Biomimetic Total Synthesis of (±)-Pallavicinolide A

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Abstract

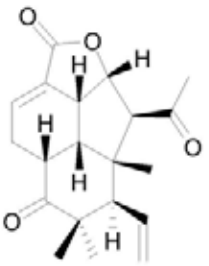
Liverworts biosynthesize many new skeletons of diterpenoids with interesting biological activities. In 1998, the diterpene pallavicinolide A was isolated from the Japanese liverwort *Pallavicinin subciliata* by Asakawa and co-workers, which contained a novel tetracyclic-fused skeleton with seven contiguous stereocenters. The intriguing structure and potential bioactivities have attracted our attention. In this thesis, we give the detailed description of the first total synthesis of (±)-pallavicinolide A (**3**) involving a biomimetic approach.

In Chapter 1, biomimetic total syntheses of natural products are reviewed with several kinds of organic reactions as examples.

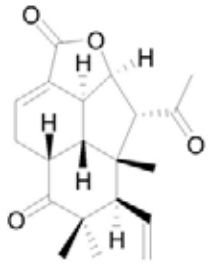
In Chapter 2, the background of (±)-pallavicinolide A (**3**) including its isolation, structural elucidation and biogenetic pathway is overviewed. Then the retrosynthetic analysis and detailed synthetic procedures are discussed. We completed the first total syntheses of (±)-pallavicinolide A (**3**) and one of its non-natural isomer (±)-neopallavicinolide A (**296**) with a linear sequence of 32 steps starting from 2-methyl-1,3-cyclohexanedione (MCD). Our synthetic route features the following three biomimetic transformations as key steps: (a) Grob fragmentation; (b) singlet oxygen oxidation; and (c) intramolecular Diels-Alder cycloaddition.

Chapter 3 provides a short summary of my research.

Chapter 4 contains experimental procedures.



Pallavicinolide A (**3**)



Neopallavicinolide A (**296**)

摘要

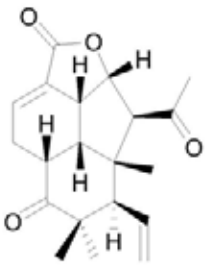
一九九八年，日本学者 Asakawa 及其同事从药用苔类植物 *pallavicinia subciliata* 中分离得到了几个结构独特的二萜。其中几个化合物的骨架尤其新颖，我们命名为 pallavicinolide A – C。分离者们研究并提出了这几个相关化合物的生源合成途径。它们复杂的分子结构和潜在的生物活性以及有趣的生源假设激励我们去进行它们的全合成研究。

本论文第一章以几种反应类型为例综述了天然产物的仿生全合成研究状况。

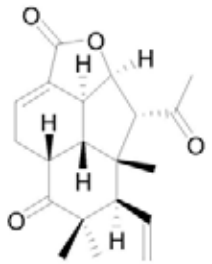
第二章是本论文的主要内容。先详细介绍了我们的目标分子 pallavicinolide A (**3**) 的分离和结构鉴定情况。根据分子结构，生源假设和我们组应用呋喃化学进行天然产物全合成的经验，我们提供了 pallavicinolide A (**3**)的逆合成分析并详细讨论了我们的全合成过程。最后，以 2-methyl-1,3-cyclohexanedione (MCD)为起始原料，通过 Grob 裂解，单线态氧化呋喃环以及分子内 Diels-Alder 环化等几步关键反应，我们完成了**(±)**-pallavicinolide A (**3**)的首次仿生全合成。此外，应用同样策略，我们也合成出了该天然产物的一个非对映异构体**(±)**-neopallavicinolide A (**296**).

第三章总结了本论文的工作。

第四章给出了与该论文相关化合物的详细实验数据。



Pallavicinolide A (**3**)



Neopallavicinolide A (**296**)

CONTENTS

ABBREVIATIONS

Å	angstrom
Ac	acetyl
Anal.	analysis
anhyd	anhydrous
aq.	aqueous
Ar	aryl
9-BBN	9-borabicyclo[3.3.1]nonane
Bn	benzyl
bp	boiling point
Bu	butyl
Bz	benzoyl
calcd	calculated
cat.	catalytic
cm	centimeter (s)
COSY	correlated spectroscopy
CSA	10-camphorsulfonic acid
d	day (s); density; doublet
D	dimension
DBN	1,5-diazabicyclo[4.3.0]non-5-ene
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DEAD	diethyl azodicarboxylate
DIBAL	diisobutylaluminum hydride
DIPEA	diisopropylethylamine
DMAP	4-(dimethylamino)pyridine

DME	1,2-dimethoxyethane
DMF	dimethylformamide
DMP	Dess-Martin periodinane
DMSO	dimethyl sulfoxide
dr	diastereomeric ratio
ee	enantiomeric excess
EI	electron impact ionization (in mass spectrometry)
ESI	electronspray ionization (in mass spectrometry)
Et	ethyl
FAB	fast atom bombardment (in mass spectrometry)
g	gram (s)
h	hour (s)
HRMS	high-resolution mass spectrum
HMBC	heteronuclear multiple-bond correlation
HMDS	hexamethyldisilazane
HMPA	hexamethylphosphorous triamide
HPLC	high performance liquid chromatography
HSQC	heteronuclear single-quantum coherence
hv	light
Hz	hertz
IBX	2-iodoxybenzoic acid
IR	infrared
KHMDS	potassium hexamethyldisilazide
LAH	lithium aluminum hydride
LDA	lithium diisopropylamide
LiHMDS	lithium hexamethyldisilazide
liq.	liquid

lit	literature
m-CPBA	*m*-chloroperbenzoic acid
MB	methylene blue
Me	methyl
MEM	2-methoxyethoxy methyl
min	minute (s)
MM2	molecular mechanics
MOM	methoxymethyl
mp	melting point
Ms	mesyl or methanesulfonyl
MS	mass spectrometry; molecular sieves
MVK	methyl vinyl ketone
m/z	mass to charge ratio (in mass spectrometry)
NaHMDS	sodium hexamethyldisilazide
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
NIS	*N*-iodosuccinimide
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
NOESY	nuclear Overhauser effect spectroscopy
ORTEP	oak ridge thermal ellipsoid plot
PCC	pyridinium chlorochromate
PDC	pyridinium dichromate
PG	protective group
Ph	phenyl
ppm	parts per million (in NMR)
PPTS	pyridinium *p*-toluenesulfonate

Pr	propyl
p-TsOH	*p*-toluenesulfonic acid
py	pyridine
Red-Al	sodium bis (2-methoxyethoxy)aluminumhydride
R_f	retardation factor (in chromatography)
ROESY	rotating frame Overhauser effect spectroscopy
rt	room temperature
TBAF	tetrabutylammonium fluoride
TBAI	tetrabutylammonium iodide
TBDMS or TBS	*t*-butyldimethylsilyl
TBDPS	*t*-butyldiphenylsilyl
TEA	triethylamine
TEMPO	2,2,6,6-tetramethylpiperidinoxyl
tert-	tertiary
TES	triethylsilyl
Tf	trifluoromethanesulfonyl
TFA	trifluoroacetic acid
THF	tetrahydrofuran
THP	tetrahydropyran
TLC	thin-layer chromatography
TIPS	triisopropylsilyl
TMEDA	*N,N,N,N*-tetramethylethylenediamine
TMS	trimethylsilyl
Tos or Ts	*p*-toluenesulfonyl
TPP	tetraphenylporphyrin

Chapter 1. Introduction:

Biomimetic Total Syntheses of Natural Products

1.1 Introduction and background

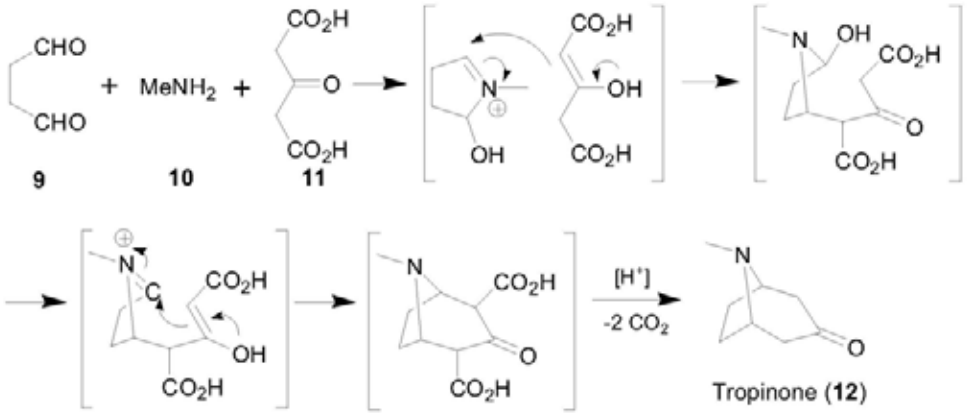
After more than a century of development contributed by Woodward, Corey, Nicolaou and many other great organic chemists, total synthesis has become a precise science and a fine art.[1] Target molecules range from the simplest urea (Wohler)[2] to the complex architectures such as vitamin B_{12} (Woodward, Eschenmoser),[3] polytoxin (Kishi)[4] and brevetoxin B (Nicolaou)[5]. The strategy toward the success in total syntheses of complex natural products was coined retrosynthetic analysis,[6] which was practiced consciously or unconsciously by Woodward and then officially introduced[7] and fully developed by Corey at Harvard University (In a mini-review about drug discovery, Schreiber divided organic synthesis into target-oriented organic synthesis and diversity-oriented organic synthesis[8]). So far, it appears that none of the total syntheses could escape from retrosynthetic analysis.

Indeed, each of these great accomplishments of total syntheses required hard work from large teams of chemists providing a few milligrams of the target molecules using more than a hundred separate reactions over a decade or more. In addition, chemists are almost helpless when confronted with the need for a significant amount of a complex organic compound (such as the anticancer drug taxol).[9] However, all natural products are made by nature, so we should learn from nature. Although the precise processes used by nature to assemble natural products are rarely known, it will be a fascinating challenge if we could match nature's wisdom in our total synthesis, even though only in one single step. While organic chemists are still working on the logic of retrosynthetic analysis, another important strategy had also been widely accepted

and guided the total syntheses of an ever-increasing number of complex natural products.[10] Biomimetic synthesis, mimicking the biosynthesis process in organism by using a chemical approach in laboratory, is therefore a method of choice.

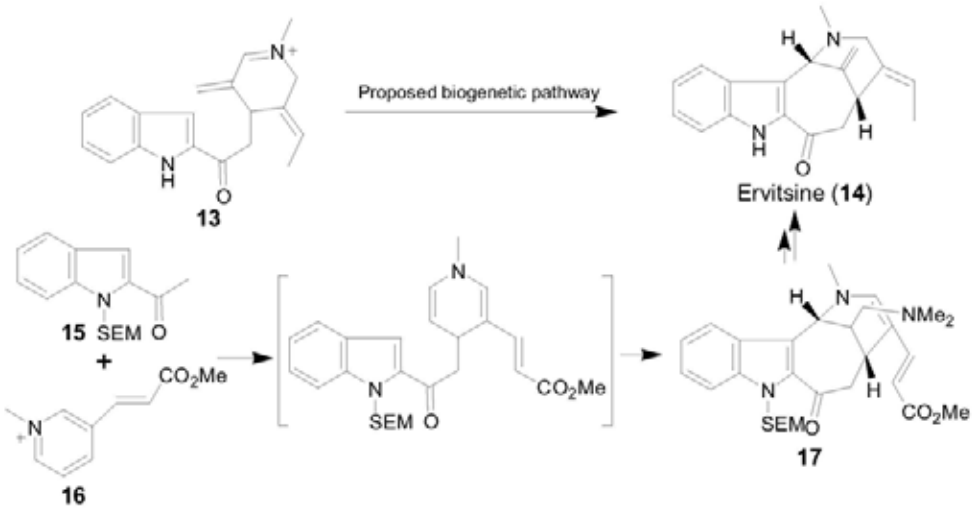
1.2 The concept, history and development of biomimetic synthesis

The concept of biomimetic synthesis was firstly introduced by Robinson in 1917, who demonstrated this concept in his intriguing one-pot synthesis of tropinone (**12**) from succindialdehyde (**9**), methylamine (**10**) and either acetone or a salt of acetonedicarboxylic acid (**11**) (Scheme 1).[11]



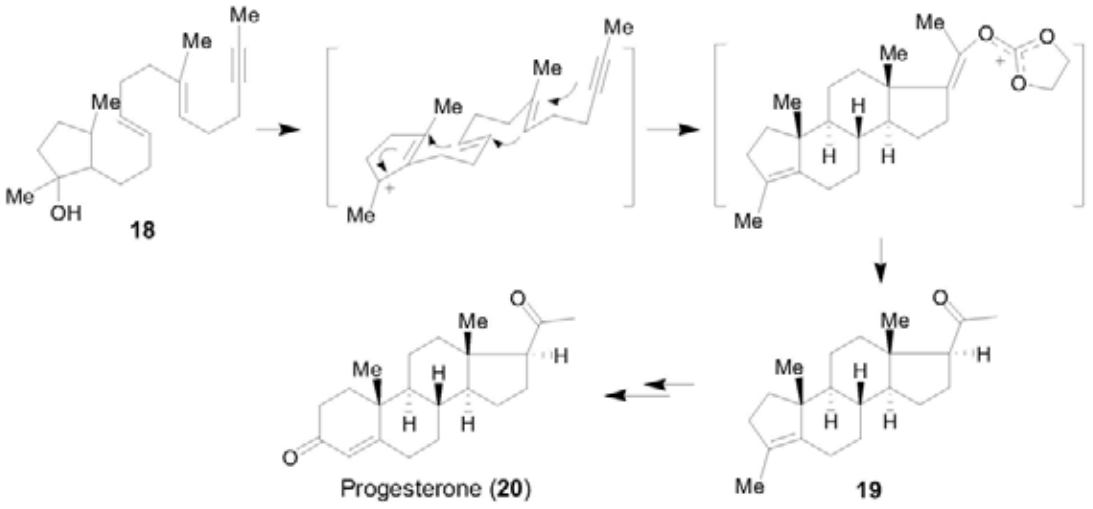
Scheme 1. Robinson's biomimetic synthesis of tropinone (**12**)

Later, van Tamelen[12] systematized different ideas and philosophy underlying biomimetic or biogenetic synthesis defined as a specific reaction or a sequence of reactions that mimic a proposed biological pathway. The process being imitated usually has a solid biochemical background. The term biomimetic synthesis was also used to describe a sequence of reactions performed to support a biogenetic hypothesis as exemplified by the straightforward and biomimetic synthesis of indole alkaloid ervitsine (**14**)[13] (Scheme 2).



Scheme 2. Bosch's synthesis of ervitsine (**14**)

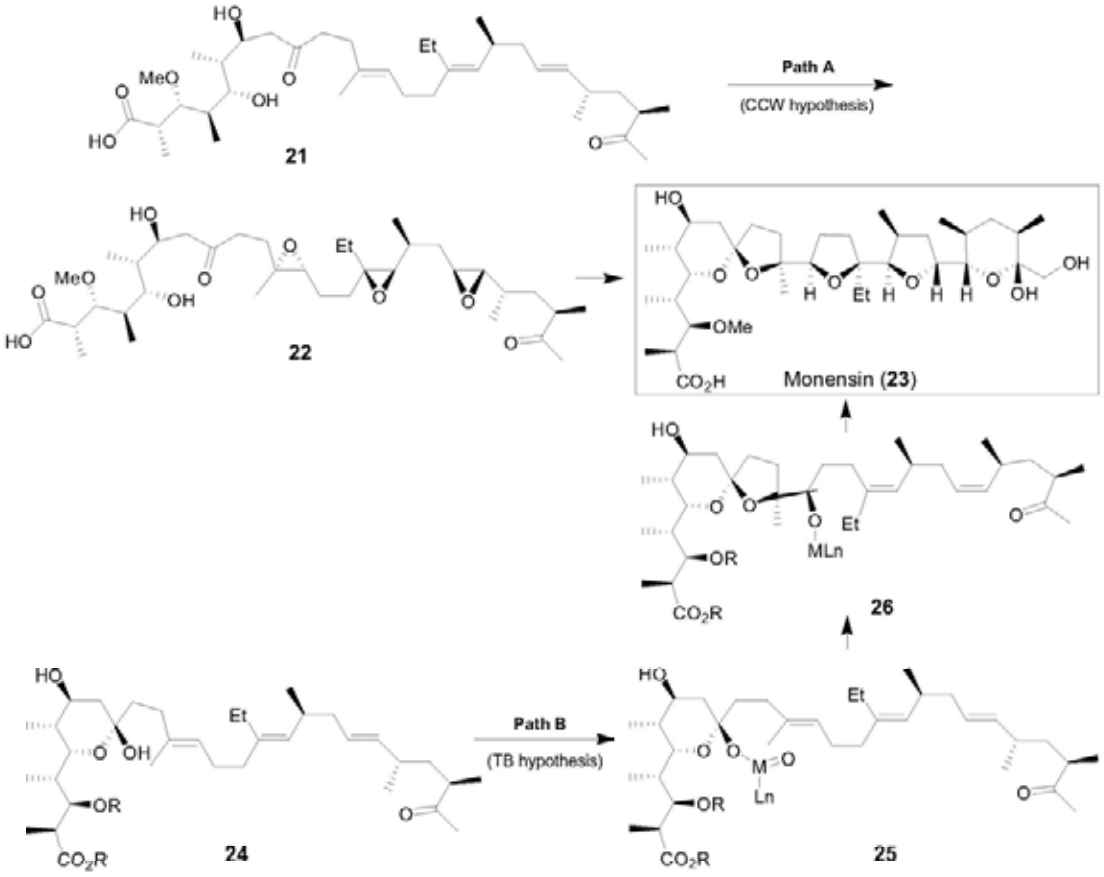
After Robinson, many great chemists devoted to biomimetic synthesis and have enriched this field to a great extent. While many achievements were not meant to be nature-inspired, others were clearly based on ideas about the structural origins of natural products. Half a century ago, Eschenmoser[14] and Stork[15] studied systematically cation cyclization stereochemistry and its relationship to squalene-triterpene biosynthesis. This evidence has provided a theoretical and empirical foundation for the beautiful synthesis of progesterone (**20**) by Johnson[16] (Scheme 3) and other magnificent accomplishments in steroid synthesis. In addition, Woodward's dramatic porphyrin-chlorin transformation in his synthesis of chlorophyll,[17] van Tamelen's definition about biomimetic synthesis[12] and tetracyclization favoring six- and five-membered rings system,[18] Eschenmoser's experiments concerning the structural origin of vitamin B_{12},[19] Nicolaou's biomimetic syntheses of the endiandric acid methyl esters[20] and Heathcock's brilliant biomimetic syntheses of the daphniphyllum alkaloids[9] are also salient achievements that have inspired others to derive lessons from nature in their own synthetic organic work.



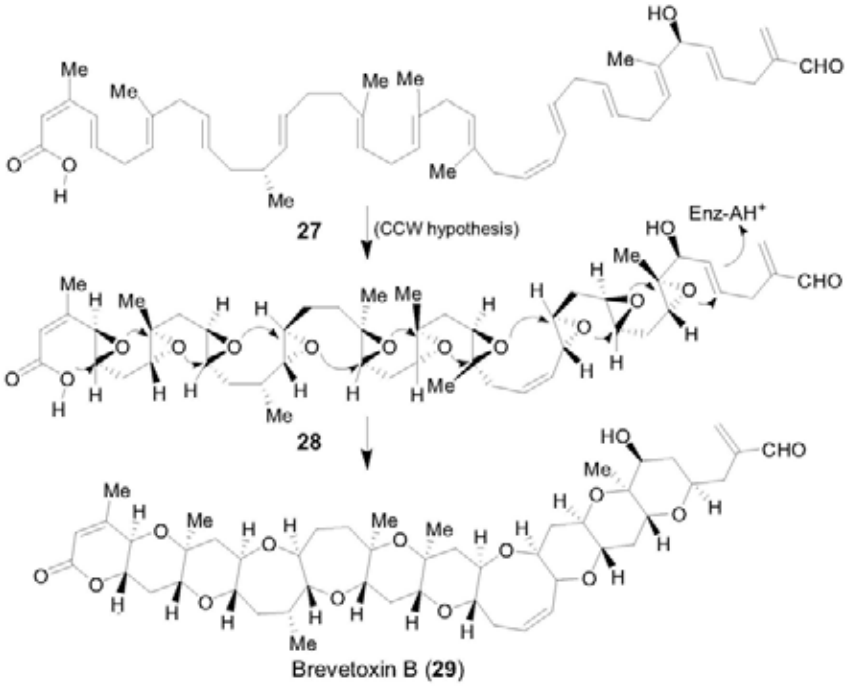
Scheme 3. Johnson's elegant cation-π cyclization to fashion the core scaffold of progesterone (**20**)

1.3 Polyether biomimetic synthesis

Polyether marine natural products, such as brevetoxin B and gymnocin A, have attracted much attention from chemists and biologists due to their novel skeletons and potential bioactivities.[21] In addition, the biosynthesis of polyether has been also one of the most appealing subjects. There are at present two biogenetic hypotheses for polyether synthesis, namely, the Cane-Celmer-Westley polyepoxide (CCW hypothesis)[22] and the Townsend-Basak oxidative cyclization (TB hypothesis),[23] as can be exemplified by the biogenesis of monensin (**23**) (Scheme 4). Currently, CCW model has gained the most acceptance. For example, Nakanishi's biogenetic hypothesis[24] for the synthesis of brevetoxin B (**29**) is closely related to the CCW hypothesis for the biosynthesis of polyether antibiotics (Scheme 5). In fact, the first total synthesis of brevetoxin B by Nicolaou[1b,25] also partially supported the above hypothesis.

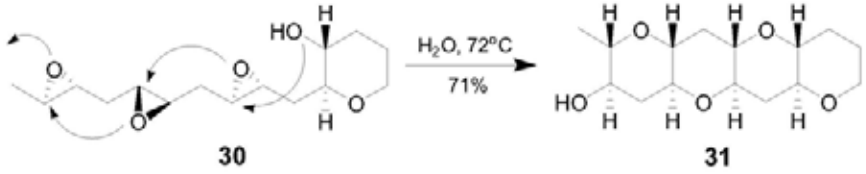


Scheme 4. The Cane-Celmer-Westley polyepoxide and the Townsend-Basak oxidative cyclization hypotheses for the biogenesis of monensin (**23**)



Scheme 5. Nakanishi's biogenetic hypothesis of brevetoxin B (**29**)

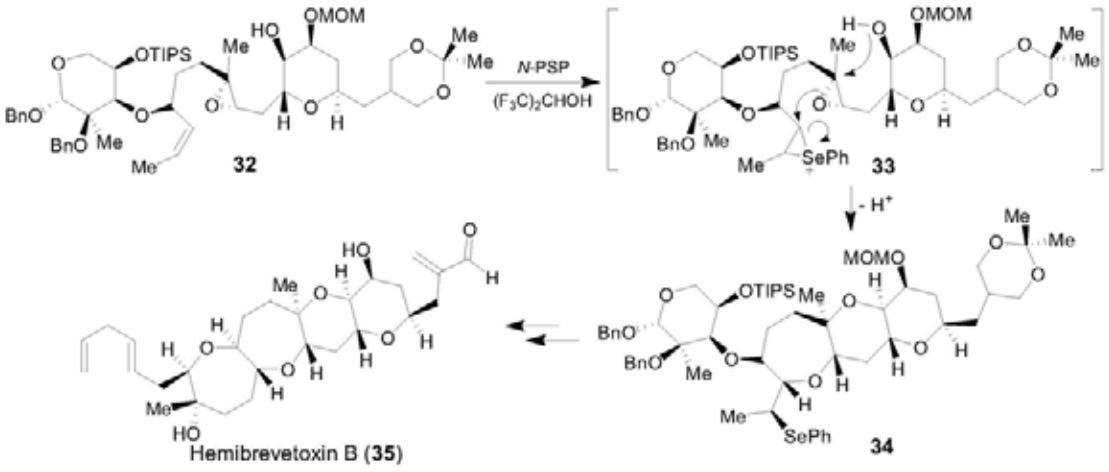
The search for the chemical evidence to support this intellectually appealing biogenesis through biomimetic synthesis was done by several research groups, including those of McDonald and Fujiwara/Murai, who have developed biomimetic approaches to the syntheses of *trans,syn,trans*-fused polycyclic ethers, with special focus on the role of the *endo*-regioselective epoxide polycyclizations.[26,27] Recently, Vilotijevic and Jamison[28] reported that highly regioselective 6-*endo* epoxide opening cascades of polyepoxide **30** in water was achieved through incorporation of a tetrahydropyran (THP) template into the polyepoxide precursor, thus producing the desired polycyclic ether **31** with *trans*,*syn*,*trans*-fusion and *anti*-stereospecific addition (Scheme 6). Notably, high *endo*-selectivity was achieved without directing groups on any of the epoxides when water was used as the cyclization promoter and solvent, although methanol and ethylene glycol were also effective. This inspiring result represented the long sought evidence in favor of Nakanishi's hypothesis of ladder-like polyether biosynthesis (or at least the feasibility).



Scheme 6. Jamison's biomimetic oxacyclization of polyepoxide

Employing a biomimetic epoxide cyclization as the key step, Holton and co-workers[29] reported a convergent total synthesis of natural product hemibrevetoxin B (**35**), which was the first example of a total synthesis accomplished using the *endo*-selective biomimetic cascade oxacyclization of an epoxide. As shown in Scheme 7, treatment of alkene **32** with *N*-phenylselenophthalimide (*N*-PSP) induced the cascade cyclization to form two rings in a single operation, thus giving **34** as a single diastereomer in high yield. The choice of solvent was critical to the success of this

synthesis, with the highly polar HFIP leading to the desired 6-*endo* mode of epoxy alcohol cyclization. This example also clearly demonstrated the power and efficacy of biomimetic synthesis.



Scheme 7. Holton's biomimetic total synthesis of hemibrevetoxin B (**35**)

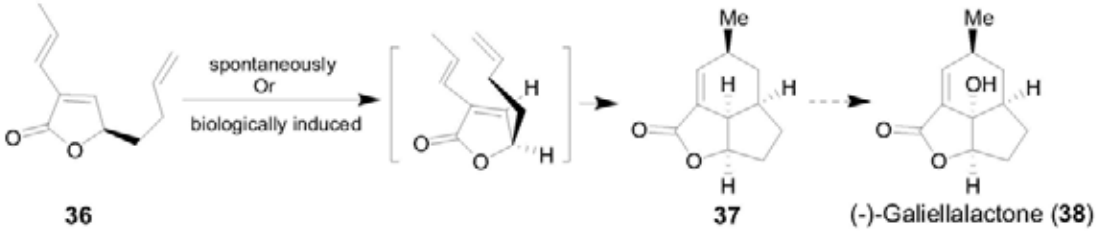
1.4 Biomimetic Diels-Alder cyclization in natural product synthesis

Amongst a large number of organic reactions, the Diels-Alder cycloaddition is perhaps the most powerful and common method to rapidly construct six-membered rings with pre-defined stereochemical outcome. Especially, by using the intramolecular (IMDA) or the transannular (TADA) Diels-Alder reaction or combining them with other transformations, structural complexity and diversity of molecules could be obtained rapidly from simple starting materials.[30] Nowdays, the Diels-Alder cycloaddition has been widely applied in total synthesis so that many total syntheses of natural products would include one Diels-Alder reaction as the key step. A long standing question is whether or not an enzyme would catalyze

Diels-Alder reaction during the biosynthesis procedure. Many research groups have done a great deal of work trying to clarify this Diels-Alderase issue. Although conclusive proof of the existence of Diels-Alderase has remained elusive, several groups have claimed the discovery and identification of a Diels-Alderase-like enzyme.[31] In addition, several investigators have conclusively established that biological macromolecules such as antibodies[32] and ribonucleic acid (RNA)[33] could catalyze the Diels-Alder reactions. As such, it would appear reasonable, despite the absence of confirmed Diels-Alderases, to assume that nature does indeed employ Diels-Alder reactions as the key C-C bond forming reactions to generate a complex array of natural products, even if these reactions proceed only due to activating encapsulation.[34]

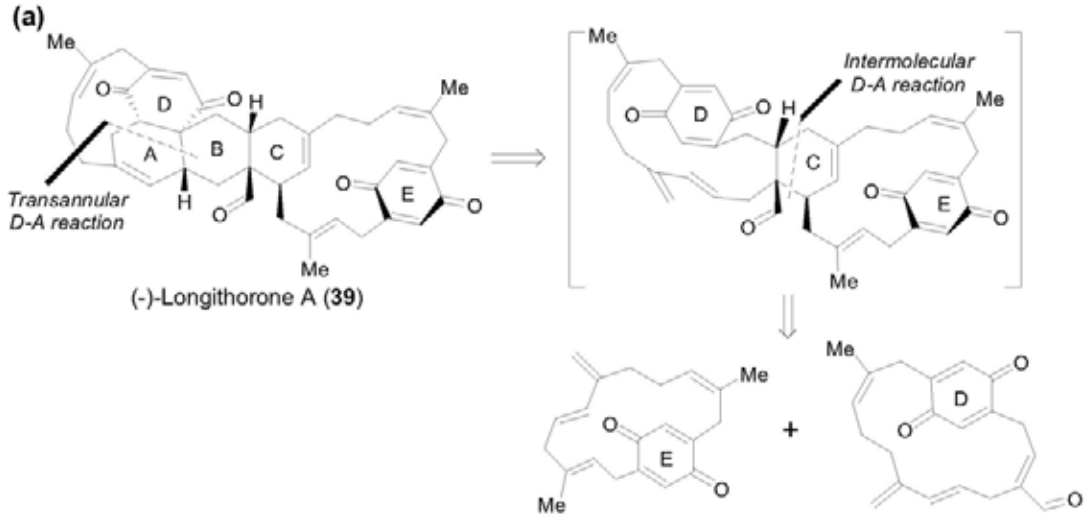
During their biosynthetic study towards (-)-galiellalactone (**38**), Sterner and co-workers[35] reported the cyclization of (-)-pregaliellalactone (**36**) to (+)-desoxygaliellalactone (**37**) which is regarded as the first example of an intramolecular Diels-Alder reaction with inverse electron demand in a polyketide biosynthetic pathway that shows a biological rate enhancement (Scheme 8). They found that the cyclization of **36** could take place spontaneously, the reaction rate could be enhanced by water and the reaction was stereospecific. Notably, they also found that the cyclization could be facilitated in the fungua *Galiella rufa* and led to the same

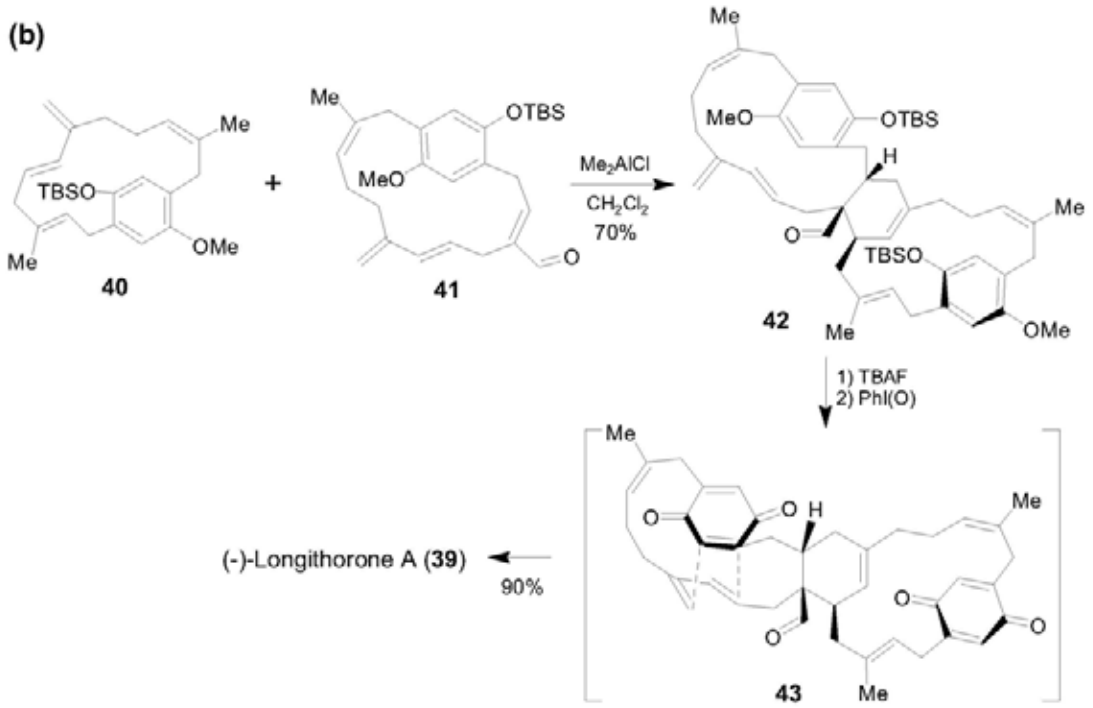
products as that of the spontaneous one. This piece of work showed that an intramolecular Diels-Alder reaction might exist in the biosynthesis of **38**.



Scheme 8. Sterner's biomimetic IMDA studies towards (-)-galiellalactone (**38**)

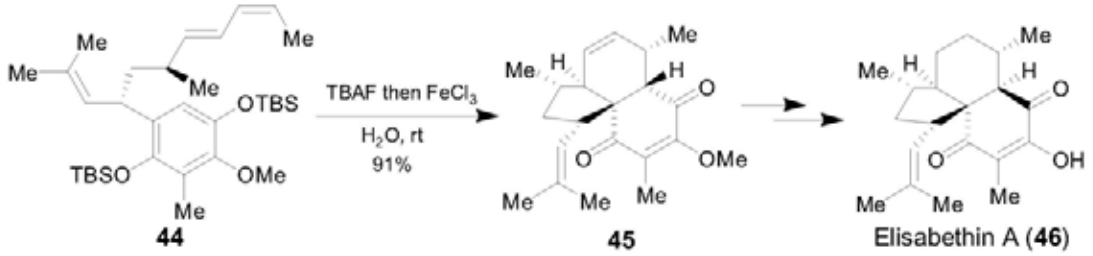
In 2002, Shair and co-workers[36] reported an elegant total synthesis of the marine natural product (-)-longithorone A (**39**) based on a biosynthetic hypothesis proposed by Schmitz and co-workers (Scheme 9(a)).[37] Thus, a Lewis acid catalyzed intermolecular Diels-Alder reaction between diene **40** and dienophile **41** smoothly provided the intermediate **42**. After deprotection, the quinine intermediate **43** underwent an anticipated transannular Diels-Alder reaction at room temperature to produce the desired natural product (-)-longithorone A (**39**) (Scheme 9(b)).





Scheme 9. (a) Schmitz's biogenetic hypothesis and (b) Shair's biomimetic total synthesis of (-)-longithorone A (**39**)

By employing a similar method, Mulzer and Heckrodt[38] reported the convergent total synthesis of diterpenoid elisabethin A (**46**) in 2003 featuring an intramolecular Diels-Alder cycloaddition as a key biomimetic step (Scheme 10).



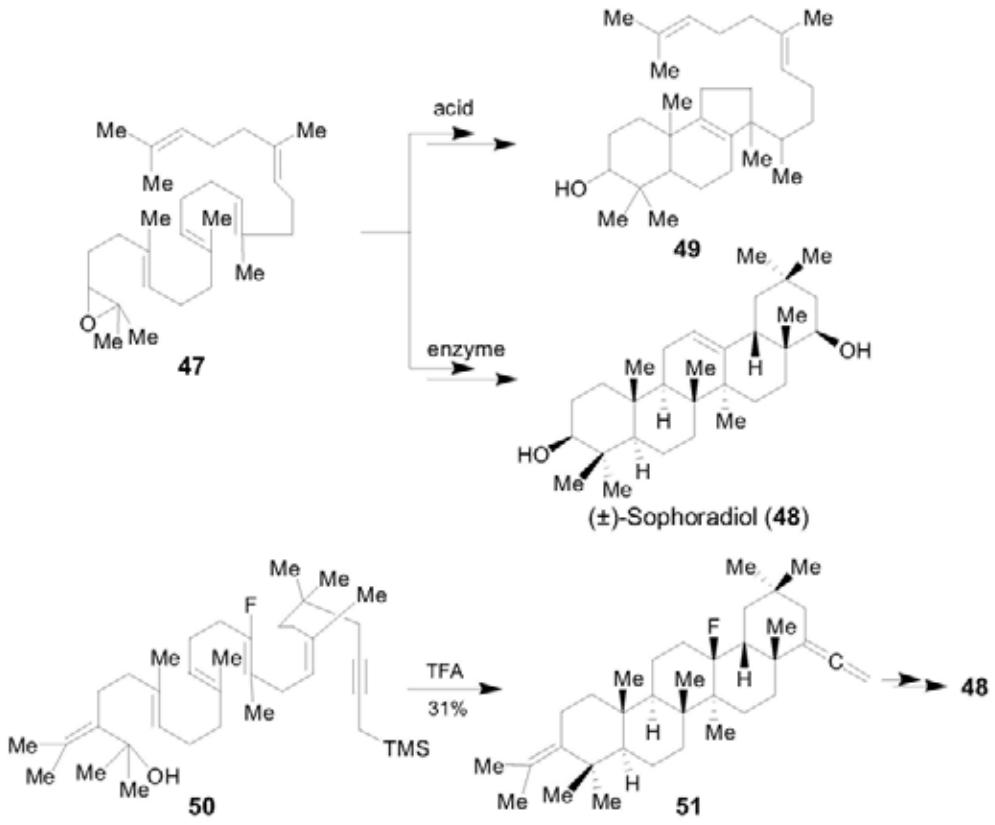
Scheme 10. Mulzer's biomimetic total synthesis of elisabethin A (**46**)

In addition, Williams[39] and Trauner[40] also reported significant work on the application of biomimetic Diels-Alder reactions to the total syntheses of natural products.

1.5 Biomimetic polyene carbocyclization in natural product synthesis

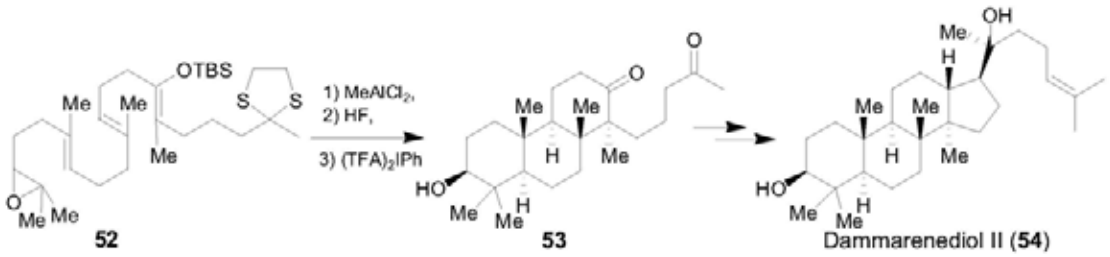
Isoprenoid natural products play a very important biological role in living organisms and are often used as potential drug candidates. The biogenetic research of polcyclic isoprenoids from simple linear polyene substrates has been regarded as the jewel of the biomimetic synthesis.[41] Biomimetic approaches to polycyclic isoprenoids were inspired primarily by the enzyme-mediated cascade cyclization-carbocyclization of squalene.[42,43] Eschenmoser[13] and Stork[14] studied systematically the cation cyclization stereochemistry and its relationship to squalene-triterpene biosynthesis, thereby providing a theoretical and empirical basis for the synthesis of progesterone (**20**) by Johnson.[15] Notably, historically significant contributions from Johnson's laboratories include the development of different initiators and terminators, which have greatly expanded the scope of polyene carbacyclizations. A landmark achieverment of the biomimetic total synthesis of triterpenoid natural prouct was the realization of (±)-sophoradiol (**48**) in 1994.[44] In the model reaction, the enzymatic cyclization of oxidasqualene **47** led to the pentacyclic triterpenoid of the oleanane series **48**, while the acid-catalyzed reaction of **47** led instead to five-membered ring containing species **49**.[45] Fish and Johnson discovered that fluoride as cation-stabilizing auxiliary played a critical role in the formation of the third six-membered ring.[44] Thus, the polyene cyclization of fluoride species **50** could give

the six-membered ring product **51** exclusively and then the natural product **48** was synthesized successfully after several further steps (Scheme 11).



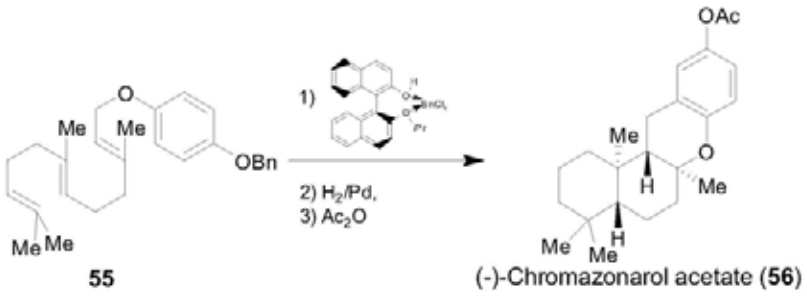
Scheme 11. Johnson's biomimetic total synthesis of (±)-sophoradiol (**48**)

Corey and co-workers[46] have contributed a great deal to the biomimetic polyene carbocyclization. In contrast to Johnson's use of fluoride as a cation-stabilizing auxiliary to control the regioselectivity of six-memered C-ring, Corey utilized the easily obtained enolsilane not only to direct regioselectivity for C-ring formation but also to assist the cascade cyclization due to its remarkable nucleophilicity. The power, efficiency and flexibility of this strategy are clearly demonstrated by many subsequent biomimetic total syntheses of natural products, for example, the synthesis of dammarenediol II (**54**) in 1996[46a] (Scheme 12).



Scheme 12. Corey's biomimetic total synthesis of dammarenediol II (**54**)

Recently, Yamamoto and co-workers[47] reported an enantioselective cyclization of polyenes with Lewis acid-assisted chiral Brønsted acids (chiral LBAs) which was the milestone in the biomimetic cyclization of polyenes. This non-enzymatic attractive method was applied to the synthesis of (-)-chromazonarol acetate (**56**)[47b] (with 44% *ee*) (Scheme 13).



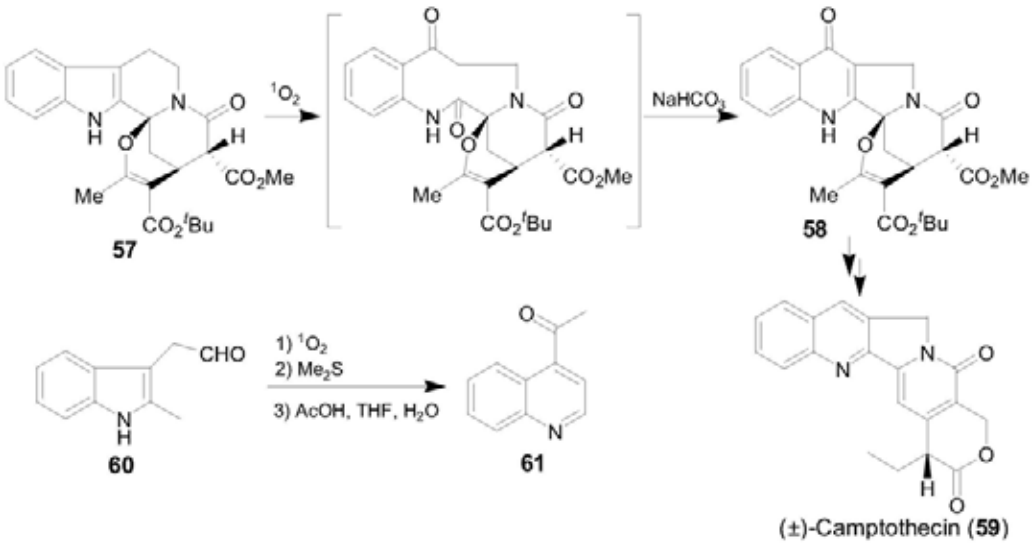
Scheme 13. Yamamoto's biomimetic synthesis of (-)-chromazonarol acetate (**56**)

1.6 Singlet oxygen chemistry in biomimetic synthesis

Singlet oxygen is a highly reactive electrophilic species and a powerful tool in the armament of synthetic organic chemists as well as possibly in that of nature itself, as written by Vassilikogiannakis,[48] *'There is perhaps no reagent that could be said to be more synonymous with biomimetic synthetic strategies than singlet oxygen. This situation arises because in plants and living organisms four crucial prerequisites are met, which favor the production and reaction of singlet oxygen. These criteria are: 1) the presence of natural sunlight providing visible spectrum irradiation; 2) the*

proliferation of photosensitizers (e.g., tannins, porphyrins, and chlorophy II) in the environment; 3) pervasive molecular dioxygen (~ 20% of atmospheric air); and, finally, 4) an abundance of oxidizable substrates, such as terpenes, in the immediate vicinity.' Furthermore, the aqueous cellular environments in plants might facilitate the oxidation by singlet oxygen.

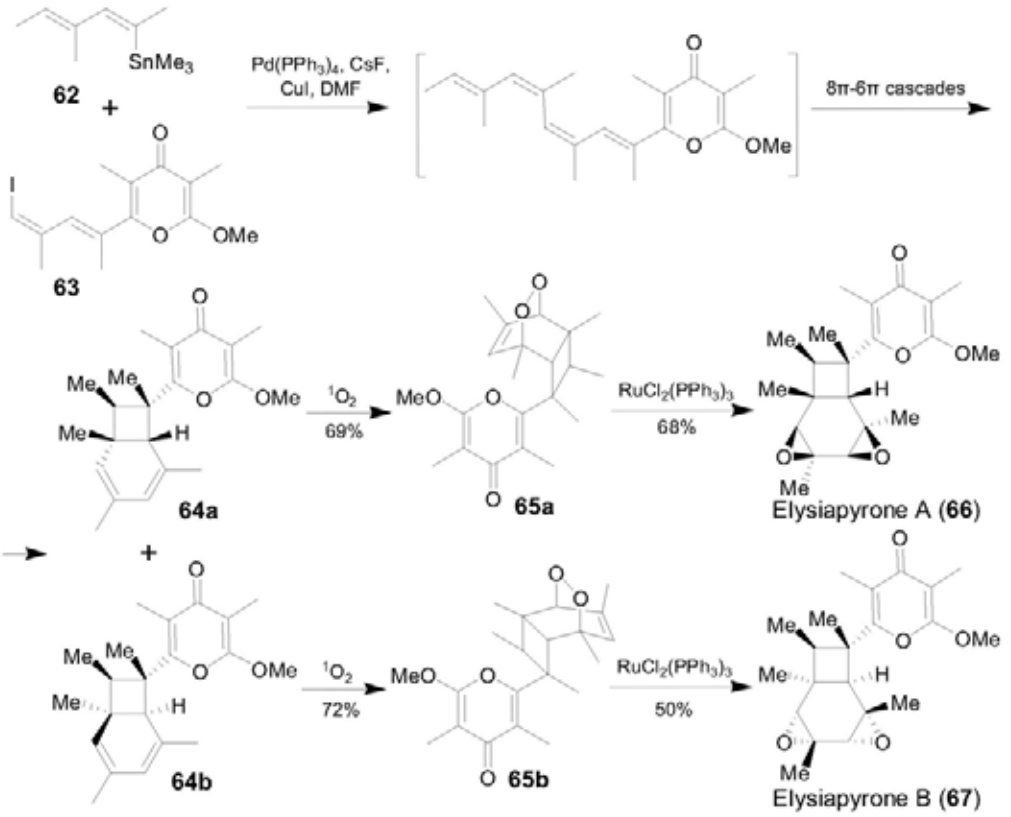
The reaction of $^1O_2$ has been investigated extensively in simple substrates[49] and it has also been applied successfully to the biomimetic total syntheses of natural products. An early example was the investigation by Fukumoto and co-workers[50] about the conversion of indoles to quinolines through singlet oxygen oxidation mediated biomimetic approach. The singlet oxygen oxidation was also applied to the biomimetic synthesis of quinine alkaloid (±)-camptothecin (**59**)[51] (Scheme 14).



Scheme 14. Fukumoto's biomimetic conversion of indoles to quinolines by using $^1O_2$

Recently, Trauner and co-workers[52] reported biomimetic total syntheses of elysiapyrones A (**66**) and B (**67**). Thus, the intermediates **64a** and **64b**, produced through the proposed biogenetic 8π-6π electrocyclization cascade reactions[53] from compounds **62** and **63**, were treated with singlet oxygen to give *endo*-peroxides **65a**

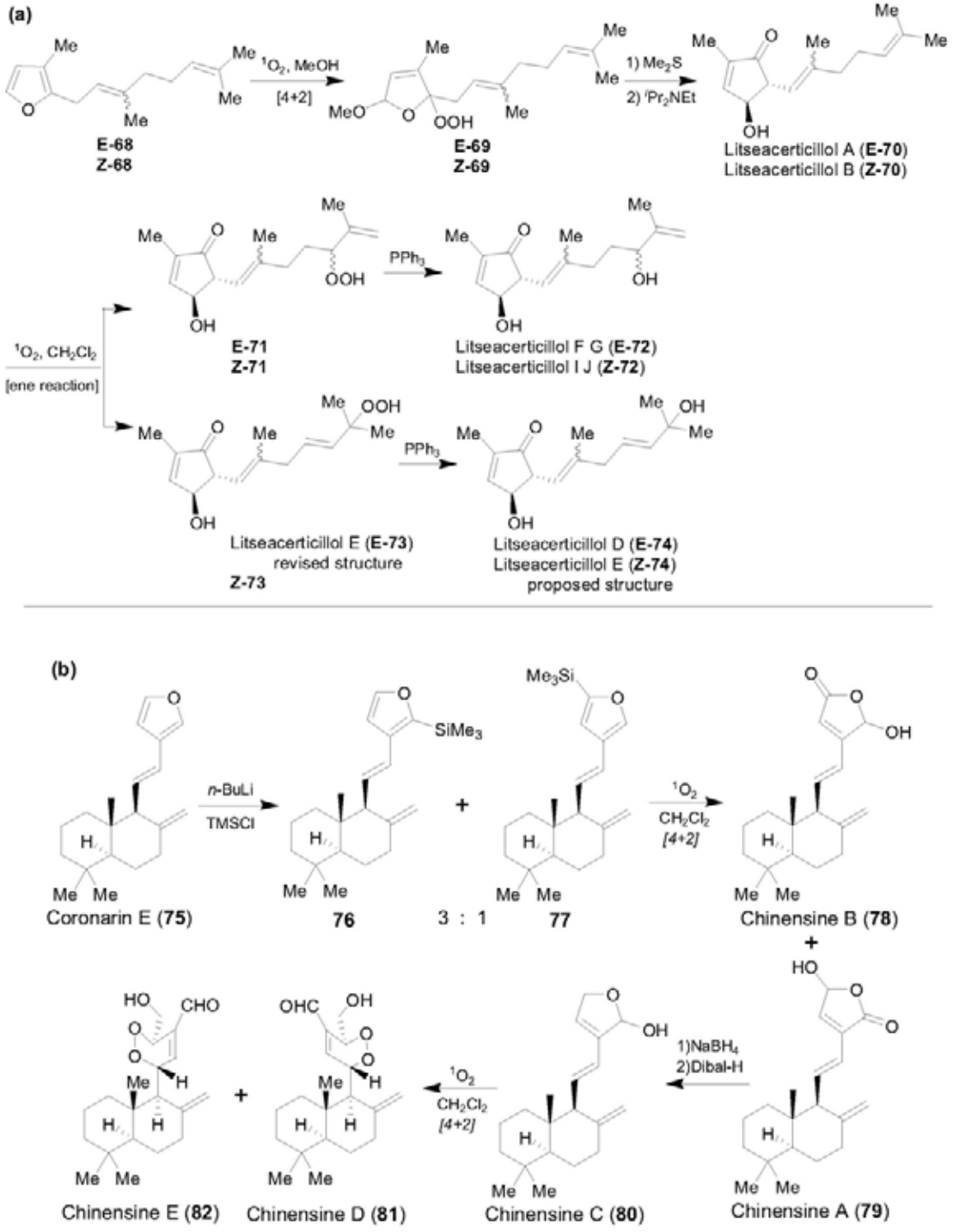
and **65b**, and the subsequent transition-metal catalyzed isomerization provided two natural products (Scheme 15).



Scheme 15. Trauner's biomimetic syntheses of elysiapyrones

The power of singlet oxygen in the biomimetic syntheses of natural products was exemplified again by the syntheses of a series of terpenoids by Vassilikogiannakis and co-workers.[48] For example, recently, they completed the biomimetic total syntheses of litseacerticillols,[54] during which two kinds of singlet oxygen oxidation, [4+2] cycloaddition with furan species and ene reaction with side chain, were applied to provide the natural products efficiently (Scheme 16 (a)). In 2007, the same group reported the biomimetic total syntheses of chinensines A-E[55] using singlet oxygen involved [4+2] cycloaddition twice by starting from naturally occurring coronarin E (**75**) (Scheme 16 (b)). These promising examples illustrate that singlet oxygen is perhaps a major player in the late stage biosynthesis and manipulation of

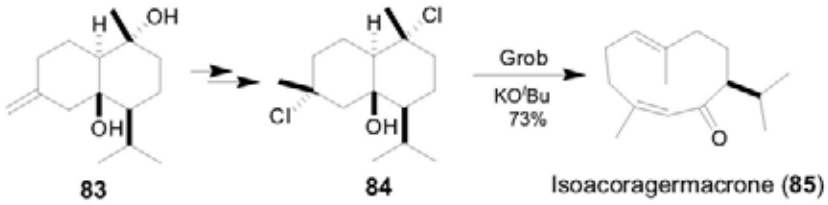
polyoxygenated terpenoid natural products.



Scheme 16. Vassilikogiannakis's biomimetic syntheses of litseacerticillols and chinensines

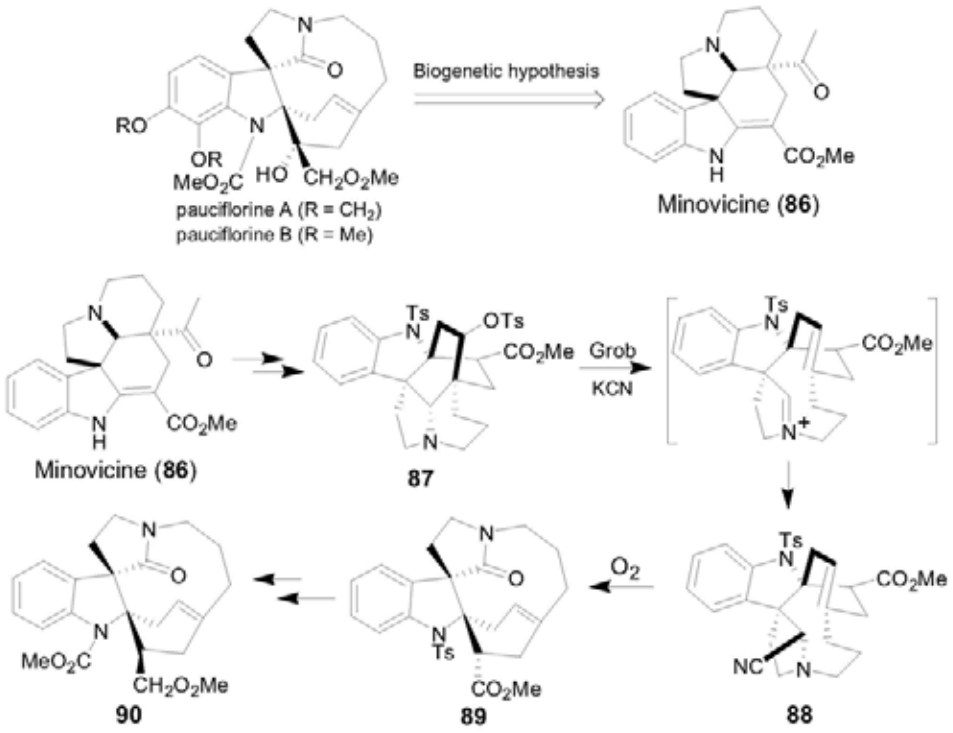
1.7 Biomimetic Grob fragmentation

Grob fragmentation is a very useful method to construct novel structures through ring-opened or ring-enlarged fashions. This reaction has been applied to many total syntheses of natural products as one of the key transformations. Holton's[56] total synthesis of taxol and Paquette's[57] total synthesis of jatrophatrione are two relevant examples. In addition, this fragmentation reaction was also involved in the biomimetic syntheses of many natural molecules. An early example was Iguchi and co-workers' biomimetic transformation of isoacoragermacrone (**85**)[58] through a key Grob fragmentation of the intermediate **84** which was a derivative of the naturally occurring sesquiterpene isocalamendiol (**83**) (Scheme 17).



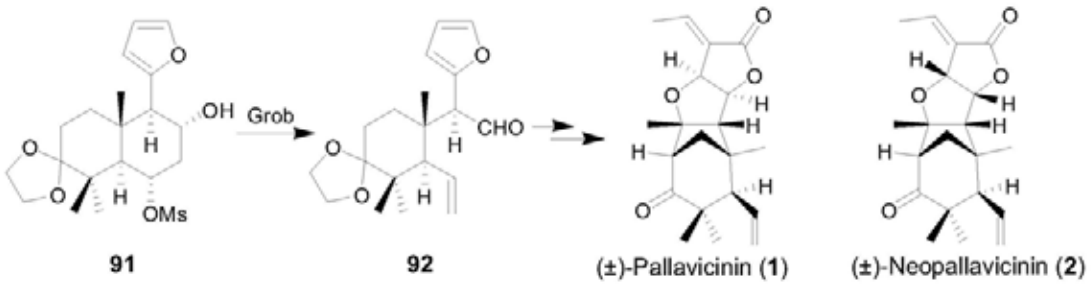
Scheme 17. Iguchi's biomimetic synthesis of isoacoragermacrone (**85**)

In 1999, Kuehne and co-worker[59] reported a biomimetic synthesis of the pauciflorine skeleton **90** from the proposed biogenetic precursor minovicine (**86**). During which, they applied a cyanide mediated Grob fragmentation of tosylate **87** and the subsequent oxidation to form the core skeleton of natural products (Scheme 18).



Scheme 18. Kuehne's biomimetic synthesis of the skeleton **90** of pauciflorine A and B

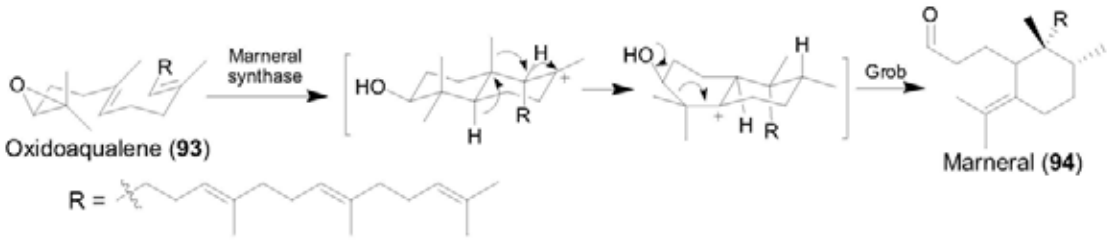
In addition, during the total syntheses of (±)-pallavicinin (**1**) and (±)-neopallavicinin (**2**)[60] achieved in our laboratory, Grob fragmentation as one of the key steps (**91** to **92**) was also employed to support the biogenetic hypothesis (Scheme 19).



Scheme 19. Biomimetic syntheses of (±)-pallavicinin and (±)-neopallavicinin

In 2006, Matsuda and co-workers[61] provided the first experimental proof of Grob fragmentation in triterpene biosynthesis. They characterized the *Arabidopsis thaliana* triterpene synthase gene *At5g42600* and found that the encoded enzyme annulated

oxidoaqualene (**93**) to a bicyclic intermediate, which underwent 1,2-shifts to a C5 cation. Ring A was then cleaved to form the 3,4-*seco* aldehyde **94** (they named **94** as marneral and named the enzyme as marneral synthase) (Scheme 20).



Scheme 20. Grob fragmentation in triterpene biosynthesis

1.8 Final episode

In addition to the above mentioned inspiring improvements in biomimetic total syntheses of natural products, Baldwin's group[62] also did a lot of excellent work in this field.

Besides, Baran, who has gradually become one of the outstanding organic chemists in the world, has done many fascinating works on organic syntheses.[1d] Actually, during Baran's intriguing syntheses, he always emphasizes the biosynthetic origins of natural products and then designs and practices the most straightforward synthetic routes during which chemoselective transformations would serve as the key points.

Biomimetic natural product synthesis is a very complex and exciting field of chemistry. By combining biomimetic synthesis and retro-synthetic analysis, chemists

can do a lot of significant work to illustrate the origin of natural molecules.[63] As written by Pettus: *Chemists should ponder probable biosynthetic pathways leading to their target, because few things are more humbling to one's best-laid plans than nature's simpler solution. Nature has been conducting and optimizing chemical experiments for millions of years, therefore, matching or exceeding nature's accumulated wisdom is a daunting challenge. However, the precise sequence used by nature to assemble its product is rarely known. In these instances, synthetic chemists are empowered with the ability to illuminate nature's hidden pathways by determining the reactivity inherent to its intermediates.*[64]

Chapter 2. Biomimetic Total Synthesis of (±)-Pallavicinolide A (3)

2.1 Introduction and background

2.1.1 General background

For a long time, the bryophytes have been used widely as medicinal plants in China to treat cuts, burns, external wounds, bacteriosis, pulmonary tuberculosis, neurasthenia, fractures, convulsions, scalds, uropathy, pneumonia, etc. Among the bryophyte species, the chemical constituents of liverworts have been investigated in most detail because the liverworts contain cellular oil bodies which are easily extracted by organic solvents. Liverworts biosynthesize a lot of lipophilic terpenoids, aromatic compounds and acetogenins which constitute the oil bodies. So far, nearly 1000 terpenoids have been isolated from or detected in the liverworts and their structures were elucidated. Many of them show interesting biological activities, such as antimicrobial, antifungal, cytotoxic, insect antifeedant, insecticidal, muscle relaxing, some enzyme inhibitory and apoptosis inducing activities.[65]

Pallavicinia species are very small thalloid liverworts. In 1994 and 1999, from the Taiwanese liverwort *Pallavicinia subciliata* (Aust.) Steph. collected at Tatung Shan, Taipei Hsien, Wu and co-workers isolated two diterpenoids with novel

skeletons, named pallavicinin (**1**)[66a] and neopallavicinin (**2**)[66b] and their structures were confirmed by NMR and/or X-ray analysis (Figure 1).

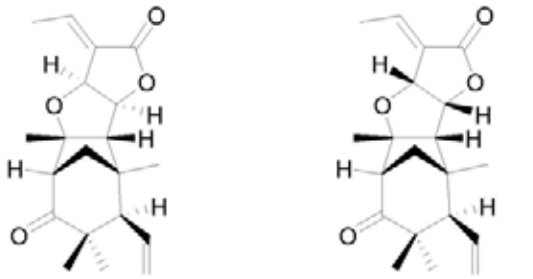


Figure 1. The structures of pallavicinin and neopallavicinin

In 1998, Asakawa and co-workers reported the isolation and structural elucidation of several pallavicinin-related diterpenoids (**1**, **3-8**)[67] isolated from the Japanese liverwort *Pallavicinia subciliata* (Aust.) Steph. collected in Tsushima, Nagasaki (Figure 2). In addition, the authors gave the general biogenetic pathway from labdane. In 2005, Lou group[68] from China isolated the natural compounds **1**, **2** and **8** again from the Chinese liverwort *Pallavicinia ambigua* (M_{ITT}) collected in Mount Wuyi, Fujian province. They also established the absolute configurations of these three molecules based on NMR and circular-dichroism (CD) analyses.

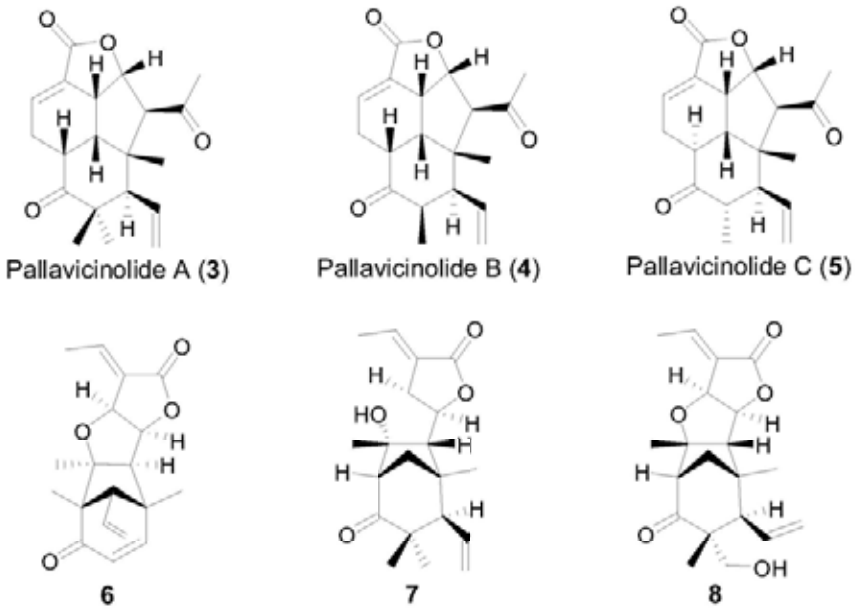


Figure 2. The structures of **3-8**

The unique structural features of these secolabdane-type diterpenoids and their potential bioactivities attracted our attention toward their total syntheses. The total syntheses of pallavicinin (**1**) and neopallavicinin (**2**) have been achieved by our group[60] and studies towards another natural product **6** are still in progress. Our present work is the biomimetic total synthesis of natural diterpene **3** and our group's future targets are the total syntheses of another two diterpenes **4** and **5**. Herein we coined them pallavicinolide A (**3**), pallavicinolide B (**4**) and pallavicinolide C (**5**).

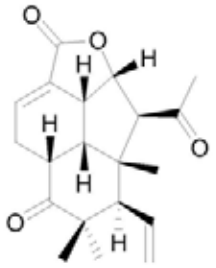
2.1.2 Collection, extraction and isolation of pallavicinolide A (3)

In 1998, Asakawa and co-workers[67] isolated several novel skeletal diterpenoids, including pallavicinolide A (**3**), from the Japanese liverwort *Pallavicinia subciliata* (#96052, dry weight 317.5 g) which was collected in Tsushima, Nagasaki, in May 1996. The diethyl ether extract was chromatographed on silica gel and then on

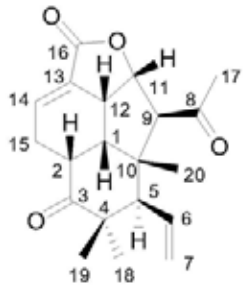
Sephadex LH-20 to give a mixture. Further purification of the mixture by preparative HPLC on silica gel afforded pallavicinolide A (**3**) in 0.56% yield of the extract. In addition, this diterpene was also isolated from *P. subciliata* (#95156) collected in Tokushima, Japan, in July 1995.[67]

2.1.3 Structural elucidation of pallavicinolide A (3)

The gross structure of pallavicinolide A (**3**) was deduced by extensive 2D-NMR experiments involving the determination of ^{1}H-^{1}H COSY, NOESY, HSQC and HMBC spectra. Furthermore, the final structure and relative stereochemistry of **3** were established by comparing its spectra data with those of known compounds, such as pallavicinin (**1**). In addition, natural pallavicinolide A (**3**) showed a optical rotation value of $[\alpha]_D = -34.2^{o}$ ($CHCl_3$, *c* 4.73). The ^{1}H NMR and ^{13}C NMR spectral data were shown in Table 1. However, the absolute stereochemistry of **3** was not established in the isolation paper.[67] We have named this natural product "pallavicinolide A".



Pallavicinolide A (**3**)



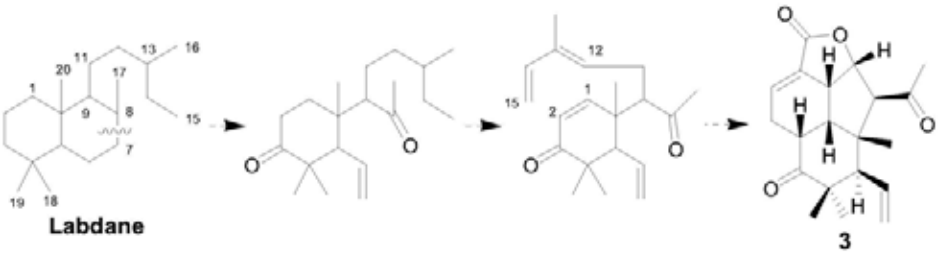
Pallavicinolide A (**3**)

Atom	^{1}H (Hz) ($CDCl_3$)	^{13}C ($CDCl_3$)
1 CH	2.99 (dd, *J*=10, 11 Hz)	48.3
2 CH	3.32 (ddd, *J*=2, 4, 11 Hz)	44.1
3 C	-	216.1
4 C	-	44.9
5 CH	2.67 (d, *J* = 11 Hz)	55.7
6 CH	5.87 (ddd, *J* =10, 11, 16) Hz)	136.4
7 CH_2	*cis*: 5.27 (dd, *J* =2, 10 Hz) *trans*: 5.15 (dd, *J* =2, 16 Hz)	119.8
8 C	-	207.0
9 CH	2.39 (d, *J* =8 Hz)	60.6
10 C	-	47.2
11 CH	5.15 (dd, *J* =8, 8 Hz)	82.2
12 CH	3.36 (dddd, *J* =3, 3, 8, 10) Hz)	40.3
13 C	-	127.1
14 CH	7.37 (ddd, *J* =3, 3, 8 Hz)	141.3
15 CH_2	α: 2.74 (ddd, *J* =2, 8, 15 Hz) β:1.91(dddd, *J* =3, 3, 4, 15 Hz)	26.1
16 C	-	168.6
17 CH_3	2.25 (s)	31.8
18 CH_3	1.07 (s)	28.7
19 CH_3	0.98 (s)	28.4
20 CH_3	1.11 (s)	23.7

Table 1. ^{1}H and ^{13}C NMR spectral data for natural pallavicinolide A (**3**)

2.1.4 Biogenetic hypothesis of pallavicinolide A (3)

Pallavicinolide A (**3**) is a modified labdane-type diterpene and its biosynthetic pathway is also a considerable interesting scientific focus. It was presumed by Asakawa that the biosynthesis was performed by C7-C8 bond cleavage of labdane analogus followed by bond reconstruction of C1-C12 and C2-C15 (Scheme 21).[67]



Scheme 21. The biogenetic hypothesis of pallavicinolide A (**3**)

From the viewpoint of chemical synthesis, C7-C8 bond cleavage to vinyl ketone species is actually a Grob fragmentation reaction and bond reconstruction of C1-C12 and C2-C15 could be achieved by intramolecular Diels-Alder cycloaddition.

2.1.5 Aim of the present work

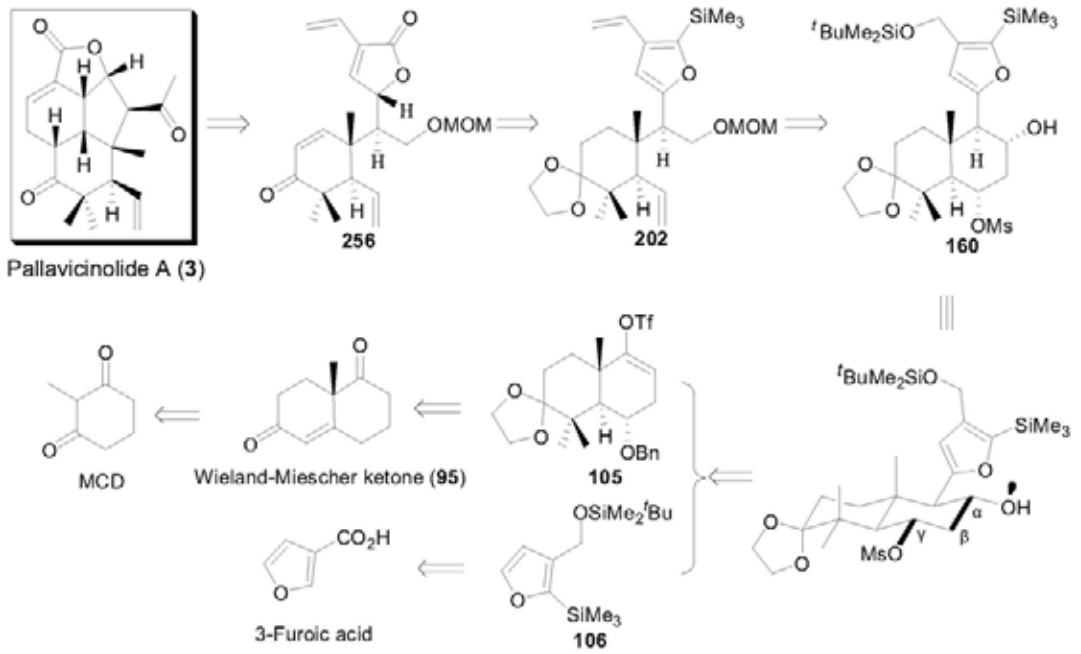
Pallavicinolide A (**3**) is a 7,8-*seco* labdane-type diterpene. The novel tetracyclic-fused skeleton with seven contiguous stereocenters makes it particularly challenging target from a chemical synthesis viewpoint. Interestingly, the fact that the four neighboring bridgehead protons point to the same face, results in a bowl-like 3-dimensional structure based on our model studies. To the best of our knowledge, this kind of framework has rarely been found in naturally occurring molecules. Besides the intriguing molecular architecture, the potential bioactivities and the biosynthetic pathway of **3** are also very interesting. Therefore, we would like to investigate the proposed biogenetic hypothesis and to better understand the

biosynthetic origins of pallavicinin family by realizing the total synthesis of **3**. In addition, in our group, the total syntheses of several natural products have been achieved by starting from furan species and our present work is the extension of furan chemistry in natural product synthesis extensively developed by our group.[60,69] Herein we describe in detail the first total synthesis of (±)-pallavicinolide A (**3**) using a biomimetic approach.

2.2 Results and discussion

2.2.1 Retrosynthetic analysis of pallavicinolide A (3)

Based on the structure of our target **3**, its proposed biosynthetic pathway and our recent success in the total syntheses of natural products starting from furan species, we present the following retrosynthetic analysis (Scheme 22).



Scheme 22. The retrosynthetic analysis of pallavicinolide A (**3**)

As shown in Scheme 22, we envision that the molecular complexity of **3** could be achieved through an intramolecular Diels-Alder (IMDA) cycloaddition[70] of butenolide **256**, in which the three new stereogenic centers could be formed

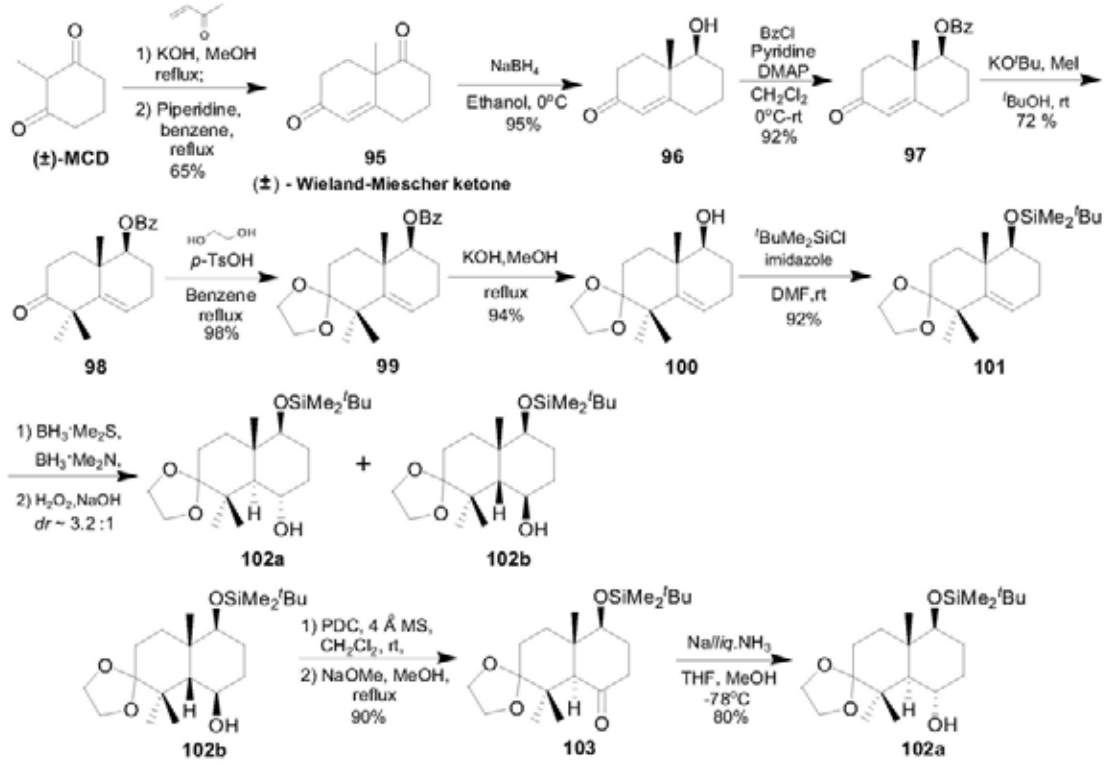
stereoselectively in one single step. Butenolide **256**, in turn, can be produced by the oxidation of furan **202**. Alkene **202** can be generated through a Grob fragmentation[71] of bicyclic mesylate **160** which is disconnected to known triflate **105**[60] and furan subunit **106**. As developed in our group, triflate **105** could be prepared easily from the simple starting material 2-methyl-1,3-cyclohexanedione (MCD) through the intermediate Wieland-Miescher ketone. Another building block **106** could be prepared from the commercially available 3-furoic acid through 3 steps.

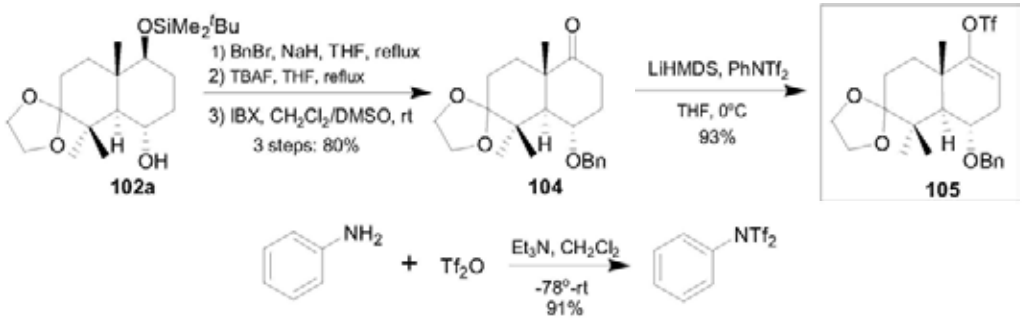
During our synthetic route, three key biomimetic transformations will be included to support the biogenetic hypothesis. They are Grob fragmentation, singlet oxygen oxidation, and intramolecular Diels-Alder reaction, respectively. The precursor of Grob fragmentation, mesylate **160**, could be produced smoothly with fully controlled stereochemistry, in which the oxygen lone pair is oriented *anti*-periplanar to the bond of cleavage [C(α)-C(β) bond and the leaving C(γ)-OMs bond]. The Grob fragmentation will take place smoothly when using KO^{t}Bu as a deprotonation reagent to yield the opened skeleton for compound **202**. In previous work of our group, the oxidation of furan species using peroxyacetic acid was successfully applied into the total syntheses of natural products containing furanone moiety.[60,69] In our present case, however, the oxidation by using similar conditions could not give the desired α,β-butenolide, and at last we discovered that the oxidation using singlet oxygen gave the desired skeleton of **256** successfully. Notably, in the literature, there have been many reports on biogenetic syntheses employing oxidation with single oxygen.[72] At last, the intramolecular Diels-Alder cycloaddition occurred rapidly once the precursor **256** was obtained and the product with full of desired stereochemistry will be formed selectively due to the more favored *cis*-fused bicyclo[3.3.0] system and the steric hindrance of methyl group. Herein, we give a detailed discussion toward the

successful total synthesis of pallavicinolide A (**3**) by using a biomimetic approach.

2.2.2 Preparation of triflate 105

Although the preparation of intermediate triflate **105** had been reported previously from our group,[60] we still made some improvements in the detailed procedures. Thus, (±)-Wieland-Miescher ketone (**95**) was prepared in large scale through the Robinson annulation between 2-methyl-1,3-cyclohexanedione (MCD) and methyl vinyl ketone (MVK).[73] It was noteworthy that piperidine as an alternatives could be used instead of pyrrolidine. In addition, during the aldol cyclization, high concentration of reaction mixture was necessary and we found that the reaction could be completed within 4 h if the solvent was removed continually (including benzene and formed H_2O) from the reaction by distillation under normal atmosphere untill no solvent remained. Then the reaction residue could be used directly for the next reduction step without further work-up or purification.



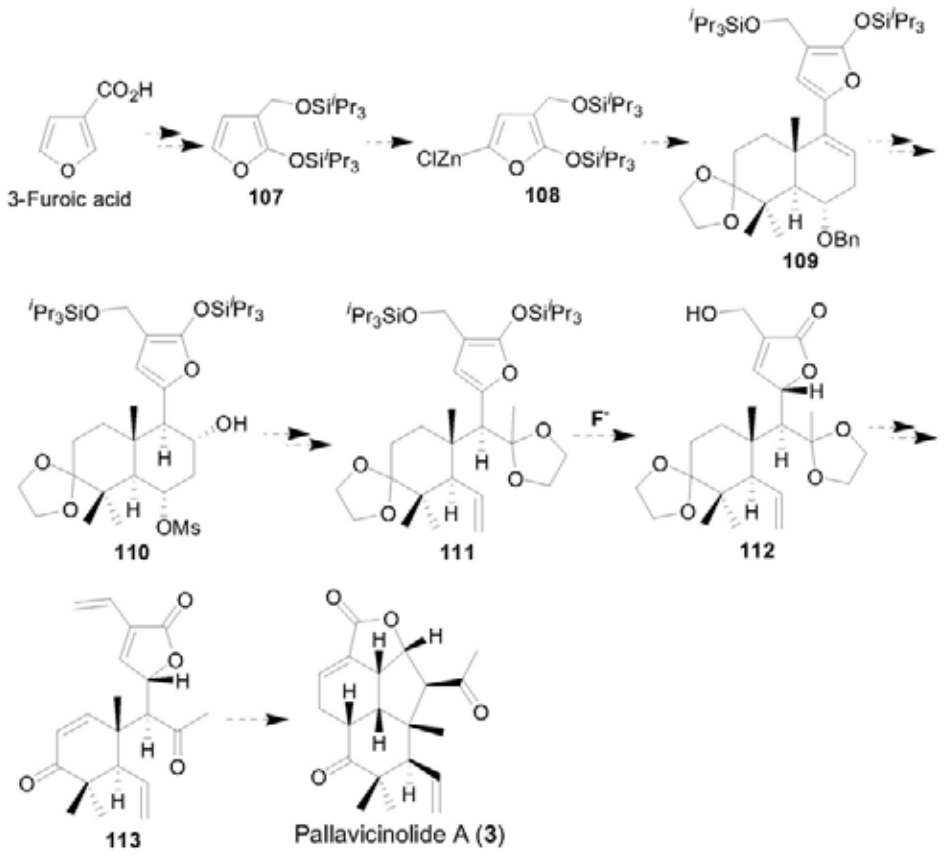


Scheme 23. The preparation of the triflate **105**

The next reduction of ketone **95** using $NaBH_4$ gave alcohol **96** in a good yield (95%) and good stereoselectivity (*dr* > 20:1). In this step, an excess of acetic acid used to quench the reaction should be neutralized using saturated $NaHCO_3$, otherwise, the next acylation will be affected. During the protection toward **97**, CH_2Cl_2 as solvent should be used and a catalytic amount of DMAP was added to speed up the reaction. The transformations from **97** to **101** were followed the previously reported procedures.[60] For the hydroboration/oxidation of **101**, we found that the reaction temperature should be controlled strictly (less than 25 °C), otherwise, it will give more side-products. Notably, we could isolate the desired alcohol **102a** in 36% yield directly with a side-product **102b** (about 11%) based on 70% conversion of olefin **101**. The side product **102b** could be converted back to **102a** through 3 steps. The transformations from **102a** to **104** were again followed the reported procedures.[60] For the last step, we found that the reaction between ketone **104** and *N*-phenyl-bis(trifluoromethanesulfonimide) ($PhNTf_2$), which was prepared from aniline and trifluoromethanesulfonic anhydride,[74] gave better reproducible results when LiHMDS was chosen as a base instead of LDA. Thus, the key intermediate **105** was yielded through 12 steps starting from MCD (Scheme 23) with an overall yield of 12.9%.

2.2.3 Preparation of furan derivative 106

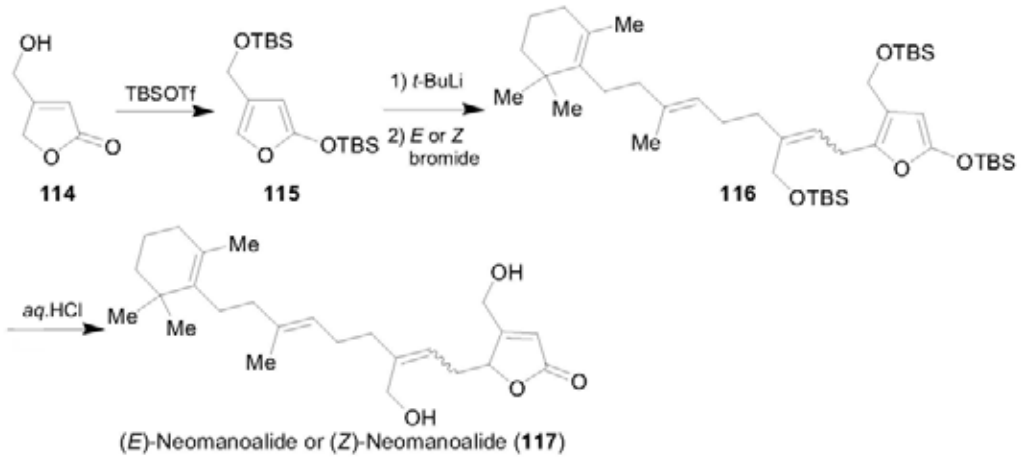
Our initial synthetic plan was to use siloxyfuran species **107** as the synthetic equivalent of butenolide as shown in Scheme 24. Thus, once we could obtain **107**, the Negishi[75] coupling between triflate **105** and furylzinc chloride **108** formed *in situ* from **107** will provide intermediate **109**. After several steps including the key Grob fragmentation, we hoped that intermediate **111** would be produced, which would be treated with fluoride to provide the desired butenolide **112** stereoselectively. Then after several subsequent steps including the key intramolecular Diels-Alder cycloaddition, the desired product **3** would be obtained (Scheme 24).



Scheme 24. The initial designed synthetic route toward **3**

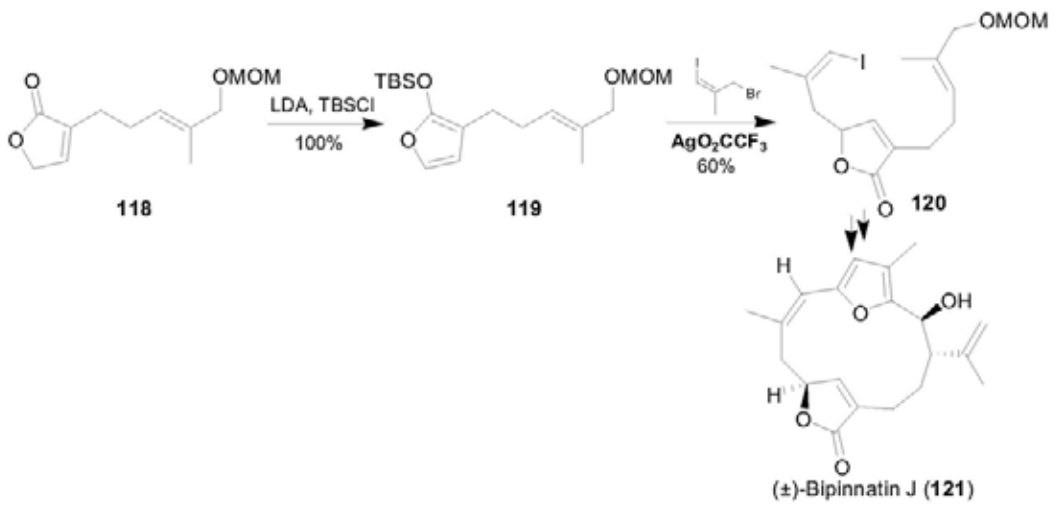
In fact, in literature, there are many examples in which 2-siloxyfuran was used as the synthetic equivalent of butenolide. Herein we give two examples using

2-siloxyfuran in organic synthesis. In 1994, Jefford and co-workers[76] reported a concise synthesis of sesterterpene, (*E*)- and (*Z*)-neomanoalides (**117**) by an appropriate application of furanolate technology. Thus, the easily obtained siloxyfuran **115** from reagent **114** was lithiated and then coupled with an allyl bromide to deliver furanolate **116**. Final treatment with acid gave the desired butenolide (*E*)- and (*Z*)-neomanoalides (**117**) (Scheme 25).



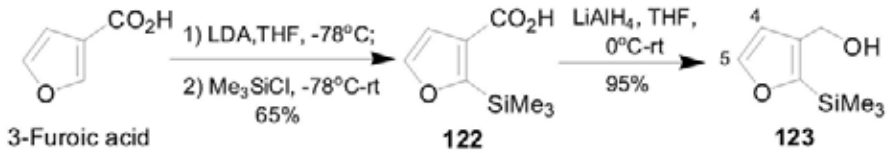
Scheme 25. The concise syntheses of (*E*)- and (*Z*)-Neomanoalides (**117**)

In 2006, Rawal[77] reported the total synthesis of (±)-bipinnatin J (**121**) featuring the use of a silver ion promoted S_N1-type γ-alkylation of a siloxyfuran. Siloxyfuran **119**, obtained from the silylation of the enolate of intermediate **118**, was treated with the requisite allylic bromide in the presence of silver trifluoroacetate, affording the desired alkylation product **120** which would elaborate to natural product (±)-bipinnatin J (**121**) through several subsequent steps (Scheme 26).



Scheme 26. The total synthesis of (±)-bipinnatin J (**121**) using siloxyfuran chemistry

Then we began to prepare siloxyfuran **107** starting from the commercially available 3-furoic acid. Thus, 3-furoic acid underwent preferentially 2-lithiation, due to the electron-withdrawing effect of the carboxyl group as well as the stabilizing coordination between the oxygen of the carboxyl group and lithium cation,[78] subsequent silylation[79] led to the formation of compound **122** in 65% yield. Reduction of compound **122** using $LiAlH_4$ provided alcohol **123** in high yield (Scheme 27).

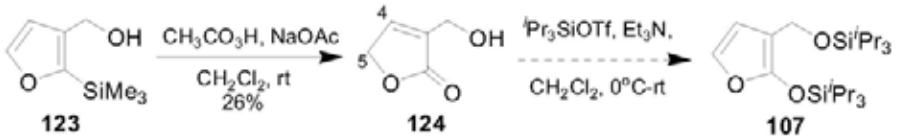


Scheme 27

In the ^1H NMR spectrum (300 MHz, $CDCl_3$), the resonance signals of TMS (δ_H 0.30, s, 9H), neighboring H-4 (δ_H 6.44, d, J = 1.4 Hz, 1H) and H-5 (δ_H 7.56, d, J = 1.4 Hz, 1H), showed that **123** was 2-silylated. The presence of a hydroxymethyl group in **123** was evident from the resonances of a hydroxyl proton (δ_H 2.26, brs, 1H) and methylene protons (δ_H 4.58, s, 2H). Thus, the structure of **123** was established.

With the success of generating compound **123**, we then moved to the next step.

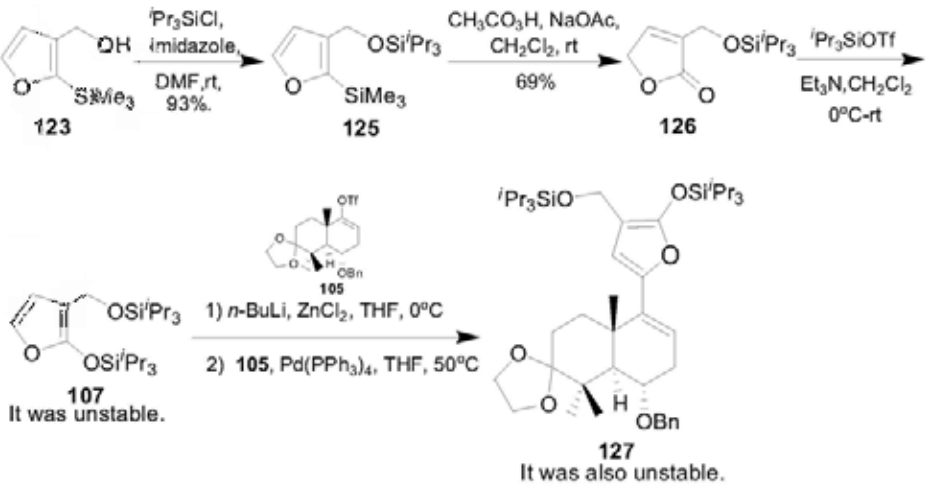
Firstly, we attempted to prepare siloxyfuran **107** through butenolide **124**. Thus, the furan derivative **123** was treated with freshly prepared peroxyacetic acid. After stirring overnight, a more polar compound **124** was obtained as the major product. After purification with column chromatography, **124** was collected as a white oil but the yield was only 26% (Scheme 28). The ^{1}H and ^{13}C NMR data of **124** were in agreement with those reported in the literature.[149] The low yield of **124** was probably due to its solubility in water and its low boiling point.



Scheme 28

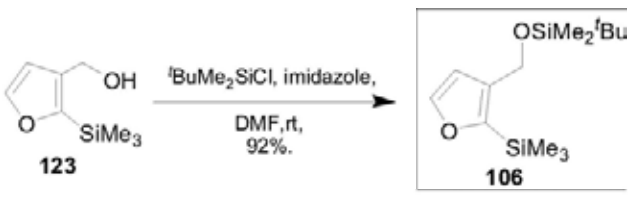
Then another route was attempted. Firstly, alcohol **123** was protected to form **125**, which was easily oxidized to the corresponding butenolide **126** in good yield. For butenolide **126**, the resonance signals at δ_H 7.39 (t, J = 2.0 Hz, 1H) in its ^{1}H NMR spectrum (300 MHz, $CDCl_3$) and δ_C 172.65 in its ^{13}C NMR spectrum (75 MHz, $CDCl_3$) demonstrated the presence of the desired α,β-unsaturated lactone motif. The molecular formula was established as $C_{14}H_{26}O_3Si$ based on its HRMS analysis. The subsequent reaction with triisopropylsilyl trifluoromethanesulfonate yielded the much less polar siloxyfuran **107**. In the crude ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **107**, the resonance signals for TIPS (δ_H 0.88-1.05, m, 42H), neighboring H-4 (δ_H 6.31, d, J = 2.3 Hz, 1H) and H-5 (δ_H 6.99, d, J = 2.3 Hz, 1H), confirmed the presence of 2,3-disubstitued furan species. The presence of a methylene group in **107** was evident from the resonance of methylene protons (δ_H 4.43, s, 2H). Thus, the structure of **107** was established. However, we found that siloxyfuran **107** was not stable and it could not be purified by column chromatography even though the silica gel used was

pretreated using base. In fact, siloxyfuran **107** was found to give butenolide **126** when it was treated with silica gel. Then the Negishi coupling between triflate **105** and crude siloxyfuran **107** was examined and the desired product **127** was formed smoothly based on TLC, crude NMR and MS analysis. Unfortunately, siloxyfuran **127** was also not stable so that column chromatography purification could not be performed (Scheme 29).



Scheme 29

In consideration of the instability of siloxyfuran species, we turned our attention to the use of more stable 2-silylfuran, such as **125**. Thus, the 2-silylfuran intermediate would be oxidized to the corresponding butenolide by using peroxyacetic acid or other methods at a late stage. Alcohol **123** was protected as the more routine TBS derivative **106** in high yield (92%), whose structure was substantiated by ^{1}H NMR, ^{13}C NMR and HRMS spectrometric analyses (Scheme 30).

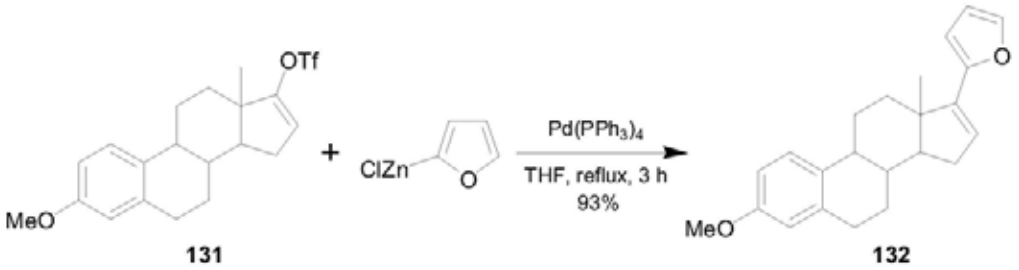


Scheme 30

2.2.4 Preparation of the precursor 160 for Grob fragmentation

With the two key intermediates **105** and **106** in hand, we began to search a good method to link them together.

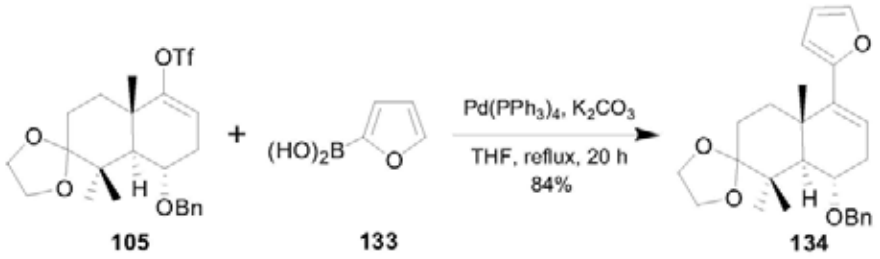
Metal-catalyzed cross coupling reactions represent the most powerful and useful C-C formation methods in organic synthesis. Most total syntheses make use of at least one metal-catalyzed coupling as a key step.[80] Pd- or Ni- catalyzed Negishi coupling between organozinc and electrophilic partners such as triflates or halides has been widely used in organic synthesis. The cross coupling of vinyl triflate with furylmetallic reagents has been examined and represents a useful tool for the syntheses of substituted furan species.[81] As shown in Scheme 31, triflate **131** was coupled with the freshly prepared furyl zinc chloride to afford vinyl furyl intermediate **132** in high yield.[82]



Scheme 31

Cross-coupling reaction of organoboron compounds under the activation of suitable base, which is called Suzuki reaction, was developed to be a routine method for carbon-carbon formation.[83] Notably, comparing with the use of other organometallic reagents, more attention was focused on that of organoboron reagent in academic and industry fields, due to their thermal stability and tolerance to water and oxygen. In the total synthesis of pallavicinin (**1**) and neopallavicinin (**2**)

completed by our group,[60] vinyl triflate **105** was coupled with 2-furylboroic acid **133** to provide furan-vinyl intermediate **134** in good yield under Suzuki coupling conditions (Scheme 32). However, Suzuki reaction needs preformed boronic acid as an electrophile and the corresponding organoboron reagent will show a relative low activity compared to organozinc species. In our case, the corresponding boronic acid or its analogs must be prepared before the coupling reaction. Suzuki coupling could serve as an alternative in our synthesis.



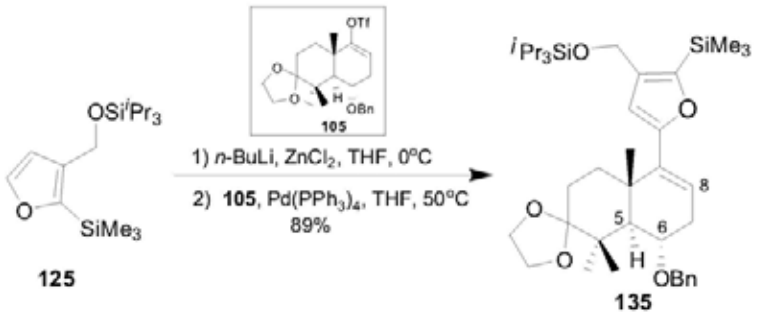
Scheme 32

The Stille coupling[84] using organotin reagent has not been our choice due to the high toxicity of organotin reagents.

The Negishi procedure was attempted initially. Thus, furan species **125** was firstly treated with *n*-butyllithium and the lithium cation was replaced with $ZnCl_2$ to form the corresponding furyl zinc chloride. This furyl zinc species was allowed to couple with vinyl triflate **105** under the catalysis of $Pd(PPh_3)_4$ to afford product **135** in good yield. After optimization, the reaction could give the desired product in 89% isolated yield and it was amenable to a large scale. In addition, we also tried another catalyst $Pd(PPh_2)Cl_2$ to perform this Negishi coupling, however, our attempt was not fruitful (Scheme 33).

The molecular formula of **135** was established as $C_{39}H_{62}O_5Si_2$ based on HRMS (ESI) and elemental analysis. The resonance signal at $\delta_{H\text{-}8}$ 5.79 (t, J = 3.9 Hz, 1H) in

the ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **135** indicated the presence of a C=C*H*-CH_2 unit. The resonance signals at δ_H 6.23 (s, 1H) and δ_H 4.65 (s, 1H) were that of furan parts. The resonance signal at $\delta_{H\text{-}5}$ 2.03 (d, J = 10.5 Hz, 1H) illustrated the *anti* axial-axial correlation in **135** ($J_{H\text{-}5,\ H\text{-}6}$ = 10.5 Hz). The compound showed benzyl resonance signals at δ_H 7.26–7.40 (m, 5H), δ_H 4.47 (d, J = 11.4 Hz, 1H), and δ_H 4.67 (d, J = 11.4 Hz, 1H); a ethylene ketal resonance signal at δ_H 3.90–4.02 (m, 4H) and three methyl resonance signals at δ_H 1.20 (s, 6H) and δ_H 1.41 (s, 3H). Thus, the structure of **135** was established.

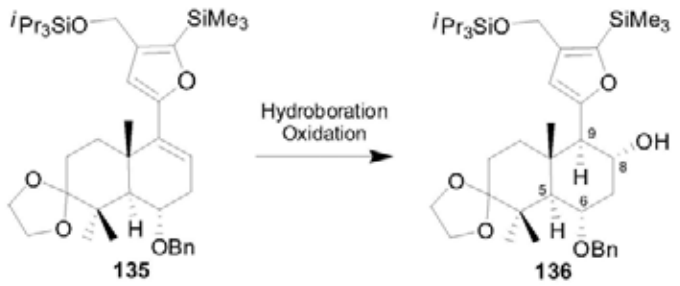


Scheme 33

After the successful preparation of vinyl furan **135**, next we focused on the synthesis of the precursor **152** for Grob fragmentation. Firstly, an equatorial hydroxyl group at C-8 should be introduced and at the same time the furyl group at an equatorial position must be arranged. Based on our knowledge, the hydroboration/oxidation[85] should produce the desired product regio- and diastereoselectively. However, the hydroboration using highly selective 9-BBN gave very low conversion (< 10%) after 48 h at 50 °C, perhaps due to steric hindrance. The reaction using less-sterically hindered reagent dicyclohexylborane at 50 °C for 15 h, followed by oxidation, increased the conversion to 76% with a 53% isolated yield. At last, the hydroboration using the simple borane dimethylsulfide complex followed by oxidation with alkaline H_2O_2 solution afforded desired alcohol **136**, with more than

90% conversion, 69% isolated yield and good diastereoselectivity (*dr* > 20:1) (Scheme 34 and Table 2).

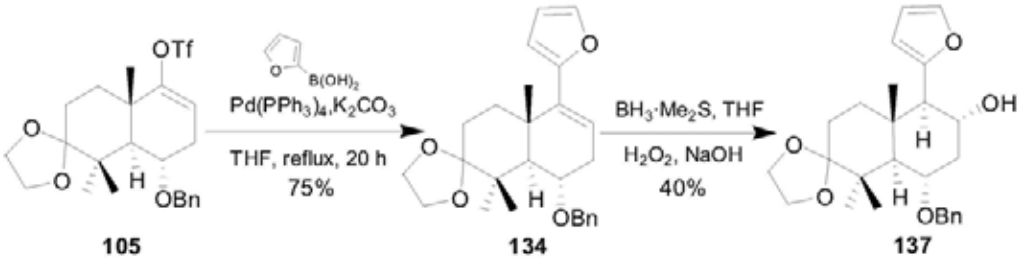
The molecular formula of **136** was established as $C_{39}H_{64}O_6Si_2$ based on HRMS (ESI) and elemental analysis. Its resonance signals at δ_H 4.11 (dt, J = 5.0, 10.8 Hz, 1H) and δ_H 3.78 (dt, J = 3.9, 10.8 Hz, 1H) in the ^{1}H NMR spectrum (300 MHz, $CDCl_3$) were assigned as H-8 and H-6 attached to oxygen atoms, respectively. The resonance signal at $\delta_{H\text{-}5}$ 1.76 (d, J = 10.8 Hz, 1H) showed the *anti* axial-axial correlation of H-5 and H-6. Similarly, the resonance signal at $\delta_{H\text{-}9}$ 2.51 (d, J = 10.8 Hz, 1H) illustrated the *anti* axial-axial correlations of H-8 and H-9 in **136** ($J_{H\text{-}5,\,H\text{-}6}$ = 10.8 Hz and $J_{H\text{-}8,\,H\text{-}9}$ = 10.8 Hz). Based on the above spectral data, an α-hydroxyl group at C-8 position was introduced successfully and the structure of **136** was established.



Entry	Experiment Conditions	Conversion (%)	Yield (%)
1	(a) 9-BBN, THF, rt to 50°C, 48 h; (b) H_2O_2, NaOH, 0°C to rt.	< 10	---
2	(a) Dicyclohexylborane, THF, rt to 50°C, 15 h; (b) H_2O_2, NaOH, 0°C to rt.	76	53
3	(a) BH_3·Me_2S, THF, rt, 15 h; (b) H_2O_2, NaOH, 0°C to rt.	> 90	69

Scheme 34 & Table 2

The relative stereochemistry of compound **136** was also indirectly confirmed by an X-ray crystallographic analysis of one of its analogs **137** prepared through the hydroboration/oxidation of **134** (Scheme 35 and Figure 3).



Scheme 35

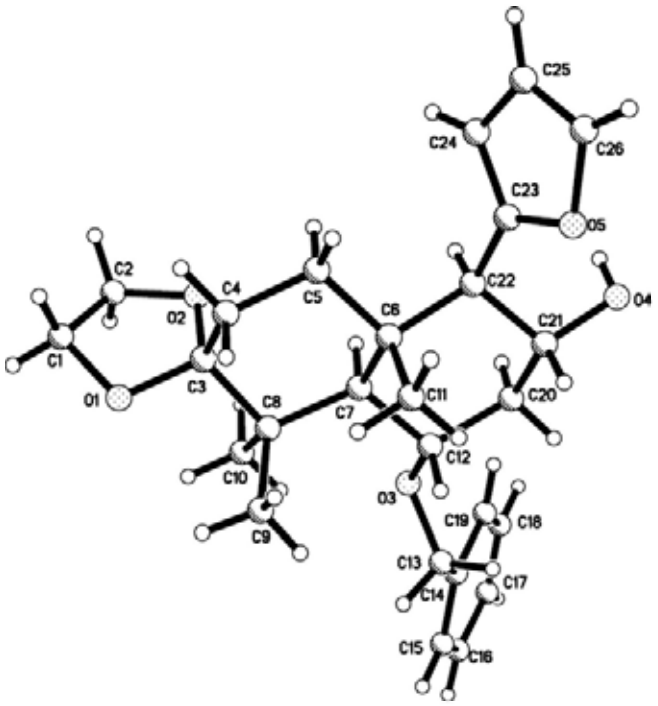
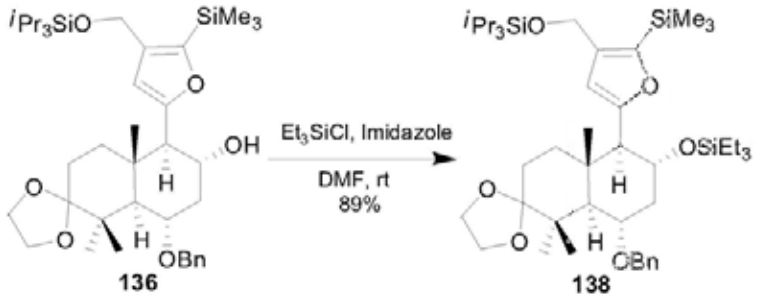


Figure 3. ORTEP drawing of compound **137**

Next we would replace the benzyl group by introducing a good leaving group at C-6 position and the masking of C-8 hydroxyl group should be considered firstly. Silyl ether as hydroxyl protective group was reported in the early 1970s.[86] This method has received much attention and a large number of such silyl protective groups are now available. Among these, TES ethers are 10-100 times more stable than TMS ethers and 10-100 times less stable than TBS ethers. TES ethers thus can tolerate a much wider range of reaction conditions but without being as hindered as their TBS counterparts. We therefore chose TES ether to protect C-8 hydroxyl group. After

reaction under standard silylation conditions, triethylsilyl ether **138** was prepared in 89% yield (Scheme 36).

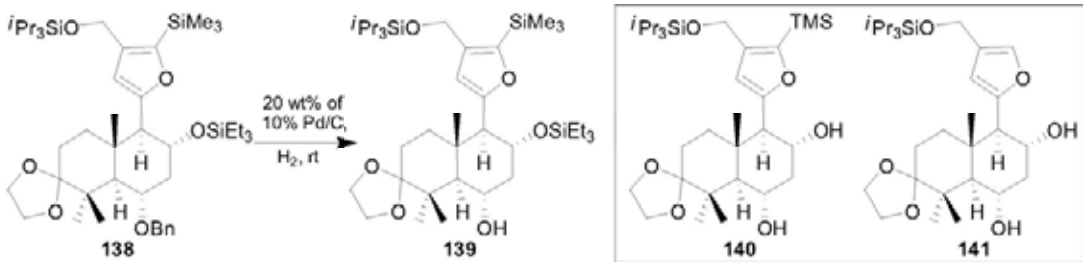
The molecular formula of **138** was established as $C_{45}H_{78}O_6Si_3$ based on HRMS (ESI) analysis. The resonance signals at δ_H 0.37 (q, J = 7.8 Hz, 6H), δ_H 0.78 (t, J = 7.8 Hz, 9H) in its ^{1}H NMR spectrum (300 MHz, $CDCl_3$) and δ_C 4.91 and 6.85 in its ^{13}C NMR spectrum (75 MHz, $CDCl_3$) illustrated the presence of a TES ether.



Scheme 36

Hydrogenolysis over palladium on charcoal was performed to deprotect the benzyl group in **138**, giving rise to the corresponding alcohol **139**. Surprisingly, we found that the catalyst purchased from different vendors gave different results. Firstly, we used 10% of palladium on charcoal purchased from Aldrich (205699-10G), together with a mixture of methanol/ethyl acetate as solvent and a hydrogen balloon as hydrogen source. We found that the reaction was slightly sluggish, with 40% conversion after 3 h and it gave the desired alcohol cleanly (more than 90% yield) after 12 h. However, when 10% of palladium on charcoal purchased from Acros (19503 0100) or BDH (29744) was used, conditions being unchanged, the reaction afforded complicated results after stirring overnight. From TLC and crude ^{1}H NMR, the triethylsilyl or trimethylsilyl group was likely destroyed to form compounds **140** or **141**. One drop of base such as triethylamine or pyridine was added to the above suspension at the beginning of reaction, but no reaction occurred. At last, the

hydrogenolysis was found to proceed rapidly when a Pd/C catalyst purchased from Acros or BDH, with ethyl acetate as solvent was used. The reaction went to completion and provided good result in 40 min to 1 hour to yield **139** cleanly. Notably, the reaction under these conditions should be monitored carefully and the reaction would become complicated when prolonging time was used (Scheme 37 and Table 3).

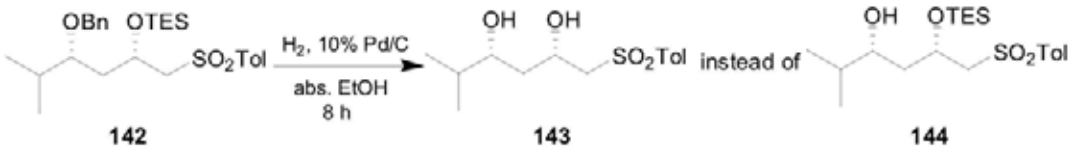


Entry	Supplier of 10% Pd/C	Reaction conditions	Results
1	Aldrich (205699-10G)	H_2, EtOAc/MeOH, rt, 3 h	40% of conversion
2	Aldrich (205699-10G)	H_2, EtOAc/MeOH, rt, 12 h	Clean, 90% yield for **139**
3	Acros (19503 0100)	H_2, EtOAc/MeOH, rt, 12 h	Complicated
4	BDH (29744)	H_2, EtOAc/MeOH, rt, 12 h	Complicated
5	Acros or BDH	H_2, EtOAc/MeOH, Et_3N or pyridine (1 drop), rt, 15 h	No reaction
6	Acros or BDH	H_2, EtOAc, rt, 40 min	Clean, 91% yield for **139**
7	Acros or BDH	H_2, EtOAc, rt, 5 h	Complicated

Scheme 37 & Table 3

A search of the literature revealed that during the total synthesis of (+)-phyllanthoside in 1991,[87] Smith and co-workers found that it was necessary to carefully monitor hydrogenolysis of benzyl ethers containing silyl group using 10% Pd/C in freshly distilled ethyl acetate in order to minimize deprotection of the silyl ethers. In 2002, Prunte and co-worker[88] reported an unexpected desilylation result when they carried out the debenzylation of TES and benzyl protected compound **142** by hydrogenolysis with 10 wt% Pd/C in methanol or ethanol, providing diol **143**

instead of the expected monosilylated product **144** (Scheme 38). After careful studies, they found that TES ethers could be cleaved by a catalytic amount of Pd/C in methanol or 95% of ethanol even though in the absence of hydrogen.

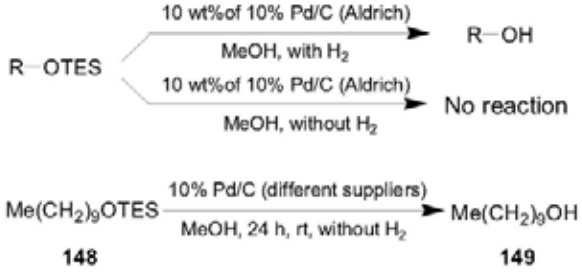


Scheme 38

In 2003, Hirota and co-workers[89] reported a remarkable solvent effect toward the Pd/C-catalyzed cleavage of TES and TBS ethers. They found that TES ethers could be easily cleaved under mild hydrogenation conditions using 10 wt% (versus substrate) of 10% Pd/C (Aldrich) in MeOH at room temperature. However, TES ether was not effected when MeCN was used as solvent and was only cleaved partially when EtOAc was used as solvent. Hirota then went on to perform more detailed investigations[90] and found that Pd/C catalyst exhibited a remarkable supplier-dependent difference in catalyst activity and property. In the absence of H_2, the cleavage of TES by Pd/C from Aldrich was not observed, instead, the reaction using Pd/C from other suppliers gave the TES cleavage product. Hirota also determined the *p*H of the aqueous suspension of Pd/C purchased from different vendors and found that those from Aldrich were much less acidic (*p*H ~ 6) than those from Acros and Merck (*p*H ~ 3). Considering the above results, Hirota concluded that Pd/C-catalyzed cleavage of TES ethers was due to the acid released from catalyst. Catalyzed solvolysis and hydrogen were also essential for the actual cleavage. In addition, Kaisalo[91] also mentioned the acidity of Pd/C catalyst in their article and explained that because Pd/C catalyst was usually prepared by the reduction of $PdCl_2$ in the presence of activated charcoal and if some residual $PdCl_2$ remained in the catalyst it would liberate HCl during the hydrogenation

(Scheme 39 and Table 4). Bearing all these facts in mind, we were able to perform the hydrogenolysis smoothly by choosing Pd/C from a suitable vendor or controlling the reaction conditions carefully without destroying the TES ether, leading to a satisfactory yield of **139** from **138**.

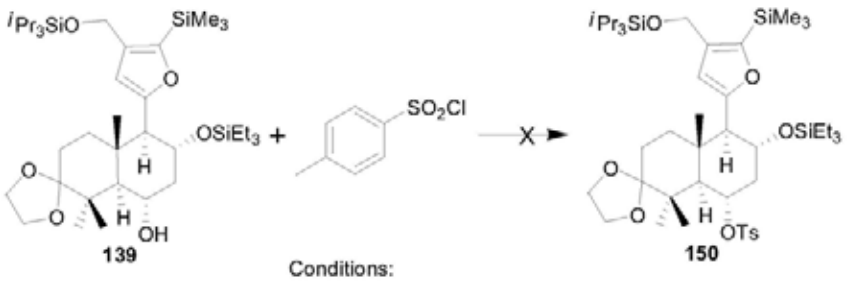
Solvent	146 :	147 (% yield)
MeOH	0	100
MeCN	100	0
EtOAc	67	33



Entry	Pd/C	148 : 149
1	Aldrich (20.569-9)	**100 : 0**
2	Wako (163-15272)	**87 : 13**
3	N. E.Chemcat (dry)	**78 : 22**
4	Nacalai (25928-84)	**75 : 25**
5	ACROS (19503-0100)	**0 : 100**
6	Kishida (400-59095)	**59 : 41**
7	Merck (807104-0010)	**0 : 100**

Scheme 39 & Table 4

With alcohol **139** in hand, a good leaving group should be introduced. Firstly, we tried to prepare tosylate **150** by treatment of the alcohol with *p*-toluenesulfonyl chloride. However, all of the attempts were not fruitful due to presumably steric hindrance. The hydroxyl group remained intact when mild conditions were employed and the substrate was found to decompose when harsh conditions were used (Scheme 40).

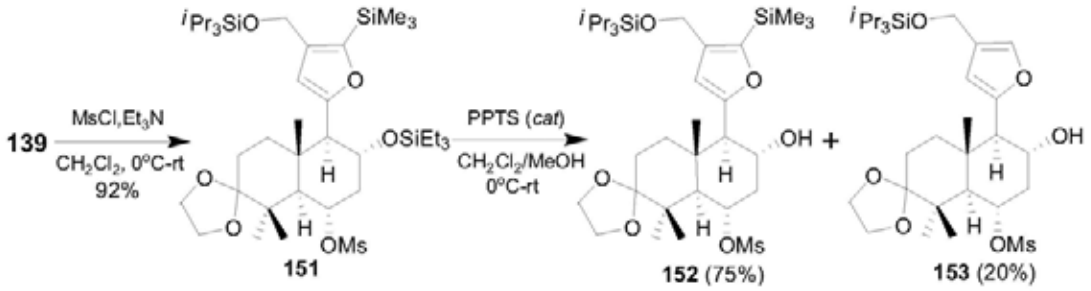


Conditions:
a) Et_3N, DMAP, CH_2Cl_2, 0°C to rt, 5 h, no reaction;
b) Et_3N, DMAP, CH_2Cl_2, reflux, 5 h, complicated;
b) Pyridine, DMAP, 0°C to rt, 3 h, complicated.

Scheme 40

Then we turned our attention to the preparation of the less sterically hindered mesylate **151**. Gratifyingly, mesylation of alcohol **139** with methanesulfonyl chloride using triethylamine as base at 0 °C for 3 h provided mesylate **151** in 92% yield, thus manifesting a good leaving group and *anti*-periplanar bonds. There are several silyl groups in **151** and the triethylsilyl group should be unmasked selectively[86b,92] to provide the free hydroxyl group in **152**. We eventually found that when mesylate **151** was dissolved in a mixture of dichloromethane and methanol at room temperature, and was treated with a catalytic amount of PPTS[93] for 40 min, most of the starting material was consumed and the desired alcohol **152** as the major product was obtained in 75% isolated yield. The molecular formula of **152** was established as $C_{33}H_{60}O_8SSi_2$ based on HRMS (ESI) analysis. The resonance signals at δ_H 5.10 (dt, J = 4.2, 11.6 Hz, 1H), δ_H 3.05 (s, 3H) in its ^{1}H NMR spectrum (300 MHz, $CDCl_3$) and δ_C 78.18 in its ^{13}C NMR spectrum (75 MHz, $CDCl_3$) illustrated the presence of a mesylate group attached to C-6. Based on the above results, the structure of **152** was established.

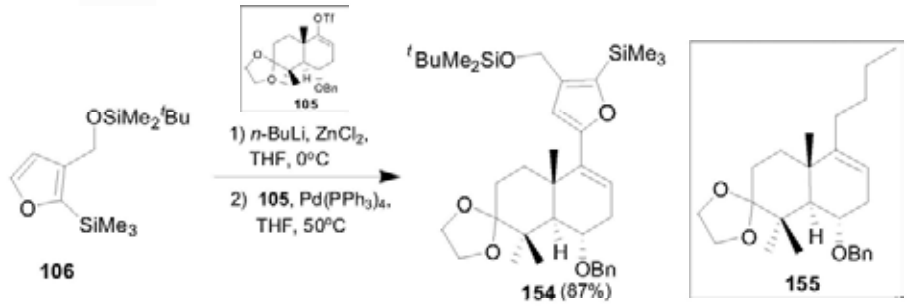
We had also worked on the modification of this reaction to optimize the yield of **152** by using different solvents, temperature and changing the amount of PPTS. However, the significant amount of the de-TMS side-product (about 20% of yield) **153** was always concomitant in the reaction. Compared to **152**, the side product **153** was slightly more polar. The molecular weight was determined to be 600 based on MS (ESI) analysis. The resonance signals of TMS in the ^{1}H NMR spectrum and ^{13}C NMR spectrum of **153** were not detected and an additional resonance signal at δ_H 7.31 (s, 1H) was observed. Thus, based on the above data, the side product was speculated to be **153** (Scheme 41).



Scheme 41

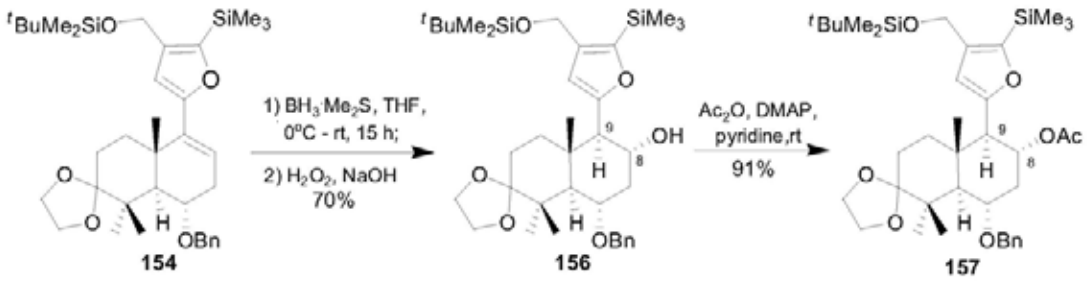
The introduction of a TES at C-8 hydroxyl group brought some inconvenience for the next hydrogenolysis and deprotection of TES although we could improve some of the conditions. We therefore tried to use another suitable protective group to replace TES. At last, we found that acetyl group was a good choice. Also, without using TES, the TIPS group in the furan ring would not be necessary because reaction conditions to remove an acetyl group would not touch the silyl group. So we used furan **106** containing more routine TBS group to undergo the Negishi coupling with triflate **105**. After purification, intermediate **154** was obtained in 82% yield but concomitant with a side-product **155** (5−10% yield) when the similar conditions as from **125** to **135** was applied. After careful investigations, we found that the amount of base *n*-BuLi should be kept to be equal to those of furan **106** and $ZnCl_2$ during the Negishi coupling. If an excess amount of *n*-BuLi was used, the reaction would be contaminated by the formation of **155**. After optimization, intermediate **154** was obtained in 87% yield from the reaction between triflate **105** (1 equiv.) and furylzinc species generated *in situ* from **106** (1.5 equiv.), *n*-BuLi (1.5 equiv.) and $ZnCl_2$ (1.5 equiv.) catalyzed by $Pd(PPh_3)_4$ (Scheme 42) and compound **155** was not detected under this condition. The structure of **154** was confirmed utilizing NMR and HRMS spectrometric analyses. Interestingly, the coupling between triflate **105** and TIPS-protected furan **125** gave normal product **135** in high yield (89%) and the side-product **155** was not produced

even though the excess amount of *n*-BuLi was used. We presume that the formation of **155** is due to the steric hindrance of TBS group.



Scheme 42

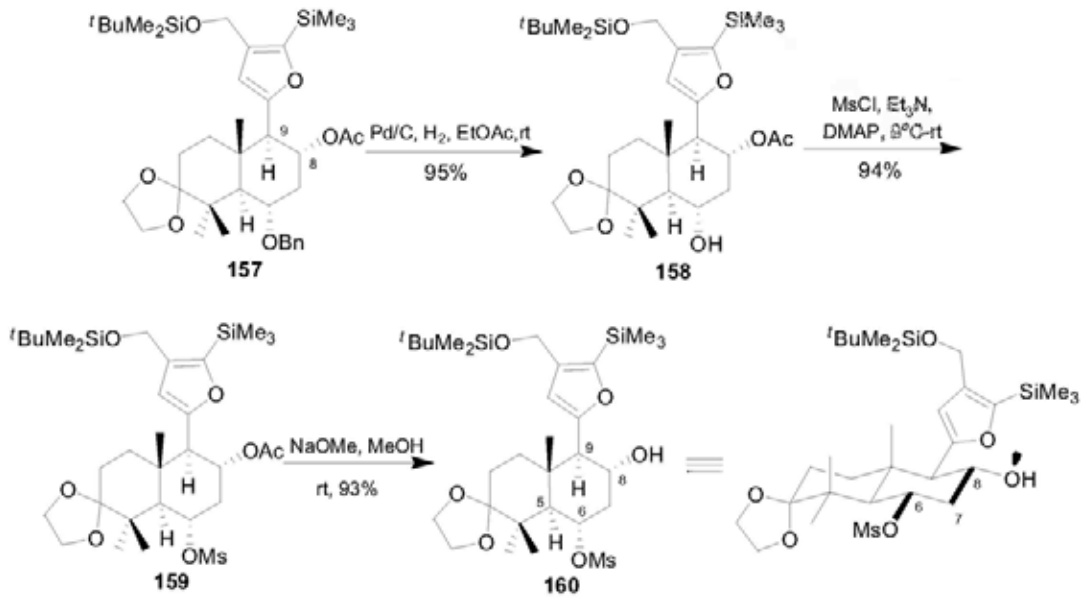
The hydroboration of **154** using borane dimethylsulfide complex followed by oxidation with alkaline H_2O_2 solution was carried out to afford the desired alcohol **156** in 70% isolated yield with excellent diastereoselectivity (*dr* > 20:1) (Scheme 43). The stereochemistry could be observed by an *anti* axial-axial correlation in **156** ($J_{H\text{-}8,\ H\text{-}9}$ = 10.8 Hz). Thereafter, the free hydroxyl group in **156** was protected as acetate **157** in high yield by allowing **156** to react with acetic anhydride in pyridine (Scheme 43). The resonance signal of $\delta_{H\text{-}8}$ at downfield (5.38, dt, J = 4.1, 11.7 Hz, 1H) meant that **157** contained an electron-withdrawing group. The resonance signals of δ_H 1.80 (s, 3H) in the ^{1}H NMR spectrum (300 MHz, $CDCl_3$) and δ_C 170.40 in the ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **157**, together with the IR absorption at 1738 cm^{-1}, indicated the presence of an OAc group. It was noteworthy that the residual pyridine from acylation should be removed thoroughly, otherwise, it will affect the next hydrogenolysis step.



Scheme 43

Removal of benzyl protective group could be achieved through hydrogenolysis using 20 wt% of 10% Pd/C in ethyl acetate under the normal atmosphere of hydrogen to afford alcohol **158** in more than 90% yield (Aldrich's Pd/C for 12 h and ACROS or BDH's Pd/C for 2 h, respectively). Mesylation of alcohol **158** with methanesulfonyl chloride using triethylamine as base at 0 ^{o}C for 3 h provided mesylate **159** in 94% yield, which was treated with sodium methoxide in MeOH for 3.5 h at room temperature to afford the precursor **160** for Grob fragmentation cleanly (Scheme 44).

The molecular formula of **160** was established as $C_{30}H_{54}O_8SSi_2$ based on HRMS (ESI) analysis. The resonance signals at δ_H 5.08 (dt, J = 4.2, 10.8 Hz, 1H) and δ_H 4.14 (dt, J = 4.1, 11.1 Hz, 1H) in its ^{1}H NMR spectrum (300 MHz, $CDCl_3$) were assigned as H-6 and H-8 attached to oxygen atoms respectively. The resonance signals at δ_H 3.04 (s, 3H) in the ^{1}H NMR spectrum and δ_C 78.10 in the ^{13}C NMR (75 MHz, $CDCl_3$) of **160** spectrum showed the existence of –OMs. The resonance signal at $\delta_{H\text{-}5}$ 1.89 (d, J = 11.1 Hz, 1H) with large coupling constants showed the *anti* axial-axial correlation of H-5 and H-6. Similarly, the resonance signal at $\delta_{H\text{-}9}$ 2.48 (d, J = 10.8 Hz, 1H) with large coupling constants illustrated the *anti* axial-axial correlations of H-8 and H-9 in **160** ($J_{H\text{-}5,\ H\text{-}6}$ = 11.1 Hz and $J_{H\text{-}8,\ H\text{-}9}$ = 10.8 Hz). Based on the above results, the structure of **160** was established and the usual stereochemical requirement for the subsequent Grob fragmentation was fully assembled, in which the oxygen lone pair was oriented *anti*-periplanar to the bond C8-C7 bond and the C6-OMs bond (Scheme 43). It must be noted that during the NMR measurements of compounds **139**, **151**, **152**, **158**, **159** and **160**, slow decomposition of materials was observed in commercial $CDCl_3$. So $CDCl_3$ must be pretreated with KOH before all NMR measurements.

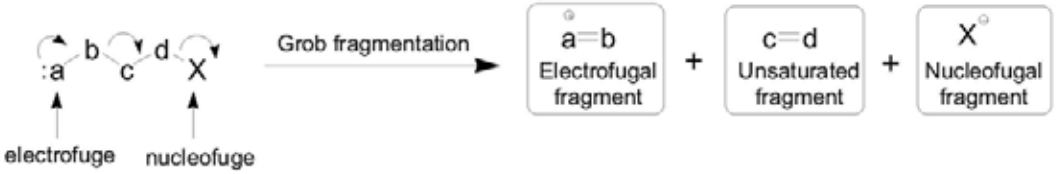


Scheme 44

2.2.5 Preparation of compound 196a

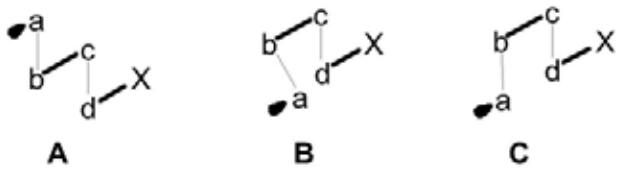
With alcohol **160** in hand, we then focused on the Grob fragmentation to generate ring-opened key intermediate **196** by disconnection of the C7-C8 bond in alcohol **160**.

Grob fragmentation refers to the regulated heterolytic cleavage reactions of molecules containing certain combinations of carbon and heteroatoms (e.g., B, O, N, S, P, halogens) which was systematically investigated by Grob.[94] As seen in its formula (Scheme 45), the Grob fragmentation is an elimination reaction taking place when an electrofuge and nucleofuge are situated in position 1 and 3 on an aliphatic chain. The reaction product is an electrofugal fragment (carbonium ion, acylium ion), an unsaturated fragment (alkene, alkyne, imine) and a nucleofugal fragment (leaving group such as tosyl, mesyl or hydroxyl).



Scheme 45

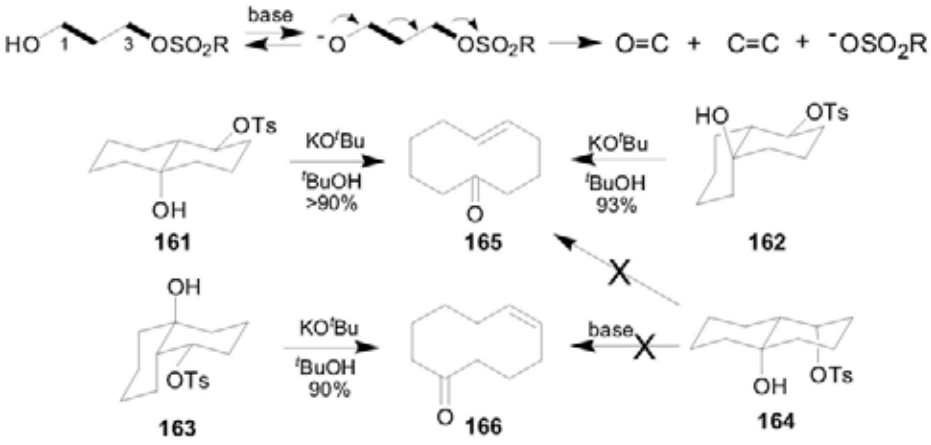
Grob fragmentation can take place by several different mechanisms based on the structural, as well as the steric and electronic factors present in the substrate. Currently, it is most accepted that the fragmentation proceeds through a concerted fashion in which the *a*=*b* and X fragments departed from the middle *c*=*d* group simultaneously. As shown in Scheme 46, the synchronous mechanism of Grob fragmentation shows that the fragmentation could be operated only if both the lone pair of electrons on electrofuge (:a) and the d-X bond are *anti*-periplanar to the cleaved bond *b*-*c*. These conditions are all satisfied by the following conformation **A**, **B**, **C** (Scheme 46).[95] In other words, if the precursor of Grob fragmentation is in accordance with one of the following models **A**, **B** or **C**, successful disconnection would take place at the relevant carbon-carbon bond, affording the corresponding fragmentation products. If a gauche relationship exists between these bonds, the compounds react very slowly and usually complex product mixtures are formed.



Scheme 46

Three closely related Grob-type fragmentations can be distinguished.[96] The first type is the base-induced Wharton reaction,[97] in which cyclic 1,3-diol monosulfonate esters undergo olefin-formation fragmentation with the release of an electrofugal

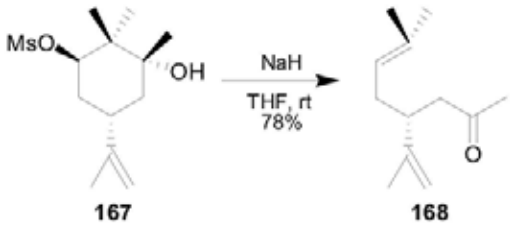
carbonyl fragment (Scheme 47). In this instance, the base does not play its usual role in elimination reactions but instead serves to abstract a proton from the hydroxyl group, which forms the more powerful electron donor O^- enabling the sulfonate ester group to be removed more readily. Warton's investigations on the fragmentation of 1,10-decalindiol monotosylates clearly displayed the stereochemical importance of the precursors for the occurrence of the fragmentation.[98] As shown in Scheme 47, under the promotion of base such as KO^{t}Bu, diol monotosylates **161**, **162**, and **163**, in which the leaving group (-OTs) are *anti*-periplanar with the corresponding carbon-carbon bond to be cleaved, underwent a rapid fragmentation to give the corresponding 5-cyclodecenone **165** and **166** in high yields. However, for monotosylate **164** having a gauche relationship between these bonds, the normal fragmentation products were not obtained.



Scheme 47

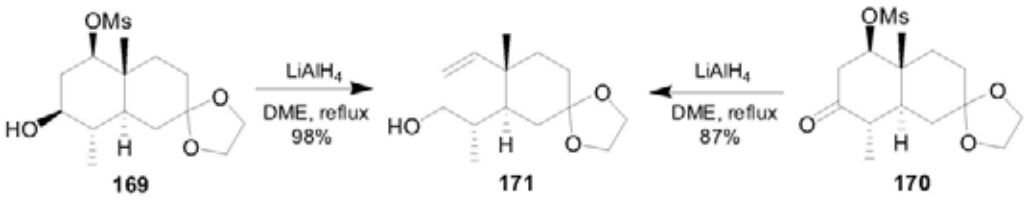
As shown in Scheme 48, the leaving group (OMs) in **167** was *anti*-periplanar with the disconnected carbon-carbon bond, though the hydroxyl group of **167** was at an equatorial position. This geometry is still in accordance with the aforementioned requirements for the synchronous mechanism of Grob fragmentation. Thus, treatment of mesylate **167** with NaH in THF afforded the fragmentation product **168** in good

yield.[99]



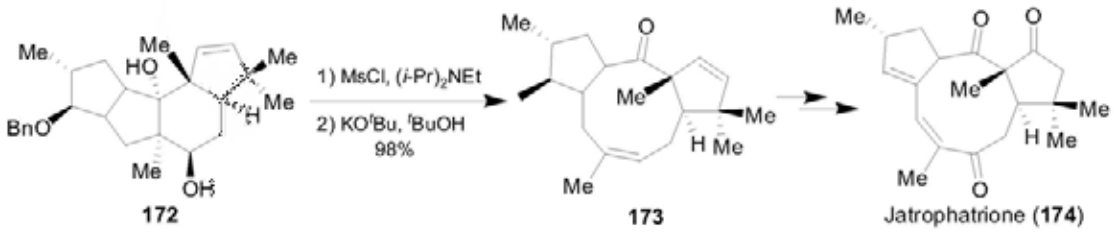
Scheme 48

Mesyloxy-alcohol **169** readily underwent Grob fragmentation with lithium aluminum hydride in refluxing 1,2-dimethoxyethane, affording olefin alcohol **171** in nearly quantitative yield. On the other hand, reductive fragmentation of oxo-mesylate **170** to **171** was also achieved by treatment of **170** with lithium aluminum hydride in refluxing 1,2-dimethoxyethane (Scheme 49).[100]



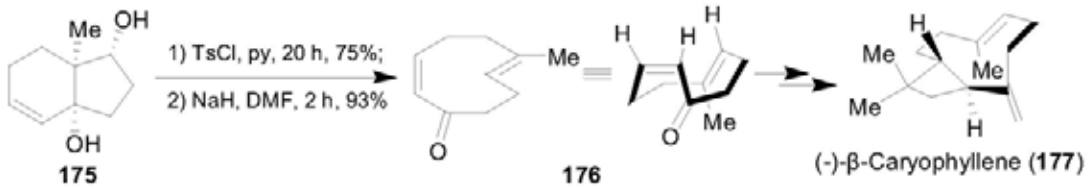
Scheme 49

Grob fragmentation is perhaps most synthetically useful for the construction of medium-sized ring systems. During the first total synthesis of jatrophatrione (**174**) by Paquette,[101] the key step in their approach was the Grob fragmentation to generate the tricyclo[5.9.5] skeleton. Thus, tetracyclic 1,3-diol **172** was monomesylated on the less hindered hydroxyl group and then treated with potassium *tert*-butoxide, producing the desired tricyclic product **173** in excellent yield after the concerted fragmentation (Scheme 50).



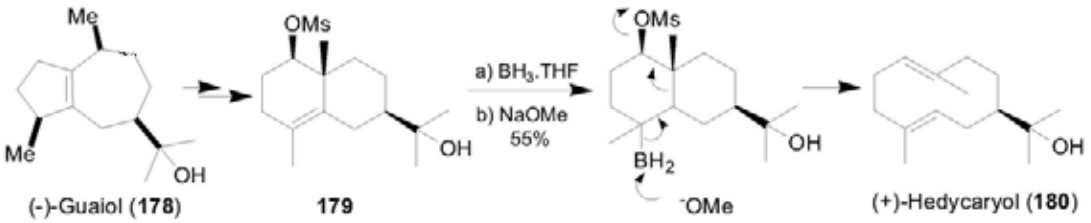
Scheme 50

In 2008, Corey and co-worker[102] reported an unconventional approach to the enantioselective synthesis of (-)-β-caryophyllene (**177**) utilizing a Grob fragmentation to build the nine-membered ring. Thus, selective tosylation of the secondary hydroxyl group in diol **175** followed by deprotonation and alkoxide-driven carbonyl-forming elimination (Grob fragmentation) gave the chiral *E*,*Z*-dienone **176** (Scheme 51).



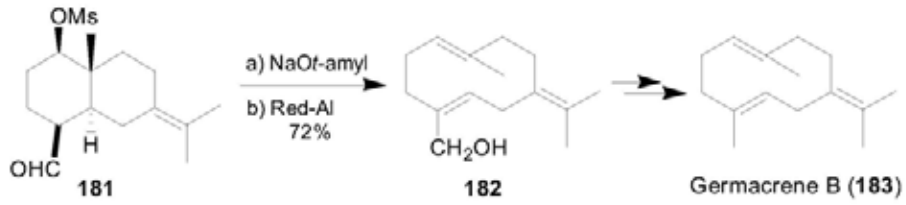
Scheme 51

The second type of Grob fragmentation is the so-called boronate fragmentation reaction introduced and studied extensively by Marshall and co-workers.[103] In contrast to the Wharton reaction in which only one endocyclic double bond is formed regio- and stereospecifically, the boronate fragmentation reaction results in the regio- and stereospecific formation of two endocyclic double bonds. The requirement for the *anti*-periplanar alignment of the bonds of cleavage also exists in the boronate fragmentation reaction. For example, during the synthesis of (+)-hedycaryol (**180**) starting from natural (-)-guaiol (**178**),[104] olefin intermediate **179** was treated with BH_3 followed by NaOMe to afford the Marshall fragment product (+)-hedycaryol (**180**) in 55% yield (Scheme 52).



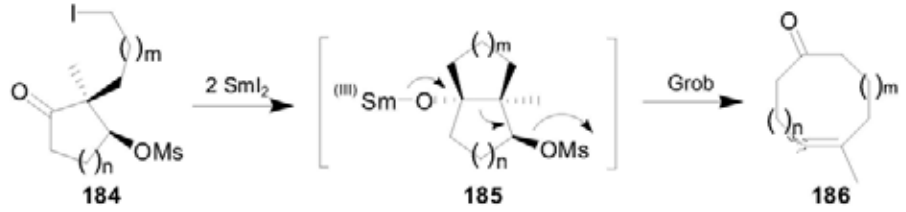
Scheme 52

The third Grob-type fragmentation reaction was developed by Mander and co-workers[105] which involves an enolate-assisted, intraannular l,4-fragmentation *via* α-deprotonation of a carbonyl function group and has been used to prepare functionalized cyclodecadiene systems. For example, in the synthetic studies toward germacrene B (**183**),[106] aldehyde **181** was treated with sodium *tert*-amylate (NaO*t*-amyl) and then the initially formed unstable germacrane aldehyde was reduced *in situ* by Red-Al to provide diene **182** (Scheme 53).



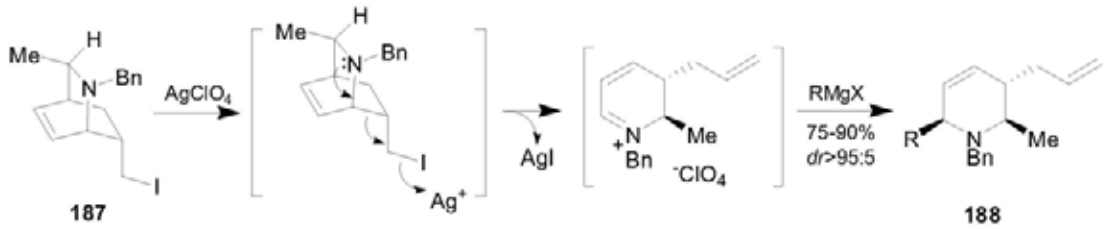
Scheme 53

In addition to the aforementioned Grob fragmentation induced by bases, Molander and coworkers reported a sequential intramolecular Barbier cyclization/Grob fragmentation for the syntheses of medium-sized carbocycles mediated by samarium (II) iodide.[107] The intramolecular Barbier reaction of substituted keto mesylates bearing iodoalkyl **184** generated a bicyclic alkoxide intermediate **185** that underwent a rapid Grob fragmentation to produce stereoselectively medium-sized carbocycles **186** with high yields (Scheme 54).



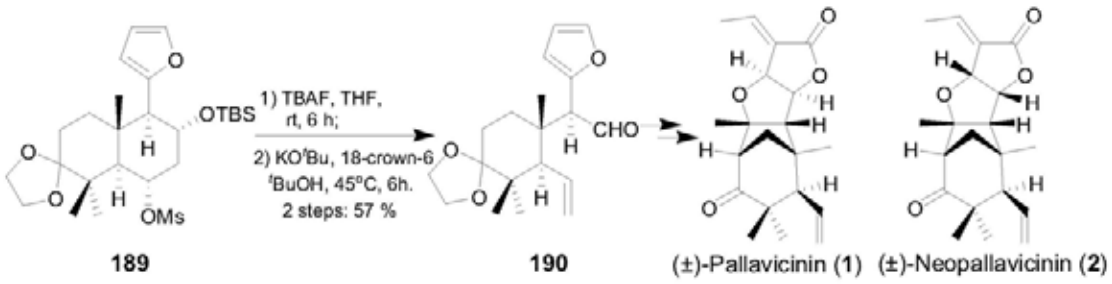
Scheme 54

In 2008, Charette and co-workers reported a silver ion-induced Grob fragmentation of γ-amino iodide **187** to form polysubstituted piperidine **188** with high stereoselectivities.[108] The stereoelectronic requirements for frangomeric effect during the fragmentation also demanded that the nitrogen lone pair should be oriented *anti*-periplanar to the carbon-carbon bond to be cleaved and the carbon-leaving group bond (Scheme 55).



Scheme 55

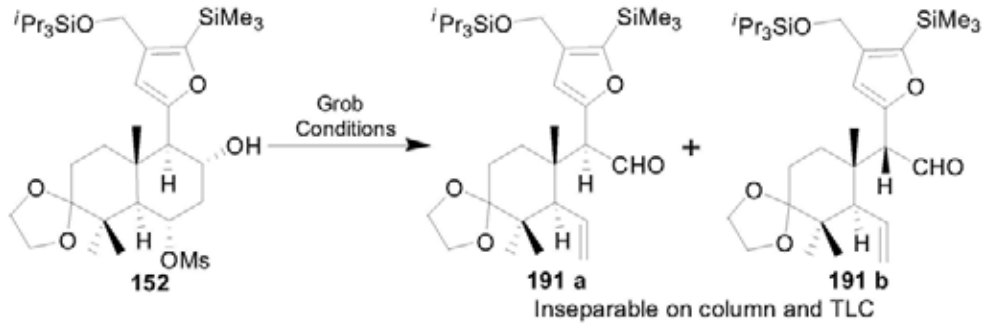
In addition, during the total syntheses of (±)-pallavicinin (**1**) and (±)-neopallavicinin (**2**) achieved in our laboratory,[60] Grob fragmentation as one of the key steps was employed successfully to convert bicyclic mesylate **189** to **190** in good yield (Scheme 56).



Scheme 56

Encouraged by the above examples, we tried to convert hydroxyl mesylate **152** to the desired aldehyde **191** under Grob fragmentation conditions. Based on the structure analysis, compound **152** encompassed the full stereochemical requirements for Grob fragmentation, i.e., the oxygen lone pair was oriented *anti*-periplanar to the bond C8-C7 bond and the C6-OMs bond. Therefore, we attempted the Grob fragmentation of mesylate **152** using similar conditions as that for **189** to **190**. However, the reaction led to a very complex mixture when compound **152** was treated with KO^{t}Bu in ^{t}BuOH at 45 °C for 2 h. The fragmentation employing other base such as NaH, NaOMe or LiHMDS in different solvents also did not give good results. Eventually, we found that crude aldehyde **191** could be obtained smoothly when substrate **152** was treated with freshly sublimed KO^{t}Bu in ^{t}BuOH for less than 10 min at below 25 °C.

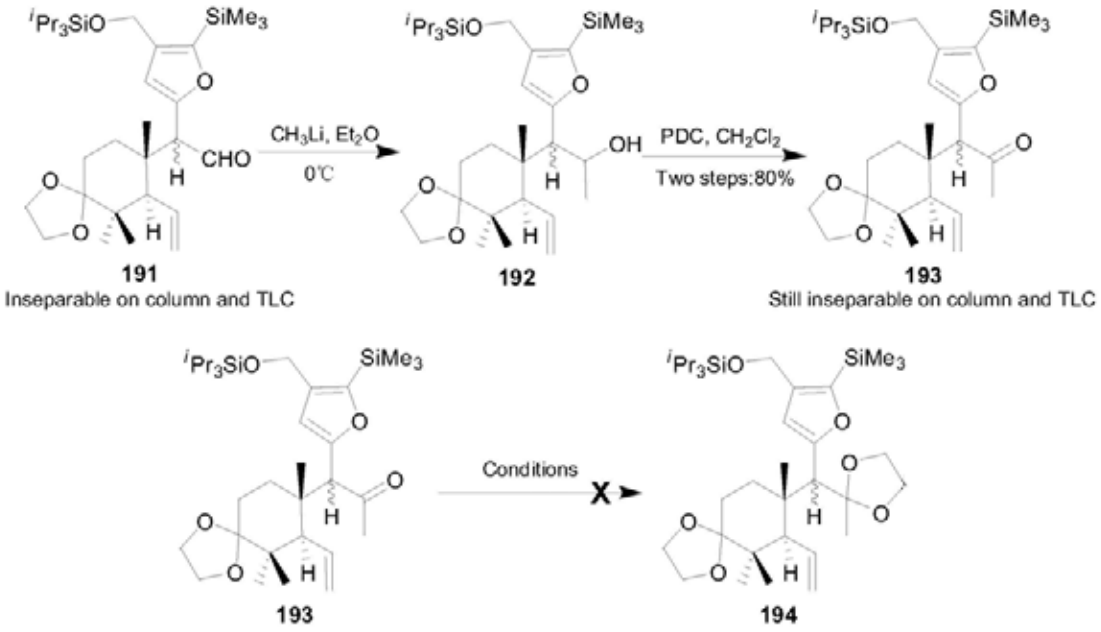
The resonance signals at δ_H 9.90 (d, J = 4.2 Hz, 1H) and δ_H 9.76 (d, J = 4.8 Hz, 1H) in the ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **191** showed the presence of aldehyde but it should be a mixture of a pair of isomers. The major resonance signals at δ_H 5.73 (ddd, J = 10.2, 10.5, 17.1 Hz, 1H), δ_H 5.29 (dd, J = 1.2, 10.2 Hz, 1H) and δ_H 5.12 (dd, J = 1.2, 17.1 Hz, 1H) in its ^{1}H NMR spectrum indicated the presence of –CH=CH_2. These spectra data showed that the Grob fragmentation gave the normal product aldehyde **191**. Significantly, the diastereoselectivity varied from 2:1 to 8:1 *dr* value based on the crude NMR analysis. Obviously, the product aldehyde underwent an epimerization easily. The overall yield ranged from 60 to 70% and the major side-product was desilylation compound (10–20%). In addition, the two isomers of aldehyde **191** were inseparable on column or thin-layer chromatography (Scheme 57 and Table 5).



Entry	Reaction conditions	Results
1	KO^{t}Bu, ^{t}BuOH, 18-Crown-6, 45 °C, 2 h	Complicated
2	KO^{t}Bu, ^{t}BuOH, 45 °C, 2 h	Complicated
3	KO^{t}Bu, ^{t}BuOH, 45 °C, 10 min	Yield<40%, dr: 1:5 – 1:8
4	KO^{t}Bu, THF, 0 °C, 40 min	No desired product was produced
5	NaH, THF, 15-Crown-5, 0 °C -rt, overnight	No desired product was produced
6	KO^{t}Bu, THF, 18-Crown-6, 0 °C- 45 °C, 40 min	Messy, Yield<10%
7	NaOMe, MeOH, rt-reflux, 1 h	Yield<20%, dr: 1:3 – 1:6
8	LiHMDS, THF, 0 °C -rt, overnight	No desired product was produced
9	KO^{t}Bu, ^{t}BuOH, 20-25 °C, 10 min	Yield: 70%, dr: 1:2 - 1:8

Scheme 57 & Table 5

As the two isomers of Grob fragmentation were inseparable, we targeted to separate them by altering the functional group on that position to convert the mixture to the corresponding methyl ketone **193**. Crude aldehyde **191** was treated with methyllithium and was followed by a subsequent PDC oxidation affording ketone **193** in a moderate yield. Unfortunately, it was still difficult to separate the mixture on column chromatography. We then tried to protect the ketone group as an acetal **194** and hoped to separate the two isomers from this step or the later steps. Also, this strategy is in accordance with our preliminary design. However, the ketalization failed although we tried several reaction conditions (Scheme 58 and Table 6).

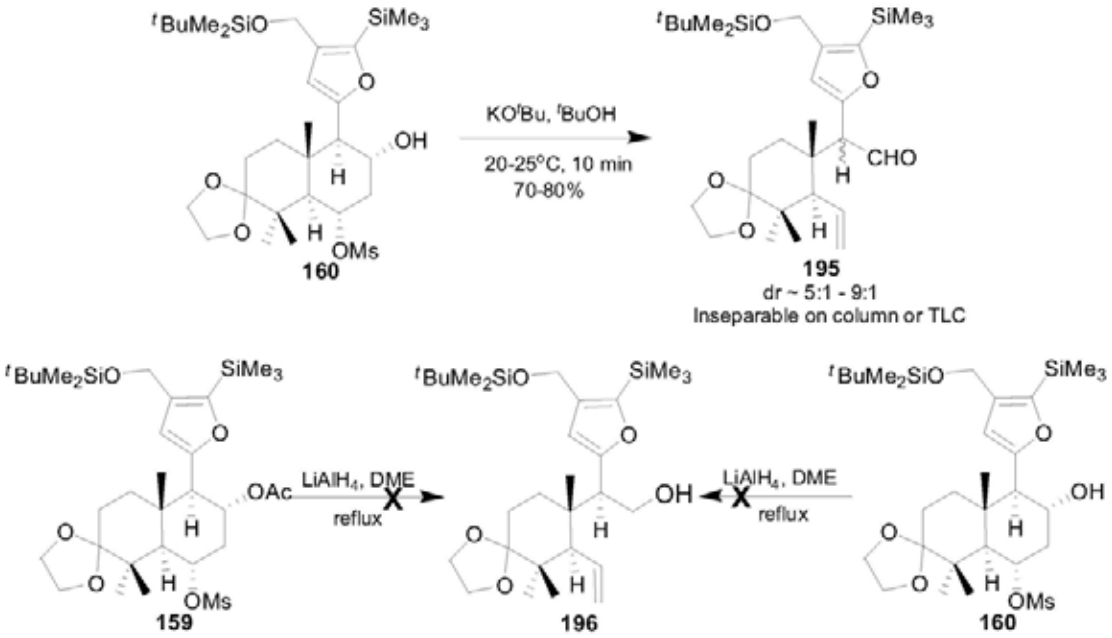


Entry	Reaction conditions	Results
1	HO, OH, TMSCl, MeOH, 0 °C - rt, 2 h	Complicated
2	HO, OH, SeO_2, $CHCl_3$, rt-50 °C, 12 h	No reaction
3	TMSO, OTMS, I_2 (*cat*), CH_2Cl_2, rt, 24 h	Complicated
4	TMSO, OTMS, $ZnCl_2$, CH_2Cl_2, rt, 24 h	No reaction
5	TMSO, OTMS, TMSOTf, CH_2Cl_2, -10 °C, 1 h	Complicated

Scheme 58 & Table 6

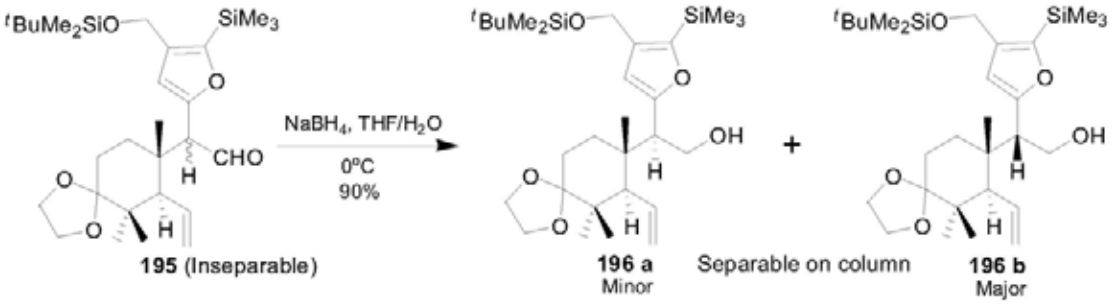
Then we tried Grob fragmentation on another mesylate **160**, which was treated with freshly sublimed KO^{t}Bu in ^{t}BuOH for less than 10 min at below 25 °C to give aldehyde **195** cleanly based on TLC. Crude NMR analysis showed that this was still a mixture of a pair of isomers and the diastereoselectivity varied from 5:1 to 9:1 *dr* value from different batches of reactions. Obviously, the product aldehyde also underwent an epimerization easily. The overall yield ranged from 70 to 80%, and a minor side-product de-TMS compound (5–10%) was also obtained. In addition, crude aldehyde **195** was again inseparable on column or thin-layer chromatography. Besides, we also tried to treat mesylate **159** and **160** with lithium aluminum hydride in

refluxing 1,2-dimethoxyethane to yield alcohol **196** through a reductive fragmentation. However, these attempts were not fruitful (Scheme 59).



Scheme 59

We then tried to do the separation from the two isomers of Grob fragmentation by reducing the mixture to the corresponding alcohol **196**. Therefore, crude aldehyde **195** was reduced to the corresponding alcohol using $NaBH_4$. Fortunately, less polar isomer **196a** as a minor product was separated from the more polar major isomer **196b** after a careful chromatographic separation (Scheme 60).



Scheme 60

The molecular formulae of both **196a** and **196b** were determined as $C_{29}H_{52}O_5Si_2$

based on HRMS (ESI) analysis which confirmed that they were diastereoisomers. For major isomer **196b**, its protons were assigned according to a ^{1}H-^{1}H COSY study. Based on ^{1}H-^{1}H COSY, the resonance signal at δ_H 2.91 (dd, J = 4.8, 8.7 Hz, 1H) in the ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **196b** was assigned as H-9 attached to the furan ring. The resonance signal at δ_H 0.85 (s, 3H) in the ^{1}H NMR spectrum was assigned as the H-11 of β-methyl. NOE correlation between H-11 of methyl and H-9 was observed based on ROESY spectrum (Figure 4) which indicated the presence of a β-H-9 in **196b**. The protons of another isomer **196a** were also assigned according to ^{1}H-^{1}H COSY experiment. Based on ^{1}H-^{1}H COSY, the resonance signal at δ_H 2.85 (dd, J = 4.0, 9.5 Hz, 1H) in the ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **196a** was assigned as the H-9 attached to the furan ring. The resonance signal at δ_H 1.19 (s, 3H) in the ^{1}H NMR spectrum was assigned as the H-11 of β-methyl.

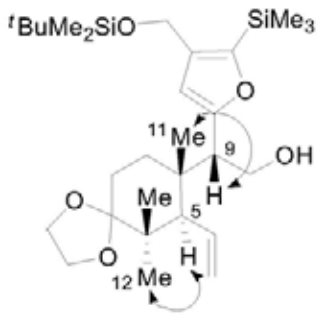
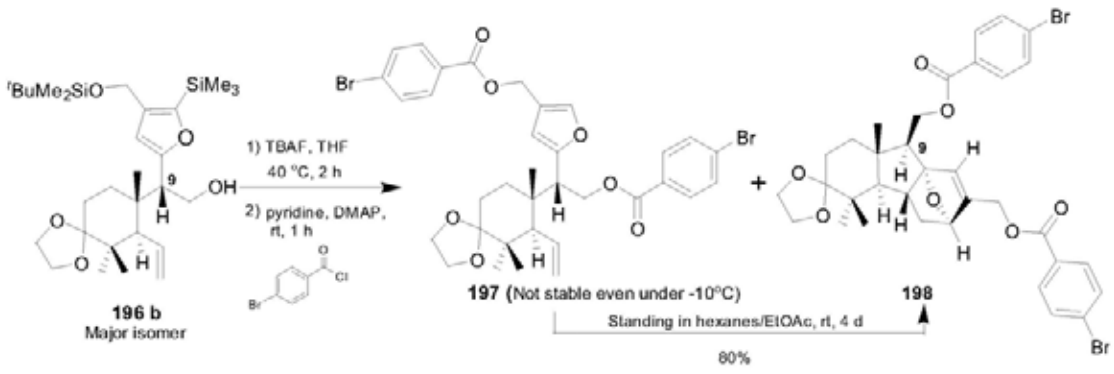


Figure 4. NOE correlations for **196b**

To obtain a full picture on the stereochemistry of **196**, we decided to resort to the use of X-ray diffraction analysis. So we removed both of the silyl group on the major isomer (more polar one) of **196** using TBAF. Without purification, the crude diol was allowed to react with an excess of 4-bromobenzoyl chloride to produce ester **197** as a white solid after rapid column chromatography. Compound **197** was primarily confirmed by NMR and MS analyses. Besides **197**, a more polar compound than that of **197** was also isolated but its structure could not be confirmed only by simple NMR

and MS analysis. We tried to prepare the single crystal of **197** in order to obtain X-ray diffraction data. Accordingly, **197** was dissolved in a mixture of hexanes and ethyl acetate and the solvents were allowed to evaporate slowly. After slow evaporation for 4 days at room temperature, fine single crystals were obtained. However, TLC showed that it was not ester **197** any more but the more polar compound identified previously. In addition, the new compound had the same molecular formula $C_{34}H_{36}Br_2O_7$ as that of **197** based on HRMS (ESI) and elemental analysis. After X-ray crystallographic analysis, the compound was confirmed to be **198**, an intramolecular Diels-Alder cycloadduct between furan and olefin. It is well known that Diels-Alder reaction concerns *syn* addition and the configuration of substrate will be retained during reaction. Based on the X-ray data, the H-9 from **196b** was confirmed to be a β-H and the major product from unoptimized Grob fragmentation was not our desired aldehyde. However, the minor one was our desired product (Scheme 61 and Figure 5).



Scheme 61

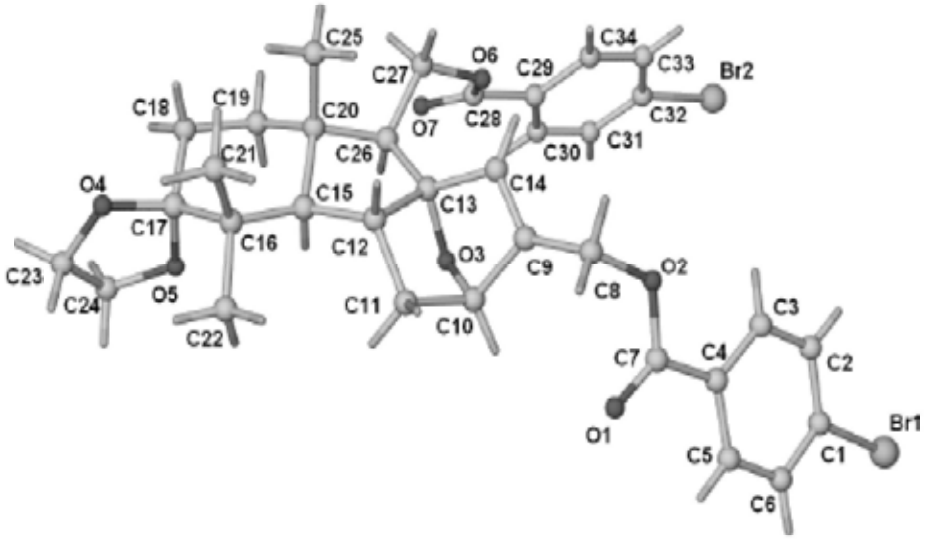
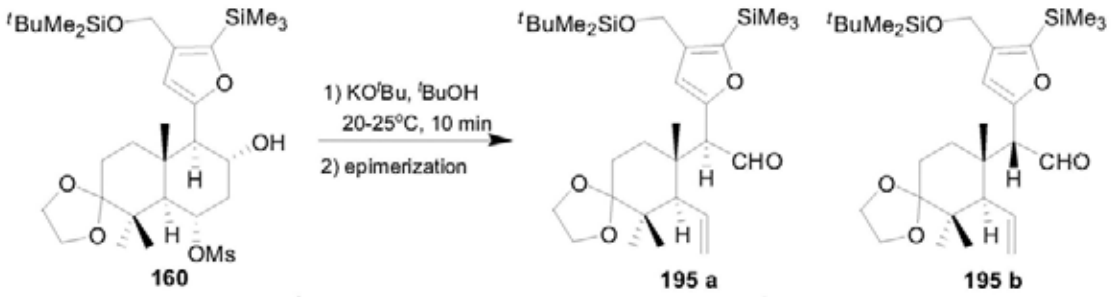


Figure 5. ORTEP drawing of compound **198**

Next, our attention was focused on the improvement of diastereoselectivity of Grob fragmentation. The Grob fragmentation product always gave different *dr* value (1:2–1:9) from different batches of reactions under the same reaction conditions. In addition, we found that the *dr* value could be increased to about 1:1.5 after column chromatography. So we thought that the epimerization would be affected by acid or base. At last, we found that the *dr* value could be changed to 1:1 when the crude aldehyde was treated with DBU in THF for 3.5 h at room temperature and the epimerization was clean. Prolonging time or raising temperature would give mixture of less than 1:1 ratio. Besides, the *dr* value also could be increased to 1:1 when the crude aldehyde was treated with silica gel for 3 h at 45 °C but this epimerization condition would give a slightly dirty result when it was scaled up (Scheme 62 and Table 7). Figure 6 showed the epimerization result (*dr* value from 0.13:1 to 1.05:1) from one batch of reaction based on crude NMR spectra [The resonance signal at slightly upfield δ_H 9.75 (d, J = 4.7 Hz, 1H) in the ^{1}H NMR spectrum (400 MHz, $CDCl_3$) showed the desired aldehyde isomer **195a**].



160 195 a 195 b

entry	Epimerization condition	a : b
1)	Just after Grob	~1:8
2)	Treated with silical gel in CH_2Cl_2 at rt for 24 h	~1:1.4
3)	Treated with silical gel in $CHCl_3$ at 45°C for 24 h	~1:1.4
4)	Treated with silical gel in THF at 45°C for 24 h	~1:1.6
5)	Treated with Amberlyst 15 in CH_2Cl_2 at rt for 2 h	Messy
6)	Treated with Amberlite XD4 in CH_2Cl_2 at rt for 2 h	~1:8
7)	Treated with silical gel (dry) at 45°C for 3 h	~1:1
8)	Treated with silical gel (dry) at 45°C for 18 h	~1:1, but not so clean
9)	Treated with DBU in THF, rt, 20 min	~1:2
10)	Treated with DBU in THF, rt, 3.5 h	~1:1
11)	Treated with DBU in THF, rt, 21 h	~1:1
12)	Treated with DBU in THF, rt, 21 h then 45°C, 3h	~1:1.7
13)	Treated with NaOMe in MeOH, rt, 21 h	~1:2, dirty
14)	Treated with phosphazene base P_2-Et in toluene, rt, 1 h	Messy

Scheme 62 & Table 7

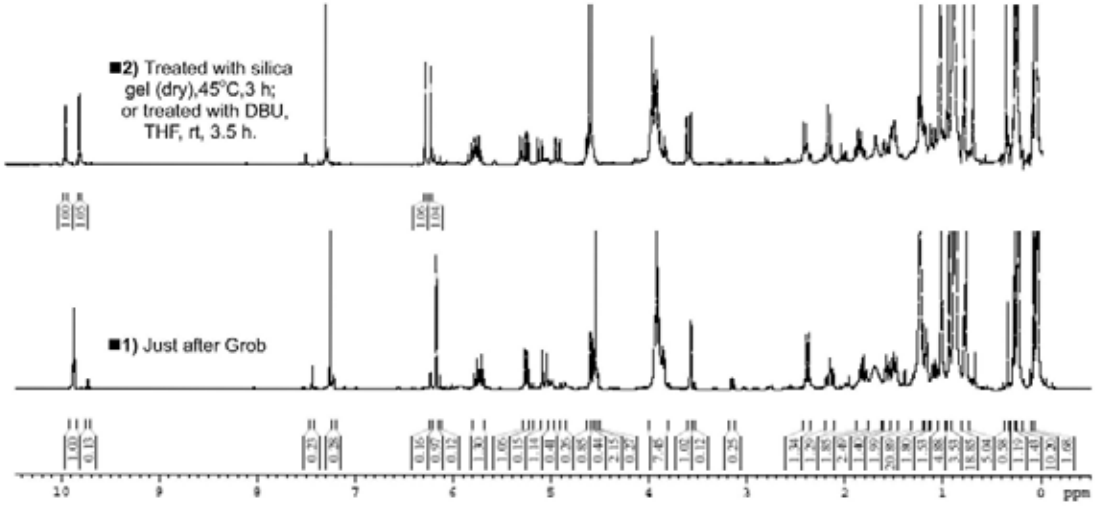


Figure 6

Based on the conformational analysis of aldehyde **195**, we envisioned that the

epimerization of **195a** to **195b** under basic condition during Grob fragmentation was due to the stabilizing effect of carbon anion by 2-silyl group and the π-π stacking between vinyl and furyl group in **195b** might also facilitate it. In addition, we calculated the minimized steric energy of **195a** and **195b** using MM2 calculation in Chem 3D and the results showed that there were similar minimized steric energy between **195a** and **195b** (Figure 7). These preliminary results could explain the epimerization between **195a** and **195b**.

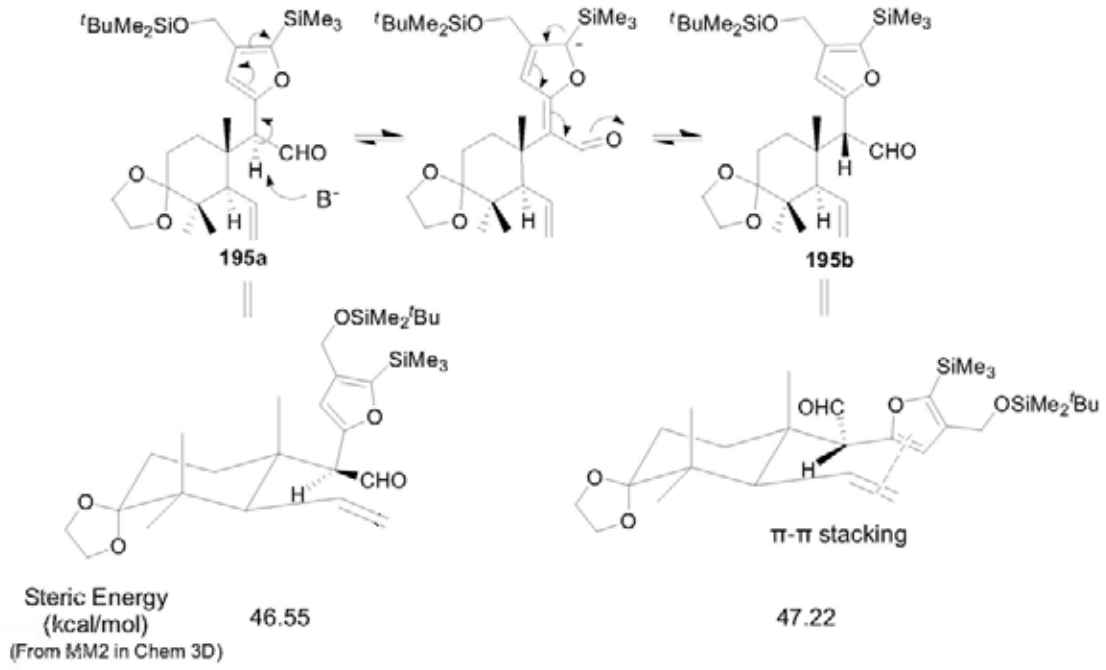
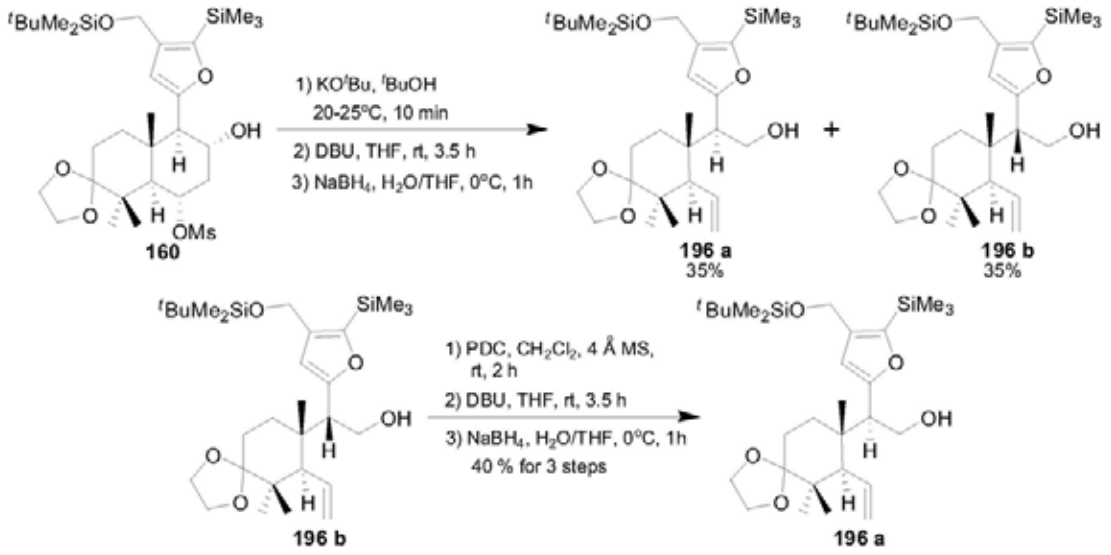


Figure 7

After the general work up, the Grob fragmentation product from mesylate **160** was dissolved in THF and then treated with DBU at room temperature for 3.5 h. Without any work up, to the above solution was added H_2O (1:10 *v:v* for H_2O:THF) followed by addition of $NaBH_4$ at 0 °C. After work up and careful purification, desired alcohol **196a** could be obtained in 35% yield over these three steps. Although the diastereoisomeric ratio was modest, the undesired alcohol isomer **196b** could be recycled to give **196a** by oxidation using PDC, equilibration and subsequent reduction

(Scheme 63).



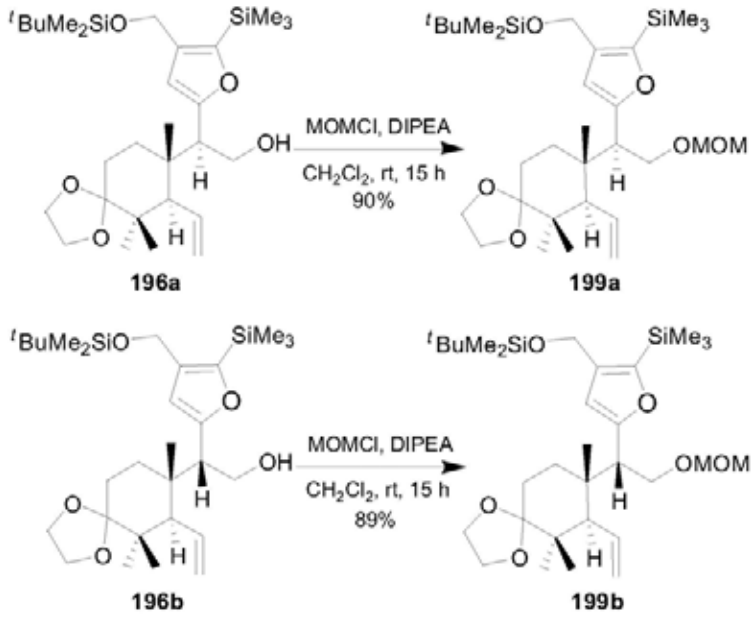
Scheme 63

As described in the first chapter, Grob fragmentation as one of the key steps had been successfully applied to the biomimetic syntheses of several natural products and the first experimental proof of Grob fragmentation in triterpene biosynthesis was also reported recently.[61] Our success in this reaction supported partially the biogenetic hypothesis towards natural pallavicinolide A (**3**) and it will undoubtedly provide another example of Grob fragmentation applied to biomimetic synthesis of a natural product.

2.2.6 Preparation of compound 202

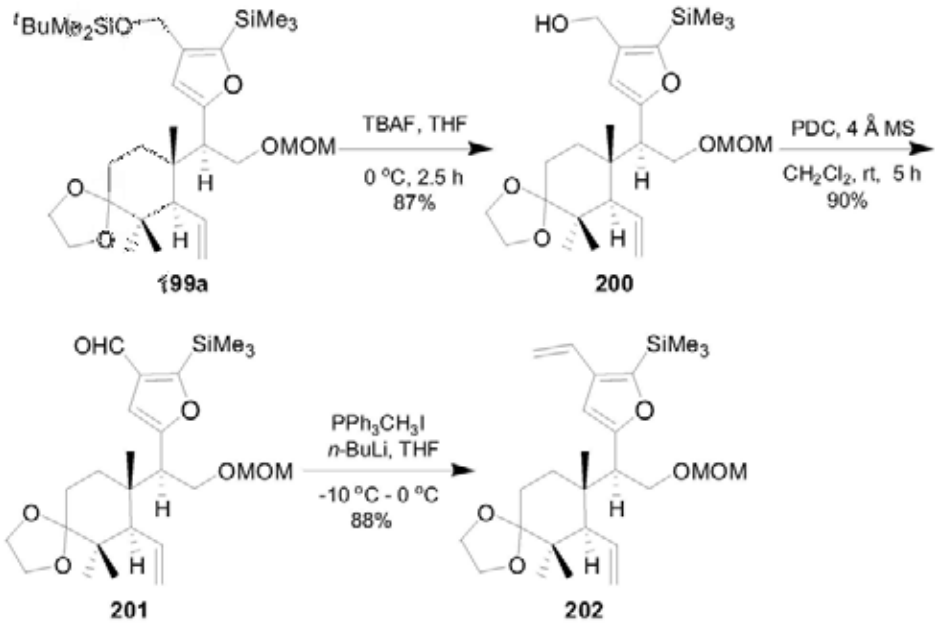
After the successful preparation of alcohol **196a**, next we focused on the synthesis of compound **202** for the oxidation of furan species to the desired α,β-butenolide. Firstly, alcohol **196a** was protected as stable MOM ether **199a** using the standard MOM etherification conditions. The resonance signals at δ_H 3.17 (s, 3H), δ_H 4.40 (d, J = 6.8 Hz, 1H) and δ_H 4.50 (d, J = 6.8 Hz, 1H) in the ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **199a** showed the presence of a MOM group. Similarily, another alcohol

196b was also protected as stable MOM ether **199b** using the standard MOM etherification conditions and the sturcure of **199b** was confirmed by NMR, HRMS and IR analysis (Scheme 64).



Scheme 64

Next, a double bond was then necessary to be placed on the furan ring in **199a** before oxidation taken place. We found that the selective removal of TBS group could be achieved to furnish alcohol **200** in good yield when substrate **199a** was treated with TBAF at low temperature. The TMS group was remained intact under this condition. Then PDC oxidation of alcohol **200** yielded the corresponding aldehyde **201** in 90% isolated yield. The resonance signals at δ_H 10.01 (s, 1H) in the ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **201** and δ_C 186.31 in its ^{13}C NMR spectrum (100 MHz, $CDCl_3$) together with IR absorption at 1677 cm^{-1} illustrated the formation of an aldehyde. Finally, a subsequent classical Wittig[109] olefination provided desired olefin **202** smoothly, which would serve as the precursor of desired α,β-butenolide (Scheme 65).



Scheme 65

For the olefin furan **202**, the molecular formula was determined as $C_{29}H_{52}O_5Si_2$ based on HRMS (ESI) and elemental analysis. The resonance signals at δ_H 3.16 (s, 3H), δ_H 4.42 (d, J = 6.8 Hz, 1H) and δ_H 4.51 (d, J = 6.8 Hz, 1H) in its ^{1}H NMR spectrum (300 MHz, $CDCl_3$) showed the presence of the MOM group. The resonance signals at δ_H 5.76 (ddd, J = 10.3, 10.5, 17.1 Hz, 1H), δ_H 5.21 (dd, J = 2.5, 10.3 Hz, 1H), δ_H 4.96 (dd, J = 2.5, 17.1 Hz, 1H) and δ_H 2.04 (d, J = 10.5 Hz, 1H) in the ^{1}H NMR spectrum showed the presence of a CH-CH=CH_2 group. The resonance signals at δ_H 6.69 (dd, J = 10.8, 17.4 Hz, 1H), δ_H 5.38 (dd, J = 1.4, 17.4 Hz, 1H) and δ_H 5.07 (dd, J = 1.4, 10.8 Hz, 1H) in the ^{1}H NMR spectrum of **202** showed the successful introduction of a C-CH=CH_2 group through the Wittig reaction. The structure of **202** was therefore confirmed.

2.2.7 Preparation of compound 255a

With olefin **202** in hand, we therefore turned our attention on the conversion of furyl intermediate **202** into the corresponding α,β-butenolide **227** then to ketone **255a**.

Herein we would firstly introduce a general background for the oxidative conversion of furan into the corresponding butenolide.

Furan and its derivatives are significant compounds in the area of organic chemistry. Not only there are furan units in many of the naturally occurring molecules,[110] but also furan species are always useful synthons in the preparation of many kinds of chemical structures,[111] especially in the field of furan oxidation.[112,113]

2-Trimethylsilylfuran derivatives play an important role in organic chemistry not only due to their presence as key structural units in many natural products as well as important pharmaceuticals,[114] but also in their use as building blocks in synthetic organic chemistry. Many transformation reactions have been documented for these molecules.[115] As illustrated in our synthesis of furan intermediate **106**, the main method of furan functionalization procedures involve metalation of the corresponding furan derivatives followed by trapping of the furyl anion with trimethylsilyl chloride.

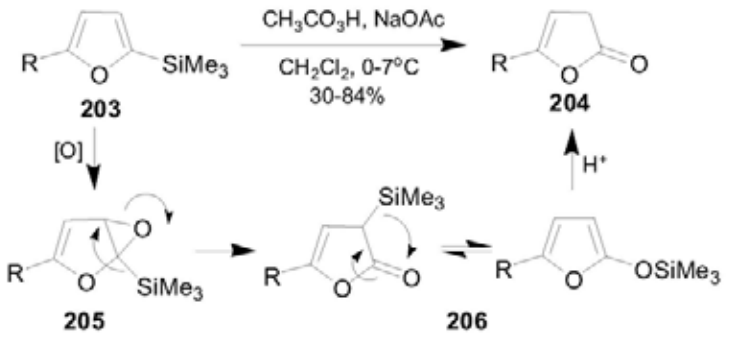
Δ^2 and Δ^3 –Butenolides are most widely employed as useful synthetic units for the syntheses of biologically and chemically significant natural products.[116] A common but old method for butenolide synthesis involved an intramolecular dehydration of the corresponding γ-keto acids. However, reaction conditions employed in this procedure, *e.g.* heating in acetic anhydride, were sometimes too vigorous to be tolerated for other functional groups, and often brought about concomitant formation of isomers. Although 2-substituted furans had also been used as precursors for butenolides through oxidation, regiochemical ambiguities had made this approach problematic. Some miscellaneous methods were also developed to prepare many functionalized butenolides.[117]

2-Siloxyfurans have widely been used as the equivalent of butenolide in organic

synthesis and we have given some examples in this field in the former part of this Chapter. As mentioned before, 2-siloxyfuran chemistry cannot be adopted in our study.

At present, the most useful method was the direct oxidative conversion of 2-trimethylsilylfurans, which was initially explored by Kuwajima,[118a] developed by Goldsmith[118c] and Tanis,[118d] and was employed in the total synthesis of *dl*-confertin by Schultz.[118b]

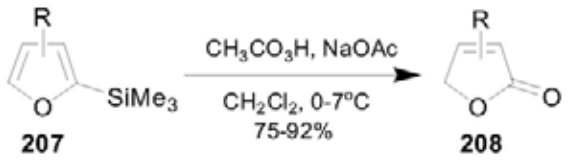
In 1981, Kuwajima and co-worker demonstrated that 5-alkyl-2-trimethylsilylfuran **203** underwent oxidation cleanly with peroxyacetic acid to afford the corresponding Δ^3–butenolide in good yield.[118a] Use of other oxidant such as *m*-CPBA or *t*-butyl hydroperoxide with titanium isopropoxide gave low yield or no reaction. The reaction mechanism was also discussed. Thus, epoxidation of **203** should take place selectively on the site bearing a σ donating trimethylsilyl group to yield epoxide **205**, which underwent a carbon-oxygen bond fission with concomitant migration of the silyl group to give **206** under acidic conditions. At last, the more acid-sensitive trimethylsilyl enol ether **206** would be converted into the corresponding Δ^3–butenolide **204** by acid (Scheme 66).



Scheme 66

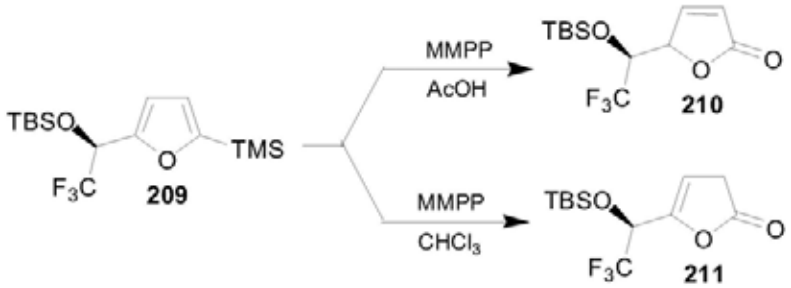
After Kuwajima, Goldsmith[118c] and Tanis[118d] also devoted to the field a great deal

and they reported that oxidation of 3- or 4-substituted 2-trimethylsilylfurans (**207**) with peroxyacetic acid directly afforded Δ^2–butenolide **208** solely (Scheme 67).



Scheme 67

In addition, 2-trimethylsilylfurans could also be oxidized to butenolides by other oxidants. Some oxidants, such as magnesium monoperoxyphthalate (MMPP), could be used to afford the related Δ^2 or Δ^3–butenolides in different solvents.[119] As shown in Scheme 68, oxidation of furyl compound **209** with MMPP in acetic acid gave the corresponding Δ^2–butenolide **210**. However, oxidation of the same substrate with MMPP in chloroform only led to the corresponding Δ^3–butenolide **211**, without double-bond migration.

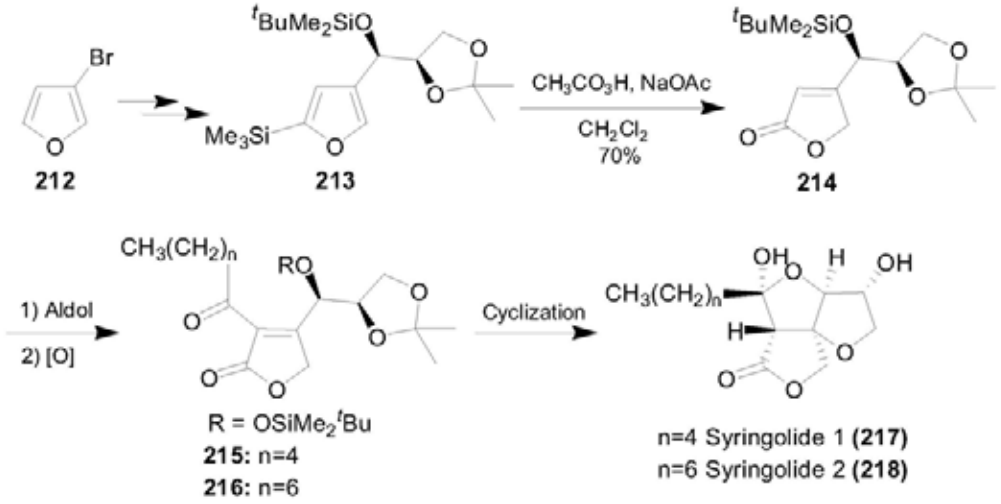


Scheme 68

In our group, the total syntheses of several natural products have been achieved by using 2-trimethylsilylfuran species as a crucial precursor[60,69] and our present work is the extension of furan chemistry in natural product synthesis extensively developed by our group. One of the pivotal steps in the synthetic endeavors towards pallavicinin and neopallavicinin,[60] prehispanolone,[69a,69c,69d] sphydrofuran,[69a] secosyrins,[69a,69c]

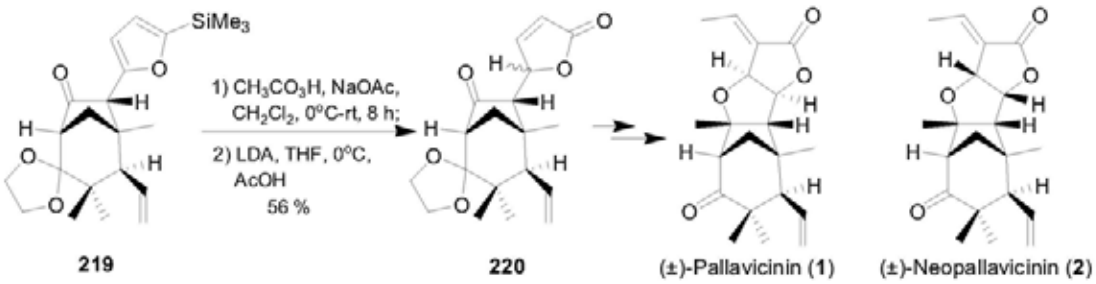
syringolides[69a,69b] and plakortone B[69f,69k] involves peracid oxidation of substituted 2-trimethylsilylfuran derivatives to the desired butenolides. We are going to use the total syntheses of syringolides, pallavicinin and neopallavicinin to illustrate this powerful method.

Yu[69a,69b] applied the above strategy as a pivotal step in the total syntheses of syringolide 1 (**217**) and syringolide 2 (**218**). 2-Trimethylsilylfuran **213,** which was obtained through several steps starting from the simple material 3-bromofuran **212**, was oxidized by peroxyacetic acid to provide butenolide **214** in good yield. Then the final products syringolide 1 (**217**) and syringolide 2 (**218**) were realized after aldol consendation, oxidation and the final cyclization (Scheme 69).



Scheme 69

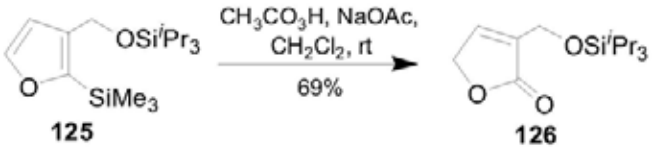
During the biomimetic total syntheses of pallavicinin (**1**) and neopallavicinin (**2**) completed by Peng,[60] peroxyacetic acid oxidation of 5-substituted-2-trimethylsilyl furan **219** followed by double-bond migration with LDA and AcOH furnished the desired butenolide mixture **220** in 57% overall yield, which afforded the final two natural products **1** and **2** after subsequent transformations (Scheme 70).



Scheme 70

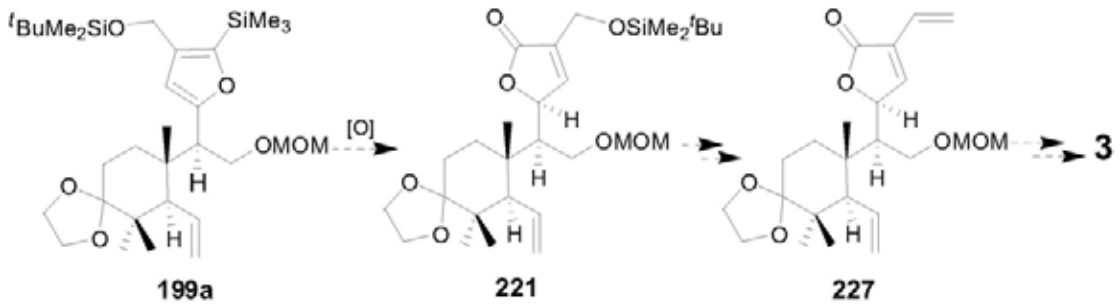
Encouraged by the previous successful experiences in our group, we aimed to oxidize our 3-substituted-2-trimethylsilylfuran derivative to the desired α,β-butenolide.

During our initial attempt to synthesize siloxyfuran intermediate **107**, we had realized the preparation of butenolide **126** from the oxidation of furan **125** using peroxyacetic acid in the yield of 69% (Scheme 71).



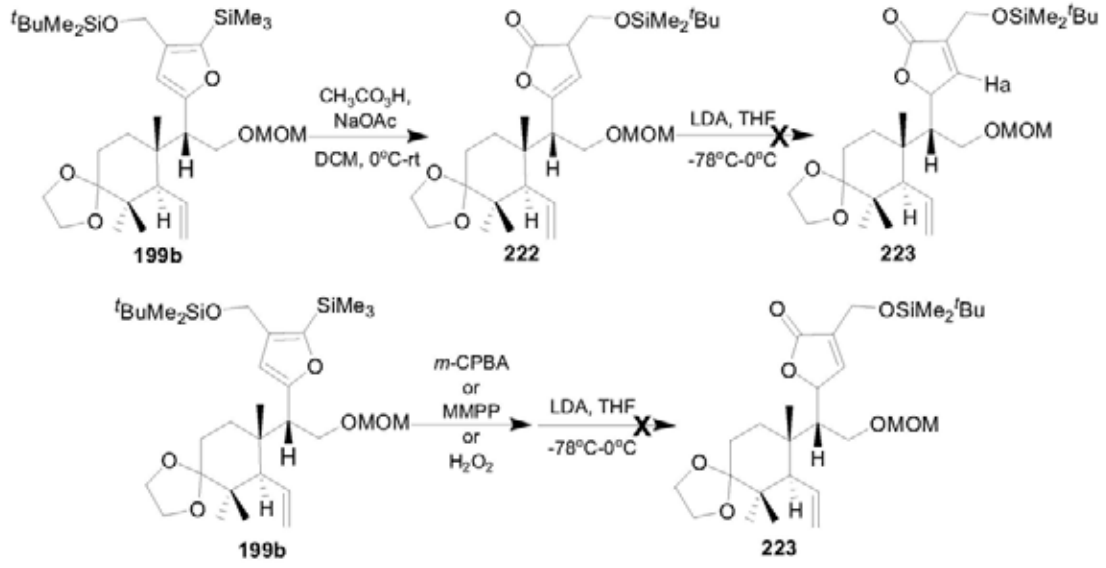
Scheme 71

In the preliminary design, we tried to oxidize furan species **199a** firstly, then modified butenolide **221** to olefin **227**, and then to the final product (Scheme 72).



Scheme 72

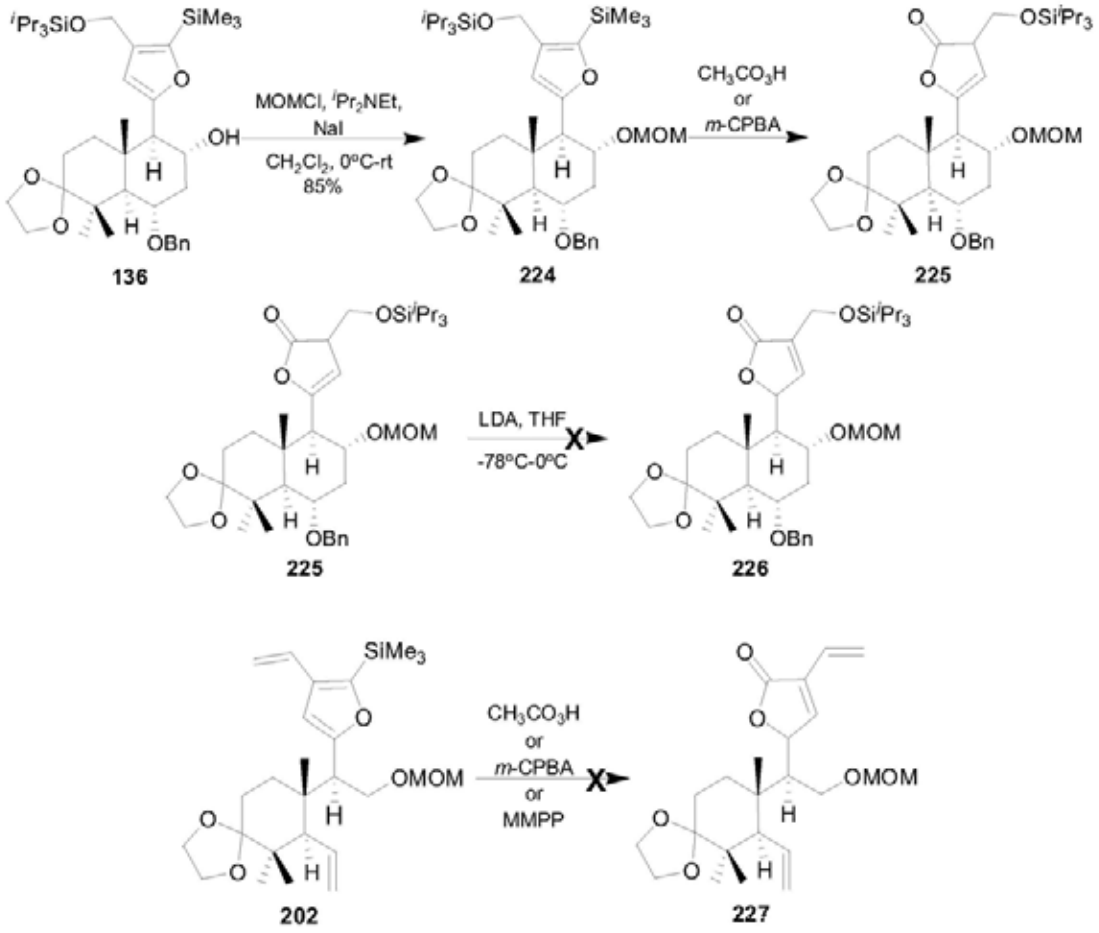
Therefore, as a model reaction, we attempted the oxidation of the diastereoisomer **199b** for the preparation of the corresponding butenolide **223** by treatment furan **199b** with freshly prepared peroxyacetic acid. After stirring for several h, TLC showed that most of the starting material was consumed and a new polar compound was generated. However, it was not our desired α,β-butenolide **223** as the crude NMR showed that there was no proton signal of α,β-butenolide (in general, $\delta_{Ha} > 7.0$ ppm). We tried several times the same reaction by changing reaction time or temperature, but the desired product was not obtained. Considering the mechanism of oxidation and the crude NMR result together with MS data, we presumed that the product might be the corresponding β,γ-butenolide **222**. So we tried the double-bond migration by treating it with LDA. However, desired α,β-butenolide **223** was still not formed. All the attempts using other oxidants such as *m*-CPBA, MMPP and H_2O_2 were also unfruitful (Scheme 73).



Scheme 73

We also tried the oxidation of bicyclic furyl **224**, derived from **136**, using peroxyacetic acid. However, it still seemed that β,γ-butenolide **225** was formed and

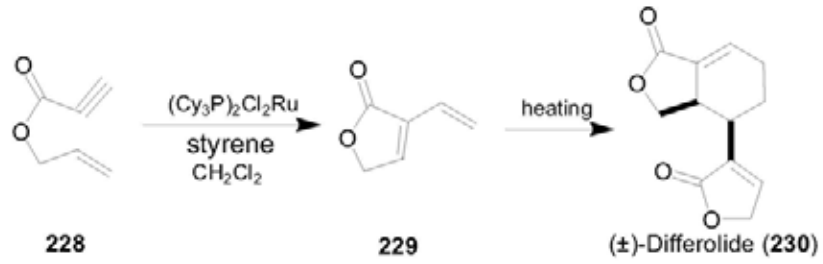
the isomerization using LDA failed to provide desired α,β-butenolide **226**. In addition, the oxidation of olefin **202** using peroxyacid also failed to give desired butenolide **227** (Scheme 74).



Scheme 74

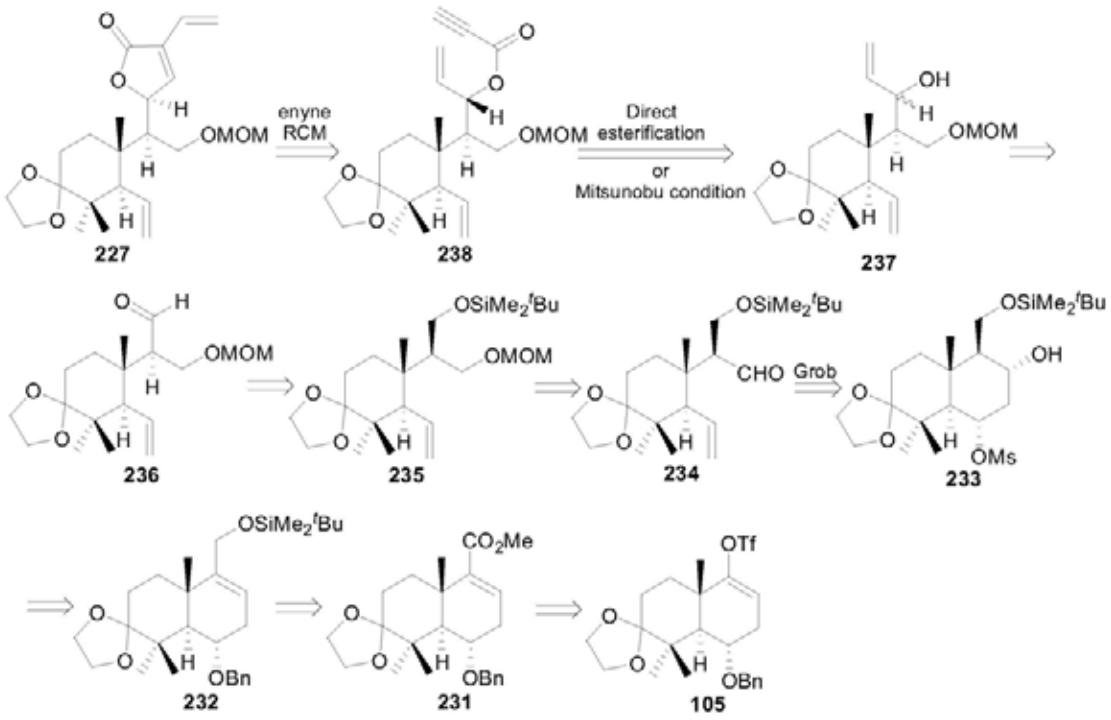
As a relative young reaction, metal-catalyzed olefin metathesis has enjoyed the considerable attention in recent years and gained widespread applications in the field of natural product synthesis.[120] During olefin metathesis, enyne metathesis was a good method to prepare conjugated diene. The enyne metathesis, especially intramolecular enyne metathesis (or ring-closing enyne metathesis), has been widely used in the total syntheses of natural products.[121] There are also some examples demonstrating the preparation of butenolide from olefin metathesis.[122] Notably, in 1999, Hoye and

co-workers[123] reported a two-step synthesis of (±)-differolide (**230**) featuring enyne metathesis of **228** to 2-vinylbutenolide **229** and subsequent [4+2] cycloaddition (Scheme 75).



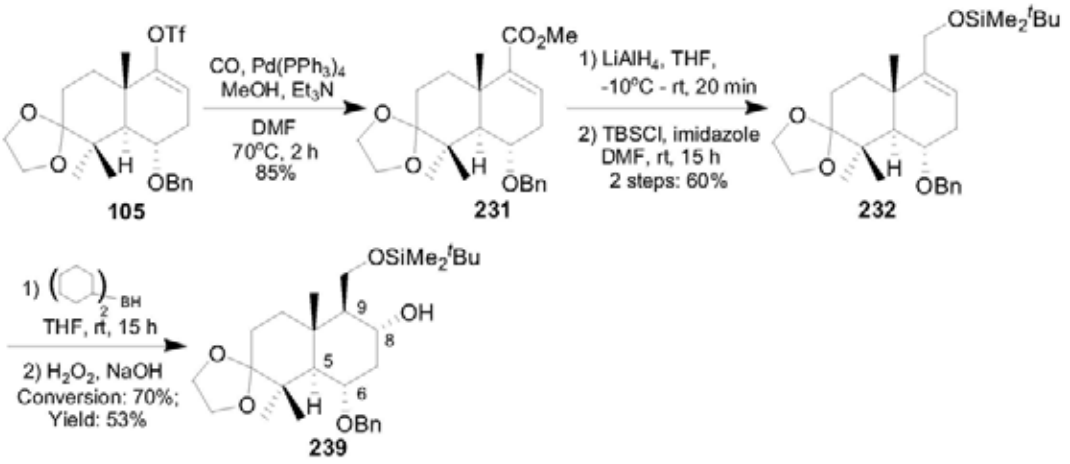
Scheme 75

In fact, our key intermediate **227** in this stage is just a 2-vinylbutenolide. So when our aforementioned investigations using peroxyacid oxidation did not materialize, we decided to try to build 2-vinylbutenolide **227** using the famous enyne metathesis. Our alternative synthetic analysis is shown in Scheme 76: a Pd-catalyzed methoxycarbonylation[124] of vinyltriflate **105** will provide ester **231**, which undergoes reduction and followed by protection to give silyl ether **232**. The next several steps are to prepare the precursor **233** for Grob fragmentation following the same protocols used previously. Once the Grob fragmentation is successful, aldehyde **234** will be converted to another aldehyde **236** using general transformations, which will be attacked by an organometallic reagent such as vinyl magnesiumchloride to provide alcohol **237**. The two alcohol isomers could be separated easily and the right alcohol could react with propiolic acid under general conditions to form ester **238**. For another isomer, a Mitsunobu reaction conditions will be used to convert the configuration. Once enyne **238** is obtained, the next enyne ring-closing metathesis (enyne RCM) will provide the desired 2-vinylbutenolide **227** selectively.



Scheme 76

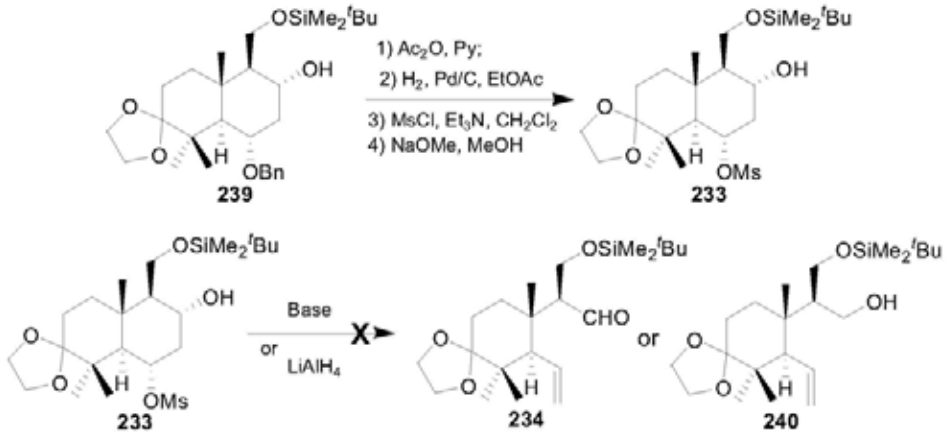
In practice, the methoxycarbonylation of triflate **105** with carbon monoxide catalyzed by $Pd(PPh_3)_4$ in hot mixture of MeOH and DMF afforded ester **231** in 85% yield. The molecular formula of **231** was established as $C_{24}H_{32}O_5$ based on HRMS (ESI) and elemental analysis. The resonance signals at δ_H 3.67 (s, 3H), δ_H 6.47 (dd, J = 3.6, 4.5 Hz, 1H) in its ^{1}H NMR spectrum (300 MHz, $CDCl_3$) and δ_C 167.72 in its ^{13}C NMR spectrum (75 MHz, $CDCl_3$) together with IR absorption at 1716 cm^{-1} illustrated the presence of an unsaturated methyl ester. The reduction using $LiAlH_4$ followed by protection as TBS ether **232** went smoothly. The hydroboration conditions of **232** were screened and the trial using cyclohexylborane could give alcohol **239** in moderate yield. The reaction using simple borane gave more of de-silyl side-product and the reaction using bulky 9-BBN led to low conversion of starting material (Scheme 77).



Scheme 77

The molecular formula of **239** was established as $C_{29}H_{48}O_5Si$ based on HRMS (ESI) analysis. The resonance signals at δ_H 4.04 (dt, J = 4.1, 10.6 Hz, 1H) and δ_H 3.64 (dt, J = 3.9, 10.5 Hz, 1H) in the ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **239** were assigned as H-8 and H-6 attached to oxygen atoms respectively. The resonance signal at $\delta_{H\text{-}5}$ 1.67 (d, J = 10.5 Hz, 1H) with large coupling constant showed the *anti* axial-axial correlation of H-5 and H-6. So based on the above spectrum data, the structure of **239** was established.

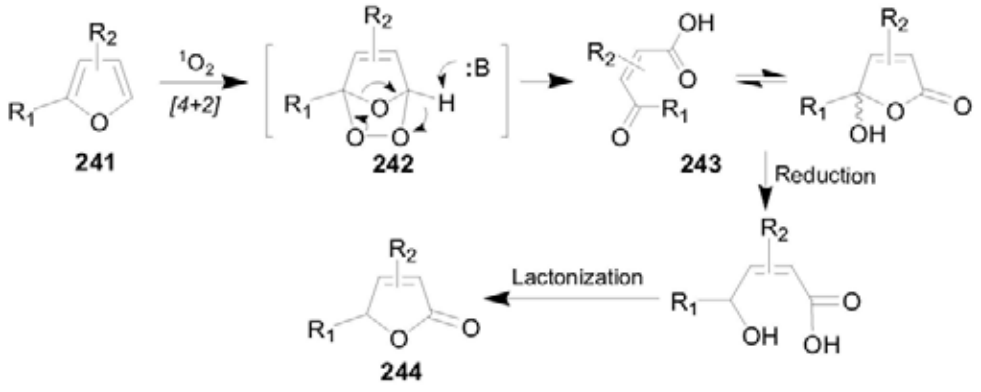
Then acetylation, hydrogenolysis, mesylation and deprotection employing similar reaction conditions as that from **156** to **160** furnished the precursor **233** for Grob fragmentation smoothly. The structure of **233** was confirmed by NMR, HRMS and IR analysis. Then the key Grob fragmentation was attempted carefully. However, all of our attempts failed to obtain desired products **234** and **240** although all kinds of reaction conditions used in our previous work were tested (Scheme 78).



Scheme 78

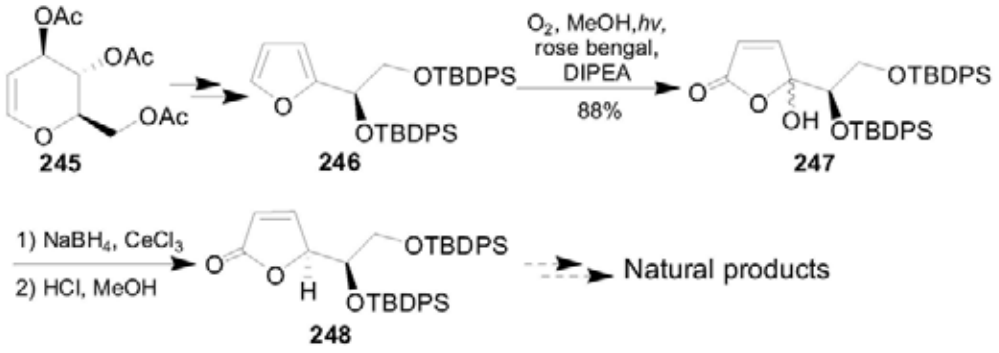
These unsuccessful investigations urged us to search other methods to prepare desired α,β-butenolide **227**.

Singlet oxygen is a highly reactive electrophilic species and a powerful tool in organic synthesis.[125] It's well known that 3-alkylfurans could be oxidized by singlet oxygen to produce the corresponding 3-alkyl-4-hydroxybutenolides[126] and many significant improvements to the basic reaction have been uncovered. Furan **241**, as an active diene, could undergo readily a [4+2] cycloaddition with photochemically generated singlet oxygen to form ozonide adduct **242**, which will be converted to the corresponding 4-hydroxybutenolide **243** in the presence of a hindered base such as diisopropylethylamine. Subsequent reduction will provide α,β-butenolide **244** (Scheme 79).



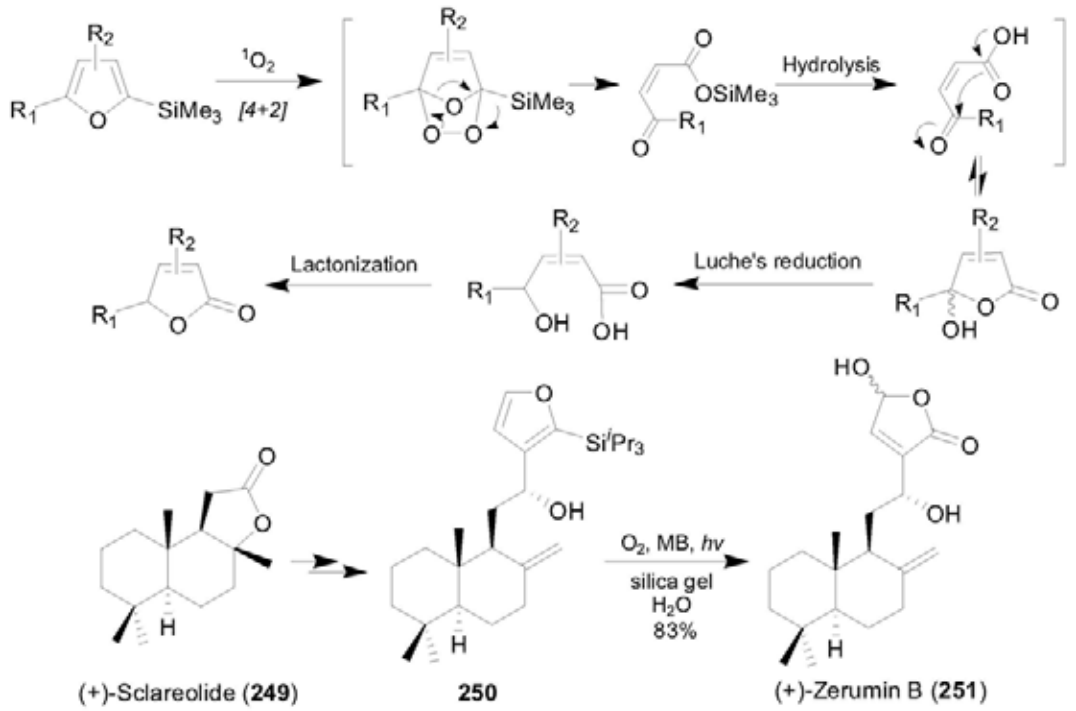
Scheme 79

There are many publications using the above method to prepare the heterocycles from furan.[115d,115e,127] For example, in 2005, Fall and co-workers[116d] reported an efficient approach to the synthesis of a chiral butenolide **248** based on the oxidation of a furan intermediate **246** with singlet oxygen followed by reduction (Scheme 80).



Scheme 80

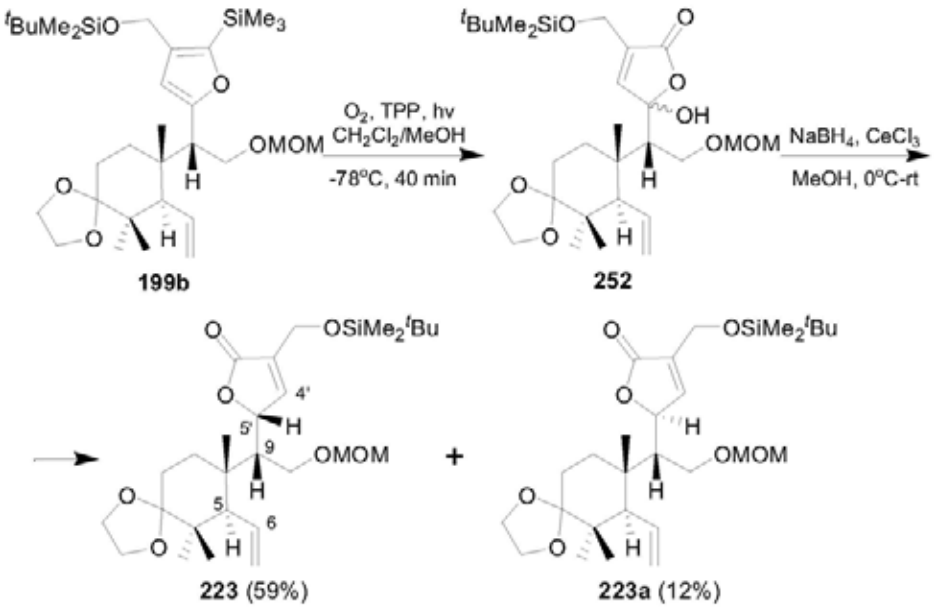
However, the transformation of the ozonide adduct into the corresponding 4-hydroxybutenolide by the action of base has always induced problems. A number of elegant solutions have been reported to solve this issue. In 1981, Adam and Rodriguez[128] found that a silyl group in furan could be used to stabilize the intermediate during the singlet oxygen oxidation, and this result was also found in other groups.[129] Many applications of singlet oxygen oxidation of 2-silylfuran to the total syntheses of natural products were reported recently. Especially, Vassilikogiannakis and co-workers[48,130] did significant work on applying singlet oxygen oxidation of furan species to the biomimetic synthesis. For example, in 2008, they reported a fast and efficient synthesis of (+)-zerumin B (**251**)[130] utilizing the regioselective singlet oxygen oxidation of 3-substituted furan **250** as the last key step (Scheme 81).



Scheme 81

Encouraged by these improvements in singlet oxygen oxidation of silylfurans, we then sought to convert 2-trimethylsilylfuran **199b** to desired α,β-butenolide **223** using singlet oxygen chemistry as a model transformation. Substrate **199b** and a catalytic amount of photosensitizer tetraphenylporphyrin (TPP) in a solvent mixture of dichloromethane and methanol was purged with oxygen 3 times and then the solution was irradiated using a 300 W of sunlamp at -78 ^{o}C under oxygen atmosphere (an oxygen balloon was used). After stirring for 40 min, TLC showed that all starting material **199b** was consumed and a new but much more polar spot was appeared. We thought the polar compound might be 4-hydroxybutenolide **252**. After general work up, the crude reaction residue was reduced under Luche condition[116d,131] and two products were isolated after careful column chromatography with nearly 5:1 diastereoisomeric ratio in more than 80% overall yield. To our delight, crude NMR showed the proton signals at downfield (δ_H 7.37 & 7.48) which supported the formation of α,β-butenolide motif. Then the structure of major product **223** was

identified using HRMS and NMR analyses (Scheme 82).



Scheme 82

The molecular formula of **223** was established as $C_{28}H_{48}O_7Si$ based on HRMS (ESI) analysis. The resonance signals at δ_H 7.37 (dd, J = 1.6, 3.4 Hz, 1H) and δ_H 5.39 (brs, 1H) in its ^{1}H NMR spectrum (300 MHz, acetone-d_6) were assigned as H-4' and H-5'. The resonance signal at δ_C 173.05 in its ^{13}C NMR spectrum (75 MHz, acetone-d_6) and IR absorption at 1727 cm^{-1} confirmed the presence of α,β-butenolide. The resonance signals at δ_H 5.85 (ddd, J = 10.2, 10.5, 17.4 Hz, 1H), δ_H 5.24 (dd, J = 2.7, 10.2 Hz, 1H), δ_H 5.07 (dd, J = 2.7, 17.4 Hz, 1H) and δ_H 2.40 (d, J = 10.5 Hz, 1H) in the ^{1}H NMR spectrum of **223** suggested the presence of CH-CH=CH$_2$ unit. Thus, based on the above results, the gross structure of **223** was established.

Ultimately, structure of **223** was confirmed by an X-ray crystallographic analysis (Figure 8). Based on the mechanism of reduction using $NaBH_4$, the other isomer should be **223a**.

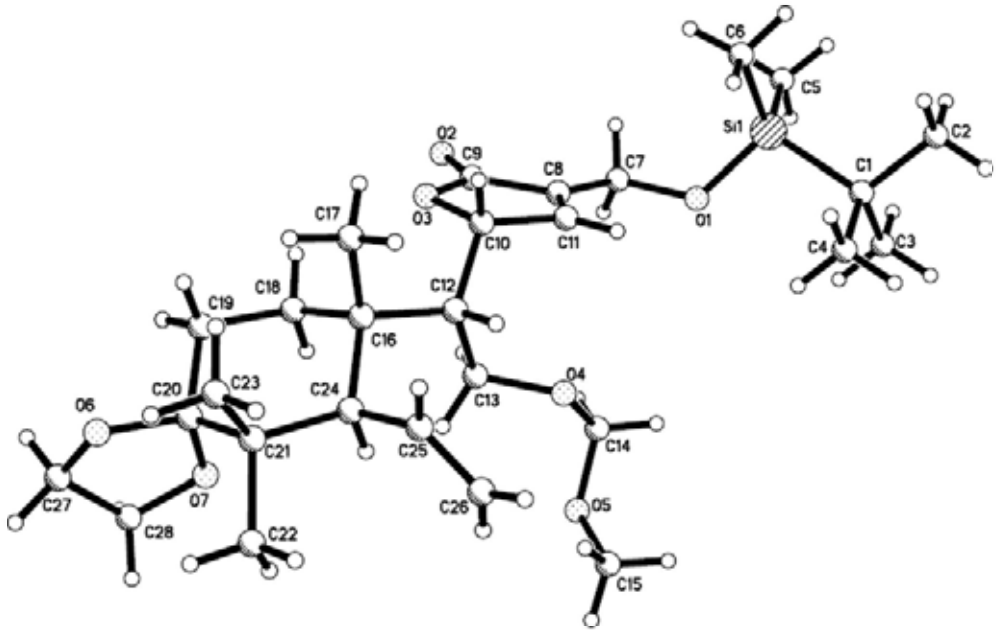
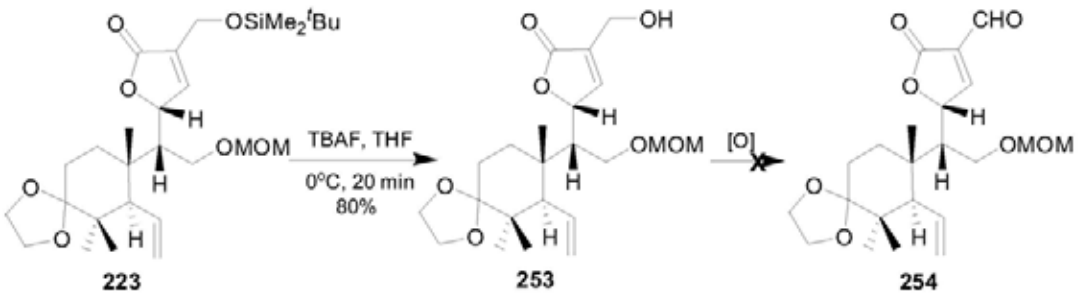
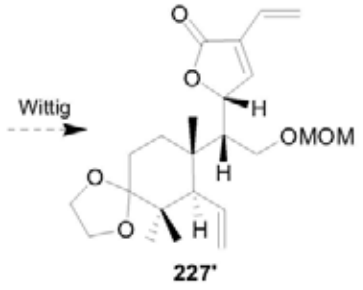


Figure 8. ORTEP drawing of compound **223**

With butenolide **223** in hand, we then tried to convert it to the corresponding vinylbutenolide **227'**. Thus, the TBS group was firstly unmasked using TBAF in tetrahydrofuran at low temperature (0 °C) and alcohol **253** was obtained in 80% yield and its structure was elucidated with NMR and HRMS analyses. However, the next oxidation was problematic. Although we had tried several oxidants such as PDC, Dess-Martin periodinane reagent[132] and Swern conditions,[133] we still failed to obtain positive result (Scheme 83). In all of the cases, no obvious spot was observed on TLC although all starting material was consumed and no aldehyde signal was detected from the crude NMR spectrum. We presumed that this kind of aldehyde in **254** was very unstable and it would be decomposed even under mild conditions.



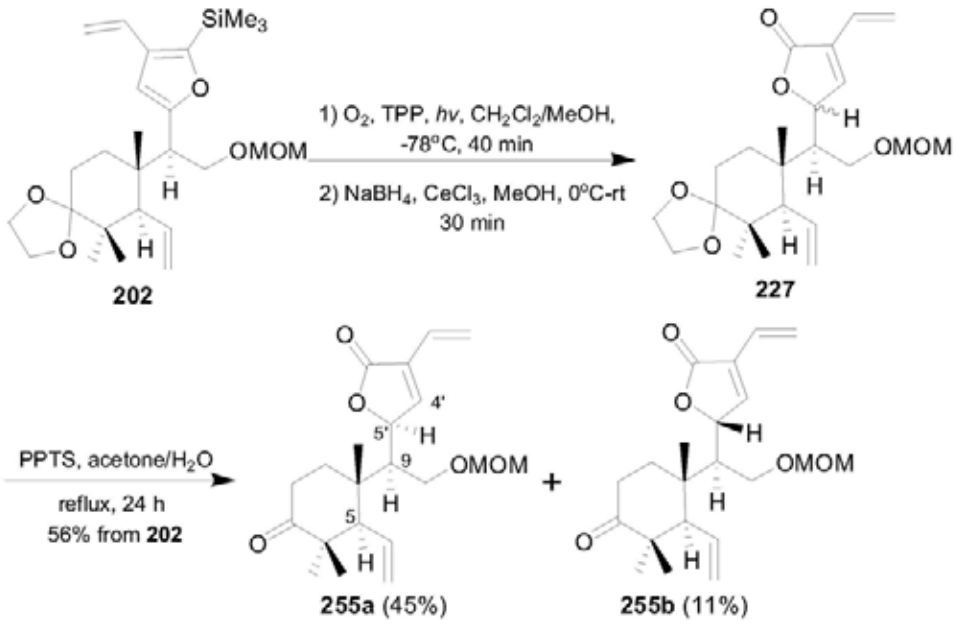
entry	oxidation condition	result
1)	PDC, CH_2Cl_2, 4 Å MS, 0°C-rt	Failed
2)	DMP, CH_2Cl_2, 0°C-rt	Failed
3)	DMP, $NaHCO_3$,CH_2Cl_2, 0°C-rt	Failed
4)	DMP, $NaHCO_3$,CH_2Cl_2/H_2O, 0°C-rt	Failed
5)	Swern conditions	Failed



Scheme 83

We next tried the singlet oxygen oxidation on vinylfuran **202** in the hope to prepare our desired **227**. Gratifyingly, the singlet oxygen oxidation followed by Luche reduction of **202** yielded vinylbutenolide **227** with a moderate yield. The formation of α,β-butenolide was characterized from the proton resonance signals at downfield (δ_H 7.48 & 7.66) based on a crude NMR spectrum. It was worthy to note that the two isomers **227a** and **227b** were not separable using column chromatography and the diastereoselectivity was judged through a crude NMR spectral analysis to be about 4:1. Based on the mechanism of reduction using $NaBH_4$ and the aforementioned preparation of **223**, the major isomer should be our desired *syn* product **227a**. After de-ketalization by treatment of **227** with PPTS in a refluxing solution of acetone/H_2O (*v*/*v* = 20:1), the two isomers of the corresponding ketone **255a** and **255b** were obtained after a careful column chromatography on silica gel (Scheme 84). We also investigated the above singlet oxygen oxidation, using other photosensitizer such as Rose Bengal, changing solvent system to MeOH, and executing the reduction at much lower temperature with an aim to increase the diastereoselectivity and the yield.

However, similar results instead of better outcome were obtained.



Scheme 84

The molecular formula of **255a** was established as $C_{21}H_{30}O_5$ based on HRMS (ESI) and elemental analysis. The resonance signals at δ_H 7.46 (m, 1H) and δ_H 5.57 (brs, 1H) in the ^{1}H NMR spectrum (400 MHz, acetone-d_6) of **255a** were assigned as H-4' and H-5' respectively. The resonance signal at δ_C 172.55 in its ^{13}C NMR spectrum (100 MHz, acetone-d_6) and IR absorption at 1706 cm^{-1} confirmed the presence of an α,β-butenolide. The resonance signal at δ_C 214.70 together with IR absorption at 1759 cm^{-1} suggested the presence of a ketone group. The resonance signals at δ_H 5.98 (ddd, J = 10.3, 10.5, 17.2 Hz, 1H), δ_H 5.32 (dd, J = 2.2, 10.3 Hz, 1H), δ_H 5.25 (dd, J = 2.2, 17.2 Hz, 1H) and δ_H 2.68 (d, J = 10.5 Hz, 1H) in the ^{1}H NMR spectrum of **255a** illustrated the presence of a CH-CH=CH$_2$ group. The resonance signals at δ_H 6.47 (dd, J = 11.4, 17.4 Hz, 1H), δ_H 6.22 (dd, J = 1.8, 17.4 Hz, 1H) and δ_H 5.40 (dd, J = 1.8, 11.4 Hz, 1H) in its ^{1}H NMR spectrum were assigned as a C-CH=CH$_2$ attached to the butenolide motif. Thus, based on the above results, the gross structure of **255a** was

established.

The stereochemistry of our major isomer **255a** was confirmed to be the desired product after an X-ray crystallographic analysis (Figure 9).

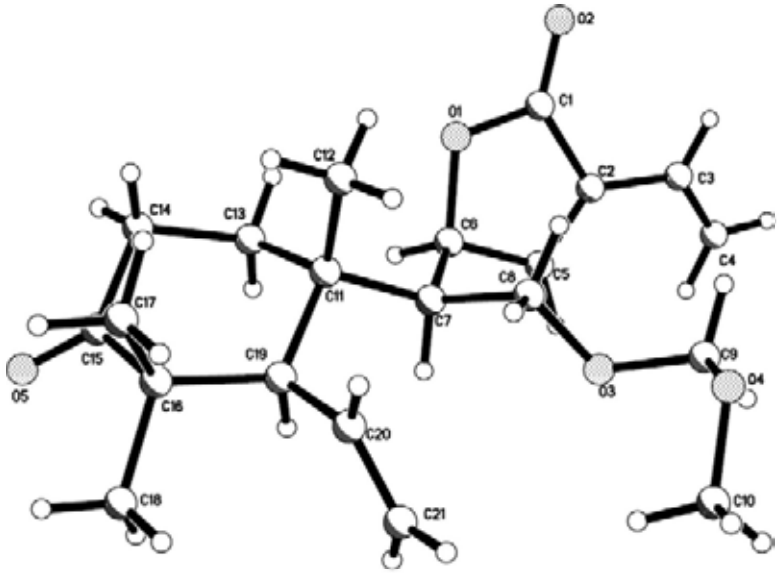
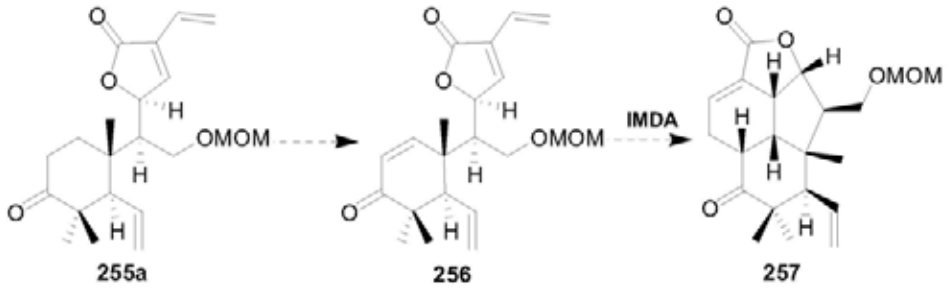


Figure 9. ORTEP drawing of compound **255a**

As demonstrated in Chapter 1, singlet oxygen oxidation of furan derivatives has been considered a possibility involved in the biosynthesis of natural molecule. Our success in this stage again supported the hypothesis of a biogenetic synthesis using singlet oxygen as an oxidant.

2.2.8 Preparation of compound 257

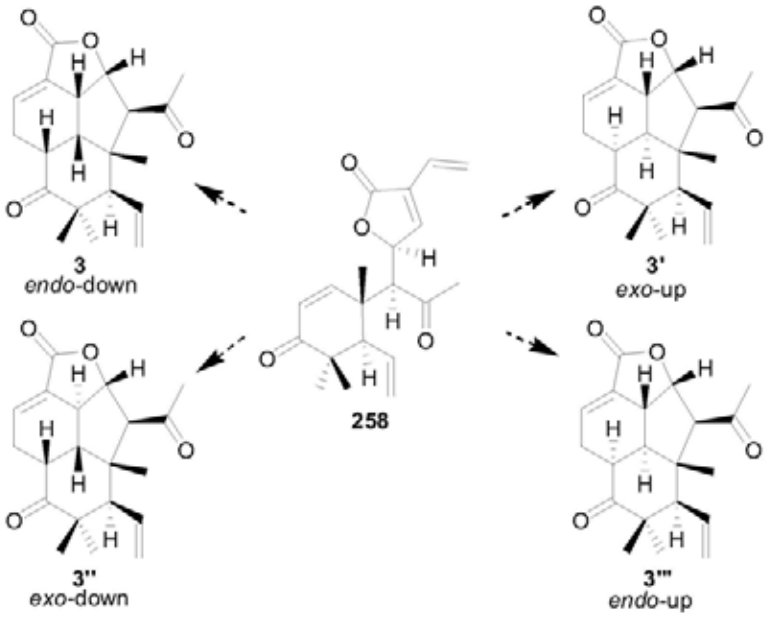
With vinylbutenolide **255a** in hand, we then turned our attention to introduce a double bond between C1 and C2 to form α,β-unsaturated ketone **256**, which would serve finally as the precursor for an intramolecular Diels-Alder cycloaddition en route to **257** (Scheme 85).



255a 256 257

Scheme 85

Initially, we chose **258** as a model to study the cycloaddition. From theory, this step could produce four possible isomers **3**, **3'**, **3''** and **3'''**. Molecules **3''** and **3'''** cannot be formed due to *trans*-fused bicyclo[3.3.0] systems. The computation (optimization and thermal correction at HF/6-31G(d) and single point computation at B3LYP/6-31G(d) level) showed that the *endo*-cycloaddition leading to **3** (ΔH = –123.9 kJ/mol, ΔS = –79.0 kJ/mol, ΔG = –100.4 kJ/mol) was more favorable by 72.8 kJ/mol than that for the formation of **3'** (ΔH = –49.6 kJ/mol, ΔS = –73.8 kJ/mol, ΔG = –27.6 kJ/mol). The activation energies computed for the transition states of *endo*-down **3** and *exo*-up **3'** were 79.0 kJ/mol and 152.1 kJ/mol, respectively. It therefore appeard that *endo*-down **3** should be the most favorable adduct from the IMDA cycloaddition (Scheme 86).



Scheme 86

Before research results are discussed, we would like to give a simple introduction to the Diels-Alder reaction.

Since its discovery in 1928 by Diels and Alder,[134] Diels-Alder reaction has become the most powerful method to rapidly construct six-membered rings in organic chemistry.

The Diels-Alder reaction refers to the cycloaddition between a conjugated diene (a diene) and a double bond (a dienophile) in a 1,4-manner ([4+2] cycloadditon). The reaction is highly stereospecific and the stereochemistry of this reaction can always be predicted based on the analysis of the HOMOs and LUMOs of the reactants.[135]

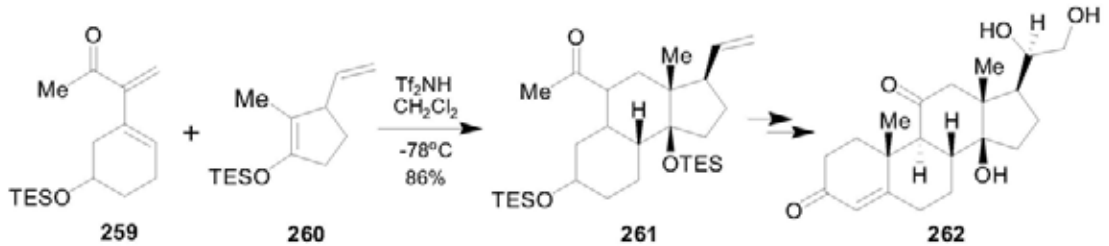
There are some general rules for the Diels-Alder reaction: (a) Electron-donating substituents in the diene accelerate the reaction and electron-withdrawing groups retard it; it is just the reverse for the dienophile: electron-donating groups decrease the rate and withdrawing groups increase it; (b) The addition does not change any stereochemistry of reactants so the cycloaddition is stereospecifically; (c) The diene

must be in the cisoid conformation or must be able to achieve it during the reaction. Otherwise, the reaction does not take place; d) The addition is predominantly *endo* in most cases; e) Although the Diels-Alder reaction is concerted, bond formation is asynchronous in the transition state; f) The Diels-Alder reaction is usually reversible; and g) The addition could be accelerated by using many methods such as high pressure, microwave irradiation, ultrasound or Lewis acid catalysis.[135]

Based on the structure of reactants, the Diels-Alder reaction involved intermolecular Diels-Alder and intramolecular Diels-Alder (IMDA) reaction and transannular Diels-Alder (TADA) reaction. From the electronic aspect, Diels-Alder reaction can be divided into a normal version and an inverse electron demand version.

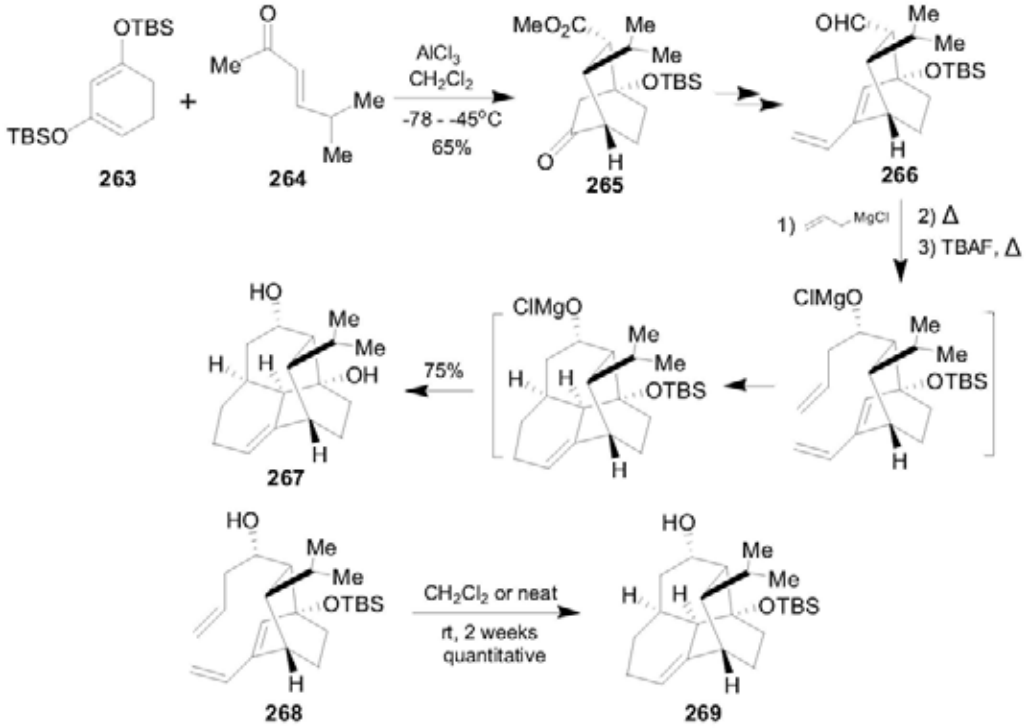
Nowdays, Diels-Alder cycloaddition has been widely applied in total synthesis so that almost each synthesis of natural product would include one Diels-Alder reaction as the key step.[70] We herein present several recent examples of total synthesis using Diels-Alder reaction.

In 2008, Chu and co-worker[136] reported an efficient synthetic route toward the core structure **262** for rhodexin A. Thus, an inverse electron demand intermolecular Diels-Alder reaction between the electron-poor acyldiene **259** and silyl enol ether **260** gave a cycloadduct **261**. It was then converted to the key intermediate **262** which could be served as an important intermediate towards rhodexin A (Scheme 87).



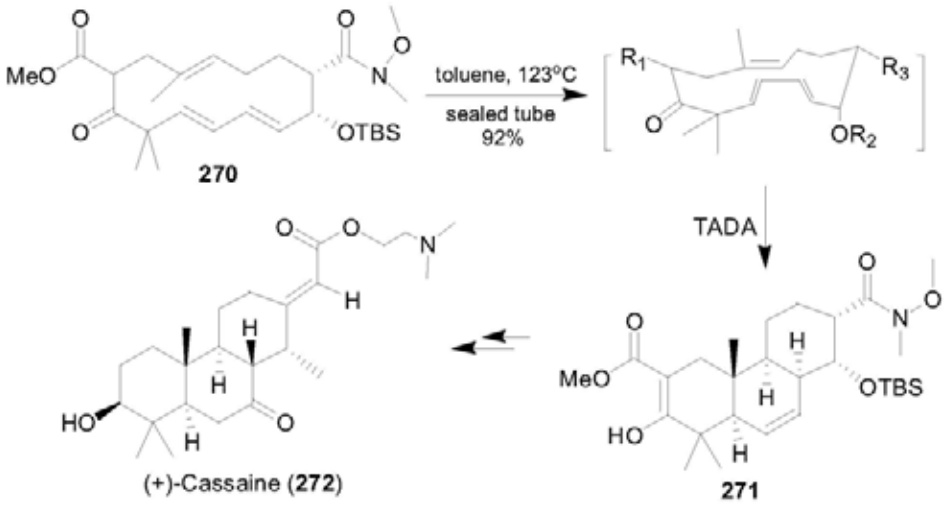
Scheme 87

Baran and co-workers[137] reported a concise approach to the carbon skeleton of diterpene vinigrol. Their endeavor started from a Lewis-acid catalyzed intermolecular Diels-Alder cycloaddition between diene **263** and dienophile **264**, producing a bicyclic ketone **265**. After several steps, a tandem addition/intramolecular Diels-Alder reaction sequence was used to provide diol **267**, which would yield the core skeleton of vinigrol. Notably, Baran found that the IMDA reaction took place even at room temperature due to a strong proximity effect and it was regarded as the only example of a noncatalyzed cycloaddition between a completely electron-neutral diene and simple olefin (**268** to **269**) happened at ambient temperature (Scheme 88).



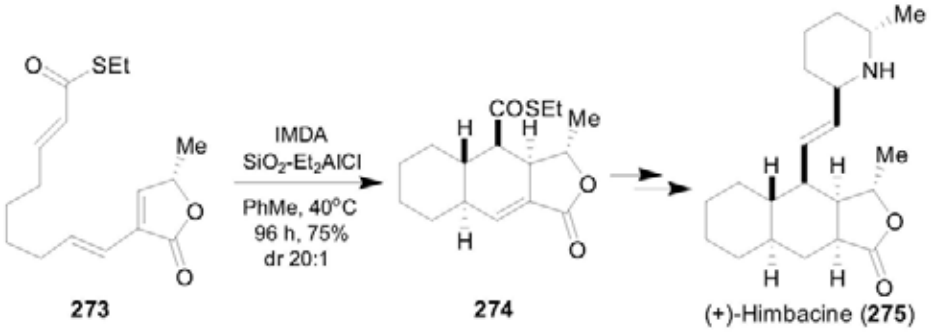
Scheme 88

Recently, transannular Diels-Alder reaction (TADA) attracted much attention because it is able to construct molecular complexity rapidly.[138] In 2008, Deslongchamps and co-workers[138d] reported the total synthesis of (+)-cassaine (**272**) using TADA reaction as the pivotal step (Scheme 89).



Scheme 89

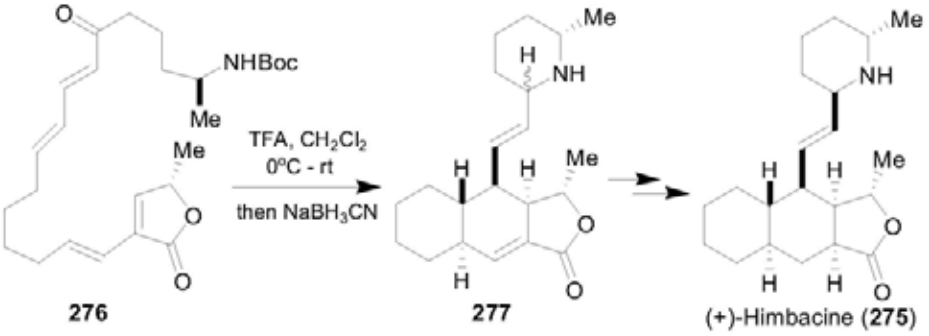
Our Diels-Alder precursor **256** is a vinylbutenolide and there are also many examples using the IMDA of vinlybutenolide to construct the skeleton of natural molecules. For example, in 1997, Hart and co-worker[139] reported the total synthesis of (+)-himbacine (**275**) using organosulfur chemistry. The key step of this work was the intramolecular Diels-Alder reaction of **273** containing a vinylbutenolide (as diene) and an unsaturated thioester group (as more reactive dienophile). Thus, compound **273** was treated with an acid promoter at 40 °C for 4 days and the *endo* product **274** was obtained predominately in 75% yield (Scheme 90).



Scheme 90

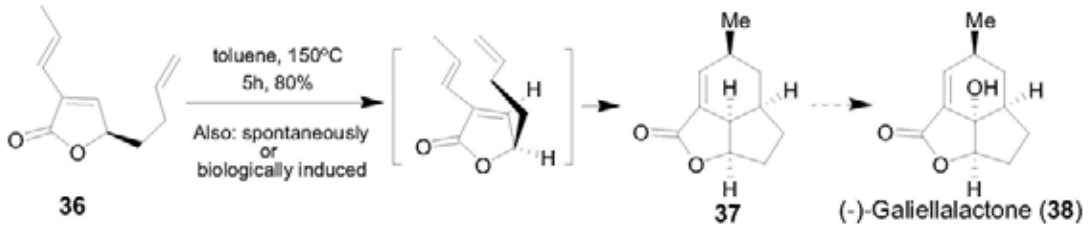
In 2005, Baldwin and co-worker[62a] also reported the biomimetic total synthesis of

(+)-himbacine (**275**). The tricyclic core skeleton was again achieved by the IMDA reaction. During the course of this reaction, trifluoroacetic acid promoted butenolide **276** to undergo *N*-deprotection and condensation followed by an iminum ion activated IMDA cycloaddition to give the precursor **277** for (+)-himbacine on reductive work up (Scheme 91).



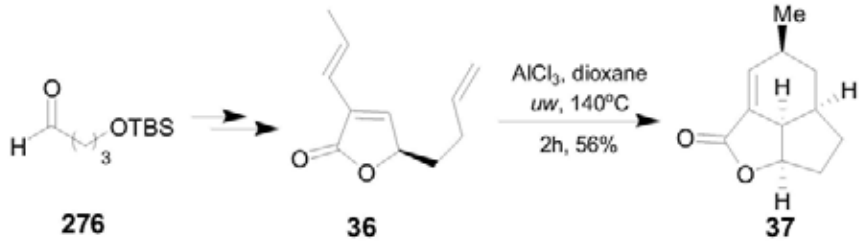
Scheme 91

As demonstrated in Chapter 1, Sterner and co-workers[35] reported the cyclization of (-)-pregaliellalactone (**36**) to (+)-desoxygaliellalactone (**37**) which was regarded as the first example of an intramolecular Diels-Alder reaction with inverse electron demand in a polyketide biosynthetic pathway (Scheme 92). They found that the cyclization of **36** could take place to give the desired product **37** in 80% yield when it was heated at 150 °C in toluene in a sealed tube for 5 h. Notably, they also found that the cyclization could take place spontaneously or faciliated in the fungua *Galiella rufa* and led to the same products.



Scheme 92

In 2007, Lebel and co-worker[140] also reported the total synthesis of (+)-desoxygaliellalactone (**37**) using the IMDA reaction of the same precursor **36**. Surprisingly, they found that the above result was irreproducible under Sterner's reaction conditions and the desired product could not be isolated. Alternatively, the desired product **37** was obtained in 56% yield when **36** was treated with aluminum trichloride at 140 °C under microwave for 2 h in a sealed tube (Scheme 93).

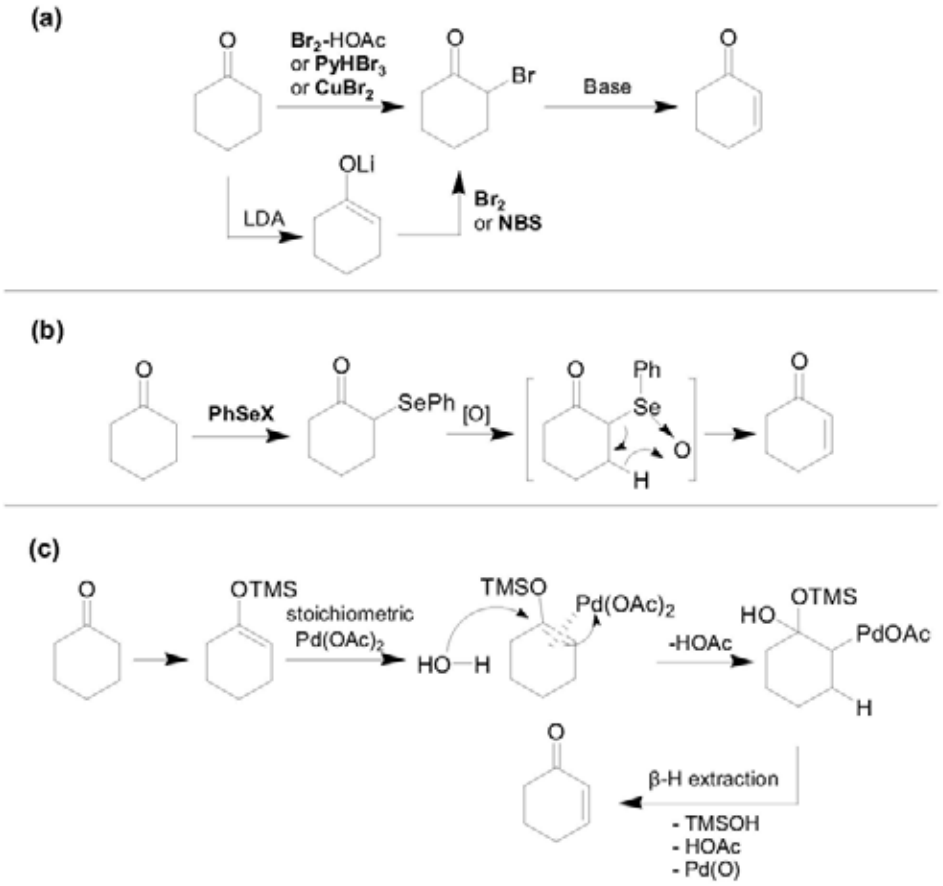


Scheme 93

Encouraged by the above information, we are convinced that the synthesis of compound **257** containing the core structure of natural product could be realized by an intramolecular Diels-Alder reaction once we obtained the precursor **256**.

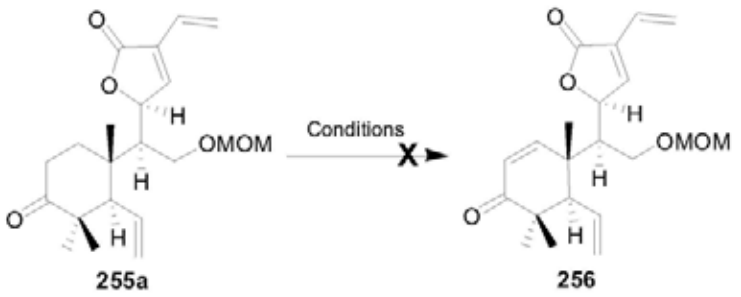
We then started to prepare **256** from ketone **255a**. There are several methods to prepare α,β-unsaturated ketone through dehydrogenation of saturated carbonyl compounds.[141] The three most popular methods are: 1) α-halogenation (bromide or iodide) and subsequent elimination in the presence of a base (Scheme 94 (a));[142a] 2) sulfenylation-sulfoxide elimination or selenylation-selenoxide elimination, which was

frequently employed in organic synthesis due to their versatility. In this reaction, α-selenium compound was prepared from the corresponding metal enolate of saturated ketone and it was then oxidized to induce elimination at a suitable temperature (Scheme 94 (b));[142c] 3) preparation of the corresponding silyl enol ethers or silyl ketene acetals followed by oxidation with palladium acetate (Saegusa oxidation) (Scheme 94 (c)).[142b]



Scheme 94

We made use of the above several routine methods in the hope to convert ketone **255a** to unsaturated ketone **256**. However, all our investigations failed to give the desired product although these reactions were performed carefully and were repeated more than 2 times (Scheme 95 and Table 8).

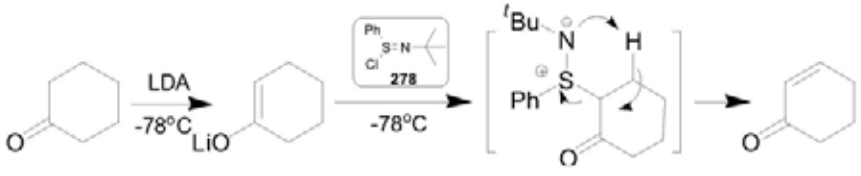


255a 256

Entry	Reaction conditions	Results
1	1) $CuBr_2$, THF, 24 h; 2) $CaCO_3$, DMF, 120 °C	Failed
2	1) LiHMDS, TMSCl; 2) NBS; 3) DBU	Failed
3	$FeCl_3$, NaI, CH_3CN, rt	Complicated
4	1) LiHMDS, PhSeCl; 2) H_2O_2, Py	Complicated
5	1) LiHMDS, PhSeSePh + Br_2; 2) H_2O_2, Py	Complicated
6	1) *p*-TsOH, PhSeCl, EA, 0°C; 2) H_2O_2, Py, CH_2Cl_2	Not desired product
7	SeO_2, ^{t}BuOH, 100 °C, 8 h	No reation
8	1) TMSOTf, Et_3N, CH_2Cl_2; 2) $Pd(OAc)_2$, CH_3CN	Failed
9	1) LiHMDS, TMSCl; 2) $Pd(OAc)_2$, CH_3CN	Failed
10	1) LDA, TMSCl; 2) $Pd(OAc)_2$, DDQ, CH_3CN	Failed

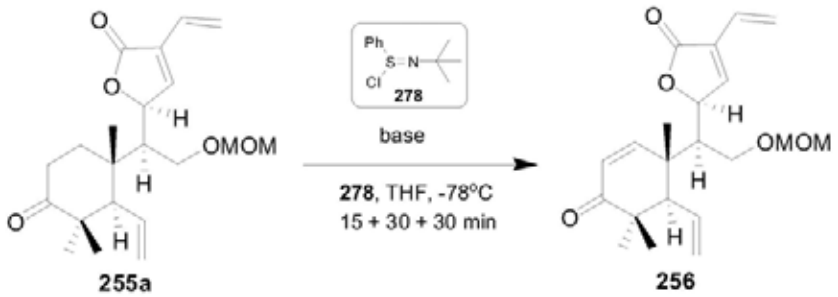
Scheme 95 & Table 8

Recently, Mukaiyama and co-workers[143] reported a new method for the dehydrogenation of ketones to form the corresponding α,β-unsaturated ketones by using *N-tert*-butyl phenylsulfinimidol chloride (**278**)[144] and the dehydrogenation step occurred in a one-pot manner under very mild conditions (Scheme 96). This mild condition had been used in organic synthesis successfully.[145]



Scheme 96

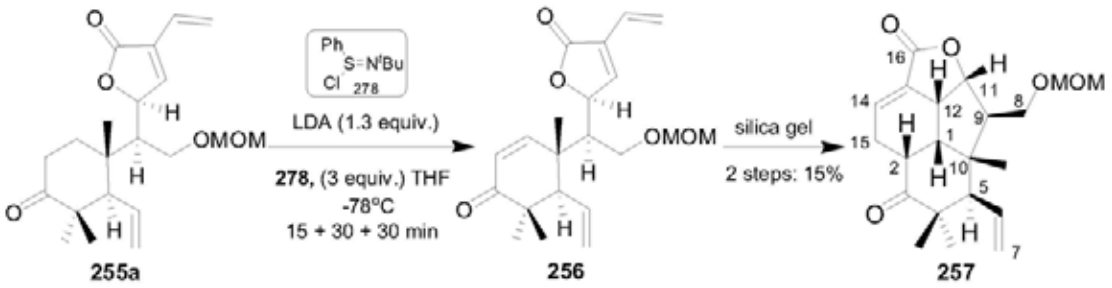
We therefore tried the Mukaiyama condition on our substrate **255a**. Thus, **255a** was treated very carefully with freshly prepared LDA (1 equiv.) and then the resulting lithium enolate was allowed to react with reagent **278** (1.1 equiv.). After 30 min, the reaction was quenched with dilute acid and the crude NMR spectrum showed that the desired double bond, assigned as δ_H 7.00 (d, J = 10.4 Hz, 1H) and δ_H 5.90 (d, J = 10.4 Hz, 1H) in the ^{1}H NMR spectrum (400 MHz, acetone-d_6), was formed but the reaction gave low conversion (< 20%). Unfortunately, TLC showed that the product almost has the same R_f value as that of the starting material. Therefore we tried to optimize this reaction. However, satisfied results could not be achieved even though we tried many reaction conditions. In addition, the reaction was very tricky and it should be carried out in a very careful manner. During the preparation of LDA, the amount of *n*-BuLi must not be in excess, otherwise, all of the starting material would be consumed and no product could be obtained. Reagent **278** should be freshly prepared and it was added to the reaction in one portion. At last, we found that the best condition was to treat substrate **255a** with freshly prepared LDA (1.3 equiv.) at –78 °C for 30 min and then the reagent *N-tert*-butyl phenylsulfinimidoyl chloride (**278**) (3 equiv.) was added in one portion rapidly. After another 30 min at –78 °C, the reaction was quenched with dilute acid and usual workup was carried out. From the crude NMR spectrum, we found that the desired product was formed. From NMR and TLC, we judged that the yield was about 20% (Scheme 97 and Table 9).



Entry	Reaction conditions	Results
1	LDA (1.0 equiv.), **278** (1.1 equiv.)	< 20% conversion
2	LDA (1.0 equiv.), **278** (3 equiv.)	< 30% conversion
3	LDA (1.2 equiv.), **278** (3 equiv.)	~ 50% conversion
4	LDA (1.3 equiv.), **278** (3 equiv.)	~ 60% conversion ~ 20% yield
5	LDA (1.5 equiv.), **278** (3 equiv.)	~ 90% conversion, messy
6	LDA (1.3 equiv.), TMEDA (2 equiv.), **278** (3 equiv.)	~40% conversion, <15% yield
7	LDA (1.3 equiv.), HMPA (2 equiv.), **278** (3 equiv.)	~60% conversion, messy
8	LiHMDS (1.3 equiv.), **278** (3 equiv.)	Failed
9	KHMDS (1.3 equiv.), **278** (3 equiv.)	Failed

Scheme 97 & Table 9

In some trials, we did purification of the crude product on a long column. However, we lost the desired material after column chromatography and a more polar compound was obtained. To our delight, it was tetracyclic compound **257** based on NMR and MS analyses. It was likely that the intramolecular Diels-Alder reaction proceeded very easily (Scheme 98). The production of *endo*-product **257** as the only isomer was due to the more favorable *cis*-fused bicyclo[3.3.0] system and the steric hindrance of the methyl group. This result was also consistent with our preliminary computation.



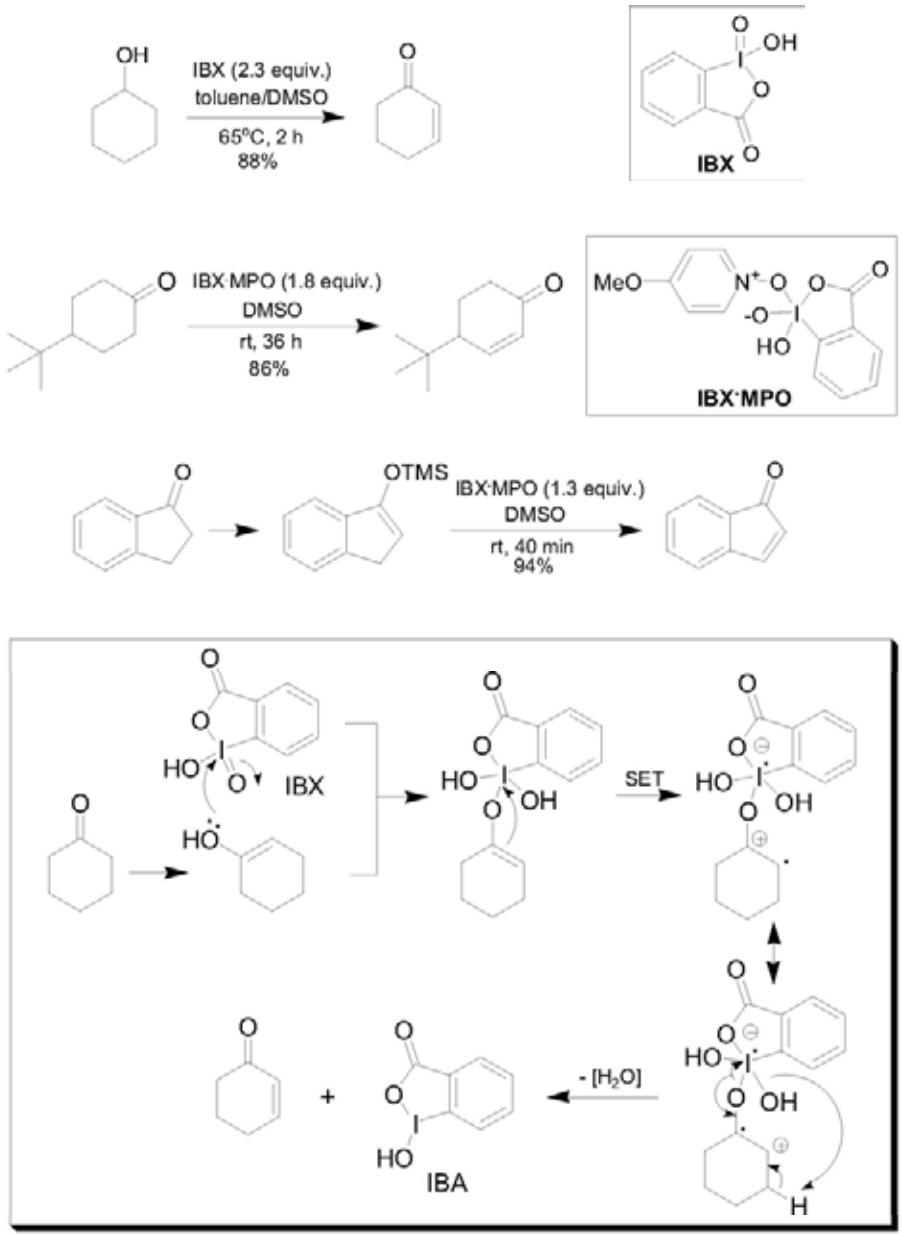
Scheme 98

The molecular formula of **257** was established as $C_{21}H_{28}O_5$ based on HRMS (EI) analysis. The resonance signal at δ_H 7.18 (ddd, J = 3.0, 3.1, 7.9 Hz, 1H) in its ^{1}H NMR spectrum (400 MHz, acetone-d_6) was assigned as H-14. The resonance signal at δ_C 169.77 in the ^{13}C NMR spectrum (100 MHz, acetone-d_6) and IR absorption at 1705 cm^{-1} suggested the presence of an α,β-unsaturated lactone. The resonance signal at δ_C 216.68 together with IR absorption at 1760 cm^{-1} demonstrated the presence of a ketone group. The resonance signals at δ_H 6.16 (ddd, J = 10.0, 11.1, 16.6 Hz, 1H), δ_H 5.19 (dd, J = 2.2, 10.0 Hz, 1H), δ_H 5.11 (dd, J = 2.2, 16.6 Hz, 1H) and δ_H 2.49 (d, J = 11.1 Hz, 1H) in the ^{1}H NMR spectrum were assigned as H-5, H-6 and H-7 in the unit of CH-CH=CH$_2$. The resonance signal at δ_H 4.93 (t, J = 8.7 Hz, 1H) in its ^{1}H NMR spectrum was assigned as H-11 of the lactone. Compound **257** showed three methyl signals at δ_H 0.93 (s, 3H), δ_H 1.03 (s, 3H) and δ_H 1.14 (s, 3H) and a signal of methyl in MOM at δ_H 3.29 (s, 3H). Thus, based on the above results, the gross structure of **257** was established. In addition, the stereochemistry of **257** was confirmed indirectly by an X-ray diffraction analysis of one of its derivatives and the detailed information will be discussed below.

The reaction under Mukaiyama conditions gave the desired product but with very low yield. So we had to continue to try other methods.

Recently, Nicolaou and co-worker reported a series of articles promoting a new

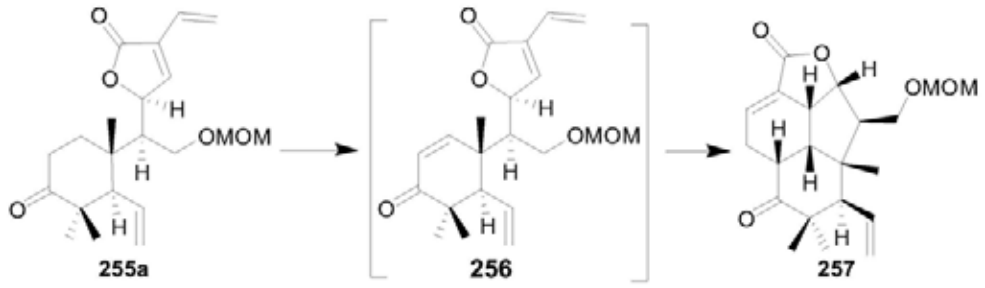
IBX-mediated dehydrogenation of carbonyl compound to realize α,β-unsaturated carbonyl through a proposed single-electron transfer mechanism (Scheme 99).[146]



Scheme 99

These mild and efficient methods attracted our attention. We then utilized the above methods to our substrate **255a**. However, the above reaction conditions failed to give any satisfied results although we tried several times very carefully. At last, we run the reaction under acidic conditions. Thus, **255a** (10 mg scale) was allowed to

react with IBX (3 equiv.) at 65 °C and a catalytic amount of *p*-TsOH (0.1 equiv.) was added to the solution to facilitate the formation of an enol. After stirring for 3.5 h at 65 °C, TLC showed the conversion was about 90% and a more polar compound as the major product was isolated. To our delight, it was the Diels-Alder cycloadduct **257** and the overall yield of these two steps was 40% (Table 10, entry 8). In fact, it was a tandem enone formation/IMDA cycloaddition sequence. We presumed that only *endo*-product **257** was formed because of the more favorable *cis*-fused bicyclo[3.3.0] system and the steric hindrance of the methyl group. The result also accorded with our preliminary computation. However, the yield decreased when the reaction was scaled up to 50 mg scale (25% yield, Table 10, entry 8). It was assumed that the strong acidity of *p*-TsOH decomposed the substrate. Then we carried out the reaction by adding weak acidic pyridinium *p*-toluenesulfonate (PPTS) in stead of *p*-TsOH to the mixture of substrate and IBX. After heating to 65 °C for 3.5 h, product **257** was produced. After optimization, we obtained the cycloaddition adduct **257** in 42% isolated yield based on 80% of conversion by using 1.5 equiv. of PPTS (Table 10, entry 10) and the reaction could be scaled up to 50 mg (Scheme 100 and Table 10).



255a **256** **257**

Entry	Reaction conditions	Results
1	IBX (3.0 equiv.), DMSO, 70 °C, 2 h	No reaction
2	IBX (3.0 equiv.), DMSO, 70 °C, 16 h	80% conversion, messy
3	IBX.NMO (1.8 equiv.), DMSO/ CH_2Cl_2, rt, 16 h	messy
4	1) LDA, TMSCl; 2) IBX.NMO (1.3 equiv.), DMSO/ CH_2Cl_2, rt, 1 h	messy

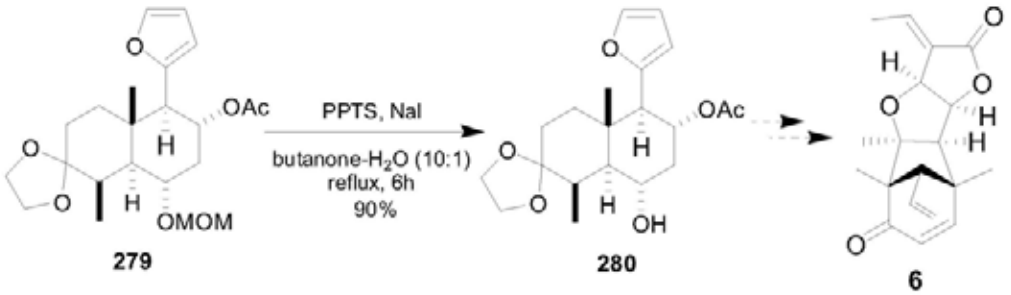
5	1) TMSOTf, Et_3N, CH_2Cl_2; 2) IBX.NMO (1.3 equiv.), DMSO/ CH_2Cl_2, rt, 1 h	messy
6	IBX (3.0 equiv.), DBU, DMSO, 70 °C, 2 h	messy
7	IBX (3.0 equiv.), *p*-TsOH (0.1 equiv.), DMSO, 65 °C, 2 h	Conversion ~ 50%
8	IBX (3.0 equiv.), *p*-TsOH (0.1 equiv.), DMSO, 65 °C,3.5 h	Conversion ~ 90% (10 mg, 40% yield; 50 mg, 25% yield)
9	IBX (3.0 equiv.), PPTS (0.5 equiv.), DMSO, 65 °C,3.5 h	Conversion ~ 40%
10	IBX (3.0 equiv.), PPTS (1.5 equiv.), DMSO, 65 °C,3.5 h	Conversion ~ 80% (50 mg, 42% yield)
11	IBX (3.0 equiv.), PPTS (3 equiv.), DMSO, 65 °C,3.5 h	Conversion ~ 90% (< 30% yield)

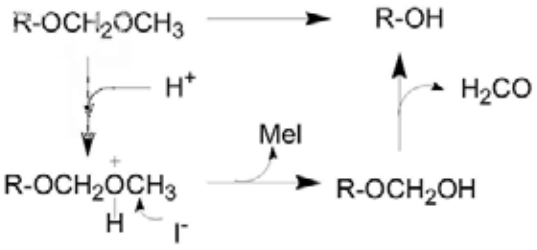
Scheme 100 & Table 10

2.2.9 Total synthesis of (±)-pallavicinolide A (3)

With the tetracyclic fused core strucrure **257** in hand, we then focused on the modification of side chain at the final stage in order to complete the total synthesis.

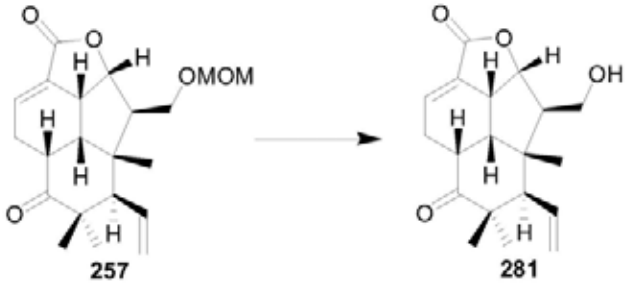
Firstly, the MOM group should be removed. During the synthetic studies toward the natural molecule **6** by Zhang in our group, he found that MOM ether **279** was deprotected easily to give alcohol **280** when it was treated with weak acidic PPTS plus a strong nuclephilic reagent NaI in refluxing 2-butanone-H_2O for 6 h (Scheme 101).[147]





Scheme 101

We then applied this method to our compound **257** and the desired alcohol **281** was obtained successfully in 75% yield. We also tried several routine acidic conditions. However, most of them gave lower yields due to the acid-labile skeleton (Scheme 102 and Table 11). The structure of **281** was characterized by NMR, HRMS and IR analyses.

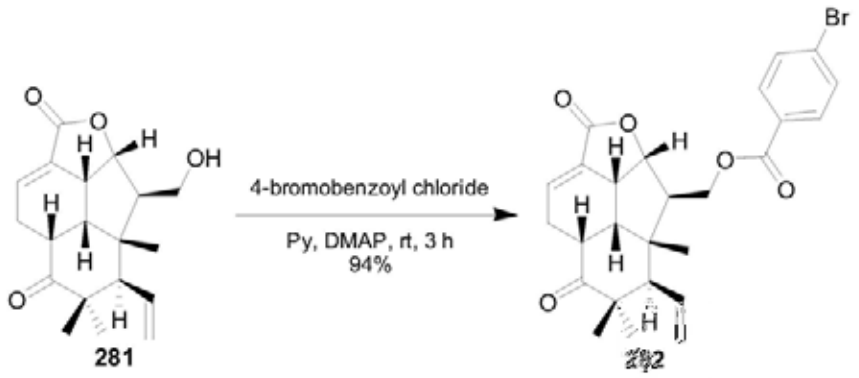


257 **281**

entry	de-MOM condition	result
1)	PPTS, NaI, butanone-H_2O (10:1) reflux, 15 h	75%
2)	*p*-TsOH, Toluene/H_2O, 70°C, 15 min	25%
3)	HCl (1%), MeOH, 60 °C, 20 min	Failed
4)	$AlCl_3$ (wet), CH_2Cl_2, -10 - 0°C, 40 min	50%

Scheme 102 & Table 11

To determine the stereochemistry of IMDA reaction, bromobenzonate **282** was prepared as a white solid in 94% yield using the esterification between alcohol **281** and 4-bromobenzoyl chloride. An X-ray crystallographic analysis of ester **282** confirmed the *endo* addition of IMDA reaction (Scheme 103 and Figure 10).



Scheme 103

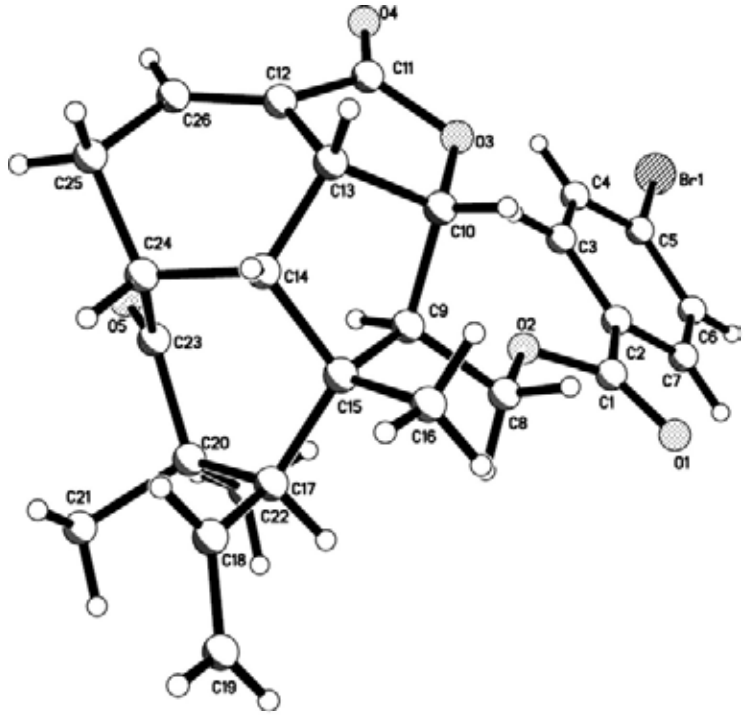
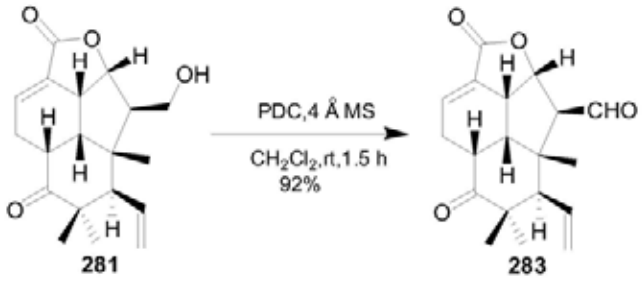


Figure 10. ORTEP drawing of compound **282**

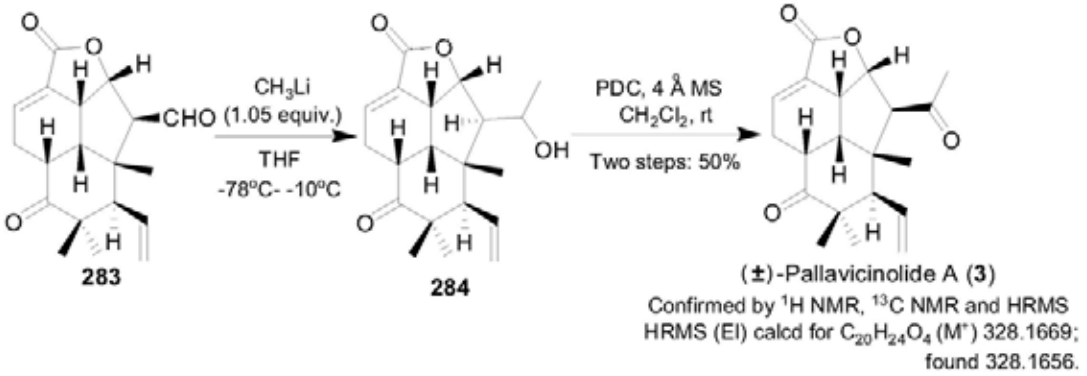
Oxidation of alcohol **281** was achieved by using PDC in dry CH_2Cl_2. After stirring for 1.5 h at room temperature, a less polar spot was appeared on TLC and aldehyde **283** was obtained in 92% yield after purification using preparative TLC. The molecular formula of **283** was established as $C_{19}H_{22}O_4$ based on HRMS (EI) analysis. The resonance signals at δ_H 9.89 (d, J = 1.8 Hz, 1H) in its ^{1}H NMR spectrum (400 MHz, acetone-d_6) and at δ_C 201.88 in its ^{13}C NMR spectrum (75 MHz, acetone-d_6)

illustrated the presence of an aldehyde (Scheme 104).



Scheme 104

The subsequent addition of MeLi (1.05 equiv.) was carried out carefully and the amount of MeLi should be controlled strictly. Otherwise, the reaction would lead to poor result. After the last oxidation of crude alcohol **284**, the desired natural product **3** was obtained successfully and the overall yield of these two steps was about 50% (Scheme 105). The ^{1}H and ^{13}C NMR spectroscopic and MS spectrometric data of synthetic (±)-pallavicinolide A (**3**) are in agreement with those reported in the literature.[67] Figure 11 showed the NMR spectra of (±)-pallavicinolide A (**3**) (the yellow data was literature value). The NMR data comparison between natural and synthetic **3** is shown in Table 12.



Scheme 105

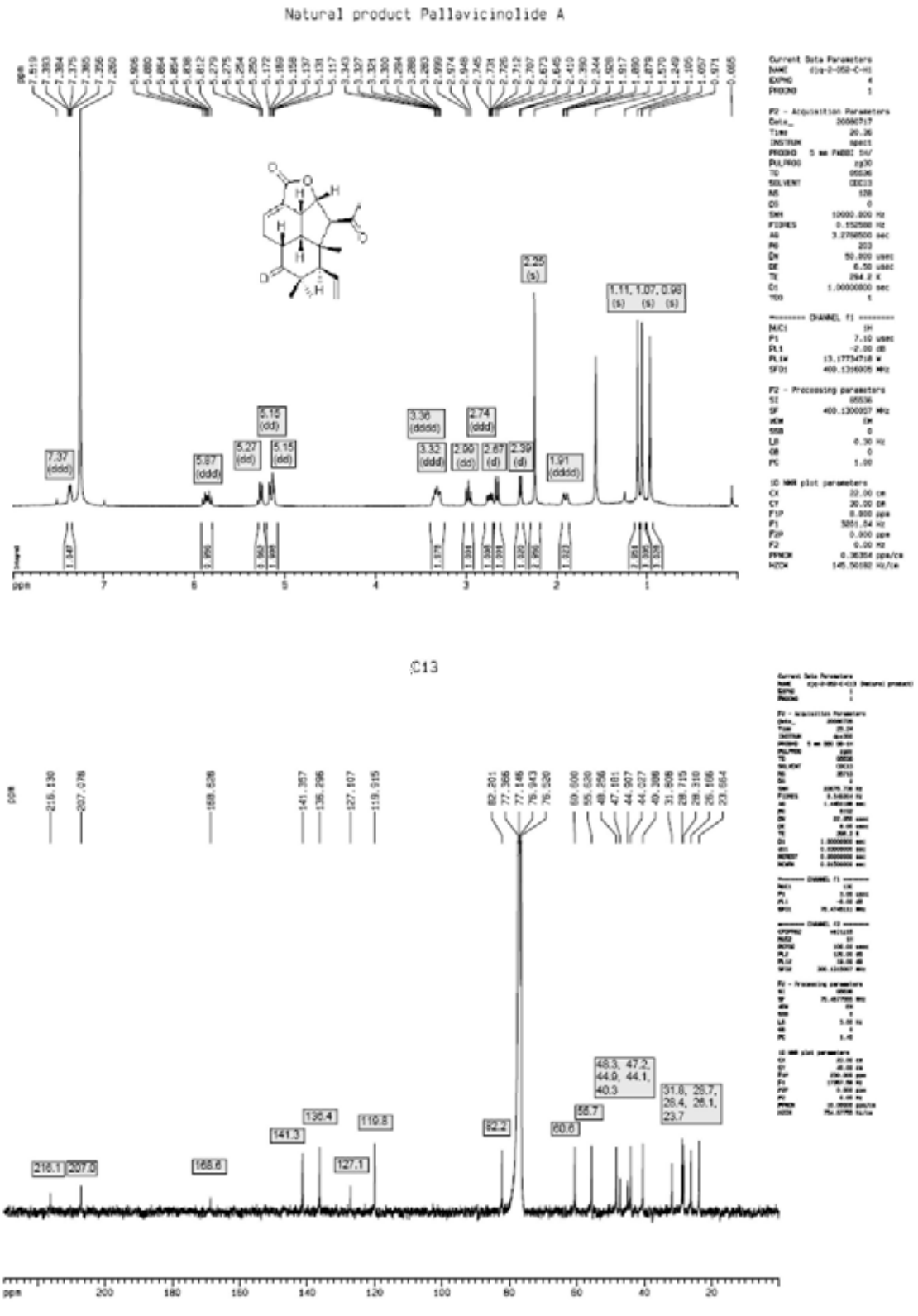


Figure 11. NMR spectra of (±)-pallavicinolide A (**3**)

H	Natural (600M, δ ppm)	Synthetic (400M, δ ppm)	△(δ ppm)
1	2.99 (dd, *J*=10, 11 Hz)	2.98 (dd, *J* = 10.0, 10.8 Hz)	0.01
2	3.32 (ddd, *J*=2, 4, 11 Hz)	3.31 (m)	0.01
5	2.67 (d, *J*= 11 Hz)	2.66 (d, *J* = 11.2 Hz)	0.01
6	5.87 (ddd, *J*=10, 11, 16 Hz)	5.86 (ddd, *J* = 10.0, 11.2, 16.4 Hz)	0.01
7(*cis*)	5.27 (dd, *J*=2, 10 Hz)	5.27 (dd, *J* = 1.8, 10.0 Hz)	
7(*trans*)	5.15 (dd, *J*=2, 16 Hz)	5.15 (m)	
9	2.39 (d, *J*=8 Hz)	2.40 (d, *J* = 8.1 Hz)	0.01
11	5.15 (dd, *J*=8, 8 Hz)	5.15 (m)	
12	3.36 (dddd, *J*=3, 3, 8, 10 Hz)	3.35 (m)	0.01
14	7.37 (ddd, *J*=3, 3, 8 Hz)	7.37 (ddd, *J* = 3.0, 3.1, 7.9 Hz)	
15	α : 2.74 (ddd, *J*=2, 8, 15 Hz) β :1.91(dddd, *J*=3, 3, 4, 15 Hz)	2.74 (ddd, *J* = 2.0, 7.9, 14.9 Hz) 1.91 (dddd, *J* = 3.0, 3.1, 4.1, 14.9 Hz)	
17	2.25 (s)	2.24 (s)	0.01
18	1.07 (s)	1.06 (s)	0.01
19	0.98 (s)	0.97 (s)	0.01
20	1.11 (s)	1.11 (s)	

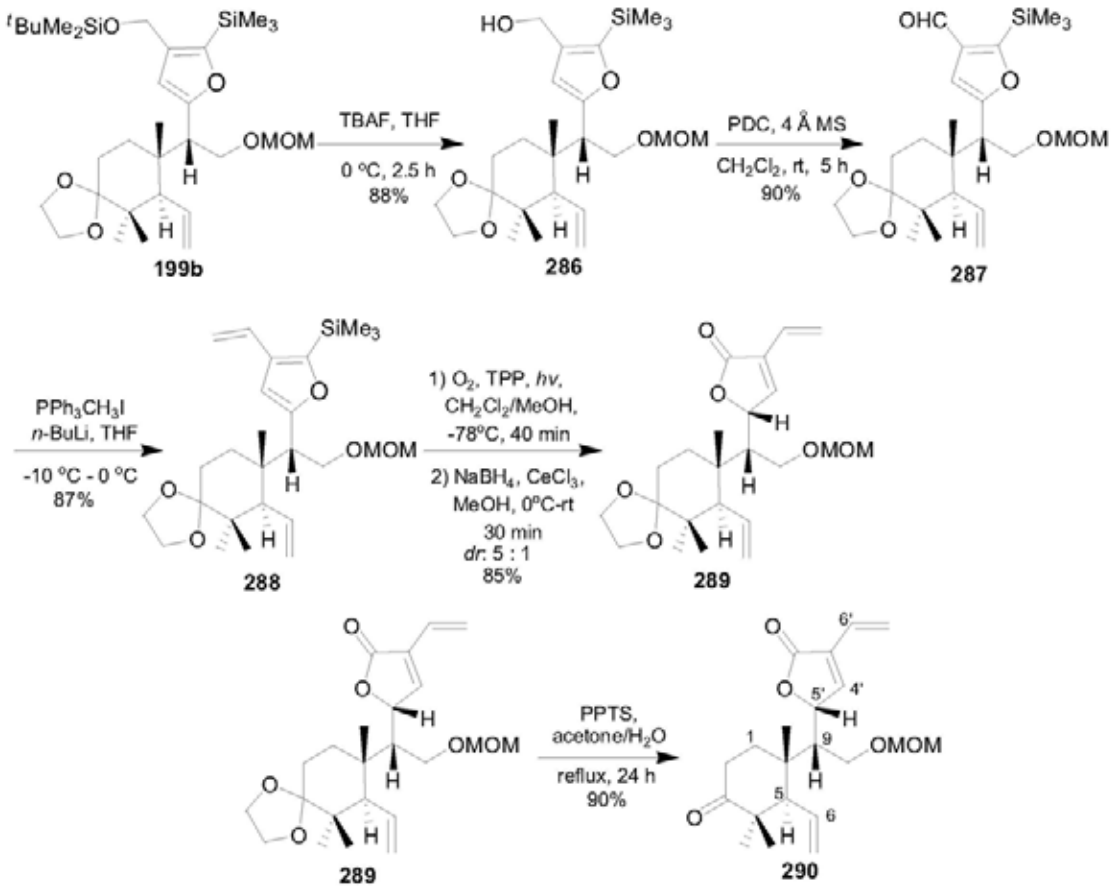
C	Natural (δ ppm)	Synthetic (δ ppm)	△(δ ppm)
1	48.3	48.26	0.04
2	44.1	44.03	0.07
3	216.1	216.13	0.03
4	44.9	44.91	0.01
5	55.7	55.62	0.08
6	136.4	136.30	0.10
7	119.8	119.92	0.12
8	207.0	207.08	0.08
9	60.6	60.60	
10	47.2	47.18	0.02
11	82.2	82.20	

12	40.3	40.39	0.09
13	127.1	127.11	0.01
14	141.3	141.36	0.06
15	26.1	26.17	0.07
16	168.6	168.63	0.03
17	31.8	31.81	0.01
18	28.7	28.72	0.02
19	28.4	28.31	0.09
20	23.7	23.66	0.04

Table 12. Spectral comparison between natural and synthetic pallavicinolide A (**3**)

2.2.10 Synthesis of (±)-neopallavicinolide A (296)

Using the same synthetic route, we also completed the total synthesis of the non-natural molecule (±)-neopallavicinolide A (**296**) starting from alcohol **199b**. Thus after 3 steps, vinylfuran **288** was prepared in similar yield as that of natural serial. The singlet oxygen oxidation/Luche reduction of **288** gave the corresponding butenolide in 85% overall yield with 5:1 diastereoisomeric ratio in favor of *syn* compound **289**. By comparison with the natural series, this step gave much higher yield (85% *v* 60%) and butenolide **289** could be separated with the other isomer easily using column chromatography. The major isomer was deketalized using PPTS in refluxing acetone/H_2O to afford ketone **290** in good yield (Scheme 106). Their structures were characterized with NMR, HRMS and IR analyses.



Scheme 106

The molecular formula of **290** was established as $C_{21}H_{30}O_5$ based on HRMS (EI) and elemental analysis. Its protons were assigned according to ^{1}H-^{1}H COSY. Based on ^{1}H-^{1}H COSY, the resonance signals at δ_H 7.54 (d, J = 1.2 Hz, 1H), 5.49 (brs, 1H) and δ_H 2.24–2.31 (m, 1H) in its ^{1}H NMR spectrum (300 MHz, acetone-d_6) were assigned as H-4', H-5' and H-9 respectively. The resonance signals at δ_H 6.47 (dd, J = 11.2, 17.7 Hz, 1H), δ_H 6.20 (dd, J = 1.9, 17.7 Hz, 1H) and δ_H 5.39 (dd, J = 1.9, 11.2 Hz, 1H) in the ^{1}H NMR spectrum were assigned as H-6', H-7' (*trans*) and H-7' (*cis*) in C-CH=CH_2 group. The resonance signals at δ_H 5.95 (ddd, J = 10.2, 10.3, 17.1 Hz, 1H), δ_H 5.29 (dd, J = 2.2, 10.2 Hz, 1H), δ_H 5.14 (dd, J = 2.2, 17.1 Hz, 1H) and δ_H 2.58 (d, J = 10.3 Hz, 1H) in its ^{1}H NMR spectrum were assigned as the H-6, H-7(*cis*), H-7(*trans*) and H-5 in CH-CH=CH_2 unit respectively. In addition, the resonance signals at δ_C

214.57 and 172.61 in its ^{13}C NMR spectrum (75 MHz, acetone-d_6) together with IR absorptions at 1765 and 1704 cm^{-1} also supported the presence of a ketone and a lactone group. Thus, based on the above result, the structure of **290** was established.

The relative stereochemistry of **290** was confirmed by X-ray crystallographic analysis (Figure 12).

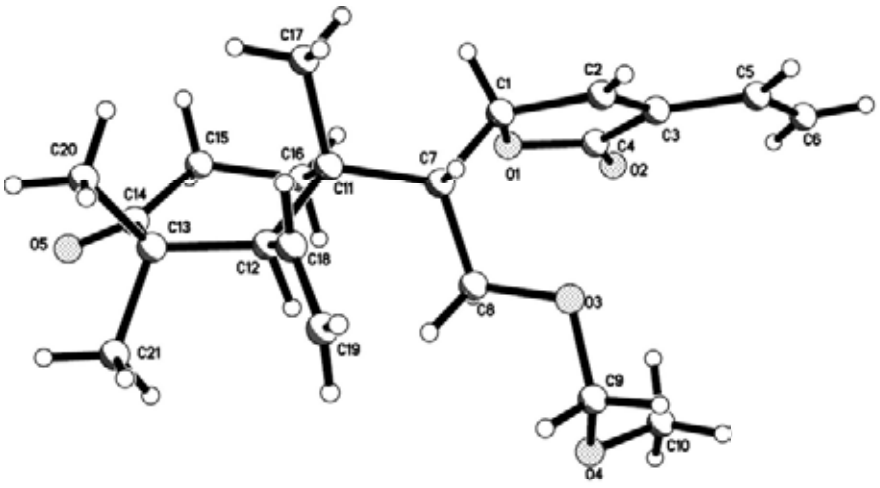
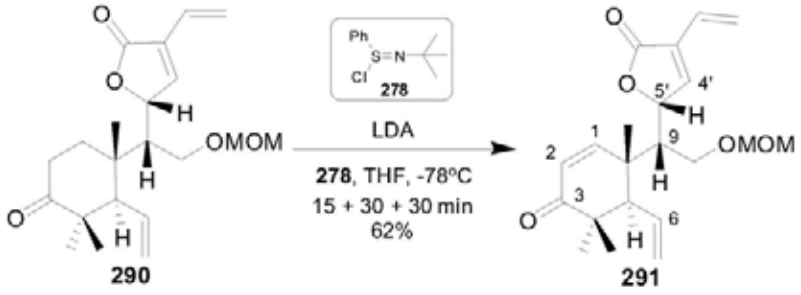


Figure 12. ORTEP drawing of compound **290**

For the preparation of α,β-unsaturated ketone **291**, we found that when **290** was allowed to react carefully with Mukaiyama's reagent, **291** could be obtained in a moderate yield. Unlike the corresponding intermediate **256** in the natural series, enone **291** was stable and it did not undergo Diels-Alder cycloaddition during column chromatography (Scheme 107).



Scheme 107

The molecular formula of **291** was established as $C_{21}H_{28}O_5$ based on HRMS (EI) and elemental analysis. Its protons were assigned according to ^1H-^1H COSY. Based on ^1H-^1H COSY, the resonance signals at δ_H 6.94 (d, J = 10.5 Hz, 1H) and δ_H 5.92 (d, J = 10.5 Hz, 1H) in the ^1H NMR spectrum (300 MHz, acetone-d_6) of **291** were assigned as H-1 and H-2 of the newly formed double bond. The resonance signals at δ_H 7.58 (d, J = 1.5 Hz, 1H), δ_H 5.51 (brs, 1H) and δ_H 2.30 (m, 1H) in its ^1H NMR spectrum were assigned as H-4', H-5' and H-9 respectively. In addition, the resonance signal at δ_C 202.87 in its ^{13}C NMR spectrum (75 MHz, acetone-d_6) also supported the formation of an α,β-unsaturated ketone. In addition, the stereochemistry of **291** was confirmed by an X-ray crystallographic analysis (Figure 13).

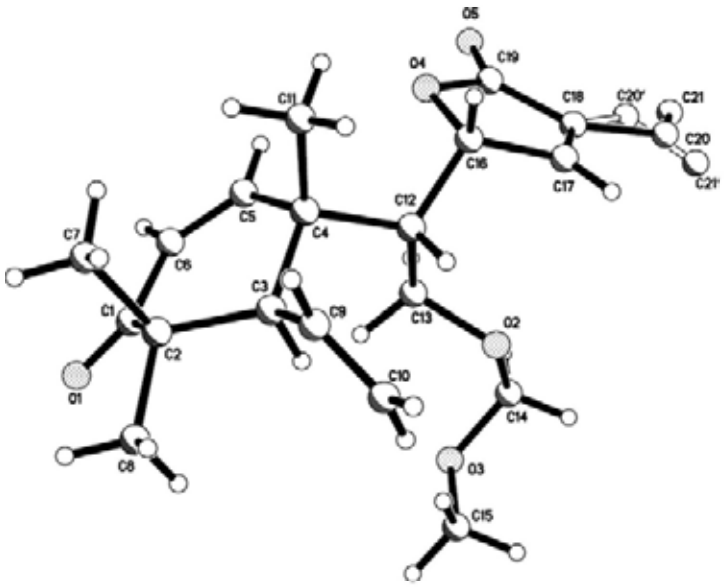
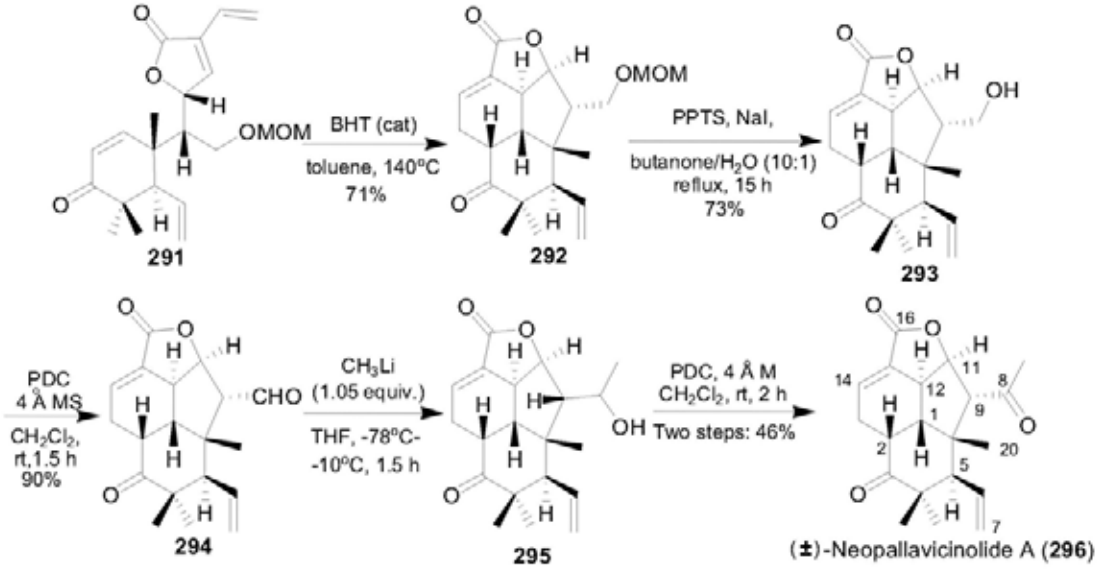


Figure 13. ORTEP drawing of compound **291**

At last, the intramolecular Diels-Alder reaction was occurred in high temperature in the presence of the radical inhibitor 2,6-di-*tert*-butyl-*p*-cresol (BHT) to give adduct **292** as the only product in 71% yield. Notably, the use of radical inhibitor such as BHT was necessary to achieve useful yield in this transformation.[148] The production of **292** as the only product was also due to the more favorable *cis*-fused bicyclo[3.3.0]

system and the steric hindrance of the methyl group. After next several steps involving deprotection, nucleophilic addition and subsequent oxidation, the non-natural molecule (±)-neopallavicinolide A (**296**) was realized and it was characterized with NMR, HRMS and IR spectrometric analyses (Scheme 108). The stereochemistry of the core skeleton of (±)-neopallavicinolide A (**296**) was confirmed by an X-ray crystallographic analysis of intermediate **293** (Figure 14). Figure 15 showed the NMR spectra of (±)-neopallavicinolide A (**296**).



Scheme 108

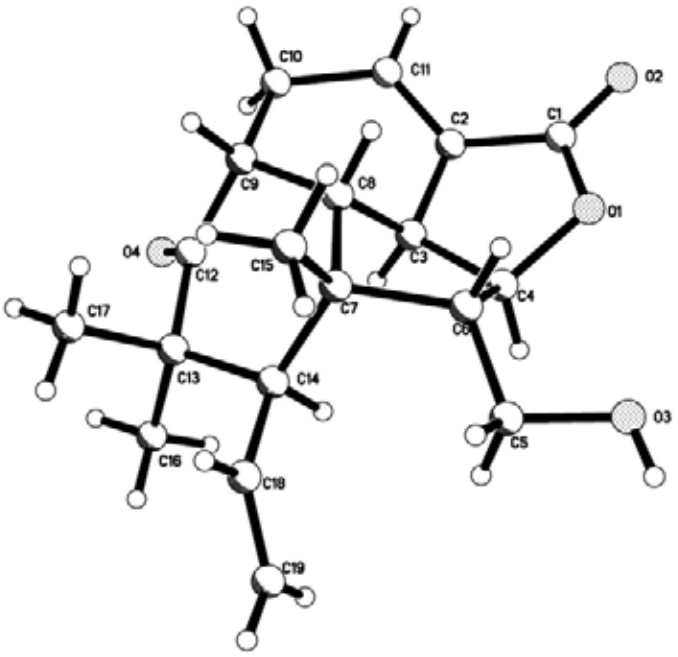
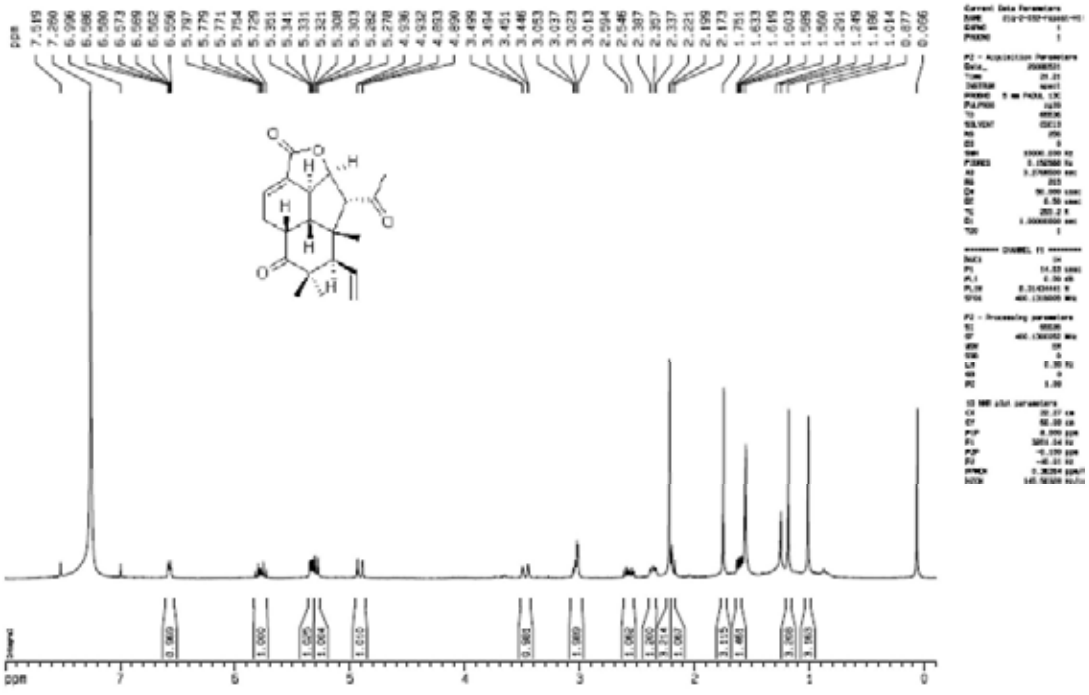


Figure 14. ORTEP drawing of compound **293**



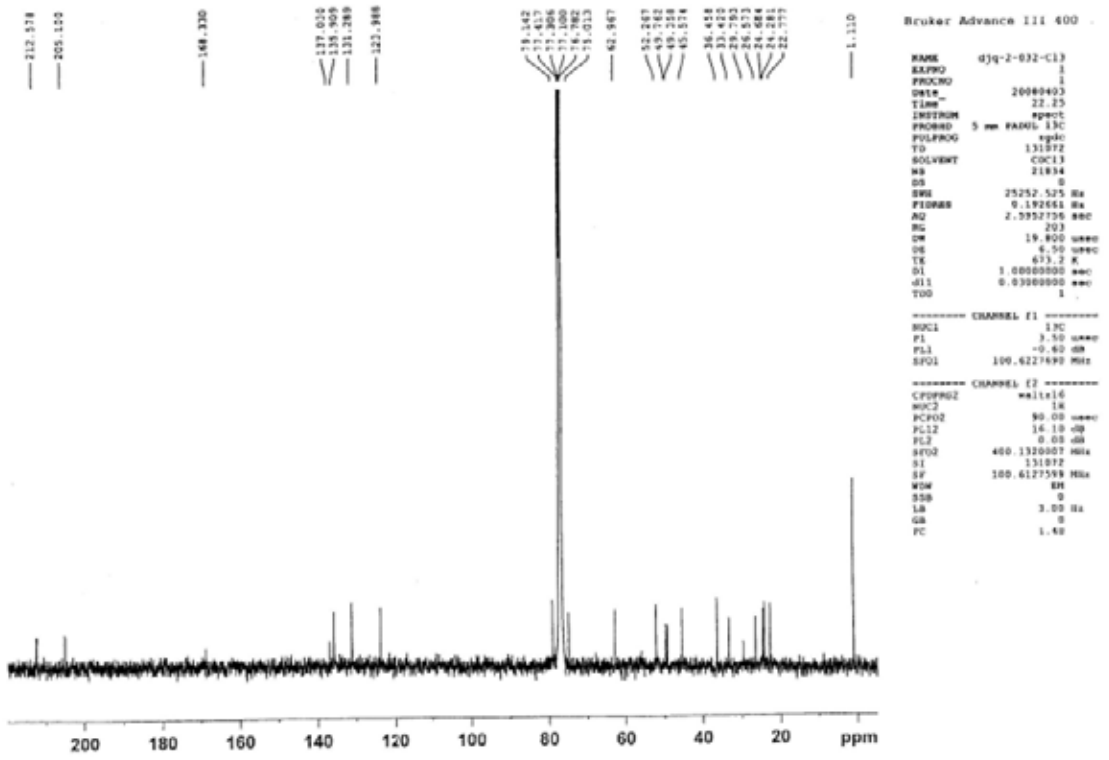


Figure 15. NMR spectra of (±)-neopallavicinolide A (**296**)

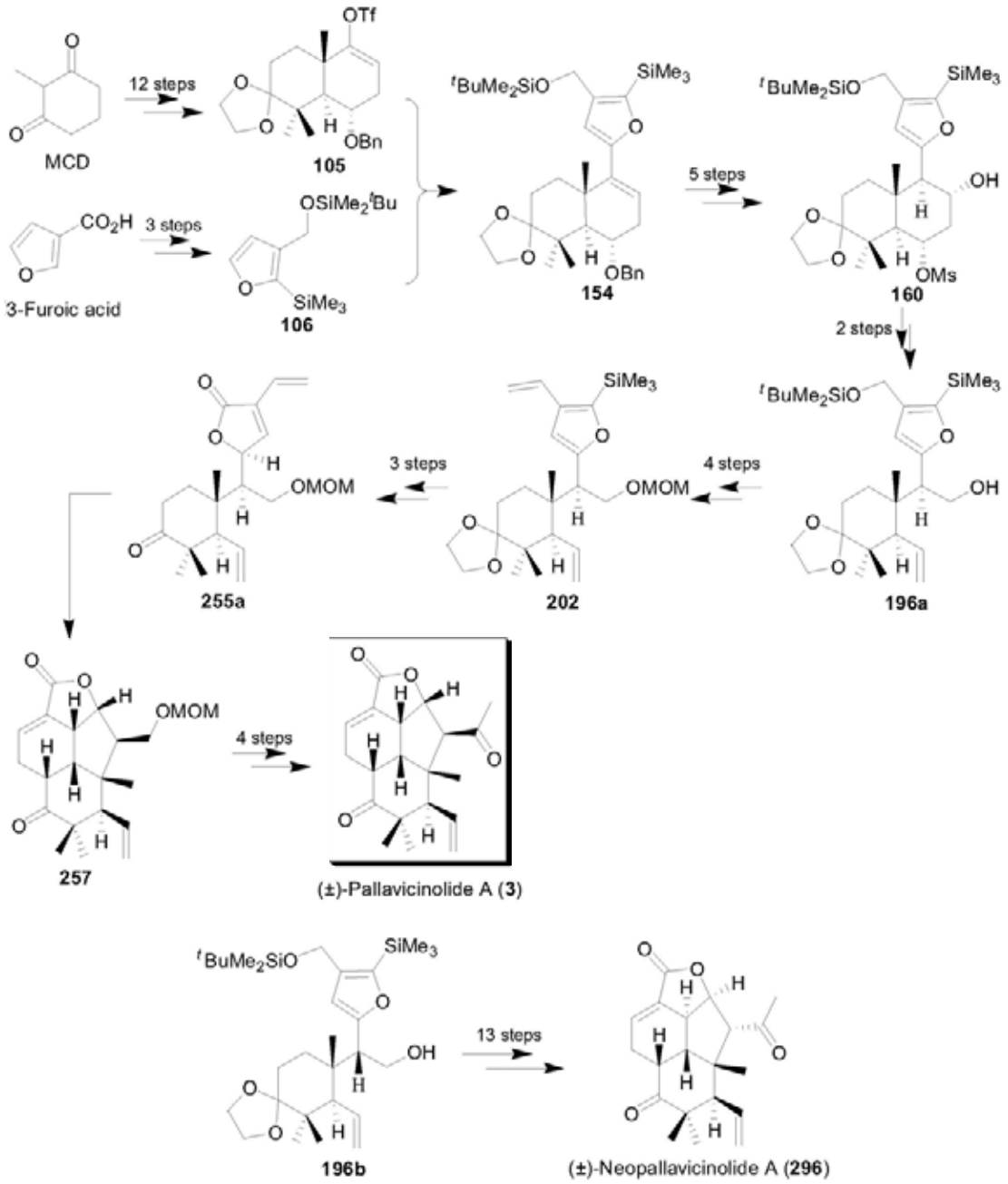
The molecular formula of (±)-neopallavicinolide A (**296**) was established as $C_{20}H_{24}O_4$ based on HRMS (EI) analysis. The resonance signals at δ_H 6.57 (ddd, J = 1.8, 2.7, 6.9 Hz, 1H), δ_H 5.34 (dd, J = 4.0, 8.0 Hz, 1H) and δ_H 2.19 (d, J = 7.8 Hz, 1H) in its ^{1}H NMR spectrum (400 MHz, $CDCl_3$) were assigned as H-14, H-11 and H-5, respectively. The resonance signals at δ_H 5.77 (ddd, J = 7.8, 10.2, 17.1 Hz, 1H), δ_H 5.29 (dd, J = 1.8, 10.2 Hz, 1H) and δ_H 4.91 (dd, J = 1.8, 17.1 Hz, 1H) in the ^{1}H NMR spectrum were assigned as H-6, H-7 (*cis*) and H-7 (*trans*) in $CH{=}CH_2$ unit. The resonance signals at δ_C 212.58, δ_C 205.10 and δ_C 168.33 in its ^{13}C NMR spectrum (75 MHz, $CDCl_3$) were assigned as C-3, C-8 and C-16 respectively. IR absorption at 1765 and 1707 cm^{-1} also suggested the presence of a carbonyl group. Thus, based on the above results and aforementioned X-ray crystallographic analyses of the precursors, the structure of (±)-neopallavicinolide A (**296**) was established.

Chapter 3. Conclusion

The natural diterpene (±)-pallavicinolide A (**3**) and non-natural compound (±)-neopallavicinolide A (**296**) were synthesized for the first time in a biomimetic approach from the simple starting material 2-methyl-1,3-cyclohexanedione (MCD) and 3-furoic acid.

Thus, the two motifs **105** and **106**, prepared from MCD and 3-furoic acid respectively, were coupled together through a Negishi coupling to give bicyclic furan **154**. Then precursor **160** underwent a KO^{t}Bu promoted Grob fragmentation and subsequent reduction to provide alcohol **196a**. Then vinyl furan **202** generated from **196a** underwent a singlet oxygenation/Luche reduction/deprotection sequence to provide vinyl butenolide **255a**. Then a domino enone formation/IMDA reaction sequence gave the core skeleton **257**. After modifying the side chain in the final steps, the total synthesis of **3** was achieved. The straightforward synthetic route involves 32 steps as the longest linear sequence and the overall yield is about 0.12%. Using the same strategy, the total synthesis of non-natural compound (±)-neopallavicinolide A (**296**) is also achieved from **196b** and the overall yield is about 0.16%.

Notable features of the synthesis are highlighted by three key biomimetic transformations: a base-promoted Grob fragmentation, a singlet oxygen oxidation, and an intramolecular Diels-Alder cycloaddition. Our biomimetic synthesis supports the biogenetic hypothesis given by Asakawa and constitutes a good example of biomimetic synthesis. Our work on total synthesis of (±)-pallavicinolide A (**3**) was published in *Angew. Chem. Int. Ed.* **2009**, *48*, 2351-2354.


MCD
12 steps
105
3-Furoic acid
3 steps
106
154
5 steps
160
2 steps
196a
4 steps
202
3 steps
255a
257
4 steps
(±)-Pallavicinolide A (3)
196b
13 steps
(±)-Neopallavicinolide A (296)

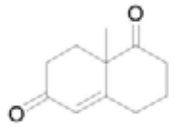
Chapter 4. Experimental Section

General Information

All reagents and solvents were reagent grade. Further purification and drying by standard methods were employed when necessary. All organic solvents were evaporated under reduced pressure with a rotary evaporator. Column chromatography was performed using E. Merck or Machery-Nagel 60 M silica gel (230 – 400 mesh). The plates used for thin-layer chromatography (TLC) were E. Merck silica gel 60 F_{254} (0.24 nm thickness) precoated on aluminum plates, and then visualized under UV light (365 nm and 254 nm) or through staining with a 5% of dodecamolybdophosphoric acid in ethanol and subsequent heating.

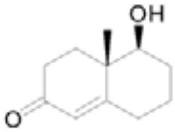
Melting points were measured on a Reichert Microscope apparatus and an Electrothermal 9100 apparatus and were uncorrected. NMR spectra were recorded on a Bruker DPX-300 spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C) and a Bruker Advance III 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) at room temperature. Chemical shifts were reported as parts per million (ppm) and in δ unit on the scale downfield from tetramethylsilane (TMS, δ 0.00 ppm) or relative to the resonance of solvent ($CDCl_3$: 7.26 ppm in ^{1}H, 77.1 ppm in ^{13}C; acetone-d_6: 2.05 ppm in ^{1}H, 30.0 ppm in ^{13}C). Coupling constants (*J*) were reported in Hz. Splitting patterns were described by using the following abbreviations: s, singlet; brs, broad singlet; d, double; t, triplet; q, quartet; m, multiplet. Mass spectra (ESI, EI and FAB) were obtained with a ThermoFinnigan MAT 95 XL spectrometer and determined at an ionized voltage of 70 eV unless otherwise stated. Elemental analyses were performed at Shanghai Institute of Organic Chemistry, the Chinese Academy of Sciences, China. Infrared spectra (IR) were recorded on a Nicolet 420 FT-IR spectrometer as thin film on potassium bromide discs.

(±)-Wieland-Miescher ketone (95).[73,60]



A mixture of 2-methyl-1,3-cyclohexanedione (63.1 g, 0.5 mol), methyl vinyl ketone (52.6 g, 0.75 mol) and potassium hydroxide (0.25 g, 4.46 mmol) in absolute methanol (250 mL) was refluxed for 4 h, then methanol and excess of methyl vinyl ketone were removed under reduced pressure. The residual solvent and water were removed azeotropically with three washings of benzene (50 mL × 3). The residue was then dissolved in benzene (300 mL) and piperidine (3 mL) was added to the solution. The mixture was refluxed for 1 h and the H_2O that formed during the reaction and all of benzene were separated from distillation under normal pressure till no solvent remained. The reddish reactiom mixture was cooled to room temperature and diluted with EtOAc (250 mL) and the solution was washed with dilute HCl (0.1 N, 150 mL). The aqueous solution was extracted with EtOAc (150 mL × 2) and the combined organic layers were washed with brine (150 mL), dried over Na_2SO_4, filtered and evaporated to give a residue which could be used into the next reduction directly without further purification. It could be purified from distillation or column chromatography following the references.

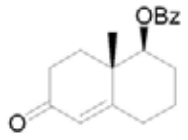
(±)-(4a*S*,5*S*)-3,4,4a,5,6,7,8-Hepahydro-5-hydroxy-4a-methylnaphthalen-2(3*H*)-one (96).[60]



To a stirred solution of ketone **95** (15.7 g, 88 mmol) in EtOH (200 mL) at 0 °C was added portionwise $NaBH_4$ (1.1 g, 30 mmol) and then the mixture was stirred for 10 min at 0 °C. The mixture was treated with AcOH (10 mL) carefully and the

mixture was stirred for another 10 min at 0 °C. The solvent was allowed to evaporate *in vacuo* and the residue was partitioned between EtOAc (300 mL) and water (150 mL). The aqueous was extracted with EtOAc (300 mL × 2) and the combined organic layers were washed with saturated $NaHCO_3$ (250 mL) to remove all AcOH and then washed with brine (150 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated to give the crude alcohol **96** which could be used into the next protection without further purification. It could be purified following the reference 60.

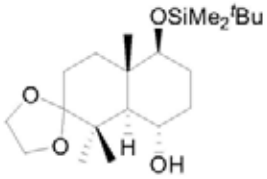
(±)-(4a*S*,5*S*)-5-Benzoyl-3,4,4a,5,6,7,8-hepahydro-4a-methylnaphthalen-2(3*H*)-one (97).[60]



To a solution of alcohol **96** (18.0 g, 0.1 mol) in dry CH_2Cl_2 (40 mL) was added pyridine (9.7 mL, 0.12 mol) and DMAP (0.5 g) at 0 °C followed by addition of benzoyl chloride (13.9 mL, 0.12 mol). After stirring for 0.5 h at 0 °C, the reaction was warmed to room temperature and continued overnight. The reaction was diluted with CH_2Cl_2 (100 mL) and then washed with H_2O (200 mL). The aqueous layer was extracted with CH_2Cl_2 (100 mL × 2) and the combined organic layers were washed with H_2O (100 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography on silica gel (650 g, hexanes:EtOAc 10:1 – 5:1) to provide benzonate **97** (26.2 g, 92%) as a white semi-solid. The spectra data were identical to those of reference 60.

The experimental procedures of intermediates **98** to **101** were the same as that for reference 60.

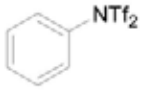
(±)-(4a*S*,5*S*,8*R*,8a*R*)-5-*tert*-Butyldimethylsiloxy-8-hydroxy-3,4,4a,5,6,7,8,8a-octahydro-1,1,4a-trimethylnaphthalen-2(3*H*)-one ethylene ketal (102a).[60]



To a solution of **101** (18.3 g, 50 mmol) in dry THF (distilled from $LiAlH_4$, 100 mL) was added $BH_3{\cdot}Me_2N$ (1.98 g, 33.5 mmol) in one portion followed by $BH_3{\cdot}Me_2S$ (10 M, 10 mL, 0.1 mol) dropwise at 0 °C under N_2. The mixture was stirred at 0 °C for 4 h and then warmed to 20 °C for 72 h. The reaction was then cooled to 0 °C and a premixed solution of H_2O_2 (30%, 50 mL) and NaOH (3 M, 50 mL) was added to the reaction dropwise. After another 1 h, the suspension was warmed to room temperature and stirred overnight. The residue was partitioned between EtOAc (350 mL) and H_2O (150 mL). The aqueous layer was extracted with EtOAc (200 mL × 2) and the combined organic layers were washed with brine (150 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography on silica gel (600 g, hexanes:EtOAc 20:1 – 10:1 – 5:1) very carefully to provide the desired alcohol **102a** (6.9 g, 36%) as a white syrup. The spectra data were identical to those reported.[60]

The experimental procedures of intermediates **103** to **104** were the same as that for reference 60.

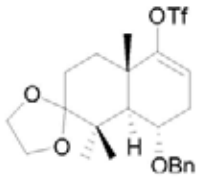
***N*-Phenyl bis(trifluoromethanesulfonimide).**[74]



To a solution of aniline (9.1 mL, 0.1 mol) and triethylamine (34.7 mL, 0.25 mol) in dry CH_2Cl_2 (150 mL) under N_2 at −78 °C was added trifluoromethanesulfonic anhydride (34 mL, 0.2 mol) slowly. The mixture was stirred at −78 °C for 2 h and then warmed to room temperature before quenching with dilute HCl (1 N, 50 mL) carefully.

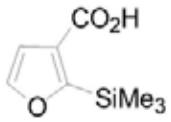
The mixture was extracted with CH_2Cl_2 (70 mL × 2) and the combined organic layers were washed with H_2O (150 mL), dried over $NaSO_4$, filtered and evaporated to give a crude product as a brown solid which was purified by recrystallization from hexanes. The product *N*-phenyl bis(trifluoromethane-sulfonimide) was obtained as a white needle-shaped crystals (32.5 g, 91%). mp 97.5–100.0 °C, lit,[74] 93–94 °C (100–102 °C, Aldrich 2009-2010, p 2106); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 119.49 (q, *J* = 323 Hz), 130.05, 131.06, 132.03, 132.20.

(±)-(4a*S*,8*S*,8a*S*)-8-Benzyloxy-5-triflate-3,4,4a,7,8,8a-hextahydro-1,1,4a-trimethyl naphthalen-2(3*H*)-one ethylene ketal (105).[60]



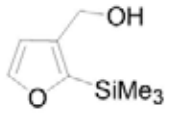
To a solution of ketone **104** (4.4 g, 12.3 mmol) in dry THF (30 mL) at −10 °C under N_2 was added dropwise LiHMDS (1 M in THF, 14.8 mL, 14.8 mmol) and then the resulting mixture was stirred at −10 °C - 0 °C for 1 h. Then a solution of *N*-phenyl bis(trifluoromethanesulfonimide) (4.6 g, 12.9 mmol) in THF (10 mL) was added dropwise to the above reactiom mixture. After 30 min at –10°C - 0 °C, the reaction was quenched with saturated $NaHCO_3$ (40 mL) and then extracted with diethyl ether (40 mL × 2). The combined organic layers were washed with NaOH (1 M, 40 mL) and brine (50 mL), dried over $NaSO_4$, filtered and evaporated to give a crude product as a brown solid which was purified by column chromatography on silica gel (200 g, hexanes:EtOAc 20:1) to yield **105** (5.6 g, 93%) as a white solid. mp 89.0–90.5 °C. The spectra data were identical to those reported.[60]

2-(Trimethylsilyl)furan-3-carboxylic acid (122).[79]



n-BuLi (1.6 M solution in hexane, 125 mL, 0.2 mol) was added to diisopropylamine (28.3 mL, 0.2 mol) in dry THF (100 mL) with stirring at –10 °C under N_2. After 20 min, the mixture was cooled to –78 °C, a solution of 3-furoic acid (11.2 g, 0.1 mol) in dry THF (60 mL) was added and then stirring at this temperature for 0.5 h was followed by addition of TMSCl (44.7 mL, 0.35 mol). Then the reaction was warmed to room temperature within 1 h. The reaction mixture was treated with H_2O (60 mL) followed by HCl (2 N, 100 mL) and it was stirred vigorously for 0.5 h, then diluted with water (100 mL) and extracted with diethyl ether (150 mL × 3). The combined organic layers were washed with brine (150 mL), dried over Na_2SO_4, filtered and evaporated. The residue was crystallized from hexanes to afford the first batch of acid **122** (5.5 g) as a white solid. The mother liquid was concentrated and then purified by column chromatography on silica gel (250 g, hexanes:EtOAc 10:1 – 5:1) to give the second batch of **122** (6.5 g). The overall yield was 65%. R_f 0.50 (hexanes:EtOAc = 3:2); mp 87.5–89.0 °C, lit,[79] 89–90 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.37 (s, 9H), 6.80 (d, J = 1.5 Hz, 1H), 7.60 (d, J = 1.5 Hz, 1H), 12.75 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –1.90, 110.90, 127.14, 146.52, 169.80, 170.57; MS (ESI) *m/z* $(M-H)^+$ 183.

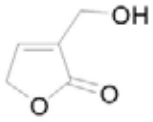
[2-(Trimethylsilyl)furan-3-yl]methanol (123).



To a suspension of $LiAlH_4$ (4.94 g, 0.13 mol) in dry diethyl ether (150 mL) was added slowly a solution of **122** (18.4 g, 0.1 mol) in diethyl ether (80 mL) at 0 °C under N_2. The mixture was stirred for 1 h at room temperature and then quenched with water

(5 mL) and NaOH (3 M, 15 mL) carefully. After stirring vigorously for 0.5 h, the solution was diluted with water (100 mL) and extracted with EtOAc (150 mL × 3). The combined organic layers were washed with brine (150 mL), dried over Na_2SO_4, filtered and evaporated. The residue was purified by column chromatography on silica gel (450 g, hexanes:EtOAc 10:1) to give 16.15 g (95%) of alcohol **123** as a white oil. [Note: the water bath was kept below 30 °C during the evaporation of solvent due to the low boiling point of the alcohol.] R_f 0.40 (hexanes:EtOAc = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.30 (s, 9H), 2.26 (br s, 1H), 4.58 (s, 2H), 6.44 (d, J = 1.4 Hz, 1H), 7.56 (d, J = 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –1.01, 57.08, 110.66, 134.82, 146.50, 156.70; HRMS (ESI) *m/z* calcd for $C_8H_{14}O_2SiNa$ $(M+Na)^+$ 193.0661, found 193.0657.

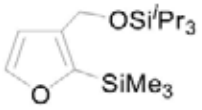
3-Hydroxymethyl-5*H*-furan-2-one (124).



A solution of furan **123** (0.84 g, 5 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a suspension of peroxyacetic acid (2 M, 10 mL) and NaOAc (1.64 g, 20 mmol) in CH_2Cl_2 (20 mL) and then the mixture was stirring for 15 min at 0 °C and 12 h at room temperature. An aqueous of $Na_2S_2O_3$ (10 mL) was added to the reaction slowly followed by neutralization to *p*H ~ 7 with $NaHCO_3$ solid. The reaction was extracted with EtOAc (15 mL × 3) and the combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, filtered and evaporated carefully (< 30 °C water bath). The residue was purified by column chromatography on silica gel (25 g, hexanes:EtOAc 5:1 – 0:1) to give 0.148 g (26%) of **124** as a light-yellow liquid. R_f 0.30 (hexanes:EtOAc = 0:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.99 (s, 1H), 4.39 (dd, J = 1.5, 3.6 Hz, 2H), 4.84 (dd, J = 1.8, 3.9 Hz, 2H), 7.42 (t, J = 1.5 Hz, 1H); ^{13}C NMR (75

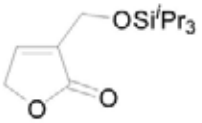
MHz, $CDCl_3$) δ 56.76, 70.87, 133.41, 146.20, 173.45; MS (EI) *m/z* (M^+) 114.

3-[(Triisopropylsilyloxy)methyl]-2-(trimethylsilyl)furan (125).



To a solution of alcohol **123** (17.0 g, 0.1 mol) in DMF (75 mL) was added imidazole (13.6 g, 0.2 mol) followed by TIPSCl (23.6 mL, 0.11 mol) at 0 °C under N_2. The mixture was stirred for 12 h at room temperature and then quenched with 5% $NaHCO_3$ (300 mL) slowly. After extraction with diethyl ether (200 mL × 3), the combined organic layers were washed with brine (200 mL), dried over Na_2SO_4, filtered and evaporated. The residue was purified by column chromatography on silica gel (600 g, hexanes:EtOAc 100:1) to give 30.4 g (93%) of **125** as a white oil. R_f 0.70 (hexanes:EtOAc = 100:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.28 (s, 9H), 1.05–1.15 (m, 22H), 4.71 (s, 2H), 6.48 (d, *J* = 1.5 Hz, 1H), 7.55 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –1.07, 12.13, 18.14, 57.83, 110.66, 135.99, 146.05, 155.08; HRMS (ESI) *m/z* calcd for $C_{17}H_{34}O_2Si_2Na$ $(M+Na)^+$ 349.1995, found 349.1998.

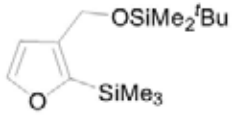
3-Triisopropylsilyloxymethyl-5*H*-furan-2-one (126).



To a solution of furan **125** (0.653 g, 2 mmol) in CH_2Cl_2 (7 mL) was added NaOAc (0.656 g, 8 mmol) in one portion. The mixture was cooled to 0 °C, a solution of peracetic acid (2 M, 4 mL) in CH_2Cl_2 (3 mL) was added dropwise to the reaction mixture and left stirring for 15 min at 0 °C and 3 h at room temperature. Saturated $Na_2S_2O_3$ (10 mL) was added to the reaction slowly followed by neutralization to *p*H ~ 8 with $NaHCO_3$ solid. The reaction was extracted with EtOAc (15 mL × 3) and the combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, filtered

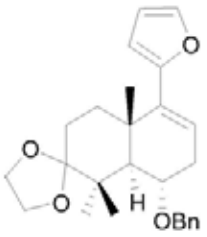
and concentrated. The residue was purified by column chromatography on silica gel (18 g, hexanes:EtOAc 10:1 – 5:1) to give 0.354 g (69%) of **126** as a colorless liquid. R_f 0.40 (hexanes:EtOAc = 5:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03–1.16 (m, 22H), 4.52 (dd, J = 2.7, 5.4 Hz, 2H), 4.84 (dd, J = 2.7, 4.5 Hz, 2H), 7.39 (t, J = 2.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.90, 17.96, 58.73, 70.97, 135.01, 144.91, 172.65; HRMS (ESI) *m/z* calcd for $C_{14}H_{26}O_3SiNa$ $(M+Na)^+$ 293.1549, found 293.1554.

3-[(*tert*-Butyldimethylsilyloxy)methyl]-2-(trimethylsilyl)furan (106).



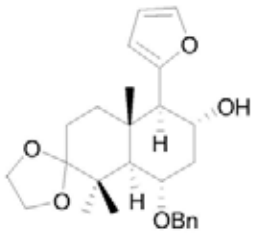
To a solution of alcohol **123** (17.0 g, 0.1 mol) in DMF (75 mL) was added imidazole (13.6 g, 0.2 mol) followed by TBSCl (16.6 g, 0.11 mol) at 0 °C under N_2. The mixture was stirred for 12 h at room temperature and then quenched with 5% $NaHCO_3$ (300 mL) slowly. After extraction with diethyl ether (200 mL × 3), the combined organic layers were washed with brine (200 mL), dried over Na_2SO_4, filtered and evaporated. The residue was purified by column chromatography on silica gel (600 g, hexanes:EtOAc 100:1) to give 26.1 g (92%) of **106** as a white oil. R_f 0.70 (hexanes:EtOAc = 100:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.14 (s, 6H), 0.32 (s, 9H), 0.98 (s, 9H), 4.69 (s, 2H), 6.47 (d, J = 1.5 Hz, 1H), 7.57 (d, J = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –5.04, –1.02, 26.07, 57.66, 110.77, 135.64, 146.07, 155.06; IR (film) 3749, 2959, 2857, 1469, 1254, 1091, 846, 769 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{28}O_2Si_2Na$ $(M+Na)^+$ 307.1520, found 307.1523.

(±)-(4a*S*,8*S*,8a*S*)-8-Benzyloxy-5-furyl-3,4,4a,7,8,8a-hextahydro-1,1,4a-trimethylnaphthalen-2(3*H*)-one ethylene ketal (134).



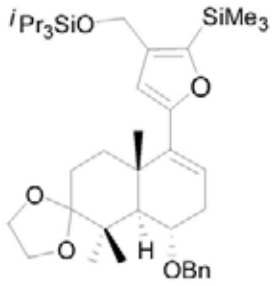
To a suspension of K_2CO_3 (0.4 g, 2.86 mmol) and $Pd(PPh_3)_4$ (50 mg, 0.044 mmol) in dry THF (4 mL) was added a solution of the triflate **105** (0.7 g, 1.43 mmol) in THF (2 mL) under N_2 and the mixture was stirred for 20 min at room temperature. 2-Furylboronic acid (0.26 g, 2.29 mmol) was added to the mixture and the reaction was heated to reflux for 15 h, then allowed to cool to room temperature. The mixture was diluted with diethyl ether (5 mL), washed with saturated $NaHCO_3$ (5 mL) and then extracted with diethyl ether (5 mL × 3). The combined extracts were washed with brine (5 mL), dried over Na_2SO_4, filtered and evaporated. The residue was purified by column chromatography on silica gel (25 g, hexanes:EtOAc 30:1 – 20:1) to give 0.44 g (75%) of **134** as a white semi-solid. R_f 0.35 (hexanes:EtOAc = 12:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (s, 6H), 1.38 (s, 9H), 1.47–1.88 (m, 4H), 2.03 (d, J = 10.5 Hz, 1H), 2.18–2.26 (m, 1H), 2.81 (dt, J = 4.6, 12.2 Hz, 1H), 3.89–3.99 (m, 5H), 4.47 (d, J = 11.1 Hz, 1H), 4.66 (d, J = 11.1 Hz, 1H), 5.78 (dd, J = 3.3, 4.7 Hz, 1H), 6.13 (dd, J = 0.5, 3.2 Hz, 1H), 6.30 (dd, J = 1.8, 3.3 Hz, 1H), 7.32 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.44, 21.98, 25.25, 26.87, 33.88, 34.38, 40.07, 42.87, 53.64, 64.93, 71.18, 75.29, 107.05, 110.25, 113.26, 125.36, 127.45, 127.95, 128.32, 138.78, 140.71, 140.82, 155.34; IR (film) 3096, 2974, 2935, 1707, 1675, 1469, 1385, 1109, 806, 723 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{32}O_4Na$ $(M+Na)^+$ 431.2193, found 431.2197; Anal. Calcd for $C_{26}H_{32}O_4$: C, 76.44; H, 7.90. Found: C, 76.17; H, 7.98.

(±)-(4a*S*,5*R*,6*R*,8*S*,8a*S*)-8-Benzyloxy-5-furyl-6-hydroxy-3,4,4a,5,6,7,8,8a-octahydr-o-1,1,4a-trimethylnaphthalen-2(3*H*)-one ethylene ketal (137).



At 0 °C, under N_2, $BH_3 \cdot Me_2S$ (10 M, 0.155 mL) was added dropwise to a solution of **134** (0.21 g, 0.515 mmol) in dry THF (2 mL) and then the reaction was stirred at room temperature for 15 h. The above solution was cooled to 0 °C and a mixture of pre-cooled H_2O_2 (30%, 1.15 mL) and NaOH (3 M, 1.15 mL) was added carefully. The mixture was stirred vigorously for 3 h at room temperature before addition of saturated Na_2SO_3 dropwise to the solution to remove the excess amount of H_2O_2. The reaction was extracted with EtOAc (4 mL × 3), washed with brine (4 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (15 g, hexanes:EtOAc 5:1 – 2:1) to give 88 mg (40%) of **137** as a white solid. A sample crystal for X-ray crystallography was obtained by dissolving the solid in hexanes:EtOAc (1:1) and the solvent was allowed to evaporate slowly for 4 days. R_f 0.40 (hexanes:EtOAc = 2:1); mp 87.0–88.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (s, 3H), 1.05 (s, 3H), 1.13 (s, 3H), 1.26–1.68 (m, 8H), 1.77 (d, J = 10.8 Hz, 1H), 2.51 (d, J = 10.8 Hz, 1H), 2.75 (dt, J = 4.6, 12.2 Hz, 1H), 3.77 (dt, J = 4.2, 10.8 Hz, 1H), 3.93–3.95 (m, 4H), 4.12 (dt, J = 4.1, 10.5 Hz, 1H), 4.46 (d, J = 11.1 Hz, 1H), 4.66 (d, J = 11.1 Hz, 1H), 6.14 (d, J = 3.0 Hz, 1H), 6.35 (dd, J = 1.8, 3.3 Hz, 1H), 7.27–7.38 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.55, 20.49, 25.54, 26.15, 36.50, 38.35, 40.47, 42.83, 55.83, 59.02, 64.91, 64.99, 66.96, 71.14, 75.58, 108.95, 110.18, 113.30, 127.53, 128.10, 128.35, 129.65, 138.47, 141.97, 153.45; IR (film) 3421, 3059, 2997, 1787, 1735, 1469, 1375, 1069, 856, 737 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{34}O_5Na$ $(M+Na)^+$ 449.2406, found 449.2409; Anal. Calcd for $C_{26}H_{34}O_5$: C, 73.21; H, 8.03. Found: C, 73.12; H, 8.11.

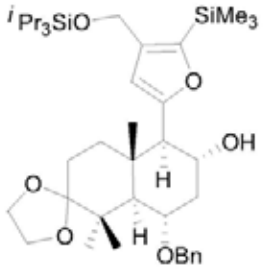
(±)-(4a*S*,8*S*,8a*R*)-8-Benzyloxy-5-{4-[(triisopropylsilyloxy)methyl]-5-(trimethylsilyl)furan-2-yl}-1,1,4a-trimethyl-4,4a,8,8a-tetrahydronaphthalen-2(1*H*,3*H*,7*H*)-one ethylene ketal (135).



To a solution of **125** (2.05 g, 6.27 mmol) in dry THF (20 mL) was added dropwise *n*-BuLi (1.6 M solution in hexane, 3.92 mL, 6.27 mmol) at 0 °C under N_2. The reaction mixture was stirred at 0 °C for 0.5 h and at room temperature for 1 h. To the above solution was added $ZnCl_2$ (powder, 0.86 g, 6.27 mmol) portionwise and then stirring for a further 1 h at room temperature. At last, the mixture of vinyl triflate **105** (2.05 g, 4.18 mmol) and $Pd(PPh_3)_4$ (0.15 g, 0.13 mmol) was added to the above reaction solution and then the reaction was heated to 50 °C. After 1 h, TLC showed that the reaction was completed and it was cooled to room temperature before diluting with diethyl ether (30 mL) followed by addition of saturated $NaHCO_3$ (20 mL). The organic layer was separated and the aqueous layer was extracted with diethyl ether (25 mL × 2), washed with brine (25 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (75 g, hexanes:EtOAc 100:1 – 50:1) to give 2.45 g (89%) of **135** as a light-yellow syrup. R_f 0.50 (hexanes:EtOAc = 20:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.27 (s, 9H), 1.07–1.09 (m, 22H), 1.20 (s, 6H), 1.41 (s, 3H), 1.50–1.60 (m, 2H), 1.73–1.86 (m, 2H), 2.03 (d, J = 10.5 Hz, 1H), 2.18–2.25 (m, 1H), 2.83 (dt, J = 5.1, 18.3 Hz, 1H), 3.90–4.02 (m, 5H), 4.47 (d, J = 11.4 Hz, 1H), 4.65 (s, 2H), 4.67 (d, J = 11.4 Hz, 1H), 5.79 (t, J = 3.9 Hz, 1H), 6.23 (s, 1H), 7.26–7.40 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$)

δ –0.96, 12.13, 18.15, 20.47, 22.01, 25.31, 26.91, 33.88, 34.53, 40.21, 42.85, 53.75, 57.92, 64.92, 71.23, 75.41, 108.32, 113.32, 124.62, 127.44, 127.96, 128.32, 136.64, 138.85, 140.93, 152.70, 158.74; IR (film) 3842, 2848, 1461, 1367, 1250, 1103, 1039, 847, 752, 691, 446 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{39}H_{62}O_5Si_2Na$ $(M+Na)^+$ 689.4028, found 689.4017; Anal. Calcd for $C_{39}H_{62}O_5Si_2$: C, 70.22; H, 9.37. Found: C, 70.87; H, 9.87.

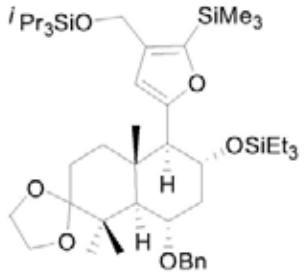
(±)-(4a*S*,5*R*,6*R*,8*S*,8a*R*)-8-Benzyloxy-5-{4-[(triisopropylsilyloxy)methyl]-5-(trimethylsilyl)furan-2-yl}-6-hydroxy-1,1,4a-trimethyl-octahydronaphthalen-2(1*H*)-one ethylene ketal (136).



At 0 °C, under N_2, $BH_3{\cdot}Me_2S$ (10 M, 2.4 mL) was added dropwise to a solution of **136** (5.33 g, 8 mmol) in dry THF (20 mL) and then the reaction was stirred at room temperature for 15 h. After cooling to 0 °C, a mixture of pre-cooled H_2O_2 (30%, 12 mL) and NaOH (3 M, 12 mL) was added to the above solution carefully and then it was stirred vigorously for 3 h at room temperature before addition of saturated Na_2SO_3 dropwise to remove the excess amount of H_2O_2. The mixture was extracted with EtOAc (25 mL × 3), washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (120 g, hexanes:EtOAc 20:1 – 5:1) to give 3.78 g (69%) of **136** as a light-yellow foam. R_f 0.35 (hexanes:EtOAc = 6:1); ^1H NMR (300 MHz, $CDCl_3$) δ 0.26 (s, 9H), 0.97 (s, 3H), 1.00–1.10 (m, 22H), 1.11 (s, 3H), 1.16 (s, 3H), 1.38–1.42 (m, 2H), 1.57–1.69 (m, 3H), 1.76 (d, J = 10.8 Hz, 1H), 2.51 (d, J = 10.8 Hz,

1H), 2.70–2.80 (m, 1H), 3.78 (dt, J = 3.9, 10.8 Hz, 1H), 3.92–3.98 (m, 4H), 4.11 (dt, J = 5.0, 10.8 Hz, 1H), 4.46 (d, J = 11.1 Hz, 1H), 4.66 (s, 2H), 4.67 (d, J = 10.8 Hz, 1H), 6.22 (s, 1H), 7.26–7.39 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –1.05, 12.11, 16.50, 18.12, 20.49, 25.57, 26.33, 36.29, 38.50, 40.17, 42.88, 55.89, 57.88, 59.14, 64.89, 65.08, 67.00, 71.15, 75.65, 110.08, 113.37, 127.54, 128.17, 128.35, 136.55, 138.48, 154.13, 156.84; IR (film) 3520, 3444, 2967, 2880, 1457, 1371, 1252, 1104, 1050, 847, 769 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{39}H_{64}O_6Si_2Na$ $(M+Na)^+$ 707.4134, found 707.4132; Anal. Calcd for $C_{39}H_{64}O_6Si_2$: C, 68.37; H, 9.42. Found: C, 68.95; H, 9.37.

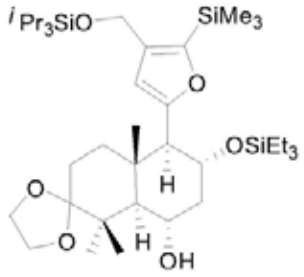
(±)-(4a*S*,5*R*,6*R*,8*S*,8a*R*)-8-Benzyloxy-5-{4-[(triisopropylsilyloxy)methyl]-5-(trimethylsilyl)furan-2-yl}-6-triethylsilyloxy-1,1,4a-trimethyl-octahydronaphthalen-2(1*H*)-one ethylene ketal (138).



To a solution of alcohol **136** (1.5 g, 2.19 mmol) in DMF (4 mL) was added imidazole (0.3 g, 4.38 mmol) and DMAP (20 mg) followed by TESCl (0.36 g, 2.40 mmol) at 0 °C under N_2. The mixture was stirred for 12 h at room temperature and then quenched with 5% $NaHCO_3$ (20 mL) slowly. After extraction with diethyl ether (20 mL × 3), the combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered and evaporated. The residue was purified by column chromatography on silica gel (50 g, hexanes:EtOAc 50:1 – 20:1) to give 1.55 g (89%) of **138** as a white oil. R_f 0.60 (hexanes:EtOAc = 12:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.24 (s, 9H), 0.37 (q, J = 7.8 Hz, 6H), 0.78 (t, J = 7.8 Hz, 9H), 1.04–1.12 (m, 28H), 1.13 (s, 3H), 1.40–1.54 (m, 4H), 1.62–1.68 (m, 1H), 1.72 (d, J = 10.5 Hz, 1H), 2.45 (d, J = 10.8 Hz,

1H), 2.46–2.50 (m, 1H), 3.72 (dt, J = 3.9, 10.8 Hz, 1H), 3.91–3.92 (m, 4H), 4.13 (dt, J = 4.2, 11.4 Hz, 1H), 4.48 (d, J = 10.8 Hz, 1H), 4.62 (d, J = 10.5 Hz, 1H), 4.64 (s, 2H), 6.13 (s, 1H), 7.26–7.39 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –0.89, 4.91, 6.85, 12.11, 16.83, 18.14, 20.65, 25.67, 26.31, 36.72, 38.20, 42.78, 42.90, 55.98, 58.01, 58.90, 64.83, 65.03, 68.02, 71.25, 75.97, 110.47, 113.43, 127.48, 128.05, 128.34, 136.53, 138.76, 152.20, 158.04; IR (film) 2957, 2885, 1473, 1370, 1250, 1131, 1057, 850, 749 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{45}H_{78}O_6Si_3Na$ $(M+Na)^+$ 821.5004, found 821.5001.

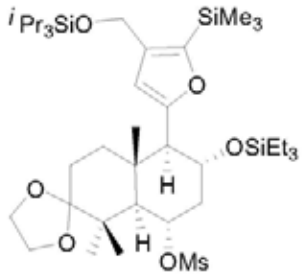
(±)-(4a*S*,5*R*,6*R*,8*S*,8a*R*)-6-Triethylsilyloxy-5-{4-[(triisopropylsilyloxy)methyl]-5-(trimethylsilyl)furan-2-yl}-8-hydroxy-1,1,4a-trimethyl-octahydronaphthalen-2(1*H*)-one ethylene ketal (139).



Palladium on charcoal (0.13 g, 10% *w/w*, Aldrich 205699-10G) was added to a solution of **138** (1 g) in MeOH/EtOAc (8/4 mL) at room temperature. The heterogeneous mixture was purged with H_2 for 3 times and then stirred for 12 h at room temperature under a hydrogen atmosphere. After that, the reaction mixture was filtered over a Celite pad and washed with EtOAc (10 mL), then concentrated and purified by column chromatography on silica gel (50 g, hexanes:EtOAc 5:1 – 3:1) to give 0.80 g (90%) of alcohol **139** as a white foam. R_f 0.40 (hexanes:EtOAc = 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.23 (s, 9H), 0.37 (q, J = 7.8 Hz, 6H), 0.77 (t, J = 7.8 Hz, 9H), 1.03–1.12 (m, 25H), 1.15 (s, 3H), 1.18 (s, 3H),1.42–1.50 (m, 4H), 1.60–1.66 (m, 2H), 2.40–2.41 (m, 1H), 2.42 (d, J = 10.5 Hz, 1H), 3.94–4.05 (m, 6H), 4.16 (dt, J =

4.2, 11.4 Hz, 1H), 4.62 (s, 2H), 6.11 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –0.88, 4.87, 6.86, 12.13, 16.57, 18.16, 20.33, 25.83, 26.22, 36.66, 38.31, 42.76, 48.29, 57.52, 58.02, 58.95, 64.87, 64.99, 67.95, 68.62, 75.97, 110.50, 113.33, 136.57, 152.34, 157.90; IR (film) 3513, 2963, 2889, 1468, 1375, 1245, 1128, 1055, 849, 754 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{38}H_{72}O_6Si_3Na$ $(M+Na)^+$ 731.4529, found 731.4534.

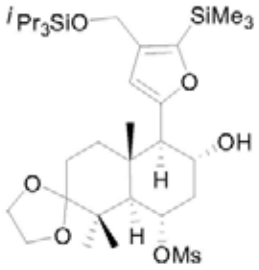
(±)-(4a*S*,5*R*,6*R*,8*S*,8a*R*)-6-Triethylsilyloxy-8-methylsulfonyloxy-5-{4-[(triisopropylsilyloxy)methyl]-5-(trimethylsilyl)furan-2-yl}-1,1,4a-trimethyl-octahydronaphthalen-2(1*H*)-one ethylene ketal (151).



To a solution of compound **139** (0.455 g, 0643 mmol) in CH_2Cl_2 (3 mL) was added Et_3N (0.196 ml, 1.41 mmol) followed by MsCl (0.09 mL, 1.16 mmol) slowly at 0 °C. The reaction was stirred for 2 h at 0 °C and then was quenched with saturated $NaHCO_3$ (40 mL). The mixture was extracted with CH_2Cl_2 (5 mL × 3), washed with brine (8 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (20 g, hexanes:EtOAc 6:1 – 3:1) to give 0.465 g (92%) of product **151** as a white foam. R_f 0.40 (hexanes:EtOAc = 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.23 (s, 9H), 0.32–0.43 (m, 6H), 0.77 (t, J = 7.9 Hz, 9H), 1.03–1.10 (m, 24H), 1.14 (s, 6H), 1.32–1.48 (m, 3H), 1.57–1.75 (m, 4H), 1.86 (d, J = 11.4 Hz, 1H), 2.44 (d, J = 10.5 Hz, 1H), 2.68–2.76 (m, 1H), 3.04 (s, 3H), 3.93–3.94 (m, 4H), 4.16 (dt, J = 4.2, 11.7 Hz, 1H), 4.62 (s, 2H), 5.08 (dt, J = 4.2, 11.4 Hz, 1H), 6.14 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –0.94, 4.75, 6.77, 12.09, 16.48, 18.12, 20.07, 25.21, 25.86, 31.61, 36.51, 38.50, 40.23, 42.38,

44.58, 46.05, 55.15, 57.94, 58.48, 64.87, 65.03, 67.32, 78.47, 110.78, 112.90, 136.58, 152.65, 156.97; IR (film) 2974, 2883, 1679, 1357, 1255, 1108, 1042, 941, 842, 776 cm^{-1}; HRMS (FAB) *m/z* calcd for $C_{33}H_{58}O_7SSi_2$ $(M-H)^+$ 654.3442, found 654.3437.

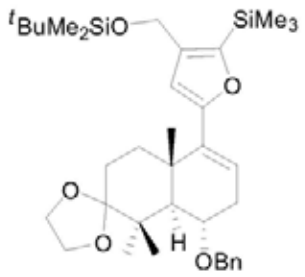
(±)-(4a*S*,5*R*,6*R*,8*S*,8a*R*)-8-Methylsulfonyloxy-5-{4-[(triisopropylsilyloxy)methyl]-5-(trimethylsilyl)furan-2-yl}-6-hydroxy-1,1,4a-trimethyl-octahydronaphthalen-2(1*H*)-one ethylene ketal (152).



To a solution of silyl ether **151** (400 mg, 0.509 mmol) in $MeOH/CH_2Cl_2$ (3/4 mL) was added PPTS (30 mg, 0.119 mmol) at 20 °C and then the reaction was stirred for 0.5 h at 20 °C. Et_3N (8 drops) was added to the reaction and then saturated $NaHCO_3$ (5 mL) was added. After 5 min, the reaction was extracted with EtOAc (10 mL × 3) and the combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (20 g, hexanes:EtOAc 7:1 – 2:1) to give 257 mg (75%) of product **152** as a white foam. R_f 0.45 (hexanes:EtOAc = 2:1); ^1H NMR (300 MHz, $CDCl_3$) δ 0.24 (s, 9H), 1.00 (s, 3H), 1.02–1.12 (m, 21H), 1.12 (s, 6H), 1.41–1.44 (m, 1H), 1.57–1.80 (m, 4H), 1.91 (d, J = 11.4 Hz, 1H), 2.50 (d, J = 10.8 Hz, 1H), 2.80–2.86 (m, 1H), 3.05 (s, 3H), 3.96–3.98 (m, 4H), 4.16 (dt, J = 4.2, 11.7 Hz, 1H), 4.65 (s, 2H), 5.10 (dt, J = 4.2, 11.6 Hz, 1H), 6.23 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –1.09, 12.08, 16.18, 18.10, 19.94, 25.05, 25.89, 36.09, 38.81, 40.35, 42.00, 42.48, 55.07, 57.80, 58.55, 64.91, 65.09, 66.29, 78.18, 110.36, 112.84, 136.60, 154.46, 155.82; IR (film) 3445, 2953, 2887, 1341, 1267, 1151, 1112, 1050, 853, 784, 634

cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{33}H_{60}O_8SSi_2Na$ $(M+Na)^+$ 695.3445, found 695.3441.

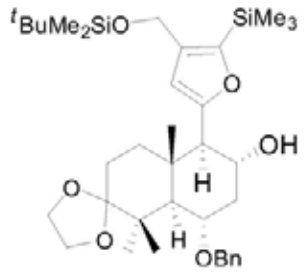
(±)-(4a*S*,8*S*,8a*R*)-8-Benzyloxy-5-{4-[(*tert*-butyldimethylsilyloxy)methyl]-5-(trimethylsilyl)furan-2-yl}-1,1,4a-trimethyl-4,4a,8,8a-tetrahydronaphthalen-2(1*H*,3*H*,7*H*)-one ethylene ketal (154).



To a solution of **106** (4.26 g, 15 mmol) in dry THF (35 mL) was added dropwise *n*-BuLi (1.6 M solution in hexane, 9.4 mL, 15 mmol) at 0 °C under N_2. The mixture was stirred at 0 °C for 0.5 h and at room temperature for 1 h. $ZnCl_2$ (powder, 2.05 g, 15 mmol) was added to the above solution portionwise and left stirring for another 1 h at room temperature. A mixture of vinyl triflate **105** (4.9 g, 10 mmol) and $Pd(PPh_3)_4$ (0.35 g, 0.3 mmol) in dry THF (25 mL) was added to the above reaction solution and then the reaction was heated to 50 °C for 20 min. TLC showed that the reaction was completed and it was cooled to room temperature before diluting with diethyl ether (70 mL) followed by quenching with saturated $NaHCO_3$ (50 mL). The organic layer was separated and the aqueous was extracted with diethyl ether (50 mL × 2), washed with brine (70 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (180 g, hexanes:EtOAc 100:1 – 40:1) to give 5.43 g (87%) of **154** as a light-yellow solid. R_f 0.50 (hexanes:EtOAc = 20:1); mp 91.5–95.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.08 (s, 6H), 0.27 (s, 9H), 0.92 (s, 9H), 1.16 (s, 3H), 1.17 (s, 3H), 1.40 (s, 3H), 1.48–1.62 (m, 2H), 1.71–1.95 (m, 2H), 2.03 (d, *J* = 10.5 Hz, 1H), 2.22 (dddd, *J* = 14.7, 6.3, 5.1,

3.3 Hz, 1H), 2.84 (dt, J = 5.1, 18.3 Hz, 1H), 3.95 (m, 5H), 4.47 (d, J = 11.4 Hz, 1H), 4.58 (s, 2H), 4.67 (d, J = 11.4 Hz, 1H), 5.79 (dd, J = 3.3, 4.5 Hz, 1H), 6.17 (s, 1H), 7.27–7.40 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –4.99, –0.92, 14.21, 18.52, 20.48, 22.02, 25.32, 26.09, 26.93, 33.92, 34.54, 40.21, 42.87, 53.76, 57.81, 64.93, 71.22, 75.41, 76.68, 108.42, 113.30, 116.79, 124.66, 127.32, 127.44, 127.96, 128.32, 136.32, 138.86, 140.92, 153.11, 158.74; IR (film) 3846, 2851, 1463, 1364, 1254, 1103, 1040, 849, 755, 696, 446 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{36}H_{56}O_5Si_2Na$ $(M+Na)^+$ 647.3558, found 647.3557; Anal. Calcd for $C_{36}H_{56}O_5Si_2$: C, 69.18; H, 9.03. Found: C, 69.67; H, 8.93.

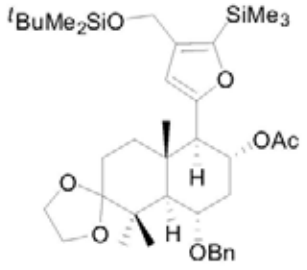
(±)-(4a*S*,5*R*,6*R*,8*S*,8a*R*)-8-Benzyloxy-5-{4-[(*tert*-butyldimethylsilyloxy)methyl]-5-(trimethylsilyl)furan-2-yl}-6-hydroxy-1,1,4a-trimethyl-octahydronaphthalen-2(1*H*)-one ethylene ketal (156).



BH_3·Me_2S (10 M, 2.4 mL) was added to a solution of **154** (4.98 g, 8 mmol) in dry THF (20 mL) dropwise at 0 °C, under N_2 and then the reaction was stirred at room temperature for 15 h. A mixture of pre-cooled H_2O_2 (30%, 12 mL) and NaOH (3 M, 12 mL) was added to the above solution at 0 °C carefully and then it was stirred vigorously for 3 h at room temperature before saturated Na_2SO_3 was added dropwise to the solution to remove the excess amount of H_2O_2. The reaction was extracted with EtOAc (25 mL × 3), washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (150 g, hexanes:EtOAc 20:1 – 10:1) to give 3.6 g (70%)

of **156** as a light-yellow foam. R_f 0.40 (hexanes:EtOAc = 6:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.07 (s, 6H), 0.26 (s, 9H), 0.90 (s, 9H), 0.97 (s, 3H), 1.05 (s, 3H), 1.14 (s, 3H), 1.42 (t, *J* = 10.5 Hz, 2H), 1.58–1.68 (m, 3H), 1.76 (d, *J* = 10.8 Hz, 1H), 2.50 (d, *J* = 10.8 Hz, 1H), 2.73–2.75 (m, 1H), 3.77 (dt, *J* = 4.0, 10.8 Hz, 1H), 3.94–3.96 (m, 4H), 4.07 (dt, *J* = 4.1, 10.8 Hz, 1H), 4.45 (d, *J* = 11.4 Hz, 1H), 4.58 (s, 2H), 4.66 (d, *J* = 11.3 Hz, 1H), 6.17 (s, 1H), 7.26–7.38 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –4.98, –1.00, 16.55, 18.47, 20.49, 25.57, 26.04, 26.32, 36.34, 38.51, 40.24, 42.90, 55.92, 57.76, 59.17, 64.90, 65.07, 67.02, 71.15, 75.66, 110.19, 113.37, 127.53, 128.15, 128.34, 136.24, 138.52, 154.46, 156.95; IR (film) 3526, 3452, 2958, 2883, 1461, 1361, 1253, 1106, 1043, 844, 770 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{36}H_{58}O_6Si_2Na$ $(M+Na)^+$ 665.3664, found 665.3663; Anal. Calcd for $C_{36}H_{58}O_6Si_2$: C, 67.24; H, 9.09. Found: C, 67.15; H, 8.86.

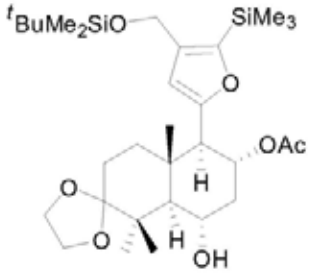
(±)-(4a*S*,5*R*,6*R*,8*S*,8a*R*)-6-Acetyloxy-8-benzyloxy-5-{4-[(*tert*-butyldimethylsilyloxy)methyl]-5-(trimethylsilyl)furan-2-yl}-1,1,4a-trimethyl-octahydronaphthalen-2-(1*H*)-one ethylene ketal (157).



A mixture of **156** (4.7 g, 7.3 mmol), Ac_2O (2.76 mL, 29.2 mmol) and DMAP (25 mg) in pyridine (25 mL) was stirred for 2 h at room temperature. Then it was quenched with saturated $NaHCO_3$ (50 mL) carefully, extracted with EtOAc (70 mL × 3), washed with saturated $CuSO_4$ (70 mL) and brine (70 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (150 g, hexanes:EtOAc 30:1 – 20:1) to give 4.54 g (91%)

of product **157** as a white foam. R_f 0.50 (hexanes:EtOAc = 10:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (s, 6H), 0.24 (s, 9H), 0.89 (s, 9H), 1.00 (s, 3H), 1.05 (s, 3H), 1.13 (s, 3H), 1.38–1.48 (m, 3H), 1.60–1.72 (m, 2H), 1.77 (d, *J* = 10.8 Hz, 1H), 1.80 (s, 3H), 2.69 (d, *J* = 11.7 Hz, 1H), 2.75–2.80 (m, 1H), 3.81 (dt, *J* = 4.1, 10.8 Hz, 1H), 3.94–3.97 (m, 4H), 4.44 (d, *J* = 11.2 Hz, 1H), 4.56 (s, 2H),4.64 (d, *J* = 11.2 Hz, 1H), 5.38 (dt, *J* = 4.1, 11.7 Hz, 1H), 6.05 (s, 1H), 7.27–7.36 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –4.96, –1.10, 16.42, 18.37, 20.46, 21.09, 25.55, 25.97, 26.34, 36.28, 37.99, 38.47, 42.84, 55.21, 55.66, 57.74, 64.88, 65.07, 69.30, 71.20, 75.43, 109.69, 113.28, 127.50, 127.99, 128.34, 136.02, 138.35, 153.66, 156.27, 170.40; IR (film) 3156, 2764, 1738, 1595, 1463, 1366, 1258, 1111, 838, 768, 630 cm^{-1}; HRMS (FAB) *m/z* calcd for $C_{38}H_{61}O_7Si_2$ $(M+H)^+$ 685.3950, found 685.3945; Anal. Calcd for $C_{38}H_{60}O_7Si_2$: C, 66.62; H, 8.83. Found: C, 66.67; H, 8.77.

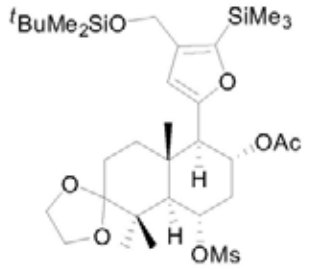
(±)-(4a*S*,5*R*,6*R*,8*S*,8a*R*)-6-Acetyloxy-5-{4-[(*tert*-butyldimethylsilyloxy)methyl]-5-(trimethylsilyl)furan-2-yl}-8-hydroxy-1,1,4a-trimethyl-octahydronaphthalen-2(1*H*)-one ethylene ketal (158).



Palladium on charcoal (0.55 g, 10% w/w) was added to a solution of compound **157** (5.5 g) in EtOAc (50 mL) at room temperature. The heterogeneous mixture was purged with H_2 for 3 times and then stirred for 2 h at room temperature under a hydrogen atmosphere. After there, the reaction mixture was filtered over a Celite pad and washed with EtOAc (50 mL), then concentrated and purified by column chromatography on silica gel (180 g, hexanes:EtOAc 5:1 – 3:1) to give 4.54 g (95%)

of alcohol **158** as a white foam. R_f 0.45 (hexanes:EtOAc = 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.01 (s, 6H), 0.20 (s, 9H), 0.86 (s, 9H), 0.96 (s, 3H), 1.11 (s, 3H), 1.16 (s, 3H), 1.41–1.51 (m, 3H), 1.53 (d, J = 10.8 Hz, 1H), 1.62–1.68 (m, 2H), 1.77 (s, 3H), 2.49–2.53 (m, 1H), 2.63 (d, J = 11.8 Hz, 1H), 3.94–3.97 (m, 4H), 4.08 (dt, J = 4.2, 10.8 Hz, 1H), 4.52 (s, 2H), 5.36 (dt, J = 4.2, 11.8 Hz, 1H), 6.02 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –4.98, –1.13, 16.16, 18.34, 20.15, 21.02, 25.62, 25.95, 26.22, 36.17, 38.53, 42.80, 43.39, 55.15, 56.86, 57.70, 64.85, 64.99, 67.99, 69.01, 75.43, 109.69, 113.18, 135.99, 153.71, 156.11, 170.27; IR (film) 3517, 2938, 2888, 1732, 1466, 1371, 1252, 1107, 1032, 844, 771, 632 cm^{-1}; HRMS (FAB) *m/z* calcd for $C_{31}H_{53}O_7Si_2$ $(M\text{-}H)^+$ 593.3324, found 593.3348.

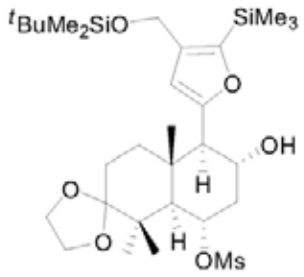
(±)-(4a*S*,5*R*,6*R*,8*S*,8a*R*)-6-Acetyloxy-8-methylsulfonyloxy-5-{4-[(*tert*-butyldimethylsilyloxy)methyl]-5-(trimethylsilyl)furan-2-yl}-1,1,4a-trimethyl-octahydronaphthalen-2(1*H*)-one ethylene ketal (159).



To a solution of compound **158** (3.7 g, 6.23 mmol) in CH_2Cl_2 (30 mL) was added Et_3N (1.9 ml, 13.7 mmol) followed by MsCl (0.88 mL, 11.24 mmol) slowly at 0 °C. The reaction mixture was stirred for 2 h at 0 °C and was then quenched with saturated $NaHCO_3$ (40 mL), and the mixture was extracted with CH_2Cl_2 (30 mL × 3), washed with brine (40 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexanes:EtOAc 5:1 – 3:1) to give 3.94 g (94%) of product **159** as a light-yellow foam. R_f 0.45 (140 g, hexanes:EtOAc = 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.02 (s, 6H),

0.21 (s, 9H), 0.87 (s, 9H), 1.03 (s, 3H), 1.06 (s, 3H), 1.13 (s, 3H), 1.43–1.45 (m, 1H), 1.65–1.71 (m, 3H), 1.77 (s, 3H), 1.91 (d, J = 11.4 Hz, 1H), 2.67 (d, J = 11.7 Hz, 1H), 2.81–2.83 (m, 1H), 3.03 (s, 3H), 3.94–3.99 (m, 4H), 4.53 (s, 2H), 5.11 (dt, J = 4.2, 11.4 Hz, 1H), 5.40 (dt, J = 4.2, 11.7 Hz, 1H), 6.05 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –4.98, –1.13, 16.10, 18.37, 19.94, 20.90, 25.03, 25.96, 36.09, 38.72, 39.91, 40.16, 42.46, 54.84, 57.65, 64.91, 65.08, 67.92, 110.03, 112.77, 136.05, 154.12, 155.25, 169.79; IR (film) 2950, 2889, 1742, 1349, 1247, 1105, 1039, 933, 842, 770, 531 cm^{-1}; HRMS (FAB) *m/z* calcd for $C_{31}H_{55}O_9SSi_2$ $(M-H)^+$ 671.3100, found 671.3082.

(±)-(4a*S*,5*R*,6*R*,8*S*,8a*R*)-8-Methylsulfonyloxy-5-{4-[(*tert*-butyldimethylsilyloxy)-methyl]-5-(trimethylsilyl)furan-2-yl}-6-hydroxy-1,1,4a-trimethyl-octahydronaphthalen-2(1*H*)-one ethylene ketal (160).



To a solution of ester **159** (4.2 g, 6.25 mmol) in THF/MeOH (30/15 mL) at room temperature was added NaOMe (1.01 g, 18.75 mmol) and then the reaction mixture was stirred for 3 h at room temperature. After cooling to 0 °C, H_2O (50 mL) was added to the reaction and then saturated NH_4Cl (25 mL). After 5 min, the reaction was extracted with EtOAc (40 mL × 3), washed with brine (40 mL), dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (120 g, hexanes:EtOAc 3:1 – 1:1) to give 3.67 g (93%) of product **160** as a light-yellow foam. R_f 0.25 (hexanes:EtOAc = 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 6H), 0.24 (s, 9H), 0.88 (s, 9H), 1.00 (s, 3H), 1.06 (s, 3H), 1.12 (s, 3H), 1.41–1.43 (m, 1H), 1.60–1.80 (m, 4H), 1.89 (d, J = 11.1 Hz, 1H), 2.48 (d,

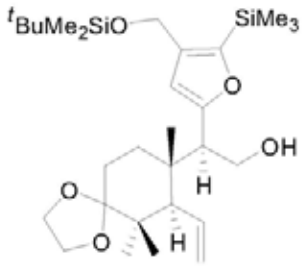
J = 10.8 Hz, 1H), 2.81–2.83 (m, 1H), 3.04 (s, 3H), 3.92–3.97 (m, 4H), 4.14 (dt, J = 4.1, 11.1 Hz, 1H), 4.56 (s, 2H), 5.08 (dt, J = 4.2, 10.8 Hz, 1H), 6.16 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –5.05, –1.07, 16.16, 18.42, 19.90, 25.01, 25.83, 25.98, 36.07, 38.75, 40.29, 42.05, 42.43, 55.00, 57.63, 58.45, 64.86, 65.04, 66.22, 78.10, 110.38, 112.78, 136.20, 154.73, 155.91; IR (film) 3442, 2951, 2889, 1343, 1254, 1172, 1105, 1046, 924, 844, 772, 526 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{30}H_{54}O_8SSi_2Na$ $(M+Na)^+$ 653.2970, found 653.2944.

(±)-(3*R*,4*S*)-4-{(*R*)-1-(4-[(*tert*-Butyldimethylsilyloxy)methyl]-5-(trimethylsilyl)-furan-2-yl)-2-hydroxyethyl}-2,2,4-trimethyl-3-vinylcyclohexanone ethylene ketal (196a). and

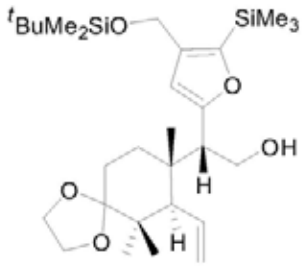
(±)-(3*R*,4*S*)-4-{(*S*)-1-(4-[(*tert*-Butyldimethylsilyloxy)methyl]-5-(trimethylsilyl)-furan-2-yl)-2-hydroxyethyl}-2,2,4-trimethyl-3-vinylcyclohexanone ethylene ketal (196b).

In one portion, KO^{t}Bu (1.28 g, 11.4 mmol, freshly sublimed) was added to a solution of **160** (2.4 g, 3.8 mmol) in ^{t}BuOH (50 mL) at 20 °C under N_2 and the resulting mixture was stirred for 10 min at 20 °C. The reaction was cooled by an ice bath and quenched by slow addition of H_2O (100 mL) followed by saturated NH_4Cl (60 mL). The mixture was extracted with diethyl ether (60 mL × 3), washed with brine (80 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure to give a residue which was subjected to the equilibration without further purification. The crude aldehyde was dissolved in THF (30 ml) and to which DBU (1.72 mL, 11.4 mmol) was added at room temperature. The mixture was stirred vigorously for 3.5 h. After cooling to 0 °C, H_2O (3 mL) was added to the above solution and then $NaBH_4$ (0.29 g, 7.6 mmol) was added portionwise. After another 1 h, saturated NH_4Cl (20 mL) and H_2O (30 mL) was added dropwise to the reaction. Then the mixture was extracted

with EtOAc (40 mL × 3), washed with brine (40 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel carefully (200 g, hexanes:EtOAc 20:1 – 5:1).



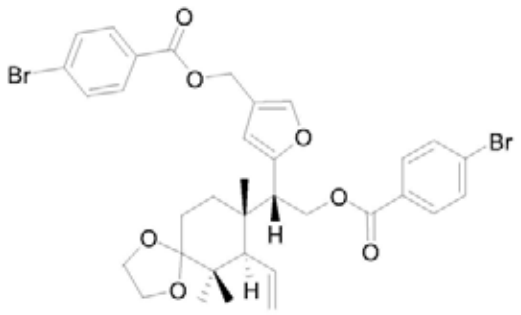
The purification gave 0.71 g (35%) of product **196a** as a white oil (the less polar one). R_f 0.40 (hexanes:EtOAc = 5:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.07 (s, 6H), 0.28 (s, 9H), 0.67 (s, 3H), 0.90 (s, 9H), 1.02 (s, 3H), 1.19 (s, 3H), 1.22–1.30 (m, 2H), 1.45 (dt, J = 3.3, 13.5 Hz, 1H), 1.79 (dt, J = 3.6, 11.0 Hz, 1H), 2.01 (d, J = 10.5 Hz, 1H), 2.22 (dt, J = 3.6, 11.0 Hz, 1H), 2.85 (dd, J = 4.0, 9.5 Hz, 1H), 3.76–3.89 (m, 6H), 4.60 (s, 2H), 4.89 (dd, J = 2.7, 17.1 Hz, 1H), 5.18 (dd, J = 2.7, 10.2 Hz, 1H), 5.74 (ddd, J = 10.2, 10.5, 17.1 Hz, 1H), 6.17 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –4.93, –1.01, 18.42, 20.45, 20.77, 23.54, 26.01, 26.92, 31.26, 38.66, 41.98, 52.54, 54.84, 57.79, 61.66, 64.73, 64.89, 111.26, 112.16, 120.00, 135.17, 135.86, 154.25, 158.17; IR (film) 3954, 3880, 2955, 2863, 1468, 1388, 1253, 1099, 1049, 843, 773 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{29}H_{52}O_5Si_2Na$ $(M+Na)^+$ 559.3256, found 559.3260.



The purification also gave 0.71 g (35%) of isomer **196b** as a white oil (the more polar one). R_f 0.35 (hexanes:EtOAc = 5:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.06 (s, 6H), 0.25 (s, 9H), 0.80 (s, 3H), 0.85 (s, 3H), 0.89 (s, 9H), 1.03 (s, 3H), 1.15–1.24 (m,

1H), 1.42–1.48 (m, 2H), 1.79 (d, J = 10.0 Hz, 2H), 2.32 (d, J = 10.5 Hz, 1H), 2.91 (dd, J = 4.8, 8.7 Hz, 1H), 3.87–3.98 (m, 6H), 4.57 (s, 2H), 5.09 (dd, J = 1.8, 17.1 Hz, 1H), 5.24 (dd, J = 1.2, 10.2 Hz, 1H), 5.79 (ddd, J = 10.2, 10.5, 17.1 Hz, 1H), 6.13 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –4.97, –0.96, 18.46, 20.57, 20.91, 23.95, 26.04, 26.99, 30.61, 39.13, 42.14, 51.49, 53.82, 57.79, 60.91, 64.85, 65.16, 111.33, 112.35, 119.56, 135.12, 136.18, 154.08, 158.62; IR (film) 3952, 3875, 2952, 2856, 1467, 1385, 1257, 1102, 1045, 847, 772 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{29}H_{52}O_5Si_2Na$ $(M+Na)^+$ 559.3256, found 559.3259.

(±)-{5-[(*S*)-1-(1*S*,2*R*)-1,3,3-trimethyl-4-one ethylene ketal-2-vinylcyclohexyl]-ethyl 4-bromobenzoate}furan-3-yl-methyl 4-bromobenzoate (197).

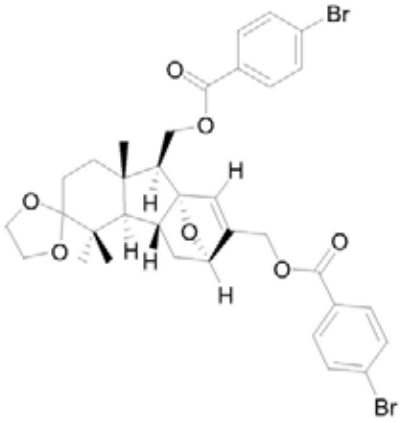


TBAF (1 M in THF, 0.32 mL) was added to a solution of compound **196b** (43 mg, 0.08 mmol) in THF (1 mL) at 0 °C. After stirring for 5 h at room temperature and 1.5 h at 45 °C, the reaction was quenched with H_2O (3 mL) and then the reaction was extracted with EtOAc (5 mL × 3). The combined organic extracts were washed with brine (5 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude material (~ 42 mg) was used in the next esterification without further purification.

A mixture of the above residue, 4-bromobenzoyl chloride (69 mg, 0.32 mmol), DMAP (2 mg) in pyridine (1 mL) was stirred for 40 min at room temperature. The reaction mixture was quenched with saturated $NaHCO_3$ (5 mL) carefully, extracted

with EtOAc (5 mL × 3), washed with saturated $CuSO_4$ (5 mL) and brine (5 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified rapidly by column chromatography on silica gel (15 g, hexanes:EtOAc 15:1 – 5:1) to give 34 mg of product **197** (59.5%) as a white semi-solid. R_f 0.50 (hexanes:EtOAc = 6:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81 (s, 3H), 0.94 (s, 3H), 1.06 (s, 3H), 1.50–1.56 (m, 2H), 1.78–1.95 (m, 2H), 2.37 (d, *J* = 10.5 Hz, 1H), 3.16 (dd, *J* = 4.5, 10.5 Hz, 1H), 3.90–3.97 (m, 4H), 4.61 (t, *J* = 10.5 Hz, 1H), 4.71 (m, 1H), 5.10–5.16 (m, 3H), 5.26 (dd, *J* = 2.1, 10.2 Hz, 1H), 5.82 (ddd, *J* = 10.2, 10.5, 17.1 Hz, 1H), 6.19 (s, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.54–7.62 (m, 4H), 7.82 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.58, 20.85, 23.90, 26.84, 29.77, 30.56, 39.08, 42.21, 47.36, 53.82, 58.70, 63.50, 64.94, 65.10, 109.62, 112.08, 119.99, 120.71, 127.89, 128.30, 129.06, 129.22, 130.98, 131.14, 131.56, 131.84, 134.82, 140.44, 155.93, 165.68; HRMS (ESI) *m/z* calcd for $C_{34}H_{36}{}^{79}Br^{81}BrO_7Na$ $(M+Na)^+$ 739.0700, found 739.0708.

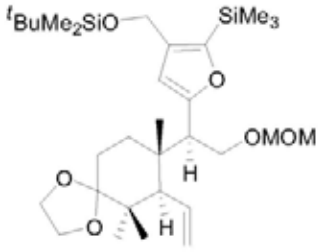
(±)-[3*S*,4*R*,4b*R*,8a*S*,9*S*,9a*S*)-3,9a,oxy-9-(Methyl 4-bromobenzoate)-5,5,8a -trimethyl-6-one ethylene ketal-4,4a,4b,5,6,7,8,8a,9,9a-decahydro-3*H*-fluorenyl]ethyl 4-bromobenzoate (198).



The purification of the above residue also gave 13 mg of a more polar compound **198** (22.8%) as a white powder. Preparation of the single crystal of **197** was attempted

by dissolving the compound in hexanes:EtOAc (1:1) and the solvent was allowed to evaporate slowly. However, after 4 days, we found that most of the compound **197** had been converted to tricyclic compound **198** through an intramolecular Diels-Alder cycloaddition. Thus, a sample crystal of **198** for X-ray crystallography was obtained and it was determined by an X-ray crystallographic analysis. R_f 0.35 (hexanes:EtOAc = 6:1); mp 101.5–103.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (s, 3H), 1.02 (s, 3H), 1.05 (s, 3H), 1.40–1.46 (m, 1H), 1.51–1.59 (m, 2H), 1.73–1.87 (m, 6H), 2.24 (t, J = 8.3 Hz, 1H), 3.88–3.97 (m, 4H), 4.49–4.56 (m, 2H), 4.90–4.96 (m, 3H), 6.37 (s, 1H), 7.54 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.7 Hz, 2H), 7.90 (d, J = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 1.09, 14.27, 16.11, 20.21, 20.91, 24.40, 27.87, 29.85, 36.22, 42.81, 44.90, 48.59, 51.38, 56.32, 61.14, 63.33, 65.13, 65.29, 80.48, 98.60, 113.14, 128.17, 128.46, 128.76, 129.05, 131.26, 131.29, 131.81, 131.92, 132.78, 143.40, 165.62, 165.91; IR (film) 2965, 2876, 1756, 1547, 1267, 1108, 1015, 841, 754 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{34}H_{36}{}^{79}Br^{81}BrO_7Na$ $(M+Na)^+$ 739.0700, found 739.0710; Anal. Calcd for $C_{34}H_{36}Br_2O_7$: C, 57.00; H, 5.06. Found: C, 57.12; H, 4.99.

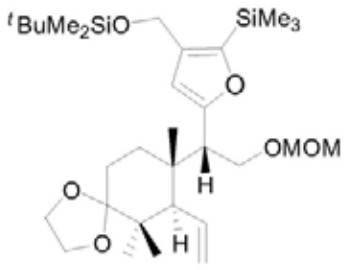
(±)-(3*R*,4*S*)-4-{(*R*)-1-[4-((*tert*-Butyldimethylsilyloxy)methyl)-5-(trimethylsilyl)-furan-2-yl]-2-(methoxymethoxy)ethyl}-2,2,4-trimethyl-3-vinylcyclohexanone ethylene ketal (199a).



To a solution of compound **196a** (0.85 g, 1.58 mmol) in dry CH_2Cl_2 (10 mL) was added DIPEA (0.83 mL, 4.74 mmol) followed by MOMCl (0.24 mL, 3.16 mmol) at 0

°C and the reactiom mixture was stirred at room temperature for 15 h, then quenched with saturated NH_4Cl (15 mL) and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4, filtered, concentrated under reduced pressure and purified by column chromatography on silica gel (40 g, hexanes:EtOAc 20:1 – 15:1) to give 0.825 g (90%) of product **199a** as a white oil. R_f 0.50 (hexanes:EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 6H), 0.27 (s, 9H), 0.68 (s, 3H), 0.89 (s, 9H), 1.01 (s, 3H), 1.22 (s, 3H), 1.22–1.27 (m, 1H), 1.45 (dt, *J* = 3.4, 13.5 Hz, 1H), 1.77 (ddd, *J* = 3.6, 13.5, 13.8 Hz, 1H), 2.05 (d, *J* = 10.4 Hz, 1H), 2.15 (ddd, *J* =3.6, 13.5, 13.8 Hz, 1H), 2.90 (dd, *J* = 3.6, 9.6 Hz, 1H), 3.17 (s, 3H), 3.74–3.81 (m, 2H), 3.82–3.90 (m, 4H), 4.40 (d, *J* = 6.8 Hz, 1H), 4.50 (d, *J* = 6.8 Hz, 1H), 4.58 (s, 2H), 4.96 (dd, *J* = 2.4, 16.8 Hz, 1H), 5.20 (dd, *J* = 2.4, 10.4 Hz, 1H), 5.74 (ddd, *J* = 10.4, 10.4, 16.8 Hz, 1H),6.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –4.92, –0.96, 18.37, 20.39, 20.81, 23.55, 25.99, 26.90, 31.29, 38.59, 41.96, 49.50, 54.72, 54.99, 57.90, 64.71, 64.85, 67.02, 96.37, 110.43, 112.16, 120.05, 135.24, 135.88, 152.95, 159.00; IR (film) 3940, 3665, 2999, 2852, 1466, 1386, 1253, 1019, 918, 849, 769, 629 cm^{-1}; HRMS (FAB) *m/z* calcd for $C_{31}H_{56}O_6Si_2$ (M^+) 580.3610, found 580.3595.

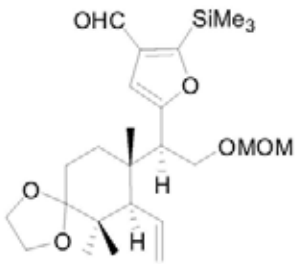
(±)-(3*R*,4*S*)-4-{(*S*)-1-[4-((*tert*-Butyldimethylsilyloxy)methyl)-5-(trimethylsilyl)-furan-2-yl]-2-(methoxymethoxy)ethyl}-2,2,4-trimethyl-3-vinylcyclohexanone ethylene ketal (199b).



Using the same procedures as that for **199a**, the MOM-ether **199b** was prepared

from alcohol **196b** in 89% yield as a white oil. R_f 0.45 (hexanes:EtOAc = 10:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (s, 6H), 0.24 (s, 9H), 0.81 (s, 3H), 0.83 (s, 3H), 0.88 (s, 9H), 1.04 (s, 3H), 1.42–1.47 (m, 2H), 1.77 (d, J = 9.3 Hz, 2H), 2.38 (d, J = 10.5 Hz, 1H), 2.96 (dd, J = 3.6, 9.9 Hz, 1H), 3.18 (s, 3H), 3.85–3.97 (m, 6H), 4.44 (d, J = 6.6 Hz, 1H), 4.53 (d, J = 6.6 Hz, 1H), 4.56 (s, 2H), 5.09 (dd, J = 2.3, 17.0 Hz, 1H), 5.25 (dd, J = 2.1, 10.2 Hz, 1H), 5.80 (ddd, J = 10.2, 10.5, 17.0 Hz, 1H),6.07 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –4.97, –0.92, 18.40, 20.48, 20.92, 24.03, 26.01, 26.96, 30.49, 38.99, 42.12, 48.21, 53.88, 54.93, 57.91, 64.82, 65.09, 66.15, 96.31, 109.60, 112.37, 119.50, 135.32, 136.21, 152.86, 159.46; IR (film) 3073, 2865, 1467, 1255, 1011, 916, 848, 766, 629 cm^{-1}; HRMS (FAB) *m/z* calcd for $C_{31}H_{56}O_6Si_2$ (M^+) 580.3610, found 580.3596.

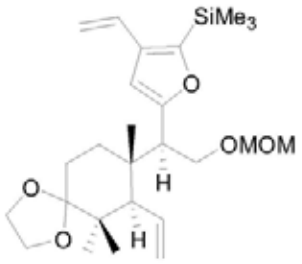
(±)-5-{(*R*)-2-(Methoxymethoxy)-1-[(1*S*,2*R*)-1,3,3-trimethyl-4-one ethylene ketal-2-vinylcyclohexyl]ethyl}-2-(trimethylsilyl)furan-3-carbaldehyde (200).



To a solution of compound **199a** (0.92 g, 1.59 mmol) in THF (10 mL) was added TBAF (1 M in THF, 3.17 mL) at 0 °C. After stirring for 2.5 h at 0 °C, the reaction was quenched with H_2O (20 mL) and followed by saturated NH_4Cl (10 mL), then extracted with EtOAc (25 mL × 3). The combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was subjected to the next oxidation without further purification. The crude alcohol was dissolved in dry CH_2Cl_2 (10 ml) and then treated with PDC (0.9 g, 2.39 mol) followed by adding 4 Å MS (0.8 g). After stirring for 5 h at room

temperature, the reaction mixture was diluted with EtOAc (10 mL) and stirred for another 15 min, filtered over a Celite pad and washed with EtOAc (10 mL), then concentrated and purified by column chromatography on silica gel (40 g, hexanes:EtOAc 10:1 – 5:1) to give 0.575 g (78 % yield for two steps) of product aldehyde **200** as a white syrup. R_f 0.50 (hexanes:EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.38 (s, 9H), 0.65 (s, 3H), 0.99 (s, 3H), 1.19 (s, 3H), 1.26 (dt, *J* = 3.3, 13.2 Hz, 1H), 1.43 (dt, *J* = 3.2, 13.4 Hz, 1H), 1.73–1.80 (m, 1H), 1.94 (d, *J* = 10.4 Hz, 1H), 2.08–2.12 (m, 1H), 2.96 (dd, *J* = 3.6, 9.6 Hz, 1H), 3.14 (s, 3H), 3.71–3.77 (m, 2H), 3.81–3.90 (m, 4H), 4.40 (d, *J* = 6.8 Hz, 1H), 4.49 (d, *J* = 6.8 Hz, 1H), 4.90 (dd, *J* = 2.2, 17.0 Hz, 1H), 5.21 (dd, *J* = 2.2, 10.2 Hz, 1H), 5.73 (ddd, *J* = 10.2, 10.4, 17.0 Hz, 1H), 6.48 (s, 1H), 10.01 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –1.06, 20.39, 20.69, 23.48, 26.79, 31.26, 38.50, 41.97, 49.35, 54.84, 55.03, 64.72, 64.86, 66.52, 96.30, 106.77, 111.93, 120.31, 134.87, 137.73, 161.33, 170.03, 186.31; IR (film) 3765, 3375, 3093, 2571, 1677, 1461, 1392, 1254, 1031, 918, 849, 766, 629 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{40}O_6SiNa$ $(M+Na)^+$ 487.2486, found 487.2489.

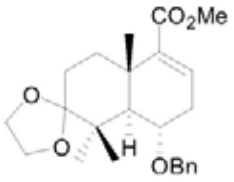
(±)-(3*R*,4*S*)-4-{(*R*)-2-(Methoxymethoxy)-1-[5-(trimethylsilyl)-4-vinylfuran-2-yl]-ethyl}-2,2,4-trimethyl-3-vinylcyclohexanone ethylene ketal (202).



At –10 °C, under N_2, to a suspension of salt Ph_3PCH_3I (0.675 g, 1.67 mmol) in dry THF (3 mL) was added *n*-BuLi (1.6 M in hexane, 0.928 mL, 1.484 mmol) and then the mixture was stirred at this temperature for 0.5 h. After that, a solution of above aldehyde **200** (0.574 g, 1.237 mmol) in THF (3 mL) was added dropwise at –10 °C

and then the mixture was stirred at –10 °C – 0 °C for another 0.5 h. H_2O (10 mL) was added to the reaction and then extracted with EtOAc (10 mL × 3). The combined organic extracts were washed with brine (10 mL), dried over Na_2SO_4, filtered, concentrated under reduced pressure and purified by column chromatography on silica gel (40 g, hexanes:EtOAc 20:1 – 10:1) to give 0.503 g (88%) of product **202** as a white semi-solid. R_f 0.30 (hexanes:EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.30 (s, 9H), 0.69 (s, 3H), 1.02 (s, 3H), 1.20 (s, 3H), 1.21–1.23 (m, 1H), 1.45 (dt, *J* = 3.6, 13..5 Hz, 1H), 1.78 (ddd, *J* = 3.6, 13.5, 13.8, 1H), 2.04 (d, *J* = 10.5 Hz, 1H), 2.15 (ddd, *J* = 3.6, 13.5, 13.8, 1H), 2.89 (dd, *J* = 3.4, 9.8 Hz, 1H), 3.16 (s, 3H), 3.76–3.80 (m, 2H), 3.82–3.90 (m, 4H), 4.42 (d, *J* = 6.8 Hz, 1H), 4.51 (d, *J* = 6.8 Hz, 1H), 4.96 (dd, *J* = 2.5, 17.1 Hz, 1H), 5.07 (dd, *J* = 1.4, 10.8 Hz, 1H), 5.21 (dd, *J* = 2.5, 10.3 Hz, 1H), 5.38 (dd, *J* = 1.4, 17.4 Hz, 1H), 5.76 (ddd, *J* = 10.3, 10.5, 17.1 Hz, 1H), 6.29 (s, 1H), 6.69 (dd, *J* = 10.8, 17.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –0.83, 20.20, 20.81, 23.60, 26.93, 31.55, 38.49, 42.02, 49.66, 54.99, 55.19, 64.75, 64.90, 66.81, 96.33, 106.74, 112.15, 112.58, 119.97, 128.62, 134.58, 135.33, 155.77, 159.67; IR (film) 2967, 2885, 1583, 1469, 1389, 1253, 1207, 1039, 913, 842, 7606, 627 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{42}O_5SiNa$ $(M+Na)^+$ 485.2694, found 485.2695; Anal. Calcd for $C_{26}H_{42}O_5Si$: C, 67.49; H, 9.15. Found: C, 67.68; H, 9.06.

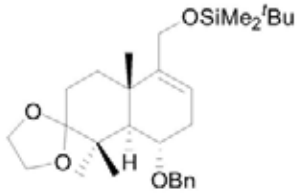
(±)-(4*S*,4a*R*,8a*S*)-Methyl 4-(benzyloxy)-5,5,8a-trimethyl-6-one ethylene ketal-3,4,4a,5, 6,7,8,8a-octahydronaphthalen-1-carboxylate (231).



To a solution of triflate **105** (0.49 g, 1 mmol) in DMF (4 mL) was added $Pd(PPh_3)_4$ (34.6 mg, 0.03 mmol), triethylamine (0.416 mL, 3 mmol) and methanol

(1.5 mL). The reaction mixture was purged for 3 times using a CO balloon and the reaction was stirred at 70 °C for 2.5 h under CO atmosphere. The reaction mixture was allowed to cool to room temperature, then poured into a saturated NH_4Cl solution (10 mL), diluted with water (10 mL) and then extracted with EtOAc (15 mL × 3). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by column chromatography on silica gel (25 g, hexanes:EtOAc 50:1 – 20:1 – 10:1) afforded the corresponding methyl ester **231** (0.34 g, 85%) as a white semi-solid. R_f 0.30 (hexanes:EtOAc = 12:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ1.13 (s, 3H), 1.14 (s, 3H), 1.35 (s, 3H), 1.47–1.62 (m, 2H), 1.80–1.86 (m, 1H), 1.90 (d, J = 10.8 Hz, 1H), 2.20 (m, 2H), 2.80 (dt, J = 5.2, 18.7 Hz, 1H), 3.67 (s, 3H), 3.89–3.97 (m, 5H), 4.45 (d, J = 11.4 Hz, 1H), 4.63 (d, J = 11.4 Hz, 1H), 6.47 (dd, J = 3.6, 4.5 Hz, 1H), 7.27–7.38 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.40, 21.54, 25.29, 26.77, 32.46, 34.48, 39.46, 42.76, 51.35, 53.46, 64.95, 71.34, 74.79, 113.13, 123.86, 127.55, 127.94, 128.36, 129.74, 134.25, 138.56, 142.04, 167.72; IR (film) 3154, 2851, 1716, 1595, 1461, 1368, 1255, 1110, 842, 768, 641, 446 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{32}O_5Na$ $(M+Na)^+$ 423.2142, found 423.2146; Anal. Calcd for $C_{24}H_{32}O_5$: C, 71.97; H, 8.05. Found: C, 71.69; H, 8.11.

(±)-(4a*S*,8*S*,8a*R*)-8-(Benzyloxy)-5-[(*tert*-butyldimethylsilyloxy)methyl]-1,1,4a-trimethyl-4,4a,8,8a-tetrahydronaphthalen-2-(1*H*,3*H*,7*H*)-one ethylene ketal (232).



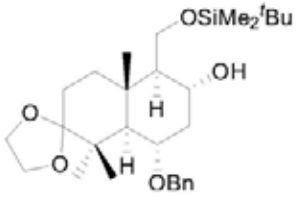
To a suspension of $LiAlH_4$ (38 mg, 1 mmol) in dry THF (2 mL) was added slowly a solution of **231** (0.28 g, 0.7 mmol) in THF (1 mL) at –10 °C under N_2. The mixture

was stirred for 10 min at –10 °C and for 15 min at room temperature before quenching with water (38 μL) and NaOH (3M, 0.12 mL) carefully. After stirring vigorously for a further 0.5 h, the solution was diluted with water (3 mL) and extracted with EtOAc (4 mL × 3). The combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, filtered and evaporated. The residue was purified by column chromatography on silica gel (30 g, hexanes:EtOAc 5:1 – 1:1) to give 0.17 g (65%) of the corresponding alcohol as a white oil. R_f 0.35 (hexanes:EtOAc = 1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (s, 3H), 1.13 (s, 3H), 1.18 (s, 3H), 1.45 (brs, 1H), 1.50–1.58 (m, 1H), 1.62–1.73 (m, 1H), 1.78–1.85 (m, 2H), 1.92 (d, J = 10.2 Hz, 1H), 2.14–2.22 (m, 1H), 2.64–2.72 (m, 1H), 3.90–3.98 (m, 5H), 4.00–4.14 (m, 2H), 4.42 (d, J = 11.4 Hz, 1H), 4.63 (d, J = 11.4 Hz, 1H), 5.54 (dd, J = 3.9, 4.2 Hz, 1H), 7.27–7.38 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.45, 22.06, 25.01, 26.75, 32.71, 33.29, 39.12, 42.82, 53.35, 63.00, 64.93, 64.97, 70.89, 75.50, 113.19, 120.29, 127.40, 127.92, 128.28, 138.74, 147.47; IR (film) 3850, 3120, 2857, 1461, 1368, 1252, 1107, 842, 766 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{23}H_{32}O_4Na$ $(M+Na)^+$ 395.2193, found 395.2193.

To a solution of the above alcohol (0.108 g, 0.29 mmol) in dry DMF (2 mL) was added imidazole (39.5 mg, 0.58 mmol), DMAP (4 mg) followed by TBSCl (48 mg, 0.319 mmol) at 0 °C under N_2. The mixture was stirred for 15 h at room temperature before quenching with 5% $NaHCO_3$ (6 mL) slowly. After extraction with diethyl ether (6 mL × 3), the combined organic layers were washed with brine (6 mL), dried over Na_2SO_4, filtered and evaporated. The residue was purified by column chromatography on silica gel (13 g, hexanes:EtOAc 20:1) to give 0.13 g (92%) of **232** as a white oil. R_f 0.40 (hexanes:EtOAc = 20:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.06 (s, 6H), 0.91 (s, 9H), 1.13 (s, 6H), 1.19 (s, 3H), 1.49–1.55 (m, 1H), 1.60–1.69 (m, 2H), 1.80–1.88 (m, 1H), 1.92 (d, J = 10.5 Hz, 1H), 2.08–2.16 (m, 1H), 2.69–2.75 (m, 1H), 3.91–3.97 (m,

5H), 4.06–4.12 (m, 2H), 4.42 (d, J = 11.4 Hz, 1H), 4.64 (d, J = 11.4 Hz, 1H), 5.51–5.55 (m, 1H), 7.27–7.39 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –5.33, –5.25, 18.46, 20.46, 21.94, 25.10, 26.06, 26.79, 32.47, 33.50, 39.17, 42.85, 53.35, 62.76, 64.93, 65.00, 70.87, 75.67, 113.28, 118.10, 127.36, 127.94, 128.27, 138.93, 146.18; IR (film) 3154, 2907, 1478, 1357, 1246, 1115, 857, 750 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{29}H_{46}O_4SiNa$ $(M+Na)^+$ 509.3058, found 509.3060.

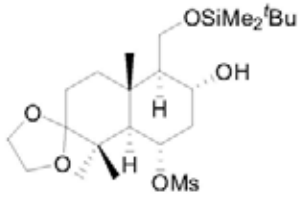
(±)-(4a*S*,5*S*,6*R*,8*S*,8a*R*)-8-(Benzyloxy)-5-[(*tert*-butyldimethylsilyloxy)methyl]-6-hydroxy-1,1,4a-trimethyl-octahydronaphthalen-2-(1*H*)-one ethylene ketal (239).



Dicyclohexylborane (0.18 g, 1.03 mmol) was added to the solution of **232** (0.1 g, 0.206 mmol) in dry THF (1 mL) at 0 °C under N_2 and then the reaction was stirred at room temperature for 15 h. After cooling to 0 °C, a mixture of pre-cooled H_2O_2 (30%, 0.5 mL) and NaOH (3 M, 0.5 mL) was added to the above solution carefully and then it was stirred vigorously for 3 h at room temperature before adding saturated Na_2SO_3 (2 mL) dropwise to the solution to remove the excess amount of H_2O_2. The reaction was extracted with EtOAc (3 mL × 3), washed with brine (3 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (12 g, hexanes:EtOAc 5:1 – 1:1) to give 55 mg (53%) of **239** as a white oil. R_f 0.45 (hexanes:EtOAc = 6:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.08 (s, 6H), 0.89 (s, 12H), 1.03 (s, 3H), 1.11 (s, 3H), 1.25–1.60 (m, 6H), 1.67 (d, J = 10.5 Hz, 1H), 1.69–1.75 (m, 2H), 2.60–2.65 (m, 1H), 3.64 (dt, J = 3.9, 10.5 Hz, 1H), 3.74 (t, J = 9.6 Hz, 1H), 3.91–3.96 (m, 5H), 4.04 (dd, J = 4.1, 10.6 Hz, 1H), 4.40 (d, J = 11.1 Hz, 1H), 4.58 (s, 1H), 4.64 (d, J = 11.4 Hz, 1H), 7.25–7.36 (m, 5H); ^{13}C NMR

(75 MHz, $CDCl_3$) δ –5.48, 17.09, 18.11, 20.67, 25.65, 25.86, 26.33, 36.06, 37.45, 41.22, 42.75, 56.18, 56.54, 64.47, 64.90, 65.05, 70.95, 75.41, 113.11, 127.43, 128.11, 128.29, 138.63; IR (film) 3931, 2917, 1456, 1367, 1255, 1108, 863, 743 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{29}H_{48}O_5SiNa$ $(M+Na)^+$ 527.3163, found 527.3166.

(±)-(1*S*,3*R*,4*S*,4a*S*,8a*R*)-4-[(*tert*-Butyldimethylsilyloxy)methyl]-3-hydroxy-4a,8,8-trimethyl-7-one ethylene ketal-decahydronaphthalen-1-yl methanesulfonate (233).



To a solution of alcohol **239** (0.3 g, 0.595 mmol) in pyridine (2 mL) was added dropwise Ac_2O (0.238 mL, 2.38 mmol) followed by DMAP (3 mg) at room temperature. The reaction mixture was stirred for 1 h at room temperature. Then it was quenched with saturated $NaHCO_3$ (8 mL) carefully, extracted with EtOAc (8 mL × 3), washed with saturated $CuSO_4$ (8 mL) and brine (8 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (25 g, hexanes:EtOAc 10:1) to give 0.30 g (94%) of the corresponding acetate as a white foam. R_f 0.45 (hexanes:EtOAc = 10:1); ^1H NMR (300 MHz, $CDCl_3$) δ –0.02 (s, 3H), –0.01 (s, 3H), 0.86 (s, 9H), 1.05 (s, 3H), 1.09 (s, 3H), 1.10 (s, 3H), 1.20–1.90 (m, 8H), 2.03 (s, 3H), 2.78–2.84 (m, 1H), 3.70–3.74 (m, 3H), 3.90–3.97 (m, 4H), 4.40 (d, J = 11.4 Hz, 1H), 4.63 (d, J = 11.4 Hz, 1H), 5.10 (dt, J = 4.2, 11.7 Hz, 1H), 7.24–7.36 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –5.80, –5.66, 17.69, 18.11, 20.55, 21.43, 25.61, 25.87, 26.29, 26.95, 36.13, 37.69, 42.60, 55.07, 56.43, 58.21, 64.83, 64.98, 68.99, 71.06, 75.53, 113.24, 127.38, 127.90, 128.27, 138.55, 170.56; IR (film) 3141, 2987, 1738, 1472, 1358, 1255, 1108, 863, 743 cm^{-1};

HRMS (ESI) *m/z* calcd for $C_{31}H_{50}O_6SiNa$ $(M+Na)^+$ 569.3269, found 569.3263.

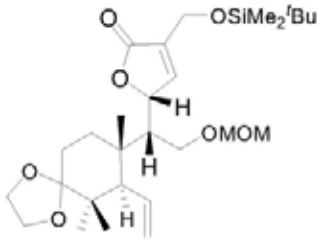
Palladium on charcoal (50 mg, 10% w/w) was added to a solution of the above benzyl ether (0.3 g) in EtOAc (4 mL) at room temperature. The heterogeneous mixture was purged with H_2 for 3 times and then stirred for 40 min under a hydrogen atmosphere. After that, the reaction mixture was filtered over a Celite pad and washed with EtOAc (4 mL), then concentrated to give the corresponding crude alcohol (0.25 g) as a white foam which was used into the next step without further purification.

To a solution of the above alcohol in CH_2Cl_2 (3 mL) at 0 °C was added Et_3N (0.19 ml, 1.37 mmol) followed by MsCl (88 μL, 1.124 mmol) slowly. The reaction was stirred for 0.5 h at 0 °C and 40 min at room temperature and then was quenched with saturated $NaHCO_3$ (4 mL). The mixture was extracted with CH_2Cl_2 (5 mL × 3), washed with brine (5 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (12 g, hexanes:EtOAc 5:1 – 3:1) to give 0.24 g (82%) of the corresponding mesylate as a light-yellow foam. R_f 0.40 (hexanes:EtOAc = 3:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ –0.05 (s, 3H), –0.02 (s, 3H), 0.83 (s, 9H), 1.01 (s, 3H), 1.09 (s, 3H), 1.12 (s, 3H), 1.27–1.33 (m, 1H), 1.50–1.90 (m, 6H), 2.00 (s, 3H), 2.79–2.83 (m, 1H), 3.00 (s, 3H), 3.65–3.71 (m, 2H), 3.92–3.98 (m, 4H), 5.02–5.11 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –5.82, –5.71, 17.32, 18.08, 20.03, 21.23, 25.01, 25.83, 35.91, 37.97, 39.46, 40.20, 42.21, 54.72, 55.53, 58.06, 64.85, 64.98, 67.73, 78.17, 112.69, 170.03; IR (film) 3015, 2887, 1757, 1350, 1247, 1108, 842, 754 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{46}O_8SSiNa$ $(M+Na)^+$ 557.2575, found 557.2574.

To a solution of the above mesylate (0.24 g, 0.449 mmol) in THF/MeOH (1.5/3 mL) at room temperature was added NaOMe (82 mg, 1.518 mmol) and then the

reaction was stirred for 2.5 h at room temperature. After cooling to 0 °C, H_2O (5 mL) was added to the reaction and then saturated NH_4Cl (3 mL) was added. After 5 min, the reaction was extracted with EtOAc (6 mL × 3), washed with brine (6 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (15 g, hexanes:EtOAc 3:1 – 1:1) to give 0.188 g (85%) of product **233** as a light-yellow foam. R_f 0.30 (hexanes:EtOAc = 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.08 (s, 6H), 0.84 (s, 3H), 0.89 (s, 9H), 1.06 (s, 3H), 1.13 (s, 3H), 1.20–1.40 (m, 3H), 1.50–1.68 (m, 3H), 1.70–1.83 (m, 3H), 2.64–2.72 (m, 1H), 3.03 (s, 3H), 3.74 (t, J = 10.5 Hz, 1H), 3.94–4.00 (m, 6H), 4.99 (dt, J = 3.9, 10.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –5.52, 16.74, 20.14, 25.14, 25.81, 35.87, 37.83, 40.24, 40.52, 42.37, 42.90, 55.68, 63.98, 64.93, 65.07, 69.95, 78.49, 112.56; IR (film) 3445, 2889, 1344, 1258, 1162, 1111, 1078, 934, 854, 762 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{23}H_{44}O_7SSiNa$ $(M+Na)^+$ 515.2475, found 515.2473.

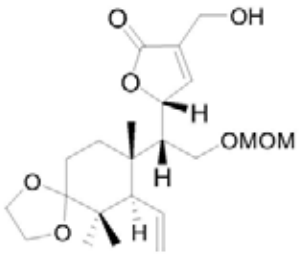
(±)-(*R*)-5-{(*R*)-3-[(*tert*-Butyldimethylsilyloxy)methyl]-5-[(*S*)-2-(methoxymethoxy)-1-[(1*S*,2*R*)-1,3,3-trimethyl-4-one ethylene ketal-2-vinylcyclohexyl]ethyl}furan-2(5*H*)-one (223).



To a solution of furan **199b** (0.58 g, 1 mmol) in CH_2Cl_2/MeOH (7/7 mL) was added TPP (2 mg). The mixture was purged several times with O_2 (balloon), cooled to –78 °C and irradiated with a 300 W lamp for 40 min, with stirring under an oxygen atmosphere. The mixture was then warmed to room temperature and the solvent was allowed to evaporate. The residue was then dissolved in MeOH (10 mL), cooled to 0

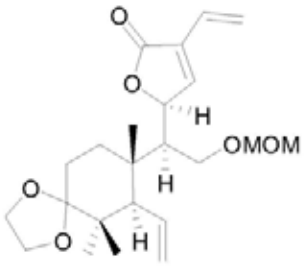
°C, to which was added $CeCl_3 \cdot 7H_2O$ (82 mg, 0.22 mmol) and $NaBH_4$ (0.19 g, 5 mmol). After being stirred for 0.5 h, the reaction mixture was acidified to *p*H ~ 3 by addition of aqueous HCl (2 N, 10 mL) and extracted with CH_2Cl_2 (15 mL × 3). The combined organic extracts were washed with water (15 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified carefully by column chromatography on silica gel (30 g, hexanes:EtOAc 20:1 – 5:1) to provide the major isomer **223** (0. 309 g, 59%) as a white solid. A sample crystal for X-ray crystallography was obtained by dissolving the solid in acetone:H_2O (5:1) and the solvent was allowed to evaporate slowly for 5 days. R_f 0.40 (hexanes:EtOAc = 5:1); mp 81.5–84.0 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 0.11 (s, 6H), 0.80 (s, 3H), 0.92 (s, 9H), 1.10 (s, 3H), 1.27 (s, 3H), 1.45–1.51 (m, 1H), 1.58–1.68 (m, 2H), 1.83 (dt, *J* = 4.5, 12.8 Hz, 1H), 2.16 (d, *J* = 7.8 Hz, 1H), 2.40 (d, *J* = 10.5 Hz, 1H), 3.00 (dd, *J* = 2.5, 8.0 Hz, 1H), 3.26 (s, 3H), 3.66 (d, *J* = 10.2 Hz, 1H), 3.85–3.95 (m, 4H), 4.37–4.47 (m, 3H), 4.51 (d, *J* = 6.3 Hz, 1H), 5.07 (dd, *J* = 2.7, 17.4 Hz, 1H), 5.24 (dd, *J* = 2.7, 10.2 Hz, 1H), 5.39 (brs, 1H), 5.85 (ddd, *J* = 10.2, 10.5, 17.4 Hz, 1H), 7.37 (dd, *J* = 1.6, 3.4 Hz, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ –5.19, 18.98, 20.95, 21.32, 24.60, 26.36, 27.10, 32.16, 39.72, 42.59, 50.01, 55.18, 55.46, 58.65, 63.58, 65.46, 65.85, 81.36, 97.28, 112.54, 120.67, 132.36, 136.79, 152.81, 173.05; IR (film) 2978, 2893, 1727, 1465, 1108, 1074, 947, 753 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{28}H_{48}O_7SiNa$ $(M+Na)^+$ 547.3062, found 547.3058.

(±)-(*R*)-3-(Hydroxymethyl)-5-{(*S*)-2-(methoxymethoxy)-1-[(1*S*,2*R*)-1,3,3-trimethyl-4-one ethylene ketal-2-vinylcyclohexyl]ethyl}furan-2(5*H*)-one (253).



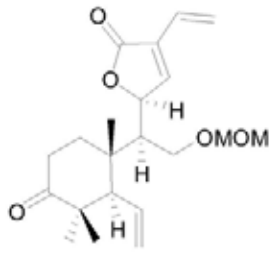
At 0 °C, TBAF (1 M in THF, 0.26 mL) was added to a solution of compound **223** (52.4 mg, 0.1 mmol) in THF (2 mL). After stirring for 20 min at 0 °C, the reaction was quenched with H_2O (2 mL) and then saturated NH_4Cl (2 mL) and extracted with EtOAc (4 mL × 3). The combined organic extracts were washed with brine (3 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (10 g, hexanes:EtOAc 2:1 – 1:2) to give 33 mg (80 %) of desired alcohol **253** as a white syrup. R_f 0.30 (hexanes:EtOAc = 1:1); ^{1}H NMR (300 MHz, acetone-d_6) δ 0.78 (s, 3H), 1.09 (s, 3H), 1.25 (s, 3H), 1.42–1.52 (m, 1H), 1.58–1.70 (m, 2H), 1.82 (dt, J = 4.5, 12.8 Hz, 1H), 2.09–2.15 (m, 1H), 1.94 (d, J = 10.5 Hz, 1H), 2.98 (dd, J = 7.8, 10.5 Hz, 1H), 3.24 (s, 3H), 3.64 (d, J = 10.2 Hz, 1H), 3.83–3.94 (m, 4H), 4.19 (brd, 1H), 4.25 (brs, 1H), 4.37 (d, J = 6.3 Hz, 1H), 4.44 (d, J = 6.6 Hz, 1H), 5.04 (dd, J = 2.7, 17.4 Hz, 1H), 5.22 (dd, J = 2.7, 10.2 Hz, 1H), 5.36 (brs, 1H), 5.84 (ddd, J = 10.2, 10.5, 17.4 Hz, 1H), 7.38 (t, J = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 20.70, 21.09, 24.38, 26.86, 31.91, 39.45, 42.34, 49.77, 54.97, 55.22, 56.88, 63.39, 65.23, 65.61, 81.04, 97.06, 112.31, 120.44, 132.63, 136.55, 152.50, 173.31; IR (film) 3467, 2981, 2873, 1725, 1464, 1111, 1076, 946, 755 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{34}O_7Na$ $(M+Na)^+$ 433.2197, found 433.2205.

(±)-(*S*)-5-{(*R*)-2-(Methoxymethoxy)-1-[(1*S*,2*R*)-1,3,3-trimethyl-4-one-4-ethylene ketal-2-vinylcyclohexyl]ethyl}-3-vinylfuran-2(5*H*)-one (227).



To a solution of furan **202** (508 mg, 1.1 mmol) in CH_2Cl_2/MeOH (5/5 mL) was added TPP (2 mg). The mixture was purged several times with O_2 (balloon), cooled to –78 °C and irradiated with a 300 W lamp for 40 min, with stirring under an oxygen atmosphere. The mixture was warmed to room temperature and the solvent was allowed to evaporate. The residue was then dissolved in MeOH (10 mL), cooled to 0 °C, to which $CeCl_3 \cdot 7H_2O$ (82 mg, 0.22 mmol) and $NaBH_4$ (0.19 g, 5 mmol) were added. After being stirred for 0.5 h, the reaction mixture was acidified to *p*H ~ 3 by addition of aqueous HCl (2 N, 10 mL) and extracted with CH_2Cl_2 (15 mL × 3). The combined organic extracts were washed with water (15 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (35 g, hexanes:EtOAc 10:1 – 2:1) to remove the catalyst and then the mixture (232 mg, 0.572 mmol) of product **227** and its isomer was obtained. (R_f 0.45 hexanes:EtOAc = 3:1).

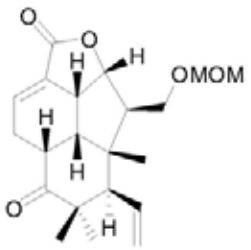
(±)-(*S*)-5-{(*R*)-2-(Methoxymethoxy)-1-[(1*S*,2*R*)-1,3,3-trimethyl-4-oxo-2-vinylcyclohexyl]ethyl}-3-vinylfuran-2(5*H*)-one (255a).



A mixture of ketal **227** and PPTS (58 mg, 0.23 mmol) in acetone/H_2O (10/0.5 mL) was heated to reflux for 24 h. The solvent was allowed to evaporate and the residue

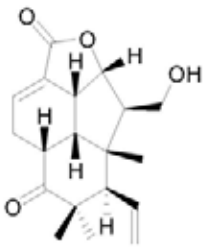
was partitioned between water (5 mL) and EtOAc (10 mL) and then the aqueous layer was extracted with EtOAc (10 mL × 2). The combined organic extracts were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel carefully (10 g, CH_2Cl_2:EtOAc 40:1 – 10:1) to provide product **255a** (179 mg, 45 % for two steps) as a white solid. A sample crystal for X-ray crystallography was obtained by dissolving the solid in hexanes:CH_2Cl_2 (1:1) and the solvent was allowed to evaporate slowly for 3 days. R_f 0.35 (CH_2Cl_2:EtOAc = 2:1); mp 86.0–88.5 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 1.06 (s, 3H), 1.13 (s, 3H), 1.30 (s, 3H), 1.70–1.78 (m, 1H), 2.10–2.14 (m, 2H), 2.37–2.41 (m, 1H), 2.64–2.66 (m, 1H), 2.68 (d, J = 10.5 Hz, 1H), 3.11 (dd, J = 6.8, 10.7 Hz, 1H), 3.20 (s, 3H), 3.57 (dd, J = 2.8, 10.8 Hz, 1H), 4.36 (d, J = 6.8 Hz, 1H), 4.44 (d, J = 6.5 Hz, 1H), 5.25 (dd, J = 2.2, 17.2 Hz, 1H), 5.32 (dd, J = 2.2, 10.3 Hz, 1H), 5.40 (dd, J = 1.8, 11.4 Hz, 1H), 5.57 (brs, 1H), 5.98 (ddd, J = 10.3, 10.5, 17.2 Hz, 1H), 6.22 (dd, J = 1.8, 17.4 Hz, 1H), 6.47 (dd, J = 11.4, 17.4 Hz, 1H), 7.45–7.46 (m, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 20.33, 23.23, 27.22, 32.99, 34.98, 39.12, 47.99, 49.84, 55.53, 57.80, 63.27, 79.34, 97.21, 120.22, 120.35, 127.03, 128.34, 136.05, 153.04, 172.55, 214.70; IR (film) 2970, 2899, 1759, 1706, 1467, 1103, 1033, 917 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{30}O_5Na$ $(M+Na)^+$ 385.1985, found 385.1992; Anal. Calcd for $C_{21}H_{30}O_5$: C, 69.59; H, 8.34. Found: C, 69.64; H, 8.26.

(±)-(3*S*,4*R*,4a*S*,5*R*,5a*S*,6*R*,8a*R*)-5-[(Methoxymethoxy)methyl]-5a,7,7-trimethyl-6-vinyl-5,5a,6,7-tetrahydro-1*H*-acenaphtho[1,8-*bc*]furan-3,8(4*H*,4a*H*,8a*H*)-dione (257).



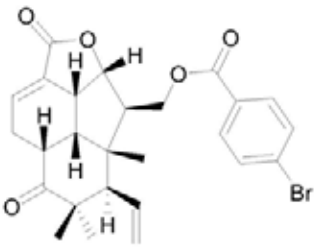
To a solution of ketone **255a** (36.2 mg, 0.1 mmol) in DMSO (0.7 mL) was added PPTS (37.7 mg, 0.15 mmol) and IBX (84 mg, 0.3 mmol), then the mixture was heated to 65 °C for 3.5 h. The reaction was diluted with EtOAc (10 mL) and washed with saturated $NaHCO_3$ (3 mL), H_2O (3 mL) and brine (3 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (8 g, hexanes:EtOAc 5:1 – 1:1) to give a white oil (15.1 mg, 42 %). R_f 0.40 (hexanes:EtOAc = 2:1); ^{1}H NMR (400 MHz, acetone-d_6) δ 0.93 (s, 3H), 1.03 (s, 3H), 1.14 (s, 3H), 1.51 (dd, J = 2.5, 5.7 Hz, 1H), 1.86 (dq, J = 3.6, 14.9 Hz, 1H), 2.49 (d, J = 11.1 Hz, 1H), 2.60 (ddd, J = 2.0, 7.9, 14.9 Hz, 1H), 3.12 (t, J = 10.2 Hz, 1H), 3.29 (s, 3H), 3.39–3.44 (m, 1H), 3.51–3.59 (m, 1H), 3.64–3.72 (m, 2H), 4.56 (dd, J = 6.6, 12.2 Hz, 2H), 4.93 (t, J = 8.7 Hz, 1H), 5.11 (dd, J = 2.1, 16.6 Hz, 1H), 5.19 (dd, J = 2.2, 10.0 Hz, 1H), 6.16 (ddd, J = 10.0, 11.1, 16.6 Hz, 1H), 7.18 (ddd, J = 3.0, 3.1, 7.9 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 24.47, 25.94, 41.05, 45.68, 47.08, 49.46, 50.06, 55.50, 57.50, 66.39, 85.44, 97.28, 118.61, 128.69, 139.58, 140.96, 169.77, 216.68; IR (film) 2971, 2931, 1760, 1705, 1463, 1212, 1024, 918, 733 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{21}H_{28}O_5$ (M^+) 360.1931, found 360.1925.

(±)-(3*S*,4*R*,4a*S*,5*R*,5a*S*,6*R*,8a*R*)-5-(Hydroxymethyl)-5a,7,7-trimethyl-6-vinyl--5, 5a,6,7-tetrahydro-1*H*-acenaphtho[1,8-*bc*]furan-3,8(4*H*,4a*H*,8a*H*)-dione (281).



A mixture of **257** (15 mg, 0.0417 mmol), PPTS (21 mg, 0.0834 mmol) and NaI (18.8 mg, 0.125 mmol) in 2-butanone/H_2O (0.6/0.06 mL) was refluxed for 12 h. The solvent was allowed to evaporate and the residue was partitioned between water (2 mL) and EtOAc (2 mL) and then the aqueous layer was extracted with EtOAc (2 mL × 2). The combined organic extracts were washed with brine (2 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (hexanes:EtOAc 1:1) to provide the product **281** (9.9 mg, 75 %) as a white semi-solid. R_f 0.30 (hexanes:EtOAc = 3:2); ^{1}H NMR (400 MHz, acetone-d_6) δ 0.93 (s, 3H), 1.03 (s, 3H), 1.15 (s, 3H), 1.41–1.45 (m, 1H), 1.85 (dq, J = 3.6, 14.9 Hz, 1H), 2.49 (d, J = 11.1 Hz, 1H), 2.60 (ddd, J = 2.0, 7.9, 14.9 Hz, 1H), 3.12 (dd, J = 10.3, 10.6 Hz, 1H), 3.36–3.40 (m, 1H), 3.51–3.57 (m, 1H), 3.64 (t, J = 5.1 Hz, 1H), 3.74–3.80 (m, 2H), 4.92 (t, J = 8.7 Hz, 1H), 5.09 (dd, J = 2.2, 16.4 Hz, 1H), 5.18 (dd, J = 2.2, 10.0 Hz, 1H), 6.15 (ddd, J = 10.0, 11.1, 16.4 Hz, 1H), 7.16 (ddd, J = 3.0, 3.1, 7.9 Hz, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 24.57, 25.97, 40.99, 45.66, 46.70, 49.61, 51.88, 55.61, 57.51, 66.60, 85.27, 118.40, 128.89, 139.72, 140.83, 169.87, 216.78; IR (film) 3482, 3443, 3067, 2974, 2893, 1756, 1702, 1462, 1219, 1187, 1066, 1016, 733 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{19}H_{24}O_4$ (M^+) 316.1669, found 316.1662.

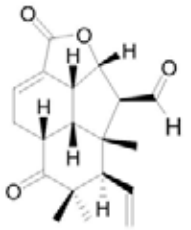
(±)-[(3*S*,4*R*,4a*S*,5*R*,5a*S*,6*R*,8a*R*)-5a,7,7-Trimethyl-3,8-dioxo-6-vinyl-3,4,4a,5,5a,6,7,8,8a-nonahydro-1*H*-acenaphtho[1,8-*bc*]furan-5-yl]methyl-4-bromobenzoate (282).



The mixture of **281** (4 mg, 0.0127 mmol), 4-bromobenzoyl chloride (11 mg, 0.0508 mmol) and DMAP (1 mg) in pyridine (0.2 mL) was stirred for 3 h at room temperature. The reaction mixture was then quenched with saturated $NaHCO_3$ (2 mL) carefully, extracted with EtOAc (2 mL × 3), washed with saturated $CuSO_4$ (3 mL) and brine (3 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by preparative TLC (hexanes:EtOAc 2:1) to give 5.9 mg (94%) of product **282** as a white solid. A sample crystal for X-ray crystallography was obtained by dissolving the solid in hexanes:CH_2Cl_2 (1:1) and the solvent was allowed to evaporate slowly for 3 days. R_f 0.40 (hexanes:EtOAc = 2:1); mp 77.5–79.5 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 0.96 (s, 3H), 1.14 (s, 3H), 1.17 (s, 3H), 1.64–1.72 (m, 1H), 1.86 (dq, J = 3.6, 14.9 Hz, 1H), 2.49 (d, J = 11.1 Hz, 1H), 2.62 (ddd, J = 2.0, 7.9, 14.9 Hz, 1H), 3.19 (dd, J = 10.3, 10.6 Hz, 1H), 3.43–3.49 (m, 1H), 3.60–3.64 (m, 1H), 4.51–4.54 (m, 2H), 5.13 (t, J = 8.7 Hz, 1H), 5.20–5.24 (m, 2H), 6.20 (ddd, J = 10.0, 11.1, 16.4 Hz, 1H), 7.21 (ddd, J = 3.0, 3.1, 7.9 Hz, 1H), 7.72 (d, J = 8.6 Hz, 2H), 7.95 (d, J = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, acetone-d_6) δ 24.89, 25.83, 41.04, 45.71, 47.10, 49.43, 49.56, 57.43, 63.98, 85.28, 118.96, 128.35, 128.58, 130.42, 132.37, 132.87, 139.19, 141.32, 166.19, 169.51, 216.50; IR (film) 2968, 1757, 1717, 1587, 1268, 1183, 1106, 1016, 804, 754 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{27}O_5BrNa$ $(M+Na)^+$ 521.0934, found 521.0936; Anal. Calcd for $C_{26}H_{27}BrO_5$: C, 62.53; H, 5.45. Found: C, 62.76; H, 5.38.

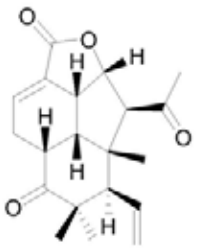
(±)-(3*S*,4*R*,4a*S*,5*S*,5a*S*,6*R*,8a*R*)-5a,7,7-Trimethyl-3,8-dioxo-6-vinyl-3,4,4a,5,5a,6,7,

8,8a-nonahydro-1*H*-acenaphtho[1,8-*bc*]furan-5-carbaldehyde (283).



To a solution of alcohol **281** (6 mg, 0.019 mmol) in dry CH_2Cl_2 (1 ml) was added PDC (14.2 mg, 0.038 mmol) and 4 Å MS (10 mg). After stirring for 1.5 h, the reaction mixture was diluted with EtOAc (1 mL) and stirred for another 15 min. The mixture was filtered over a Celite pad and washed with EtOAc (2 mL), then concentrated and purified by preparative TLC (hexanes:EtOAc 2:1) to give 5.5 mg (92%) of aldehyde **283** as a white syrup. R_f 0.40 (hexanes:EtOAc = 2:1); ^{1}H NMR (400 MHz, acetone-d_6) δ 0.99 (s, 3H), 1.14 (s, 3H), 1.27 (s, 3H), 1.90 (dq, J = 3.6, 14.9 Hz, 1H), 2.25 (dd, J = 1.6, 8.8 Hz, 1H), 2.59 (d, J = 11.1 Hz, 1H), 2.62 (ddd, J = 2.0, 7.9, 14.9 Hz, 1H), 3.21 (dd, J = 9.6, 10.6 Hz, 1H), 3.50–3.54 (m, 1H), 3.61–3.65 (m, 1H), 5.16 (dd, J = 2.2, 16.6 Hz, 1H), 5.23 (dd, J = 2.2, 10.0 Hz, 1H), 6.17 (ddd, J = 10.0, 11.1, 16.6 Hz, 1H), 7.23 (ddd, J = 3.0, 3.1, 7.9 Hz, 1H), 9.89 (d, J = 1.8 Hz, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 25.08, 25.79, 40.61, 45.64, 45.86, 48.90, 49.89, 58.02, 61.85,80.73, 119.27, 127.76, 138.74, 141.93, 169.28, 201.88, 216.34; IR (film) 2975, 2922, 1764, 1709, 1463, 1186, 1020, 803 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{19}H_{22}O_4$ (M^+) 314.1513, found 314.1510.

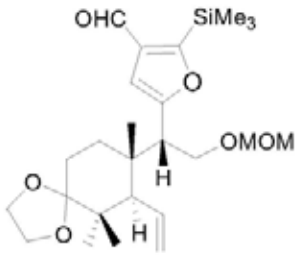
(±)-Pallavicinolide A (3).



To a solution of aldehyde **283** (3.8 mg, 0.0121 mmol) in dry THF (0.2 mL) was

added MeLi (1.6 M in THF, 8 μL, 0.0127 mmol) at –78 °C under N_2 and the resulting solution was stirred for 40 min at this temperature then another 40 min at –10 °C. The reaction mixture was quenched with saturated NH_4Cl (1 mL) and extracted with EtOAc (1 mL × 3). The combined organic extracts were washed with brine (1 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was dissolved in dry CH_2Cl_2 (0.5 ml) and then PDC (7 mg, 0.019 mmol) and 4 Å MS (5 mg) were added. After stirring for 2 h, the reaction mixture was diluted with EtOAc (0.5 mL) and stirred for another 15 min, filtered over a Celite pad and washed with EtOAc (1.5 mL), then concentrated and purified by preparative TLC (hexanes:EtOAc 2:1) to give 2 mg (50% yield for the two steps) of target product **3** as a white syrup. R_f 0.35 (hexanes:EtOAc = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (s, 3H), 1.06 (s, 3H), 1.11 (s, 3H), 1.91 (dddd, *J* = 3.0, 3.1, 4.1, 14.9 Hz, 1H), 2.24 (s, 3H), 2.40 (d, *J* = 8.1 Hz, 1H), 2.66 (d, *J* = 11.2 Hz, 1H), 2.74 (ddd, *J* = 2.0, 7.9, 14.9 Hz, 1H), 2.98 (dd, *J* = 10.0, 10.8 Hz, 1H), 3.29–3.32 (m, 1H), 3.33–3.36 (m, 1H), 5.14–5.16 (m, 2H), 5.27 (dd, *J* = 1.8, 10.0 Hz, 1H), 5.86 (ddd, *J* = 10.0, 11.2, 16.4 Hz, 1H), 7.37 (ddd, *J* = 7.9, 3.1, 3.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.66, 26.17, 28.31, 28.72, 31.81, 40.39, 44.03, 44.03, 47.18, 48.26, 55.62, 60.60, 82.20, 119.92, 127.11, 136.30, 141.36, 168.63, 207.08, 216.13; IR (film) 2978, 2927, 1766, 1705, 1363, 1181, 1063, 1017, 921, 734 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{20}H_{24}O_4$ (M^+) 328.1669, found 328.1656.

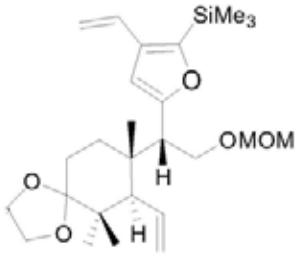
(±)-5-{(*S*)-2-(Methoxymethoxy)-1-[(1*S*,2*R*)-1,3,3-trimethyl-4-one ethylene ketal-2-vinylcyclohexyl]ethyl}-2-(trimethylsilyl)furan-3-carbaldehyde (287).



Using the same procedures as that for **200**, aldehyde **287** was prepared from ether

199b in 79% yield as a light-yellow oil. R_f 0.45 (hexanes:EtOAc = 5:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.34 (s, 9H), 0.78 (s, 3H), 0.82 (s, 3H), 1.02 (s, 3H), 1.30–1.50 (m, 2H), 1.75 (d, J = 10.5 Hz, 1H), 2.34 (d, J = 10.5 Hz, 1H), 3.00 (dd, J = 3.8, 10.4 Hz, 1H), 3.16 (s, 3H), 3.82–3.94 (m, 6H), 4.44 (d, J = 6.9 Hz, 1H), 4.51 (d, J = 6.6 Hz, 1H), 5.06 (dd, J = 2.1, 17.0 Hz, 1H), 5.24 (dd, J = 2.1, 10.2 Hz, 1H), 5.76 (ddd, J = 10.2, 10.5, 17.0 Hz, 1H), 6.44 (s, 1H), 9.98 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –1.02, 20.47, 20.83, 23.93, 26.82, 30.50, 38.93, 42.10, 48.25, 53.83, 54.98, 64.81, 65.07, 65.76, 96.23, 105.81, 112.09, 119.64, 134.96, 137.97, 161.79, 169.80, 186.11; IR (film) 3745, 3373, 3085, 2568, 1679, 1470, 1395, 1254, 1033, 921, 847, 764, 629 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{40}O_6SiNa$ $(M+Na)^+$ 487.2486, found 487.2490.

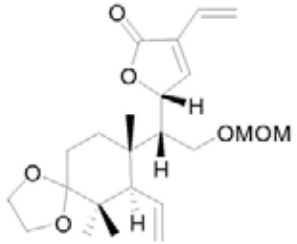
(±)-(3*R*,4*S*)-4-{(*S*)-2-(Methoxymethoxy)-1-[5-(trimethylsilyl)-4-vinylfuran-2-yl]-ethyl}-2,2,4-trimethyl-3-vinylcyclohexanone ethylene ketal (288).



Using the same procedures as that for **202**, vinyl furan **288** was prepared from aldehyde **287** in 87% yield as a white syrup. R_f 0.30 (hexanes:EtOAc = 8:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.27 (s, 9H), 0.81 (s, 3H), 0.85 (s, 3H), 1.05 (s, 3H), 1.46 (d, J = 9.0 Hz, 2H), 1.78 (d, J = 9.3, 2H), 2.38 (d, J = 10.5 Hz, 1H), 2.98 (dd, J = 3.7, 10.1 Hz, 1H), 3.19 (s, 3H), 3.85–3.97 (m, 6H), 4.47 (d, J = 6.6 Hz, 1H), 4.55 (d, J = 6.6 Hz, 1H), 5.04–5.16 (m, 2H), 5.25 (dd, J = 2.4, 10.2 Hz, 1H), 5.38 (dd, J = 1.5, 17.4 Hz, 1H), 5.80 (ddd, J = 10.2, 10.5, 17.1 Hz, 1H), 6.25 (s, 1H), 6.65 (dd, J = 10.8, 17.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –0.81, 20.52, 20.92, 24.03, 26.94, 30.46, 38.90, 42.13, 48.11, 53.91, 54.95, 64.83, 65.10, 65.94, 96.27, 105.83, 112.32, 112.74, 119.56, 128.44, 134.89, 135.26, 155.70, 160.11; IR (film) 3080, 2988, 2878, 1632, 1587, 1473,

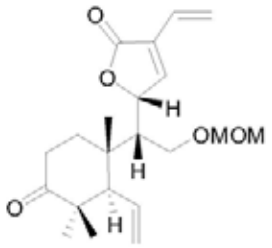
1390, 1253, 1102, 1046, 840, 627 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{42}O_5SiNa$ $(M+Na)^+$ 485.2694, found 485.2696.

(±)-(*R*)-5-{(*S*)-2-(Methoxymethoxy)-1-[(1*S*,2*R*)-1,3,3-trimethyl-4-one ethylene-ketal-2-vinylcyclohexyl]ethyl}-3-vinylfuran-2(5*H*)-one (289).



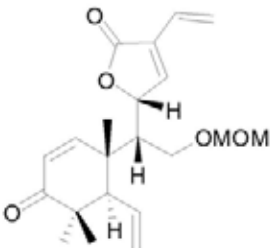
Using the same procedures as that for **227**, vinyl butenolide **289** was prepared from furan **288**. The residue was purified carefully by column chromatography on silica gel (hexanes:EtOAc 10:1 – 2:1) to give product **289** in 71% yield as a white semi-solid. R_f 0.40 (hexanes:EtOAc = 3:1); ^{1}H NMR (300 MHz, acetone-d_6) δ 0.80 (s, 3H), 1.11 (s, 3H), 1.28 (s, 3H), 1.45–1.65 (m, 3H), 1.75–1.90 (m, 1H), 2.16–2.20 (m, 1H), 2.40 (d, J = 10.5 Hz, 1H), 3.03 (dd, J = 8.1, 10.2 Hz, 1H), 3.22 (s, 3H), 3.64 (dd, J = 1.2, 10.5 Hz, 6H), 3.85–3.96 (m, 4H), 4.34 (d, J = 6.6 Hz, 1H), 4.45 (d, J = 6.6 Hz, 1H), 5.06 (dd, J = 2.4, 17.1 Hz, 1H), 5.24 (dd, J = 2.7, 10.2 Hz, 1H), 5.35–5.40 (m, 2H), 5.86 (ddd, J = 10.2, 10.5, 17.1 Hz, 1H), 6.18 (dd, J = 2.1, 17.7 Hz, 1H), 6.42–6.52 (m, 1H), 7.50 (d, J = 1.8, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 20.98, 21.33, 24.62, 27.11, 32.17, 39.73, 42.64, 50.26, 55.26, 55.56, 63.62, 65.48, 65.86, 80.39, 97.31, 112.54, 119.83, 120.64, 127.28, 127.62, 136.82, 153.91, 172.78; IR (film) 3076, 2986, 2878, 1748, 1469, 1398, 1351, 1209, 911, 627 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{23}H_{34}O_6Na$ $(M+Na)^+$ 429.2248, found 429.2249.

(±)-(*R*)-5-{(*S*)-2-(Methoxymethoxy)-1-[(1*S*,2*R*)-1,3,3-trimethyl-4-oxo-2-vinylcyclohexyl]ethyl}-3-vinylfuran-2(5*H*)-one (290).



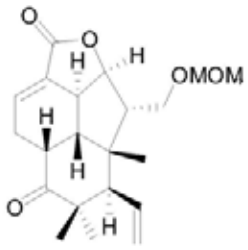
Using the same procedures as that for **255a**, ketone **290** was prepared from ketal **289** in 90% yield as a white solid. A sample crystal for X-ray crystallography was obtained by dissolving the solid in Et_2O:CH_2Cl_2:EtOH (1:1:1) and the solvent was allowed to evaporate slowly for 4 days. R_f 0.30 (hexanes:EtOAc = 2:1); mp 77.5–80.0 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 1.03 (s, 3H), 1.15 (s, 3H), 1.41 (s, 3H), 1.70–1.82 (m, 1H), 2.02–2.12 (m, 1H), 2.24–2.31 (m, 2H), 2.58 (d, J = 10.3 Hz, 1H), 2.62–2.72 (m, 1H), 3.11 (dd, J = 8.1, 10.5 Hz, 1H), 3.21 (s, 3H), 3.66 (dd, J = 2.1, 10.5 Hz, 1H), 4.34 (d, J = 6.6 Hz, 1H), 4.46 (d, J = 6.6 Hz, 1H), 5.14 (dd, J = 2.4, 17.1 Hz, 1H), 5.29 (dd, J = 2.4, 10.2 Hz, 1H), 5.39 (dd, J = 1.9, 11.2 Hz, 1H), 5.49 (brs, 1H), 5.95 (ddd, J = 10.2, 10.3, 17.1 Hz, 1H), 6.20 (dd, J = 1.9, 17.7 Hz, 1H), 6.47 (dd, J = 11.2, 17.7 Hz, 1H), 7.54 (d, J = 1.2 Hz, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 20.73, 23.41, 27.22, 33.45, 34.95, 39.71, 47.91, 49.63, 55.62, 57.95, 63.06, 80.36, 97.25, 119.96, 120.62, 127.20, 127.60, 136.11, 153.65, 172.61, 214.57; IR (film) 2975, 2896, 1765, 1704, 1467, 1110, 1041, 915 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{30}O_5Na$ $(M+Na)^+$ 385.1985, found 385.1991; Anal. Calcd for $C_{21}H_{30}O_5$: C, 69.59; H, 8.34. Found: C, 69.70; H, 8.25.

(±)-(*R*)-5-{(*S*)-2-(Methoxymethoxy)-1-[(1*S*,6*R*)-1,5,5-trimethyl-4-oxo-2-vinylcyclohex-2-enyl]ethyl}-3-vinylfuran-2(5*H*)-one (291).



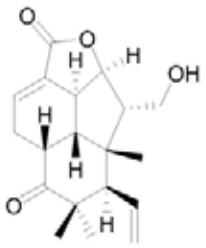
Under a N_2 atmosphere, to the mixture of diisopropylamine (11.7 μL, 0.083 mmol) in dry THF (0.2 mL) was added *n*-BuLi (1.6 M in hexane, 47 μL, 0.075 mmol) at –78 °C and the resulting mixture was stirred for 15 min. Then a solution of ketone **290** (18.1 mg, 0.05 mmol) in THF (0.15 mL) was added in one portion and the mixture was stirred for 15 min at –78 °C. Finally, to the reaction was added reagent *N*-*tert*-butyl phenylsulfinimidoyl chloride (**278**) (32.5 mg, 0.15 mmol) in one portion at –78 °C and the resulting pale yellow solution was stirred for 40 min at the same temperature. The reaction was quenched by addition of 1% HCl (1 mL). The reaction was extracted with CH_2Cl_2 (3 mL × 3), washed with brine (3 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (7 g, hexanes:EtOAc 10:1 – 3:1) carefully to give 11.1 mg (62%) of product **291** as a white solid. A sample crystal for X-ray crystallography was obtained by dissolving the solid in hexanes:CH_2Cl_2 (1:1) and the solvent was allowed to evaporate slowly for 4 days. R_f 0.30 (hexanes:EtOAc = 2:1); mp 74.0–77.0 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 1.03 (s, 3H), 1.17 (s, 3H), 1.44 (s, 3H), 2.30 (m, 1H), 2.64 (d, J = 10.2 Hz, 1H), 3.00 (dd, J = 7.2, 10.8 Hz, 1H), 3.18 (s, 3H), 3.33 (dd, J = 1.8, 11.1 Hz, 1H), 4.34 (d, J = 6.6 Hz, 1H), 4.46 (d, J = 6.6 Hz, 1H), 5.20 (dd, J = 2.2, 17.0 Hz, 1H), 5.36 (dd, J = 2.4, 9.9 Hz, 1H), 5.42 (dd, J = 1.8, 11.4 Hz, 1H), 5.51 (brs, 1H), 5.92 (d, J = 10.5 Hz, 1H), 6.04 (ddd, J = 10.2, 10.5, 17.0 Hz, 1H), 6.22 (dd, J = 1.8, 17.5 Hz, 1H), 6.49 (dd, J = 11.4, 17.8 Hz, 1H), 6.94 (d, J = 10.5 Hz, 1H),7.58 (d, J = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 20.17, 23.55, 25.24, 42.72, 44.82, 48.93, 54.50, 55.64, 63.65, 80.39, 97.21, 120.40, 121.85, 127.09, 127.31, 128.28, 135.01, 152.83, 153.88, 172.36, 202.87; HRMS (EI) *m/z* calcd for $C_{21}H_{28}O_5$ (M^+) 360.1931, found 360.1917; Anal. Calcd for $C_{21}H_{28}O_5$: C, 69.98; H, 7.83. Found: C, 69.77; H, 7.94.

(±)-(3*S*,4*S*,4a*R*,5*S*,5a*S*,6*R*,8a*R*)-5-[(Methoxymethoxy)methyl]-5a,7,7-trimethyl-6-vinyl-5,5a,6,7-tetrahydro-1*H*-acenaphtho[1,8-*bc*]furan-3,8(4*H*,4a*H*,8a*H*)-dione (292).



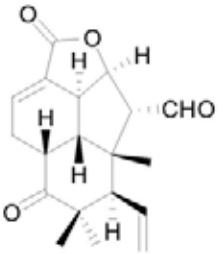
A solution of ketone **291** (9 mg) and a trace amount of 2,6-di-*tert*-butyl-4-methyl phenol (1 mg) in toluene (3 mL) was heated to 140 °C in a sealed tube for 5 h. The reaction was cooled to room temperature and then concentrated. The residue was purified by column chromatography on silica gel (4 g, hexanes:EtOAc 5:1 – 1:1) to afford 6.5 mg of product **292** (71%) as a light yellow oil. R_f 0.35 (hexanes:EtOAc = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (s, 3H), 1.18 (s, 3H), 1.50–1.53 (m, 1H), 1.51 (s, 3H), 2.15 (d, J = 9.9 Hz, 1H), 2.24–2.28 (m, 1H), 2.33–2.39 (m, 1H), 2.55 (dt, J = 7.8, 19.2 Hz, 1H), 3.04–3.08 (m, 1H), 3.36 (s, 3H), 3.42–3.48 (m, 1H), 3.56 (t, J = 10.1 Hz, 1H), 3.65–3.69 (m, 1H), 4.56–4.63 (m, 2H), 5.08 (dd, J = 1.5, 17.0 Hz, 1H), 5.27 (dd, J = 1.5, 10.2 Hz, 1H), 5.91 (ddd, J = 9.9, 10.2, 17.0 Hz, 1H), 6.54 (ddd, J = 1.8, 2.7, 6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.73, 22.93, 24.63, 26.60, 36.51, 45.90, 47.16, 49.47, 53.13, 55.61, 61.97, 65.88, 66.40, 82.79, 96.45, 120.76, 134.38, 135.27, 136.94, 168.73, 213.49; IR (film) 2975, 2927, 1762, 1714, 1474, 1209, 1031, 916, 743 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{21}H_{28}O_5$ (M^+) 360.1931, found 360.1924.

(±)-(3*S*,4*S*,4a*R*,5*S*,5a*S*,6*R*,8a*R*)-5-(Hydroxymethyl)-5a,7,7-trimethyl-6-vinyl-5,5a,6,7-tetrahydro-1*H*-acenaphtho[1,8-*bc*]furan-3,8(4*H*,4a*H*,8a*H*)-dione (293).



Using the same procedures as that for **281**, alcohol **293** was prepared as a white solid from ether **292** in 73% yield. A sample crystal for X-ray crystallography was obtained by dissolving the solid in hexanes:CH_2Cl_2 (1:1) and the solvent was allowed to evaporate slowly for 3 days. R_f 0.30 (hexanes:EtOAc = 1:1); mp 76.5–80.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.04 (s, 3H), 1.19 (s, 3H), 1.52 (s, 3H), 2.15–2.21 (m, 2H), 2.31–2.37 (m, 1H), 2.50–2.63 (m, 1H), 3.04–3.09 (m, 1H), 3.45 (dd, *J* = 2.0, 18.9 Hz, 1H), 3.73–3.85 (m, 2H), 4.64 (dd, *J* = 4.6, 8.0 Hz, 1H), 5.14 (dd, *J* = 1.2, 17.1 Hz, 1H), 5.31 (dd, *J* = 1.5, 10.2 Hz, 1H), 6.00 (ddd, *J* = 10.2, 10.5, 17.1 Hz, 1H), 6.55 (ddd, *J* = 1.8, 2.7, 6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.66, 23.14, 24.57, 26.54, 36.38, 45.71, 47.28, 49.37, 52.94, 61.03, 61.99, 67.97, 81.60, 120.51, 135.08, 135.36, 136.82, 168.62, 213.26; IR (film) 3481, 3445, 3069, 2964, 2890, 1758, 1704, 1456, 1205, 1193, 1056, 1013, 732 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{19}H_{24}O_4$ (M^+) 316.1669, found 316.1661.

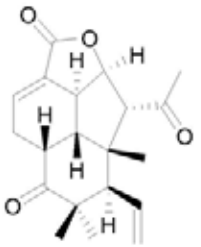
(±)-(3*S*,4*S*,4a*R*,5*R*,5a*S*,6*R*,8a*R*)-5a,7,7-Trimethyl-3,8-dioxo-6-vinyl-3,4,4a,5,5a,6,7,8,8a-nonahydro-1*H*-acenaphtho[1,8-*bc*]furan-5-carbaldehyde (294).



Using the same procedures as that for **283**, aldehyde **294** was prepared from alcohol **293** in 90% yield as a light-yellow oil. R_f 0.35 (hexanes:EtOAc = 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.01 (s, 3H), 1.23 (s, 3H), 1.61 (dd, *J* = 6.0, 11.7 Hz, 1H),

1.78 (s, 3H), 2.08 (d, J = 10.2 Hz, 1H), 2.35–2.38 (m, 1H), 2.62 (ddd, J = 2.0, 7.9, 14.9 Hz, 1H), 2.90 (d, J = 4.2 Hz, 1H), 3.08 (t, J = 6.5 Hz, 1H), 3.46 (dd, J = 1.8, 19.2 Hz, 1H), 4.92 (d, J = 17.1 Hz, 1H), 5.34–5.40 (m, 2H), 5.90 (ddd, J = 10.2, 10.5, 17.1 Hz, 1H), 6.58 (ddd, J = 1.8, 2.7, 6.9 Hz, 1H), 9.82 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.53, 23.48, 24.67, 26.59, 36.26, 45.76, 49.31, 50.73, 53.34, 62.30, 74.90, 75.87, 124.17, 132.25, 135.70, 136.50, 168.11, 197.51, 212.30; IR (film) 2976, 2925, 1762, 1707, 1463, 1187, 1021, 804 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{19}H_{22}O_4$ (M^+) 314.1513, found 314.1509.

(±)-Neopallavicinolide A (296).



Using the same procedures as that for (±)-pallavicinolide A (**3**), (±)-neopallavicinolide A (**296**) was prepared from aldehyde **294** in 46% yield as a white syrup. R_f 0.35 (hexanes:EtOAc = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (s, 3H), 1.01 (s, 3H), 1.11 (s, 3H), 1.60–1.64 (m, 1H),1.75 (s, 3H), 2.19 (d, J = 7.8 Hz, 1H), 2.22 (s, 3H), 2.33–2.39 (m, 1H), 2.57 (ddd, J = 7.5, 10.0, 16.9 Hz, 1H), 3.01–3.06 (m, 2H), 3.47 (dd, J = 2.0, 19.2 Hz, 1H), 4.91 (dd, J = 1.8, 17.1 Hz, 1H), 5.29 (dd, J = 1.8, 10.2 Hz, 1H), 5.34 (dd, J = 4.0, 8.0 Hz, 1H), 5.77 (ddd, J = 7.8, 10.2, 17.1 Hz, 1H), 6.57 (ddd, J = 1.8, 2.7, 6.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.78, 24.28, 24.68, 26.57, 33.42, 36.46, 45.57, 49.36, 49.76, 52.27, 62.97, 75.01, 79.14, 123.99, 131.29, 135.91, 137.03, 168.33, 205.10, 212.58; IR (film) 2976, 2931, 1765, 1707, 1361, 1178, 1065, 1009, 925, 733 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{20}H_{24}O_4$ (M^+) 328.1669, found 328.1671.

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Appendix I

List of X-ray crystallographic data

Table 1. Crystal data and structure refinement for 137

Identification code	djq-1-045-1
Empirical formula	C26 H34 O5
Formula weight	426.53
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 6.9786(8) A alpha = 104.439(2) deg.
	b = 11.6573(14) A beta = 100.463(2) deg.
	c = 14.6639(18) A gamma = 92.687(3) deg.
Volume	1130.7(2) A^3
Z, Calculated density	2, 1.253 Mg/m^3
Absorption coefficient	0.085 mm^-1
F(000)	460
Crystal size	0.50 x 0.20 x 0.20 mm
Theta range for data collection	1.46 to 25.00 deg.
Limiting indices	-8<=h<=8, -10<=k<=13, -17<=l<=17
Reflections collected / unique	6210 / 3957 [R(int) = 0.0217]
Completeness to theta = 25.00	99.2 %
Absorption correction	SADABS
Max. and min. transmission	1.00000 and 0.554511
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3957 / 0 / 280
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0742, wR2 = 0.2163
R indices (all data)	R1 = 0.0964, wR2 = 0.2438
Largest diff. peak and hole	0.700 and -0.575 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **137.**
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	3802(3)	6555(2)	4522(2)	48(1)

O(2)	2434(3)	7945(2)	5543(2)	47(1)
O(3)	8644(3)	9753(2)	7323(2)	46(1)
O(4)	6689(4)	9327(2)	10169(2)	64(1)
O(5)	4733(6)	6690(4)	9799(3)	120(2)
C(1)	1963(6)	6723(4)	4006(3)	65(1)
C(2)	1490(6)	7900(4)	4586(3)	61(1)
C(3)	3844(4)	7089(3)	5520(2)	38(1)
C(4)	3187(5)	6159(3)	5985(2)	40(1)
C(5)	3189(4)	6706(3)	7040(2)	37(1)
C(6)	5218(4)	7275(2)	7608(2)	33(1)
C(7)	5988(4)	8207(2)	7106(2)	32(1)
C(8)	5917(4)	7726(3)	5997(2)	36(1)
C(9)	7476(5)	6865(3)	5759(2)	47(1)
C(10)	6218(5)	8753(3)	5535(2)	49(1)
C(11)	6562(5)	6293(3)	7715(2)	42(1)
C(12)	7954(5)	8838(3)	7710(2)	39(1)
C(13)	10715(5)	9937(3)	7470(3)	50(1)
C(14)	11329(5)	11222(3)	7568(2)	44(1)
C(15)	12877(6)	11522(4)	7176(3)	73(1)
C(16)	13469(8)	12731(5)	7306(4)	98(2)
C(17)	12587(8)	13598(4)	7829(4)	82(2)
C(18)	11055(7)	13299(3)	8207(3)	70(1)
C(19)	10425(6)	12123(3)	8075(3)	54(1)
C(20)	7793(5)	9433(3)	8740(2)	49(1)
C(21)	6919(5)	8635(3)	9247(2)	47(1)
C(22)	4967(4)	7998(3)	8636(2)	37(1)
C(23)	3974(5)	7296(3)	9170(2)	44(1)
C(24)	2016(4)	7228(3)	9071(2)	37(1)
C(25)	1510(7)	6582(4)	9668(3)	72(1)
C(26)	3056(8)	6259(4)	10127(3)	79(1)

Table 3. Bond lengths [A] and angles [deg] for **137.**

O(1)-C(1)	1.415(4)
O(1)-C(3)	1.434(3)
O(2)-C(2)	1.425(4)

O(2)-C(3)	1.433(4)
O(3)-C(13)	1.420(4)
O(3)-C(12)	1.430(4)
O(4)-C(21)	1.432(4)
O(5)-C(23)	1.346(5)
O(5)-C(26)	1.457(6)
C(1)-C(2)	1.509(6)
C(3)-C(4)	1.512(4)
C(3)-C(8)	1.552(4)
C(4)-C(5)	1.519(4)
C(5)-C(6)	1.532(4)
C(6)-C(11)	1.534(4)
C(6)-C(22)	1.578(4)
C(6)-C(7)	1.581(4)
C(7)-C(12)	1.532(4)
C(7)-C(8)	1.573(4)
C(8)-C(10)	1.538(4)
C(8)-C(9)	1.542(4)
C(12)-C(20)	1.524(4)
C(13)-C(14)	1.502(5)
C(14)-C(19)	1.377(5)
C(14)-C(15)	1.382(5)
C(15)-C(16)	1.406(7)
C(16)-C(17)	1.354(7)
C(17)-C(18)	1.360(7)
C(18)-C(19)	1.375(5)
C(20)-C(21)	1.499(5)
C(21)-C(22)	1.530(4)
C(22)-C(23)	1.492(4)
C(23)-C(24)	1.344(4)
C(24)-C(25)	1.368(5)
C(25)-C(26)	1.289(7)
C(1)-O(1)-C(3)	107.0(2)
C(2)-O(2)-C(3)	109.4(3)
C(13)-O(3)-C(12)	114.1(2)
C(23)-O(5)-C(26)	104.8(4)
O(1)-C(1)-C(2)	103.7(3)
O(2)-C(2)-C(1)	103.4(3)

O(2)-C(3)-O(1)	105.9(2)
O(2)-C(3)-C(4)	108.0(2)
O(1)-C(3)-C(4)	109.7(2)
O(2)-C(3)-C(8)	109.9(2)
O(1)-C(3)-C(8)	108.8(2)
C(4)-C(3)-C(8)	114.2(2)
C(3)-C(4)-C(5)	110.8(2)
C(4)-C(5)-C(6)	112.4(2)
C(5)-C(6)-C(11)	109.3(2)
C(5)-C(6)-C(22)	107.6(2)
C(11)-C(6)-C(22)	109.2(2)
C(5)-C(6)-C(7)	108.9(2)
C(11)-C(6)-C(7)	114.8(2)
C(22)-C(6)-C(7)	106.9(2)
C(12)-C(7)-C(8)	115.8(2)
C(12)-C(7)-C(6)	109.0(2)
C(8)-C(7)-C(6)	115.5(2)
C(10)-C(8)-C(9)	107.3(3)
C(10)-C(8)-C(3)	107.0(3)
C(9)-C(8)-C(3)	109.7(2)
C(10)-C(8)-C(7)	111.2(2)
C(9)-C(8)-C(7)	113.4(2)
C(3)-C(8)-C(7)	108.0(2)
O(3)-C(12)-C(20)	106.7(2)
O(3)-C(12)-C(7)	111.1(2)
C(20)-C(12)-C(7)	111.7(2)
O(3)-C(13)-C(14)	109.8(3)
C(19)-C(14)-C(15)	118.6(3)
C(19)-C(14)-C(13)	121.3(3)
C(15)-C(14)-C(13)	120.1(3)
C(14)-C(15)-C(16)	119.1(4)
C(17)-C(16)-C(15)	121.1(4)
C(16)-C(17)-C(18)	119.6(4)
C(17)-C(18)-C(19)	120.3(4)
C(18)-C(19)-C(14)	121.3(4)
C(21)-C(20)-C(12)	115.0(3)
O(4)-C(21)-C(20)	109.1(3)
O(4)-C(21)-C(22)	111.6(3)

C(20)-C(21)-C(22)	110.1(3)
C(23)-C(22)-C(21)	111.0(3)
C(23)-C(22)-C(6)	114.9(2)
C(21)-C(22)-C(6)	111.3(2)
C(24)-C(23)-O(5)	109.7(3)
C(24)-C(23)-C(22)	120.1(3)
O(5)-C(23)-C(22)	130.2(3)
C(23)-C(24)-C(25)	107.9(3)
C(26)-C(25)-C(24)	110.0(4)
C(25)-C(26)-O(5)	107.6(4)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **137.**
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

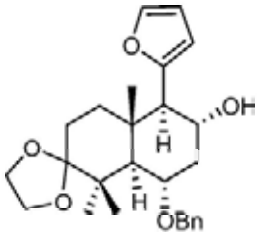
	U11	U22	U33	U23	U13	U12
O(1)	47(1)	63(2)	28(1)	2(1)	4(1)	2(1)
O(2)	44(1)	54(1)	42(1)	15(1)	5(1)	13(1)
O(3)	39(1)	37(1)	59(1)	14(1)	-2(1)	-5(1)
O(4)	70(2)	75(2)	31(1)	-8(1)	2(1)	3(1)
O(5)	104(3)	139(4)	134(4)	78(3)	5(3)	17(3)
C(1)	58(2)	92(3)	38(2)	12(2)	-3(2)	2(2)
C(2)	48(2)	88(3)	51(2)	35(2)	-1(2)	8(2)
C(3)	39(2)	40(2)	29(2)	2(1)	4(1)	5(1)
C(4)	40(2)	35(2)	36(2)	1(1)	0(1)	-4(1)
C(5)	42(2)	34(2)	35(2)	7(1)	6(1)	0(1)
C(6)	36(2)	30(1)	30(1)	5(1)	3(1)	5(1)
C(7)	34(2)	27(1)	32(2)	4(1)	4(1)	5(1)
C(8)	37(2)	36(2)	33(2)	5(1)	6(1)	2(1)
C(9)	43(2)	49(2)	42(2)	-2(1)	11(1)	5(2)
C(10)	57(2)	50(2)	40(2)	15(1)	10(2)	-2(2)
C(11)	49(2)	34(2)	44(2)	12(1)	6(1)	10(1)
C(12)	40(2)	31(2)	42(2)	6(1)	3(1)	1(1)
C(13)	42(2)	43(2)	59(2)	5(2)	10(2)	1(1)

C(14)	46(2)	48(2)	34(2)	10(1)	-1(1)	-8(1)
C(15)	69(3)	78(3)	75(3)	17(2)	30(2)	-11(2)
C(16)	92(4)	109(4)	100(4)	46(3)	26(3)	-39(3)
C(17)	100(4)	57(3)	83(3)	33(2)	-10(3)	-26(3)
C(18)	85(3)	43(2)	71(3)	12(2)	-3(2)	-8(2)
C(19)	59(2)	42(2)	56(2)	7(2)	7(2)	-6(2)
C(20)	50(2)	43(2)	39(2)	-5(1)	-1(2)	-6(2)
C(21)	47(2)	54(2)	30(2)	-1(1)	-1(1)	6(2)
C(22)	40(2)	37(2)	30(2)	6(1)	3(1)	8(1)
C(23)	55(2)	45(2)	30(2)	11(1)	4(1)	9(2)
C(24)	22(1)	53(2)	43(2)	27(1)	5(1)	9(1)
C(25)	67(3)	81(3)	77(3)	24(2)	32(2)	6(2)
C(26)	96(4)	91(3)	63(3)	45(2)	17(2)	-6(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **137.**

	x	y	z	U(eq)
H(4A)	5747	9715	10102	96
H(1A)	981	6087	3970	78
H(1B)	2046	6755	3360	78
H(2A)	2006	8555	4376	73
H(2B)	88	7923	4534	73
H(4B)	4058	5532	5926	48
H(4C)	1878	5808	5655	48
H(5A)	2751	6094	7319	45
H(5B)	2270	7307	7093	45
H(7A)	5073	8821	7162	38
H(9A)	7358	6603	5075	70
H(9B)	7284	6190	6008	70
H(9C)	8757	7267	6047	70
H(10A)	6180	8436	4861	73
H(10B)	7464	9195	5836	73
H(10C)	5196	9270	5621	73
H(11A)	5991	5768	8026	64

H(11B)	7817	6645	8095	64
H(11C)	6718	5850	7091	64
H(12A)	8919	8254	7718	46
H(13A)	11165	9438	6930	59
H(13B)	11304	9718	8046	59
H(15A)	13518	10933	6832	88
H(16A)	14483	12939	7027	117
H(17A)	13026	14394	7929	99
H(18A)	10429	13892	8556	84
H(19A)	9369	11932	8334	65
H(20A)	9091	9757	9106	58
H(20B)	7003	10096	8735	58
H(21A)	7821	8036	9342	56
H(22A)	4125	8623	8535	44
H(24A)	1157	7560	8669	44
H(25A)	237	6403	9733	86
H(26A)	3096	5829	10585	95



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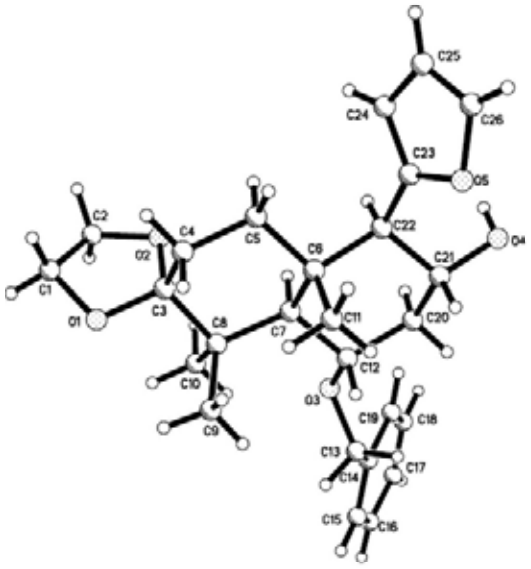


Table 1. Crystal data and structure refinement for 198.

Identification code	djq-1-077-2
Empirical formula	C34 H37 Br2 O7
Formula weight	717.46
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 6.0993(7) A alpha = 111.282(2) deg.
	b = 15.8880(17) A beta = 97.599(2) deg.
	c = 17.514(2) A gamma = 99.056(3) deg.
Volume	1528.3(3) A^3
Z, Calculated density	2, 1.559 Mg/m^3
Absorption coefficient	2.701 mm^-1
F(000)	734
Crystal size	0.11 x 0.16 x 0.31 mm
Theta range for data collection	1.41 to 25.01 deg.
Limiting indices	-7<=h<=6, -16<=k<=18, -20<=l<=20
Reflections collected / unique	8407 / 5360 [R(int) = 0.0545]
Completeness to theta = 25.01	99.5 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5360 / 0 / 388
Goodness-of-fit on F^2	0.926
Final R indices [I>2sigma(I)]	R1 = 0.0593, wR2 = 0.1171
R indices (all data)	R1 = 0.1406, wR2 = 0.1544
Largest diff. peak and hole	0.749 and -0.466 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **198**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	1731(1)	3421(1)	732(1)	58(1)
Br(2)	-353(2)	8798(1)	3126(1)	74(1)

C(1)	−231(11)	3572(4)	−116(4)	39(2)
C(2)	−2048(11)	3963(4)	48(4)	44(2)
C(3)	−3421(12)	4088(5)	−560(4)	45(2)
C(4)	−3005(12)	3814(4)	−1369(4)	39(2)
C(5)	−1223(12)	3383(4)	−1535(4)	43(2)
C(6)	159(12)	3255(4)	−915(5)	47(2)
C(7)	−4388(13)	3949(5)	−2054(5)	47(2)
C(8)	−7571(12)	4528(5)	−2447(5)	55(2)
C(9)	−6687(11)	5443(5)	−2468(4)	44(2)
C(10)	−4755(11)	5694(5)	−2878(4)	42(2)
C(11)	−5823(11)	5644(4)	−3752(4)	42(2)
C(12)	−7093(10)	6442(4)	−3500(4)	31(2)
C(13)	−6306(10)	6862(4)	−2522(4)	31(2)
C(14)	−7562(11)	6185(5)	−2227(4)	41(2)
C(15)	−6454(9)	7298(4)	−3697(3)	26(1)
C(16)	−7124(10)	7252(4)	−4587(4)	31(2)
C(17)	−6200(10)	8230(4)	−4566(4)	36(2)
C(18)	−6784(12)	9012(4)	−3863(4)	46(2)
C(19)	−6065(11)	8992(4)	−3003(4)	38(2)
C(20)	−7143(10)	8076(4)	−2979(4)	31(2)
C(21)	−9678(10)	6948(4)	−4965(4)	44(2)
C(22)	−6043(11)	6540(4)	−5189(4)	42(2)
C(23)	−5221(12)	8507(5)	−5704(5)	59(2)
C(24)	−3146(13)	8775(6)	−5045(5)	64(2)
C(25)	−9709(10)	7984(4)	−3035(4)	42(2)
C(26)	−6118(11)	7906(4)	−2204(4)	35(2)
C(27)	−7132(11)	8332(4)	−1430(4)	43(2)
C(28)	−4093(12)	8910(5)	−266(4)	44(2)
C(29)	−3198(11)	8874(4)	553(4)	41(2)
C(30)	−953(12)	9261(5)	941(4)	48(2)
C(31)	−101(12)	9238(5)	1699(5)	52(2)
C(32)	−1514(12)	8859(4)	2100(4)	43(2)
C(33)	−3781(12)	8493(4)	1736(4)	43(2)
C(34)	−4614(12)	8489(4)	965(4)	43(2)
O(1)	−3987(11)	3755(4)	−2738(3)	82(2)
O(2)	−6121(8)	4335(3)	−1821(3)	48(1)
O(3)	−4034(7)	6674(3)	−2420(3)	38(1)
O(4)	−7035(7)	8287(3)	−5346(3)	50(1)

O(5)	-3791(7)	8391(3)	-4474(3)	41(1)
O(6)	-5958(8)	8264(3)	-694(3)	44(1)
O(7)	-3193(9)	9477(4)	-509(3)	67(2)

Table 3. Bond lengths [A] and angles [deg] for **198**.

Br(1)-C(1)	1.892(7)
Br(2)-C(32)	1.883(7)
C(1)-C(2)	1.366(8)
C(1)-C(6)	1.371(8)
C(2)-C(3)	1.359(9)
C(2)-H(2A)	0.9300
C(3)-C(4)	1.394(8)
C(3)-H(3A)	0.9300
C(4)-C(5)	1.381(8)
C(4)-C(7)	1.474(9)
C(5)-C(6)	1.380(9)
C(5)-H(5A)	0.9300
C(6)-H(6A)	0.9300
C(7)-O(1)	1.192(7)
C(7)-O(2)	1.340(8)
C(8)-O(2)	1.467(7)
C(8)-C(9)	1.484(9)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(14)	1.323(8)
C(9)-C(10)	1.532(8)
C(10)-O(3)	1.431(7)
C(10)-C(11)	1.550(9)
C(10)-H(10A)	0.9800
C(11)-C(12)	1.547(8)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(15)	1.525(8)
C(12)-C(13)	1.570(8)
C(12)-H(12A)	0.9800

C(13)-O(3)	1.464(7)
C(13)-C(14)	1.503(8)
C(13)-C(26)	1.526(8)
C(14)-H(14A)	0.9300
C(15)-C(16)	1.531(8)
C(15)-C(20)	1.569(7)
C(15)-H(15A)	0.9800
C(16)-C(21)	1.535(8)
C(16)-C(22)	1.542(8)
C(16)-C(17)	1.553(8)
C(17)-O(5)	1.428(7)
C(17)-O(4)	1.433(7)
C(17)-C(18)	1.526(8)
C(18)-C(19)	1.525(8)
C(18)-H(18A)	0.9700
C(18)-H(18B)	0.9700
C(19)-C(20)	1.517(8)
C(19)-H(19A)	0.9700
C(19)-H(19B)	0.9700
C(20)-C(25)	1.535(8)
C(20)-C(26)	1.550(8)
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
C(23)-O(4)	1.400(7)
C(23)-C(24)	1.483(10)
C(23)-H(23A)	0.9700
C(23)-H(23B)	0.9700
C(24)-O(5)	1.414(7)
C(24)-H(24A)	0.9700
C(24)-H(24B)	0.9700
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600
C(26)-C(27)	1.538(8)

C(26)-H(26A)	0.9800
C(27)-O(6)	1.438(7)
C(27)-H(27A)	0.9700
C(27)-H(27B)	0.9700
C(28)-O(7)	1.216(8)
C(28)-O(6)	1.326(8)
C(28)-C(29)	1.491(9)
C(29)-C(30)	1.378(9)
C(29)-C(34)	1.400(8)
C(30)-C(31)	1.375(9)
C(30)-H(30A)	0.9300
C(31)-C(32)	1.379(9)
C(31)-H(31A)	0.9300
C(32)-C(33)	1.379(9)
C(33)-C(34)	1.375(9)
C(33)-H(33A)	0.9300
C(34)-H(34A)	0.9300
C(2)-C(1)-C(6)	120.0(6)
C(2)-C(1)-Br(1)	121.3(5)
C(6)-C(1)-Br(1)	118.7(5)
C(3)-C(2)-C(1)	121.1(6)
C(3)-C(2)-H(2A)	119.5
C(1)-C(2)-H(2A)	119.5
C(2)-C(3)-C(4)	120.3(6)
C(2)-C(3)-H(3A)	119.8
C(4)-C(3)-H(3A)	119.8
C(5)-C(4)-C(3)	118.0(6)
C(5)-C(4)-C(7)	118.7(6)
C(3)-C(4)-C(7)	123.3(6)
C(4)-C(5)-C(6)	121.3(6)
C(4)-C(5)-H(5A)	119.3
C(6)-C(5)-H(5A)	119.3
C(1)-C(6)-C(5)	119.2(6)
C(1)-C(6)-H(6A)	120.4
C(5)-C(6)-H(6A)	120.4
O(1)-C(7)-O(2)	123.4(7)
O(1)-C(7)-C(4)	123.9(7)
O(2)-C(7)-C(4)	112.7(6)

O(2)-C(8)-C(9)	112.7(5)
O(2)-C(8)-H(8A)	109.0
C(9)-C(8)-H(8A)	109.0
O(2)-C(8)-H(8B)	109.0
C(9)-C(8)-H(8B)	109.0
H(8A)-C(8)-H(8B)	107.8
C(14)-C(9)-C(8)	127.4(6)
C(14)-C(9)-C(10)	104.8(5)
C(8)-C(9)-C(10)	127.4(6)
O(3)-C(10)-C(9)	101.9(5)
O(3)-C(10)-C(11)	101.1(5)
C(9)-C(10)-C(11)	108.0(5)
O(3)-C(10)-H(10A)	114.7
C(9)-C(10)-H(10A)	114.7
C(11)-C(10)-H(10A)	114.8
C(10)-C(11)-C(12)	100.8(5)
C(10)-C(11)-H(11A)	111.6
C(12)-C(11)-H(11A)	111.6
C(10)-C(11)-H(11B)	111.6
C(12)-C(11)-H(11B)	111.6
H(11A)-C(11)-H(11B)	109.4
C(15)-C(12)-C(11)	121.7(5)
C(15)-C(12)-C(13)	101.3(4)
C(11)-C(12)-C(13)	101.1(5)
C(15)-C(12)-H(12A)	110.5
C(11)-C(12)-H(12A)	110.5
C(13)-C(12)-H(12A)	110.5
O(3)-C(13)-C(14)	100.5(4)
O(3)-C(13)-C(26)	109.5(5)
C(14)-C(13)-C(26)	128.0(5)
O(3)-C(13)-C(12)	101.7(4)
C(14)-C(13)-C(12)	105.9(5)
C(26)-C(13)-C(12)	108.2(4)
C(9)-C(14)-C(13)	106.5(5)
C(9)-C(14)-H(14A)	126.7
C(13)-C(14)-H(14A)	126.7
C(12)-C(15)-C(16)	120.7(5)
C(12)-C(15)-C(20)	103.3(4)

C(16)-C(15)-C(20)	116.9(5)
C(12)-C(15)-H(15A)	104.8
C(16)-C(15)-H(15A)	104.8
C(20)-C(15)-H(15A)	104.8
C(21)-C(16)-C(15)	115.4(5)
C(21)-C(16)-C(22)	105.3(5)
C(15)-C(16)-C(22)	109.9(5)
C(21)-C(16)-C(17)	109.4(5)
C(15)-C(16)-C(17)	107.2(5)
C(22)-C(16)-C(17)	109.5(5)
O(5)-C(17)-O(4)	105.5(4)
O(5)-C(17)-C(18)	108.7(5)
O(4)-C(17)-C(18)	108.4(5)
O(5)-C(17)-C(16)	109.4(5)
O(4)-C(17)-C(16)	110.9(5)
C(18)-C(17)-C(16)	113.6(5)
C(17)-C(18)-C(19)	112.9(5)
C(17)-C(18)-H(18A)	109.0
C(19)-C(18)-H(18A)	109.0
C(17)-C(18)-H(18B)	109.0
C(19)-C(18)-H(18B)	109.0
H(18A)-C(18)-H(18B)	107.8
C(20)-C(19)-C(18)	111.3(5)
C(20)-C(19)-H(19A)	109.4
C(18)-C(19)-H(19A)	109.4
C(20)-C(19)-H(19B)	109.4
C(18)-C(19)-H(19B)	109.4
H(19A)-C(19)-H(19B)	108.0
C(19)-C(20)-C(25)	110.5(5)
C(19)-C(20)-C(26)	114.9(5)
C(25)-C(20)-C(26)	108.9(5)
C(19)-C(20)-C(15)	106.7(5)
C(25)-C(20)-C(15)	114.9(5)
C(26)-C(20)-C(15)	100.8(4)
C(16)-C(21)-H(21A)	109.5
C(16)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(16)-C(21)-H(21C)	109.5

H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(16)-C(22)-H(22A)	109.5
C(16)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(16)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
O(4)-C(23)-C(24)	105.9(6)
O(4)-C(23)-H(23A)	110.6
C(24)-C(23)-H(23A)	110.6
O(4)-C(23)-H(23B)	110.6
C(24)-C(23)-H(23B)	110.6
H(23A)-C(23)-H(23B)	108.7
O(5)-C(24)-C(23)	104.9(6)
O(5)-C(24)-H(24A)	110.8
C(23)-C(24)-H(24A)	110.8
O(5)-C(24)-H(24B)	110.8
C(23)-C(24)-H(24B)	110.8
H(24A)-C(24)-H(24B)	108.9
C(20)-C(25)-H(25A)	109.5
C(20)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(20)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(13)-C(26)-C(27)	115.9(5)
C(13)-C(26)-C(20)	104.9(5)
C(27)-C(26)-C(20)	114.2(5)
C(13)-C(26)-H(26A)	107.1
C(27)-C(26)-H(26A)	107.1
C(20)-C(26)-H(26A)	107.1
O(6)-C(27)-C(26)	112.8(5)
O(6)-C(27)-H(27A)	109.0
C(26)-C(27)-H(27A)	109.0
O(6)-C(27)-H(27B)	109.0
C(26)-C(27)-H(27B)	109.0
H(27A)-C(27)-H(27B)	107.8

O(7)-C(28)-O(6)	124.0(7)
O(7)-C(28)-C(29)	123.0(7)
O(6)-C(28)-C(29)	113.0(6)
C(30)-C(29)-C(34)	118.3(6)
C(30)-C(29)-C(28)	120.2(6)
C(34)-C(29)-C(28)	121.4(6)
C(31)-C(30)-C(29)	121.0(6)
C(31)-C(30)-H(30A)	119.5
C(29)-C(30)-H(30A)	119.5
C(30)-C(31)-C(32)	120.1(7)
C(30)-C(31)-H(31A)	119.9
C(32)-C(31)-H(31A)	119.9
C(33)-C(32)-C(31)	119.9(7)
C(33)-C(32)-Br(2)	119.5(5)
C(31)-C(32)-Br(2)	120.5(6)
C(34)-C(33)-C(32)	119.8(6)
C(34)-C(33)-H(33A)	120.1
C(32)-C(33)-H(33A)	120.1
C(33)-C(34)-C(29)	120.8(7)
C(33)-C(34)-H(34A)	119.6
C(29)-C(34)-H(34A)	119.6
C(7)-O(2)-C(8)	117.4(5)
C(10)-O(3)-C(13)	95.5(4)
C(23)-O(4)-C(17)	110.1(5)
C(24)-O(5)-C(17)	109.0(5)
C(28)-O(6)-C(27)	116.8(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **198**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	49(1)	74(1)	61(1)	33(1)	10(1)	25(1)
Br(2)	86(1)	91(1)	46(1)	23(1)	5(1)	35(1)

C(1)	41(4)	42(4)	31(4)	10(3)	13(3)	8(3)
C(2)	53(5)	54(5)	32(4)	18(3)	21(4)	22(4)
C(3)	51(5)	54(5)	42(4)	22(4)	18(4)	29(4)
C(4)	53(5)	31(4)	38(4)	16(3)	15(4)	12(3)
C(5)	57(5)	40(4)	42(4)	20(3)	25(4)	16(4)
C(6)	48(5)	34(4)	66(6)	20(4)	25(4)	17(4)
C(7)	73(6)	39(4)	39(5)	22(4)	16(4)	19(4)
C(8)	50(5)	57(5)	59(5)	35(4)	−6(4)	0(4)
C(9)	42(4)	44(4)	51(5)	28(4)	2(4)	7(4)
C(10)	33(4)	47(5)	59(5)	33(4)	10(4)	15(3)
C(11)	56(5)	34(4)	40(4)	17(3)	11(4)	13(3)
C(12)	31(4)	34(4)	32(4)	15(3)	6(3)	12(3)
C(13)	25(4)	39(4)	33(4)	19(3)	5(3)	7(3)
C(14)	35(4)	61(5)	36(4)	30(4)	10(3)	4(4)
C(15)	20(3)	33(3)	24(3)	12(3)	4(3)	3(3)
C(16)	27(4)	32(4)	35(4)	14(3)	6(3)	7(3)
C(17)	28(4)	52(4)	35(4)	26(3)	−1(3)	12(3)
C(18)	47(4)	44(4)	51(5)	21(4)	11(4)	15(4)
C(19)	42(4)	28(4)	39(4)	6(3)	9(3)	10(3)
C(20)	30(4)	32(4)	28(4)	9(3)	6(3)	8(3)
C(21)	29(4)	54(4)	40(4)	19(4)	−6(3)	0(3)
C(22)	56(5)	42(4)	25(4)	11(3)	6(3)	9(4)
C(23)	59(5)	77(6)	55(5)	44(5)	15(4)	6(4)
C(24)	58(5)	97(6)	63(6)	61(5)	17(5)	16(5)
C(25)	33(4)	52(4)	43(4)	19(3)	8(3)	17(3)
C(26)	33(4)	44(4)	25(4)	12(3)	9(3)	8(3)
C(27)	43(4)	38(4)	44(5)	10(3)	8(4)	10(3)
C(28)	45(5)	46(5)	39(5)	11(4)	13(4)	15(4)
C(29)	43(4)	37(4)	33(4)	5(3)	8(4)	3(3)
C(30)	42(5)	50(5)	49(5)	20(4)	15(4)	−1(4)
C(31)	32(4)	57(5)	53(5)	13(4)	−1(4)	0(4)
C(32)	50(5)	40(4)	37(4)	9(3)	14(4)	19(4)
C(33)	48(5)	47(4)	37(4)	15(3)	17(4)	11(4)
C(34)	44(4)	37(4)	43(5)	9(3)	12(4)	5(3)
O(1)	132(5)	95(4)	42(4)	33(3)	29(4)	63(4)
O(2)	51(3)	51(3)	50(3)	32(2)	6(3)	12(3)
O(3)	32(3)	44(3)	41(3)	21(2)	4(2)	12(2)
O(4)	38(3)	79(4)	52(3)	45(3)	3(2)	20(3)

O(5)	31(3)	60(3)	46(3)	36(2)	9(2)	13(2)
O(6)	48(3)	45(3)	29(3)	10(2)	2(2)	-1(2)
O(7)	69(4)	78(4)	56(4)	41(3)	9(3)	-5(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **198**.

	x	y	z	U(eq)
H(2A)	-2348	4146	584	53
H(3A)	-4645	4359	-436	54
H(5A)	-949	3175	-2075	52
H(6A)	1341	2957	-1037	56
H(8A)	-9079	4508	-2325	66
H(8B)	-7698	4047	-2996	66
H(10A)	-3553	5351	-2878	50
H(11A)	-6859	5052	-4084	51
H(11B)	-4672	5755	-4058	51
H(12A)	-8738	6196	-3663	38
H(14A)	-8727	6271	-1933	49
H(15A)	-4791	7454	-3570	31
H(18A)	-8409	8965	-3976	55
H(18B)	-6043	9601	-3858	55
H(19A)	-4427	9089	-2868	46
H(19B)	-6509	9493	-2584	46
H(21A)	-10454	7369	-4618	65
H(21B)	-10241	6334	-4997	65
H(21C)	-9936	6950	-5517	65
H(22A)	-4430	6696	-4989	63
H(22B)	-6373	6550	-5737	63
H(22C)	-6654	5933	-5217	63
H(23A)	-5386	9015	-5872	71
H(23B)	-5152	7976	-6192	71
H(24A)	-1925	8524	-5282	76
H(24B)	-2651	9444	-4772	76
H(25A)	-9980	8486	-2576	62

H(25B)	-10361	7406	-3009	62
H(25C)	-10390	8001	-3554	62
H(26A)	-4498	8201	-2051	41
H(27A)	-7077	8979	-1322	52
H(27B)	-8713	8019	-1548	52
H(30A)	-1	9541	687	57
H(31A)	1432	9479	1942	62
H(33A)	-4745	8249	2011	52
H(34A)	-6136	8228	715	52

Table 6. Torsion angles [deg] for **198**.

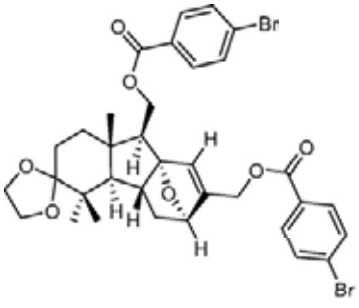
C(6)-C(1)-C(2)-C(3)	-3.4(10)
Br(1)-C(1)-C(2)-C(3)	178.5(5)
C(1)-C(2)-C(3)-C(4)	0.3(10)
C(2)-C(3)-C(4)-C(5)	2.4(10)
C(2)-C(3)-C(4)-C(7)	-178.5(6)
C(3)-C(4)-C(5)-C(6)	-2.2(10)
C(7)-C(4)-C(5)-C(6)	178.7(6)
C(2)-C(1)-C(6)-C(5)	3.6(10)
Br(1)-C(1)-C(6)-C(5)	-178.3(5)
C(4)-C(5)-C(6)-C(1)	-0.8(10)
C(5)-C(4)-C(7)-O(1)	-4.4(11)
C(3)-C(4)-C(7)-O(1)	176.5(7)
C(5)-C(4)-C(7)-O(2)	177.1(6)
C(3)-C(4)-C(7)-O(2)	-2.0(9)
O(2)-C(8)-C(9)-C(14)	-110.5(8)
O(2)-C(8)-C(9)-C(10)	78.3(9)
C(14)-C(9)-C(10)-O(3)	30.7(6)
C(8)-C(9)-C(10)-O(3)	-156.6(6)
C(14)-C(9)-C(10)-C(11)	-75.3(6)
C(8)-C(9)-C(10)-C(11)	97.5(7)
O(3)-C(10)-C(11)-C(12)	-41.1(6)
C(9)-C(10)-C(11)-C(12)	65.4(6)
C(10)-C(11)-C(12)-C(15)	116.1(6)
C(10)-C(11)-C(12)-C(13)	5.3(6)

C(15)-C(12)-C(13)-O(3)	-95.0(5)
C(11)-C(12)-C(13)-O(3)	30.8(5)
C(15)-C(12)-C(13)-C(14)	160.4(5)
C(11)-C(12)-C(13)-C(14)	-73.8(6)
C(15)-C(12)-C(13)-C(26)	20.2(6)
C(11)-C(12)-C(13)-C(26)	146.0(5)
C(8)-C(9)-C(14)-C(13)	-169.6(6)
C(10)-C(9)-C(14)-C(13)	3.1(7)
O(3)-C(13)-C(14)-C(9)	-35.1(6)
C(26)-C(13)-C(14)-C(9)	-160.2(6)
C(12)-C(13)-C(14)-C(9)	70.4(6)
C(11)-C(12)-C(15)-C(16)	75.5(7)
C(13)-C(12)-C(15)-C(16)	-173.7(5)
C(11)-C(12)-C(15)-C(20)	-151.5(5)
C(13)-C(12)-C(15)-C(20)	-40.8(5)
C(12)-C(15)-C(16)-C(21)	58.3(7)
C(20)-C(15)-C(16)-C(21)	-68.7(7)
C(12)-C(15)-C(16)-C(22)	-60.6(7)
C(20)-C(15)-C(16)-C(22)	172.4(5)
C(12)-C(15)-C(16)-C(17)	-179.6(5)
C(20)-C(15)-C(16)-C(17)	53.5(6)
C(21)-C(16)-C(17)-O(5)	-161.7(5)
C(15)-C(16)-C(17)-O(5)	72.5(6)
C(22)-C(16)-C(17)-O(5)	-46.7(6)
C(21)-C(16)-C(17)-O(4)	-45.7(6)
C(15)-C(16)-C(17)-O(4)	-171.5(4)
C(22)-C(16)-C(17)-O(4)	69.3(6)
C(21)-C(16)-C(17)-C(18)	76.7(6)
C(15)-C(16)-C(17)-C(18)	-49.1(6)
C(22)-C(16)-C(17)-C(18)	-168.3(5)
O(5)-C(17)-C(18)-C(19)	-68.4(7)
O(4)-C(17)-C(18)-C(19)	177.4(5)
C(16)-C(17)-C(18)-C(19)	53.7(7)
C(17)-C(18)-C(19)-C(20)	-57.7(7)
C(18)-C(19)-C(20)-C(25)	-69.1(6)
C(18)-C(19)-C(20)-C(26)	167.1(5)
C(18)-C(19)-C(20)-C(15)	56.4(6)
C(12)-C(15)-C(20)-C(19)	166.8(5)

C(16)-C(15)-C(20)-C(19)	-58.1(6)
C(12)-C(15)-C(20)-C(25)	-70.3(6)
C(16)-C(15)-C(20)-C(25)	64.8(7)
C(12)-C(15)-C(20)-C(26)	46.6(5)
C(16)-C(15)-C(20)-C(26)	-178.3(5)
O(4)-C(23)-C(24)-O(5)	19.8(8)
O(3)-C(13)-C(26)-C(27)	-114.7(6)
C(14)-C(13)-C(26)-C(27)	6.8(9)
C(12)-C(13)-C(26)-C(27)	135.3(5)
O(3)-C(13)-C(26)-C(20)	118.4(5)
C(14)-C(13)-C(26)-C(20)	-120.2(6)
C(12)-C(13)-C(26)-C(20)	8.4(6)
C(19)-C(20)-C(26)-C(13)	-147.0(5)
C(25)-C(20)-C(26)-C(13)	88.5(5)
C(15)-C(20)-C(26)-C(13)	-32.8(5)
C(19)-C(20)-C(26)-C(27)	85.0(6)
C(25)-C(20)-C(26)-C(27)	-39.5(7)
C(15)-C(20)-C(26)-C(27)	-160.8(5)
C(13)-C(26)-C(27)-O(6)	65.2(7)
C(20)-C(26)-C(27)-O(6)	-172.7(5)
O(7)-C(28)-C(29)-C(30)	-22.0(10)
O(6)-C(28)-C(29)-C(30)	158.1(6)
O(7)-C(28)-C(29)-C(34)	155.2(7)
O(6)-C(28)-C(29)-C(34)	-24.8(8)
C(34)-C(29)-C(30)-C(31)	2.4(10)
C(28)-C(29)-C(30)-C(31)	179.7(6)
C(29)-C(30)-C(31)-C(32)	-2.7(10)
C(30)-C(31)-C(32)-C(33)	0.7(10)
C(30)-C(31)-C(32)-Br(2)	178.5(5)
C(31)-C(32)-C(33)-C(34)	1.4(10)
Br(2)-C(32)-C(33)-C(34)	-176.5(5)
C(32)-C(33)-C(34)-C(29)	-1.6(9)
C(30)-C(29)-C(34)-C(33)	-0.3(9)
C(28)-C(29)-C(34)-C(33)	-177.5(6)
O(1)-C(7)-O(2)-C(8)	-0.3(10)
C(4)-C(7)-O(2)-C(8)	178.1(5)
C(9)-C(8)-O(2)-C(7)	-86.5(8)
C(9)-C(10)-O(3)-C(13)	-50.2(5)

C(11)-C(10)-O(3)-C(13)	61.1(5)
C(14)-C(13)-O(3)-C(10)	51.8(5)
C(26)-C(13)-O(3)-C(10)	-171.3(5)
C(12)-C(13)-O(3)-C(10)	-57.0(5)
C(24)-C(23)-O(4)-C(17)	-10.9(8)
O(5)-C(17)-O(4)-C(23)	-2.1(7)
C(18)-C(17)-O(4)-C(23)	114.2(6)
C(16)-C(17)-O(4)-C(23)	-120.4(6)
C(23)-C(24)-O(5)-C(17)	-21.6(8)
O(4)-C(17)-O(5)-C(24)	15.2(7)
C(18)-C(17)-O(5)-C(24)	-100.9(6)
C(16)-C(17)-O(5)-C(24)	134.5(6)
O(7)-C(28)-O(6)-C(27)	-9.0(9)
C(29)-C(28)-O(6)-C(27)	170.9(5)
C(26)-C(27)-O(6)-C(28)	83.1(6)

Symmetry transformations used to generate equivalent atoms:



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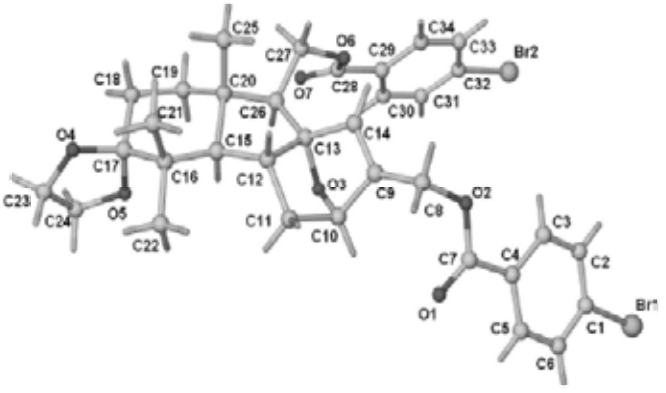

Table 1. Crystal data and structure refinement for 223.

Identification code	djq-1-087-c
Empirical formula	C28 H48 O7 Si
Formula weight	524.75
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 6.8709(19) A alpha = 77.041(5) deg.
	b = 20.653(6) A beta = 84.299(5) deg.
	c = 22.273(6) A gamma = 81.836(5) deg.
Volume	3041.5(15) A^3
Z, Calculated density	4, 1.146 Mg/m^3
Absorption coefficient	0.117 mm^-1
F(000)	1144
Crystal size	0.50 x 0.40 x 0.20 mm
Theta range for data collection	0.94 to 28.09 deg.
Limiting indices	-8<=h<=9, -27<=k<=26, -26<=l<=29
Reflections collected / unique	20699 / 14283 [R(int) = 0.0397]
Completeness to theta = 28.09	96.5 %
Absorption correction	SADABS
Max. and min. transmission	1.000 and 0.086541
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14283 / 0 / 649
Goodness-of-fit on F^2	0.994
Final R indices [I>2sigma(I)]	R1 = 0.0660, wR2 = 0.1565
R indices (all data)	R1 = 0.1571, wR2 = 0.2086
Largest diff. peak and hole	0.246 and -0.234 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **223.**

U(eq) is defined as one third of the trace of the orthogonalize Uij tensor.

	x	y	z	U(eq)

Si(1)	8908(1)	5178(1)	7130(1)	62(1)
Si(1')	2657(1)	9841(1)	7880(1)	61(1)
O(1)	7133(3)	5641(1)	7439(1)	65(1)
O(1')	1604(3)	9349(1)	7567(1)	66(1)
O(2)	6504(3)	7823(1)	7248(1)	63(1)
O(2')	2384(3)	7169(1)	7794(1)	59(1)
O(3)	7576(3)	7552(1)	8199(1)	50(1)
O(3')	1570(3)	7423(1)	6812(1)	48(1)
O(4)	5096(3)	6071(1)	9259(1)	50(1)
O(4')	4203(3)	8920(1)	5774(1)	50(1)
O(5)	1799(3)	5885(1)	9466(1)	73(1)
O(5')	7564(3)	9046(1)	5665(1)	67(1)
O(6)	5444(4)	8993(1)	10660(1)	82(1)
O(6')	6317(4)	6567(1)	4751(1)	80(1)
O(7)	3343(3)	8451(1)	10273(1)	74(1)
O(7')	4298(4)	6022(1)	4336(1)	91(1)
C(1)	8566(5)	4301(2)	7536(1)	65(1)
C(1')	1910(6)	10697(2)	7427(1)	69(1)
C(2)	10284(7)	3809(2)	7353(2)	122(2)
C(2')	3037(9)	11197(2)	7624(2)	136(2)
C(3)	6637(6)	4110(2)	7384(2)	106(1)
C(3')	-312(7)	10891(2)	7522(2)	130(2)
C(4)	8501(7)	4245(2)	8239(2)	107(1)
C(4')	2430(7)	10727(2)	6738(2)	97(1)
C(5)	8601(7)	5308(2)	6284(2)	111(2)
C(5')	1759(7)	9748(2)	8708(2)	97(1)
C(6')	5383(6)	9611(2)	7819(2)	104(1)
C(6)	11327(6)	5408(2)	7246(2)	113(2)
C(7)	6802(5)	6351(2)	7267(1)	64(1)
C(7')	1794(5)	8645(2)	7775(1)	68(1)
C(8)	7308(4)	6664(1)	7760(1)	47(1)
C(8')	1538(4)	8321(1)	7263(1)	46(1)
C(9)	7048(4)	7397(1)	7681(1)	49(1)
C(9')	1899(4)	7591(1)	7346(1)	46(1)
C(10)	8251(4)	6937(1)	8633(1)	46(1)
C(10')	921(4)	8032(1)	6363(1)	45(1)
C(11)	8013(4)	6405(1)	8304(1)	50(1)
C(11')	995(4)	8571(1)	6700(1)	46(1)

C(12)	7135(4)	6899(1)	9266(1)	40(1)
C(12')	2187(4)	8084(1)	5750(1)	41(1)
C(13)	5020(4)	6776(1)	9227(1)	42(1)
C(13')	4275(4)	8213(1)	5833(1)	44(1)
C(14)	3455(5)	5876(2)	9055(1)	63(1)
C(14')	5784(5)	9116(2)	6012(1)	59(1)
C(15)	2105(5)	5436(2)	10043(2)	86(1)
C(15')	7562(5)	9487(2)	5073(2)	79(1)
C(16)	7415(4)	7463(1)	9609(1)	44(1)
C(16')	2042(4)	7522(1)	5394(1)	48(1)
C(17)	9638(4)	7519(2)	9568(1)	61(1)
C(17')	-160(5)	7441(2)	5398(2)	72(1)
C(18)	6296(5)	8139(1)	9313(1)	54(1)
C(18')	3201(5)	6855(1)	5690(1)	62(1)
C(19)	6341(5)	8671(1)	9683(1)	64(1)
C(19')	3275(6)	6321(2)	5311(1)	75(1)
C(20)	5395(5)	8477(2)	10328(1)	61(1)
C(20')	4298(5)	6533(2)	4677(2)	67(1)
C(21)	6356(5)	7803(2)	10700(1)	60(1)
C(21')	3332(5)	7212(2)	4299(1)	69(1)
C(22)	5004(6)	7577(2)	11281(1)	88(1)
C(22')	4760(6)	7460(2)	3746(2)	92(1)
C(23)	8319(6)	7899(2)	10926(2)	88(1)
C(23')	1448(6)	7102(2)	4031(2)	100(1)
C(24')	2978(5)	7745(1)	4714(1)	54(1)
C(24)	6527(4)	7264(1)	10296(1)	48(1)
C(25')	1950(5)	8390(2)	4377(1)	67(1)
C(25)	7514(5)	6605(2)	10630(1)	61(1)
C(26')	2694(6)	8951(2)	4187(1)	85(1)
C(26)	6654(6)	6075(2)	10868(1)	83(1)
C(27')	7482(7)	6018(2)	4565(2)	111(2)
C(27)	3598(7)	9379(2)	10644(2)	126(2)
C(28')	6180(8)	5666(2)	4329(3)	142(2)
C(28)	2197(6)	8967(2)	10514(2)	96(1)

Table 3. Bond lengths [A] and angles [deg] for **223.**

Si(1)-O(1)	1.636(2)
Si(1)-C(6)	1.851(4)
Si(1)-C(1)	1.870(3)
Si(1)-C(5)	1.871(3)
Si(1')-O(1')	1.633(2)
Si(1')-C(1')	1.859(3)
Si(1')-C(5')	1.863(3)
Si(1')-C(6')	1.865(4)
O(1)-C(7)	1.420(3)
O(1')-C(7')	1.414(3)
O(2)-C(9)	1.201(3)
O(2')-C(9')	1.208(3)
O(3)-C(9)	1.359(3)
O(3)-C(10)	1.460(3)
O(3')-C(9')	1.360(3)
O(3')-C(10')	1.465(3)
O(4)-C(14)	1.398(3)
O(4)-C(13)	1.437(3)
O(4')-C(14')	1.399(3)
O(4')-C(13')	1.429(3)
O(5)-C(14)	1.389(4)
O(5)-C(15)	1.422(4)
O(5')-C(14')	1.387(4)
O(5')-C(15')	1.426(3)
O(6)-C(27)	1.399(5)
O(6)-C(20)	1.432(3)
O(6')-C(27')	1.408(4)
O(6')-C(20')	1.427(4)
O(7)-C(28)	1.407(4)
O(7)-C(20)	1.437(4)
O(7')-C(28')	1.394(6)
O(7')-C(20')	1.432(3)
C(1)-C(3)	1.525(5)
C(1)-C(2)	1.529(5)
C(1)-C(4)	1.542(4)
C(1')-C(4')	1.528(4)
C(1')-C(3')	1.529(5)

C(1')-C(2')	1.535(5)
C(7)-C(8)	1.486(4)
C(7')-C(8')	1.481(4)
C(8)-C(11)	1.319(4)
C(8)-C(9)	1.471(4)
C(8')-C(11')	1.315(3)
C(8')-C(9')	1.464(4)
C(10)-C(11)	1.485(4)
C(10)-C(12)	1.528(3)
C(10')-C(11')	1.485(3)
C(10')-C(12')	1.535(3)
C(12)-C(13)	1.524(3)
C(12)-C(16)	1.571(3)
C(12')-C(13')	1.533(3)
C(12')-C(16')	1.564(3)
C(16)-C(18)	1.536(4)
C(16)-C(17)	1.540(4)
C(16)-C(24)	1.577(3)
C(16')-C(18')	1.535(4)
C(16')-C(17')	1.544(4)
C(16')-C(24')	1.580(4)
C(18)-C(19)	1.519(4)
C(18')-C(19')	1.525(4)
C(19)-C(20)	1.508(4)
C(19')-C(20')	1.513(4)
C(20)-C(21)	1.546(4)
C(20')-C(21')	1.560(5)
C(21)-C(23)	1.538(4)
C(21)-C(22)	1.539(4)
C(21)-C(24)	1.568(4)
C(21')-C(22')	1.537(4)
C(21')-C(23')	1.543(5)
C(21')-C(24')	1.568(4)
C(24')-C(25')	1.492(4)
C(24)-C(25)	1.500(4)
C(25')-C(26')	1.300(4)
C(25)-C(26)	1.300(4)
C(27')-C(28')	1.434(6)

C(27)-C(28)	1.460(5)
O(1)-Si(1)-C(6)	110.01(16)
O(1)-Si(1)-C(1)	104.29(14)
C(6)-Si(1)-C(1)	112.56(18)
O(1)-Si(1)-C(5)	109.22(16)
C(6)-Si(1)-C(5)	109.7(2)
C(1)-Si(1)-C(5)	110.95(17)
O(1')-Si(1')-C(1')	104.65(13)
O(1')-Si(1')-C(5')	109.50(15)
C(1')-Si(1')-C(5')	111.75(17)
O(1')-Si(1')-C(6')	109.48(16)
C(1')-Si(1')-C(6')	111.81(17)
C(5')-Si(1')-C(6')	109.53(19)
C(7)-O(1)-Si(1)	124.24(19)
C(7')-O(1')-Si(1')	123.36(19)
C(9)-O(3)-C(10)	109.4(2)
C(9')-O(3')-C(10')	109.1(2)
C(14)-O(4)-C(13)	115.3(2)
C(14')-O(4')-C(13')	114.7(2)
C(14)-O(5)-C(15)	112.6(3)
C(14')-O(5')-C(15')	112.8(2)
C(27)-O(6)-C(20)	108.1(3)
C(27')-O(6')-C(20')	109.1(3)
C(28)-O(7)-C(20)	109.6(2)
C(28')-O(7')-C(20')	108.3(3)
C(3)-C(1)-C(2)	109.4(3)
C(3)-C(1)-C(4)	108.2(3)
C(2)-C(1)-C(4)	108.5(3)
C(3)-C(1)-Si(1)	111.0(2)
C(2)-C(1)-Si(1)	110.4(3)
C(4)-C(1)-Si(1)	109.3(2)
C(4')-C(1')-C(3')	108.3(3)
C(4')-C(1')-C(2')	108.0(3)
C(3')-C(1')-C(2')	110.3(4)
C(4')-C(1')-Si(1')	110.2(2)
C(3')-C(1')-Si(1')	110.6(2)
C(2')-C(1')-Si(1')	109.4(3)
O(1)-C(7)-C(8)	111.3(2)

O(1')-C(7')-C(8')	110.3(2)
C(11)-C(8)-C(9)	107.8(2)
C(11)-C(8)-C(7)	131.9(3)
C(9)-C(8)-C(7)	120.4(2)
C(11')-C(8')-C(9')	108.1(2)
C(11')-C(8')-C(7')	131.5(3)
C(9')-C(8')-C(7')	120.4(2)
O(2)-C(9)-O(3)	121.8(3)
O(2)-C(9)-C(8)	129.6(3)
O(3)-C(9)-C(8)	108.6(2)
O(2')-C(9')-O(3')	121.3(3)
O(2')-C(9')-C(8')	130.0(3)
O(3')-C(9')-C(8')	108.7(2)
O(3)-C(10)-C(11)	103.1(2)
O(3)-C(10)-C(12)	111.3(2)
C(11)-C(10)-C(12)	116.2(2)
O(3')-C(10')-C(11')	103.1(2)
O(3')-C(10')-C(12')	111.5(2)
C(11')-C(10')-C(12')	115.6(2)
C(8)-C(11)-C(10)	111.1(2)
C(8')-C(11')-C(10')	111.0(2)
C(13)-C(12)-C(10)	109.5(2)
C(13)-C(12)-C(16)	116.4(2)
C(10)-C(12)-C(16)	115.5(2)
C(13')-C(12')-C(10')	110.5(2)
C(13')-C(12')-C(16')	116.0(2)
C(10')-C(12')-C(16')	114.8(2)
O(4)-C(13)-C(12)	105.9(2)
O(4')-C(13')-C(12')	106.5(2)
O(5)-C(14)-O(4)	113.8(2)
O(5')-C(14')-O(4')	114.5(2)
C(18)-C(16)-C(17)	109.8(2)
C(18)-C(16)-C(12)	111.5(2)
C(17)-C(16)-C(12)	107.5(2)
C(18)-C(16)-C(24)	107.4(2)
C(17)-C(16)-C(24)	112.5(2)
C(12)-C(16)-C(24)	108.16(19)
C(18')-C(16')-C(17')	110.2(2)

C(18')-C(16')-C(12')	111.7(2)
C(17')-C(16')-C(12')	107.7(2)
C(18')-C(16')-C(24')	107.7(2)
C(17')-C(16')-C(24')	111.5(2)
C(12')-C(16')-C(24')	108.1(2)
C(19)-C(18)-C(16)	112.3(2)
C(19')-C(18')-C(16')	112.6(3)
C(20)-C(19)-C(18)	111.8(2)
C(20')-C(19')-C(18')	111.4(2)
O(6)-C(20)-O(7)	105.5(3)
O(6)-C(20)-C(19)	110.2(2)
O(7)-C(20)-C(19)	107.4(3)
O(6)-C(20)-C(21)	109.4(3)
O(7)-C(20)-C(21)	110.5(2)
C(19)-C(20)-C(21)	113.4(3)
O(6')-C(20')-O(7')	106.0(3)
O(6')-C(20')-C(19')	108.3(3)
O(7')-C(20')-C(19')	109.2(2)
O(6')-C(20')-C(21')	110.5(2)
O(7')-C(20')-C(21')	109.1(3)
C(19')-C(20')-C(21')	113.5(3)
C(23)-C(21)-C(22)	106.7(3)
C(23)-C(21)-C(20)	109.9(2)
C(22)-C(21)-C(20)	108.8(3)
C(23)-C(21)-C(24)	114.6(3)
C(22)-C(21)-C(24)	107.9(2)
C(20)-C(21)-C(24)	108.7(2)
C(22')-C(21')-C(23')	106.7(3)
C(22')-C(21')-C(20')	108.7(3)
C(23')-C(21')-C(20')	109.7(3)
C(22')-C(21')-C(24')	108.2(2)
C(23')-C(21')-C(24')	113.8(3)
C(20')-C(21')-C(24')	109.5(2)
C(25')-C(24')-C(21')	110.9(2)
C(25')-C(24')-C(16')	112.4(3)
C(21')-C(24')-C(16')	117.6(2)
C(25)-C(24)-C(21)	110.7(2)
C(25)-C(24)-C(16)	112.0(2)

C(21)-C(24)-C(16)	117.2(2)
C(26')-C(25')-C(24')	126.4(3)
C(26)-C(25)-C(24)	125.8(3)
O(6')-C(27')-C(28')	106.8(4)
O(6)-C(27)-C(28)	106.9(3)
O(7')-C(28')-C(27')	108.4(4)
O(7)-C(28)-C(27)	105.7(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **223**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Si(1)	63(1)	62(1)	56(1)	-14(1)	6(1)	2(1)
Si(1')	72(1)	63(1)	51(1)	-17(1)	-6(1)	-11(1)
O(1)	70(2)	61(1)	63(1)	-21(1)	6(1)	-2(1)
O(1')	85(2)	51(1)	65(1)	-14(1)	-18(1)	-6(1)
O(2)	71(2)	58(1)	50(1)	5(1)	-9(1)	-2(1)
O(2')	59(1)	57(1)	51(1)	7(1)	-1(1)	-5(1)
O(3)	57(1)	45(1)	44(1)	-4(1)	-2(1)	-6(1)
O(3')	54(1)	41(1)	46(1)	-6(1)	0(1)	-4(1)
O(4)	45(1)	37(1)	68(1)	-8(1)	-10(1)	-6(1)
O(4')	47(1)	40(1)	62(1)	-6(1)	-9(1)	-7(1)
O(5)	47(1)	59(1)	109(2)	-3(1)	-15(1)	-9(1)
O(5')	46(1)	60(1)	88(2)	6(1)	-16(1)	-5(1)
O(6)	101(2)	71(2)	92(2)	-47(1)	12(1)	-32(2)
O(6')	83(2)	67(2)	98(2)	-41(1)	13(1)	-18(1)
O(7)	70(2)	64(1)	99(2)	-44(1)	9(1)	-13(1)
O(7')	116(2)	78(2)	98(2)	-54(1)	23(2)	-34(2)
C(1)	72(2)	61(2)	62(2)	-11(2)	-7(2)	-1(2)
C(1')	88(3)	61(2)	61(2)	-21(2)	2(2)	-10(2)
C(2)	127(4)	68(3)	154(4)	-19(3)	21(3)	20(2)
C(2')	223(6)	80(3)	122(4)	-29(3)	-34(4)	-49(4)
C(3)	110(4)	92(3)	120(3)	-16(3)	-23(3)	-30(3)

C(3')	122(4)	96(3)	133(4)	11(3)	22(3)	32(3)
C(4)	136(4)	105(3)	66(2)	12(2)	-19(2)	-15(3)
C(4')	126(4)	92(3)	66(2)	-4(2)	-4(2)	-8(3)
C(5)	170(5)	98(3)	54(2)	-14(2)	7(2)	8(3)
C(5')	139(4)	96(3)	57(2)	-19(2)	-4(2)	-13(3)
C(6')	76(3)	108(3)	123(3)	-11(3)	-16(2)	-6(2)
C(6)	70(3)	100(3)	162(4)	-19(3)	7(3)	-19(2)
C(7)	81(2)	56(2)	53(2)	-16(2)	-9(2)	10(2)
C(7')	97(3)	56(2)	51(2)	-9(2)	-4(2)	-14(2)
C(8)	43(2)	51(2)	45(2)	-11(1)	3(1)	4(1)
C(8')	44(2)	45(2)	46(2)	-8(1)	3(1)	-4(1)
C(9)	40(2)	57(2)	45(2)	-6(1)	4(1)	-4(1)
C(9')	39(2)	48(2)	47(2)	-6(1)	6(1)	-5(1)
C(10)	39(2)	48(2)	45(2)	-5(1)	-6(1)	2(1)
C(10')	43(2)	44(2)	46(2)	-5(1)	-9(1)	-2(1)
C(11)	49(2)	48(2)	49(2)	-12(1)	3(1)	5(1)
C(11')	45(2)	43(2)	45(2)	-5(1)	2(1)	1(1)
C(12)	37(2)	38(1)	42(1)	-5(1)	-4(1)	-2(1)
C(12')	43(2)	39(1)	40(1)	-7(1)	-3(1)	-4(1)
C(13)	44(2)	37(1)	46(2)	-8(1)	-4(1)	-5(1)
C(13')	45(2)	37(1)	48(2)	-8(1)	-3(1)	-3(1)
C(14)	75(2)	49(2)	69(2)	-8(2)	-16(2)	-20(2)
C(14')	73(2)	51(2)	57(2)	-9(1)	-14(2)	-18(2)
C(15)	72(3)	96(3)	87(3)	-7(2)	4(2)	-28(2)
C(15')	61(2)	77(2)	84(2)	8(2)	2(2)	-4(2)
C(16)	47(2)	42(2)	43(2)	-8(1)	0(1)	-9(1)
C(16')	53(2)	47(2)	48(2)	-14(1)	1(1)	-13(1)
C(17)	52(2)	65(2)	70(2)	-17(2)	-1(2)	-24(2)
C(17')	69(2)	79(2)	78(2)	-31(2)	4(2)	-30(2)
C(18)	67(2)	44(2)	50(2)	-8(1)	-1(1)	-7(1)
C(18')	86(2)	42(2)	56(2)	-13(1)	11(2)	-8(2)
C(19)	75(2)	47(2)	72(2)	-16(2)	7(2)	-14(2)
C(19')	104(3)	48(2)	77(2)	-24(2)	19(2)	-19(2)
C(20)	70(2)	55(2)	71(2)	-33(2)	9(2)	-25(2)
C(20')	81(3)	60(2)	73(2)	-36(2)	14(2)	-26(2)
C(21)	79(2)	59(2)	51(2)	-21(2)	-1(2)	-27(2)
C(21')	88(3)	74(2)	56(2)	-28(2)	4(2)	-28(2)
C(22)	123(3)	89(3)	60(2)	-30(2)	19(2)	-35(2)

C(22')	133(4)	86(3)	60(2)	-27(2)	27(2)	-27(2)
C(23)	105(3)	94(3)	80(2)	-36(2)	-26(2)	-25(2)
C(23')	117(4)	119(3)	84(3)	-50(2)	-21(2)	-32(3)
C(24')	63(2)	56(2)	47(2)	-12(1)	-2(1)	-18(2)
C(24)	52(2)	51(2)	45(2)	-10(1)	-2(1)	-15(1)
C(25')	82(3)	70(2)	50(2)	-8(2)	-13(2)	-12(2)
C(25)	76(2)	59(2)	48(2)	-4(2)	-13(2)	-14(2)
C(26')	110(3)	70(2)	65(2)	3(2)	-2(2)	-11(2)
C(26)	119(3)	62(2)	69(2)	1(2)	-15(2)	-27(2)
C(27')	122(4)	99(3)	120(4)	-58(3)	7(3)	11(3)
C(27)	100(4)	92(3)	208(5)	-97(3)	49(3)	-28(3)
C(28')	123(4)	105(4)	224(6)	-110(4)	62(4)	-36(3)
C(28)	97(3)	82(3)	120(3)	-54(2)	8(2)	-4(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **223.**

	x	y	z	U(eq)
H(2A)	10090	3362	7565	184
H(2B)	11495	3918	7463	184
H(2C)	10346	3839	6915	184
H(2'A)	2653	11640	7390	204
H(2'B)	4427	11078	7549	204
H(2'C)	2733	11186	8056	204
H(3A)	6493	3659	7598	159
H(3B)	6649	4142	6947	159
H(3C)	5554	4408	7512	159
H(3'A)	-672	11333	7283	194
H(3'B)	-660	10885	7952	194
H(3'C)	-998	10578	7393	194
H(4A)	8325	3795	8449	160
H(4B)	7422	4549	8362	160
H(4C)	9715	4356	8345	160
H(4'A)	2029	11171	6509	146
H(4'B)	1759	10412	6606	146

H(4'C)	3827	10619	6668	146
H(5A)	8784	5760	6085	167
H(5B)	7301	5225	6224	167
H(5C)	9561	5004	6109	167
H(5'A)	2179	9302	8928	146
H(5'B)	346	9829	8741	146
H(5'C)	2289	10064	8883	146
H(6'A)	5714	9168	8061	156
H(6'B)	6008	9924	7971	156
H(6'C)	5831	9622	7395	156
H(6A)	11488	5336	7681	169
H(6B)	11390	5872	7059	169
H(6C)	12359	5137	7060	169
H(7A)	5427	6490	7185	77
H(7B)	7596	6503	6890	77
H(7'A)	808	8526	8110	82
H(7'B)	3085	8487	7930	82
H(10A)	9657	6930	8680	55
H(10B)	-452	8023	6284	54
H(11A)	8321	5948	8461	59
H(11B)	698	9026	6534	55
H(12A)	7740	6484	9523	48
H(12B)	1611	8497	5484	49
H(13A)	4178	6907	9567	51
H(13B)	4512	7031	8841	51
H(13C)	4687	7976	6236	52
H(13D)	5201	8063	5520	52
H(14A)	3134	6172	8664	76
H(14C)	3795	5427	8981	76
H(14B)	5464	9581	6040	71
H(14D)	5943	8852	6427	71
H(15A)	930	5466	10313	129
H(15B)	3178	5553	10227	129
H(15C)	2415	4987	9981	129
H(15D)	8813	9413	4850	119
H(15E)	7333	9942	5123	119
H(15F)	6537	9404	4848	119
H(17A)	9857	7863	9771	91

H(17B)	10117	7629	9143	91
H(17C)	10326	7099	9766	91
H(17D)	-292	7096	5184	108
H(17E)	-861	7856	5196	108
H(17F)	-697	7321	5817	108
H(18A)	6878	8289	8899	65
H(18B)	4937	8081	9281	65
H(18C)	4536	6928	5737	74
H(18D)	2594	6694	6099	74
H(19A)	7697	8739	9707	77
H(19B)	5652	9091	9473	77
H(19C)	3972	5905	5526	90
H(19D)	1944	6242	5267	90
H(22A)	4880	7899	11537	132
H(22B)	5561	7149	11506	132
H(22C)	3726	7540	11161	132
H(22D)	5967	7528	3893	138
H(22E)	4173	7875	3506	138
H(22F)	5031	7133	3494	138
H(23A)	8092	8238	11166	132
H(23B)	9219	8033	10576	132
H(23C)	8872	7485	11175	132
H(23D)	508	6949	4363	149
H(23E)	1770	6773	3782	149
H(23F)	893	7516	3782	149
H(24A)	4297	7844	4764	65
H(24B)	5168	7189	10264	58
H(25A)	648	8391	4295	81
H(25B)	8860	6573	10671	73
H(26A)	3991	8976	4258	102
H(26B)	1931	9328	3980	102
H(26C)	5310	6084	10838	100
H(26D)	7384	5686	11068	100
H(27A)	8127	5728	4913	134
H(27B)	8486	6172	4247	134
H(27C)	3630	9783	10323	151
H(27D)	3223	9505	11037	151
H(28A)	6633	5626	3911	170

H(28B)	6154	5219	4583	170
H(28C)	1436	8785	10889	115
H(28D)	1298	9230	10216	115

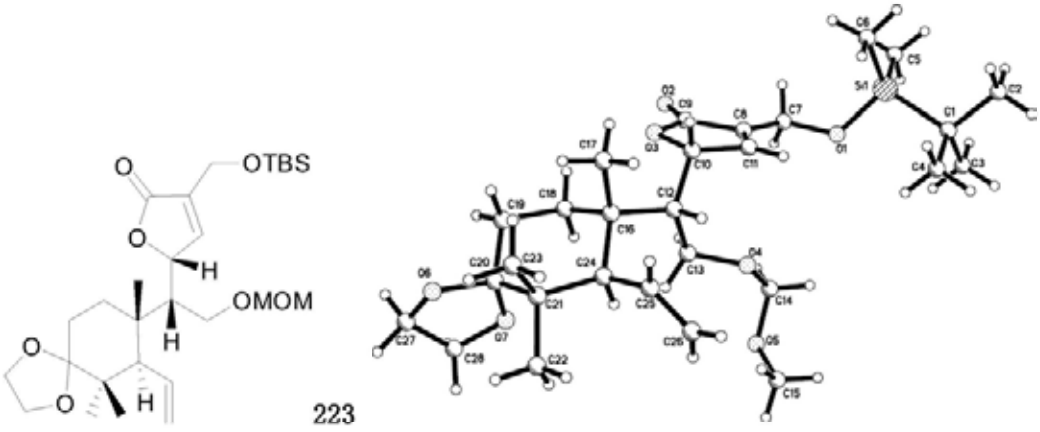

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Table 1. Crystal data and structure refinement for 255a.

Identification code	djq-2-046-2
Empirical formula	C21 H30 O5
Formula weight	362.45
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 7.4106(12) A alpha = 94.842(3) deg.
	b = 7.9291(14) A beta = 101.651(3) deg.
	c = 17.692(3) A gamma = 99.217(3) deg.
Volume	997.7(3) A^3
Z, Calculated density	2, 1.207 Mg/m^3
Absorption coefficient	0.085 mm^-1
F(000)	392
Crystal size	0.40 x 0.30 x 0.20 mm
Theta range for data collection	1.18 to 28.04 deg.
Limiting indices	-8<=h<=9, -8<=k<=10, -23<=l<=23
Reflections collected / unique	6853 / 4763 [R(int) = 0.0250]
Completeness to theta = 28.04	98.1 %
Absorption correction	SADABS
Max. and min. transmission	1.0000 and 0.351258
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4763 / 0 / 235
Goodness-of-fit on F^2	1.012
Final R indices [I>2sigma(I)]	R1 = 0.0600, wR2 = 0.1609
R indices (all data)	R1 = 0.1052, wR2 = 0.2024
Largest diff. peak and hole	0.277 and -0.239 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **255a**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	7086(2)	5682(2)	5691(1)	48(1)
O(2)	7959(2)	5292(2)	4560(1)	64(1)
O(3)	9955(2)	3478(2)	7284(1)	51(1)
O(4)	13209(3)	3853(3)	7724(1)	85(1)
O(5)	3623(3)	9107(3)	8493(1)	98(1)
C(1)	7555(3)	4688(3)	5122(1)	48(1)
C(2)	7436(3)	2922(3)	5318(1)	50(1)

C(3)	7890(4)	1555(4)	4814(2)	70(1)
C(4)	7497(5)	-59(5)	4845(2)	91(1)
C(5)	6889(3)	2895(3)	5986(1)	50(1)
C(6)	6596(3)	4625(3)	6276(1)	44(1)
C(7)	7742(3)	5376(3)	7098(1)	39(1)
C(8)	9803(3)	5214(3)	7158(1)	41(1)
C(9)	11645(4)	3035(4)	7159(2)	67(1)
C(10)	13201(5)	3353(5)	8478(2)	103(1)
C(11)	7427(3)	7220(3)	7384(1)	40(1)
C(12)	8841(3)	8613(3)	7155(1)	50(1)
C(13)	5422(3)	7435(3)	7015(1)	50(1)
C(14)	4858(4)	9054(4)	7363(2)	66(1)
C(15)	4964(4)	8998(3)	8213(2)	63(1)
C(16)	6837(3)	8806(3)	8700(1)	60(1)
C(17)	8151(4)	10576(4)	8816(2)	87(1)
C(18)	6587(5)	8329(5)	9505(2)	92(1)
C(19)	7574(3)	7296(3)	8289(1)	47(1)
C(20)	9473(4)	7149(4)	8739(1)	66(1)
C(21)	9814(6)	5884(6)	9147(2)	111(2)

Table 3. Bond lengths [A] and angles [deg] for **255a**.

O(1)-C(1)	1.361(3)
O(1)-C(6)	1.450(2)
O(2)-C(1)	1.210(3)
O(3)-C(9)	1.407(3)
O(3)-C(8)	1.431(2)
O(4)-C(9)	1.394(4)
O(4)-C(10)	1.425(4)
O(5)-C(15)	1.208(3)
C(1)-C(2)	1.464(3)
C(2)-C(5)	1.325(3)
C(2)-C(3)	1.470(3)
C(3)-C(4)	1.275(4)
C(5)-C(6)	1.488(3)
C(6)-C(7)	1.544(3)
C(7)-C(8)	1.536(3)
C(7)-C(11)	1.575(3)
C(11)-C(12)	1.536(3)
C(11)-C(13)	1.540(3)
C(11)-C(19)	1.577(3)
C(13)-C(14)	1.531(3)

C(14)-C(15)	1.495(4)
C(15)-C(16)	1.516(4)
C(16)-C(18)	1.543(4)
C(16)-C(17)	1.547(4)
C(16)-C(19)	1.576(3)
C(19)-C(20)	1.498(3)
C(20)-C(21)	1.312(4)
C(1)-O(1)-C(6)	109.40(17)
C(9)-O(3)-C(8)	113.03(17)
C(9)-O(4)-C(10)	113.5(2)
O(2)-C(1)-O(1)	120.9(2)
O(2)-C(1)-C(2)	130.0(2)
O(1)-C(1)-C(2)	109.10(18)
C(5)-C(2)-C(1)	107.2(2)
C(5)-C(2)-C(3)	131.3(3)
C(1)-C(2)-C(3)	121.5(2)
C(4)-C(3)-C(2)	126.3(3)
C(2)-C(5)-C(6)	111.1(2)
O(1)-C(6)-C(5)	103.12(16)
O(1)-C(6)-C(7)	111.68(17)
C(5)-C(6)-C(7)	115.65(17)
C(8)-C(7)-C(6)	109.45(16)
C(8)-C(7)-C(11)	114.70(16)
C(6)-C(7)-C(11)	114.51(16)
O(3)-C(8)-C(7)	107.36(16)
O(4)-C(9)-O(3)	113.4(2)
C(12)-C(11)-C(13)	109.39(17)
C(12)-C(11)-C(7)	110.26(16)
C(13)-C(11)-C(7)	109.59(16)
C(12)-C(11)-C(19)	113.76(18)
C(13)-C(11)-C(19)	107.02(16)
C(7)-C(11)-C(19)	106.70(16)
C(14)-C(13)-C(11)	113.66(19)
C(15)-C(14)-C(13)	109.8(2)
O(5)-C(15)-C(14)	121.3(3)
O(5)-C(15)-C(16)	122.2(3)
C(14)-C(15)-C(16)	116.5(2)
C(15)-C(16)-C(18)	109.6(2)
C(15)-C(16)-C(17)	107.4(2)
C(18)-C(16)-C(17)	108.4(2)
C(15)-C(16)-C(19)	109.06(19)
C(18)-C(16)-C(19)	108.0(2)
C(17)-C(16)-C(19)	114.4(2)
C(20)-C(19)-C(16)	109.82(19)

C(20)-C(19)-C(11)	113.67(17)
C(16)-C(19)-C(11)	117.71(18)
C(21)-C(20)-C(19)	124.3(3)

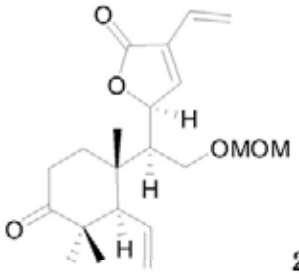
Symmetry transformations used to generate equivalent atoms:

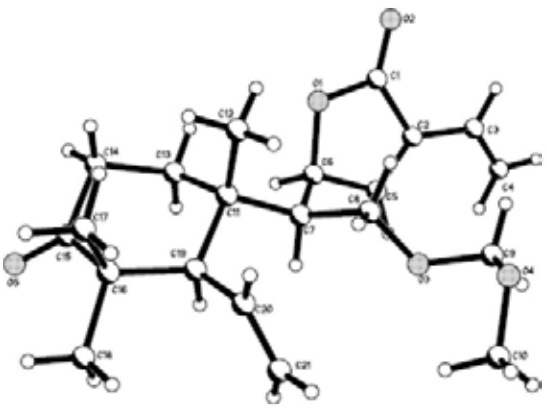
Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **255a**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	54(1)	52(1)	38(1)	10(1)	7(1)	12(1)
O(2)	63(1)	90(1)	41(1)	17(1)	11(1)	13(1)
O(3)	47(1)	47(1)	64(1)	16(1)	17(1)	13(1)
O(4)	48(1)	78(1)	132(2)	47(1)	12(1)	12(1)
O(5)	62(1)	131(2)	106(2)	-17(2)	34(1)	25(1)
C(1)	39(1)	67(2)	35(1)	6(1)	1(1)	10(1)
C(2)	43(1)	60(1)	42(1)	-3(1)	-1(1)	9(1)
C(3)	63(2)	74(2)	67(2)	-9(1)	6(1)	16(1)
C(4)	83(2)	83(2)	98(2)	-18(2)	3(2)	29(2)
C(5)	50(1)	48(1)	46(1)	6(1)	3(1)	2(1)
C(6)	40(1)	50(1)	40(1)	8(1)	8(1)	4(1)
C(7)	39(1)	44(1)	35(1)	7(1)	8(1)	5(1)
C(8)	40(1)	44(1)	40(1)	10(1)	9(1)	9(1)
C(9)	63(2)	58(2)	92(2)	24(1)	31(2)	26(1)
C(10)	85(2)	105(3)	116(3)	41(2)	-6(2)	26(2)
C(11)	37(1)	45(1)	39(1)	8(1)	8(1)	8(1)
C(12)	48(1)	49(1)	55(1)	12(1)	15(1)	5(1)
C(13)	41(1)	58(1)	50(1)	5(1)	6(1)	13(1)
C(14)	53(2)	71(2)	75(2)	6(1)	9(1)	26(1)
C(15)	53(1)	59(2)	78(2)	-10(1)	21(1)	13(1)
C(16)	53(1)	70(2)	54(1)	-9(1)	14(1)	12(1)
C(17)	74(2)	75(2)	97(2)	-28(2)	6(2)	4(2)
C(18)	99(2)	128(3)	59(2)	-9(2)	35(2)	36(2)
C(19)	47(1)	55(1)	39(1)	3(1)	11(1)	8(1)
C(20)	61(2)	99(2)	38(1)	1(1)	6(1)	25(1)
C(21)	128(3)	174(4)	53(2)	37(2)	16(2)	84(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **255a**.

	x	y	z	U(eq)
H(3A)	8527	1902	4435	84
H(4A)	6861	-468	5214	109
H(4B)	7846	-827	4498	109
H(5A)	6711	1922	6240	60
H(6A)	5262	4570	6269	52
H(7A)	7281	4611	7452	47
H(8A)	10187	5478	6682	49
H(8B)	10600	6009	7587	49
H(9A)	11558	1799	7150	80
H(9B)	11815	3332	6654	80
H(10A)	14299	3970	8841	155
H(10B)	13195	2139	8464	155
H(10C)	12103	3613	8639	155
H(12A)	8675	8496	6599	75
H(12B)	10091	8483	7386	75
H(12C)	8640	9730	7335	75
H(13A)	5318	7476	6462	60
H(13B)	4551	6434	7079	60
H(14A)	5689	10069	7285	79
H(14B)	3591	9122	7104	79
H(17A)	7609	11425	9068	131
H(17B)	8312	10898	8319	131
H(17C)	9346	10505	9132	131
H(18A)	6143	9235	9768	138
H(18B)	7768	8177	9807	138
H(18C)	5695	7278	9441	138
H(19A)	6749	6247	8353	57
H(20A)	10476	8012	8729	80
H(21A)	8842	5001	9169	133
H(21B)	11028	5869	9414	133





255a

Table 1. Crystal data and structure refinement for **282**.

Identification code	djq-2-064
Empirical formula	C26.50 H32 Br Cl O7
Formula weight	577.88
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.969(3) A alpha = 92.078(6) deg.
	b = 11.895(4) A beta = 96.398(5) deg.
	c = 15.094(5) A gamma = 108.522(5) deg.
Volume	1512.8(8) A^3
Z, Calculated density	2, 1.269 Mg/m^3
Absorption coefficient	1.485 mm^-1
F(000)	598
Crystal size	0.40 x 0.30 x 0.20 mm
Theta range for data collection	1.81 to 25.00 deg.
Limiting indices	-10<=h<=10, -14<=k<=14, -17<=l<=13
Reflections collected / unique	8188 / 5277 [R(int) = 0.0661]
Completeness to theta = 25.00	99.0 %
Absorption correction	SADABS
Max. and min. transmission	1.0000 and 0.074209
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5277 / 0 / 335
Goodness-of-fit on F^2	1.057
Final R indices [I>2sigma(I)]	R1 = 0.1282, wR2 = 0.3080
R indices (all data)	R1 = 0.1993, wR2 = 0.3912
Extinction coefficient	0.76(7)
Largest diff. peak and hole	0.908 and -0.483 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **282**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	7778(2)	11645(1)	5997(1)	100(1)
O(1)	9452(9)	6411(6)	5672(5)	87(2)
O(1W)	8140(30)	9916(18)	8442(15)	278(11)
O(2)	7813(8)	6262(6)	4423(5)	78(2)
O(2W)	9110(50)	1500(40)	-760(40)	560(40)
O(3)	4300(8)	5234(7)	3936(5)	84(2)

O(4)	2798(11)	6188(9)	3216(7)	117(3)
O(5)	5874(9)	5483(7)	1098(5)	90(2)
C(1)	8655(12)	6836(9)	5186(7)	71(3)
C(2)	8433(11)	8011(8)	5322(7)	68(2)
C(3)	7196(11)	8305(9)	4880(7)	73(3)
C(4)	7021(12)	9381(9)	5077(7)	77(3)
C(5)	8054(13)	10180(9)	5716(8)	80(3)
C(6)	9343(13)	9916(10)	6152(7)	82(3)
C(7)	9525(12)	8815(9)	5963(7)	71(3)
C(8)	7819(11)	5056(8)	4210(7)	70(3)
C(9)	6461(11)	4548(8)	3447(6)	66(2)
C(10)	4827(11)	4218(9)	3758(7)	73(3)
C(11)	3303(13)	5360(10)	3227(8)	80(3)
C(12)	3127(11)	4410(10)	2523(8)	74(3)
C(13)	3720(10)	3481(8)	2920(7)	65(2)
C(14)	4780(10)	3026(8)	2366(6)	64(2)
C(15)	6439(10)	3408(8)	2911(6)	59(2)
C(16)	6539(13)	2466(9)	3572(7)	77(3)
C(17)	7787(11)	3601(8)	2315(6)	66(2)
C(18)	7722(13)	2413(10)	1885(7)	80(3)
C(19)	8939(15)	2011(11)	1938(8)	96(3)
C(20)	7766(11)	4550(9)	1620(7)	76(3)
C(21)	8280(16)	4224(12)	724(8)	101(4)
C(22)	8930(13)	5794(10)	1991(9)	93(4)
C(23)	6111(11)	4623(9)	1381(7)	69(2)
C(24)	4746(11)	3455(9)	1401(7)	72(3)
C(25)	3146(12)	3597(11)	1034(7)	82(3)
C(26)	2839(11)	4498(9)	1657(7)	75(3)
C(27)	5330(70)	8030(30)	1830(30)	171(17)
Cl(1)	6377(18)	8686(19)	2519(9)	261(10)
Cl(2)	5610(30)	8746(16)	722(10)	274(9)

Table 3. Bond lengths [A] and angles [deg] for **282**.

Br(1)-C(5)	1.877(11)
O(1)-C(1)	1.202(12)
O(2)-C(1)	1.336(12)
O(2)-C(8)	1.461(11)
O(3)-C(11)	1.361(13)
O(3)-C(10)	1.457(12)
O(4)-C(11)	1.208(12)
O(5)-C(23)	1.193(11)

C(1)-C(2)	1.484(14)
C(2)-C(3)	1.378(14)
C(2)-C(7)	1.391(14)
C(3)-C(4)	1.365(13)
C(4)-C(5)	1.366(15)
C(5)-C(6)	1.394(16)
C(6)-C(7)	1.393(14)
C(8)-C(9)	1.532(13)
C(9)-C(10)	1.524(13)
C(9)-C(15)	1.548(12)
C(10)-C(13)	1.561(14)
C(11)-C(12)	1.481(15)
C(12)-C(26)	1.317(14)
C(12)-C(13)	1.488(14)
C(13)-C(14)	1.539(13)
C(14)-C(15)	1.539(12)
C(14)-C(24)	1.561(14)
C(15)-C(16)	1.544(13)
C(15)-C(17)	1.550(12)
C(17)-C(18)	1.515(14)
C(17)-C(20)	1.572(13)
C(18)-C(19)	1.320(15)
C(20)-C(23)	1.518(14)
C(20)-C(21)	1.551(15)
C(20)-C(22)	1.556(15)
C(23)-C(24)	1.536(14)
C(24)-C(25)	1.543(14)
C(25)-C(26)	1.510(15)
C(27)-Cl(1)	1.35(5)
C(27)-Cl(2)	1.91(4)
C(1)-O(2)-C(8)	117.7(7)
C(11)-O(3)-C(10)	110.6(8)
O(1)-C(1)-O(2)	122.3(9)
O(1)-C(1)-C(2)	127.2(9)
O(2)-C(1)-C(2)	110.5(9)
C(3)-C(2)-C(7)	120.3(9)
C(3)-C(2)-C(1)	123.5(9)
C(7)-C(2)-C(1)	116.2(9)
C(4)-C(3)-C(2)	120.1(10)
C(3)-C(4)-C(5)	121.0(10)
C(4)-C(5)-C(6)	119.8(10)
C(4)-C(5)-Br(1)	120.6(9)
C(6)-C(5)-Br(1)	119.6(9)
C(7)-C(6)-C(5)	119.7(10)

C(2)-C(7)-C(6)	119.1(10)
O(2)-C(8)-C(9)	104.6(7)
C(10)-C(9)-C(8)	113.2(8)
C(10)-C(9)-C(15)	104.0(7)
C(8)-C(9)-C(15)	116.6(7)
O(3)-C(10)-C(9)	113.9(8)
O(3)-C(10)-C(13)	106.7(7)
C(9)-C(10)-C(13)	102.5(8)
O(4)-C(11)-O(3)	121.3(11)
O(4)-C(11)-C(12)	130.2(11)
O(3)-C(11)-C(12)	108.3(9)
C(26)-C(12)-C(11)	125.0(10)
C(26)-C(12)-C(13)	124.3(10)
C(11)-C(12)-C(13)	109.0(9)
C(12)-C(13)-C(14)	115.7(8)
C(12)-C(13)-C(10)	100.1(8)
C(14)-C(13)-C(10)	106.3(7)
C(15)-C(14)-C(13)	106.7(7)
C(15)-C(14)-C(24)	114.5(7)
C(13)-C(14)-C(24)	111.8(7)
C(14)-C(15)-C(16)	109.8(8)
C(14)-C(15)-C(9)	101.6(7)
C(16)-C(15)-C(9)	108.8(8)
C(14)-C(15)-C(17)	112.9(7)
C(16)-C(15)-C(17)	109.4(7)
C(9)-C(15)-C(17)	114.2(7)
C(18)-C(17)-C(15)	109.3(7)
C(18)-C(17)-C(20)	113.2(8)
C(15)-C(17)-C(20)	112.5(7)
C(19)-C(18)-C(17)	123.8(11)
C(23)-C(20)-C(21)	105.6(9)
C(23)-C(20)-C(22)	109.8(9)
C(21)-C(20)-C(22)	107.6(9)
C(23)-C(20)-C(17)	111.7(8)
C(21)-C(20)-C(17)	111.6(9)
C(22)-C(20)-C(17)	110.4(9)
O(5)-C(23)-C(20)	122.8(9)
O(5)-C(23)-C(24)	121.2(9)
C(20)-C(23)-C(24)	115.4(8)
C(23)-C(24)-C(25)	110.7(9)
C(23)-C(24)-C(14)	109.6(8)
C(25)-C(24)-C(14)	113.4(8)
C(26)-C(25)-C(24)	107.7(8)
C(12)-C(26)-C(25)	117.4(10)

Cl(1)-C(27)-Cl(2)	113(2)

Symmetry transformations used to generate equivalent atoms:

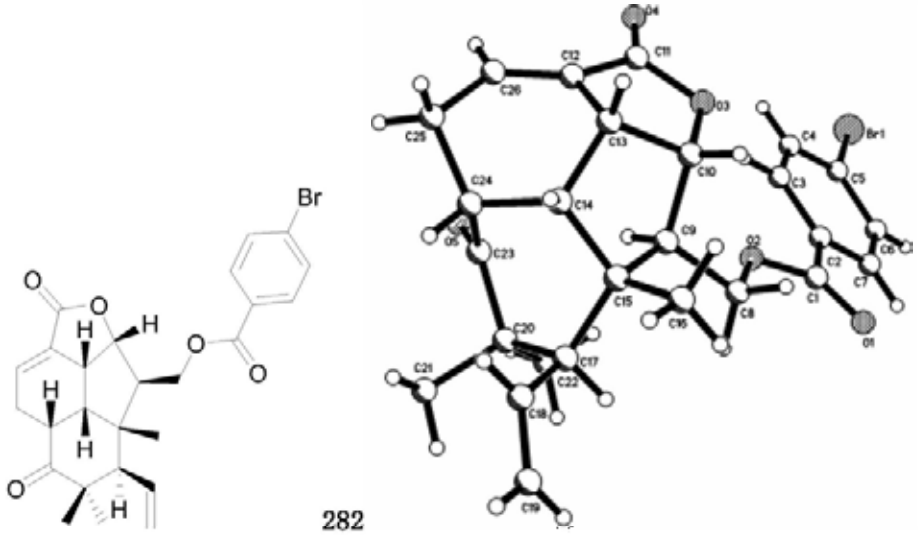
Table 4. Anisotropic displacement parameters (Å^2 x 10^3) for **282**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
Br(1)	111(1)	92(1)	107(1)	4(1)	13(1)	50(1)
O(1)	79(5)	90(5)	93(5)	3(4)	-19(4)	42(4)
O(1W)	310(30)	200(16)	260(20)	-38(15)	49(18)	-7(17)
O(2)	81(5)	82(4)	73(5)	-1(4)	-8(4)	37(3)
O(2W)	330(40)	580(70)	700(80)	400(70)	170(50)	-10(40)
O(3)	70(4)	111(5)	84(5)	-15(4)	1(4)	51(4)
O(4)	103(7)	130(7)	132(8)	-21(6)	-8(5)	70(6)
O(5)	70(5)	108(6)	99(6)	29(5)	12(4)	36(4)
C(1)	59(6)	74(6)	80(7)	-7(5)	8(5)	25(5)
C(2)	63(6)	72(5)	66(6)	5(5)	5(5)	22(4)
C(3)	54(5)	86(6)	78(7)	4(5)	-2(5)	26(5)
C(4)	68(6)	85(6)	89(8)	11(6)	3(5)	40(5)
C(5)	78(7)	85(7)	75(7)	17(6)	7(6)	25(5)
C(6)	80(7)	83(7)	77(7)	2(5)	2(6)	23(5)
C(7)	71(6)	83(6)	66(6)	6(5)	9(5)	37(5)
C(8)	64(6)	78(6)	75(7)	-2(5)	-3(5)	34(5)
C(9)	57(5)	79(6)	69(6)	3(5)	5(4)	30(4)
C(10)	61(6)	95(7)	67(6)	2(5)	0(5)	34(5)
C(11)	64(6)	99(7)	87(8)	6(6)	1(5)	45(6)
C(12)	55(6)	101(7)	77(7)	6(6)	12(5)	39(5)
C(13)	49(5)	74(5)	74(6)	7(5)	8(4)	23(4)
C(14)	54(5)	76(5)	65(6)	3(4)	4(4)	27(4)
C(15)	50(5)	76(5)	56(5)	0(4)	2(4)	29(4)
C(16)	73(7)	89(7)	77(7)	20(5)	11(5)	38(5)
C(17)	51(5)	80(6)	71(6)	8(5)	6(4)	26(4)
C(18)	73(7)	95(7)	85(8)	1(6)	3(5)	47(6)
C(19)	89(8)	105(8)	103(9)	2(7)	9(7)	47(7)
C(20)	56(6)	91(7)	84(7)	26(6)	9(5)	27(5)
C(21)	108(9)	130(10)	92(9)	32(7)	48(7)	62(8)
C(22)	63(6)	94(7)	123(10)	20(7)	11(6)	24(5)
C(23)	64(6)	86(6)	66(6)	17(5)	11(5)	35(5)
C(24)	56(6)	101(7)	65(6)	4(5)	0(4)	37(5)
C(25)	62(6)	117(8)	65(7)	7(6)	-3(5)	31(6)

C(26)	61(6)	91(7)	79(8)	11(6)	6(5)	34(5)
C(27)	270(50)	88(19)	150(30)	30(20)	20(30)	40(20)
Cl(1)	186(12)	390(20)	115(8)	35(11)	-19(8)	-29(13)
Cl(2)	370(30)	265(17)	156(12)	-56(11)	-51(13)	99(16)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **282**.

	x	y	z	U(eq)
H(3A)	6478	7768	4446	87
H(4A)	6186	9574	4772	93
H(6A)	10078	10471	6567	98
H(7A)	10364	8621	6261	85
H(8A)	7638	4588	4724	85
H(8B)	8823	5068	4022	85
H(9A)	6525	5164	3025	80
H(10A)	4774	3736	4274	88
H(13A)	2853	2822	3093	78
H(14A)	4367	2155	2315	77
H(16A)	5699	2340	3938	115
H(16B)	7543	2740	3945	115
H(16C)	6436	1733	3244	115
H(17A)	8794	3910	2711	79
H(18A)	6768	1938	1565	96
H(19A)	9908	2466	2253	115
H(19B)	8828	1273	1660	115
H(21A)	8251	4818	315	152
H(21B)	7569	3465	473	152
H(21C)	9339	4188	830	152
H(22A)	8636	6023	2545	140
H(22B)	8882	6368	1567	140
H(22C)	9990	5760	2089	140
H(24A)	4931	2854	1005	87
H(25A)	3187	3869	436	99
H(25B)	2302	2841	1006	99
H(26A)	2462	5091	1439	90
H(27A)	4259	7935	1966	205
H(27B)	5437	7249	1777	205


Br
O
O
H
H
O
O
H
H
O
H
O4
C11
C12
C26
O3
C25
C13
C4
Br1
C10
C3
C5
C24
C14
C9
O2
C2
C6
C7
O5
C23
C15
C16
C8
C1
O1
C20
C17
C21
C22
C18
C19

282

Table 1. Crystal data and structure refinement for 290.

Identification code	djq-1-094
Empirical formula	C21 H30 O5
Formula weight	362.45
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 6.780(2) A alpha = 76.160(6) deg.
	b = 11.908(4) A beta = 86.026(6) deg.
	c = 13.365(5) A gamma = 74.330(6) deg.
Volume	1008.8(6) A^3
Z, Calculated density	2, 1.193 Mg/m^3
Absorption coefficient	0.084 mm^-1
F(000)	392
Crystal size	0.40 x 0.30 x 0.20 mm
Theta range for data collection	1.82 to 28.10 deg.
Limiting indices	-8<=h<=8, -13<=k<=15, -17<=l<=14
Reflections collected / unique	6890 / 4772 [R(int) = 0.0283]
Completeness to theta = 28.10	97.2 %
Absorption correction	SADABS
Max. and min. transmission	1.0000 and 0.209078
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4772 / 0 / 235
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0717, wR2 = 0.1946
R indices (all data)	R1 = 0.1204, wR2 = 0.2311
Largest diff. peak and hole	0.485 and -0.316 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **290**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	1062(2)	3584(2)	948(1)	62(1)
O(2)	-1438(3)	3497(2)	0(2)	80(1)
O(3)	4459(3)	872(1)	1150(1)	66(1)
O(4)	2937(4)	-699(2)	1781(2)	82(1)
O(5)	3178(8)	3339(6)	5714(3)	316(5)
C(1)	3229(3)	3513(2)	833(2)	53(1)
C(2)	3715(4)	3283(2)	-210(2)	55(1)

C(3)	2042(4)	3292(2)	-674(2)	53(1)
C(4)	338(4)	3467(2)	72(2)	58(1)
C(5)	1848(5)	3170(2)	-1721(2)	68(1)
C(6)	207(6)	3105(3)	-2136(3)	90(1)
C(7)	4481(3)	2613(2)	1748(2)	45(1)
C(8)	3866(4)	1439(2)	1984(2)	52(1)
C(9)	4746(5)	-375(2)	1445(2)	76(1)
C(10)	1514(7)	-385(4)	976(4)	122(2)
C(11)	4524(3)	3159(2)	2700(2)	48(1)
C(12)	5779(4)	2173(2)	3591(2)	52(1)
C(13)	5776(5)	2507(3)	4659(2)	71(1)
C(14)	3711(6)	3331(4)	4870(3)	106(1)
C(15)	2348(5)	4118(3)	4051(3)	84(1)
C(16)	2359(4)	3593(2)	3119(2)	63(1)
C(17)	5506(5)	4229(2)	2340(2)	73(1)
C(18)	7921(4)	1635(3)	3247(2)	65(1)
C(19)	8757(5)	505(3)	3313(3)	92(1)
C(20)	7435(7)	3110(5)	4791(3)	122(2)
C(21)	6117(7)	1353(4)	5496(3)	110(1)

Table 3. Bond lengths [A] and angles [deg] for **290**.

O(1)-C(4)	1.351(3)
O(1)-C(1)	1.448(3)
O(2)-C(4)	1.204(3)
O(3)-C(9)	1.405(3)
O(3)-C(8)	1.418(3)
O(4)-C(9)	1.397(4)
O(4)-C(10)	1.408(5)
O(5)-C(14)	1.162(4)
C(1)-C(2)	1.482(4)
C(1)-C(7)	1.545(3)
C(2)-C(3)	1.327(4)
C(3)-C(5)	1.459(4)
C(3)-C(4)	1.477(4)
C(5)-C(6)	1.306(4)
C(7)-C(8)	1.522(3)
C(7)-C(11)	1.567(3)
C(11)-C(16)	1.533(3)
C(11)-C(17)	1.555(3)
C(11)-C(12)	1.566(3)
C(12)-C(18)	1.509(4)

C(12)-C(13)	1.570(4)
C(13)-C(21)	1.524(5)
C(13)-C(20)	1.528(4)
C(13)-C(14)	1.529(5)
C(14)-C(15)	1.453(5)
C(15)-C(16)	1.520(4)
C(18)-C(19)	1.295(4)
C(4)-O(1)-C(1)	109.68(19)
C(9)-O(3)-C(8)	112.86(19)
C(9)-O(4)-C(10)	111.9(3)
O(1)-C(1)-C(2)	103.41(19)
O(1)-C(1)-C(7)	111.94(18)
C(2)-C(1)-C(7)	117.75(19)
C(3)-C(2)-C(1)	111.0(2)
C(2)-C(3)-C(5)	128.1(2)
C(2)-C(3)-C(4)	106.9(2)
C(5)-C(3)-C(4)	125.0(2)
O(2)-C(4)-O(1)	120.8(3)
O(2)-C(4)-C(3)	130.3(3)
O(1)-C(4)-C(3)	108.9(2)
C(6)-C(5)-C(3)	126.7(3)
C(8)-C(7)-C(1)	110.51(19)
C(8)-C(7)-C(11)	115.24(18)
C(1)-C(7)-C(11)	113.50(18)
O(3)-C(8)-C(7)	109.22(18)
O(4)-C(9)-O(3)	112.8(2)
C(16)-C(11)-C(17)	110.0(2)
C(16)-C(11)-C(12)	107.0(2)
C(17)-C(11)-C(12)	111.6(2)
C(16)-C(11)-C(7)	111.22(19)
C(17)-C(11)-C(7)	107.53(19)
C(12)-C(11)-C(7)	109.59(18)
C(18)-C(12)-C(11)	111.7(2)
C(18)-C(12)-C(13)	111.7(2)
C(11)-C(12)-C(13)	117.1(2)
C(21)-C(13)-C(20)	106.9(3)
C(21)-C(13)-C(14)	107.7(3)
C(20)-C(13)-C(14)	107.4(3)
C(21)-C(13)-C(12)	107.9(3)
C(20)-C(13)-C(12)	115.4(2)
C(14)-C(13)-C(12)	111.2(2)
O(5)-C(14)-C(15)	117.5(4)
O(5)-C(14)-C(13)	119.8(4)
C(15)-C(14)-C(13)	122.7(3)

C(14)-C(15)-C(16)	113.8(3)
C(15)-C(16)-C(11)	112.5(2)
C(19)-C(18)-C(12)	125.9(3)

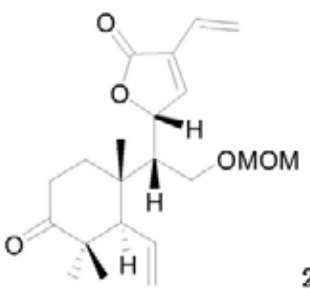
Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **290**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	48(1)	75(1)	58(1)	-17(1)	0(1)	-5(1)
O(2)	50(1)	99(2)	86(2)	-15(1)	-5(1)	-16(1)
O(3)	106(2)	48(1)	45(1)	-13(1)	13(1)	-23(1)
O(4)	125(2)	69(1)	60(1)	-11(1)	0(1)	-46(1)
O(5)	262(6)	462(9)	64(2)	-59(4)	18(3)	168(6)
C(1)	51(1)	48(1)	57(2)	-6(1)	0(1)	-14(1)
C(2)	51(1)	55(1)	48(1)	6(1)	4(1)	-14(1)
C(3)	56(1)	45(1)	49(1)	2(1)	-4(1)	-9(1)
C(4)	52(2)	53(1)	60(2)	-6(1)	-4(1)	-7(1)
C(5)	77(2)	60(2)	55(2)	-3(1)	-7(1)	-4(1)
C(6)	96(2)	97(2)	73(2)	-25(2)	-18(2)	-6(2)
C(7)	45(1)	44(1)	44(1)	-6(1)	5(1)	-13(1)
C(8)	69(2)	46(1)	43(1)	-13(1)	9(1)	-18(1)
C(9)	112(2)	48(2)	63(2)	-18(1)	7(2)	-12(2)
C(10)	157(4)	129(3)	104(3)	-29(3)	-26(3)	-69(3)
C(11)	49(1)	47(1)	51(1)	-12(1)	6(1)	-18(1)
C(12)	52(1)	62(1)	45(1)	-11(1)	5(1)	-22(1)
C(13)	79(2)	95(2)	47(2)	-23(2)	7(1)	-33(2)
C(14)	114(3)	142(3)	48(2)	-33(2)	20(2)	-4(2)
C(15)	75(2)	97(2)	96(3)	-57(2)	22(2)	-23(2)
C(16)	55(2)	67(2)	75(2)	-36(1)	7(1)	-13(1)
C(17)	90(2)	63(2)	76(2)	-12(1)	1(2)	-40(2)
C(18)	53(2)	84(2)	56(2)	-14(1)	-3(1)	-15(1)
C(19)	67(2)	95(3)	96(3)	-19(2)	-4(2)	6(2)
C(20)	150(4)	175(4)	89(3)	-63(3)	1(3)	-92(3)
C(21)	148(4)	126(3)	50(2)	2(2)	-16(2)	-42(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **290**.

	x	y	z	U(eq)
H(1A)	3406	4306	819	63
H(2A)	5020	3151	-500	66
H(5A)	3013	3136	-2135	82
H(6A)	-998	3135	-1755	109
H(6B)	244	3028	-2814	109
H(7A)	5900	2421	1500	54
H(8A)	4529	919	2611	62
H(8B)	2395	1593	2087	62
H(9A)	5292	-721	863	91
H(9B)	5748	-707	1994	91
H(10A)	292	-617	1237	183
H(10B)	2097	-790	442	183
H(10C)	1183	465	702	183
H(12A)	5102	1522	3722	62
H(15A)	2742	4865	3831	101
H(15B)	964	4301	4323	101
H(16A)	1531	4196	2580	75
H(16B)	1740	2925	3310	75
H(17A)	4700	4816	1796	110
H(17B)	6872	3947	2093	110
H(17C)	5552	4584	2909	110
H(18A)	8711	2161	2961	78
H(19A)	8023	-54	3594	110
H(19B)	10092	252	3081	110
H(20A)	7306	3287	5460	183
H(20B)	7280	3840	4270	183
H(20C)	8760	2581	4725	183
H(21A)	6142	1533	6157	165
H(21B)	7399	814	5377	165
H(21C)	5025	985	5481	165



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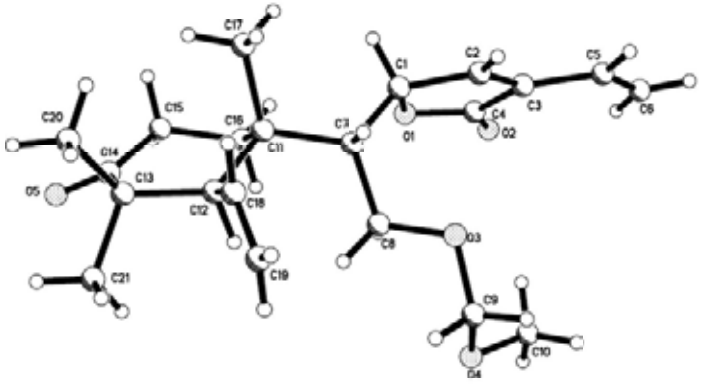


Table 1. Crystal data and structure refinement for **291**.

Identification code	DJQ-2-023
Empirical formula	C21 H28 O5
Formula weight	360.43
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 6.9604(10) A alpha = 90 deg. b = 22.356(3) A beta = 100.420(3) deg. c = 13.4868(19) A gamma = 90 deg.
Volume	2064.0(5) A^3
Z, Calculated density	4, 1.160 Mg/m^3
Absorption coefficient	0.082 mm^-1
F(000)	776
Crystal size	0.40 x 0.30 x 0.20 mm
Theta range for data collection	1.79 to 28.05 deg.
Limiting indices	-8<=h<=9, -19<=k<=29, -17<=l<=17
Reflections collected / unique	13885 / 4969 [R(int) = 0.0529]
Completeness to theta = 28.05	99.2 %
Absorption correction	SADABS
Max. and min. transmission	1.0000 and 0.503189
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4969 / 31 / 254
Goodness-of-fit on F^2	0.991
Final R indices [I>2sigma(I)]	R1 = 0.0650, wR2 = 0.1772
R indices (all data)	R1 = 0.1621, wR2 = 0.2363
Largest diff. peak and hole	0.360 and -0.196 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **291**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	8294(5)	4095(2)	5229(2)	66(1)
C(2)	6598(4)	3663(1)	5084(2)	61(1)
C(3)	6196(4)	3491(1)	6145(2)	55(1)
C(4)	5913(4)	4029(1)	6857(2)	51(1)
C(5)	7203(4)	4542(1)	6684(2)	61(1)

C(6)	8304(5)	4566(2)	5976(2)	70(1)
C(7)	4904(5)	3987(2)	4397(2)	81(1)
C(8)	7097(6)	3099(2)	4541(3)	89(1)
C(9)	4615(5)	3035(2)	6081(2)	77(1)
C(10)	4896(8)	2494(2)	6442(3)	114(2)
C(11)	3790(4)	4253(2)	6701(2)	75(1)
C(12)	6545(4)	3795(1)	7970(2)	50(1)
C(13)	8743(4)	3717(1)	8267(2)	53(1)
C(14)	11047(6)	3142(2)	9354(3)	99(1)
C(15)	11588(9)	2430(3)	8223(5)	155(2)
C(16)	5731(4)	4140(1)	8783(2)	62(1)
C(17)	6316(5)	3897(2)	9813(2)	79(1)
C(18)	7233(6)	4293(2)	10432(3)	91(1)
C(19)	7301(5)	4843(2)	9858(3)	89(1)
O(1)	9593(4)	4070(1)	4720(2)	103(1)
O(2)	9085(3)	3218(1)	8926(2)	69(1)
O(3)	12189(4)	2980(2)	8678(3)	124(1)
O(4)	6430(3)	4750(1)	8869(2)	73(1)
O(5)	7946(4)	5335(1)	10109(2)	117(1)
C(20)	7804(13)	4109(4)	11553(6)	89(4)
C(21)	8883(16)	4465(5)	12165(8)	122(5)
C(20')	8379(15)	4448(5)	11461(6)	93(4)
C(21')	8720(30)	3980(6)	12030(11)	157(6)

Table 3. Bond lengths [A] and angles [deg] for **291**.

C(1)-O(1)	1.231(3)
C(1)-C(6)	1.456(4)
C(1)-C(2)	1.510(4)
C(2)-C(8)	1.530(4)
C(2)-C(7)	1.543(4)
C(2)-C(3)	1.554(4)
C(3)-C(9)	1.493(4)
C(3)-C(4)	1.572(4)
C(4)-C(5)	1.501(4)
C(4)-C(11)	1.538(4)
C(4)-C(12)	1.576(4)
C(5)-C(6)	1.329(4)
C(9)-C(10)	1.305(5)
C(12)-C(13)	1.520(4)
C(12)-C(16)	1.531(4)

C(13)-O(2)	1.419(3)
C(14)-O(3)	1.362(5)
C(14)-O(2)	1.394(4)
C(15)-O(3)	1.403(6)
C(16)-O(4)	1.446(4)
C(16)-C(17)	1.478(4)
C(17)-C(18)	1.302(5)
C(18)-C(19)	1.458(6)
C(18)-C(20')	1.511(8)
C(18)-C(20)	1.548(8)
C(19)-O(5)	1.213(4)
C(19)-O(4)	1.377(4)
C(20)-C(21)	1.286(8)
C(20')-C(21')	1.294(8)
O(1)-C(1)-C(6)	120.4(3)
O(1)-C(1)-C(2)	122.4(3)
C(6)-C(1)-C(2)	117.2(3)
C(1)-C(2)-C(8)	110.4(3)
C(1)-C(2)-C(7)	105.8(2)
C(8)-C(2)-C(7)	108.3(3)
C(1)-C(2)-C(3)	107.8(2)
C(8)-C(2)-C(3)	109.4(2)
C(7)-C(2)-C(3)	115.1(2)
C(9)-C(3)-C(2)	111.7(2)
C(9)-C(3)-C(4)	112.7(2)
C(2)-C(3)-C(4)	115.9(2)
C(5)-C(4)-C(11)	108.5(2)
C(5)-C(4)-C(3)	110.2(2)
C(11)-C(4)-C(3)	112.9(2)
C(5)-C(4)-C(12)	109.2(2)
C(11)-C(4)-C(12)	109.5(2)
C(3)-C(4)-C(12)	106.5(2)
C(6)-C(5)-C(4)	125.5(3)
C(5)-C(6)-C(1)	122.5(3)
C(10)-C(9)-C(3)	123.6(4)
C(13)-C(12)-C(16)	110.8(2)
C(13)-C(12)-C(4)	112.5(2)
C(16)-C(12)-C(4)	116.1(2)
O(2)-C(13)-C(12)	107.6(2)
O(3)-C(14)-O(2)	113.7(3)
O(4)-C(16)-C(17)	103.9(3)
O(4)-C(16)-C(12)	111.6(2)
C(17)-C(16)-C(12)	114.4(3)
C(18)-C(17)-C(16)	111.8(4)

C(17)-C(18)-C(19)	107.0(3)
C(17)-C(18)-C(20')	149.4(6)
C(19)-C(18)-C(20')	103.4(5)
C(17)-C(18)-C(20)	117.0(5)
C(19)-C(18)-C(20)	135.7(5)
C(20')-C(18)-C(20)	33.2(4)
O(5)-C(19)-O(4)	118.9(5)
O(5)-C(19)-C(18)	131.5(4)
O(4)-C(19)-C(18)	109.6(3)
C(14)-O(2)-C(13)	113.4(2)
C(14)-O(3)-C(15)	111.2(4)
C(19)-O(4)-C(16)	107.6(3)
C(21)-C(20)-C(18)	118.6(10)
C(21')-C(20')-C(18)	111.7(12)

Symmetry transformations used to generate equivalent atoms:

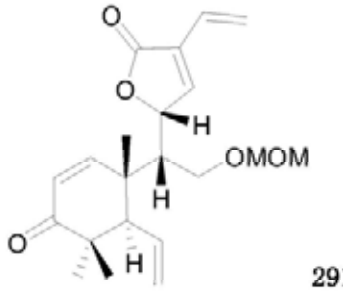
Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **291**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	68(2)	82(2)	51(2)	10(2)	14(2)	3(2)
C(2)	63(2)	68(2)	52(2)	-4(1)	10(1)	3(2)
C(3)	55(2)	57(2)	50(2)	-3(1)	7(1)	1(1)
C(4)	45(2)	56(2)	50(2)	-4(1)	4(1)	2(1)
C(5)	68(2)	49(2)	66(2)	0(1)	8(2)	3(1)
C(6)	71(2)	69(2)	68(2)	9(2)	11(2)	-12(2)
C(7)	79(2)	101(3)	58(2)	6(2)	0(2)	6(2)
C(8)	111(3)	91(3)	70(2)	-14(2)	29(2)	9(2)
C(9)	91(3)	79(2)	62(2)	-18(2)	14(2)	-26(2)
C(10)	164(4)	81(3)	95(3)	-13(2)	23(3)	-55(3)
C(11)	54(2)	101(2)	67(2)	-5(2)	1(2)	16(2)
C(12)	44(2)	57(2)	48(2)	-6(1)	8(1)	-5(1)
C(13)	50(2)	58(2)	50(2)	2(1)	7(1)	-2(1)
C(14)	74(3)	112(3)	103(3)	36(2)	-8(2)	6(2)
C(15)	134(5)	137(5)	215(7)	28(5)	84(5)	46(4)
C(16)	46(2)	83(2)	58(2)	-13(2)	11(1)	-5(2)
C(17)	75(2)	111(3)	54(2)	-8(2)	23(2)	2(2)
C(18)	80(3)	140(4)	54(2)	-19(2)	12(2)	25(2)
C(19)	47(2)	129(3)	91(3)	-66(3)	13(2)	2(2)

O(1)	87(2)	150(3)	81(2)	-6(2)	37(2)	-17(2)
O(2)	53(1)	77(1)	74(1)	24(1)	7(1)	4(1)
O(3)	68(2)	131(3)	179(3)	51(2)	40(2)	20(2)
O(4)	65(1)	77(1)	77(2)	-25(1)	15(1)	-1(1)
O(5)	81(2)	130(2)	137(2)	-80(2)	16(2)	-8(2)
C(20)	81(5)	96(7)	83(6)	-9(5)	-5(4)	-1(5)
C(21)	144(7)	147(8)	73(6)	-28(5)	9(5)	-9(6)
C(20')	102(7)	120(7)	58(5)	-21(5)	14(5)	0(5)
C(21')	191(10)	167(9)	105(8)	19(7)	5(7)	-7(8)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **291**.

	x	y	z	U(eq)
H(3A)	7385	3288	6480	65
H(5A)	7235	4871	7108	74
H(6A)	9111	4895	5957	84
H(7A)	5277	4076	3761	121
H(7B)	4612	4353	4713	121
H(7C)	3770	3735	4288	121
H(8A)	8148	2891	4960	134
H(8B)	7486	3209	3918	134
H(8C)	5971	2844	4405	134
H(9A)	3361	3141	5766	93
H(10A)	6136	2375	6761	136
H(10B)	3857	2227	6382	136
H(11A)	3700	4581	7151	113
H(11B)	2953	3934	6838	113
H(11C)	3394	4385	6017	113
H(12A)	5998	3391	7972	60
H(13A)	9315	3648	7672	64
H(13B)	9327	4074	8603	64
H(14A)	11542	3512	9675	119
H(14B)	11147	2837	9873	119
H(15A)	12408	2329	7748	233
H(15B)	10257	2461	7880	233
H(15C)	11686	2125	8731	233
H(16A)	4301	4143	8609	74
H(17A)	6061	3508	9997	94



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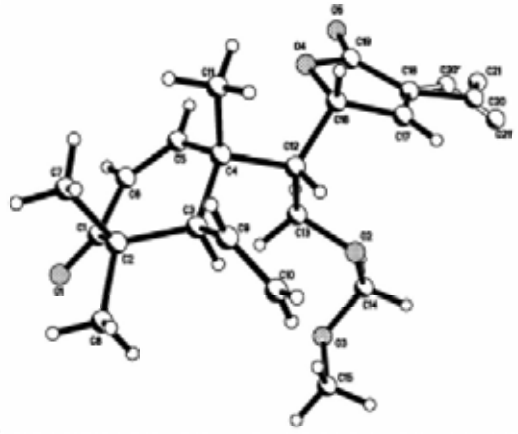


Table 1. Crystal data and structure refinement for **293**.

Identification code	djq-2-024byproduct
Empirical formula	C19 H24 O4
Formula weight	316.38
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 14.087(3) A alpha = 90 deg.
	b = 8.1861(16) A beta = 90 deg.
	c = 28.200(5) A gamma = 90 deg.
Volume	3251.9(11) A^3
Z, Calculated density	8, 1.292 Mg/m^3
Absorption coefficient	0.089 mm^-1
F(000)	1360
Crystal size	0.40 x 0.30 x 0.20 mm
Theta range for data collection	1.44 to 28.04 deg.
Limiting indices	-13<=h<=18, -9<=k<=10, -37<=l<=32
Reflections collected / unique	20682 / 3941 [R(int) = 0.1070]
Completeness to theta = 28.04	100.0 %
Absorption correction	SADABS
Max. and min. transmission	1.0000 and 0.726354
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3941 / 0 / 208
Goodness-of-fit on F^2	0.948
Final R indices [I>2sigma(I)]	R1 = 0.0578, wR2 = 0.1459
R indices (all data)	R1 = 0.1618, wR2 = 0.2161
Largest diff. peak and hole	0.466 and -0.248 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **293**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	7305(2)	7274(3)	4477(1)	50(1)
O(2)	8781(2)	7257(3)	4181(1)	58(1)
O(3)	5468(2)	7952(4)	5225(1)	73(1)
O(4)	5419(2)	3986(4)	2842(1)	82(1)
C(1)	7946(2)	6933(4)	4133(1)	43(1)
C(2)	7447(2)	6274(4)	3717(1)	41(1)
C(3)	6449(2)	6040(4)	3857(1)	33(1)

C(4)	6369(2)	6548(4)	4368(1)	39(1)
C(5)	4911(2)	7568(5)	4822(1)	52(1)
C(6)	5526(2)	7754(4)	4386(1)	40(1)
C(7)	5007(2)	7582(3)	3888(1)	35(1)
C(8)	5884(2)	7309(4)	3583(1)	35(1)
C(9)	5840(2)	6695(4)	3077(1)	44(1)
C(10)	6874(2)	6359(5)	2890(1)	61(1)
C(11)	7651(2)	6468(5)	3257(1)	55(1)
C(12)	5213(2)	5195(5)	3070(1)	47(1)
C(13)	4272(2)	5250(4)	3347(1)	45(1)
C(14)	4358(2)	6043(4)	3855(1)	39(1)
C(15)	4511(2)	9190(4)	3761(1)	54(1)
C(16)	3910(3)	3503(5)	3408(1)	74(1)
C(17)	3587(3)	6169(5)	3015(1)	70(1)
C(18)	3384(2)	6314(5)	4068(1)	50(1)
C(19)	2975(3)	5387(6)	4390(1)	67(1)

Table 3. Bond lengths [A] and angles [deg] for **293**.

O(1)-C(1)	1.354(4)
O(1)-C(4)	1.480(4)
O(2)-C(1)	1.213(3)
O(3)-C(5)	1.418(4)
O(4)-C(12)	1.215(4)
C(1)-C(2)	1.470(4)
C(2)-C(11)	1.339(4)
C(2)-C(3)	1.473(4)
C(3)-C(4)	1.505(4)
C(3)-C(8)	1.519(4)
C(4)-C(6)	1.545(4)
C(5)-C(6)	1.511(4)
C(6)-C(7)	1.590(4)
C(7)-C(8)	1.521(4)
C(7)-C(15)	1.533(4)
C(7)-C(14)	1.560(4)
C(8)-C(9)	1.514(4)
C(9)-C(12)	1.513(5)
C(9)-C(10)	1.573(4)
C(10)-C(11)	1.509(5)
C(12)-C(13)	1.540(4)
C(13)-C(16)	1.527(5)
C(13)-C(17)	1.541(4)

C(13)-C(14)	1.577(4)
C(14)-C(18)	1.514(4)
C(18)-C(19)	1.315(5)
C(1)-O(1)-C(4)	111.3(2)
O(2)-C(1)-O(1)	121.4(3)
O(2)-C(1)-C(2)	129.3(3)
O(1)-C(1)-C(2)	109.2(2)
C(11)-C(2)-C(1)	128.8(3)
C(11)-C(2)-C(3)	118.7(3)
C(1)-C(2)-C(3)	106.9(2)
C(2)-C(3)-C(4)	107.0(2)
C(2)-C(3)-C(8)	106.0(2)
C(4)-C(3)-C(8)	105.0(2)
O(1)-C(4)-C(3)	104.1(2)
O(1)-C(4)-C(6)	115.0(2)
C(3)-C(4)-C(6)	105.4(2)
O(3)-C(5)-C(6)	108.3(3)
C(5)-C(6)-C(4)	113.7(3)
C(5)-C(6)-C(7)	116.5(2)
C(4)-C(6)-C(7)	105.6(2)
C(8)-C(7)-C(15)	111.4(2)
C(8)-C(7)-C(14)	108.9(2)
C(15)-C(7)-C(14)	114.4(2)
C(8)-C(7)-C(6)	98.0(2)
C(15)-C(7)-C(6)	109.8(2)
C(14)-C(7)-C(6)	113.1(2)
C(9)-C(8)-C(3)	105.9(2)
C(9)-C(8)-C(7)	123.2(2)
C(3)-C(8)-C(7)	103.8(2)
C(12)-C(9)-C(8)	107.8(2)
C(12)-C(9)-C(10)	113.2(3)
C(8)-C(9)-C(10)	109.6(2)
C(11)-C(10)-C(9)	115.6(3)
C(2)-C(11)-C(10)	120.1(3)
O(4)-C(12)-C(9)	121.9(3)
O(4)-C(12)-C(13)	119.9(3)
C(9)-C(12)-C(13)	118.2(3)
C(16)-C(13)-C(12)	108.5(3)
C(16)-C(13)-C(17)	108.5(3)
C(12)-C(13)-C(17)	104.1(3)
C(16)-C(13)-C(14)	108.0(3)
C(12)-C(13)-C(14)	114.0(2)
C(17)-C(13)-C(14)	113.6(3)
C(18)-C(14)-C(7)	112.9(2)

C(18)-C(14)-C(13)	110.6(2)
C(7)-C(14)-C(13)	115.5(2)
C(19)-C(18)-C(14)	125.8(3)

Symmetry transformations used to generate equivalent atoms:

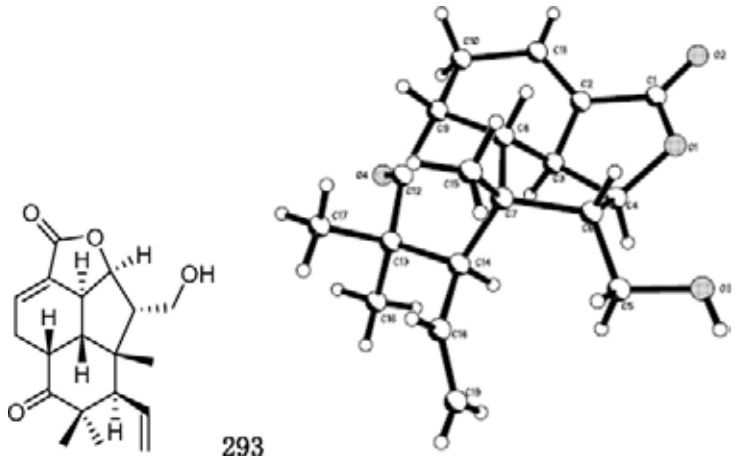
Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **293**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	37(1)	70(2)	44(1)	-7(1)	-8(1)	-2(1)
O(2)	34(1)	70(2)	72(2)	8(1)	-11(1)	-2(1)
O(3)	60(2)	117(2)	41(1)	-21(1)	1(1)	-1(2)
O(4)	67(2)	93(2)	86(2)	-49(2)	2(2)	0(2)
C(1)	32(2)	46(2)	50(2)	8(2)	-4(1)	3(1)
C(2)	36(2)	44(2)	43(2)	-1(1)	-1(1)	7(1)
C(3)	30(1)	38(2)	32(2)	-1(1)	0(1)	3(1)
C(4)	38(2)	44(2)	34(2)	1(1)	-3(1)	-2(1)
C(5)	46(2)	75(2)	34(2)	-16(2)	5(1)	-6(2)
C(6)	36(2)	45(2)	38(2)	-7(1)	-1(1)	-2(1)
C(7)	31(1)	39(2)	35(2)	-2(1)	-2(1)	4(1)
C(8)	34(2)	39(2)	33(2)	3(1)	0(1)	3(1)
C(9)	38(2)	62(2)	32(2)	4(2)	-1(1)	6(2)
C(10)	47(2)	97(3)	38(2)	-8(2)	7(2)	2(2)
C(11)	36(2)	80(3)	50(2)	-6(2)	10(2)	5(2)
C(12)	43(2)	63(2)	36(2)	-11(2)	-10(1)	6(2)
C(13)	41(2)	55(2)	40(2)	-2(2)	-9(1)	-1(2)
C(14)	34(2)	48(2)	34(2)	1(1)	-3(1)	-1(1)
C(15)	51(2)	45(2)	67(2)	3(2)	1(2)	12(2)
C(16)	88(3)	65(3)	68(3)	-15(2)	-1(2)	-30(2)
C(17)	46(2)	113(3)	50(2)	4(2)	-19(2)	13(2)
C(18)	31(2)	66(2)	52(2)	-1(2)	-3(1)	1(2)
C(19)	48(2)	96(3)	58(2)	-4(2)	11(2)	-16(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **293**.

	x	y	z	U(eq)

H(3A)	5128	7976	5461	109
H(3B)	6224	4924	3801	40
H(4A)	6247	5599	4571	46
H(5A)	4370	8299	4802	62
H(5B)	4677	6457	4844	62
H(6A)	5797	8856	4397	48
H(8A)	6252	8326	3583	42
H(9A)	5548	7540	2879	53
H(10A)	6889	5275	2751	73
H(10B)	7012	7135	2639	73
H(11A)	8273	6671	3163	66
H(14A)	4662	5214	4055	46
H(15A)	4197	9078	3461	82
H(15B)	4973	10050	3742	82
H(15C)	4052	9451	4001	82
H(16A)	3843	3000	3103	111
H(16B)	3306	3521	3566	111
H(16C)	4355	2891	3595	111
H(17A)	3566	5627	2713	104
H(17B)	3806	7270	2972	104
H(17C)	2963	6182	3152	104
H(18A)	3044	7218	3962	60
H(19A)	3288	4471	4506	81
H(19B)	2372	5647	4501	81



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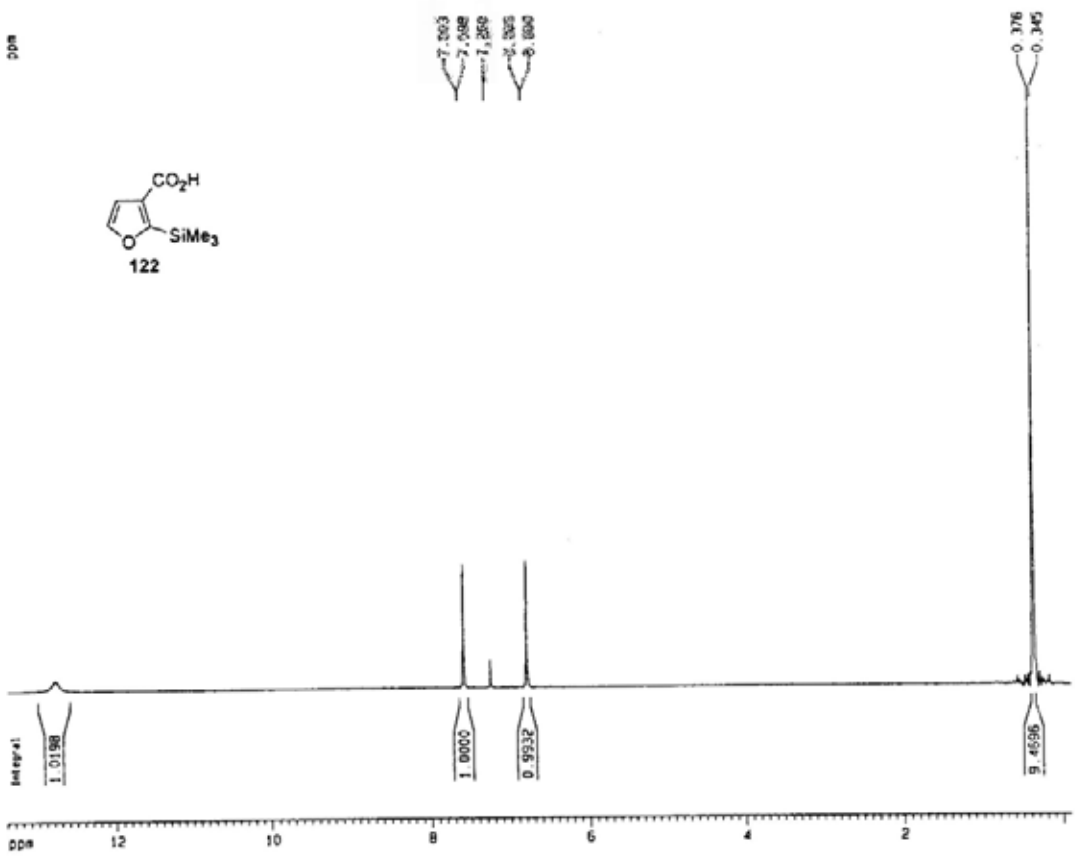
Appendix II

Index of NMR spectra of compounds

1H



Current Data Parameters
NAME dongjq-11-H1
EXPNO 1
PROCNO 1

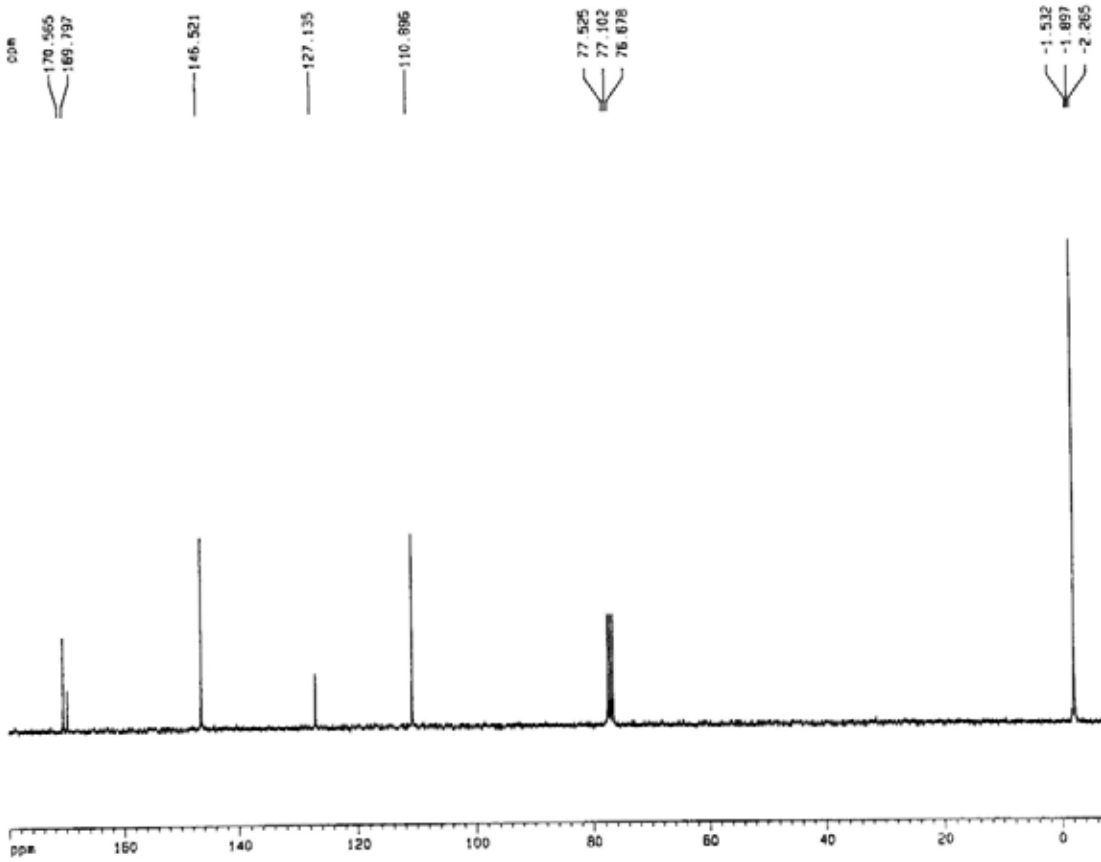
F2 - Acquisition Parameters
Date_ 20081009
Time 10.57
INSTRUM spx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 64
DW 55.600 usec
DE 79.43 usec
TE 295.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 300.1300055 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 35.00 cm
F1P 13.400 ppm
F1 4021.74 Hz
F2P -0.100 ppm
F2 -30.01 Hz
PPMCM 0.61364 ppm/cm
HZCM 184.17068 Hz/cm

C13



Current Data Parameters
NAME dongjq-11-C13
EXPNO 1
PROCNO 1

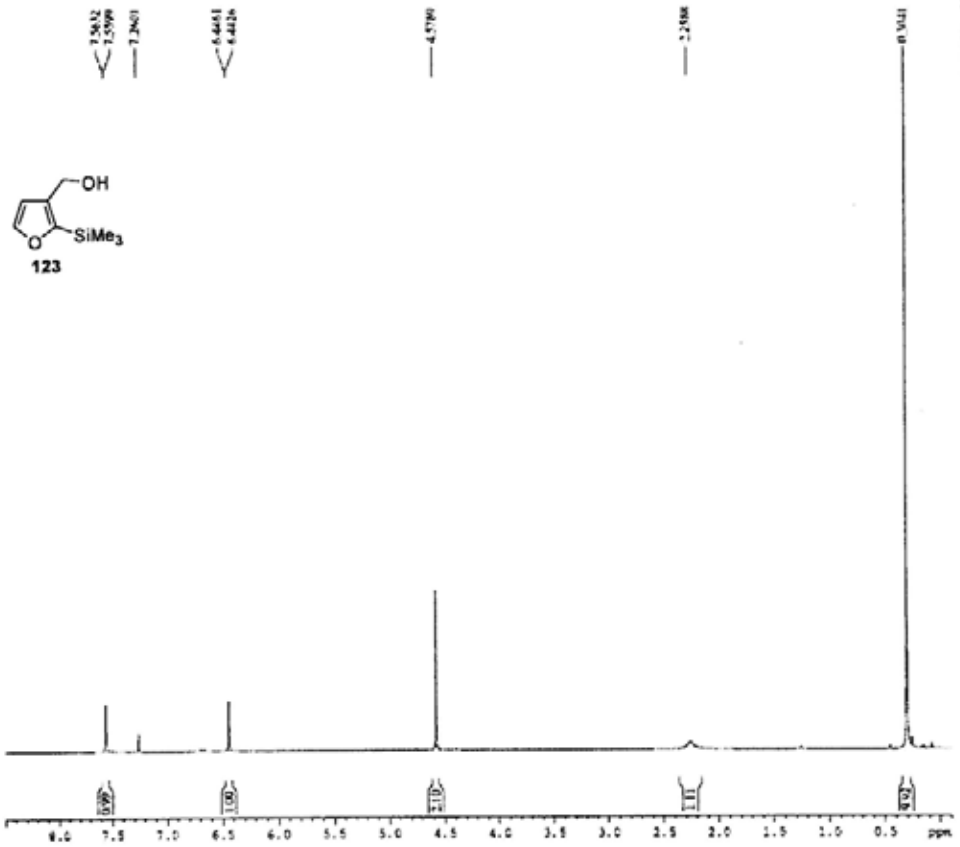
F2 - Acquisition Parameters
Date_ 20081009
Time 11.02
INSTRUM spx300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 126
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 295.2 K
D1 1.00000000 sec
D11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== 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 75.4677431 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
CY 10.00 cm
F1P 180.000 ppm
F1 13584.19 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 8.26087 ppm/cm
HZCM 623.42920 Hz/cm

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Bruker Advance III 400

NAME          donajq-12-H1
EXPNO                    1
PROCNO                   1
Date_          20081010
Time                12.48
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     0
SWH           10000.000 Hz
FIDRES        0.152588 Hz
AQ            3.2768500 sec
RG                    64
DW               50.000 usec
DE                4.50 usec
TE                295.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                1H
P1                14.63 usec
PL1               0.00 dB
PLW1         8.31434441 W
SFO1       400.1316005 MHz
SI                 65536
SF         400.1320049 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
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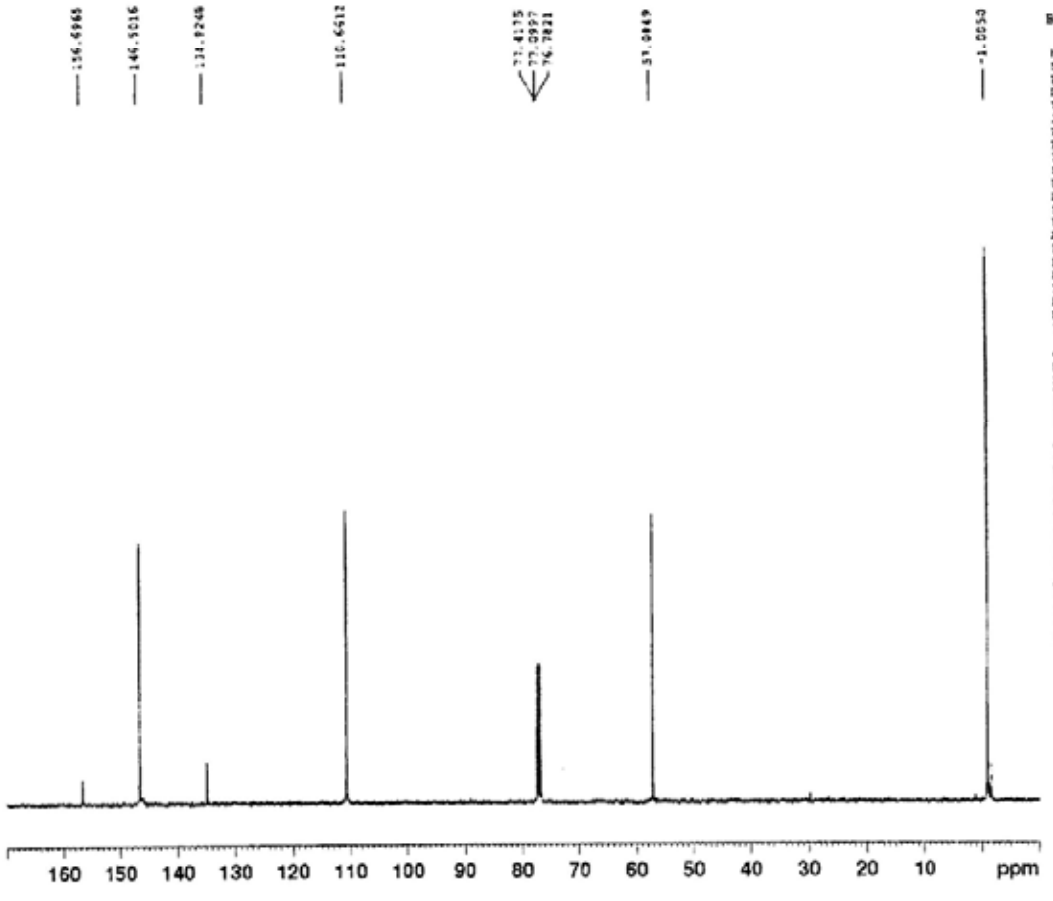


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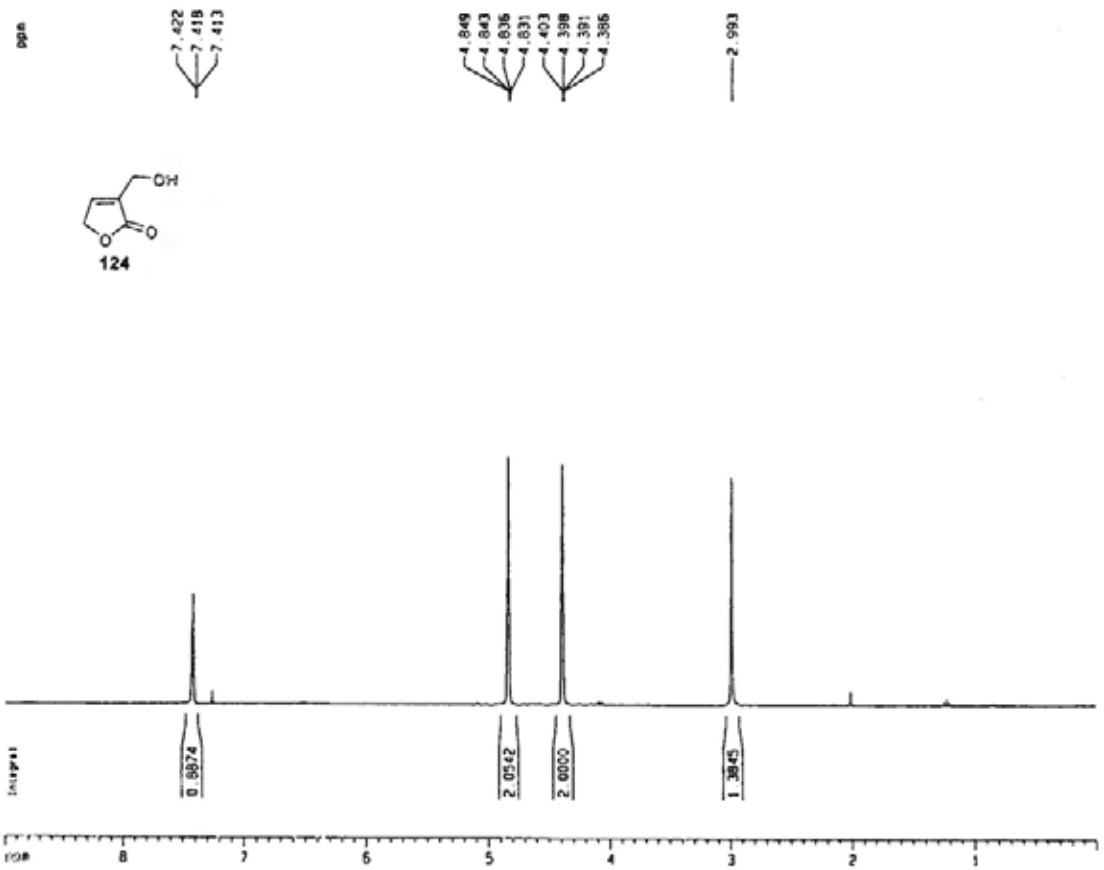
Bruker Advance III 400

NAME          donajq-12-C13
EXPNO                    1
PROCNO                   1
Date_          20081010
Time                12.09
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                131072
SOLVENT            CDCl3
NS                   394
DS                     0
SWH          29761.904 Hz
FIDRES        0.227065 Hz
AQ            2.2020995 sec
RG                   203
DW               16.800 usec
DE                6.50 usec
TE                295.9 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                13C
P1                9.60 usec
PL1              -0.40 dB
PLW1        61.26166943 W
SFO1       100.6228180 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             90.00 usec
PL2               0.00 dB
PL12             15.46 dB
PLW2         8.31434441 W
PLW12        0.22865611 W
SFO2       400.1320007 MHz
SI                131072
SF         100.6227930 MHz
WDW                   EM
SSB                    0
LB                3.00 Hz
GB                     0
PC                1.40
```

1H



Current Data Parameters
NAME dongja-14-2-H1
EXPNO 1
PROCNO 1

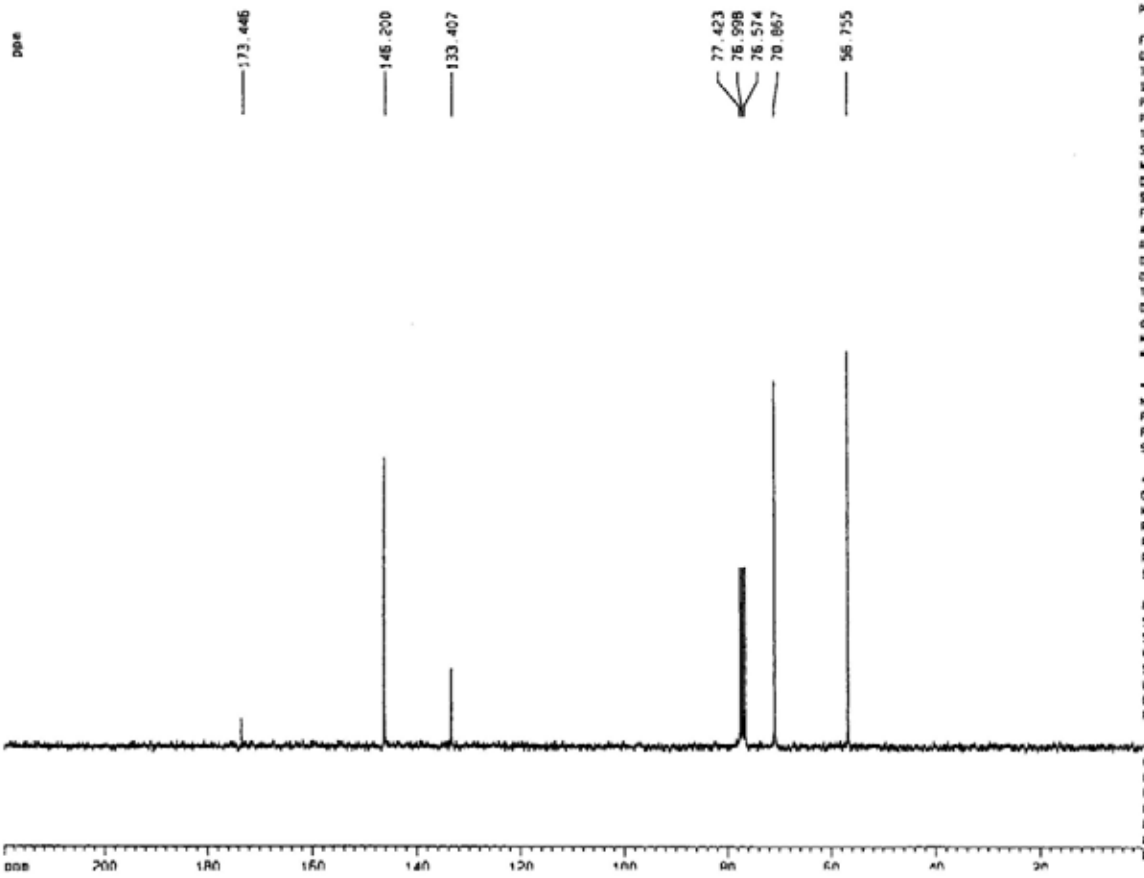
F2 - Acquisition Parameters
Date_ 20060915
Time 20.16
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 101.6
DW 55.600 usec
DE 79.43 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 300.1300057 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 5.00 cm
F1P 9.000 ppm
F1 2701.17 Hz
F2P -0.000 ppm
F2 -0.00 Hz
PPMCM 0.40909 ppm/cm
HZCM 122.78046 Hz/cm

C13



Current Data Parameters
NAME dongja-14-2-C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060915
Time 20.22
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 223
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

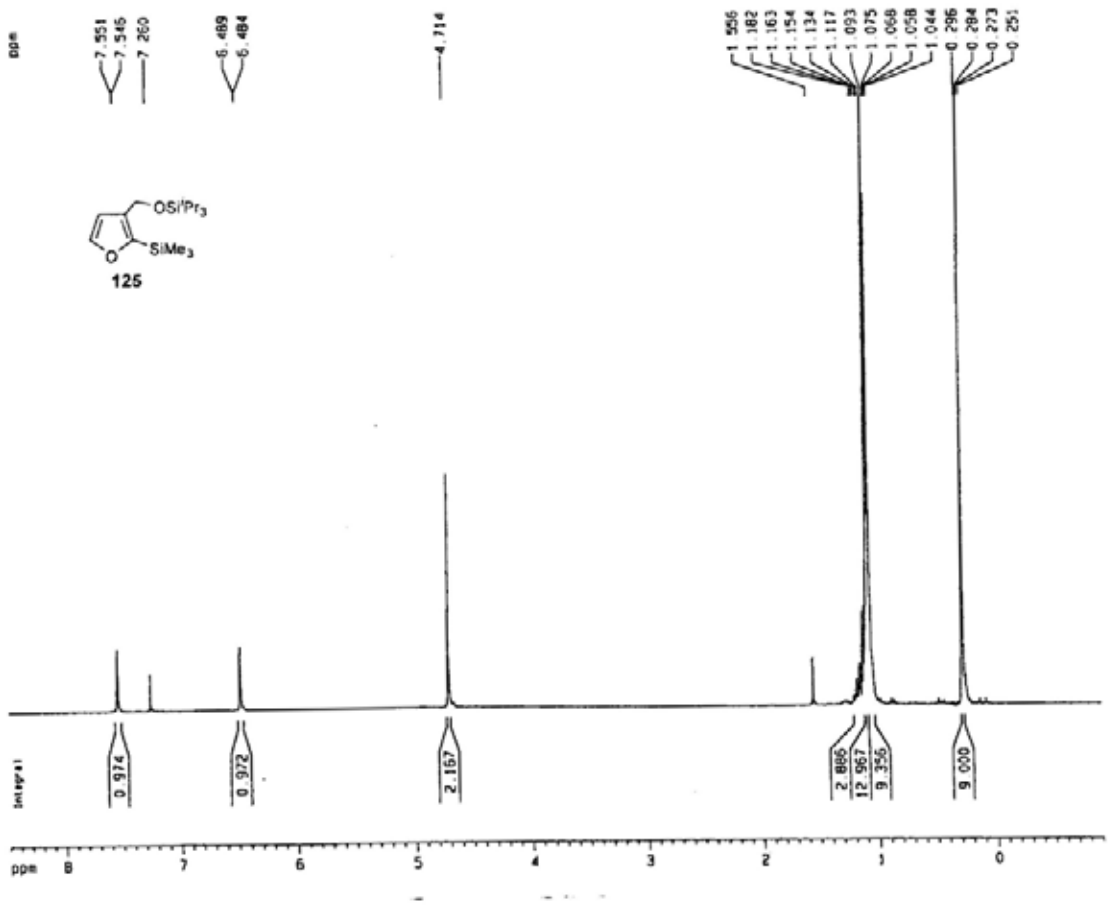
-------- CHANNEL f1 --------
NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SFO1 75.4745111 MHz

-------- 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 75.4577562 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
CY 8.00 cm
F1P 220.000 ppm
F1 16602.91 Hz
F2P -0.000 ppm
F2 -0.00 Hz
PPMCM 9.56522 ppm/cm

1H



Current Data Parameters
NAME ompjs-19-H1
EXPNO 1
PROCNO 1

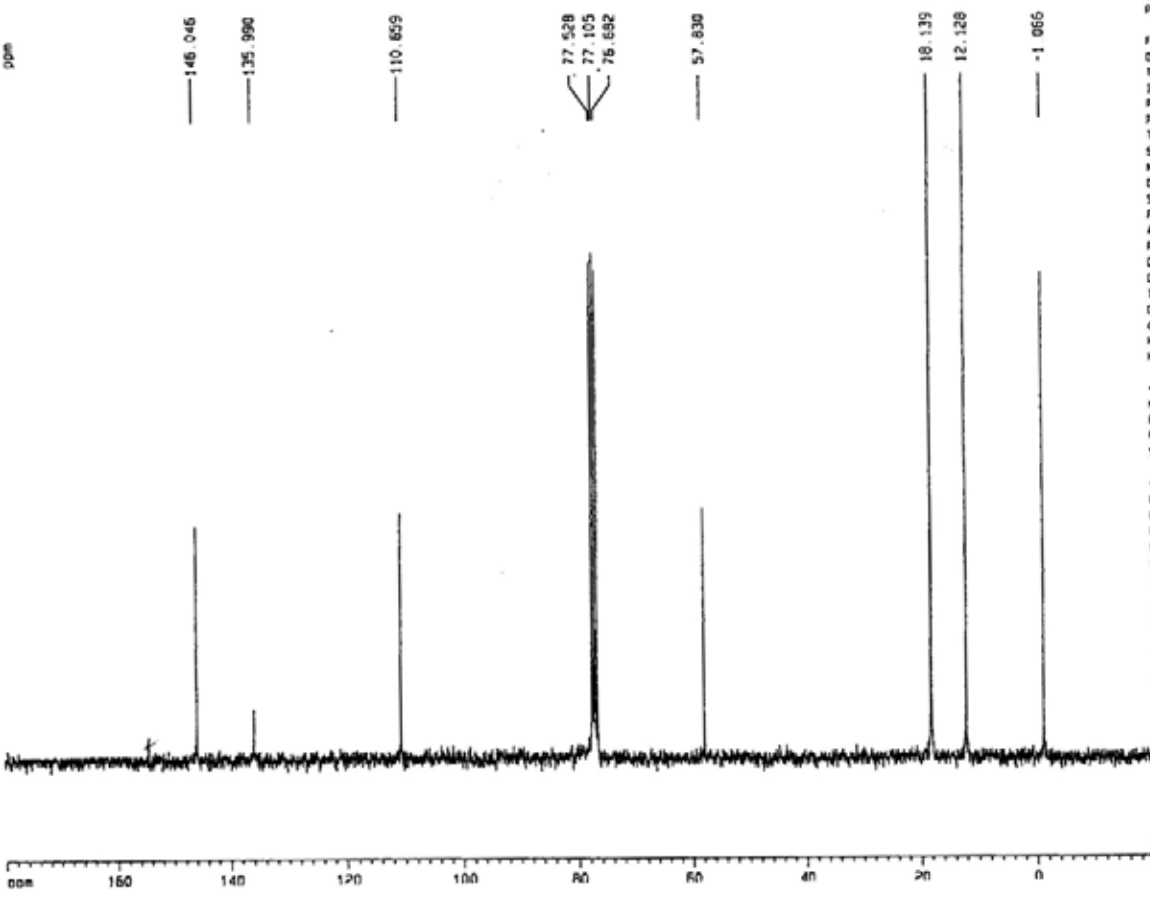
F2 - Acquisition Parameters
Date_ 20060920
Time 11 54
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 12
DS 0
SWH 8992.806 Hz
FIDRES 0.274438 Hz
AQ 1.8219508 sec
RG 101.6
DW 55.600 usec
DE 79.43 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 300.1300060 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 24.00 cm
F1P 8.500 ppm
F1 2551.10 Hz
F2P -0.900 ppm
F2 -270.12 Hz
PPMCM 0.42727 ppm/cm
HZCM 128.23737 Hz/cm

C13



Current Data Parameters
NAME ompjs-19-C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060920
Time 11 59
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 500
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

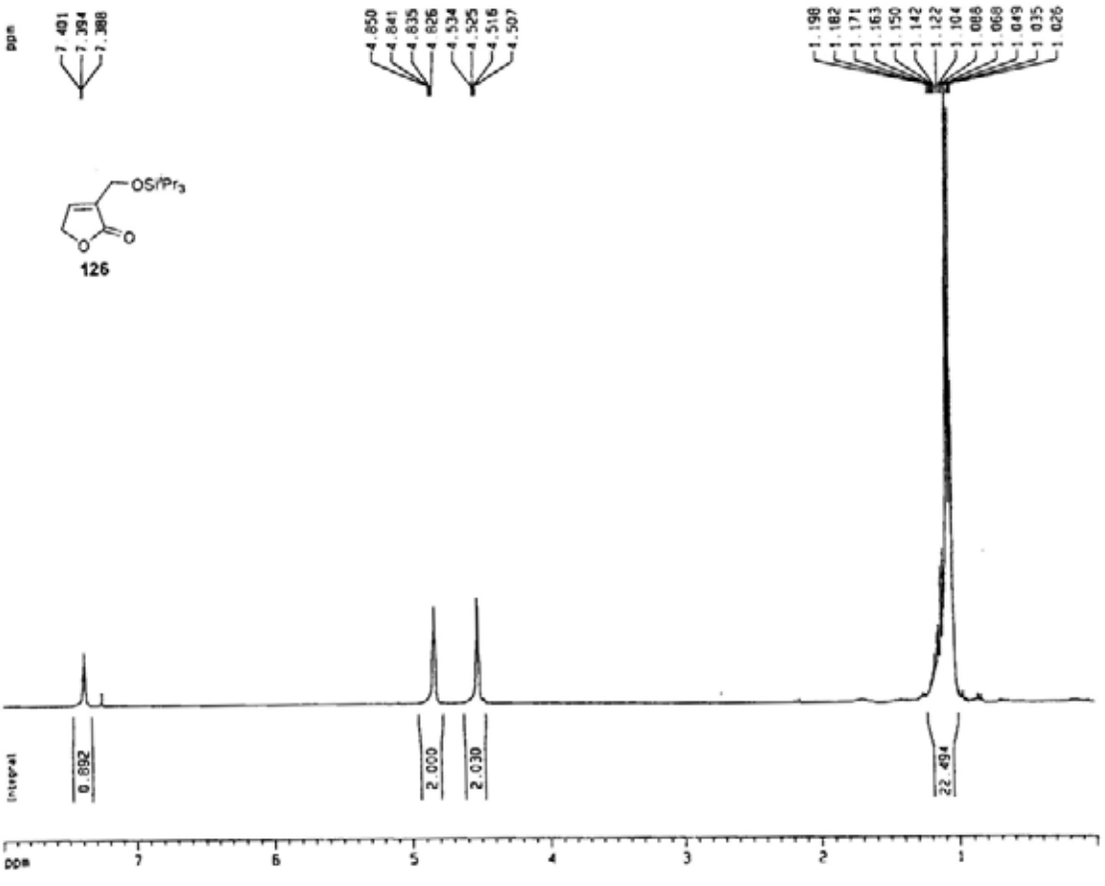
-------- CHANNEL f1 --------
NUC1 13C
P1 3.00 usec
PL1 +6.00 dB
SFO1 75.4745111 MHz

-------- 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 75.4677421 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
CY 30.00 cm
F1P 180.000 ppm
F1 13584.19 Hz
F2P -20.000 ppm
F2 -1509.35 Hz
PPMCM 8.68565 ppm/cm

1H

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Current Data Parameters
NAME            dongjq-21-H1
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_                20060921
Time                    10.35
INSTRUM                spect300
PROBHD     5 mm BBO BB-1H
PULPROG                    zg
TD                      32768
SOLVENT                 CDCl3
NS                         12
DS                          0
SWH                8992.806 Hz
FIDRES             0.274439 Hz
AQ                 1.8219508 sec
RG                       50.8
DW                     55.600 usec
DE                     79.43 usec
TE                      0.0 K
D1                 1.00000000 sec
HCREST             0.00000000 sec
HCWRK              0.01500000 sec

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

F2 - Processing parameters
SI                         32768
SF                 300.1300097 MHz
WDW                        EM
SSB                         0
LB                      0.30 Hz
GB                          0
PC                      1.00

1D NMR plot parameters
CX                     22.00 cm
CY                     24.00 cm
F1P                    8.000 ppm
F1                   2401.04 Hz
F2P                    0.000 ppm
F2                      0.00 Hz
PPMCM               0.36364 ppm/cm
HZCM              109.13818 Hz/cm
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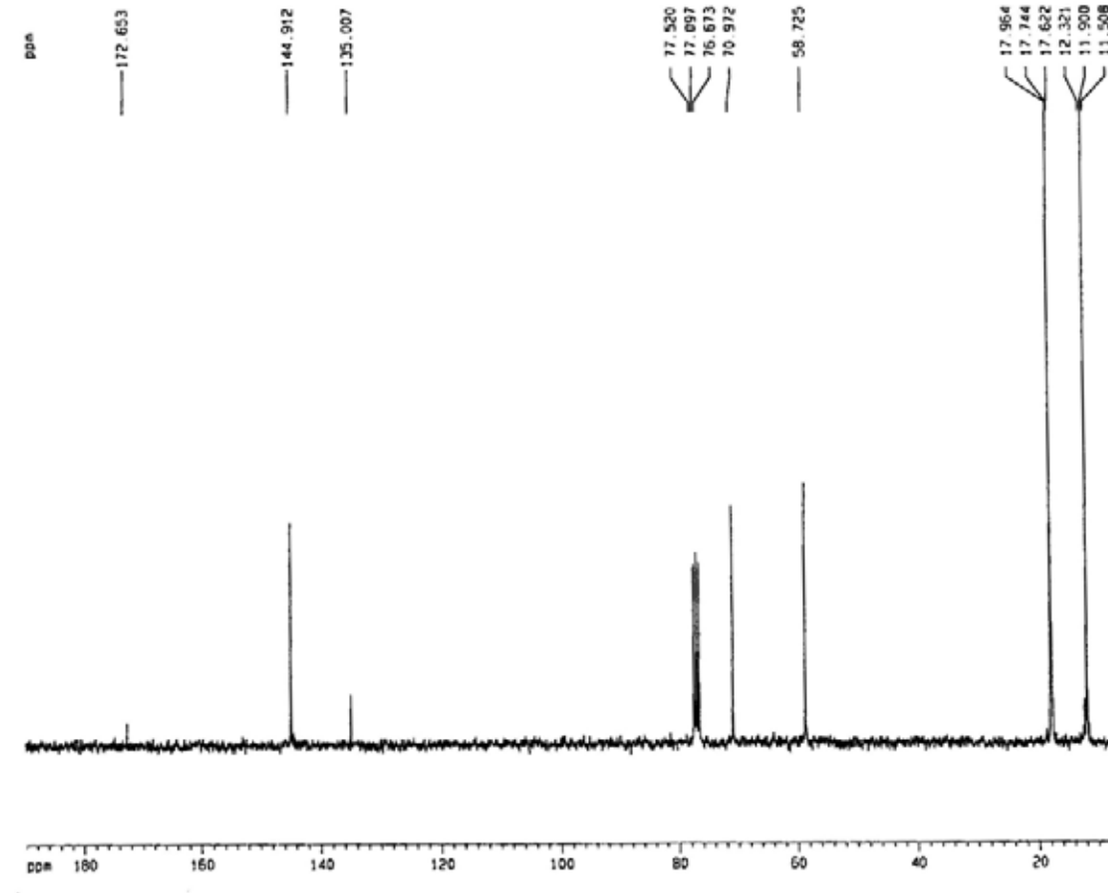
C13

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Current Data Parameters
NAME          dongjq-21-C13
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_               20060921
Time                   10.40
INSTRUM               spect300
PROBHD     5 mm BBO BB-1H
PULPROG                zgpg
TD                     65536
SOLVENT                CDCl3
NS                       154
DS                         0
SWH               22675.736 Hz
FIDRES            0.346004 Hz
AQ                1.4451188 sec
RG                      8192
DW                    22.050 usec
DE                     6.00 usec
TE                      0.0 K
D1                1.00000000 sec
d11               0.03000000 sec
HCREST            0.00000000 sec
HCWRK             0.01500000 sec

======== 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                75.4677455 MHz
WDW                        EM
SSB                         0
LB                      3.00 Hz
GB                          0
PC                      1.40

1D NMR plot parameters
CX                     23.00 cm
CY                     30.00 cm
F1P                  190.000 ppm
F1                 14338.87 Hz
F2P                   -0.000 ppm
F2                    -0.00 Hz
PPMCM               8.26087 ppm/cm
HZCM              623.42914 Hz/cm
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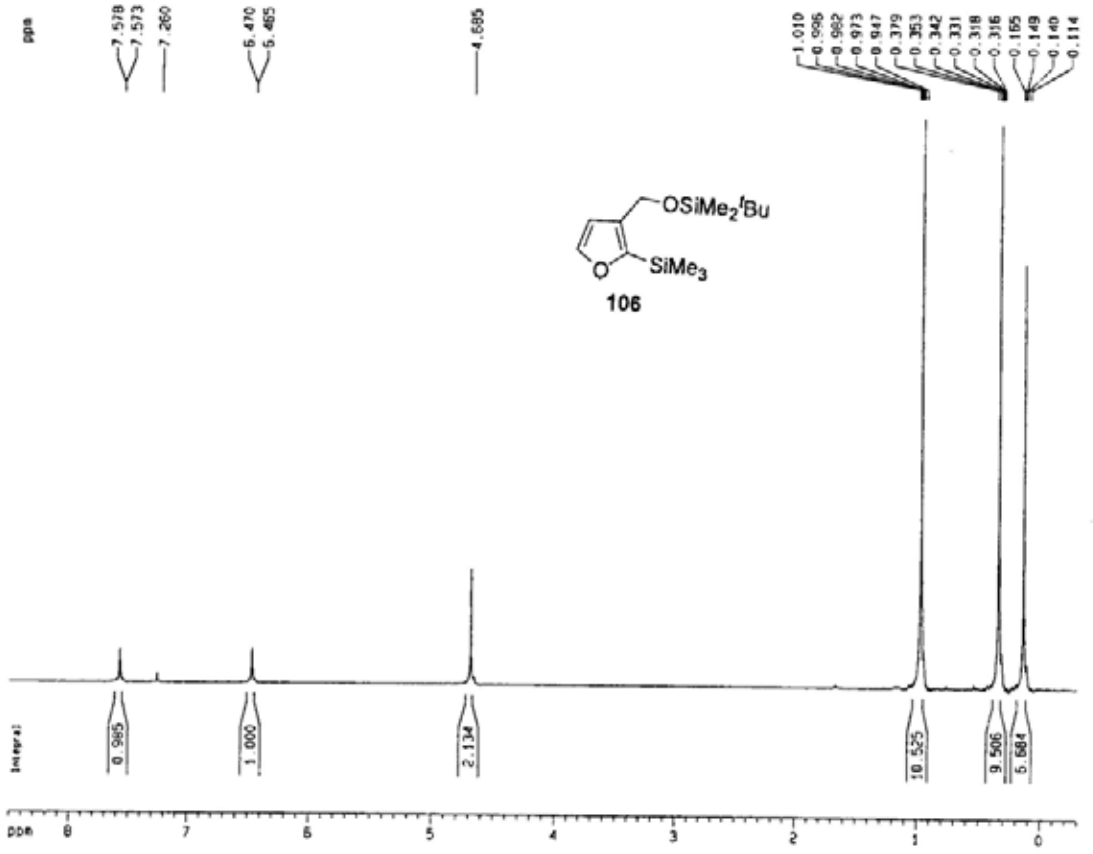
1H



Current Data Parameters
NAME bjq-2-053-H1
EXPNO 2
PROCNO 1

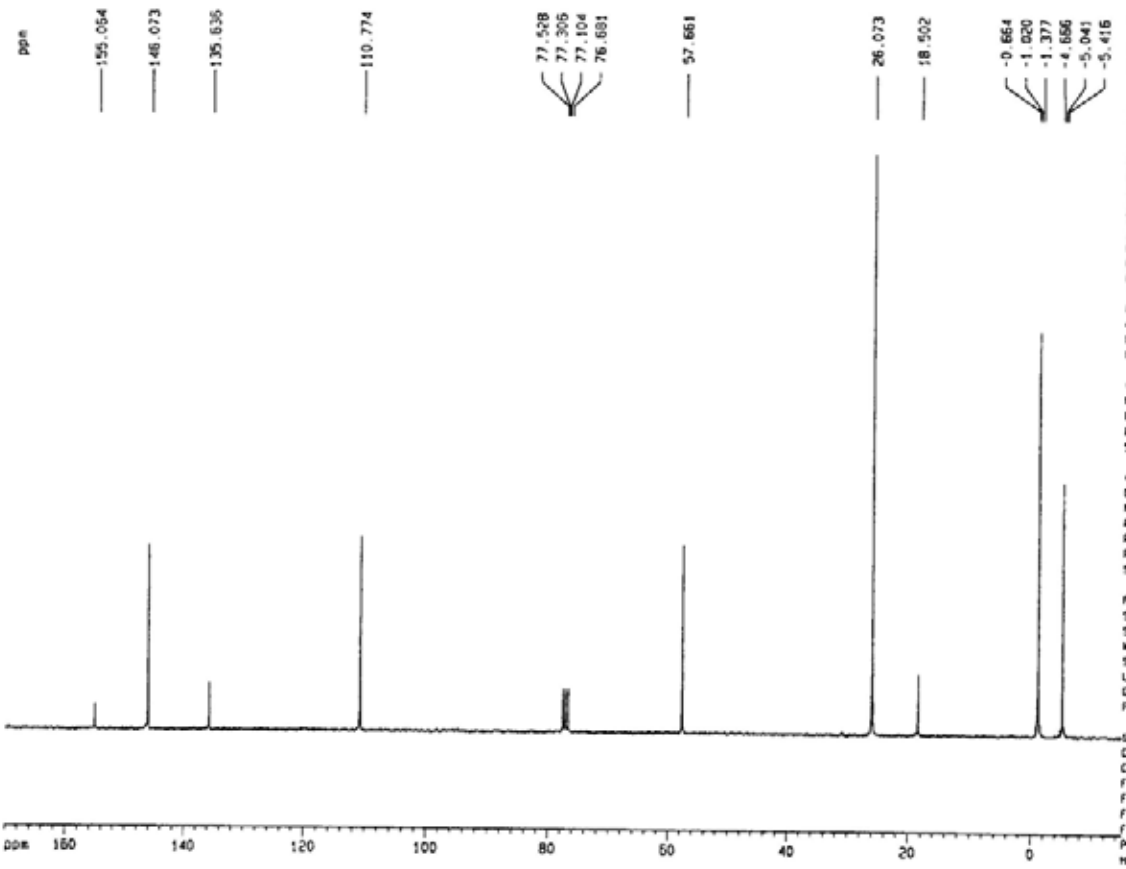
F2 - Acquisition Parameters
Date_ 20080718
Time 16.38
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 8992.806 Hz
FIDRES 0.274435 Hz
AQ 1.8219506 sec
RG 14.3
DW 55.600 usec
DE 75.43 usec
TE 298.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 300.1300060 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 12.00 cm
F1P 8.500 ppm
F1 2551.10 Hz
F2P -0.300 ppm
F2 -90.04 Hz
PPMCM 0.40000 ppm/cm
HZCM 120.05200 Hz/cm

C13



Current Data Parameters
NAME bjq-2-053-C13
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080718
Time 16.43
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 104
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
D11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

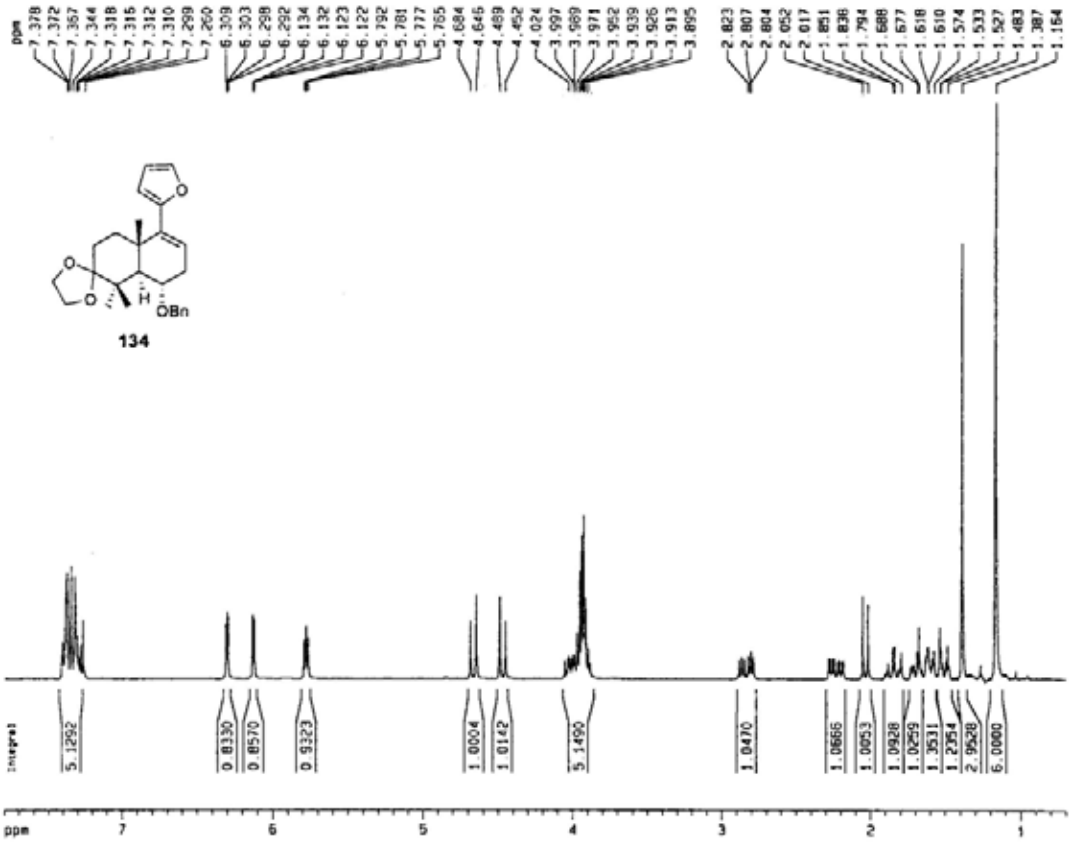
******** CHANNEL f1 ********
NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SFO1 75.4745111 MHz

******** 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 75.4677445 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
CY 12.00 cm
F1P 170.000 ppm
F1 12829.52 Hz
F2P -15.000 ppm
F2 -1132.62 Hz
PPMCM 8.04348 ppm/cm
HZCM 607.02313 Hz/cm

1H



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Current Data Parameters
NAME djq-1-044-H1
EXPNO 1
PROCNO 1

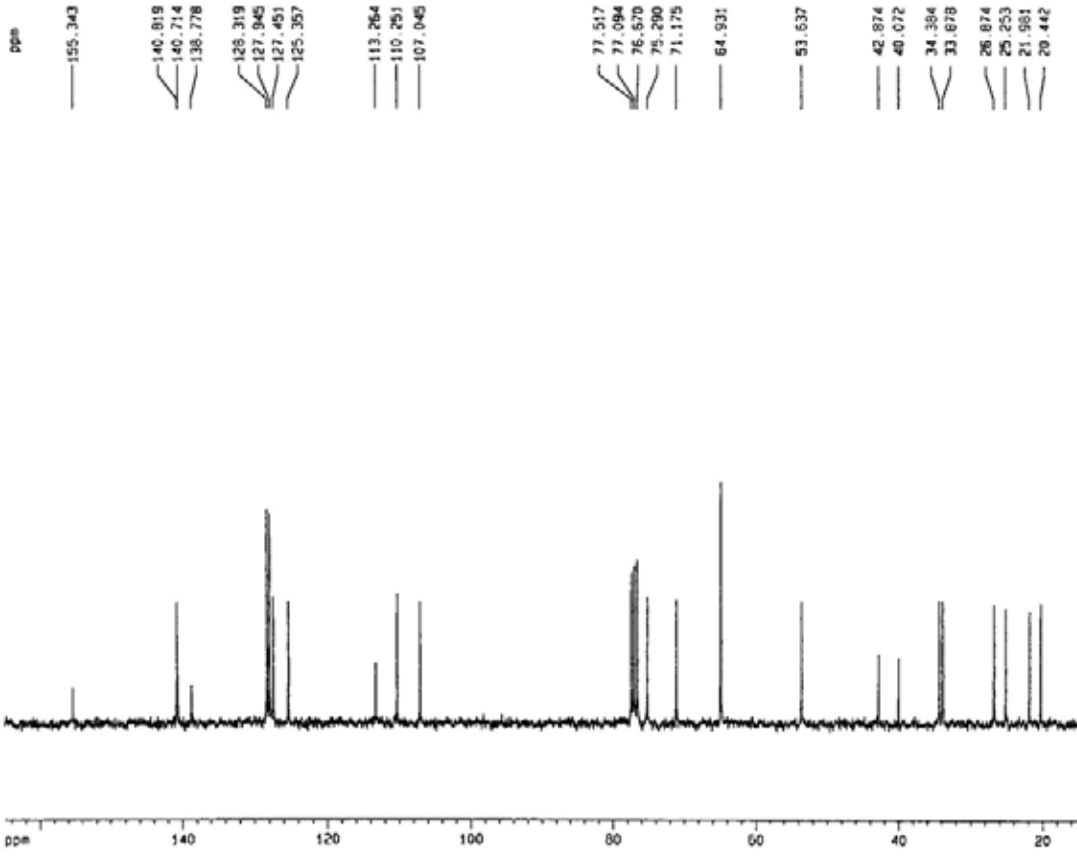
F2 - Acquisition Parameters
Date_ 20070716
Time 15.22
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219568 sec
RG 64
DW 55.600 usec
DE 79.43 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 300.1300055 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 12.00 cm
F1P 7.800 ppm
F1 2341.01 Hz
F2P 0.700 ppm
F2 210.09 Hz
PPMCM 0.32273 ppm/cm
HZCM 96.86814 Hz/cm

C13



Current Data Parameters
NAME djq-1-044-C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070716
Time 19.18
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 165
DS 0
SWH 22675.736 Hz
FIDRES 0.345804 Hz
AQ 1.4451188 sec
RG 3649.1
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

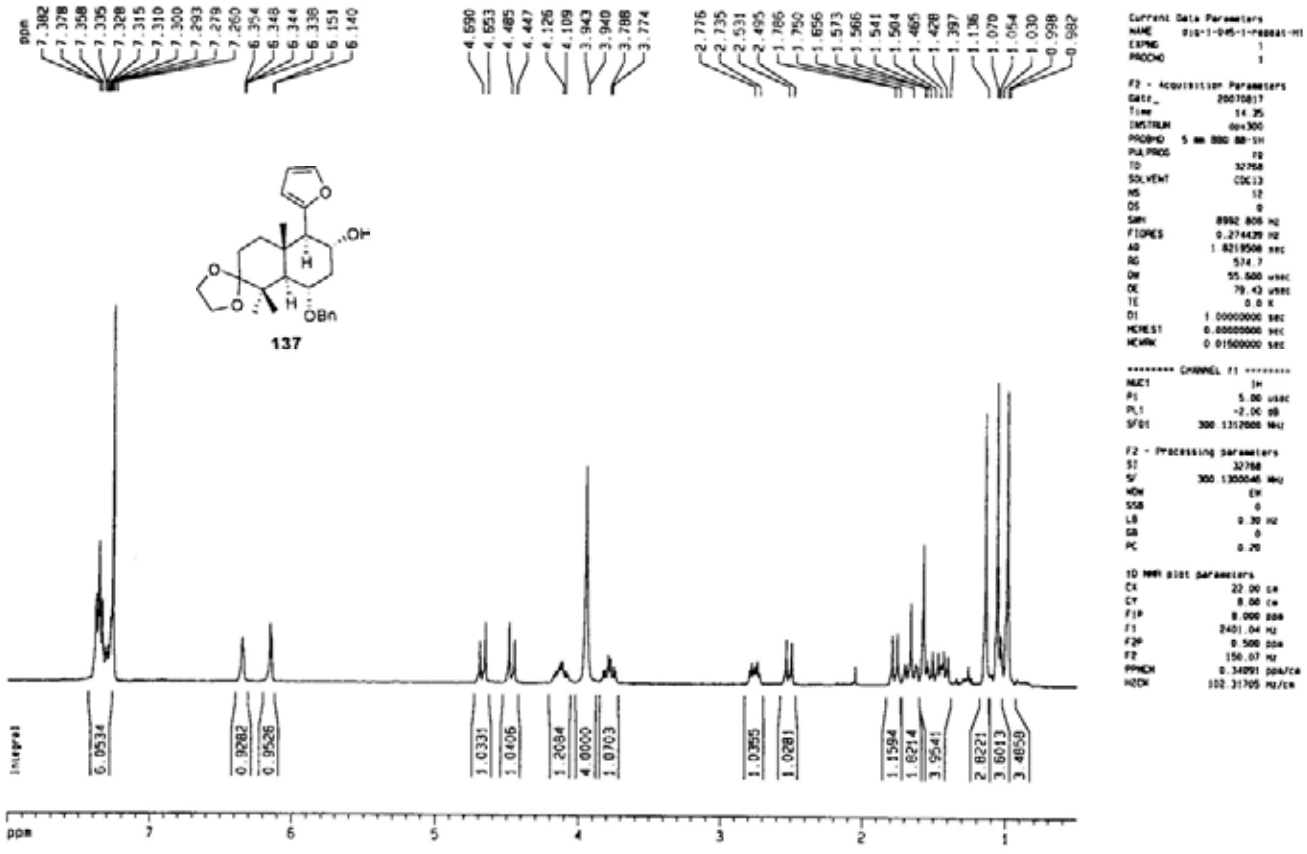
-------- CHANNEL f1 --------
NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SFO1 75.4745111 MHz

-------- 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 75.4677452 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
CY 5.00 cm
F1P 155.000 ppm
F1 12452.18 Hz
F2P 10.000 ppm
F2 754.68 Hz
PPMCM 6.73913 ppm/cm
HZCM 506.58698 Hz/cm

1H



Current Data Parameters
NAME 01b-1-045-repeat-H1
EXPNO 1
PROCNO 1

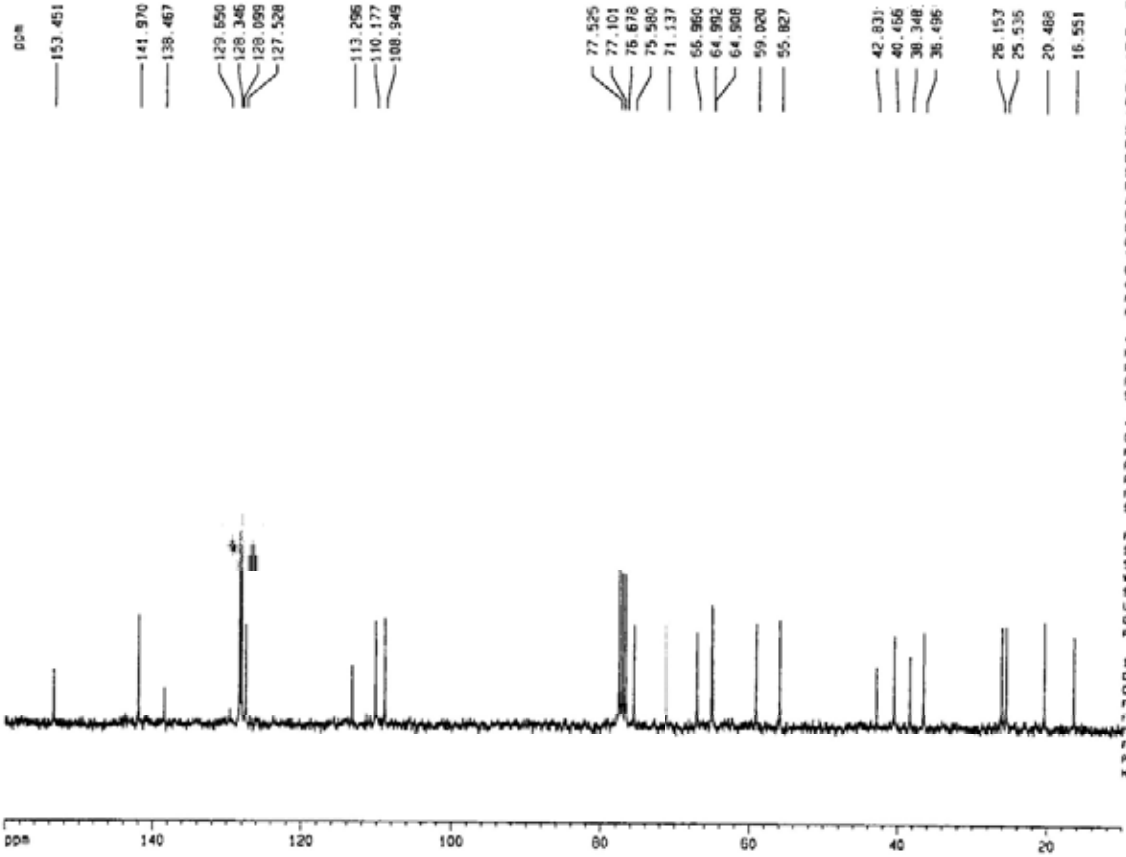
F2 - Acquisition Parameters
Date_ 20070817
Time 14.35
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 12
DS 0
SWH 8992.806 Hz
FIDRES 0.274429 Hz
AQ 1.8219508 sec
RG 574.7
DW 55.600 usec
DE 79.43 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 300.1300046 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.20

1D NMR plot parameters
CX 22.00 cm
CY 8.00 cm
F1P 8.000 ppm
F1 2401.04 Hz
F2P 0.500 ppm
F2 150.07 Hz
PPMCM 0.34091 ppm/cm
HZCM 102.31705 Hz/cm

C13



Current Data Parameters
NAME 01b-1-045-repeat-C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070820
Time 19.42
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 111
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4455188 sec
RG 10321.3
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

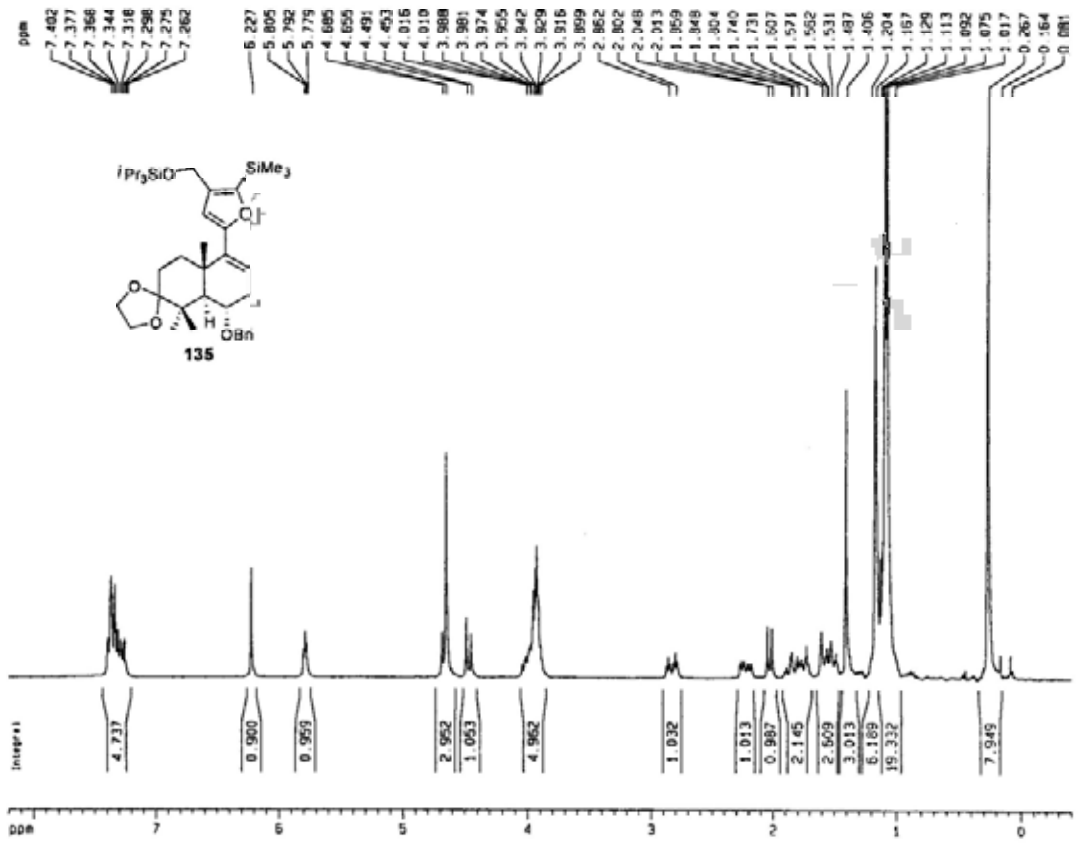
======== CHANNEL f1 ========
NUC1 13C
P1 5.00 usec
PL1 -6.00 dB
SFO1 75.4745111 MHz

======== 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 75.4677455 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
CY 4.00 cm
F1P 160.000 ppm
F1 12074.84 Hz
F2P 10.000 ppm
F2 754.68 Hz
PPMCM 6.52174 ppm/cm
HZCM 492.18091 Hz/cm

1H



Current Data Parameters
NAME dongjq-42-H1
EXPNO 1
PROCNO 1

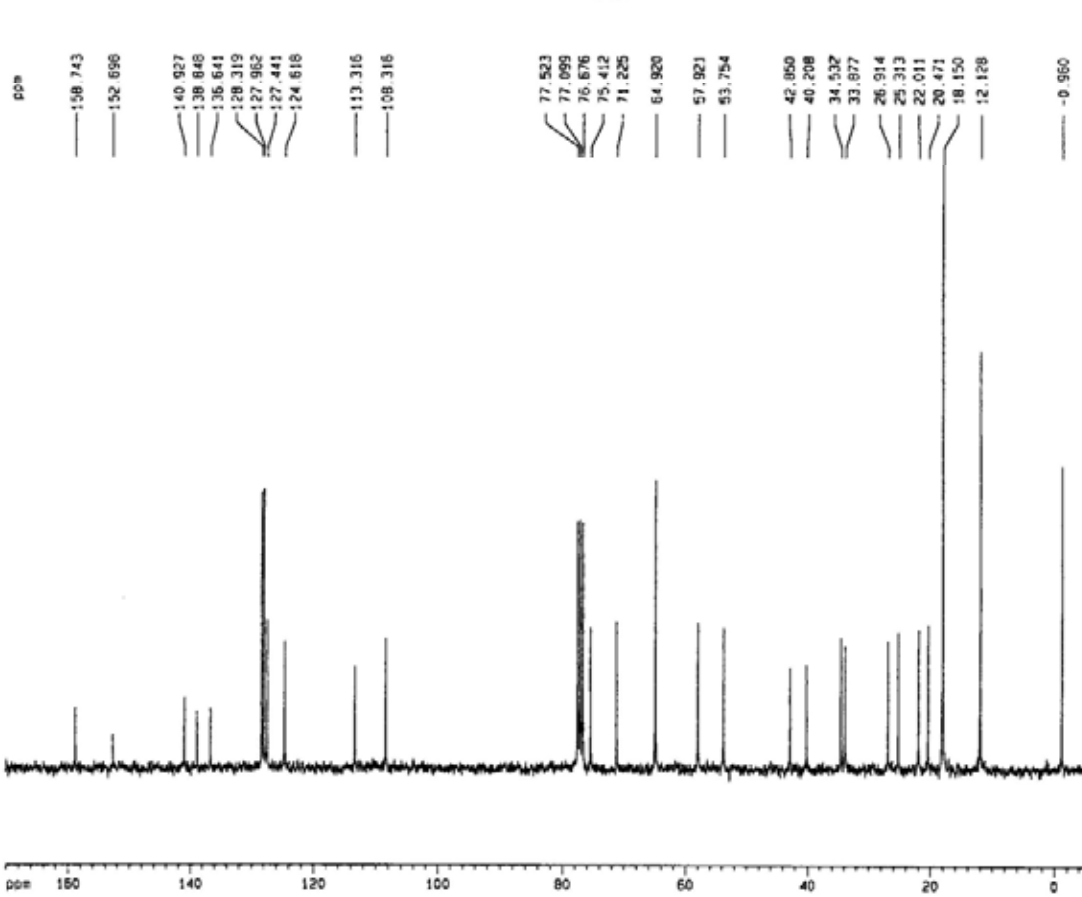
F2 - Acquisition Parameters
Date_ 20061027
Time 19.38
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 6392.006 Hz
FIDRES 0.274439 Hz
AQ 2.5619508 sec
RG 64
DW 55.600 usec
DE 79.43 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 300.1300049 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 24.00 cm
F1P 8.200 ppm
F1 2461.07 Hz
F2P -0.400 ppm
F2 -120.05 Hz
PPMCM 0.39091 ppm/cm
HZCM 117.32355 Hz/cm

C13



Current Data Parameters
NAME dongjq-42-C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061027
Time 19.44
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 373
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8502
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
D11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

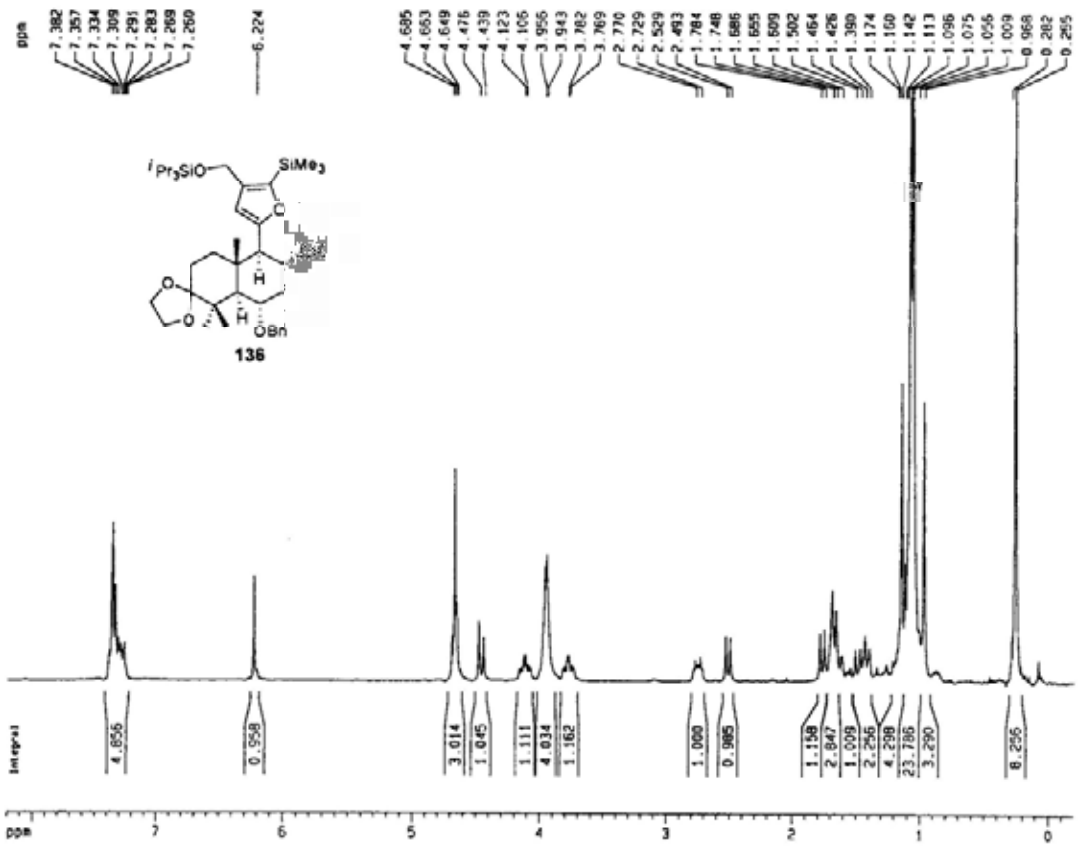
-------- CHANNEL f1 --------
NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SFO1 75.4745111 MHz

-------- 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 75.4677438 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
CY 18.00 cm
F1P 170.000 ppm
F1 12829.52 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 7.82609 ppm/cm
HZCM 590.61707 Hz/cm

1H



Current Data Parameters
NAME dongjq-46-2-h1
EXPNO 1
PROCNO 1

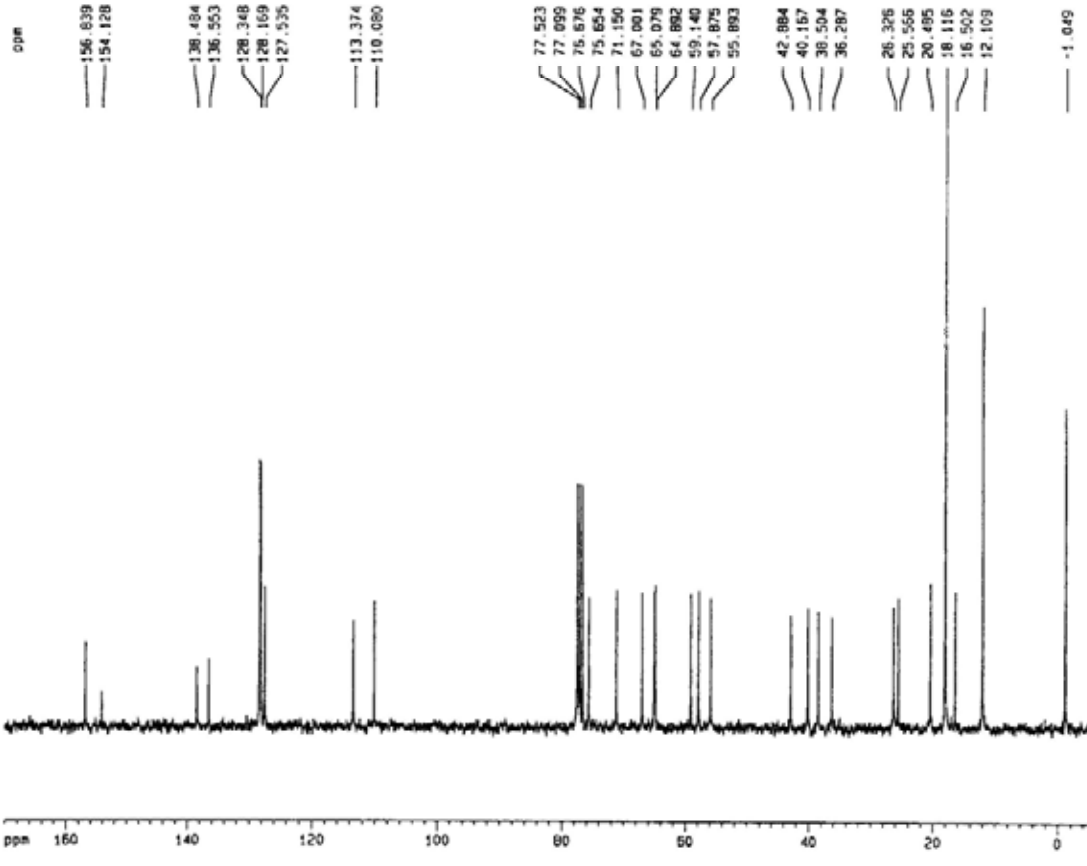
F2 - Acquisition Parameters
Date_ 20061115
Time 19.04
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 12
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219500 sec
RG 64
DW 55.600 usec
DE 79.43 usec
TE 0.0 K
D1 1.00000000 sec
HCREST 0.00000000 sec
HCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 300.1300049 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 24.00 cm
F1P 8.250 ppm
F1 2461.87 Hz
F2P -0.250 ppm
F2 -60.83 Hz
PPMCM 0.38182 ppm/cm
HZCM 114.59509 Hz/cm

C13



Current Data Parameters
NAME dongjq-46-2-C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061115
Time 19.13
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 277
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 1290.2
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
D11 0.03000000 sec
HCREST 0.00000000 sec
HCWRK 0.01500000 sec

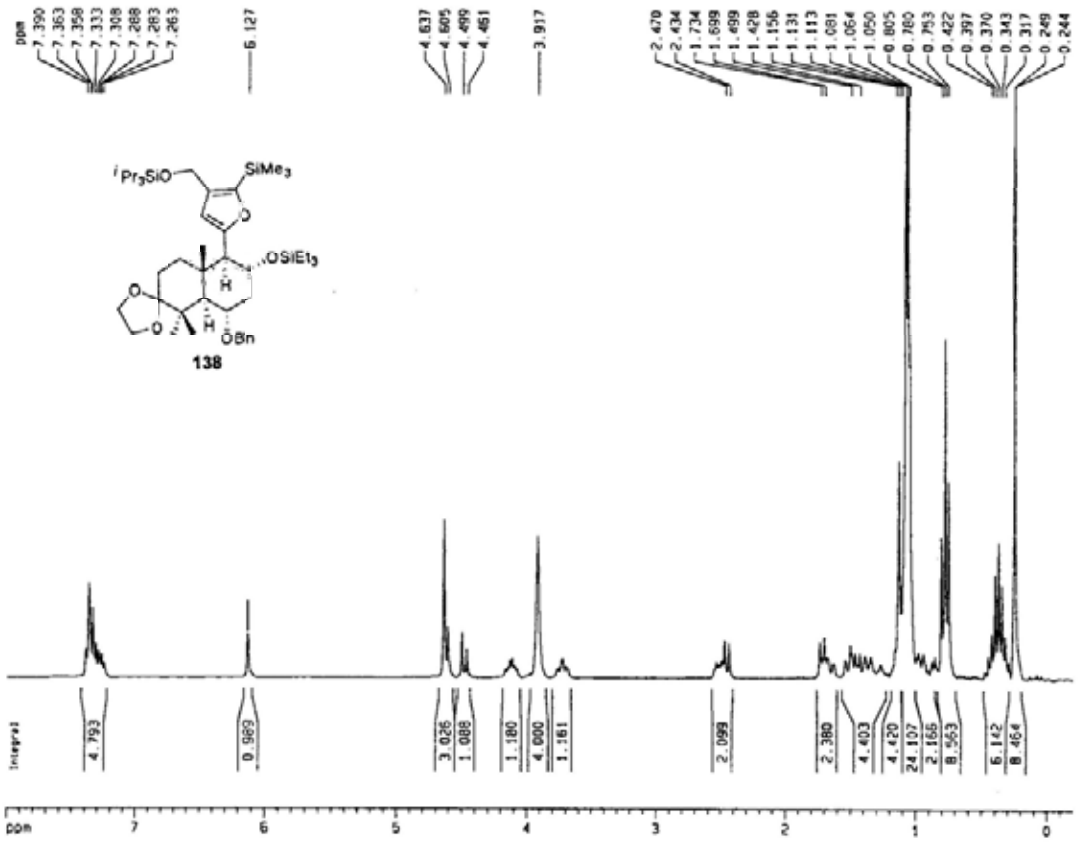
======== CHANNEL f1 ========
NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SFO1 75.4745111 MHz

======== 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 75.4677445 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
CY 18.00 cm
F1P 170.000 ppm
F1 12829.52 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 7.82609 ppm/cm
HZCM 590.61707 Hz/cm

1H



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```
Current Data Parameters
NAME            dongjs-54-H1
EXPNO                      1
PROCNO                     1

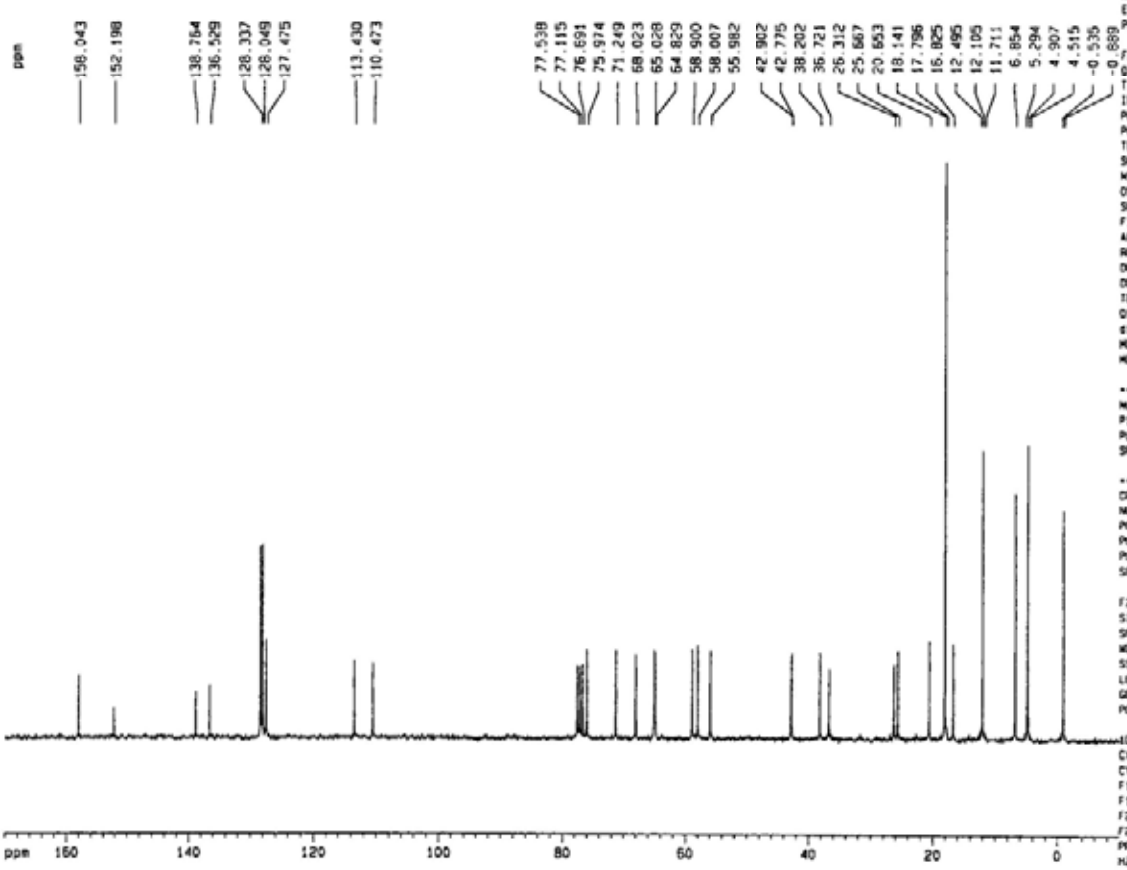
F2 - Acquisition Parameters
Date_           20061211
Time                   11.29
INSTRUM                spx300
PROBHD     5 mm BBO BB-1H
PULPROG                 zg
TD                     32768
SOLVENT                CDCl3
NS                        10
DS                         0
SWH              8992.806 Hz
FIDRES           0.274439 Hz
AQ               1.8219568 sec
RG                      20.2
DW                   55.600 usec
DE                   79.43 usec
TE                      0.0 K
D1               1.00000000 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

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

F2 - Processing parameters
SI                     32768
SF            300.1300095 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                   22.00 cm
CY                   18.00 cm
F1P                  8.000 ppm
F1                 2401.04 Hz
F2P                 -0.200 ppm
F2                  -60.03 Hz
PPMCM              0.33273 ppm/cm
HZCM             111.86684 Hz/cm
```

C13




```
Current Data Parameters
NAME            dongjs-54-C13
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_           20061211
Time                   11.34
INSTRUM                dsx300
PROBHD     5 mm BBO BB-1H
PULPROG                zgpg
TD                     65536
SOLVENT                CDCl3
NS                       107
DS                         0
SWH              22675.736 Hz
FIDRES           0.346004 Hz
AQ               1.4451188 sec
RG                      8192
DW                   22.050 usec
DE                    6.00 usec
TE                      0.0 K
D1               1.00000000 sec
d11              0.03000000 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

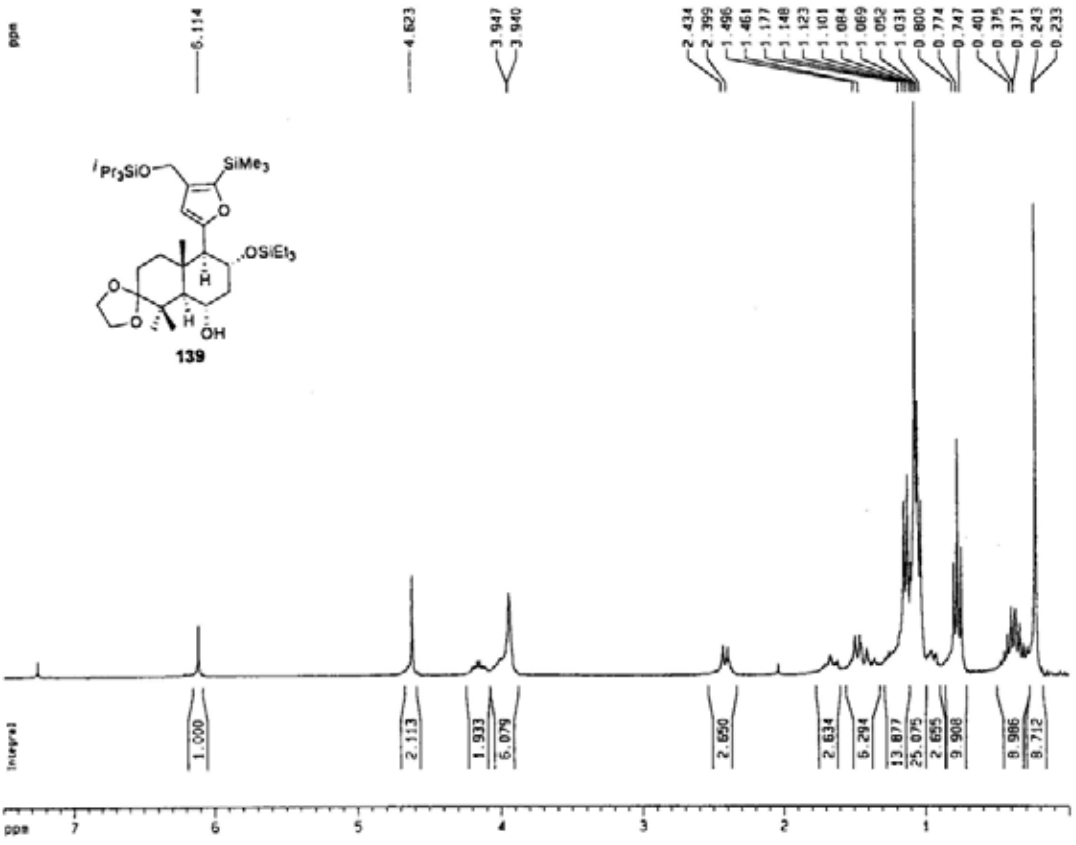
======== CHANNEL f1 ========
NUC1                    13C
P1                   3.00 usec
PL1                  -6.00 dB
SFO1          75.4745111 MHz

======== 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            75.4577445 MHz
WDW                    EM
SSB                     0
LB                   3.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                   23.00 cm
CY                   12.00 cm
F1P                170.000 ppm
F1               12829.52 Hz
F2P                -10.000 ppm
F2                -754.68 Hz
PPMCM             7.82609 ppm/cm
HZCM            590.61767 Hz/cm
```

1H



139

```
Current Data Parameters
NAME        oongja-56-H1
EXPNO               1
PROCNO              1

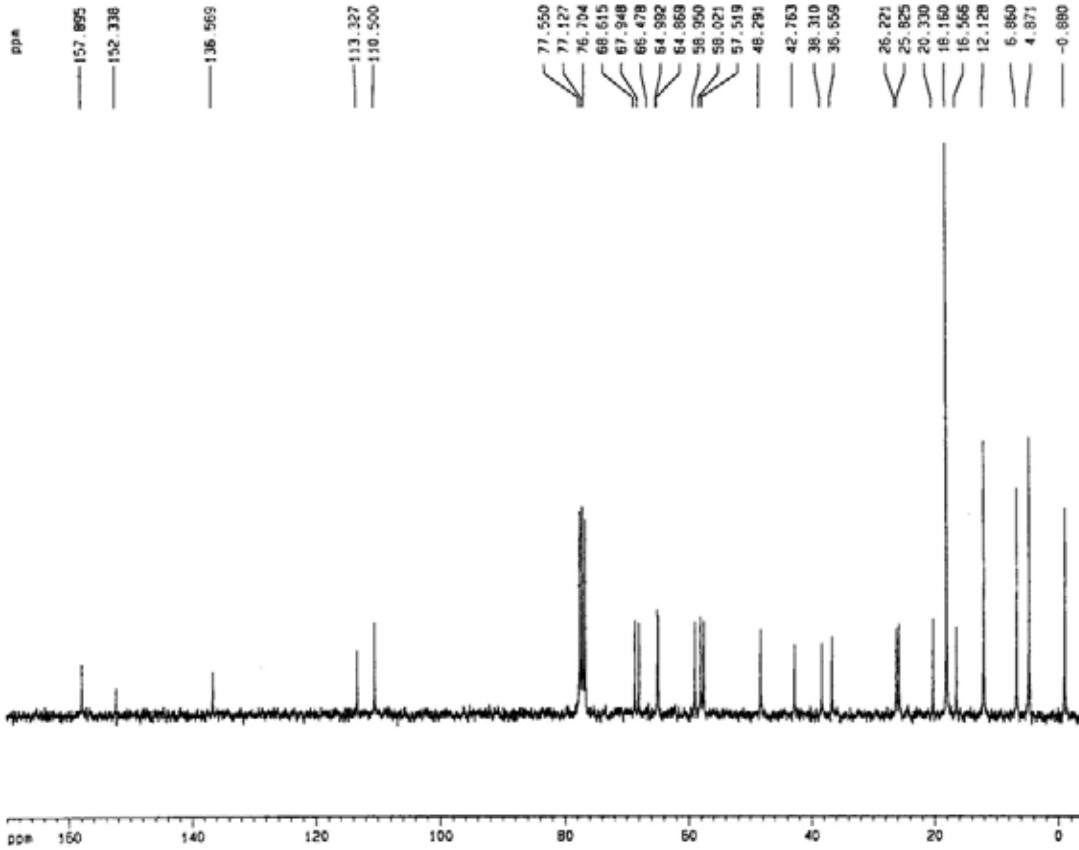
F2 - Acquisition Parameters
Date_         20061212
Time              9.23
INSTRUM          dpx300
PROBHD  5 mm BBO BB-1H
PULPROG             zg
TD                32768
SOLVENT           CDCl3
NS                  12
DS                   0
SWH           8992.806 Hz
FIDRES        0.274439 Hz
AQ            1.8219568 sec
RG                  64
DW               55.600 usec
DE               75.43 usec
TE                0.0 K
D1            1.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

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

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

1D NMR plot parameters
CX               22.00 cm
CY               12.00 cm
F1P              7.500 ppm
F1              2250.98 Hz
F2P              0.000 ppm
F2               0.00 Hz
PPMCM            0.34091 ppm/cm
HZCM          102.31705 Hz/cm
```

C13




```
Current Data Parameters
NAME        oongja-56-C13
EXPNO               1
PROCNO              1

F2 - Acquisition Parameters
Date_         20061212
Time              9.24
INSTRUM          dpx300
PROBHD  5 mm BBO BB-1H
PULPROG          zgpg
TD                65536
SOLVENT           CDCl3
NS                 240
DS                   0
SWH          22675.736 Hz
FIDRES        0.346004 Hz
AQ            1.4451188 sec
RG                2048
DW               22.050 usec
DE                6.00 usec
TE                0.0 K
D1            1.00000000 sec
D11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

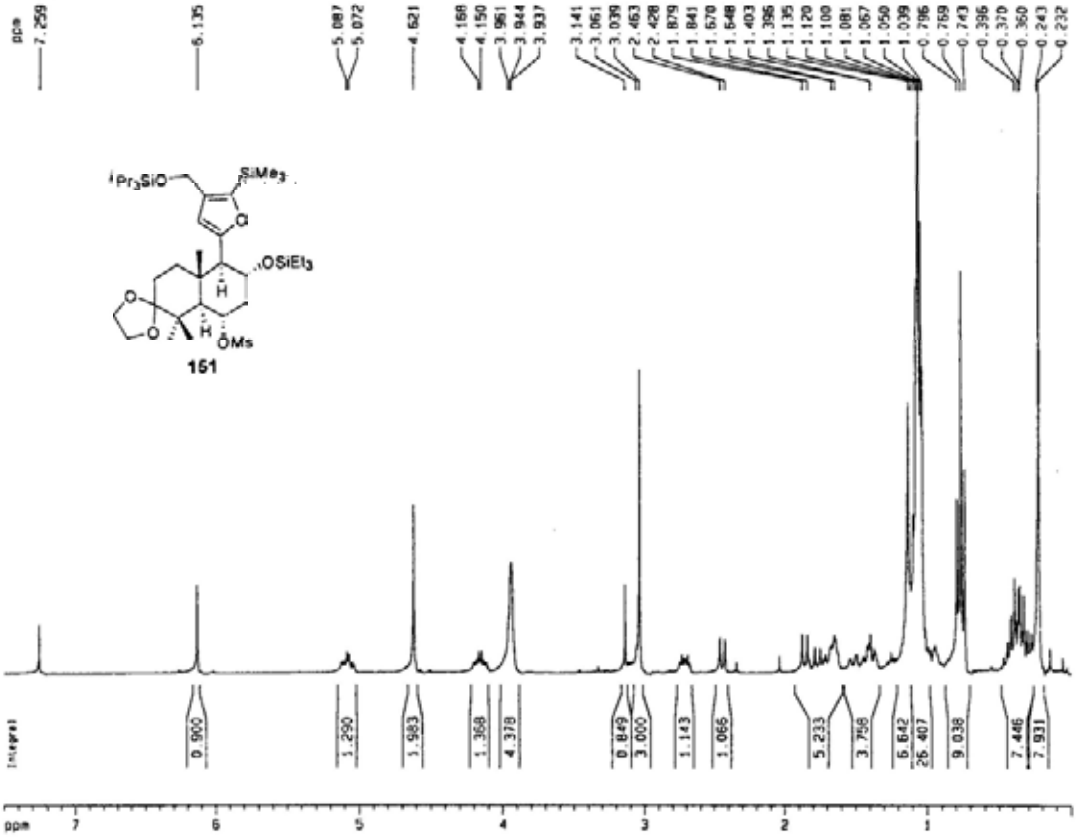
-------- CHANNEL f1 --------
NUC1                13C
P1               3.00 usec
PL1             -6.00 dB
SFO1        75.4745111 MHz

-------- 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          75.4677410 MHz
WDW                 EM
SSB                  0
LB               3.00 Hz
GB                   0
PC                1.40

1D NMR plot parameters
CX               23.00 cm
CY               12.00 cm
F1P             170.000 ppm
F1            12829.52 Hz
F2P             -10.000 ppm
F2             -754.68 Hz
PPMCM            7.82609 ppm/cm
HZCM          590.61707 Hz/cm
```

1H



151

```
Current Data Parameters
NAME        oanglo-57-0-H1
EXPNO               1
PROCNO              1

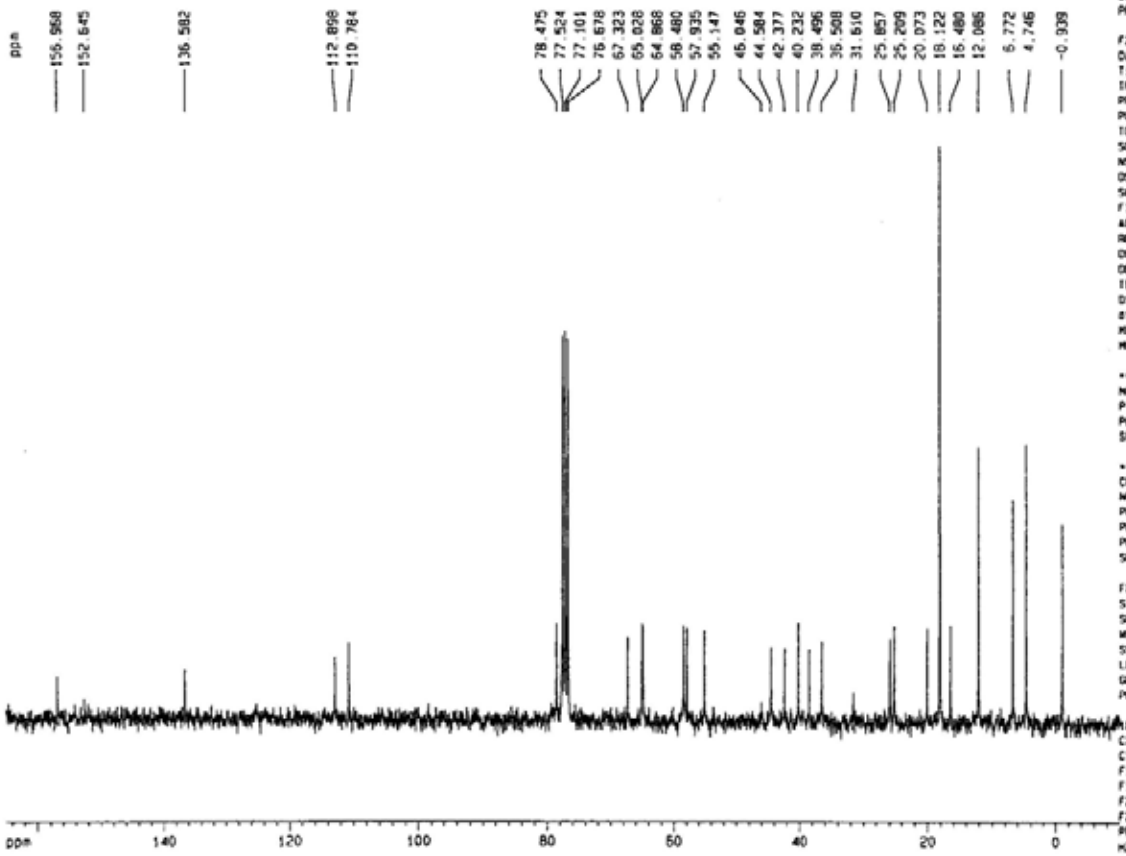
F2 - Acquisition Parameters
Date_         20061213
Time              11.08
INSTRUM           dpx300
PROBHD  5 mm BBO BB-1H
PULPROG             zg
TD                32768
SOLVENT           CDCl3
NS                  16
DS                   0
SWH           8992.806 Hz
FIDRES        0.274439 Hz
AQ            1.8219508 sec
RG                  64
DW             55.600 usec
DE             79.43 usec
TE                0.0 K
D1            1.00000000 sec
HCREST        0.00000000 sec
HCWRK         0.01500000 sec

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

F2 - Processing parameters
SI                32768
SF          300.1300055 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00

1D NMR plot parameters
CX               22.00 cm
CY               20.00 cm
F1P              7.500 ppm
F1             2250.98 Hz
F2P              0.000 ppm
F2               0.00 Hz
PPMCM         0.34091 ppm/cm
HZCM        102.31795 Hz/cm
```

C13




```
Current Data Parameters
NAME        oanglo-57-0-C13
EXPNO               1
PROCNO              1

F2 - Acquisition Parameters
Date_         20061213
Time              11.18
INSTRUM           dpx300
PROBHD  5 mm BBO BB-1H
PULPROG           zgpg
TD                65536
SOLVENT           CDCl3
NS                 254
DS                   0
SWH          22675.736 Hz
FIDRES        0.346004 Hz
AQ            1.4451188 sec
RG                8192
DW             22.050 usec
DE              6.00 usec
TE                0.0 K
D1            1.00000000 sec
D11           0.03000000 sec
HCREST        0.00000000 sec
HCWRK         0.01500000 sec

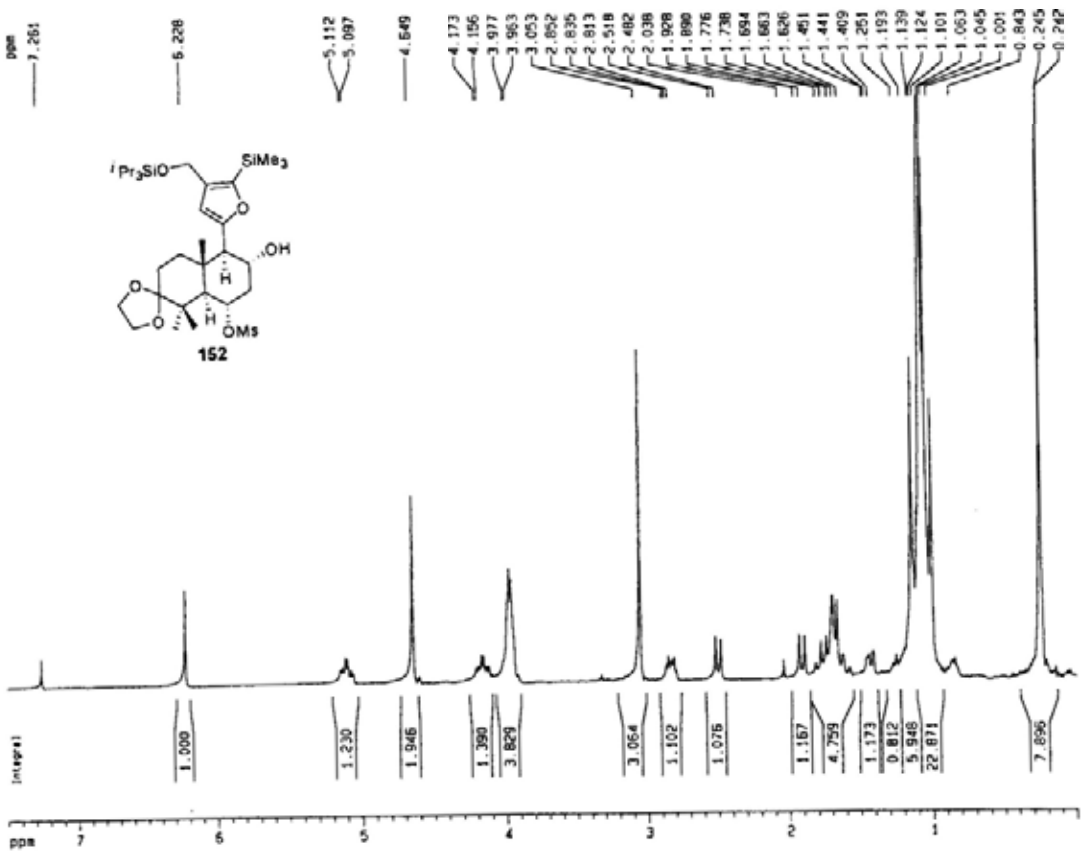
======== CHANNEL f1 ========
NUC1                13C
P1               3.00 usec
PL1             -6.00 dB
SFO1        75.4745111 MHz

======== 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          75.4677434 MHz
WDW                 EM
SSB                  0
LB                3.00 Hz
GB                   0
PC                1.40

1D NMR plot parameters
CX               23.00 cm
CY               12.00 cm
F1P             165.000 ppm
F1            12452.18 Hz
F2P             -10.000 ppm
F2             -754.68 Hz
PPMCM         7.60870 ppm/cm
HZCM        574.21112 Hz/cm
```

1H



Current Data Parameters
NAME dongjo-58-1-H1
EXPNO 1
PROCNO 1

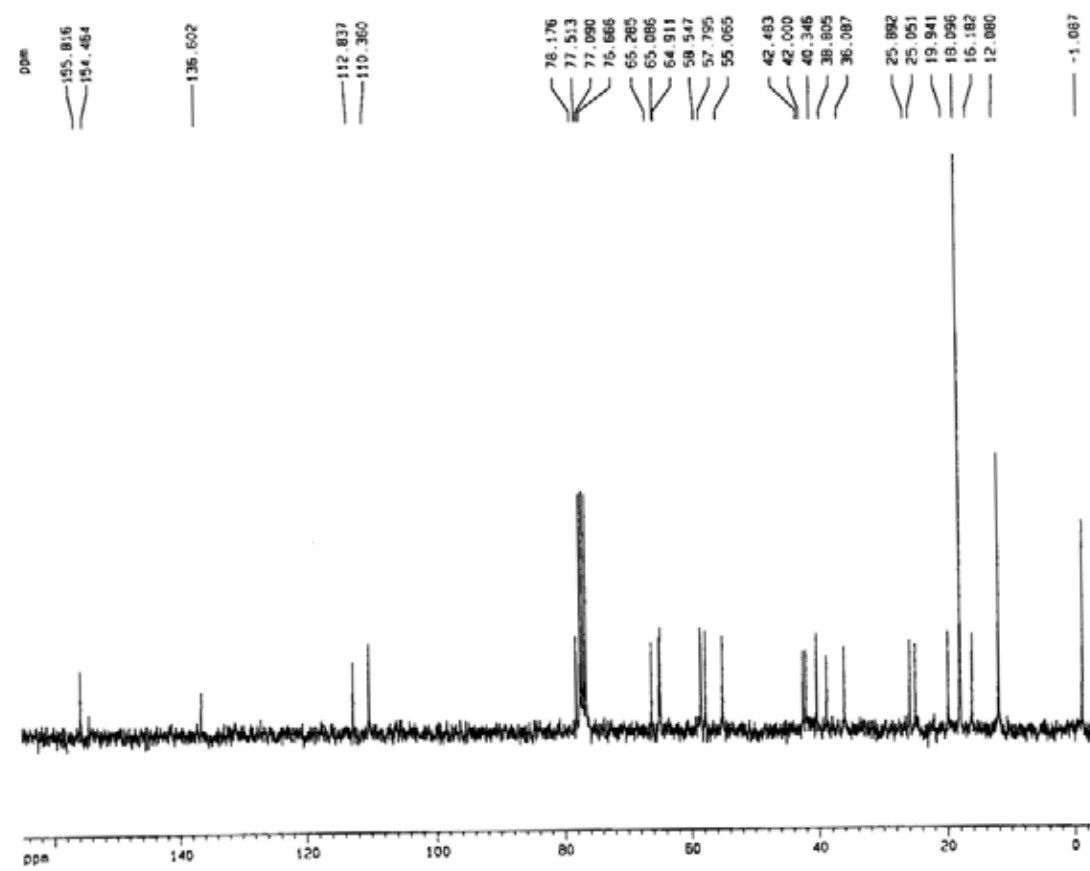
F2 - Acquisition Parameters
Date_ 20061213
Time 17.20
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 12
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219568 sec
RG 64
DW 55.600 usec
DE 79.43 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 300.1300046 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 24.00 cm
F1P 7.500 ppm
F1 2250.98 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.34091 ppm/cm
HZCM 102.31705 Hz/cm

C13



Current Data Parameters
NAME dongjo-58-1-C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061213
Time 17.21
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 84
DS 0
SWH 20675.735 Hz
FIDRES 0.346004 Hz
AQ 1.4451308 sec
RG 8192
DW 22.850 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
D11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

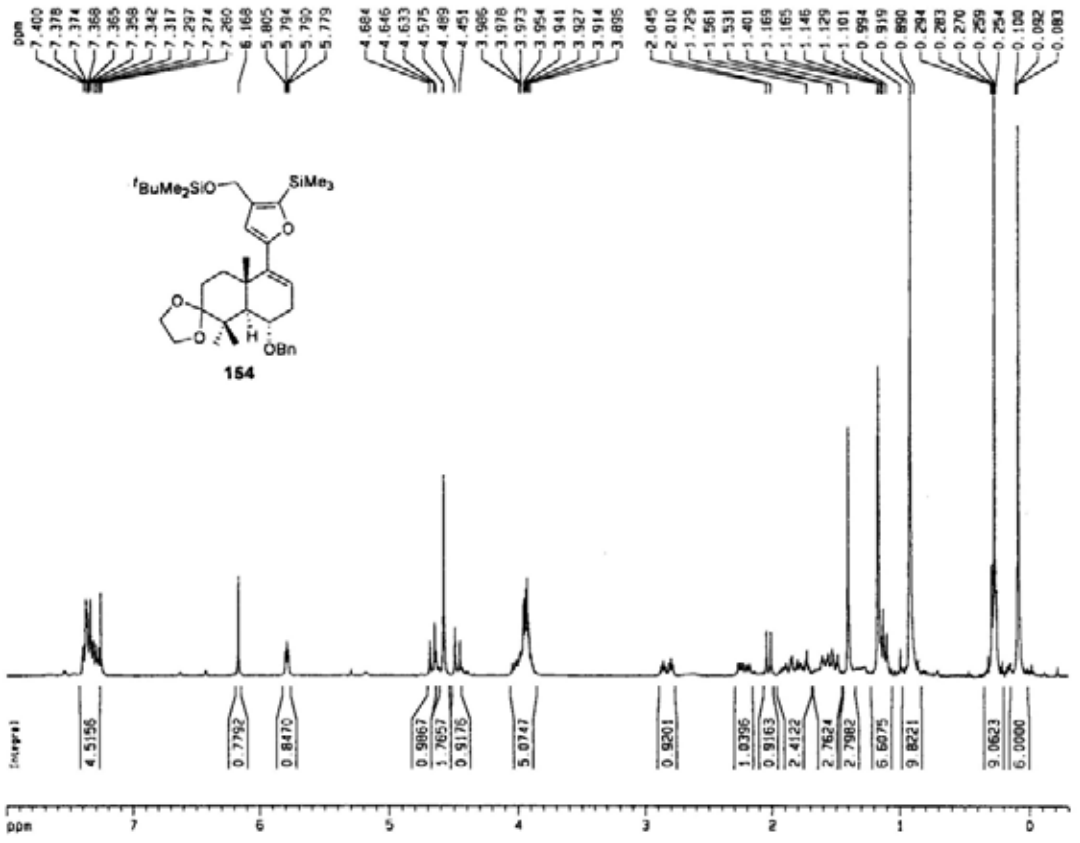
======== CHANNEL f1 ========
NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SFO1 75.4745111 MHz

======== 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 75.4677448 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
CY 12.00 cm
F1P 165.000 ppm
F1 12452.18 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 7.50870 ppm/cm
HZCM 574.21112 Hz/cm

1H

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Current Data Parameters
NAME          dja-1-057-H1
EXPNO                    1
PROCNO                   1

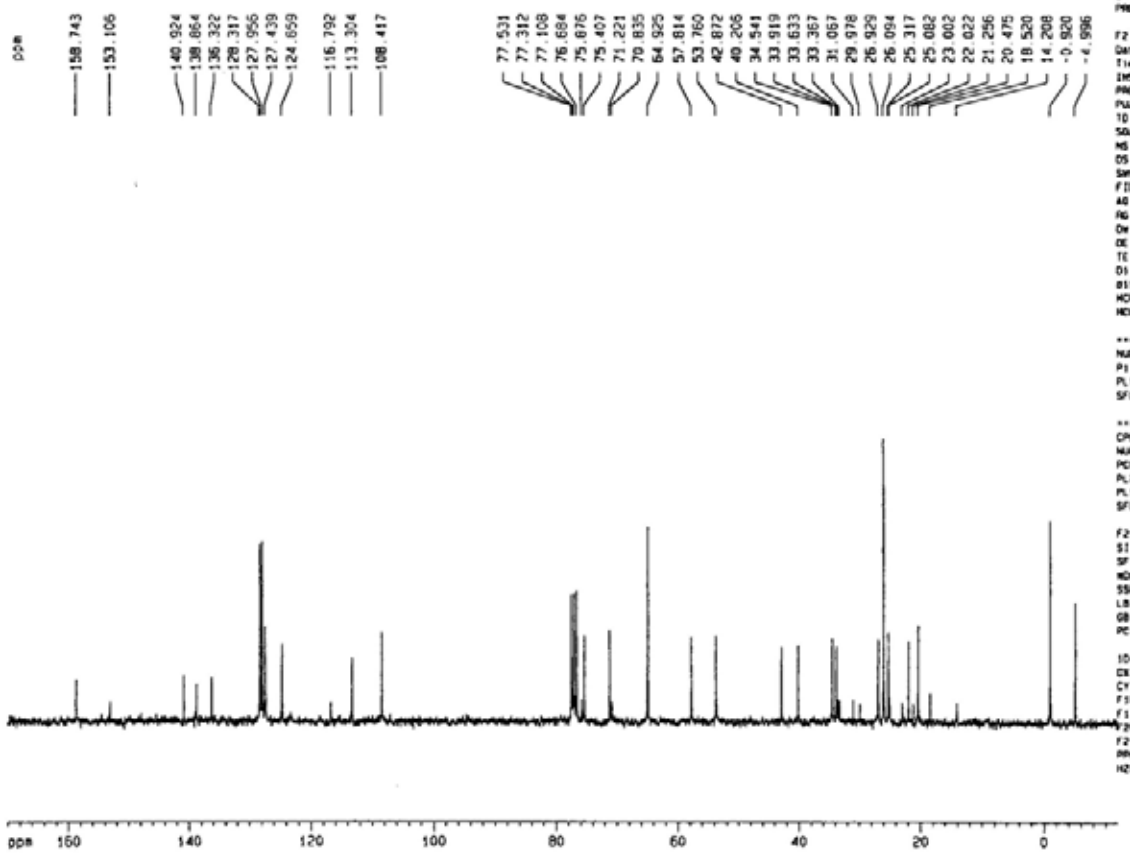
F2 - Acquisition Parameters
Date_              20070813
Time                  19.10
INSTRUM                dpx300
PROBHD     5 mm BBO BB-1H
PULPROG                  zg
TD                    32768
SOLVENT               CDCl3
NS                        8
DS                        0
SWH                8992.806 Hz
FIDRES             0.274439 Hz
AQ                 1.8219508 sec
RG                       64
DW                   55.600 usec
DE                    79.43 usec
TE                      0.0 K
D1                 1.00000000 sec
HCREST             0.00000000 sec
HCWFK              0.01500000 sec

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

F2 - Processing parameters
SI                    32768
SF             300.1300055 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00

1D NMR plot parameters
CX                    22.00 cm
CY                    24.00 cm
F1P                   8.000 ppm
F1                 2401.54 Hz
F2P                  -0.300 ppm
F2                   -90.04 Hz
PPMCM              0.37227 ppm/cm
HZCM             113.23087 Hz/cm
```

C13

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Current Data Parameters
NAME          dja-1-057-repeat-C13
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20071025
Time                  14.51
INSTRUM                dbx300
PROBHD     5 mm BBO BB-1H
PULPROG                zgpg
TD                    65536
SOLVENT               CDCl3
NS                      108
DS                        0
SWH               22675.736 Hz
FIDRES             0.346004 Hz
AQ                 1.4451188 sec
RG                    1625.5
DW                   22.050 usec
DE                    6.00 usec
TE                      0.0 K
D1                 1.00000000 sec
D11                0.03000000 sec
HCREST             0.00000000 sec
HCWFK              0.01500000 sec

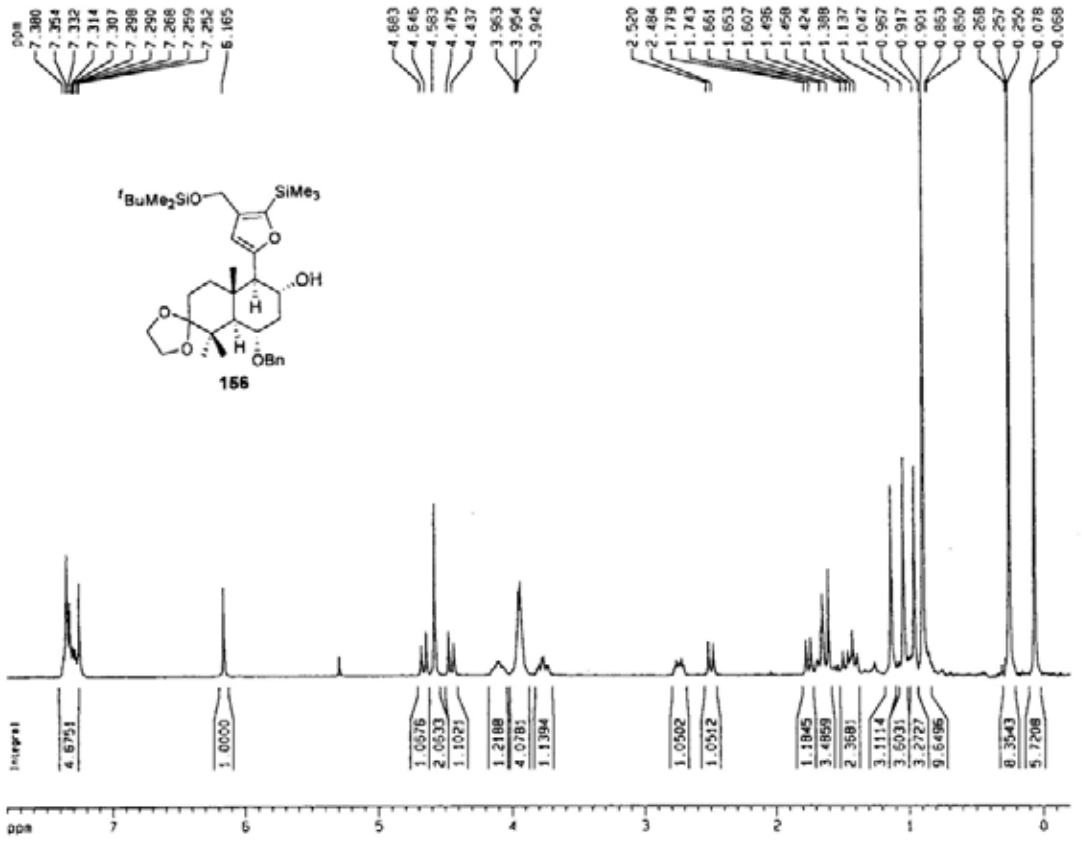
======== CHANNEL f1 ========
NUC1                     13C
P1                    3.00 usec
PL1                   -6.00 dB
SFO1           75.4745111 MHz

======== 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             75.4577438 MHz
WDW                      EM
SSB                       0
LB                     3.00 Hz
GB                        0
PC                     1.80

1D NMR plot parameters
CX                    23.00 cm
CY                     6.00 cm
F1P                 170.000 ppm
F1                 12829.52 Hz
F2P                 -12.000 ppm
F2                  -905.55 Hz
PPMCM              7.91304 ppm/cm
HZCM             597.17950 Hz/cm
```

1H



156

Current Data Parameters
NAME djq-1-059-H1
EXPNO 1
PROCNO 1

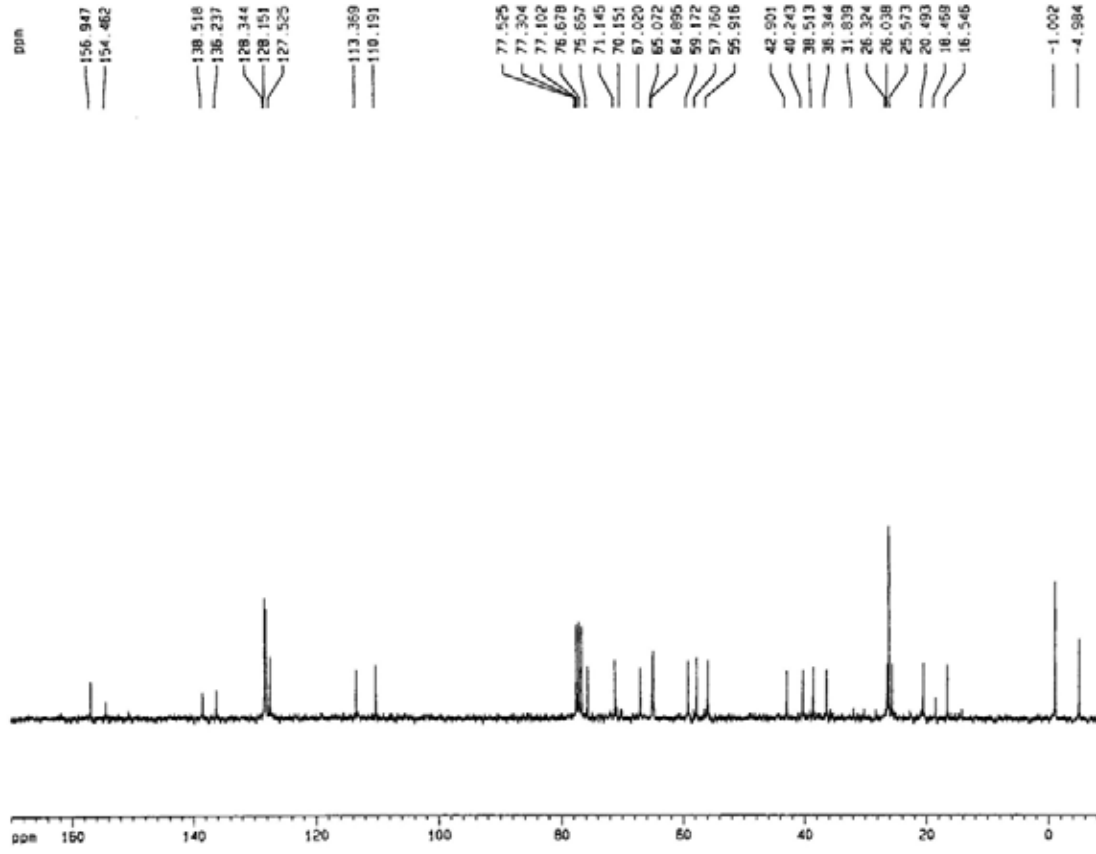
F2 - Acquisition Parameters
Date_ 20070813
Time 19.46
INSTRUM spx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 128
DW 55.600 usec
DE 79.43 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 300.1300060 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 20.00 cm
F1P 7.800 ppm
F1 2341.01 Hz
F2P -0.200 ppm
F2 -60.03 Hz
PPMCM 0.36354 ppm/cm
HZCM 109.13818 Hz/cm

C13



Current Data Parameters
NAME djq-1-059-repeat-C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20071025
Time 15.02
INSTRUM spx300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 158
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 1625.5
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

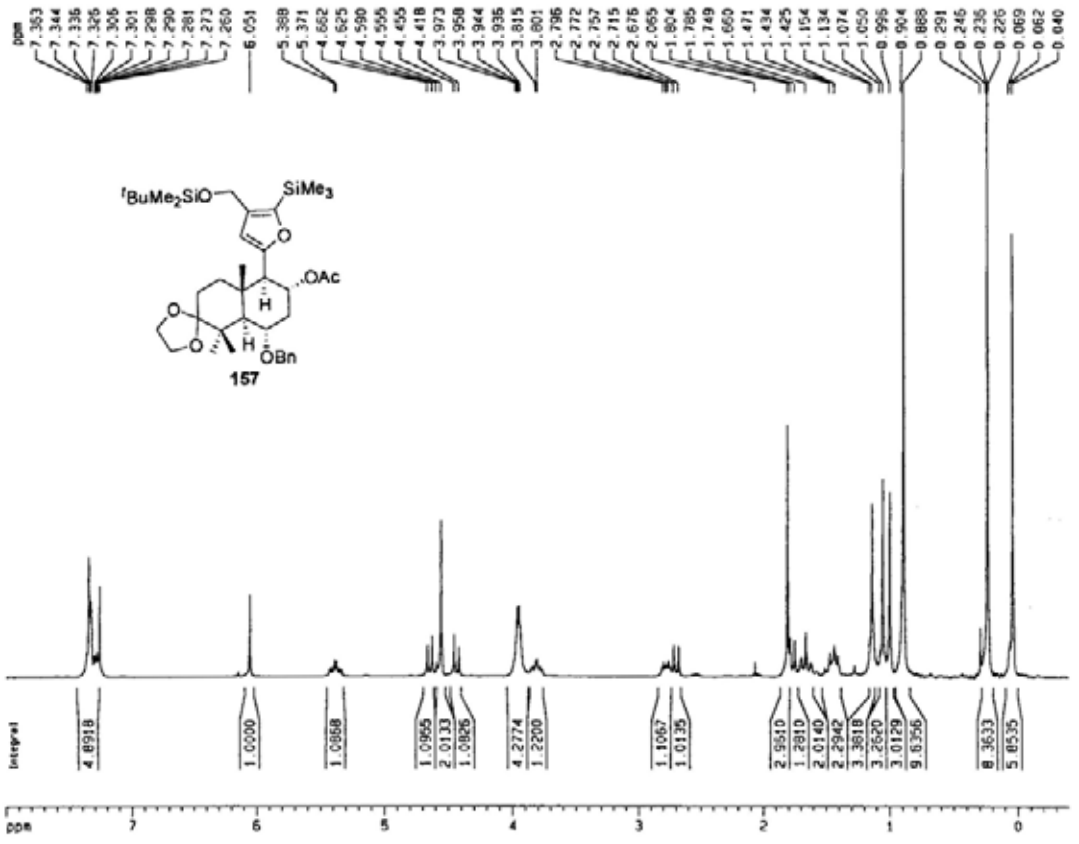
--------- CHANNEL f1 ---------
NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SFO1 75.4745111 MHz

--------- 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 75.4677441 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.80

1D NMR plot parameters
CX 23.00 cm
CY 8.00 cm
F1P 170.000 ppm
F1 12829.52 Hz
F2P -12.000 ppm
F2 -905.61 Hz
PPMCM 7.91304 ppm/cm
HZCM 967.17990 Hz/cm

1H



Current Data Parameters
NAME djq-1-060-H1
EXPNO 1
PROCNO 1

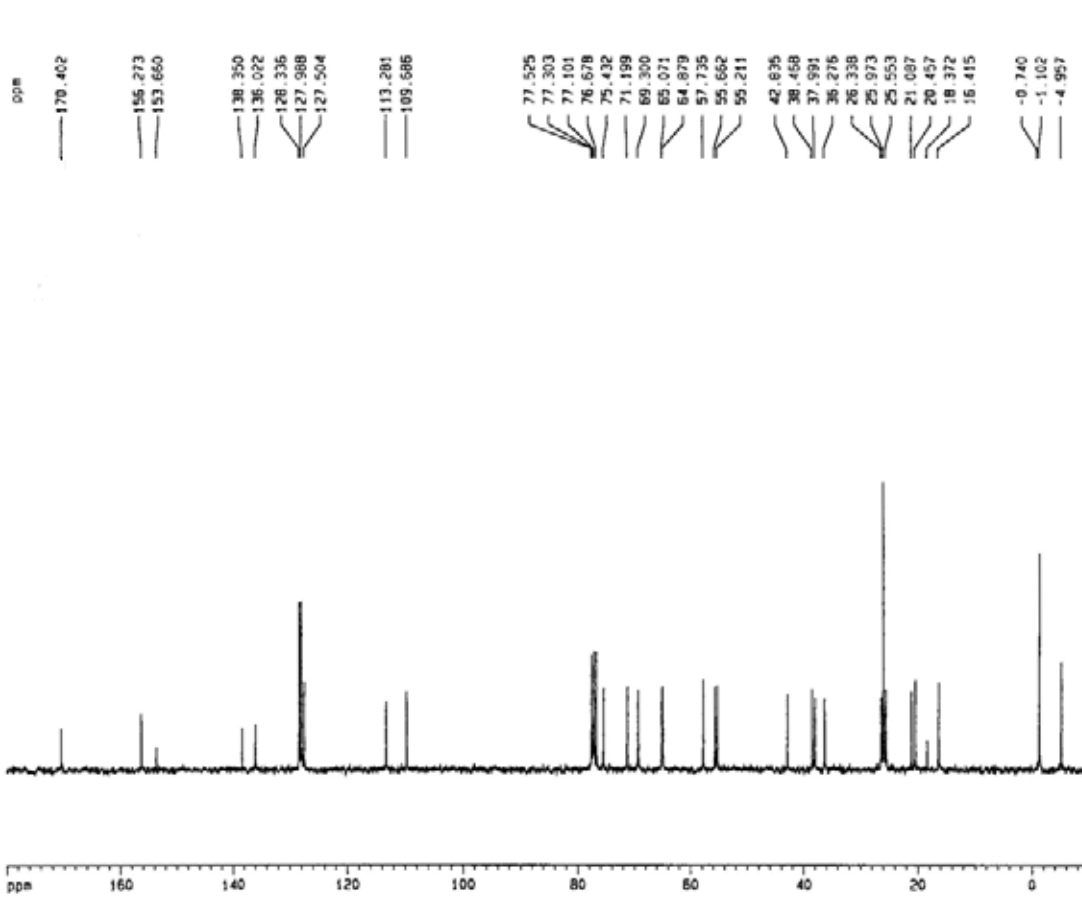
F2 - Acquisition Parameters
Date_ 20080419
Time 13.23
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 35.9
DW 55.600 usec
DE 75.43 usec
TE 295.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

******** 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

1D NMR plot parameters
CX 22.00 cm
CY 18.00 cm
F1P 8.000 ppm
F1 2401.04 Hz
F2P -0.400 ppm
F2 -120.05 Hz
PPMCM 0.38182 ppm/cm
HZCM 114.58509 Hz/cm

C13



Current Data Parameters
NAME djq-1-060-C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080419
Time 13.27
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 155
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 10321.3
DW 22.050 usec
DE 6.00 usec
TE 295.2 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

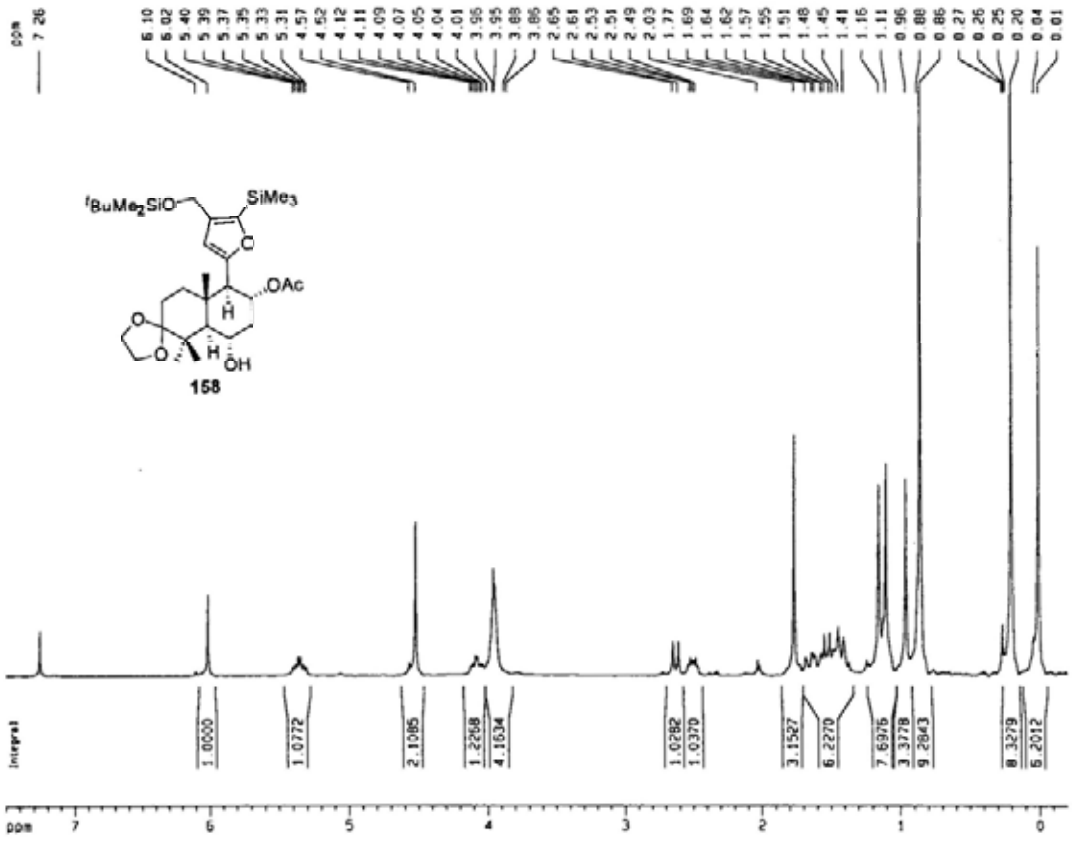
******** CHANNEL f1 ********
NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SFO1 75.4745111 MHz

******** 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 75.4577462 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
CY 6.00 cm
F1P 180.000 ppm
F1 13584.19 Hz
F2P -15.000 ppm
F2 -1132.02 Hz
PPMCM 8.47826 ppm/cm
HZCM 639.83521 Hz/cm

1H



Current Data Parameters
NAME dip-1-083-8-H1
EXPNO 2
PROCNO 1

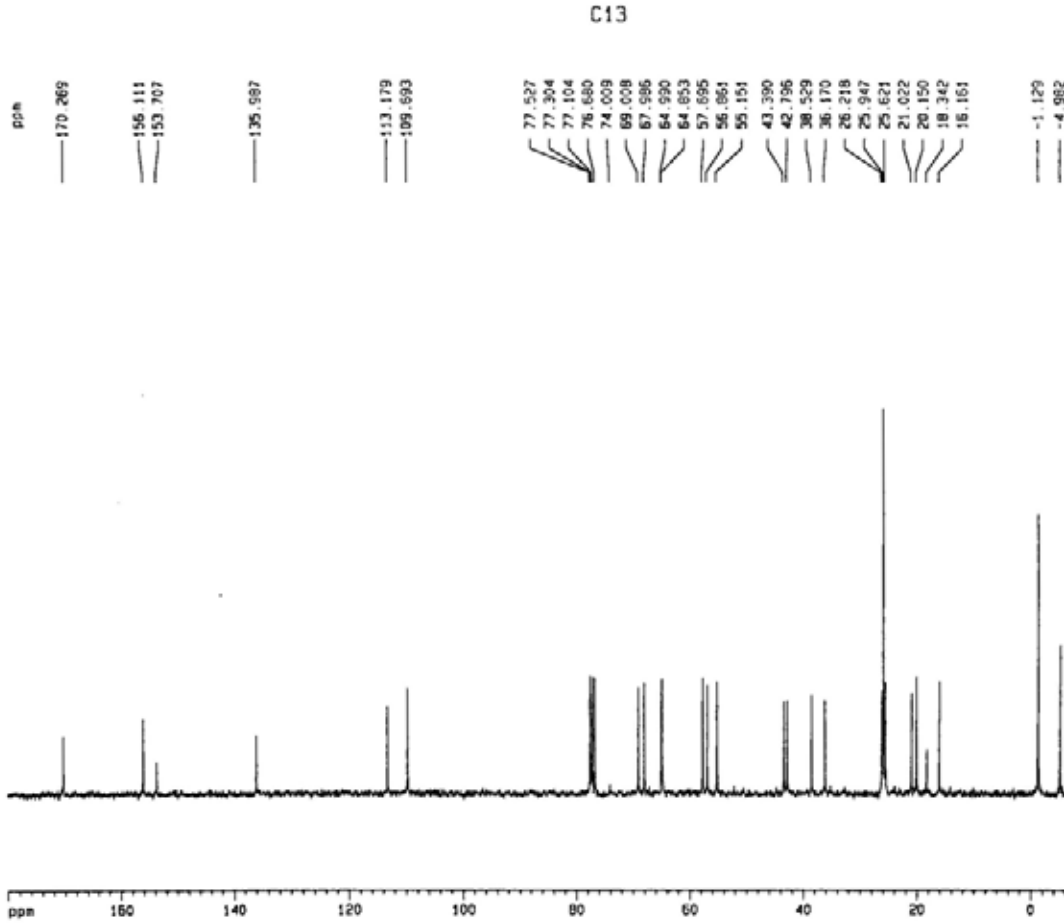
F2 - Acquisition Parameters
Date_ 20080419
Time 10.54
INSTRUM spx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 25.4
DW 55.600 usec
DE 78.43 usec
TE 295.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

******** 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

1D NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 7.500 ppm
F1 2250.98 Hz
F2P -0.200 ppm
F2 -60.03 Hz
PPMCM 0.35000 ppm/cm
HZCM 105.04551 Hz/cm

C13



Current Data Parameters
NAME dip-1-083-8-C13
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080419
Time 10.59
INSTRUM spx300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 116
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 295.2 K
D1 1.00000000 sec
D11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

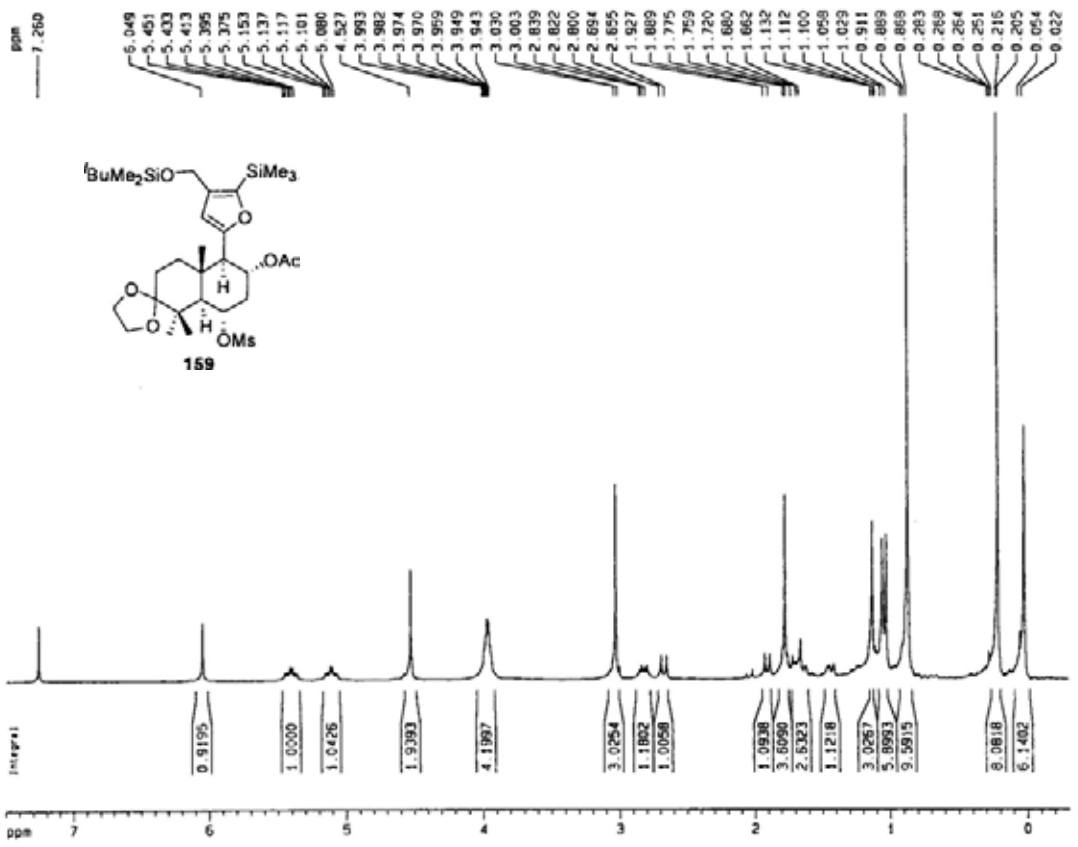
******** CHANNEL f1 ********
NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SFO1 75.4745111 MHz

******** 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 75.4677462 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
CY 8.00 cm
F1P 180.000 ppm
F1 13584.19 Hz
F2P -15.000 ppm
F2 -1132.62 Hz
PPMCM 8.47826 ppm/cm
HZCM 639.83521 Hz/cm

1H



Current Data Parameters
NAME dlq-1-083-C-H1
EXPNO 10
PROCNO 1

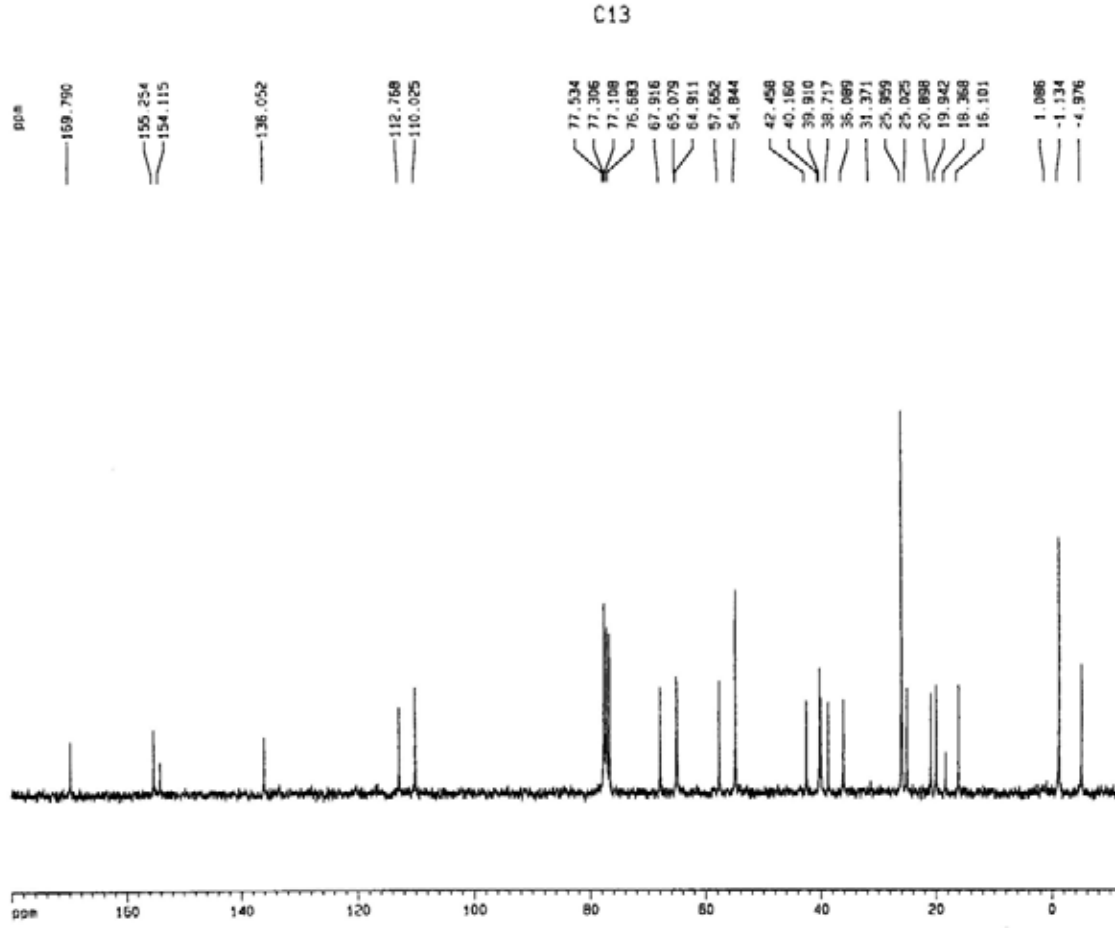
F2 - Acquisition Parameters
Date_ 20080423
Time 13.53
INSTRUM spx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 64
DW 55.600 usec
DE 75.43 usec
TE 296.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 300.1300066 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 12.00 cm
F1P 7.500 ppm
F1 2250.98 Hz
F2P -0.300 ppm
F2 -90.04 Hz
PPMCM 0.35495 ppm/cm
HZCM 106.40973 Hz/cm

C13



Current Data Parameters
NAME dlq-1-083-C-C13
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080423
Time 13.58
INSTRUM spx300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 209
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 295.2 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

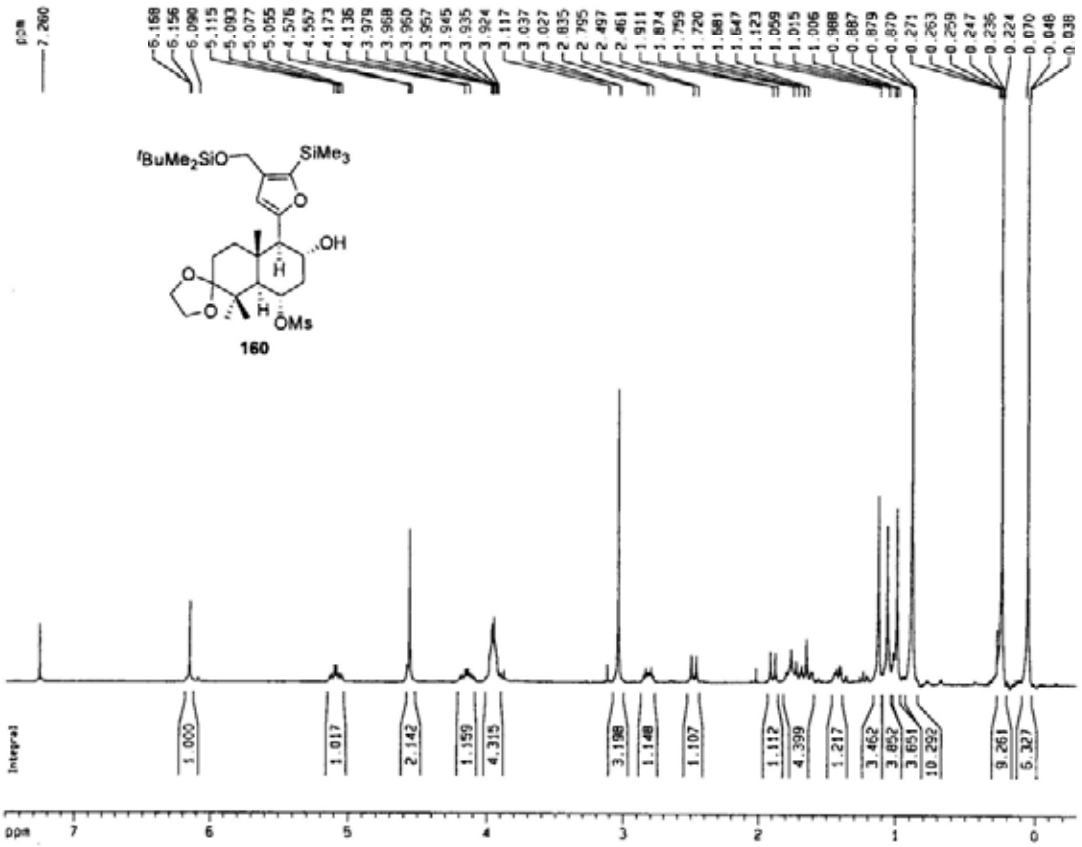
======== CHANNEL f1 ========
NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SFO1 75.4745111 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 19.00 dB
SFO2 300.1315002 MHz

F2 - Processing parameters
SI 65536
SF 75.4677408 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
CY 8.00 cm
F1P 180.000 ppm
F1 13584.20 Hz
F2P -12.000 ppm
F2 -905.61 Hz
PPMCM 8.34783 ppm/cm
HZCM 629.99164 Hz/cm

1H



Current Data Parameters
NAME djq-1-084-B-H1
EXPNO 1
PROCNO 1

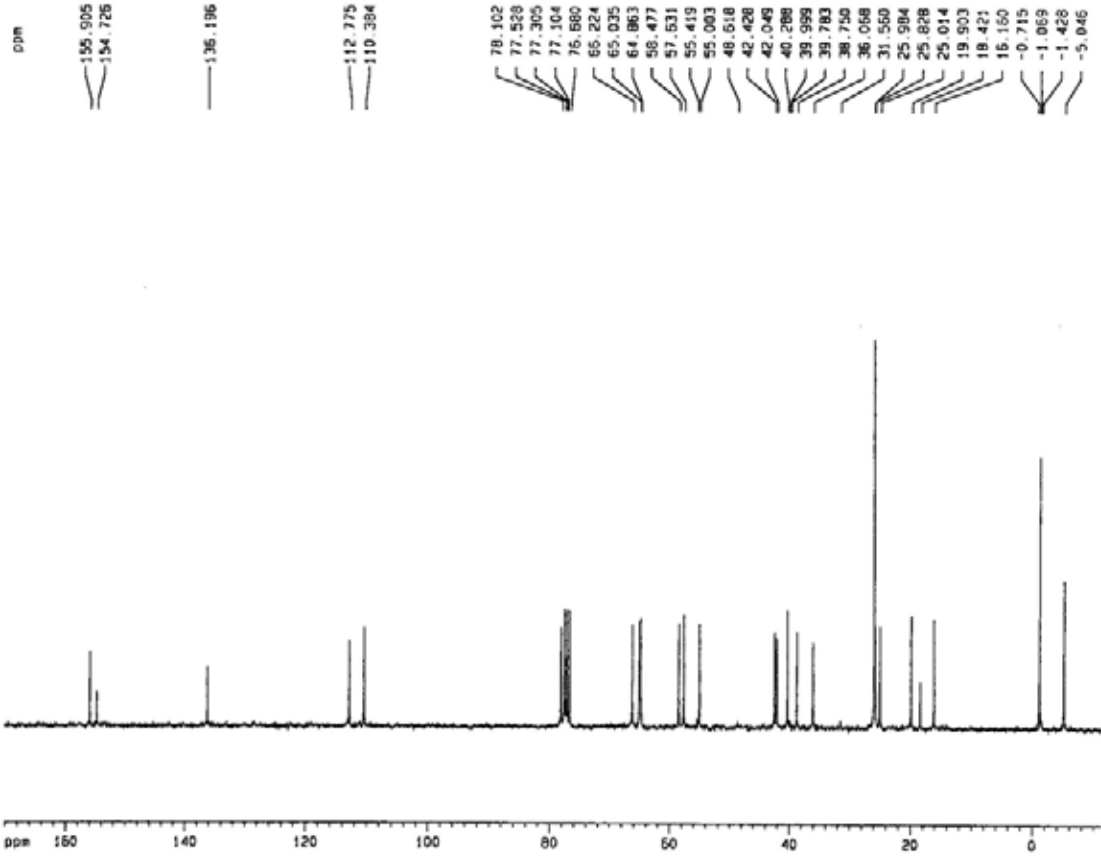
F2 - Acquisition Parameters
Date_ 20080419
Time 13.35
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 28.5
DW 55.600 usec
DE 78.43 usec
TE 296.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== 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

1D NMR plot parameters
CX 22.00 cm
CY 18.00 cm
F1P 7.500 ppm
F1 2250.98 Hz
F2P -0.300 ppm
F2 -90.04 Hz
PPMCM 0.35455 ppm/cm
HZCM 106.40973 Hz/cm

C13



Current Data Parameters
NAME djq-1-084-B-C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080419
Time 13.39
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 211
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 296.2 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

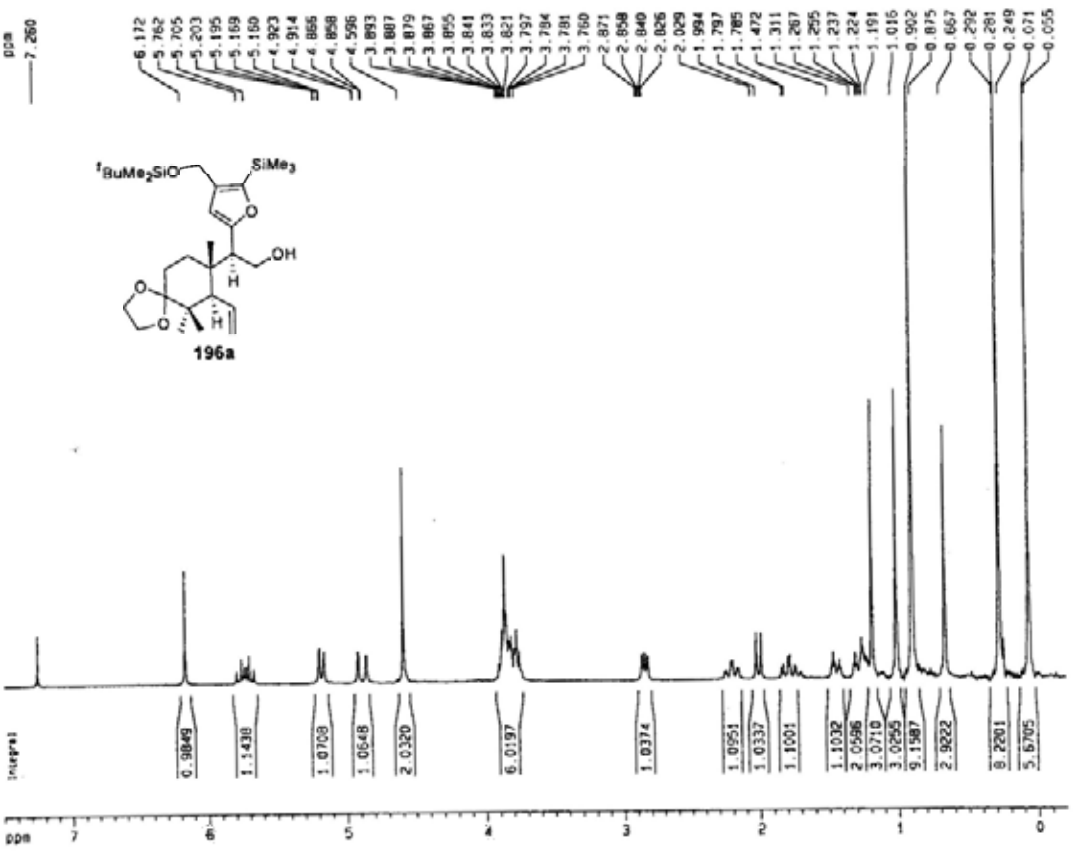
======== CHANNEL f1 ========
NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SFO1 75.4745111 MHz

======== 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 75.4677476 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
CY 8.00 cm
F1P 170.000 ppm
F1 12829.52 Hz
F2P -15.000 ppm
F2 -1132.02 Hz
PPMCM 8.04348 ppm/cm
HZCM 607.02319 Hz/cm

1H



Current Data Parameters
NAME dja-1-065-NaBH4-1-H1
EXPNO 1
PROCNO 1

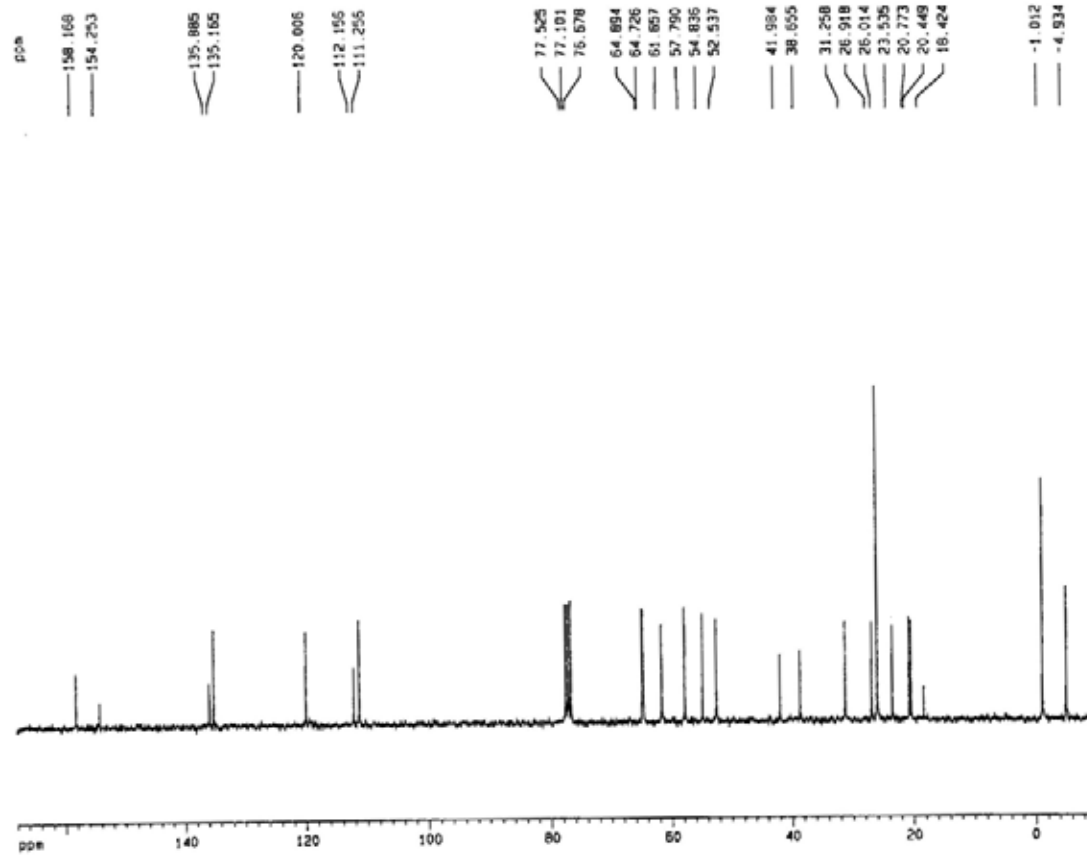
F2 - Acquisition Parameters
Date_ 20070830
Time 14.32
INSTRUM dds300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219568 sec
RG 64
DW 55.600 usec
DE 75.43 usec
TE 0.0 K
D1 1.00000000 sec
HCREST 0.00000000 sec
HCWFK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 300.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.05

1D NMR plot parameters
CX 22.00 cm
CY 24.00 cm
F1P 7.500 ppm
F1 2250.98 Hz
F2P -0.200 ppm
F2 -60.03 Hz
PPMCM 0.35000 ppm/cm
HZCM 105.04590 Hz/cm

C13



Current Data Parameters
NAME dja-1-065-NaBH4-1-C13
EXPNO 1
PROCNO 1

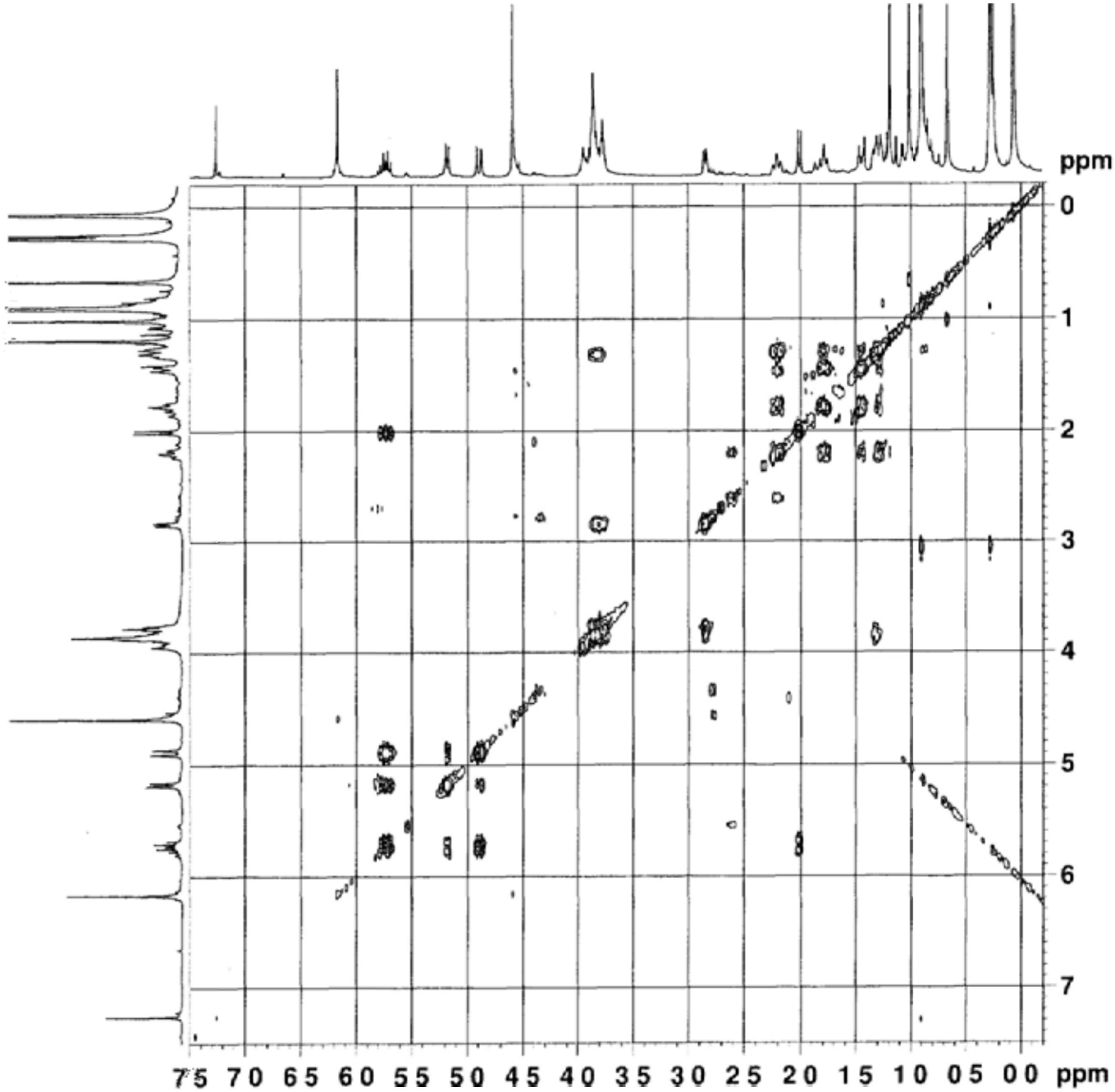
F2 - Acquisition Parameters
Date_ 20070830
Time 14.37
INSTRUM dds300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 256
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
d11 0.03000000 sec
HCREST 0.00000000 sec
HCWFK 0.01500000 sec

======== 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 300.1315067 MHz

F2 - Processing parameters
SI 65536
SF 75.4677431 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

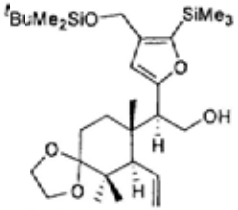
1D NMR plot parameters
CX 23.00 cm
CY 7.00 cm
F1P 158.000 ppm
F1 12678.56 Hz
F2P -15.000 ppm
F2 -1132.02 Hz
PPMCM 7.95652 ppm/cm
HZCM 600.48075 Hz/cm




```
NAME        djq-1-085-1 H-H Cosy
EXPNO                         2
PROCNO                        1
Date_                  20080603
Time                      15.57
INSTRUM                   spect
PROBHD    5 mm PADUL 13C
PULPROG          cosygpmfqf
TD                         2048
SOLVENT                  CDCl3
NS                            14
DS                             8
SWH                  3906.250 Hz
FIDRES               1.907349 Hz
AQ                   0.2621940 sec
RG                           203
DW                   128.000 us
DE                     6.50 us
TE                     294.9 K
D0                   0.00000300 se
D1                   1.08355701 se
D13                  0.00000400 se
D16                  0.00020000 se
IN0                  0.00025600 se

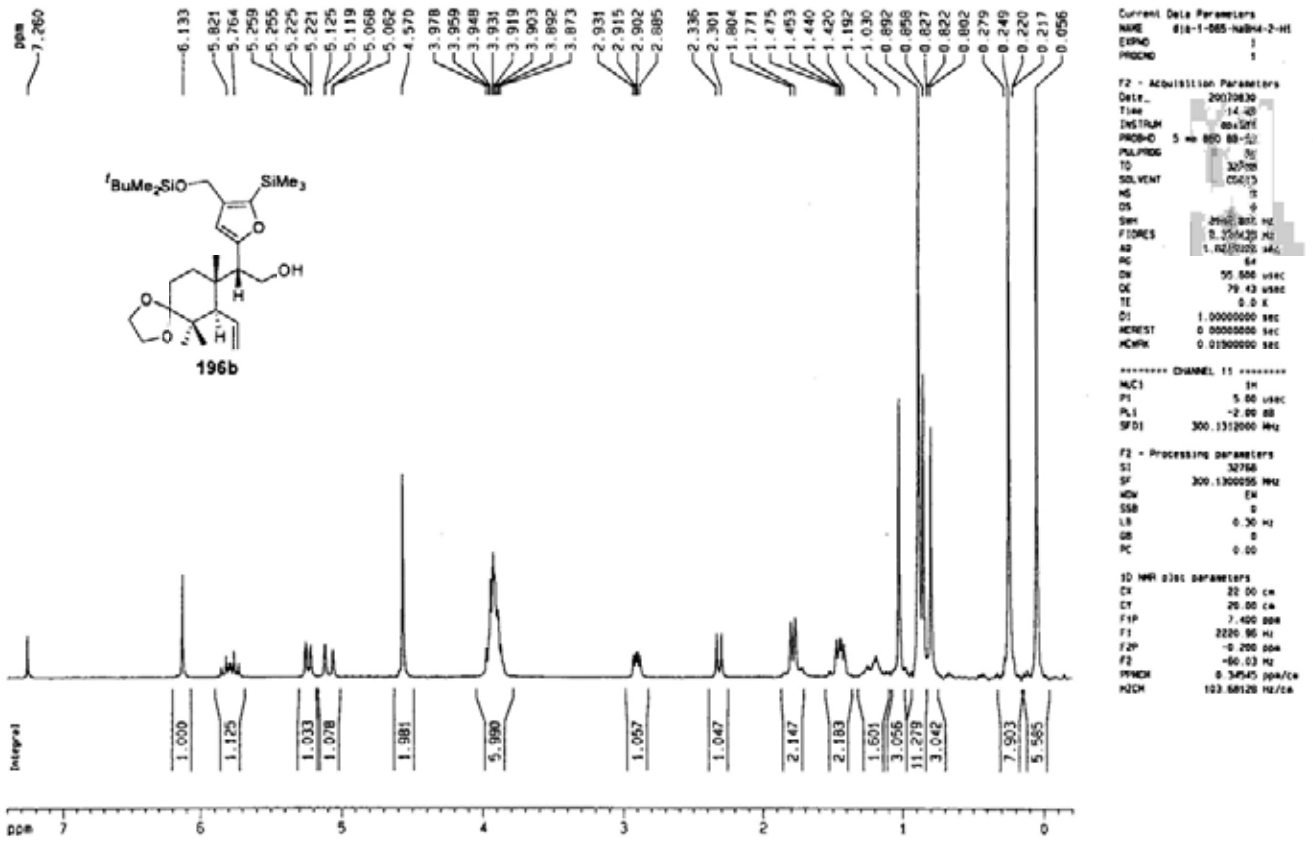
======== CHANNEL f1 ======
NUC1                         1H
P1                     14.83 us
PL1                     0.00 dB
PL1W                 8.31434441 W
SFO1               400.1312112 MHz

====== GRADIENT CHANNEL =====
GPNAM1                SINE.100
GPNAM2                SINE.100
GPNAM3                SINE.100
GPZ1                    16.00 %
GPZ2                    12.00 %
GPZ3                    40.00 %
P16                   1000.00 usec
ND0                          1
TD                         128
SFO1               400.1312 MHz
FIDRES              30.517578 Hz
SW                      9.762 ppm
FnMODE                     QF
SI                       1024
SF                 400.1300022 MHz
WDW                      SINE
SSB                         0
LB                      0.00 Hz
GB                          0
PC                       1.40
SI                       1024
MC2                        QF
SF                 400.1300009 MHz
WDW                      SINE
SSB                         0
LB                      0.00 Hz
GB                          0
```



^{1}H-^{1}H COSY of **196a**

1H



196b

Current Data Parameters
NAME dja-1-065-NaBH4-2-H1
EXPNO 1
PROCNO 1

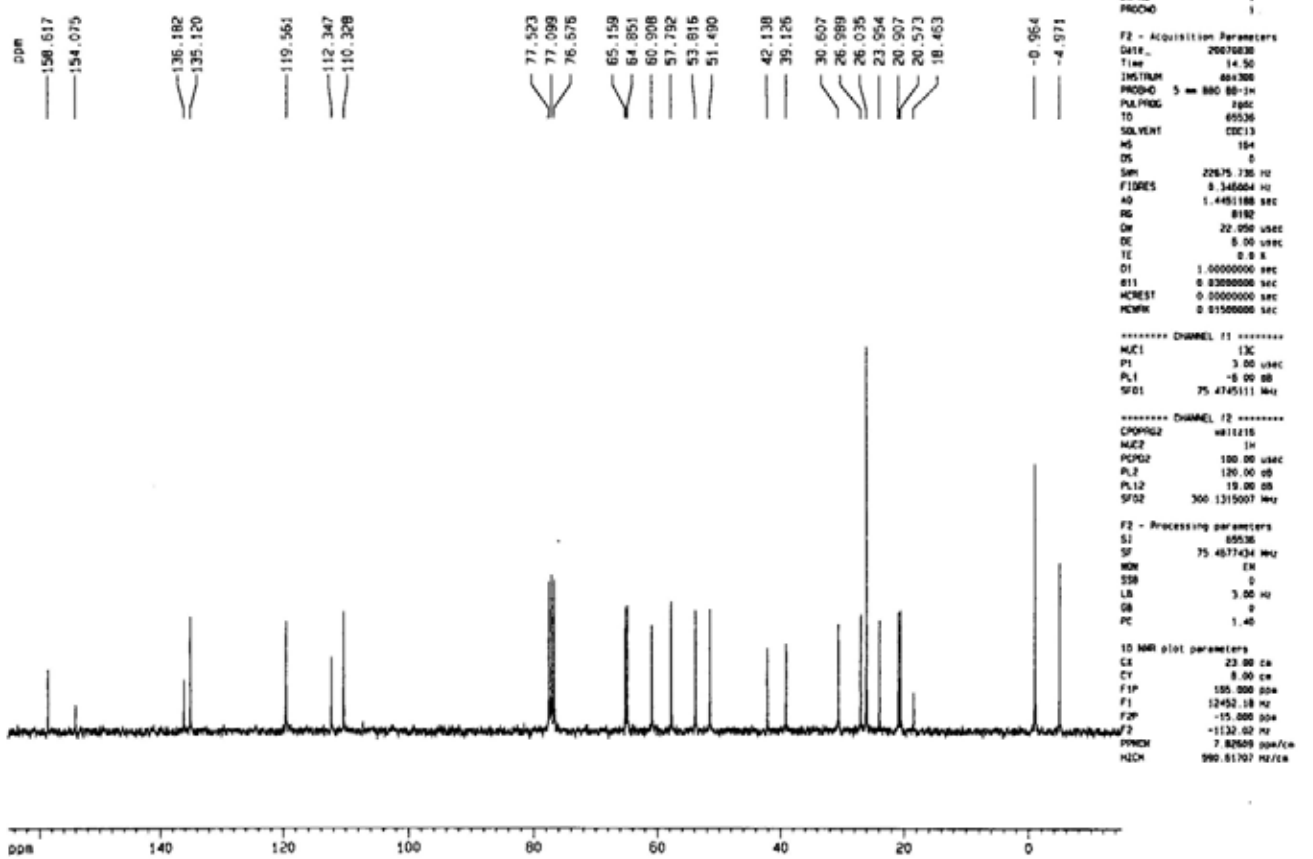
F2 - Acquisition Parameters
Date_ 20070830
Time 14.48
INSTRUM spect
PROBHD 5 mm BBO BB-H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 2998.801 Hz
FIDRES 0.091492 Hz
AQ 1.0929920 sec
RG 64
DW 55.800 usec
DE 79.43 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 300.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.00

1D NMR plot parameters
CX 22.00 cm
CY 20.00 cm
F1P 7.400 ppm
F1 2220.96 Hz
F2P -0.200 ppm
F2 -60.03 Hz
PPMCM 0.34545 ppm/cm
HZCM 103.68128 Hz/cm

C13



Current Data Parameters
NAME dja-1-065-NaBH4-2-C13
EXPNO 1
PROCNO 1

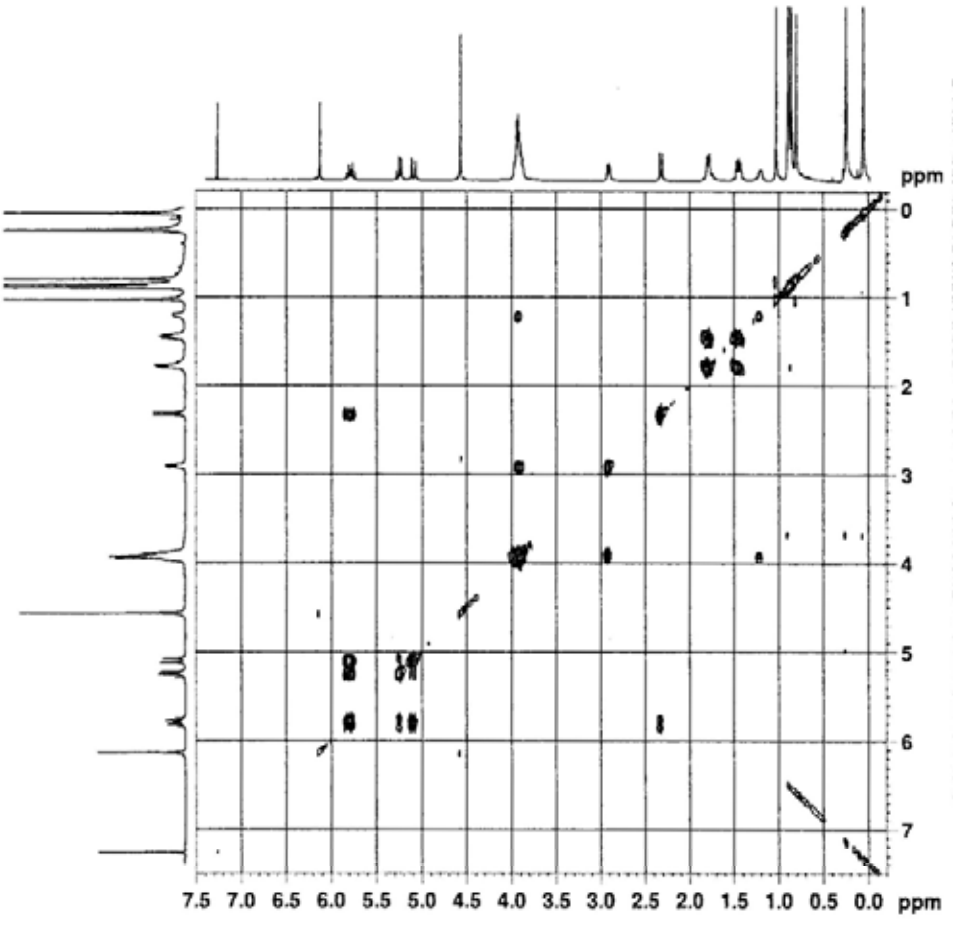
F2 - Acquisition Parameters
Date_ 20070830
Time 14.50
INSTRUM dpx300
PROBHD 5 mm BBO BB-H
PULPROG zgdc
TD 65536
SOLVENT CDCl3
NS 164
DS 0
SWH 22675.736 Hz
FIDRES 0.345804 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
D11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== 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 75.4677434 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

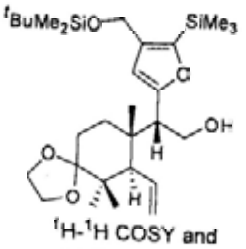
1D NMR plot parameters
CX 22.00 cm
CY 8.00 cm
F1P 185.000 ppm
F1 13452.18 Hz
F2P -15.000 ppm
F2 -1132.02 Hz
PPMCM 7.82609 ppm/cm
HZCM 590.61707 Hz/cm



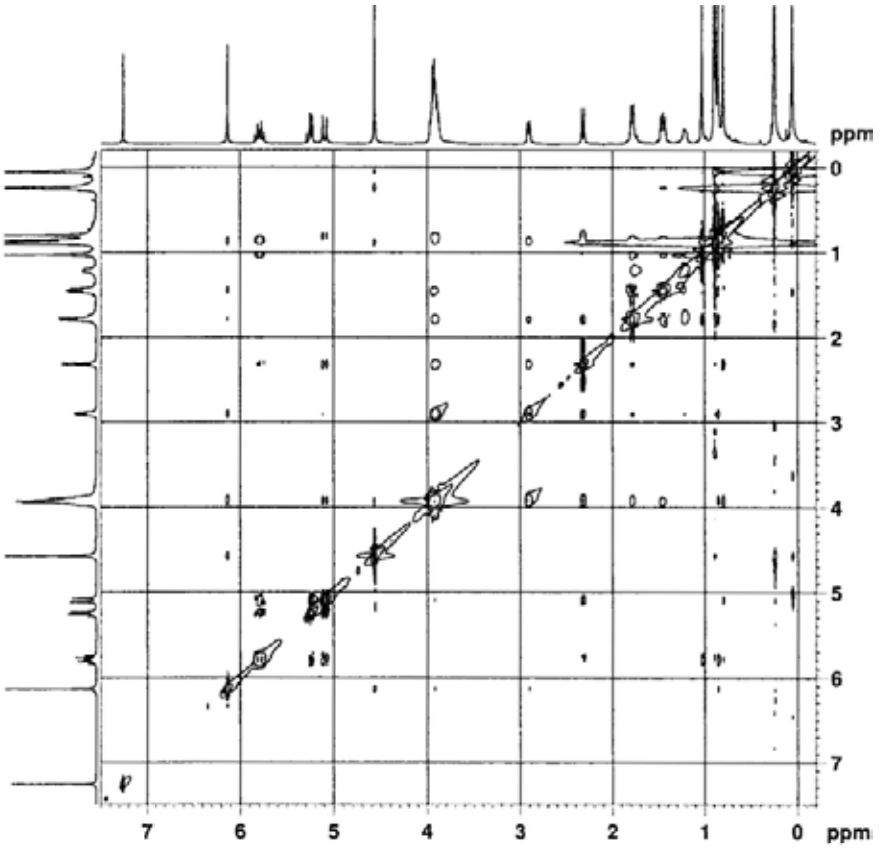

```
NAME        djq-1-085-2 H-H Cosy
EXPNO                 2
PROCNO                1
Date_          20080530
Time               9.39
INSTRUM           spect
PROBHD   5 mm PADUL 13C
PULPROG       cosygpmfqf
TD                 2048
SOLVENT            CDCl3
NS                    6
DS                    8
SWH           3267.974 Hz
FIDRES        1.595690 Hz
AQ            0.3133940 sec
RG                  203
DW              153.000 usec
DE                6.50 usec
TE              297.4 K
D0            0.00000300 sec
D1            2.03235793 sec
D13           0.00000400 sec
D16           0.00020000 sec
IN0           0.00030600 sec

======== CHANNEL f1 ========
NUC1                1H
P1                14.83 usec
PL1                0.00 dB
PL1W         8.31434441 W
SFO1        400.1314784 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPNAM3          SINE.100
GPZ1              16.00 %
GPZ2              12.00 %
GPZ3              40.00 %
P16             1000.00 usec
NDO                   1
TD                  104
SFO1          400.1315 MHz
FIDRES        31.422825 Hz
SW                8.167 ppm
FnMODE               QF
SI                 1024
SF          400.1299986 MHz
WDW              SINE
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.40
SI                 1024
MC2                  QF
SF          400.1299987 MHz
WDW              SINE
```



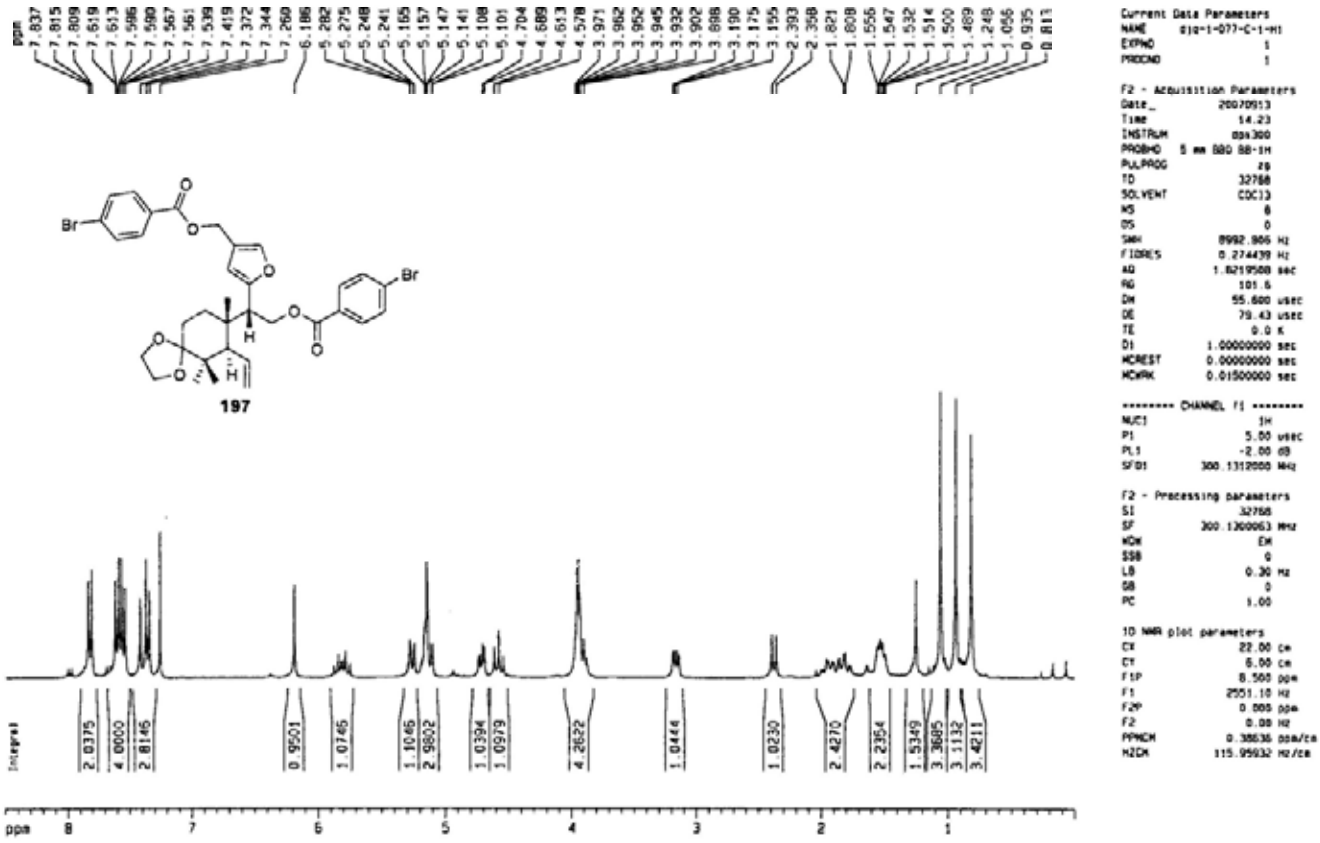
^{t}H-^{1}H COSY and ROESY of **196b**




```
NAME        djq-1-085-2-Roesy
EXPNO                 2
PROCNO                1
Date_          20080530
Time               3.28
INSTRUM           spect
PROBHD   5 mm PADUL 13C
PULPROG          roesyph
TD                 2048
SOLVENT            CDCl3
NS                   16
DS                    4
SWH           3703.704 Hz
FIDRES        1.808449 Hz
AQ            0.2765300 sec
RG                 28.5
DW              135.000 usec
DE                6.50 usec
TE              295.3 K
D0            0.00012156 sec
D1            2.06922102 sec
D12           0.00002000 sec
IN0           0.00027000 sec

======== CHANNEL f1 ========
NUC1                1H
P1                14.83 usec
P15           300000.00 usec
PL1                0.00 dB
PL11              15.66 dB
PL1W         8.31434441 W
PL11W        0.22585411 W
SFO1        400.1313103 MHz
NDO                   1
TD                  256
SFO1          400.1313 MHz
FIDRES        14.467592 Hz
SW                9.256 ppm
FnMODE       States-TPPI
SI                 1024
SF          400.1300037 MHz
WDW              QSINE
SSB                   2
LB                 0.00 Hz
GB                    0
PC                 1.00
SI                 1024
MC2          States-TPPI
SF          400.1300037 MHz
WDW              QSINE
SSB                   2
LB                 0.00 Hz
GB                    0
```

1H



Current Data Parameters
NAME djg-1-077-C-1-H1
EXPNO 1
PROCNO 1

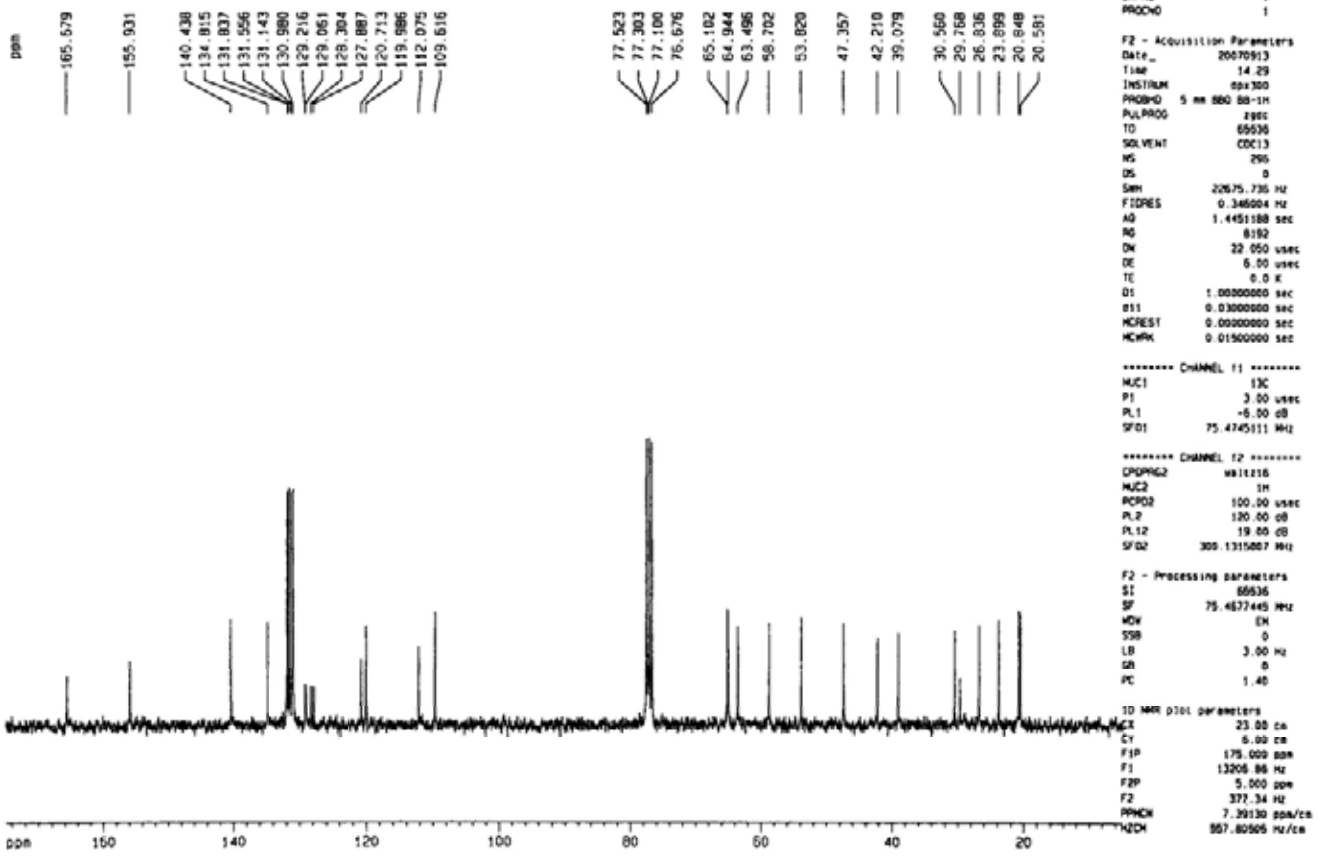
F2 - Acquisition Parameters
Date_ 20070913
Time 14.23
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219588 sec
RG 101.6
DW 55.600 usec
DE 79.43 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

-------- 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

1D NMR plot parameters
CX 22.00 cm
CY 6.00 cm
F1P 8.560 ppm
F1 2551.10 Hz
F2P 0.005 ppm
F2 0.00 Hz
PPMCM 0.38536 ppm/cm
HZCM 115.95932 Hz/cm

C13



Current Data Parameters
NAME djg-1-077-C-1-C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070913
Time 14.29
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 256
DS 0
SWH 22675.735 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
D11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

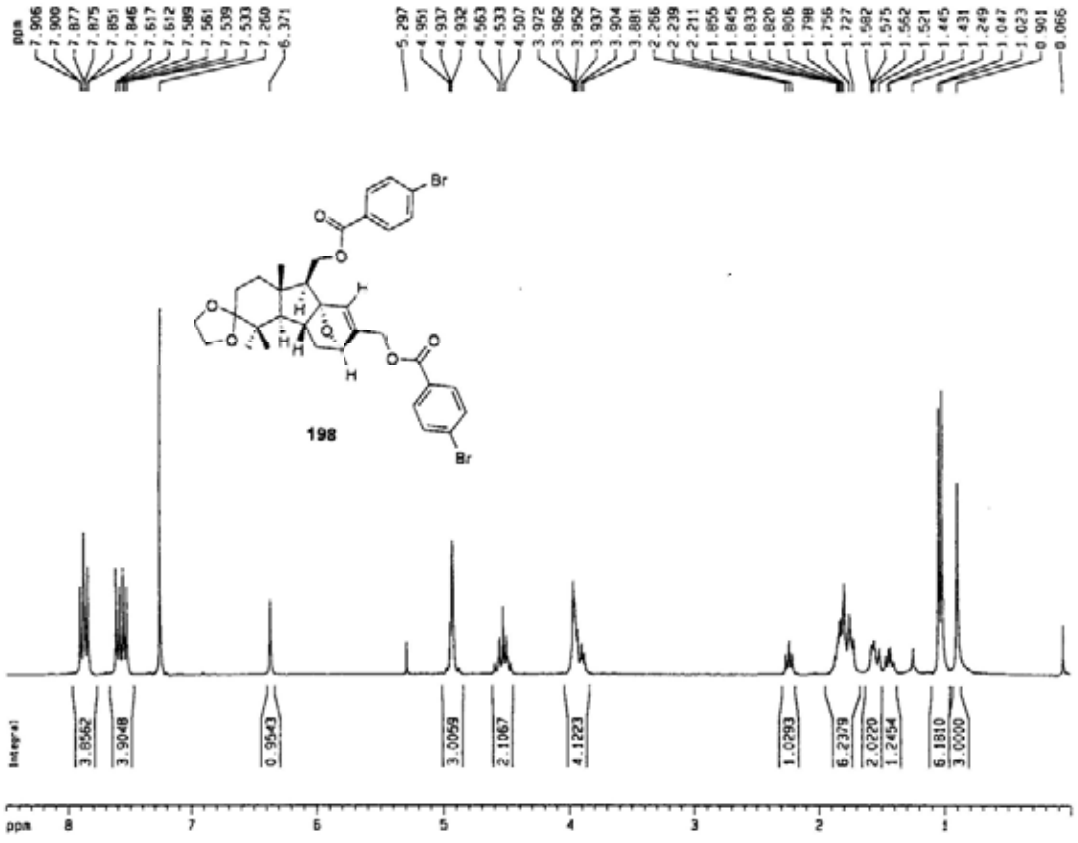
-------- CHANNEL f1 --------
NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SFO1 75.4745111 MHz

-------- 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 75.4677445 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
CY 6.00 cm
F1P 175.000 ppm
F1 13206.86 Hz
F2P 5.000 ppm
F2 377.34 Hz
PPMCM 7.39130 ppm/cm
HZCM 867.80505 Hz/cm

1H



Current Data Parameters
NAME dig-1-077-C-2-H1
EXPNO 1
PROCNO 1

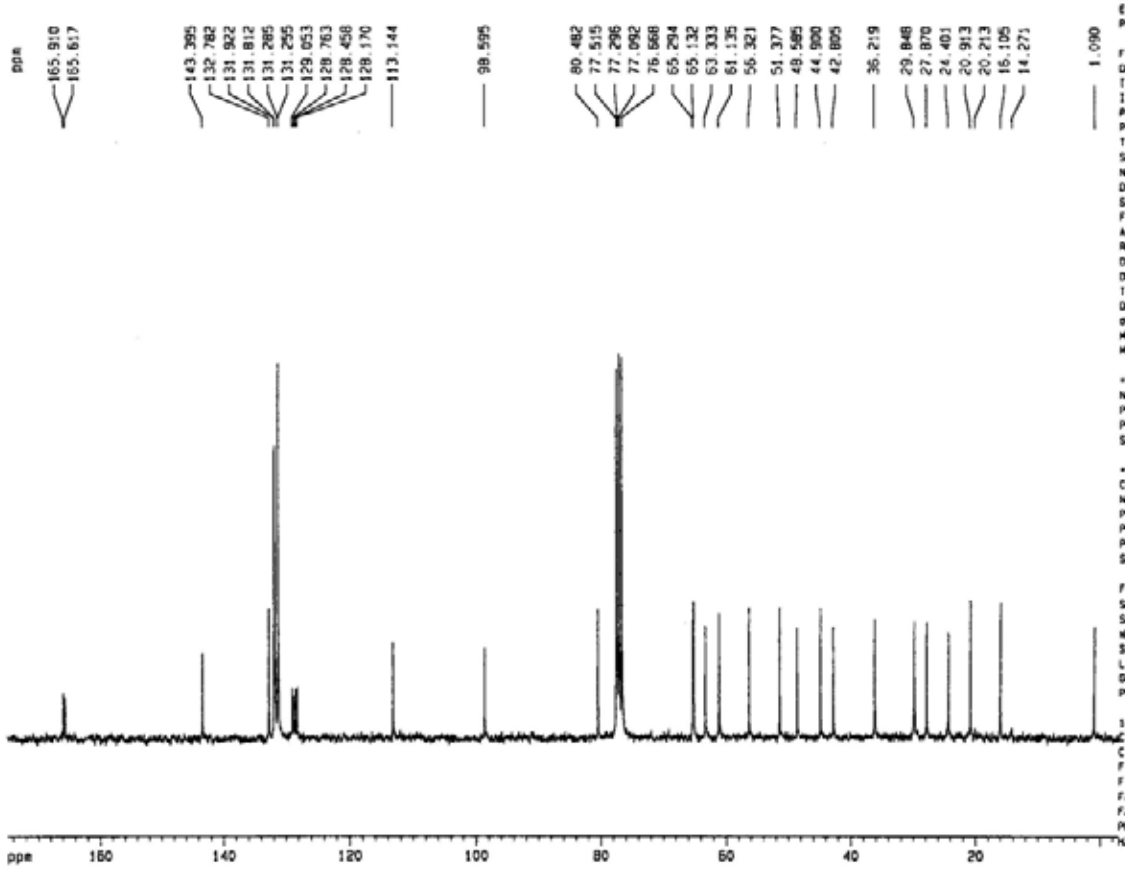
F2 - Acquisition Parameters
Date_ 20070913
Time 14.15
INSTRUM spx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 8992.806 Hz
FIDRES 0.274435 Hz
AQ 1.8219588 sec
RG 287.4
DW 55.500 usec
DE 79.43 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 300.1300057 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.20

1D NMR plot parameters
CX 22.00 cm
CY 8.00 cm
F1P 8.500 ppm
F1 2551.10 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.38636 ppm/cm
HZCM 115.95832 Hz/cm

C13



Current Data Parameters
NAME dig-1-077-C-2-C13
EXPNO 1
PROCNO 1

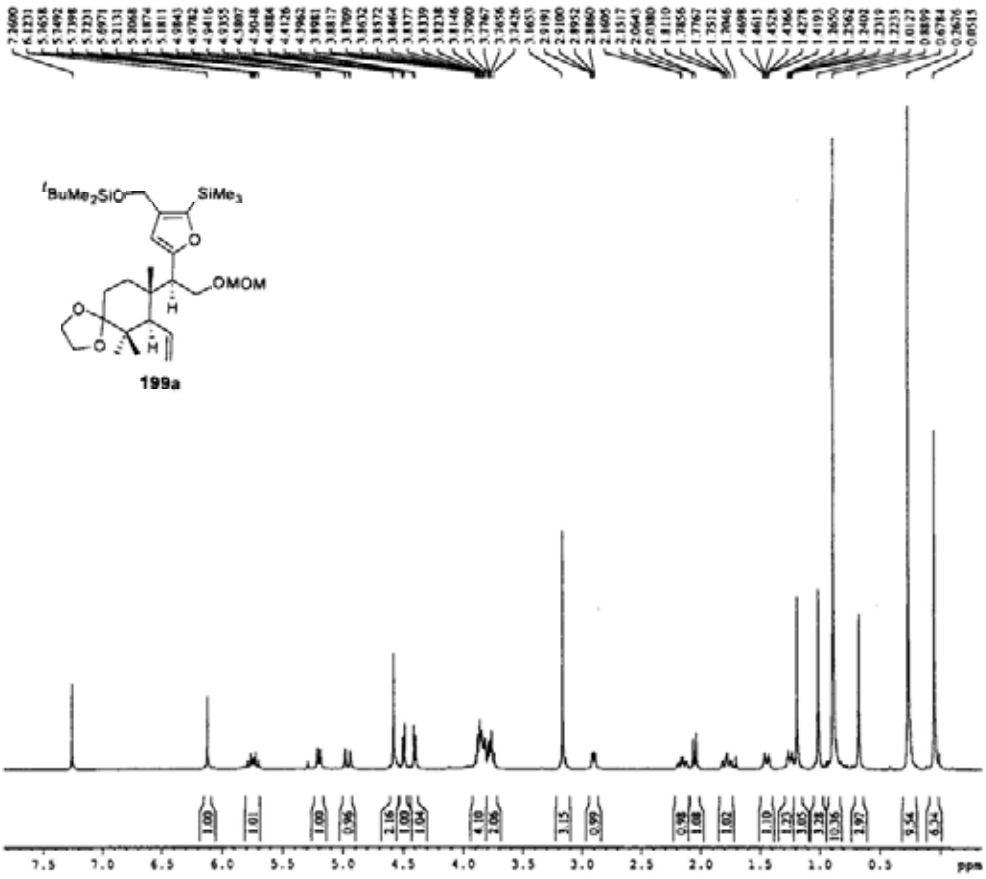
F2 - Acquisition Parameters
Date_ 20070927
Time 14.32
INSTRUM spx300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 1933
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 7298.2
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
D11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== 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 75.4677441 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

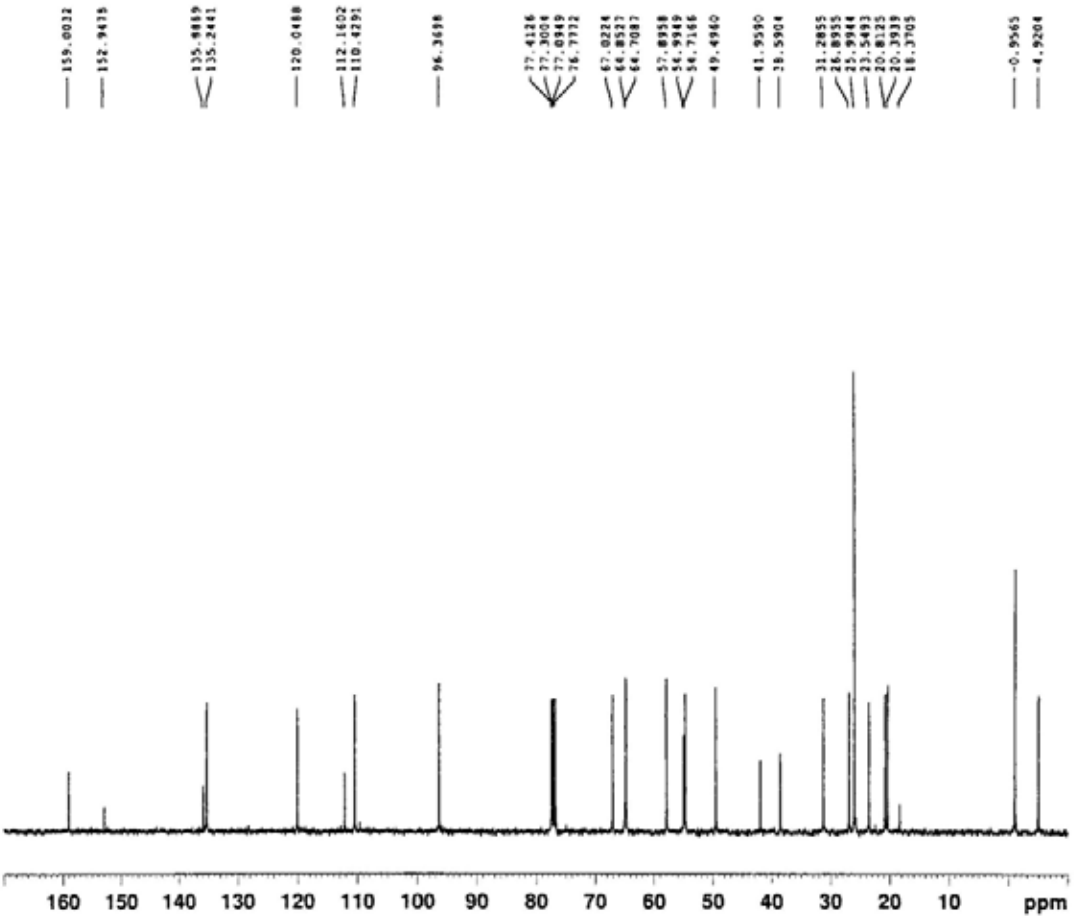
1D NMR plot parameters
CX 23.00 cm
CY 8.00 cm
F1P 175.000 ppm
F1 13206.86 Hz
F2P -3.000 ppm
F2 -226.40 Hz
PPMCM 7.73913 ppm/cm
HZCM 584.05469 Hz/cm



199a

Bruker Advance III 400

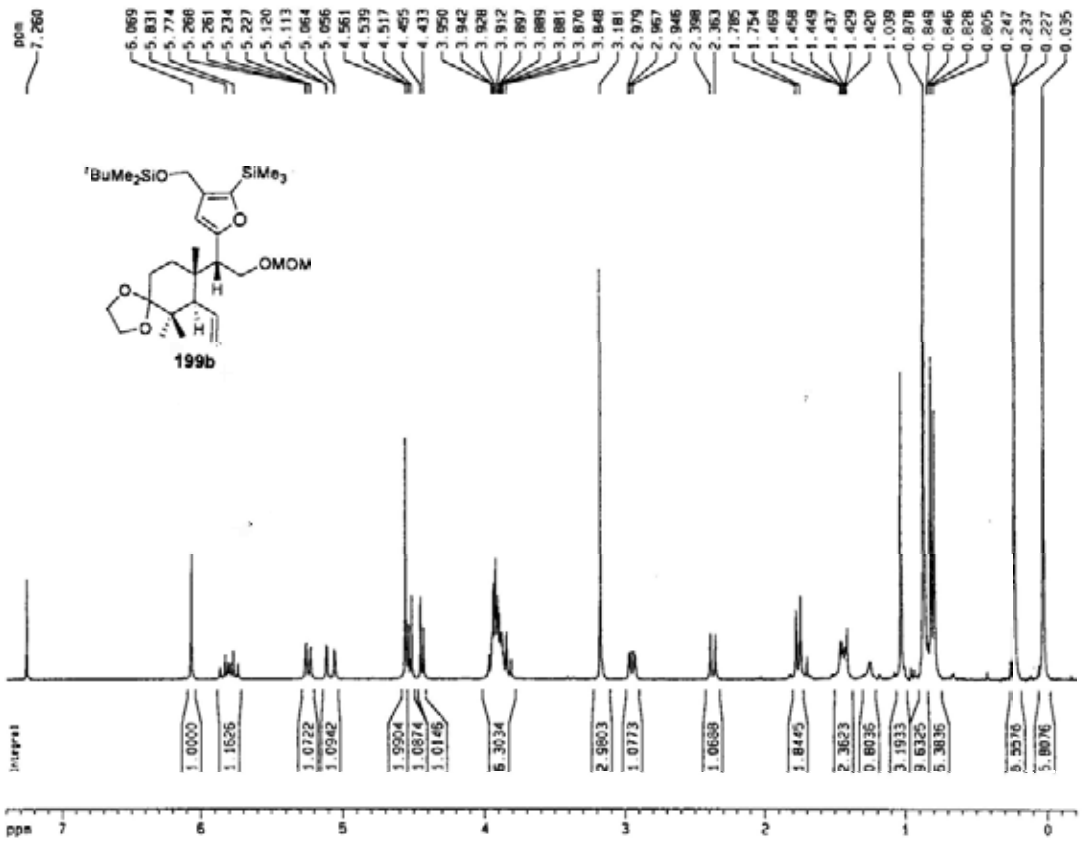
NAME	djq-2-042-1-H1
EXPNO	1
PROCNO	1
Date_	20080531
Time	9.14
INSTRUM	spect
PROBHD	5 mm PADUL 13C
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	12
DS	0
SWH	10000.000 Hz
FIDRES	0.152588 Hz
AQ	3.27685000 sec
RG	50.8
DW	50.000 use
DE	6.50 use
TE	294.7 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.83 use
PL1	0.00 dB
PL1W	8.31434441 W
SFO1	400.1316005 MHz
SI	65536
SF	400.1300053 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



Bruker Advance III 400

NAME	djq-2-042-1-C13
EXPNO	1
PROCNO	1
Date_	20080531
Time	9.22
INSTRUM	spect
PROBHD	5 mm PADUL 13C
PULPROG	zgpg
TD	131072
SOLVENT	CDCl3
NS	140
DS	0
SWH	29761.904 Hz
FIDRES	0.227065 Hz
AQ	2.2020595 sec
RG	203
DW	16.800 usec
DE	6.50 usec
TE	294.9 K
D1	1.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.68 usec
PL1	-0.60 dB
PL1W	41.24164963 W
SFO1	100.6208180 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	0.00 dB
PL12	15.66 dB
PL2W	8.31434441 W
PL12W	0.22585411 W
SFO2	400.1320007 MHz
SI	131072
SF	100.6127619 MHz
WDW	EM
SSB	0
LB	3.00 Hz
GB	0
PC	1.40

1H



Current Data Parameters
NAME dip-1-086-H1
EXPNO 1
PROCNO 1

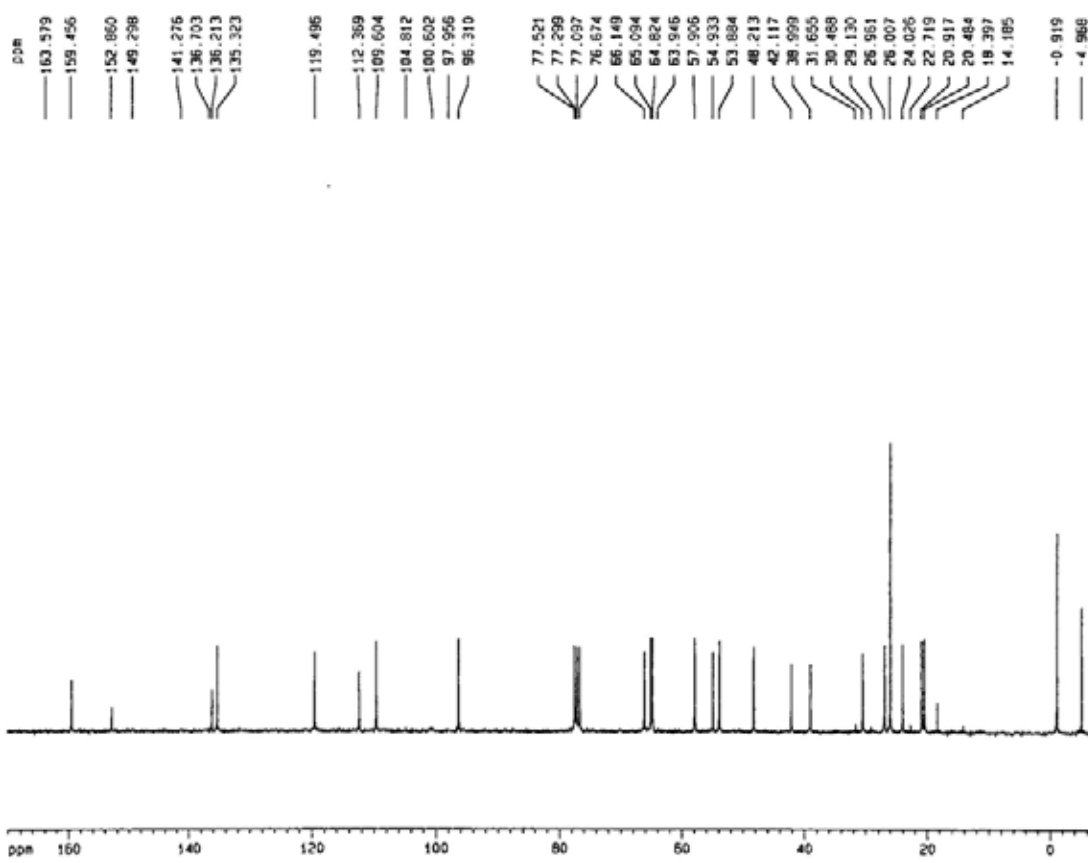
F2 - Acquisition Parameters
Date_ 20071101
Time 14.17
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 32
DW 55.600 usec
DE 79.43 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 300.1300055 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.40

1D NMR plot parameters
CX 22.00 cm
CY 24.00 cm
F1P 7.400 ppm
F1 2220.96 Hz
F2P -0.200 ppm
F2 -60.03 Hz
PPMCM 0.34545 ppm/cm
HZCM 103.68128 Hz/cm

C13



Current Data Parameters
NAME dip-1-086-C13
EXPNO 1
PROCNO 1

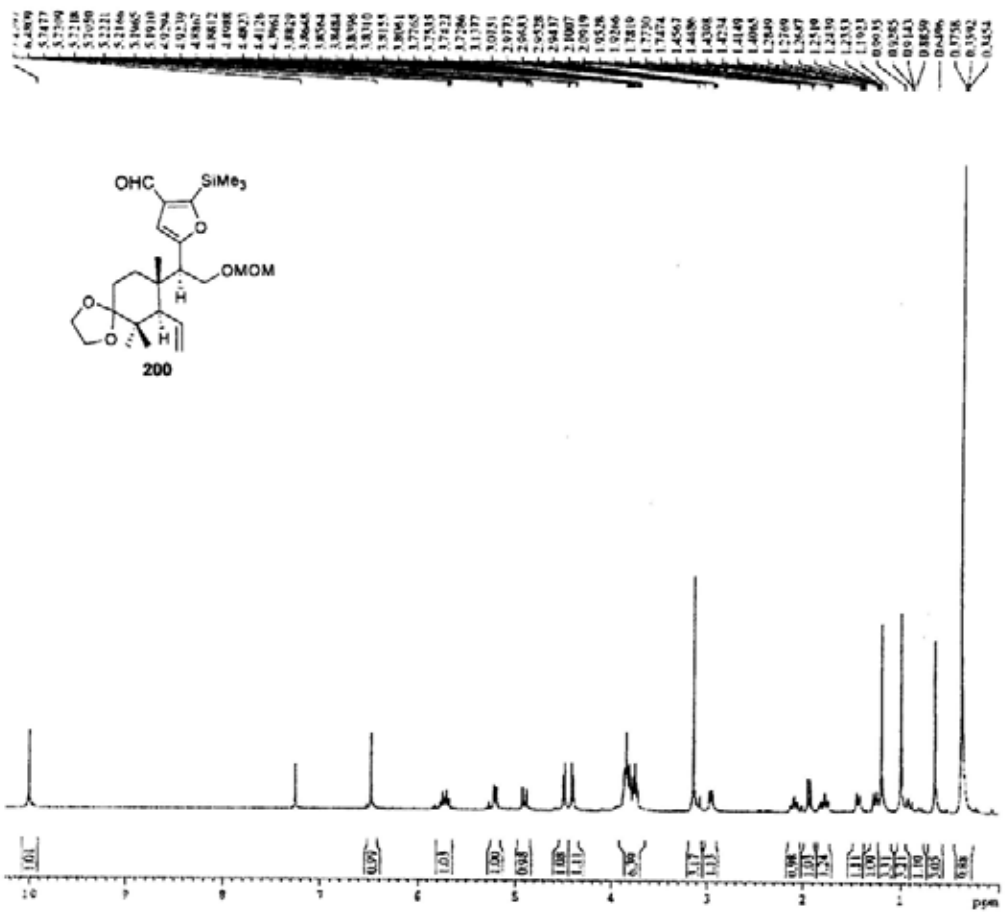
F2 - Acquisition Parameters
Date_ 20071101
Time 14.22
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 201
DS 0
SWH 22675.736 Hz
FIDRES 0.345804 Hz
AQ 1.4451168 sec
RG 2580.3
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

-------- 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 75.4677431 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
CY 5.00 cm
F1P 170.000 ppm
F1 12829.52 Hz
F2P -12.000 ppm
F2 -905.61 Hz
PPMCM 7.91304 ppm/cm
HZCM 597.17950 Hz/cm

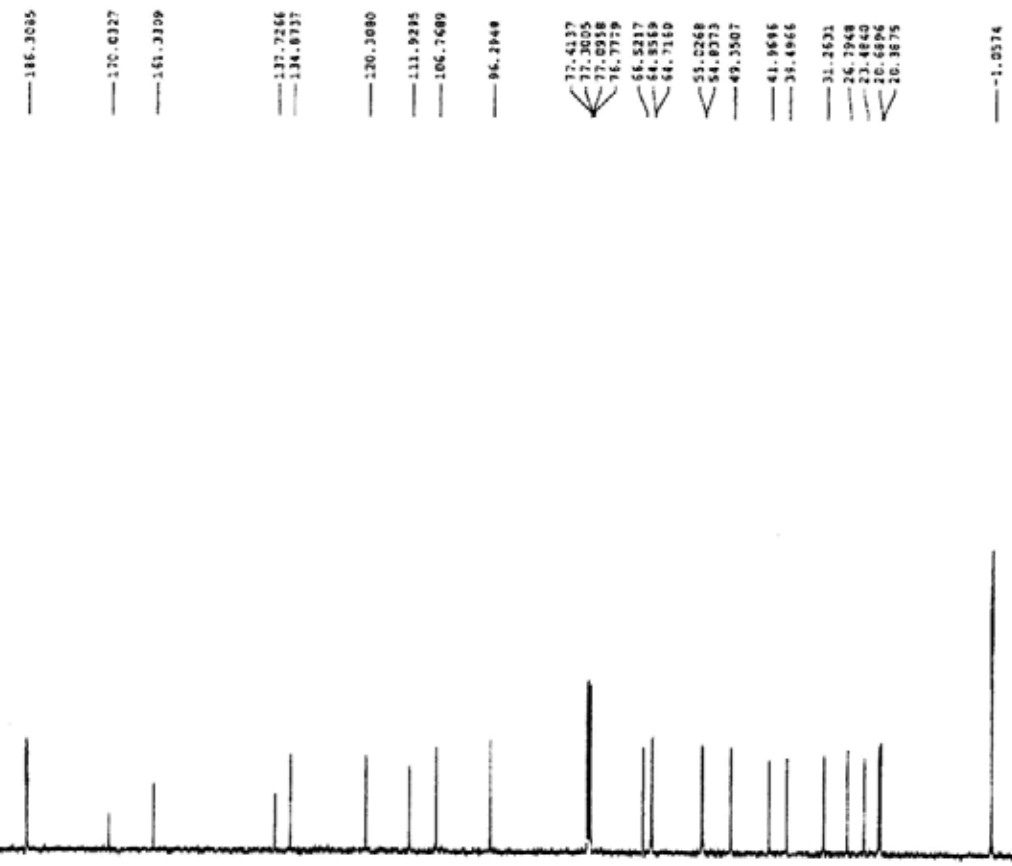


200


```
Bruker Advance III 400

NAME          djq-2-043-c-H1
EXPNO                      1
PROCNO                     1
Date_               20080602
Time                   14.38
INSTRUM                spect
PROBHD   5 mm PABBO BB/19F-1
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        32
DS                         0
SWH               10000.000 Hz
FIDRES                0.152588 Hz
AQ                3.2768000 sec
RG                     45.2
DW                    50.000 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
PL1W              8.31434441 W
SFO1            400.1316005 MHz
SI                    65536
SF              400.1300041 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

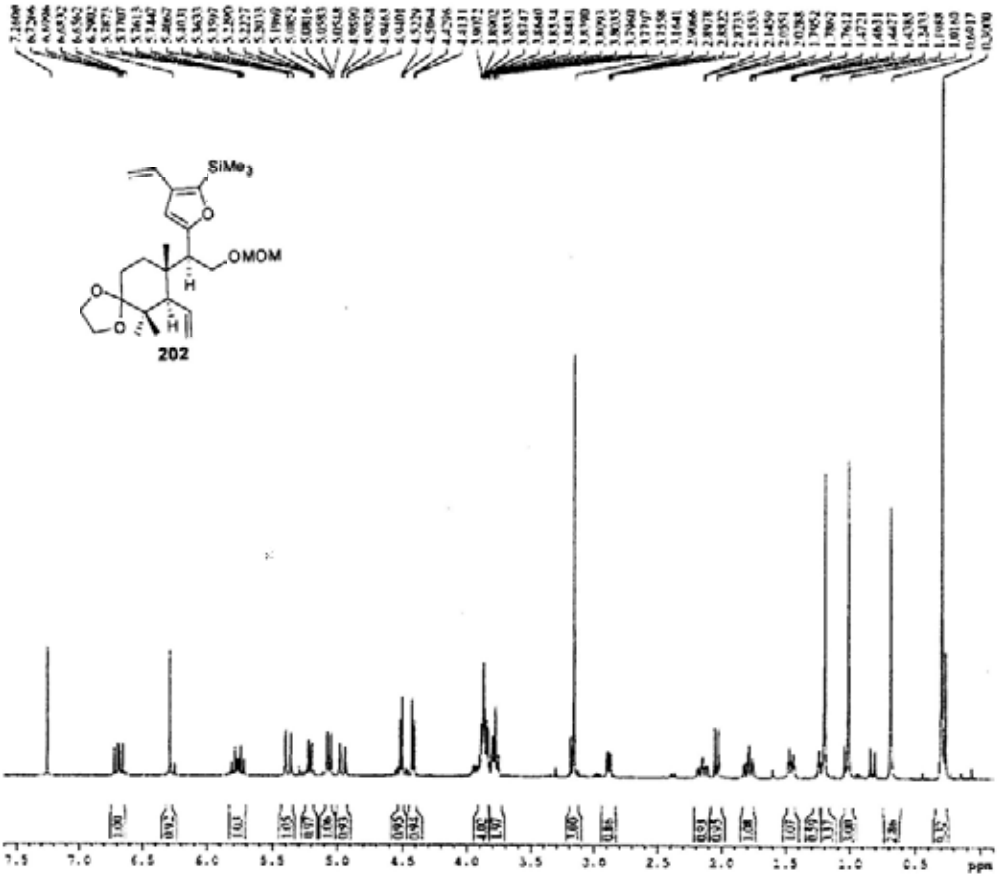


```
Bruker Advance III 400

NAME          djq-2-043-C13
EXPNO                      1
PROCNO                     1
Date_               20080602
Time                   14.39
INSTRUM                spect
PROBHD   5 mm PABBO BB/19F-1
PULPROG             zgpg30
TD                   131072
SOLVENT               CDCl3
NS                        99
DS                         0
SWH              25252.525 Hz
FIDRES                0.192661 Hz
AQ                2.59527552 sec
RG                       203
DW                   19.800 usec
DE                     6.50 usec
TE                   295.0 K
D1                1.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      13C
P1                     3.50 usec
PL1                   -0.60 dB
PL1W             41.24164963 W
SFO1            100.6227690 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                      1H
PCPD2                 90.00 usec
PL2                    0.00 dB
PL12                  16.10 dB
PL2W              8.31434441 W
PL12W             0.20409295 W
SFO2            400.1320007 MHz
SI                    131072
SF              100.6127681 MHz
WDW                       EM
SSB                        0
LB                     3.00 Hz
GB                         0
PC                      1.40
```

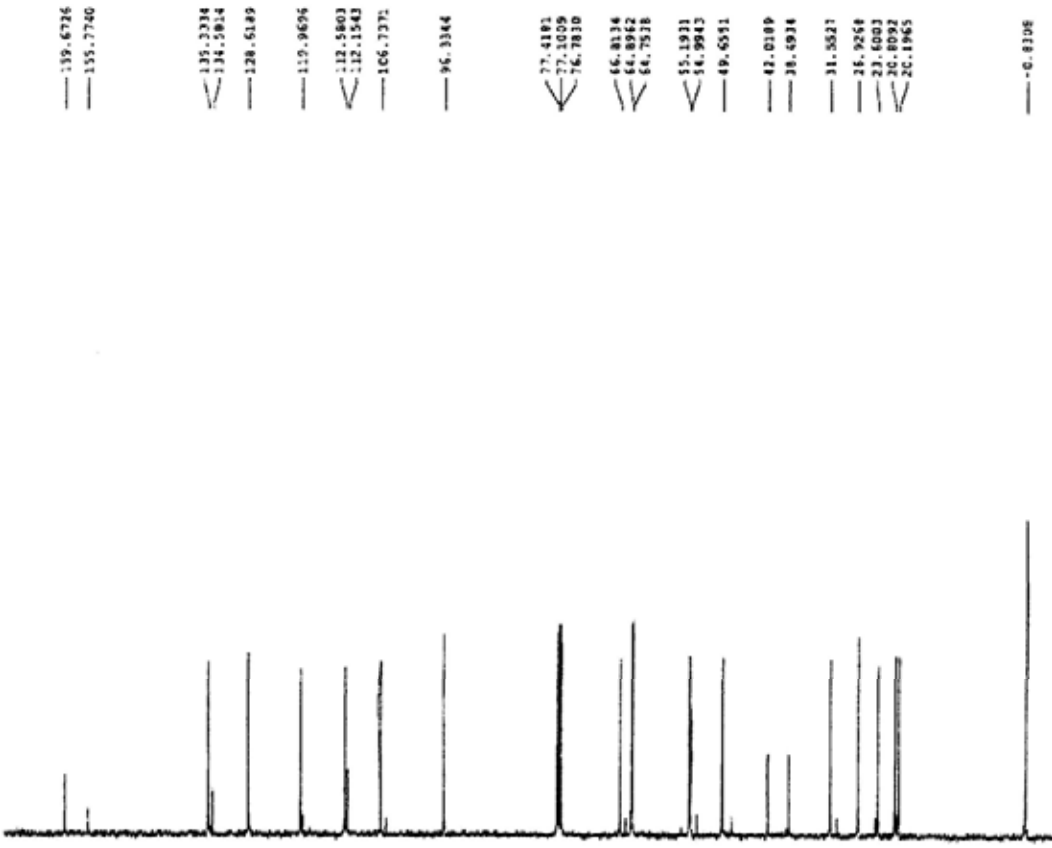


202


```
Bruker Advance III 400

NAME        djq-2-044-c-H1
EXPNO               1
PROCNO              1
Date_        20081124
Time              17.13
INSTRUM           spect
PROBHD  5 mm PADUL 13C
PULPROG          zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   0
SWH          10000.000 Hz
FIDRES        0.152588 Hz
AQ            3.2768500 sec
RG                 144
DW              50.000 usec
DE               4.50 usec
TE              295.4 K
D1           1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               1H
P1               14.83 usec
PL1               0.00 dB
PLIW         8.31434441 W
SFO1       400.1316005 MHz
SI               65536
SF         400.1300000 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```



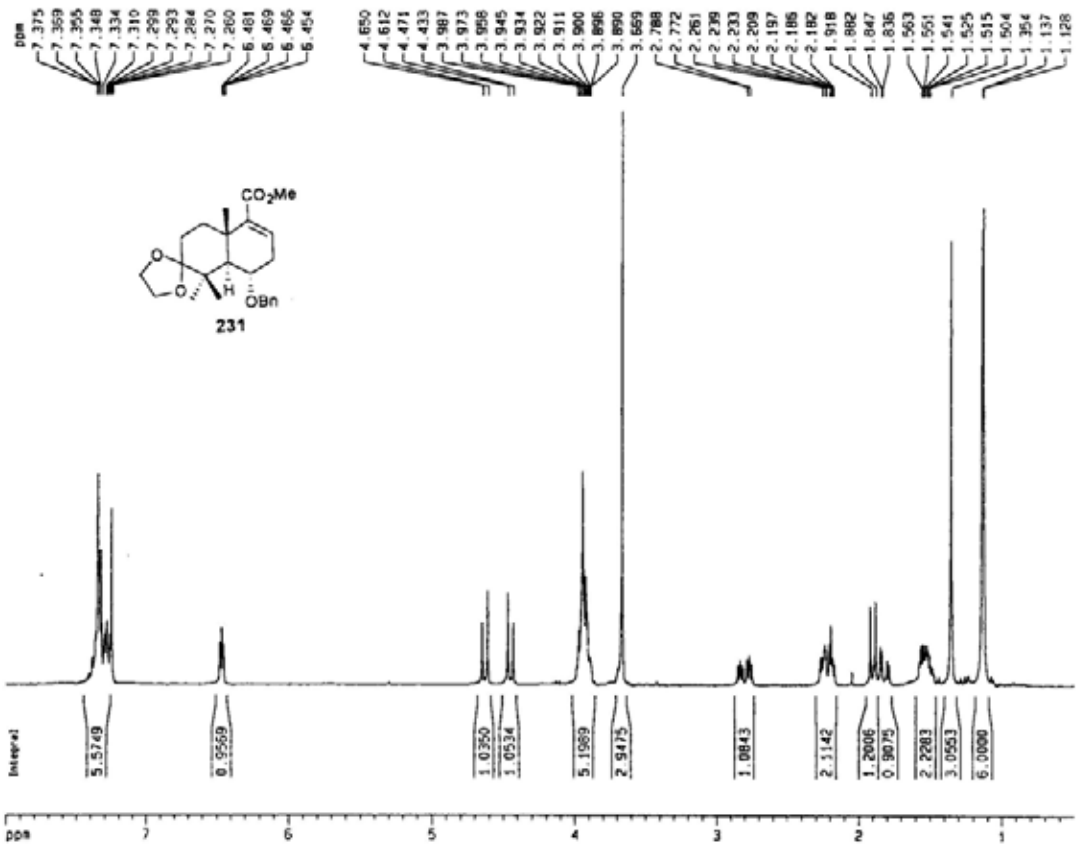
```
Bruker Advance III 400

NAME        djq-2-044-c-C13
EXPNO               1
PROCNO              1
Date_        20081124
Time              17.25
INSTRUM           spect
PROBHD  5 mm PADUL 13C
PULPROG        zgdc
TD             131072
SOLVENT          CDCl3
NS                 617
DS                   0
SWH          29761.904 Hz
FIDRES        0.227065 Hz
AQ            2.2020595 sec
RG                 203
DW              16.800 usec
DE               6.50 usec
TE              296.1 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               13C
P1                9.60 usec
PL1              -0.60 dB
PLIW        41.24164843 W
SFO1       100.6208150 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2            90.00 usec
PL2               0.00 dB
PL12             15.46 dB
PL12W        8.31434441 W
PL12W        0.22585411 W
SFO2       400.1320007 MHz
SI             131072
SF         100.6127610 MHz
WDW                EM
SSB                 0
LB               3.00 Hz
GB                  0
PC               1.40
```

1H



Current Data Parameters
NAME djq-1-058-2-H1
EXPNO 1
PROCNO 1

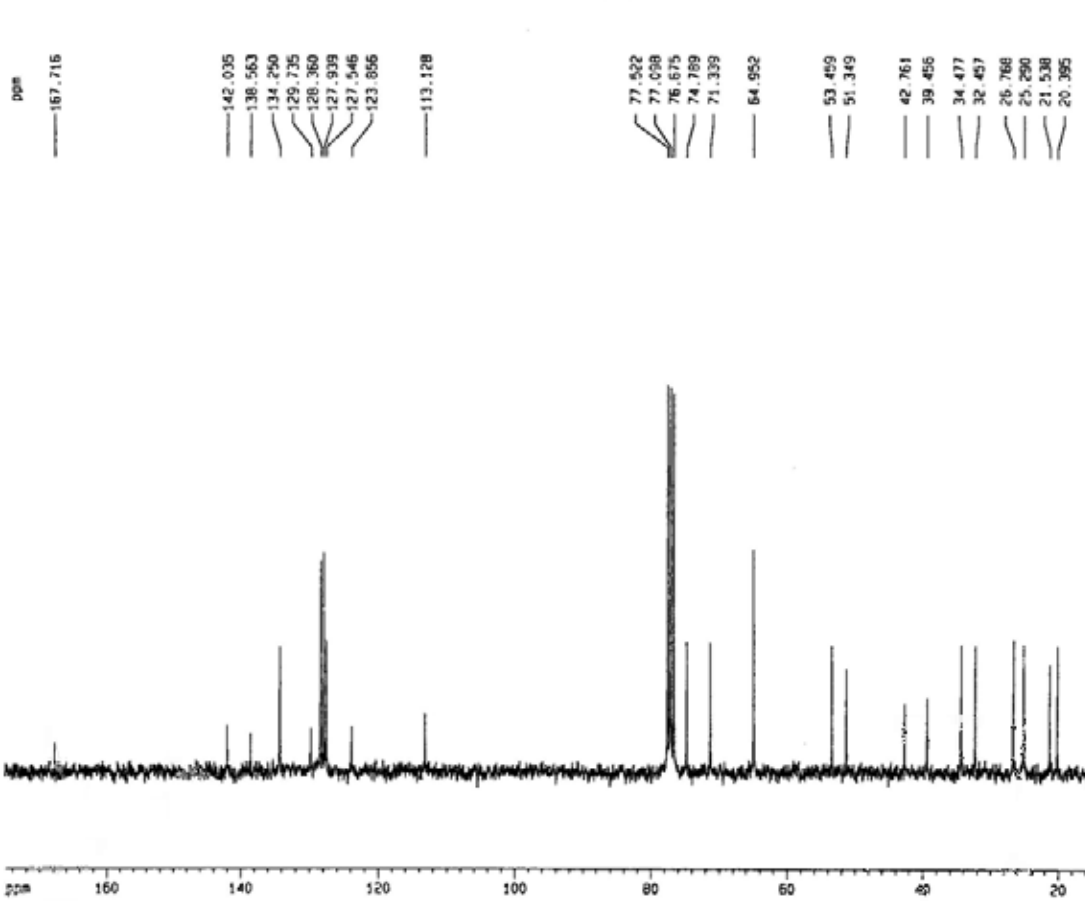
F2 - Acquisition Parameters
Date_ 20070813
Time 19.24
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 12
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 203.2
DW 55.600 usec
DE 75.43 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 300.1300055 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 12.00 cm
F1P 8.000 ppm
F1 2401.04 Hz
F2P 0.500 ppm
F2 150.07 Hz
PPMCM 0.34091 ppm/cm
HZCM 102.31705 Hz/cm

C13



Current Data Parameters
NAME djq-1-058-2-C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070813
Time 19.28
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 361
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

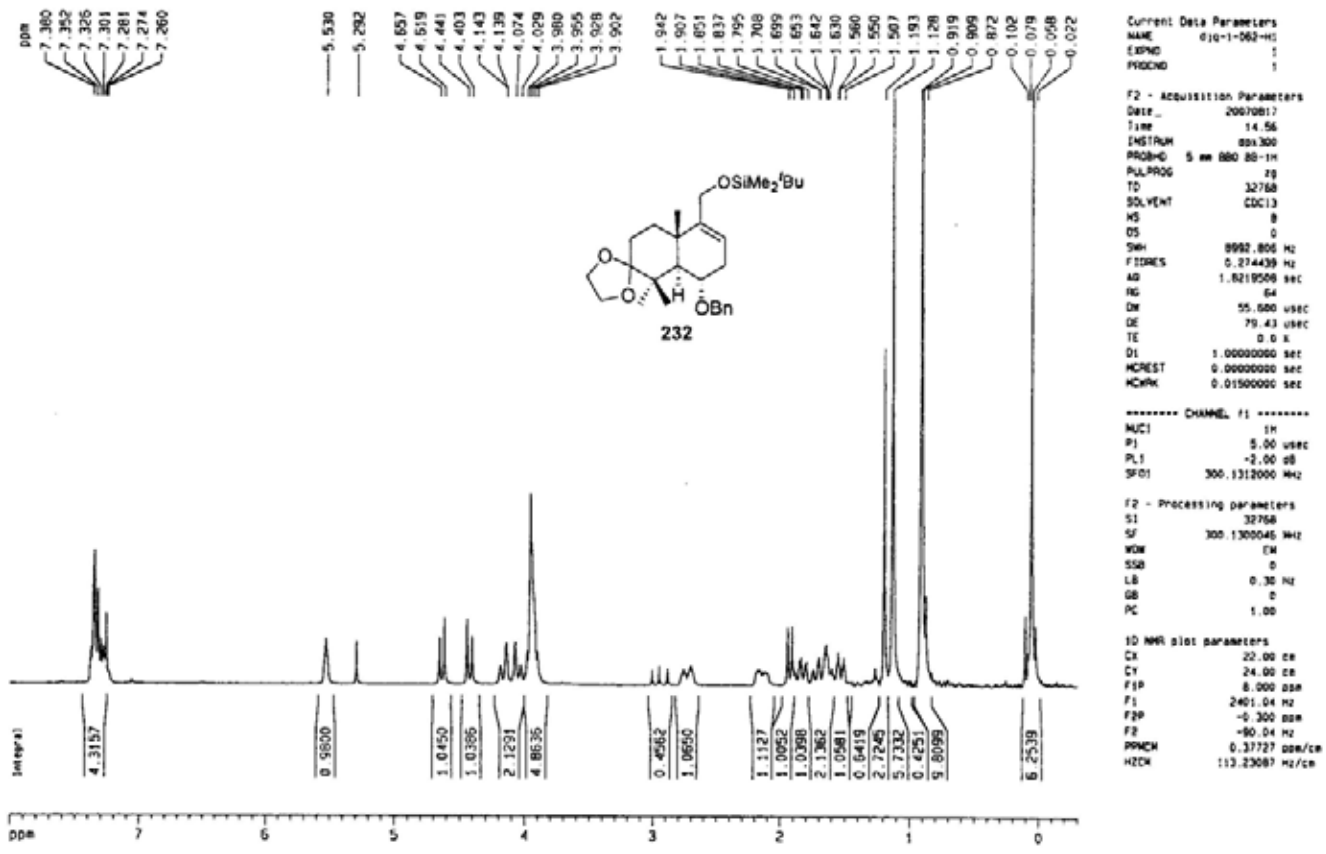
======== CHANNEL f1 ========
NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SFO1 75.4745111 MHz

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

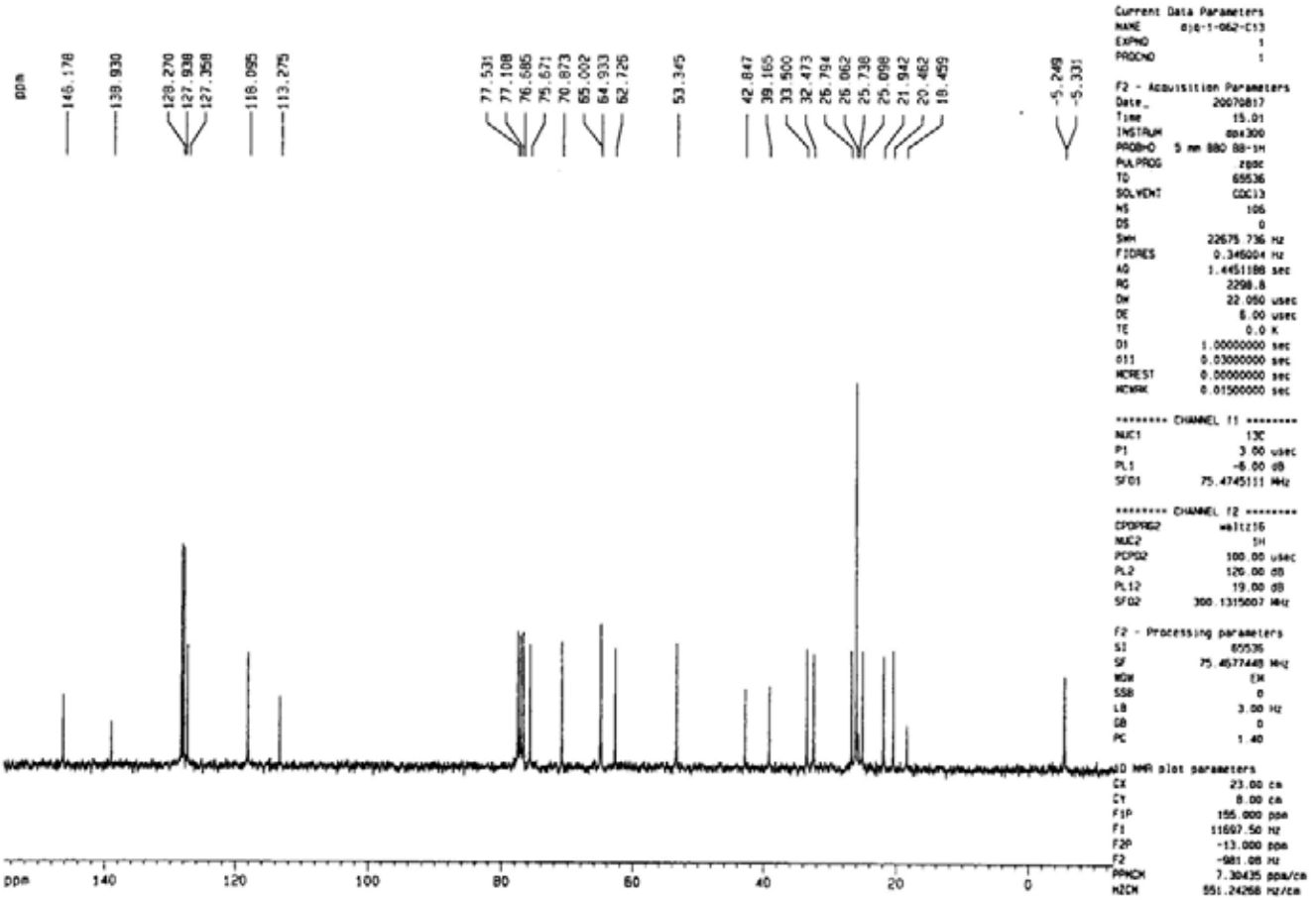
F2 - Processing parameters
SI 65536
SF 75.4677436 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
CY 8.00 cm
F1P 175.000 ppm
F1 13205.86 Hz
F2P 11.000 ppm
F2 830.15 Hz
PPMCM 7.13043 ppm/cm
HZCM 538.11780 Hz/cm

1H



C13



Current Data Parameters
NAME djq-1-062-H1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070817
Time 14.56
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219506 sec
RG 64
DW 55.600 usec
DE 79.43 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

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

1D NMR plot parameters
CX 22.00 cm
CY 24.00 cm
F1P 8.000 ppm
F1 2401.04 Hz
F2P -0.300 ppm
F2 -90.04 Hz
PPMCM 0.37727 ppm/cm
HZCM 113.23087 Hz/cm

Current Data Parameters
NAME djq-1-062-C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070817
Time 15.01
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 106
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 2298.8
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
D11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

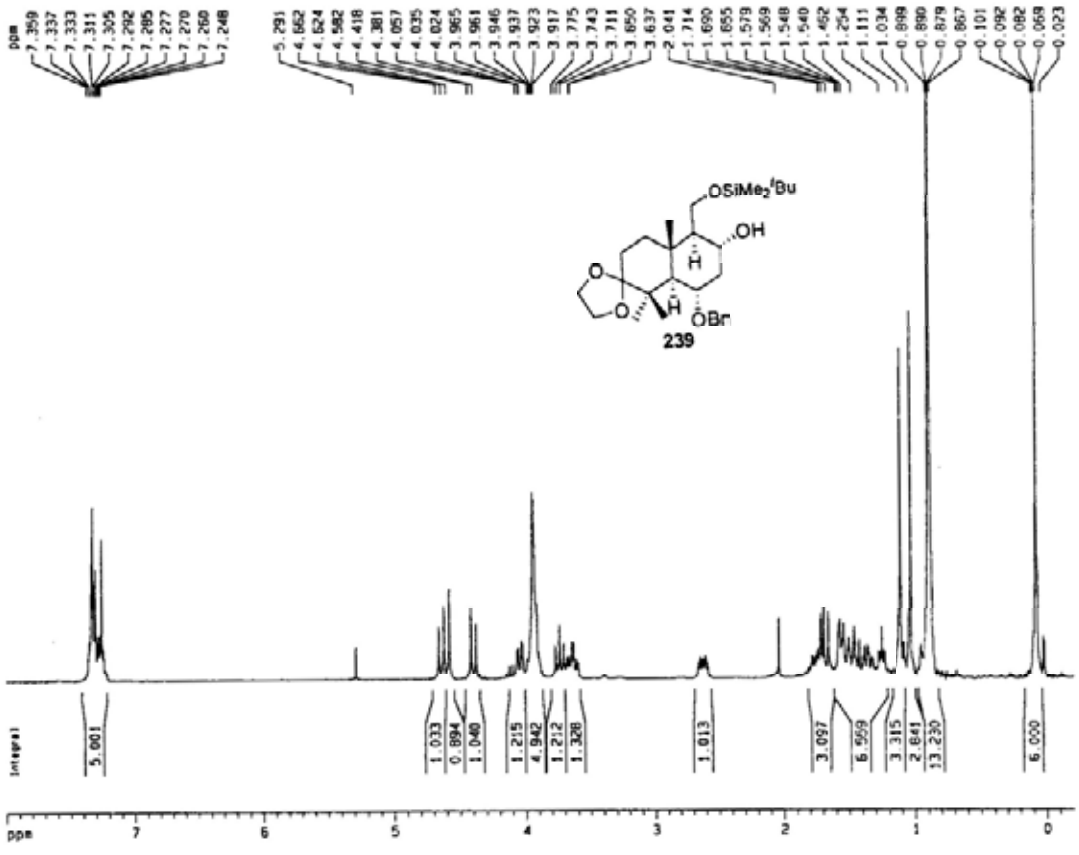
======== CHANNEL f1 ========
NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SFO1 75.4745111 MHz

======== 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 75.4577448 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
CY 8.00 cm
F1P 155.000 ppm
F1 11692.50 Hz
F2P -13.000 ppm
F2 -981.08 Hz
PPMCM 7.30435 ppm/cm
HZCM 551.24268 Hz/cm

1H



Current Data Parameters
NAME djq-1-063-1-H1
EXPNO 1
PROCNO 1

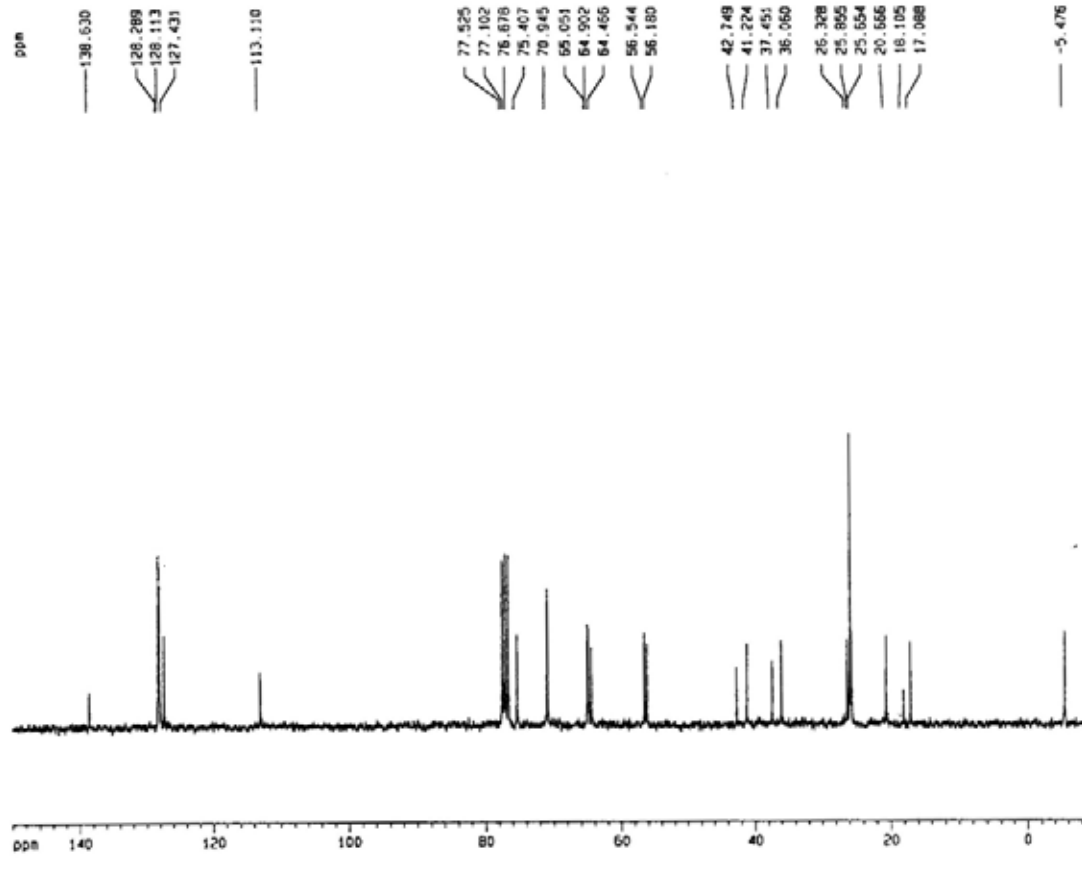
F2 - Acquisition Parameters
Date_ 20070821
Time 18.31
INSTRUM spx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219568 sec
RG 64
DW 55.600 usec
DE 75.43 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 300.1300052 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 36.00 cm
F1P 9.000 ppm
F1 2401.04 Hz
F2P -0.260 ppm
F2 -60.03 Hz
PPMCM 0.37273 ppm/cm
HZCM 111.86664 Hz/cm

C13



Current Data Parameters
NAME djq-1-063-1-C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070821
Time 18.36
INSTRUM spx300
PROBHD 5 mm BBO BB-1H
PULPROG zgdc
TD 65536
SOLVENT CDCl3
NS 240
DS 0
SWH 22675.736 Hz
FIDRES 0.345804 Hz
AQ 1.4451188 sec
RG 11585.2
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
D11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

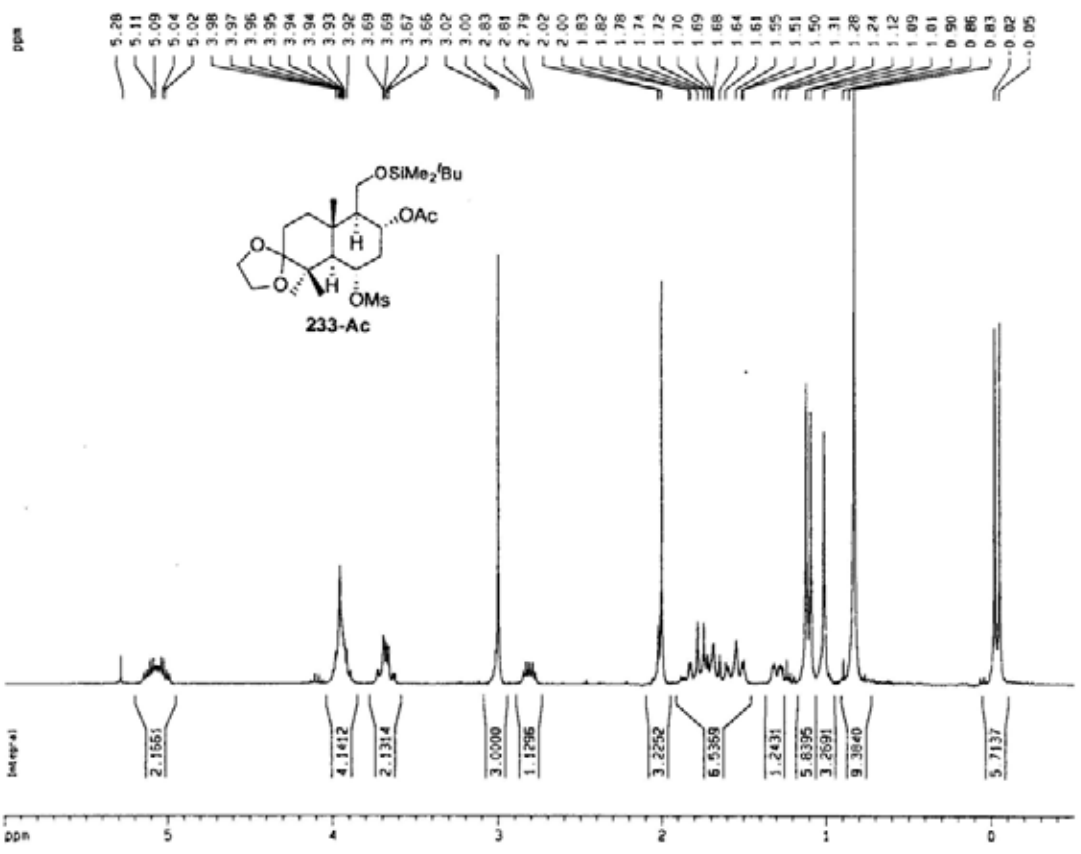
-------- CHANNEL f1 --------
NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SFO1 75.4745111 MHz

-------- CHANNEL f2 --------
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 19.05 dB
SFO2 300.1315007 MHz

F2 - Processing parameters
SI 65536
SF 75.4677445 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
CY 6.00 cm
F1P 150.000 ppm
F1 11320.16 Hz
F2P -15.000 ppm
F2 -1132.02 Hz
PPMCM 7.17391 ppm/cm
HZCM 541.39911 Hz/cm

1H




```
Current Data Parameters
NAME            dje-1-072-H1
EXPNO                      1
PROCNO                     1

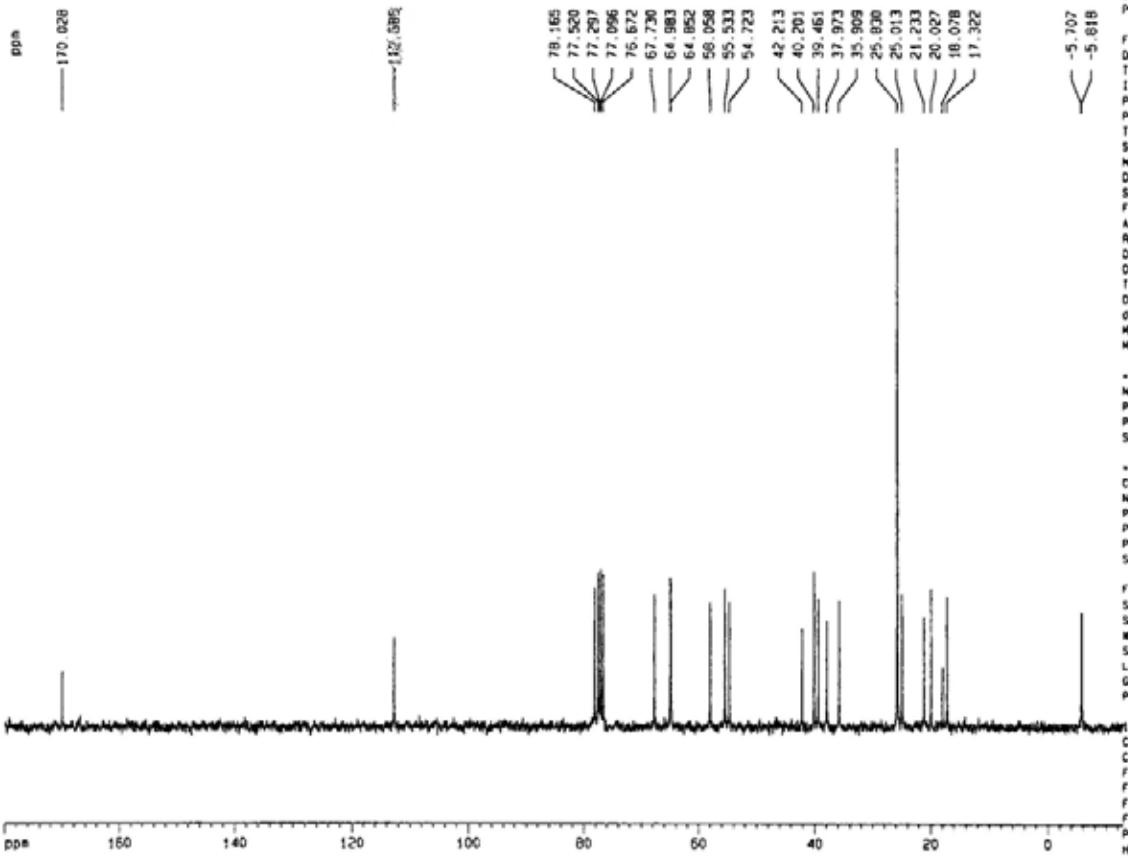
F2 - Acquisition Parameters
Date_          20070904
Time               18.08
INSTRUM          dpx300
PROBHD  5 mm BBO BB-1H
PULPROG                 zg
TD                   32768
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              8992.806 Hz
FIDRES           0.274436 Hz
AQ               1.8219508 sec
RG                    50.8
DW                  55.600 usec
DE                  79.43 usec
TE                   0.0 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

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

F2 - Processing parameters
SI                   32768
SF            300.1300049 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.00 cm
CY                  24.00 cm
F1P                 6.000 ppm
F1                1800.78 Hz
F2P                -0.500 ppm
F2                -150.06 Hz
PPMCM             0.29545 ppm/cm
HZCM              88.67477 Hz/cm
```

C13



```
Current Data Parameters
NAME            dje-1-072-C13
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_          20070904
Time               18.12
INSTRUM          dpx300
PROBHD  5 mm BBO BB-1H
PULPROG              zgpg
TD                   65536
SOLVENT              CDCl3
NS                      98
DS                       0
SWH              22675.736 Hz
FIDRES           0.346004 Hz
AQ               1.4451188 sec
RG                    8192
DW                  22.050 usec
DE                   6.00 usec
TE                   0.0 K
D1              1.00000000 sec
D11             0.03000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

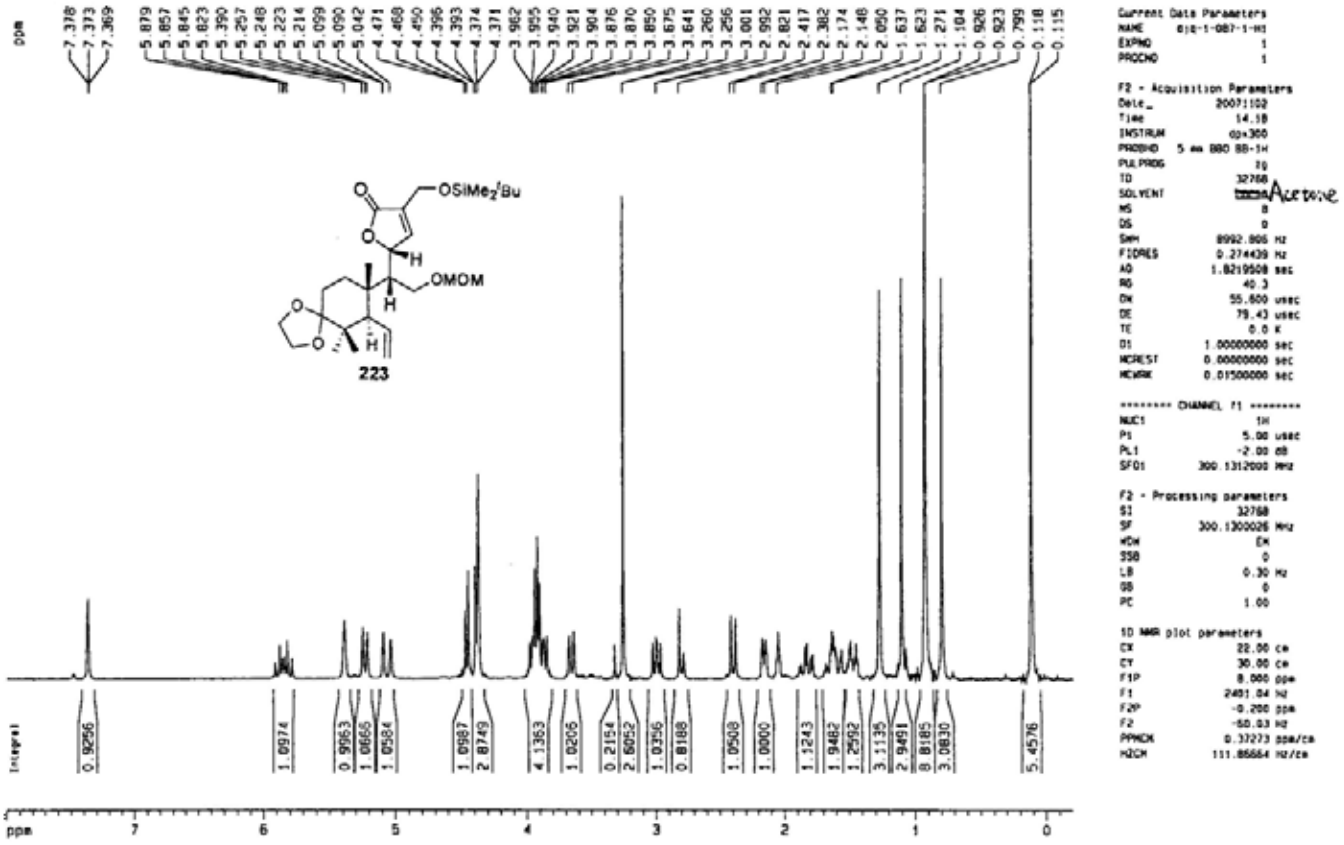
======== CHANNEL f1 ========
NUC1                   13C
P1                   3.00 usec
PL1                 -6.00 dB
SFO1          75.4745111 MHz

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

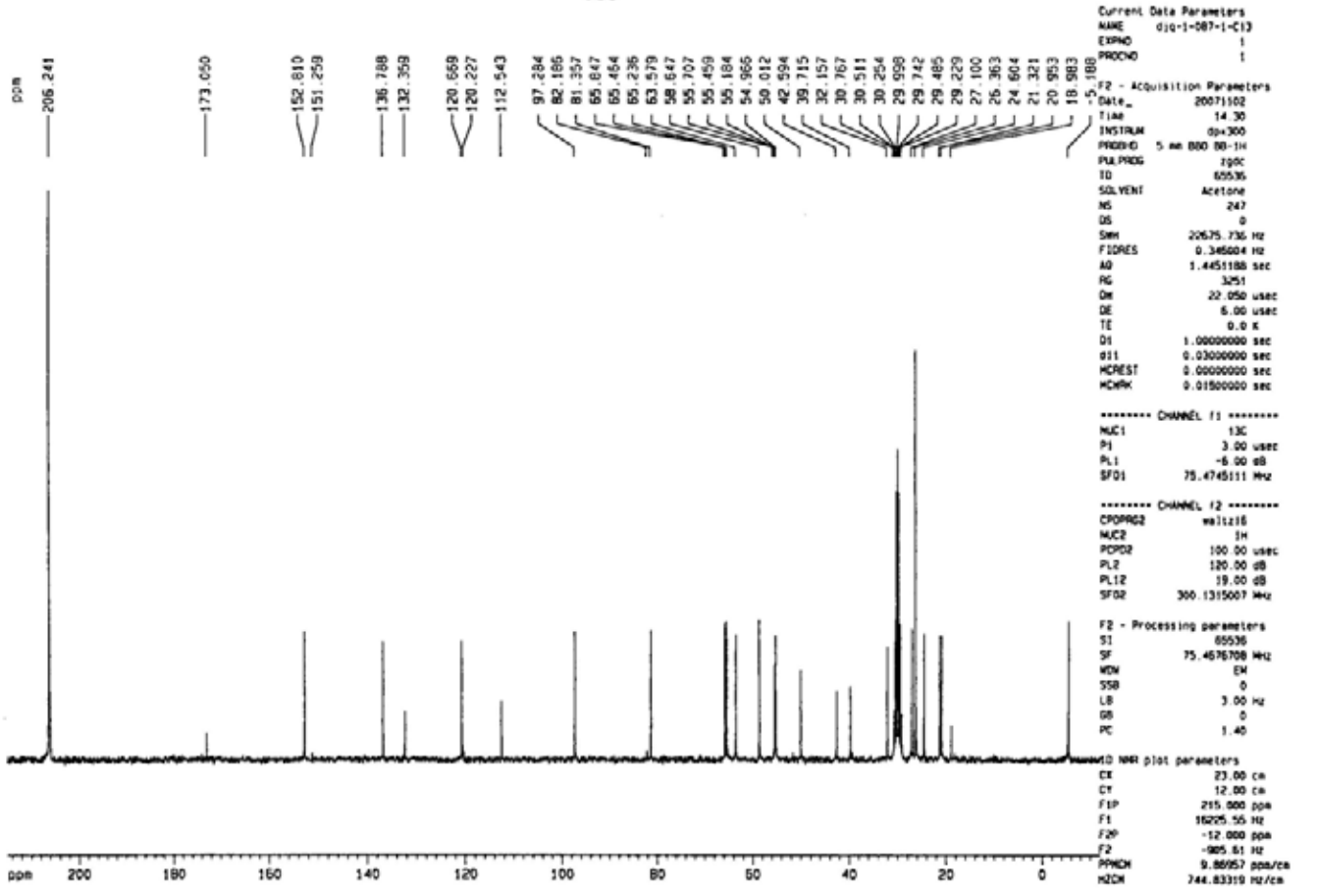
F2 - Processing parameters
SI                   65536
SF            75.4577459 MHz
WDW                    EM
SSB                     0
LB                   3.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  23.00 cm
CY                  12.00 cm
F1P               180.000 ppm
F1              13584.19 Hz
F2P               -13.000 ppm
F2               -981.08 Hz
PPMCM             8.39130 ppm/cm
HZCM              633.27277 Hz/cm
```

1H



C13



Current Data Parameters
NAME djq-1-087-1-H1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20071102
Time 14.18
INSTRUM dp+300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT Acetone
NS 8
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 40.3
DW 55.600 usec
DE 79.43 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 300.1300026 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 30.00 cm
F1P 8.000 ppm
F1 2401.04 Hz
F2P -0.200 ppm
F2 -60.03 Hz
PPMCM 0.37273 ppm/cm
HZCM 111.85684 Hz/cm

Current Data Parameters
NAME djq-1-087-1-C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20071102
Time 14.30
INSTRUM dp+300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT Acetone
NS 247
DS 0
SWH 22675.736 Hz
FIDRES 0.345884 Hz
AQ 1.4451188 sec
RG 3251
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

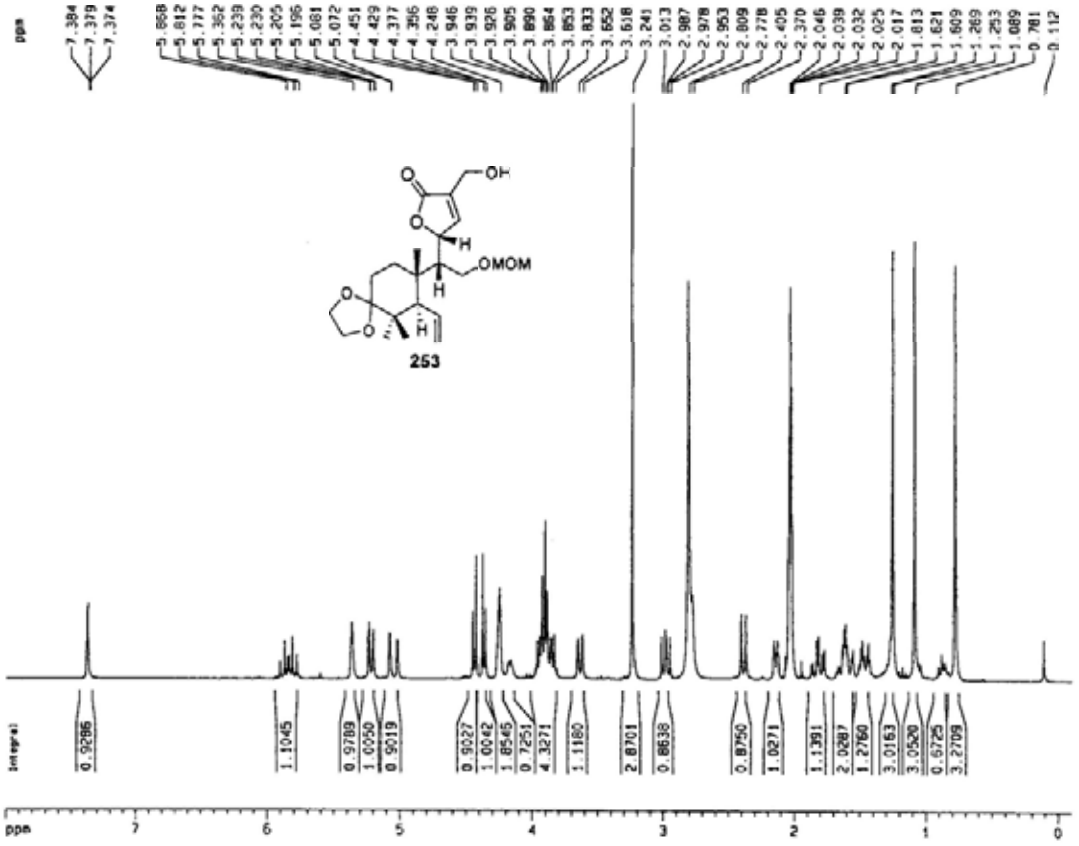
======== CHANNEL f1 ========
NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SFO1 75.4745111 MHz

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

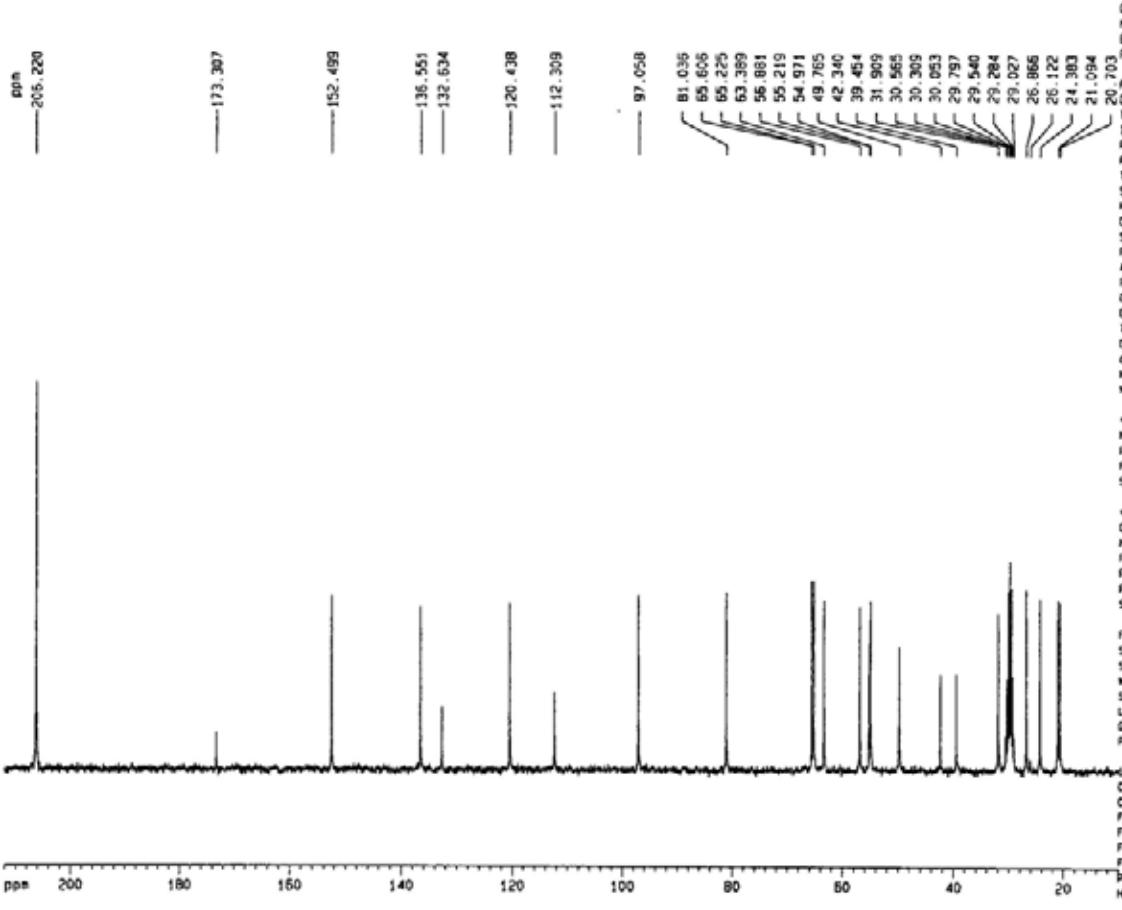
F2 - Processing parameters
SI 65536
SF 75.4676708 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

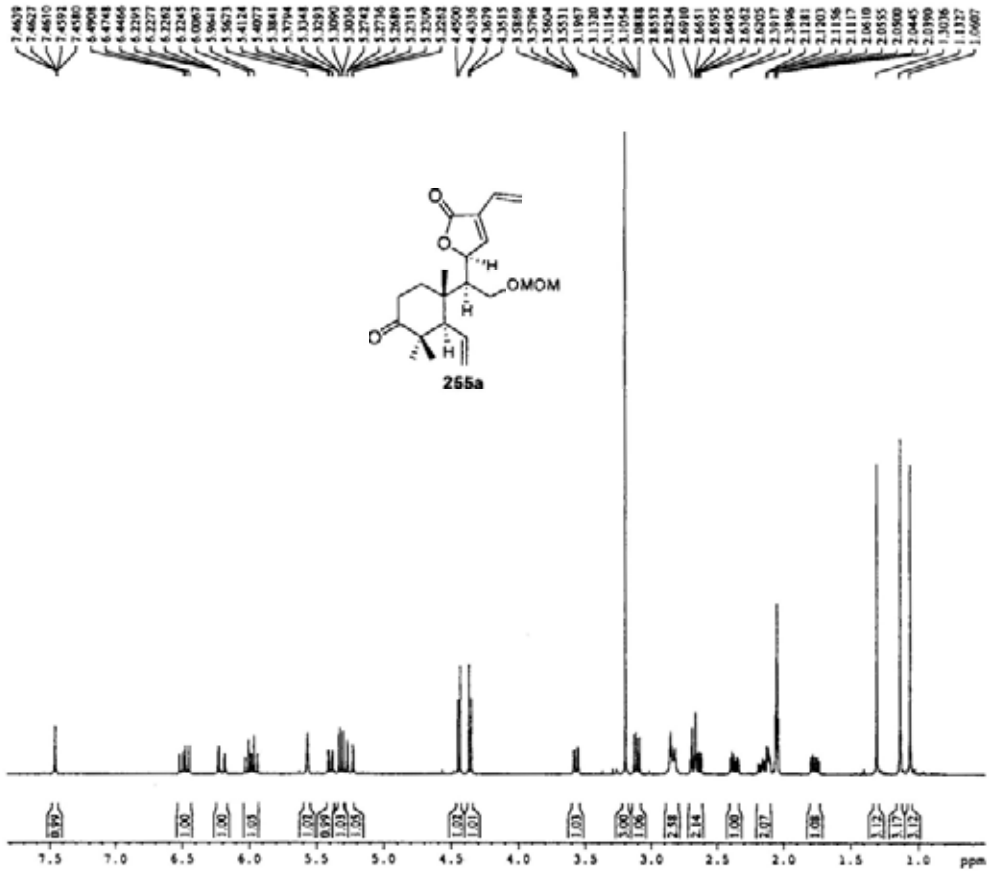
1D NMR plot parameters
CX 23.00 cm
CY 12.00 cm
F1P 215.000 ppm
F1 16225.55 Hz
F2P -12.000 ppm
F2 -905.61 Hz
PPMCM 9.86957 ppm/cm
HZCM 744.83319 Hz/cm

1H



C13

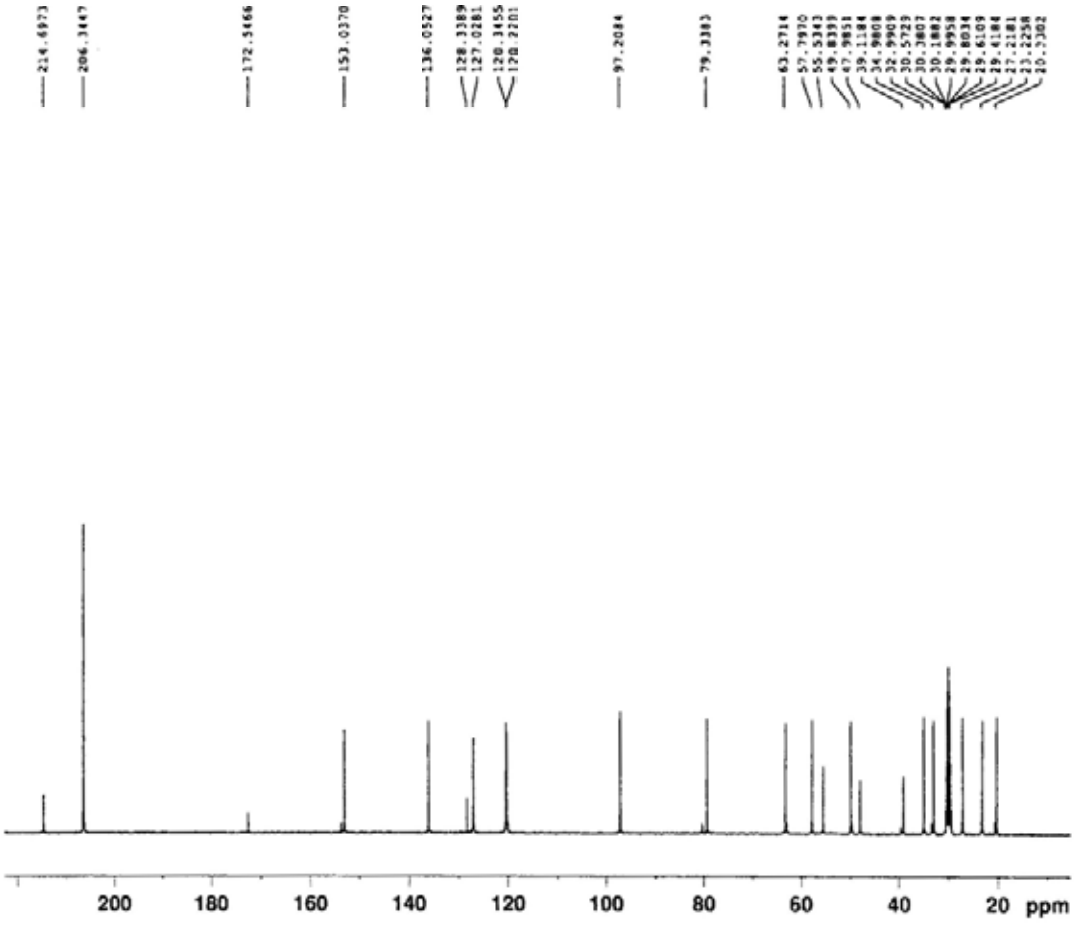





```
Bruker Advance III 400

NAME          djq-2-046-2-H1
EXPNO                  1
PROCNO                 1
Date_           20080626
Time               14.45
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG            zg30
TD                65536
SOLVENT         Acetone
NS                    33
DS                     0
SWH           10000.000 Hz
FIDRES        0.152588 Hz
AQ            3.2768500 sec
RG                   203
DW              50.000 usec
DE                6.50 usec
TE              293.4 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.83 usec
PL1                0.00 dB
PL1W         8.31434441 W
SFO1        400.1316005 MHz
SI                 65536
SF          400.1300047 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

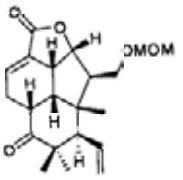



```
Bruker Advance III 400

NAME          djq-2-046-2-C13
EXPNO                  1
PROCNO                 1
Date_           20080626
Time               14.27
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG            zgdc
TD                131072
SOLVENT         Acetone
NS                   312
DS                     0
SWH           29761.904 Hz
FIDRES        0.227065 Hz
AQ            2.2020595 sec
RG                   203
DW              16.800 usec
DE                6.50 usec
TE              294.1 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 5.00 usec
PL1               -0.60 dB
PL1W         41.24184963 W
SFO1        100.6208160 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             90.00 usec
PL2                0.00 dB
PL12              16.10 dB
PL2W         8.31434441 W
PL12W        0.20409293 W
SFO2        400.1320007 MHz
SI                131072
SF          100.6126713 MHz
WDW                   EM
SSB                    0
LB                3.00 Hz
GB                     0
PC                1.40
```



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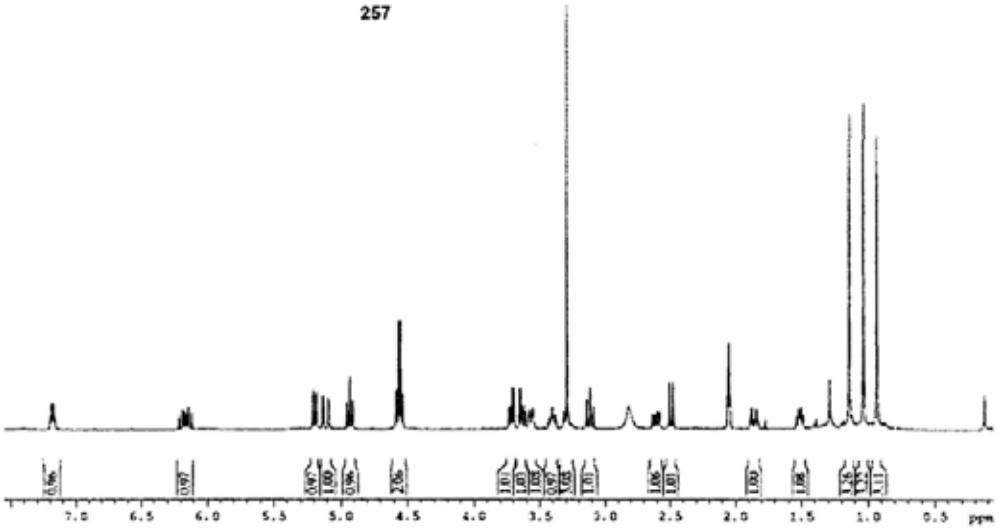
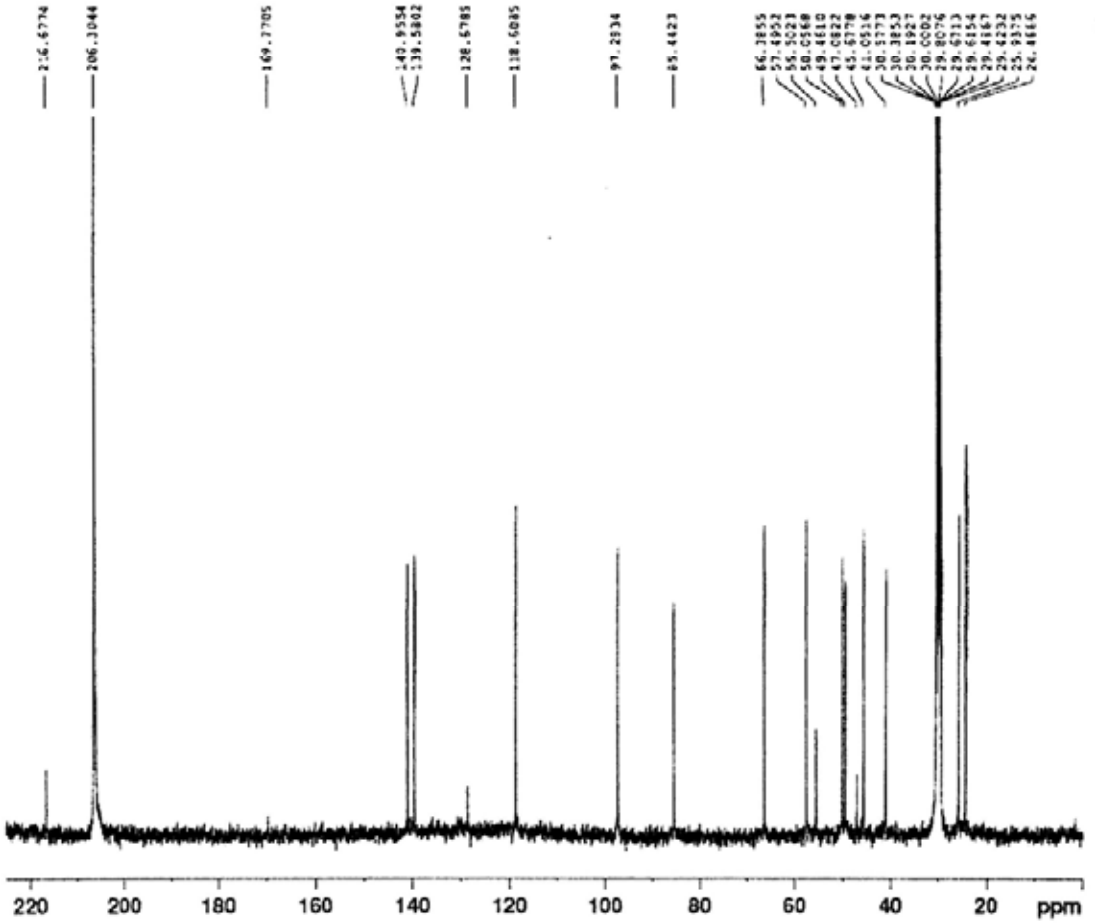



```
Bruker Advance III 400

NAME          djq-2-045-H1
EXPNO                    1
PROCNO                   1
Date_             20080707
Time                 16.27
INSTRUM              spect
PROBHD   5 mm PABBI 1H/
PULPROG              zg30
TD                  65536
SOLVENT           Acetone
NS                      16
DS                       0
SWH           10000.000 Hz
FIDRES            0.152588 Hz
AQ                3.2768500 sec
RG                     114
DW                50.000 usec
DE                 6.50 usec
TE                298.2 K
D1            1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                 7.10 usec
PL1               -2.00 dB
PL1W        13.17734718 W
SFO1       400.1316005 MHz
SI                  65536
SF         400.1300050 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 1.00
```

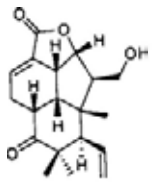



```
Bruker Advance III 400

NAME          djq-2-049-C13
EXPNO                    3
PROCNO                   1
Date_             20080707
Time                 16.18
INSTRUM              spect
PROBHD   5 mm PABBI 1H/
PULPROG          zgdc
TD                  131072
SOLVENT           Acetone
NS                    2555
DS                       0
SWH           29761.904 Hz
FIDRES            0.227065 Hz
AQ                2.2020595 sec
RG                     203
DW                16.800 usec
DE                 6.50 usec
TE                298.2 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                  13C
P1                14.50 usec
PL1               -4.00 dB
PL1W        90.22689819 W
SFO1       100.6208180 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                   1H
PCPD2             80.00 usec
PL2               -2.00 dB
PL12              18.80 dB
PL2W        13.17734718 W
PL12W        0.15962442 W
SFO2       400.1320007 MHz
SI                  131072
SF         100.6226628 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 0.20
```



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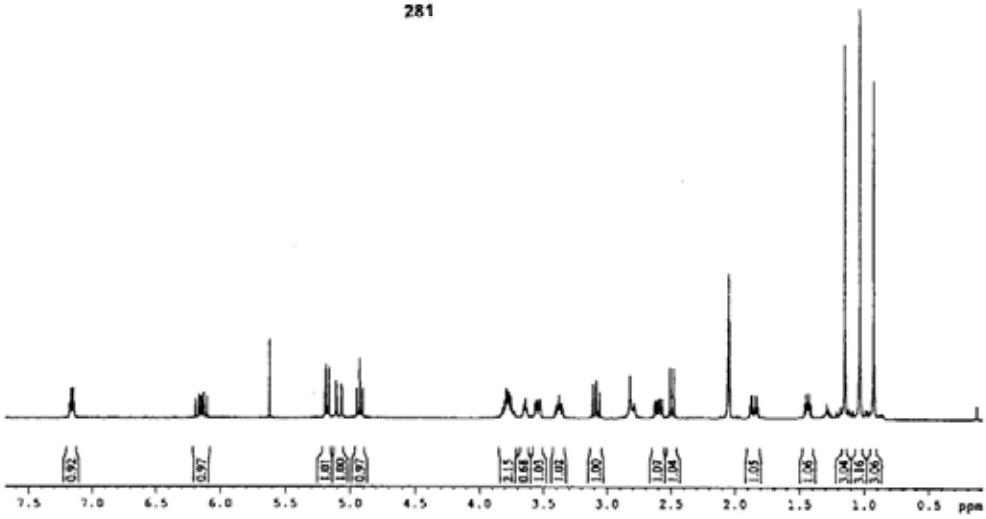
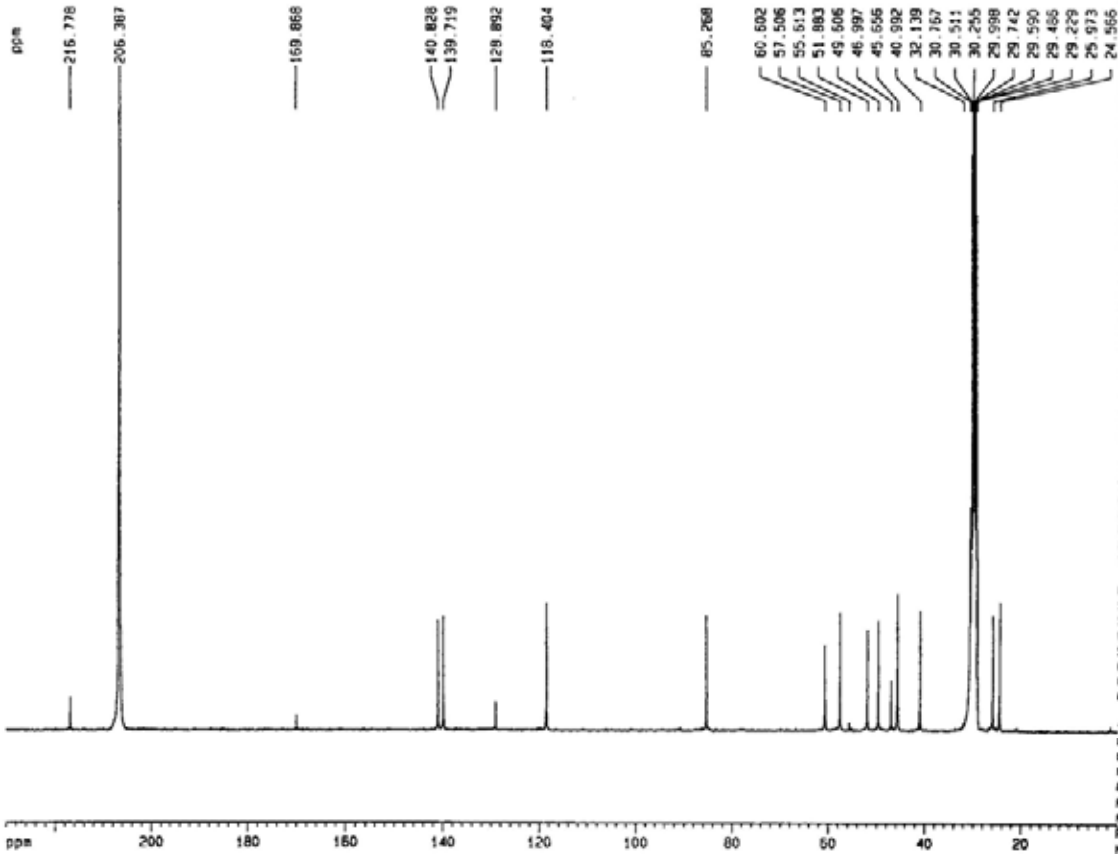


```
Bruker Advance III 400

NAME          djq-2-050-H1
EXPNO                    1
PROCNO                   1
Date_             20080712
Time                 11.33
INSTRUM               spect
PROBHD  5 mm PABBI 1H/
PULPROG               zg30
TD                   65536
SOLVENT            Acetone
NS                       8
DS                       0
SWH           10000.000 Hz
FIDRES        0.152588 Hz
AQ            3.2768500 sec
RG                    50.8
DW                50.000 use
DE                 6.50 use
TE                298.2 K
D1            1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                 14.83 use
PL1                0.00 dB
PL1W          8.31434441 W
SFO1        400.1316005 MHz
SI                   65536
SF          400.1300049 MHz
WDW                     EM
SSB                      0
LB                 0.30 Hz
GB                       0
PC                 1.00
```

C13



```
Current Data Parameters
NAME          djq-2-050-C13
EXPNO                   10
PROCNO                   1

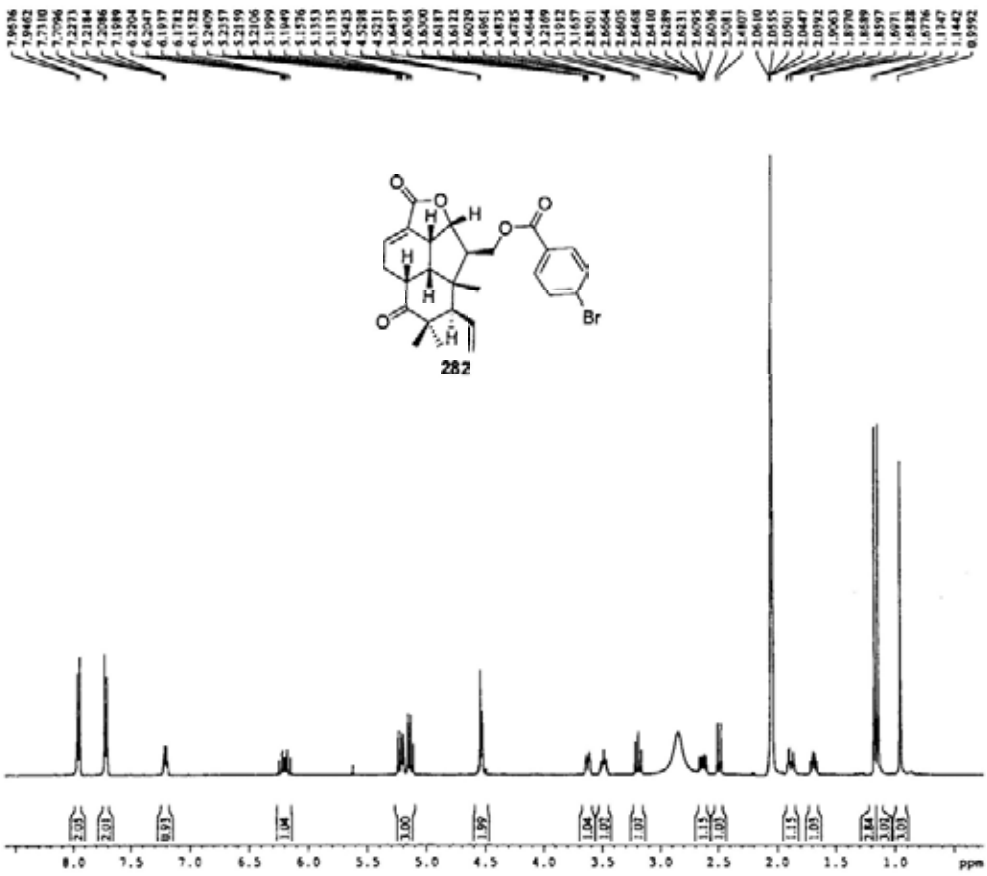
F2 - Acquisition Parameters
Date_             20080712
Time                 21.53
INSTRUM              dp+300
PROBHD  5 mm BBO BB-1H
PULPROG              zgpc
TD                   65536
SOLVENT            ------
NS                   51864
DS                       0
SWH           22675.736 Hz
FIDRES        0.346004 Hz
AQ            1.4451188 sec
RG                    8192
DW                22.050 usec
DE                 6.00 usec
TE                298.2 K
D1            1.00000000 sec
d11           0.03000000 sec
HCREST        0.00000000 sec
HCWRK         0.01500000 sec

======== 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            75.4676712 MHz
WDW                     EM
SSB                      0
LB                 3.00 Hz
GB                       0
PC                 1.40

1D NMR plot parameters
CX                 23.00 cm
CY                 50.00 cm
F1P               230.000 ppm
F1                17357.56 Hz
F2P                 0.000 ppm
F2                  0.00 Hz
PPMCM             10.00000 ppm/cm
HZCM              754.67676 Hz/cm
```



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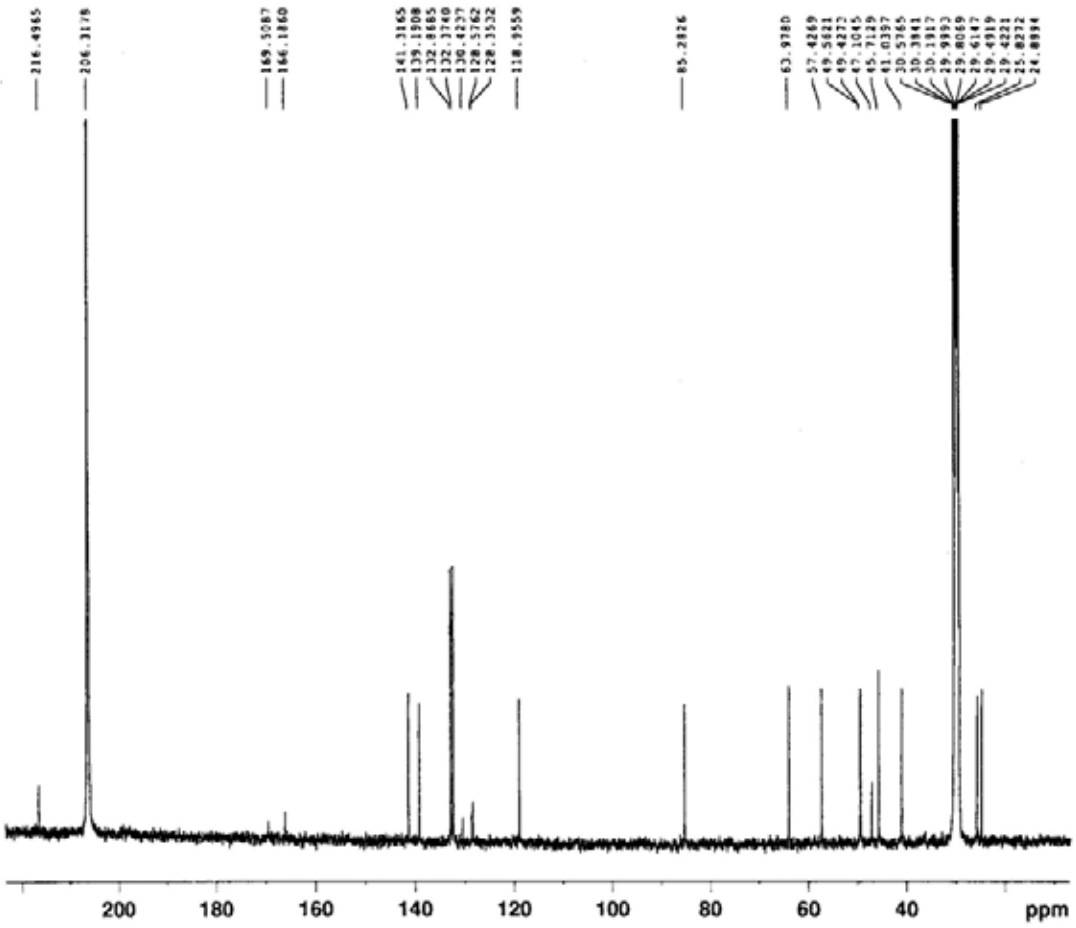
```
Bruker Advance III 400

NAME          djq-2-064-H1
EXPNO                    1
PROCNO                   1
Date_             20080917
Time                 14.05
INSTRUM              spect
PROBHD   5 mm PADUL 13C
PULPROG              zg30
TD                  65536
SOLVENT           Acetone
NS                      32
DS                       0
SWH           10000.000 Hz
FIDRES        0.152588 Hz
AQ            3.2768500 sec
RG                     203
DW              50.000 usec
DE               6.50 usec
TE                296.4 K
D1            1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.83 usec
PL1                   0.00 dB
PL1W          8.31434441 W
SFO1        400.1316005 MHz
SI                   65536
SF          400.1300049 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

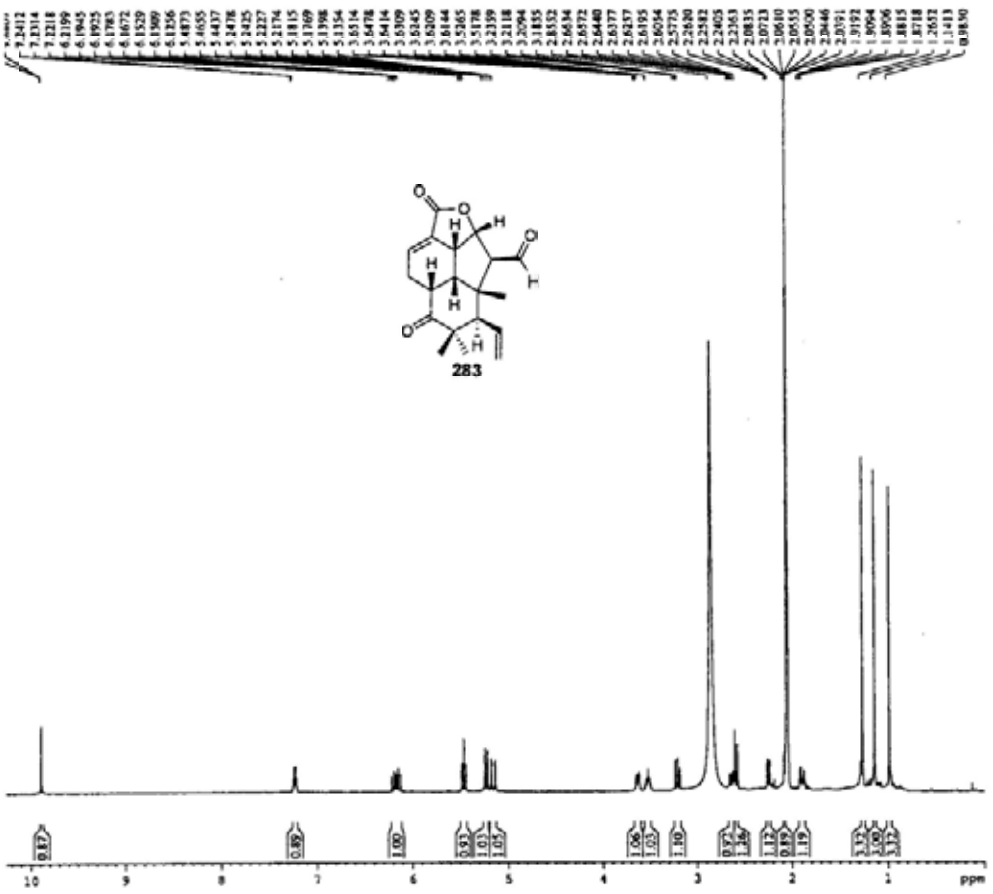



```
Bruker Advance III 400

NAME          djq-2-064-C13
EXPNO                    1
PROCNO                   1
Date_             20080917
Time                 22.41
INSTRUM              spect
PROBHD   5 mm PADUL 13C
PULPROG              zgdc
TD                  131072
SOLVENT           Acetone
NS                    8840
DS                       0
SWH           25252.525 Hz
FIDRES        0.192661 Hz
AQ            2.5952756 sec
RG                     203
DW              19.800 usec
DE               6.50 usec
TE                298.7 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        100.6227690 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                   0.00 dB
PL12                 15.66 dB
PL2W          8.31434441 W
PL12W         0.22585611 W
SFO2        400.1320007 MHz
SI                  131072
SF          100.6126626 MHz
WDW                     EM
SSB                      0
LB                    3.00 Hz
GB                       0
PC                    1.40
```



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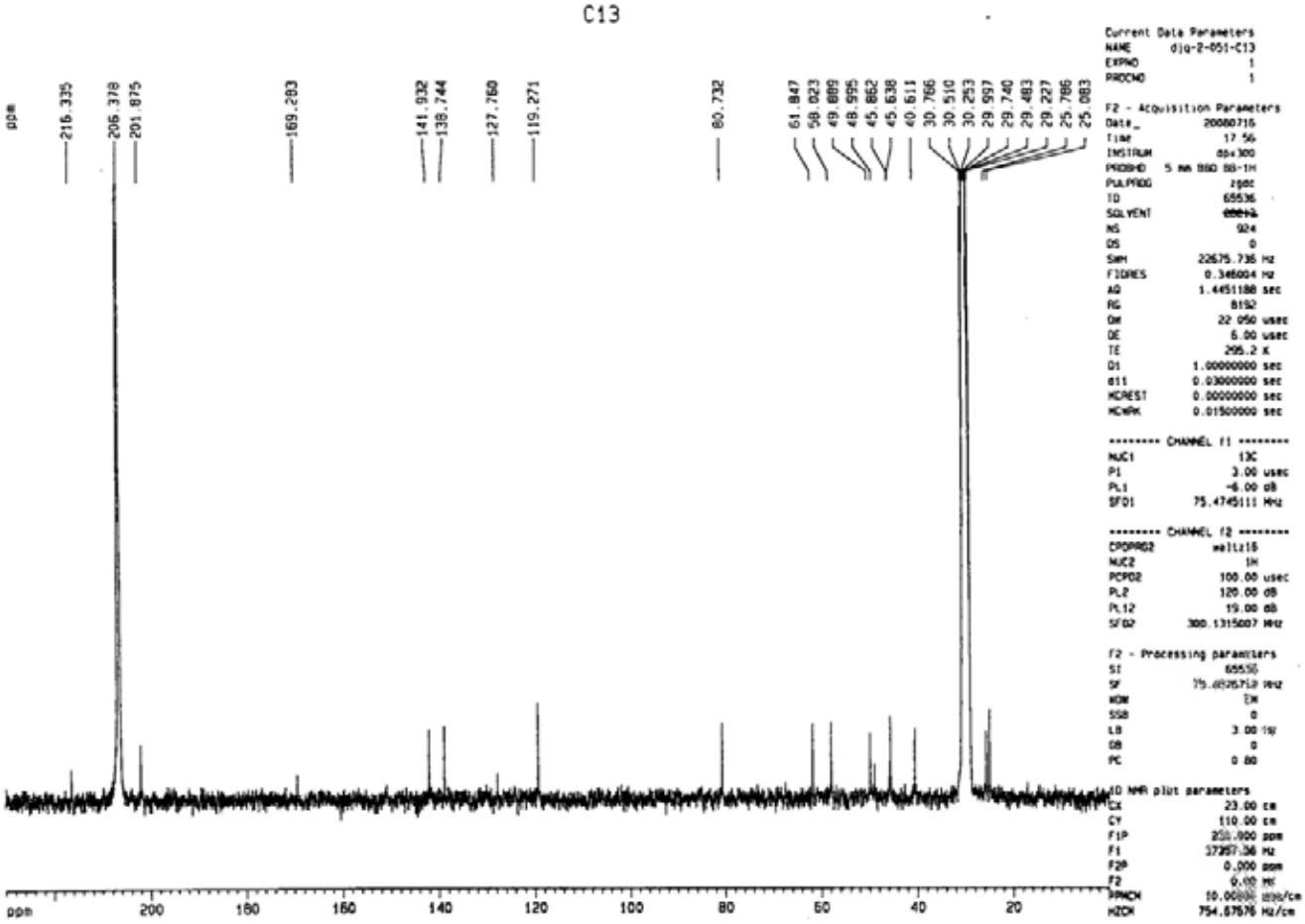
```
Bruker Advance III 400

NAME          djq-2-051-h1
EXPNO                    2
PROCNO                   1
Date_             20080722
Time                 17.40
INSTRUM               spect
PROBHD   5 mm PABBI 1H/
PULPROG              zg30
TD                  65536
SOLVENT           Acetone
NS                      50
DS                       0
SWH           10000.000 Hz
FIDRES        0.152588 Hz
AQ            3.2768500 sec
RG                     203
DW              50.000 usec
DE               6.50 usec
TE              295.0 K
D1            1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.10 usec
PL1                 -2.00 dB
PL1W          13.17734718 W
SFO1          400.1316005 MHz
SI                  65536
SF            400.1300050 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```




```
Current Data Parameters
NAME        djq-2-051-C13
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080715
Time                17.56
INSTRUM           dpx300
PROBHD  5 mm BBO BB-1H
PULPROG             zgdc
TD                 65536
SOLVENT          ======
NS                   924
DS                     0
SWH           22675.736 Hz
FIDRES        0.346004 Hz
AQ            1.4451188 sec
RG                  8192
DW              22.050 usec
DE               6.00 usec
TE              295.2 K
D1            1.00000000 sec
d11           0.03000000 sec
HCREST        0.00000000 sec
HCNPK         0.01500000 sec

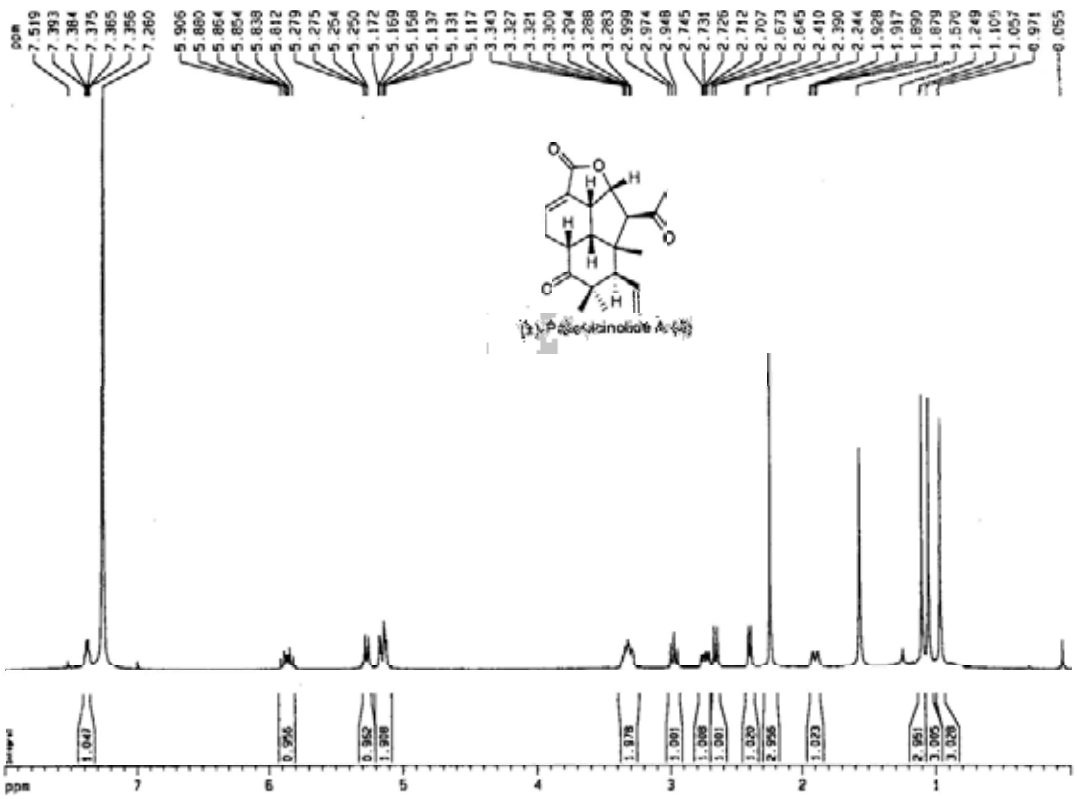
======== CHANNEL f1 ========
NUC1                   13C
P1                   3.00 usec
PL1                 -6.00 dB
SFO1          75.4745111 MHz

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

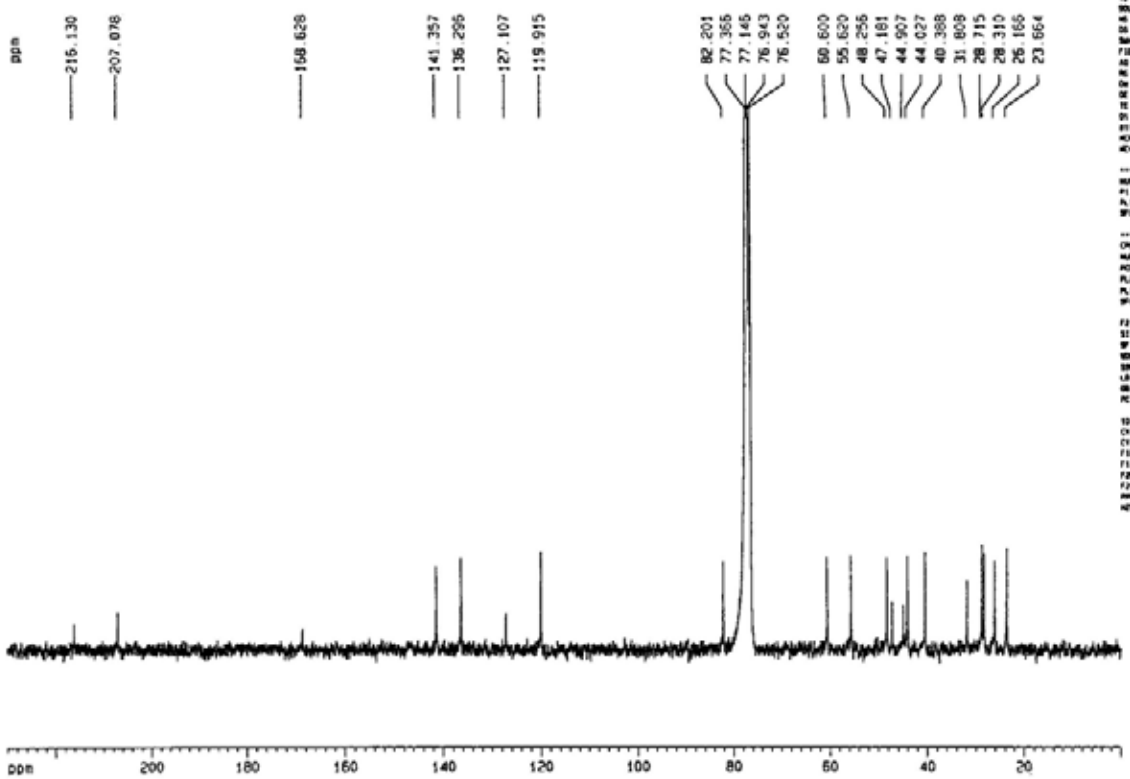
F2 - Processing parameters
SI                  65536
SF            75.4826713 MHz
WDW                    EM
SSB                     0
LB                   3.00 Hz
GB                      0
PC                   0.80

1D NMR plot parameters
CX                  23.00 cm
CY                 110.00 cm
F1P               220.000 ppm
F1              17297.36 Hz
F2P                 0.000 ppm
F2                  0.00 Hz
PPMCM            10.00000 ppm/cm
HZCM            754.67576 Hz/cm
```

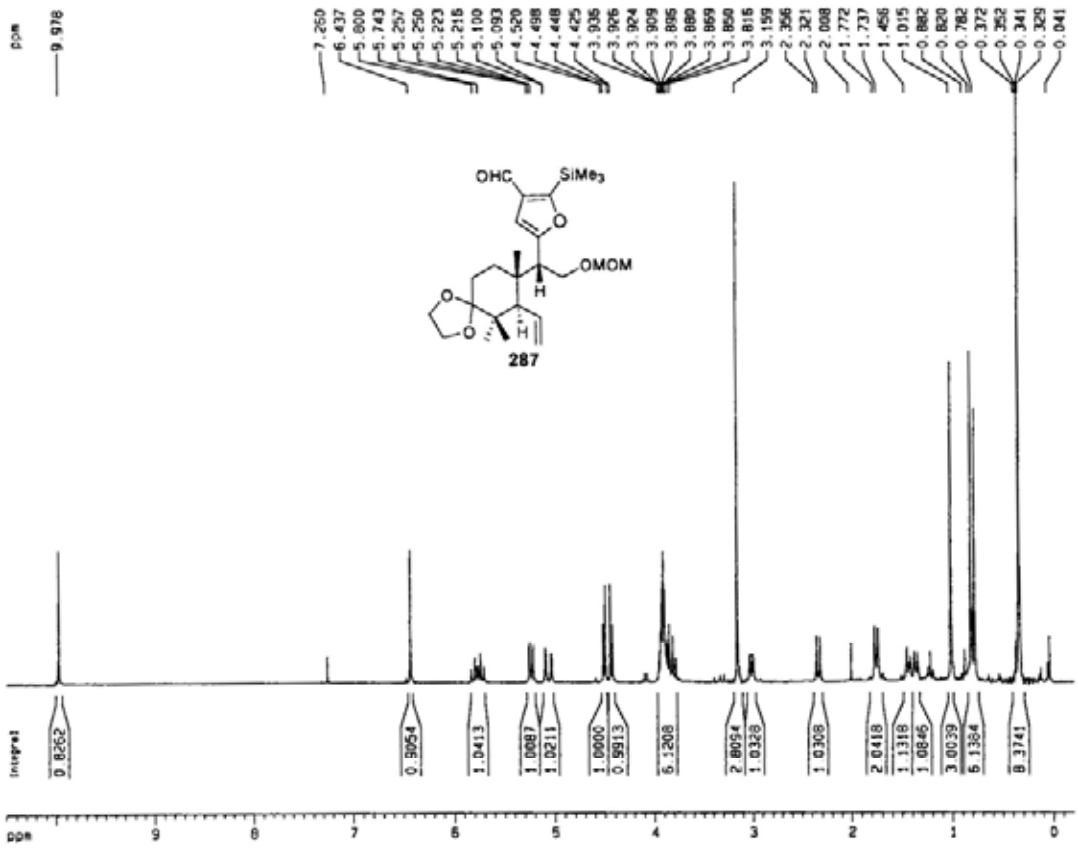
Natural product Pallavicinolide A



C13



1H




```
Current Data Parameters
NAME          ojo-1-091-C2-H1
EXPNO                       1
PROCNO                      1

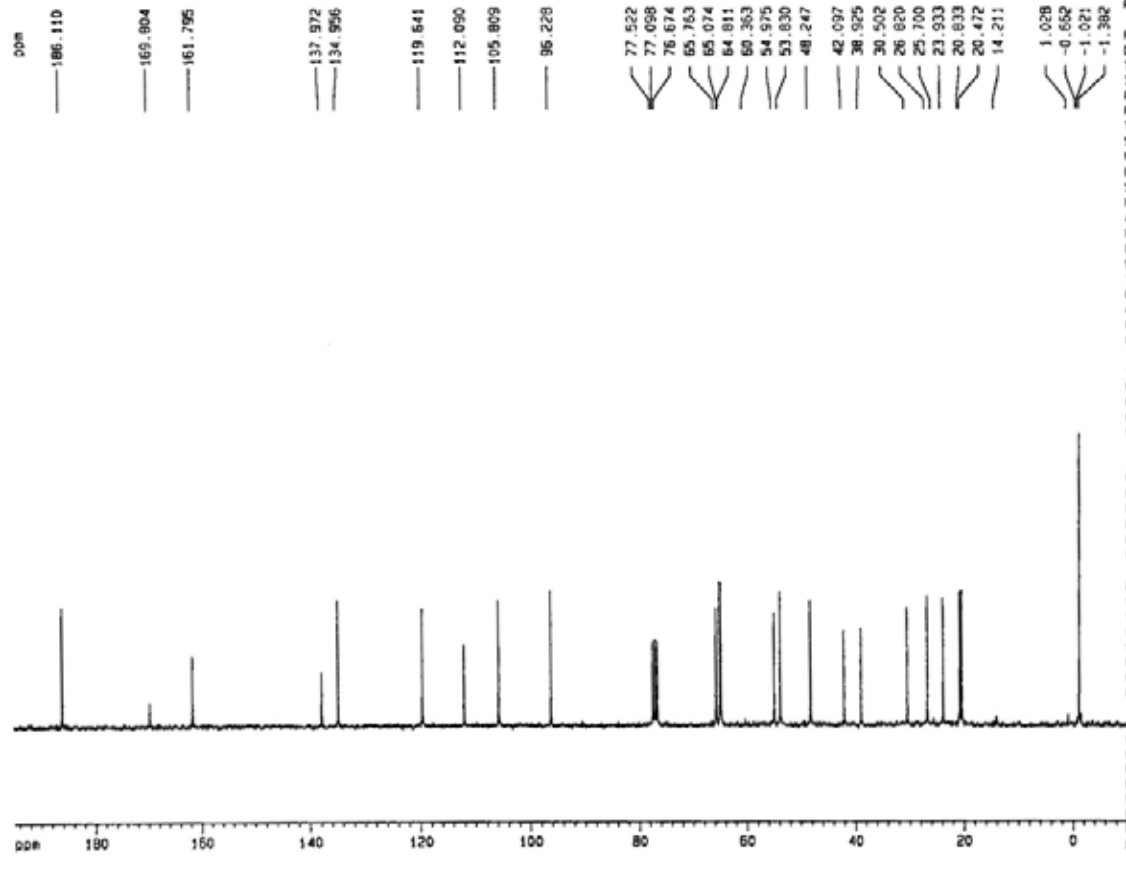
F2 - Acquisition Parameters
Date_              20071116
Time                   15.01
INSTRUM                spx300
PROBHD  5 mm BBO BB-1H
PULPROG                   zg
TD                     32768
SOLVENT                CDCl3
NS                         8
DS                         0
SWH                8992.806 Hz
FIDRES             0.274439 Hz
AQ                 1.8219508 sec
RG                        32
DW                    55.600 usec
DE                    79.43 usec
TE                     0.0 K
D1                 1.00000000 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

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

F2 - Processing parameters
SI                         32768
SF                300.1300095 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          0.20

1D NMR plot parameters
CX                         22.00 cm
CY                         30.00 cm
F1P                      10.500 ppm
F1                     3151.38 Hz
F2P                     -0.200 ppm
F2                      -60.03 Hz
PPMCM                  0.48635 ppm/cm
HZCM                 145.97232 Hz/cm
```

C13



```
Current Data Parameters
NAME          ojo-1-091-C2-C13
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20071116
Time                   15.07
INSTRUM                spx300
PROBHD  5 mm BBO BB-1H
PULPROG                 zgpg
TD                     65536
SOLVENT                CDCl3
NS                       193
DS                         0
SWH               22675.736 Hz
FIDRES             0.346004 Hz
AQ                 1.4451188 sec
RG                      8192
DW                    22.050 usec
DE                     6.00 usec
TE                     0.0 K
D1                 1.00000000 sec
D11                0.03000000 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

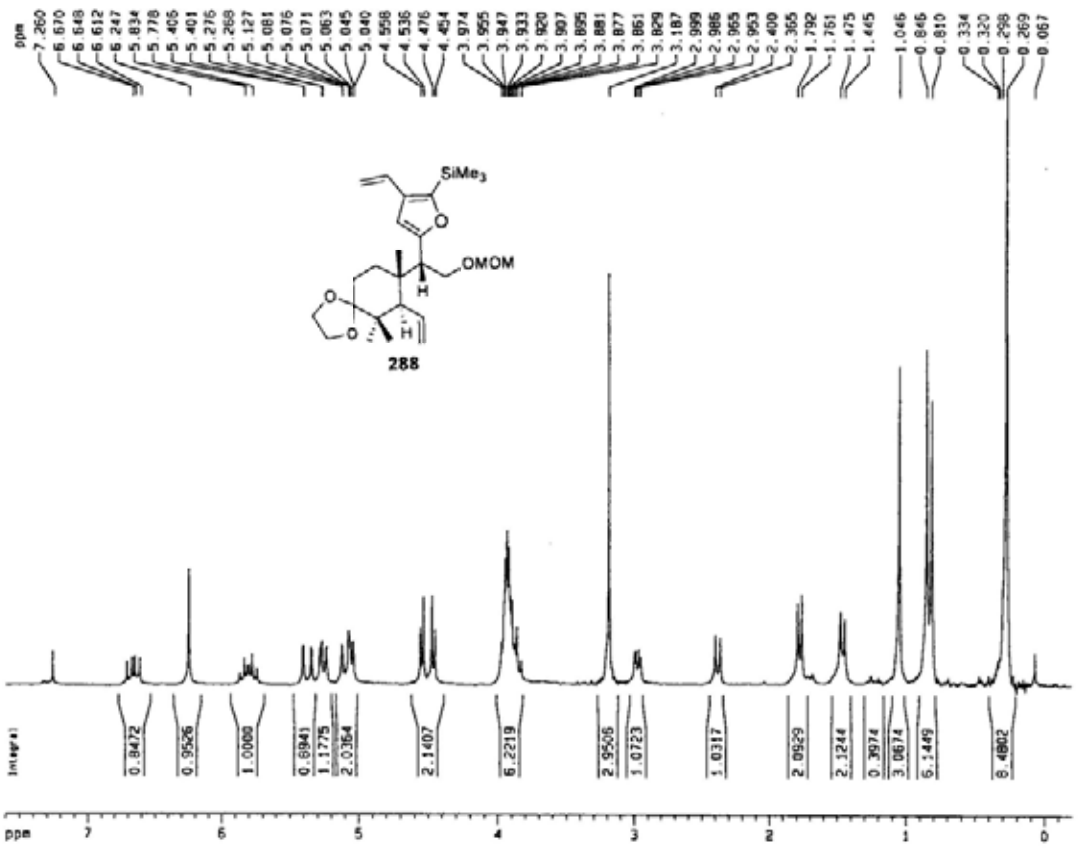
======== CHANNEL f1 ========
NUC1                      13C
P1                      3.00 usec
PL1                    -6.00 dB
SFO1             75.4745111 MHz

======== 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                75.4677459 MHz
WDW                           EM
SSB                            0
LB                          3.00 Hz
GB                             0
PC                          1.40

1D NMR plot parameters
CX                         23.00 cm
CY                          6.00 cm
F1P                     195.000 ppm
F1                     14716.21 Hz
F2P                    -10.000 ppm
F2                      -754.68 Hz
PPMCM                  8.91304 ppm/cm
HZCM                 672.64734 Hz/cm
```

1H



Current Data Parameters
NAME djq-1-092-H1
EXPNO 1
PROCNO 1

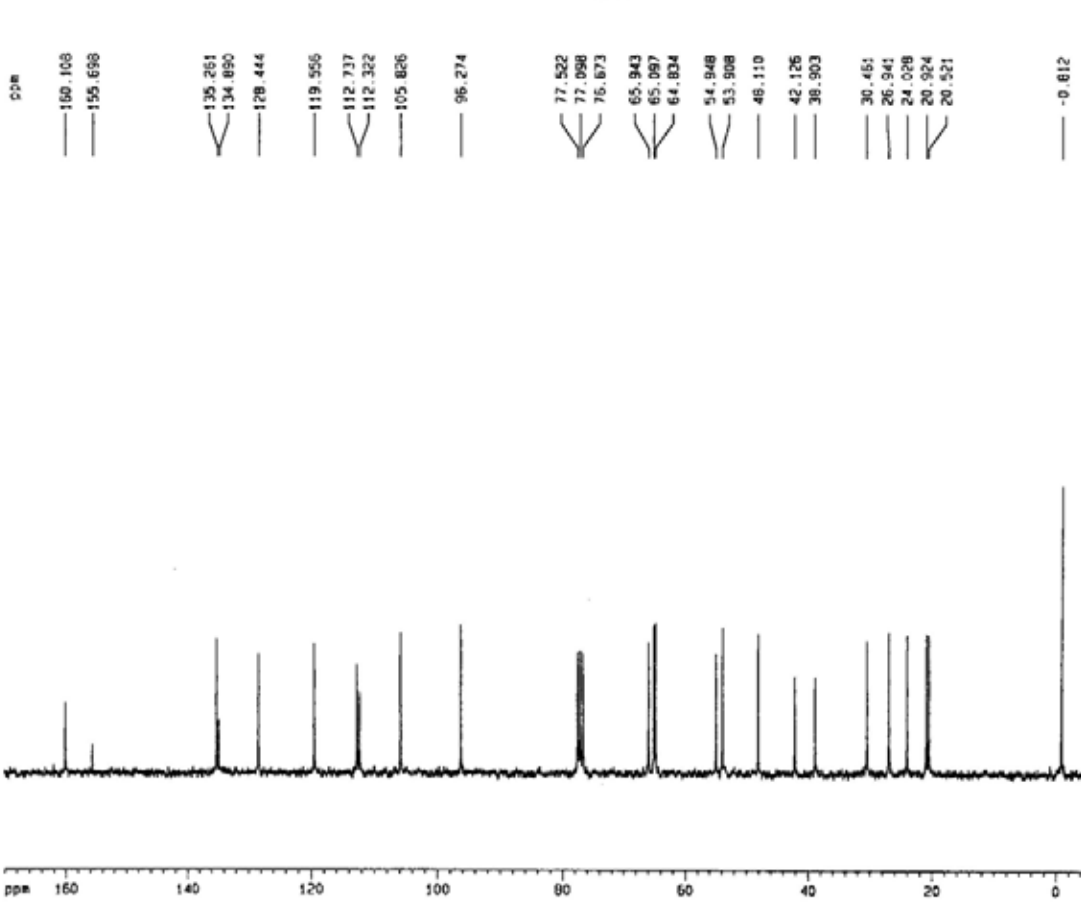
F2 - Acquisition Parameters
Date_ 20071117
Time 14.01
INSTRUM qp+300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 12
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219598 sec
RG 64
DW 55.600 usec
DE 78.43 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 300.1300044 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 24.00 cm
F1P 7.500 ppm
F1 2250.99 Hz
F2P -0.200 ppm
F2 -60.03 Hz
PPMCM 0.35455 ppm/cm
HZCM 106.40972 Hz/cm

C13



Current Data Parameters
NAME djq-1-092-C13
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20071117
Time 14.08
INSTRUM qp+300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 243
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4455188 sec
RG 11585.2
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

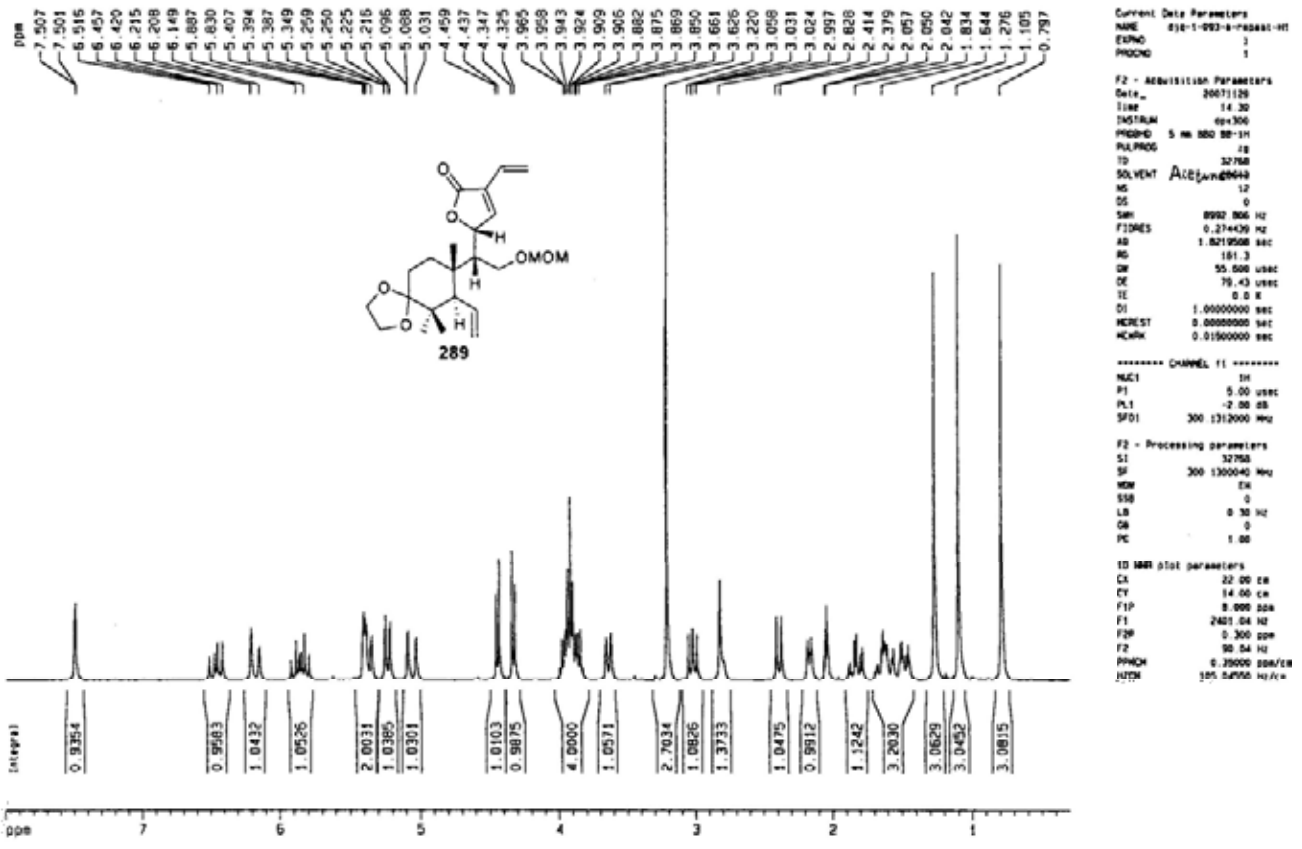
======== CHANNEL f1 ========
NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SFO1 75.4745111 MHz

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

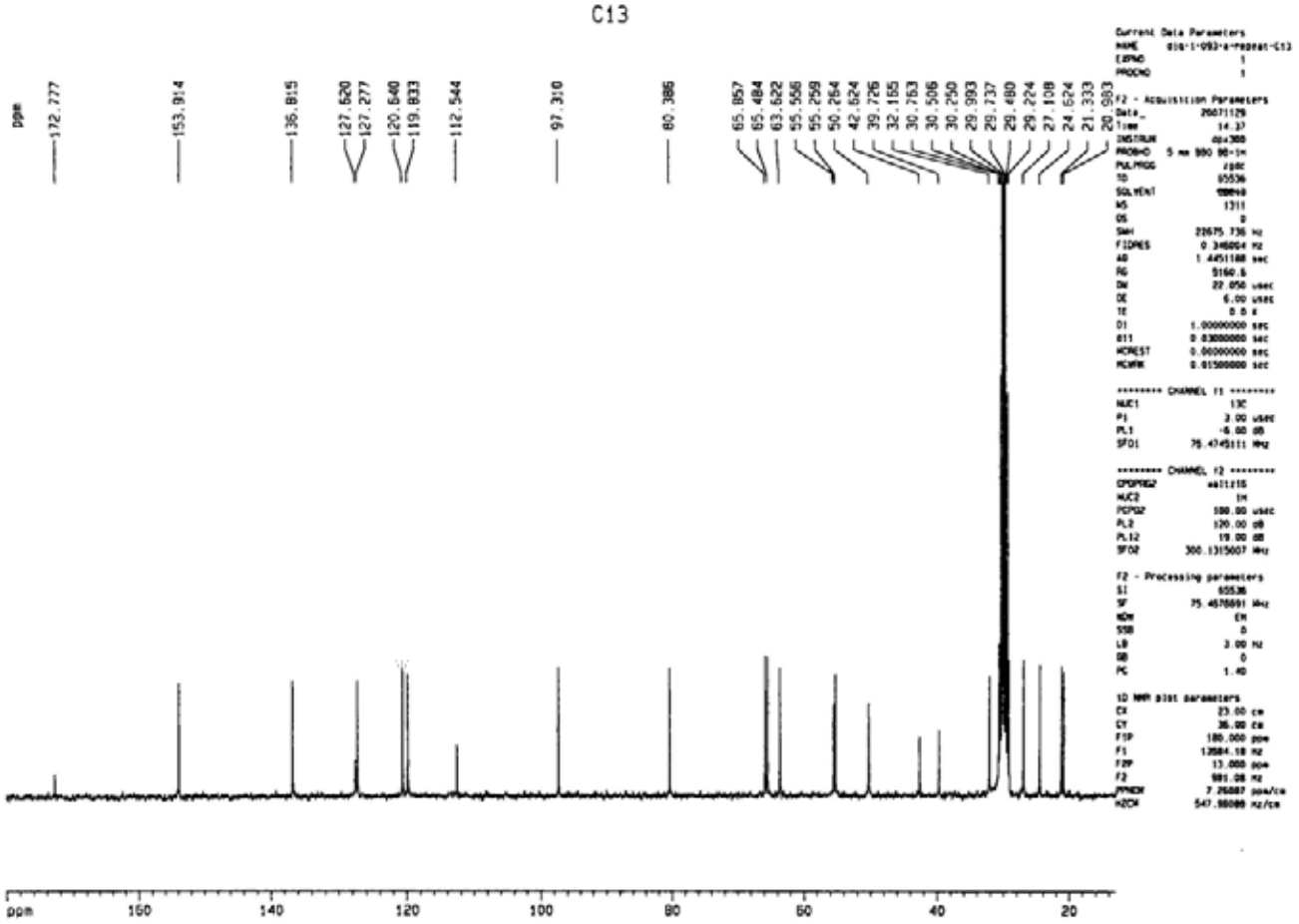
F2 - Processing parameters
SI 65536
SF 75.4677434 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 23.00 cm
CY 6.00 cm
F1P 170.000 ppm
F1 12829.52 Hz
F2P -10.000 ppm
F2 -754.88 Hz
PPMCM 7.82609 ppm/cm
HZCM 590.61713 Hz/cm

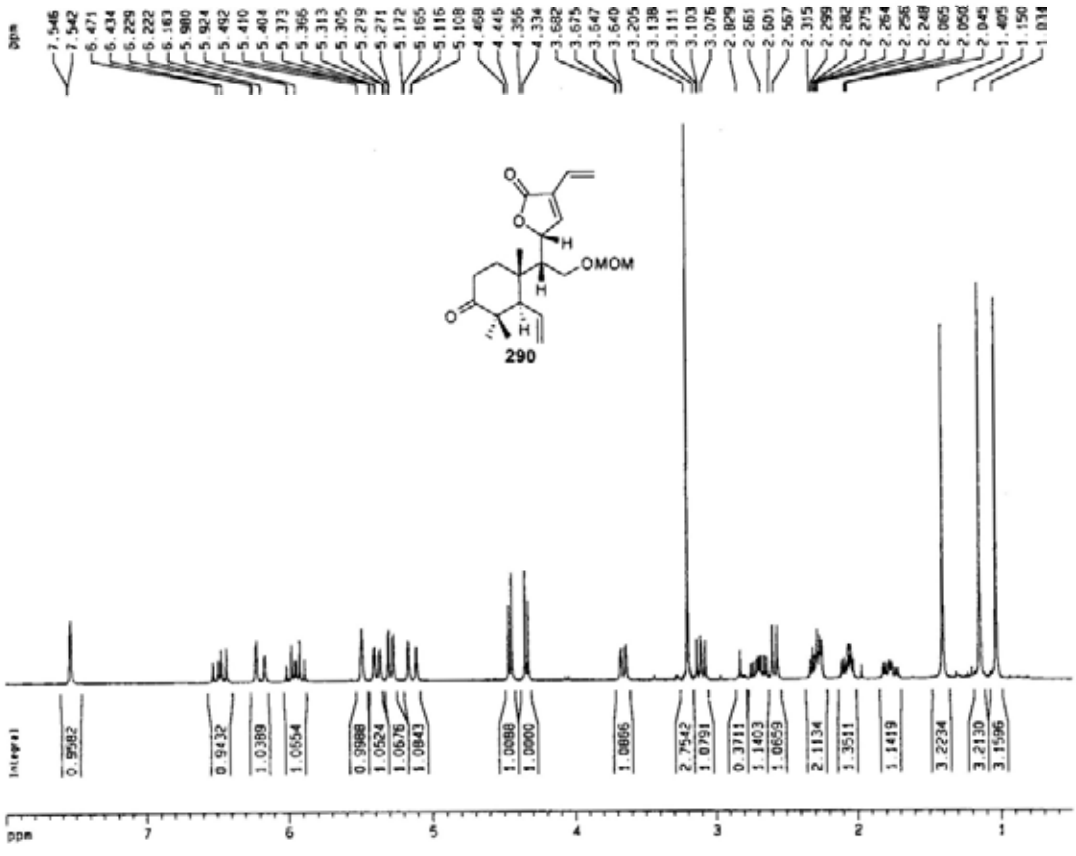
1H



C13



1H



Current Data Parameters
NAME djq-1-094-H1
EXPNO 1
PROCNO 1

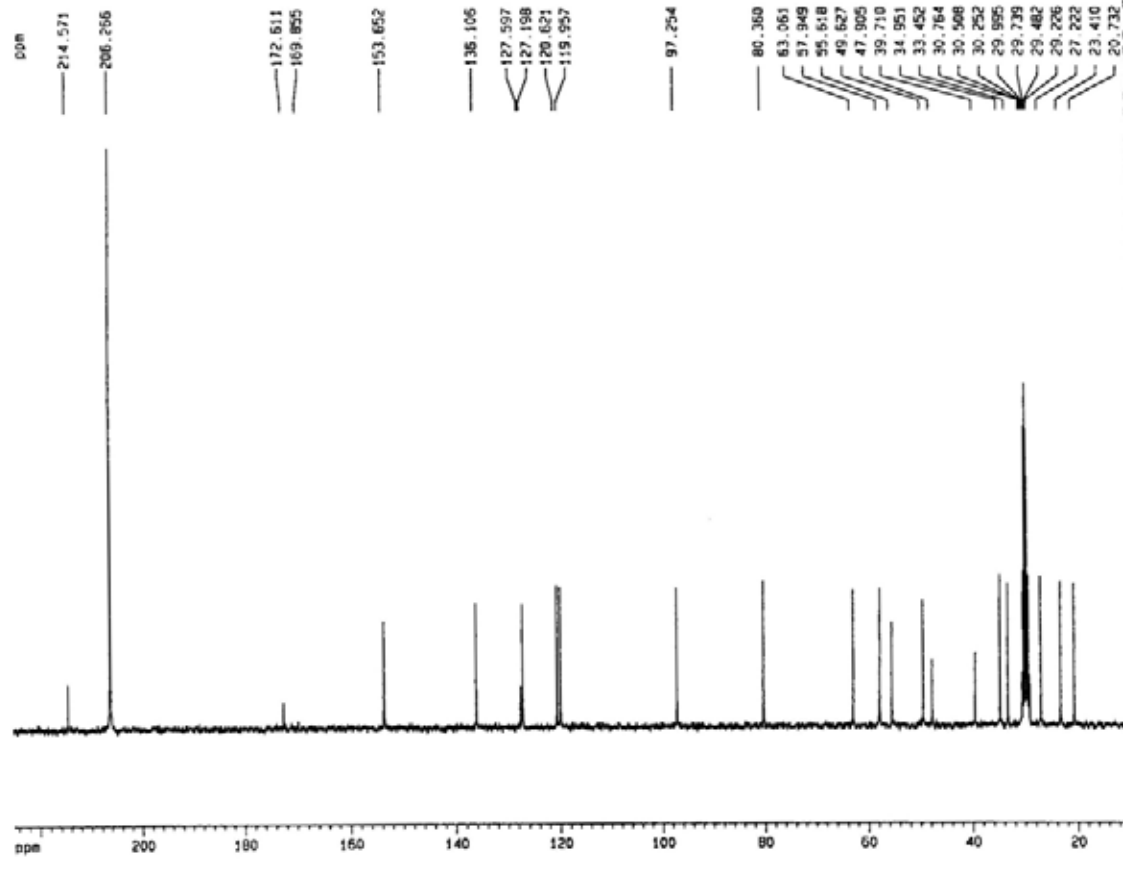
F2 - Acquisition Parameters
Date_ 20071129
Time 15.57
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT ~~CDCl3~~ Acetone
NS 12
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 64
DW 55.600 usec
DE 79.43 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 300.1300018 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 12.00 cm
F1P 8.000 ppm
F1 2401.04 Hz
F2P 0.500 ppm
F2 150.07 Hz
PPMCM 0.34091 ppm/cm
HZCM 102.31705 Hz/cm

C13



Current Data Parameters
NAME djq-1-094-C13
EXPNO 1
PROCNO 1

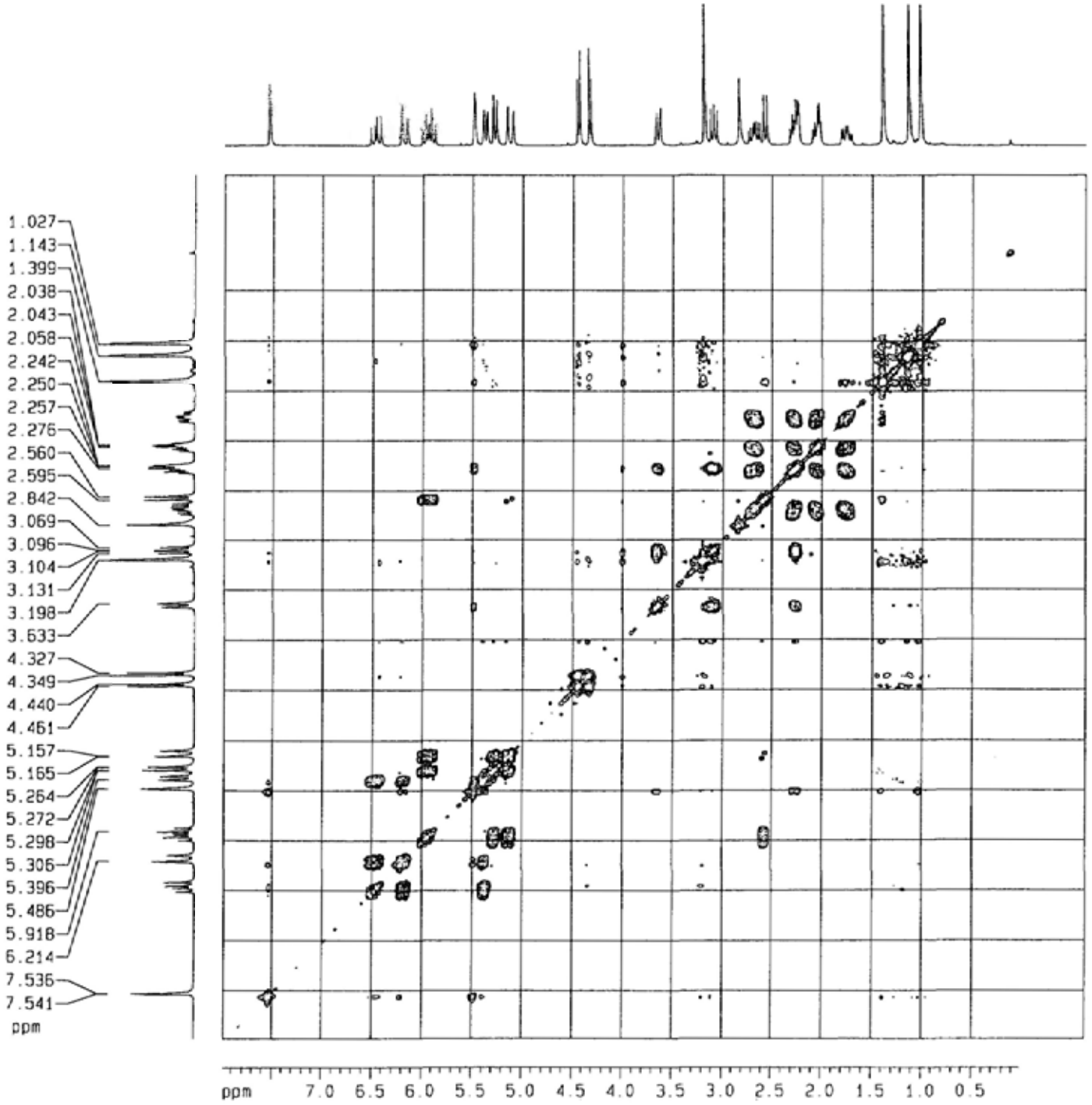
F2 - Acquisition Parameters
Date_ 20071129
Time 15.41
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zgdc
TD 65536
SOLVENT ~~CDCl3~~
NS 156
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== 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 75.4676722 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

2D NMR plot parameters
CX 23.00 cm
CY 12.00 cm
F1P 225.000 ppm
F1 16980.23 Hz
F2P 10.000 ppm
F2 754.68 Hz
PPMCM 9.34783 ppm/cm
HZCM 705.45868 Hz/cm




```
                Current Data Parameters
NAME        dqq-1-094 H-H cosy
EXPNO                      301
PROCNO                       1

        F2 - Acquisition Parameters
Date_               20071213
Time                   13.50
INSTRUM                dpx300
PROBHD   5 mm BBO BB-1H
PULPROG             cosyqf45
TD                      1024
SOLVENT               Acetone
NS                          4
DS                         16
SWH                2394.636 Hz
FIDRES             2.338512 Hz
AQ                 0.2138612 sec
RG                     101.6
DW                   208.800 usec
DE                     6.00 usec
TE                      0.0 K
d0                 0.00000300 sec
D1                 3.00000000 sec
IN0                0.00041649 sec
MCREST             0.00000000 sec
MCWRK              3.00000000 sec

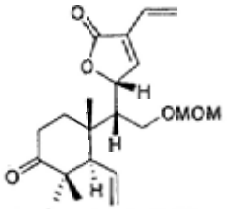
        ======== CHANNEL f1 ========
NUC1                       1H
P1                       9.30 usec
PL1                     -2.00 dB
SFO1             300.1312045 MHz

        F1 - Acquisition parameters
NDO                         1
TD                        256
SFO1             300.1312 MHz
FIDRES             9.379033 Hz
SW                     8.000 ppm
FnMODE                    QF

        F2 - Processing parameters
SI                        512
SF               300.1300034 MHz
WDW                      SINE
SSB                         0
LB                       0.00 Hz
GB                          0
PC                       1.00

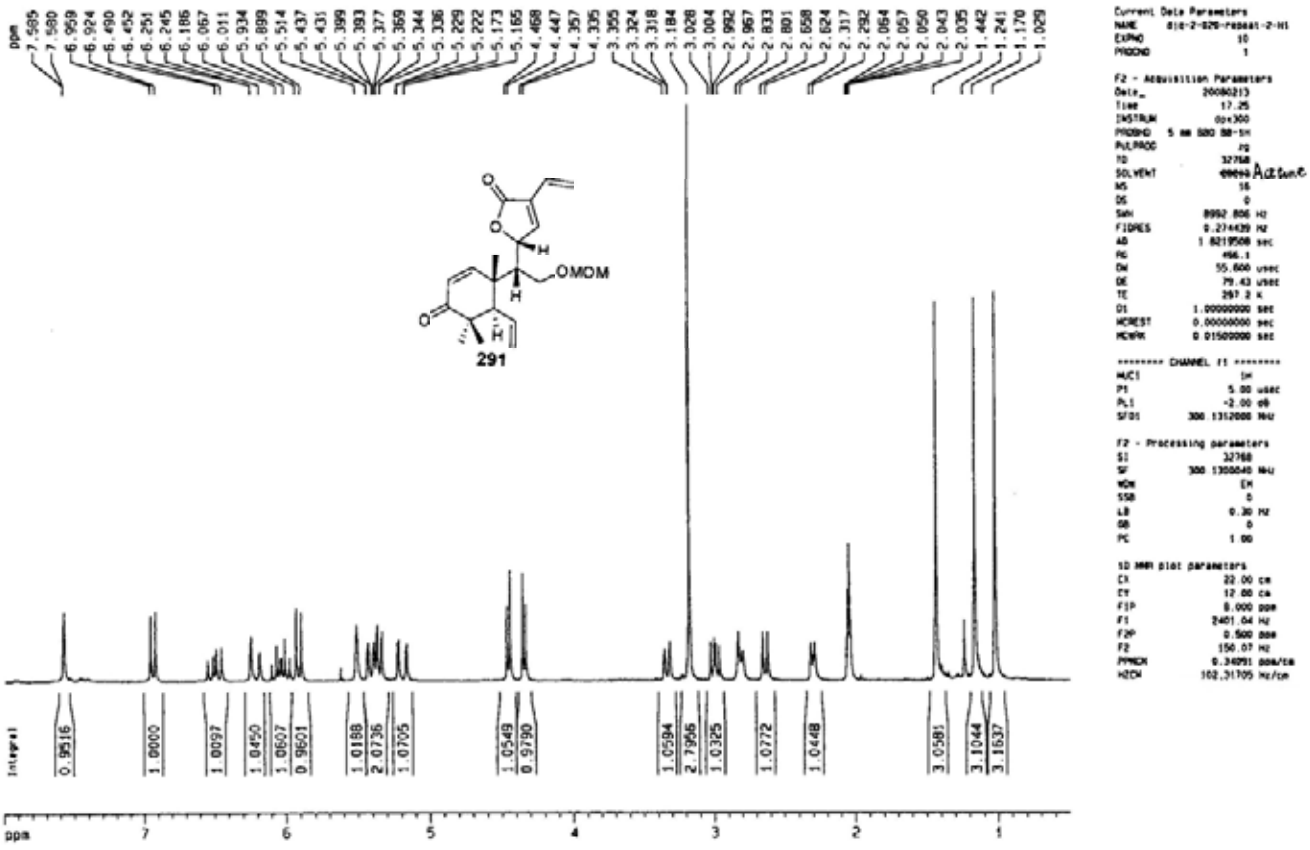
        F1 - Processing parameters
SI                        512
MC2                       QF
SF               300.1299972 MHz
WDW                      SINE
SSB                         0
LB                       0.00 Hz
GB                          0

        2D NMR plot parameters
CX2                     15.00 cm
CX1                     15.00 cm
F2PLO                   7.987 ppm
F2LO                 2397.07 Hz
F2PHI                  -0.636 ppm
F2HI                 -190.93 Hz
F1PLO                   7.963 ppm
F1LO                 2395.97 Hz
F1PHI                  -0.640 ppm
F1HI                 -192.03 Hz
F2PPMCM              0.57486 ppm/cm
F2HZCM             172.53348 Hz/cm
F1PPMCM              0.57486 ppm/cm
F1HZCM             172.53348 Hz/cm
```

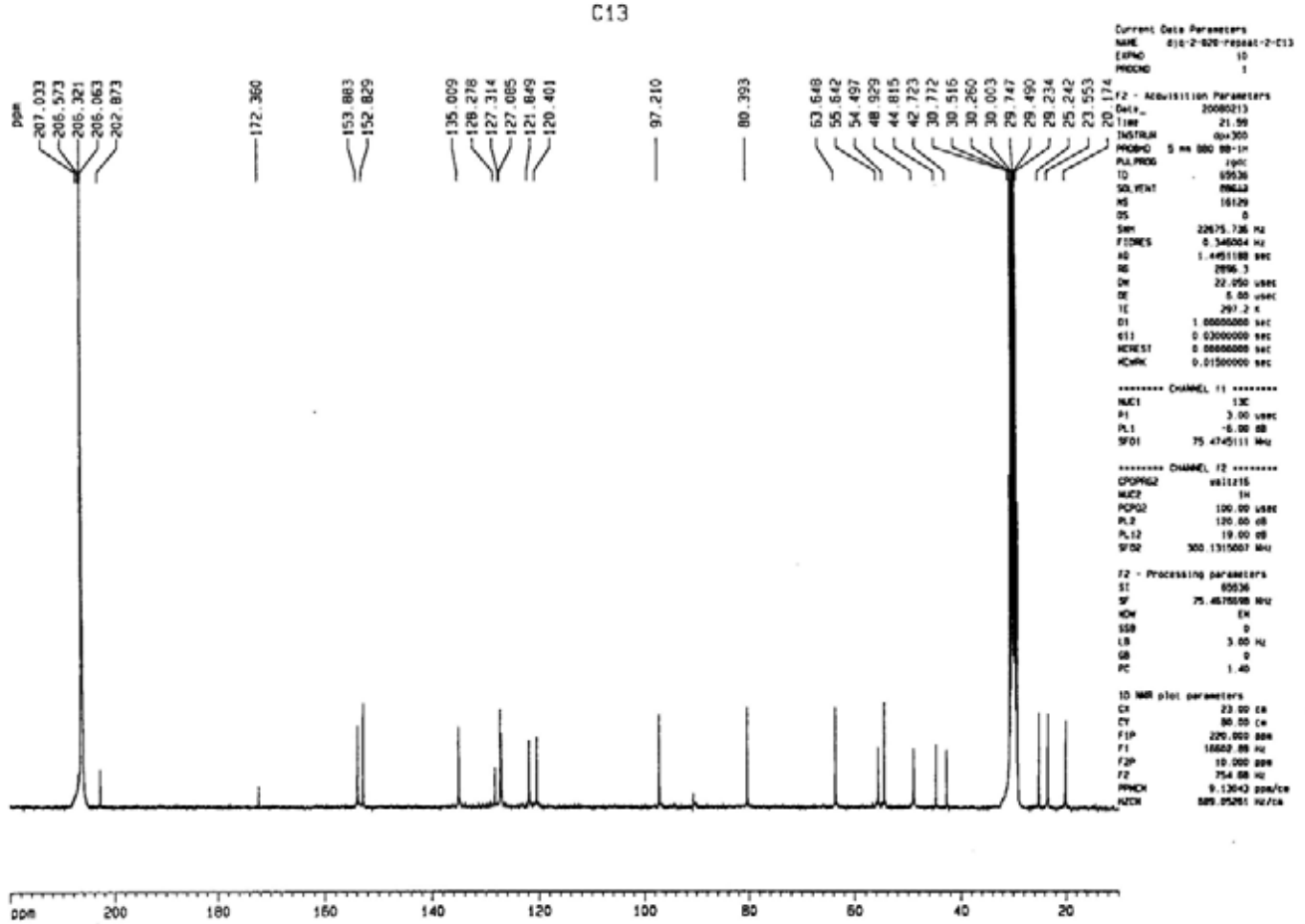


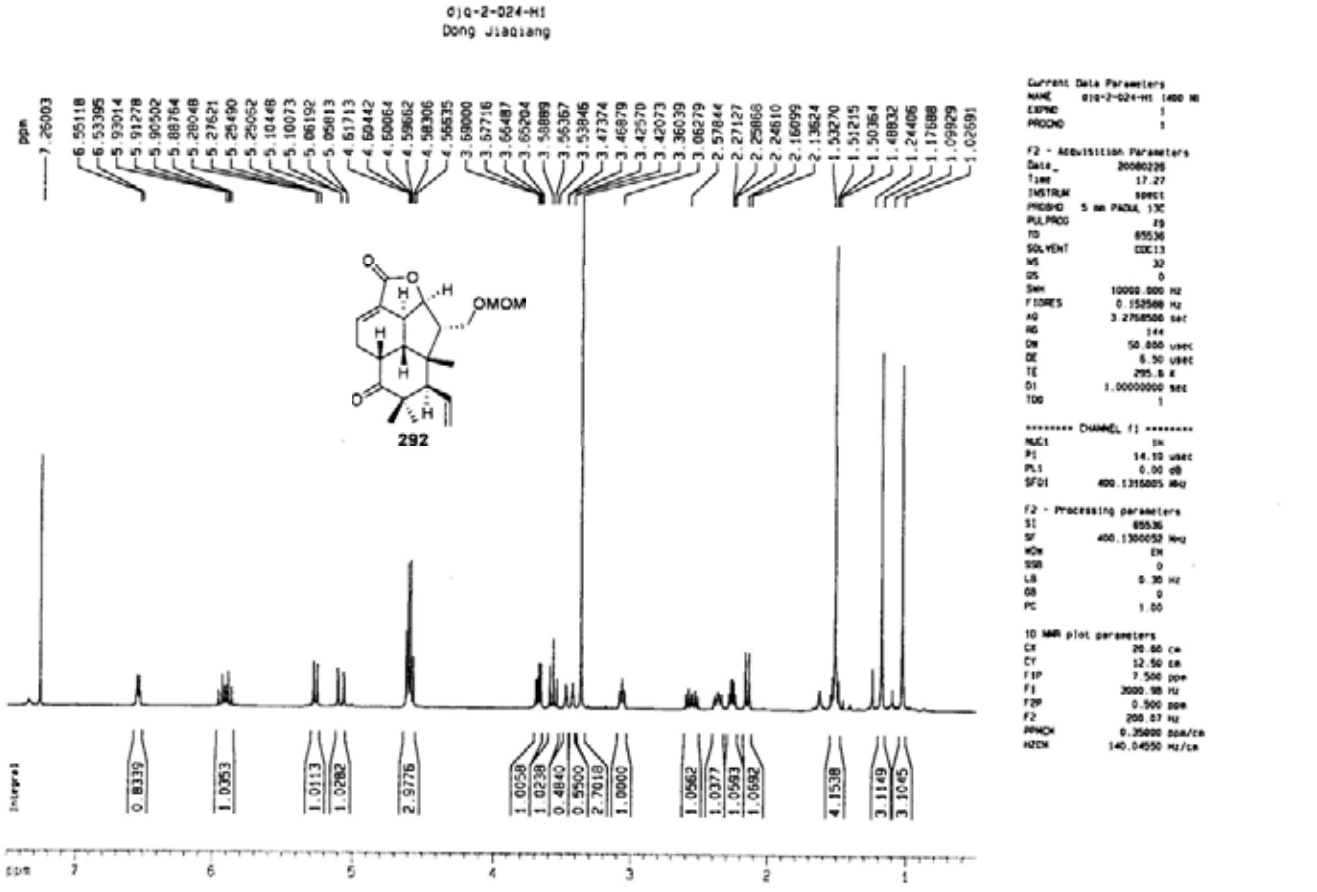
^{1}H-^{1}H COSY of **290**

1H

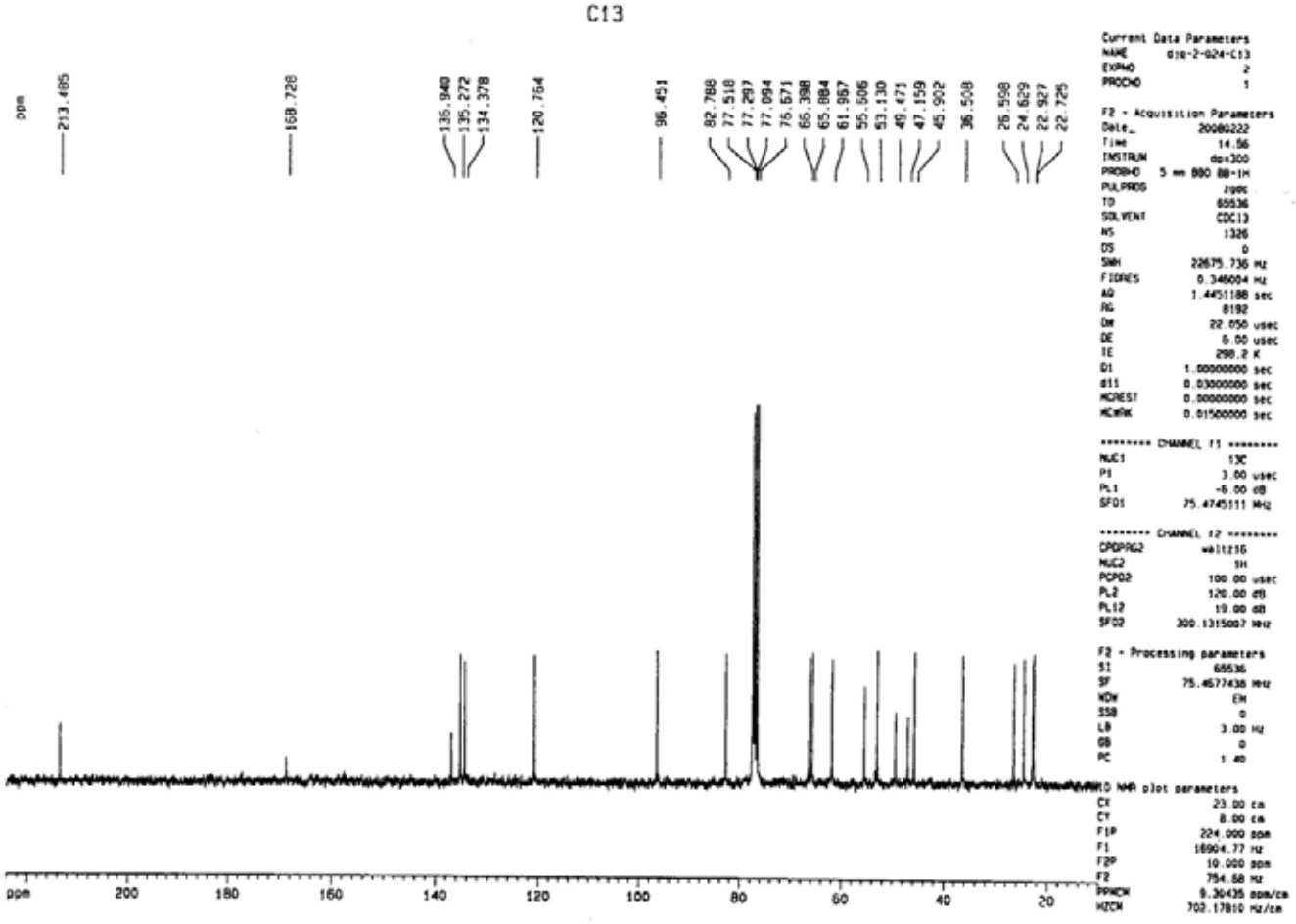

OMOM
291
Acetone

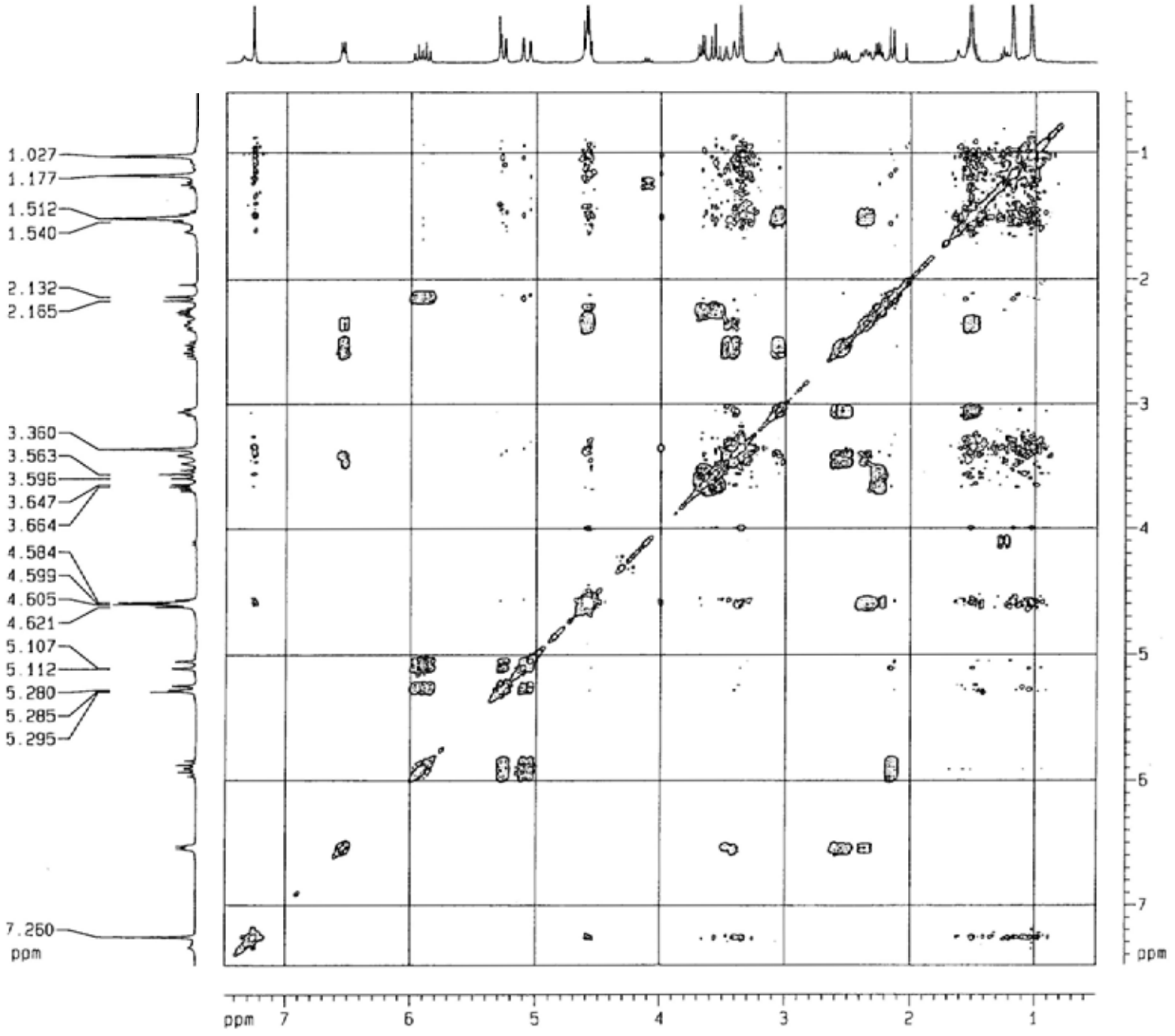
C13


207.033
206.573
206.321
206.063
202.873
172.360
153.883
152.829
135.009
128.278
127.314
127.085
121.849
120.401
97.210
80.393
63.648
55.642
54.497
48.929
44.815
42.723
30.772
30.516
30.260
30.003
29.747
29.490
29.234
25.242
23.553
20.174


djq-2-024-H1
Dong Jiaqiang
OMOM
292
Current Data Parameters
NAME djq-2-024-H1 1400 MI
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080226
Time 17.27
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 32
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2768500 sec
RG 144
DW 50.000 usec
DE 6.50 usec
TE 295.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.50 usec
PL1 0.00 dB
SFO1 400.1315005 MHz
F2 - Processing parameters
SI 65536
SF 400.1300052 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 12.50 cm
F1P 7.500 ppm
F1 3000.98 Hz
F2P 0.500 ppm
F2 200.07 Hz
PPMCM 0.35000 ppm/cm
HZCM 140.04550 Hz/cm
ppm
Integral
0.8339
1.0063
1.0113
1.0282
2.9776
1.0058
1.0238
0.4840
0.5500
2.7018
1.0000
1.0562
1.0377
1.0593
1.0692
4.1538
3.1149
3.1045

C13


Current Data Parameters
NAME djq-2-024-C13
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080222
Time 14.56
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 1326
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== 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 75.4577436 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 23.00 cm
CY 8.00 cm
F1P 224.000 ppm
F1 16904.77 Hz
F2P 10.000 ppm
F2 754.58 Hz
PPMCM 9.30435 ppm/cm
HZCM 702.17810 Hz/cm
ppm
213.485
168.728
135.940
135.272
134.378
120.764
96.451
82.786
77.518
77.297
77.094
76.671
66.398
65.884
61.967
55.506
53.130
49.471
47.159
45.902
36.508
26.598
24.629
22.927
22.725




```
                Current Data Parameters
NAME        djq-2-024 H-H cosy
EXPNO                    301
PROCNO                     1

        F2 - Acquisition Parameters
Date_               20080225
Time                   19.35
INSTRUM                dpx300
PROBHD  5 mm BBO BB-1H
PULPROG             cosygf45
TD                      1024
SOLVENT                 CDCl3
NS                         4
DS                        16
SWH                 2097.315 Hz
FIDRES              2.048160 Hz
AQ                  0.2445716 sec
RG                      101.6
DW                    238.400 usec
DE                      6.00 usec
TE                     298.2 K
D0                  0.00000300 sec
D1                  3.00000000 sec
IN0                 0.00047599 sec
HCREST              0.00000000 sec
HCWRK               3.00000000 sec

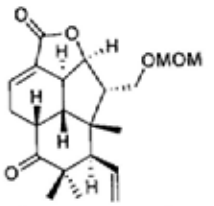
        ======== CHANNEL f1 ========
NUC1                       1H
P1                       9.30 usec
PL1                     -2.00 dB
SFO1                300.1312057 MHz

        F1 - Acquisition parameters
NDD                        1
TD                       256
SFO1                300.1312 MHz
FIDRES              8.206623 Hz
SW                      7.000 ppm
FnMODE                    QF

        F2 - Processing parameters
SI                       512
SF                  300.1289570 MHz
WDW                     SINE
SSB                        0
LB                      0.00 Hz
GB                         0
PC                      1.00

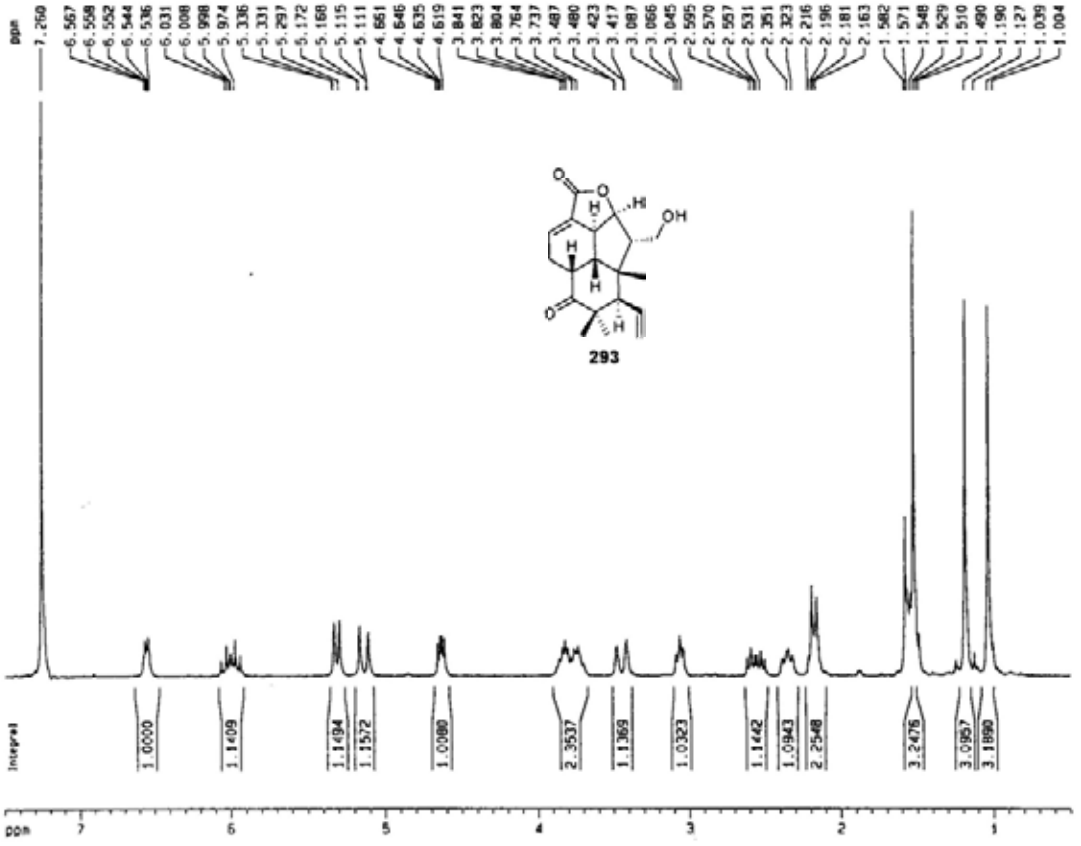
        F1 - Processing parameters
SI                       512
MC2                       QF
SF                  300.1289556 MHz
WDW                     SINE
SSB                        0
LB                      0.00 Hz
GB                         0

        2D NMR plot parameters
CX2                    15.00 cm
CX1                    15.00 cm
F2PLO                  7.479 ppm
F2LO                2244.62 Hz
F2PHI                  0.504 ppm
F2HI                 151.40 Hz
F1PLO                  7.484 ppm
F1LO                2246.02 Hz
F1PHI                  0.525 ppm
F1HI                 157.44 Hz
F2PPMCM             0.46498 ppm/cm
F2HZCM             139.54794 Hz/cm
F1PPMCM             0.46393 ppm/cm
F1HZCM             139.23004 Hz/cm
```



^{1}H-^{1}H COSY of **292**

1H



293

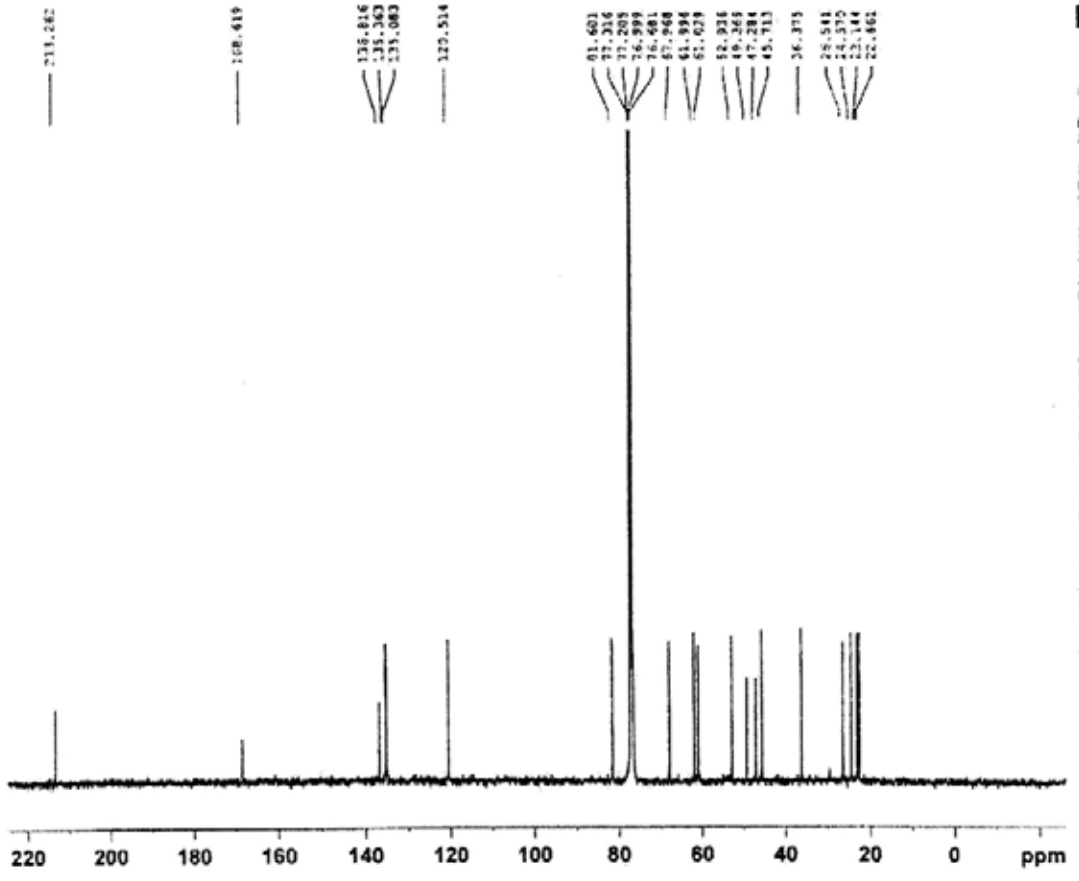
Current Data Parameters
NAME eja-2-027-H1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080306
Time 17.53
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219500 sec
RG 406.4
DW 55.600 usec
DE 79.43 usec
TE 298.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 32768
SF 300.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 12.00 cm
F1P 7.500 ppm
F1 2250.98 Hz
F2P 0.500 ppm
F2 150.06 Hz
PPMCM 0.31818 ppm/cm
HZCM 95.49091 Hz/cm



BRUKER

Current Data Parameters
NAME dpq-2-027-c13
EXPNO 1
PROCNO 1

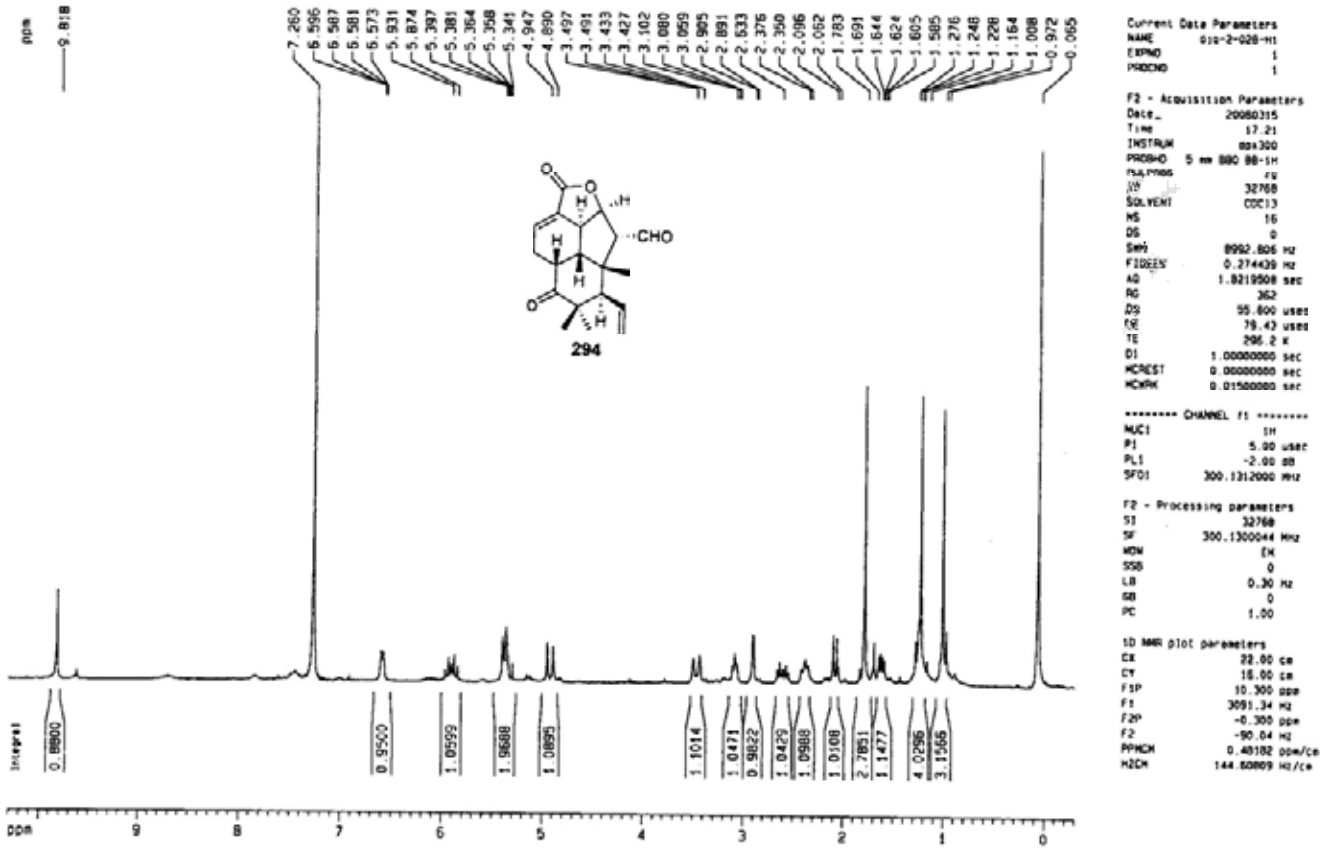
F2 - Acquisition Parameters
Date_ 20080213
Time 22.15
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgdc
TD 131072
SOLVENT CDCl3
NS 10990
DS 0
SWH 25252.525 Hz
FIDRES 0.192661 Hz
AQ 2.5952756 sec
RG 203
DW 19.800 usec
DE 6.50 usec
TE 295.5 K
D1 1.00000000 sec
d11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 3.50 usec
PL1 -0.60 dB
SFO1 100.6227690 MHz

======== CHANNEL f2 ========
CPDPG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL12 16.10 dB
PL2 0.00 dB
SFO2 400.1320007 MHz

F2 - Processing parameters
SI 131072
SF 100.6127705 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1H



Current Data Parameters
NAME 01s-2-028-H1
EXPNO 1
PROCNO 1

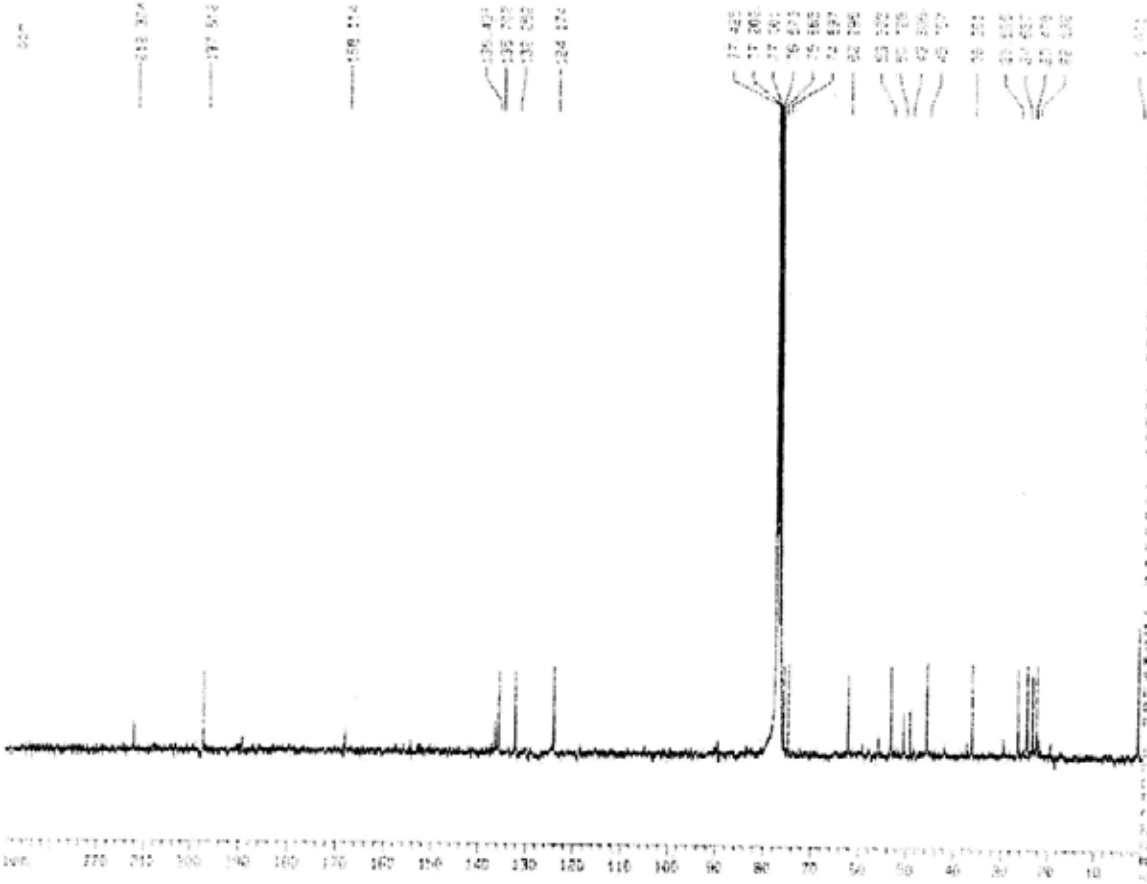
F2 - Acquisition Parameters
Date_ 20060315
Time 17.21
INSTRUM spx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 362
DW 55.600 usec
DE 78.43 usec
TE 296.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

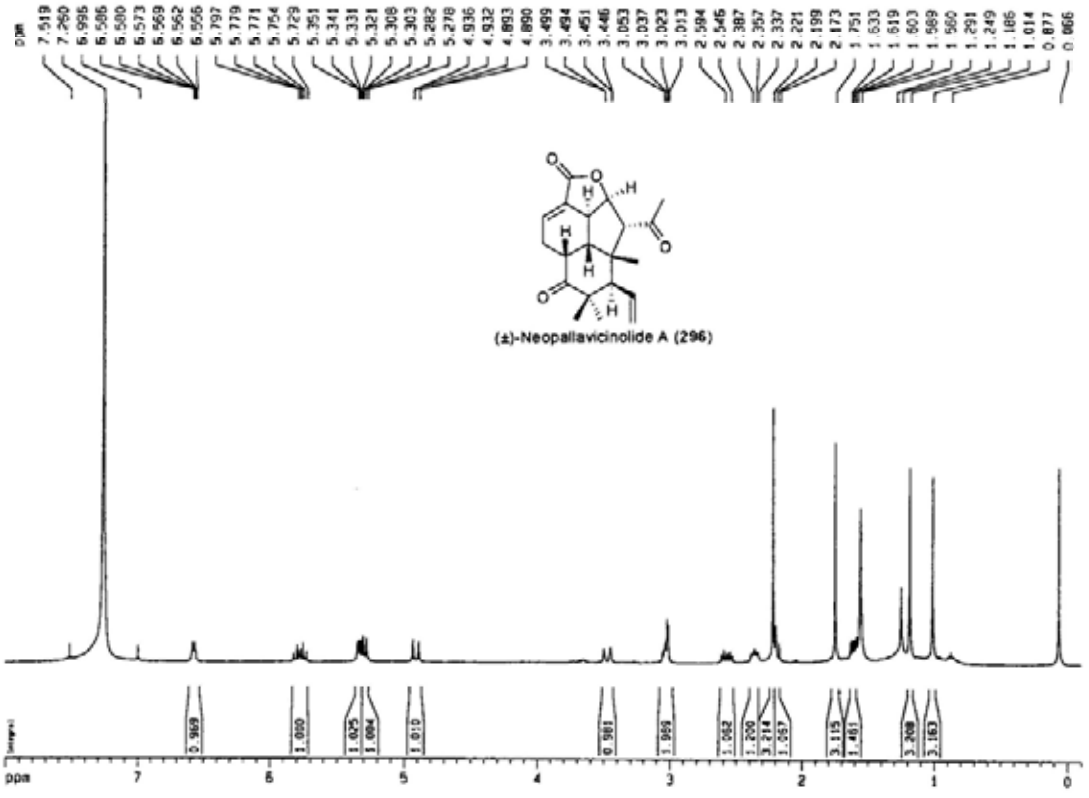
F2 - Processing parameters
SI 32768
SF 300.1300044 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

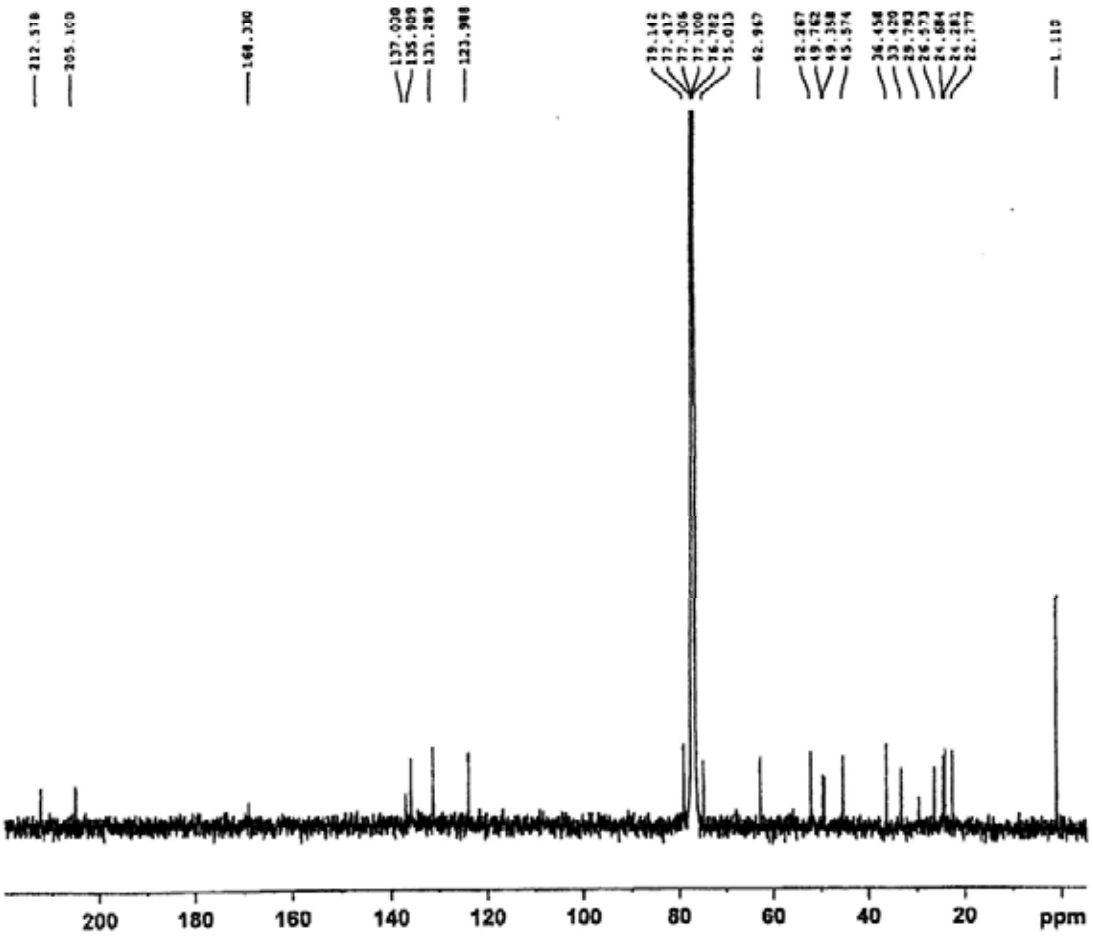
1D NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 10.300 ppm
F1 3091.34 Hz
F2P -0.300 ppm
F2 -90.04 Hz
PPMCM 0.40182 ppm/cm
HZCM 144.80809 Hz/cm

13C



The isomer of Pallavicinolide A





Bruker Advance III 400