Ibrahim Ahmed Ibrahim Ali

Novel Trichloroacetimidates and their Reactions

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Novel Trichloroacetimidates and their Reactions

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First of all, I thank God for giving me the time and effort to accomplish this work

Contents

List of Abbreviations

Ac	Acetyl
AcOH	Acetic acid
Ac_2O	Acetic anhydride
All	Allyl
Bn	Benzyl
$BF_3.Et_2O$	Borontrifluoride-diethylether
CAN	Cerium(IV) ammonium nitrate
Cb	Cyclobutyl
Cpm	Cyclopropyl methyl
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DMF	*N,N*-Dimethylformamide
DPM	Diphenyl methyl
eq.	Equivalent
Et	Ethyl
Et_2O	Diethylether
FAB	Fast atom bombardment
Fl	9-Fluorenyl
Gal	Galactose
LG	Leaving group
MALDI	Matrix-assisted laser desorption
Man	Mannose
Me	Methyl
m.p.	Melting point
MeOH	Methanol
MS	Mass spectrometry
NEt_3	Triethylamine
NIS	*N*-Iodosuccinimide
NMR	Nuclear magnetic resonance
Nu	Nucleophile
Ph	Phenyl
Pim	Phthalimidomethyl
PM	4-Methoxyphenyl
ppm	Parts per million

Py	Pyridine
r.t.	Room temperature
THF	Tetrahydrofuran
TLC	Thin-layer chromatography
TMS	Trimethylsilyl
TMSOTf	Trimethylsilyl trifluoromethanesulfonate

1. Introduction and objectives

1.1 *O*-Glycoside bond formation

Glycoside synthesis is a very common reaction in nature providing a great variety of oligosaccharides and glycoconjugates as glycolipids, glycoproteins and glycopeptides. As recognized only recently, the structural diversity of the oligosaccharide portion, which is inherent in the variability in the glycoside bond formation, makes them ideal as carrier of biological information and specificity. For this fact, the field of the synthetic carbohydrate chemistry grew up exponentially in the last twenty years in order to synthesize oligosaccharides for specific purposes which include their use in antibody production, screening of antibodies, lectin and selectin specificity, interaction studies with virus[1,2] and bacterial receptors,[3-5] substrates for glycosidases [6,7] and glycosyltransferases[8] and probes in molecular recognition studies including conformational analysis. To date, it is the challenge for the synthetic chemist to build up glycosidic linkages with high regio- and stereocontrol similar to the naturally occurring ones. Two different approaches are generally used for the *O*-glycoside bond formation:

- Enzymatic *O*-glycoside bond formation
- Chemical *O*-glycoside bond formation

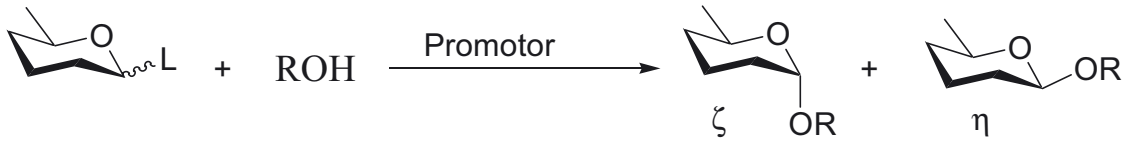
1.1.1 Enzymatic *O*-glycoside bond formation

The enzymatic *O*-glycosylation is generally based on specific glycosyl-transferases which use nucleoside diphosphate or, in some cases, nucleoside monophosphate sugars as glycosyl donors. The nucleoside di- or monophosphate residues are the leaving groups and sugars, or other aglycones are the glycosyl acceptors.[9] The driving force for the irreversible *O*-glycoside bond formation is the cleavage of the nucleoside of the di- or monophosphate residue from the activated sugar, while the glycosyltransferase provides the desired regio- and diastereoselectivity. The limited

availability of the glycosyltransferases, the complex generation of expensive glycosyl donors and the difficulty in carrying out the enzymatic reactions limit the use of this method for the synthesis of complex oligosaccharides. In most of the cases, the fragments of complex oligosaccharides are prepared through a total chemical synthesis and then used as efficient acceptors for specific enzymes (fucosyltransferase, sialyltransferase and galactosyltransferase).

1.1.2 Chemical *O*-glycoside bond formation

The chemical synthesis of oligosaccharides is based on the glycosylation reactions, coupling different building blocks with generating a glycosidic bond. As a general principle of most of the glycosylation methods a glycosyl donor is formed by combining a leaving group with the anomeric centre of one approperiately protected glycosyl building block. In the glycosylation reaction the activated glycosyl donor reacts with one hydroxy group of the completely or partially protected glycosyl acceptor (Scheme 1).



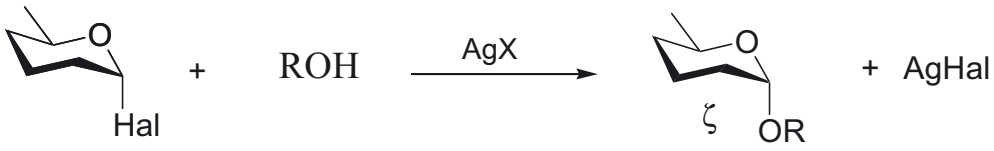
Scheme 1: Glycosylation reactions

When an ζ&η-mixture of the glycoside product is formed, the anomers must be separated by different techniques as chromatography, crystallization, distillation, etc…. Successful glycosylation reactions require high regio- and stereoselectivity preferably leading to only one pure anomer.

1.1.2.1 The Koenigs-Knorr method

The oldest glycosylation method was published by *Koenigs* and *Knorr* in 1901,[10] it was variously modified and it is still in use.[11] The glycosyl donors are usually

chlorides and bromides which are activated with various silver or mercury salts (Scheme 2). Advanced modifications make use of glycosyl fluorides as donor compounds.[12, 13]

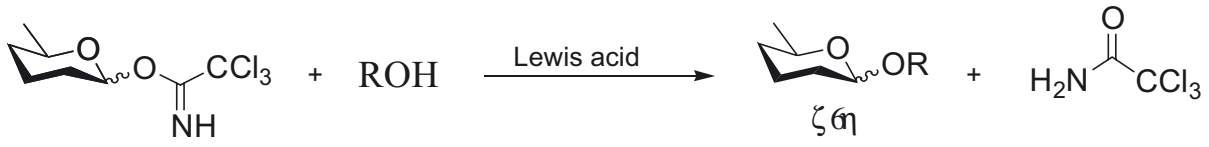


Scheme 2: Koenigs-Knorr glycosylation method

In order to favour a stereocontrolled S_N2-type reaction, solvents of low polarity (dichloromethane, cyclohexane and petroleum ether) and low temperatures are commonly used. The application of this method led to excellent results, for example the synthesis of numerous oligosaccharides including the blood group A-, B-, and Le^a-determinants.[14] However, the main disadvantages of the Koenigs-Knorr method are the need of at least stoichiometric amounts of the promoters and the thermal instability of many glycosyl halides.

1.1.2.2 The trichloroacetimidate method

A universal glycosylation method which avoids the use of heavy metal salts as promoters was developed by *R. R. Schmidt* and *J. Michel*[15] in 1980. *O*-Glycosyl trichloroacetimidates were introduced as a new type of glycosyl donors. It is easily prepared, sufficiently stable and it can be activated for the glycosylation reactions with catalytic amounts of Lewis acids such as TMSOTf, $BF_3.Et_2O$, $Sn(OTf)_2$, AgOTf and $ZnCl_2.Et_2O$[16,17] (Scheme 3).



Scheme 3: The trichloroacetimidate glycosylation method

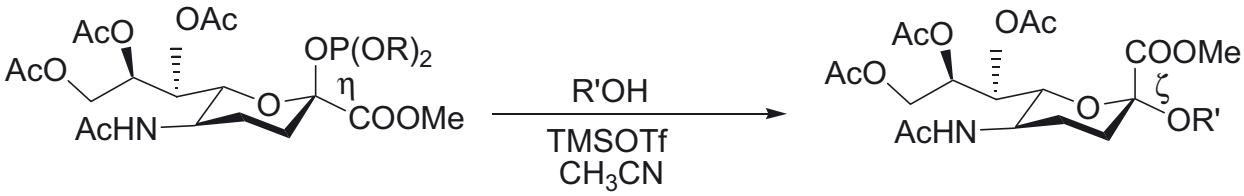
The anomeric configuration /ζ#or#η) of the trichloroacetimidate donors is crucial for the anomeric sterocontrol of the glycosidic bond formation. η-Trichloroacetimidates can be selectively prepared with K_2CO_3 as base[18] (kinetic control), whereas the use of NaH, $CsCO_3$ or KOH[19] with phase transfer catalyst[97] exclusively gives the ζ-trichloroacetimidates (thermodynamic control).

1.1.2.3 Anomeric stereocontrol in *O*-glycoside bond formation

The main advantages of the trichloroacetimidate method include the various possibilities for stereocontrol in the *O*-glycoside bond formation. Excellent stereoconterol can be achieved by using trichloroacetimidates as donors bearing a participating neighbouring group at the 2-position (neighbouring group effect) as well as by performing the reaction in a suitable combination solvent/catalyst (ether and nitrile effect). The trichloroacetimidate glycosylation method will be explained later in detail.

1.1.2.4 The phosphite method

In 1992, R. R. Schmidt and co-workers[21-23] developed the phosphite method as supplementary procedure to the trichloroacetimidate. This method found their best applications in the activation of deoxysugars (KDO and Neu5Ac) and is universally used for the sialylation step in the synthesis of many neuraminic acid glycosides. Glycosyl phosphites are synthesized starting from the unprotected anomeric oxygen of sugars by reaction with phosphorochloridites or phosphoroamidites and Hünig's base. The η-glycosyl phosphites of neuraminic acid can be activated with catalytic amounts of TMSOTf (Scheme 5).

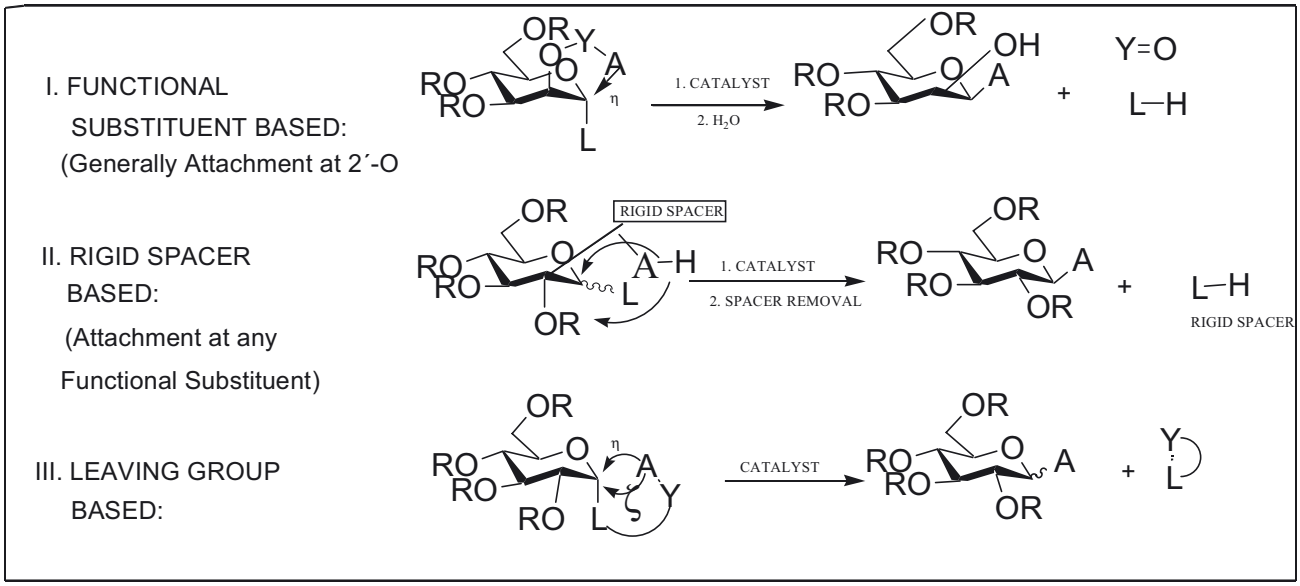


Scheme 5: Phosphite method

1.1.2.5 Intramolecular glycosylation method

An ideal approach which, in principle, could overcome the activation and stereochemical issues involves holding the component sugar donor and acceptor units in appropriate orientations within the same molecule in such a way that they can be forced to couple intramolecularly. Although this method is in its infancy, it appears that it will have high potential for the synthesis of specific sugar-sugar bonds of oligosaccharides. In general, the intramolecular methods are divided into three main classes (Scheme 6)

- Functional substituent based
- Rigid spacer based
- Leaving group based [24]



Scheme 6: Intramolecular glycoside bond formation[25]

The rigid spacer based approach was the most investigated one used for glycoside bond formation since 1992, when the first examples of the synthesis of ζ-glycosides[26] were reported. Later, the method was extended to the synthesis of η-glycosides,[27,28] ζ6η4rhamnosides[29] and η-mannosides.[30] Recently, *Schmidt and co-workers*[25] reported several successful examples of disaccharide formation prepared by an intramolecular rigid spacer based approach in which the *m*-xylylene residue is used as rigid spacer.[31] The thioglycoside donor and acceptor were attached to ζ3ζ-dibromoxylene by a nucleophilic substitution and then activated with NIS/TMSOTf under different reaction conditions. The stereoselectivity is controlled by the ring size (14-or 15-membered ring) and the configuration of the acceptor residue within the macrocyclic ring.

1.1.2.6 Other glycosylation methods

A lot of efforts has been made to improve the yields and the steroselectivity of the glycosylation reactions. In additional methods, glycals,[32] sugar epoxides,[33] thioglycosides, sulfoxides and 4-pentenyl glycosides[34] were used as donors. The anomeric *O*-alkylation method which was introduced by Schmidt et al.[35] forms the *O*-glycosidic bond in a different way; it is based on the base-catalyzed activation of the anomeric hydroxy group of the glycosyl donor. The anomeric *C*-*O* bond is not cleaved and the anomeric configuration is retained during the reaction course. This method has been extensively employed for unprotected, less reactive *O*-acetyl protected or more reactive benzyl protected sugars as donors in the presence of alkylating agents such as benzyl or allyl bromides, long-chain alkylating agents and sulfates.[36]

Although numerous methods have been employed for the chemical *O*-glycoside bond formation so far, the trichloroacetimidate method has found particularly wide application and it is now considered as the most efficient method for the *O*-glycoside bond formation in simple and complex oligosaccharide synthesis.

1.2. The trichloroacetimidate glycosylation methods

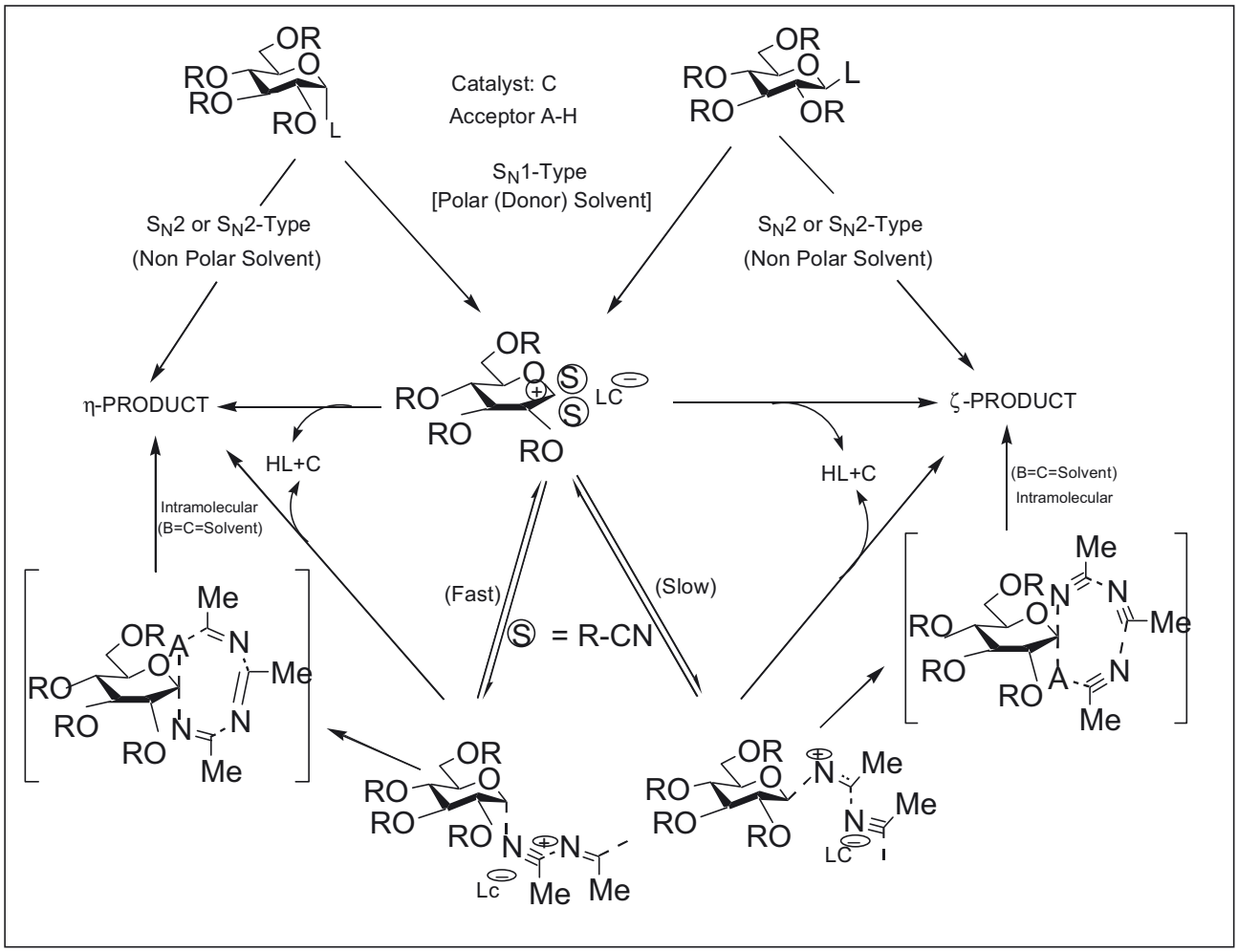
1.2.1. Trichloroacetimidate formation (activation step)

Electron-deficient nitriles are known to undergo direct and reversible base-catalyzed addition of alcohols to the triple-bond system, thereby providing *O*-alkyl imidates.[37,38] This imidate synthesis has the advantage that the free imidates can be directly isolated as stable adducts, which are less sensitive to hydrolysis than the corresponding salts. Therefore, base-catalyzed transformation of the anomeric oxygen atom into a good-leaving group should be possible, for instance, by addition to trichloroacetonitrile in the presence of base. Thus, with different bases (K_2CO_3, $CaCO_3$, NaH, DBU, or others) trichloroacetimidates can be isolated, often in pure form and in high yields.

Ether and nitrile effect[39,42]

The choice of the combination catalyst/solvent in the glycosylation reactions plays a crucial role for the anomeric stereocontrol. In general, if any paricipating protecting group is present in the second position of the trichloroacetimidate donor, the glycosylation reaction follows a S_N2-type pathway in non-polar solvents using weak Lewis acids as $BF_3.Et_2O$ at low temperature (Scheme 4).

The influence of the solvent under S_N1-type conditions is of particular interest and it was extensively studied for ethers and nitriles.[39,42] In diethyl ether, using stronger acid catalysts as TMSOTf, the S_N1-type reaction is favoured. The participation of the ethers, due to the reverse anomeric effect, results in the formation of equatorial oxonium ions which favour thermodynamically ζ-glycosides.



Scheme 4: Nitrile and ether effect in the glycosylation reaction

The influence of the nitriles is more complex. The highly reactive carbenium ion intermediate is attacked by nitriles preferentially on the (ζ)-face to give the kinetically controlled ζ-nitrilium-nitrile conjugate and, therefore, give the η4product. On the contrary, the thermodynamically more stable η-nitrilium-nitrile conjugate affords the ζ4product

1.2.2. Glycosylation reactions (glycosylation step)

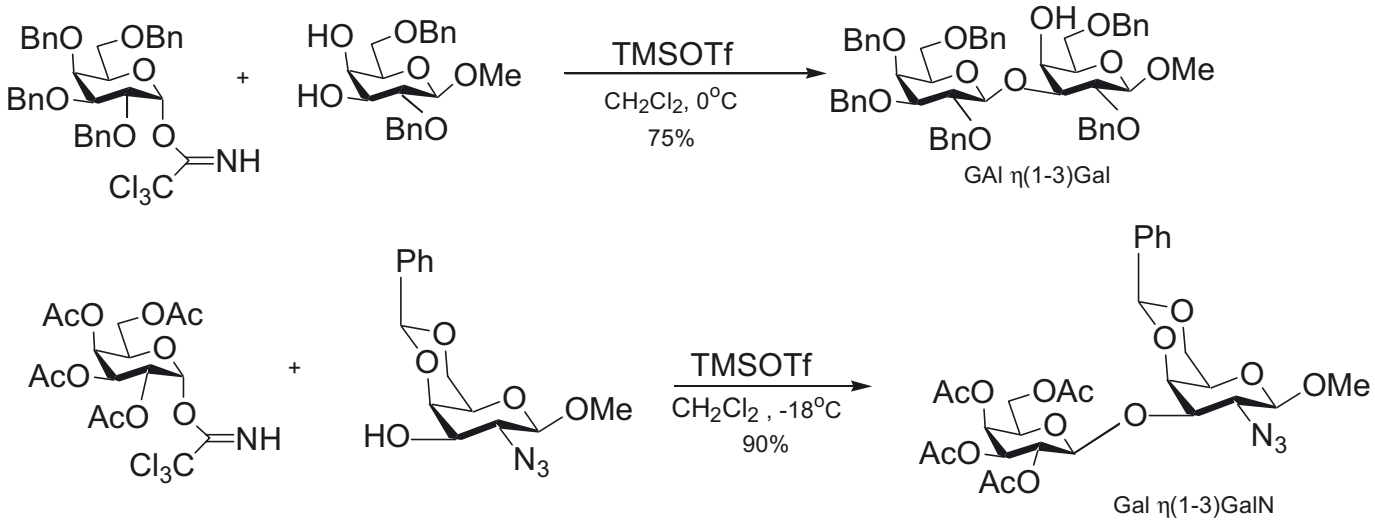
After base-catalyzed generation of *O*-glycosyl trichloroacetimidates (activation step), mild acid treatment in the presence of acceptors leads to the desired glycosides in an

irreversible manner. Under the reaction conditions, the Lewis acid ($BF_3.OEt_2$) or the strong acidic catalysts (TMSOTf, TfOH) are requird for the activation of the basic *O*-glycosyl trichloroacetimidates.

1.2.3. *O*-Glycosides

1.2.3.1. Synthesis of oligosaccharides

Trichloroacetimidates have been used for the glycosylation of oligosaccharides and all glycosides were obtained in high yileds and high stereoselectivity. Such as Gal η(1-3)Gal[43] and Gal η(1-3)GalN[44] (Scheme 7) .

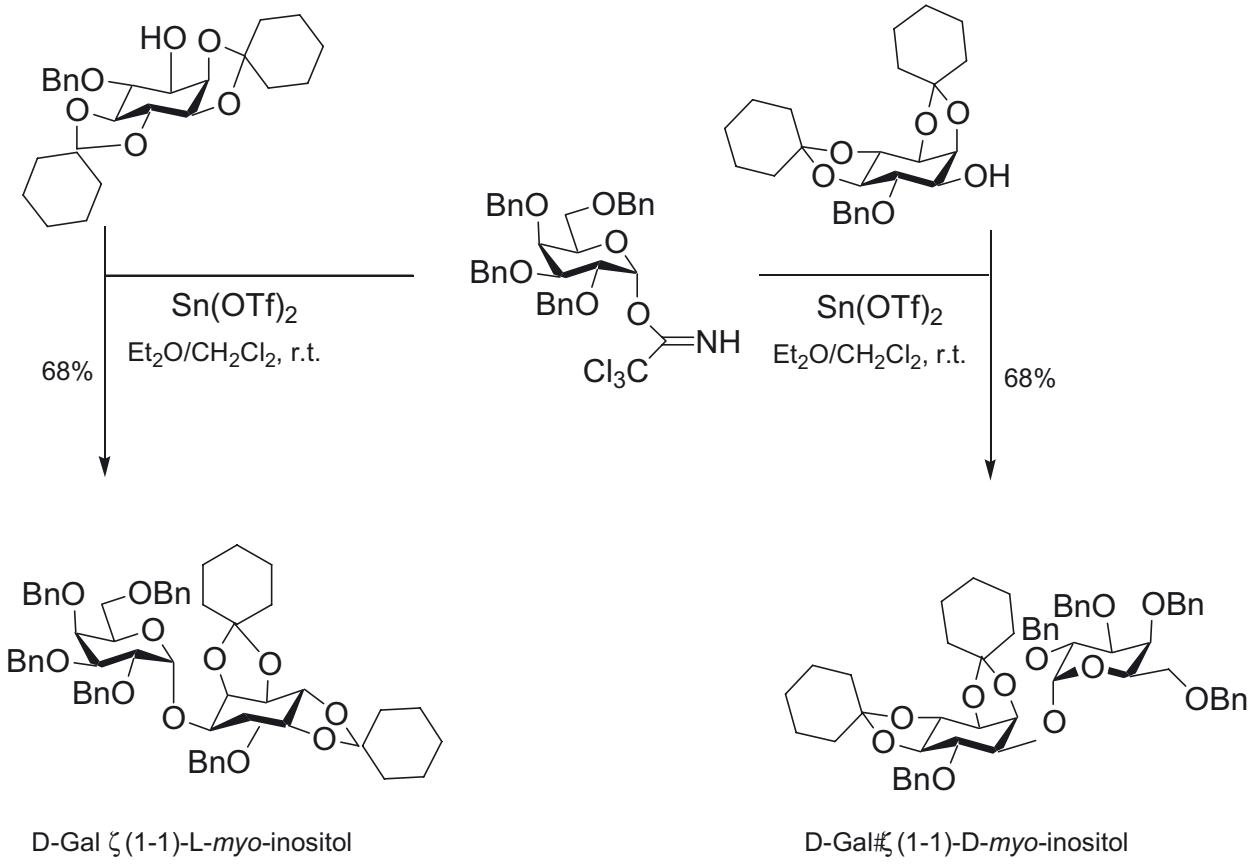


Scheme 7: Synthesis of oligosaccharides

1.2.3.2. Glycosylation of inositol derivatives

The synthesis of galactinol [D-Galζ#(1-1)-L-*myo*-inositol] which is involved in the biosynthesis of the raffinose family, has been reported (Scheme 8).[45] The suitable L-*myo*-inositol derivative was glycosylated with the *O*-benzyl protected galactosyl trichloroacetimidate under reaction conditions favoring an S_N1-type reaction mechanism, whereby the ζ-glycoside was formed exclusively. In the same way D-

Galζ(1-1)-D-*myo*-inositol was obtained from the corresponding D-*myo*-inositol derivative.

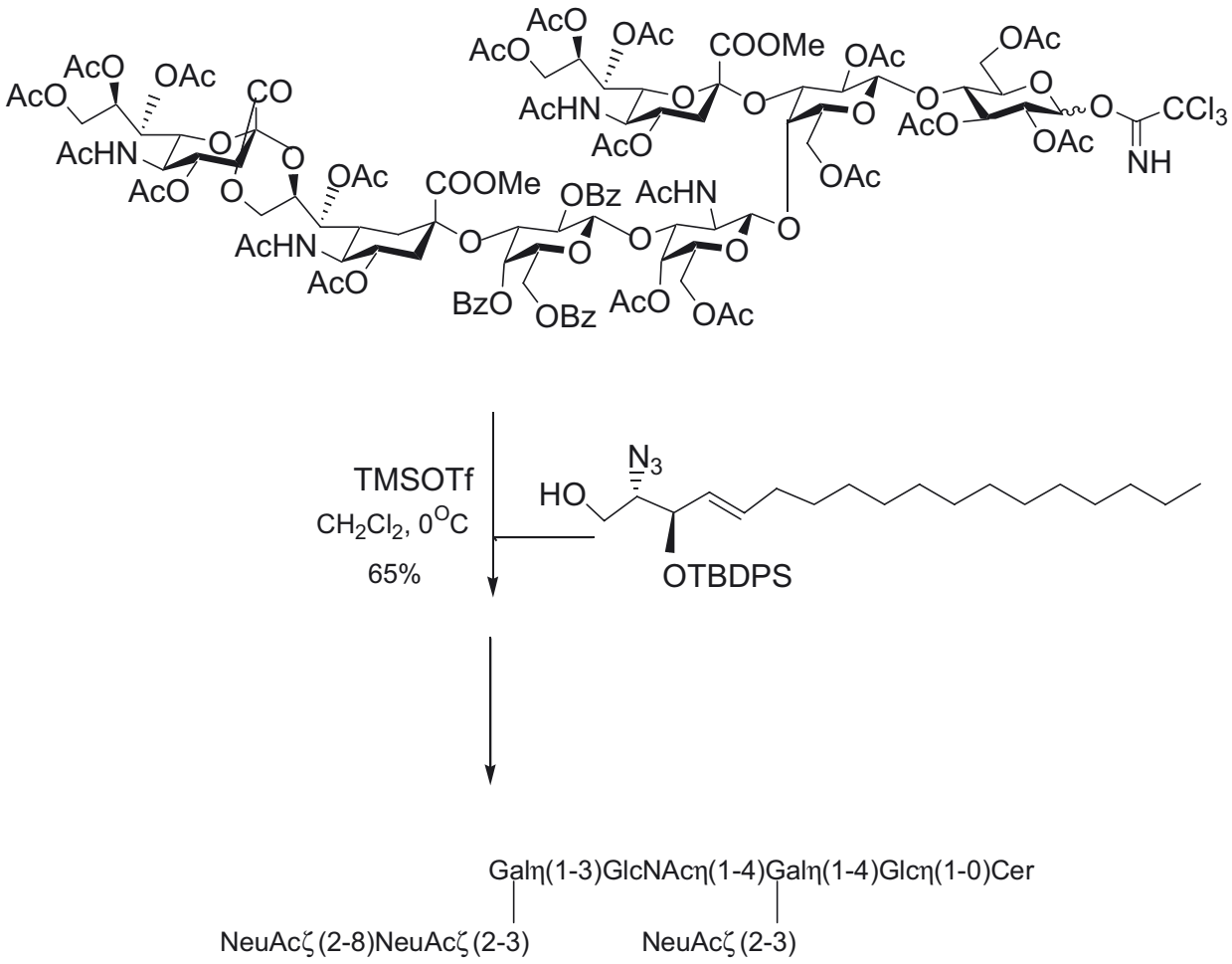


D-Gal ζ(1-1)-L-*myo*-inositol D-Galζ(1-1)-D-*myo*-inositol

Scheme 8: Synthesis of inositol glycosides derivatives

1.2.3.3. Glycosylation of sphingosine derivatives

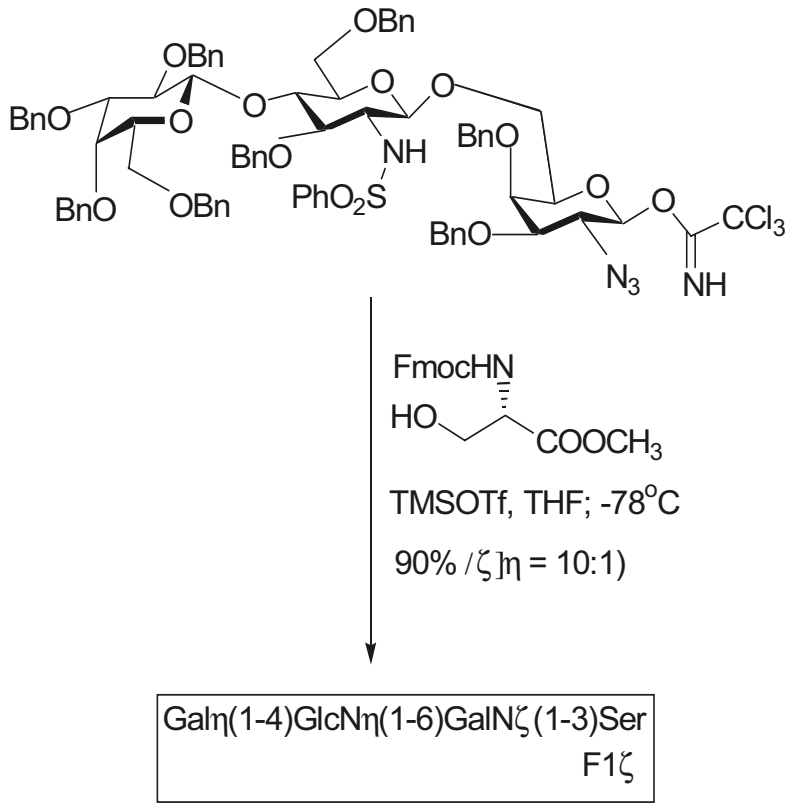
The trichloroacetimide method has been preferentially chosen for the coupling of the oligoglycosyl donor to the azidosphingosine (Scheme 9).[46]



Scheme 9: Glycosylation of sphingosine derivatives

1.2.3.4 Glycosylation of amino acids

The well established method[47] for the preparation of ζ-glycosylated serine and threonine derivatives has also been applied to the attachment of complex oligosaccharides (Scheme 10). Glycosylation of the serine acceptor with the η-configured trisaccharide trichloroacetimidate gave the ζ-glycosylated product stereospecifically, thus furnishing a derivative of the F1ζ-antigen.[48]

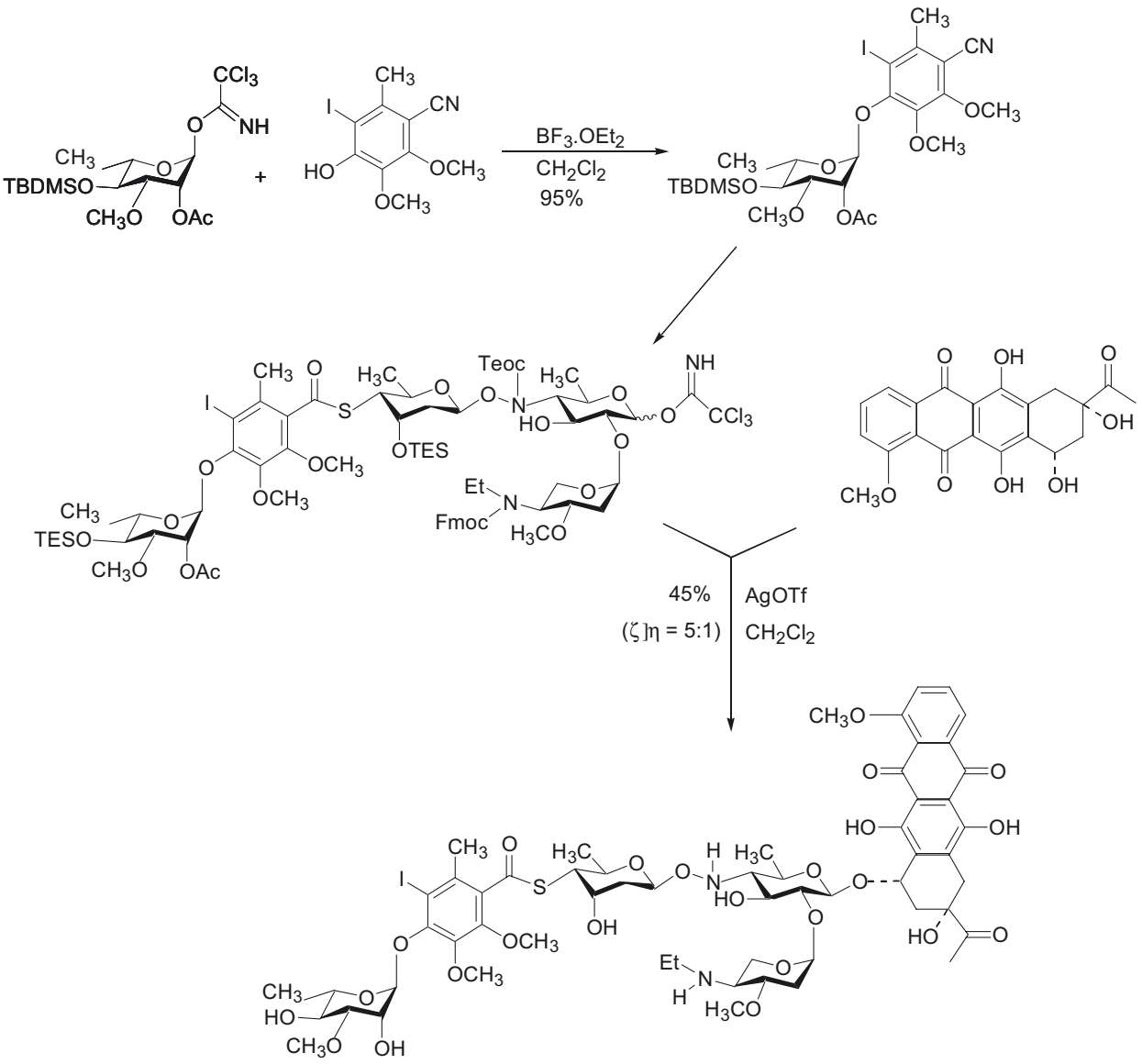


Scheme 10: Synthesis of the F1ζ-antigen

1.2.3.5 Polycyclic and macrocyclic glycosides

Glycosides of polycycles or macrocycles (anthracyclines, chalicheamicin, macrolactones, *etc*.) are of great interest because of their antibiotic and antitumor activities. The synthesis of calichearubicin A and B, which have the same carbohydrate moiety as calicheamicin, has recently been reported (Scheme 11).[49,50] The phenolic acceptor was stereospecifically glycosylated with rhamnosyl trichloroacetimidate in a very good yield. The resulting ζ4glycoside was transformed into the trichloroacetimidate donor which was used for the glycosylation of the anthracycline acceptor with silver triflate as catalyst. The ζ-glycosidically linked calichearubicin A was stereoselectively (ζ:η = 5:1) obtained. The η-glycosidically

linked calichearubicin B was similarly prepared from the same trichloroacetimidate donor with boron trifluoride-diethyl ether as the catalyst.

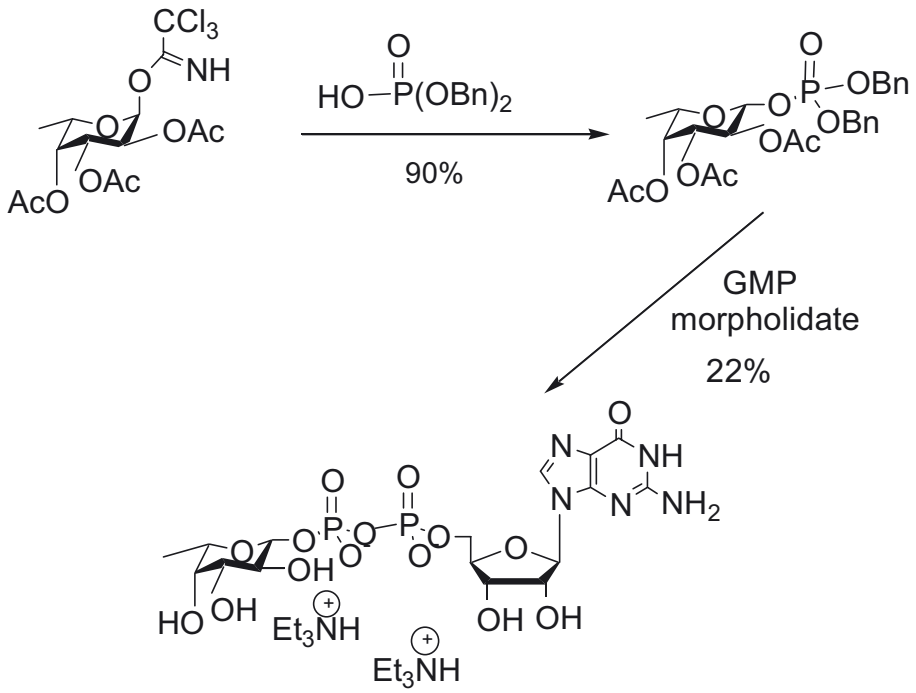


Scheme 11: Synthesis of calichearubicin A

1.2.3.6 Glycosides of phosphoric and carboxylic acids

Trichloroacetimidates can be used for glycosylation of phosphoric and carboxylic acids without additional Lewis acid. Reaction of the ζ-fucosyl trichloroacetimidate

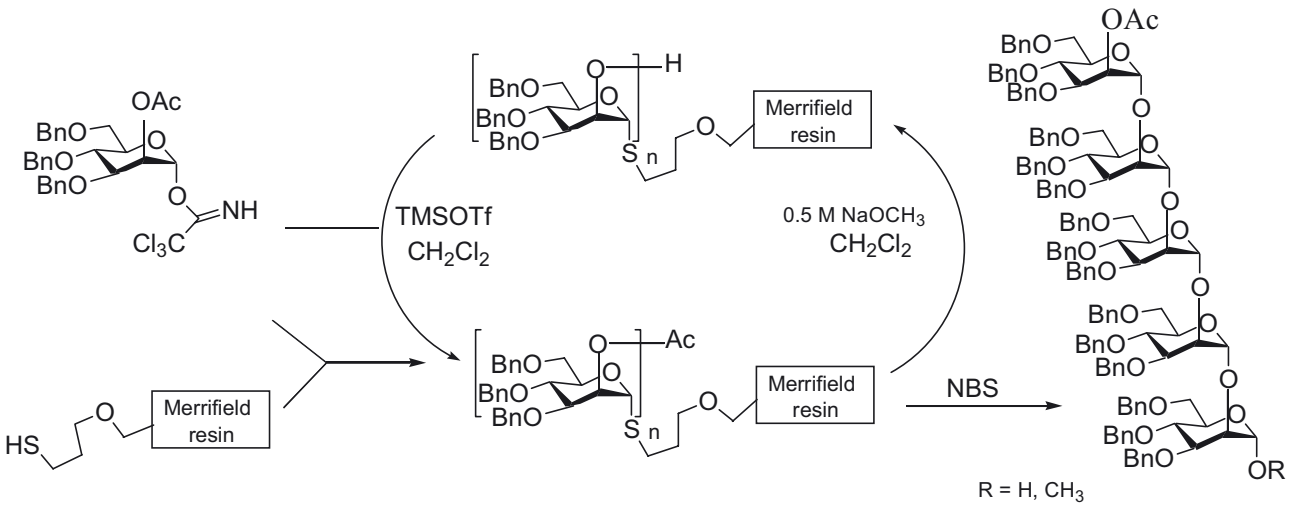
with dibenzyl phosphate gave the η-fucosyl phosphate with stereospecific inversion of configuration (Scheme 12).[51] Deprotection and coupling with GMP morpholidate yielded GMP fucose.



Scheme 12

1.2.3.7 Solid-phase synthesis

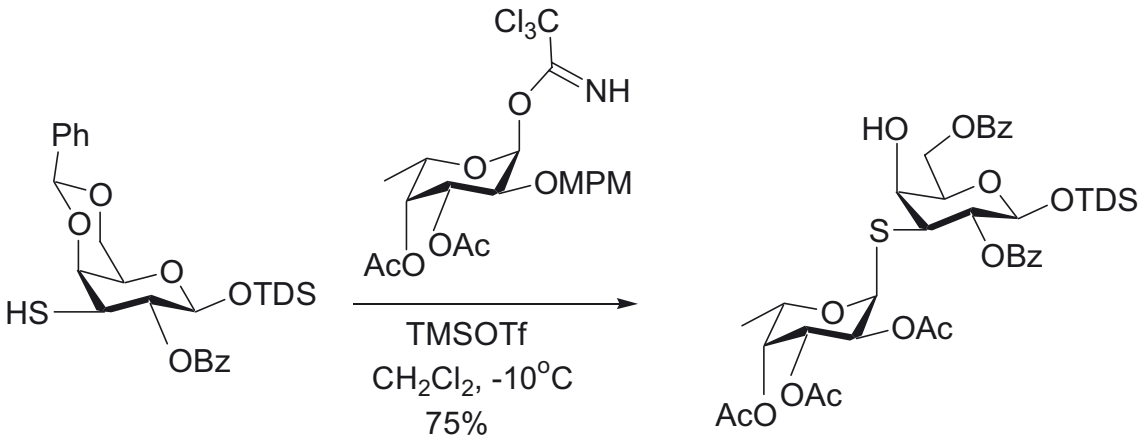
Although solid-phase chemistry is well developed, progress has not yet been fully extended to oligosaccharide chemistry, because of the high demands on the polymer support and the lack of powerful analytical tools for monitoring reactions on solid phases. The synthesis of an ζ-(1-2)-linked pentamannose moiety has recently been reported (Scheme 13);[52] a Merrifield resin, a thio-linker, and a 2-*O*-acetyl protected mannosyl trichloroacetimidate were used.



Scheme 13

1.2.4 S-Glycosides

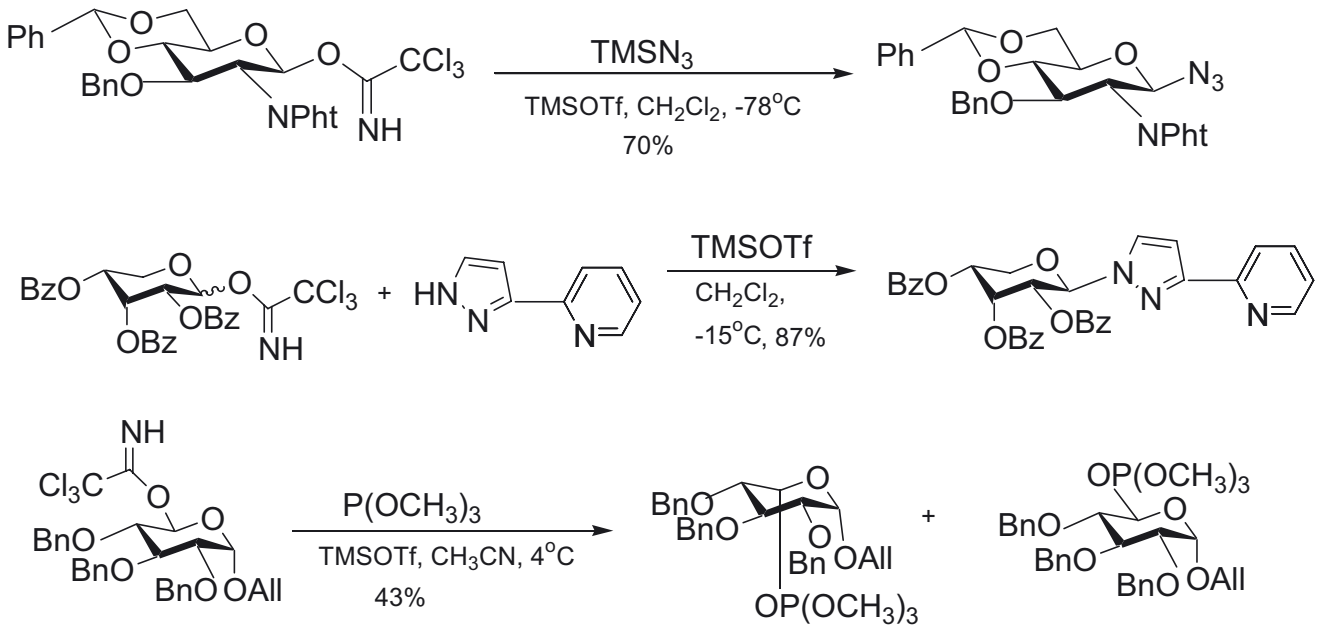
Thio-linked analogs of oligosaccharides are of interest because of their improved stability to glycosidases. The synthesis of several examples by the trichloroacetimidate glycosylation method has been described (Scheme 14).[53,54] Glycosylation of the 3-thio galactose acceptor with a fucosyl trichloroacetimidate gave the ζ-disaccharide stereospecifcally.



Scheme 14

1.2.5 *N*- and *P*-Glycosides

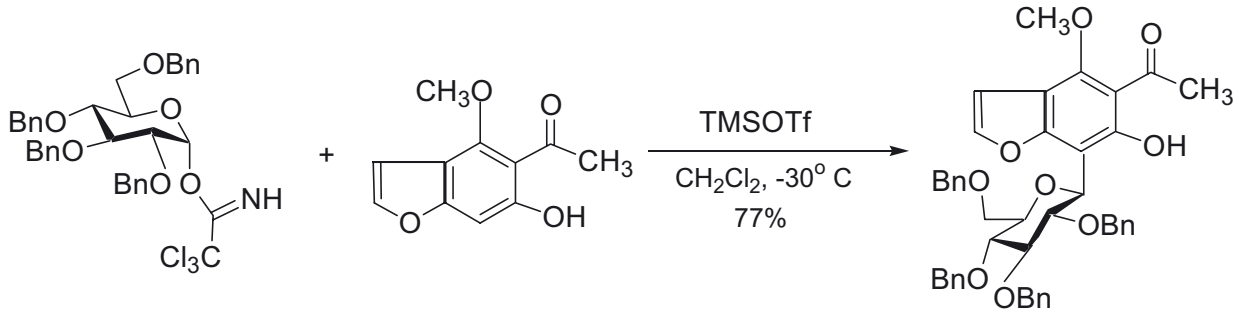
Trichloroacetimidates are also suitable glycosyl donors for the synthesis of *N*-glycosides. For instance, reaction of *N*-phthaloyl-protected glucosamine trichloroacetimidate with trimethylsilyl azide gave, owing to neighbouring group participation, only the η-glycosyl azide (Scheme 15).[55] Another example of the synthesis of *N*-glycosides is the reaction of the ribopyranosyl trichloroacetimidate with 2-(3-pyrazolyl)pyridine.[56] A *P*-glycoside has been prepared from the reaction of the hemiacetal-type trichloroacetimidate with trimethyl phosphite.[57] The resulting diastereomeric phosphonates can be considered as *P*-analogs of uronic acids, and their glycosides are of interest in investigations with glycosidases.



Scheme 15

1.2.6 *C*-Glycosides

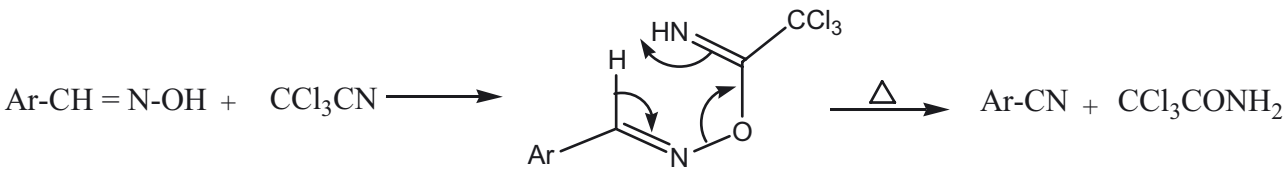
Application of trichloroacetimidates to the synthesis of aromatic *C*-glycosides, *i.e.* vitexin, isovitexin, isoembigenin, etc. which are of interest because of their physiological properties, is well established.[58,59] A benzofuran derivative was recently glycosylated with glucosyl trichloroacetimidate to yield the respective η4glycoside stereo-specifically which has served as intermediate in the synthesis of visnagine analogs (Scheme 16).[60]



Scheme 16

1.3 Synthesis of aryl cyanides by using trichloroacetimidate: Dehydration

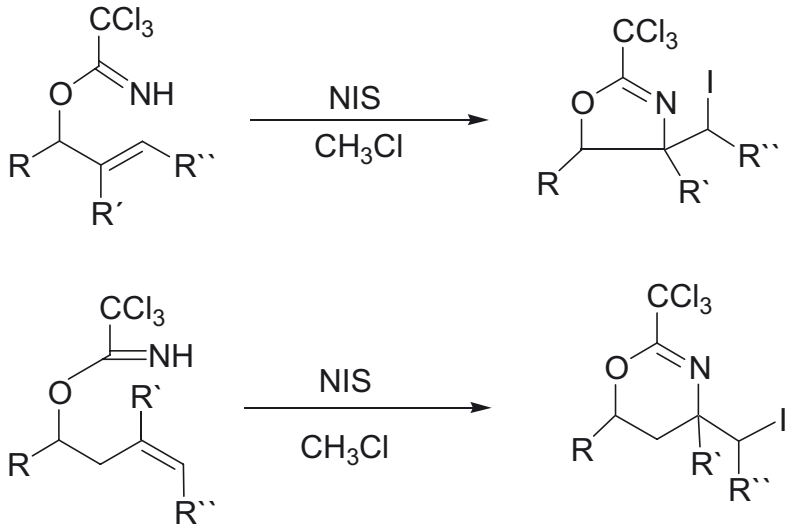
The aryl aldoximes are readily dehydrated upon refluxing with trichloroaceonitrile. The by-product, trichloroacetamide, is generally obtained in quantitative yield and can be easily removed. The reaction can be depicted as follows as shown in scheme 17.[61]



Scheme 17

1.4 Cyclization *via* imidates: Introduction of an amino group

The unsaturated imidates are easily obtained by treating a solution of the appropriate unsaturated alcohol with trichloroacetonitrile in the presence of a catalytic amount of NaH. Cyclization of such imidates can be carried out under kinetic conditions by adding either iodine in THF in the presence of pyridine, or NIS in chloroform to a solution of the allylic or homoallylic trichloroacetimidate.[62] Cyclization of the allylic derivatives shows total regioselectivity to afford 4,5-dihydro-1,3-oxazoles, while the homoallylic derivatives give 4,5-dihydro-1,3-oxazines exclusively.



Scheme 18

2.0 Theortical Part

2.1 Preface

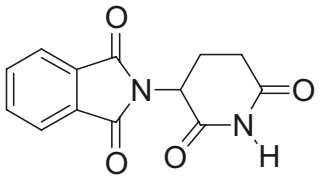
The most widely used glycosylation protocol today is without any doubt the trichloroacetimidate method developed by Schmidt.[15] This method displays several key advantages making it the first choice for most glycosylation endeavors. Besides its general efficiency in glycosylation reactions, trichloroacetimidates are easily accessible from the corresponding hemiacetals by base catalyzed addition to trichloroacetonitrile and the resulting glycosyl trichloroacetimidates are suitable for storage. Glycosyl trichloroacetimidates are activated by Lewis acid catalysis; hence, they do not require drastic conditions and necessitate only catalytic activation. Moreover, protecton/deprotection methodologies are of great significance in organic synthesis. Particularly, under mild conditions. Consequently, the uses of some derived trichloroacetimidate compounds as electrophilic reagents have been investigated. Upon activation of these trichloroacetimidates carbenium ion intermediates will be presumably the electrophilic species that could react with nucleophiles. Rearrangement of such carbenium ions may take place when it is possible; thus providing products based on the reactant of such rearrangements. These reagents have the advantage to provide compounds derivatized or functionalized by groups that may have some biological significance. Moreover, they can be used as protecting groups and as reagents for generating *C-C* bonds. As a consequence of the strategy developed in this thesis is the use of the trichloroacetimidates of the pthalimidomethyl-, diphenylmethyl-, 9-fluorenyl groups as protecting groups. In this respect, it became interesting to study the effect of these groups on the stereoselectivity during the glycosylation reaction.

Also, the reactions of trichloroacetimidates of cyclopropylmethyl, cyclobutyl, 3-buten-2- and 2-buten-1-yl alcohols with some nucleophiles have been investigated.

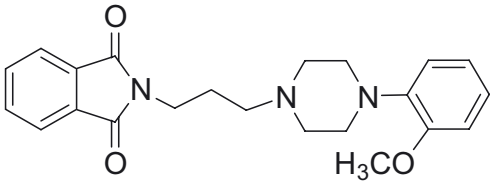
2.2 Phthalimidomethylation of *O*-nucleophiles with *O*-phthalimidomethyl trichloroacetimidate.

Tumor necrosis factor alpha (TNF-ζ) is an important cytokine secreted by activated monocytes/macrophages and possesses favorable biological activities including direct tumor toxicity,[63,64] stimulation of the host immune system,[64] and η-cell growth stimulation.[65] The unfavourable effects of TNF-ζ include induction of endotoxic shock that causes hemorrhagic necrosis of transplanted solid tumors, [63] tissue inflammation,[66] tumor-promoting action as well as stimulation of tumor metastasis, angiogenesis[67,68] and stimulation of HIV replication.[69]

Thalidomide [*N*-(ζ)-phthalimidoglutarimide] was introduced as a sedative drug but was removed from the market because of its teratogenicity.[70, 71] Recently, thalidomide proved its activity as potential inhibitor of TNF-ζ production[69,72] and this immunosuppressive property led to its use in the treatment of graft-versus-host disease (GVHD), leprosy, AIDS, Behcet's disease, lupus erythe-matosus, malaria, and other related diseases.[69,73-77] Recently, a new pharmacologically interesting compound within the series of phthalimides, NAN-190, is reported as a well recognized antagonist of postsynaptic receptors 5-HT_{1A}.[78]



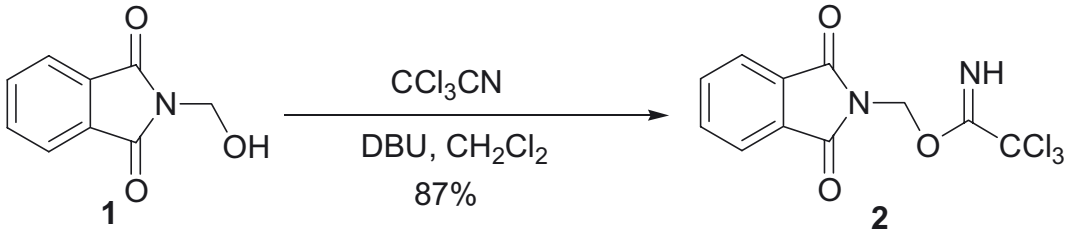
Thalidomide



NAN-190

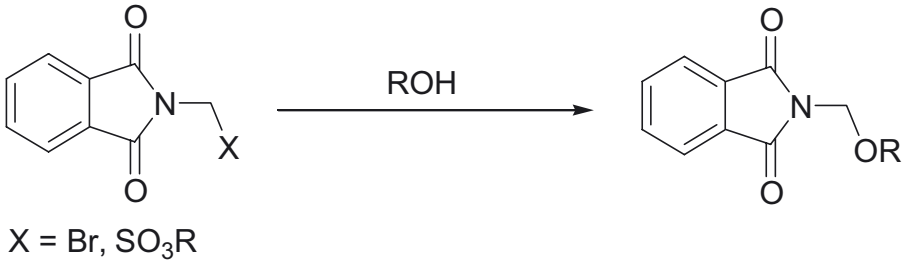
A study on the hypolipidemic activity of phthalimidomethyl (Pim)-tetra-*O*-acyl-ζ-D-mannopyranosides in mice showed significant reduction of plasma cholesterol and triglyceride levels.[79] Moreover, the phthalamidomethyl and phthalimide derivatives

possess analgesic,[80] hypolipidemic,[81,82] anticonvulsant,[83] and antitumor activities.[84] They are also useful as synthetic intermediates,[85-94] for instance in polymer chemistry.[95] The phthalimidomethyl derivatives have been used for the identification[96-100] of amines and alcohols *via* nucleophilic substitution[101] of a leaving group on the Pim moiety. The biological activities as well as our interest in the reactivity of trichloroacetimidates[102-104] attracted our attention to develop a method for introducing the phthalimidomethyl group on nucleophiles to form, for instance, *C*- and *O*-bonds under acid catalysis. *O*-(Phthalimidomethyl)trichloroacetimidate (**2**) (Scheme 19) was expected to serve as imidomethylating agent; ensuing removal of the phthaloyl residue in the products will readily provide the corresponding aminomethyl derivatives. In the case of *O*-nucleophiles the *O*-aminomethyl intermediate will liberate the hydroxy group, thus exhibiting that Pim is also a useful protecting group.



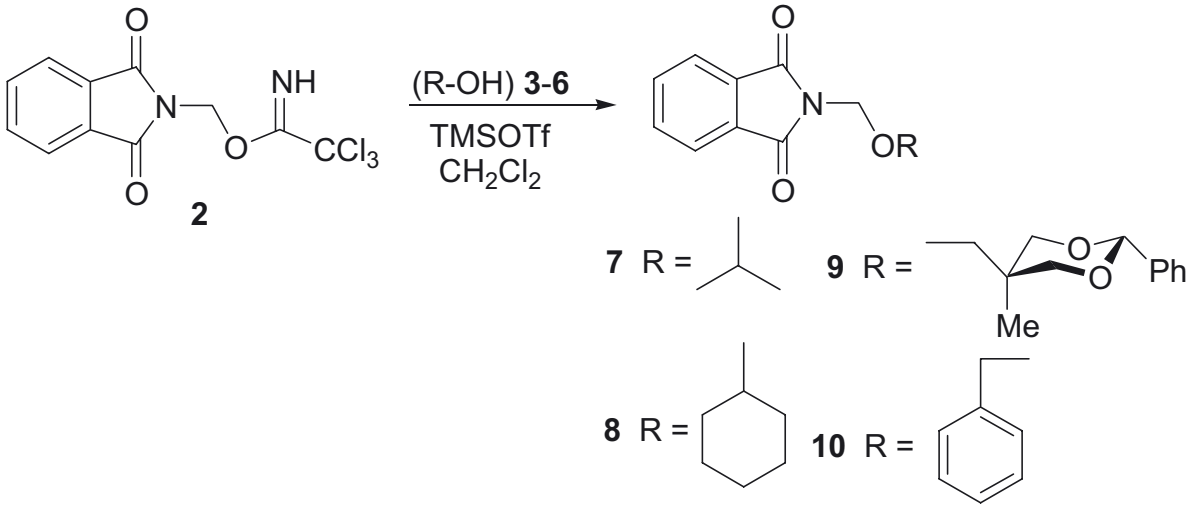
Scheme 19: Synthesis of the trichloroacetimidate **2**

The synthesis of **2** was achieved by reaction of *N*-hydroxymethyl phthalimide (**1**) with trichloroacetonitrile in dichloromethane as solvent and in the presence of 1,8-diaza-bicyclo[5.4.0]undec-7-ene (DBU) as a base which promotes the addition to the nitrile group (Scheme 19). The product **2** was isolated in 87% yield after column chromatography and its structure was readily assigned from its ^{1}H NMR spectrum [ι = 5.90 (s, 2 H, CH_2), 8.59 (br s, 1 H, NH)]. The phthalimidomethyl ethers are usually prepared from the reaction of *N*-bromomethyl phthalimide[79] and phthalimidomethyl sulfonate derivatives with alcohols (Scheme 20).[80]



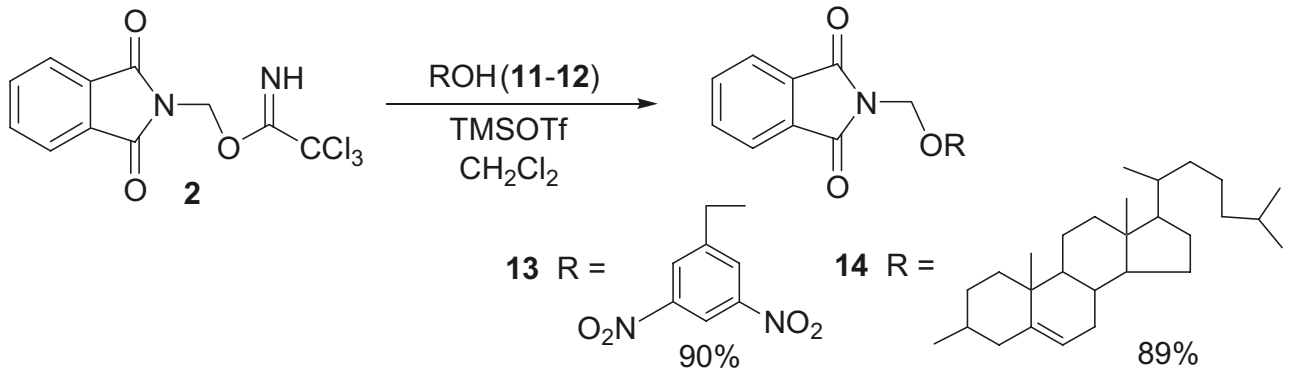
Scheme 20

In the present work, the pthalimidomethyl trichloroacetimidate (**2**) has been found to react smoothly with alcohols such as isopropyl alcohol (**3**), cyclohexyl alcohol (**4**), benzyl alcohol (**5**) and 5-methyl-2-phenyl-1,3-dioxane-5-methanol (**6**)[105] in high yields (77%-90%) to give the phthalimidomethyl ether derivatives **7**-**9**[99-100] (Scheme 21).



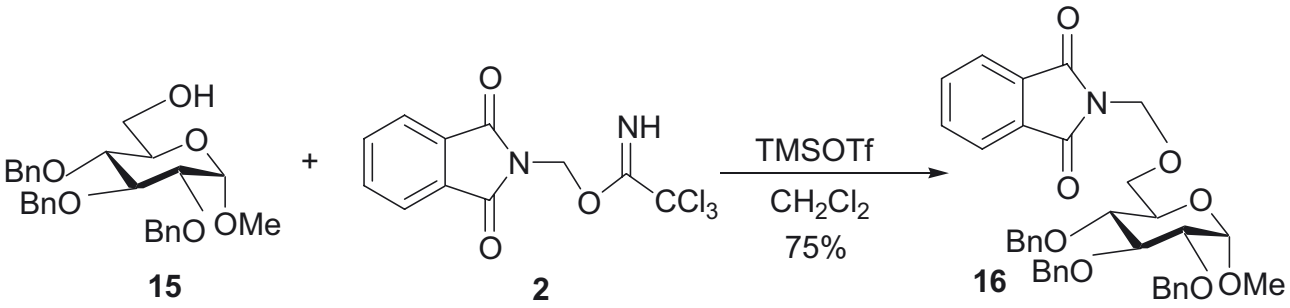
Scheme 21

Trichloroacetimidate **2** has also been reacted with 3,5-dinitrobenzyl alcohol (**11**) and cholesterol (**12**) under the same conditions to give 3,5-dinitrobenzyl phthalimidomethyl ether (**13**) and cholesteryl phthalimidomethyl ether (**14**) (Scheme 22). The structure of ether **13** was confirmed by ^{1}H NMR spectroscopy [ι = 4.80, 5.30 (2 s, 4 H, 2 CH_2), 7.70-8.93 (m, 7 H, Ar-H)].



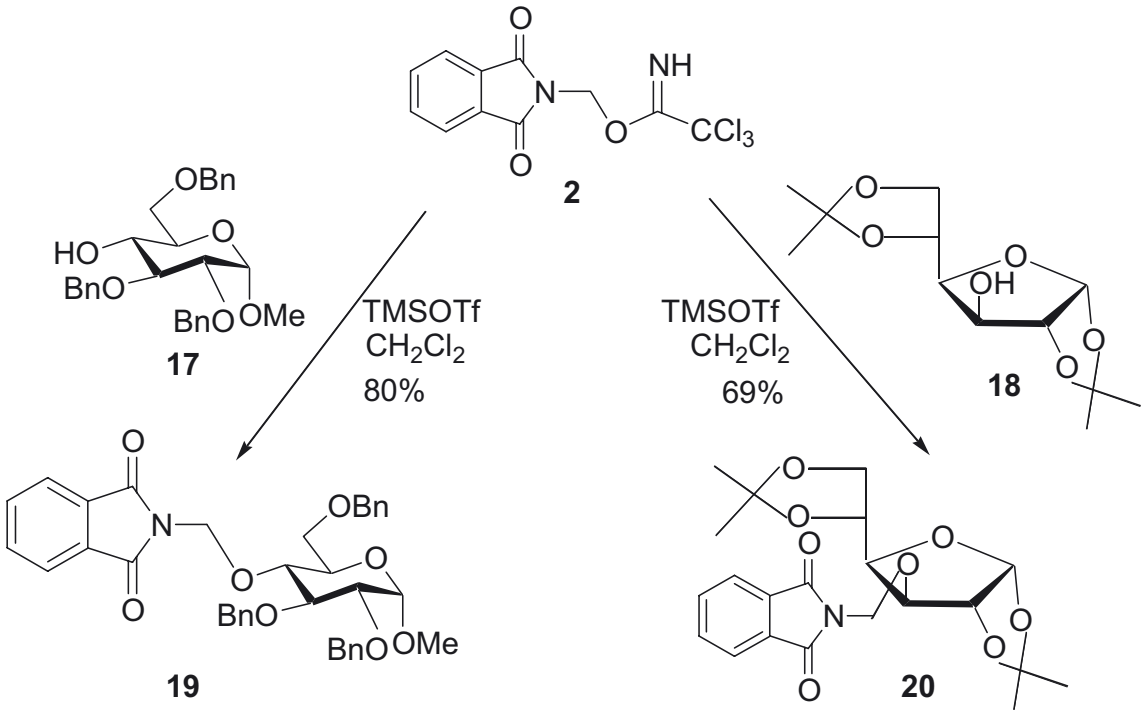
Scheme 22

The imidomethylation procedure has been also extended to a series of carbohydrate derivatives. Thus, the trichloroacetimidate **2** was reacted with the primary hydroxyl group in *O*-6-unprotected glucoside **15**[106] to give methyl 2,3,4-tri-*O*-benzyl-6-*O*-phthalimidomethyl-ζ-D-glucopyranoside (**16**) as shown in Scheme 23.



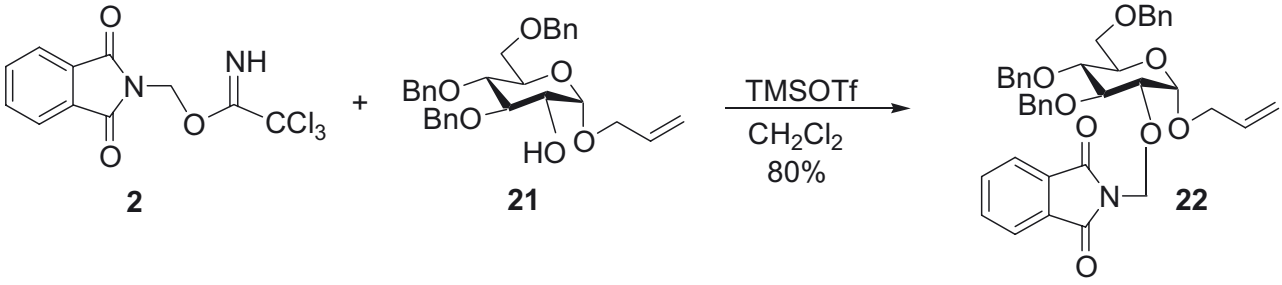
Scheme 23

Similarily, the etherification of secondary hydroxyl groups in various types of partially protected carbohydrates has been successfully carried out (Scheme 24). Thus, reaction of trichloroacetimidate **2** with *O*-4-unprotected glucopyranose **17**[107] and *O*-3-unprotected glucofuranose **18**[108] gave **19** and **20**, respectively. The ^{1}H NMR spectrum of **19** showed the absence of the singlet of the NH of trichloroacetimidate. The ζ-configuration of the anomeric proton could be assigned from the ^{1}H NMR data [ι = 4.40 (d, $J_{1,2}$ = 3.3 Hz, 1-H].



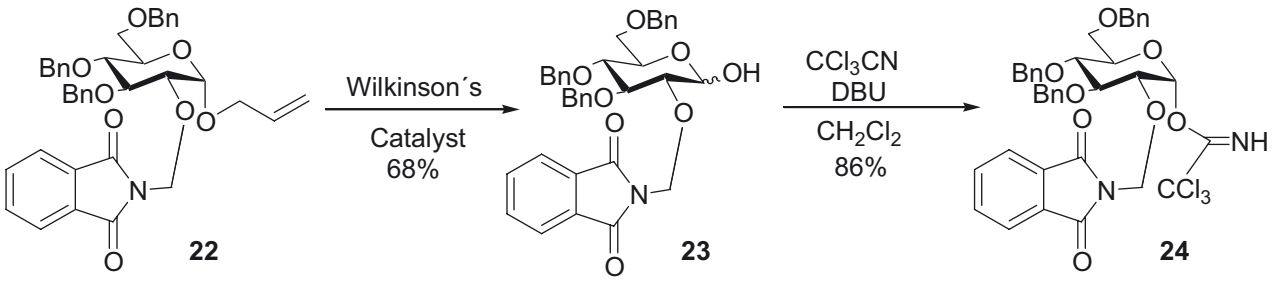
Scheme 24

The stereoselectivity of the glycosyl bond formation is a subject which is still attracting many investigators. In this respect, it became interesting to study the effect of the phthalimidomethyl group on the stereoselectivity during the glycosylation reaction. Towards this objective the allyl 3,4,6-tri-*O*-benzyl-ζ-D-glucopyranoside (**21**)[109] was reacted with the trichloroacetimidate **2** to give the glucose derivative **22**, which has the phthalimidomethyl group on *O*-2 (Scheme 25).



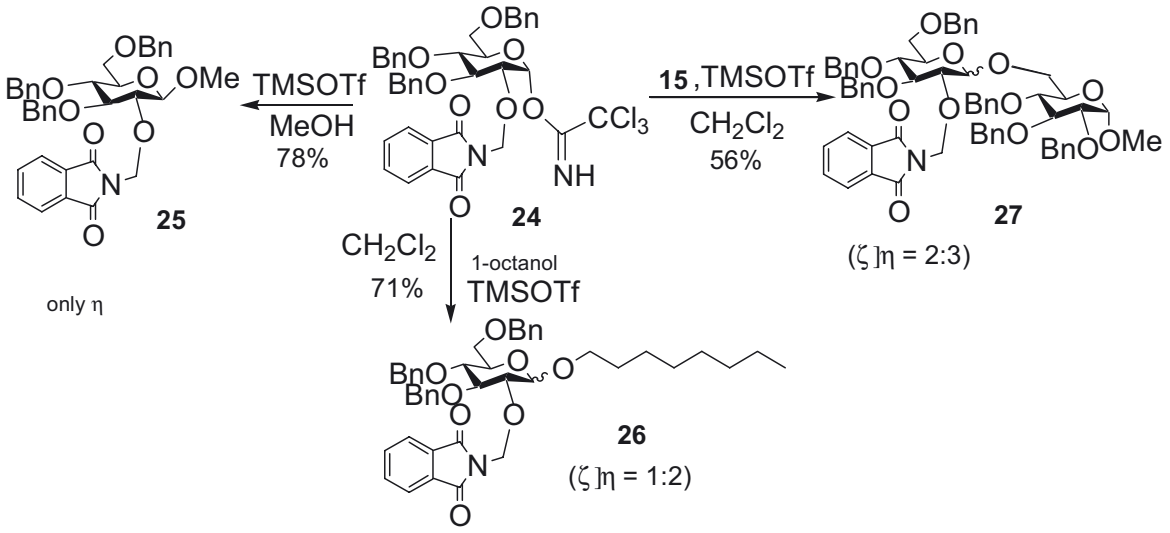
Scheme 25

The deallylation of *O*-1 in **22** with Wilkinson´s catalyst afforded the glucose derivative **23** (ζ/η 2:3). Reaction of **23** with trichloroacetonitrile in the presence of DBU as a base led to the trichloroacetimidate **24**; only the ζ-anomer was obtained ^{1}H NMR [ι = 6.54 (d, $J_{1,2}$ = 3.3 Hz, 1-H)].



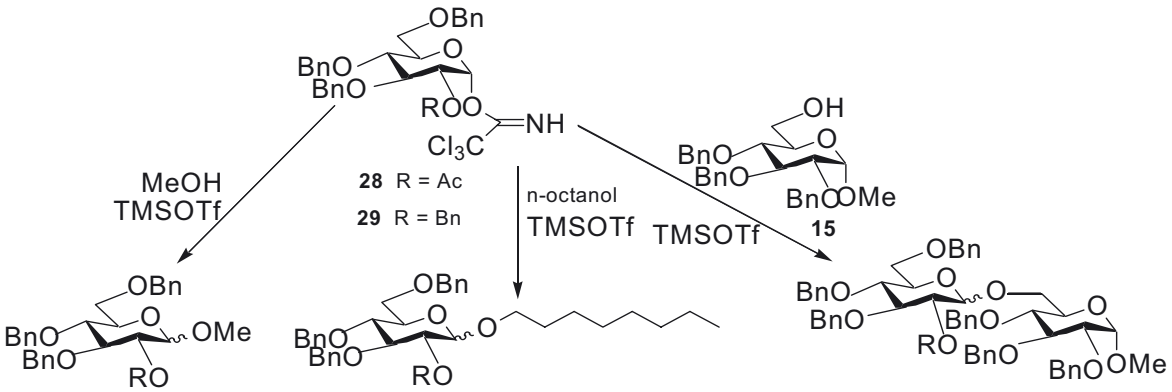
Scheme 26

Glycosylation of methanol, n-octanol and 6-*O*-unprotected glucopyranoside **15** with **24** as a glycosyl donor in the presence of TMSOTf as a catalyst afforded glucosides **25**-**27** in high yields; the η-anomers were main products. The preference for the η-product may be due to the steric effect and/or neighboring group participation *via* a seven-membered intermediate. Thus, in terms of glycosyl donor properties and anomeric control there is a big difference between a 2-*O*-acyl group and a 2-*O*-phthalimidomethyl group. The phthalimidomethyl group rather resembles the 2-*O*-benzyl group which offers high glycosyl donor properties with little interference in anomeric stereocontrol (Scheme 27).



Scheme 27

This conclusion has been deduced from a parallel study using donors with acetyl or benzyl groups in 2-position as in the glucose derivative **28**[110] and **29**[111] and reacting them with the acceptors methanol, n-octanol and glucose derivative **15** under similar conditions. The glucosides derivatives **30-35**[112-114] were formed (Scheme 28). The ζ6η-ratios differ markedly from the results of the reaction of **24** with the same acceptors.



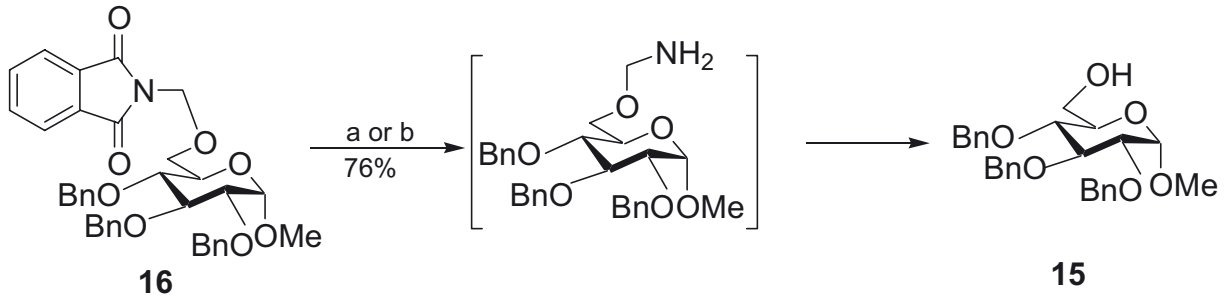
R	ζ:η	yield
30 Ac	1 : 8	73%
31 Bn	2 : 5	85%

R	ζ:η	yield
32 Ac	only η	77%
33 Bn	1 : 2	82%

R	ζ:η	yield
34 Ac	1 : 2	65%
35 Bn	2 : 1	70%

Scheme 28

Attempted cleavage of the phthalimidomethyl group with hydrazine hydrate or methylamine in methanol gave from **16** the respective alcohol **15** whose formation is the result of hydrolysis of the intermediate aminomethyl derivative (Scheme 29).

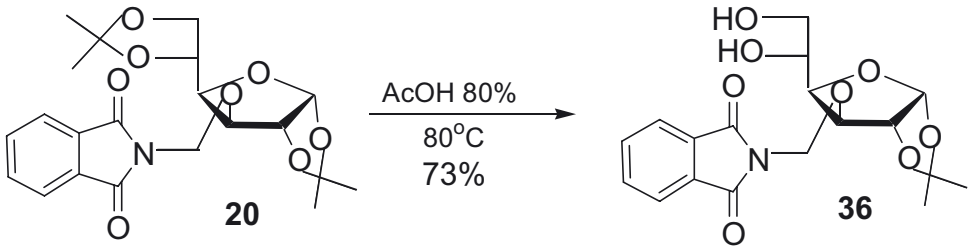


a = $NH_2NH_2.H_2O$

b = $MeNH_2$, MeOH

Scheme 29

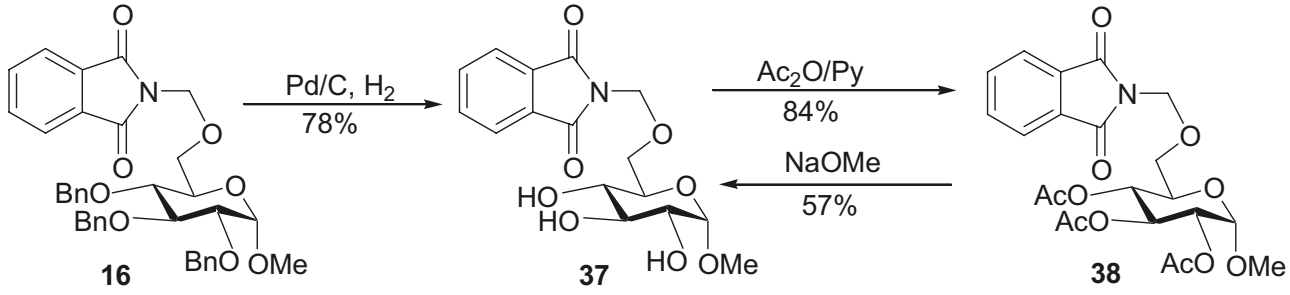
Treatment of 1:2,5:6-di-*O*-isopropylidene-3-*O*-phthalimidomethyl-ζ-D-glucofuranose (**20**) with aqueous acetic acid (80%) at 80 °C led to selective removal of the 5:6-*O*-isopropylidene group without affecting the phthalimidomethyl moiety (Scheme 30).



Scheme 30

Also hydrogenolysis of **16** in methanol with palladium on carbon as catalyst cleanly furnished the 2,3,4-*O*-unprotected intermediate **37**; subsequent transformation into the 2,3,4-tri-*O*-acetyl derivative **38** with pyridine/acetic anhydride and de-*O*-acetylation with sodium methoxide in methanol afforded the 2,3,4-*O*-unprotected compound **37** again without affecting the phthalimidomethyl group. Hence the pthalimidomethyl

group is compatible with and orthogonal to all important hydroxyl protecting groups; it offers selective removal with strong nucleophiles, thus complementing the repertoire of the available hydroxyl protecting groups which are generally sensitive to acid, base, or hydrogenolysis, respectively (Scheme 31).



Scheme 31

2.3 Protection of hydroxyl groups with diphenylmethyl and 9-fluorenyl trichloroacetimidates-effect on anomeric stereocontrol.

The protection-deprotection methodologies are of great significance in organic synthesis. As a consequence of the extensive use of the benzyl group as protecting group, the diphenylmethyl (DPM) group has been used for the protection of hydroxyl groups. Its hydrogenolytic cleavage could be achieved as cleanly as in the case of benzyl ethers.[115]

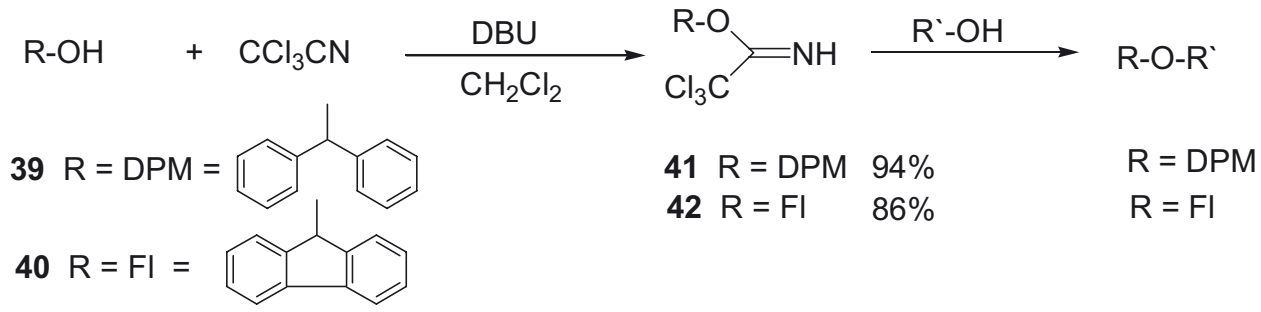
The synthesis of DPM ethers can be carried out by using DPM chloride and bromide in the presence of a base,[115] diphenyldiazomethane,[116,117] diphenylmethylphosphate in the presence of trifluoroacetic acid,[116, 117] diphenylmethanol in the presence of various acids such as xenon difluoride,[118] *p*-toluenesulfonic acid,[119] concentrated sulfuric acid,[119] ytterbium(III)triflate-ferric chloride,[120] ferric chloride or ferric perchlorate,[121] and ferric nitrate.[122] Direct transformation of silyl ethers or alkyl tetrahydropyranyl ethers into the respective DPM alkyl ethers was also reported to take place with

DPM-formate under the influence of trimethylsilyltrifluoromethanesulfonate (TMSOTf).[123] The DPM group was generated when orthoesters of *myo*-inositol were reacted with Grignard reagents.[124] Beside the alcohol protection, the DPM group was also used for the protection of acids.[125-127] Moreover, the DPM ethers are valuable as therapeutic agents.[128-130]

On the other hand, the 9-fluorenyl (Fl) ethers have comparatively attracted less attention and the studies on them are mainly concerned with the photolytic reactions.[131-134] Their synthesis was carried out by the reaction of 9-bromo- or 9-diazo-fluorene with alcohols.[135-137] As expected, the solvolysis of 9-fluorenyl ethers under acid conditions is slower than the solvolysis of the corresponding diphenylmethyl derivatives, which reflects the different stability of the diphenylmethyl and the fluorenyl carbenium ion intermediates.[132-134] Therefore it is worthwhile to investigate the properties of these two structurally related compounds, which due to different carbenium ion stabilization and steric demand could exhibit different protecting group characteristics.

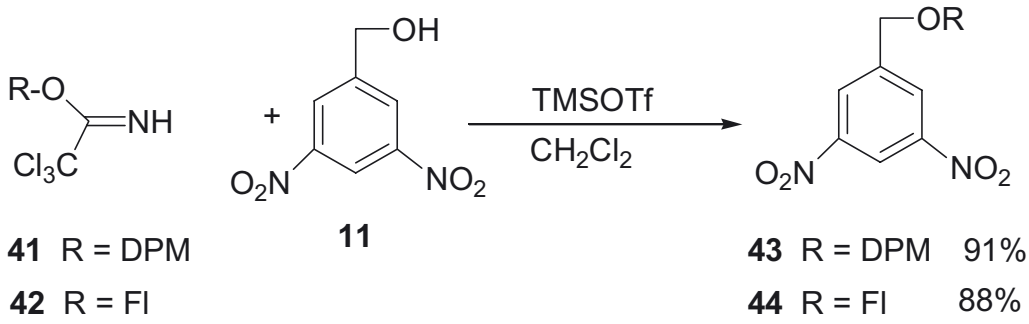
As a consequence of the interest in the DPM and Fl groups and the need for efficient methods for introducing them to alcohols, their trichloroacetimidates were considered as donors of the DPM[138] and Fl groups, respectively; obviously, we had in mind the importance of *O*-glycosyl trichloroacetimidates as glycosyl donors.[102-104] Moreover, the ready formation of the trichloroacetimidates from DPM-OH and 9-Fl-OH as well as the mild condition of introducing these groups in the presence of acid and base sensitive groups should be of significance. Therefore, the introduction of the DPM and Fl groups as protecting groups particularly in the carbohydrate field as well as their effect on the anomeric ratio in the glycosidation reaction have been investigated. The required *O*-DPM[138] and *O*-Fl trichloroacetimidates **41** and **42** respectively, were prepared by the reaction of the diphenylmethanol (**39**) and 9-fluorenol (**40**), with trichloroacetonitrile in presence of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) as

base (Scheme 32). Their formation was confirmed by the spectroscopic data [ι = 8.40, 8.67 ppm (NH)].



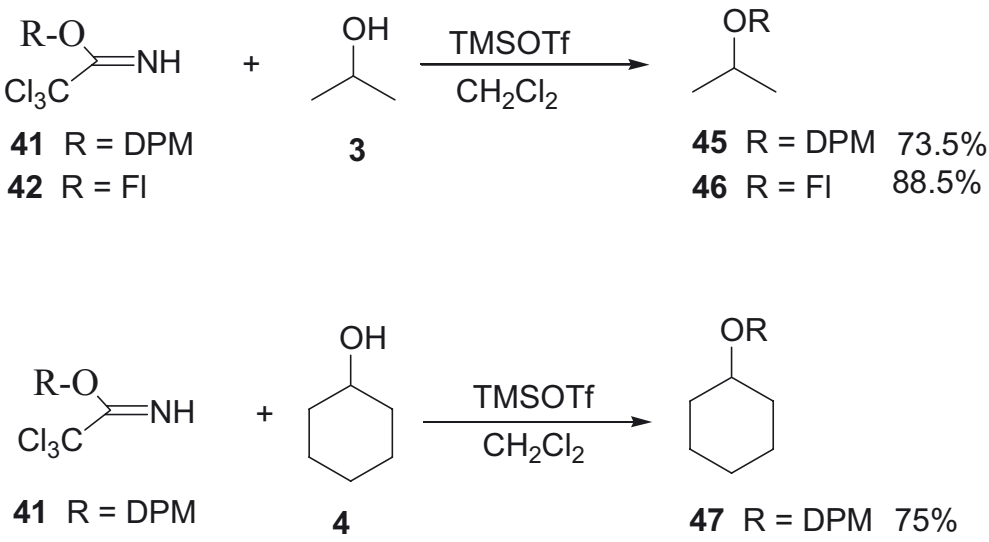
Scheme 32

The trichloroacetimidates **41** and **42** are crystalline compounds and characterized by their stability at room temperature for long periods of time without detected decomposition. Reaction of the trichloroacetimidate **41** and **42** with model compounds containing a primary hydroxyl group such as dinitrobenzyl alcohol (**11**) and in the presence of TMSOTf readily afforded the respective DPM ethers **43** and Fl ethers **44**, respectively, in high yields. The ^{1}H NMR spectra of **43** and **44** exhibit the presence of CH_2 of dinitrobenzyl at ι = 4.71 (s, 2 H, CH_2), 5.50 (s, 1 H, CH) and Fl at# = 4.26 (s, 2 H, CH_2), 5.89 (s, 1 H, CH), respectively (Scheme 33).



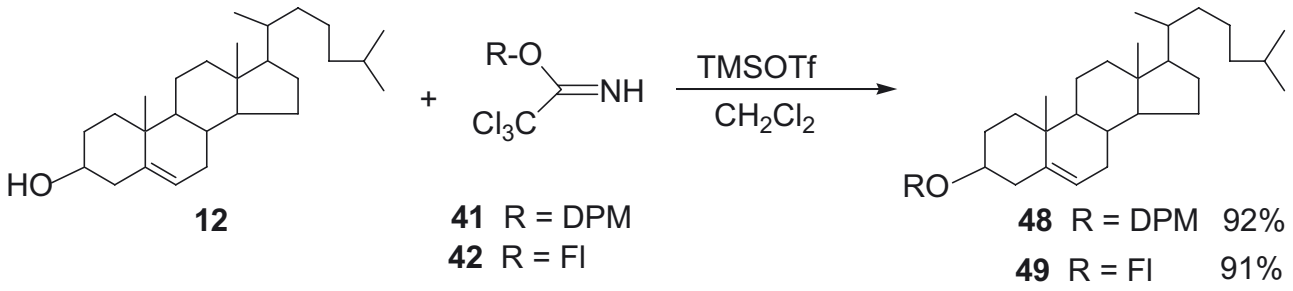
Scheme 33

Similarily, the ethers **45**[139], **46** [135] and **47**[140] could be synthesized by the reaction of the secondary alcohols, isopropyl alcohol (**3**) and cyclohexyl alcohol (**4**) with trichloroacetimidates **41** and **42** (Scheme 34).



Scheme 34

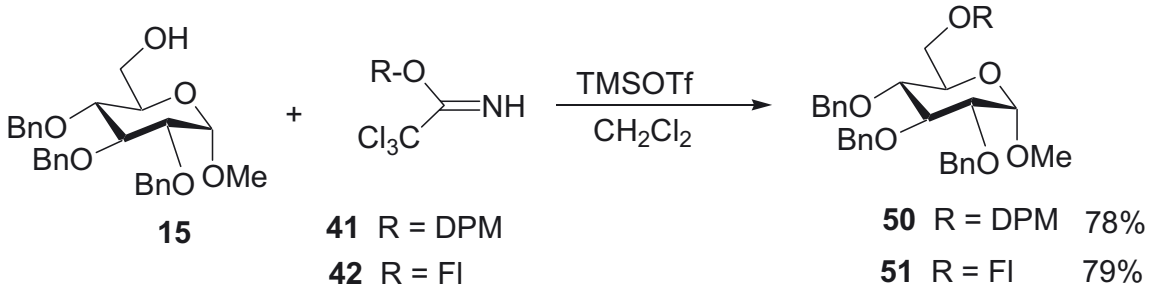
Cholesteryl ether derivatives **48** and **49** were synthesized through etherification reaction between trichloroacetimidates **41**, **42** as donor and cholesterol (**12**) as acceptor using TMSOTf as promoter. The structure of **49** was established through the ^{1}H NMR spectrum [ι♯ 0.64-2.40 (m, cholesterol), 3.40 (m, CH), 5.22 (d, CH), 5.60 (s, CH), 7.22-7.72 (m, Ar-H)].



Scheme 35

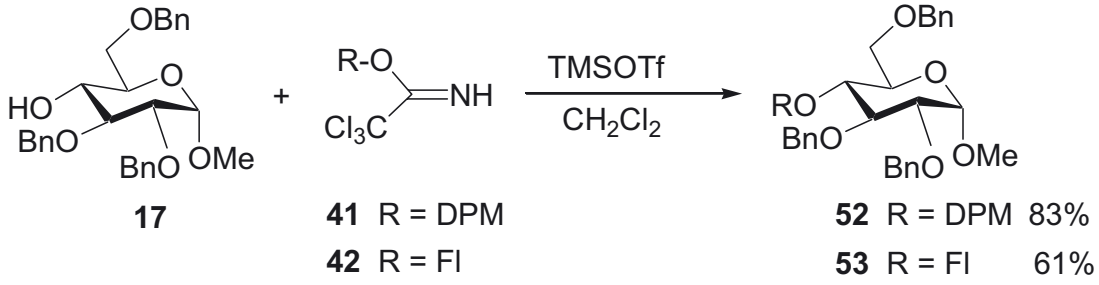
A successful multistep synthesis of complex oligosaccharide structures requires an appropriate protecting group strategy. Generally, the presence of three or more hydroxyl groups in each sugar residue necessitates the protection of those hydroxyl groups which are not involved in the glycosylation step.

In carbohydrate chemistry, protecting groups are distinguished as either temporary or permanent. In oligosaccharide synthesis some hydroxyl groups need to be selectively protected in a different manner (temporary) than others (permanent) so that they can be deprotected in a desired intermediate and made available for the subsequent glycosylation. For our study, the diphenylmethyl (DPM) protecting group has been used for the protection of hydroxyl groups; a consequence of the extensive use of the benzyl group. The synthesis of DPM ethers of primary groups in partially protected carbohydrates has been successfully carried out. Thus reaction of **41** and **42** with the *O*-6 unprotected glucoside **15**[106] gave **50** and **51**, respectively (Scheme 36).



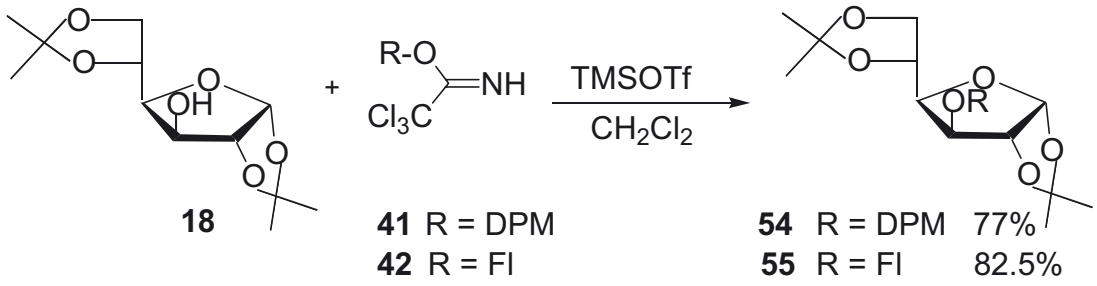
Scheme 36

Similarily, the etherification of secondary hydroxyl groups in various types of partially protected carbohydrates such as *O*-4-unprotected glucoside **17**[107] has been carried out by the reaction with trichloroacetimidates **41** and **42** to give **52** and **53**, respectively (Scheme 37).



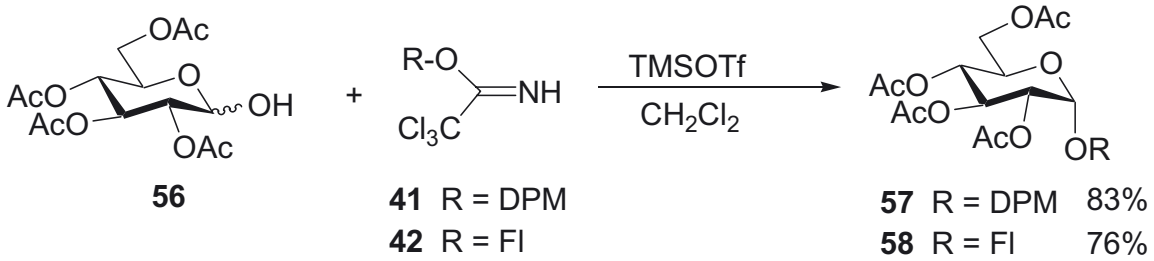
Scheme 37

Also, 1:2,5:6-di-*O*-isopropylidene-ζ-D-glucofuranose[108] was reacted with **41** and **42** in the presence of TMSOTf as promoter to afford the corresponding ethers **54** and **55** (Scheme 38). The introductions of the DPM and Fl group were confirmed by the presence of the anticipated signals for the DPM and Fl groups in their ^{1}H NMR spectra.



Scheme 38

The introduction of DPM and Fl on the anomeric hydroxyl group of 2,3,4,6-tetra-*O*-acetyl-ζ,η-glucose (**56**)[141] gave the corresponding ethers **57** and **58,** and the Fl on mannose derivative **59**[142] gave **60** in high yield (Scheme 39). The ζ-configuration was assigned for these derivatives on the basis of their spectral data [**57**, ι = 5.15 (d, $J_{1,2}$ = 3.7 Hz, 1-H), 94.3 (C-1); **58**, ι = 5.30 (d, $J_{1,2}$ = 3.7 Hz, 1-H), 95.0 (C-1)].



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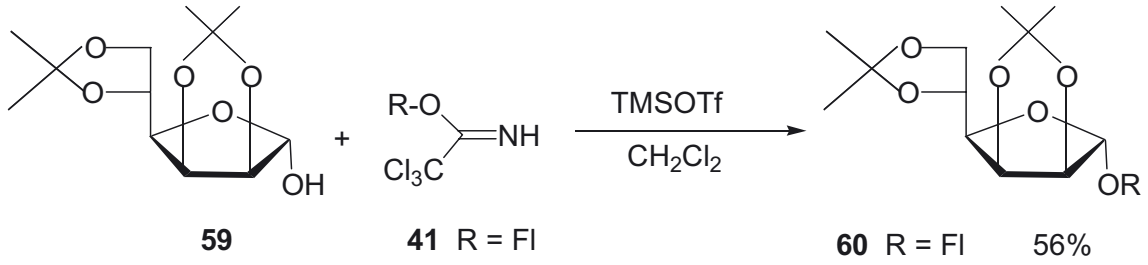
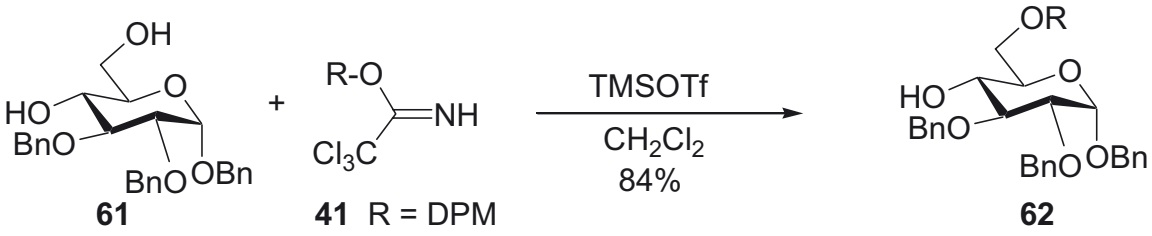


59 **41** R = Fl **60** R = Fl 56%

Scheme 39

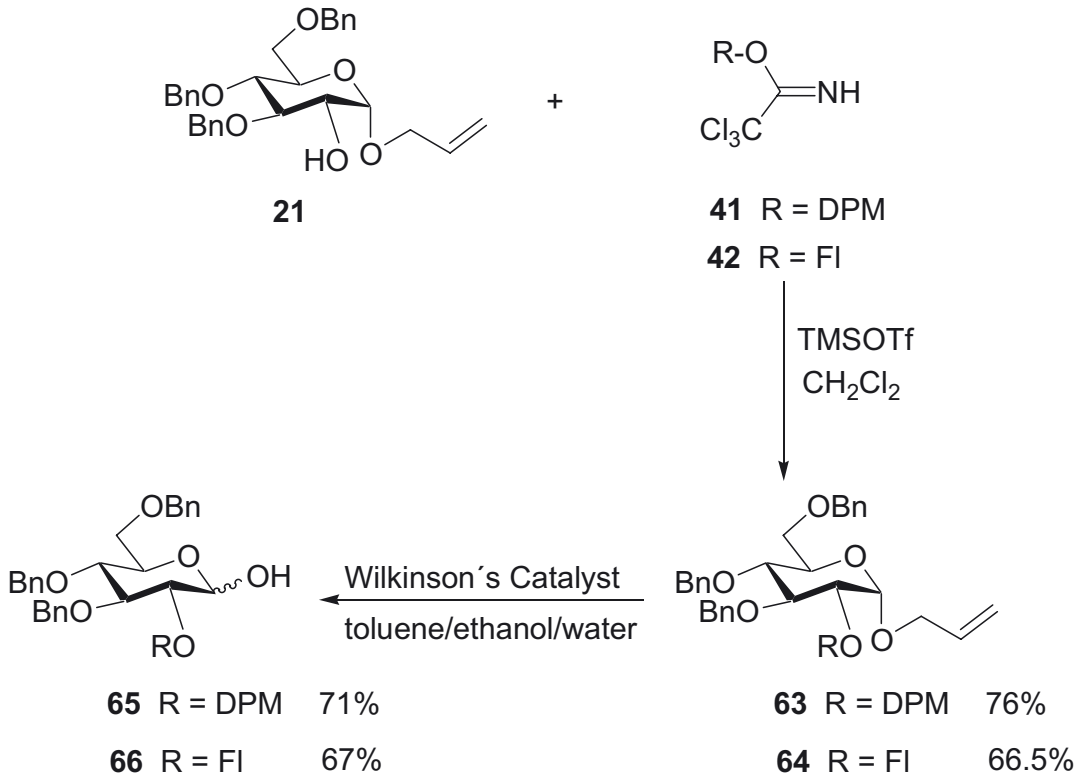
When the trichloroacetimidate **41** was reacted with a partially protected glucose such as 1,2,3-tri-*O*-benzyl-ζ-D-glucose (**61**)[143] under similar reaction conditions, the DPM was introduced on position 6 to give **62** according to the relative reactivity of the hydroxy (6-OH >>3-OH >2-OH > 4-OH) groups in sugars[144] (Scheme 40).



61 **41** R = DPM **62**

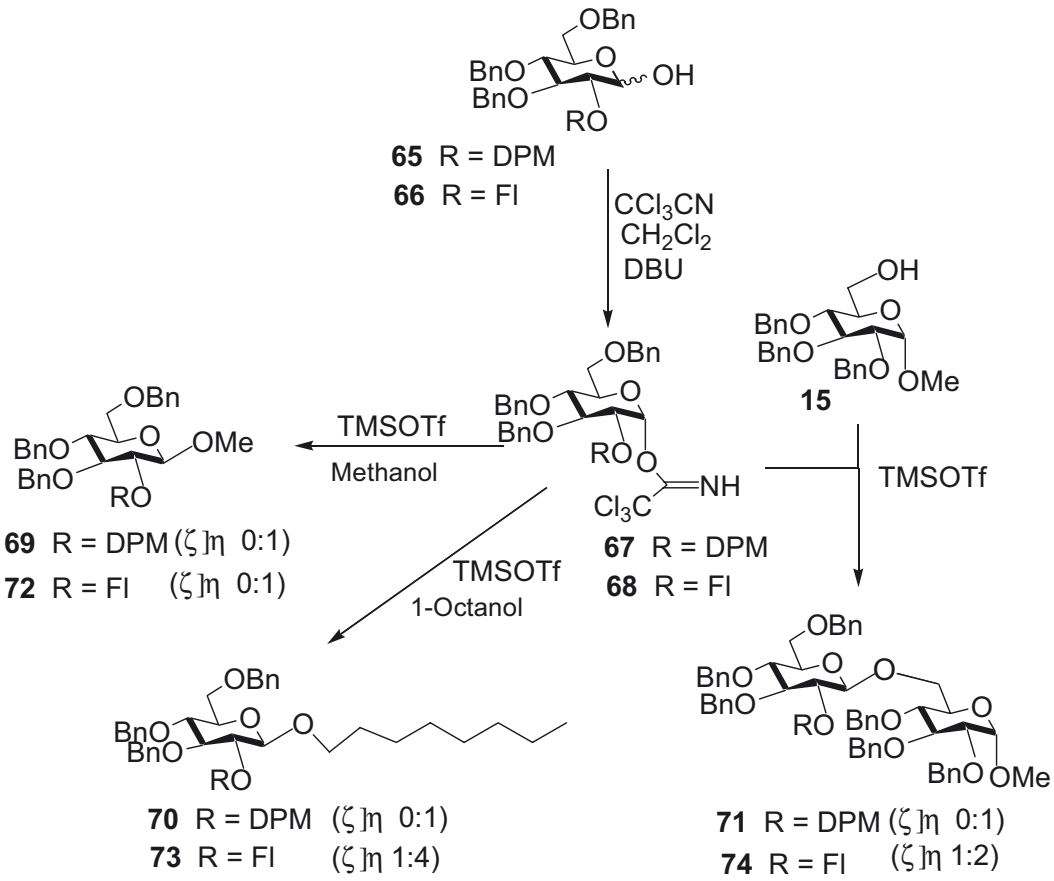
Scheme 40

The stereoselectivity of the glycosyl bond formation is a subject which is still attracting many investigators. In this respect, it became interesting to study the effect of the DPM and Fl group on the stereoselectivity during the glycosylation reaction. The first step of this strategy is the synthesis of *O*-2-DPM/Fl-glucose derivatives by the reaction of trichloroacetimidates **41** and **42** with allyl 3,4,6-tri-*O*-benzyl-ζ-D-glucopyranoside (**21**)[109] to afford **63** and **64**, respectively, in high yields [^{1}H NMR of **63**: ι = 4.69 (d, $J_{1,2}$ = 3.5 Hz, 1-H); **64**: ι = 4.31 (d, $J_{1,2}$ = 2.9 Hz, 1-H)]. Deallylation of *O*-1 in **63** and **64** using Wilkinson´s catalyst $(Ph_3P)_3RhCl$ gave **65** and **66**, respectively (Scheme 41).



Scheme 41

Activation of the anomeric center in **65** and **66** by reaction with trichloroacetonitrile in presence of DBU as a catalyst gave the corresponding trichloroacetimidates **67** and **68**. Glycosylation of methyl and octyl alcohols as well as the glycosyl acceptor **15** with the DPM-trichloroacetimidate **67** gave exclusively the corresponding η-glucosides **69**, **70** and **71** in good yields without detection of the ζ-anomers. However, the analogues with Fl group gave with the same acceptors, the respective η-glucosides **72**, **73** and **74** predominantly (Scheme 42), but accompanied by the respective ζ-glucoside whose ratio was dependent on the structure of the acceptor.



Scheme 42

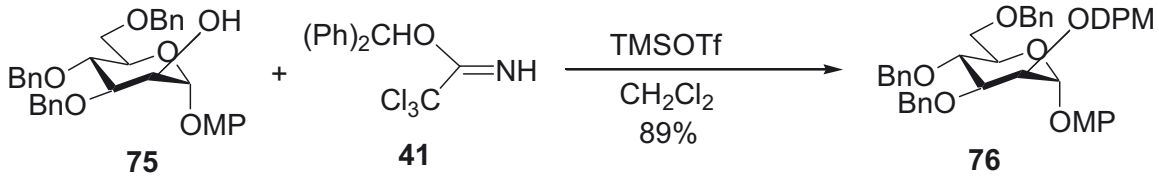
In conclusion, the presence of the DPM group on *O*-2 of D-glucosyl donors is recommended to give stereoselectively the η-anomers without contamination by the respective ζ-anomers. These results can be explained to be due to the steric effect of the DPM group leading to the attack of the acceptor from the η-side. The steric effect of the DPM group seems to be more pronounced than the one of the fluorenyl group, which has a central ring connecting the two phenyl groups and benzyl groups. For instance, poor anomeric η]ζ ratio 1:0.1-2 was observed when we had fluorenyl and benzyl groups on *O*-2 of the glucosyl donors. Moreover, during the glucosidation reactions the steric effect operates more effectively than the neighboring group participation. For example, glycosyl donor, which has acetyl group on *O*-2, resulted in a mixture (η]ζ ratio, 1:0-0.5).

The η-linked mannopyranoside unit has been found in various natural sources as *Hyriopsis Schlegeli* glycosphingolipid,[145,146] the fungal metabolite deacetyl caloproside,[147,148] complex carbohydrate antibiotics such as Everninomycins,[149] a number of serotypes of the capsular polysaccharides Klebsiella[150] and the bacterial *O*-antigen of Salmonella serogroups.[151, 152] Furthermore important is its incorporation in the pentasaccharide core structure (Fig. 1) which is a common feature in the *N*-linked glycoproteins that are attached to oligomeric chains.[153-156] One of them is 4GlNAcη8 ⟶ 4GlNAc-Asn (Fig.1). Consequently, a key step for the synthesis of such a core region is the availability of a precursor capable of generating a η-mannosidic linkage that can be linked to the 4-position of an *N*-acetyl-D-glucopyranoside derivative.

Fig.1

One of the most difficult tasks is the synthesis of such *cis*-η-D-mannopyranoside linkages. This led to the development of less direct routes such as the reduction of uloses,[157] inversion of η-glucosides,[158] anomeric inversion of ζ-mannosides,[159] direct *O*-alkylation of pyranoses,[160] preattachment of the aglycon by means of suitable tether to the *O*-2 position of mannosyl donors.[161-165] However, the selectivity towards the secondary position of sugar derivatives was less satisfactory. More promising results were reported[166] by using benzylsulfonyl group on *O*-2, but it did not find wide application because of the low reactivity of the donors employed. Despite the tremendous progress shown above for constructing η-D-mannopyranosidic linkages, it still remains a challenging synthetic problem. In our study, promising results from the combination of the DPM group on *O*-2 with the activation of the anomeric position by a trichloroacetimidate group or a 2-thio-nitrogen heterocycle have been

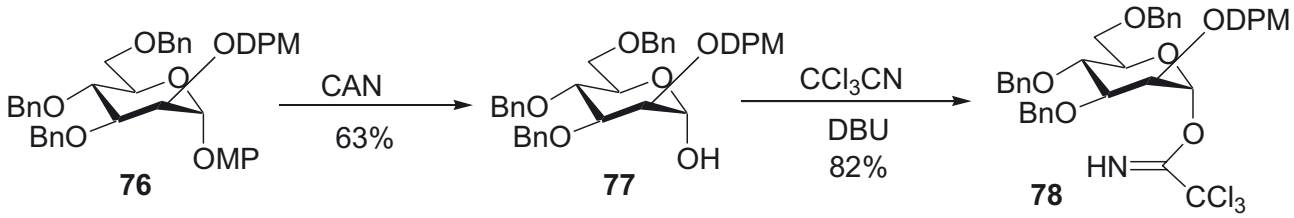
achieved. The first step of this strategy is the synthesis of 4-methoxyphenyl 3,4,6-tri-*O*-benzyl-*O*-2-diphenylmethyl-ζ-D-mannopyrnoside (**76**) which was achieved in high yield (89%) by the reaction of trichloroacetimidate **41** with mannose derivative **75**[167] (Scheme 43).



Scheme 43

The 4-methoxyphenyl (MP) group at the anomeric carbon was removed by treatment with ammonium cerium (IV) nitrate in a mixture of acetonitrile/water, 4:1 at 0 °C to afford **77** in 63% yield. The ^{1}H NMR spectrum showed the disappearance of the singlet of the OCH_3 of the MP group. The ζ-configuration of the anomeric proton could be assigned from the ^{1}H NMR data (ι = 5.34 (d, $J_{1,2}$ = 1.5 Hz, 1-H).

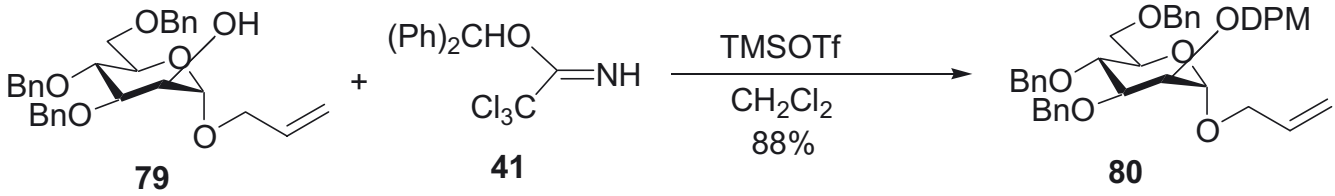
Treatment of **77** with trichloroacetonitrile in the presence of catalytic amounts of DBU afforded the corresponding trichloroacetimidate **78** in 82% (Scheme 44). Its ζ-configuration was indicated by the appearance of the anomeric proton as a doublet at ι = 6.78 (d, $J_{1,2}$ = 1.9 Hz, 1-H). The introduction of the trichloroacetimidate group was confirmed by the presence in its ^{1}H NMR spectrum, a singlet (D_2O exchangeable) at 8.81 corresponding to NH group.



Scheme 44

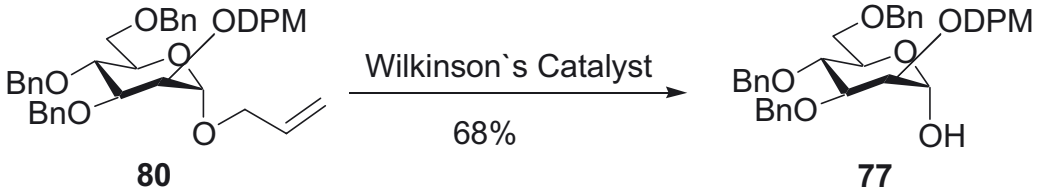
Alternatively, compound **77** could be synthesized in 7 steps from mannose by another synthetic route. The allyl protecting group at the anomeric position of the mannose

was used. The trichloroacetimidate **41** was reacted with allyl 3,4,6-tri-*O*-benzyl-ζ-D-mannopyranoside (**79**)[168] to afford **80** in high yield (Scheme 45). The ζ-configuration of **80** was indicated by the appearance of the anomeric proton as doublet at ι 4.92 with coupling constant value of $J_{1,2}$ = 1.5 Hz.



Scheme 45

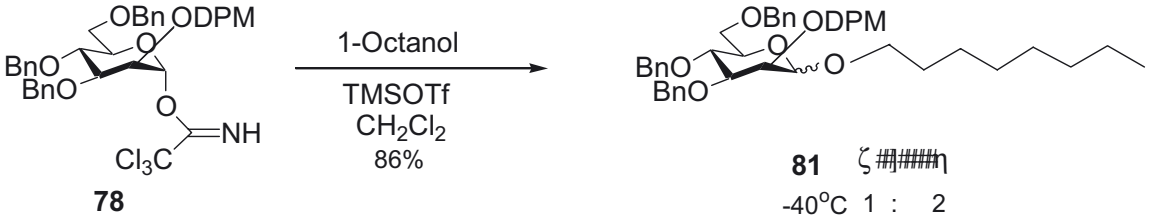
The deallylation of *O*-1 in **80** using Wilkinson´s catalyst $(Ph_3P)_3RhCl$ gave **77** (Scheme 46). The structure of **77** was established through ^{1}H NMR which reveals the presence of OH at ι = 1.96 ppm and the absence of the allyl group, thus confirming the proposed structure.



Scheme 46

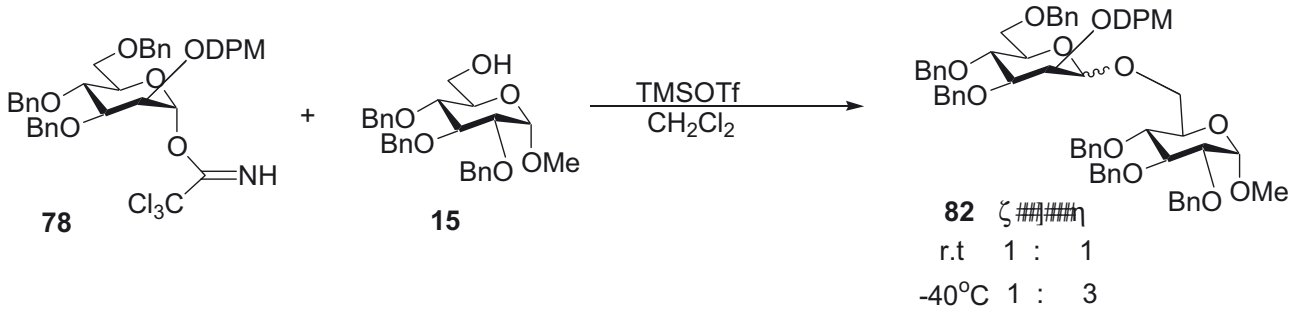
The coupling of the trichloroacetimidate donor **78** with n-octanol as acceptor was carried out in dry dichloromethane at room temperature and -40 °C in presence of TMSOTf to afford the desired **81** in 86% yield (Scheme 47). The ζ:η ratio in **81** was found to be dependent on the temperature at which the reaction was carried out. At room temperature the ratio was 1:1 and at -40 °C it was 1:2. The anomers could be separated by flash column chromatography. The ζ- and η-configuration of the anomers could be assigned from the coupling constant values of $J_{1CH,1H}$ of the

anomeric protons. The $J_{1CH,1H}$ value of the ζ-anomer = 170.3 Hz and for η-anomer = 152.6 Hz, respectively.[165]



Scheme 47

By the same coupling procedure, the acceptor derivative **15**[106] was treated with the trichloroacetimidate donor **78** to afford **82** in 76% yield and the ζ:η ratio was 1:1 at room temperature and 1:3 at -40 °C. The coupling constants of $J_{1CH,1H}$ for the ζ-anomer are 171.6 Hz and for η-anomer are 155.1 Hz.[165]

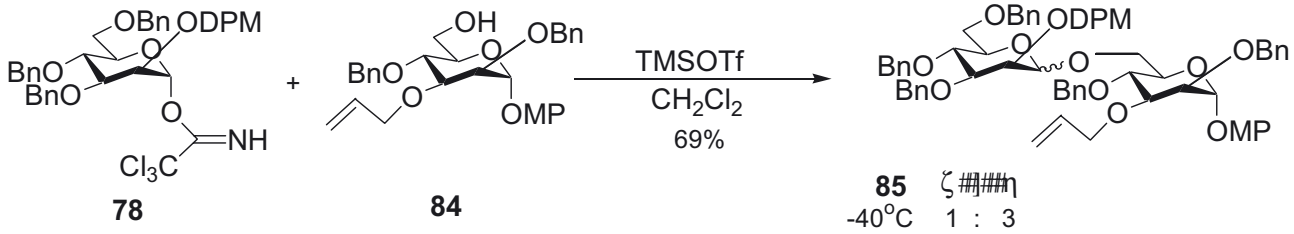


Scheme 48

The required *O*-6-unprotected acceptor **84** was obtained in high yield through a reductive benzylidene opening of compound **83**[169] using $LiAlH_4$ in ether.

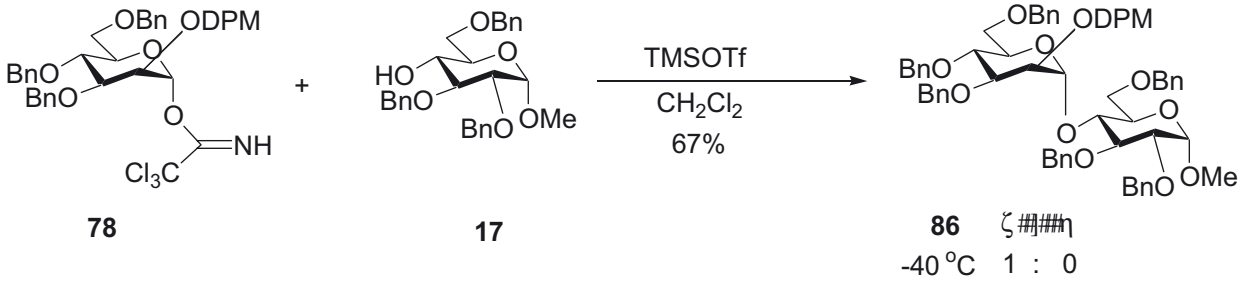
Scheme 49

Reaction of trichloroacetimidate **78** with **84** at -40 °C in the presence TMSOTf as a catalyst and under the same conditions gave **85** (ζ6η mixture, 1:3) (Scheme 50). The ζ- and η-anomer of the anomeric mixture could be assigned from the coupling constant values of $J_{1CH,1H}$. The $J_{1CH,1H}$ value of the ζ-anomer = 170.5 Hz, and for η-anomer = 154.3 Hz, respectively.



Scheme 50

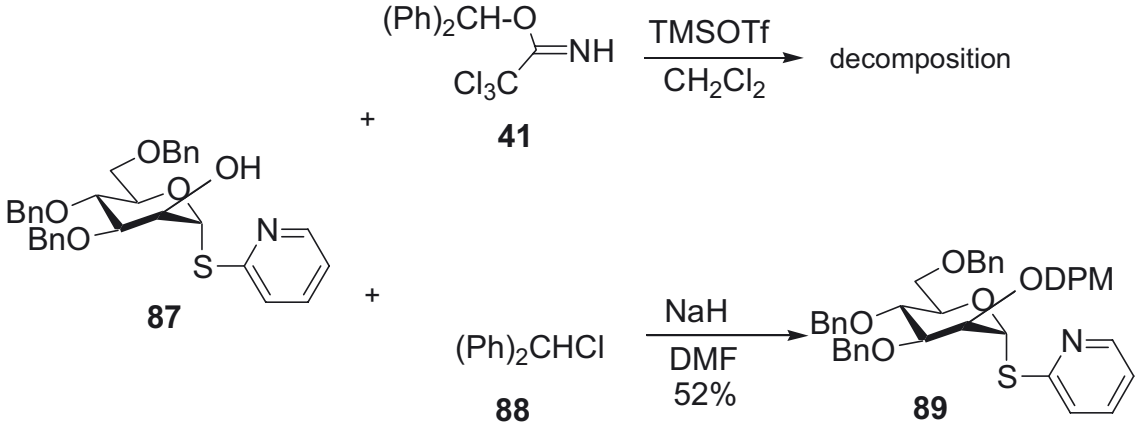
On the other hand, reaction of trichloroacetimidate **78** with the 4-OH free glucose derivative **17**[107] gave **86** in 67% yield (Scheme 51). The ζ-configuration of **86** was indicated by the appearance of the anomeric proton as a doublet at ι 5.41 with coupling constant value of $J_{1,2}$ = 1.1 Hz, and the $J_{1CH,1H}$ value of the ζ-anomer = 172.3 Hz.



Scheme 51

Activation of the anomeric center by a thio group instead of the trichloroacetimidate was also carried out. Thus, the target donor **89** was designed for this study. Thus, treatment of pyridin-2-yl 3,4,6-tri-*O*-benzyl-1-thio4ζ-D-mannopyranoside[165] (**87**) with diphenymethyl trichloroacetimidate (**41**) in the presence of a catalytic amount of

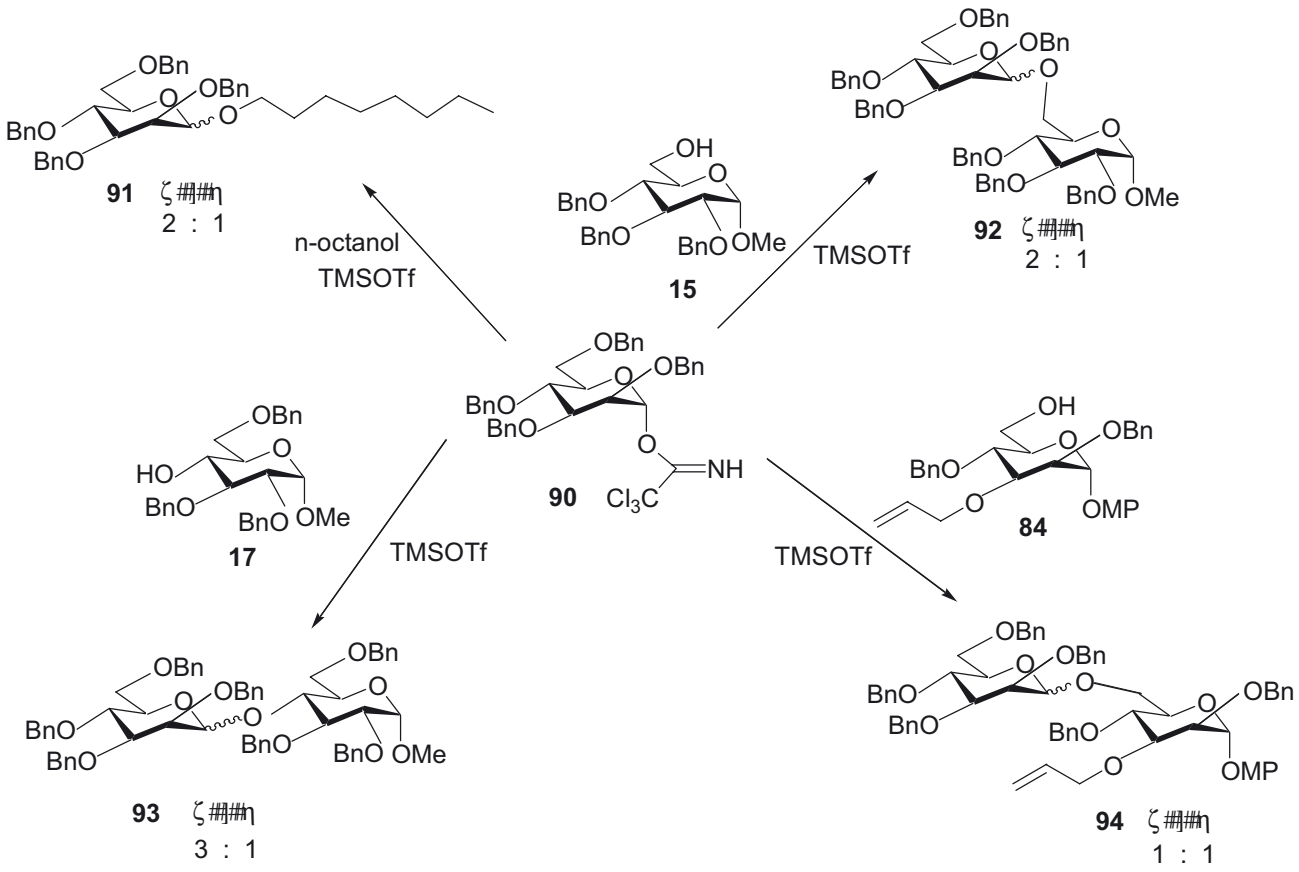
TMSOTf under argon at -40 °C, was carried out, however the expected product **89** was decomposed during the reaction. On the other hand, the DPM group could be successfully introduced on **87** by reaction with chlorodiphenylmethane (**88**) in the presence of NaH as base to give **89** (Scheme 52). The structure of **89** was confirmed by studying its ^{1}H NMR spectrum, which showed the [CH(Ph)$_2$] as a singlet at ι = 5.85 and#he anomeric proton as a doublet (ι = 6.56 ppm, $J_{1,2}$ = 1.5 Hz).



Scheme 52

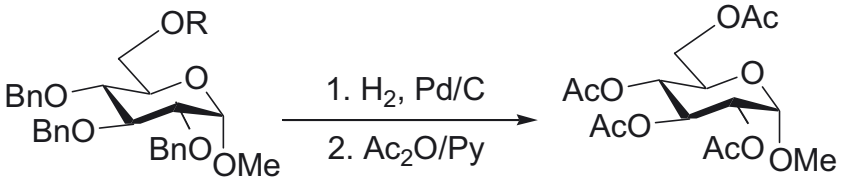
By using the same coupling procedure, the acceptor derivative **15** was treated with thio mannose derivative **89** as donor in presence of *N*-iodosuccinimide (NIS) to afford **82** in 56% yield and ζ6η ratio 1:3 at -40 °C.

In this respect, it became interesting to study the effect of the benzyl group on the stereoselectivity during the glycosylation reactions. Towards this study the glycosylation of various glycosyl acceptors **15**, **17**, **84** with **90**,[170] which has a benzyl group on *O*-2, gave the corresponding products **91**-**94**,[171] in good yields (Scheme 53). It was observed that sterically demanding 2-*O*-substituents at mannopyranosyl donors rather enforce than inhibit η-mannopyranoside formation because bulky substituents at 2-*O* support generation of a twist boat intermediate which should be preferentially attacked from the η-side.[169]



Scheme 53

Moreover, the DPM and Fl groups can be readily deprotected by hydrogenation as shown by the examples **50** and **51** which upon deprotection and acetylation gave **95**.[172] Also disaccharides **71** and **74** gave **96**[25] (Scheme 54).

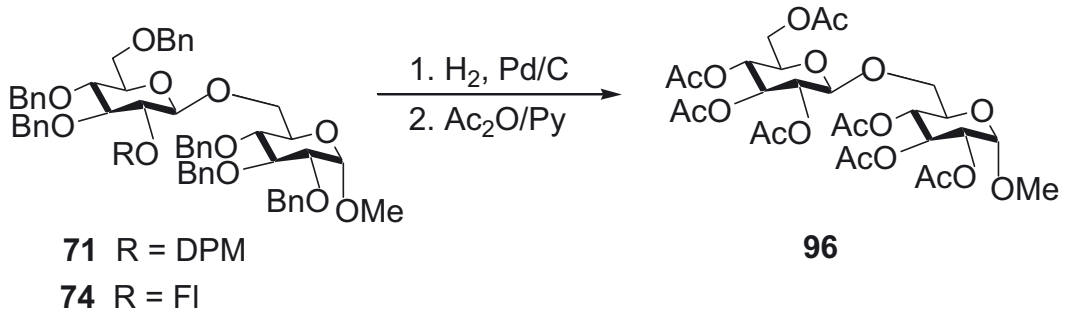


50 R = DPM

51 R = Fl

95

Also



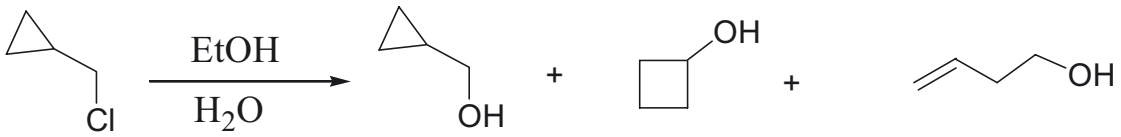
71 R = DPM
74 R = Fl

96

Scheme 54

2.4 Generation of the cyclopropylmethyl cation from the trichloroacetimidate of cyclopropylmethanol synthesis of cyclopropylmethyl and cyclobutyl ethers.

A considerable amount of work has been devoted towards the search for *C-C* participation in the cyclopropylmethyl systems.[173-177] Thus, the rate of solvolysis of primary cyclopropylmethyl systems is enhanced because of participation by the ω# bonds of the ring[172-178] in the symmetrically stabilized cyclopropylmethyl cation.[179-181] A similar participation of ω bonds has been also given for the ion formed from the solvolysis of secondary cyclobutyl substrates which leads to the same products resulting from the cyclopropylmethyl substrates. The rearrangement may take place *via* a nonplanar cyclobutyl cation intermediate or transition state. The products from such solvolysis often include almost equal amounts of the cyclopropylmethyl **98** and the respective cyclobutyl **99** in addition to a minor amount (5%) of the homoallyl compounds **100** (Scheme 55).[182]

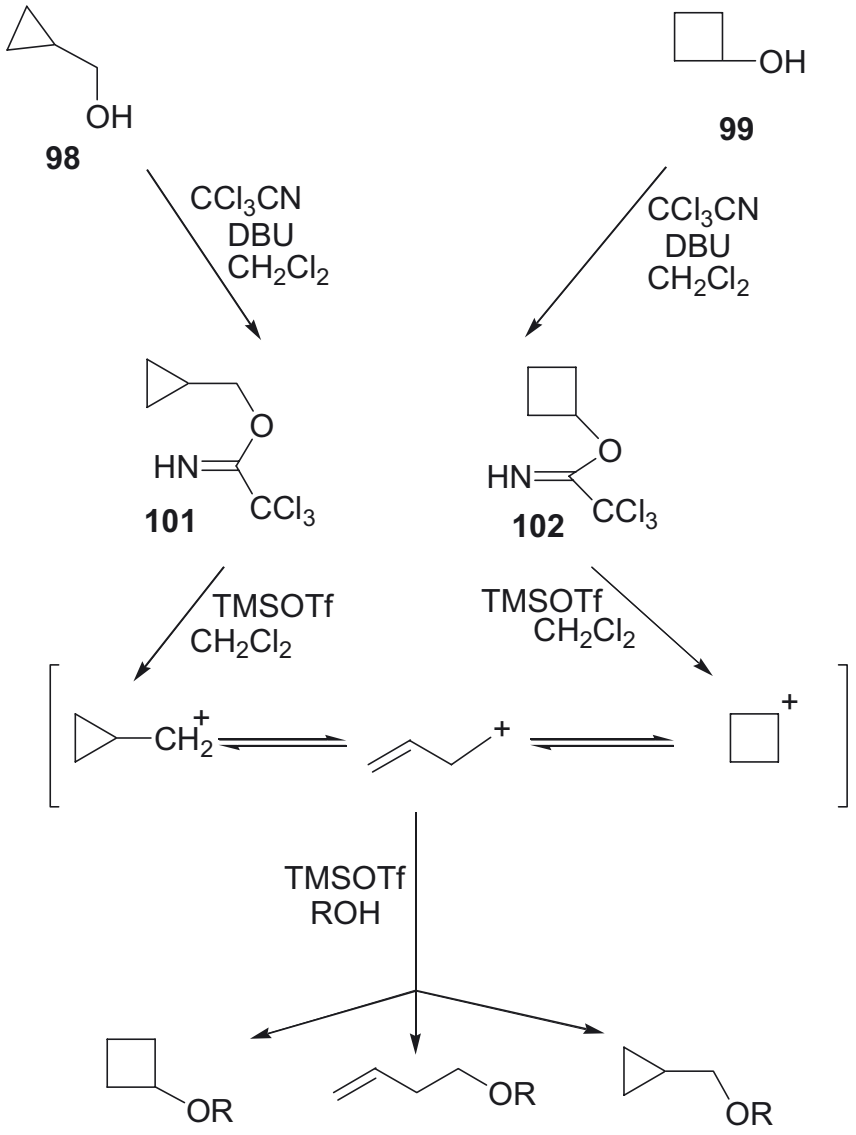


97 **98** **99** **100**

Scheme 55

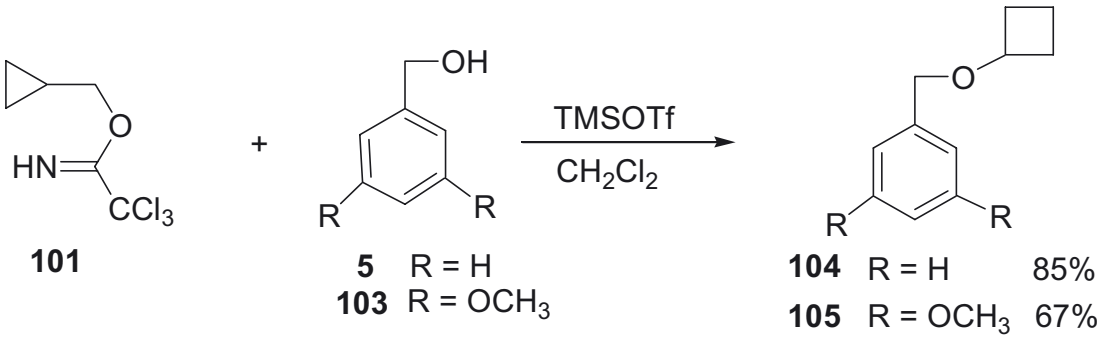
The formation of such products can be rationalized by assuming a type of nonclassical homoallyl-cyclopropylmethyl-cyclobutyl cation as the reactive intermediates.[183] Such rearrangement has been achieved with high stereoselectivity.[184-186] Factors such as the nucleophilicity of the medium may play a role in this respect. The rearrangement of the respective radical intermediate attracted also the attention.[187-193] Having the above aspects in mind and continuing the work on the glycosyl bond formation utilizing the trichloroacetimidate procedure,[102-104] this part describes the reaction of cyclopropylmethyl and cyclobutyl trichloroacetimidates with hydroxyl groups of varied nucleophilicities in order to investigate its use as alkylating agent under mildly acidic condition and to shed some light on the mechanism of the trichloroacetimidate procedure in forming glycosyl bonds. Thus, it has proved to be a useful precursor for the synthesis of cyclopropylmethyl (Cpm) and cyclobutyl (Cb) ethers (Scheme 56).

The required cyclopropylmethyl trichloroacetimidate (**101**) was prepared in 92% yield by the reaction of cyclopropylmethanol (**98**) with trichloroacetonitrile. The reaction has been activated by a catalytic amount of DBU (Scheme 56). The trichloroacetimidate **101** can be stored without any problem and its structure was confirmed by ^{1}H NMR spectroscopy [ι♯ 0.38-1.32 (m, 5 H, cyclopropyl), 4.13 (d, *J* = 7.1 Hz, 2 H, CH_2), 8.23 (brs, 1 H, NH)]. The cyclopropylmethyl cation has been found to be formed readily from the trichloroacetimidate **101** in the presence of trimethylsilyltrifluoromethanesulfonate (TMSOTf).



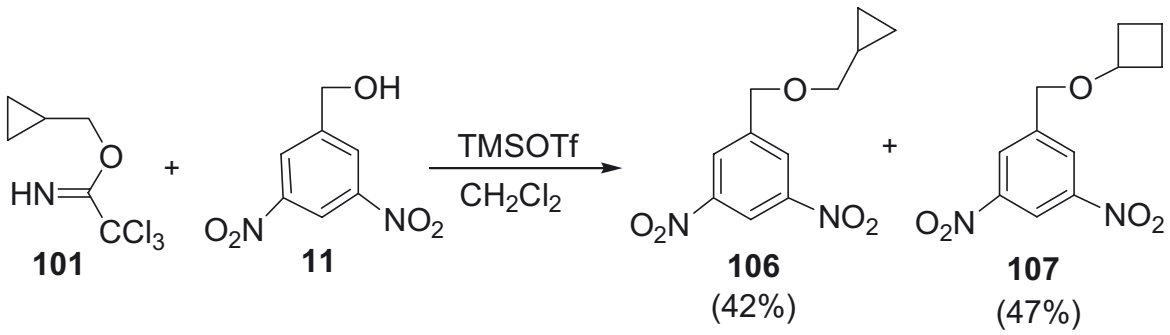
Scheme 56

Thus, under such catalysis reaction of **101** with benzyl alcohol (**5**) and its 3,5-dimethoxy derivative **103**, the respective cyclobutyl ethers **104**[194] and **105** were the only isolated products. The acidic condition in this synthesis could be some times preferable over the base catalysis normally used for alkylation processes such as in preparation of **104** from benzyl chloride and cyclobutanol[194] (Scheme 57).



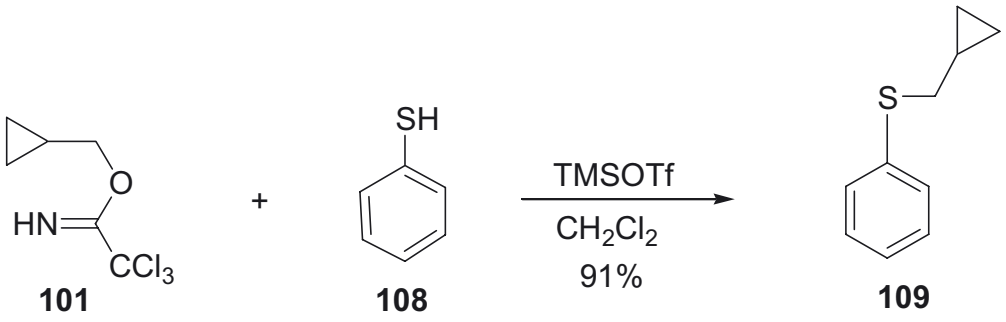
Scheme 57

When two nitro groups are present on the benzyl alcohol such as in 3,5-dinitrobenzyl alcohol (**11)**, both the cyclopropylmethyl **106** and cyclobutyl derivatives **107** were obtained. The cyclopropylmethyl and cyclobutyl ethers can be readily identified by ^{1}H NMR spectroscopy where the former group appeared at ι # #0.28-1.15 ppm and the cyclobutyl group at ι = 1.55-2.30 ppm, in accordance with the reported spectral data for respective ethers[195] (Scheme 58).



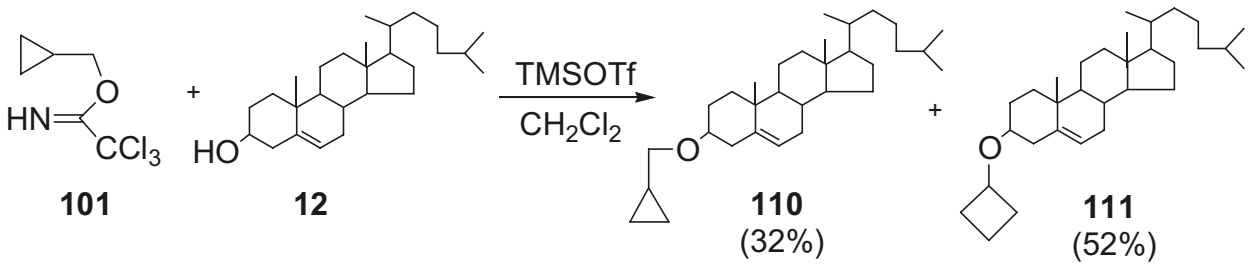
Scheme 58

On the other hand, the thiophenol (**108**) gave under similar conditions the cyclopropylmethyl derivative[196] **109** as the only isolated product in high yield (91%) (Scheme 59).



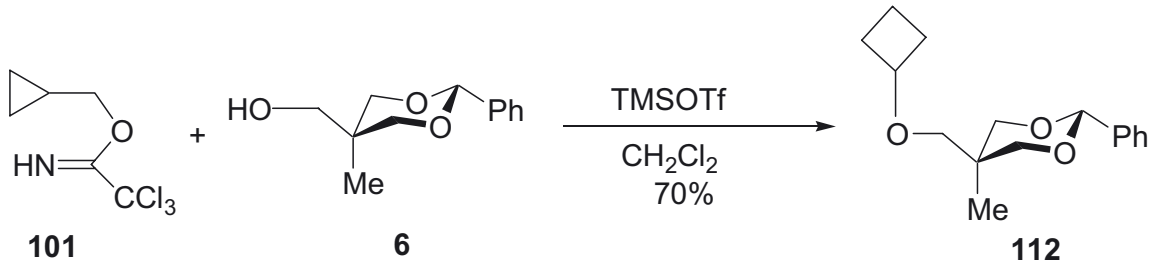
Scheme 59

Applying the same reaction on cholesterole **12** gave the two products, cholesterolyl cyclopropylmethyl ether (**110**) and cholesterolyl cyclobutyl ether (**111**) (Scheme 60).



Scheme 60

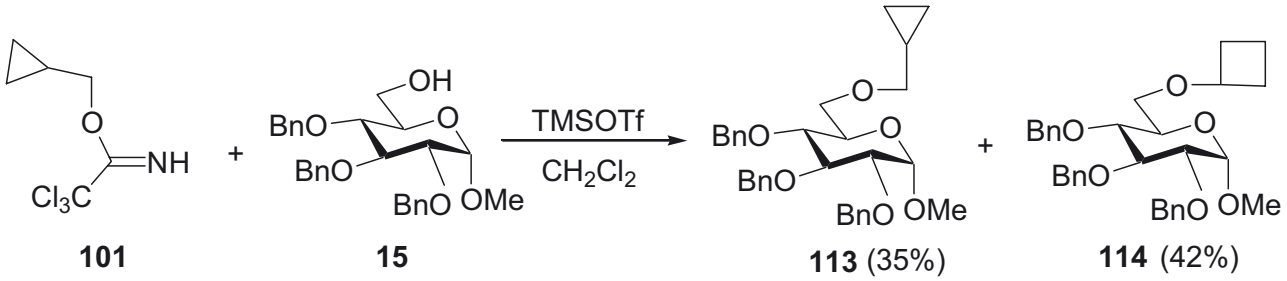
5-Methyl-2-phenyl-5-cyclobutyl-1,3-dioxane (**112**) was synthesized through a reaction between acceptor **6**[105] and trichloroacetimidate **101** whereby the cyclobutyl derivative was only isolated in good yield (70%) (Scheme 61).



Scheme 61

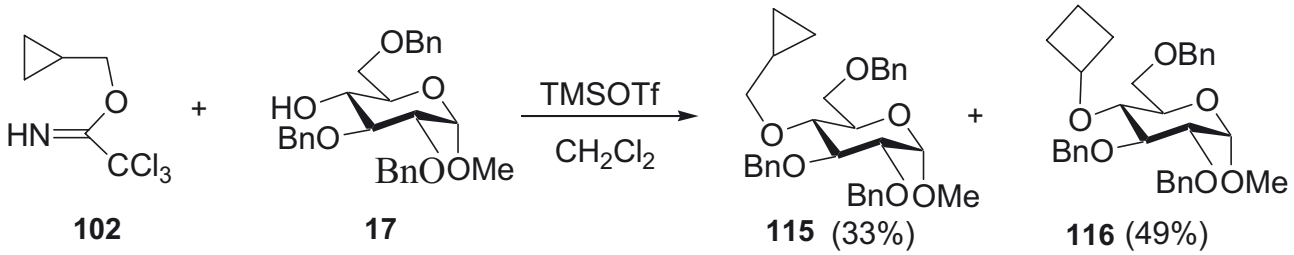
The direct reaction of secondary hydroxyl groups in various types of partially protected carbohydrates has been also successfully carried out (Scheme 62). Thus

reaction of trichloroacetimidate **101** with the *O*-6 unprotected glucoside **15**[106] gave the cyclopropylmethyl **113** and the cyclobutyl glucose derivatives **114**.



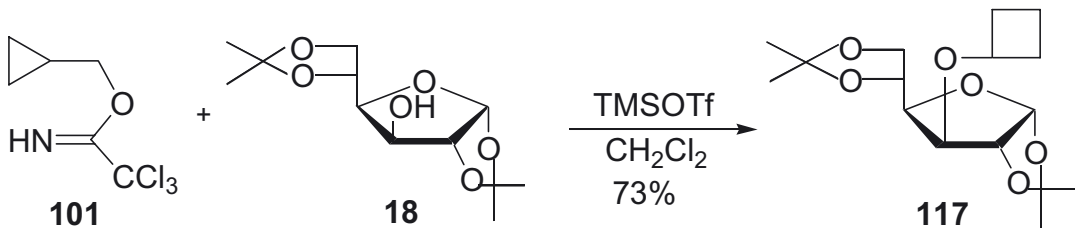
Scheme 62

Again, the 4-OH free glucose derivative **17**[107] was submitted to the alkylation with the trichloroacetimidate donor **101**. The above conditions for the reaction was the same using dichloromethane as solvent and TMSOTf as catalyst. The two derivatives **115** and **116** were obtained with almost the same ratio as above (Scheme 63).



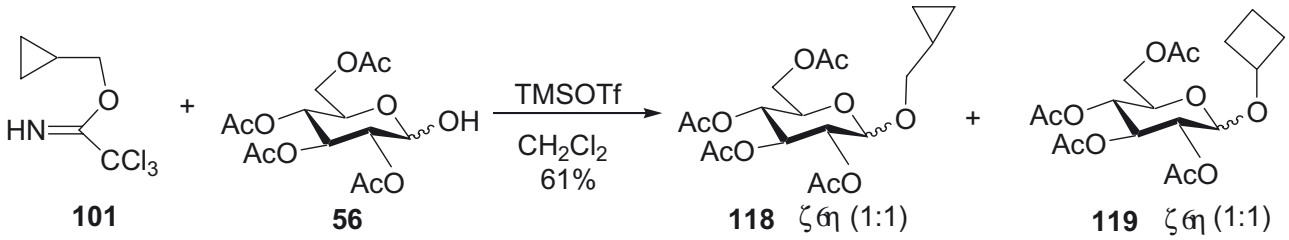
Scheme 63

On the other hand, the etherification of the secondary hydroxyl group in glucofuranose **18**[108] with trichloroacetimidate **101** gave only the respective cyclobutyl derivative **117** (Scheme 64).



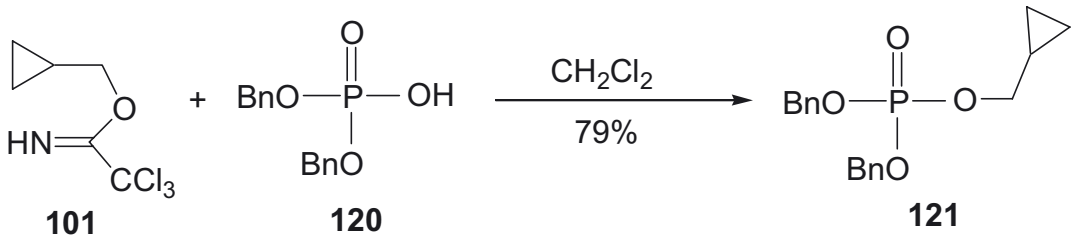
Scheme 64

Under such catalysis, reaction of cyclopropylmethyl trichloroacetimidate (**101**) with the unprotected anomeric hydroxyl group of glucose derivative **56**[141] gave a mixture of the ζ and η anomers of the cyclopropyl **118**[197] and cyclobutyl derivatives **119** (Scheme 65).



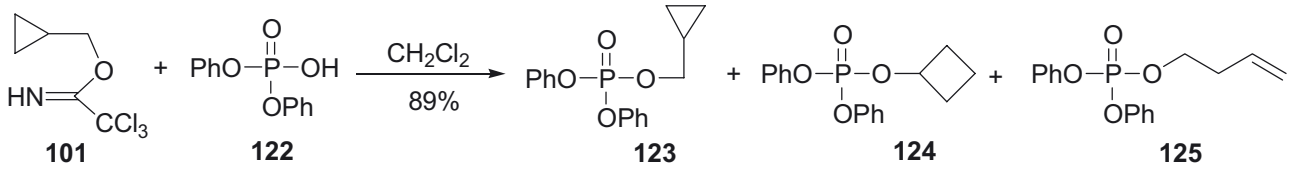
Scheme 65

In this respect, it became interesting to study the acidity effect of the acceptor on the rearrangement during the reaction. The difference in the type of the isolated products was found to be dependent on the acidity of the acceptors. For example, dibenzyl phosphate (**120**), which is a weak acid, gave only the cyclopropylmethyl derivative **121**[198] without any catalyst and the reaction proceeds without rearrangement (Scheme 66).



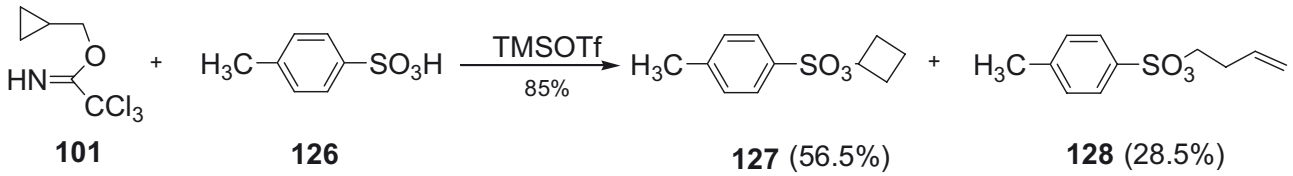
Scheme 66

When the acceptor have slight acidic character such as diphenyl phosphate (**122**), the acidity of the acceptor was found to be sufficient to cause rearrangement of the generated cyclopropylmethyl cation in the reaction. Thus, reaction of **101** with **122** afforded cyclopropylmethyl, cyclobutyl and homoallyl derivatives **123**, **124**[199] and **125** in a ratio of 4:2:1 (Scheme 67).



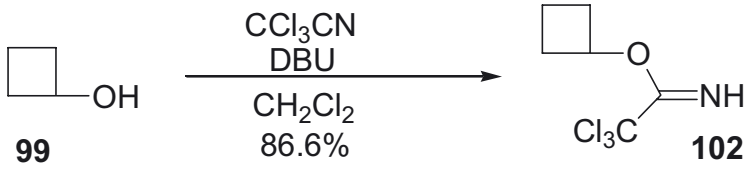
Scheme 67

In the case of the sulfonic acid **126**, where the acidity is higher than in **120** and **122**, the rearrangement during the reaction of **101** with **126** was found to readily take place whereby the cyclobutyl **127**[200] and allyl derivative **128**[201] were formed and no cylopropyl derivative could be detected (Scheme 68).



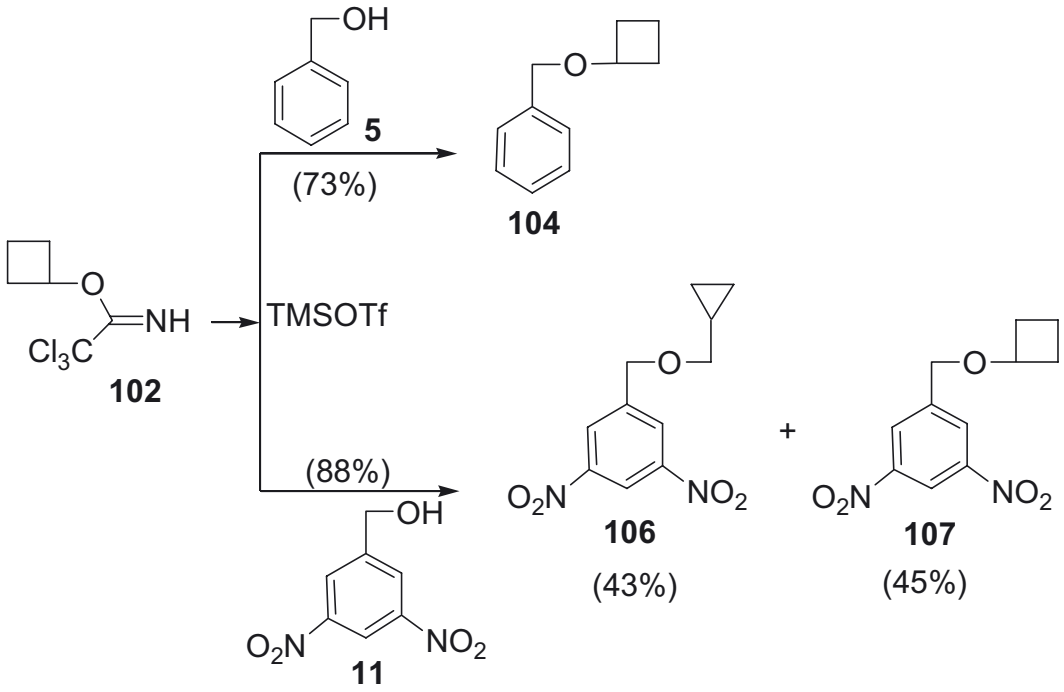
Scheme 68

It will be interesting to investigate whether the cyclobutyl trichloroacetimidate (**102**) will have a similar effect or a different one compared with the cyclopropyl trichloroacetimidate **101**. The required cyclobutyl trichloroacetimidate (**102**) was prepared in 87% yield by the reaction of cyclobutanol (**99**) with trichloroacetonitrile in presence of DBU as catalyst. The product **102** can be identified by ^{1}H NMR spectroscopy where the cyclobutyl group appeared as a multiplet at ι = 1.61-2.40 (m, 6 H, 3 CH_2), 5.12 (m, 1 H, CH), 8.21 (s,1 H, NH).



Scheme 69

The cyclobutyl trichloroacetimidate (**102**) was reacted with benzyl alcohol (**5**), dinitrobenzyl alcohol (**11**) and *O*-6-unprotected glucose derivative **15**, to give the same ratio of the cyclopropyl and cyclobutyl products as those resulting from the reaction with the cyclopropylmethyl trichloroacetimidate (**101**).



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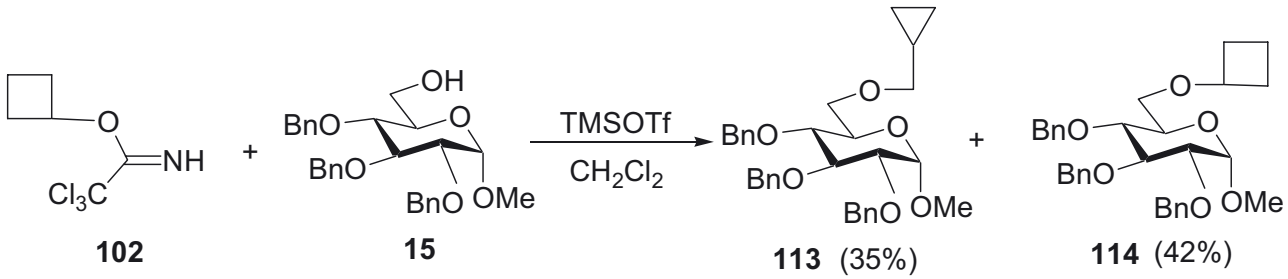
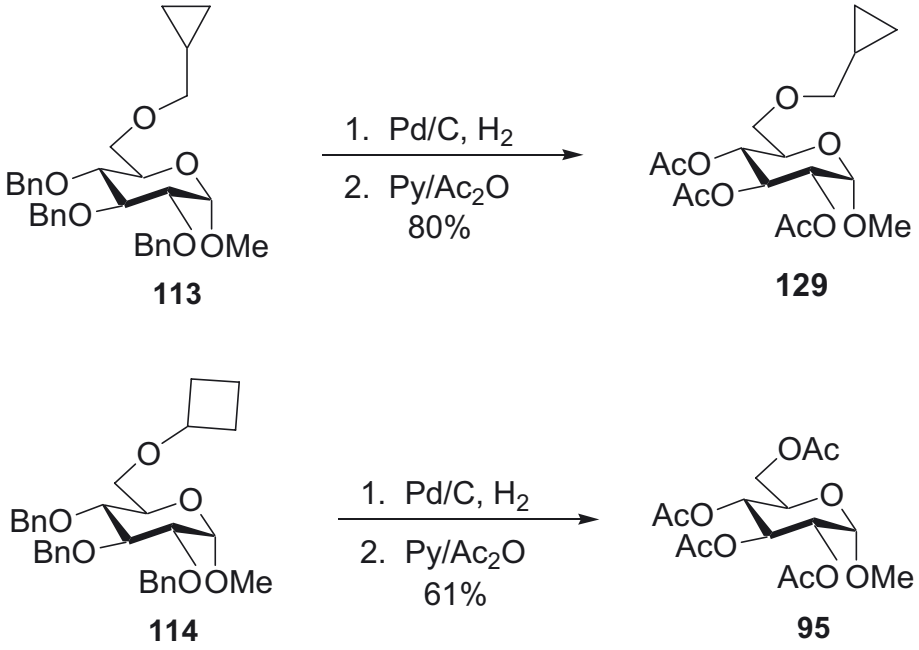


Scheme 70

In order to study the effect of temperature on the ratio of the products of the above reactions, the same reactions with alcohols **5**, **11** and glucose derivative **15** with

trichloroacetimidate **101** and **102** at lower temperature (-40 °C) were carried out. However, almost the same results as above were obtained.

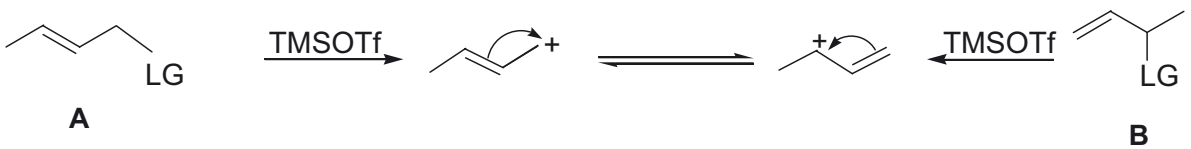
Catalytic hydrogenation of **113** and **114** in the presence of Pd/C and formic acid and subsequent acetylation, led to the cleavage of the cyclobutyl group in addition to the deprotection of benzyl groups from **114** to give **95**[25] whereas the cyclopropylmethyl group was not removed whereby the product was identified as **129** (Scheme 71).



113 **129** **114** **95**

Scheme 71

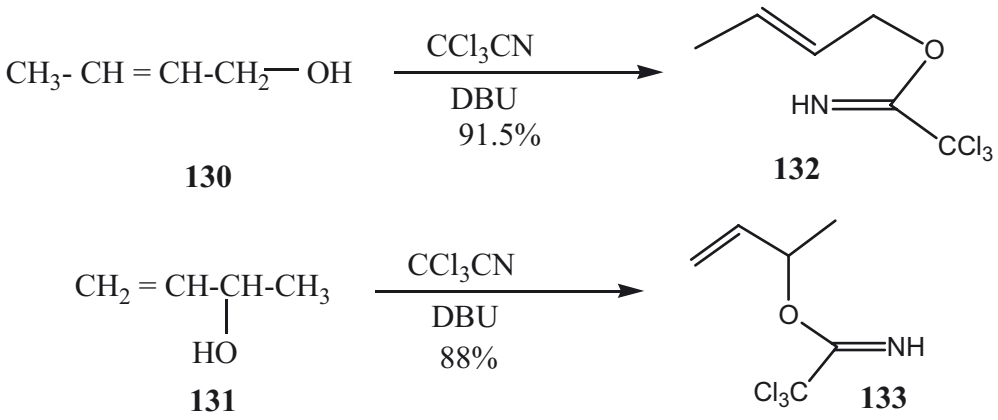
The double bond rearrangement of many unsaturated compounds can take place on treatment with acids.[202] Thus, rearrangement of allyl compounds carrying a leaving group of the type shown in the following scheme may take place in presence of acids *via* carbonium ions, which in presence of alcohol may give two products (Scheme 72).



A **B**

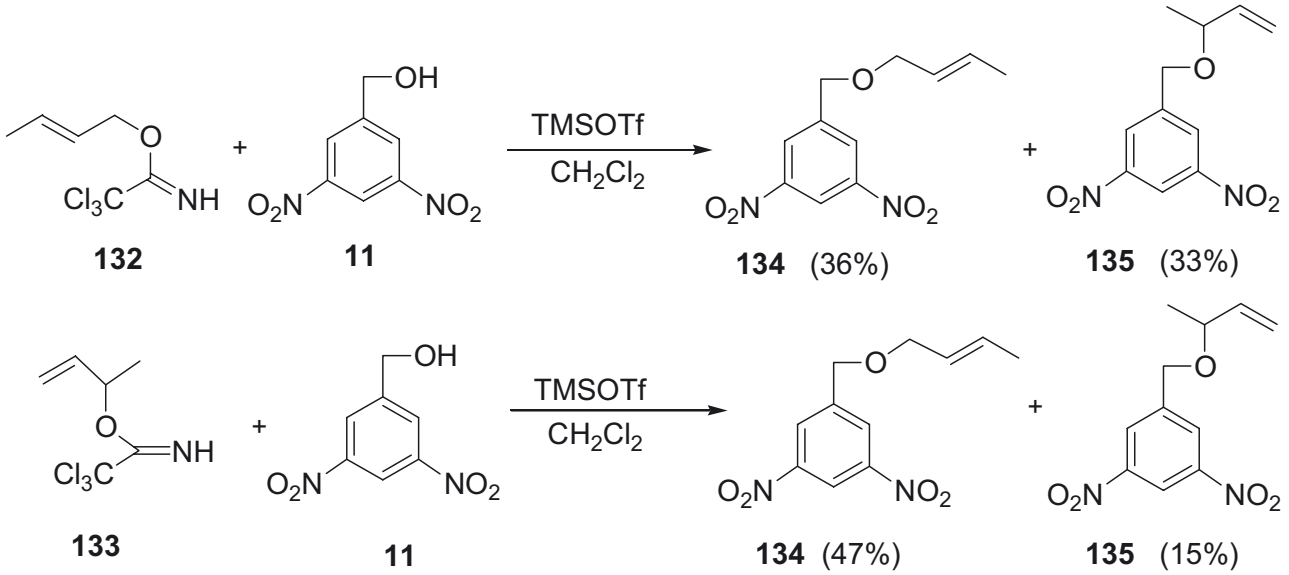
Scheme 72

The *O*-(2-buten-1-yl)trichloroacetimidate (**132**)[138] and *O*-(3-buten-2-yl) trichloroacetimidate (**133**)[138] were prepared in 91.5% and 88% yield, respectively, by the reaction of 2-buten-1-ol (**130**) or 3-buten-2-ol (**131**) with trichloroacetonitrile. The reaction has been activated by catalytic amounts of DBU. The structure of **133** was confirmed by ^{1}H NMR spectroscopy [ι♯ ♯1.41 (d, 3 H, CH_3), 5.14 (dd, 2 H, CH_2), 5.51 (m, 1 H, CH), 5.92 (m, 1 H, CH), 8.31 (brs, 1 H, NH)].



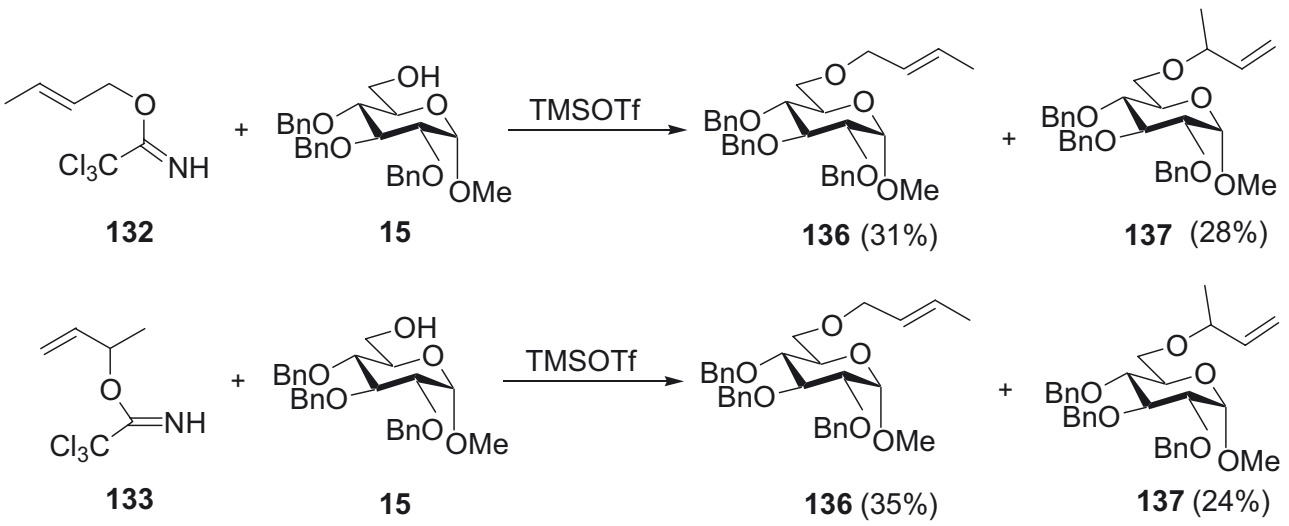
Scheme 73

Thus, reaction of **132** or **133** with 3,5-dinitrobenzyl alcohol (**11**) in the presence of catalytic amount of TMSOTf, gave a mixture of two products **134** and **135** (Scheme 74) which were identified by ^{1}H NMR spectroscopy. The formation of the two types of products can be rationalized by assuming a type of 3-butenyl and 2-butenyl cation as the reactive intermediates. The results indicated that the rearrangement of the 3- and 2-butenyl cation have been achieved in the reaction as soon as it started whereby the ratio of the 2-butenyl ether is higher than the 3-butenyl derivative.



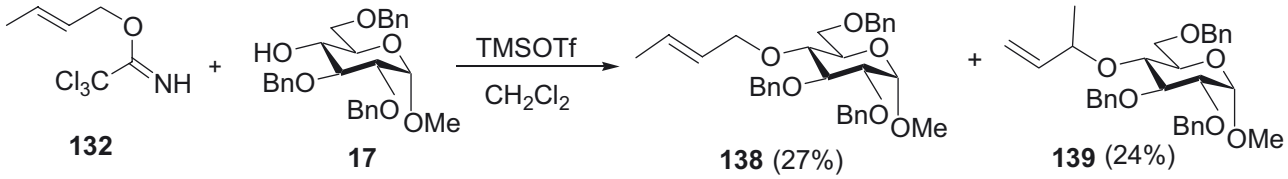
Scheme 74

Thus, under such catalysis, reaction of **132** or **133** with a number of monosaccharide derivatives, possessing one unprotected hydroxyl group such as 6-*O*-unprotected glucose derivative **15** was performed. The 3- and 2-butenyl-glucose ether derivatives **136** and **137** were synthesized through etherification reaction between trichloroacetimidate **132**, **133** as donor and glucose derivative **15** as acceptor using TMSOTf as promoter (Scheme 75).



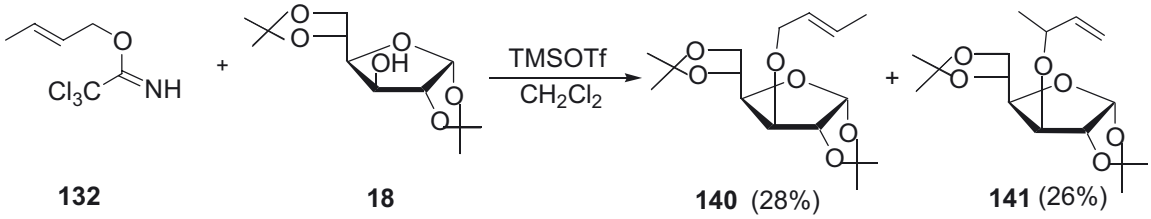
Scheme 75

Similarily, the etherification of secondary hydroxyl groups in glucose derivative **17** with trichloroacetimidate **132** gave the respective butenyl glucose derivatives **138** and **139** (Scheme 76).



Scheme 76

Treatment of trichloroacetimidate **132** with glucofuranose **18** in the presence of catalytic amounts of TMSOTf afforded the corresponding ethers **140** and **141** (Scheme 77).



Scheme 77

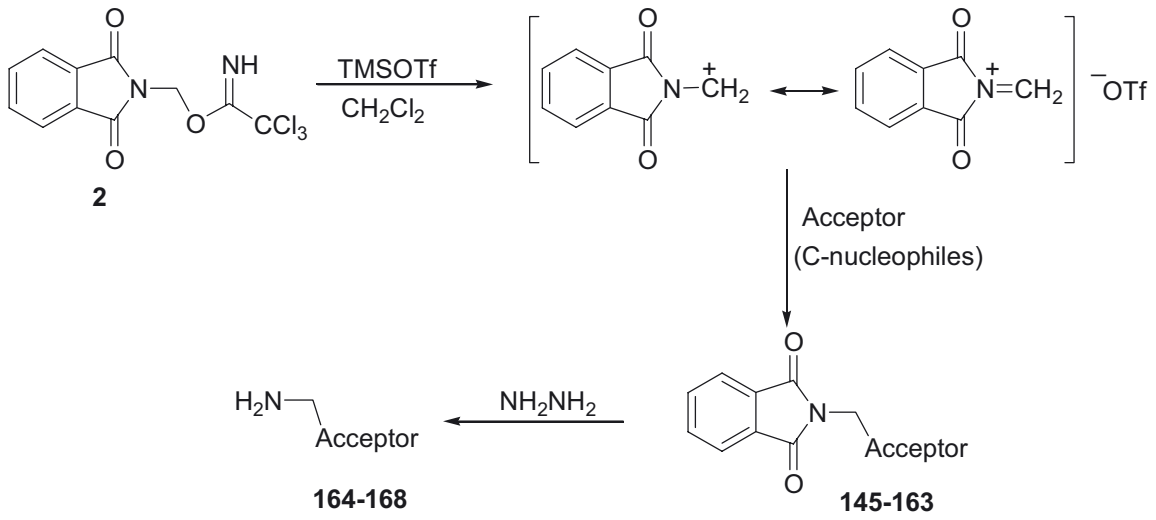
In conclusion, alkyl ether protection of the several hydroxy groups was carried out using trichloroacetimidates. In every reaction a mixture of 2-butenyl ethers and 3-butenyl ethers was obtained.

2.5 Intermolecular imidomethylation of *C*-nucleophiles using Pim trichloroacetimidate and catalytic amounts of TMSOTf: a novel approach to the synthesis η-amino ketones and acids.

The development of methodologies for *C-C* bond formation,[203] particularily those involving introduction of one carbon atom bearing a functional group into the skeleton of organic molecules, is of high interest and required in the organic synthesis of natural products and biologically significant molecules. When such a functional group is an alkyl- or an acyl-amino group linked *via* the nitrogen to a methylene leaving group such as halogen, OR or NR_2, the process is called amino or amidomethylation.[203-207] Usually, such reagents are electrophilic and require for linkage in the other reactant are nucleophilc center. Much work was done on the aminomethylation of activated carbon atoms by reaction with formaldehyde and amines.[203]

Organometallic derivatives derived from alkenes and aromatic compounds can be aminomethylated.[203-211] Such aminomethylation processes are usually providing products with amino alkyl groups. On the other hand, amidomethylations provide amides that could be readily hydrolysed to the corresponding amines. The use of formaldehyde and amides for the amidomethylation of activated carbons was unsuccessful.[203] However, such reaction had taken place by using hydroxymethyl amides in 1930,[212] and then developed.[213-217] The hydroxy group in the latter reagent has been replaced by a leaving group such as esters,[217] halogens[215] and substituted amines.[214,218,219] The respective cyclic imides of dicarboxylic or sulfocarboxylic acids were also used.[214,220-224] The reaction required the use of strong acid and heating for long period of time which could reach 24 hours. Owing to the importance of amino and amidomethylation in organic synthesis and compounds possessing such a group, it became interesting to develop a method which requires mild reaction conditions and

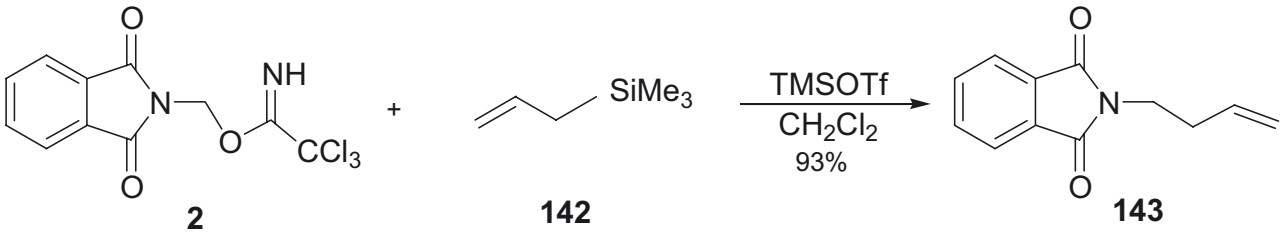
only catalytic amounts of the promoters. Towards this end, we have investigated the reaction of the recently developed[225] reagent, *O*-phthalimidomethyl trichloroacetimidate (**2**) with different types of *C*-nucleophiles; this reagent has been successfully used as a protecting group *via* imidomethylation of *O*-nucleophiles.



Scheme 78

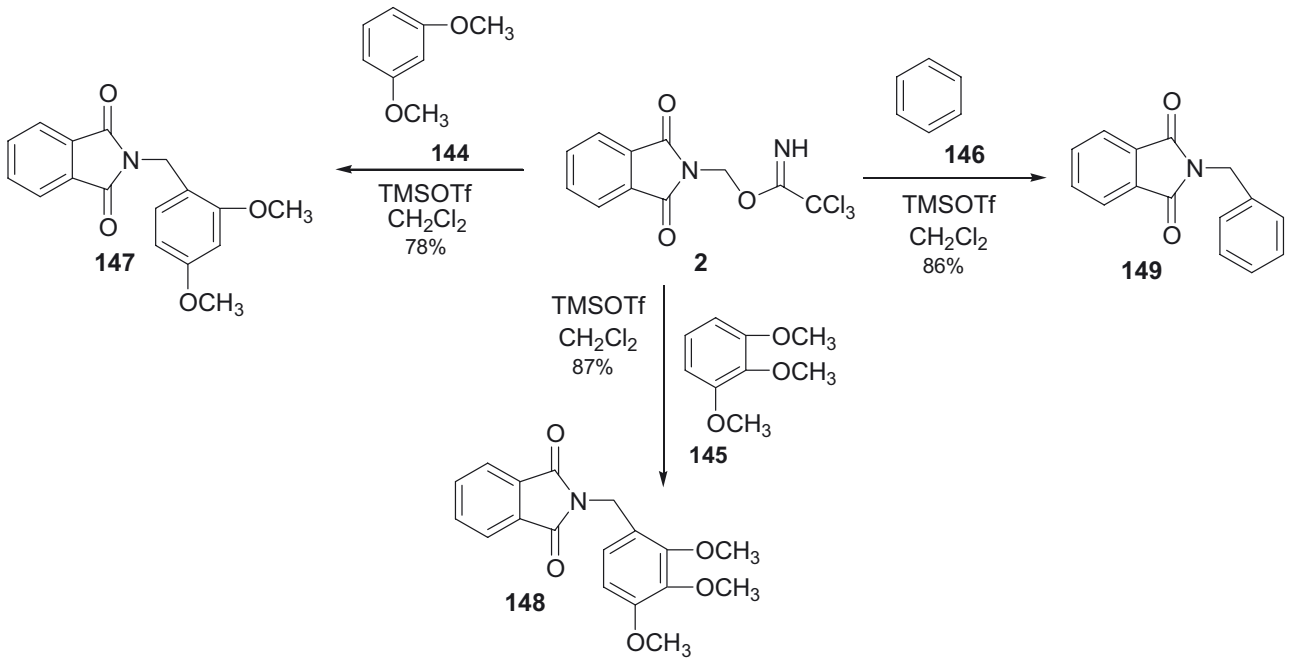
In this respect, a methodology has been developed for introducing the aminomethyl group on carbon nucleophiles to form a *C*-*C* bond using *O*-phthalimidomethyl (Pim) trichloroacetimidate (**2**)[213] as an aminomethylating agent with the phthalimido group as a latent protecting group. The reaction proceeded smoothly in the presence of catalytic amounts of TMSOTf under mild conditions and at room temperature. Moreover, a practical approach for the synthesis of η-amino ketones and esters has been achieved.

Reaction of the trichloroacetimidate **2** with the silylated *C*-nucleophile allyl trimethylsilane (**142**) in the presence of TMSOTf gave **143** in 93% yield; compound **143** was prepared by the nucleophilic displacement of the tosyloxy group in 1-tosyloxy-3-butene with potassium phthalimide.[226]



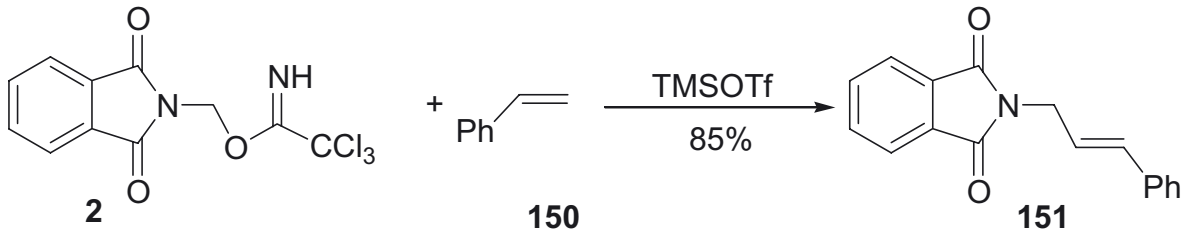
Scheme 79

Similarily, the trichloroacetimidate **2** was reacted with 1,3-dimethoxybenzene (**144**) and 1,2,3-trimethoxybenzene (**145**) to give **147** and **148** in 78% and 87% yield, respectively. Also **2** was reacted with benzene (**146**) to give **149** in 86% yield; **149** was available by Mitsunobu reaction of benzyl alcohol with phthalimide[227-230] and by reaction of benzylamine[231] or benzylazide[231,232] with phthalic anhydride. These compounds **147-149** were readily identified by ^{1}H NMR spectroscopy which showed a singlet at ι#4.82-4.84 characteristic for the introduced methylene group, in addition to the signals of the aromatic protons which confirm the position of the imidomethyl group on the ring (Scheme 80).



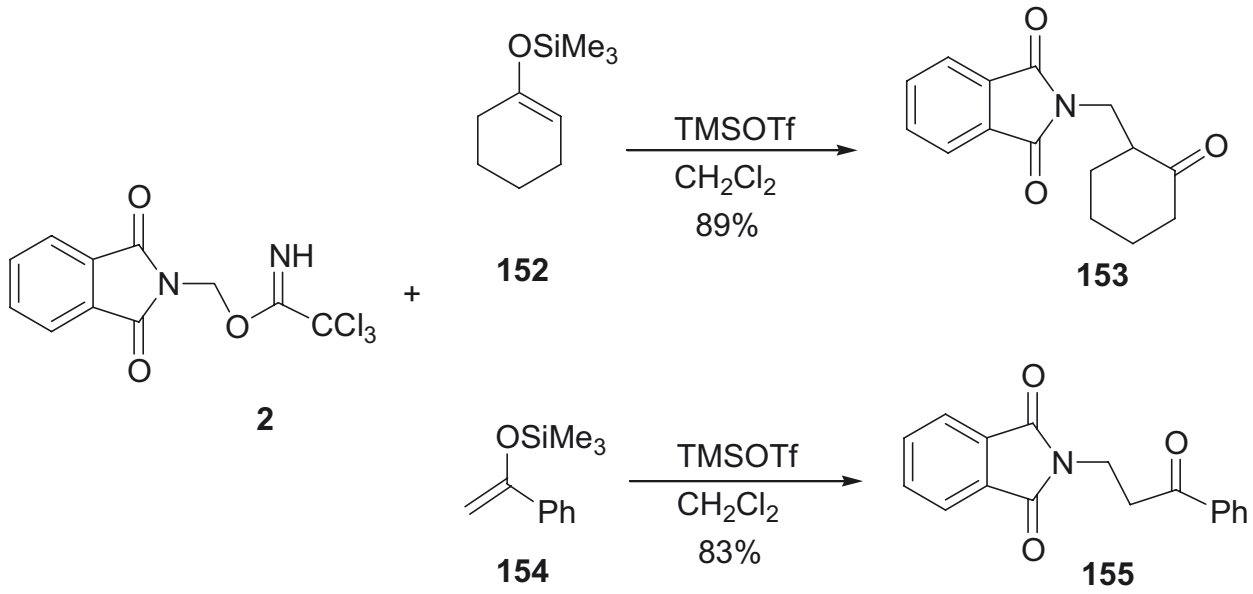
Scheme 80

The (*Z/E*)-1-phenyl-3-phthalimido-2-propene (**151**) was synthesized[233] by reaction of (3-chloro-allyl)-benzene with phthalimide potassium salt. The trichloroacetimidate **2** was found to be also a suitable precursor for the synthesis of **151** in 85% yield upon reaction with pheneylethylene (styrene) (**150**). The ratio of *Z/E* in **151** is 1:1 as determined from its ^{1}H NMR spectrum (Scheme 81).



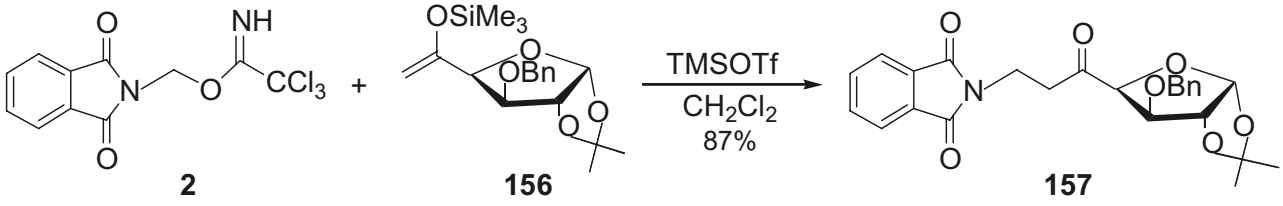
Scheme 81

The trichloroacetimidate **2** has been also found to be an excellent reagent for the imidomethylation of the ζ-position in ketones and acids. Thus, compound **153**[234] was readily prepared by reaction of trichloroacetimidate **2** with 1-trimethylsiloxy-cyclohexene (**152**) as a *C*-nucleophile. The synthesis of **155** was reported [235] by using Michael addition of phthalimide to phenyl vinyl ketone. The reaction of trichloroacetimidate **2** with 1-phenyl-1-trimethylsiloxy-ethylene (**154**) in the presence of TMSOTf gave **155** in 83% yield (Scheme 82).



Scheme 82

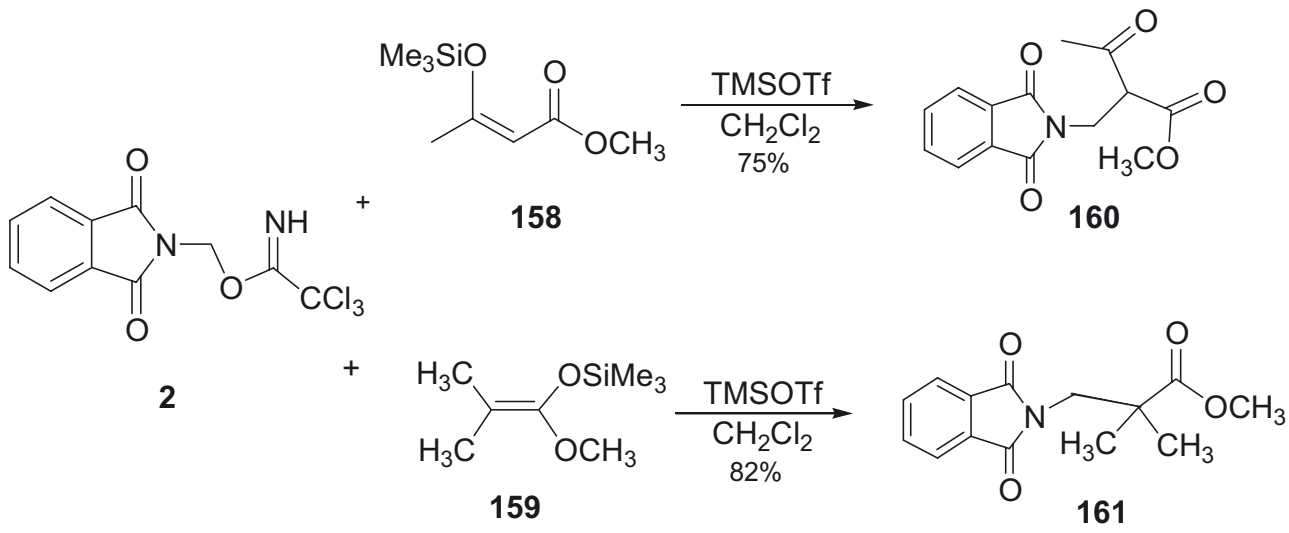
The reaction of **2** on the 6-position of glucose derivative **156**[236] gave 3-*O*-benzyl-6,7-dideoxy- 1:2-*O*-isopropylidene-7-(*N*-phthalimido)-ζ-D-xylo-heptofuranos-5-ulose (**157**) in 87% yield. The generated *C*-*C* linkage in the product was confirmed by the presence of two signals at ι 4.04 and 3.96 for the CH_2-CH_2 group and confirmed from its ^{13}C NMR spectrum which showed them at ι 32.4 and 39.0 (Scheme 83).



Scheme 83

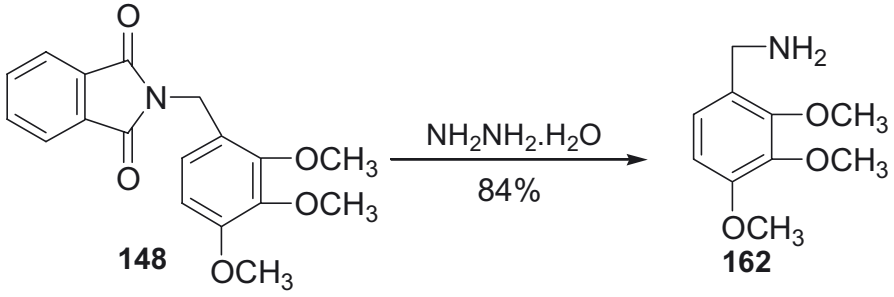
η-Amino acids and their derivatives are an important class of compounds. They are present in many biologically active compounds and in the free form they show interesting pharmacological effects.[237] They are also precursors of the η-lactam moiety which is present in some antibiotics. Again, the trichloroacetimidate **2** was reacted with silylated reagents such as 3-trimethylsiloxy-2-butenic acid methyl ester (**158)** and

1-methoxy-2-methyl-1-trimethylsiloxy-propene (**159**) in the presence of TMSOTf to give in 75% and 82% yield of **160** and **161**,[238] respectively. Compound **160** was identified by ^{1}H NMR spectroscopy which showed newly introduced imidomethylene group at ι 4.13 and signals of the benzene ring at ι 7.61-7.88 (Scheme 84).



Scheme 84

After performing the imidomethylation successfully on the selected *C*-nucleophiles, it became interesting to achieve a deprotection of the amino group. Hydrazine hydrate in refluxing methanol has been selected to remove the phthalimido group, which worked successfully to give the respective amines **162**,[239] **163** and **164**[240] from **148**, **149** and **151** respectively (Scheme 85).



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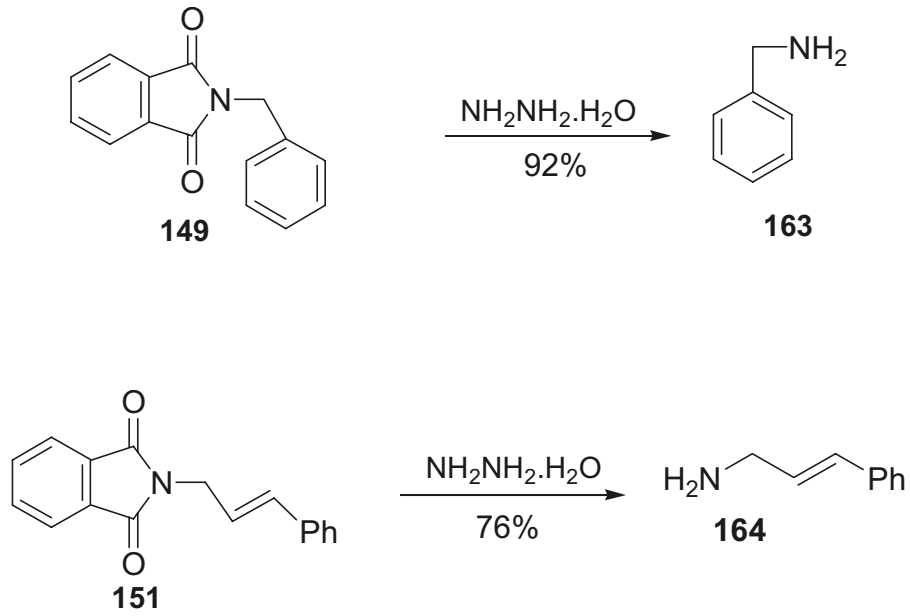
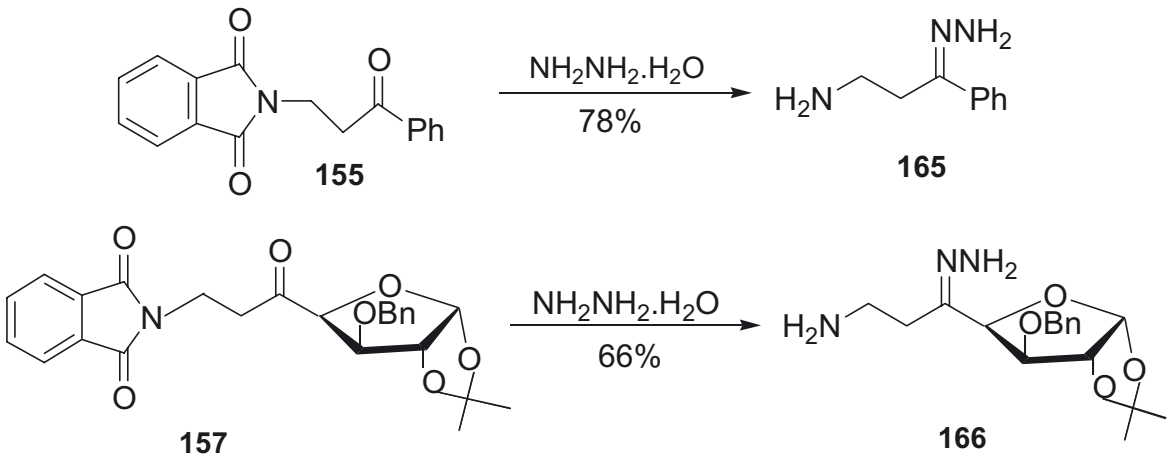


Scheme 85

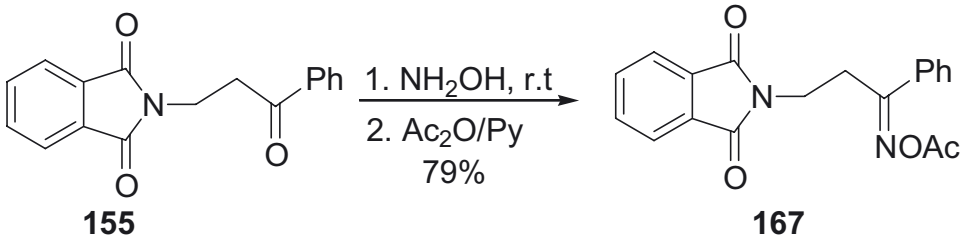
In case of the η-aminoketones **155** and **157**, a concomitant reaction of the carbonyl groups with hydrazine, in addition to the deprotection, had taken place to give the hydrazones **165** and **166**, respectively (Scheme 86).



Scheme 86

Attempted deprotection of the phthalimide group by heating with hydroxylamine even for long time and with more reagent did not cause its hydroxylaminolysis and

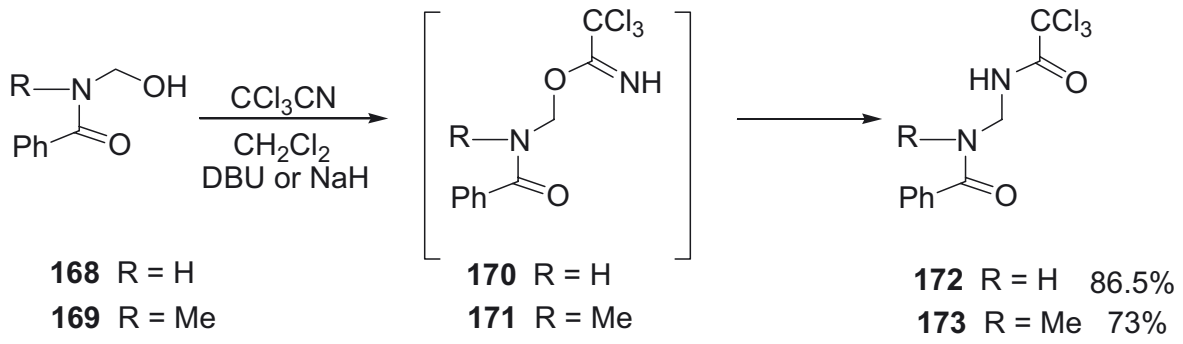
the product from the reaction was found to be the corresponding oxime whose acetylation gave **167**. The failure of the cleavage could be due to the lower nucleophilicity of the hydroxylamine compared to hydrazine (Scheme 87).



155 **167**

Scheme 87

The successful imidomethylation *via* the trichloroacetimidate **2** as shown above and on the other hand, the failure of reacting formaldehyde and amides with activated carbons, attracted our attention to explore the reactivity of the *N*-methylol amides as amidomethylating agents *via* their trichloroacetimidates. Thus methylol benzamide (**168**)[241] and *N*-methylmethylol benzamide (**169**)[242] were reacted with trichloroaceonitrile in dichloromethane as solvent and in the presence of DBU or NaH for activating the hydroxyl group towards the reaction with the nitrile group.[102-104] The reaction was carried out at different temperatures (-50 ^{o}C, 0 ^{o}C, room temp.). However, in each case the expected trichloroacetimidates **170** and **171** could not be obtained, but the isolated products were found to have the structure of the trichloroacetamides **172** and **173**. The structures of **172** and **173** were established through their ^{1}H NMR spectra which reveal the presence of a methylene moiety between two NH groups for **172** which appeared as a dd at ι 4.98, whereas that of **173** appeared as a doublet at ι 5.00 (Scheme 88).



168 R = H
169 R = Me

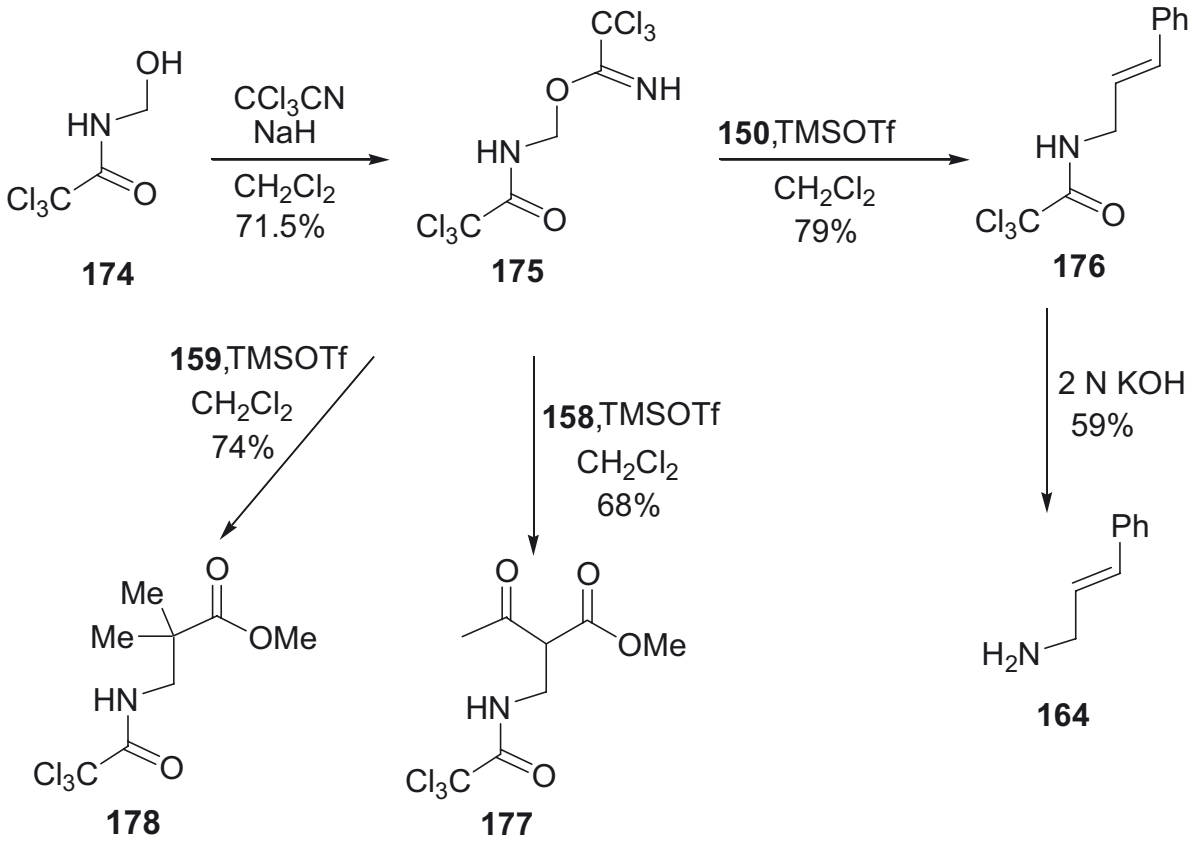
170 R = H
171 R = Me

172 R = H 86.5%
173 R = Me 73%

Scheme 88

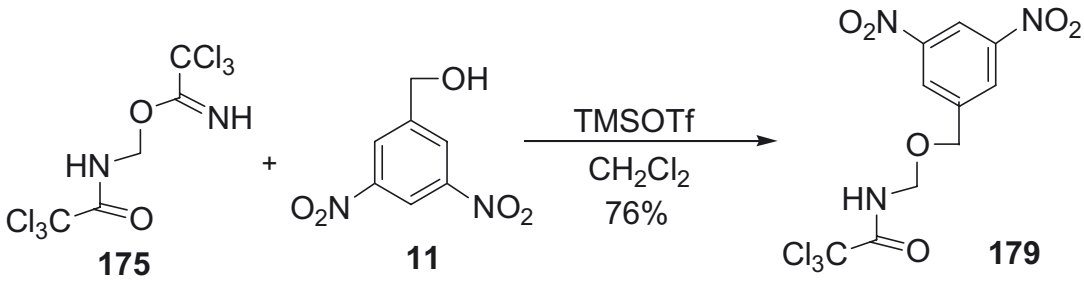
When the phenyl group in the above amides was changed to the trichloromethyl group as in *N*-hydroxymethyl trichloroacetamide (**174**),[243] and reacting the latter with trichloroacetonitrile in presence of NaH at room temperature, the trichloroacetimidate **175** was formed without rearrangement and in good yield. The structure of **175** was confirmed from its ^{1}H NMR spectrum which showed a doublet at ι 4.93 due to the CH_2 group in addition to a signal at ι 3.95 for the NH, whereas the other NH appeared at ι 7.81.

The trichloroacetimidate **175** was reacted readily with styrene **150** to give **176**[244] which can be hydrolysed to the amine **164** with 1N KOH. It was also reacted with the *O*-silylated nucleophiles 3-trimethylsiloxy-2-butenoic acid methyl ester (**158**) and 1-methoxy-2-methyl-1-trimethylsiloxy-propene (**159**) under the same conditions to afford **177** and **178** respectively, in good yield (Scheme 89).



Scheme 89

Reaction of **175** with 3,5-dinitrobenzyl alcohol (**11**) as *O*-nucleophile in the presence of TMSOTf gave the respective ether **179**. Its structure was readily assigned from its ^{1}H NMR spectrum [ι = 4.84 (s, CH_2), 5.04 (d, J = 6.9 Hz, CH_2), 7.43 (brs, NH), 8.53-8.96 (m, Ar-H)].



Scheme 90

In conclusion, a general method has been developed for introducing the *N*-phthalimidomethyl group (Pim) on a variety of carbon nucleophiles. The trichloroacetimidate of Pim can be considered as a reagent of choice for forming *C-C* bonds with nucleophiles under mild conditions. Trichloroacetimidate **2** is characterized by a high reactivity in electrophilic reactions. The high reactivity is due to the electron withdrawing nature of the carbonyl groups which increased its electrophilicity.[245] The reagent **2** can be stored without decomposition and the respective derivatives can be easily isolated and identified. On the other hand, deprotection of the phthalimido group to give the aminomethylated analogues could be readily achieved. Thus, novel approaches for the η-amino ketones and acids have been achieved. Preliminary results with **177** proved also its successful applications as amidoalkylating agent.

3.0 Experimental Part

3.1 General Method

Solvents: were purified and dried in the usual way. The boiling range of the petroleum ether used was 35 °C-65 °C.

Thin layer chromatography (TLC): silica gel 60 F_{254} plastic plates (E. Merk, layer thickness 0.2 mm) detected by UV absorption and by treatment with one of the following reagents followed by heating at 120 °C.

a) Mostaine: a solution of 20 g of ammonium molibdate and 0.4 g of cerium (IV) sulfate in 400 ml of 10% aq. sulfuric acid.

b) 15% aq. sulfuric acid.

Optical rotation: were determined at 20 °C with a Perkin-Elmer 241 MC polarimeter (1-dm cell).

Melting points were determined on a Büchi 510 melting-point apparatus and the values are uncorrected.

NMR spectra: measured with the following instruments;

a) Bruker AC 250 (250 MHz)

b) Bruker DRX 600 (600 MHz)

TMS (0.00 ppm) or the signal of the deuterated solvent were used as internal standard. The chemical shifts were given in ppm and the coupling constants in Hz.

Explanation to the ^{1}H-NMR data: s = singulet, brs = broad singulet, d = doublet, t = triplet, dd = doublet doublet, m = multiplet.

In case of di-and oligosaccharide the monosugar unit was indicated by a, b, c beginning from the sugar at right end.

FAB-MS: modified Finningan MAT 312/ AMD 5000 spectrometer at 790 eV and T = 70 °C.

MALDI-MS: the mass spectra were measured with a KRATOS Analytical Kompact **MALDI 1**: spectrometer using 2,5 di-hydroxy benzoic acid (DHB) as matrix.

***O*-Phthalimidomethyl trichloroacetimidate (2).**

A stirred solution of *N*-hydroxymethyl phthalimide (**1**, 0.58 g, 5 mmol) in dry dichloromethane (30 ml) and trichloroacetonitrile (5 ml, 50 mmol) was treated with DBU (71µl) at room temperature and then left for 2 h. The solvent was evaporated and the product was purified by column chromatography 5% triethylamine in toluene/ethyl acetate, 25:1 to give **2** (1.3 g, 87%) as a white powder. m.p. 145-147 ^{o}C. ^{1}H-NMR (250 MHz, $CDCl_3$):#ι # #5.90#s, 2 H, CH_2), 7.79-7.99 (m, 4 H, Ar-H), 8.59 (s, 1 H, NH). ^{13}C-NMR (62.8 MHz, $CDCl_3$): ι#= 64.9 (CH_2), 90.6 (CCl_3), 124.0, 131.8, 134.7 (C-Ar), 161.2 (CNH), 166.5 (CO). EI-MS: m/z = 321.0.

General procedure for reaction of trichloroacetimidate 2 with alcohols.

A solution of **2** (0.45 g, 1.4 mmol) and alcohol (1.4 mmol) in dry dichloromethane (40 ml) was stirred under nitrogen at room temperature and then TMSOTf (13 µl, 0.06 mmol) was added. After 20 min-3 h. The reaction mixture was neutralized with solid sodium bicarbonate, filtered and concentrated in vacuo. The residue was purified by flash chromatography.

Isopropyl phthalimidomethyl ether (7).

White powder (0.25 g, 81%); R_f = 0.54 (petroleum ether/ethylacetate 5:1). m.p. 92 ^{o}C, Lit.[99] 92-93 ^{o}C. The analytical data **7** are identical with the published values.[99]

Cyclohexyl phthalimidomethyl ether (8).

White powder (0.45 g, 90%); R_f = 0.81 (petroleum ether/ethylacetate 5:1). m.p. 83 ^{o}C, Lit.[100] 81-83 ^{o}C. The analytical data **8** are identical with the published values.[100]

5-Methyl-2-phenyl-5-(phthalimidomethyloxy)methyl-1,3-dioxane (9).

White powder (0.4 g, 77%); R_f = 0.65 (petroleum ether/ethyl acetate, 5:1). m.p.76 ^{o}C.

^{1}H-NMR (250 MHz, $CDCl_3$): ι#= 0.76 (s, 3 H, CH_3), 3.52 (d, J_{gem} = 11.8 Hz, 2 H, CH_2), 3.84 (s, 2 H, CH_2), 4.00 (d, J_{gem} = 11.8 Hz, 2 H, CH_2), 5.20 (s, 2 H, CH_2), 5.32 (s, 1 H, CH), 7.26-7.87 (m, 9 H, Ar-H). ^{13}C-NMR (62.8 MHz, $CDCl_3$): ι#= 17.2 (CH_3), 34.4, 67.8, 71.6, 73.1 (4 CH_2), 101.8 (CH), 123.5, 123.6, 126.0, 128.1, 128.7, 131.8, 134.2, 138.1 (C-Ar), 163.7 (C), 168.0 (CO). EI-MS: m/z = 367.0.

Benzyl phthalimidomethyl ether (10).

White powder (0.32 g, 87%); R_f = 0.82 (petroleum ether/ethyl acetate 5/1). m.p. 80 ^{o}C, Lit.[99] 81 ^{o}C.

3,5-Dinitrobenzyl alcohol (11).

3,5-Dinitrobenzyl alcohol (**11**) was purchased from Fluka and used as received.

Cholesterol (12).

Cholesterol (**12**) was purchased from Fluka and used as received.

(3,5-Dinitrobenzyl) phthalimidomethyl ether (13).

Yellow powder (0.45 g, 90%); R_f = 0.53 (petroleum ether/ethyl acetate, 4:1). m.p. 115 ^{o}C. ^{1}H-NMR (250 MHz, $CDCl_3$): ι#= 4.80 (s, 2 H, CH_2), 5.30 (s, 2 H, CH_2), 7.70-8.93 (m, 7 H, H-Ar). ^{13}C-NMR (62.8 MHz, $CDCl_3$): ι#= 67.2, 69.4 (2 CH_2), 117.9, 123.9, 134.7 (C-Ar), 167.7 (CO). EI-MS: m/z = 357.0.

$C_{16}H_{11}N_3O_7$ (357.3) Calcd: C: 53.78 H: 3.10 N: 11.76

Found: C: 53.51 H: 3.05 N: 11.43

Cholesteryl phthalimidomethyl ether (14).

White powder (0.7 g, 89%); R_f = 0.74 (petroleum ether/ethyl acetate, 25:1). m.p. 132 ^{o}C. ^{1}H-NMR (250 MHz, $CDCl_3$): ι#= 0.64-2.41 (m, 43 H, Cholesteryl), 3.45 (m, 1

H,CH), 5.11 (m, 2 H,CH_2), 5.36 (m, 1 H, CH), 7.20-7.90 (m, 4 H, Ar-H).

$C_{36}H_{51}NO_3$ (545.8) Calcd: C: 79.22 H: 9.41 N: 2.56

Found: C: 79.07 H: 9.49 N. 2.55

Methyl 2,3,4-tri-*O*-benzyl-ζ-D-glucopyranoside (15).

(a) Compound **15** was synthesized following a published procedure. The analytical data are identical with the published values.[106]

(b) Removal of the phthaloyl group

Methyl 2,3,4-tri-*O*-benzyl-ζ-D-glucopyranoside (15).

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-phthalimidomethyl-ζ-D-glucopyranoside (**16**, 0.2 g, 0.32 mmol) was dissolved in (10 ml) of methyl alcohol and (1 ml) of hydrazine and the reaction mixture refluxed for 1 h, the solvent was evaporated in vacuo and the residue was purified by flash chromatography petrolum ether/ethyl acetate, 2:1 to give methyl 2,3,4-tri-*O*-benzyl-ζ-D-glucopyranoside (**15**) (76%) as a white powder.

Methyl amine can be used instead of hydrazine.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-phthalimidomethyl-ζ-D-glucopyranoside (16).

White powder (0.65 g, 75%); R_f = 0.38 (petroleum ether/ethyl acetate, 4:1); $[Ŭ]_D$ = 51.5 (c =1.5, CH_2Cl_2); m.p. 89 °C.

^{1}H-NMR (600 MHz, $CDCl_3$): ι# 3.30 (s, 3 H, OCH_3), 3.45 (dd, $J_{1,2}$ = 3.5, $J_{2,3}$ = 9.6 Hz, 1 H, 2-H), 3.55 (dd, $J_{4,3}$ = 9.3, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 3.67 (m, 1 H, 5-H), 3.78 (m, 1 H, 6-H), 3.87 (m, 1 H, 6′-H), 3.92 (dd, $J_{3,4}$ = 9.3, $J_{3,2}$ = 9.6 Hz, 1 H, 3-H), 4.35 (d, $J_{1,2}$ = 3.4 Hz, 1 H, 1-H), 4.52 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.60 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.74 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.78 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.83 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.94 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 5.18 (q, J_{gem} = 10.9 Hz, 2 H, CH_2Phth), 7.11-7.79 (m, 19 H, Ar-H). ^{13}C-NMR (150.8

MHz, $CDCl_3$): ι# 55.1 (OCH_3), 67.8 (CH_2), 68.6 (C-6), 69.9 (C-5), 77.5 (C-4), 79.8 (C-2), 82.0 (C-3), 89.2 (C-1), 73.4, 74.9, 75.6 (3 CH_2), 123.6, 127.5, 127.8, 127.9, 128.1, 128.2, 128.3, 128.4, 131.8, 134.2, 138.2, 138.3, 138.8 (C-Ar), 167.8 (CO). EI-MS: m/z = 623.0.

$C_{37}H_{37}NO_8$ (623.7)	Calcd:	C: 71.25	H: 5.97	N: 2.24
	Found:	C: 70.94	H: 5.82	N: 1.89

Methyl 2,3,6-tri-*O*-benzyl-ζ-D-glucopyranoside (17).

Compound **17** was synthesized following a published procedure. The analytical data are identical with the published values.[107]

1:2, 5:6-Di-*O*-isopropylidene-ζ-D-glucofuranose (18).

Compound **18** was synthesized following a published procedure. The analytical data are identical with the published values.[108]

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-phthalimidomethyl-ζ-D-glucopyranoside (19).

White powder (0.70 g, 80%); R_f = 0.35 (petroleum ether/ethyl acetate, 5:1); $[Ŭ]_D$ = 3.5 (c =2.0, CH_2Cl_2); m.p. 62 °C.

^{1}H-NMR (600 MHz, $CDCl_3$): ι# 3.26 (s, 3 H, OCH_3), 3.44 (dd, $J_{1,2}$ = 3.3, $J_{2,3}$ = 9.2 Hz, 1 H, 2-H), 3.52 (m, 2 H, 4-H, 5-H), 3.72 (m, 1 H, 3-H), 3.84 (m, 2 H, 6-H, 6´-H), 4.40 (d, $J_{1,2}$ = 3.3 Hz, 1 H, 1-H), 4.55 (d, J_{gem}= 12.1 Hz, 1 H, CHPh), 4.60 (d, J_{gem}= 12.1 Hz, 1 H, CHPh), 4.71 (d, J_{gem}= 12.1 Hz, 1 H, CHPh), 4.88 (d, J_{gem}= 12.1 Hz, 1 H, CHPh), 5.02 (d, J_{gem}= 11.2 Hz, 1 H, CHPh), 5.04 (d, J_{gem}= 11.2 Hz, 1 H, CHPh), 5.17 (dd, J_{gem} = 7.5 Hz, 2 H, CH_2), 7.26-7.73 (m, 19 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι# 55.0 (OCH_3), 67.8 (C-6), 69.4 (C-4), 69.8 (C-5) 73.3, 79.4, 79.7 (3 CH_2), 79.2 (C-2), 80.9 (C-3), 81.3 (CH_2), 123.3, 123.4, 123.5, 127.2, 127.6, 127.8, 127.9, 128.1, 128.3, 128.4, 131.7, 131.8, 132.0, 133.9, 134., 134.1, 137.9, 138.0, 138.6,

138.7 (C-Ar), 167.3, 167.8 (CO). EI-MS: m/z = 623.0.

$C_{37}H_{37}NO_8$ (623.7)	Calcd:	C: 71.25	H: 5.97	N: 2.24
	Found:	C:70.79	H: 6.03	N: 1.80

1:2, 5:6-Di-*O*-isopropylidene-3-*O*-phthalimidomethyl-ζ-D-glucofuranose (20).

Colorless oil (0.4 g, 69%); R_f = 0.65 (petroleum ether/ethyl acetate, 4:1); $[Ŭ]_D$ = -12.5 (c = 2.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι# 1.04, 1.24, 1.28, 1.44 (4 s, 12 H, 4 CH_3), 3.94 (m, 3 H, 4-H, 6-H, 6´-H), 4.16 (m, 1 H, 5-H), 4.30 (d, *J* = 2.7 Hz, 1 H, 3-H), 4.58 (d, *J* = 3.5 Hz, 1 H, 2-H), 5.23 (s, 2 H, CH_2), 5.85 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 7.75- 7.91 (m, 4 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι# 23.8, 24.2, 26.2, 26.8 (4 CH_3), 67.1 (C-6), 67.9 (CH_2), 72.1 (C-5), 80.8 (C-4), 81.0 (C-3), 83.7 (C-2), 105.2 (C-1), 108.8, 112.1, 123.6, 123.7, 131.9, 123.7, 131.9, 132.2, 134.2, 134.3 (C-Ar), 167.9 (CO). EI-MS: m/z = 419.0.

$C_{21}H_{25}NO_8$ (419.4)	Calcd:	C: 60.13	H: 6.00	N: 3.34
	Found:	C: 60.43	H: 5.90	N: 3.31

Allyl 3,4,6-tri-*O*-benzyl-ζ-D-glucopyranoside (21).

Compound **21** was synthesized following a published procedure. The analytical data are identical with the published values.[109]

Allyl 3,4,6-tri-*O*-benzyl-2-*O*-phthalimidomethyl-ζ-D-glucopyranoside (22).

Colourless oil (0.7 g, 80%); R_f = 0.43 (petroleum ether/ethyl acetate, 5:1); $[Ŭ]_D$ = -2.4 (c = 2.0, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$): ι# 3.65 (m, 3 H, 6-H, 2-H, 4-H), 3. 78 (m, 2 H, 6´-H, 5-H), 3.92 (m, 2 H, 3-H, CH-allyl), 4.11 (m, 1 H, CH-allyl), 4.42 (d, J_{gem} = 10.5 Hz, 1 H, CHPh), 4.46 (d, J_{gem} = 10.5 Hz, 1 H, CHPh), 4.60 (d, J_{gem} = 10.4 Hz, 1 H, CHPh),

4.70 (d, J_{gem} = 10.4 Hz, 1 H, CHPh), 4.81 (m, 2 H, $\underline{CH_2}$=CH), 4.91 (d, J_{gem} = 10.5 Hz, 1 H, CHPh), 5.02 (d, $J_{1,2}$ = 3.2 Hz, 1 H, 1-H), 5.17 (d, J_{gem} = 10.5 Hz, 1 H, CHPh), 5.23 (s, 2 H, CH_2), 5.80 (m, 1 H, CH_2=$\underline{CH}$), 7.07-7.40 (m, 15 H, Ar-H), 7.68-7.90 (m, 4 H, Ar-H). MS (MALDI, positive mode, Matrix: DHB): m/z = 672.0 $(M+Na)^+$, 688.0 $(M+K)^+$.

$C_{39}H_{39}NO_8$ (649.7) Calcd: C: 72.09 H: 6.05 N: 2.15

Found: C: 72.31 H: 6.23 N: 1.92

3,4,6-Tri-*O*-benzyl-2-*O*-phthalimidomethyl-ζ,η-D-glucopyranose (23).

To a solution of **22** (1.2 g, 1.85 mmol) in a mixture of toluene/EtOH/H_2O (40:40:2 ml) was added Wilkinson´s catalyst (342 mg, 0.36 mmol) and the reaction mixture was refluxed at 110 °C. After 8 h. the solvent was evaporated in vacuo and the residue was purified by flash chromatography petroleum ether/ethyl acetate, 8:1 to give ζ,η mixture of **23** (0.77 g, 68%) as a colorless oil; R_f = 0.35 (petroleum ether/ethyl acetate, 5:1); $[\breve{U}]_D$ = 50.5 (c = 2.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι#= 1.50 (brs, 1 H, OH), 3.47 (m, 1 H, η-5-H), 3.56 (m, 3 H, η-2-H, η-3-H, η-4-H), 3.65 (m, 3 H, ζ-4-H, 6-H, 6´-H), 3.80 (dd, $J_{2,1}$ = 3.5, $J_{2,3}$ = 9.4 Hz, 1 H, ζ-2-H), 3.90 (dd, J = 9.4, J = 9.3 Hz, 1 H, 3-H), 4.02 (m, 1 H, ζ-5-H), 4.44 (d, J_{gem} = 10.4 Hz, 1 H, 1 CHPh), 4.48 (d, J_{gem} = 12.2 Hz, 1 H, 1 CHPh), 4.58 (d, J_{gem} = 10.4 Hz, 1 H, 1 CHPh), 4.62 (d, $J_{1,2}$ = 6.4 Hz, 1 H, η-1-H), 4.73 (m, 2 H, 2 CHPh), 4.83 (d, J_{gem} = 10.4 Hz, 1 H, 1 CHPh), 5.25 (m, 2 H, η CH_2), 5.37 (d, $J_{1,2}$ = 3.4 Hz, 1 H, ζ-1-H), 5.45 (d, J_{gem} = 11.2 Hz, 2 H, ζ CH_2), 7.08-7.32 (m, 15 H, Ar-H), 7.45-7.84 (m, 4 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι#= 67.3, 67.9 (2 CH_2), 68.6 (C-6), 70.3 (C-5), 73.4, 74.8 (2 CH_2), 77.8 (C-4), 79.7 (C-2), 80.8 (C-3), 96.8 (C-1), 123.6, 123.7, 127.4, 127.6, 127.8, 127.9, 128.2, 128.4, 131.7, 134.2, 134.4,137.8, 138.3, 138.5 (C-Ar), 167.6, 168.1 (2 CO). MS (MALDI, positive mode, Matrix:

DHB): m/z = 632.5 $(M+Na)^+$.

$C_{36}H_{35}NO_8$ (609.7) Calcd: C: 70.92 H: 5.78 N: 2.29

Found: C: 70.48 H: 6.20 N: 2.33

***O*-(3,4,6-Tri-*O*-benzyl-2-*O*-phthalimidomethyl-ζ-D-glucopyranosyl) trichloroacetimidate (24).** A stirred solution of glucose derivative **23** (0.61 g, 1.0 mmol) in dry dichloromethane (30 ml) and trichloroaceonitrile (1 ml, 10 mmol) was treated with DBU (10 µl) at room temperature and then left for 1.5 h. The solvent was evaporated and the product was purified by column chromatography 5% triethylamine in toluene/ethyl acetate, 25:1 to give **24** (0.65 g, 86%) as yellow oil ; R_f = 0.43 (2% triethylamine in toluene); $[Ŭ]_D$ = 34.5 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$): ι# 3.68 (m, 2 H, 6-H, 6´-H), 4.05 (m, 2 H, 4-H, 5-H), 4.60 (m, 3 H, 2 CHPh, 3-H), 4.80 (d, J_{gem} = 9.7 Hz, 1 H, CHPh), 4.83 (d, J_{gem} = 11.1 Hz, 1 H, CHPh), 4.85 (d, J_{gem} = 11.1 Hz, 1 H, CHPh), 5.15 (d, J_{gem} = 9.7 Hz, 1 H, CHPh), 5.20 (d, J_{gem} = 12.7 Hz, 2 H, CH_2), 6.54 (d, $J_{1,2}$ = 3.3 Hz, 1 H, 1-H), 7.00-7.28 (m, 15 H, Ar-H), 7.61-7.77 (m, 4 H, Ar-H), 8.36 (s, 1 H, NH).

Methyl 3,4,6-tri-*O*-benzyl-2-*O*-phthalimidomethyl-η-D-glucopyranoside (25).

A solution of the trichloroacetimidate **24** (0.53 g, 0.7 mmol) and methyl alcohol (0.28 ml, 7.0 mmol) in dry dichloromethane (20 ml) was treated with TMSOTf (13 µl, 0.07 mmol), and then stirred for 1 h. The reaction was quenched by the addition of solid sodium bicarbonate, filtered and concentrated. The crude residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate, 15:1 to afford **25** (0.34 g, 78%) as a colorless oil; R_f = 0.68 (petroleum ether/ethyl acetate, 5:1); $[Ŭ]_D$ = 10.7 (c = 0.5, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι# 3.29 (s, 3 H, OCH_3), 3.40 (m, 1 H, 5-H), 3.54 (m, 1 H, 3-H), 3.55 (m, 1 H, 4-H), 3.59 (dd, $J_{2,1}$ = 7.7, $J_{2,3}$ = 7.4 Hz, 1 H, 2-H), 3.64 (dd, $J_{6,5}$

= 4.8, J_{gem} = 10.7 Hz, 1 H, 6-H), 3.72 (m, 1 H, 6′-H), 4.17 (d, $J_{1,2}$ = 7.7 Hz, 1 H, 1-H), 4.48 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.53 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.59 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.70 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.76 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.82 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 5.33 (q, J_{gem} = 11.1 Hz, 2 H, CH_2), 7.08-7.32 (m, 15 H, Ar-H), 7.66-7.79 (m, 4 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι#= 57.1 (OCH_3), 68.2 (CH_2), 68.8 (C-6), 73.5 (CH_2), 74.8 (C-5), 74.9, 75.5 (2 CH_2), 77.8 (C-4), 81.7 (C-2), 84.1 (C-3), 103.7 (C-1), 123.5, 127.2, 127.3, 127.6, 127.7, 127.8, 127.9, 128.2, 128.3, 132.0, 134.0, 137.9, 138.1, 138.4 (C-Ar), 167.9 (CO). MS (MALDI, positive mode, Matrix: DHB): m/z = 646.2 $(M+Na)^+$, 662.2 $(M+K)^+$.

$C_{37}H_{37}NO_8$ (623.7) Calcd: C: 71.25 H: 5.97 N: 2.24

Found: C: 71.41 H: 6.05 N: 2.18

Octyl 3,4,6-tri-*O*-benzyl-2-*O*-phthalimidomethyl-ζ6η-D-glucopyranoside (26).

A solution of the trichloroacetimidate **24** (0.53 g, 0.7 mmol) and 1-octanol (1.10 ml, 7.0 mmol) in dry dichloromethane (10 ml) was treated with TMSOTf (13 µl, 0.07 mmol), and then stirred for 1.5 h. The reaction was processed as above and the product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate, 20:1 to afford **26** (ζ]η = 1:2, 0.36 g, 71%) as colorless oil; R_f = 0.43 (petroleum ether/ethyl acetate, 10:1); [Ŭ]$_D$ = 2.6 (c = 2.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι = 0.84-1.36 [(m, 13 H, $CH_3(CH_2)_5$)], 1.57-1.60 (m, 2 H, CH_2), 3.40 (m, 3 H, η-5-H, CH_2), 3.53 (m, 4 H, ζ-4-H, ζ-6-H, η-3-H, η-4-H), 3.64 (m, 3 H, η-2-H, η-6-H, ζ-6′-H), 3.71 (m, 2 H, η-6′-H, ζ-5-H), 3.79 (m, 1 H, ζ-2-H), 3.90 (dd, $J_{3,2}$ = 9.2, $J_{3,4}$ = 9.3 Hz, 1 H, ζ-3-H), 4.27 (d, $J_{2,1}$ = 7.8 Hz, 0.67 H, η-1-H), 4.52 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.64 (d, J_{gem} = 11.2 Hz, 1 H, CHPh), 4.72 (m, 2 H, 2 CHPh), 4.75 (d, J_{gem} = 11.2 Hz, 1 H, CHPh), 4.81 (d, J_{gem} = 11.2 Hz, 1 H, CHPh), 4.98 (d, $J_{1,2}$ = 3.4 Hz, 0.33 H, ζ-1-H), 5.32 (s, 2 H, CH_2), 7.09-7.32 (m, 15 H,

Ar-H), 7.66-7.67 (m, 4 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι# 14.1, 22.6, 25.8, 26.0, 29.1, 31.8, 32.7 [$CH_3(CH_2)_5$)], 67.3, 68.4 (2 CH_2), 68.7 (C-6), 70.2 (C-5), 73.5, 75.3, 75.4 (3 CH_2), 78.0 (C-4), 79.7 (C-2), 81.3 (C-3), 96.7 (C-1), 123.5, 127.1, 127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.1, 128.3, 133.9, 134.3 (C-Ar), 167.6, 167.8 (2 CO). MS (MALDI, positive mode, Matrix: DHB): m/z = 744.4 $(M+Na)^+$, 760.0 $(M+K)^+$.

$C_{44}H_{51}NO_8$ (721.9) Calcd: C: 73.21 H: 7.12 N: 1.94

Found: C: 73.04 H: 7.32 N: 1.83

Methyl *O*-(3,4,6-tri-*O*-benzyl-2-*O*-phthalimidomethyl-ζθη-D-glucopyranosyl)-(1-6)-2,3,4-tri-*O*-benzyl-ζ-D-glucopyranoside (27). A solution of the trichloroacetimidate **24** (0.53 g, 0.7 mmol) and methyl 2,3,4-tri-*O*-benzyl-ζ-D-glucopyranoside (**15**, 0.32 g, 0.7 mmol) in dry dichloromethane (30 ml) was treated with TMSOTf (13 µl, 0.07 mmol), and then stirred for 1.5 h. The reaction was processed as above. The crude residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate, 20:1 to afford **27** (ζ]η = 2:3, 0.42 g, 56%) as colorless oil; R_f = 0.68 (petroleum ether/ethyl acetate, 5:1); [Ŭ]$_D$ = 13.7 (c = 1.0, CH_2Cl_2).

27 ζ] Colourless oil (0.17 g, 22%); R_f = 0.72 (petroleum ether/ethyl acetate 5:1); [Ŭ]$_D$ = 9.1 (c = 0.5, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι# 3.33 (s, 3 H, OCH_3), 3.51 (dd, $J_{2,1}$ = 3.3, $J_{2,3}$ = 9.6 Hz, 1 H, 2-H_a), 3.58 (m, 3 H, 4-H_a, 4-H_b, 6-H_b), 3.63 (dd, $J_{6',5}$ = 3.8, J_{gem} = 10.8 Hz, 1 H, 6′-H_b), 3.71 (m, 2 H, 5-H_a, 6-H_a), 3.73 (m, 2 H, 2-H_b, 5-H_b), 3.79 (m, 1 H, 6′-H_a), 3.85 (dd, $J_{3,2}$ = 9.1, $J_{3,4}$ = 9.2 Hz, 1 H, 3-H_b), 3.96 (dd, $J_{3,2}$ = 9.2, $J_{3,4}$ = 9.3 Hz, 1 H, 3-H_a), 4.41 (d, J_{gem}= 10.7 Hz, 1 H, CHPh), 4.44 (d, J_{gem}= 10.7 Hz, 1 H, CHPh), 4.52 (d, $J_{1,2}$ = 3.3 Hz, 1 H, 1-H_a), 4.58 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.61 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.69 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.71 (d, J_{gem} = 12.1 Hz, 1 H, CHPh),

4.74 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.77 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.79 (m, 1 H, CHPh), 4.85 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.89 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.94 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 5.13 (d, $J_{1,2}$ = 3.3 Hz, 1 H, 1-H_b), 5.16 (q, J_{gem} = 11.0 Hz, 2 H, CH_2Phth), 7.08-7.36 (m, 34 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι# 55.1 (OCH_3), 65.9 (C_a-6), 66.6 (CH_2), 68.6 (C_b-6), 70.1 (C_b-5), 70.2 (C_a-5), 73.3, 73.4, 73.8, 74.9, 75.3, 75.7 (6 CH_2), 77.8 (C_a-4), 77.9 (C_b-4), 79.1 (C_b-2), 79.8 (C_a-2), 81.1 (C_b-3), 82.0 (C_a-3), 97.0 (C_b-1), 97.9 (C_a-1), 123.6, 127.2, 127.5, 127.6, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.6, 131.8, 134.2, 138.0, 138.2, 138.4, 138.6 (C-Ar), 167.6 (CO). MS (MALDI, positive mode, Matrix: DHB): m/z = 1080.0 $(M+Na)^+$, 1096.0 $(M+K)^+$.

$C_{64}H_{65}NO_{13}$ (1056.2)	Calcd:	C: 72.77	H: 6.20	N: 1.32
	Found:	C: 72.30	H: 6.32	N: 1.32

27 η]#Colourless oil (0.25 g, 34%); R_f = 0.68 (petroleum ether/ethyl acetate 5:1); [Ŭ]$_D$ = 13.7 (c= 0.5, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι# 3.41 (s, 3 H, OCH_3), 3.43 (m, 2 H, 4-H_a, 5-H_b), 3.51 (m, 2 H, 2-H_a, 3-H_b), 3.57 (dd, $J_{4,3}$ = 9.2, $J_{4,5}$ = 9.4 Hz, 1 H, 4-H_b), 3.66 (m, 2 H, 6-H_b, 6´-H_b), 3.70 (m, 1 H, 6-H_a), 3.74 (dd, $J_{2,1}$ = 7.8, $J_{2,3}$ = 8.6 Hz, 1 H, 2-H_b), 3.84 (m, 1 H, 5-H_a), 3.99 (dd, $J_{3,2}$ = 9.2, $J_{3,4}$ = 9.3 Hz, 1 H, 3-H_a), 4.11 (m, 1 H, 6´-H_a), 4.36 (d, $J_{1,2}$ = 7.8 Hz, 1 H, 1-H_b), 4.48 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.54 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.61 (d, $J_{1,2}$ = 3.3 Hz, 1 H, 1-H_a), 4.62 (m, 2 H, 2 CHPh), 4.66 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.72 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.75 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.78 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.80 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.83 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.88 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.97 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 5.37 (q, J_{gem} = 11.1 Hz, 2 H, CH_2Phth), 7.06-7.55 (m, 34 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι# 55.2 (OCH_3), 68.1 (CH_2), 68.5 (C_b-6), 68.8 (C_a-6), 70.0 (C_a-5), 73.3, 73.4, 73.8, (3 CH_2), 74.9 (C_b-5), 75.0, 75.1, 75.7 (3

CH_2), 77.8 (C_b-4), 78.1 (C_a-4), 79.8 (C_a-2), 81.2 (C_b-2), 81.9 (C_a-3), 83.8 (C_b-3), 97.8 (C_a-1), 103.1 (C_b-1), 123.5, 126.7, 126.9, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 131.7, 134.0, 137.8, 138.1, 138.2, 138.3 (C-Ar), 167.6, 167.8 (2 CO). MS (MALDI, positive mode, Matrix: DHB): m/z = 1080.0 $(M+Na)^+$, 1096.0 $(M+K)^+$.

$C_{64}H_{65}NO_{13}$ (1056.2) Calcd: C: 72.77 H: 6.20 N: 1.32

Found: C: 72.41 H: 6.18 N: 1.25

_O_-(3,4,6-Tri-_O_-benzyl-2-_O_-acetyl-ζ-D-glucopyranosyl) trichloroacetimidate (28).

Colorless oil (0.5 g, 79%); R_f = 0.53 (2% triethylamine in toluene); Compound **28** was synthesized following a published procedure. The analytical data are identical with the published values.[110]

_O_-(2,3,4,6-Tetra-_O_-benzyl-ζ-D-glucopyranosyl) trichloroacetimidate (29).

Colorless oil (0.6 g, 82%); R_f = 0.64 (2% triethylamine in toluene); Compound **29** was synthesized following a published procedure. The analytical data are identical with the published values.[111]

Methyl 2-_O_-acetyl- 3,4,6-tri-_O_-benzyl-ζ/η-D-glucopyranoside (30).[114]

A solution of the trichloroacetimidate **28** (0.45 g, 0.7 mmol) and methanol (0.28 ml, 7.0 mmol) in dry dichloromethane (10 ml) was treated with TMSOTf (13 µl, 0.07 mmol), and then stirred for 2 h. The reaction was processed as above and the product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate, 15:1 to afford **30** (0.26 g, 73%) as colorless oil; R_f = 0.32 (petroleum ether/ethyl acetate, 5:1); $[Ŭ]_D$ = 9.5 (c = 1.0, CH_2Cl_2).

Methyl 2,3,4,6-tetra-*O*-benzyl-ζ/η-D-glucopyranoside (31). [112]

A solution of the trichloroacetimidate **29** (0.48 g, 0.7 mmol) and methanol (0.28 ml, 7.0 mmol) in dry dichloromethane (10 ml) was treated with TMSOTf (13 µl, 0.07 mmol), and then stirred for 1.5 h. The reaction was processed as above and the product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate, 15:1 to afford **31** (0.26 g, 73%) as colorless oil; R_f = 0.49 (petroleum ether/ethyl acetate, 5:1); $[Ŭ]_D$ = 14.3 (c = 1.0, CH_2Cl_2).

Octyl 2-*O*-acetyl- 3,4,6-tri-*O*-benzyl-η-D-glucopyranoside (32).[114]

A solution of the trichloroacetimidate **28** (0.45 g, 0.7 mmol) and 1-octanol (1.10 ml, 7.0 mmol) in dry dichloromethane (10 ml) was treated with TMSOTf (13 µl, 0.07 mmol), and then stirred for 2.5 h. The reaction was processed as above and the product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate, 20:1 to afford **32** (0.33 g, 77%) as colorless oil; R_f = 0.39 (petroleum ether/ethyl acetate, 10:1); $[Ŭ]_D$ = 9.6 (c = 1.0, CH_2Cl_2).

Octyl 2,3,4,6-tetra-*O*-benzyl-ζ/η-D-glucopyranoside (33). [113]

A solution of the trichloroacetimidate **29** (0.48 g, 0.7 mmol) and 1-octanol (1.10 ml, 7.0 mmol) in dry dichloromethane (10 ml) was treated with TMSOTf (13 µl, 0.07 mmol), and then stirred for 1.5 h. The reaction was processed as above and the product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate, 20:1 to afford **33** (0.37 g, 82%) as colorless oil; R_f = 0.44 (petroleum ether/ethyl acetate, 10:1); $[Ŭ]_D$ = 5.8 (c = 1.0, CH_2Cl_2).

Methyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-ζ6η-D-glucopyranosyl)-(1-6)-2,3,4-tri-*O* benzyl-ζ-D-glucopyranoside (34).[114] A solution of the trichloroacetimidate **28** (0.45 g, 0.7 mmol) and giucose derivative **15** (0.32 g, 0.7 mmol) in dry dichloromethane (30

ml) was treated with TMSOTf (13 µl, 0.07 mmol), and then stirred for 1.5 h. The reaction was processed as above. The crude residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate, 15:1 to afford **34** (0.43 g, 65%) as colorless oil; R_f = 0.51 (petroleum ether/ethyl acetate, 5:1); $[\alpha]_D$ = 32.5 (c = 1.0, CH_2Cl_2).

Methyl *O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-(1-6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (35).[112] A solution of the trichloroacetimidate **29** (0.48 g, 0.7 mmol) and glucose derivative **15** (0.32 g, 0.7 mmol) in dry dichloromethane (30 ml) was treated with TMSOTf (13 µl, 0.07 mmol), and then stirred for 1.5 h. The reaction was processed as above. The crude residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate, 15:1 to afford **35** (0.48 g, 70%) as colorless oil; R_f = 0.62 (petroleum ether/ethyl acetate, 5:1); $[\alpha]_D$ = 46.2 (c = 1.0, CH_2Cl_2).

1:2-*O*-Isopropylidene-3-*O*-phthalimidomethyl-α-D-glucofuranose (36).
To a solution of **20** (0.4 g, 0.9 mmol) in acetic acid (15 ml, 80%) was added and the reaction mixture refluxed. After stirring for 3 h. the solvent was evaporated in vacuo and the residue was purified by flash chromatograph petrolum ether/ethyl acetate, 2:1 to give **36** (0.26 g, 73%) as colorless oil; R_f = 0.32 (petroleum ether/ethyl acetate 1:1); $[\alpha]_D$ = 15.6 (c = 1.0, CH_2Cl_2).
^{1}H-NMR (250 MHz, $CDCl_3$): ι# 1.30, 1.46 (2 s, 6 H, 2 CH_3), 2.81 (brs, 1 H, OH), 4.02 (brs, 1 H, OH), 4.12 (m, 2 H, 6-H, 4-H), 4.31 (m, 1 H, 6′-H), 4.39 (m, 1 H, 5-H), 4.63 (d, *J* = 3.7 Hz, 1 H, 3-H), 5.13 (d, J_{gem} = 10.0 Hz, 1 H, CHPh), 5.27 (d, J_{gem} = 10.0 Hz, 1 H, CHPh), 5.30 (d, $J_{2,1}$ = 3.5 Hz, 1 H, 2-H), 5.86 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 7.72-7.91 (m, 4 H, Ar-H). MS (MALDI, positive mode, Matrix: DHB): m/z = 402.0 $(M+Na)^+$, 418.0 $(M+K)^+$.

$C_{18}H_{21}NO_8$ (379.4) Calcd: C: 56.99 H: 5.57 N: 3.69
Found: C: 57.21 H: 5.87 N: 3.23

Methyl 2,3,4-tri-*O*-acetyl-6-*O*-phthalimidomethyl-ζ-D-glucopyranoside (38).

A mixture of **16** (0.3 g, 0.48 mmol) and palladium on carbon (0.25 g, 10%) in ethanol/ethyl acetate (20 ml, 1:1) and formic acid (0.2 ml) is stirred under hydrogen for 12 h. After filtration and concentration in vauco, the residue is dissolved in pyridine/acetic anhydride (10 ml, 1:1), and the mixture is stirred for 15 h. The solution is concentrated in vacuo and coevaporated with toluene and the product was purified by column chromatography petrolum ether/ethyl acetate, 5:1 to give **38** (0.19 g, 81%) as colorless oil; R_f = 0.41 (petroleum ether/ethyl acetate, 2:1); $[Ŭ]_D$ = 7.5 (c = 0.5, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$): ι# 1.89, 1.94, 2.01 (3 s, 9 H, 3 AcO), 3.31 (s, 3 H, OCH_3), 3.71 (m, 3 H, 6-H, 5-H, 6´-H), 4.70 (d, $J_{1,2}$ = 2.7 Hz, 1 H, 1-H), 4.74 (m, 1 H, 2-H), 5.00 (dd, $J_{4,3}$ = 9.5, $J_{4,5}$ = 9.8 Hz, 1 H, 4-H), 5.15 (s, 2 H, CH_2), 5.41 (dd, $J_{3,4}$ = 9.5, $J_{3,2}$ = 9.7 Hz, 1 H, 3-H), 7.72-7.91 (m, 4 H, Ar-H). MS (MALDI, positive mode,Matrix: DHB): m/z = 502.0 $(M+Na)^+$, 518.0 $(M+K)^+$.

$C_{22}H_{25}NO_{11}$ (479.4) Calcd: C: 55.11 H: 5.25 N: 2.92
Found: C: 55.35 H: 5.47 N: 3.08

Diphenylcarbinol (39).

Diphenylcarbinol (**39**) was purchased from Fluka and used as received.

9-Hydroxyfluorene (40).

9-Hydroxyfluorene (**40**) was purchased from Fluka and used as received.

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_O_-Diphenylmethyl trichloroacetimidate (41).[138]

A mixture of diphenycarbinol (**39**, 0.92 g, 5.0 mmol), trichloroacetonitrile (5 ml, 50 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (71 µl) in dry dichloromethane (10 ml) was stirred under nitrogen at room temperature for 3 h; then the reaction mixture was concentrated in vacuo and the residue was purified by flash chromatography 3% triethylamine in petroleum ether/ethyl acetate, 80:1 to give as a white powder **41** (1.5 g, 94%); R_f = 0.70 (3% triethylamine in toluene); m.p. 85 °C.

^{1}H-NMR (250 MHz, $CDCl_3$): ι# 6.94 (s, 1 H, CH), 7.28-7.44 (m, 10 H, Ar-H), 8.40 (brs, 1 H, NH). ^{13}C-NMR (62.8 MHz, $CDCl_3$): ι# 81.4 (CH), 91.6 (CCl_3), 126.9, 127.9, 128.5, 139.8 (C-Ar), 161.3 (CNH).

($C_{15}H_{12}Cl_3NO$) 328.6; EI-MS: m/z = 328.0.

_O_-(9-Fluorenyl) trichloroacetimidate (42).

A stirred solution of 9-hydroxyfluorene (**40**, 0.91 g, 5.0 mmol) in dry dichloromethane (10 ml) and trichloroacetonitrile (5 ml, 50 mmol) was treated with DBU (71 σl) at room temperature and then left for 0.5 h. The solvent was evaporated and the product was purified by column chromatography 3% triethylamine in toluene to give **42** as a white powder (1.4 g, 86%); R_f = 0.56 (3% triethylamine in toluene); m.p. 59 °C.

^{1}H-NMR (250 MHz, $CDCl_3$): ι = 6.99 (s, 1 H, CH), 7.25-7.67 (m, 8 H, Ar-H), 8.67 (brs, 1 H, NH). ^{13}C-NMR (62.5 MHz, $CDCl_3$): ι = 79.6 (CH), 91.5 (CCl_3), 120.0, 126.0, 127.8, 129.6, 141.0, 141.7 (C-Ar), 163.6 (CNH).

($C_{15}H_{10}Cl_3NO$) 326.6; EI-MS: m/z = 326.0.

General procedure for the reaction of trichloroacetimidate 41 with alcohols.

A solution of **41** (0.2 g, 0.6 mmol) and alcohol (0.6 mmol) in dry dichloromethane (10 ml) was stirred under nitrogen at room temperature for 5 min. and then TMSOTf

(13 µl, 0.06 mmol) was added. After 45 min-2.5 h the reaction mixture was neutralized with solid sodium bicarbonate, filtered and concentrated in vacuo. The residue was purified by flash chromatography.

General procedure for the reaction of trichloroacetimidate 42 with alcohols.

A solution of the trichloroacetimidate **42** (0.46 g, 1.4 mmol) and alcohol (1.6 mmol) in dry dichloromethane (10 ml) was cooled to -40 ^{o}C and was treated with TMSOTf (26 µl, 0.14 mmol), and then stirred for 10-120 min. The reaction was quenched by the addition of solid sodium bicarbonate, filtered and concentrated. The crude residue was purified by column chromatography on silica gel using (petroleum ether/ethyl acetate).

3,5-Dinitrobenzyl diphenylmethyl ether (43).

Yellow powder (0.2 g, 91%); R_f = 0.66 (petroleum ether/ethyl acetate, 5:1); m.p. 127 ^{o}C. ^{1}H-NMR (250 MHz, $CDCl_3$): ι#= 4.71 (s, 2 H, CH_2), 5.50 (s, 1 H, CH), 7.31-7.40 (m, 10 H, Ar-H), 8.52 (m, 2 H, Ar-H), 8.91 (dd, *J* = 2.1 Hz, 1 H, Ar-H); ^{13}C-NMR (62.8 MHz, $CDCl_3$): ι#= 68.7 (CH_2), 84.3 (CH), 117.8, 126.9, 127.1, 128.0, 128.7, 141.0, 143.3, 148.6 (C-Ar). EI-MS: m/z = 364.0.

$C_{20}H_{16}N_2O_5$ (364.4)	Calcd:	C: 65.93	H: 4.43	N: 7.68
	Found:	C: 65.80	H: 4.60	N: 7.20

9-(3,5-Dinitrobenzyloxy) fluorene (44).

Yellow powder (0.45 g, 88%); R_f = 0.47 (petroleum ether/ethyl acetate, 4:1); m.p. 108 ^{o}C. ^{1}H-NMR (250 MHz, $CDCl_3$): ι = 4.26 (s, 2 H, CH_2), 5.89 (s, 1 H, CH), 7.25-7.73 (m, (H, Ar-H), 8.42 (d, *J*= 2.1 Hz, 2 H, Ar-H), 8.88 (dd, *J*= 2.1 Hz, 1 H, Ar-H). ^{13}C-NMR (62.8 MHz, $CDCl_3$):#ι# 63.8 (CH_2), 81.0 (CH), 117.6, 120.3, 125.5, 127.1, 127.9, 129.7, 141.1, 141.5, 143.7, 148.4, (C-Ar). EI-MS: m/z = 362.0.

$C_{20}H_{14}N_2O_5$ (362.3) Calcd: C: 66.29 H: 3.89 N: 7.73

Found: C: 66.61 H: 4.06 N: 7.97

Diphenylmethyl isopropyl ether (45).

Colorless oil (0.1 g, 73.5%); R_f = 0.76 (petroleum ether/ethyl acetate, 5:1); Compound **45** was synthesized following a published procedure. The analytical data are identical with the published values.[139]

9- Isopropoxy fluorene (46).

White powder **46** (0.28 g, 88.5%); R_f = 0.64 (petroleum ether/ethyl acetate, 10:1); m.p. 44 °C, Lit.[135] 43-44 °C.

Cyclohexyl diphenylmethyl ether (47).

Colorless oil (0.12 g, 75%); R_f = 0.66 (petroleum ether/ethyl acetate, 6:1). Compound **47** was synthesized following a published procedure. The analytical data are identical with the published values.[140]

Cholesteryl diphenylmethyl ether (48).

White powder (0.31 g, 92%); R_f = 0.42 (petroleum ether/ethyl acetate, 10:1); m.p. 136 °C. ^{1}H-NMR (250 MHz, $CDCl_3$):#t # #0.64-2.44#m3#43#T 3#cholesterol), 3.31 (m, 1 H, CH), 5.35 (d, 1 H, CH), 5.61 (s, 1 H, CH), 7.20-7.52 (m, 10 H, Ar-H). EI-MS: m/z = 552.0.

$C_{40}H_{56}O$ (552.9) Calcd: C: 86.80 H: 10.21

Found: C: 87.04 H: 9.82

Cholesteryl fluorenyl ether (49).

Colorless oil (0.70 g, 91%); R_f = 0.80 (petroleum ether/ethyl acetate, 20:1).

^{1}H-NMR (250 MHz, $CDCl_3$) δ = 0.64-2.40 (m, 43 H, cholesterol), 3.40 (m, 1 H, CH), 5.22 (m, 1 H, CH), 5.60 (s, 1 H, CH), 7.22-7.72 (m, 8 H, Ar-H). EI-MS: m/z = 550.0.

$C_{40}H_{54}O$ (550.9)	Calcd:	C: 87.21	H: 9.88
	Found:	C: 87.15	H: 9.81

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-diphenylmethyl-α-D-glucopyranside (50).

Colorless oil (0.30 g, 78%); R_f = 0.51 (petroleum ether/ethyl acetate, 5:1); $[\alpha]_D$ = -8.6 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 3.40 (s, 3 H, OCH_3), 3.57 (dd, $J_{1,2}$ = 3.6, $J_{2,3}$ = 9.3 Hz, 1 H, 2-H), 3.64 (m, 3 H, 4-H, 6-H, 6´-H), 3.80 (m, 1 H, 5-H), 4.04 (dd, $J_{3,2}$ = 9.3, $J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 4.52 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 4.67 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.69 (m, 2 H, 2 CHPh), 4.73 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.81 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 4.86 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 5.40 (s, 1 H, CH), 7.13-7.48 (m, 25 H, Ar-H). MS (MALDI, positive mode, Matrix: DHB): m/z = 653.0 $(M+Na)^+$, 669.0 $(M+K)^+$.

$C_{41}H_{42}O_6$ (630.8)	Calcd:	C: 78.07	H: 6.71
	Found:	C: 78.04	H: 6.61

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(9-fluorenyl)-α-D-glucopyranoside (51).

White foam (0.69 g, 79%); R_f = 0.52 (petroleum ether/ethyl acetate, 5:1); $[\alpha]_D$ = 25.5 (c = 2.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 3.44 (s, 3 H, OCH_3), 3.51 (m, 2 H, 6-H, 6´-H), 3.60 (dd, $J_{4,3}$ = 9.3, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 3.63 (dd, $J_{1,2}$ = 3.1, $J_{2,3}$ = 9.2 Hz, 1 H, 2-H), 3.74 (m, 1 H, 5-H), 4.02 (dd, $J_{3,2}$ = 9.2, $J_{3,4}$ = 9.3 Hz, 1 H, 3-H), 4.50 (d, J_{gem}= 10.6 Hz, 1 H, CHPh), 4.73 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 4.74 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.83 (d, J_{gem} = 11.3 Hz, 1 H, CHPh), 4.86 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.88 (d, J_{gem} = 11.3 Hz, 1 H, CHPh), 5.05 (d, J_{gem} = 11.3 Hz, 1 H, CHPh), 5.74 (s, 1 H, CH), 7.05-

7.42 (m, 8 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι = 54.9 (OCH_3), 63.4 (C-6), 70.0 (C-5), 73.1, 74.7, 75.6 (3 CH_2), 77.5 (C-4), 79.7 (C-2), 80.8 (CH), 82.0 (C-3), 97.8 (C-1), 119.8, 125.4, 127.1, 127.2, 127.4, 128.2, 129.1, 137.9, 138.6, 140.7, 142.2, 142.4 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 650.0 (M+Na)+.

$C_{41}H_{40}O_6$ (628.8) Calcd: C: 78.32 H: 6.41

Found: C: 78.71 H: 6.37

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-diphenylmethyl–Ŭ-D-glucopyranoside (52).

Colorless oil (0.32 g, 83%); R_f = 0.63 (petroleum ether/ethyl acetate, 4:1); $[Ŭ]_D$ = -35.0 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$): ι = 3.20 (dd, $J_{6,5}$ = 5.1, J_{gem}= 10.6 Hz, 1 H, 6- H), 3.44 (s, 3 H, OCH_3), 3.45 (m, 1 H, 6´-H), 3.55 (dd, $J_{1,2}$ = 3.6, $J_{2,3}$ = 9.6 Hz, 1 H, 2-H), 3.70 (m, 1 H, 4-H), 3.81 (m, 1 H, 5-H), 4.04 (dd, $J_{3,2}$ = 9.6, $J_{3,4}$ = 9.3 Hz, 1 H, 3-H), 4.19 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.23 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.50 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.63 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.65 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.78 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.95 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 5.91 (s, 1 H, CH). MS (MALDI, positive mode, Matrix: DHB): m/z = 653.0 $(M+Na)^+$, 669.0 $(M+K)^+$.

$C_{41}H_{42}O_6$ (630.8) Calcd: C: 78.07 H: 6.71

Found: C: 78.03 H: 6.50

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(9-fluorenyl)-Ŭ-D-glucopyranoside (53).

White foam (0.54 g, 61%); R_f = 0.48 (petroleum ether/ethyl acetate, 4:1); $[Ŭ]_D$ = 13.3 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι = 3.29 (m, 1 H, 6-H), 3.34 (s, 3 H, OCH_3), 3.38 (dd, $J_{6,5}$ = 3.3, J_{gem} = 10.2 Hz, 1 H, 6´-H), 3.50 (m, 2 H, 2-H, 5-H), 3.63 (dd, $J_{4,3}$ = 9.1, $J_{4,5}$

= 9.5 Hz, 1 H, 4-H), 3.73 (dd, $J_{3,2}$ = 9.2, $J_{3,4}$ = 9.1 Hz, 1 H, 3-H), 4.58 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 4.62 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.64 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.66 (d, J_{gem} = 11.6 Hz, 1 H, CHPh), 4.73 (d, J_{gem} = 11.6 Hz, 1 H, CHPh), 4.76 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.97 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 5.68 (s, 1 H, CH), 7.21-7.64 (m, 23 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι = 55.1 (OCH_3), 63.5 (C-6), 69.8 (C-5), 70.6 (C-4), 73.1, 75.4, 77.2 (3 CH_2), 79.4 (C-2), 80.7 (CH), 81.5 (C-3), 98.1 (C-1), 119.8, 119.9, 120.2, 125.2, 125.4, 125.6, 127.3, 127.7, 127.9, 128.0, 128.4, 128.5, 129.1, 140.8, 140.9, 142.4 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 629.0 $(M+H)^+$.

$C_{41}H_{40}O_6$ (628.8) Calcd: C: 78.32 H: 6.41

Found: C: 78.51 H: 6.49

3-*O*-Diphenylmethyl-1:2, 5:6-di-*O*-isopropylidene-Ŭ-D-glucofuranose (54).

White foam (0.20 g, 77%); R_f = 0.67 (petroleum ether/ethyl acetate, 4:1); $[Ŭ]_D$ = -21.1 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$): ι # 1.22, 1.30, 1.35, 1.42 (4 s, 12 H, 4 CH_3), 4.02 (m, 2 H, 6-H, 6´-H), 4.09-4.20 (m, 2 H, 4-H, 3-H), 4.35 (m, 1 H, 5- H), 4.51 (d, $J_{2,1}$ = 3.7 Hz, 1 H, 2-H), 5.60 (s, 1 H, CH), 5.87 (d, $J_{1,2}$ = 3.7 Hz, 1 H, 1-H), 7.16-7.41 (m, 10 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$) ι = 25.5, 26.3, 26.7, 26.9 (4 CH_3), 67.6 (C-6), 72.7 (C-5), 80.0 (C-3), 81.6 (C-4), 82.6 (CH), 83.0 (C-2), 105.4 (C-1), 109.0, 111.8, 126.9, 127.4, 127.7, 128.4, 128.5, 141.3, 142.1 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 449.0 $(M+Na)^+$, 465.0 $(M+K)^+$.

$C_{25}H_{30}O_6$ (426.5) Calcd: C: 70.40 H: 7.01

Found: C: 70.26 H: 7.02

3-*O*-(9-Fluorenyl)-1:2, 5:6-di-*O*-isopropylidene-Ŭ-D-glucofuranose (55).

Colorless oil (0.49 g, 82.5%); R_f = 0.38 (petroleum ether/ethyl acetate, 5:1); $[Ŭ]_D$ = +

9.8 (c = 2.0, CH_2Cl_2). ^{1}H-NMR (250 MHz, $CDCl_3$):# = 1.22, 1.42, 1.44, 1.51 (4 s, 12 H, 4 CH_3), 4.05 (dd, $J_{6,5}$ = 5.7, J_{gem} = 8.6 Hz, 1 H, 6-H), 4.20 (m, 2 H, 4-H, 6′-H), 4.42 (d, J = 2.9 Hz, 1 H, 3-H), 4.52 (m, 2 H, 5-H, 2-H), 5.66 (s, 1 H, CH), 5.88 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 7.27-7.70 (m, 8 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): = 24.1, 25.4, 27.0 (4 CH_3), 67.7 (C-6), 72.5 (C-5), 81.7 (C-3), 81.9 (C-4), 82.1 (CH), 84.1 (C-2), 105.4 (C-1), 109.0, 111.7, 119.8, 119.9, 125.1, 125.7, 127.3, 127.6, 129.0, 129.3, 140.3, 140.8, 142.6, 143.1 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 447 $(M+Na)^+$.

$C_{25}H_{28}O_6$ (424.5)	Calcd:	C: 70.73	H: 6.65
	Found:	C: 70.92	H: 6.70

Diphenylmethyl 2,3,4,6-tetra-*O*-acetyl-ζ-D-glucopyranoside (57).

White powder (0.26 g, 83%); R_f = 0.45 (petroleum ether/ethyl acetate, 2:1); $[Ŭ]_D$ = 107.6 (c = 1.0, CH_2Cl_2); m.p. 127 °C.

^{1}H-NMR (600 MHz, $CDCl_3$): # = 2.00, 2.01, 2.02, 2.07 (4 s, 12 H, 4 AcO), 3.92 (m, 1 H, 6-H), 3.97 (m, 1 H, 5-H), 4.15 (dd, $J_{6,5}$ = 3.9, J_{gem} = 9.9 Hz, 1 H, 6′-H), 4.89 (dd, $J_{1,2}$ = 3.7, $J_{2,3}$ = 9.9 Hz, 1 H, 2-H), 5.06 (dd, $J_{4,3}$ = 9.8, $J_{4,5}$ = 9.9 Hz, 1 H, 4-H), 5.15 (d, $J_{1,2}$ = 3.7 Hz, 1 H, 1-H), 5.60 (dd, $J_{3,2}$ = 9.9, $J_{3,4}$ = 9.8 Hz, 1 H, 3-H), 5.67 (s, 1 H, CH), 7.26-7.37 (m, 10 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): # = 20.5, 20.6 (4 AcO), 61.6 (C-6), 67.7 (C-5), 68.4 (C-4), 70.2 (C-3), 70.6 (C-2), 81.0 (CH), 94.3 (C-1), 126.8, 127.1, 127.7, 128.0, 128.4, 128.5, 140.4, 141.4 (C-Ar), 169.5, 169.8, 170.1, 170.6 (4 CO). MS (MALDI, positive mode, Matrix: DHB): m/z = 537.0 $(M+Na)^+$, 553.0 $(M+K)^+$.

$C_{27}H_{30}O_{10}$ (514.5)	Calcd:	C: 63.02	H: 5.87
	Found:	C: 63.15	H: 5.97

9-Fluorenyl 2,3,4,6-tetra-*O*-acetyl-ζ-D-glucopyranoside (58).

Colorless foam (0.55 g, 76%); R_f = 0.37 (petroleum ether/ethyl acetate, 2:1); [Ŭ]$_D$= 17.4 (c =1.0, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$) ι = 2.00, 2.02, 2.06, 2.08 (4 s, 12 H, 4 AcO), 3.90 (m, 1 H, 6-H), 4.20 (m, 2 H, 5-H, 6′-H), 4.83 (dd, $J_{2,1}$ = 3.7, $J_{2,3}$ = 9.9 Hz, 1 H, 2-H), 5.11 (dd, $J_{4,3}$ = 9.4, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 5.30 (d, $J_{1,2}$ = 3.7 Hz, 1 H, 1-H), 5.51 (dd, $J_{3,2}$ = 9.9, $J_{3,4}$ = 9.4 Hz, 1 H, 3-H), 5.70 (s, 1 H, CH), 7.20-7.61 (m, 8 H, Ar-H). ^{13}C-NMR (62.8 MHz, $CDCl_3$): ι = 20.5, 20.6, 20.7 (4 AcO), 61.7 (C-6), 67.6 (C-5), 68.5 (C-4), 70.0 (C-3), 70.8 (C-2), 81.1 (CH), 95.0 (C-1), 120.1, 125.1, 125.8, 127.5, 127.6, 129.4, 129.6, 140.5, 141.1, 141.5, 142.5, 147.7 (C-Ar), 169.5, 170.0, 170.6 (CO). MS (MALDI, positive mode, Matrix: DHB): m/z = 535.0 $(M+Na)^+$, 551.0 $(M+K)^+$.

$C_{27}H_{28}O_{10}$ .0.5 H_2O (521.5)	Calcd:	C: 62.18	H: 5.75
	Found:	C: 61.87	H: 5.77

2:3, 5:6-di-*O*-isopropylidene-Ŭ-D-mannofuranose (59).

Compound **59** was synthesized following a published procedure. The analytical data are identical with the published values.[142]

9-Fluorenyl 2:3, 5:6-di-*O*-isopropylidene-Ŭ-D-mannofuranoside (60).

White foam (0.33 g, 56%); R_f = 0.43 (petroleum ether/ethyl acetate, 5:1); [Ŭ]$_D$ = -3.5 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$): ι = 1.30, 1.36, 1.43, 1.47 (4 s, 12 H, 4 CH_3), 3.71 (dd, $J_{6,5}$ = 4.4, J_{gem} = 8.6 Hz, 1 H, 6-H), 3.90 (dd, $J_{6,5}$ = 6.3, J_{gem} = 8.6 Hz, 1 H, 6′-H), 4.11 (dd, $J_{4,3}$ = 3.6, $J_{4,5}$ = 7.3 Hz, 1 H, 4-H), 4.29 (m, 1 H, 5-H), 4.67 (d, $J_{2,3}$ = 5.9 Hz, 1 H, 2-H), 4.77 (dd, $J_{3,4}$ = 3.6, $J_{3,2}$ = 5.9 Hz, 1 H, 3-H), 5.41 (s, 1 H, 1-H), 5.63 (s, 1 H, CH), 7.20-7.71 (m, 8 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι# 66.4 (C-6), 73.2 (C-5), 79.5 (C-3), 80.3 (C-4, CH), 85.5 (C-2), 105.8 (C-1), 109.1, 112.6, 119.9, 120.0,

125.2, 126.1, 127.6, 127.7, 129.0, 129.2, 140.2, 140.9, 142.0, 143.7 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 447.0 $(M+Na)^+$.

$C_{25}H_{28}O_6$ (424.5) Calcd: C: 70.73 H: 6.65

Found: C: 70.91 H: 6.87

1,2,3-Tri-O-benzyl-ζ-D-glucose (61).

Compound **61** was synthesized following a published procedure. The analytical data are identical with the published values.[143]

Benzyl 2,3-di-*O*-benzyl-6-*O*-diphenylmethyl-Ŭ-D-glucopyranoside (62).

Colorless oil (0.31 g, 84%); R_f = 0.35 (petroleum ether/ethyl acetate, 4:1); $[Ŭ]_D$ = 17.5 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι#= 2.56 (brs, 1 H, OH), 3.62 (dd, $J_{2,1}$ = 3.6, $J_{2,3}$ = 9.5 Hz, 1 H, 2-H), 3.72 (m, 3 H, 6-H, 6´-H, 4-H), 3.93 (m, 1 H, 5-H), 3.96 (dd, $J_{3,2}$ = 9.5, $J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 4.61 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.63 (d, J_{gem} = 12.1 Hz,1 H, CHPh), 4.71 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.78 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.83 (d, J_{gem} = 11.3 Hz, 1 H, CHPh), 4.94 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 5.09 (d, J_{gem} = 11.3 Hz, 1 H, CHPh), 5.49 (s, 1 H, $CH(Ph)_2$), 7.30-7.46 (m, 25 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι#= 68.6 (C-6), 68.7 (CH_2), 70.3 (C-5), 71.1 (C-4), 72.6 (CH_2), 75.4 (CH_2), 79.6 (C-2), 81.5 (C-3), 84.2 (CH), 95.0 (C-1), 126.8, 126.9, 127.4, 127.7, 127.8, 127.9, 128.3, 128.4, 137.0, 138.0, 138.7, 141.9 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 639.4 $(M+Na)^+$.

$C_{40}H_{40}O_6$ (616.8) Calcd: C: 77.89 H: 6.53

Found: C: 77.73 H: 6.41

Allyl 3,4,6-tri-*O*-benzyl-2-*O*-diphenylmethyl-Ŭ-D-glucopyranoside (63).

Colorless oil (0.30 g, 76%); R_f = 0.72 (petroleum ether/ethyl acetate, 4:1); $[Ŭ]_D$ =

25.0 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι#= 3.62 (m, 3 H, 4-H, 5-H, 6-H), 3.73 (dd, $J_{2,1}$ = 3.5, $J_{2,3}$ = 10.5 Hz, 1 H, 2-H), 3.80 (m, 1 H, 6´-H), 3.91 (dd, *J* = 6.3, *J* = 12.9 Hz, 1 H, CH-allyl), 4.10 (m, 2 H, 3-H, CH-allyl), 4.44 (d, J_{gem} = 11.8 Hz, 1 H, CHPh), 4.48 (d, J_{gem} = 10.5 Hz, 1 H, CHPh), 4.58 (d, J_{gem} = 11.8 Hz, 1 H, CHPh), 4.69 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 4.81 (d, J_{gem} = 10.5 Hz, 1 H, CHPh), 4.86 (d, J_{gem} = 10.5 Hz, 1 H, CHPh), 4.95 (d, J_{gem} = 10.5 Hz, 1 H, CHPh), 5.21 (m, 2 H, CH=$\underline{CH_2}$), 5.61 (s, 1 H, CH), 5.92 (m, 1 H, $\underline{CH}$=CH_2), 7.14-7.39 (m, 25 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι#= 68.3 (CH_2), 68.4 (C-6), 70.1 (OCH_2), 73.4 (C-5), 74.9, 75.7 (2 CH_2), 78.6 (C-4), 79.7 (C-2), 82.5 (C-3), 84.9 (CH), 96.3 (C-1), 117.7 (CH=$\underline{CH_2}$), 126.7, 127.3, 127.3, 127.4, 127.6, 127.8, 127.9, 128.3, 128.4, 133.9, 138.3, 142.1, 142.7 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 680.0 $(M+Na)^+$.

$C_{43}H_{44}O_6$ (656.8) Calcd: C: 78.63 H: 6.75

Found: C: 78.46 H: 6.63

Allyl 3,4,6-tri-*O*-benzyl-2-*O*-(9-fluorenyl)-Ŭ-D-glucopyranoside (64).

Colorless oil (0.27 g, 66.5%); R_f = 0.54 (petroleum ether/ethyl acetate, 4/1); $[Ŭ]_D$ = -5.7 (c = 2.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$0]#ι#ǂ#3.50#m, 3 H, 6-H, 4-H, 2-H), 3.64 (dd, $J_{6',5}$ = 3.2, J_{gem} = 10.5 Hz, 1 H, 6´-H), 3.69 (m, 1 H, 5-H), 3.78 (dd, *J* = 6.1, *J* = 12.1 Hz, 1 H, CH-allyl), 3.97 (dd, $J_{3,4}$ = 9.2, $J_{3,2}$ = 9.4 Hz, 1 H, 3-H), 4.01 (m, 1 H, CH-allyl), 4.31 (d, $J_{1,2}$ = 2.9 Hz, 1 H, 1-H), 4.36 (d, J_{gem} = 10.5 Hz, 1 H, CHPh), 4.38 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.54 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.77 (d, J_{gem} = 12.5 Hz, 1 H, CHPh), 4.87 (d, J_{gem} = 11.2 Hz, 1 H, CHPh), 5.15 (d, J_{gem} = 11.2 Hz , 1 H, CHPh), 5.19 (d, *J* = 10.2 Hz, 1 H, CH-allyl), 5.30 (d, *J* = 18.5 Hz, 1 H, CH-allyl), 5.78 (s, 1 H, CH), 6.01 (m, 1 H, $\underline{CH}$=CH_2), 7.05-7.74 (m, 23 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι#= 68.2 (C-6), 68.3 (CH_2), 69.7 (C-5), 73.1 (CH_2), 75.1, 75.8 (2 CH_2), 76.8

(C-2), 77.7 (C-4), 80.8 (CH), 81.7 (C-3), 96.9 (C-1), 117.8 (CH=$\underline{CH_2}$), 119.8, 119.9, 125.9, 126.7, 127.3, 127.4, 127.5, 127.7, 127.8, 127.9, 128.0, 128.3, 129.1, 134.0, 137.7, 138.2, 140.4, 140.9, 141.4, 143.8 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 677.0 $(M+Na)^+$, 693.0 $(M+K)^+$.

$C_{43}H_{42}O_6$ (654.8) Calcd: C: 78.87 H: 6.46

Found: C: 78.61 H: 6.50

3,4,6-Tri-*O*-benzyl-2-*O*-diphenylmethyl–Ŭ/η-D-glucopyranose (65).

To a solution of **63** (1.2 g, 1.85 mmol) in a mixture of toluene/EtOH/H_2O (40:40:2 ml) was added Wilkinson´s catalyst (342 mg, 0.36 mmol) and the reaction mixture was refluxed at 110 °C. After 10 h. the solvent was evaporated in vacuo and the residue was purified by flash chromatography petroleum ether/ethyl acetate, 10:1 to give ζ6η mixture of **65** (ζ]η = 4:1, 0.80 g, 71%) as a colorless oil; R_f = 0.45 (petroleum ether/ethyl acetate, 3:1); $[Ŭ]_D$ = 17.8 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι#= 3.08 (brs, 1 H, ζ-OH), 3.22 (brs, 1 H, η-OH), 3.53 (m, 2 H, η-4-H, η-5-H), 3.63 (m, 2 H, ζ-4-H, 6-H), 3.72 (m, 2 H, ζ-2-H, η-3-H,#6´-H), 4.04 (m, 2 H, ζ-3-H, ζ-5-H), 4.46 (d, J_{gem} = 9.6 Hz, 1 H, CHPh), 4.48 (d, J_{gem} = 9.6 Hz, 1 H, CHPh), 4.51 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.75 (d, $J_{1,2}$ = 8.2 Hz, 0.2 H, η-1-H), 4.83 (d, J_{gem} = 9.6 Hz, 1 H, CHPh), 4.86 (d, J_{gem} = 9.6 Hz, 1 H, CHPh), 4.99 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 5.07 (d, $J_{1,2}$ = 2.9 Hz, 0.8 H, ζ-1-H), 5.72 (s, 1 H, CH), 7.16-7.38 (m, 25 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι#= 67.0 (CH_2), 68.4 (C-6), 70.2 (C-5), 73.4, 74.7 (2 CH_2), 77.7 (C-4), 78.2 (C-2), 81.8 (C-3), 82.9 (CH), 91.1 (C-ζ-1), 97.6 (C-η-1), 126.6, 127.1, 127.3, 127.4, 127.6, 127.7, 127.8, 127.9, 128.0, 128.3, 128.6, 137.7, 137.9, 138.1, 138.5, 141.7, 142.3, 142.8 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 639.0 $(M+Na)^+$.

$C_{40}H_{40}O_6$ (616.8) Calcd: C: 77.89 H: 6.53

Found: C: 78.21 H: 6.83

3,4,6-Tri-*O*-benzyl-2-*O*-(9-fluorenyl)–Ŭ-D-glucopyranose (66).

To a solution of **64** (1.21 g, 1.85 mmol) in a mixture of toluene/EtOH/H_2O (40:40:2 ml) was added Wilkinson`s catalyst (342 mg, 0.36 mmol) and the reaction mixture was refluxed at 110 °C. for 16 h. The reaction was processed as above and the product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate, 8:1 to afford **66** (0.75 g, 67%) as colorless oil; R_f = 0.36 (petroleum ether/ethyl acetate, 2:1); $[Ŭ]_D$ = 15.2 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$):#ŧ ǂ #2.02#brs, 1 H, OH), 3.65 (m, 2 H, 6-H, 5-H), 3.77 (m, 2 H, 6´-H, 4-H), 4.06 (m, 1 H, 3-H), 4.51 (dd, $J_{2,1}$ = 3.8, $J_{2,3}$ = 9.8 Hz, 1 H, 2-H), 4.62 (d, J_{gem} = 11.6 Hz, 1 H, CHPh), 4.71 (d, J_{gem} = 11.6 Hz, 1 H, CHPh), 4.80 (d, J_{gem} = 9.5 Hz, 1 H, CHPh), 4.86 (d, J_{gem} = 11.6 Hz, 1 H, CHPh), 4.88 (m, 1 H, 1 CHPh), 4.95 (d, J_{gem} = 11.6 Hz, 1 H, CHPh), 5.47 (d, $J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 5.70 (s, 1 H, CH), 7.11- 7.72 (m, 23 H, Ar-H). MS (MALDI, positive mode, Matrix: DHB): m/z = 636.0 $(M+Na)^+$, 652.0 $(M+K)^+$.

$C_{40}H_{38}O_6$ (614.7) Calcd: C: 78.15 H: 6.23

Found: C: 78.35 H: 6.28

***O*-(3,4,6-Tri-*O*-benzyl-2-*O*-diphenylmethyl–Ŭ-D-glucopyranosyl)trichloroaceti-midate (67).** A stirred solution of **65** (1.54 g, 2.5 mmol) in dry dichloromethane (40 ml) and trichloroacetonitrile (2.5 ml, 25 mmol) was treated with DBU (35 µl) at room temperature and then left for 1.5 h. The solvent was evaporated and the product was purified by column chromatography 3% triethylamine in toluene to give **67** (1.86 g, 84%) as a yellow oil ; R_f = 0.65 (3% triethylamine in toluene) $[Ŭ]_D$ = 6.5 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$): ι#= 3.76 (m, 3 H, 6-H, 6´-H, 4-H), 3.81 (dd, $J_{2,1}$ = 3.4,

$J_{2,3}$ = 9.5 Hz, 1 H, 2-H), 4.02 (m, 1 H, 5-H), 4.22 (dd, $J_{3,2}$ = 9.3, $J_{3,4}$ = 9.5 Hz, 1 H, 3-H), 4.48 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.55 (d, J_{gem} = 10.3 Hz, 1 H, CHPh), 4.62 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.91 (m, 2 H, 2 CHPh), 4.97 (d, J_{gem} = 10.3 Hz, 1 H, CHPh), 5.76 (s, 1 H, CH), 6.38 (d, $J_{1,2}$ = 3.4 Hz, 1 H, 1-H), 7.21-7.53 (m, 25 H, Ar-H), 8.62 (brs, 1 H, NH).

***O*-[3,4,6-Tri-*O*-benzyl-2-*O*-(9-fluorenyl)–Ŭ-D-glucopyranosyl]trichloroacetimidate (68).** A stirred solution of **66** (1.54 g, 2.5 mmol) in dry dichloromethane (40 ml) and trichloroacetonitrile (2.5 ml, 25 mmol) was treated with DBU (35 µl) at room temperature and then left for 2 h. The reaction was processed as above and the product was purified by column chromatography 3% triethylamine in toluene to give **68 (**1.46 g, 77%) as a yellow oil; R_f = 0.65 (3% triethylamine in toluene); $[Ŭ]_D$ = -32.4 (c = 2.0, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$):#ł# #3.51 (m, 1 H, 6-H), 3.67 (m, 2 H, 2-H, 6´-H), 3.80 (m, 1 H, 3-H), 4.05 (m, 1 H, 5-H), 4.20 (dd, $J_{4,3}$ = 9.2, $J_{4,3}$ = 9.3 Hz, 1 H, 4-H), 4.46 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.50 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.61 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.75 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.83 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.95 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 5.69 (s, 1 H, CH), 5.88 (d, $J_{1,2}$ = 3.4 Hz, 1 H, 1-H), 7.12-7.76 (m, 23 H, Ar-H), 8.45 (brs, 1 H, NH).

Methyl 3,4,6-tri-*O*-benzyl-2-*O*-diphenylmethyl-η-D-glucopyranoside (69).

A solution of **67** (0.46 g, 0.6 mmol) and methanol (0.24 ml, 6.0 mmol) in dry dichloromethane (20 ml) was treated with TMSOTf (13 µl, 0.06 mmol), and then stirred for 1.5 h. at room temperature. The reaction was quenched by the addition of solid sodium bicarbonate, filtered and concentrated. The crude residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate, 15:1 to afford **69** (0.31 g, 81%) as a colorless oil; R_f = 0.65 (petroleum ether/ethyl acetate

5:1); $[\breve{U}]_D$ = -15.6 (c = 2.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι# 3.40 (s, 3 H, OCH_3), 3.45 (m, 1 H, 5-H), 3.53 (m, 2 H, 4-H, 2-H), 3.63 (dd, $J_{6,5}$ = 4.7, J_{gem} = 10.7 Hz, 1 H, 6-H), 3.71 (m, 2 H, 3-H, 6´-H), 4.32 (d, $J_{1,2}$ = 7.6 Hz, 1 H, 1-H), 4.45 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.52 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.59 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.74 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.78 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.93 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 6.03 (s, 1 H, CH), 7.10- 7.34 (m, 25 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι# 56.8 (OCH_3), 68.9 (C-6), 73.5 (CH_2), 74.8 (C-5), 74.9, 75.7 (2 CH_2), 77.9 (C-4), 78.9 (C-2), 83.1 (CH), 84.5 (C-3), 105.1 (C-1), 126.7, 126.9, 127.4, 127.6, 127.7, 127.8, 128.0, 128.1, 128.2, 128.3, 138.1, 138.6, 141.8, 143.4 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 653.0 $(M+Na)^+$, 669.0 $(M+K)^+$.

$C_{41}H_{42}O_6$ (630.8) Calcd: C: 78.06 H: 6.71

Found: C: 77.80 H: 6.50

Octyl 3,4,6- tri-*O*-benzyl-2-*O*-diphenylmethyl-η-D-glucopyranoside (70).

A solution of the trichloroacetimidate **67** (0.46 g, 0.6 mmol) and octanol (0.94 ml, 6.0 mmol) in dry dichloromethane (20 ml) was treated with TMSOTf (13 µl, 0.06 mmol), and then stirred for 1 h. The reaction was processed as above and the product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate, 20:1 to afford **70** (0.37 g, 86%) as a colorless oil; R_f = 0.82 (petroleum ether/ethyl acetate, 5:1); $[\breve{U}]_D$ = -27.6 (c = 2.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι# 0.87-1.56 [$CH_3(CH_2)_5$], 3.36 (m, 1 H, CH), 3.46 (m, 1 H, CH), 3.54 (dd, $J_{2,1}$ = 7.6, $J_{2,3}$ = 8.7 Hz, 1 H, 2-H), 3.67 (m, 2 H, 6-H, 6´-H), 3.71 (m, 1 H, 3-H), 3.87 (m, 2 H, CH_2), 4.43 (d, $J_{1,2}$ = 7.6 Hz, 1 H, 1-H), 4.45 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.51 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.58 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.73 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.80 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.95 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 6.14 (s, 1 H, CH), 7.17-7.34 (m, 25 H, Ar-H).

^{13}C-NMR (150.8 MHz, $CDCl_3$): ι# 14.1, 22.7, 26.2, 29.4, 29.7, 31.8 [$CH_3(CH_2)_5$], 68.9 (CH_2), 70.0 (C-6), 73.4 (CH_2), 74.8 (C-5), 74.9, 75.7 (2 CH_2), 77.9 (C-4), 78.2 (C-2), 82.8 (CH), 84.6 (C-3), 104.1 (C-1), 126.6, 126.9, 127.4, 127.5, 127.6, 127.7, 127.9, 128.1, 128.2, 128.3, 138.1, 138.7, 141.8 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 751.0 $(M+Na)^+$, 767.0 $(M+K)^+$.

$C_{48}H_{56}O_6$ (728.9) Calcd: C: 79.09 H: 7.74

Found: C: 79.32 H: 7.85

Methyl *O*-(3,4,6-tri-*O*-benzyl-2-*O*-diphenylmethyl-η-D-glucopyranosyl)-(1-6)-2,3,4-tri-*O*-benzyl-ζ-D-glucopyranoside (71).

Colorless oil (0.43 g, 68%); R_f = 0.47 (petroleum ether/ethyl acetate, 5:1); $[Ŭ]_D$ = 34.8 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι# 3.27 (s, 3 H, OCH_3), 3.35 (m, 1 H, 5-H_b), 3.39 (m, 1 H, 3-H_b), 3.43 (dd, $J_{2,1}$ = 3.4, $J_{2,3}$ = 9.7 Hz, 1 H, 2-H_a), 3.47 (dd, $J_{2,1}$ = 7.8, $J_{2,3}$ = 10.1 Hz, 1 H, 2-H_b), 3.51 (m, 2 H, 6-H_b, 4-H_b), 3.56 (dd, $J_{6,5}$ = 4.8, J_{gem} = 10.2 Hz, 1 H, 6-H_a), 3.60 (m, 2 H, 6′-H_a, 4-H_a), 3.74 (m, 1 H, 5-H_a), 3.92 (dd, $J_{3,2}$ = 9.2, $J_{3,4}$ = 9.7 Hz, 1 H, 3-H_a), 4.04 (m, 1 H, 6′-H_b), 4.31 (d, $J_{1,2}$ = 7.8 Hz, 1 H, 1-H_b), 4.37 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.41 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.43 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.47 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.53 (d, $J_{1,2}$ = 3.3 Hz, 1 H, 1-H_a), 4.56 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.60 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.64 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.70 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.74 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.75 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.90 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.93 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 6.12 (s, 1 H, CH), 7.09-7.27 (m, 40 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι# 55.2 (OCH_3), 68.2 (C_b-6), 68.9 (C_a-6), 69.0 (C_b-4), 69.6 (C_a-5), 73.2, 73.4, 73.7 (3 CH_2), 74.9 (C_b-5), 75.1, 75.5, 75.6 (3 CH_2), 77.1 (C_b-2), 77.9 (C_b-3), 79.6 (C_a-4), 81.7 (C_a-3), 82.3 (CH), 84.7 (C_a-2), 97.9 (C_a-1), 104.1 (C_b-1), 126.6, 127.3, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3,

128.4, 128.5, 138.0, 138.1, 138.3, 138.6, 138.9, 141.6, 142.9 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 1085.9 $(M+Na)^+$, 1101.1 $(M+K)^+$.

$C_{68}H_{70}O_{11}$ (1063.3) Calcd: C: 76.81 H: 6.63

Found: C: 76.90 H: 7.01

Methyl 3,4,6-tri-*O*-benzyl-2-*O*-(9-fluorenyl)-η-D-glucopyranoside (72).

Colorless oil (0.24 g, 64%); R_f = 0.54 (petroleum ether/ethyl acetate, 4/1); $[Ŭ]_D$ = -5.7 (c = 2.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$0]#t # #3.54 (m, 1 H, 5-H), 3.65 (dd, $J_{3,2}$ = 9.1, $J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 3.71 (s, 3 H, OCH_3), 3.73 (m, 2 H, 6-H, 4-H), 3.79 (m, 1 H, 6´-H), 4.09 (dd, $J_{2,1}$ = 8.0, $J_{2,3}$ = 9.1 Hz, 1 H, 2-H), 4.49 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1-H), 4.50 (d, J_{gem} = 11.5 Hz, 1 H, CHPh), 4.53 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.57 (d, J_{gem} = 11.5 Hz, 1 H, CHPh), 4.59 (d, J_{gem} = 11.5 Hz, 1 H, CHPh), 4.61 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.88 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 5.96 (s, 1 H, CH), 6.98-7.64 (m, 23 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι = 57.2 (OCH_3), 68.8 (C-6), 73.5, 74.9, 76.0 (3 CH_2), 75.1 (C-5), 77.9 (C-4), 82.4 (CH), 83.2 (C-2), 84.5 (C-3), 105.2 (C-1), 119.7, 125.5, 127.3, 127.5, 127.7, 128.0, 128.4, 128.6, 138.1, 138.3, 140.0, 140.2, 144.3, 144.5 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 652.0 $(M+Na)^+$.

$C_{41}H_{40}O_6$ (628.8) Calcd: C: 78.32 H: 6.40

Found: C: 78.64 H: 6.42

Octyl 3,4,6-tri-*O*-benzyl-2-*O*-(9-fluorenyl)–Ŭ/η-D-glucopyranoside (73).

Colorless oil (ζ]η =1:4, 0.35 g, 80%); R_f = 0.63 (petroleum ether/ethyl acetate, 5:1); $[Ŭ]_D$ = 23.5 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$0]#t # #0.82-1.71 [$CH_3(CH_2)_5$], 3.49 (m, 2 H, ζ-2-H, ζ-4-H), 3.55 (m, 3 H, 5-H, 6-H, 6´-H), 3.64 (dd, $J_{2,1}$ = 8.7, $J_{2,3}$ = 9.0 Hz, 0.8 H, η-3-H), 3.69 (m, 4 H, η-2-H, η-CH_2, η-4-H), 3.95 (m, 0.2 H, ζ-3-H), 4.09 (m, 2 H, ζ-CH_2),

4.27 (d, $J_{1,2}$ = 3.4 Hz, 0.2 H, ζ-1-H), 4.42 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.47 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.53 (m, 1 H, CHPh), 4.58 (d, $J_{1,2}$ = 8.1 Hz, 0.8 H, η-1-H), 4.60 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.64 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.86 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 5.77 (s, 0.2 H,#ζ-CH), 6.1 (s, 0.8 H, η-CH), 6.93-7.38 (m, 23 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι = 14.1, 22.6, 26.1, 26.3, 29.1, 29.2, 31.7 [$CH_3(CH_2)_5$], 67.7 (CH_2), 68.3 (C-6), 68.9, 69.4, 70.3 (3 CH_2), 74.9 (C-5), 76.9 (C-ζ-2), 77.8 (C-4), 81.8 (CH), 82.7 (C-η-2), 84.6 (C-3), 97.4 (C-ζ-1), 104.2 (C-η-1), 119.7, 119.8, 125.5, 125.8, 127.3, 127.4, 127.6, 127.7, 127.9, 128.2, 128.3, 128.6, 128.8, 129.1, 138.2, 140.2 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 750.7 $(M+Na)^+$.

Methyl *O*-[3,4,6-tri-*O*-benzyl-2-*O*-(9-fluorenyl)-ζ/η-D-glucopyranosyl]-(1-6)-2,3,4-tri-*Λ*-benzyl-ζ-D-glucopyranoside (74).

Colorless oil ((ζ]η =1:2, 0.38 g, 61%); R_f = 0.43 (petroleum ether/ethyl acetate, 5:1); [Ŭ]$_D$ = 24.6 (c = 2.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$0]#ǂ #Ƀ.37 (m, 1 H, η-2-H_a), 3.42 (s, 3 H, OCH_3), 3.45 (m, 4 H, 5-H_b, ζ44-H_a, η-4-H_a, 6-H_b), 3.54 (m, 2 H, ζ-3-H_b, ζ-2-H_b), 3.58 (m, 2 H, 6-H_a, ζ-2-H_a), 3.70 (m, 3 H, ζ-4-H_b, η-3-H_b, 6′-H_b), 3.88 (m, 3 H, 5-H_a, η-3-H_a, ζ-3-H_a), 4.01 (m, 2 H, η-2-H_b, 6′-H_a), 4.29 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.35 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 4.43 (m, 2 H, 1-H_a, η-1-H_b), 4.47 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.58 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 4.63 (d, $J_{1,2}$ = 3.6 Hz, 1 H, ζ-1-H_b), 4.65 (m, 3 H, 3 CHPh), 4.76 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.81 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 4.94 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 4.98 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 5.29 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 5.72 (s, 1 H, CH), 7.03-7.36 (m, 38 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι = 55.1 (OCH_3), 66.2 (C_b-6), 68.1 (C_b-5), 69.2 (C_b-4), 69.6 (C_a-6), 69.7 (C_a-5), 73.3, 73.4, 73.5, 73.8 (4 CH_2), 75.0 (C_a-η-4), 75.7, 75.8 (2 CH_2),

77.5 (C_a-ζ-2), 77.7 (C_a-ζ-4), 78.0 (C_b-ζ-3), 78.2 (C_b4η-4), 79.4 (C_b-η-2), 80.2 (C_b-ζ-2), 81.3 (C_b-η-2), 81.7 (C_a-ζ-3), 81.9 (C_a-η-3), 85.3 (C_b-η-3), 97.5 (C_a-1), 97.9 (C_b-ζ-1), 103.9 (C_b-η-1), 119.7, 119.8, 126.1, 127.3, 127.5, 127.6, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 138.5, 140.2, 143.9 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 1083.0 $(M+Na)^+$.

$C_{68}H_{68}O_{11}$ (1061.3) Calcd: C: 76.95 H: 6.65

Found: C: 77.27 H: 6.70

4-Methoxyphenyl *O*-3,4,6-tri-*O*-benzyl-2-*O*-diphenylmethyl–Ŭ-D-mannopyranoside (76). A solution of the diphenylmethyl trichloroacetimidate **41** (0.46 g, 1.4 mmol) and methoxyphenyl 3,4,6-tri-*O*-benzyl-Ŭ-D-mannopyranoside (**75**, 0.78 g, 1.4 mmol) in dry dichloromethane (30 ml) was treated with TMSOTf (26 µl, 0.14 mmol), and then stirred for 1.5 h. The reaction was quenched by the addition of solid sodium bicarbonate, filtered and concentrated. The crude residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate, 10:1 to afford **76** (0.90 g, 89%) as colorless oil; R_f = 0.37 (petroleum ether/ethyl acetate, 5:1); $[Ŭ]_D$ = 32.0 (c = 2.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$)0]#ŧ #3.72 (s, 3 H, OCH_3), 3.77 (m, 1 H, 6-H), 3.86 (dd, $J_{6,5}$ = 4.4, J_{gem} = 10.0 Hz, 1 H, 6´-H), 3.94 (m, 1 H, 5-H), 4.09 (m, 1 H, 2-H), 4.13 (dd, $J_{3,2}$ = 2.7, $J_{3,4}$ = 9.5 Hz, 1 H, 3-H), 4.29 (dd, $J_{4,3}$ = 9.5, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 4.50 (d, J_{gem} = 11.9 Hz, 1 H, CHPh), 4.59 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.63 (d, J_{gem} = 11.9 Hz, 1 H, CHPh), 4.66 (d, J_{gem} = 11.9 Hz, 1 H, CHPh), 4.71 (d, J_{gem} = 11.9 Hz, 1 H, CHPh), 4.94 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 5.49 (d, $J_{1,2}$ = 1.1 Hz, 1 H, 1-H), 5.82 (s, 1 H, CH), 6.78 (d, J = 9.0 Hz, 2 H, Phenyl), 6.94 (d, J = 9.0 Hz, 2 H, Phenyl), 7.23-7.37 (m, 25 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι = 55.6 (OCH_3), 67.1 (CH_2), 69.1 (C-6), 72.2 (CH_2), 72.4 (C-5), 72.7 (C-2), 73.2 (CH_2), 74.7 (C-4), 80.1 (C-3), 82.6 (CH), 97.2 (C-1), 114.5, 117.7, 127.3, 127.4, 127.5, 127.9, 128.2, 128.3,

128.4, 128.5, 138.4, 138.5, 142.0, 142.1, 150.1, 154.8 (C-Ar). (MALDI, positive mode, Matrix: DHB): m/z = 745.0 $(M+Na)^+$, 761.0 $(M+K)^+$.

$C_{47}H_{46}O_7$ (722.9) Calcd: C: 78.09 H: 6.41

Found: C: 78.21 H: 6.50

3,4,6-Tri-*O*-benzyl-2-*O*-diphenylmethyl–Ŭ-D-mannopyranose (77).

(a) To a solution of **76** (2.4 g, 3.3 mmol) was dissolved in a mixture of acetonitrile/water (60 ml, 4:1). Ammonium cerium(IV) nitrate (4.96 gm, 9 mmol) was added at 0 °C and after 30 min diluted with dichloromethane (50 ml) and saturated $NaHCO_3$ solution. The aqueous layer was extracted twice with dichloromethane. The organic layer was dried with $MgSO_4$ and the solvents were removed in vacuum. The residue was purified by flash chromatography petroleum ether/ethyl acetate, 10:1 to give **77** (1.3 g, 63%).

(b) To a solution of **80** (2.4 g, 3.7 mmol) in a mixture of toluene/EtOH/H_2O (80:80:5 ml) was added Wilkinson´s catalyst (684 mg, 0.72 mmol) and the reaction mixture was refluxed at 110 °C. After 8 h., the solvent was evaporated in vacuo and the residue was purified by flash chromatography petroleum ether/ethyl acetate, 10:1 to give ζ#mixture of **77** (1.53 g, 68%) as a colorless oil; R_f = 0.45 (petroleum ether/ethyl acetate, 3:1); $[Ŭ]_D$ = 17.8 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$): ι#= 1.96 (brs, 1 H, OH), 3.76 (m, 2 H, 6-H, 6`-H), 3.95 (m, 1 H, 5-H), 4.07 (m, 3 H, 2-H, 4-H, 3-H), 4.62 (m, 3 H, 3 CHPh), 4.65 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.69 (d, J_{gem} = 10.9 Hz, 1 H, CHPh), 4.98 (d, J_{gem} = 10.9 Hz, 1 H, CHPh), 5.34 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1-H), 5.80 (s, 1 H, CH), 7.22-7.46 (m, 25 H, Ar-H). (MALDI, positive mode, Matrix: DHB): m/z = 639.0 $(M+Na)^+$, 655.0 $(M+k)^+$.

$C_{40}H_{40}O_6$ .1.5 H_2O (643.8) Calcd: C: 74.63 H: 6.70

Found: C: 74.62 H: 6.44

***O*-(3,4,6-Tri-*O*-benzyl-2-*O*-diphenylmethyl–Ŭ-D-mannopyranosyl)trichloroacetimidate (78).** A stirred solution of **77** (3.1 g, 5 mmol) in dry dichloromethane (40 ml) and trichloroacetonitrile (2.5 ml, 25 mmol) was treated with DBU (70 µl) at room temperature and then left for 2 h. The solvent was evaporated and the product was purified by column chromatography 3% triethylamine in toluene to give **78 (**3.1 g, 82%) as a yellow oil; R_f = 0.72 (3% triethylamine in toluene) $[Ŭ]_D$ = -9.5 (c = 2.0, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$): ι# 4.15 (m, 1 H, 6-H), 4.25 (m, 1 H, 6′-H), 4.35 (m, 2 H, 5-H, 2-H), 4.42 (m, 1 H, 3-H), 4.70 (dd, $J_{4,3}$ = 9.6, $J_{4,5}$ = 9.7 Hz, 1 H, 4-H), 4.87 (m, 2 H, 2 CHPh), 4.91 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 5.01 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 5.11 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 5.31 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 6.20 (s, 1 H, CH), 6.78 (d, $J_{1,2}$ = 1.9 Hz, 1 H, 1-H), 7.52-7.91 (m, 25 H, Ar-H), 8.81 (s, 1 H, NH).

Allyl 3,4,6-tri-*O*-benzyl-Ŭ-D-mannopyranoside (79).

Compound **79** was synthesized following a published procedure. The analytical data are identical with the published values.[168]

Allyl 3,4,6-tri-*O*-benzyl-2-*O*-diphenylmethyl-Ŭ-D-mannopyranoside (80)

A solution of the diphenylmethyl trichloroacetimidate **41** (0.46 g, 1.4 mmol) and allyl 3,4,6-tri-*O*-benzyl-Ŭ-D-mannopyranoside[168] (**79**, 0.69 g, 1.4 mmol) in dry dichloromethane (30 ml) was treated with TMSOTf (26 µl, 0.14 mmol), and then stirred for 30 min. The reaction was quenched by the addition of solid sodium bicarbonate, filtered and concentrated. The crude residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate, 15:1 to afford **80** (0.81 g, 88%) as colorless oil; R_f = 0.48 (petroleum ether/ethyl acetate, 5:1); $[Ŭ]_D$ = -12.0 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$0]#ɨ#ɨ#Ƀ.75 (m, 3 H, 6-H, 6′-H, 5-H), 3.91 (m, 3 H, 4-H, 2-H, CH-allyl), 4.15 (m, 2 H, 3-H, CH-allyl), 4.51 (m, 2 H, 2 CHPh), 4.53 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.57 (d, J_{gem} = 11.1 Hz, 1 H, CHPh), 4.73 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.90 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.92 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1-H), 5.15 (m, 2 H, CH=$\underline{CH_2}$), 5.71 (s, 1 H, CH), 5.80 (m, 1 H, $\underline{CH}$=CH_2), 7.14-7.50 (m, 25 H, Ar-H). (MALDI, positive mode, Matrix: DHB): m/z = 679.7 $(M+Na)^+$, 695.7 $(M+K)^+$.

$C_{43}H_{44}O_6$ (656.8) Calcd: C: 78.63 H: 6.75

Found: C: 78.51 H: 6.68

Octyl 3,4,6- tri-*O*-benzyl-2-*O*-diphenylmethyl–ζϭη-D-mannopyranoside (81).

A solution of the trichloroacetimidate **78** (0.46 g, 0.6 mmol) and octanol (0.94 ml, 6.0 mmol) in dry dichloromethane (20 ml) was treated with TMSOTf (13 µl, 0.06 mmol), and then stirred for 10 min. The reaction was quenched by the addition of solid sodium bicarbonate, filtered and concentrated. The crude residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate, 30:1 to afford **81** (0.37 g, 86%) as a colorless oil.

81ǯ]#A colorless oil (0.12 g, 28.5%); R_f = 0.42 (petroleum ether/ethyl acetate, 10:1); $[Ŭ]_D$ = 15.5 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι#= 0.90-1.60 [$CH_3(CH_2)_5$], 3.36 (m, 1 H, CH), 3.66 (m, 1 H, CH), 3.79 (m, 2 H, 6-H, 5-H), 3.87 (dd, $J_{6',5}$ = 4.8, J_{gem} = 10.8 Hz, 1 H, 6′-H), 3.90 (m, 1 H, 2-H), 3.95 (dd, $J_{3,2}$ = 2.8, $J_{3,4}$ = 9.4 Hz, 1 H, 3-H), 4.18 (dd, $J_{4,3}$ = 9.4, $J_{4,5}$ = 9.7 Hz, 1 H, 4-H), 4.54 (d, J_{gem} = 11.6 Hz, 1 H, CHPh), 4.58 (m, 3 H, 3 CHPh), 4.73 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.89 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.90 (d, J_{gem} = 11.6 Hz, 1 H, CHPh), 5.75 (s, 1 H, CH), 7.25-7.36 (m, 25 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι#= 14.1, 22.6, 26.1, 29.2, 29.3, 29.4, 31.8 [$CH_3(CH_2)_6$], 67.6 (CH_2), 69.4 (C-6), 71.9 (CH_2), 72.0 (C-5), 73.3 (C-2), 74.9 (CH_2), 75.1 (C-4), 80.5 (C-3), 82.4 (CH_2), 98.0 (C-1), 82.5 (CH), 127.2, 127.3, 127.4, 127.5, 127.6, 128.0, 128.1,

128.2, 128.3, 138.1, 138.5, 138.6, 142.2, 142.3 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 751.0 $(M+Na)^+$, 767.0 $(M+K)^+$.

$C_{48}H_{56}O_6$ (728.9) Calcd: C: 79.09 H: 7.74

Found: C: 78.72 H: 7.71

81#η]#Colorless oil (0.25 g, 57%); R_f = 0.38 (petroleum ether/ethyl acetate, 10:1); [Ŭ $]_D$ = -27.0 (c = 2.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι#= 0.92-1.68 [$CH_3(CH_2)_5$], 3.41 (m, 1 H, CH), 3.51 (m, 2 H, 3-H, 5-H), 3.85 (m, 2 H, 6-H, 6′-H), 4.01 (m, 1 H, CH), 4.04 (m, 1 H, 2-H), 4.10 (dd, $J_{4,3} = J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 4.34 (d, J_{gem} = 11.9 Hz, 1 H, CHPh), 4.41 (d, $J_{1,2}$ = 3.0 Hz, 1 H, 1-H), 4.43 (d, J_{gem} = 11.9 Hz, 1 H, CHPh), 4.62 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.66 (d, J_{gem} = 11.9 Hz, 1 H, CHPh), 4.72 (d, J_{gem} = 11.9 Hz, 1 H, CHPh), 4.96 (d, J_{gem} = 11.9 Hz, 1 H, CHPh), 6.28 (s, 1 H, CH), 7.27-7.49 (m, 25 H, Ar-H).

^{13}C-NMR (150.8 MHz, $CDCl_3$): ι#= 14.1, 22.7, 26.2, 29.3, 29.4, 29.7, 31.8 [$CH_3(CH_2)_6$], 69.5 (C-6), 69.9 (CH_2), 71.1 (CH_2), 71.4 (C-2), 73.3 (CH_2), 74.7 (C-4), 75.1 (CH_2), 76.0 (C-5), 82.2 (CH), 82.5 (C-3), 102.0 (C-1), 126.7, 127.3, 127.4, 127.5, 127.6, 127.7, 128.0, 128.2, 128.6, 138.3, 138.4, 138.6, 142.1, 142.9 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 751.0 $(M+Na)^+$, 767.0 $(M+K)^+$.

$C_{48}H_{56}O_6$ (728.9) Calcd: C: 79.09 H: 7.74

Found: C: 78.60 H: 7.84

Methyl (3,4,6-tri-*O*-benzyl-2-*O*-diphenylmethyl-ζ/η-D-mannopyranosyl)-(1-6)-2,3,4-tri-*O*-benzyl-ζ-D-glucopyranoside (82).

(a) 82#ξ]#Colorless oil (0.12 g, 19%); R_f = 0.41 (petroleum ether/ethyl acetate, 5:1); [Ŭ$]_D$ = 21.5 (c = 2.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι#= 3.31 (s, 3 H, OCH_3), 3.39 (dd, $J_{4,5}$ = 9.5, $J_{4,3}$ = 9.6 Hz, 1 H, 4-H_a), 3.44 (dd, $J_{2,1}$ = 3.4, $J_{2,3}$ = 9.6 Hz, 1 H, 2-H_a), 3.64 (m, 3 H, 5-H_a, 6-H_a,

6-H_b), 3.73 (m, 2 H, 5-H_b, 6´-H_b), 3.83 (dd, $J_{6',5}$ = 4.1, J_{gem} = 11.5 Hz, 1 H, 6´-H_a), 3.90 (m, 2 H, 2-H_b, 3-H_b), 3.97 (dd, $J_{3,2}$ = 9.2, $J_{3,4}$ = 9.3 Hz, 1 H, 3-H_a), 4.19 (dd, $J_{4,3}$ = 9.2, $J_{4,5}$ = 9.3 Hz, 1 H, 4-H_b), 4.47 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.51 (d, J_{gem} = 11.2 Hz, 1 H, CHPh), 4.54 (m, 3 H, 3 CHPh), 4.58 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H_a), 4.66 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.70 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.79 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.83 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.87 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.90 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.99 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 5.02 (d, $J_{1,2}$ = 4.8 Hz, 1 H, 1-H_b), 5.74 (s, 1 H, CH), 7.25-7.41 (m, 40 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι# 55.0 (OCH_3), 65.5 (C_a-6), 68.9 (CH_2), 69.1 (C_b-6), 69.7 (C_a-5), 71.8 (CH_2), 71.9 (C_b-5), 72.5 (CH_2), 72.7 (C_b-2), 73.1, 74.4, 74.7 (3 CH_2), 74.9 (C_b-4-C_b), 75.0, 75.7 (2 CH_2), 77.5 (C_a-4), 79.7 (C_b-3), 80.0 (C_a-2), 82.0 (C_a-3), 82.2 (CH), 97.7 (C_a-1), 98.3 (C_b-1), 112.2, 114.6, 116.0, 127.3, 127.4, 127.5, 127.6, 127.8, 127.9, 128.1, 128.2, 128.3, 128.4, 138.0, 138.1, 138.3, 138.5, 142.1, 142.2 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 1085.2 $(M+Na)^+$, 1102.1 $(M+K)^+$;

$C_{68}H_{70}O_{11}$ (1063.3) Calcd: C: 76.81 H: 6.63

Found: C: 76.39 H: 6.58

#

82#η]#Colorless oil (0.36 g, 57%); R_f = 0.38 (petroleum ether/ethyl acetate, 5:1); [Ŭ]$_D$ = 2.3 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι# 3.18 (s, 3 H, OCH_3), 3.31 (m, 2 H, 4-H_a, 6-H_a), 3.37 (m, 1 H, 6-H_b), 3.38 (m, 2 H, 6´-H_a, 6´-H_b), 3.64 (m, 2 H, 5-H_a, 5-H_b), 3.73 (m, 1 H, 2-H_a), 3.92 (m, 2 H, 3-H_a, 3-H_b), 4.01 (m, 3 H, 4-H_b, 2-H_b, 1-H_b), 4.26 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.29 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.44 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.48 (d, $J_{1,2}$ = 3.4 Hz, 1 H, 1-H_a), 4.49 (m, 2 H, 2 CHPh), 4.53 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.58 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.68 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.70 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.76 (d, J_{gem} = 11.0 Hz, 1 H, CHPh),

4.82 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.95 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 6.06 (s, 1 H, CH), 7.09-7.23 (m, 40 H, Ar-H). MS (MALDI, positive mode, Matrix: DHB): m/z = 1085.2 $(M+Na)^+$, 1102.1 $(M+K)^+$.

$C_{68}H_{70}O_{11}$ (1063.3)	Calcd:	C: 76.81	H: 6.63
	Found:	C: 76.59	H: 6.96

(b) A stirred solution of **89** (0.20 g, 0.28 mmol) and glucose derivative **15** (0.13 g, 0.28 mmol) in dry dichloromethane (20 ml) was stirred under nitrogen at -40 ^oC and then *N*-iodosuccinimide (0.08 g, 0.36 mmol) in dry dichloromethane. The mixture was stirred for 30 min. The solution was concentrated in vacuo and then flash chromatography petroleum ether/ethyl acetate, 15:1 to afford **82** (0.23 g, 56 %).

Methoxyphenyl-3-O-allyl-2-O-benzyl-4,6-O-benzylidene-ζ-D-mannopyranoside (83). Compound **83** was synthesized following a published procedure. The analytical data are identical with the published values.[169]

4-Methoxphenyl 3-*O*-allyl-2,4-di-*O*-benzyl-ζ-D-mannopyranoside (84).

To a solution of methoxyphenyl-3-O-allyl-2-O-benzyl-4,6-O-benzylidene-ζ-D-mannopyranoside (**83**,[169] 1.63 g, 3.2 mmol) in 50 ml diethyl ether-dichloromethane (1:1), (0.5 g, 13.1 mmol) of $LiAlH_4$ was added in three portions with stirring, and the mixture was slowly heated to the boiling point to the hot solution $AlCl_3$ (1.5 g) in ether (20 ml) was added during 30 min. The mixture was refluxed for 2 h. and the reaction mixture was cooled, the excess of $LiAlH_4$ was decomposed with ethyl acetate (8 ml). After addition of water (15 ml) and dilution with ether (50 ml) the organic layer was washed with water (3 x30 ml), dried and evaporation under vacuum. The crude material was purified by flash Chromatography petroleum ether/ethyl acetate, 3:1 to obtain **84** (1.42 g, 87%) as a colorless oil; R_f = 0.34 (petroleum ether/ethyl

acetate, 5:1); $[\alpha]_D$ = 17.6 (c = 0.5, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.30 (brs, 1 H, OH), 3.69 (s, 3 H, OCH_3), 4.02 (m, 2 H, 6-H, 5-H), 4.13 (m, 1 H, 6′-H), 4.18 (m, 3 H, 3-H, OCH_2), 4.21 (m, 1 H, 2-H), 4.72 (m, 1 H, 4-H), 4.86 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.91 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.97 (d, J_{gem} = 10.5 Hz, 1 H, CHPh), 5.23 (d, J_{gem} = 10.5 Hz, 1 H, CHPh), 5.36 (m, 2 H, CH=$\underline{CH_2}$), 5.44 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1-H), 6.00 (m, 1 H, $\underline{CH}$=CH_2), 6.75 (m, 4 H, Ar-H), 7.31 (m, 10 H, Ar-H). MS (MALDI, positive mode, Matrix: DHB): m/z = 528.5 $(M+Na)^+$, 545.0 $(M+K)^+$.

$C_{30}H_{34}O_7$ (506.6) Calcd: C: 71.13 H: 6.76

Found: C: 71.45 H: 6.86

4-Methoxphenyl *O*-(3,4,6-tri-*O*-benzyl-2-*O*-diphenylmethyl-α/β-D-mannopyranosyl)-(1-6)-3-*O*-allyl-2,4-di-*O*-benzyl-α-D-mannopyranoside (85). A solution of the trichloroacetimidate **78** (0.46 g, 0.6 mmol) and 4-methoxphenyl 3-*O*-allyl-2,4-tri-*O*-benzyl-α-D-mannopyranoside (**84**, 0.30 ml, 0.6 mmol) in dry dichloromethane (20 ml) was treated with TMSOTf (13 µl, 0.06 mmol), and then stirred for 30 min. The reaction was processed as above and the product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate, 15:1 to afford **85** (0.47 g, 69%) as a colorless oil.

85: Colorless oil (0.11 g, 17%); R_f = 0.34 (petroleum ether/ethyl acetate, 5:1); $[\alpha]_D$ = 30.0 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 3.56 (s, 3 H, OCH_3), 3.61 (m, 1 H, 6-H_a), 3.71 (m, 1 H, 6-H_b), 3.80 (m, 2 H, 5-H_a, 6′-H_b), 3.87 (m, 3 H, 3-H_b, 4-H_a, 5-H_b), 3.90 (m, 1 H, 6′-H_a), 3.93 (m, 2 H, 2-H_a, 2-H_b), 3.96 (dd, $J_{3,2}$ = 2.9, $J_{3,4}$ = 10.7 Hz, 1 H, 3-H_a), 4.13 (m, 2 H, OCH_2), 4.19 (dd, $J_{4,3}$ = 9.5, $J_{4,5}$ = 9.7 Hz, 1 H, 4-H_b), 4.30 (m, 2 H, 2 CHPh), 4.48 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.52 (d, J_{gem} = 11.1 Hz, 1 H, CHPh), 4.57 (d, J_{gem} = 11.1 Hz, 1 H, CHPh), 4.69 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.71 (d, J_{gem} = 12.0 Hz, 1

H, CHPh), 4.74 (d, J_{gem} = 11.1 Hz, 1 H, CHPh), 4.89 (d, J_{gem} = 11.1 Hz, 1 H, CHPh), 4.94 (d, J_{gem} = 11.1 Hz, 1 H, CHPh), 4.99 (d, $J_{1,2}$ = 1.1 Hz, 1 H, 1-H_b), 5.20 (m, 1 H, CH-allyl), 5.36 (m, 2 H, CH-allyl, 1-H_a), 5.67 (s, 1 H, CH), 6.05 (m, 1 H, CH=CH_2), 6.75 (d, J = 9.0 Hz, 2 H, phenyl), 6.93 (d, J = 9.0 Hz, 2 H, phenyl), 7.21-7.39 (m, 35 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι = 55.4 (OCH_3), 66.1 (C_a-6), 67.1 (CH_2), 69.2 (C_b-6), 71.1 (OCH_2), 71.5 (C_a-5), 71.9 (C_b-5), 72.7 (CH_2), 72.9 (C_b-2), 73.2, 73.3, 74.4 (3 CH_2), 74.5 (C_a-4), 74.6 (CH_2), 74.7 (C_b-4), 79.8 (C_b-3), 82.2 (CH), 85.0 (CH=CH_2), 96.9 (C_a-1), 98.0 (C_b-1), 114.6 (CH_2=CH), 127.2, 127.4, 127.5, 127.6, 127.8, 127.9, 128.1, 128.2, 128.3, 128.4, 134.8, 138.6, 142.3, 142.5, 150.3, 154.8 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 1128.0 $(M+Na)^+$, 1144.0 $(M+K)^+$.

$C_{70}H_{72}O_{12}$ (1105.3)	Calcd:	C: 76.06	H: 6.55
	Found:	C: 76.48	H: 6.62

85]Colorless oil (0.36 g, 52%); R_f = 0.31 (petroleum ether/ethyl acetate, 5:1); [α]$_D$ = 7.9 (c = 2.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι = 3.34 (dd, $J_{6,5}$ = 2.5, J_{gem} = 9.4 Hz, 1 H, 6-H_b), 3.41 (m, 1 H, 5-H_b), 3.63 (s, 3 H, OCH_3), 3.64 (dd, $J_{6,5}$ = 5.3, J_{gem} = 9.8 Hz, 1 H, 6-H_a), 3.72 (m, 3 H, 3-H_b, 4-H_a, 6′-H_a), 3.79 (m, 2 H, 2-H_b, 6′-H_b), 3.94 (m, 1 H, 5-H_a), 4.03 (m, 2 H, 3-H_a, 4-H_b), 4.15 (m, 1 H, 2-H_a), 4.17 (m, 2 H, OCH_2), 4.18 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H_b), 4.20 (d, J_{gem} = 11.8 Hz, 1 H, CHPh), 4.27 (d, J_{gem} = 11.8 Hz, 1 H, CHPh), 4.49 (m, 3 H, 3 CHPh), 4.58 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.65 (d, J_{gem} = 11.8 Hz, 1 H, CHPh), 4.75 (d, J_{gem} = 11.8 Hz, 1 H, CHPh), 4.90 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.93 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 5.26 (m, 1 H, CH-allyl), 5.38 (d, $J_{1,2}$ = 2.8 Hz, 1 H, 1-H_a), 5.45 (m, 1 H, CH-allyl), 6.15 (m, 1 H, CH=CH_2), 6.24 (s, 1 H, CH), 6.65 (d, J = 9.0 Hz, 2 H, Phenyl), 6.90 (d, J = 9.0 Hz, 2 H, Phenyl), 7.22-7.34 (m, 35 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι = 55.4 (OCH_3), 67.1, 68.0, 69.3, 70.1, 71.0 (5

CH_2), 74.4 (C_b-2), 76.4 (C_b-6), 76.5 (C_a-6), 78.0 (CH_2), 78.1 (C_a-4), 79.6 (C_a-5), 81.3 (C_a-3), 81.4 (C_b-4), 81.5 (C_a-2), 83.0 (C_b-5), 89.0 (C_b-3), 89.6 (CH), 97.4 (C_a-1), 109.1 (C_b-1), 114.5, 116.6, 117.1, 117.9, 118.1, 126.6, 127.1, 127.3, 127.4, 127.6, 127.7, 127.8, 128.0, 128.1, 128.3, 128.8, 134.6, 134.9, 138.1, 138.4, 138.6, 142.0, 143.2 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 1127.3 $(M+Na)^+$, 1143.3 $(M+K)^+$.

$C_{70}H_{72}O_{12}$ (1105.3) Calcd: C: 76.06 H: 6.55

Found: C: 76.27 H: 6.57

Methyl (3,4,6-tri-*O*-benzyl-2-*O*-diphenylmethyl-ζ-D-mannopyranosyl)-(1-4)-2,3,6-tri-*O*-benzyl-ζ-D-glucopyranoside (86). Colorless oil (0.42 g, 67%); R_f = 0.41 (petroleum ether/ethyl acetate, 5:1); $[Ŭ]_D$ = 36.5 (c = 2.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι# 3.37 (s, 3 H, OCH_3), 3.49 (dd, $J_{2,1}$ = 3.4, $J_{2,3}$ = 9.6 Hz, 1 H, 2-H_a), 3.62 (m, 1 H, 5-H_b), 3.69 (m, 1 H, 6-H_a), 3.72 (m, 2 H, 6′-H_a, 6-H_b), 3.75 (m, 1 H, 6′-H_b), 3.81 (m, 2 H, 3-H_a, 5-H_a), 3.83 (dd, $J_{3,2}$ = 2.8, $J_{3,4}$ = 9.4 Hz, 1 H, 3-H_b), 3.90 (m, 1 H, 2-H_b), 4.10 (dd, $J_{4,3}$ = 9.4, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H_b), 4.15 (m, 1 H, 4-H_a), 4.30 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.39 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.45 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.49 (m, 2 H, 2 CHPh), 4.52 (m, 2 H, 2 CHPh), 4.55 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 4.58 (d, $J_{1,2}$ = 3.4 Hz, 1 H, 1-H_a), 4.66 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.87 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 4.96 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 5.41 (m, 2 H, CH, 1-H_b), 7.12-7.31 (m, 40 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι# 55.2 (OCH_3), 69.3 (C_a-6), 69.4 (C_b-6), 69.8 (C_b-5), 71.6, 72.2, 72.6 (3 CH_2), 73.0 (C_a-5), 73.2, 73.3 (2 CH_2), 73.8 (C_b-2), 74.5 (CH_2), 74.7 (C_a-4), 79.6 (C_b-3), 79.8 (C_a-2), 81.0 (C_b-4), 81.4 (C_a-3), 81.5 (CH), 97.7 (C_a-1), 99.6 (C_b-1), 126.4, 126.9, 127.2, 127.3, 127.4, 127.5, 127.6, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 137.8, 138.2, 138.6, 138.9, 142.0, 142.4 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 1086.0 $(M+Na)^+$, 1102.0 $(M+K)^+$.

$C_{68}H_{70}O_{11}$ (1063.3) Calcd: C: 76.81 H: 6.63
Found: C: 76.27 H: 6.60

Pyridin-2-yl-3,4,6-tri-*O*-benzyl-1-thio-ζ-D-mannopyranoside (87).

Compound **87** was synthesized following a published procedure. The analytical data are identical with the published values.[165]

Chlorodiphenylmethan (88).

Chlorodiphenylmethan (**88**) was purchased from Fluka and used as received.

Pyridin-2-yl-3,4,6-tri-*O*-benzyl-2-*O*-diphenylmethyl-1-thio-ζ-D-mannopyranoside (89). To a solution of **87**[165] (0.54 g, 1 mmol) and chlorodiphenylmethan (**88**, 0.21 ml, 1.2 mmol) in dry DMF (20 ml), NaH (0.03 g, 1.25 mmol) was added. The reaction mixture was stirred at 0 °C under argon for 2 h. and also at room temperature for 10 h. The solvent was evaporated under reduced pressure and the crude residue was purified by column chromatography petroleum ether/ethyl acetate, 10:1 to afford **89** (0.37 g, 52%) as a colorless oil; R_f = 0.62 (petroleum ether/ethyl acetate, 5:1); $[\check{U}]_D$ = 23.0 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$): ι# 3.75 (dd, $J_{6,5}$ = 1.5, J_{gem}= 10.9 Hz, 1 H, 6-H), 3.95 (m, 2 H, 6′-H, 5-H), 4.11 (dd, $J_{3,2}$ = 2.8, $J_{3,4}$ = 9.6 Hz, 1 H, 3-H), 4.18 (m, 1 H, 2-H), 4.32 (dd, $J_{4,3}$ = 9.6 Hz, $J_{4,5}$ = 9.7 Hz, 1 H, 4-H), 4.44 (d, J_{gem}= 10.8 Hz, 1 H, CHPh), 4.55 (d, J_{gem}= 12.0 Hz, 1 H, CHPh), 4.62 (d, J_{gem}= 10.8 Hz, 1 H, CHPh), 4.65 (d, J_{gem}= 10.8 Hz, 1 H, CHPh), 4.73 (d, J_{gem}= 12.0 Hz, 1 H, CHPh), 4.99 (d, J_{gem}= 10.8 Hz, 1 H, CHPh), 5.85 (s, 1 H, CH), 6.56 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1-H), 7.03-7.54 (m, 18 H, Ar-H), 8.48 (m, 1 H, Ar-H). MS (MALDI, positive mode, Matrix: DHB): m/z = 731.9 $(M+Na)^+$, 748.3 $(M+K)^+$.

$C_{45}H_{43}NO_5S$ (709.9) Calcd: C: 76.13 H: 6.10 N: 1.97

Found: C: 76.17 H: 6.11 N: 1.97

***O*-(2,3,4,6-Tetra-*O*-benzyl–Ŭ-D-mannopyranosyl)trichloroacetimidate (90).**
Compound **90** was synthesized following a published procedure. The analytical data are identical with the published values.[170]

Octyl 2,3,4,6- tetra-*O*-benzyl-ζ/η-D-mannopyranoside (91).[171]
A solution of the trichloroacetimidate **90** (0.41 g, 0.6 mmol) and octanol (0.14 ml, 0.9 mmol) in dry dichloromethane (20 ml) was treated with TMSOTf (13 µl, 0.06 mmol), and then stirred for 45 min. The reaction was processed as above and the product purified by column chromatography on silica gel using petroleum ether/ethyl acetate, 15:1 to afford **91** (0.29 g, 75%) as a colorless oil; R_f = 0.63 (petroleum ether/ethyl acetate, 5:1); $[Ŭ]_D$ = 35.7 (c = 1.0, CH_2Cl_2). Ref. for ζ-compound.[171]: $[Ŭ]_D$ = 25.6 (c = 6.4, $CHCl_3$).

Methyl (2,3,4,6-tetra-*O*-benzyl-ζ/η-D-mannopyranosyl)-(1-6)-2,3,4-tri-*O*-benzyl-ζ-D-glucopyranoside (92).[171] A solution of the trichloroacetimidate **90** (0.41 g, 0.6 mmol) and glucose derivative **15** (0.28 ml, 0.6 mmol) in dry dichloromethane (20 ml) was treated with TMSOTf (13 µl, 0.06 mmol), and then stirred for 30 min. The reaction was processed as above and the product purified by column chromatography on silica gel using petroleum ether/ethyl acetate, 10:1 to afford **92** (0.41 g, 69%) as a colorless oil; R_f = 0.32 (petroleum ether/ethyl acetate, 5:1); $[Ŭ]_D$ = 34.0 (c = 1.0, CH_2Cl_2).

Methyl (2,3,4,6-tetra-*O*-benzyl-ζ/η-D-mannopyranosyl)-(1-4)-2,3,6-tri-*O*-benzyl-ζ-D-glucopyranoside (93).[171] A solution of the trichloroacetimidate **90** (0.41 g, 0.6 mmol) and glucose derivative **17** (0.28 ml, 0.6 mmol) in dry dichloromethane (20 ml)

was treated with TMSOTf (13 µl, 0.06 mmol), and then stirred for 45 min. The reaction was processed as above and the product purified by column chromatography on silica gel using petroleum ether/ethyl acetate, 10:1 to afford **92** (0.48 g, 81%) as a colorless oil; R_f = 0.37 (petroleum ether/ethyl acetate, 5:1); [Ŭ]$_D$ = 18.5 (c = 1.0, CH_2Cl_2). Ref. for ζ-compound.[171]: [Ŭ]$_D$ = 13.5 (c = 1.9, $CHCl_3$).

4-Methoxphenyl *O*-(2,3,4,6-tetra-*O*-benzyl-ζ/η-D-mannopyranosyl)-(1-6)-3-*O*-allyl-2,4-di-*O*-benzyl-ζ-D-mannopyranoside (94). A solution of the trichloroacrtimidate (**90,** 0.41 g, 0.6 mmol) and 4-methoxphenyl 3-*O*-allyl-2,4-tri-*O*-benzyl-ζ-D-mannopyranoside (**84**, 0.30 ml, 0.6 mmol) in dry dichloromethane (20 ml) was treated with TMSOTf (13 µl, 0.06 mmol), and then stirred for 75 min. The reaction was processed as above and the product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate, 15:1 to afford **94** (0.47 g, 76%) as a colorless oil; R_f = 0.42 (petroleum ether/ethyl acetate, 5:1); [Ŭ]$_D$ = 23.3 (c = 2.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι# = 3.35 (m, 2 H, 3-H_b, 5-H_b), 3.57 (s, 3 H, OCH_3), 3.61 (m, 2 H, 2-H_b, 6-H_a), 3.71 (dd, $J_{6,5}$ = 5.6, J_{gem} = 10.6 Hz, 1 H, 6-H_b), 3.74 (m, 2 H, 4-H_b, 6′-H_b), 3.90 (m, 3 H, 4-H_a, 5-H_a, 2-H_a), 4.00 (m, 1 H, 3-H_a), 4.16 (m, 2 H, 6′-H_a, CH-allyl), 4.19 (m, 2 H, CH-allyl, η-1-H_b), 4.37 (d, J_{gem}= 11.0 Hz, 1 H, CHPh), 4.41 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.49 (d, J_{gem}= 11.0 Hz, 1 H, CHPh), 4.51 (m, 3 H, 3 CHPh), 4.66 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.76 (d, J_{gem} = 10.0 Hz, 1 H, CHPh), 4.80 (d, J_{gem} = 10.0 Hz, 1 H, CHPh), 4.83 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.86 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.90 (d, J_{gem} = 10.0 Hz, 1 H, CHPh), 5.20 (m, 1 H, CH-allyl), 5.25 (d, $J_{1,2}$ = 1.1 Hz, 1 H, ζ-1-H_b), 5.38 (m, 1 H, CH-allyl), 5.42 (d, $J_{1,2}$ = 1.1 Hz, 1 H, 1-H_a), 5.43 (m, 2 H, CH=$\underline{CH_2}$), 6.01 (m, 1 H, $\underline{CH}$=CH_2), 6.67 (d, J = 9.0 Hz, 2 H, Ar-H), 6.90 (d, J = 9.0 Hz, 2 H, Ar-H), 7.17-7.38 (m, 30 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι# = 55.4 (OCH_3), 68.5 (C_a-6), 69.7 (C_b-6), 71.1 (OCH_2), 71.2 , 71.4 (2

CH_2), 72.5 (C_a-5), 72.6, 72.8 (2 CH_2), 73.3 (C_b-2), 73.6 (CH_2), 74.4 (C_a-2), 74.8 (CH_2), 74.5 (C_a-4), 74.9 (C_b-4), 75.8 (C_b-5), 79.7 (C_a-3), 82.2 (C_b-3), 92.1 ($\underline{CH}$=CH_2), 94.8 (C_b-ζ-1), 96.9 (C_a-1), 101.9 (C_b-η41), 117.8 (CH=$\underline{CH_2}$), 127.2, 127.3, 127.4, 127.6, 127.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 128.5, 134.9, 138.4, 138.8 (C-Ar). MS (MALDI, positive mode, Matrix: DHB): m/z = 1052.4 $(M+Na)^+$, 1068.8 $(M+K)^+$.

Methyl 2,3,4,6-tetra-*O*-acetyl-ζ-D-glucopyranoside (95).

(a) Diphenylmethyl glucose derivative **50** or **51** (0.1 g, 0.16 mmol) was dissolved in dry methanol (10 ml) and stirred together with Pd/C (0.05 g) under hydrogen atmosphere for 16 h. The catalyst was filtered off and washed carefully with methanol. The solvent was removed under reduced pressure and then treated with acetic anhydride (2 ml) and pyridine (2 ml). The reaction mixture was stirred for 15 h., and then concentrated and purified by flash chromatography (petroleum ether/ethyl acetate, 2:1) to affored **95** as a white powder (0.04 g, 70%). The analytical data are identical with the published values.[172]

(b) Catalytic hydrogenation of methyl 2,3,4-tri-O-benzyl-6-O-cyclobutyl-ζ-D-glucopyranoside (114). Cyclobutyl glucose derivative **114** (0.1 g, 0.2 mmol) was dissolved in dry methanol (10 ml) and stirred together with Pd/C (0.05 g) under hydrogen atmosphere for 12 h. The catalyst was filtered off and washed carefully with methanol. The solvent was removed under reduced pressure and then treated with acetic anhydride (2 ml) and pyridine (2 ml). The reaction mixture was stirred for 15 h., and then concentrated and purified by flash chromatography (petroleum ether/ethyl acetate, 2:1) to affored **95**.

Methyl-*O*-(2,3,4,6-tetra-*O*-acetyl-ζ-D-glucopyranosyl)-(1-6)-2,3,4-tri-*O*-acetyl-ζ-D-glucopyranoside (96). Diphenylmethyl glucose derivative **71** or **74** (0.1 g, 0.16 mmol) was dissolved in dry methanol (10 ml) and stirred together with Pd/C (0.05 g) under hydrogen atmosphere for 16 h. The catalyst was filtered off and washed carefully with methanol. The solvent was removed under reduced pressure and then treated with acetic anhydride (2 ml) and pyridine (2 ml). The reaction mixture was stirred for 15 h., and then concentrated and purified by flash chromatography (petroleum ether/ethyl acetate, 2:1) to afforded **95** as a colorless oil (0.03 g, 50%). The analytical data are identical with the published values.[25]

Cyclopropylmethanol (98).

Cyclopropylmethanol (**98**) was purchased from Lancaster and used as received.

Cyclobutyl alcohol (99).

Cyclobutyl alcohol (**99**) was purchased from Lancaster and used as received.

Cyclopropylmethyl trichloroacetimidate (101).

A stirred solution of cyclopropylmethanol (**98**, 1.8 g, 25.3 mmol) in dry dichloromethane (40 ml) and trichloroacetonitrile (25 ml, 250 mmol) was treated with DBU (0.35 ml) at room temperature and then left for 0.5 h. The solvent was evaporated and the product was purified by column chromatography 3% triethylamine in toluene to give **101** (5.0 g, 92%) as yellow oil; R_f = 0.83 (3% triethylamine in toluene).

^{1}H-NMR (250 MHz, $CDCl_3$):#ǂ #7538#m, 2 H, CH_2), 0.64 (m, 2 H, CH_2), 1.32 (m, 1 H, CH), 4.13 (d, *J* = 7.1 Hz, 2 H, CH_2), 8.23 (brs, 1 H, NH).

Cyclobutyl trichloroacetimidate (102).

It was prepared as above and the product was purified by column chromatography on silica gel using 3% triethyl amine in toluene to afford **102** (4.7 g, 86.6%) as a yellow colorless oil; R_f = 0.90 (3% triethylamine in toluene).

^{1}H-NMR (250 MHz, $CDCl_3$):## #1.61 (m, 1 H, CH), 1.80 (m, 1 H, CH), 2.15 (m, 2 H, CH_2), 2.40 (m, 2 H, CH_2), 5.12 (m, 1 H, CH), 8.21 (brs, 1 H, NH).

General procedure for reaction of cyclopropylmethyl trichloroacetimidate (101) with alcohols.

A solution of cyclopropylmethyl trichloroacetimidate (**101**, 0.3 g, 1.4 mmol) and alcohol (1.4 mmol) in dry methylene chloride (10 ml) was treated with TMSOTf (0.15 ml). The reaction mixture was stirred for 0.5-3.0 h. and then was quenched with solid sodium bicarbonate, filtered and concentrated. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate).

General procedure for reaction of cyclopropylmethyl trichloroacetimidate (101) with acids. #

A solution of cyclopropylmethyl trichloroacetimidate (**101**, 0.3 g, 1.4 mmol) and acid (1.4 mmol) in dry methylene chloride (20 ml) was stirred for 0.5-3.0 h. The reaction mixture was quenched with solid sodium bicarbonate, filtered and concentrated. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate).

Benzyl cyclobutyl ether (104).

Colorless oil (0.38 g, 85%);# R_f = 0.41 (petroleum ether/ethyl acetate, 6:1). The analytical data are identical with the published values.[194]

3,5-Dimethoxybenzyl cyclobutyl ether (105).

Colorless oil (0.20 g, 67%);#R_f = 0.48 (petroleum ether/ethyl acetate, 5:1).

^{1}H-NMR (250 MHz, $CDCl_3$)#t]#1.45-2.46#m, 6 H, 3 CH_2), 3.77, 3.79 (2 s, 6 H, 2 OCH_3), 4.00 (m, 1 H, CH), 4.35 (s, 2 H, CH_2), 6.13-6.50 (m, 3 H, Ar-H); EI-MS: m/z = 222.0.

$C_{13}H_{18}O_3$ (222.3) Calcd: C: 70.24 H: 8.16

Found: C: 70.25 H: 8.42

3,5-Dinitrobenzyl cyclopropylmethyl ether (106) And 3,5-Dinitrobenzyl cyclobutyl ether (107).

106: Yellow colorless oil (0.15 g, 42%); R_f = 0.58 (petroleum ether/ethyl acetate, 6:1). ^{1}H-NMR (250 MHz, $CDCl_3$)#t]#0.28#m, 2 H, CH_2), 0.63 (m, 2 H, CH_2), 1.15 (m, 1 H, CH), 3.45 (d, *J* = 6.9 Hz, 2 H, CH_2), 4.72 (s, 2 H, CH_2), 8.55 (m, 2 H, Ar-H), 8.96 (dd, *J* = 2.1 Hz, 1 H, Ar-H). ^{13}C-NMR (62.8 MHz, $CDCl_3$) ι: 3.1 (2 CH_2), 10.4 (CH), 70.2 (CH_2), 76.1 (CH_2), 117.7, 127.0, 143.7, 148.6 (C-Ar).

($C_{11}H_{12}N_2O_5$) 252.2; EI-MS: m/z = 252.0.

107: Yellow colorless oil (0.16 g, 47%); R_f = 0.62 (petroleum ether/ethyl acetate, 6:1). ^{1}H-NMR (250 MHz, $CDCl_3$)#t]#1.55#m, 1 H, CH), 1.70 (m, 1 H, CH), 2.05 (m, 2 H, CH_2), 2.30 (m, 2 H, CH_2), 4.10 (m, 1 H, CH), 4.60 (s, 2 H, CH_2), 8.50-9.00 (m, 3 H, Ar-H). ^{13}C-NMR (62.8 MHz, $CDCl_3$) ι: 12.4 (CH_2), 30.2 (2 CH_2), 67.5 (CH_2), 73.8 (CH), 117.7, 127.1, 143.6, 148.5 (C-Ar).

($C_{11}H_{12}N_2O_5$) 252.2; EI-MS: m/z = 252.0.

Thiophenol (108).

Thiophenol (**108**) was purchased from Fluka and used as received.

(Phenyl thio-methyl)-cyclopropane (109).

Colorless oil (0.4 g, 91%); R_f = 0.75 (petroleum ether/ethyl acetate, 6:1). The analytical data are identical with the published values.[196]

Cholesteryl cyclopropylmethyl ether (110)and cholesteryl cyclobutyl ether(111).

110: Colorless oil (0.20 g, 32%); R_f = 0.76 (petroleum ether/ethyl acetate, 10:1).

^{1}H-NMR (250 MHz, $CDCl_3$)#t]#0.18#m, 2 H, CH_2), 0.52 (m, 2 H, CH_2), 0.65-2.28 (m, 43 H, cholesteryl, CH), 3.41 (d, *J* = 7.0 Hz, 1 H, CH_2), 3.50 (m, 1 H, CH), 5.32 (m, 1 H, CH). EI-MS: m/z = 442.0.

$C_{31}H_{52}O$ (442.8) Calcd: C: 84.09 H: 12.29

Found: C: 84.12 H: 12.40

111: Colorless oil (0.32 g, 52%); R_f = 0.82 (petroleum ether/ethyl acetate, 10:1).

^{1}H-NMR (250 MHz, $CDCl_3$)#t]#0.66-2.50#m, 49 H, cholesteryl, 3 CH_2), 3.50 (m, 1 H, CH), 4.20 (m, 1 H, CH), 5.33 (m, 1 H, CH). EI-MS: m/z = 442.0.

$C_{31}H_{52}O$ (442.8) Calcd: C: 84.09 H: 12.29

Found: C: 83.87 H: 11.95

5-Cyclobutyl-5-methyl-2-phenyl-1,3-dioxane (112).

Colorless oil (0.25 g, 70%); R_f = 0.64 (petroleum ether/ethyl acetate, 5:1).

^{1}H-NMR (250 MHz, $CDCl_3$): ι#= 0.76 (s, 3 H, CH_3), 1.40 (m, 1 H, CH), 1.60 (m, 1 H, CH), 1.82 (m, 2 H, CH_2), 2.28 (m, 2 H, CH_2), 3.64 (d, J_{gem} = 11.8 Hz, 2 H, 2 CH), 3.84 (s, 2 H, CH_2), 4.05 (d, J_{gem} = 11.8 Hz, 2 H, 2 CH), 4.17 (m, 1 H, CH), 5.39 (s, 1 H, CH), 7.30-7.52 (m, 5 H, Ar-H). EI-MS: m/z = 262.35.

$C_{16}H_{22}O_3$ (262.3) Calcd: C: 73.25 H: 8.45

Found: C: 73.00 H: 8.14

Methyl 2,3,4-tri-O-benzyl-6-O-cyclopropylmethyl-ζ-D-glucopyranoside (113) and methyl 2,3,4-tri-O-benzyl-6-O-cyclobutyl-ζ-D-glucopyranoside (114).

113: Colorless oil (o.5 g, 35%) it was obtained in 73% yield when the alcohol was reacted with cyclobutyl trichloroacetimidate under the same condition. R_f = 0.61 (petroleum ether/ethyl acetate, 5:1). $[Ŭ]_D$ = 35.3 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι # #0.18 (m, 2 H, CH_2), 0.51 (m, 2 H, CH_2), 1.06 (m, 1 H, CH), 3.20 (dd, *J* = 7.1, *J* = 10.6 Hz, 1 H, CH), 3.39 (s, 3 H, OCH_3), 3.41 (m, 1 H, CH), 3.56 (dd, $J_{2,1}$ = 3.5, $J_{2,3}$ = 9.3 Hz, 1 H, 2-H), 3.67 (m, 2 H, 4-H, 6-H), 3.73 (m, 2 H, 6′-H, 5-H), 4.00 (dd, $J_{3,2}$ = 9.3, $J_{3,4}$ = 9.6 Hz, 1 H, 3-H), 4.60 (m, 1 H, CHPh), 4.63 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 4.66 (d, J_{gem} = 12.6 Hz, 1 H, CHPh), 4.82 (d, J_{gem} = 12.6 Hz, 1 H, CHPh), 4.84 (d, J_{gem} = 10.9 Hz, 1 H, CHPh), 4.89 (d, J_{gem} = 10.9 Hz, 1 H, CHPh), 4.98 (d, J_{gem} = 10.9 Hz, 1 H, CHPh), 7.15-7.38 (m, 15 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι #= 2.9, 3.1 (2 CH_2), 10.4 (CH), 55.1 (OCH_3), 66.0 (CH_2), 68.4 (CH_2), 68.6 (C-6), 69.8 (CH_2), 70.0 (C-5), 76.1 (CH_2), 77.6 (C-4), 79.8 (C-2), 82.1 (C-3), 98.1 (C-1), 127.5, 127.6, 127.7, 127.8, 127.9, 128.1, 128.3, 128.4, 138.2, 138.4, 138.8 (C-Ar). MS (FAb, positive mode, M+ NaI): 518.0.

$C_{32}H_{38}O_6$ (518.6)	Calcd:	C: 74.10	H: 7.38
	Found:	C: 73.80	H: 7.35

114: Colorless oil (0.6 g, 42%); R_f = 0.64 (petroleum ether/ethyl acetate, 5:1). $[Ŭ]_D$ = 85.4 (c = 0.5, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$): ι #= 1.46 (m, 1 H, CH), 1.64 (m, 1 H, CH), 1.92 (m, 2 H, CH_2), 2.15 (m, 2 H, CH_2), 3.36 (s, 3 H, OCH_3), 3.48 (m, 1 H, 6-H), 3.54 (dd, $J_{2,1}$ = 3.6, $J_{2,3}$ = 9.3 Hz, 1 H, 2-H), 3.57 (m, 1 H, 6′-H), 3.62 (dd, $J_{4,3}$ = 9.3, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 3.70 (m, 1 H, 5-H), 3.88 (m, 1 H, CH), 3.98 (dd, $J_{3,2}$ = 9.3, $J_{3,4}$ = 9.3 Hz, 1 H, 3-H), 4.59 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.62 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 4.64 (d, J_{gem} = 12.3 Hz, 1 H, CHPh), 4.78 (d, J_{gem} = 12.3 Hz, 1 H, CHPh), 4.82 (d, J_{gem} = 10.8

Hz, 1 H, CHPh), 4.88 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 4.99 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 7.27-7.35 (m, 15 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$): ι# 12.3 (CH_2), 30.0, 30.3 (2 CH_2), 55.1 (OCH_3), 65.9 (6-C), 69.2 (CH_2), 69.7 (CH_2), 69.8 (C-5), 73.5 (CH), 75.6 (CH_2), 77.6 (C-4), 79.7 (C-2), 82.1 (C-3), 98.1 (C-1), 116.4, 127.4, 127.6, 127.7, 127.8, 127.9, 128.1, 128.3, 138.1, 138.4, 138.8 (C-Ar). MS (FAB, positive mode, M+ NaI): 518.0.

$C_{32}H_{38}O_6$ (518.6) Calcd: C: 74.10 H: 7.38

Found: C: 73.72 H: 7.54

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-cyclopropylmethyl-Ŭ-D-glucopyranoside (115) and Methyl 2,3,6-tri-*O*-benzyl-4-*O*-cyclobutyl-Ŭ-D-glucopyranoside (116).

115: Colorless oil (0.5 g, 33%); R_f = 0.53 (petroleum ether/ethyl acetate, 5:1). $[Ŭ]_D$ = 9.3 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$): ι# 0.15 (m, 2 H, CH_2), 0.37 (m, 2 H, CH_2), 1.05 (m, 1 H, CH), 3.21 (m, 1 H, 6-H), 3.35 (s, 3 H, OCH_3), 3.60 (m, 3 H, 6´-H, 2-H, 5-H), 3.72 (m, 3 H, 4-H, CH_2), 3.90 (dd, $J_{3,2}$ = $J_{3,4}$ = 9.6 Hz, 1 H, 3-H), 4.56 (m, 1 H, CHPh), 4.65 (m, 2 H, CHPh), 4.71 (m, 1 H, CHPh), 4.74 (d, $J_{1,2}$ = 2.7 Hz, 1 H, 1-H), 4.86 (m, 2 H, 2 CHPh), 7.19-7.41 (m, 15 H, Ar-H). MS (FAb, positive mode, M+ NaI): 518.0.

$C_{32}H_{38}O_6$ (518.6) Calcd: C: 74.10 H: 7.38

Found: C: 73.98 H: 7.52

116: Colorless oil (0.67 g, 49%); R_f = 0.58 (petroleum ether/ethyl acetate, 5:1).$[Ŭ]_D$ = 53.6 (c = 2.0, CH_2Cl_2). ^{1}H-NMR (250 MHz, $CDCl_3$): ι# 1.40 (m, 1 H, CH), 1,65 (m, 1 H, CH), 1.90 (m, 2 H, CH_2), 2.18 (m, 2 H, CH_2), 3.37 (s, 3 H, OCH_3), 3.55 (m, 2 H, 6-H, 6´-H), 3.60-3.80 (m, 3 H, 2-H, 5-H, 4-H), 3.86 (m, 1 H, CH), 4.00 (dd, $J_{3,2}$ = $J_{3,4}$ = 9.7 Hz, 1 H, 3-H), 4.62 (d, $J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 4.65-4.88 (m, 2 H, 2 CHPh), 4.77 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.84 (m, 3 H, 3 CHPh), 7.25-7.40 (m, 15 H, Ar-

H). MS (FAB, positive mode, M+ NaI): 518.0.

$C_{32}H_{38}O_6$ (518.6) Calcd: C: 74.10 H: 7.38

Found: C: 74.46 H: 7.05

3-*O*-Cyclobutyl 1:2, 5:6-di-*O*-isopropylidene-ζ-D-glucofuranose (117).

Colorless oil (0.31 g, 73%); R_f = 0.53 (petroleum ether/ethyl acetate, 5:1). $[Ŭ]_D$ = -11.5 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$): ι≠ 1.29, 1.34, 1.42, 1.47 (4 s, 12 H, 4 CH_3), 1.52-1.90 (m, 4 H, 2 CH_2), 2.25 (m, 2 H, CH_2), 3.96 (m, 2 H, 6-H, 4-H), 4.15 (m, 2 H, 6´-H, 5-H), 4.30 (m, 2 H, 3-H, CH), 4.51 (d, $J_{2,1}$ = 3.6 Hz, 1 H, 2-H), 5.92 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H). (MALDI, positive mode, Matrix: DHB): m/z = 337.6 $(M+Na)^+$, 353.7 $(M+K)^+$.

$C_{16}H_{26}O_6$ (314.4) Calcd: C: 61.13 H: 8.33

Found: C: 61.51 H: 8.02

Cyclobutyl/cyclopropylmethyl 2,3,4,6-tetra-*O*-acetyl-ζ6η-D-glucopyranoside (118/119). Colorless foam (0.68 g, 61%); R_f = 0.35 (petroleum ether/ethyl acetate, 2:1); $[Ŭ]_D$= +26.74 (c = 2.0, CH_2Cl_2).

^{1}H-NMR (600 MHz, $CDCl_3$) ι: 0.20 (m, 2 H, cyclopropyl-CH_2), 0.54 (m, 2 H, cyclopropyl-CH_2), 1.04 (m, 1 H, cyclopropyl-CH), 1.50 (m, 1 H, cyclobutyl-CH), 1.70 (m, 2 H, cyclobutyl-CH_2), 1.80 (m, 1 H, cyclobutyl-CH), 2.10 (m, 12 H, 4 AcO), 2.20 (m, 2 H, cyclobutyl-CH_2), 3.39 (m, 2 H, cyclopropyl-CH_2), 3.67 (m, 2 H, η-5-H, ß-CH), 4.04 (m, 3 H, ß-6-H, CH, ζ-6-H), 4.13 (m, 1 H, 5-H), 4.23 (m, 2 H, ζ-6´-H, ß-6`-H), 4.46 (d, $J_{1,2}$ = 8.0 Hz, 1 H, ß-1-H), 4.60 (d, $J_{1,2}$ = 8.0 Hz, 1 H, ß-1-H), 4.85 (dd, $J_{2,1}$ = 3.6, $J_{2,3}$ = 10.2 Hz, 1 H, ζ-2-H), 4.87 (dd, $J_{2,1}$ = 3.2, $J_{2,3}$ = 10.2 Hz, 1 H, ζ-2-H), 4.94 (m, 1 H, ß-2-H), 5.06 (d, $J_{1,2}$ = 3.2 Hz, 1 H, 1-H), 5.07 (m, 2 H, ζ-4-H, ß-4-H),

5.16 (d, $J_{1,2}$ = 3.6 Hz, 1 H, ζ-1-H), 5.21 (m, 2 H, ß-3-H), 5.51 (m, 2 H, ζ-3-H). (MALDI, positive mode, Matrix: DHB): m/z = 337.6 $(M+Na)^+$, 353.7 $(M+K)^+$.

$C_{16}H_{26}O_6$ (314.4) Calcd: C: 61.13 H: 8.33

Found: C: 61.51 H: 8.02

Dibenzyl phosphate (120).

Dibenzyl phosphate (**120**) was purchased from Fluka and used as received.

Reaction of 101 with phosphoric acid dibenzyl ester: 121.

Colorless oil of phosphoric acid dibenzyl cyclopropylmethyl ester[198] (**121**, 0.36 g, 79%); R_f = 0.45 (petroleum ether/ethyl acetate, 5:1).

^{1}H-NMR (250 MHz, $CDCl_3$) ι: 0.24 (m, 2 H, CH_2), 0.53 (m, 2 H, CH_2), 1.16 (m, 1 H, CH), 3.81 (t, J = 7.3 Hz, 2 H, CH_2), 5.00 (2 s, 4 H, 2 CH_2), 7.21-7.49 (m, 10 H, Ar-H). EI-MS: m/z = 332.0.

$C_{18}H_{21}O_4P$ (332.3) Calcd: C: 65.05 H: 6.37

Found: C: 64.81 H: 6.45

Diphenyl phosphate (122).

Diphenyl phosphate (**122**) was purchased from Fluka and used as received..

Reaction of 101 with phosphoric acid diphenyl ester:123, 124 and 125.

Colorless oil of **123**, **124** and **125** (ratio 4:2:1, 0.37 g, 89%); R_f = 0.42 (petroleum ether/ethyl acetate, 5:1)

^{1}H-NMR (250 MHz, $CDCl_3$) ι: 0.35 (m, 2 H, cyclopropyl-CH_2), 0.67 (m, 2 H, cyclopropyl-CH_2), 1.22 (m, 1 H, cyclopropyl-CH), 1.55 (m, 2 H, cyclobutyl-CH_2), 1.82 (m, 2 H, cyclobutyl-CH_2), 2.35 (m, 6 H, cyclobutyl-CH_2, allyl-2 CH_2), 4.15 (m, 2 H, cyclopropyl-CH_2), 4.35 (m, 1 H, cyclobutyl-CH), 5.00 (m, 2 H, allyl-CH_2), 5.80

(m, 1 H, allyl-CH), 7.19-7.51 (m, 10 H, Ar-H). EI-MS: m/z = 304.0.

$C_{16}H_{17}O_4P$ (332.3) Calcd: C: 63.15 H: 5.63

Found: C: 63.10 H: 5.46

_p_-Toluenesulphonic acid (126).

_p_-Toluenesulphonic acid (**126**) was purchased from Fluka and used as received.

Reaction of 101 with _p_-toluenesulphonic acid: 127 and 128.

Colorless oil of **127** and **128** (ratio 2:1, 0.37 g, 85%); R_f = 0.58 (petroleum ether/ethyl acetate, 5:1).

^{1}H-NMR (250 MHz, $CDCl_3$) ι: 1.41 (m, 2 H, cyclobutyl-CH_2), 1.65 (m, 2 H, cyclobutyl-CH_2), 2.11 (m, 4 H, cyclobutyl-CH_2, allyl-CH_2), 2.42 (s, 3 H, CH_3), 4.00 (m, 2 H, allyl-CH_2), 4.70 (m, 1 H, cyclobutyl-CH_2), 5.00 (m, 2 H, allyl-CH_2), 5.55 (m, 1 H, allyl-CH), 7.20-7.81 (m, 4 H, Ar-H). MS: m/z = 226.0.

$C_{16}H_{17}O_4P$ (226.3) Calcd: C: 58.38 H: 6.23

Found: C: 58.18 H: 6.44

Methyl 2,3,4-tri-_O_-acetyl-6-_O_-cyclopropylmethyl-ζ-D-glucopyranoside (129).

A solution of **113** (0.10 g, o.2 mmol) was catalytic hydrogenated by the same procedure as a above followed by acetylation to give methyl 2,3,4-tri-_O_-actyl-6-_O_-cyclopropylmethyl-ζ-D-glucopyranoside (**129**) as a colorless oil (0.06 g, 80%); R_f = 0.32 (petroleum ether/ethyl acetate, 3:1). $[Ŭ]_D$ = 70.8 (c = 2.0, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$) ι: 0.15 (m, 2 H, CH_2), 0.45 (m, 2 H, CH_2), 1.00 (m, 1 H, CH), 1.96, 1.98, 2.00 (3 s, 9 H, 3 AcO) , 3.20 (m, 2 H, CH_2), 3.36 (s, 3 H, OCH_3), 3.53 (m, 2 H, 6-H, 6′-H), 3.88 (m, 1 H, 5-H), 4.87 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.94 (dd, $J_{1,2}$ = 3.6, $J_{2,3}$ = 9.7 Hz, 1 H, 2-H), 5.12 (dd, $J_{4,3}$ = 9.6, $J_{4,5}$ = 9.7 Hz, 1 H, 4-H), 5.41 (dd, $J_{3,2}$ = 9.7, $J_{3,4}$ = 9.6 Hz, 1 H, 3-H). (MALDI, positive mode, Matrix: DHB):

m/z = 397.0 $(M+Na)^+$, 413.0 $(M+K)^+$.

$C_{17}H_{26}O_9$ (374.4) Calcd: C: 54.53 H: 7.00

Found: C: 54.90 H: 6.80

2-Buten-1-ol (130).

2-Buten-1-ol (**130**) was purchased from Fluka and used as received.

3-Buten-2-ol (131).

3-Buten-2-ol (**131**) was purchased from Fluka and used as received.

***O*-(2-Buten-1-yl) trichloroacetimidate (132).**[138]

A stirred solution of 2-buten-1-ol (**130**) (1.82 g, 25.3 mmol) in dry dichloromethane (40 ml) and trichloroacetonitrile (25 ml, 250 mmol) was treated with DBU (0.35 ml) at room temperature and then left for 0.5 h. The solvent was evaporated and the product was purified by column chromatography 3% triethylamine in toluene to give **132** (5.0 g, 91.5%) as yellow oil; R_f = 0.73 (3% triethylamine in toluene).

^{1}H-NMR (250 MHz, $CDCl_3$):#ι#ι#85>8#d, *J* = 6.5 Hz, 3 H, CH_3), 4.70 (d, *J* = 6.4 Hz, 2 H, CH_2), 5.75 (m, 2 H, 2 CH), 8.30 (brs, 1 H, NH). ^{13}C-NMR (150.8 MHz, $CDCl_3$) ι: 17.8 (CH_3), 69.8 (CH_2), 91.5 (CCl_3), 124.4 (CH), 131.6 (CH), 162.5 (CN).

***O*-(3-Buten-2-yl) trichloroacetimidate (133).**[138]

133 was prepared from 3-buten-2-ol (**131**) as described above. Yellow oil (4.8 g, 88%); R_f = 0.67 (3% triethylamine in toluene). ^{1}H-NMR (250 MHz, $CDCl_3$):#ι#ι#85;8#d, *J* = 6.4 Hz, 3 H, CH_3), 5.14 (dd, *J* = 11.7, *J* = 18.3 Hz, 2 H, CH_2), 5.51 (m, 1 H, CH), 5.92 (m, 1 H, CH), 8.31 (brs, 1 H, NH). ^{13}C-NMR (62.8 MHz, $CDCl_3$) ι: 19.3 (CH_3), 75.6 (CH), 91.7 (CCl_3), 115.9 (CH_2), 136.7 (CH), 161.6 (CN). ($C_6H_8Cl_3NO$) 216.5.

General procedure for reaction of trichloroacetimidate 132 with alcohols. Trichloroacetimidate **132** (0.3 g, 1.4 mmol) and alcohol (1.4 mmol) in dry methylene chloride (10 ml) were treated with TMSOTf (0.015 ml). The reaction mixture was stirred for 0.5-3.0 h. It was quenched with solid sodium bicarbonate, filtered and concentrated. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate).

2-Buten-1-yl 3,5-dinitrobenzyl ether (134) and 3-Buten-2-yl 3,5-dinitrobenzyl ether (135).

134: Yellow oil (0.13 g, 36%); R_f = 0.48 (petroleum ether/ethyl acetate, 5:1). ^{1}H-NMR (250 MHz, $CDCl_3$):#t # #1.72#d, *J* = 6.2 Hz, 3 H, CH_3), 4.04 (d, *J* = 6.2 Hz, 2 H, OCH_2), 4.65 (s, 2 H, CH_2Ph), 5.55 (m, 1 H, CH-CH_3), 5.75 (m, 1 H, CH=CH), 8.51 (m, 2 H, Ar-H), 8.90 (s, 1 H, Ar-H).
($C_{11}H_{12}N_2O_5$) 252.2; MS: m/z = 252.0.

135: Yellow oil (0.12 g, 33%); R_f = 0.44 (petroleum ether/ethyl acetate, 5:1). ^{1}H-NMR (250 MHz, $CDCl_3$):#t # #1.34#d, *J* = 6.4 Hz, 3 H, CH_3), 4.00 (m, 1 H, CH), 4.59 (d, J_{gem} = 13.4 Hz, 1 H, CHPh), 4.69 (d, J_{gem} = 13.4 Hz, 1 H, CHPh), 5.24 (m, 2 H, CH_2), 5.76 (m, 1 H, CH=CH_2), 8.50 (m, 2 H, Ar-H), 8.88 (s, 1 H, Ar-H).
($C_{11}H_{12}N_2O_5$) 252.2; MS: m/z = 252.0.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2-buten-1-yl)-Ŭ-D-glucopyranoside (136) and Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3-buten-2-yl)-Ŭ-D-glucopyranoside (137).

136: White foam (0.22 g, 31%); R_f = 0.57 (petroleum ether /ethyl acetate 5:1); $[Ŭ]_D$= 36.7 (c = 1.0, CH_2Cl_2).
^{1}H-NMR (250 MHz, $CDCl_3$):#t # #1.68#d, *J* = 6.1 Hz, 3 H, CH_3), 3.36 (s, 3 H, OCH_3), 3.60 (m, 3 H, 6-H, 4-H, 6´-H), 3.66 (m, 2 H, 2-H, 5-H), 3.90 (m, 3 H, 3-H, OCH_2),

4.61 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.64 (d, J_{gem} = 12.0 Hz, 1 H, 1 CHPh), 4.76 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.81 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.84 (m, 1 H, CHPh), 4.89 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.97 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 5.60 (m, 2 H, CH=CH), 7.25-7.45 (m, 15 H, Ar-H). (MALDI, positive mode, Matrix: DHB): m/z = 541.0 $(M+Na)^+$, 557.0 $(M+K)^+$.

$C_{32}H_{38}O_6$ (518.7) Calcd: C: 74.10 H: 7.38

Found: C: 74.06 H: 7.40

137: White foam (0.2 g, 28%); R_f = 0.53 (petroleum ether/ethyl acetate, 5:1); $[\alpha]_D$= 49.6 (c = 2.0, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$):#.##-#.26 (2 d, 3 H, CH_3), 3.35 (2 s, 3 H, OCH_3), 3.64 (m, 2 H, 6-H, 6′-H), 3.70 (m, 3 H, 4-H, 2-H, 5-H), 3.90 (m, 2 H, CH, 3-H), 4.59 (d, $J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 4.61 (m, 2 H, 2 CHPh), 4.80 (m, 3 H, 3 CHPh), 4.90 (m, 1 H, CHPh), 5.11 (m, 2 H, CH=$\underline{CH_2}$), 5.70 (m, 1 H, CH=CH_2), 7.24-7.43 (m, 15 H, Ar-H). (MALDI, positive mode, Matrix: DHB): m/z = 541.1 $(M+Na)^+$, 557.1 $(M+K)^+$.

$C_{32}H_{38}O_6$ (518.7) Calcd: C: 74.10 H: 7.38

Found: C: 73.91 H: 7.22

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2-buten-1-yl)-α-D-glucopyranoside (138) and Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(3-buten-2-yl)-α-D-glucopyranoside (139).

138: Colorless oil (0.2 g, 27%); R_f = 0.52 (petroleum ether/ethyl acetate, 5:1); $[\alpha]_D$= 82.2 (c = 1.5, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$):#.##-#.62 (d, J = 5.1 Hz, 3 H, CH_3), 3.41 (s, 3 H, OCH_3), 3.52 (dd, $J_{6,5}$ = 4.2, J_{gem}= 9.3 Hz, 1 H, 6-H), 3.61 (m, 2 H, 5-H, 6′-H), 3.70 (m, 2 H, 2-H, 4-H), 3.83 (m, $J_{3,2}$ = $J_{3,4}$ = 9.4 Hz, 1 H, 3-H), 3.95 (d, J = 5.4 Hz, 2 H, OCH_2), 4.61 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.65 (d, J_{gem} = 11.2 Hz, 1 H, CHPh), 4.71 (d, J_{gem} = 12.4 Hz, 1 H, CHPh), 4.80 (m, 3 H, 3 CHPh), 5.05 (d, J_{gem} = 12.4 Hz, 1 H, CHPh), 5.51

(m, 1 H, CH=CH), 5.73 (m, 1 H, CH=CH), 7.21-7.45 (m, 15 H, Ar-H). (MALDI, positive mode, Matrix: DHB): m/z = 541.0 $(M+Na)^+$, 557.0 $(M+K)^+$.

$C_{32}H_{38}O_6$ (518.7) Calcd: C: 74.10 H: 7.38

Found: C: 74.04 H: 7.06

139: Colorless oil (0.17 g, 24%); R_f = 0.49 (petroleum ether/ethyl acetate, 5:1); $[\alpha]_D$= 129.6 (c = 1.0, CH_2Cl_2).

^{1}H-NMR (250 MHz, $CDCl_3$):δ = 1.25 (d, *J* = 6.1 Hz, 3 H, CH_3), 3.31 (s, 3 H, OCH_3), 3.50 (m, 2 H, 6-H, 5-H), 3.65 (m, 3 H, 6´-H, 4-H, 2-H), 3.80 (m, 2 H, 3-H, CH-CH_3), 4.60 (d, $J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 4.62 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.70 (m, 3 H, 3 CHPh), 4.82 (m, 2 H, 2 CHPh), 5.10 (m, 2 H, CH=CH_2), 5.75 (m, 1 H, CH=CH_2), 7.22-7.48 (m, 15 H, Ar-H). (MALDI, positive mode, Matrix: DHB): m/z = 541.0 $(M+Na)^+$, 557.0 $(M+K)^+$.

$C_{32}H_{38}O_6$ (518.7) Calcd: C: 74.10 H: 7.38

Found: C: 74.12 H: 7.31

3- *O*-(2-Buten-1-yl)-1:2,5:6- di-*O*- isopropylidene- α-D- glucofuranose (140) and 3- *O*- (3-buten-2-yl)- 1:2,5:6- di-*O*- isopropylidene-α-D- glucofuranose (141).

140: Colorless oil (0.13 g, 28%); R_f = 0.51 (petroleum ether/ethyl acetate, 5:1); $[\alpha]_D$ = -11.2 (c = 2.0, CH_2Cl_2). ^{1}H-NMR (250 MHz, $CDCl_3$):δ = 1.25, 135, 1.42, 1.49 (4 s, 12 H, 4 CH_3), 1.70 (d, *J* = 6.2 Hz, 3 H, CH_3), 3.98 (m, 3 H, 6-H, 6´-H, 5-H), 4.08 (m, 3 H, CH_2, 4-H), 4.30 (m, 1 H, 3-H), 4.52 (d, *J* = 3.6 Hz, 1 H, 2-H), 5.55 (m, 1 H, CH), 5.75 (m, 1 H, CH), 5.86 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H). MALDI, positive mode, Matrix: DHB): m/z = 337.2 $(M+Na)^+$, 353.3 $(M+K)^+$.

$C_{18}H_{26}O_{10}$ (314.4) Calcd: C: 61.12 H: 8.33

Found: C: 61.53 H: 8.40

141: Colorless oil (0.11 g, 26%); R_f = 0.48 (petroleum ether/ethyl acetate, 5:1); $[\check{U}]_D$ = -4.5 (c = 1.0, CH_2Cl_2). ^{1}H-NMR (250 MHz, $CDCl_3$):# = 1.22 (d, *J* = 6.4 Hz, 3 H, CH_3), 1.30, 1.35, 1.41, 1.44 (4 s, 12 H, 4 CH_3), 3.98 (m, 3 H, 6-H, 6´-H, 5-H), 4.10 (m, 2 H, 4-H, 2-H), 4.30 (m, 1 H, CH), 4.50 (m, 1 H, 2-H), 5.20 (m, 2 H, CH_2), 5.88 (d, *J* = 3.8 Hz, 1 H, 1-H). MALDI, positive mode, Matrix: DHB): m/z = 337.2 $(M+Na)^+$, 353.3 $(M+K)^+$.

$C_{18}H_{26}O_{10}$ (314.4)	Calcd:	C: 61.12	H: 8.33
	Found:	C: 61.47	H: 8.52

General procedure for reaction of trichloroacetimidate 2.

A solution of **2** (0.45 g, 1.4 mmol) and C-nucleophiles as acceptor (1.4 mmol) in dry dichloromethane (40 ml) was stirred under nitrogen at room temperature and then TMSOTf (13 µl, 0.06 mmol) was added. After 20 min-3 h. The reaction mixture was neutralized with solid sodium bicarbonate, filtered and concentrated in vacuo. The residue was purified by flash chromatography.

Allyl trimethylsilane (142).

Allyl trimethylsilane (**142**) was purchased from Fluka and used as received.

***N*-But-3-enyl-phthalimide (143).**

White powder (0.26 g, 93%); R_f = 0.64 (petroleum ether/ethylacetate, 5:1). m.p. 48 ^{o}C, Lit.[226] 49-50 ^{o}C. The analytical data are identical with the published values.[226]

1,3-Dimethoxybenzene (144).

1,3-Dimethoxybenzene (**144**) was purchased from Aldrich and used as received.

1,2,3-Trimethoxybenzene (145).

1,2,3-Trimethoxybenzene (**145**) was purchased from Aldrich and used as received.

Benzene (146).

Benzene (**146**) was purchased from Fluka and used as received.

***N*-(2,4-Dimethoxy)benzyl-phthalimide (147).**

White powder (0.32 g, 78%); R_f = 0.43 (petroleum ether/ethylacetate, 5:1). m.p. 91 ^oC. ^1H-NMR (250 MHz, $CDCl_3$):# = 3.76 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 4.82 (s, 2 H, CH_2), 6.38-7.13 (m, 3 H, Ar-H), 7.67-7.87 (m, 4 H, Ar-H). ^{13}C-NMR (62.8 MHz, $CDCl_3$) ι: 36.5 (CH_2), 55.2, 55.3 (2 OCH_3), 98.5, 103.8, 116.6, 122.8, 123.1, 129.7, 132.1, 133.5, 133.8 (C-Ar), 160.5, 163.7 (2 CO). MS: m/z = 297.0.

$C_{17}H_{15}NO_4$ (297.3)	Calcd:	C: 68.68	H: 5.08	N: 4.71
	Found:	C: 68.58	H: 5.16	N: 4.78

***N*-(2,3,4-Trimethoxy)benzyl-phthalimide (148).**

White powder (0.40 g, 87%); R_f = 0.48 (petroleum ether/ethylacetate, 5:1). m.p. 106 ^oC. ^1H-NMR (250 MHz, $CDCl_3$):# = 3.81, 3.84, 3.95 (3 s, 9 H, 3 OCH_3), 4.84 (s, 2 H, NCH_2), 6.58 (d, *J* = 8.6 Hz, 1 H, Ar-H), 6.94 (d, *J* = 8.6 Hz, 1 H, Ar-H), 7.69-7.88 (m, 4 H, Ar-H). MS: m/z = 327.0.

$C_{18}H_{17}NO_5$ .0.25 H_2O (331.8)	Calcd:	C: 65.15	H: 5.23	N: 4.22
	Found:	C: 65.27	H: 5.13	N: 4.27

***N*-Benzyl-phthalimide (149).**

White powder (0.29 g, 86%); R_f = 0.45 (petroleum ether/ethylacetate, 5:1); m.p. 118 ^oC, Lit. 118 ^oC. The analytical data are identical with the published values.[231]

Styrene (150).

Styrene (**150**) was purchased from Fluka and used as received.

***N*-(Z/E)-Cinnamyl-phthalimide (151).**

White powder (0.31 g, 85%); R_f = 0.67 (petroleum ether/ethylacetate, 5:1). m.p. 155 ^oC, Lit. 158-159 ^oC. The analytical data are identical with the published values.[233]

1- Trimethylsiloxy-cyclohexene (152).

1- Trimethylsiloxy-cyclohexene (**152**) was purchased from Fluka and used as received.

***N*-(2-Oxo-cyclohexylmethyl)-phthalimide (153).**

White powder (0.32 g, 89%); R_f = 0.57 (petroleum ether/ethylacetate, 5:1). m.p. 133 ^oC, Lit. 134 ^oC. The analytical data are identical with the published values.[234]

1-Phenyl-1-trimethylsiloxy-ethylene (154).

1-Phenyl-1-trimethylsiloxy-ethylene (**154**) was purchased from Fluka and used as received.

***N*-(3-Oxo-3-phenyl-propyl)-phthalimide (155).**

White powder (0.32 g, 83%); R_f = 0.52 (petroleum ether/ethylacetate, 5:1). m.p. 128 ^oC, Lit. 130 ^oC. The analytical data are identical with the published values.[235]

4-*C*-(1-Trimethylsilyl)oxy) ethenyl-3-*O*-benzyl-1:2-*O*-isopropylidene-ζ-D-glucofuranose (156).

Compound **156** was synthesized following a published procedure. The analytical data are identical with the published values.[236]

3-*O*-Benzyl-6,7-dideoxy-1:2-*O*-isoproylidene-7-(*N*-phthalimido)-ζ-D-xylo-heptofuranos-5-ulose (157).

Colorless oil (0.55 g, 87%); R_f = 0.72 (petroleum ether/ethylacetate, 5:1); $[\breve{U}]_D$ = -18.5 (c = 0.5, CH_2Cl_2). ^{1}H-NMR (600 MHz, $CDCl_3$):#t = 1.29, 1.44 (2 s, 6 H, 2 CH_3), 3.04 (m, 2 H, CH_2), 3.96 (m, 2 H, CH_2), 4.24 (d, J = 3.5 Hz, 1 H, 4-H), 4.46 (d, J_{gem} = 11.9 Hz, 1 H, CHPh), 4.53 (d, J_{gem} = 11.9 Hz, 1 H, CHPh), 4.55 (d, J = 3.4 Hz, 1 H, 2-H), 4.64 (d, J = 3.5 Hz, 1 H, 3-H), 6.01 (d, J = 3.4 Hz, 1 H, 1-H), 7.20-7.33 (m, 5 H, Ar-H), 7.67-7.80 (m, 4 H, Ar-H); ^{13}C-NMR (150.8 MHz, $CDCl_3$) ι: 26.3, 26.9 (2 CH_3), 32.4, 39.0, 72.4 (3 CH_2), 81.7 (C-2), 83.5 (C-4), 85.2 (C-3), 105.9 (C-1), 112.4, 123.1, 123.8, 127.6, 128.0, 128.5, 132.1, 133.8, 134.5, 136.7 (C-Ar), 167.9, 206.3 (2 CO). MALDI, positive mode, Matrix: DHB): m/z = 473.9 $(M+Na)^+$, 490.0 $(M+K)^+$.

$C_{25}H_{25}NO_7 . H_2O$(469.5) Calcd: C: 63.90 H: 5.75 N: 2.98

Found: C: 63.84 H: 5.66 N: 3.03

3-Trimethylsiloxy-2-butenic acid methyl ester (158).

3-Trimethylsiloxy-2-butenic acid methyl ester (**158**) was purchased from Fluka and used as received.

1-Methoxy-2-methyl-1-trimethylsiloxy-propene (159).

1-Methoxy-2-methyl-1-trimethylsiloxy-propene (**159**) was purchased from Fluka and used as received.

Methyl 3-oxo-2-(*N*-phthalimidomethyl)butanoate (160).

Colorless oil (0.29 g, 75%); R_f = 0.48 (petroleum ether/ethylacetate, 5:1).

^{1}H-NMR (250 MHz, $CDCl_3$):#t = 2.20 (s, 3 H, CH_3), 3.62 (s, 3 H, OCH_3), 3.95 (m, 1 H, CH), 4.13 (m, 2 H, CH_2), 7.61-7.88 (m, 4 H, Ar-H). m/z = 275.0.

$C_{14}H_{13}NO_5$ (275.3) Calcd: C: 61.09 H: 4.76 N: 5.09

Found: C: 60.81 H: 4.68 N: 5.68

Methyl 2,2-dimethyl-3-(*N*-phthalimidomethyl)propionate (161).

White powder (0.30 g, 82%); R_f = 0.53 (petroleum ether/ethylacetate, 5:1). m.p. 92 ^oC, Lit. 92-94 ^oC. The analytical data are identical with the published values.[226]

General procedure for the removal of the phthaloyl group.

The phthalimide derivative (0.50 mmol) was dissolved in methyl alcohol (30 ml) and (2 ml) of hydrazine and the reaction mixture refluxed for 1 h. the solvent was evaporated in vacuo and the residue was dissolved in dichloromethane (50 ml). The organic layer was extracted with 1N NaOH (5x 50ml) and the organic layer was dried with magnesium sulfate and concentrated in vacuo. The residue was purified by flash chromatography (dichloromethane/methanol).

2,3,4-Trimethoxybenzyl amine (162).

Yellow oil (0.08 g, 84%); The analytical data are identical with the published values.[239]

Benzylamine (163).

Yellow oil (0.05 g, 92%); The analytical data with an authentic sample.

3-Phenyl-allylamine (164).

Yellow oil (0.05 g, 76%); The analytical data are identical with the published values.[240]

3-Amino-1-phenyl propan-1-one hydrazone (165).

Yellow oil (0.05 g, 78%); R_f = 0.34 (chloroform/methanol 2:1).

^{1}H-NMR (250 MHz, $CDCl_3$):# = 2.81 (m, 2 H, CH_2), 2.97 (m, 2 H, CH_2), 3.51-4.20 (brs, 4 H, 2 NH_2), 7.18-7.68 (m, 5 H, Ar-H). m/z = 163.0.

7-Amino-3-*O*-benzyl-6,7-dideoxy-1:2-*O*-isopropylidene-ζ-D-xylo-heptofuranos-5-ulose hydrazone (166). Colorless oil (0.44 g, 66%); R_f = 0.41 (chloroform/methanol 2:1); $[\check{U}]_D$ = - 4.5 (c = 0.5, CH_2Cl_2). ^{1}H-NMR (250 MHz, $CDCl_3$):#t = 1.27, 1.44 (2 s, 6 H, 2 CH_3), 2.45 (m, 2 H, CH_2), 2.85 (m, 2 H, CH_2), 4.01 (d, *J* = 3.5 Hz, 1 H, 4-H), 4.42 (d, J_{gem} = 11.8 Hz, 1 H, CHPh), 4.45 (d, J_{gem} = 11.8 Hz, 1 H, CHPh), 4.55 (d, *J* = 3.5 Hz, 1 H, 2-H), 4.70 (d, *J* = 3.5 Hz, 1 H, 3-H), 5.11 (brs, 2 H, NH_2), 5.95 (d, *J* = 3.5 Hz, 1 H, 1-H), 7.13-7.31 (m, 5 H, Ar-H).

$C_{17}H_{25}N_3O_4$ .0.25 H_2O (340.4) Calcd: C: 60.07 H: 7.41 N: 12.36

Found: C: 60.14 H: 7.49 N: 11.74

1-Phenyl-3-(*N*-phthalimido)-propan-1-one *O*-acetyloxime (167).

Compound **155** (0.2, 0.7 mmol) was dissolved in dry methanol (20 ml) and hydroxyamine hydrochloride (0.15 g) was added. Dropwise of NaOMe was added to (PH = 10), stirring for 1 h. The mixture was filterated and evaporated in vacuo. The residue was dissolved in pyridine (5 ml), treated with acetic anhydride (2.5 ml) and the mixture stirred at room temp. for 12 h. The solvent was evaporated in vacuo by coevaporation with toluene and the residue purified by flash chromatography dichloromethane/methanol 10:1 to afford **167** (0.19 g, 79%) as colorless oil; R_f = 0.71 (chloroform/methanol 5:1).

^{1}H-NMR (250 MHz, $CDCl_3$):#t = 2.17 (s, 3 H, AcO), 3.24 (t, *J* = 7.2 Hz, 2 H, CH_2), 3.96 (t, *J* = 7.2 Hz, NCH_2), 7.24-7.38 (m, 5 H, Ar-H), 7.67-7.82 (m, 4 H, Ar-H). (MALDI, positive mode, Matrix: DHB): m/z = 358.4 $(M+Na)^+$, 375.1 $(M+K)^+$.

$C_{19}H_{16}N_2O_4$ .0.5 H_2O (345.3) Calcd: C: 66.08 H: 4.95 N: 8.11

Found: C: 66.14 H: 4.90 N: 7.91

***N*-hydroxymethylol benzamide (168).**

168 was prepared according to reference 241.

***N*-hydroxymethyl *N*-methyl benzamide (169).**

169 was prepared according to reference 242.

***N*-[(Trichloroacetylamino)methyl]benzamide (172).**

A stirred solution of *N*-hydroxymethylol benzamide **168** (0.76 g, 5.0 mmol) in dry dichloromethane (20 ml) and trichloroacetonitrile (5 ml, 50 mmol) was treated with DBU (71µl) at room temperature and then left for 12 h. The solvent was evaporated and the product was purified by column chromatography 2% triethylamine in toluene to give **172** (0.80 g, 54%) as a oil; R_f = 0.62 (2% triethylamine in toluene). NaH can be used instesd of DBU to give (1.3 g, 86.5%).

^{1}H-NMR (250 MHz, $CDCl_3$): 4.98 (d, *J* = 7.0 Hz, 2 H, CH_2), 7.41-7.81 (m, 5 H, Ar-H, NH), 8.12 (brs, 1 H, NH). m/z =295.5.

$C_{10}H_9Cl_3N_2O_2$ (295.6) Calcd: C: 40.64 H: 3.07 N: 9.48

Found: C: 40.62 H: 3.10 N: 9.35

***N*-[(Trichloroacetylamino)methyl]-*N*-methyl-benzamide (173).**

A stirred solution of *N*-hydroxymethyl *N*-methyl benzamide **169** (0.83 g, 5.0 mmol) in dry dichloromethane (20 ml) and trichloroacetonitrile (5 ml, 50 mmol) was treated with NaH (0.12 g, 5 mmol) at room temperature and then left for 8 h. The reaction was processed as above. The crude residue was purified by column chromatography 2% triethylamine in toluene to give **173** (0.1 g, 73%) as a oil; R_f = 0.71 (2% triethylamine in toluene).

^{1}H-NMR (250 MHz, $CDCl_3$): 3.11 (s, 3 H, CH_3), 5.00 d, *J* = 5.8 Hz, 2 H, CH_2), 7.42 (m, 5 H, Ar-H), 8.01 (brs, 1 H, NH). (MALDI, positive mode, Matrix: DHB): m/z = 332.0 $(M+Na)^+$.

$C_{11}H_{11}Cl_3N_2O_2$ (309.6) Calcd: C: 42.68 H: 3.58 N: 9.05

Found: C: 42.69 H: 3.59 N: 9.20

***N*-Hydroxymethyl trichloroacetamide (174).**

174 was prepared according to reference 243.

***O*-(*N*-Trichloroacetamide methyl) trichloroacetimidate (175).**

A stirred solution of *N*-hydroxymethyltrichloroacetamide **174** (0.96 g, 5.0 mmol) in dry dichloromethane (20 ml) and trichloroacetonitrile (5 ml, 50 mmol) was treated with NaH (0.12 g, 5 mmol) at room temperature and then left for 8 h. The reaction was processed as above. The crude residue was purified by column chromatography 2% triethylamine in toluene to give **175** (1.2 g, 71.5%) as a oil; R_f = 0.69 (2% triethylamine in toluene).

^{1}H-NMR (250 MHz, $CDCl_3$):### 8.95 (brs, 1 H, NH), 4.93 (d, *J* = 6.4 Hz, 2 H, CH_2), 7.81 (brs, 1 H, NH).

($C_5H_4Cl_6N_2O_2$) 337.0; m/z = 337.0.

General procedure for reaction of trichloroacetimidate 175 with *C*-nucleophiles.

A solution of **175** (0.47 g, 1.4 mmol) and acceptor (1.4 mmol) in dry dichloromethane (40 ml) was stirred under nitrogen at room temperature and then TMSOTf (13 µl, 0.06 mmol) was added. After 1-3 h. The reaction mixture was neutralized with solid sodium bicarbonate, filtered and concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethylacetate).

***N*-(3-Phenyl-allyl)-trichloroacetamide (176).**[244]

Yellow oil (0.21g, 79%); The analytical data are identical with the published values.[244]

Methyl 3-oxo-2-(trichloroacetylamino)methyl-butanoate (177).

Colorless oil (0.27 g, 68%); R_f = 0.46 (petroleum ether/ethylacetate, 5:1).

^{1}H-NMR (250 MHz, $CDCl_3$):δ = 2.35 (s, 3 H, CH_3), 3.79 (s, 3 H, CH_3), 3.92 (m, 3 H, NCH_2), 7.51 (brs, 1 H, NH). MS: m/z = 290.0.

$C_8H_{10}Cl_3NO_4$ (290.5) Calcd: C: 33.07 H: 3.47 N: 4.82

Found: C: 32.55 H: 3.54 N: 5.01

Methyl 3-(trichloroacetyl)amino-2,2-dimethyl-propanoate (178).

Colorless oil (0.28 g, 74%); R_f = 0.53 (petroleum ether/ethylacetate, 5:1).

^{1}H-NMR (250 MHz, $CDCl_3$):δ = 1.19 (s, 6 H, 2 CH_3), 3.39 (d, *J* = 6.1 Hz, 2 H, CH_2), 3.68 (s, 3 H, OCH_3), 7.51 (brs, 1 H, NH). MS: m/z = 276.54.

$C_8H_{12}Cl_3NO_3$ (276.5) Calcd: C: 34.74 H: 4.37 N: 5.06

Found: C: 34.67 H: 4.73 N: 4.97

Trichloroacetamidmethyl-3,5-dinitrobenzyl ether (179).

Yellow powder (0.39 g, 76%); R_f = 0.45 (petroleum ether/ethylacetate, 4:1); m.p.108 ^{o}C.

^{1}H-NMR (250 MHz, $CDCl_3$):δ = 4.84 (s, 2 H, CH_2), 5.04 (d, *J* = 6.9 Hz, 2 H, CH_2), 7.43 (brs, 1 H, NH), 8.53-8.96 (m, 3 H, Ar-H). ^{13}C-NMR (150.8 MHz, $CDCl_3$) ι: 69.1, 71.9 (2 CH_2), 118.0, 127.0, 142.3, 148.5 (C-Ar), 163.1 (CO). MS: m/z = 372.0.

$C_{10}H_8Cl_3N_3O_6$ (372.6) Calcd: C: 32.24 H: 2.16 N: 11.28

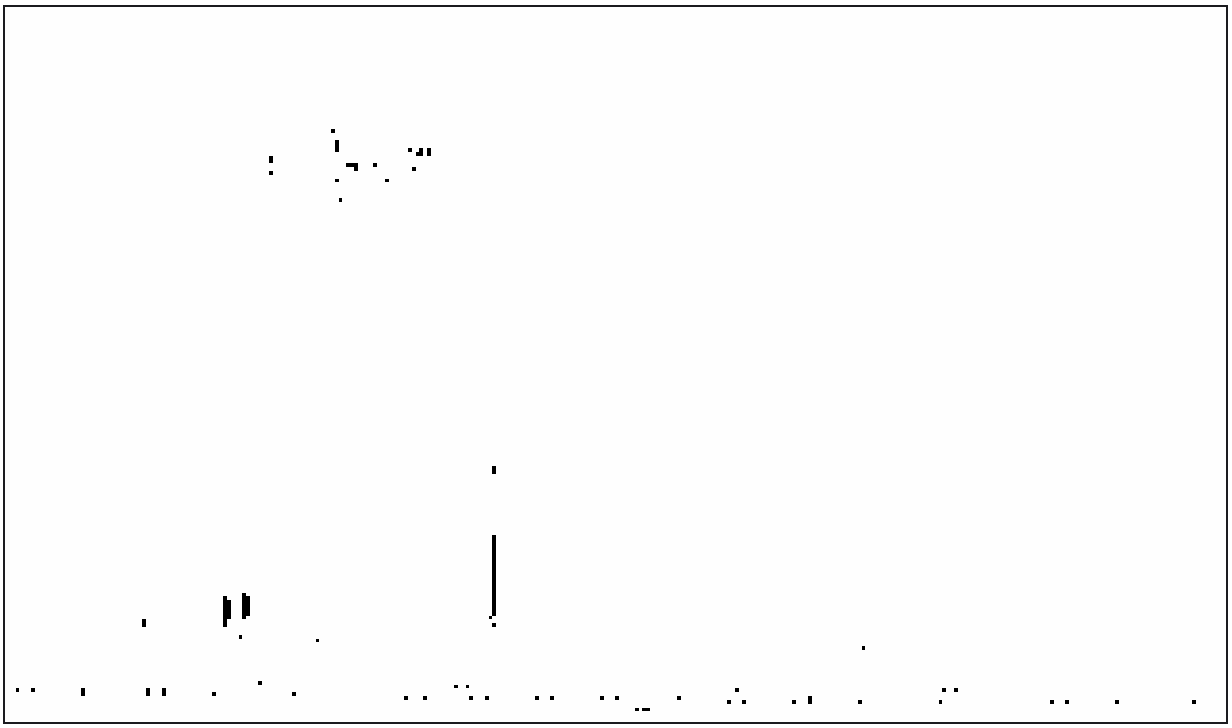
Found: C: 32.24 H: 2.23 N: 10.81

Removal of the trichloroacetimide group.

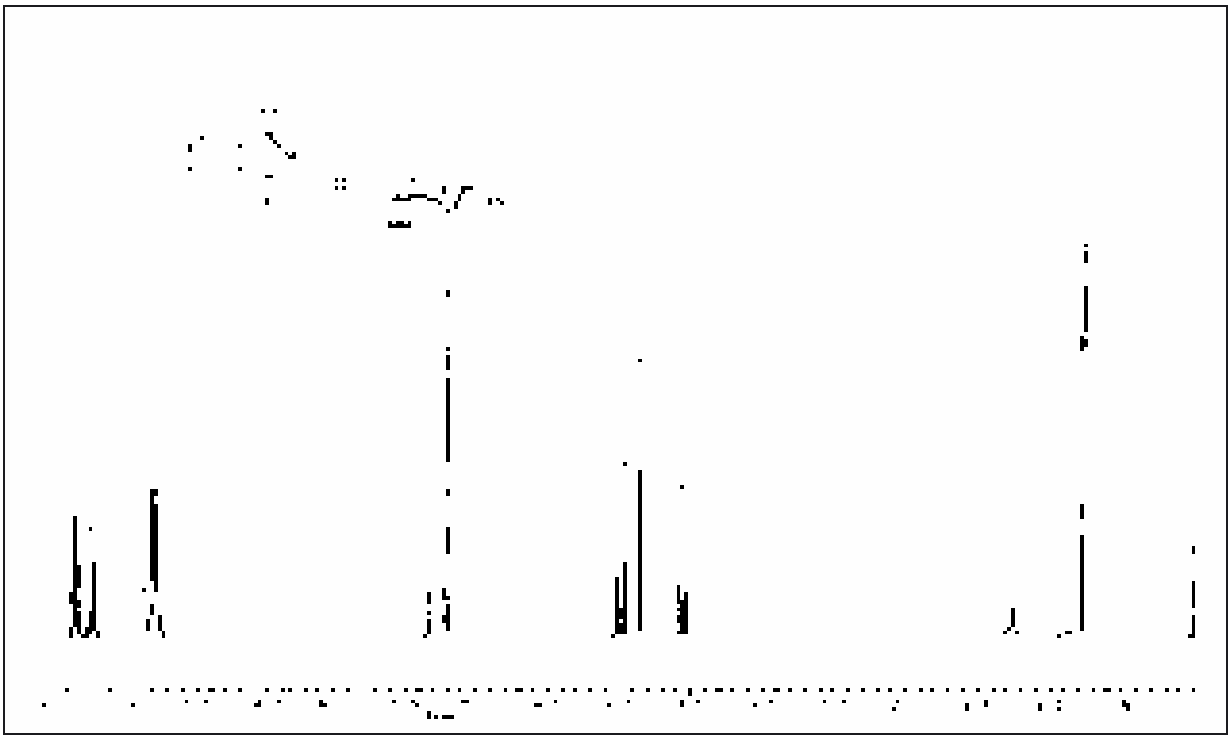
The trichloroacetimide derivative **176** (0.5 g, 1.87 mmol) was dissolved in methy alcohol (10 ml) and 2 N KOH (5 ml) and the reaction mixture was refluxed for 1 h. The solvent was evaporated in vacuo and the residue was dissolved in

dichloromethane (50 ml). The solution was extracted with 1N NaOH (5x 50ml) and the organic layer was dried with magnesium sulfate and concentrated in vacuo to give **166**.[240]

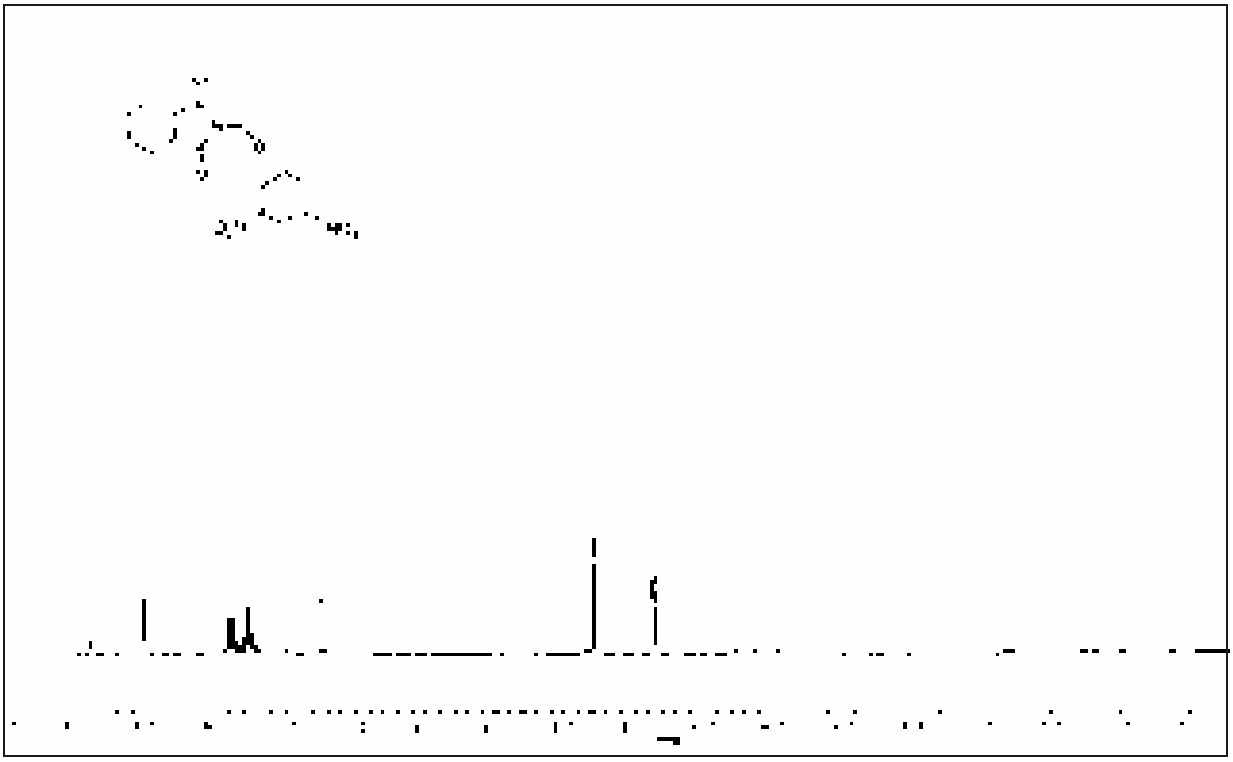
3.3 NMR Spectra



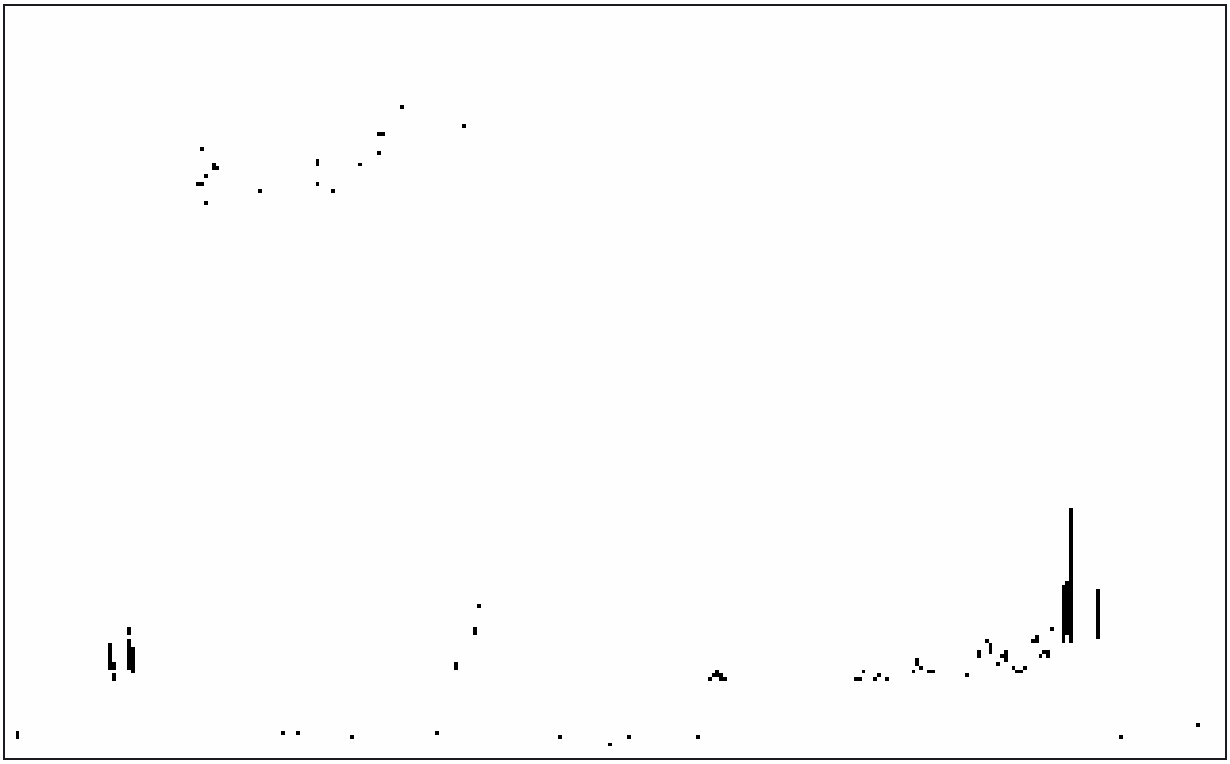
^{1}H-NMR Spectrum of Compound **2** (250 MHz, $CDCl_3$)



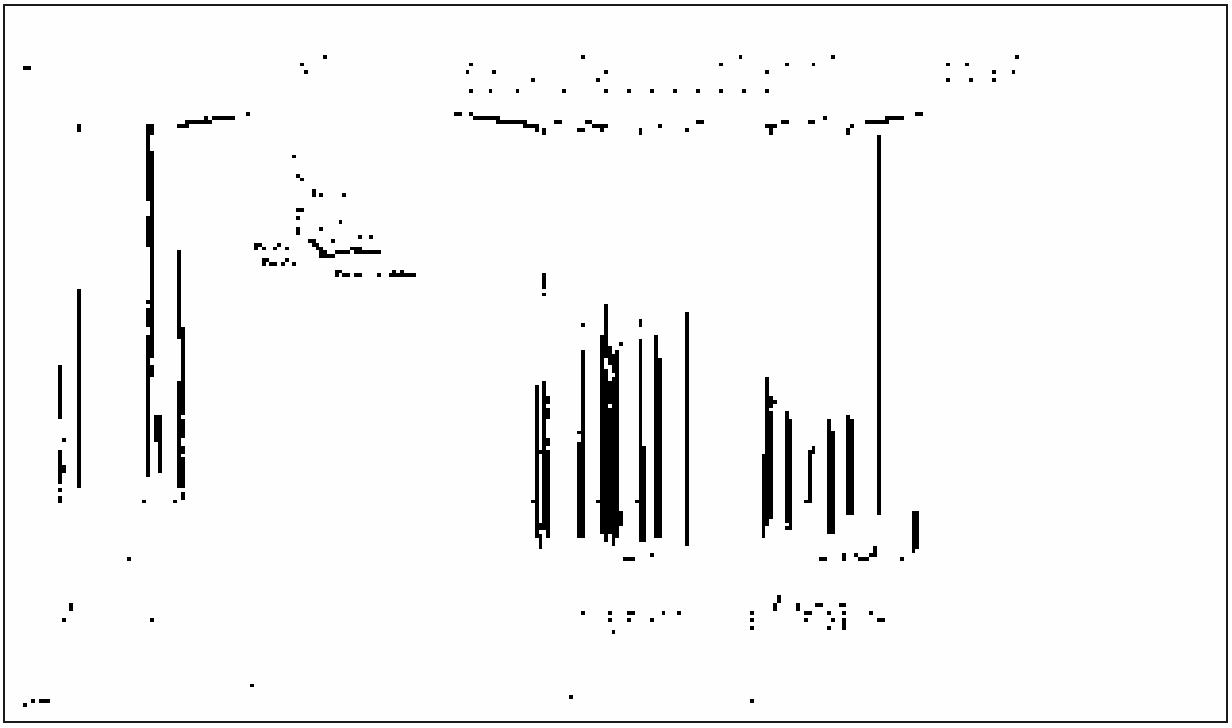
^{1}H-NMR Spectrum of Compound **9** (250 MHz, $CDCl_3$)



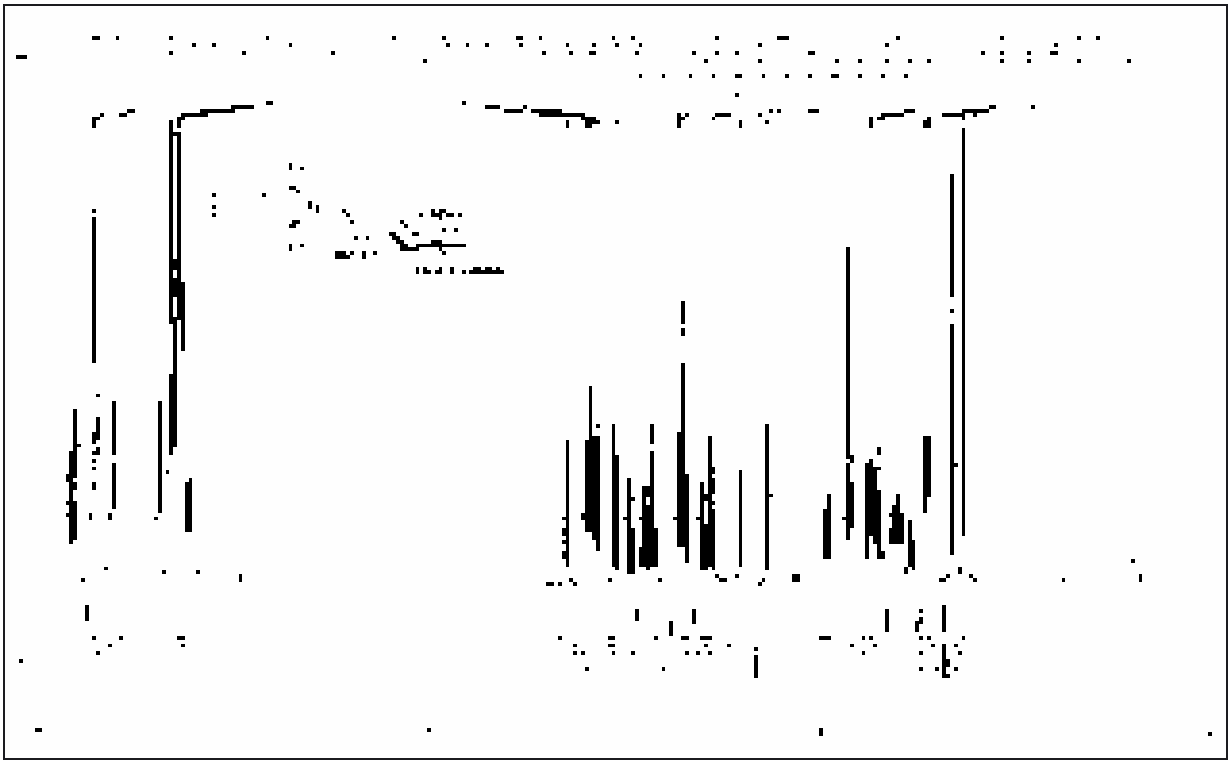
^{1}H-NMR Spectrum of Compound **13** (250 MHz, $CDCl_3$)



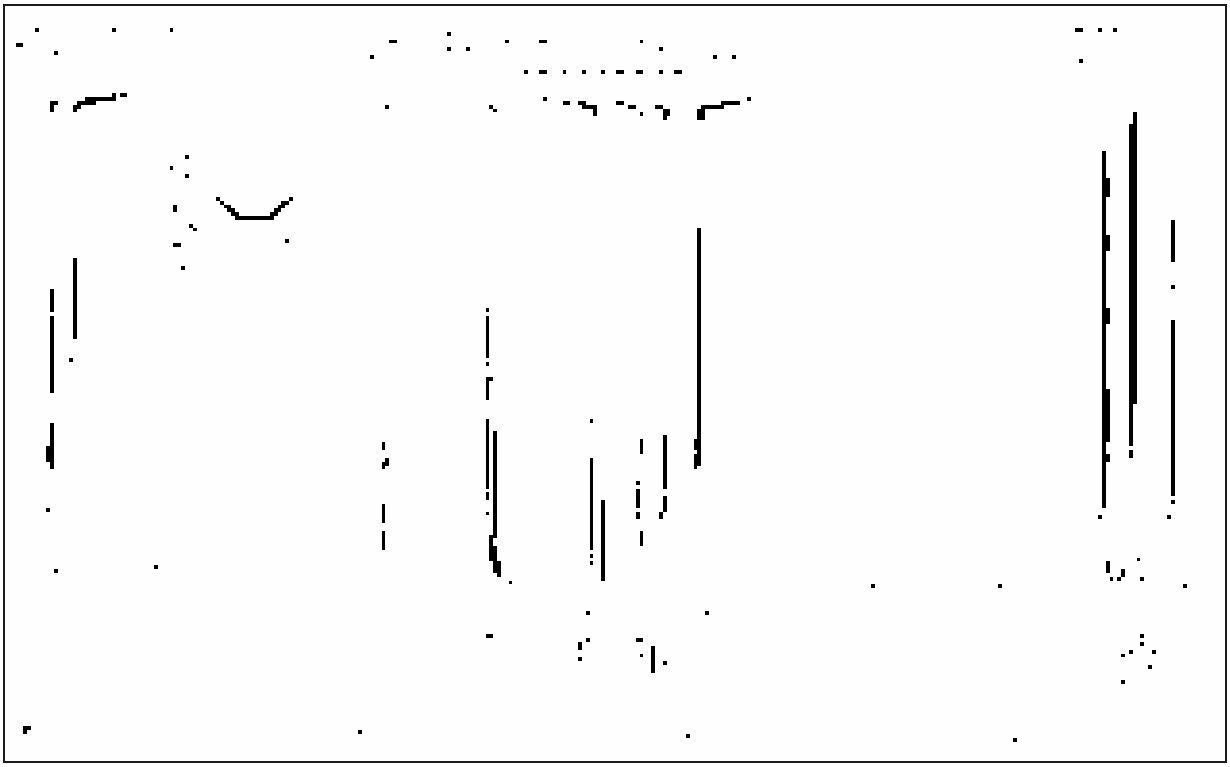
^{1}H-NMR Spectrum of Compound **14** (250 MHz, $CDCl_3$)



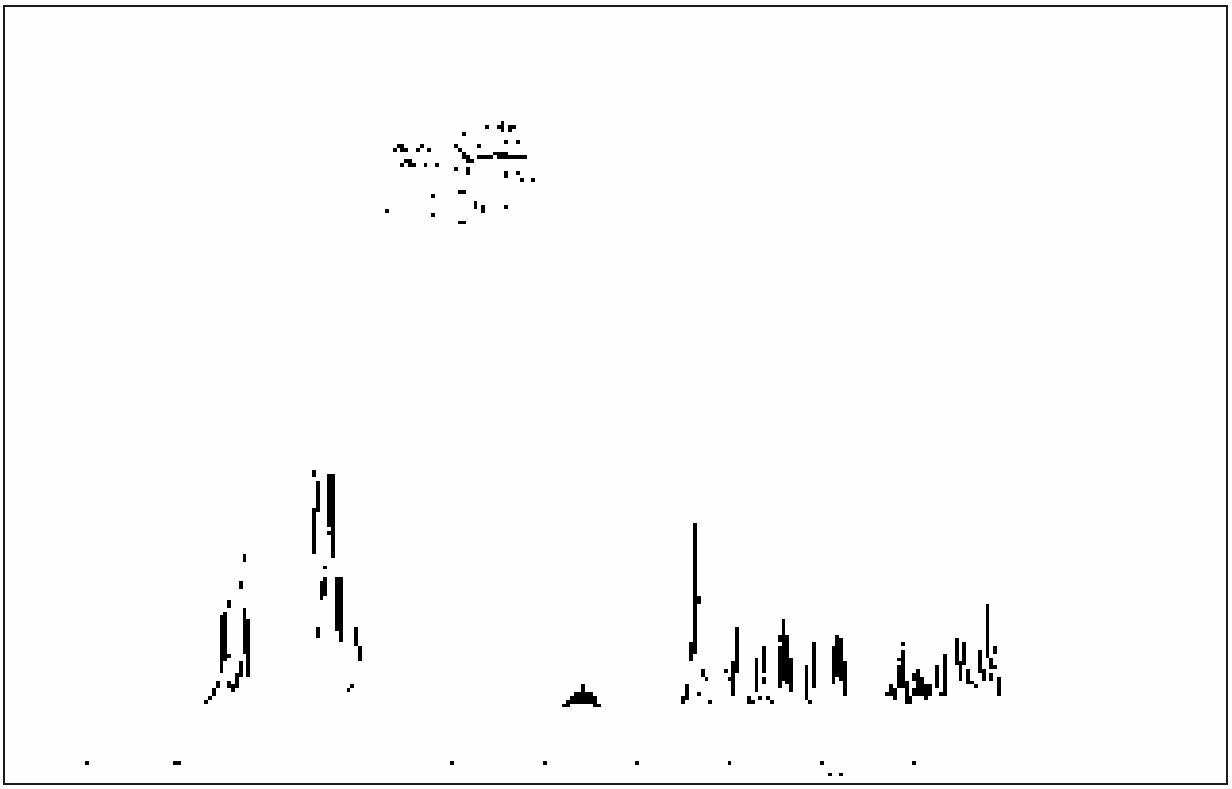
^{1}H-NMR Spectrum of Compound **16** (600 MHz, $CDCl_3$)



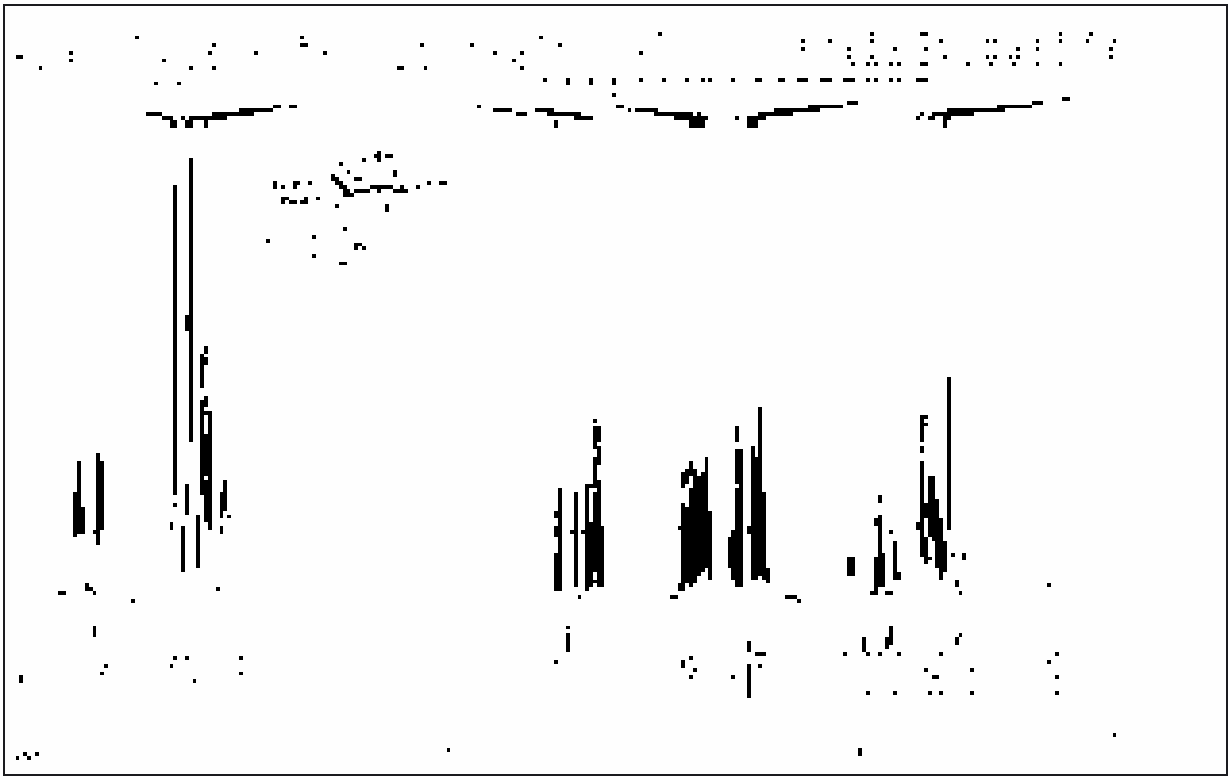
^{1}H-NMR Spectrum of Compound **19** (600 MHz, $CDCl_3$)



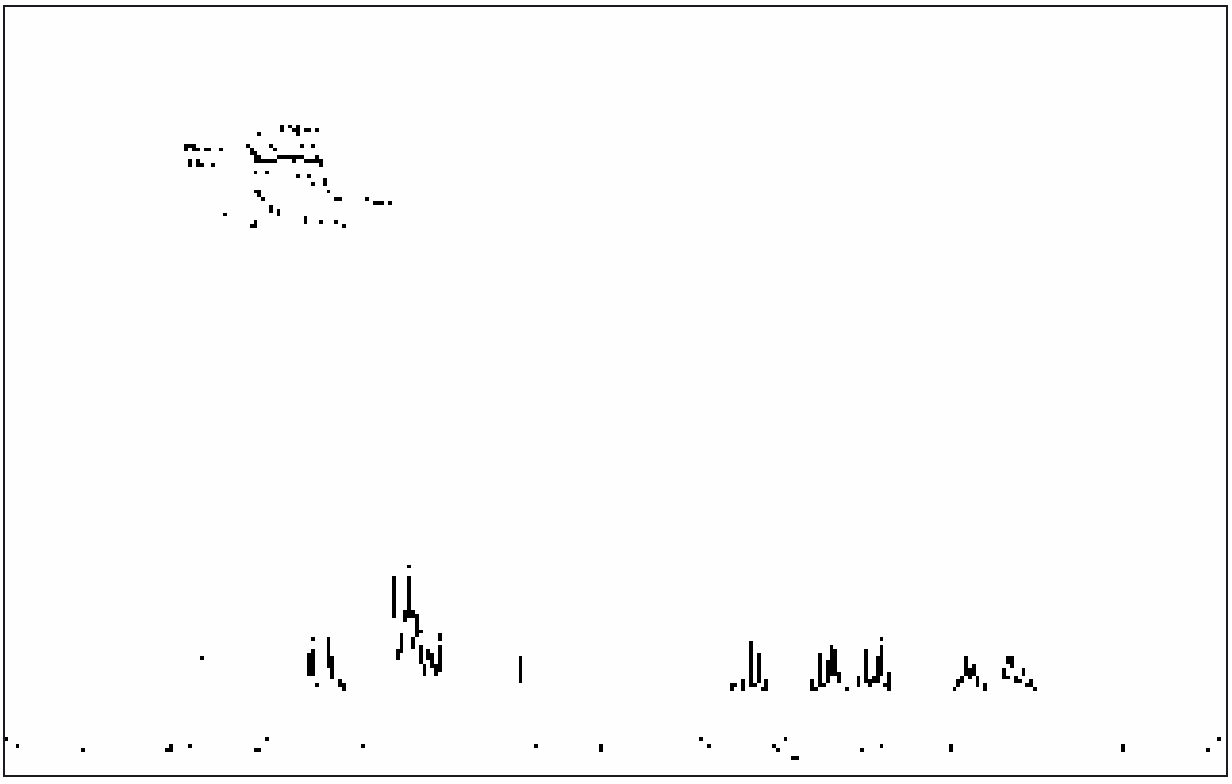
^{1}H-NMR Spectrum of Compound **20**(600 MHz, $CDCl_3$)



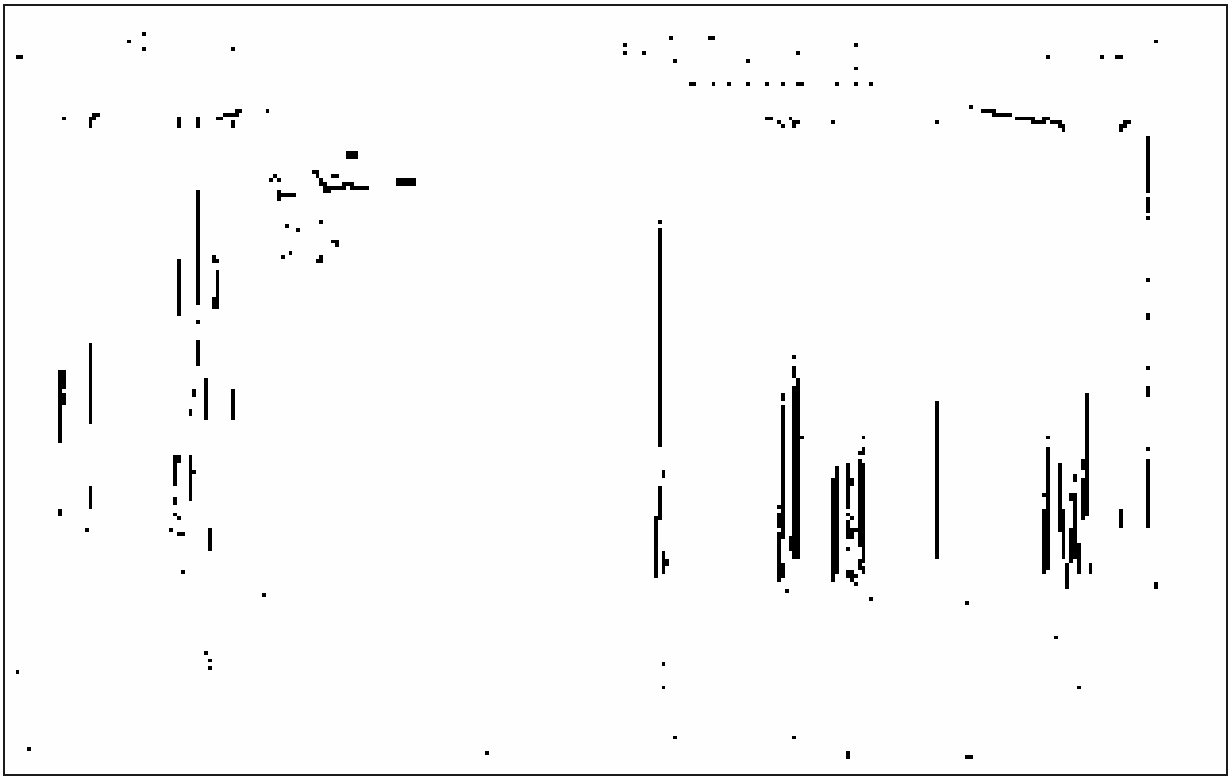
^{1}H-NMR Spectrum of Compound **22** (250 MHz, $CDCl_3$)



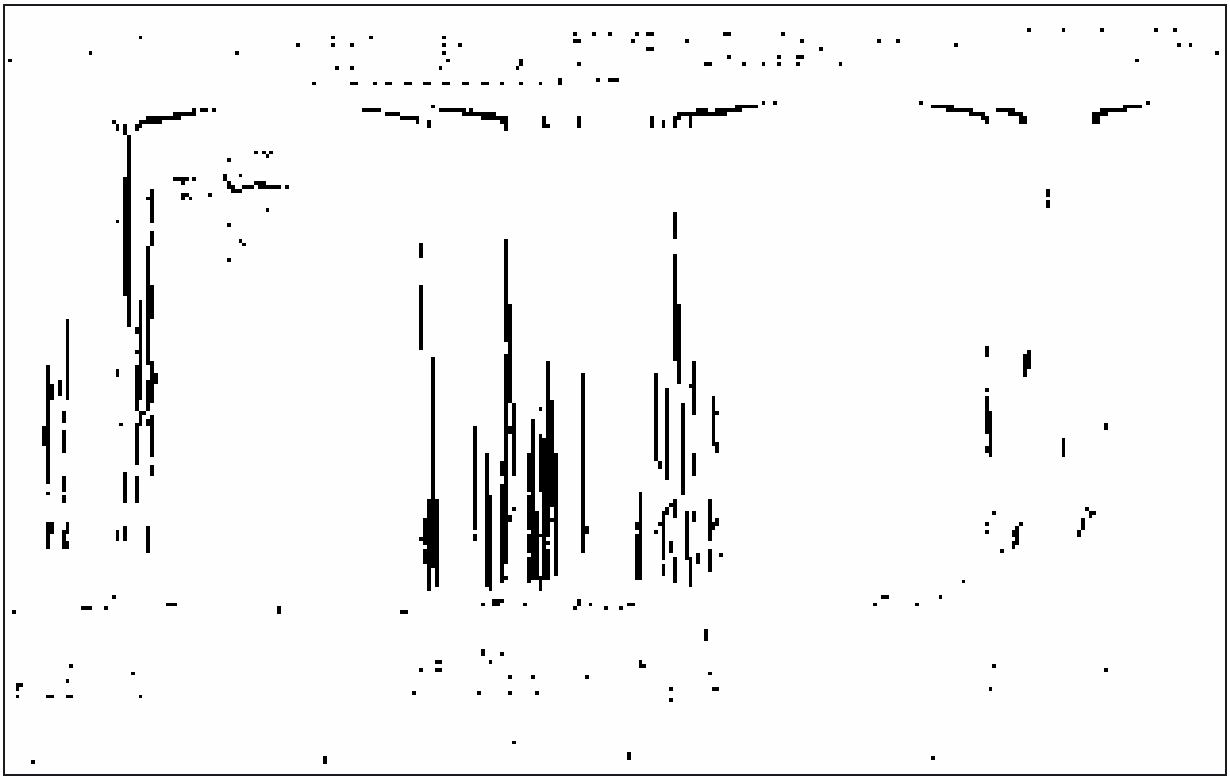
^{1}H-NMR Spectrum of Compound **23** (600 MHz, $CDCl_3$)



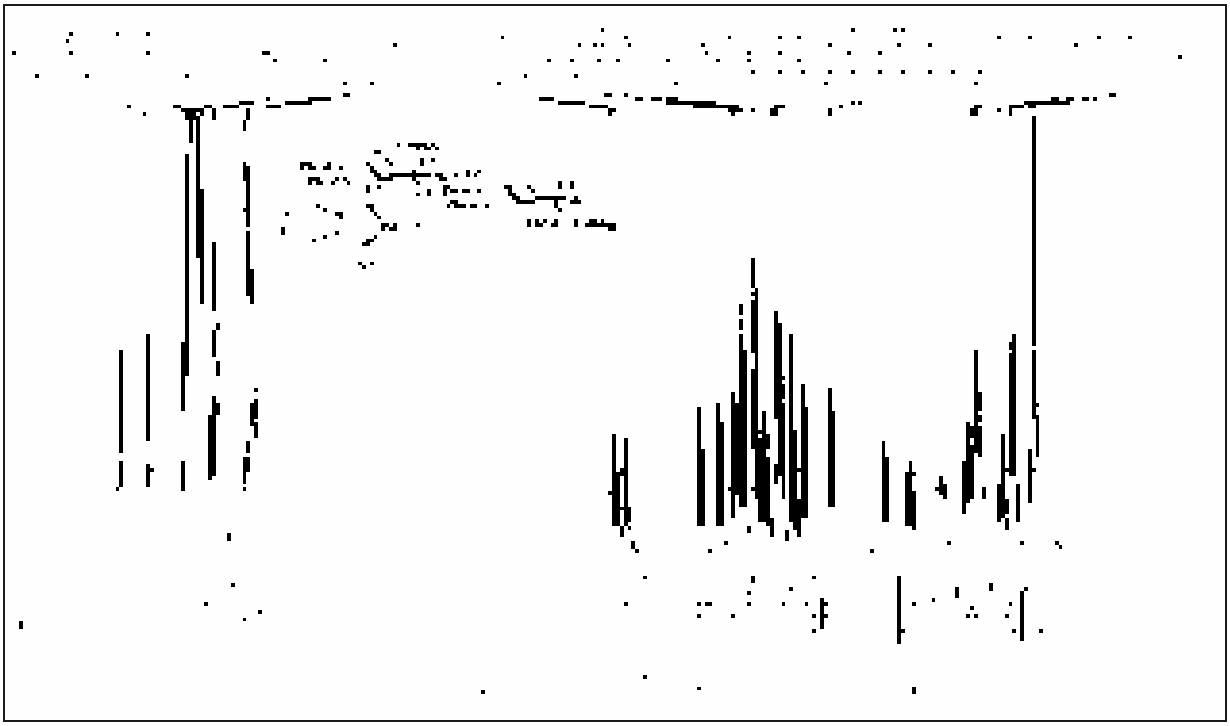
^{1}H-NMR Spectrum of Compound **24** (250 MHz, $CDCl_3$)



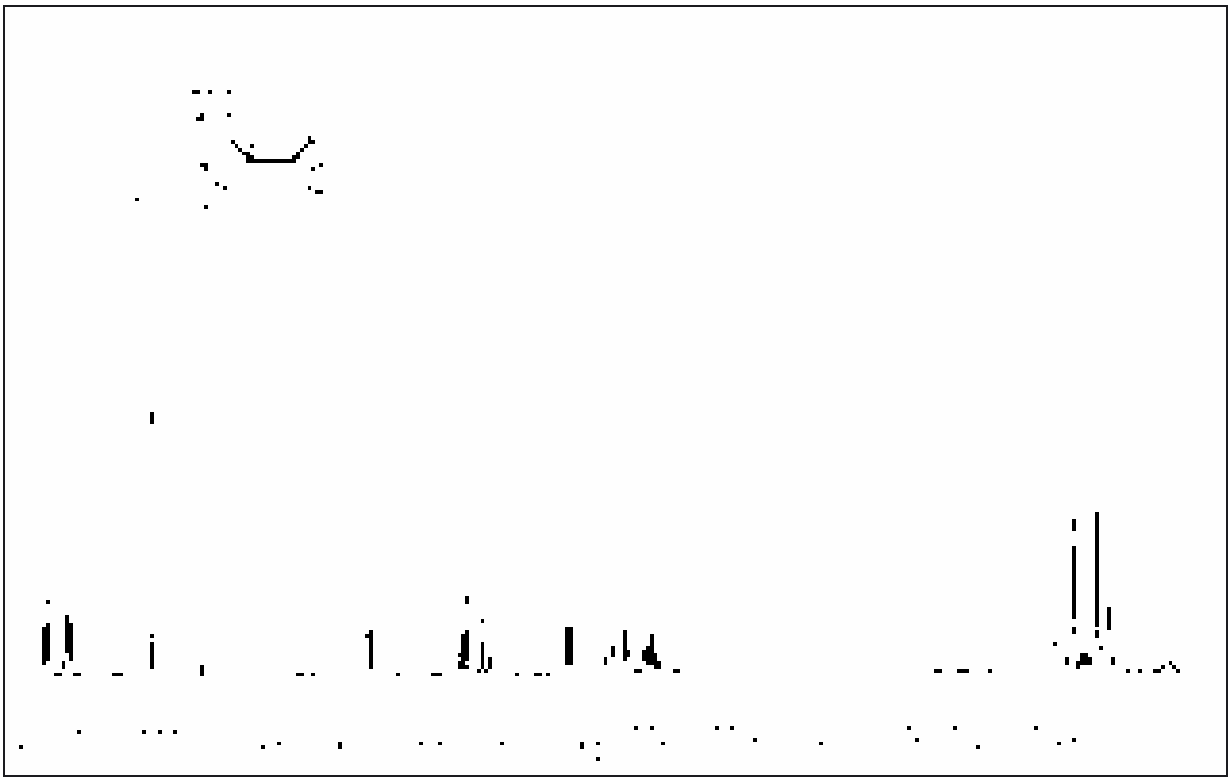
^{1}H-NMR Spectrum of Compound **25** (600 MHz, $CDCl_3$)



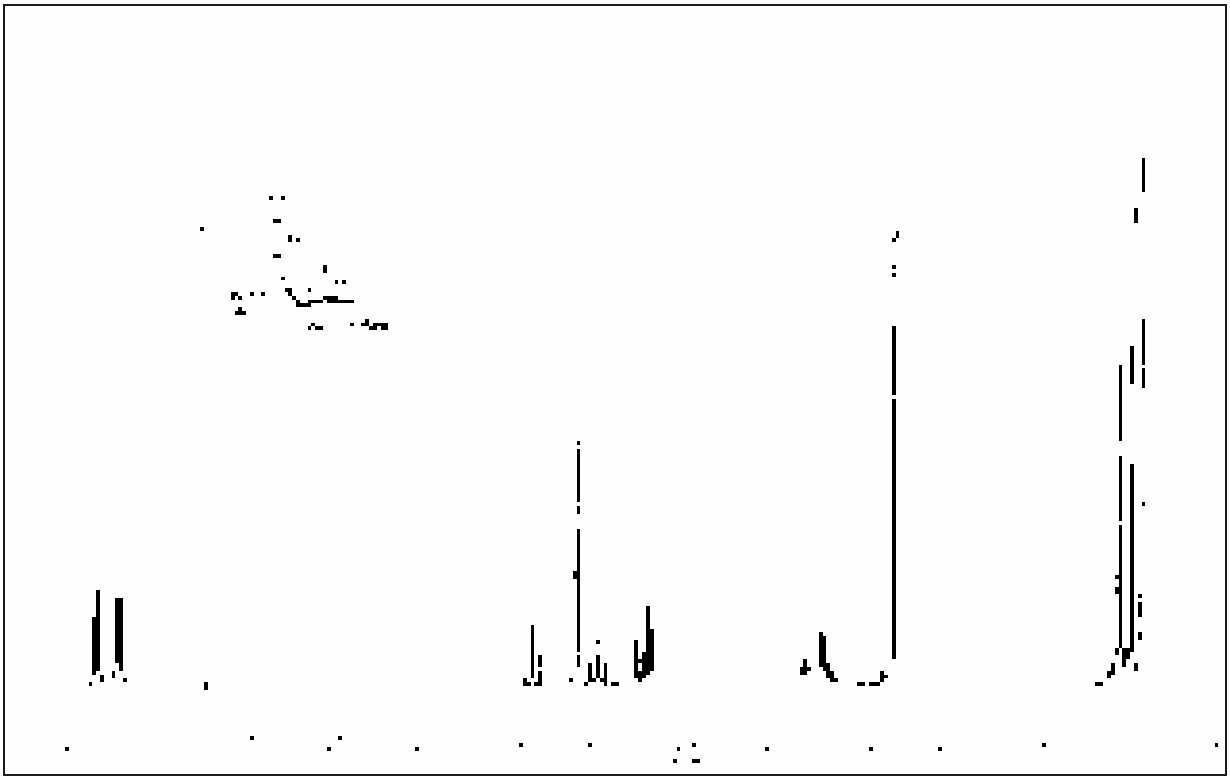
^{1}H-NMR Spectrum of Compound **26** (600 MHz, $CDCl_3$)



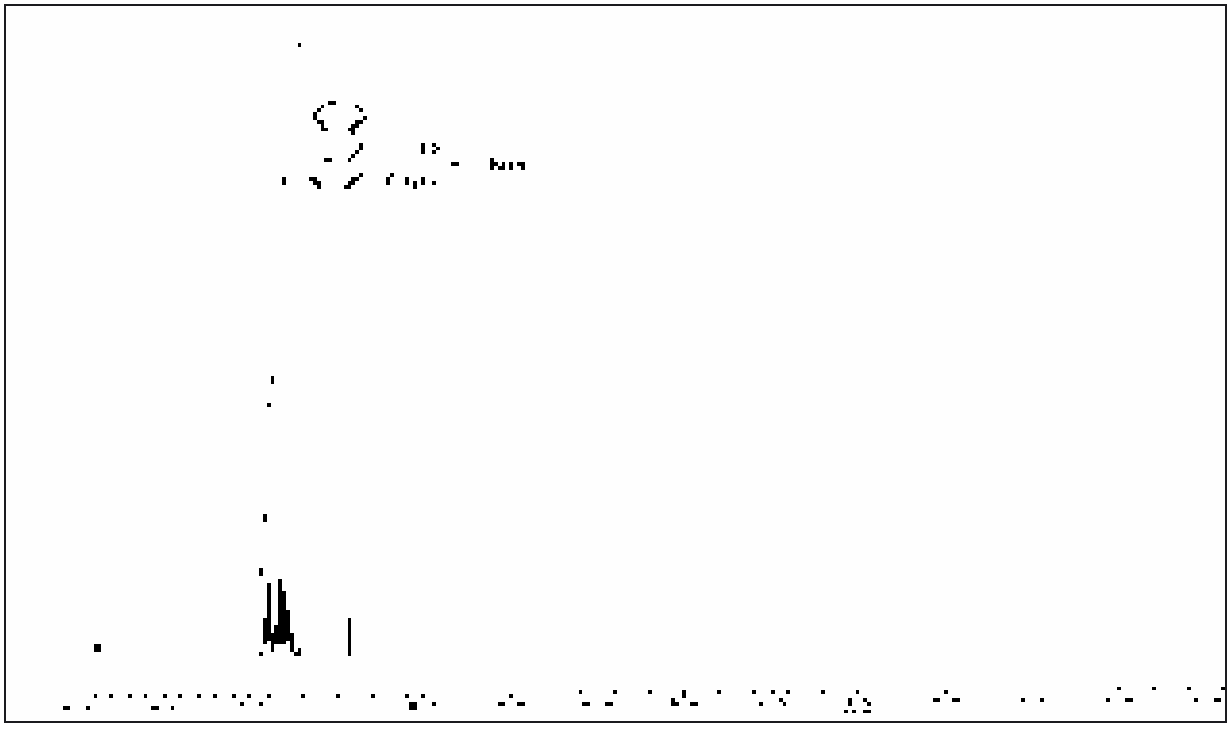
^{1}H-NMR Spectrum of Compound **27η** (600 MHz, $CDCl_3$)



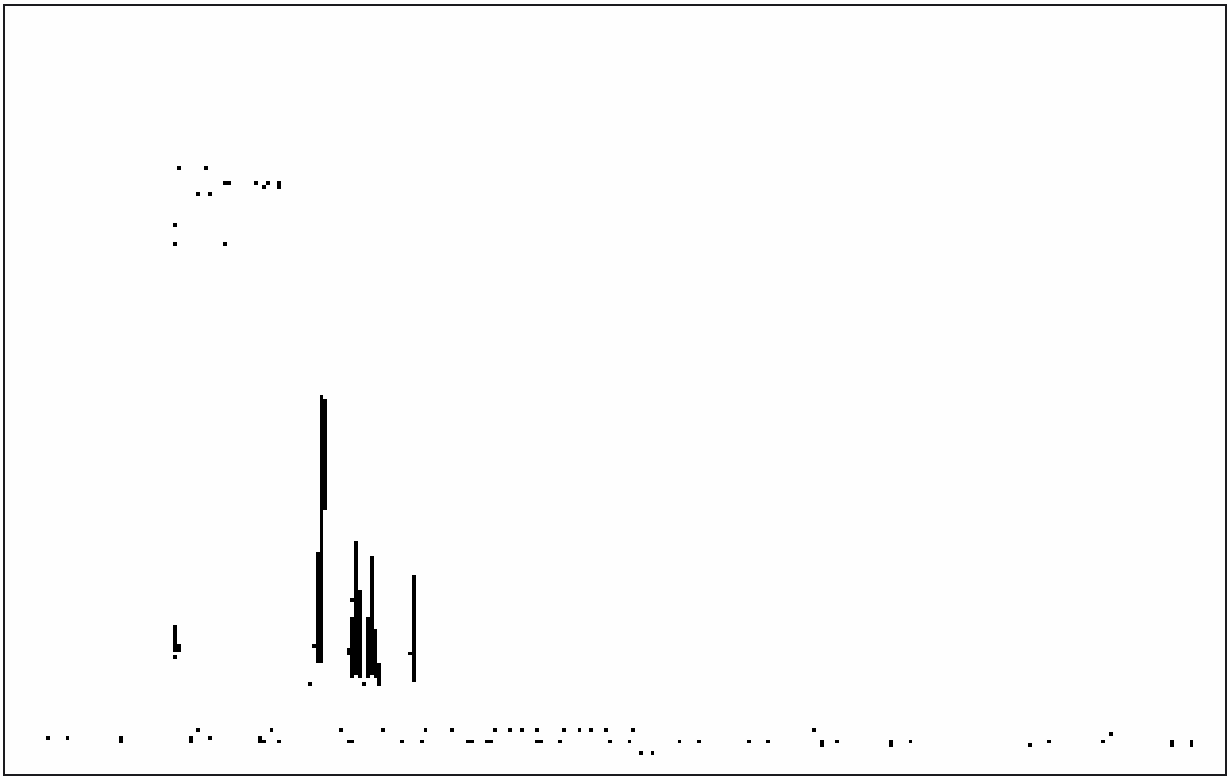
^{1}H-NMR Spectrum of Compound **36** (250 MHz, $CDCl_3$)



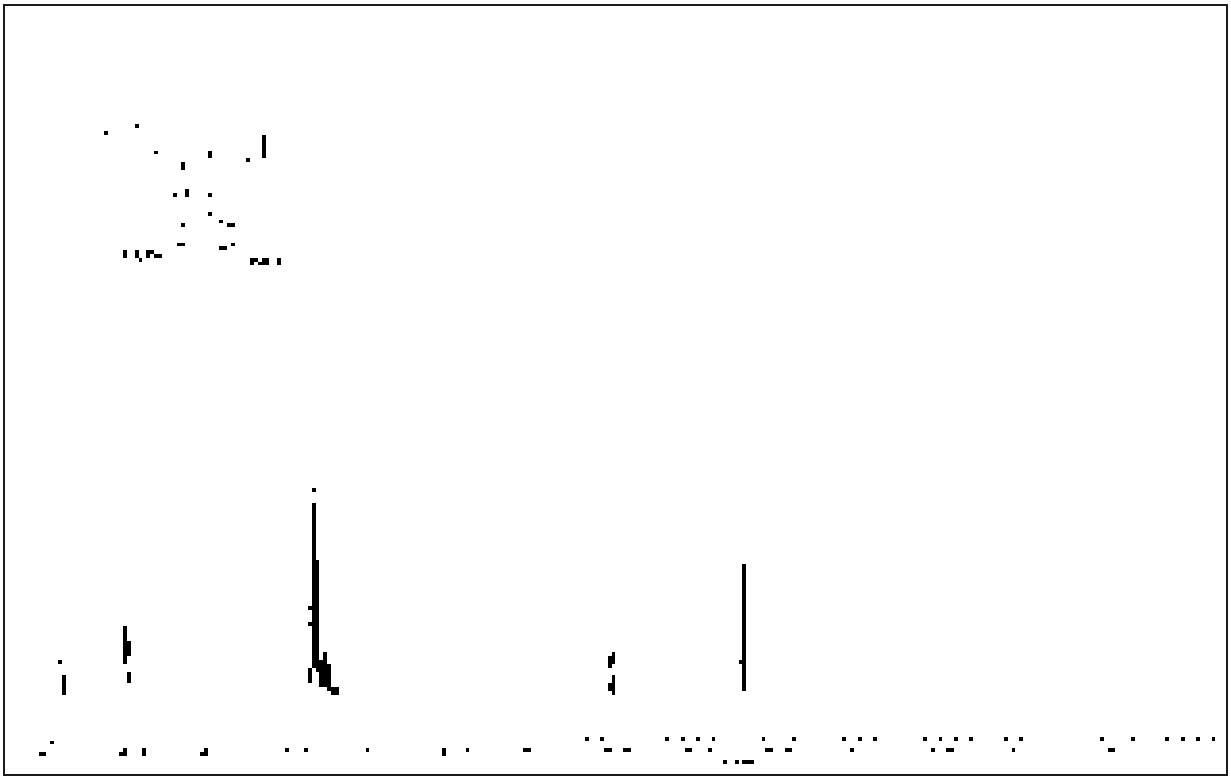
^{1}H-NMR Spectrum of Compound **38** (250 MHz, $CDCl_3$)



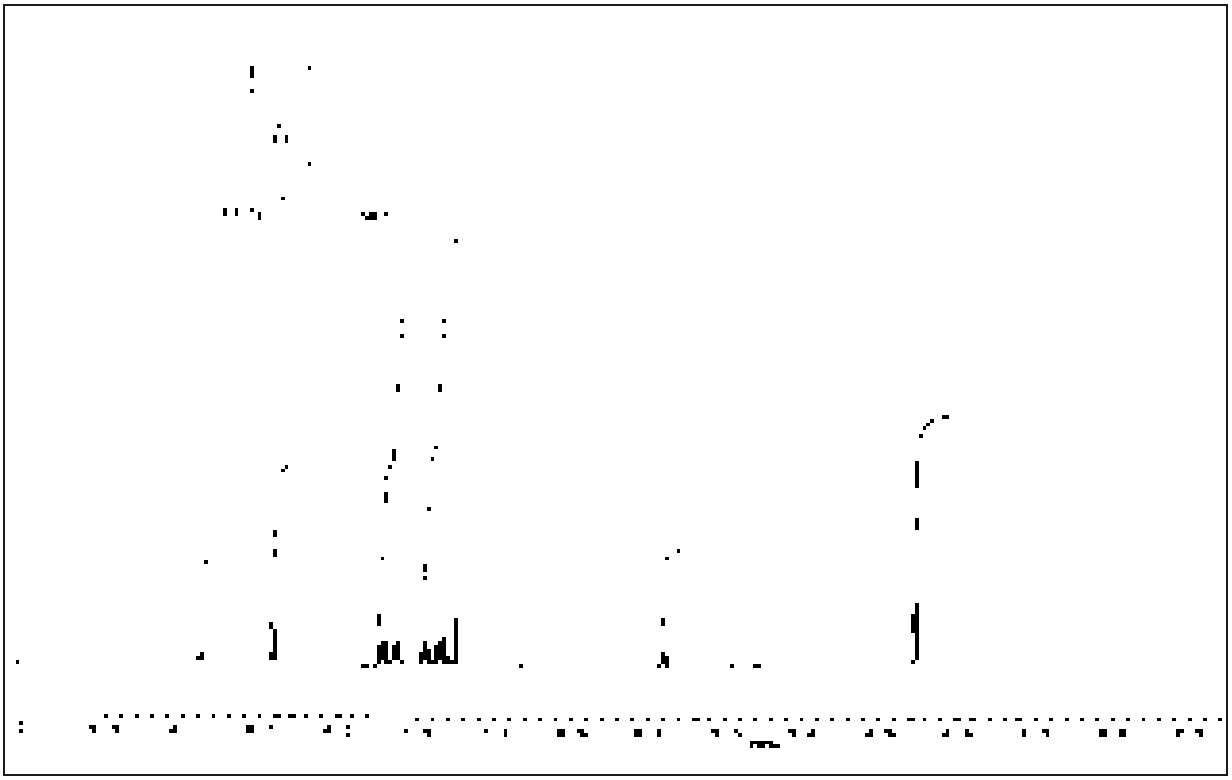
^{1}H-NMR Spectrum of Compound **41** (250 MHz, $CDCl_3$)



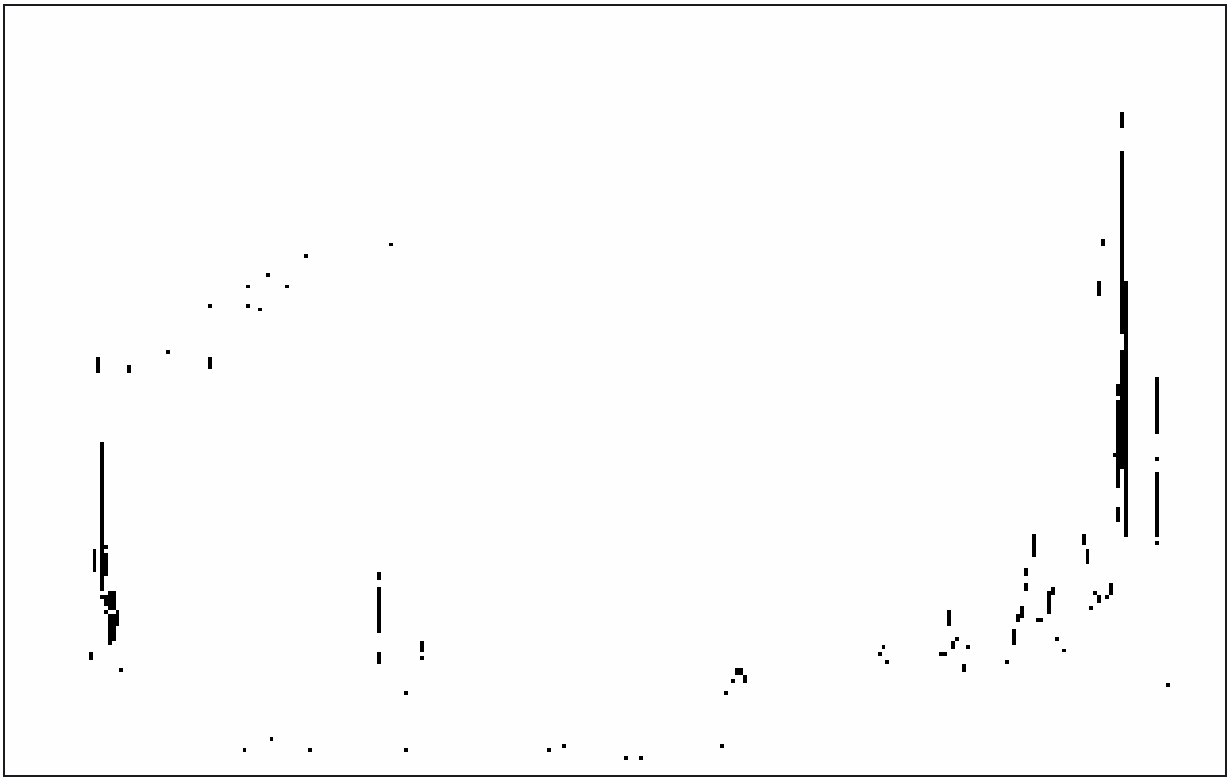
^{1}H-NMR Spectrum of Compound **42** (250 MHz, $CDCl_3$)



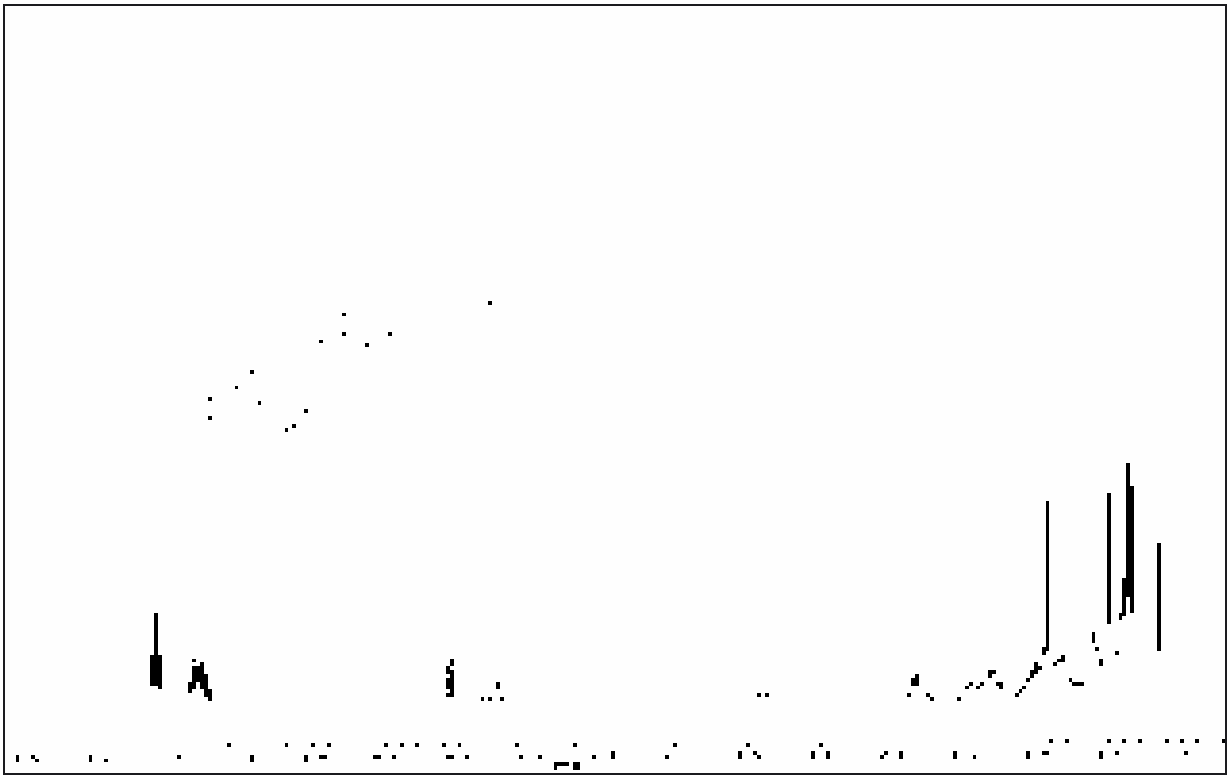
^{1}H-NMR Spectrum of Compound **43** (250 MHz, $CDCl_3$)



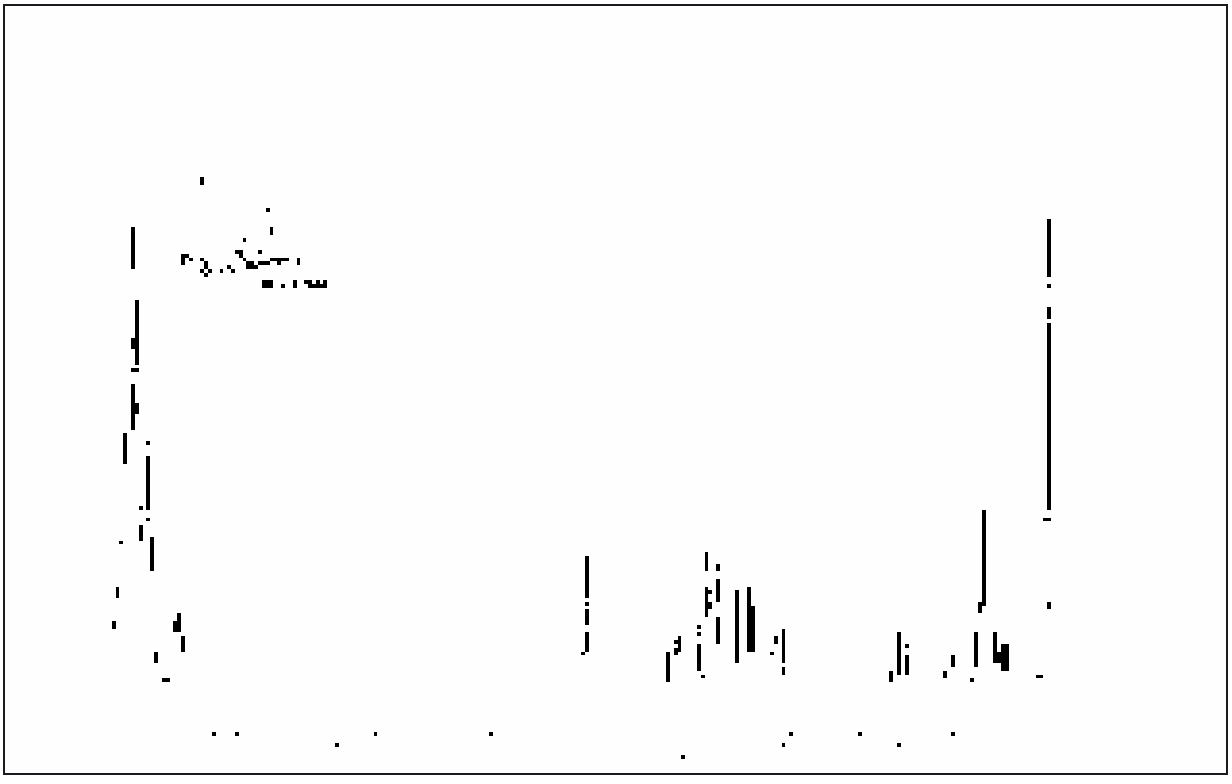
^{1}H-NMR Spectrum of Compound **44** (250 MHz, $CDCl_3$)



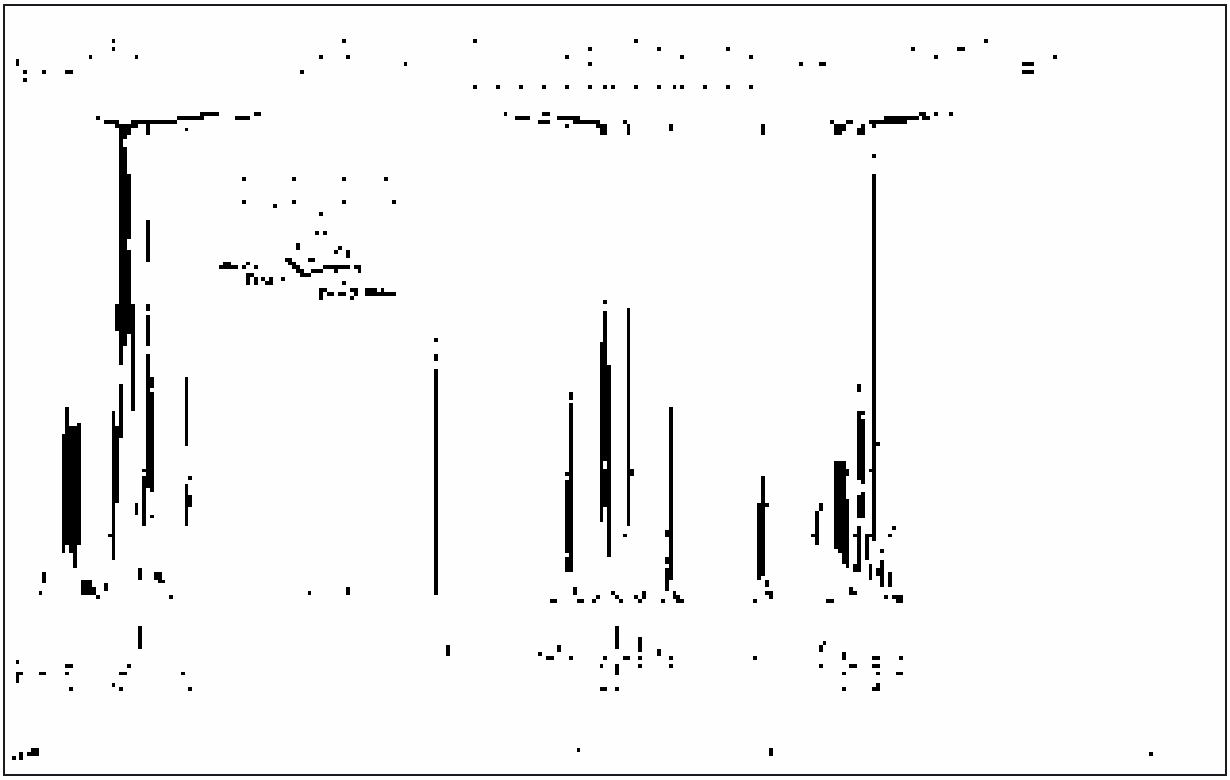
^{1}H-NMR Spectrum of Compound **48** (250 MHz, $CDCl_3$)



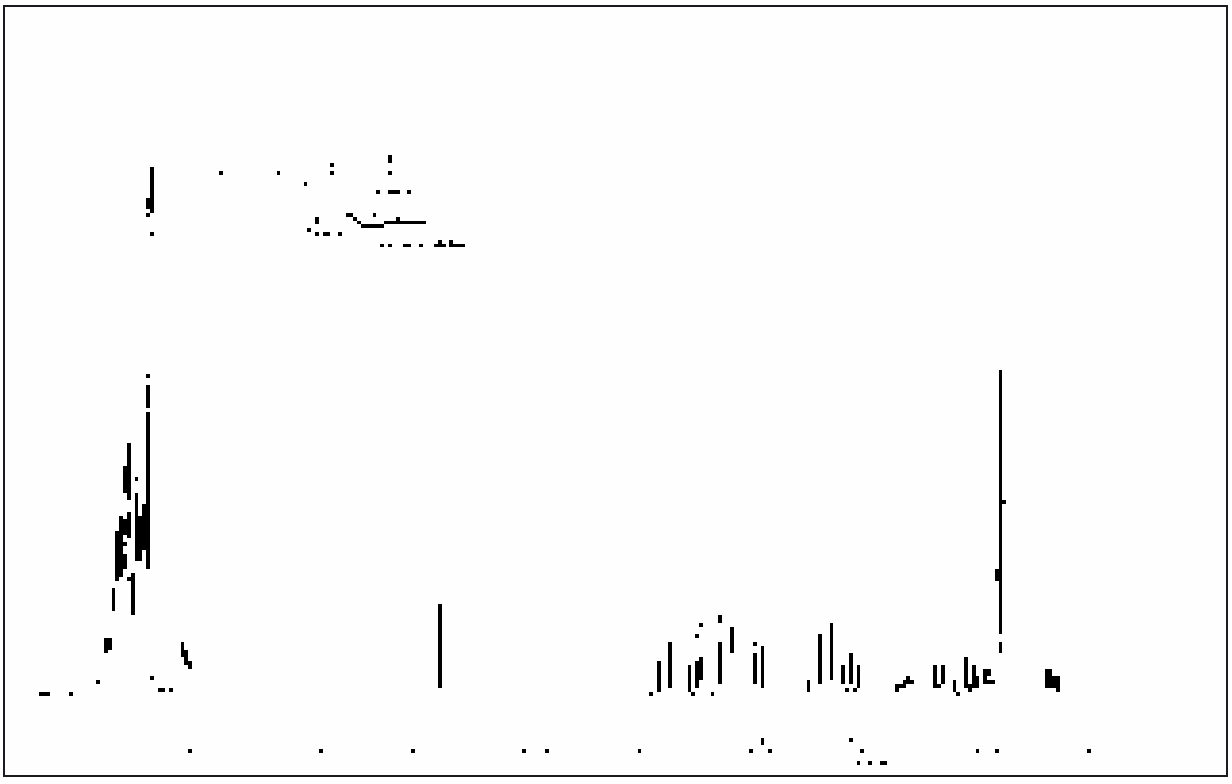
^{1}H-NMR Spectrum of Compound **49** (250 MHz, $CDCl_3$)



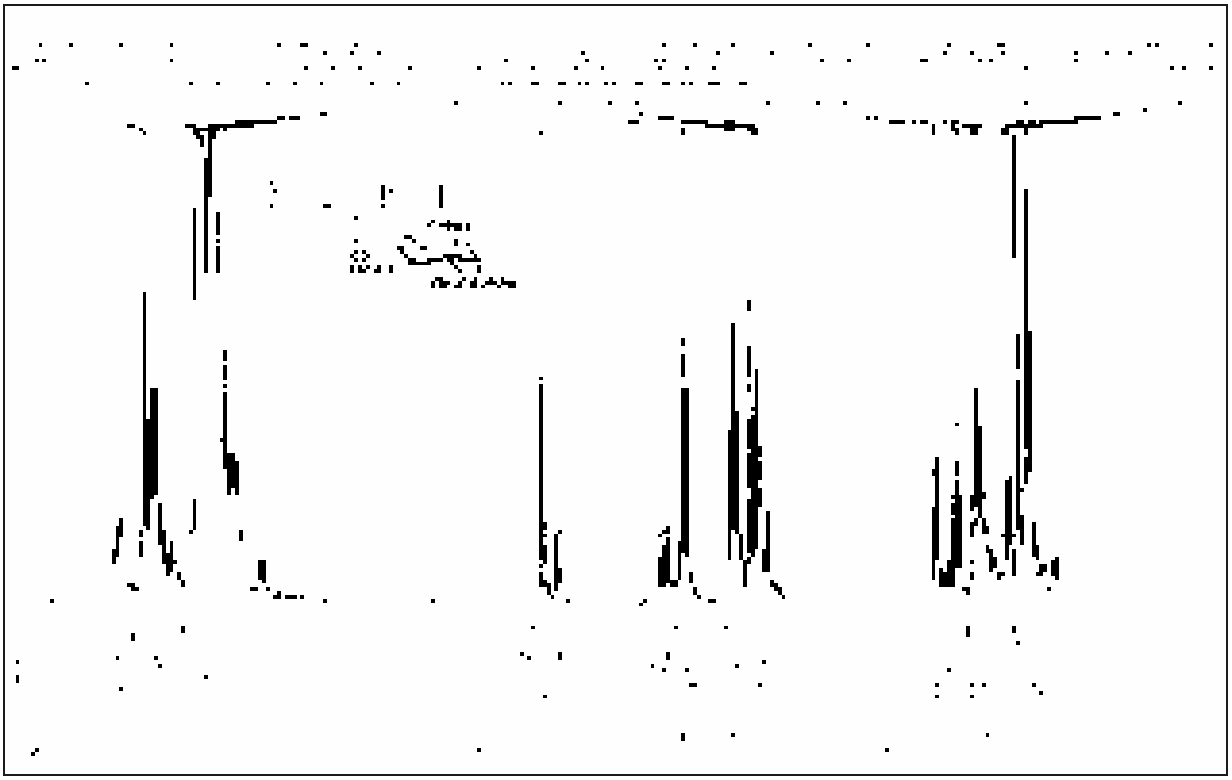
^{1}H-NMR Spectrum of Compound **50** (250 MHz, $CDCl_3$)



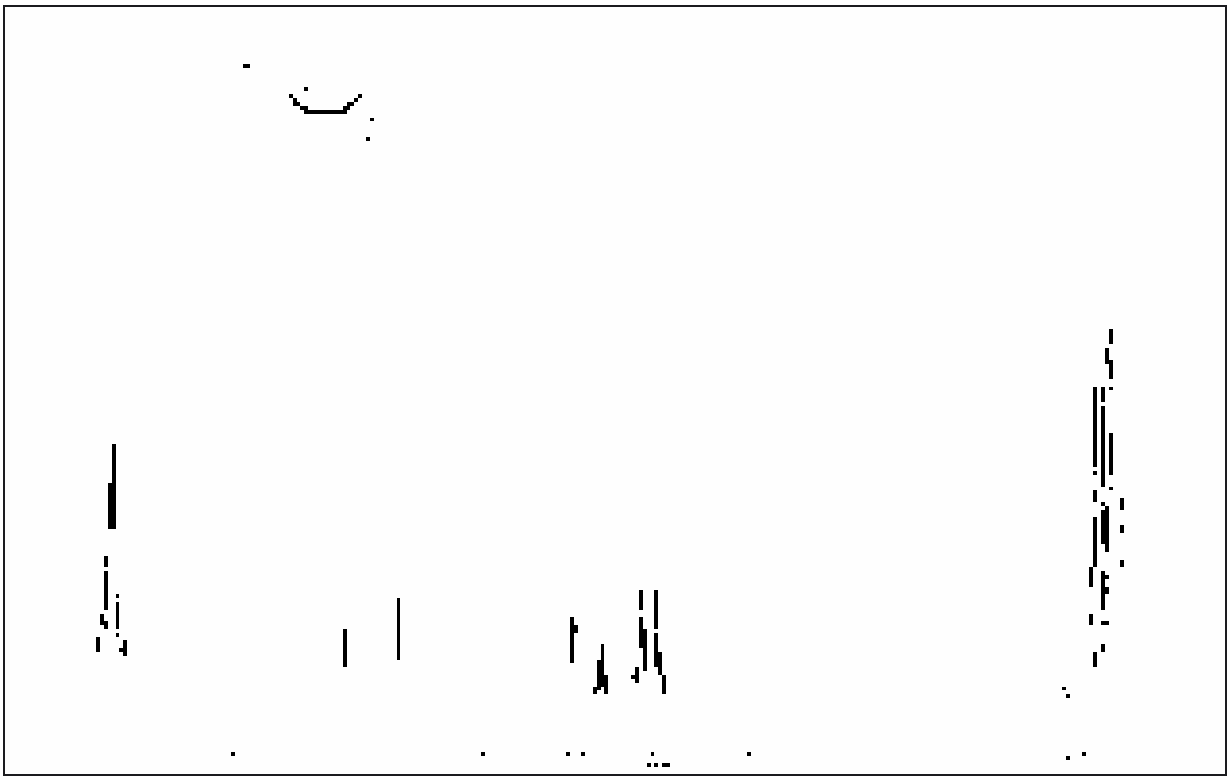
^{1}H-NMR Spectrum of Compound **51** (600 MHz, $CDCl_3$)



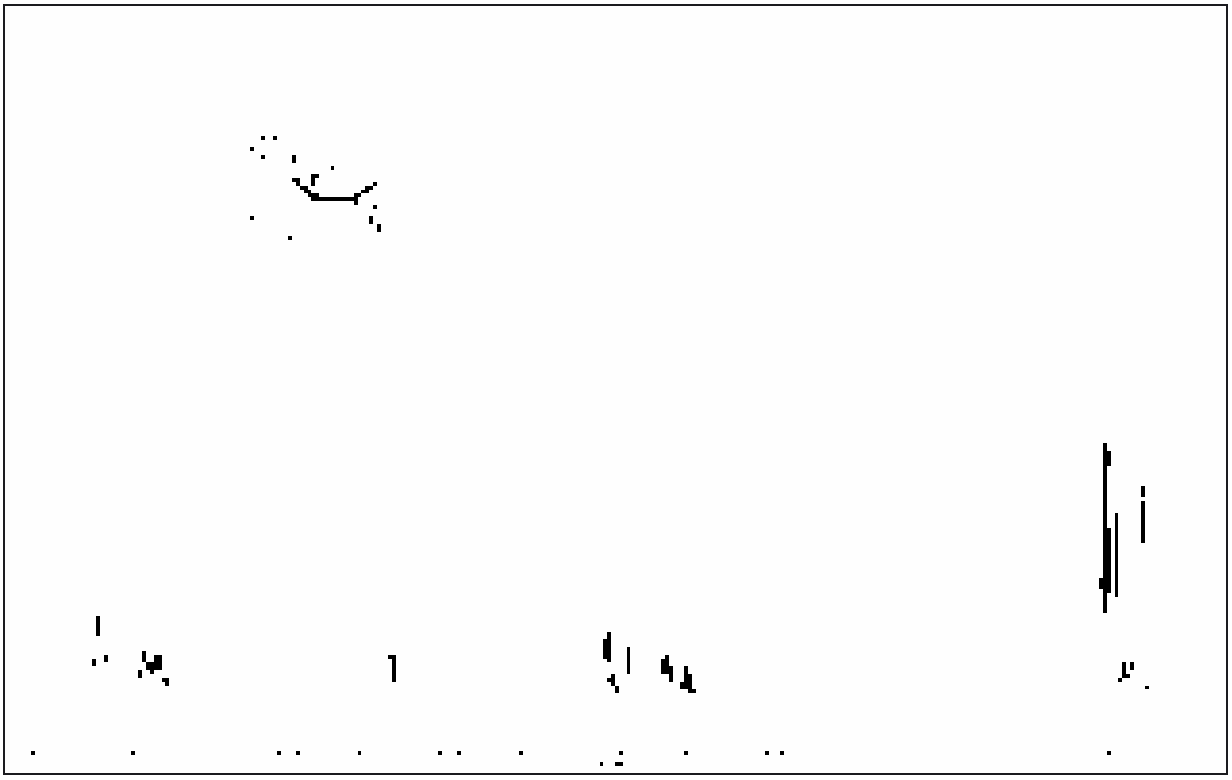
^{1}H-NMR Spectrum of Compound **52** (250 MHz, $CDCl_3$)



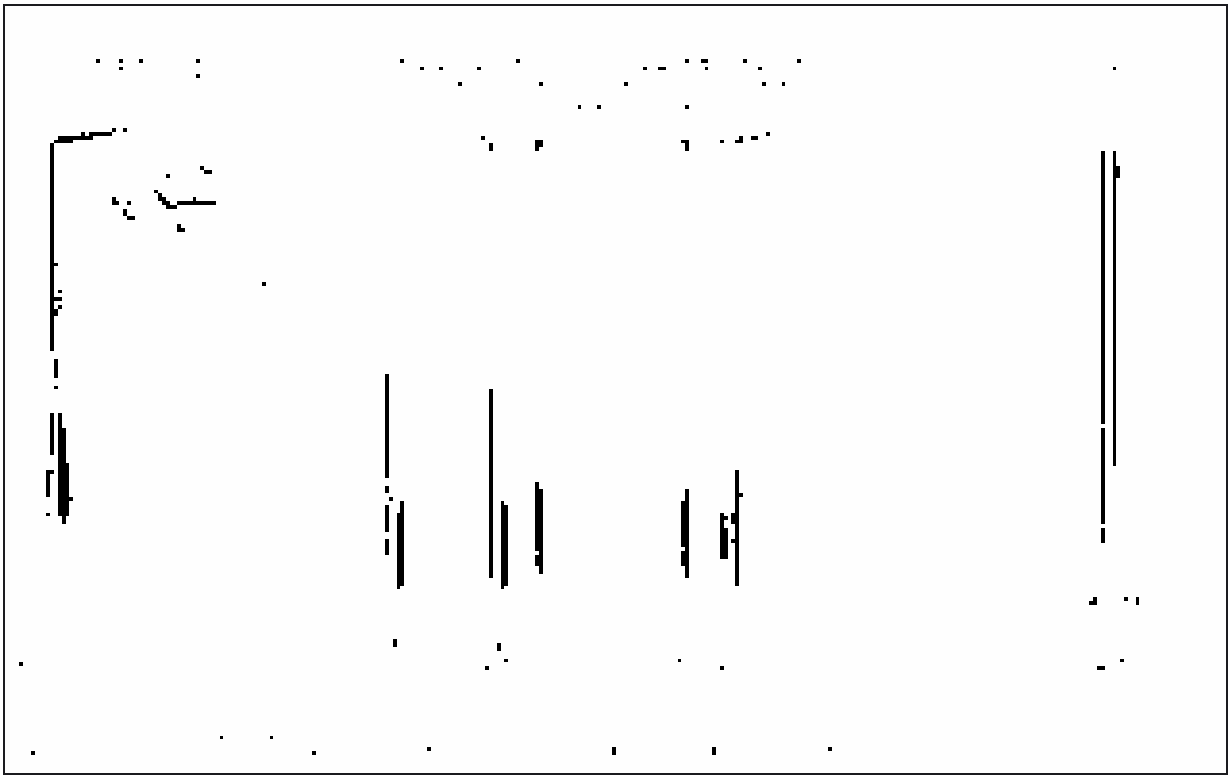
^{1}H-NMR Spectrum of Compound **53** (600 MHz, $CDCl_3$)



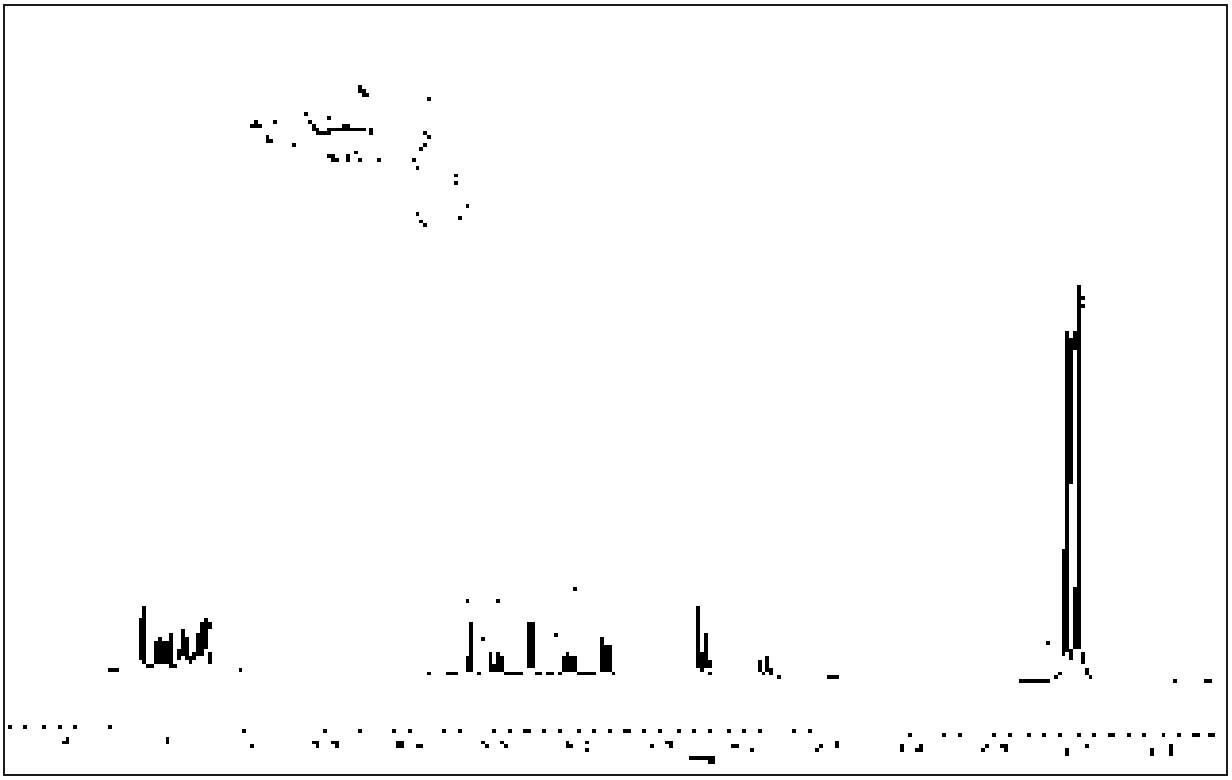
^{1}H-NMR Spectrum of Compound **54** (250 MHz, $CDCl_3$)



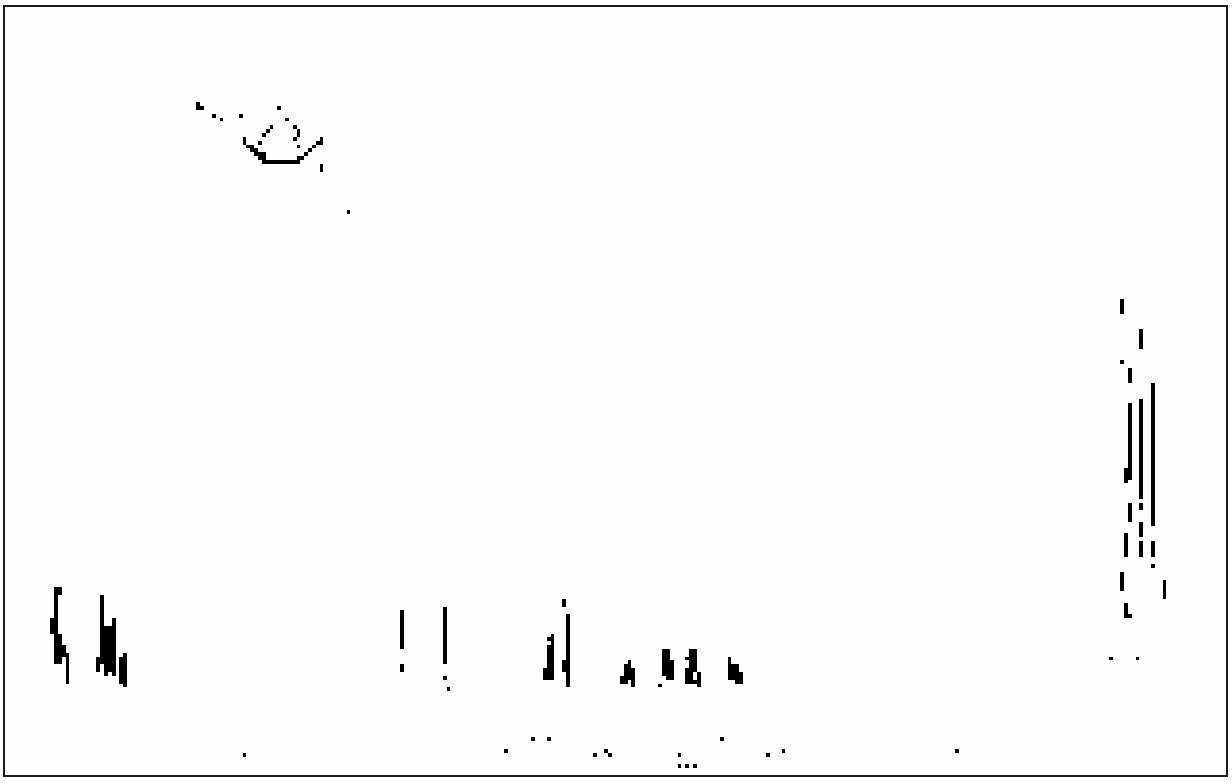
^{1}H-NMR Spectrum of Compound **55** (250 MHz, $CDCl_3$)



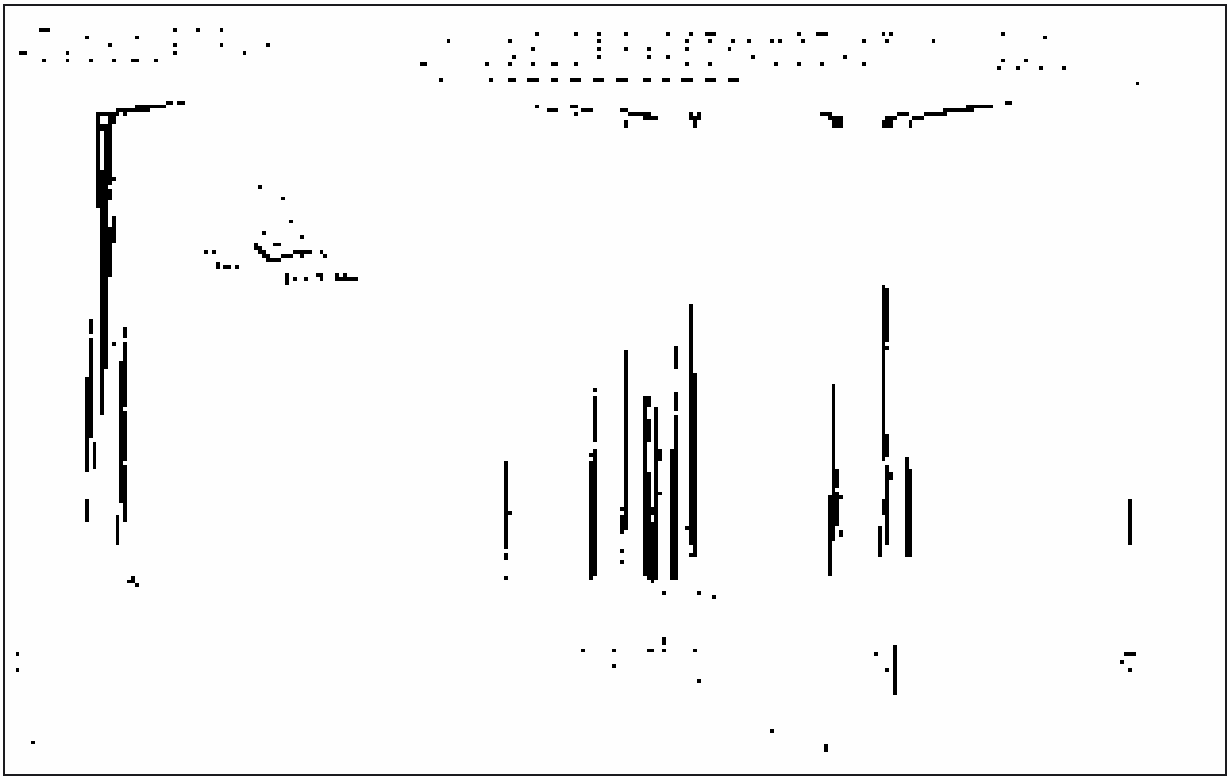
^{1}H-NMR Spectrum of Compound **57** (600 MHz, $CDCl_3$)



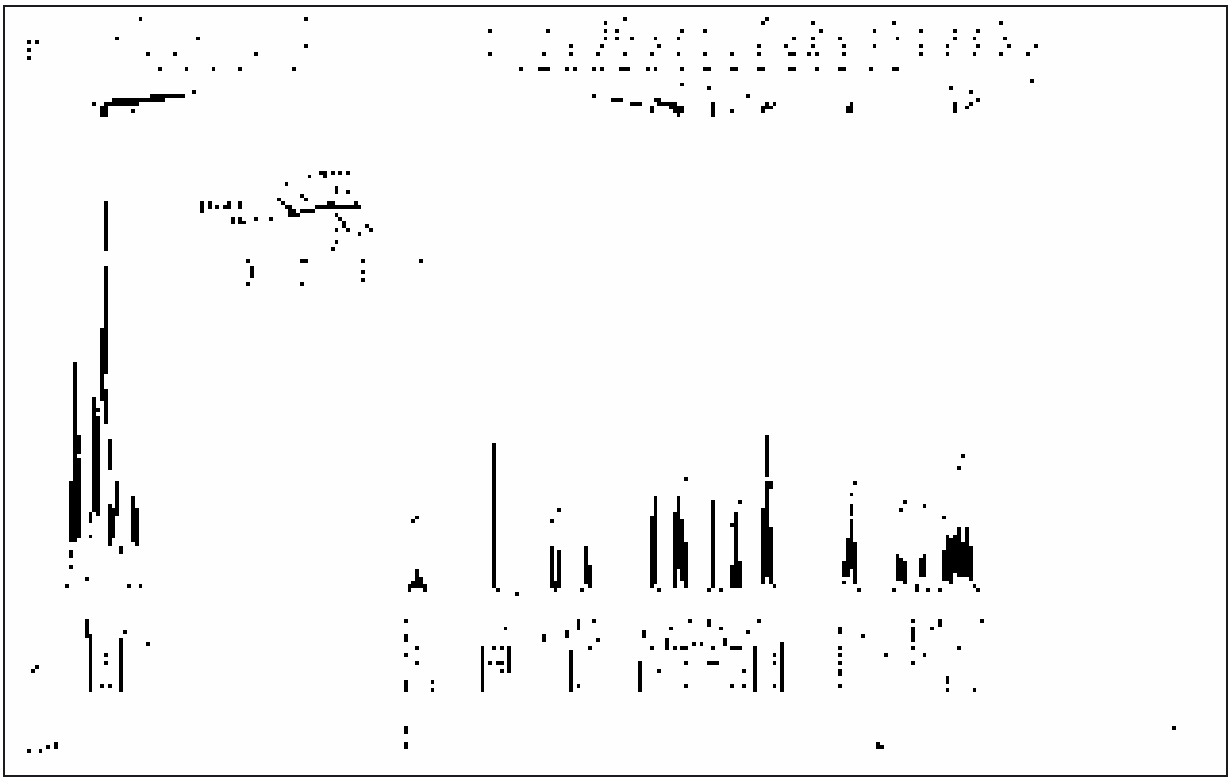
^{1}H-NMR Spectrum of Compound **58** (250 MHz, $CDCl_3$)



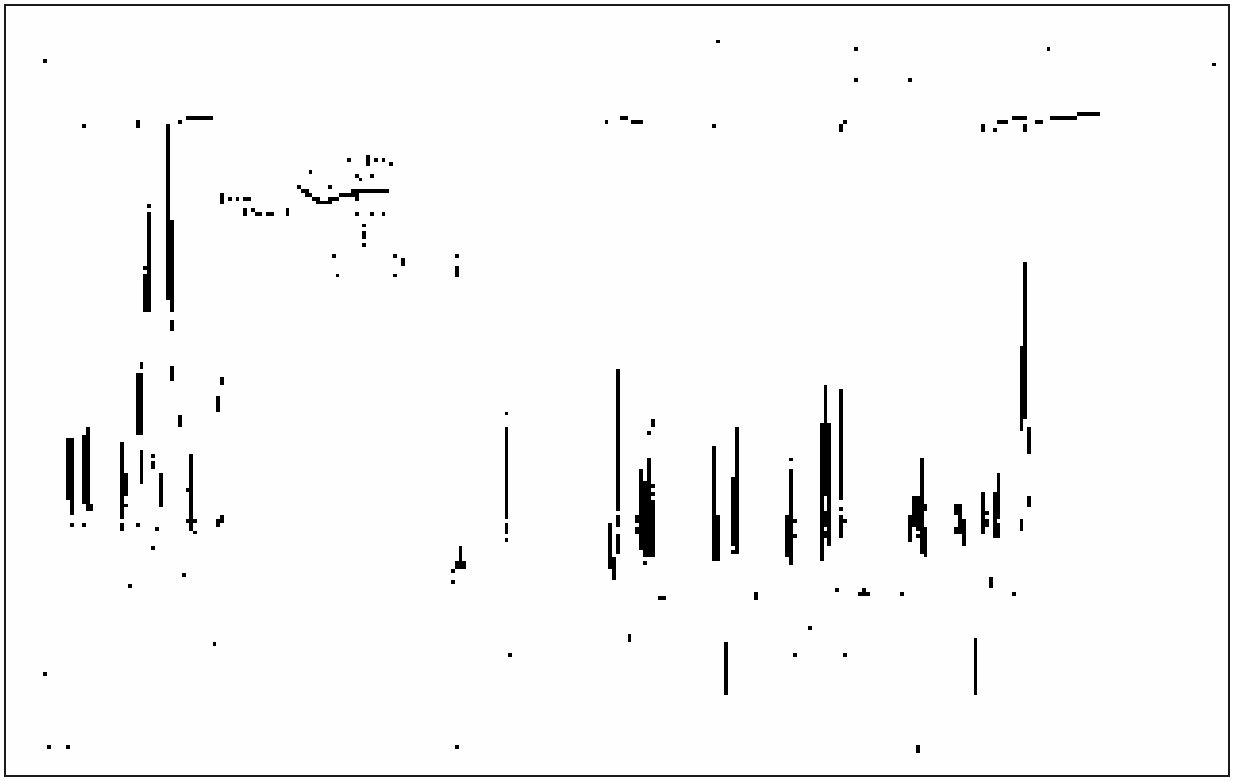
^{1}H-NMR Spectrum of Compound **60** (250 MHz, $CDCl_3$)



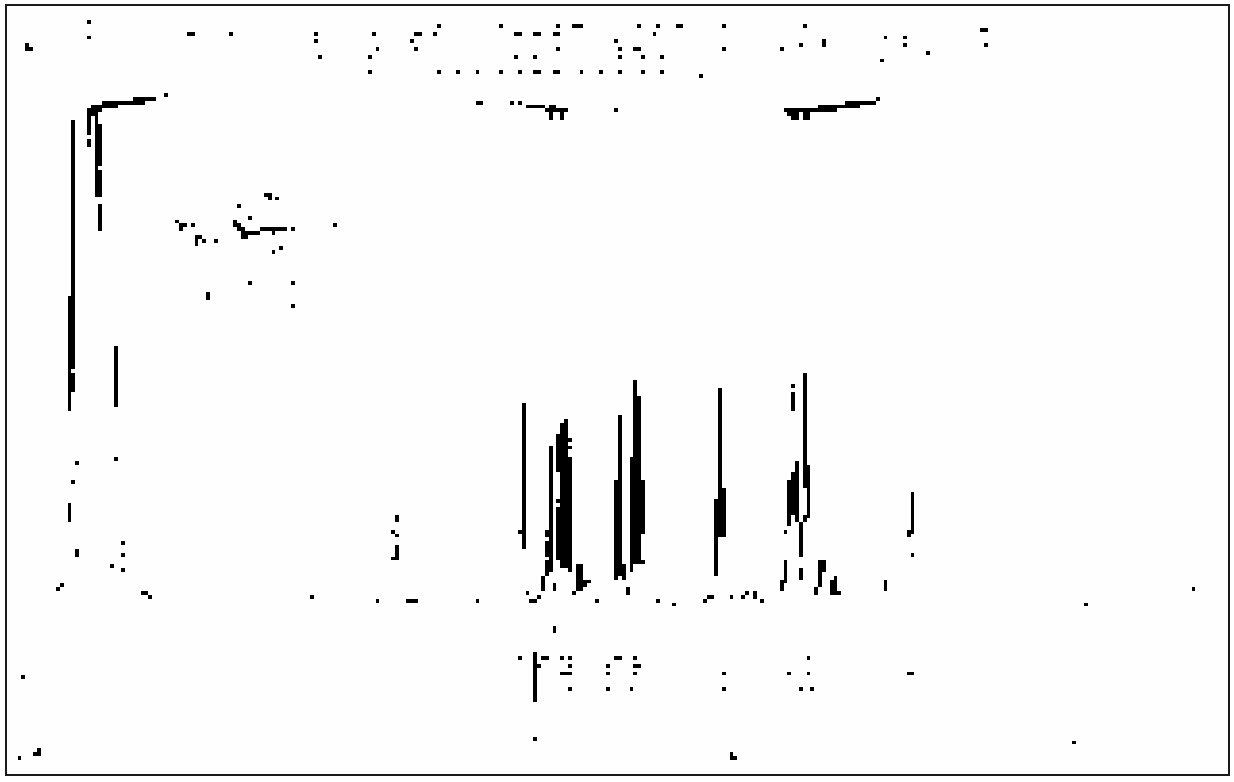
^{1}H-NMR Spectrum of Compound **62** (600 MHz, $CDCl_3$)



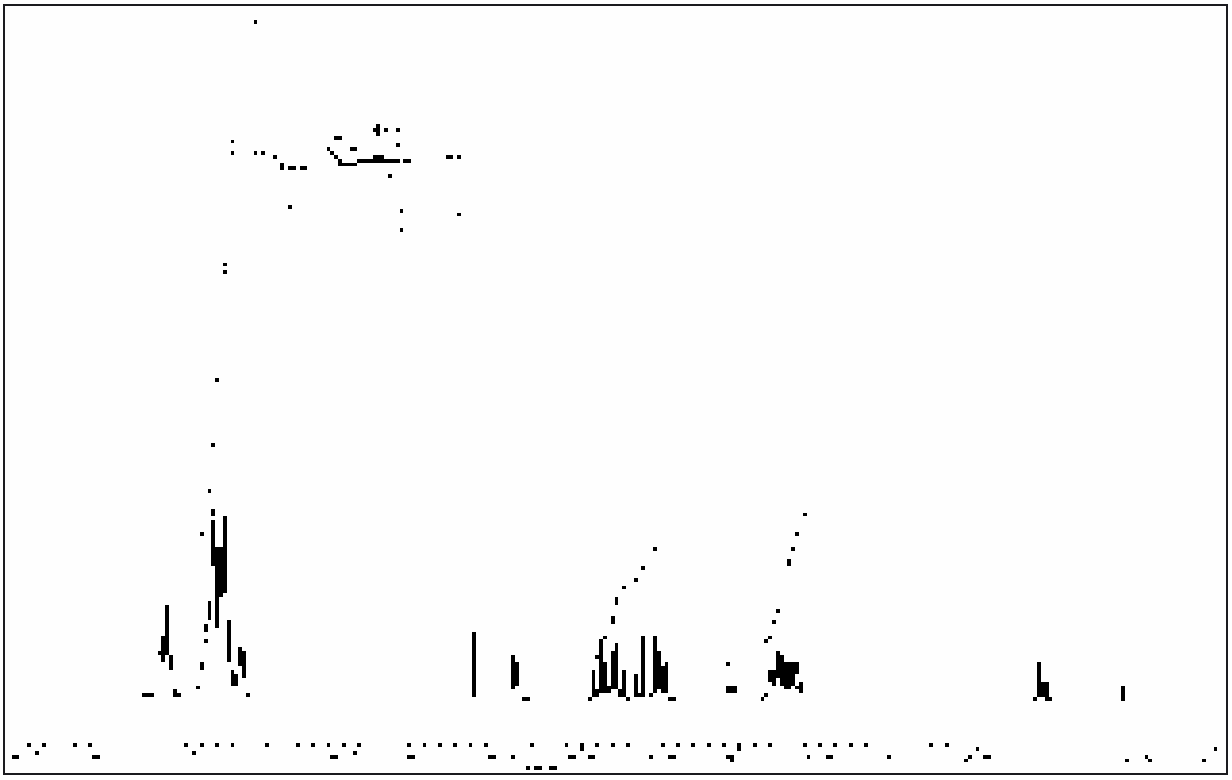
^{1}H-NMR Spectrum of Compound **63** (600 MHz, $CDCl_3$)



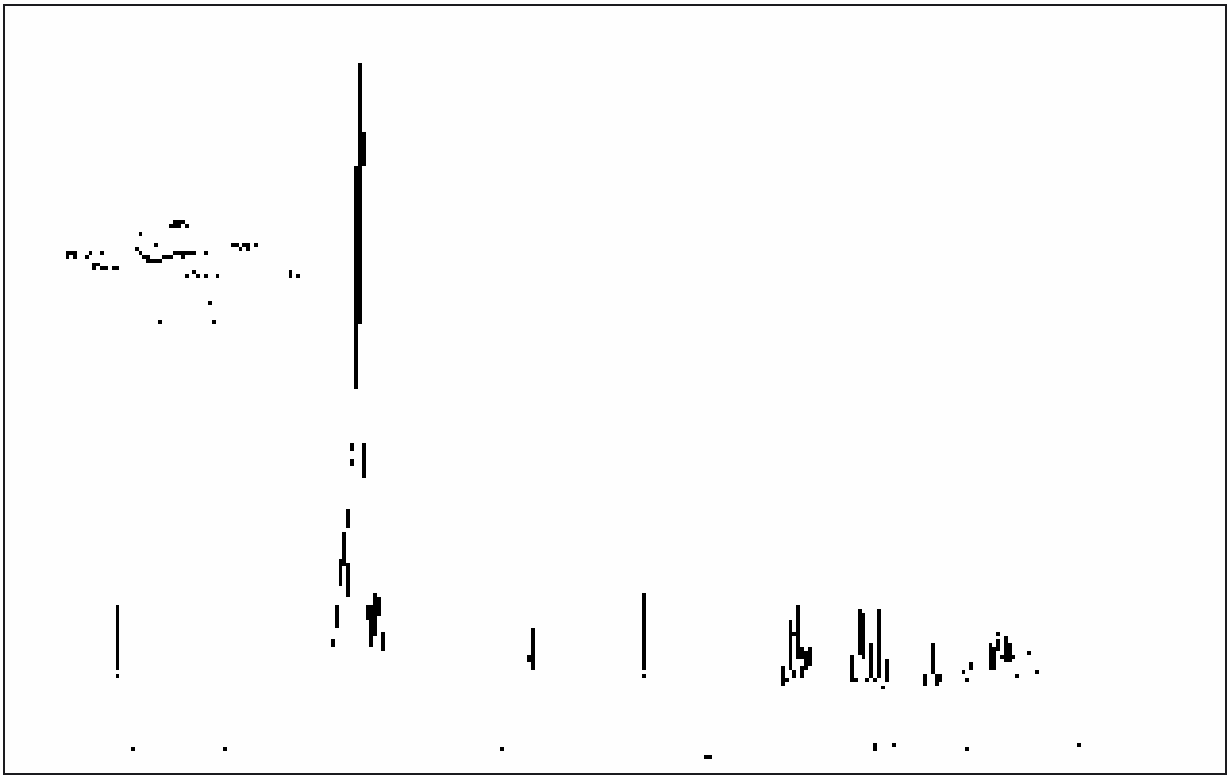
^{1}H-NMR Spectrum of Compound **64** (250 MHz, $CDCl_3$)



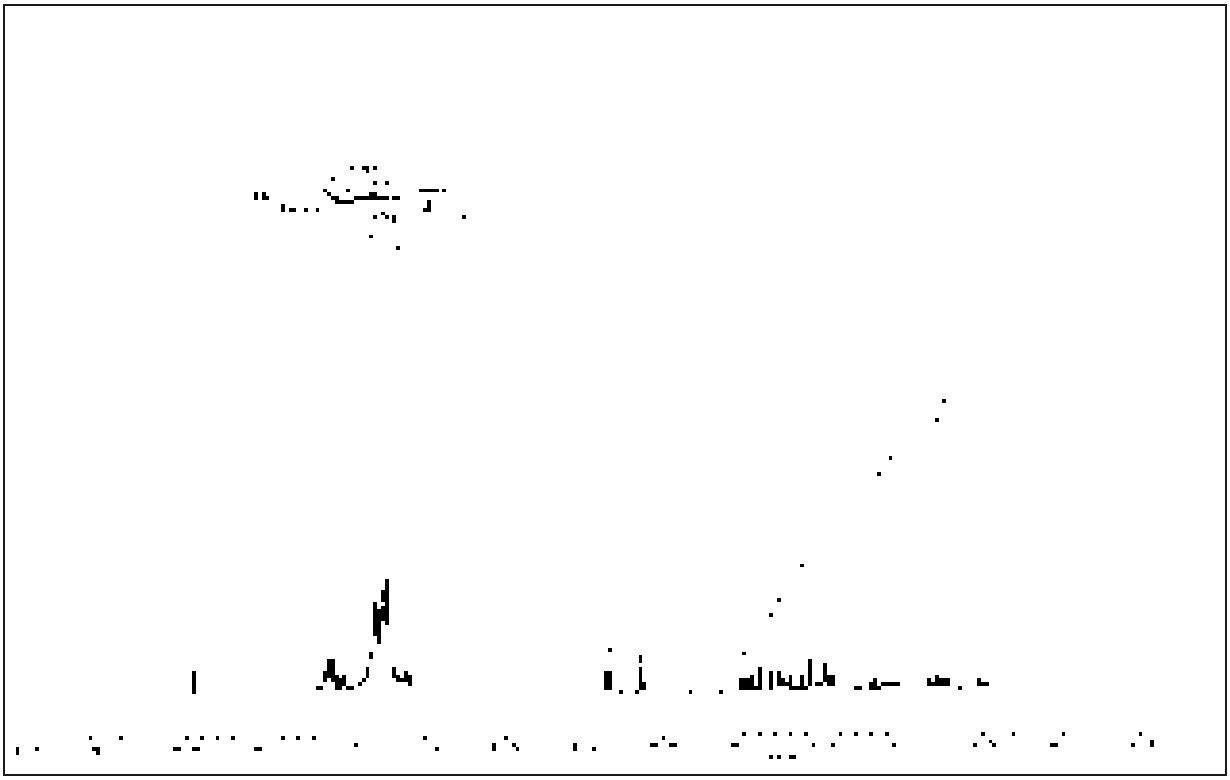
^{1}H-NMR Spectrum of Compound **65** (600 MHz, $CDCl_3$)



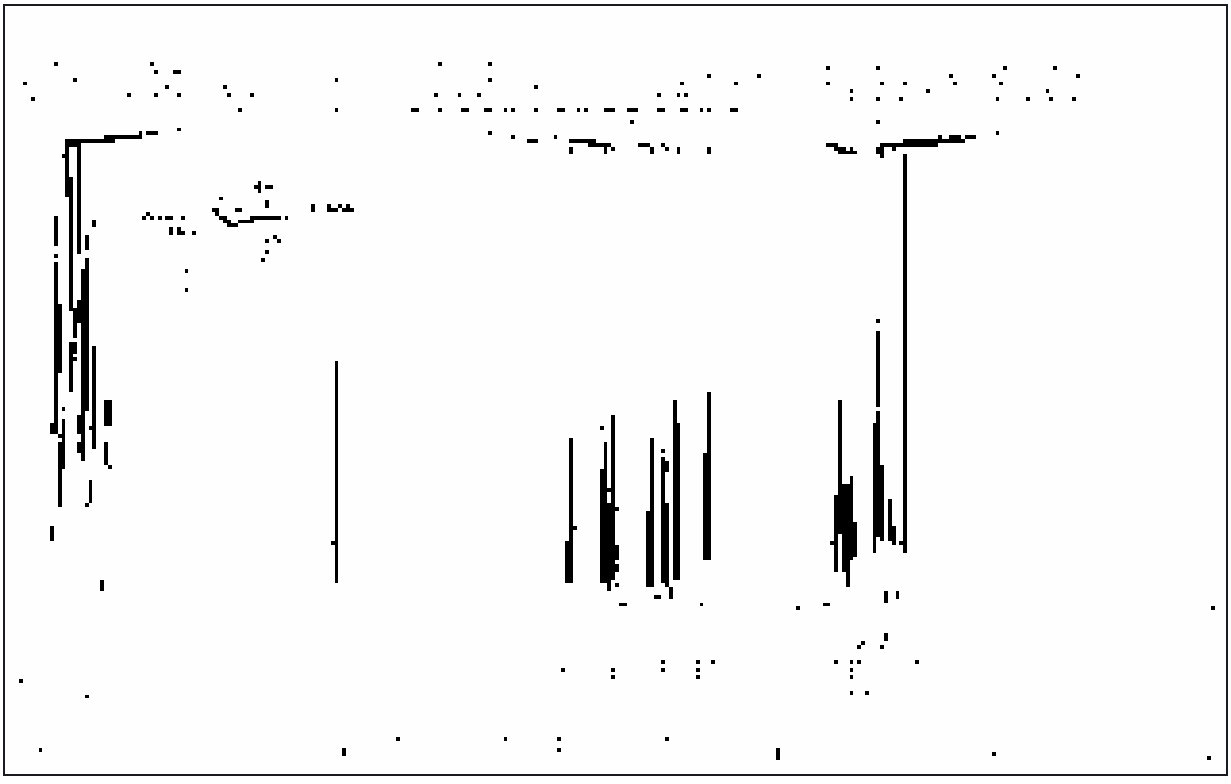
^{1}H-NMR Spectrum of Compound **66** (250 MHz, $CDCl_3$)



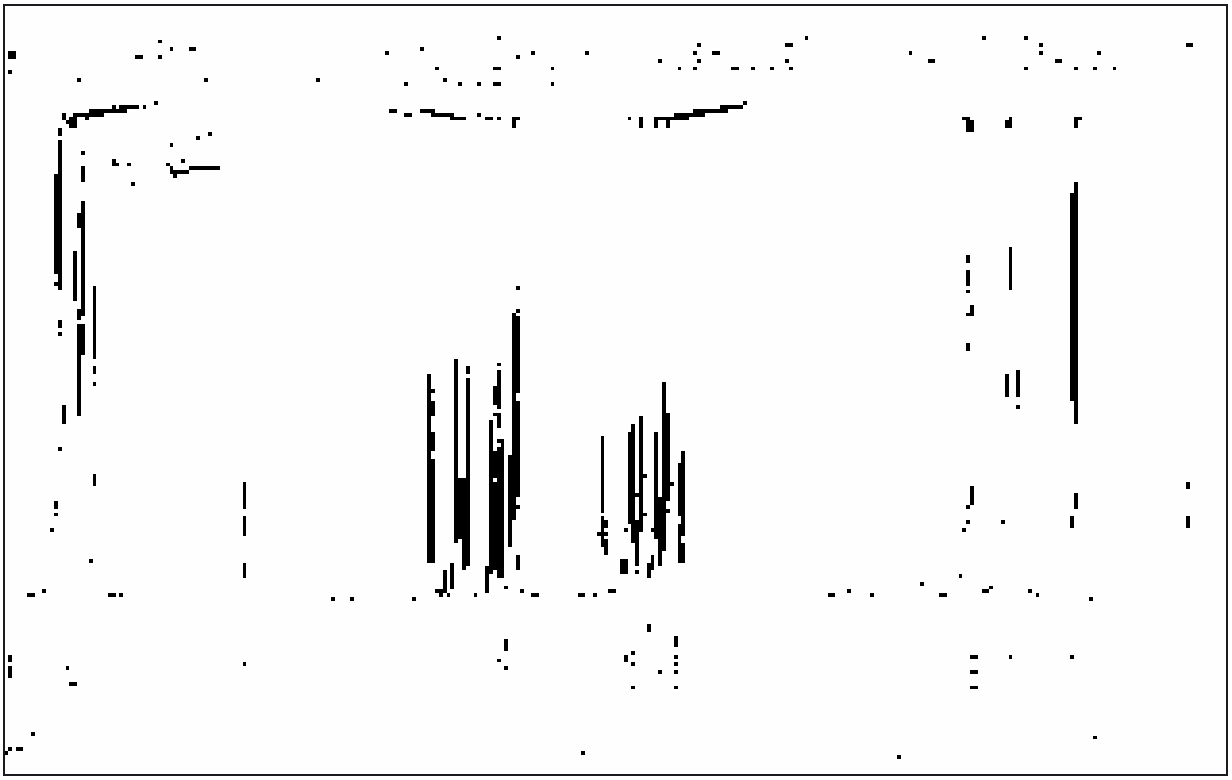
^{1}H-NMR Spectrum of Compound **67** (250 MHz, $CDCl_3$)



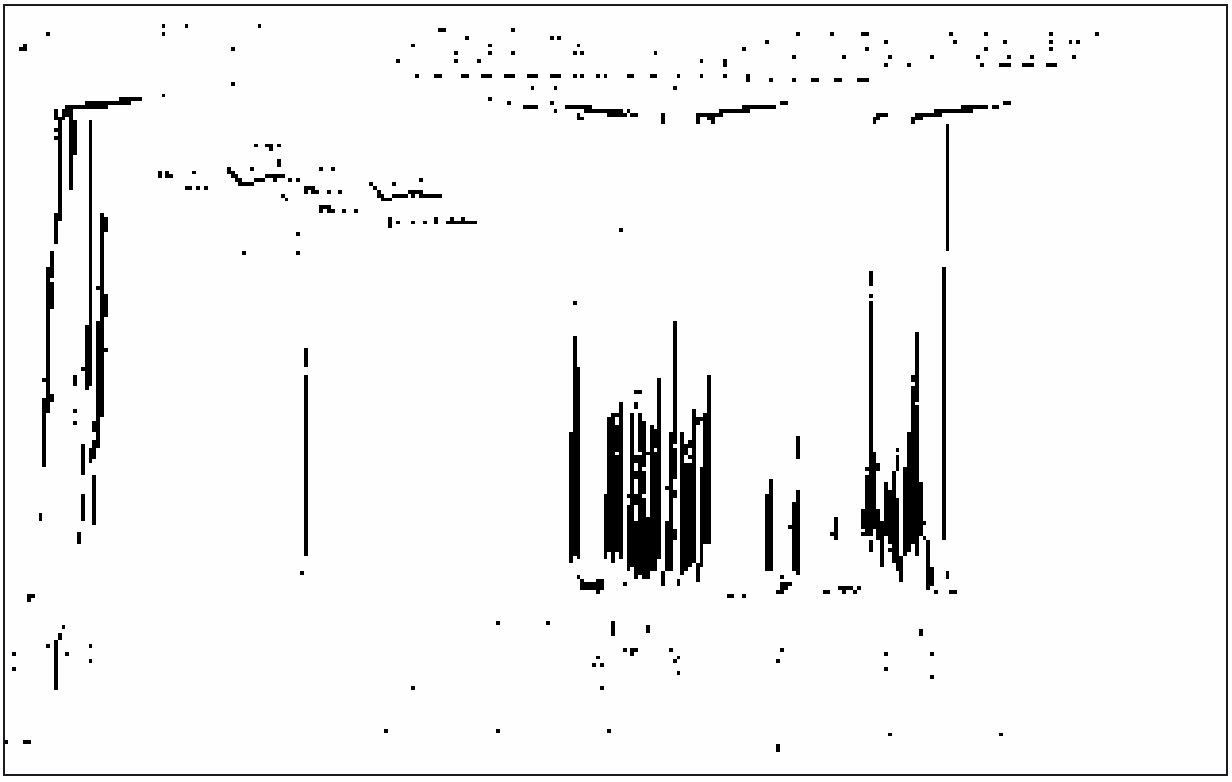
^{1}H-NMR Spectrum of Compound **68** (250 MHz, $CDCl_3$)



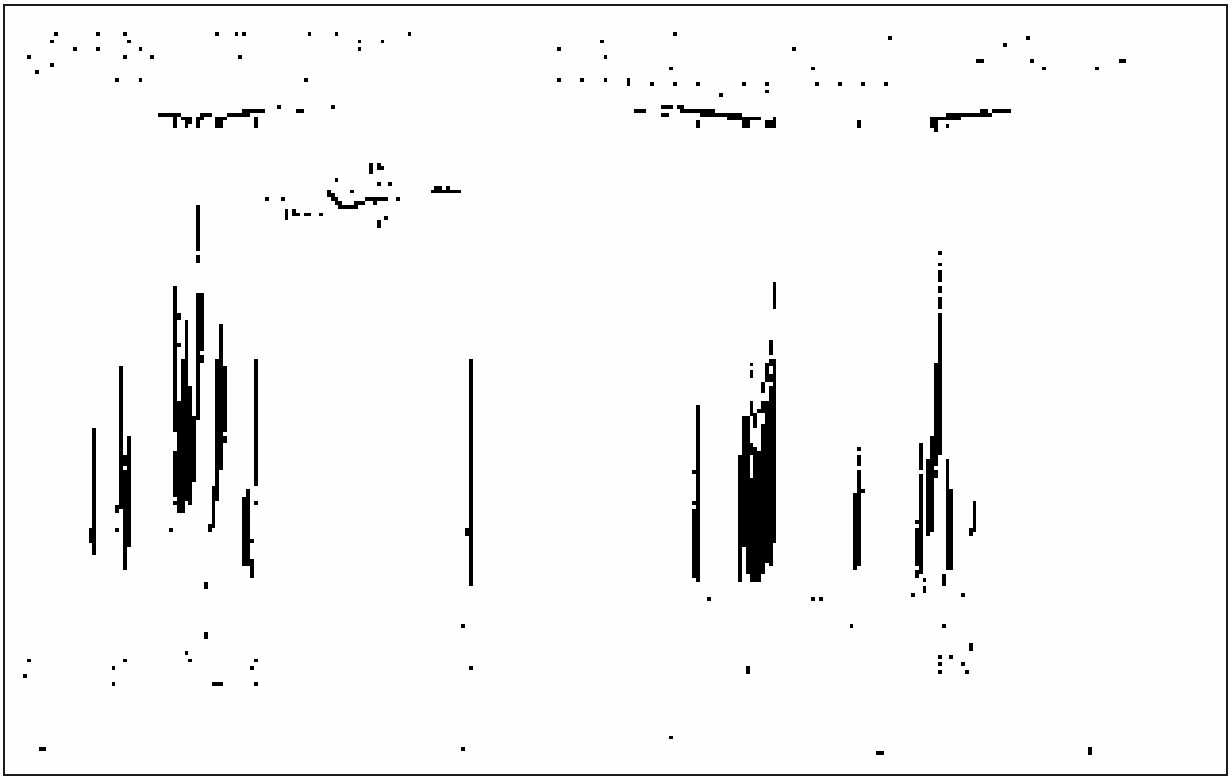
^{1}H-NMR Spectrum of Compound **69** (600 MHz, $CDCl_3$)



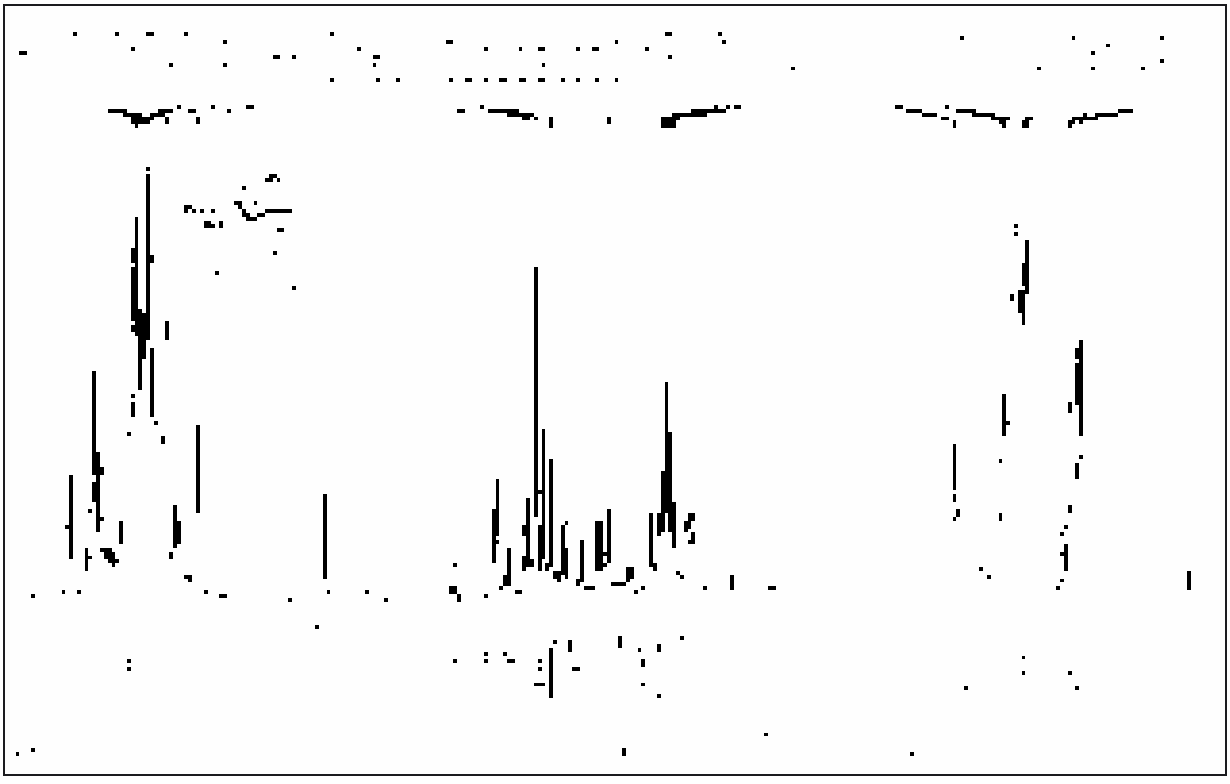
^{1}H-NMR Spectrum of Compound **70** (600 MHz, $CDCl_3$)



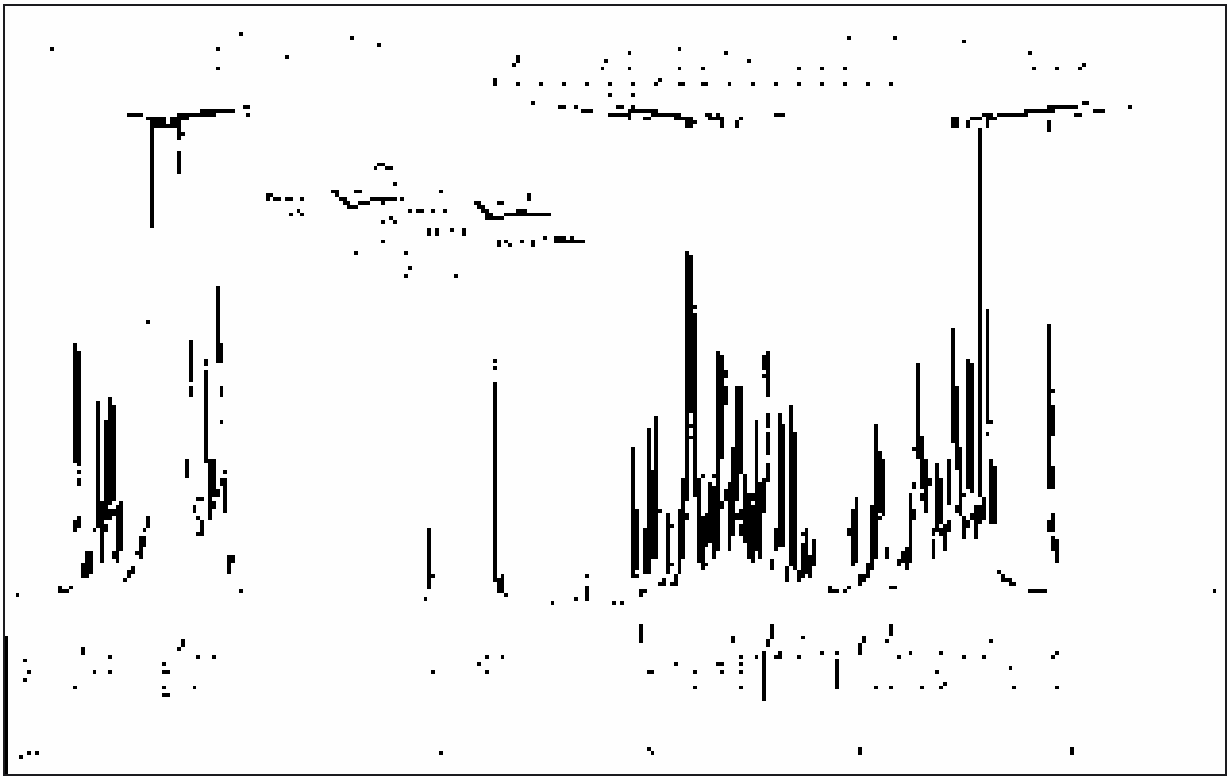
^{1}H-NMR Spectrum of Compound **71** (600 MHz, $CDCl_3$)



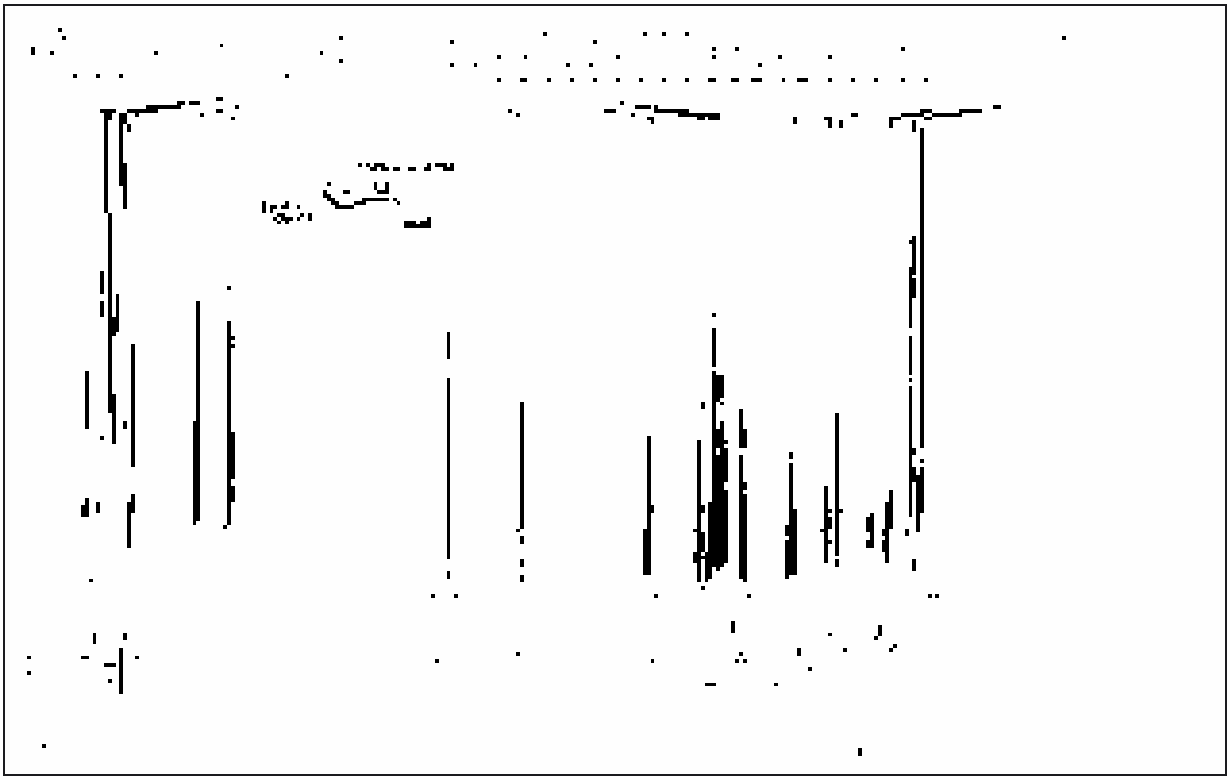
^{1}H-NMR Spectrum of Compound **72** (600 MHz, $CDCl_3$)



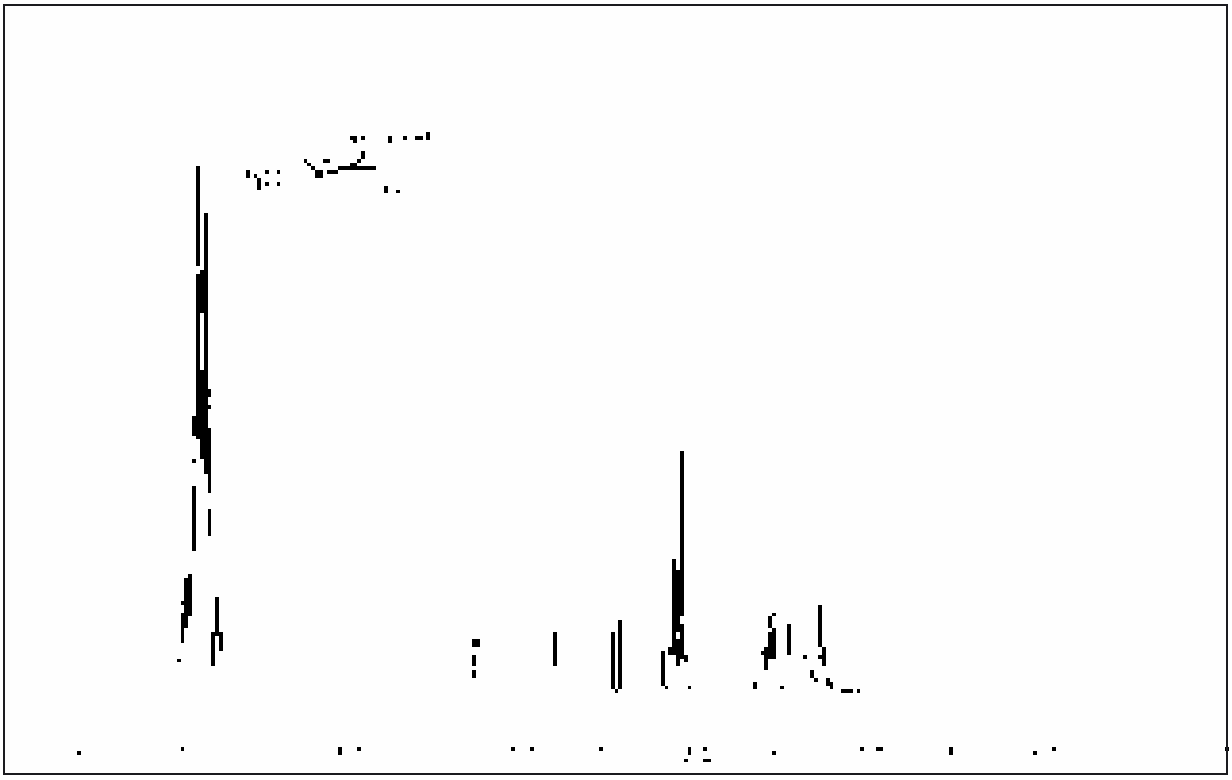
^{1}H-NMR Spectrum of Compound **73** (600 MHz, $CDCl_3$)



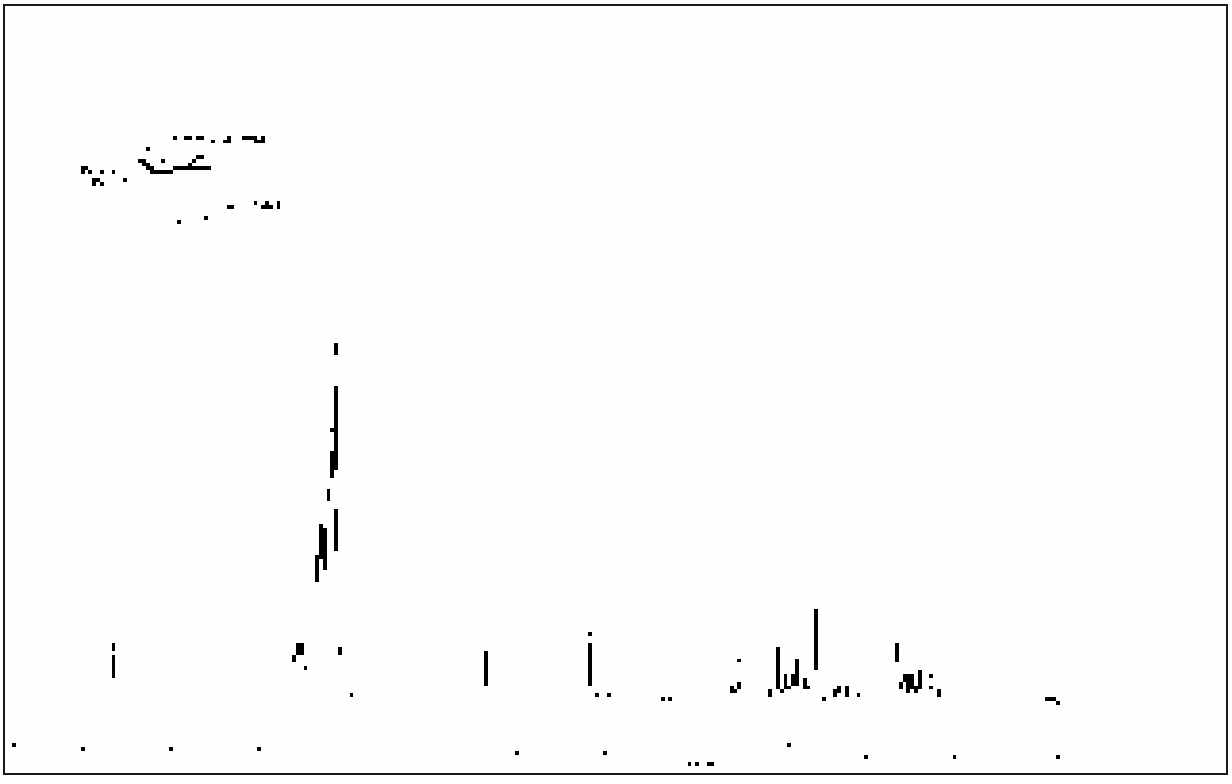
^{1}H-NMR Spectrum of Compound **74** (600 MHz, $CDCl_3$)



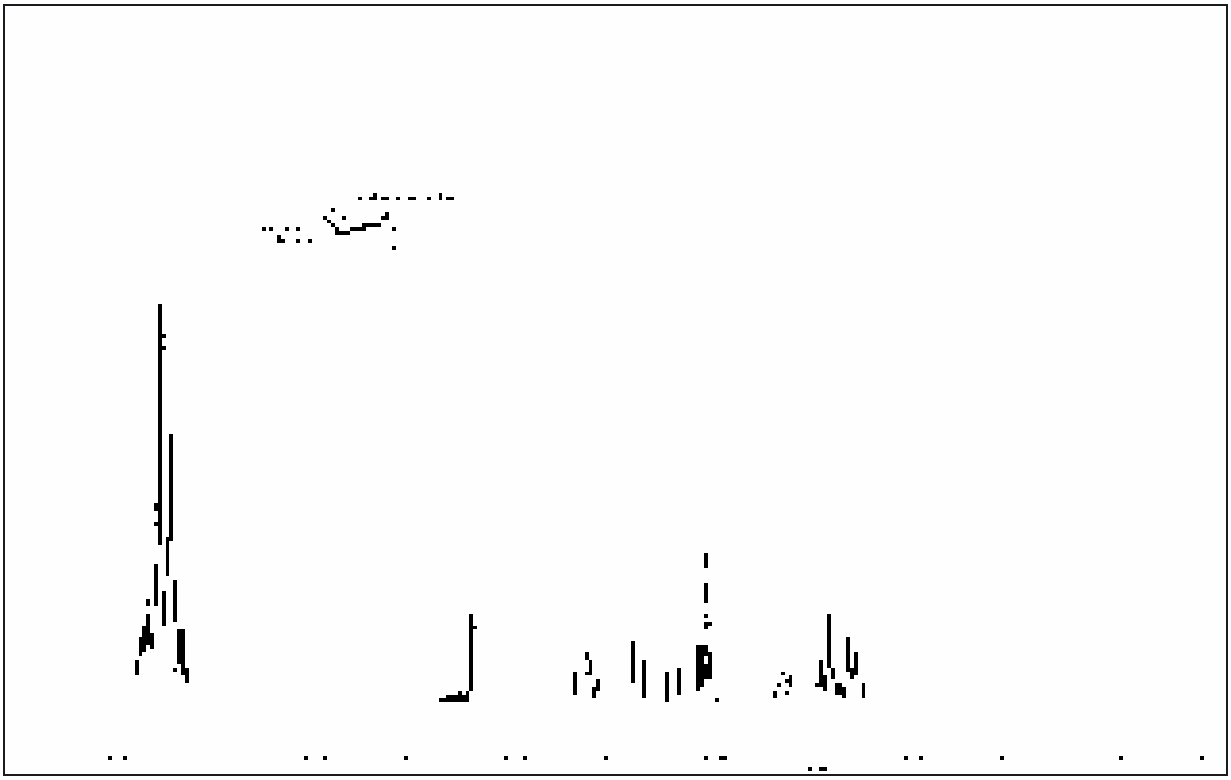
^{1}H-NMR Spectrum of Compound **76** (600 MHz, $CDCl_3$)



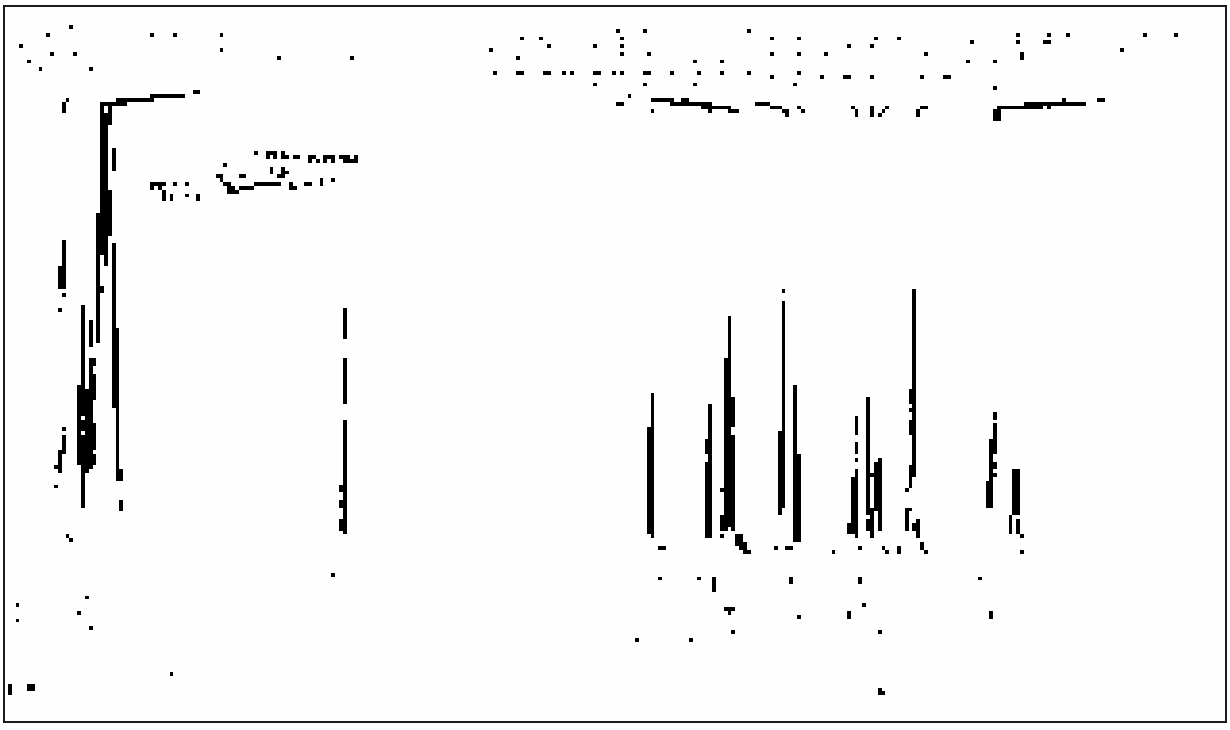
^{1}H-NMR Spectrum of Compound **77** (250 MHz, $CDCl_3$)



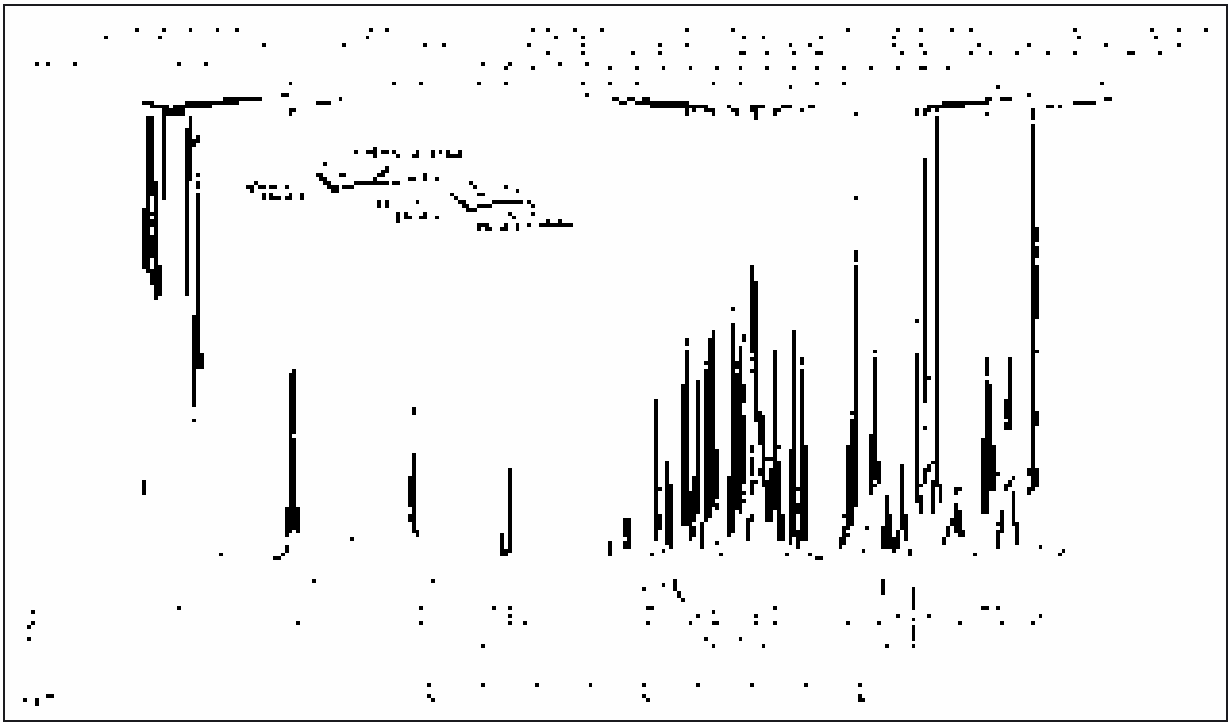
^{1}H-NMR Spectrum of Compound **78** (250 MHz, $CDCl_3$)



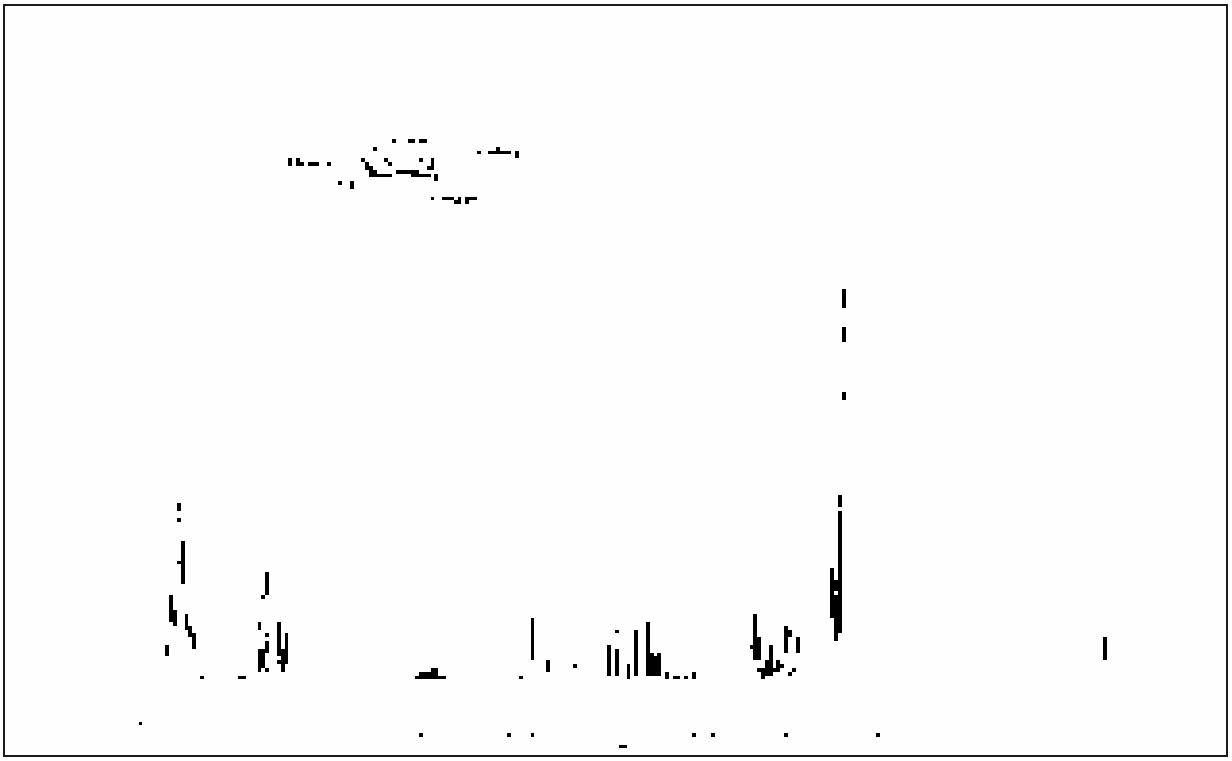
^{1}H-NMR Spectrum of Compound **80** (250 MHz, $CDCl_3$)



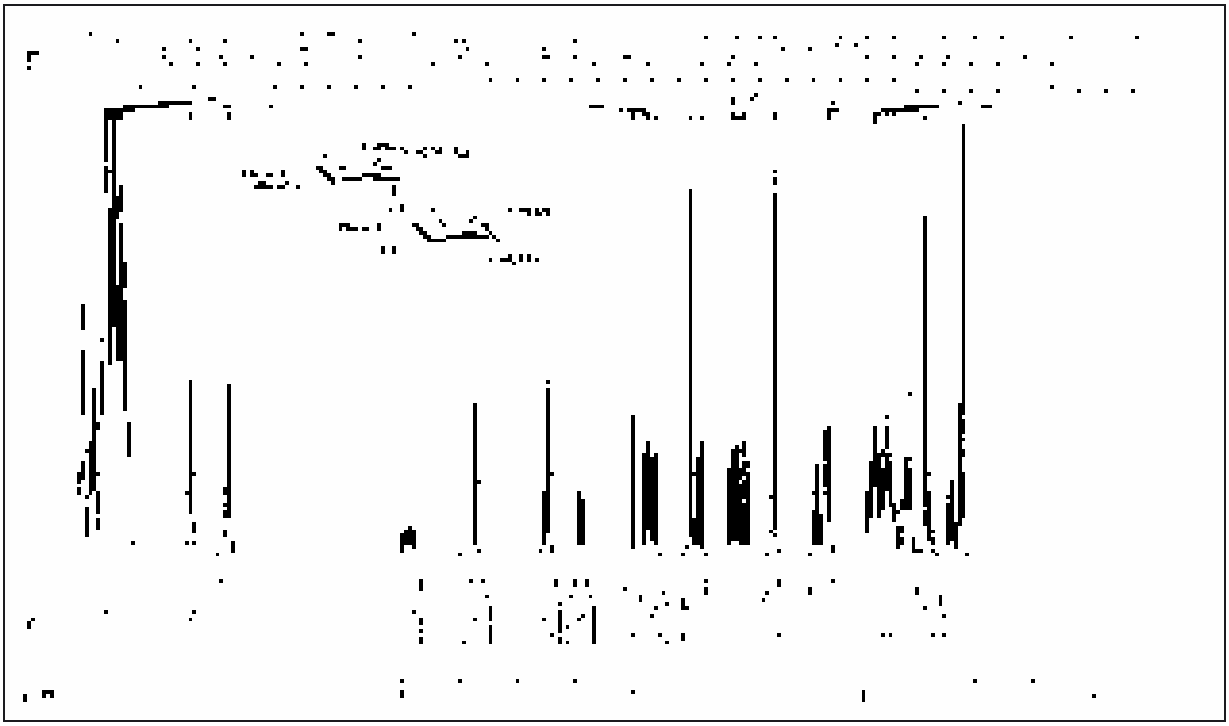
^{1}H-NMR Spectrum of Compound **81η** (600 MHz, $CDCl_3$)



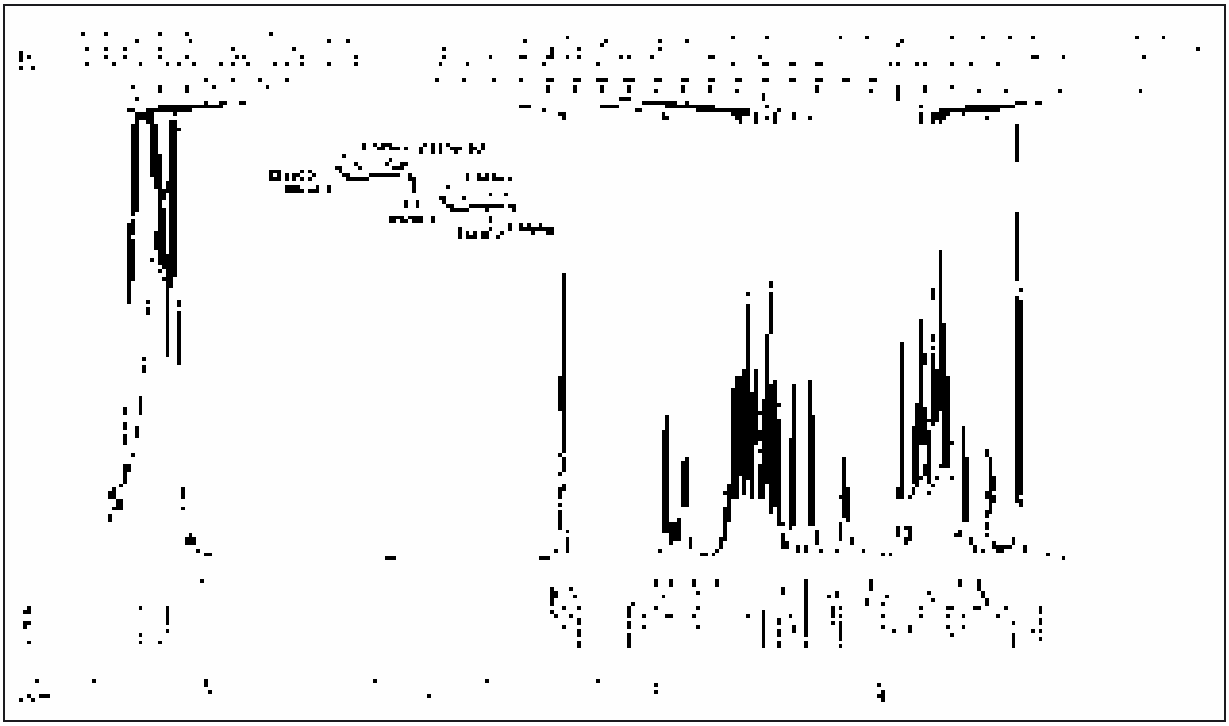
^{1}H-NMR Spectrum of Compound **82η** (600 MHz, $CDCl_3$)



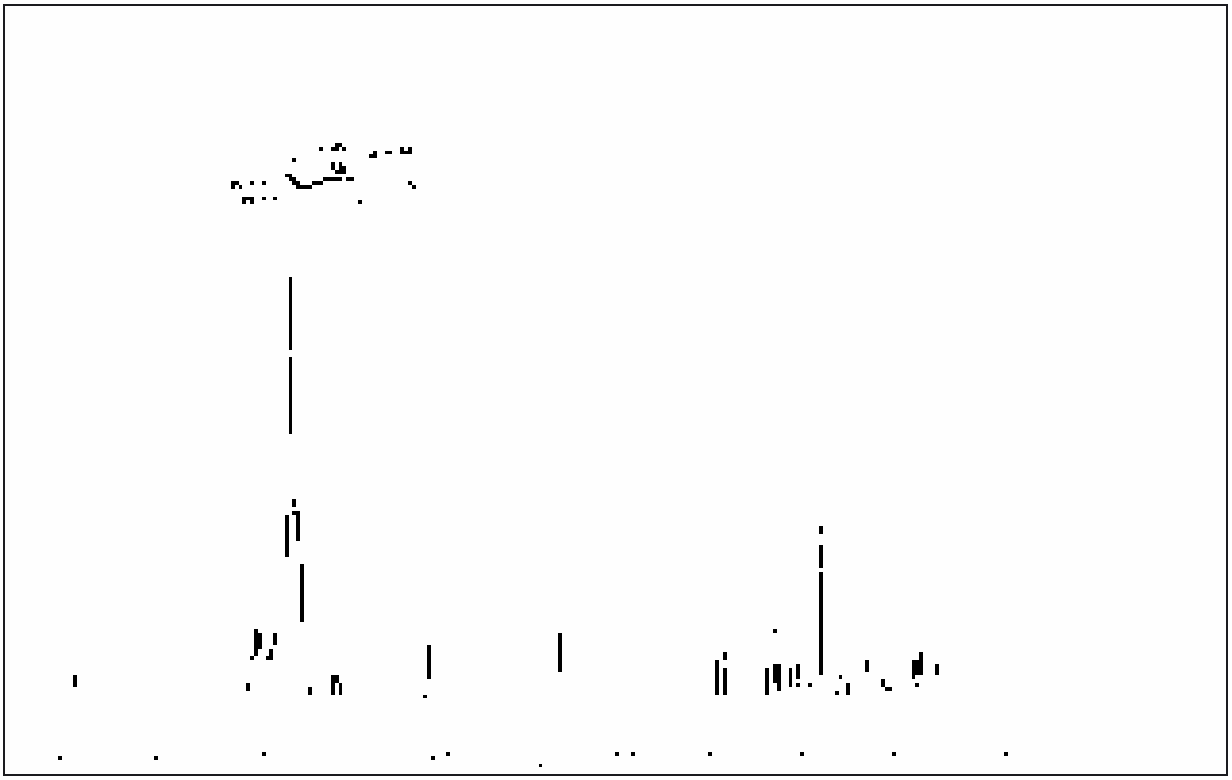
^{1}H-NMR Spectrum of Compound **84** (250 MHz, $CDCl_3$)



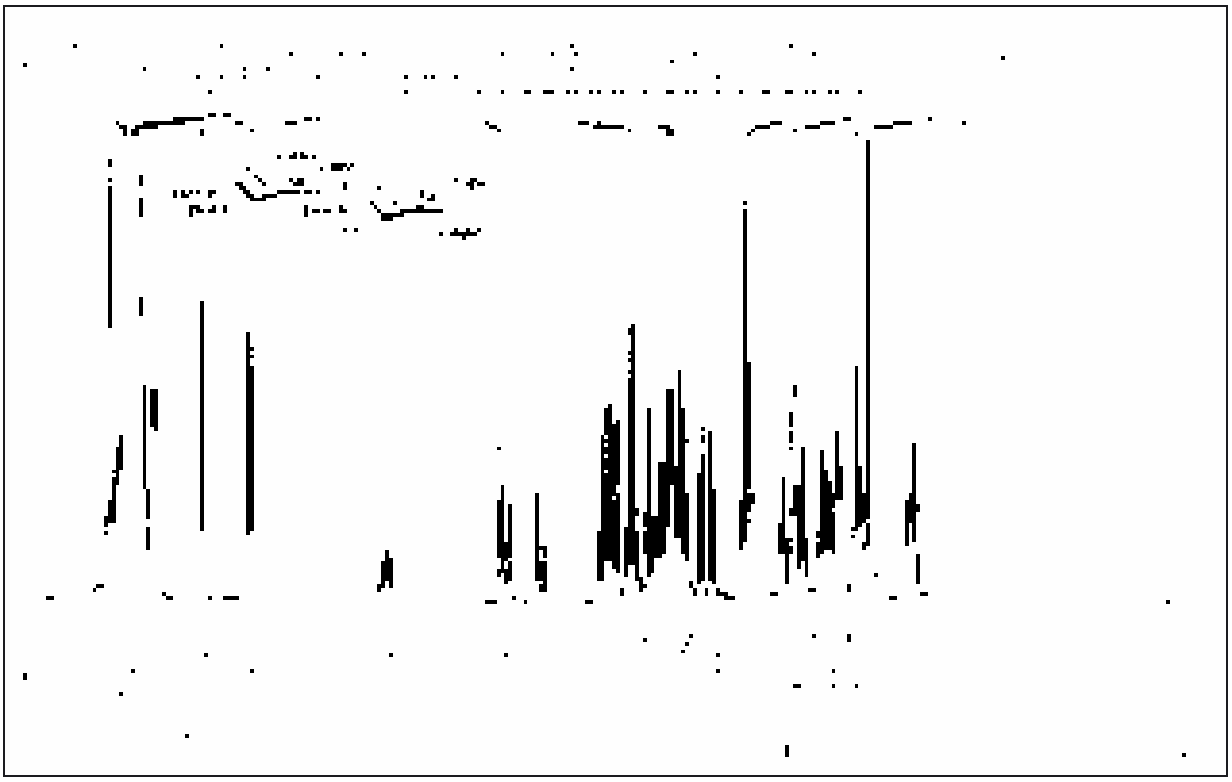
^{1}H-NMR Spectrum of Compound **85ζ** (600 MHz, $CDCl_3$)



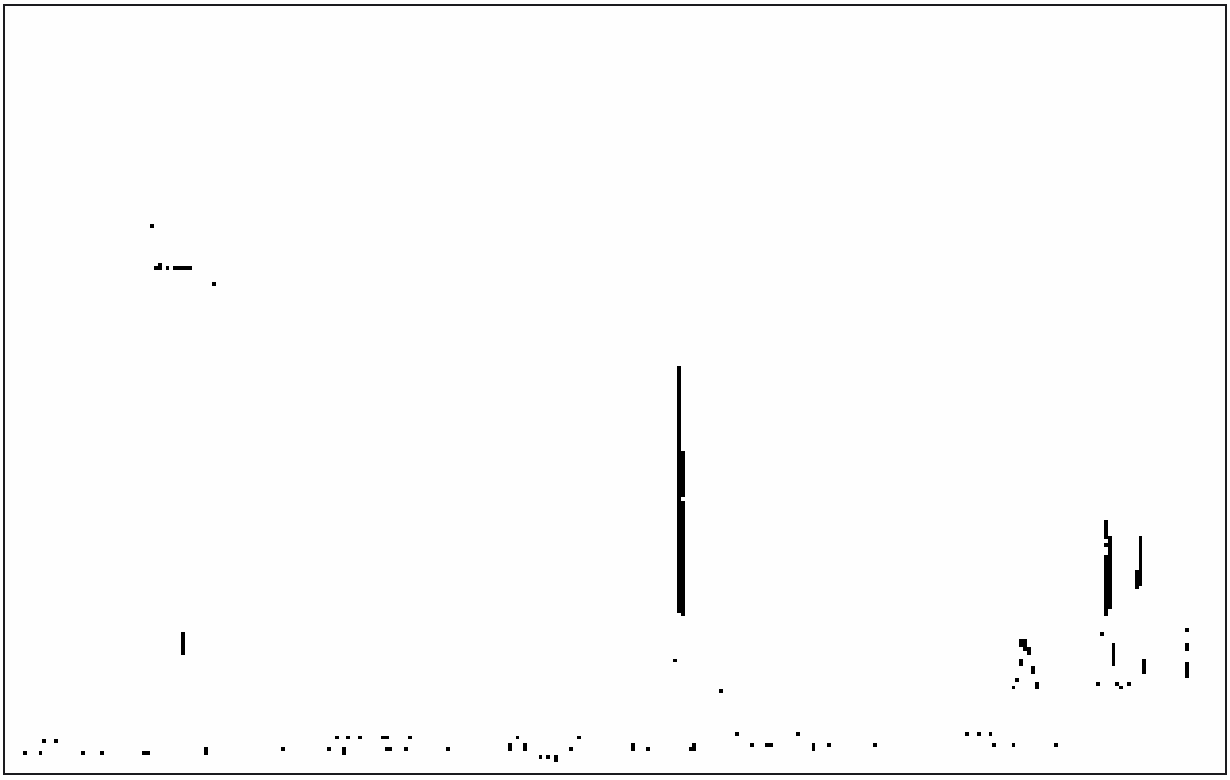
^{1}H-NMR Spectrum of Compound **86** (600 MHz, $CDCl_3$)



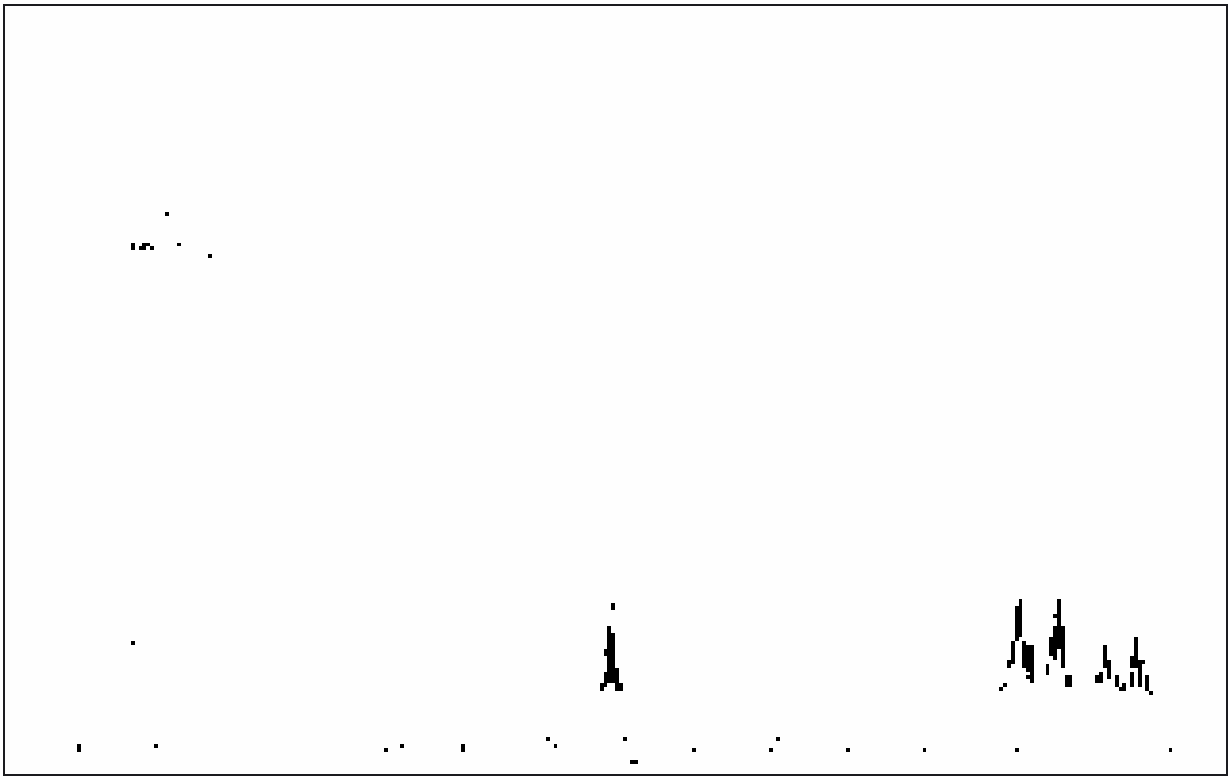
^{1}H-NMR Spectrum of Compound **89** (250 MHz, $CDCl_3$)



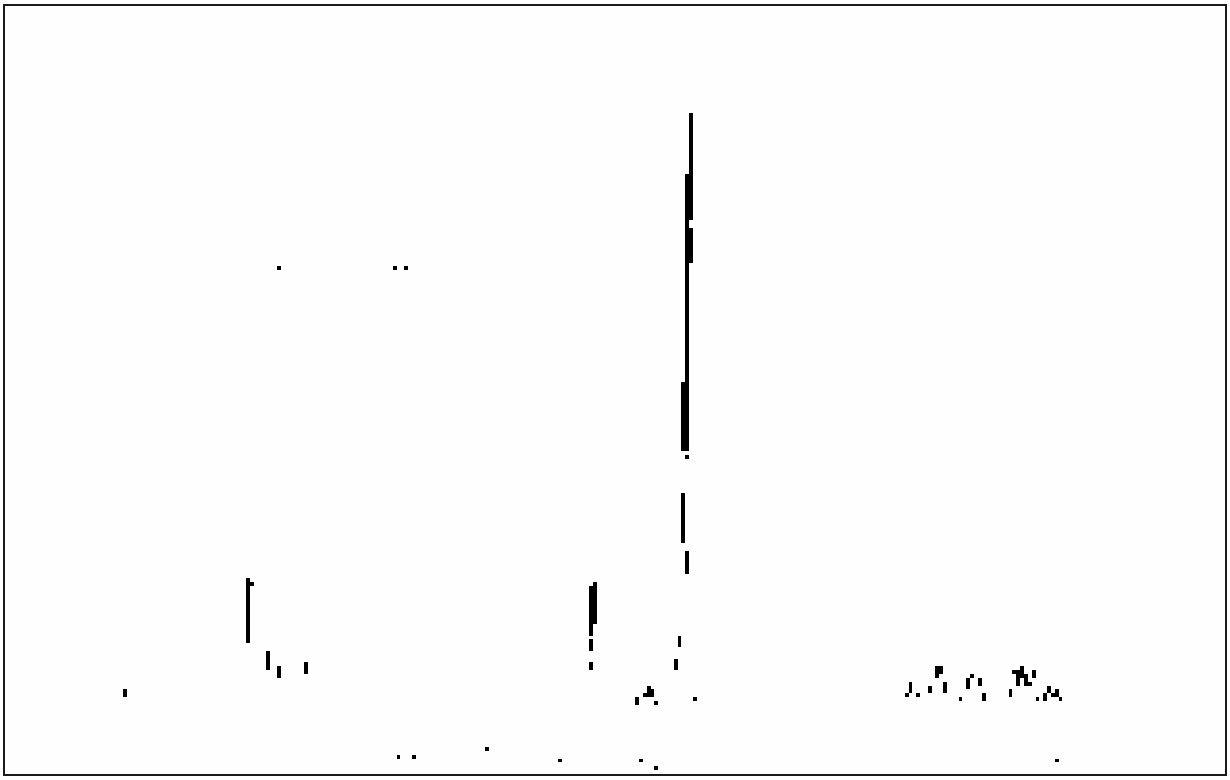
^{1}H-NMR Spectrum of Compound **94** (600 MHz, $CDCl_3$)



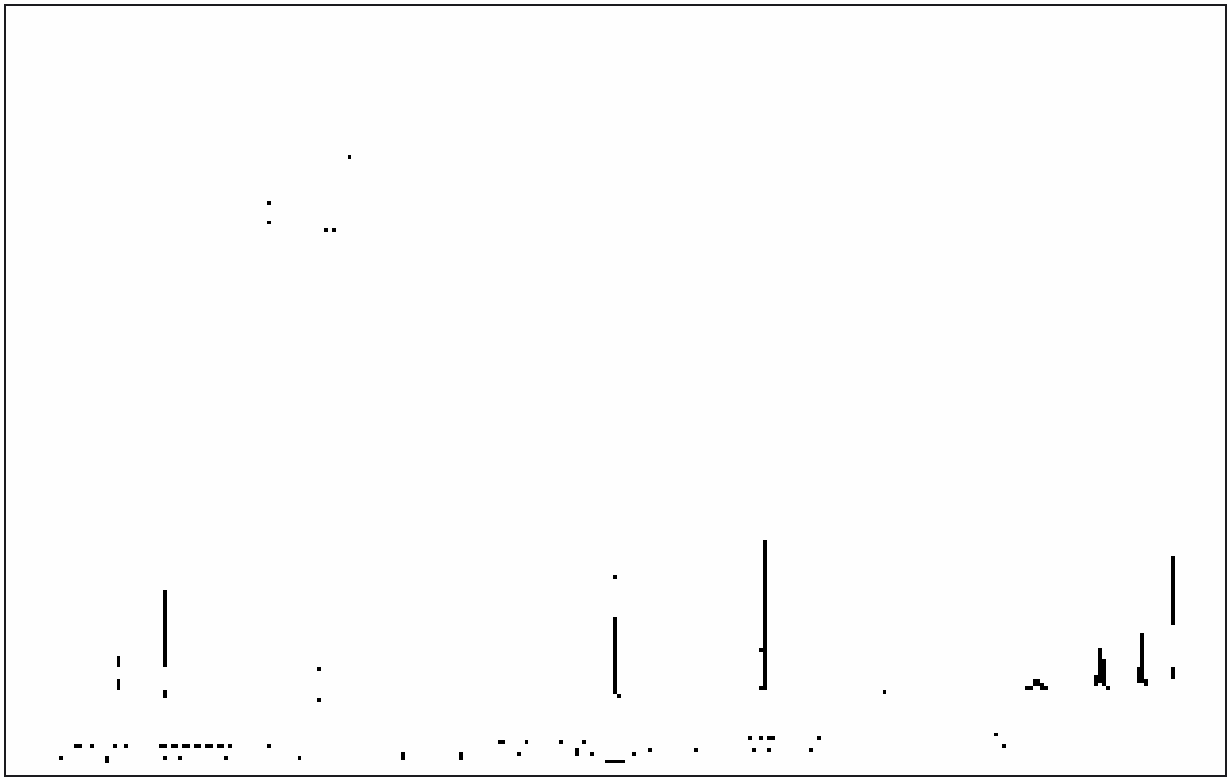
^{1}H-NMR Spectrum of Compound **101** (250 MHz, $CDCl_3$)



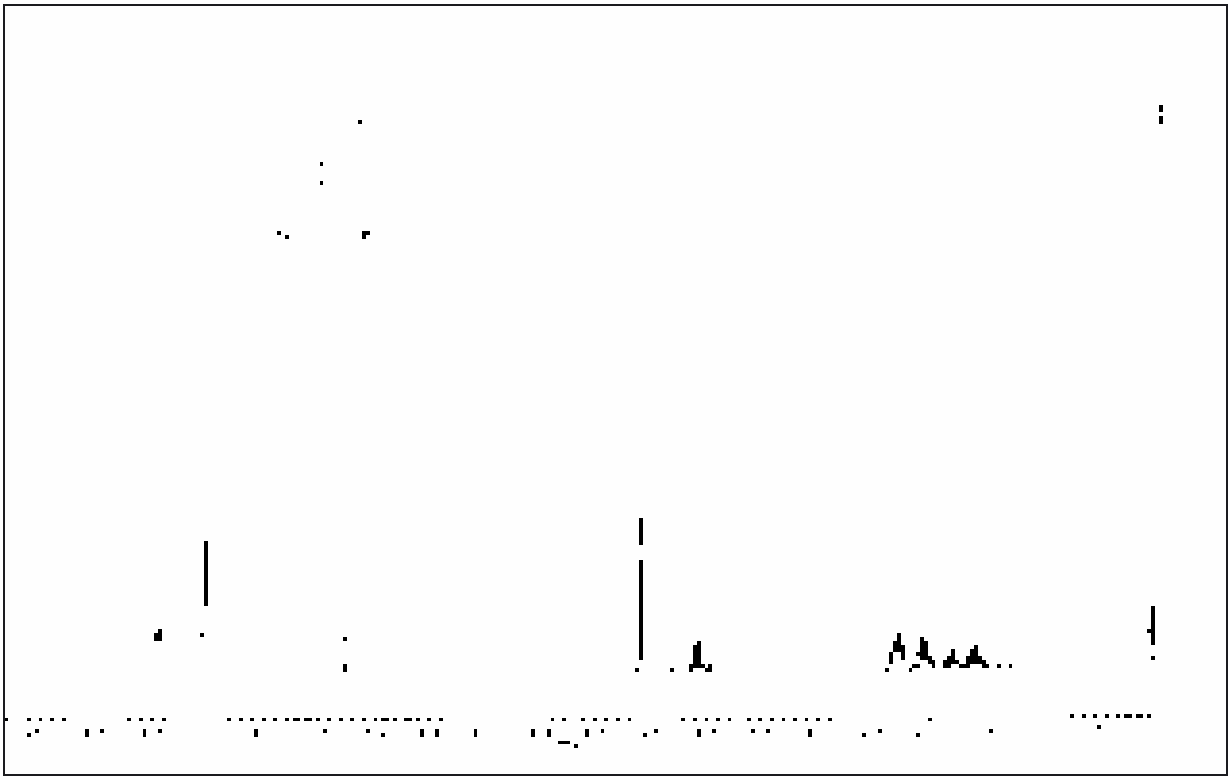
^{1}H-NMR Spectrum of Compound **102** (250 MHz, $CDCl_3$)



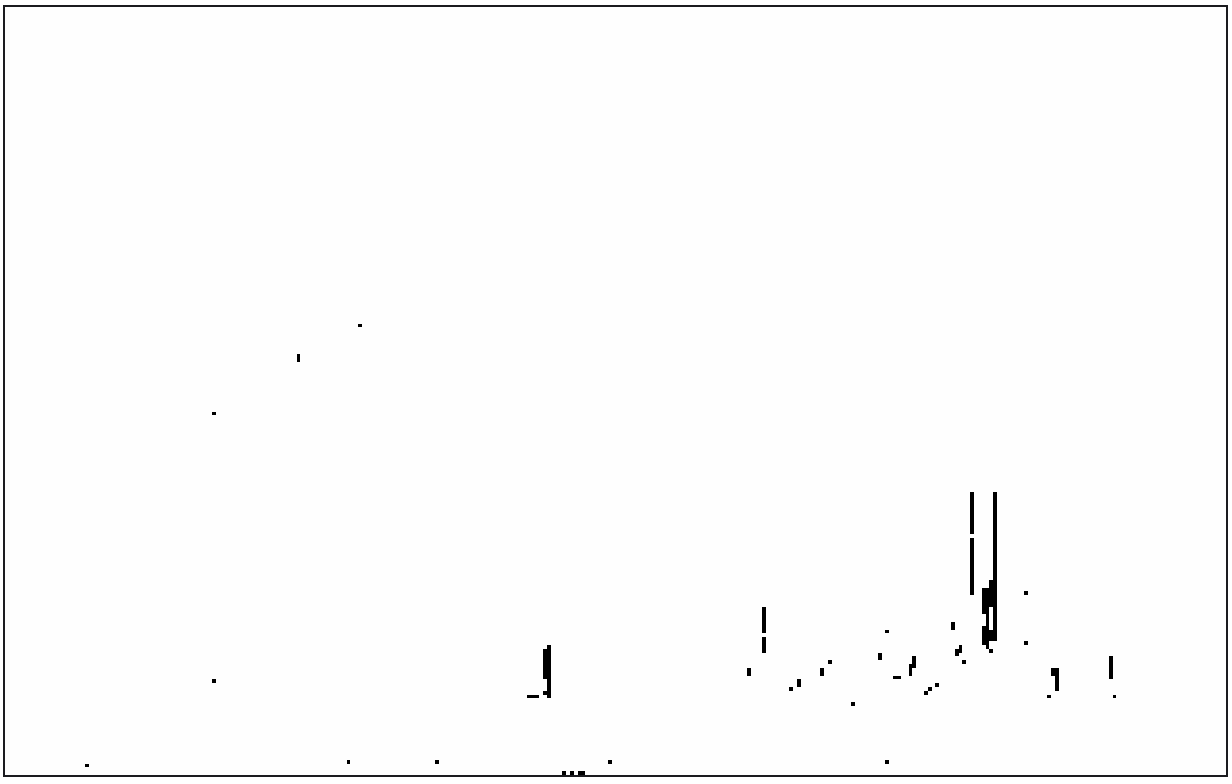
^{1}H-NMR Spectrum of Compound **105** (250 MHz, $CDCl_3$)



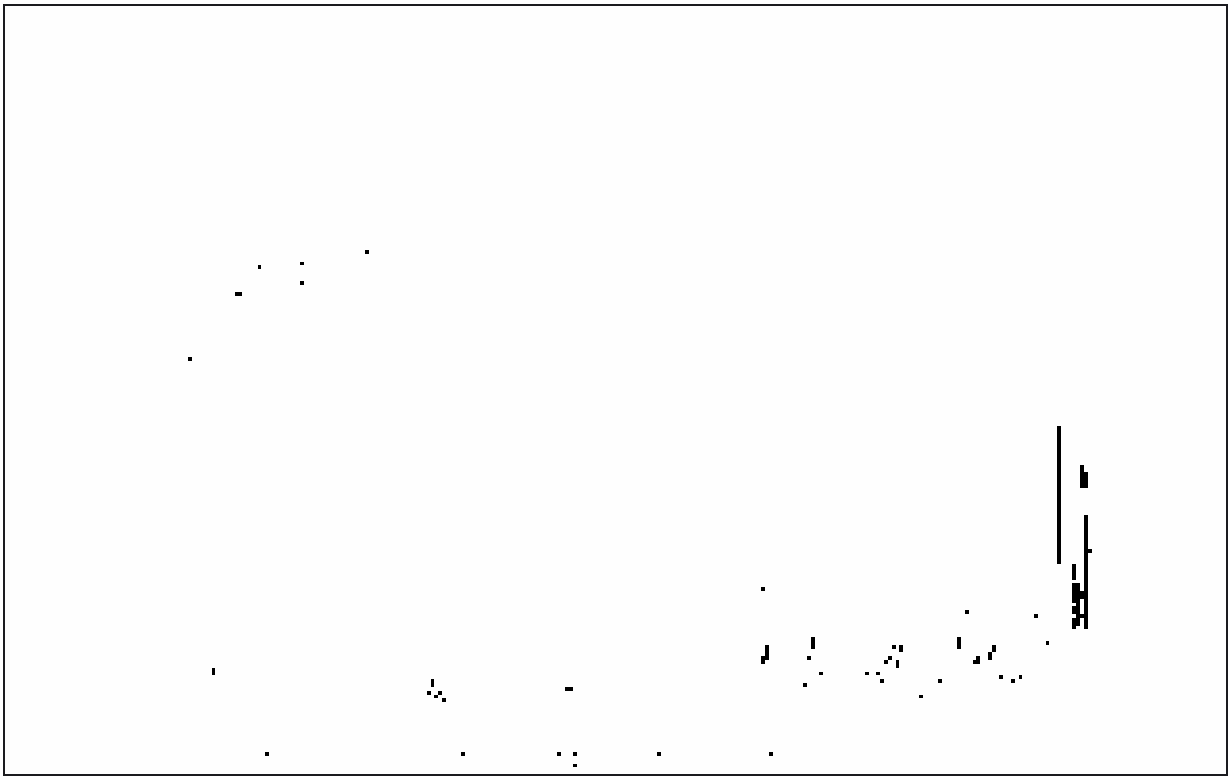
^{1}H-NMR Spectrum of Compound **106** (250 MHz, $CDCl_3$)



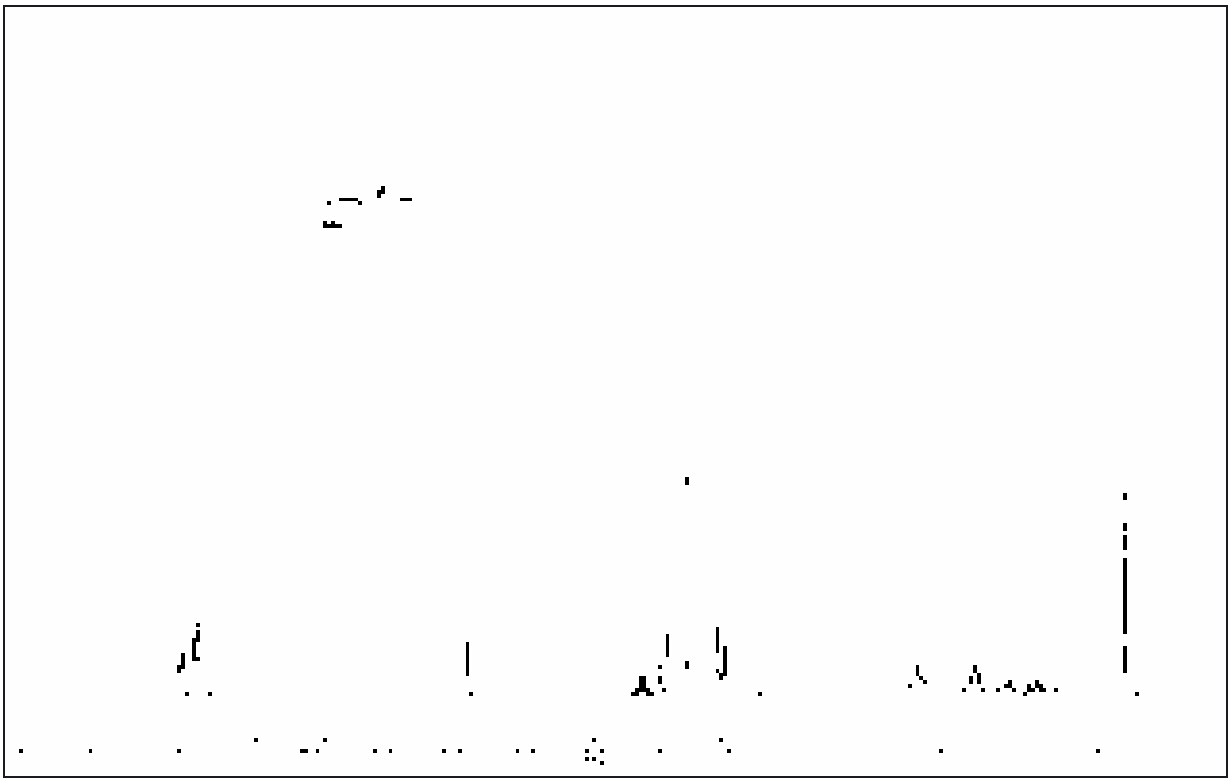
^{1}H-NMR Spectrum of Compound **107** (250 MHz, $CDCl_3$)



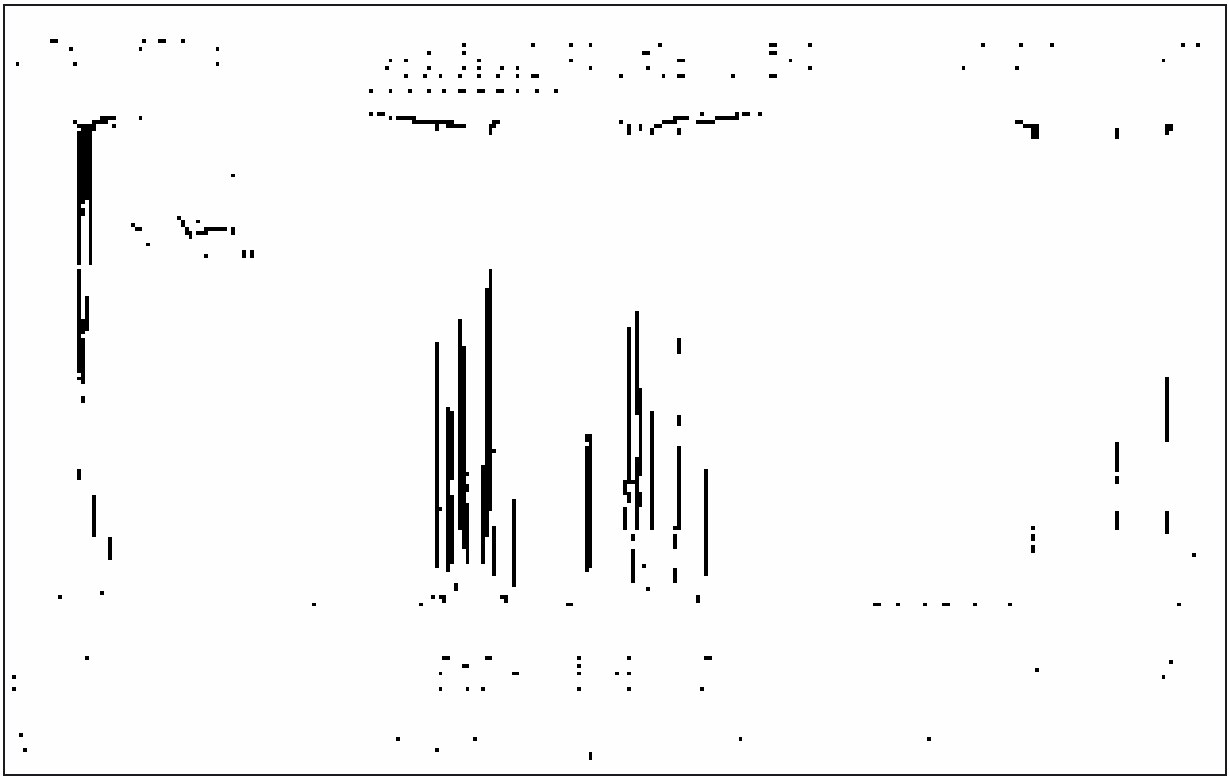
^{1}H-NMR Spectrum of Compound **110** (250 MHz, $CDCl_3$)



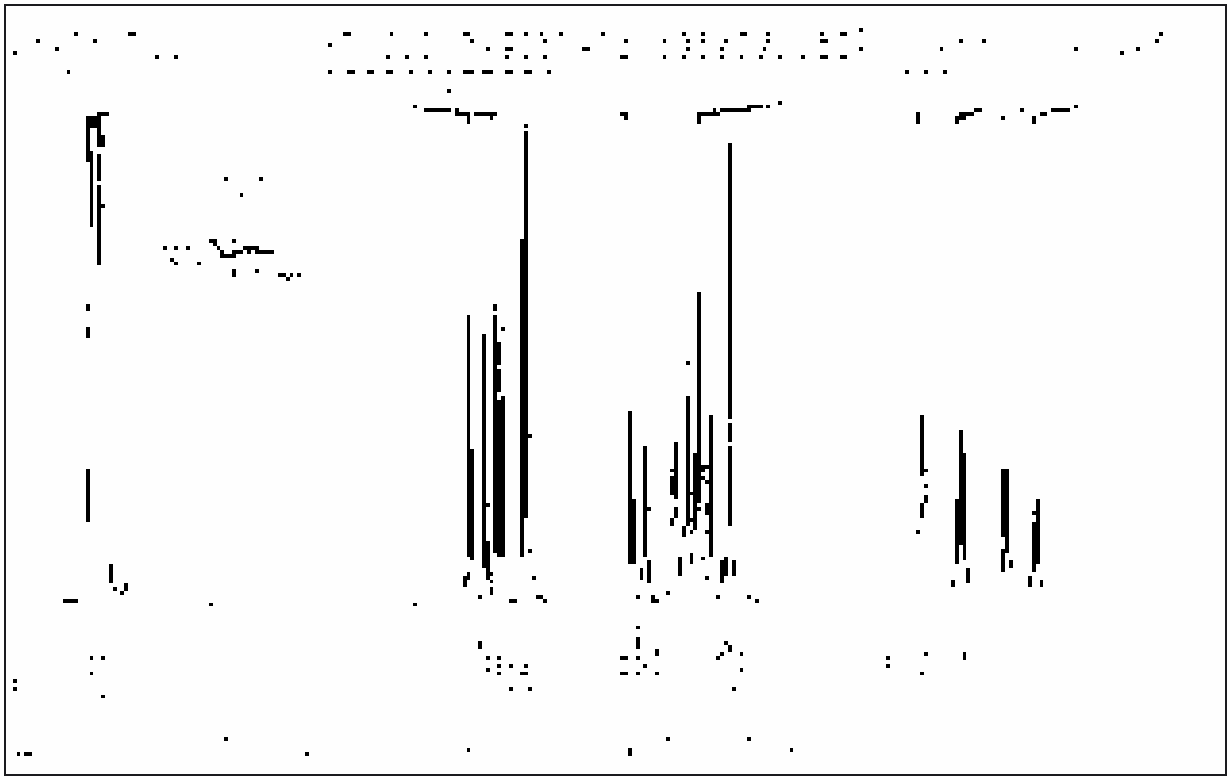
^{1}H-NMR Spectrum of Compound **111** (250 MHz, $CDCl_3$)



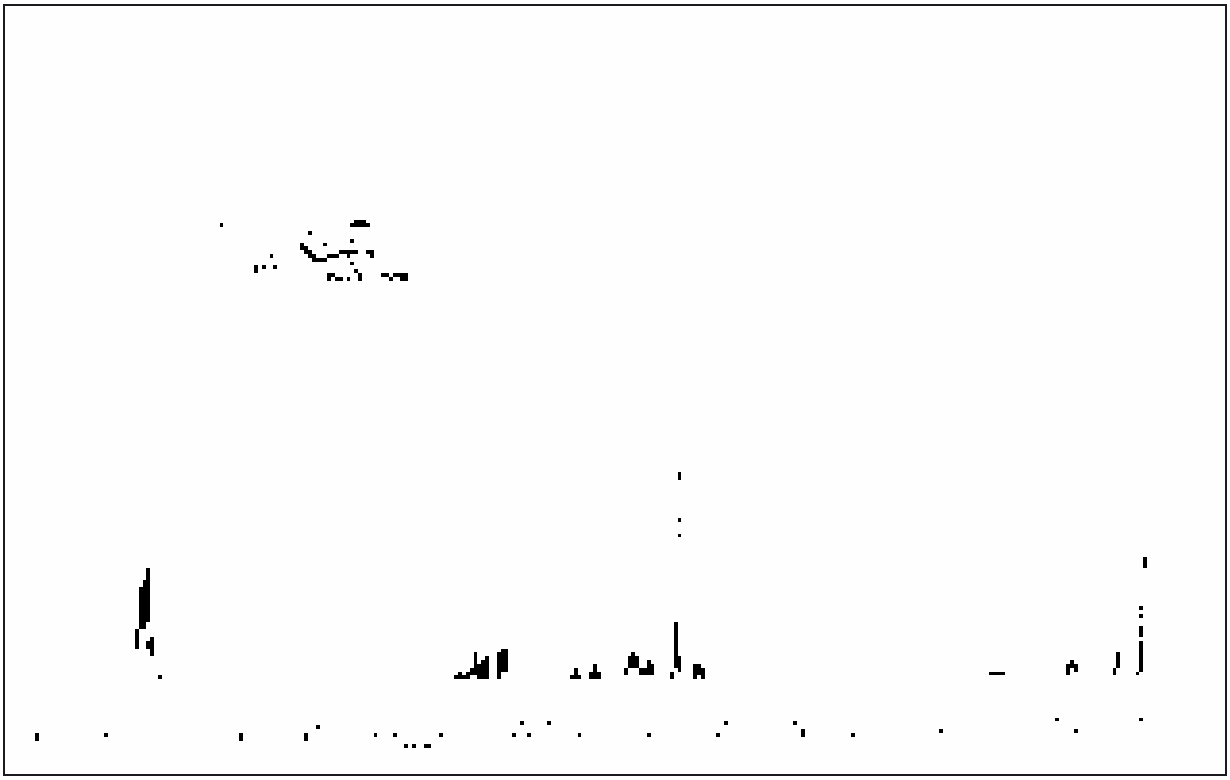
^{1}H-NMR Spectrum of Compound **112** (250 MHz, $CDCl_3$)



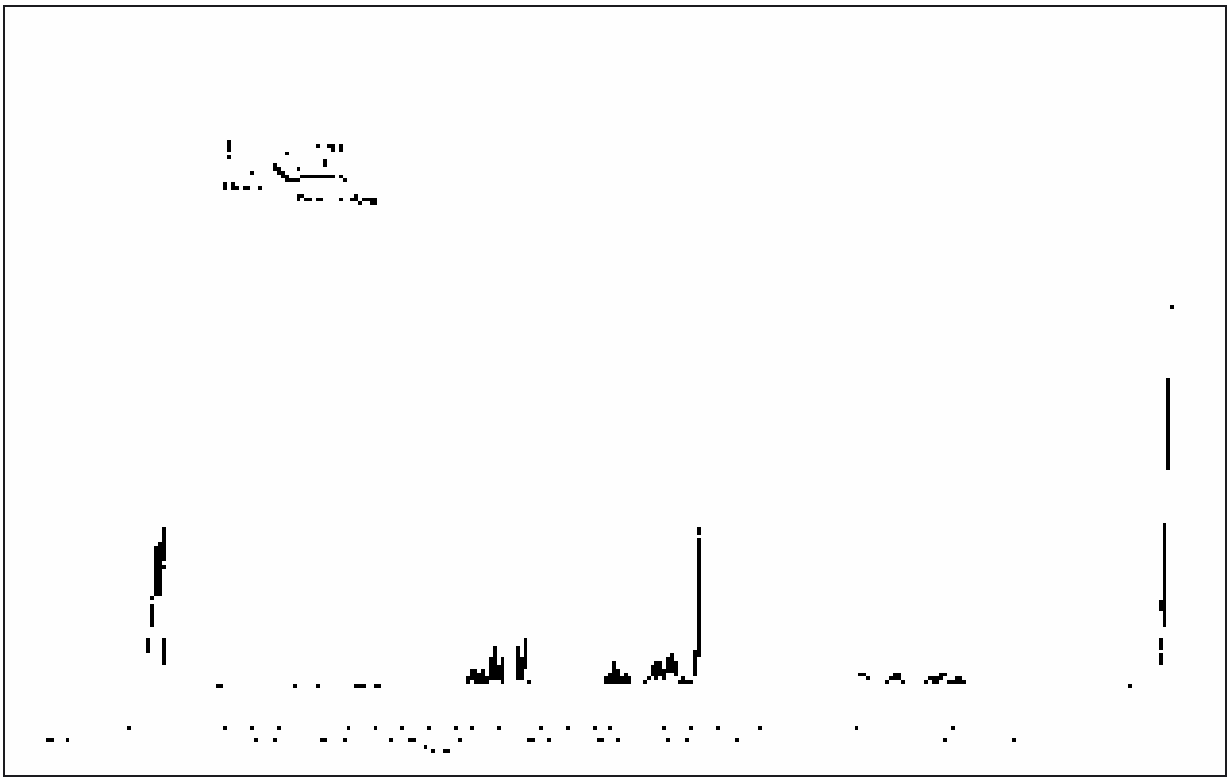
^{1}H-NMR Spectrum of Compound **113** (600 MHz, $CDCl_3$)



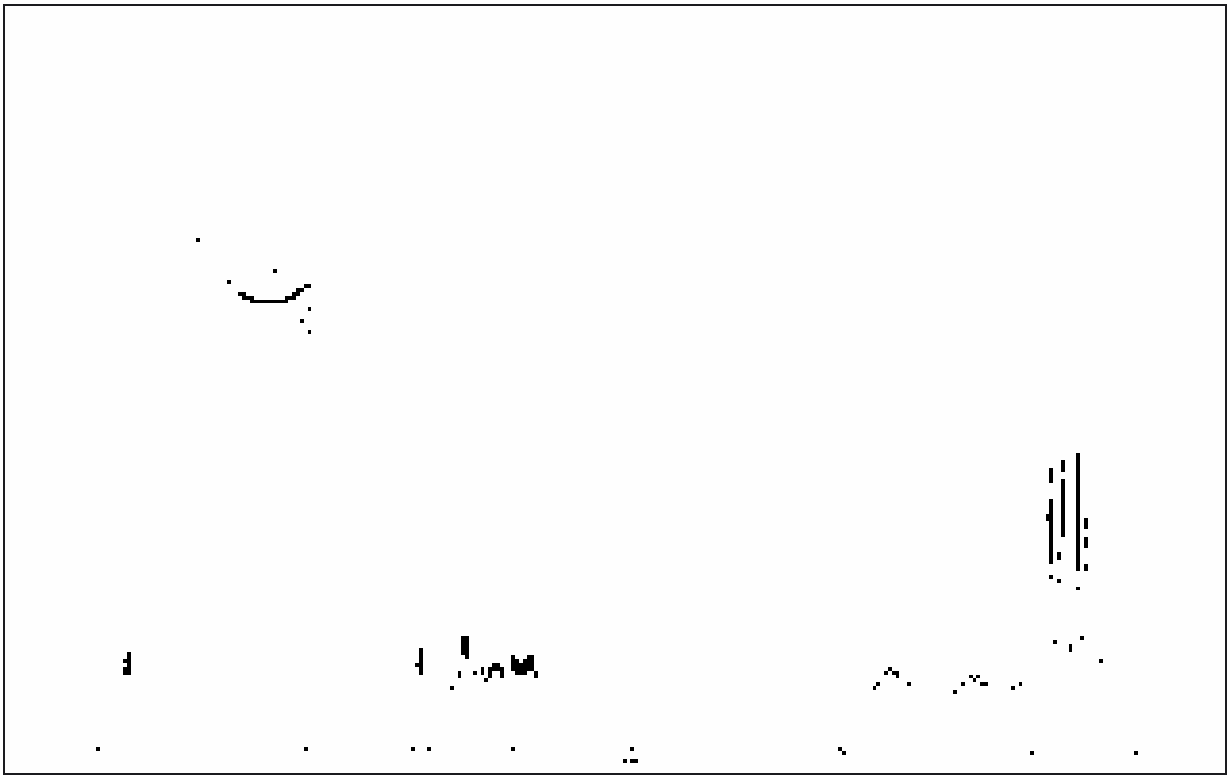
^{1}H-NMR Spectrum of Compound **114** (600 MHz, $CDCl_3$)



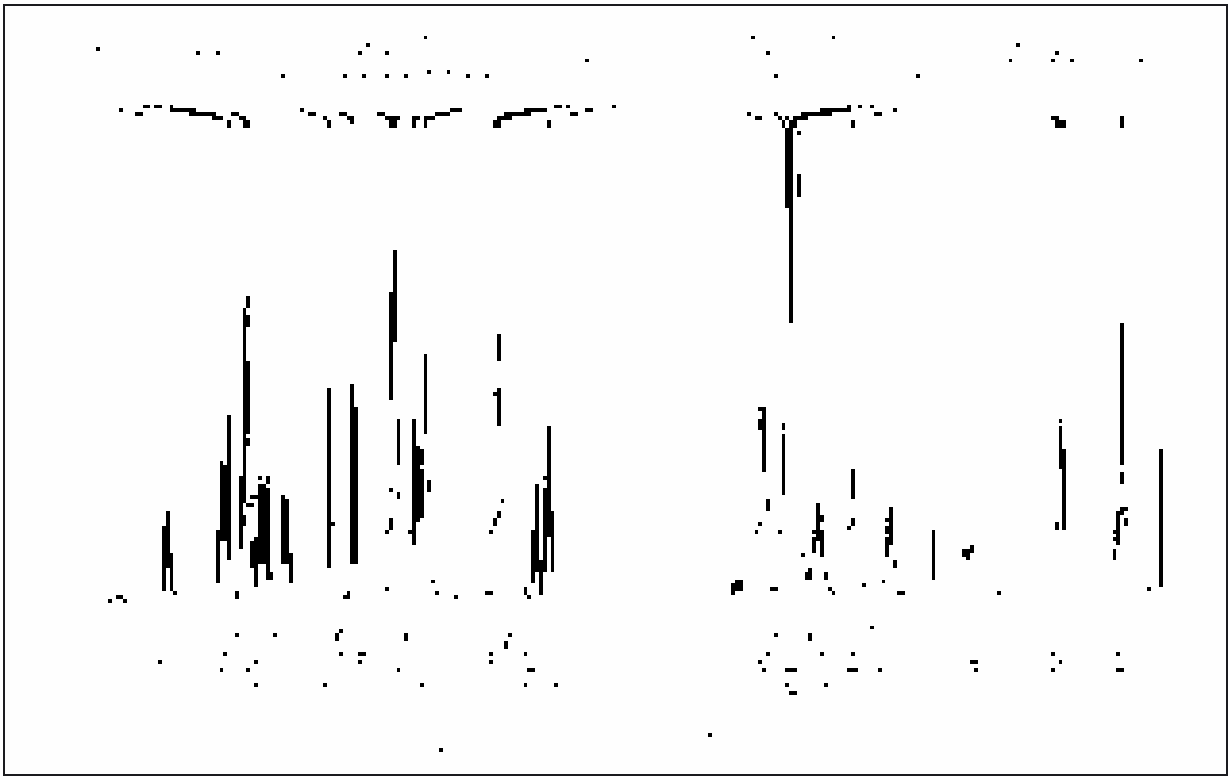
^{1}H-NMR Spectrum of Compound **115** (250 MHz, $CDCl_3$)



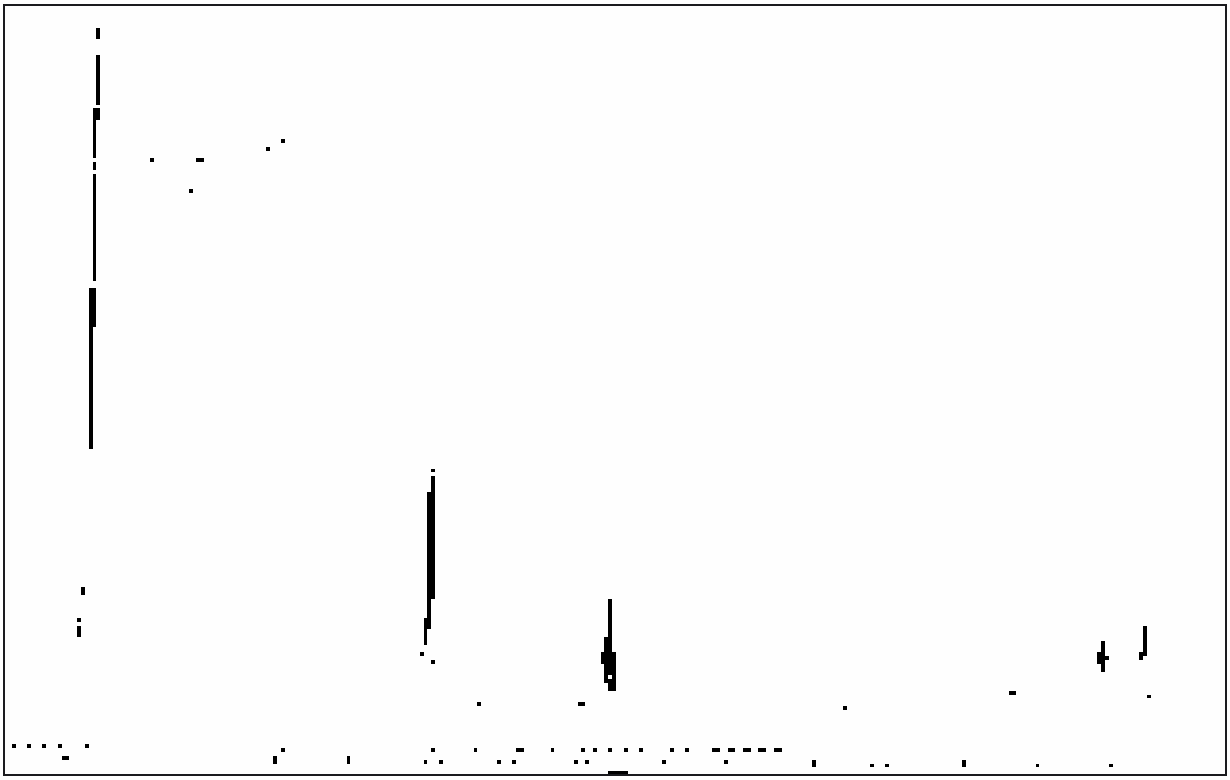
^{1}H-NMR Spectrum of Compound **116** (250 MHz, $CDCl_3$)



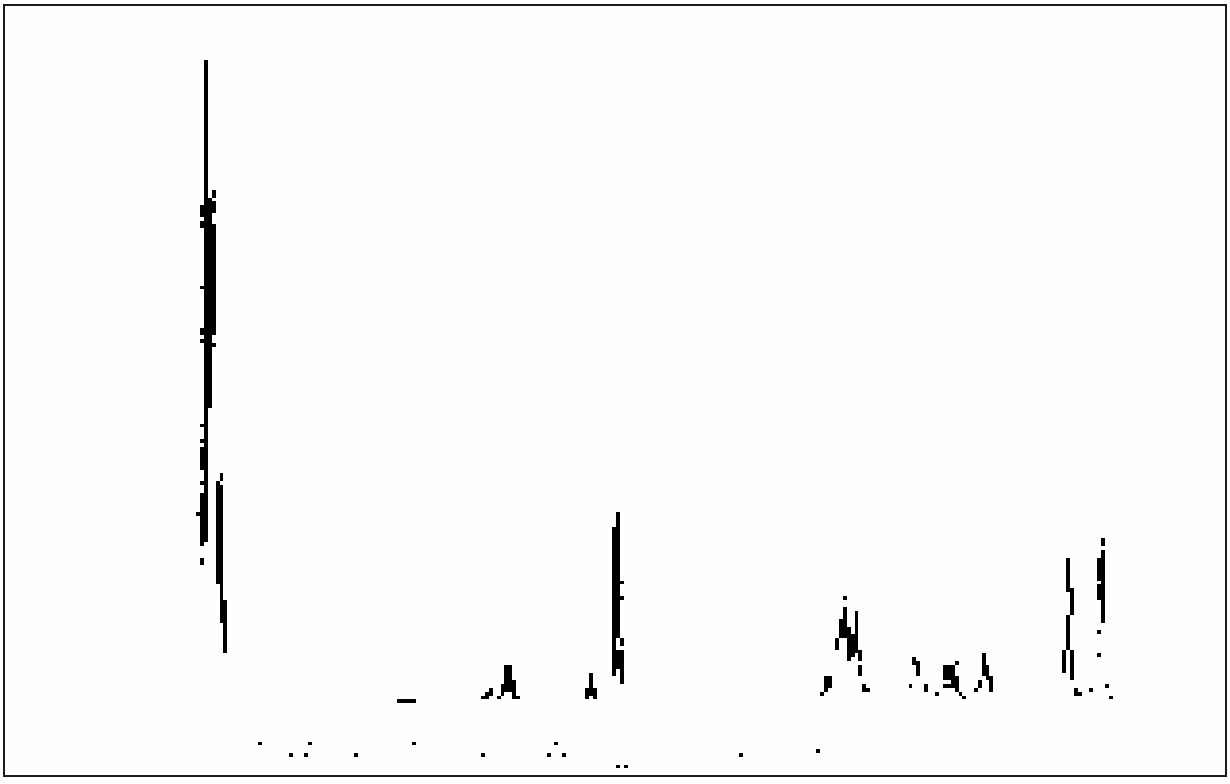
^{1}H-NMR Spectrum of Compound **117** (250 MHz, $CDCl_3$)



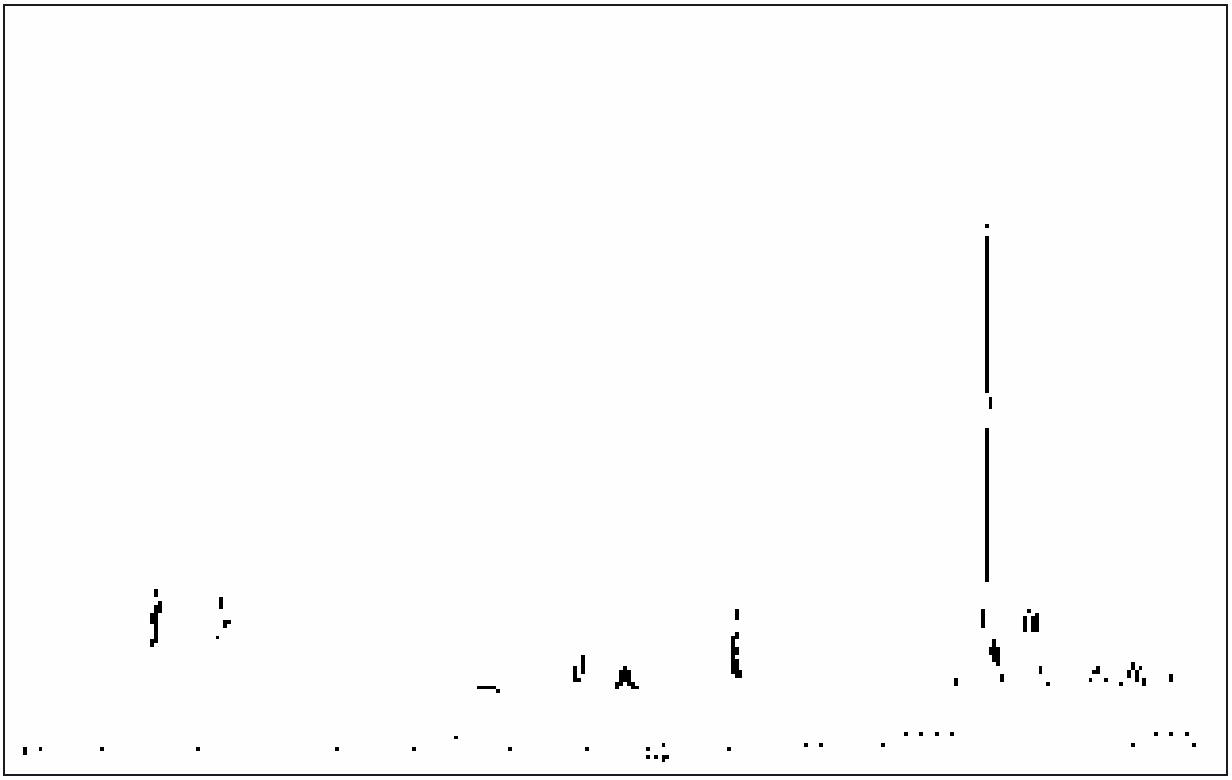
^{1}H-NMR Spectrum of Compound **118** and **119** (600 MHz, $CDCl_3$)



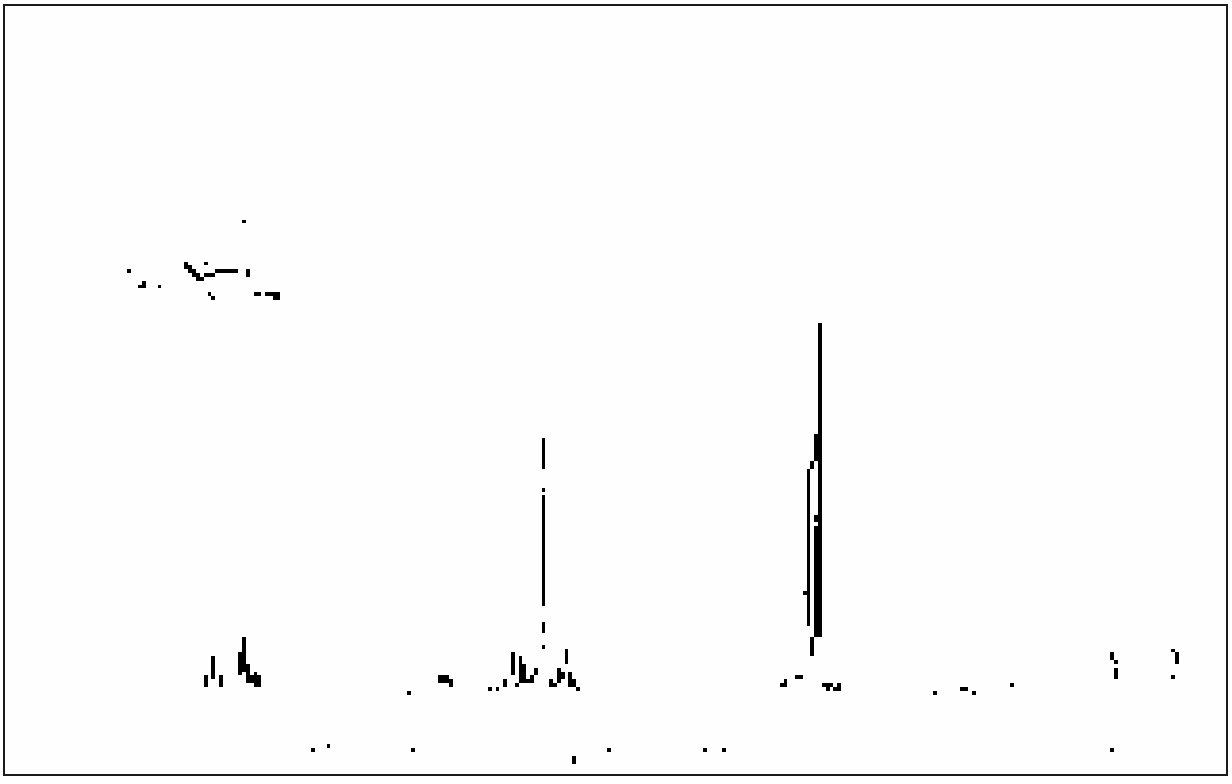
^{1}H-NMR Spectrum of Compound **121** (250 MHz, $CDCl_3$)



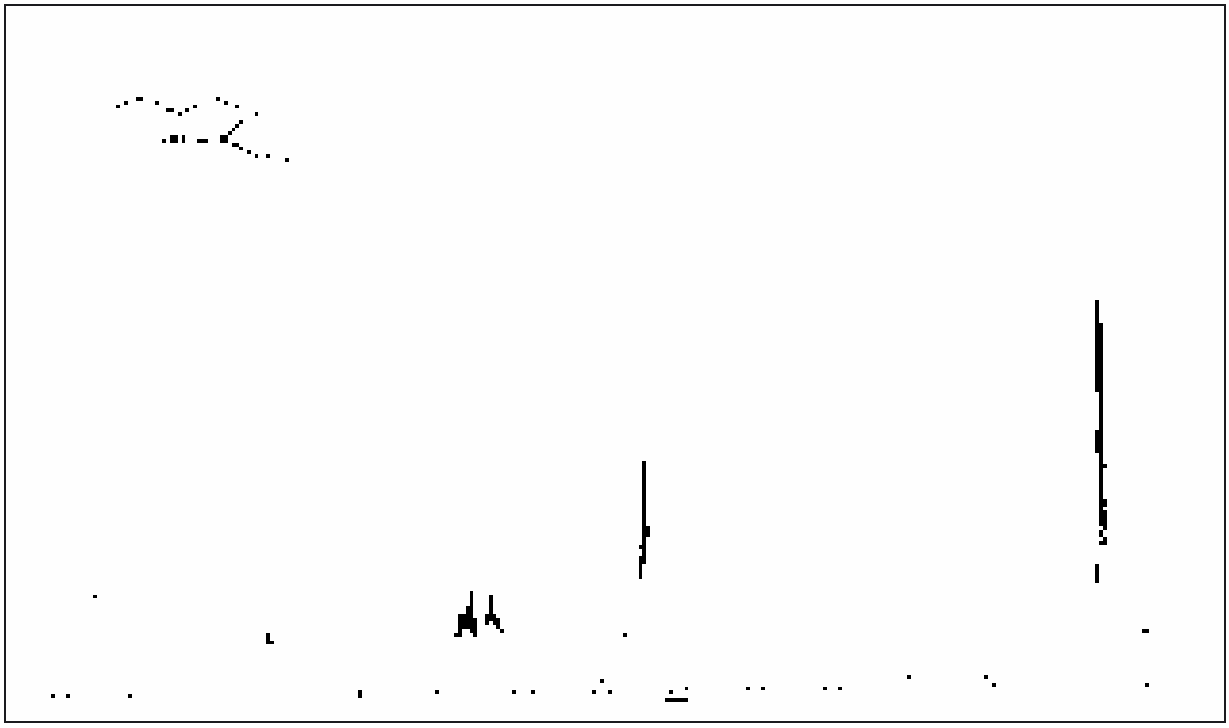
^{1}H-NMR Spectrum of Compound **123, 124** and **125** (250 MHz, $CDCl_3$)



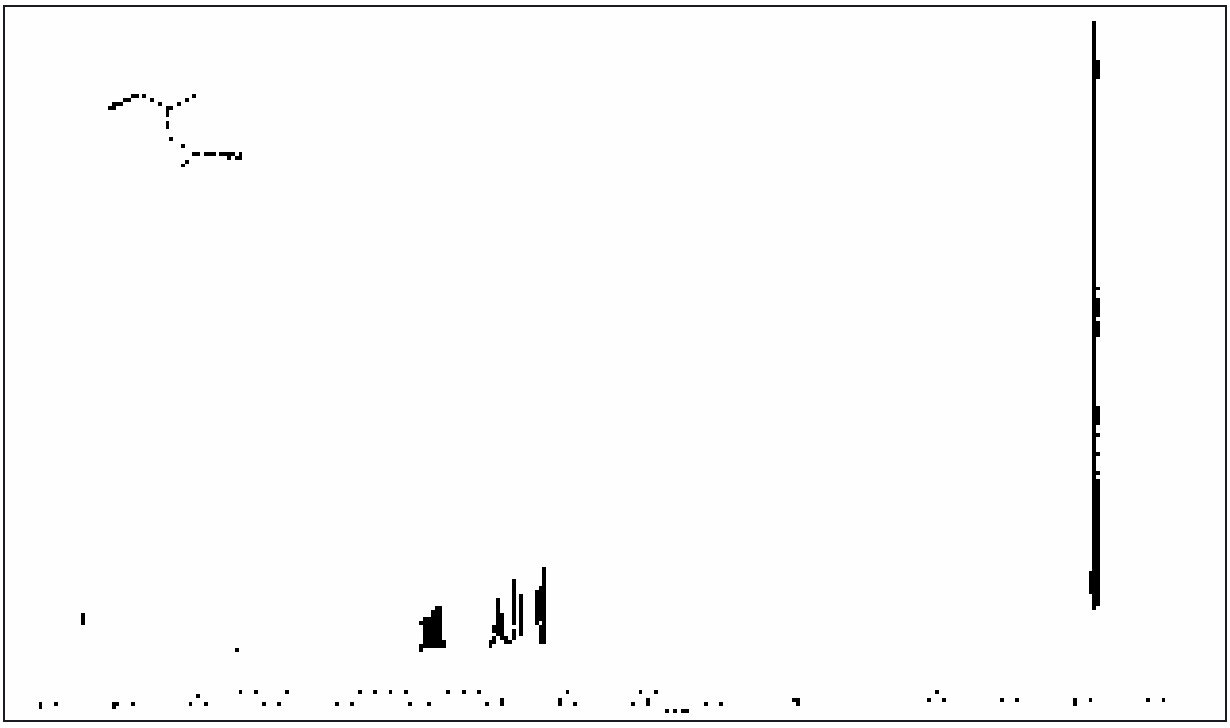
^{1}H-NMR Spectrum of Compound **127** and **128** (250 MHz, $CDCl_3$)



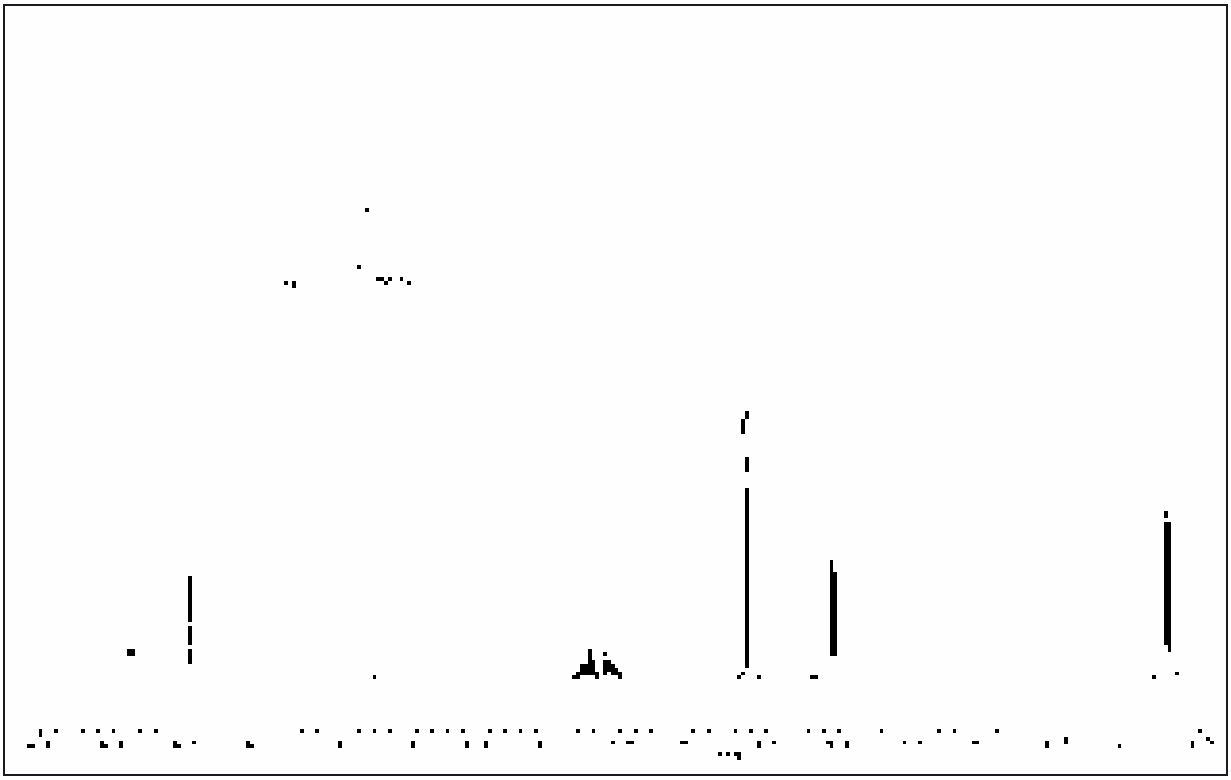
^{1}H-NMR Spectrum of Compound **129** (250 MHz, $CDCl_3$)



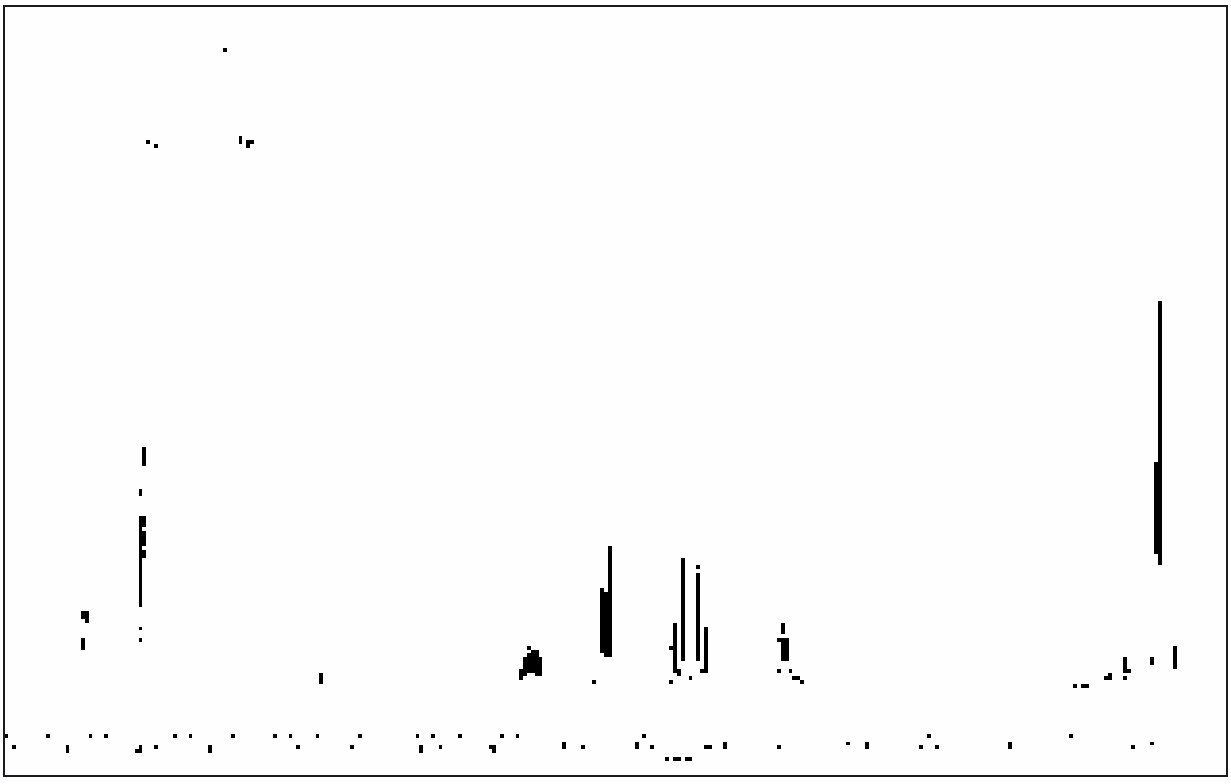
^{1}H-NMR Spectrum of Compound **132** (250 MHz, $CDCl_3$)



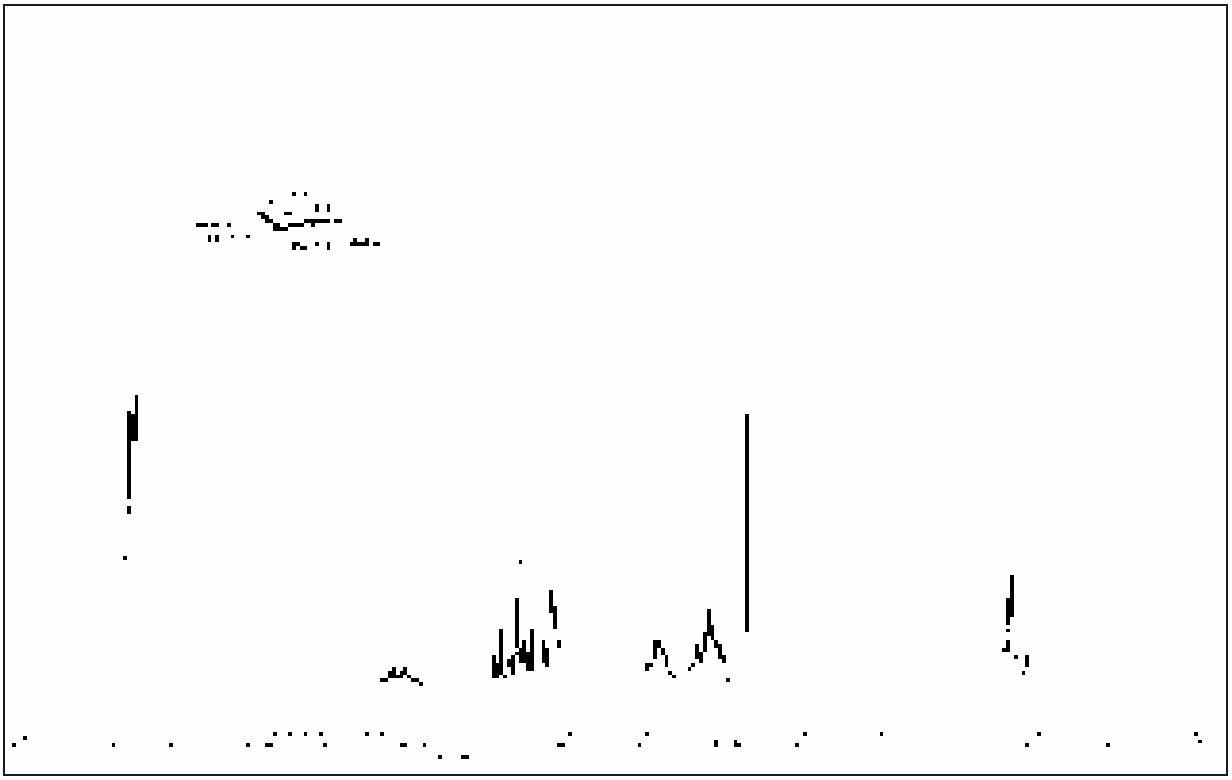
^{1}H-NMR Spectrum of Compound **133** (250 MHz, $CDCl_3$)



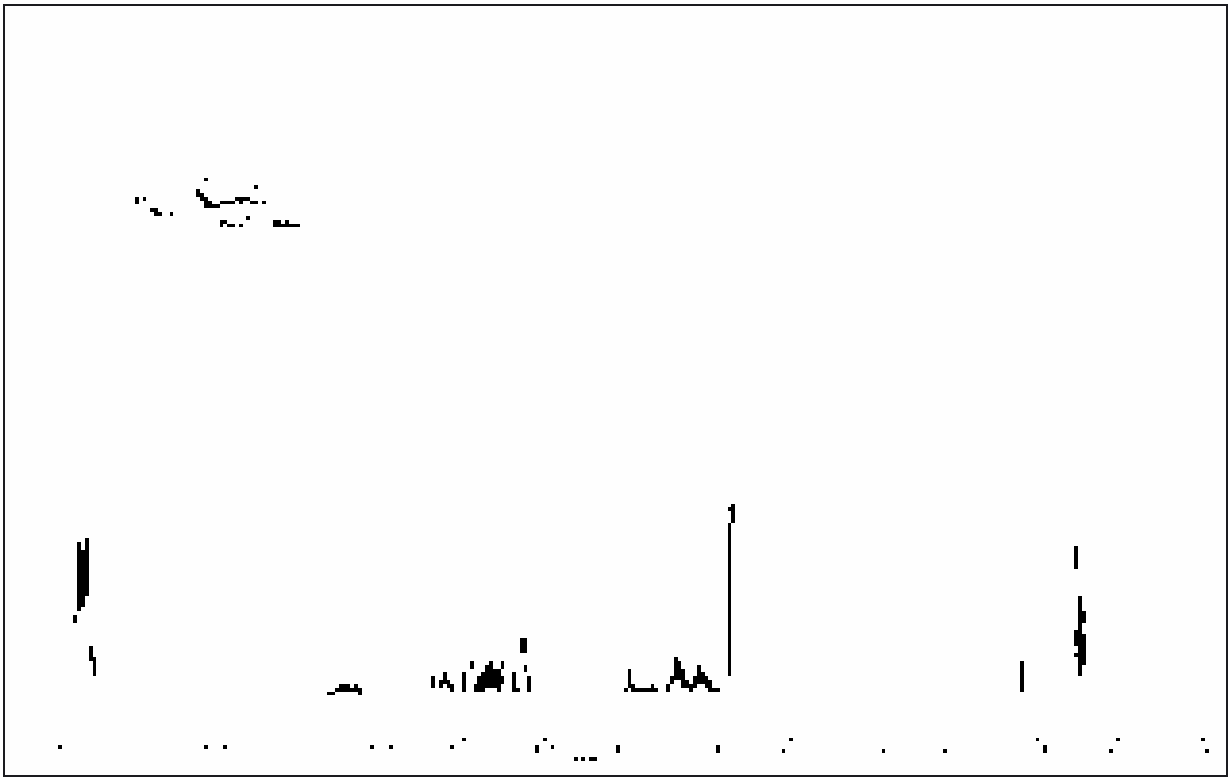
^{1}H-NMR Spectrum of Compound **134** (250 MHz, $CDCl_3$)



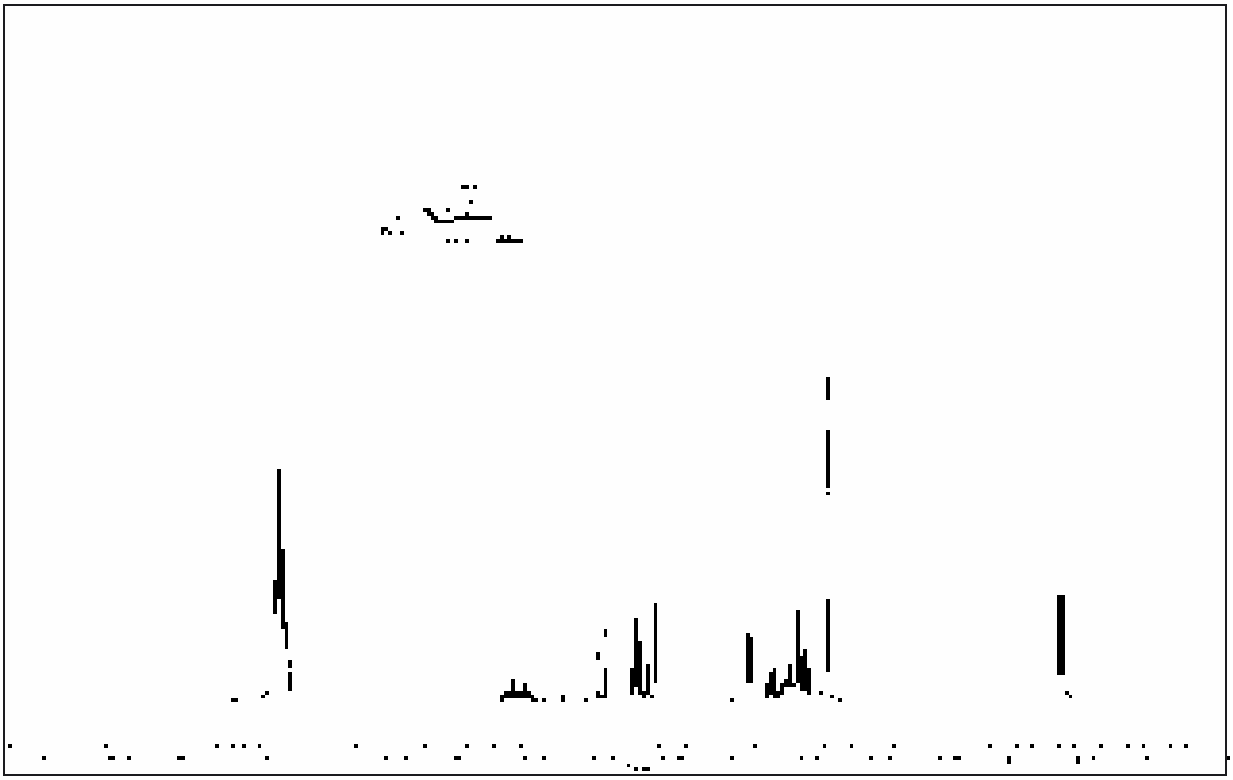
^{1}H-NMR Spectrum of Compound **135** (250 MHz, $CDCl_3$)



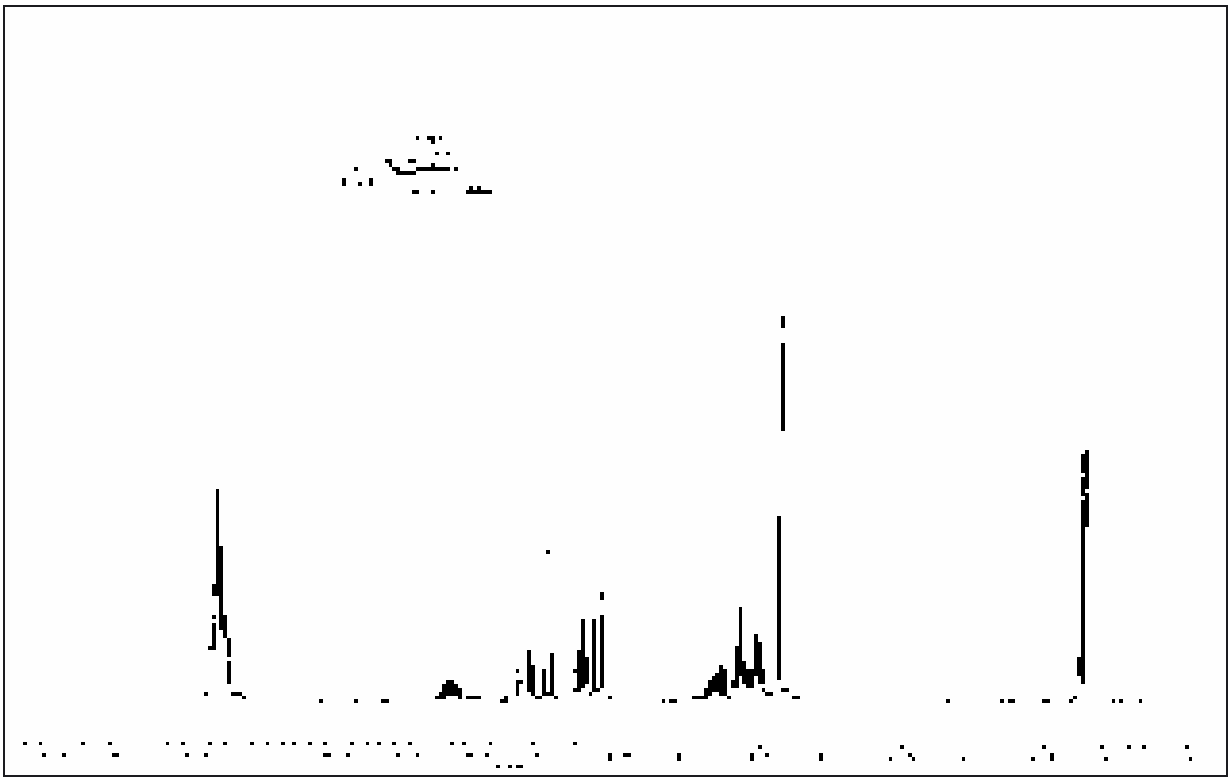
^{1}H-NMR Spectrum of Compound **136** (250 MHz, $CDCl_3$)



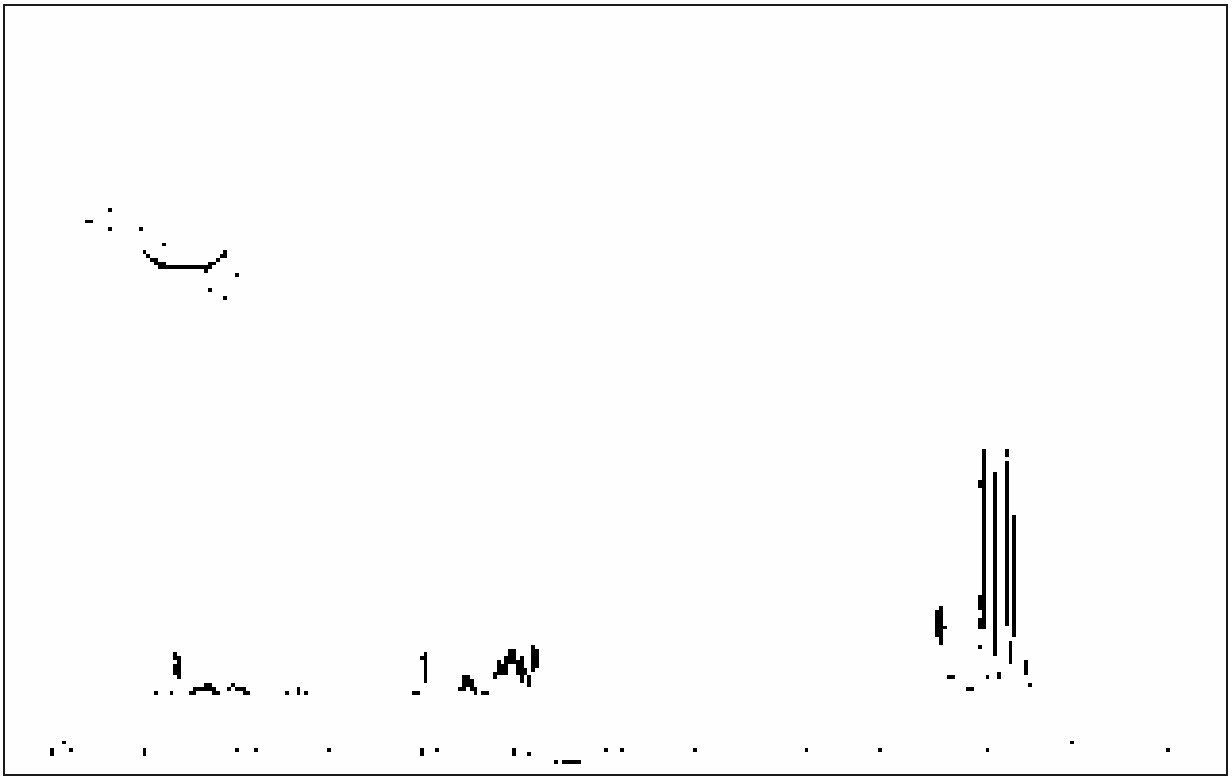
^{1}H-NMR Spectrum of Compound **137** (250 MHz, $CDCl_3$)



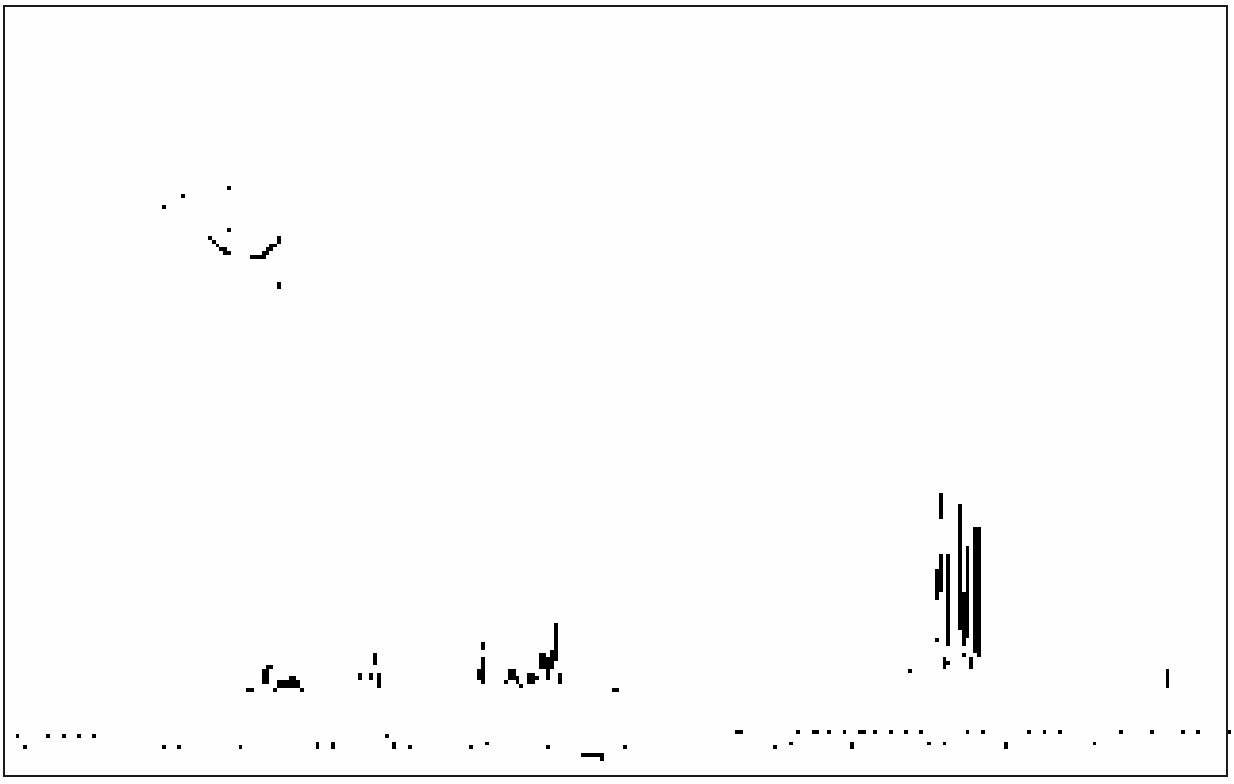
^{1}H-NMR Spectrum of Compound **138** (250 MHz, $CDCl_3$)



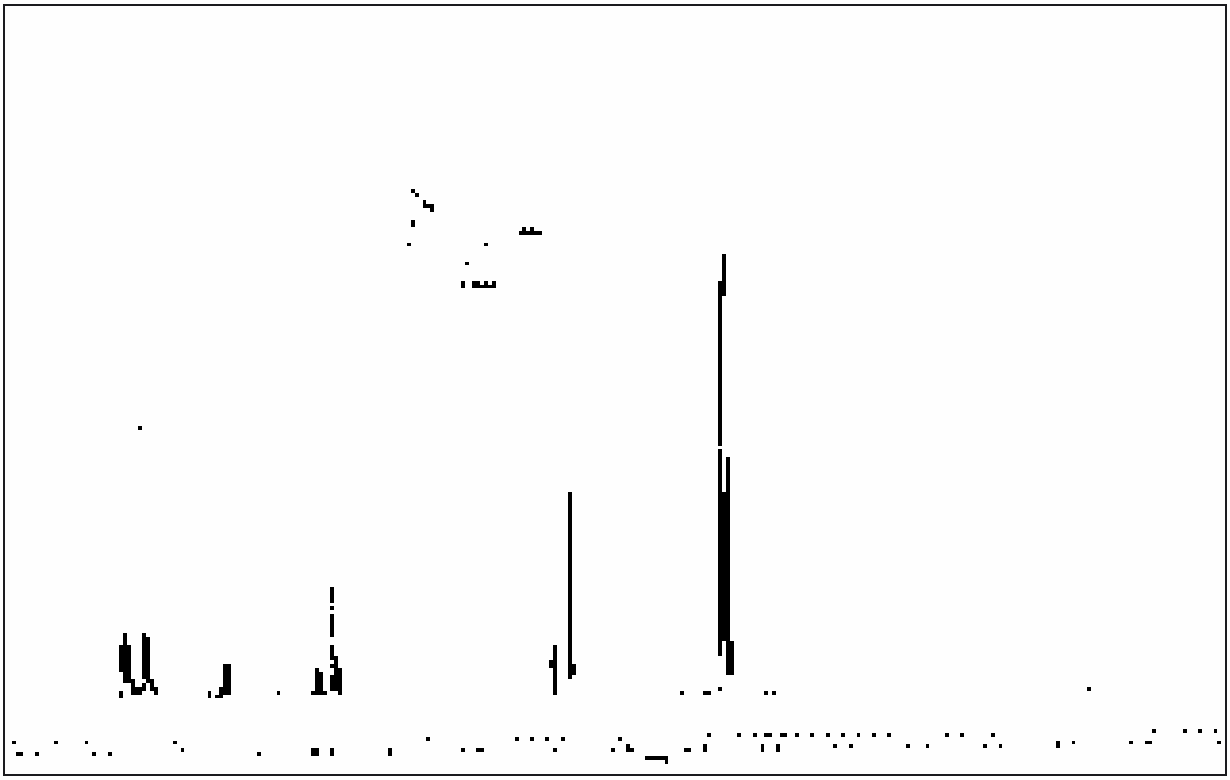
^{1}H-NMR Spectrum of Compound **139** (250 MHz, $CDCl_3$)



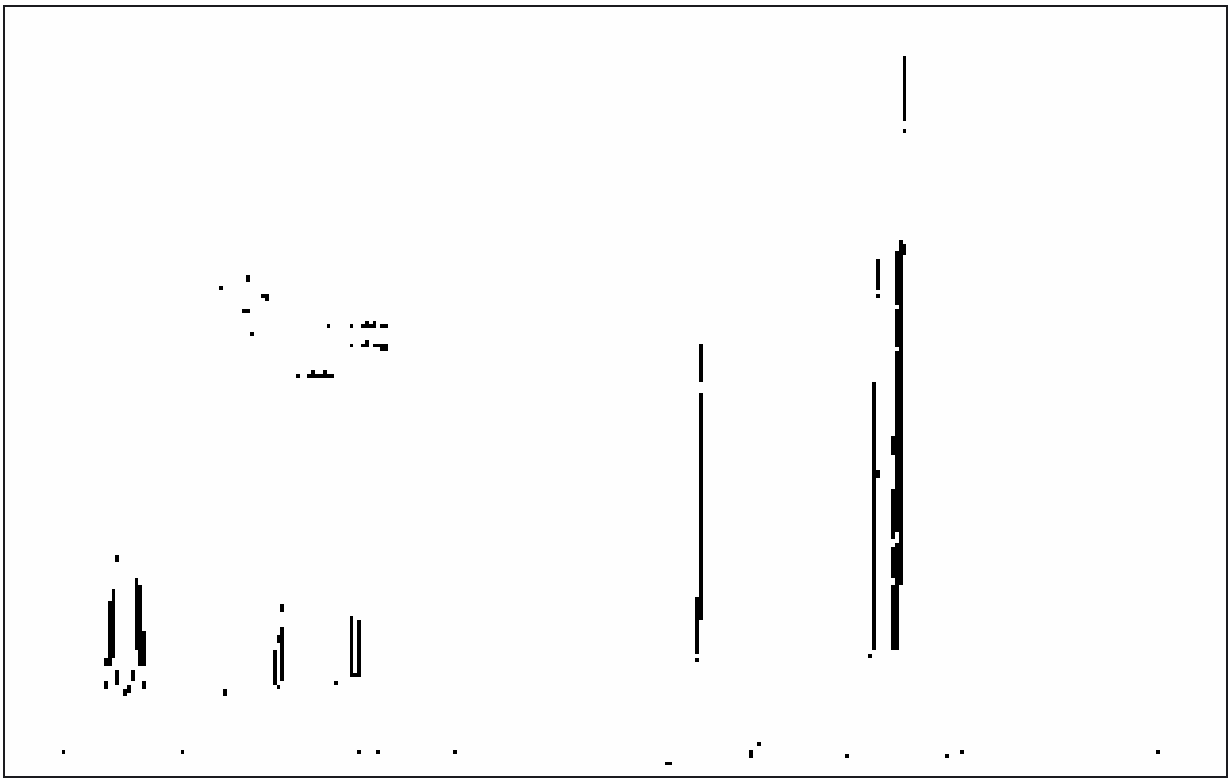
^{1}H-NMR Spectrum of Compound **140** (250 MHz, $CDCl_3$)



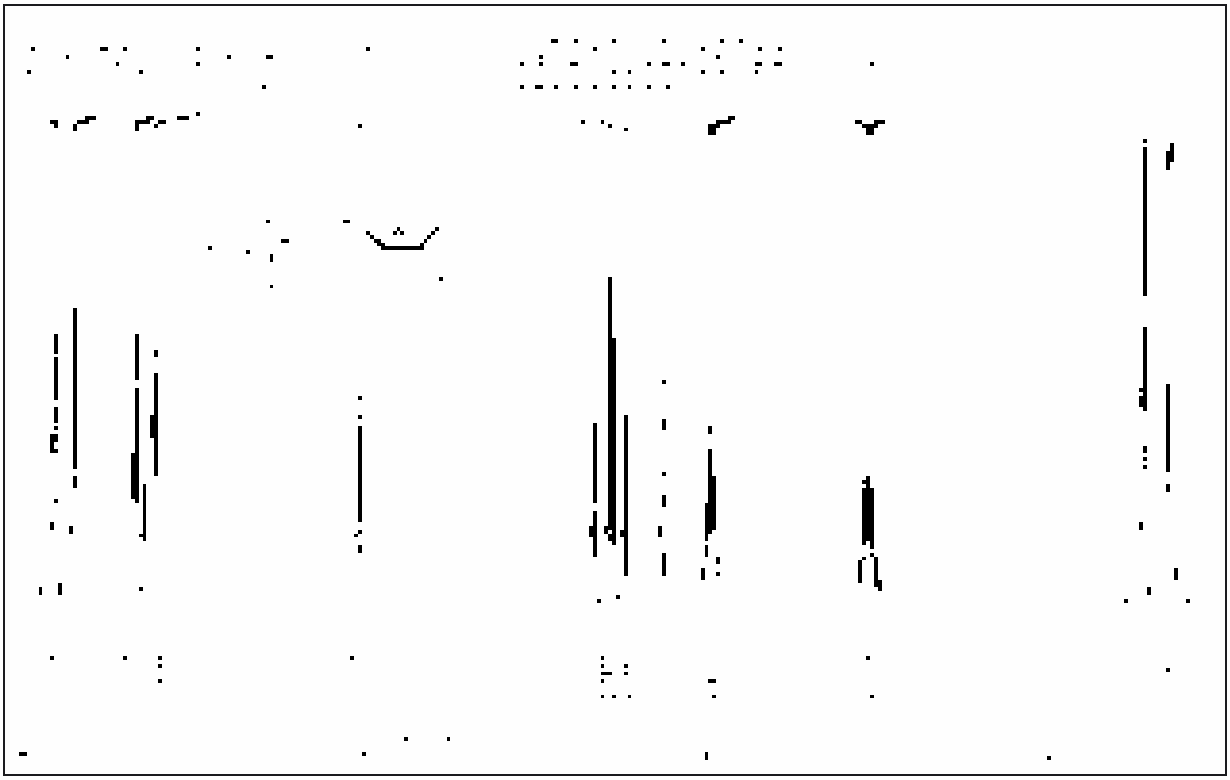
^{1}H-NMR Spectrum of Compound **141** (250 MHz, $CDCl_3$)



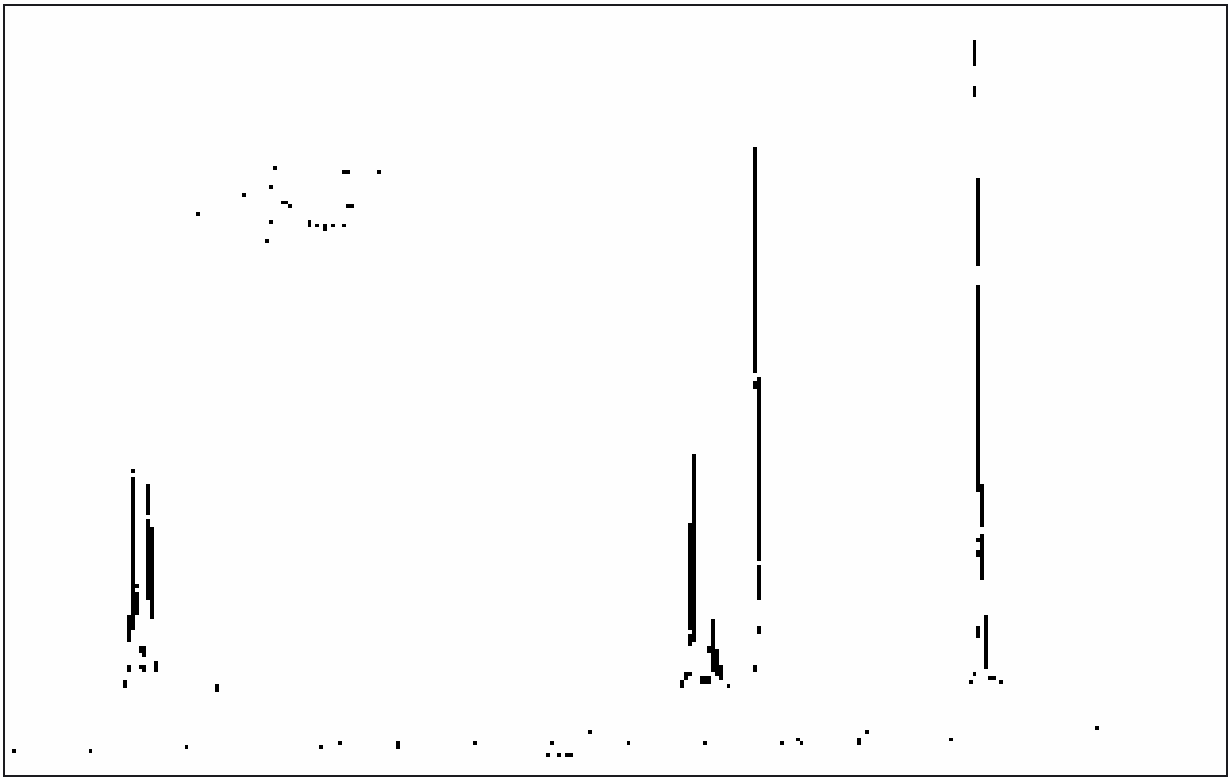
^{1}H-NMR Spectrum of Compound **147** (250 MHz, $CDCl_3$)



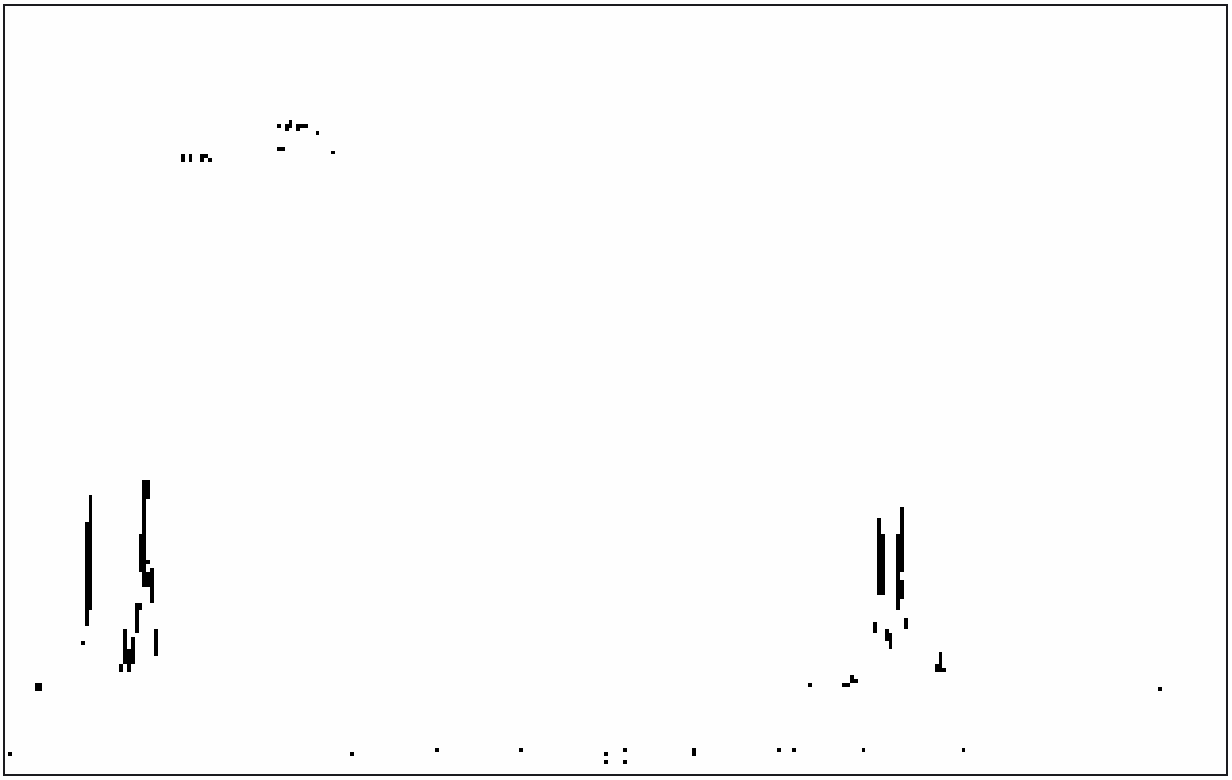
^{1}H-NMR Spectrum of Compound **148** (250 MHz, $CDCl_3$)



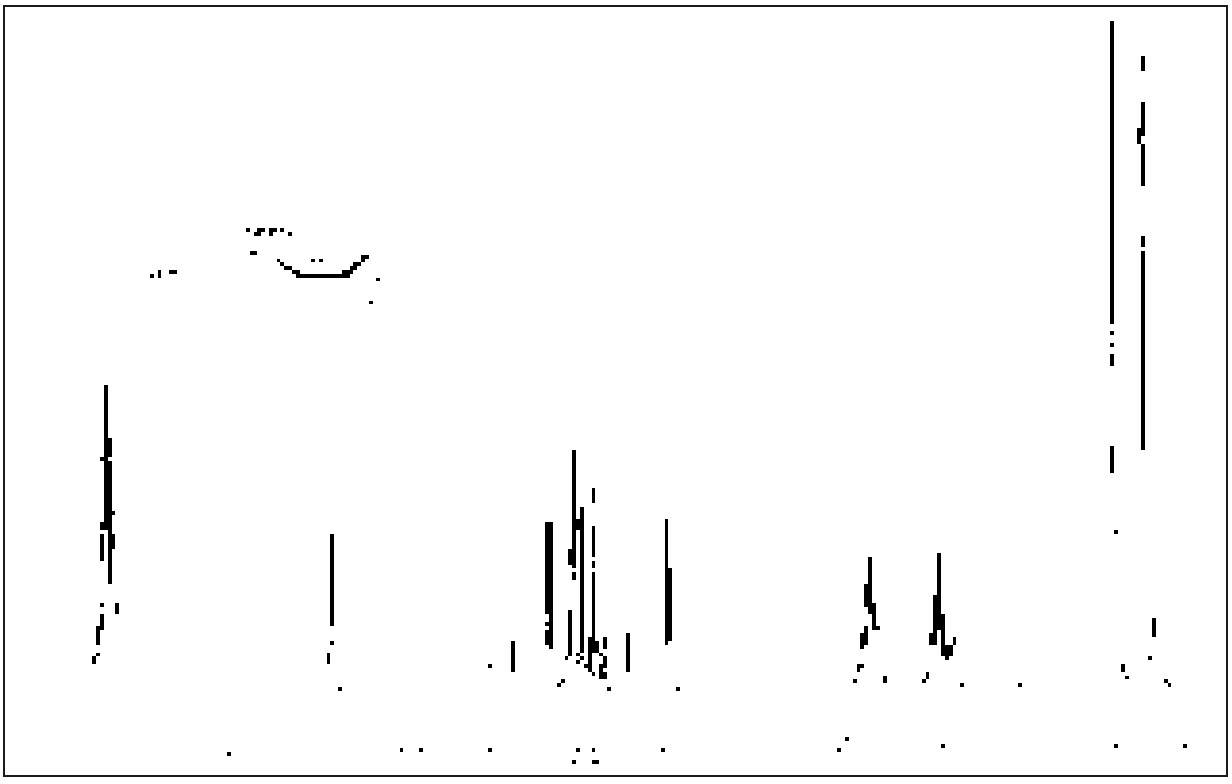
^{1}H-NMR Spectrum of Compound **157** (600 MHz, $CDCl_3$)



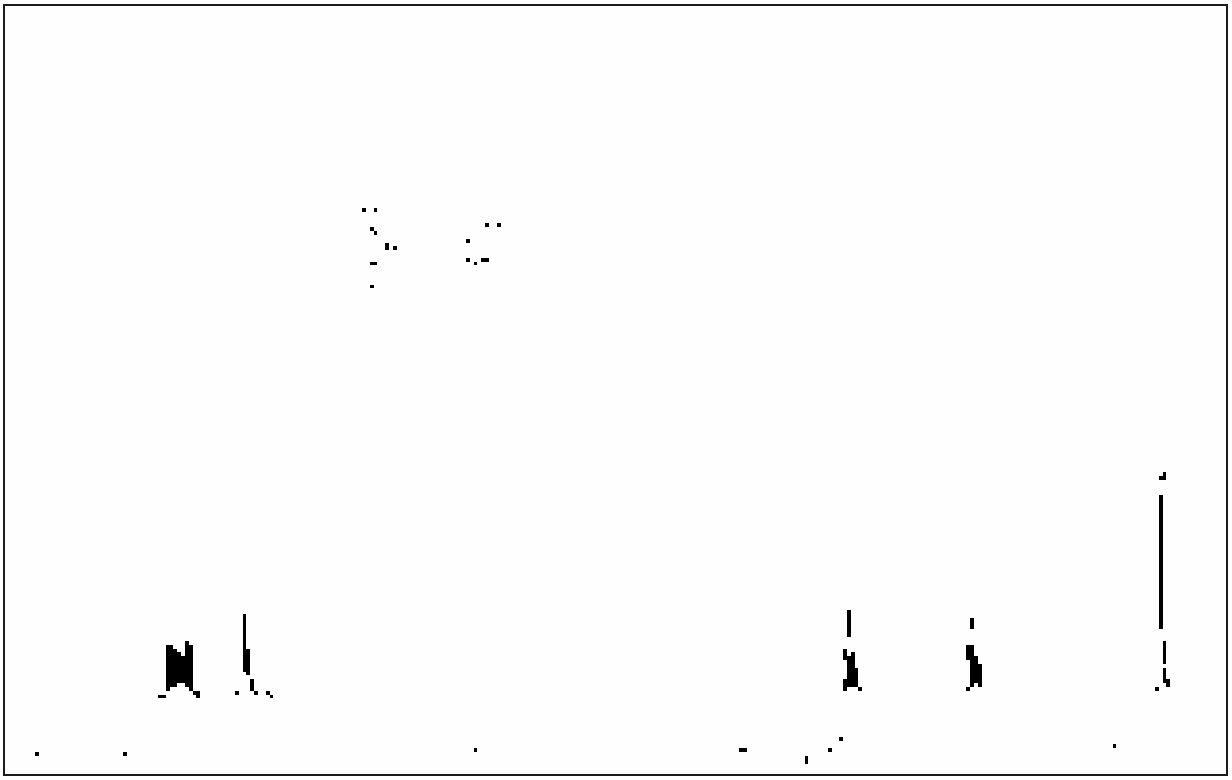
^{1}H-NMR Spectrum of Compound **160** (250 MHz, $CDCl_3$)



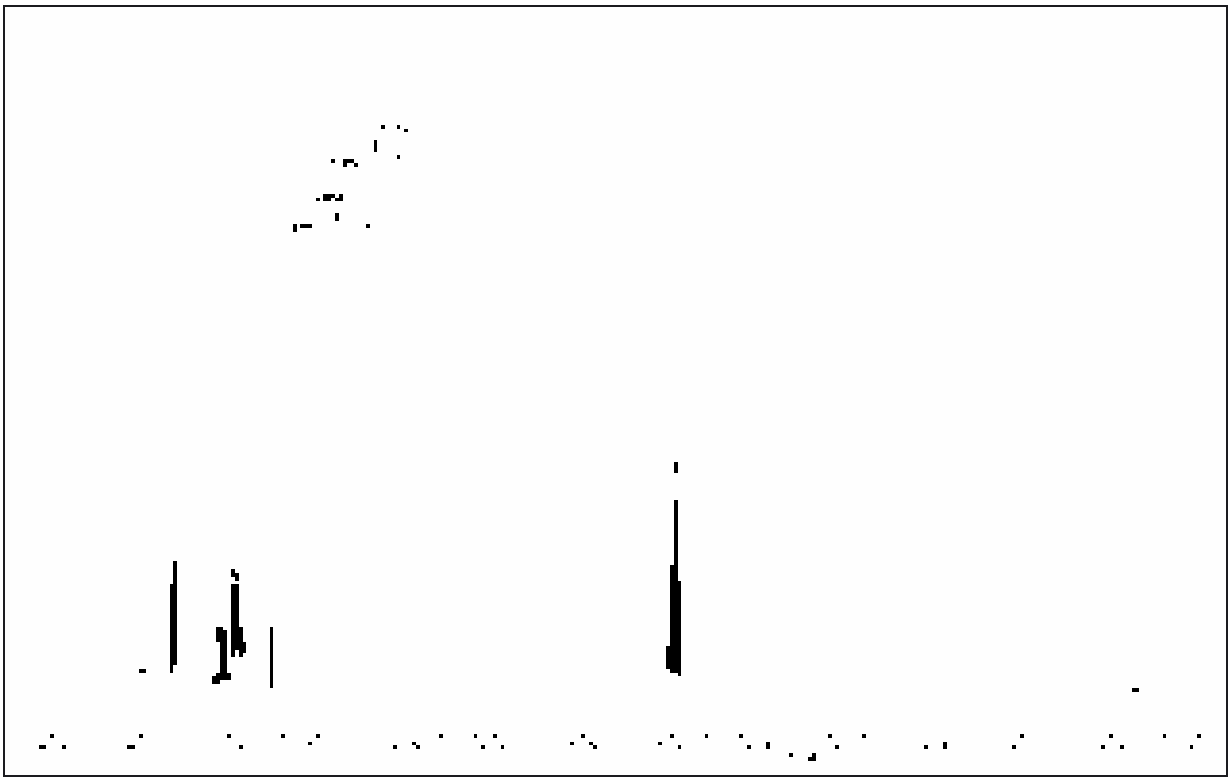
^{1}H-NMR Spectrum of Compound **165** (250 MHz, $CDCl_3$)



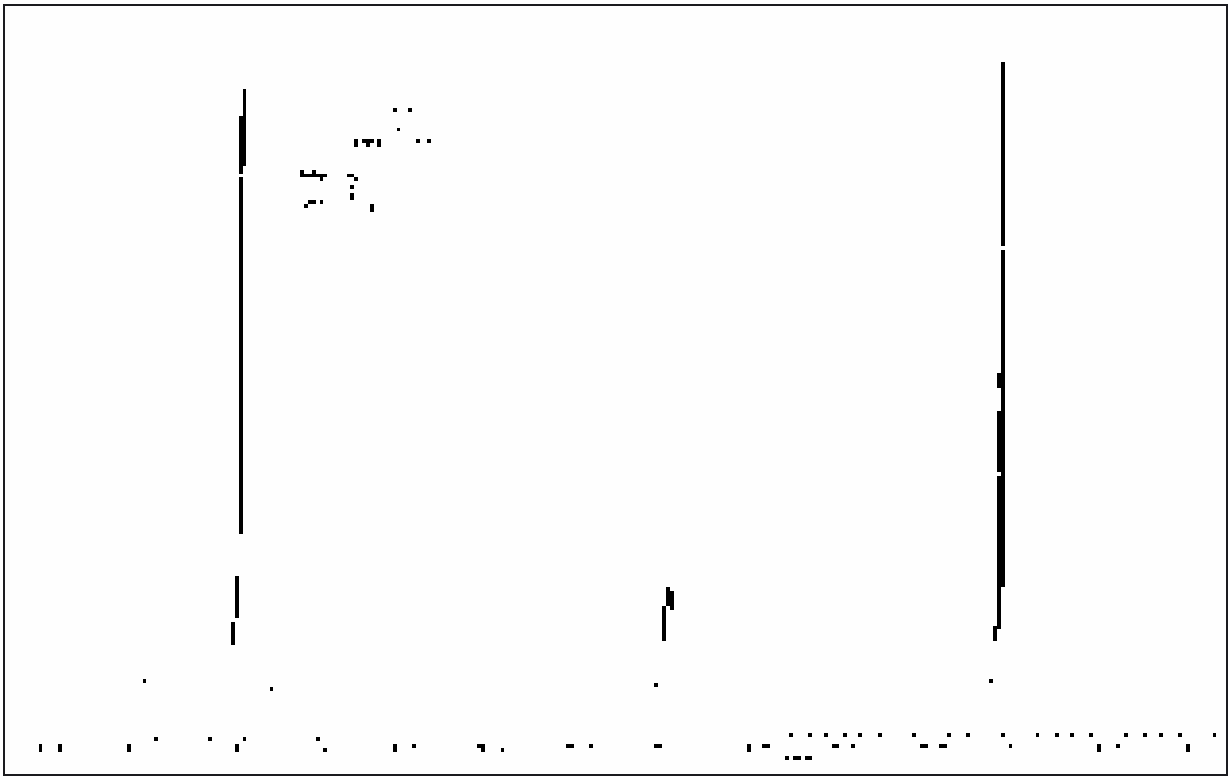
^{1}H-NMR Spectrum of Compound **166** (250 MHz, $CDCl_3$)



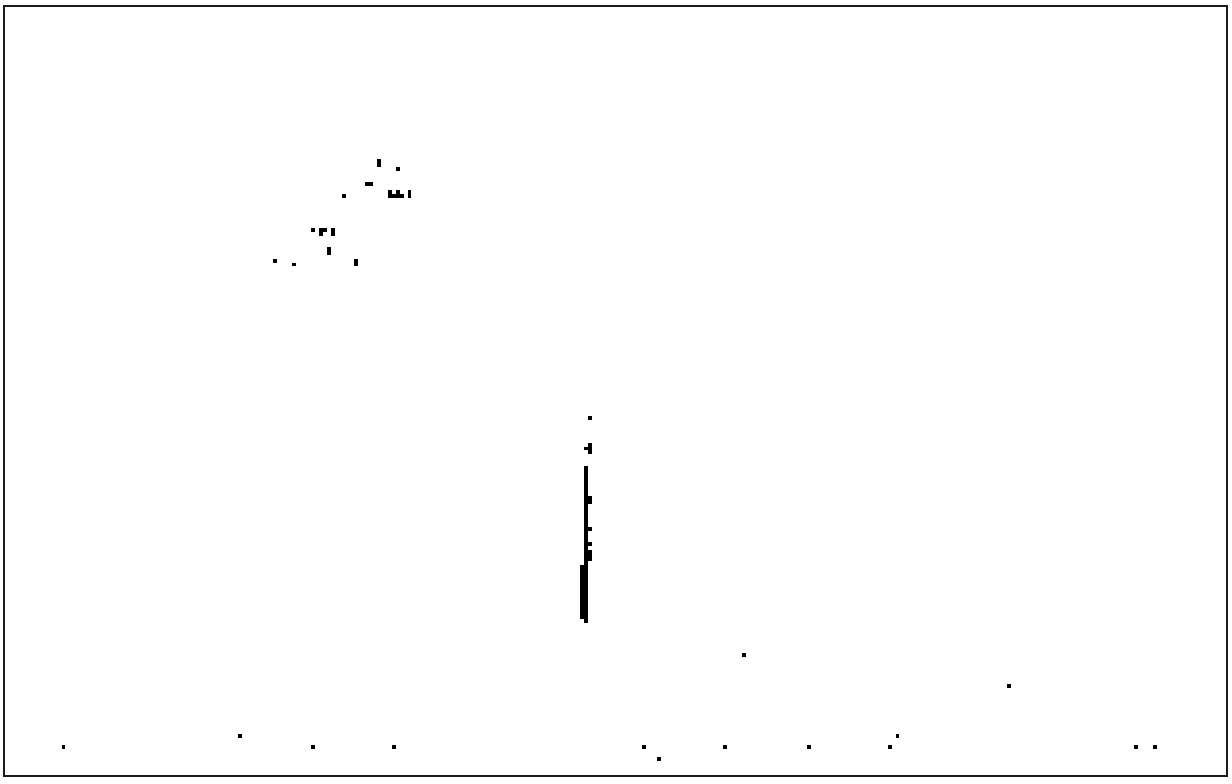
^{1}H-NMR Spectrum of Compound **167** (250 MHz, $CDCl_3$)



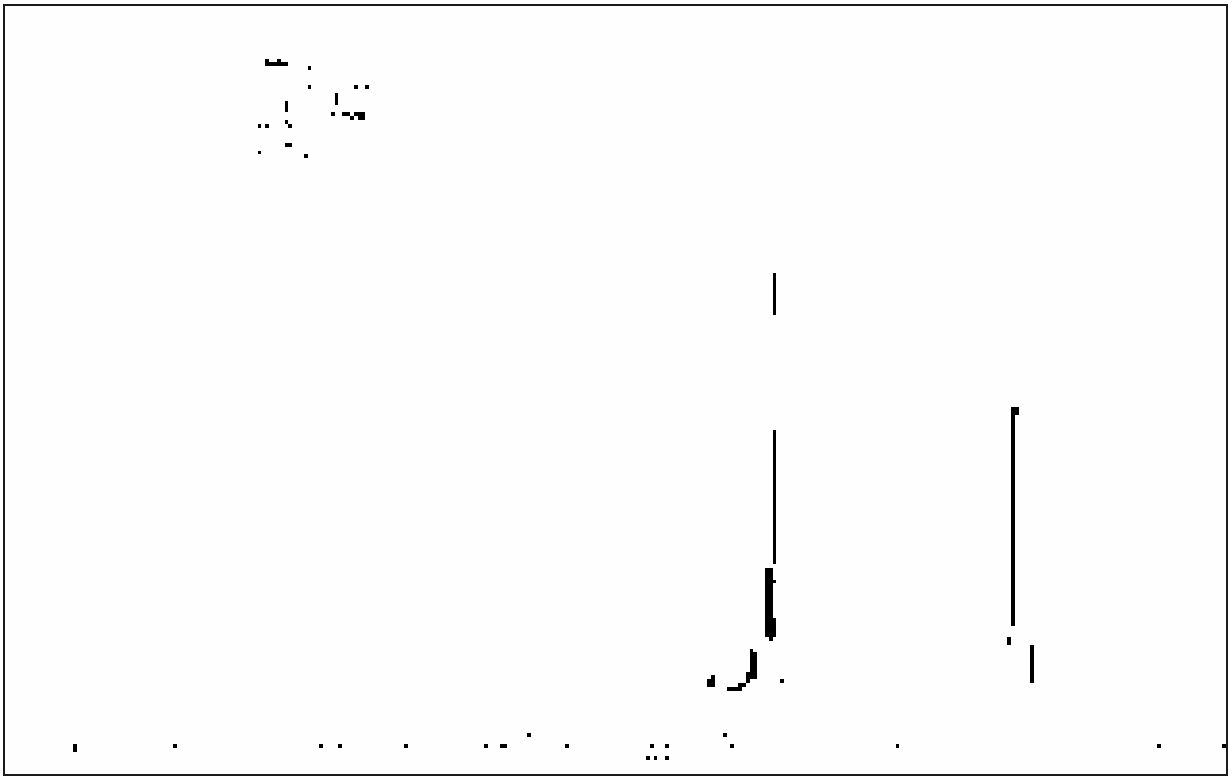
^{1}H-NMR Spectrum of Compound **172** (250 MHz, $CDCl_3$)



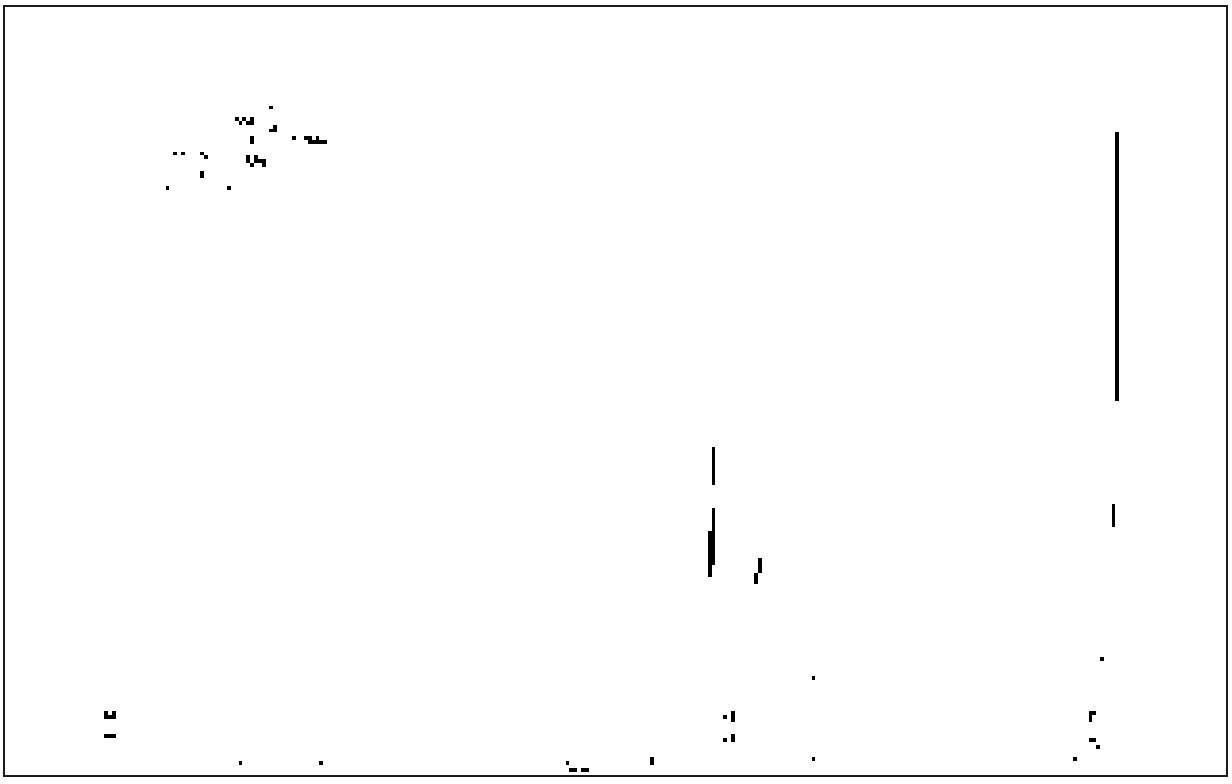
^{1}H-NMR Spectrum of Compound **173** (250 MHz, $CDCl_3$)



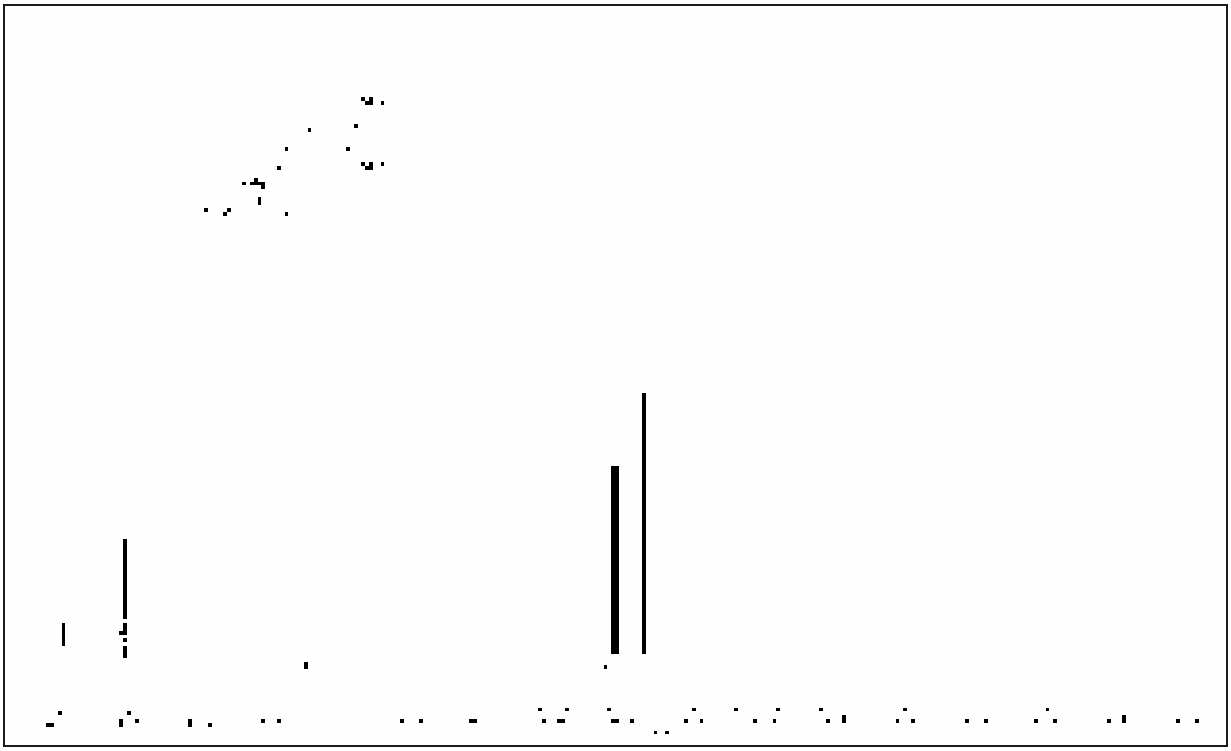
^{1}H-NMR Spectrum of Compound **175** (250 MHz, $CDCl_3$)



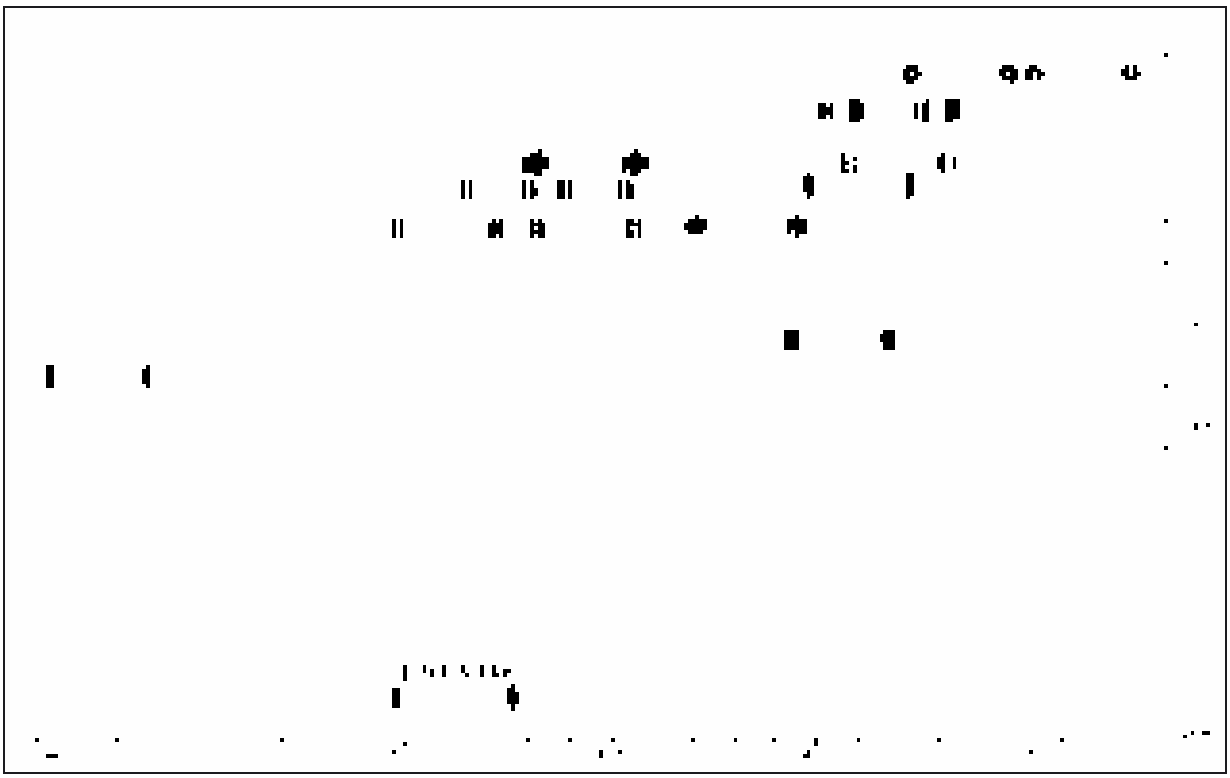
^{1}H-NMR Spectrum of Compound **177** (250 MHz, $CDCl_3$)



^{1}H-NMR Spectrum of Compound **178** (250 MHz, $CDCl_3$)

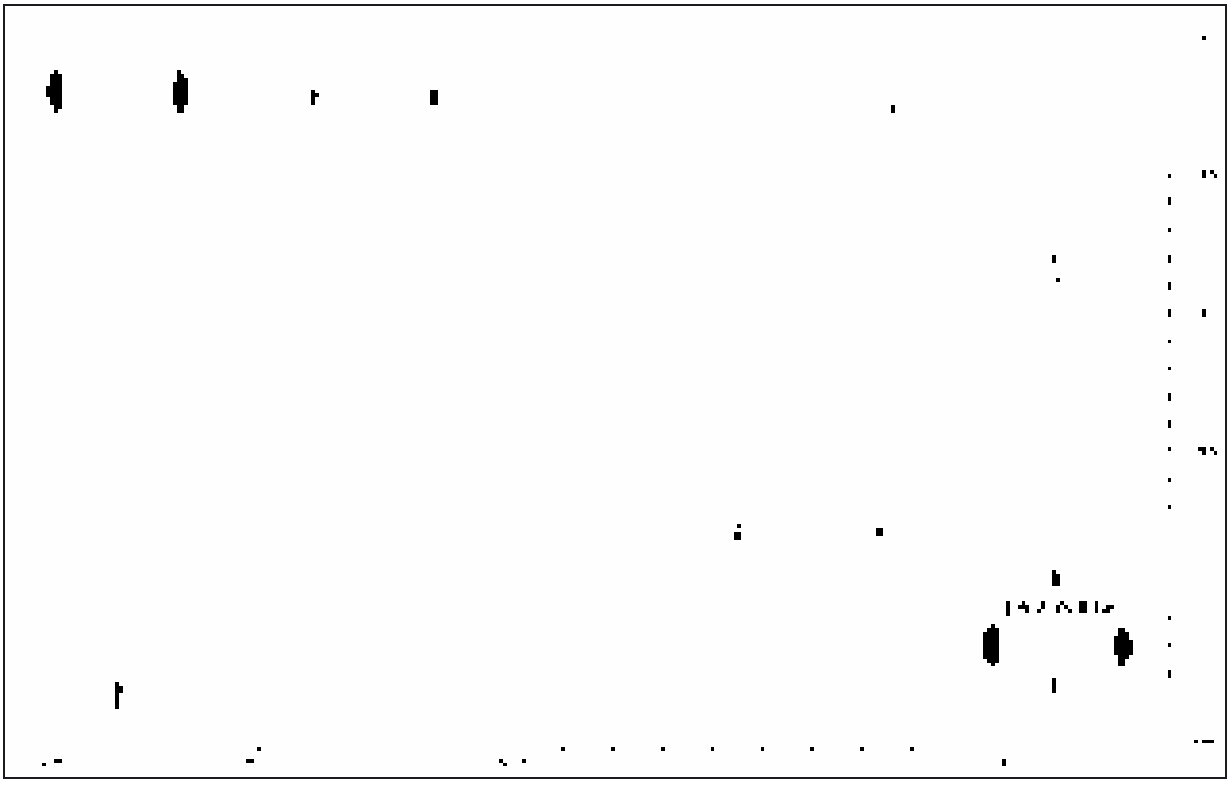


^{1}H-NMR Spectrum of Compound **179** (250 MHz, $CDCl_3$)



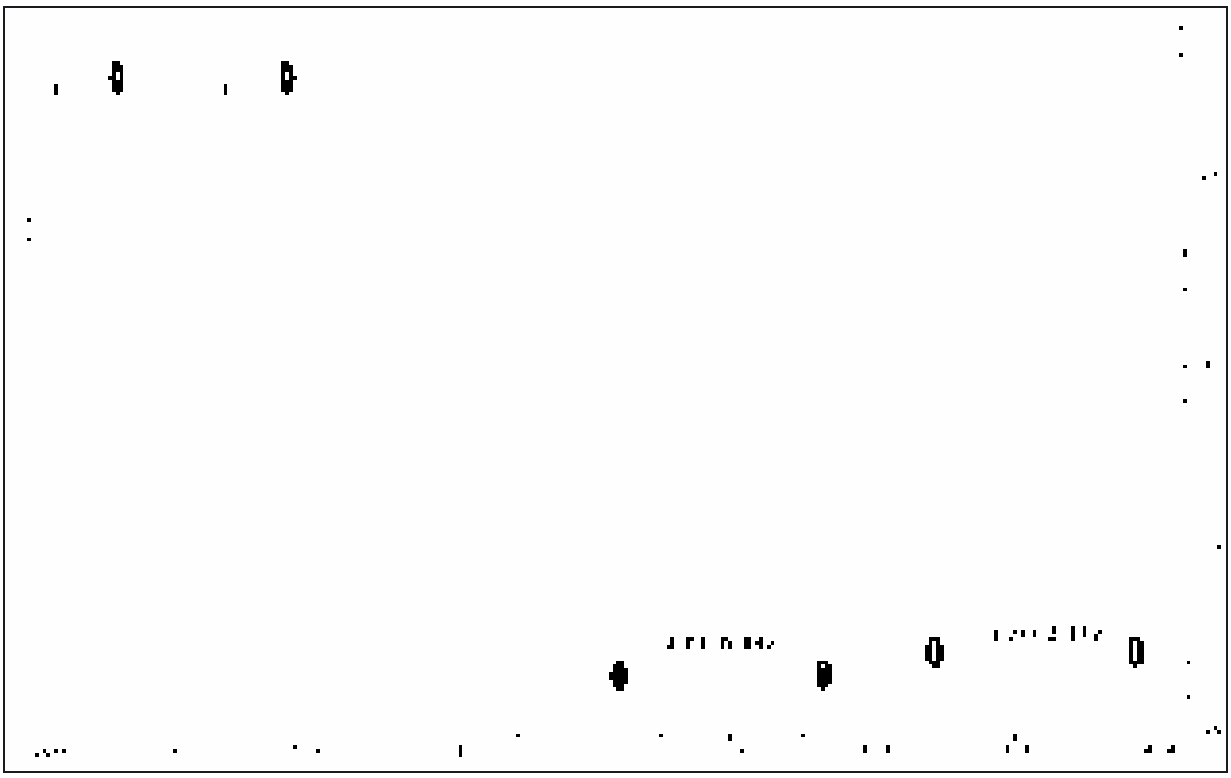
HMQC Spectrum of Compound **81** ζ#

#

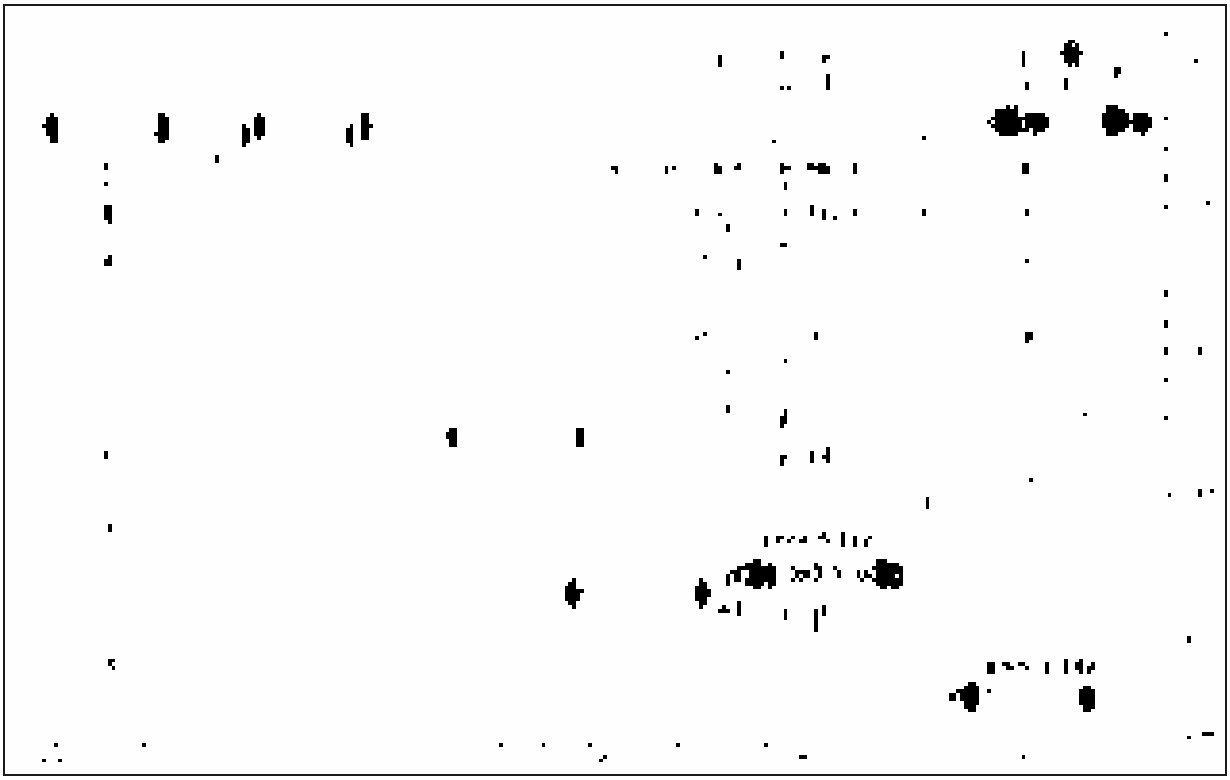


HMQC Spectrum of Compound **81**η#

#

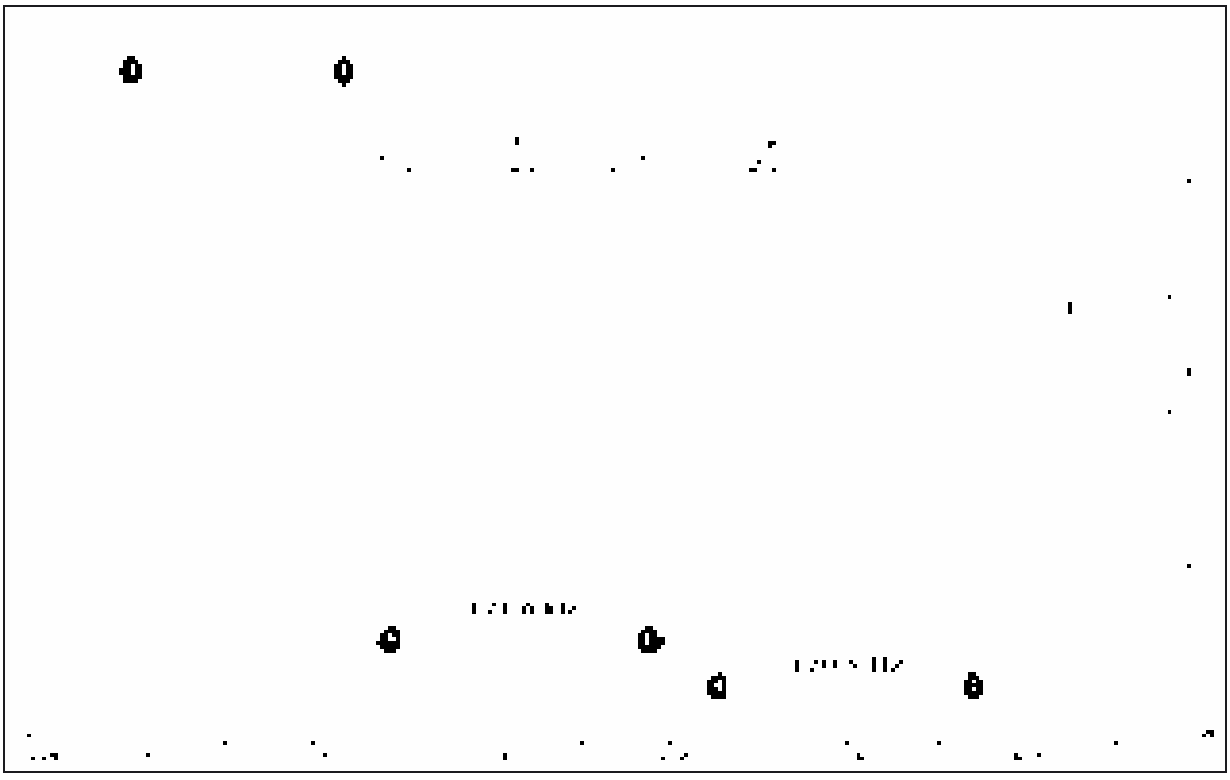


HMQC Spectrum of Compound **82** ζ#

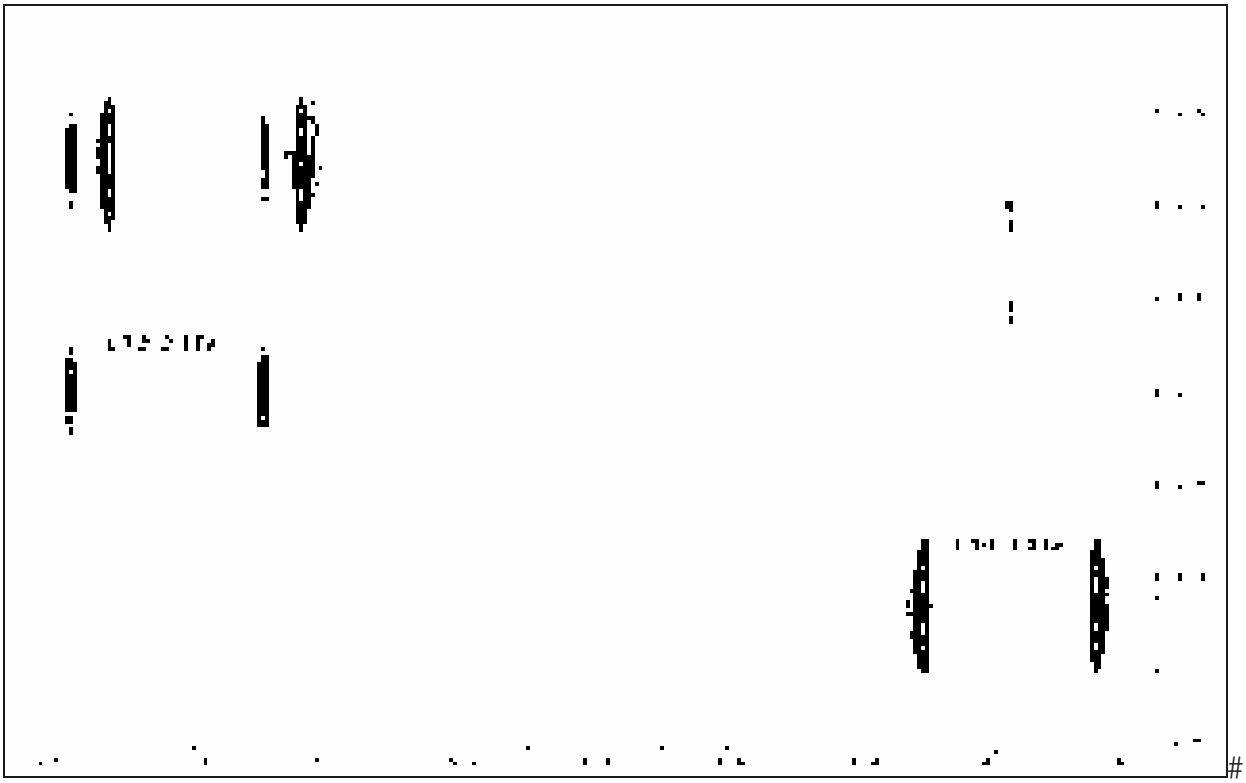


HMQC Spectrum of Compound **82** η#

#



HMQC Spectrum of Compound **85** ζ#

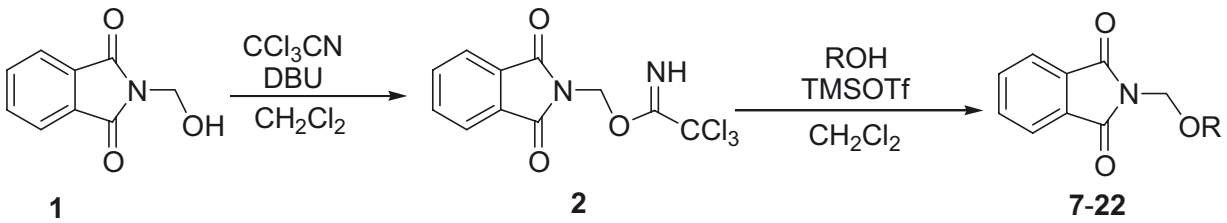


HMQC Spectrum of Compound **85** η#

4. Summary Part

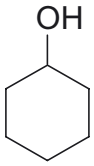
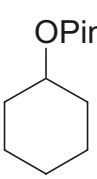
4.1 Phthalimidomethyl as protecting group.

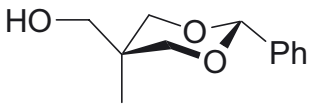
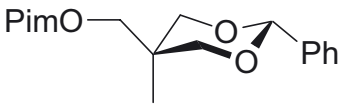
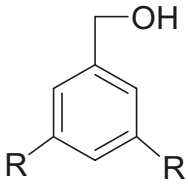
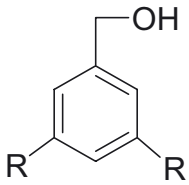
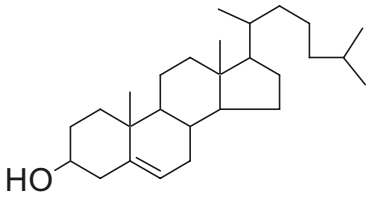
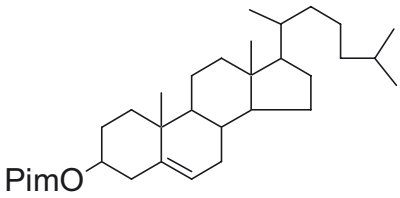
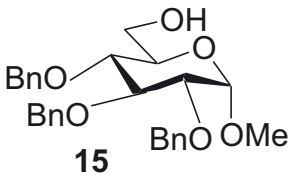
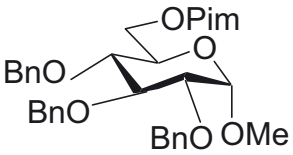
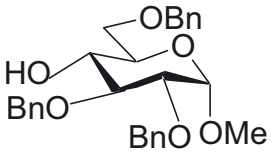
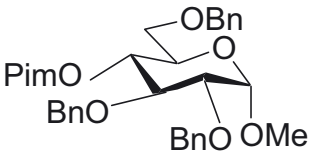
A successful multi-step synthesis of complex oligosaccharide structures requires an appropriate protecting group strategy. Generally, the presence of three or more hydroxy groups in each sugar residue necessitates the protection of those hxdroxy groups which are not involved in the glycosylation step. In our study, the phthalimidomethyl protecting group has been used for the protection of hydroxy groups. The trichloroacetimidate **2** was prepared by the reaction of *N*-hydroxymethyl phthalimide (**1**) with trichloroacetonitrile in dichloromethane as solvent and in the presence of DBU in 87 % yield. The trichloroacetimidate **2** was reacted with primary and secondary hydroxy groups in various types of organic compounds (Table 4.1).

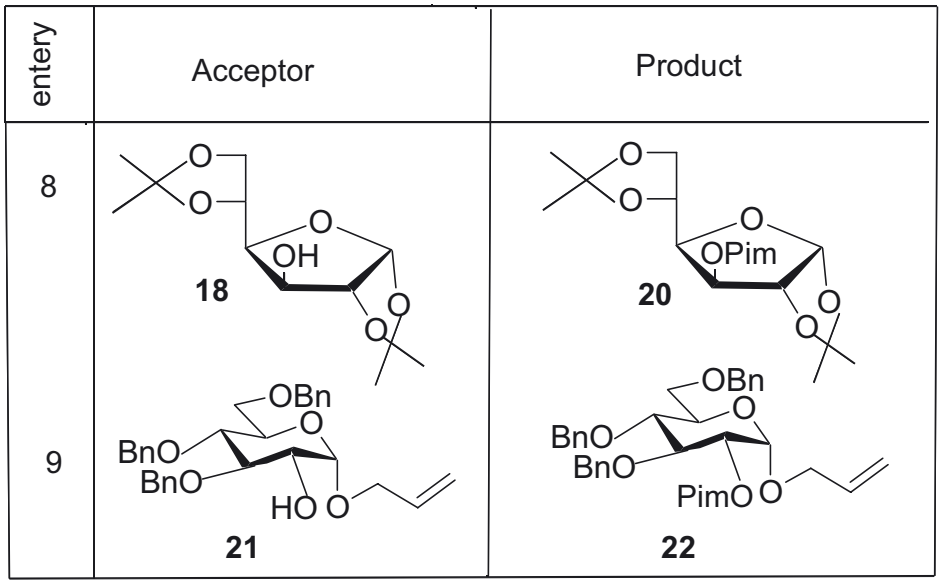


1 **2** **7-22**

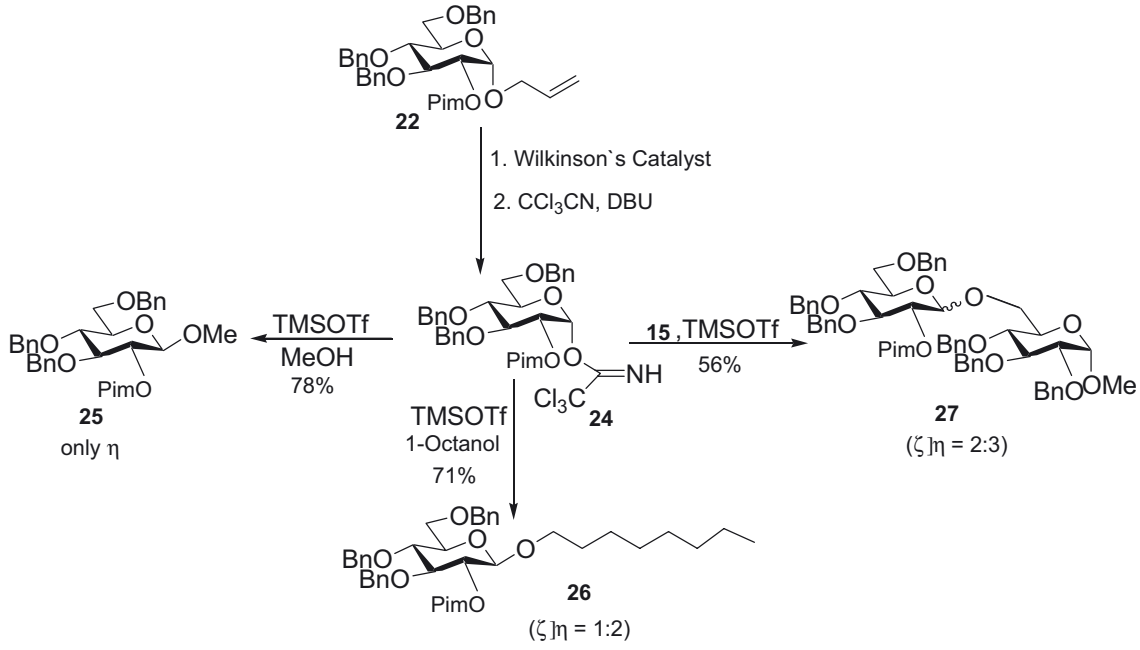
Table 4.1 Reaction of alcohols **3-21** with phthalimido trichloroacetimidate

entery	Acceptor	Product
1	 **3**	 **7**
2	 **4**	 **8**

entery	Acceptor	Product
3	 **6**	 **9**
4	 **5** R = H **11** R = NO_2	 **10** R = H **13** R = NO_2
5	 **12**	 **14**
6	 **15**	 **16**
7	 **17**	 **19**

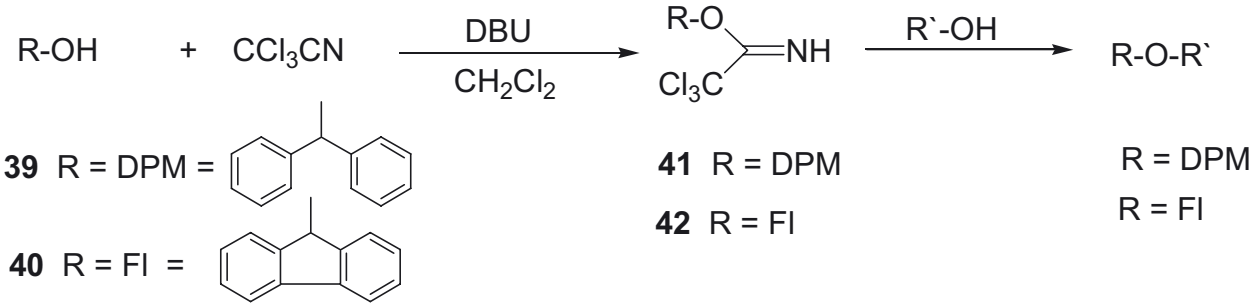


The deallylation of *O*-1 in **22** which possesses a phthalimidomethyl group on *O*-2 and reaction with trichloroacetonitrile in the presence of DBU as a base led to trichloroacetimidate **24**. Glycosylation of methanol, n-octanol and 6-*O*-unprotected glucopyranoside **15** with **24** as glycosyl donor in the presence of TMSOTf as a catalyst afforded glucosides **25**-**27** in high yields. Thus, it was demonstrated that the Pim group on *O*-2 controls the anomeric selectivity essentially based on steric hindrance.



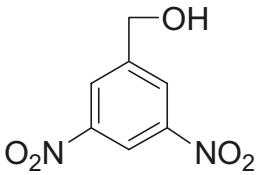
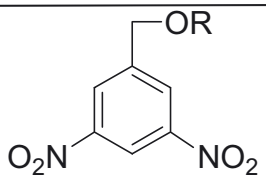
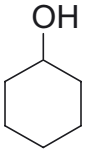
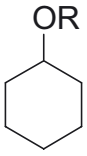
4.2 Diphenyl carbinol and fluorenol as protecting groups.

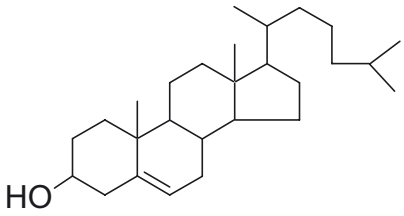
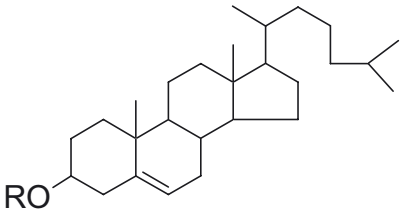
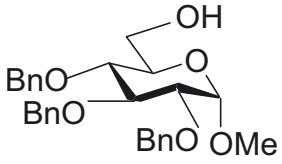
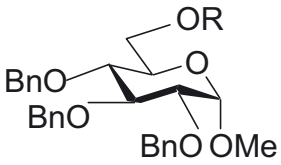
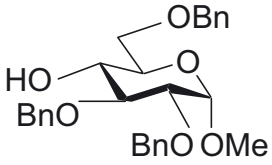
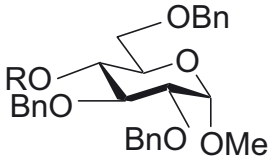
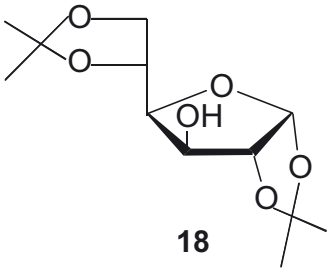
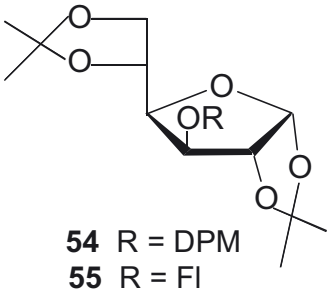
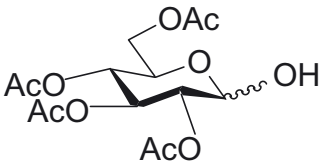
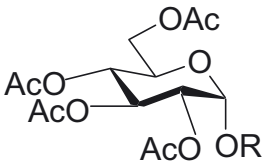
The required trichloroacetimidates **41** and **42** of the DPM [128] and Fl, respectively, were prepared by the reaction of diphenylmethanol (**39**) and 9-fluorenol (**40**), with trichloroacetonitrile in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as catalyst.

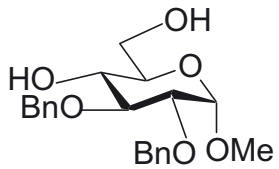
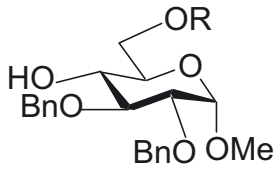
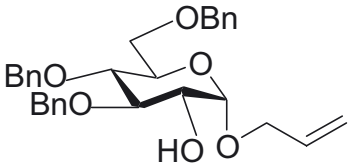
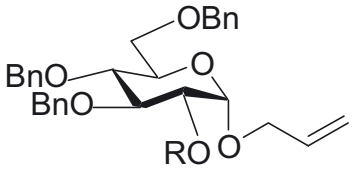


Also, trichloroacetimidates **41** and **42** were reacted with different hydroxy groups in alcohols and carbohydrates (Table 4.2).

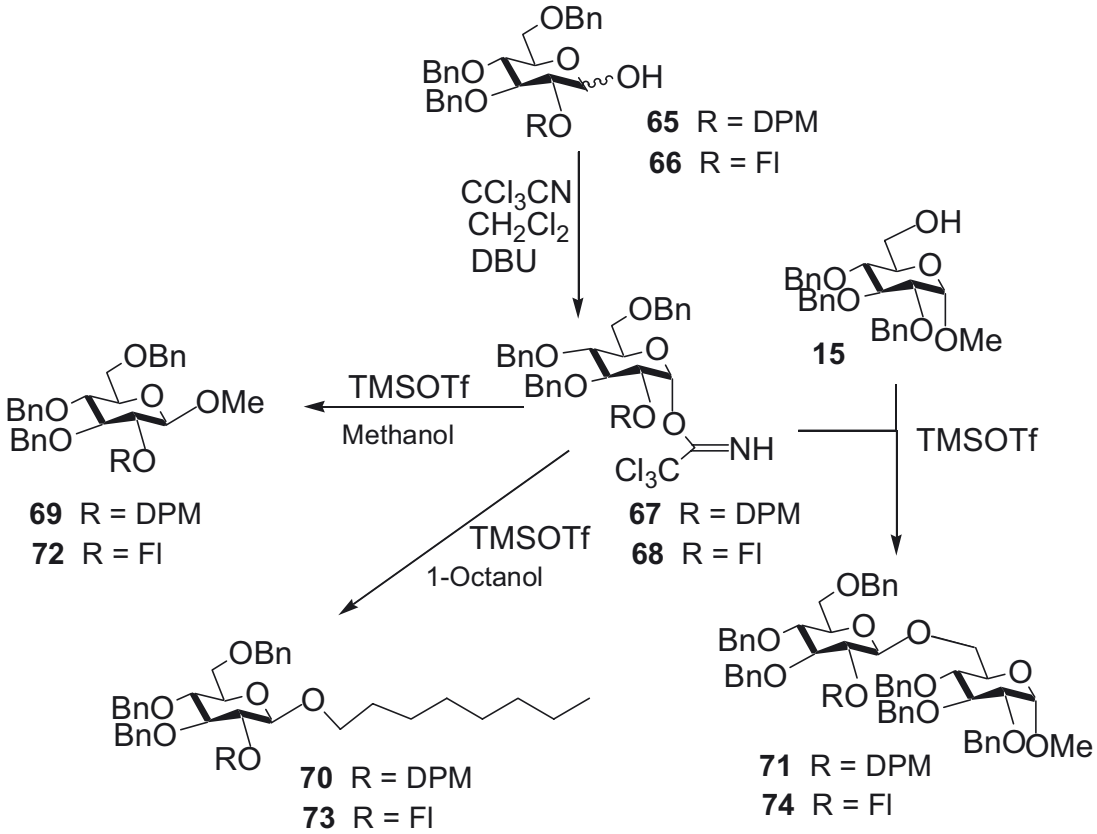
Table 4.2. Reaction of alcohols **3**-**21** with *O*-DPM and *O*-Fl trichloroacetimidates

Entery	Acceptor	Product
1	 **11**	 **43** R = DPM **44** R = Fl
2	 **3**	 **45** R = DPM **46** R = Fl
3	 **4**	 **47** R = DPM

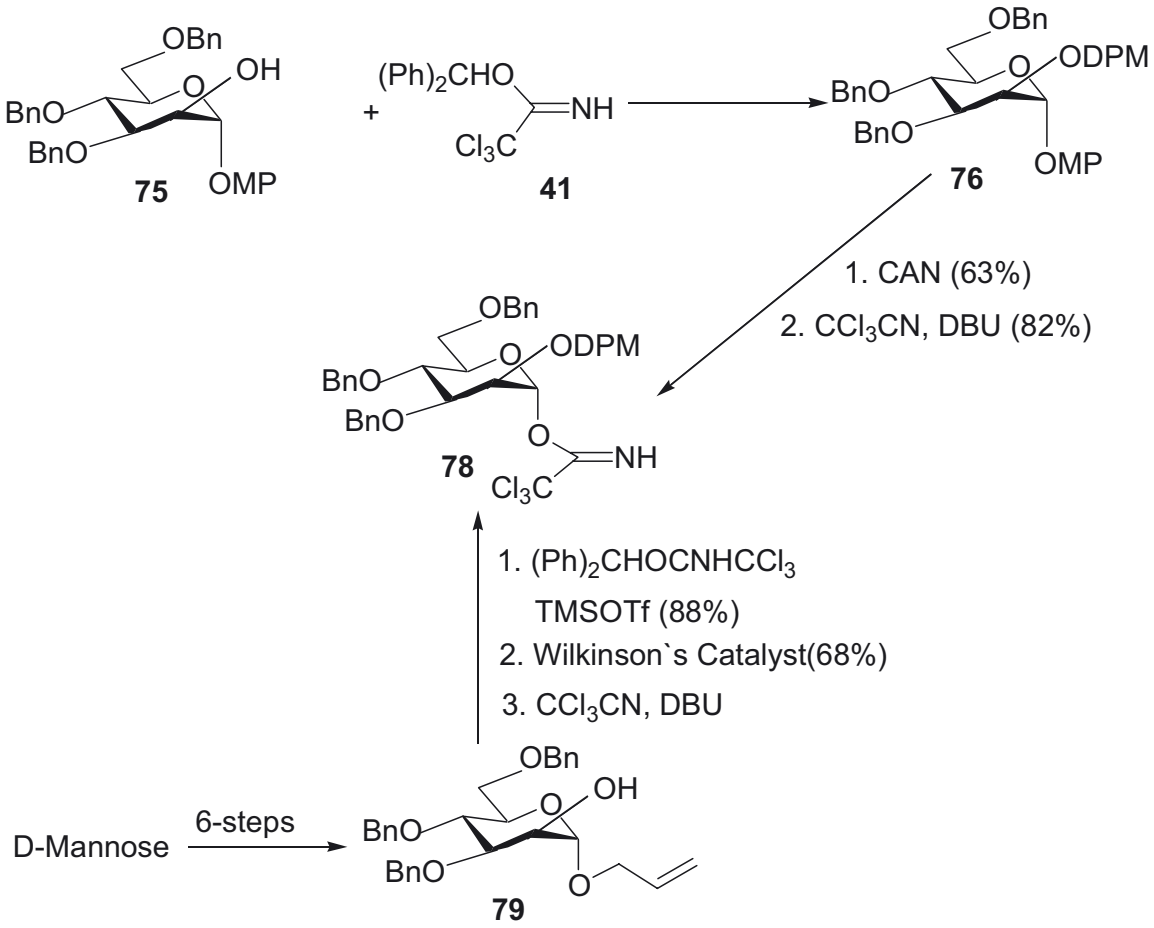
Entery	Acceptor	Product
4	 **12**	 **48** R = DPM **49** R = Fl
5	 **15**	 **50** R = DPM **51** R = Fl
6	 **17**	 **52** R = DPM **53** R = Fl
7	 **18**	 **54** R = DPM **55** R = Fl
8	 **56**	 **57** R = DPM **58** R = Fl

Entery	Acceptor	Product
9	 **61**	 **62** R = DPM
10	 **21**	 **63** R = DPM **64** R = Fl

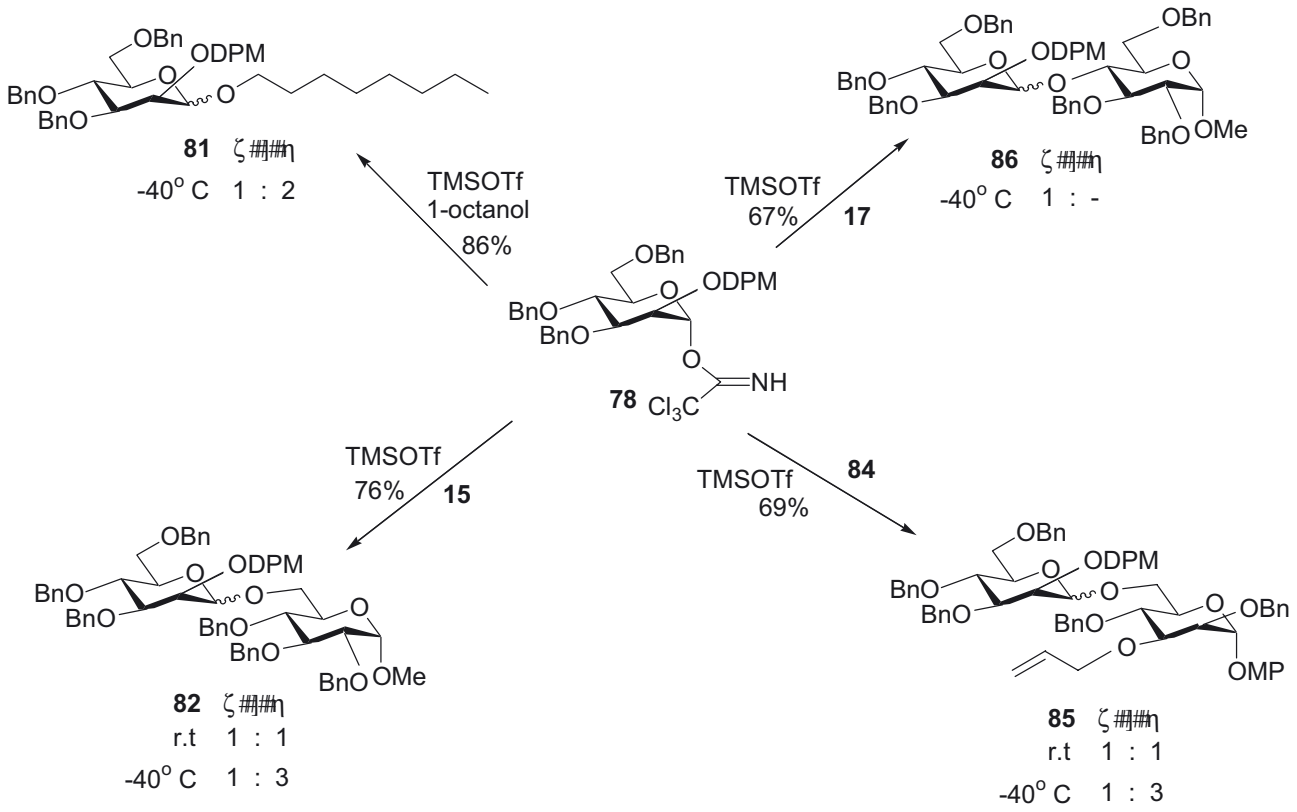
It became interesting to study the effect of the DPM and Fl group of glycosyl donors **67** and **68** on the stereoselectivity during the glycosylation reaction as shown for the reactions leading to compounds **69**-**74**.



Also, the stereoselectivity in mannosylation reactions was studied.

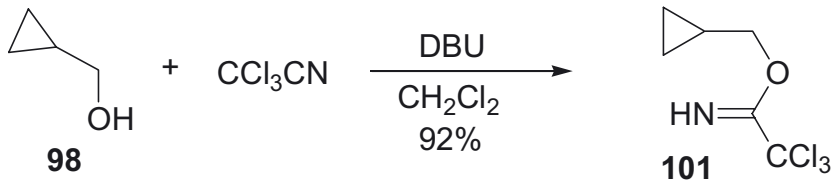


The coupling of the trichloroacetimidate donor **78** with n-octanol, glucose derivatives **15**, **84** and 4-OH free glucose derivative **17** as acceptor was carried in dry dichloromethane at room temperature and at -40°C in the presence of TMSOTf as catalyst to afford the desired mannopyranosides **81**, **82**, **85** and **86**. Thus, it became obvious, that compared with the benzyl group the DPM group supports in most cases η-mannopyranoside formation.



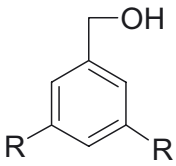
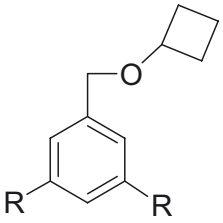
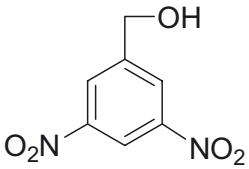
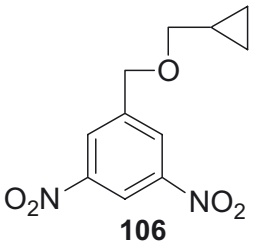
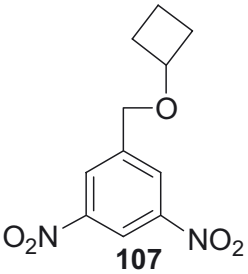
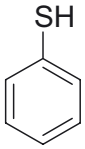
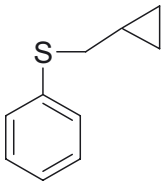
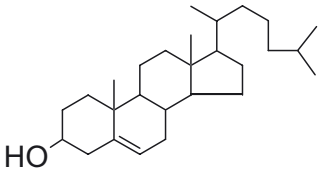
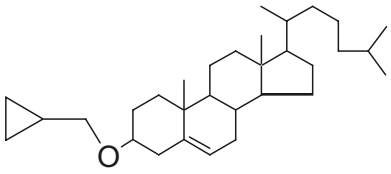
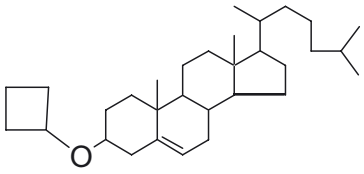
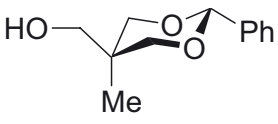
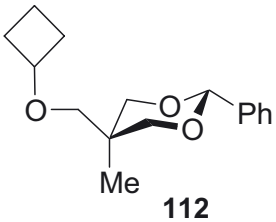
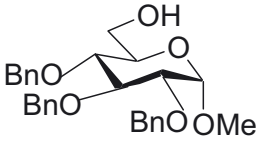
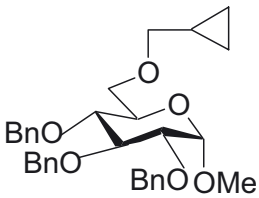
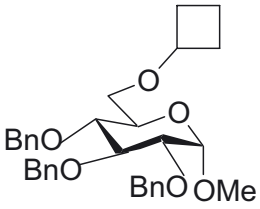
4.3 Cyclopropylmethyl and cyclobutyl trichloroacetimidate.

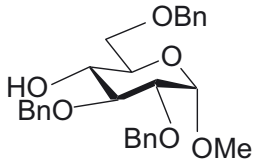
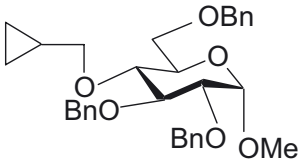
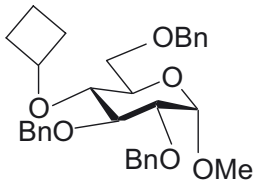
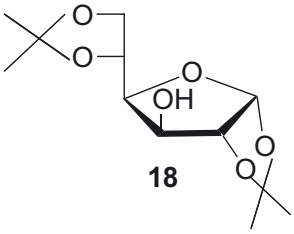
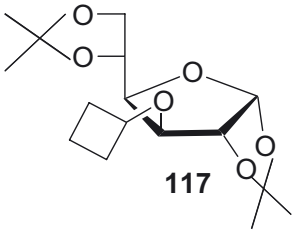
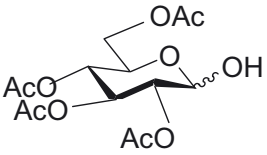
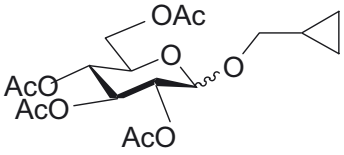
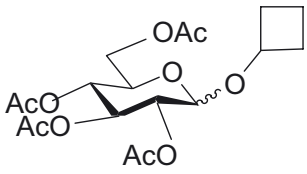
This part describes the reaction of cyclopropylmethyl and cyclobutyl trichloroacetimidates, respectively, with hydroxy groups of varied nucleophilicities in order to investigate its use as alkylating agent under mildly acidic condition and to throw some light on the mechanism of the trichloroacetimidate procedure in forming glycosyl bonds.



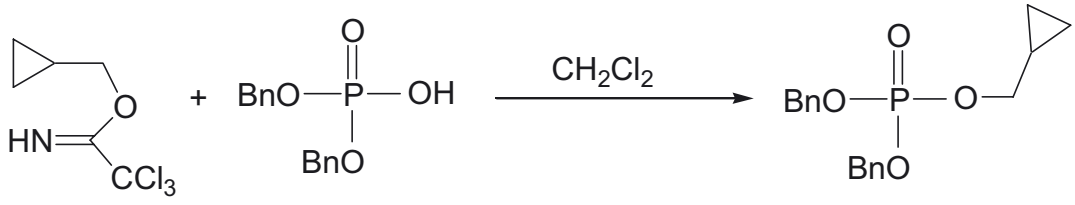
The cyclopropylmethyl cation has been found to be formed readily from the trichloroacetimidate **101** in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) as catalyst (Table 4.3).

Table 4.3 Reaction of alcohols with cyclopropylmethyl trichloroacetimidate

Entry	Acceptor	Product	
		Cyclopropyl deivatives	Cyclobutyl derivatives
1	 **5** R = H **103** R = OCH_3	 **104** R = H **105** R = OCH_3	
2	 **11**	 **106**	 **107**
3	 **108**	 **109**	
4	 **12**	 **110**	 **111**
5	 **6**		 **112**
6	 **15**	 **113**	 **114**

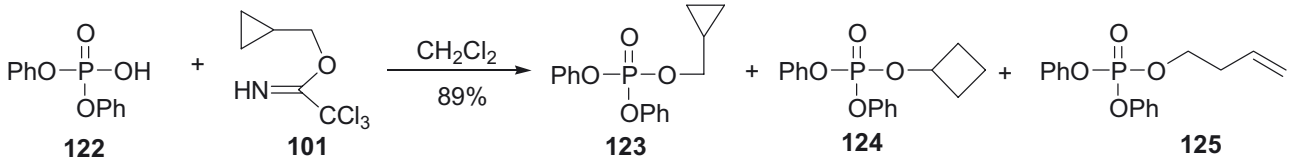
Entry	Acceptor	Product	
		Cyclopropyl derivatives	Cyclobutyl derivatives
7	 **17**	 **115**	 **116**
8	 **18**	 **117**	
9	 **56**	 **118**	 **119**

Dibenzyl phosphate **120,** as weak acid, gave only cyclopropylmethyl derivative **121** without any catalyst and the reaction proceeded without rearrangement.



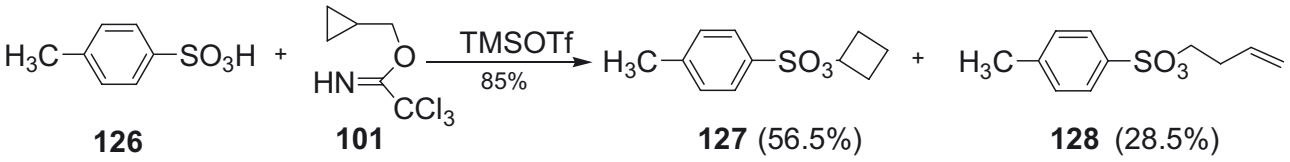
101 **120** **121**

When the acceptor has a slightly more acidic character such as diphenyl phosphate **122** reaction with trichloroacetimidate **101** gave, in addition to **123**, rearrangement products **124** and **125**.



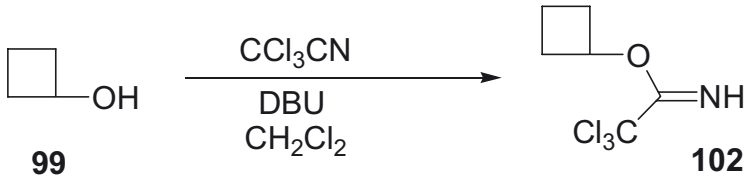
122 **101** **123** **124** **125**

In the case of 4-toluenesulfonic acid, the cyclobutyl **127** [182] and homoallyl derivatives **128** were formed.



126 **101** **127** (56.5%) **128** (28.5%)

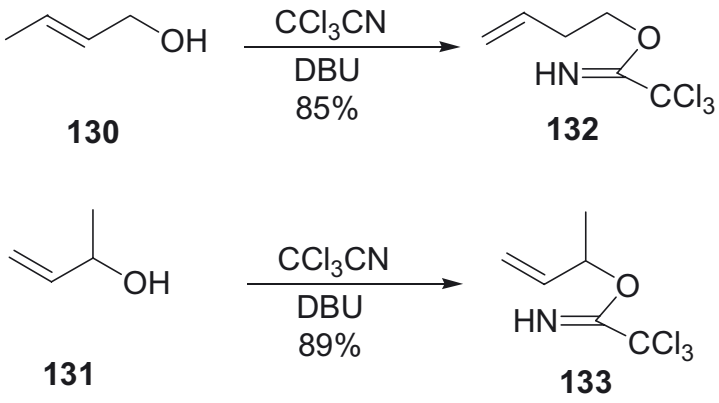
The required cyclobutyl trichloroacetimidate **102** was prepared in 87% yield by the reaction of cyclobutanol **99** with trichloroacetonitrile in the presence of DBU as catalyst.



99 **102**

The cyclobutyl trichloroacetimidate **102** was reacted with acceptors such as benzyl alcohol (**5**), dinitrobenzyl alcohol (**11**) and the *O*-6-unprotected hydroxy group in glucose derivative **15**; it gave the same reaction products as cyclopropylmethyl trichloroacetimidate **101** and also in about the same ratio.

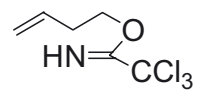
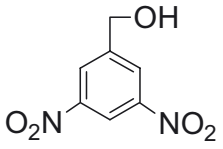
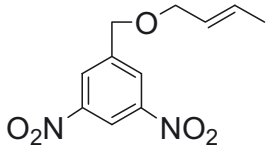
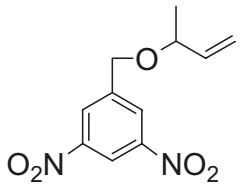
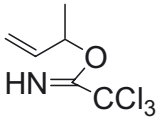
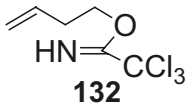
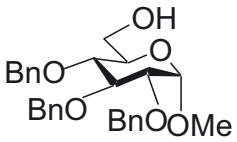
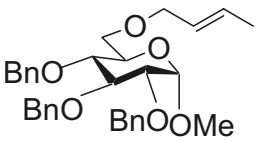
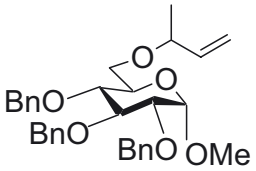
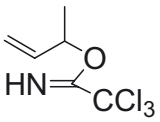
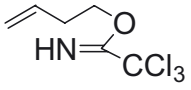
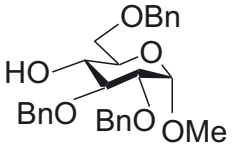
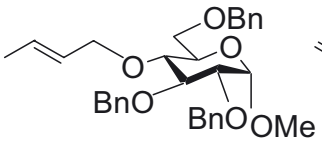
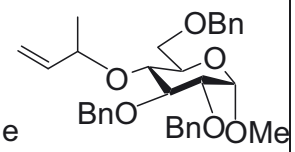
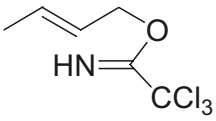
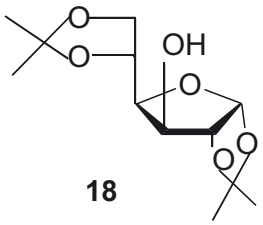
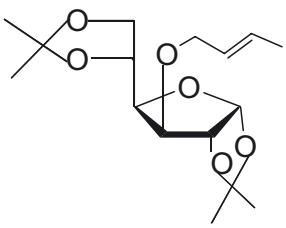
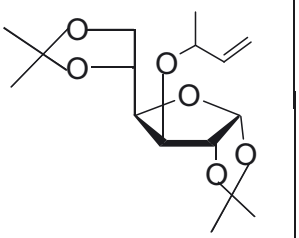
The double bond rearrangement of many unsaturated compounds can take place on treatment with acids. Thus, rearrangement of allyl compounds carrying a leaving group of the type shown in the following scheme may take place in presence of acids *via* carbonium ions, which in presence of alcohol may give two products (table 4.4).



130 **132**

131 **133**

Table 4.4 Reaction of acohols with trichloroacetimidates **132** and **133**

Reagent	Acceptor	Product	
 **132**	 **11**	 **134** (36%) from **132** **134** (47%) from **133**	 **135** (33%) from **132** **135** (15%) from **133**
 **133**			
 **132**	 **15**	 **136** (31%) from **132** **136** (35%) from **133**	 **137** (28%) from **132** **137** (24%) from **133**
 **133**			
 **132**	 **17**	 **138** (27%) from **132**	 **139** (24%) from **132**
 **132**	 **18**	 **140** (28%) from **132**	 **141** (26%) from **132**

4.4 Aminomethylation with *O*-(phthalimidomethyl)trichloroactimidate.

It has been found that the phthalimidomethyl group (Pim) can be used as an aminomethylating agent for *C*-nucleophiles (Table 4.5).

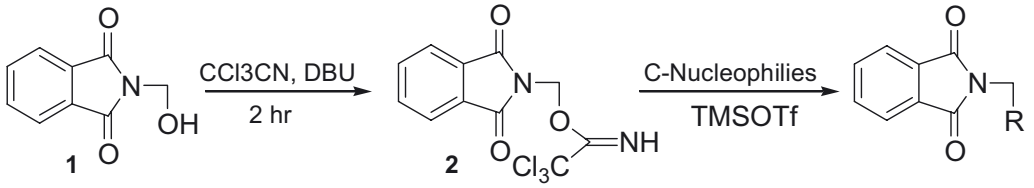
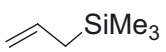
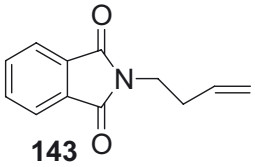
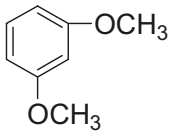
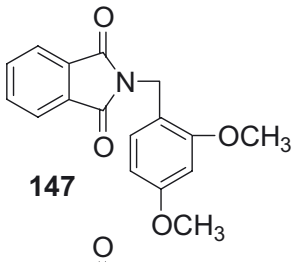
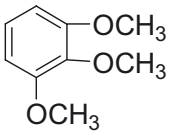
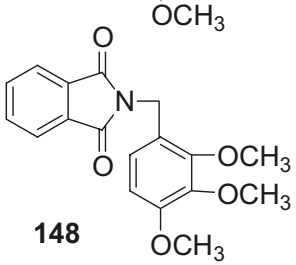
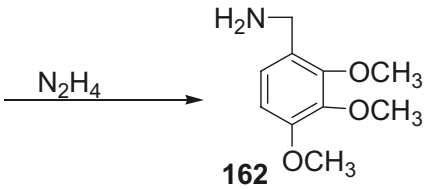
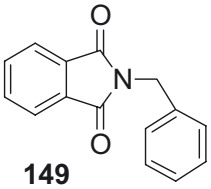
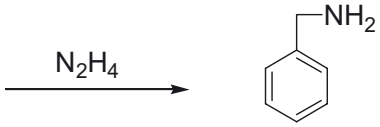
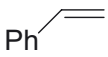
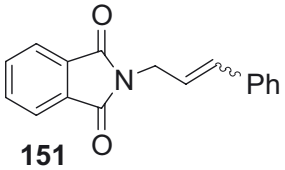
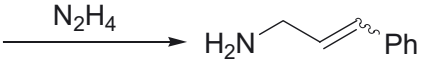
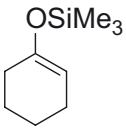
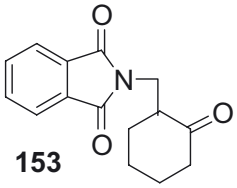
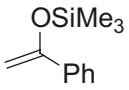
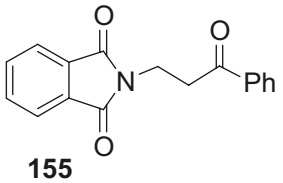
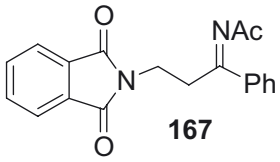
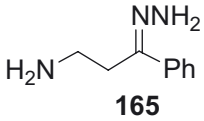
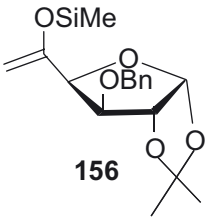
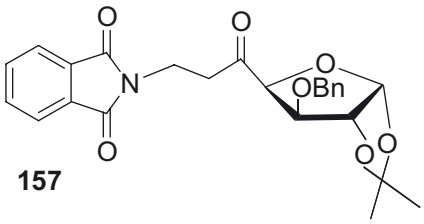
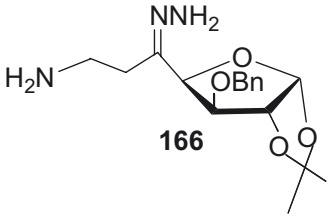
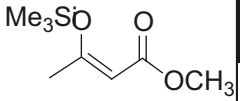
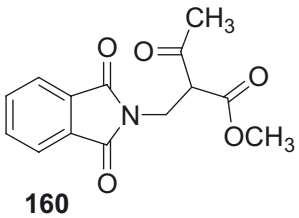
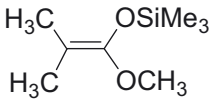
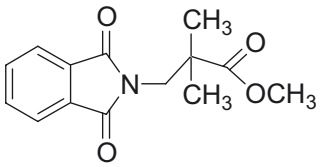
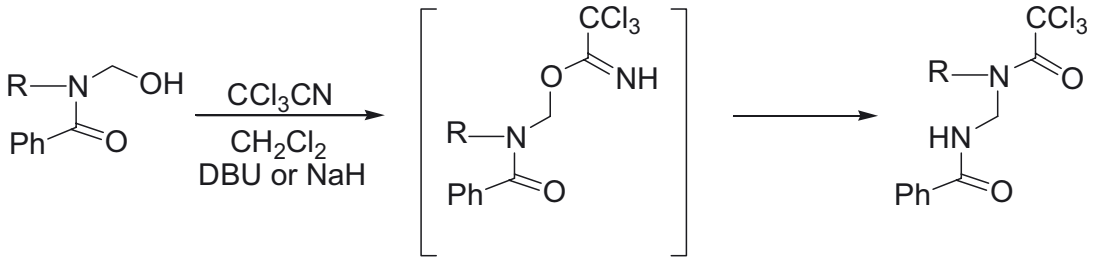


Table 4.5 Phthalimidomethylation of *C*-nucleophiles

NO	Acceptor	Product	Deprotection
1	 **142**	 **143**	
2	 **144**	 **147**	
3	 **145**	 **148**	 **162**
4	 **146**	 **149**	 **163**
5	 **150**	 **151**	 **164**
6	 **152**	 **153**	

NO	Acceptor	Product	Deprotection
7	 **154**	 **155**	 **167**  **165**
8	 **156**	 **157**	 **166**
9	 **158**	 **160**	
10	 **159**	 **161**	

In order to extend the scope of aminomethylation using *N*-methylol benzamide **168** [209], *N*-methylmethylol benzamide **169**[210] the compounds **168** and **169** were reacted with trichloroaceonitrile in dichloromethane as a solvent and in the presence of DBU or NaH for activating the hydroxyl group towards the reaction with the nitrile group at different temperature (-50°C, 0°C, room temp.). The trichlorocetamides **172** and **173** were obtained through the intermediate trichloroacetimidates **170** and **171**.

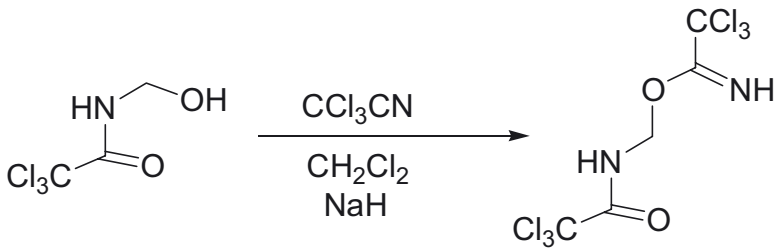


168 R = H
169 R = CH_3

170 R = H
171 R = CH_3

172 R = H
173 R = CH_3

Then the phenyl group was changed to trichloromethyl in *N*-hydroxymethyl trichloroacetamide[211] **174**. The trichloroacetimidate **175** was formed without rearrangement when **174** reacted with trichloroacetonitrile in the presence of NaH at room temperature in good yield.

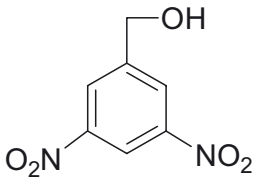
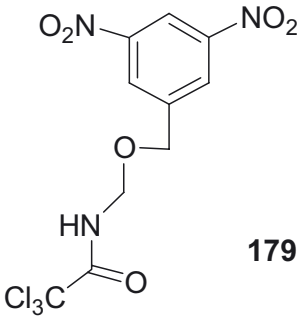
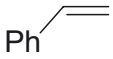
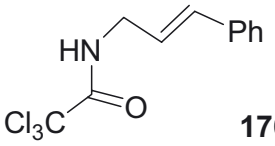
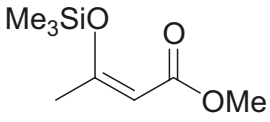
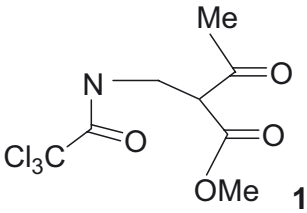
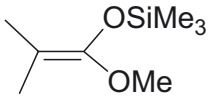
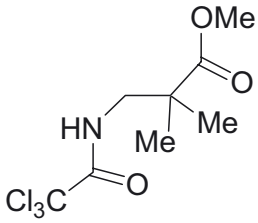


174 **175**

Scheme 93

Reaction of the trichloroacetimidate **175** with different acceptors in the presence of TMSOTf as catalyst gave the respective *O*- and *C*-amidomethylation products.

Table 4.6 Reaction of trichloroacetimidate derivative **177** with *C*-nucleophiles

No	Acceptor	Product
1	 **11**	 **179**
2	 **150**	 **176**
3	 **158**	 **177**
4	 **159**	 **178**

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