

**Construction of Carbocycles from Carbohydrates via
1,3-Dipolar Cycloaddition**

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of the Requirements for the Degree of
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in

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Abstract

In this thesis, the background information on the construction of carbocycles from carbohydrates via intramolecular 1,3-dipolar cycloaddition is presented. A review regarding the syntheses of gabosine B and cocaine are also described.

By using intramolecular nitrile oxide-alkene cycloaddition (INOC) as the key step to construct hydroxylated carbocycles, gabosine F was synthesized for the first time from L-arabinose. Hence, theoretically, gabosine B, which is the enantiomer of gabosine F, can also be synthesized from D-arabinose by the same synthetic strategy.

A 5-membered INOC cycloadduct **84** was employed to prepare alcohol **91**, which was transformed into several cyclopent-2-enone derivatives **94–96**.

The regioselectivity of intramolecular nitron-alkene cycloaddition (INAC) was studied. The INAC of hept-6-enose nitron **98**, with a 3,4-*trans*-pentylidene acetal as the only blocking group, afforded *endo*-cycloadduct **97** (cycloheptane) exclusively. This result concluded that the regiospecific outcome of this INAC reaction is due to the presence of the 3,4-*trans*-pentylidene acetal blocking group.

Starting with D-ribose, INAC of nitrones **113**, **129**, and **140**, bearing an α,β -unsaturated ester as the dipolarophile was studied. The INAC *endo*-cycloadduct **141** (cycloheptane) was converted into natural cocaine successfully, together with cocaine analogues **162**, **169**, **170**, **173**, **175**, and **177**.

To investigate the regioselectivity in INAC of hex-5-enose with a 2,3-*trans*-pentylidene acetal blocking group, nitrones **178** and **195** were prepared from D-mannitol. *endo*-Cycloadducts (cyclohexanes) were afforded exclusively.

摘要

本文描述了以單糖為起始原料，應用分子內 1,3-偶極環加成反應製備碳環的背景資料。另外，本文還綜述了 gabosine B 和可卡因之合成的研究進展。

以 L-阿拉伯糖作為起始原料，通過分子內腈氧化物環加成 (INOC) 反應為關鍵的一步，首次地合成了 gabosine F。所以理論上，利用相同的合成方法便能把 D-阿拉伯糖合成為 gabosine F 的對映體，即是 gabosine B。

通過製備分子內腈氧化物環加成五員環化合物 **84**，製備了合成中間體 **91**，以及另外三種環戊-2-烯酮的衍生物 **94-96**。

為了研究分子內硝酮環加成 (INAC) 反應的區域選擇性，製備了擁有 3,4-反式亞戊基縮醛保護的硝酮 **98**，其分子內硝酮環加成反應只生成了一種七員環內產物 **97**。這證明 3,4-反式亞戊基縮醛保護能引導生成七員環內產物。

以 D-核糖作為起始原料，研究了以 α , β -不飽和酯作為親偶極體的硝酮 **113**, **129** 和 **140** 之分子內硝酮環加成反應。其中以七員環內產物 **141** 能製備成天然產物可卡因，以及另外六種可卡因的類似物 **162**, **169**, **170**, **173**, **175** 和 **177**。

其後，以 D-甘露醇作為起始原料，製備了擁有 2,3-反式亞戊基縮醛保護的硝酮 **178** 和 **195** 並研究其分子內硝酮環加成反應的區域選擇性。結果這些環加成反應只生成了六員環內產物。

Abbreviation

[α]	specific rotation	DEPT	Distortionless
Å	angstrom (s)		Enhancement by
Ac	acetyl		Polarization Transfer
Anal.	analytical	DMAP	4-dimethylaminopyridine
aq.	aqueous	DMF	dimethylformamide
atm.	atmosphere	DMSO	dimethyl sulfoxide
Boc	<i>t</i> -butyloxycarbonyl	ee	enantiomeric excess
BORSM	based on recovering starting material	EI	Electron Impact
Bn	benzyl	ESI	Electrospray Ionization
br	broad (spectral)	Et	ethyl
Bz	benzoyl	Et ₂ O	diethyl ether
ⁿ Bu	<i>n</i> -butyl	FAB	Fast Atom Bombardment
^t Bu	<i>tert</i> -butyl	FT	Fourier transform
°C	degree Celsius	g	gram
calcd	calculated	h	hour
cat.	catalytic	HRMS	high-resolution mass spectrum
Chloramine-T	<i>N</i> -chloro- <i>p</i> -toluenesulfona mide sodium salt	Hz	hertz
CI	chemical ionization	IBX	2-iodoxybenzoic acid
conc.	concentrated	INAC	Intramolecular nitron-alkene
COSY	Correlated Spectroscopy		cycloaddition
COTC	2-crotonyloxymethyl-(4 <i>R</i> ,5 <i>R</i> ,6 <i>R</i>)-4,5,6-trihydroxy-2-c yclohexenone	INOC	Intramolecular nitrile oxide-alkene cycloaddition
(±)-CSA	(±)-10-camphorsulfonic acid	IR	infrared
δ	chemical shift in parts per million downfield from tetramethylsilane (spectral)	<i>J</i>	coupling constant (in NMR)
δ+	delta positive charge	KHMDS	potassium hexamethyldisilylamide
δ-	delta negative charge	L	liter(s)
d	day (s) or doublet (spectral)	lit.	literature
DBU	1,8-Diazabicyclo[5.4.0] undec-7-ene	μ	micro-
		M	moles per liter
		m	multiplet (spectral), milli-
		Me	methyl
		MHz	megahertz

min	minute	<i>rac</i>	racemic
mp	melting point	R _f	retention factor
Ms	methanesulfonyl	rt	room temperature
MS	molecular sieves or mass spectrum	s	singlet (spectral)
MTO	methyltrioxorhenium	sat.	saturated
<i>m/z</i>	mass-to-charge ratio	S _N 2	bimolecular nucleophilic substitution
n	nano	t	triplet (spectral)
NCS	<i>N</i> -chlorosuccinimide	TBAF	tetrabutylammonium fluoride
NMO	4-methylmorpholine <i>N</i> -oxide	TBS	<i>tert</i> -butyldimethylsilyl
NMR	nuclear magnetic resonance	Tf	trifluoromethanesulfonate
NOESY	nuclear overhauser enhancement spectroscopy	TFA	trifluoroacetic acid
Nu	nucleophile	THF	tetrahydrofuran
Ph	phenyl	TLC	thin layer chromatography
ppm	parts per million (in NMR)	TPAP	tetra- <i>n</i> -propylammonium perruthenate
py	pyridine	<i>p</i> -TsOH	<i>p</i> -toluenesulfonic acid
q	quartet (spectral)	TS	transition state
quin	quintet (spectral)	UHP	urea hydrogen peroxide

Chapter 1

Introduction

1.1 General background

Construction of carbocycles from their acyclic precursors have drawn great attention in organic synthesis, mainly due to the majority of natural products consists of carbocycles, especially the 5-, 6-, and 7-membered carbocyclic rings. For example, natural products like (-)-neplanocin A (**1**), (+)-gabosine F (**2**), and (-)-cocaine (**3**) consist of carbocycle with a 5-, 6-, and 7-membered rings respectively (Figure 1). For these natural products, most of them are enantiopure substances. That is, the syntheses of these compounds require either asymmetric synthesis from achiral precursors or using chiral starting materials.

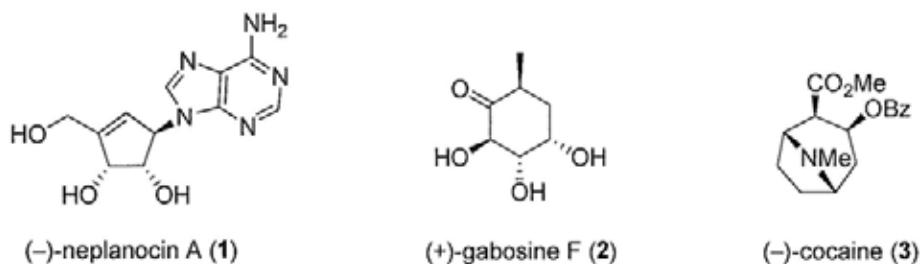


Figure 1

Carbohydrates have been considered as the most versatile starting materials for natural product synthesis because it is readily available and in large quantities. More importantly, carbohydrates are enantiopure substances so the final products must be

optically pure. Thus, there is no need to worry about the presence of undesired enantiomer that may affect the bioactivity of the synthesized product. The 1,3-dipolar cycloaddition is a powerful tool for preparing carbocycles as this reaction can create new chiral centers and can form a new carbon-carbon bond.¹⁻⁴ When carbohydrates are used to prepare the chiral 1,3-dipolar to perform the cycloaddition, the cycloadducts generally contain newly formed chiral centers in high diastereoselectivity.

In this chapter, the 1,3-dipolar cycloaddition in organic synthesis and its applications to the construction of carbocycles are presented in detail.

1.2 1,3-Dipolar Cycloaddition

The 1,3-dipole is defined as a species that is represented by the zwitterionic octet structures, which contains four electrons in three parallel atomic p orbitals.¹ It can be divided into two different types: the allyl anion type and the propargyl/allenyl anion type (Figure 2).²

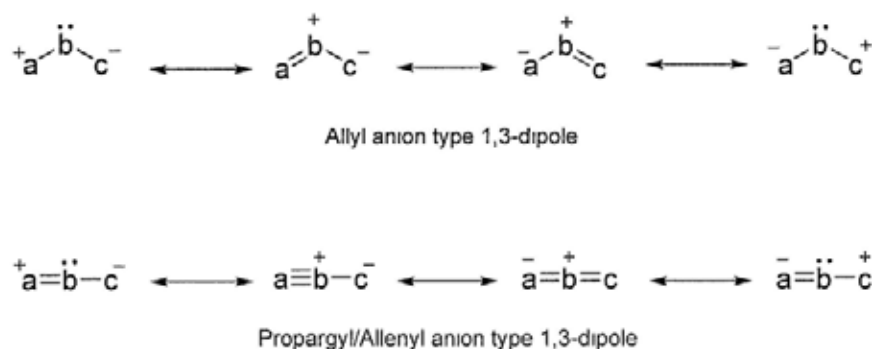


Figure 2

Where atoms a and c are mainly carbon, nitrogen, oxygen and sulphur. The allyl anion type has four electrons in those three p orbitals with perpendicular to the plane of the dipole and the dipole is bent. The central atom b in allyl anion type 1,3-dipole can be nitrogen, oxygen and sulphur. The propargyl/allenyl anion type has one extra π orbital located in the plane orthogonal to the four-electrons π molecular orbital of the dipole, the extra π orbital hence will not involved in the resonance structures and will not take part in the cycloaddition reaction. The propargyl/allenyl anion type 1,3-dipole is linear and the central atom b is limited to nitrogen only.

For all of the 1,3-dipoles, 1,3-dipolar cycloaddition can take place with the dipolarophile, usually alkenes and alkynes, which involves 4 π electrons from the dipole and 2 π electrons from the dipolarophile. When the cycloaddition proceeds through the concerted mechanism, thermally allowed $[\pi 4_s + \pi 2_s]$ cycloaddition will occur in which the π orbital of dipole and the π orbital of the dipolarophile are combined suprafacially (Figure 3).⁴

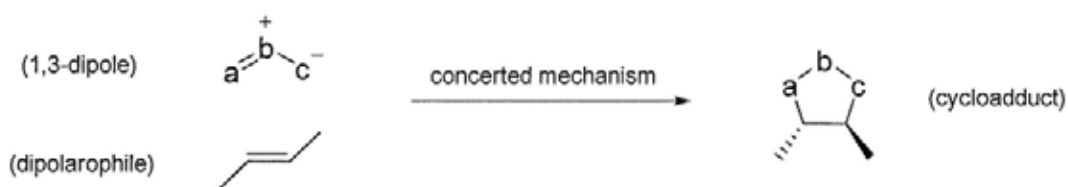


Figure 3

The result is that, a *trans*-cycloadduct will be formed as the only diastereomer when *trans*-alkene is used as the dipolarophile (Figure 3).

1.2.1 Intramolecular Nitrile Oxide-Alkene Cycloaddition (INOC)

Intramolecular nitrile oxide-alkene cycloaddition (INOC) is the 1,3-dipolar cycloaddition reaction between a nitrile oxide (1,3-dipole) and an alkene (dipolarophile) within the same molecule (Figure 4).

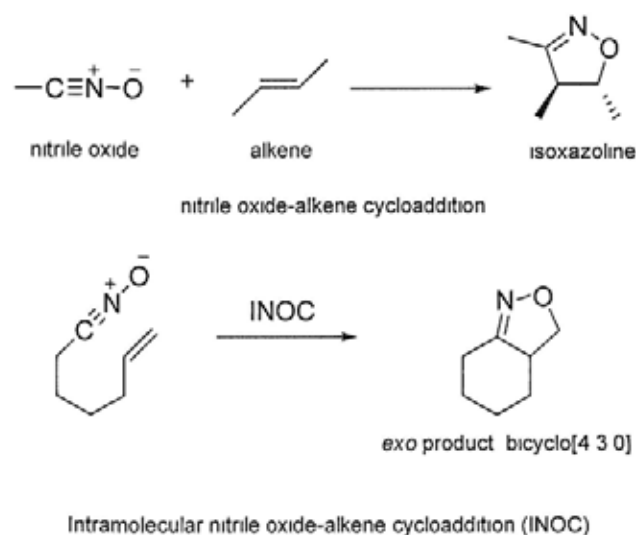
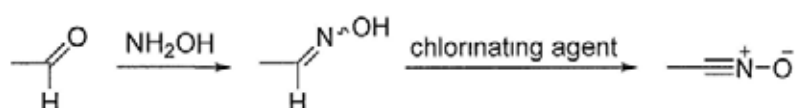


Figure 4

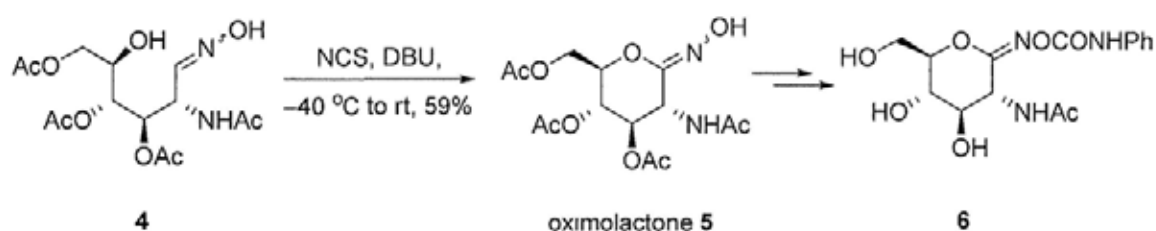
This reaction allows the formation of one carbon-carbon bond and the creation of up to two carbon stereocenters within one step. It had been used to construct many bi- and polycyclic isoxazolines. As the nitrile oxide functional group is in a linear structure, the INOC almost always proceeds to give the bicyclo[$x.3.0$] derivatives (*exo* product) for $x = 3 - 5$ (Figure 4).²

The nitrile oxides are commonly generated from treatment of a chlorinating agent (e.g. sodium hypochlorite, chloramine-T and *N*-chlorosuccinimide) and a weak base to an oxime,⁵ which can be readily synthesized by condensation of aldehyde with hydroxylamine (Scheme 1).



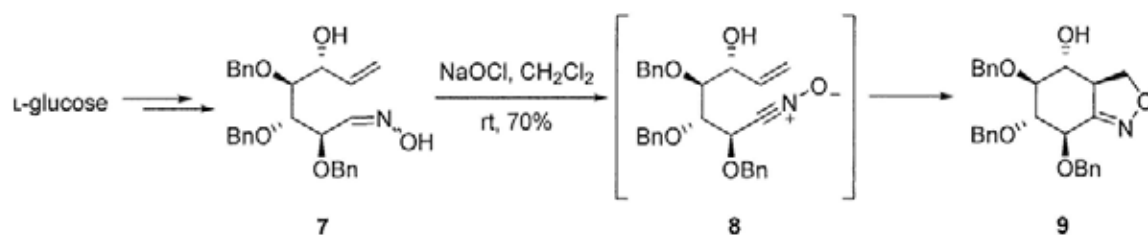
Scheme 1

These reaction conditions for generating nitrile oxide are basic and could deprotonate the acidic proton(s) of the substrates. Since nitrile oxides derived from sugars are highly oxygenated, the presence of free hydroxyl group(s) could attack the electrophilic carbon of the nitrile oxide, forming the oximolactone as the side product. The formation of oximolactone side product was reported by Vasella and co-workers in the synthesis of phenylcarbamate **6** with oximolactone **5** as the key intermediate (Scheme 2).⁶



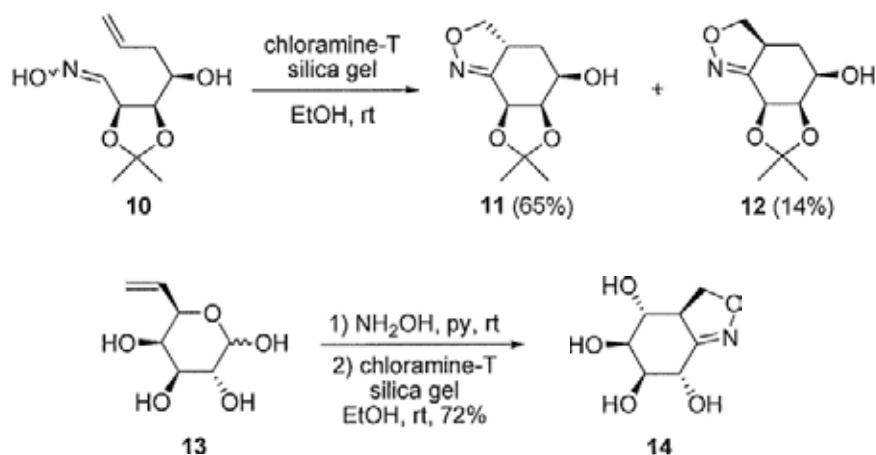
Scheme 2

Reports on INOC reactions in the presence of free hydroxyl group(s) are rare. Tatsuta *et al.* had prepared oxime **7**, which had a free hydroxyl group in the δ position, to react with NaOCl at room temperature to generate nitrile oxide **8** which then cyclized to give isoxazoline **9** (Scheme 3).⁷



Scheme 3

Recently, Shing *et al.* had used chloramine-T in the presence of silica gel to perform INOC reaction of many sugar derivatives with one or more hydroxyl groups (Scheme 4).⁸



Scheme 4

Adding silica gel to the reaction allows improvement of the yield of the cycloadduct(s). It was believed that the silica gel can provide a slightly acidic environment for the INOC reaction so to prevent the formation of undesired oximolactone product.⁸ In the thesis, INOC reactions were carried out by this chloramine-T/silica gel methodology in order to attain maximum yield of cycloadducts.

1.2.2 Intramolecular Nitron-Alkene Cycloaddition (INAC)

Intramolecular nitron-alkene cycloaddition (INAC) is the 1,3-dipolar cycloaddition reaction between a nitron (1,3-dipole) and an alkene (dipolarophile) within the same molecule (Figure 5).

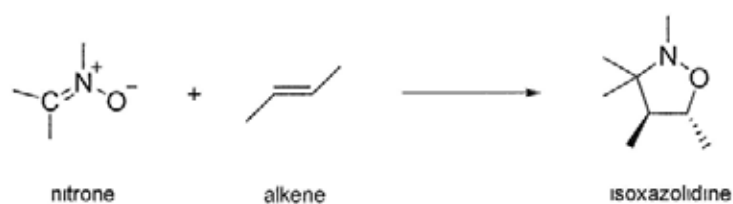
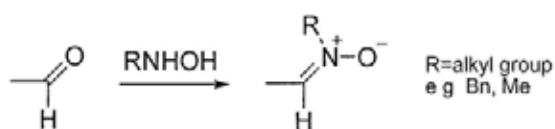


Figure 5

Throughout this reaction, formation of a carbon-carbon bond and up to three carbon stereocenters will take place. It is a powerful synthetic method for the preparation of polyhydroxylated carbocycles of different ring sizes from sugars. Also, the introduction of a nitrogen functionality to the substrate during INAC reaction allows the formation of alkaloids and related natural products from INAC cycloadducts. The nitronium can be prepared by reacting aldehyde with alkyl hydroxylamine (Scheme 5).



Scheme 5

Unlike INOC reactions, INAC reactions have two modes of cyclization, namely the *exo* or the *endo* mode, which lead to the formation of a fused or a bridged cycloadduct respectively (Figure 6).²

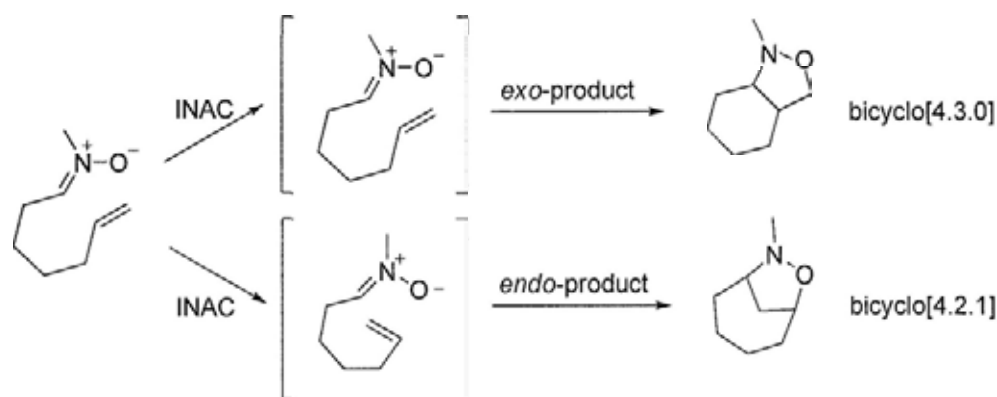
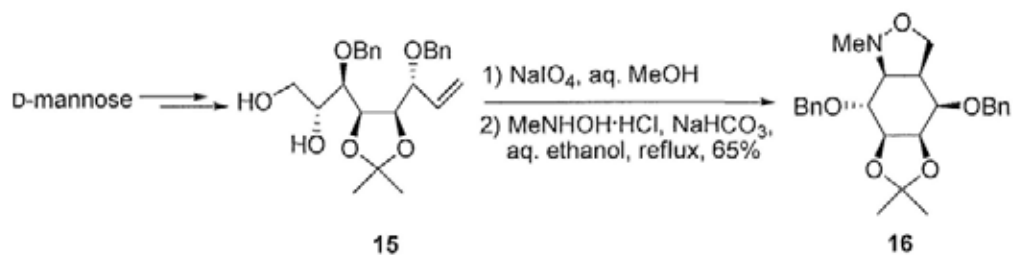


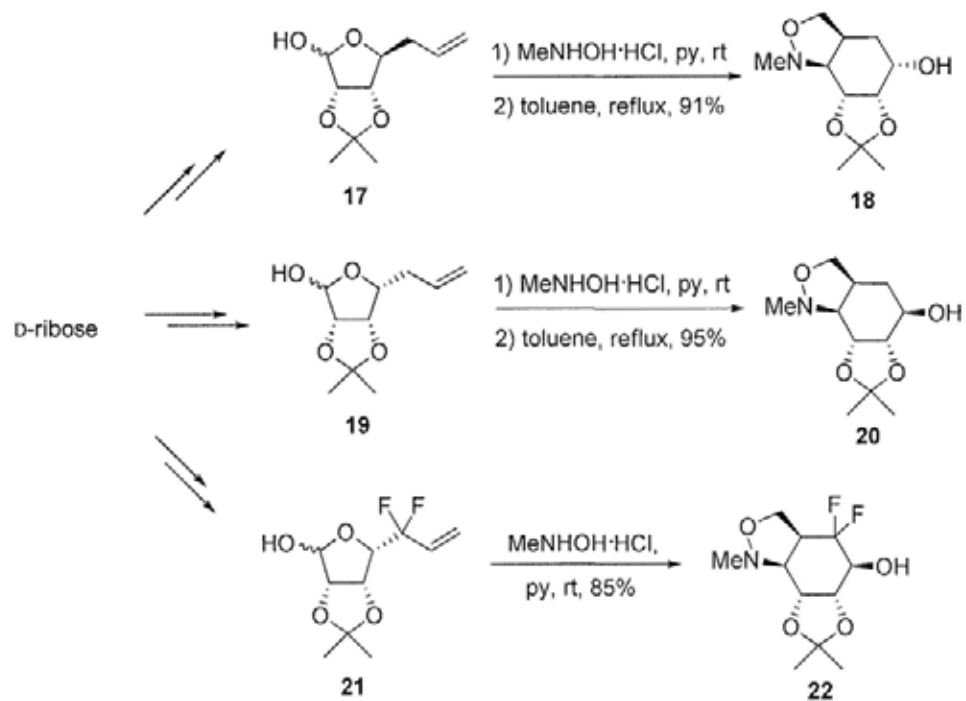
Figure 6

In most cases, INAC reactions lead to the formation of the *exo*-cycloadducts instead of *endo*-cycloadducts. For example, Shing and co-workers reported⁹ an entry to *cis*-fused cyclohexane **16** from D-mannose through the unbranched sugar derivative **15** (Scheme 6).



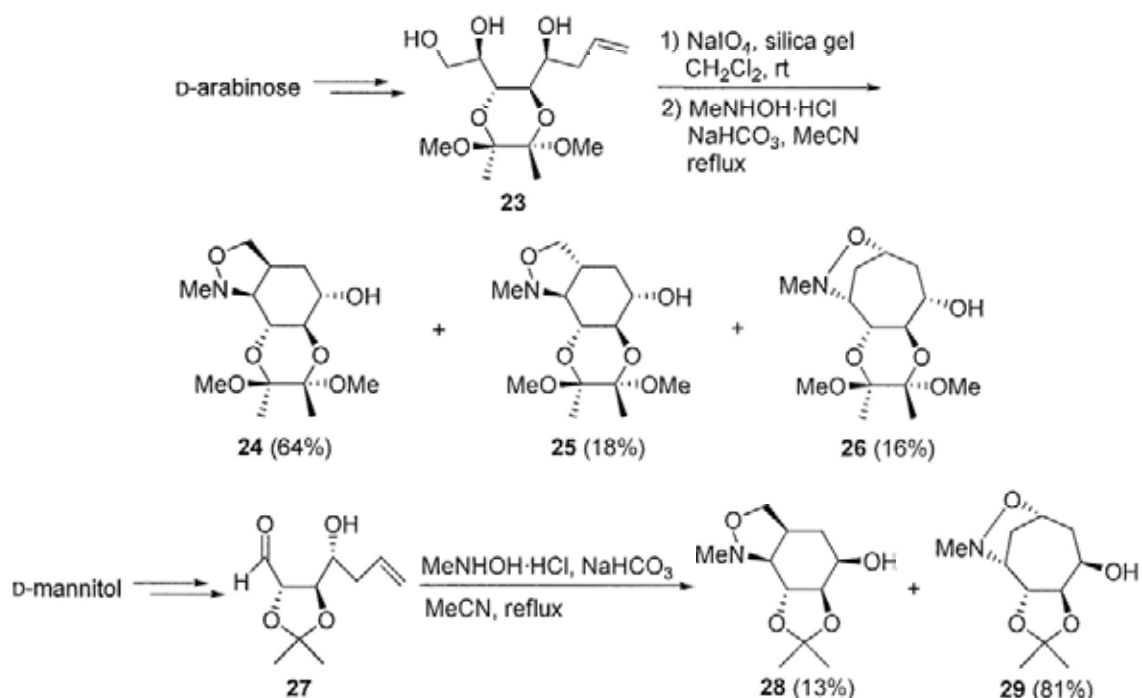
Scheme 6

Singh *et al.* had prepared three unbranched sugar derivatives **17**, **19** and **21** from D-ribose to give *cis*-fused cyclohexanes, **18**, **20** and **22**, respectively through the *exo*-mode INAC reaction (Scheme 7).^{10,11}



Scheme 7

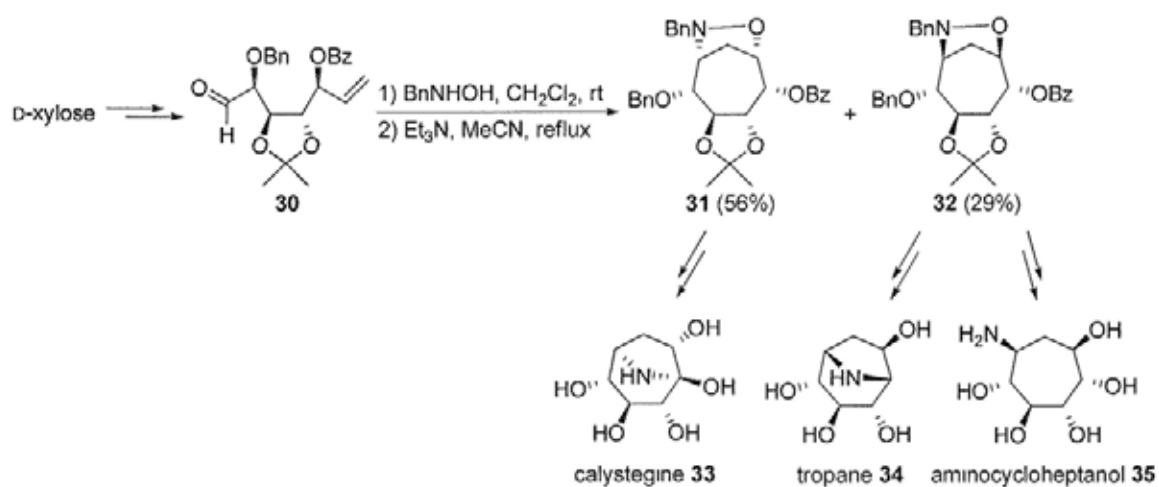
However the formation of *endo*-cycloadducts from sugar derivatives is rare¹² until 2006. Shing *et al.* had discovered the formation of *endo*-cycloadducts was enhanced when the acyclic INAC precursor contains a *trans*-blocking protecting group (Scheme 8).¹³⁻¹⁵



Scheme 8

It was suggested that the presence of *trans*-blocking group will impose a torsional strain that can affect the conformation of the transition states of INAC reactions hence enhance the formation of *endo*-cycloadducts. These suggestions were further supported by the theoretical analysis performed by Yamada *et al.*¹³⁻¹⁵

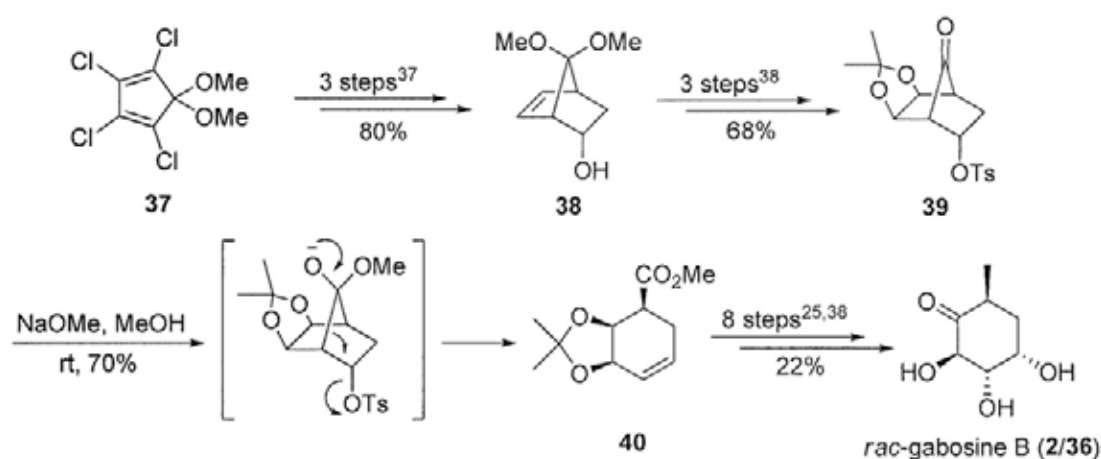
It was found that when a 3,4-*trans*-acetonide was employed, the INAC reactions of hept-6-enoses yielded *endo*-cycloadducts exclusively. The cycloadducts formed could be transformed to optically active calystegines, tropanes and aminocycloheptanols (Scheme 9).¹⁴



Scheme 9

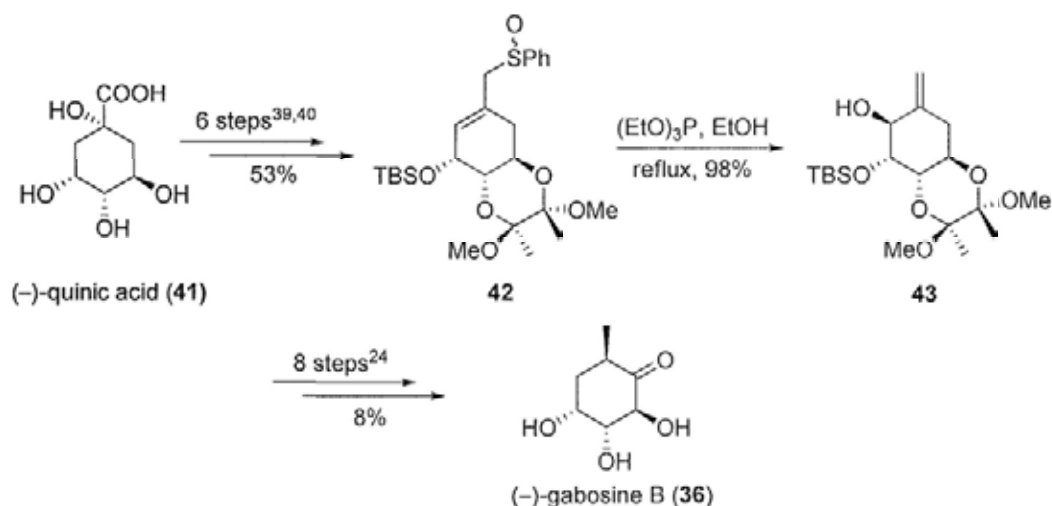
In this thesis, further studies on the regioselectivity of INAC reactions of sugar derivatives and transformation of cycloadducts to some natural products or analogues with biological importance are discussed.

gabosines (some were synthesized as the enantiomer of natural gabosines) were found.¹⁸⁻³⁶ The most recent reports include (i) the synthesis of (+)-gabosine N and (+)-gabosine O by Rao *et al.* using ring-closing metathesis as the key step for carbocyclization,³⁰ (ii) synthesis of (-)-gabosine E by Gallos *et al.* using INAC as the key step,³¹ (iii) synthesis of (-)-gabosine A and (-)-gabosine N by Madsen and co-workers using ring-closing metathesis as the key step,³² (iv) synthesis of (+)-gabosine A, (-)-gabosine B, (+)-gabosine D, (+)-gabosine E, (+)-gabosine F, (-)-gabosine G, (-)-gabosine I, (-)-gabosine K and (-)-gabosine O by Shing and co-workers.³³⁻³⁶ (-)-Gabosine B (**36**) and (+)-gabosine F (**2**) are a pair of enantiomers which belong to the class of hydroxylated cyclohexanones (saturated carbocycle). The first synthesis of racemic gabosine B (**36**) was achieved by Mehta and Lakshminath in 15 steps with 8.4% overall yield from 5,5-dimethoxy-tetrachloro-cyclopenta-diene (**35**), giving a mixture of *rac*-gabosines B (**33**) and F (**34**), using the Grob-like 'top-to-bottom' fragmentation as the key step (Scheme 10).²⁵



Scheme 10

Enantiopure gabosine B (**36**), was constructed by Shinada *et al.*, starting from (–)-quinic acid (**41**) and using a Mislow-Evans rearrangement as the key step, in 15 steps with 4.3% overall yield (Scheme 11).²⁴



Scheme 11

However, there is still no report on the synthesis of enantiopure gabosine F (**2**). Since the products of intramolecular nitrile oxide-alkene cycloaddition (INOC) can be easily transformed into saturated carbocyclic ketone, the enantiopure (+)-gabosine F (**2**) could be synthesized from the INOC cycloadduct in a few steps. The synthesis of (+)-gabosine F (**2**) from carbohydrate via INOC reaction is described in the following chapter.

1.3.2 Cocaine and Cocaine Analogues

Natural (–)-cocaine (**3**) (Figure 8) is a tropane alkaloid component of coca leaves of *Erythroxylum Coca*.⁴¹ It is a powerful stimulant of the central nervous system and its

neuronal reinforcing properties are due to its inhibition of dopamine reuptake.⁴² However its addictive properties makes cocaine abuse become one of the greatest concerns of the public today and long-term cocaine abuse can produce neurophysiological alternations in the central nervous system.⁴³

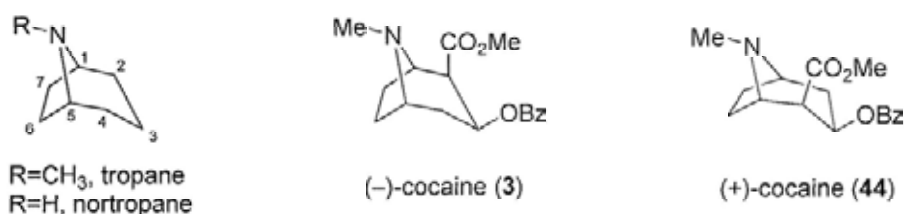
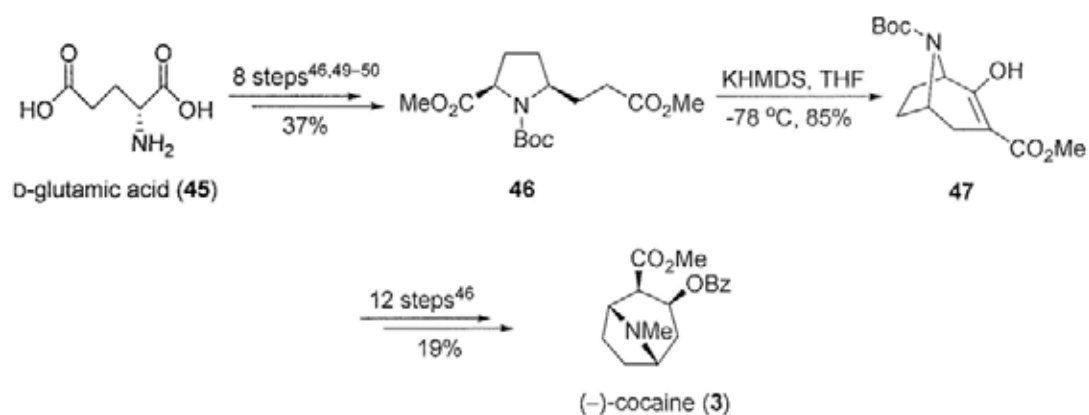


Figure 8

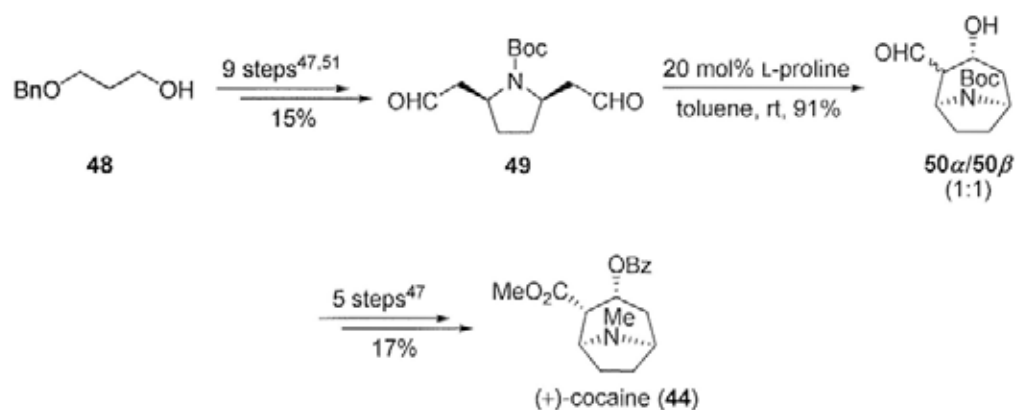
The total synthesis of cocaine has been a challenging task to numerous synthetic chemists for nearly a century, mainly due to the difficulties on building the tropane skeleton as well as to functionalize this skeleton in correct stereochemistry, especially the axial 2-carbomethoxy group which is less thermodynamically stable. The early synthesis of cocaine yield racemic mixture hence optical resolution of *rac*-cocaine was needed.^{44,45} Until now only three syntheses of optically pure cocaine were reported.^{46–48}

In 1998, Rapoport and co-workers had using D- and L-glutamic acid to synthesize natural (–)-cocaine (**3**) and unnatural (+)-cocaine (**44**) respectively in 21 steps with 5.9% overall yield, in which the 8-azabicyclo[3.2.1]octane framework was constructed by Dieckmann condensation (Scheme 12).⁴⁶



Scheme 12

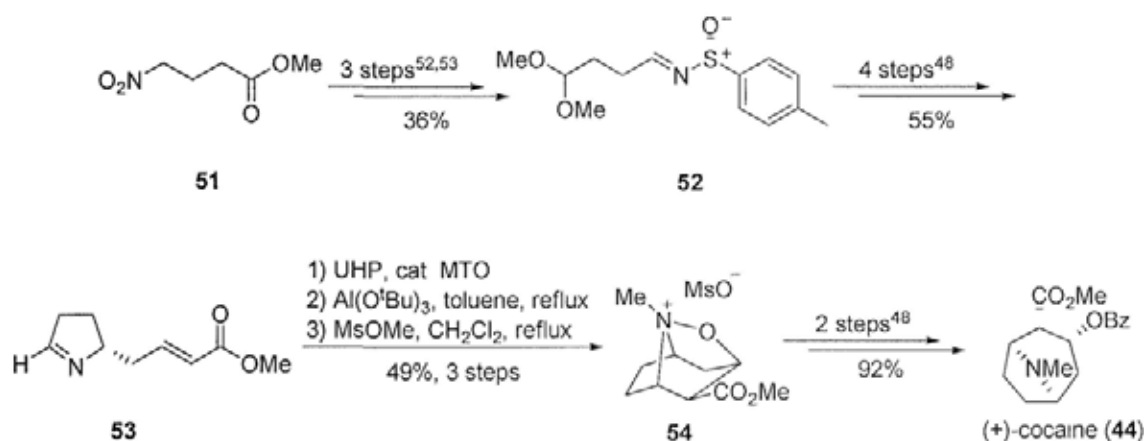
Pearson *et al.* reported an asymmetric synthesis of (+)-cocaine (44) using L-proline catalyzed intramolecular aldol reaction to form the tropane skeleton. However, 1:1 mixture of C-2 epimers was obtained during this key reaction. This synthesis involved 15 steps, 2.2% overall yield and 86% ee starting from commercially available 3-benzyloxy-1-propanol (48) (Scheme 13).⁴⁷



Scheme 13

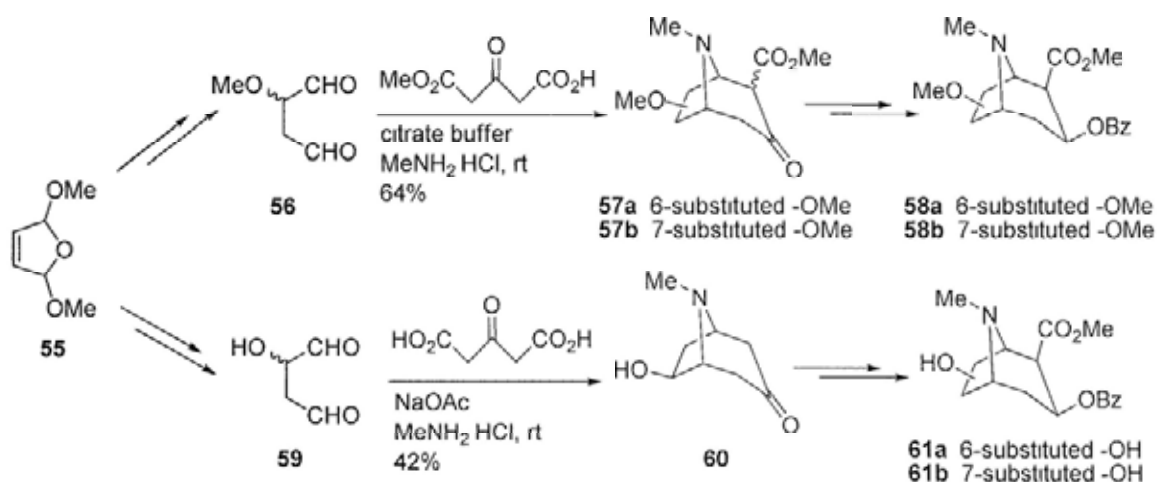
The latest asymmetric total synthesis of cocaine was reported by Davis *et al.* in 2010.⁴⁸ Starting with a chiral masked oxo sulfinimine 52 to prepare a chiral imine

intermediate **53**, the tropane skeleton was constructed in the same strategy as in Tufariello's *rac*-cocaine synthesis, using INAC as the key step.⁴⁵ Both (-)- and (+)-cocaine could be synthesized in 12 steps and 9% overall yield from methyl 4-nitrobutanoate (**51**) (Scheme 14).



Scheme 14

Since cocaine abuse is one of the greatest concerns in the society, much effort had been used to obtain cocaine analogues for abuse treatment. Because of the difficulties on the synthesis of optically pure natural (-)-cocaine (**3**), preparation of cocaine analogues was limited and analogues were mainly derived from natural (-)-cocaine (**3**).⁵⁴⁻⁵⁷ A few examples were based on minor modification of the reported synthetic strategies.^{48,58-60} Kozikowski and co-workers had prepared racemic 6- and 7-methoxylated and hydroxylated cocaine analogues using Willstätter's synthesis,⁴⁴ followed by optical resolution (Scheme 15).⁵⁸⁻⁶⁰



Scheme 15

This 7 β -hydroxylated cocaine **61b** had been used by Dickerson and Janda to synthesize haptens for immunopharmacotherapy in cocaine abuse (Figure 9).⁶¹

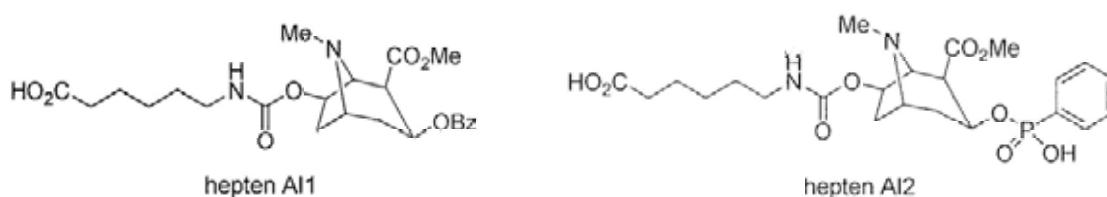
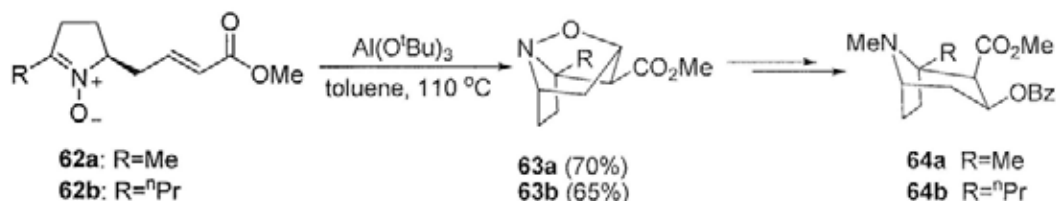


Figure 9

In 2010, Davis *et al.* prepared optically pure cocaine C-1 analogues **64a** and **64b**, starting from the chiral masked oxo sulfinimine to prepare chiral intermediates **62** and following the same strategy as Tufariello's synthesis (Scheme 16).⁴⁸



Scheme 16

However, there are still no therapeutically useful cocaine derivative reported hence further syntheses of cocaine analogues syntheses are needed.

The *endo*-mode INAC reaction of hept-6-enoses allows the construction of 7-membered ring carbocycles with nitrogen functionality on the carbocycles. These *endo*-cycloadducts had been shown to be transformed into optically pure tropanes.¹⁴ In this thesis, synthetic studies on natural (-)-cocaine (**3**) and its analogues are discussed.

Chapter 2

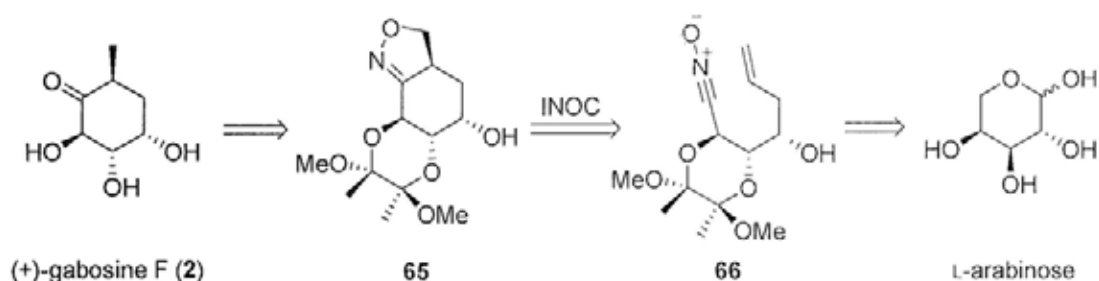
Results and Discussion

2.1 Construction of Carbocycles via Intramolecular Nitrile Oxide-Alkene Cycloaddition (INOC)

The intramolecular nitrile oxide-alkene cycloaddition (INOC) allows the formation of saturated carbocycles from sugar derivatives in good diastereoselectivity. These cycloadducts can be transformed into either natural products or their analogues with biological interests. In this section, application of INOC cycloadducts in the syntheses of gabosine F and a potentially bio-active cyclopent-2-enone is discussed.

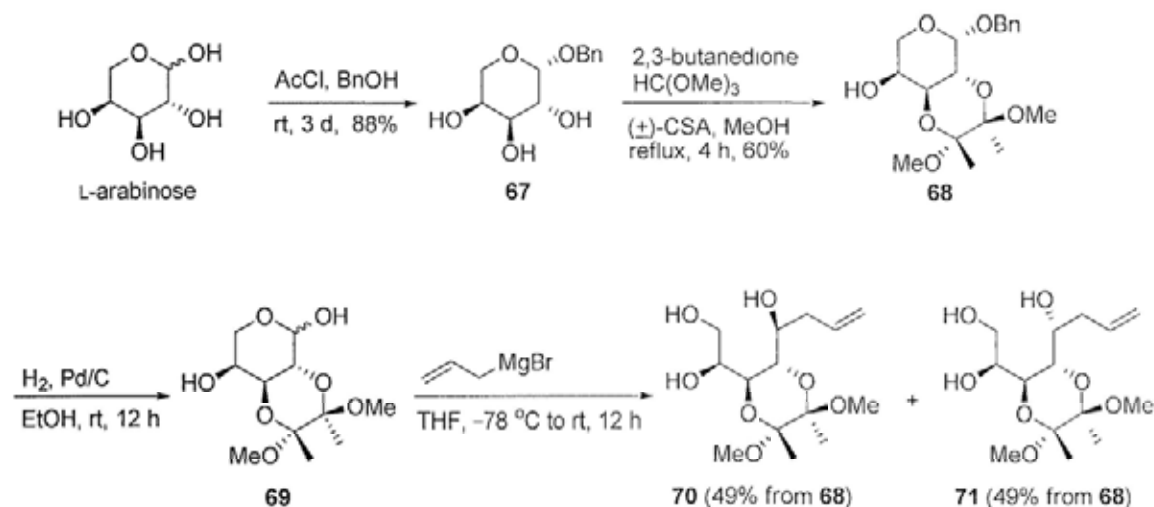
2.1.1 Synthesis of Optically Pure (+)-Gabosine F (2) from L-Arabinose

Retrosynthesis of (+)-gabosine F (2) shows that it could be synthesized from isoxazoline 65, which should be prepared from L-arabinose as shown below, using INOC as the key step (Scheme 17).



Scheme 17

Starting with *L*-arabinose, it was subjected to Fischer glycosidation to give benzyl- β -*L*-arabinopyranoside (**67**)⁶² by reacting with acidic benzyl alcohol (Scheme 18). Protection of the 2,3-*trans*-diol in **67** as butane 2,3-bisacetal³⁹ gave acetal **68**.

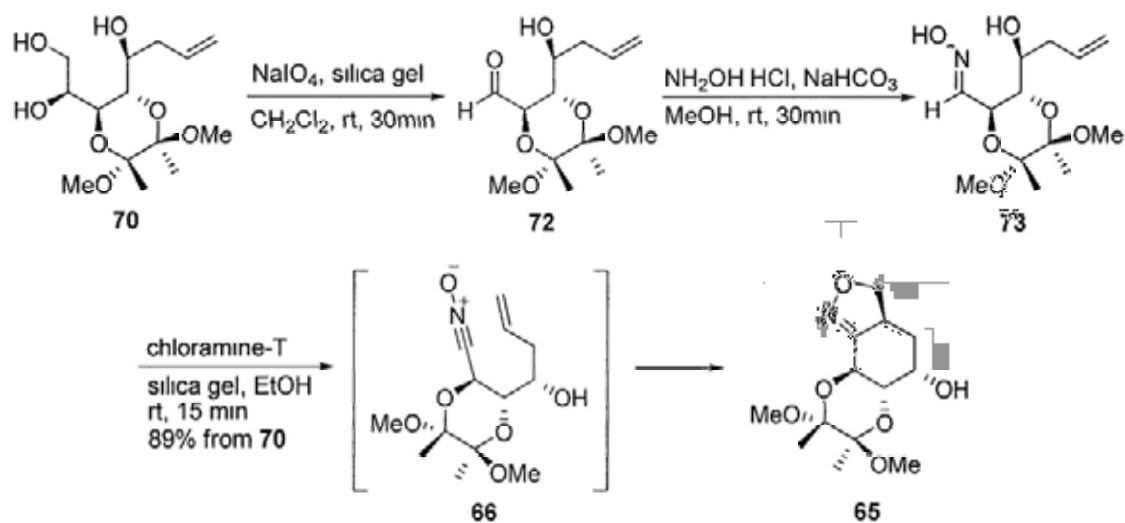


Scheme 18

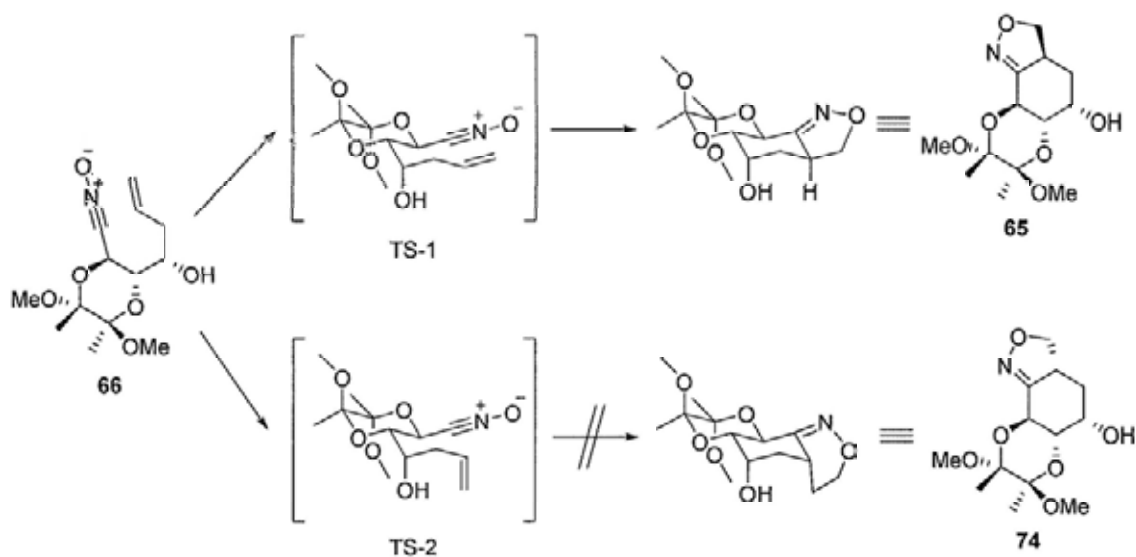
The benzyl group in acetal **68** was removed by hydrogenolysis using palladium-on-charcoal as catalyst to yield lactol **69**, which was then reacted with an excess of allylmagnesium bromide to give alkenes **70** and **71** in equal amounts.¹³ The poor diastereoselectivity of this allylation might be due to the inherent multi-oxygen functionalities of the *trans*-diacetal blocking group, which could offer chelation and complicate the transition state model, making no preference for either side of the addition.¹³

The alkene **70** was then transformed into the INOC cycloadduct, isoxazoline **65**, in excellent overall yield via a reaction sequence involving (i) silica-gel mediated glycol

cleavage oxidation,⁶³ (ii) oximation with hydroxylamine and (iii) chloramine-T/silica gel mediated INOC of oxime **73** (Scheme 19).⁸

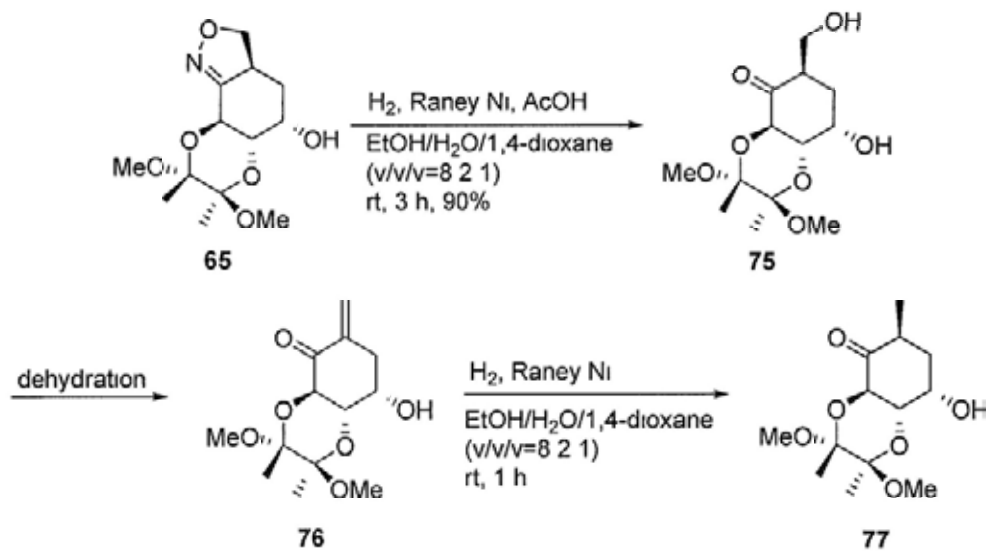


In this INOC reaction, isoxazoline **65** was obtained as the only one diastereomer. The reason of the diastereospecific outcome for this reaction can be explained by the following proposed transition states (Figure 10).



Due to the rigidity of the *trans*-diacetal blocking group, the acyclic carbon chain on hept-6-enose is occupying the equatorial position of the *trans*-diacetal ring, as shown in both TS-1 and TS-2. For TS-1, bonding orbitals of the nitrile oxide group and the alkene moiety are aligned in the same plane in space hence a better overlapping of orbitals leads to lower TS energy, resulting in the formation of isoxazoline **65**. On the other hand, there are no good overlapping of bonding orbitals in TS-2 and this cycloaddition pathway is not favoured, hence no isoxazoline **74** was formed.

The isoxazoline **65** obtained was subjected to Raney[®]-Nickel catalyzed hydrogenolysis to yield ketone **75** smoothly (Scheme 20). In order to remove the primary hydroxyl group in **75**, it was first dehydrated to give exocyclic enone **76**, which then was hydrogenated to provide the corresponding β -methyl ketone **77**.



Scheme 20

The ketone **75** was dehydrated under different conditions and the results are summarized in Table 1.

Table 1. Dehydration conditions of ketone **75**.

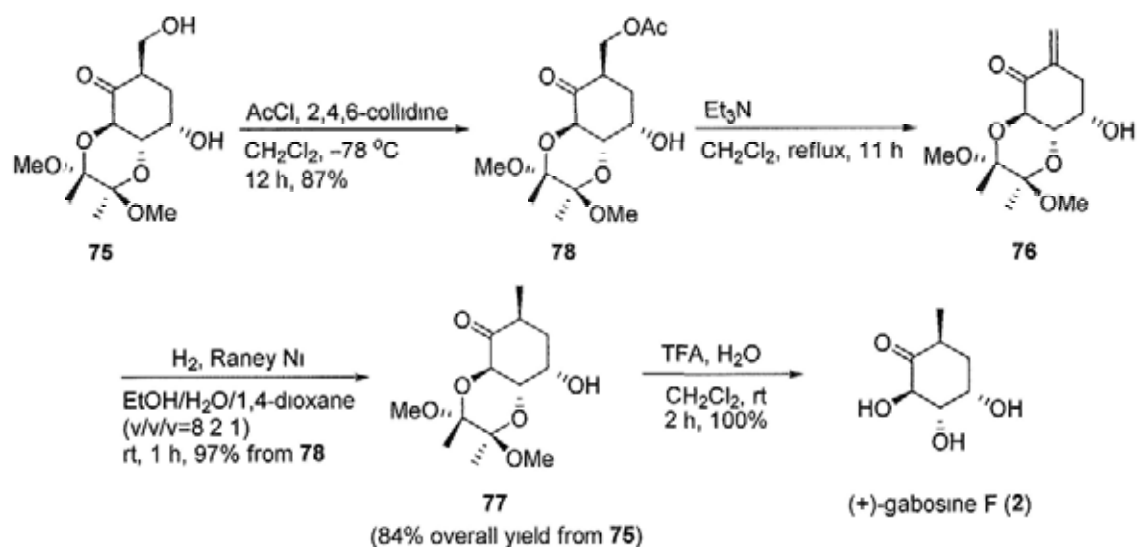
Entry	Dehydration Conditions	Yield of 77 from 75
1	Martin's sulfurane, THF, $-78\text{ }^{\circ}\text{C}$	No reaction
2	Martin's sulfurane, THF, rt	Decomposed
3	Burgess reagent, THF, $-78\text{ }^{\circ}\text{C}$	No reaction
4	Burgess reagent, CH_2Cl_2 , $-78\text{ }^{\circ}\text{C}$	No reaction
5	Burgess reagent, CH_2Cl_2 , rt	No reaction
6	Burgess reagent, CH_2Cl_2 , reflux, 18 h	38%
7	Burgess reagent, THF, reflux, 2 h	34%
8	MsCl (1 eq.), 2,4,6-collidine, CH_2Cl_2 , $-78\text{ }^{\circ}\text{C}$ to rt, 15 h then add Et_3N , rt, 1 h	43%
9	AcCl (1 eq.), 2,6-lutidine, CH_2Cl_2 , $-78\text{ }^{\circ}\text{C}$, 18 h then add Et_3N reflux, 10 h	61%
10	AcCl (1 eq.), 2,4,6-collidine, CH_2Cl_2 , $-78\text{ }^{\circ}\text{C}$, 18 h then add Et_3N reflux, 10 h	61%

Ketone **75** was first attempted to be dehydrated by Martin's sulfurane, which is a mild dehydrating agent which can do the activation and elimination in one pot without the addition of an external base.⁶⁴ No reaction was observed with ketone **75** at $-78\text{ }^{\circ}\text{C}$ (entry 1), but at room temperature the starting material was decomposed and did not lead to ketone **75** or any product (entry 2). It was suggested that at room temperature the dehydration may have take place, but the exocyclic enone **76** formed may be unstable and destroyed by Martin's sulfurane. Another mild dehydrating agent, Burgess reagent,⁶⁵ was then used to react with ketone **75**. It had no reaction with **75** at $-78\text{ }^{\circ}\text{C}$ (entries 3 and 4). When the reaction was risen to room temperature, ketone **75** still remained inert but no decomposition was observed (entry 5). The dehydration finally

occurred when reacting under boiling CH₂Cl₂ to afford enone **76**, which was then subjected to Raney[®]-Nickel catalyzed hydrogenation to yield the β -methyl ketone **77**, in 38% overall yield from ketone **75** (entry 6). Changing the reaction solvent for dehydration from CH₂Cl₂ to THF gave similar yields (entry 7).

The primary alcohol of ketone **75** was also mesylated regioselectively⁶⁶ by methanesulfonyl chloride with 2,4,6-collidine as base to give the corresponding mono-mesylate (entry 8), it was observed that some of the mesylate had been converted into the enone **76** from the TLC, but the elimination was not complete. The elimination reaction was completed by adding triethylamine into the same reaction flask to afford enone **76**, and the subsequent hydrogenation yielded **77** in 43% overall yield from ketone **75**. When ketone **75** was subjected to regioselective acetylation⁶⁶ with either 2,6-lutidine or 2,4,6-collidine as base, the corresponding mono-acetate **78** was formed without enone **76** showing on TLC (entries 9 and 10). Triethylamine was then added and the reaction was heated to cause the elimination to take place. Hydrogenation of resulting enone **76** afforded β -methyl ketone **77** in 61% overall yield from ketone **75**.

The acetate **78** was recognized to be fairly stable and could be isolated in a pure form. It was isolated prior to the elimination process in order to avoid any side reaction that might affect the elimination (Scheme 21). Regioselective acetylation of ketone **75** in the same conditions as mentioned previously furnished acetate **78** in an excellent yield.

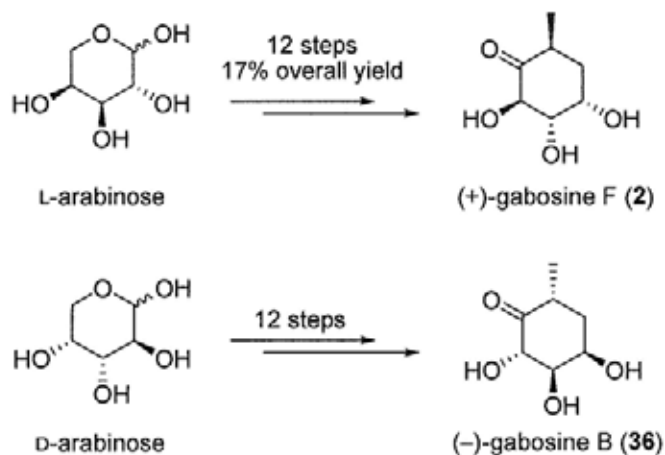


Scheme 21

The purified acetate **78** was reacted with triethylamine in CH_2Cl_2 under reflux to afford enone **76**, followed by hydrogenation to give β -methyl ketone **77** in 97% overall yield from acetate **78**. That is, 84% overall yield from ketone **75** and these condition furnished the highest yield to form β -methyl ketone **77** from ketone **75**. It should be noted that the Raney[®]-Nickel catalyzed hydrogenation of enone **76** afforded β -methyl ketone **77** as the sole product. The stereospecific outcome of this reaction might be due to the “anchor effect” of the axial free α -alcohol,⁶⁷ which directed the approach of the hydrogen from the α -face, resulting in the formation of β -methyl ketone **77**.

The remaining *trans*-diacetal blocking group of β -methyl ketone **77** was hydrolyzed with trifluoroacetic acid to give the target molecule (+)-gabosine F (**2**) in a quantitative yield (Scheme 21). The specific rotation, $[\alpha]_D^{20} +88.4$ (c 0.69, MeOH) {lit. $[\alpha]_D^{20} +94$ (c 1.0, MeOH)}, and the NMR spectral data are in good agreement with the

literature values.^{16a} The enantiopure (+)-gabosine F (**2**) was hence synthesized for the first time by using L-arabinose as the starting material, in 12 steps and 17% overall yield (Scheme 22).

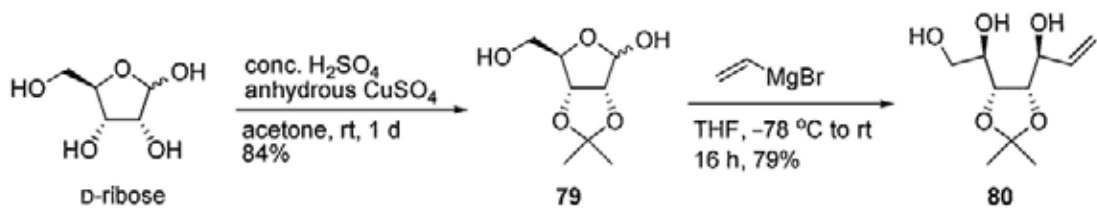


Scheme 22

Using the same synthetic strategy, (-)-gabosine B (**36**), which is the enantiomer of (+)-gabosine F (**2**), in theory can also be synthesized from D-arabinose, the enantiomer of L-arabinose (Scheme 22). This synthesis of (-)-gabosine B (**36**) is believed to be superior than the previous synthesis (15 steps, 4.3% overall yield) reported by Shinada *et al.*²⁴

2.1.2 Synthesis of Cyclopent-2-enone Derivatives

In the previous section, an INOC cycloadduct had been transformed into (+)-gabosine F (**2**), which is a hydroxylated cyclohexanone. In this section, preparation of hydroxylated cyclopent-2-enone derivatives from another INOC cycloadduct is discussed.



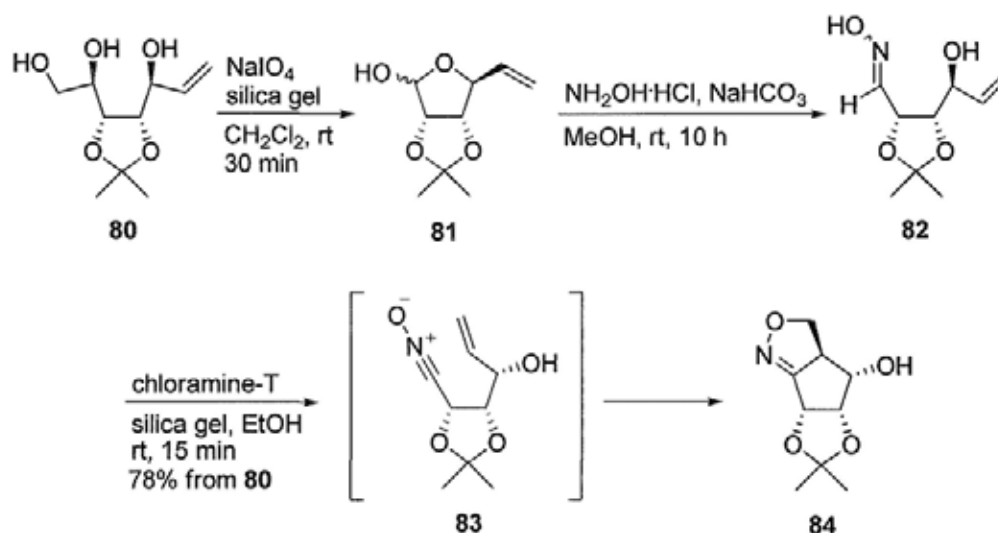
Scheme 23

The acetonide **79**,⁶⁸ synthesized from D-ribose by isopropylideneation, was reacted with vinylmagnesium bromide to afford alkene **80** in a good yield (Scheme 23).⁹ The highly stereoselectivity of vinylation was explained with the chelation controlled transition model⁹ shown in Figure 11.



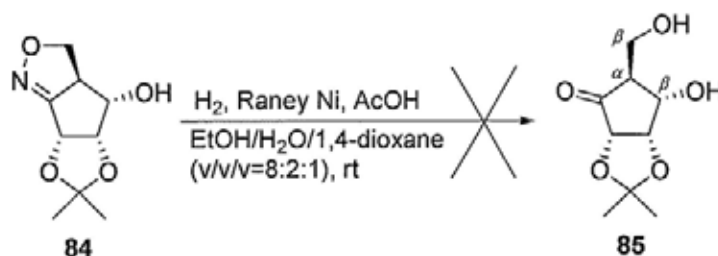
Figure 11

As the α -face of **79** is hindered by the bulky isopropylidene group, the vinylmagnesium bromide attack on the β -side, resulting in the formation of alkene **80**. The alkene **80** was then subjected to glycol cleavage oxidation to give crude lactol **81**, which was followed by oximation to afford oxime **82** (Scheme 24). The crude oxime **82** was then reacted with chloramine-T in the presence of silica gel to generate nitrile oxide **83** in situ and cyclized through INOC to form isoxazoline **84** as a single diastereomer.⁸



Scheme 24

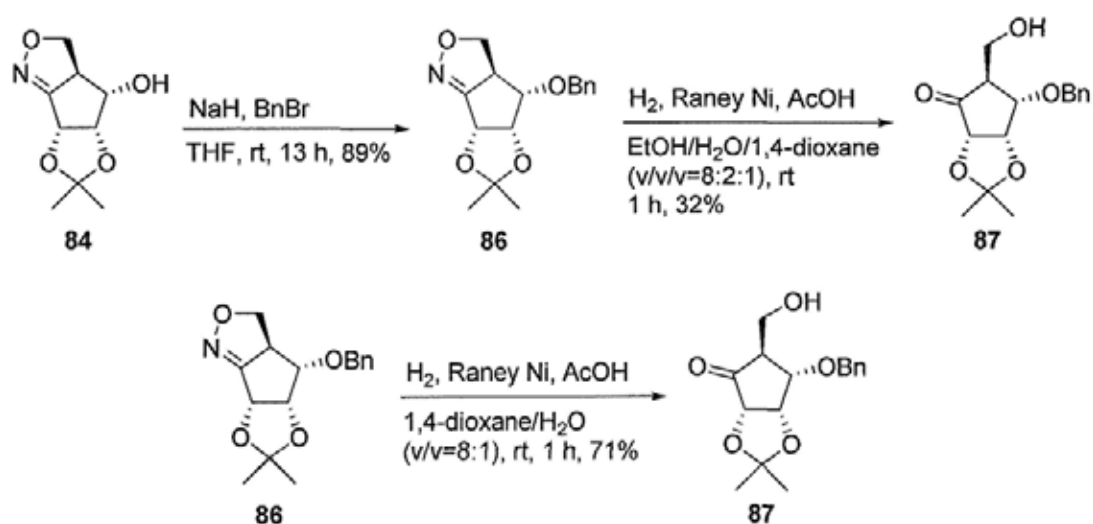
In order to convert isoxazoline **84** into the cyclopentanone moiety, the nitrogen-oxygen bond was attempted to cleave by hydrogenolysis to give β -hydroxyl ketone **85** (Scheme 25).



Scheme 25

However, Raney[®]-Nickel catalyzed hydrogenolysis of isoxazoline **84** did not afford β -hydroxyl ketone **85**. Surprisingly the starting material decomposed into a complex mixture of products which cannot be characterized. It was suggested that the presence of two β -hydroxyl groups in ketone **85** would allow the retro-aldol reaction to occur readily, leading the decomposition of ketone **85**.

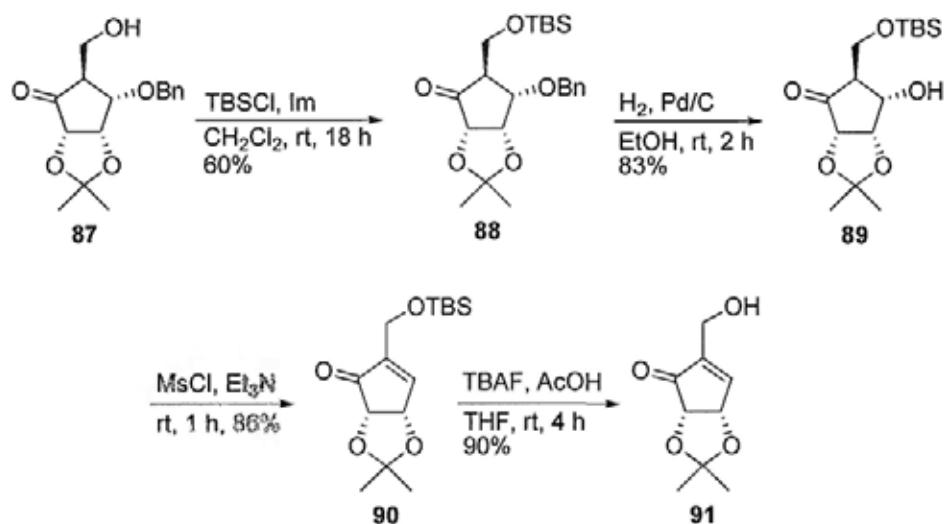
If the instability of ketone **85** was really due to the retro-aldol reaction, the stability of the cyclopentanone may be increased on reducing the number of β -hydroxyl groups. Isoxazoline **84** was therefore protected as a benzyl ether to form **86**, which was followed by hydrogenolysis in the same conditions as before to afford ketone **87** in moderate yield (Scheme 26).



Scheme 26

Changing the reaction solvent from EtOH/H₂O/dioxane (v/v/v=8:2:1) to dioxane/H₂O (v/v=8:1) improved the reaction yield of ketone **87**. Although ketone **87** is more stable than ketone **85**, ketone **87** is still not very stable and prone to decompose upon prolonged standing. Ketone **87** was hence directed quickly to the next step after purification by short column chromatography without characterization. Silylation of ketone **87** with *t*-butyldimethylsilyl chloride and imidazole in CH₂Cl₂ furnished silyl ether **88** (Scheme 27). Unlike the previous β -hydroxyl ketones, this silyl ether **88** is

stable enough to be characterized. The benzyl group in **88** was then removed by hydrogenolysis using palladium-on-charcoal as catalyst to give alcohol **89** in good yield.

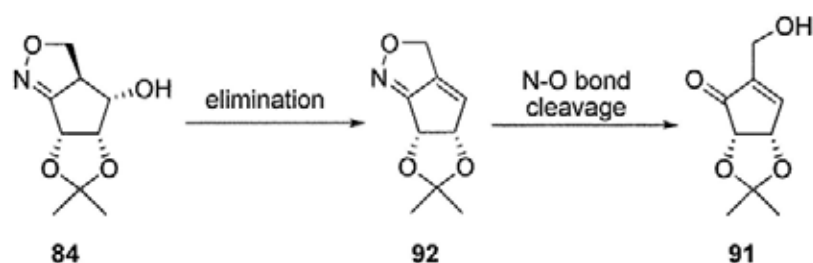


Scheme 27

In order to synthesize the target molecules, cyclopent-2-enone derivatives, the secondary hydroxyl group in silyl ether **89** had to be eliminated to give the resulting enone. Reacting silyl ether **89** with methanesulfonyl chloride and triethylamine at room temperature furnished the enone **90** directly. Alcohol **91**, was obtained easily by removing the silyl group of enone **90** with tetra-*n*-butylammonium fluoride, in an excellent yield. This alcohol **91** has a primary allylic alcohol in a cyclopent-2-enone moiety hence can be functionalized easily by replacing the allylic alcohol with different substituents. Alcohol **91** is actually the key intermediate of Khan's synthesis of (\pm)-neplanocin A.⁶⁹ Now, using the mentioned strategy, optically pure alcohol **91** can be synthesized from isoxazoline **84**, and this is a formal synthesis of natural (-)-neplanocin A (**1**).⁶⁹ A survey of neplanocin A syntheses from literatures showed that another approach⁷⁰ is more efficient than Khan's synthesis, but Khan's synthesis showed that the

alcohol **91** is an useful intermediate for natural product synthesis, as well as a potential anti-tumor substance.

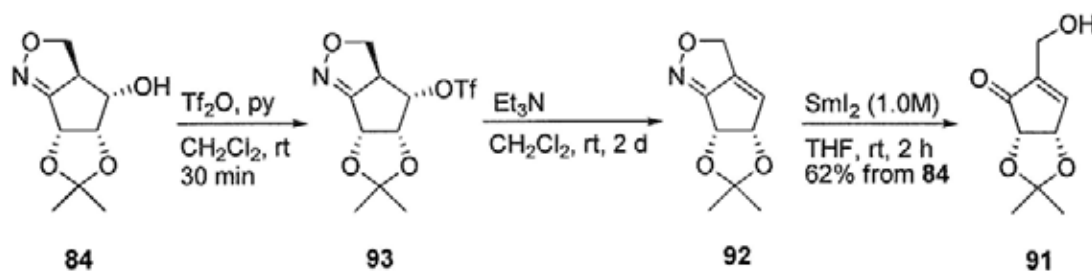
Starting from D-ribose, the cyclopent-2-enone derivative, alcohol **91**, was synthesized through the INOC cycloadduct, isoxazoline **84**, in 11 steps and 13% overall yield. Obviously this synthetic scheme requires too many steps and is not practical. Especially one of the intermediates, ketone **87**, is not stable upon prolonged standing. In order to make the synthesis more efficient, another synthetic pathway had to be explored.



Scheme 28

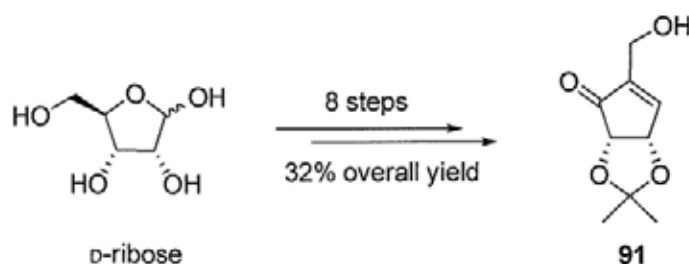
Another approach to cyclopent-2-enone **91** is to carry out elimination prior to nitrogen-oxygen bond cleavage (Scheme 28). As the intermediate **92** is already unsaturated, attempts to cleave the nitrogen-oxygen bond in **92** by hydrogenolysis would lead to hydrogenation on the alkene moiety as well. In order to obtain the alcohol **91**, the nitrogen-oxygen bond should be cleaved by another strategy. It was found that samarium(II) iodide is capable to perform nitrogen-oxygen bond cleavage,⁷¹ without saturating the alkene moiety. Thus starting with isoxazoline **84** as in the previous synthesis, the free hydroxyl group was first activated by trifluoromethanesulfonic anhydride to afford triflate **93** (Scheme 29). Elimination of crude triflate **93** under mild conditions furnished **92** smoothly, and this was followed by the samarium(II) iodide

mediated N-O bond cleavage to give the alcohol **91**, in 62% overall yield from isoxazoline **84**.



Scheme 29

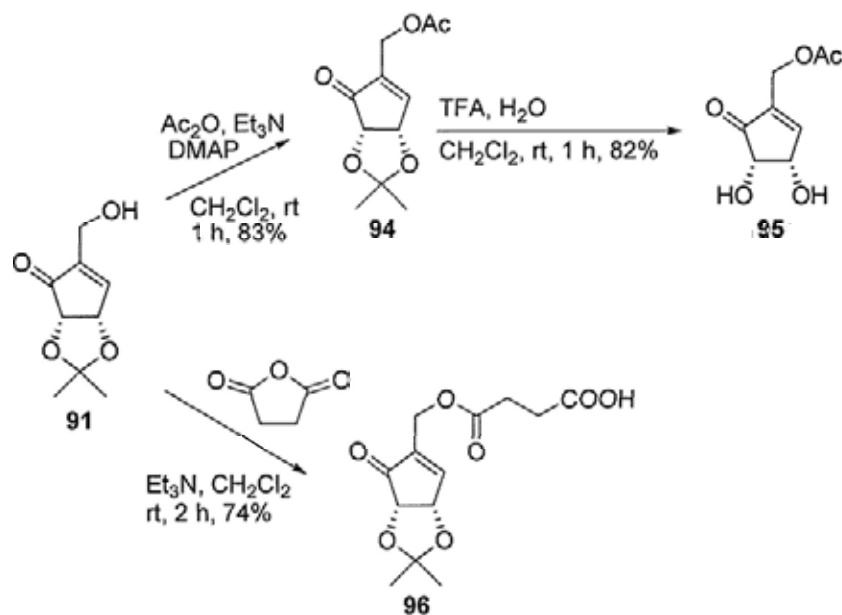
Using this new synthetic strategy, alcohol **91** was obtained from D-ribose in 8 steps with 32% overall yield (Scheme 30), providing an efficient approach to prepare optically pure alcohol **91**.



Scheme 30

With the alcohol **91** in hand, it can be transformed into several cyclopent-2-enone derivatives (Scheme 31). The allylic alcohol of **91** was reacted with acetic anhydride to give acetate **94** in 83% yield. The isopropylidene group in acetate **94** can be removed by TFA hydrolysis, yielding diol **95**. Both acetate **94** and diol **95** can be recognized as the 5-membered ring versions of COTC⁷² analogues and their anti-tumor activities would be investigated. Reacting alcohol **91** with succinic anhydride and

triethylamine, followed by acid work-up afforded carboxylic acid **96**. The carboxylic acid functionality in **96** is capable to form peptide linkage with any proteins or peptides and the bioactivity of these conjugates would be studied.



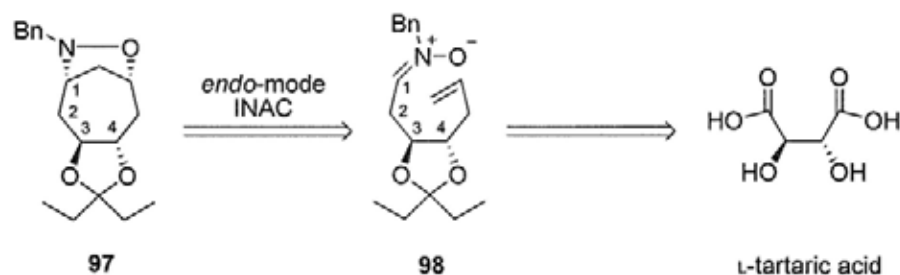
Scheme 31

2.2 Construction of Carbocycles via Intramolecular Nitron-Alkene Cycloaddition (INAC)

As mentioned in the previous section, optically pure carbocycles were formed from carbohydrates via INOC reactions. In this section 6- and 7-membered carbocycles were prepared by INAC reactions. Also, synthetic studies towards optically pure (-)-cocaine (**3**) and its analogues from carbohydrates are discussed.

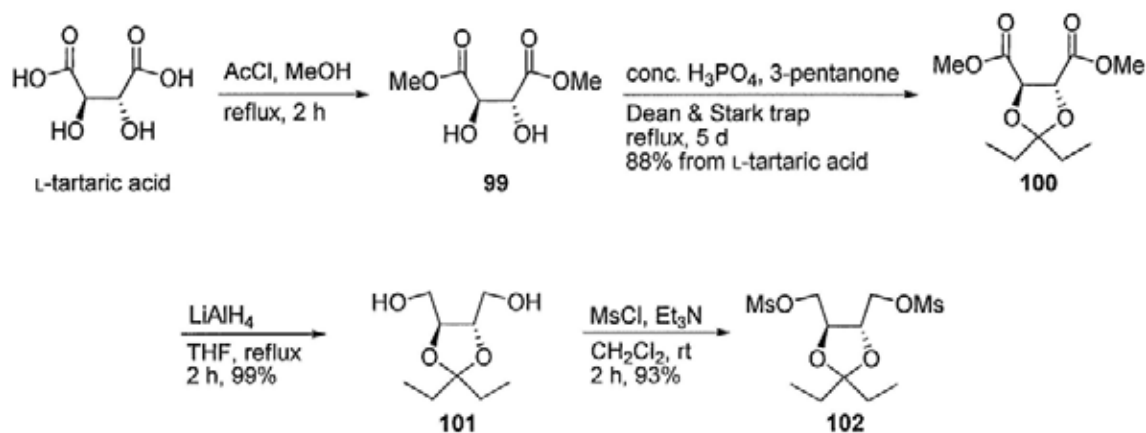
2.2.1 Studies on Regioselectivity of INAC on Hept-6-enose from L-Tartaric Acid with a 3,4-*trans*-Pentylidene Blocking Group

From the works conducted by my previous colleague, Dr. Wong Wai Fun, INAC of hept-6-enose containing 3,4-*trans*-isopropylidene blocking group furnished exclusive formation of 7-membered *endo*-cycloadducts due to the torsional strain of the blocking group.¹⁴ In order to further support this explanation, INAC of nitron **98**, a hept-6-enose bearing a 3,4-*trans*-pentylidene as the only blocking group, which providing the same torsional strain as 3,4-*trans*-isopropylidene moiety, was studied (Scheme 32). If the *endo*-cycloaddition is really due to the torsional strain of the *trans*-blocking group, INAC of nitron **98** would also lead to exclusive formation of an *endo*-cycloadduct. As one of the synthetic intermediates towards nitron **98** is volatile, using a pentylidene instead of isopropylidene as the blocking group can increase the molecular weight of this intermediate hence reduce its volatility.



Scheme 32

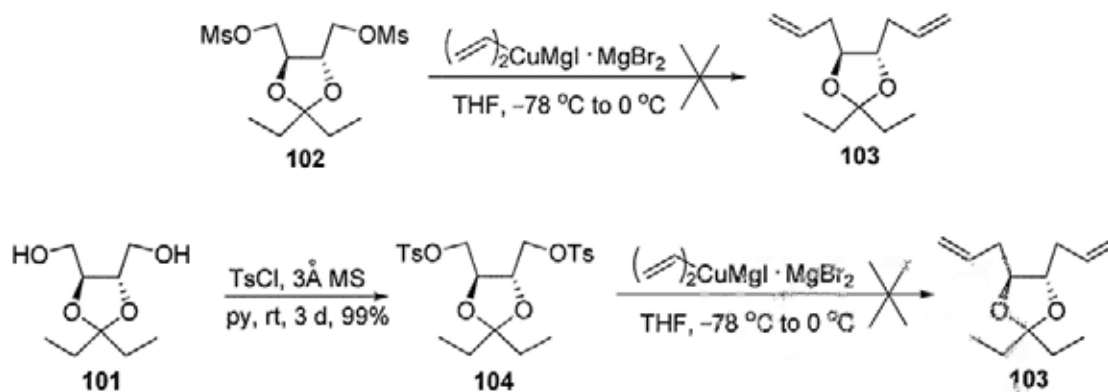
Thus starting with L-tartaric acid, it was first transformed into its methyl ester **99** through Fischer esterification⁷³ (Scheme 33). The 2,3-*trans*-diol of ester **99** were then protected by a pentydene group by heating in 3-pentanone with a catalytic amount of H₃PO₄. A Dean and Stark trap allowed continuous removal of water from the reaction mixture, hence, forcing the equilibrium toward the product side, resulting in an excellent overall yield of diester **100** from L-tartaric acid.



Scheme 33

Reduction of ester **100** with LiAlH₄ in THF under reflux led to the formation of diol **101**, followed by activation of two hydroxyl groups by methanesulfonyl chloride to give dimesylate **102** (Scheme 33). The dimesylate **102** was attempted to carry out vinyl

substitution with cuprate,^{74a} which was generated from mixing vinylmagnesium bromide with copper(I) iodide at low temperature, in order to afford the desired dialkene **103** (Scheme 34).

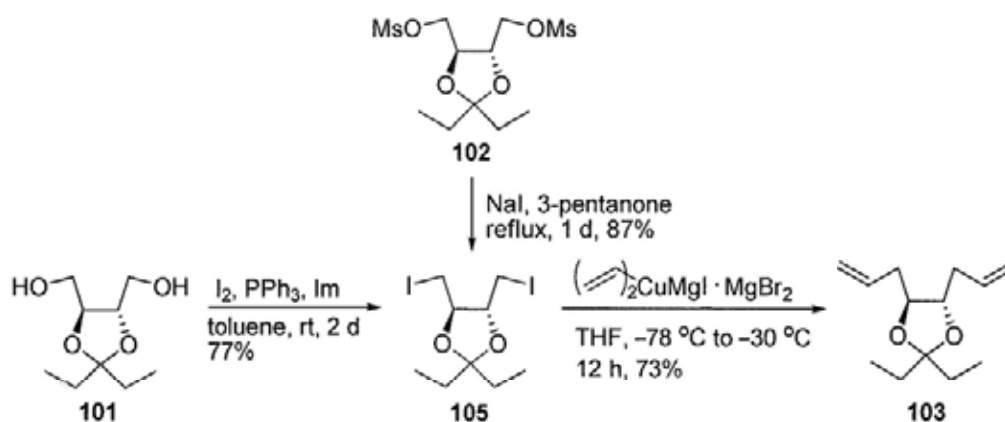


Scheme 34

However, no desired dialkene **103** was formed and the starting material decomposed into a mixture of products which could not be isolated as pure compound. The ditosylate **104**, formed by tosylation of diol **101**, showed no reaction under the same reaction conditions. Unlike dimesylate **102**, reacting divinyl cuprate with ditosylate **104** did not lead to the decomposition of the starting material. It was suggested that the methyl protons in the mesylate moiety of **102** were acidic enough to be deprotonated by the cuprate, leading to a series of undesired rearrangement reactions.

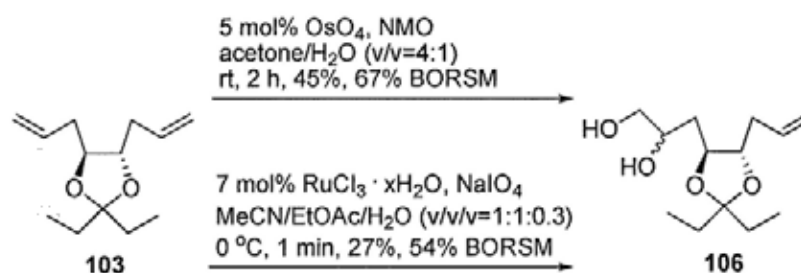
Besides activating diol **101** by sulfonate esters, transformation of **101** into the corresponding iodide **105** was also performed in order to realize the vinyl substitution (Scheme 35). Thus diiodide **105** was prepared by either (i) reacting diol **101** with iodine, triphenylphosphine and imidazole in toluene or (ii) displacement of mesylates in **102** with iodide ions. This diiodide **105** was then subjected to vinylation with the cuprate.

The dialkene **103**, which was found to be a volatile substance, was formed in good yield, especially when performing this reaction at lower temperature ($-30\text{ }^{\circ}\text{C}$ instead of $0\text{ }^{\circ}\text{C}$).



Scheme 35

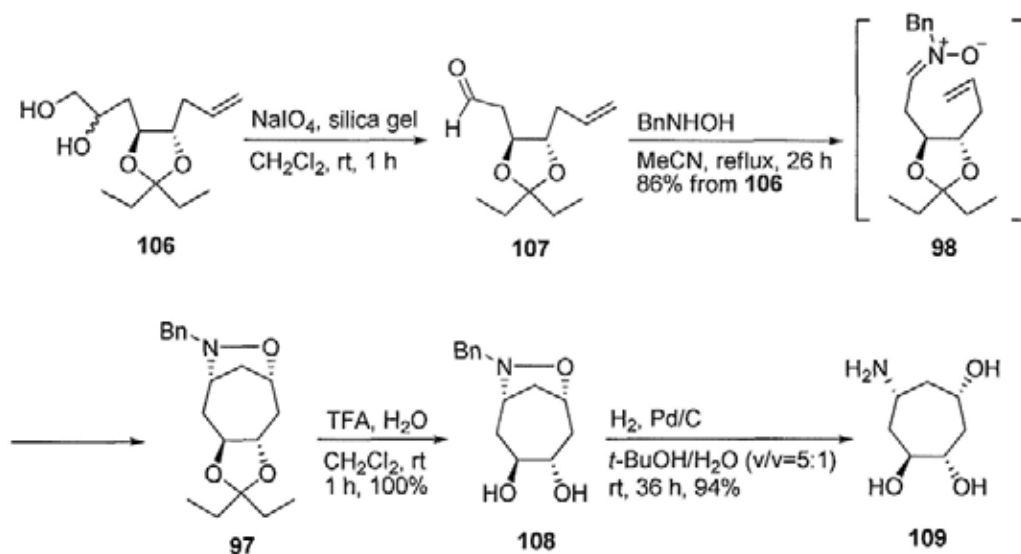
The difference in reactivity between disulfonates **102/104** and diiodide **105** probably because they were reacting under different mechanisms.^{74b,c} According to literature, the reaction between alkyl iodide and cuprate reagent was not a classical $\text{S}_{\text{N}}2$ substitution.^{74c} This can explain why diiodide **105** but not disulfonates **102/104** was vinylated.



Scheme 36

With the dialkene **103** in hand, one of its alkene moieties was dihydroxylated to form diol **106** (Scheme 36). Catalytic osmium tetroxide dihydroxylation with one

equivalent of 4-methylmorpholine *N*-oxide as co-oxidant furnished diol **106** in good yield in counting the recovery of starting material. The ruthenium tetroxide catalyzed flash dihydroxylation⁷⁵ afforded a lower yield of diol **106**, although the reaction proceeded much faster.



Scheme 37

The diol **106** was then subjected to glycol cleavage oxidation to form aldehyde **107** (Scheme 37), which was condensed with *N*-benzylhydroxylamine to form nitron **98**. Subsequent INAC reaction by heating the reaction mixture to reflux yielded the *endo*-cycloadduct isoxazolidine **97** as the only diastereomer. The ring size of cycloadduct was confirmed by the ¹³C DEPT NMR spectrum of isoxazolidine **97**. There are five resonances in the upfield region (δ 25–40 ppm) were assigned to be methylene group, two of which are the methylene carbons of pentyldene moiety, the other three are belonged to the cycloheptane ring. If *exo*-cycloadduct cyclohexane had been formed, only four methylene resonances in upfield region would have been found. Both the

regio- and stereochemistry of diol **108** were further confirmed by X-ray crystallographic analysis (Figure 12). Diol **108** was obtained from TFA hydrolysis of isoxazolidine **97** in quantitative yield.

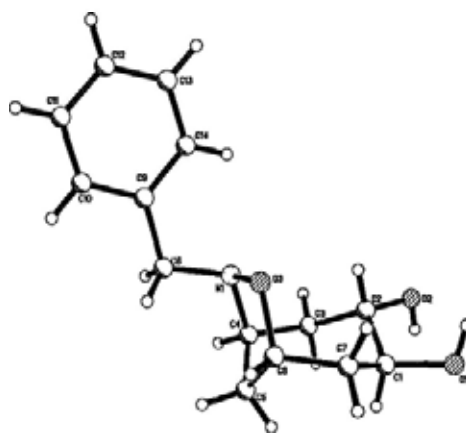


Figure 12. X-ray crystallographic structure of diol **108**.

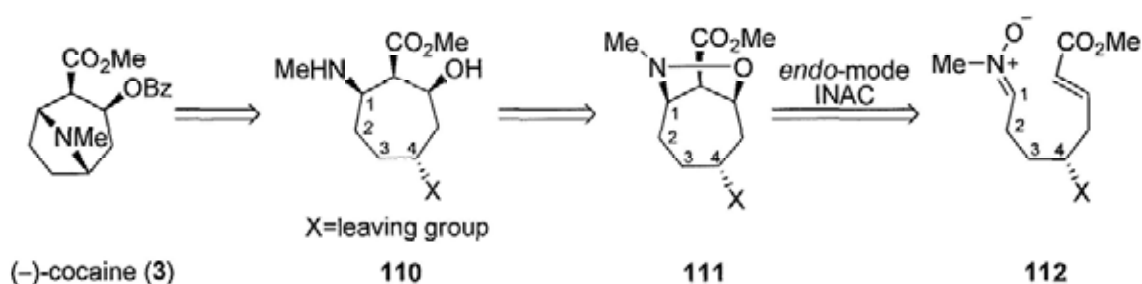
Since the INAC of nitron **98**, which consists of 3,4-*trans*-pentylidene as the only blocking group, afforded exclusive formation of *endo*-cycloadduct, isoxazolidine **97**. It is concluded that the presence of 3,4-*trans*-pentylidene (or isopropylidene) can induce the *endo*-mode INAC reaction to perform exclusively. Thus the regioselectivity of INAC reactions can be certainly controlled by changing the blocking group of substrates.

In addition, the diol **108** was transformed into aminocycloheptanol **109**, by hydrogenolysis catalyzed by palladium-on-charcoal (Scheme 37). Both nitrogen-oxygen bond and nitrogen-benzyl moiety were cleaved, resulting in the formation of **109** in 94% yield. Thus aminocycloheptanol **109** were synthesized from L-tartaric acid in 10 steps

with 27% overall yield, thus providing a high yielding approach of aminocycloheptanol synthesis.

2.2.2 Synthetic Studies towards (-)-Cocaine (3) and (-)-Cocaine Analogues

By analyzing the structure of (-)-cocaine (3), it was noted that the structure of cocaine consists of a 7-membered carbocycle, with a carboxylate ester moiety connected to the carbocyclic ring (Scheme 38). The tropane skeleton might be constructed by allowing the amine group in C-1 position to attack the C-4 of **110**, obtained from hydrogenolysis of isoxazolidine **111**. The isoxazolidine **111** might be prepared by *endo*-mode INAC reaction of **112**, using an α,β -unsaturated ester as the dipolarophile.



Scheme 38

In this section, approaches towards (-)-cocaine (3) and (-)-cocaine analogues syntheses from carbohydrate via *endo*-mode INAC reaction as the key step are discussed.

2.2.2.1 INAC of Nitrones with a 2,3-*cis*-Isopropylidene as Blocking Group and an α,β -Unsaturated Ester as Dipolarophile

It was attempted to use the nitron **113**, which bearing an α,β -unsaturated ester moiety, to perform INAC reaction to furnish *endo*-cycloadduct **114** (Scheme 39). The C-4 free hydroxyl group of cycloadduct **114** could be activated by MsCl hence allowing the formation of a tropane skeleton in the next step. Although previous studies¹³ showed that the INAC of hept-6-ene bearing 2,3-*cis*-isopropylidene would lead to an exclusive formation of 6-membered *exo*-cycloadduct, it was hoped that the presence of α,β -unsaturated ester moiety in nitron **113** could induce the *endo*-mode INAC reaction, by electronic effect.



Scheme 39

Obviously, the α,β -unsaturated ester is an electron deficient alkene with the β -carbon bearing slightly positive charge (Figure 13).

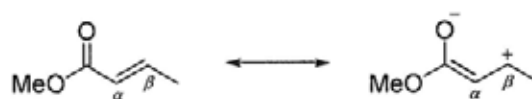
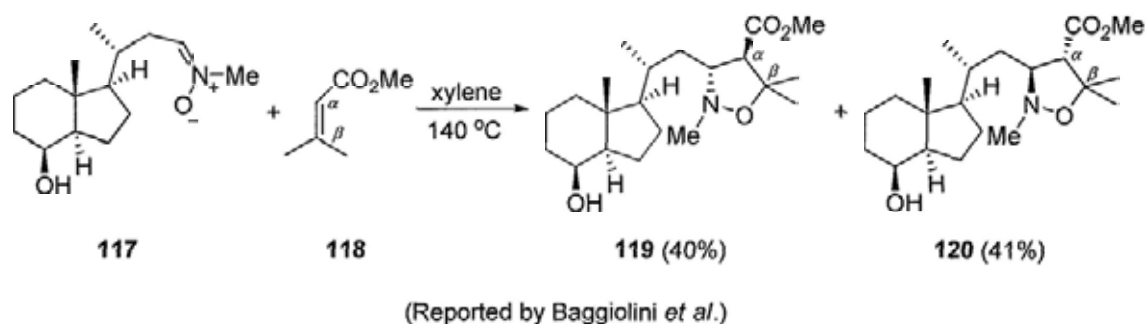


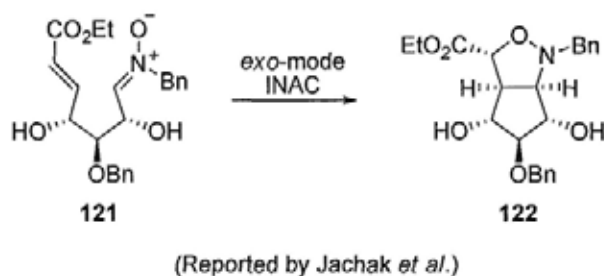
Figure 13. Resonance structures of the α,β -unsaturated ester.

During 1,3-dipolar cycloaddition between a nitron and the α,β -unsaturated ester, the oxygen atom of nitron, bearing a negative charge, would attack the β -carbon of the α,β -unsaturated ester.⁴ This regiochemical outcome was supported by several literature reports of intermolecular 1,3-dipolar cycloaddition between the nitron and the α,β -unsaturated ester.⁷⁶⁻⁷⁸ For example, Baggiolini *et al.* reported the formation of 1:1 mixture of isoxazolidine esters **119** and **120** by intermolecular nitron-alkene cycloaddition, in which the oxygen atom of nitron attacked the β -carbon of the methyl 3,3-dimethylacrylate (**118**) (Scheme 40).⁷⁶



Scheme 40

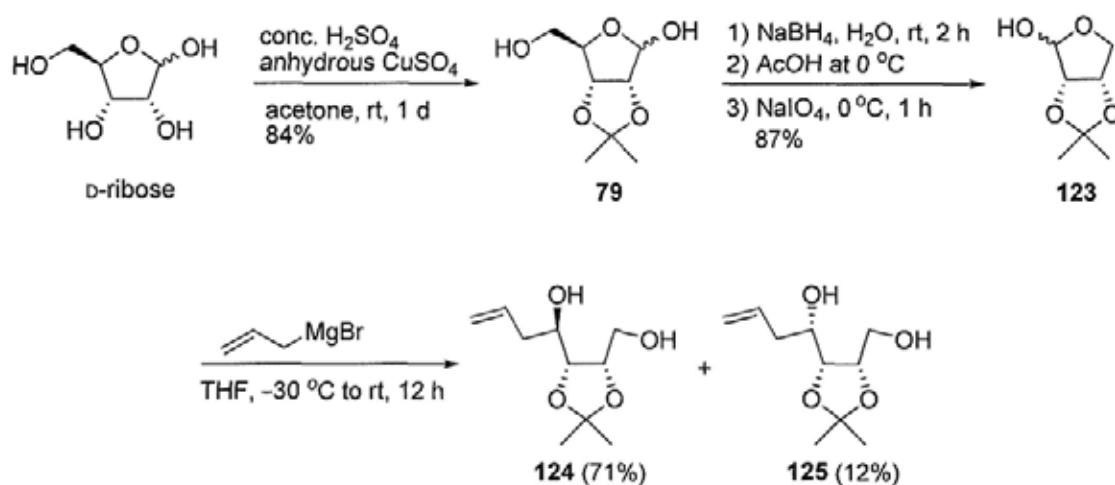
However, it was reported that the INAC reaction of nitron **121**, bearing an α,β -unsaturated ester as the dipolarophile, had led to the formation of an 5-membered *exo*-cycloadduct rather than a 6-membered *endo*-cycloadduct (Scheme 41).⁷⁹



Scheme 41

In contrast to the nitrone **121**, the INAC of nitrone **113** involved selectivity between the formations of 6- or 7-membered cycloadducts (Scheme 39). Such regiochemical studies of INAC reaction are discussed in this thesis.

Starting from acetonide **79**, it was transformed into lactol **123** in an one pot reaction, firstly sodium borohydride reduction (Scheme 42), followed by glycol cleavage oxidation, as reported by Baxter *et al.*⁸⁰ The lactol **123** was subjected to Grignard reaction with allylmagnesium bromide, affording alkene **124** as the major product and its 4-epimer alkene **125** as the minor product.⁸¹



Scheme 42

The diastereoselectivity of the allylation can be explained by the chelation controlled transition model as shown in Figure 14. The α -face of **123** is blocked by the bulky isopropylidene moiety, causing the allyl group more likely to attack on the β -face of carbonyl carbon, yielding **124** as the major product.

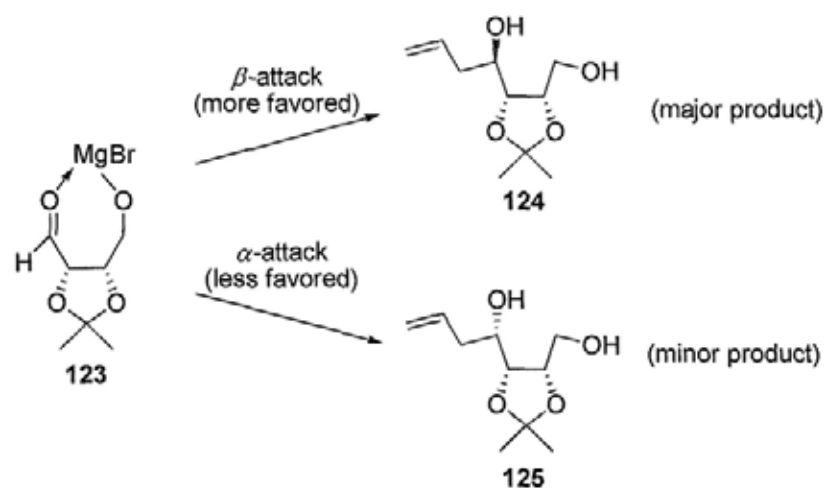
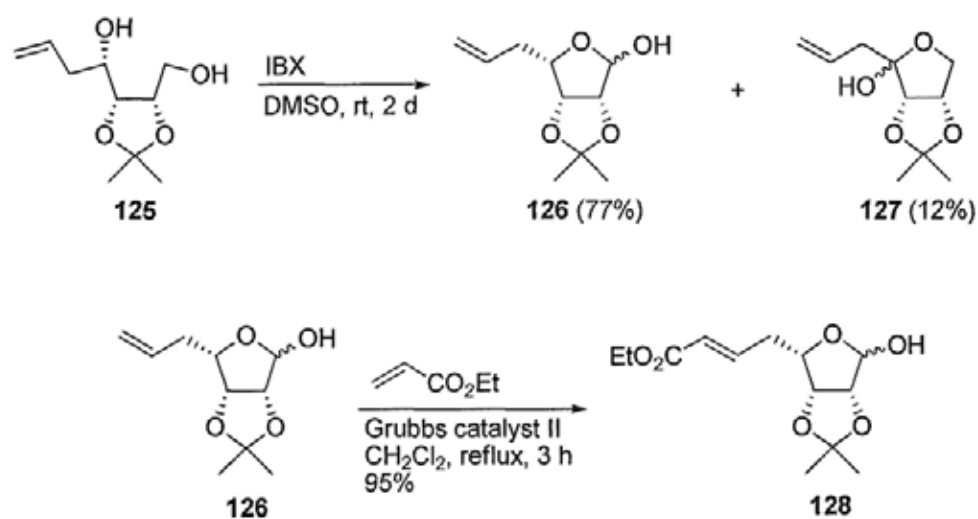


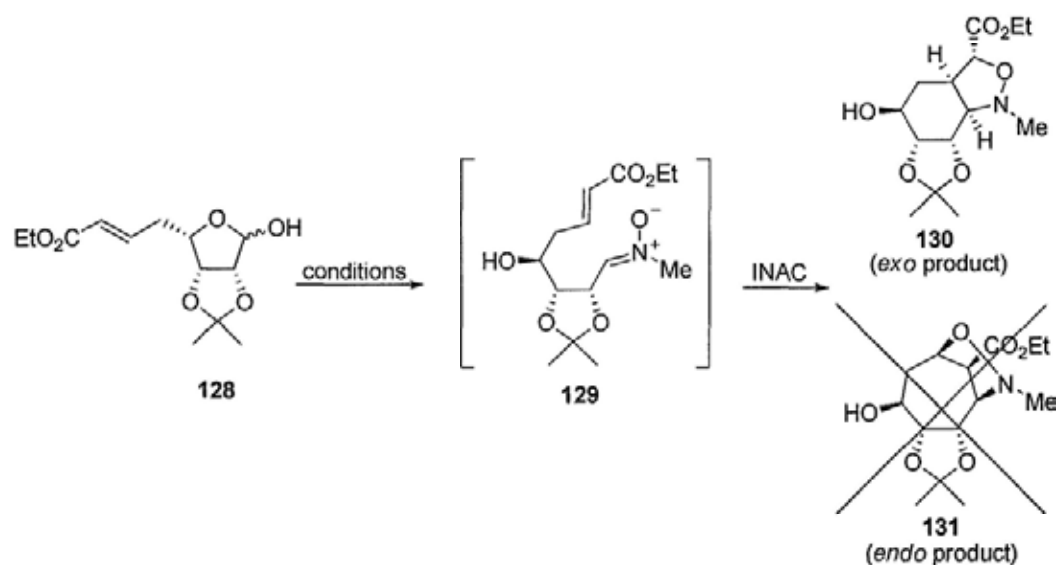
Figure 14

Firstly, the alkene **125** was used to prepare the nitrone for studying INAC reaction. It was subjected to selective oxidation of its primary alcohol by one equivalent of 2-iodoxybenzoic acid⁸² in DMSO to give the desired lactol **126** in a good yield. Lactol **127**, formed by oxidizing the secondary alcohol of **125**, was isolated as the minor product (Scheme 43).



Scheme 43

The lactol **126** was then carried out cross-metathesis with ethyl acrylate, catalyzed by the second generation Grubbs catalyst,⁸³ to furnish α,β -unsaturated ester **128** as the only product in an excellent yield (Scheme 43). The large coupling constant ($J = 15.6$ Hz) of the two alkene signals (δ 5.95 and 7.00 ppm) in the ^1H NMR spectrum of **128** indicated that a *trans*-alkene was formed.



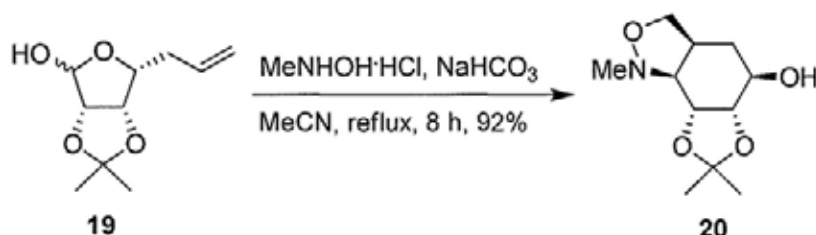
Scheme 44

With the α,β -unsaturated ester **128** in hand, it was subjected to condensation with N -methylhydroxylamine to give nitron **129** in order to perform the INAC reaction (Scheme 44). Several INAC conditions were tried and the results are summarized in Table 2.

Table 2. Reaction conditions between ester **128** and *N*-methylhydroxylamine.

Entry	Conditions	Yield of 130
1	MeNHOH·HCl, NaHCO ₃ , MeCN, rt	nil
2	MeNHOH·HCl, NaHCO ₃ , MeCN, reflux	decomposed
3	MeNHOH·HCl, py, MeCN, reflux, 17 h	41%
4	MeNHOH·HCl, py, CH ₂ Cl ₂ , reflux, 34 h	67%
5	MeNHOH·HCl, py, EtOH, reflux, 2 h	72%

When α,β -unsaturated ester **128** was reacted with *N*-methylhydroxylamine hydrochloride and sodium hydrogen carbonate, no desired INAC cycloadduct formed, with a mixture of products in which none of them could be purely isolated (entry 1). This result was in contrast to the INAC reaction of lactol **19**, the enantiomer of **126**, which was able to furnish the INAC cycloadduct in an excellent yield (Scheme 45).¹³

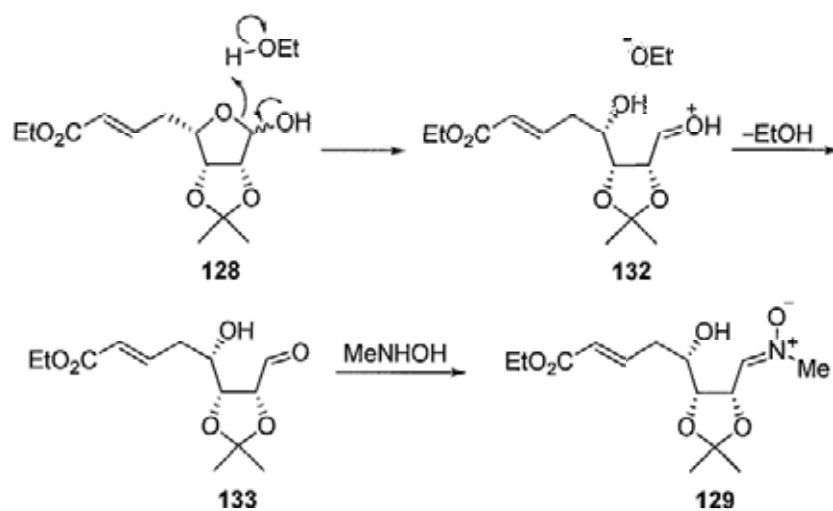
**Scheme 45**

The same reaction conditions were then repeated on the α,β -unsaturated ester **128** as shown in entry 2. However, decomposition of **128** occurred after prolonged heating instead of yielding any INAC cycloadduct. Actually the only difference in structure between lactol **19** and α,β -unsaturated ester **128** is the alkene moiety, with lactol **19** bearing a terminal alkene and the α,β -unsaturated ester **128** having an ethyl carboxylate substituted alkene. Thus the difference in reactivity should be due to the presence of α,β -unsaturated ester moiety in **128**, which is more likely to be attached by nucleophiles.

It was suggested that the base (NaHCO_3) used in the entries 1 and 2 was too basic, causing 1,4-Michael addition of *N*-methylhydroxylamine to the ester **128** hence did not afford any INAC cycloadduct.

When allowing ester **128** to react with *N*-methylhydroxylamine hydrochloride and pyridine in MeCN and heated under reflux (entry 3), the INAC *exo*-cycloadduct **130** was formed as the only product (Scheme 44). Changing the reaction solvent for INAC reaction did not encourage the formation of any desired *endo*-cycloadduct, even though some improvements of reaction yields (*exo*-cycloadduct) were observed (entries 4 and 5).

It should be noted that using EtOH as reaction solvent allowed the formation of the INAC cycloadduct **130** in much shorter time (entry 5). It is probably due to the protic nature of EtOH, which facilitated the opening of lactol **128** into its aldehyde form **133**. Aldehyde **133** then reacted with *N*-methylhydroxylamine to give nitrone **129** (Scheme 46). Whereas in aprotic solvents like CH_2Cl_2 and MeCN such the lactol ring opening to free aldehyde **133** was not facilitated, resulting in a longer reaction time (entries 3 and 4).



Scheme 46

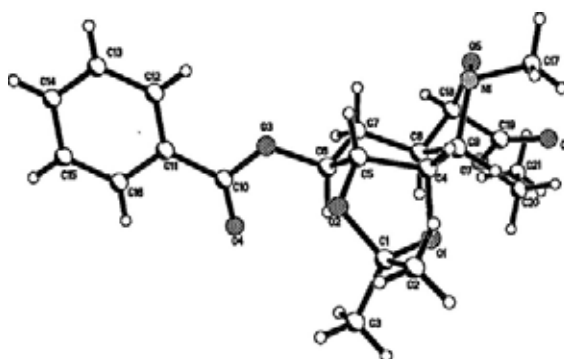
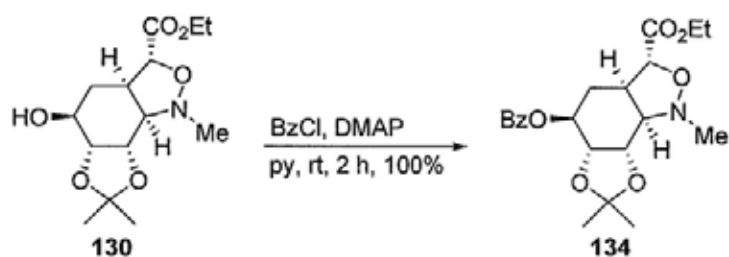


Figure 15. X-ray crystallographic structure of benzoate **134**.

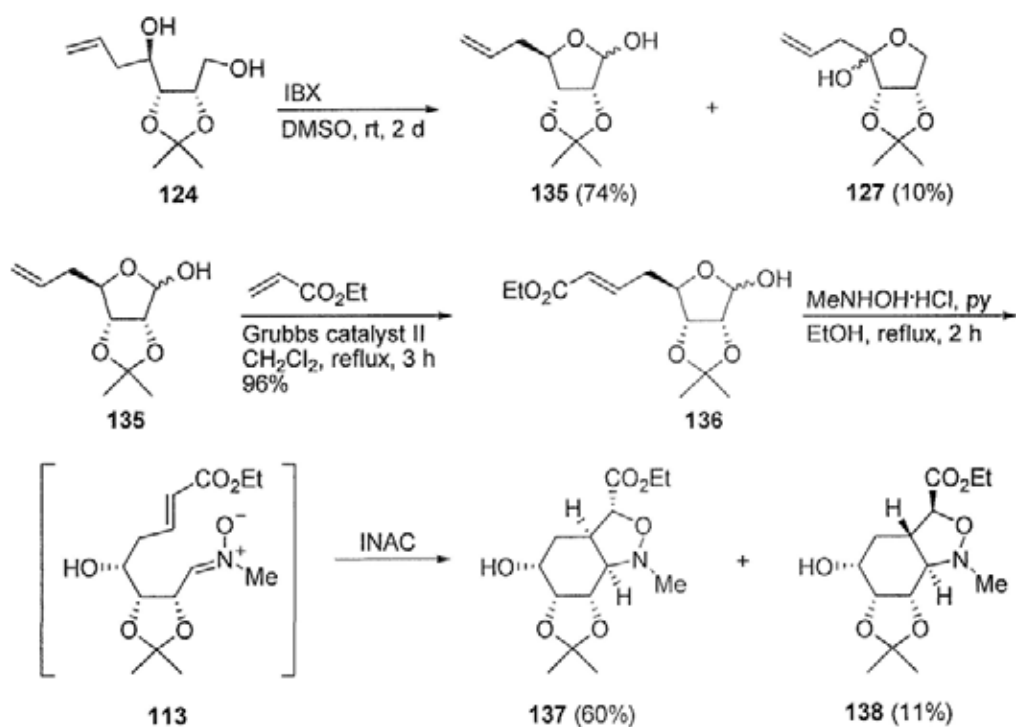
Although the ring size of this cycloadduct could not be convincingly confirmed by ^{13}C DEPT NMR, both the regio- and stereochemistry of cycloadduct **130** were assigned by X-ray crystallographic analysis of its benzoate **134** (Figure 15), formed in quantitative yield by reacting cycloadduct **130** with benzoyl chloride (Scheme 47).



Scheme 47

From the X-ray crystallographic structure of benzoate **134** (Figure 15), it clearly shows that a 6-membered *exo*-cycloadduct was formed. That is, the α,β -unsaturated ester moiety in nitrone **129** cannot direct the *endo*-mode INAC reaction, by means of electronic effect.

Then the INAC of nitrone **113**, which is the 4-epimer of nitrone **129**, was also studied (Scheme 48). Following the same strategy as described previously, alkene **124** was subjected to selective IBX oxidation, giving lactol **135** as the major product. Lactol **135** was then reacted with ethyl acrylate in the presence of second generation Grubbs catalyst to give *trans*- α,β -unsaturated ester **136** in an excellent yield. The nitrone **113** was formed by reacting the α,β -unsaturated ester **136** with *N*-methylhydroxylamine hydrochloride and pyridine under boiling EtOH, and cyclized to give two INAC *exo*-cycloadducts, isoxazolidines **137** and **138**.



Scheme 48

The regio- and stereochemistry of the minor cycloadduct **138** was confirmed by X-ray crystallography (Figure 16).

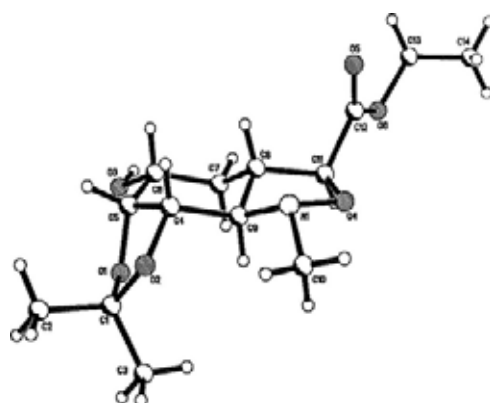
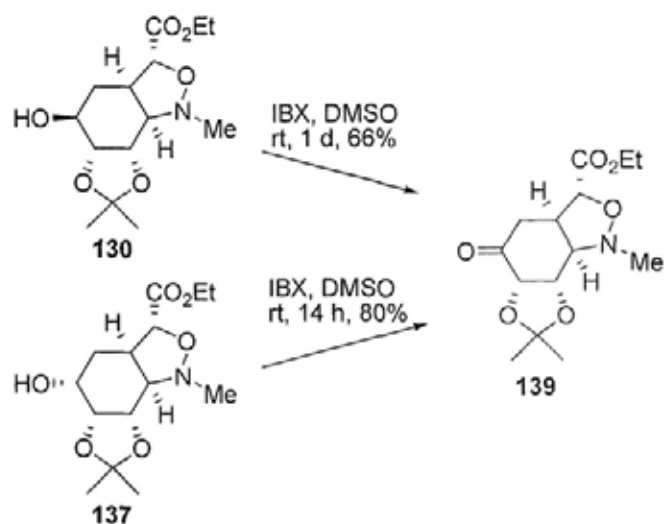


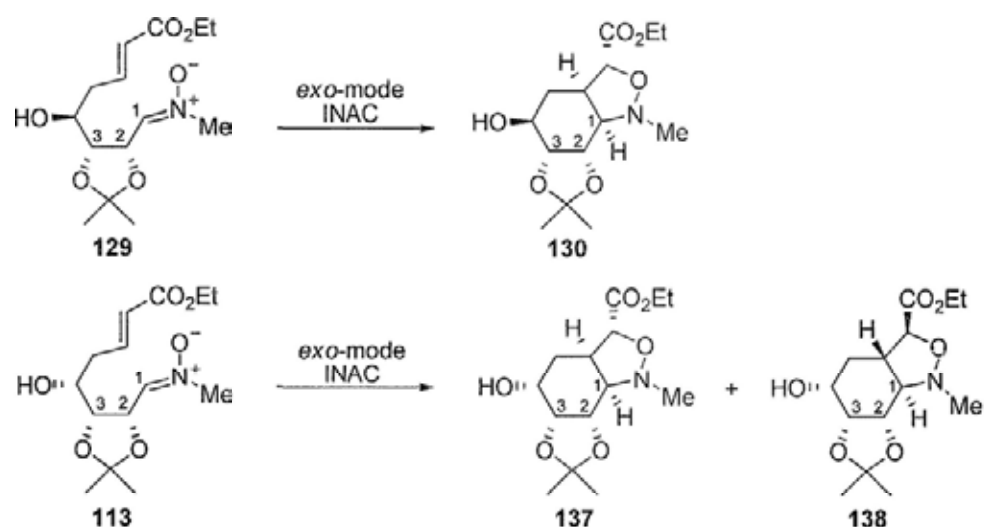
Figure 16. X-ray crystallographic structure of isoxazolidine **138**.

The ring size and stereochemistry of the other cycloadduct, isoxazolidine **137**, formed in this INAC reaction, was assigned as follows. Both isoxazolidines **130** and **137** were able to afford the identical ketone **139** by IBX oxidation (Scheme 49).



Scheme 49

To summarize this section, the INAC reactions of both nitron **113** and **129** resulted exclusive formation of *exo*-cycloadducts (Scheme 50). No desired *endo*-cycloadduct was formed with α,β -unsaturated ester moiety as the dipolarophile in the presence of a 2,3-*cis*-isopropylidene blocking group.



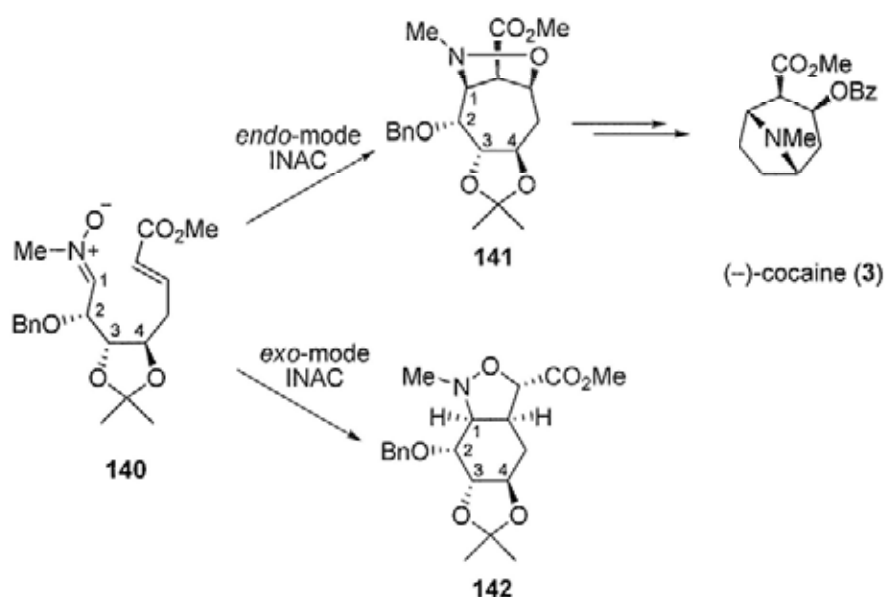
Scheme 50

Since these 6-membered carbocycles are not useful for cocaine synthesis, another synthetic strategy towards cocaine was developed and is to be discussed in the next section.

2.2.2.2 INAC of Nitrone with a 3,4-*trans*-Isopropylidene as Blocking Group and an α,β -Unsaturated Ester as Dipolarophile

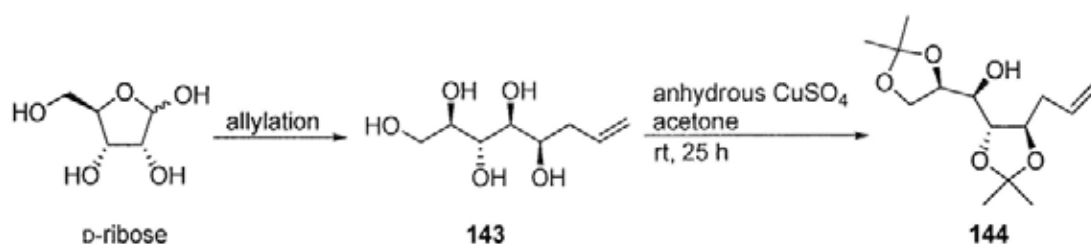
In section 2.2.1 of this thesis, it was concluded that the presence of 3,4-*trans*-isopropylidene blocking group in hept-6-enoses can induce exclusive formation of INAC *endo*-cycloadducts. In section 2.2.2.1 it was discovered that using α,β -unsaturated ester as the dipolarophile did not cause any *endo*-cycloadduct formation during INAC of nitrone bearing a 2,3-*cis*-isopropylidene moiety. In order to obtain the desired 7-membered *endo*-cycloadduct, which is the synthetic precursor of cocaine and its

analogues, INAC of the nitron **140**, with a 3,4-*trans*-isopropylidene moiety and an α,β -unsaturated ester as dipolarophile, was studied (Scheme 51).



Scheme 51

The diacetone **144** was prepared from D-ribose through two synthetic steps, firstly aqueous allylation of D-ribose afforded alkene **143**,⁸⁴ which was followed by isopropylideneation of the crude alkene **143** (Scheme 52). The allylation conditions performed are listed in Table 3.

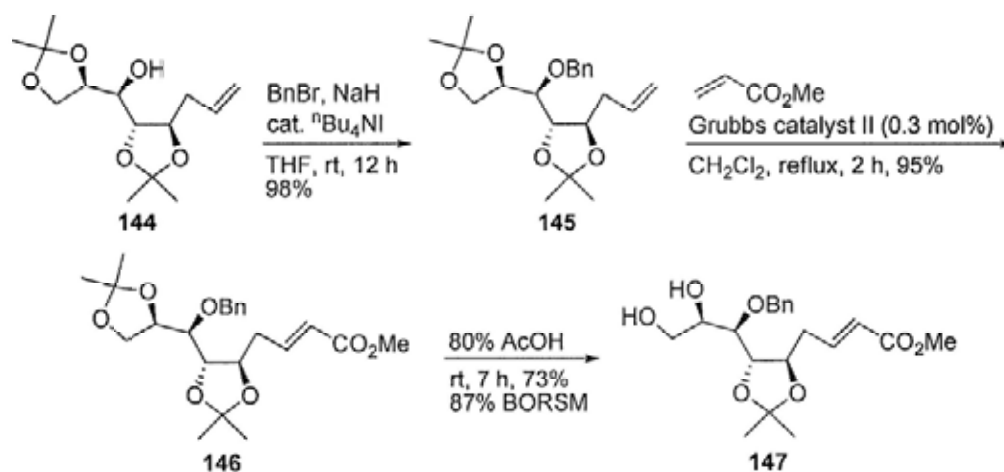


Scheme 52

Table 3. Sequential allylation and isopropylideneation of D-ribose.

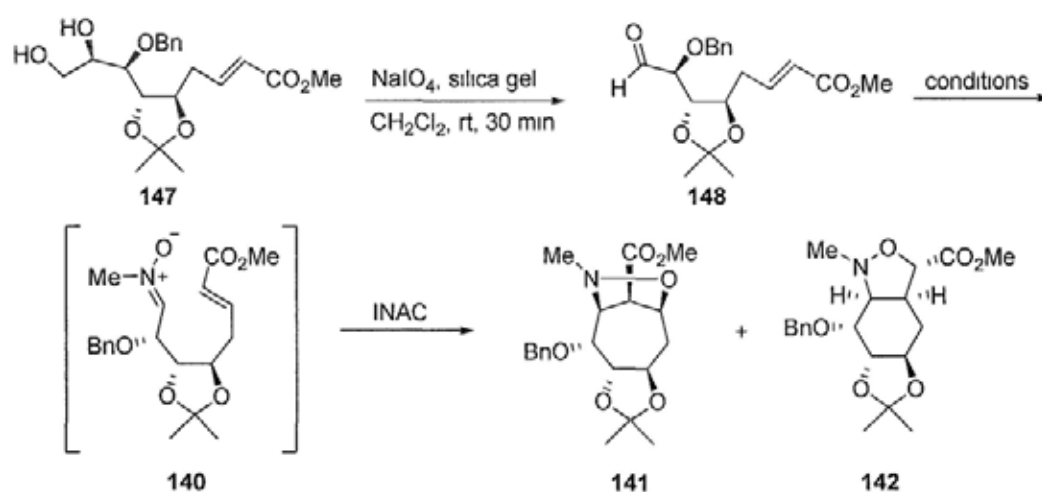
Entry	Allylation Conditions	Overall Yield of 144 from D-ribose
1	In, allyl bromide, EtOH/H ₂ O (v/v=4:1), rt, 12 h	64%
2	Sn, allyl bromide, EtOH/H ₂ O (v/v=4:1), reflux, 2 h	50%

Indium metal is able to perform allylation of D-ribose smoothly at room temperature, giving alkene **143** (entry 1). Subsequent isopropylideneation furnished alkene **144** in a good overall yield from D-ribose. When indium was replaced by tin, which is a more economical reagent, no allylation occurred unless the reaction was heated, and afforded a moderate yield of **144** finally (entry 2).

**Scheme 53**

Benzoylation of alcohol **144** with sodium hydride and benzyl bromide gave benzyl ether **145** in an excellent yield (Scheme 53).¹⁴ Cross metathesis of benzyl ether **145** with methyl acrylate catalyzed by a trace amount (0.3 mol%) of the second generation Grubbs catalyst afforded α,β -unsaturated ester **146** in 95% yield. The large coupling constant ($J = 15.7$ Hz) of the two alkene signals (δ 5.86 and 5.96 ppm) in ¹H NMR confirmed that a *trans*-alkene was formed. The α,β -unsaturated ester **146** was then

subjected to regioselective acid hydrolysis to give 1,2-diol **147** in 87% yield based on starting material recovery.



Scheme 54

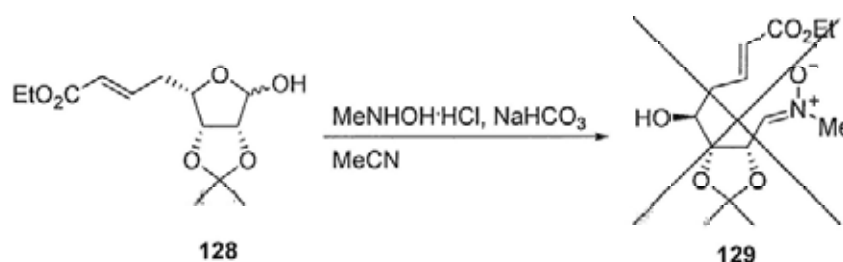
With the diol **147** in hand, silica gel mediated glycol cleavage oxidation furnished aldehyde **148** (Scheme 54). The aldehyde **148** was then subjected to several conditions to afford nitron **140** that carried out the INAC reaction (Table 4).

Table 4. Reaction conditions between aldehyde **148** and *N*-methylhydroxylamine.

Entry	Conditions	Yield of 141/142 from 147	141:142 by NMR
1	MeNHOH·HCl, NaHCO ₃ , MeCN, reflux, 4 h	70%	8:1
2	MeNHOH·HCl, NaHCO ₃ , MeOH, rt to reflux	decomposed	–
3	1) MeNHOH·HCl, NaHCO ₃ , MeCN, rt, 30 min 2) MeOH, reflux, 29 h	63%	14:1
4	1) MeNHOH·HCl, NaHCO ₃ , MeCN, rt, 30 min 2) CH ₂ Cl ₂ , reflux, 72 h	62%	10:1
5	MeNHOH·HCl, NaHCO ₃ , DMF, reflux, 1 h	64%	13:1
6	MeNHOH·HCl, py, toluene, reflux, 2 h	72%	14:1
7	MeNHOH·HCl, Et ₃ N, toluene, reflux, 2 h	75%	15:1

When using MeCN as solvent, reaction between aldehyde **148** and *N*-methylhydroxylamine with NaHCO₃ as base afforded nitron **140** as shown in the TLC (entry 1). Without isolating the nitron, the reaction mixture was heated to reflux and furnishing an inseparable mixture of two INAC cycloadducts. The major cycloadduct was found to be a 7-membered *endo*-cycloadduct **141**, with 6-membered *exo*-cycloadduct **142** as the minor product (Scheme 54). Their ratio was determined by measuring the integration of the individual *N*-methyl group in the ¹H NMR spectrum of the mixture of cycloadducts. Although in this stage the mixture of isoxazolidines **141** and **142** could neither be separated nor their regiochemistry be characterized, these two cycloadducts were separated in the following step and their regiochemistry was confirmed, as described later.

It should be noted that the reaction conditions in entry 1 is actually identical with the INAC reaction conditions of α,β -unsaturated ester **128** as mentioned in the last section, where no nitron **129** was formed under the conditions (Scheme 55).



Scheme 55

However, INAC of aldehyde **148** in such conditions did give nitron **140** which cyclized to INAC cycloadducts **141/142** (Scheme 54). The difference in reactivity

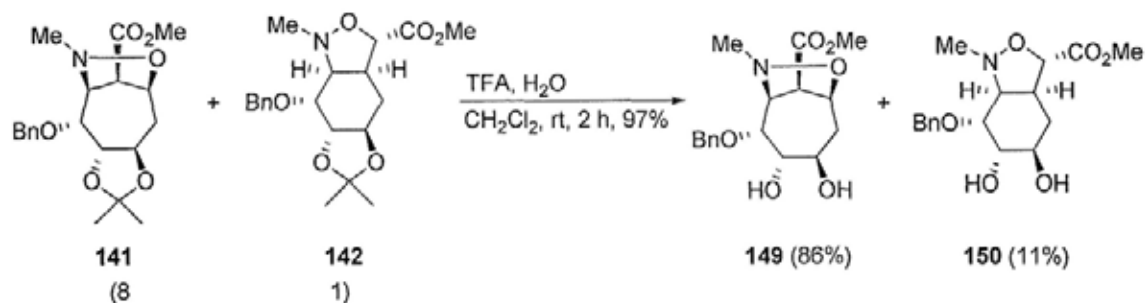
between lactol **128** and aldehyde **148** under the same reaction conditions is probably due to the **128** exists in lactol form, which makes condensation to MeNHOH more difficult hence nucleophilic MeNHOH may attack on the α,β -unsaturated ester moiety instead. On the other hand, aldehyde **148** exists as the free aldehyde form and hence it is more likely to condense with MeNHOH to give the nitrone **140**.

In order to study the solvent effect on the regioselectivity of INAC of nitrone **140**, solvents other than MeCN were used as well (entries 2–7). The reaction between aldehyde **148** and *N*-methylhydroxylamine with NaHCO₃ as base in MeOH did not furnish complete conversion into nitrone **140** at room temperature and decomposed upon heating (entry 2). It was suggested that the mixture of MeOH and NaHCO₃ produced a trace amount of the strongly basic methoxide anion that destroyed the α,β -unsaturated ester moiety, resulting in no INAC reaction.

Using the conditions as shown in entry 3 instead, INAC reaction of nitrone **140** in boiling MeOH occurred, resulting higher *endo/exo* ratio (**141:142** = 14:1) although a longer reaction time was needed and a lower reaction yield was afforded. When CH₂Cl₂ and DMF were used as INAC reaction solvents (entries 4 and 5), also higher *endo/exo* ratios were observed than using MeCN.

It was also found that mixing aldehyde **148** with either pyridine or triethylamine in boiling toluene also allowed the formation of INAC cycloadducts in a short reaction time with higher *endo/exo* selectivity (entries 6 and 7). Thus the conditions in entry 7 was considered as the most efficient approach towards the desired *endo*-cycloadduct **141**.

When this inseparable mixture of isoxazolidines **141** and **142** was subjected to hydrolysis by trifluoroacetic acid, diols **149** and **150** were formed and now they could be separated by column chromatography (Scheme 56).



Scheme 56

The diol **149** was isolated and its structure was confirmed by X-ray crystallography (Figure 17), which in turns confirmed the regio- and stereochemistry of the *endo*-cycloadduct **141**.

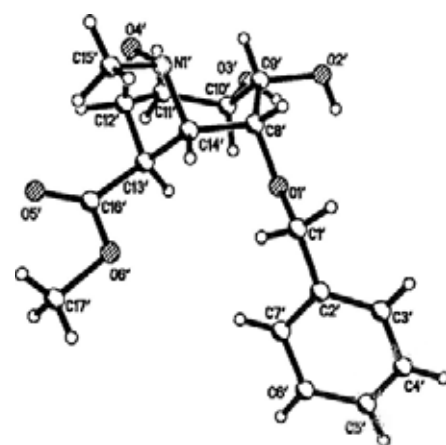


Figure 17. X-ray crystallographic structure of diol **149**.

Although diol **150** is not a solid at room temperature and pressure, it crystallized in a hydrated form hence its structure can also be confirmed (Figure 18).

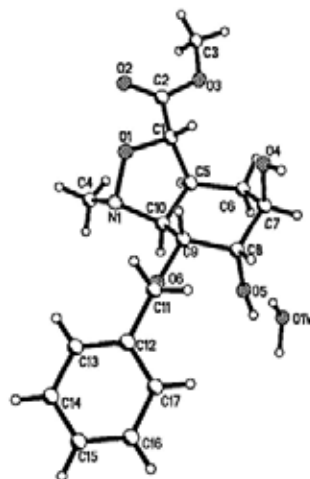
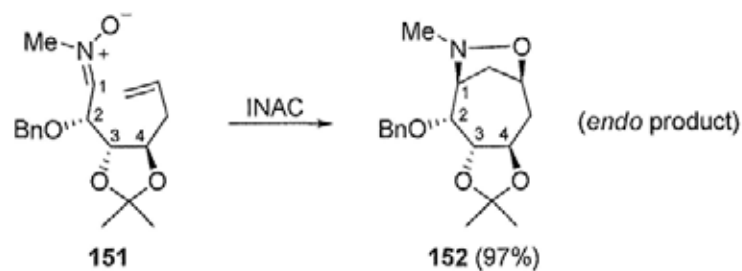


Figure 18. X-ray crystallographic structure of hydrated diol **150**.

Thus it was concluded that INAC reaction nitron **140** gave 7-membered *endo*-cycloadduct **141** as the major product, with a small amount of 6-membered *exo*-cycloadduct **142**. This result was in contrast to the INAC reaction of nitron **151**, which gave exclusive formation of *endo*-cycloadduct **152** (Scheme 57).¹⁴



Scheme 57

Both nitrones **140** and **151** bearing the same 3,4-*trans*-isopropylidene moiety, but nitrone **140**, with an α,β -unsaturated ester as the dipolarophile, yielded a small amount of *exo*-cycloadduct upon INAC reaction. Thus adding a carboxylate ester moiety into the terminal alkene did not induce the formation of *endo*-cycloadduct by electronic effect, but favoured more *exo*-cycloadduct formation instead. The reason may be due to the somewhat bulky carboxylate ester moiety, preventing the dipolarophile to perform *endo*-cyclization as the carboxylate ester moiety is closer to the isoxazolidine ring in *endo*-cycloadduct. The steric effect of the substituted alkene on the regioselectivity of INAC reaction was not further studied and the aim of this project, that is the synthetic studies of cocaine and its analogues, was focused again.

2.2.2.3 Transformation of Isoxazolidine **141** into (-)-Cocaine (**3**) and Cocaine Analogues

The INAC reaction of nitrone **140** gave preponderantly isoxazolidine **141**. Through this reaction, three new stereocenters were formed, and all of them have the correct stereochemistry when compared to the natural (-)-cocaine (**3**) (Figure 19).

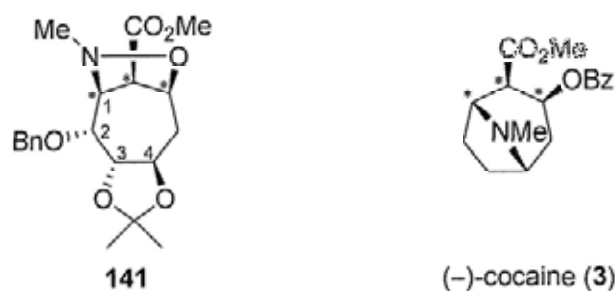
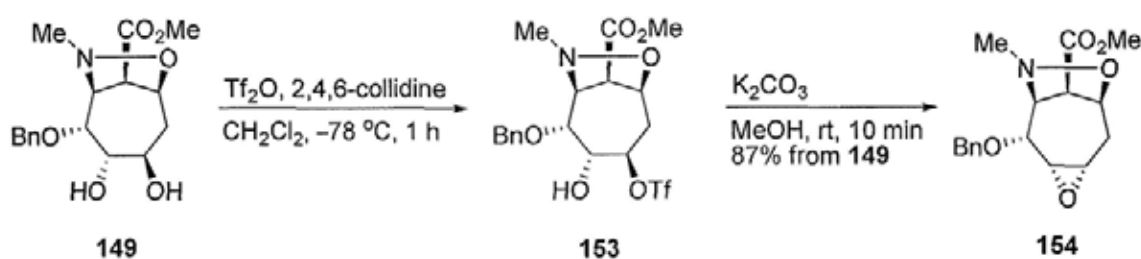


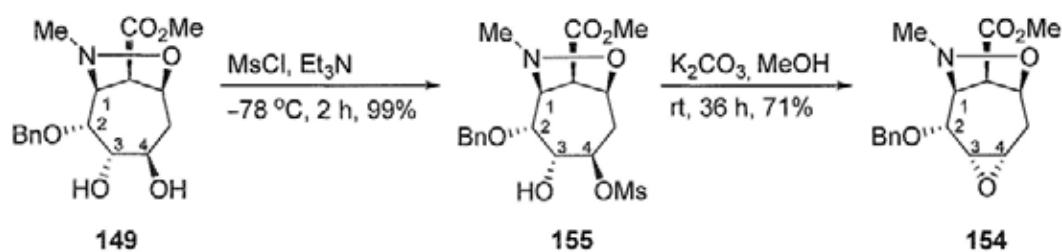
Figure 19

In order to construct the tropane skeleton for cocaine synthesis, the C-4 hydroxyl group in **141** would be converted into a leaving group like a sulfonate ester. Hydrogenolysis of nitrogen-oxygen bond would give an amino function that could undergo intramolecular S_N2 displacement to form the tropane skeleton. However, it was noted that the stereochemistry of C-4 hydroxyl group in **141** is *syn* to the C-1, causing the corresponding sulfonate would also be *syn* to C-1, which would make intramolecular S_N2 displacement not feasible. Thus isoxazolidine **141** should be transformed into tropane skeleton by another strategy.



Scheme 58

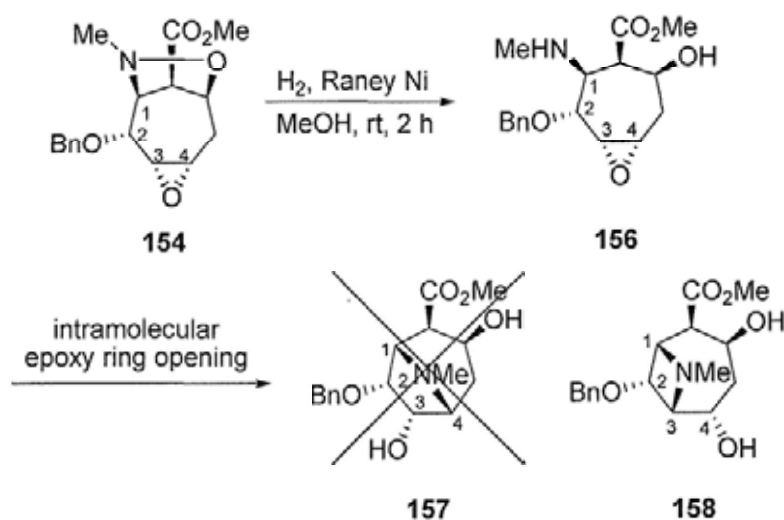
The diol **149**, which was obtained from isoxazolidine **141** as described in the previous section, was converted into the corresponding monotriflate **153** by reacting with trifluoromethanesulfonic anhydride and 2,4,6-collidine under low temperature (Scheme 58). The triflate **153** isolated was found to be unstable upon prolonged standing at room temperature, hence it was subjected to the next synthetic step once formed. Reacting triflate **153** with potassium carbonate in MeOH at room temperature allowed the formation of epoxide **154** in 87% overall yield from diol **149**.



Scheme 59

The epoxide **154** could also be synthesized by another method (Scheme 59). Selective mesylation of diol **149** furnished mesylate **155** in an excellent yield, the mesylate **155** was then reacted with potassium carbonate in MeOH to afford the same epoxide **154**. However, the overall yield of epoxide **154** from diol **149** is lower using this strategy hence the previous triflate strategy is considered to be more efficient.

It should be noted that after converting diol **149** into the corresponding epoxide **154**, the C-4 stereochemistry was inverted, which is *anti* to the C-1 so that intramolecular $\text{S}_{\text{N}}2$ displacement to form the tropane skeleton became possible.



Scheme 60

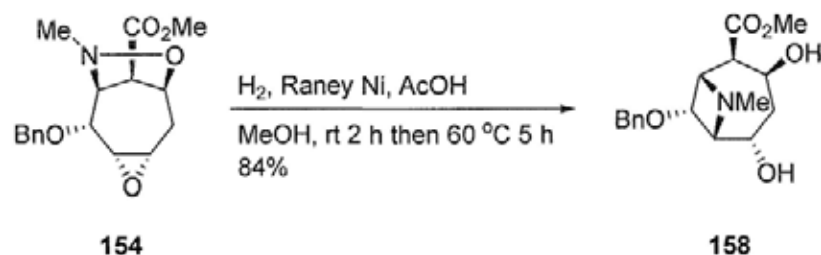
It was attempted to transform epoxide **154** into the corresponding tropane **157** by first hydrogenolysis of nitrogen-oxygen bond to obtain amine **156**, which was followed by intramolecular epoxy ring opening reaction by the amino function (Scheme 60). Thus the epoxide **154** was subjected to Raney[®]-Nickel hydrogenolysis to furnish amine **156**. However, when amine **156** was attempted to be characterized by ¹H NMR, the presence of another product was observed and the amount of this product was found to increase with time at room temperature. After 21 days at room temperature, all amine **156** was found to be consumed (Table 5, entry 1), but no desired tropane **157** was formed. Instead the diol **158**, formed by the amino function in **156** attacking on the C-3 position, was obtained. Other intramolecular epoxy ring opening conditions are shown in the Table 5 as well.

Table 5. Intramolecular epoxy ring opening conditions of amine **156**.

Entry	Conditions	Yield of 158 from 154
1	neat, rt, 21 d	60%
2	neat, 70 °C, 29 h	88%
3	CH ₂ Cl ₂ , reflux	no reaction
4	toluene, 90 °C	no reaction
5	AcOH, MeOH, reflux, 4 h	88%

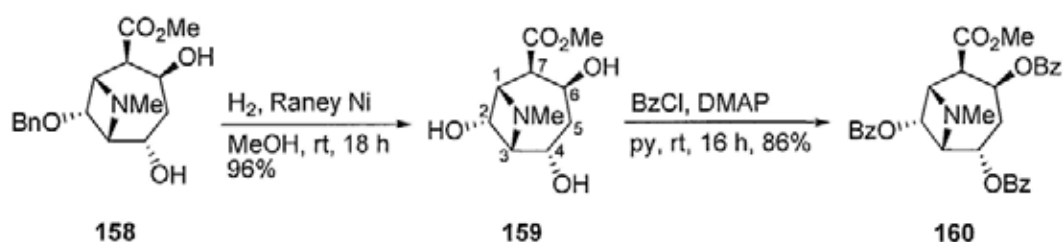
Since it was found that the neat amine **156** could be transformed into diol **158** under solvent free conditions at room temperature (entry 1), elevation of reaction temperature furnished diol **158** in 88% overall yield from epoxide **154** (entry 2). However, when amine **156** was heated in the presence of solvents like CH₂Cl₂ and toluene, no reaction resulted (entries 3 and 4), probably due to the aprotic nature of such

solvents that disfavoured epoxy ring opening to afford diol **158**. Thus protic solvent like MeOH was then used, in addition to a catalytic amount of acetic acid, which also gave diol **158** in 88% overall yield (entry 5).



Scheme 61

Actually this diol **158** could be prepared from epoxide **154** in one step. Hydrogenolysis of epoxide **154** catalyzed by Raney[®]-Nickel at room temperature, after all starting material epoxide **154** was consumed, the reaction mixture was heated up to 60 °C for 5 more hours to furnish diol **158** (Scheme 61). As the reaction yield is still comparable to the previous two-step synthesis (Scheme 60) hence this one-step synthesis (Scheme 61) is a more efficient approach.



Scheme 62

The benzyl ether **158** was then subjected to hydrogenolysis with a stoichiometric amount of Raney[®]-Nickel to give triol **159** (Scheme 62). If Raney[®]-Nickel was added in a catalytic amount, the reaction was sluggish and the starting material **158** was not

completely consumed. After analyzing the ^1H NMR and 2D COSY NMR spectra of triol **159**, the proton's assignment was supported by the ^1H - ^1H connectivities (Figure 20). The three most downfield proton signals (δ 5.15, 4.53, and 4.10 ppm) were assigned as H_2 , H_6 , and H_4 respectively as the C-2, C-6, and C-4 are bonded to oxygen atoms, whereas two more upfield proton signals (δ 4.00 and 3.41 ppm) were assigned as H_1 and H_3 respectively as the C-1 and C-3 are bonded to nitrogen atoms. H_2 is correlated to both H_1 and H_3 and this evidence indicated that the triol **159** and hence diol **158** consist of a bicyclo[4.1.1] skeleton instead of a tropane skeleton.

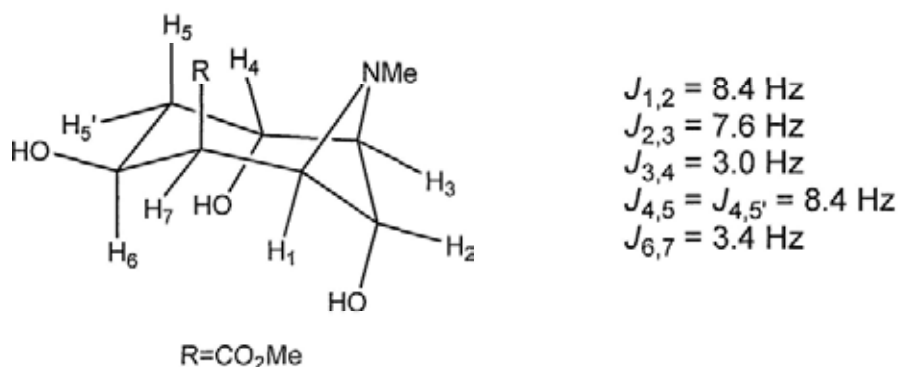


Figure 20. Conformation of triol **159**.

The presence of such bicyclo[4.1.1] skeleton in diol **158** and triol **159** was confirmed by X-ray crystallographic analysis of tribenzoate **160** (Figure 21), which was formed by benzylation of triol **159** (Scheme 62). It means that no tropane ring was formed by intramolecular epoxy ring opening reaction of amine **156**.

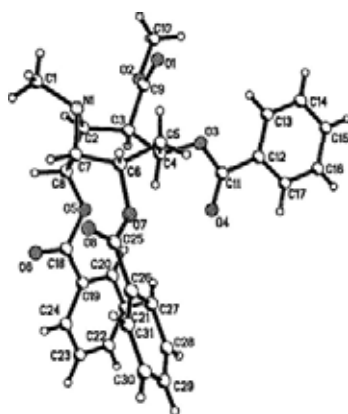
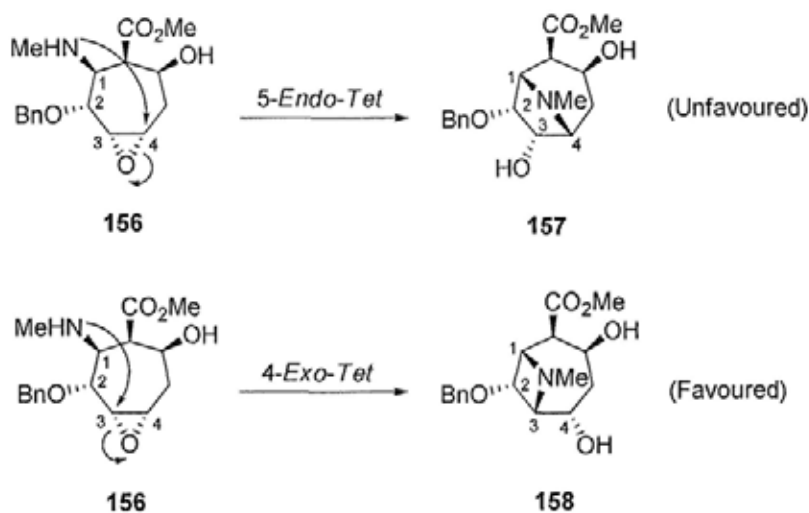


Figure 21. X-ray crystallographic structure of tribenzoate **160**.

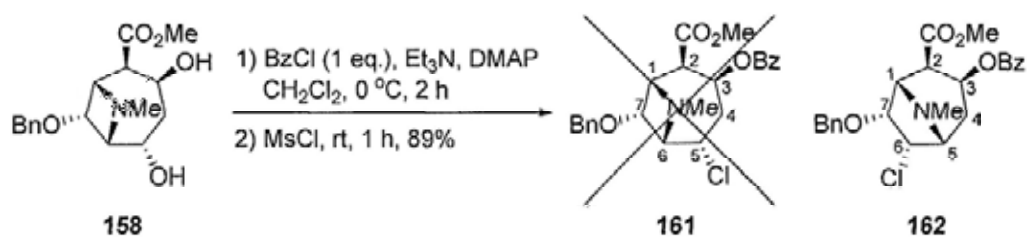
The formation of the bicyclo[4.1.1] skeleton instead of the tropane ring after intramolecular epoxy ring opening reaction of amine **156** can be explained by Baldwin's rule.⁸⁵ When amine **156** was carry out intramolecular epoxy ring opening reaction, the amino function could attack either C-3 or C-4 position of the epoxy moiety (Scheme 63).



Scheme 63

When the amino function attacked the C-4 position of the epoxy moiety, a tropane skeleton would be formed through the *5-Endo-Tet* cyclization, which is an unfavoured process according to Baldwin's rule (Scheme 63). If the amino function attacked the C-3 position of the epoxy moiety instead, a bicyclo[4.1.1] skeleton would be formed through the *4-Exo-Tet* cyclization, a favoured process according to Baldwin's rule, hence the diol **158** instead of tropane **157** was formed.

As the diol **158** does not consist of a tropane skeleton, it seems that the desired cocaine cannot be synthesized by this strategy. However, when diol **158** was first benzoylated with one equivalent of benzoyl chloride, followed by the addition of methanesulfonyl chloride, chloride **162** was obtained in an excellent yield (Scheme 64).



Scheme 64

The presence of a chlorine atom in chloride **162** was confirmed by mass spectrometry, in which the intensity of $M + 2$ peak is one-third of the molecular ion (M) peak. The existence of a tropane skeleton in chloride **162** was assigned by determining the ^1H - ^1H connectivities from the 2D COSY NMR (Figure 22). It should be noted that a strong correlation between H_6 and H_7 was found, which belonged to the methine proton next to chloride group and benzyloxy moiety respectively (Figure 22). If the product existed as a bicyclo[4.1.1] skeleton as shown in the chloride **161** instead (Scheme 64),

no such strong correlation between these two proton signals (between H₅ and H₇ in this case) should be found in the 2D COSY NMR. Thus the existence of tropane structure in chloride **162** was supported by the presence of correlation between these two proton signals (H₆ and H₇).

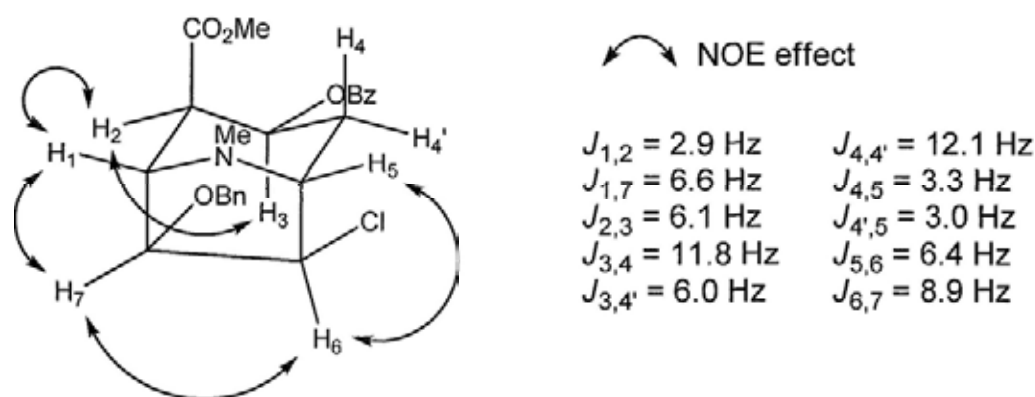
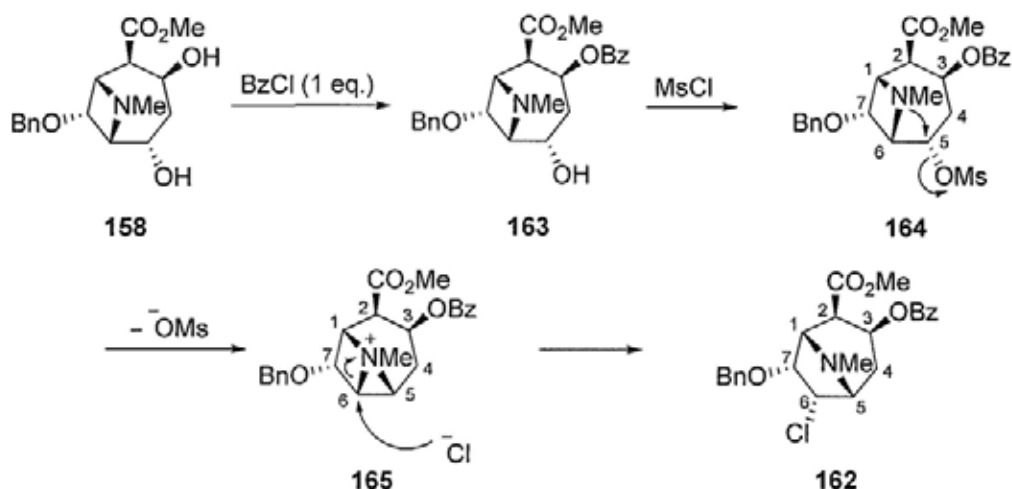


Figure 22. NOE correlations of chloride **162**.

From the 2D NOESY NMR spectrum of chloride **162**, there was NOE correlation between H₆ and H₇, showing that the chloride function is *syn* to the benzyl group in **162** (Figure 22). Since the α -stereochemistry of the benzyl group was already confirmed by X-ray crystallographic analysis of both diol **149** and benzoate **160**, the chloride function in **162** should also have the α -stereochemistry, as shown in Figure 22.

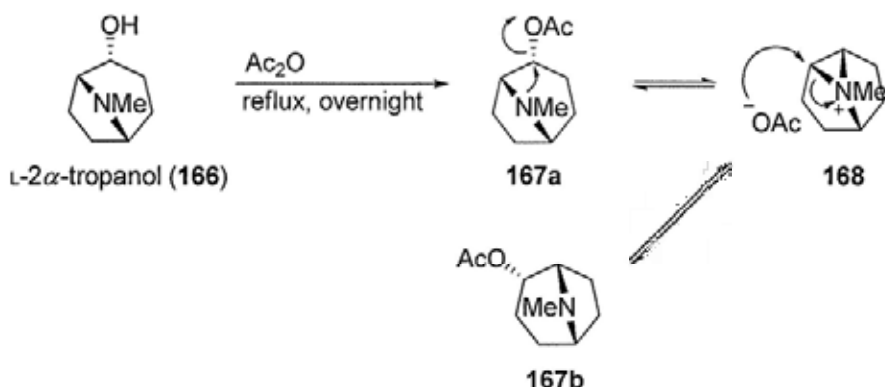
The formation of chloride **162** from diol **158** in Scheme 64 can be explained as follows. First, the regioselective esterification of diol **158** with one equivalent of benzoyl chloride afforded monobenzoate **163** (Scheme 65). Then, the addition of methanesulfonyl chloride to the reaction mixture produced mesylate **164**, in which the mesylate moiety is now *anti* to the adjacent aza-bridge. Due to this neighboring-group participation, the mesylate **164** would dissociate easily to give ammonium ion **165**.

Then the nucleophilic chloride ion attacked the α -face of C-6 position in **165** to furnish α -chloride **162**.



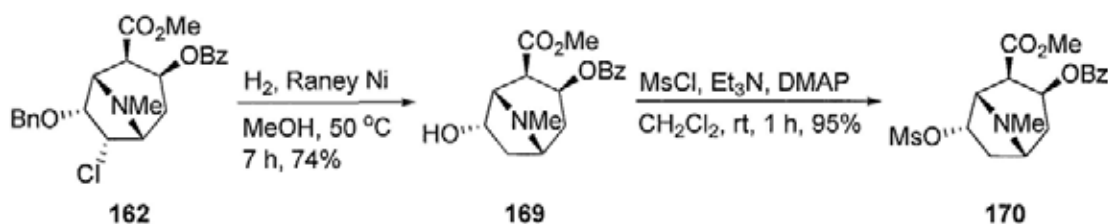
Scheme 65

The release of ring strain from bicyclo[4.1.1] skeleton to tropane ring is probably the driving force of C-6 attack instead of C-5. The formation of ammonium ion **165** is the result of neighboring-group participation, and the existence of this ammonium ion **165** was supported by a similar example reported by Archer *et al.* Racemic acetates **167a/167b** were obtained via ammonium ion **168** upon acetylation of L-2 α -tropanol (**166**) under prolonged heating in acetic anhydride (Scheme 66).⁸⁶



Scheme 66

The chloride **162** obtained is actually one of the (-)-cocaine analogue, with a chloride in C-6 position and a benzyloxy moiety in C-7 position. Thus natural (-)-cocaine (**3**) could be obtained easily by simply eliminating both the chloride and benzyloxy moieties in **162**. When chloride **162** was subjected to hydrogenolysis in the presence of a stoichiometric amount of Raney[®]-Nickel at 50 °C, alcohol **169** was afforded in 74% yield (Scheme 67).



Scheme 67

Both the benzyl group and the chloride moiety were removed during this reaction. It should be noted that if Raney[®]-Nickel was added in a catalytic amount, the reaction was sluggish and even the starting material chloride **162** was not be completely consumed.

This alcohol **169** is another (-)-cocaine analogue, with α -hydroxyl group in the C-7 position, which is the 7-epimer of a cocaine analogue **61b** reported by Kozikowski and co-workers⁵⁹ (Figure 23). According to Kozikowski's publication, there is no coupling between H-1 and H-7 from their ¹H NMR spectra when the H-7 is in the α -stereochemistry.^{58,59} They also observed that there is a coupling ($J_{1,7} = 6.0$ Hz) between

H-1 and H-7 in the ^1H NMR spectrum of the pseudococaine analogue **171**, in which the H-7 has the β -stereochemistry (Figure 23).⁵⁸

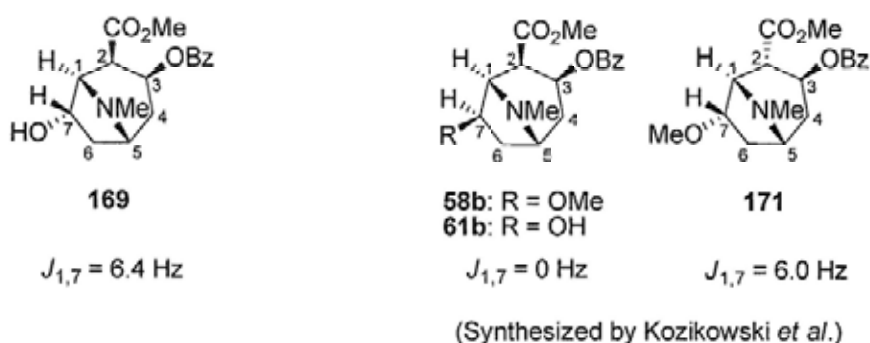
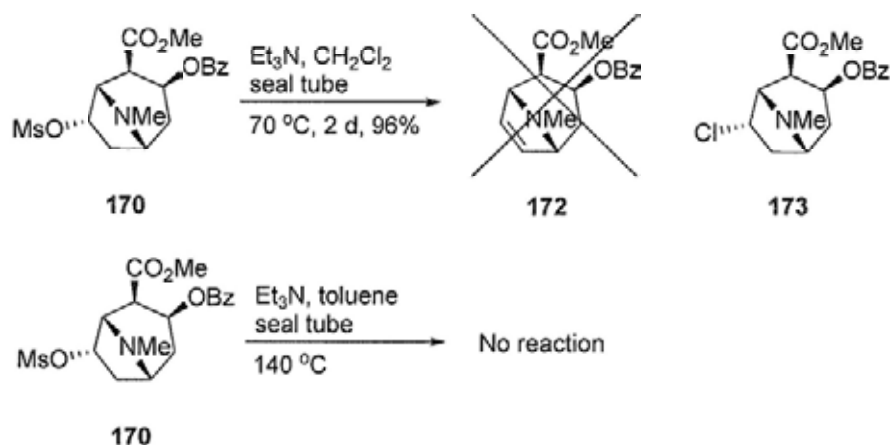


Figure 23

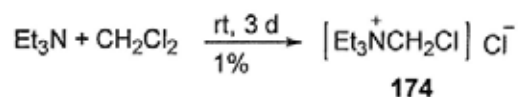
In the ^1H NMR spectrum of alcohol **169**, it was found that there is also a coupling ($J_{1,7} = 6.4 \text{ Hz}$) between H-1 and H-7 hence confirmed the β -stereochemistry of the H-7 (Figure 23). More importantly, the stereochemistry of H-7 in other cocaine analogues can also be assigned by analyzing their ^1H NMR spectra.

The alcohol **169** was then subjected to mesylation to give mesylate **170** in an excellent yield (Scheme 67). It was attempted to afford alkene **172** by performing elimination reaction on mesylate **170** (Scheme 68). However, no alkene **172** was found and chloride **173** was obtained instead when mesylate **170** was reacted with triethylamine in CH_2Cl_2 at 70°C inside a seal tube.



Scheme 68

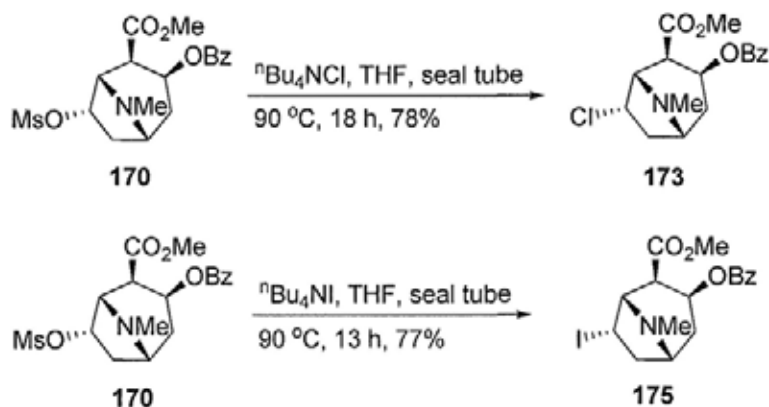
However, when the reaction solvent CH_2Cl_2 was replaced by toluene, no reaction was observed even the reaction was heated at higher temperature (Scheme 68). It seems that CH_2Cl_2 itself may be also one of the reagents in this reaction. After searching for examples from literature it was found that chloromethyltriethylammonium chloride (**174**) would be formed upon mixing triethylamine and CH_2Cl_2 at room temperature (Scheme 69).⁸⁷



Scheme 69

Although the authors did not perform this reaction at higher temperature, they did realize the formation of **174** was inhibited at lower temperature.⁸⁷ Thus in the reaction conditions shown in Scheme 68, in which the mixture of triethylamine and CH_2Cl_2 was heated at $70\text{ }^\circ\text{C}$, more ionic salt **174** would probably be formed. As the salt **174** consists of chloride anion, this chloride anion could act as a nucleophile to displace

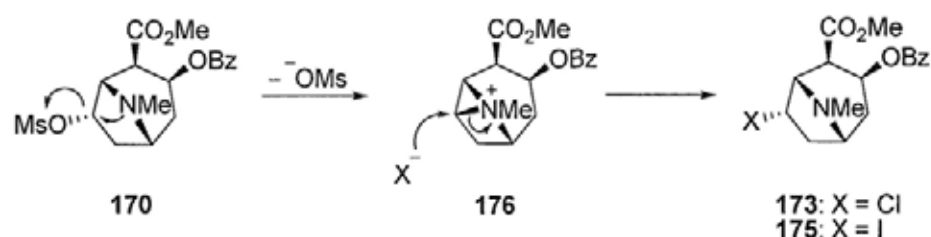
the mesylate moiety in mesylate **170** to give chloride **173**. This formation of chloride **173** from displacement of mesylate by chloride was corroborated by the formation of the same chloride **173** via reaction of mesylate **170** with tetra-*n*-butylammonium chloride (Scheme 70). It showed that the mesylate moiety in **170** was readily displaced by chloride ion.



Scheme 70

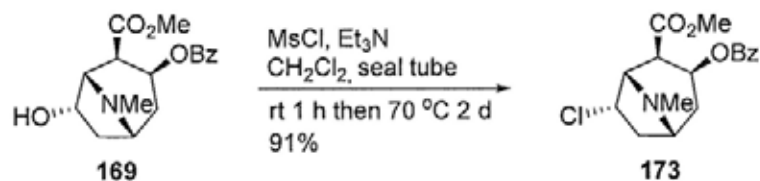
By replacing chloride ion with iodide ion, iodide **175** could be synthesized by reacting mesylate **170** with tetra-*n*-butylammonium iodide (Scheme 70). Thus two more (–)-cocaine analogues, namely 7 α -chlorococaine (**173**) and 7 α -iodococaine (**175**), were prepared as well. The presence of a chlorine atom in chloride **173** was confirmed by mass spectrometry, in which the intensity of the $M + 2$ peak is one-third of the molecular ion (M) peak. The presence of iodine atom in iodide was also supported by mass spectrometry. In addition, from the ^{13}C DEPT NMR spectrum of iodide **175**, there is an upfield methine carbon signal (δ 19.0 ppm), which corresponds to the iodo-substituted methine carbon at 7-position.

After analyzing the ^1H NMR spectra of chloride **173** and iodide **175**, it was found that both of these two cocaine analogues had coupling ($J_{1,7} = 6.4$ Hz in chloride **173** and $J_{1,7} = 6.1$ Hz in iodide **175**) between H-1 and H-7. According to these results, both chloride **173** and iodide **175** were found to be α -substituted. The retention of configuration upon displacement reactions of α -mesylate **170** can be explained by the neighboring-group participation of aza-bridge, which forcing the nucleophile to attack on the α -face of the ammonium ion **176** (Scheme 71).



Scheme 71

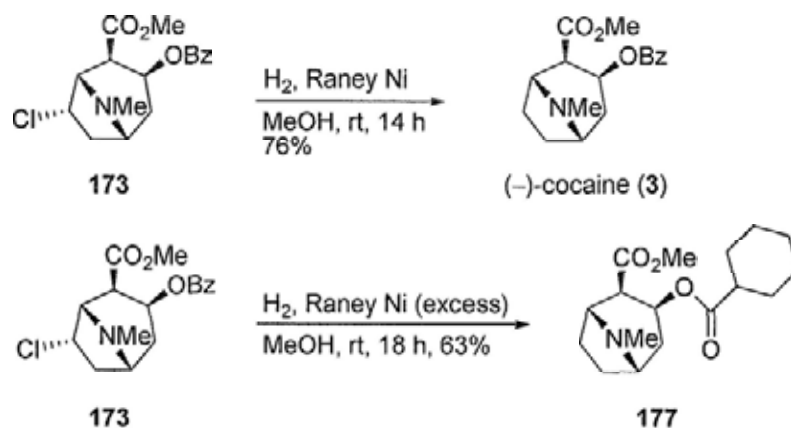
Actually the chloride **173** could be synthesized from alcohol **169** in one step, by the reaction of alcohol **169** with methanesulfonyl chloride and an excess of triethylamine in CH_2Cl_2 at room temperature, followed by heating (Scheme 72).



Scheme 72

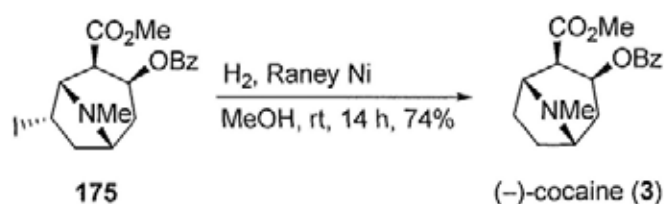
With the chloride **173** in hand, the natural product (-)-cocaine (**3**) can be obtained by simply hydrogenolysis of chloride **173**, with a stoichiometric amount of Raney[®]-Nickel (Scheme 73). The specific rotation, $[\alpha]_D^{20} -16.9$ (c 0.18, CHCl_3) {lit. $[\alpha]_D^{23}$

-16.2 (*c* 1.2, CHCl₃}}, and all NMR spectral data of the synthesized (-)-cocaine (**3**) are in good agreement with the literature values.⁴⁶



Scheme 73

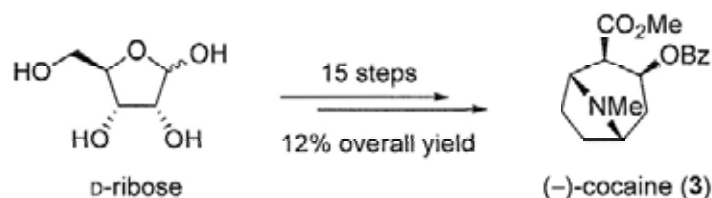
It should be noted that if the amount of Raney[®]-Nickel used was in highly excess, amine **177** instead of (-)-cocaine (**3**) would be obtained (Scheme 73). Beside the carbon-chlorine bond in chloride **173** was cleaved, the benzoate moiety was also fully hydrogenated as well. Surprisingly this amine **177**, with just replacing the benzoyl group in (-)-cocaine (**3**) with cyclohexanecarbonyl moiety, has not been reported in the literature hence the first synthesis of amine **177** is reported in this thesis.



Scheme 74

The iodide **175** was also transformed into the same (-)-cocaine (**3**) by Raney[®]-Nickel hydrogenolysis (Scheme 74).

To summarize this section, the natural product (–)-cocaine (**3**) was synthesized from D-ribose via an *endo*-mode INAC reaction as the key step, with 15 steps in 12% overall yield (Scheme 75).



Scheme 75

This synthesis is more efficient than both Rapoport's⁴⁶ (21 steps, 5.9% overall yield) and Pearson's⁴⁷ (15 steps, 2.2% overall yield) cocaine syntheses. Although this new strategy required three more synthetic steps than the latest Davis' cocaine synthesis (12 steps, 9% overall yield),⁴⁸ it produced cocaine in higher overall yield. More importantly, the readily available D-ribose was used as the starting material hence this new synthetic strategy is considered to be more practical.

In addition to the natural product (–)-cocaine (**3**), six more (–)-cocaine analogues were synthesized as well (Figure 24).

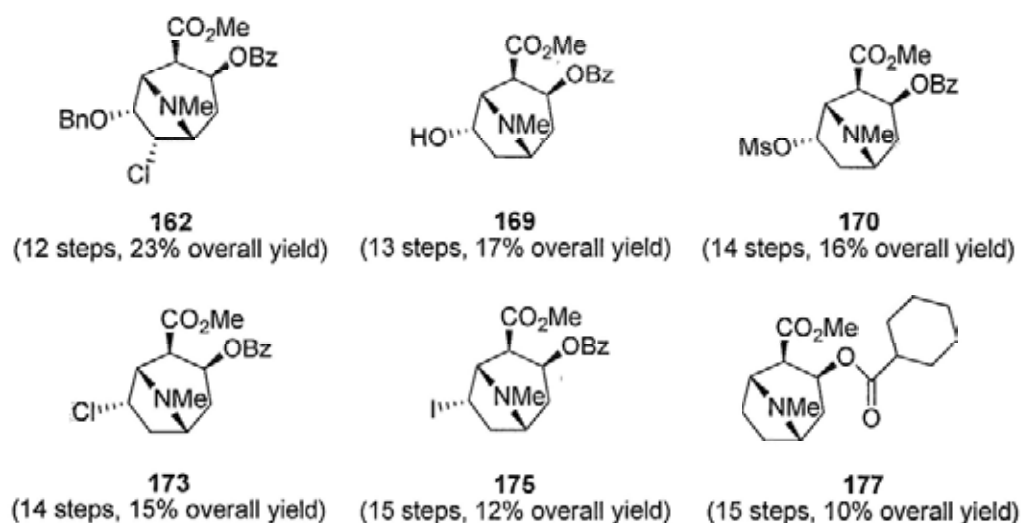
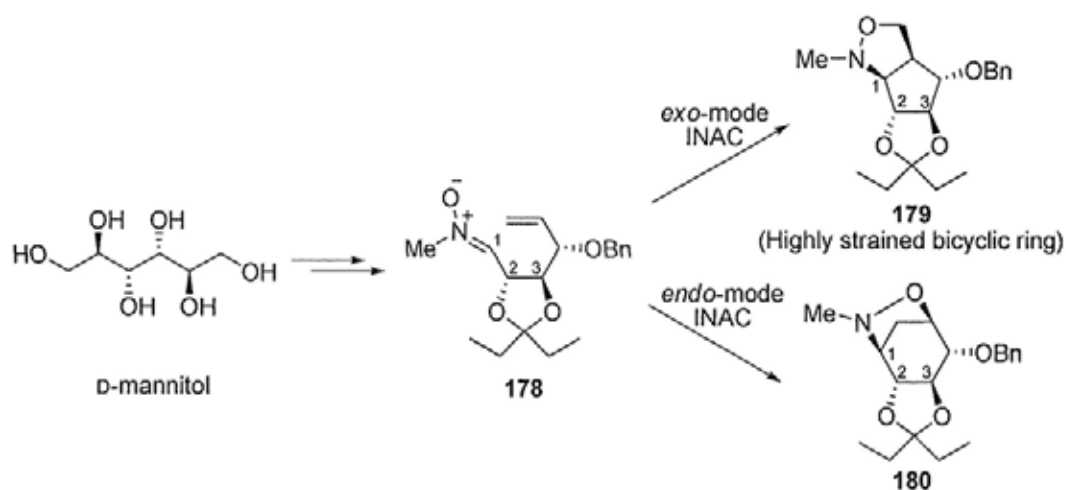


Figure 24

2.2.3 Studies on Regioselectivity of INAC on Hex-5-enoses from D-Mannitol with a 2,3-*trans*-Pentylidene Blocking Group

In this section, regioselectivity of INAC reactions on hex-5-enoses with a 2,3-*trans*-pentylidene moiety are studied (Scheme 76). Due to the severe torsional strain of the 5-5 *trans*-fused bicyclic ring in isoxazolidine **179**, formation of *exo*-cycloadducts from INAC of such hex-5-enoses are not expected to be observed.



Scheme 76

With the 1,2-diol **182** in hand, it was first subjected to glycol cleavage oxidation to furnish aldehyde **183**, followed by Grignard addition with vinylmagnesium bromide to give alkenes **184** and **185** in ratio of 3:2 (Scheme 78). The configuration of the newly formed stereocenter of alkene **184** was assigned by an X-ray crystallographic analysis of the INAC cycloadduct synthesized later.

The diastereoselectivity of this vinylation can be explained by the chelation controlled transition model shown in Figure 25. As the α -face of **183** was blocked by the pentylidene group, the Grignard reagent would like to attack the β -face of **183**, the formation of alkene **184** is more favoured.

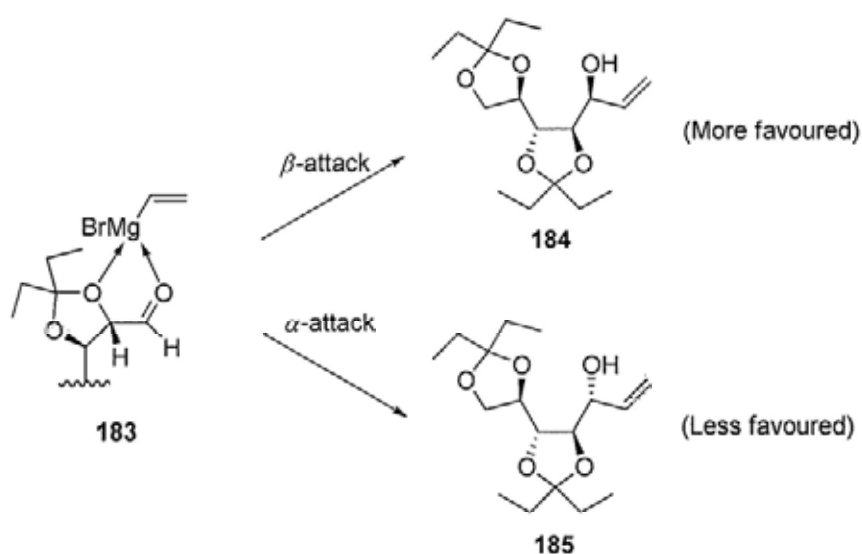
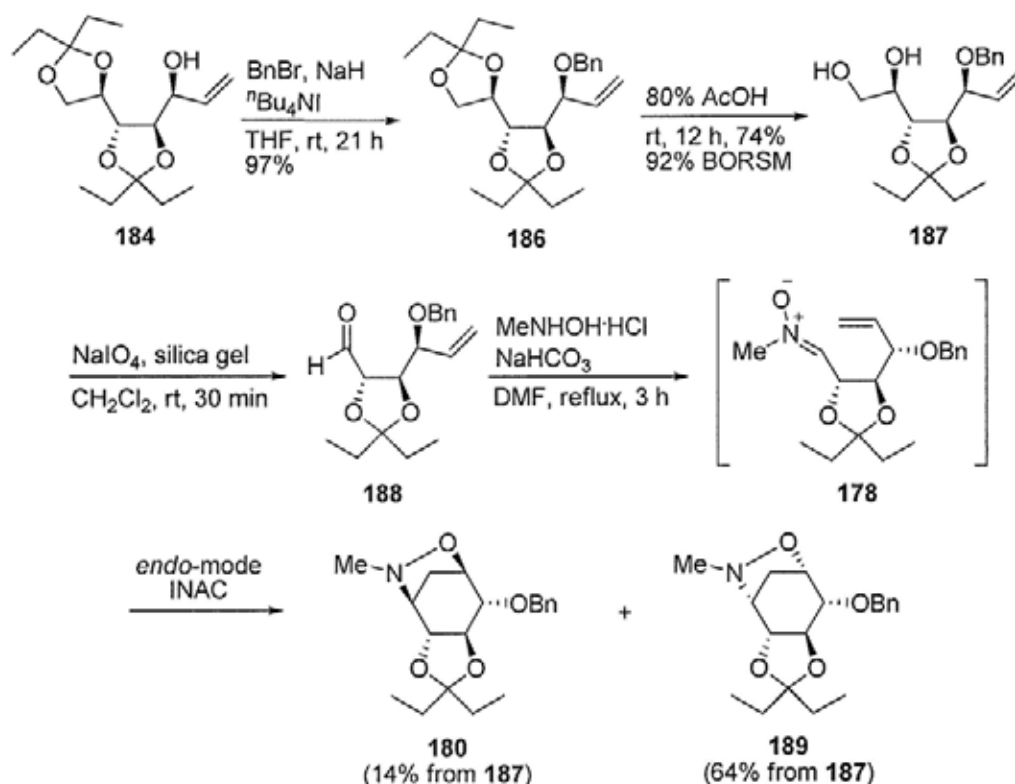


Figure 25

The alkene **184** was then transformed into the corresponding nitron by the following synthetic sequence. First, the free hydroxyl group of alkene **184** was protected as a benzyl ether to afford compound **186**, which was followed by

regioselective acid hydrolysis of its terminal pentyldiene group to give 1,2-diol **187** (Scheme 79). Glycol cleavage oxidation of diol **187** furnished aldehyde **188**. Then the nitrone **178** was prepared by reacting the aldehyde with *N*-methylhydroxylamine. Subsequent heating of the resulting mixture allowed the INAC reaction to take place, yielding two 6-membered *endo*-cycloadducts, isoxazolidines **180** and **189**.



Scheme 79

The ring size of both isoxazolidines **180** and **189** were assigned by their ^{13}C DEPT NMR spectra. For both isoxazolidines **180** and **189**, each having three resonances in the upfield region (δ 25–40 ppm) were assigned to a methylene group, two of which are the methylene carbons of pentyldiene group and the remaining one is the methylene carbon in the cyclohexane ring. If a 5-membered *exo*-cycloadduct had been formed

instead, only two methylene carbon resonances have been found. The structure of the major cycloadduct **189** was confirmed by X-ray crystallography (Figure 26).

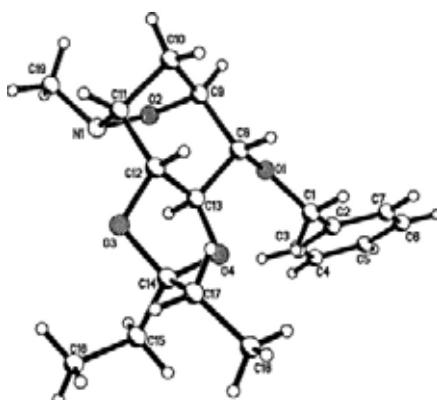


Figure 26. X-ray crystallographic structure of isoxazolidine **189**.

It shows that isoxazolidine **189** consists of a 6-membered carbocycle with the isoxazolidine ring *cis* to the benzyloxy moiety, which in turn concluded that the isoxazolidine ring of another cycloadduct, isoxazolidine **180**, is *trans* to its benzyloxy moiety as shown in Scheme 79.

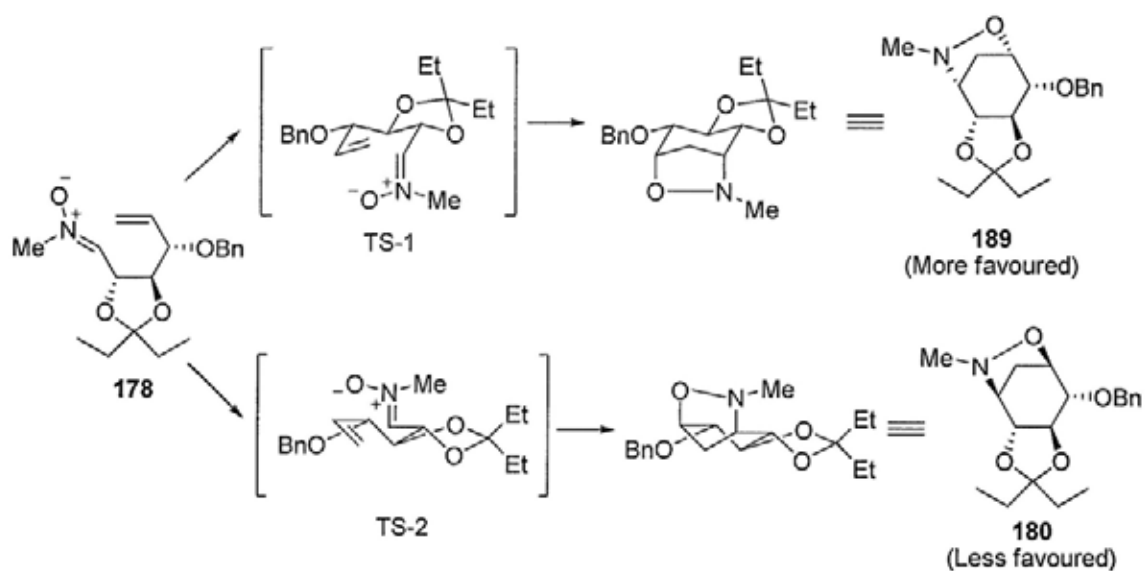
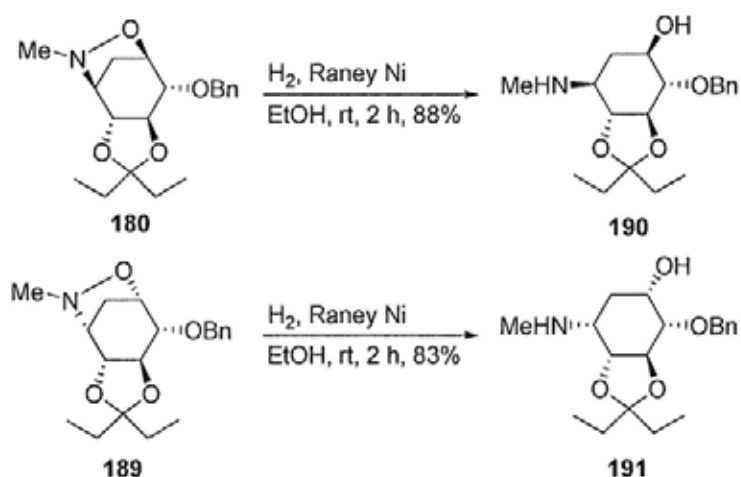


Figure 27

During this INAC reaction, isoxazolidine **189** rather than isoxazolidine **180** was formed as the major product. The reason of this outcome can be explained by the proposed transition states (Figure 27). In order to minimize the torsional strain of the 5-membered *trans*-pentylidene ring, this pentylidene ring would occupy the *trans*-diequatorial position as shown in both TS-1 and TS-2. For TS-1, the carbocycle was formed by adopting a chair-like conformation which led to lower TS energy, resulting in the formation of isoxazolidine **189** as the major product. On the other hand, a boat-like conformation was adopted during the formation of carbocycle in TS-2. As the TS energy is higher than that in TS-1, the isoxazolidine **180** was formed as the minor product.

The stereochemistry of the newly formed chiral centers of the INAC cycloadducts **180** and **189** was also assigned by converting them into their corresponding hydrogenolysis products. Isoxazolidine **180** and **189** were subjected to Raney[®]-Nickel catalyzed hydrogenolysis to afford amines **190** and **191** respectively (Scheme 80).



Scheme 80

Now the carbocyclic ring of both amines **190** and **191** are aligned in chair conformation, with the pentyldiene group occupying the *trans*-diequatorial position (Figure 28). After analyzing their ^1H NMR spectra, it was found that the coupling patterns of methylene protons (H_6 and $\text{H}_{6'}$) in the carbocyclic ring of amines **190** are different from that of amine **191**. In amine **190**, as both H_1 and H_5 are occupying in the axial position, the $J_{1,6}$ and $J_{5,6}$ have large values (Figure 28). Thus together with the large geminal coupling of $J_{6,6'}$, the H_6 was observed as quartet (q, $J = 11.5$ Hz). Since the $\text{H}_{6'}$ is occupying the equatorial position, it has smaller magnitude of both $J_{1,6'}$ and $J_{5,6'}$. The $\text{H}_{6'}$ was hence observed as a doublet of triplets (dt, $J = 13.0, 4.7$ Hz).

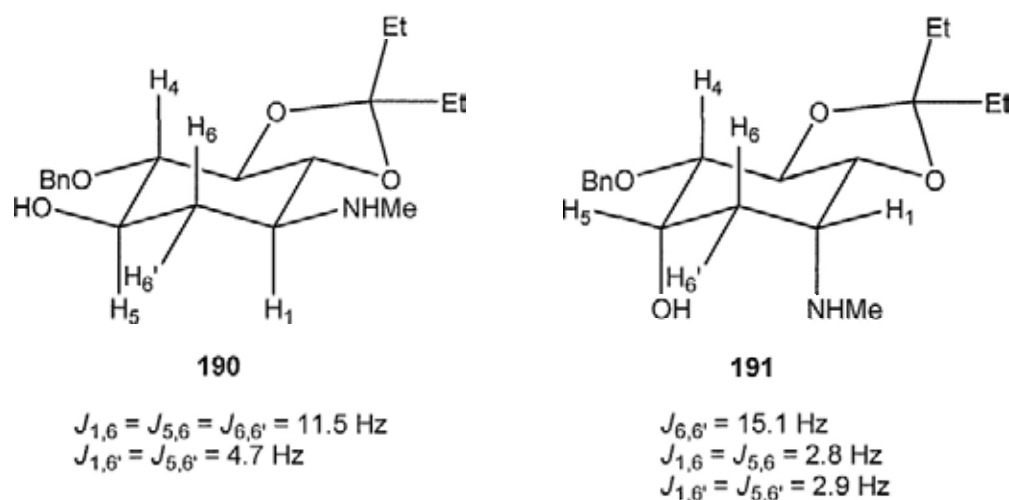
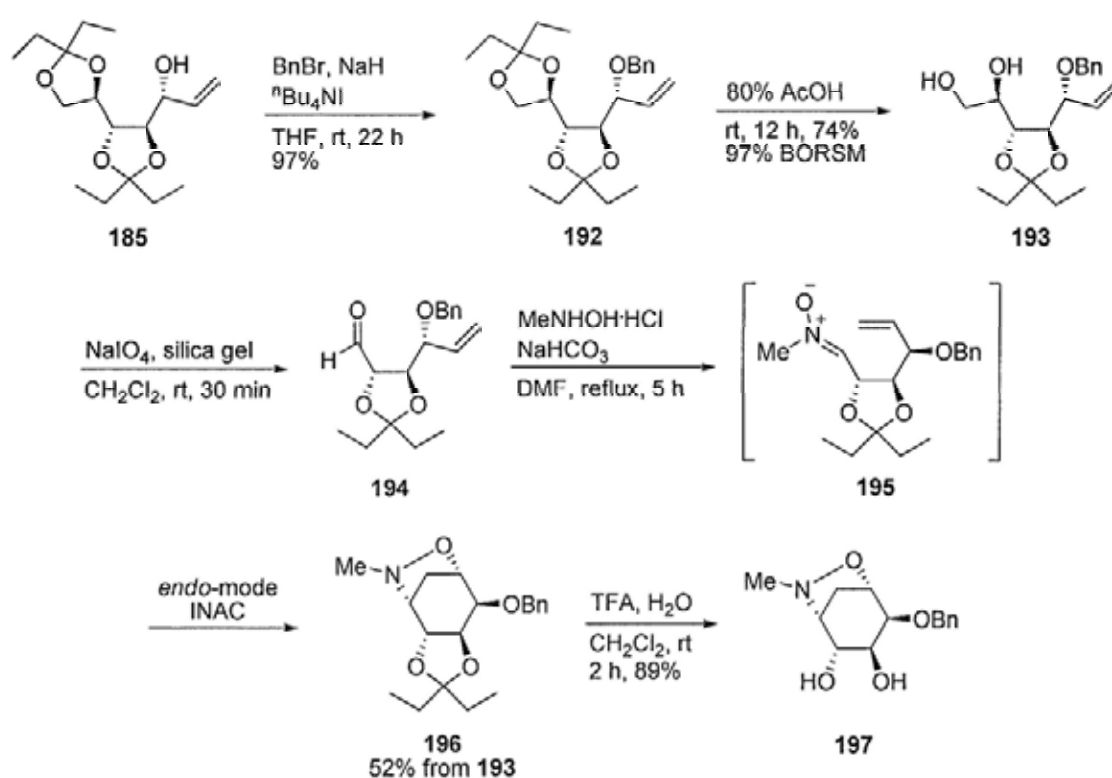


Figure 28. Conformations of **190** and **191**.

However, both H_1 and H_5 in amine **191** are occupying the equatorial position hence all of the $J_{1,6}$, $J_{5,6}$, $J_{1,6'}$, and $J_{5,6'}$ are small in magnitude (Figure 28). Both H_6 and $\text{H}_{6'}$ were observed as a doublet of triplets (dt, $J = 15.1, 2.8$ Hz and dt, $J = 15.2, 2.9$ Hz) in the ^1H NMR spectrum, which is different from the case in amine **190** (one quartet and one doublet of triplets). Hence by analyzing the coupling patterns of H_6 and $\text{H}_{6'}$ from

the ^1H NMR spectra, the stereochemistry of the amine and hydroxyl moieties can be assigned.

The alkene **185**, which is the minor product of the previous Grignard vinylation shown in Scheme 78, was also transformed into its corresponding nitrone **195** by the same synthetic strategy (Scheme 81). First, benzylation of alcohol **185** gave benzyl ether **192**, which was followed by regioselective acid hydrolysis to furnish 1,2-diol **193**. Glycol cleavage oxidation of diol **193** afforded aldehyde **194**. This aldehyde **194** was then reacted with *N*-methylhydroxylamine to yield nitrone **195**. After heating the nitrone **195**, the INAC reaction occurred and one 6-membered *endo*-cycloadduct **196** was formed in a moderate overall yield from diol **193**.



Scheme 81

The ring size of the INAC cycloadduct **196** was confirmed by its ^{13}C DEPT NMR spectrum as mentioned previously. Isoxazolidine **196** has three resonances in the upfield region (δ 25–40 ppm) which were assigned to be a methylene group, two of which are the methylene carbons of pentylidene group and the remaining one is the methylene carbon in the cyclohexane ring. Thus the formation of a 6-membered cycloadduct was confirmed.

In contrast to the INAC reaction of nitrene **178** which gave two INAC cycloadducts (Scheme 79), the INAC reaction of nitrene **195** furnished only one INAC cycloadduct. The reason can be explained by the following proposed transition states (Figure 29). In order to minimize the torsion strain of both TS-1 and TS-2, the pentylidene group is occupying *trans*-diequatorial position, and then the benzyl group should occupy the axial position. For TS-2, the carbocycle was formed by adopting a boat-like conformation which led to higher TS energy. Also, there is steric repulsion between the axial benzyl group and the nitrene moiety. These two factors make the formation of isoxazolidine **198** became highly unfavoured. Thus no isoxazolidine **198** was formed. On the other hand, there is no such steric repulsion between the benzyl group and nitrene moiety in TS-1, and the formation of carbocycle in TS-1 adopted a chair-like conformation which led to lower TS energy. Hence isoxazolidine **196** was obtained as the sole product during this INAC reaction.

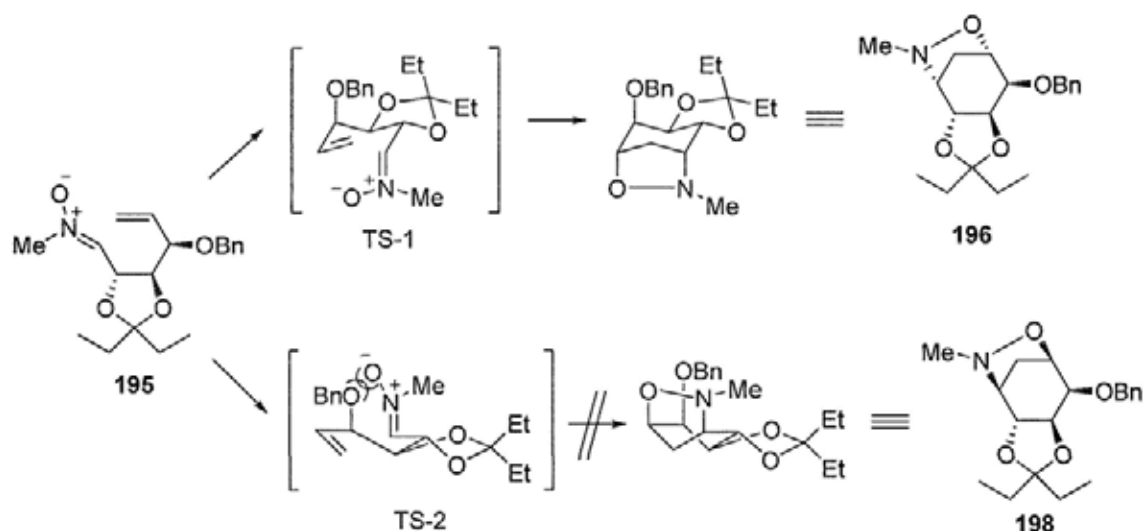
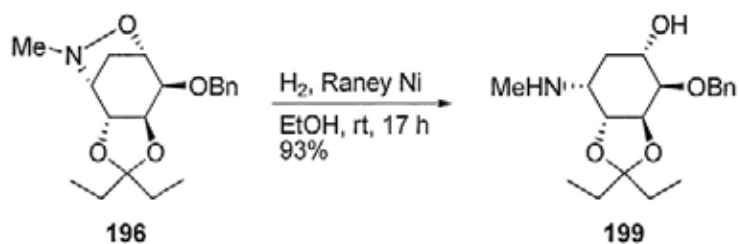


Figure 29

The pentaerythritol group of isoxazolidine **196** was removed by trifluoroacetic acid hydrolysis to afford diol **197** in 89% yield (Scheme 81). Although diol **197** is a solid at room temperature and pressure, it cannot be crystallized in good single crystals hence its structure cannot be confirmed by X-ray crystallography. However, the stereochemistry of this INAC cycloadduct was confirmed by the ^1H NMR spectrum of amine **199**, which was formed by Raney[®]-Nickel hydrogenolysis of isoxazolidine **196** (Scheme 82).



Scheme 82

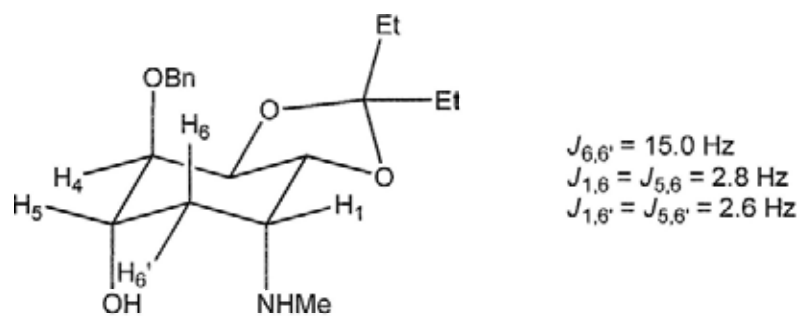


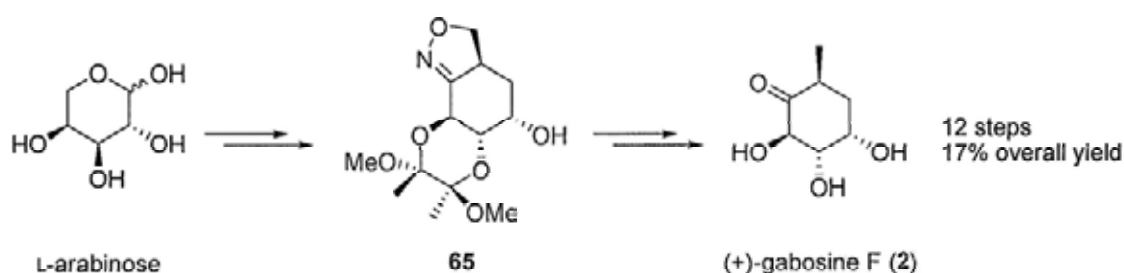
Figure 30. Conformation of amine **199**

In order to adopt the most stable conformation, the carbocycle of amine **199** is in chair conformation with a pentyldene group occupying the *trans*-diequatorial position (Figure 30). From the ^1H NMR spectrum of amine **199**, both H_6 and $\text{H}_{6'}$ were observed as a doublet of triplets (dt, $J = 15.0, 2.8 \text{ Hz}$ and dt, $J = 15.0, 2.6 \text{ Hz}$). This observation is comparable to the coupling patterns of H_6 and $\text{H}_{6'}$ in amine **191** (Figure 28), in which both the amine and hydroxyl moieties are occupied in the α -position. Hence the hydroxyl and amine moieties in amine **199** should also have such α -stereochemistry as well.

Chapter 3

Conclusion

Enantiopure (+)-gabosine F (**2**) was successfully synthesized from L-arabinose via intramolecular nitrile oxide-alkene cycloaddition (INOC) as the key step, in 12 steps and 17% overall yield (Scheme 83).



Scheme 83

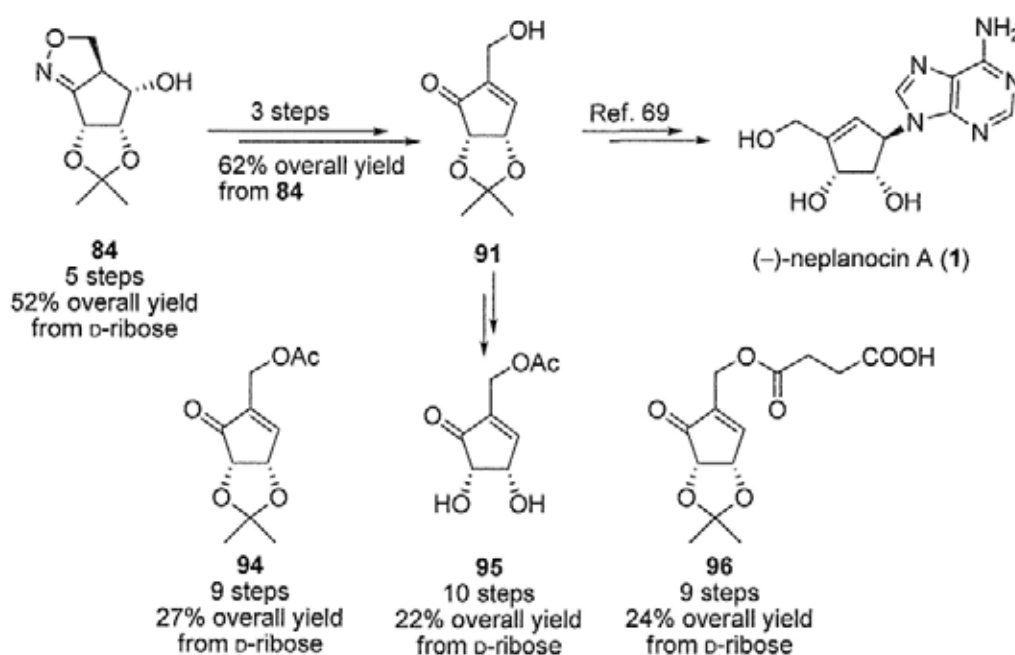
Theoretically, by following the same synthetic strategy, another natural product (–)-gabosine B (**36**), which is the enantiomer of (+)-gabosine F (**2**), can also be synthesized from D-arabinose (Scheme 84).



Scheme 84

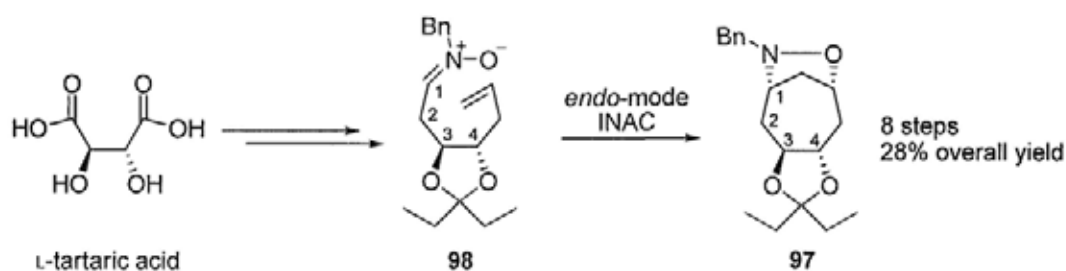
The INOC cycloadduct isoxazoline **84** was transformed into optically pure alcohol **91**, which is the key intermediate of Khan's synthesis of (±)-neplanocin A.⁶⁹

This alcohol **91** was also converted into cyclopent-2-enone derivatives **94–96** (Scheme 85).



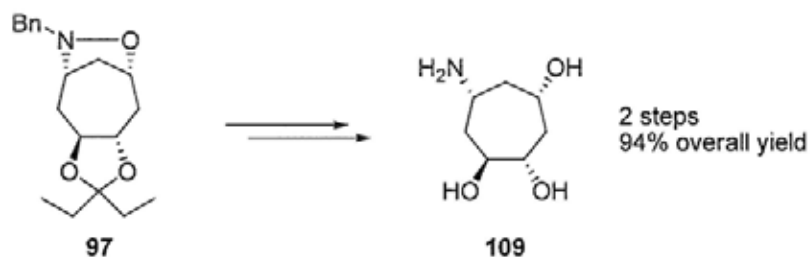
Scheme 85

In the studies on regioselectivity of INAC of hept-6-ene bearing a 3,4-*trans*-pentyldiene blocking group, the INAC of nitron **98**, which was prepared from L-tartaric acid, gave exclusive formation of *endo*-cycloadduct isoxazolidine **97** (Scheme 86). As the nitron **98** consists of only nitron, alkene and 3,4-*trans*-pentyldiene moieties, its exclusive formation of *endo*-cycloadduct concluded that the presence of 3,4-*trans*-pentyldiene group can induce the *endo*-mode INAC reaction to take place.



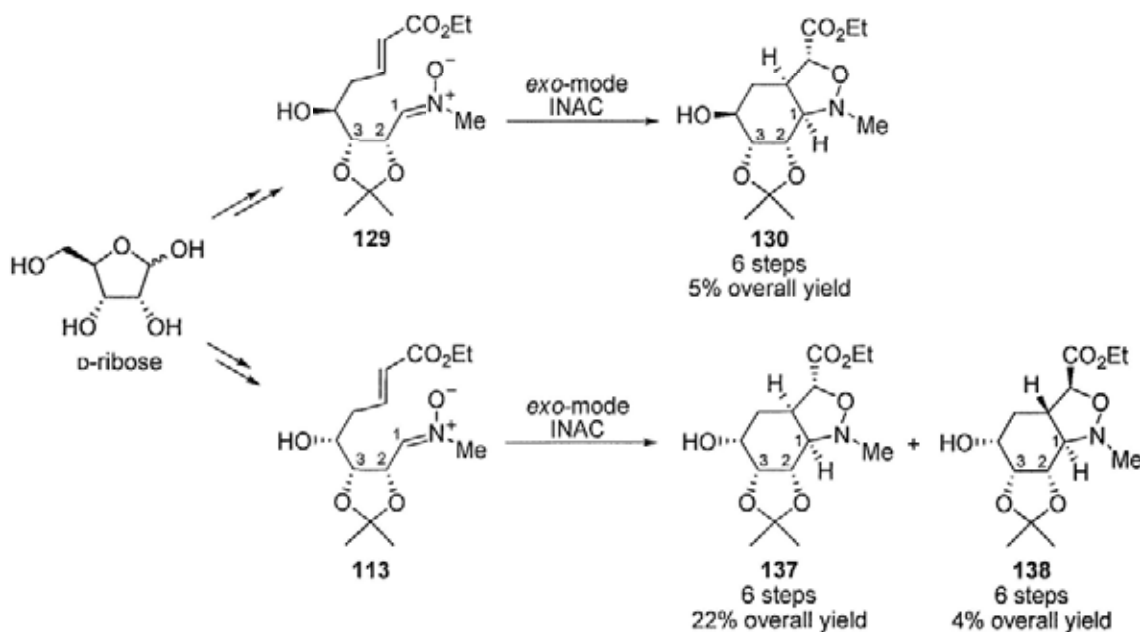
Scheme 86

The cycloadduct isoxazolidine **97** was transformed into aminocycloheptanol **109** readily (Scheme 87).



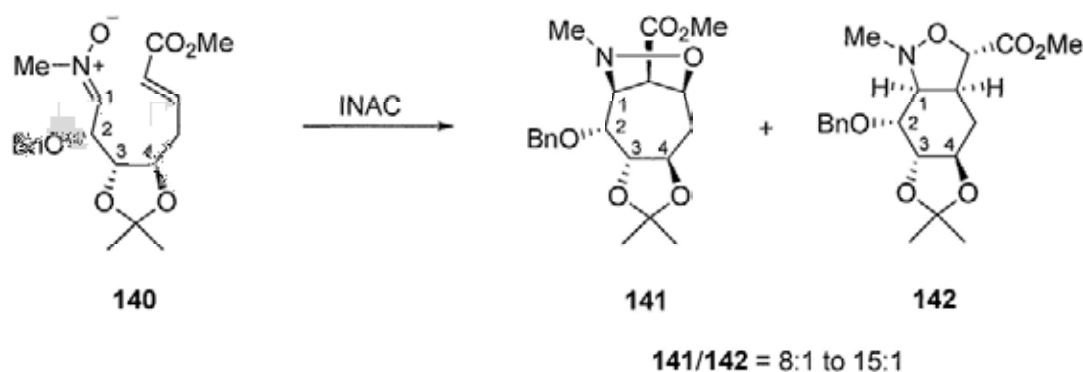
Scheme 87

In the studies of INAC reaction between nitrono moiety and α,β -unsaturated ester, exclusive formation of 6-membered *exo*-cycloadducts **130**, **137** and **138** was observed when substrates were bearing a 2,3-*cis*-isopropylidene group (nitrones **129** and **113**) (Scheme 88).



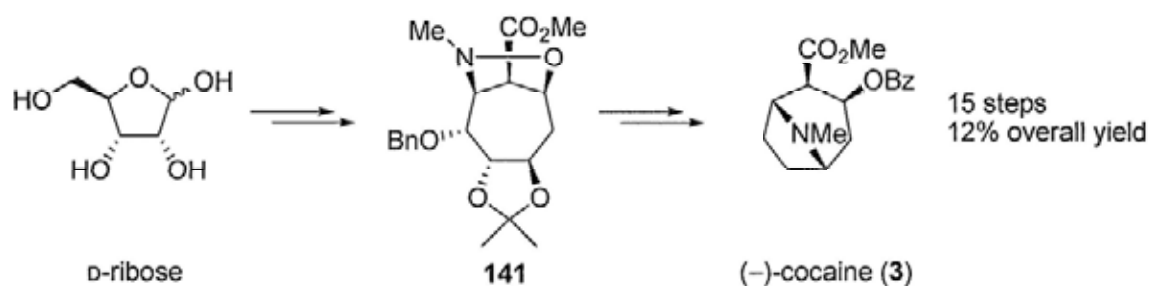
Scheme 88

When the substrate was bearing a 3,4-*trans*-isopropylidene (nitron 140), INAC reaction between nitron moiety and α,β -unsaturated ester afforded 7-membered *endo*-cycloadduct 141 as the major product, with 6-membered *exo*-cycloadduct 142 formed as the minor product (Scheme 89).



Scheme 89

Through this *endo*-cycloadduct isoxazolidine 141, natural product (–)-cocaine (3) was hence synthesized from D-ribose in 15 steps and 12% overall yield (Scheme 90).



Scheme 90

By using this synthetic strategy, six more (–)-cocaine analogues were obtained as well (Figure 31).

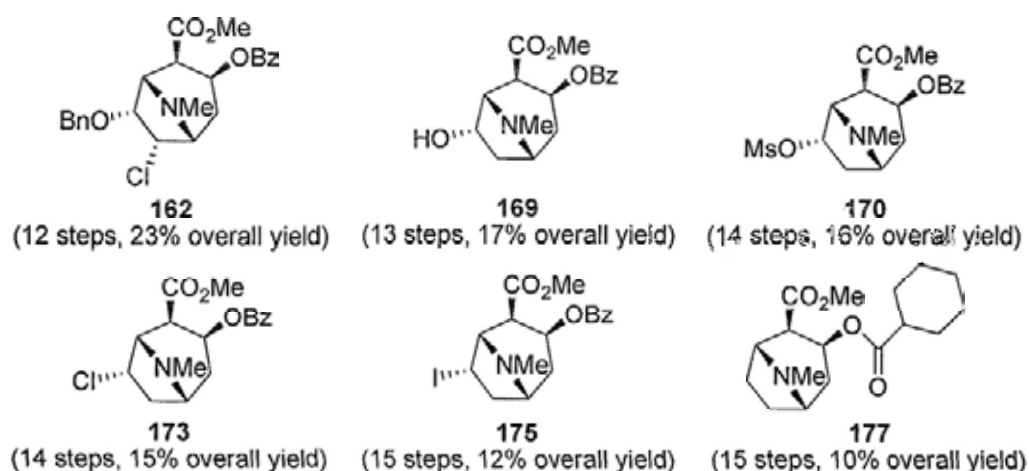
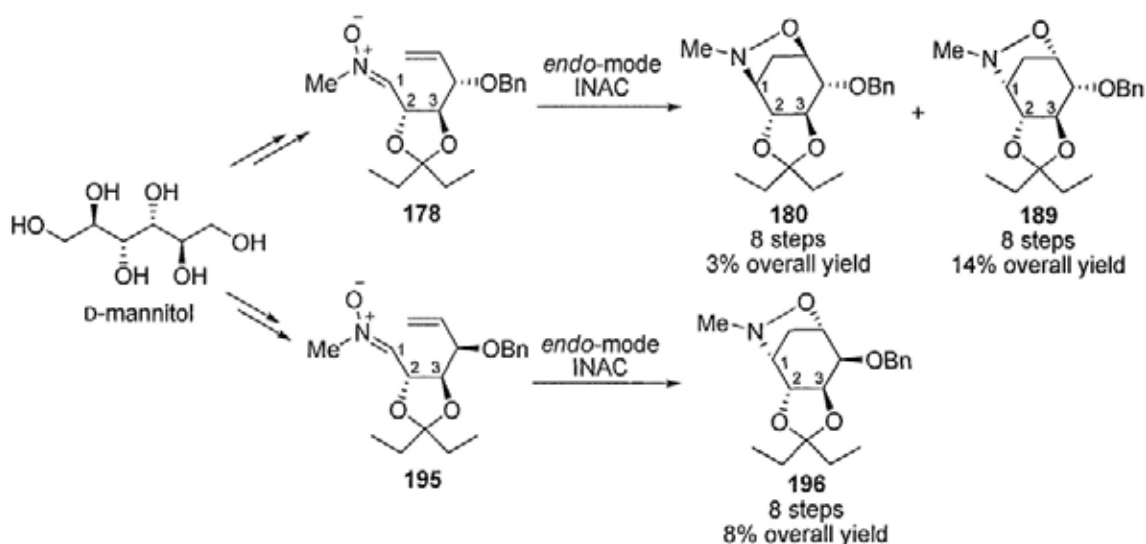


Figure 31

The regioselectivity of INAC reaction of hex-5-enoses with 2,3-*trans*-pentylidene blocking group were also studied. Exclusive formation of 6-membered *endo*-cycloadducts were observed during INAC reaction of nitrones **178** and **195**, which were accessed from D-mannitol, in 8 steps (Scheme 91).



Scheme 91

Experimental Section

Melting points were measured with a Reichert apparatus in Celsius degrees and are uncorrected. Optical rotations were obtained with a Perkin-Elmer model 341 polarimeter, operating at 589nm. Infrared (IR) spectra were recorded on a Nicolet 205 or a Perkin-Elmer 1600 FT-IR spectrophotometer as thin films on potassium bromide discs. Nuclear magnetic resonance (NMR) spectra were measured with either (i) Bruker DPX300 NMR spectrometer at 300.13 MHz (^1H) or at 75.47 MHz (^{13}C) or (ii) Bruker Avance III 400 NMR spectrometer at 400.19 MHz (^1H) or at 100.62 MHz (^{13}C) as mentioned, in CDCl_3 solutions, unless stated otherwise. All chemical shifts were recorded in ppm relative to tetramethylsilane ($\delta = 0.0$). Spin-spin coupling constants (J value) recorded in Hz were measured directly from the spectra. MS and HRMS were measured on a ThermoFinnigan MAT 95 KL at the Department of Chemistry, The Chinese University of Hong Kong, Hong Kong, China. Elemental analyses were carried out by MEDAC Ltd, Department of Chemistry, Brunel University, Uxbridge, UK. All reactions were monitored by analytical thin-layer chromatography (TLC) on Merck aluminium-precoated plates of silica gel 60 F254 with detection by spraying with 5% (w/v) dodecamolybdophosphoric acid in ethanol or 5% (w/v) ninhydrin in ethanol, and subsequent heating. E. Merck silica gel 60 (230-400 mesh) was used for flash chromatography. All reagents and solvents were general reagent grade unless otherwise stated. Pyridine was distilled from barium oxide and stored in the presence of potassium hydroxide pellets. DMF was dried by magnesium sulfate, filtered and the filtrate was then distilled under reduced pressure. Acetonitrile was freshly distilled from P_2O_5 under

nitrogen. Acetone was dried by CaSO_4 and filtered. THF and toluene were freshly distilled from Na/benzophenone ketyl under nitrogen. Et_2O was freshly distilled from K/benzophenone ketyl under nitrogen. Dichloromethane was freshly distilled from P_2O_5 under nitrogen. Other reagents were purchased from commercial suppliers and were used without purification.

General procedure for glycol cleavage reaction. NaIO_4 (3 eq.) was dissolved in a minimum amount of hot water ($\sim 80^\circ\text{C}$) followed by the addition of silica gel (230–400 mesh, $10 \times$ weight of diol) with vigorous swirling and shaking. The mixture was suspended in CH_2Cl_2 and then a solution of diol (1 eq.) in CH_2Cl_2 was added. After vigorous stirring at room temperature for 1 h, the mixture was filtered then concentrated under reduced pressure to give the crude aldehyde product.

Generation of allylmagnesium bromide. To a suspension of magnesium powder (3.65 g, 150 mmol) in Et_2O (10 mL) was added a catalytic amount of iodine and the mixture was stirred at room temperature for 15 min. A solution of allyl bromide (4.30 mL, 50.0 mmol) in Et_2O (50 mL) was added dropwise to the mixture at a rate to maintain a gentle reflux of the Et_2O . After the addition of the allyl bromide solution, the mixture was heated under reflux for 30 min and then cooled down for use. The concentration of the allylmagnesium bromide solution generated was around 1.5 M.

Generation of vinylmagnesium bromide. Vinyl bromide (1.34 mL, 19.0 mmol) was condensed with an acetone-dry ice cold finger and diluted with THF (20 mL) at -78°C . To a suspension of magnesium powder (1.48 g, 60.9 mmol) in THF (30 mL) was

added 1,2-dibromoethane (0.2 mL) and the vinyl bromide solution was added dropwise to the reaction mixture at a rate that a moderate reflux was maintained. After the addition had been completed, the solution was heated to reflux for 30 min and then cooled down for use. The concentration of the vinylmagnesium bromide solution generated was around 1.5 M.

Generation of BnNHOH.⁸⁸ Hydroxylamine hydrochloride (3.76 g, 54.1 mmol) and NaHCO₃ (6.20 g, 73.8 mmol) were added to a solution of benzaldehyde (5.0 mL, 49.2 mmol) in CH₃CN (50 mL) and the mixture was stirred at room temperature for 1 h. The reaction mixture was partitioned between Et₂O (50 mL) and water (50 mL). The aqueous layer was extracted with Et₂O (2 × 50 mL). The combined organic extracts were washed with brine, dried over anhydrous MgSO₄, and filtered. Concentration of the filtrate followed by flash chromatography (hexane:Et₂O, 1:2) gave benzylaldehyde oxime as a colorless oil. To a solution of benzylaldehyde oxime in MeOH (24 mL) was added a trace amount of bromocresol green to give a clear yellow solution. NaBH₃CN (3.55 g, 56.5 mmol) was added to the reaction mixture which turned the mixture into dark blue and 2 M HCl in MeOH was added dropwise with stirring until the color of the mixture turned yellow. The addition of 2 M HCl in MeOH was continued whenever the color of the mixture turned blue. After stirring at room temperature for 1 h, the reaction was completed indicated by the permanent yellow color of the mixture without the addition of the acid. The solvent was then removed under reduced pressure and the residue was dissolved in water (20 mL). 6 M NaOH was added to attain a pH value greater than 9. After saturation of the mixture with NaCl, the aqueous phase was

extracted with CHCl_3 (4×30 mL). The solvent was removed under reduced pressure and the residue was purified by recrystallization from hexane- CH_2Cl_2 to give benzylhydroxylamine (4.92 g, 81%) as a white solid.

General procedure for INAC reaction (Method A). *N*-Methylhydroxylamine hydrochloride (1.05 eq.) and NaHCO_3 (2.10 eq.) were then added to a solution of aldehyde in the selected solvent. The reaction mixture was stirred at room temperature for until the disappearance of the aldehyde as shown on TLC. It was then heated under reflux until the disappearance of the nitron as shown on TLC. After cooling, the reaction mixture was partitioned between EtOAc and water. The aqueous layer was extracted with EtOAc for three times. The combined organic extracts were washed with brine, dried over anhydrous MgSO_4 , and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography to give the cycloadduct(s).

General procedure for INAC reaction (Method B). *N*-Methylhydroxylamine hydrochloride (1.05 eq.) and NaHCO_3 (2.10 eq.) were added to a solution of aldehyde in MeCN. The reaction mixture was stirred at room temperature for until the disappearance of the aldehyde as shown on TLC. Et_2O was added to the reaction mixture to precipitate out most of the salt. The salt was filtered off through a thin layer of silica gel and washed with EtOAc. Concentration of the filtrate gave the crude product of nitron. The crude nitron was then redissolved in the selected solvent and the solution was heated under reflux until the disappearance of the nitron as shown on

TLC. The reaction mixture was then concentrated under reduced pressure and the residue was purified by flash chromatography to give the cycloadduct(s).

General procedure for INAC reaction (Method C). *N*-Methylhydroxylamine hydrochloride (1.05 eq.) and the selected base (3 eq.) were added to a solution of aldehyde/lactol in the selected solvent. The mixture was then heated under reflux. After the completion of the reaction, the mixture was filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography to yield the cycloadduct(s).

(+)-Gabosine F (2). To a stirred solution of ketone **77** (9.3 mg, 0.034 mmol) in CH₂Cl₂ (1 mL) were added deionized water (0.05 mL) and TFA (0.25 mL, 3.4 mmol) at room temperature to form a clear solution. The mixture was stirred at room temperature for 2 h. Concentration of the mixture under reduced pressure and the residue was purified by flash chromatography (CHCl₃:MeOH, 20:1) furnished (+)-gabosine F (**2**) (5.5 mg, 100%) as colorless crystals: mp 88–90 °C {lit.^{16a} mp 82–85 °C}; [α]_D²⁰ +88.4 (*c* 0.69, MeOH) {lit.^{16a} [α]_D²⁰ +94 (*c* 1.0, MeOH)}; *R*_f 0.20 (CHCl₃:MeOH, 9:1); IR (thin film) 3390, 2969, 2931, 1716, 1455, 1379, 1347, 1199, 1122, 1080 cm⁻¹; ¹H NMR (300 MHz, CD₃OD) δ 1.03 (3H, d, *J* = 6.6 Hz), 1.41 (1H, td, *J* = 13.8, 2.4 Hz), 2.12 (1H, ddd, *J* = 14.1, 6.0, 3.3 Hz), 2.86–2.99 (1H, m), 3.46 (1H, dd, *J* = 9.9, 3.0 Hz), 4.09 (1H, q, *J* = 2.7 Hz), 4.40 (1H, d, *J* = 10.2 Hz); ¹³C NMR (75 MHz, CD₃OD) δ 13.7, 37.8, 38.1, 69.7, 78.1, 79.2, 211.4; MS (ESI) *m/z* (relative intensity) 183 ([M+Na]⁺, 100), 159 ([M-H]⁺, 55); HRMS (ESI) calcd for C₇H₁₂O₄ [M+Na]⁺ 183.0628, found 183.0632.

(-)-Cocaine (3). To a solution of chloride **173** (1.9 mg, 0.006 mmol) in MeOH (0.5 mL) was added Raney[®]-Nickel (2 mg). The mixture was activated with an atmosphere of H₂ (balloon) by three times followed by stirring under the same H₂ atmosphere at room temperature for another 14 h. The reaction mixture was filtered and washed with MeOH. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (CH₂Cl₂:MeOH, 19:1) to afford (-)-cocaine (**3**) (1.3 mg, 76%) as a white solid: mp 92–93 °C {lit.⁴⁶ mp 93–94 °C}; [α]_D²⁰ -16.9 (*c* 0.18, CHCl₃) {lit.⁴⁶ [α]_D²³ -16.2 (*c* 1.2, CHCl₃)}; R_f 0.48 (CH₂Cl₂:MeOH, 5:1); IR (thin film) 2947, 1749, 1714, 1450, 1315, 1278, 1229, 1176, 1114 cm⁻¹; ¹H NMR (400 MHz) δ 1.68–1.77 (2H, m), 1.84–1.90 (1H, m), 2.06–2.20 (2H, m), 2.23 (3H, s), 2.44 (1H, td, *J* = 11.8, 2.8 Hz), 3.02 (1H, dd, *J* = 5.2, 3.4 Hz), 3.30 (1H, s), 3.56–3.58 (1H, m), 3.71 (3H, s), 5.24 (1H, dt, *J* = 11.9, 6.0 Hz), 7.42 (2H, t, *J* = 7.8 Hz), 7.54 (1H, tt, *J* = 7.4, 1.2 Hz), 8.01–8.03 (2H, m); ¹³C NMR (100 MHz) δ 25.6 (CH₂), 25.8 (CH₂), 35.9 (CH₂), 41.5 (CH₃), 50.6 (CH), 51.8 (CH₃), 61.9 (CH), 65.2 (CH), 67.3 (CH), 128.7 (CH), 130.1 (CH), 130.6 (C), 133.3 (CH), 166.6 (C), 171.1 (C); MS (ESI) *m/z* (relative intensity) 304 ([M+H]⁺, 100); HRMS (ESI) calcd for C₁₇H₂₁NO₄ [M+H]⁺ 304.1543, found 304.1539.

(-)-Cocaine (3) from iodide 175. To a solution of iodide **175** (4.0 mg, 0.009 mmol) in MeOH (1 mL) was added Raney Nickel (4 mg). The mixture was activated with an atmosphere of H₂ (balloon) by three times followed by stirring under the same H₂ atmosphere at room temperature for another 14 h. The reaction mixture was filtered and washed with MeOH. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (CH₂Cl₂:MeOH, 19:1) to afford (-)-cocaine (**3**) (2.1 mg, 74%) as a white solid.

Isoxazoline 65. Following the glycol cleavage produce, alkene **70** (69.1 mg, 0.226 mmol) was converted into aldehyde **72** as a colorless oil. NaHCO₃ (38.0 mg, 0.452 mmol) and hydroxylamine hydrochloride (23.6 mg, 0.339 mmol) were added to the solution of aldehyde **72** in MeOH (3 mL). The mixture was stirred at room temperature for 30 min. Deionized water (8 mL) was added to the reaction mixture and the MeOH was removed under reduced pressure. The remaining aqueous solution was then extracted with EtOAc (3 × 10 mL) and the combined organic extracts were washed with brine, dried over anhydrous MgSO₄, and filtered. Concentration of the filtrate afforded crude oxime **73**. To the stirred suspension the crude oxime **73** and silica gel (230–400 mesh, 300 mg) in EtOH (10 mL) was added chloramine-T trihydrate (95.5 mg, 0.339 mmol) in small portions. After stirring at room temperature for 15 min, the silica gel was filtered. Concentration of the filtrate and the residue was purified by flash chromatography (hexane:EtOAc, 2:1 to 1:2) afforded isoxazoline **65** (57.4 mg, 89% overall yield from **70**) as a white solid: mp 232–233 °C; $[\alpha]_D^{20}$ -10.9 (*c* 1.96, CHCl₃); *R_f* 0.29 (hexane:EtOAc, 1:4); IR (thin film) 3545, 2949, 1377, 1118, 1032, 873 cm⁻¹; ¹H NMR (300 MHz) δ 1.33 (3H, s), 1.37 (3H, s), 1.53 (1H, ddd, *J* = 14.1, 11.7, 2.4 Hz), 2.32 (1H, ddd, *J* = 14.1, 6.6, 3.3 Hz), 3.22 (3H, s), 3.30 (3H, s), 3.66–3.87 (3H, m), 4.15 (1H, q, *J* = 2.7 Hz), 4.55 (1H, dd, *J* = 10.2, 7.5 Hz), 4.95 (1H, d, *J* = 9.9 Hz); ¹³C NMR (75 MHz) δ 18.0, 35.0, 44.9, 48.4, 48.7, 64.6, 68.8, 73.9, 74.1, 100.7, 100.8, 157.2; MS (ESI) *m/z* (relative intensity) 310 ([M+Na]⁺, 100); HRMS (ESI) calcd for C₁₃H₂₁NO₆ [M+Na]⁺ 310.1261, found 310.1265.

Benzyl β -L-arabinopyranoside (67). Acetyl chloride (9.47 mL, 133 mmol) was added dropwise to BnOH (140 mL) at 0 °C over 30 min. L-Arabinose (20.6 g, 133 mmol) was then added to the reaction mixture which was stirred vigorously at room temperature for 3 d. Et₂O (700 mL) was added to precipitate the benzyl glycoside that was filtered and the crude white solid was washed with Et₂O. Recrystallization from EtOH afforded glycoside **67** (29.1 g, 88%) as white crystals: mp 171–172 °C {lit.⁸⁹ mp 167–169 °C}; [α]_D²⁰ +217.9 (*c* 1.11, MeOH) {lit.⁸⁹ [α]_D²⁰ -217 (*c* 0.400, H₂O)}; R_f 0.50 (CH₃Cl:MeOH, 5:1); ¹H NMR (300 MHz, CD₃OD) δ 3.60 (1H, dd, *J* = 12.6, 2.4 Hz), 3.80–3.88 (4H, m), 4.52 (1H, d, *J* = 12 Hz), 4.71 (1H, d, *J* = 11.7 Hz), 7.25–7.42 (5H, m); ¹³C NMR (75 MHz, CD₃OD) δ 65.2, 71.2, 71.6, 71.7, 100.8, 129.6, 130.0, 130.2, 139.9; MS (ESI) *m/z* (relative intensity) 263 ([M+Na]⁺, 100); HRMS (ESI) calcd for C₁₂H₁₆O₅ [M+Na]⁺ 263.0890, found 263.0897.

Benzyl-2,3-*O*-[(2*R*,3*R*)-2,3-dimethoxybutan-2,3-dioxy]- β -L-arabinopyranoside (68). To a suspension of **67** (23.0 g, 95.9 mmol) in methanol (500 mL), 2,3-butanedione (12.6 mL, 144 mmol), trimethylorthoformate (52.5 mL, 480 mmol) and (\pm)-10-camphorsulfonic acid (2.23 g, 9.59 mmol) were added and the mixture was heated under reflux for 4 h. Powdered NaHCO₃ (3.99 g) was then added to the cooled reaction mixture and stirred for 5 h. The mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was dissolved in EtOAc and the solution was washed with saturated NaHCO₃ solution. The organic layer was dried over anhydrous MgSO₄ and filtered. The filtrate was concentrated under reduced pressure and the crude residue was purified by flash chromatography (hexane:EtOAc, 1:1) to

afford product **68** (20.4 g, 60%) as a white solid: mp 143–144 °C; $[\alpha]_D^{20} +3.9$ (c 1.27, CHCl_3); R_f 0.32 (hexane:EtOAc, 1:1); IR (thin film) 3480, 2945, 1455, 1378, 1136, 1038, 885 cm^{-1} ; ^1H NMR (300 MHz) δ 1.31–1.33 (6H, 2s), 2.02 (1H, br s), 3.22 (3H, s), 3.26 (3H, s), 3.68 (1H, dd, $J = 12.6, 1.5$ Hz), 3.79 (1H, dd, $J = 12.6, 1.5$ Hz), 3.92–3.93 (1H, m), 4.11 (1H, dd, $J = 10.5, 3$ Hz), 4.16 (1H, dd, $J = 10.5, 3$ Hz), 4.65 (1H, d, $J = 12.3$ Hz), 4.73 (1H, d, $J = 12.6$ Hz), 4.95 (1H, d, $J = 3$ Hz), 7.26–7.42 (5H, m); ^{13}C NMR (75 MHz) δ 18.0, 48.1, 48.2, 63.4, 65.4, 66.1, 68.2, 69.5, 97.1, 100.3, 100.4, 127.8, 128.2, 128.5, 137.9; MS (ESI) m/z (relative intensity) 377 ($[\text{M}+\text{Na}]^+$, 100); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{26}\text{O}_7$ $[\text{M}+\text{Na}]^+$ 377.1571, found 377.1572.

Alkenes 70 and 71. To a solution of *trans*-diacetal **68** (23.2 g, 65.5 mmol) in EtOH (200 mL) was added 10% Pd-on-charcoal (696 mg, 0.655 mmol) and the mixture was stirred under an atmosphere of H_2 (balloon). After stirring at room temperature under H_2 for 12 h, the mixture was filtered and the filtrate was concentrated to give lactol **69** as a white solid. A solution of allylmagnesium bromide was generated with magnesium powder (39.8 g, 1.64 mol) and allyl bromide (85.0 mL, 982 mmol) in Et_2O (500 mL). The Et_2O solution of allylmagnesium bromide was added dropwise to a stirred solution of lactol **69** in THF (400 mL) at -78 °C under N_2 over 2 h. After stirring at -78 °C for a further 1 h and then room temperature for 12 h, the mixture was quenched with saturated NH_4Cl solution and the aqueous phase was extracted with EtOAc (2 \times 500 mL). The combined organic extracts were dried over anhydrous MgSO_4 , and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (CHCl_3 :EtOAc, 1:4) to afford firstly

alkene **70** (9.89 g, 49% overall yield from **68**) as a colorless oil and secondly alkene **71** (9.77 g, 49% overall yield from **68**) as a colorless oil: Data for **70**: $[\alpha]_D^{20} -147.5$ (*c* 2.52, CHCl₃); *R_f* 0.33 (CHCl₃:EtOAc, 1:3); IR (thin film) 3371, 2949, 1376, 1128, 1037 cm⁻¹; ¹H NMR (300 MHz) δ 1.26–1.27 (6H, 2s), 2.15 (1H, dt, *J* = 14.1, 8.4 Hz), 2.81 (1H, dddd, *J* = 14.1, 6.0, 2.7, 1.5 Hz), 3.01–3.34 (9H, m), 3.55 (1H, ddd, *J* = 10.8, 8.1, 2.7 Hz), 3.70–3.90 (5H, m), 5.17–5.22 (2H, m), 5.84 (1H, dddd, *J* = 17.7, 9.3, 8.4, 6.0 Hz); ¹H NMR (300 MHz, CDCl₃-D₂O) δ 1.26–1.27 (6H, 2s), 2.15 (1H, dt, *J* = 14.4, 9.0 Hz), 2.80 (1H, dddd, *J* = 14.1, 6.0, 2.7, 1.5 Hz), 3.25–3.26 (6H, 2s), 3.54 (1H, dd, *J* = 9.3, 8.1 Hz), 3.70–3.90 (5H, m), 5.16–5.22 (2H, m), 5.83 (1H, dddd, *J* = 17.7, 9.3, 8.4, 6.0 Hz); ¹³C NMR (75 MHz) δ 17.7, 17.8, 37.8, 48.6, 63.8, 70.6, 70.9, 73.6, 73.9, 99.8, 99.0, 119.3, 135.0; MS (ESI) *m/z* (relative intensity) 329 ([M+Na]⁺, 100); HRMS (ESI) calcd for C₁₄H₂₆O₇ [M+Na]⁺ 329.1571, found 329.1575.

Data for **71**: $[\alpha]_D^{20} -148.9$ (*c* 1.26, CHCl₃); *R_f* 0.24 (CHCl₃:EtOAc, 1:3); IR (thin film) 3393, 2949, 1377, 1127, 1037 cm⁻¹; ¹H NMR (300 MHz) δ 1.25–1.28 (6H, 2s), 2.32–2.51 (2H, 1ddd, *J* = 14.4, 6.9, 5.7 Hz, 1ddd, *J* = 14.4, 8.4, 7.2 Hz), 3.13 (3H, s), 3.22–3.24 (6H, 2s), 3.68 (1H, dd, *J* = 9.9, 1.8 Hz), 3.72–3.81 (3H, m), 3.92 (1H, ddd, *J* = 8.1, 5.1, 1.8 Hz), 3.99 (1H, dd, *J* = 9.9, 6.3 Hz), 5.08–5.15 (2H, m), 5.83 (1H, ddt, *J* = 17.1, 10.2, 6.9 Hz); ¹H NMR (300 MHz, CDCl₃-D₂O) δ 1.25–1.27 (6H, 2s), 2.30–2.51 (2H, 1ddd, *J* = 14.1, 6.6, 5.4 Hz, 1ddd, *J* = 14.4, 8.4, 7.2 Hz), 3.22–3.24 (6H, 2s), 3.67 (1H, dd, *J* = 9.9, 1.8 Hz), 3.70–3.79 (3H, m), 3.91–3.99 (2H, 1ddd, *J* = 8.1, 5.1, 1.8 Hz, 1dd, *J* = 9.9, 6.3 Hz), 5.06–5.15 (2H, m), 5.83 (1H, ddt, *J* = 17.1, 10.2, 6.9 Hz); ¹³C NMR (75 MHz) δ 17.8, 17.9, 37.9, 48.8, 48.5, 63.7, 69.7, 70.4, 71.5, 72.2, 99.0, 99.2, 117.9, 135.5; MS (ESI) *m/z* (relative intensity) 329 ([M+Na]⁺, 100); HRMS (ESI) calcd for C₁₄H₂₆O₇ [M+Na]⁺ 329.1571, found 329.1579.

Ketone 75. To a solution of isoxazoline **65** (220 mg, 0.765 mmol) in EtOH/H₂O/1,4-dioxane (v/v/v = 8:2:1, 12 mL) were added AcOH (0.08 mL, 1.53 mmol) and Raney[®]-Nickel (59 mg). The mixture was activated with an atmosphere of H₂ (balloon) by three times followed by stirring under the same H₂ atmosphere at room temperature for another 3 h. The mixture was filtered and washed with EtOH. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (EtOAc) to afford ketones **75** (200 mg, 90%) as a colorless oil: $[\alpha]_D^{20} - 89.9$ (*c* 0.47, CHCl₃); *R_f* 0.21 (EtOAc); IR (thin film) 3455, 2997, 2951, 1727, 1461, 1379, 1212, 1139, 1116, 1008 cm⁻¹; ¹H NMR (300 MHz) δ 1.31 (3H, s), 1.37 (3H, s), 1.74 (1H, td, *J* = 14.1, 2.4 Hz), 2.16 (1H, ddd, *J* = 14.4, 6.3, 3.3 Hz), 2.43 (2H, br s), 2.96–3.03 (1H, m), 3.21 (3H, s), 3.24 (3H, s), 3.65 (1H, dd, *J* = 11.7, 6.0 Hz), 3.78–3.88 (2H, m), 4.22 (1H, q, *J* = 2.7 Hz), 4.82 (1H, dd, *J* = 10.8, 1.2 Hz); ¹³C NMR (75 MHz) δ 18.0, 31.2, 45.5, 48.5, 48.8, 61.7, 67.2, 72.5, 73.8, 100.4, 100.6, 206.6; MS (ESI) *m/z* (relative intensity) 313 ([M+Na]⁺, 100); HRMS (ESI) calcd for C₁₃H₂₂O₇ [M+Na]⁺ 313.1256, found 313.1258.

Ketone 77. To a stirred solution of **75** (32.5 mg, 0.112 mmol) in CH₂Cl₂ (4 mL) at room temperature was added Burgess reagent (48.1 mg, 0.202 mmol). The mixture was heated to reflux for 18 h then the solvent was removed under reduced pressure to give the crude enone **76**. The crude product was redissolved in EtOH/H₂O/1,4-dioxane (v/v/v = 8:2:1, 4 mL) followed by the addition of Raney[®]-Nickel (10 mg). The mixture was activated with an atmosphere of H₂ (balloon) by three times followed by stirring under the same H₂ atmosphere at room temperature for another 1 h. The mixture was

filtered and washed with EtOH. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (hexane:Et₂O, 1:2) to yield **77** (11.7 mg, 38% overall yield from **75**) as colorless crystals: mp 190 °C; [α]_D²⁰ -81.0 (*c* 0.62, CHCl₃); *R*_f 0.17 (hexane:Et₂O, 1:2); IR (thin film) 3516, 2926, 1731, 1455, 1379, 1206, 1138, 1036 cm⁻¹; ¹H NMR (300 MHz) δ 1.05 (3H, d, *J* = 6.6 Hz), 1.31 (3H, s), 1.37 (3H, s), 1.44 (1H, td, *J* = 13.8, 2.4 Hz), 1.76 (1H, br s), 2.23 (1H, ddd, *J* = 14.4, 6.0, 3.0 Hz), 2.83–2.96 (1H, m), 3.20 (3H, s), 3.23 (3H, s), 3.78 (1H, dd, *J* = 10.8, 2.7 Hz), 4.15 (1H, q, *J* = 2.7 Hz), 4.78 (1H, d, *J* = 10.8 Hz); ¹³C NMR (75 MHz) δ 13.7, 18.0, 18.1, 37.0, 38.2, 48.4, 48.7, 67.5, 72.5, 73.9, 100.3, 100.6, 205.3; MS (ESI) *m/z* (relative intensity) 297 ([M+Na]⁺, 100); HRMS (ESI): calcd for C₁₃H₂₂O₆ [M+Na]⁺ 297.1309, found 297.1314.

Ketone 77 by mesylation of 75. To a stirred solution of **75** (13.8 mg, 0.048 mmol) and 2,4,6-collidine (0.02 mL, 0.152 mmol) in CH₂Cl₂ (1 mL) at -78 °C was added methanesulfonyl chloride (0.006 mL, 0.076 mmol). The mixture was stirred at -78 °C for 1 h and then room temperature for 12 h to afford a mixture of mesylate and enone **76**. Et₃N (0.01 mL, 0.072 mmol) was added to the reaction mixture and stirred at room temperature for 1 h to allow the complete elimination of mesylate to enone **76**. The reaction mixture was quenched by saturated NaHCO₃ solution. The aqueous phase was extracted with EtOAc (2 × 15 mL) and the combined organic extracts were washed with 1 M hydrochloric acid then saturated NaHCO₃ solution. The organic phase was then dried over anhydrous MgSO₄ and filtered. The filtrate was concentrated under reduced pressure to give crude enone **76**. The crude product was redissolved in EtOH/H₂O/1,4-dioxane (v/v/v = 8:2:1, 1 mL) and Raney[®]-Nickel (4 mg) was added to

the solution. The mixture was activated with an atmosphere of H₂ (balloon) by three times followed by stirring under the same H₂ atmosphere at room temperature for another 1 h. The mixture was filtered and washed with EtOH. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (hexane:Et₂O, 1:2) to yield **77** (5.6 mg, 43% overall yield from **75**) as colorless crystals.

Ketone 77 by acetylation of 75. To a stirred solution of **75** (14.0 mg, 0.048 mmol) and 2,4,6-collidine (0.015 mL, 0.116 mmol) in CH₂Cl₂ (2 mL) at -78 °C was added acetyl chloride (0.004 mL, 0.058 mmol). The mixture was stirred at -78 °C for 18 h to afford crude acetate **78**. Et₃N (0.02 mL, 0.144 mmol) was added to the reaction mixture and the mixture was heated to reflux for 10 h. The reaction mixture was quenched by saturated NaHCO₃ solution. The aqueous phase was extracted with EtOAc (2 × 15 mL) and the combined organic extracts were washed with 1 M hydrochloric acid then saturated NaHCO₃ solution. The organic phase was then dried over anhydrous MgSO₄ and filtered. The filtrate was concentrated under reduced pressure to give crude enone **76**. The crude product was redissolved in EtOH/H₂O/1,4-dioxane (v/v/v = 8:2:1, 2 mL) and Raney[®]-Nickel (4 mg) was added to the solution. The mixture was activated with an atmosphere of H₂ (balloon) by three times followed by stirring under the same H₂ atmosphere at room temperature for another 1 h. The mixture was filtered and washed with EtOH. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (hexane:Et₂O, 1:2) to yield **77** (8.0 mg, 61% overall yield from **75**) as colorless crystals.

Ketone 77 from acetate 78. To a stirred solution of **78** (46.7 mg, 0.141 mmol) in CH₂Cl₂ (5 mL) was added Et₃N (0.059 mL, 0.42 mmol). The mixture was heated to reflux for 11 h then the solvent was removed under reduced pressure to give the crude enone **76**. The crude product was redissolved in EtOH/H₂O/1,4-dioxane (v/v/v = 8:2:1, 5 mL) and Raney[®]-Nickel (10 mg) was added to the solution. The mixture was activated with an atmosphere of H₂ (balloon) by three times followed by stirring under the same H₂ atmosphere at room temperature for another 1 h. The mixture was filtered and washed with EtOH. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (hexane:Et₂O, 1:2) to yield ketone **77** (37.2 mg, 97% overall yield from acetate **78**) as colorless crystals.

Acetate 78. To a stirred solution of **75** (51.3 mg, 0.177 mmol) and 2,4,6-collidine (0.056 mL, 0.424 mmol) in CH₂Cl₂ (5 mL) at -78 °C was added acetyl chloride (0.015 mL, 0.212 mmol). The reaction mixture was stirred at -78 °C for 12 h then was quenched by saturated NaHCO₃ solution. The aqueous phase was extracted with EtOAc (2 × 25 mL) and the combined organic extracts were washed with 1 M hydrochloric acid then saturated NaHCO₃ solution. The organic phase was then dried over anhydrous MgSO₄ and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (hexane:EtOAc, 2:3) to yield acetate **78** (49.3 mg, 87%) as colorless crystals: mp 140–141 °C; $[\alpha]_D^{20}$ -67.7 (*c* 0.63, CHCl₃); *R_f* 0.19 (hexane:EtOAc, 2:3); IR (thin film) 3472, 2995, 2952, 1739, 1456, 1378, 1241, 1139, 1117, 1037 cm⁻¹; ¹H NMR (300 MHz) δ 1.32 (3H, s), 1.37 (3H, s), 1.60 (1H, td, *J* = 14.1, 2.4 Hz), 2.03 (3H, s), 2.32 (1H, ddd, *J* = 14.1, 6.0, 3.3 Hz), 3.13–3.21 (1H, m), 3.21 (3H, s), 3.25 (3H, s), 3.82 (1H, dd, *J* = 10.8, 2.4 Hz), 4.15 (1H, dd, *J* = 11.4, 5.7

Hz), 4.22 (1H, q, $J = 2.4$ Hz), 4.37 (1H, dd, $J = 11.4, 5.4$ Hz), 4.80 (1H, d, $J = 10.8$ Hz); ^{13}C NMR (75 MHz) δ 18.0, 21.3, 32.0, 42.7, 48.5, 48.8, 62.4, 67.1, 72.5, 73.7, 100.4, 100.7, 171.3, 202.2; MS (ESI) m/z (relative intensity) 355 ($[\text{M}+\text{Na}]^+$, 100), 295 (17); HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{24}\text{O}_8$ $[\text{M}+\text{Na}]^+$ 355.1363, found 355.1365.

2,3-*O*-Isopropylidene- α,β -D-ribofuranose (79). Concentrated H_2SO_4 (0.19 mL, 3.59 mmol) and anhydrous CuSO_4 (11.0 g) were added to a suspension of D-ribose (10.8 g, 71.7 mmol) in dry acetone (350 mL). The reaction mixture was stirred at room temperature for 1 d. The mixture was neutralized with saturated NaHCO_3 solution and then filtered. The filtrate was partitioned between EtOAc (200 mL) and water (200 mL). The aqueous layer was extracted with EtOAc (2×200 mL). The combined organic extracts were washed with brine, dried over anhydrous MgSO_4 , and filtered. Concentration of the filtrate and the residue was purified by flash chromatography (hexane:EtOAc, 1:1) gave acetonide **79** (11.5 g, 84%) as a colorless oil: $[\alpha]_{\text{D}}^{20} -23.6$ (c 2.65, CHCl_3) {lit.⁶⁸ $[\alpha]_{\text{D}}^{20} -27.4$ (c 4.17, acetone)}; R_f 0.28 (hexane:EtOAc, 1:1); IR (thin film) 3403, 2988, 2942, 1459 cm^{-1} ; ^1H NMR (300 MHz, mixture of α and β isomer with ratio $\alpha:\beta=1:10$) δ 1.31 (3.0H, s), 1.38 (0.3H, s), 1.47 (3.0H, s), 1.56 (0.3H, s), 3.65–3.75 (2.2H, m), 3.92 (1.0H, br s), 4.16 (0.1H, t, $J = 3.3$ Hz), 4.38 (1.0H, t, $J = 2.7$ Hz), 4.56 (1.0H, d, $J = 5.7$ Hz), 4.62 (0.1H, dd, $J = 6.9, 4.2$ Hz), 4.70 (0.1H, dd, $J = 6.6, 2.4$ Hz), 4.80 (1.0H, d, $J = 6$ Hz), 5.18 (1.0H, d, $J = 4.8$ Hz), 5.39–5.44 (1.1H, m); ^{13}C NMR (75 MHz) δ 24.9, 26.3, 26.5, 63.3, 63.6, 79.6, 81.3, 81.7, 81.8, 86.8, 87.7, 97.3, 102.8, 112.4, 114.3; MS (FAB) m/z (relative intensity) 190 ($[\text{M}]^-$, 10), 189 ($[\text{M}-\text{H}]^-$, 100), 183 (55),

127 (51), 91 (68), 71 (59); HRMS (FAB) calcd for $C_8H_{14}O_5$ $[M-H]^-$ 189.0768, found 189.0764.

Alkene 80. To the stirred solution of acetone **79** (10.6 g, 55.6 mmol) in THF (200 mL) was added vinylmagnesium bromide solution in THF (300 mL, 342 mmol) at -78 °C. The mixture was stirred at -78 °C for 1 h and then room temperature for 16 h. The reaction mixture was quenched by saturated NH_4Cl solution. The aqueous phase was extracted with EtOAc (3×300 mL) and the combined organic extracts were dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (hexane:Et₂O, 1:4) to afford alkene **80** (9.54 g, 79%) as a white solid: mp 75 °C {lit.⁹ mp 74 °C}; $[\alpha]_D^{20}$ -36.9 (c 1.77, $CHCl_3$) {lit.⁹ $[\alpha]_D^{20}$ -31 (c 1.8, $CHCl_3$)}; R_f 0.24 (hexane:EtOAc, 1:2); IR (thin film) 3172, 2983, 2920, 1458, 1371, 1259, 1216, 1167, 1069 cm^{-1} ; 1H NMR (400 MHz) δ 1.33 (3H, s), 1.39 (3H, s), 3.30 (3H, br s), 3.71 (1H, dd, $J = 10.9, 5.7$ Hz), 3.88–3.94 (2H, m), 4.05 (1H, dd, $J = 9.2, 5.3$ Hz), 4.14 (1H, dd, $J = 9.3, 5.4$ Hz), 4.33 (1H, dd, $J = 9.0, 6.1$ Hz), 5.29 (1H, d, $J = 10.5$ Hz), 5.40 (1H, d, $J = 17.2$ Hz), 6.03 (1H, ddd, $J = 16.9, 10.5, 5.8$ Hz); ^{13}C NMR (100 MHz) δ 25.8, 28.3, 64.8, 69.8, 71.1, 78.0, 80.3, 109.4, 117.4, 137.9; MS (ESI) m/z (relative intensity) 241 ($[M+Na]^+$, 100); HRMS (ESI) calcd for $C_{10}H_{18}O_5$ $[M+Na]^+$ 241.1046, found 241.1047.

Isoxazoline 84. Following the glycol cleavage produce, alkene **80** (4.71 g, 21.6 mmol) was converted into lactol **81** as a colorless oil. $NaHCO_3$ (7.26 g, 86.4 mmol) and hydroxylamine hydrochloride (4.50 g, 64.8 mmol) were added to the solution of lactol **81** in MeOH (40 mL). The mixture was stirred at room temperature for 10 h. Deionized

water (100 mL) was added to the reaction mixture and the MeOH was removed under reduced pressure. The remaining aqueous solution was then extracted with EtOAc (3 × 100 mL) and the combined organic extracts were washed with brine, dried over anhydrous MgSO₄, and filtered. Concentration of the filtrate afforded crude oxime **82**. To a stirred suspension the crude oxime **82** and silica gel (230–400 mesh, 23.6 g) in EtOH (300 mL) was added chloramine-T trihydrate (9.13 g, 32.4 mmol) in small portions. After stirring at room temperature for 15 min, the silica gel was filtered. Concentration of the filtrate and the residue was purified by flash chromatography (hexane:EtOAc, 1:1) to yield isoxazoline **84** (3.36 g, 78% overall yield from alkene **80**) as a white solid: mp 75 °C; $[\alpha]_D^{20} +127.7$ (*c* 1.23, CHCl₃); *R_f* 0.19 (hexane:EtOAc, 1:1); IR (thin film) 3305, 2987, 2939, 1647, 1381, 1267, 1212, 1159, 1103, 1053 cm⁻¹; ¹H NMR (400 MHz) δ 1.39 (3H, s), 1.54 (3H, s), 2.54 (1H, br s), 3.74 (1H, dd, *J* = 8.7, 5.1 Hz), 3.88 (1H, q, *J* = 9.3 Hz), 4.20 (1H, t, *J* = 9.0 Hz), 4.63 (1H, dd, *J* = 10.6, 8.8 Hz), 4.85 (1H, t, *J* = 5.2 Hz), 5.02 (1H, d, *J* = 5.3 Hz); ¹³C NMR (100 MHz) δ 24.3, 26.3, 56.9, 72.3, 74.3, 74.5, 83.3, 113.3, 161.0; MS (ESI) *m/z* (relative intensity) 222 ([M+Na]⁺, 100), 200 ([M+H]⁺, 42); HRMS (ESI) calcd for C₉H₁₃NO₄ [M+Na]⁺ 222.0737, found 222.0740.

Benzyl ether 86. Sodium hydride (60%, 110 mg, 2.76 mmol) was suspended in dry THF (5 mL) under nitrogen at 0 °C. A solution of the **84** (183 mg, 0.920 mmol) in THF (10 mL) was added dropwise over 1 h at 0 °C, and then the mixture was stirred at 0 °C for 1 h. Benzyl bromide (0.16 mL, 1.38 mmol) was added dropwise over 15 min. The reaction mixture was stirred at room temperature for 13 h. Water was then added

slowly at 0 °C to destroy the excess of hydride, and this was followed by the addition of saturated NH₄Cl solution. The aqueous layer was extracted with Et₂O (2 × 20 mL). The combined organic extracts were washed with brine, dried over MgSO₄, and filtered. Concentration of the filtrate and the residue was purified by flash chromatography (hexane:Et₂O, 3:2) to afford benzyl ether **86** (237 mg, 89%) as a white solid: mp 90 °C; [α]_D²⁰ +51.4 (*c* 2.06, CHCl₃); R_f 0.13 (hexane:Et₂O, 3:2); IR (thin film) 2986, 2937, 2872, 1457, 1377, 1266, 1210, 1158, 1117, 1054 cm⁻¹; ¹H NMR (400 MHz) δ 1.39 (3H, s), 1.58 (3H, s), 3.53 (1H, dd, *J* = 9.3, 4.3 Hz), 3.87 (1H, dd, *J* = 10.0, 8.6 Hz), 4.09 (1H, qd, *J* = 10.2, 0.9 Hz), 4.45 (1H, dd, *J* = 10.4, 8.5 Hz), 4.58 (1H, d, *J* = 12.4 Hz), 4.66 (1H, d, *J* = 12.4 Hz), 4.94 (1H, dd, *J* = 5.2, 0.9 Hz), 4.98 (1H, t, *J* = 5.2 Hz), 7.29–7.39 (5H, m); ¹³C NMR (100 MHz) δ 24.3 (CH₃), 26.5 (CH₃), 54.7 (CH), 71.9 (CH), 72.5 (CH₂), 74.3 (CH₂), 79.9 (CH), 83.4 (CH), 113.3 (C), 128.3 (CH), 128.7 (CH), 129.0 (CH), 137.4 (C), 161.8 (C); MS (ESI) *m/z* (relative intensity) 312 ([M+Na]⁺, 100), 290 ([M+H]⁺, 70); HRMS (ESI) calcd for C₁₆H₁₉NO₄ [M+Na]⁺ 312.1206, found 312.1206.

Silyl ether 88. To a solution of isoxazoline **86** (251 mg, 0.869 mmol) in 1,4-dioxane/H₂O (v/v = 8:1, 12 mL) were added AcOH (1 mL, 17.4 mmol) and Raney[®]-Nickel (25 mg). The mixture was activated with an atmosphere of H₂ (balloon) by three times followed by stirring under the same H₂ atmosphere at room temperature for another 2 h. The mixture was filtered and washed with EtOH. The filtrate was concentrated under reduced pressure. The residue was purified by short column chromatography (hexane:EtOAc, 3:2) to afford ketone **87** (194 mg, 76%) as a colorless oil. The ketone **87** was then immediately redissolved in CH₂Cl₂ (10 mL), followed by

the addition of imidazole (109 mg, 1.60 mmol) and TBSCl (120 mg, 0.798 mmol). The mixture was stirred at room temperature for 18 h and was then quenched by saturated NaHCO₃ solution. The aqueous phase was extracted with EtOAc (3 × 25 mL) and the combined organic extracts were washed with brine, dried over anhydrous MgSO₄, and filtered. Concentration of the filtrate followed by flash chromatography (hexane:Et₂O, 8:1) to yield silyl ether **88** (162 mg, 60%) as a colorless oil: $[\alpha]_D^{20} +52.9$ (*c* 0.30, CHCl₃); R_f 0.40 (hexane:Et₂O, 2:1); IR (thin film) 2930, 2858, 1761, 1462, 1378, 1255, 1213, 1099 cm⁻¹; ¹H NMR (400 MHz) δ -0.03 (6H, s), 0.78 (9H, s), 1.39 (3H, s), 1.44 (3H, s), 2.71 (1H, dd, *J* = 9.5, 1.3 Hz), 3.69 (1H, dd, *J* = 10.0, 2.7 Hz), 4.06 (1H, dd, *J* = 10.0, 2.1 Hz), 4.12 (1H, dd, *J* = 4.6, 1.0 Hz), 4.33 (1H, dd, *J* = 9.5, 3.8 Hz), 4.71 (1H, d, *J* = 12.2 Hz), 4.78 (1H, t, *J* = 4.2 Hz), 4.84 (1H, d, *J* = 12.2 Hz), 7.29–7.42 (5H, m); ¹³C NMR (100 MHz) δ -5.4 (CH₃), -5.3 (CH₃), 18.5 (C), 25.8 (CH₃), 26.1 (CH₃), 27.4 (CH₃), 53.4 (CH), 59.1 (CH₂), 72.1 (CH₂), 72.9 (CH), 76.1 (CH), 81.4 (CH), 113.5 (C), 128.4 (CH), 128.9 (CH), 138.1 (C), 212.5 (C); MS (ESI) *m/z* (relative intensity) 429 ([M+Na]⁺, 100), 413 (48); HRMS (ESI) calcd for C₂₂H₃₄O₅Si [M+Na]⁺ 429.2068, found 429.2070.

Alcohol 89. To a solution of silyl ether **88** (29.9 mg, 0.074 mmol) in EtOH (3 mL) was added 10% Pd-on-charcoal (5.0 mg). The mixture was activated with an atmosphere of H₂ (balloon) by three times followed by stirring under the same H₂ atmosphere at room temperature for another 2 h. The reaction mixture was filtered and washed with EtOH. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (hexane:Et₂O, 2:1) to afford alcohol **89** (19.4 mg, 83%) as a white solid: mp 69 °C; $[\alpha]_D^{20} +112.6$ (*c* 0.16, CHCl₃); R_f 0.13 (hexane:Et₂O,

2:1); IR (thin film) 3474, 2936, 2854, 1744, 1461, 1427, 1254, 1109, 1071 cm^{-1} ; ^1H NMR (400 MHz) δ 0.03 (3H, s), 0.05 (3H, s), 0.85 (9H, s), 1.40 (3H, s), 1.47 (3H, s), 2.62–2.66 (1H, m), 3.90 (1H, dd, $J = 10.0, 3.3$ Hz), 3.99 (1H, dd, $J = 10.0, 4.0$ Hz), 4.22 (1H, dd, $J = 5.2, 1.2$ Hz), 4.43 (1H, dd, $J = 8.4, 4.6$ Hz), 4.82 (1H, t, $J = 4.9$ Hz); ^{13}C NMR (100 MHz) δ -5.3 (CH_3), -5.3 (CH_3), 18.5 (C), 25.5 (CH_3), 26.2 (CH_3), 27.0 (CH_3), 55.3 (CH), 60.2 (CH_2), 69.2 (CH), 77.8 (CH), 80.9 (CH), 113.9 (C), 211.6 (C); MS (ESI) m/z (relative intensity) 339 ($[\text{M}+\text{Na}]^+$, 100); HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{28}\text{O}_5\text{Si}$ $[\text{M}+\text{Na}]^+$ 339.1598, found 339.1591.

Enone 90. To a stirred solution of alcohol **89** (79.1 mg, 0.250 mmol) and triethylamine (0.10 mL, 0.750 mmol) in CH_2Cl_2 (7 mL) at 0 $^\circ\text{C}$ were added methanesulfonyl chloride (0.03 mL, 0.375 mmol). The reaction mixture was stirred at room temperature for 1 h and was quenched by saturated NaHCO_3 solution. The aqueous phase was extracted with EtOAc (3 \times 20 mL) and the combined organic extracts were washed with brine, dried over anhydrous MgSO_4 , and filtered. Concentration of the filtrate and the residue was purified by flash chromatography (hexane:Et₂O, 8:1) to yield enone **90** (64.4 mg, 86%) as a colorless oil: $[\alpha]_D^{20}$ -11.0 (c 0.36, CHCl_3); R_f 0.13 (hexane:Et₂O, 8:1); IR (thin film) 2932, 2857, 1725, 1376, 1255, 1204, 1123, 1089 cm^{-1} ; ^1H NMR (400 MHz) δ 0.07–0.08 (6H, 2s), 0.91 (9H, s), 1.40–1.41 (6H, 2s), 4.36 (2H, t, $J = 1.8$ Hz), 4.53 (1H, d, $J = 5.4$ Hz), 5.22 (1H, dq, $J = 5.6, 1.8$ Hz), 7.43 (1H, q, $J = 2.1$ Hz); ^{13}C NMR (100 MHz) δ -5.2 (CH_3), -5.1 (CH_3), 18.6 (C), 26.2 (CH_3), 26.5 (CH_3), 27.9 (CH_3), 58.2 (CH_2), 77.3 (CH), 78.4 (CH), 115.8 (C), 147.7 (C), 152.9 (CH), 202.0 (C); MS (ESI) m/z (relative intensity) 299 ($[\text{M}+\text{H}]^+$, 100); HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{26}\text{O}_4\text{Si}$ $[\text{M}+\text{H}]^+$ 299.1673, found 299.1666.

Alcohol 91. To a solution of enone **90** (33.3 mg, 0.112 mmol) in THF (3 mL) was added AcOH (0.12 mL, 2.10 mmol) a 1 M THF solution of TBAF (0.12 mL, 0.123 mmol). The reaction mixture was stirred at room temperature for 4 h and the solvent was removed under reduced pressure. Flash chromatography of the residue (hexane:EtOAc, 1:1) afforded alcohol **91** (18.4 mg, 90%) as a colorless oil: $[\alpha]_D^{20} +16.2$ (*c* 1.54, CHCl₃); *R*_f 0.19 (hexane:EtOAc, 1:1); IR (thin film) 3428, 2990, 2933, 1720, 1380, 1206, 1101, 1061 cm⁻¹; ¹H NMR (400 MHz) δ 1.38–1.39 (6H, 2s), 2.72 (1H, br s), 4.34 (2H, s), 4.51 (1H, d, *J* = 5.5 Hz), 5.21–5.23 (1H, m), 7.44 (1H, q, *J* = 1.7 Hz); ¹H NMR (400 MHz, CDCl₃-D₂O) δ 1.38–1.39 (6H, 2s), 4.33 (2H, s), 4.51 (1H, d, *J* = 5.4 Hz), 5.21–5.23 (1H, m), 7.44 (1H, d, *J* = 1.3 Hz); ¹³C NMR (100 MHz) δ 26.3 (CH₃), 27.7 (CH₃), 57.4 (CH₂), 77.3 (CH), 78.0 (CH), 115.9 (C), 146.3 (C), 153.5 (CH), 202.8 (C); MS (ESI) *m/z* (relative intensity) 207 ([M+Na]⁺, 100); HRMS (ESI) calcd for C₉H₁₂O₄ [M+Na]⁺ 207.0628, found 207.0632.

Alcohol 91 by reacting 92 with SmI₂. To a stirred solution of isoxazoline **84** (49.7 mg, 0.249 mmol) and pyridine (0.044 mL, 0.549 mmol) in CH₂Cl₂ (4 mL) was added trifluoromethanesulfonic anhydride (0.046 mL, 0.274 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 30 min and was quenched by saturated NaHCO₃ solution. The aqueous phase was extracted with EtOAc (3 × 15 mL) and the combined organic extracts were concentrated under reduced pressure to give crude triflate **93**. The crude product was then redissolved in CH₂Cl₂ (2 mL) and triethylamine (0.17 mL, 1.25 mmol) was added. The reaction mixture was stirred at room temperature for 2 d and then was filtered. Concentration of filtrate gave crude **92**

and then 0.1 M THF solution of SmI₂ (7.4 mL, 0.750 mmol) was added. The mixture was stirred at room temperature for 2 h and then quenched by water. The aqueous phase was extracted with EtOAc (3 × 15 mL) and the combined organic extracts were concentrated under reduced pressure. The residue was purified by flash chromatography (hexane:EtOAc, 1:1) to afford alcohol **91** (28.3 mg, 62% overall yield from isoxazoline **84**) as a colorless oil.

Acetate 94. To a stirred solution of alcohol **91** (17.1 mg, 0.093 mmol) and triethylamine (0.031 mL, 0.223 mmol) in CH₂Cl₂ (2 mL) at 0 °C were added acetic anhydride (0.010 mL, 0.111 mmol) and DMAP (1.1 mg, 0.009 mmol). The reaction mixture was stirred at room temperature for 1 h and was quenched by saturated NaHCO₃ solution. The aqueous phase was extracted with EtOAc (3 × 15 mL) and the combined organic extracts were washed with brine, dried over anhydrous MgSO₄, and filtered. Concentration of the filtrate and the residue was purified by flash chromatography (hexane:Et₂O, 1:1) to yield acetate **94** (17.5 mg, 83%) as a colorless oil: [α]_D²⁰ +6.2 (c 0.53, CHCl₃); R_f 0.22 (hexane:Et₂O, 1:1); IR (thin film) 2991, 2939, 1746, 1726, 1373, 1226, 1204, 1099, 1055 cm⁻¹; ¹H NMR (400 MHz) δ 1.39 (3H, s), 1.40 (3H, s), 2.10 (3H, s), 4.53 (1H, d, *J* = 5.5 Hz), 4.73–4.81 (2H, m), 5.21–5.24 (1H, m), 7.40 (1H, q, *J* = 1.7 Hz); ¹³C NMR (100 MHz) δ 21.1, 26.5, 27.8, 58.1, 77.3, 77.8, 116.0, 142.3, 154.6, 170.7, 201.1; MS (ESI) *m/z* (relative intensity) 249 ([M+Na]⁺, 88), 213 (100); HRMS (ESI) calcd for C₁₁H₁₄O₅ [M+Na]⁺ 249.0733, found 249.0732.

Diol 95. To a stirred solution of acetate **94** (17.5 mg, 0.077 mmol) in CH₂Cl₂ (2 mL) were added deionized water (0.05 mL) and TFA (0.5 mL) at room temperature to

form a clear solution. The mixture was stirred at room temperature for 1 h. Concentration of the reaction mixture under reduced pressure and the residue was purified by flash chromatography (hexane:EtOAc, 1:8) furnished diol **95** (11.8 mg, 82%) as a white solid: mp 40–41 °C; $[\alpha]_D^{20}$ -24.4 (*c* 0.44, CHCl₃); *R_f* 0.21 (hexane:EtOAc, 1:8); IR (thin film) 3409, 2924, 1728, 1372, 1244, 1146, 1065 cm⁻¹; ¹H NMR (400 MHz, MeOD) δ 2.09 (3H, s), 4.11 (1H, d, *J* = 5.4 Hz), 4.73–4.77 (3H, m), 7.45 (1H, dt, *J* = 3.0, 1.5 Hz); ¹³C NMR (100 MHz) δ 21.1 (CH₃), 58.2 (CH₂), 68.0 (CH), 72.1 (CH), 141.8 (C), 156.1 (CH), 171.0 (C), 205.2 (C); MS (ESI) *m/z* (relative intensity) 209 ([M+Na]⁺, 100); HRMS (ESI) calcd for C₈H₁₀O₅ [M+Na]⁺ 209.0420, found 209.0421.

Carboxylic acid 96. To a stirred solution of alcohol **91** (11.7 mg, 0.063 mmol) and triethylamine (0.020 mL, 0.140 mmol) in CH₂Cl₂ (0.8 mL) at 0 °C were added succinic anhydride (7.0 mg, 0.070 mmol). The reaction mixture was stirred at room temperature for 30 min until the disappearance of the starting material as shown on TLC. Acetic acid (0.072 mL, 1.30 mmol) was added at room temperature and the mixture was stirred for 2 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash chromatography (CHCl₃:MeOH, 40:1) to give carboxylic acid **96** (13.3 mg, 74%) as a colorless oil: $[\alpha]_D^{20}$ -2.9 (*c* 0.63, CHCl₃); *R_f* 0.31 (CHCl₃:MeOH, 19:1); IR (thin film) 3498, 2988, 2923, 1725, 1374, 1204, 1155, 1098, 1046 cm⁻¹; ¹H NMR (400 MHz) δ 1.39 (3H, s), 1.41 (3H, s), 2.65–2.73 (4H, m), 4.54 (1H, d, *J* = 5.5 Hz), 4.78 (1H, d, *J* = 15.1 Hz), 4.84 (1H, dt, *J* = 15.1, 1.4 Hz), 5.22–5.24 (1H, m), 7.42 (1H, q, *J* = 2.0 Hz); ¹³C NMR (100 MHz, C₆D₆) δ 26.3 (CH₃), 27.6 (CH₃), 28.6 (CH₂), 28.8 (CH₂), 58.2 (CH₂), 77.3 (CH), 77.6 (CH), 115.2 (C), 141.8 (C), 154.1

(CH), 171.4 (C), 178.0 (C), 200.2 (C); MS (ESI) m/z (relative intensity) 307 ($[M+Na]^+$, 100); HRMS (ESI) calcd for $C_{13}H_{16}O_7$ $[M+Na]^+$ 307.0788, found 307.0787.

Isoxazolidine 97. Following the glycol cleavage produce, diol **106** (137 mg, 0.56 mmol) was converted into aldehyde **107** as a colorless oil. The crude product was then redissolved in CH_3CN (15 mL), followed by addition of *N*-benzylhydroxylamine (72.5 mg, 0.59 mmol) at room temperature. The mixture was stirred at room temperature for 30 min until the disappearance of the starting material as shown on TLC. The mixture was then heated under reflux for 26 h. After cooling, the reaction mixture was concentrated under reduced pressure and the residue was purified by flash chromatography (hexane:Et₂O, 4:1) to furnish isoxazolidine **97** (153 mg, 86% overall yield from diol **106**) as a colorless oil: $[\alpha]_D^{20} +116.6$ (c 0.44, $CHCl_3$); R_f 0.18 (hexane:Et₂O, 7:2); IR (thin film) 2970, 2939, 1496, 1454, 1353, 1304, 1201, 1167, 1146, 1080 cm^{-1} ; ¹H NMR (300 MHz) δ 0.90 (6H, t, $J = 7.5$ Hz), 1.38 (1H, ddd, $J = 13.2, 11.1, 2.7$ Hz), 1.63 (4H, q, $J = 7.5$ Hz), 1.73 (1H, ddd, $J = 14.1, 10.2, 0.6$ Hz), 1.94 (1H, d, $J = 13.2$ Hz), 2.19 (1H, ddd, $J = 14.1, 6.3, 3.9$ Hz), 2.30 (1H, dt, $J = 12.9, 3.9$ Hz), 2.52 (1H, dt, $J = 13.2, 8.4$ Hz), 3.51 (1H, quin, $J = 3.9$ Hz), 3.68–3.79 (2H, m), 4.04 (1H, d, $J = 12.9$ Hz), 4.18 (1H, td, $J = 10.8, 4.2$ Hz), 4.70 (1H, dd, $J = 9.6, 3.9$ Hz), 7.24–7.38 (5H, m); ¹³C NMR (75 MHz) δ 8.5 (CH₃), 8.8 (CH₃), 30.9 (CH₂), 31.2 (CH₂), 33.4 (CH₂), 35.3 (CH₂), 37.3 (CH₂), 60.2 (CH), 63.1 (CH₂), 75.7 (CH), 76.9 (CH), 78.4 (CH), 112.2 (C), 128.0 (CH), 129.0 (CH), 129.4 (CH), 137.8 (C); MS (ESI) m/z (relative intensity) 340 ($[M+Na]^+$, 100), 318 ($[M+H]^+$, 76); HRMS (ESI) calcd for $C_{19}H_{27}NO_3$ $[M+Na]^+$ 340.1883, found 340.1882.

Dimethyl-2,3-O-(3,3-pentylidene)-L-tartrate (100). Acetyl chloride (2.61 mL, 33.3 mmol) was added dropwise to methanol (200 mL) at 0 °C. L-Tartaric acid (5.39 g, 33.3 mmol) was added and the mixture was heated to reflux for 2 h. The solvent was removed under reduced pressure to give crude **99**. It was then redissolved in 3-pentanone (50 mL). Concentrated phosphoric acid (1 mL) was added and the mixture was heated to reflux with Dean and Stark apparatus for 5 d. The mixture was cooled to room temperature, concentrated and redissolved in EtOAc (100 mL). The mixture was washed with saturated NaHCO₃ solution (2 × 50 mL). The combined aqueous solution was then extracted with EtOAc (2 × 50 mL) and the combined organic extracts were washed with brine, dried over anhydrous MgSO₄, and filtered. Concentration of the filtrate and the residue was purified by flash chromatography (hexane:Et₂O, 3:1) to give **100** (7.82 g, 88% overall yield from L-tartaric acid) as a colorless oil: $[\alpha]_D^{20} -17.6$ (*c* 0.96, CHCl₃) {lit.⁹⁰ $[\alpha]_D^{25} -16.4$ (*c* 3.35, CHCl₃)}; *R*_f 0.25 (hexane:Et₂O, 3:1); IR (thin film) 2977, 2954, 2855, 1761, 1463, 1439, 1361, 1205, 1172, 1113, 1021 cm⁻¹; ¹H NMR (300 MHz) δ 0.94 (6H, t, *J* = 7.5 Hz), 1.73 (4H, q, *J* = 7.5 Hz), 3.82 (6H, s), 4.75 (2H, s); ¹³C NMR (75 MHz) δ 8.3, 30.0, 53.2, 77.7, 118.4, 170.4; MS (ESI) *m/z* (relative intensity) 269 ([M+Na]⁺, 100); HRMS (ESI) calcd for C₁₁H₁₈O₆ [M+Na]⁺ 269.1007, found 269.1105.

Diol 101. To a stirred solution of **100** (1.36 g, 5.52 mmol) in THF (40 mL) at 0 °C were added LiAlH₄ (0.23 g, 6.09 mmol) and the mixture was heated to reflux for 2 h. The reaction mixture was cooled to 0 °C and was quenched with water and saturated NH₄Cl solution. The aqueous phase was extracted with EtOAc (3 × 100 mL) and the

combined organic extracts were dried over anhydrous MgSO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (hexane:EtOAc, 1:2) to afford diol **101** (1.04 g, 99%) as a white solid: mp 43–45 °C {lit.⁹⁰ mp 43.5–45 °C}; $[\alpha]_D^{20} +1.6$ (*c* 0.48, CHCl_3) {lit.⁹⁰ $[\alpha]_D^{25} +2.80$ (*c* 5.0, CHCl_3)}; R_f 0.23 (hexane:EtOAc, 1:2); IR (thin film) 3396, 2974, 2940, 2883, 1464, 1201, 1173, 1084, 1055 cm^{-1} ; ^1H NMR (300 MHz) δ 0.91 (6H, t, $J = 7.5$ Hz), 1.66 (4H, q, $J = 7.5$ Hz), 2.13 (2H, br s), 3.69–3.83 (4H, m), 3.96–3.98 (2H, m); ^{13}C NMR (75 MHz) δ 8.5, 30.8, 62.6, 78.7, 113.4; MS (ESI) m/z (relative intensity) 213 ($[\text{M}+\text{Na}]^+$, 100); HRMS (ESI) calcd for $\text{C}_9\text{H}_{18}\text{O}_4$ $[\text{M}+\text{Na}]^+$ 213.1108, found 213.1113.

Dimesylate 102. To a stirred solution of diol **101** (1.28 g, 6.75 mmol) and triethylamine (5.64 mL, 40.5 mmol) in CH_2Cl_2 (100 mL) at 0 °C was added methanesulfonyl chloride (1.57 mL, 20.2 mmol). The mixture was stirred at room temperature for 2 h then was quenched by saturated NaHCO_3 solution. The aqueous phase was extracted with Et_2O (2 \times 100 mL) and the combined organic extracts were dried over anhydrous MgSO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (hexane:EtOAc, 1:1) to give dimesylate **102** (2.18 g, 93%) as a colorless oil: $[\alpha]_D^{20} -4.4$ (*c* 3.82, CHCl_3); R_f 0.47 (hexane:EtOAc, 1:2); IR (thin film) 2977, 2943, 1464, 1356, 1175, 1088 cm^{-1} ; ^1H NMR (300 MHz) δ 0.90 (6H, t, $J = 7.5$ Hz), 1.66 (4H, q, $J = 7.5$ Hz), 3.07 (6H, s), 4.14–4.15 (2H, m), 4.35–4.36 (4H, m); ^{13}C NMR (75 MHz) δ 8.3, 30.6, 38.1, 68.3, 75.8, 115.2; MS (ESI) m/z (relative intensity) 369 ($[\text{M}+\text{Na}]^+$, 100); HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{22}\text{S}_2\text{O}_8$ $[\text{M}+\text{Na}]^+$ 369.0648, found 369.0646.

Dialkene 103. The solution of vinylmagnesium bromide in THF (4.0 mL, 2.3 mmol) freshly generated was added to the solution of copper (I) iodide (49.8 mg, 0.26 mmol) in THF (2 mL) at $-78\text{ }^{\circ}\text{C}$. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min, followed by the adding a solution of diiodide **105** (104 mg, 0.25 mmol) in THF (2 mL). The mixture was stirred at $-30\text{ }^{\circ}\text{C}$ for 12 h. The reaction was then quenched by saturated NH_4Cl solution. The aqueous phase was extracted with Et_2O ($3 \times 20\text{ mL}$) and the combined organic extracts were dried over anhydrous MgSO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (hexane: CH_2Cl_2 , 3:1) to afford dialkene **103** (39.0 mg, 73%) as a colorless oil: $[\alpha]_{\text{D}}^{20} -33.6$ (c 1.22, CHCl_3); R_f 0.33 (hexane: CH_2Cl_2 , 3:1); IR (thin film) 2974, 2940, 1464, 1357, 1176, 1084 cm^{-1} ; ^1H NMR (300 MHz) δ 0.90 (6H, t, $J = 7.5$ Hz), 1.63 (4H, q, $J = 7.5$ Hz), 2.29–2.37 (4H, m), 3.68–3.73 (2H, m), 5.07–5.11 (3H, m), 5.14–5.16 (1H, m), 5.86 (2H, ddt, $J = 17.1, 10.2, 7.2$ Hz); ^{13}C NMR (75 MHz) δ 8.5, 31.1, 37.5, 80.2, 112.3, 117.8, 134.5; MS (CI) m/z (relative intensity) 211 ($[\text{M}+\text{H}]^+$, 100), 181 (81), 169 (30) 125 (37); HRMS (CI) calcd for $\text{C}_{13}\text{H}_{22}\text{O}_2$ $[\text{M}+\text{H}]^+$ 211.1693, found 211.1692.

Ditosylate 104. To a mixture of 3 Å molecular sieves (0.5 g) and diol **101** (102 mg, 0.54 mmol) in pyridine (6 mL) at $0\text{ }^{\circ}\text{C}$ was added *p*-toluenesulfonyl chloride (829 mg, 4.35 mmol) then the mixture was stirred at room temperature for 3 d. The mixture was filtered, diluted with EtOAc and washed with 0.2 M NaOH solution ($2 \times 10\text{ mL}$). The aqueous layer was extracted with EtOAc ($2 \times 25\text{ mL}$) and the combined organic extracts were dried over anhydrous MgSO_4 and filtered. The filtrate was concentrated

under reduced pressure and the residue was purified by flash chromatography (hexane:Et₂O, 1:1) to afford tosylate **104** (264 mg, 99%) as a white solid: mp 86–88 °C; $[\alpha]_D^{20}$ -10.2 (*c* 1.28, CHCl₃); *R_f* 0.24 (hexane:Et₂O, 1:1); IR (thin film) 2975, 2941, 2883, 1598, 1495, 1463, 1363, 1307, 1190, 1177, 1096 cm⁻¹; ¹H NMR (300 MHz) δ 0.78 (6H, t, *J* = 7.5 Hz), 1.53 (4H, q, *J* = 7.5 Hz), 2.46 (6H, s), 3.97–3.98 (2H, m), 4.09–4.10 (4H, m), 7.36 (4H, d, *J* = 8.4 Hz), 7.78 (4H, d, *J* = 8.1 Hz); ¹³C NMR (75 MHz) δ 8.2, 22.1, 30.5, 68.8, 75.7, 115.1, 128.5, 130.4, 132.9, 145.7; MS (ESI) *m/z* (relative intensity) 537 (100), 521 ([M+Na]⁺, 66); HRMS (ESI) calcd for C₂₃H₃₀S₂O₈ [M+Na]⁺ 521.1274, found 521.1300.

Diiodide 105 from diol 101. To a stirred solution of diol **101** (491 mg, 2.58 mmol), triphenylphosphine (2.03 g, 7.74 mmol) and imidazole (703 mg, 10.3 mmol) in toluene (50 mL) were added iodine (1.64 g, 6.45 mmol) and the mixture was stirred at room temperature for 2 d. The reaction was quenched with saturated Na₂S₂O₃ solution, the aqueous phase was extracted with Et₂O (2 × 50 mL). The combined organic extracts were dried over anhydrous MgSO₄ and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (hexane:CH₂Cl₂, 5:1) to yield diiodide **105** (813 mg, 77%) as a yellowish oil: $[\alpha]_D^{20}$ -3.1 (*c* 0.55, CHCl₃); *R_f* 0.21 (hexane:CH₂Cl₂, 5:1); IR (thin film) 2972, 2938, 2880, 1463, 1354, 1271, 1203, 1169, 1107, 1068 cm⁻¹; ¹H NMR (300 MHz) δ 0.93 (6H, t, *J* = 7.5 Hz), 1.69 (4H, q, *J* = 7.5 Hz), 3.33–3.43 (4H, m), 3.74–3.81 (2H, m); ¹³C NMR (75 MHz) δ 6.4, 8.6, 31.0, 80.7, 114.0; MS (EI) *m/z* (relative intensity) 381 ([M-C₂H₅]⁺, 45), 57 (68), 44 (100); HRMS (EI) calcd for C₉H₁₆I₂O₂ [M-C₂H₅]⁺ 380.8843, found 380.8847.

Diiodide 105 from dimesylate 102. Sodium iodide (526 mg, 3.50 mmol) were added to a solution of dimesylate **102** (304 mg, 0.88 mmol) in 3-pentanone (15 mL). The mixture was heated to reflux for 1 d. The reaction mixture was partitioned between Et₂O (20 mL) and saturated Na₂S₂O₃ solution (15 mL). The aqueous layer was extracted with Et₂O (2 × 20 mL). The combined organic extracts were dried over anhydrous MgSO₄ and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (hexane:CH₂Cl₂, 5:1) to give diiodide **105** (314 mg, 87%) as a yellowish oil.

Diol 106 by OsO₄ dihydroxylation. NMO (75.9 mg, 0.65 mmol) was added to a solution of dialkene **103** (118 mg, 0.56 mmol) in acetone/H₂O (v/v = 4:1, 10 mL) with a catalytic amount of osmium tetroxide (0.72 mL of 10 mg mL⁻¹ *t*-butanol solution, 0.028 mmol) at room temperature and stirred for 2 h. The reaction mixture was then diluted with EtOAc (25 mL) and quenched with saturated Na₂S₂O₃ solution (15 mL). The resultant mixture was extracted with EtOAc (2 × 25 mL). The combined extracts were washed with brine, dried over MgSO₄, and filtered. The filtrate was concentrated and the residue was purified by flash chromatography (hexane:CH₂Cl₂, 3:1 to hexane:EtOAc, 1:1) to afford firstly starting material dialkene **103** (39.8 mg, 34%) and secondly diol **106** (61.6 mg, 45%) as a colorless oil: $[\alpha]_D^{20} -35.8$ (c 0.70, CHCl₃); R_f 0.22 (hexane:EtOAc, 1:1); IR (thin film) 3401, 2975, 2940, 2882, 1643, 1465, 1355, 1202, 1175, 1084 cm⁻¹; ¹H NMR (300 MHz) δ 0.89 (6H, t, $J = 7.5$ Hz), 1.55–1.86 (6H, m), 2.35 (2H, t, $J = 5.7$ Hz), 2.56 (2H, br s), 3.50–3.75 (1H, m), 3.63–3.74 (2H, m), 3.83 (1H, qd, $J = 8.7, 2.7$ Hz), 3.91–3.98 (1H, m), 5.08–5.16 (2H, m), 5.77–5.91 (1H, m); ¹³C

NMR (75 MHz) δ 8.4, 8.5, 8.6, 31.0, 31.0, 31.1, 35.8, 36.4, 37.0, 66.8, 67.2, 70.4, 71.6, 78.3, 80.3, 80.6, 81.3, 112.8, 113.3, 118.1, 118.2, 134.0, 134.1; MS (ESI) m/z (relative intensity) 267 ($[M+Na]^+$, 100); HRMS (ESI) calcd for $C_{13}H_{24}O_4$ $[M+Na]^+$ 267.1578, found 267.1571.

Diol 106 by RuO_4 dihydroxylation. $NaIO_4$ (10.8 mg, 0.050 mmol) in deionized water (0.3 mL) was added to a solution of dialkene **103** (10.6 mg, 0.050 mmol) and ruthenium trichloride (0.7 mg, 0.004 mmol) in $CH_3CN/EtOAc$ (v/v = 1:1, 2 mL) at room temperature and stirred for 1 min. The reaction was quenched with saturated $Na_2S_2O_3$ solution (5 mL). The resultant mixture was extracted with $EtOAc$ (3×10 mL). The combined extracts were washed with brine, dried over $MgSO_4$, and filtered. The filtrate was concentrated and the residue was purified by flash chromatography (hexane: CH_2Cl_2 , 3:1 to hexane: $EtOAc$, 1:1) to afford firstly starting material dialkene **103** (5.3 mg, 50%) and secondly diol **106** (3.3 mg, 27%) as a colorless oil.

Diol 108. To a stirred solution of isoxazolidine **97** (203 mg, 0.64 mmol) in CH_2Cl_2 (15 mL) were added deionized water (0.8 mL) and TFA (3 mL) at room temperature to form a clear solution. The mixture was stirred at room temperature for 1 h. Concentration of the mixture under reduced pressure and the residue was purified by flash chromatography ($CHCl_3:MeOH$, 50:1) to yield diol **108** (162 mg, 100%) as a white solid: mp 127–128 °C; $[\alpha]_D^{20} +170.8$ (c 0.50, $MeOH$); R_f 0.12 ($CHCl_3:MeOH$, 50:1); IR (thin film) 3355, 2922, 2853, 1495, 1453, 1314, 1077, 1028 cm^{-1} ; 1H NMR (300 MHz,

MeOD) δ 1.42 (1H, ddd, $J = 13.5, 10.2, 2.7$ Hz), 1.61 (1H, dd, $J = 14.7, 9.3$ Hz), 1.97 (1H, d, $J = 12.6$ Hz), 2.02–2.07 (1H, m), 2.15 (1H, ddd, $J = 14.7, 6.3, 3.9$ Hz), 2.52–2.62 (1H, m), 3.46–3.49 (1H, m), 3.59 (1H, td, $J = 9.0, 6.3$ Hz), 3.73, (1H, d, $J = 12.6$ Hz), 3.82 (1H, td, $J = 9.9, 3.9$ Hz), 3.96 (1H, d, $J = 12.6$ Hz), 4.63 (1H, s), 7.27–7.37 (5H, m); ^{13}C NMR (75 MHz, MeOD) δ 34.0, 40.4, 41.8, 61.0, 63.2, 71.9, 73.4, 76.7, 128.6, 129.4, 130.6, 138.4; MS (ESI) m/z (relative intensity) 272 ($[\text{M}+\text{Na}]^+$, 100), 250 ($[\text{M}+\text{H}]^+$, 57); HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_3$ $[\text{M}+\text{Na}]^+$ 272.1257, found 272.1259.

Amine 109. To a solution of diol **108** (17.8 mg, 0.071 mmol) in $^t\text{BuOH}/\text{H}_2\text{O}$ (v/v = 5:1, 1.5 mL) was added 10% Pd-on-charcoal (5.0 mg). The mixture was activated with an atmosphere of H_2 (balloon) by three times followed by stirring under the same H_2 atmosphere at room temperature for another 36 h. The reaction mixture was filtered and washed with EtOH. The filtrate was concentrated under reduced pressure. The residue was purified by Sephadex LH-20 (eluent: EtOH) to afford amine **109** (10.8 mg, 94%) as a colorless oil: $[\alpha]_{\text{D}}^{20} -6.1$ (c 0.84, CHCl_3); R_f 0.34 (CHCl_3 :MeOH:30% aq. NH_3 , 1.2:1.8:0.5); ^1H NMR (400 MHz, MeOD) δ 1.47 (1H, q, $J = 11.0$ Hz), 1.72 (1H, dt, $J = 13.6, 10.4$ Hz), 1.84–1.89 (1H, m), 1.97–2.09 (2H, m), 2.16–2.20 (1H, m), 3.22–3.29 (1H, m), 3.55 (1H, ddd, $J = 10.1, 7.0, 2.9$ Hz), 3.75 (1H, dt, $J = 7.1, 4.4$ Hz), 3.84 (1H, tt, $J = 10.6, 3.8$ Hz); ^{13}C NMR (100 MHz, MeOD) δ 41.0 (CH_2), 43.9 (CH_2), 44.5 (CH), 46.4 (CH_2), 68.2 (CH), 73.7 (CH), 73.9 (CH); MS (ESI) m/z (relative intensity) 162 ($[\text{M}+\text{H}]^+$, 100), 149 (90); HRMS (ESI) calcd for $\text{C}_7\text{H}_{15}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 162.1125, found 162.1127.

2,3-O-Isopropylidene- α,β -L-erythrose (123). To a stirred solution of acetonide **79** (11.5 g, 60.3 mmol) in deionized water (250 mL) at 0 °C was added NaBH₄ (3.42 g, 90.5 mmol). The mixture was stirred at 0 °C for 1 h and then at room temperature for a further 2 h. The reaction mixture was quenched by dropwise addition of AcOH (20 mL) at 0 °C. NaIO₄ was then added to the reaction mixture at 0 °C and stirred at 0 °C for 1 h. MeOH (500 mL) was added to precipitate out most of the salt. The salt was filtered off and washed with EtOAc. Concentration of filtrate under reduced pressure and the residue was purified by flash chromatography (hexane:Et₂O, 2:3) to yield lactol **123** (8.44 g, 87%) as a colorless oil: $[\alpha]_D^{20} +73.6$ (*c* 1.70, CHCl₃) {lit.⁸⁰ $[\alpha]_D^{25} +72$ (*c* 2.4, MeOH)}; *R_f* 0.38 (hexane:Et₂O, 2:3); IR (thin film) 3427, 2943, 1376, 1210, 1100, 1068 cm⁻¹; ¹H NMR (300 MHz) δ 1.32 (3H, s), 1.47 (3H, s), 2.74 (1H, d, *J* = 2.4 Hz), 4.00 (1H, d, *J* = 10.2 Hz), 4.05 (1H, dd, *J* = 10.5, 3.3 Hz), 4.57 (1H, d, *J* = 6.0 Hz), 4.82 (1H, dd, *J* = 6.0, 3.3 Hz), 5.42 (1H, d, *J* = 2.4 Hz); ¹³C NMR (75 MHz) δ 25.1, 26.6, 72.4, 80.3, 85.5, 102.1, 112.7; MS (ESI) *m/z* (relative intensity) 183 ([M+Na]⁺, 100), 149 (19), 143 ([M-OH]⁺, 14); HRMS (ESI) calcd for C₇H₁₂O₄ [M+Na]⁺ 183.0628, found 183.0635.

Alkenes 124 and 125. To a stirred solution of lactol **123** (15.0 g, 93.6 mmol) in dry THF (300 mL) was added a Et₂O solution of allylmagnesium bromide (89 mL, 1.03 mol) dropwise at 0 °C under N₂. After the addition, the mixture was allowed to rise to room temperature and stirred for another 12 h. The mixture was quenched with saturated NH₄Cl solution and the aqueous phase was extracted with EtOAc (3 × 500 mL). The combined organic extracts were dried over anhydrous MgSO₄ and filtered.

The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (hexane:Et₂O, 2:3) to afford firstly alkene **124** (13.4 g, 71%) as a colorless oil and secondly its 4-epimer alkene **125** (4.01 g, 21%) as a colorless oil. Data for **124**: $[\alpha]_D^{20}$ -5.4 (*c* 2.14, CHCl₃); *R*_f 0.21 (hexane:Et₂O, 2:3); IR (thin film) 3386, 3078, 2982, 2927, 1641, 1381, 1219, 1166 cm⁻¹; ¹H NMR (300 MHz) δ 1.35 (3H, s), 1.41 (3H, s), 2.15 (1H, dt, *J* = 14.1, 8.4 Hz), 2.31 (3H, br s), 2.59–2.66 (1H, m), 3.73 (1H, dd, *J* = 11.4, 4.5 Hz), 3.79–3.89 (2H, m), 3.96 (1H, dd, *J* = 9.0, 5.7 Hz), 4.29 (1H, dt, *J* = 8.1, 5.4 Hz), 5.18 (1H, d, *J* = 2.4 Hz), 5.23 (1H, s), 5.81–5.95 (1H, m); ¹³C NMR (75 MHz) δ 25.7, 28.3, 39.0, 61.1, 69.0, 77.6, 79.7, 108.8, 119.0, 134.4; MS (ESI) *m/z* (relative intensity) 225 ([M+Na]⁺, 100), 222 (5), 185 ([M-OH]⁺, 3); HRMS (ESI) calcd for C₁₀H₁₈O₄ [M+Na]⁺ 225.1097, found 225.1105.

Data for **125**: $[\alpha]_D^{20}$ -16.4 (*c* 1.12, CHCl₃); *R*_f 0.14 (hexane:Et₂O, 2:3); IR (thin film) 3410, 3077, 2985, 2936, 1642, 1381, 1217, 1166 cm⁻¹; ¹H NMR (300 MHz) δ 1.38 (3H, s), 1.52 (3H, s), 2.00 (3H, br s), 2.29–2.45 (2H, m), 3.74–3.85 (3H, m), 4.09 (1H, dd, *J* = 6.9, 3.0 Hz), 4.20 (1H, dt, *J* = 6.9, 5.1 Hz), 5.12 (1H, s), 5.16 (1H, d, *J* = 10.8 Hz), 5.80–5.93 (1H, m); ¹³C NMR (75 MHz) δ 25.2, 27.3, 39.4, 61.0, 68.8, 77.5, 78.5, 108.4, 118.0, 134.6; MS (ESI) *m/z* (relative intensity) 225 ([M+Na]⁺, 100), 222 (4), 185 ([M-OH]⁺, 2); HRMS (ESI) calcd for C₁₀H₁₈O₄ [M+Na]⁺ 225.1097, found 225.1101.

Lactols 126 and 127. To a solution of alkene **125** (484 mg, 2.93 mmol) in DMSO (10 mL) was added IBX (822 mg, 2.93 mmol) and the mixture was stirred at room temperature for 2 d. The mixture was partitioned between Et₂O (50 mL) and water (25 mL). The aqueous layer was extracted with Et₂O (2 × 50 mL). The combined

organic extracts were dried over anhydrous MgSO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (hexane: Et_2O , 3:2) to give firstly lactol **126** (371 mg, 77%) as a colorless oil and secondly its regioisomer **127** (56.6 mg, 12%) as a white solid. Data for **126**: $[\alpha]_D^{20} -16.6$ (*c* 2.01, CHCl_3); R_f 0.43 (hexane: Et_2O , 2:3); IR (thin film) 3429, 3071, 2983, 2942, 1644, 1374, 1210, 1165, 1064 cm^{-1} ; ^1H NMR (300 MHz) δ 1.32 (3H, s), 1.46 (3H, s), 2.45 (2H, t, $J = 6.9$ Hz), 2.72 (1H, br s), 4.16 (1H, td, $J = 6.9, 3.6$ Hz), 4.59 (1H, d, $J = 6.0$ Hz), 4.66 (1H, dd, $J = 6.0, 3.6$ Hz), 5.07 (1H, dd, $J = 10.2, 0.9$ Hz), 5.14 (1H, dd, $J = 17.1, 1.5$ Hz), 5.40 (1H, d, $J = 2.1$ Hz), 5.80–5.94 (1H, m); ^{13}C NMR (75 MHz) δ 25.3, 26.4, 33.3, 80.0, 80.6, 86.0, 101.2, 112.8, 117.6, 134.7; MS (ESI) m/z (relative intensity) 223 ($[\text{M}+\text{Na}]^+$, 100), 200 ($[\text{M}]^+$, 12), 195 (12), 185 ($[\text{M}-\text{CH}_3]^+$, 15), 183 ($[\text{M}-\text{OH}]^+$, 25); HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{16}\text{O}_4$ $[\text{M}+\text{Na}]^+$ 223.0941, found 223.0944.

Data for **127**: mp 38–39 $^\circ\text{C}$; $[\alpha]_D^{20} +38.4$ (*c* 2.08, CHCl_3); R_f 0.20 (hexane: Et_2O , 3:2); IR (thin film) 3423, 3078, 2983, 2938, 1643, 1458, 1382, 1210, 1097 cm^{-1} ; ^1H NMR (300 MHz, mixture of stereomer in ratio of 1:4) δ 1.32 (3.0H, s), 1.37 (0.8H, s), 1.48 (3.0H, s), 1.56 (0.8H, s), 2.29 (0.3H, dd, $J = 14.4, 7.8$ Hz), 2.40 (1.0H, br s) 2.45 (1.3H, dd, $J = 14.1, 8.7$ Hz), 2.64 (1.0H, dd, $J = 14.1, 6.3$ Hz), 3.68 (0.3H, dd, $J = 10.8, 4.5$ Hz), 3.91–4.02 (2.3H, m), 4.33 (0.3H, d, $J = 6.3$ Hz), 4.42 (1.0H, d, $J = 6.0$ Hz), 4.76 (0.3H, ddd, $J = 6.3, 4.5, 1.8$ Hz) 4.84 (1.0H, dd, $J = 5.7, 3.6$ Hz), 5.12 (0.3H, d, $J = 6.6$ Hz), 5.17 (0.3H, s), 5.22 (1.0H, d, $J = 8.1$ Hz), 5.28 (1.0H, s), 5.85–5.99 (1.3H, m); ^{13}C NMR (75 MHz) δ 25.3, 26.6, 26.7, 40.3, 40.8, 69.2, 71.5, 80.5, 81.0, 85.4, 104.0, 106.1, 112.9, 114.3, 119.3, 121.0, 132.4, 132.7; MS (ESI) m/z (relative intensity) 239 (53), 223

($[M+Na]^+$, 100), 183 ($[M-OH]^+$, 92); HRMS (ESI) calcd for $C_{10}H_{16}O_4$ $[M+Na]^+$ 223.0941, found 223.0948.

Ester 128. To the solution of lactol **126** (52.0 mg, 0.26 mmol) in CH_2Cl_2 (5 mL) were added ethyl acrylate (0.11 mL, 1.04 mmol) and the 2nd generation Grubbs catalyst (4.2 mg, 0.005 mmol). The mixture was heated to reflux for 3 h. It was then concentrated under reduced pressure and the residue was purified by flash chromatography (hexane:Et₂O, 3:2) to furnish ester **128** (67.3 mg, 95%) as a colorless oil: $[\alpha]_D^{20}$ -17.5 (*c* 0.66, $CHCl_3$); R_f 0.23 (hexane:Et₂O, 1:1); IR (thin film) 3431, 2984, 2939, 1720, 1657, 1373, 1321, 1271, 1211, 1164, 1068 cm^{-1} ; ¹H NMR (300 MHz, mixture of *α* and *β* isomer with ratio *α:β* = 1:5) δ 1.28 (3.6H, t, *J* = 7.2 Hz), 1.32 (3.0H, s), 1.37 (0.6H, s), 1.46 (3.0H, s), 1.53 (0.6H, s), 2.39 (1.2H, br s), 2.58–2.64 (2.2H, m), 2.99–3.10 (0.2H, m), 3.59 (0.2H, td, *J* = 6.6, 3.3 Hz), 4.13–4.22 (2.4H, m), 4.28 (1.0H, td, *J* = 6.6, 3.3 Hz), 4.51 (0.2H, dd, *J* = 6.0, 3.6 Hz), 4.60–4.62 (1.2H, m), 4.69 (1.0H, dd, *J* = 6.0, 3.6 Hz), 4.97 (0.2H, d, *J* = 3.3 Hz), 5.37 (1.0H, s), 5.86 (0.2H, dt, *J* = 11.7, 1.8 Hz), 5.95 (1.0H, dt, *J* = 15.6, 1.5 Hz), 6.36 (0.2H, dt, *J* = 11.7, 7.5 Hz), 7.00 (1.0H, dt, *J* = 15.6, 6.9 Hz); ¹³C NMR (75 MHz) δ 14.7, 25.3, 25.5, 26.3, 26.5, 31.7, 32.0, 60.8, 74.8, 79.0, 79.2, 80.4, 80.7, 86.0, 97.1, 101.4, 113.0, 123.9, 124.2, 144.5, 145.2, 167.0; MS (ESI) *m/z* (relative intensity) 295 ($[M+Na]^+$, 100); HRMS (ESI) calcd for $C_{13}H_{20}O_6$ $[M+Na]^+$ 295.1152, found 295.1157.

Isoxazolidine 130. Following the INAC reaction procedure (Method C) using pyridine as base and EtOH (2 mL) as the reaction solvent and the product was purified by flash chromatography (hexane:EtOAc, 2:3), ester **128** (12.3 mg, 0.045 mmol) was

converted into isoxazolidine **130** (9.8 mg, 72%) as a colorless oil: $[\alpha]_D^{20} +40.0$ (c 0.80, CHCl_3); R_f 0.20 (hexane:EtOAc, 2:3); IR (thin film) 3403, 2982, 2934, 1751, 1458, 1380, 1242, 1212, 1058 cm^{-1} ; ^1H NMR (400 MHz) δ 1.29 (3H, t, $J = 7.1$ Hz), 1.34 (3H, s), 1.45 (3H, s), 1.74–1.81 (1H, m), 2.12 (1H, ddd, $J = 14.2, 7.8, 3.0$ Hz), 2.86 (3H, s), 2.93–2.99 (1H, m), 3.08 (1H, dd, $J = 7.5, 2.6$ Hz), 3.77–3.78 (1H, m), 4.17–4.24 (3H, m), 4.26 (1H, dd, $J = 7.0, 2.6$ Hz), 4.31 (1H, br s), 4.40 (1H, d, $J = 4.2$ Hz); ^1H NMR (400 MHz, $\text{CDCl}_3\text{-D}_2\text{O}$) δ 1.29 (3H, t, $J = 7.1$ Hz), 1.34 (3H, s), 1.46 (3H, s), 1.78 (1H, dt, $J = 14.0, 5.6$ Hz), 2.13 (1H, ddd, $J = 14.3, 7.9, 3.0$ Hz), 2.86 (3H, s), 2.93–3.00 (1H, m), 3.09 (1H, dd, $J = 7.5, 2.6$ Hz), 3.77 (1H, quin, $J = 3.3$ Hz), 4.18–4.24 (3H, m), 4.26 (1H, dd, $J = 7.0, 2.6$ Hz), 4.41 (1H, d, $J = 4.2$ Hz); ^{13}C NMR (100 MHz) δ 14.5 (CH_3), 24.6 (CH_3), 27.2 (CH_3), 29.3 (CH_2), 42.7 (CH), 44.6 (CH_3), 61.9 (CH_2), 67.2 (CH), 68.7 (CH), 72.1 (CH), 77.2 (CH), 82.8 (CH), 108.8 (C), 171.0 (C); MS (ESI) m/z (relative intensity) 324 ($[\text{M}+\text{Na}]^+$, 100); HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{23}\text{NO}_6$ $[\text{M}+\text{Na}]^+$ 324.1418, found 324.1414.

Benzoate 134. To a stirred solution of isoxazolidine **130** (10.2 mg, 0.034 mmol) in pyridine (0.16 mL) at 0 °C were added benzoyl chloride (0.008 mL, 0.068 mmol) and DMAP (0.4 mg, 0.003 mmol). The mixture was stirred at room temperature for 2 d and was quenched by saturated NaHCO_3 solution. The aqueous phase was extracted with EtOAc (3×10 mL) and the combined organic extracts were washed with brine, dried over anhydrous MgSO_4 , and filtered. Concentration of the filtrate and the residue was purified by flash chromatography (hexane:Et₂O, 3:2) to yield benzoate **134** (13.7 mg, 100%) as a white solid: mp 116 °C; $[\alpha]_D^{20} +62.3$ (c 0.36, CHCl_3); R_f 0.16 (hexane:Et₂O, 3:2); IR (thin film) 2983, 2930, 1719, 1373, 1272, 1209, 1114, 1065, 1026 cm^{-1} ; ^1H

NMR (400 MHz) δ 1.30 (3H, t, $J = 7.1$ Hz), 1.37 (3H, s), 1.52 (3H, s), 1.83 (1H, q, $J = 12.2$ Hz), 2.21 (1H, dt, $J = 12.5, 4.6$ Hz), 2.95 (3H, s), 3.08–3.11 (1H, m), 3.19 (1H, dd, $J = 6.3, 2.2$ Hz), 4.18–4.27 (4H, m), 4.38 (1H, dd, $J = 7.7, 6.0$ Hz), 5.16 (1H, ddd, $J = 11.9, 7.9, 3.8$ Hz), 7.44 (2H, t, $J = 7.6$ Hz), 7.56 (1H, t, $J = 7.4$ Hz), 8.04–8.06 (2H, m); ^{13}C NMR (100 MHz) δ 14.5, 26.2, 28.2, 29.9, 44.8, 45.6, 62.0, 67.7, 73.1, 74.3, 76.6, 81.3, 109.5, 128.7, 130.1, 130.3, 133.5, 166.4, 171.3; MS (ESI) m/z (relative intensity) 428 ($[\text{M}+\text{Na}]^+$, 100), 413 (33); HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{27}\text{NO}_7$ $[\text{M}+\text{Na}]^+$ 428.1680, found 428.1687.

Lactols 135 and 127. To a solution of alkene **124** (949 mg, 4.69 mmol) in DMSO (30 mL) was added IBX (1.58 g, 5.16 mmol) and the mixture was stirred at room temperature for 2 d. The mixture was partitioned between Et_2O (100 mL) and water (100 mL). The aqueous layer was extracted with Et_2O (2×100 mL). The combined organic extracts were dried over anhydrous MgSO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (hexane: Et_2O , 3:2) to give firstly lactol **135** (693 mg, 74%) as a colorless oil and secondly its regioisomer **127** (94.2 mg, 10.0%) as a white solid. Data for **135**: $[\alpha]_{\text{D}}^{20} -5.3$ (c 2.53, CHCl_3); R_f 0.45 (hexane: Et_2O , 2:3); IR (thin film) 3434, 3079, 2984, 2941, 1642, 1438, 1375, 1211, 1075 cm^{-1} ; ^1H NMR (300 MHz, mixture of α and β isomer with ratio $\alpha:\beta=1:5.6$) δ 1.31 (3.00H, s), 1.38 (0.54H, s), 1.47 (3.00H, s), 1.56 (0.54H, s), 2.21–2.53 (2.36H, m), 3.08 (1.00H, d, $J = 2.1$ Hz), 3.91 (0.18H, d, $J = 9.0$ Hz), 4.11 (0.18H, td, $J = 9.0, 2.7$ Hz), 4.22 (1.00H, t, $J = 8.1$ Hz), 4.47 (0.18H, dd, $J = 6.6, 2.7$ Hz), 4.60 (1.00H, d, $J = 6.0$ Hz), 4.63 (1.00H, d, $J = 6.0$ Hz), 5.10 (1.18H, s),

5.14 (1.18H, d, $J = 4.2$ Hz), 5.26 (0.18H, dd, $J = 9.3, 4.2$ Hz), 5.44 (1.00H, d, $J = 2.4$ Hz), 5.72–5.87 (1.18H, m); ^{13}C NMR (75 MHz) δ 25.4, 26.7, 26.9, 37.5, 40.4, 79.9, 80.3, 83.5, 84.1, 86.5, 86.8, 96.3, 103.6, 112.8, 115.2, 118.2, 118.7, 133.6, 134.5; MS (ESI) m/z (relative intensity) 223 ($[\text{M}+\text{Na}]^+$, 100), 185 ($[\text{M}-\text{CH}_3]^+$, 7), 183 ($[\text{M}-\text{OH}]^+$, 3), 149 (3); HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{16}\text{O}_4$ $[\text{M}+\text{Na}]^+$ 223.0941, found 223.0945.

Ester 136. To the solution of lactol **135** (63.1 mg, 0.32 mmol) in CH_2Cl_2 (4 mL) were added ethyl acrylate (0.14 mL, 1.26 mmol) and the 2nd generation Grubbs catalyst (2.7 mg, 0.003 mmol). The mixture was heated to reflux for 2 h. It was then concentrated under reduced pressure and the residue was purified by flash chromatography (hexane: Et_2O , 2:1) to afford ester **136** (82.3 mg, 96%) as a colorless oil: $[\alpha]_{\text{D}}^{20} +20.9$ (c 0.82, CHCl_3); R_f 0.15 (hexane: Et_2O , 2:1); IR (thin film) 3428, 2984, 2940, 1718, 1654, 1373, 1274, 1211, 1162, 1073 cm^{-1} ; ^1H NMR (300 MHz, mixture of α and β isomer with ratio $\alpha:\beta = 1:2$) δ 1.28 (4.5H, t, $J = 7.2$ Hz), 1.31 (3.0H, s), 1.38 (1.5H, s), 1.47 (3.0H, s), 1.56 (1.5H, s), 2.41–2.65 (3.0H, m), 4.14–4.21 (3.5H, m), 4.30 (1.0H, t, $J = 7.5$ Hz), 4.46 (0.5H, dd, $J = 6.9, 3.0$ Hz), 4.59–4.67 (2.5H, m), 5.29 (0.5H, d, $J = 3.9$ Hz), 5.46 (1.0H, s), 5.87–5.95 (1.5H, m), 6.85–6.99 (1.5H, m); ^{13}C NMR (75 MHz) δ 14.7, 25.5, 26.8, 26.9, 35.8, 38.8, 60.9, 79.6, 80.0, 83.6, 84.5, 86.0, 86.5, 96.3, 103.7, 113.0, 115.7, 124.3, 124.9, 143.4, 144.7, 166.5, 166.8; MS (ESI) m/z (relative intensity) 295 ($[\text{M}+\text{Na}]^+$, 100); HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{20}\text{O}_6$ $[\text{M}+\text{Na}]^+$ 295.1152, found 295.1150.

Isoxazolidines 137 and 138. Following the INAC reaction procedure (Method C) using pyridine as base and EtOH (10 mL) as the reaction solvent and the product was purified by flash chromatography (hexane:EtOAc, 1:1 to 1:3), ester **136** (75.0 mg, 0.275 mmol) was converted to firstly isoxazolidine **137** (49.6 mg, 60%) as a colorless oil then secondly isoxazolidine **138** (9.1 mg, 11%) as a white solid. Data for **137**: $[\alpha]_{\text{D}}^{20} +26.4$ (*c* 1.82, CHCl₃); *R_f* 0.18 (hexane:EtOAc, 1:1); IR (thin film) 3491, 2983, 2936, 1751, 1451, 1380, 1262, 1209, 1055 cm⁻¹; ¹H NMR (400 MHz, C₆D₆) δ 0.87 (3H, t, *J* = 7.1 Hz), 1.15 (3H, s), 1.34 (3H, s), 1.41 (1H, d, *J* = 12.8 Hz), 2.04–2.11 (1H, m), 2.35 (1H, d, *J* = 5.2 Hz), 2.63 (3H, s), 3.12–3.15 (2H, m), 3.88 (2H, q, *J* = 7.1 Hz), 3.94–3.97 (1H, m), 4.02 (1H, dd, *J* = 7.7, 3.4 Hz), 4.07 (1H, br s), 4.15 (1H, d, *J* = 6.0 Hz); ¹H NMR (400 MHz, C₆D₆-D₂O) δ 0.87 (3H, t, *J* = 7.1 Hz), 1.15 (3H, s), 1.34 (3H, s), 1.41 (1H, d, *J* = 12.6 Hz), 2.04–2.11 (1H, m), 2.63 (3H, s), 3.12 (2H, s), 3.88 (2H, q, *J* = 7.1 Hz), 3.94–3.97 (1H, m), 4.02 (1H, dd, *J* = 7.7, 3.4 Hz), 4.06–4.09 (1H, m), 4.15 (1H, d, *J* = 5.7 Hz); ¹³C NMR (100 MHz, C₆D₆) δ 14.1 (CH₃), 24.1 (CH₃), 26.3 (CH₃), 28.9 (CH₂), 43.2 (CH), 44.7 (CH₃), 61.0 (CH₂), 64.5 (CH), 68.4 (CH), 74.3 (CH), 75.1 (CH), 82.1 (CH), 108.4 (C), 170.7 (C); MS (ESI) *m/z* (relative intensity) 324 ([M+Na]⁺, 100); HRMS (ESI) calcd for C₁₄H₂₃NO₆ [M+Na]⁺ 324.1418, found 324.1420.

Data for **138**: mp 123–124 °C; $[\alpha]_{\text{D}}^{20} +62.3$ (*c* 0.88, CHCl₃); *R_f* 0.10 (hexane:EtOAc, 1:2); IR (thin film) 3227, 2987, 2931, 2877, 1745, 1461, 1381, 1218, 1167, 1039 cm⁻¹; ¹H NMR (400 MHz) δ 1.28 (3H, t, *J* = 7.1 Hz), 1.36 (3H, s), 1.53 (3H, s), 1.77 (1H, td, *J* = 13.2, 9.1 Hz), 2.17–2.27 (2H, m), 2.44 (1H, br s), 2.66 (1H, dd, *J* = 11.3, 8.8 Hz), 2.83 (3H, s), 4.02 (1H, quin, *J* = 4.6 Hz), 4.16 (1H, dd, *J* = 7.9, 5.7 Hz), 4.19–4.26 (3H, m), 4.32 (1H, t, *J* = 4.8 Hz); ¹³C NMR (100 MHz) δ 14.6 (CH₃), 26.1 (CH₃), 28.2 (CH₃), 31.2 (CH₂), 46.2 (CH), 47.0 (CH₃), 61.8 (CH₂), 69.4 (CH), 73.6 (CH),

76.3 (CH), 76.7 (CH), 78.0 (CH), 110.1 (C), 117.3 (C); MS (ESI) m/z (relative intensity) 302 ($[M+H]^+$, 100); HRMS (ESI) calcd for $C_{14}H_{23}NO_6$ $[M+H]^+$ 302.1598, found 302.1591.

Ketone 139 from isoxazolidine 130. To the solution of isoxazolidine **130** (4.6 mg, 0.015 mmol) in DMSO (0.015 mL) was added IBX (6.4 mg, 0.023 mmol) and the mixture was stirred at room temperature for 1 d. The reaction mixture was partitioned between Et_2O (10 mL) and water (10 mL). The aqueous layer was extracted with Et_2O (3×10 mL). The combined extracts were washed with brine, dried over $MgSO_4$, and filtered. The filtrate was concentrated and the residue was purified by flash chromatography (hexane: Et_2O , 2:3) to afford ketone **139** (3.0 mg, 66%) as a colorless oil: $[\alpha]_D^{20} +30.2$ (c 0.91, $CHCl_3$); R_f 0.20 (hexane: Et_2O , 2:3); IR (thin film) 2984, 2937, 1736, 1461, 1433, 1374, 1213, 1165, 1080, 1039 cm^{-1} ; 1H NMR (400 MHz) δ 1.26 (3H, t, $J = 7.2$ Hz), 1.35 (3H, s), 1.44 (3H, s), 2.65 (1H, dd, $J = 13.4, 9.4$ Hz), 2.74 (1H, dd, $J = 13.4, 6.2$ Hz), 2.92 (3H, s), 3.19 (1H, dtd, $J = 9.0, 6.0, 2.7$ Hz), 3.24 (1H, dd, $J = 6.0, 1.8$ Hz), 4.12–4.25 (3H, m), 4.37–4.42 (2H, m); ^{13}C NMR (100 MHz) δ 14.4 (CH_3), 25.7 (CH_3), 27.2 (CH_3), 39.1 (CH_2), 45.3 (CH_3), 47.3 (CH), 62.0 (CH_2), 66.3 (CH), 76.8 (CH), 77.2 (CH), 80.9 (CH), 110.6 (C), 170.7 (C), 205.8 (C); MS (ESI) m/z (relative intensity) 322 ($[M+Na]^+$, 100), 301 (40), 242 (27), 130 (20); HRMS (ESI) calcd for $C_{14}H_{21}NO_6$ $[M+Na]^+$ 322.1261, found 322.1262.

Ketone 139 from isoxazolidine 137. To the solution of isoxazolidine **137** (59.8 mg, 0.198 mmol) in DMSO (2 mL) was added IBX (83.3 mg, 0.298 mmol) and the mixture was stirred at room temperature for 14 h. The reaction mixture was partitioned

between Et₂O (20 mL) and water (20 mL). The aqueous layer was extracted with Et₂O (3 × 20 mL). The combined extracts were washed with brine, dried over MgSO₄, and filtered. The filtrate was concentrated and the residue was purified by flash chromatography (hexane:Et₂O, 2:3) to afford ketone **139** (47.3 mg, 80%) as a colorless oil.

Isoxazolidines 141 and 142 using MeCN as the INAC reaction solvent.

Following the glycol cleavage procedure, diol **147** (6.39 g, 16.8 mmol) was converted into aldehyde **148** as a colorless oil. Following the INAC reaction procedure (Method A) using MeCN (300 mL) as the reaction solvent and the product was purified by flash chromatography (hexane:Et₂O, 3:2), aldehyde **148** was converted into an inseparable mixture of isoxazolidines **141** and **142** (4.45 g, 70% overall yield from diol **147**) as a colorless oil: R_f 0.17 (hexane:Et₂O, 3:2); ¹H NMR (400 MHz, mixture of **141** and **142** with ratio **141**:**142** = 8:1) δ 1.42 (6.00H, s), 1.44 (0.39H, s), 1.48 (0.39H, s), 1.73 (1.00H, d, *J* = 14.3, 9.1 Hz), 1.87 (0.13H, q, *J* = 11.8 Hz), 2.22–2.28 (1.00H, m), 2.35–2.41 (0.13H, m), 2.58 (3.00H, s), 2.82 (0.39H, s), 2.96–3.03 (0.26H, m), 3.47 (1.00H, s), 3.75 (0.39H, s), 3.78 (3.00H, s), 3.96–3.98 (0.13H, m), 4.02–4.07 (2.26H, m), 4.14–4.23 (2.13H, m), 4.62 (0.13H, d, *J* = 11.8 Hz), 4.72 (1.00H, d, *J* = 11.8 Hz), 4.90 (1.00H, d, *J* = 11.8 Hz), 4.94 (0.13H, d, *J* = 11.8 Hz), 5.18–5.19 (1.00H, m), 7.27–7.40 (5.65H, m); ¹³C NMR (100 MHz) δ 26.9, 26.9, 27.2, 27.3, 32.4, 34.6, 45.5, 46.1, 46.9, 49.4, 52.5, 52.8, 53.6, 69.7, 71.0, 71.1, 72.1, 73.8, 73.9, 74.7, 76.5, 78.5, 80.0, 80.5, 108.2, 110.0, 127.6, 127.7, 127.9, 128.4, 128.5, 138.3, 138.7, 172.2, 172.9.

Isoxazolidines 141 and 142 using CH₂Cl₂ as the INAC reaction solvent.

Following the glycol cleavage procedure, diol **147** (22.4 mg, 0.059 mmol) was converted into aldehyde **148**. Following the INAC reaction procedure (Method B) using CH₂Cl₂ (3 mL) as reaction solvent and the product was purified by flash chromatography (hexane:Et₂O, 3:2), aldehyde **148** was converted into an inseparable mixture of isoxazolidines **141** and **142** (13.8 mg, 62% overall yield from diol **147**, **141:142** = 10:1 by NMR) as a colorless oil.

Isoxazolidines 141 and 142 using MeOH as the INAC reaction solvent.

Following the glycol cleavage procedure, diol **147** (38.2 mg, 0.100 mmol) was converted into aldehyde **148**. Following the INAC reaction procedure (Method B) using MeOH (4 mL) as the reaction solvent and the product was purified by flash chromatography (hexane:Et₂O, 3:2), aldehyde **148** was converted into an inseparable mixture of isoxazolidines **141** and **142** (23.9 mg, 63% overall yield from diol **147**, **141:142** = 14:1 by NMR) as a colorless oil.

Isoxazolidines 141 and 142 using DMF as the INAC reaction solvent.

Following the glycol cleavage procedure, diol **147** (30.4 mg, 0.080 mmol) was converted into aldehyde **148**. Following the INAC reaction procedure (Method A) using DMF (3 mL) as the reaction solvent and the product was purified by flash chromatography (hexane:Et₂O, 3:2), aldehyde **148** was converted into an inseparable mixture of isoxazolidines **141** and **142** (19.2 mg, 64% overall yield from diol **147**, **141:142** = 13:1 by NMR) as a colorless oil.

Isoxazolidines 141 and 142 using toluene as the INAC reaction solvent.

Following the glycol cleavage procedure, diol **147** (38.7 mg, 0.102 mmol) was converted into aldehyde **148**. Following the INAC reaction procedure (Method C) using triethylamine as base and toluene (5 mL) as the reaction solvent and the product was purified by flash chromatography (hexane:Et₂O, 3:2), aldehyde **148** was converted into an inseparable mixture of isoxazolidines **141** and **142** (28.9 mg, 75% overall yield from diol **147**, **141:142** = 15:1 by NMR) as a colorless oil.

Diacetonide 144. To a solution of D-ribose (1.44 g, 9.58 mmol) in EtOH (40 mL) and H₂O (10 mL) were added indium (1.21 g, 10.5 mmol) and allyl bromide (3.32 mL, 38.3 mmol). The mixture was stirred vigorously at room temperature for 12 h until the disappearance of the starting material as shown on TLC. The solvent was removed under reduced pressure and the residue was dissolved in acetone (50 mL). Anhydrous CuSO₄ (1.40 g) was added and the reaction mixture was stirred at room temperature for 25 h. The mixture was neutralized with saturated NaHCO₃ solution and then filtered. The filtrate was partitioned between Et₂O (50 mL) and water (50 mL). The aqueous layer was extracted with Et₂O (2 × 50 mL). The combined organic extracts were washed with brine, dried over anhydrous MgSO₄, and filtered. Concentration of the filtrate and the residue was purified by flash chromatography (hexane:Et₂O, 3:1) to give diacetonide **144** (1.66 g, 64% overall yield from D-ribose) as a colorless oil: [α]_D²⁰ +25.0 (*c* 4.07, CHCl₃); R_f 0.54 (hexane:Et₂O, 1:1); IR (thin film) 3475, 2987, 2936, 1372, 1216, 1166, 1068, 849, 514 cm⁻¹; ¹H NMR (400 MHz) δ 1.36 (3H, s), 1.39 (3H, s), 1.40 (3H, s), 1.43 (3H, s), 1.68 (1H, br s), 2.30–2.38 (1H, m), 2.52–2.59 (1H, m), 3.68 (1H, dd, *J* = 7.8, 6.0

Hz), 3.87 (1H, t, $J = 5.5$ Hz), 3.97 (1H, dd, $J = 8.2, 6.7$ Hz), 4.07 (1H, dd, $J = 8.2, 6.4$ Hz), 4.12 (1H, td, $J = 7.6, 3.6$ Hz), 4.19 (1H, td, $J = 6.5, 5.4$ Hz), 5.10–5.18 (2H, m), 5.90 (1H, ddt, $J = 17.2, 10.2, 7.0$ Hz); ^{13}C NMR δ 25.5, 26.8, 27.3, 27.6, 38.0, 65.7, 71.8, 75.9, 78.1, 80.1, 109.2, 109.4, 117.8, 134.5; MS (EI) m/z (relative intensity) 257 ($[\text{M}-\text{OCH}_3]^+$, 46), 101 (79), 84 (69), 83 (61), 59 (55), 49 (64), 44 (92), 43 (100); HRMS (EI) calcd for $\text{C}_{14}\text{H}_{24}\text{O}_5$ $[\text{M}-\text{OCH}_3]^+$ 257.1384, found 257.1385.

Diacetonide 144 by tin allylation. To a solution of D-ribose (5.29 g, 35.2 mmol) in EtOH/H₂O (v/v = 4:1, 150 mL) were added tin (4.60 g, 38.7 mmol) and allyl bromide (12.2 mL, 0.14 mol). The mixture was heated to reflux for 2 h until the disappearance of the starting material as shown on TLC. The solvent was removed under reduced pressure and the residue was dissolved in acetone (50 mL). The reaction mixture was stirred at room temperature for 25 h. The mixture was neutralized with saturated NaHCO₃ solution and was partitioned between Et₂O (200 mL) and water (200 mL). The aqueous layer was extracted with Et₂O (2 × 200 mL). The combined organic extracts were washed with brine, dried over anhydrous MgSO₄, and filtered. Concentration of the filtrate and the residue was purified by flash chromatography (hexane:Et₂O, 3:1) to yield diacetonide **144** (4.77 g, 50% overall yield from D-ribose) as a colorless oil.

6-O-Benzyl-1,2,3-trideoxy-4,5:7,8-di-O-isopropylidene-D-altro-oct-1-enitol (145). Sodium hydride (60%, 217 mg, 5.43 mmol) was suspended in dry THF (10 mL) under nitrogen at 0 °C. A solution of the diacetonide **144** (604 mg, 2.22 mmol) in THF (30 mL) was added dropwise over 1 h at 0 °C, and then the mixture was stirred at 0 °C for 1 h. Benzyl bromide (0.32 mL, 2.71 mmol) was added dropwise over 15 min and

tetra-*n*-butylammomium iodide (83.6 mg, 0.23 mmol) was added. The reaction mixture was stirred at room temperature for 12 h. Water was then added slowly at 0 °C to destroy the excess of hydride, and followed by the addition of saturated NH₄Cl solution. The aqueous layer was extracted with Et₂O (2 × 30 mL). The combined organic extracts were washed with brine, dried over MgSO₄, and filtered. Concentration of the filtrate and the residue was purified by flash chromatography (hexane:Et₂O, 10:1) to furnish benzyl ether **145** (786 mg, 98%) as a colorless oil: $[\alpha]_D^{20} +23.6$ (*c* 1.08, CHCl₃) {lit.¹⁴ $[\alpha]_D^{20} +28.0$ (*c* 2.71, CHCl₃)}; *R_f* 0.55 (hexane:Et₂O, 2:1); IR (thin film) 2986, 2935, 1372, 1215, 1072, 849, 699 cm⁻¹; ¹H NMR (400 MHz) δ 1.36 (3H, s), 1.38 (6H, s), 1.44 (3H, s), 2.24–2.32 (1H, m), 2.40–2.47 (1H, m), 3.72–3.79 (2H, m), 3.94 (1H, dd, *J* = 8.0, 7.2 Hz), 4.01–4.08 (2H, m), 4.27 (1H, td, *J* = 6.8, 4.6 Hz), 4.74 (1H, d, *J* = 11.4 Hz), 4.79 (1H, d, *J* = 11.4 Hz), 5.06–5.10 (2H, m), 5.76–5.88 (1H, m), 7.28–7.37 (5H, m); ¹³C NMR (100 MHz) δ 25.6, 26.8, 27.3, 27.5, 38.4, 66.1, 74.9, 76.2, 78.0, 78.9, 80.4, 109.2, 109.3, 117.7, 128.2, 128.5, 128.8, 134.5, 138.4; MS (ESI) *m/z* (relative intensity) 385 ([M+Na]⁺, 100); HRMS (ESI) calcd for C₂₁H₃₀O₅ [M+Na]⁺ 385.1985, found 385.1986.

Ester 146. To the solution of benzyl ether **145** (8.98 g, 24.8 mmol) in CH₂Cl₂ (250 mL) were added methyl acrylate (4.46 mL, 49.6 mmol) and the 2nd generation Grubbs catalyst (63.0 mg, 0.074 mmol). The mixture was heated to reflux for 2 h. It was then concentrated under reduced pressure and the residue was purified by flash chromatography (hexane:Et₂O, 4:1) to yield ester **146** (9.87 g, 95%) as a white solid: mp 56–57 °C; $[\alpha]_D^{20} +31.9$ (*c* 0.52, CHCl₃); *R_f* 0.12 (hexane:Et₂O, 4:1); IR (thin film) 2985, 2936, 2890, 1725, 1660, 1454, 1435, 1371, 1214, 1166, 1076 cm⁻¹; ¹H NMR (400 MHz)

δ 1.36 (3H, s), 1.37 (6H, s), 1.44 (3H, s), 2.33–2.41 (1H, m), 2.57 (1H, dddd, $J = 15.2, 6.8, 3.2, 1.5$ Hz), 3.69 (1H, dd, $J = 7.8, 5.6$ Hz), 3.73 (3H, s), 3.76 (1H, t, $J = 5.4$ Hz), 3.91 (1H, dd, $J = 7.8, 7.2$ Hz), 4.03–4.08 (2H, m), 4.23 (1H, td, $J = 6.7, 5.1$ Hz), 4.73 (1H, d, $J = 11.4$ Hz), 4.79 (1H, d, $J = 11.4$ Hz), 5.86 (1H, d, $J = 15.7$ Hz), 6.96 (1H, dt, $J = 15.7, 7.1$ Hz), 7.28–7.37 (5H, m); ^{13}C NMR (100 MHz) δ 25.5 (CH₃), 26.7 (CH₃), 27.3 (CH₃), 27.5 (CH₃), 36.7 (CH₂), 51.8 (CH₃), 66.2 (CH₂), 75.1 (CH₂), 76.2 (CH), 77.2 (CH), 79.0 (CH), 80.2 (CH), 109.5 (C), 109.6 (C), 123.6 (CH), 128.3 (CH), 128.5 (CH), 128.9 (CH), 138.3 (C), 145.1 (CH), 167.1 (C); MS (ESI) m/z (relative intensity) 443 ([M+Na]⁺, 55), 435 (50), 403 (100); HRMS (ESI) calcd for C₂₃H₃₂O₇ [M+Na]⁺ 443.2040, found 443.2036.

Diol 147. A solution of ester **146** (815 mg, 1.94 mmol) in 80% aqueous AcOH (50 mL) was stirred at room temperature for 7 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (hexane:Et₂O, 4:1 to hexane:EtOAc, 1:1) to afford firstly starting material ester **146** (131 mg, 16%) and secondly diol **147** (538 mg, 73%) as a colorless oil: $[\alpha]_{\text{D}}^{20} +16.0$ (c 0.55, CHCl₃); R_f 0.12 (hexane:EtOAc, 1:1); IR (thin film) 3443, 2986, 2939, 1719, 1658, 1453, 1381, 1274, 1214, 1173, 1071 cm⁻¹; ^1H NMR (400 MHz) δ 1.36 (3H, s), 1.39 (3H, s), 2.35–2.43 (2H, m), 2.60–2.67 (1H, m), 3.00 (1H, d, $J = 3.3$ Hz), 3.60 (1H, dd, $J = 7.6, 5.4$ Hz), 3.73 (3H, s), 3.79 (2H, br s), 3.84 (1H, t, $J = 7.6$ Hz), 3.90–3.92 (1H, m), 3.99 (1H, td, $J = 7.9, 3.0$ Hz), 4.60 (1H, d, $J = 11.2$ Hz), 4.75 (1H, d, $J = 11.2$ Hz), 5.85 (1H, d, $J = 15.8$ Hz), 6.96 (1H, dt, $J = 15.7, 7.1$ Hz), 7.29–7.38 (5H, m); ^{13}C NMR (100 MHz) δ 27.2 (CH₃), 27.5 (CH₃), 36.8 (CH₂), 51.9 (CH₃), 63.1 (CH₂), 72.5 (CH), 74.3 (CH₂), 78.7 (CH), 79.5 (CH), 80.7 (CH), 109.9 (C), 123.5 (CH), 128.6 (CH), 129.0 (CH), 137.6 (C), 145.2 (CH),

167.1 (C); MS (ESI) m/z (relative intensity) 403 ($[M+Na]^+$, 100), 368 (60); HRMS (ESI) calcd for $C_{20}H_{28}O_7$ $[M+Na]^+$ 403.1727, found 403.1729.

Diols 149 and 150. To a stirred solution of isoxazolidines **141** and **142** (337 mg, 0.89 mmol, **141:142** = 8:1 by NMR) in CH_2Cl_2 (20 mL) were added deionized water (0.5 mL) and TFA (3 mL) at room temperature to form a clear solution. The mixture was stirred at room temperature for 2 h. Concentration of the mixture under reduced pressure and the residue was purified by flash chromatography (hexane:EtOAc, 1:2 to 1:4) to afford firstly diol **149** (258 mg, 86%) as a white solid then secondly diol **150** (34.3 mg, 11%) as a colorless oil. Data for **149**: mp 113–114 °C; $[\alpha]_D^{20}$ -82.9 (c 1.88, $CHCl_3$); R_f 0.21 (hexane:EtOAc, 1:2); IR (thin film) 3386, 2950, 2892, 1735, 1436, 1333, 1216, 1070, 1019 cm^{-1} ; 1H NMR (400 MHz, CD_3OD) δ 1.64–1.67 (1H, m), 2.17–2.23 (1H, m), 2.59 (3H, s), 3.69 (1H, br s), 3.75 (3H, s), 3.83 (1H, br s), 3.94–3.97 (3H, m), 4.71–4.78 (2H, m), 5.00 (1H, br s), 7.29–7.31 (1H, m), 7.33–7.37 (2H, m), 7.42–7.44 (2H, m); ^{13}C NMR (100 MHz) δ 36.5, 45.8, 50.5, 52.7, 67.8, 68.2, 72.1, 72.6, 77.6, 79.0, 128.1, 128.3, 128.7, 137.6, 172.9; MS (ESI) m/z (relative intensity) 360 ($[M+Na]^+$, 100); HRMS (ESI) calcd for $C_{17}H_{23}NO_6$ $[M+Na]^+$ 360.1418, found 360.1410; Anal. Calcd for $C_{17}H_{23}NO_6$: C, 60.52; H, 6.87; N, 4.15, found: C, 60.53; H, 6.68; N, 4.14.

Data for **150**: $[\alpha]_D^{20}$ -43.6 (c 1.60, $CHCl_3$); R_f 0.07 (hexane:EtOAc, 1:2); IR (thin film) 3402, 2951, 2883, 1749, 1455, 1436, 1357, 1210, 1077 cm^{-1} ; 1H NMR (400 MHz) δ 1.77 (1H, q, J = 11.1 Hz), 2.13 (1H, dt, J = 12.9, 5.0 Hz), 2.42 (2H, br s), 2.81 (3H, s), 2.90–2.96 (1H, m), 3.05 (1H, s), 3.69–3.74 (5H, m), 3.84–3.90 (1H, m), 4.28 (1H, s), 4.60 (1H, d, J = 11.7 Hz), 4.68 (1H, d, J = 11.7 Hz), 7.30–7.38 (5H, m); 1H NMR (400 MHz, $CDCl_3$ - D_2O) δ 1.72 (1H, q, J = 11.2 Hz), 2.08 (1H, dt, J = 13.0, 5.2 Hz), 2.76 (3H,

s), 2.87–2.92 (1H, m), 2.99 (1H, s), 3.68–3.72 (5H, m), 3.83–3.89 (1H, m), 4.24 (1H, s), 4.60–4.66 (2H, m), 7.27–7.35 (5H, m); ^{13}C NMR (100 MHz) δ 33.0 (CH₂), 45.3 (CH), 45.8 (CH₃), 52.7 (CH₃), 68.4 (CH), 69.2 (CH), 73.3 (CH), 73.7 (CH₂), 76.8 (CH), 80.6 (CH), 128.2 (CH), 128.4 (CH), 128.9 (CH), 138.0 (C), 172.7 (C); MS (ESI) m/z (relative intensity) 338 ([M+H]⁺, 100); HRMS (ESI) calcd for C₁₇H₂₃NO₆ [M+H]⁺ 338.1598, found 338.1607.

Epoxide 154. To a stirred solution of diol **149** (136 mg, 0.40 mmol) and 2,4,6-collidine (0.12 mL, 0.89 mmol) in CH₂Cl₂ (8 mL) was added trifluoromethanesulfonic anhydride (0.07 mL, 0.44 mmol) at –78 °C. The reaction mixture was stirred at –78 °C for 1 h and was quenched by saturated NaHCO₃ solution. The aqueous phase was extracted with EtOAc (3 × 20 mL) and the combined organic extracts were washed with 1 M hydrochloric acid then saturated NaHCO₃ solution. The organic phase was then concentrated under reduced pressure to give crude triflate **153**. The crude product was then redissolved in MeOH (8 mL) and potassium carbonate (83.5 mg, 0.60 mmol) was added. The mixture was stirred at room temperature for 10 min. Deionized water (20 mL) was added to the reaction mixture and the MeOH was removed under reduced pressure. The remaining aqueous solution was then extracted with EtOAc (3 × 20 mL) and the combined organic extracts were washed with brine, dried over anhydrous MgSO₄, and filtered. Concentration of the filtrate and the residue was purified by flash chromatography (hexane:EtOAc, 3:2) to yield epoxide **154** (112 mg, 87% overall yield from diol **149**) as a colorless oil: $[\alpha]_{\text{D}}^{20} +18.6$ (c 0.95, CHCl₃); R_f 0.21 (hexane:EtOAc, 3:2); IR (thin film) 2954, 1734, 1436, 1242, 1204, 1072, 1052 cm⁻¹; ^1H NMR (400 MHz)

δ 2.30 (1H, d, $J = 16.0$ Hz), 2.55 (1H, dd, $J = 16.8, 4.9$ Hz), 2.67 (3H, s), 3.34 (2H, d, $J = 3.4$ Hz), 3.69 (1H, d, $J = 3.4$ Hz), 3.71 (3H, s), 3.92 (1H, t, $J = 3.6$ Hz), 3.96 (1H, s), 4.68 (1H, d, $J = 3.8$ Hz), 4.74 (1H, d, $J = 12.0$ Hz), 4.80 (1H, d, $J = 12.0$ Hz), 7.29–7.42 (5H, m); ^{13}C NMR (100 MHz) δ 33.4 (CH₂), 46.4 (CH₃), 49.6 (CH), 52.8 (CH₃), 57.9 (CH), 58.7 (CH), 68.7 (CH), 71.7 (CH₂), 75.4 (CH), 77.7 (CH), 128.3 (CH), 128.3 (CH), 128.8 (CH), 138.0 (C), 173.1 (C); MS (ESI) m/z (relative intensity) 320 ([M+H]⁺, 100); HRMS (ESI) calcd for C₁₇H₂₁NO₅ [M+H]⁺ 320.1492, found 320.1493.

Epoxide 154 from mesylate 155. To a stirred solution of mesylate **155** (23.4 mg, 0.056 mmol) in MeOH (1.5 mL) were added potassium carbonate (11.7 mg, 0.084 mmol). The reaction mixture was stirred at room temperature for 36 h and deionized water (10 mL) was added to the reaction mixture and the MeOH was removed under reduced pressure. The remaining aqueous solution was then extracted with EtOAc (3 \times 10 mL) and the combined organic extracts were washed with brine, dried over anhydrous MgSO₄, and filtered. Concentration of the filtrate and the residue was purified by flash chromatography (hexane:EtOAc, 3:2) to yield epoxide **154** (12.7 mg, 71%) as a colorless oil.

Mesylate 155. To a stirred solution of diol **149** (54.9 mg, 0.163 mmol) and triethylamine (0.05 mL, 0.358 mmol) in CH₂Cl₂ (1.5 mL) at -78 °C were added methanesulfonyl chloride (0.017 mL, 0.179 mmol) and DMAP (2.0 mg, 0.016 mmol). The reaction mixture was stirred at -78 °C for 2 h and was quenched by saturated NaHCO₃ solution. The aqueous phase was extracted with EtOAc (3 \times 20 mL) and the

combined organic extracts were washed with brine, dried over anhydrous MgSO₄, and filtered. Concentration of the filtrate and the residue was purified by flash chromatography (hexane:EtOAc, 1:1) to yield mesylate **155** (66.8 mg, 99%) as a colorless oil: $[\alpha]_D^{20}$ -104.0 (*c* 0.90, CHCl₃); R_f 0.17 (hexane:EtOAc, 1:1); IR (thin film) 3537, 2951, 1734, 1438, 1348, 1222, 1172, 1080 cm⁻¹; ¹H NMR (400 MHz) δ 1.98 (1H, ddd, *J* = 14.7, 9.6, 1.7 Hz), 2.38 (1H, ddd, *J* = 14.8, 7.1, 4.4 Hz), 2.55 (3H, s), 2.78 (1H, d, *J* = 7.5 Hz), 3.02 (3H, s), 3.36 (1H, s), 3.76 (3H, s), 3.96–4.00 (2H, m), 4.13 (1H, t, *J* = 8.0 Hz), 4.73 (1H, d, *J* = 11.6 Hz), 4.78 (1H, d, *J* = 11.6 Hz), 4.89 (1H, td, *J* = 9.8, 7.2 Hz), 5.06–5.07 (1H, m), 7.30–7.37 (5H, m); ¹H NMR (400 MHz, CDCl₃-D₂O) δ 1.97 (1H, ddd, *J* = 14.6, 9.6, 1.6 Hz), 2.38 (1H, ddd, *J* = 14.7, 7.1, 4.4 Hz), 2.54 (3H, s), 3.02 (3H, s), 3.37 (1H, s), 3.76 (3H, s), 3.96–4.00 (2H, m), 4.12 (1H, dd, *J* = 10.3, 1.8 Hz), 4.73 (1H, d, *J* = 11.6 Hz), 4.78 (1H, d, *J* = 11.6 Hz), 4.88 (1H, td, *J* = 9.8, 7.2 Hz), 5.06–5.07 (1H, m), 7.28–7.37 (5H, m); ¹³C NMR (100 MHz) δ 38.3 (CH₂), 38.5 (CH₃), 46.9 (CH₃), 49.3 (CH), 53.2 (CH₃), 67.9 (CH), 70.7 (CH), 73.8 (CH₂), 75.4 (CH), 78.0 (CH), 79.6 (CH), 128.1 (CH), 128.4 (CH), 128.9 (CH), 137.9 (C), 172.6 (C); MS (ESI) *m/z* (relative intensity) 416 ([M+H]⁺, 100); HRMS (ESI) calcd for C₁₈H₂₅NO₈S [M+H]⁺ 416.1374, found 416.1378.

Diol 158. To a solution of epoxide **154** (616 mg, 1.93 mmol) in MeOH (20 mL) was added Raney[®]-Nickel (60 mg). The mixture was activated with an atmosphere of H₂ (balloon) by three times followed by stirring under the same H₂ atmosphere at room temperature for another 2 h. The mixture was filtered and washed with MeOH. The filtrate was concentrated under reduced pressure to give crude amine **156**. The crude

product was redissolved in MeOH (50 mL) and was added AcOH (0.01 mL, 0.19 mmol). The mixture was heated to reflux for 4 h. Concentration of the reaction mixture under reduced pressure and the residue was purified by flash chromatography (CHCl₃:MeOH, 80:1) to afford diol **158** (543 mg, 88% overall yield from epoxide **154**) as a colorless oil: $[\alpha]_D^{20} +9.4$ (*c* 0.95, CHCl₃); *R_f* 0.23 (CHCl₃:MeOH, 30:1); IR (thin film) 3403, 2948, 1734, 1457, 1436, 1270, 1173, 1119, 1060, 1015 cm⁻¹; ¹H NMR (400 MHz) δ 1.68 (2H, br s), 2.24 (1H, ddd, *J* = 13.5, 10.2, 1.4 Hz), 2.63–2.70 (4H, m), 2.74 (1H, d, *J* = 3.5 Hz), 3.53–3.56 (1H, m), 3.73 (3H, s), 4.06 (1H, ddd, *J* = 8.0, 2.9, 1.1 Hz), 4.21 (1H, br s), 4.44 (1H, d, *J* = 11.6 Hz), 4.54–4.57 (2H, m), 4.89 (1H, t, *J* = 7.8 Hz), 7.27–7.38 (5H, m); ¹H NMR (400 MHz, CDCl₃-D₂O) δ 2.23 (1H, dd, *J* = 12.4, 10.3 Hz), 2.63–2.69 (4H, m), 2.74 (1H, d, *J* = 3.5 Hz), 3.53–3.56 (1H, m), 3.73 (3H, s), 4.06 (1H, dd, *J* = 8.0, 1.8 Hz), 4.19 (1H, ddd, *J* = 10.0, 6.7, 3.2 Hz), 4.44 (1H, d, *J* = 11.6 Hz), 4.52–4.57 (2H, m), 4.89 (1H, t, *J* = 7.8 Hz), 7.27–7.38 (5H, m); ¹³C NMR (100 MHz) δ 40.8 (CH₂), 44.2 (CH₃), 48.0 (CH), 52.4 (CH₃), 69.4 (CH), 70.4 (CH), 70.8 (CH), 72.4 (CH₂), 73.2 (CH), 128.0 (CH), 128.4 (CH), 128.9 (CH), 137.6 (C), 173.8 (C); MS (ESI) *m/z* (relative intensity) 322 ([M+H]⁺, 100); HRMS (ESI) calcd for C₁₇H₂₃NO₅ [M+H]⁺ 322.1649, found 322.1652.

Diol 158 by heating the neat amine 156. To a solution of epoxide **154** (69.2 mg, 0.217 mmol) in MeOH (5 mL) was added Raney[®]-Nickel (8 mg). The mixture was activated with an atmosphere of H₂ (balloon) by three times followed by stirring under the same H₂ atmosphere at room temperature for another 2 h. The mixture was filtered and washed with MeOH. The filtrate was evaporated to dryness under reduced pressure

to give crude amine **156**. The neat crude product was heated at 70 °C for 29 h. The resulting residue was purified by flash chromatography (CHCl₃:MeOH, 80:1) to afford diol **158** (61.2 mg, 88% overall yield from epoxide **154**) as a colorless oil.

Diol 158 from epoxide 154 in one step reaction. To a solution of epoxide **154** (24.1 mg, 0.076 mmol) in MeOH (5 mL) was added AcOH (0.4 μL, 0.008 mmol) and Raney[®]-Nickel (3 mg). The mixture was activated with an atmosphere of H₂ (balloon) by three times followed by stirring under the same H₂ atmosphere at room temperature for 2 h. The H₂ balloon was removed and then the mixture was heated to 60 °C for another 5 h. The reaction mixture was filtered and washed with MeOH. Concentration of filtrate under reduced pressure and the residue was purified by flash chromatography (CHCl₃:MeOH, 80:1) to yield diol **158** (20.3 mg, 84%) as a colorless oil.

Triol 159. To a solution of diol **158** (5.8 mg, 0.018 mmol) in MeOH (1 mL) was added Raney[®]-Nickel (15 mg). The mixture was activated with an atmosphere of H₂ (balloon) by three times followed by stirring under the same H₂ atmosphere at room temperature for another 18 h. The mixture was filtered and washed with MeOH. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (CHCl₃:MeOH, 8:1) to afford triol **159** (4.0 mg, 96%) as a colorless oil: $[\alpha]_D^{20} +12.2$ (*c* 0.60, CHCl₃); *R_f* 0.27 (CHCl₃:MeOH, 8:1); IR (thin film) 3380, 2943, 1733, 1437, 1269, 1175, 1058 cm⁻¹; ¹H NMR (400 MHz, MeOD) δ 2.46 (2H, dd, *J* = 8.5, 3.4 Hz), 2.65 (3H, s), 2.94 (1H, d, *J* = 3.4 Hz), 3.41 (1H, dt, *J* = 7.6, 3.0 Hz), 3.73 (3H,

s), 4.00 (1H, dd, $J = 8.4, 1.5$ Hz), 4.10 (1H, td, $J = 8.4, 3.1$ Hz), 4.53 (1H, m), 5.15 (1H, t, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, MeOD) δ 40.4 (CH₂), 44.1 (CH₃), 48.5 (CH), 52.5 (CH₃), 64.1 (CH), 71.1 (CH), 71.5 (CH), 71.9 (CH), 75.2 (CH), 175.2 (C); MS (ESI) m/z (relative intensity) 232 ([M+H]⁺, 100); HRMS (ESI) calcd for C₁₀H₁₇NO₅ [M+H]⁺ 232.1179, found 232.1181.

Tribenzoate 160. To a stirred solution of triol **159** (18.4 mg, 0.080 mmol) in pyridine (0.7 mL) at 0 °C were added benzoyl chloride (0.032 mL, 0.279 mmol) and DMAP (1.0 mg, 0.008 mmol). The reaction mixture was stirred at room temperature for 16 h. Toluene (3 mL) was added and the mixture was then filtered. Concentration of the filtrate and the residue was purified by flash chromatography (hexane:Et₂O, 3:2) to yield tribenzoate **160** (37.0 mg, 86%) as a white solid: mp 151–152 °C; $[\alpha]_{\text{D}}^{20} -87.7$ (c 2.00, CHCl₃); R_f 0.18 (hexane:Et₂O, 3:2); IR (thin film) 2946, 1720, 1450, 1273, 1109 cm⁻¹; ^1H NMR (400 MHz) δ 2.38 (1H, d, $J = 12.1$ Hz), 2.85 (3H, s), 3.38 (1H, br s), 3.47 (1H, s), 3.65 (3H, s), 4.04 (1H, s), 4.14 (1H, d, $J = 7.3$ Hz), 5.59 (1H, q, $J = 5.2$ Hz), 6.15 (1H, t, $J = 7.9$ Hz), 6.38 (1H, br s), 7.12 (2H, t, $J = 7.3$ Hz), 7.38 (1H, t, $J = 7.3$ Hz), 7.42–7.47 (4H, m), 7.54–7.62 (2H, m), 7.74 (2H, d, $J = 7.9$ Hz), 8.07 (4H, d, $J = 7.7$ Hz); ^{13}C NMR (100 MHz, C₆D₆) δ 33.9 (CH₂), 43.9 (CH₃), 47.9 (CH), 51.2 (CH₃), 65.5 (CH), 68.7 (CH), 69.1 (CH), 69.4 (CH), 72.0 (CH), 128.2 (CH), 128.6 (CH), 128.8 (CH), 130.0 (CH), 130.2 (CH), 130.4 (CH), 130.6 (C), 131.1 (C), 132.6 (CH), 133.0 (CH), 133.3 (CH), 165.3 (C), 165.6 (C), 166.0 (C), 170.1 (C); MS (ESI) m/z (relative intensity) 544 ([M+H]⁺, 100); HRMS (ESI) calcd for C₃₁H₂₉NO₈ [M+H]⁺ 544.1966, found 544.1969.

Chloride 162. To a stirred solution of diol **158** (345 mg, 1.07 mmol) and triethylamine (0.60 mL, 4.30 mmol) in CH₂Cl₂ (11 mL) at 0 °C were added benzoyl chloride (0.14 mL, 1.18 mmol) and DMAP (13.1 mg, 0.11 mmol). The reaction mixture was stirred at 0 °C for 2 h and then was added methanesulfonyl chloride (0.16 mL, 1.61 mmol) at 0 °C. The mixture was stirred at room temperature for another 1 h and was quenched by saturated NaHCO₃ solution. The aqueous phase was extracted with EtOAc (3 × 25 mL) and the combined organic extracts were washed with brine, dried over anhydrous MgSO₄, and filtered. Concentration of the filtrate and the residue was purified by flash chromatography (hexane:Et₂O, 2:3) to furnish chloride **162** (424 mg, 89%) as a colorless oil: $[\alpha]_D^{20} +43.5$ (*c* 1.02, CHCl₃); *R_f* 0.19 (hexane:Et₂O, 2:3); IR (thin film) 3029, 2948, 2901, 1748, 1717, 1452, 1314, 1279, 1175, 1116, 1027 cm⁻¹; ¹H NMR (400 MHz, C₆D₆) δ 1.87 (3H, s), 2.43 (1H, ddd, *J* = 12.2, 6.0, 3.0 Hz), 2.68 (1H, td, *J* = 12.1, 3.3 Hz), 2.84–2.86 (1H, m), 3.36 (3H, s), 3.49 (1H, ddd, *J* = 6.5, 2.9, 1.2 Hz), 3.68 (1H, dd, *J* = 6.1, 2.9 Hz), 3.87 (1H, dd, *J* = 8.9, 6.6 Hz), 4.09 (1H, dd, *J* = 8.9, 6.4 Hz), 4.30 (1H, d, *J* = 12.2 Hz), 4.80 (1H, d, *J* = 12.2 Hz), 6.19 (1H, dt, *J* = 11.8, 6.2 Hz), 7.01–7.14 (4H, m), 7.28 (2H, t, *J* = 7.9 Hz), 7.52 (2H, d, *J* = 7.7 Hz), 8.27–8.30 (2H, m); ¹³C NMR (100 MHz) δ 29.9 (CH₂), 40.8 (CH₃), 44.6 (CH), 51.8 (CH₃), 57.3 (CH), 64.2 (CH), 65.8 (CH), 66.4 (CH), 73.7 (CH₂), 74.9 (CH), 127.5 (CH), 127.9 (CH), 128.6 (CH), 128.8 (CH), 130.0 (CH), 130.9 (C), 133.0 (CH), 138.1 (C), 166.0 (C), 171.9 (C); MS (ESI) *m/z* (relative intensity) 444 ([M+H]⁺, 100), 413 (30), 301 (27); HRMS (ESI) calcd for C₂₄H₂₆ClNO₅ [M+H]⁺ 444.1572, found 444.1580.

Alcohol 169. To a solution of chloride **162** (39.2 mg, 0.088 mmol) in MeOH (4 mL) was added Raney[®]-Nickel (70 mg). The mixture was activated with an atmosphere

of H₂ (balloon) by three times followed by stirring under the same H₂ atmosphere at 50 °C for another 7 h. The reaction mixture was filtered and washed with MeOH. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (CHCl₃:MeOH, 15:1) to afford alcohol **169** (20.9 mg, 74%) as a colorless oil: $[\alpha]_D^{20}$ -23.3 (*c* 1.05, CHCl₃); R_f 0.12 (CHCl₃:MeOH, 15:1); IR (thin film) 3411, 2950, 2805, 1743, 1717, 1602, 1584, 1451, 1316, 1281, 1177, 1118, 1071 cm⁻¹; ¹H NMR (400 MHz) δ 1.63 (1H, dd, *J* = 14.0, 3.6 Hz), 1.84 (1H, br s), 1.97 (1H, ddd, *J* = 11.1, 5.6, 3.3 Hz), 2.34 (3H, s), 2.49 (1H, td, *J* = 11.8, 2.8 Hz), 2.65 (1H, ddd, *J* = 13.8, 10.5, 7.5 Hz), 3.24–3.26 (1H, m), 3.43 (1H, dd, *J* = 6.1, 2.8 Hz), 3.53–3.55 (1H, m), 3.71 (3H, s), 4.89 (1H, ddd, *J* = 10.2, 6.4, 3.6 Hz), 5.71 (1H, dt, *J* = 11.8, 6.2 Hz), 7.41 (2H, t, *J* = 7.8 Hz), 7.53 (1H, tt, *J* = 7.4, 1.3 Hz), 8.02–8.05 (2H, m); ¹³C NMR (100 MHz) δ 34.8 (CH₂), 35.7 (CH₂), 41.1 (CH₃), 45.1 (CH), 51.9 (CH₃), 60.7 (CH), 67.3 (CH), 67.8 (CH), 71.5 (CH), 128.7 (CH), 130.1 (CH), 130.9 (C), 133.2 (CH), 166.5 (C), 172.3 (C); MS (ESI) *m/z* (relative intensity) 320 ([M+H]⁺, 100); HRMS (ESI) calcd for C₁₇H₂₁NO₅ [M+H]⁺ 320.1492, found 320.1487.

Mesylate 170. To a stirred solution of alcohol **169** (22.2 mg, 0.70 mmol) and triethylamine (0.023 mL, 0.167 mmol) in CH₂Cl₂ (0.7 mL) at 0 °C were added methanesulfonyl chloride (0.008 mL, 0.083 mmol) and DMAP (0.8 mg, 0.007 mmol). The reaction mixture was stirred at room temperature for 1 h and was quenched by saturated NaHCO₃ solution. The aqueous phase was extracted with EtOAc (3 × 15 mL) and the combined organic extracts were washed with brine, dried over anhydrous MgSO₄, and filtered. Concentration of the filtrate and the residue was purified by flash chromatography (hexane:EtOAc, 2:3) to yield mesylate **170** (26.3 mg, 95%) as a

colorless oil: $[\alpha]_D^{20}$ -14.1 (*c* 1.32, CHCl₃); *R_f* 0.22 (hexane:EtOAc, 2:3); IR (thin film) 2952, 1748, 1717, 1451, 1359, 1281, 1232, 1179, 1116, 1071 cm⁻¹; ¹H NMR (400 MHz) δ 1.89–2.00 (2H, m), 2.35 (3H, s), 2.57 (1H, td, *J* = 11.9, 3.0 Hz), 2.77 (1H, ddd, *J* = 14.8, 10.7, 7.3 Hz), 3.20 (3H, s), 3.32–3.34 (1H, m), 3.39 (1H, dd, *J* = 5.8, 2.9 Hz), 3.71 (3H, s), 3.81 (1H, d, *J* = 5.4 Hz), 5.47–5.53 (2H, m), 7.42 (2H, t, *J* = 7.8 Hz), 7.55 (1H, t, *J* = 7.4 Hz), 8.02 (2H, d, *J* = 7.2 Hz); ¹³C NMR (100 MHz) δ 32.7 (CH₂), 34.7 (CH₂), 38.8 (CH₃), 41.3 (CH₃), 45.2 (CH), 52.0 (CH₃), 60.4 (CH), 66.4 (CH), 66.5 (CH), 77.5 (CH), 128.7 (CH), 130.0 (CH), 130.5 (C), 133.4 (CH), 166.5 (C), 170.7 (C); MS (ESI) *m/z* (relative intensity) 398 ([M+H]⁺, 100); HRMS (ESI) calcd for C₁₈H₂₃NO₇ [M+H]⁺ 398.1268, found 398.1267.

Chloride 173. To a solution of mesylate **170** (16.9 mg, 0.043 mmol) in CH₂Cl₂ (0.4 mL) in a seal tube was added triethylamine (0.03 mL, 0.21 mmol). The solution was degassed and heated at 70 °C for 2 d. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash chromatography (hexane:Et₂O, 2:3) to give chloride **173** (13.8 mg, 96%) as a colorless oil: $[\alpha]_D^{20}$ -39.4 (*c* 0.69, CHCl₃); *R_f* 0.21 (hexane:Et₂O, 2:3); IR (thin film) 2950, 2805, 1750, 1717, 1602, 1451, 1345, 1315, 1280, 1176, 1116 cm⁻¹; ¹H NMR (400 MHz) δ 1.88 (1H, dd, *J* = 14.4, 4.9 Hz), 1.96–2.01 (1H, m), 2.35 (3H, s), 2.48 (1H, td, *J* = 11.8, 2.8 Hz), 2.86 (1H, ddd, *J* = 14.6, 11.4, 7.4 Hz), 3.30–3.31 (1H, m), 3.53 (1H, dd, *J* = 5.9, 2.9 Hz), 3.68–3.70 (1H, m), 3.73 (3H, s), 4.66 (1H, ddd, *J* = 11.3, 6.4, 5.0 Hz), 5.61 (1H, dt, *J* = 12.0, 6.2 Hz), 7.42 (2H, t, *J* = 7.8 Hz), 7.54 (1H, tt, *J* = 7.4, 1.3 Hz), 8.02–8.05 (2H, m); ¹³C NMR (100 MHz) δ 35.1 (CH₂), 36.4 (CH₂), 41.3 (CH₃), 46.2 (CH), 52.0 (CH₃), 55.4 (CH), 61.0 (CH), 66.4 (CH), 68.6 (CH), 128.7 (CH), 130.1 (CH), 130.6 (C), 133.3 (CH), 166.3 (C),

171.2 (C); MS (ESI) m/z (relative intensity) 338 ($[M+H]^+$, 100); HRMS (ESI) calcd for $C_{17}H_{20}ClNO_4$ $[M+H]^+$ 338.1154, found 338.1163.

Chloride 173 from alcohol 169 in one step reaction. To a solution of alcohol **169** (7.2 mg, 0.023 mmol) in CH_2Cl_2 (0.2 mL) in a seal tube at 0 °C was added triethylamine (0.03 mL, 0.184 mmol) and methanesulfonyl chloride (0.002 mL, 0.025 mmol). The reaction mixture was stirred at room temperature for 1 h and was then degassed and heated at 70 °C for 2 d. The reaction mixture was quenched by saturated $NaHCO_3$ solution. The aqueous phase was extracted with EtOAc (3×15 mL) and the combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, and filtered. Concentration of the filtrate and the residue was purified by flash chromatography (hexane:Et₂O, 2:3) to furnish chloride **173** (6.9 mg, 91%) as a colorless oil.

Chloride 173 by reacting mesylate 170 with nBu_4NCl . To a solution of mesylate **170** (3.9 mg, 0.010 mmol) in THF (0.09 mL) in a seal tube was added tetra-*n*-butylammomium chloride (3.3 mg, 0.012 mmol). The solution was degassed and heated at 90 °C for 18 h. The reaction mixture was then filtered and the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (hexane:Et₂O, 2:3) to yield chloride **173** (2.6 mg, 78%) as a colorless oil.

Iodide 175. To a solution of mesylate **170** (5.5 mg, 0.014 mmol) in THF (0.14 mL) in a seal tube was added tetra-*n*-butylammomium iodide (6.1 mg, 0.017 mmol). The solution was degassed and heated at 90 °C for 13 h. The reaction mixture was then

filtered and the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (hexane:Et₂O, 1:1) to yield iodide **175** (4.6 mg, 77%) as a colorless oil: $[\alpha]_D^{20}$ -48.7 (*c* 0.43, CHCl₃); *R_f* 0.16 (hexane:Et₂O, 1:1); IR (thin film) 2947, 2854, 1748, 1718, 1451, 1277, 1171, 1116, 1026 cm⁻¹; ¹H NMR (400 MHz) δ 1.91–2.00 (2H, m), 2.30 (3H, s), 2.35 (1H, td, *J* = 11.8, 2.8 Hz), 2.82 (1H, ddd, *J* = 14.3, 11.7, 7.2 Hz), 3.26–3.28 (1H, m), 3.57 (1H, dd, *J* = 5.8, 3.0 Hz), 3.65–3.66 (1H, m), 3.73 (3H, s), 4.53 (1H, dt, *J* = 11.9, 6.1 Hz), 5.50 (1H, dt, *J* = 12.0, 6.1 Hz), 7.42 (2H, t, *J* = 7.6 Hz), 7.54 (1H, t, *J* = 7.4 Hz), 8.03–8.05 (2H, m); ¹³C NMR (100 MHz) δ 19.0 (CH), 35.6 (CH₂), 38.2 (CH₂), 41.4 (CH₃), 49.9 (CH), 52.0 (CH₃), 61.8 (CH), 66.3 (CH), 69.7 (CH), 128.7 (CH), 130.1 (CH), 130.6 (C), 133.3 (CH), 166.3 (C), 171.2 (C); MS (ESI) *m/z* (relative intensity) 430 ([M+H]⁺, 100); HRMS (ESI) calcd for C₁₇H₂₀INO₄ [M+H]⁺ 430.0510, found 430.0505.

Amine 177. To a solution of chloride **173** (4.7 mg, 0.014 mmol) in MeOH (1 mL) was added Raney[®]-Nickel (20 mg). The mixture was activated with an atmosphere of H₂ (balloon) by three times followed by stirring under the same H₂ atmosphere at room temperature for another 18 h. The reaction mixture was filtered and washed with MeOH. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (CH₂Cl₂:MeOH, 19:1) to afford amine **177** (2.7 mg, 63%) as a colorless oil: $[\alpha]_D^{20}$ -53.6 (*c* 0.15, CHCl₃); *R_f* 0.43 (CH₂Cl₂:MeOH, 5:1); IR (thin film) 2932, 2854, 1750, 1727, 1449, 1248, 1174, 1140, 1045 cm⁻¹; ¹H NMR (400 MHz) δ 1.17–1.31 (4H, m), 1.34–1.43 (2H, m), 1.59–1.71 (5H, m), 1.83–1.85 (2H, m), 2.00–2.13 (2H, m), 2.19 (3H, s), 2.23–2.33 (2H, m), 2.92 (1H, dd, *J* = 5.5, 3.4 Hz), 3.24 (1H, s), 3.48–3.49 (1H, m), 3.70 (3H, s), 4.95 (1H, dt, *J* = 11.9, 6.0 Hz); ¹³C NMR (100

MHz) δ 25.5 (CH₂), 25.7 (CH₂), 25.8 (CH₂), 25.8 (CH₂), 26.1 (CH₂), 29.1 (CH₂), 29.3 (CH₂), 35.7 (CH₂), 41.5 (CH₃), 43.4 (CH), 50.4 (CH), 51.7 (CH₃), 61.9 (CH), 65.1 (CH), 66.4 (CH), 171.2 (C), 176.4 (C); MS (ESI) m/z (relative intensity) 310 ([M+H]⁺, 100); HRMS (ESI) calcd for C₁₇H₂₇NO₄ [M+H]⁺ 310.2013, found 310.2014.

1,2:3,4:5,6-Tri-*O*-pentylidene-*D*-mannitol (181). To a solution of *D*-mannitol (1.01 g, 5.57 mmol) in 3-pentanone (50 mL) was added concentrated phosphoric acid (0.5 mL). The mixture was heated to reflux with Dean and Stark apparatus for 12 h. It was then cooled down to room temperature and NaHCO₃ (3 g) was added. The solution was then filtered, concentration of the filtrate and the residue was purified by flash chromatography (hexane:Et₂O, 12:1) to give **181** (2.02 g, 94%) as a colorless oil: $[\alpha]_D^{20}$ +21.3 (*c* 1.99, CHCl₃); R_f 0.21 (hexane:Et₂O, 12:1); IR (thin film) 2974, 2942, 2883, 1464, 1357, 1201, 1174, 1085, 1059 cm⁻¹; ¹H NMR (400 MHz) δ 0.84–0.91 (18H, m), 1.57–1.67 (12H, m), 3.87–3.95 (4H, m), 4.06 (1H, dd, *J* = 8.0, 6.6 Hz), 4.15–4.19 (2H, m); ¹³C NMR (100 MHz) δ 8.3, 8.5, 8.6, 29.4, 29.8, 30.5, 67.2, 77.0, 80.1, 113.7, 113.8; MS (ESI) m/z (relative intensity) 409 ([M+Na]⁺, 100); HRMS (ESI) calcd for C₂₁H₃₈O₆ [M+Na]⁺ 409.2561, found 409.2566.

1,2:3,4-Di-*O*-pentylidene-*D*-mannitol (182). A solution of **181** (11.7 g, 30.3 mmol) in 80% aqueous AcOH (160 mL) was stirred at room temperature for 3 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (hexane:Et₂O, 12:1 to hexane:EtOAc, 3:1) to afford firstly starting material **181** (5.93 g, 51%) and secondly diol **182** (2.79 g, 29%) as a colorless oil: $[\alpha]_D^{20}$ +14.9 (*c* 0.86, CHCl₃); R_f 0.14 (hexane:EtOAc, 3:1); IR (thin film) 3437, 2973, 2940,

2882, 1464, 1201, 1174, 1130, 1084, 1058 cm^{-1} ; ^1H NMR (400 MHz) δ 0.84–0.93 (12H, m), 1.56–1.71 (8H, m), 2.43 (1H, t, $J = 6.9$ Hz), 3.68–3.89 (6H, m), 3.94 (1H, dd, $J = 8.4, 6.5$ Hz), 4.02 (1H, dt, $J = 8.8, 6.4$ Hz), 4.25 (1H, dd, $J = 8.4, 6.1$ Hz); ^1H NMR (400 MHz, $\text{CDCl}_3\text{-D}_2\text{O}$) δ 0.84–0.93 (12H, m), 1.57–1.71 (8H, m), 3.68–3.82 (4H, m), 3.87 (1H, t, $J = 7.7$ Hz), 3.92–3.97 (1H, m), 4.00–4.05 (1H, m), 4.23–4.27 (1H, m); ^{13}C NMR (100 MHz) δ 8.3, 8.4, 8.5, 29.1, 29.6, 30.5, 30.6, 64.5, 69.2, 72.6, 76.8, 81.9, 82.0, 113.7, 114.9; MS (ESI) m/z (relative intensity) 341 ($[\text{M}+\text{Na}]^+$, 100); HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{30}\text{O}_6$ $[\text{M}+\text{Na}]^+$ 341.1935, found 341.1930.

Alkenes 184 and 185. Following the glycol cleavage produce, diol **182** (3.34 g, 10.5 mmol) was converted into aldehyde **183** as a colorless oil. The crude product was redissolved in THF (40 mL) and was cooled to -78 $^\circ\text{C}$. A solution of vinylmagnesium bromide in THF (90 mL, 31.5 mmol) freshly generated was added at -78 $^\circ\text{C}$. The mixture was stirred at -78 $^\circ\text{C}$ for 15 h and was then quenched by saturated NH_4Cl solution. The aqueous phase was extracted with EtOAc (3×100 mL) and the combined organic extracts were dried over anhydrous MgSO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (hexane:Et₂O, 8:1) to afford firstly alkene **184** (1.45 g, 44% overall yield from diol **182**) as a colorless oil and secondly alkene **185** (0.97 g, 29% overall yield from diol **182**) as a colorless oil. Data for **184**: $[\alpha]_{\text{D}}^{20} -18.0$ (c 0.91, CHCl_3); R_f 0.35 (hexane:Et₂O, 4:1); IR (thin film) 3481, 2973, 2941, 2883, 1464, 1357, 1272, 1174, 1082, 1059 cm^{-1} ; ^1H NMR (400 MHz) δ 0.85–0.90 (12H, m), 1.57–1.65 (8H, m), 2.86 (1H, d, $J = 9.8$ Hz), 3.80 (1H, t, $J = 8.2$ Hz), 3.89 (1H, dd, $J = 8.1, 6.6$ Hz), 3.98–4.03 (2H, m), 4.18 (1H, dd, $J = 8.1, 6.4$ Hz), 4.35–4.37 (1H, m), 5.23 (1H, d, $J = 10.6$ Hz),

5.38 (1H, d, $J = 17.3$ Hz), 6.01 (1H, ddd, $J = 17.0, 10.6, 4.6$ Hz); ^1H NMR (400 MHz, $\text{CHCl}_3\text{-D}_2\text{O}$) δ 0.84–0.90 (12H, m), 1.57–1.65 (8H, m), 3.80 (1H, t, $J = 8.2$ Hz), 3.88 (1H, dd, $J = 8.2, 6.6$ Hz), 3.98–4.03 (2H, m), 4.18 (1H, dd, $J = 8.1, 6.3$ Hz), 4.35 (1H, s), 5.23 (1H, dd, $J = 10.6, 1.5$ Hz), 5.37 (1H, dd, $J = 17.3, 1.5$ Hz), 6.01 (1H, ddd, $J = 17.0, 10.6, 4.6$ Hz); ^{13}C NMR (100 MHz) δ 8.4, 8.4, 8.4, 8.5, 29.1, 29.8, 30.5, 30.5, 69.1, 71.1, 77.3, 78.0, 83.3, 113.4, 114.4, 116.1, 137.8; MS (ESI) m/z (relative intensity) 337 ($[\text{M}+\text{Na}]^+$, 100); HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{30}\text{O}_5$ $[\text{M}+\text{Na}]^+$ 337.1985, found 337.1992.

Data for **185**: $[\alpha]_D^{20} +31.0$ (c 0.45, CHCl_3); R_f 0.28 (hexane: Et_2O , 4:1); IR (thin film) 3473, 2973, 2940, 2882, 1464, 1357, 1200, 1174, 1084, 1059 cm^{-1} ; ^1H NMR (400 MHz) δ 0.84–0.93 (12H, m), 1.57–1.70 (8H, m), 3.51 (1H, d, $J = 2.3$ Hz), 3.71 (1H, t, $J = 8.0$ Hz), 3.79 (1H, t, $J = 7.0$ Hz), 3.94 (1H, dd, $J = 8.4, 6.6$ Hz), 4.04 (1H, dt, $J = 8.4, 6.4$ Hz), 4.15 (1H, t, $J = 5.9$ Hz), 4.23 (1H, dd, $J = 8.4, 6.2$ Hz), 5.25 (1H, dt, $J = 10.5, 1.4$ Hz), 5.40 (1H, dt, $J = 17.3, 1.5$ Hz), 6.03 (1H, ddd, $J = 16.8, 10.5, 5.8$ Hz); ^1H NMR (400 MHz, $\text{CHCl}_3\text{-D}_2\text{O}$) δ 0.84–0.93 (12H, m), 1.57–1.71 (8H, m), 3.71 (1H, t, $J = 8.0$ Hz), 3.79 (1H, t, $J = 7.0$ Hz), 3.94 (1H, dd, $J = 8.4, 6.6$ Hz), 4.04 (1H, dt, $J = 8.4, 6.4$ Hz), 4.12–4.16 (1H, m), 4.23 (1H, dd, $J = 8.4, 6.2$ Hz), 5.25 (1H, dt, $J = 10.5, 1.4$ Hz), 5.40 (1H, dt, $J = 17.2, 1.6$ Hz), 6.03 (1H, ddd, $J = 17.1, 10.5, 5.8$ Hz); ^{13}C NMR (100 MHz) δ 8.3, 8.4, 8.5, 29.1, 29.7, 30.6, 30.6, 69.1, 73.8, 76.9, 81.7, 84.2, 113.6, 114.7, 116.9, 137.3; MS (ESI) m/z (relative intensity) 337 ($[\text{M}+\text{Na}]^+$, 100); HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{30}\text{O}_5$ $[\text{M}+\text{Na}]^+$ 337.1985, found 337.1989.

Benzyl ether 186. Sodium hydride (60%, 140 mg, 3.49 mmol) was suspended in dry THF (10 mL) under nitrogen at 0 °C. A solution of the alkene **184** (457 mg, 1.45 mmol) in THF (10 mL) was added dropwise over 1 h at 0 °C, and then the mixture was

stirred at 0 °C for 1 h. Benzyl bromide (0.21 mL, 1.75 mmol) was added dropwise over 15 min and tetra-*n*-butylammomium iodide (53.7 mg, 0.15 mmol) was added. The reaction mixture was stirred at room temperature for 21 h. Water was then added slowly at 0 °C to destroy the excess of hydride, and this was followed by the addition of saturated NH₄Cl solution. The aqueous layer was extracted with Et₂O (2 × 20 mL). The combined organic extracts were washed with brine, dried over MgSO₄, and filtered. Concentration of the filtrate and the residue was purified by flash chromatography (hexane:Et₂O, 20:1) to give benzyl ether **186** (570 mg, 97%) as a colorless oil: $[\alpha]_D^{20} +40.5$ (*c* 0.96, CHCl₃); *R_f* 0.24 (hexane:Et₂O, 19:1); IR (thin film) 2973, 2940, 2881, 1457, 1201, 1173, 1123, 1083, 1059 cm⁻¹; ¹H NMR (400 MHz) δ 0.84–0.89 (12H, m), 1.52–1.68 (8H, m), 3.88 (1H, dd, *J* = 7.2, 5.4 Hz), 3.92–3.98 (2H, m), 4.04–4.13 (3H, m), 4.37 (1H, d, *J* = 12.0 Hz), 4.67 (1H, d, *J* = 12.0 Hz), 5.31–5.34 (1H, m), 5.36 (1H, s), 5.94 (1H, ddd, *J* = 16.7, 10.9, 7.9 Hz), 7.24–7.35 (5H, m); ¹³C NMR (100 MHz) δ 8.3, 8.5, 8.6, 29.3, 30.0, 30.4, 30.5, 68.3, 70.7, 77.6, 77.8, 80.5, 83.1, 113.8, 119.4, 127.0, 127.8, 128.6, 136.0, 138.8; MS (ESI) *m/z* (relative intensity) 427 ([M+Na]⁺, 100), 413 (38); HRMS (ESI) calcd for C₂₄H₃₆O₅ [M+Na]⁺ 427.2455, found 427.2450.

Diol 187. A solution of benzyl ether **186** (327 mg, 0.81 mmol) in 80% aqueous AcOH (15 mL) was stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (hexane:Et₂O, 19:1 to hexane:EtOAc, 2:1) to afford firstly starting material benzyl ether **186** (62.7 mg, 19%) and secondly diol **187** (203 mg, 74%) as a colorless oil: $[\alpha]_D^{20} +14.8$ (*c* 0.95, CHCl₃); *R_f* 0.19 (hexane:EtOAc, 2:1); IR (thin film) 3427, 2973, 2938, 2880,

1456, 1203, 1121, 1085, 1059 cm^{-1} ; ^1H NMR (400 MHz) δ 0.83–0.89 (6H, m), 1.55–1.63 (4H, m), 2.32 (1H, t, $J = 6.2$ Hz), 3.62–3.66 (1H, m), 3.67–3.71 (1H, m), 3.75–3.80 (2H, m), 3.91 (1H, t, $J = 8.0$ Hz), 4.02 (1H, dd, $J = 8.2, 4.1$ Hz), 4.25 (1H, dd, $J = 6.6, 4.2$ Hz), 4.45 (1H, d, $J = 11.6$ Hz), 4.72 (1H, d, $J = 11.6$ Hz), 5.39–5.46 (2H, m), 5.90 (1H, ddd, $J = 17.4, 10.6, 7.0$ Hz), 7.30–7.38 (5H, m); ^1H NMR (400 MHz, $\text{CHCl}_3\text{-D}_2\text{O}$) δ 0.82–0.88 (6H, m), 1.55–1.63 (4H, m), 3.60–3.64 (1H, m), 3.66–3.70 (1H, m), 3.77 (1H, dd, $J = 11.3, 3.9$ Hz), 3.91 (1H, t, $J = 8.1$ Hz), 4.01 (1H, dd, $J = 8.2, 4.2$ Hz), 4.25 (1H, dd, $J = 6.8, 4.2$ Hz), 4.45 (1H, d, $J = 11.6$ Hz), 4.72 (1H, d, $J = 11.6$ Hz), 5.39–5.46 (2H, m), 5.90 (1H, ddd, $J = 17.4, 10.6, 6.9$ Hz), 7.30–7.38 (5H, m); ^{13}C NMR (100 MHz) δ 8.3, 8.3, 30.4, 30.4, 64.6, 71.8, 73.0, 77.5, 78.8, 81.8, 113.3, 120.7, 128.5, 128.6, 129.0, 133.5, 137.2; MS (ESI) m/z (relative intensity) 359 ($[\text{M}+\text{Na}]^+$, 100); HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{28}\text{O}_5$ $[\text{M}+\text{Na}]^+$ 359.1829, found 359.1829.

Isoxazolidines 180 and 189. Following the glycol cleavage produce, diol **187** (30.7 mg, 0.091 mmol) was converted into aldehyde **188** as a colorless oil. Following the INAC reaction procedure (Method A) using DMF (6 mL) as the reaction solvent and the product was purified by flash chromatography (hexane: Et_2O , 2:1 to 1:1), aldehyde **188** was converted into firstly isoxazolidine **180** (4.4 mg, 14% overall yield from diol **187**) as a colorless oil and secondly isoxazolidine **189** (19.4 mg, 64% overall yield from diol **187**) as a white solid. Data for **180**: $[\alpha]_{\text{D}}^{20} -94.5$ (c 0.75, CHCl_3); R_f 0.15 (hexane: Et_2O , 2:1); IR (thin film) 2972, 2941, 2882, 1461, 1199, 1176, 1119, 1072, 1057, 1003 cm^{-1} ; ^1H NMR (400 MHz) δ 0.92–0.97 (6H, m), 1.65–1.76 (4H, m), 2.12 (1H, ddd, $J = 13.0, 5.2, 4.0$ Hz), 2.42 (1H, d, $J = 13.0$ Hz), 2.61 (3H, s), 3.46 (1H, d, $J = 8.0$ Hz), 3.53–3.63 (3H, m), 4.42 (1H, d, $J = 5.6$ Hz), 4.60 (1H, d, $J = 11.6$ Hz), 4.73

(1H, d, $J = 11.6$ Hz), 7.27–7.37 (5H, m); ^{13}C NMR (100 MHz) δ 8.6 (CH₃), 8.7 (CH₃), 26.2 (CH₂), 29.9 (CH₂), 30.2 (CH₂), 45.7 (CH₃), 60.9 (CH), 71.9 (CH₂), 77.7 (CH), 78.6 (CH), 79.3 (CH), 81.5 (CH), 116.4 (C), 128.1 (CH), 128.2 (CH), 128.8 (CH), 138.2 (C); MS (ESI) m/z (relative intensity) 334 ($[\text{M}+\text{H}]^+$, 100); HRMS (ESI) calcd for C₁₉H₂₇NO₄ $[\text{M}+\text{H}]^+$ 334.2013, found 334.2007.

Data for **189**: mp 81–82 °C; $[\alpha]_{\text{D}}^{20} +24.1$ (c 0.45, CHCl₃); R_f 0.14 (hexane:Et₂O, 1:1); IR (thin film) 2969, 2941, 2881, 1455, 1127, 1084, 1061 cm⁻¹; ^1H NMR (400 MHz) δ 0.92–0.99 (6H, m), 1.66–1.75 (4H, m), 1.77–1.88 (1H, m), 2.34 (1H, dt, $J = 12.0, 5.8$ Hz), 2.68 (3H, s), 3.28 (1H, d, $J = 9.1$ Hz), 3.45 (1H, d, $J = 9.0$ Hz), 3.57 (1H, d, $J = 5.4$ Hz), 4.12 (1H, t, $J = 9.1$ Hz), 4.51 (1H, d, $J = 6.1$ Hz), 4.63 (1H, d, $J = 12.2$ Hz), 4.82 (1H, d, $J = 12.2$ Hz), 7.24–7.39 (5H, m); ^{13}C NMR (100 MHz) δ 8.6 (CH₃), 8.9 (CH₃), 29.9 (CH₂), 30.0 (CH₂), 33.1 (CH₂), 47.6 (CH₃), 62.2 (CH), 71.5 (CH₂), 78.8 (CH), 79.9 (CH), 79.9 (CH), 80.0 (CH), 115.2 (C), 127.8 (CH), 128.2 (CH), 128.6 (CH), 138.7 (C); MS (ESI) m/z (relative intensity) 356 ($[\text{M}+\text{Na}]^+$, 100), 248 (29); HRMS (ESI) calcd for C₁₉H₂₇NO₄ $[\text{M}+\text{Na}]^+$ 356.1832, found 356.1833; Anal. Calcd for C₁₉H₂₇NO₄: C, 68.44; H, 8.16; N, 4.20, found: C, 68.73; H, 8.34; N, 4.33.

Amine 190. To a solution of isoxazolidine **180** (9.0 mg, 0.027 mmol) in EtOH (1 mL) was added Raney[®]-Nickel (2 mg). The mixture was activated with an atmosphere of H₂ (balloon) by three times followed by stirring under the same H₂ atmosphere at room temperature for another 2 h. The reaction mixture was filtered and washed with EtOH. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (CH₂Cl₂:MeOH, 20:1) to afford amine **190** (8.0 mg, 88%) as a colorless oil: $[\alpha]_{\text{D}}^{20} -36.4$ (c 0.20, CHCl₃); R_f 0.16 (CHCl₃:MeOH, 10:1);

IR (thin film) 3315, 2969, 2933, 2883, 1460, 1357, 1167, 1073 cm^{-1} ; ^1H NMR (400 MHz) δ 0.92–0.96 (6H, m), 1.29 (1H, q, $J = 11.5$ Hz), 1.66–1.73 (4H, m), 2.07 (2H, br s), 2.30 (1H, dt, $J = 13.0, 4.7$ Hz), 2.47 (3H, s), 2.72 (1H, ddd, $J = 11.0, 9.8, 4.3$ Hz), 3.38 (1H, t, $J = 9.2$ Hz), 3.42–3.50 (2H, m), 3.63–3.69 (1H, m), 4.65 (1H, d, $J = 11.5$ Hz), 4.97 (1H, d, $J = 11.6$ Hz), 7.28–7.40 (5H, m); ^{13}C NMR (100 MHz) δ 8.6 (CH_3), 30.6 (CH_2), 30.6 (CH_2), 34.2 (CH_3), 35.8 (CH_2), 56.5 (CH), 71.5 (CH), 73.0 (CH_2), 80.8 (CH), 82.1 (CH), 82.7 (CH), 115.8 (C), 128.2 (CH), 128.5 (CH), 128.8 (CH), 138.6 (C); MS (ESI) m/z (relative intensity) 336 ($[\text{M}+\text{H}]^+$, 100), 250 (43), 142 (27); HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{29}\text{NO}_4$ $[\text{M}+\text{H}]^+$ 336.2169, found 336.2178.

Amine 191. To a solution of isoxazolidine **189** (18.7 mg, 0.056 mmol) in EtOH (2 mL) was added Raney[®]-Nickel (5 mg). The mixture was activated with an atmosphere of H_2 (balloon) by three times followed by stirring under the same H_2 atmosphere at room temperature for another 2 h. The reaction mixture was filtered and washed with EtOH. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (CH_2Cl_2 :MeOH, 40:1) to afford amine **191** (15.6 mg, 83%) as a white solid: mp 60 $^\circ\text{C}$; $[\alpha]_{\text{D}}^{20}$ -27.8 (c 0.26, CHCl_3); R_f 0.12 (CHCl_3 :MeOH, 40:1); IR (thin film) 3316, 2968, 2932, 2879, 1460, 1356, 1093 cm^{-1} ; ^1H NMR (400 MHz) δ 0.93–0.99 (6H, m), 1.23 (1H, dt, $J = 15.1, 2.8$ Hz), 1.68–1.76 (4H, m), 2.33 (1H, dt, $J = 15.2, 2.9$ Hz), 2.48 (3H, s), 3.22–3.23 (1H, m), 3.38–3.43 (2H, m), 4.10–4.11 (1H, m), 4.34 (1H, t, $J = 9.8$ Hz), 4.79 (1H, d, $J = 12.5$ Hz), 4.87 (1H, d, $J = 12.6$ Hz), 7.25–7.28 (1H, m), 7.33 (2H, t, $J = 7.6$ Hz), 7.42 (2H, d, $J = 7.3$ Hz); ^{13}C NMR (100 MHz) δ 8.5 (CH_3), 8.9 (CH_3), 30.4 (CH_2), 30.4 (CH_2), 30.5 (CH_2), 34.8 (CH_3), 56.9 (CH), 71.2 (CH), 71.5 (CH_2), 75.3 (CH), 79.4 (CH), 80.2 (CH), 114.0 (C),

127.8 (CH), 128.4 (CH), 128.6 (CH), 139.0 (C); MS (ESI) m/z (relative intensity) 336 ($[M+H]^+$, 100), 250 (23); HRMS (ESI) calcd for $C_{19}H_{29}NO_4$ $[M+H]^+$ 336.2169, found 336.2157.

Benzyl ether 192. Sodium hydride (60%, 26.3 mg, 0.657 mmol) was suspended in dry THF (4 mL) under nitrogen at 0 °C. A solution of the alkene **185** (93.9 mg, 0.299 mmol) in THF (4 mL) was added dropwise over 1 h at 0 °C, and then the mixture was stirred at 0 °C for 1 h. Benzyl bromide (0.039 mL, 0.329 mmol) was added dropwise over 15 min and tetra-*n*-butylammomium iodide (11.0 mg, 0.030 mmol) was added. The reaction mixture was stirred at room temperature for 22 h. Water was then added slowly at 0 °C to destroy the excess of hydride, and this was followed by the addition of saturated NH_4Cl solution. The aqueous layer was extracted with Et_2O (2×10 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and filtered. Concentration of the filtrate and the residue was purified by flash chromatography (hexane: Et_2O , 20:1) to yield benzyl ether **192** (117 mg, 97%) as a colorless oil: $[\alpha]_D^{20}$ -24.0 (c 0.41, $CHCl_3$); R_f 0.17 (hexane: Et_2O , 20:1); IR (thin film) 2974, 2941, 2882, 1456, 1174, 1080, 1059 cm^{-1} ; 1H NMR (400 MHz) δ 0.79 (3H, t, $J = 7.5$ Hz), 0.84 (3H, t, $J = 7.5$ Hz), 0.85–0.90 (6H, m), 1.52–1.66 (8H, m), 3.72 (1H, t, $J = 7.8$ Hz), 3.84 (1H, dd, $J = 7.6, 6.4$ Hz), 3.96 (1H, dd, $J = 8.5, 3.2$ Hz), 4.03–4.13 (3H, m), 4.41 (1H, d, $J = 12.3$ Hz), 4.69 (1H, d, $J = 12.3$ Hz), 5.23 (1H, dd, $J = 17.4, 1.3$ Hz), 5.41 (1H, dd, $J = 10.3, 1.7$ Hz), 5.97 (1H, ddd, $J = 17.4, 10.3, 8.5$ Hz), 7.23–7.30 (5H, m); ^{13}C NMR (100 MHz) δ 8.4 (CH_3), 8.4 (CH_3), 8.5 (CH_3), 8.6 (CH_3), 29.3 (CH_2), 29.9 (CH_2), 30.5 (CH_2), 30.5 (CH_2), 68.4 (CH_2), 70.5 (CH_2), 77.7 (CH), 79.0 (CH), 80.7 (CH), 82.8 (CH), 113.7

(C), 114.0 (C), 121.0 (CH₂), 127.9 (CH), 128.3 (CH), 128.6 (CH), 134.7 (CH), 138.5 (C); MS (ESI) *m/z* (relative intensity) 427 ([M+Na]⁺, 100), 413 (55), 149 (70); HRMS (ESI) calcd for C₂₄H₃₆O₅ [M+Na]⁺ 427.2455, found 427.2446.

Diol 193. A solution of benzyl ether **192** (64.4 mg, 0.16 mmol) in 80% aqueous AcOH (5 mL) was stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (hexane:Et₂O, 20:1 to hexane:EtOAc, 2:1) to afford firstly starting material benzyl ether **192** (15.2 mg, 24%) and secondly diol **193** (39.7 mg, 74%) as a colorless oil: [α]_D²⁰ -41.9 (*c* 0.33, CHCl₃); R_f 0.19 (hexane:EtOAc, 2:1); IR (thin film) 3396, 2973, 2939, 2881, 1457, 1203, 1087, 1058 cm⁻¹; ¹H NMR (400 MHz) δ 0.83–0.87 (6H, m), 1.55–1.62 (4H, m), 2.28 (1H, t, *J* = 6.1 Hz), 3.61–3.65 (1H, m), 3.66–3.72 (1H, m), 3.75–3.90 (5H, m), 4.38 (1H, d, *J* = 11.4 Hz), 4.69 (1H, d, *J* = 11.3 Hz), 5.41 (1H, d, *J* = 17.3 Hz), 5.48 (1H, dd, *J* = 10.3, 1.2 Hz), 5.87 (1H, ddd, *J* = 17.2, 10.4, 7.7 Hz), 7.30–7.38 (5H, m); ¹H NMR (400 MHz, CHCl₃-D₂O) δ 0.82–0.87 (6H, m), 1.55–1.63 (4H, m), 3.60–3.64 (1H, m), 3.68 (1H, dd, *J* = 11.4, 4.2 Hz), 3.74–3.90 (4H, m), 4.38 (1H, d, *J* = 11.3 Hz), 4.69 (1H, d, *J* = 11.3 Hz), 5.41 (1H, d, *J* = 17.3 Hz), 5.48 (1H, d, *J* = 10.3 Hz), 5.87 (1H, ddd, *J* = 17.4, 10.3, 7.8 Hz), 7.30–7.39 (5H, m); ¹³C NMR (100 MHz) δ 8.2 (CH₃), 8.4 (CH₃), 30.4 (CH₂), 30.6 (CH₂), 64.5 (CH₂), 70.9 (CH₂), 73.1 (CH), 81.5 (CH), 81.9 (CH), 82.3 (CH), 114.0 (C), 121.1 (CH₂), 128.7 (CH), 128.8 (CH), 129.0 (CH), 135.4 (CH), 136.9 (C); MS (ESI) *m/z* (relative intensity) 359 ([M+Na]⁺, 100), 301 (15), 149 (33); HRMS (ESI) calcd for C₁₉H₂₈O₅ [M+Na]⁺ 359.1829, found 359.1824.

Isoxazolidine 196. Following the glycol cleavage produce, diol **193** (32.0 mg, 0.095 mmol) was converted into aldehyde **194** as a colorless oil. Following the INAC reaction procedure (Method A) using DMF (5 mL) as the reaction solvent and the product was purified by flash chromatography (hexane:Et₂O, 2:1), aldehyde **194** was converted into isoxazolidine **196** (16.5 mg, 52% overall yield from diol **193**) as a colorless oil: $[\alpha]_D^{20} +47.1$ (*c* 0.61, CHCl₃); *R_f* 0.27 (hexane:Et₂O, 3:2); IR (thin film) 2966, 2938, 2880, 1457, 1167, 1142, 1111, 1071, 1057 cm⁻¹; ¹H NMR (400 MHz) δ 0.93–0.99 (6H, m), 1.69–1.84 (4H, m), 2.18–2.23 (1H, m), 2.31 (1H, d, *J* = 12.2 Hz), 2.67 (3H, s), 3.59 (1H, d, *J* = 5.4 Hz), 3.73 (1H, d, *J* = 9.6 Hz), 4.00 (1H, dd, *J* = 9.6, 3.3 Hz), 4.10 (1H, dd, *J* = 4.7, 3.4 Hz), 4.53–4.55 (2H, m), 4.93 (1H, d, *J* = 11.7 Hz); ¹³C NMR (100 MHz) δ 8.6 (CH₃), 8.8 (CH₃), 30.1 (CH₂), 30.2 (CH₂), 31.5 (CH₂), 47.6 (CH₃), 63.0 (CH), 73.2 (CH₂), 74.4 (CH), 77.4 (CH), 77.7 (CH), 78.4 (CH), 114.3 (C), 127.9 (CH), 127.9 (CH), 128.7 (CH), 139.0 (C); MS (ESI) *m/z* (relative intensity) 334 ([M+H]⁺, 100); HRMS (ESI) calcd for C₁₉H₂₇NO₄ [M+H]⁺ 334.2013, found 334.2005.

Diol 197. To a stirred solution of isoxazolidine **196** (26.0 mg, 0.078 mmol) in CH₂Cl₂ (3 mL) were added deionized water (0.05 mL) and TFA (0.2 mL) at room temperature to form a clear solution. The mixture was stirred at room temperature for 2 h. Concentration of the mixture under reduced pressure and the residue was purified by flash chromatography (CHCl₃:MeOH, 40:1) to furnish diol **197** (18.5 mg, 89%) as a white solid: mp 159 °C; $[\alpha]_D^{20} +20.7$ (*c* 0.35, CHCl₃); *R_f* 0.25 (CHCl₃:MeOH, 19:1); IR (thin film) 3332, 2927, 1442, 1240, 1164, 1110, 1081, 1047 cm⁻¹; ¹H NMR (400 MHz) δ 2.13 (1H, dt, *J* = 12.2, 5.6 Hz), 2.31 (1H, d, *J* = 12.2 Hz), 2.50 (1H, d, *J* = 9.7 Hz), 2.61–2.63 (4H, m), 3.24 (1H, dd, *J* = 5.5, 2.2 Hz), 3.43 (1H, t, *J* = 7.4 Hz), 3.74–3.82

(2H, m), 4.47 (1H, t, $J = 4.6$ Hz), 4.56 (1H, d, $J = 11.6$ Hz), 4.62 (1H, d, $J = 11.6$ Hz), 7.30–7.38 (5H, m); ^1H NMR (400 MHz, $\text{CHCl}_3\text{-D}_2\text{O}$) δ 2.13 (1H, dt, $J = 12.2, 5.6$ Hz), 2.31 (1H, d, $J = 12.2$ Hz), 2.63 (3H, s), 3.24 (1H, dd, $J = 5.2, 1.6$ Hz), 3.43 (1H, d, $J = 8.1$ Hz), 3.74–3.80 (2H, m), 4.46 (1H, t, $J = 4.9$ Hz), 4.55 (1H, d, $J = 11.6$ Hz), 4.62 (1H, d, $J = 11.6$ Hz), 7.30–7.37 (5H, m); ^{13}C NMR (100 MHz) δ 28.9 (CH_2), 47.6 (CH_3), 66.9 (CH), 73.8 (CH_2), 74.1 (CH), 75.5 (CH), 76.7 (CH), 77.8 (CH), 128.3 (CH), 128.6 (CH), 129.0 (CH), 138.0 (C); MS (ESI) m/z (relative intensity) 266 ($[\text{M}+\text{H}]^+$, 100), 149 (40); HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_4$ $[\text{M}+\text{H}]^+$ 266.1387, found 266.1386.

Amine 199. To a solution of isoxazolidine **196** (8.3 mg, 0.025 mmol) in EtOH (1 mL) was added Raney[®]-Nickel (2 mg). The mixture was activated with an atmosphere of H_2 (balloon) by three times followed by stirring under the same H_2 atmosphere at room temperature for another 17 h. The reaction mixture was filtered and washed with EtOH. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography ($\text{CH}_2\text{Cl}_2\text{:MeOH}$, 80:1) to afford amine **199** (7.8 mg, 93%) as a colorless oil: $[\alpha]_D^{20} +11.2$ (c 0.32, CHCl_3); R_f 0.40 ($\text{CHCl}_3\text{:MeOH}$, 19:1); IR (thin film) 3314, 2968, 2931, 1459, 1359, 1131, 1095 cm^{-1} ; ^1H NMR (400 MHz) δ 0.97 (6H, t, $J = 7.4$ Hz), 1.61 (1H, dt, $J = 15.0, 2.8$ Hz), 1.67–1.79 (4H, m), 2.12 (1H, dt, $J = 15.0, 2.6$ Hz), 2.48 (3H, s), 3.31 (1H, d, $J = 2.7$ Hz), 3.98 (1H, d, $J = 2.8$ Hz), 4.08 (1H, dd, $J = 10.2, 3.4$ Hz), 4.19 (1H, t, $J = 2.8$ Hz), 4.32 (1H, dd, $J = 10.2, 2.4$ Hz), 4.63 (1H, d, $J = 11.8$ Hz), 4.91 (1H, d, $J = 11.8$ Hz), 7.28–7.33 (5H, m); ^{13}C NMR (100 MHz) δ 8.6 (CH_3), 8.7 (CH_3), 27.5 (CH_2), 30.5 (CH_2), 30.6 (CH_2), 34.7 (CH_3), 58.1 (CH), 72.1 (CH), 73.5 (CH_2), 74.0 (CH), 75.6 (CH), 78.0 (CH), 113.0 (C), 127.7 (CH), 127.8 (CH),

128.6 (CH), 139.2 (C); MS (ESI) m/z (relative intensity) 336 ($[M+H]^+$, 100), 250 (35);
HRMS (ESI) calcd for $C_{19}H_{29}NO_4$ $[M+H]^+$ 336.2169, found 336.2176.

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II-13	¹ H NMR and ¹³ C NMR spectra of carboxylic acid 96	213
II-14	¹ H NMR and ¹³ C NMR spectra of isoxazolidine 97	215
II-15	¹ H NMR and ¹³ C NMR spectra of dimesylate 102	217
II-16	¹ H NMR and ¹³ C NMR spectra of dialkene 103	219
II-17	¹ H NMR and ¹³ C NMR spectra of ditosylate 104	221
II-18	¹ H NMR and ¹³ C NMR spectra of diiodide 105	223
II-19	¹ H NMR and ¹³ C NMR spectra of diol 106	225
II-20	¹ H NMR and ¹³ C NMR spectra of diol 108	227
II-21	¹ H NMR and ¹³ C NMR spectra of amine 109	229
II-22	¹ H NMR and ¹³ C NMR spectra of ester 128	231
II-23	¹ H NMR and ¹³ C NMR spectra of isoxazolidine 130	233
II-24	¹ H NMR and ¹³ C NMR spectra of benzoate 134	236
II-25	¹ H NMR and ¹³ C NMR spectra of ester 136	238

II-26	¹ H NMR and ¹³ C NMR spectra of isoxazolidine 137	240
II-27	¹ H NMR and ¹³ C NMR spectra of isoxazolidine 138	243
II-28	¹ H NMR and ¹³ C NMR spectra of ketone 139	245
II-29	¹ H NMR and ¹³ C NMR spectra of isoxazolidines 141/142	247
II-30	¹ H NMR and ¹³ C NMR spectra of ester 146	249
II-31	¹ H NMR and ¹³ C NMR spectra of diol 147	251
II-32	¹ H NMR and ¹³ C NMR spectra of diol 149	253
II-33	¹ H NMR and ¹³ C NMR spectra of diol 150	255
II-34	¹ H NMR and ¹³ C NMR spectra of epoxide 154	258
II-35	¹ H NMR and ¹³ C NMR spectra of mesylate 155	260
II-36	¹ H NMR and ¹³ C NMR spectra of diol 158	263
II-37	¹ H NMR, ¹³ C NMR and COSY spectra of triol 159	266
II-38	¹ H NMR and ¹³ C NMR spectra of tribenzoate 160	269
II-39	¹ H NMR, ¹³ C NMR, COSY and NOESY spectra of chloride 162	271
II-40	¹ H NMR and ¹³ C NMR spectra of alcohol 169	275
II-41	¹ H NMR and ¹³ C NMR spectra of mesylate 170	277
II-42	¹ H NMR and ¹³ C NMR spectra of chloride 173	279
II-43	¹ H NMR and ¹³ C NMR spectra of iodide 175	281
II-44	¹ H NMR and ¹³ C NMR spectra of amine 177	283
II-45	¹ H NMR and ¹³ C NMR spectra of isoxazolidine 180	285
II-46	¹ H NMR and ¹³ C NMR spectra of diol 182	287
II-47	¹ H NMR and ¹³ C NMR spectra of alkene 184	290
II-48	¹ H NMR and ¹³ C NMR spectra of alkene 185	293
II-49	¹ H NMR and ¹³ C NMR spectra of benzyl ether 186	296
II-50	¹ H NMR and ¹³ C NMR spectra of diol 187	298
II-51	¹ H NMR and ¹³ C NMR spectra of isoxazolidine 189	301
II-52	¹ H NMR and ¹³ C NMR spectra of amine 190	303
II-53	¹ H NMR and ¹³ C NMR spectra of amine 191	305
II-54	¹ H NMR and ¹³ C NMR spectra of benzyl ether 192	307
II-55	¹ H NMR and ¹³ C NMR spectra of diol 193	309
II-56	¹ H NMR and ¹³ C NMR spectra of isoxazolidine 196	312
II-57	¹ H NMR and ¹³ C NMR spectra of diol 197	314
II-58	¹ H NMR and ¹³ C NMR spectra of amine 199	317

NMR spectra were measured in CDCl₃ solutions, unless stated otherwise.

X-ray crystallographic data and structure of diol 108

Table 1. Crystal data and structure refinement for p.

Identification code	shb32	
Empirical formula	C14 H19 N O3	
Formula weight	249.30	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, C2	
Unit cell dimensions	a = 8.750(2) Å	alpha = 90 deg.
94.372(7) deg.	b = 7.445(2) Å	beta =
deg.	c = 20.096(6) Å	gamma = 90
Volume	1305.3(6) Å ³	
Z, Calculated density	4, 1.269 Mg/m ³	
Absorption coefficient	0.089 mm ⁻¹	
F(000)	536	
Crystal size	0.40 x 0.30 x 0.30 mm	
Theta range for data collection	1.02 to 24.99 deg.	
Limiting indices	-9<=h<=10, -8<=k<=8, -19<=l<=23	
Reflections collected / unique	3521 / 2154 [R(int) = 0.0643]	
Completeness to theta = 24.99	100.0 %	
Absorption correction	SADBS	
Max. and min. transmission	1.000 and 0.089585	
Refinement method	Full-matrix least-squares on	
F ²		
Data / restraints / parameters	2154 / 1 / 164	
Goodness-of-fit on F ²	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0679, wR2 = 0.1657	

R indices (all data)

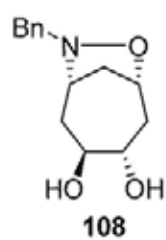
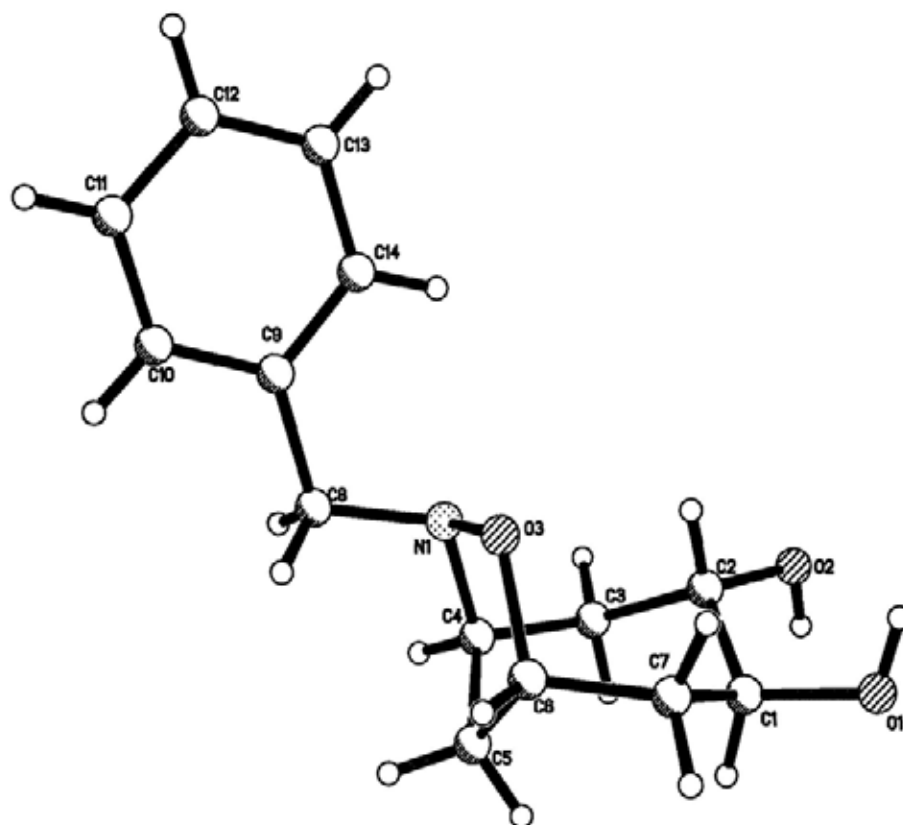
R1 = 0.1219, wR2 = 0.2226

Absolute structure parameter

1(3)

Largest diff. peak and hole

0.308 and -0.513 e.A⁻³

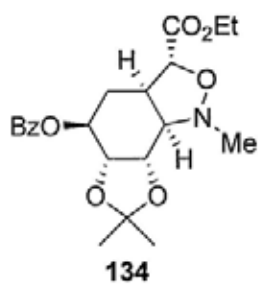
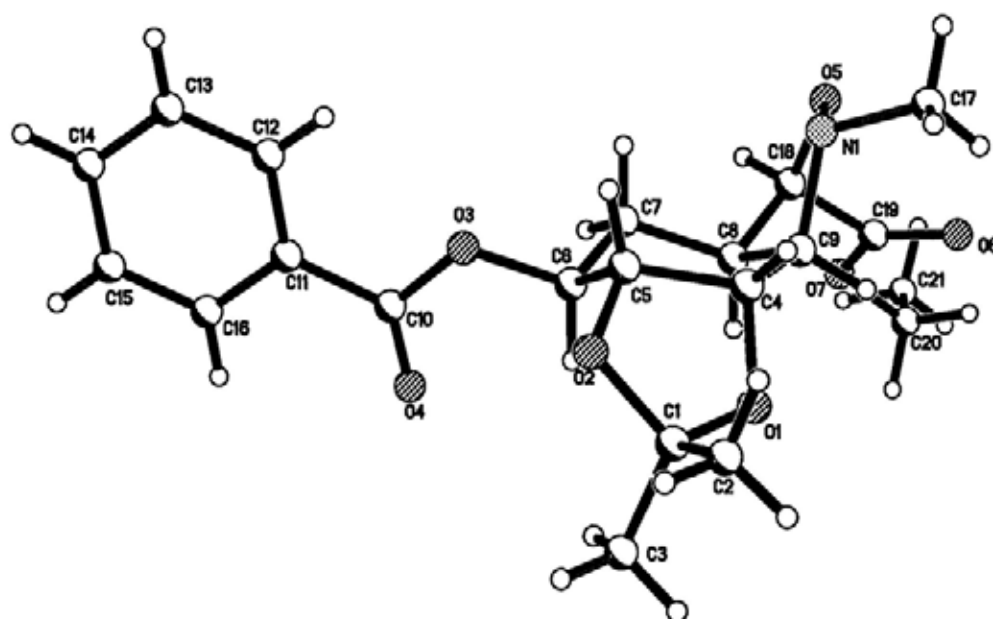


X-ray crystallographic data and structure of benzoate 134

Table 1. Crystal data and structure refinement for p.

Identification code	skh78(cu)
Empirical formula	C21 H27 N O7
Formula weight	405.44
Temperature	296(2) K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 8.7187(2) Å alpha = 90
deg.	b = 10.0275(2) Å beta =
103.938(2) deg.	c = 12.7718(3) Å gamma = 90
deg.	
Volume	1083.72(4) Å ³
Z, Calculated density	2, 1.242 Mg/m ³
Absorption coefficient	0.776 mm ⁻¹
F(000)	432
Crystal size	0.40 x 0.20 x 0.20 mm
Theta range for data collection	3.57 to 67.31 deg.
Limiting indices	-10<=h<=9, -7<=k<=11, -
15<=l<=14	
Reflections collected / unique	3660 / 2326 [R(int) = 0.0291]
Completeness to theta = 67.31	91.4 %
Absorption correction	Multiscan
Max. and min. transmission	1.0000 and 0.162000
Refinement method	Full-matrix least-squares on
F ²	
Data / restraints / parameters	2326 / 1 / 263
Goodness-of-fit on F ²	1.063

Final R indices [I>2sigma(I)]	R1 = 0.0473, wR2 = 0.1449
R indices (all data)	R1 = 0.0561, wR2 = 0.1600
Absolute structure parameter	-0.3(4)
Extinction coefficient	0.0084(16)
Largest diff. peak and hole	0.193 and -0.192 e.A ⁻³

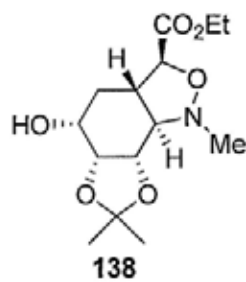
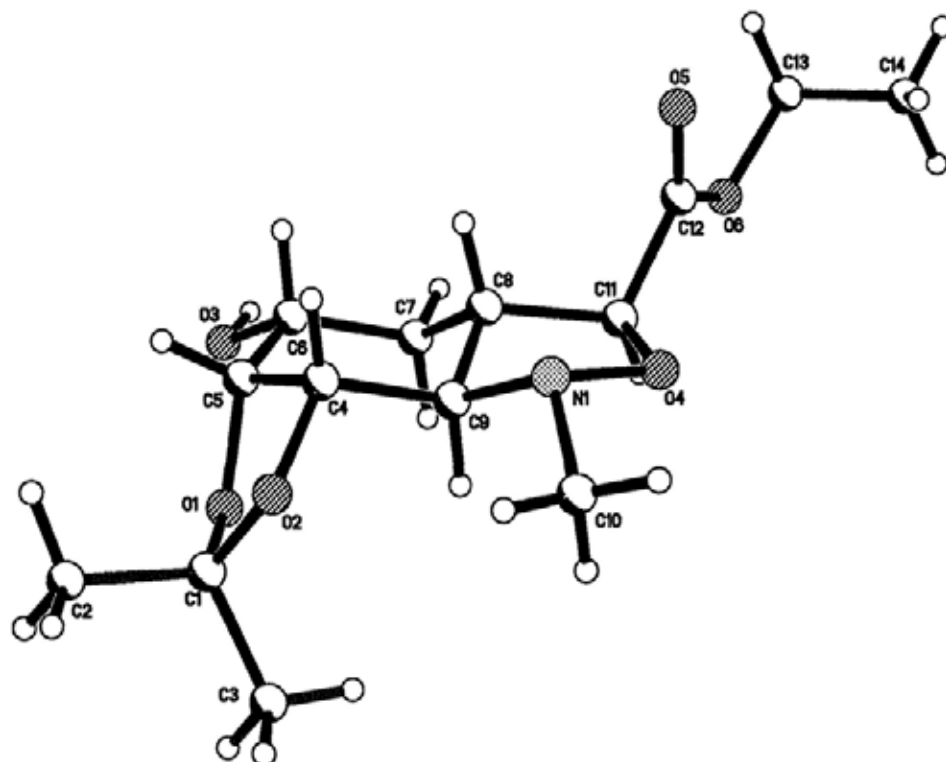


X-ray crystallographic data and structure of isoxazolidine 138

Table 1. Crystal data and structure refinement for p.

Identification code	skh73-3
Empirical formula	C14 H23 N O6
Formula weight	301.33
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 10.4120(8) Å alpha = 90
deg.	b = 6.8959(5) Å beta =
107.878(2) deg.	c = 11.3411(9) Å gamma = 90
deg.	
Volume	774.97(10) Å ³
Z, Calculated density	2, 1.291 Mg/m ³
Absorption coefficient	0.101 mm ⁻¹
F(000)	324
Crystal size	0.40 x 0.40 x 0.30 mm
Theta range for data collection	1.89 to 27.89 deg.
Limiting indices	-13<=h<=13, -9<=k<=9, -14<=l<=8
Reflections collected / unique	6452 / 3402 [R(int) = 0.0182]
Completeness to theta = 27.89	98.2 %
Absorption correction	Multiscan
Max. and min. transmission	1.000 and 0.826843
Refinement method	Full-matrix least-squares on
F ²	
Data / restraints / parameters	3402 / 1 / 191
Goodness-of-fit on F ²	1.049

Final R indices [I>2sigma(I)]	R1 = 0.0489, wR2 = 0.1351
R indices (all data)	R1 = 0.0629, wR2 = 0.1478
Absolute structure parameter	-0.4(13)
Largest diff. peak and hole	0.279 and -0.239 e.A ⁻³

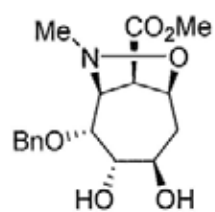
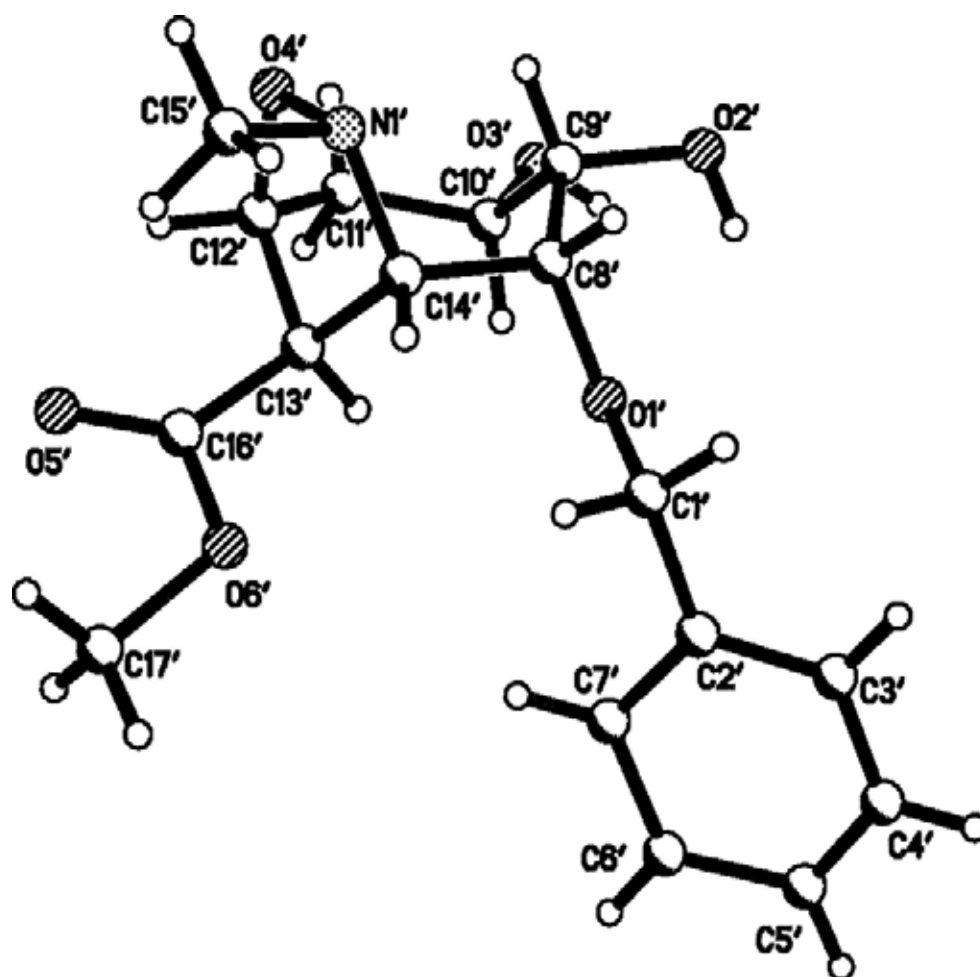


X-ray crystallographic data and structure of diol 149

Table 1. Crystal data and structure refinement for p.

Identification code	shr11
Empirical formula	C17 H23 N O6
Formula weight	337.36
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 12.322(2) Å alpha = 90
deg.	b = 10.019(2) Å beta =
112.203(3) deg.	c = 15.678(3) Å gamma = 90
deg.	
Volume	1791.9(6) Å ³
Z, Calculated density	4, 1.251 Mg/m ³
Absorption coefficient	0.095 mm ⁻¹
F(000)	720
Crystal size	0.40 x 0.30 x 0.20 mm
Theta range for data collection	2.47 to 25.00 deg.
Limiting indices	-13<=h<=14, -9<=k<=11, -
18<=l<=17	
Reflections collected / unique	11292 / 5789 [R(int) = 0.0480]
Completeness to theta = 25.00	99.4 %
Absorption correction	Multiscan
Max. and min. transmission	0.7456 and 0.5126
Refinement method	Full-matrix least-squares on
F ²	
Data / restraints / parameters	5789 / 1 / 433
Goodness-of-fit on F ²	0.908

Final R indices [$I > 2\sigma(I)$]	R1 = 0.0609, wR2 = 0.1431
R indices (all data)	R1 = 0.1200, wR2 = 0.1626
Absolute structure parameter	2.3(15)
Largest diff. peak and hole	0.376 and -0.270 e. \AA^{-3}



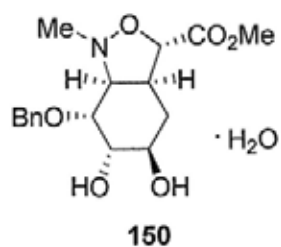
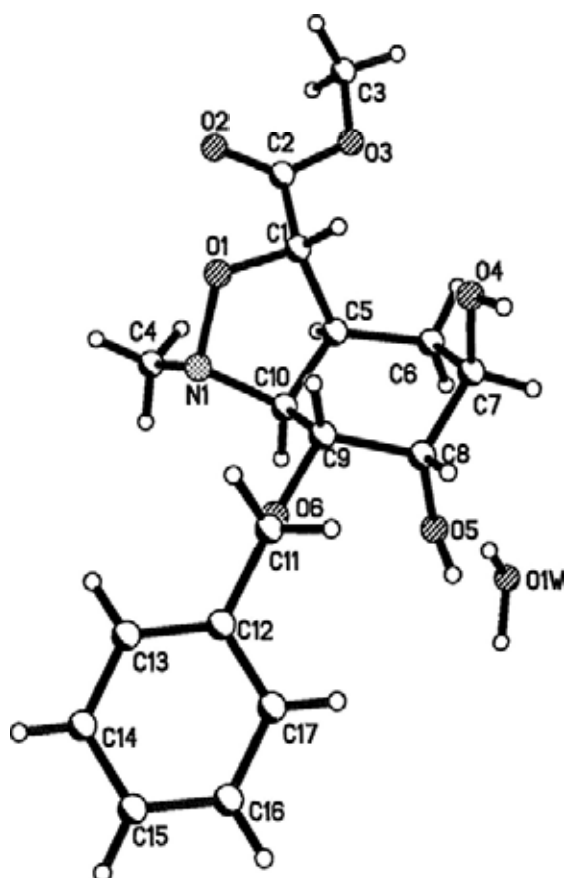
149

X-ray crystallographic data and structure of hydrated diol 150

Table 1. Crystal data and structure refinement for p.

	Identification code	SHR12
	Empirical formula	C17 H25 N O7
	Formula weight	355.38
	Temperature	296(2) K
	Wavelength	0.71073 Å
	Crystal system, space group	Monoclinic, P2(1)2(1)2(1)
deg.	Unit cell dimensions	a = 8.7316(8) Å alpha = 90
deg.		b = 11.9598(11) Å beta = 90
deg.		c = 16.9623(15) Å gamma = 90
	Volume	1771.3(3) Å ³
	Z, Calculated density	4, 1.333 Mg/m ³
	Absorption coefficient	0.103 mm ⁻¹
	F(000)	760
	Crystal size	0.40 x 0.30 x 0.20 mm
	Theta range for data collection	2.08 to 25.25 deg.
	Limiting indices	-10<=h<=10, -14<=k<=14, -
	20<=l<=20	
	Reflections collected / unique	15155 / 1856 [R(int) = 0.0377]
	Completeness to theta = 25.25	100.0 %
	Absorption correction	multi-scan
	Max. and min. transmission	0.7456 and 0.6563
F ²	Refinement method	Full-matrix least-squares on
	Data / restraints / parameters	1856 / 0 / 226
	Goodness-of-fit on F ²	1.086

Final R indices [I>2sigma(I)]	R1 = 0.0427, wR2 = 0.1195
R indices (all data)	R1 = 0.0535, wR2 = 0.1316
Absolute structure parameter	0.6(19)
Largest diff. peak and hole	0.334 and -0.281 e.A ⁻³



X-ray crystallographic data and structure of tribenzoate 160

Table 1. Crystal data and structure refinement for p.

Identification code	SHR65
Empirical formula	C31 H29 N O8
Formula weight	543.55
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 9.897(6) Å alpha = 90 deg.
deg.	b = 11.401(8) Å beta = 90
deg.	c = 24.683(16) Å gamma = 90
Volume	2785(3) Å ³
Z, Calculated density	4, 1.296 Mg/m ³
Absorption coefficient	0.094 mm ⁻¹
F(000)	1144
Crystal size	0.40 x 0.30 x 0.20 mm
Theta range for data collection	1.65 to 25.25 deg.
Limiting indices	-5<=h<=11, -13<=k<=13, -
29<=l<=29	
Reflections collected / unique	16943 / 5034 [R(int) = 0.1148]
Completeness to theta = 25.25	99.9 %
Absorption correction	multi-scan
Max. and min. transmission	0.7456 and 0.4761
Refinement method	Full-matrix least-squares on
F ²	
Data / restraints / parameters	5034 / 0 / 361
Goodness-of-fit on F ²	0.987
Final R indices [I>2sigma(I)]	R1 = 0.0781, wR2 = 0.1676

R indices (all data)

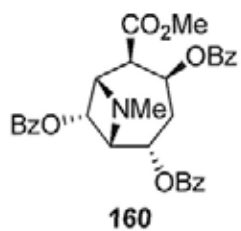
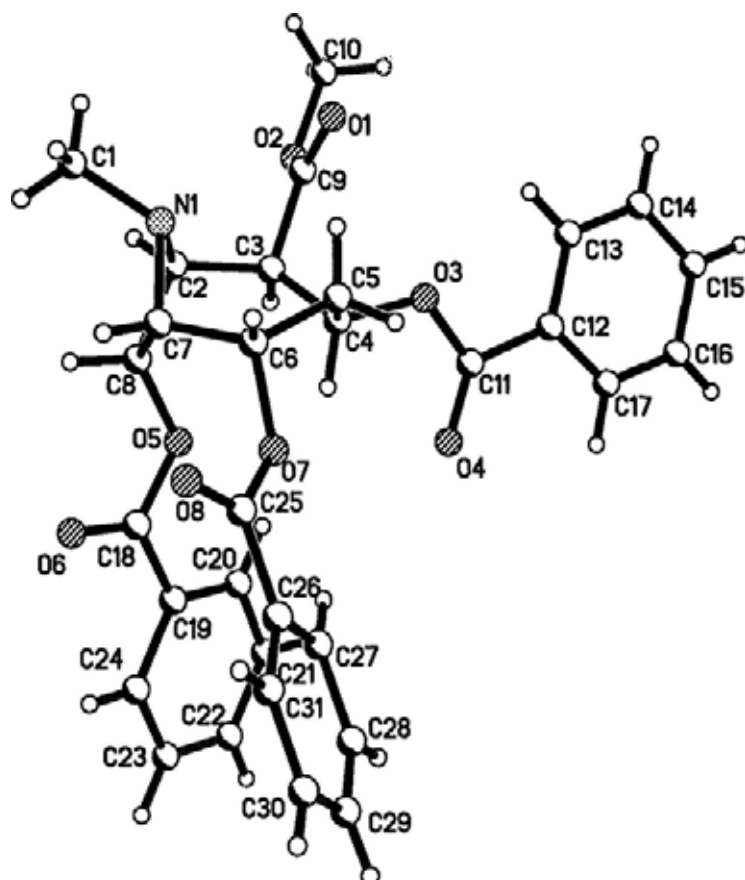
R1 = 0.1712, wR2 = 0.2127

Absolute structure parameter

2(2)

Largest diff. peak and hole

0.399 and -0.274 e.A⁻³

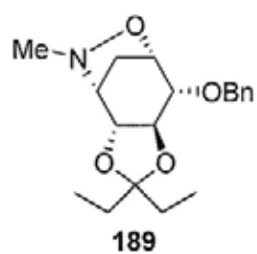
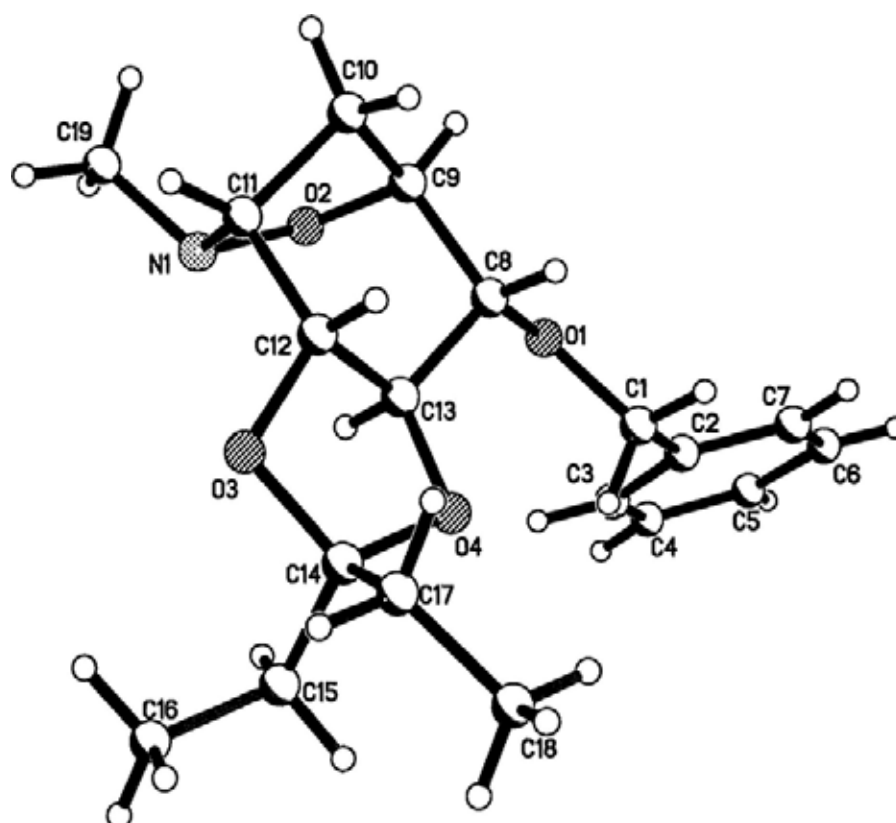


X-ray crystallographic data and structure of isoxazolidine **189**

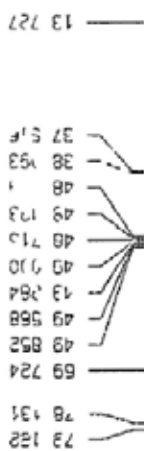
Table 1. Crystal data and structure refinement for p.

Identification code	sha37
Empirical formula	C19 H27 N O4
Formula weight	333.42
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 8.9665(5) Å alpha = 90
deg.	b = 10.5916(7) Å beta = 90
deg.	c = 19.6233(14) Å gamma = 90
deg.	
Volume	1863.6(2) Å ³
Z, Calculated density	4, 1.188 Mg/m ³
Absorption coefficient	0.083 mm ⁻¹
F(000)	720
Crystal size	0.40 x 0.30 x 0.20 mm
Theta range for data collection	2.08 to 25.25 deg.
Limiting indices	-5<=h<=10, -12<=k<=12, -
23<=l<=23	
Reflections collected / unique	13263 / 3375 [R(int) = 0.0487]
Completeness to theta = 25.25	100.0 %
Absorption correction	multi-scan
Max. and min. transmission	0.7456 and 0.6385
Refinement method	Full-matrix least-squares on
F ²	
Data / restraints / parameters	3375 / 0 / 217
Goodness-of-fit on F ²	1.047

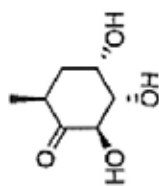
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0435, wR2 = 0.1073
R indices (all data)	R1 = 0.0582, wR2 = 0.1213
Absolute structure parameter	0.6(13)
Largest diff. peak and hole	0.154 and -0.211 e. \AA^{-3}



¹³C NMR (Solvent CD₃OD)



2.1177
ppm

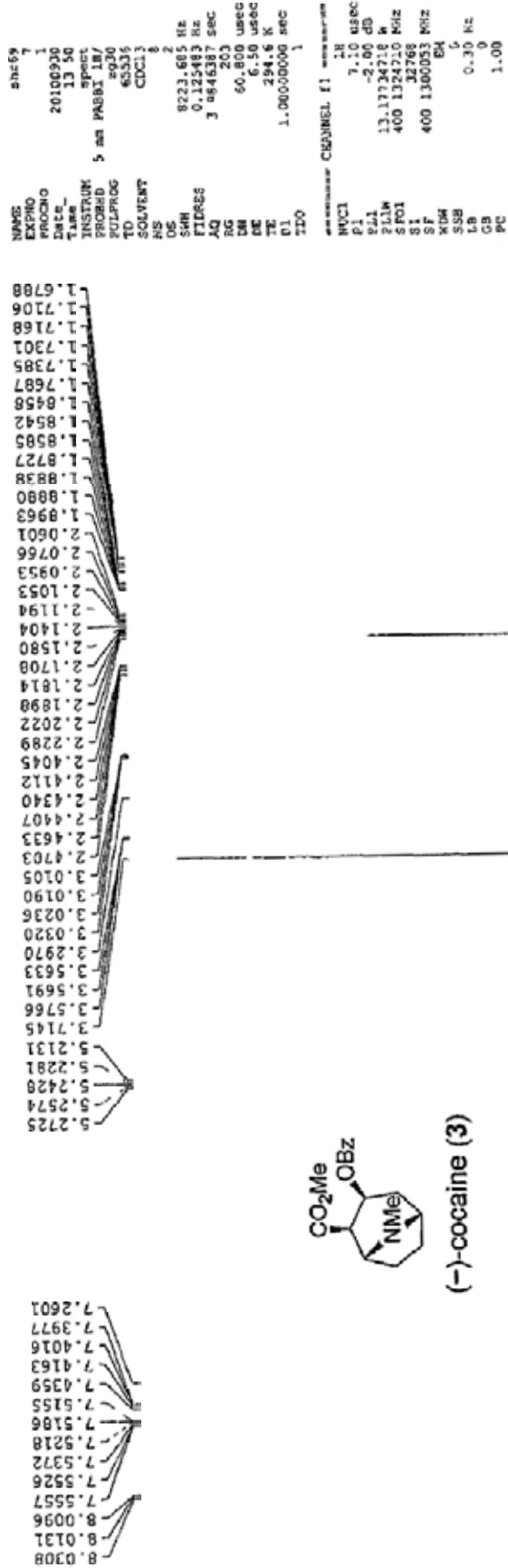


(+)-gabosine F (2).

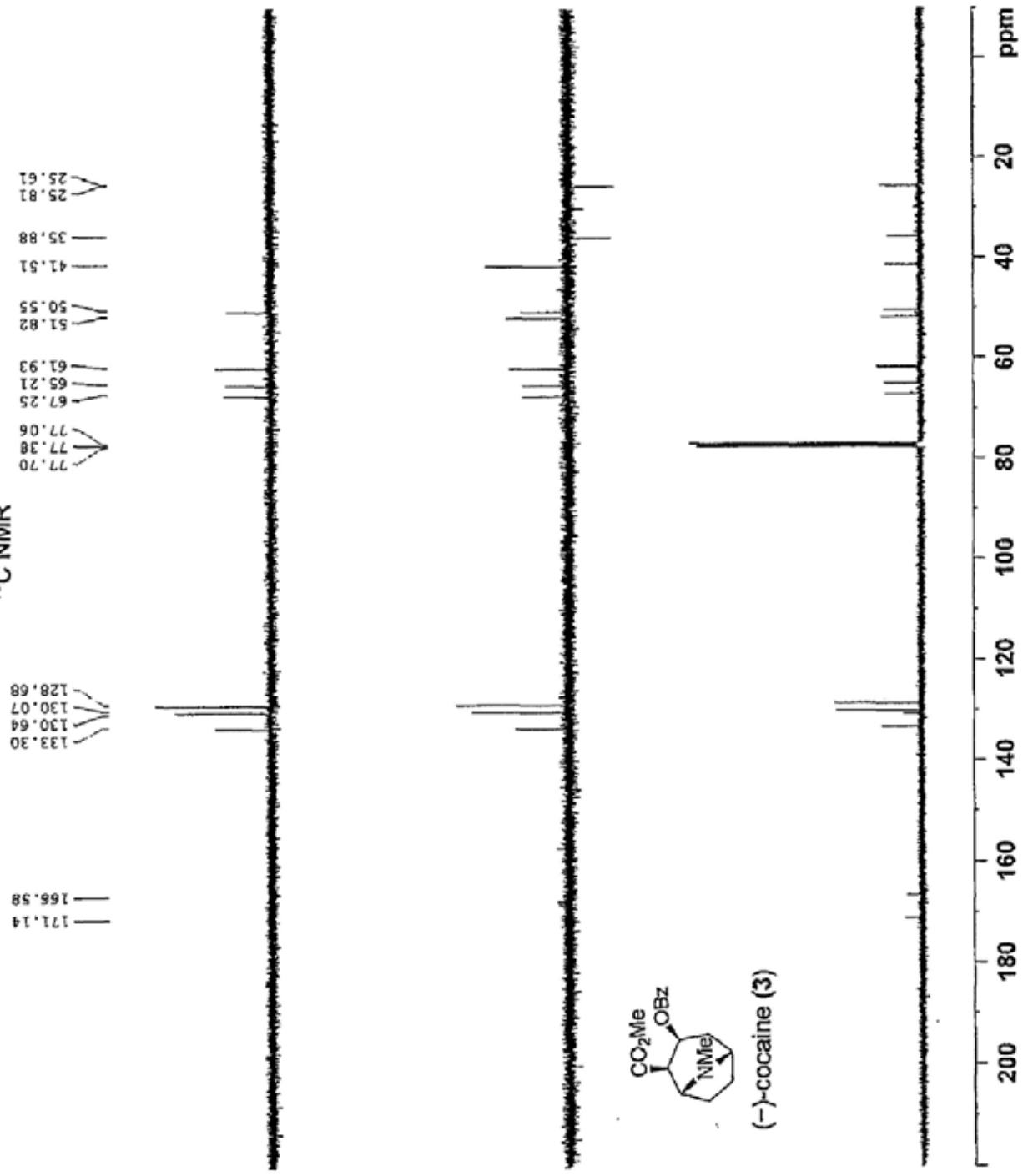
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*PROCNO 1
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NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SFO2 300.1315007 MHz
** CHANNEL f2 **
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NUC2 1H
P2 100.00 usec
PL2 120.00 dB
PL12 19.00 dB
SFO2 300.1315007 MHz
*2 Processing parameters
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RG 4096
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
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CY 11.30 cm
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F 16602.88 Hz
ZP -20.000 ppm
SFO1 125.761 MHz
SFO2 300.1315007 MHz
PC 1.40
  
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¹H NMR



¹³C NMR



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PROCNO 1
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Time_ 12.06
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PULPROG zgpg30
TD 65536
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DS 4
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FIDRES 0.366798 Hz
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RG 203
DM 20.000 usec
DE 6.50 usec
TE 294.7 K
D1 2.0000000 sec
D11 0.0300000 sec
TD0 1

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PL1W 90.2269819 W
SFO1 100.6228258 MHz

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PL3 18.80 dB
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SFO2 400.1316005 MHz
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¹³C NMR

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 PROCNO 1

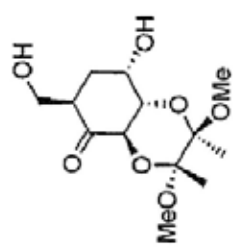
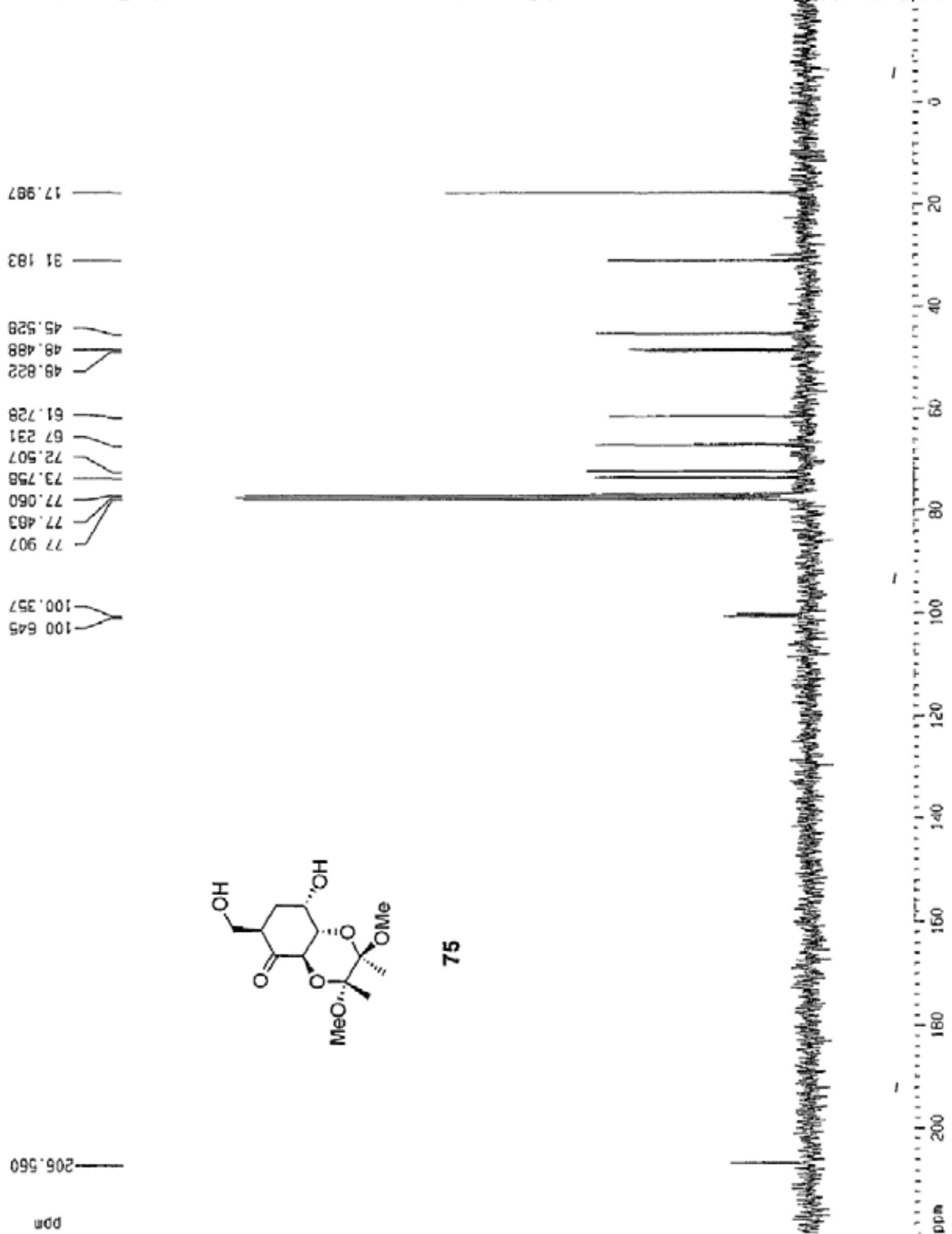
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 FIDRES 0.346004 Hz
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 RG 5160 5
 DM 22.050 usec
 DE 6.00 usec
 IE 0 0 K
 D1 1 000000.00 sec
 D11 0 030000.00 sec
 ACQRES 0 000000.00 sec
 ANRES 0 015000.00 sec

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 SF01 75.4745111 MHz

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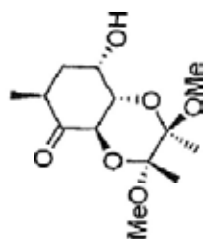
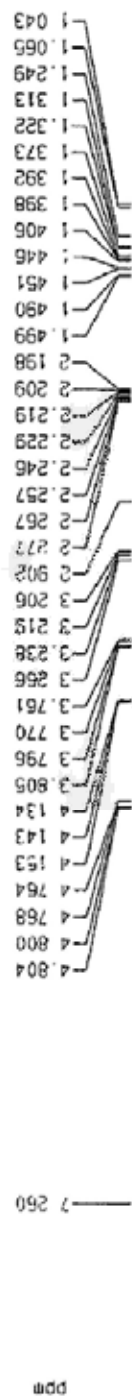
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75

¹H NMR



77

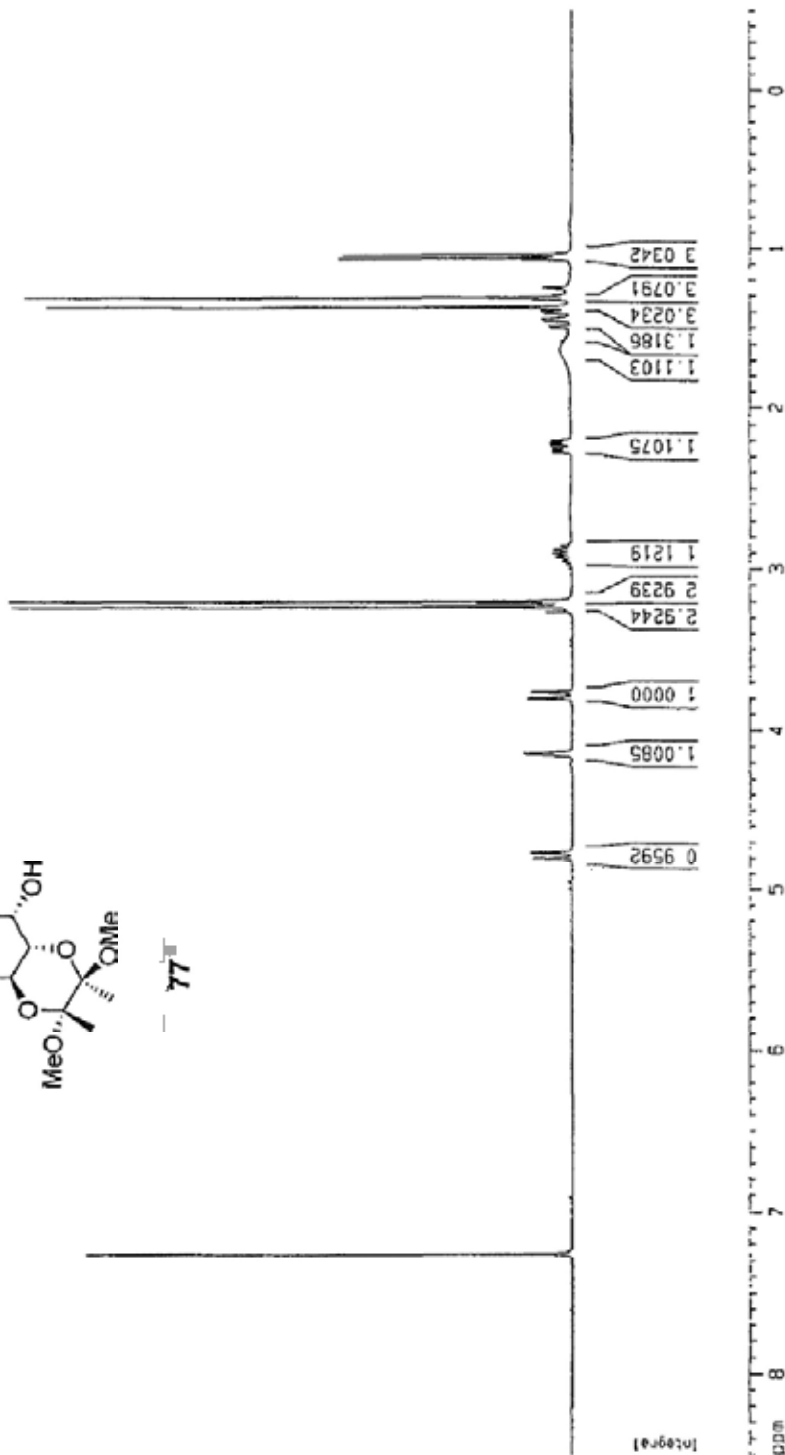
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 PROCNO 1

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 FIDRES 0.274438 Hz
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 ACQRES 0.0000000 SEC
 HCHW 0.0150000 SEC

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 PL1 -2.00 dB
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F2 - Processing parameters
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 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
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 F2 2551.10 Hz
 F3 -0.500 ppm
 F4 -150.07 Hz
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 GYOH 172.78845 Hz/cm



Current Data Parameters
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 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
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 d11 0.0300000 sec
 MCREST 0.0000000 sec
 MCKRR 0.0150000 sec

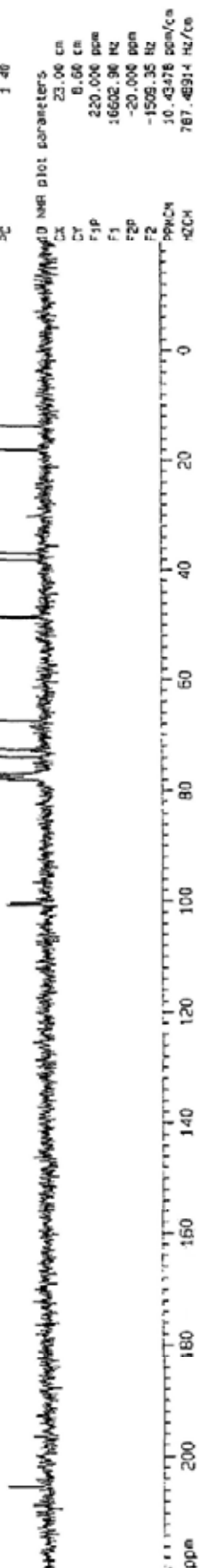
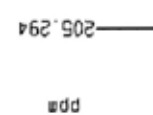
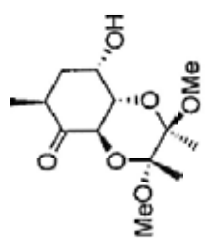
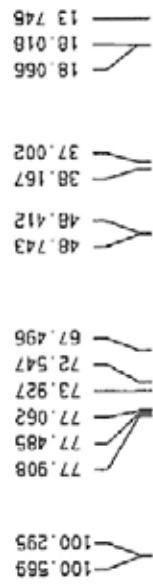
***** CHANNEL f1 *****
 NUC1 13C
 P1 3.00 usec
 PL1 -5.00 dB
 SF01 75.474511 MHz

***** CHANNEL f2 *****
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 usec
 PL2 120.00 dB
 PL12 19.00 dB
 SF02 300.1315007 MHz

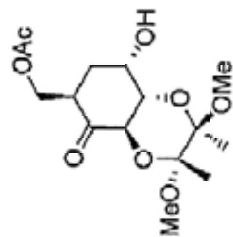
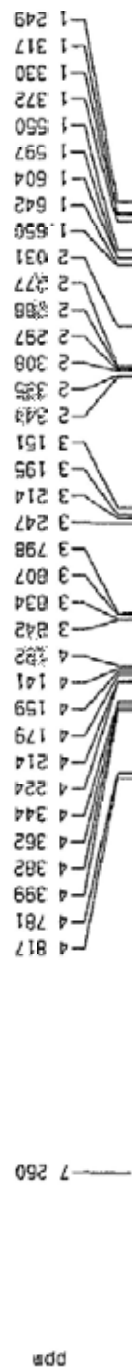
F2 - Processing parameters
 SI 65536
 SF 75.4677143 MHz
 RG 655
 SFO 0
 LB 3.00 Hz
 GB 0
 CB 0
 SC 1.40

F2 - NMR plot parameters
 CK 23.00 cm
 CY 8.66 cm
 F1P 220.000 ppm
 F1 16602.96 Hz
 F2P -20.000 ppm
 F2 -1505.35 Hz
 PPMCH 10.4328 ppm/ce
 XCH 787.49314 Hz/ce

¹³C NMR



¹H NMR



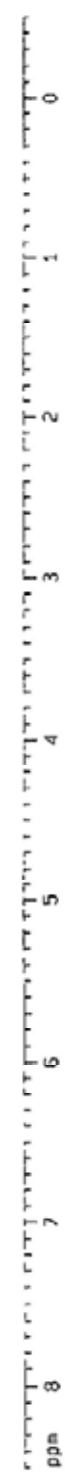
Current Data Parameters
 NAME snf13c
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20071105
 Time 10 13
 INSTRUM dpx300
 PROBHD 5 mm BBO BB-1H
 PULPROG zg
 TD 32768
 SOLVENT CCCl3
 NS 16
 DS 0
 SWH 8882.806 Hz
 FIDRES 0.274439 Hz
 AQ 1.8219508 sec
 RG 362
 DN 55.600 usec
 DE 79.43 usec
 TE 0.0 K
 D1 1.00000000 sec
 ACQEST 0.00000000 sec
 NUC1 1H
 P1 5.00 usec
 PL1 -2.00 dB
 SF01 300.1312800 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300663 MHz
 NUX EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

10 NMR plot parameters
 CX 22.00 cm
 CY 11.15 cm
 F1P 8.500 ppm
 F1 2551.10 Hz
 F2P -0.500 ppm
 F2 -150.07 Hz
 PPMCM 0.40369 ppm/cm
 AZCM 122.78066 Hz/cm

***** CHANNEL f1 *****



¹³C NMR

Current Data Parameters
 NAME snf13carbomic
 EXPNO 1
 PROCNO 1

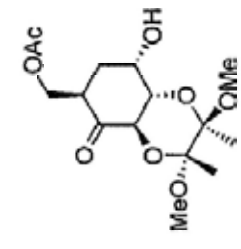
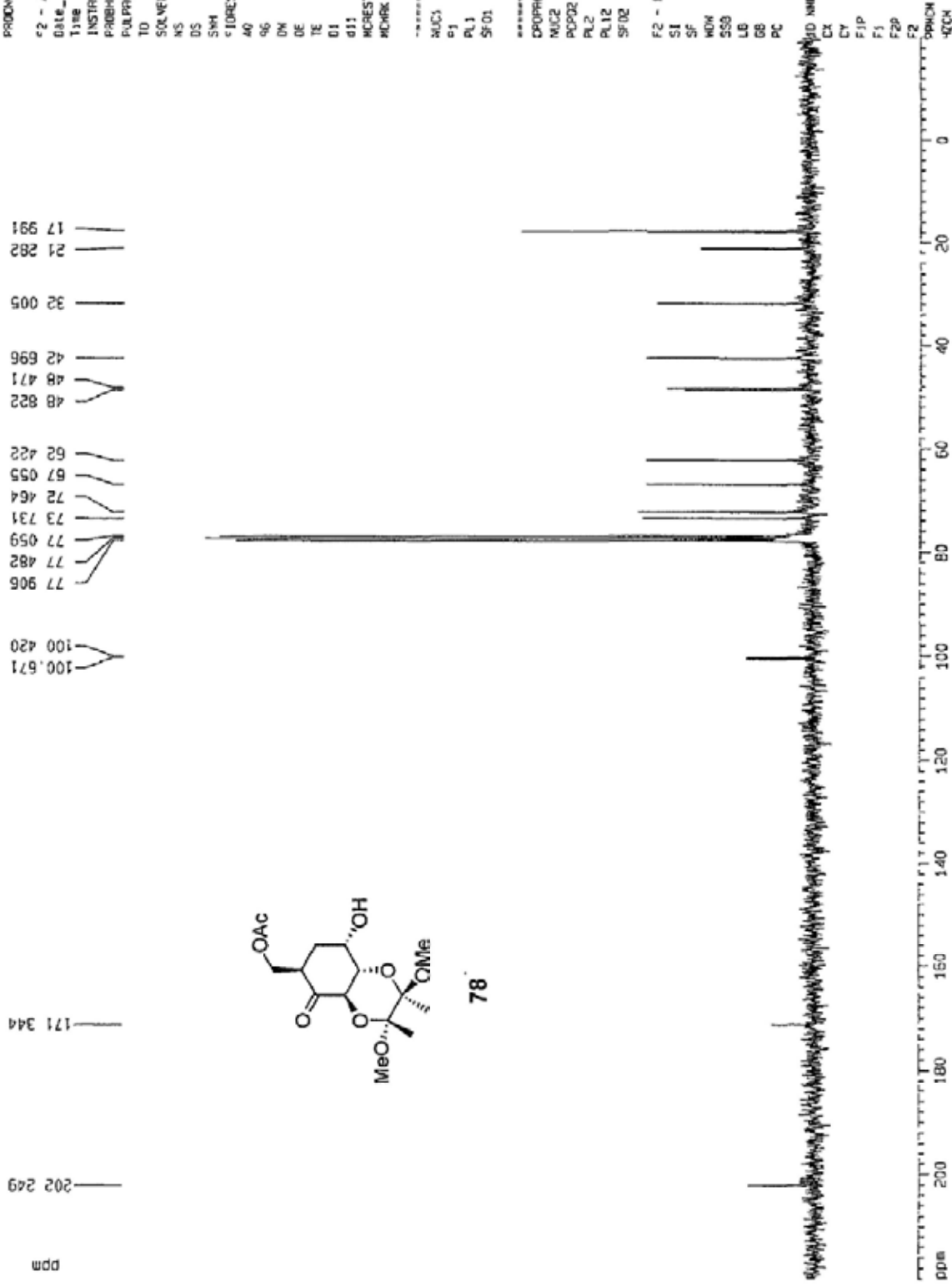
F2 - Acquisition Parameters
 Date_ 20071123
 Time 16.16
 INSTRUM spect
 PULPROG zgpg30
 FREQ0 500.136
 TD 65536
 SOLVENT MeOD
 NS 430
 DS 0
 SWH 22675.736 Hz
 FIDRES 0.346304 Hz
 AQ 1.4651188 Sec
 RG 5792.6
 DN 22.050 usec
 DE 6.00 usec
 TE 0.0 K
 D1 1.0000000 Sec
 d11 0.0300000 Sec
 ACQRES 0.0300000 Sec
 PCPRG2 0.0150000 Sec

***** CHANNEL f1 *****
 NUC1 13C
 P1 3.00 usec
 PL1 -6.00 dB
 SF01 75.4745111 MHz

***** CHANNEL f2 *****
 CPDPRG2 MBLD3E
 NUC2 1H
 PCDPRG 100.00 usec
 PL2 120.00 dB
 PL12 19.00 dB
 SF02 300.1315007 MHz

F2 - Processing parameters
 SI 65536
 SF 75.4677135 MHz
 MDW FH
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40

***** NMR plot parameters *****
 CX 23.00 cm
 CY 11.21 cm
 F1P 220.000 ppm
 F1 16502.90 Hz
 F2P -20.000 ppm
 F2 -1509.35 Hz
 GPCN 10.43478 ppm/Hz
 HZCN 787.46920 Hz/Hz



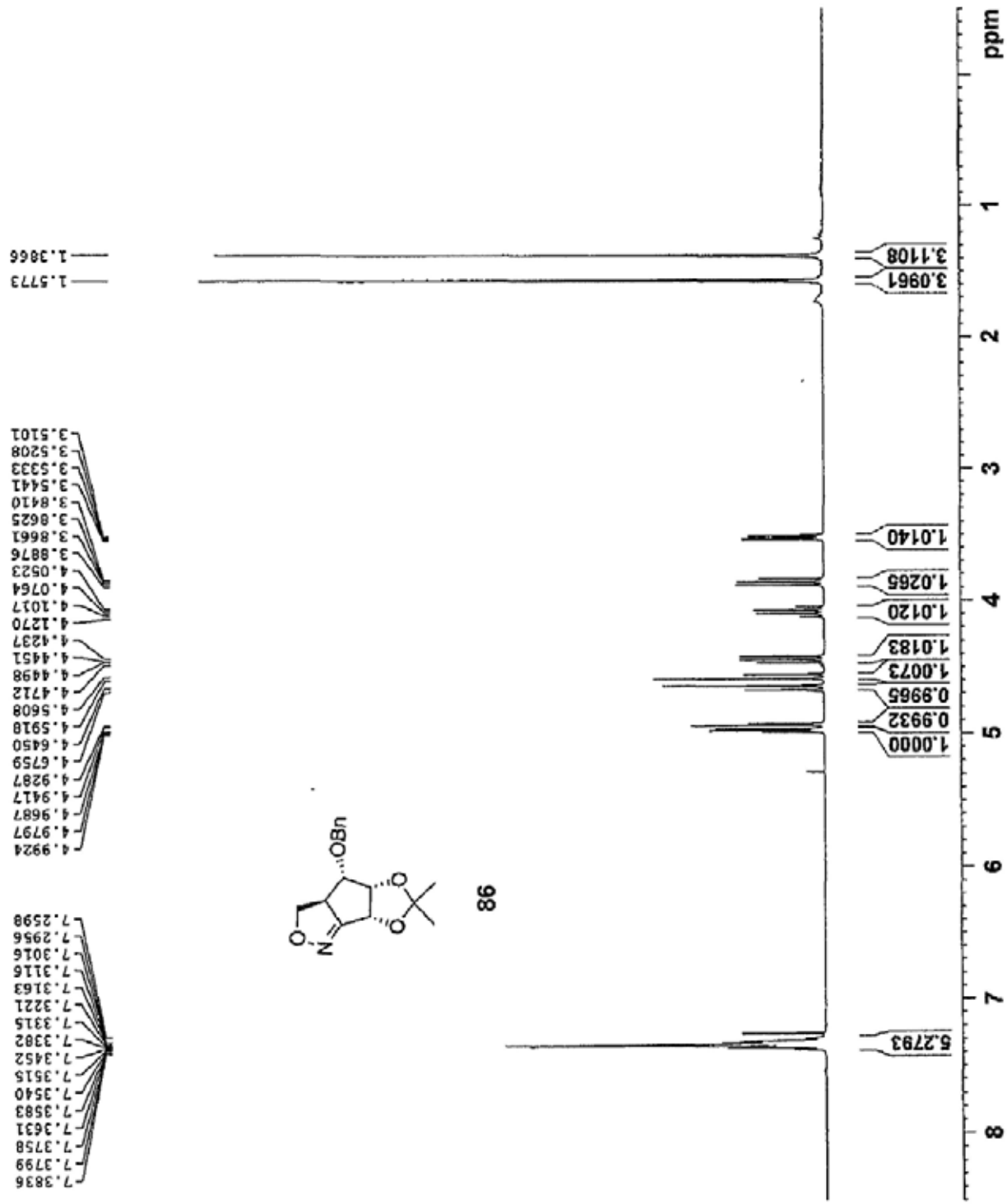
78

¹H NMR

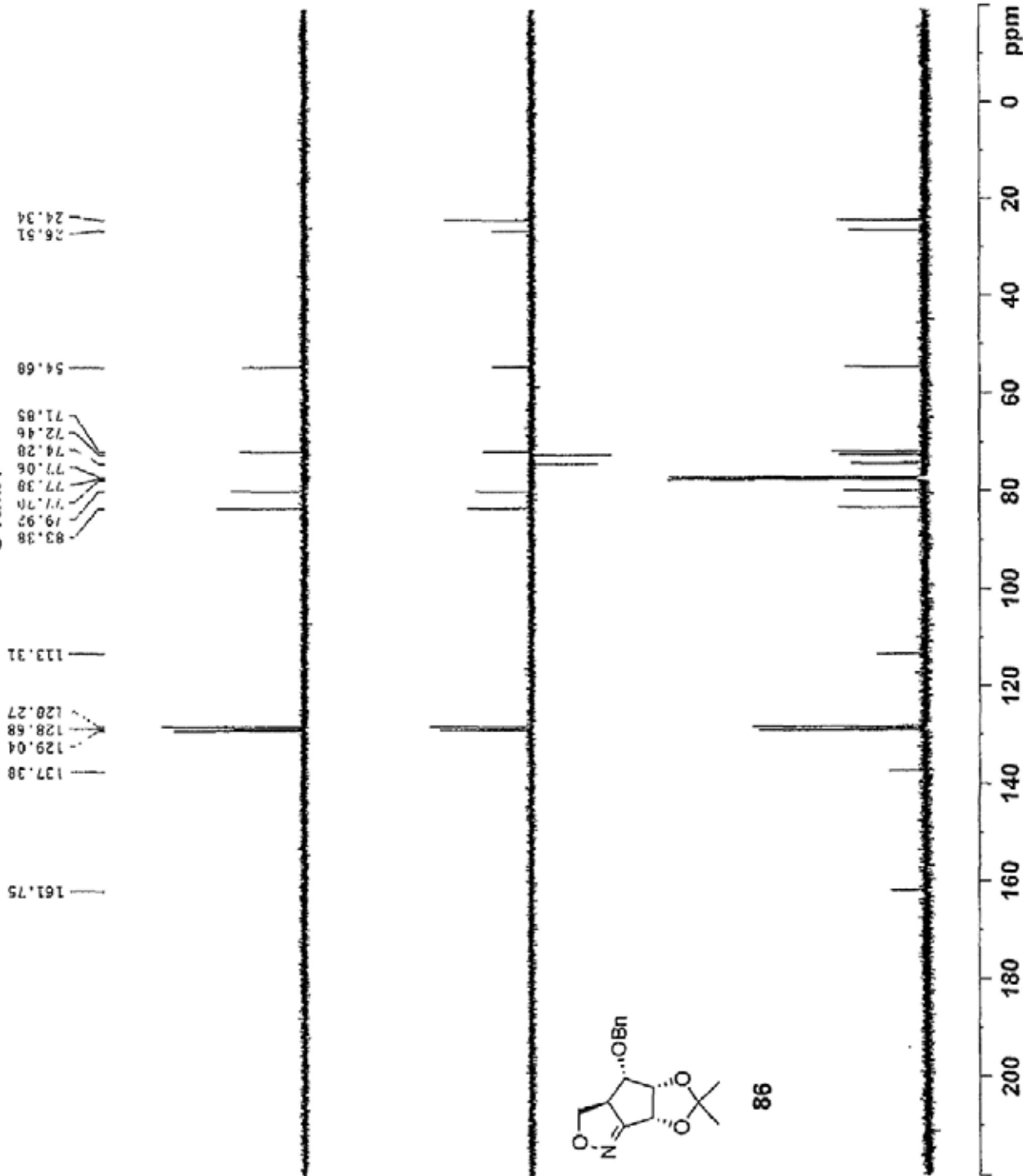
```

NAME:                               shd0
EXPNO:                               1
PROCNO:                              1
Date_   :                           20081114
Time    :                            15.48
INSTRUM:                             spect
PROBHD: 5 mm PABOL 13C
PULPROG:                              zg30
TD      :                             65536
SOLVENT :                             CDCl3
NS      :                              4
DS      :                              2
SWH     : 8223.685 Hz
FIDRES : 0.125483 Hz
AQ      : 3.3846387 sec
RG      : 101
DK      : 60.800 usec
DE      : 6.30 usec
TE      : 293.2 K
TA      :
TT0    : 1.00000000 sec

***** CHANNEL f1 *****
NUC1   : 1H
P1     : 14.83 usec
PL1    : 0.00 dB
PL1M   : 8.31434441 W
SFO1   : 400.1324710 MHz
SI     : 32768
SF     : 400.1380046 MHz
WDW    : EM
SSB    : 0
LB     : 0.30 Hz
GB     : 0
PC     : 1.00
  
```



¹³C NMR



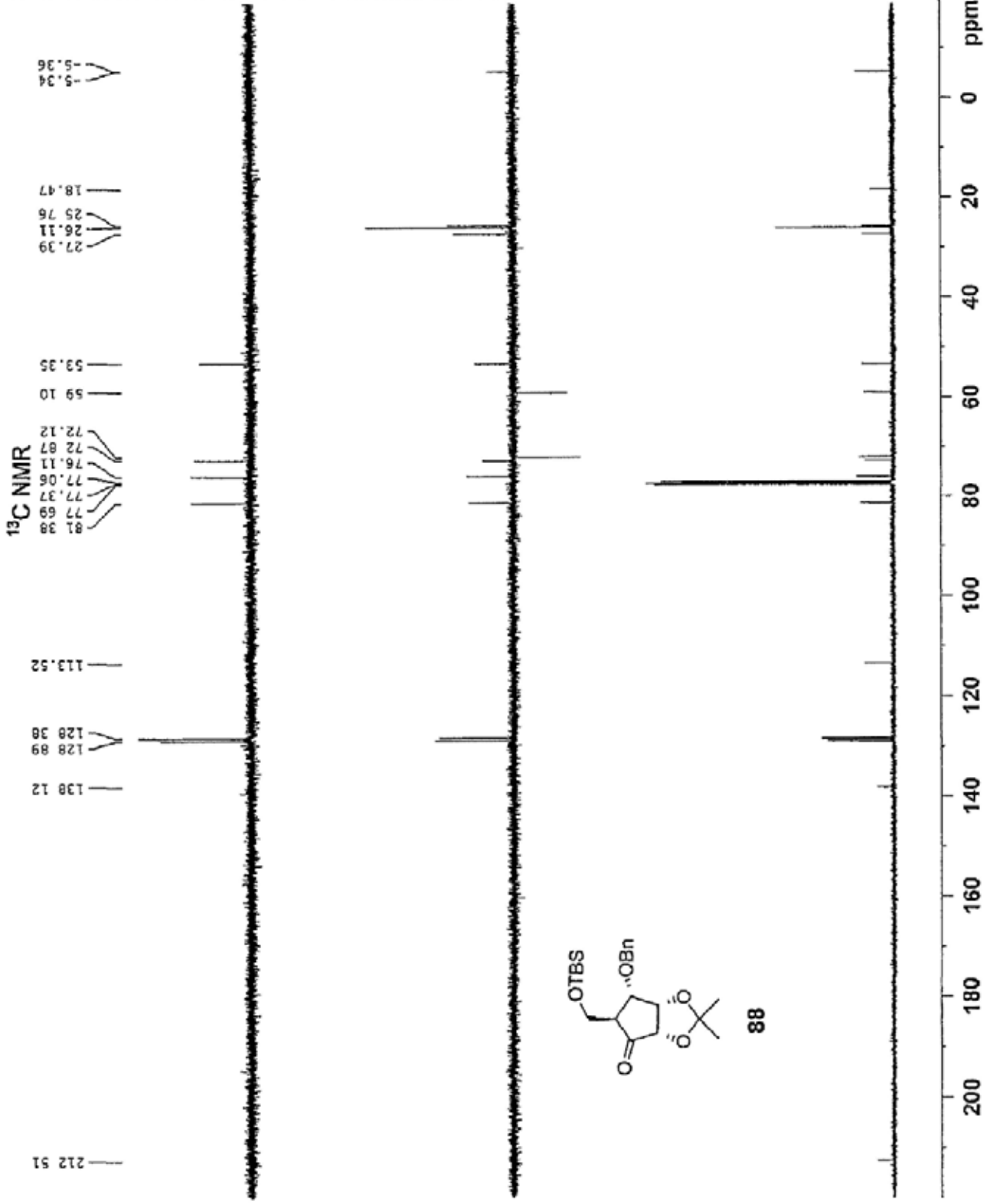
NAME eth10carbon
EXENO 2
PROCNO 1
EXPNO 20100924
Time 11.09
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 123
DS 4
SNK 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
CW 20.800 usec
DE 6.50 usec
TE 294.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 ¹³C
P1 14.50 usec
PL1 -1.00 dB
EL1 90.22698615 Hz
SFO1 100.6228298 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 ¹H
PCPD2 80.00 usec
PL2 -2.00 dB
EL2 18.80 dB
ELI3 18.80 dB
PL2W 13.17734718 W
ELI2W 0.10960442 W
ELI3W 0.10960442 W
SFO2 400.1315005 MHz
SI 32768
SF 100.6127353 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.60


```

Current Date Parameters
NAME          JH11601001
PROCNO       1
===== Acquisition Parameters =====
Date_         20050811
Time         13:59
INSTRUM      spect
PROBHD       5 mm PABUL 13C
PULPROG      zgpg30
NUC1         13C
NUC2         13C
SOLVENT      CDCl3
MS           177
RG          24000
AQ          0.34000000
RG          1.00000000
AD          1.00000000
AB          1.00000000
SFO          200
AQ          20.00000000
RG          1.00000000
SFO          200.62500000
AQ          2.00000000
RG          1.00000000
SFO          0.00000000
===== CHANNEL f1 13C =====
NUC1         13C
P1           9.00 usec
PL1          -0.00 dB
PL1M         -1.00000000
SFO1         100.625000 MHz
===== CHANNEL f2 =====
COPROG2     zgpg30
NUC2         13C
P2           0.00 usec
PL2          0.00 dB
PL2M         -1.00000000
SFO2         100.625000 MHz
===== Processing parameters =====
SI          32768
SF          100.625000 MHz
WDW         EM
SSB         0
LB          1.00 Hz
GB          0
PC          1.00
  
```



¹H NMR

```

NAME                               sh16
EXPNO                               1
PROCNO                               1
Date_                                20081208
Time_                                13.06
INSTRUM                             spect
PROBHD                               5 mm PABBO 13C
PULPROG                             zgpg30
SOLVENT                               CDCl3
NS                                   15
DS                                   2
SWH                                     8273.685 Hz
F2                                     0.125483 Hz
AQ                                     3.9846387 sec
RG                                     203
EN                                     60.800 usec
DE                                     6.50 usec
TE                                     294.7 K
D1                                     1.00000000 sec
TD0                                   1
===== CHANNEL f1 =====
NUC1                                  1H
P1                                     14.83 usec
PL1                                    0.00 dB
SFO1                                  6.21336431 M
SF01                                  400.1324710 MHz
SI                                     32768
SF                                     400.13000000 MHz
WDW                                    EM
SSB                                    0
GB                                     0.30 Hz
PC                                     1.00
  
```

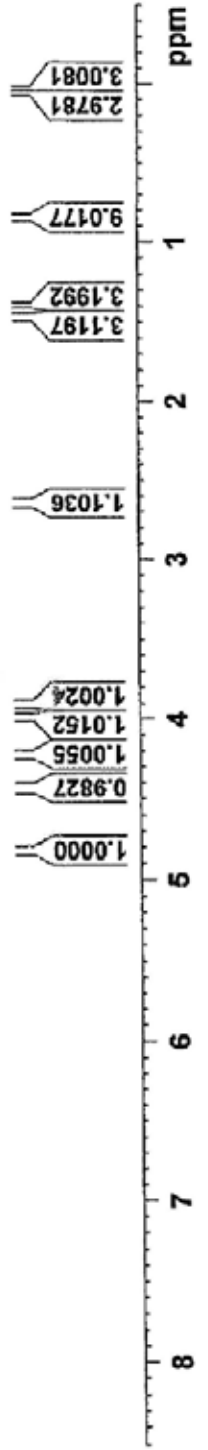
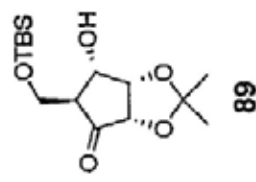
0.0332
0.0543

0.8487

1.3967
1.4680

2.6221
2.6250
2.6326
2.6431
2.6536
2.6614
2.6642
3.8842
3.8925
3.9092
3.9175
3.9692
3.9793
3.9942
4.0043
4.2137
4.2167
4.2267
4.2297
4.4132
4.4246
4.4342
4.4456
4.8062
4.8185
4.8307

7.2600



¹H NMR

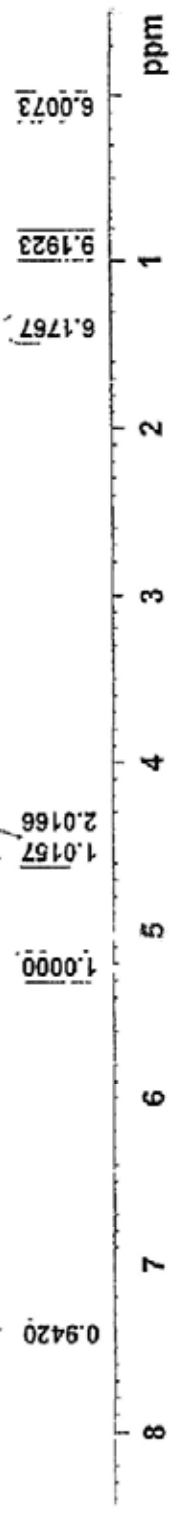
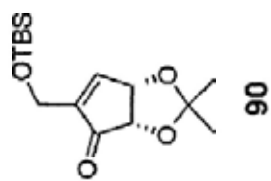
NAME
 EXPNO 1
 PROCNO 1
 Date_ 20101021
 Time 12.40
 INSTRUM spect
 PROBRD 5 mm PAULI-13C
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 8225.685 Hz
 FIDRES 0.125483 Hz
 AQ 3.9846387 sec
 RG 203
 DM 60.800 usec
 DE 6.50 usec
 TE 294.5 K
 D1 1.00000000 sec
 TDO 1

----- CHANNEL f1 -----
 NUC1 13H
 ST 14.83 usec
 PL1 0.00 dB
 SFO 400.1324210 MHz
 SF 400.1324210 MHz
 ST 32768
 SFO 400.1300004 MHz
 EM G
 NS 6
 DS 0
 SWH 6.30 Hz
 ZG 0
 ZC 1.00

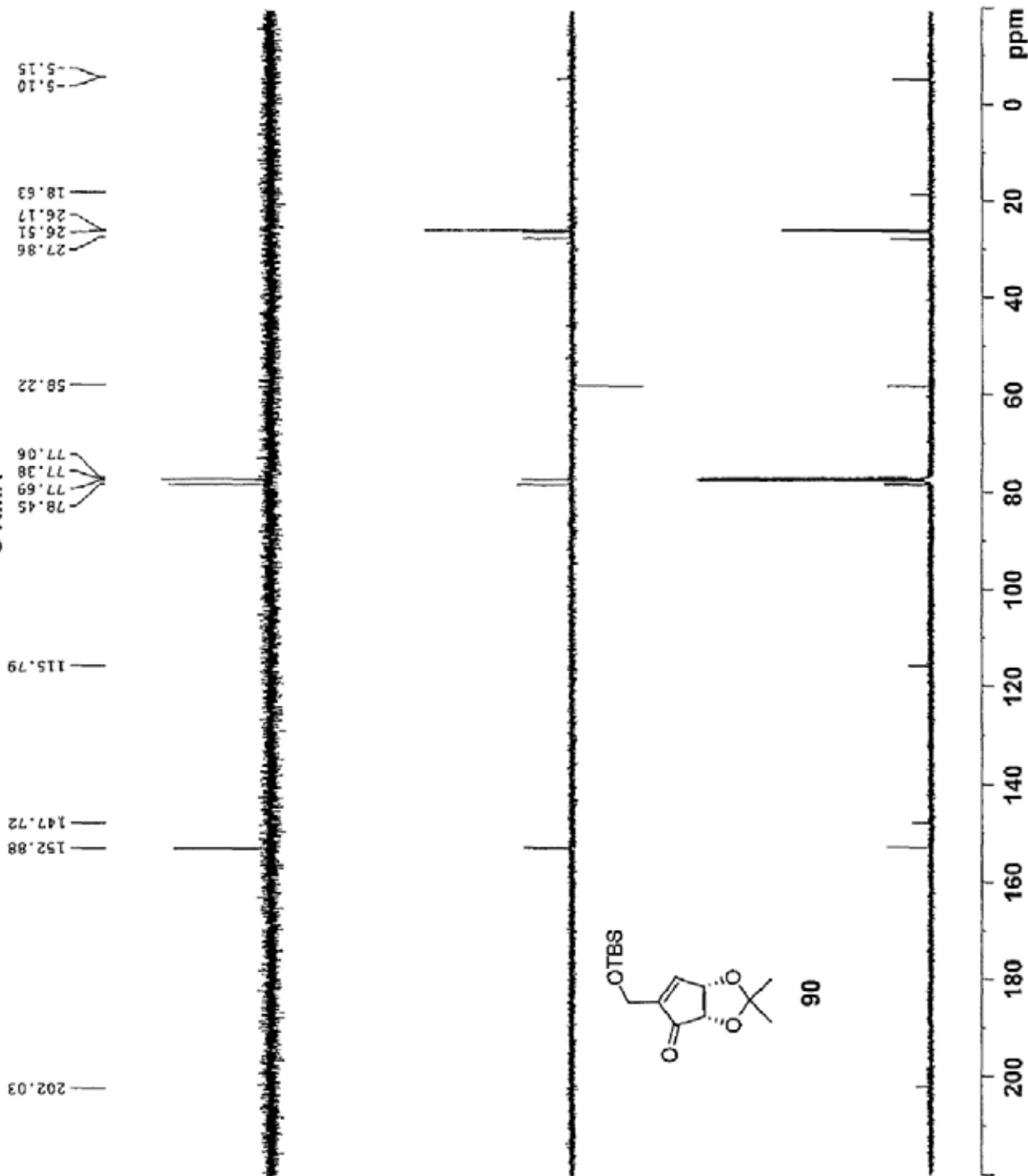
0.0781
 0.0709
 0.9107
 1.4032
 1.4105
 1.6077

4.2598
 4.3643
 4.3690
 4.5226
 4.5361
 5.2087
 5.2130
 5.2187
 5.2227
 5.2266
 5.2322
 5.2366

7.4342
 7.4290
 7.4237
 7.4186
 7.2602



¹³C NMR



NAME sh:9earbon
EXPNO 2
PROCNO 1
Date_ 20101021
Time_ 12:57
INSTRUM spect
PROBHD 5 mm PABUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 305
DS 4
SWH 24038.461 Hz
FIDRES 0.366786 Hz
AQ 1.3631986 sec
RG 203
DM 20.800 usec
DE 6.50 usec
TE 295.4 K
O1 2.0000000 sec
C11 6.0300000 sec
T100 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.68 usec
PL1 -0.60 dB
PL1N 41.24164963 Hz
SFO1 100.6228298 MHz

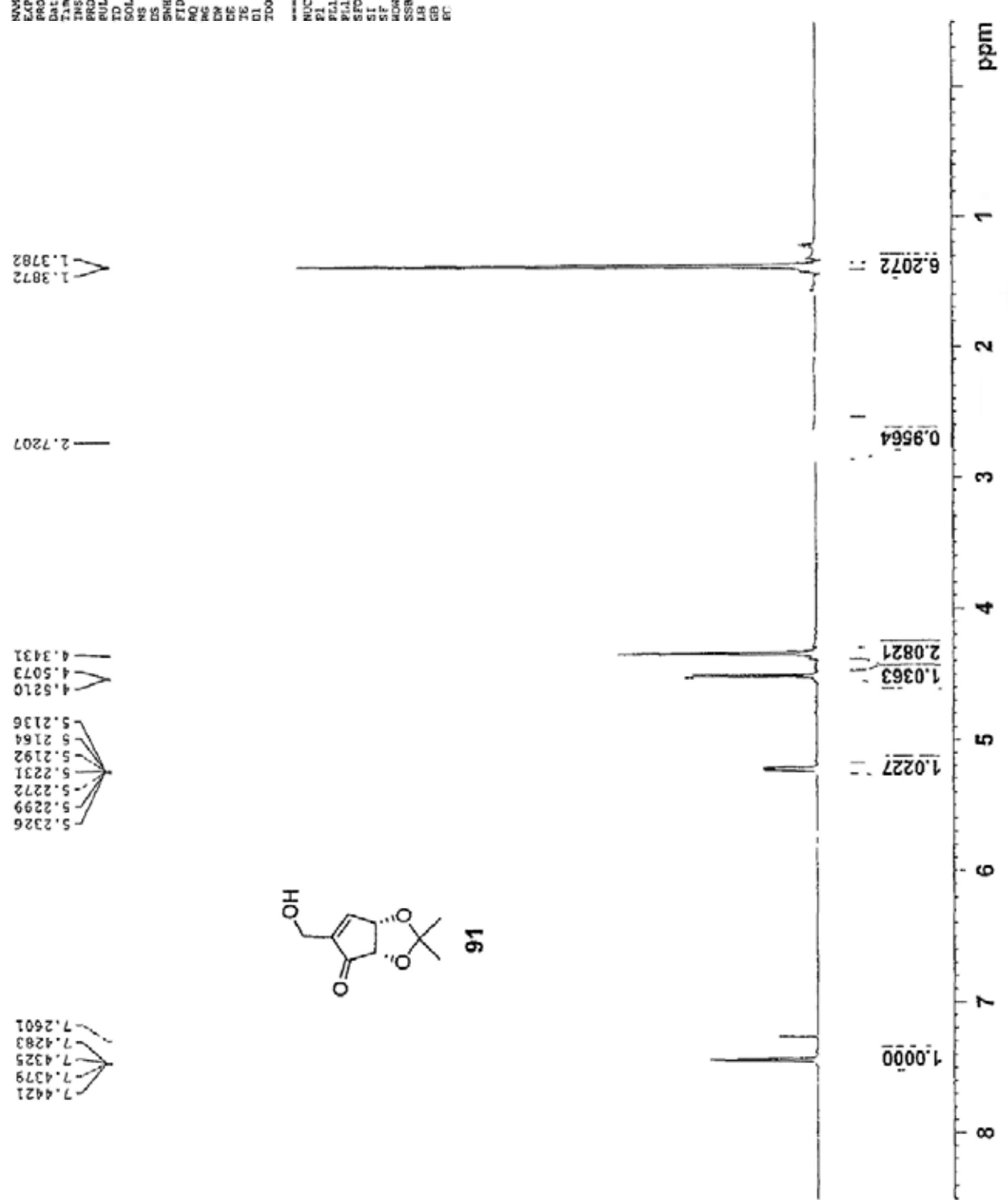
===== CHANNEL f2 =====
CFPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL2 15.66 dB
PL3 15.92 dB
PL2H 8.3143441 Hz
PL2N 0.22585411 Hz
PL3W 0.21272903 Hz
SFO2 400.1316005 MHz
SI 32768
SF 100.6127331 MHz
WDW EM
SSB 0
LB 0
GB 0
PC 1.40

```

NAME          AB30
EXPNO         2
PROCNO        1
DATE_         20101006
TIME         18:09
INSTRUM       spect
PROBHD        5 mm PABBO1 1H7
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            4
DS            2
SFO          8123.635 Hz
SFRES        0.125483 Hz
AQ           3.9846337 sec
RG           32
DM           60.800 usec
DE           6.50 usec
TE           294.1 K
D1           1.00000000 sec
ZOO          1

***** CHANNEL f1 *****
NUC1          1H
P1           7.10 usec
PL1          -2.00 dB
PL12         13.17734718 W
SFO1         400.1324710 MHz
SI           32768
SF           400.1300001 MHz
WDW          EM
SSB          0
LR           0.30 Hz
GB           0
PC           1.00
  
```

¹H NMR

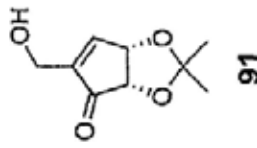


¹H NMR (Solvent: CDCl₃-D₂O)

7.4373
7.4340
7.2602

5.2297
5.2268
5.2229
5.2190
5.2165
5.2135
4.7629
4.5204
4.5069
4.3279

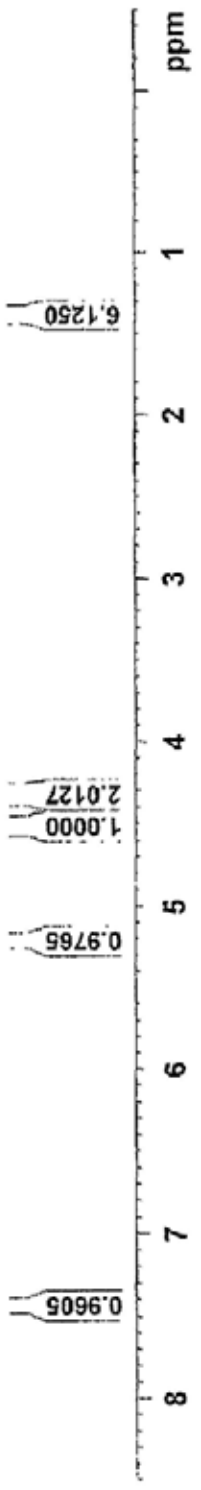
1.3856
1.3766

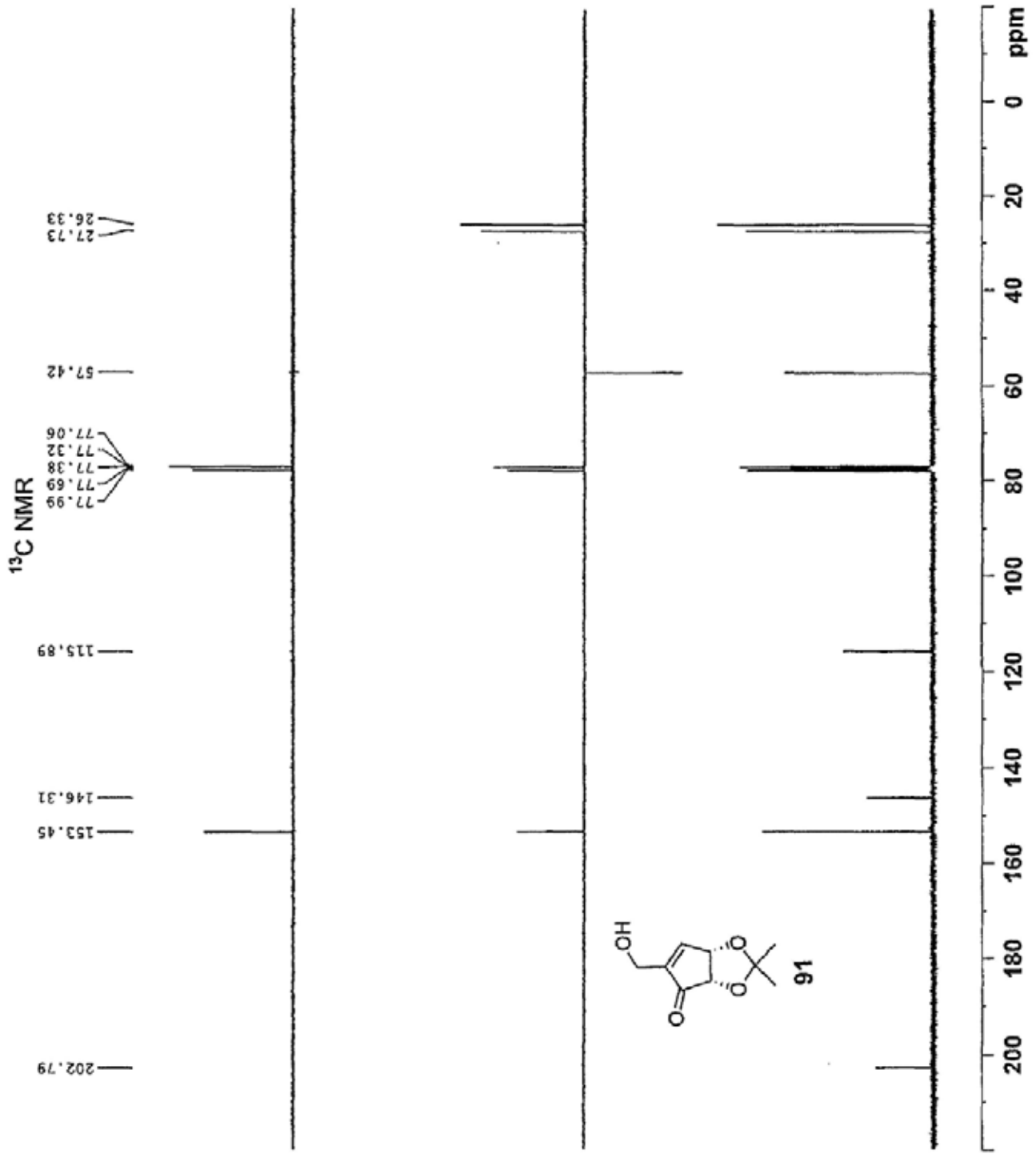


```

NAME          sh10020
EXPNO         1
PROCNO        1
Date_         20101006
Time          19.18
INSTRUM       spect
PROBHD        5 mm PWBH11N7
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            4
DS            2
SHR           8223.695 Hz
FIDRES        0.125483 Hz
AQ            3.9816387 sec
RG            32
EW            60.800 usec
DC            6.50 usec
TE            294.1 K
D1            1.00000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          1H
P1            7.10 usec
PL            -2.00 dB
PL1          13.17734718 dB
PL1N         400.1324710 MHz
SFO1         400.1324710 MHz
SI           32768
SF           400.1300053 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
    
```





```

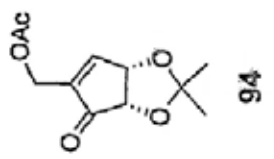
NAME          sh30carbon
EXPNO         2
PROCNO        1
Date_         20101005
Time_        10.37
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            65
DS            4
SME           24038.461 Hz
FIDRES        0.366788 Hz
AQ            1.363188 sec
RG            228
DE            20.800 usec
TE            298.5 K
D1            2.0000000 sec
D11           0.0300000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          13C
P1            9.90 usec
PL1           -2.00 dB
PL1W          55.33689499 Hz
SFO1          100.6278183 MHz

===== CHANNEL f2 =====
CFDPRG2       waiczi6
NUC2          1H
P2            90.00 usec
PL2           -1.00 dB
PL2W          15.16 dB
PL13         18.62 dB
PL2W         13.56617059 W
PL12W        0.32844096 W
PL13W        0.14806664 W
SFO2          400.1916008 MHz
SI            32768
SF            100.6278263 MHz
WDW           EM
SSB           0
GB            1.00 Hz
PC            1.60
  
```

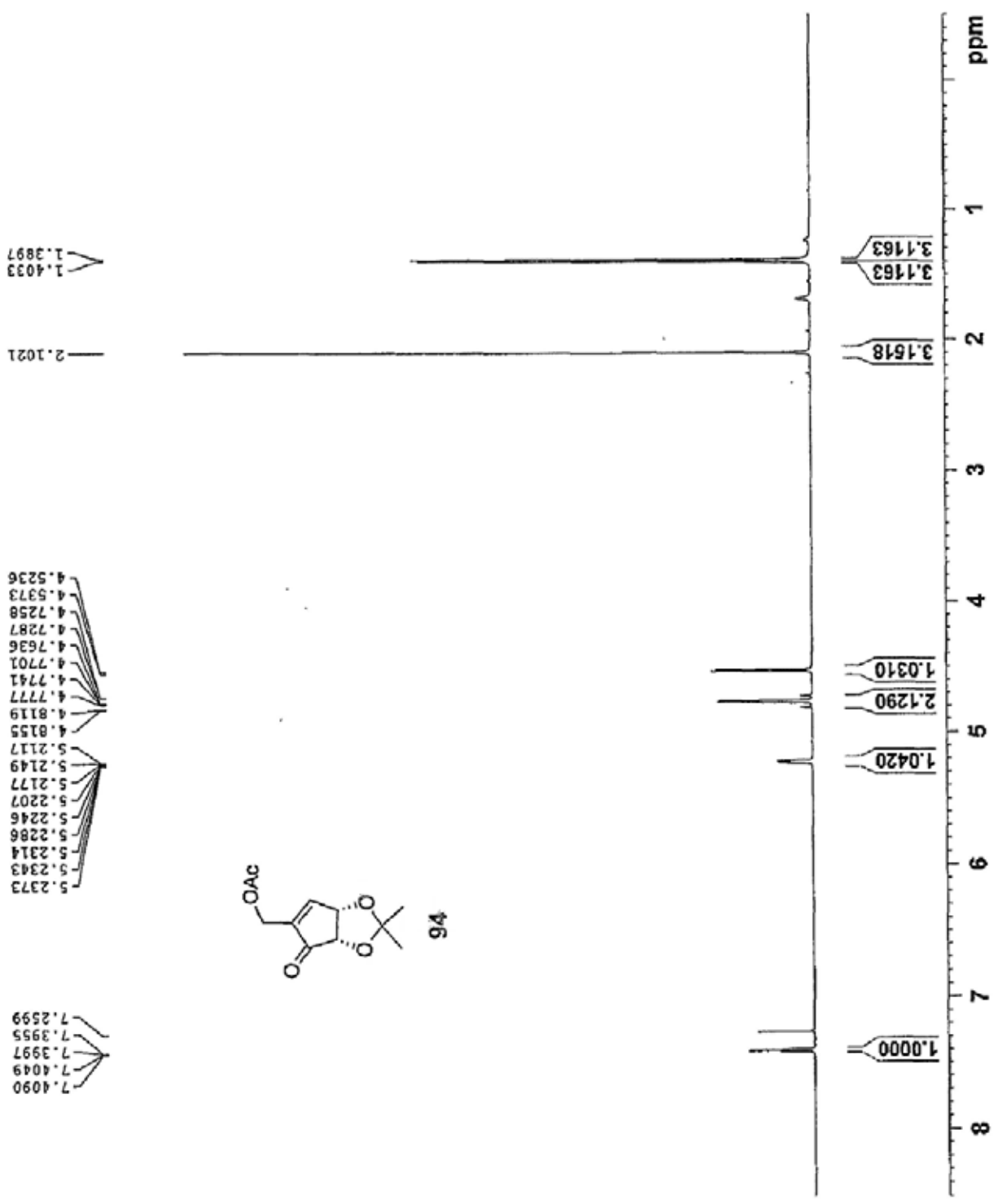

¹H NMR

- 7.4090
- 7.4049
- 7.3997
- 7.3955
- 7.2599
- 5.2373
- 5.2343
- 5.2314
- 5.2286
- 5.2246
- 5.2207
- 5.2177
- 5.2149
- 5.2117
- 4.8155
- 4.8119
- 4.7777
- 4.7741
- 4.7701
- 4.7636
- 4.7287
- 4.7258
- 4.5973
- 4.5236
- 1.4033
- 1.3897

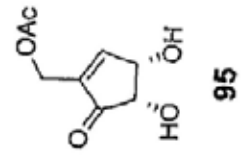


NAME sh31
 EXPNO 3
 F2PROC 1
 Date_ 20090212
 Time 15.35
 INSTRUM spect
 PULPROG 5 mm PABUL 13C
 PRGNAME 6230
 SOLVENT CDCl3
 NS 4
 DS 2
 SMR 8223.685 Hz
 FIDRES 0.125483 Hz
 AQ 3.9846387 sec
 RG 144
 RW 60.800 usec
 EX 6.50 usec
 ZE 285.4 K
 TE 1.0000000 sec
 TDL 1
 TDO

***** CHANNEL f1 *****
 NUC1 13
 P1 14.83 usec
 PL1 0.00 dB
 FLLW 8.3143441 N
 SFO1 400.1328710 MHz
 SI 32768
 SF 400.1300040 MHz
 ZR
 GB 0.30 Hz
 G0 1.00

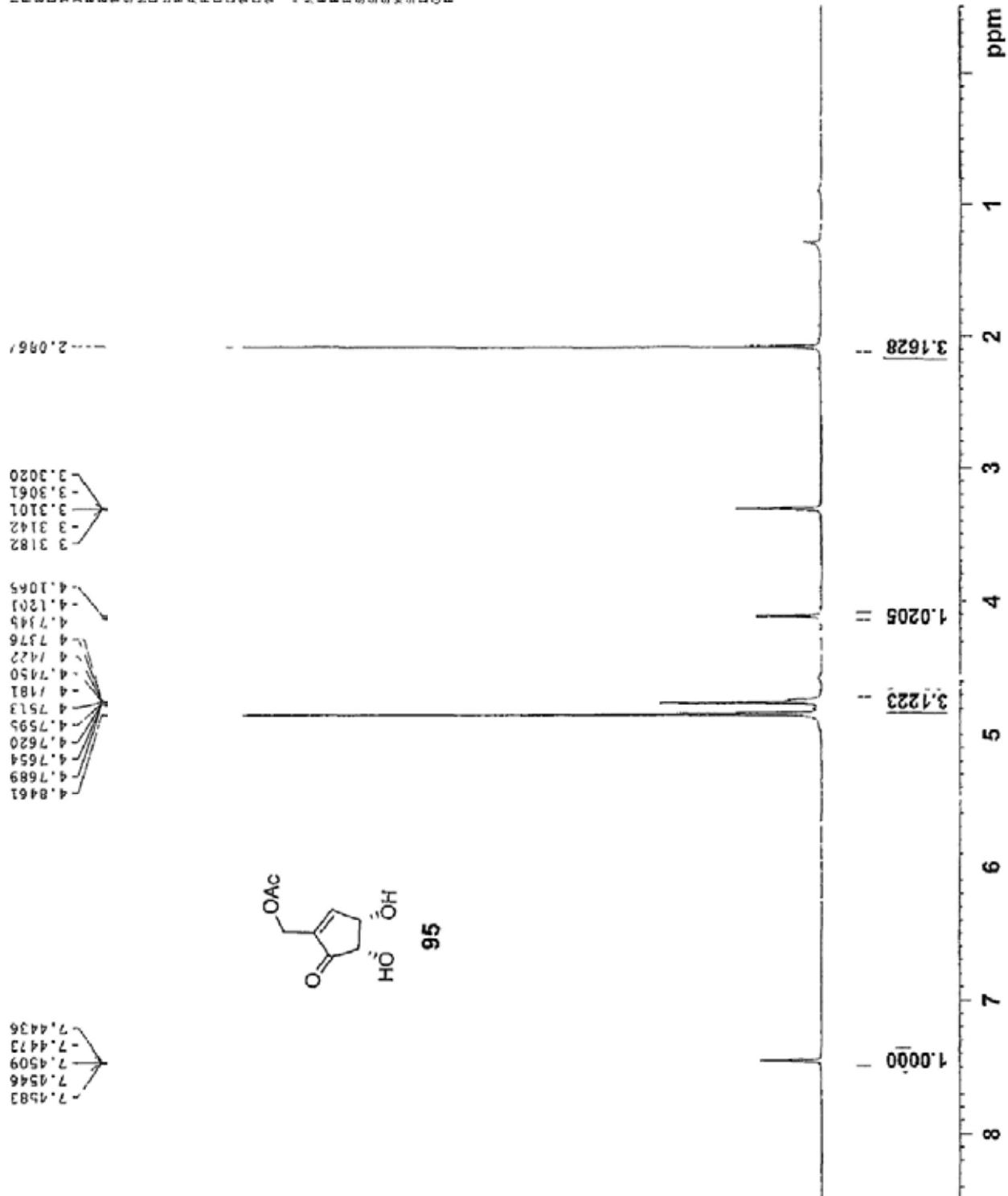


¹H NMR (Solvent: CD₃OD)



NAME
 CARNO
 PROCNO
 DUEC
 TAREM
 INSTRUM
 PROGRAM
 PULPROG
 TO
 SOLVENT
 NS
 DS
 SARH
 FTURNS
 AQ
 RG
 DK
 DE
 TE
 DI
 TD0

***** CHANNEL f1 *****
 NUCL
 P1
 P2
 P3
 SFO1
 SFO2
 SFO3
 SFO4
 SFO5
 SFO6
 SFO7
 SFO8
 SFO9
 SFO10
 SFO11
 SFO12
 SFO13
 SFO14
 SFO15
 SFO16
 SFO17
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 SFO19
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 SFO94
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 SFO96
 SFO97
 SFO98
 SFO99
 SFO100



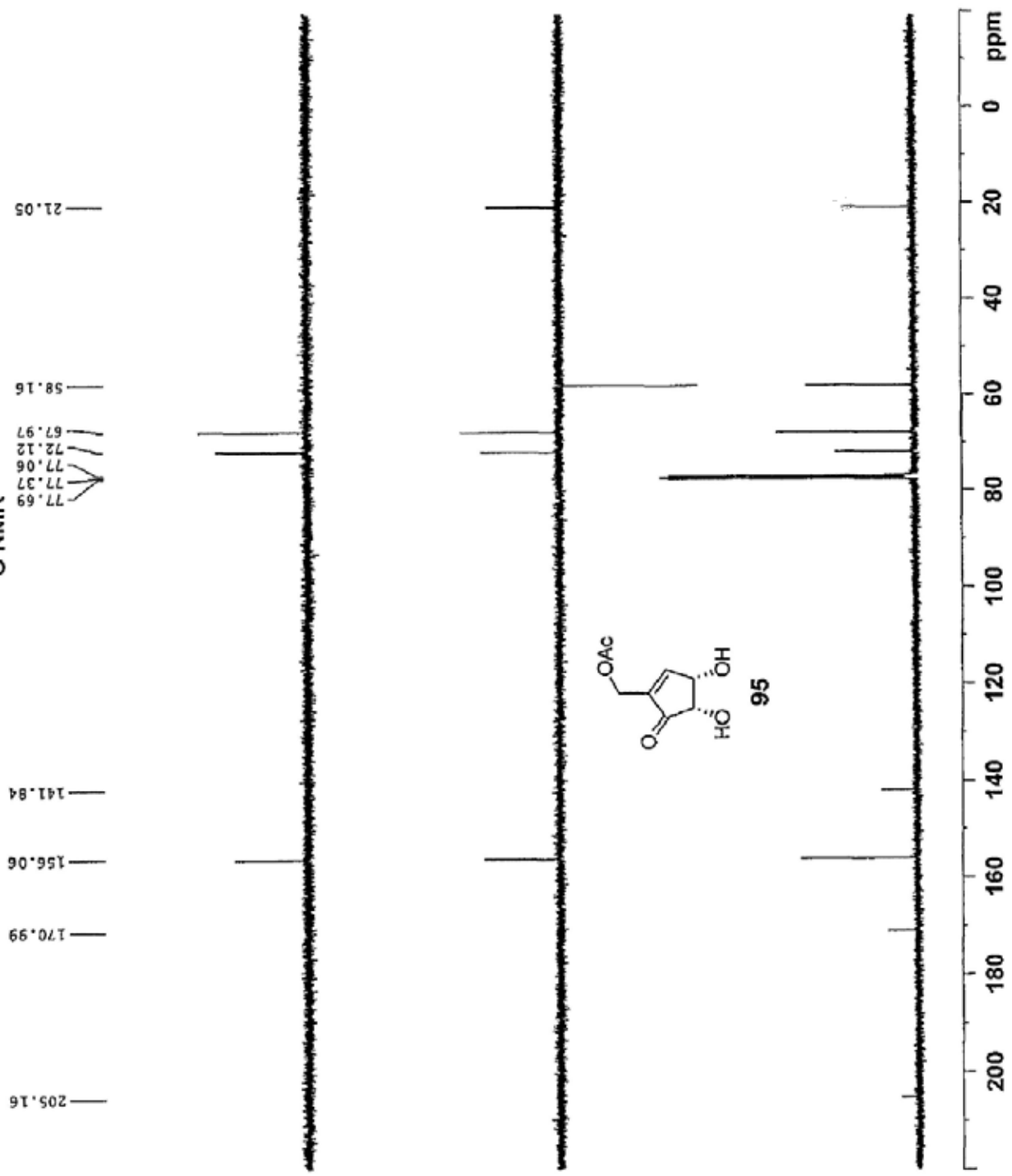
¹³C NMR

```

NAME sh38carbon
EXPNO 1
PROCNO 1
Date_ 20101011
Time 18.08
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 205
DS 4
SWH 24038.451 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 181
DW 20.800 usec
DE 6.50 usec
TE 299.6 K
D1 2.0000000 sec
D11 0.0300000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.90 usec
PL1 -2.00 dB
PL1W 95.33689499 W
SFO1 100.627183 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPDZ 90.00 usec
PL2 -1.00 dB
PL12 15.16 dB
PL13 18.62 dB
PL1Z 13.56617069 W
PL1ZW 0.32844056 W
PL13W 0.14806664 W
SFO2 400.1916008 MHz
SI 32768
SF 100.6278227 MHz
WDW 256
SSB 0
LA 1.00 Hz
GB 0
PC 1.40
    
```

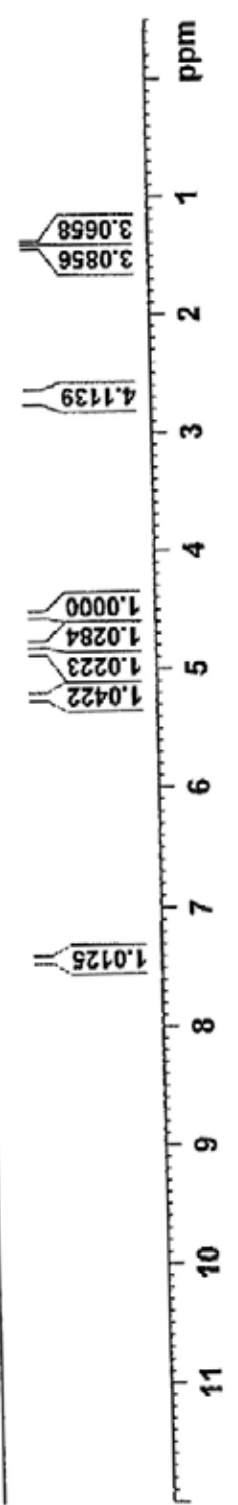
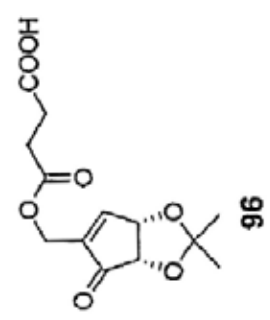


¹H NMR

```

NAME
EXPNO 2
PROCNO 1
Date_ 20100611
Time 18.01
INSTRUM spect
PROBHD 5 mm PABBI
PULPROG zgpg30
TD 65536
SOLVENT ccd13
NS 2
DS 2
SMR 8223.685 Hz
F2 0.125483 Hz
F3 3.9846387 sec
AQ 101
RG 60.800 usec
DS 6.50 usec
TE 294.4 K
CL 1.00000000 sec
TD0 1
===== CHANNEL f1 =====
NUC1 1H
P1 7.10 usec
PL -2.00 dB
PC 13.1724718 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300048 MHz
SK 0
SM 0
SSB 0
LB 0
GB 0
PC 1.00
  
```

1.4061
 1.3892
 2.5513
 2.6516
 2.6782
 2.6864
 2.6909
 2.6982
 2.7032
 2.7154
 2.7260
 4.5283
 4.5420
 4.7650
 4.8027
 4.8204
 4.8241
 4.8276
 4.8580
 4.8618
 4.8654
 5.2231
 5.2259
 5.2299
 5.2342
 5.2367
 5.2392
 7.4250
 7.4201
 7.2597



¹³C NMR (Solvent: C₆D₆)

28.81
28.59
28.59
27.63
26.25

58.21

77.31
77.61

119.21

127.82
128.06
128.30

141.82

154.07

171.38

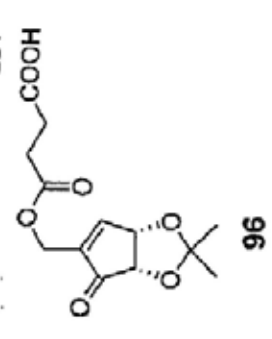
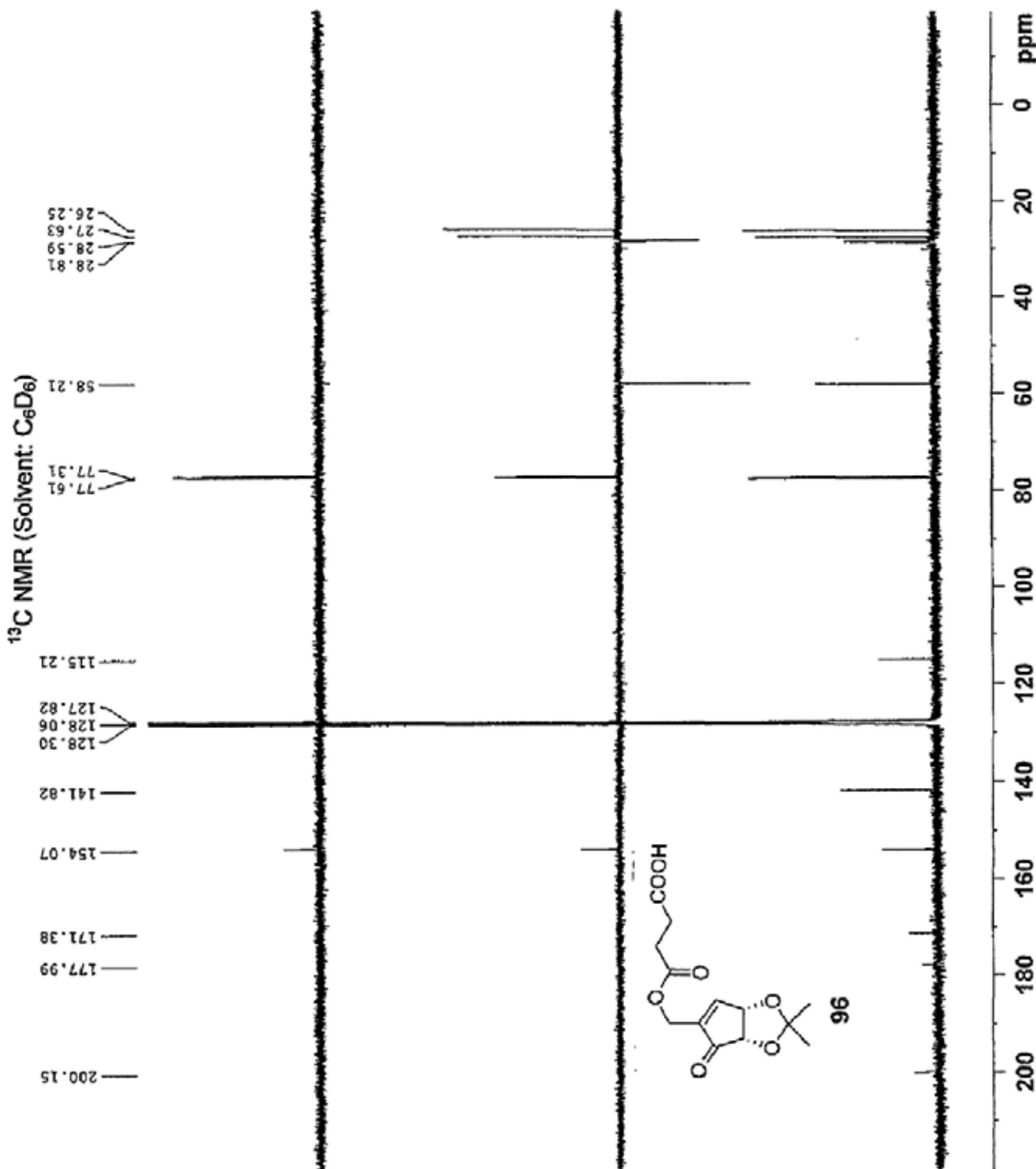
177.99

200.15

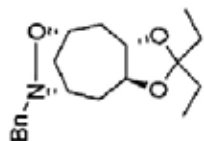
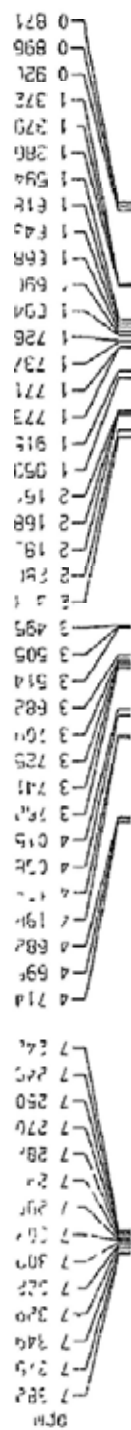
NAME eh50carbon_CED6
EXNO 1
PROCNO 1
Date 20100716
Time 15.35
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT C6D6
NS 240
DS 4
SWH 24036.461 Hz
FIDRES 0.366788 Hz
AQ 1.36531988 sec
RG 101
ZG 101
DW 20.800 usec
DE 6.50 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

CHANNEL F1
NUC1 ¹³C
P1 9.90 usec
PL1 -2.00 dB
PL1W 55.33689499 W
SFO1 100.6319183 MHz

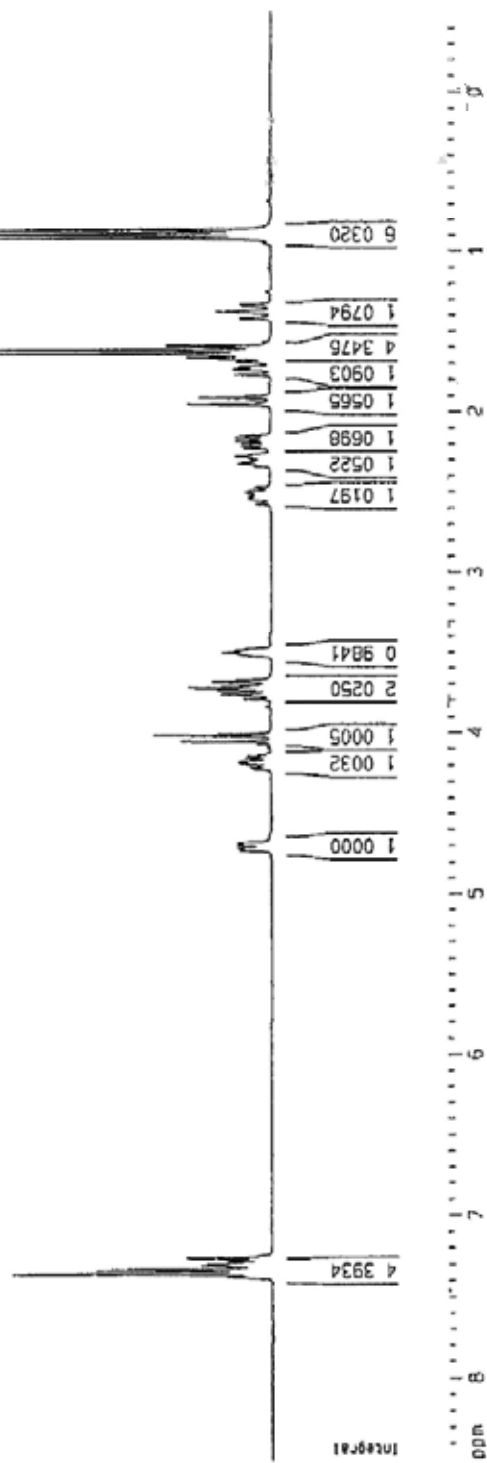
CHANNEL F2
CFDPRG2 waltz16
NUC2 ¹H
PCPDZ 90.00 usec
PL2 -1.00 dB
PL2 15.15 dB
PL2 18.82 dB
PL2W 13.56617089 W
PL2W 0.32844096 W
PL2W 0.14806664 W
SFO2 400.1916008 MHz
SI 32768
SF 100.6278199 MHz
MDW EX
SSB 0
LB 1.00 kHz
GB 0
PC 1.40



¹H NMR



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----- Data Parameters
 DATE 5/27
 -PROG 1
 -PROC 1
 ----- Acquisition Parameters
 Date_ 20080425
 Time 12 12
 INSTRUM gdx300
 PROBHD 5 mm BBO BB-1H
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 8
 DS 0
 SSB 0
 SHH 8532.606 Hz
 FIDRES 0.274438 Hz
 AQ 1.8239508 sec
 RG 128
 DM 55.600 usec
 DE 79.43 usec
 TE 295.2 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCHRG 0.01500000 sec
 ----- CHANNEL f1 -----
 NUC1 1H
 P1 5.00 usec
 PL1 -2.00 dB
 SF01 300.1312000 MHz
 ----- Processing parameters
 S1 32768
 SF 300.1300066 MHz
 MDH EH
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00
 ----- 10 MHz plot parameters
 CX 22.00 cm
 CY 10.56 cm
 F1P 8.500 ppm
 F1 2551.10 Hz
 F2P -0.500 ppm
 F2 -150.07 Hz
 PPM0M 0.40909 ppm/cm
 HZCM 122.78045 Hz/cm

Current Data Parameters
 NAME SFD27carbonic
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20070210
 Time 15 12
 INSTRUM dpa300
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpgc
 TD 65536
 SOLVENT DMS-D6
 NS 286
 DS 0
 SWH 22675.736 Hz
 FIDRES 0.346004 Hz
 AQ 1.4451188 sec
 RG 2580.3
 BN 22.050 usec
 BE 6.00 usec
 TE 0.0 K
 D1 1.0000000 sec
 d11 0.0300000 sec
 MCREST 0.0000000 sec
 MCHRG 0.0150000 sec

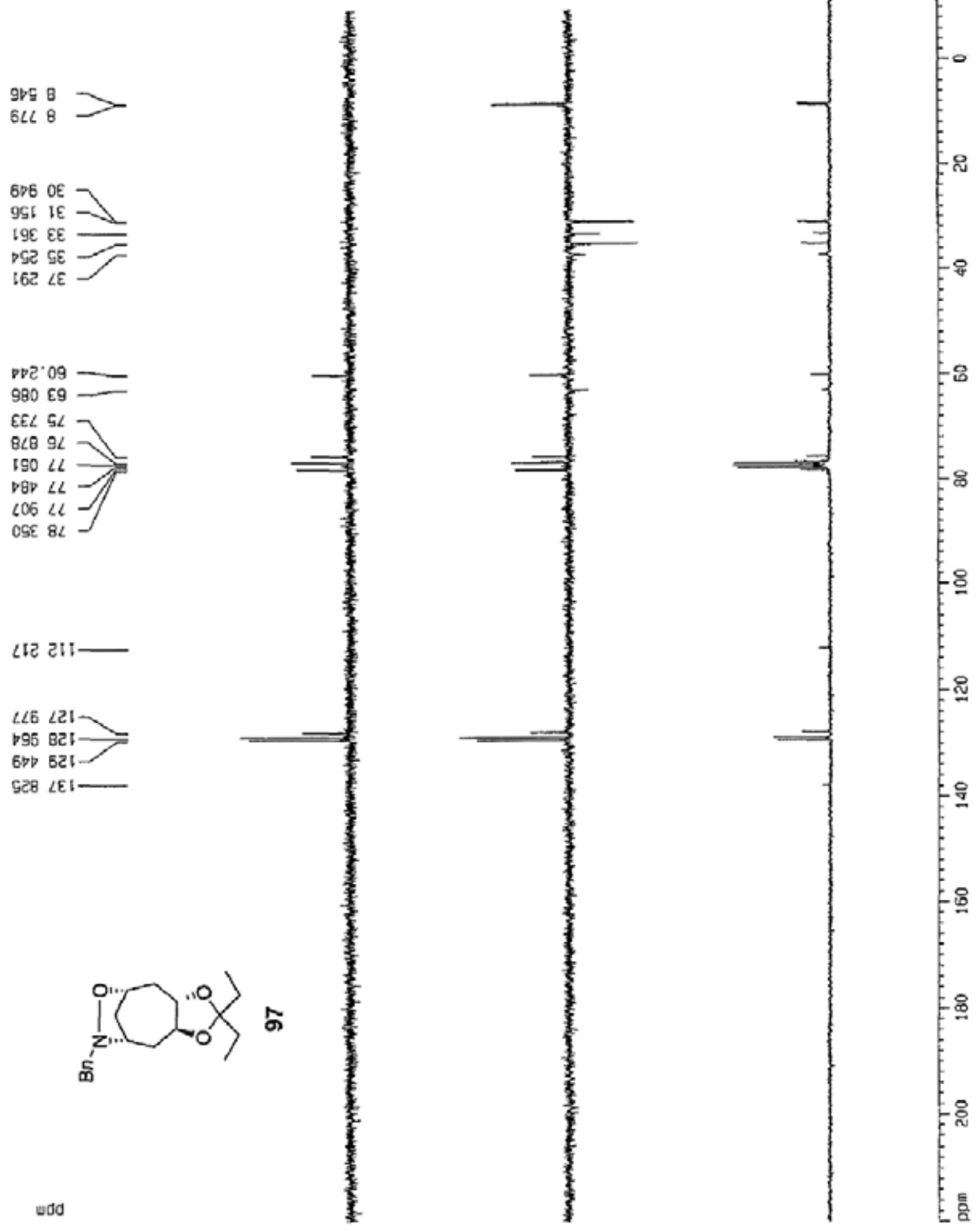
***** CHANNEL f1 *****
 NUC1 13C
 P1 3.00 usec
 PL1 -5.00 dB
 SF01 75.4745111 MHz

***** CHANNEL f2 *****
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 usec
 PL2 120.00 dB
 PL12 19.00 dB
 SF02 300.1315007 MHz

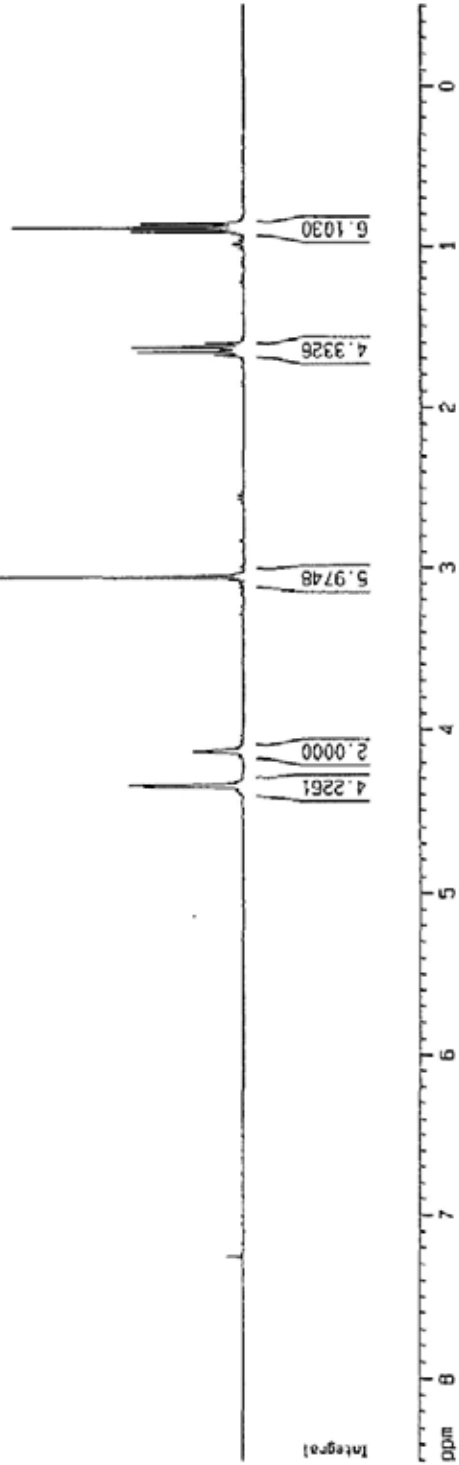
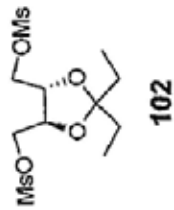
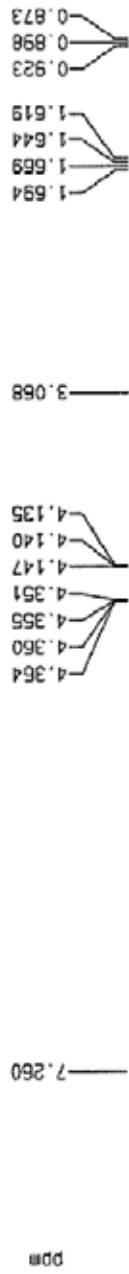
F2 - Processing parameters
 SI 65535
 SF 75.4677143 MHz
 NDM EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40

F0 MMR plot parameters
 CX 23.00 cm
 CY 1.75 cm
 F1P 220.000 ppm
 F1 16502.90 Hz
 F2P -20.000 ppm
 F2 -1509.36 Hz
 PPMX 10.43478 ppm/cm
 HzCM 767.48620 Hz/cm

¹³C NMR



¹H NMR



Current Data Parameters
NAME sb11b
EXPNO 1
PROCNO 1

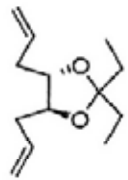
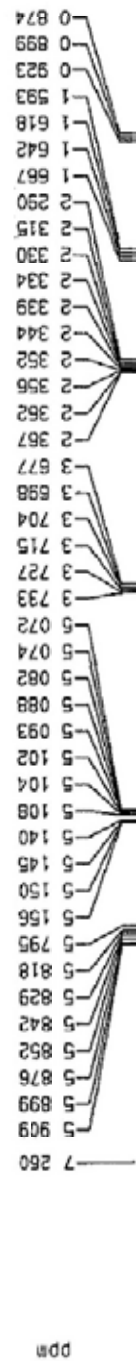
F2 - Acquisition Parameters
Date_ 20061012
Time 21.12
INSTRUM GPC300
PROBHD 5 mm BBO BB-JH
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 4
DS 0
SWH 8892.806 Hz
FIDRES 0.274639 Hz
AQ 1.8215908 sec
RG 71.8
OR 55.800 usec
DE 79.43 usec
TE 0.0 K
D1 1.00000000 sec
HCREST 0.00000000 sec
MCORR 0.00500000 sec

***** CHANNEL f1 *****
NUC1 ¹H
P1 5.00 usec
PL1 -2.00 dB
SFO1 300.1312000 MHz

F2 - Processing parameters
SI 32768
SF 300.1300063 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

ID NMR plot parameters
CX 22.00 cm
CY 8.37 cm
FIP 8.500 ppm
F1 2551.10 Hz
F2 -0.500 ppm
PCORR -150.07 Hz
PCORR 0.40909 ppm/cm
KZDN 122.78006 Hz/cm

¹H NMR



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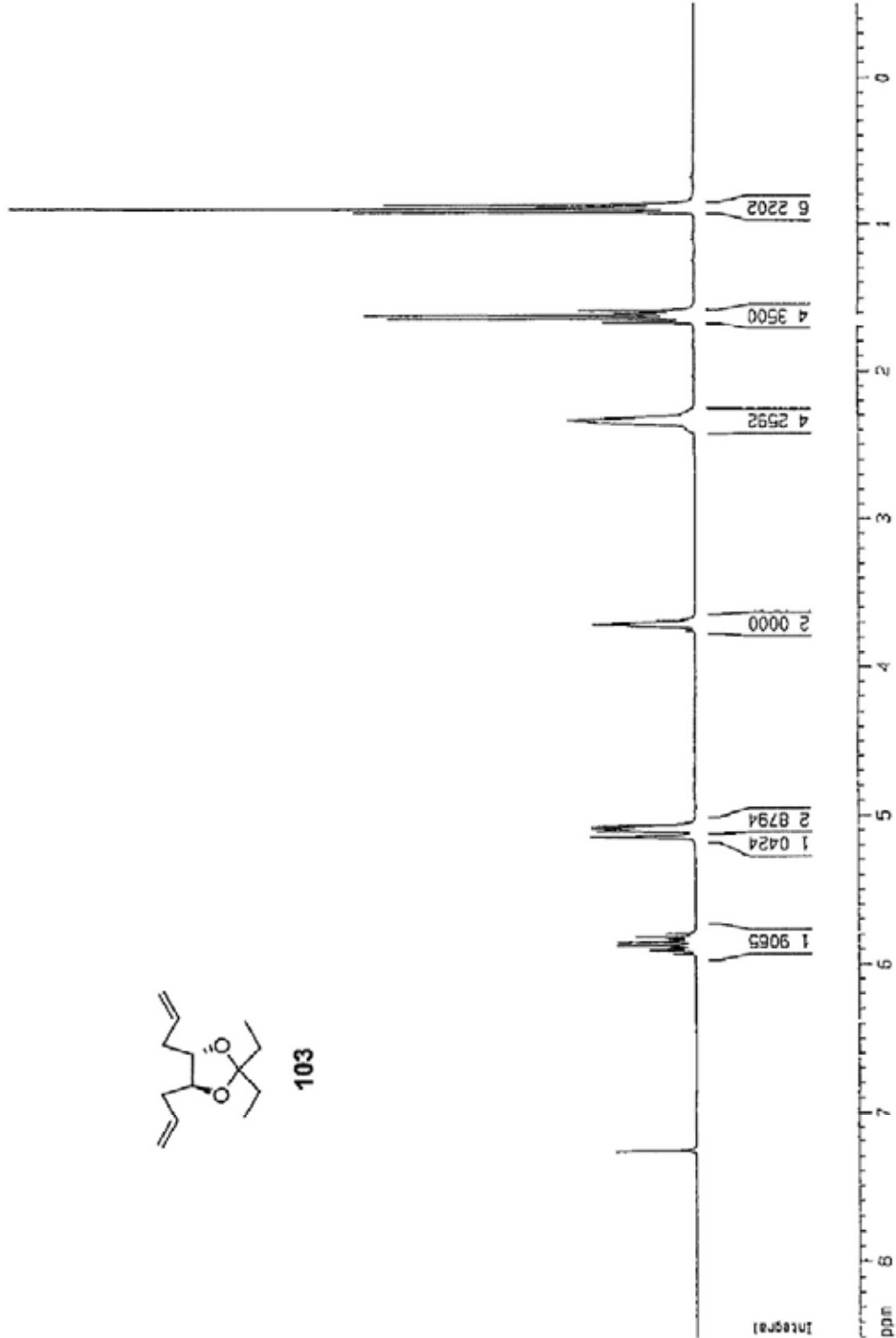
Current Data Parameters
 NAME : 9612h
 EXPNO : 1
 PROCNO : 1

F2 - Acquisition Parameters
 Date_ : 20080228
 Time : 9.46
 INSTRUM : dpc300
 PROBHD : 5 mm BB-1H
 PULPROG : zg
 TD : 32768
 SOLVENT : CDCl3
 NS : 8
 DS : 4
 SWH : 10000.000 MHz
 FIDRES : 0.24130 MHz
 AQ : 0.00050000 sec
 RG : 5
 DM : 55.600 usec
 DE : 79.43 usec
 TE : 300.2 K
 D1 : 0.00000000 sec
 sFOF : 0.00000000 sec
 ACQRES : 0.00000000 sec
 NUC1 : 1H
 P1 : 5.00 usec
 PL1 : -2.00 dB
 SFO1 : 300.1312000 MHz

***** CHANNEL f3 *****
 NUC1 : 1H
 P1 : 5.00 usec
 PL1 : -2.00 dB
 SFO1 : 300.1312000 MHz

F2 - Processing parameters
 SI : 32768
 SF : 300.1300050 MHz
 MD : EM
 SS : 0
 LB : 0.30 Hz
 GB : 0
 PC : 1.00

1D NMR plot parameters
 EX : 22.00 cm
 CY : 11.28 cm
 F1 : 8.500 ppm
 F2 : 255.11 Hz
 F2P : -0.500 ppm
 PPHOM : 0.40909 ppm/cm
 HZCM : 177.76047 Hz/cm



Current Data Parameters
 NAME methcarbene
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080228
 Time 9 54
 INSTRUM dpx300
 PROBHD 5 mm BBO BB-3H
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 270
 DS 0
 SMI 28675.736 Hz
 FIDRES 0.346004 Hz
 AQ 1.4451188 sec
 RG 13004
 DH 22.050 usec
 DE 6.00 usec
 TE 299.2 K
 D1 1.0000000 sec
 d11 0.0300000 sec
 WREST 0.0000000 sec
 MCRMK 0.0150000 sec

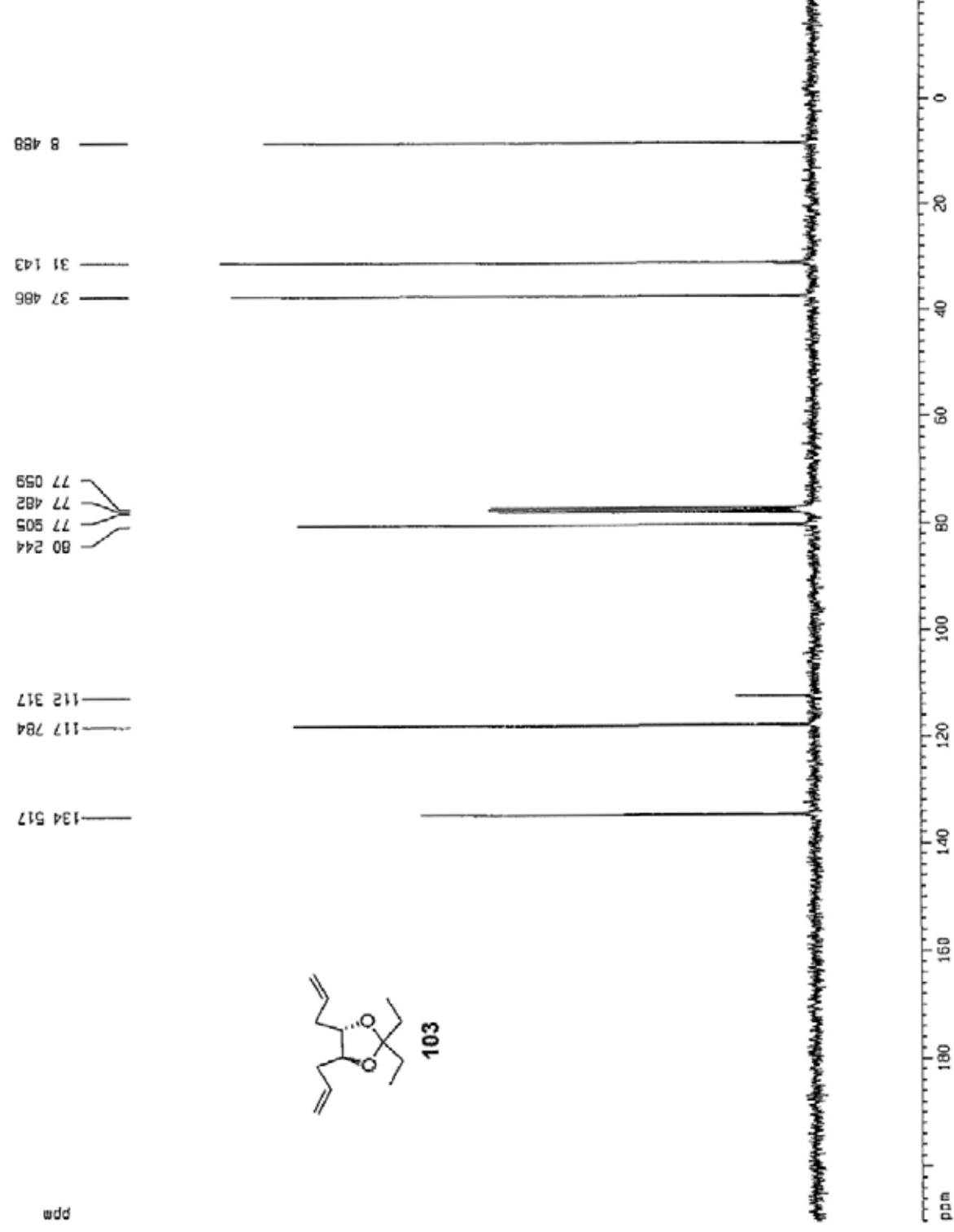
***** CHANNEL f1 *****
 NUC1 13C
 P1 3.00 usec
 PL1 -6.00 dB
 SF01 75.4745111 MHz

***** CHANNEL f2 *****
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 usec
 PL2 120.00 dB
 PL12 19.00 dB
 SF02 300.1315007 MHz

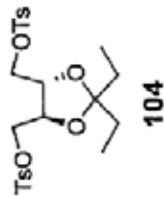
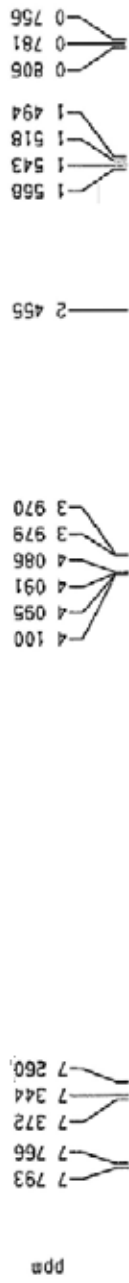
F2 - Processing parameters
 SI 65536
 SF 75.4677143 MHz
 NDM EX
 SSB C
 LB 3.00 Hz
 GB 0
 PC 1.40

F2 - Acquisition Parameters
 CX 23.00 cm
 CY 11.04 cm
 F1P 210.000 ppm
 F1 158.4822 Hz
 F2P -20.000 ppm
 F2 -1509.36 Hz
 PUNCH 10.00000 ppm/cm
 KZDN 754.67712 Hz/cm

¹³C NMR



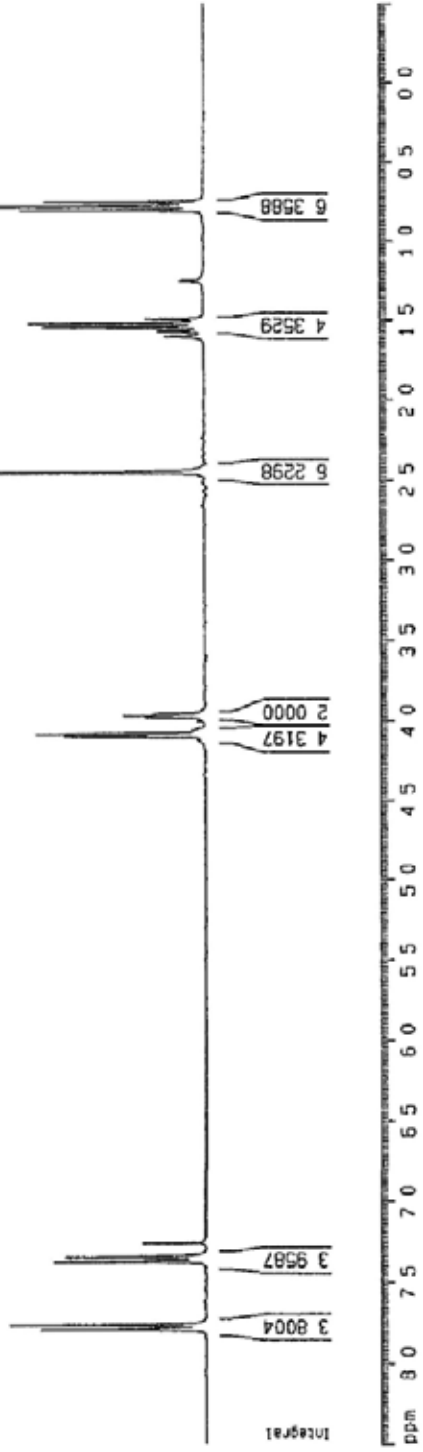
¹H NMR



Current Data Parameters
 NAME shd14
 EXPNO 3
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20061024
 Time 14 04
 INSTRUM dpx300
 PROBNM 5 mm BBO BB-3H
 PULPROG zg
 TO 32789
 SOLVENT CCl3
 NS 4
 DS 0
 SMH 8982.805 Hz
 FIDRES 0.274435 Hz
 AQ 1.9215509 sec
 RG 181
 DW 55.600 usec
 DE 79.43 usec
 TE 0.0 K
 D1 1.00000000 sec
 NUCREST 0.00000000 sec
 NUCRKE 0.01500000 sec

***** CHANNEL f1 *****
 NUC1 1H
 P1 5.00 usec
 PL1 -2.00 dB
 SF01 300.1312000 MHz
 F2 - Processing parameters
 SI 32789
 SF 300.1307483 MHz
 KW EK
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 22.00 cm
 CY 9.25 cm
 F1P 8.500 ppa
 F1 2551.10 Hz
 F2P -0.500 ppa
 F2 -150.07 Hz
 PPHC 0.49509 ppa/cm
 KZCM 122.78845 Hz/cm



Current Data Parameters
 NAME snc14_carbon
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20061024
 Time 14 09
 INSTRUM dxt300
 PROBNM 5 mm BBO BB-1H
 PULPROG zgpg30
 TO 65536
 SOLVENT CDCl3
 NS 55
 DS 0
 SMH 22575.736 Hz
 FIDRES 0.345664 Hz
 AQ 1.445180 sec
 RG 10321.3
 DW 22.650 usec
 DE 5.00 usec
 TE 0.0 K
 D1 1.0000000 sec
 d11 0.0000000 sec
 MCREST 0.0000000 sec
 MCMRK 0.01500000 Hz

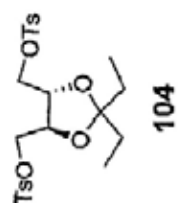
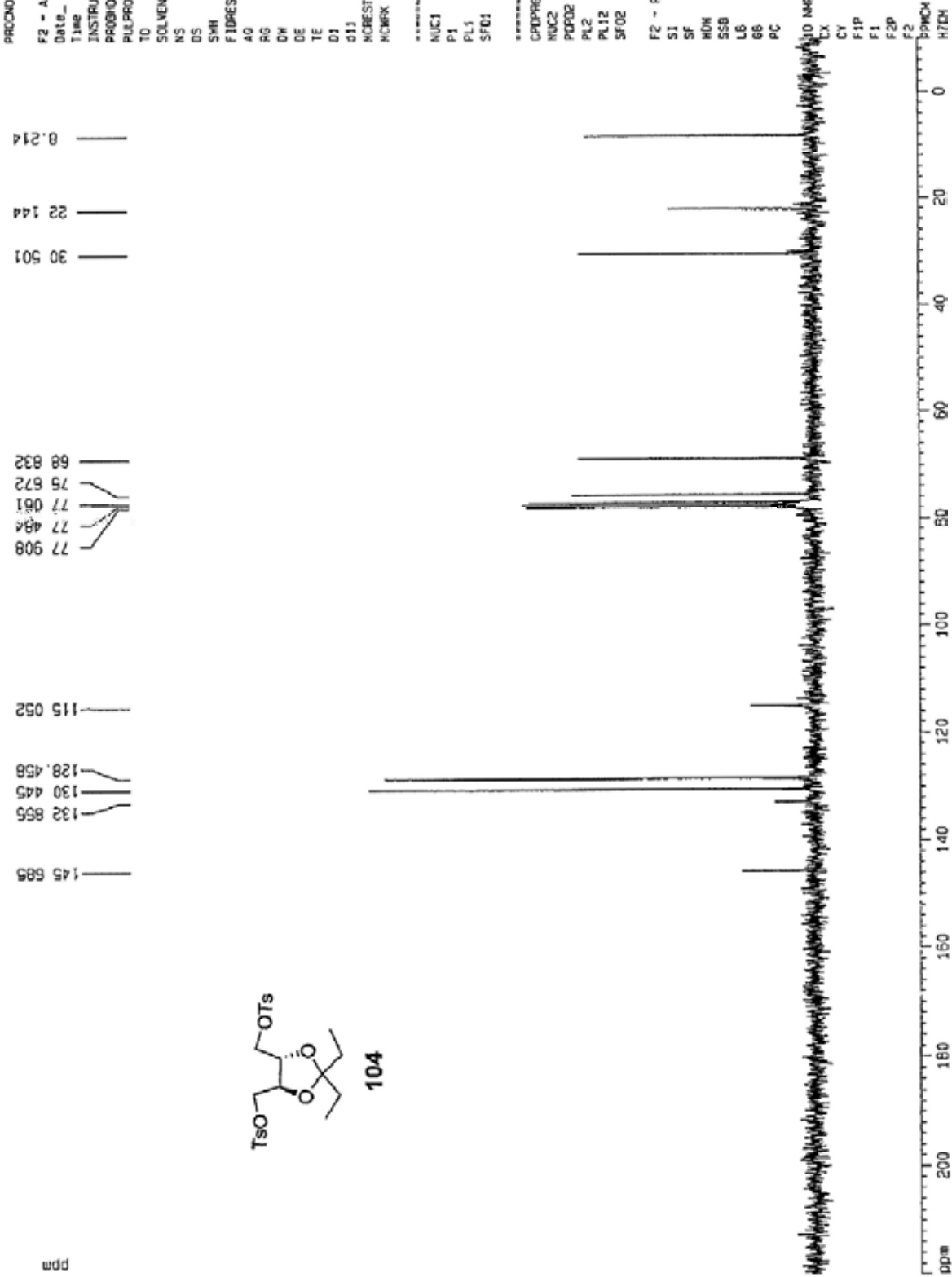
***** CHANNEL F1 *****
 NUC1 13C
 P1 3.00 usec
 PL1 -6.00 dB
 SF01 75.474511 MHz

***** CHANNEL F2 *****
 CPDPRG2 waltz16
 NUC2 1H
 PDP02 100.00 usec
 PL2 120.00 dB
 PL12 19.00 dB
 SF02 300.1315007 MHz

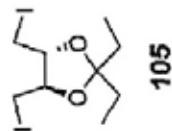
F2 - Processing parameters
 SI 65536
 SF 75.4677153 MHz
 HN EN
 SS 0
 LB 3.00 Hz
 GB 0
 PC 1.40

10 MHz plot parameters
 CX 23.00 cm
 CY 6.31 cm
 F1P 220.000 ppm
 F1 16502.90 Hz
 F2P -10.000 ppm
 F2 -754.66 Hz
 PPMX 10.00000 ppm/cm
 HZCN 754.67712 Hz/cm

¹³C NMR



¹H NMR



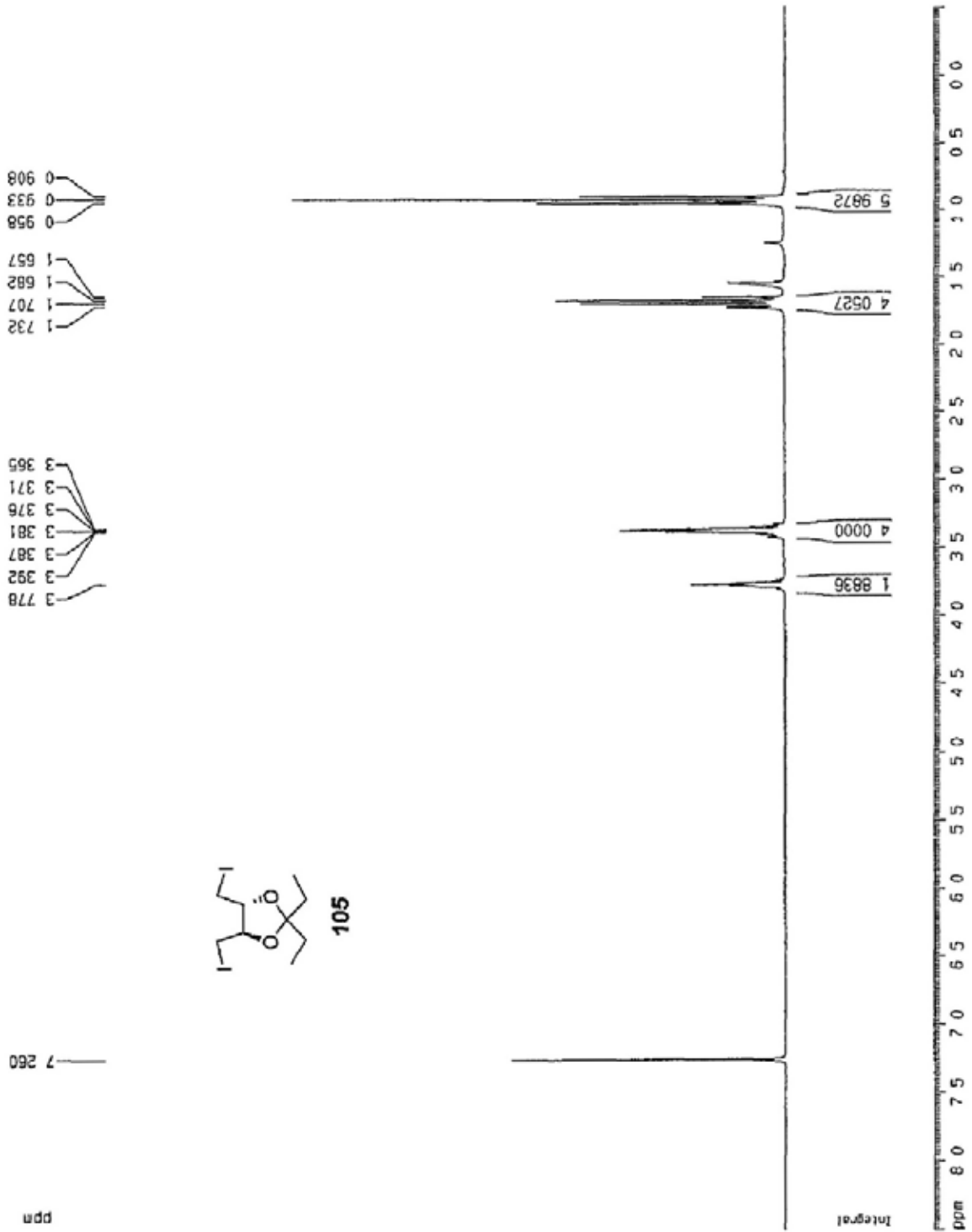
Current Data Parameters
 NAME srb16b
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20051104
 Time 14 02
 INSTRUM 40x300
 PROBHD 5 mm 880 SB-1H
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 8
 DS 0
 SWH 8892.806 Hz
 FIDRES 0.276439 Hz
 AQ 1.8219508 sec
 RG 574.7
 DW 55.800 usec
 DE 79.43 usec
 TE 0.0 K
 D1 1.06000000 sec
 MCREST 0.06000000 sec
 MCNRK 0.01800000 sec

***** CHANNEL f1 = *****
 NU1 1H
 P1 5.00 usec
 PL1 -2.00 dB
 SF01 300.1312000 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300063 MHz
 NQW EH
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CK 22.00 cm
 CY 8.97 cm
 F1P 8.500 ppm
 F1 2553.10 Hz
 F2P -0.500 ppm
 F2 150.07 Hz
 PPMCK 0.40809 ppm/cm
 HZCM 122.78046 Hz/cm



¹³C NMR

Current Data Parameters
 NAME sb15_carbonyl
 EXPNO 1
 PROCNO 1

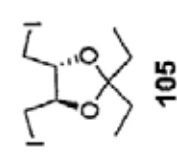
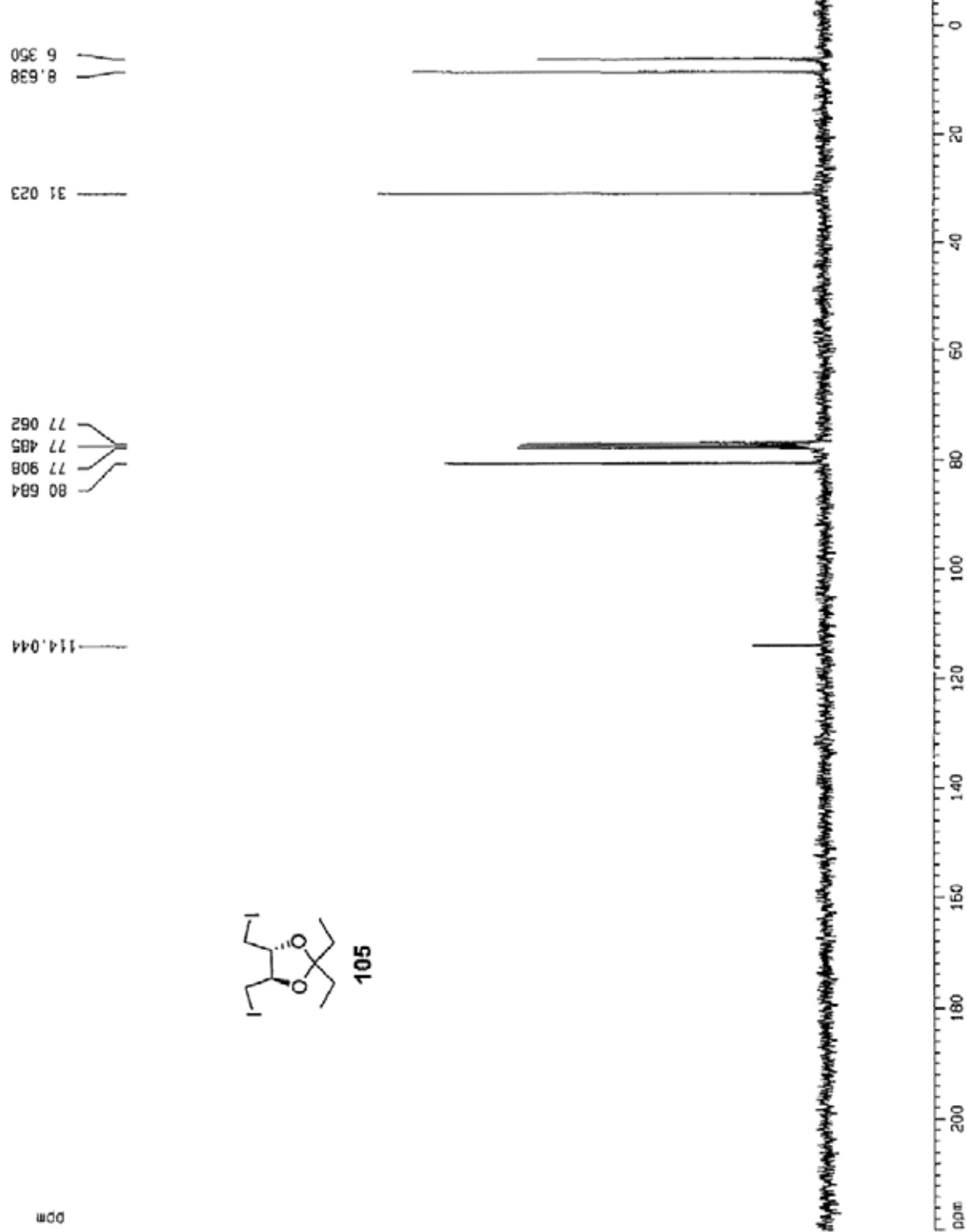
F2 - Acquisition Parameters
 Date_ 20051109
 Time 21.18
 INSTRUM dpx300
 PROBDH 5 mm BBO BB-1H
 PULPROG zgpg
 TD 65536
 SOLVENT COCl3
 NS 201
 DS 0
 SWH 22675.735 Hz
 FIDRES 0.346904 Hz
 AQ 1.451168 sec
 RG 10321.3
 DM 22.850 usec
 DE 6.00 usec
 TE 0.0 K
 D1 1.0000000 sec
 d11 0.0300000 sec
 ACQRES 0.0000000 sec
 HZMRX 0.0150000 sec

***** CHANNEL f1 *****
 NUC1 ¹³C
 P1 3.00 usec
 PL1 -6.00 dB
 SF01 75.4745111 MHz

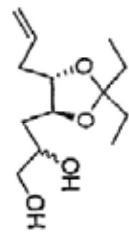
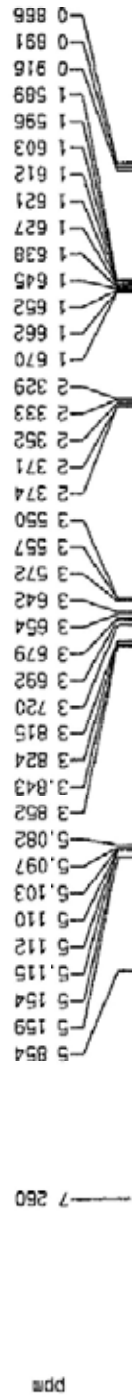
***** CHANNEL f2 *****
 CDPGR2 waltz16
 NUC2 ¹H
 PCPD2 100.00 usec
 PL2 120.00 dB
 PL12 19.00 dB
 SF02 300.1315007 MHz

F2 - Processing parameters
 SI 65536
 SF 75.4677153 MHz
 HDH CM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40

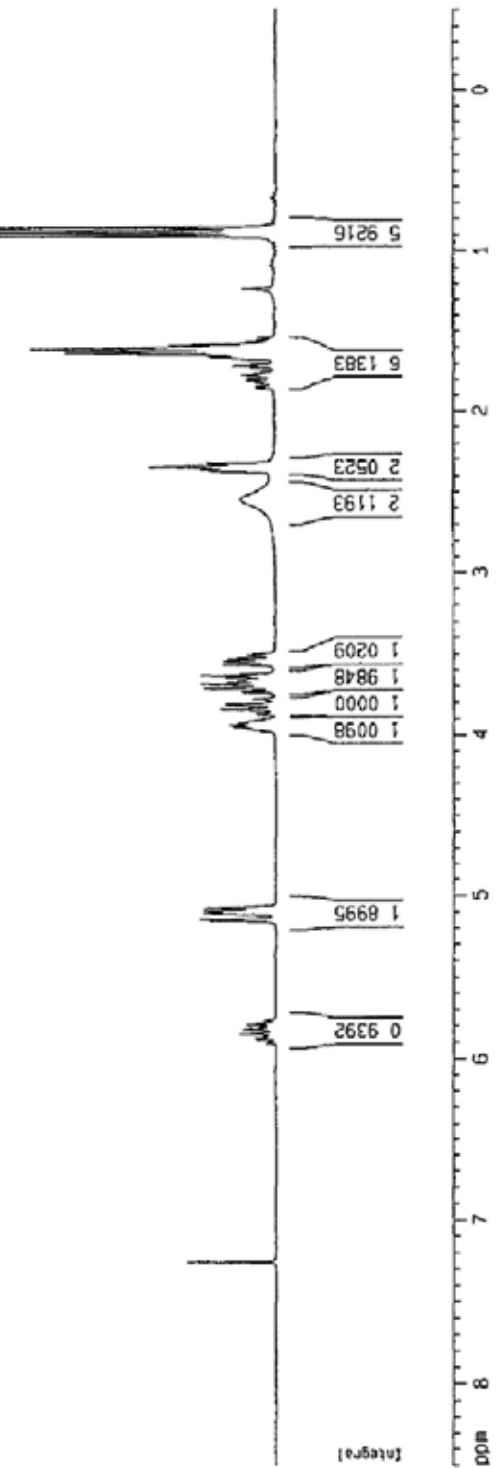
***** DMR plot parameters *****
 CX 23.00 cm
 CY 18.00 cm
 F1P 220.000 ppm
 F1 18602.90 Hz
 F2P -10.000 ppm
 F2 -754.68 Hz
 PHO0 10.00000 ppm/cm
 HZ00 754.67712 Hz/cm



¹H NMR



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Current Data Parameters
 NAME: chb25g
 EXPNO: 3
 PROCNO: 1

F2 - Acquisition Parameters
 Date_: 20070118
 Time: 21:37
 INSTRUM: dbx300
 PROBHD: 5 mm BBO BB-1H
 PULPROG: zg
 TD: 32768
 SOLVENT: COCl3
 NS: 8
 DS: 0
 SWH: 6982.006 Hz
 FIDRES: 0.274439 Hz
 AQ: 1.8219508 sec
 RG: 161.3
 OR: 05.600 usec
 DE: 79.43 usec
 TE: 0.0 K
 D5: F 00000000 sec
 ACQRES: 0.0000000 sec
 HEMARK: 0 015000000 sec

===== CHANNEL f1 =====
 NUC1: 1H
 P1: 5.00 usec
 PL1: -2.00 dB
 SFO1: 300.1312000 MHz

F2 - Processing parameters
 SI: 32768
 SF: 300.1300653 MHz
 WDW: EM
 SSB: 0
 LB: 0.30 Hz
 GB: 0
 PC: 1.00

ID NMR plot parameters
 AX: 22.00 cm
 AY: 10.25 cm
 FIP: 8.500 ppm
 F1: 2551.10 Hz
 F2: -0.500 ppm
 F2: -150.07 Hz
 PPMX: 0.46509 ppm/cm
 HZCX: 122.78546 Hz/cm

Current Data Parameters
 NAME sbd25carb00b
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20070118
 Time 21 47
 INSTRUM dpx300
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpg30
 TO 65536
 SOLVENT CDCl3
 NS 706
 DS 0
 SWH 22675.736 Hz
 FIDRES 0.346004 Hz
 AQ 1.6451188 sec
 RG 6192
 DM 22.050 usec
 DE 6.00 usec
 TE 0.0 K
 D1 1.0000000 sec
 D11 0.0300000 sec
 ACQRES 0.0000000 sec
 MCNRC 0.0150000 sec

***** CHANNEL f1 *****
 NU1 13C
 P1 3.00 usec
 PL1 -5.00 dB
 SF01 75.477143 MHz

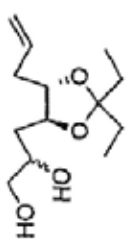
***** CHANNEL f2 *****
 CPDPRG2 waltz16
 NU12 1H
 PCP02 100.00 usec
 PL2 120.00 dB
 PL12 19.00 dB
 SF02 300.1315007 MHz

F2 - Processing parameters
 S1 65536
 SF 75.4677143 MHz
 WDM EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40

F2 M9 plot parameters
 CX 23.00 cm
 CY 10.12 cm
 FIP 220.000 ppm
 F1 16502.90 Hz
 F2P -10.000 ppm
 F2 -754.68 Hz
 PUNCH :0 000000 ppm/cm
 KICK 754.67712 Hz/cm

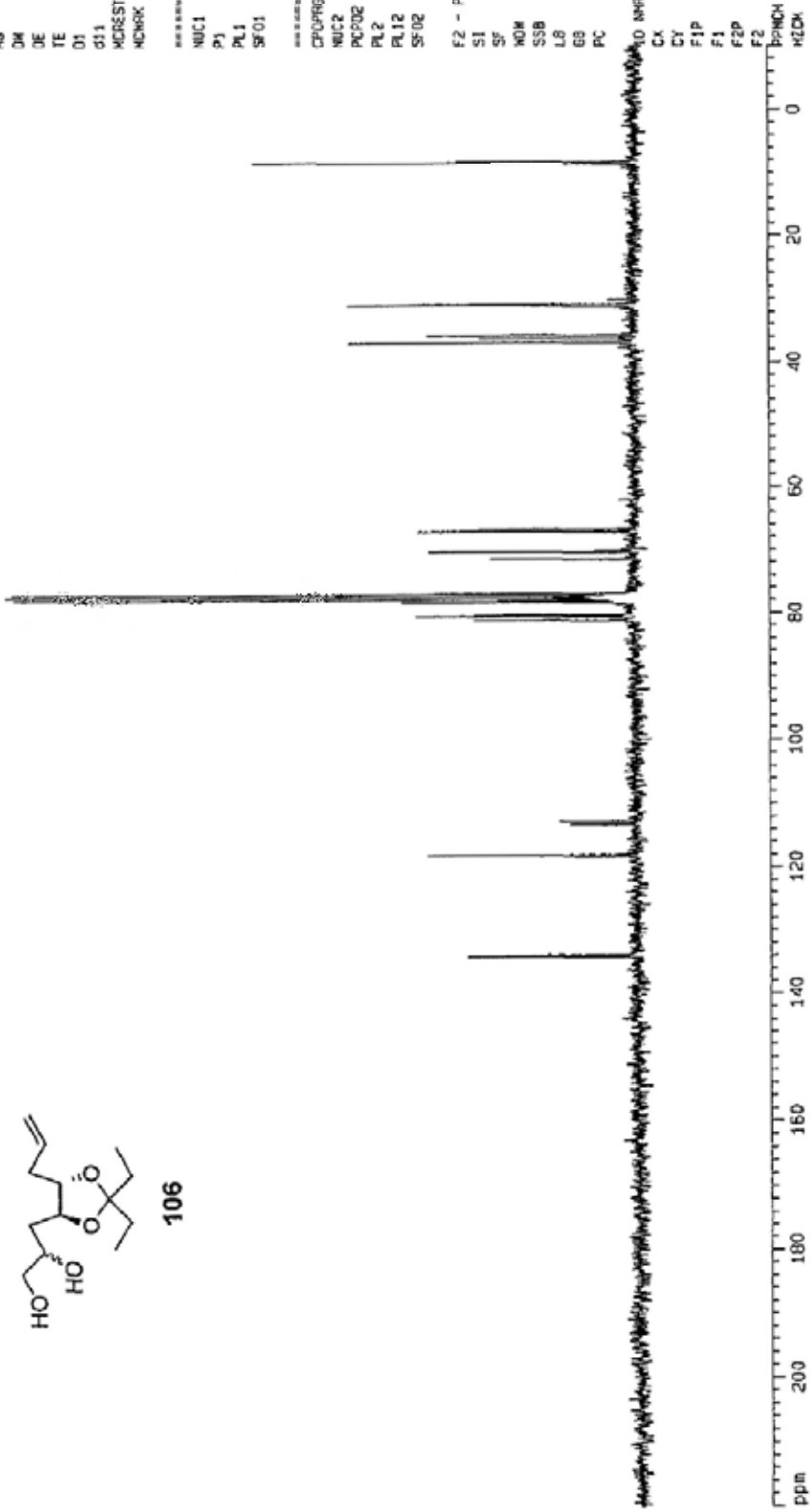
¹³C NMR

- 8 427
- 8 519
- 8 579
- 30 965
- 31 018
- 31 104
- 35 849
- 36 363
- 37 018
- 66 821
- 67 224
- 70 376
- 71 551
- 77 060
- 77 484
- 77 907
- 78 333
- 80 338
- 80 596
- 81 264
- 112 826
- 113 272
- 118 119
- 118 213
- 133 974
- 134 133

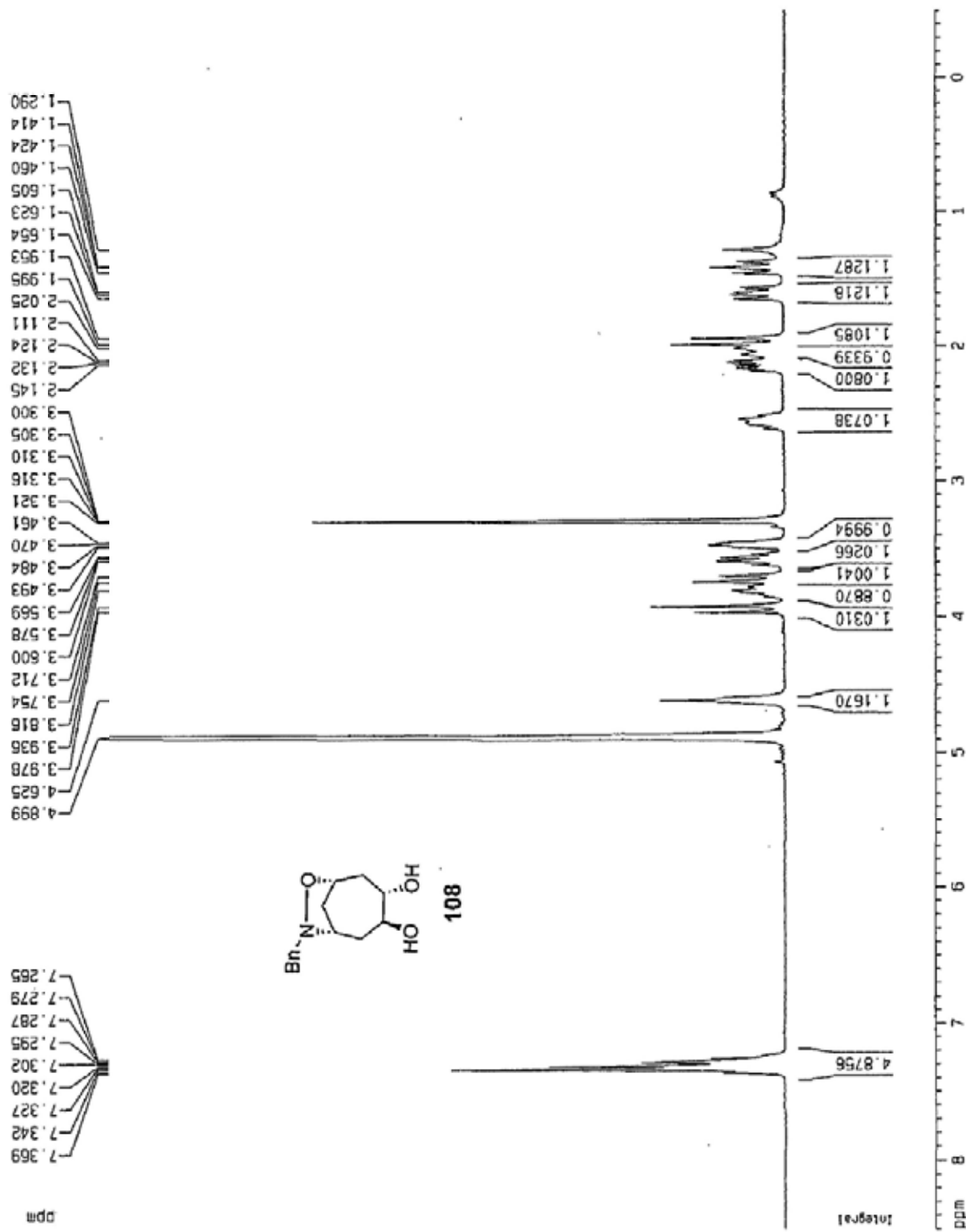


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ppm



¹H NMR (Solvent: CD₃OD)



Current Data Parameters
 NAME sh032e
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20071012
 Time 16.26
 INSTRUM dp+300
 PROBRD 5 mm BBO BB-JH
 PULPROG zg30
 TD 32768
 SOLVENT MeOD
 NS 16
 DS 0
 SHH 6992.806 Hz
 FIDRES 0.274439 Hz
 AQ 1.9219508 sec
 RG 362
 DM 55.500 usec
 DE 79.43 usec
 TE 0.0 K
 D1 1.0000000 sec
 XDREST 0.0000000 sec
 MDPRK 0.0150000 sec

***** CHANNEL f1 *****
 NUCL1 1H
 P1 5.00 usec
 PL1 -2.00 dB
 SFO1 300.1312000 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300045 MHz
 MDW EN
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 22.00 cm
 CY 90.38 cm
 FXP 8.500 BPR
 F1 2631.10 Hz
 F2P -0.500 BPR
 F2 -150.07 Hz
 PPMCH 0.40909 ppm/cm
 HZCH 122.78046 Hz/cm

¹³C NMR (Solvent: CD₃OD)

Current Data Parameters
 NAME shd3cc-bn-Me00
 EXPNO 1
 PROCNO 1

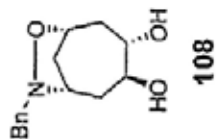
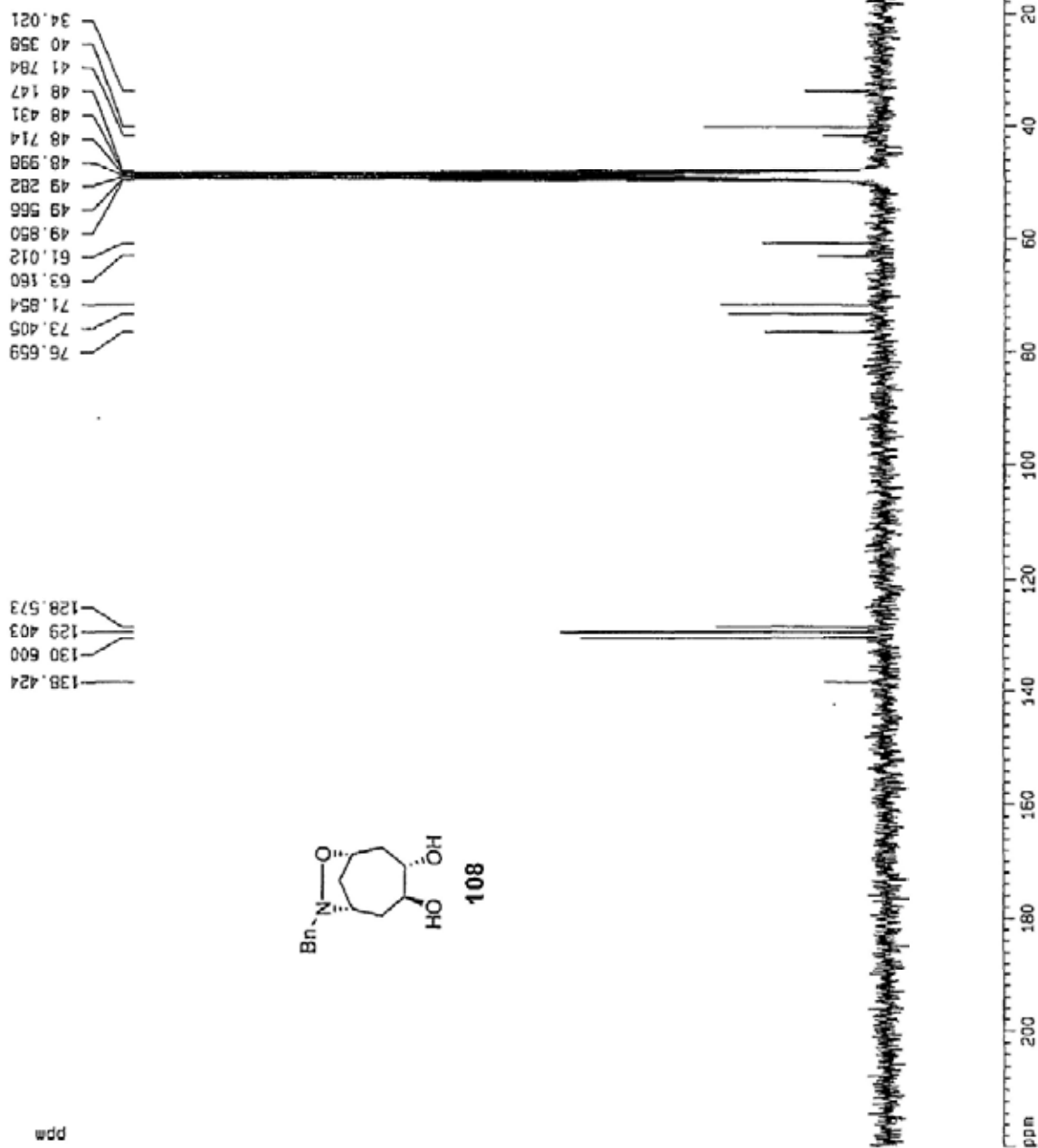
F2 - Acquisition Parameters
 Date_ 20071032
 Time 16.34
 INSTRUM gdx300
 PROBHD 5 mm BBO BB-3H
 PULPROG zgpg
 TD 65536
 SOLVENT CDCL3
 NS 1005
 DS 0
 SWH 22675.736 Hz
 FIDRES 0.346004 Hz
 AQ 1.4451198 sec
 RG 3649.1
 CW 22.050 usec
 DE 6.00 usec
 TE 0.0 K
 D1 1.0000000 sec
 D11 0.0000000 sec
 ACQRES 0.0000000 sec
 HZMRK 0.01500000 sec

***** CHANNEL F1 *****
 NUC1 13C
 P1 3.00 usec
 PL1 -6.00 dB
 SFO1 75.476313 MHz

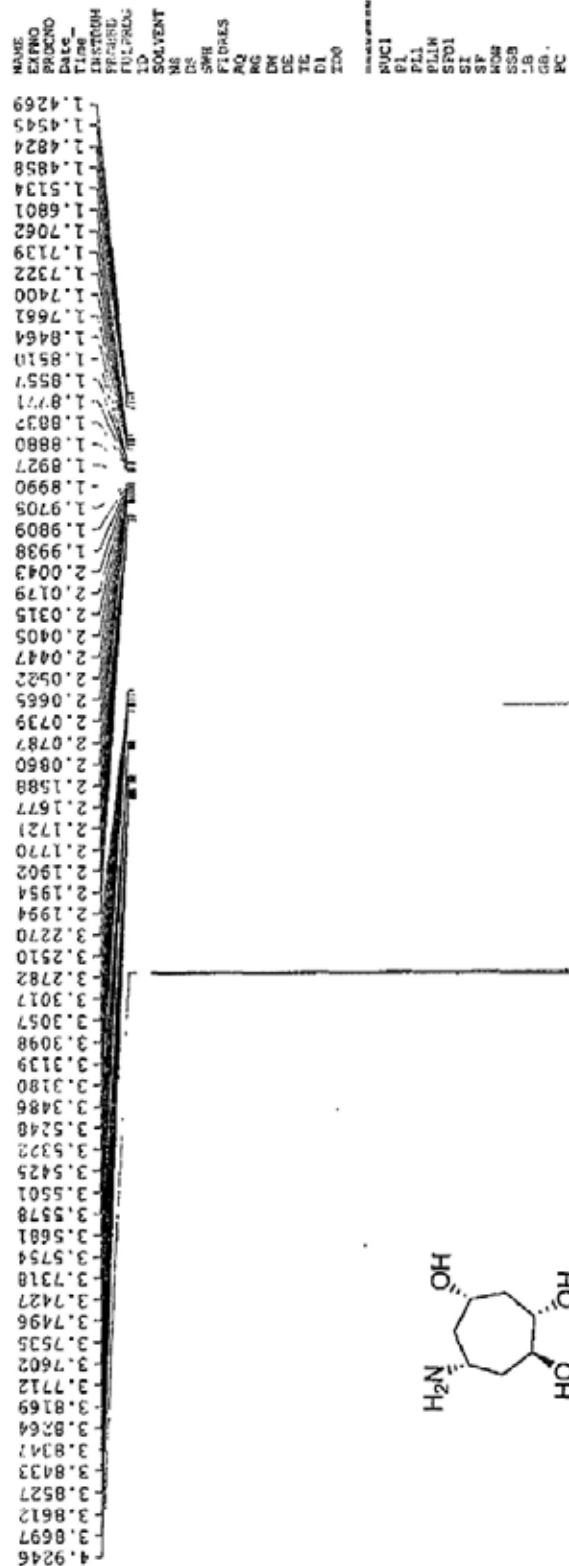
***** CHANNEL F2 *****
 CPDPRG2 waltz16
 NUC2 1H
 P2 100.00 usec
 PL2 120.00 dB
 PL12 15.00 dB
 SFO2 300.1315067 MHz

F2 - Processing parameters
 SI 65536
 SF 75.4676424 MHz
 XCH EN
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.00

10 wa plot parameters
 CX 23.00 cm
 CY 50.50 cm
 FIP 220.000 ppm
 F1 16602.88 Hz
 F2P -20.000 ppm
 F2 -1509.35 Hz
 PPMIN 10.43478 ppm/cx



¹H NMR (Solvent: CD₃OD)



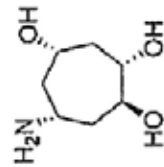
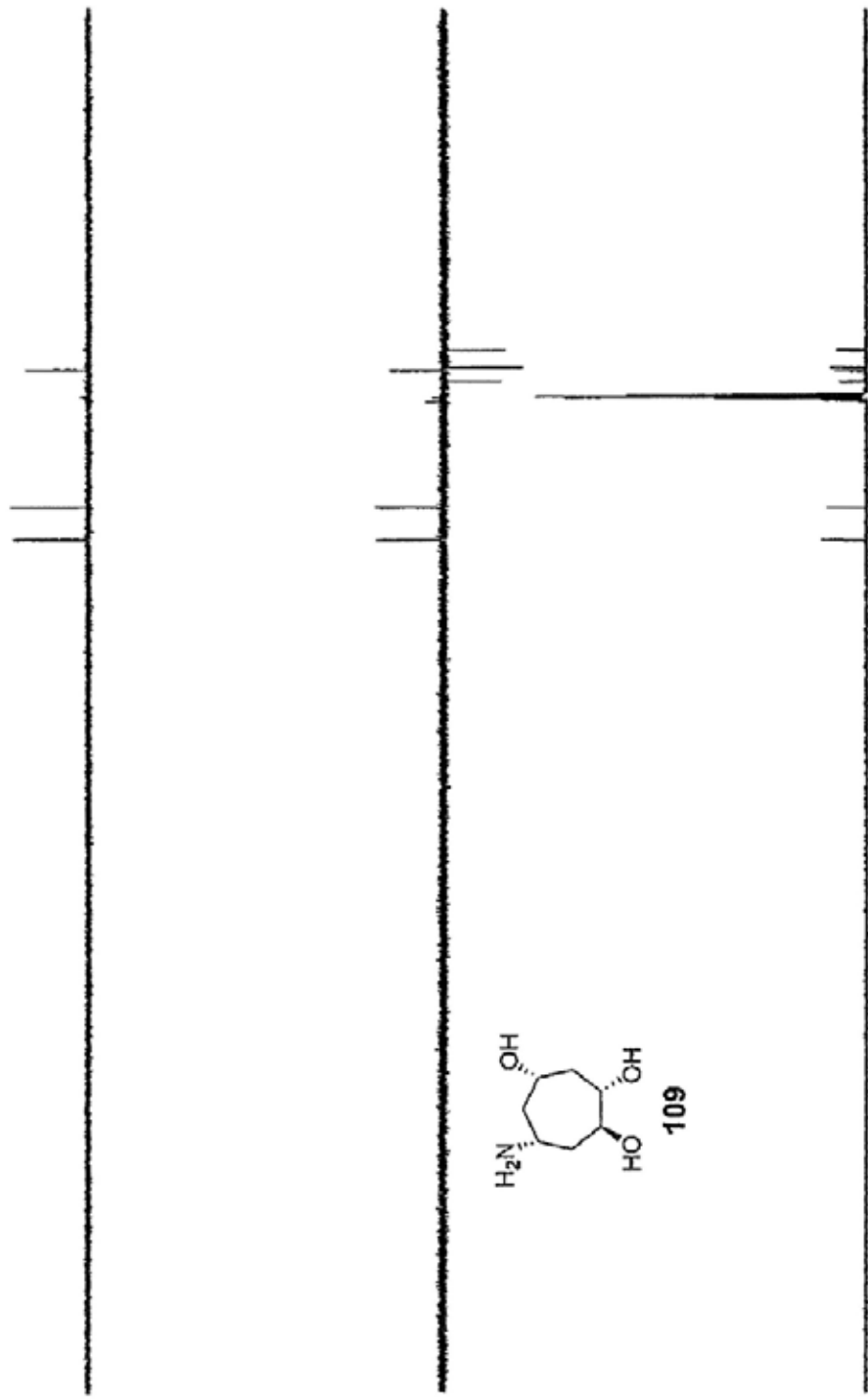
¹³C NMR (Solvent: CD₃OD)

73.88
73.70
68.16
49.42
49.42
49.21
49.00
48.79
48.57
48.36
48.36
46.36
44.49
43.94
41.03

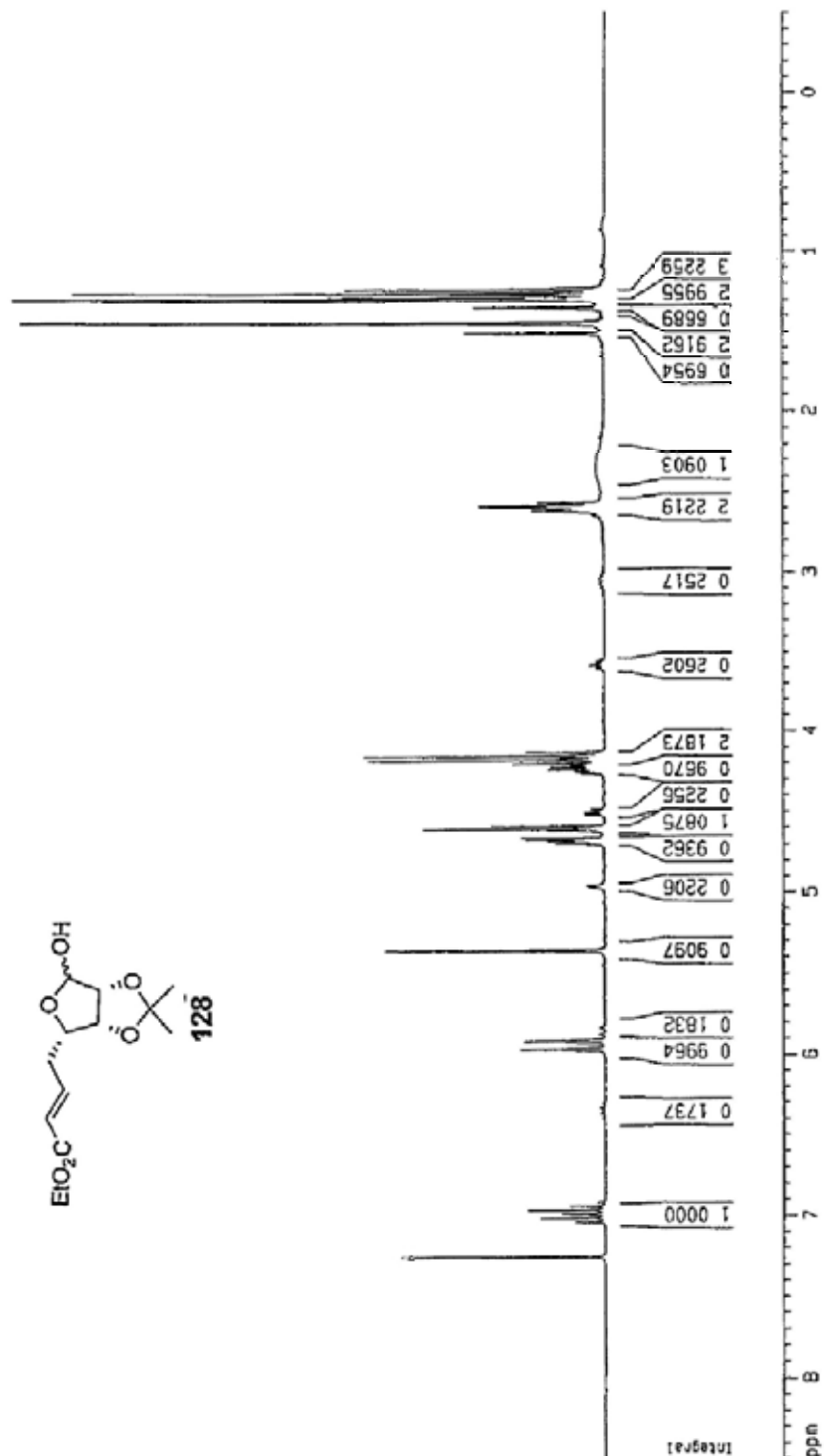
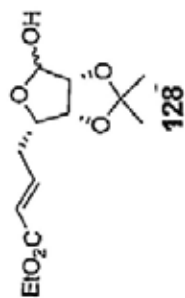
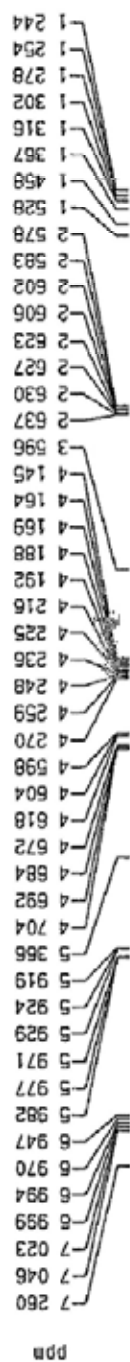
NAME sbh46carbon
EXPNO 1
PROCNO 1
Date_ 20100928
Time_ 18.11
INSTRUM spect
PROBHD 5 mm PABBD-8B-
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 89
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 1620
DM 20.800 usec
DE 6.50 usec
TE 298.5 K
D1 2.0000000 sec
D11 0.0300000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.90 usec
PL1 -2.00 dB
PL1W 55.33689499 W
SFO1 100.6179183 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.16 dB
PL13 18.62 dB
PL12W 13.56617069 W
PL12W 0.32844096 W
PL13W 0.14806664 W
SFO2 400.1916008 MHz
SI 32768
SF 100.6271170 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



¹H NMR



Current Data Parameters
 NAME EXPNO 1
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20070911
 Time 22.02
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpg30
 TO 32768
 SOLVENT CDCl₃
 NS 8
 DS 0
 SWH 8932.806 Hz
 FIDRES 0.274439 Hz
 AQ 1.8219506 sec
 RG 181
 DV 55.500 usec
 DE 79.43 usec
 TE 0.0 K
 D1 1.0000000 sec
 MCREST 0.0001000 sec
 MDPRK 0.01500000 sec
 ----- CHANNEL f1 -----
 NUC1 1H
 P1 5.00 usec
 PL1 -2.00 dB
 SFO1 300.1312000 MHz
 F2 - Processing parameters
 S1 32768
 SF 300.130063 MHz
 MDH EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00
 3D NMR plot parameters
 CX 32.00 cm
 CY 8.01 cm
 FIP 8.500 ppm
 F1 2551.10 Hz
 F2 0.500 ppm
 PPMCM -350.07 Hz
 NZCM 0.40395 ppm/cm
 NZCN 122.78046 Hz/cm

```

Current Data Parameters
NAME      suk513carbon
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20070311
Time     22 13
INSTRUM  gpc300
PROBHD   5 mm BBO BB-1H
PULPROG  zgpg
TD        65536
SOLVENT  DMS-D6
NS        380
DS        0
SMH       22675.736 Hz
FIDRES   0.346004 Hz
AQ        1.465188 sec
RG        4597.6
DM        22.058 usec
DE        6.00 usec
TE        0.0 K
O1        1.0000000 sec
O11       0.0300000 sec
MCREST   0.0000000 sec
MCHRGK   0.0150000 sec

***** CHANNEL f1 *****
NUC1      13C
P1        3.00 usec
PL1       -6.00 dB
SF01      75.4745111 MHz

***** CHANNEL f2 *****
CPDPRG2  waltz16
NUC2      1H
PCPD2     160.00 usec
PL2       19.00 dB
PL12      19.00 dB
SF02      300.1315007 MHz

F2 - Processing parameters
SI        65536
SF        75.4677146 MHz
WDW       EM
SSB       0
LB        3.00 Hz
GB        0
PC        1.40

***** F2 MDW plot parameters *****
CX        23.00 cm
CY        10.44 cm
FIP       220.000 ppm
F1        15602.50 Hz
F2p       -20.000 ppm
F2        -1509.35 Hz
PPM01    10.43078 ppm/cx
M001     767.46814 Hz/cm

```

¹³C NMR

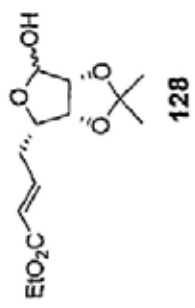
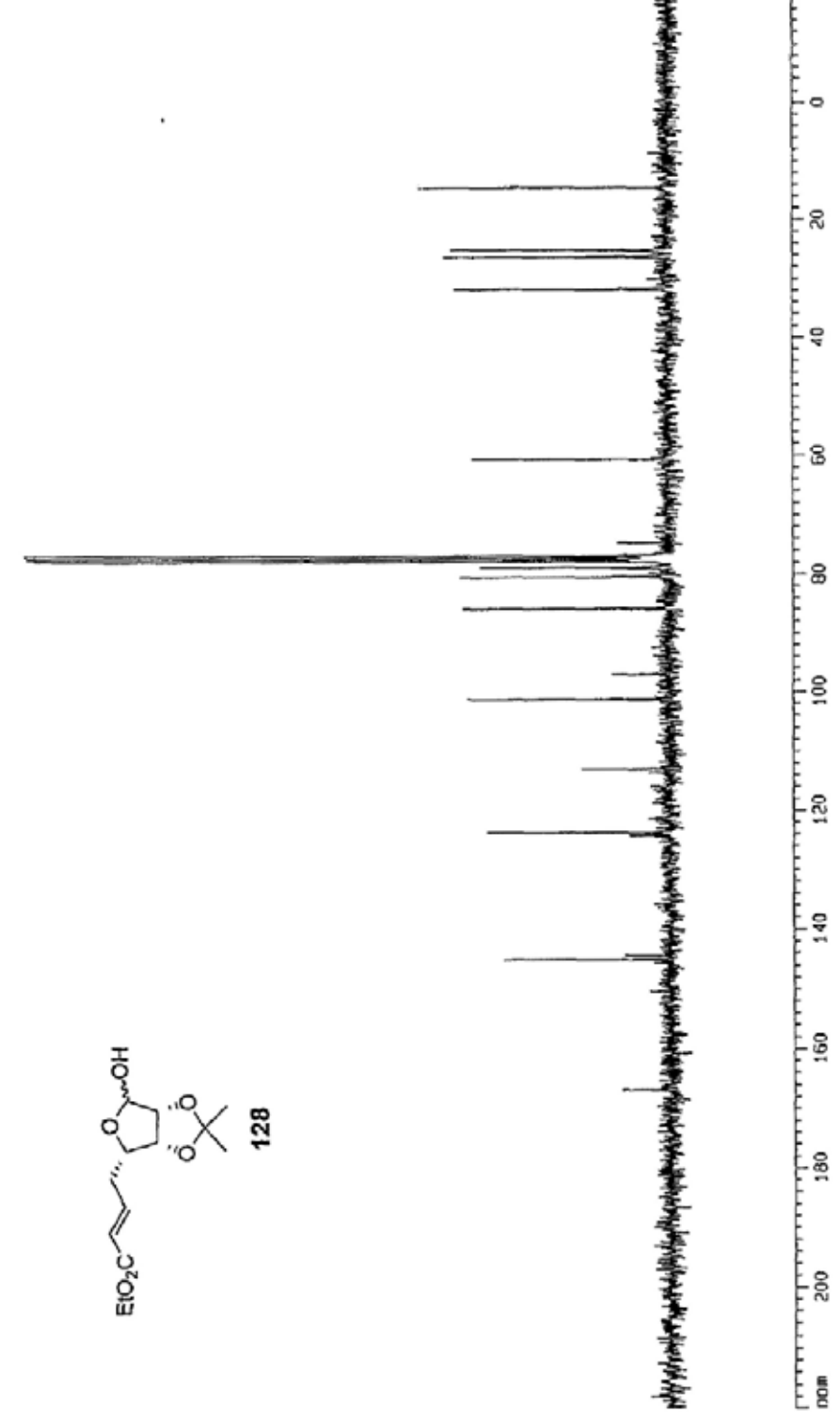
14 713
25 320
25 482
26 290
26 482
31 742
31 955

60 799
74 794
77 059
77 483
77 906
78 982
79 168
80 445
80 666
86 029
97 129
101 359

113 049
123 885
124 240

144 528
145 205

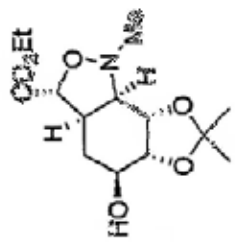
166 973



¹H NMR

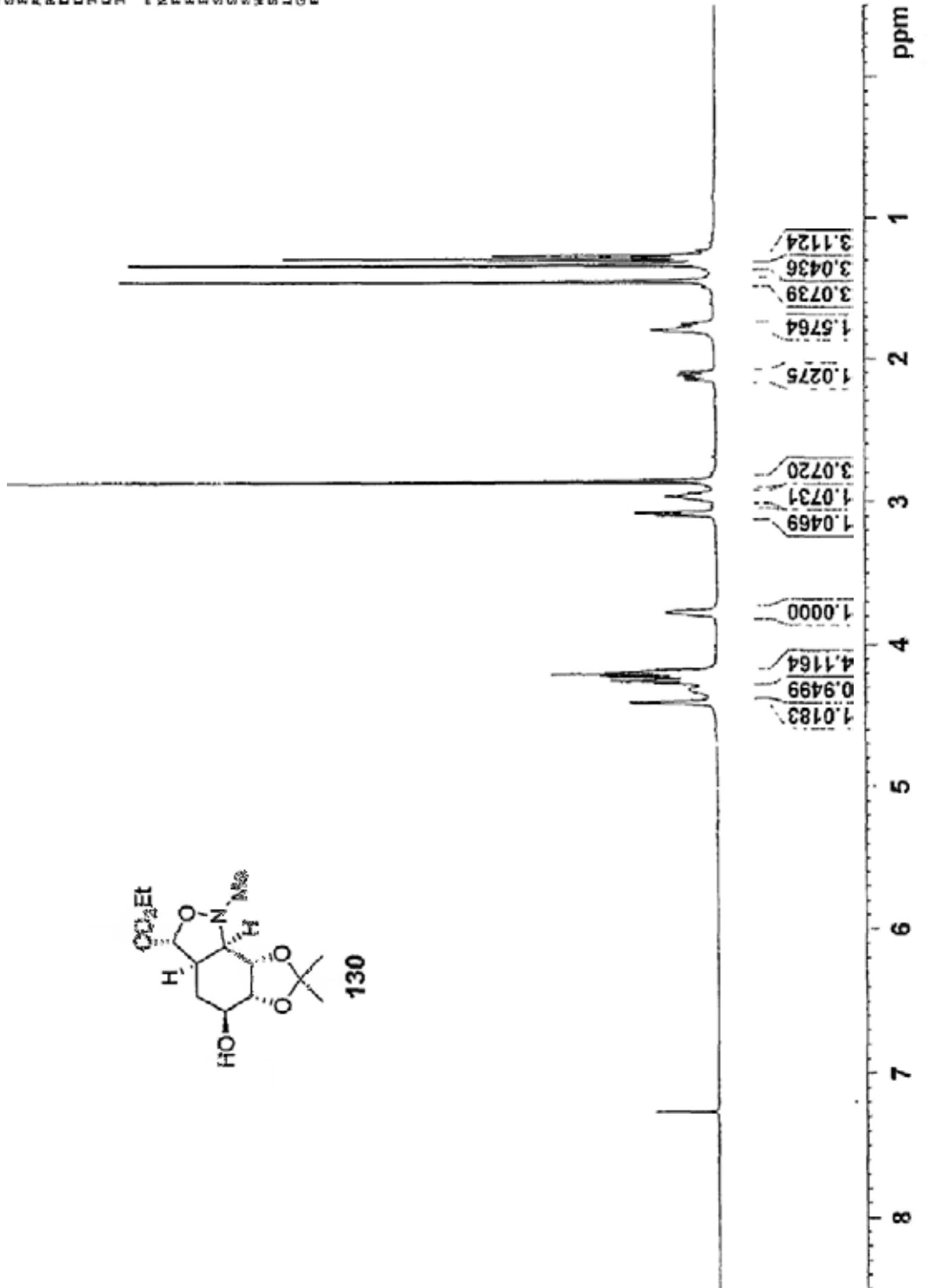
4.4076
4.3971
4.3133
4.2717
4.2652
4.2543
4.2471
4.2368
4.2278
4.2190
4.2099
4.2099
4.2099
4.1910
4.1833
4.1729
3.7800
3.7731
3.7661
3.0964
3.0899
3.0776
3.0711
3.0916
2.9798
2.9718
2.9611
2.9500
2.9425
2.9307
2.8590
2.1526
2.1451
2.1330
2.1255
2.1170
2.1095
2.0974
2.0899
1.8056
1.7937
1.7781
1.7572
1.7430
1.4532
1.3350
1.3048
1.2870
1.2692

7.2597



NAME
EXPNO 1
PROCNO 1
Date_ 20100826
Time 11.15
INSTRUM spect
PROBHD 5 mm PABBO 1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2
DS 2
SWH 8223.685 Hz
FIDRES 0.123483 Hz
AQ 3.9866387 sec
RG 64
WDW EM
SSB 60.800 usec
LB 6.50 usec
GB 67.2 K
PC 1.0000000 sec
1

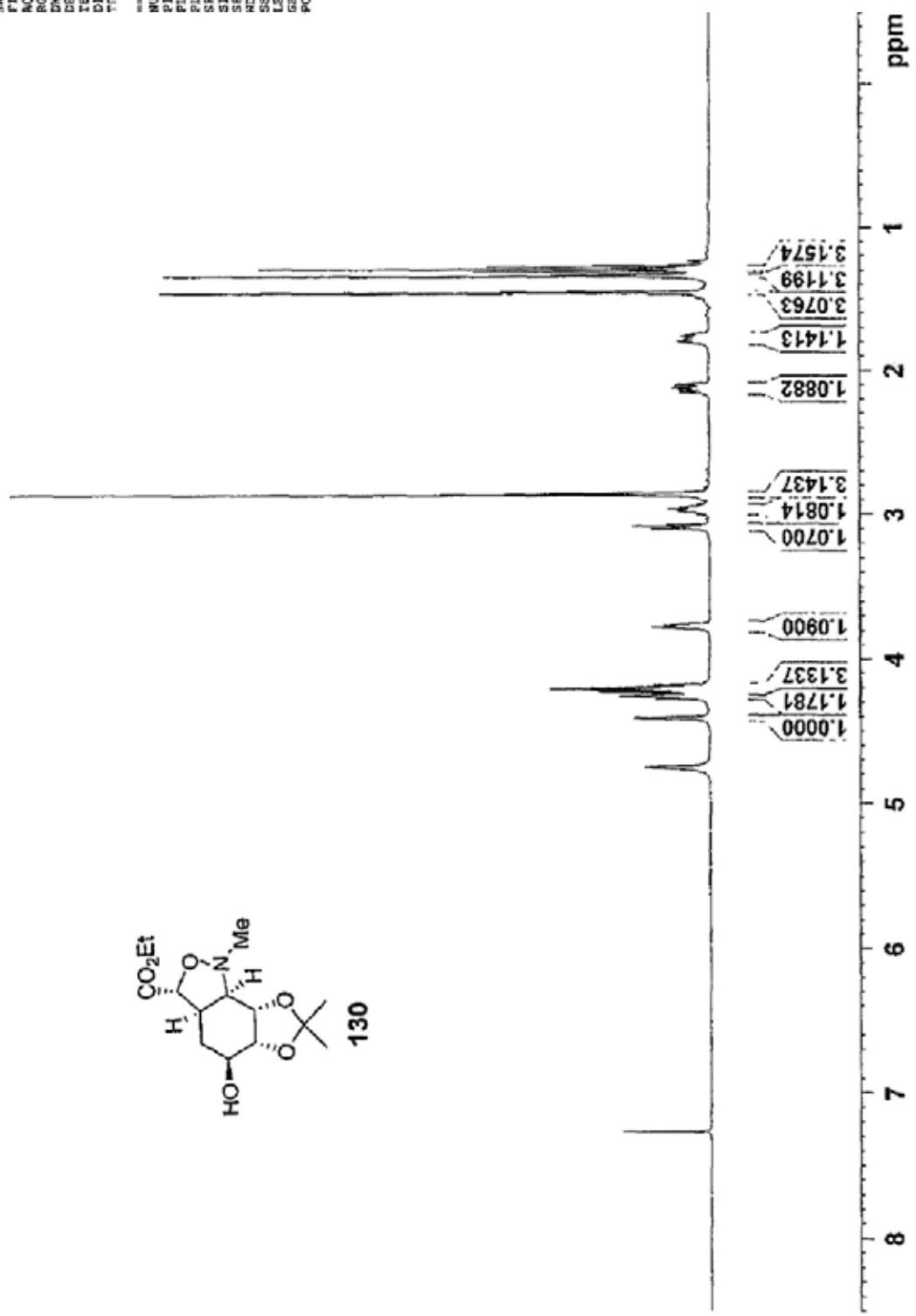
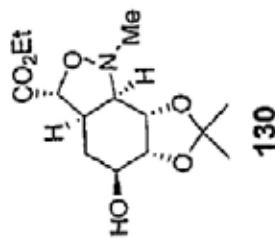
***** CHANNEL f1 *****
NUC1 13C
P1 13.00 usec
PL 0.00 dB
F2 13.17734718 MHz
SFO 400.1324310 MHz
SI 32768
SF 400.1300053 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



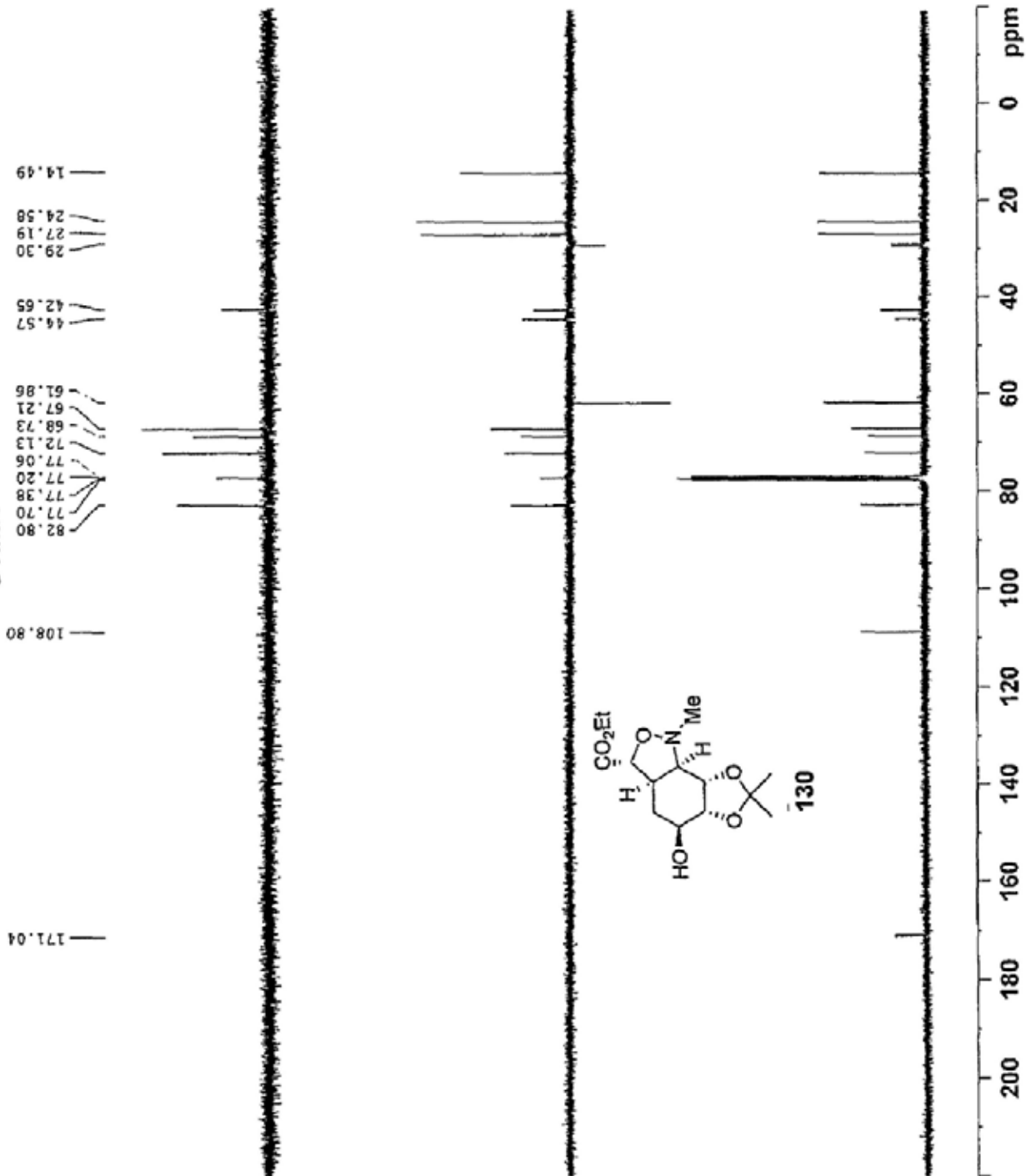
¹H NMR (Solvent: CDCl₃-D₂O)

7.2601
4.7491
4.4129
4.4023
4.2765
4.2701
4.2589
4.2525
4.2404
4.2313
4.2226
4.2135
4.2049
4.1957
4.1874
4.1781
3.7868
3.7785
3.7700
3.7624
3.7529
3.1004
3.0938
3.0816
3.0750
2.9953
2.9838
2.9756
2.9649
2.9537
2.9459
2.9344
2.8618
2.1567
2.1491
2.1370
2.1294
2.1210
2.1134
2.1014
2.0938
1.8110
1.7971
1.7824
1.7761
1.7615
1.7477
1.4568
1.3386
1.3083
1.2904
1.2726

NAME
EXPNO
PROCNO
DATE_
TIME
INSTRUM
PROBHD
PULPROG
TD
SOLVENT
NS
DS
SWH
FIDRES
AQ
RG
DVI
DE
TE
D1
D11
TD0
***** CHANNEL f1 *****
NUC1
P1
PL1
PLN
SFO1
SI
SF
NDM
SSB
LB
GB
PC
ahh3_d2o
1
20100827
10.33
spect
5 mm PWBH1 1H/
2530
45536
CDCl3
1
2
8223.685 Hz
0.125483 Hz
3.5846387 sec
80.6
60.800 usec
6.50 usec
294.4 K
1.00000000 sec
1
1H
7.10 usec
-2.00 dB
15.17254718 W
400.1324710 MHz
32768
r00 13000048 MHz
EM
C
0.30 Hz
0
1.00



¹³C NMR



NAME skh53carbon
EXPNO 1
PROCNO 1
Date_ 20100826
Time_ 11.20
INSTRUM spect
PROBHD 5 mm PABBI 1H/1
PULPROG zgpg30
TD 65536
SOLVENT CDCl₃
NS 270
DS 4
SWH 24038.463 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DM 20.800 usec
DE 6.50 usec
TE 673.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

CHANNEL f1
NUC1 13C
P1 14.50 usec
PL1 -4.00 dB
PL1W 90.22689819 W
SFO1 100.6228258 MHz

CHANNEL f2
CFPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL2W 18.80 dB
PL3 18.80 dB
PL2W 13.17734718 W
PL12W 0.10960442 W
PL13W 0.10960442 W
SFO2 400.1316000 MHz
SI 32768
SF 100.6127946 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

¹H NMR

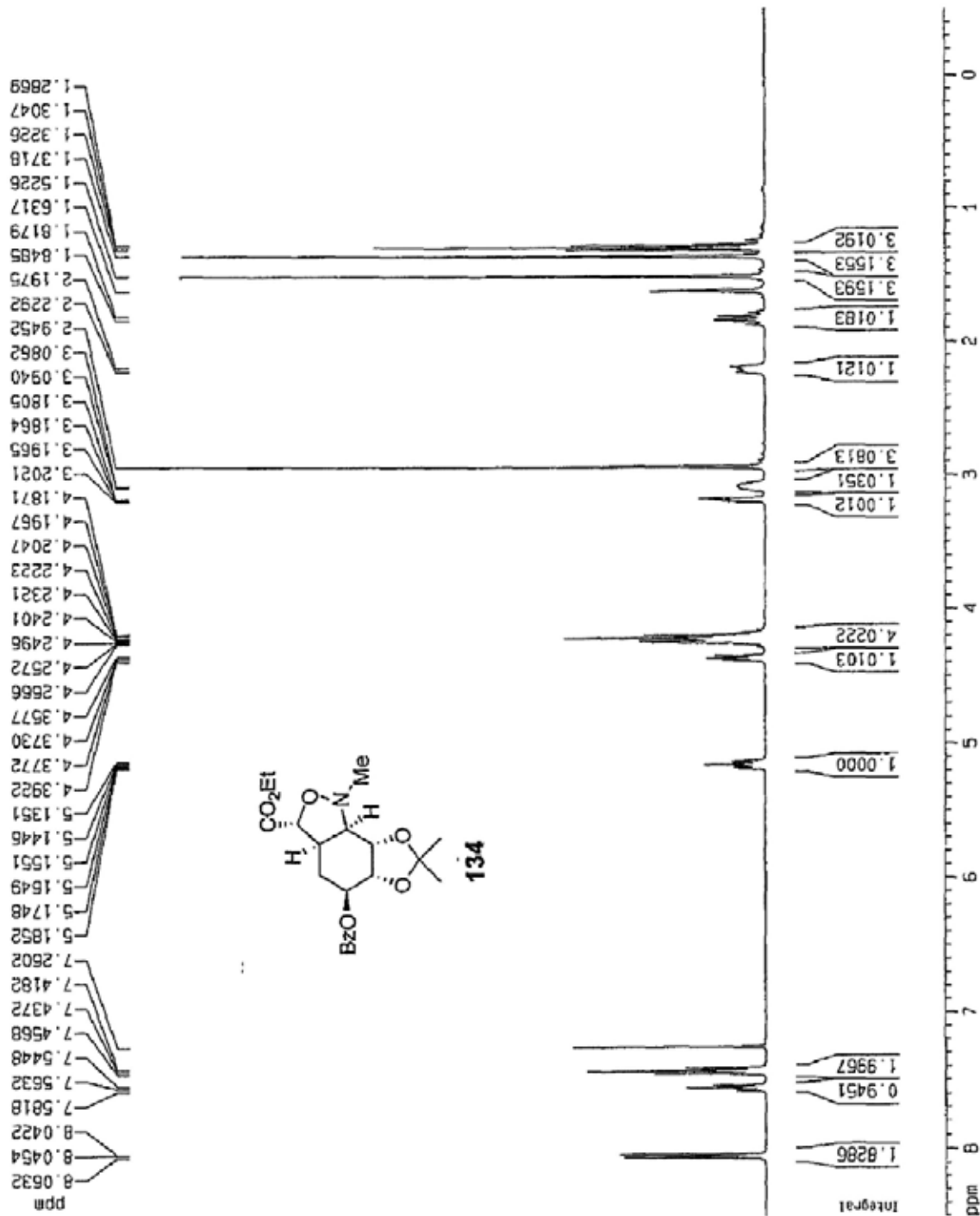
Current Data Parameters
NAME skh78b
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080214
Time 12:22
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg
TD 65535
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.152569 Hz
AQ 3.2768500 sec
RG 71.8
DM 50.000 usec
DE 6.50 usec
TE 293.4 K
D1 1.00000000 sec
D10 1

***** CHANNEL f1 *****
NUC1 1H
P1 14.10 usec
PL1 0.00 dB
SFO1 400.1316005 MHz

F2 - Processing parameters
SI 65536
SF 400.1300054 MHz
WDW EN
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 10.91 cm
F1P 6.500 ppm
F1 3401.10 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PRND 0.45000 ppm/cm
HZCN 180.05849 Hz/cm



Current Data Parameters

NAME skh78carbon
 EXPNC 1
 PROCNC 1

F2 - Acquisition Parameters

Date_ 20080317
 Time_ 15.33
 INSTRUM spect
 PROBHD 5 mm PADUL 13C
 PULPRG zgdc
 TD 131072
 SOLVENT CDCl3
 NS 698
 DS 0
 SWH 25252.525 Hz
 FIDRES 0.192661 Hz
 AQ 2.5952756 sec
 RG 203
 DM 19.800 usec
 DE 6.50 usec
 TE 295.8 K
 D1 1.0000000 sec
 d11 0.0300000 sec
 TDR 1

==== CHANNEL f1 =====

NUC1 13C
 P1 3.50 usec
 PL1 -0.60 dB
 SFO1 100.6227690 MHz

==== CHANNEL f2 =====

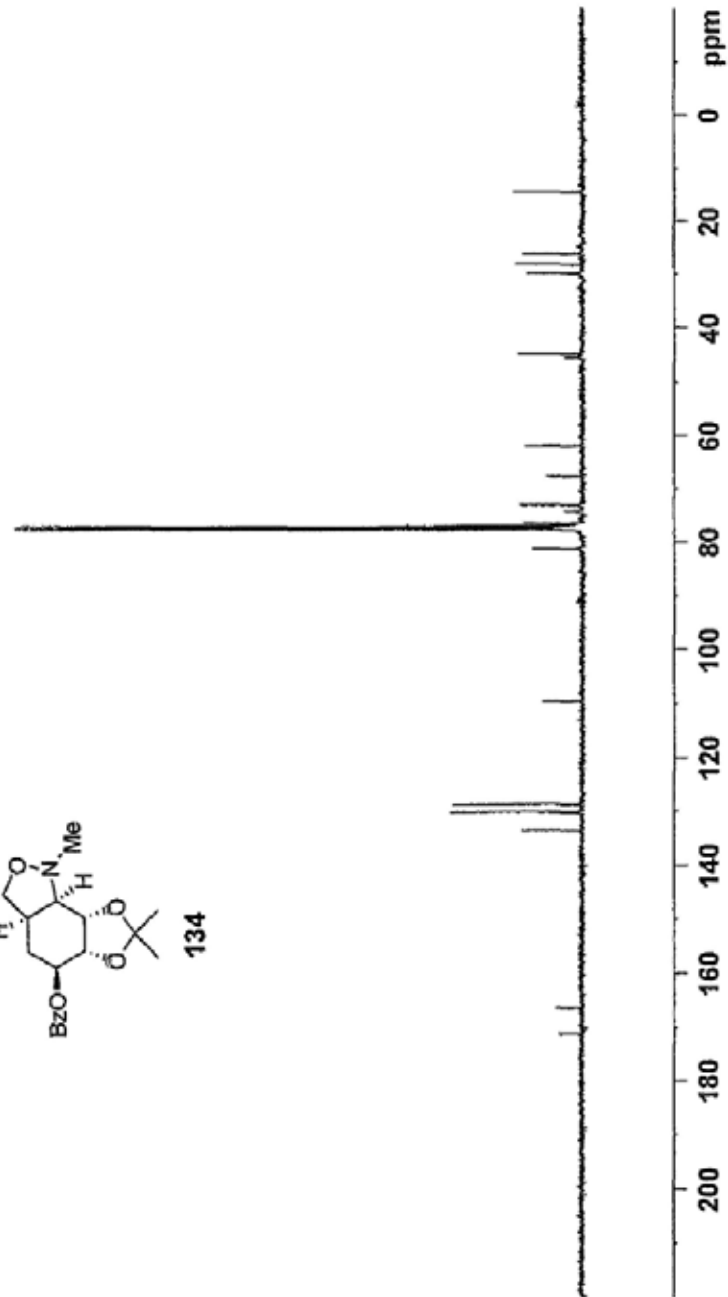
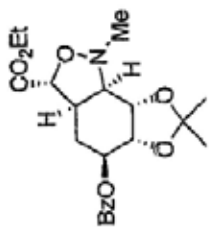
CPDPRG2 waltz16
 NUC2 1H
 FCPD2 90.00 usec
 PL2 16.10 dB
 PL2 0 dB
 SFO2 400.1320007 MHz

F2 - Processing parameters

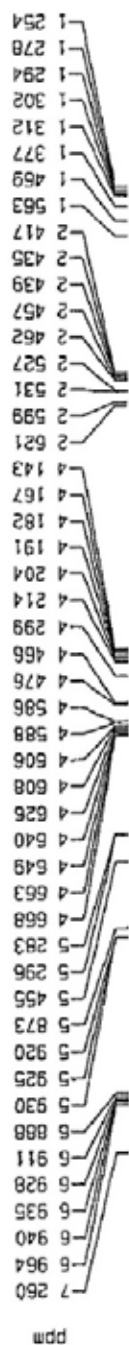
SF 131072
 SF 100.6127336 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40

¹³C NMR

- 171.33
- 166.39
- 133.53
- 130.27
- 130.13
- 128.73
- 109.51
- 81.26
- 77.69
- 77.38
- 77.06
- 76.60
- 74.33
- 73.08
- 67.70
- 62.02
- 45.55
- 44.81
- 29.89
- 28.21
- 26.15
- 14.52



¹H NMR



Current Data Parameters
 NAME sth70carbon
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20071026
 Time 17 12
 INSTRUM GPC300
 PROBRD 5 mm BBO BB-1H
 PULPROG zgpg
 TD 65535
 SOLVENT CDCl3
 NS 484
 DS 0
 SWH 22675.735 Hz
 FIDRES 0.3460004 Hz
 AQ 1.4431188 sec
 RG 5160.6
 DM 22.050 usec
 DE 6.00 usec
 TE 0.0 K
 D1 1.0000000 sec
 d11 0.0300000 sec
 NUCRES1 D
 NUCRES2 D
 NUCRES3 D
 NUCRES4 D
 NUCRES5 D
 NUCRES6 D
 NUCRES7 D
 NUCRES8 D
 NUCRES9 D
 NUCRES10 D
 NUCRES11 D
 NUCRES12 D
 NUCRES13 D
 NUCRES14 D
 NUCRES15 D
 NUCRES16 D
 NUCRES17 D
 NUCRES18 D
 NUCRES19 D
 NUCRES20 D
 NUCRES21 D
 NUCRES22 D
 NUCRES23 D
 NUCRES24 D
 NUCRES25 D
 NUCRES26 D
 NUCRES27 D
 NUCRES28 D
 NUCRES29 D
 NUCRES30 D
 NUCRES31 D
 NUCRES32 D
 NUCRES33 D
 NUCRES34 D
 NUCRES35 D
 NUCRES36 D
 NUCRES37 D
 NUCRES38 D
 NUCRES39 D
 NUCRES40 D
 NUCRES41 D
 NUCRES42 D
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 NUCRES46 D
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 NUCRES61 D
 NUCRES62 D
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 NUCRES66 D
 NUCRES67 D
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 NUCRES71 D
 NUCRES72 D
 NUCRES73 D
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 NUCRES78 D
 NUCRES79 D
 NUCRES80 D
 NUCRES81 D
 NUCRES82 D
 NUCRES83 D
 NUCRES84 D
 NUCRES85 D
 NUCRES86 D
 NUCRES87 D
 NUCRES88 D
 NUCRES89 D
 NUCRES90 D
 NUCRES91 D
 NUCRES92 D
 NUCRES93 D
 NUCRES94 D
 NUCRES95 D
 NUCRES96 D
 NUCRES97 D
 NUCRES98 D
 NUCRES99 D
 NUCRES100 D

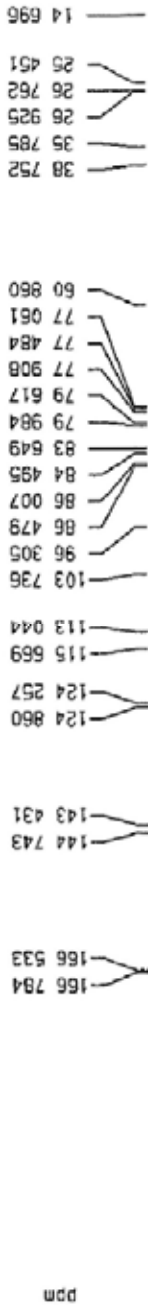
***** CHANNEL f1 *****
 NUC1 13C
 P1 3.00 usec
 PL1 -6.00 dB
 SFO1 75.4745111 MHz

***** CHANNEL f2 *****
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 usec
 PL2 120.00 dB
 PL12 19.00 dB
 SFO2 300.1315007 MHz

F2 - Processing parameters
 SI 65536
 SF 4677136 MHz
 NDM EN
 SSB C
 LB 3.00 Hz
 GB 6
 PC 1.40

10 MHz plot parameters
 CX 23.90 cm
 CY 10.90 cm
 F1P 220.000 ppm
 F1 16502.90 Hz
 F2P -20.000 ppm
 F2 -1508.35 Hz
 PPH0H 10.43478 ppm/cx
 APM 187.48620 Hz/cx

¹³C NMR

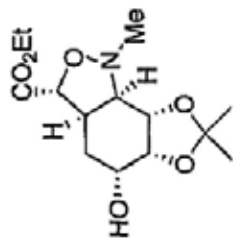


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¹H NMR (Solvent: C₆D₆)

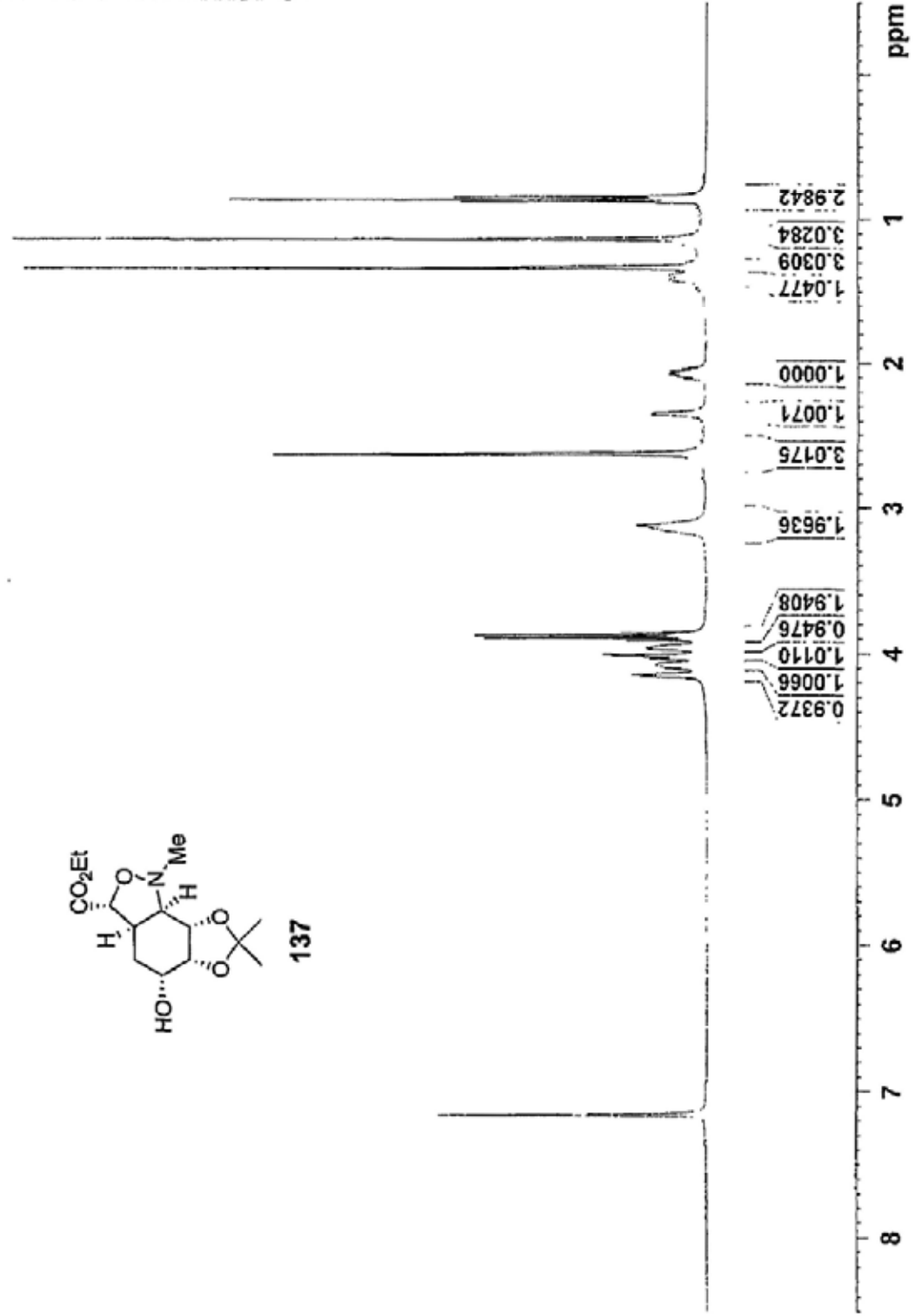
7.1600

4.1585
4.1435
4.0749
4.0368
4.0282
4.0175
4.0089
3.9702
3.9618
3.9102
3.8923
3.8745
3.8568
3.1521
3.1233
2.6297
2.3589
2.3459
2.1133
2.0910
2.0791
2.0613
2.0392
-1.4212
-1.3893
-1.3399
-1.1463
-0.8901
-0.8722
0.8545



137

NAME s1h73_1st_6565
EXNO 1
PROCNO 1
Date_ 20100823
Time_ 19.38
INSTRUM spect
PROBRD 5 mm PABBI 1H
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 4
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.984537 sec
RG 32
DM 60.800 usec
DE 6.50 usec
TE 294.5 K
D1 1.00000000 sec
TD0 1
***** CHANNEL f1 *****
NUC1 1H
P1 7.10 usec
PL1 -2.00 dB
SFO1 13.1734718 MHz
SFO2 450.1324710 MHz
SFO3 537.68 MHz
SFO4 490.1300457 MHz
SFO5 50 MHz
SFO6 C
LB 0.30 Hz
GB 0
PC 1.00



¹H NMR (Solvent: C₆D₆-D₂O)

```

NAME          smn73_1st_cf606_d2o
EXPNO         1
PROCNO        1
Date_         20100824
Time_         15.55
INSTRUM       spect
PROBHD        5 mm TMRBBI 1H/
PULPROG       zg30
TD             65536
SOLVENT       CDCl3
NS            4
DS            2
SFO          400.1360426 MHz
AQ           3.5846367 sec
RG           32
DW           60.800 usec
DE           6.50 usec
TE           294.2 K
D1           1.00000000 sec
D0           1
===== CHANNEL f1 =====
NUC1          1H
P1            1.10 usec
PL1          -2.00 dB
PL12         13.1774718 dB
SFO1         400.1360426 MHz
SI           32768
SF           400.1360426 MHz
WDW          EM
SSB          0
LB           0.30 KHz
GB           0
PC           1.00
  
```

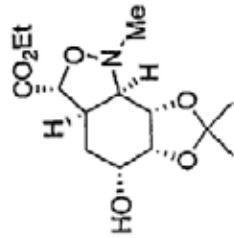
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-1.4218
-1.3902
-1.3407
1.1470
0.8910
0.8732
0.8554

2.1147
2.0926
2.0804
2.0624
2.0412

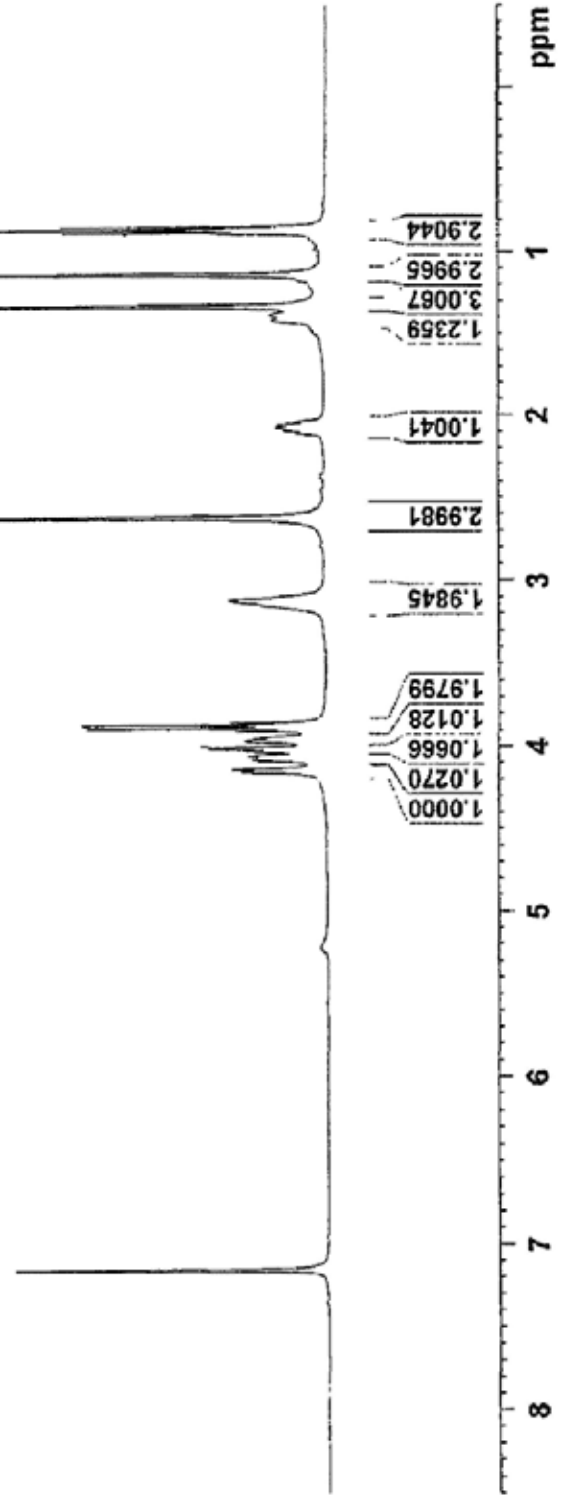
2.6295

3.1234
3.0572
3.0750
3.8927
3.9105
3.9648
4.0099
4.0181
4.0290
4.0374
4.0625
4.0786
4.0852
4.1440
4.1583
  
```

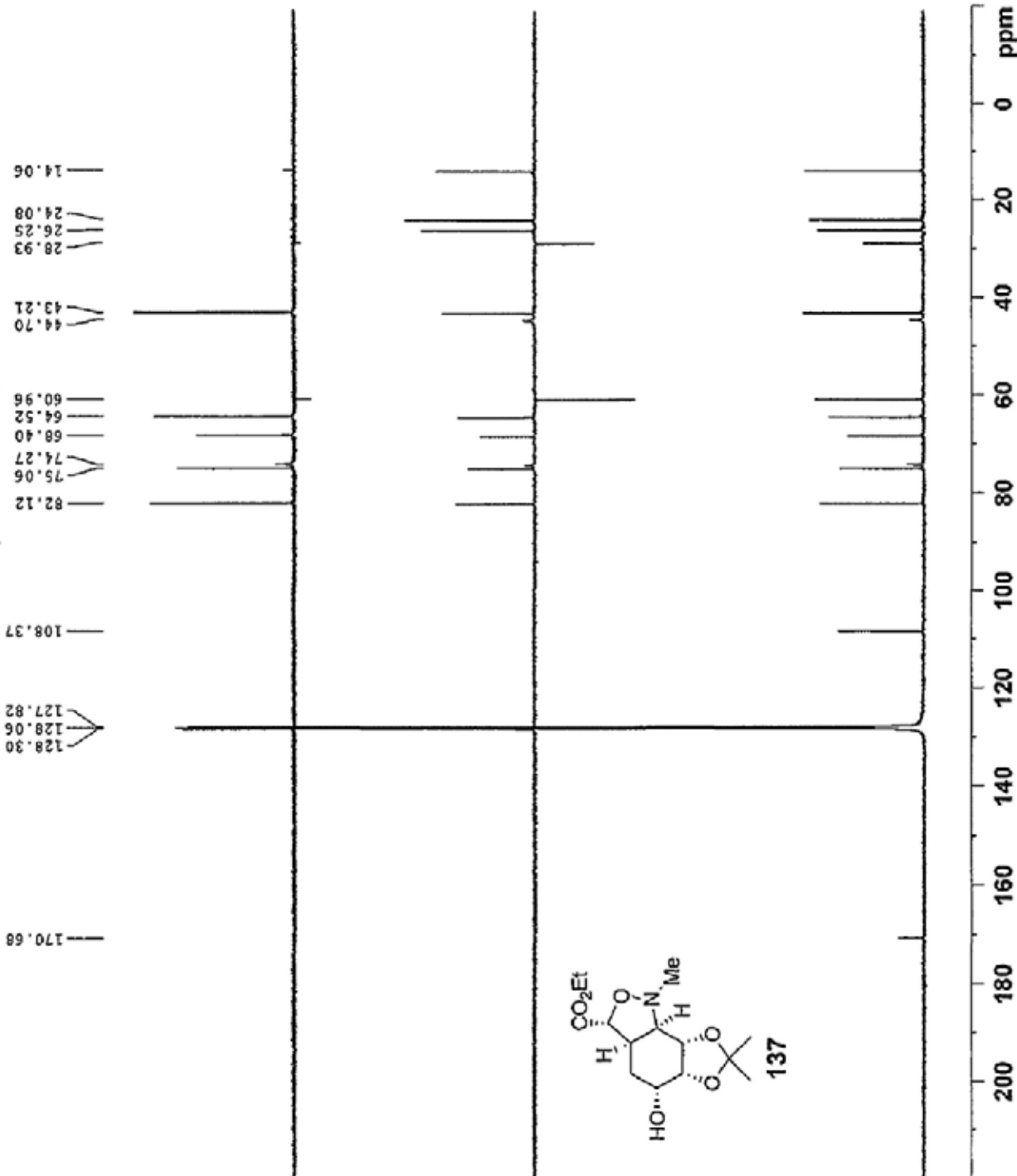


137

7.1600



¹³C NMR (Solvent: C₆D₆)

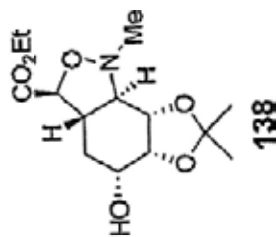
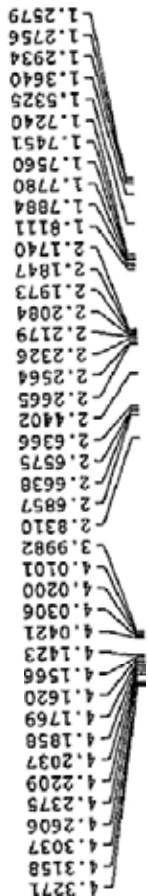


NAME skh73_1st_carbon
 EXPNO 1
 PROCNO 1
 Date_ 20100823
 Time 14.36
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT C6D6
 MS 293
 DS 4
 SWH 24039.461 Hz
 FIDRES 0.366759 Hz
 AQ 1.3631988 sec
 RG 203
 DM 20.800 usec
 DE 6.50 usec
 TE 298.5 K
 D1 2.0000000 sec
 D11 0.0000000 sec
 TDO 1

CHANNEL f3
 NUC1 13C
 P1 9.90 usec
 PL1 -2.00 dB
 PL1W 55.33689499 W
 SFO1 100.6278192 MHz

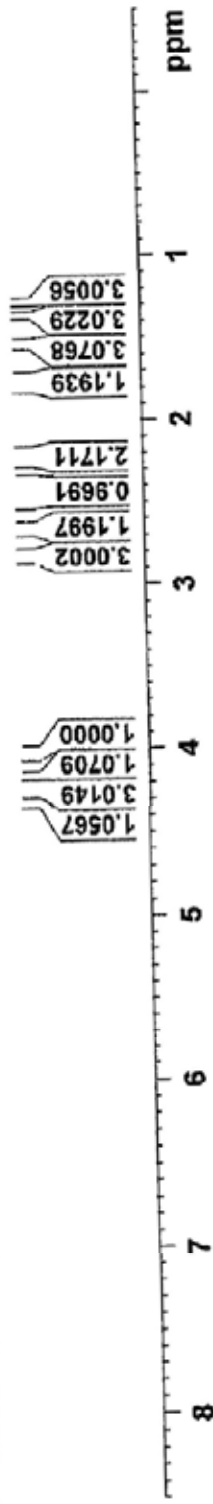
CHANNEL f2
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 90.00 usec
 PL2 -1.00 dB
 PL12 15.16 dB
 PL13 18.62 dB
 PL2W 13.56617069 W
 PL1W 0.3284096 W
 PL13W 0.14806664 W
 SFO2 400.1915008 MHz
 SI 32768
 SF 100.6278192 MHz
 MDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

¹H NMR

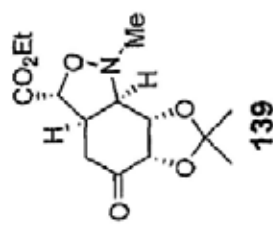


```

NAME          sht33_3rd
EXPNO         2
PROCNO        1
Date_         20100817
Time          21.32
INSTRUM       spect
PROBHD        5 mm QNP60
PULPROG       zgpg30
SOLVENT       CDCl3
NS            4
DS            2
SWH           8223.685 Hz
F2          0.125483 Hz
F1          3.9846387 sec
AQ           50.6
RG           60.800 usec
DE           6.50 usec
TE           298.0 K
D1           1.0000000 sec
TD            1
===== CHANNEL f1 =====
NUC1          1H
P1           14.00 usec
PL1          -1.00 dB
SFO1         300.13637069 MHz
SFO2         400.1524713 MHz
SFO3         327.68
SF           400.1500146 MHz
WDW           EM
SSB           0
GB           0
PC           1.00
  
```

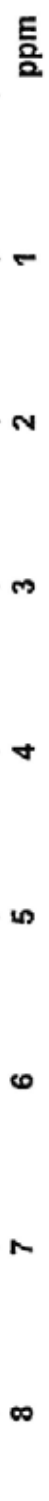
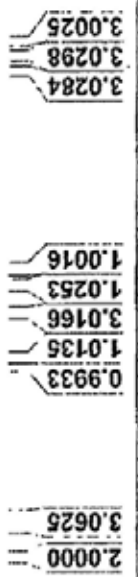


¹H NMR

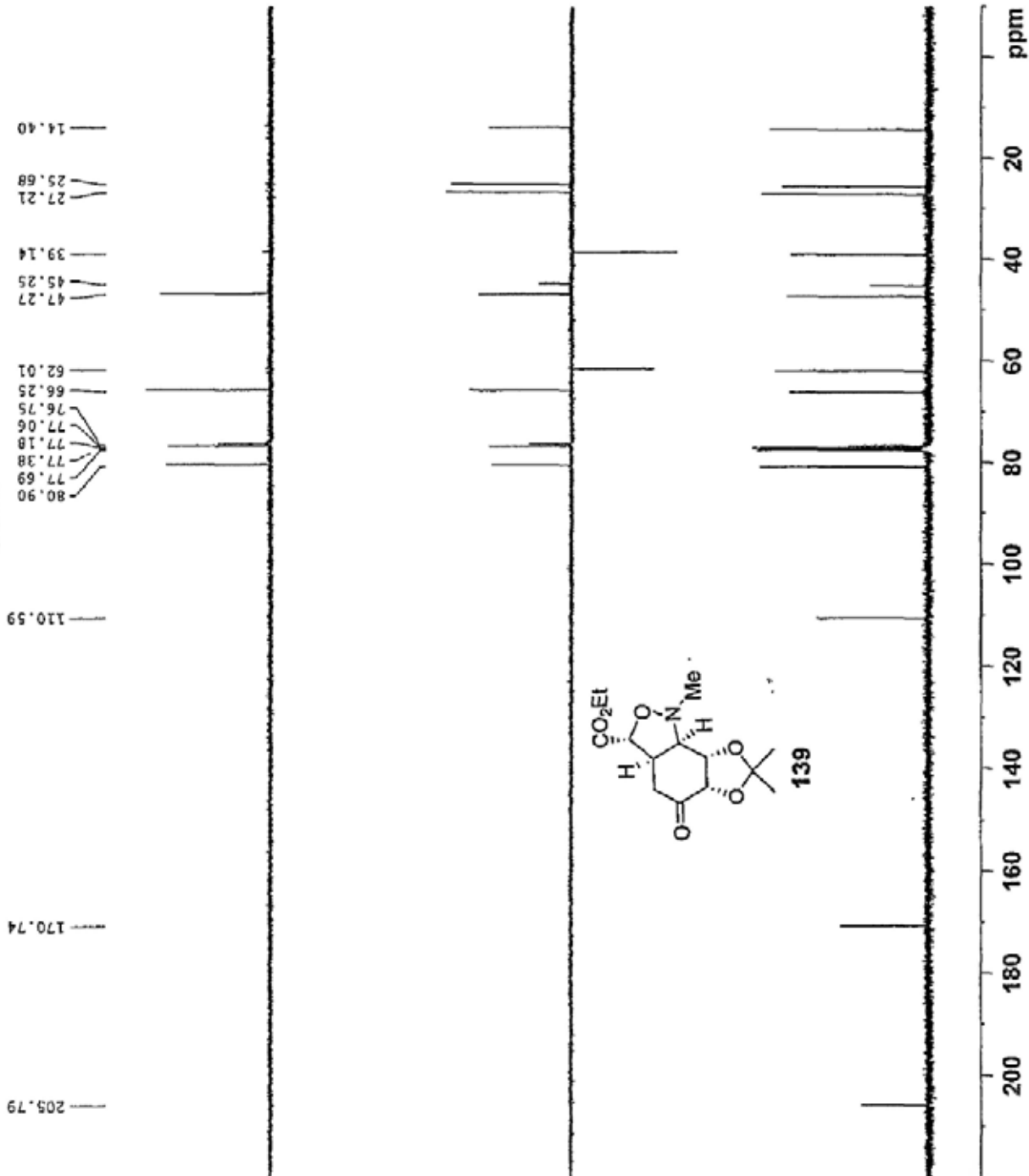


NAME sh103
EXPNO 43
PROCNO 2010080
Date_ 21.51
Time 21.51
INSTRUM spect
PROBHD zgpg30
PULPROG zgpg30
TD 65536
SOLVENT COCL2
NS 2
DS 2
SWH 8223.695 Hz
F2RES 0.125483 Hz
AQ 3.9846387 sec
RG 32
WDW 60.800 usec
DE 6.50 usec
TE 294.8 K
SI 1
SFO 400.1300041 MHz
SF 400.1300041 MHz
MAG 8.94
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

***** CHANNEL f1 *****
NUC1 1H
P1 7.10 usec
PL1 -2.00 dB
PL1H 13.17134718 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300041 MHz
MAG 8.94
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



¹³C NMR

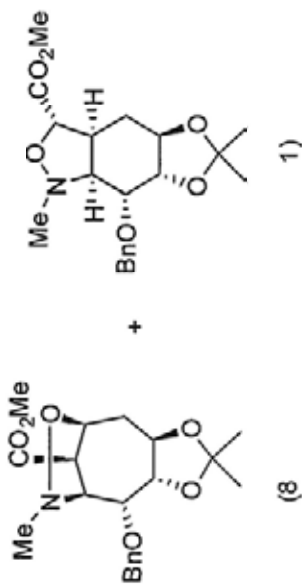
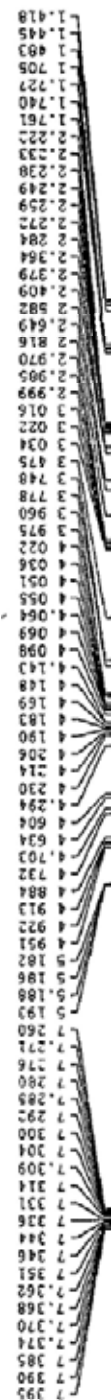


NAME skh103carbon
EXPNO 2
PROCNO 7
Date_ 20100806
Time 21.56
INSTRUM spect
PROBHD 5 mm F40G1 IH/
PULPROG zgpg30
TD 65536
SOLVENT CDCl₃
NS 73
DS 4
SNK 24038.461 Hz
FIDRES 0.366198 Hz
AQ 1.363188 sec
RG 203
DM 20.800 usec
DE 6.50 usec
TE 295.0 K
D1 2.0000000 sec
D11 0.0300000 sec
TD0 1

***** CHANNEL f1 *****
NUC1 ¹³C
PI 14.50 usec
PL1 -4.00 dB
PL1W 90.22689819 W
SFO1 100.628298 MHz

***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC2 ¹H
PCPD2 80.00 usec
PL2 -2.00 dB
PL2W 18.80 dB
PL13 18.80 dB
PL2W 13.17734718 W
PL12W 0.10960442 W
PL13W 0.10960442 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127390 MHz
RGW EM
SSB 0
LB 1.00 Kz
GB 0
PC 1.40

¹H NMR



141/142

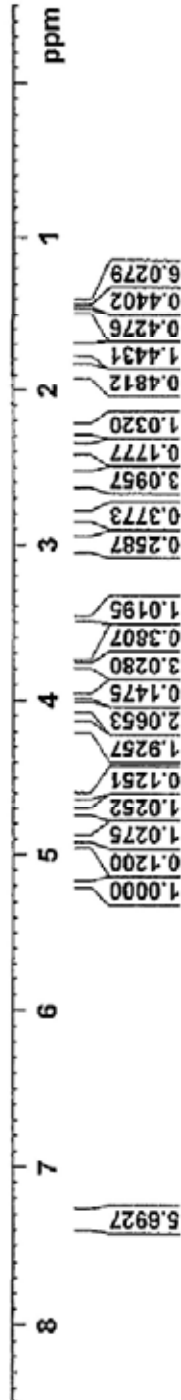
Current Data Parameters
 NAME shr09
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters

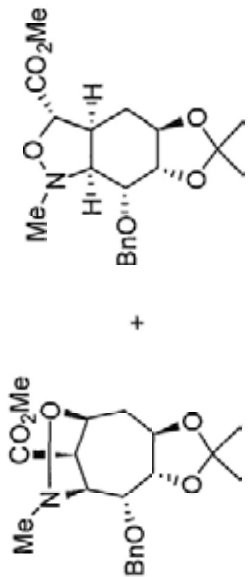
Date_ 20090514
 Time_ 17.59
 INSTRUM spect
 PROBHD 5 mm PABBI 1H/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 8223.685 Hz
 FIDRES 0.125483 Hz
 AQ 3.9846387 sec
 RG 144
 DM 60.800 usec
 DE 6.50 usec
 TE 294.3 K
 D1 1.00000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 7.10 usec
 PL1 -2.00 dB
 PL1W -1.0000000 W
 SF01 400.1324710 MHz

F2 - Processing parameters
 SI 32768
 SF 400.1300053 MHz
 WDW EM
 SSB 0
 LB 0
 GB 0
 PC 1.00

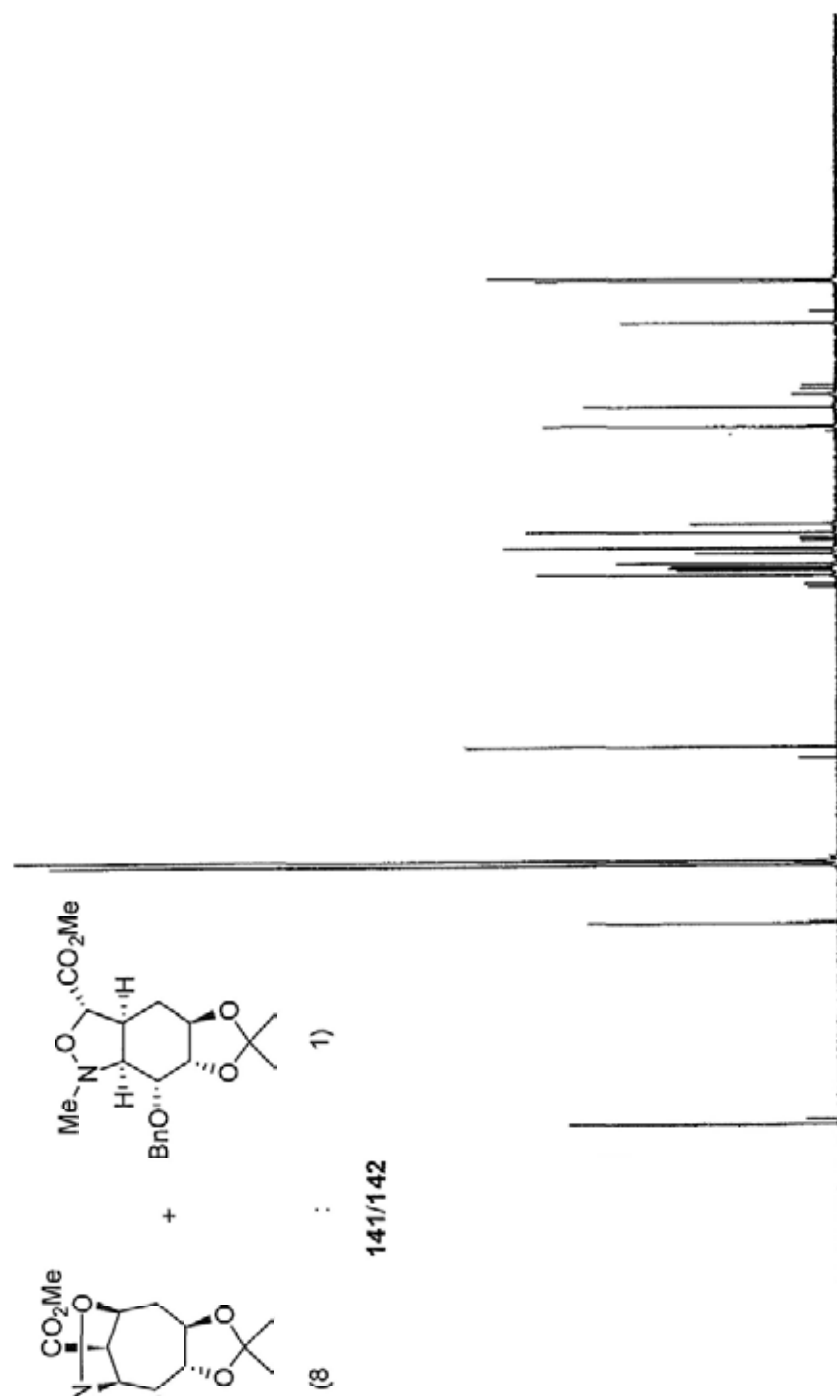


¹³C NMR



(8) : (1)

141/142



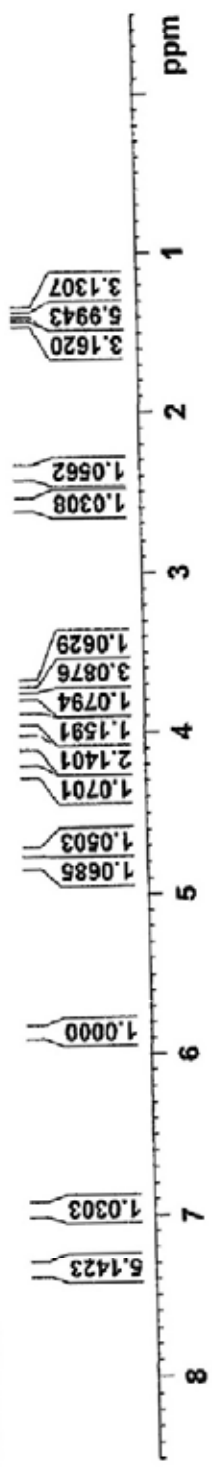
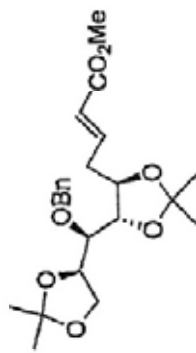
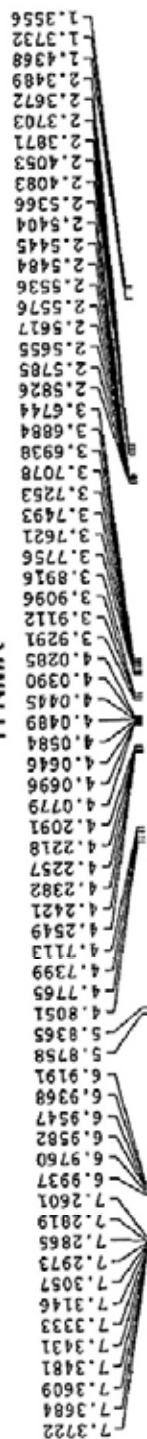
```

NAME          shc09_10carbon
EXPNO         1
PROCNO        20020610
Pulse         14.00
INSTRUM       spect
PROBHD        5 mm HANNI 1H/
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            236
DS            4
SR           24039.461 Hz
FIDRES        0.365198 Hz
AQ            1.3631263 sec
RG            20.860 usec
DE            20.860 usec
TE            294.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          13C
P1            14.50 usec
PL1           0.00 dB
PL12          99.22698300 dB
PL13          100.6221230 dB
SFO1          100.6221230 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
P2            80.00 usec
PL2           -2.00 dB
PL12          19.00 dB
PL13          19.00 dB
PL14          13.1792128 dB
PL15          0.1086142 dB
PL16          0.1086142 dB
SFO2          400.1311005 MHz
SI            32768
SF            100.6231551 MHz
RG            65536
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
    
```


¹H NMR

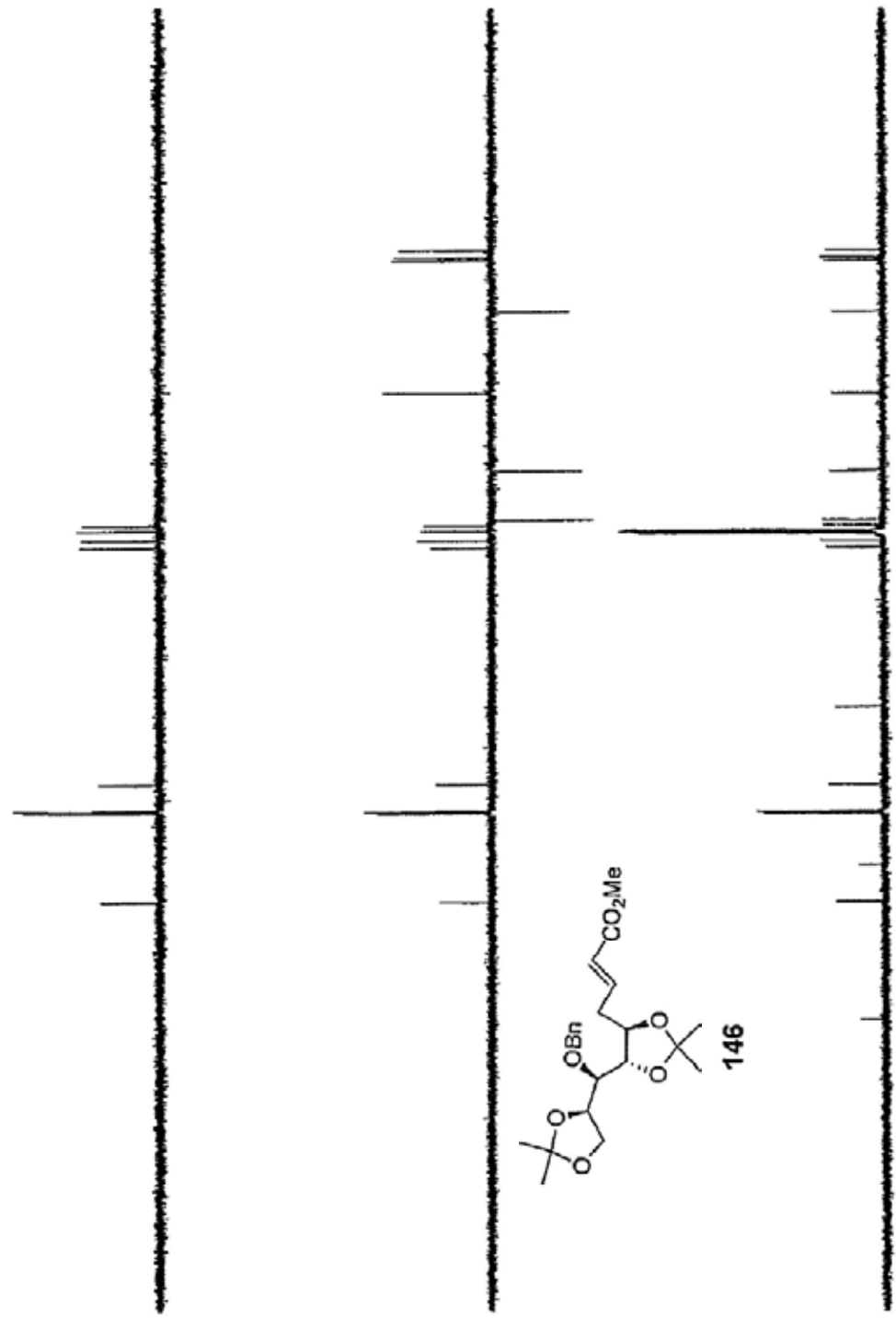


NAME: EABBO
 EABBO
 Date: 20100619
 Time: 20:09
 INST: spect
 PROG: 5 mm EABBO h
 PULPROG: zgpg30
 TD: 65536
 SOLVENT: CDCl3
 NS: 2
 DS: 4
 SWH: 8223.685 Hz
 FIDRES: 0.125183 Hz
 AQ: 3.9846387 sec
 RG: 64
 DM: 60.800 usec
 DE: 6.50 usec
 TE: 298.4 K
 D1: 1.00000000 sec
 TEO: 1

***** CHANNEL f1 *****
 NUCL1: 1H
 P1: 14.00 usec
 PL1: -1.00 dB
 PL3: -1.00 dB
 PL4: -1.00 dB
 PL5: -1.00 dB
 PL6: -1.00 dB
 PL7: -1.00 dB
 PL8: -1.00 dB
 PL9: -1.00 dB
 PL10: -1.00 dB
 PL11: -1.00 dB
 PL12: -1.00 dB
 PL13: -1.00 dB
 PL14: -1.00 dB
 PL15: -1.00 dB
 PL16: -1.00 dB
 PL17: -1.00 dB
 PL18: -1.00 dB
 PL19: -1.00 dB
 PL20: -1.00 dB
 PL21: -1.00 dB
 PL22: -1.00 dB
 PL23: -1.00 dB
 PL24: -1.00 dB
 PL25: -1.00 dB
 PL26: -1.00 dB
 PL27: -1.00 dB
 PL28: -1.00 dB
 PL29: -1.00 dB
 PL30: -1.00 dB
 PL31: -1.00 dB
 PL32: -1.00 dB
 PL33: -1.00 dB
 PL34: -1.00 dB
 PL35: -1.00 dB
 PL36: -1.00 dB
 PL37: -1.00 dB
 PL38: -1.00 dB
 PL39: -1.00 dB
 PL40: -1.00 dB
 PL41: -1.00 dB
 PL42: -1.00 dB
 PL43: -1.00 dB
 PL44: -1.00 dB
 PL45: -1.00 dB
 PL46: -1.00 dB
 PL47: -1.00 dB
 PL48: -1.00 dB
 PL49: -1.00 dB
 PL50: -1.00 dB
 PL51: -1.00 dB
 PL52: -1.00 dB
 PL53: -1.00 dB
 PL54: -1.00 dB
 PL55: -1.00 dB
 PL56: -1.00 dB
 PL57: -1.00 dB
 PL58: -1.00 dB
 PL59: -1.00 dB
 PL60: -1.00 dB
 PL61: -1.00 dB
 PL62: -1.00 dB
 PL63: -1.00 dB
 PL64: -1.00 dB
 PL65: -1.00 dB
 PL66: -1.00 dB
 PL67: -1.00 dB
 PL68: -1.00 dB
 PL69: -1.00 dB
 PL70: -1.00 dB
 PL71: -1.00 dB
 PL72: -1.00 dB
 PL73: -1.00 dB
 PL74: -1.00 dB
 PL75: -1.00 dB
 PL76: -1.00 dB
 PL77: -1.00 dB
 PL78: -1.00 dB
 PL79: -1.00 dB
 PL80: -1.00 dB
 PL81: -1.00 dB
 PL82: -1.00 dB
 PL83: -1.00 dB
 PL84: -1.00 dB
 PL85: -1.00 dB
 PL86: -1.00 dB
 PL87: -1.00 dB
 PL88: -1.00 dB
 PL89: -1.00 dB
 PL90: -1.00 dB
 PL91: -1.00 dB
 PL92: -1.00 dB
 PL93: -1.00 dB
 PL94: -1.00 dB
 PL95: -1.00 dB
 PL96: -1.00 dB
 PL97: -1.00 dB
 PL98: -1.00 dB
 PL99: -1.00 dB
 PL100: -1.00 dB

¹³C NMR

- 167.06
- 145.10
- 138.27
- 128.86
- 128.53
- 128.34
- 123.61
- 109.58
- 109.52
- 80.24
- 78.96
- 77.70
- 77.38
- 77.23
- 77.06
- 76.21
- 75.14
- 66.15
- 51.81
- 36.70
- 27.48
- 27.26
- 26.86
- 25.53

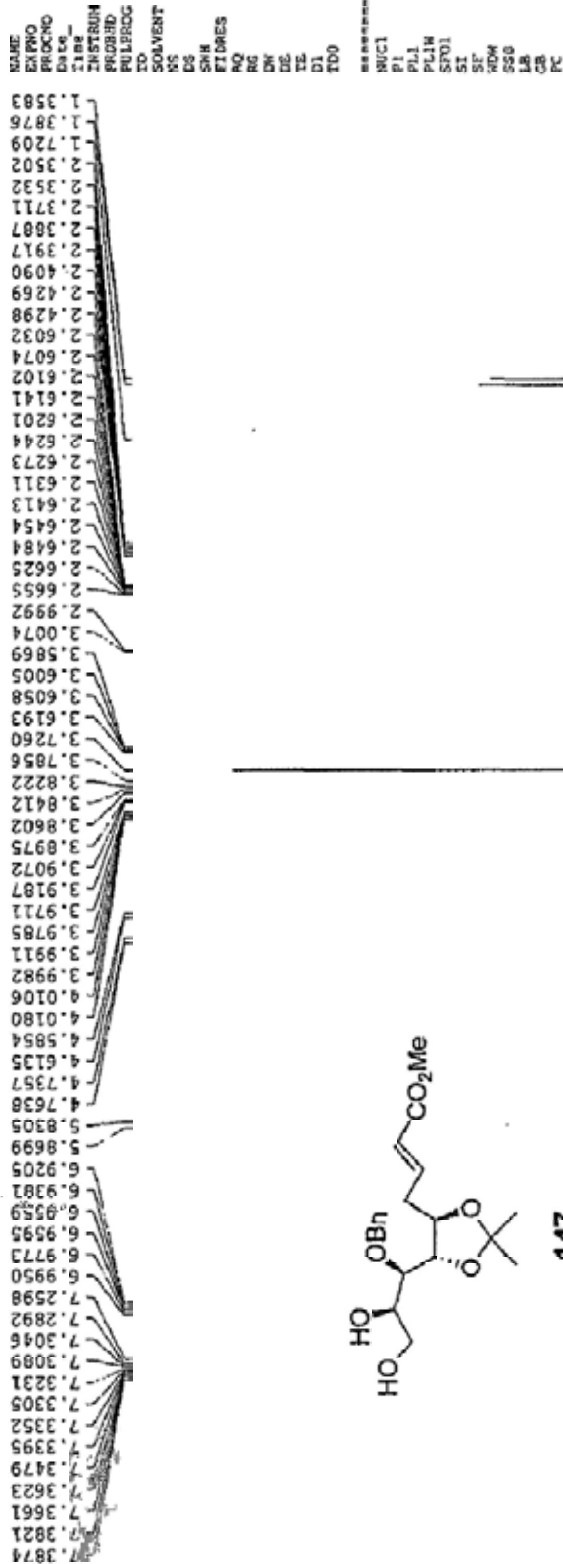


NAME ehro5carbon
 EXPNO 1
 PROCNO 1
 Date_ 20100819
 Time_ 20.15
 INSTRUM spect
 PROBR0 5 mm BBOBO BB
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 91
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3531988 sec
 RG 181
 DW 20.800 usec
 DE 6.50 usec
 TE 299.2 K
 D1 2.0000000 sec
 D11 0.83000000 sec
 TDO 1

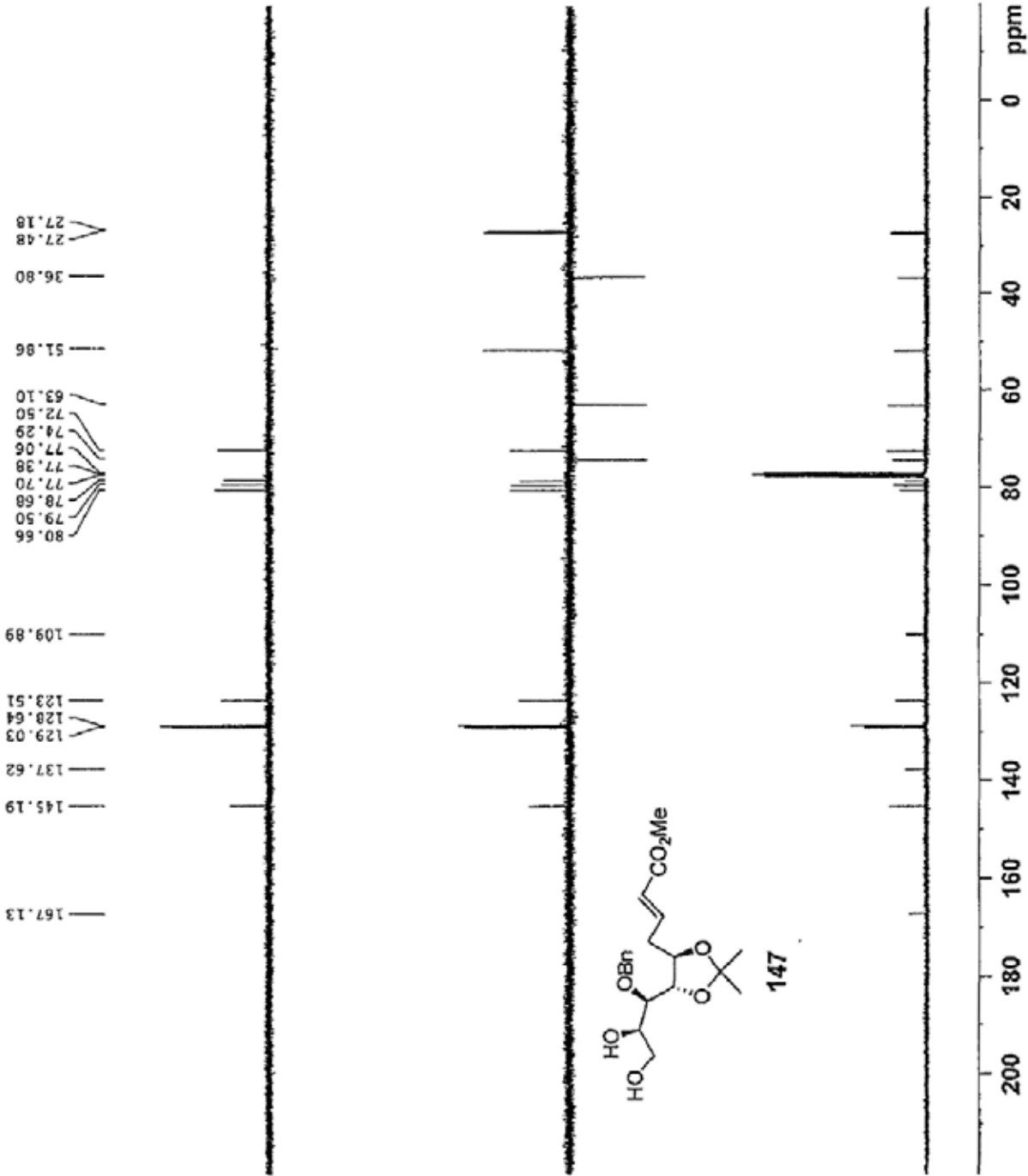
CHANNEL f1
 NUC1 13C
 P1 9.50 usec
 PL1 -2.00 dB
 PL1W 55.33689499 W
 SFO1 100.6279183 MHz

CHANNEL f2
 NUC2 1H
 P2 90.00 usec
 PL2 -1.00 dB
 PL2W 15.16 dB
 PL3 18.52 dB
 PL3W 13.56617069 W
 PL4 0.32844096 W
 PL5W 0.14806684 W
 SFO2 400.1516008 MHz
 SI 32768
 SF 100.6278212 MHz
 NDW 5M
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

¹H NMR



¹³C NMR



NAME shr06carbon
 EXPNO 2
 PROCNO 1
 Date_ 20090609
 Time_ 13.41
 INSTRUM spect
 PROBHD 5 mm PABBI 1H/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 248
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366796 Hz
 AQ 1.3631988 sec
 RG 203
 DM 20.800 usec
 DE 6.50 usec
 TE 294.7 K
 OI 2.0000000 sec
 D11 0.0300000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 14.50 usec
 PL1 -4.00 dB
 PL1W 90.2269819 K
 SFO1 100.6220299 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 MUC2 1H
 P2 80.00 usec
 PL2 -2.00 dB
 PL12 18.80 dB
 PL13 18.80 dB
 PL2W 13.17734718 W
 PL12W 0.10960442 W
 PL13W 0.10960442 W
 SFO2 400.1316005 MHz
 S1 32768
 SF 100.6127346 MHz
 MDW 0
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

¹H NMR (Solvent: CD₃OD)

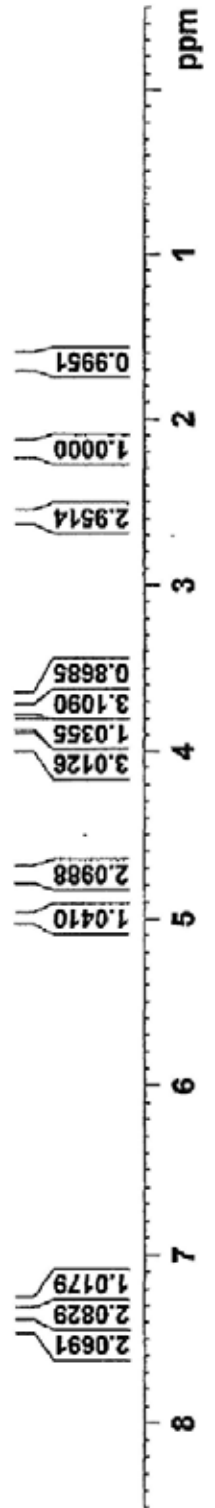
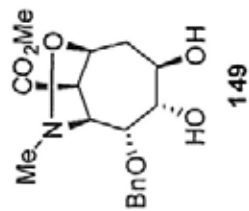
```

NAME          shx11_MeOP
EXPNO         1
PROCNO        1
Date_         20090605
Time          13.09
INSTRUM       spect
PROBHD        5 mm FAPBZ 1H/
PULPROG       zg30
TD            65536
SOLVENT       MeOD
NS            8
DS            2
SWH           6223.695 Hz
FIDRES        0.126483 Hz
AQ            3.9846387 sec
RG            144
DM            60.800 usec
DE            6.50 usec
TE            284.6 K
D1            1.00000000 sec
TDO           1

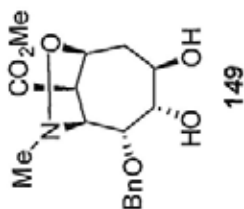
----- CHANNEL f1 -----
NUC1          1H
P1            7.16 usec
PL1           -2.00 dB
PL12          13.17734718 W
SFO1          400.1324710 MHz
SI            32768
SF            400.1300033 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
  
```

1.6374
 1.6558
 1.6747
 2.1686
 2.1787
 2.1827
 2.1931
 2.2062
 2.2162
 2.2294
 2.5892
 3.3018
 3.3058
 3.3100
 3.3141
 3.3181
 3.6225
 3.7546
 3.8329
 3.9368
 3.9513
 3.9558
 3.9714
 4.7110
 4.7407
 4.7510
 4.7713
 4.7799
 4.8885
 4.9966

7.2916
 7.2975
 7.3056
 7.3092
 7.3332
 7.3373
 7.3479
 7.3518
 7.3693
 7.4205
 7.4332
 7.4386



¹³C NMR

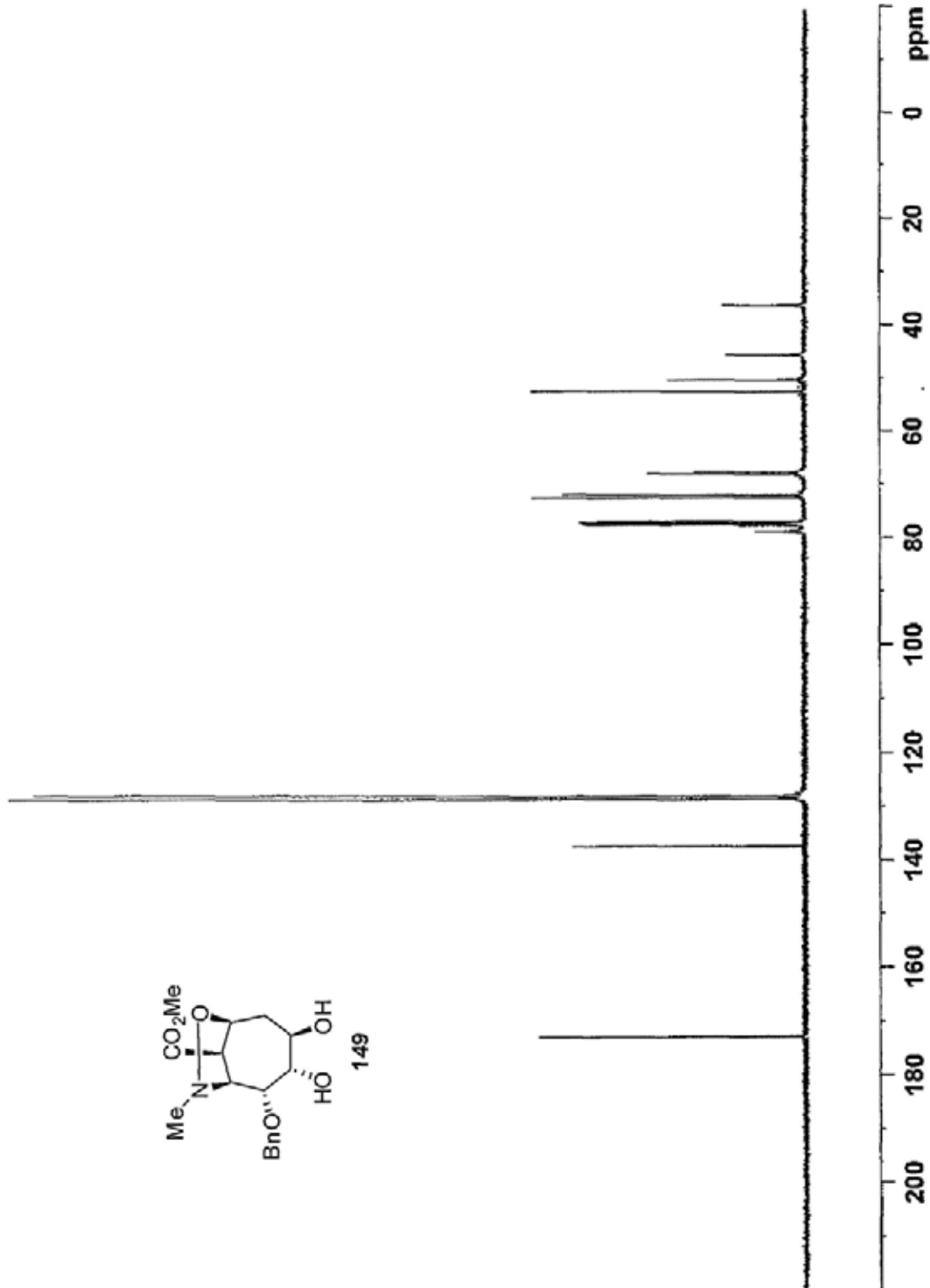


```

NAME sh:11acetbon
EXPNO 2
PROCNO 1
Date_ 20090620
Time 18.38
INSTRUM spect
PROBHD 5 mm PABBO 1H/1
PULPROG zgpg30
TD 65536
SFO1 100.6228238 MHz
SOLVENT CDCl3
NS 191
DS 4
SFR 24036.461 Hz
FIDRES 0.366758 Hz
AQ 1.3631988 sec
RG 203
DM 20.800 usec
DE 6.50 usec
TE 294.7 K
D1 2.0000000 sec
D11 0.0300000 sec
TBO 1

===== CHANNEL f1 =====
NUC1 13C
P1 14.50 usec
PL1 0.00 dB
PL12 0.00 dB
PL13 18.80 dB
SFO1 100.6228238 MHz

===== CHANNEL f2 =====
SFO2 100.6228238 MHz
NUC2 1H
P2 14.50 usec
PL2 -2.00 dB
PL22 18.80 dB
PL23 18.80 dB
SFO2 400.1316005 MHz
SI 32768
SF 109.622773 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
EC 1.40
    
```



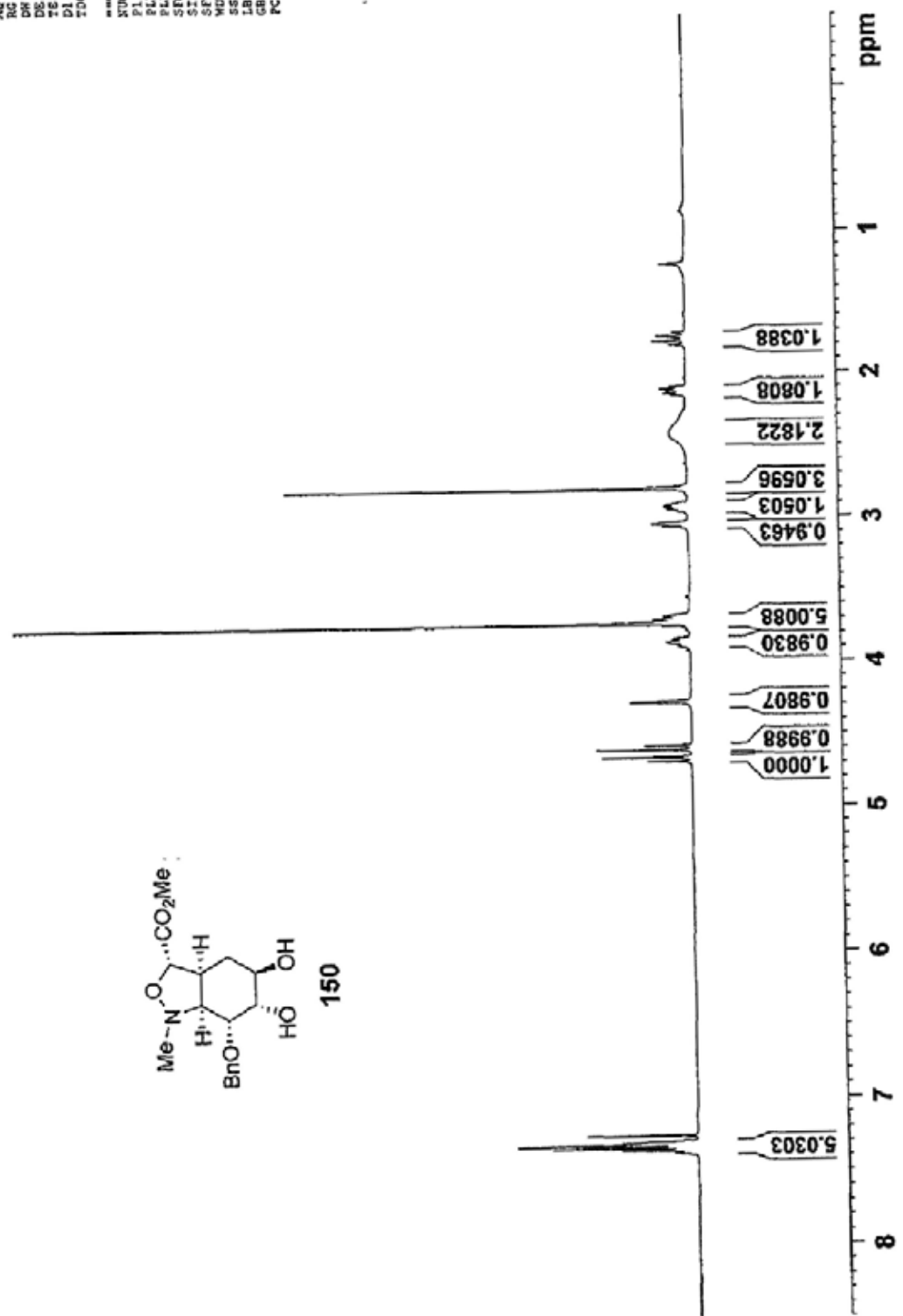
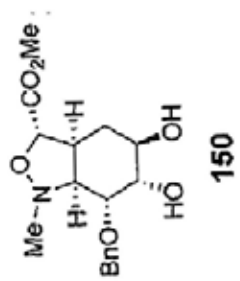
¹H NMR :

```

NAME          shr12
EXPNO         1
PROCNO        1
Date_         20090619
Time          13.14
INSTRUM       spect
PROBHD        5 mm PABBO1 1H/
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            8
DS            2
SWH           8221.685 Hz
FIDRES        0.125483 Hz
AQ            3.9816397 sec
RG            80.6
DWD           60.800 usec
DE            6.50 usec
TE            294.4 K
D1            1.00000000 sec
D2            1
D3            1
D5            1
D6            1
===== CHANNEL f1 =====
NUC1          1H
P1            7.10 usec
PL1          -2.00 dB
SFO1         13.17334718 MHz
SFO2         400.1324710 MHz
SFO3         400.1324710 MHz
SF           400.13000000 MHz
RG           80.6
WDW           EM
SSB           0
LB            0
GB            0
PC            1.00
  
```

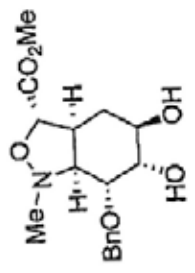
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 1.7841
 1.8119
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 2.1287
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 2.1486
 2.1610
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 2.8068
 2.9019
 2.9067
 2.9164
 2.9206
 2.9298
 2.9347
 2.9438
 2.9481
 2.9579
 2.9627
 3.0538
 3.6850
 3.6922
 3.7141
 3.7296
 3.7419
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 3.8730
 3.8768
 3.8885
 3.8994
 4.2832
 4.5867
 4.6159
 4.6661
 4.6953

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 7.3464
 7.3253
 7.3158
 7.3071
 7.2973
 7.2598

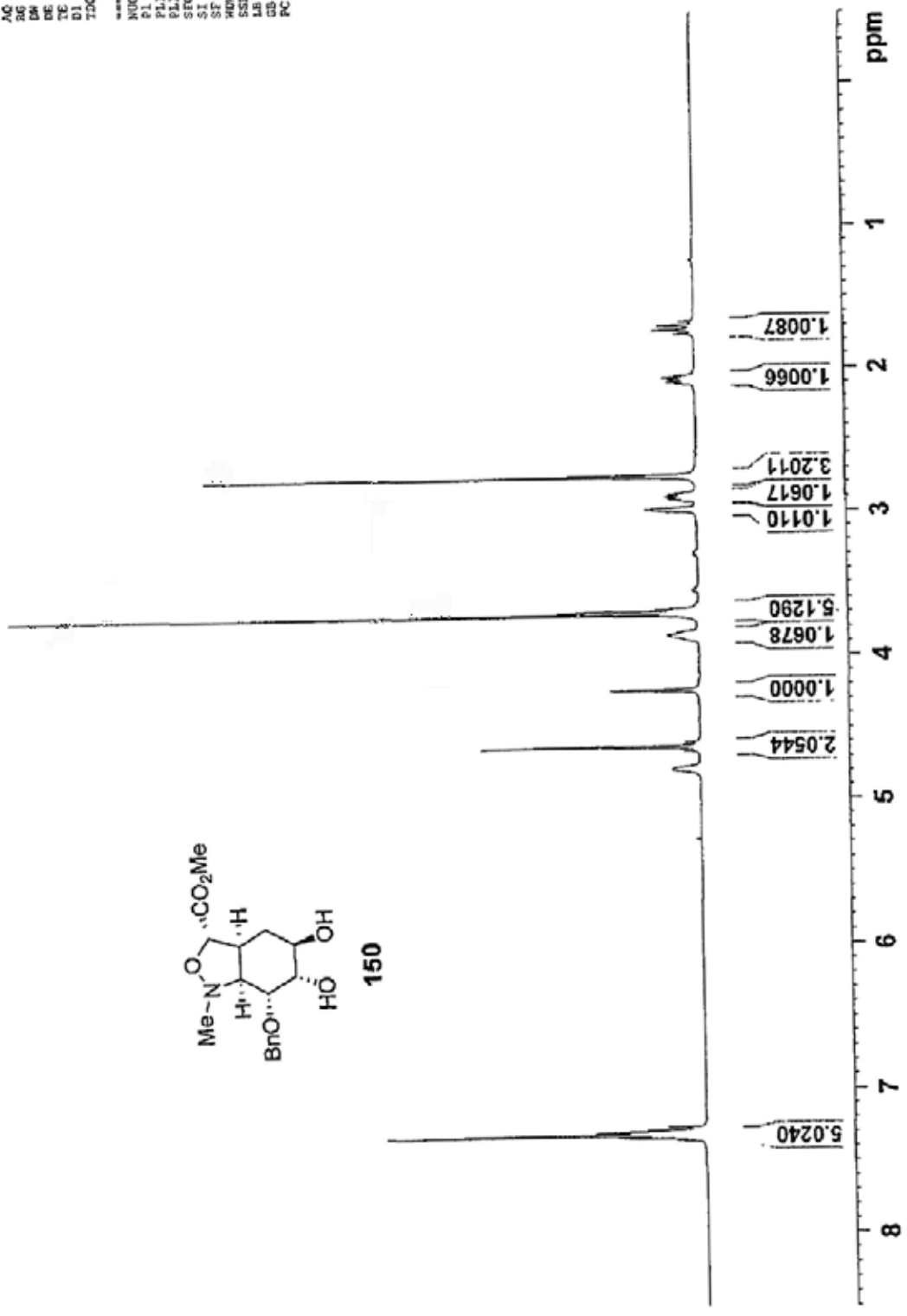


¹H NMR (Solvent: CDCl₃-D₂O)

- 7.3533
- 7.3355
- 7.3319
- 7.3178
- 7.3123
- 7.3012
- 7.2913
- 7.2825
- 7.2727
- 7.2665
- 7.2600
- 4.7877
- 4.6649
- 4.6349
- 4.6322
- 4.6018
- 4.2412
- 3.8910
- 3.8800
- 3.8693
- 3.8600
- 3.8438
- 3.8330
- 3.7170
- 3.7028
- 3.6829
- 2.9871
- 2.9248
- 2.9142
- 2.9103
- 2.9011
- 2.8964
- 2.8865
- 2.8831
- 2.8732
- 2.8684
- 2.7589
- 2.1132
- 2.1003
- 2.0868
- 2.0808
- 2.0679
- 2.0549
- 1.7620
- 1.7341
- 1.7023
- 1.6744



150



NAME abc12_020
 EXPNO 2
 PROCNO 1
 Date_ 20100705
 Time 11.23
 INSTRUM spect
 PROBRD 5 mm PABOL L3C
 PULPROG zg30
 TB 65315
 SOLVENT CDCl₃
 NS 4
 DS 2
 SWH 823.685 Hz
 FIDRES 0.125883 Hz
 AQ 3.984637 sec
 RG 71.8
 DW 60.000 usec
 DE 6.56 usec
 TE 294.7 K
 D1 1.00000000 usec
 T20 1
 CHANNEL f1
 NUC1 13C
 P1 14.83 usec
 PL1 0.00 dB
 PL1W 8.31436441 H
 SFO1 400.1324718 MHz
 SI 32768
 SF 400.13000416 MHz
 SM 5M
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

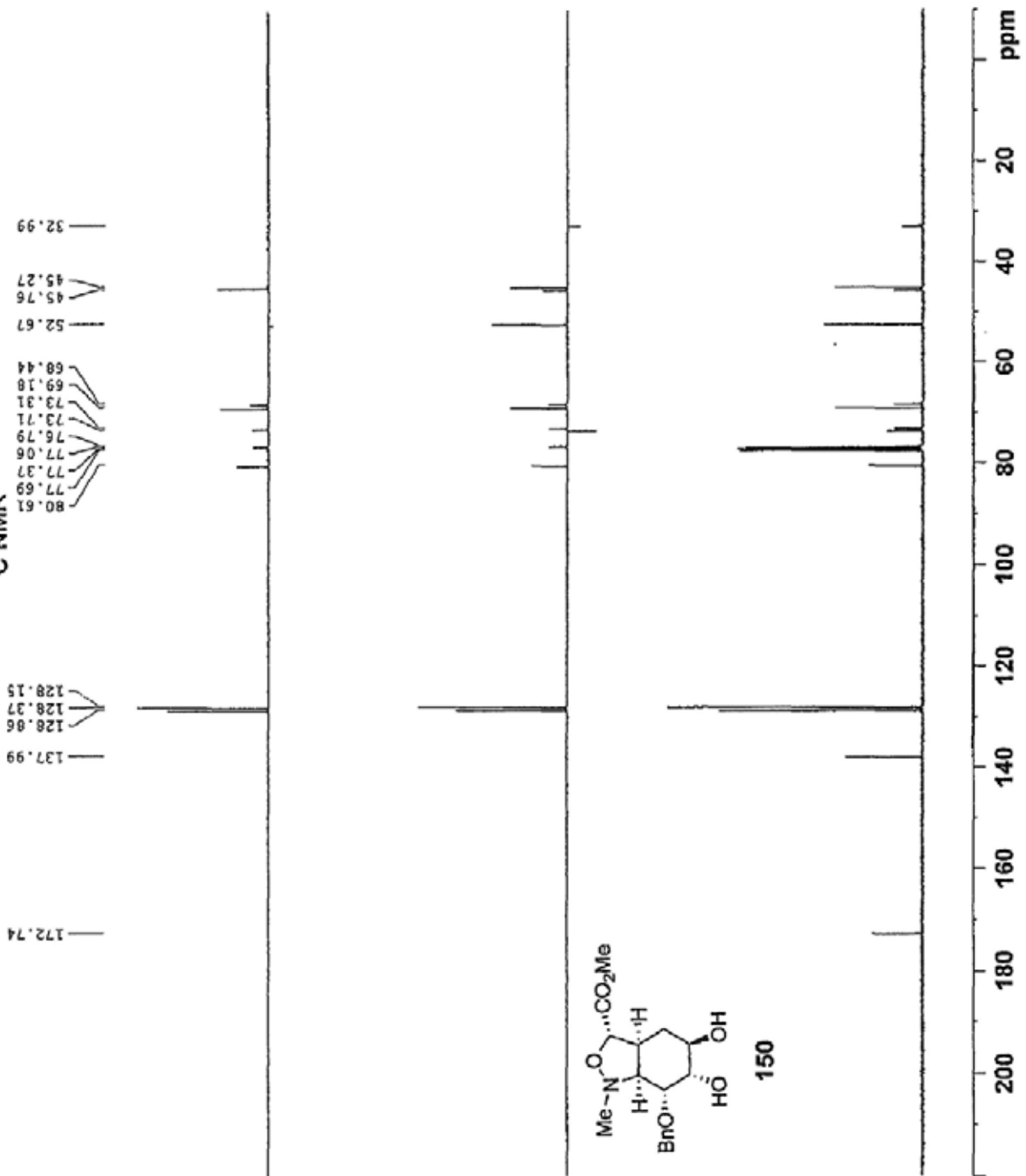
¹³C NMR

```

NAME          ehr12carbox
EXPNO         1
PROCNO        1
Date_         20100709
Time          10.55
INSTRUM       spect
PROBHD        5 mm ENDU-13C
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            202
DS            4
SNR           24038.461 Hz
FIDRES        0.356798 Hz
AQ           1.363198 sec
RG            203
DW            20.800 usec
DE            6.50 usec
TE            295.4 K
D1            2.0000000 sec
D11           0.0300000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          13C
P1            9.58 usec
PL            -0.60 dB
PL1N         41.24164963 W
SFO1         100.6228296 MHz

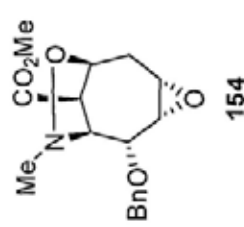
===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         90.00 usec
PL2           0.00 dB
PL12         15.56 dB
PL13         15.92 dB
PL2N         6.3143441 W
PL12N        0.2258541 W
PL13N        0.21272953 W
SFO2         400.1315005 MHz
SI            32768
SF           100.6127404 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.00
  
```



¹H NMR

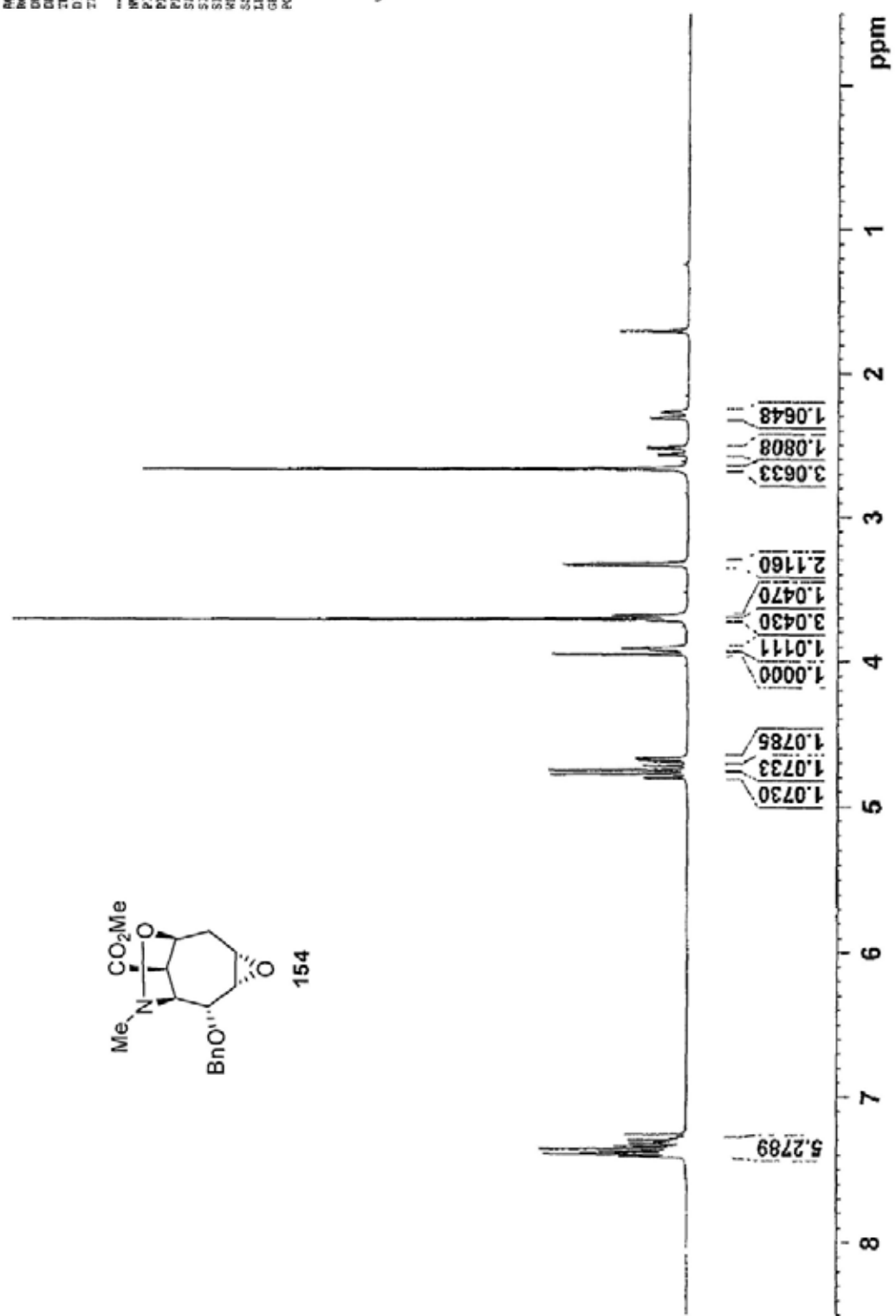
7.4163
7.4123
7.3951
7.3802
7.3775
7.3729
7.3602
7.3561
7.3412
7.3239
7.3202
7.3160
7.3096
7.3027
7.2954
7.2886
7.2850
7.2598

4.8101
4.7800
4.7544
4.7243
4.6856
4.6760
3.9556
3.9281
3.9191
3.9101
3.7145
3.6949
3.6865
3.3393
3.3309
2.6723
2.5747
2.5626
2.5327
2.5205
2.3178
2.2779
1.7115

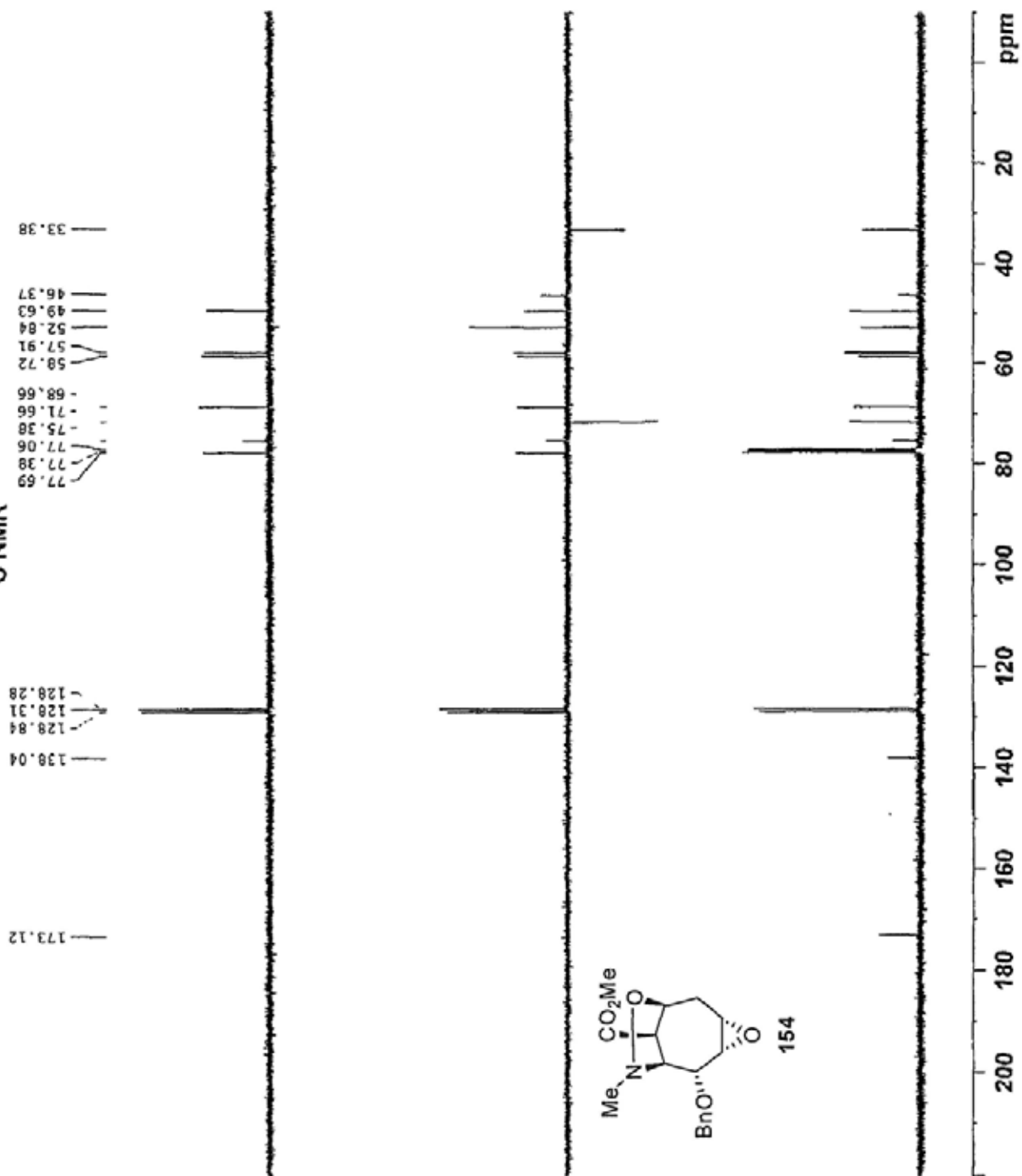


NAME shz16
EXPNO 1
PROCNO 2
Date_ 20100906
Time 10.37
INSTRUM spect
PROBHD 5 mm PABBI 1H7
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 4
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 64
DM 60.800 usec
DE 6.50 usec
TE 673.2 K
D1 1.00800000 sec
ZD0 1

***** CHANNEL f1 *****
NUC1 1H
P1 1K
PL1 7.10 usec
RF1 -2.00 dB
EL1H 13.17734716 K
SFO1 400.1324710 MHz
SI 32768
SF 160.1300046 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



¹³C NMR



```

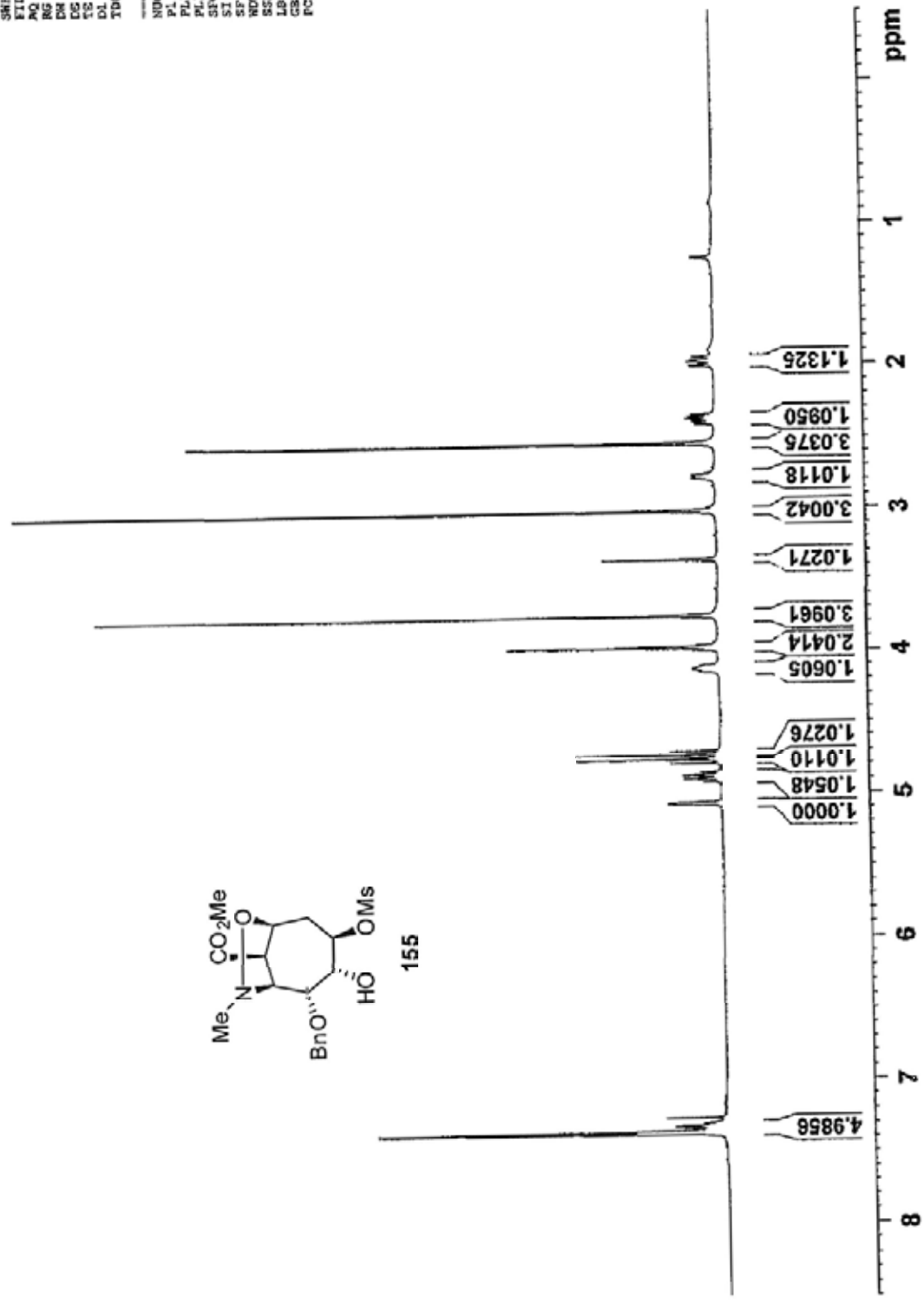
NAME: shricarbon
EXPNO: 1
PROCNO: 1
Date_ : 20100806
Time_ : 10.43
INSTRUM : spect
PROBHD : 5 mm PABBI 1H
PULPROG : zgpg30
TD : 65536
SOLVENT : CDCl3
NS : 138
DS : 4
SWH : 24038.461 Hz
FIDRES : 0.366798 Hz
AQ : 1.3631988 sec
RG : 203
DM : 20.800 USEC
DE : 6.50 USEC
TE : 673.2 K
D1 : 2.0000000 sec
D11 : 0.0300000 sec
TDO : 1

===== CHANNEL f1 =====
NUC1 : 13C
P1 : 14.50 USEC
PL1 : -4.00 dB
PL1W : 90.22689815 W
SFO1 : 100.6229298 MHz

===== CHANNEL f2 =====
CPDPRG2 : waltz16
NUC2 : 1H
PCPD2 : 80.00 USEC
PL2 : -2.00 dB
PL2W : 18.60 dB
PL3 : 18.60 dB
PL3W : 18.60 dB
PL2W : 13.17734718 W
PL3W : 0.10960442 W
PL13W : 0.10960442 W
SFO2 : 400.1316005 MHz
SI : 32768
SF : 100.6127360 MHz
RGW : 3M
SSB : 0
LB : 1.00 Hz
GB : 0
PC : 1.40
  
```

¹H NMR

1.9441
1.9485
1.9681
1.9725
1.9809
1.9852
2.0048
2.0091
2.3447
2.3556
2.3625
2.3734
2.3816
2.3925
2.3994
2.4103
2.5479
2.7112
2.7900
3.0232
3.3646
3.7610
3.9618
3.9764
3.9827
3.9979
4.1081
4.1281
4.1473
4.7111
4.7401
4.7683
4.7972
4.8563
4.8744
4.8808
4.8990
4.9056
4.9236
5.0647
5.0698
5.0747
7.2599
7.2976
7.3025
7.3081
7.3146
7.3193
7.3292
7.3383
7.3455
7.3586
7.3695



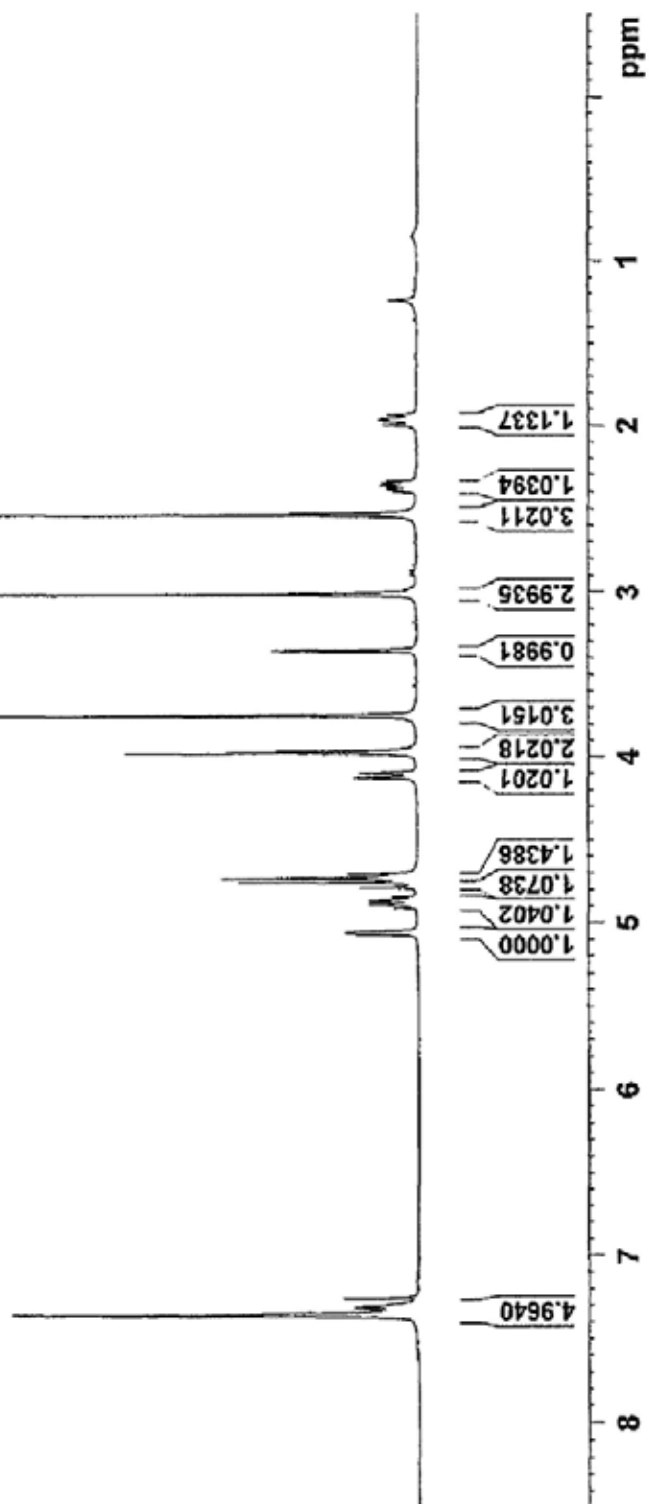
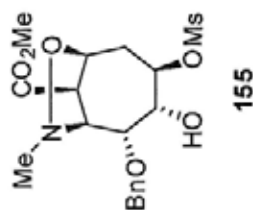
NAME shz12
EXPNO 2
PROCNO 1
Date_ 20180928
Time 20:15
INSTRUM spect
PROBHD 5 mm QNP300
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 4
DS 2
SWH 823.685 Hz
FIDRES 0.125483 Hz
AQ 3.984587 sec
RG 36
DM 69.800 usec
DE 6.50 usec
TE 298.5 K
TS 1.0000000 sec
D1 1.0000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 14.00 usec
PL1 -1.00 dB
PL14 13.56617069 W
SFO1 400.1524113 MHz
SF 400.1500143 MHz
WDW EM
SSB 0
LB 0.30 Kz
GB 0
PC 1.00

¹H NMR (Solvent: CDCl₃-D₂O)

7.3674
7.3566
7.3375
7.3271
7.3170
7.3120
7.3059
7.3000
7.2952
7.2843
7.2599

5.0731
5.0683
5.0634
4.9182
4.9002
4.8937
4.8753
4.8692
4.8510
4.7935
4.7646
4.7402
4.7113
4.1332
4.1287
4.1074
4.1031
3.9960
3.9813
3.9766
3.9615
3.7591
3.3650
3.0223
2.5449
2.4081
2.3973
2.3904
2.3795
2.3713
2.3604
2.3535
2.3426
2.0058
2.0018
1.9779
1.9693
1.9652
1.9452
1.9413

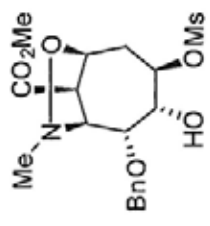
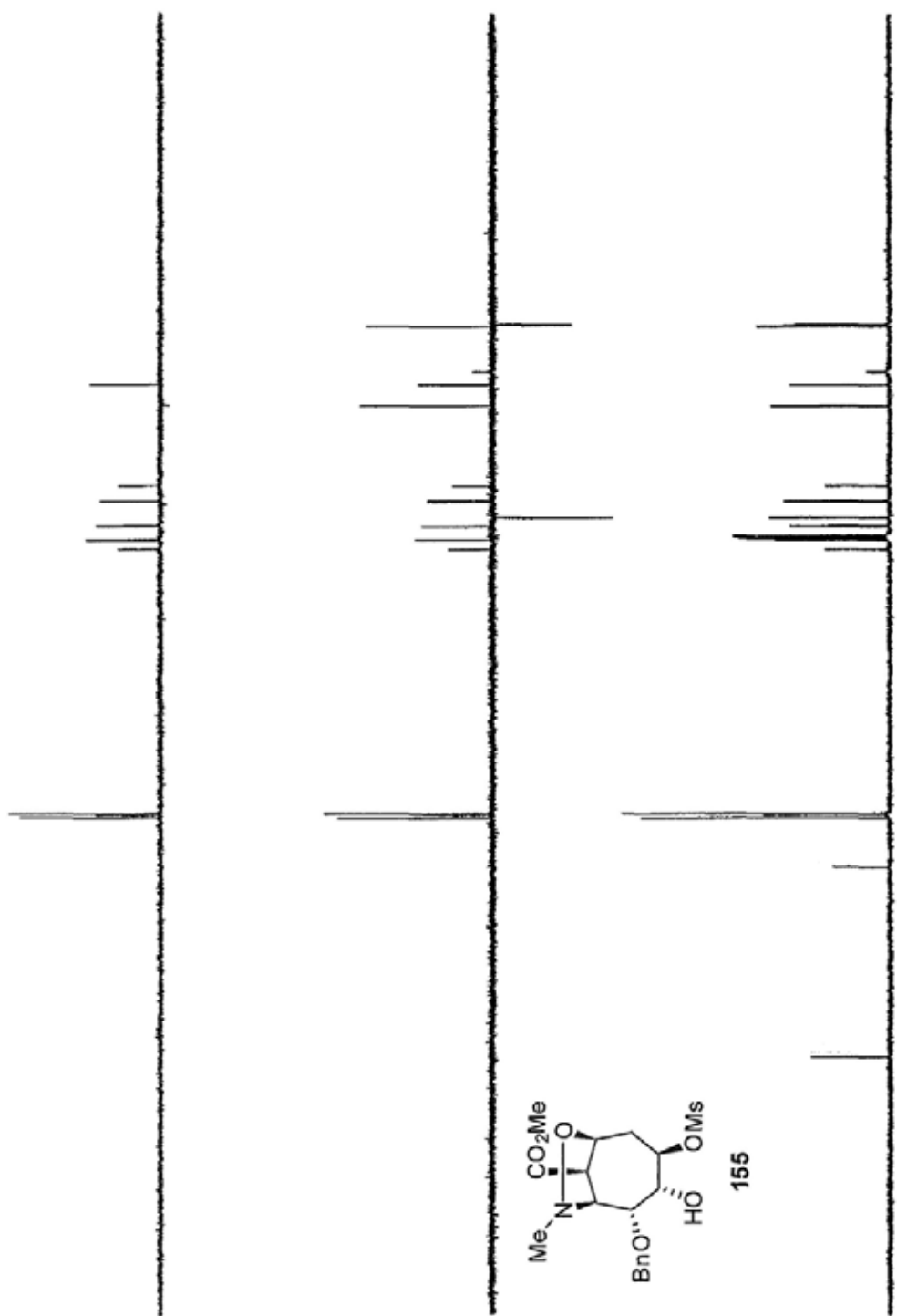


NAME shr1330
EXPNO 1
PROCNO 1
Date_ 20100929
Time 11.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
ID 65536
SOLVENT CDCl3
NS 4
DS 2
SS 8213.685 Hz
SFO 0.125483 Hz
FIDRES 3.9846387 sec
AQ 32
RG 60.800 usec
DF 6.50 usec
DE 298.4 K
TE 1.00000000 sec
D1 1
TD0 1

***** CHANNEL f1 *****
NUC1 1H
P1 14.00 usec
PL1 -1.00 dB
PL1W 13.56617069 W
SFO1 600.1924713 MHz
SI 32768
SF 600.1900188 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

¹³C NMR

172.62
 137.86
 128.87
 128.37
 128.09
 79.63
 78.01
 77.70
 77.38
 77.06
 75.41
 73.75
 70.72
 67.92
 53.15
 49.26
 46.89
 38.52
 38.28

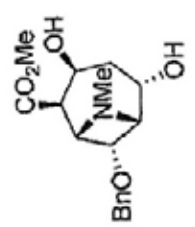


NAME shr13carbon
 EXPNO 2
 PROCNO 1
 Date_ 20100929
 Time_ 10.52
 INSTRUM spect
 PROBHD 5 mm PABBO Bg-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 107
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 228
 DW 20.800 USEC
 DE 6.50 USEC
 TE 298.8 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TDO 1

CHANNEL f1
 NUC1 13C
 P1 9.90 USEC
 PL1 -2.00 DB
 PL1W 55.32680499 W
 SFO1 100.6271183 MHz

CHANNEL f2
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 90.00 USEC
 PL2 -1.00 DB
 PL12 15.16 DB
 PL13 19.62 DB
 PL1W 13.56617059 W
 PL2W 0.3284056 W
 PL3W 0.14806664 W
 SFO2 400.1915008 MHz
 SI 32768
 SF 100.6278285 MHz
 WDW ES
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

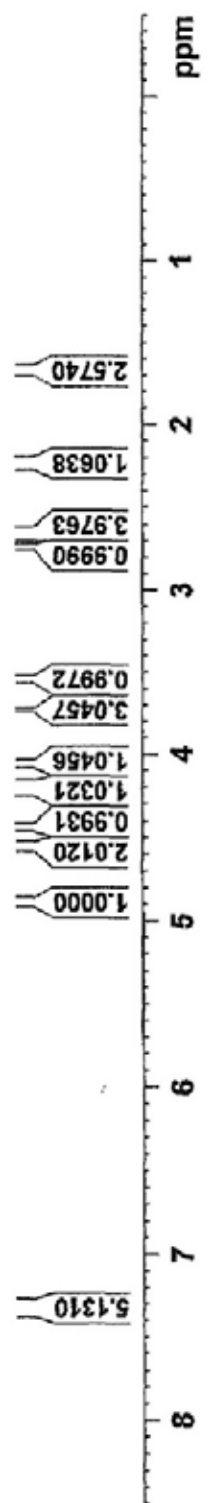
¹H NMR



158

```

NAME          ehz20
EXPNO         3
PROCNO       1
Date_         20090706
Time         13.40
INSTRUM      spect
PROBHD       5 mm PAULI 13C
PULPROG      zgpg30
TD            65536
SOLVENT      CDCl3
NS            32
DS            2
SWH           8123.685 Hz
FIDRES        0.125483 Hz
AQ            3.9846387 sec
RG            203
DN            60.800 usec
DE            6.50 usec
TE            284.5 K
D1            1.00000000 sec
D11           1
===== CHANNEL f1 =====
NUC1          13C
P1            14.83 usec
PL            0.00 dB
FLL           B-3143441 W
FLAN          400.1324710 MHz
SFO1          32768
SI            400.1300018 MHz
SF            400.1300018 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
  
```

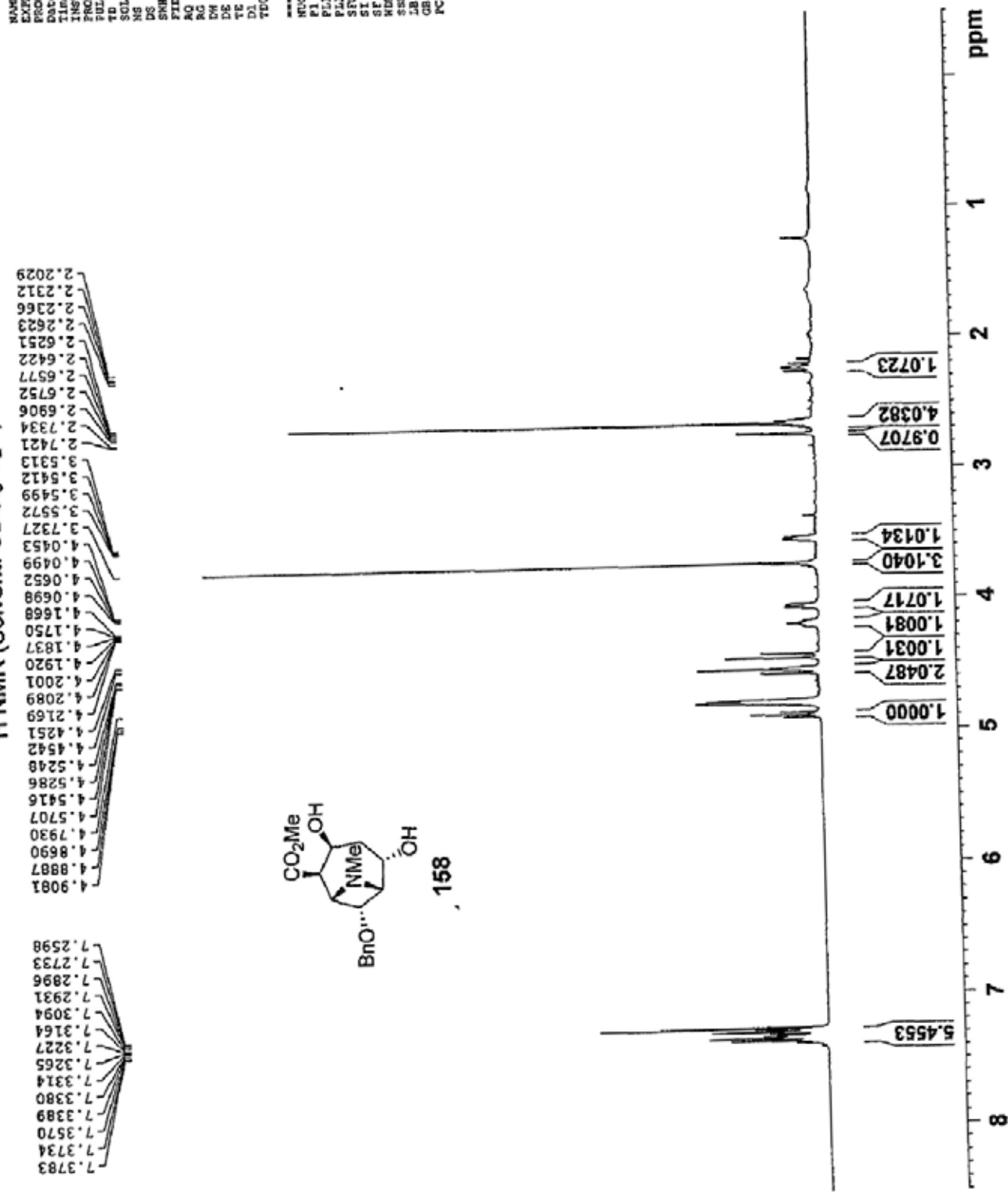


¹H NMR (Solvent: CDCl₃-D₂O)

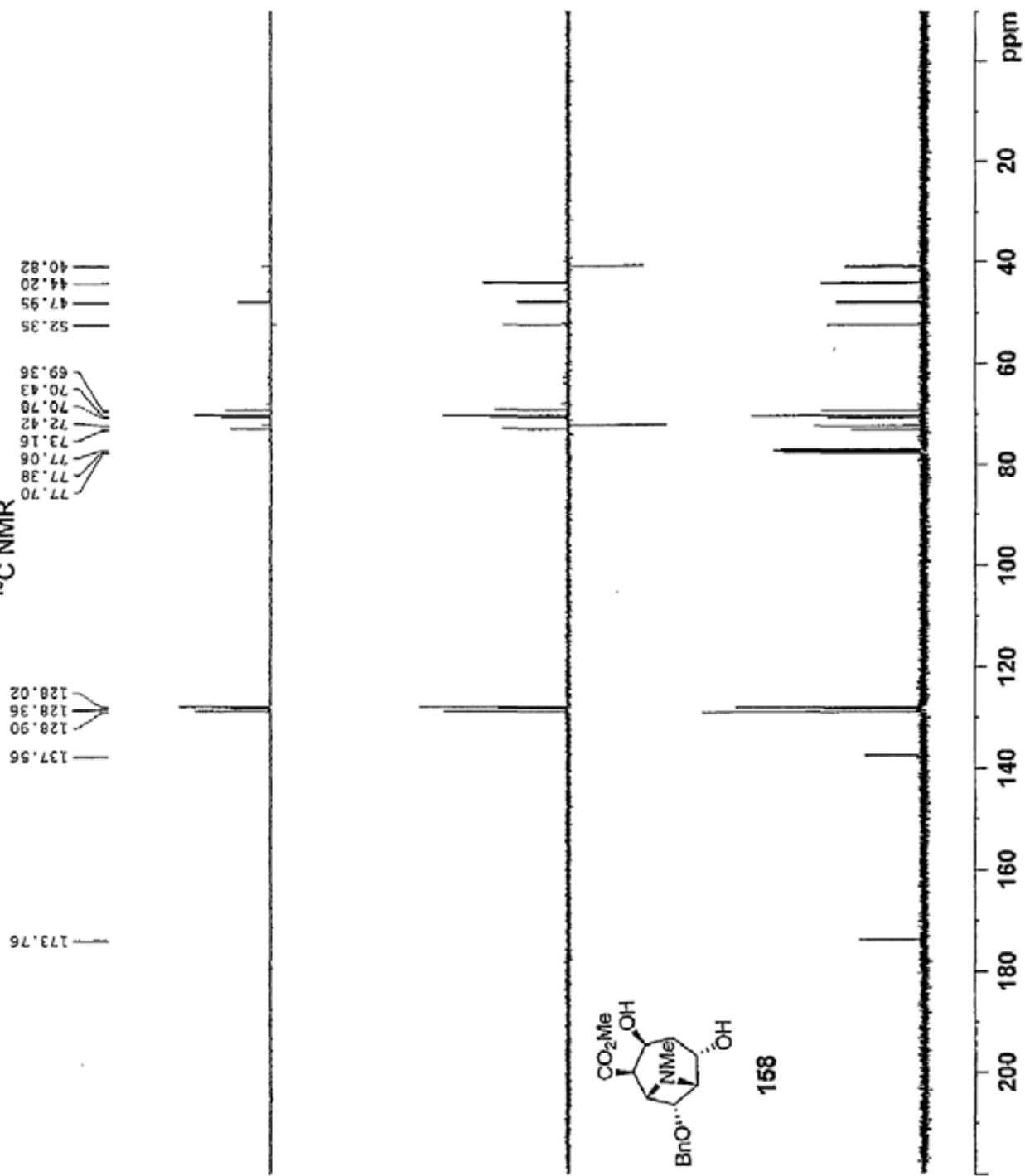
```

NAME          ahr20_mxd
EXPNO         1
PROCNO        1
Date_         20090706
Time          14 00
INSTRUM       spect
PROBHD        5 mm BBOUL 13C
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            2
SWH           8223.685 Hz
FIDRES        0.125463 Hz
AQ            3.9846387 sec
RG            203
DM            60.800 usec
DE            6.50 usec
TE            294.7 K
D1            1.00000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          13C
P1            14.83 usec
PL1           0.00 dB
PL12         8.31434441 W
PL13         100.1334710 MHz
ST1          32768
SI           1600.1330051 MHz
SF           100.6261260 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
  
```



¹³C NMR



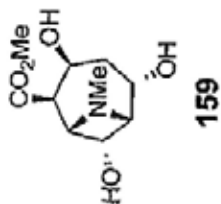
NAME sh120catdon
 EXPNO 7
 PROCNO 1
 Date_ 20100720
 Time_ 16.06
 INSTRUM spect
 PROBRD 5 mm BBBI 1H/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 41
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631986 sec
 RG 203
 DW 20.800 usec
 DE 6.50 usec
 TE 294.5 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

CHANNEL f1
 NUC1 13C
 P1 14.50 usec
 PL1 -4.00 dB
 PL1W 90.22688819 W
 SFO1 100.6228298 MHz

CHANNEL f2
 CPDPRG2 waltz16
 NUC2 1H
 P2 80.00 usec
 PL2 -2.00 dB
 PL12 18.80 dB
 PL13 18.80 dB
 PL1W 13.17734718 W
 PL12W 0.10968042 W
 PL13W 0.10968042 W
 SFO2 400.1316005 MHz
 S1 32768
 SF 100.6127419 MHz
 MDR 0
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

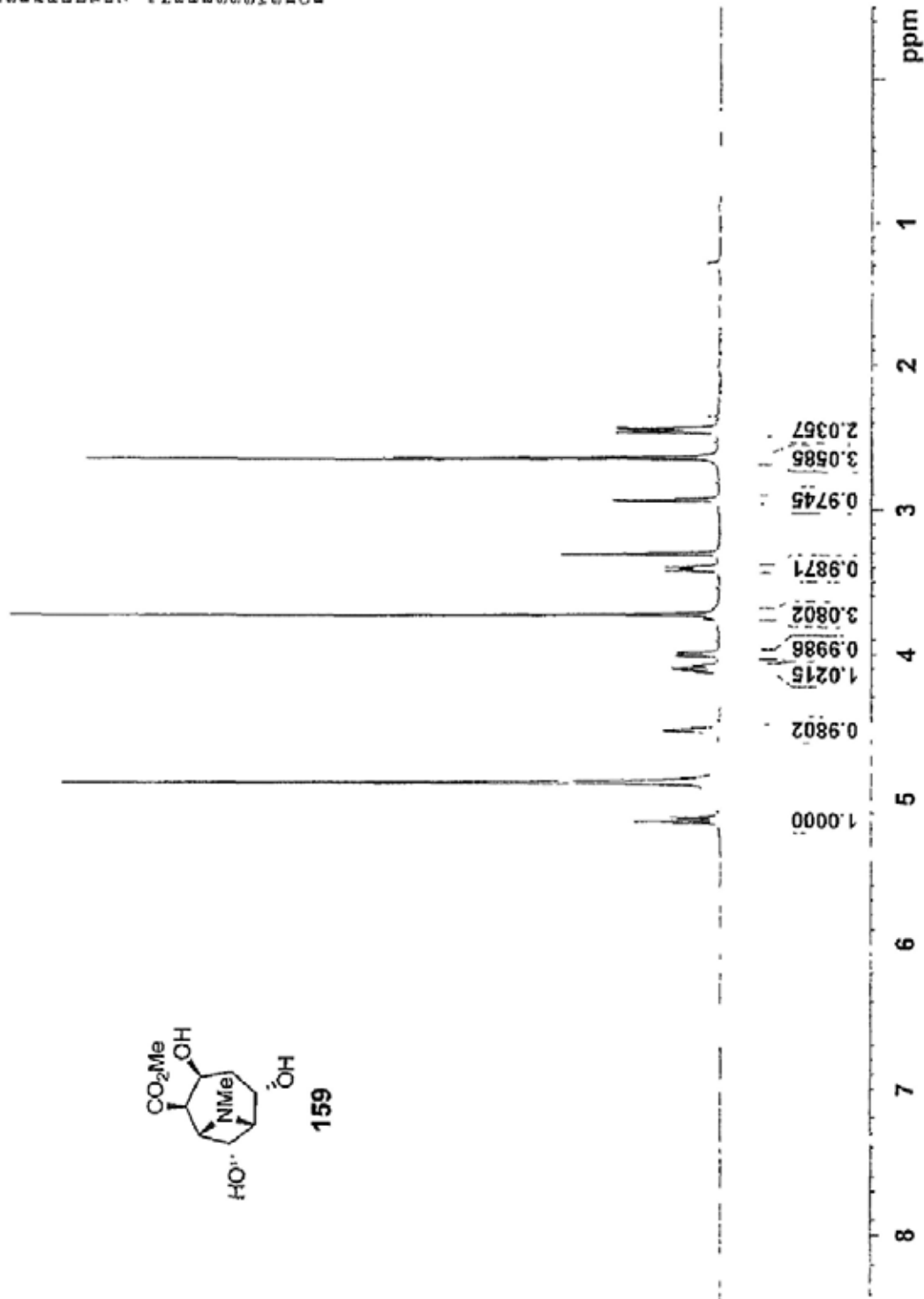
¹H NMR (Solvent: CD₃OD)

5.1730
5.1530
5.1331
4.8900
4.5346
4.5264
4.1291
4.1214
4.1080
4.1002
4.0869
4.0792
4.0161
4.0125
3.9954
3.9916
3.7293
3.4285
3.4210
3.4106
3.4021
3.3946
3.3181
3.3141
3.3103
3.3062
3.3024
2.9455
2.9370
2.6511
2.4725
2.4641
2.4512
2.4421

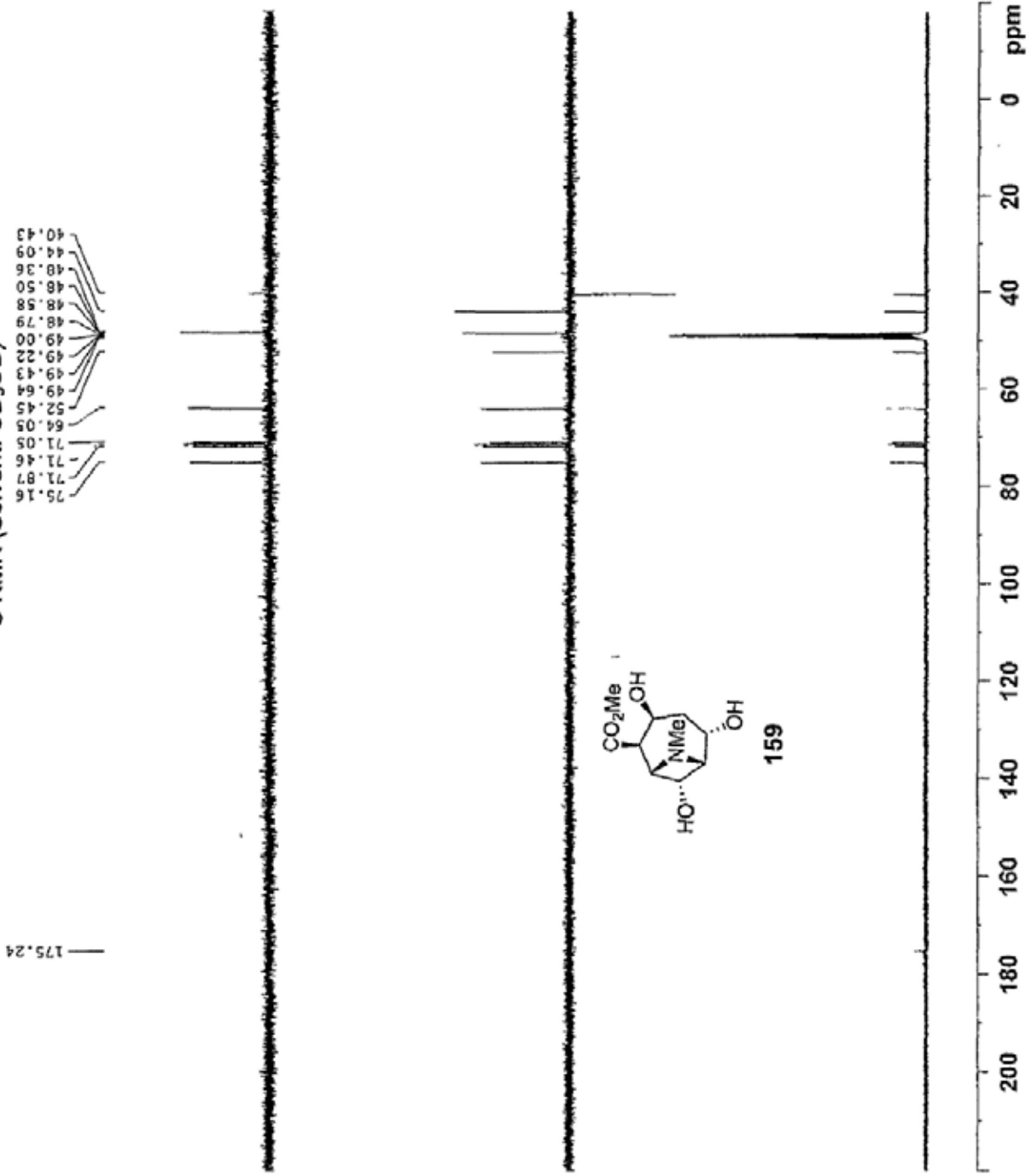


NAME shz28600
EXPNO 1
PROCNO 1
Date_ 20100117
Time 11 04
INSTRUM spect
PROBHD 5 mm PABBI 1H/7
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 8
DS 2
SS 2
SME 8223.655 Hz
FIDRES 0.125483 Hz
AQ 3.9886387 sec
RG 39.5
DM 60 800 usec
DE 5 50 usec
TE 284.3 K
EC 1
OL 1 00000000 sec
TDO 1

***** CHANNEL f1 *****
NUC1 1H
P1 7.10 usec
PL1 -2.00 dB
PL14 13.17734718 N
SFO1 400.1321710 MHz
SI 32768
SF 400.1300020 MHz
WDW EM
SSB 0
AB 0
CB 0
PC 1.00



¹³C NMR (Solvent: CD₃OD)



```

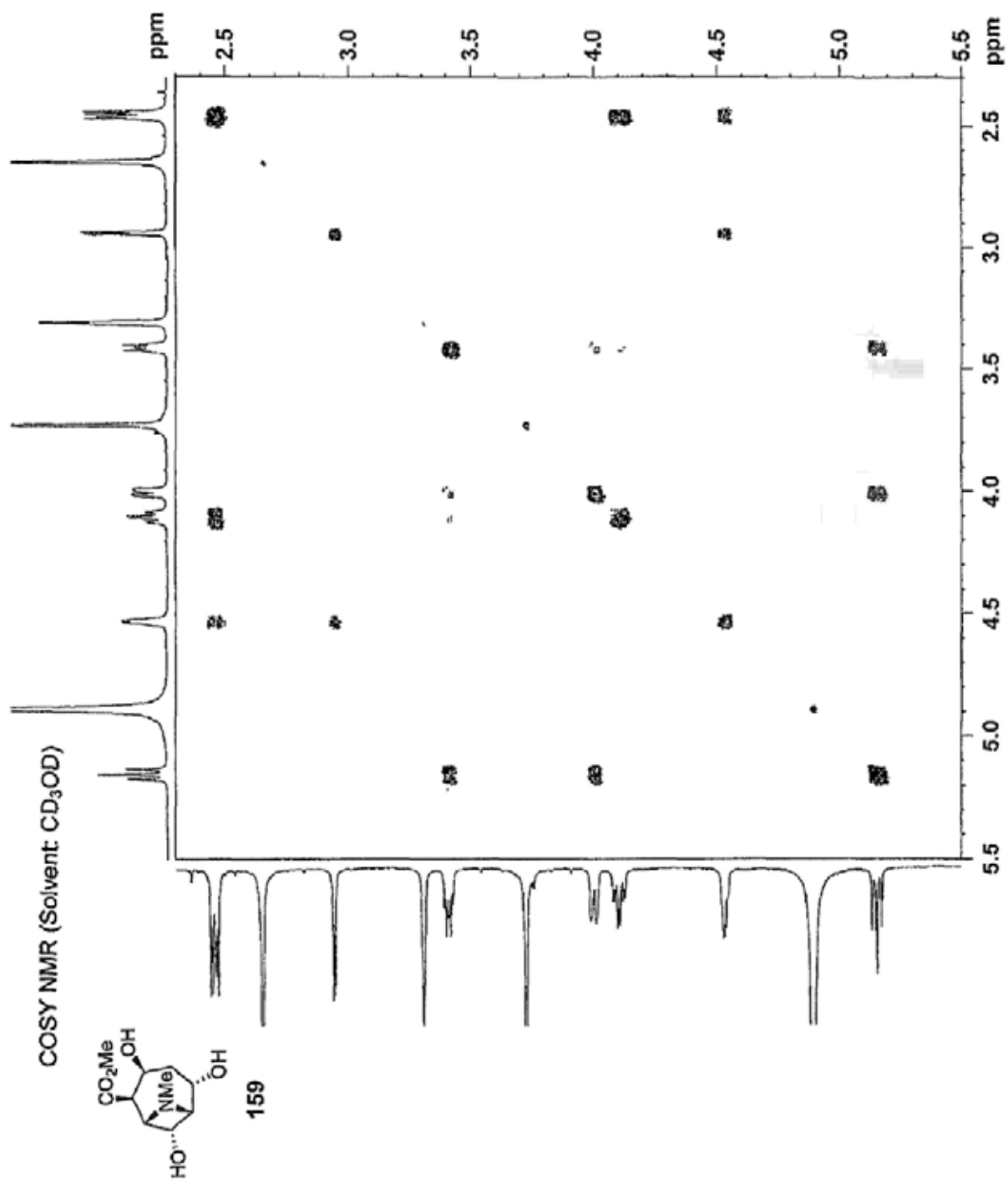
NAME          shr28me000qacben
EXPNO         1
PROCNO        1
Date_         20100917
Time_         11.08
INSTRUM       spect
PROBHD        5 mm PABBI 1H/
PULPROG       zgpg30
TD            65536
SOLVENT       MeCO
NS            268
DS            4
SMH           24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631988 sec
RG            203
DM            20.800 usec
DE            6.50 usec
TE            294.6 K
D1            2.0000000 sec
D11           0.0300000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          13C
P1            14.50 usec
PL1           -4.00 dB
PL1W          90.22688633 W
SE01          100.6223238 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
P2            83.00 usec
PCPD2         -2.00 dB
PL2           18.80 dB
PL12          18.80 dB
PL13          18.80 dB
PL2W          13.1773178 W
PL12W         0.10960442 W
PL13W         0.10960442 W
SF02          400.1316003 MHz
SI            32768
SE            100.6125271 MHz
KDN           EK
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
  
```

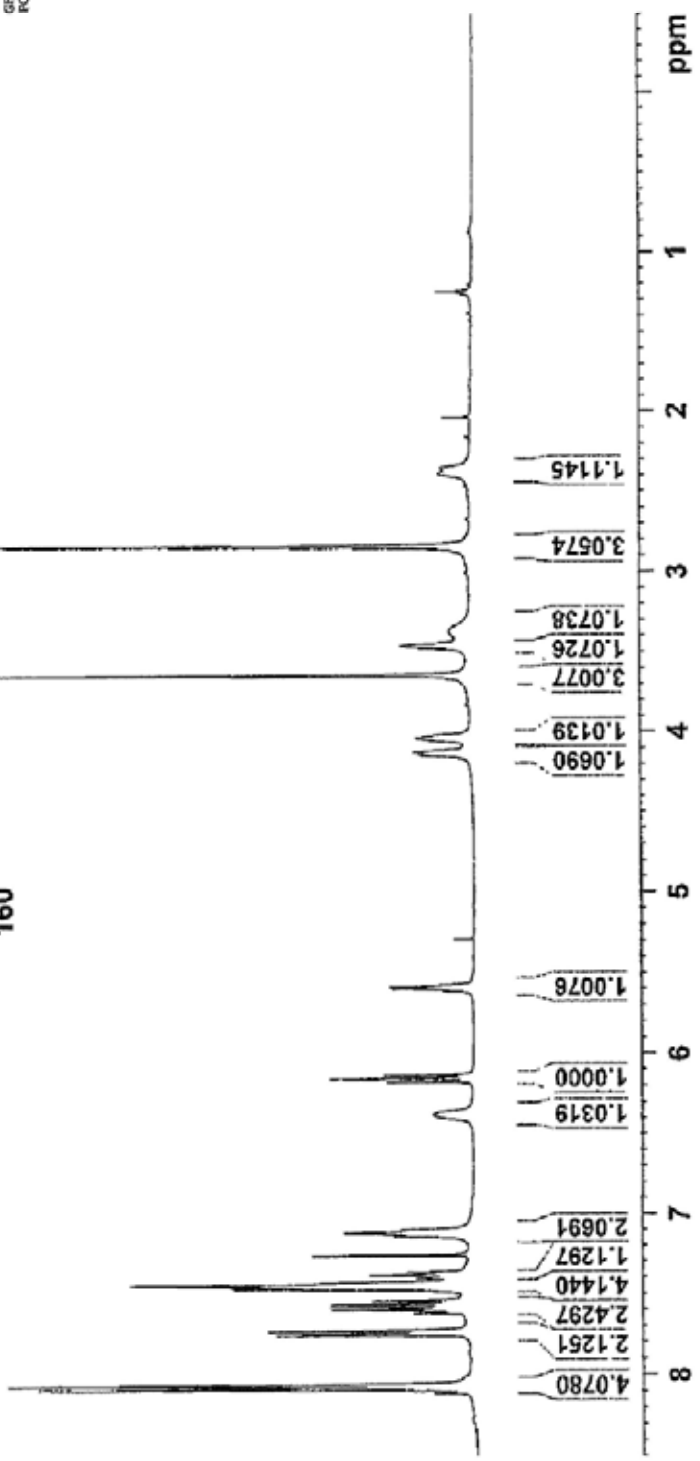
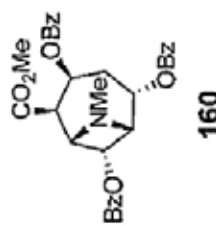
NAME sbr28MeOCosy
 EXPNO 1
 PROCNO 1
 Date_ 20100917
 Time_ 11.40
 INSTRUM spect
 FROBHD 5 mm PABBI 1H/
 PULPROG cosygpmzfg
 TD 2048
 SOLVENT MeOD
 MeOD
 NS 4
 DS 8
 SFO1 2408.478 Hz
 FIDRES 1.176015 Hz
 AQ 0.4252148 sec
 RG 203
 EN 207.600 usec
 DE 6.50 usec
 TE 294.3 K
 D0 0.00000300 sec
 D1 2.00000000 sec
 D13 0.00000400 sec
 D16 0.00020000 sec
 INO 0.00041520 sec

CHANNEL f1
 MOC1 1H
 P1 7.10 usec
 PL1 -2.00 dB
 PL1W 13.17734718 W
 SFO1 400.1318066 MHz
 GRADIENT CHANNEL
 GPRM1 SINE.100
 GPRM2 SINE.100
 GPRM3 SINE.100
 GP21 16.00 k
 GP22 12.00 k
 GP23 80.00 k
 P16 1000.00 usec
 MDQ 1
 TD 128
 SFO1 400.1318 MHz
 FIDRES 18.816198 Hz
 SW 6.019 ppm
 FTMODE CF
 SI 1024
 SF 400.1299985 MHz
 SSB SINE
 LB 0
 GB 0
 I1 0.00 Hz
 I2 0
 I3 0
 I4 1.40
 I5 1024
 MC2 CF
 SF 400.1299985 MHz
 SSB SINE
 LB 0
 GB 0



¹H NMR

- 7.5974
- 7.5794
- 7.5613
- 7.5429
- 7.4726
- 7.4632
- 7.4532
- 7.4437
- 7.4346
- 7.4249
- 7.4029
- 7.3842
- 7.3659
- 7.2598
- 7.1361
- 7.1179
- 7.0999
- 6.3788
- 6.1738
- 6.1536
- 6.1338
- 5.6121
- 5.5990
- 5.5859
- 5.5730
- 4.1458
- 4.1276
- 4.0421
- 3.6517
- 3.4652
- 3.3768
- 2.8468
- 2.3930
- 2.3628

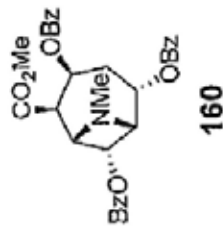
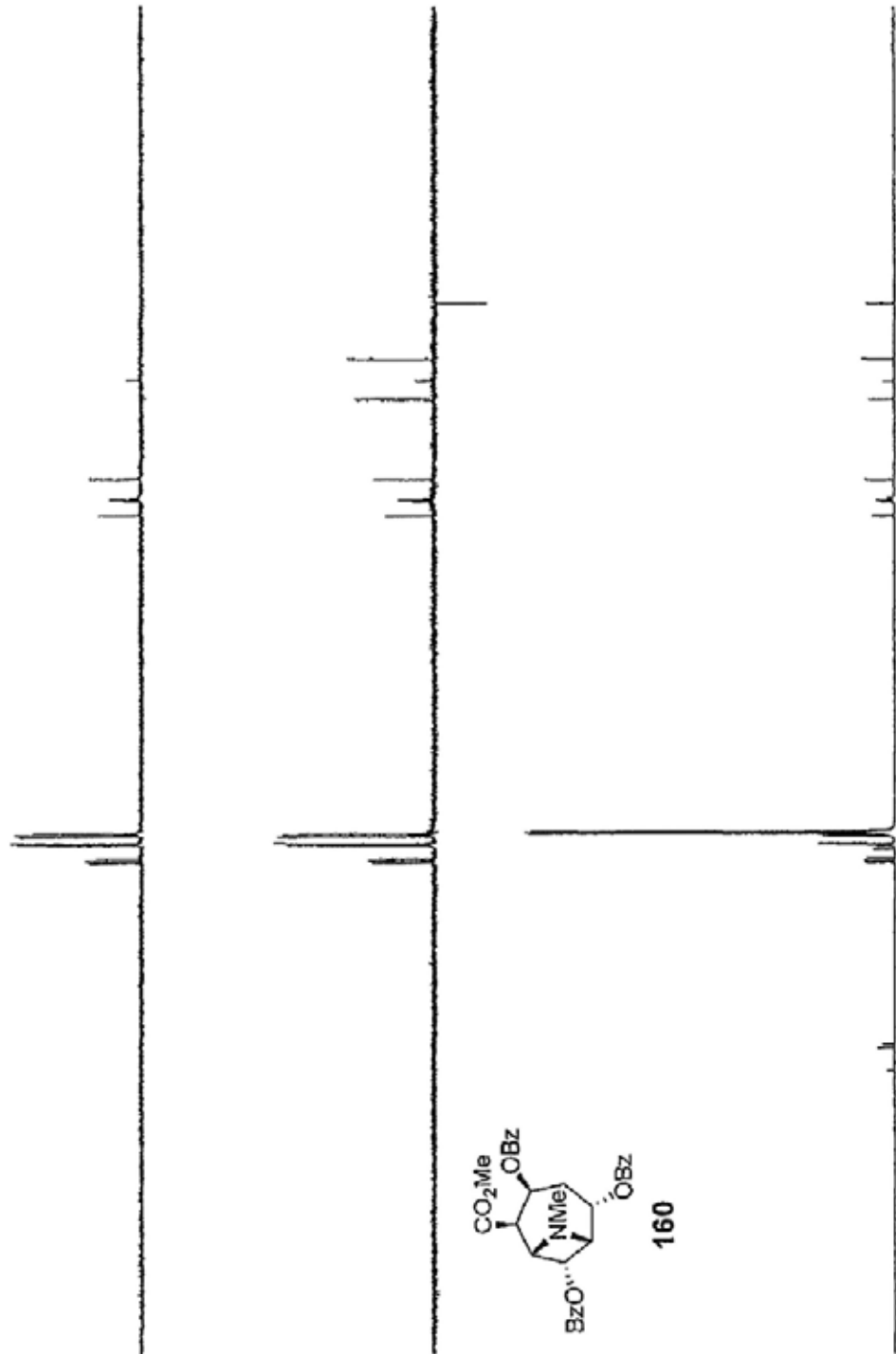
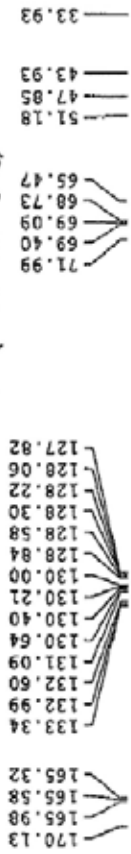


```

NAME          SH163
EXPNO         4
PROCNO       1
Date_         20101101
Time         22.23
INSTRUM      spect
PROBHD       5 mm EASYBO BB-
PULPROG      zg30
TD           65536
SOLVENT      CDCl3
NS           4
DS           2
SWH          8223.695 Hz
FIDRES      0.125461 Hz
AQ          3.981637 sec
RG           64
AQ           60.800 usec
DE           8.728 usec
TE           298.2 K
D1           1.00000000 sec
TD0          1

===== CHANNEL f1 =====
NUC1          1H
P1           14.00 usec
PL1          -1.00 dB
PL12         13.56617069 K
SFO1         100.1924713 MHz
SI           32768
SF           100.1900116 MHz
WDW          EM
SSB          0
LB           0.30 Hz
GB           0
PC           1.00
  
```

¹³C NMR (Solvent: C₆D₆)



NAME shr65c6d6carbon
 EXPNO 1
 PROCNO 1
 Date_ 20101103
 Time 10.37
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT C6D6
 NS 201
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 80.6
 DW 20.800 usec
 DE 5.50 usec
 TE 298.3 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 9.90 usec
 PL1 -2.00 dB
 PL1W 55.33689499 W
 SFO1 100.6175183 MHz

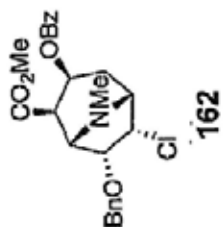
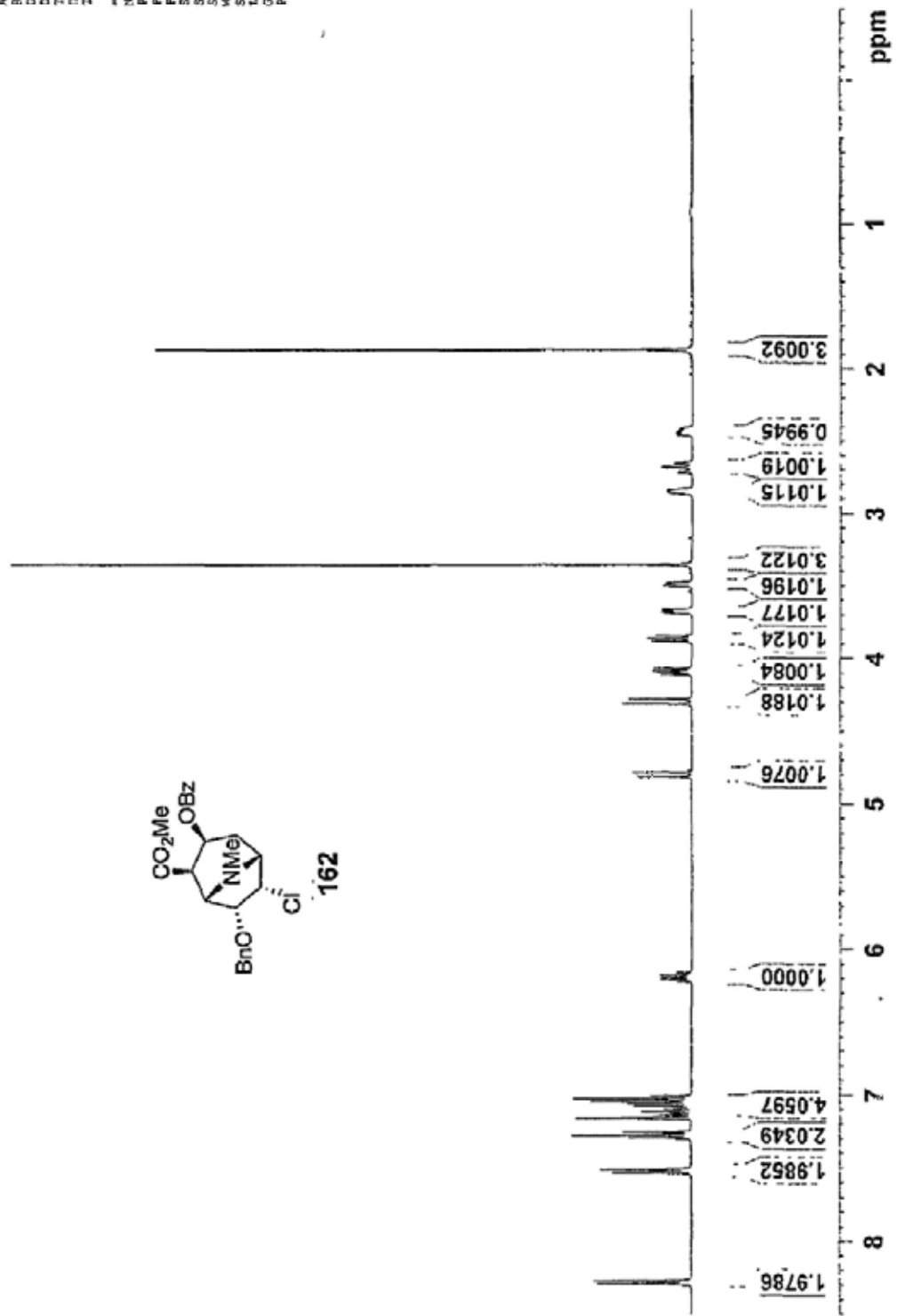
===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 90.00 usec
 PL2 -1.00 dB
 PL2W 15.15 dB
 PL3 18.62 dB
 PL3W 13.56617069 W
 PL4W 0.32844095 W
 PL5W 0.14806664 W
 SFO2 400.1915008 MHz
 SI 32768
 SF 100.6278207 MHz
 NDW EX
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

¹H NMR (Solvent: C₆D₆)

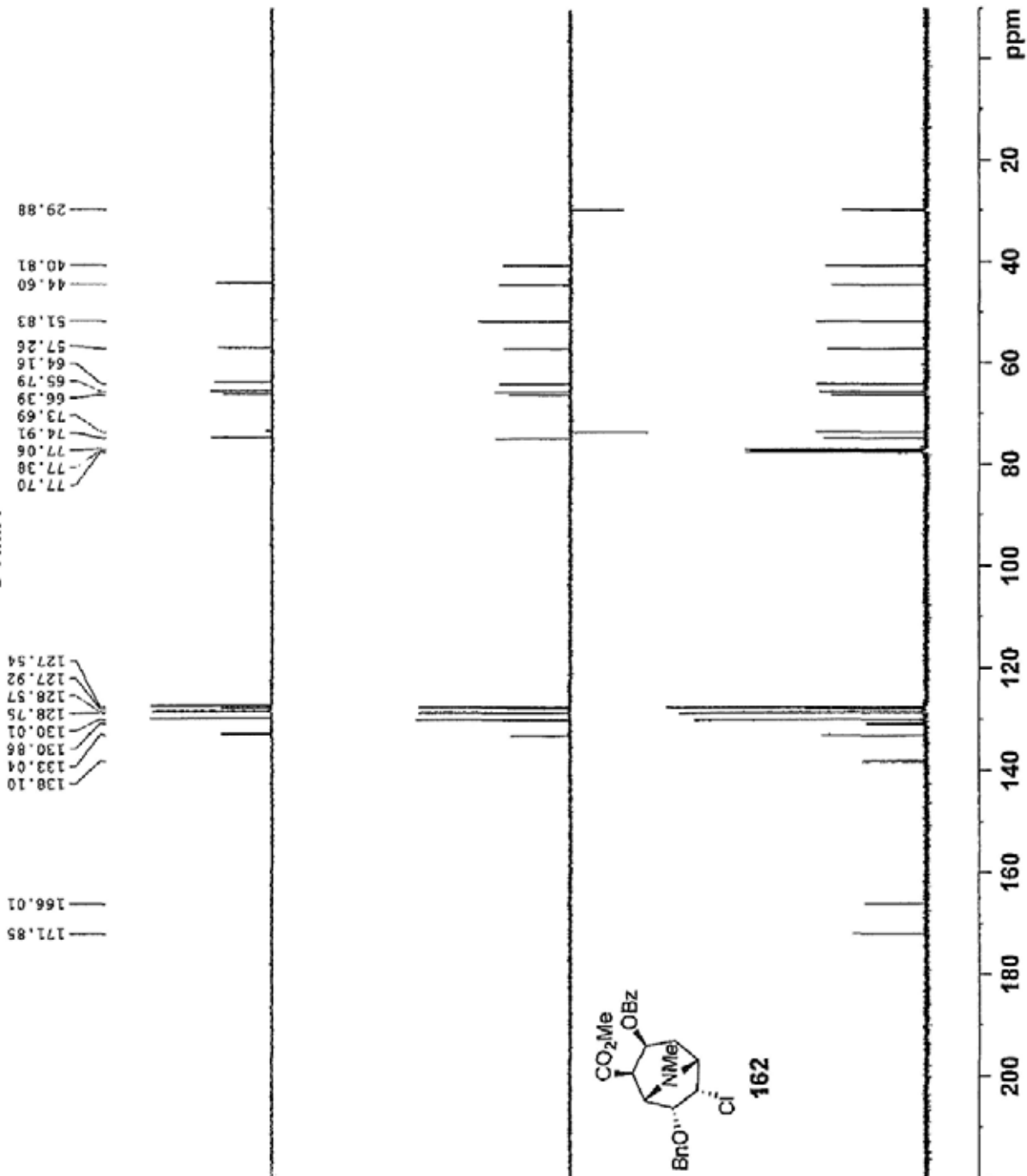


```

NAME          shz42c6d6
EXPNO         1
PROCNO        1
Date_         20011211
Time          16.03
SOLVENT       5 mm PABUL 4 JC
PROBHD        5mm
PULPROG       zgpg30
TD            65536
SOLVENT       C6D6
NS            2
DS            4
SWH           8223.665 Hz
F2           0.1254817 Hz
NUC1          13
NUC2          13
RG            3.981436 sec
AQ            60.116
SFO1          400.136110 MHz
SF           400.1360413 MHz
SE           0
ME1           EM
SSB           0
LB           0.30 Hz
GB           0
PC           1.00
  
```



¹³C NMR

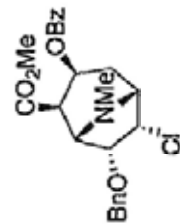


NAME shr42carbon
 EXPNO 4
 PROCNO 1
 Date_ 20100719
 Time 14.17
 INSTRUM spect
 PROBRD 5 cm PABBI 1H/
 PULPROG zgpg30
 TO 65136
 SOLVENT CDCl3
 NS 161
 DS 4
 SNH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631988 sec
 RG 203
 DM 20.800 usec
 DE 6.50 usec
 TE 294.7 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TDO 1

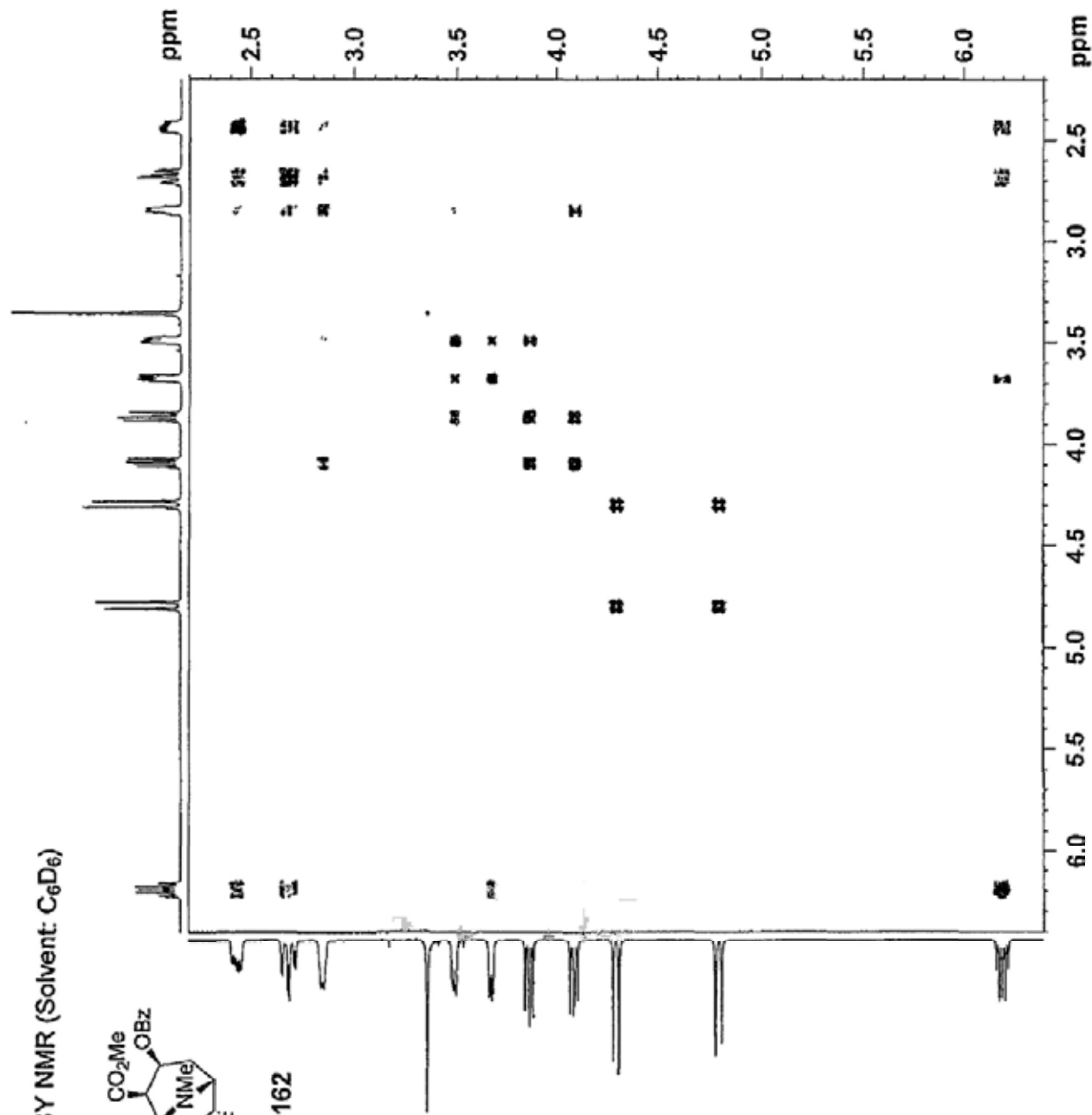
----- CHANNEL f1 -----
 NUC1 13C
 P1 14.50 usec
 PL1 -4.00 dB
 PL1W 90.22689619 W
 SF01 100.628298 MHz

----- CHANNEL f2 -----
 CPDPRG2 waltz16
 NUC2 1H
 PCPDZ 90.00 usec
 PL2 -2.00 dB
 PL12 18.80 dB
 PL13 18.80 dB
 PL2W 13.17734718 W
 PL12W 0.10966442 W
 PL13W 0.10966442 W
 SF02 400.1315005 MHz
 SI 32768
 SF 100.6127404 MHz
 NSM Em
 SSB 0
 LB 1.00 Hz
 CB 0
 PC 1.40

COSY NMR (Solvent: C₆D₆)



162



```

NAME shr42C606cosy
EXPNO 1
PROCNO 1
Date_ 20091221
Time 16.56
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG cosygpmrf
TD 2048
SOLVENT C6D6
NS 4
DS 8
SWH 1726.519 Hz
FIDRES 0.643027 Hz
AQ 0.5931508 sec
RG 203
DE 6.50 usec
TE 673.2 K
D0 0.0000000 sec
D1 2.0000000 sec
D13 0.0000000 sec
D16 0.0002000 sec
IN0 0.00057920 sec

***** CHANNEL f1 *****
NUC1 13C
P1 14.63 usec
PL1 0.00 dB
PL1W 8.31434441 W
SF01 400.1317431 MHz

***** GRADIENT CHANNEL *****
GPRAM1 SINE.100
GPRAM2 SINE.100
GPRAM3 SINE.100
GPZ1 16.00 %
GPZ2 12.00 %
GPZ3 40.00 %
P16 1000.00 usec
NU0 1
TD 128
SF01 400.1317 MHz
FIDRES 13.488503 Hz
SW 4.315 ppm
PRMODE QF
SI 1024
SF 400.1300422 MHz
SSB 0
L5 0.00 Hz
GB 0
PC 1.40
SI 1024
MC2 QF
SF 400.1300422 MHz
SSB 0
LB 0.00 Hz
GB 0
    
```

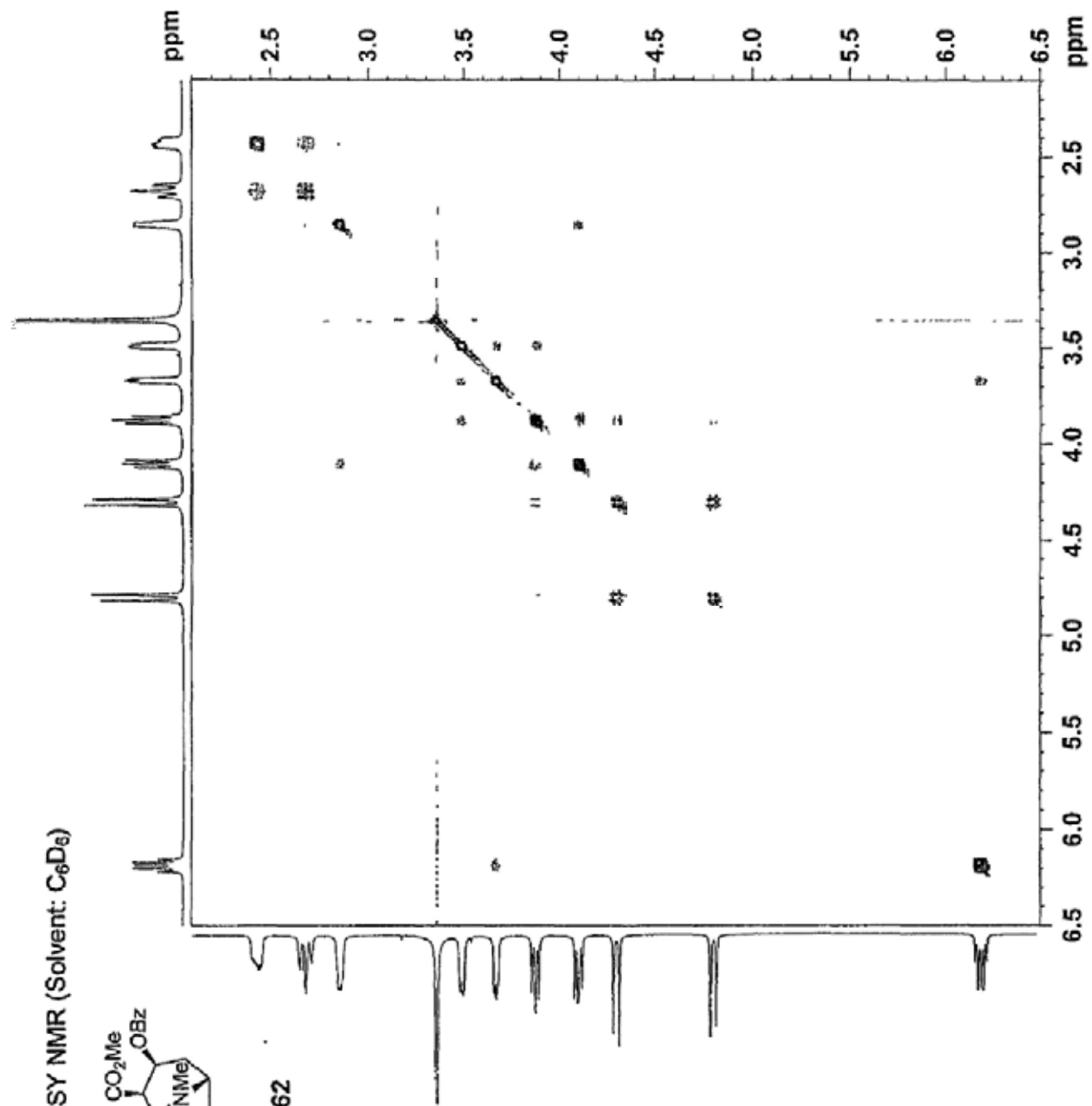
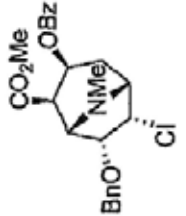
shr42c6d6noesy

NAME
EXPNO 1
PROCNO 1
Date_ 20100806
Time_ 22.31
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG noesyph
TD 2048
SOLVENT C6D6
NS 32
DS 4
SWH 1822.157 Hz
FIDRES 0.889725 Hz
AQ 0.5620212 sec
RG 32
DW 274.400 usec
DE 6.50 usec
TE 294.5 K
DO 0.00026536 sec
D1 2.00000000 sec
D8 0.69999999 sec
INO 0.00054880 sec

=====
CHANNEL f1
=====

NUC1	1H
P1	7.10 usec
PL1	-2.00 CB
PL1W	13.17734718 W
SFO1	400.1317575 MHz
ND0	1
TD	256
SFO1	400.1318 MHz
FIDRES	7.117813 Hz
SW	4.554 ppm
FMODE	States-TPPI
SI	1024
SF	400.1300418 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0
PC	1.00
SI	1024
MC2	States-TPPI
SF	400.1300421 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0

NOESY NMR (Solvent: C₆D₆)

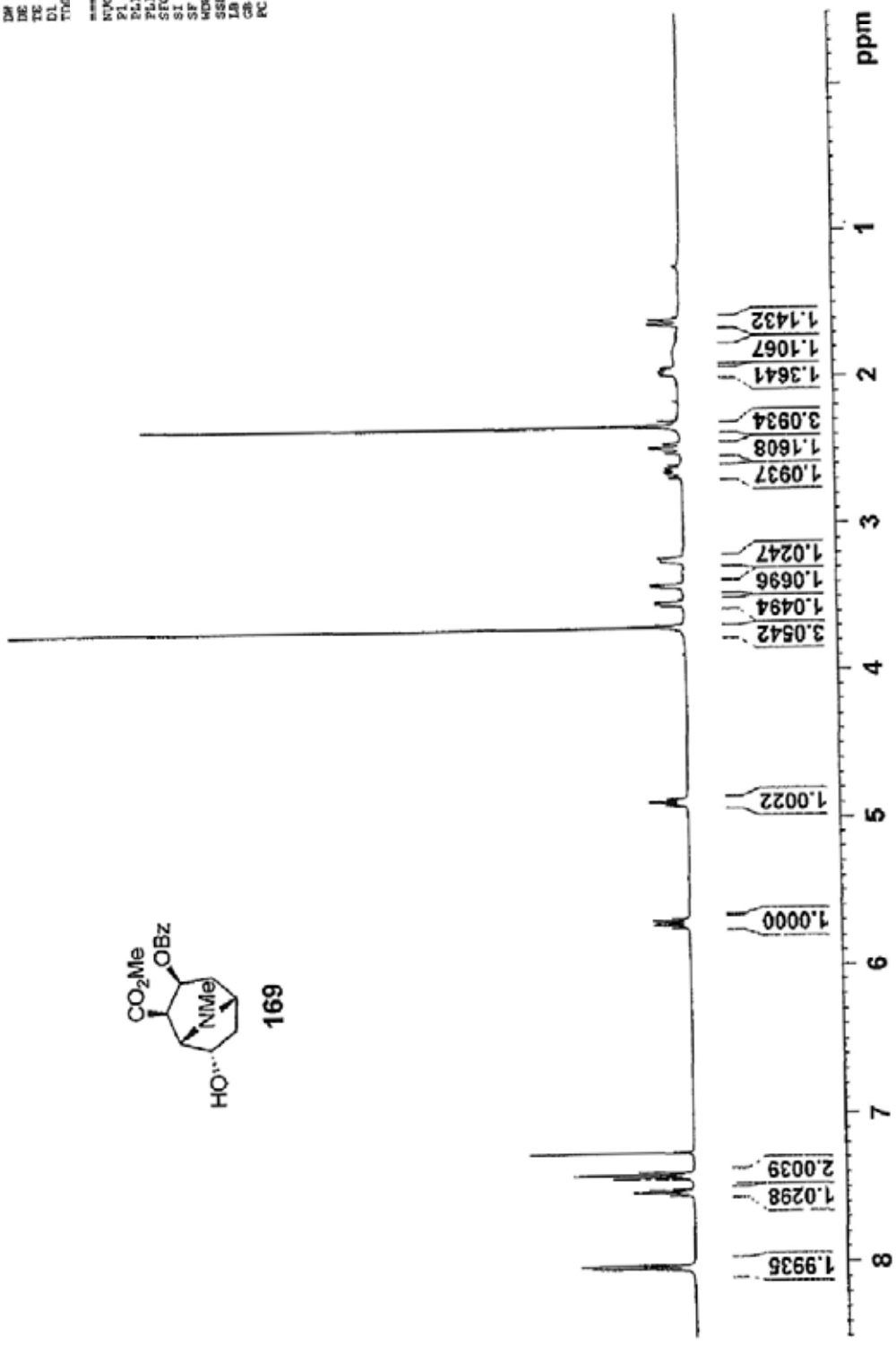


¹H NMR

NAME	169
EXPNO	6
PROCNO	1
Date_	20100721
Time	20.45
INSTRUM	5 mm PRBBO-1H
PROBHD	5 mm PRBBO-1H
PULPROG	zgpg30
TD	65534
SOLVENT	CDCl3
NS	2
DS	2
SWH	8273.685 Hz
F2RES	0.125483 Hz
AQ	3.5646387 sec
RG	90.5
DM	60.800 usec
DE	6.50 usec
TE	297.5 K
D1	1.00000000 sec
TXB	1

===== CHANNEL f1 =====
 NUC1 1H
 P1C1 14.00 usec
 PL1 -1.00 dB
 F1LH 13.56617059 Hz
 SFO1 400.1524713 MHz
 SF 400.1500143 MHz
 MSB 0
 SSB 0
 TB 0.30 Hz
 GB 0
 PC 1.00

1.6052
1.6141
1.6401
1.6490
1.6498
1.9491
1.9547
1.9652
1.9686
1.9790
1.9846
1.9929
2.3436
2.4583
2.4654
2.4879
2.4952
2.5177
2.5248
2.6284
2.6358
2.6446
2.6540
2.6628
3.2398
3.2490
3.2579
3.4142
3.4211
3.4293
3.4363
3.5331
3.5369
3.5437
3.5487
3.5527
3.7112
4.8689
4.8779
4.8849
4.8944
4.9039
4.9109
4.9199
5.6815
5.6971
5.7119
5.7266
5.7422
7.2601
7.3956
7.3996
7.4142
7.4301
7.4337
7.5090
7.5123
7.5156
7.5261
7.5308
7.5357
7.5461
7.5493
8.0185
8.0221
8.0269
8.0396
8.0425
8.0469

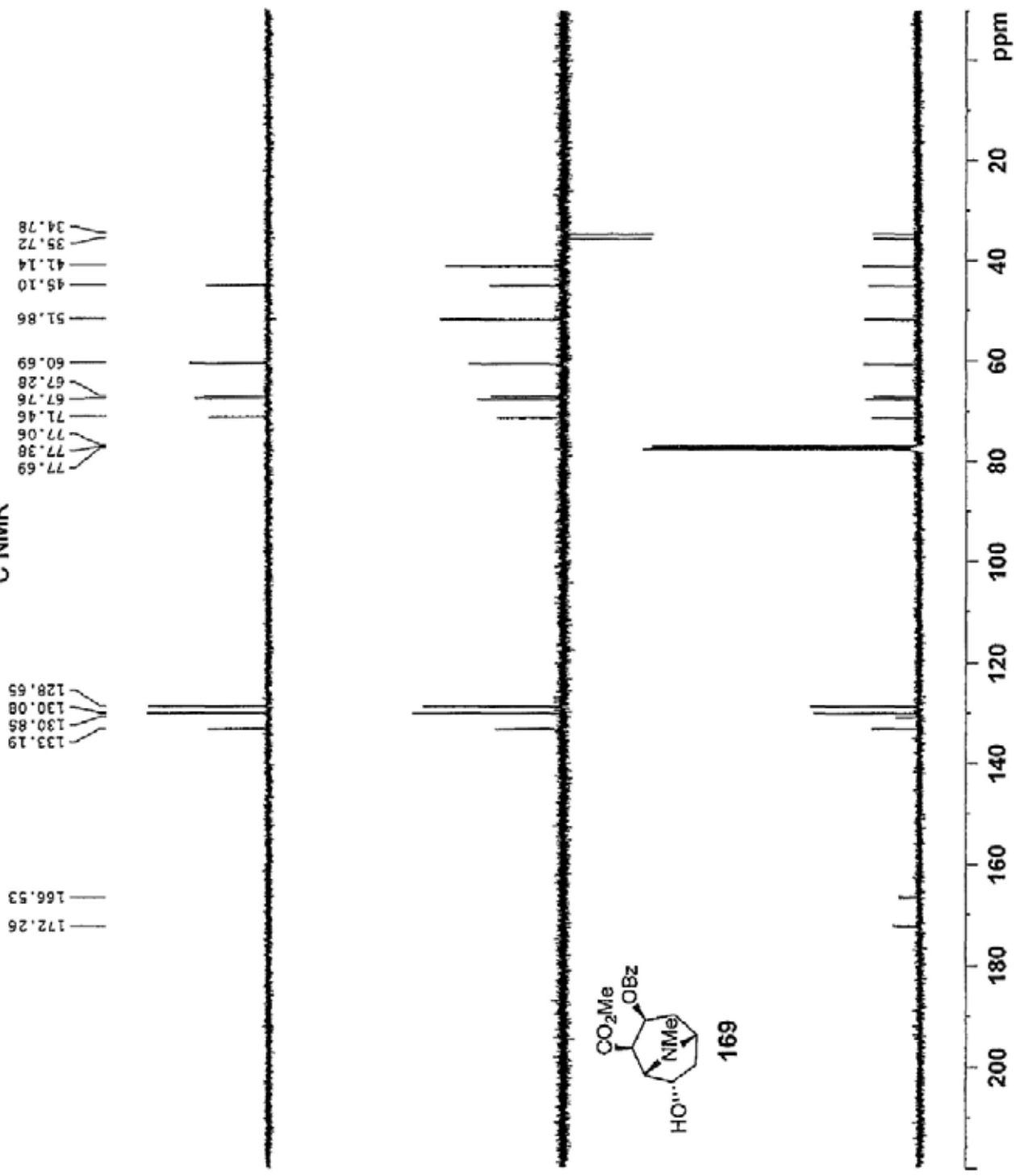


¹³C NMR

NAME shr45carbon 4
EXPNO 1
PROCNO 1
Date_ 20100722
Time 20.11
INSTRUM spect
PROBHD 5 mm BBOBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 112
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 181
DW 20.800 usec
DE 6.50 usec
TE 298.2 K
D1 2.0000000 sec
D11 0.0300000 sec
TD0 1

***** CHANNEL f1 *****
NUC1 13C
P1 9.90 usec
PL1 -2.00 dB
PL1W 55.33689499 W
SFO1 100.6379183 MHz

***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL2W 15.16 dB
PL3 18.62 dB
PL3W 13.56617069 W
PL4W 0.32844096 W
PL3M 0.14806664 W
SFO2 400.1936000 MHz
SI 32968
SF 100.6278219 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



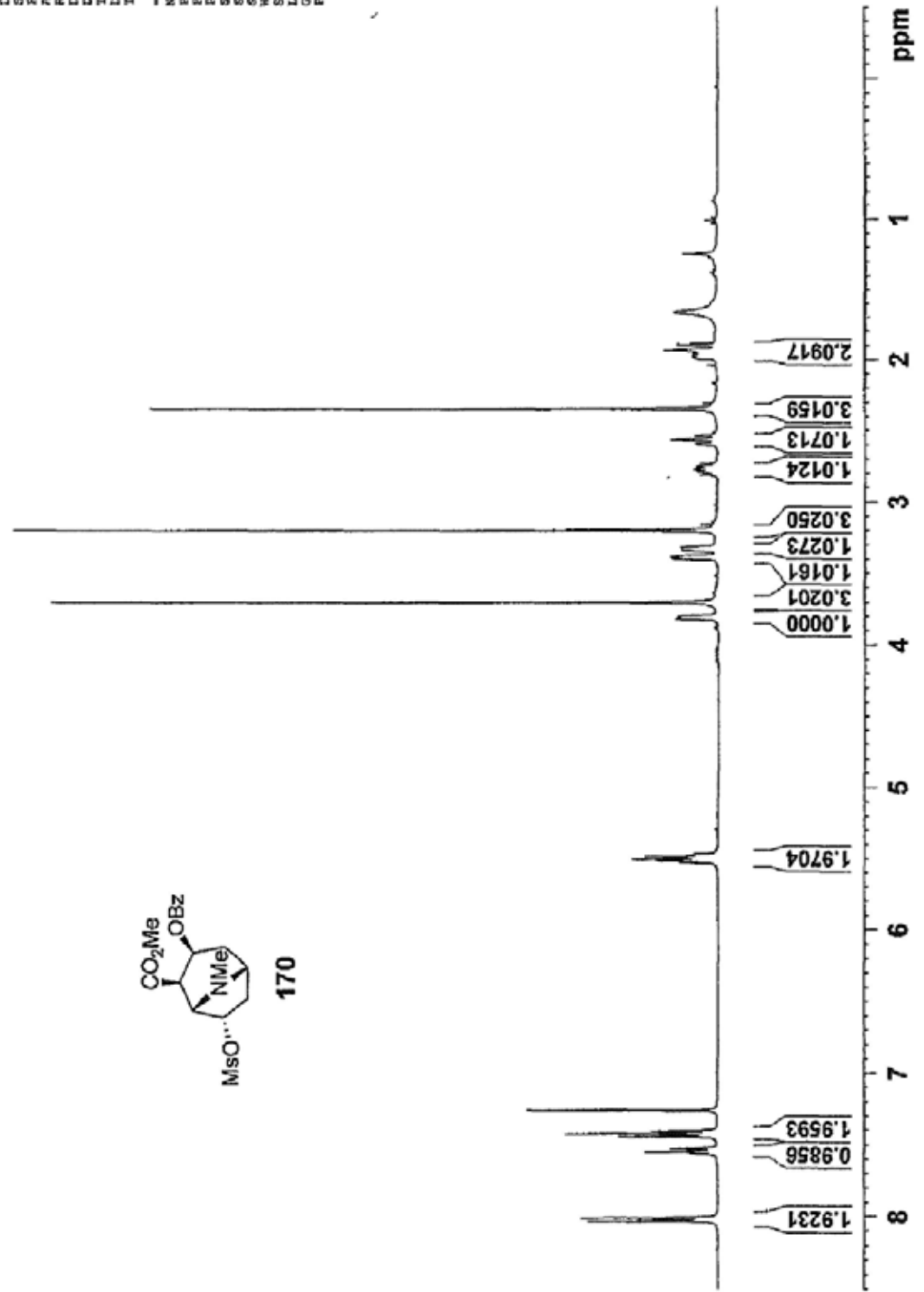
¹H NMR

1.8929
1.9015
1.9300
1.9300
1.9392
1.9504
1.9570
1.9717
1.9811
1.9871
1.9955
2.3485
2.5327
2.5396
2.5627
2.5699
2.5922
2.5997
2.7340
2.7521
2.7607
2.7711
2.7786
2.7889
2.7974
2.8156
3.2013
3.3226
3.3303
3.3383
3.3801
3.3874
3.3946
3.4019
3.7058
3.8053
3.8188
5.4727
5.4784
5.4875
5.4945
5.5034
5.5172
5.5310

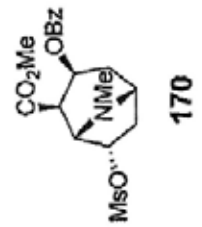
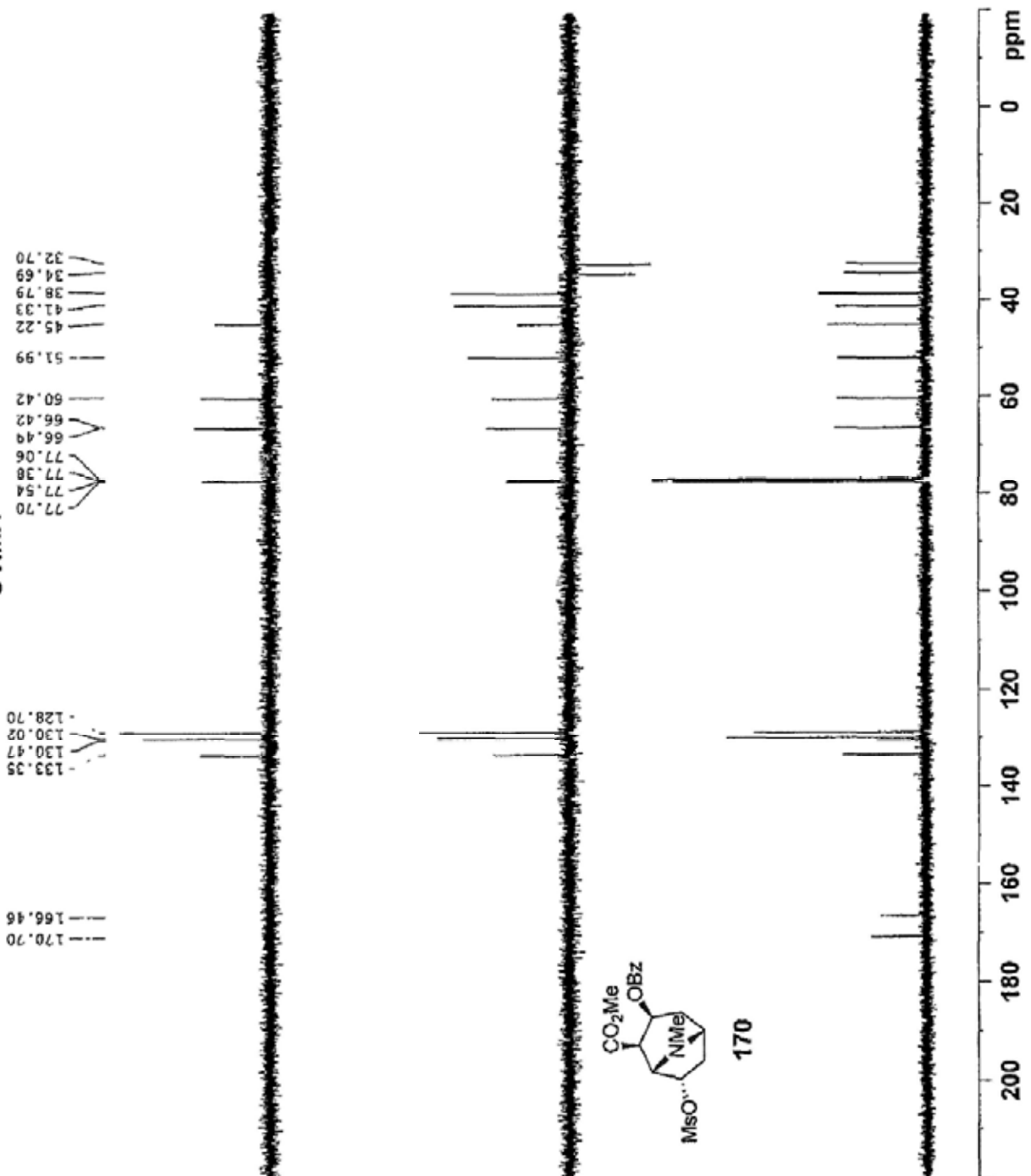
7.2599
7.4056
7.4246
7.4440
7.5288
7.5472
7.5658
8.0105
8.0285

NAME shrg7
EXPNO 4
PROCNO 1
Date_ 20100517
Time 15.33
INSTRUM spect
PROBHD 5 mm BBO1 1H/7
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SM 623.685 Hz
FIDRES 0.125483 Hz
AQ 3.8846387 sec
RG 114
DM 60.800 usec
DE 6.50 usec
TE 294.3 K
D1 1.00000000 sec
D11 1

***** CHANNEL f1 *****
NUC1 1H
P1 7.10 usec
PL -2.00 dB
PL1W 13.17734718 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300656 MHz
SFO2 524
WDW 0
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



¹³C NMR



```

NAME          shr57carbon
EXPNO         2
PROCNO        1
Date_         20100525
Time_         9.41
INSTRUM       spect
PROBHD        5 mm PABBI 1H/
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            74
DS            4
SWH           24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631988 sec
RG            203
DM            20.800 usec
DE            6.50 usec
TE            294.7 K
D1            2.0000000 sec
D11          0.0300000 sec
TDO           1

----- CHANNEL f1 -----
NUC1          13C
P1            14.50 usec
PL1           -4.00 dB
PL1W          90.22689619 W
SFO1          100.6228299 MHz

----- CHANNEL f2 -----
CPDPRG2      Waltz16
NUC2          1H
PCPD2        80.00 usec
PL2           -2.00 dB
PL12         18.80 dB
PL13         18.80 dB
PL1W         13.1773718 W
PL1ZM        0.10960442 W
SFO2         400.1315005 MHz
SI           32768
SF           100.6127368 MHz
WDW          EM
SSB          0
LB           1.00 Hz
GB           0
PC           1.40
  
```

```

NAME          sh77z602_1
EXPNO         1
PROCNO       1
DATE_         20101027
TIME         10.41
INSTRUM      spect
PROBHD       5 mm PABBO BB-
PULPROG      zg30
TD           65536
SOLVENT      CDCl3
NS           8
DS           2
SWH          8223.685 Hz
FIDRES       0.125483 Hz
AQ           3.9876367 sec
RG           144
AQ           144
CF           60.800 usec
DE           6.50 usec
TE           298.0 K
D1           1.00000000 sec
TD0          1
===== CHANNEL f1 =====
NUC1          1H
P1           14.00 usec
PL1          -1.00 dB
G1           1.00 dB
NUC2          13C
P2           13.56617069 usec
PL2          0.00 dB
G2           1.00 dB
NUC3          15N
P3           460.2524713 usec
PL3          0.00 dB
G3           1.00 dB
===== CHANNEL f2 =====
NUC4          1H
P4           14.00 usec
PL4          -1.00 dB
G4           1.00 dB
===== CHANNEL f3 =====
NUC5          13C
P5           13.56617069 usec
PL5          0.00 dB
G5           1.00 dB
===== CHANNEL f4 =====
NUC6          15N
P6           460.2524713 usec
PL6          0.00 dB
G6           1.00 dB
===== CHANNEL f5 =====
NUC7          1H
P7           14.00 usec
PL7          -1.00 dB
G7           1.00 dB
===== CHANNEL f6 =====
NUC8          13C
P8           13.56617069 usec
PL8          0.00 dB
G8           1.00 dB
===== CHANNEL f7 =====
NUC9          15N
P9           460.2524713 usec
PL9          0.00 dB
G9           1.00 dB
===== CHANNEL f8 =====
NUC10         1H
P10          14.00 usec
PL10         -1.00 dB
G10          1.00 dB
===== CHANNEL f9 =====
NUC11         13C
P11          13.56617069 usec
PL11         0.00 dB
G11          1.00 dB
===== CHANNEL f10 =====
NUC12         15N
P12          460.2524713 usec
PL12         0.00 dB
G12          1.00 dB
===== CHANNEL f11 =====
NUC13         1H
P13          14.00 usec
PL13         -1.00 dB
G13          1.00 dB
===== CHANNEL f12 =====
NUC14         13C
P14          13.56617069 usec
PL14         0.00 dB
G14          1.00 dB
===== CHANNEL f13 =====
NUC15         15N
P15          460.2524713 usec
PL15         0.00 dB
G15          1.00 dB
===== CHANNEL f14 =====
NUC16         1H
P16          14.00 usec
PL16         -1.00 dB
G16          1.00 dB
===== CHANNEL f15 =====
NUC17         13C
P17          13.56617069 usec
PL17         0.00 dB
G17          1.00 dB
===== CHANNEL f16 =====
NUC18         15N
P18          460.2524713 usec
PL18         0.00 dB
G18          1.00 dB
===== CHANNEL f17 =====
NUC19         1H
P19          14.00 usec
PL19         -1.00 dB
G19          1.00 dB
===== CHANNEL f18 =====
NUC20         13C
P20          13.56617069 usec
PL20         0.00 dB
G20          1.00 dB
===== CHANNEL f19 =====
NUC21         15N
P21          460.2524713 usec
PL21         0.00 dB
G21          1.00 dB
===== CHANNEL f20 =====
NUC22         1H
P22          14.00 usec
PL22         -1.00 dB
G22          1.00 dB
===== CHANNEL f21 =====
NUC23         13C
P23          13.56617069 usec
PL23         0.00 dB
G23          1.00 dB
===== CHANNEL f22 =====
NUC24         15N
P24          460.2524713 usec
PL24         0.00 dB
G24          1.00 dB
===== CHANNEL f23 =====
NUC25         1H
P25          14.00 usec
PL25         -1.00 dB
G25          1.00 dB
===== CHANNEL f24 =====
NUC26         13C
P26          13.56617069 usec
PL26         0.00 dB
G26          1.00 dB
===== CHANNEL f25 =====
NUC27         15N
P27          460.2524713 usec
PL27         0.00 dB
G27          1.00 dB
===== CHANNEL f26 =====
NUC28         1H
P28          14.00 usec
PL28         -1.00 dB
G28          1.00 dB
===== CHANNEL f27 =====
NUC29         13C
P29          13.56617069 usec
PL29         0.00 dB
G29          1.00 dB
===== CHANNEL f28 =====
NUC30         15N
P30          460.2524713 usec
PL30         0.00 dB
G30          1.00 dB
===== CHANNEL f29 =====
NUC31         1H
P31          14.00 usec
PL31         -1.00 dB
G31          1.00 dB
===== CHANNEL f30 =====
NUC32         13C
P32          13.56617069 usec
PL32         0.00 dB
G32          1.00 dB
===== CHANNEL f31 =====
NUC33         15N
P33          460.2524713 usec
PL33         0.00 dB
G33          1.00 dB
===== CHANNEL f32 =====
NUC34         1H
P34          14.00 usec
PL34         -1.00 dB
G34          1.00 dB
===== CHANNEL f33 =====
NUC35         13C
P35          13.56617069 usec
PL35         0.00 dB
G35          1.00 dB
===== CHANNEL f34 =====
NUC36         15N
P36          460.2524713 usec
PL36         0.00 dB
G36          1.00 dB
===== CHANNEL f35 =====
NUC37         1H
P37          14.00 usec
PL37         -1.00 dB
G37          1.00 dB
===== CHANNEL f36 =====
NUC38         13C
P38          13.56617069 usec
PL38         0.00 dB
G38          1.00 dB
===== CHANNEL f37 =====
NUC39         15N
P39          460.2524713 usec
PL39         0.00 dB
G39          1.00 dB
===== CHANNEL f38 =====
NUC40         1H
P40          14.00 usec
PL40         -1.00 dB
G40          1.00 dB
===== CHANNEL f39 =====
NUC41         13C
P41          13.56617069 usec
PL41         0.00 dB
G41          1.00 dB
===== CHANNEL f40 =====
NUC42         15N
P42          460.2524713 usec
PL42         0.00 dB
G42          1.00 dB
===== CHANNEL f41 =====
NUC43         1H
P43          14.00 usec
PL43         -1.00 dB
G43          1.00 dB
===== CHANNEL f42 =====
NUC44         13C
P44          13.56617069 usec
PL44         0.00 dB
G44          1.00 dB
===== CHANNEL f43 =====
NUC45         15N
P45          460.2524713 usec
PL45         0.00 dB
G45          1.00 dB
===== CHANNEL f44 =====
NUC46         1H
P46          14.00 usec
PL46         -1.00 dB
G46          1.00 dB
===== CHANNEL f45 =====
NUC47         13C
P47          13.56617069 usec
PL47         0.00 dB
G47          1.00 dB
===== CHANNEL f46 =====
NUC48         15N
P48          460.2524713 usec
PL48         0.00 dB
G48          1.00 dB
===== CHANNEL f47 =====
NUC49         1H
P49          14.00 usec
PL49         -1.00 dB
G49          1.00 dB
===== CHANNEL f48 =====
NUC50         13C
P50          13.56617069 usec
PL50         0.00 dB
G50          1.00 dB
===== CHANNEL f49 =====
NUC51         15N
P51          460.2524713 usec
PL51         0.00 dB
G51          1.00 dB
===== CHANNEL f50 =====
NUC52         1H
P52          14.00 usec
PL52         -1.00 dB
G52          1.00 dB
===== CHANNEL f51 =====
NUC53         13C
P53          13.56617069 usec
PL53         0.00 dB
G53          1.00 dB
===== CHANNEL f52 =====
NUC54         15N
P54          460.2524713 usec
PL54         0.00 dB
G54          1.00 dB
===== CHANNEL f53 =====
NUC55         1H
P55          14.00 usec
PL55         -1.00 dB
G55          1.00 dB
===== CHANNEL f54 =====
NUC56         13C
P56          13.56617069 usec
PL56         0.00 dB
G56          1.00 dB
===== CHANNEL f55 =====
NUC57         15N
P57          460.2524713 usec
PL57         0.00 dB
G57          1.00 dB
===== CHANNEL f56 =====
NUC58         1H
P58          14.00 usec
PL58         -1.00 dB
G58          1.00 dB
===== CHANNEL f57 =====
NUC59         13C
P59          13.56617069 usec
PL59         0.00 dB
G59          1.00 dB
===== CHANNEL f58 =====
NUC60         15N
P60          460.2524713 usec
PL60         0.00 dB
G60          1.00 dB
===== CHANNEL f59 =====
NUC61         1H
P61          14.00 usec
PL61         -1.00 dB
G61          1.00 dB
===== CHANNEL f60 =====
NUC62         13C
P62          13.56617069 usec
PL62         0.00 dB
G62          1.00 dB
===== CHANNEL f61 =====
NUC63         15N
P63          460.2524713 usec
PL63         0.00 dB
G63          1.00 dB
===== CHANNEL f62 =====
NUC64         1H
P64          14.00 usec
PL64         -1.00 dB
G64          1.00 dB
===== CHANNEL f63 =====
NUC65         13C
P65          13.56617069 usec
PL65         0.00 dB
G65          1.00 dB
===== CHANNEL f64 =====
NUC66         15N
P66          460.2524713 usec
PL66         0.00 dB
G66          1.00 dB
===== CHANNEL f65 =====
NUC67         1H
P67          14.00 usec
PL67         -1.00 dB
G67          1.00 dB
===== CHANNEL f66 =====
NUC68         13C
P68          13.56617069 usec
PL68         0.00 dB
G68          1.00 dB
===== CHANNEL f67 =====
NUC69         15N
P69          460.2524713 usec
PL69         0.00 dB
G69          1.00 dB
===== CHANNEL f68 =====
NUC70         1H
P70          14.00 usec
PL70         -1.00 dB
G70          1.00 dB
===== CHANNEL f69 =====
NUC71         13C
P71          13.56617069 usec
PL71         0.00 dB
G71          1.00 dB
===== CHANNEL f70 =====
NUC72         15N
P72          460.2524713 usec
PL72         0.00 dB
G72          1.00 dB
===== CHANNEL f71 =====
NUC73         1H
P73          14.00 usec
PL73         -1.00 dB
G73          1.00 dB
===== CHANNEL f72 =====
NUC74         13C
P74          13.56617069 usec
PL74         0.00 dB
G74          1.00 dB
===== CHANNEL f73 =====
NUC75         15N
P75          460.2524713 usec
PL75         0.00 dB
G75          1.00 dB
===== CHANNEL f74 =====
NUC76         1H
P76          14.00 usec
PL76         -1.00 dB
G76          1.00 dB
===== CHANNEL f75 =====
NUC77         13C
P77          13.56617069 usec
PL77         0.00 dB
G77          1.00 dB
===== CHANNEL f76 =====
NUC78         15N
P78          460.2524713 usec
PL78         0.00 dB
G78          1.00 dB
===== CHANNEL f77 =====
NUC79         1H
P79          14.00 usec
PL79         -1.00 dB
G79          1.00 dB
===== CHANNEL f78 =====
NUC80         13C
P80          13.56617069 usec
PL80         0.00 dB
G80          1.00 dB
===== CHANNEL f79 =====
NUC81         15N
P81          460.2524713 usec
PL81         0.00 dB
G81          1.00 dB
===== CHANNEL f80 =====
NUC82         1H
P82          14.00 usec
PL82         -1.00 dB
G82          1.00 dB
===== CHANNEL f81 =====
NUC83         13C
P83          13.56617069 usec
PL83         0.00 dB
G83          1.00 dB
===== CHANNEL f82 =====
NUC84         15N
P84          460.2524713 usec
PL84         0.00 dB
G84          1.00 dB
===== CHANNEL f83 =====
NUC85         1H
P85          14.00 usec
PL85         -1.00 dB
G85          1.00 dB
===== CHANNEL f84 =====
NUC86         13C
P86          13.56617069 usec
PL86         0.00 dB
G86          1.00 dB
===== CHANNEL f85 =====
NUC87         15N
P87          460.2524713 usec
PL87         0.00 dB
G87          1.00 dB
===== CHANNEL f86 =====
NUC88         1H
P88          14.00 usec
PL88         -1.00 dB
G88          1.00 dB
===== CHANNEL f87 =====
NUC89         13C
P89          13.56617069 usec
PL89         0.00 dB
G89          1.00 dB
===== CHANNEL f88 =====
NUC90         15N
P90          460.2524713 usec
PL90         0.00 dB
G90          1.00 dB
===== CHANNEL f89 =====
NUC91         1H
P91          14.00 usec
PL91         -1.00 dB
G91          1.00 dB
===== CHANNEL f90 =====
NUC92         13C
P92          13.56617069 usec
PL92         0.00 dB
G92          1.00 dB
===== CHANNEL f91 =====
NUC93         15N
P93          460.2524713 usec
PL93         0.00 dB
G93          1.00 dB
===== CHANNEL f92 =====
NUC94         1H
P94          14.00 usec
PL94         -1.00 dB
G94          1.00 dB
===== CHANNEL f93 =====
NUC95         13C
P95          13.56617069 usec
PL95         0.00 dB
G95          1.00 dB
===== CHANNEL f94 =====
NUC96         15N
P96          460.2524713 usec
PL96         0.00 dB
G96          1.00 dB
===== CHANNEL f95 =====
NUC97         1H
P97          14.00 usec
PL97         -1.00 dB
G97          1.00 dB
===== CHANNEL f96 =====
NUC98         13C
P98          13.56617069 usec
PL98         0.00 dB
G98          1.00 dB
===== CHANNEL f97 =====
NUC99         15N
P99          460.2524713 usec
PL99         0.00 dB
G99          1.00 dB
===== CHANNEL f98 =====
NUC100        1H
P100         14.00 usec
PL100        -1.00 dB
G100         1.00 dB
===== CHANNEL f99 =====
NUC101        13C
P101         13.56617069 usec
PL101        0.00 dB
G101         1.00 dB
===== CHANNEL f100 =====
NUC102        15N
P102         460.2524713 usec
PL102        0.00 dB
G102         1.00 dB
===== CHANNEL f101 =====
NUC103        1H
P103         14.00 usec
PL103        -1.00 dB
G103         1.00 dB
===== CHANNEL f102 =====
NUC104        13C
P104         13.56617069 usec
PL104        0.00 dB
G104         1.00 dB
===== CHANNEL f103 =====
NUC105        15N
P105         460.2524713 usec
PL105        0.00 dB
G105         1.00 dB
===== CHANNEL f104 =====
NUC106        1H
P106         14.00 usec
PL106        -1.00 dB
G106         1.00 dB
===== CHANNEL f105 =====
NUC107        13C
P107         13.56617069 usec
PL107        0.00 dB
G107         1.00 dB
===== CHANNEL f106 =====
NUC108        15N
P108         460.2524713 usec
PL108        0.00 dB
G108         1.00 dB
===== CHANNEL f107 =====
NUC109        1H
P109         14.00 usec
PL109        -1.00 dB
G109         1.00 dB
===== CHANNEL f108 =====
NUC110        13C
P110         13.56617069 usec
PL110        0.00 dB
G110         1.00 dB
===== CHANNEL f109 =====
NUC111        15N
P111         460.2524713 usec
PL111        0.00 dB
G111         1.00 dB
===== CHANNEL f110 =====
NUC112        1H
P112         14.00 usec
PL112        -1.00 dB
G112         1.00 dB
===== CHANNEL f111 =====
NUC113        13C
P113         13.56617069 usec
PL113        0.00 dB
G113         1.00 dB
===== CHANNEL f112 =====
NUC114        15N
P114         460.2524713 usec
PL114        0.00 dB
G114         1.00 dB
===== CHANNEL f113 =====
NUC115        1H
P115         14.00 usec
PL115        -1.00 dB
G115         1.00 dB
===== CHANNEL f114 =====
NUC116        13C
P116         13.56617069 usec
PL116        0.00 dB
G116         1.00 dB
===== CHANNEL f115 =====
NUC117        15N
P117         460.2524713 usec
PL117        0.00 dB
G117         1.00 dB
===== CHANNEL f116 =====
NUC118        1H
P118         14.00 usec
PL118        -1.00 dB
G118         1.00 dB
===== CHANNEL f117 =====
NUC119        13C
P119         13.56617069 usec
PL119        0.00 dB
G119         1.00 dB
===== CHANNEL f118 =====
NUC120        15N
P120         460.2524713 usec
PL120        0.00 dB
G120         1.00 dB
===== CHANNEL f119 =====
NUC121        1H
P121         14.00 usec
PL121        -1.00 dB
G121         1.00 dB
===== CHANNEL f120 =====
NUC122        13C
P122         13.56617069 usec
PL122        0.00 dB
G122         1.00 dB
===== CHANNEL f121 =====
NUC123        15N
P123         460.2524713 usec
PL123        0.00 dB
G123         1.00 dB
===== CHANNEL f122 =====
NUC124        1H
P124         14.00 usec
PL124        -1.00 dB
G124         1.00 dB
===== CHANNEL f123 =====
NUC125        13C
P125         13.56617069 usec
PL125        0.00 dB
G125         1.00 dB
===== CHANNEL f124 =====
NUC126        15N
P126         460.2524713 usec
PL126        0.00 dB
G126         1.00 dB
===== CHANNEL f125 =====
NUC127        1H
P127         14.00 usec
PL127        -1.00 dB
G127         1.00 dB
===== CHANNEL f126 =====
NUC128        13C
P128         13.56617069 usec
PL128        0.00 dB
G128         1.00 dB
===== CHANNEL f127 =====
NUC129        15N
P129         460.2524713 usec
PL129        0.00 dB
G129         1.00 dB
===== CHANNEL f128 =====
NUC130        1H
P130         14.00 usec
PL130        -1.00 dB
G130         1.00 dB
===== CHANNEL f129 =====
NUC131        13C
P131         13.56617069 usec
PL131        0.00 dB
G131         1.00 dB
===== CHANNEL f130 =====
NUC132        15N
P132         460.2524713 usec
PL132        0.00 dB
G132         1.00 dB
===== CHANNEL f131 =====
NUC133        1H
P133         14.00 usec
PL133        -1.00 dB
G133         1.00 dB
===== CHANNEL f132 =====
NUC134        13C
P134         13.56617069 usec
PL134        0.00 dB
G134         1.00 dB
===== CHANNEL f133 =====
NUC135        15N
P135         460.2524713 usec
PL135        0.00 dB
G135         1.00 dB
===== CHANNEL f134 =====
NUC136        1H
P136         14.00 usec
PL136        -1.00 dB
G136         1.00 dB
===== CHANNEL f135 =====
NUC137        13C
P137         13.56617069 usec
PL137        0.00 dB
G137         1.00 dB
===== CHANNEL f136 =====
NUC138        15N
P138         460.2524713 usec
PL138        0.00 dB
G138         1.00 dB
===== CHANNEL f137 =====
NUC139        1H
P139         14.00 usec
PL139        -1.00 dB
G139         1.00 dB
===== CHANNEL f138 =====
NUC140        13C
P140         13.56617069 usec
PL140        0.00 dB
G140         1.00 dB
===== CHANNEL f139 =====
NUC141        15N
P141         460.2524713 usec
PL141        0.00 dB
G141         1.00 dB
===== CHANNEL f140 =====
NUC142        1H
P142         14.00 usec
PL142        -1.00 dB
G142         1.00 dB
===== CHANNEL f141 =====
NUC143        13C
P143         13.56617069 usec
PL143        0.00 dB
G143         1.00 dB
===== CHANNEL f142 =====
NUC144        15N
P144         460.2524713 usec
PL144        0.00 dB
G144         1.00 dB
===== CHANNEL f143 =====
NUC145        1H
P145         14.00 usec
PL145        -1.00 dB
G145         1.00 dB
===== CHANNEL f144 =====
NUC146        13C
P146         13.56617069 usec
PL146        0.00 dB
G146         1.00 dB
===== CHANNEL f145 =====
NUC147        15N
P147         460.2524713 usec
PL147        0.00 dB
G147         1.00 dB
===== CHANNEL f146 =====
NUC148        1H
P148         14.00 usec
PL148        -1.00 dB
G148         1.00 dB
===== CHANNEL f147 =====
NUC149        13C
P149         13.56617069 usec
PL149        0.00 dB
G149         1.00 dB
===== CHANNEL f148 =====
NUC150        15N
P150         460.2524713 usec
PL150        0.00 dB
G150         1.00 dB
===== CHANNEL f149 =====
NUC151        1H
P151         14.00 usec
PL151        -1.00 dB
G151         1.00 dB
===== CHANNEL f150 =====
NUC152        13C
P152         13.56617069 usec
PL152        0.00 dB
G152         1.00 dB
===== CHANNEL f151 =====
NUC153        15N
P153         460.2524713 usec
PL153        0.00 dB
G153         1.00 dB
===== CHANNEL f152 =====
NUC154        1H
P154         14.00 usec
PL154        -1.00 dB
G154         1.00 dB
===== CHANNEL f153 =====
NUC155        13C
P155         13.56617069 usec
PL155        0.00 dB
G155         1.00 dB
===== CHANNEL f154 =====
NUC156        15N
P156         460.2524713 usec
PL156        0.00 dB
G156         1.00 dB
===== CHANNEL f155 =====
NUC157        1H
P157         14.00 usec
PL157        -1.00 dB
G157         1.00 dB
===== CHANNEL f156 =====
NUC158        13C
P158         13.56617069 usec
PL158        0.00 dB
G158         1.00 dB
===== CHANNEL f157 =====
NUC159        15N
P159         460.2524713 usec
PL159        0.00 dB
G159         1.00 dB
===== CHANNEL f158 =====
NUC160        1H
P160         14.00 usec
PL160        -1.00 dB
G160         1.00 dB
===== CHANNEL f159 =====
NUC161        13C
P161         13.56617069 usec
PL161        0.00 dB
G161         1.00 dB
===== CHANNEL f160 =====
NUC162        15N
P162         460.2524713 usec
PL162        0.00 dB
G162         1.00 dB
===== CHANNEL f161 =====
NUC163        1H
P163         14.00 usec
PL163        -1.00 dB
G163         1.00 dB
===== CHANNEL f162 =====
NUC164        13C
P164         13.56617069 usec
PL164        0.00 dB
G164         1.00 dB
===== CHANNEL f163 =====
NUC165        15N
P165         460.2524713 usec
PL165        0.00 dB
G165         1.00 dB
===== CHANNEL f164 =====
NUC166        1H
P166         14.00 usec
PL166        -1.00 dB
G166         1.00 dB
===== CHANNEL f165 =====
NUC167        13C
P167         13.56617069 usec
PL167        0.00 dB
G167         1.00 dB
===== CHANNEL f166 =====
NUC168        15N
P168         460.2524713 usec
PL168        0.00 dB
G168         1.00 dB
===== CHANNEL f167 =====
NUC169        1H
P169         14.00 usec
PL169        -1.00 dB
G169         1.00 dB
===== CHANNEL f168 =====
NUC170        13C
P170         13.56617069 usec
PL170        0.00 dB
G170         1.00 dB
===== CHANNEL f169 =====
NUC171        15N
P171         460.2524713 usec
PL171        0.00 dB
G171         1.00 dB
===== CHANNEL f170 =====
NUC172        1H
P172         14.00 usec
PL172        -1.00 dB
G172         1.00 dB
===== CHANNEL f171 =====
NUC173        13C
P173         13.56617069 usec
PL173        0.00 dB
G173         1.00 dB
===== CHANNEL f172 =====
NUC174        15N
P174         460.2524713 usec
PL174        0.00 dB
G174         1.00 dB
===== CHANNEL f173 =====
NUC175        1H
P175         14.00 usec
PL175        -1.00 dB
G175         1.00 dB
===== CHANNEL f174 =====
NUC176        13C
P176         13.56617069 usec
PL176        0.00 dB
G176         1.00 dB
===== CHANNEL f175 =====
NUC177        15N
P177         460.2524713 usec
PL177        0.00 dB
G177         1.00 dB
===== CHANNEL f176 =====
NUC178        1H
P178         14.00 usec
PL178        -1.00 dB
G178         1.00 dB
===== CHANNEL f177 =====
NUC179        13C
P179         13.56617069 usec
PL179        0.00 dB
G179         1.00 dB
===== CHANNEL f178 =====
NUC180        15N
P180         460.2524713 usec
PL180        0.00 dB
G180         1.00 dB
===== CHANNEL f179 =====
NUC181        1H
P181         14.00 usec
PL181        -1.00 dB
G181         1.00 dB
===== CHANNEL f180 =====
NUC182        13C
P182         13.56617069 usec
PL182        0.00 dB
G182         1.00 dB
===== CHANNEL f181 =====
NUC183        15N
P183         460.2524713 usec
PL183        0.00 dB
G183         1.00 dB
===== CHANNEL f182 =====
NUC184        1H
P184         14.00 usec
PL184        -1.00 dB
G184         1.00 dB
===== CHANNEL f183 =====
NUC185        13C
P185         13.56617069 usec
PL185        0.00 dB
G185         1.00 dB
===== CHANNEL f184 =====
NUC186        15N
P186         460.2524713 usec
PL186        0.00 dB
G186         1.00 dB
===== CHANNEL f185 =====
NUC187        1H
P187         14.00 usec
PL187        -1.00 dB
G187         1.00 dB
===== CHANNEL f186 =====
NUC188        13C
P188         13.56617069 usec
PL188        0.00 dB
G188         1.00 dB
===== CHANNEL f187 =====
NUC189        15N
P189         460.2524713 usec
PL189        0.00 dB
G189         1.00 dB
===== CHANNEL f188 =====
NUC190        1H
P190         14.00 usec
PL190        -1.00 dB
G190         1.00 dB
===== CHANNEL f189 =====
NUC191        13C
P191         13.56617069 usec
PL191        0.00 dB
G191         1.00 dB
===== CHANNEL f190 =====
NUC192        15N
P192         460.2524713 usec
PL192        0.00 dB
G192         1.00 dB
===== CHANNEL f191 =====
NUC193        1H
P193         14.00 usec
PL193        -1.00 dB
G193         1.00 dB
===== CHANNEL f192 =====
NUC194        13C
P194         13.56617069 usec
PL194        0.00 dB
G194         1.00 dB
===== CHANNEL f193 =====
NUC195        15N
P195         460.2524713 usec
PL195        0.00 dB
G195         1.00 dB
===== CHANNEL f194 =====
NUC196        1H
P196         14.00 usec
PL196        -1.00 dB
G196         1.00 dB
===== CHANNEL f195 =====
NUC197        13C
P197         13.56617069 usec
PL197        0.00 dB
G197         1.00 dB
===== CHANNEL f196 =====
NUC198        15N
P198         460.2524713 usec
PL198        0.00 dB
G198         1.00 dB
===== CHANNEL f197 =====
NUC199        1H
P199         14.00 usec
PL199        -1.00 dB
G199         1.00 dB
===== CHANNEL f198 =====
NUC200        13C
P200         13.56617069 usec
PL200        0.00 dB
G200         1.00 dB
===== CHANNEL f199 =====
NUC201        15N
P201         460.2524713 usec
PL201        0.00 dB
G201         1.00 dB
===== CHANNEL f200 =====
NUC202        1H
P202         14.00 usec
PL202        -1.00 dB
G202         1.00 dB
===== CHANNEL f201 =====
NUC203        13C
P203         13.56617069 usec
PL203        0.00 dB
G203         1.00 dB
===== CHANNEL f202 =====
NUC204        15N
P204         460.2524713 usec
PL204        0.00 dB
G204         1.00 dB
===== CHANNEL f203 =====
NUC205        1H
P205         14.00 usec
PL205        -1.00 dB
G205         1.00 dB
===== CHANNEL f204 =====
NUC206        13C
P206         13.56617069 usec
PL206        0.00 dB
G206         1.00 dB
===== CHANNEL f205 =====
NUC207        15N
P207         460.2524713 usec
PL207        0.00 dB
G207         1.00 dB
===== CHANNEL f206 =====
NUC208        1H
P208         14.00 usec
PL208        -1.00 dB
G208         1.00 dB
===== CHANNEL f207 =====
NUC209        13C
P209         13.56617069 usec
PL209        0.00 dB
G209         1.00 dB
===== CHANNEL f208 =====
NUC210        15
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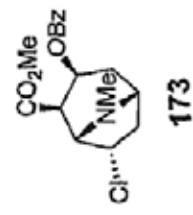
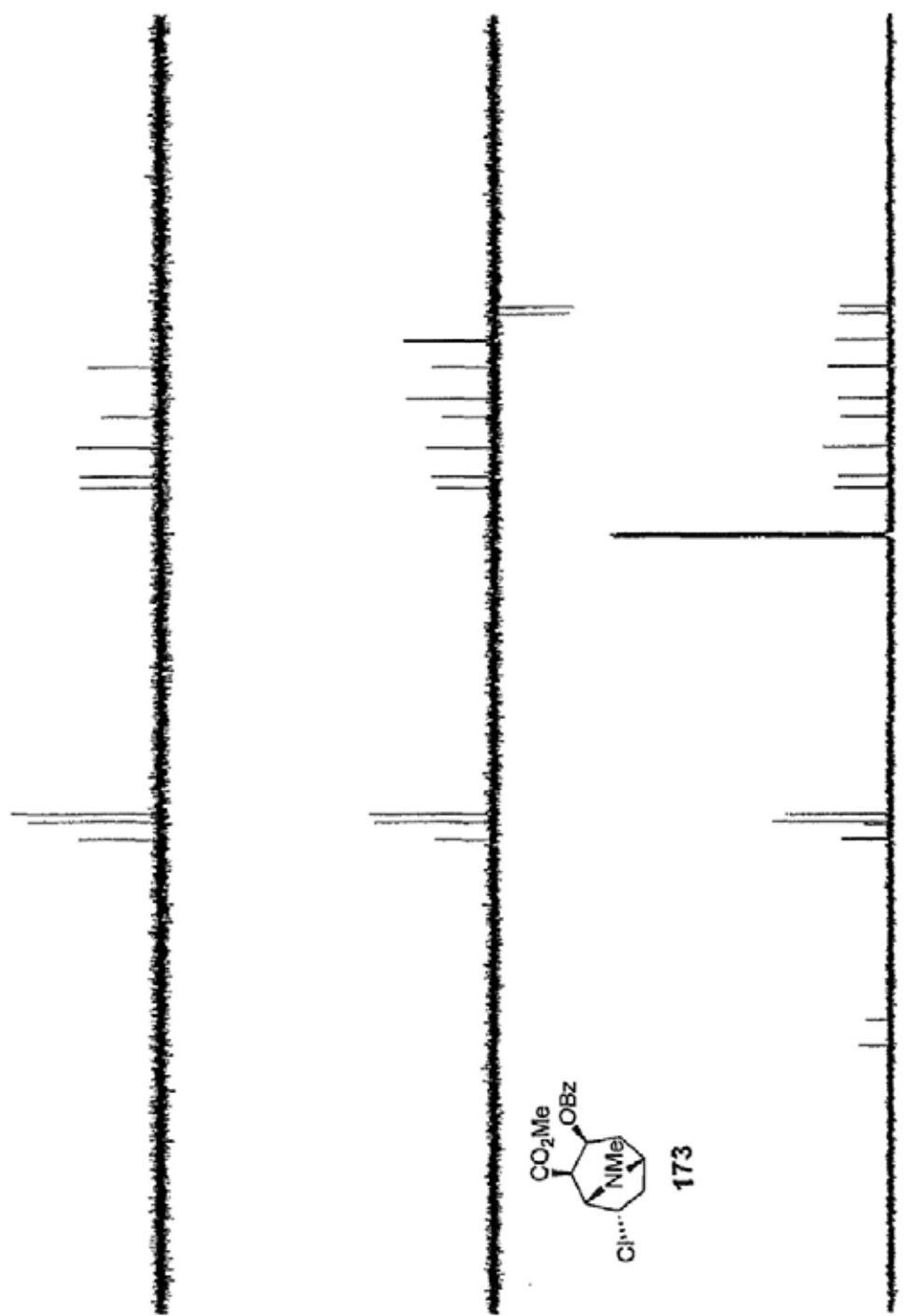
¹³C NMR

171.18
166.32
133.30
130.59
130.08
128.69
77.69
77.38
77.06
68.57
66.42
62.02
59.40
52.99
46.20
41.28
36.40
35.14

shir77:carbon
RNAME 1
EXPNO 1
PROCNO 1
Date_ 20100528
Time_ 9.35
INSTRUM spect
PROBHD 5 mm EBBBI 1B7
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 201
DS 4
SWH 24038.461 Hz
FIDRES 0.365798 Hz
AQ 1.3631988 sec
RG 203
DN 20.800 usec
DE 5.50 usec
TE 294.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TDO 1

----- CHANNEL f1 -----
NUC1 ¹³C
P1 14.50 usec
PL1 -4.00 dB
PL1W 90.22689815 W
SE01 100.6228298 MHz

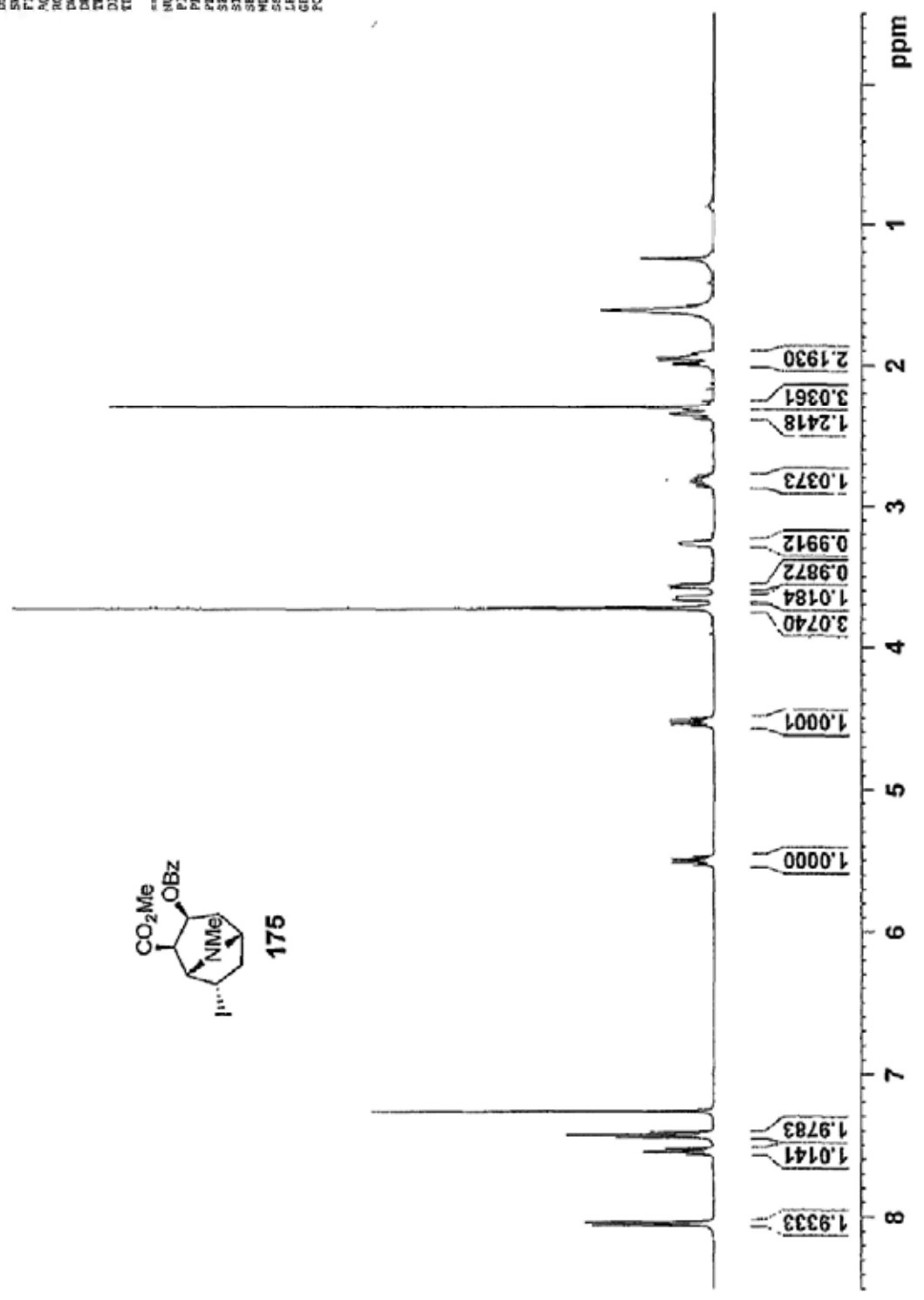
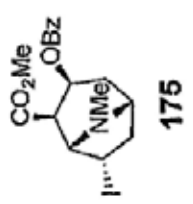
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CDPRG2 waltz16
NUC2 ¹H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 18.80 dB
PL13 18.80 dB
PL2W 13.17734718 W
PL12W 0.10960442 W
PL13W 0.10960442 W
SE02 400.1316005 MHz
SI 32768
SF 100.6127346 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



¹H NMR

8.0508, 8.0330, 8.0297, 7.5625, 7.5441, 7.5255, 7.4437, 7.4242, 7.4053, 7.2600

5.5308, 5.5155, 5.5009, 5.4864, 5.4711, 4.5597, 4.5444, 4.5299, 4.5154, 4.5002, 3.7282, 3.6628, 3.6598, 3.6472, 3.5827, 3.5753, 3.5681, 3.5607, 3.2752, 3.2670, 3.2586, 2.8645, 2.8466, 2.8352, 2.8287, 2.8175, 2.8110, 2.7996, 2.7816, 2.3855, 2.3785, 2.3559, 2.3488, 2.3263, 2.3193, 2.3005, 1.9979, 1.9832, 1.9620, 1.9472, 1.9240, 1.9188, 1.9102, 1.6144



NAME shr76
 EXPNO 2
 PROCNO 1
 Date_ 20100719
 Time_ 19.03
 INSTRUM spect
 PROBHD 5 mm PABBI 1H/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8223.685 Hz
 FIDRES 0.125483 Hz
 AQ 3.9946387 sec
 RG 203
 TM 60.800 usec
 DE 6.30 usec
 TE 294.6 K
 TD 1.00000000 sec
 TDO 1

CHANNEL f1
 NUC1 1H
 P1 7.10 usec
 PL1 -2.00 dB
 FWH 13.17734718 W
 SF01 400.1324710 MHz
 SI 32768
 SF 400.1300046 MHz
 EQ
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

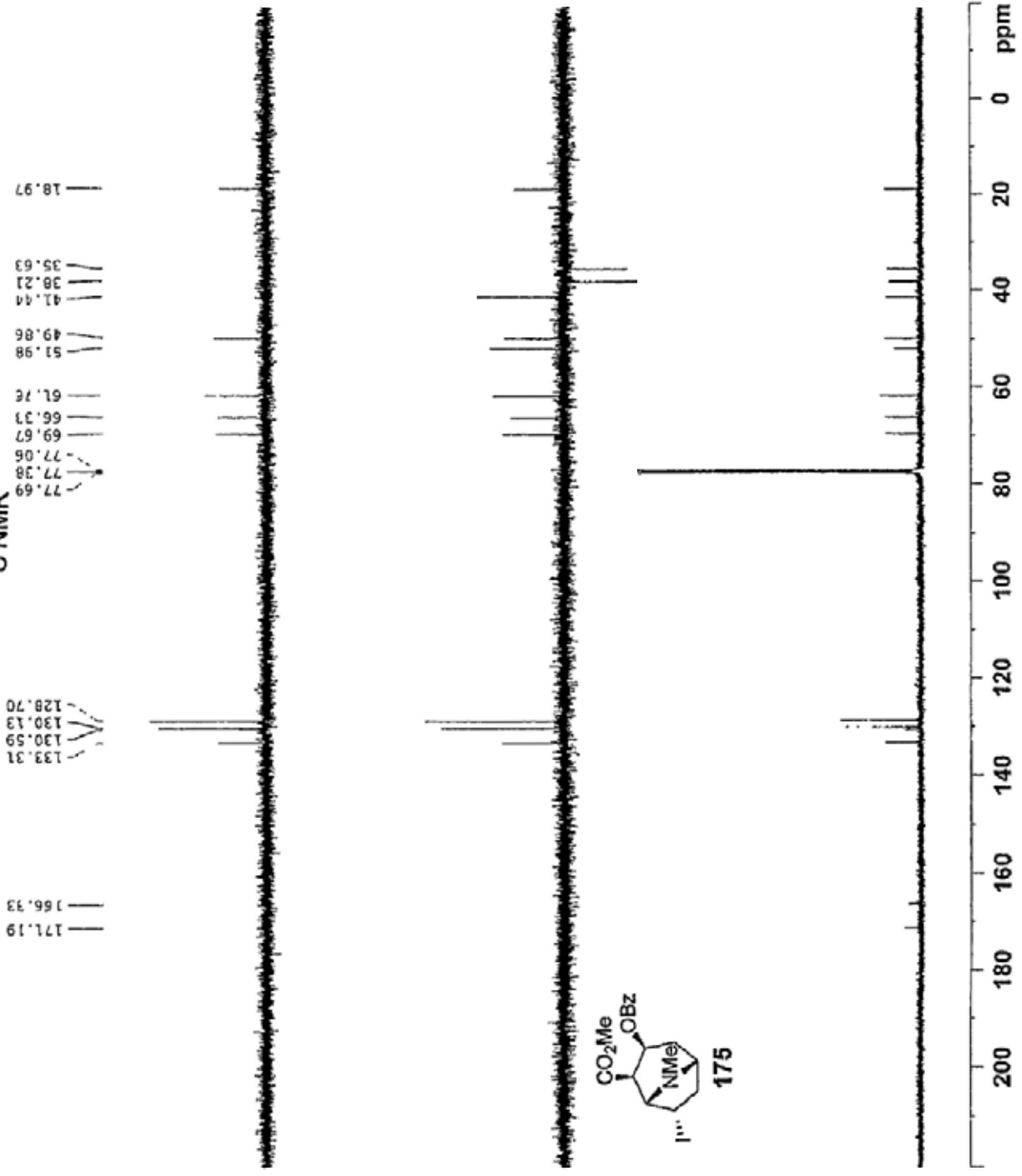
¹³C NMR

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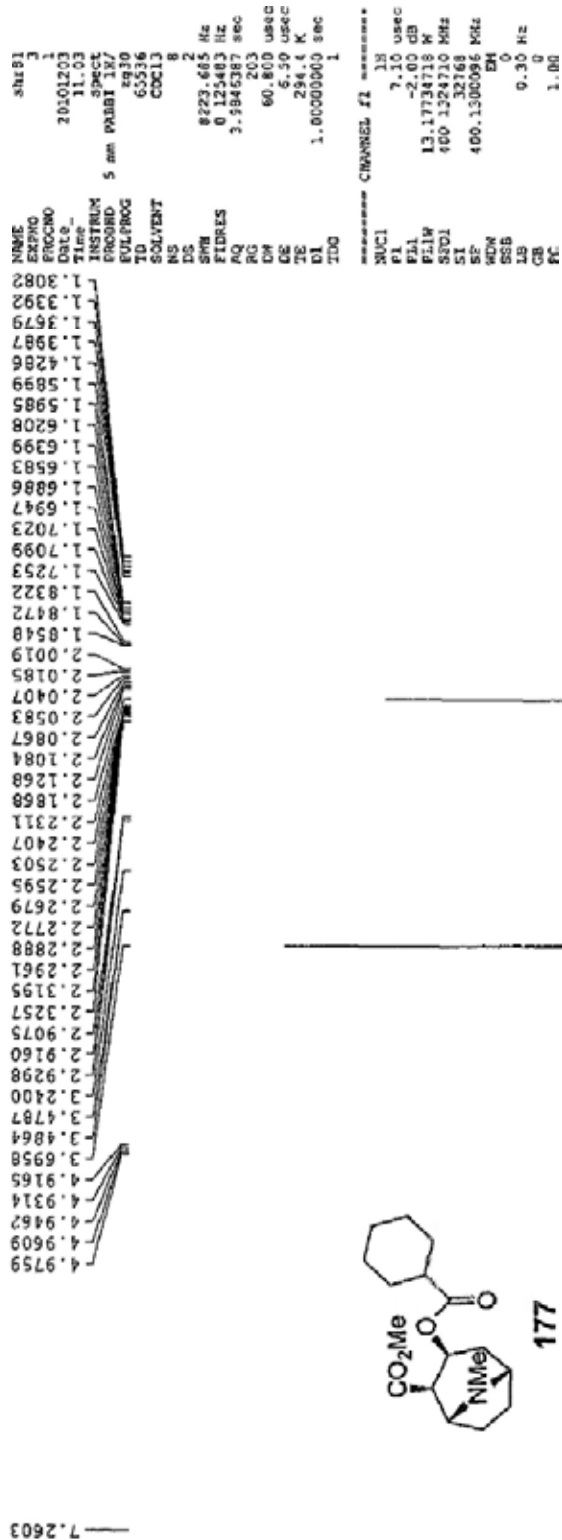
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Time_         11.18
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PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            348
DS            4
SWH           24038.461 Hz
FLORES        0.366798 Hz
AQ            1.3631988 sec
RG            203
DN            20.000 usec
DE            6.50 usec
TE            295.7 K
D1            2.0000000 sec
D11           0.0300000 sec
TDO           1

===== CHANNEL f1 =====
NUC1          13C
P1            9.68 usec
PL1          -0.60 dB
PL1W         41.24164963 MHz
SFO1         100.6228298 MHz

===== CHANNEL f2 =====
CPDPRG2      vbitz16
NUC2          1H
PCPD2        90.00 usec
PL2          0.00 dB
PL12         15.56 dB
PL13         15.22 dB
PL1W         8.21434441 MHz
PL1W         0.22585411 MHz
PL13W        0.1272963 MHz
SFO2         400.1316005 MHz
SI           327.66
SF           100.6127338 MHz
WDW          EM
SSB          0
LB           1.00 Hz
GB           0
PC           1.40
  
```



¹H NMR



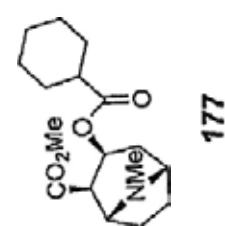
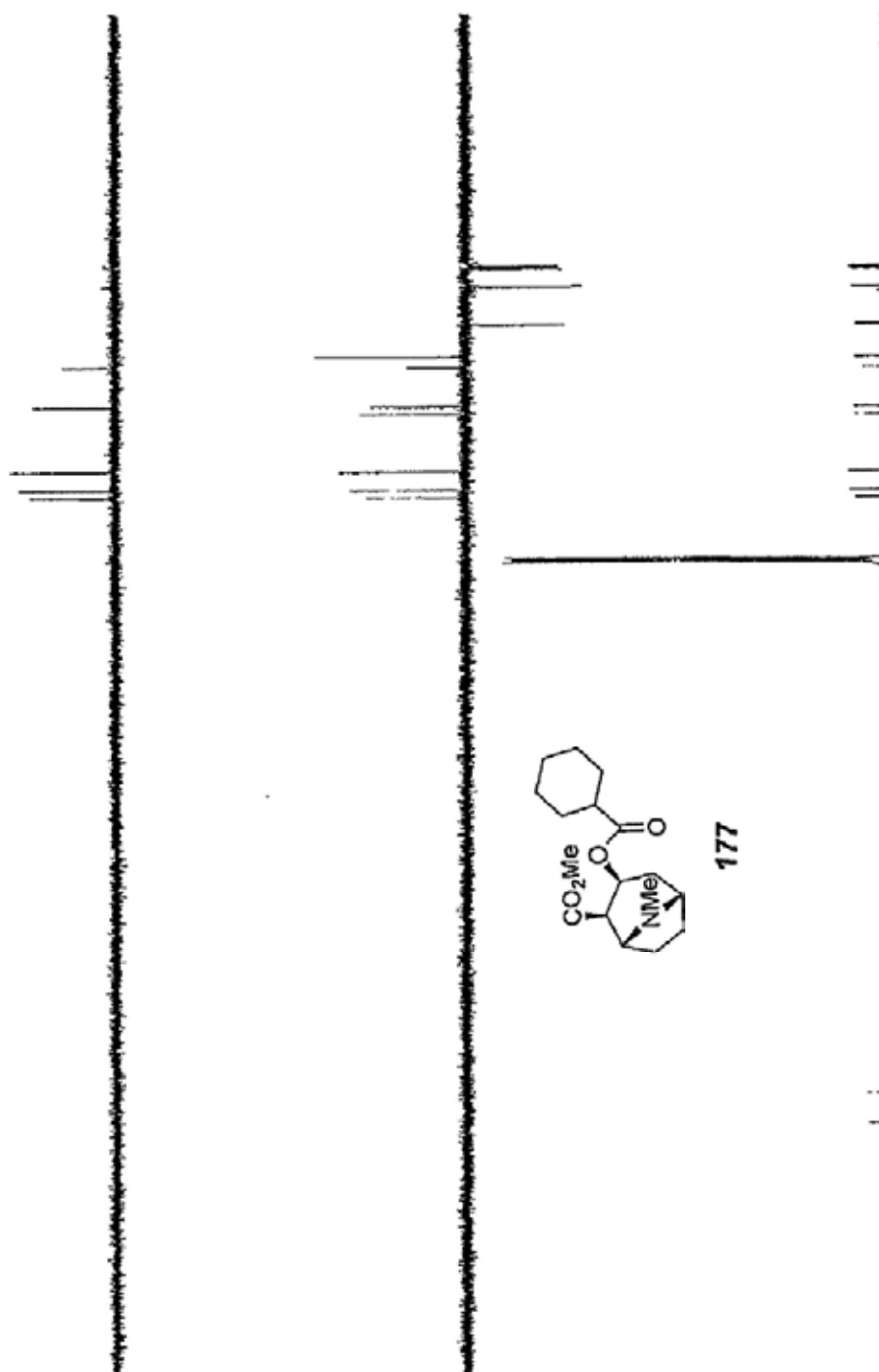
¹³C NMR

176.37
171.17
77.70
77.38
77.06
66.41
65.12
61.90
51.73
50.39
43.08
41.48
35.72
29.03
29.13
26.09
25.81
25.75
25.66
25.52

NAME SHELDCARBON J
EXPNO 1
PROCNO 1
Date_ 20101203
Time 22.48
INSTRUM spect
PROBHD 5 mm PABUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 7000
DS 4
SWH 24338.461 Hz
FIDRES 0.266798 Hz
AQ 1.3631988 sec
RG 203
CW 20.800 usec
DE 4.50 usec
TE 293.2 K
D1 2.0000000 sec
D11 0.0500000 sec
TD0 1

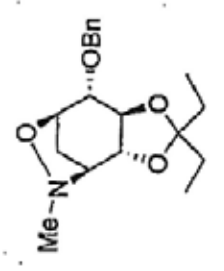
***** CHANNEL f1 *****
NUC1 13C
P1 9.68 usec
PL1 -0.60 dB
PL12 41.71164983 %
SFO1 100.628258 MHz

***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 15.66 dB
PL13 15.92 dB
PL28 8.31476441 W
PL12W 0.22585411 W
PL13W 0.21272963 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127331 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

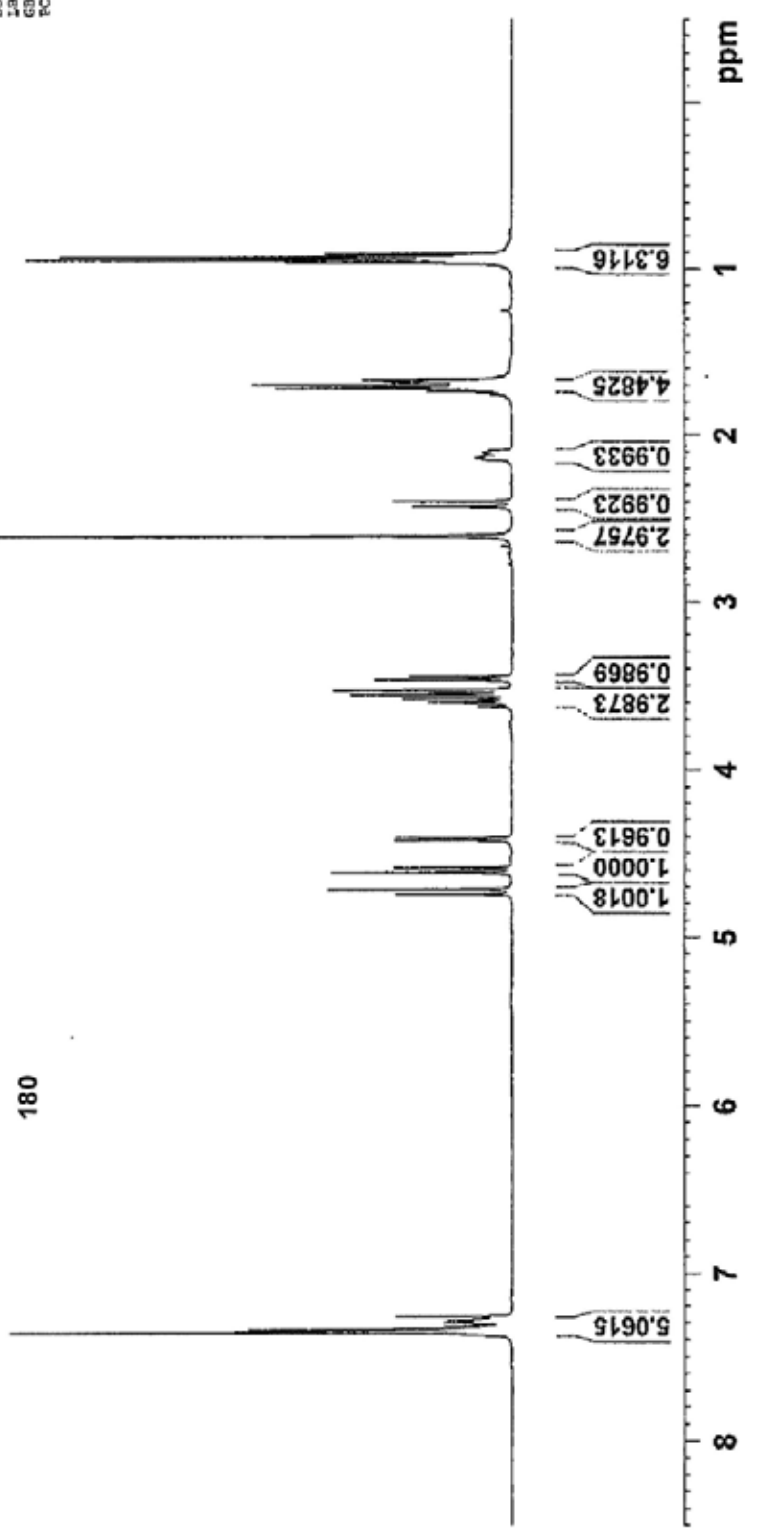


¹H NMR

7.3690
7.3546
7.3492
7.3389
7.3244
7.3190
7.3018
7.2958
7.2889
7.2802
7.2708
7.2598
4.7455
4.7164
4.6179
4.5888
4.4270
4.4129
3.6264
3.6012
3.5809
3.5568
3.5364
3.5304
3.4691
3.4491
2.6092
2.4325
2.3999
2.3512
2.1383
2.1288
2.1188
2.1061
2.0962
1.7566
1.7388
1.7207
1.7019
1.6893
1.6830
1.6723
1.6541
0.9684
0.9499
0.9353
0.9166



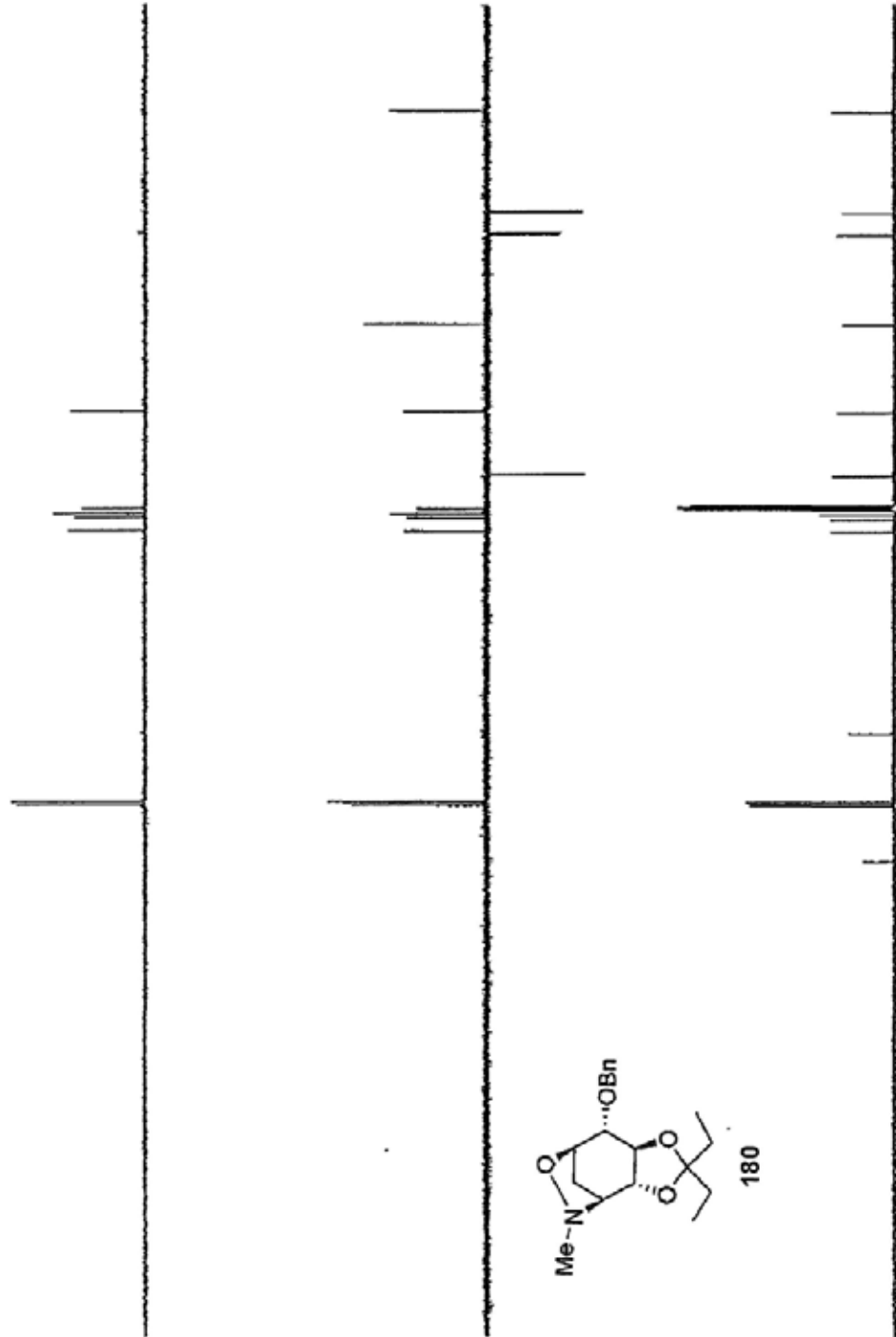
180



NAME shwa36
EXPNO 2
PROCNO 1
Date_ 20100706
Time 15.57
INSTRUM spect
PROBHD 5 mm PAUCL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 4
DS 2
SWH 8223.685 Hz
FIDRES 0.175483 Hz
AQ 3.9846317 sec
RG 214
CW 60.810 usec
CZ 8.35 usec
TE 284.7 K
DE 1.00000000 sec
TDO 1
===== CHANNEL f1 =====
NUC1 1H
P1 24.83 usec
PL1 0.00 dB
PC1W 8.31434441 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300048 MHz
WDW EM
SSB 0
GB 0
PC 1.00

¹³C NMR

136.22
128.75
128.22
128.09
116.39
81.53
79.33
78.64
77.70
77.38
77.06
71.87
60.90
45.74
30.15
29.91
26.20
8.74
8.63

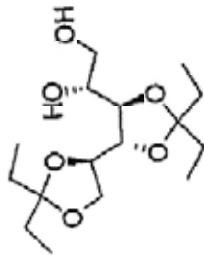


NAME sha36catbot
EXPNO 1
PROCNO 1
Date_ 20100706
Time 16.04
INSTRUM spect
PROBHD 5 mm PABUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 187
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DN 20.800 USEC
DE 6.50 USEC
TE 295.4 K
D1 2.0000000 sec
D11 0.0300000 sec
TDO 1

----- CHANNEL f1 -----
NUC1 13C
P1 9.68 usec
PL1 -0.60 dB
PL1W 41.24164963 W
SFO1 100.628288 MHz

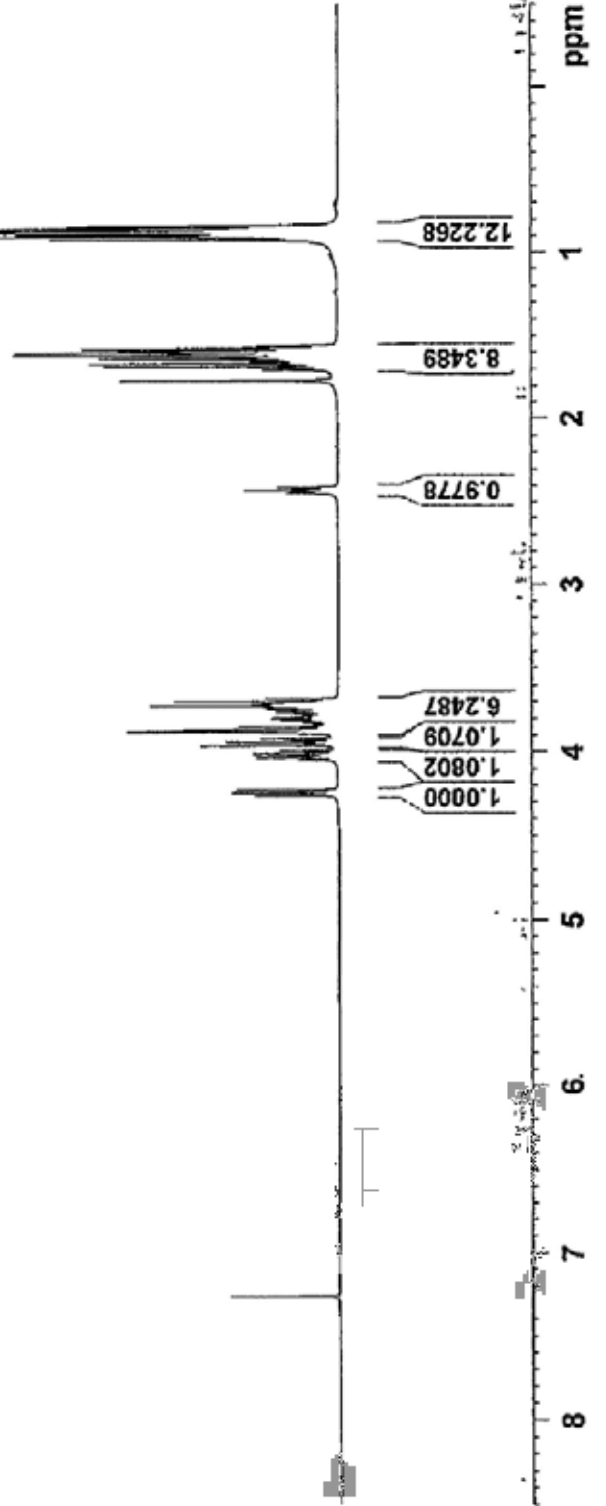
----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 13C
PCPD2 90.00 usec
PL2 0.00 dB
PL12 15.66 dB
PL13 15.52 dB
PL2W 6.31434441 W
PL12W 0.22585411 W
PL13W 0.21272963 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127346 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

¹H NMR



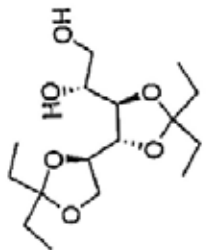
182

NAME shw29
EXRNO 1
PROCNO 20100501
Date_ 13-45
Time_ 13-45
INSTRUM spect
PROBHD 5 mm EASY 1H/1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 4
DS 7
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 36
WDW 60.600 usec
DE 6.50 usec
TE 294.7 K
D1 1.0000000 sec
TD0 1
----- CHANNEL f1 -----
NUC1 1H
P1 7.10 usec
PL1 -2.00 dB
PL1W 13.17734718 W
SFO1 400.132410 MHz
SI 32768
SF 400.1300053 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



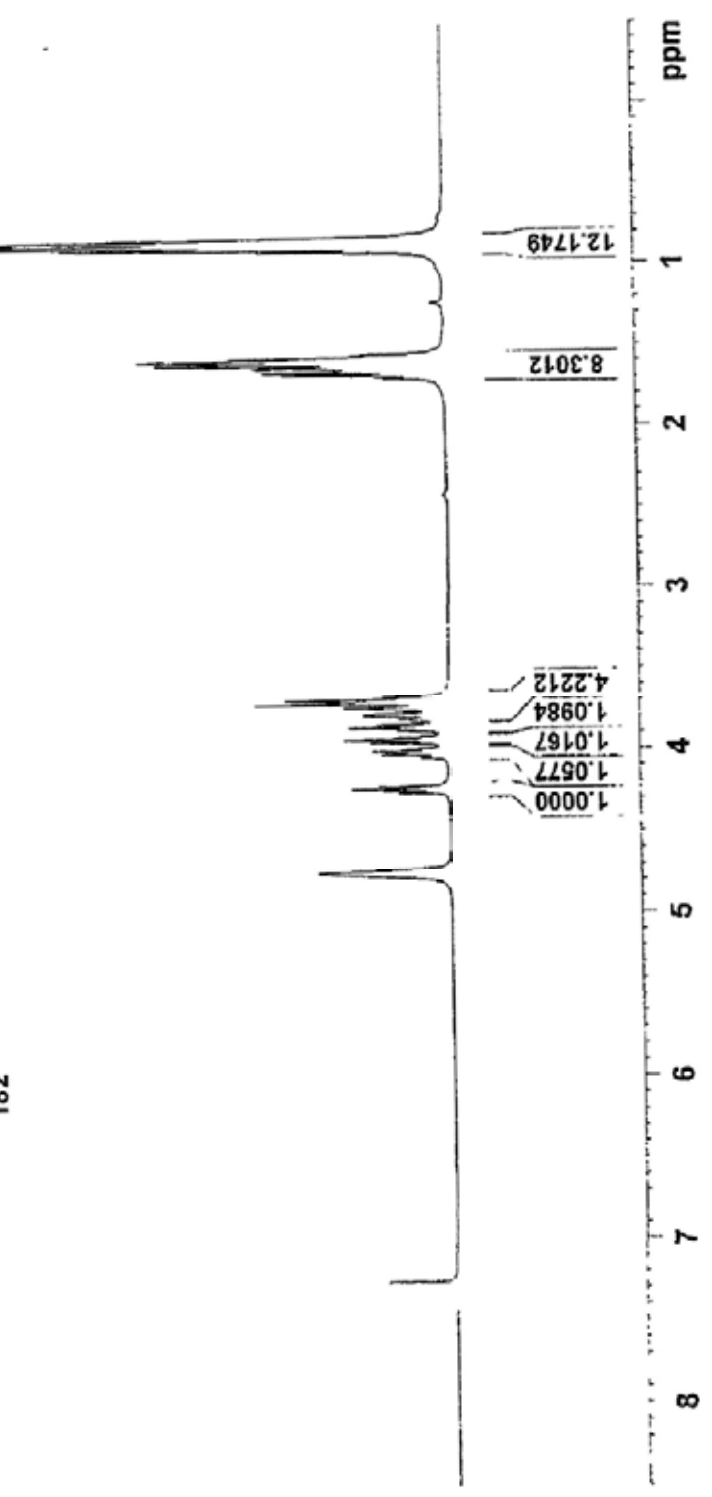
¹H NMR (Solvent: CDCl₃-D₂O)

7.2603
 4.7550
 4.2674
 4.2632
 4.2473
 4.2311
 4.2271
 4.0490
 4.0325
 4.0160
 3.9998
 3.9650
 3.9607
 3.9441
 3.9275
 3.9234
 3.8849
 3.8697
 3.8505
 3.8210
 3.8151
 3.7928
 3.7869
 3.7561
 3.7489
 3.7215
 3.7009
 3.6822
 1.7076
 1.6890
 1.6703
 1.6519
 1.6414
 1.6378
 1.6183
 1.6030
 1.5930
 1.5848
 1.5807
 1.5666
 0.9226
 0.9264
 0.9079
 0.9035
 0.9001
 0.8951
 0.8910
 0.8768
 0.8624
 0.8484
 0.8439
 0.8439



sha2382c
 2
 20100904
 1317
 5 mm PAB3B1K7
 65316
 CDCl₃
 4
 2
 4223.685 Hz
 0.125483 Hz
 3.9846387 sec
 71.8
 60.800 usec
 6.30 usec
 294.4 K
 1.00000000 sec
 1

===== CHANNEL f1 =====
 NUCL1 1H
 P1 7.10 usec
 PL -2.00 dB
 F1LW 13.17784718 M
 SFOL 400.1324110 MHz
 SI 32768
 CF 400.1300058 MHz
 CH 0
 SSB 0 30 Kz
 LA 0
 GB 0
 PC 1.00



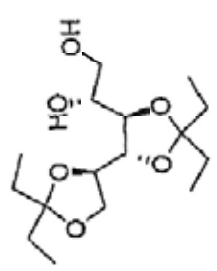
¹³C NMR

133.12
 134.88
 82.04
 81.86
 77.70
 77.38
 77.06
 76.81
 72.58
 69.21
 64.45
 30.67
 30.51
 29.64
 29.05
 8.49
 8.35
 8.29

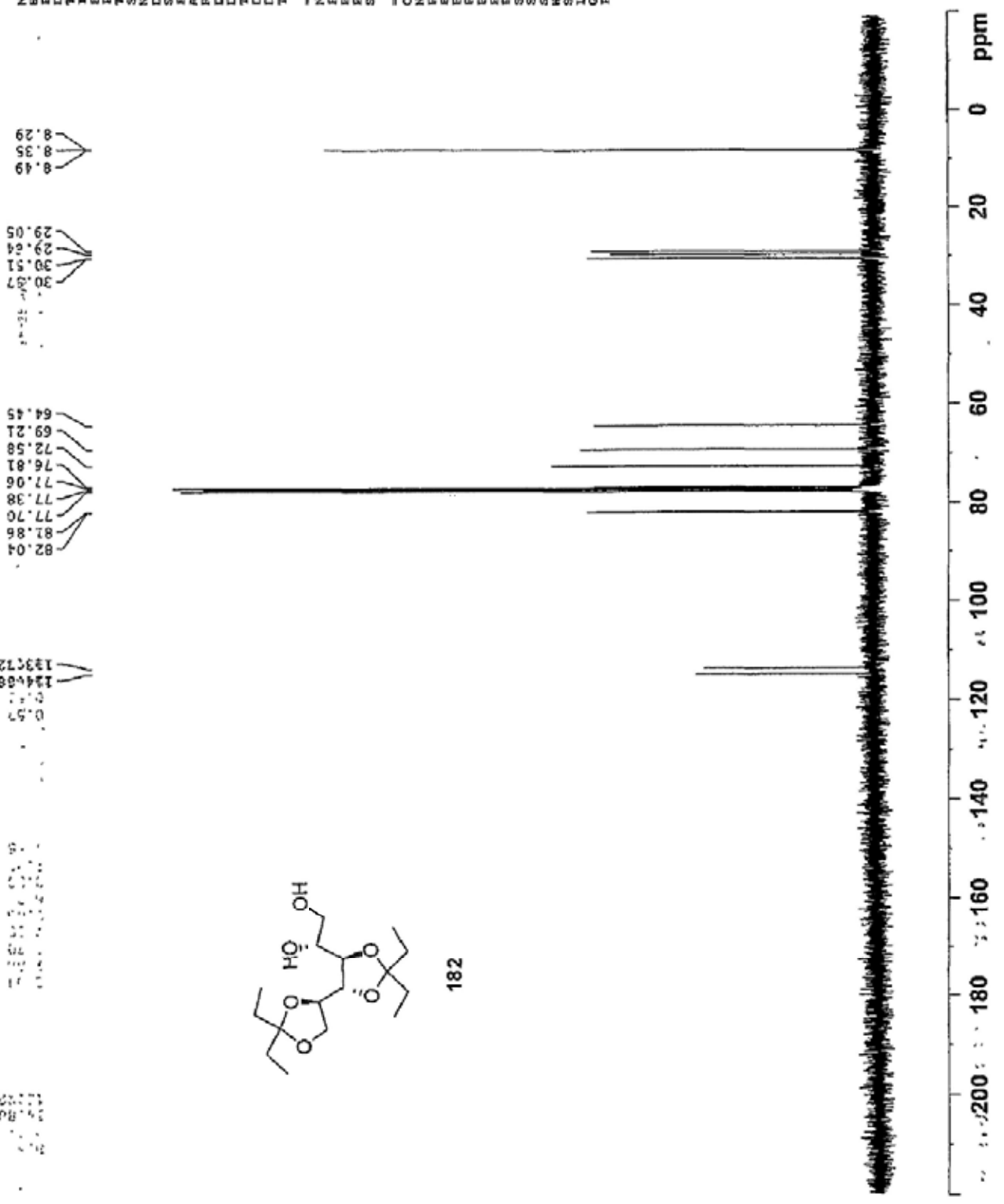
NAME sha2carbon
 EXPNO 1
 PROCNO 1
 Date_ 20100301
 Time 13.51
 INSTRUM spect
 PROBHD 5 mm PABBI JN/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 178
 DS 4
 SWH 24038.461 Hz
 FIDRES 0.365798 Hz
 AQ 1.3631988 sec
 RG 203
 DW 20.800 usec
 DE 6.50 usec
 TE 295.0 K
 D1 2.0000000 sec
 D11 3.0300000 sec
 TDO 1

CHANNEL f1 13C
 NUC1 13C
 P1 14.50 usec
 PL -4.00 dB
 FLLW 90.2269819 MHz
 SFO1 100.6228298 MHz

CHANNEL f2 1H
 NUC2 1H
 P2 80.00 usec
 PL -2.00 dB
 FLL2 18.80 dB
 FLL3 18.80 dB
 EL2W 13.17734718 MHz
 FLLW 0.10950442 MHz
 FLL3W 0.10950442 MHz
 SFO2 400.1316005 MHz
 SI 32168
 SF 100.6127338 MHz
 HF 0
 HZ 3.00 Hz
 CB 0
 PC 1.40

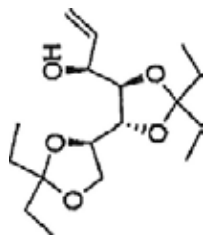


182



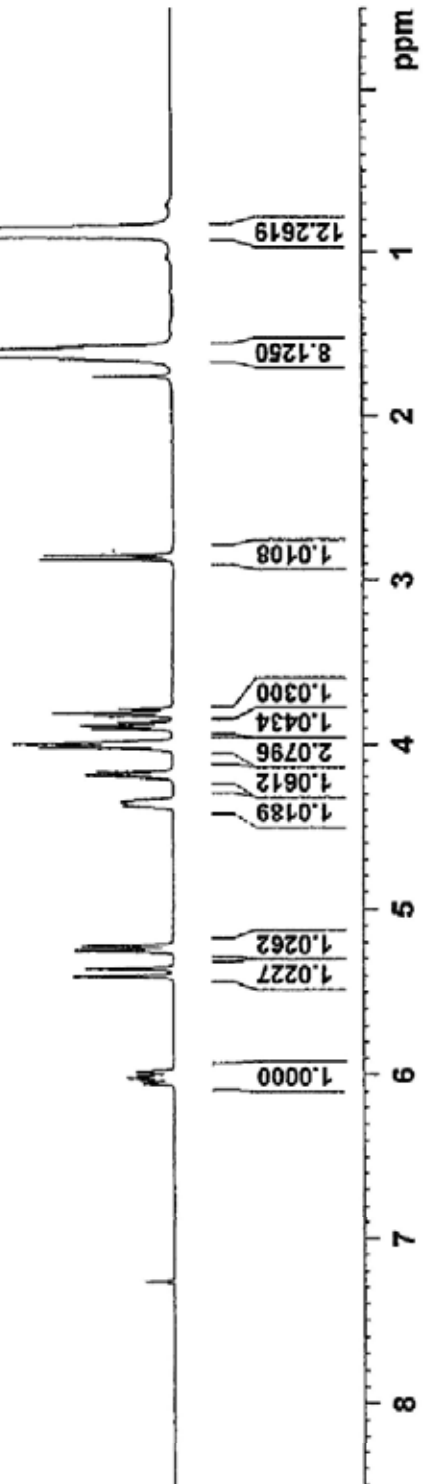
¹H NMR

7.2602
 6.0555
 6.0441
 6.0289
 6.0169
 6.0130
 6.0010
 5.9857
 5.9743
 5.4011
 5.3579
 5.2479
 5.2213
 4.3696
 4.3614
 4.3568
 4.3484
 4.2013
 4.1853
 4.1811
 4.1650
 4.0302
 4.0144
 4.0087
 3.9941
 3.9779
 3.9053
 3.8850
 3.8684
 3.8252
 3.8046
 3.7840
 2.8751
 2.8505
 1.7613
 1.6543
 1.6357
 1.6307
 1.6244
 1.6122
 1.5934
 1.5748
 0.9008
 0.8854
 0.8826
 0.8643
 0.8490
 0.8461



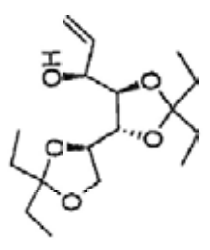
184

NAME: ahead
 EXPNO: 1
 PROCNO: 1
 Date_: 20100609
 Time: 11.36
 INSTRUM: spect
 PROBHD: 5 mm WBXBI 1H/
 PULPROG: zgpg30
 TD: 65536
 SOLVENT: CDCl3
 NS: 4
 DS: 2
 SWH: 8123.081 Hz
 FIDRES: 0.1225881 Hz
 AQ: 3.3846381 sec
 RG: 22.6
 DR: 60.000 usec
 DE: 8.13 usec
 TE: 294.3 K
 D1: 1.00000000 sec
 D2: 1
 ===== CHANNEL f1 =====
 NUC1: 13C
 P1: 1.10 usec
 PL1: -2.00 dB
 FLLW: 13.37734718 Hz
 SFO1: 400.1324710 MHz
 SI: 32768
 SF: 400.1300061 MHz
 MDW: EX
 SSB: 0
 LB: 0.30 Hz
 GB: 0
 PC: 1.00



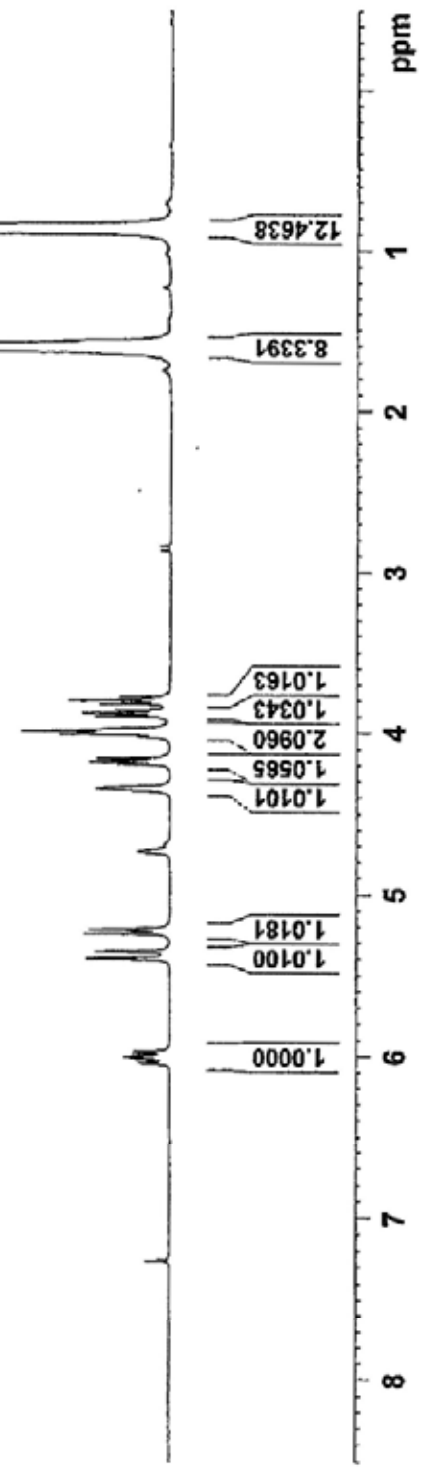
¹H NMR (Solvent: CDCl₃-D₂O)

7.2602
6.0510
6.0395
6.0245
6.0128
6.0086
5.9963
5.9813
5.9698
5.983
5.9945
5.9551
5.9513
5.9445
5.9408
5.9180
5.9143
4.7366
4.3452
4.1982
4.1825
4.1779
4.1618
4.0286
4.0109
4.0034
3.9988
3.9914
3.9833
3.9019
3.8855
3.8815
3.8650
3.8235
3.8030
3.7825
1.6531
1.6416
1.6348
1.6302
1.6238
1.6116
1.6074
1.5930
1.5887
1.5745
1.5703
0.9026
0.8991
0.8839
0.8808
0.8663
0.8631
0.8496
0.8448



NAME ehaj30d5
EXPNO 1
PROCNO 1
F2 - 2010091
F3 - 18.21
INSTRUM spect
PROBHD 5 mm PABBO-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 4
DS 2
SWH 8223.685 Kz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 25.4
WE 60.800 usec
DE 6.50 usec
TE 297.5 K
D1 1.0000000 sec
TDO 1

***** CHANNEL f1 *****
NUC1 1H
P1 14.00 usec
PL -1.00 dB
FLLF 23.56637059 Kz
STOL 400.192713 MHz
RF 400.1900151 MHz
K1 0
K2 0
SSB 0.30 Hz
LB 0
GB 0
PC 1.00



¹³C NMR

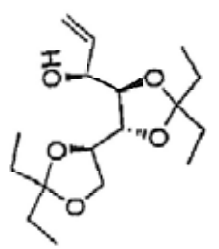
137.77

116.09
114.36
113.38

83.27
78.01
77.69
77.38
77.31
77.06
71.14
69.07

30.53
30.50
29.83
29.10

8.51
8.44
8.40
8.36



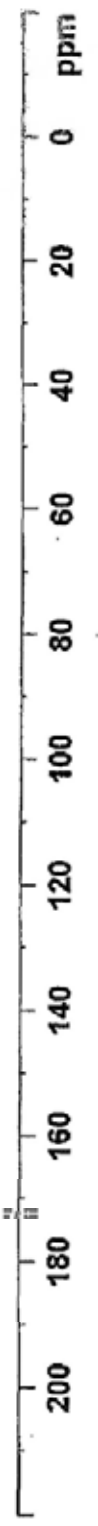
184

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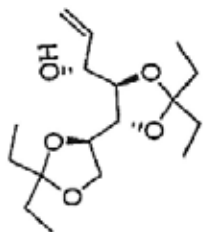
NAME          sha30c.zbon
EXPNO         1
PROCNO        1
Date_         20100609
Time          11.44
INSTRUM       spect
PROBHD        5 mm PROBI JH/
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            104
DS            4
SH            24038.461 Hz
FIDRES        0.266788 Hz
AQ            1.5631588 sec
RG            703
DM            20.800 usec
DE            8.50 usec
TE            284.6 K
D1            2.0000000 sec
D11           0.0300000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          13C
P1            14.50 usec
PL1           -1.00 dB
PL1W          90.2268815 W
SFO1          100.6228298 MHz

===== CHANNEL f2 =====
CDEPRG2       waltz16
NUC2          1H
PCPD2         80.00 usec
PL2           -2.00 dB
PL2W          18.80 dB
PL13          18.80 dB
PL1W          18.80 dB
PL2W          13.17734728 W
PL12W         0.10960442 W
PL13W         0.10960442 W
SFO2          400.1315005 MHz
SI            32769
SF            100.6127345 MHz
EM            0
NDW           1.00 Hz
SSB           0
LB            0
GB            0
PC            1.40
    
```



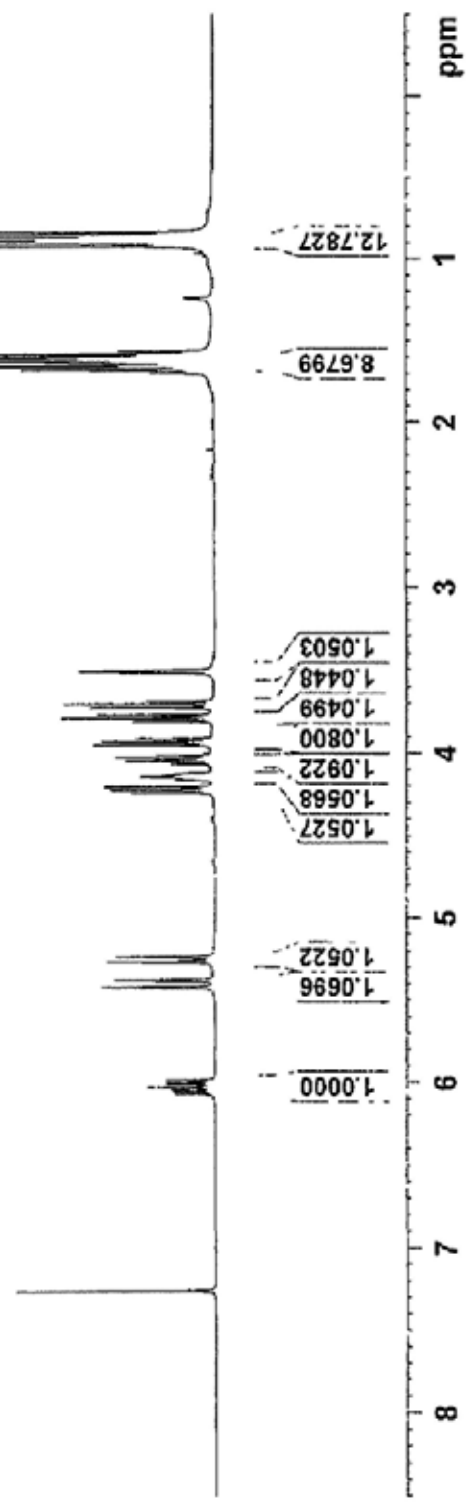
¹H NMR



185

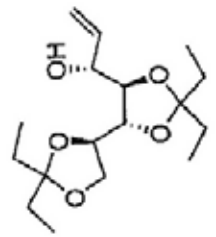
NAME shw31
EXPNO 2
PROCNO 1
Date_ 20100812
Time 11 02
INSTRUM spect
PROBHD 5 mm EMEB1 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
OS 0223.625 Hz
SMH 0.125483 Hz
FIDRES 3.5846387 sec
RG 80.6
DM 60.800 usec
DC 6.50 usec
TE 294.2 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 7.10 usec
PL -2.00 dB
F2V 13.17734718 W
SFO1 400.1324110 MHz
SI 32768
SF 400.1300043 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

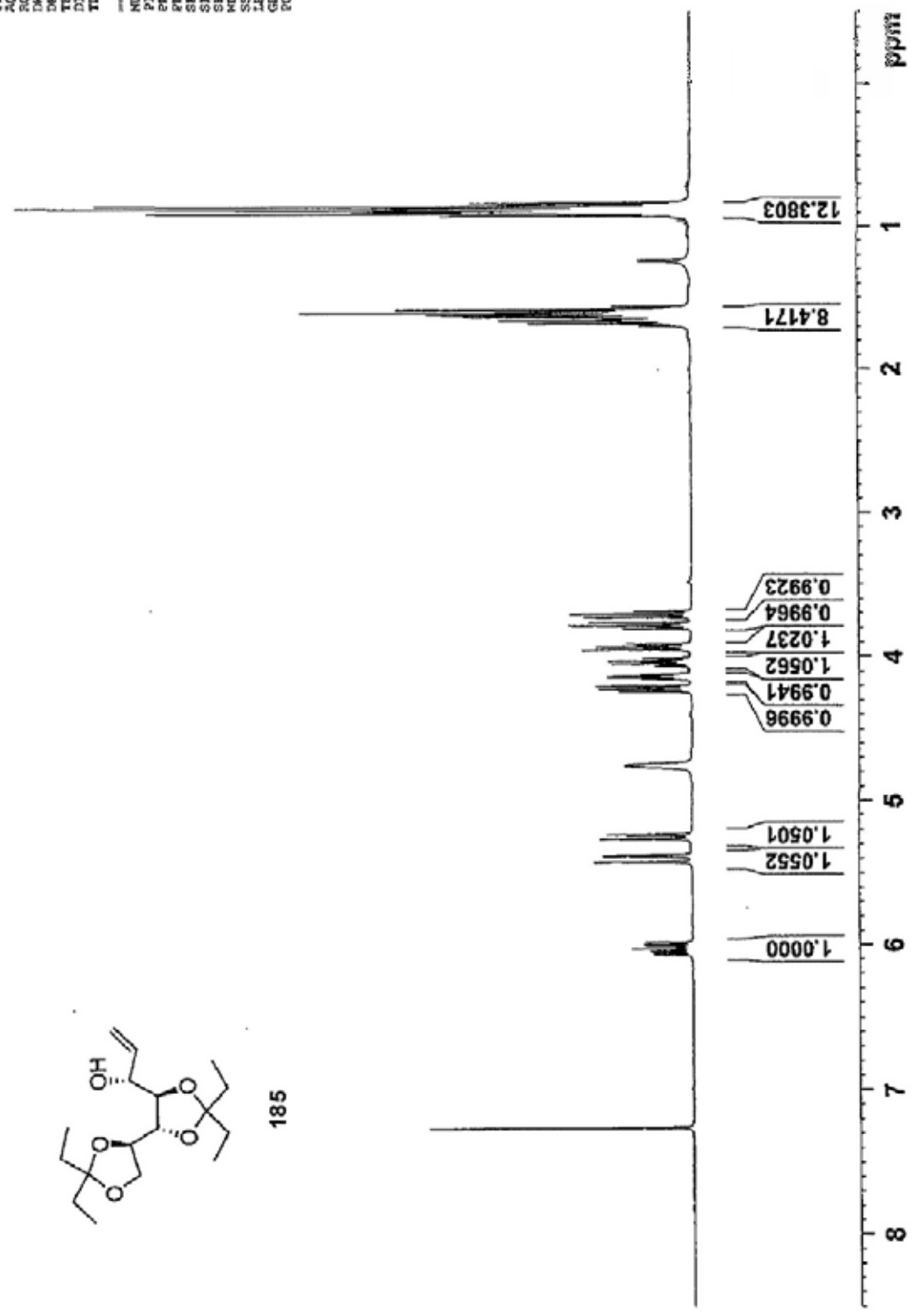


¹H NMR (Solvent: CDCl₃-D₂O)

7.2599
6.0699
6.0555
6.0437
6.0291
6.0271
6.0124
6.0006
5.9862
5.9274
5.4235
5.4196
5.3843
5.3804
5.3764
5.2674
5.2638
5.2599
5.2411
5.2375
5.2337
4.7554
4.2443
4.2288
4.2233
4.2077
4.1577
4.1433
4.1404
4.1290
4.1260
4.0690
4.0529
4.0480
4.0370
4.0320
4.0162
3.9552
3.9388
3.9342
3.9178
3.8097
3.7906
3.7731
3.7304
3.7100
3.6900
1.7060
1.6871
1.6678
1.6615
1.6488
1.6423
1.6298
1.6236
1.6109
1.6055
1.5922
1.5738
0.9316
0.9130
0.9069
0.9021
0.8941
0.8883
0.8835
0.8694
0.8694
0.8629
0.8440



NS SOLVENT CDCl₃
 TD 5 mm PABDO B8
 FT/PROG 293C
 Date 20100914
 Time 18.22
 INSTRUM spect
 NS 2
 DS 8223.655 Hz
 FIDRES 0.123487 Hz
 AQ 3.384838 sec
 RG 96.5
 DM 60.800 usec
 DE 9.50 usec
 XT 2.977.7 X
 DI 1.00000000 sec
 TDO 1
 CHANNEL F1
 NUC1 ¹H
 P1 14.00 usec
 PL 14.00 dB
 FLL 13.5667100 MHz
 SFO1 400.1524713 MHz
 SI 327.68
 SF 400.150000000 MHz
 ED 252
 CB 0.30 Hz
 GB 0
 PC 1.00



¹³C NMR

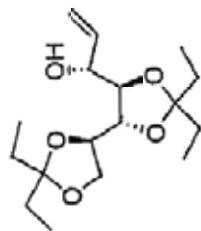
137.27

116.95
118.66
113.59

84.15
81.73
77.70
77.38
77.06
76.94
73.77

30.60
30.56
29.73
29.10

8.50
8.40
8.32



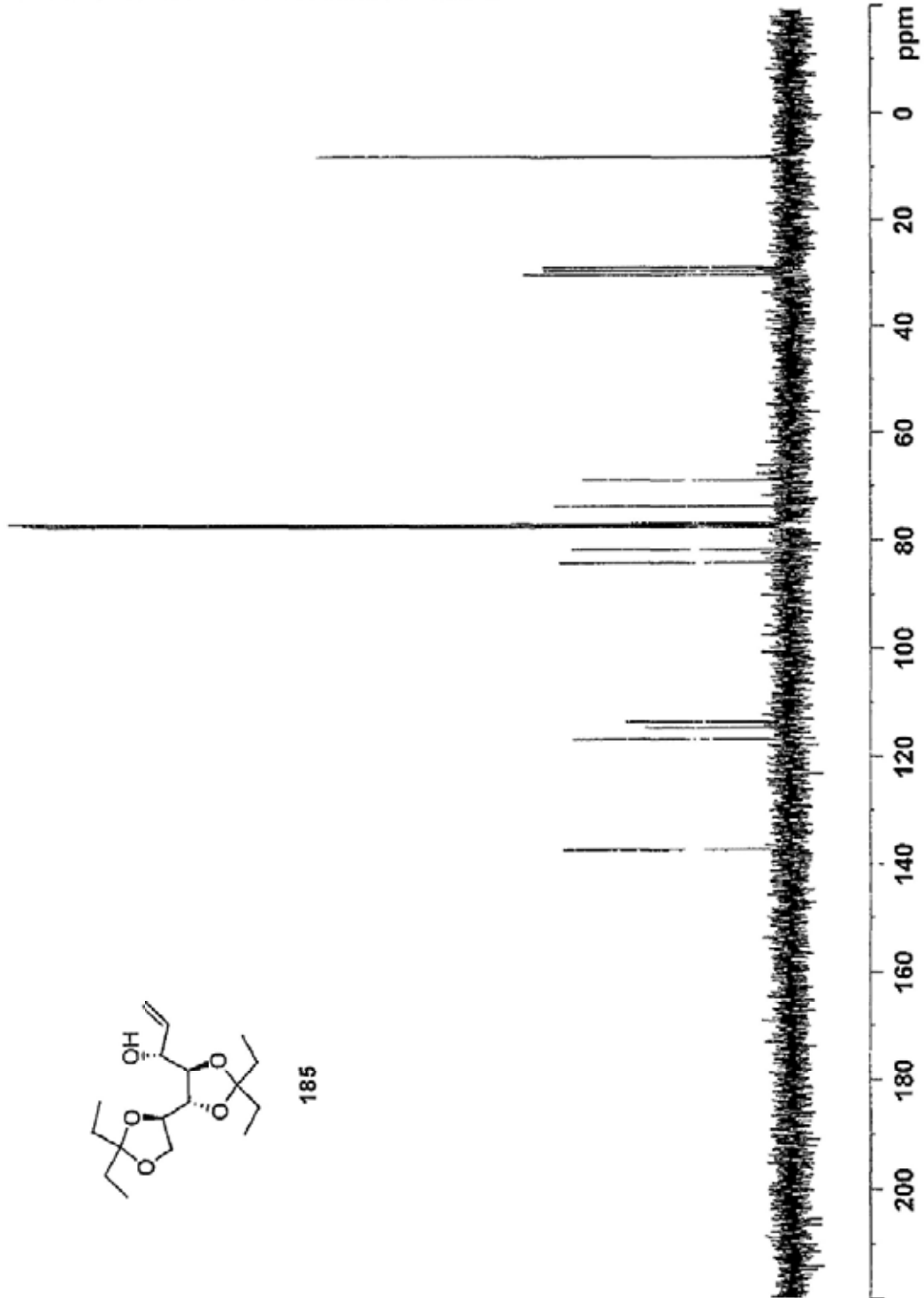
185

```

NAME shallicarben
EXPNO 1
PROCNO 1
Date_ 20100715
Time 11.40
INSTRUM spect
PROBHD 5 mm ZABD1 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 303
EN 20.000 usec
TE 29.50 K
D1 2.0000000 sec
D11 0.03000000 sec
T00 1

===== CHANNEL F1 =====
NUC1 13C
P1 14.50 usec
PL1 -4.00 dB
PL1W 90.2769919 W
SFO1 100.628298 MHz

===== CHANNEL F2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL2W 18.80 dB
PL3 18.80 dB
PL3W 18.80 dB
PL4W 13.1772418 W
PL5W 0.10569442 W
PL6W 0.10569442 W
SFO2 400.136005 MHz
SI 32
SF 100.6127331 MHz
WDW 8K
SSB 0
LB 1.00 Hz
GB 0
EC 1.40
    
```



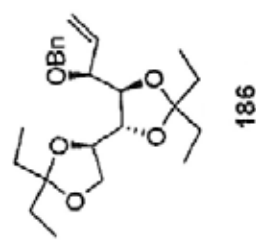
¹³C NMR

113.77
119.44
127.70
127.84
128.57
135.97
138.83

68.25
70.69
77.06
77.38
77.64
77.69
77.78
80.45
83.13

30.53
30.37
29.96
29.29

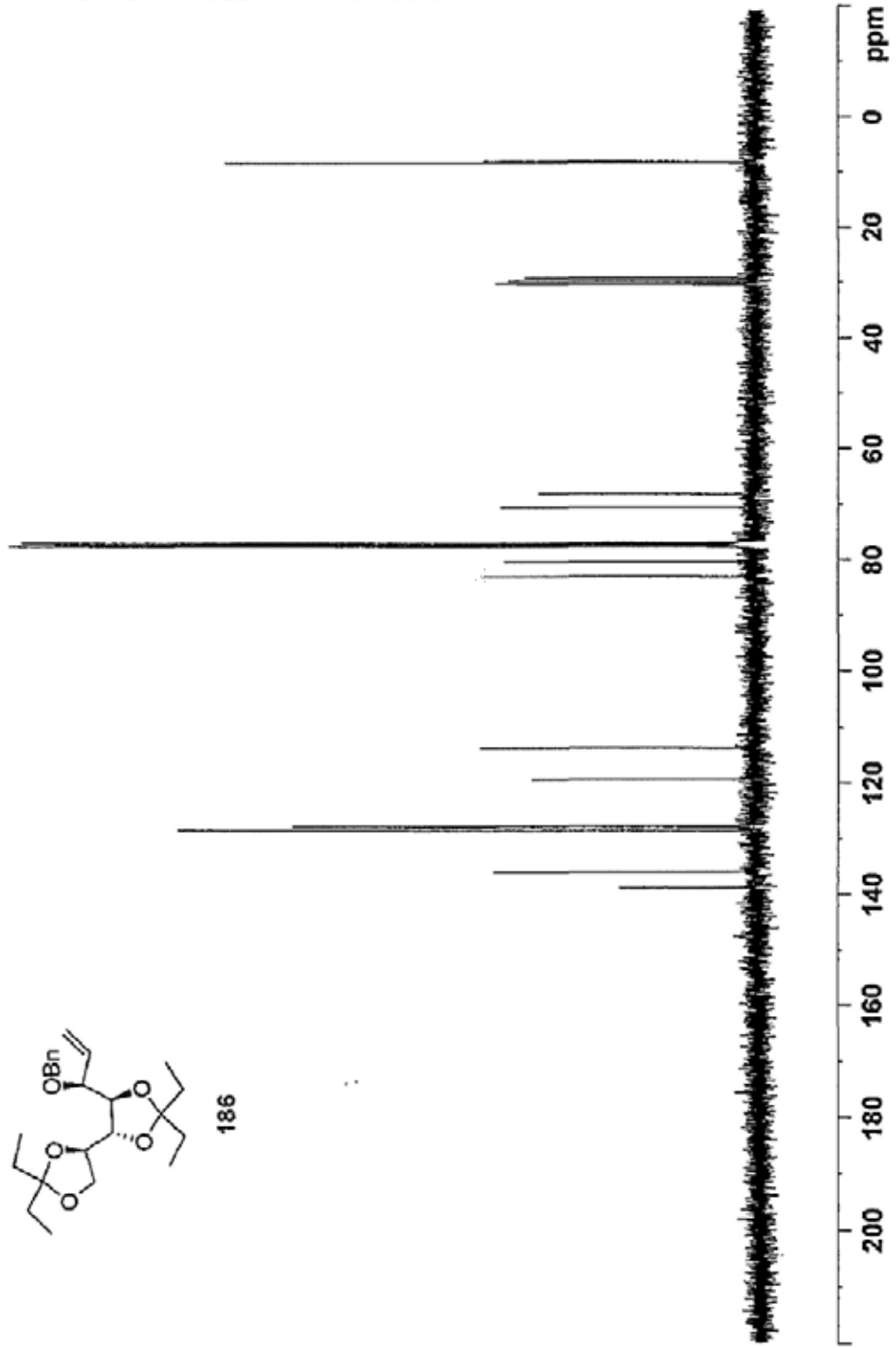
8.94
8.51
8.29



NAME etha32carbon
EXPNO 1
PROCNO 1
F2 - 20100623
Time 19.53
INSTRUM spect
PROBHD 5 mm PABBE 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 186
DS 4
SWH 24039.461 Hz
FIDRES 0.366796 Hz
AQ 1.3631986 sec
RG 203
DM 20.000 usec
DE 6.50 usec
TE 294.7 K
D1 2.0000000 sec
D11 0.0300000 sec
TEO 1

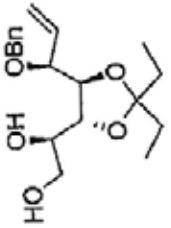
===== CHANNEL f1 =====
NUC1 ¹³C
P1 14.50 usec
PL1 -4.00 dB
PL1W 90.2269815 W
SFO1 100.628256 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 ¹H
PCPD2 90.00 usec
PL2 -2.00 dB
PL3 18.80 dB
PL12 18.80 dB
PL13 18.80 dB
PL1W 13.17734718 W
PL1M 0.10950442 W
PL1W 0.10950442 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127338 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

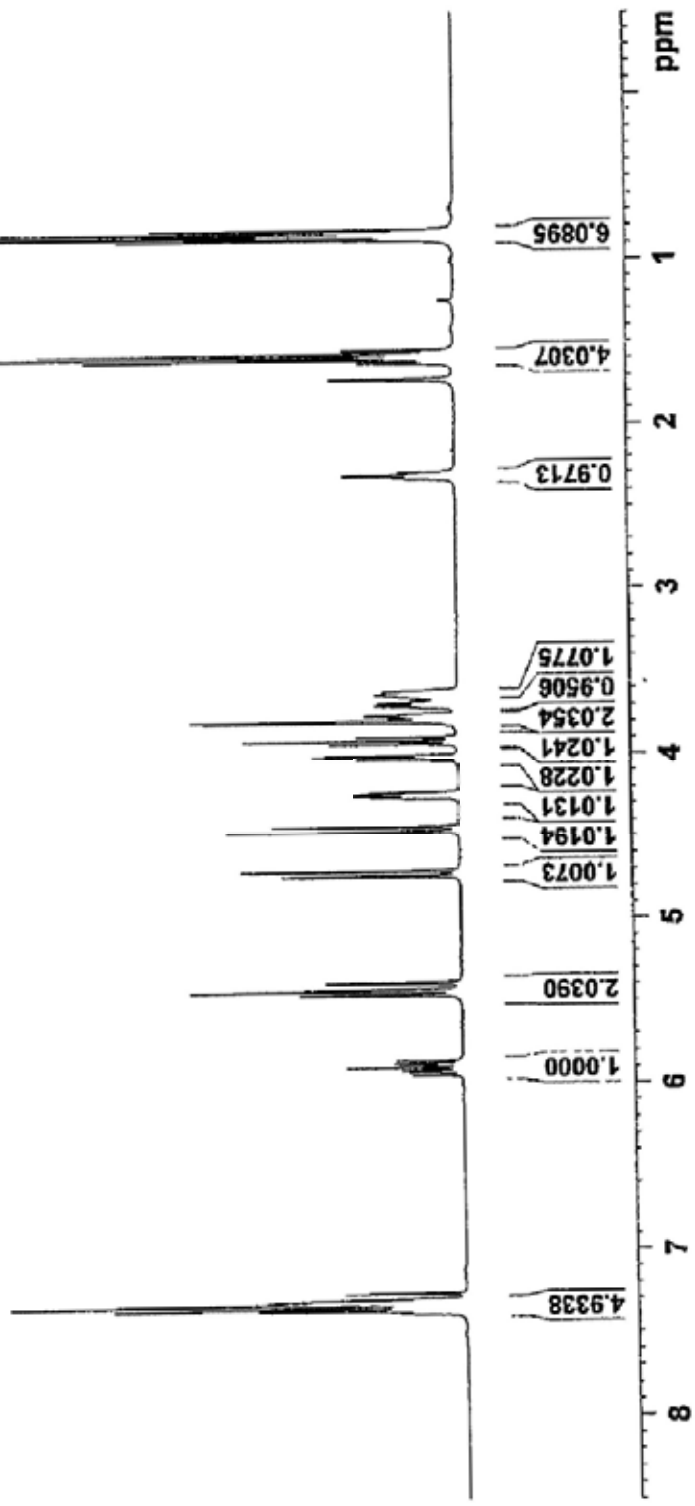


¹H NMR

7.3780
7.3574
7.3430
7.3199
7.3103
7.3015
7.2598
5.9462
5.9288
5.9197
5.9027
5.8857
5.8766
5.8592
5.4610
5.4323
5.3882
4.7385
4.7095
4.4686
4.4395
4.2623
4.2518
4.2457
4.2349
4.0337
4.0234
4.0133
4.0030
3.9342
3.9144
3.8943
3.8003
3.7957
3.7766
3.7644
3.7531
3.7148
3.7016
3.6871
3.6745
3.6589
3.6506
3.6326
3.6226
2.3313
2.3164
2.3010
1.7291
1.6284
1.6100
1.5916
1.5732
1.5548
0.8850
0.8661
0.8452
0.8262



187

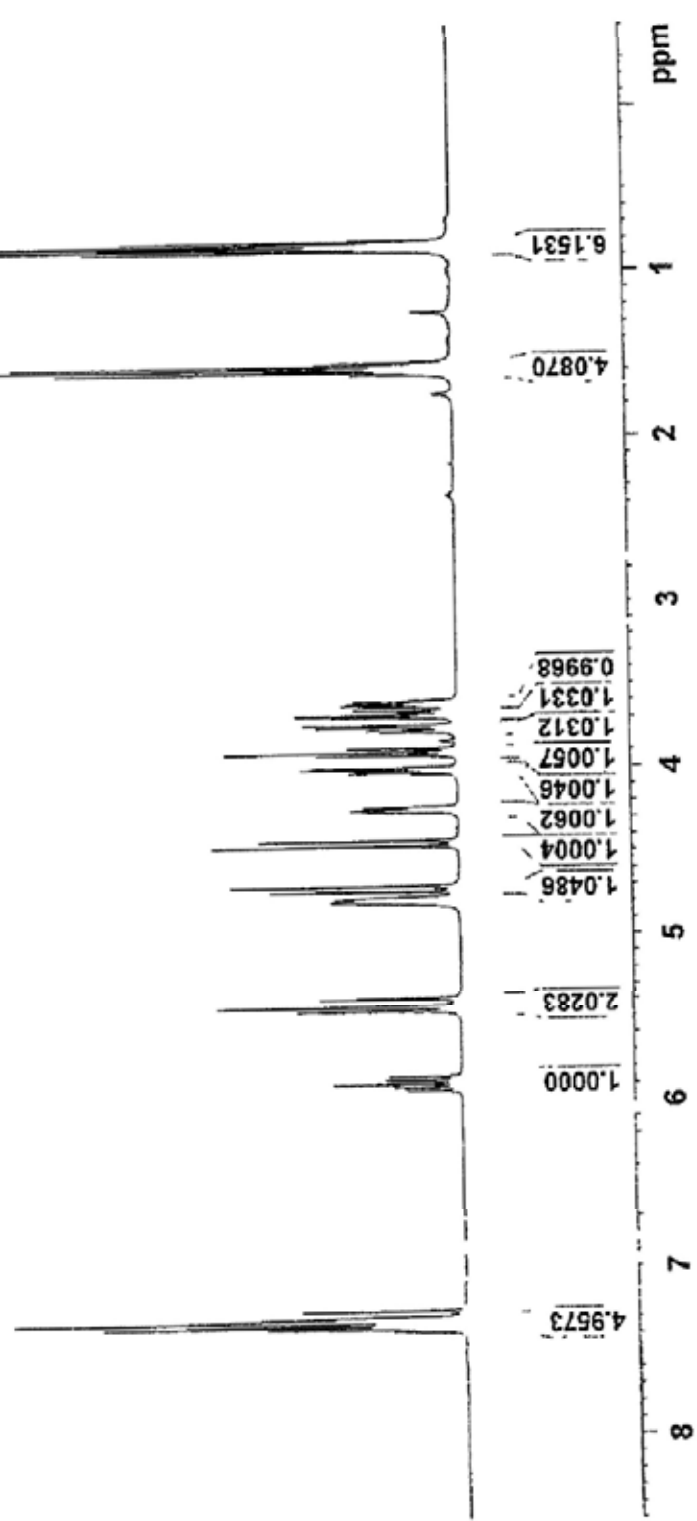
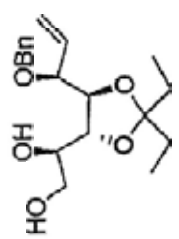


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SIRNO 1
PROCNO 1
Date_ 20100708
Time_ 20.04
INSTRUM spect
PROBHD 5 mm PABBO BBO
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 4
DS 2
SS 8223.682 Hz
SMH 0.123483 Hz
FIDRES 3.9816391 sec
AQ 50.8
RG 60.000 usec
DB 6.50 usec
DE 287.5 X
TE 1.00000000 sec
D1 1
===== CHANNEL f1 =====
NUC1 13C
P1 14.00 usec
PL1 0.00 dB
PR1 1.00 dB
SFO1 101.625313 MHz
SI 32714
SF 400.1300146 MHz
WDW EM
SSB 0
GB 0.30 Hz
CB 0
PC 1.00

¹H NMR (Solvent: CDCl₃-D₂O)

NAME sha33020
 EXPNO 1
 PROCNO 1
 Date_ 20100809
 Time 13.24
 INSTRUM spect
 PROBHD 5 mm 2HDDZ1H7
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl₃
 NS 2
 DS 2
 SMR 8223.685 Hz
 ETOMES 0.123483 Hz
 AQC 3.984638 sec
 RG 71.8
 DH 60.800 usec
 DE 6.50 usec
 TE 294.5 K
 D1 1.00000000 sec
 TTM 1
 ===== CHANNEL f1 =====
 NUC1 1H
 P1 7.10 usec
 PL -7.00 dB
 PL1W 13.17734718 W
 SFO1 400.1324710 MHz
 SI 42768
 SF 400.1300051 MHz
 EM C
 SSS C
 LB 0.30 Hz
 GB C
 PC 1.00

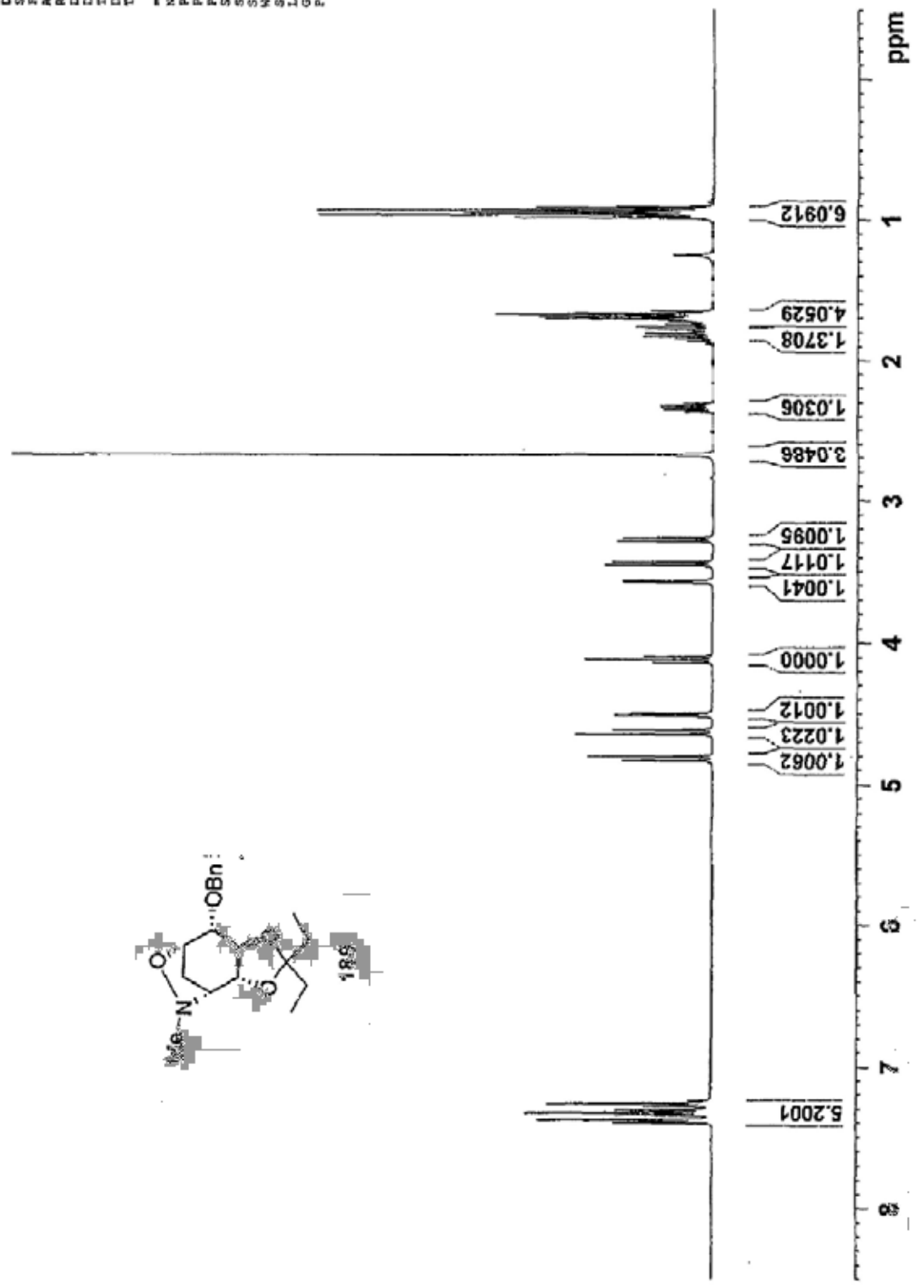
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 7.3255
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 7.3110
 7.3003
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 5.9423
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 5.9159
 5.8989
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 1.5513
 0.8619
 0.8418
 0.8532
 0.8229



¹H NMR

7.3930
7.3752
7.3416
7.3370
7.3240
7.3204
7.3051
7.2784
7.2657
7.2603
7.2427

4.8329
4.8023
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4.6183
4.5197
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4.1210
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3.5809
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3.2674
2.6814
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0.9510
0.9391
0.9163



NAME she37
EXPNO 1
PROCNO 1
Date_ 20100615
Time 19.07
INSTRUM spect
PROBHD 5 mm PR0B1 1H7
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 4
DS 2
SSN 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.5846387 sec
RG 64
EM 60.800 usec
EC 6.50 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 1.10 usec
PL1 -2.00 dB
SFO1 13.17724718 MHz
SFO2 400.13257210 MHz
SFO3 22.768 MHz
SFO4 400.1300046 MHz
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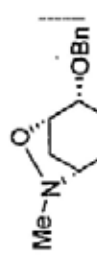
¹³C NMR

138.70
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8.58

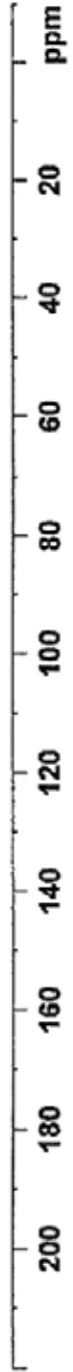
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Date_ 20100615
Time 19.31
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PULPROG dept90
TD 65536
SOLVENT CDCl3
DS 107
NS 4
SWH 24036.861 Hz
FIDRES 0.366298 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 297.2 K
CSST2 145.0000000
D1 2.0000000 sec
D2 0.0034828 sec
D12 0.0000200 sec
TDO 1

CHANNEL f1
NUC1 13C
P1 14.50 usec
P2 29.00 usec
PL1 -4.00 dB
PL1W 90.22689819 W
SFO1 100.6228298 MHz

CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
P3 7.20 usec
P4 14.40 usec
PCPD2 80.00 usec
PL2 -2.00 dB
PL2W 18.90 dB
PL12 13.17734718 W
PL12W 0.10960442 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127650 MHz
MDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



189

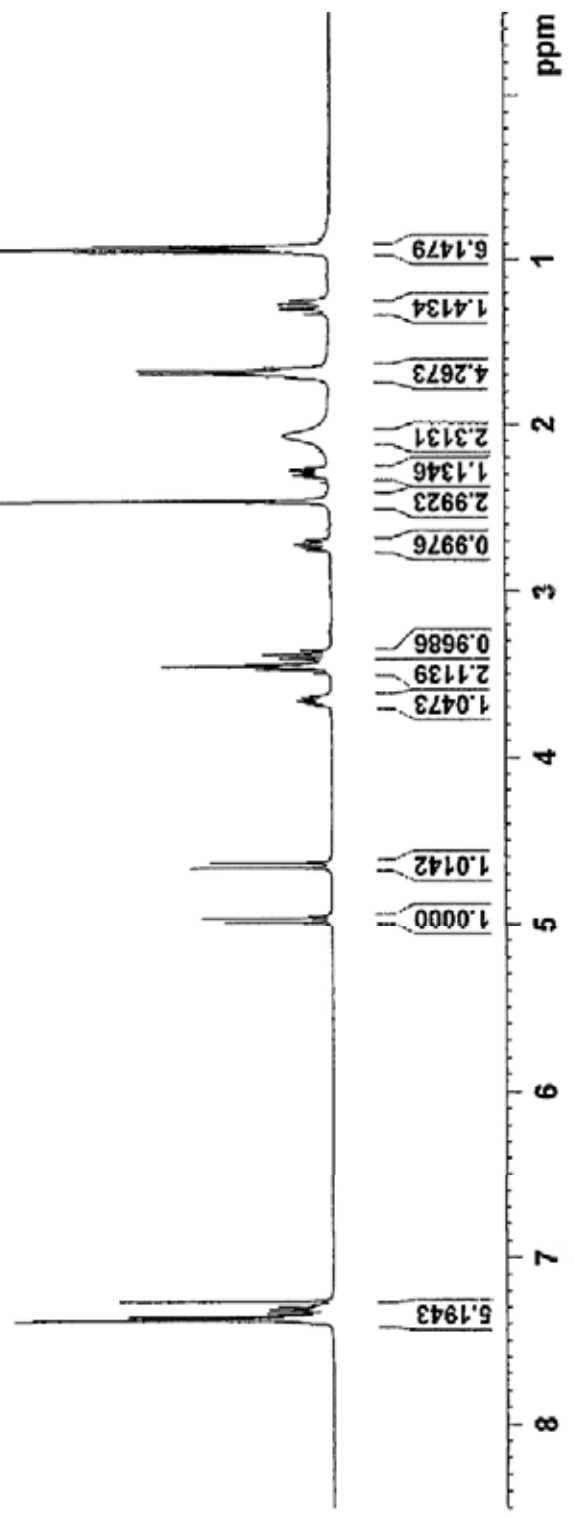
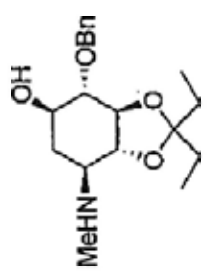


¹H NMR

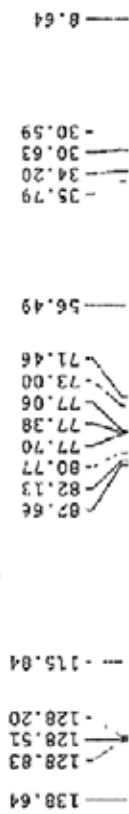


NAME EXPNO PROCNO
Date_ Time_
INSTRUM spect
PROBHD 5 mm PABUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2
DS 2
SWH 6223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DM 60.800 usec
DS 6.50 usec
TS 295.2 K
D1 1.00000000 sec
D11 1

CHANNEL f1 1H
NUC1 1H
P1 14.63 usec
PL1 0.00 dB
PL1M 6.31434441 M
STO1 400.1324710 MHz
SI 32768
ST 400.1300094 MHz
EM D
SSB 0.30 dB
LB 0 D
GB 0 D
PC 1.00



¹³C NMR



```

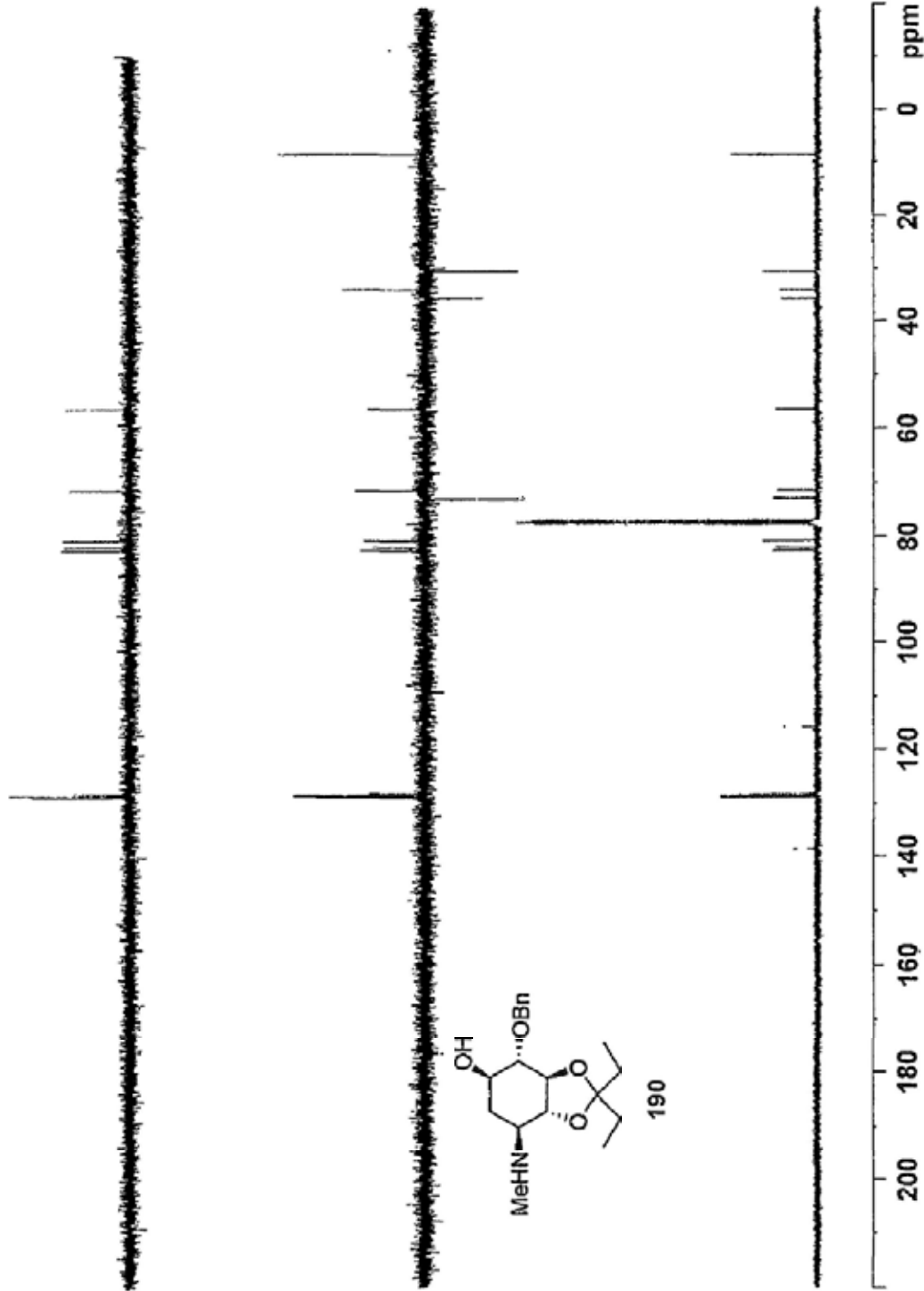
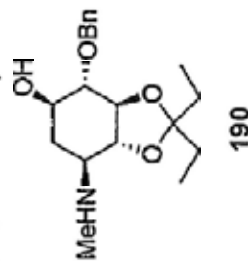
NAME          sha51carbou
EXPNO         2
PROCNO        1
Date_         20101115
Time_         14.28
INSTRUM       spect
PROBHD        5 mm PABUL-13C
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            261
DS            4
SWH           24038.461 Hz
FIDRES        0.366799 Hz
AQ            1.4631948 sec
RG            203
DE            10.400 usec
TE            295.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0           1
  
```

```

***** CHANNEL f1 *****
NUC1          13C
P1            9.68 usec
PL1           -0.60 dB
PL1M          41.2116963 W
SFO1          100.625258 MHz
  
```

```

***** CHANNEL f2 *****
CPDPRG2       /alt=16
NUC2          1H
PCPD2         90.00 usec
PL2           0.00 dB
PL12          15.16 dB
PL13          15.52 dB
PL2M          8.31434441 W
PL12M         0.22585411 W
PL13M         0.21272963 W
SFO2          400.1316005 MHz
SI            32768
SF            100.6127338 MHz
MOM           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
  
```



¹H NMR

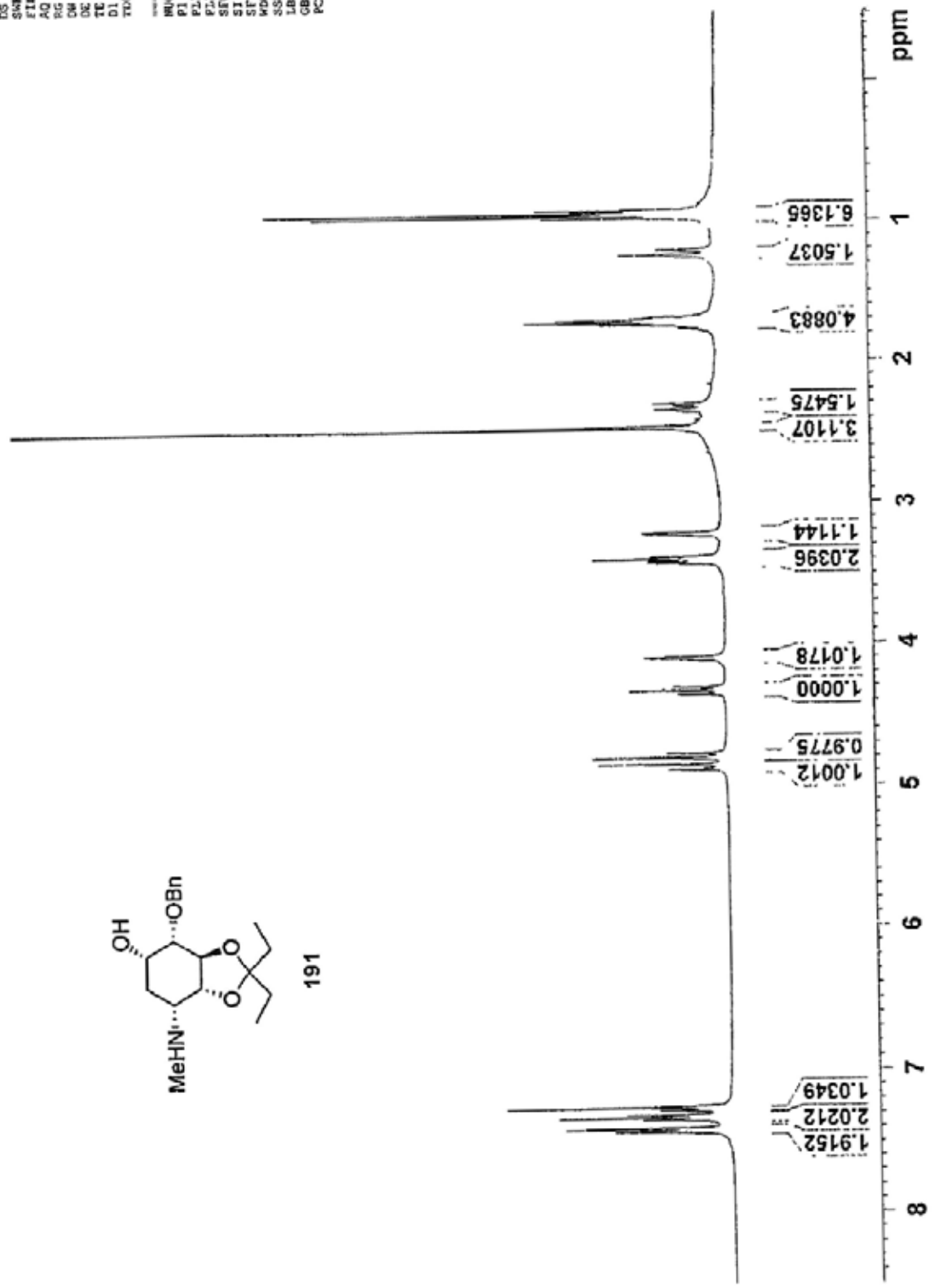
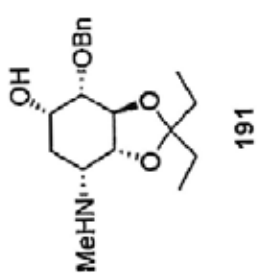
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NAME: sha49
EXPNO: 1
PROCNO: 1
Date_ 20101105
Time: 11.07
INSTRUM: spect
PROBHD: 5 mm PABUL 13C
PULPROG: zg30
TD: 65536
SOLVENT: CDCl3
NS: 8
DS: 2
SS: 8223.685 Hz
SMH: 0.125483 Hz
FIDRES: 3.8846381 SEC
AQ: 203
RG: 203
CM: 60.800 USEC
DE: 6.40 USEC
TE: 295.1 K
D1: 1.0000000 sec
T00: 1

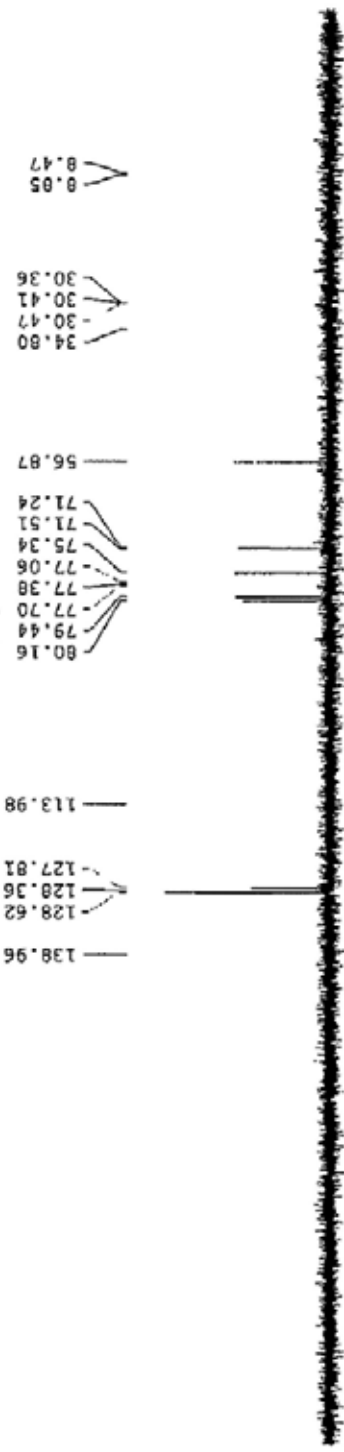
===== CHANNEL f1 =====
NUC1: 1H
P1: 14.83 USEC
PL1: 0.00 dB
P2: 8.31434441 W
SFO1: 400.1324710 MHz
SI: 32768
SF: 400.1300094 MHz
WDW: EM
SSB: 0
LB: 0.30 HZ
GB: 0
PC: 1.00
  
```

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0.9877
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1.2112
1.2181
1.2427
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1.7149
1.7288
1.7336
1.7475
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2.3448
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4.8072
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7.4298



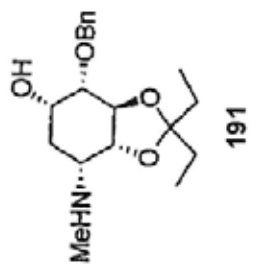
¹³C NMR



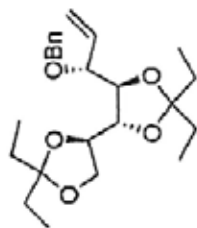
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EXPNO 1
PROCNO 1
Date_ 20101105
Time_ 11-12
INSTRUM spect
PROBHD 5 mm exBBL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 280
DS 4
SWH 24038.401 Hz
FIDRES 0.366798 Hz
AQ 1.3631948 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 295.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

----- CHANNEL f1 -----
NUC1 13C
P1 9.68 usec
PL1 -0.60 dB
PL1W 41.24164963 W
SFO1 100.6228298 MHz

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL2 15.66 dB
PL3 15.92 dB
PL2W 8.31438441 W
PL2M 0.22595433 W
PL1W 0.21272963 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127338 MHz
XCHW 0
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



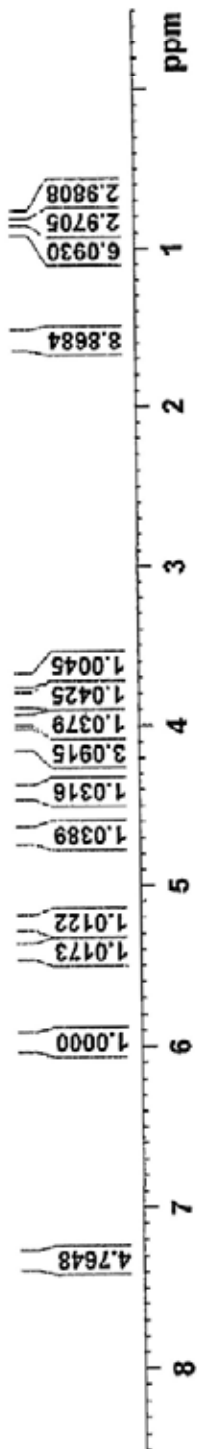
¹H NMR



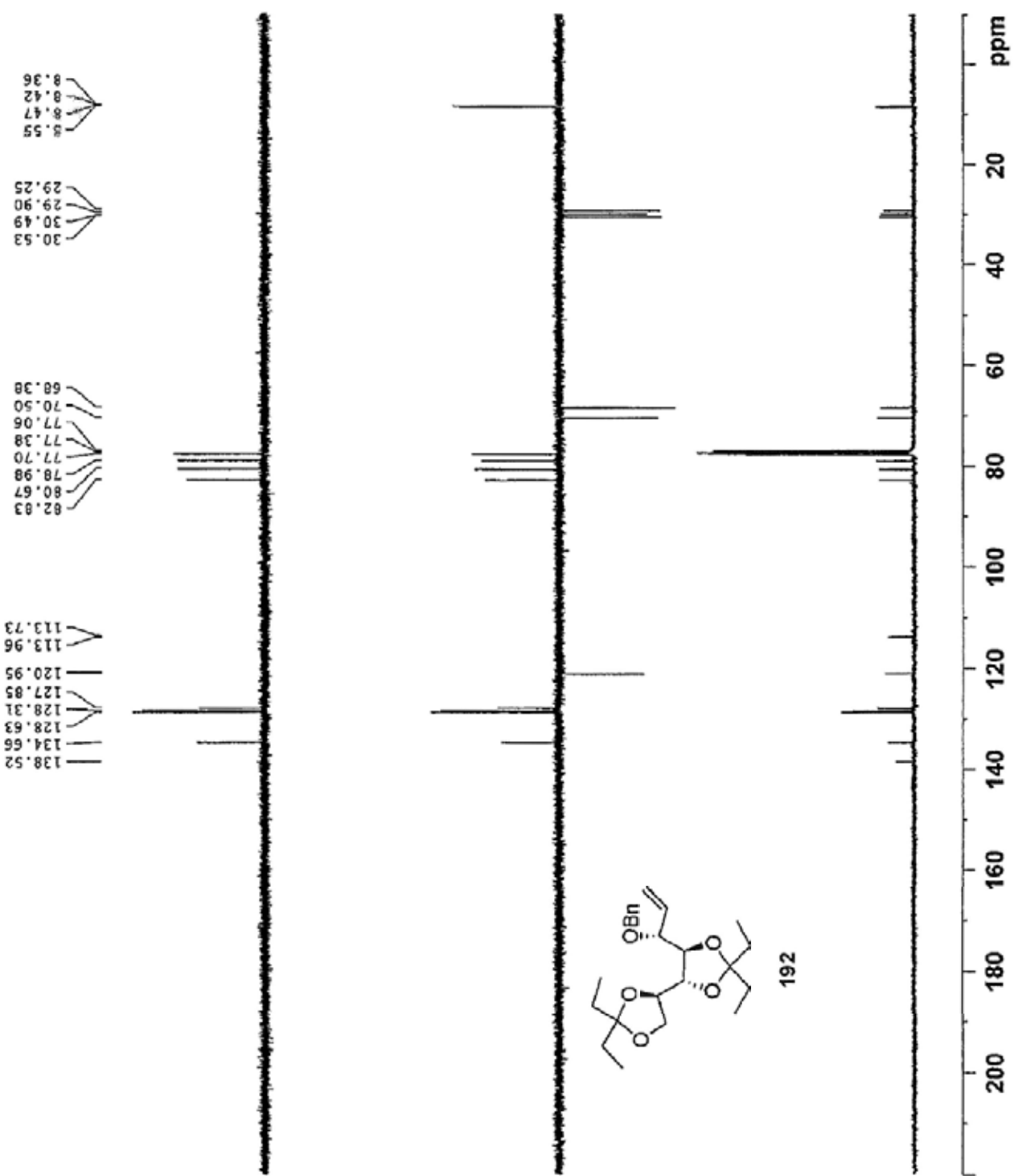
192

NAME
EXPNO
PROCNO
PROCPS
PULPROG
PROBHD
INSTRUM
SOLVENT
SOLVENT
NS
DS
SWH
FIDRES
AQ
RG
DM
DB
TE
DL
TD0
1
2
9223.695 Hz
0.125483 Hz
3.9816387 sec
80.6
60.800 usec
6.50 usec
298.2 K
1.00000000 sec
1

NAME CHANNEL F1
NUC1 1H
P1 14.00 usec
PL1 -1.00 dB
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¹³C NMR



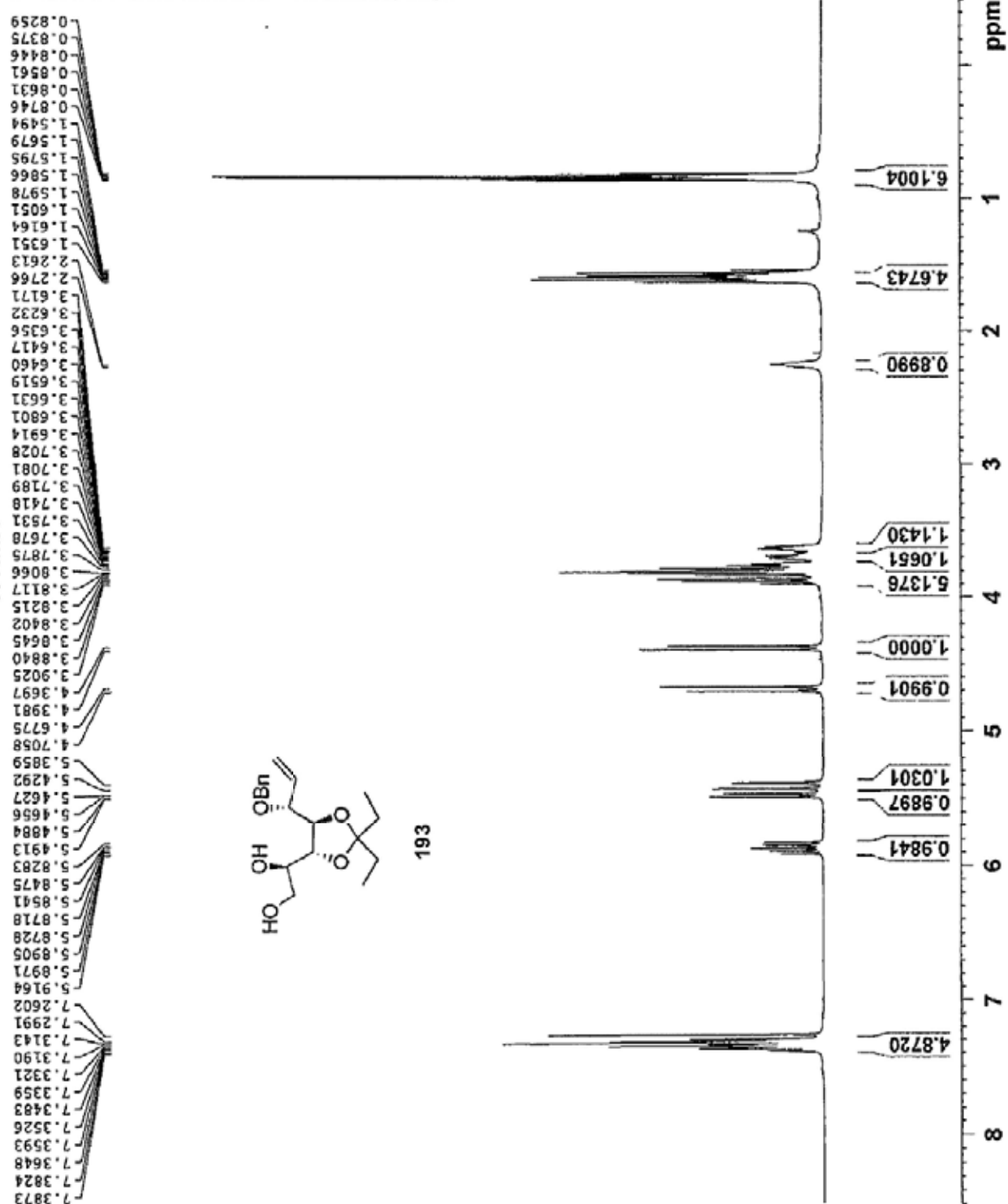
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sha38carbon: 1
EXPNO 1
PROCNO 1
Date_ 20100723
Time 15.56
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 170
DS 4
SN1 24038.461 Hz
FIDRES 0.366788 Hz
AQ 1.3631989 sec
RG 203
DM 20.800 usec
DE 6.50 usec
TE 298.8 K
D1 2.0000000 sec
D11 0.0300000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.90 usec
PL1 -2.00 dB
PL1F 55.33669392 MHz
SFO1 100.6131813 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.16 dB
PL13 18.62 dB
PL12W 13.56617069 W
PL13W 0.32844096 W
PL13M 0.14806664 W
SFO2 400.1916006 MHz
SI 32768
SF 100.6278205 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
  
```

¹H NMR



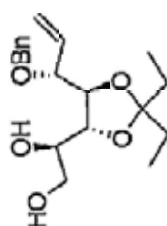
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NAME
EXPNO 1
PROCNO 1
Date_ 20100730
Time 15.39
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SMK 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.384537 sec
RG 80.6
DM 60.800 usec
DE 6.50 usec
TE 298.2 K
ZS 1
TD0 1.00000000 sec
----- CHANNEL f1 -----
NUC1 1H
P1 14.00 usec
PL1 -1.00 dB
PL12 13.56017009 M
SFO1 400.1524713 MHz
SI 32768
SF 400.1500143 MHz
WDW EM
SSB 0
RI 0
GB 0
PC 1.00

```

¹H NMR (Solvent: CDCl₃-D₂O)

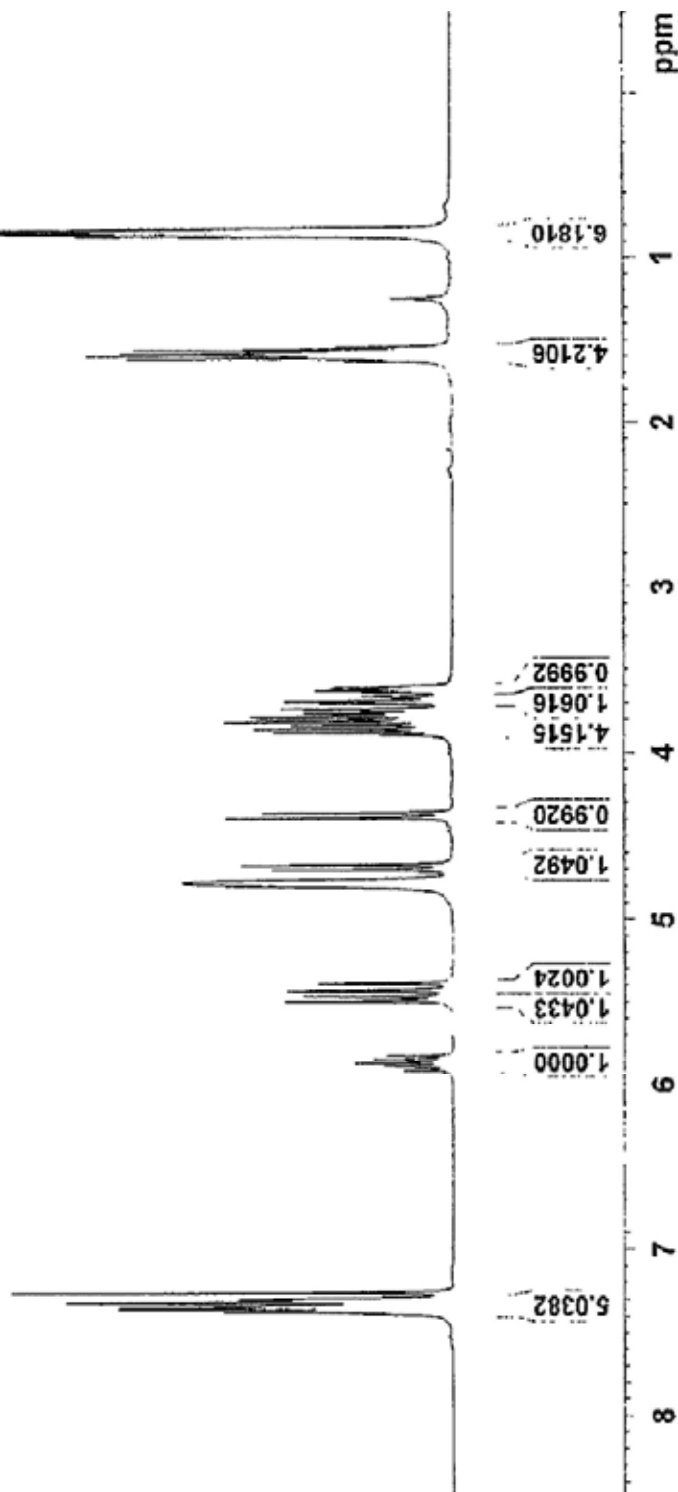
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0.8338
0.8230



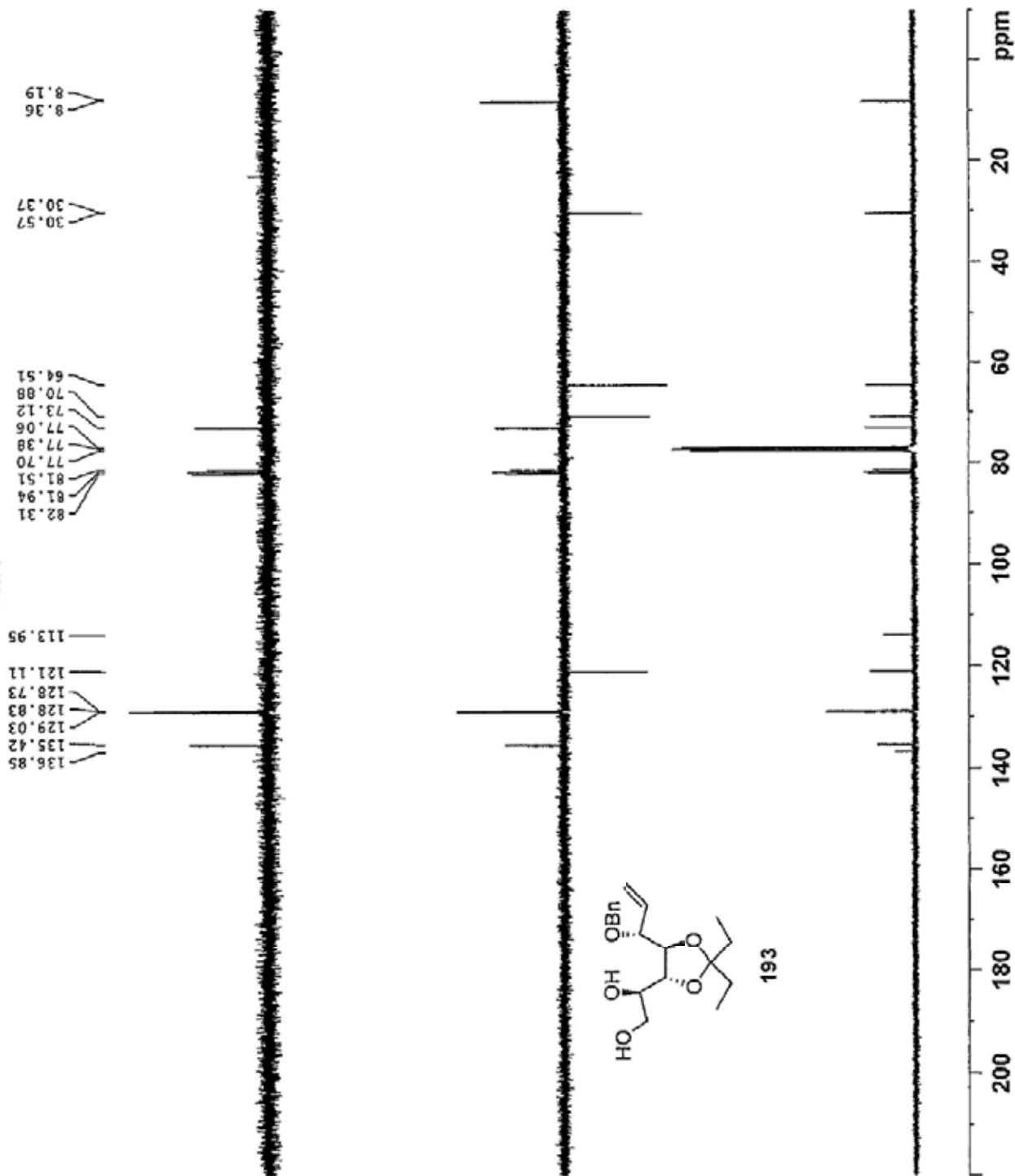
193

NAME sha39dfo
EXPNO 1
PROCNO 1
Date_ 20100909
Time 13.35
INSTRUM spect
PROBHD 5 mm PABBI 1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 823.685 Hz
FIDRES 0.125483 Hz
AQ 3.8646387 sec
RG 203
DM 60.800 usec
DE 6.50 usec
TE 294.5 K
D1 1.0000000 sec
TNO 1

===== CHANNEL f1 =====
NUC1 1H
P1 7.10 usec
PL1 -2.00 dB
PL1H 13.17734718 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300053 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



¹³C NMR

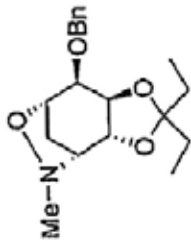
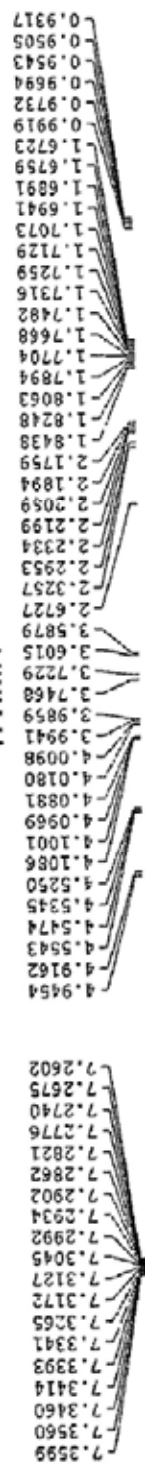


NAME sha39carbon
EXPNO 1
PROCNO 1
Date_ 20100730
Time 15.45
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 168
DS 4
SWH 24036.461 Hz
FIDRES 0.366798 Hz
AQC 1.3631986 sec
RG 161
DM 20.800 usec
DE 6.50 usec
TE 298.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

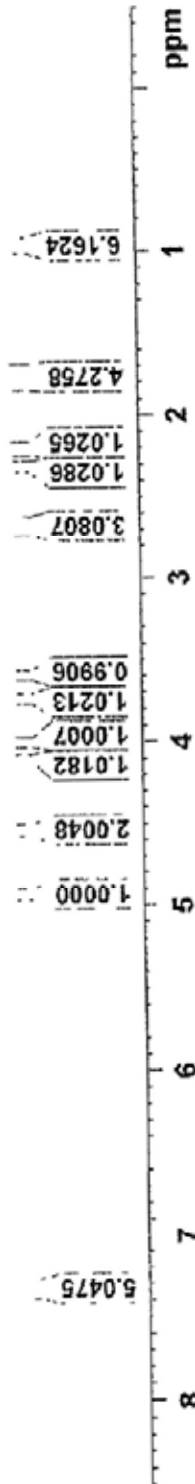
===== CHANNEL F1 =====
NUC1 ¹³C
P1 9.90 usec
PL1 -2.00 dB
PL1W 55.23689499 W
SFO1 100.6379183 MHz

===== CHANNEL F2 =====
CPDPRG2 waltz16
NUC2 ¹³C
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.16 dB
PL13 18.62 dB
PL2W 13.56617069 W
PL12W 0.32844096 W
PL13W 0.14806664 W
SFO2 400.1916008 MHz
S1 32768
SF 100.6278212 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

¹H NMR



196



NAME
EXPNO 1
PROCNO 1
F2 -
Time 14.51
Date_ 20100721
INSTRUM spect
PROBHD 5 mm EBBBO
PULPROG zgpg30
SOLVENT COCL3
NS 4
DS 2
SWH 8233.685 Hz
FIDRES 0.125413 Hz
AQ 3.9846387 sec
RG 57
EQ 60.800 usec
RF 6.50 usec
TE 298.0 K
D1 1.0000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 14.00 usec
PL1 -1.00 dB
SFO1 300.13647062 MHz
SF01 400.1424713 MHz
SI 32768
SF 400.1400128 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

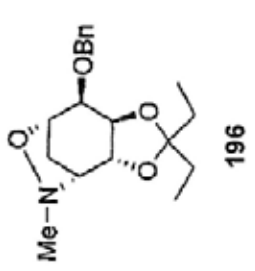
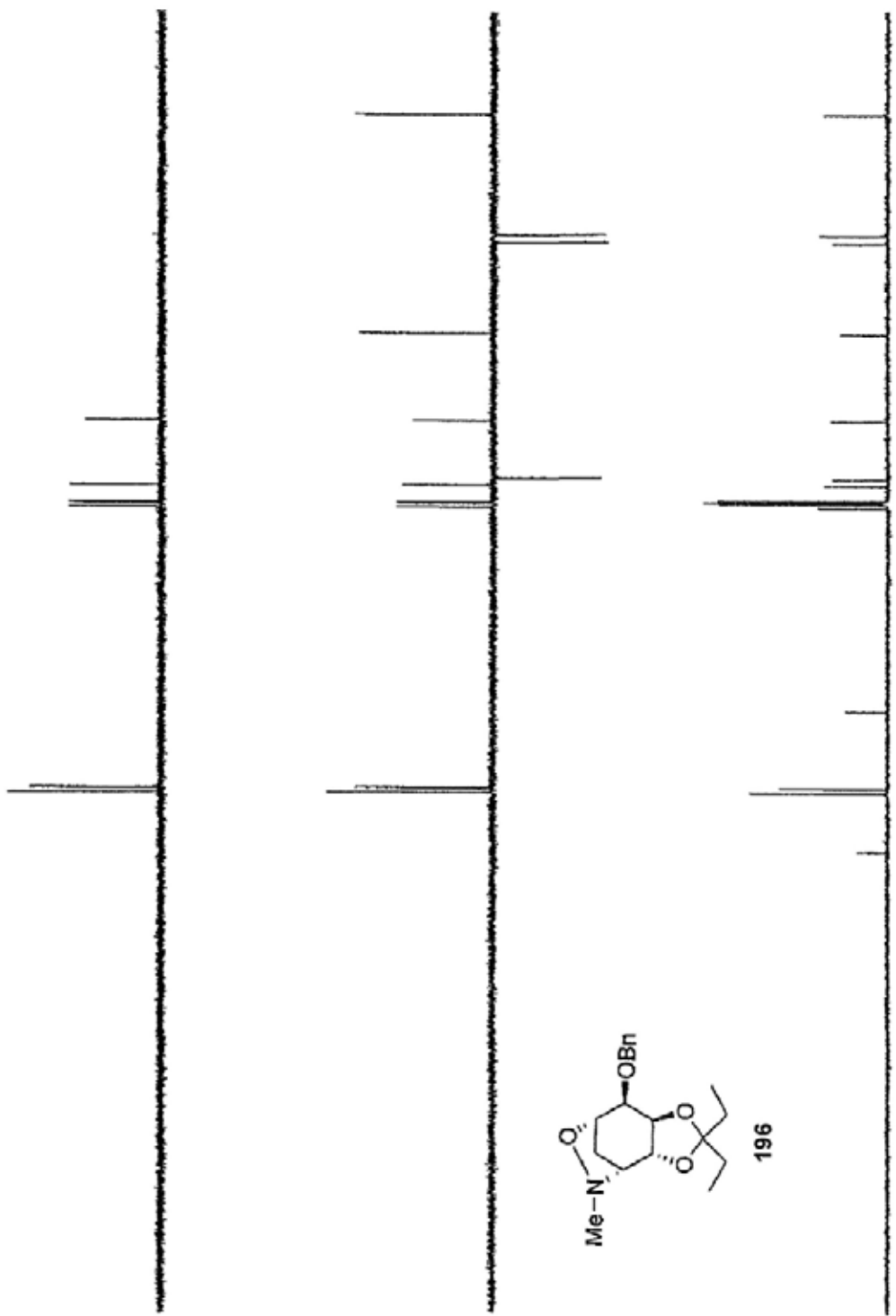
¹³C NMR

138.95
128.68
127.94
127.86
114.28
78.36
77.70
77.65
77.40
77.38
77.06
74.41
73.23
62.95
47.57
31.51
30.21
30.14
8.75
5.63

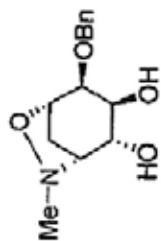
NAME sha12car3on
EXPNO 1
PROCNO 1
Date_ 20100721
Time 15.09
INSTRUM spect
F2PROB 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 142
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.362198 sec
RG 203
DW 20.810 usec
DE 7.50 usec
TE 298.6 K
D1 2.0000000 sec
D11 0.0300000 sec
T00 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.90 usec
PL1 -0.00 dB
PL1W 55.33659499 W
SFO1 100.625133 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD 30.00 usec
ECFDC -2.00 dB
PL2 15.16 dB
PL13 16.62 dB
PL1W 13.56617659 W
PL1W 0.32844095 W
PL1W 0.14806654 W
SFO2 400.1416008 MHz
SI 32708
SF 160.625133 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
FC 1.40

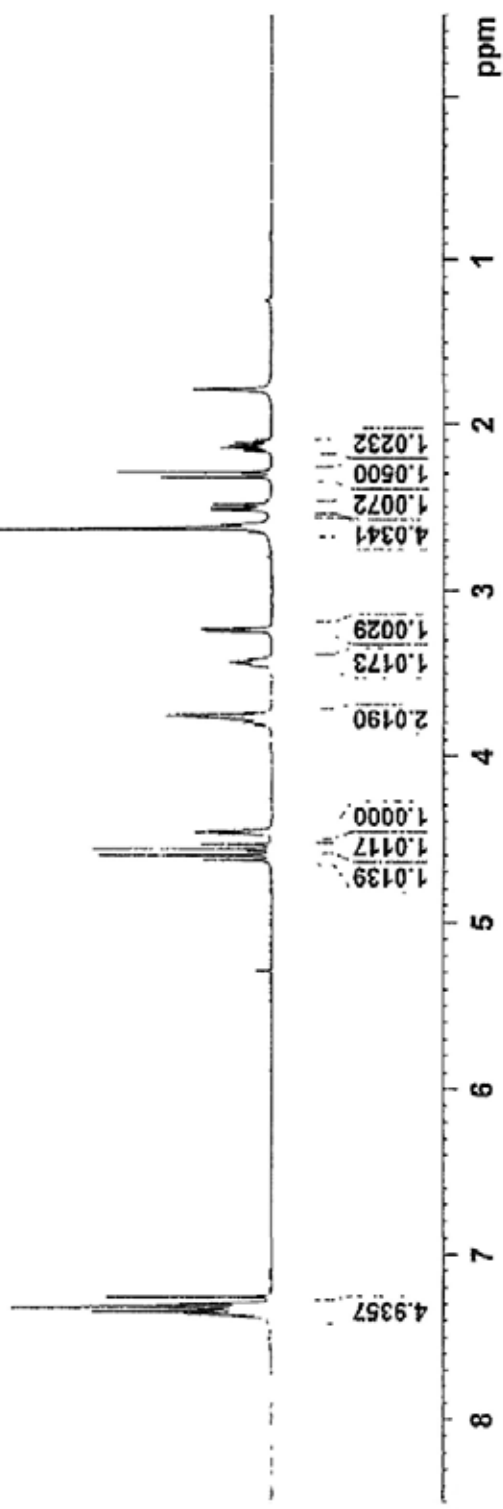


¹H NMR



197

NAME
EXPNO
PROCNO
PROC-
NAME
TIME
INSTRUM
PROBHD
PULPROG
TO
SOLVENT
NS
DS
SWH
FIDRES
AQ
RG
DC
BPC
SFO
DQ
DELTA
TEO
===== CHANNEL f1 =====
NUC1
P1
FL1
PL1
SFO1
SI
SF
SFO
SSB
LB
GB
PC
sh415
2
20100911
12.58
SPECT
5 mm PABBI
KQ70
65436
COG13
8
2
8223.695 Hz
0.125483 Hz
3.9846397 sec
3141
60.800 usec
5.50 usec
294.0 K
1.00000000 sec
1
1H
1H
-2.10 usec
-2.10 usec
13.1732710 dB
13.1732710 dB
400.1324710 MHz
32766
400.1300051 MHz
EM
0
0.30 Hz
1.00
1.00



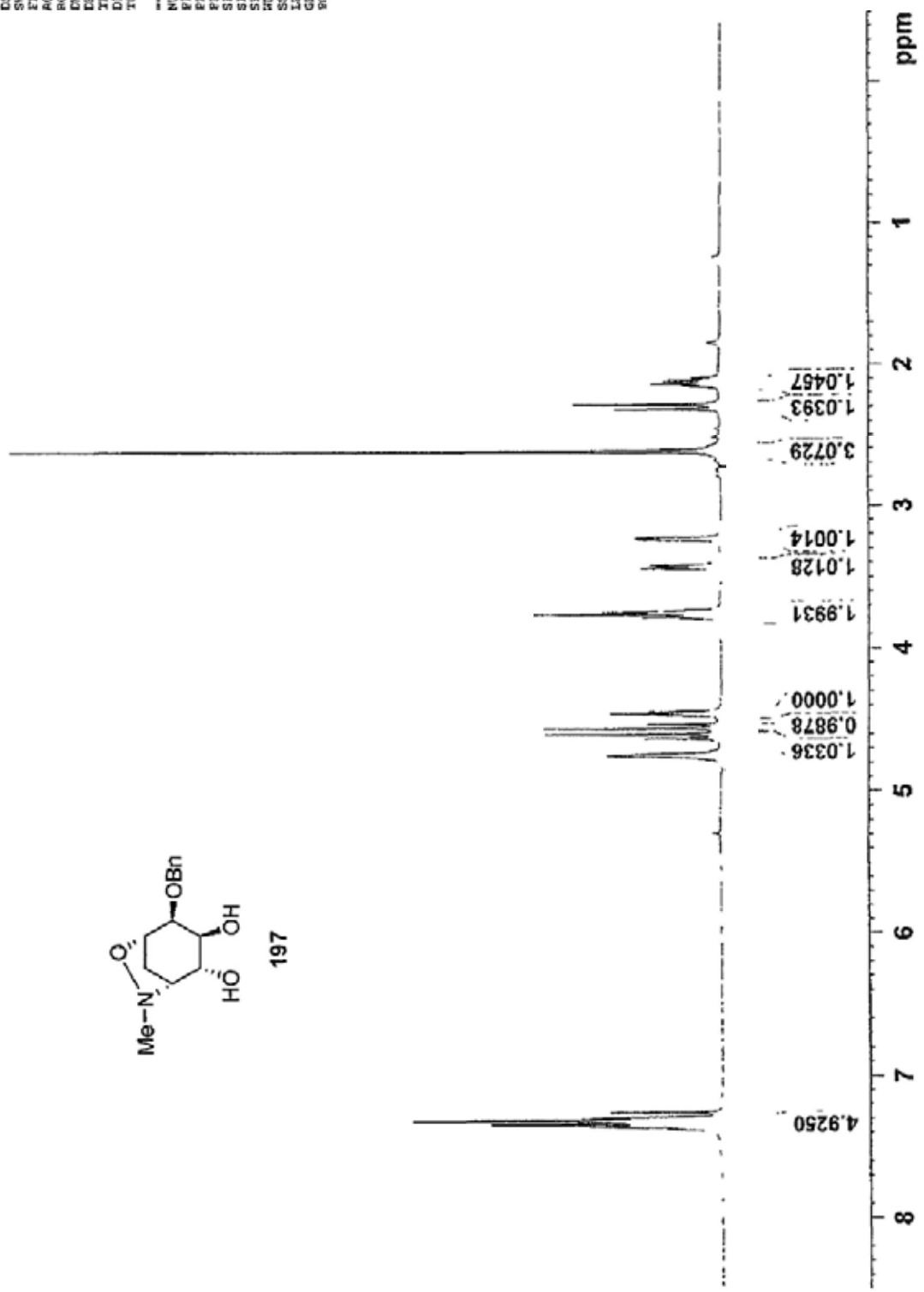
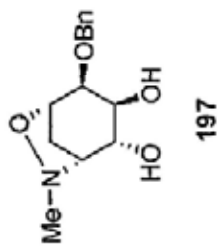
¹H NMR (Solvent: CDCl₃-D₂O)

```

NAME: sha45d2o
EXPNO: 1
PROCNO: 1
Date_ : 20100916
Time: 13.2
INSTRUM: spect
PROBHD: 5 mm PABBI 1H/
PULPROG: zgpg30
TD: 65536
SOLVENT: CDCl3
NS: 8
DS: 2
SMB: 8223.685 Hz
FIDRES: 0.125483 Hz
AQ: 3.9806387 sec
RG: 128
EM: 60.800 usec
EE: 6.50 usec
TE: 298.2 K
D1: 1.00000000 sec
TDO: 1
===== CHANNEL f1 =====
NUC1: 13C
P1: 7.10 usec
PL1: -2.00 dB
SFO: 13.1734738 MHz
STO1: 400.1324110 MHz
SI: 32768
SF: 400.1300000 MHz
WDW: EM
SSB: 0
GB: 0
PC: 1.00
  
```

4.7533
4.6360
4.6071
4.5670
4.5380
4.4735
4.4612
4.4490
3.7989
3.7862
3.7652
3.7411
3.4401
3.4199
3.2452
3.2362
3.2321
2.6287
2.3224
2.2919
2.1597
2.1456
2.1307
2.1152
2.1011

7.3727
7.3540
7.3468
7.3394
7.3250
7.3143
7.2964
7.2597
7.2577



¹³C NMR

```

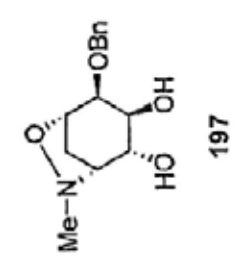
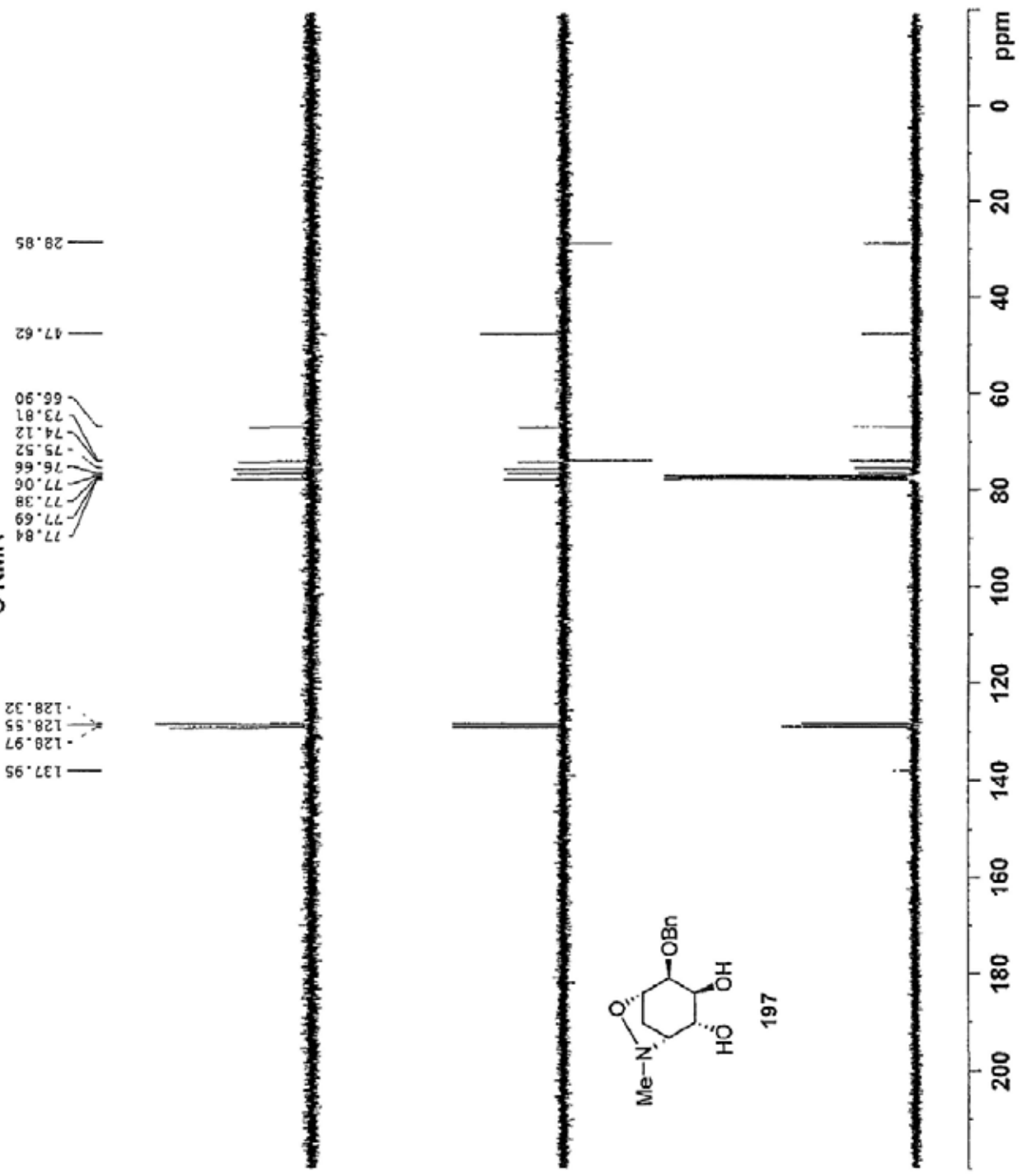
NAME sha45carbon
EXPNO 1
PROCNO 1
Date_ 20100916
Time_ 13.02
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 194
DS 4
SNH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DM 20.800 usec
DE 6.50 usec
TE 295.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
  
```

```

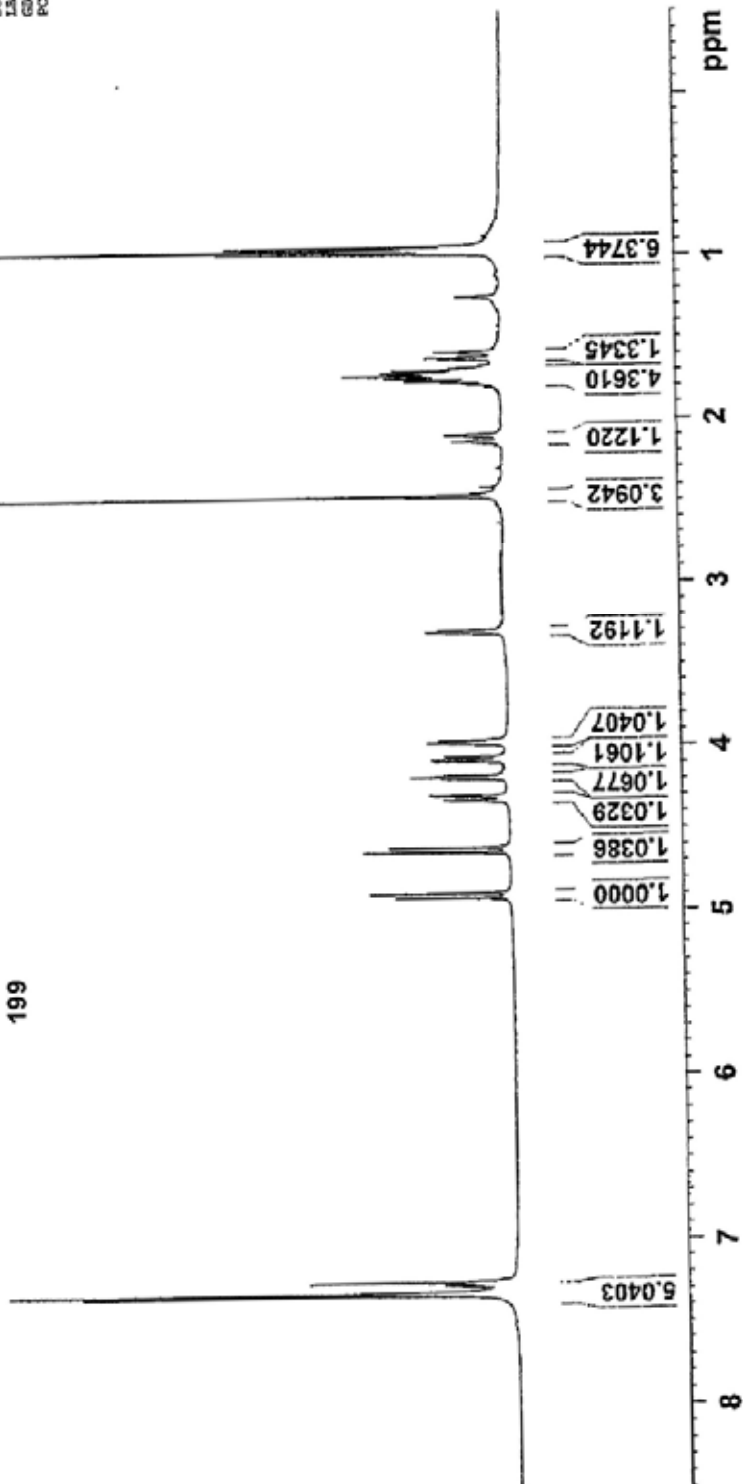
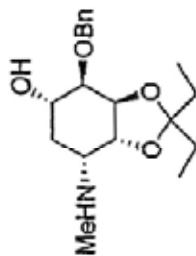
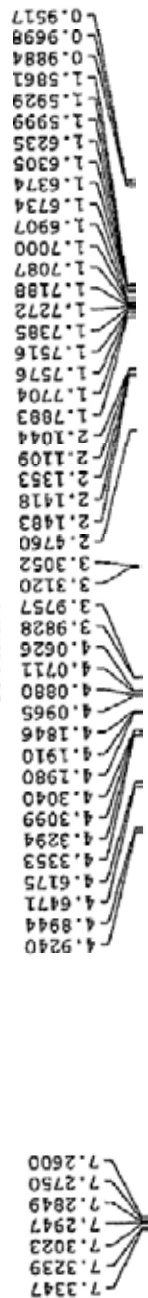
***** CHANNEL f1 *****
NUCL 13C
P1 14.30 usec
PL1 -4.00 dB
PL1W 90.22689819 W
SF01 100.6228298 MHz
  
```

```

***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC2 1H
NUC2 80.00 usec
PCPD2 -2.00 dB
PL2 18.80 dB
PL12 18.80 dB
PL13 18.80 dB
PL2W 13.17734718 W
PL12W 0.10960442 W
PL13W 0.10960442 W
SF02 400.1316005 MHz
SI 32768
SF 100.6127346 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
  
```



¹H NMR



NAME sha48
EXPNO 1
PROCNO 1
Date_ 20101030
Time 12.45
INSTRUM spect
PROBHD 5 mm PABBO BM-
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.984587 sec
RG 90.5
DQ 60.800 uSec
DC 6.50 uSec
TE 297.8 K
D1 1.00000000 sec
TD0 1

CHANNEL f1
NUC1 13C
P1 14.80 uSec
PC1 -1.00 dB
PL1 13.56617069 Hz
SFO1 400.1524713 MHz
SI 32768
SF 400.1500143 MHz
WDW EM
SSB 0
LA 0
GB 0
PC 1.00

¹³C NMR

139.19
128.64
127.80
127.70
112.96
77.98
77.70
77.38
77.06
75.75
73.97
73.52
72.09
58.06
34.69
30.63
30.53
27.49
8.66
8.57

NAME shaft8carbon
EXPNO 1
PROCNO 1
Date_ 20101030
Time 12.50
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
F2 331
SOLVENT
NS 331
DS 4
SWH 24039.461 Hz
FIDRES 0.166798 Hz
AQ 1.3631968 sec
RG 181
DW 20.800 usec
DE 6.50 usec
TE 298.5 K
D1 2.0000000 sec
D11 0.0300000 sec
TDO 1

CHANNEL f1
NUC1 ¹³C
P1 9.90 usec
PL1 -2.00 dB
PL1W 55.32683489 M
SFO1 100.6179183 MHz

CHANNEL f2
CPDPRG2 waltz16
NUC2 ¹H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 18.16 dB
PL13 18.92 dB
PL1W 13.56617069 W
PL12W 0.32844096 W
PL13W 0.14806654 W
SFO2 400.1516038 MHz
SI 32768
SF 100.6276212 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.60

