfluorinated organic compounds are used in numerous commercial products like fire protection agents, textile protection [65].

Z. kaleta [67] attempted the synthesis of fluorous cinchonidine, as a potentially reusable cinchona alkaloid. Scheme(1-19).



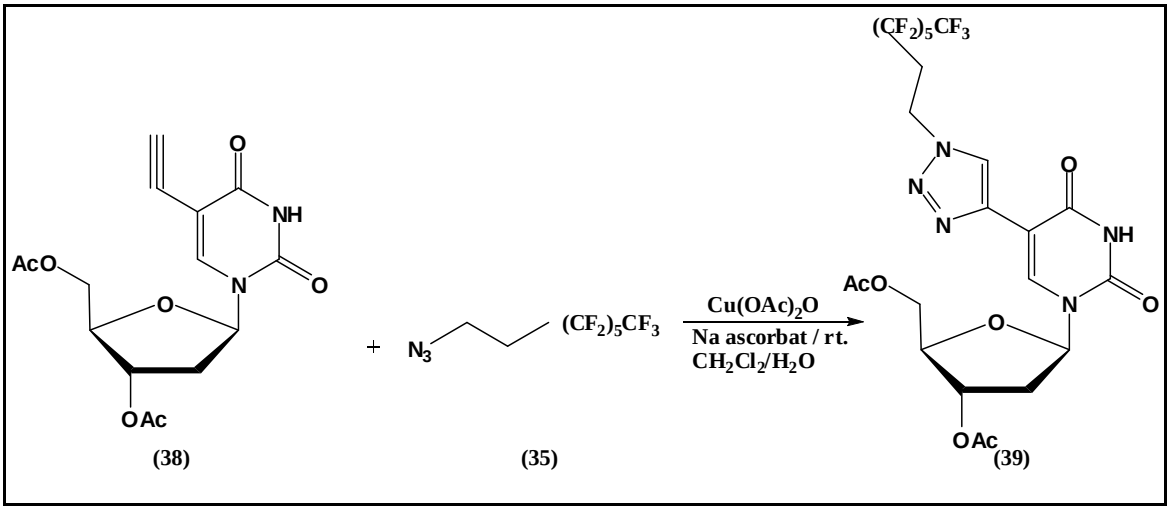
Scheme (1-19) Synthesis fluorous cinchonidine (34)

X.-Y. Zhu [68] *et al.* synthesized 1,4-disubstituted 1,2,3-triazoles *via* 1,3-dipolar cycloaddition of fluoroalkylated azide (35) with terminal alkyne (36) in presence of Cu(I) as catalyst at room temperature. Scheme (1-20).



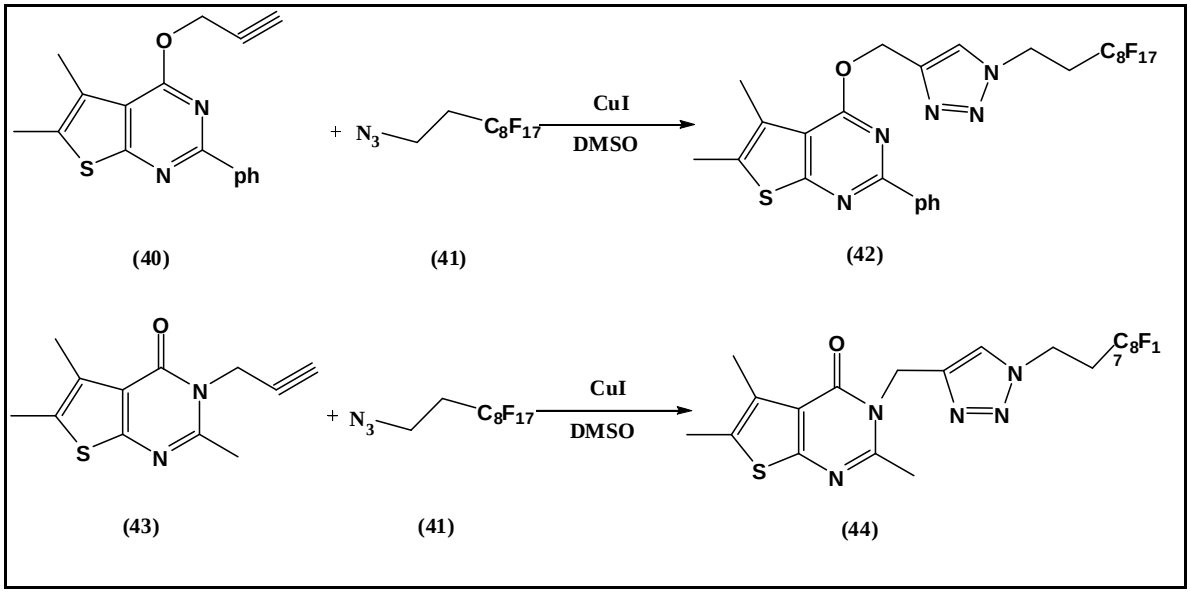
Scheme (1-20) Synthesis 1,4-disubstituted perfluoro triazole

S.M. Park[69] *et al.* synthesized perfluoroalkyl azides (35) for use in cycloaddition reaction under the conditions of the Sharpless click reaction. Scheme (1-21).



Scheme (1-21) Formation of compound (33)

Furthermore the O- and N-propargylated (40) and (43) respectively, were independently reacted with perfluoroalkyl azide (41), using copper (I) iodide as catalyst and resulted in exclusively 1,4-disubstituted-1,2,3-triazole derivatives (42) and (44), respectively[70] according to Schemes (1-22).



Scheme (1-22) Reaction of perfluoroazide with O- and N-propergyl

(1.4.1) physical and chemical properties of florous compounds:

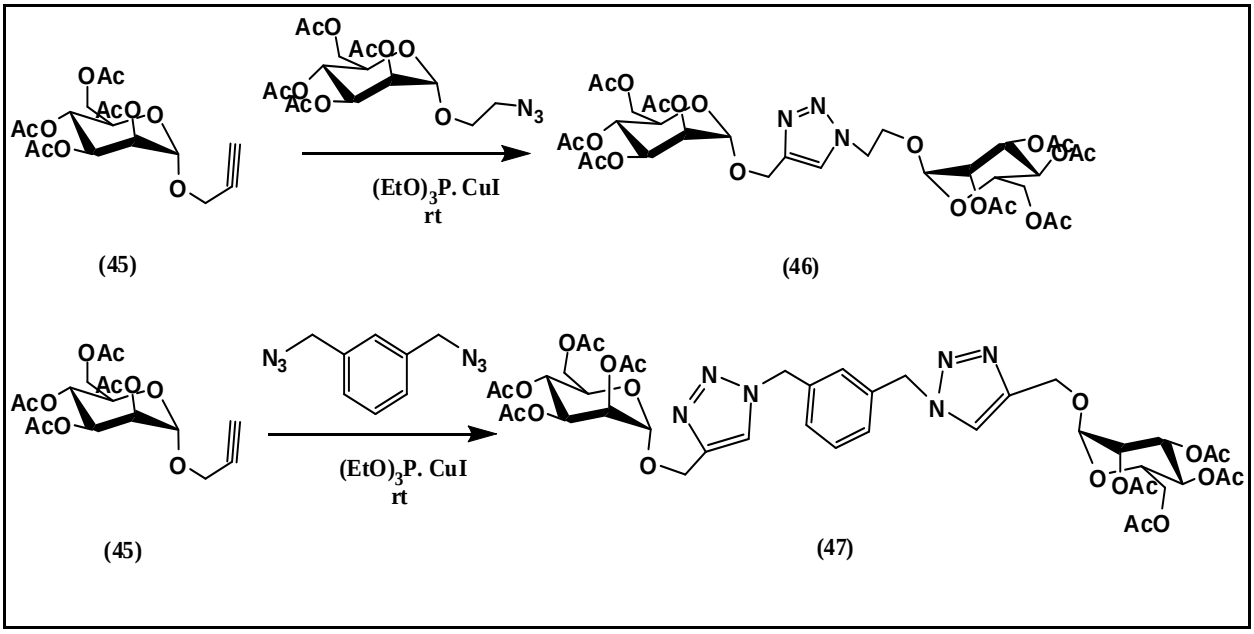
Fluorous compounds have lower the surface tension of water down to a value half [71] the fluorinated or hydrogenated chains and sugar as a polar heads have potential pharmaceutical (biocompatible formulations) and biological (extraction of membrane proteins) applications[72].

The fluorous groups are usually attached to parent molecules through a$(CH2)_m$ segment to insulate the reaction site from the electron withdrawing fluorines. A florous alkyl chain C_nF_{2n+1} C_mH_{2m}. There are two broad classes of fluorous molecules in fluorous synthesis, the first class of fluorous molecules including reagents, scavengers, and catalysts is employed for the single reaction steps. The scond class of fluorous molecules including reactants, protecting groups, and related tags are used to attach to the substrate and used for multistep reactions[73].

(1.5) Sugar triazoles:

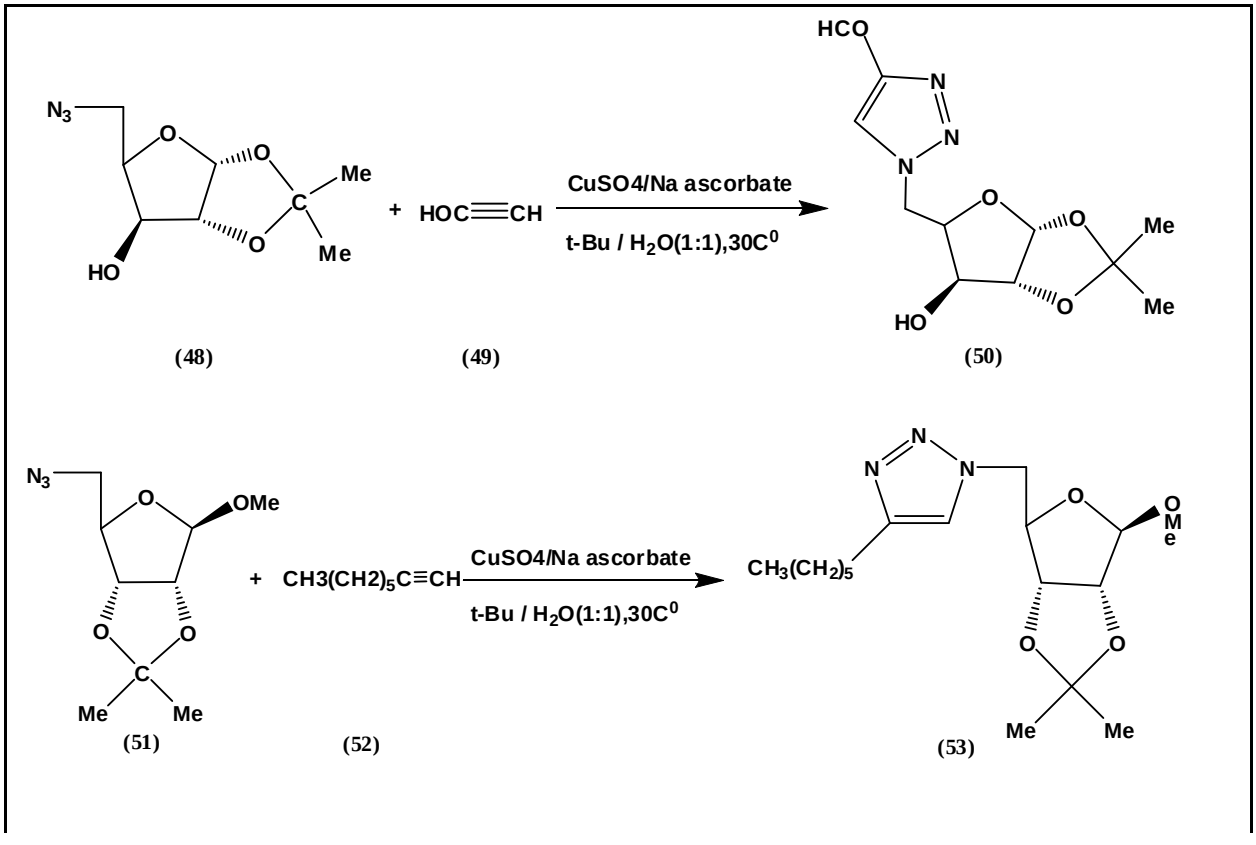
The incorporation of an azide and/or an alkyne moiety on a carbohydrate scaffold unleashes the potential to access a new dimension of structural diversity to complement the vast structural diversity already inherent to carbohydrates and so it is anticipate that interest in the 1,3-dipolar cycloaddition reaction with carbohydrate substrate will grow [74]. Triazole substituted sugars have been explored as potential monoralent and multivalent glectin ligands[75] .

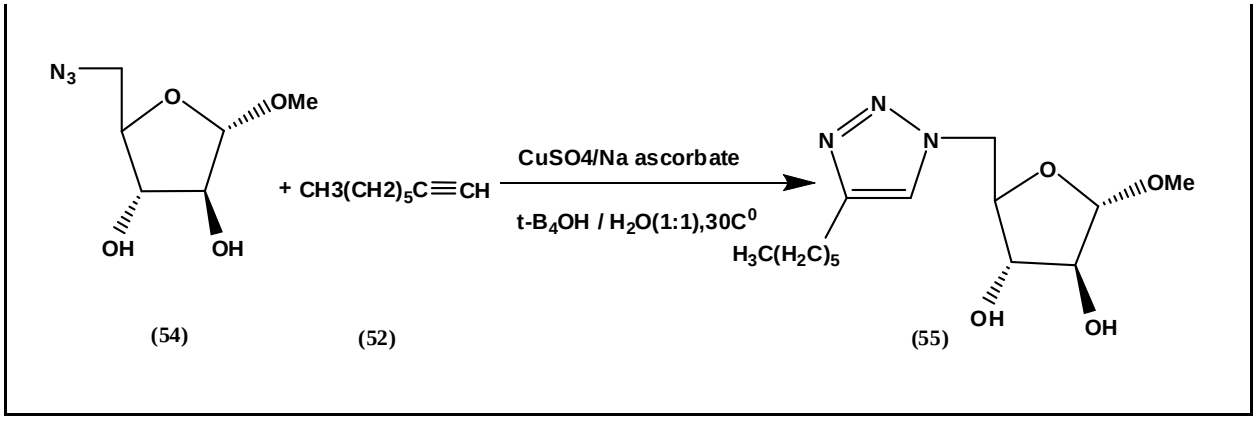
The Cu(I)-catalysed azide–alkyne dipolar cycloaddition reactions in the carbohydrate field are many and varied, S. Dedola[76] *et al*. synthesized cluster of sugar with triazole-linked. Sheme (1-23).



Scheme (1-23) Triazole linked of sugar cluster

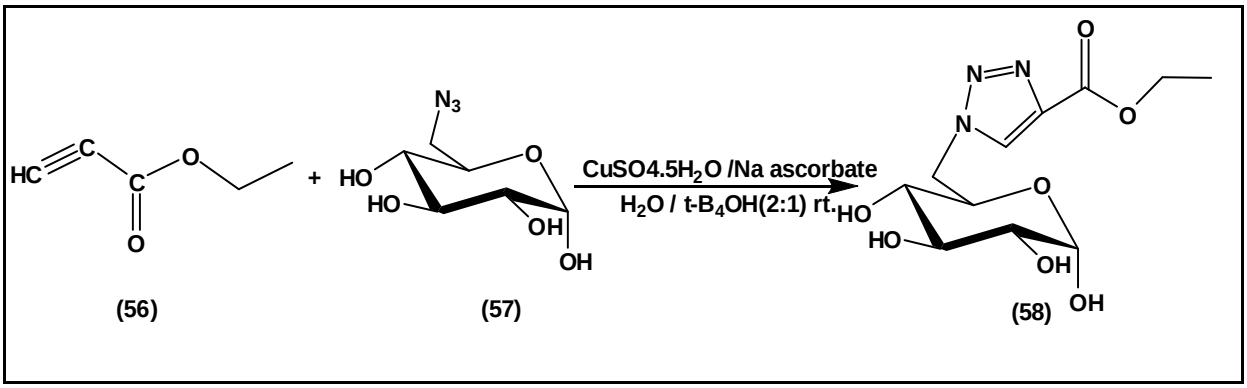
B.K.Singh[77] *et al.* have synthesized suger triazoles starting with three pentofuranoses, D-xylose, D-ribose and D-arabinose. Scheme (1-24).





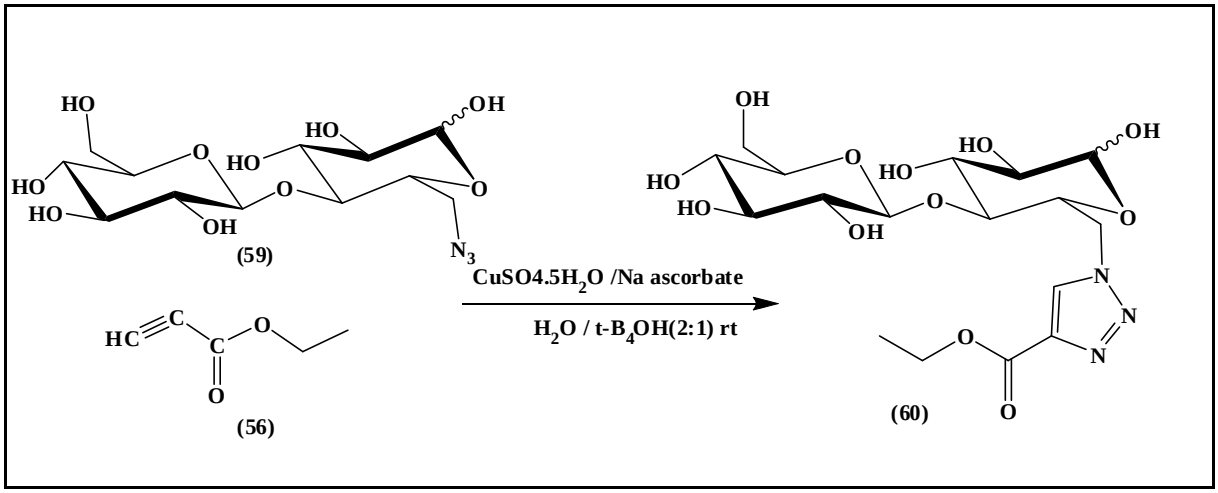
Scheme (1-24) Sugar triazole derivatives

Scheme (1-25) shows the formation of a 1,2,3-triazole derivative (58) from ethyl propiolate as alkyne (56) and 6-azido-6-deoxy-D-glucose (57) as azido sugar [78].



Scheme (1-25) Formation of glucose triazole

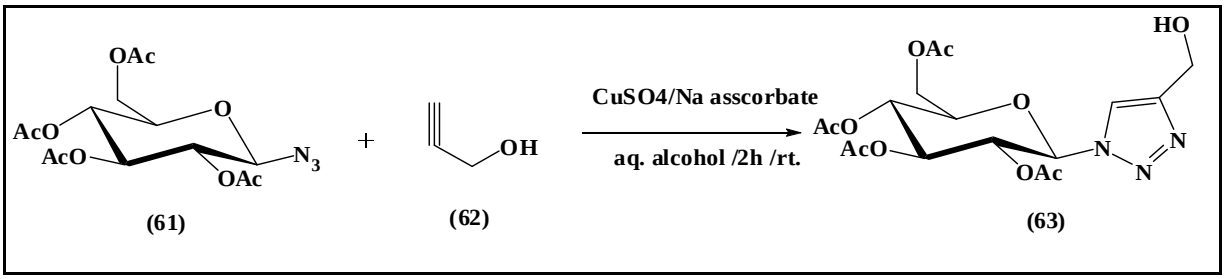
In a similar way, 6-azido-6-deoxy-cellobiose (59) could be coupled with the same alkyne (56) to afford the 1,4-di-substituted triazole[79] as show in scheme (1-26).



(59) (56) (60)

Scheme (1-26) Formation of compound (60)

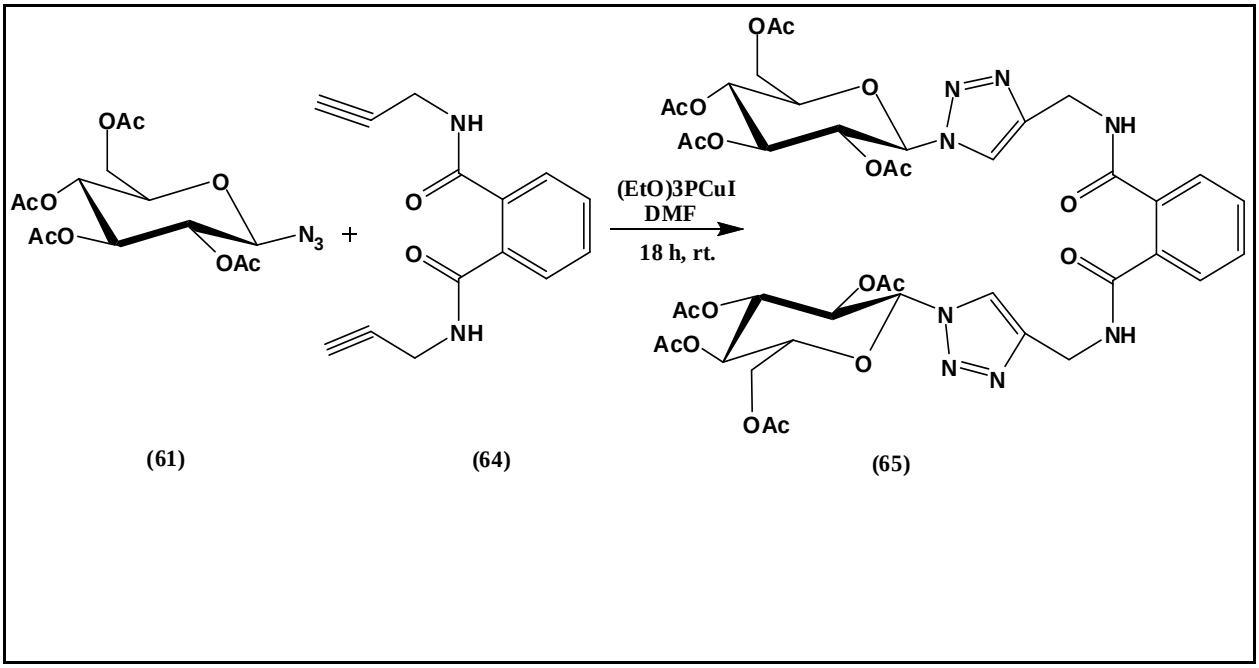
B.L Wilkinson[74] *et al.* are used 1.3dipolar cycloaddition reaction to conducted propargyl alcohol (58) with tetra-O-acetyl glucopyranosyl azide (61) by using click chemistry in presence of a $CuSo_4$ /Na ascorbate mixture in aqueous alcohol . Scheme (1-27).



(61) (62) (63)

Scheme (1-27) Formation of compound (63)

Multivalent carbohydrate interactions play fundamental roles in many biological processes, T. Ziegler[80] *et al.* describe a flexible and straightforward synthesis multidentate carbohydrate ligands *via* Cu(I)- catalyzed, 1,3-dipolar cycloaddition of glycosyl azide (61) with bivalent 2 propynyl derivative (69) was clicked to obtained 1,2,3-triazole-linked multidentate carbohydrate ligand(65). Scheme (1-28).



Scheme (1-28) Synthesis multivalent carbohydrate *via* click reaction

(1.6) The Thermodynamics:

Thermodynamics, as the most fundamental subject in the field of thermal sciences, is simply defined as the science that deals with matter, energy, and the laws governing their interactions. The name thermodynamics stems from the Greek words therme (heat) and dynamis (power), which is most descriptive of the early efforts to convert heat into power. Today the same name is broadly interpreted to include all aspects of energy and energy transformations, including power production, refrigeration, and relationships among the properties of matter[81].

A change from one equilibrium state of the system to another is called a thermodynamic process. Thermodynamics cannot determine how much time such a process will take, and the final state is independent of the amount of time it takes to reach equilibrium. It is convenient to consider thermodynamic processes where a system is taken from an initial to a final state by a continuous succession of intermediate states. To describe a process in terms of thermodynamic variables, the

system must be in thermodynamic equilibrium. However, for the process to occur, the system cannot be exactly in thermodynamic equilibrium because at least one of the thermodynamic variables is changing. However, if the change is sufficiently slow, the process is quasistatic, and the system can be considered to be in a succession of equilibrium states. A quasistatic process is an idealized concept. Although no physical process is quasistatic[82].

In practice, the primary objective of chemical thermodynamics is to establish a criterion for determining the feasibility or spontaneity of a given physical or chemical transformation on the basis of laws of thermodynamics, which are expressed in terms of Gibbs's functions, several additional theoretical concepts and mathematical functions have been developed that provide a powerful approach to the solution of these questions[83]. Once the spontaneous direction of a natural process is determined, we may wish to know how far the process will proceed before reaching equilibrium. For example, might find the maximum yield of an industrial process. Thermodynamic methods provide the mathematical relations required to estimate such quantities[81].

Although the main objective of chemical thermodynamics is the analysis of spontaneity and equilibrium, the methods also are applicable to many other problems[83]. Similarly, the energy changes that accompany a physical or chemical transformation, in the form of either heat or work, are of great interest, whether the transformation is the combustion of a fuel[84], or the fission of a uranium nucleus[85]. Thermodynamic concepts and methods provide a powerful approach to the understanding of such problems.

Although descriptions of chemical change are permeated with the terms and language of molecular theory, the concepts of thermodynamics are independent of molecular theory; thus, these concepts do not require modification as our knowledge of molecular structure changes. This feature is an advantage in a formal

sense, but it is also a distinct limitation because we cannot obtain information at a molecular level from thermodynamics[86]. In contrast to molecular theory, thermodynamics deals only with measurable properties of matter in bulk (for example, pressure, temperature, volume, cell potential, magnetic susceptibility, and heat capacity). It is an empirical and phenomenological science, and in this sense, it resembles classic mechanics. The latter also is concerned with the behavior of macroscopic systems, with the position and the velocity of a body as a function of time, without regard to the body's molecular nature[83].

The essence of thermodynamics can be summarized by four laws[87, 88]:

1- Zeroth law of thermodynamics : If two bodies are in thermal equilibrium with a third body, they are in thermal equilibrium with each other.

2- The first law of thermodynamics : Energy can be transported or converted from one form to another, but cannot be either created or destroyed. It is simply an expression of the conservation of energy principle, and it asserts that energy is a thermodynamic property.

$$\Delta E = W + Q \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1\text{-}1)$$

The quantity Q is the change in the system's energy due to heating ($Q > 0$) or cooling ($Q < 0$) and W is the work done on the system. This equation is equivalent to saying that there are two macroscopic ways of changing the internal energy of a system: doing work and heating.

3- The second law of thermodynamics: (increase of entropy principle) is expressed as the entropy of an isolated system during a process always increases or, in the limiting case of a reversible process, remains constant. In other words, the entropy of an isolated system never decreases. It also asserts that energy has quality as well as quantity, and actual processes occur in the direction of decreasing quality of energy.

$$\Delta S_{\text{Isolated system}} \geq 0$$

4- The third law of thermodynamics: most important consequence of the third law is that all heat capacities must go to zero as the temperature approaches zero.

$$S_T - S_0 = \int_0^T \frac{C_P}{T} dT \xrightarrow{\text{Since } S_0 = 0,} S_T = \int_0^T \frac{C_P}{T} dT$$

(1.6.1) Thermochemistry:

Thermochemistry is a branch of thermodynamics which are inhomogeneous both thermally and chemically, thermochemical analysis can be used successfully to define the permissible reactions occurring during a wide variety of joining processes[89]. Thus can use calorimetry to measure the energy supplied or discarded as heat by a reaction, and can identify q with a change in internal energy (if the reaction occurs at constant volume) or a change in enthalpy (if the reaction occurs at constant pressure). Conversely, if know as ΔU or ΔH for a reaction, we can predict the energy (transferred as heat) the reaction can produce[90].

The internal energy (*U*) is the sum of the kinetic and potential energies of the particles that make up a system Internal energy is a state function. A state function depends only on the present state of the system and is completely determined by variables such as temperature and pressure. As a system changes from one state to another, the internal energy changes from one definite value to a new definite value. The change in internal energy (Δ*U*) equals the difference in internal energy between the final and initial states[91].

(1.6.2) Enthalpy

The enthalpy (*H*) is a property of a substance that can be used to calculate the heat produced or absorbed in a chemical reaction. Enthalpy is also a state function,

and calculate the enthalpy change for a chemical reaction by finding the difference in enthalpy between the starting and ending state. Enthalpy is related to internal energy via its precise definition[92]:

$H = U + PV$ ……(1-3)

where P is the pressure and V is the volume.

(1.6.3) Entropy

The entropy (S) is a measure of the amount of disorder, or randomness, in a system. Entropy is another state function. For reactions involving different phases, we can often predict the sign of the entropy change. Solids have a more ordered structure since the constituent units (atoms, molecules, or ions) have definite locations[93].

(1.6.4) Gibbs free energy

The Gibbs free energy (G), or Gibbs energy, is the thermodynamic quantity defined by the equation:

$G = H – TS$ ……(1-4)

where T is the temperature. As a chemical reaction proceeds, both H and S change. These changes, denoted using the Δ symbol, allow the change in the Gibbs energy to be calculated[94]:

$\Delta G = \Delta H – T\Delta S$ ……(1-5)

(1.7) Thermal analysis

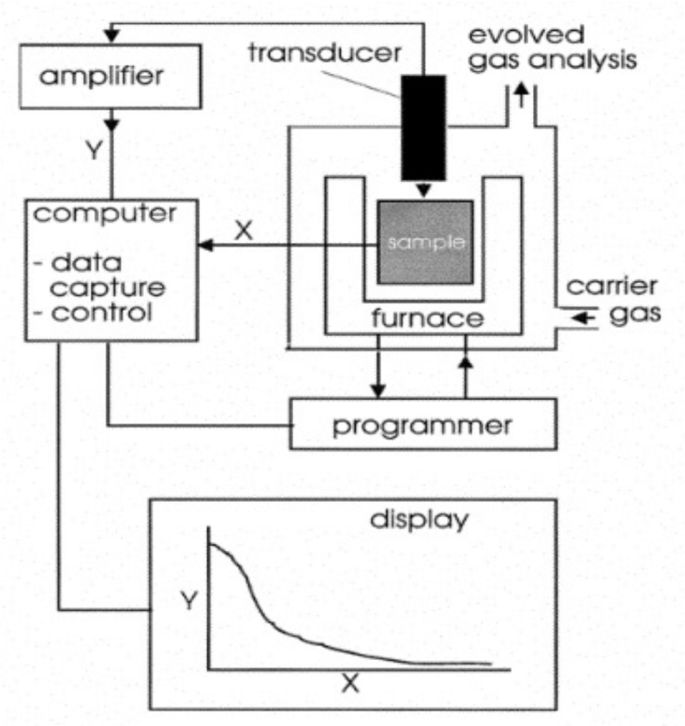


Fig. 1.1 : A generalized Thermal analysis instrument and the resulting Thermal analysis curve

Thermal analysis, in its various guises, is widely employed in both scientific and industrial domains. The ability of these techniques to characterize, quantitatively and qualitatively, a huge variety of materials over a considerable temperature range has been pivotal in their acceptance as analytical techniques **(Table 1.1)**. The application of thermal analysis to the study of materials stems from the fact that they undergo physicochemical changes on heating[(95)].

Table 1.1. Conventional forms of Thermal analysis

Property	Thermal analysis method	Abbreviation
Mass	Thermogravimetry	TG
Difference temperature	Differential thermal analysis	DTA

Alternating temperature	Alternating current calorimetry	ACC
Enthalpy	Differential scanning calorimetry	DSC
Length, volume	Dilatometry	-
Deformation	Thermomechanical analysis	TMA
Dimemsions or mechanical Properties	Dynamic mechanical analysis	DMA
Electric current	Thermostimulated current	TSC
Luminescence	Thermoluminescence	TL

The advantages of thermal analysis over other analytical methods can be summarized as follows[(96)]:

(i) The sample can be studied over a wide temperature range using various temperature programmes.

(ii) Almost any physical form of sample (solid, liquid or gel) can be accommodated using a variety of sample vessels or attachments.

(iii) A small amount of sample (0.1 μg-10 mg) is required.

(iv) The atmosphere in the vicinity of the sample can be standardized.

(v) The time required to complete an experiment ranges from several minutes to several hours.

(vi) Thermal analysis instruments are reasonably priced.

(1.7.1) Differential scanning calorimetry

A differential scanning calorimeter (DSC) measures the energy transferred as heat to or from a sample at constant pressure during a physical or chemical change. The term 'differential' refers to the fact that the behavior of the sample is compared to that of a reference material which does not undergo a physical or chemical change during the analysis. The term 'scanning' refers to the fact that the temperatures of the sample and reference material are increased, or scanned,

during the analysis. The exact ICTA definition of (DSC) is a technique that records the energy (in the form of heat) required to yield a zero temperature difference between a substance and a reference, as a function of either temperature or time at a predetermined heating and/or cooling rate, once again assuming that both the sample and the reference material are in the same environment[97].

The main goal of any enthalpic experiment, which is to determine the enthalpy of a sample as a function of temperature, is attained by measuring the energy obtained from a sample heated at a constant rate with a linear temperature or time programming[98].

The plot obtained from differential scanning calorimetry instrument is known as a DSC curve and shows the amount of heat applied as a function of temperature or time. this technique can be yield the several thermodynamic data such as enthalpy, entropy, Gibbs' free energy, and specific heat, as well as kinetic data[99]. The integration of a DSC curve is directly proportional to the enthalpy change[100].

Differential scanning calorimetry is used in the chemical industry to characterize the materials such as polymers and in the biochemistry laboratory to assess the stability of proteins, nucleic acids, and membranes. Large molecules, such as synthetic or biological polymers , attain complex three dimensional structures due to intra- and intermolecular inter - actions, such as hydrogen bonding and hydrophobic interactions. At higher temperatures , the protein undergoes an endothermic conformational change that results in the loss of its three-dimensional structure. The same principles also apply to the study of structural integrity and stability of synthetic polymers, such as plastics[97].

Aim of the Work

The target of this study is synthesis, characterization and measurement of some thermodynamic functions (ΔH, ΔG and ΔS) of two types of novel sugar based perfluorotriazoles *via*Cu (I) catalyzed 1,3-dipolarcycloaddition with three different perfluoro chains (C_4F_9, C_6F_{13} and C_8F_{17}) with ethyl spacer, and study the effect of increasing the perfluoro chain on the ΔH and ΔS , and comparison the values of the two types.

Chapter Two

2

EXPERIMENTAL PART

EXPERIMENTAL PART

(2.1) Materials

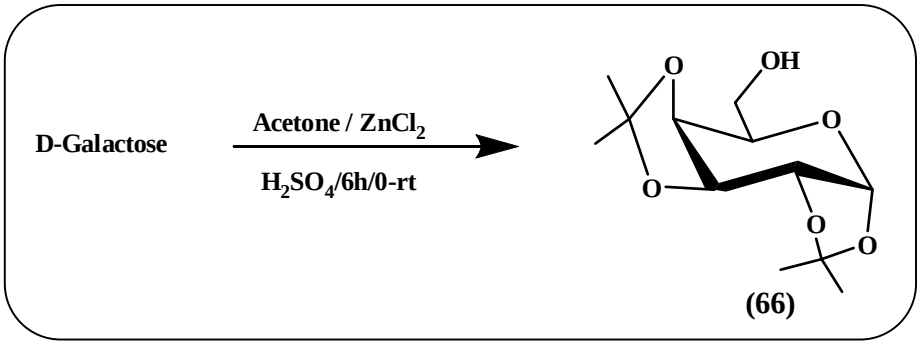
Chemical reagents and starting materials were obtained from Ajax, Merck and Sigma-Aldrich Chemical.

(2.2) Instrumentations

Infrared spectra were recorded using AVATAR 320 FT-IR. ^{1}H and ^{13}C NMR spectra were recorded using 300 MHz Bruker DPX spectrometers. DSC spectra were recorded using PERKIN ELMER DSC7. Silica TLC plates were used with an aluminum backing (0.2 mm, 60 F_{254}). The reactions were monitored by TLC and visualized by development of the TLC plates with an alkaline potassium permanganate dip.

(2.3) Synthesis of organic compounds

(2.3.1) Synthesis of 1,2:3,4-di-O-isopropylidene-α-D-galactose(66)[101]

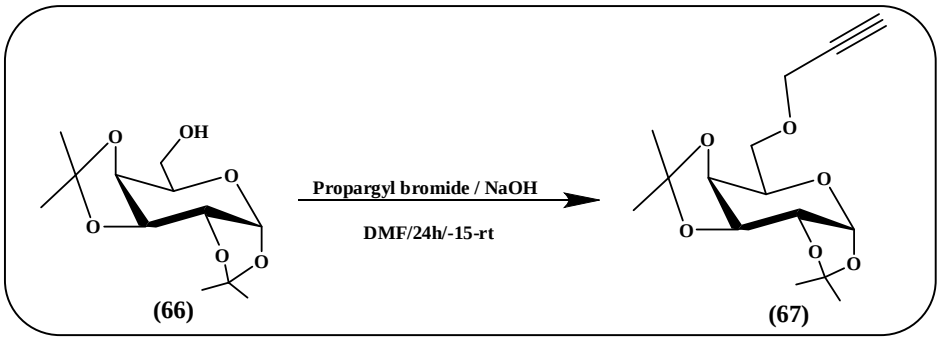


Scheme (2-1) Synthesis of compound (66)

Zinc chloride (40 g, 0.29 mol) was partially dissolved in acetone (450 mL) and conc. H_2SO_4 (1.0 mL) was added at room temperature to give a clear solution. α-D-Galactose (33.5 g, 0.18 mol) was added in one portion and the resulting white suspension stirred for 6 h at rt. A suspension of Na_2CO_3 (66.5 g, 0.63 mol) in H_2O

(100 mL) was added to the yellow reaction mixture at 0 °C. The suspension was allowed to stir for 30 min then filtered and the solid discarded. Volatile solvent was removed *in vacuo* below 30 °C. The resulting yellow oil and aqueous layer were separated and aqueous layer further extracted with Et_2O (3×100 mL). The combined organic layers were dried over Na_2SO_4, and the solvent removed *in vacuo* to yield 1,2:3,4-di-O-isopropylidene-α-D-galactopyranose **(66)** as a pale yellow oil (38.0 g, 81%) R_f = 0.45 (1:1 Et_2O/Hexane).

(2.3.2) Synthesis of 6-O-prop-2-ynyl-1,2:3,4-di-O-isopropylidene-α-D-galactose (67)

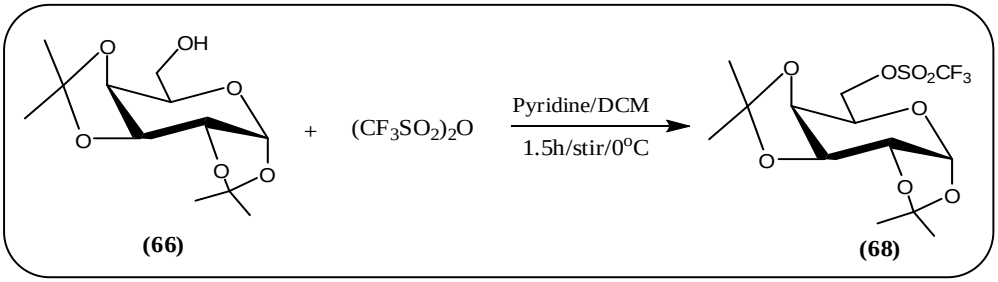


Scheme (2-2) Synthesis of compound (67)

Alcohol 1,2:3,4-di-O-isopropylidene-α-D-galactose **(66)** (0.52 g, 2 mmol) was dissolved in DMF (10 mL) in a dry flask and NaOH pellets (0.32 g, 8 mmol) were added. The flask was cooled in a salt- ice bath at -15 °C and the contents stirred for 10 min before propargyl bromide (2.2 mmol) was added dropwise. The reaction mixture was then allowed to stir for 24 h, gradually warming to rt. The reaction mixture was partitioned between Et_2O (50 mL) and water (100 mL), the layers separated, and the aqueous layer extracted with more Et_2O (3 x 50 mL). The combined extracts were dried over Na_2SO_4, and evaporated to dryness under reduced pressure. The residue was flash chromatographed (silica gel, Et_2O/*n*-

Hexane 1:9) to give 6-O-prop-2-ynl-1,2:3,4-di-O-isopropylidene-α-D-galactose **(67)** as a white needles precipitate (1.10 g, 88%), R_f = 0.41 (1:1 Hexane/ Et_2O).

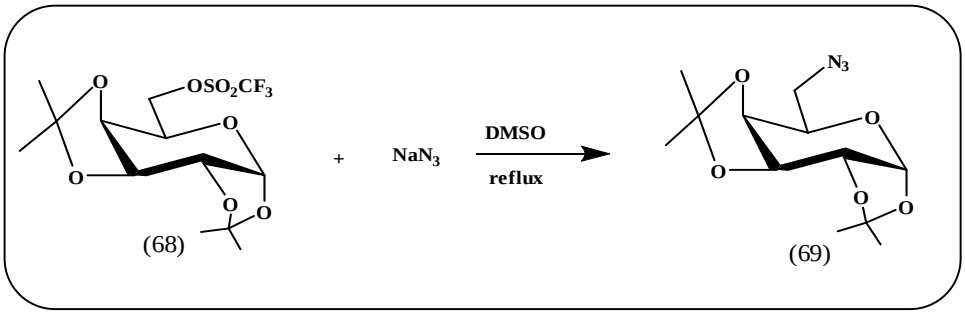
(2.3.3) Synthesis of 1,2:3,4-di-O-isopropylidene-α-D-galactose-6-O-triflate (68)[102]



Scheme (2-3) Synthesis of compound (68)

In dry round flask dichloromethane (50mL) and dry pyridine (1.35mL) was added, the flask cooled to 0 °C in ice bath and the trifluoromethanesulfonic anhydride (2.7mL, 22mmol) was added dropwise. A thick white precipitate began to form during addition, the stirring allowed for an additional 10 min. The 1,2:3,4-di-O-isopropylidene-α-D-galactose **(66)** solution (22 mmol, 5.4g in 30 mL DCM) was added dropwise and stirring continued for 1.5 h. The reaction mixture was poured into 100mL ice-water, the layer was separated and the aqueous layer was extracted with dichloromethane (3x50mL). The combined extracts were dried over sodium sulfate and the solvent was removed in vacuo, the residue was flash chromatographed (silica gel, Et2O/n-hexane 1:3) to give white solid **(68)** (4.6g, 63%), R_f =0.62 (ether).

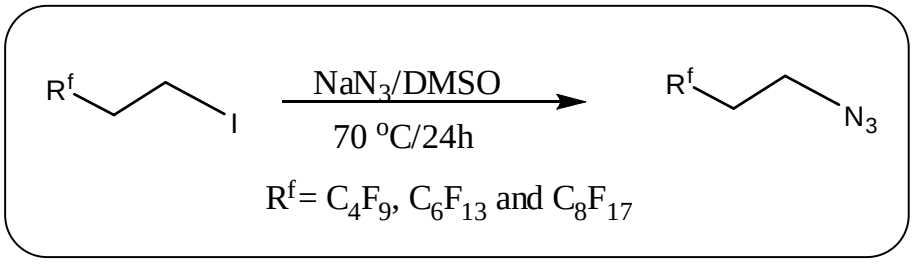
(2.3.4) Synthesis of 6-azido-6-deoxy-1,2:3,4-di-O-isopropylidene α-D-galactose (69)



Scheme (2-4) Synthesis of compound (69)

6-O-triflate-6-deoxy-1:2,3:4-di-O-isopropylidene-α-D-galactose **(68)** (1mmol) was dissolved in DMSO (50mL), sodium azide (1.2mmol) was added and allowed to the reflux overnight. Water (50mL) was added, the mixture was extracted with ether (3x50mL) and the organic layer dried over sodium sulfate and evaporated in vacuo, the residue was flash chromatographed (silica gel, Et2O/n-Hexane 3:1) to give colorless liquid **(69)** (1.3g, 71%), R_f = 0.64 (1:1 hexane/ether).

(2.3.5) Synthesis of perfluoroalkylethyl azides (35, 41and 70)



Scheme (2-5) Synthesis of perfluoroalkylethyl azides(35, 41and 70)

Sodium azide (0.98 g, 15 mmol) was added to the stirred solution of perfluoroalkylethyl iodide (5mmol) in DMSO (30 mL), the mixture was heated to 70 °C for (24), the reaction was poured in water (50 mL) and extracted with ether

(3 x 50 mL), the combined organic layers was washed with brine (50 mL), water (50 mL), dried over Na_2SO_4 and evaporated under reduced pressure to give a pale yellow liquid. The residue was flash chromatographed (silica gel, light petroleum) followed by Kugelrohr distillation (describe in Fig.(2-1)) gave perfluoroalkyethyl azide as a colorless liquid.

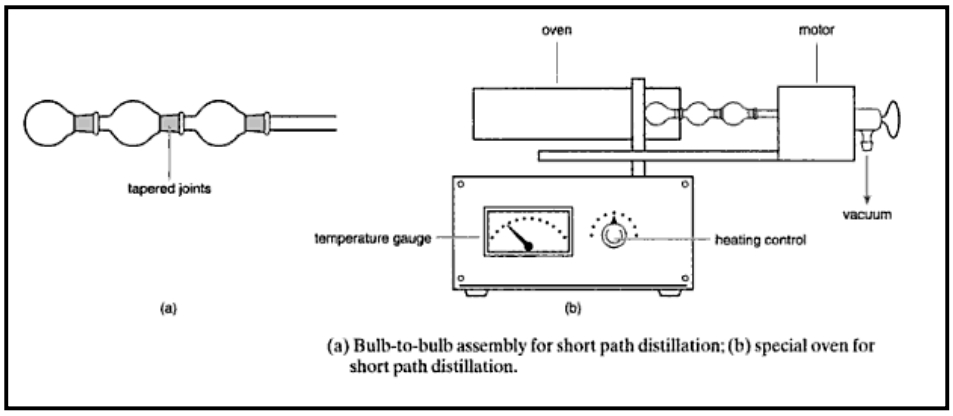
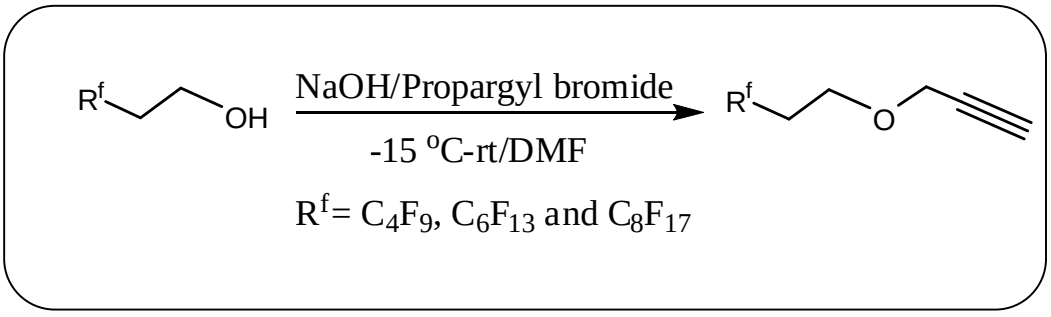


Fig. (2-1) Kugelrohr distillation

(2.3.6) Synthesis of perfluoroalkylethyl propargyl ethers (71-73)

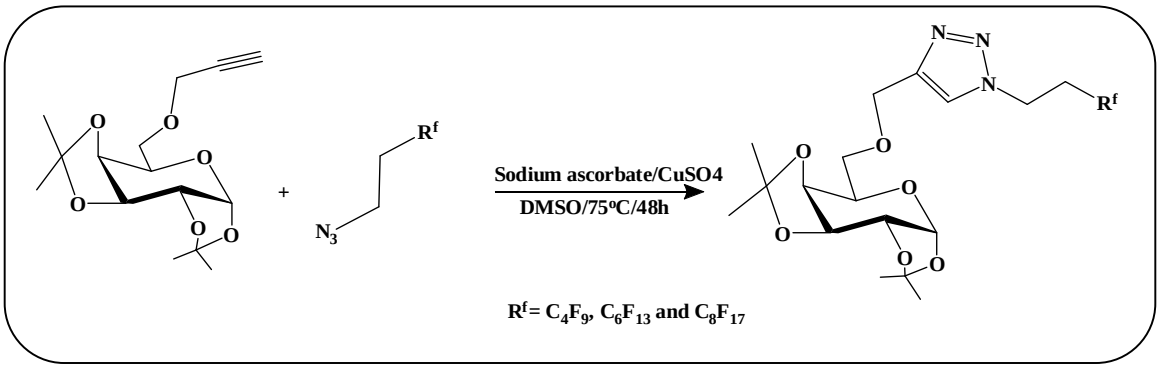


Scheme (2-6) Synthesis of perfluoroalkylethyl propargyl ethers (71-73)

Perfluoroalkylethyl alcohol (2 mmol) was dissolved in DMF (10 mL) in a dry flask and NaOH pellets (0.32 g, 8 mmol) were added. The flask was cooled in ice bath to -15 °C and the contents stirred for 10 min. before propargyl bromide (2.2 mmol) was added dropwise. The reaction mixture was then allowed to stir for 24 h, gradually warming to rt. The reaction mixture was partitioned between Et_2O (30

mL) and water (50 mL), the layers separated, the aqueous layer extracted with more Et_2O (30 mL × 3). The combined extracts were washed with 10% HCl (25 mL × 3), water (30 mL × 3), dried over Na_2SO4, and evaporated to dryness under reduced pressure. The residue was flash chromatographed (silica gel, Et_2O/light petroleum 1:20) followed by Kulgelrohr distillation gave perfluorooctylethyl propargyl ethers as a colorless liquid.

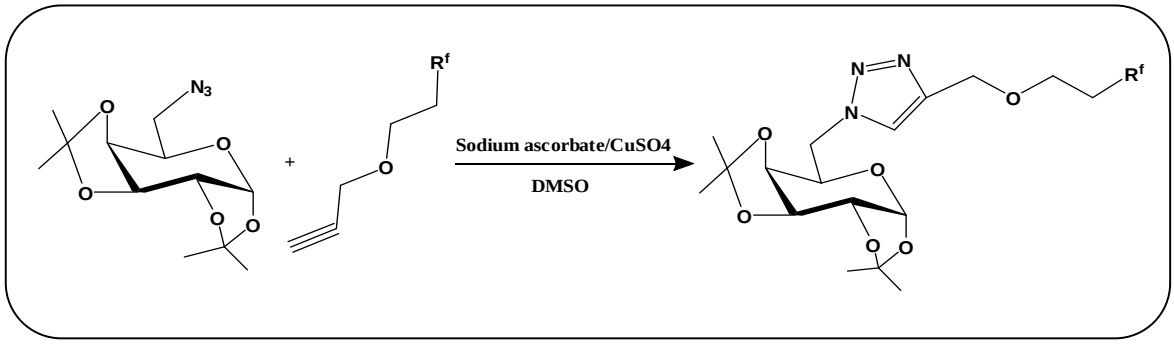
(2.3.7) General procedure for synthesis of perfluoroalkylethyl triazoles (74-76)



Scheme (2-7) Synthesis of perfluoroalkylethyl triazoles (74-76)

Propargyl ether **(67)** (0.274 g, 1.0 mmol) and perfluoroalkylethyl azide (70, 35 and 40) (1.0 mmol) were added to a suspension of sodium ascorbate (0.018 g, 0.09 mmol) and $CuSO_4$•$5H_2O$ (0.011g, 0.045 mmol) in DMSO (10 mL). The mixture was heated to 75°C with stirring for 48 h. The reaction mixture was diluted with water (30 mL), extracted with EtOAc (3×30 mL), and the combined organic layers washed with brine (2 × 20 mL), dried over Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was flash chromatographed (silica gel, Et_2O/Hexane 1:1) to yield the desired compounds, which were recrystallized.

(2.3.8) General procedure for synthesis of perfluoroalkylethyl triazoles (77-79)



Scheme (2-8) Synthesis of perfluoroalkylethyl triazoles (77-79)

Azide derivative **(69)** (0.427g, 1.5mmol) and perfluoroalkylethyl propargyl ethers (71, 72 and 73) (1.0 mmol) were added to a suspension of sodium ascorbate (0.018 g, 0.09 mmol) and $CuSO_4 \bullet 5H_2O$ (0.011g, 0.045 mmol) in DMSO (10 mL). The mixture was heated to 75°C and stirred for 48 h. The reaction mixture was diluted with water (30 mL), extracted with EtOAc (3×50 mL), and the combined organic layers washed with brine (2 × 40 mL), dried over Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was flash chromatographed (silica gel, Et_2O/hexane 1:1) to yield the desired compounds, which were recrystallized.

(2.4) Preparation of DSC samples

Samples (74-79) derivatives were weighted (5 mg) and placed in the pan, covered with lid than pressed, the sample running in the DSC instrument with another empty pan as a blank, heating gradually (10 °C/m) for three cycle heating and cooling respectively. ΔH, T_{fusion} and onset using software supplied by "PERKIN-ELMER THERMAL ANALYSIS".

(2.5) Calculation of thermodynamic functions:

Thermodynamics functions *(*ΔH, ΔG and ΔS) were calculated for synthesized compounds (74-79) using (Differential Scanning Calorimeter) (DSC) and gave the following curve Fig.(2-2)[95]

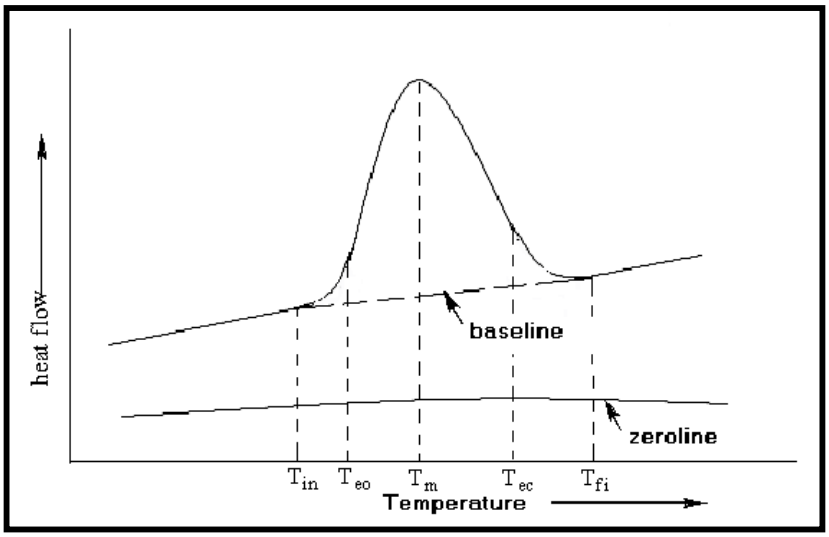


Fig. (2-2) Describe of DSC curve

Where:

T_{in}: initial peak temperature.
T_{eo}: extrapolated peak onset.
T_m: peak maximum temperature.
T_{ec} extrapolated peak completion temperature.
T_{fi}: final peak temperature.

Once a satisfactory baseline has been defined, the area of the endotherm or exotherm is determined by numerical integration. The measured area, A, is assumed to be proportional to the enthalpy change, ΔH, for the thermal event represented.

Enthalpy (Δ*H*) calculation enthalpy of transition, this is done by integrating the peak corresponding to a given transition. It can be shown that the enthalpy of transition can be expressed using the following equation:

$$\Delta H = KA$$

Where:
Δ*H* is the enthalpy of transition
K is the calorimetric constant
A is the area under the curve

Gibbs free energy (Δ*G*) equal to zero resulting from the equilibrium between solid phase to liquid phase.

Entropy (Δ*S*) was calculated from celebrated equation as shown bellow:-

$$\Delta S = \frac{\Delta H}{T}$$

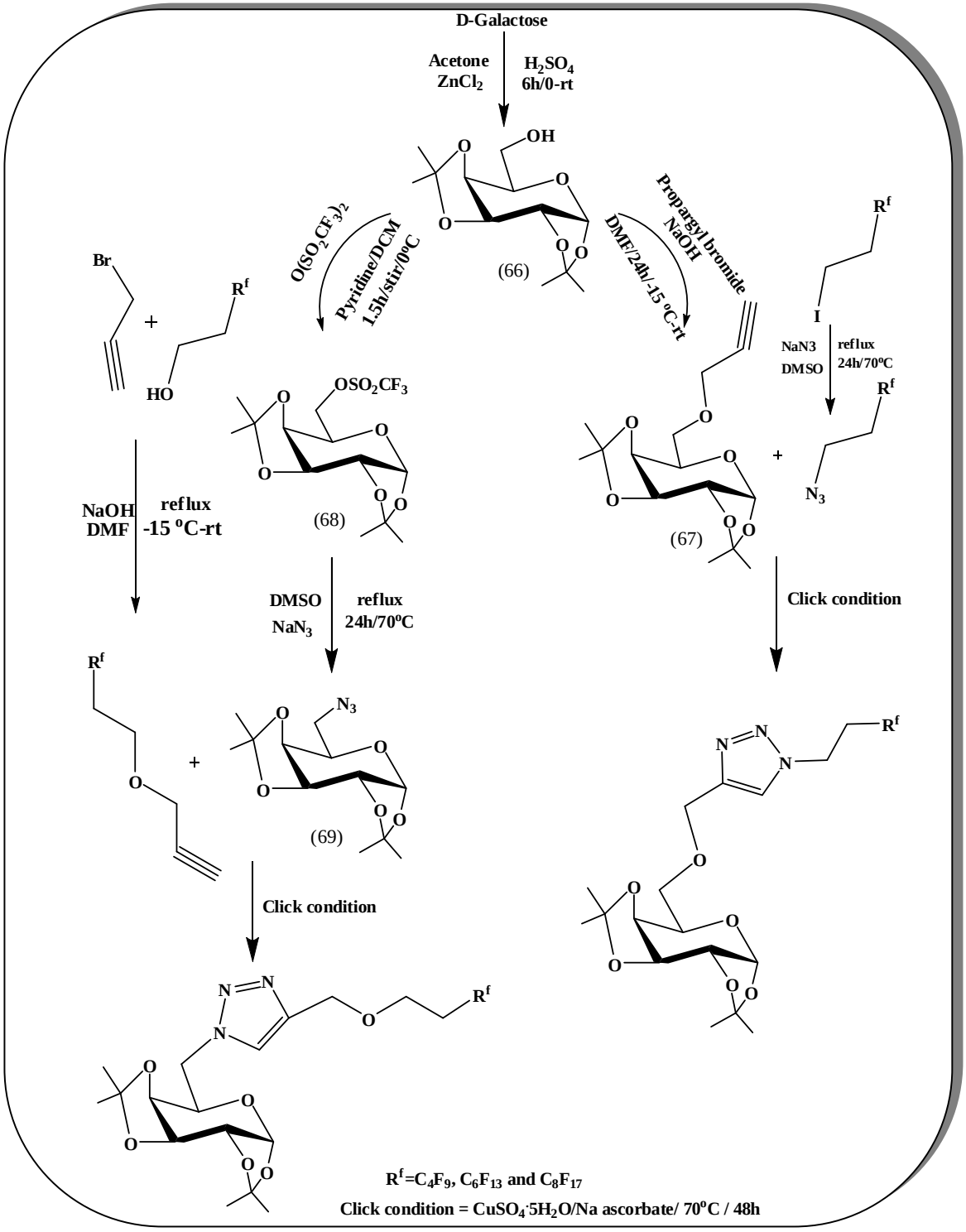
Chapter Three

3

RESULTS & DISCUSSION

Results and Discussion

Generally, overall synthesized compounds described in the scheme (3-1):

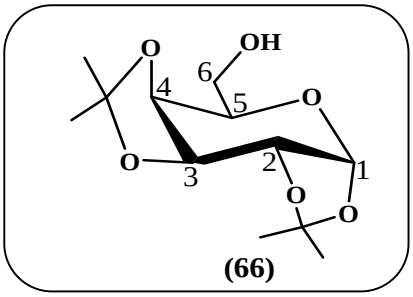


Scheme (3-1) Synthetic method of perfluoro triazoles

(3.1) Synthesis of target compounds:

(3.1.1) 1,2:3,4-di-O-isopropylidene-α-D-galactose(66)

D-Galactose contains five free hydroxyl groups (in cyclic form) as active groups, in work its only one free hydroxyl group is required, that means it is necessary to protect four groups, so 1,2:3,4-di-O-isopropylidene-α-D-galactose has been synthesized according to the following scheme from the reaction of D-Galactose with acetone in presence of $ZnCl_2$ as a catalysis acidic media (H_2SO_4) to produced 81% yield of compound (66):



(66)

Scheme (3-2) Structure of compound (66)

FT-IR spectrum Fig. (3-1) of compound (66) showed the following bands at $\bar{\upsilon}$ cm^{-1} (Nujol): 3483 (υ_{O-H}), 2987 ($\upsilon_{C-H,\ CH3}$), 2936 ($\upsilon_{C-H,CH2}$), 1382 ($\delta_{C-H,\ CH3}$), 1070 (υ_{C-O}).

^{1}H NMR spectrum Fig. (3-2) showed the following signals at δ (ppm) ($CDCl_3$): 1.36, 1.45, 1.5 (s, 12H, $4CH_{3\ isopropylidene}$), 2.37 (br s, 1H, OH), 3.74 (dd,*J* 10.7, 7.3 Hz, 1H, H_a6), 3.83 (dd, *J* 10.7, 4.7 Hz, 1H, H_b6), 3.86 (ddd, *J* 7.3, 4.7, 2.0 Hz, H5), 4.26 (dd, *J* 7.9, 1.6 H_Z, 1H, H4), 4.32 (dd, *J* 5.0, 2.4 H_Z, 1H, H2), 4.60 (dd, *J* 8.0, 2.4 H_Z, 1H, H3), 5.56 (d, *J* 5.0 H_Z,1H, H1).

The ^{13}C NMR spectrum Fig. (3-3) showed the following signals at δ ($CDCl_3$) (ppm): 24.3, 24.9, 25.9, 26.0, (4C, $CH_{3\ isopropylidene}$), 62.3 (C6), 68.6 (C5), 70.5 (C2), 70.7 (C3), 71.5 (C4), 96.3 (C1), 108.6, 109.4 (2C, $CH_{3\ isopropylidene}$).

^{1}H and ^{13}C NMR spectra indicated that only four hydroxyl groups are protected it is showed form the shifting signals (3.74 and 3.83) to the high value of δ which referred to two protons that shielded by hydroxyl group.

* *The signals around 7.35 ppm and 77.00 ppm in ^{1}H & ^{13}C NMR spectra respectively are attributed to $CDCl_3$* [103].

HSQC spectrum Fig. (3-4) of compound (66) showed the signals summarized in table (3-1).

Table (3-1) HSQC values of compound (66)

13C NMR	HSQC
24.3, 24.9, 25.9, 26.0, (4C, $CH_{3\ isopropylidene}$)	1.32, 1.44, 1.52
62.3 (C6)	3.74, 3.85
68.4 (C5)	3.85
70.5 (C2)	4.33
70.7 (C3)	4.59
71.5 (C4)	4.27
96.3 (C1)	5.56
108.6, 109.4 (2C, $CH_{3\ isopropylidene}$)	-

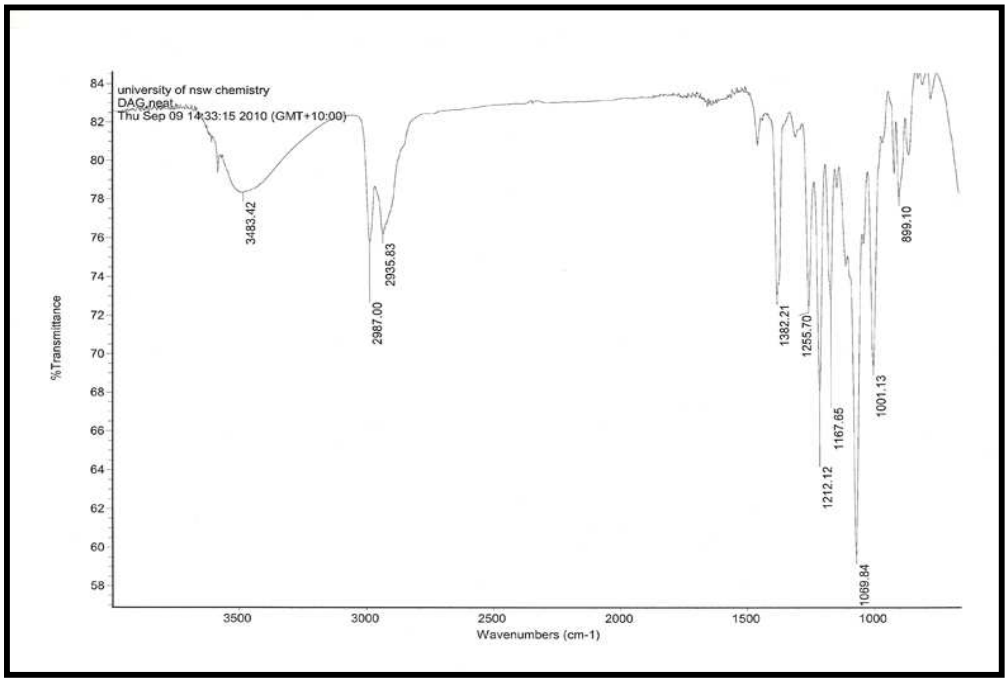


Fig. (3-1) FT-IR spectrum of compound (66)

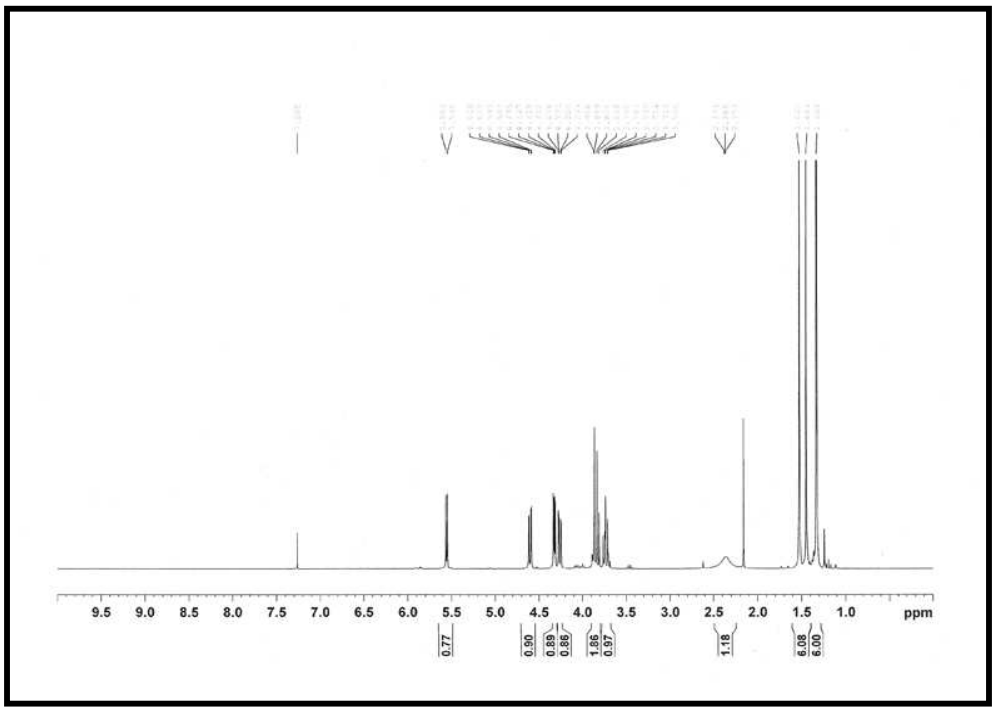


Fig. (3-2) ^{1}H NMR spectrum of compound (66)

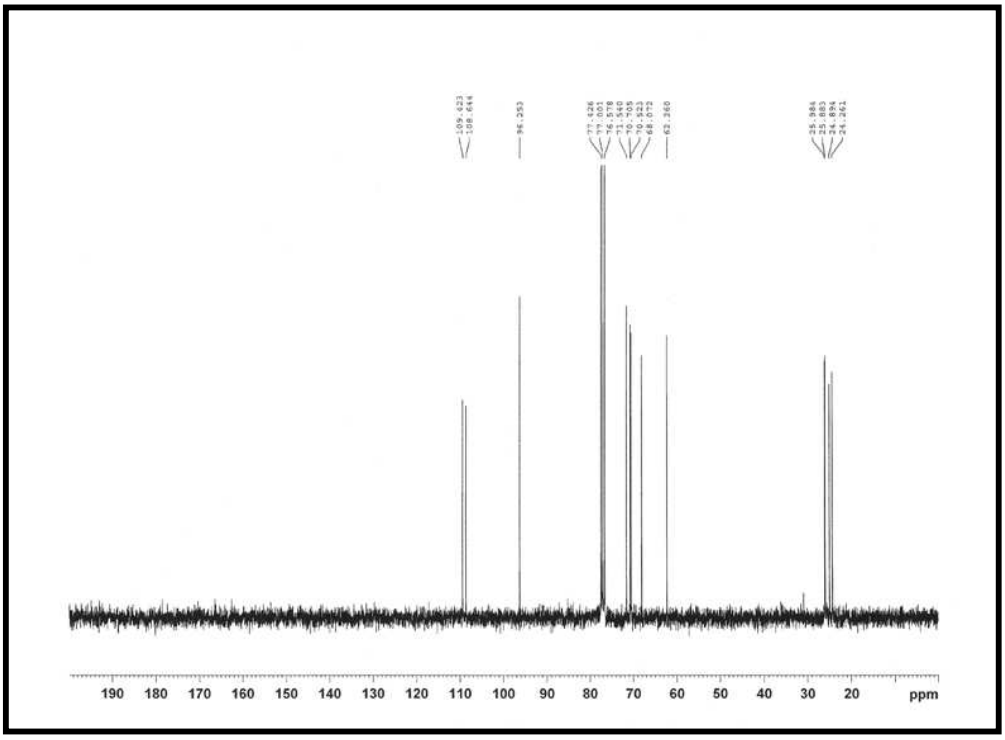


Fig. (3-3) ^{13}C NMR spectrum of compound (66)

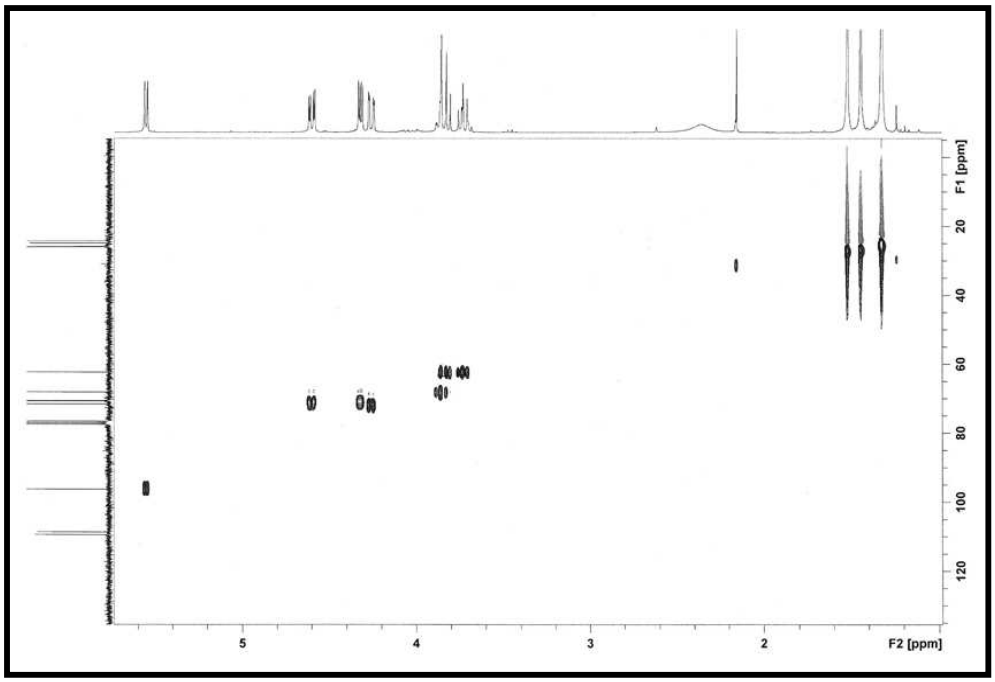
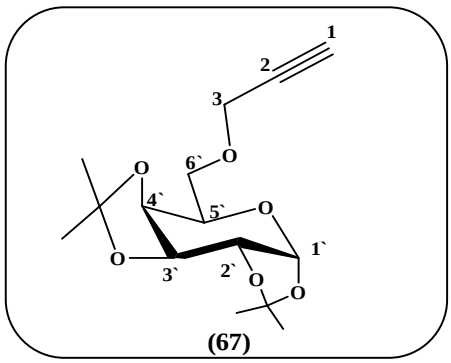


Fig. (3-4) HSQC spectrum of compound (66)

(3.1.2) 6-O-prop-2-ynyl-1,2:3,4-di-O-isopropylidene-α-D-galactose (67)

Williamson etherfication of compound **(66)** with propargyl bromide in presence of basic media (NaOH pellets) produced the terminal alkyne compound **(67)** in very good yield (88%) as showen bellow:



(67)

Scheme (3-3) Structure of compound (67)

FT-IR spectra Fig. (3-5) of compound **(67)** showed the following bands at $\bar{\upsilon}$ (cm^{-1}) (Nujol): 3253($\upsilon_{C–H\ alkyne}$), 2923($\upsilon_{C–H,\ CH3}$), 2110($\upsilon_{C\equiv C}$), 1459 ($\delta_{C–H}$), 1377($\delta_{C–H,CH3}$), 1101 ($\upsilon_{C–O}$).

FT-IR spectrum illustrate good evidence that the reaction happened successfully through conceal broad band for (-OH) group at (3483 cm^{-1}), and showed sharp bands at (3253 and 2110 cm^{-1}) which indicated that the terminal alkyne was formed.

^{1}H NMR spectrum Fig. (3-6) of compound **(67)** appeared the following signals at δ (ppm) ($CDCl_3$): 1.32, 1.34, 1.45, 1.54 (s, 12H, $4CH_{3isopropylidene}$), 2.42 (t, *J* 2.4 Hz, 1H, H1), 3.66 (dd, *J* 10.1, 7.1 Hz , H, H_a6'), 3.77 (dd, *J* 10.1, 6.2 Hz, 1H, H_b6'), 3.99 (ddd, *J* 7.1, 6.2, 2.0 Hz, 1H, H5'), 4.19 (dd, *J* 15.9, 2.4 Hz, 1H, H_a3), 4.24 (dd, *J* 15.9, 2.4 Hz, 1H, H_b3), 4.26 (dd, *J* 7.9, 2.0 Hz, 1H, H4'), 4.31 (dd, *J* 5.0, 2.4 Hz, 1H, H2'), 4.60 (dd, *J* 7.9, 2.4 Hz, 1H, H3'), 5.54 (d, *J* 5.0 Hz, 1H, H1').

The ^{1}H NMR spectrum showed triplet signal at (2.42 ppm) for the acetylenic proton which caused by the long range coupling.

While ^{13}C NMR spectrum Fig. (3-7) of compound **(67)** showed the following signals at δ (ppm) ($CDCl_3$): 24.4, 24.9, 25.9, 26.0 (4C, $CH_{3\ isopropylidene}$), 58.4 (C3), 66.7 (C5'), 68.7 (C6'), 70.4 (C2'), 70.6 (C3'), 71.2 (C4'), 74.6 (C1), 79.6 (C2), 96.3(C1'), 108.6, 109.3 (2C, $C_{\ isoprpylidene}$).

Table (3-2) summarized values of HSQC Fig. (3-8) and COSY Fig. (3-9) spectra.

Table (3-2) Summarized HSQC and COSY values of compound (67)

^{1}H NMR (ppm)	COSY	^{13}C NMR (ppm)	HSQC
1.32, 1.34, 1.45, 1.54 (s, 12H, 4CH3isopropylidene)	1.32, 1.34, 1.45, 1.54	24.4, 24.9, 25.9, 26.0 (4C, $CH_{3\ isopropylidene}$)	1.32, 1.34, 1.45, 1.54
2.42 (t, J 2.4 Hz, 1H, H1)	5.54	58.4 (C3)	4.22
3.66 (dd, J 10.1, 7.1 Hz , H, Ha6')	3.77, 399	66.7 (C5')	3.99
3.77 (dd, J 10.1, 6.2 Hz, 1H, Hb6')	3.66, 3.99	68.7 (C6')	3.77
3.99 (ddd, J 7.1, 6.2, 2.0 Hz, 1H, H5')	3.66, 3.77	70.4 (C2')	4.31
4.19 (dd, J 15.9, 2.4 Hz, 1H, Ha3)	4.24, 4.26	70.6 (C3')	4.60
4.24 (dd, J 15.9, 2.4 Hz, 1H, Hb3)	4.19, 4.26	71.2 (C4')	4.26
4.26 (dd, J 7.9, 2.0 Hz, 1H, H4')	4.19, 4.24, 4.60	74.6 (C1)	2.42
4.31 (dd, J 5.0, 2.4 Hz, 1H, H2')	5.54	79.6 (C2)	-
4.60 (dd, J 7.9, 2.4 Hz, 1H, H3')	4.26	96.3(C1')	5.54
5.54 (d, J 5.0 Hz, 1H, H1')	4.31	108.6, 109.3 (2C, $C_{\ isoprpylidene}$)	-

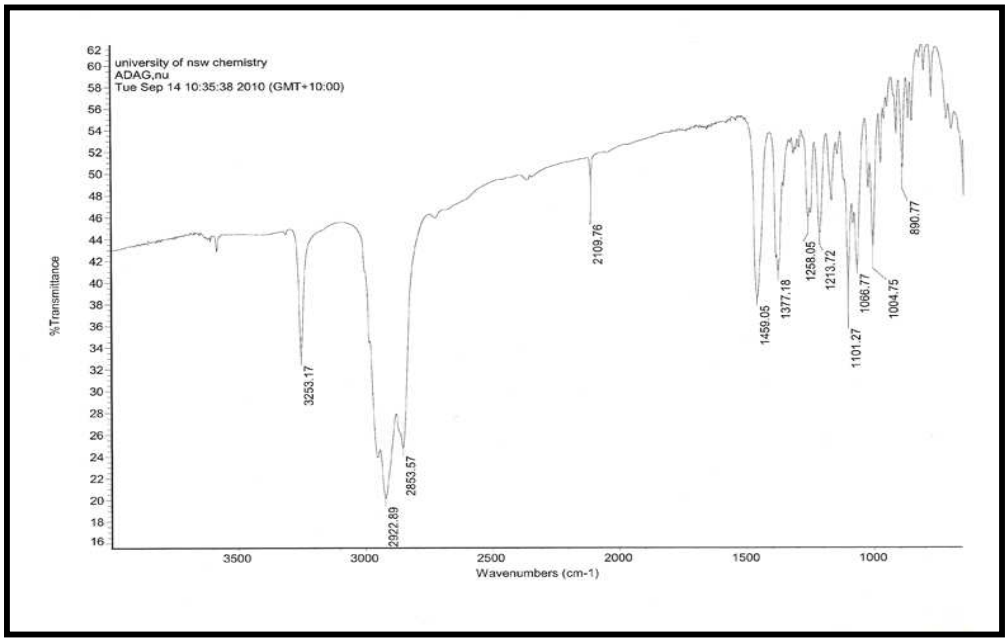


Fig. (3-5) FT-IR spectrum of compound (67)

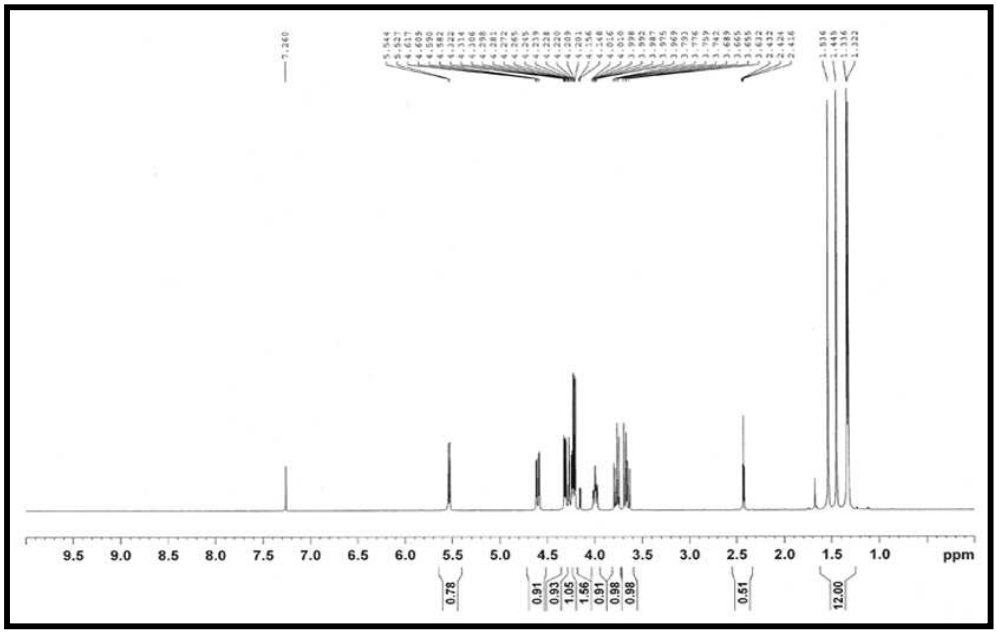


Fig. (3-6) ^{1}H NMR spectrum of compound (67)

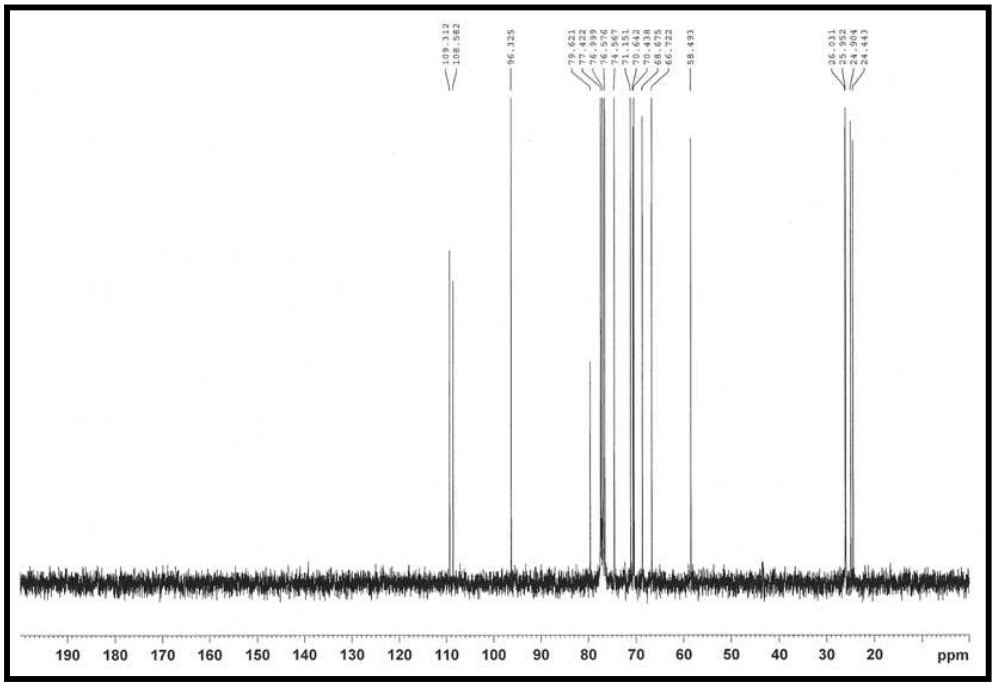


Fig. (3-7) ^{13}C NMR spectrum of compound (67)

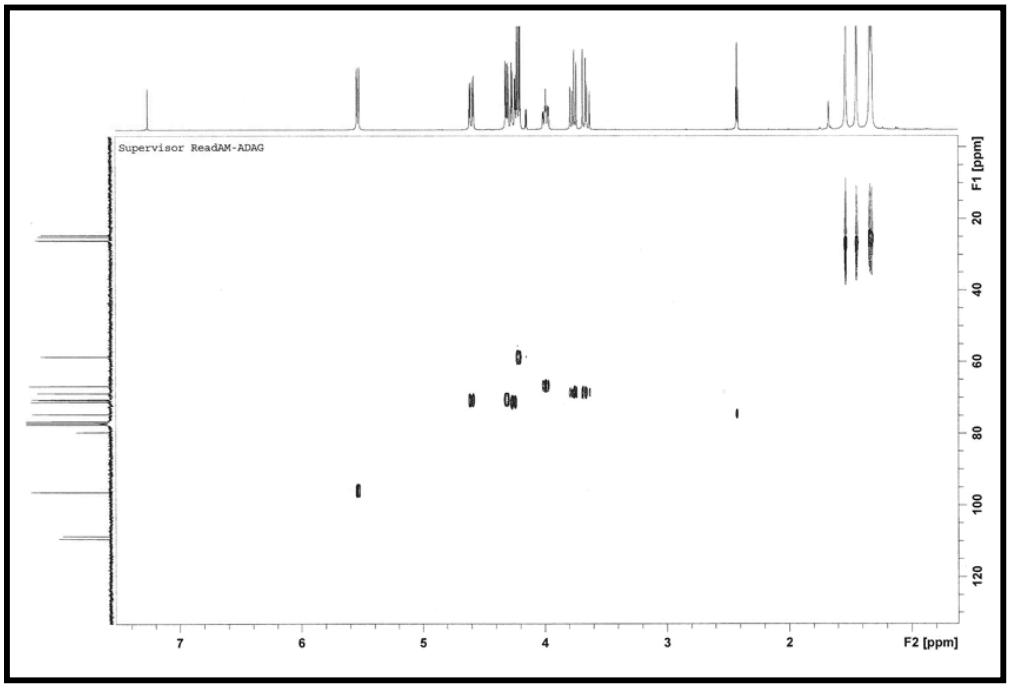


Fig. (3-8) HSQC spectrum of compound (67)

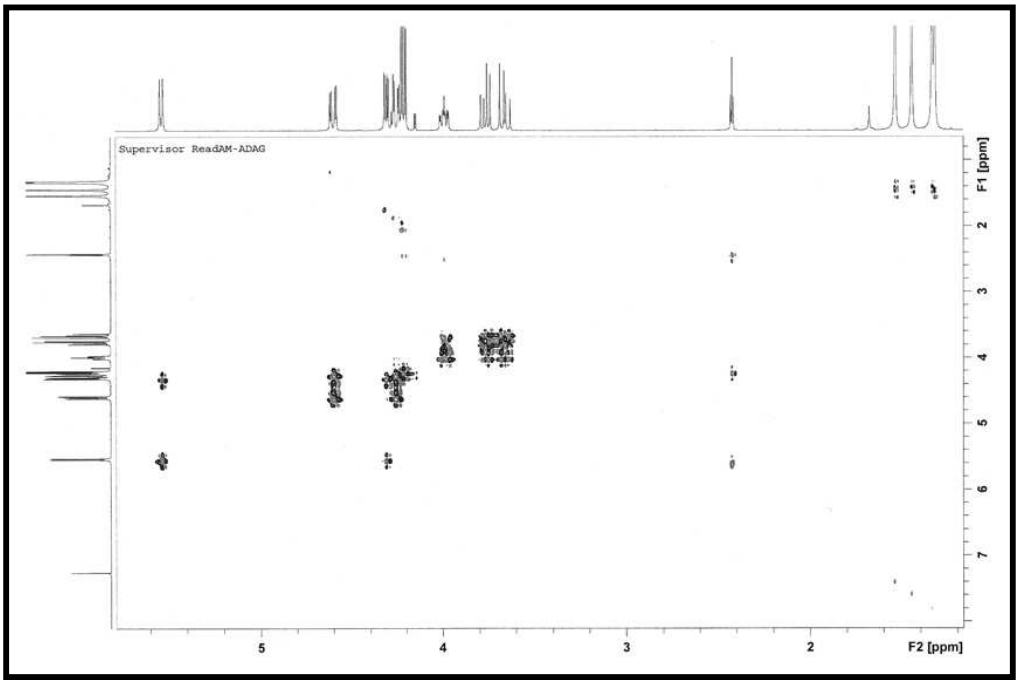
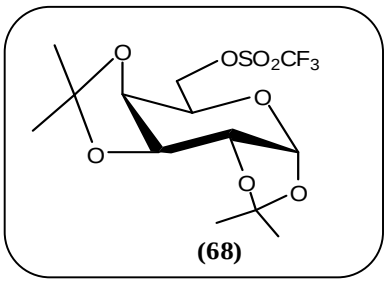


Fig. (3-9) COSY spectrum of compound (67)

(3.1.3) 1,2:3,4-di-O-isopropylidene-α-D-galactose-6-O-triflate(68)

The substitution reaction cannot occur when the OH group at (C6) converted to -OMs and –OTs due to the axial group at (C4) of galactopyranose ring . the only way is converting the OH group into an excellent leaving group like triflate ester [104]. Esterfication of compound (66) with trifluoro methane sulfonic anhydride produced the triflate ester (68) yielded (63%).



Scheme (3-4) Structure of compound (68)

FT-IR spectrum Fig. (3-10) of compound **(68)** showed the following bands at $\bar{\upsilon}$ (cm^{-1}) (Nujol): 2991 ($\upsilon_{C-H,\ CH3}$), 1417 ($\delta_{C-H,\ CH2}$), 1385(δ_{C-H}), 1248 and 1148 ($\upsilon_{S=O}$), 1212 ($\upsilon_{C-O-C,}$), 1072 (υ_{C-O}).

While ^{1}H NMR spectrum Fig. (3-11) of compound **(68)** showed the following signals at δ (ppm) ($CDCl_3$): 1.33, 1.34, 1.44, 1.53 (s, 12H, $4CH_{3\ isopropylidene}$), 4.11 (ddd, *J* 7.3, 4.7, 2.0 Hz, 1H, H5), 4.24 (dd, *J* 7.8, 2.0 Hz, 1H, H4), 4.36 (dd, *J* 5.0, 2.6 Hz, 1H, H2), 4.58 (dd, *J* 10.7, 7.3 Hz, 1H, H_a6), 4.64 (dd, *J*10.7, 4.7 Hz, 1H, H_b6), 4.65 (dd, *J* 7.8, 2.6 Hz, 1H, H3), 5.54 (d, *J* 5.0 Hz, 1H, H1).

^{13}C NMR spectrum Fig. (3-12) of compound **(68)** showed the following signals at δ (ppm) ($CDCl_3$): 24.4, 24.8, 25.8, 25.9 (4C, $CH_{3\ isopropylidene}$), 66.0 (C5), 70.2 (C2), 70.4 (C4), 70.6 (C3), 74.6 (C6), 96.1 (C1), 109.1, 110.1 (2C, $CH_{3\ isopropylidene}$).

The FT-IR spectrum signified that the compound **(68)** was formed by means of that band at (3483 cm^{-1}) concealed and ^{1}H NMR spectrum gave shifting two protons at (4.58 and 4.64 ppm) for higher value of δ scale.

The HSQC values summarized in table (3-3):

Table (3-3) HSQC values of compound (68)

13C NMR	HSQC
24.4, 24.8, 25.8, 25.9 (4C, $CH_{3\ isopropylidene}$)	1.33, 1.34, 1.44, 1.52
66.0 (C5)	4.11
70.2 (C2)	4.36
70.4 (C4)	4.24
70.6 (C3)	4.65
74.6 (C6)	4.64
96.1 (C1)	5.54
109.1, 110.1 (2C, $CH_{3\ isopropylidene}$)	-

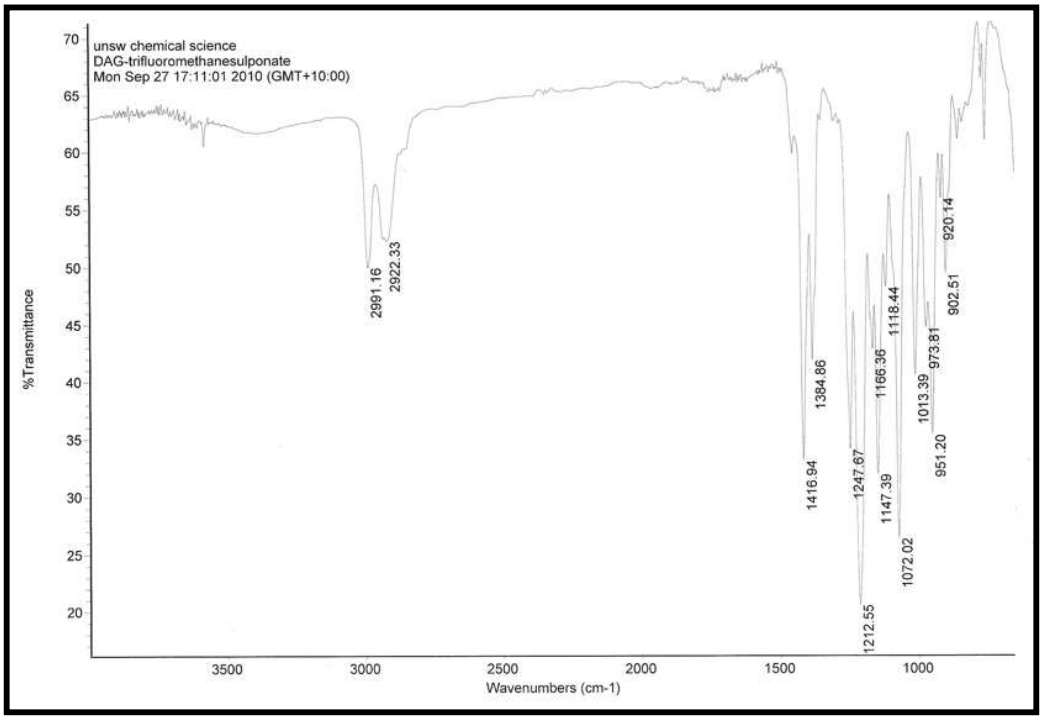


Fig. (3-10) FT-IR spectrum of compound **(68)**

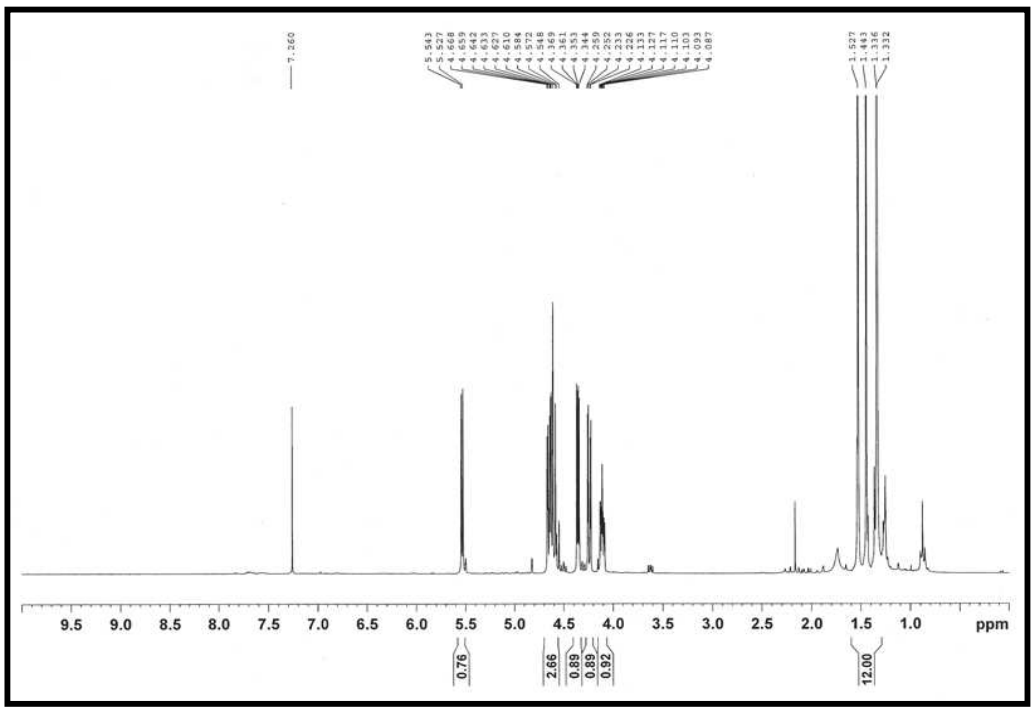


Fig. (3-11) ^{1}H NMR spectrum of compound **(68)**

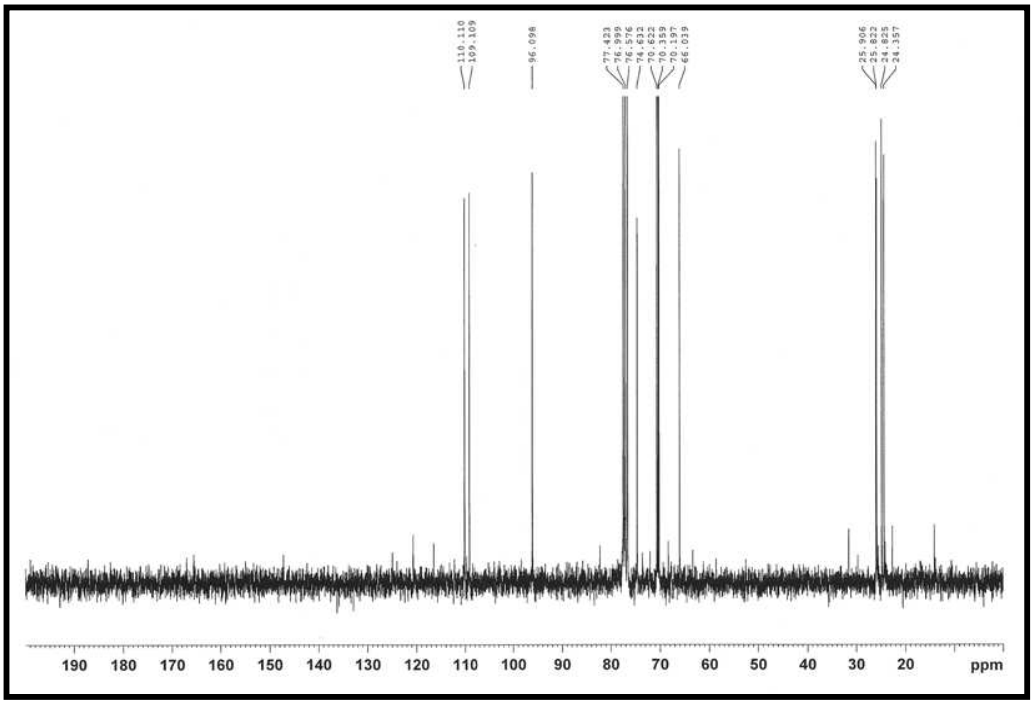


Fig. (3-12) ^{13}C NMR spectrum of compound **(68)**

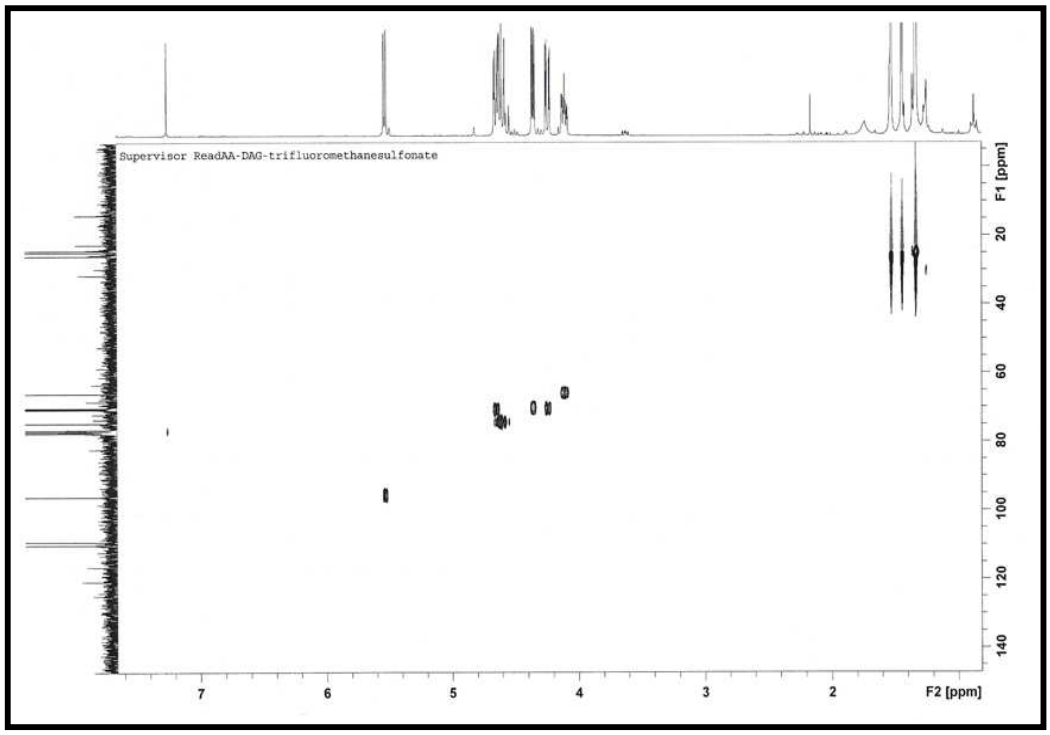
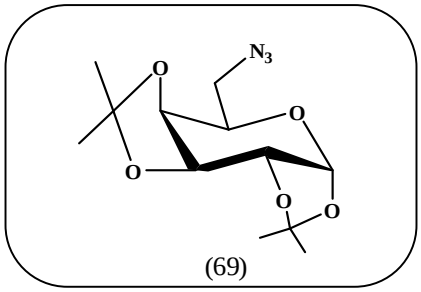


Fig. (3-13) HSQC spectrum of compound **(68)**

(3.1.4) 6-azido-6-deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactose (69)

The S_N2 reaction of compound (68) with sodium azide in DMSO afforded the sugar azide **(69)** in good yield (71%). An azide is a functional group which is important to starting click reaction, synthesis of compound **(69)** described in the following scheme:



(69)

Scheme (3-5) Structure of compound (69)

Characterization of compound **(69)** according to the following figures: FT-IR spectrum Fig. (3-14) showed the following bands at $\bar{\upsilon}$ (cm^{-1}) (Nujol): 2989 ($\upsilon_{C\text{-}H,\ CH3}$), 2103 ($\upsilon_{N=N=N,\ of\ azide}$), 1457($\delta_{C–H}$), 1212 ($\upsilon_{C\text{-}O\text{-}C}$), 1070($\upsilon_{C\text{-}O}$). The FT-IR spectrum of which showed the highly characteristic azide group absorption at 2103 cm^{-1} is an excellent evidence for the formation of compound **(69)**

^{1}H NMR spectrum Fig. (3-15) showed the following signals at δ (ppm) ($CDCl_3$): 1.33, 1.34, 1.45, 1.54 (12H, $4CH_{3isopropylidene}$), 3.36 (dd, *J* 12.7, 5.4 Hz, 1H, H_a6), 3.51 (dd, *J* 12.7, 7.8 Hz, 1H, H_b6), 3.90 (ddd, *J* 7.8, 5.4, 2.0 Hz, 1H, H5), 4.19 (dd, *J* 7.9, 2.0 Hz, 1H, H4), 4.33 (dd, *J* 5.0 , 2.5 Hz, 1H, H2), 4.63 (dd, *J* 7.9, 2.5, Hz, 1H, H3), 5.54 (d, *J* 5.0 Hz, 1H, H1).

^{13}C NMR spectrum Fig. (3-16) showed the following signals at δ ($CDCl_3$) (ppm): 24.4, 24.9, 25.9, 26.0 (4C, $CH_{3\ isopropylidene}$), 50.6 (C6), 67.0 (C5), 70.4 (C2), 70.8 (C3), 71.1 (C4), 96.3(C1), 108.8, 109.6 (2C, $C_{\ isopropylidene}$).

HSQC and COSY spectra Fig. (3-17) and (3-18) respectively, gave signals clarified in the table (3-4):

Table (3-4) Summarized HSQC and COSY values of compound **(69)**

1H NMR	COSY	13C NMR	HSQC
1.33, 1.34, 1.45, 1.54 (12H, $4CH_{3isopropylidene}$)	1.33, 1.34, 1.45, 1.54	24.4, 24.9, 25.9, 26.0 (4C, $CH_{3\ isopropylidene}$)	1.33, 1.34, 1.45, 1.54
3.36 (dd, *J* 12.7, 5.4 Hz, 1H, H_a6),	3.51, 3.90	50.6 (C6)	3.51
3.51 (dd, *J* 12.7, 7.8 Hz, 1H, H_b6)	3.36, 3.90	67.0 (C5)	3.90
3.90 (ddd, *J* 7.8, 5.4, 2.0 Hz, 1H, H5)	3.36, 3.51	70.4 (C2)	4.33
4.19 (dd, *J* 7.9, 2.0 Hz, 1H, H4)	4.63	70.8 (C3)	4.63
4.33 (dd, *J* 5.0 , 2.5 Hz, 1H, H2)	5.54	71.1 (C4)	4.19
4.63 (dd, *J* 7.9, 2.5, Hz, 1H, H3)	4.19	96.3(C1)	5.54
5.54 (d, *J* 5.0 Hz, 1H, H1)	4.33	108.8, 109.6 (2C, $C_{\ isopropylidene}$)	

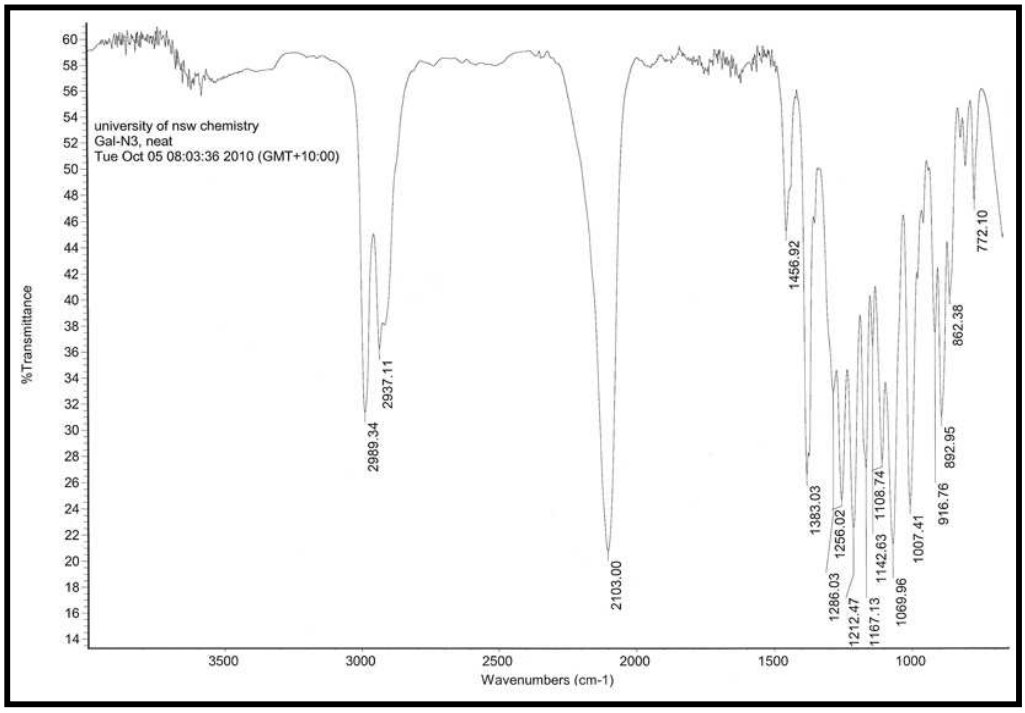


Fig. (3-14) FT-IR spectrum of compound **(69)**

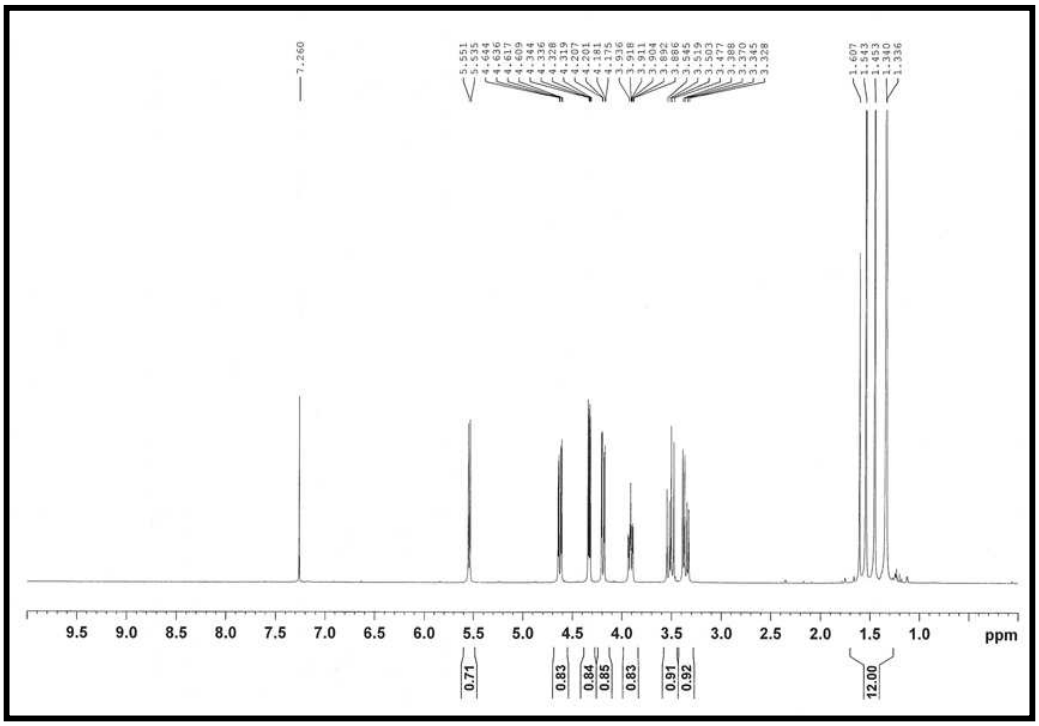


Fig. (3-15) ^{1}H NMR spectrum of compound **(69)**

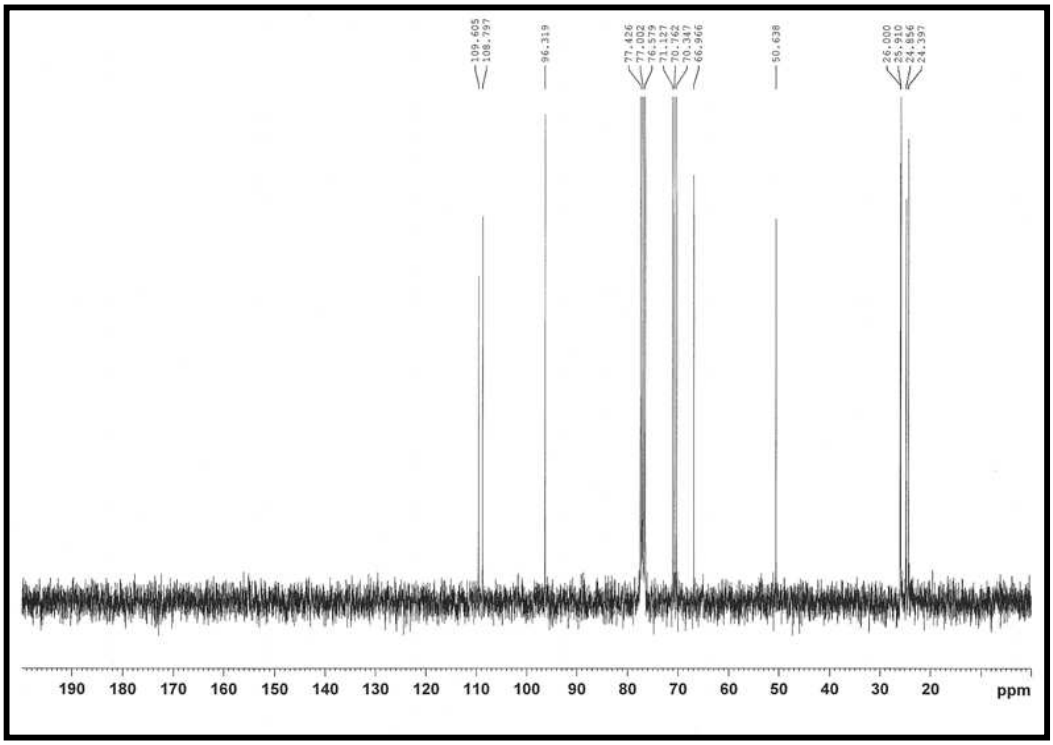


Fig. (3-16) ^{13}C NMR spectrum of compound **(69)**

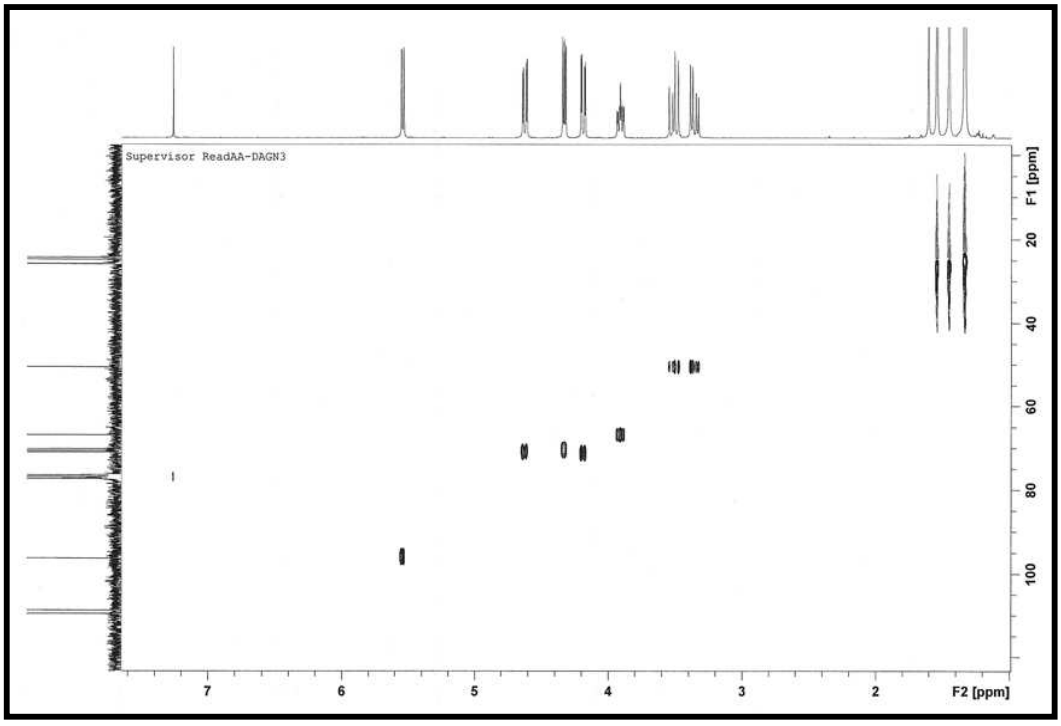


Fig. (3-17) HSQC spectrum of compound **(69)**

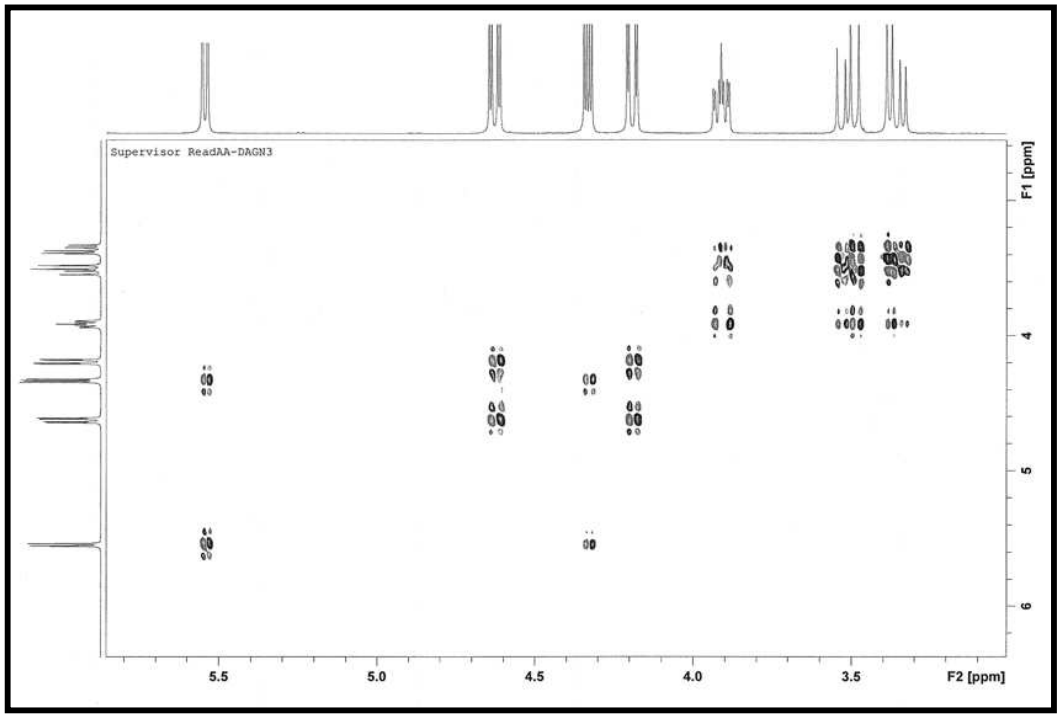
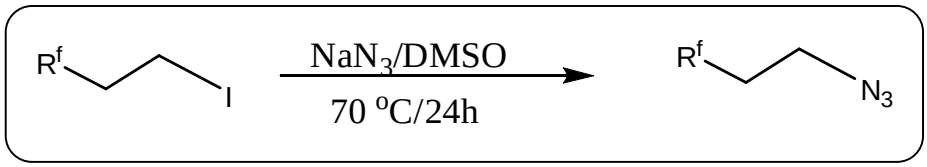


Fig. (3-18) COSY spectrum of compound **(69)**

(3.1.5) Perfluoroalkylethyl azides (70, 35 and 41)

Perfluoro chain which used in this study can be classified in to two lines: perfluoroalkylethyl azides and perfluoroalkylethyl propargyl ethers each line contains three different perfluoro chains (-C_4F_9, -C_6F_{13} and -C_8F_{17}) with (-CH_2CH_2-) as a spacer.



Scheme (3-6) Synthesis of perfluoroalkylethyl azides

FT-IR, ^{1}H NMR, ^{13}C NMR data and percentage yield of perfluoroalkyyl ethyl azide summarized in table (3-5):

Table (3-5) Summarized FT-IR, ^{1}H NMR, ^{13}C NMR and percentage yield of compound **(35, 41, 70)**

Compound No.	R^f	Yield	FT-IR (cm^{-1})(neat)	^{1}H NMR δ(ppm)($CDCl_3$)	^{13}C NMR δ(ppm)($CDCl_3$)
35	C_6F_{13}	77%	2955 (υ C-H, CH2), 2109 (υ N=N=N), 1393 (δ C-H, CH2), 1318, 1238 (υ C-F).	2.38 (m, 2H, H2), 3.61 (t, *J* 7.2 Hz, 2H, H1)	30.8 (C2), 43.3 (C1)
41	C_8F_{17}	75%	2955 (υ C-H, CH2), 2108 (υ N=N=N), 1242 (δ C-H, CH2), 1206 (υ C-F).	2.38 (m, 2H, H2), 3.61 (t, *J* 7.2 Hz, 2H, H1)	30.8 (C2), 43.3 (C1)
70	C_4F_9	71%	2955 (υ C-H, CH2), 2108 (υ N=N=N), 1393 (δ C-H, CH2), 1227(υ C-F).	2.38 (m, 2H, H2), 3.61 (t, *J* 7.2 Hz, 2H, H1)	30.7 (C2), 43.3 (C1)

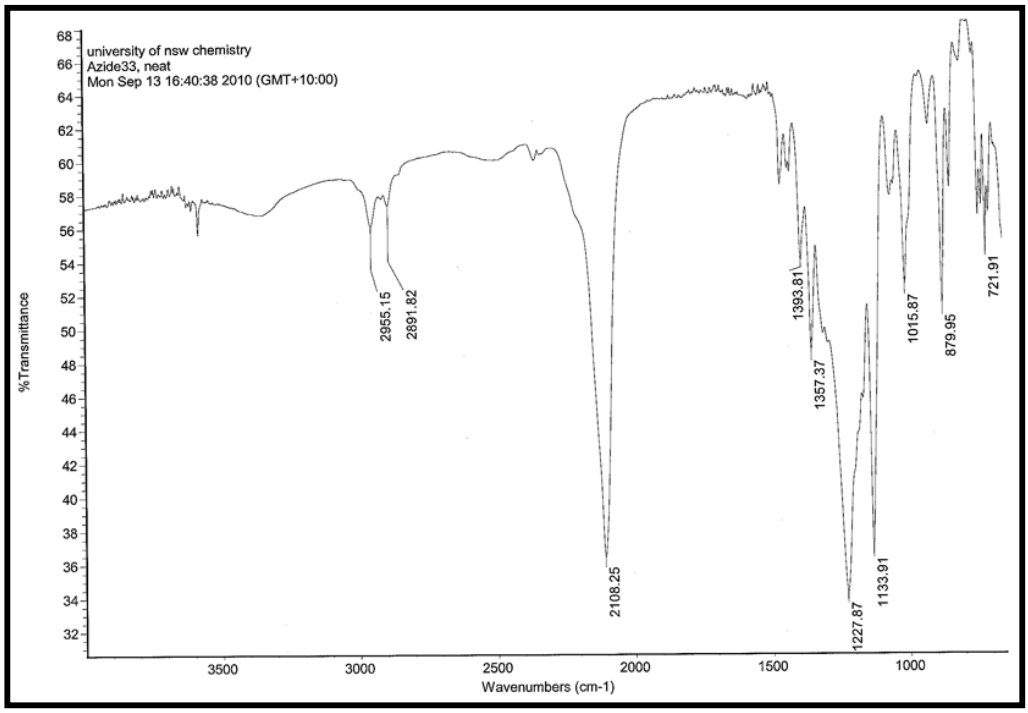


Fig. (3-19) FT-IR spectrum of compound **(70)**

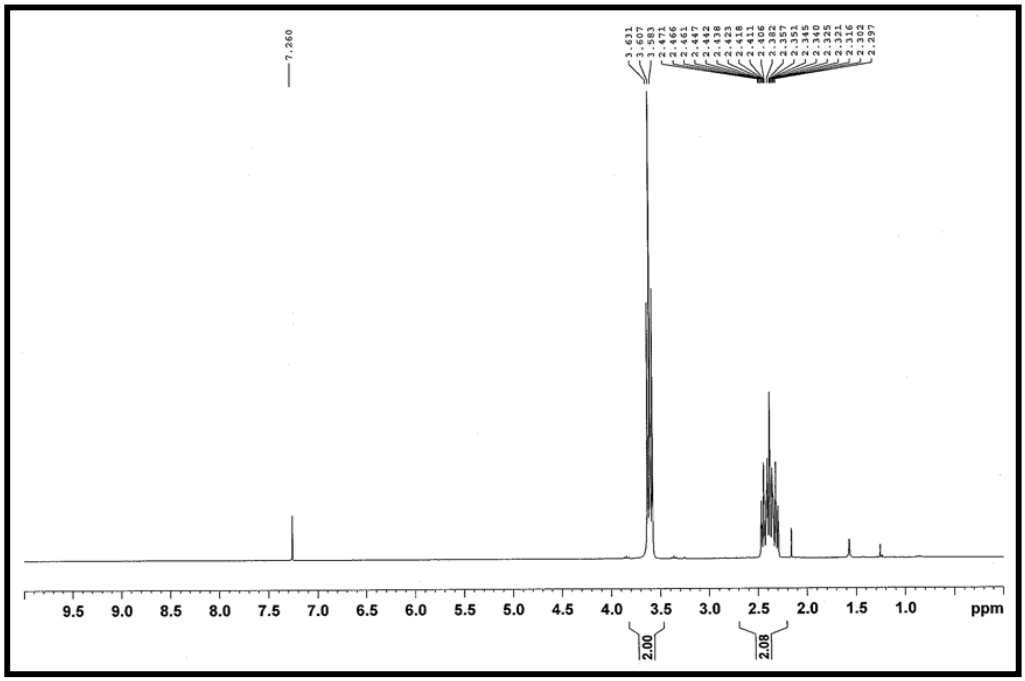


Fig. (3-20) ^{1}H NMR spectrum of compound **(70)**

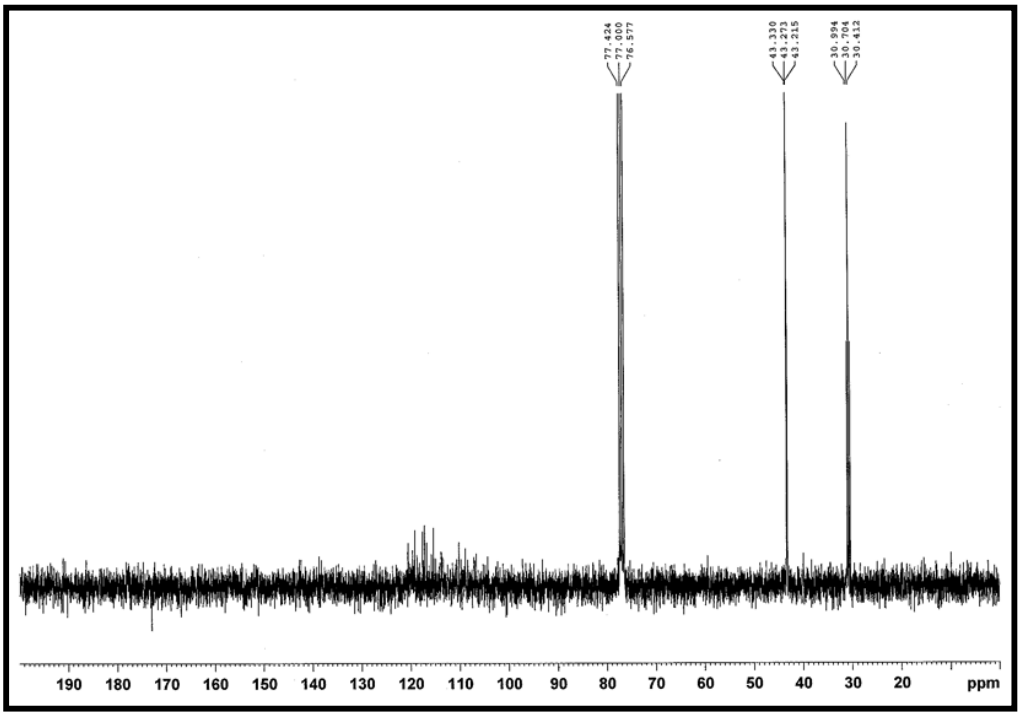


Fig. (3-21) ^{13}C NMR spectrum of compound **(70)**

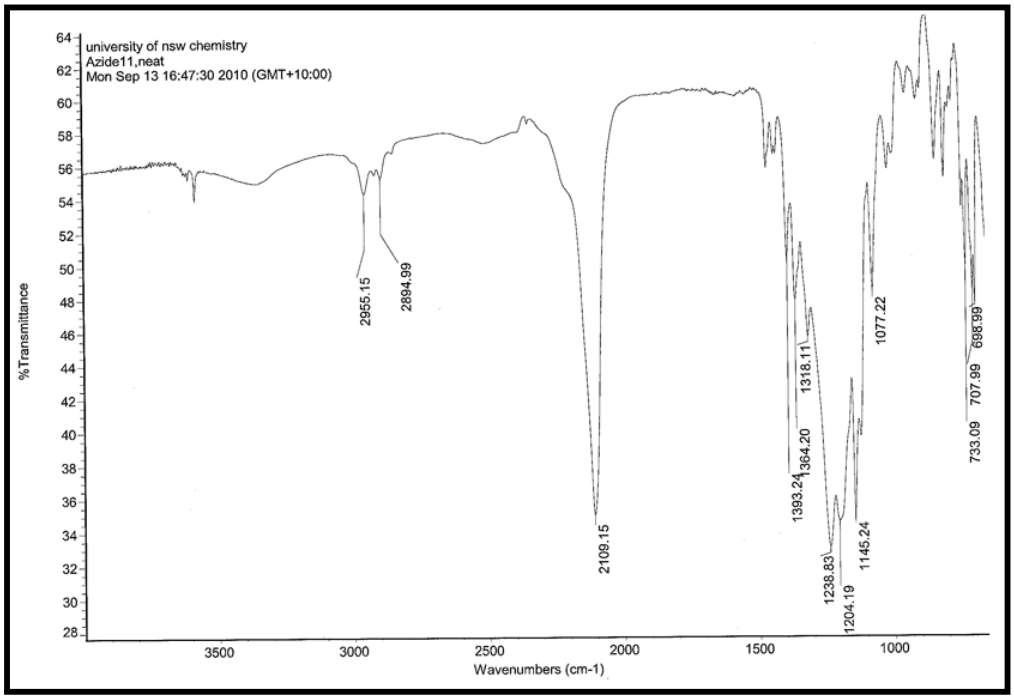


Fig. (3-22) FT-IR spectrum of compound **(35)**

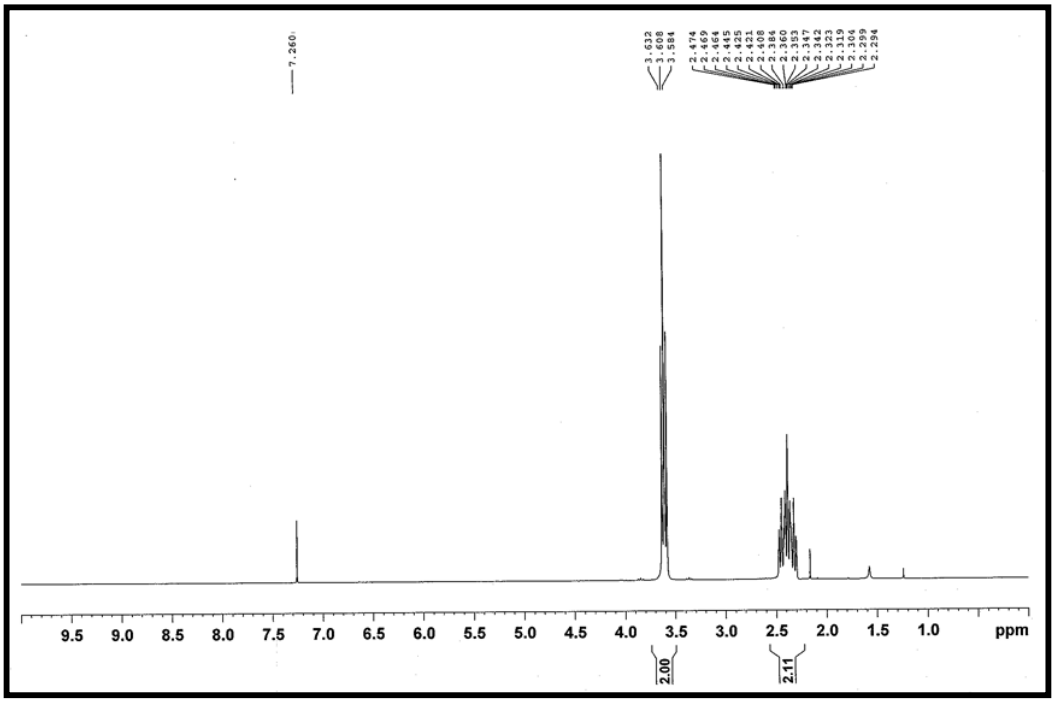


Fig. (3-23) ^{1}H NMR spectrum of compound **(35)**

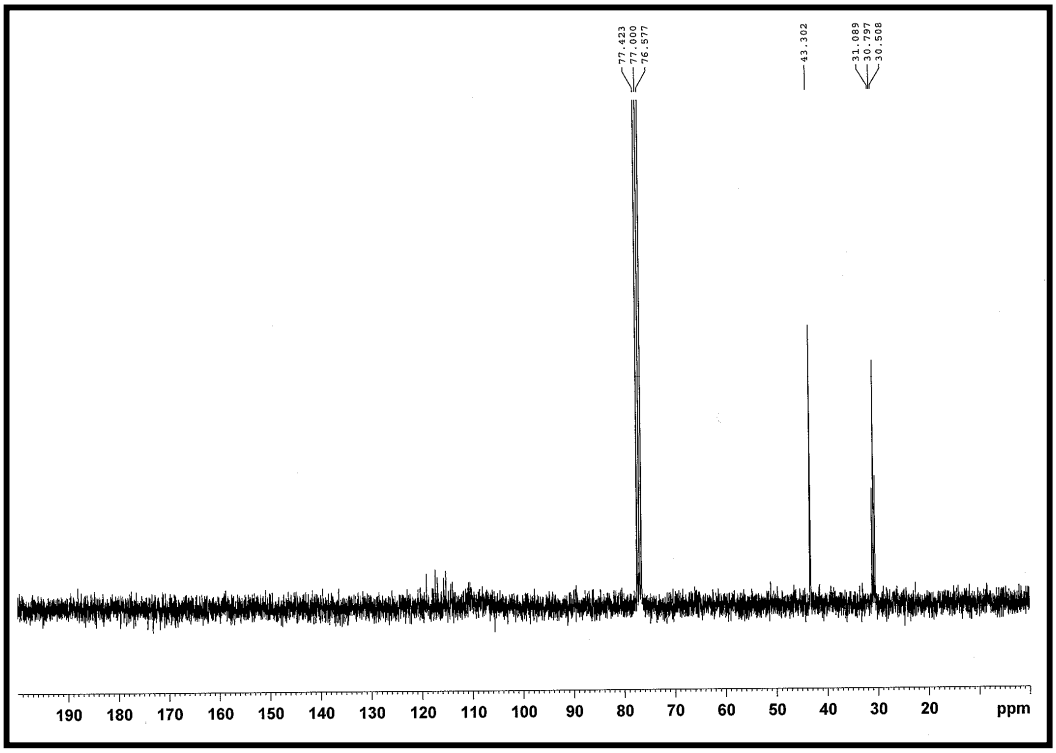


Fig. (3-24) ^{13}C NMR spectrum of compound **(35)**

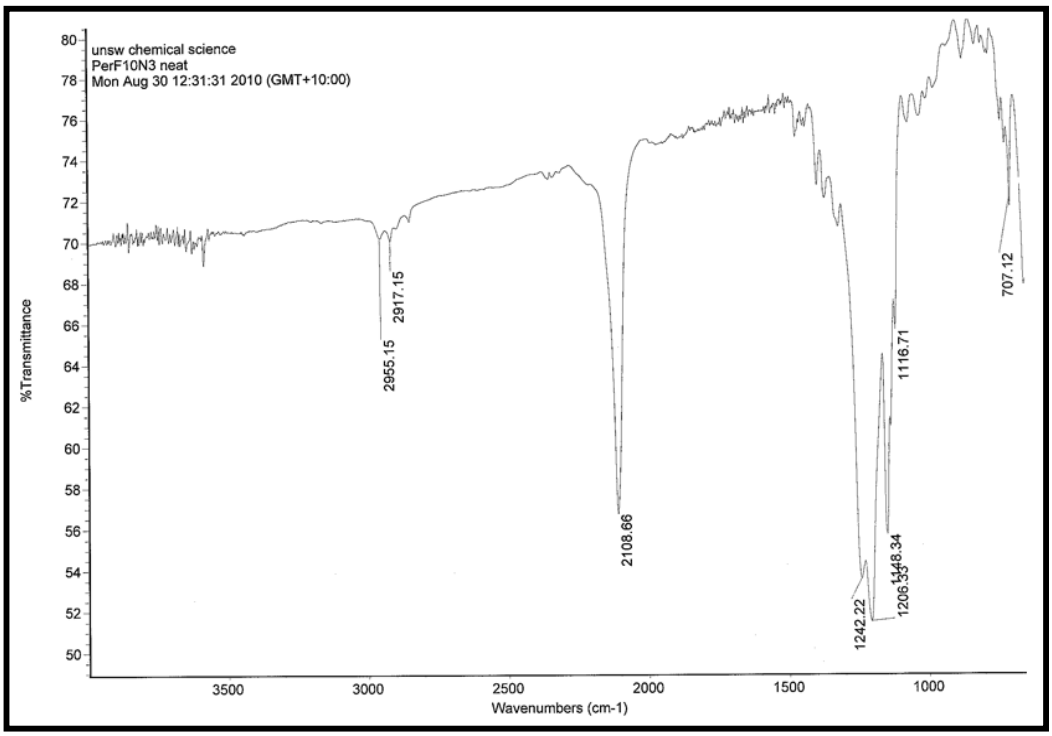


Fig (3-25) FT-IR spectrum of compound **(41)**

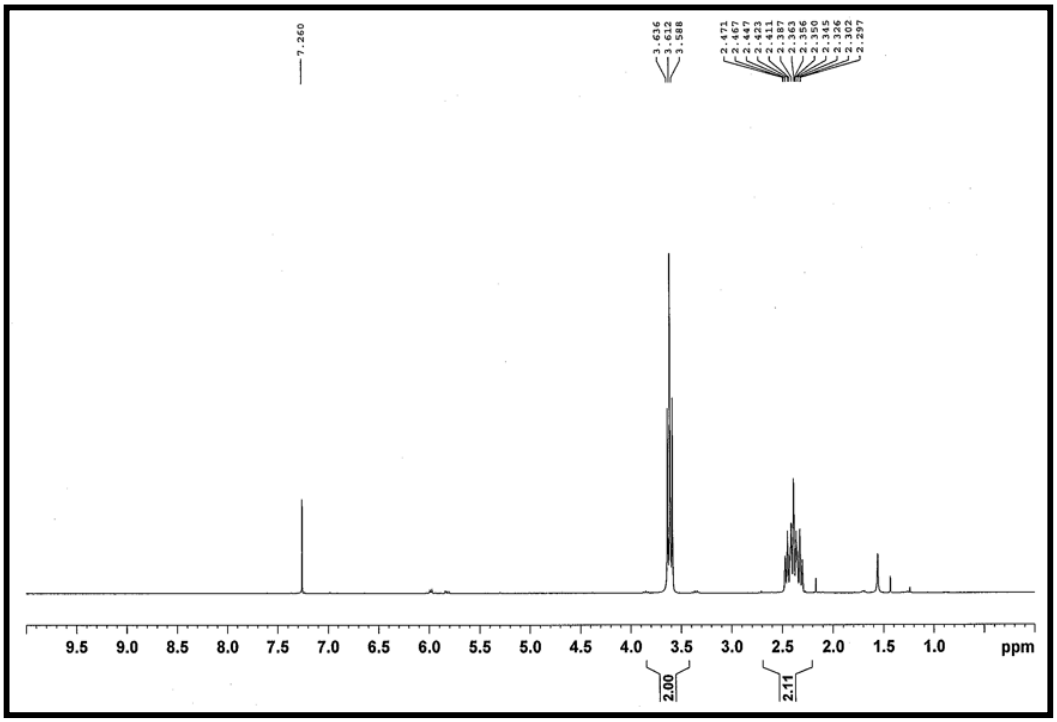


Fig. (3-26) ^{1}H NMR spectrum of compound **(41)**

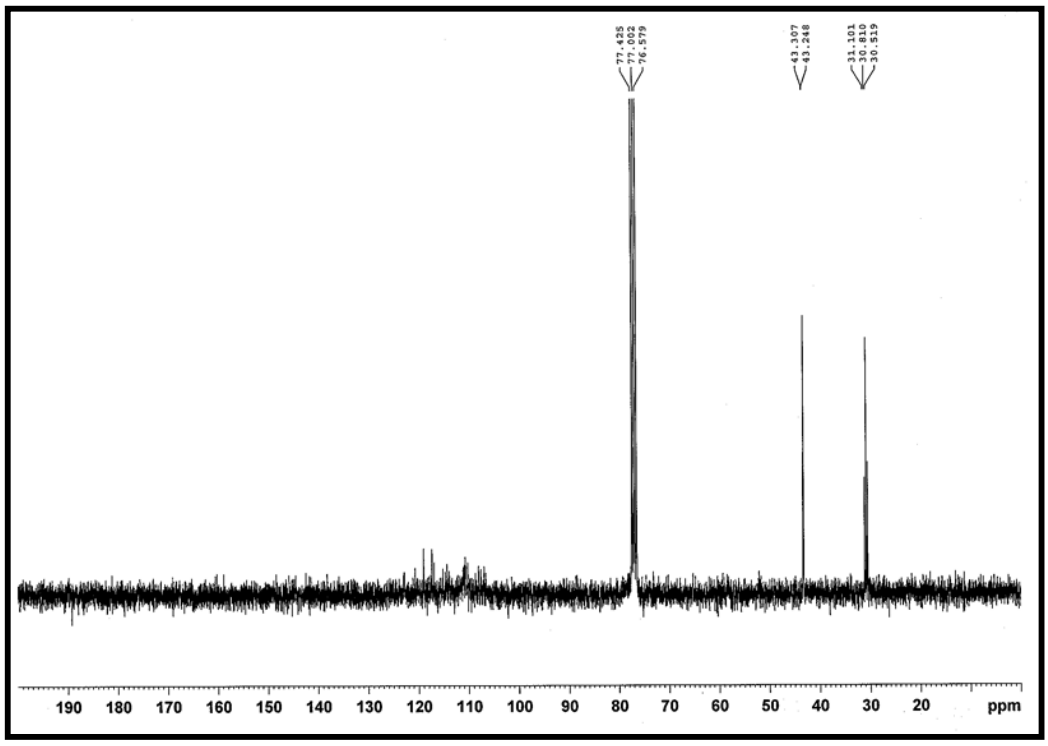
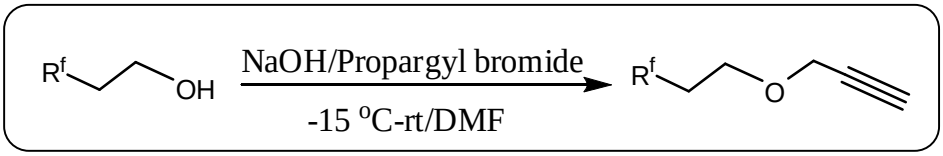


Fig. (3-27) ^{13}C NMR spectrum of compound **(41)**

FT-IR spectrum showed strong band at (2108cm^{-1}) as a specify that the compound with azide group was produced, and there are no band for (-OH) group was appeared. While the ^{1}H NMR spectrum showed signal at (tt, 3.61ppm) which referred to the effect of fluorine atoms spin in perfluoro chain overlapping with protons spin of ethylene group.

(3.1.6) Perfluoroalkylethyl propargyl ethers (71-73)

The second category of perfluoro compounds in this study that contains terminal Carbon-Carbon triple bond as an active group, Williamson etherfication of perfluoroalkyl ethyl alcohol with propargyl ether in basic media and DMF gave the perfluoroalkylethyl propargyl ethers as shown in scheme (3-6).



Scheme (3-7) Synthesis of perfluoroalkylethyl propargyl ethers

FT-IR, ^{1}H NMR, ^{13}C NMR data and percentage yield of Perfluoroalkylethyl propargyl ethers summarized in table (3-6).

Table (3-6) Summarized FT-IR, ^{1}H NMR, ^{13}C NMR and percentage yield of compound **(71-73)**

Compound No.	R^f	Yield	FT-IR (neat)(cm^{-1})	1H NMR δ(CDCl3) (ppm)	13C NMR δ(CDCl3) (ppm)
71	C_4F_9	71%	3315 (υ C-H, alkyne), 2896 (υ C-H, CH2), 2122 (υ C≡C), 1357 (δ C-H, CH2), 1234 (υ C-F), 1134 (υ C-O-C).	2.43 (m, 2H, H2`), 2.45 (t, *J* 2.4 Hz, 1H, H3), 3.82 (t, *J* 6.9 Hz, 2H, H2`), 4.18 (d, *J* 2.4 Hz, 2H, H1)	31.4 (C2`), 58.3 (C1), 61.6 (C1`), 74.9 (C3), 78.8 (C2)
			3316 (υ C-H, alkyne), 2894 (υ C-H, CH2),	2.43 (m, 2H, H2`), 2.46 (t, *J*	31.4 (C2`), 58.3 (C1),

72	C_6F_{13}	77%	2122 (υ $_{C\equiv C}$), 1361 (δ $_{C-H, CH2}$), 1239 (υ $_{C-F}$), 1145 (υ $_{C-O-C}$).	2.4 Hz, 1H, H3), 3.82 (t, *J* 6.9 Hz, 2H, H2`), 4.19 (d, *J* 2.4 Hz, 2H, H1)	61.7 (C1`), 74.9 (C3), 78.9 (C2)
73	C_8F_{17}	75%	3317 (υ $_{C-H, alkyne}$), 2897 (υ $_{C-H, CH2}$), 2122 (υ $_{C\equiv C}$), 1361 (δ $_{C-H, CH2}$), 1203 (υ $_{C-F}$), 1147 (υ $_{C-O-C}$).	2.43 (m, 2H, H2`), 2.45 (t, *J* 2.4 Hz, 1H, H3), 3.82 (t, *J* 6.9 Hz, 2H, H2`), 4.18 (d, *J* 2.4 Hz, 2H, H1)	31.4 (C2`), 58.3 (C1), 61.7 (C1`), 74.9 (C3), 78.9 (C2)

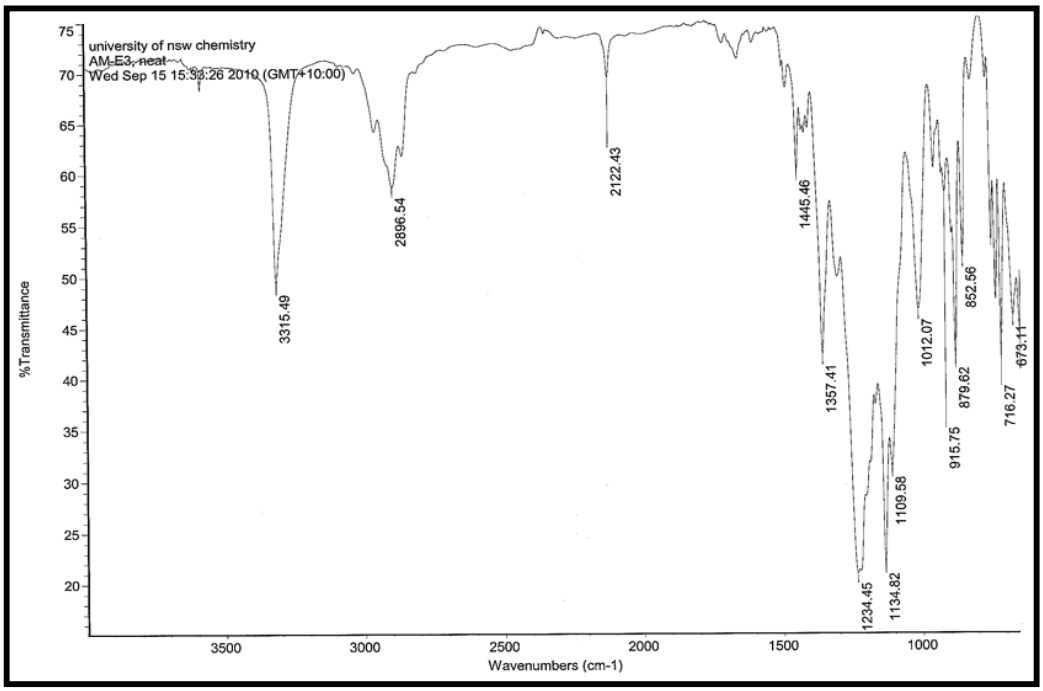


Fig. (3-28) FT-IR spectrum of compound **(71)**

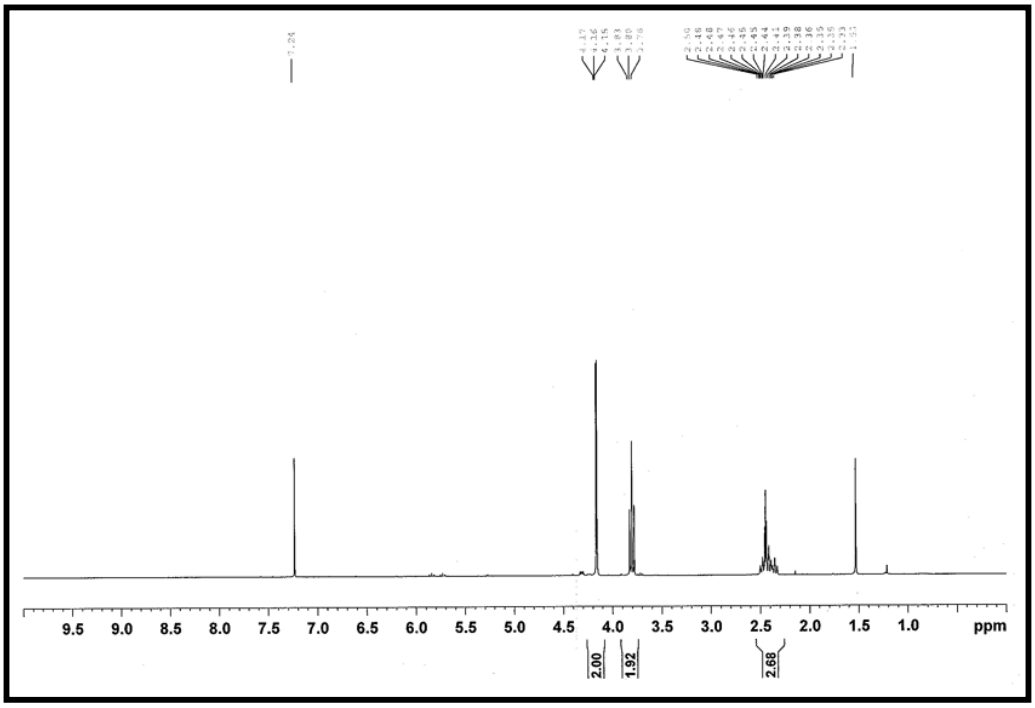


Fig. (3-29) ^{1}H NMR spectrum of compound **(71)**

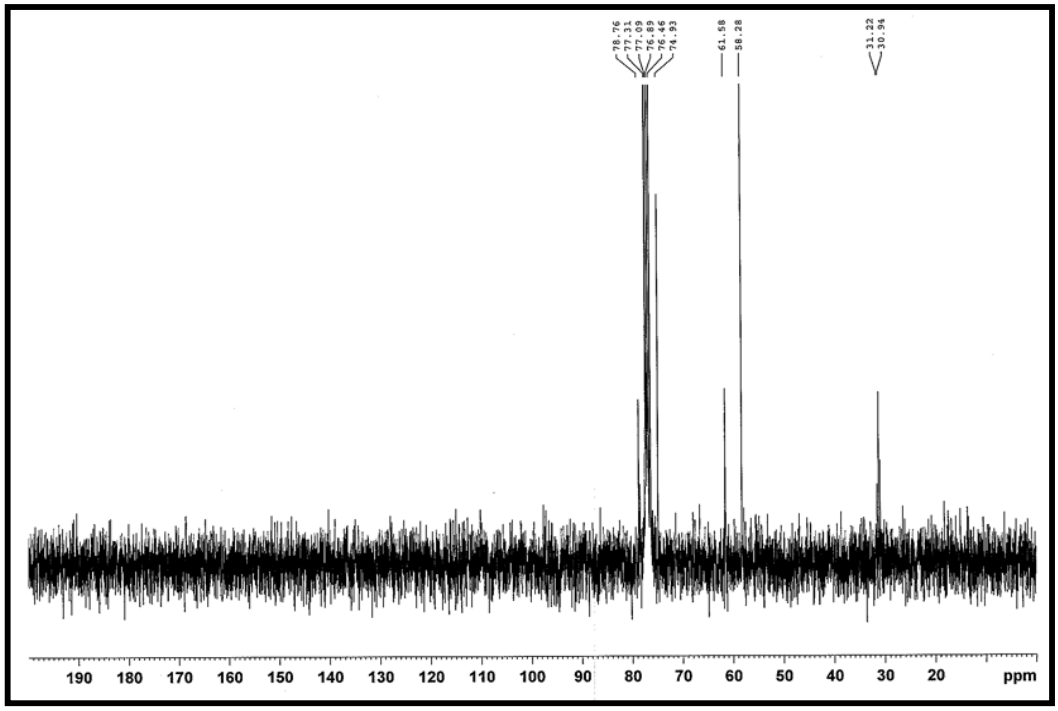


Fig. (3-30) ^{13}C NMR spectrum of compound **(71)**

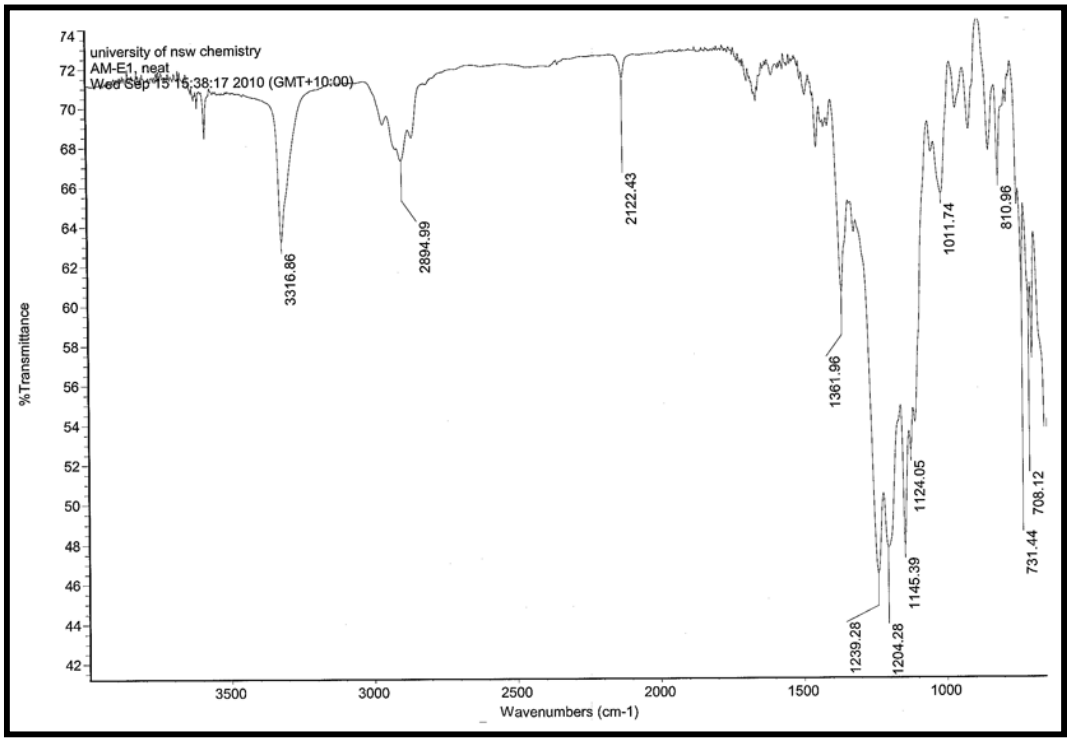


Fig. (3-31) FT-IR spectrum of compound **(72)**

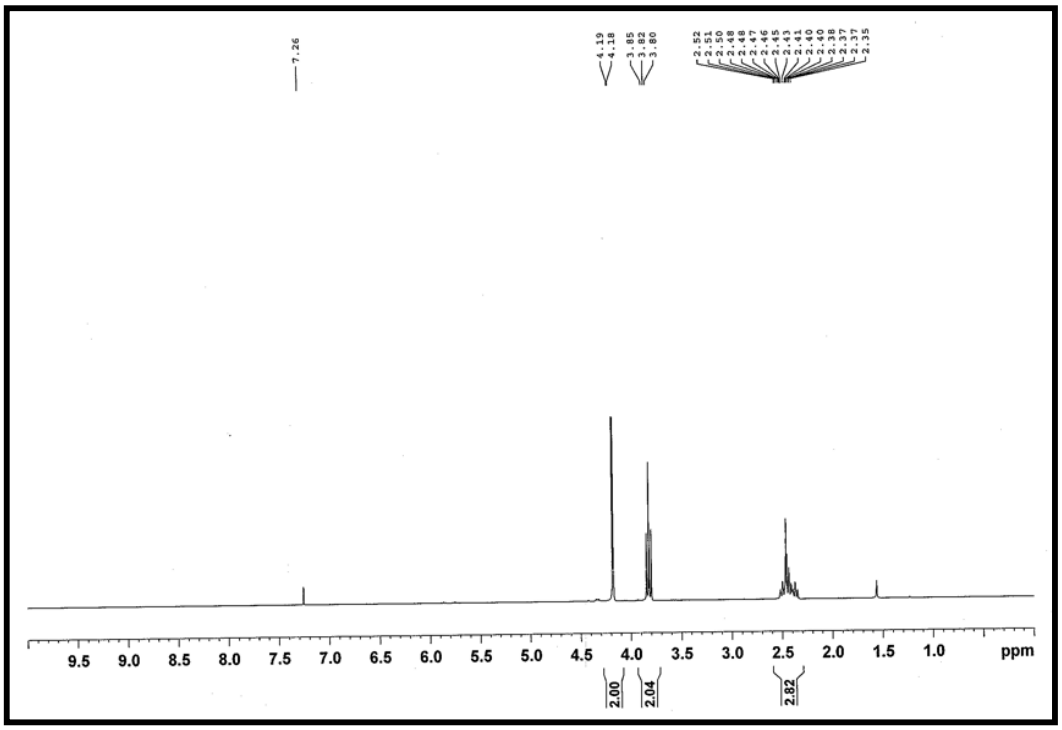


Fig. (3-32) ^{1}H NMR spectrum of compound **(72)**

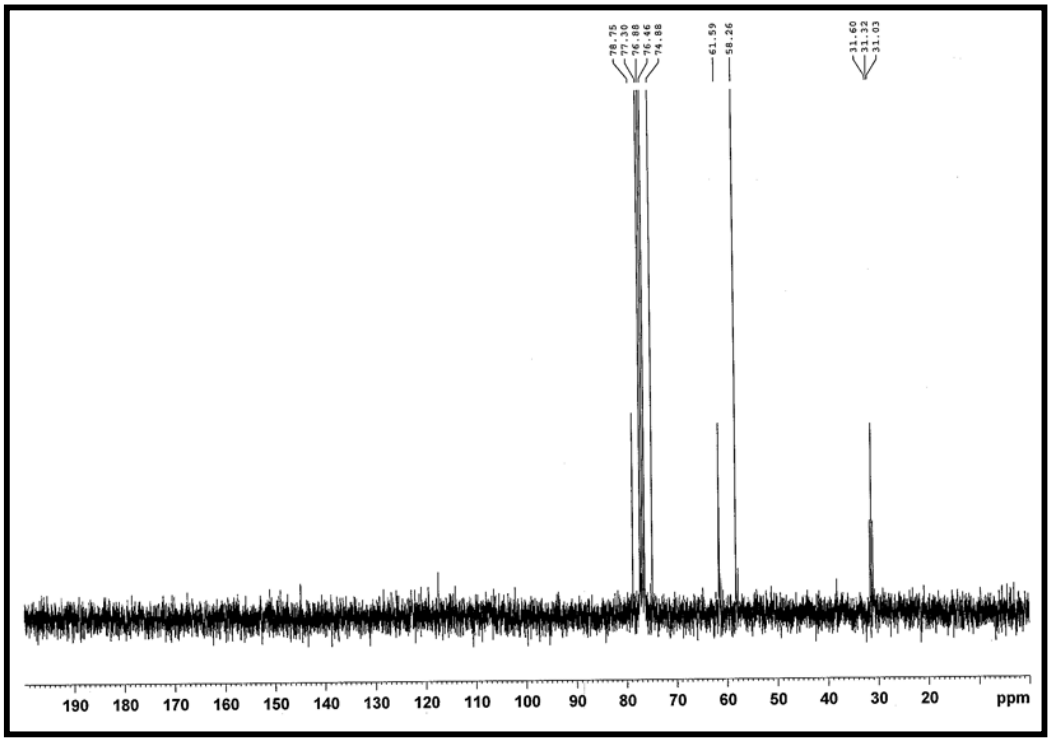


Fig. (3-33) ^{13}C NMR spectrm of compound **(72)**

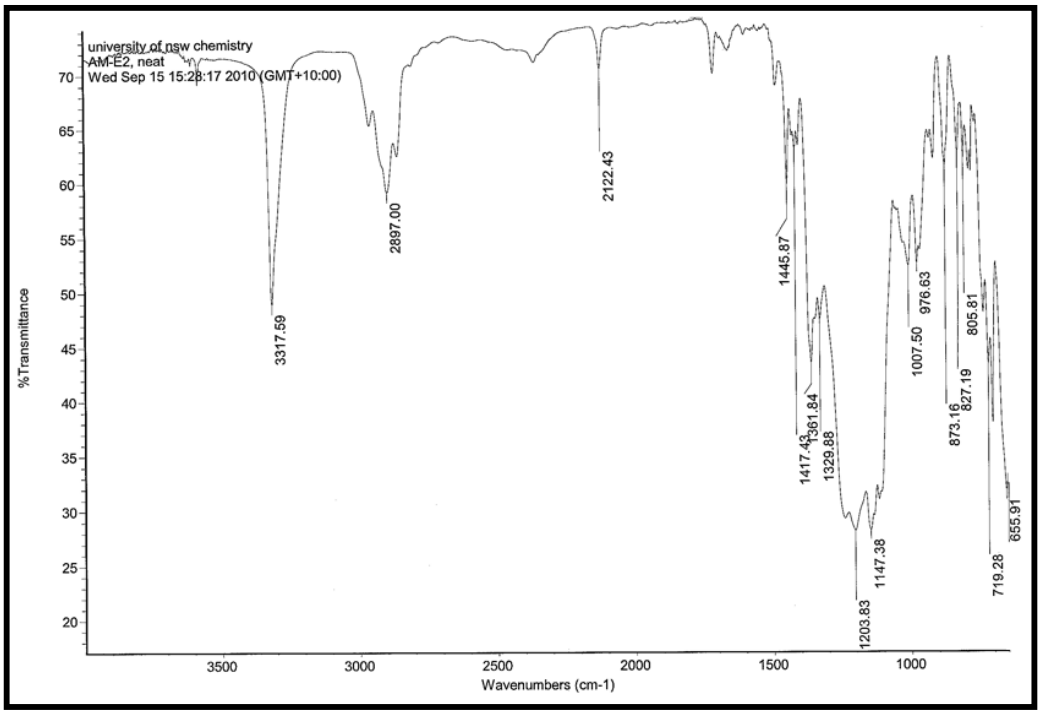


Fig. (3-34) FT-IR spectrum of compound **(73)**

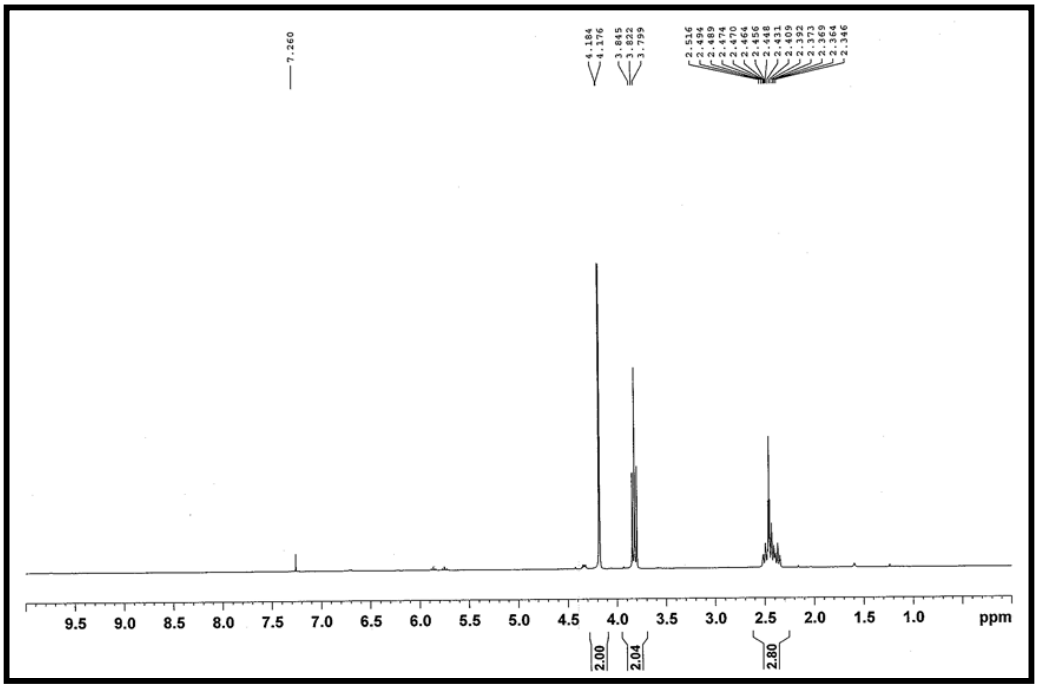


Fig. (3-35) ^{1}H NMR spectrum of compound **(73)**

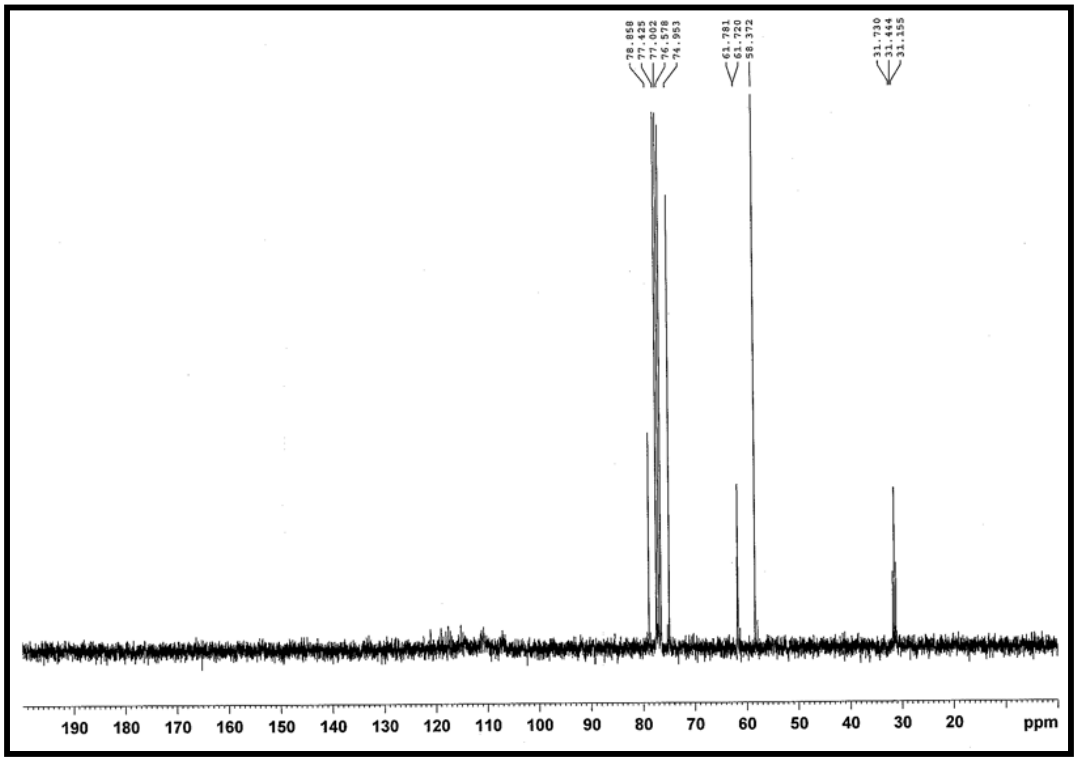


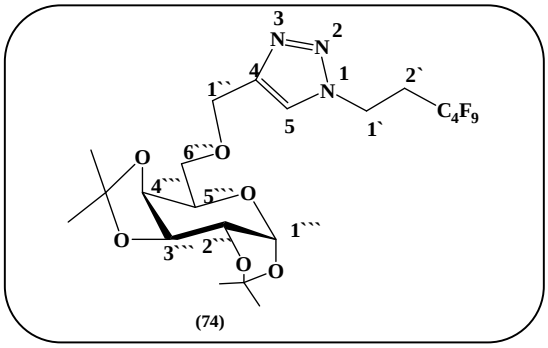
Fig. (3-36) ^{13}C NMR spectrum of compound **(73)**

The characterization spectra was showed good evidence for the formation of compounds **(71-73)**, FT-IR spectrum gave bands at (3315 and 2122 cm^{-1}) for the terminal acetylene vibrations, while ^{1}H NMR and ^{13}C NMR spectra gave triplet signals which referred to the effect of fluorine atoms spin in perfluoro chain overlapping with protons spin of ethylene group.

(3.1.7) 4-(6-galactosyloxy)methyl-1-(2-perfluorobutyl)ethyl-1*H*-1,2,3-triazole-1,2:3,4-diacetonide (74)

Click chemistry was used in this study to get 1,4-disubstitutes 1,2,3-triazoles with terminal perfluoro chain and carbohydrate derivatives as another substituent, so it is important to click of the terminal alkyne with perfluoroazides to produce N-substituted ethyl perfluoro chain.

Cu(I) catalyzed 1,3-dipolar cycloaddition of protected acetylenic sugar **(67)** with perfluoroalkyl ethyl azide to afforded 1,4-disubstituted triazole scheme (3-7)



Scheme (3-8) Structure of compound **(74)**

FT-IR spectrum Fig. (3-37) of compound **(74)** showed the following bands at $\bar{\upsilon}$ (Nujol) (cm^{-1}): 2923($\upsilon_{C\text{-}H,\ CH3}$), 1456($\delta_{C\text{-}H,\ CH3}$), 1377($\upsilon_{C\text{-}N}$), 1217($\upsilon_{C\text{-}F}$), 1168($\upsilon_{C\text{-}O\text{-}C}$).

While ^{1}H NMR Fig. (3-38) for the same compound showed the following signals at δ ($CDCl_3$) (ppm): 1.23, 1.33, 1.43, 1.53 (s, 12H, $4CH_{3isopropylidene}$), 2.82 (tt, *J* 18.0,

7.6 Hz, 2H, H2`), 3.68 (dd, *J* 10.3, 7.1 Hz, 1H, H_a6```a), 3.74 (dd, *J* 10.3, 5.6 Hz, 1H, H_b6```), 4.00 (m, 1H, H5```), 4.24 (dd, *J* 7.9, 1.9 Hz, 1H, H4```), 4.31 (dd, *J* 5.0, 2.4 Hz, 1H, H2```), 4.60 (dd, *J* 7.9, 2.4 Hz, 1H,H3```), 4.67(t, *J* 7.5 Hz, 2H, H1`), 4.73 (s, 2H, H1``), 5.54 (d, *J* 5.0 Hz, 1H, H1```), 7.66 (s, 1H, H5).

^{13}C NMR spectrum Fig. (3-39) of compound **(74)** gives the following signals at ($CDCl_3$) δ (ppm): 24.4, 24.8, 25.9, 26.0 (4C, $CH_{3\ isopropylidene}$), 31.7 (C2`), 42.3 (C1`), 64.6 (C1``), 66.8 (C5```), 69.5 (C6```), 70.4 (C2```), 70.6 (C3```), 71.1 (C4```), 96.3 (C1```), 108.5. 109.3 (2C, $C_{\ isopropylidene}$), 123.2 (C5), 145.6 (C4). MS (ESI) *m/z*: 610 ($[M+Na]^+$).

HSQC Fig. (3-40) and COSY Fig. (3-41) of compound **(74)** showed signals summarized in table (3-7):

Table (3-7) Summarized HSQC and COSY values of compound **(74)**

^{1}H NMR	COSY	^{13}C NMR	HSQC
1.23, 1.32, 1.43, 1.52 (s, 12H, $4CH_{3isopropylidene}$)	1.23, 1.32, 1.43, 1.52	24.4, 24.8, 25.9, 26.0 (4C, $CH_{3\ isopropylidene}$)	1.23, 1.32, 1.43, 1.52
2.82 (tt, *J* 18.0, 7.5 Hz, 2H, H2`)	4.67	31.7 (C2`)	2.82
3.68 (dd, *J* 10.3, 7.1 Hz, 1H, H_a6```)	3.74, 4.00	42.3 (C1`)	4.67
3.74 (dd, *J* 10.3, 5.6 Hz, 1H, H_b6```)	3.68, 4.00	64.6 (C1``)	4.73
4.00 (m, 1H, H5```)	3.68, 3.74	66.8 (C5```)	4.00
4.24 (dd, *J* 7.9, 1.9 Hz, 1H, H4```)	4.60	69.5 (C6```)	3.74
4.31 (dd, *J* 5.1, 2.4 Hz, 1H, H2```)	5.54	70.4 (C2```)	4.31
4.60 (dd, *J* 7.9, 2.4 Hz, 1H,H3```)	4.24	70.6 (C3```)	4.60
4.67(t, *J* 7.5 Hz, 2H, H1`)	2.82	71.1 (C4```)	4.24

4.73 (s, 2H, H1``)	-	96.3 (C1```)	5.54
5.54 (d, *J* 5.1 Hz, 1H, H1```)	4.31	108.5. 109.3 (2C, C isopropylidene)	-
7.65 (s, 1H, H5)	-	123.2 (C5)	7.65
-	-	145.6 (C4)	-

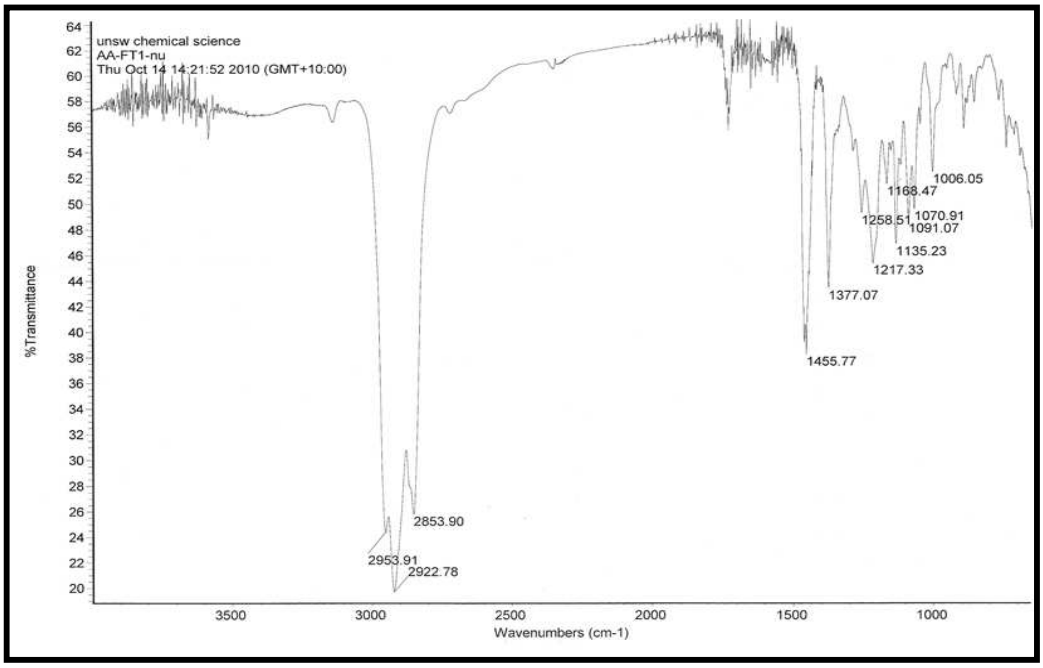


Fig. (3-37) FT-IR spectrum of compound **(74)**

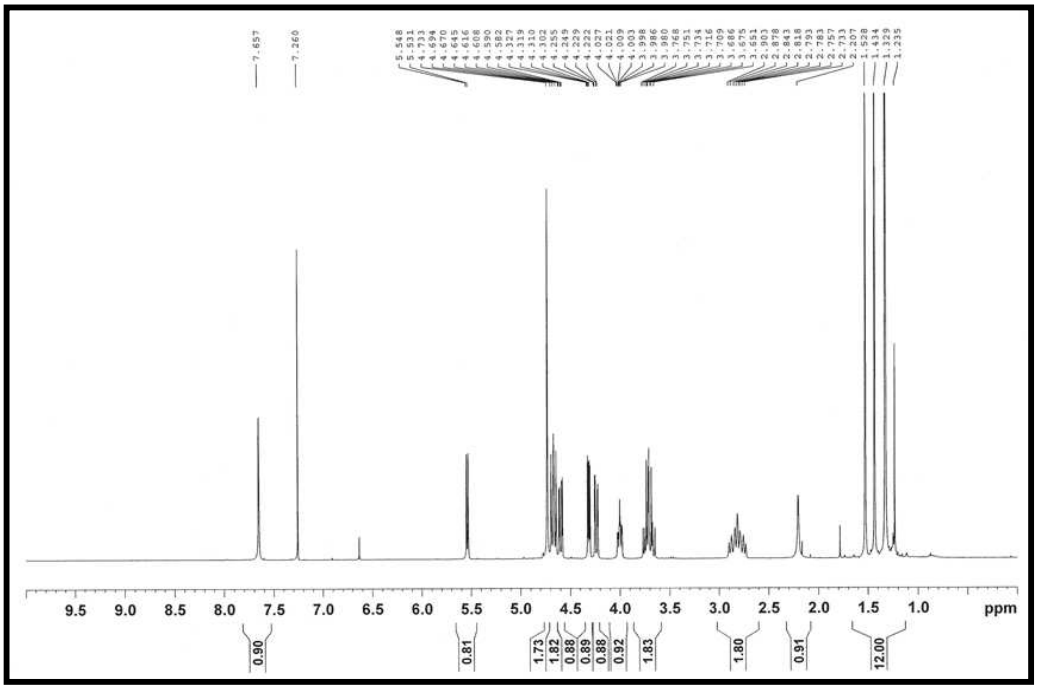


Fig. (3-38) ^{1}H NMR spectrum of compound **(74)**

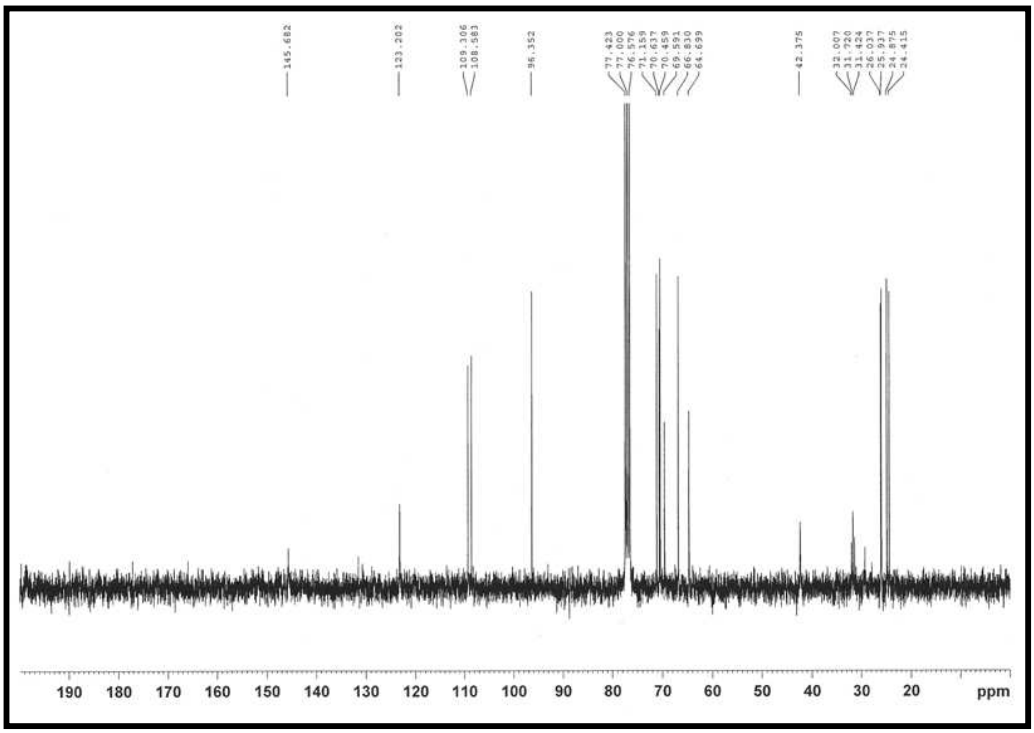


Fig. (3-39) ^{13}C NMR spectrum of compound **(74)**

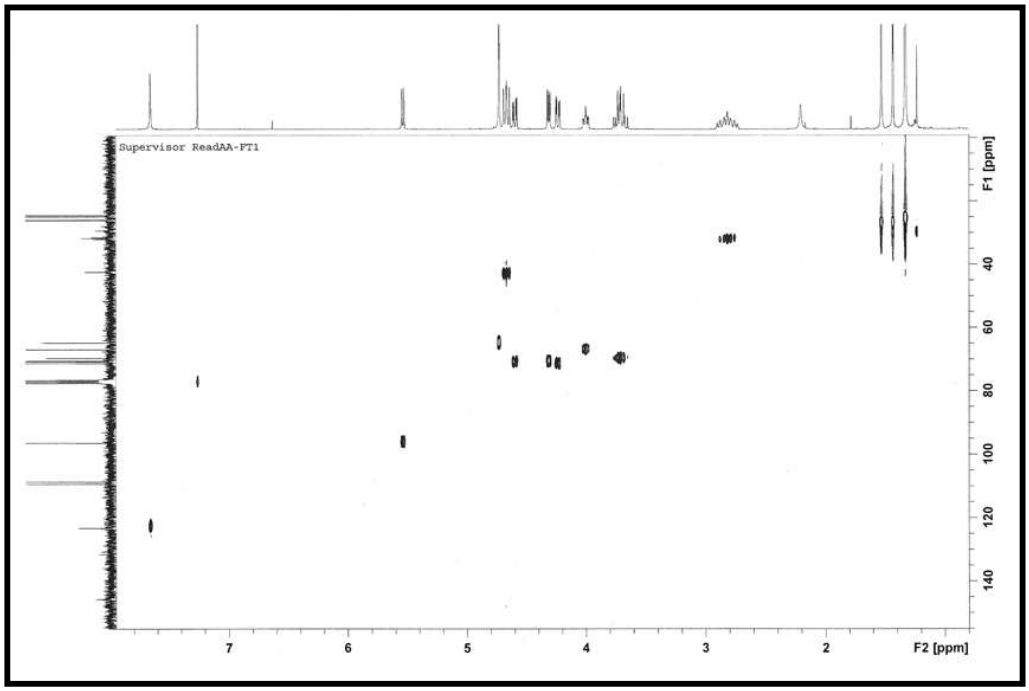


Fig. (3-40) HSQC spectrum of compound **(74)**

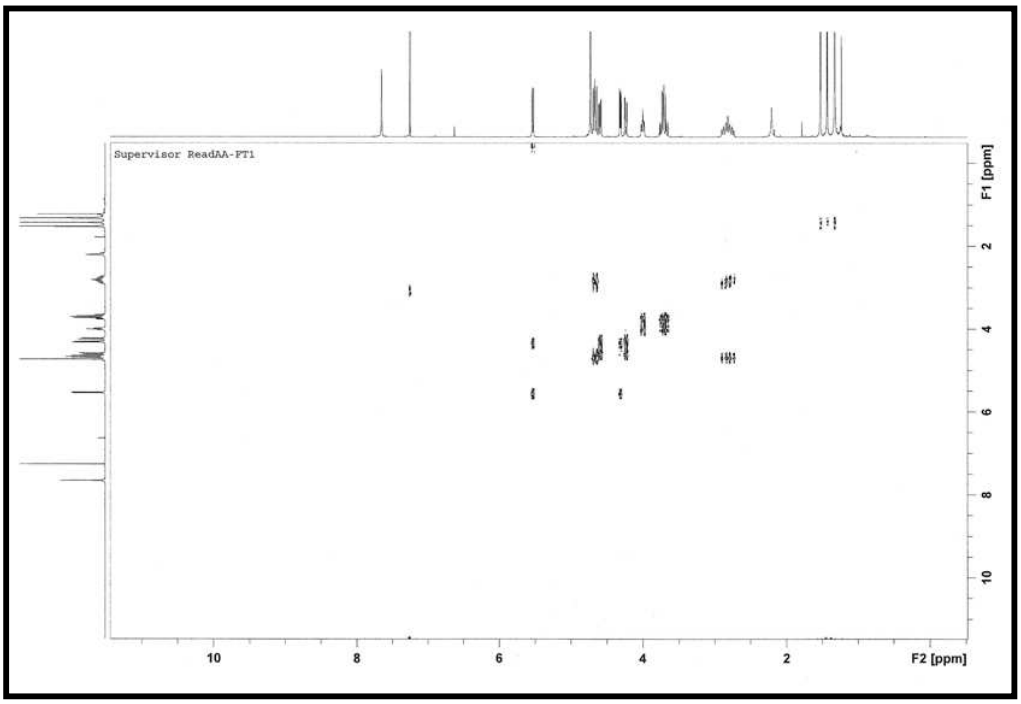


Fig. (3-41) COSY spectrum of compound **(74)**

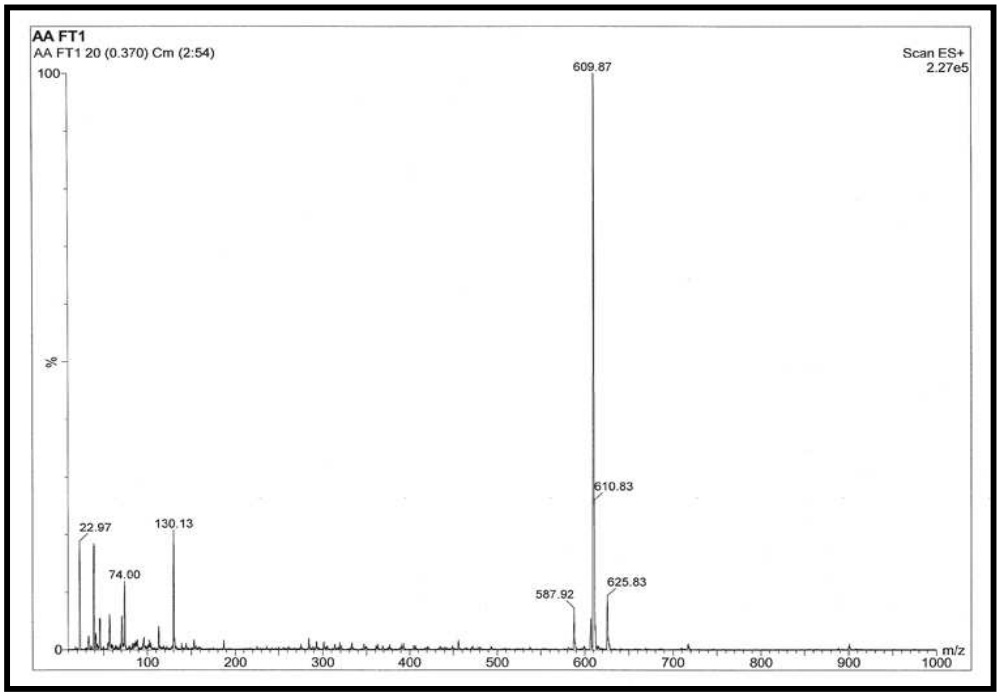
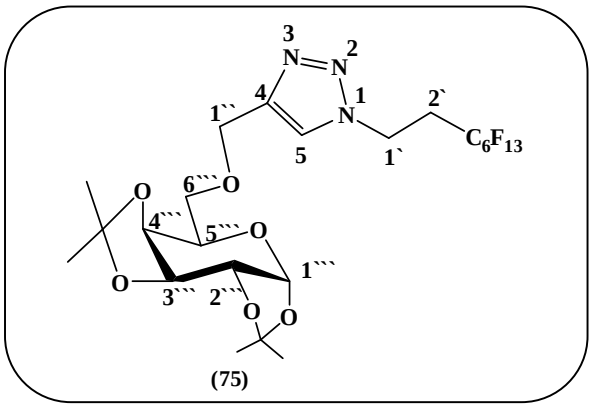


Fig. (3-42) LC-MS spectrum of compound **(74)**

(3.1.8) 4-(6-galactosyloxy)methyl-1-(2-perfluorohexyl)ethyl-1*H*-1,2,3-triazole-1,2:3,4-diacetonide (75)

Compound **(75)** synthesized in the presence Cu(I) catalysis to produce 1,4-disubstituted triazole with terminal perfluoro chain in good yield (76%) scheme (3-8).



Scheme (3-9) Structure of compound **(75)**

FT-IR spectrum Fig. (3-43) of compound **(75)** showed the following bands at $\bar{\upsilon}$ (cm^{-1}) (Nujol): 2923 ($\upsilon_{C-H, CH3}$), 1456 ($\delta_{C-H, CH3}$), 1377 (υ_{C-N}), 1213 (υ_{C-F}), 1142 (υ_{C-O-C}).

^{1}H NMR spectrum Fig. (3-44) for the same compound showed signals at δ (ppm) ($CDCl_3$): 1.32, 1.33, 1.43, 1.52 (s, 12H, $4CH_{3\ isopropylidene}$), 2.81 (tt, *J* 17.9, 7.5, Hz, 2H, H2`), 3.68 (dd, *J* 10.3, 7.1 Hz, 1H, $H_a6```$), 3.73 (dd, *J* 10.3, 5.2 Hz, 1H, $H_b6```$), 4.01 (m, 1H,H5```), 4.25 (dd, *J* 7.9, 1.9 Hz, 1H, H4```), 4.31 (dd, *J* 5.0, 2.4 Hz, 1H, H2```), 4.61 (dd, *J* 7.9, 2.4 Hz, 1H, H3```), 4.67 (t, *J* 7.5 Hz, 2H, H1`), 4.73 (s, 2H, H1``), 5.54 (d, *J* 5.0 Hz, 1H, H1```), 7.65 (s, 1H, H5).

^{13}C NMR spectrum Fig. (3-45) of compound **(75)** showed signals at δ (ppm) ($CDCl_3$): 24.4, 24.8, 25.9, 26.0 (4C, $CH_{3\ isopropylidene}$), 31.8 (C2`), 42.3 (C1`), 64.7 (C1``), 66.8 (C5```), 69.5 (C6```), 70.4 (C2```), 70.6 (C3```), 71.1 (C4```), 96.3 (C1```), 108.5, 109.3 (2C, $C_{isopropylidene}$), 123.1 (C5), 145.7 (C4). MS (ESI) *m/z*: 710 ($[M+Na]^+$).

Table (3-8) summarized values of HSQC spectrum Fig. (3-46) and COSY spectrum Fig. (3-47) of compound **(75)**.

Table (3-8) Summarized HSQC and COSY values of compound **(75)**

^{1}H NMR	**COSY**	**^{13}C NMR**	**HSQC**
1.32, 1.43, 1.52 (s, 12H, $4CH_{3\ isopropylidene}$)	1.32, 1.43, 1.52	24.4, 24.8, 25.9, 26.0 (4C, $CH_{3\ isopropylidene}$)	1.32, 1.43, 1.52
2.81 (tt, *J* 17.9, 7.5, Hz, 2H, H2`)	4.67	31.8 (C2`)	2.81
3.68 (dd, *J* 10.3, 7.1 Hz, 1H, $H_a6```$)	3.74, 4.01	42.3 (C1`)	4.67
3.73 (dd, *J* 10.3, 5.2 Hz, 2H, $H_b6```$)	3.68, 4.01	64.7 (C1``)	4.73
4.01 (m, 1H,H5```)	3.68, 3.74	66.8 (C5```)	4.01
4.25 (dd, *J* 7.9, 1.9	4.61	69.5 (C6```)	3.73

Hz, 1H, H4```)			
4.31 (dd, *J* 5.1, 2.4 Hz, 1H, H2```)	5.54	70.4 (C2```)	4.31
4.61 (dd, *J* 7.9, 2.4 Hz, 1H, H3```)	4.25	70.6 (C3```)	4.61
4.67 (t, *J* 7.5 Hz, 2H, H1`)	2.81	71.1 (C4```)	4.25
4.73 (s, 2H, H1``)	-	96.3 (C1```)	5.54
5.54 (d, *J* 5.4 Hz, 1H, H1```)	4.31	108.5, 109.3 (2C, C isopropylidene)	-
7.65 (s, 1H, H5)	-	123.1 (C5)	-
-	-	145.7 (C4)	

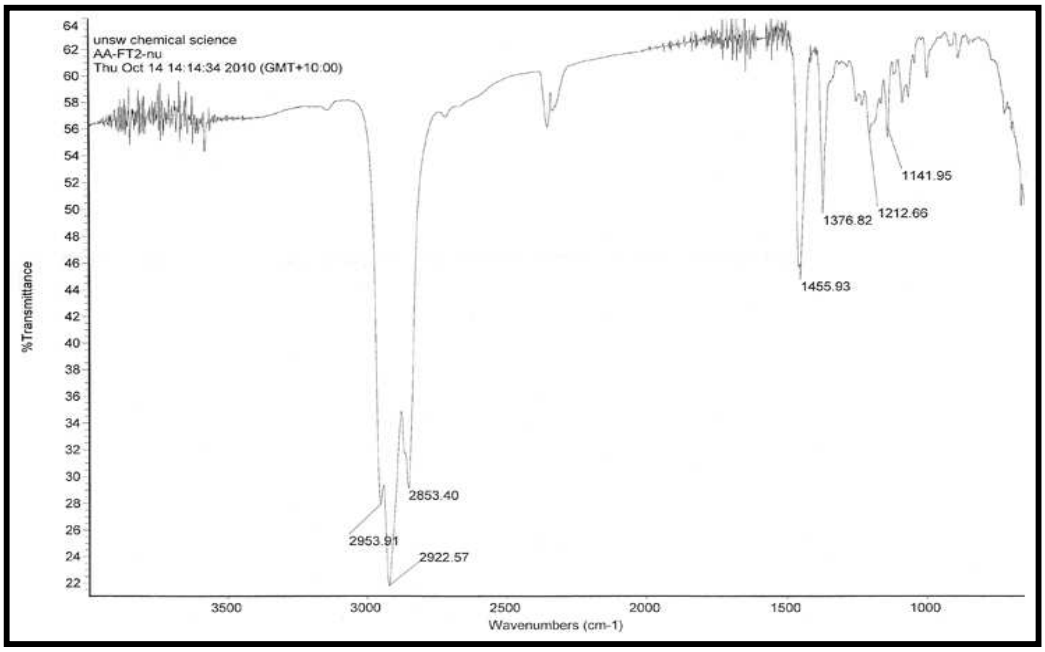


Fig. (3-43) FT-IR spectrum of compound **(75)**

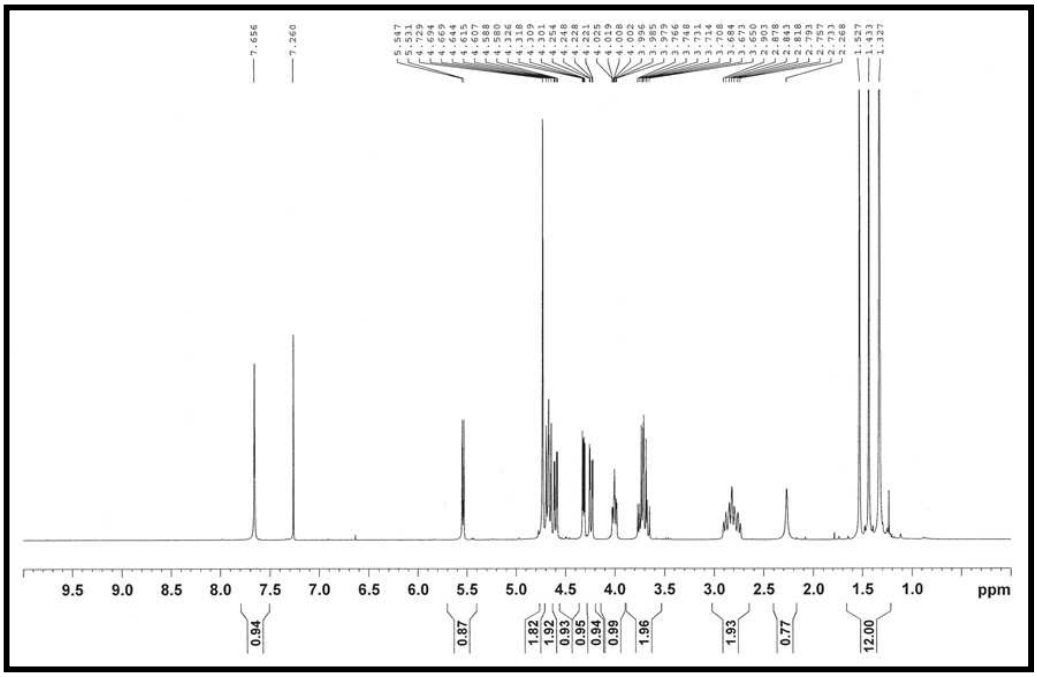


Fig. (3-44) ^{1}H NMR spectrum of compound **(75)**

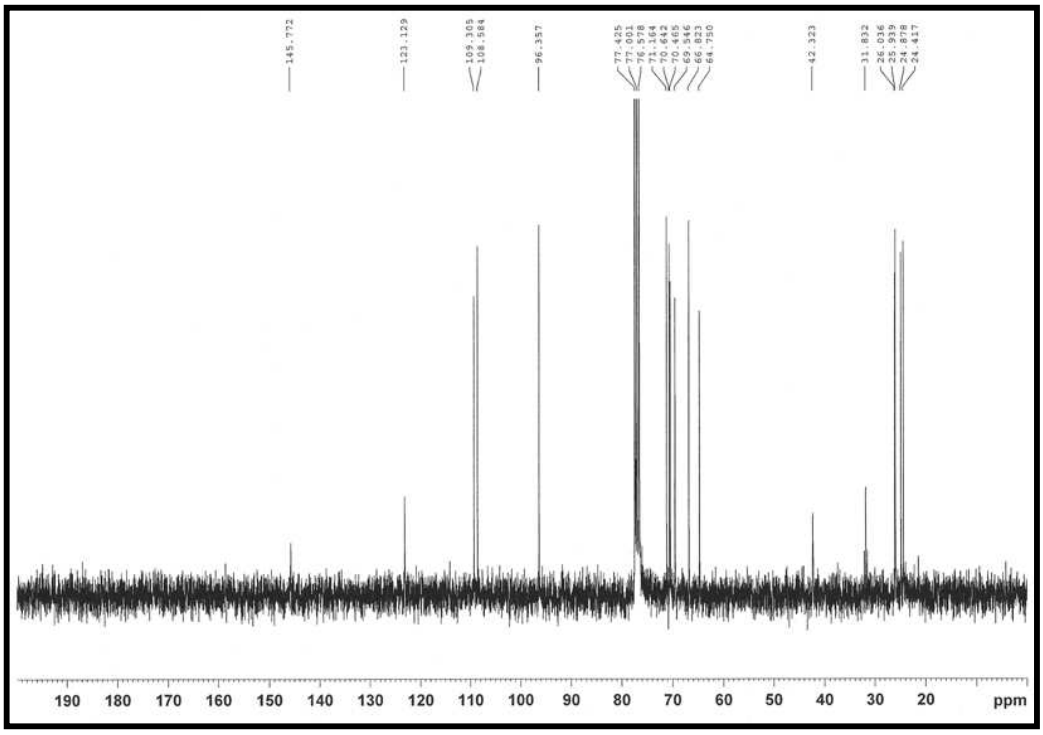


Fig. (3-45) ^{13}C NMR spectrum of compound **(75)**

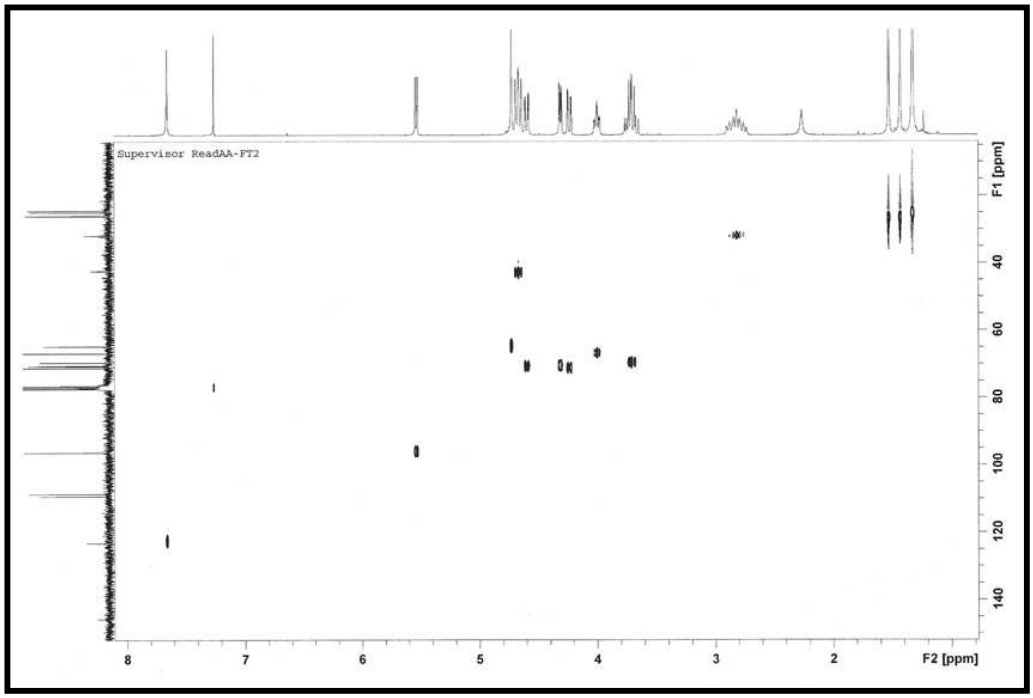


Fig. (3-46) HSQC spectrum of compound **(75)**

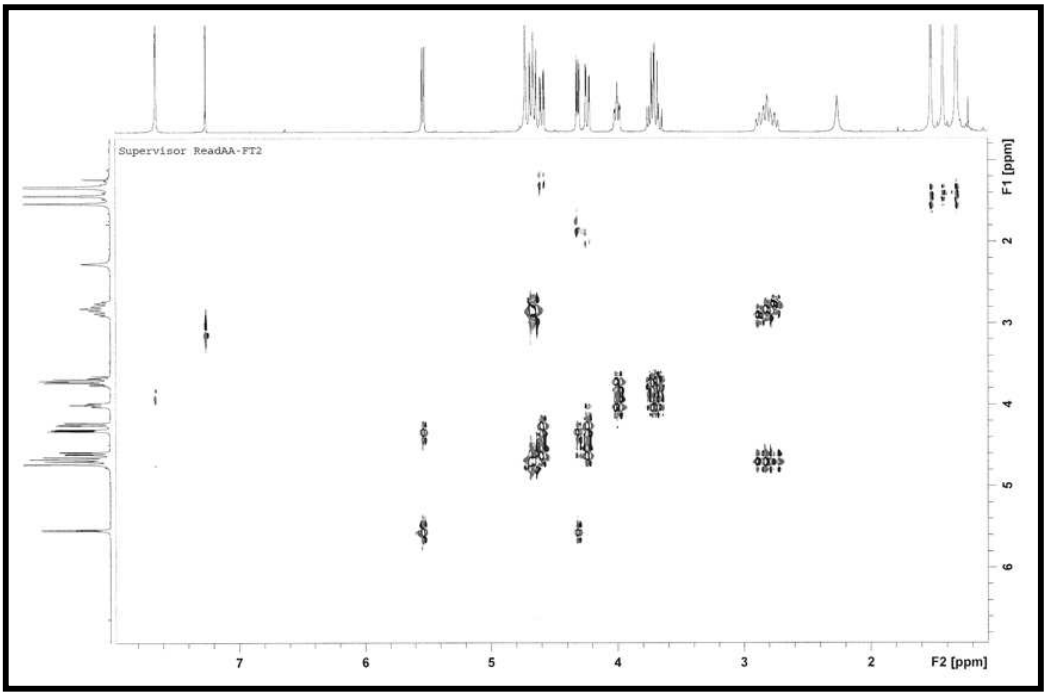


Fig. (3-47) COSY spectrum of compound **(75)**

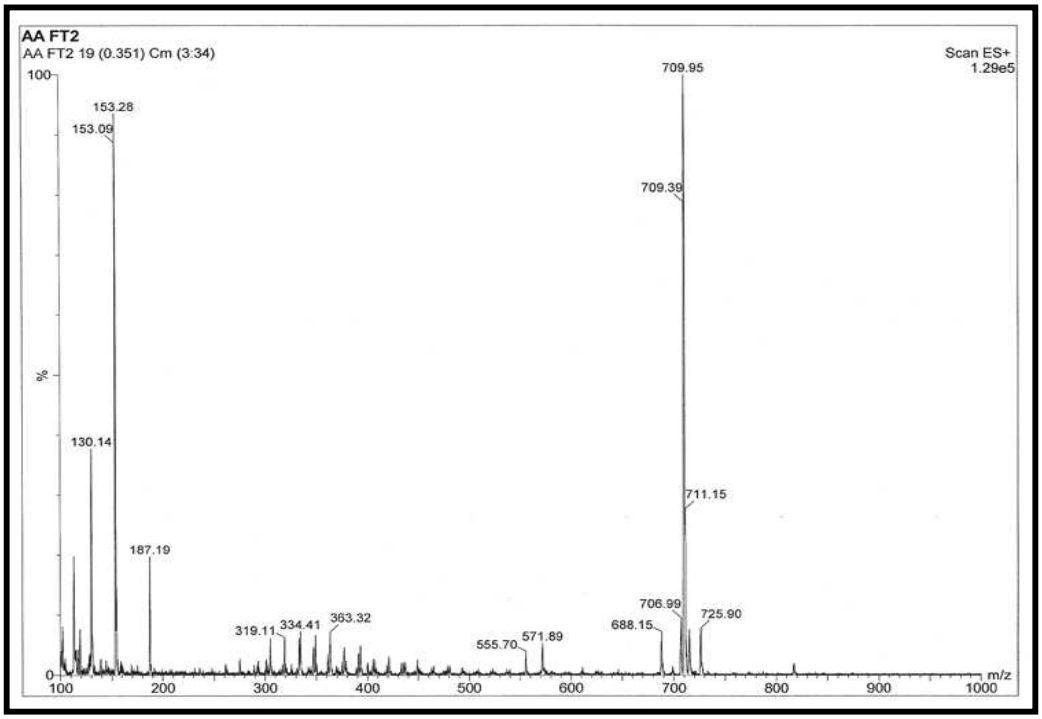
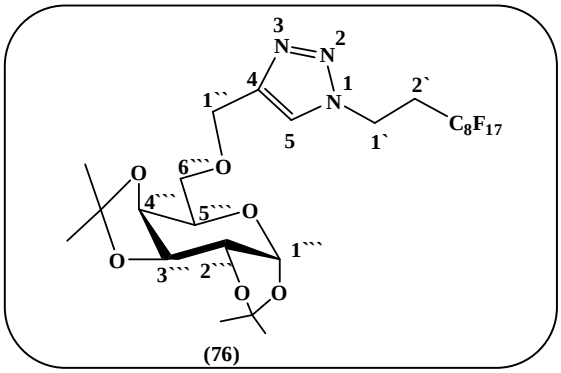


Fig. (3-48) LC-MS spectrum of compound **(75)**

(3.1.9) 4-(6-galactosyloxy)methyl-1-(2-perfluorooctyl)ethyl-1*H*-1,2,3-triazole-1,2:3,4-diacetonide (76)

Compound **(76)** synthesized using click condition to producing triazole with longer perfluoro chain in good yield (78%) scheme (3-9).



Scheme (3-10) Structure of compound (76)

FT-IR spectrum Fig. (3-49) of compound **(76)** showed bands at $\bar{\upsilon}$ (cm^{-1}) (Nujol): 2923($\upsilon_{C-H, CH3}$), 2853, 1456 ($\delta_{C-H, CH3}$), 1377 (υ_{C-N}), 1200 (υ_{C-F}), 1146 (υ_{C-O-C}).

^{1}H NMR spectrum Fig. (3-50) of compound **(76)** showed signals at δ (ppm) ($CDCl_3$): 1.33, 1.43, 1.52 (12H, $4CH_{3isopropylidene}$), 2.84 (tt, *J* 18.0, 7.5 Hz, 2H, H2`), 3.68 (dd, *J* 10.4, 7.1 Hz, 1H, H_a6```), 3.74 (dd, *J* 10.4, 5.2 Hz, 2H, H_b6```), 4.01 (m, 1H, H5```), 4.25 (dd, *J* 7.9, 1.9 Hz, 1H, H4```), 4.31 (dd, *J* 5.0, 2.4 Hz, 1H, H2```), 4.61 (dd, *J* 7.9, 2.4 Hz, 1H, H3```), 4.67 (t, *J* 7.5 Hz, 2H, H1`), 4.73 (s, 2H, H1``), 5.54 (d, *J* 5.0 Hz, 1H, H1```), 7.66 (s, 1H, H5).

^{13}C NMR spectrum Fig. (3-51) of compound **(76)** showed signals at δ (ppm) ($CDCl_3$): 24.4, 24.8, 25.9, 26.0 (4C, $CH_{3\ isopropylidene}$), 31.8 (C2`), 42.3 (C1`), 64.7 (C1``), 66.8 (C5```), 69.5 (C6```), 70.4 (C2```), 70.6 (C3```), 71.1 (C4```), 96.3 (C1```), 108.5, 109.3 (2C, $C_{isopropylidene}$), 123.1 (C5), 145.7 (C4). MS (ESI) *m/z*: 810 ($[M+Na]^+$)

Table (3-9) summarized values of HSQC spectrum Fig. (3-52) and COSY spectrum Fig. (3-53) of compound **(76)**.

Table (3-9) Summarized values of HSQC and COSY spectra of compound (76)

^{1}H NMR	COSY	^{13}C NMR	HSQC
1.33, 1.43, 1.52 (12H, $4CH_{3isopropylidene}$)	1.33, 1.43, 1.52	24.4, 24.8, 25.9, 26.0 (4C, $CH_{3\ isopropylidene}$)	1.33, 1.43, 1.52
2.84 (tt, *J* 18.0, 7.5 Hz, 2H, H2`)	4.67	31.8 (C2`)	2.84
3.68 (dd, *J* 10.4, 7.1 Hz, 1H, H_a6```)	3.74, 4.01	42.3 (C1`)	4.67
3.74 (dd, *J* 10.4, 5.2 Hz, 2H, H_b6```)	3.68, 4.01	64.7 (C1``)	4.73
4.01 (m, 1H, H5```)	3.68, 3.74	66.8 (C5```)	4.01

4.25 (dd, *J* 7.9, 1.9 Hz, 1H, H4```)	4.61	69.5 (C6```)	3.71
4.31 (dd, *J* 5.0, 2.4 Hz, 1H, H2```)	5.54	70.4 (C2```)	4.31
4.61 (dd, *J* 7.9, 2.4 Hz, 1H, H3```)	4.25	70.6 (C3```)	4.61
4.67 (t, *J* 7.5 Hz, 2H, H1`)	2.84	71.1 (C4```)	4.25
4.73 (s, 2H, H1``)	-	96.3 (C1```)	5.54
5.54 (d, *J* 5.0 Hz, 1H, H1```)	4.31	108.5, 109.3 (2C, C isopropylidene)	-
7.66 (s, 1H, H5)	-	123.1 (C5)	7.66
-	-	145.7 (C4)	-

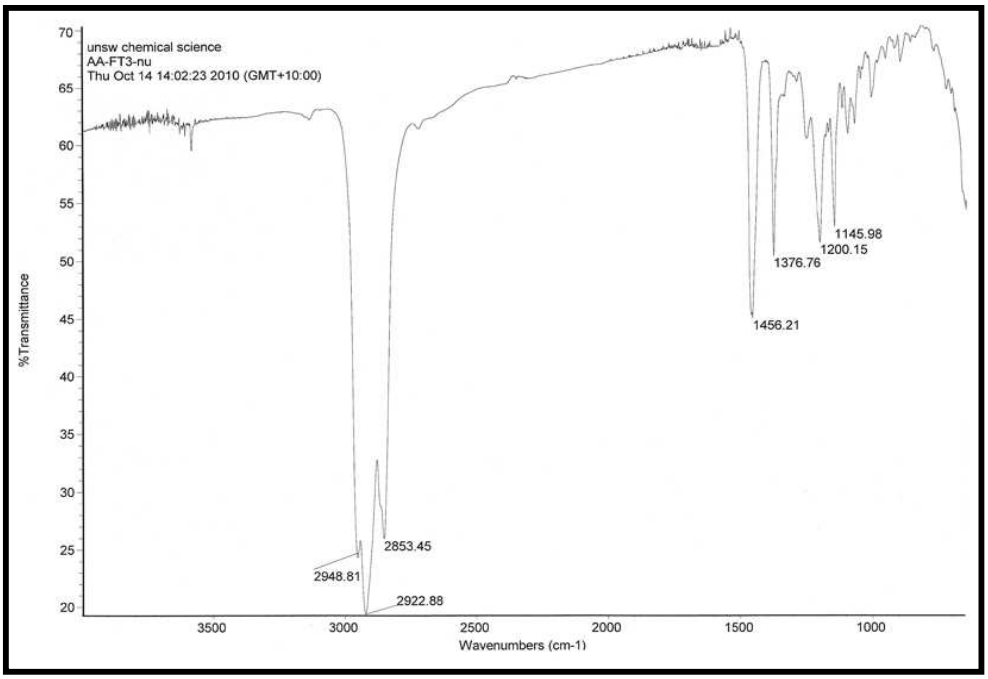


Fig. (3-49) FT-IR of compound **(76)**

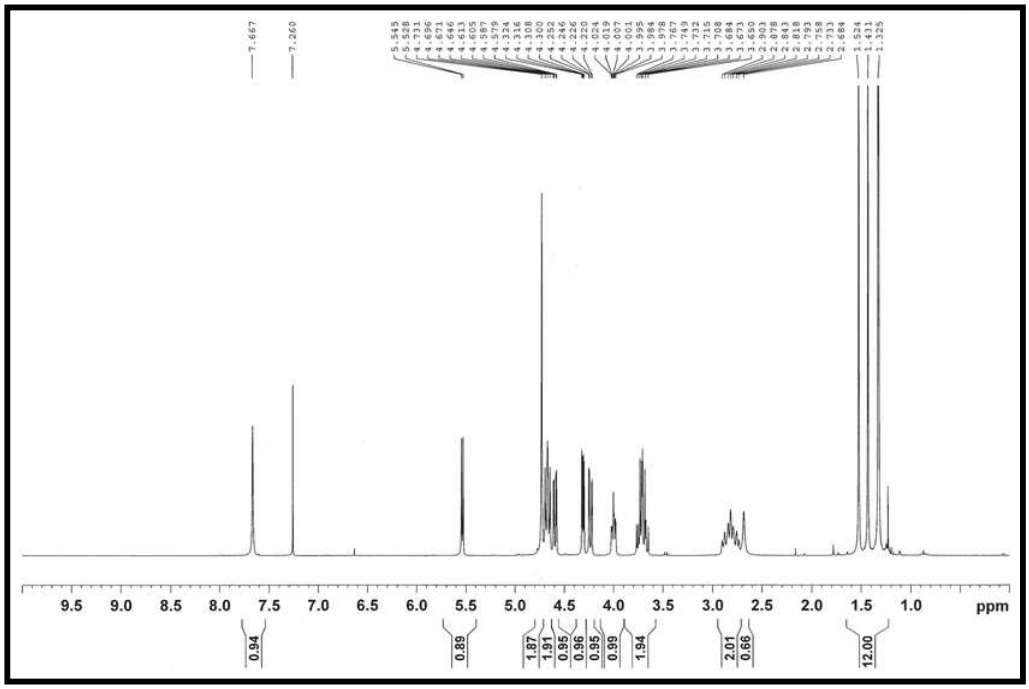


Fig. (3-50) ^{1}H NMR of compound **(76)**

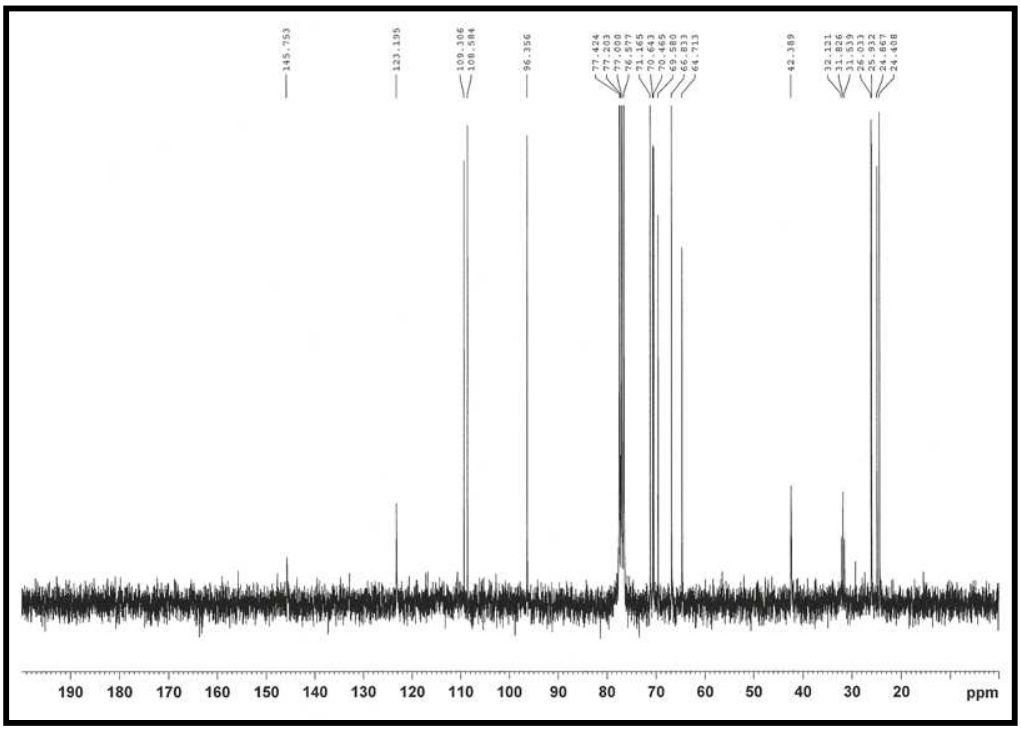


Fig. (3-51) ^{13}C NMR of compound **(76)**

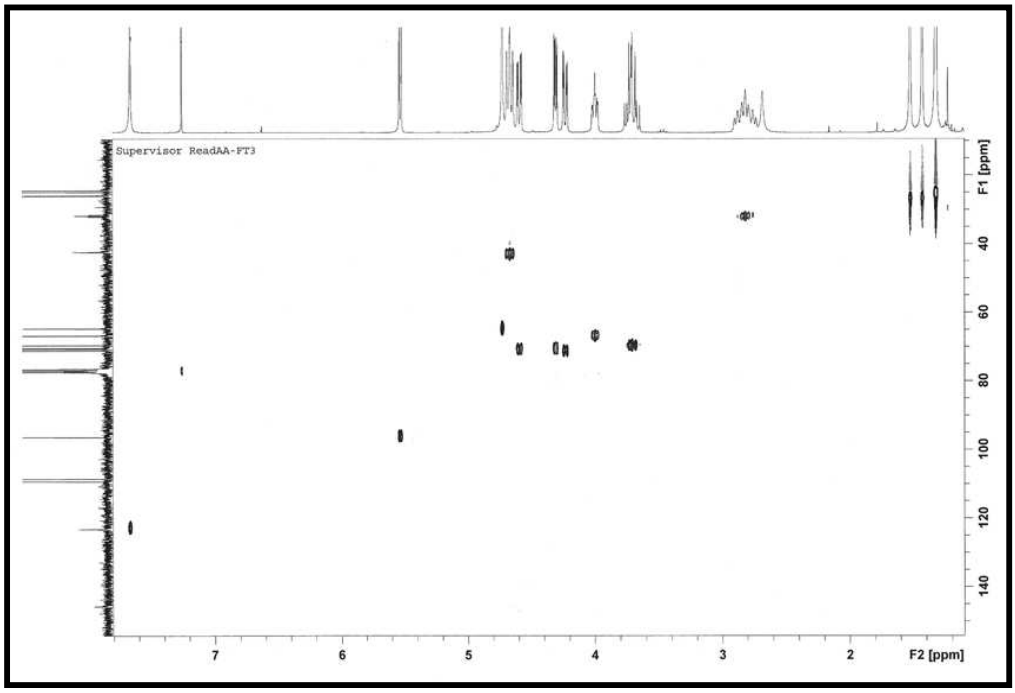


Fig. (3-52) HSQC of compound **(76)**

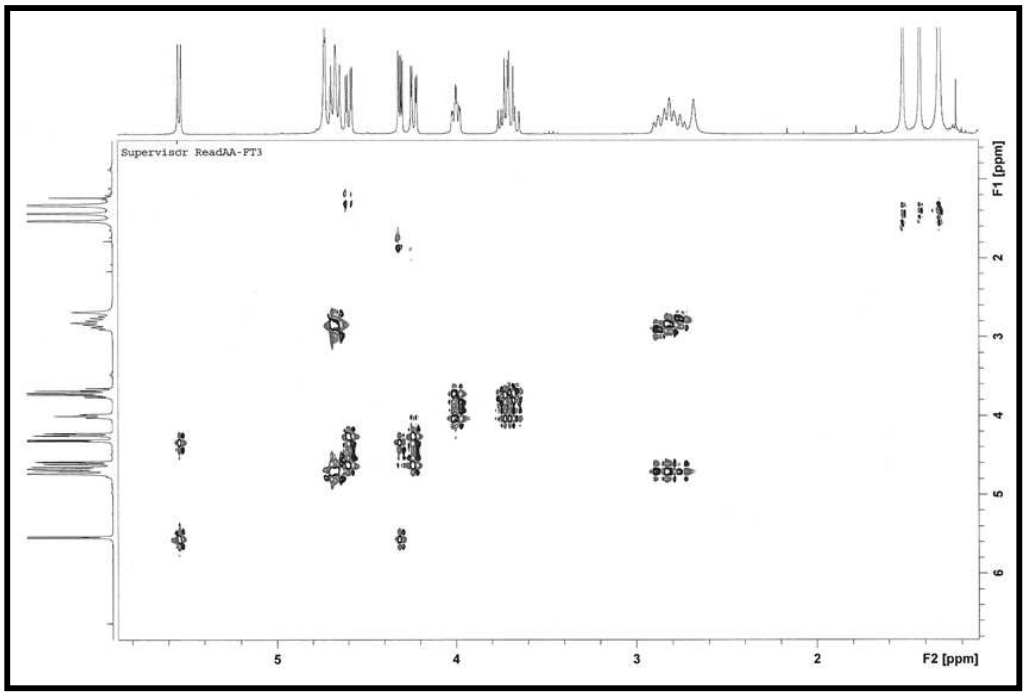


Fig. (3-53) COSY of compound **(76)**

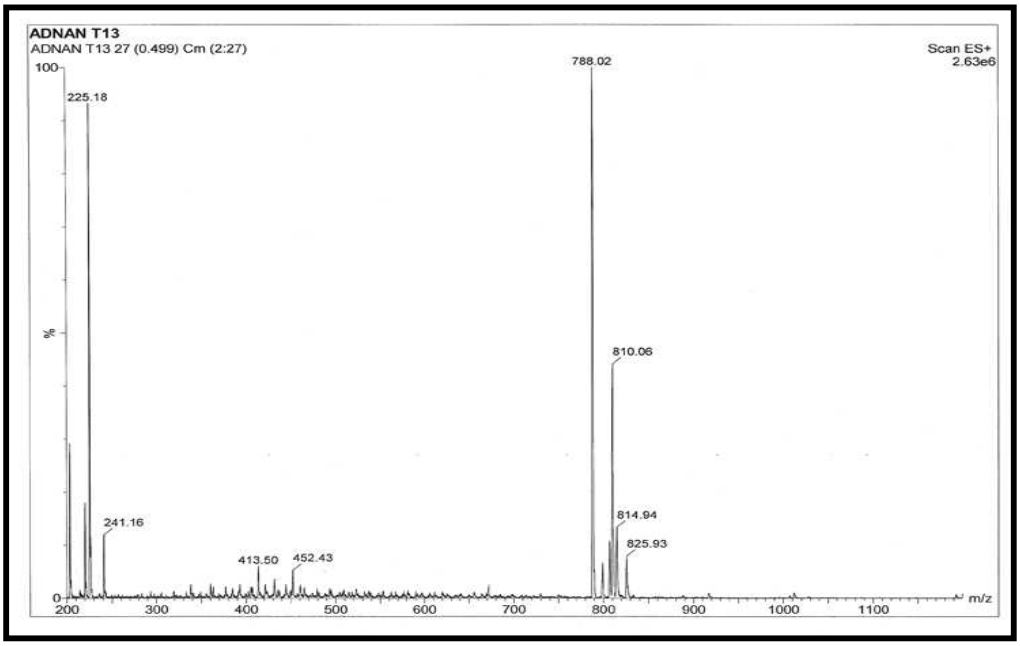
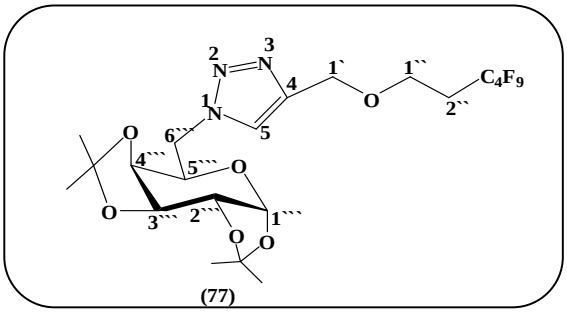


Fig. (3-54) LC-MS spectrum of compound **(76)**

(3.1.10) 1-(6-galactosyl)-4-((2-(perfluorobutyl)ethoxy)methyl-1*H*-1,2,3-triazole 1,2:3,4-diacetonide (77)

This study included a second series of triazole derivatives synthesized *via* click reaction contained ethers as a spacer.

Compound **(77)** synthesized by 1,3-dipolar cycloaddition Cu(I) catalysis in good yield (79%) compatible with scheme (3-10):



Scheme (3-11) Structure of compound (77)

FT-IR spectrum Fig. (3-54) of compound **(77)** showed bands at $\bar{\upsilon}$ (cm^{-1}) (Nujol): 2923($\upsilon_{C-H, CH3}$), 1456 (υ_{C-C}), 1220(υ_{C-N}), 1137 (υ_{C-O}).

^{1}H NMR spectrum Fig. (3-55) of compound **(77)** showed signals at δ (ppm) ($CDCl_3$): 1.27, 1.35, 1.37, 1.48 (s, 12H, $4CH_{3isopropylidene}$), 2.43 (tt, *J* 18.8, 6.7 Hz, 2H, H2``), 3.80 (t, *J* 6.7 Hz, 2H, H1``), 4.17 (ddd, *J* 8.5, 4.2, 1.8 Hz, 1H, H5```), 4.20 (dd, *J* 7.7, 1.8 Hz, 1H, H4```), 4.33 (dd, *J* 4.9, 2.6 Hz, 1H, H2```), 4.50 (m, 2H, H6```), 4.64 (dd, *J* 7.7, 2.6 Hz, 1H, H3```), 4.70 (s, 2H, H1`), 5.51 (d, *J* 4.9 Hz, 1H, H1```), 7.76 (s, 1H, H5).

^{13}C NMR spectrum Fig. (3-56) of compound **(77)** showed signals at ($CDCl_3$) δ (ppm): 24.3, 24.7, 25.8, 25.9 (4C, $CH_{3\ isopropylidene}$), 31.3 (C2``), 50.9 (C6```), 62.1 (C1``), 64.1 (C1`), 67.0 (C5```), 70.2 (C2```), 70.7 (C3```), 71.0 (C4```), 96.1 (C1```), 109.0, 109.9 (2C, $C_{\ isopropylidene}$), 124.2 (C5), 143.7 (C4). MS (ESI) *m/z*: 588 ($[M+H]^{+}$)

Table (3-10) summarized values of HSQC spectrum Fig. (3-57) and COSY spectrum Fig. (3-58) of compound **(77)**.

Table (3-10) Describe values of HSQC and COSY of compound (77)

^{1}H NMR	COSY	^{13}C NMR	HSQC
1.27, 1.35, 1.37, 1.48 (s, 12H, $4CH_{3isopropylidene}$)	1.27, 1.35, 1.37, 1.48	24.3, 24.7, 25.8, 25.9 (4C, $CH_{3\ isopropylidene}$)	1.27, 1.35, 1.37, 1.48
2.43 (tt, *J* 18.8, 6.7 Hz, 2H, H2``)	3.80	31.3 (C2``)	2.43
3.80 (t, *J* 6.7 Hz, 2H, H1``)	2.43	50.9 (C6```)	4.50
4.17 (ddd, *J* 8.5, 4.2, 1.8 Hz, 1H, H5```)	4.20, 4.50	62.1 (C1``)	3.80
4.20 (dd, *J* 7.7, 1.8 Hz, 1H, H4```)	4.17	64.1 (C1`)	4.70
4.33 (dd, *J* 4.9, 2.6 Hz, 1H, H2```)	4.64, 5.51	67.0 (C5```)	4.17

4.50 (m, 2H, H6```)	4.17	70.2 (C2```)	4.33
4.64 (dd, *J* 7.7, 2.6 Hz, 1H, H3```)	4.20	70.7 (C3```)	4.64
4.70 (s, 2H, H1`)	-	71.0 (C4```)	4.20
5.51 (d, *J* 4.9 Hz, 1H, H1```)	4.33	96.1 (C1```)	5.51
7.76 (s, 1H, H5)	-	109.0, 109.9 (2C, C isopropylidene)	-
-	-	124.2 (C5)	7.76
-	-	143.7 (C4)	-

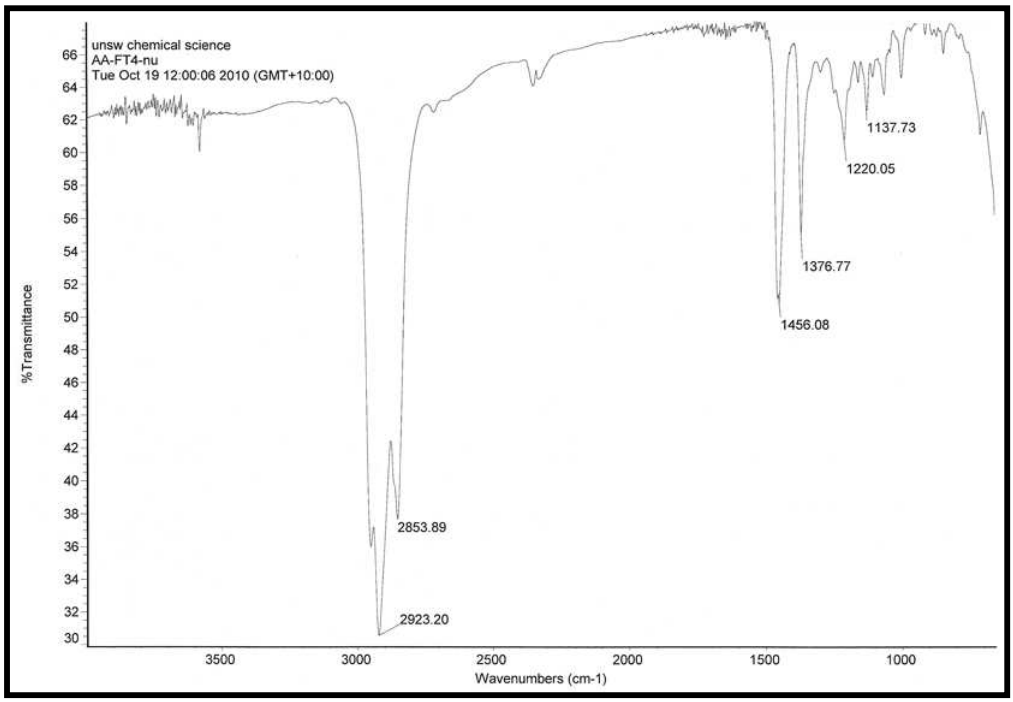


Fig. (3-55) FT-IR spectrum of compound **(77)**

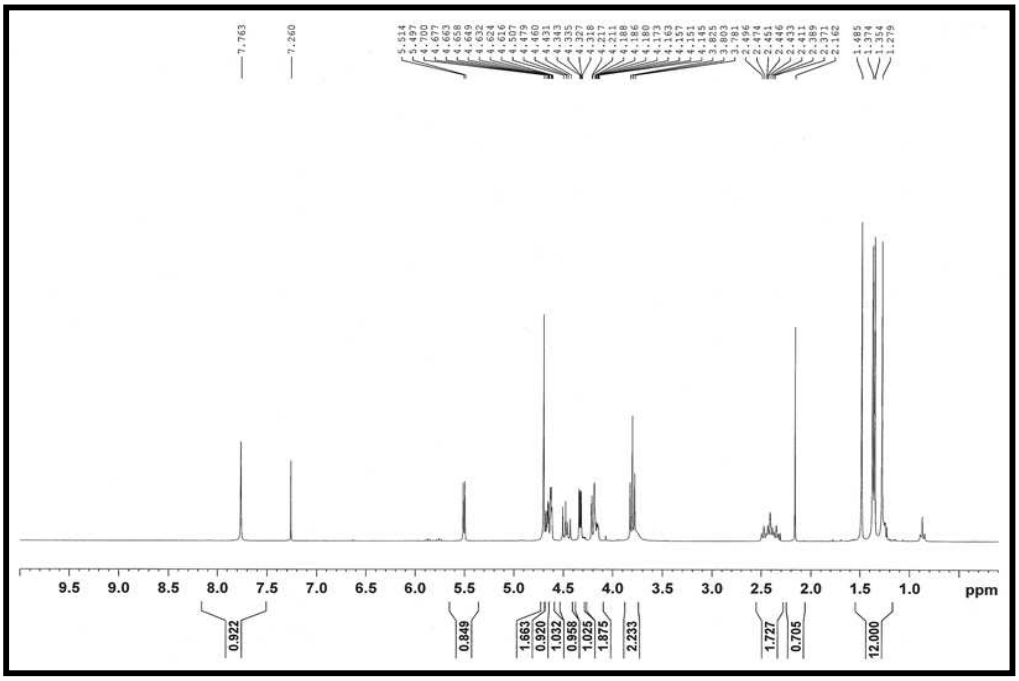


Fig. (3-56) ^{1}H NMR spectrum of compound **(77)**

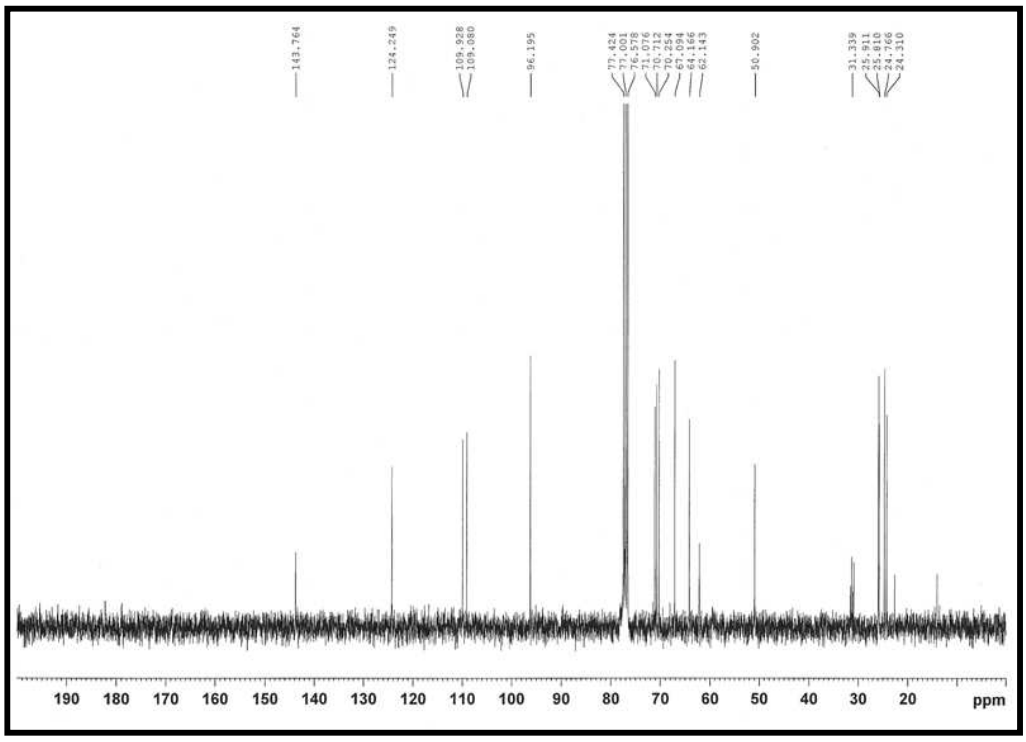


Fig. (3-57) ^{13}C NMR spectrum of compound **(77)**

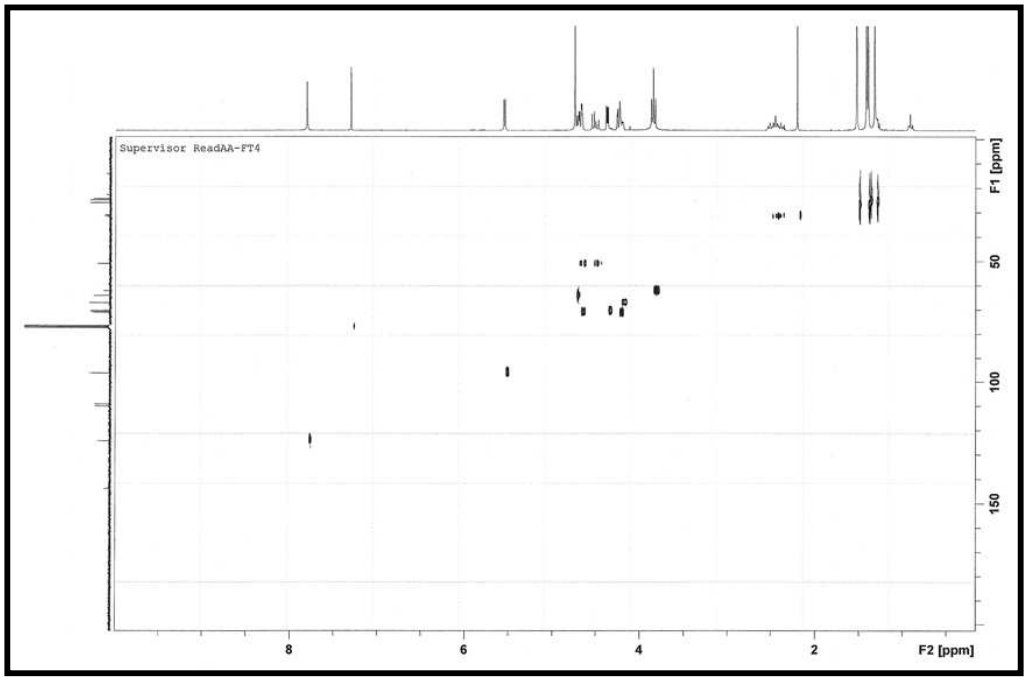


Fig. (3-58) HSQC spectrum of compound **(77)**

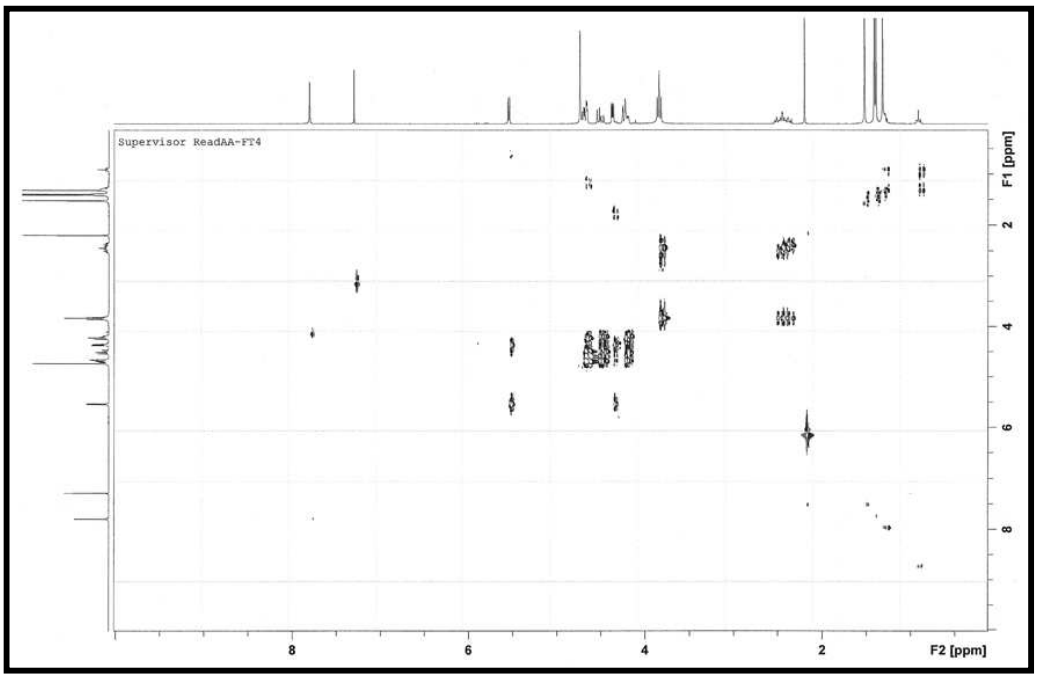


Fig. (3-59) COSY spectrum of compound **(77)**

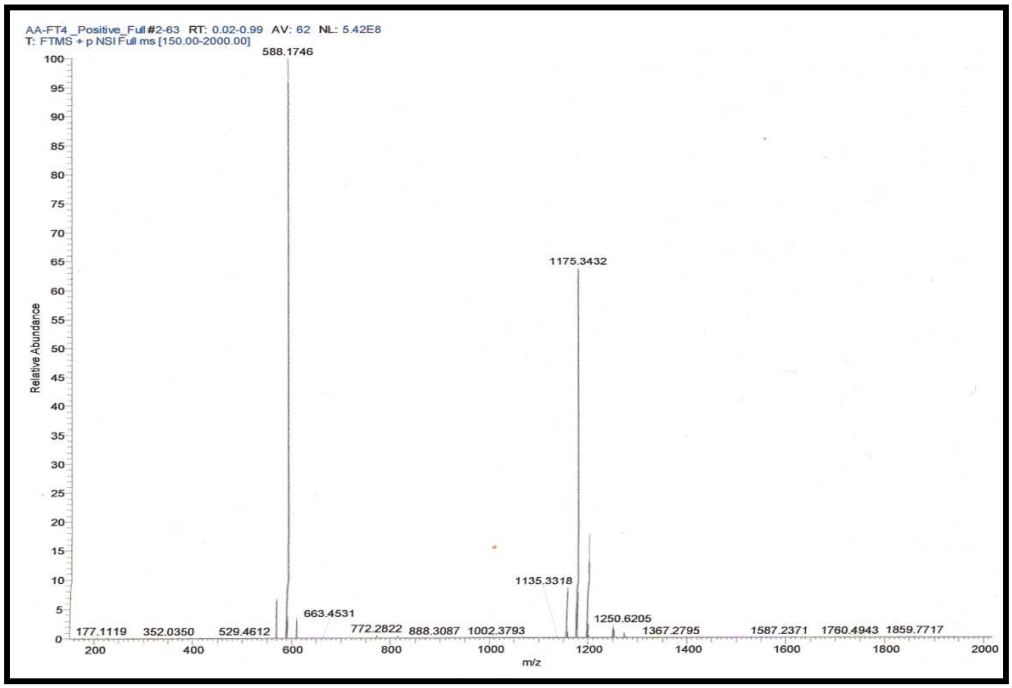
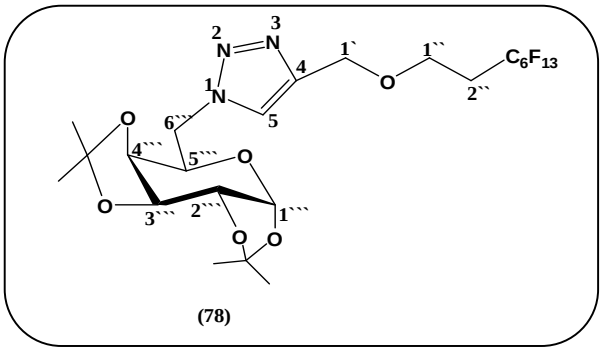


Fig. (3-60) HR-MS spectrum of compound **(77)**

(3.1.11) 1-(6-galactosyl)-4-((2-(perfluorohexyl)ethoxy)methyl-1*H*-1,2,3-triazole 1,2:3,4-diacetonide (78)

Compound **(78)** synthesized by reacting 6-azido-6-deoxy-1:2,3:4-di-o-isopropylidene-α-D-galactose with perfluoroalkylethyl propargyl ether in presence click condition to produced compound **(78)** in good yield (77%) this reaction describe in scheme (3-11).



Scheme (3-12) Structure of compound **(78)**

FT-IR spectrum Fig. (3-60) of compound **(78)** showed the following bands at $\bar{\upsilon}$ (cm^{-1}) (Nujol): 2923 ($\upsilon_{C-H, CH3}$), 2853.96, 1456 (υ_{C-C}), 1376 (υ_{C-N}), 1144 (υ_{C-O}).

^{1}H NMR spectrum Fig. (3-61) of compound **(78)** showed signals at δ (ppm) ($CDCl_3$): 1.28, 1.36, 1.37, 1.49 (s, 12H, $4CH_{3isopropylidene}$), 2.41 (tt, *J* 18.8, 6.8 Hz, 2H, H2``), 3.79 (t, *J* 6.7 Hz, 2H, H1``), 4.17 (dd, *J* 7.7, 1.9 Hz, 1H, H5```), 4.19 (dd, *J* 7.7, 1.9 Hz, 1H, H4```), 4.33 (dd, *J* 5.0, 2.5 Hz, 1H, H2```), 4.49 (m, 2H, H6```), 4.64 (dd, *J* 7.8, 2.6 Hz, 1H, H3```), 4.67 (s, 2H, H1`), 5.51 (d, *J* 4.9 Hz, 1H, H1```), 7.73 (s, 1H, H5).

^{13}C NMR spectrum Fig. (3-62) of compound **(78)** gives showed signals at δ (ppm) ($CDCl_3$): 24.2, 24.6, 25.7, 25.8 (4C, $CH_{3\ isopropylidene}$), 31.3(C2``), 50.6 (C6```), 64.2 (C1`), 67.0 (C5```), 70.1 (C2```), 70.6 (C3```), 71.0 (C4```), 96.1 (C1```), 108.9, 109.8 (2C, $C_{\ isopropylidene}$), 124.0 (C5), 143.8 (C4). MS (ESI) *m/z*: 688 ($[M+H]^+$)

Table (3-11) summarized values of HSQC spectrum Fig. (3-63) and COSY spectrum Fig. (3-64) of compound **(78)**.

Table (3-11) Describe values of HSQC and COSY of compound (78)

1H NMR	COSY	13C NMR	HSQC
1.28, 1.36, 1.37, 1.49 (s, 12H, $4CH_{3isopropylidene}$)	1.28, 1.36, 1.37, 1.49	24.2, 24.6, 25.7, 25.8 (4C, $CH_{3\ isopropylidene}$)	1.28, 1.36, 1.37, 1.49
2.41 (tt, *J* 18.8, 6.8 Hz, 2H, H2``)	3.79	31.3(C2``)	2.41
3.79 (t, *J* 6.7 Hz, 2H, H1``)	2.41	50.6 (C6```)	4.49
4.17 (dd, *J* 7.7, 1.9 Hz, 1H, H5```)	4.19, 4.49	64.2 (C1`)	4.67
4.19 (dd, *J* 7.7, 1.9 Hz, 1H, H4```)	4.17, 4.64	67.0 (C5```)	4.17
4.33 (dd, *J* 5.0, 2.5 Hz, 1H, H2```)	5.51	70.1 (C2```)	4.33

4.49 (m, 2H, H6```)	4.17	70.6 (C3```)	4.64
4.64 (dd, *J* 7.8, 2.6 Hz, 1H, H3```)	4.19	71.0 (C4```)	4.19
4.67 (s, 2H, H1`)	-	96.1 (C1```)	5.51
5.51 (d, *J* 4.9 Hz, 1H, H1```)	4.33	108.9, 109.8 (2C, C isopropylidene)	-
7.73 (s, 1H, H5).	-	124.0 (C5)	7.73
-	-	143.8 (C4)	-

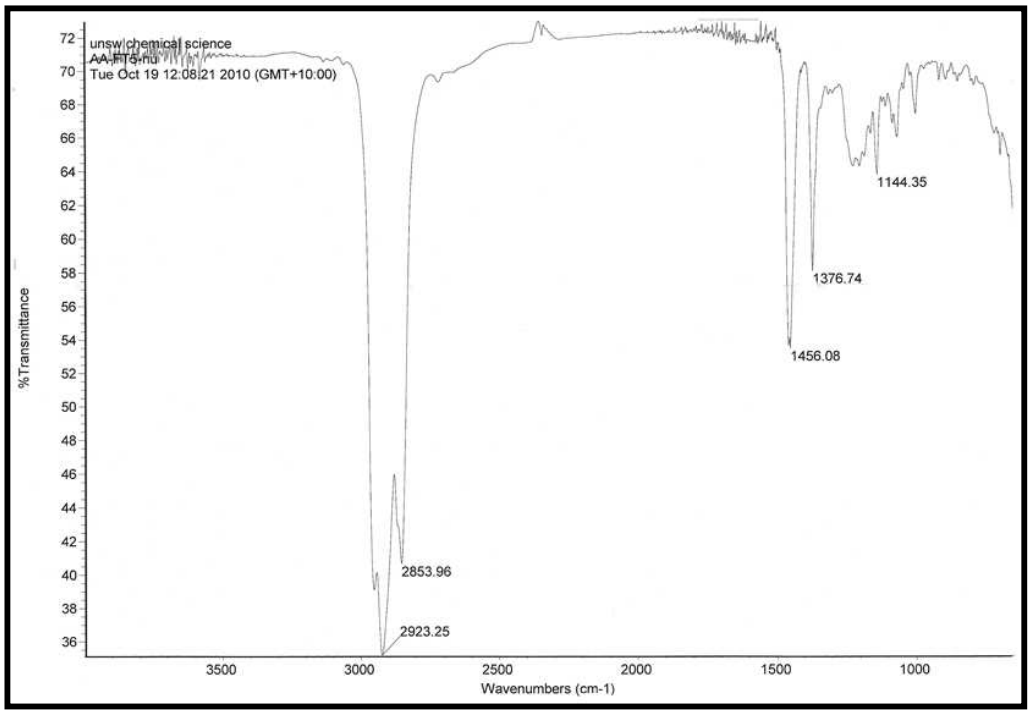


Fig. (3-61) FT-IR spectrum of compound **(78)**

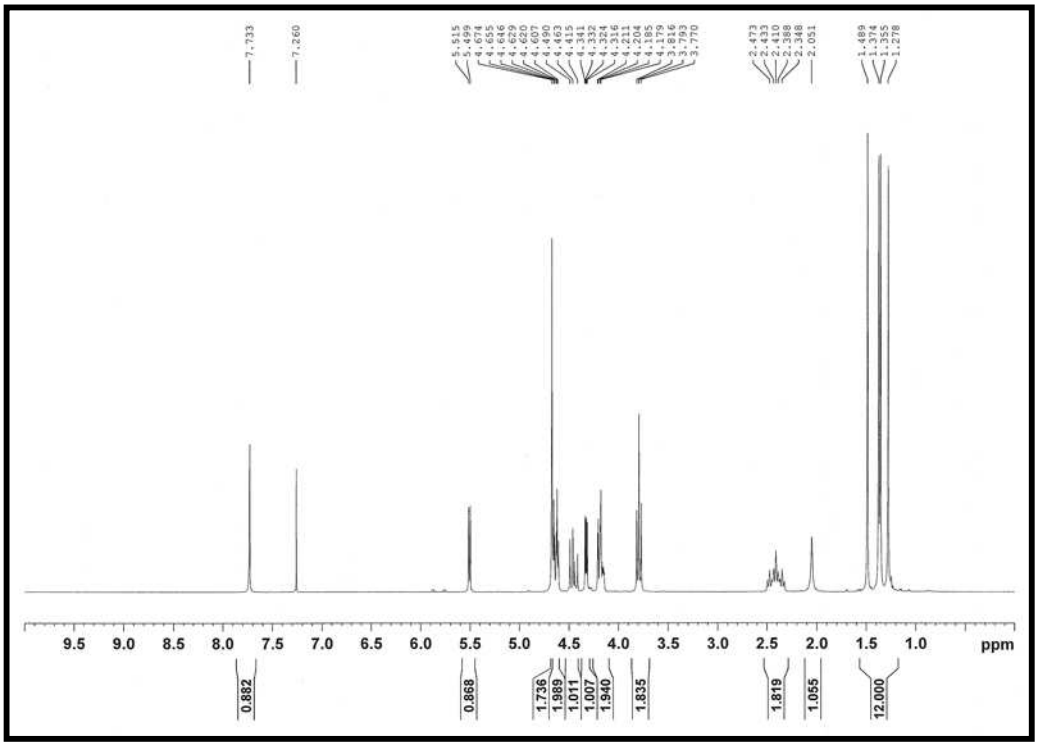


Fig. (3-62) ^{1}H NMR spectrum of compound **(78)**

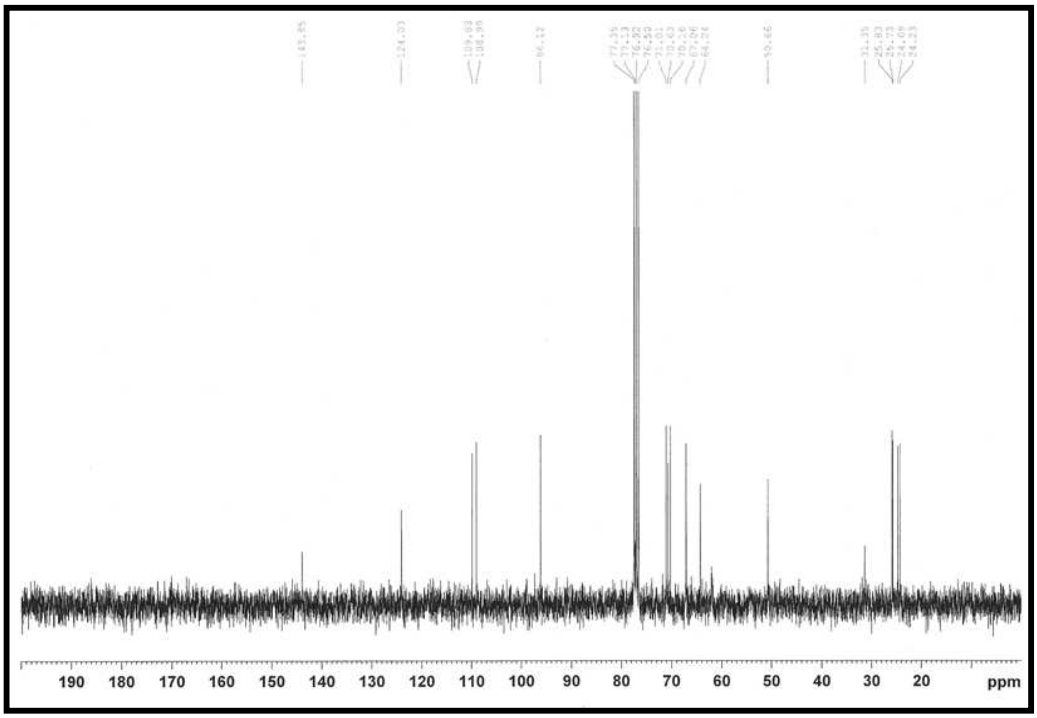


Fig. (3-63) ^{13}C NMR spectrum of compound **(78)**

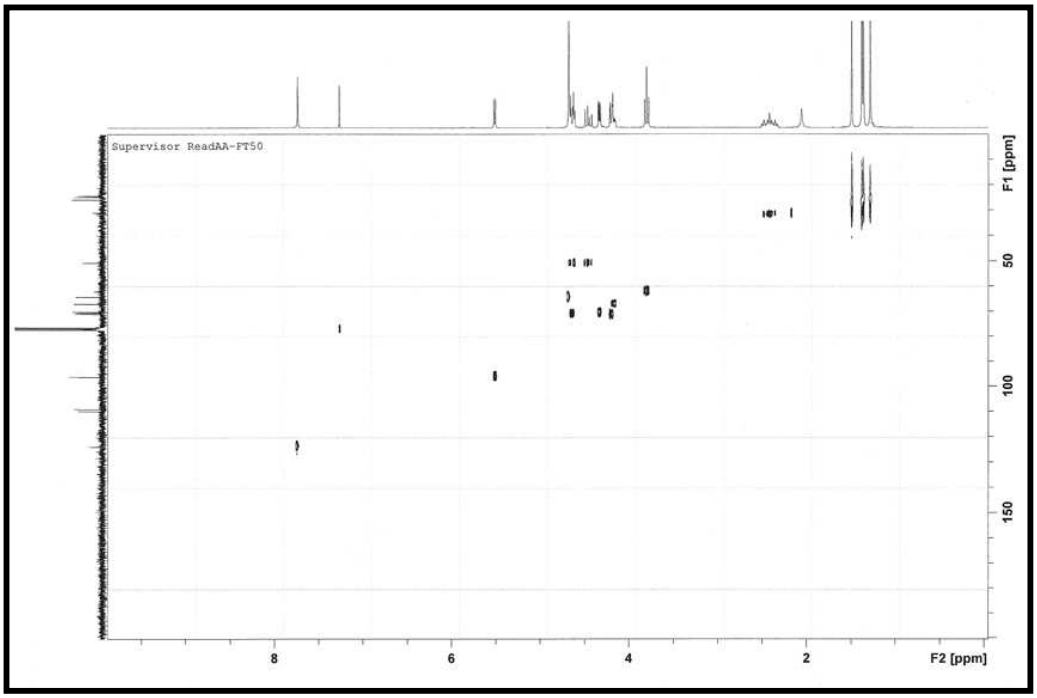


Fig. (3-64) HSQC spectrum of compound **(78)**

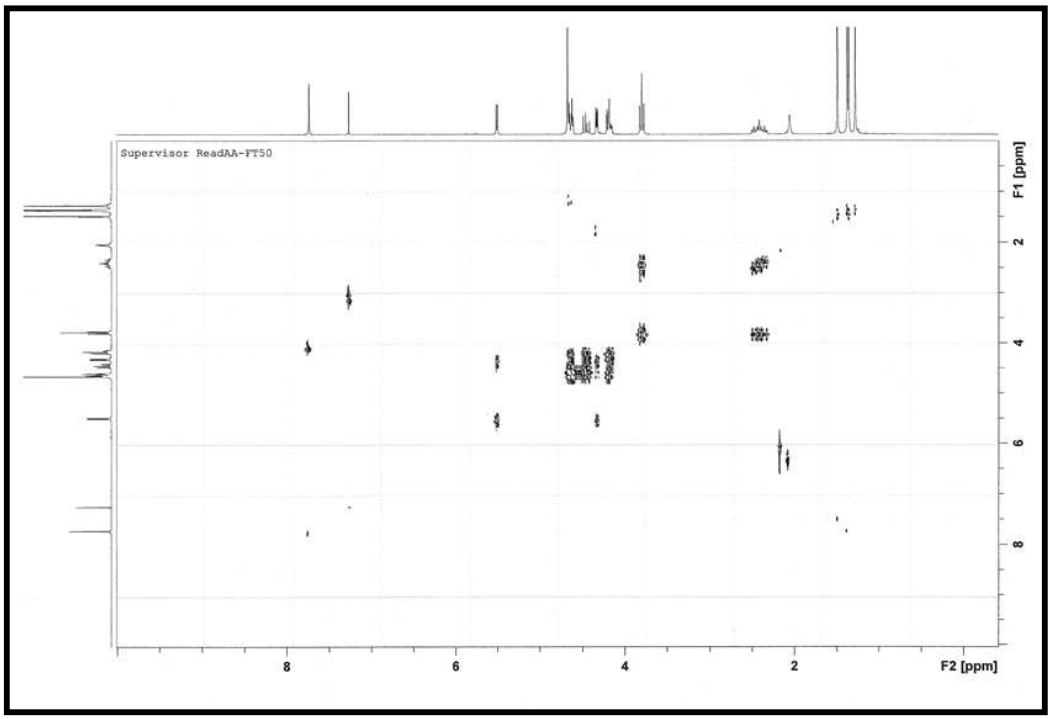


Fig. (3-65) COSY spectrum of compound **(78)**

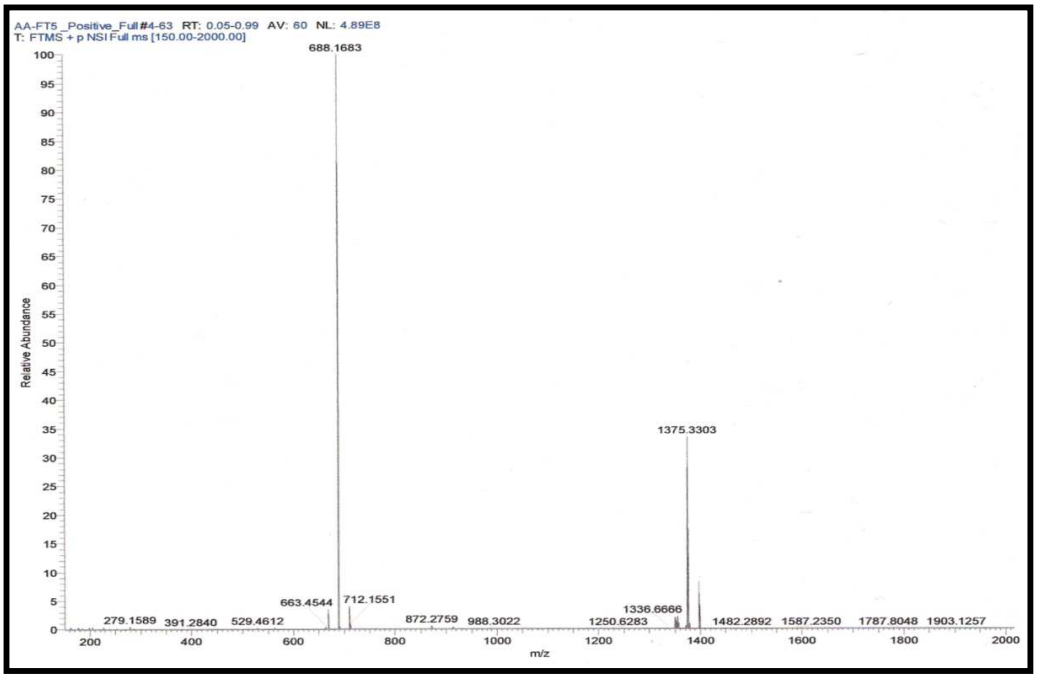
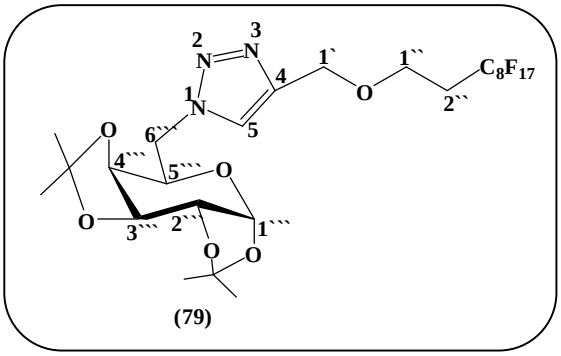


Fig. (3-66) HR-MS spectrum of compound **(78)**

(3.1.12) 1-(6-galactosyl)-4-((2-(perfluorooctyl)ethoxy)methyl-1*H*-1,2,3-triazole 1,2:3,4-diacetonide (79)

Compound **(79)** synthesized with long perfluoro chain longer than compound **(77)** and **(78)** with ether as a spacer.

Compound **(79)** synthesized *via* click reaction in good yield (75%) show in scheme (3-12).



Scheme (3-13) Structure of compound (79)

FT-IR spectrum Fig. (3-66) of compound **(79)** showed bands at $\bar{\upsilon}$ (cm^{-1}) (Nujol): 2922 ($\upsilon_{C-H, CH3}$), 1456 (υ_{C-C}), 1376 (υ_{C-N}), 1200.80, 1149 (υ_{C-O}).

^{1}H NMR spectrum Fig. (3-67) of compound **(79)** showed signals at δ (ppm) ($CDCl_3$): 1.28, 1.35, 1.38, 1.48 (s, 12H, $4CH_{3isopropylidene}$), 2.44 (tt, *J* 18.7, 6.7Hz, 2H, H2``), 3.81 (t, *J* 6.7 Hz, 2H, H1``), 4.17 (dd, *J* 8.5, 1.8 Hz, 1H, H5```), 4.21 (dd, *J* 7.8, 1.8 Hz, 1H, H4```), 4.33 (dd, *J* 5.0, 2.6 Hz, 1H, H2```), 4.52 (m, 2H, H6```), 4.65 (dd, *J* 7.8, 2.6 Hz, 1H, H3```), 4.72 (s, 2H, H1`), 5.51 (d, *J* 5.0 Hz, 1H, H1```), 7.78 (s, 1H, H5).

^{13}C NMR spectrum Fig. (3-68) of compound **(79)** showed signals at ($CDCl_3$) δ (ppm): 24.3, 24.7, 25.8, 25.9 (4C, $CH_{3\ isopropylidene}$), 31.3(C2``), 51.1 (C6```), 64.0 (C1`), 67.0 (C5```), 70.2 (C2```), 70.7 (C3```), 71.0 (C4```), 96.2 (C1```), 109.1, 109.9 (2C, $C_{isopropylidene}$), 124.1 (C5), 143.8 (C4). MS (ESI) *m/z*: 788 ($[M+H]^+$)

Table (3-12) summarized values of HSQC spectrum Fig. (3-69) and COSY spectrum Fig. (3-70) of compound **(79)**.

Table (3-12) Describe values of HSQC and COSY of compound (79)

1H NMR	COSY	13C NMR	HSQC
1.28, 1.35, 1.38, 1.48 (s, 12H, $4CH_{3isopropylidene}$)	1.28, 1.35, 1.38, 1.48	24.3, 24.7, 25.8, 25.9 (4C, $CH_{3\ isopropylidene}$)	1.28, 1.35, 1.38, 1.48
2.44 (tt, *J* 18.7, 6.7Hz, 2H, H2``)	3.81	31.3(C2``)	2.44
3.81 (t, *J* 6.7 Hz, 2H, H1``)	2.44	51.1 (C6```)	4.52
4.17 (dd, *J* 8.5, 1.8 Hz, 1H, H5```)	4.21, 4.52	64.0 (C1`)	4.72
4.21 (dd, *J* 7.8, 1.8 Hz, 1H, H4```)	4.17, 4.65	67.0 (C5```)	4.17
4.33 (dd, *J* 5.0, 2.6 Hz, 1H, H2```)	5.51	70.2 (C2```)	4.33
4.52 (m, 2H, H6```)	4.17	70.7 (C3```)	4.65
4.65 (dd, *J* 7.8, 2.6	4.33, 4.21	71.0 (C4```)	4.21

Hz, 1H, H3```)			
4.72 (s, 2H, H1`)	-	96.2 (C1```)	5.51
5.51 (d, *J* 5.0 Hz, 1H, H1```)	4.33	109.1, 109.9 (2C, C isopropylidene)	-
7.78 (s, 1H, H5)	-	124.1 (C5)	7.78
-	-	143.8 (C4)	-

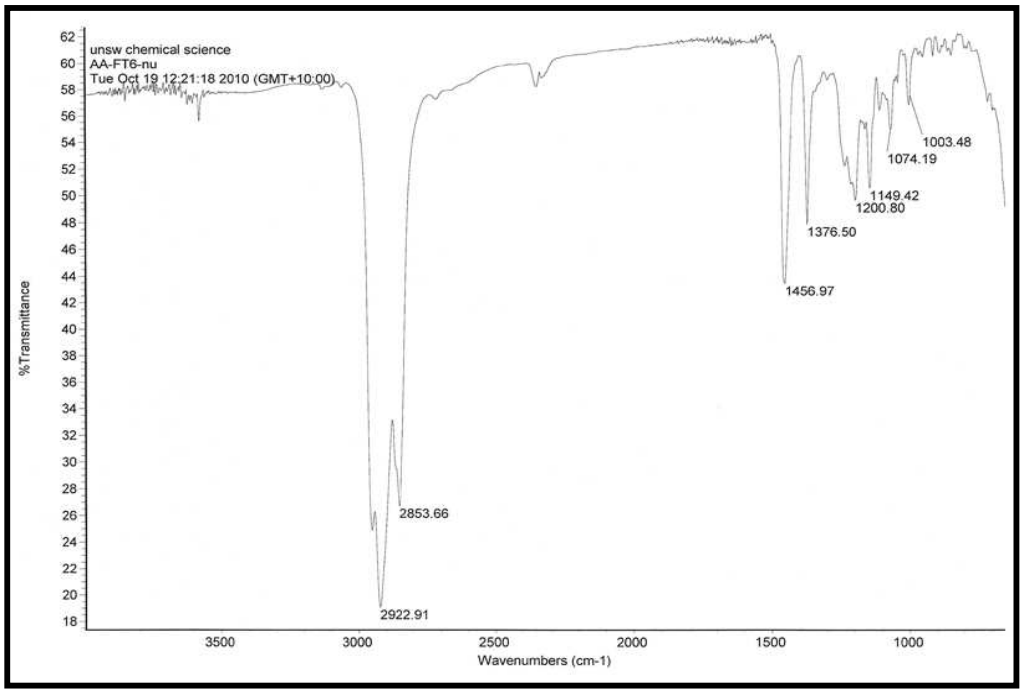


Fig. (3-67) FT-IR spectrum of compound **(79)**

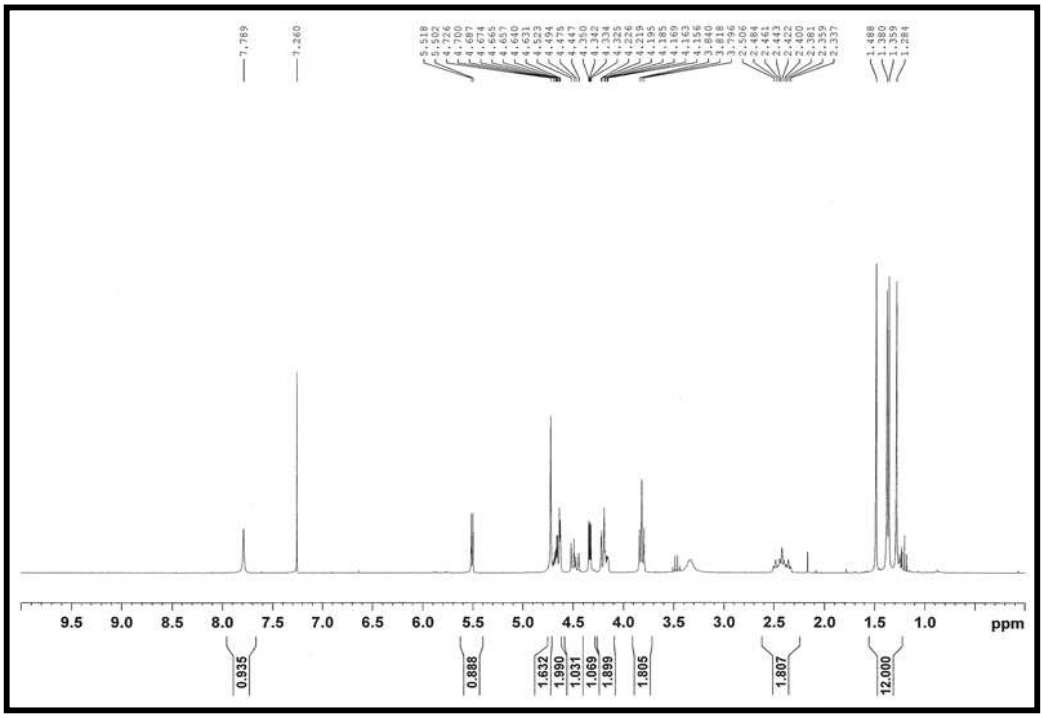


Fig. (3-68) ^{1}H NMR spectrum of compound **(79)**

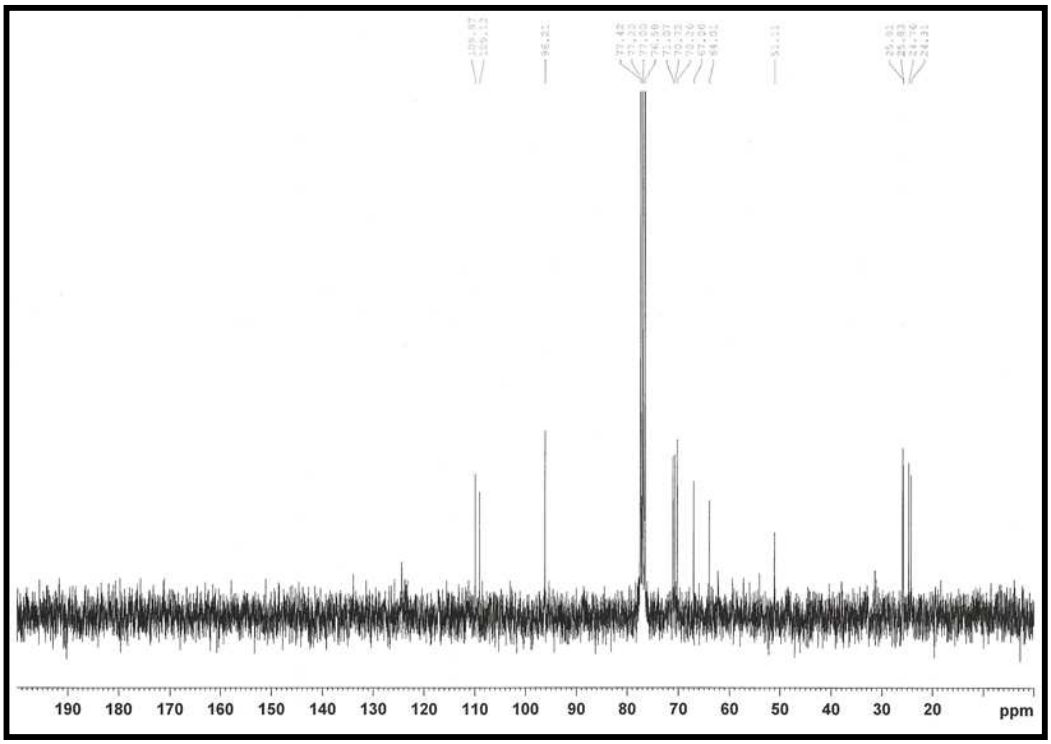


Fig. (3-69) ^{13}C NMR spectrum of compound **(79)**

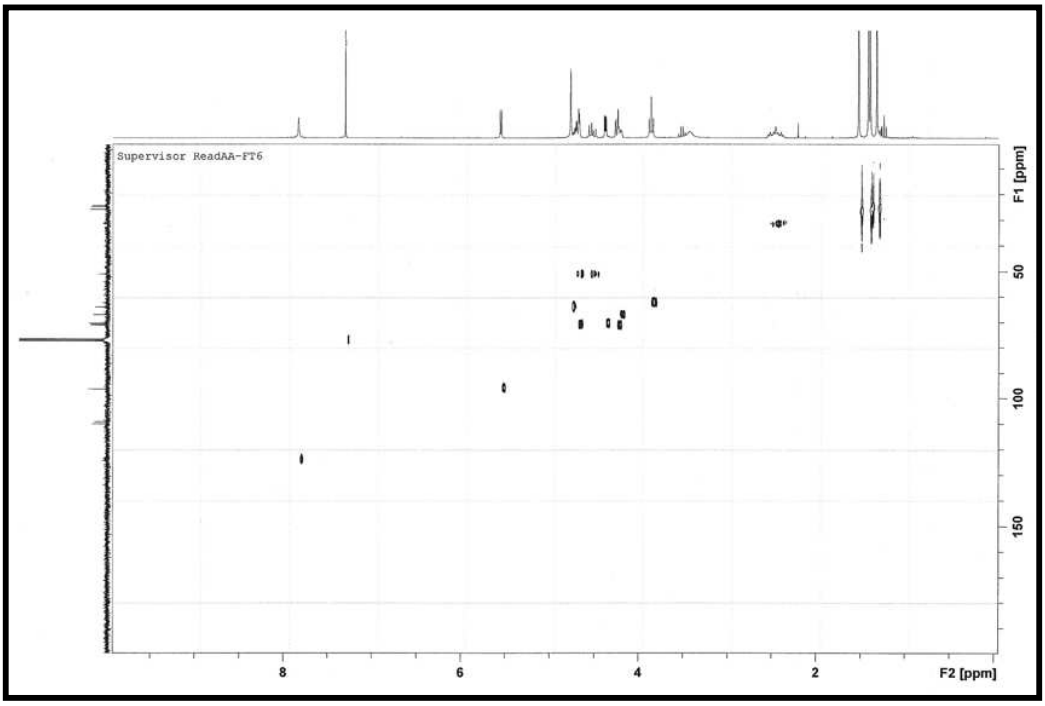


Fig. (3-70) HSQC spectrum of compound **(79)**

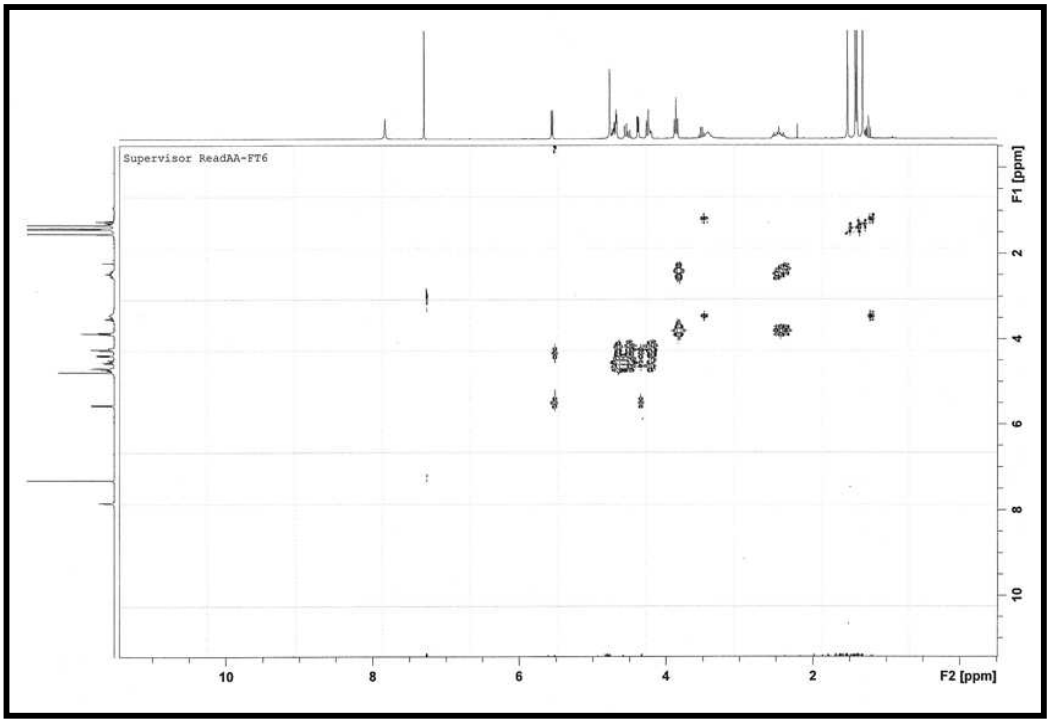


Fig. (3-71) COSY spectrum of compound **(79)**

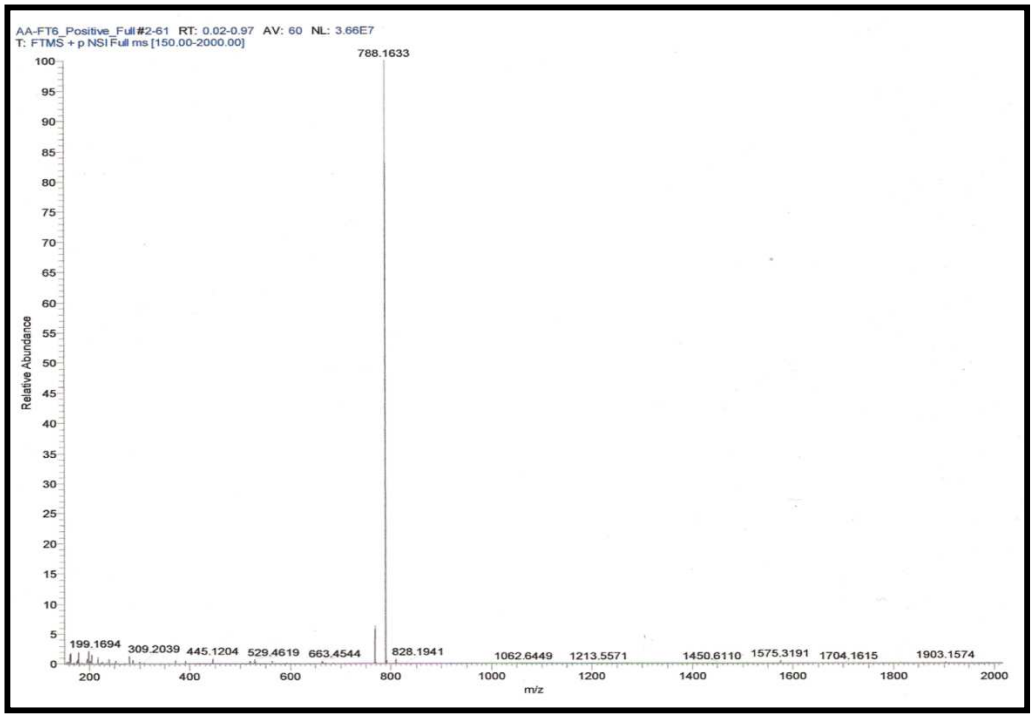


Fig. (3-72) HR-MS spectrum of compound **(79)**

Microelemental analysis Table (3-13) showed closely values of compounds (74-79).

Table (3-13) Values of Microelemental analysis

Compound	Formula	Calculated			found		
		%C	%H	%N	%C	%H	%N
74	$C_{21}H_{26}F_9N_3O_6$	42.94	4.46	7.15	43.17	4.34	6.92
75	$C_{23}H_{26}F_{13}N_3O_6$	40.18	3.81	6.11	40.21	3.50	5.92
76	$C_{25}H_{26}F_{17}N_3O_6$	38.13	3.33	5.34	38.29	3.08	5.12
77	$C_{21}H_{26}F_9N_3O_6$	42.94	4.46	7.15	43.19	4.45	7.30
78	$C_{23}H_{26}F_{13}N_3O_6$	40.18	3.81	6.11	40.62	3.62	6.24
79	$C_{25}H_{26}F_{17}N_3O_6$	38.13	3.33	5.34	38.44	3.29	5.34

Table (3-14) Percentage yield and melting point of compounds (74-79)

Compound No.	% Yield	m.p./^{o}C
74	73	92-94
75	76	97-99
76	78	112-114
77	79	95-97
7	77	106-108
79	75	121-123

(3.2) Thermodynamic Functions:

Phases, which are thermodynamically stable, have a finite number of degrees of freedom. Each phase is separated by a boundary where the phase change occurs. As one crosses the boundary, a new phase appears to the detriment of the other, and, since the overall free energy of the process is zero, the thermodynamic parameters such as ΔS, and ΔH must change in a quantitative manner at the border. Since different types of phase boundaries are encountered, different types of enthalpies are obtained, for example, entropy of fusion; enthalpy of transition, ΔH_t *;* etc. The discussion shows that a great deal information can be obtained from a DSC curve, and that the interpretation of such a curve can yield valuable insight into the nature of the material being investigated. It is important to be able to identify what type of phase transition is occurring in the substance by looking at the curve of DSC[(105)].

The enthalpy values of fusion for the pure compounds **(74-79)** are determined by the DSC method[(106)] and have been reported in Table (3-14)

Table (3-15) values of thermodynamic functions

Compound	ΔH (KJ.mol^{-1})	ΔS (KJ.mol^{-1}.K^{-1})	T (K)
74	27.050	0.072	375.5
75	32.421	0.087	371.5
76	38.911	0.100	386.8
77	27.309	0.073	369.4
78	35.547	0.093	380.4
79	41.873	0.105	395.5

Because there is a change in heat capacity, but there is no latent heat involved with the glass transition, we call the glass transition a *second order transition*. Transitions like melting and crystallization, which do have latent heats, are called *first order transitions*

(3.3) The Crystallinity

DSC can also tell us how much of a polymer is crystalline and how much is amorphous. If you read the page dealing with, compounds crystallinity many compounds contain both amorphous and crystalline material. DSC can tell us. If we know the latent heat of melting, ΔH_m.

The first thing we have to do is measure the area of that big peak we have for the melting of the compound **(74-79).** Now our plot is a plot of heat flow per gram of material, versus temperature. Heat flow is heat given off per second, so the area of

the peak is given is units of heat x temperature x time^{-1} x mass^{-1}. We usually would put this in units such as joules x kelvins x (seconds)$^{-1}$ x (grams)$^{-1}$:

$$\text{area} = \frac{\text{heat} \times \text{temperature}}{\text{time} \times \text{mass}} = \frac{\text{J K}}{\text{s g}}$$

Don't worry. It gets simpler. We usually divide the area by the heating rate of our DSC experiment. The heating rate is in units of K/s. So the expression becomes simpler:

$$\frac{\text{area}}{\text{heating rate}} = \frac{\frac{\text{J K}}{\text{s g}}}{\frac{\text{K}}{\text{s}}} = \frac{\text{J}}{\text{g}}$$

Now we have a number of joules per gram. But because we know the mass of the sample, we can make it simpler. We just multiply this by the mass of the sample:

$$\left(\frac{\text{J}}{\text{g}}\right) \times \text{g} = \text{J}$$

Now we just calculated the total heat given off when the polymer melted. Neat, huh? Now if we do the same calculation for our dip that we got on the DSC plot for the crystallization of the polymer, we can get the total heat absorbed during the crystallization. We'll call the heat *total* heat given off during melting $H_{\text{m, total}}$, and we'll call the heat of the crystallization $H_{\text{c, total}}$.

Now we're going to subtract the two:

$$H_{\text{m, total}} - H_{\text{c, total}} = H'$$

Why did we just do that? And what does that number *H*' mean? *H*' is the heat given off by that part of the polymer sample which was already in the crystalline state

before we heated the polymer above the T_c. We want to know how much of the polymer was crystalline before we induced more of it to become crystalline. That's why we subtract the heat given off at crystallization. Is everyone following me?

Now with our magic number *H*' we can figure up the percent crystallinity. We're going to divide it by the specific heat of melting, H_c^*. The specific heat of melting? That's the amount of heat given off by a certain amount, usually one gram, of a polymer. *H*' is in joules, and the specific heat of melting is usually given in joules per gram, so we're going to get an answer in grams, which we'll call m_c.

$$\frac{H'}{H^*_m} = m_c \qquad \frac{\frac{J}{J}}{\frac{g}{g}} = g$$

This is the total amount of grams of polymer that were crystalline below the T_c. Now if we divide this number by the weight of our sample, m_{total}, we get the fraction of the sample that was crystalline, and then of course, the percent crystallinity:

$$\frac{m_c}{m_{total}} = \text{crystalline fraction}$$

$$\text{crystalline fraction} \times 100 = \text{\% crystallinity}$$

Table (3-15) showed the percentage of crystalline phase for the compounds (76-79) while crystalline phase was disappearance for the compounds (74 and 75), this phenomena caused by the arrangement of perfluoro chain whereas absorb or lose the heat[107].

Table (3-16) values of the crystallinity percentage

Compound No.	Crystallinity %
74	-
٧٥	-
٧٦	٧٠,٣
٧٧	٧١,٢
٧٨	٧٢,٥
٧٩	٨٣,٧

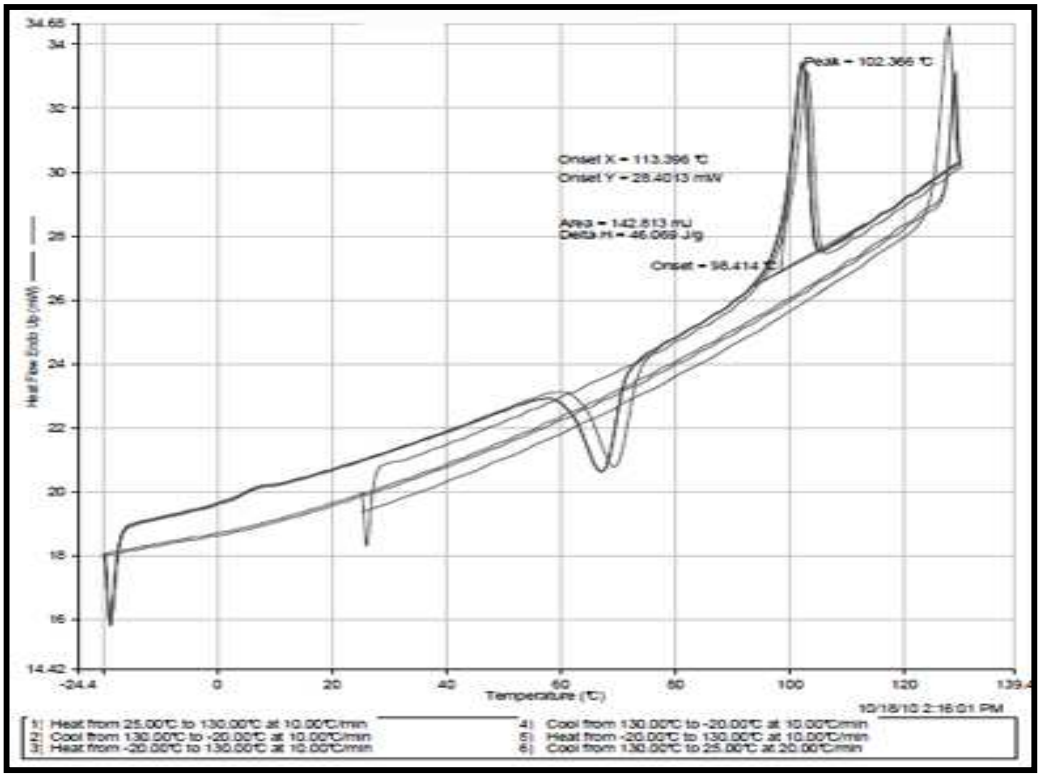


Fig. (3-73) DSC chart of compound (74)

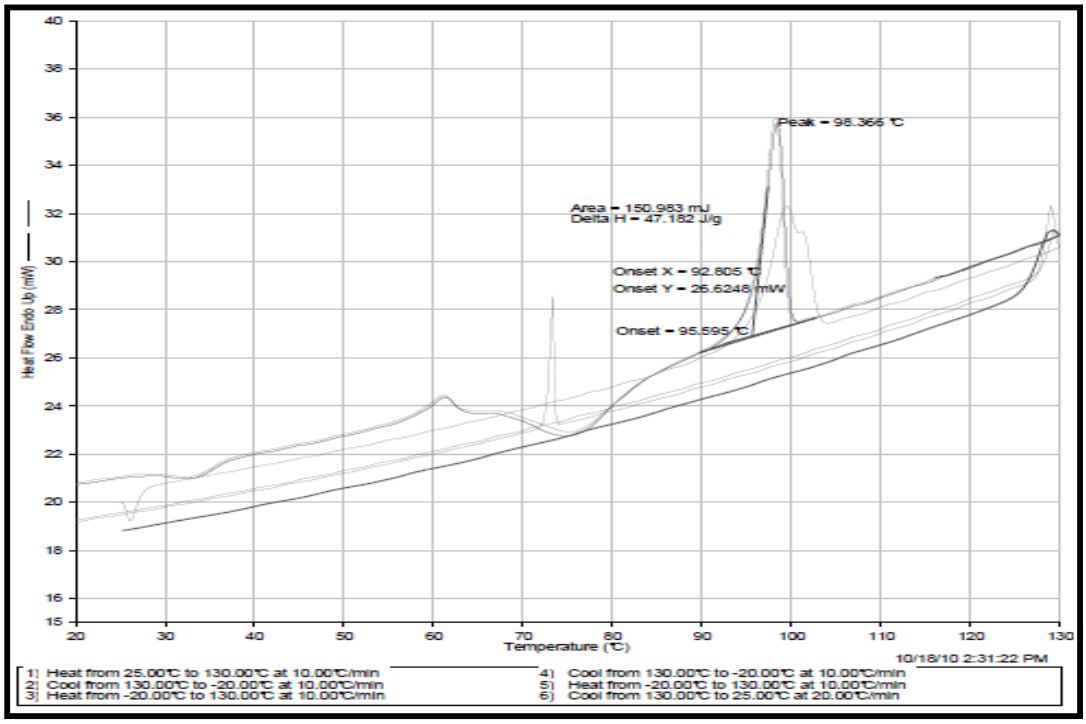


Fig. (3-74) DSC chart of compound (75)

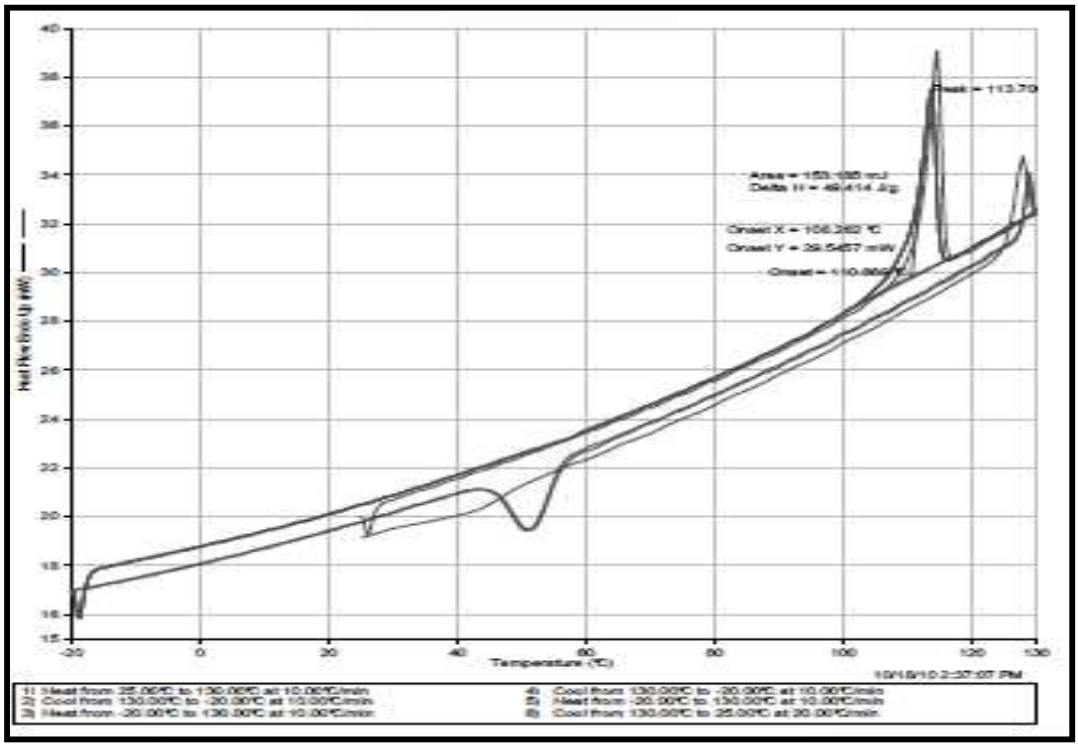


Fig. (3-75) DSC chart of compound (76)

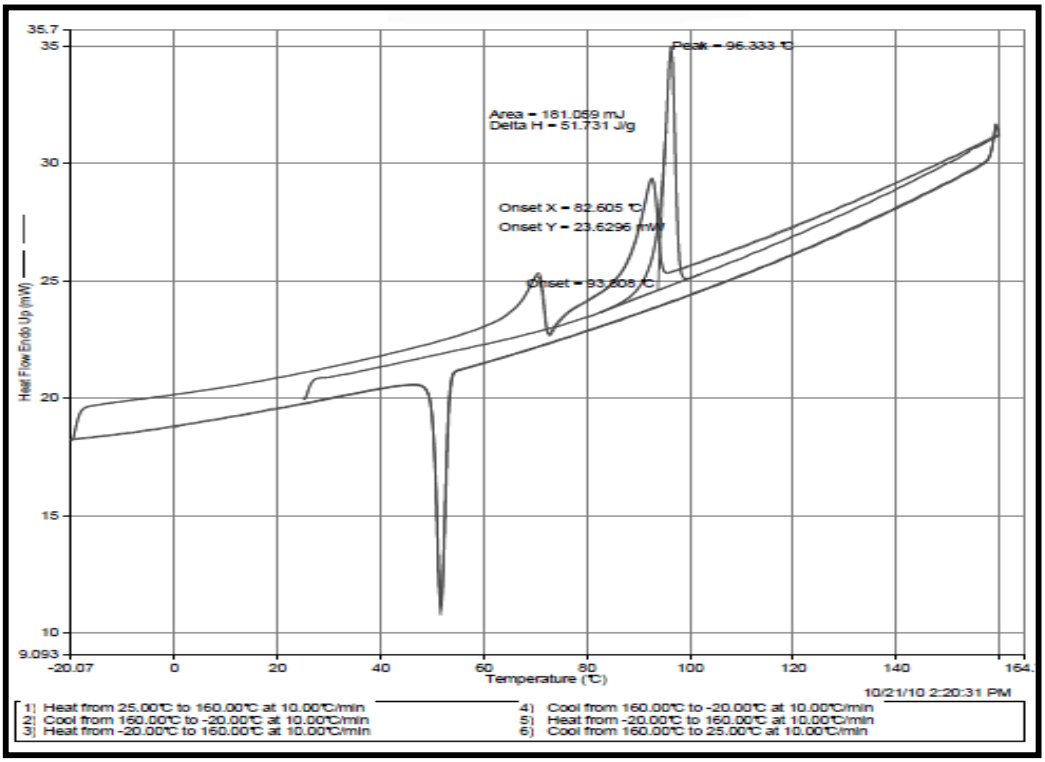


Fig. (3-76) DSC chart of compound (77)

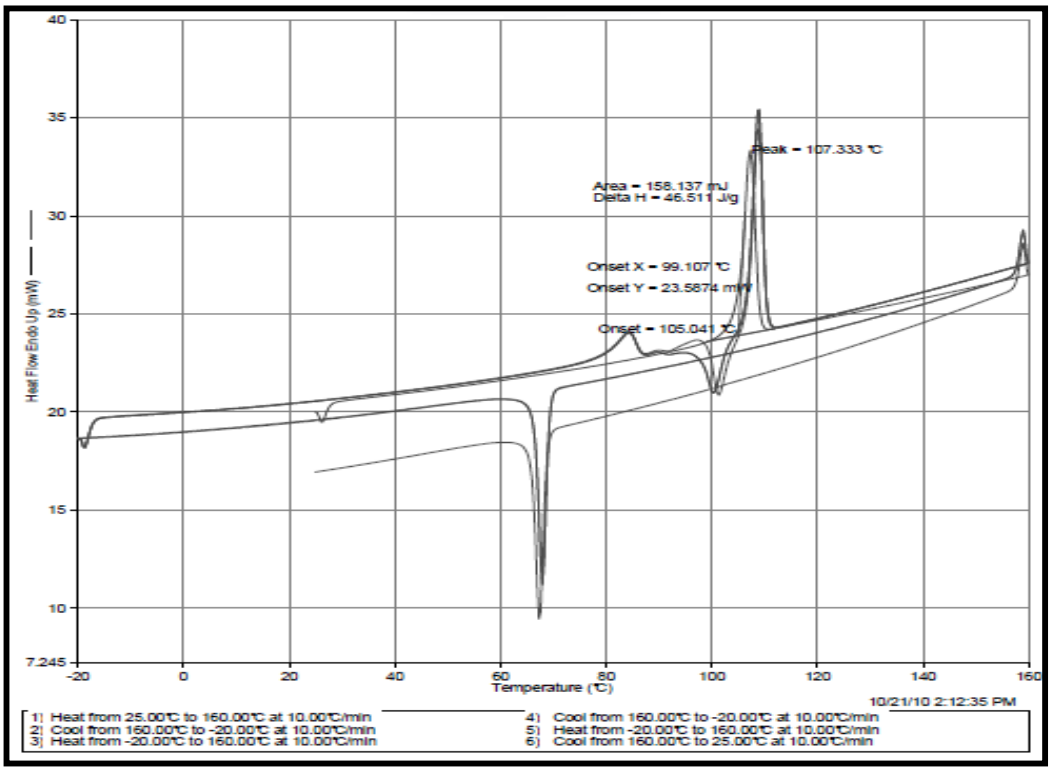


Fig. (3-77) DSC chart of compound (78)

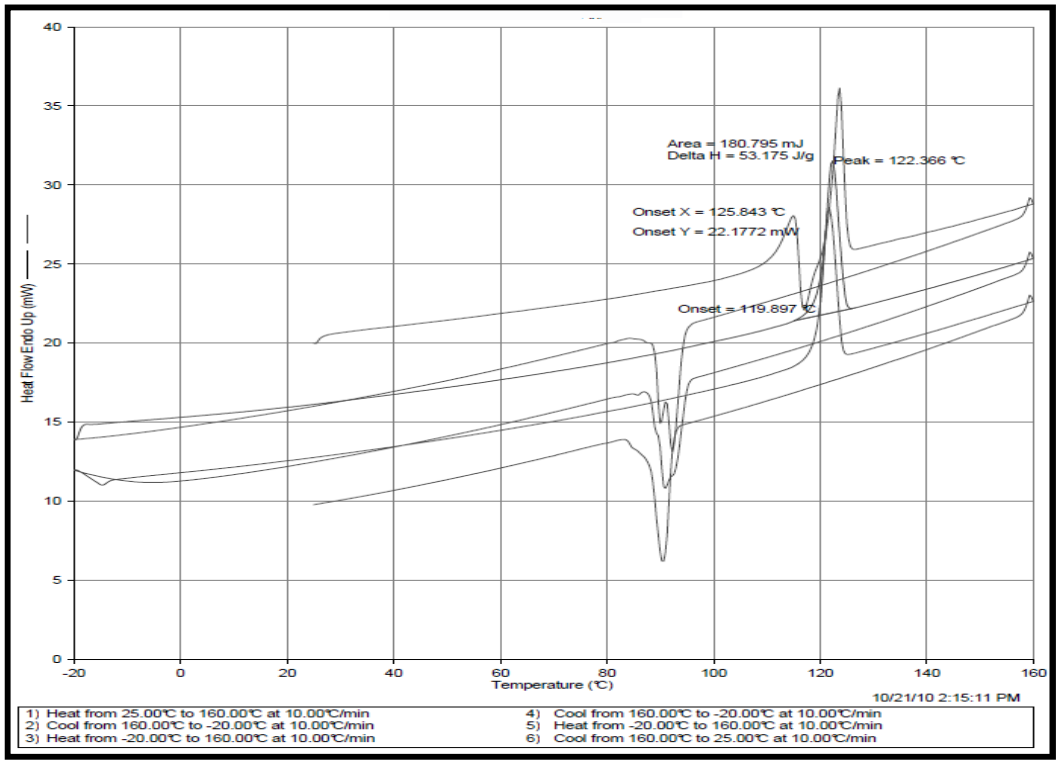


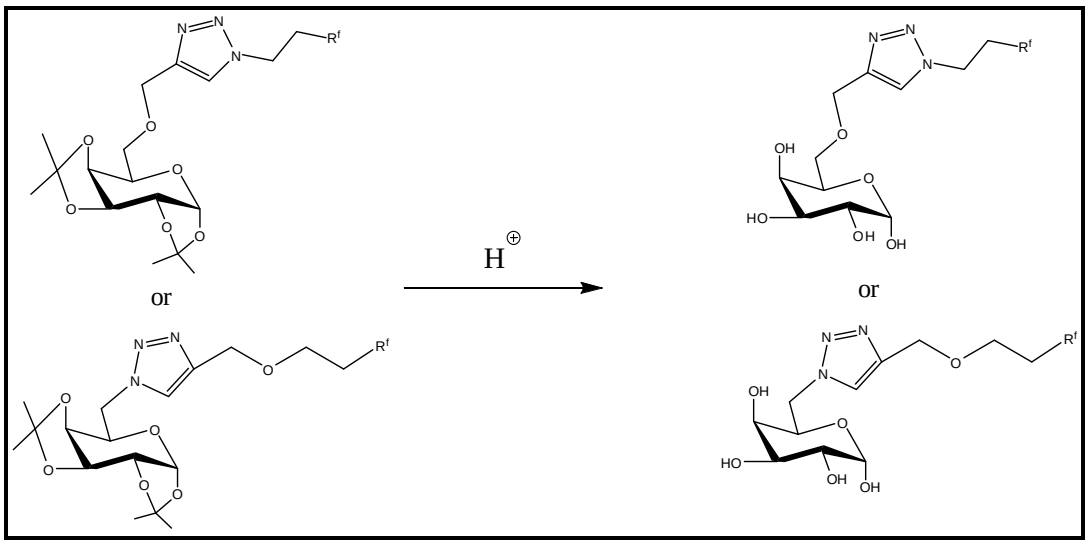
Fig. (3-78) DSC chart of compound (79)

Conclusions

Sugars 1,2,3-triazoles was synthesized by using copper (I) catalyzed alkyne-azide cycloaddition 'Click Chemistry' from galactose derivatives containing either sugar-propargyl alkyne group or sugar-azide group, these compounds containing triazole segment was synthesized in good yield. In general, the increase length of perfluoro chain leading to increasing the enthalpy values corresponding with increase melting temperature, this phenomena caused by presence the rigidity of perfluoro chain.

Prospective studies:

1. Deprotection of synthesized compounds.



2. Study the thermodynamic functions for the deprotection compounds and comparing with protected compounds.
3. Study surface activity of the perfluorotriazole derivatives.
4. Click chemistry it is important to synthesis of heterocycle ring and coupling terminal alkyne with azide producing only one product, so can be used to synthesis another sugar derivatives.
5. Study the biological activity for the perfluorotriazole derivatives.

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جمهورية العراق
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قسم الكيمياء

تحضير بيرفلورو اثيل ترايازولات جديدة مشتقة من سكر D. كالكتوز باستخدام كيمياء النَقرّة ودراسة بعض دوالها الثيرموديناميكية

رسالة مقدمة إلى
مجلس كلية العلوم-جامعة كربلاء
كجزء من متطلبات نيل درجة الماجستير في الكيمياء

من قبل
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1432 هـ　　2011 م

الخلاصة

تضمنت هذه الدراسة تحضير مجموعة من بيرفلورو ترايزولات جديدة مبتدأ من سكر D.كالكتوز.

المركب (٦٦) الذي حُضر من سكر D.كالكتوز, الاسيتون وحامض الكبريتيك المركز بوجود كلوريد الخارصين. وبعد ذلك انقسم العمل الى خطوتين رئيسيتين:

القسم الاول: تضمن طريقة وليامسون لتحضير الايثرات من المركب (٦٦) مع بروميد بروبيرجايل في وسط قاعدي اعطى مشتق الالكاين الطرفي(67) .

بينما تضمن القسم الثاني استرة المركب (٦٦) من خلال معاملتهِ مع كبريتيد ثلاثي فلوريد الميثان اللامائي في وسط من البريدين الجاف منتجاً المركب (٦٨) الحامل لمجموعة مغادرة جيدة. عومل المركب (٦٨) مع ازيد الصوديوم اعطى المركب (٦٩) مع حصيلة منتوج جيدة.

استخدم المركبان (٦٧) و (٦٩) لتحضير بيرفلوروترايزولات بوجود Cu(I) كعامل مساعد: ان تفاعل المشتق (٦٧) مع سلاسل بيرفلورو مختلفة الاطوال الحاوية على مجاميع فعالة من الازايد, والتي حُضرت من معاملة بيرفلورو يوديد الاثيل perfluoroethyl iodide مع ازيد الصوديوم في مذيب DMSO معطياً المركبات (٣٥, ٤١ و٧٠), منتجاً المركبات (٧٤-٧٦).

بينما تفاعل المركب (٦٩) مع ايثرات بيرفلورو بروبيرجايل perfluoroethyl propargyl ethers (٧١-٧٣) باستخدام نفس ظروف التفاعل وتحفيز بواسطة Cu(I) منتجا المركبات (٧٧-٧٩).

تم تشخيص المركبات المحضرة بالطرق الطيفية باستخدام تقنيات مطيافية الأشعة تحت الحمراء والرنين النووي المغناطيسي للـ[^{1}H و ^{13}C], بينما المركبات النهائية (٧٤-٧٩) تم تشخيصها باستخدام [مطيافية الأشعة تحت الحمراء ومطيافية الكتلة والرنين النووي المغناطيسي للـ ^{1}H و ^{13}C و HSQC و COSY].

درست الدوال الثيرموديناميكية للمركبات **(٧٤-٧٩)** باستخدام جهاز المسح المسعري التفاضلي (DSC) حيث بينت الدراسة زيادة في قيمة الانثالبي بزيادة طول سلسلة الفلور الناتجة من صلابة سلسلة الفلور.