DEANTIAROMATIZATION AS A DRIVING FORCE IN AN ELECTROCYCLIZATION OF CYCLOPENTADIENONE AND THE TOTAL SYNTHESIS OF 1-*EPI*- *SECO* - PSEUDOPTEROXAZOLE

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PART 1 DEANTIAROMATIZATION AS A DRIVING FORCE IN AN ELECTROCYCLIZATION OF CYCLOPENTADIENONE AND

PART 2 TOTAL SYNTHESIS OF 1-*EPI*-*SECO*-PSEUOPTEROXAZOLE

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To Rong Xu and Ryan Miancheng Zheng

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PART 1 DEANTIAROMATIZATION AS A DRIVING FORCE IN AN ELECTROCYCLIZATION OF CYCLOPENTADIENONE

PART 2 TOTAL SYNTHESIS OF 1-epi-*seco*-PSEUDOPTEROXAZOLE

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ABSTRACT

Deantiaromatization has been successfully demonstrated as a driving force in an electrocyclization of cyclopentadienones. The reaction was found to be general for a number of substrates and provides a unique way to access tricyclic ring systems with high stereoselectivity. Some evidence was uncovered to show that the process is indeed an 8π conrotatory electrocyclic ring closure.

During the exploration of substituent effects in the electrocyclization, a novel coupling reaction of an organolithium with primary halides was discovered. The experimental data suggested the engagement of the silicon atom and the important role of terminal alkene in the coupling reaction. However, the application of thiw methodology to other silane systems was successful.

The total synthesis of 1-epi-*seco*-pseudopteroxazole was accomplished in 17 steps, featuring the Buchwald-Hartwig coupling, a stereoselective intramolecular Michael reaction, a Heck coupling and asymmetric reduction of trisubstituted alkene.

In the course of reductive cleavage of the C-I bond to access key intermediate **358**, a novel dephenylation of Harmata benzothiazines was discovered to provide chiral cyclic

sulfinamides with complete stereocontrol. Preliminary mechanistic studies were carried out and a plausible mechanism was proposed based on our experimental results.

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Chapter I

Deantiaromatization as a Driving Force in an Electrocyclic Reaction

1 Background on Electrocyclization

Electrocyclic reactions have been long considered as powerful approaches to access different ring systems ranging from 3- to 8-membered rings by the simple rearrangement of a carbon-carbon bond. In general, electrocyclic reactions are stereoselective and the products can be well predicted by Woodward-Hoffmann rules.

No. of electrons	thermal	photochemical
$4n$	conrotatory	disrotatory
$4n+2$	disrotatory	conrotatory

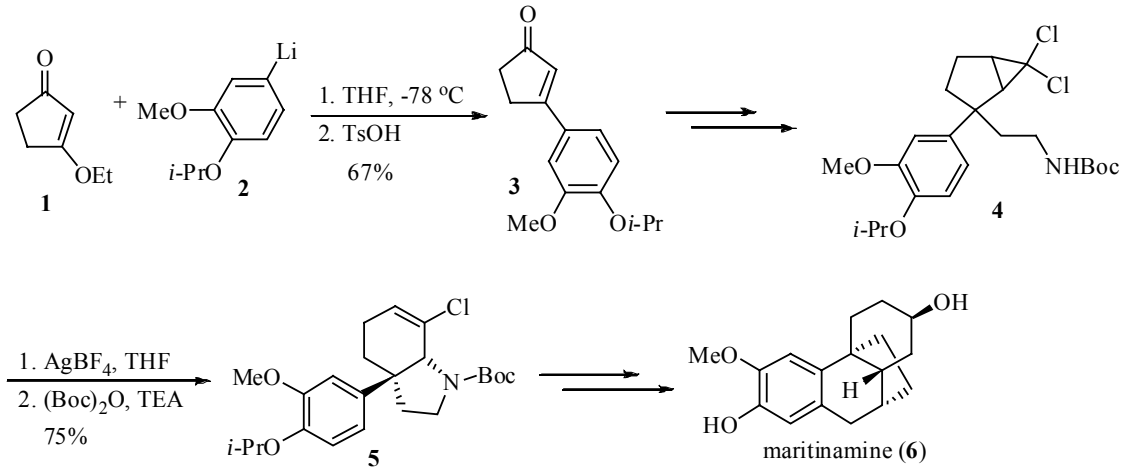
Electrocyclic reactions are usually classified by the number of electrons in the reaction. And they can also be divided into an all-carbon system or a heteroatom system based on the atoms involved in the electrocyclic reaction.[1]

Over 480 papers have been published since 2000 on this topic. Other than the progress in methodological development, electrocyclic reactions have been engaged in a number of biomimetic total synthesis of natural products, which have been well reviewed by Trauner.[1] In order to show the power of electrocyclic reactions in the limited space, we will focus on the application of electrocyclic reactions in the total synthesis of natural products published since 2000.

1.1 All-Carbon Systems

1.1.1 2π Systems

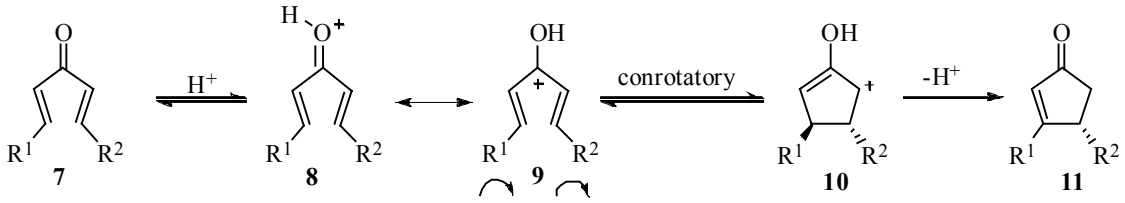
There is only one synthesis involving 2π electrons documented since 2000. Maritinamine **6**, isolated in 1989, showed potential antimalarial and cytotoxic activities.[2] In 2001, Banwell reported the first total synthesis of **6**. Addition of phenyllithium to 3-ethoxycyclopentenone **1** provided **3**. **3** was converted into intermediate **4** in a few steps. Key intermediate **5** was obtained by the silver(I)-catalyzed the electrocyclic ring-opening of cyclopropane ring, followed by intramolecular nucleophilic cyclization (Scheme 1).[3]



Scheme 1 Banwell's Total Synthesis of Maritinamine **6**

1.1.2 4π Systems

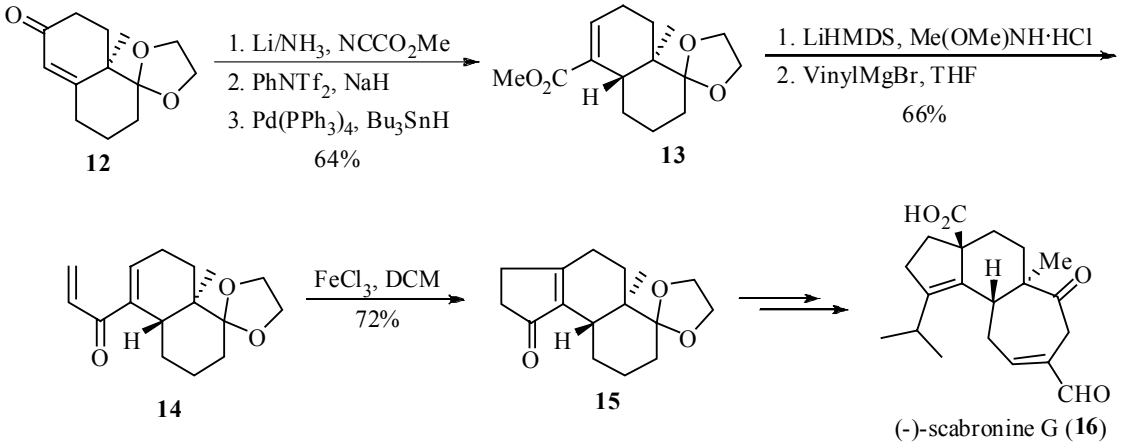
Of the electrocyclic reactions involving 4π-electrons, the Nazarov cyclization is well known. It involves the conversion of divinyl ketones **7** to cyclopentenones **11** by Lewis acid activiation. The process likely involves the complexation with Lewis acid (**8**), conrotatory cyclization to form **10** and subsequent loss of one proton (Scheme 2).



Scheme 2 Nazarov Reaction

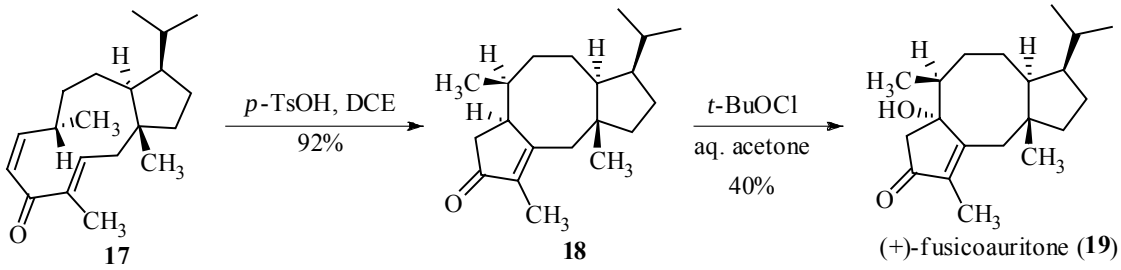
Remarkable progress has been made on the Nazarov cyclization, which has been reviewed by Denmark,[4] Tius,[5] and Frontier.[6] Herein, only applications in the total synthesis will be discussed.

Scabronine G (**16**) was isolated from metabolites from the mushroom *Sarcodon scabrosus* in 1998.[7] It was found to promote the excretion of the nerve growth factor. Encouraged by the potent bioactivity and challenging tricyclic structure, Danishefsky and coworkers[8] reported the first total synthesis of **16**. The synthesis started from (-)-Wieland-Miescher ketone (**12**). Dissolving metal reduction of the α, β-unsaturated ketone and acylation afforded a β-ketoester (not shown), which was converted to unsaturated ester **13** by the sequential triflation and hydride reduction. Vinyl ketone **14** was formed in 66% yield with the addition of Grignard reagent to Weinreb amide. Lewis acid-mediated classic Nazarov cyclization occurred smoothly to provide **15** in 72% yield. The total synthesis of (-)-**16** was accomplished in a few more steps (Scheme 3).



Scheme 3 Danishefsky's Total Synthesis of (-)-scabronine G **16**

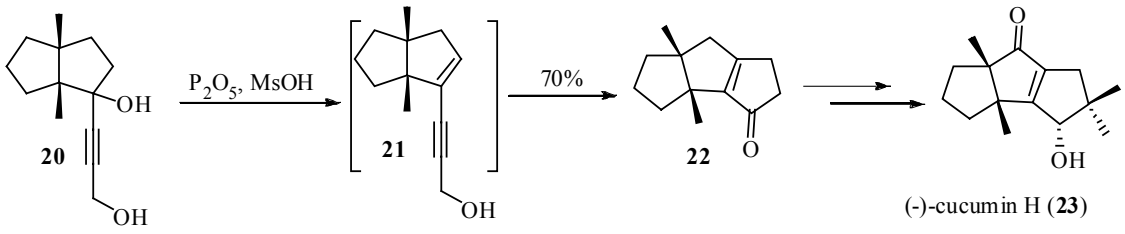
Very recently Willams reported the biomimetic total synthesis of (+)-fusicoauritone **19** featuring the Nazarov reaction of proposed biogenic precursor dolabelladienone **17**. Under acidic conditions, **17** was successfully converted to cyclopentenone **18** in 92% yield with retention of double-bond geometry. Stereoselective allylic oxidation provided **19** in moderate yield (Scheme 14).



Scheme 4 Williams's Total Synthesis of (+)-fusicoauritone **19**

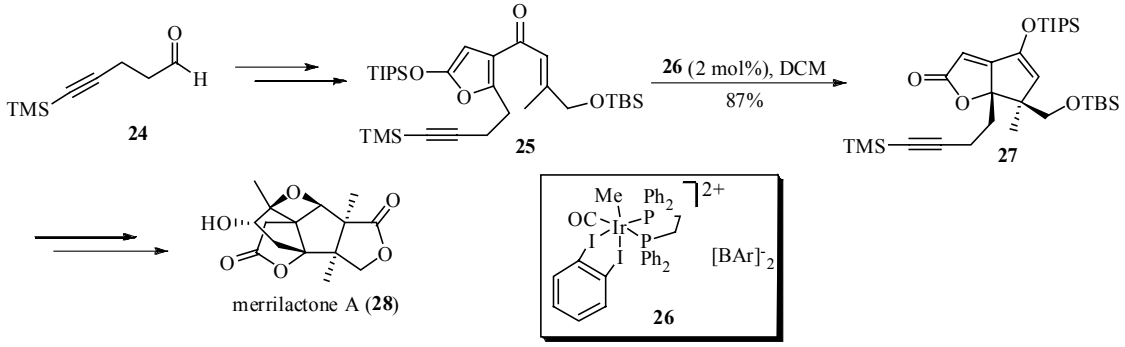
Other than divinylketone, propargyl diol **20** was demonstrated as a valuable precursor in the Nazarov reaction in the total synthesis of (-)-cucumin H **23**.[9] When **20** was exposed to Eaton's reagent (P_2O_5, MsOH), Nazarov cyclization occurred smoothly to

provide tricyclic product **22** in 70% yield, which presumably proceed via enyne **21** intermediate (Scheme 5).



Scheme 5 Srikrishna's Total Synthesis of (-)-cucumin H **23**

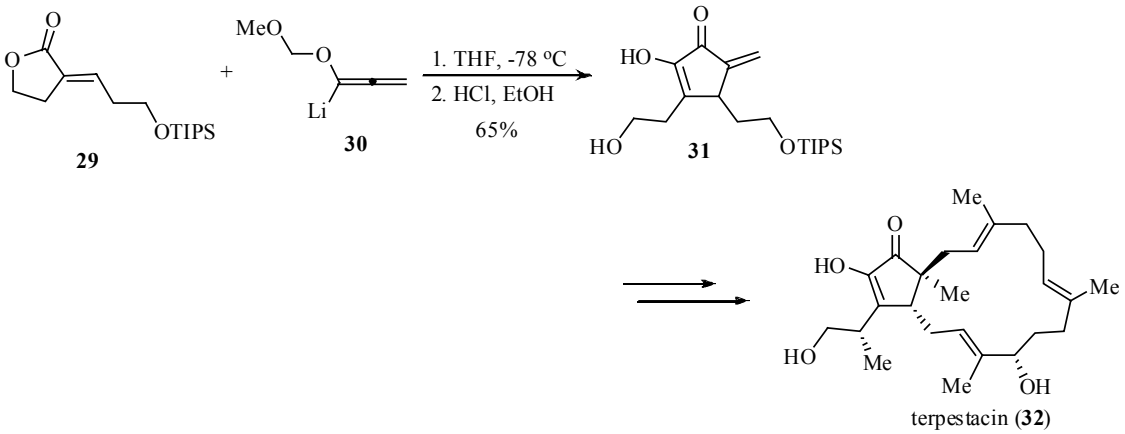
Catalytic Nazarov cyclization utilizing silyloxyfuran **25** was successfully applied to the total synthesis of (±)-merrilactone A in the Frontier group.[10] The requisite silyoxyfuran **25** was prepared from known aldehyde **24** in 5 steps. Catalyzed by the dicationic iridium catalyst **26**, Nazarov cyclization of **25** proceeded successfully to give key intermediate **27** as a single diastereomer. Finally, **27** was converted into merrilactone A **28** after a few manipulations (Scheme 6).



Scheme 6 Frontier's Total Synthesis of (±)-merrilactone **28**

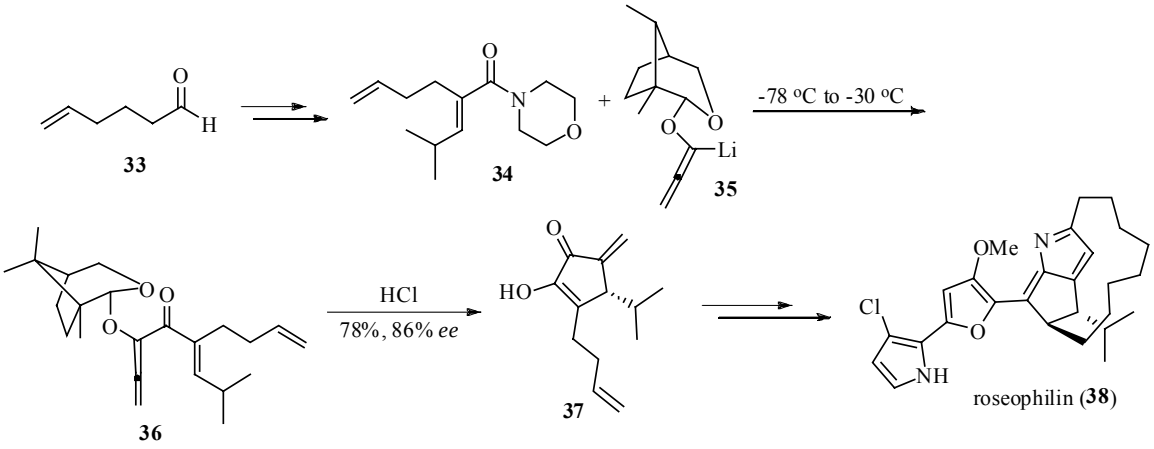
The Nazarov cyclization of allenyl vinyl ketone was another variant of the Nazarov reaction that was developed by Tius.[11] This methodology was employed in the total

synthesis of (±)-terpestacin (**32**).[12] Highly substituted cyclopentenone **31** was prepared by the reaction of γ-lactone **29** with lithioallene **30** in moderate yield. The 15-membered ring was constructed to deliver terpestacin **32** in a few steps (Scheme 7).



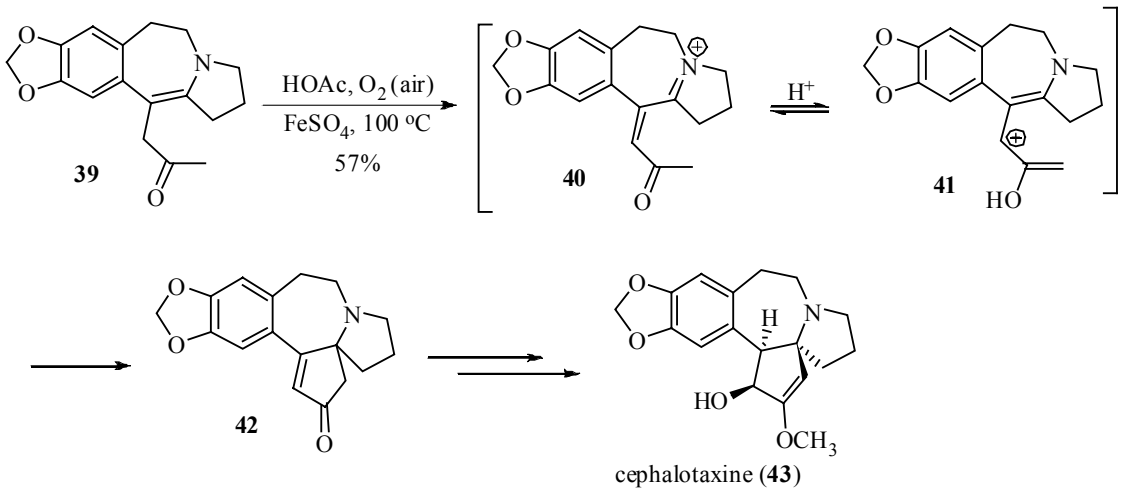
Scheme 7 Tius' Total Synthesis of (±)-terpestacin **32**

Asymmetric Nazarov cyclization of allenyl vinyl ketones was developed by Tius and developed in the total synthesis of roseophilin **38**. The chemistry of **38** has attracted considerable attention since the isolation from *Streptomyces griseoviridis* in 1992 by Seto.[13] The strong *in vitro* activity against several cancer cell lines, together with an unusual 13-membered macrocyclic ring and pyrrolylfuran core structure have made roseophilin one of the most popular target in the past decade.[14] In 2001, Tius[15] reported the enantiospecific total synthesis of **38**. Key intermediate **34** was prepared from commercially available 5-hexenal in 6 steps. Addition of chiral lithioallene **35** to the α, β-unsaturated amide **34** proceeded smoothly to give allenyl ketone **36**. Upon treatment with HCl, **36** spontaneously underwent a Nazarov cyclization to form cyclopentenone **37** in 78% yield with 86% *ee*. The first enantiospecific total synthesis of roseophilin **38** was accomplished by a few transformations (Scheme 8).



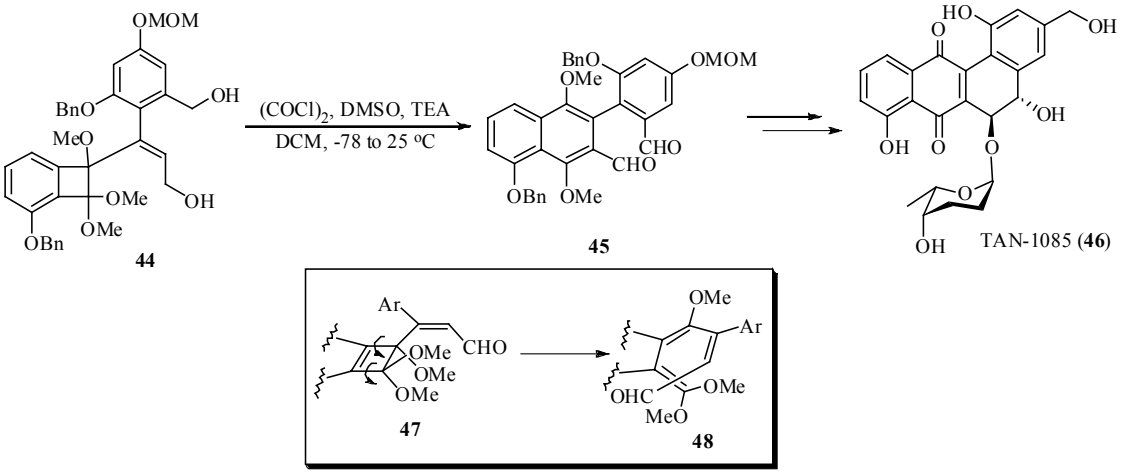
Scheme 8 Tius's Total Synthesis of Enantiomerically Pure Roseophilin **38**

During the total synthesis of cephalotaxine **43**, Li and coworkers[16] found that upon treatment with $FeSO_4$ in hot acetic acid in air, enamine **39** underwent cyclization to produce **42** in 57% yield. They proposed a mechanism involving an azo-Nazarov cyclization. Acid-mediated oxidation of enamine **39** provided iminium salt **40**, which could tautomerize to divinyl cation **41**. Nazazov cyclization of **41** would deliver **42**, which is a key intermediate to cephalotaxine **43** (Scheme 9).



Scheme 9 Li's Total Synthesis of (±)-cephalotaxine **43**

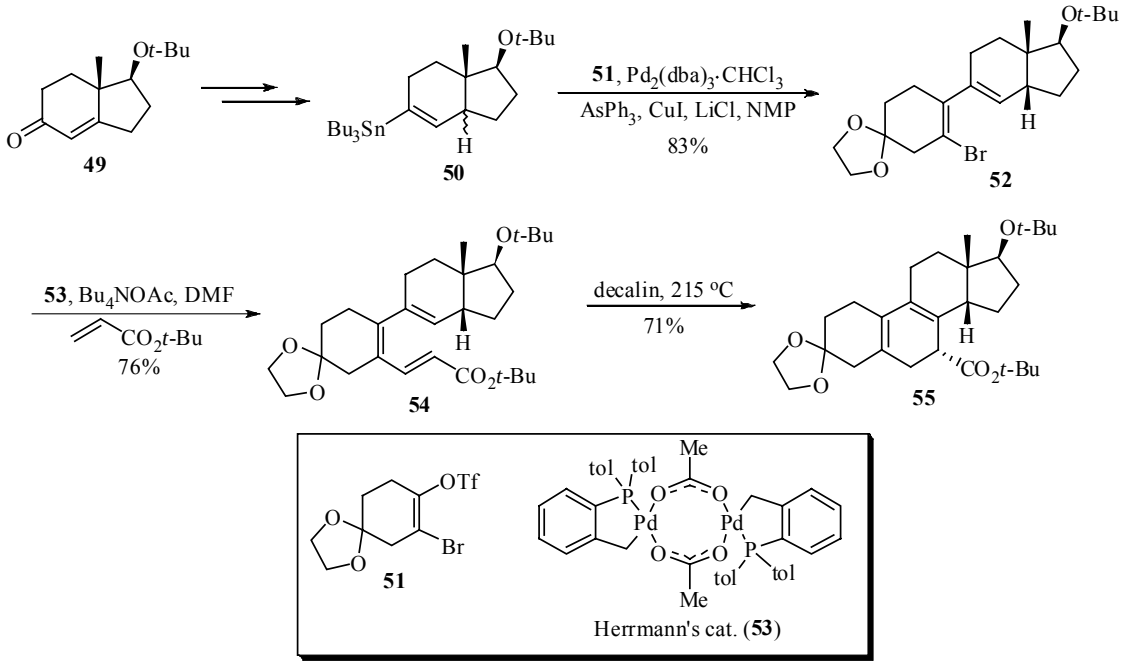
Besides the Nazarov reaction, electrocyclic ring opening reactions involving 4π electrons have been adopted by Suzuki in the total synthesis TAN-1085 (**46**).[17] Swern oxidation of diol **44** was carried out at –78 ^{o}C and the reaction was warmed up to 25 ^{o}C. Key intermediate **45** was formed. The reaction proceeded through the electrocyclic 4π electron ring-opening reaction and subsequent 6π electron cyclization (**47**→ **48**).



Scheme 10 Suzuki's Total Synthesis of TAN-1085 **46**

1.1.3 6π Systems

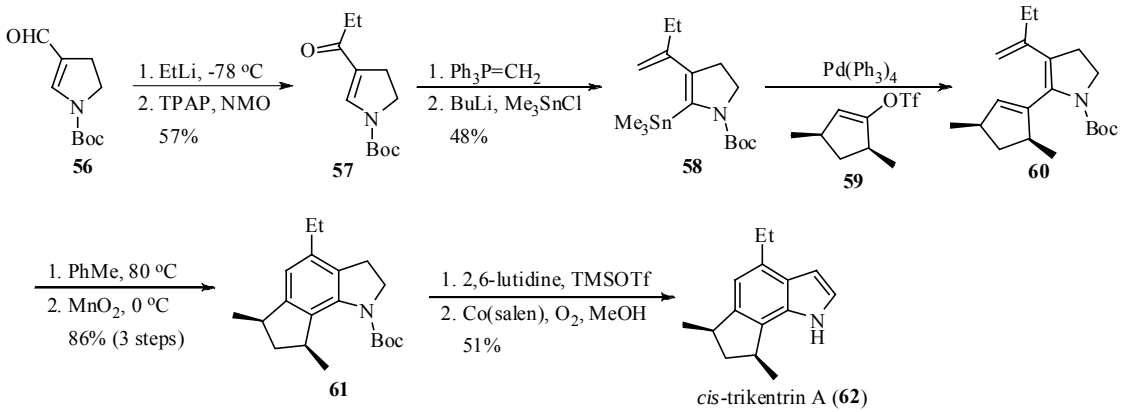
Electrocyclic reaction of hexatriene provides rapid access to 6-membered rings. Recently, Meijere and coworkers[18] demonstrated the total synthesis of steroids and their analogues featuring a 6π electrocyclization. Vinylstannane **50** was prepared from the known bicyclic ketone **49**. Compound **50** was selectively coupled with triflate **51** to form **52**. Subsequent intermolecular Heck coupling with *t*-butyl acrylate was fulfilled to provide **54** in the presence of Herrmann's catalyst. Finally, 6π-electrocyclic ring closure smoothly formed steroid **55** in reasonable yield (Scheme 11).



Scheme 11 Total Synthesis of Steroid **55**

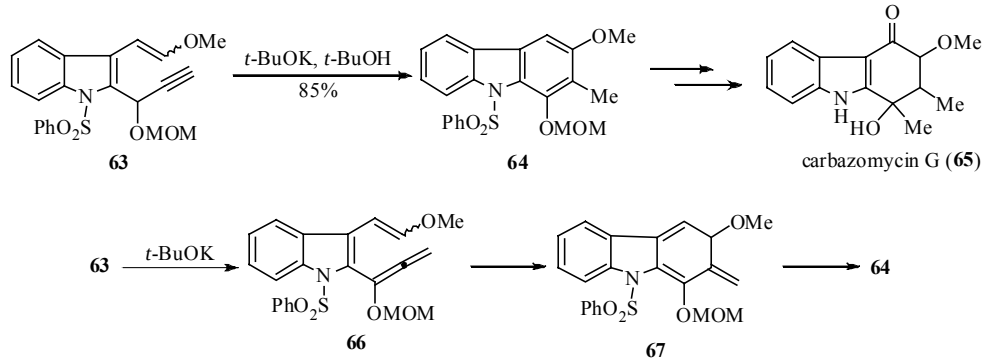
Electrocyclic ring closure of 6π electrons system was also employed to access the polysubstituted phenyl rings. One such example is the concise total synthesis of *cis*-trikentrin A (**62**) from Funk's group in 2006.[19] *cis*-Trikentrin A (**62**) was isolated from a marine sponge in 1986.[20] Due to its interesting tricyclic structure and potent antibacterial activity, **62** has attracted much interest in the organic synthetic community. Funk started from readily avaible pyrroline aldehyde **56**. Compound **56** was converted to vinyl stannane **58** by a routine reaction sequence. Subsequent Pd(0)-catalyzed Stille coupling of **58** with triflate **59** gave rise to the labile triene **60**. The crude **60** was further converted to indoline **61** utilizing facile electrocyclic ring-closure and *in situ* oxidation with MnO_2. The total synthesis of **62** was accomplished by the deprotection of the Boc group and aromatization (Scheme 12). Due to its rapid access to polysubstituted phenyl ring, the

sequence of electrocyclic ring-closure of triene and subsequent aromatization has been widely applied in the total synthesis of natural products.[21-25]



Scheme 12 Funk's Total Synthesis of *cis*-Trikentrin A **62**

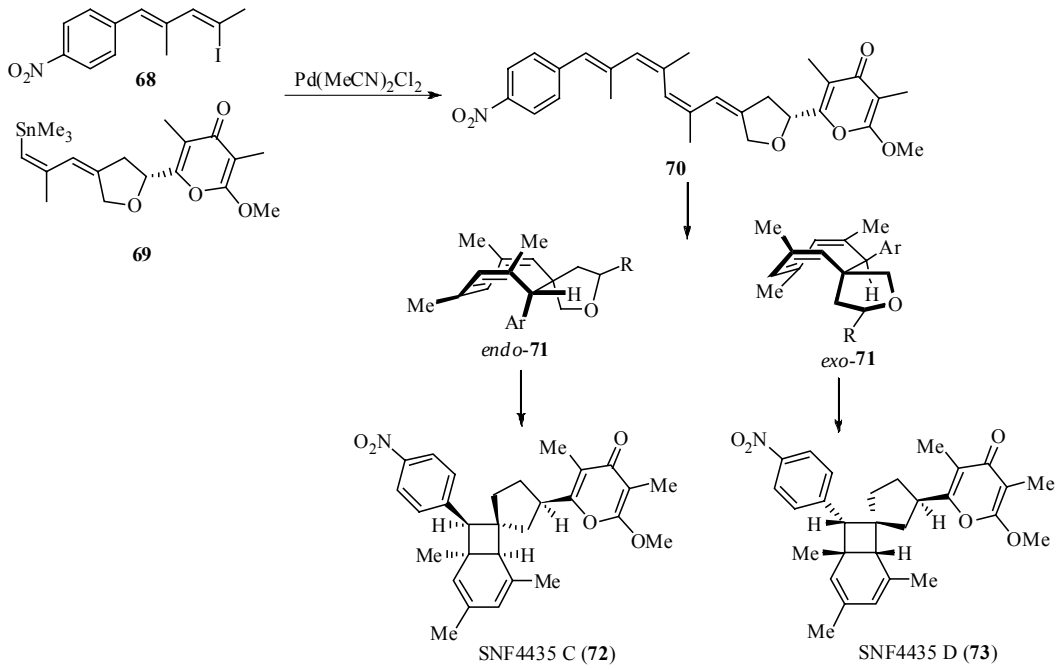
Other than the triene as the precursor of electrocyclization, dienyl propargyl alcohol was also used as starting material. In Hibino's total synthesis of carbazomycin G, propargyl alcohol **64** was converted to **64** in good yield. When **63** was subjected to *t*-BuOK, the propragyl moiety would rearrange to allene intermediate **66**, which could undergo rapid electrocyclization to afford intermediate **67**. **64** could be generated by the aromatization of **67** (Scheme 13). Application of this methodology was made in the total synthesis of murrayaquinone A[26] and calothrixin B.[27]



Scheme 13 Total Synthesis of Carbazomycin G **65**

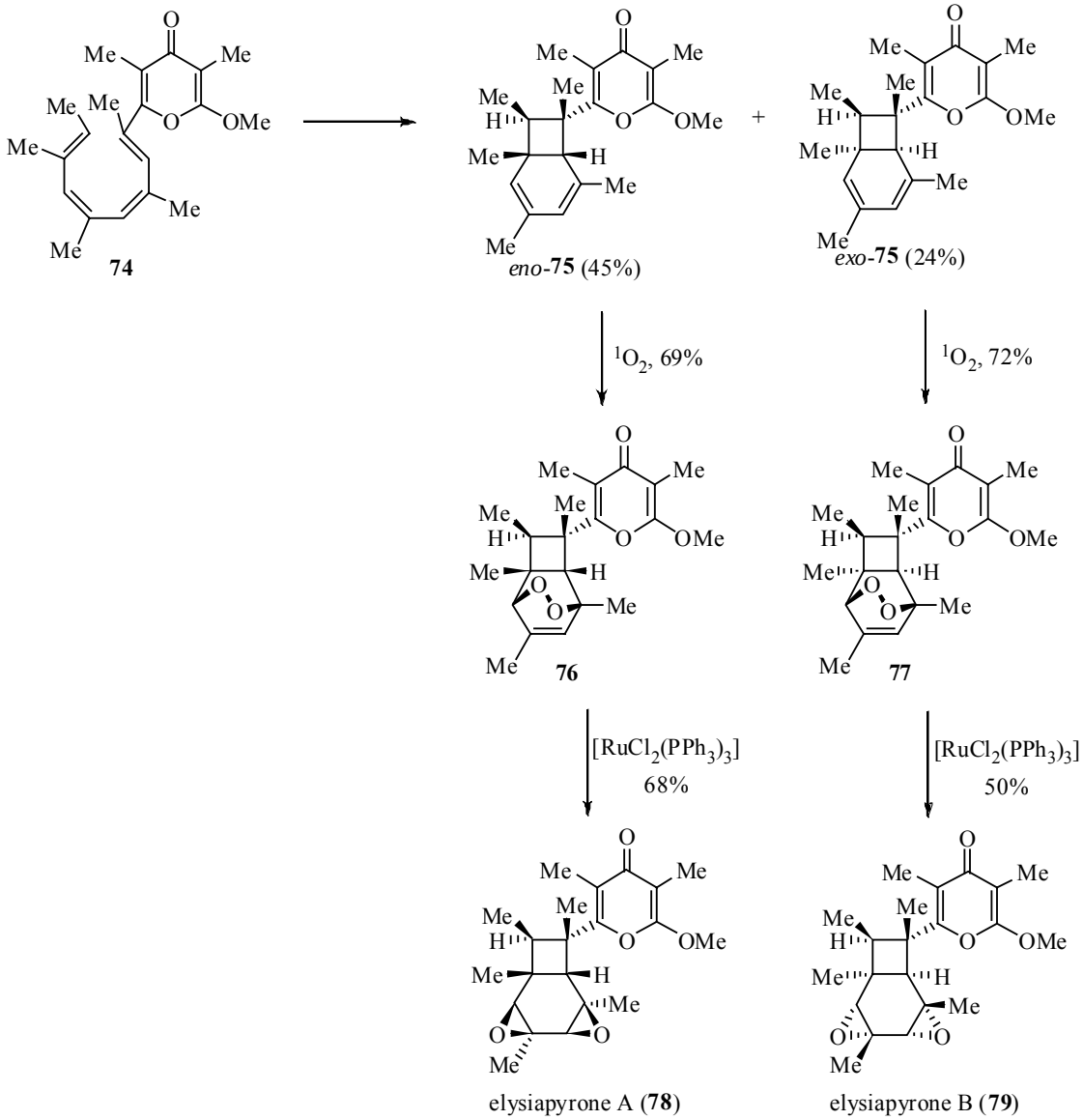
1.1.4 8π Systems

Due to the low activation barrier, the octatetraene system tends to undergo facile conrotatory ring-closure electrocyclization to provide cyclooctatriene, which can further undergo 6π electron ring-closing to afford a bicyclo[4.2.0]-octadiene system. Such a biomimetic process involving an 8π-6π cascade electrocylization was first developed by Nicolaou,[28] which offered an intriguing and rapid approach to access a number of complex natural products. Recent application of this process was made in the total synthesis of SNF4435 by Parker. In Parker's synthesis,[29] Stille coupling of iodide **68** and stannane **69** delivered octatetraene **70**. Tandem electrocyclization took place spontaneously to afford a mixture of *endo* and *exo* isomers of **71**. Subsequent disrotatory cyclization of **71** provided a 4: 1 mixture of two isomers of SNF4435 C (**72**) and SNF4435 D (**73**) in 53% yield (Scheme 14). Similar strategies were applied to the total synthesis of SNF4435[30,31] and ocellapyrone A.[32]



Scheme 14 Parker's Total Synthesis of SNF4435 C and D

In the elegant total synthesis of elysiapyrone A and B, Trauner also employed the 8π-6π cascade electrocylization to convert an octatetraene to bicyclic products **75** with a 2:1 ratio of *endo* and *exo*. Cycloaddition of singlet oxygen, followed by isomerization of peroxides into epoxides furnished the total synthesis of **78** and **79** (Scheme 15).[33]



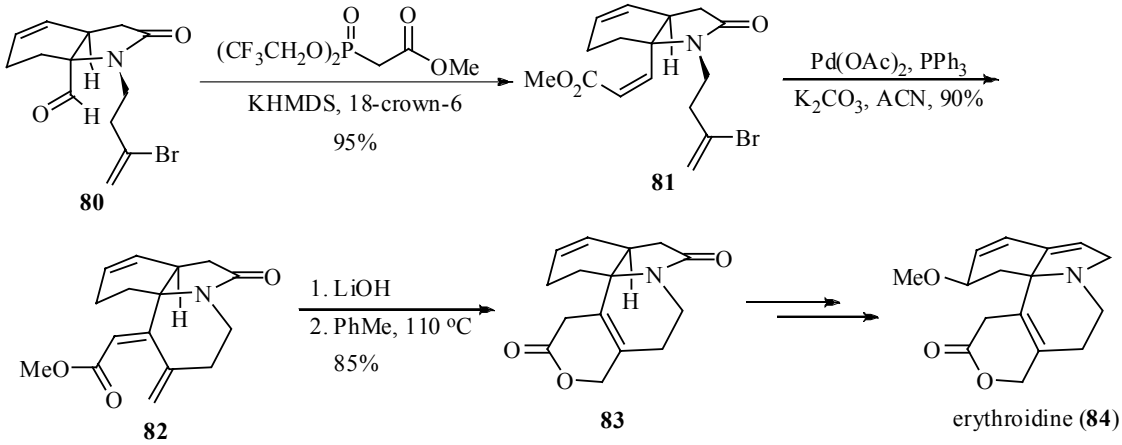
Scheme 15 Trauner's Total Synthesis of Elysiapyrone A and B

1.2 Heteroatom-containing Systems

1.2.1 Oxa-6π Systems

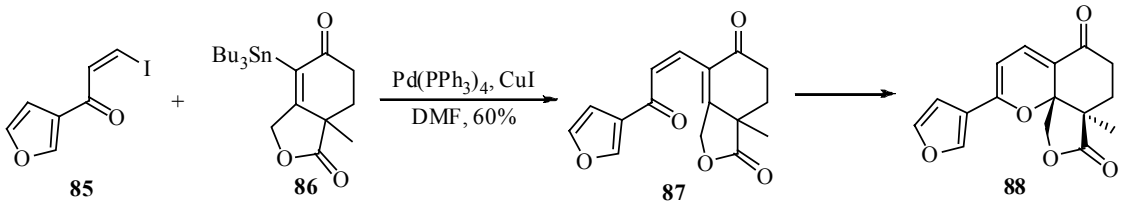
1.2.1.1 Access 2*H*-pyran Ring System

Funk[34] elegantly set up two rings of erythroidine **84** by a sequential intramolecular Heck coupling and electrocyclic ring-closure of dienyl ester. Aldehyde was reacted with Still-Gennari reagent to give the single *Z*-unsaturated ester **81** in excellent yield. Intramolecular Heck coupling smoothly furnished dienyl ester **82** in 90% yield. Hydrolysis of methyl ester and heating the resulting carboxylic acid in refluxing toluene promoted a clean 6π-electrocyclic ring-closure to furnish lactone **83** (Scheme 16).



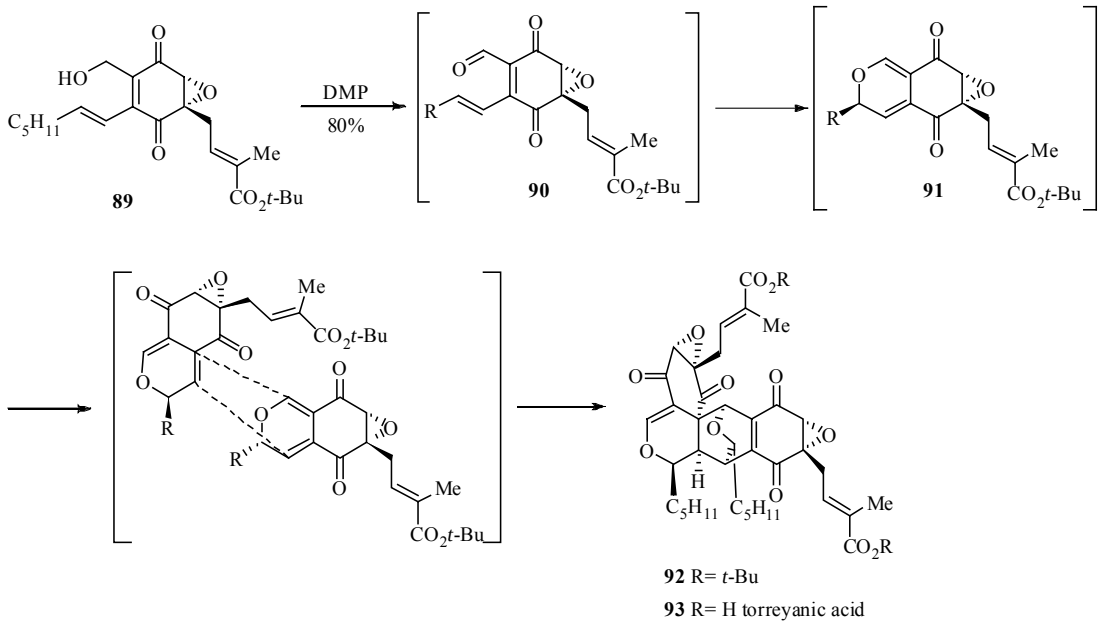
Scheme 16 Funk's Total Synthesis of (±)-β-erythroidine **84**

In the model studies toward the total synthesis of saudin, Stoltz[35] employed the oxa-6π electrocyclic reaction to establish the quaternary carbon. Stille coupling of **85** with **86** gave dienyl ketone **87**. Tandem oxa-electrocyclization of **87** provided the core of the saudin (Scheme 17).



Scheme 17 Stoltz's Synthesis of the Core of Saudin

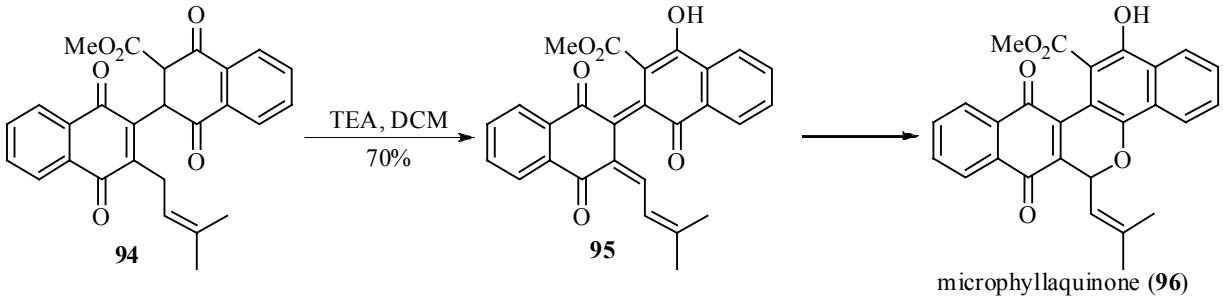
One should note that *2H*-pyran intermediate from oxa-electrocyclization can also act as either a diene or a dienophile in the Diels-Alder reaction, which was well demonstrated by Porco[36] in the biomimetic total synthesis of (+)-torreyanic acid. Alcohol **89** was converted to dienyl aldehyde **90** by treatment of Dess-Martin periodinane. Electrocyclization proceeded smoothly to form *2H*-pyran intermediate **91**, which is ready for the intermolecular Diels-Alder dimerization to provide **92**. Acidic hydrolysis of **92** furnished the total synthesis of (+)-**93** (Scheme 18). Similar strategies were also shown in the total synthesis of expoxyquinol A[37-40] and naphthoquinones[41].



Scheme 18 Porco's Total Synthesis of (+)-torreyanic acid **93**

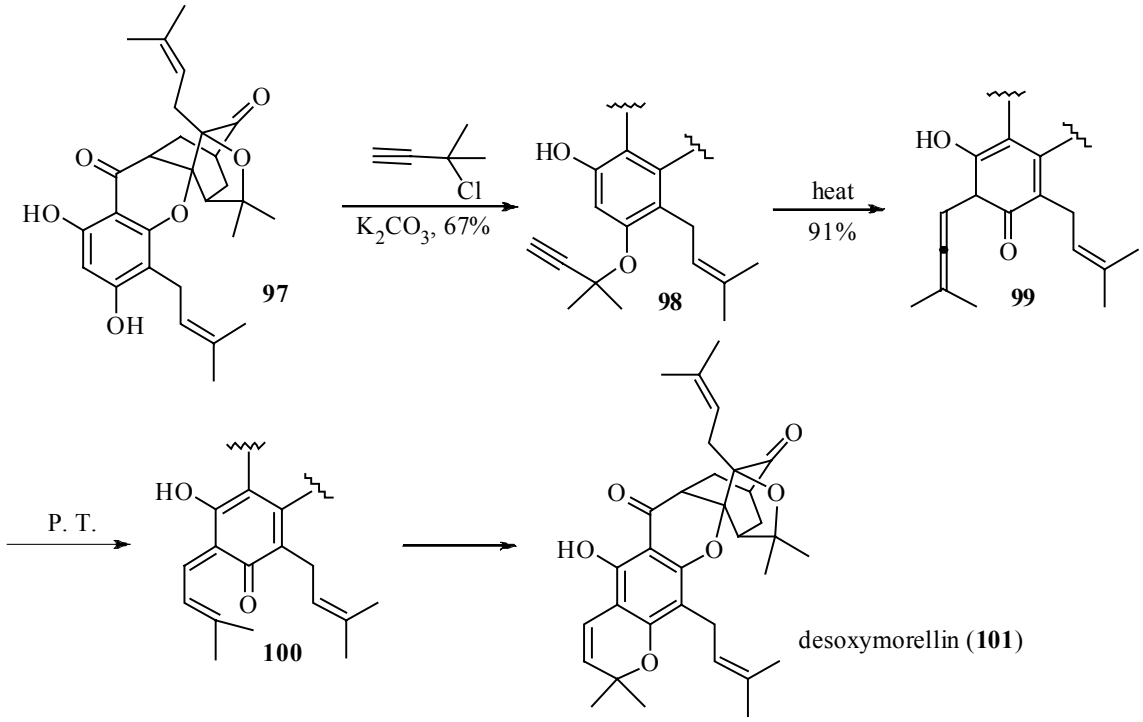
1.2.1.2 Access 2*H*-chromene Ring System

Electrocyclization of an oxa-triene also provided an excellent approach to access a polysubstituted *2H*-chromene ring system. In the biomimetic synthesis microphyllaquinone **96**,[42] base-induced tautomerization of **94** delivered **95**, which underwent an oxa-electrocyclization to form **96** (Scheme 19).



Scheme 19 Trauner's Total Synthesis of Microphyllaquinone **96**

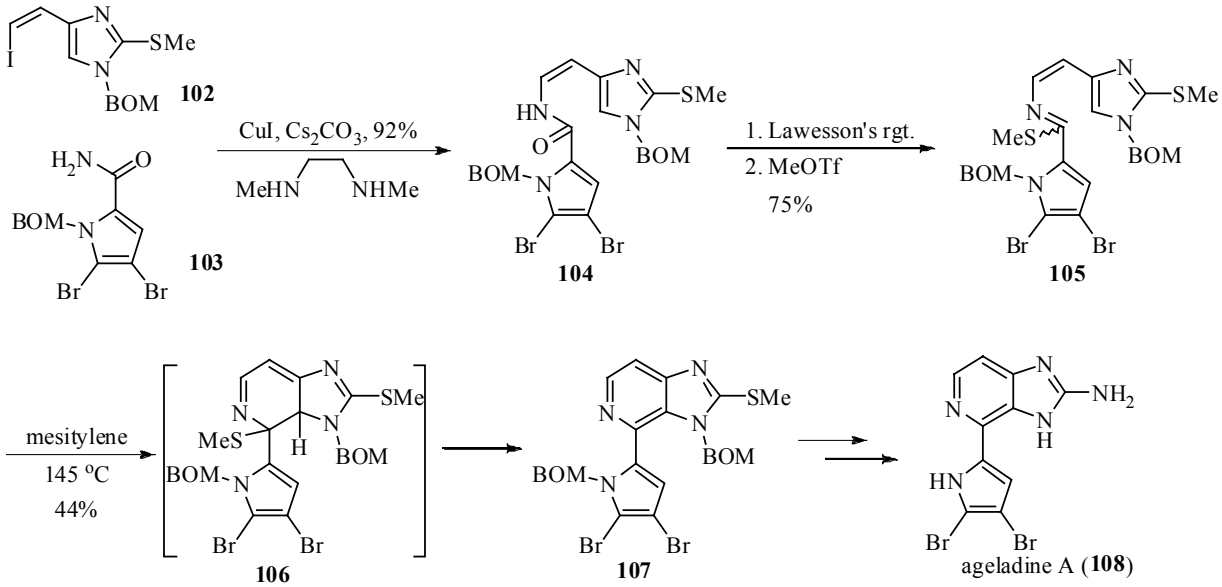
In the total synthesis of desoxymorellin **101**, Theodorakis[43] developed a tandem Claisen/electrocyclization reaction to establish the chromene ring system at a late stage of the process. Selective alkylation gave **98** in 67% yield. Claisen rearrangement of the resulting propargyl ether **98** delivered **99**, which could be further converted to **100**. Oxa-6π electrocyclization occurred smoothly to provide the target product **101** in 91% yield (Scheme 20).



Scheme 20 Theodorakis's Total Synthesis of Desoxymorellin **101**

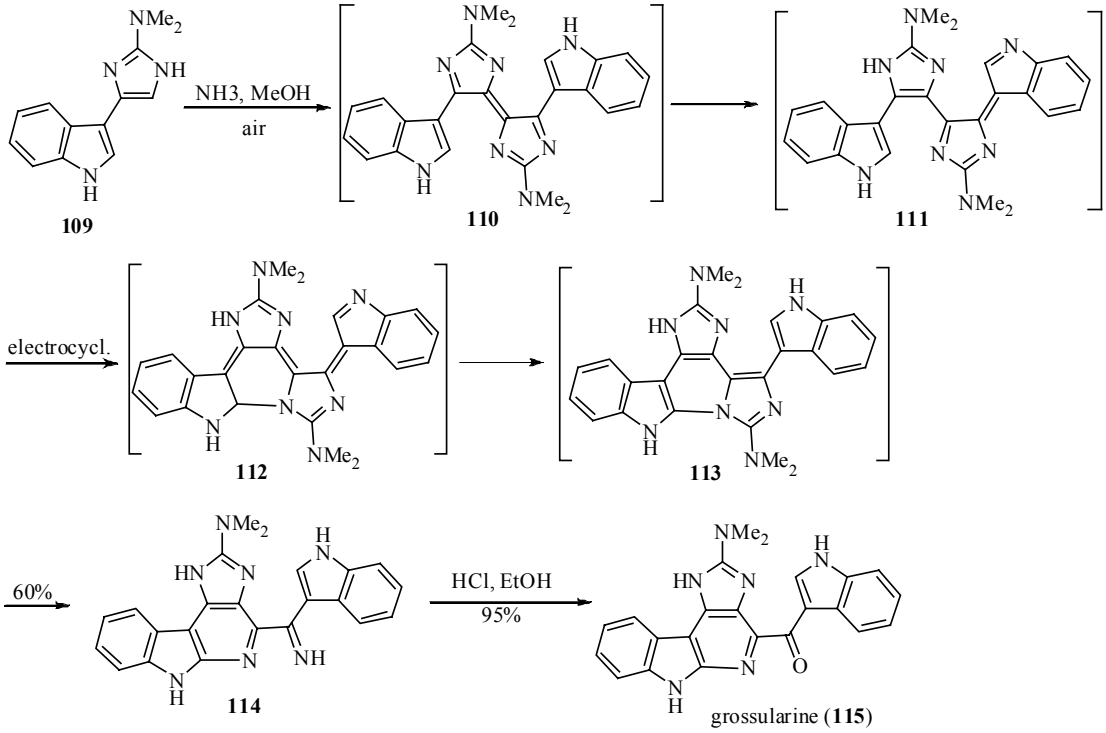
1.2.2 Aza-6π Systems

Electrocyclization of azatrienes can form dihydropyridines, which can be easily oxidized to pyridines. The overall process is particularly useful in the synthesis of pyridine-containing natural products. Recently, Weinreb[44] applied aza-6π electrocyclization into the total synthesis of ageladine A, which showed high inhibitory activity against zinc matrixmetalloproteinase (MMPs). Iodide **102** was coupled with amide in the presence of CuI to form **104** in excellent yield, which was then converted to key intermediate **105** in two steps. Thermal electrocyclization of azatriene provided **107** in moderate yield, which was a key intermediate in the total synthesis of ageladine A (Scheme 21).



Scheme 21 Weinreb's Total Synthesis of Ageladine A **108**

In an elegant biomimetic synthesis of grossularine **115**,[45] imine **114** was produced in 60% yield when **109** was exposed with the ammonia in methanol solution in the air. The mechanism was proposed as follows. Oxidative coupling of **109** could form dimer **110**, which could further tautomerize into the azatriene system **111**. Aza-6π electrocyclization took place to offer **112**, which could be converted into imine **114** by tautomerization and cleavage with ammonia. Finally, grossularine **115** was achieved by the alcoholysis of imine (Scheme 22).



Scheme 22 Horne's Biomimetic Total Synthesis of Grossularine **115**

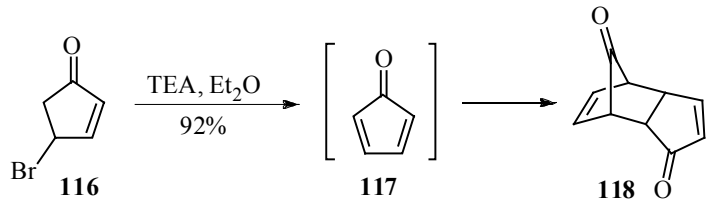
2 Background on the Cyclopentadienones Chemistry

Since the pioneering work from Depuy[46,47] and Hafner[48] in the early 1960s, the chemistry of cyclopentadienones has been of great interest in the organic chemistry community.[49] Due to the labile property of cyclopentadienones, monomeric cyclopentadienone dimerizes rapidly. The existence of cyclopentadienone intermediacy was elucidated by "three-phase" experiments.[50,51] Monomeric cyclopentadienone was finally characterized by IR spectroscopy in matrix studies.[52]

Theoretical chemist Caramella[53] proposed a bispericyclic transition structure model to explain the high reactivity and endo selectivity in the dimerization. Secondary orbital interactions accounted for the endo selectivity and deantiaromatization was believed to the driving force for the dimerization.

2.1 Preparation

Depuy[46] reported the generation of cyclopentadienones from 4-bromo-cyclopentenone **116**. When **116** was treated with triethylamine in the ether solution, cyclopentadienone **117** was formed and underwent rapid dimerzation to provide cyclopentadienone dimer **118** in 92% yield (Scheme 23). Attempts at characterization of **117** utilizing UV spectroscopy turned out to be fruitless.

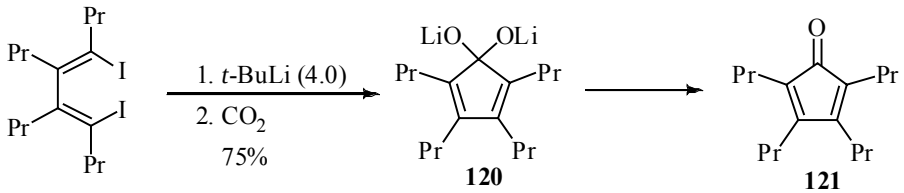


116 **117** **118**

Scheme 23 Generation of **118** from 4-bromocyclopentenone

Other than the bromo precursors, 4-acetoxycyclopentenone,[46] 4-hydroxy-cyclopentenone,[54] and 4-(phenylsulfonyl)-cyclopentenone[55] can also serve as precursors to **117**.

Synthesis of cyclopentadienone by the condensation of dithio species **120** with CO_2 was developed by Xi in 2000.[56] Cyclopentadienone **121** was synthesized in 75% yield by the lithium-halide exchange, followed by double addition to carbon dioxide (Scheme 24).



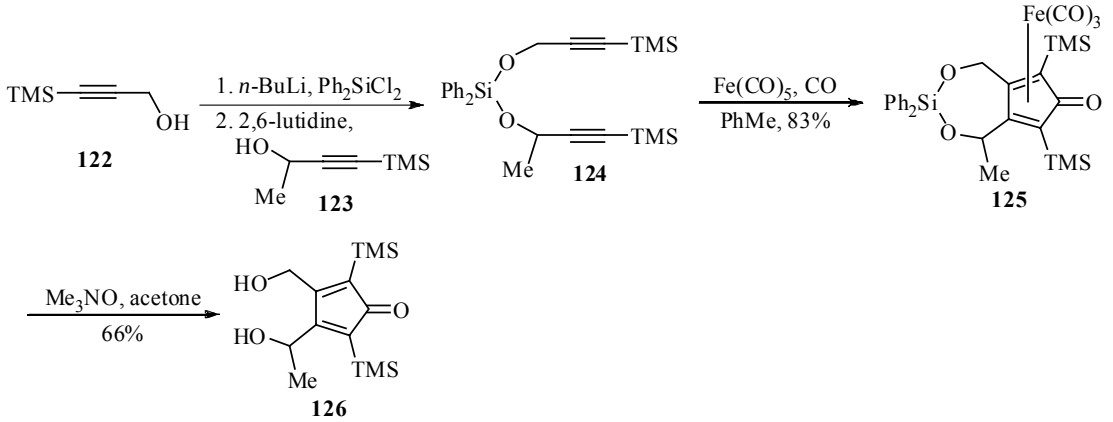
119 **120** **121**

Scheme 24 Synthesis of **121** from 1,4-diiodo-1,3-diene

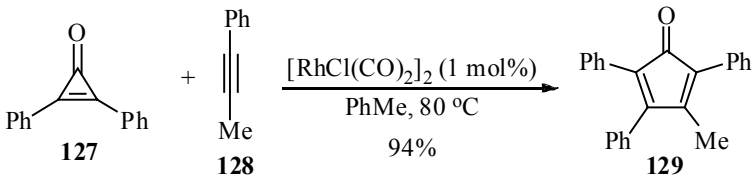
Metal-catalyzed cycloaddition reactions of alkynes provide another powerful approach to access cyclopentadienones. Pearson and coworkers[57] demonstrated the synthesis of unsymmetrically substituted cyclopentadienones. Two different propargyl alcohols were reacted with dichlorosilane respectively to form **124**. $Fe(CO)_5$ –mediated [2+2+1] cyclocarbonylation reaction to provide iron complex **125** in 83% yield. Oxidative decomplexation produced **126** in reasonable yield (Scheme 25).

Recently, Wender[58] employed a [3+2] cycloaddition approach to access cyclopentadienones. When cyclopropenone **127** reacted with alkyne **128** in the presence of 1 mol% $[RhCl(CO)_2]_2$, only one regioisomer **129** was isolated in 94% yield (Scheme 26).

Besides $Fe(CO)_5$ and $[RhCl(CO)_2]_2$, other metal complexes, such as $CpCo(CO)_2$,[59] $[Ir(COD)Cl]_2$[60] and a chromium-carbene complex,[61] also participate in cycloaddition reactions to afford cyclopentadienones.



Scheme 25 [2+2+1] Cycloaddition Approach to **126**

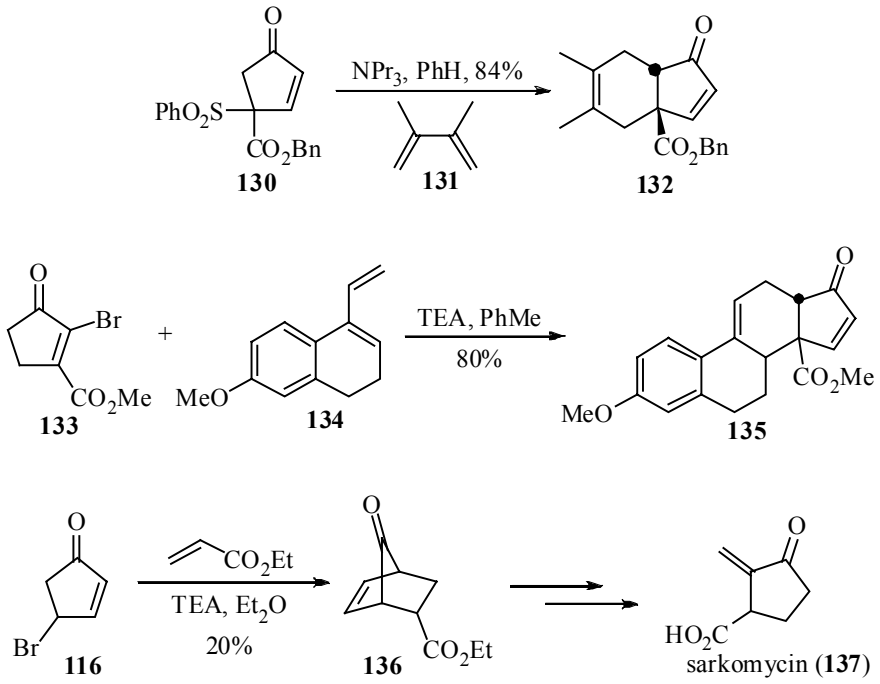


Scheme 26 [3+2] Cycloaddition Approach to **129**

2.2 Reactions of Cyclopentadienones

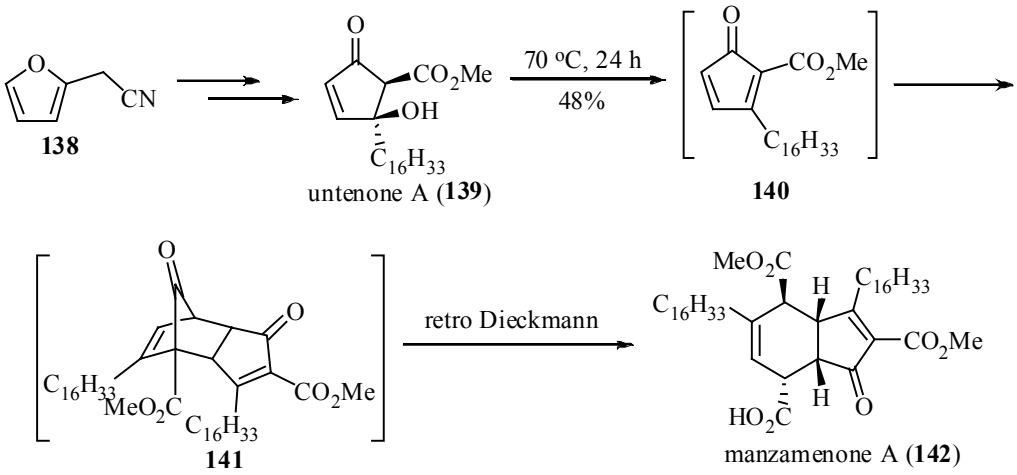
Diels-Alder reactions are best known in the cyclopentadienone chemistry. Cyclopentadienones can act as dienophiles in the Diels-Alder reaction. Fuchs demonstrated that cyclcopentadienone intermediate, which was generated *in situ* by the treatment of **130** with base, reacted with different dienes to afford Diels-Alder adducts in good yield.[55] Very recently, Harmata and coworkers[62] systematically investigated the Diels-Alder reaction of methyl 3-oxo-cyclopenta-1,4-dienecarboxylate with a wide range of dienes. The Diels-Alder adducts were formed in good to excellent yield with excellent diastereoselectivity.

Cyclopentadienones can also participate in the Diels-Alder reaction as a diene. One such example is the synthesis of (±)-sarkomycin **137**. Cycloadduct **136** was obtained in moderate yield when bromocyclopentenone **116** was treated with ethyl acrylate in the presence of base. Compound **136** was further converted to **137** in a few steps (Scheme 27).



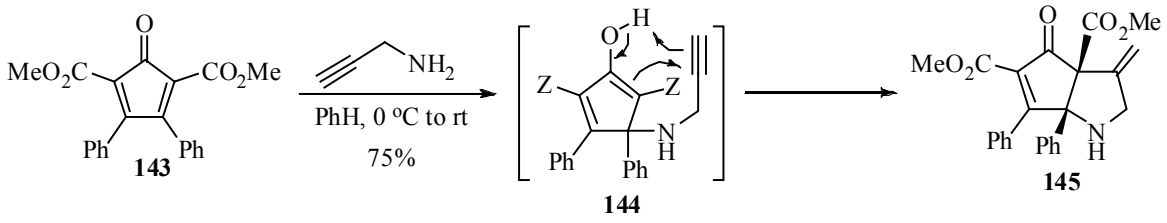
Scheme 27 Cyclopentadienone in the Diels-Alder Reaction

As mentioned before, cyclopentadienone tends to react with itself to generate dimer in the absence of dienes or dienophiles. One such example was demonstrated by Whitehead in the biomimetic total synthesis of manzamenone A **142**.[63] Compound **142** was isolated from Okinawan marine sponge *Plakortis*, together with its biogenetic precursor untenone A **139**.[64] Compound **139** was synthesized from readily available 2-furanacetonitrile **138** in a few steps. When a neat sample of **139** was heated at 70 ^{o}C for 24 hours, **142** was obtained in very respectable yield. Dehydration of **139** could provide cyclopentadienone **140**, which would readily dimerize to afford **141**. Natural product **142** could be generated by retro Dieckmann ring-opening reaction (Scheme 28).



Scheme 28 Whitehead's Biomimetic Total Synthesis of Manzamenone A

Interestingly, when stabilized cyclopentadienone **143** was treated with propargyl amine at 0 °C to room temperature, bicyclic product **145** was isolated in 75% yield. No Diels-Alder adduct was observed. A proposed mechanism is as follows. 1,4-conjugate addition of amine could deliver intermediate **144**, which would set up for ene rearrangement to afford compound **145**[65,66] (Scheme 29).

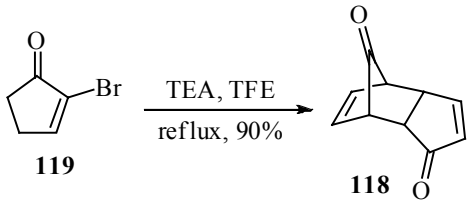


Scheme 29 Unusual Reaction of Cyclopentadienone

3 Results and Discussion[67,68]

3.1 Discovery of Electrocyclization Reaction

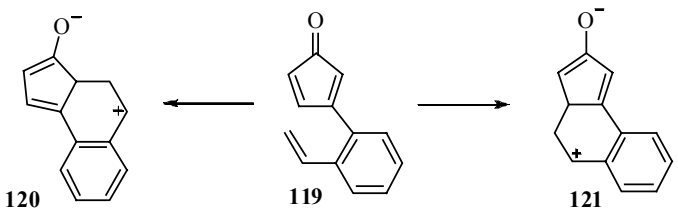
During the exploration of 2-bromocyclopentenone as a possible oxyvinyl cation in the [4+3] cycloaddition reaction, Harmata and coworkers[69] discovered a mild procedure for the formation of cyclopentadienone. When 2-bromocyclopentenone **119** was refluxed in the presence of triethylamine, **118** was isolated in 90% yield. It was believed that intermediate cyclopentadienone **117** was slowly generated from bromocyclopentenone **119** via a 2,5-elimination of HBr (Scheme 30).



119 **118**

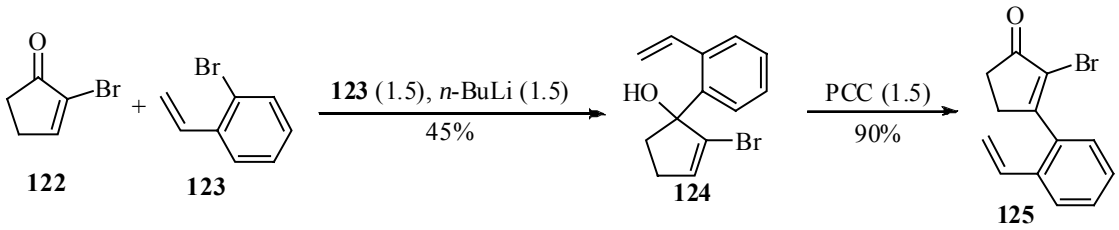
Scheme 30 Generation of **118** from 2-bromocyclopentenone

As a part of continuing interest in this reaction, we wondered whether the transient cyclopentadienone could be intercepted rather than dimerize. We chose to examine the electrocyclic ring closing reaction of cyclopentadienones represented by **119**. Even though research showed that the electrocyclization via 8π conrotatory pathway (**121**) usually prevails over 6π disrotatory (**120**),[1] we were still interested in whether this would be the case and wished to establish the role of deantiaromatization as a driving force in organic chemistry.



Scheme 31 Possible Electrocyclizations of Cyclopentadienone **119**

The synthesis of **125** was quite straightforward. Addition of 2-lithiostyrene to 2-bromocyclopentenone **122** afforded **124** in 45% yield, which was further converted to **125** in 90% yield with PCC oxidation (Scheme 32).

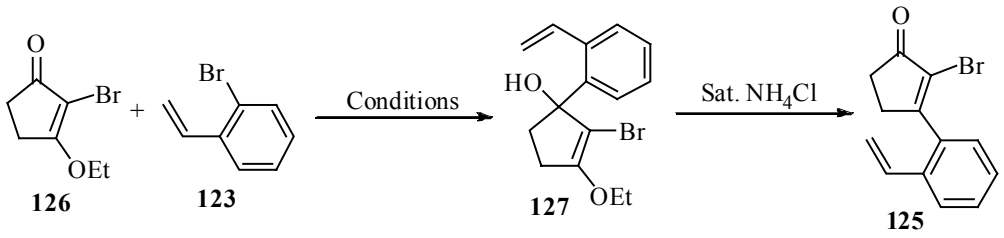


Scheme 32 Preparation of **125** from 2-bromocyclopentenone **122**

Alternatively, we also explored a one-pot process to access **125** from 2-bromo-3-ethoxycyclopentenone. The results were summarized in Table 1. Addition of organolithium to **126** provided desired product in only 21% yield, together with some complicated mixture (entry 1, 2). Switching to a non-cordination solvent toluene significantly suppressed the deprotonation (entry 3). Not surprisingly, a complicated mixture was obtained with the addition of HMPA, which decreases the aggregation state of organolithium and enhances the reactivity of organolithium reagent. (entry 4). We turned to an organocerate, which possessed enhanced oxophilicity and reduced basicity.

61% and 71% yields of **125** were obtained respectively when different methods[70,71] were used to dry $CeCl_3$ (entry 5, 6).

Table 1 Synthesis of **125** from **126**

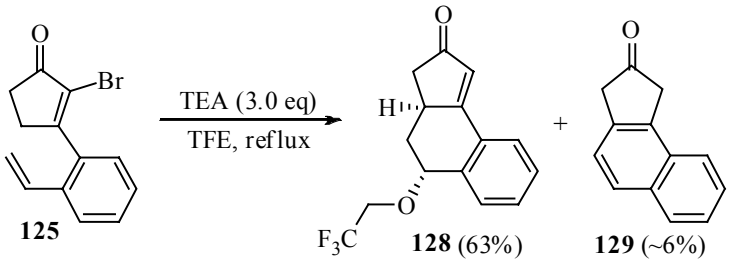


entry	Reagent (eq), solvent	T (^oC), t (h or m)	**125** (%)
1	*n*-BuLi (1.5), THF	-78 ^oC, 30 m; -10 ^oC, 50 m	21[a]
2	*n*-BuLi (1.1), THF	-78 ^oC, 1 h; rt, 1 h	20[b]
3	*n*-BuLi (1.5), PhMe	-78 ^oC, 5 h; -10 ^oC, 30 m	38[b]
4	*n*-BuLi (1.5), HMPA (20%), THF	-78 ^oC, 5 h; -10 ^oC, 30 m	0[a]
5	*n*-BuLi (2.0), $CeCl_3$ (2.5)[c], THF	-78 ^oC, 2 h	38 (61)
6	*n*-BuLi (1.5), $CeCl_3$ (1.5)[d], THF	-78 ^oC, 24 h	61 (77)

[a] A complicated mixture was obtained. [b] Significant amount of starting material was recovered. [c] $CeCl_3$ was dried using Paquette's procedure[70]. [d] $CeCl_3$ was dried using Bunnelle's procedure[71].

When **125** was subjected to 3.0 equiv. of TEA in refluxing TFE solution, **128** was formed in 63% yield, along with the elimination product **129** (ca. 6%)[72] and recovered starting material (16%). The fact that TFE was incorporated into **128** was clearly evident in both the ^{13}C and ^1H-NMR spectra of the product. For example, a quartet appeared at δ = 66.1 ppm (J = 34.1 Hz) in the ^{13}C-NMR spectrum, which is indicative of the trifluoro

methyl group (Scheme 33). The structural assignment based on this and other NMR data was later confirmed by X-ray analysis (Figure 1).



Scheme 33 Electrocyclization of **125** via a Cyclopentadienone Intermediate

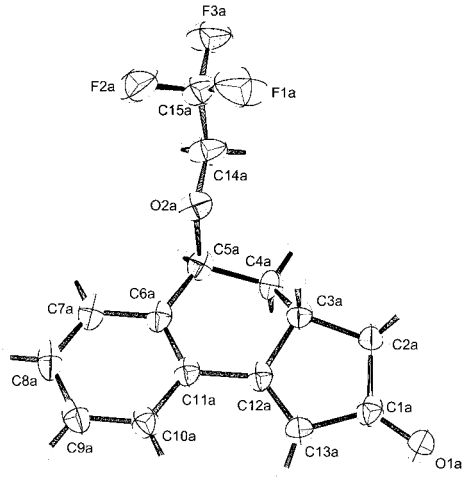
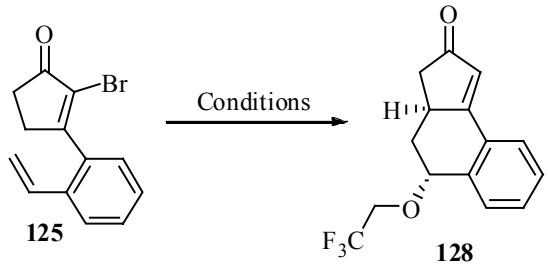


Figure 1 X-ray Structure of **128**

Excited by this result, we carried out optimization of reaction conditions that might minimize the formation of **129**, while promoting complete conversion of starting material. The results are shown in Table 2.

Table 2 Optimization of the Electrocyclization Reaction of **125**



Entry	Base (equiv)	Solvent	T °C, t	Yield %
1	TEA (3)	TFE	reflux, 2 d	63
2	TEA (3)	TFE	50, 50 h	56
3	TEA (3)	TFE	50, 7 d	66
4	TEA (3)	TFE	60, 3 d	66
5	TEA (3)	TFE	70, 2 d	69
6	TEA (3)	TFE	90-5, 2 d	60[a]
7	TEA (3)	ACN	reflux, 12 h	[b]
8	TEA (3)	THF	reflux, 12 h	[b]
9	TEA (3)	EtOH	50, 2 d	[b]
10	TEA (3)	HFIP	50, 2 d	[b]
11	TEA (3)	HFIP	50, 2 d	[b]
12	TEEDA (1.2)	TFE	50, 2 d	39
13	TEEDA (1.2)	ACN	reflux, 2 d	[b]
14	DIPEA (1.2)	TFE	50, 2 d	43
15	DIPEA (1.2)	ACN	reflux, 2 d	[b]
16	DBU (1.2)	TFE	50, 2 d	63
17	DBU (1.2)	ACN	50, 2 d	[c]
18	DBU (1.2)	THF	50, 2 d	[c]
19	HMPP (1.5)	TFE	70, 2 d	54

[a] A 29% yield of **129** was also isolated. [b] Only starting material was recovered during the reaction. [c] Only cyclopentadienone dimers were isolated in ~30% yield.

When the reaction was carried out at 50 ^{o}C for 50 hours, **128** was isolated in 56% yield with no evidence for the formation of **129** (entry 2). NMR analysis of crude reaction mixture showed a 71: 29 ratio of **128** to **125**. The ratio grew to 88:12 with the prolonged reaction time (7 days). In the hope that small rises in temperature would increase the rate of the reaction without lowering the yield of **128**, a series of experiments running at 60, 70 and 90 ^{o}C were carried out and found that the reaction at 70 ^{o}C for 2 days proceeded to give product in good yield (69%) with minimal formation of **129**, though some starting material still remained (entry 5). The reaction at 60 ^{o}C worked reasonably well (entry 4), but that at 90 ^{o}C provided significant amounts of **129** (entry 6). Interestingly, when **128** was refluxed in TFE in the presence of TEA for 2 days the formation of **129** was not observed, indicating that **128** might not be an intermediate in the formation of **129**.

We also investigated other solvents in the electrocyclization reaction (entries 7-11). TFE was the only solvent that worked in the reaction. It was both surprising and interesting to find that no reaction took place in hexafluoroisopropanol. The exact reasons for this are unclear at this time.

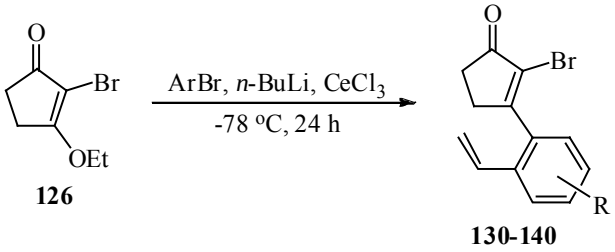
Other bases were also examined in the reaction, but none were superior to TEA (Table 1, entries 12-19). Interestingly, DBU promoted the dimerization in ACN and THF solution (entry 17, 18). Even though DBU also worked effectively, TEA was used for further exploration when considering cost analysis.

3.2 Exploration of Electrocyclization of a Number of Substrates

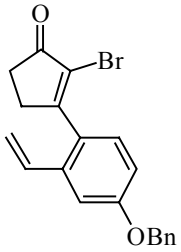
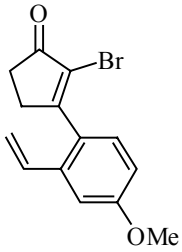
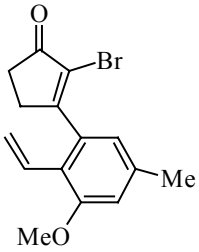
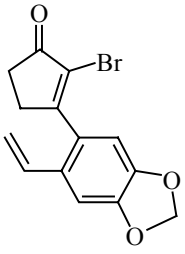
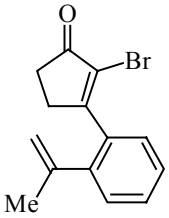
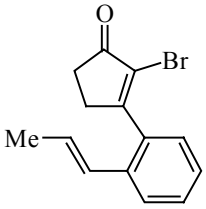
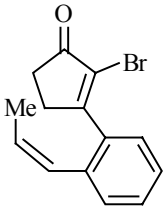
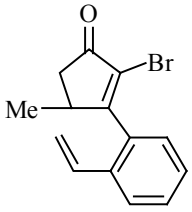
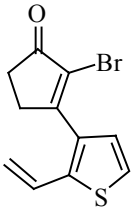
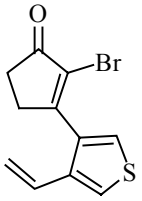
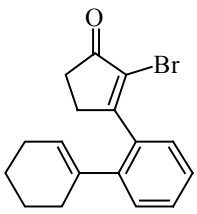
A series of bromides were converted to organocerates via a sequence of lithium-halide exchange and transmetallation with $CeCl_3$. Subsequent treatment of cerate with

cyclopentenone **126** provided cyclopentenones **132-140**. The reaction worked reasonably well (Table 3). Low (unoptimized) yields of **134** and **136** might be ascribed to steric effects, but may also be due to the quality (e.g., dryness) of the $CeCl_3$.[73,74] In our hands, drying protocols for this salt do not always produce consistent results.[70,75]

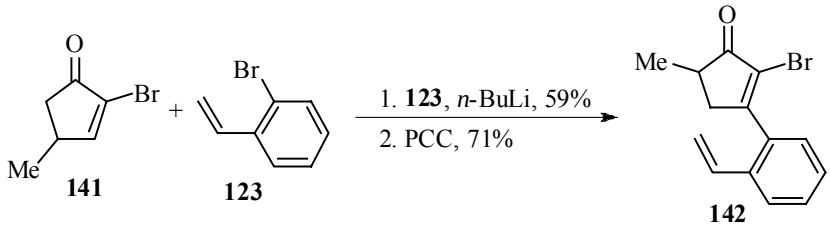
Table 3 Preparation of 2-bromocyclopentenones



126 **130-140**

 **130** (51%)	 **131** (46%)	 **132** (71%)	 **133** (56%)
 **134** (32%)	 **135** (85%)	 **136** (78%)	 **137** (33%)
 **138** (57%)	 **139** (34%)	 **140** (48%)	

Compound **142** was prepared by a two-step sequence of addition and oxidation from 4-methyl-2-bromocyclopentenone **141** (Scheme 34).



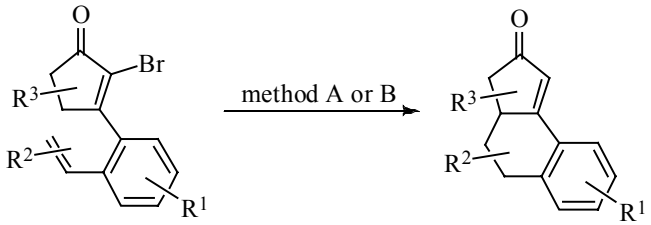
Scheme 34 Synthesis of **142**

With a series of bromocyclopentenone derivatives in hand, we carried out the electrocyclization reaction on a number of substrates using the conditions of TEA, TFE, 50 ^{o}C, 7 days. The results are shown in Table 4 together with those that were run at higher temperature (70 ^{o}C) for a shorter time (2 days).

The reaction showed reasonable generality. Electron rich aromatic systems worked better compared with less substituted aromatic rings. Compounds **146** and **148** were formed in high yields (entry 5, 7). Diastereoselectivity decreased when the reaction was carried out at higher temperature (method B). For example, the diastereomeric ratio of **148** was high at 50 ^{o}C (10:1) but deteriorated to 5.4: 1 at 70 ^{o}C (entry 7). We attributed this to a slower trapping of the intermediate cation by solvent, which perhaps allowed certain conformational changes to take place, resulting in some loss in facial selectivity.

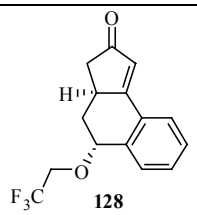
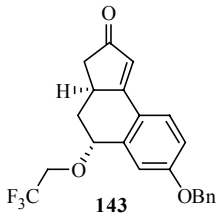
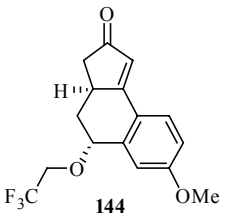
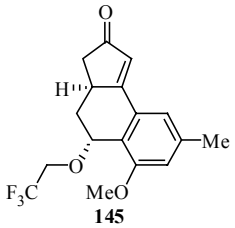
Interestingly, **149** was obtained in 24% and 33% yield. It might be suggested that an electron-donating group on the cyclopentadienone does not prevent the cyclization reaction from occurring. The structure of **149** was established securely by X-ray analysis (entry 8).

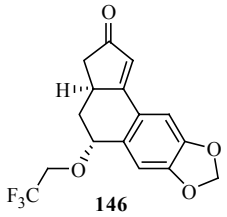
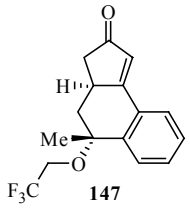
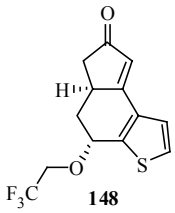
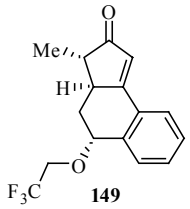
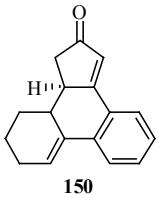
Table 4 Electrocyclization of a series of Bromocyclopentenones



method A: TEA, TFE, 50 °C, 7 d

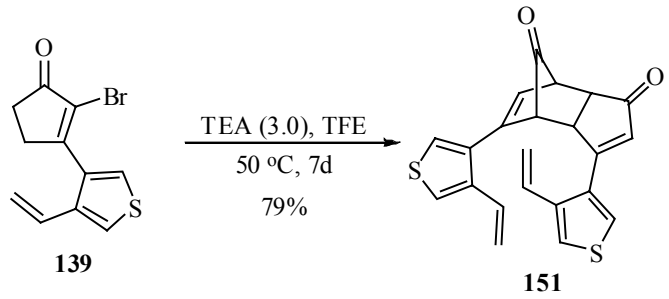
method B: TEA, TFE, 70 °C, 2 d

Entry	Product	Yield (%), 50 °C [a]	Yield (%), 70 °C [a]
1	 **128**	56	69
2	 **143**	64	61
3	 **144**	54(72)	64
4	 **145**	39(58)	61(72)

5	 **146**	71	78
6	 **147**	27(48)	50(71)
7	 **148**	84[b]	86[c]
8	 **149**	24(44)[d]	33(67)[e]
9	 **150**	23	---

[a] Yield in parentheses based on recovered starting material. [b] Diastereomeric ratio = 10:1. [c] Diastereomeric ratio = 5.4:1. [d] Diastereomeric ratio: 5.5:1. [e] Diastereomeric ratio: 4.5:1.

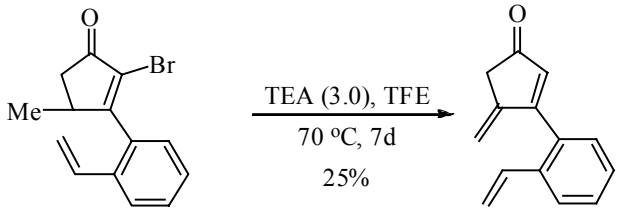
Surprisingly, when **139** was subjected under the standard condition, no electro-cyclization product was observed. Dimer **151** was generated in 79% yield with a single diastereomer (Scheme 35).



139 **151**

Scheme 35 Dimerization of **139**

When 4-methyl-2-bromocyclopentenone **137** was treated under the optimized condition, elimination product **152** was isolated in ca. 25% yield. The fact that no cyclization product was observed indicated that the steric hindrance at C-4 position might slow down the ring-closure reaction and elimination could prevail in the reaction.

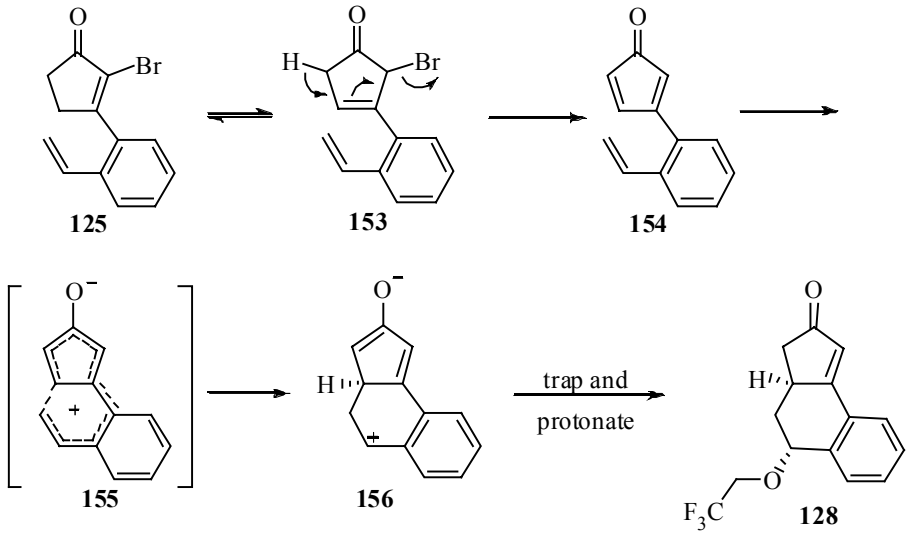


137 **152**

Scheme 36 Reaction with 4-methyl-2-bromocyclopentenone

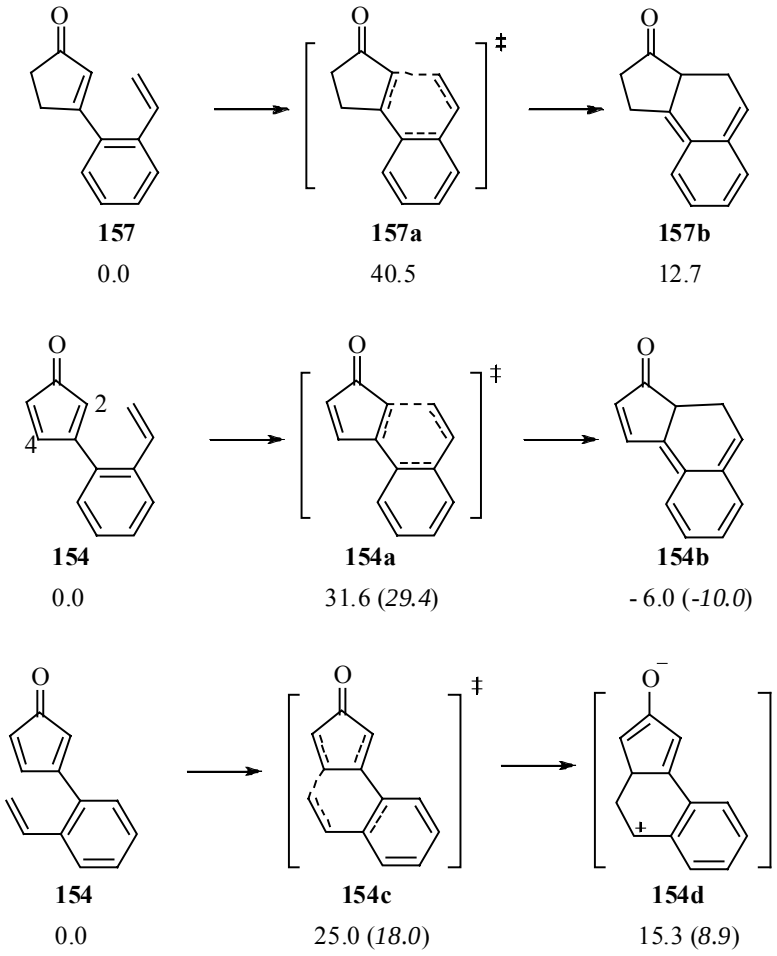
A plausible mechanism involving electrocyclization was proposed. Tautomerization of **125** might give **153**. Subsequent 1,4-debromination provides the cyclopentadienone intermediate **154**. 8π-Electrocyclization would occur driven by deantiaromatization to afford zwitterionic intermediate **156**. Product **128** would be

formed by the axial attack of TFE (Scheme 37).



Scheme 37 Proposed Mechanism for the Conversion of **128**

Schreiner and Navarro-Vázquez[67] carried out B3LYP/6-31G* calculations to examine our proposed mechanism. The results showed that the disrotatory cyclization of antiaromatic system **154** is both thermodynamically and kinetically preferred as compared with system **157**. Furthermore, cyclization of **154** at C-4 position (**154c**) has a kinetic preference, ($\Delta\Delta G_{298.15\ K}$ = -6.6 Kcal/mol). This preference increased to $\Delta\Delta G_{298.15\ K}$ = -11.4 Kcal/mol with the incorporation of solvent effects The computational results strongly supported the proposed mechanism, that is, an 8π conrotatory electrocyclization driven by the antiaromatization. (Scheme 38).

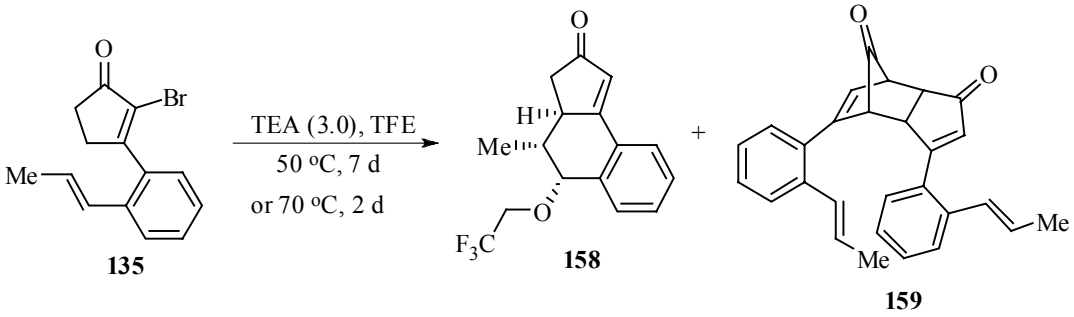


Scheme 38 Computed relative free energies $\Delta G_{298.15\,K}$.
Regular font: gas phase values; italics: PCM (TFE) data

Besides the theoretical computation, some new experimental evidence was also uncovered to support the 8π-electron conrotatory mechanism. Two isomeric compounds (**135** (*E*) and **136** (*Z*)) were prepared for this purpose. When *E* isomer **135** (*E*: *Z*, 24:1) was subjected to our standard conditions (50 ^{o}C, 7 days), the desired product **158** was obtained in 43% yield with nearly complete diastereoselectivity (10:1), together with 33% recovered starting material and some dimer **159**. The amount of dimer increased significantly at higher temperature (70 ^{o}C). The ratio of **135**, **158** and **159** in the crude reaction mixture changed from 0.39: 0.51: 0.10 (50 ^{o}C) to 0.33: 0.48: 0.19 (70 ^{o}C)

(Scheme 39). A NOESY spectrum showed a correlation of H_2 with methyl group and H_3 with H_4. It suggested that the methyl group is *cis* to H_2 and the OTFE group (Figure 2 and 3). Ultimately, the stereochemistry of **158** was firmly established by X-ray crystallography (Figure 4).

In contrast to **135**, the reaction of *Z* isomer **136** turned out to be very clean. Desired product **160** was obtained in 56% yield as a single diastereomer, accompanied by 27% recovered starting material. The stereochemistry of **160** was established by a NOESY experiment. A $^3J_{H3\text{-}H4}$ equatorial-equatorial coupling constant of 2.2 Hz agreed well with the calculated value (2.0 Hz) by Schreiner and Navarro-Vázquez[68] employing the Hassnoot-Altona empirical equation.[76] Also, no NOE was observed for H_2 and methyl group (Figure2 and 5).



Scheme 39 Electrocyclization of **135**

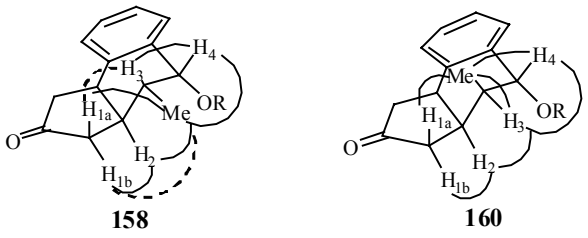


Figure 2 NOE Correlations for **158** and **160**. Dashed lines indicated the weak NOEs

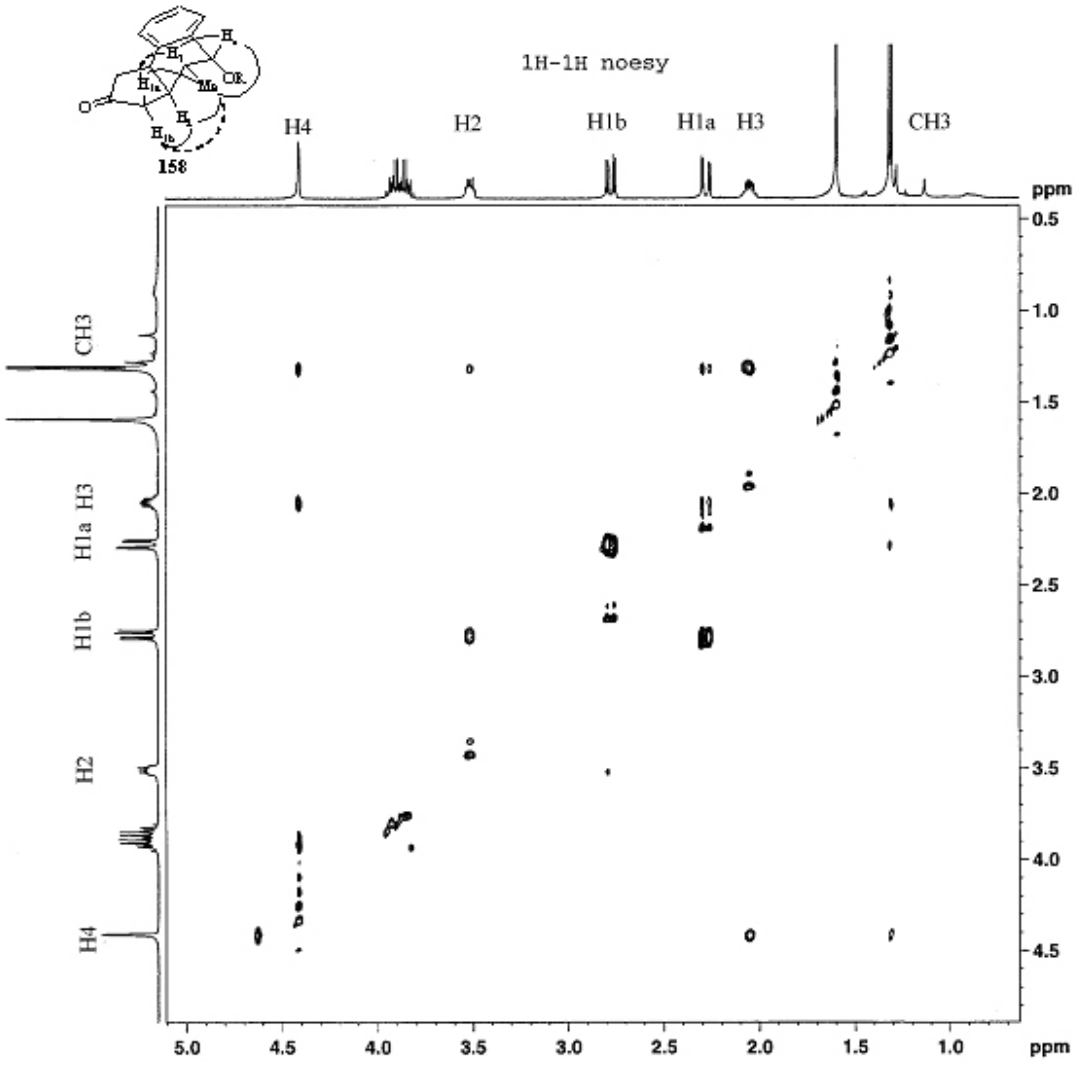


Figure 3 NOESY Spectrum of **158**

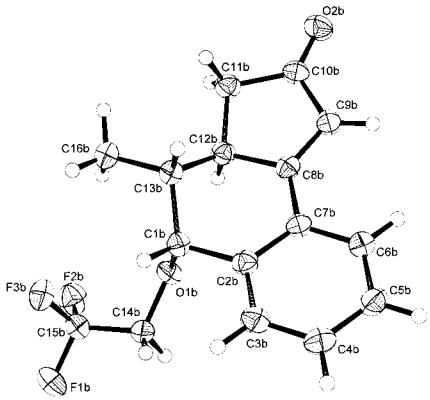


Figure 4 X-ray structure of **158**

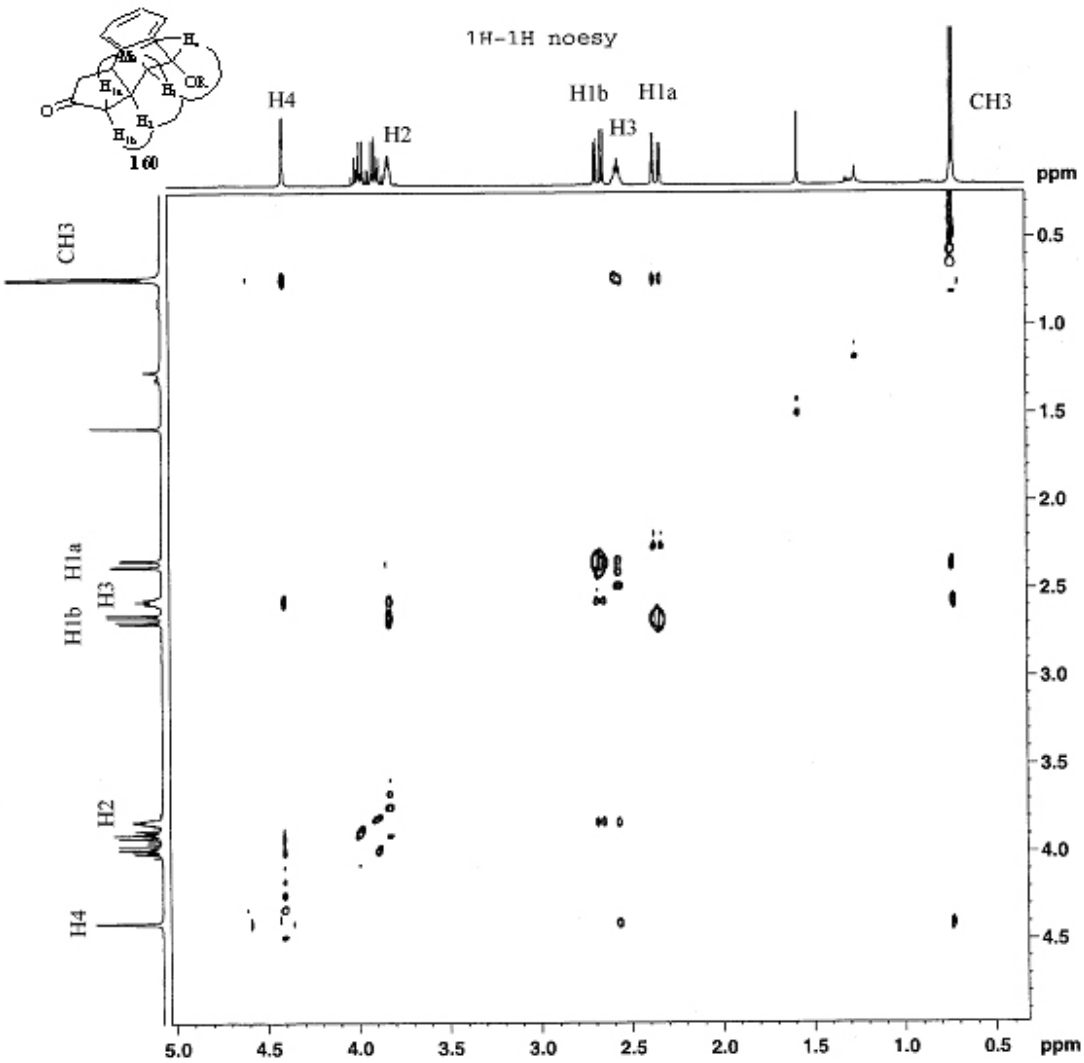
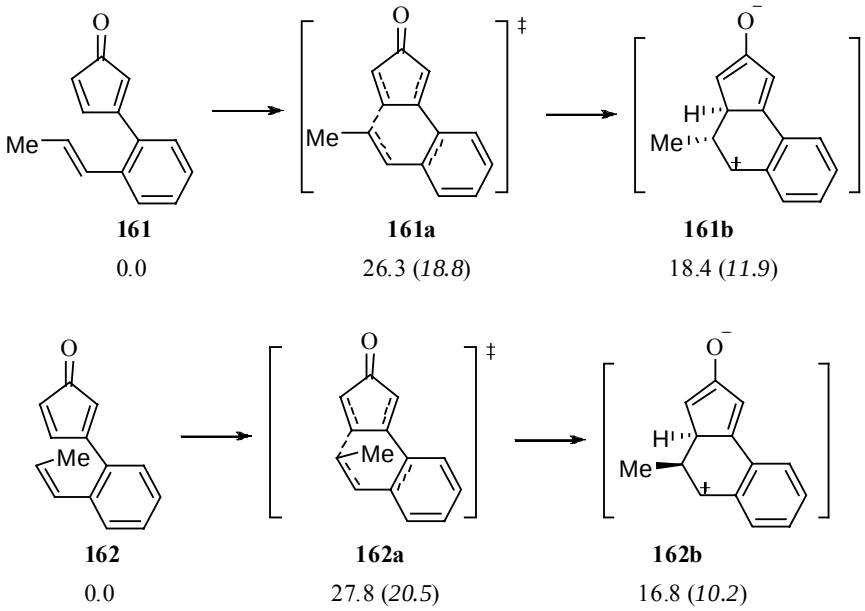


Figure 5 NOESY Spectrum of **160**

The different behaviour of isomeric system **161** and **162** in the electrocylization was further explored by Schreiner and Navarro-Vázquez[68] using B3LYP/6-31G* calculations. Even though it possesses a slightly higher activation free energy, the cyclization of **162** is less endothermic, which results in faster reaction and less side reactions as compared system **161** (Scheme 40).



Scheme 40 Computed relative free energies $\Delta G_{298.15\,K}$.
Regular font: gas phase values; italics: PCM (TFE) data

4 Summary

We have discovered an electrocyclization of cyclopentadienones driven by antiaromatization. We also uncovered some evidence that this process is indeed an 8π conrotatory electrocyclic ring closure. The reaction provides a good way to access the tricyclic ring system with high stereoselectivity. Further application in the total synthesis is still going on in our lab.

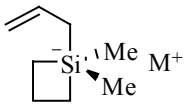
Chapter II

An Unusual Observation During a Lithium-bromine Exchange Reaction

1 Introduction

1.1 Characterization of Pentaorganosilicates

Reactions involving pentaorganosilicate intermediates have been known for several decades.[77-79] In 1981, Depuy reported the first observation of pentavalent organosilicate intermediate **163** in the gas phase by using a flowing afterglow experiment.[80] The addition of allyl anion to 1,2-dimethylsilacyclobutane was favored by the relief of strain by allowing the cyclobutane ring to span one equatorial and one axial position.

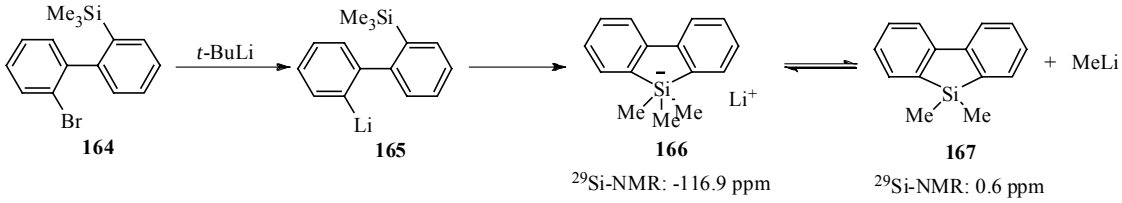


163

Figure 6 Pentaorganosilicate

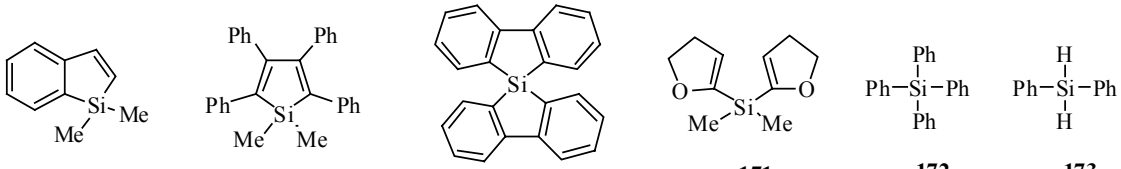
However, due to its lability and high reactivity in solution, the pentaorganosilicate intermediate had not been observed until 1996. Klumpp and coworkers[81] successfully observed this transient species employing low temperature NMR techniques. When **164** was treated with *t*-BuLi at –80 ^{o}C, the exceptionally high-field ^{29}Si-NMR signal (δ: -116.9 ppm) clearly indicated the presence of pentavalent silicon intermediate **166**. As the temperature rised, this pentavalent intermediate **166** converted reversibly into methyllithium and 5,5-dimethyldibenzosilole **167** (δ: 0.6 ppm) (Scheme 39). With the coordination of HMPA, **167** was found to be as the only species present up to room

tempterature. In contrast, no ^{29}Si-NMR signal of pentacoordinated silicon was detected at –80 ^{o}C in ethyl ether solution. An order of stabilization in solvents was proposed as followed: HMPA> THF > Et_2O.



Scheme 41 The First Observation of Pentaorganosilicate in Solution

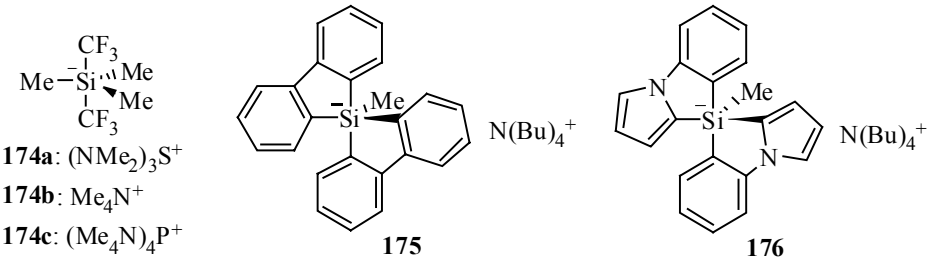
Furthermore, Klumpp and coworkers[81,82] also carried out NMR studies on a number of different organosilicates to investigate the structural requisites for stable pentaorganosilicates. Compound **168** was found to form pentaorganosilicate in the presence of HMPA at the low temperature. The hypervalent intermediate of **169** was obtained in 10% yield by ^{29}Si-NMR, together with 90% of **169**. Unexpectedly, [**170-Me**]$^{-}$**[Li(THF)$_4$]**$^{+}$ was found to be very stable and did not decompose up to 50 ^{o}C. No hypervalent species was observed with the substrate **171**. Two phenyl silanes (tetraphenyl silane **172** and biphenyl silane **173**) were also subjected to this examination. A weak signal for **[172-Ph]**$^{-}$**[Li(HMPA)$_4$]**$^{+}$ (5-10% intensity) was obtained.[82] In sharp contrast, [**173-Ph**]$^{-}$**[Li(HMPA)$_4$]**$^{+}$ was obtained as the only product when phenyllithium was added to **173** at –78 ^{o}C. Moreover, this complex even survived prolonged time (14 h) at room temperature (Figure 7).[83]



168 **169** **170** **171** **172** **173**

Figure 7 Some Organosilicates under Investigation

Other than the solvent effects and structural factors, countercations also played an important role in the stabilization of hypervalent intermediates. It was found that **174a** was stable up to 0 ^{o}C, whereas **174b** rapidly decomposed at –30 ^{o}C. And the corresponding **174c** was found to decompose at –10-0 ^{o}C.[84] Surprisingly, **175** was obtained as a highly stable white solid with a melting point of 177-182 ^{o}C.[85] Its phenylpyrrole analogue **176** also showed high stability (Figure 8).[86]



174a: $(NMe_2)_3S^+$
174b: Me_4N^+
174c: $(Me_4N)_4P^+$

175 **176**

Figure 8 Some Stable Pentaorganosilicates

X-ray diffraction has been employed as another powerful tool for the characterization of pentaorganosilicate compounds. In 1999, Kolomeitsev[84] reported the first X-ray structure of hypervalent silicate **174a**, which showed perfect trigonal-bipyramidal geometry at silicon atom. Two trifluoromethyl groups occupied two axial positions and methyl groups resided the remaining equatorial position. X-ray structures of **175**[85,87] and **176**[86] showed the slightly distorted trigonal bipyramidal geometry towards

square-pyramidal. Methyl groups were in an equatorial positions and the biaryl groups were in axial-equatorial positions.

Excited and curious about the high stability of **175** and **176**, Lammertsma[88] performed the B3LYP/6-31G(d) calculations on **175** and **176**. With the comparison of bidentate biaryl pentaorganosilicates **175**, **176** with other silicates, they found that biaryl ligands can provide electronic stabilization similar to two individual aryl groups, while avoiding the steric crowding between the axial aryl group and the *ortho*-hydrogen atoms on the equatorial aryl group. They also found the preference of axial over equatorial substitution on **175** and **176**, which was consistent with previous experimental results.[87]

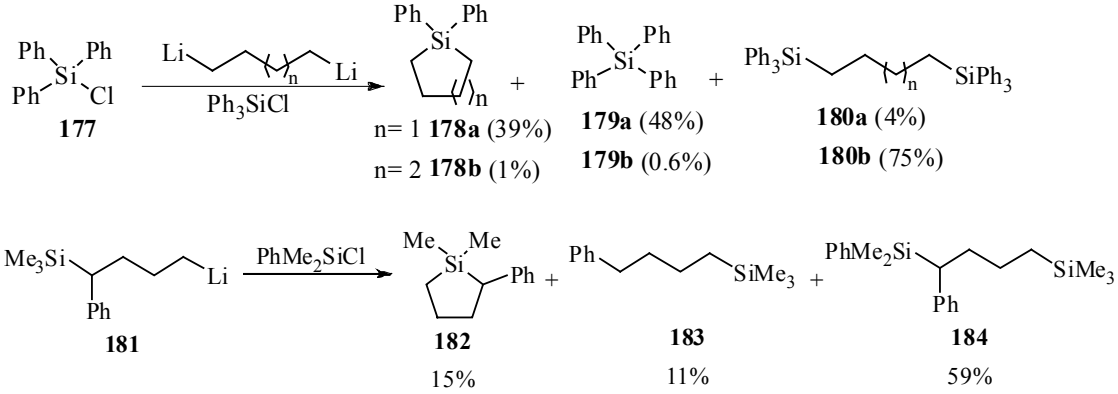
1.2 Reactions Involving Pentaorganosilicate Intermediates

1.2.1 Nucleophilic Substitution

Even though remarkable progress has been achieved in the preparation of pentaorganosilicates, the chemistry of pentaorganosilicates remains less developed. Nucleophilic substitution on the silicon atom was one of few known areas in a hypervalent organosilicate chemistry.

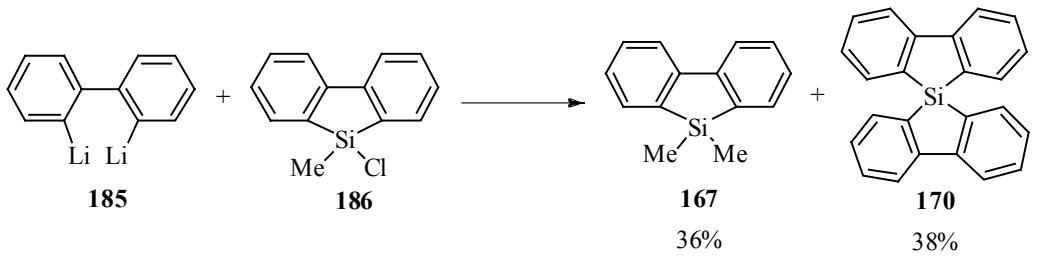
In the attempts to prepare 1,4-bis(triphenylsilyl)butane **180a**, only 4.4% yield of **180a** was obtained when the dilithiobutane was slowly added to chlorotriphenylsilane in cold diethyl ether solution.[77] Diphenylsilacyclopentane **178a** was formed in 39%, together with 48% of tetraphenylsilane **179a**. In contrast, bis(triphenylsilyl)pentane **180b** was generated in 75% yield when dilithiopentane was employed. Trace amounts of cyclosilahexane **178b** were also obtained.

Similar 5-*exo*-tet cyclization was reported by the Maercker group.[89] Significant amount of 1,4-TMS rearranged product (**183**, **184**) was obtained together with silacyclopentane **182** when organolithium **181** was quenched by chlorodimethylphenylsilane (Scheme 42).



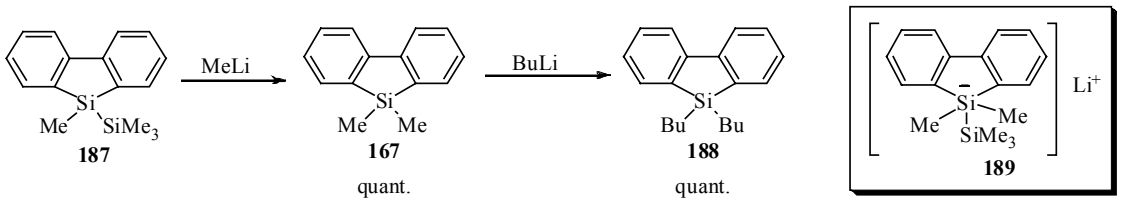
Scheme 42 Reactions Involving Pentaorganosilicates

Moreover, Gilman uncovered an interesting cyclization for silane system.[77,79] 38% of 5,5'-spirobi-[dibenzosilole] **188** and 36% of 5,5-dimethyldibenzosilole **187** were obtained upon treatment of 2,2-dilithiobiphenyl **185** with 2.0 equivalents of 5-chloro-5-methyldibenzosilole **186**. The fact that nearly equal amounts of **167** and **170** were found suggested that **170** was highly stable in ethereal solution and the formation of **170** might involve rapid bond cleavage and formation (Scheme 43).



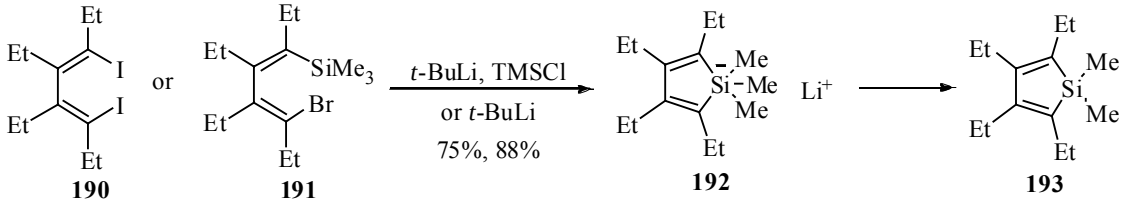
Scheme 43 Unusual reaction of **186** with Dilithiobiphenyl **185**

A similar nucleophilic substitution on the silicon atom was also observed by Ishikawa during the attempts to prepare a stable silacyclopentadienide anion.[90,91] TMS groups were replaced by methyllithium in quantitative yields and no 5-hydro-5-methyldibenzosilole was observed. Furthermore, 5,5-dimethyldibenzosilole **167** was converted to 5,5-dibutyldibenzosilole **188** upon the treatment with excess *n*-BuLi. A pentacoordinated organosilicate **189** was proposed as a key intermediate for the unusually reactively silole. However, any attempt to trap this transient intermediate was unsuccessful (Scheme 44).



Scheme 44 Nucleophilic Substitution Reaction of **187**

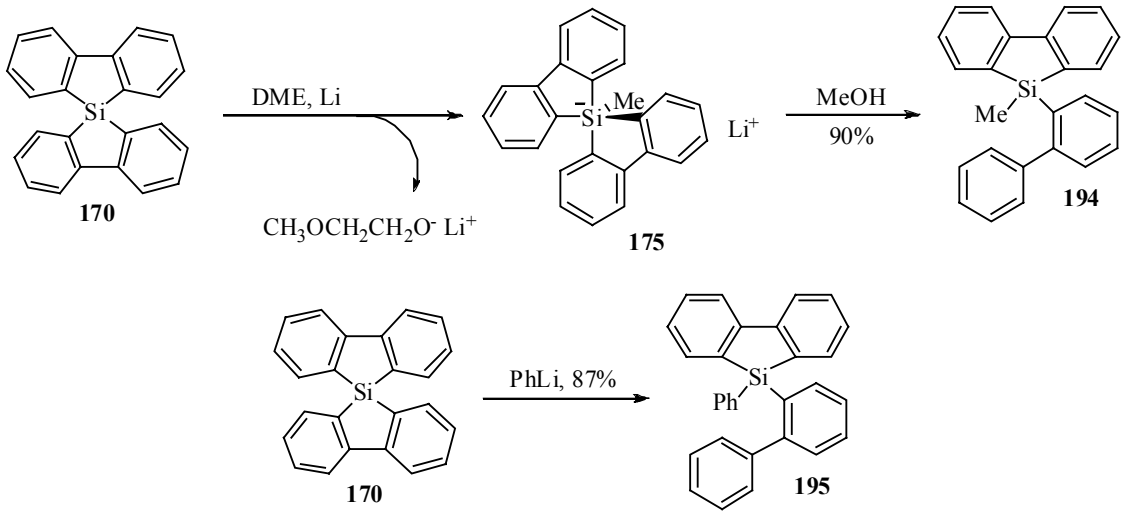
The formation of silole **193** by intramolecular nucleophilic substitution was achieved by Xi[92] and Hudrlik[93]. Lithium-halide exchange followed by treatment of TMSCl gave silole **193** via hypervalent intermediate **192**. Alternatively, **193** was also prepared upon treatment of bromosilane **191** with *t*-BuLi (Scheme 45).



Scheme 45 Synthesis of Tetraethylsilole **193**

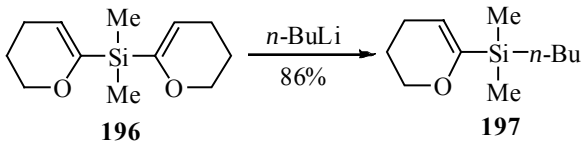
However, the formation of 5-membered siloles is reversible. When **170** was treated with lithium in DME solution, **194** was formed in 90% yield.[87] Similarly, **195** was

obtained in 87% yield upon the treatment of **170** with excess amount of PhLi (Scheme 46).[78]



Scheme 46 Reactions of 5,5'-spirobi-[dibenzosilole] **170**

Intermolecular nucleophilic substitution on the silicon atom was also investigated by Lukevics and coworkers.[94] A dihydropyran ligand was selectively cleaved by butyllithium in the presence of methyl group. The sequence of nucleophiles with different reactivities is as follows: *n*-BuLi > 2-lithiofuran > 2-lithiodihydropyran ~ 2-lithio-dihydrofuran > PhLi.

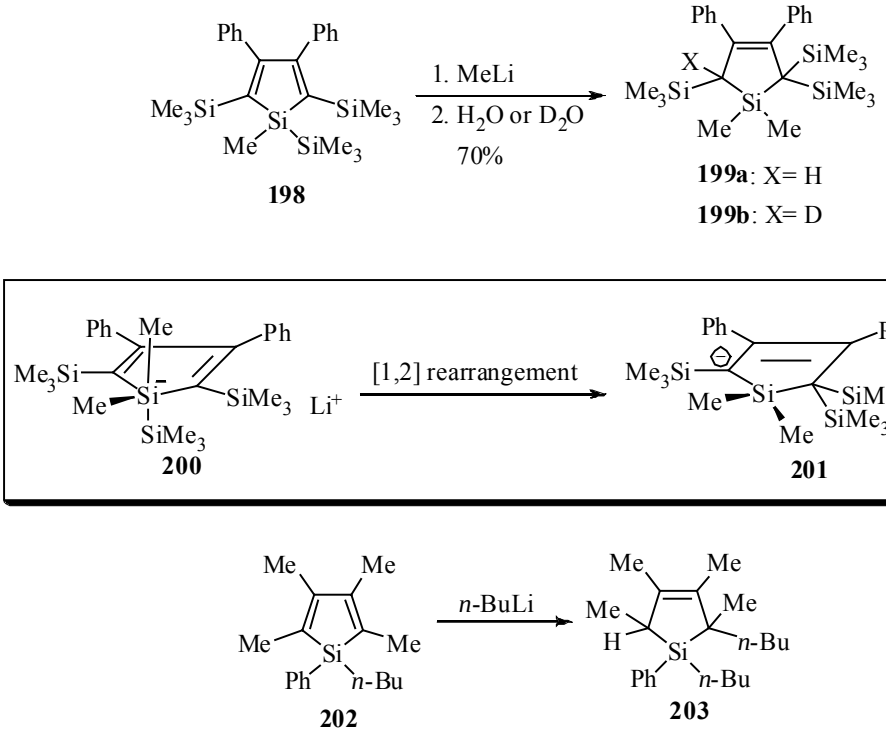


Scheme 47 Nucleophilic Substitution Reaction of **197**

1.2.2 Rearrangement Involving Pentaorganosilicate Intermediates

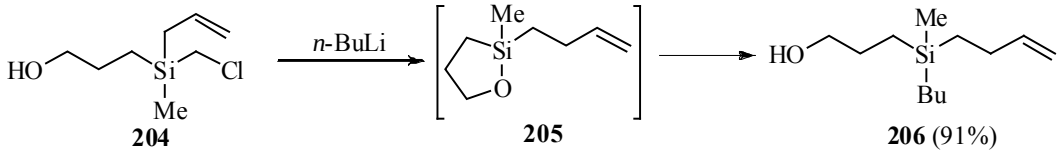
Ishikawa[90,91] and Jutzi[95] demonstrated that 70% yield of **199a** was obtained on the treatment of silole **198** with excess MeLi, accompanied by 7% of 1,1-dimethyl-2,5-

bis(trimethylsilyl)-3,4-diphenylsilole (not shown) via nucleophilic displacement on the silicon atom. The reaction may proceed through pentacoordinated intermediate **200**, which could undergo facile 1,2-migration of TMS group to form **201**. The fact that excellent deuterium incorporation was observed strongly supports the proposed mechanism. Furthermore, a butyl group can also participate the rearrangement (**202** to **203**) (Scheme 48).



Scheme 48 1, 2-rearrangement of **198** and **202**

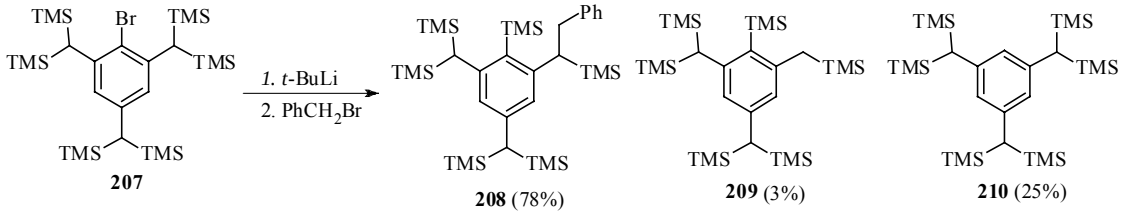
α-Chlorosilane **204** was also found to undergo 1,2-migration of allyl group to give **206** in excellent yield. **205** was assumed as the key intermediate in this rearrangement (Scheme 49). The reaction also worked for a number of ligands on the silicon atom, like phenyl, Me, 2-furyl.[96]



204 **205** **206** (91%)

Scheme 49 1, 2-rearragement of Allyl Group

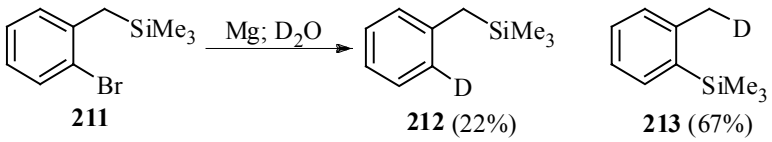
Other than 1,2-rearrangement, 1,3-rearrangement was also observed in the silane system. Lithium-halide exchange of **207**, followed by addition of benzyl bromide delivered **208** in 78% yield (Scheme 50).[97]



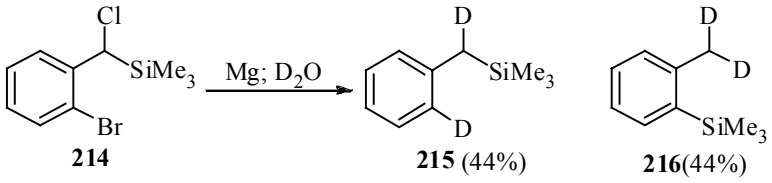
207 **208** (78%) **209** (3%) **210** (25%)

Scheme 50 1, 3-rearrangement of TMS Group

When 1-bromo-2-((trimethylsilyl)methyl)benzene **211** was treated with magnesium, followed by deuterolysis,[98] 1,3-silyl rearranged product **213** was obtained in moderate yield, accompanied by benzyltrimethylsilane **212** from the unreacted Grignard reagent. More interestingly, the deuterium hydrolysis of di-Grignard reagent of **214** offered an equal amount of 1,3-dideutero product **215** and 1,1-dideutero product **216**.[99] Both of reactions might proceed through a transient hypervalent organosilicate intermediate (Scheme 51).



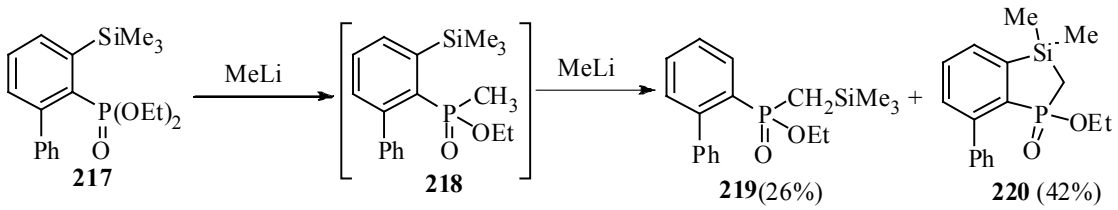
211 **212** (22%) **213** (67%)



214 **215** (44%) **216**(44%)

Scheme 51 1, 3-rearrangement of TMS Group

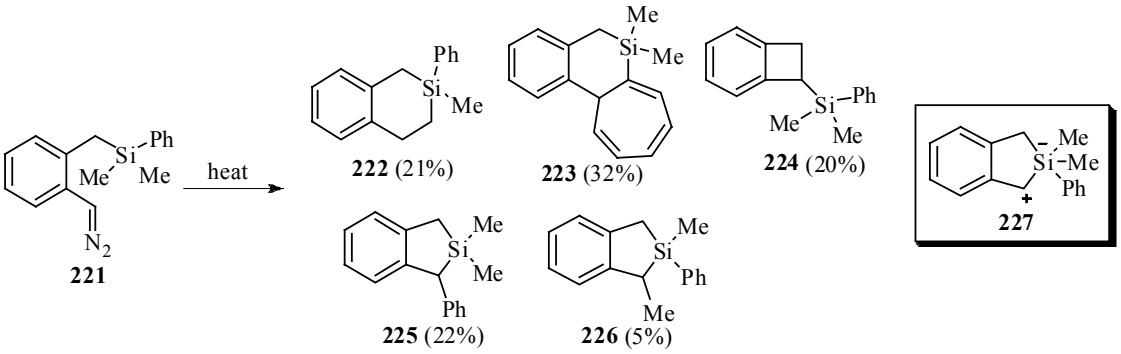
1,4-Rearrangement was found by Vedejs and coworkers[100] during the studies of chiral phosphines. Compound **219** was isolated in 26% yield and **220** was obtained in 42% yield when **217** was treated with MeLi. The mechanism proposed for the explanation of unexpected products is that first addition of MeLi to phosphonate **217**, which could lead to **218**. Deprotonation, subsequent formation of cyclosilapentane and hydrolysis could produce **219** and **220** (Scheme 52).



217 **218** **219**(26%) **220** (42%)

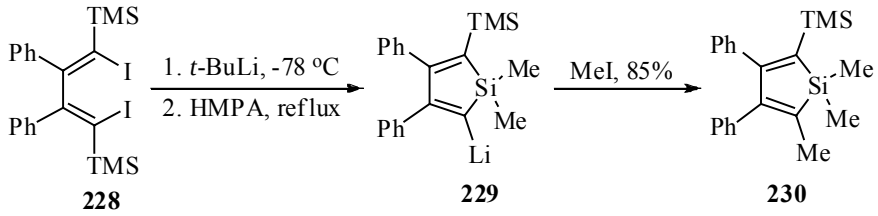
Scheme 52 1,4-rearrangement of TMS Group

In the course of the investigation of reactivity of arylcarbene,[101] aryl diazo compound **221** was prepared and subjected to heat under reduced pressure. As a result, 5 major products were obtained. Among these, **222** and **223** were formed by the C-H insertion to methyl group and phenyl ring respectively. Zwitterionic **227** was proposed to explain the formation of product **224**, **225** and **226** via 1,2-migration (Scheme 53).



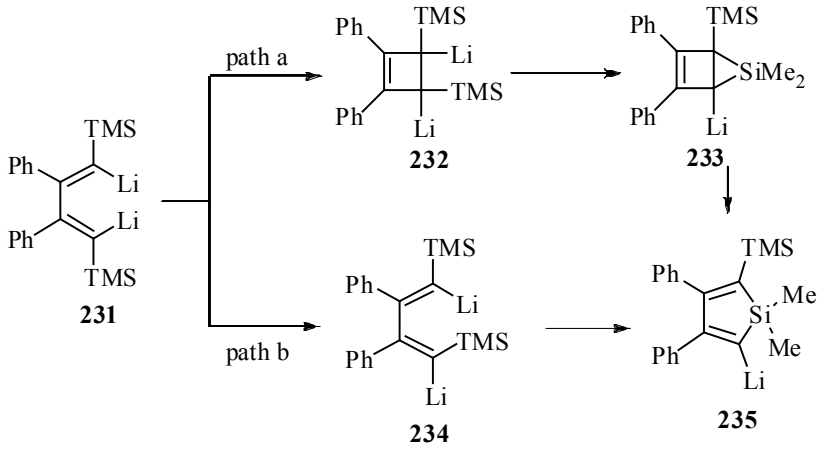
Scheme 53 Carbene Rearrangement of Silyl Group

Xi and coworkers[102] demonstrated a novel approach to access lithiosiloles from 1,4-bis(trimethylsilyl)-2,3-diphenyl-1,4-diiodo-1,3-diene **228**. Compound **228** was converted to corresponding 1,4-dilithio intermediate **229** by the addition of *t*-BuLi at –78 °C. The resulting solution was then refluxed in the presence of HMPA for 1 h before it was quenched by MeI. Compound **230** was generated in 85% yield (Scheme 54).



Scheme 54 Synthesis of Silole from 1,4-diiodo-1,3-diene **228**

Two different mechanisms were proposed (Scheme 55). In path a, electrocyclic ring-closure of **231** could deliver **232**, which might be further converted to lithio silole **235** by subsequent cyclosilapropane formation and electrocyclic ring opening. On the other hand, double bond isomerization of dilithiate **231** might give **234**. Intramolecular anionic attack could result in **235**.

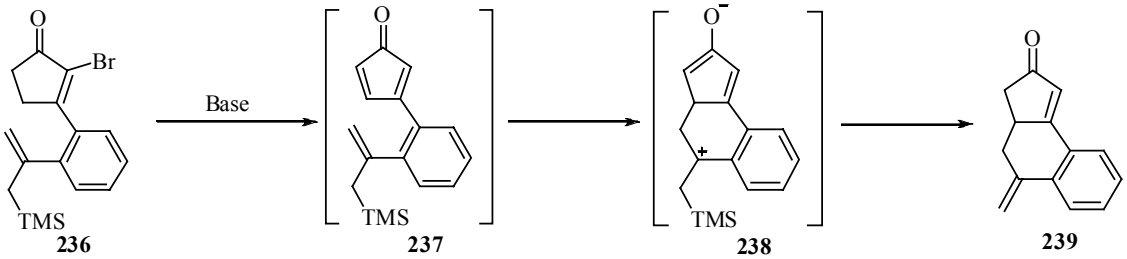


Scheme 55 Proposed Mechanism

2 Results and Discussion

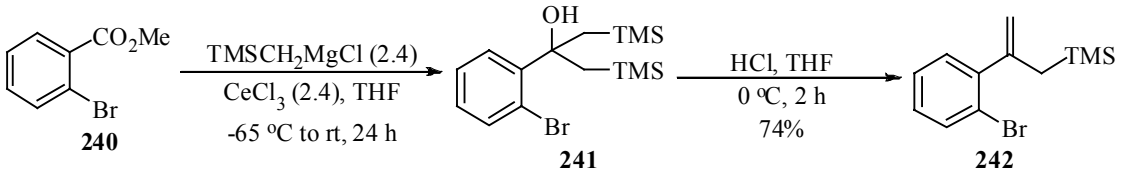
2.1 Discovery of a Novel Coupling Reaction with Primary Halides

During the exploration of substituent effects on the electrocyclic ring-closure of cyclopentadienones, we were quite interested in the trimethylsilyl-substituted cyclopentenone **236**. We assume that **236** would undergo 1,4-debromination reaction to give cyclopentadienone intermediate **237**, which could be further converted to **238** via 8πe electrocyclic ring-closure. Desilylation of **238** would deliver the product **239** (Scheme 56). The ability of a silicon-carbon bond to stabilize an adjacent carbonium ion might accelerate this electrocyclic ring-closure reaction.[103]



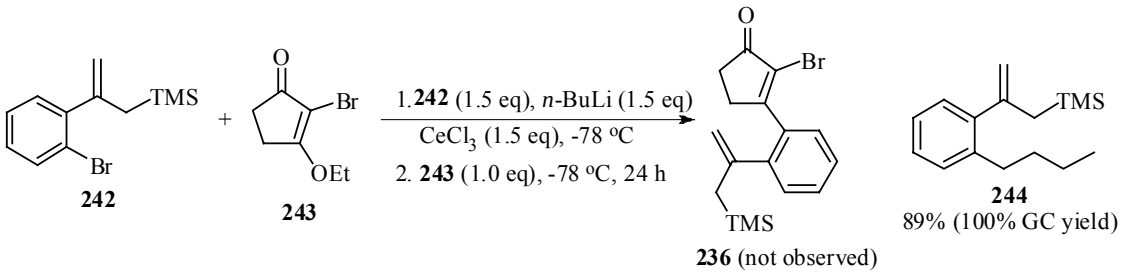
Scheme 56 Proposed Electrocyclization of **236**

The synthesis of **236** was quite straightforward. Commercially available methyl 2-bromobenzoate **240** was converted to **241** by the addition of Grignard reagent in the presence of cerium chloride. Compound **6** further underwent Peterson olefination to give **242** in 59% yield under acidic conditions (Scheme 57).[104]



Scheme 57 Synthesis of Bromosilane **242**

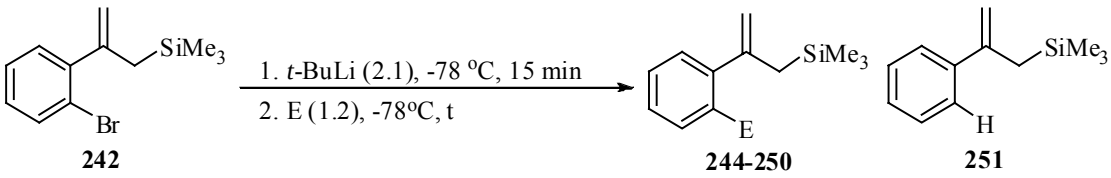
Organocerate of **242** was prepared by lithium-bromine exchange, followed by transmetallation with $CeCl_3$. Addition of organocerate reagent to ketone **243** gave none of desired **236**. However, a very interesting reaction color change did draw our attention: when *n*-BuLi was added dropwise to the cold THF solution of bromide compound **242**, the color of the reaction mixture changed from colorless to bright yellow, which is the typical color for an aryl lithium species. The yellow color changed to pale yellow (almost colorless) when the addition of *n*-BuLi was complete. After workup of some of the reaction mixture, butylated product **244** was obtained in 89% yield (Scheme 58). To the best of our knowledge, no coupling reaction of this type has been observed before.[105-107]



Scheme 58 An Unusual Observation during the Attempt to Access **236**

We assumed that **244** might be formed by lithium-bromine exchange and sequential nucleophilic attack of *n*-BuBr. The idea was confirmed by the following experiments. When **242** was treated 2.1 equivalents of *t*-BuLi, followed by quenching with *n*-BuBr, compound **244** was formed in nearly quantitative yield (94% NMR yield) (Table 5, entry 1).

Table 5 Halogen-metal Exchange of **242,** Followed by Alkylation



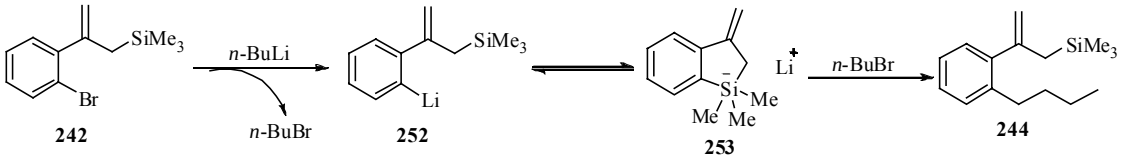
242 **244-250** **251**

Entry	Electrophiles	Time (15+t)	Product	NMR Yield (%)[a]
1	*n*-BuBr	30 m	**244**	94
2	n-PrBr	30 m	**245**	83
3	EtBr	30 m	**246**	89
4	1-bromo-3-chloropropane	30 m	**247**	58
5	Allyl bromide	3 h	**248**	74
6	$PhCH_2Cl$	3 h	**249**	94
7	PhCHO	6 h	**250**	68[a]

[a] Yields were calculated based on the mass of the mixture of alkylated product and **251** and molecular ratios that obtained from NMR integration and mass of the mixture. [b] Isolated yield.

Furthermore, the reaction worked well for a number of electrophiles (Table 5). The reaction worked well with primary bromides to afford alkylated products in good yields (entry 2 and 3). Bromide was selectively reacted in the presence of chloride (entry 4). Allyl bromide and benzyl chloride were also good electrophiles in this reaction (entry 5 and 6). Finally, the lithium reagent of **242** was also treated with benzaldehyde to afford **250** in 68% yield. The major byproduct in this alkylation reaction is **251**, which might be formed by the protonation of unreacted organolithium **251** during the workup or the competitive E_2 elimination of 1-bromobutane.

Based on the experimental results and previous literature reports, we proposed a silicon-assisted coupling mechanism (Scheme 59). Lithium-bromine exchange of **242** would give the organolithium intermediate **252**, which might cyclize to produce pentacoordinated silicon intermediate **253**. This would then undergo rapid attack by the primary bromide to afford **244**.



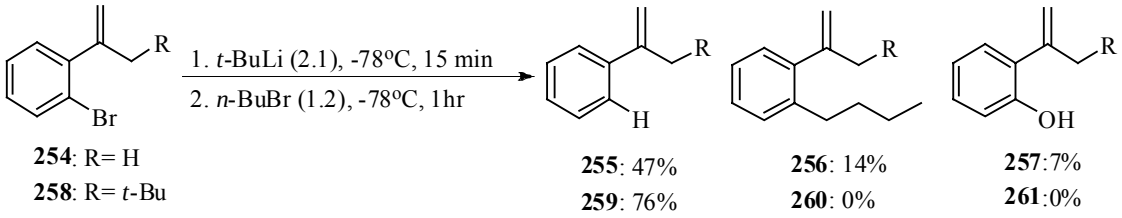
Scheme 59 Proposed Mechanism

2.2 Preliminary Mechanistic Studies

To probe the possible mechanism of the coupling reaction, we carried out some preliminary mechanistic studies.

The role of the silicon atom in the coupling reaction was explored by the replacement of TMS group with a H atom and *t*-butyl group. 2-Bromo-α-methyl styrene **254** and *t*-Bu substituted substrate **258** were prepared for this purpose. When **254** was

treated with *t*-BuLi and 1-bromobutane, 14% of alkylated product **256** was obtained. A yield of 76% of protonated product **259** was formed in the case of lithium-bromine exchange of **258** (Scheme 60). These results strongly suggested the involvement of silicon in the unprecedented coupling reaction of phenyllithium and primary alkyl halide.



254: R= H
258: R= *t*-Bu

255: 47%
259: 76%

256: 14%
260: 0%

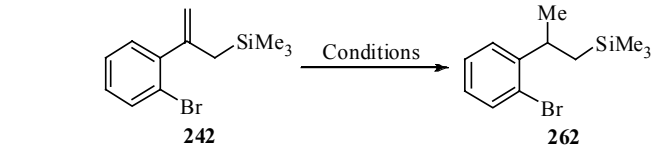
257:7%
261:0%

Scheme 60 Preliminary Mechanistic Studies

In order to fully understand the role of the alkene in this novel coupling reaction, (2-(2-bromophenyl)propyl)trimethylsilane **262** was prepared. Even though the synthesis seemed straightforward, the reaction from **242** to **262** was not simple due to labile properties of aryl bromide and allylsilane. The results were shown in Table 6.

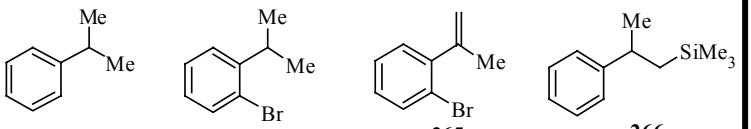
Compound **242** was first subjected to hydrogenation using Pd/C (10%) catalyst. But the desired bromosilane **262** was obtained in only 30% yield (entry 1). The major product was 1-bromo-2-isopropyl benzene **264** (51%), formed by the cleavage of TMS group. The cleavage of aryl bromide was also found in significant amounts in the crude reaction mixture (**266**, 19%). Lower reaction times did not show significant change (entry 2).

Table 6 Reduction of **242**



242 **262**

Side product



263 **264** **265** **266**

entry	Conditions[a]	**242** (%)	**262** (%)	**263** (%)	**264** (%)	**265** (%)	**266** (%)
1	Pd/C (10%) H_2 (1 atm), 4.5 h	0	30	0	51	0	19
2	Pd/C (10%) H_2 (1 atm), 20 m	4	15	3	56	9	13
3	Pd/C (5%) H_2 (1 atm), 20 m	0	17	15	21	27	19
4	Pd/C (1%) H_2 (1 atm), 30 m	55	15	0	9	0	21
5	Lindlar cat. (5%) H_2 (1 atm), 30 m	88	7	0	5	0	0
6	$TsNHNH_2$ (5.0) NaOAc (7.0) reflux, 3.5 h	68	32	0	0	0	0
7	$TsNHNH_2$ (5.0) NaOAc (7.0) reflux, 2.5 d	50	50	0	0	0	0
8	$TsNHNH_2$ (10.0) NaOAc (20.0) reflux, 7 d	0	100 (1.0:7.9)	0	0	0	0

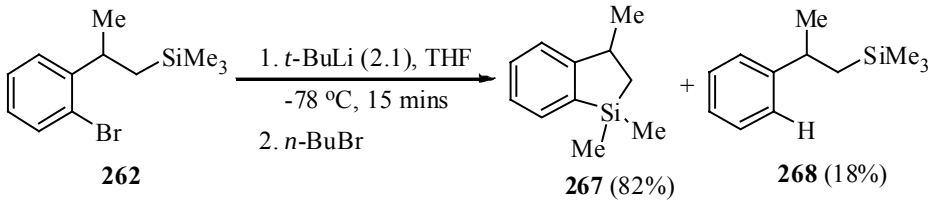
[a] GC percentage was determined by GC-MS analysis of crude reaction mixture.

Deactivation of catalyst by employing 5% Pd/C did not yield any promising result (entry 3). Significant amounts of side product **264** and **265** were obtained with the treatment of 1% Pd/C (entry 4). When the hydrogenation reaction of **242** was catalyzed by Lindlar catalysis, almost equal amount of desired product **262** and desilylation product **264** was obtained, together with 89% of starting material (entry 5). Our experimental data suggest the order of reactivity of functional group under Pd-catalyzed hydrogenation reaction of **242** to the: $C{=}CH_2 \geq C\text{-}SiMe_3 \geq C\text{-}Br$.

Finally, we turned to diimide reduction and hoped it would avoid the facile cleavage of $C\text{-}SiMe_3$ and C-Br bond. Diimide was prepared in situ by refluxing tosylhydrazine with NaOAc in the mixture of THF and water. When **242** was treated with diimide for 3.5 h, desired product **262** was obtained for 33% yield and 68% of unreacted **242** (entry 6). No side product was detected. Prolonged reaction time did not significantly improve the yield (2.5 d, entry 7). We hypothesized that the reduction reaction might be competitive with the disproportionation reaction of diimide to produce nitrogen and hydrazine under the reaction conditions.[108] To our pleasure, a higher loading of reagent afforded better quality of **262** (88% NMR pure), which was obtained in pure form after Kugelrohr distillation (entry 8).

Pure (2-(2-bromophenyl)propyl)trimethylsilane **262** was subjected to our standard coupling reaction condition. Surprisingly, benzosilole **267** was produced in 82% yield along with 18% of **268** (determined by GC-MS). No butylated product was observed in GC-MS. We concluded that the double bond played an important role in the coupling reaction. In the absence of double bond, the pentaorganosilicate intermediate

corresponding to **262** may have a lower ring strain to facilitate the release of the methyl anion to form the stable benzosilole **267** (Scheme 61).



262

267 (82%)

268 (18%)

Scheme 61 Lithium-halide Exchange of **262**

In addition to structural modifications of **242** in the mechanistic studies, **242** was also subjected to a low temperature (-78 ^{o}C, THF-d_8) ^{29}Si-NMR experiment employing the intensitive nuclei enhanced by polarization transfer (INEPT) technique to detect the existence of the proposed pentaorganosilicates intermediates. A few silicon peaks were observed at –3.76, -3.81 and –6.46 ppm. The absence of silicon peak at –116.9 ppm[81] indicated that the pentavalent organosilicates **253** did not exist in an observable concentration in the equilibrium with phenyllithium intermediate **252**, but it does not rule out its intermediacy in the reaction.

The relative intensity of silicon peaks changed significantly after the addition of 5 equiv. of HMPA. A new peak at –4.82 ppm appeared as the major peak, which may suggest the changes in the aggregation state of phenyllithium upon treatment with HMPA (Figure 9).

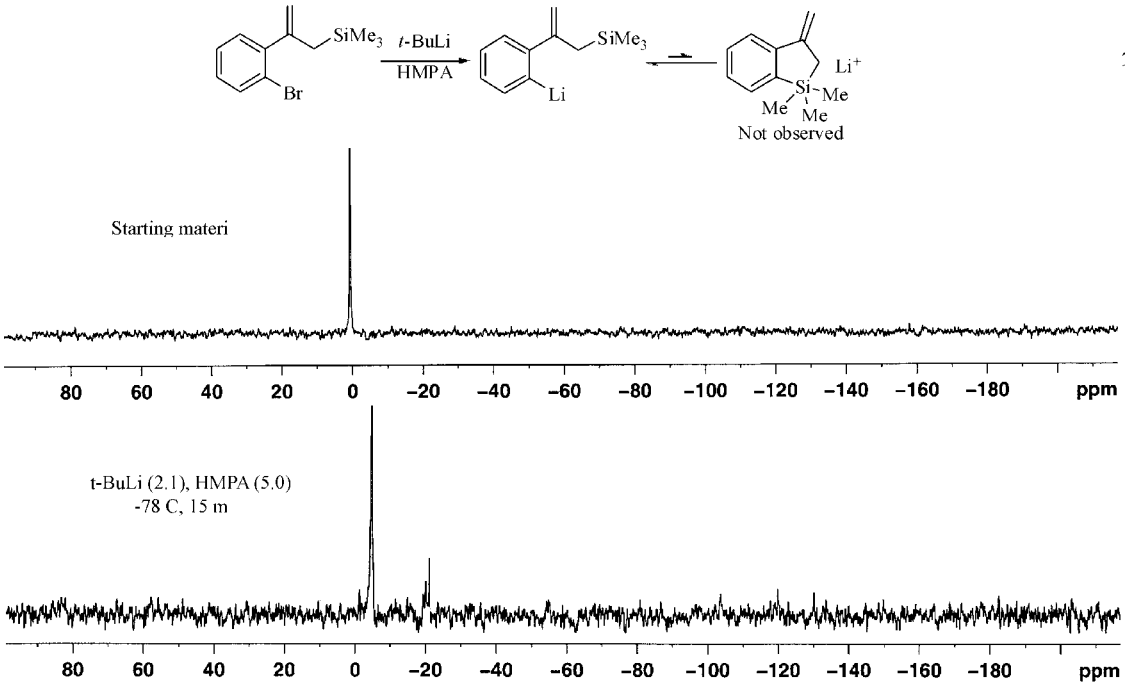


Figure 9 ^{29}Si-NMR Experiment of **242** with *t*-BuLi and HMPA

Compound **262** was also subjected to low temperature ^{29}Si-NMR studies (Figure 10). Interestingly, the peak at ca. 10.0 ppm showed up right after the treatment of **262** with *t*-BuLi. This peak prevailed in the mixture during the reaction and even after the quenching with *n*-BuBr. This peak was assigned as **267** with NMR and GC-MS data, which is consistent with our previous result.

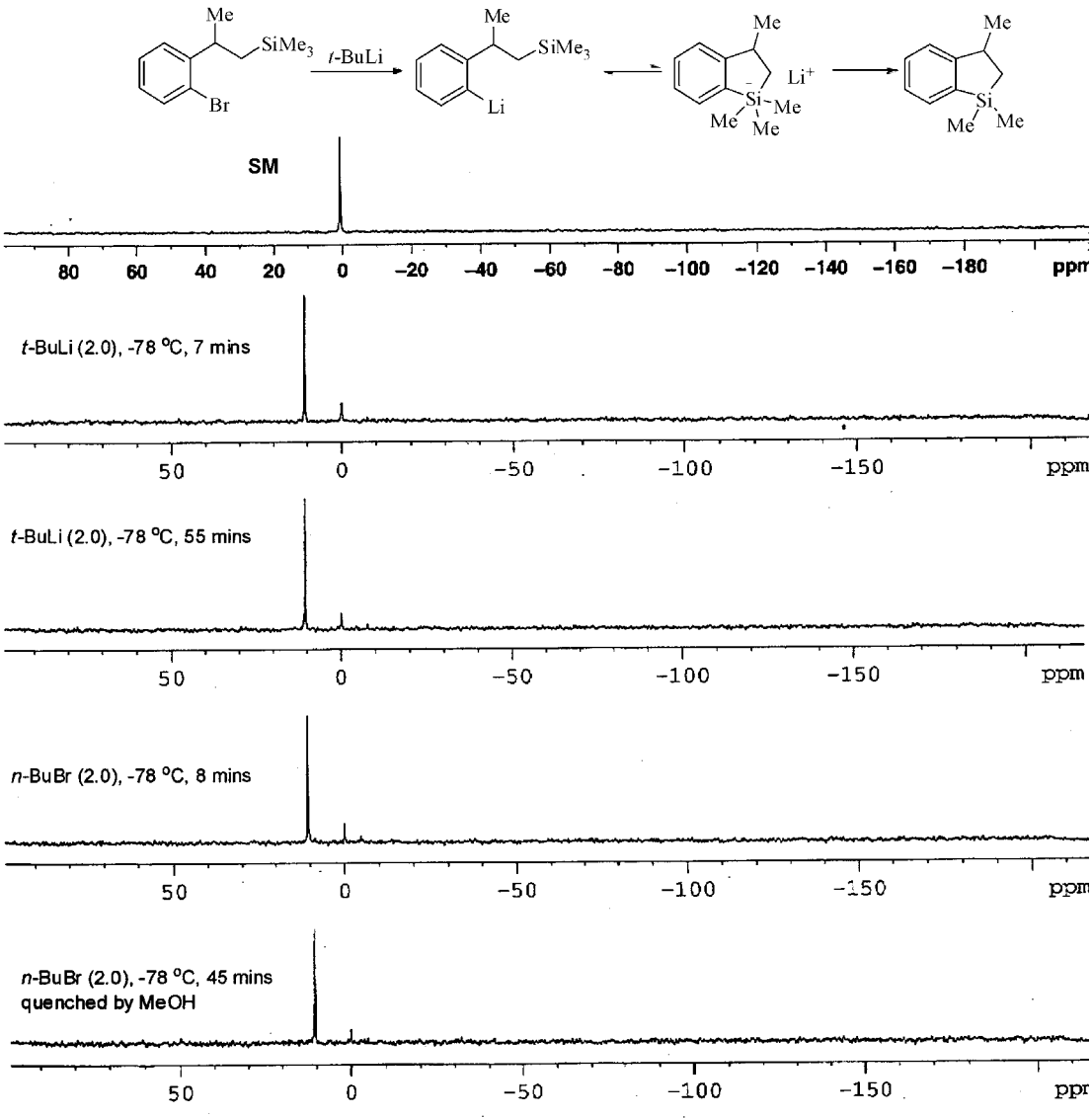
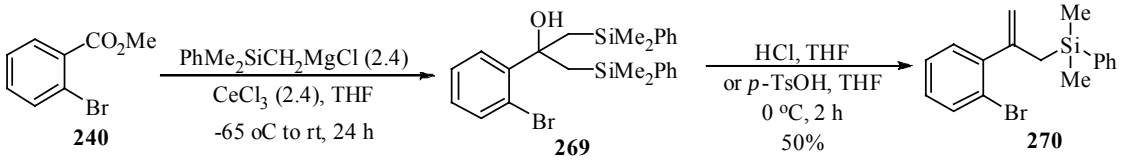


Figure 10 ^{29}Si-NMR Experiment of **262** with *t*-BuLi

2.3 Phenyldimethylsilane Derivative

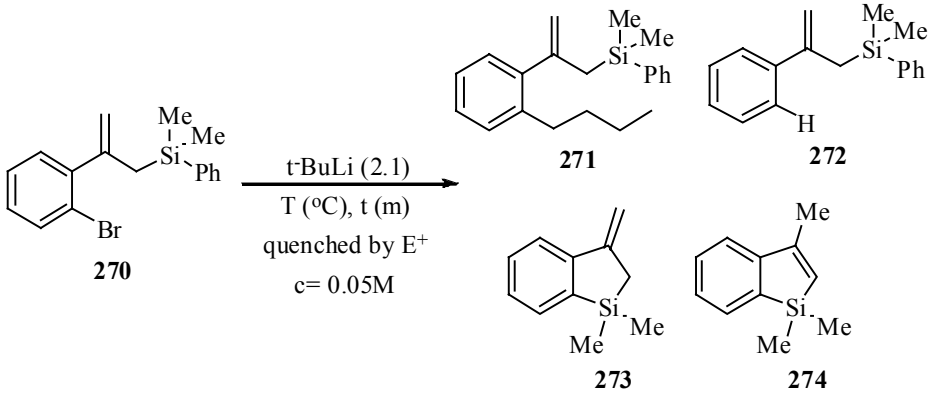
We attributed the absence of pentaorganosilicate signal to the relative instability of **253**. We designed the phenyl substrate **270** so as to stabilize the transient hypervalent intermediate. Following the procedure for **242**, **270** was obtained in 50% yield by the sequential addition of the organocerate to ester **240** followed by Peterson olefination (Scheme 62).



Scheme 62 Preparation of Phenyldimethylsilane Derivative **270**

Dimethylphenylsilane **270** was treated with 2.1 eqiuv. of *t*-BuLi and quenched by BuBr. Butylated product **271** was obtained in 64% yield, together with 11% protonation product **272**. Interestingly, 2,3-dihydro-benzosilole **273** was formed in 6% yield (Table 7, entry 1). The yield of **273** increased to 38% when the reaction was left at 0 ^{o}C for 2.5 h (entry 2). After prolonged reaction time at room temperature, benzosilole **274** was formed in 44% yield with conjugation having occurred due to the presence of excess base (entry 3). The presence of **273** and **274** showed the evidence for the formation of pentaorganosilicate intermediate during the reaction.

Table 7 Halogen-lithium Exchange of **270** under Different Tempearatures



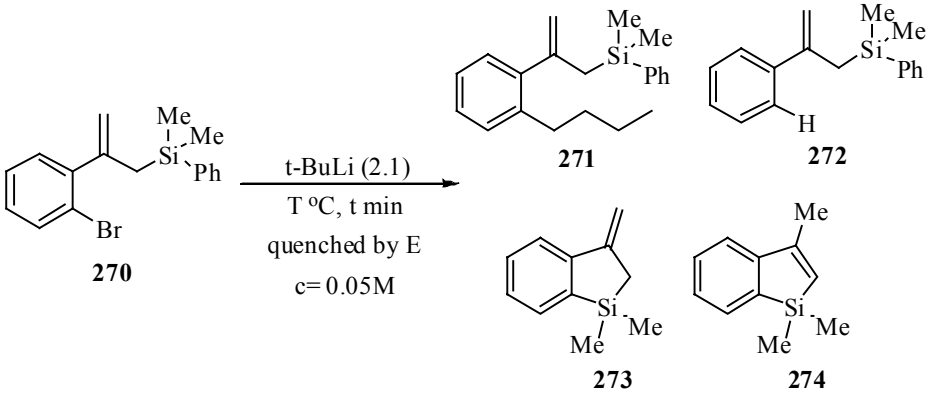
entry	T (°C), t (m)	E^+	**271** (%)	**272** (%)	**273** (%)	**274** (%)
1	-78 °C, 15 m	*n*-BuBr	64	11	6	-
2	-78 °C, 15 m -25 °C, 30 m 0 °C, 2.5 h	Sat. NH_4Cl	-	32	38	2
3	-78 °C, 15 m rt, 20 h	Sat. NH_4Cl	-	15	10	44

[a] Percentage conversion was determined by GC-MS.

Low temperature ^{29}Si-NMR experiments were also carried out with phenyldimethyl analogue **270** (Table 8). One major silicon peak (7.49 ppm) was observed together with several small peaks at –78 °C in THF solvent (Figure 11). Butylated product **271** was obtained in 93% yield upon the quenching with BuBr (entry 1). When the reaction was warmed up slowly to room temperature, the peak at 7.49 ppm gradually converted to the new peak at –8.71 ppm. No hypervalent organosilicate peak was observed under these

conditions (entry 2). When *t*-BuLi was added to mixture of **270** and 5.0 equiv. of HMPA in THF, a pentaorganosilicate intermediate (-108.04 ppm) was found to dominate in the reaction mixture. It remained intact when the reaction temperature was elevated to –40 ^{o}C. Coupling product **271** was obtained in 63% yield, together with 16% of protonated product **272** and trace amount of **273**.

Table 8 Low Temperature ^{29}Si-NMR Experiments



entry	Conditions	Major Si peak (ppm)	**271** (%)	**272** (%)	**273** (%)	**274** (%)
1	-78 ^{o}C, 25 m	7.49	-	-	-	-
	n-BuBr, 10 m	-10.7	93	7	-	-
2	-78~ -20 ^{o}C, 20 m	7.76	-	-	-	-
	0 ^{o}C, 30 m	7.44, -8.83	-	-	-	-
	rt, 1 h	-8.71	-	-	-	-
	H_2O	7.49, -0.01 -4.75, -8.71	-	28	7	13
3	d^0-THF, HMPA -80 ~ -40 ^{o}C, 20 m	-108.0	-	-	-	-
	-78 ^{o}C, BuBr, 5 m	-	63	16	-	3

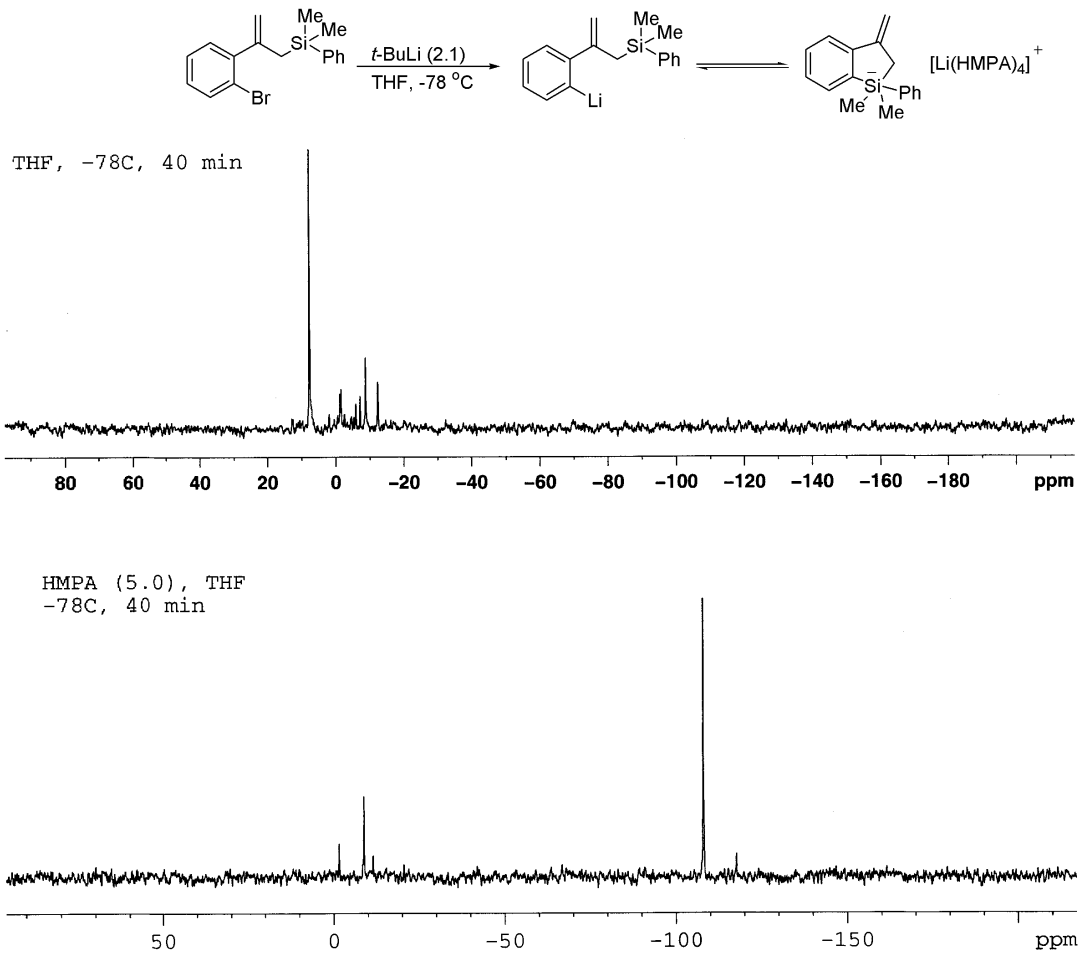
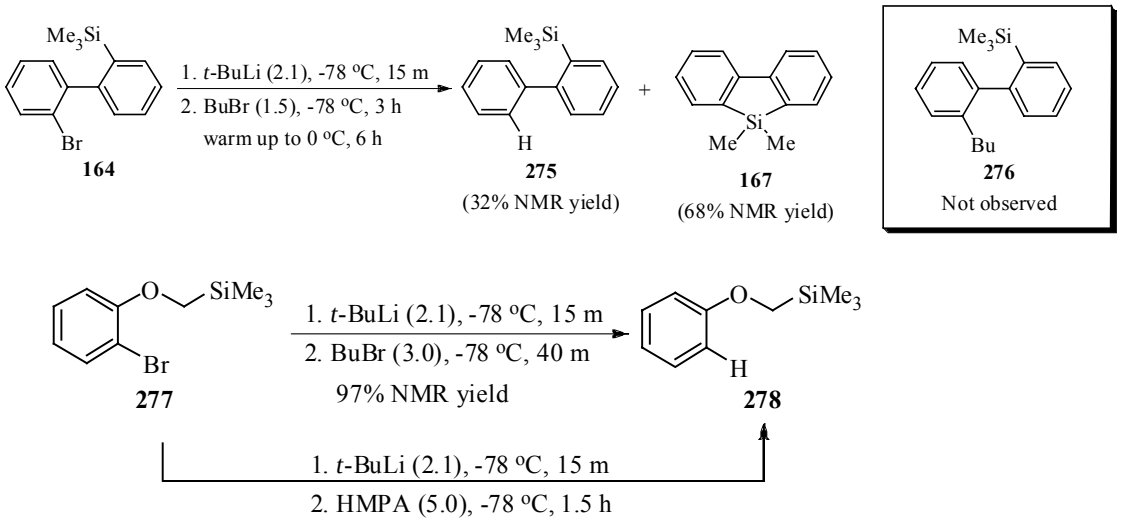


Figure 11 ^{29}Si-NMR Experiments of **270** with *t*-BuLi and HMPA

2.4 Attempts of Coupling Reaction on other Silane Substrates

Excited by the results of the novel coupling reaction of the bromosilane system, we started to explore the generality of this coupling reaction. Known bromosilane **164** was prepared. When **164** was treated with *t*-BuLi and subsequently treated with bromobutane, compounds **275** and **167** were obtained in 32% and 68% yields, respectively. No coupling product **276** was observed in the reaction mixture. Compound **277** was also subjected to the sequence of lithium-halide exchange and quenching with electrophiles

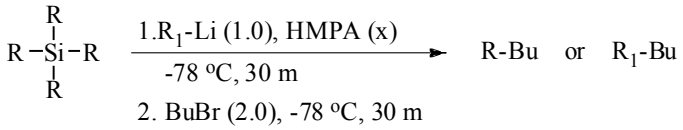
both in the absence and presence of HMPA. Compound **278** was obtained as the sole product in both cases.

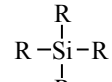
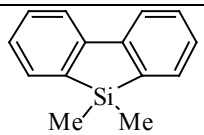
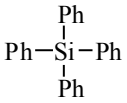
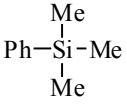


Scheme 63 Attempts of Intramolecular Coupling Reaction on **164** and **277**

The intermolecular coupling reaction was also explored on three different silane systems that were known to form the pentaorganosilicate intermediates upon treatment with an organolithium (Table 9). When 5,5-dimethyldibenzosilole **167** was treated with 1.0 equiv of phenyllithium followed by the quenching with 1-bromobutane, no reaction was observed with or without 10 equiv. of HMPA (entry 1). Similarly, no reaction took place with the tetraphenylsilane **172** and phenyltrimethylsilane **279** (entries 2 and 3).

Table 9 Attempts of Intermolecular Coupling Reaction



entry		R_1-Li	HMPA (x eq)	Coupling Pdt. R-Bu or R_1-Bu
1	 **167**	Ph-Li	0	0[a]
		Ph-Li	10	0[a]
2	 **172**	Bu-Li	0	0[a]
		Bu-Li	5.0	0[a]
3	 **279**	Ph-Li	0	0[a]
		Ph-Li	5.0	0[a]

[a]: Only clean starting material was recovered.

3 Summary

In short, we have made an unusual observation during a lithium-halide exchange reaction and discovered a novel coupling reaction of an organolithium with several primary bromides with the apparent assistance of silicon. The reaction shows generality with several primary bromides with trimethylsilane substrate **243** and phenyldimethylsilane substrate **270**. We hypothesized that a pentaorganosilicate intermediate might be involved in this unusual coupling with alkyl bromides. Detailed mechanistic studies were carried out that support our hypothesis.

The following observations are of key importance:

1. The silicon atom is apparently necessary for the coupling reaction. Only small amounts of coupling products were obtained for **254** (R= H) and **258** (R= *t*-Bu).
2. The presence of alkene is needed to prevent ring closure. The alkene may increase the ring strain of pentaorganosilicate intermediate to facilitate coupling with primary bromides. In contrast, only the release of a methyl group was observed for **262**.
3. A pentaorganosilicate for phenyldimethylsilane **270** was observed by ^{29}Si-NMR, while no pentavalent species was detected for trimethylsilane **243** due to its instablity.
4. Other attempts at coupling reactions with other silane systems turned out to be fruitless.

The experimental results implied that the silicon group plays a role in the process, but that a pentaorganosilicate need not be involved. Further studies might be needed to establish the detailed mechanism of this novel coupling reaction.

Chapter III

Total synthesis of 1-epi-*seco*-pseudopteroxazole

1 Introduction

Since the first isolation of seco-pseudopterosins and pseudopterosins by the Fenical group in the 1980s,[109,110] over 100 marine natural products, bearing diterpenoid structure, have been isolated. The chemistry of diterpenoid marine natural products has gained a lot of attention due to the structural diversity, as well as the large spectrum of biological activities.[111] In the following section, only the diterpenoid compounds bearing serrulatane carbon skeleton will be discussed, including the isolation, biological activities, and related synthesis.

1.1 Serrulatane Diterpenoids from Pseudopterogorgia Elisabethae

Serrulatane diterpenoids (as shown in Figure 12) have a backbone structure, which is comprised of a bicyclic ring and 20 total carbons.

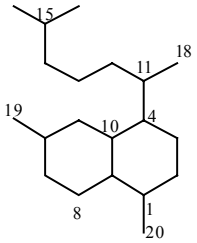
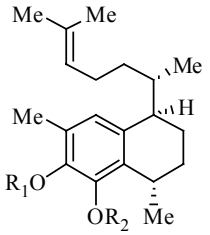
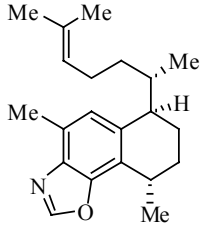


Figure 12 Frame Structure of Serrulatane

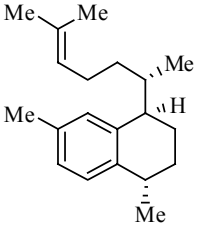
Figure 13 shows nine serrulatane-based natural products that have been isolated from *Pseudopterogorgia elisabethae* up to date. One of the best-known members of this class, *seco*-pseudopterosin aglycone (**280**) was isolated as different glycoside forms.[110,112] S*eco*-pseudopteroxazole (**281**), which bears an unusual benzoxazole moiety, was isolated in 1999.[113] Another notable member, erogorgiaene (**282**), was isolated in 2001 together with its analogue hydroxyerogorgiaene (**283**) and dimer (**288**).[114] Elisabethadione (**284**)[112] also has three closely related analogues: *tert*-hydroxyelisabethadione (**285**)[115], *sec*-hydroxyelisabethadione (**286**)[116] and elisabethamine (**287**)[117]. However, the structure of **287** with labile aminohydroquinone functionality was questioned by Davies group during the attempt of total synthesis of **287**.[118]



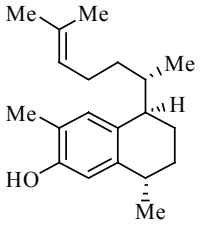
seco-pseudopterosin aglycone (**280**)



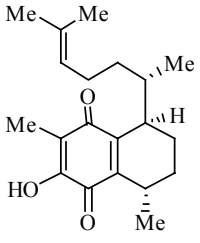
seco-pseudopteroxazole (**281**)



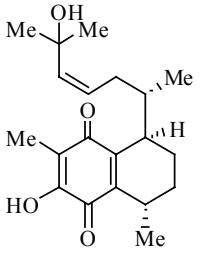
erogorgiaene (**282**)



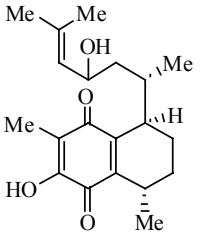
hydroxyerogorgiaene (**283**)



elisabethadione (**284**)



tert-hydroxyelisabethadione (**285**)



seco-hydroxyelisabethadione (**286**)

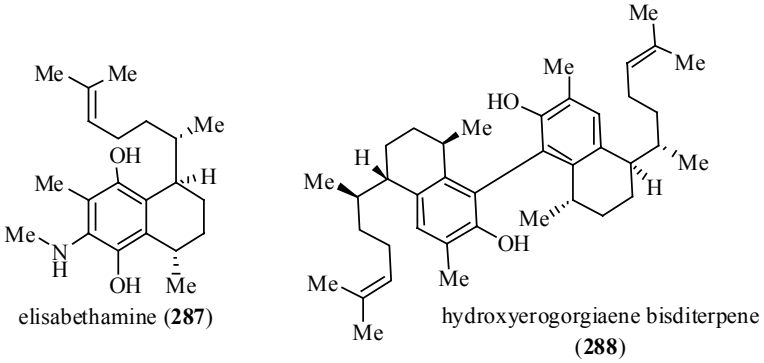


Figure 13 Serrulatane-based Marine Natural Products

Seco-pseudopterosin (**280**) and its glycosides showed promising anti-inflammatory and analgesic activity in a mouse ear anti-inflammatory assay. Moreover, the mechanism of action is distinct from those cyclooxygenase-inhibiting anti-inflammatory nonsteroidal drugs.[119] Another family member, elisabethadione (**284**), also showed moderate anti-inflammatory activity.[112]

Antituberculosis studies were carried out for *seco*-pseudopteroxazole (**281**), erogorgiaene (**282**) and related compounds. Compound **282** was found to have excellent inhibition (96%) against *M. tuberculosis* H37Rv, while **281** and **283** induced 66% and 77% inhibition respectively at a concentration of 12.5 μg/mL.[113,114] The results suggested that the hydroxy group and the benzoxazole moiety are not crucial for the activity.

Additionally, elisabethamine (**287**) exhibited moderate activity against lung cancer and prostate cancer cell lines with IC_{50} values of 10.35 and 20 μg/mL respectively.[117]

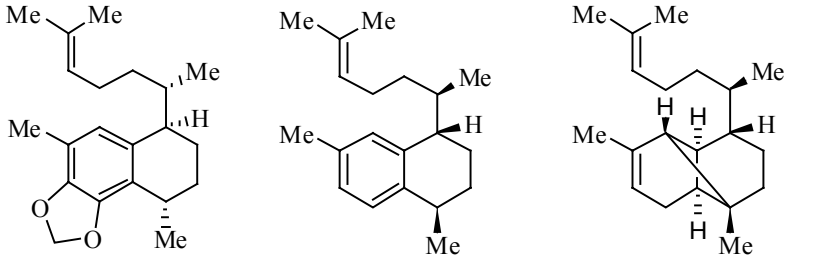
1.2 Serrulatane Diterpenoids from Other Sources

Other than being isolated from the sea whip *Pseudopterogorgia elisabethae*, the serrulatane-type diterpenoids were also found in the blue coral *Heliopora coerulea*, the

far-eastern brown algae *Dictyota dichotoma*, and in the Australian herb *Eremophila* species (Figure 14).

Helioporin D (**289**) was isolated from blue coral *Heliopora coerula* by a Japanese research group.[120] Compound **289** was originally assigned as C-1 epimer of seco-pseudopterosin, which was later revised by Schmalz's group.[121]

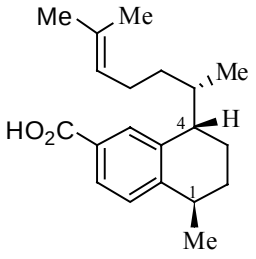
Ent-erogorgiaene (**282**) was found in the far-eastern algae, together with another complex tricyclic compound tetrahydroerogorgiaene (**290**). Both compounds showed moderate activity against human tumor cell lines.[122]



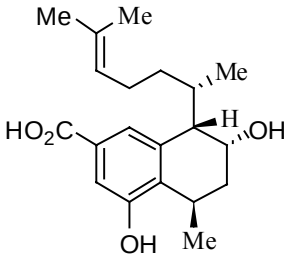
helioporin D (**289**) *ent*-erogorgiaene (**282**) tetrahydroerogorgiaene (**290**)

Figure 14 Natural Products Isolated from *Heliopora Coerulea* and *Dictyota Dichotoma*

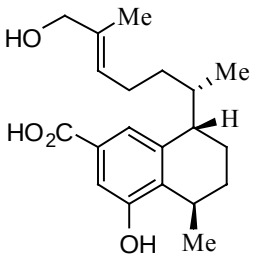
Serrulatic acid (**291**)[123], dihydroxyserrulatic acid (**292**[123], **293**[124]) and trihydroxyserrulatic acid (**294**, **295**)[125] were isolated from the land plant *Eremophila* species in recent years (Figure 15). It is worth pointing out that the configurations of C-1 and C-4 position are opposite to what was observed in the previous marine natural products. Compound **291** and **292** were subjected to the antibacterial and antiflammatory tests. Of particular interest is that **291** showed strong bactericidal activity against *S. aureus* with the minimum bactericidal concentration of 15 μg/mL and potent inhibitory against COX-1 (27 μg/mL) and COX-2 (73 μg/mL).



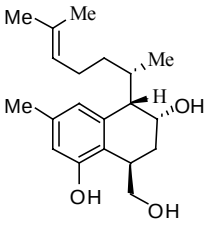
serrulatic acid (**291**)



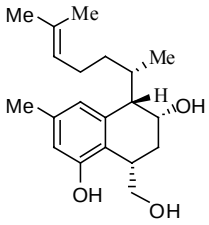
3, 8-dihydroxyserrulatic acid (**292**)



3, 16-dihydroxyserrulatic acid (**293**)



3, 8, 20β-trihydroxyserrulatic acid (**294**)

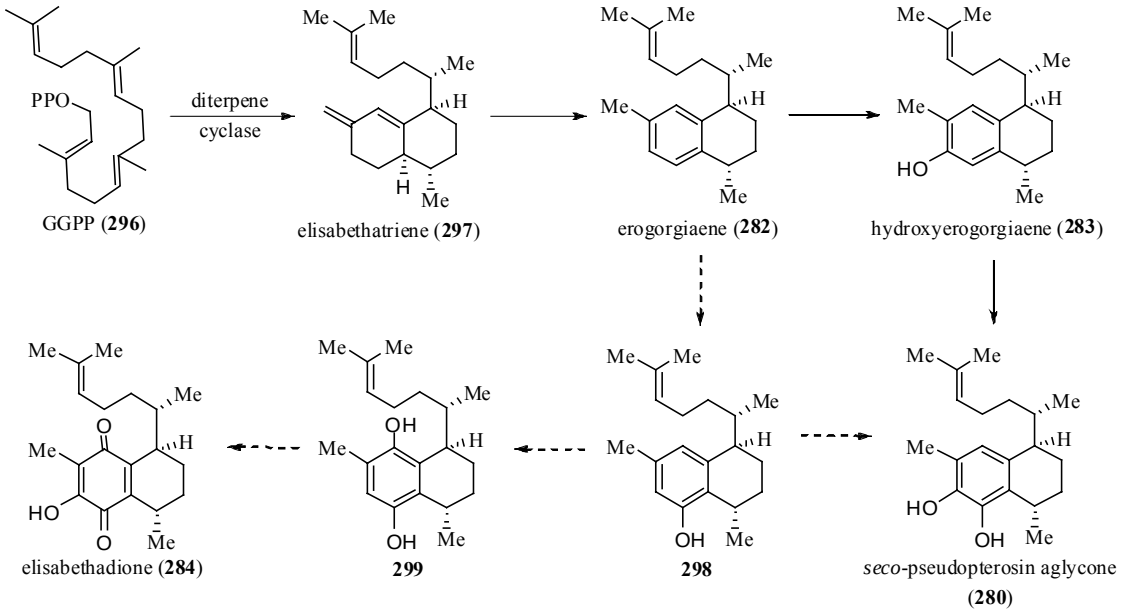


3, 8, 20α-trihydroxyserrulatic acid (**295**)

Figure 15 Natural Products Isolated from *Eremophila* Species

1.3 Biosynthesis of Serrulatane Diterpenoids

Extensive biosynthetic studies of serrulatane diterpenes have been carried out using various techniques in the Kerr group.[126-129] With the assistance of the enzyme diterpene cyclase, geranylgeranyl pyrophosphate (GGPP **296**) was transformed into elisabethatriene (**297**), which undergoes aromatization to form erogorgiaene (**282**). Oxidation at C-7 position and C-8 position produces *seco*-pseudopterosin aglycone (**280**). 5, 8-dihydroxylation of **282** could deliver the intermediate **299**, which could further transform into elisabethadione (**284**). Finally, serrulatane diterpene natural products are generally considered the biosynthetic precursors of other complex polycyclic members, which are also isolated from *Pseudopterogorgia elisabethae* (Scheme 64).



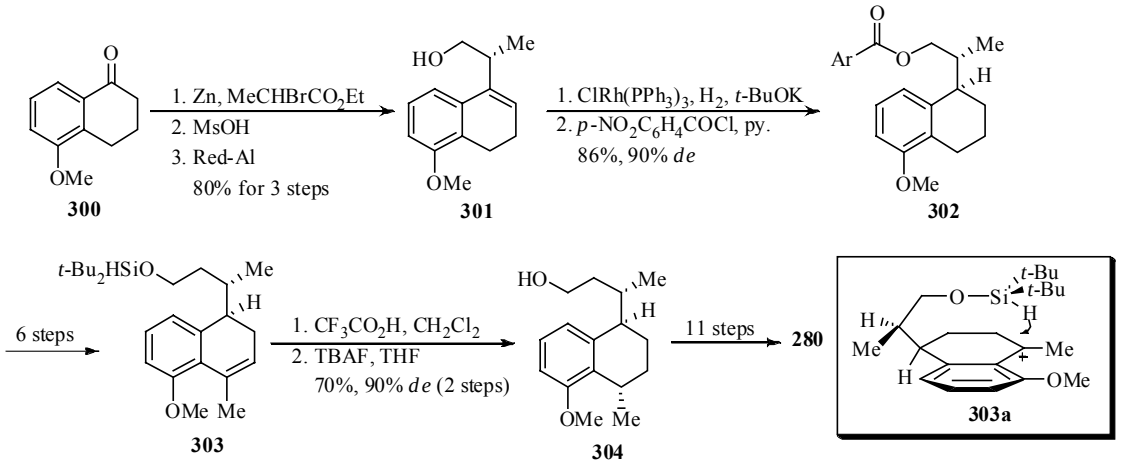
Scheme 64 Biosynthesis of Serrulatane Diterpenoids

1.4 Synthetic Efforts

Stimulated by the wide spectrum of biological activities and the potential biogenetic relationship to many other complex polycyclic diterpenoid natural products, serrulatane diterpenoids have been of particular synthetic interest in recent years. Several elegant routes have been published on the synthesis of the serrulatane and its closely related amphilectane diterpenes. However, due to the fact that I don't want to work too much on this chapter, only those synthetic approaches from starting materials carrying no stereocenter will be discussed. The strategies starting from terpene-derived units with established stereocenters will not be presented.[130-136] Also the elegant syntheses of C-1 epimeric pseudopterosins and pseudopteroxazole from Kocienski[137] and Corey [138] will not be addressed.

1.4.1 *seco*-pseudopterosin Aglycone

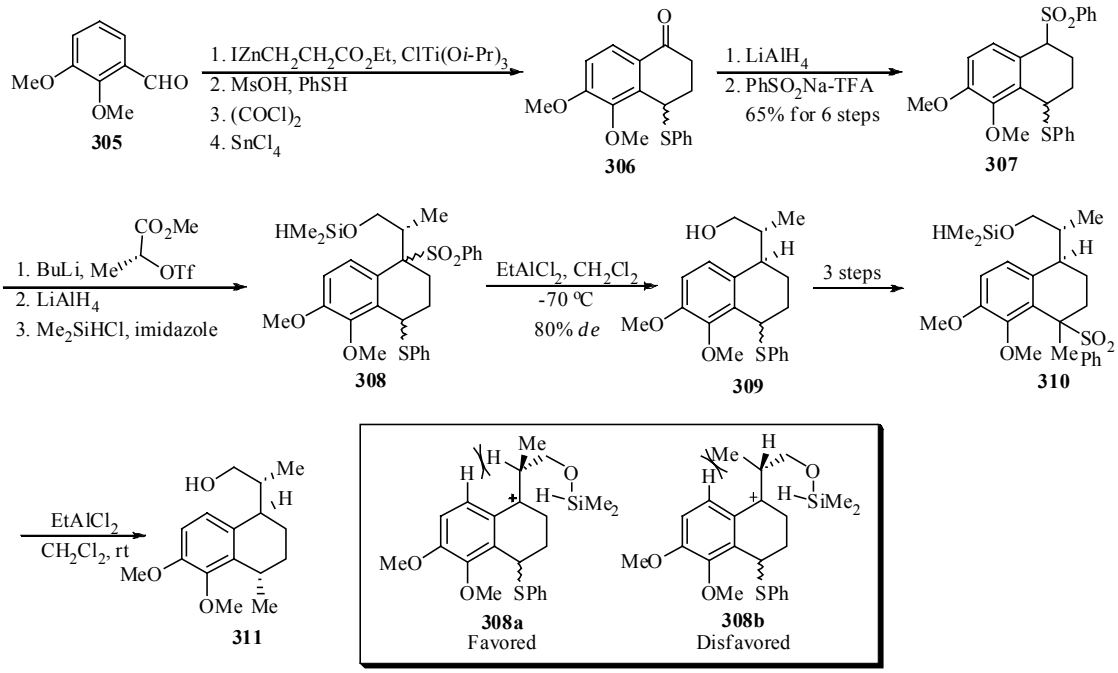
McCombie reported the first total synthesis of the *seco*-pseudopterosin aglycone (**280**) utilizing a novel intramolecular ionic hydrogenation.[139] Commercially available 5-methoxytetralone (**300**) was converted to alcohol **301**. The relative stereochemistry of C-4 and C-11 position was set up nicely by directed hydrogenation using Wilkinson's catalyst to minimize the 1,4- allylic strain. Regioselctive benzylic oxidation and several steps of functionality transformation furnished olefin **303**. Catalytic hydrogenation (H_2, Pd/C) exclusively gave C-1 epimer, generated by the attack from the less hindered face (*Re* face) of benzylic alkene. Ionic reduction (Et_3SiH, TFA) gave **304** and its C-1 epimer with a raio of 2:3. Finally, an intramolecular ionic reduction delivered **304** in 70% yield with 90% *de*. It presumably proceeded through the 9-membered ring transition state intermediate **303a**. The total synthesis of racemic **280** was completed in several steps (Scheme 65).



Scheme 65 McCombie's Total Synthesis of Racemic *seco*-pseudopterosin Aglycone

Two years later, the same group published an enantioselective route to the key intermediate dimethoxy derivative **311**.[140] Compound **307** was prepared from aldehyde

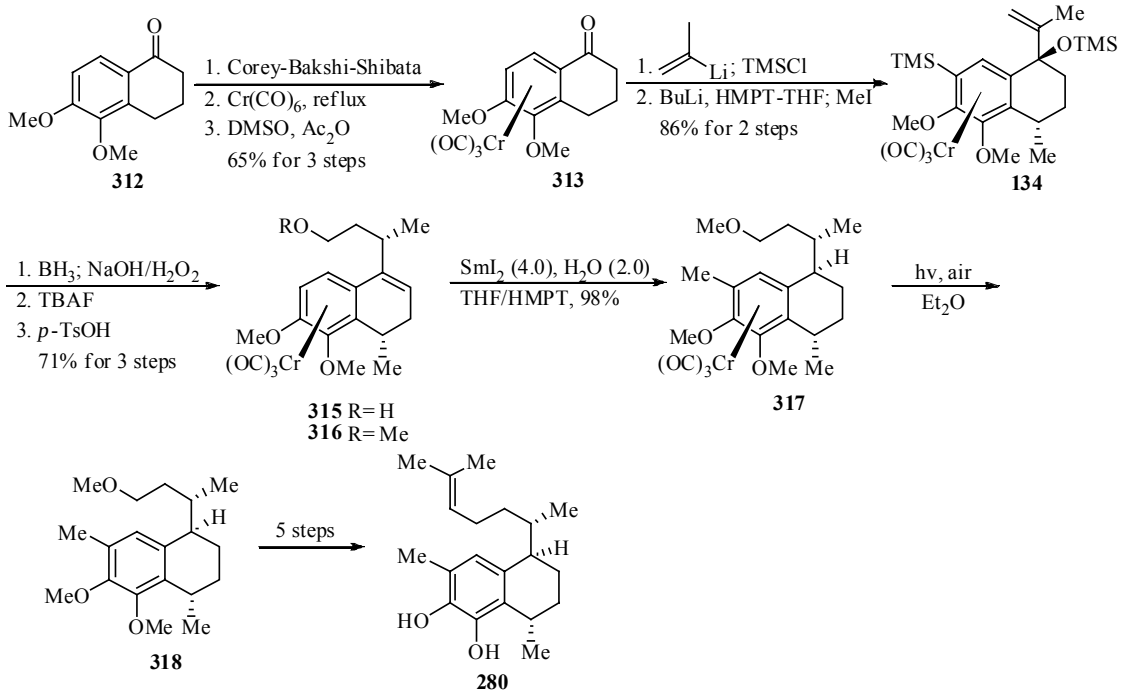
305 in 6 steps in 65% overall yield. S_N2 displacement of a triflate set the C-11 stereocenter with 90% *de* as indicated by chiral HPLC. The ester was reduced and then converted to dimethylsilyl ether **308**, which was then treated with $EtAlCl_2$ in CH_2Cl_2 at – 70 ^oC. The desired isomer **309** was generated in a 9:1 diastereomer ratio. Again, the stereochemical outcome could be explained by minimizing the 1, 4-allylic strain (as shown **308a** and **308b**). Several steps of operations delivered sulfone **310**, which underwent the intramolecular ionic reduction to give key intermediate **311** (Scheme 66).



Scheme 66 McCombie's Enantioselective Synthesis of Key Intermediate **311**

The second synthesis of **280** was accomplished in the Schmalz group.[141] Enantiomerically pure η^6-arene chromium tricarbonyl complex **313** was prepared from tetralone **312** by a sequence of enantioselective reduction, diastereoselective complexation, and oxidation. Both the nucleophilic addition of ketone and the methylation at the benzylic position took place exclusively from the less hindered *exo*

face to provide **314** with high diastereoselectivity. Stereoselective hydroboration followed by deprotection and elimination delivered **315**. Compound **315** was initially subjected to different reducing reagents. No conversion was observed under ionic reduction (TFA/$SiHEt_3$) or catalytic hydrogenation (Pd/C or Raney-Ni). Only 65% conversion was observed when it was reduced by SmI_2 in THF/HMPT/H_2O. However, methylated compound **316** afforded **317** in quantitative yield, which was further converted to **318** by oxidative decomplexation and then *seco*-pseudopterosin aglycone **280**. This synthesis requires 17 steps with a 13.2% overall yield from commercial available veratrole (Scheme 67).



Scheme 67 Schmaltz's Enantioselective Total Synthesis of *seco*-Pseudopterosin Aglycone

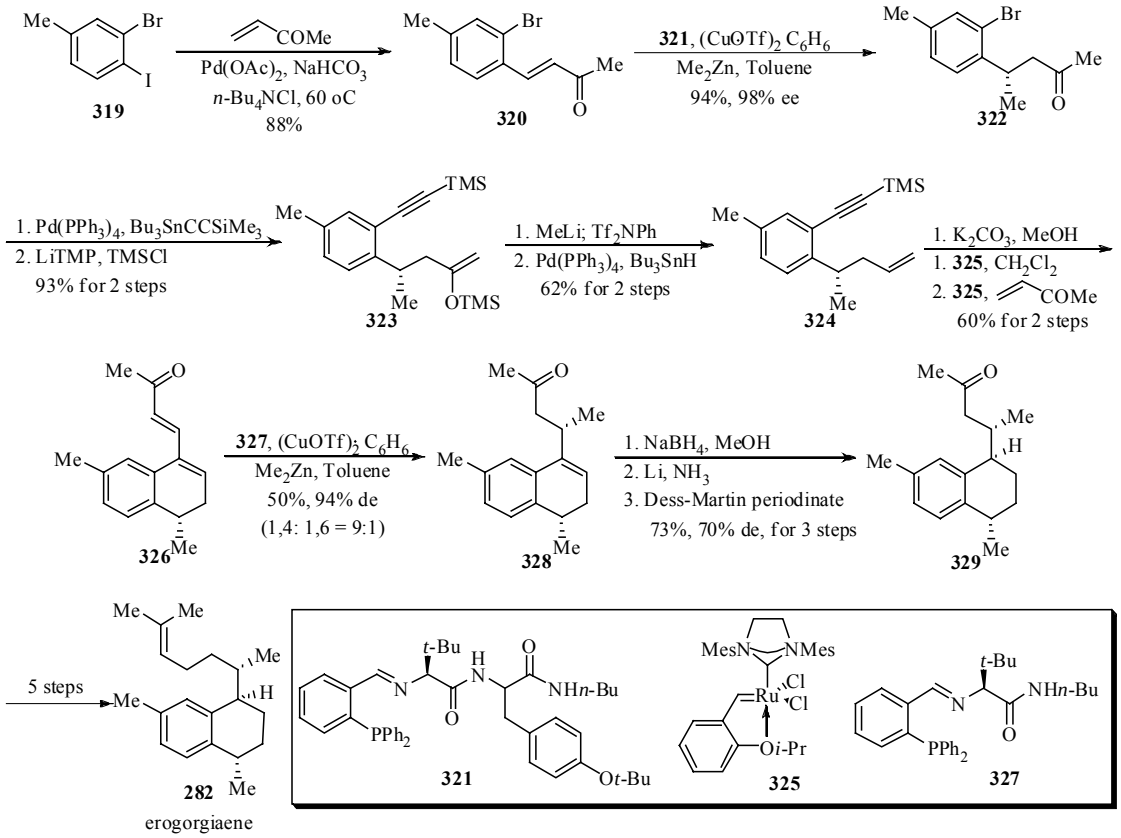
1.4.2 Erogorgiaene

Erogorgiaene (**282**) is another popular target in the synthetic community due to its potent antituberculosis activity. So far, there have been three published total syntheses of **282** and one formal synthesis.

The first enantioselective total synthesis of **282** was published by Hoveyda group in 2004.[142] Bromoketone **320** was prepared from the commercially available dihalide **319** through an intermolecular Heck coupling reaction. Cu-catalyzed asymmetric conjugate addition was carried out in the presence of chiral phosphine ligand **321** to deliver β-methyl ketone **322** in 94% yield with 98% *ee*. Stille coupling followed by regioselective deprotonation gave the intermediate compound **323**. The TMS enol ether was further converted to enyne **324** by a 3-step sequence of triflation, reduction and deprotection. Intramolecular ring-closing metathesis and cross metathesis produced α, β-unsaturated ketone **326** in good yield. After screening various reaction conditions, chiral phosphine ligand **327** gave conjugate addition product **328** with excellent diastereoselectivity and high regioselectivity.

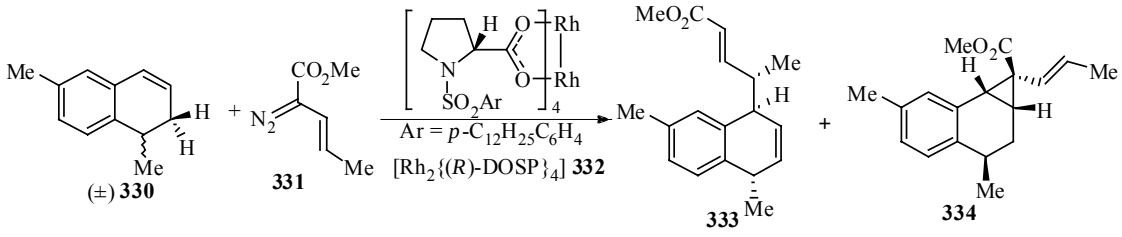
Diastereoselective reduction of **328** employing catalytic or ionic hydrogenation predominantly afforded the thermodynamically more stable *cis* product, reaction occurring from the less hindered face of benzylic alkene. Reduction of the ketone, dissolving metal reduction (Li, NH_3) and Dess-Martin oxidation afforded **329** in 73% overall yield with 85:15 diastereoselectivity. The desired diastereomer was isolated after chromatography. Compound **329** was converted to erogorgiaene after several functional group transformations. The first enantioselective total synthesis of

erogorgiaene was accomplished with a 4% overall yield in 18 steps from commercially available 2-bromo-1-iodo-4-methyl benzene (Scheme 68).



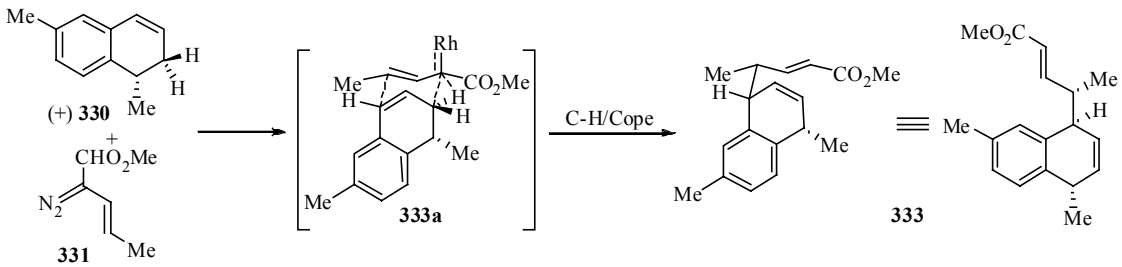
Scheme 68 Hoveyda's Enantioselective Total Synthesis of Erogorgiane **282**

In 2005, Davies group[143] reported an elegant total synthesis of erogorgiaene utilizing the strategy of the combined C-H activation / Cope rearrangement. The synthesis started from readily available racemic dihydronaphthalene **330**. Compound **333** was obtained in an enantiopure form together with cyclopropane **334** as a 1:1 mixture (Scheme 69).



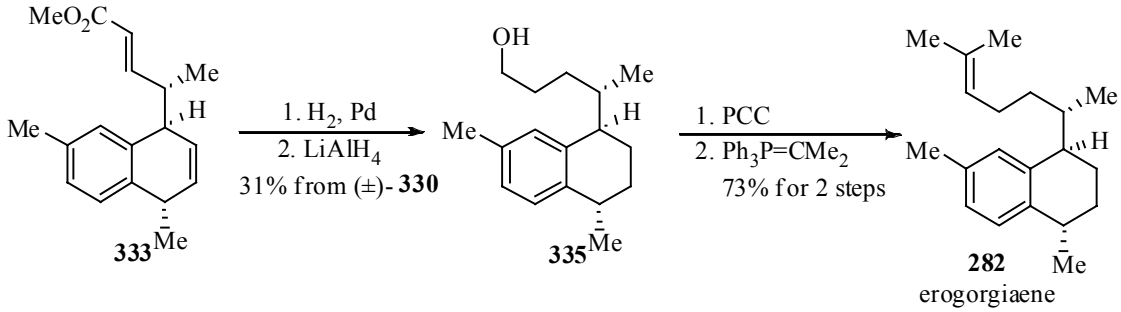
Scheme 69 Davies's Synthesis of Key Intermediate **333**

The key to the kinetic enantiodifferentiating step is to take advantage of the different reactivity of (*R*)-**330** and (*S*)-**330**. C-H activation, followed by Cope rearrangement could deliver the 1, 5-diene **333**. The stereochemical outcome could be rationalized by the chair transition intermediate **333a**. When (±)-**330** was reacted with **331** in the presence of *R*-dosp catalyst, (*S*)-**330** fit into the catalyst to give the matched combined C-H activation/Cope rearrangement product **333**. In contrast, mismatched (*R*)-**330** delivered cyclopropane **334** (Scheme 70).



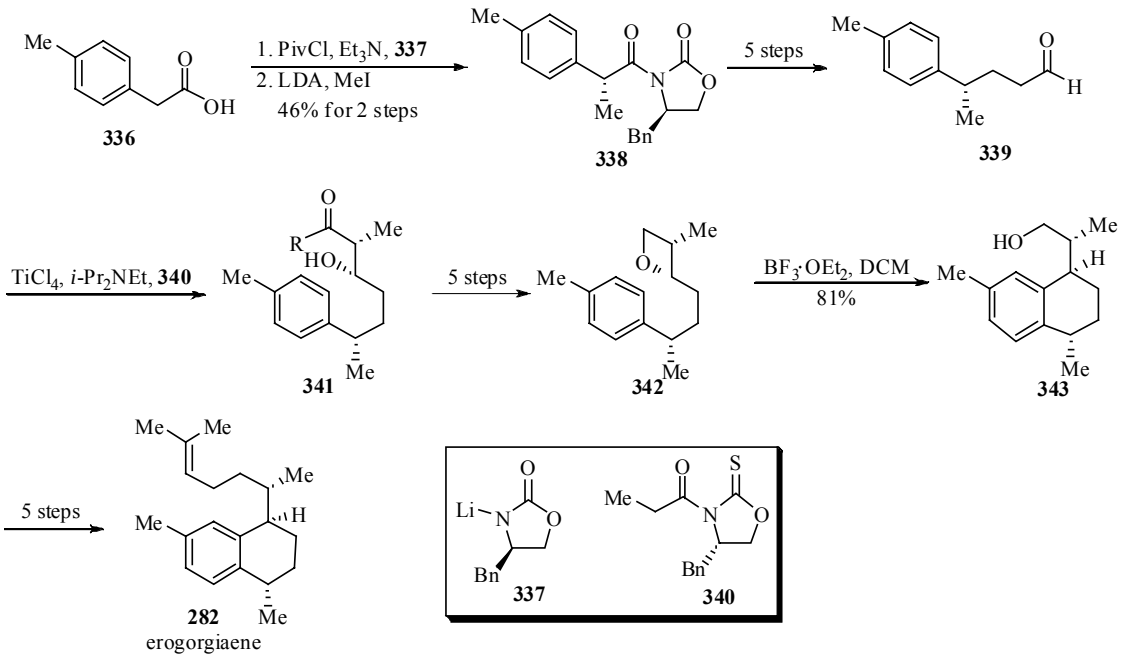
Scheme 70 Mechanism of C-H Activation/Cope Rearrangement

Compound **333** was further converted to **335** by catalytic hydrogenation and LAH reduction. PCC oxidation and Wittig olefination finished the total synthesis of erogorgiaene. This synthesis required 12 steps and gave a 6.3% overall yield from 4-oxo-4-tolylbutanoic acid (Scheme 71). The same C-H activation/Cope rearrangement strategy was also applied to the total synthesis of elisabethadione (**284**).[144]



Scheme 71 Davies's Enantioselective Total Synthesis of Erogorgiaene

Very recently, the Yadav group published another total synthesis of erogorgiaene, featuring an intramolecular Friedel–Crafts reaction of an oxetane. (Scheme 62).[145] The synthesis began with the readily available *p*-tolylacetic acid, which was alkylated with the assistant of an Evans chiral auxiliary to afford **339** with excellent stereoselectivity. Functional group interconversions converted amide **338** to **339**, which underwent *syn* aldol reaction in the presence of titanium chloride under Crimmins conditions. The amide functionality was converted to oxetane **342** in 5 steps. The key step, an intramolecular Friedel-Crafts reaction, was carried out in the presence of a Lewis acid. Cyclization occurred smoothly, resulting in **343** as a single diastereomer. The total synthesis of erogorgiaene was completed in 19 steps with an overall yield of 7% (Scheme 72).

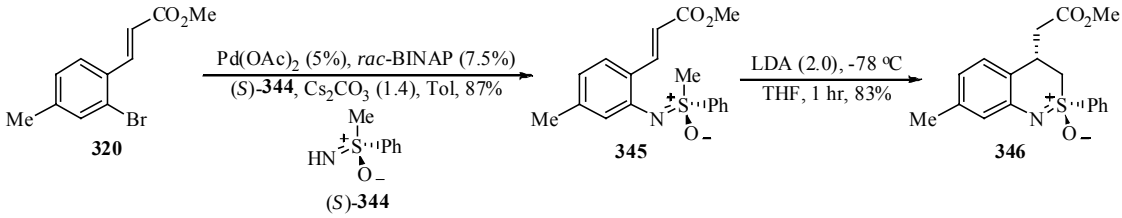


Scheme 72 Yadav's Total Synthesis of Erogorgiaene

1.4.3 Synthetic Efforts from Our Group

1.4.3.1 Formal Synthesis of Erogorgiaene

In 2005, our group published a novel approach to the synthesis of erogorgiaene featuring the highly stereoselective intramolecular Michael reaction.[146] α, β-Unsaturated ester **320** was synthesized from readily available 2-bromo-4-methylbenzaldehyde. Compound **320** was coupled with (*S*)-sulfoximine **344** under the Buchwald-Hartwig condition to give **345** in 87% yield. Base-induced intramolecular Michael addition delivered **346** in 83% yield as a single stereoisomer (Scheme 73).[147]



Scheme 73 Harmata's Benzothiazine Chemistry

The stereochemical outcome of this reaction could be rationalized complying the following two transition state configurations (Figure 16). When subjected to LDA or LiHMDS, the methyl group attached to sulfur was deprotonated to give a carbanion. The unsaturated ester approached the carbanion from the back face to avoid interaction with the phenyl group. Transition state **345a** is more favored than **345b** because **345b** exhibits the unfavorable gauche interaction of α-hydrogen with sulfoximine oxygen.

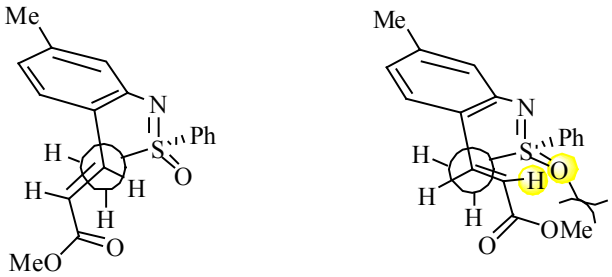
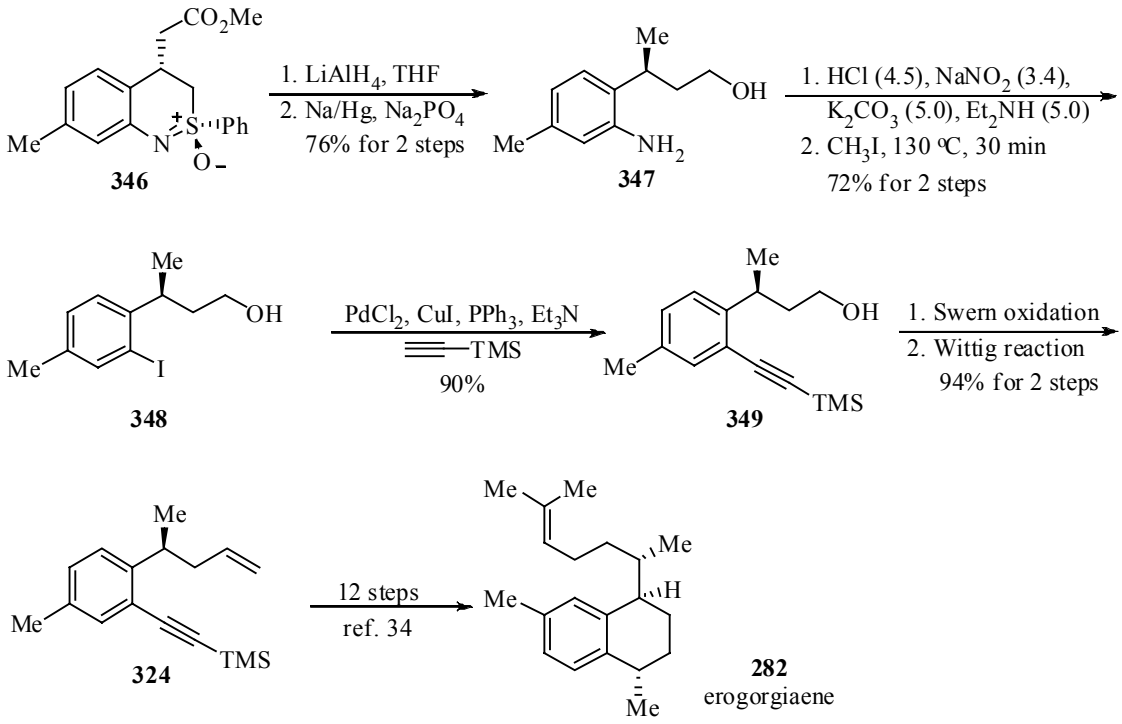


Figure 16 Configuration Analysis

With ester **346** in hand, reduction of the ester to the alcohol and reductive cleavage of sulfoximine auxiliary produced aniline **347** in 76% yield. Aryl iodide **348** was obtained by a sequence of triazene formation and iodination. Sonogarshira coupling with TMs-acetylene gave **349** in 90% yield. Finally, the primary alcohol was converted to the Hoveyda intermediate **324** in two more steps (Scheme 74).



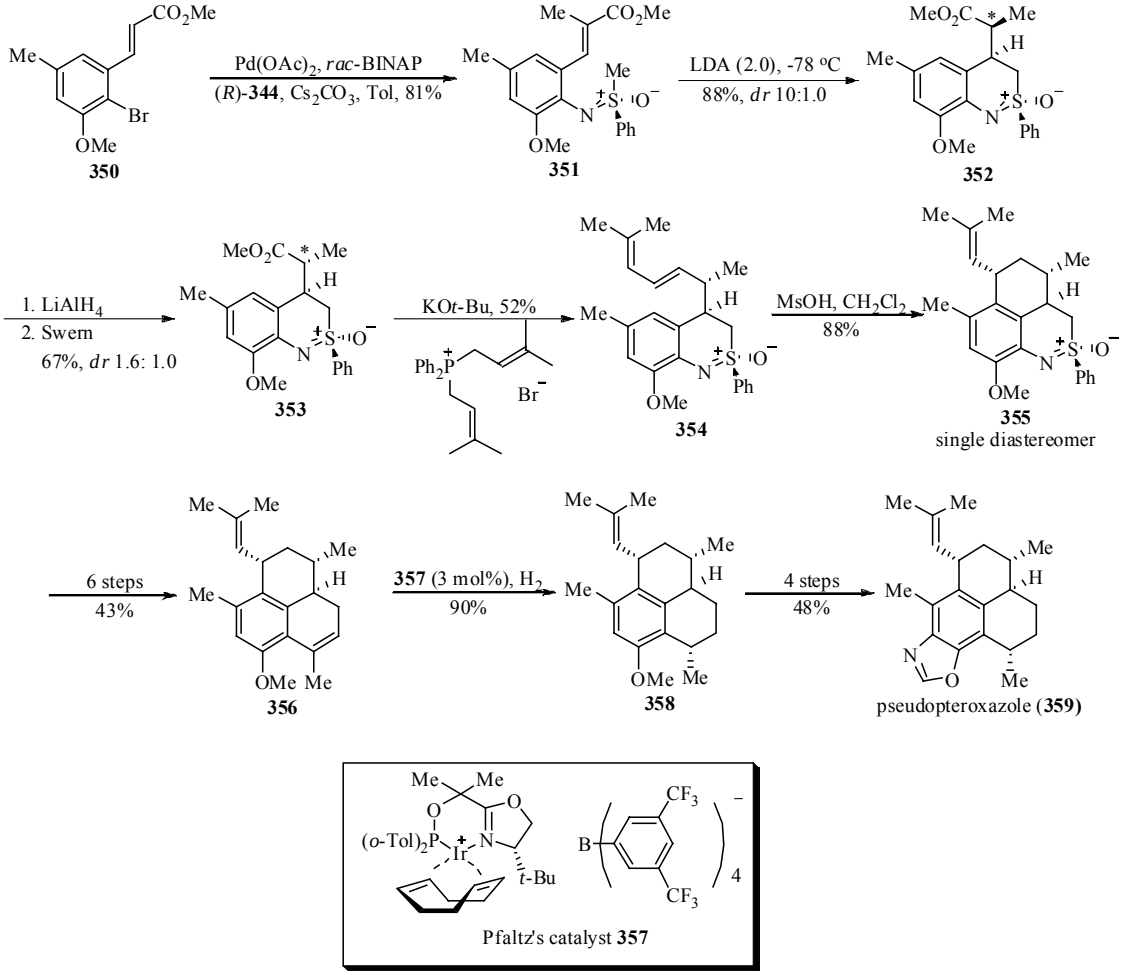
Scheme 74 Harmata's Synthesis of Key Intermediate Benzothiazine Chemistry

1.4.3.2 Total Synthesis of Pseudopteroxazole

As a part of a program aimed at the synthesis of antitubercular active products, we became interested in the synthesis of pseudopteroxazole,[148,149] a close relative to *seco*-pseudopteroxazole but with higher inhibitory activity against *M. tuberculosis* H37Rv.

Beginning with α, β-unsaturated ester **350**, coupling product **351** was obtained in 81% yield. Compound **351** was converted to benzothiazine ester **352** with incorrect stereochemistry at the methyl-bearing center in 88% yield and 90% *de*. Reduction and aldehyde formation with concomitant epimerization gave the desired *R* stereochemistry in a ratio of 1.6: 1.0 *d.r.*. When the diastereomeric mixture **353** was subjected to Wittig reaction, the desired product **354** was isolated in 52% yield after column chromatography. Intramolecular Friedel-Crafts alkylation gave tricyclic compound **355** in

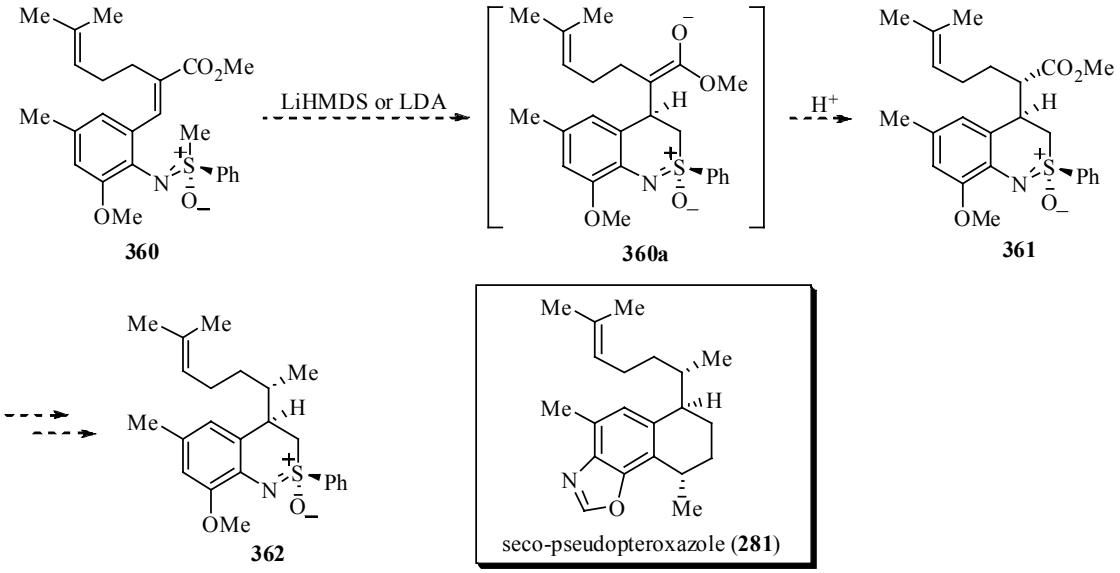
88% yield as a single diastereomer. Hydrogenation precursor **356** was generated in 43% yield in 6 steps. Asymmetric hydrogenation using Pfatlz's chiral catalyst **357** gave the desired isomer **358** with 158:1.0 *d.r.*. Installation of the oxazole ring led to the second total synthesis of pseudopteroxazole **359**. This synthesis required 17 steps and proceeded in 4.1% overall yield (Scheme 75).



Scheme 75 Harmata's Total Synthesis of Pseudopteroxazole **359**

2 The Studies Towards the Total Synthesis of *seco*-Pseudopteroxazole

Even though our group successfully accomplished the total synthesis of pseupteroxazole (**359**), we still wanted to solve the stereochemical problem faced in the synthesis of **352**. Our idea was as follows (Scheme 76). An intramolecular Michael reaction could be carried out on the substrate **360** bearing an alkyl chain. The resulting enolate could be kinetically protonated to give **361**. The ester group could be further converted to methyl group in a few steps. As a part of our synthetic program, we became interested in applying this idea to the total synthesis of *seco*-pseudopteroxazole **281**.

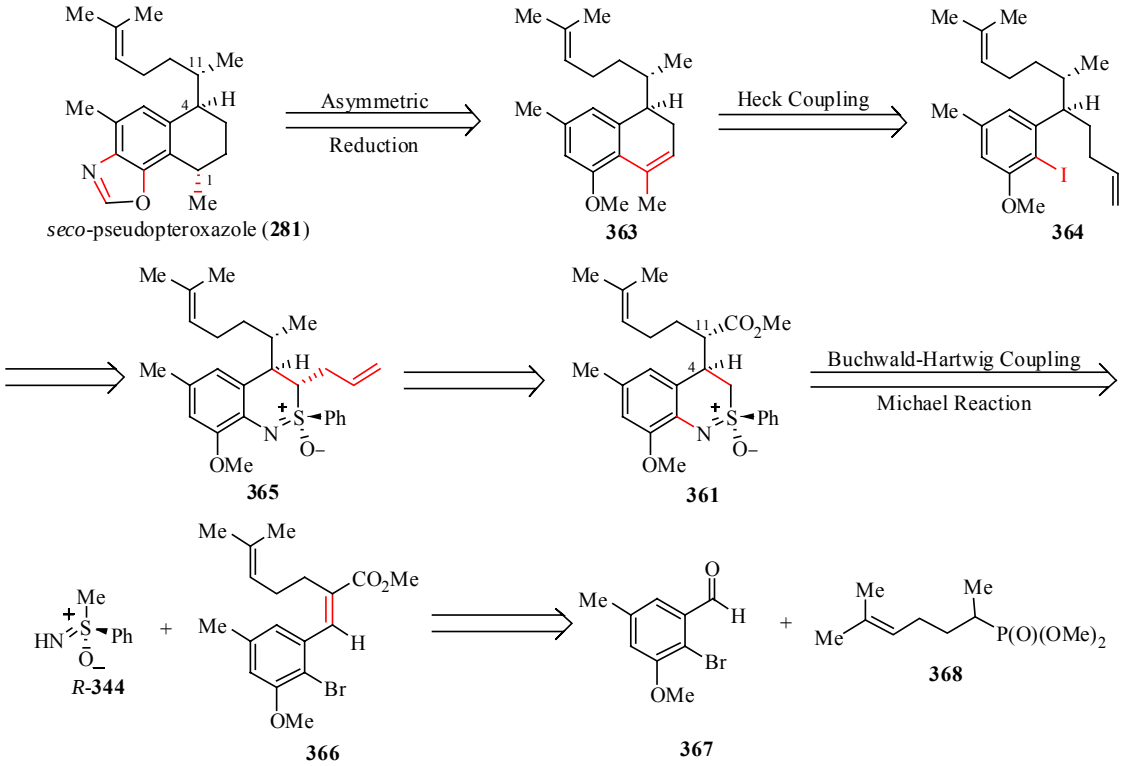


Scheme 76 Proposed Synthesis of Key Intermediate **362**

2.1 Synthetic Plan

Seco-pseudopteroxazole (**281**) could be synthesized from **363** by installation of oxazole ring and asymmetric reduction. Compound **363** could be obtained by intramolecular Heck coupling of aryl iodide **364**. Cleavage of the sulfoximine auxiliary could convert **365** to **364**. **365** could be produced from α,β-unsaturated ester **366** by our

benzothiazine chemistry. Roush-modified Horner-Wadsworth-Emmons reaction could access ester **366** with good stereoselectivity (Scheme 77).

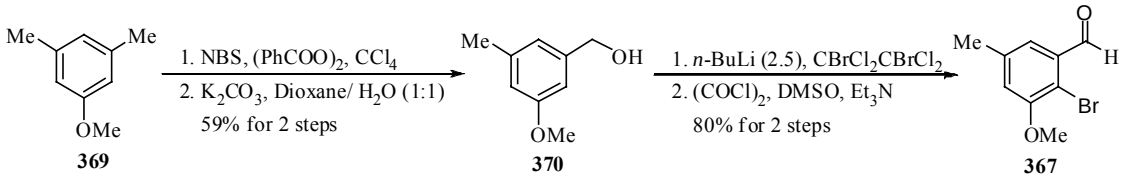


Scheme 77 Synthetic Plan to *seco*-pseudopteroxazole **281**

2.2 Results and Discussion

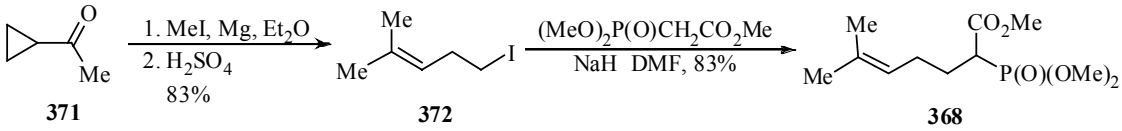
2.2.1 First Approach to Introduce the Stereochemistry at C-4 and C-11 Position

Starting from commercially available 3,5-dimethylanisole **369**, benzylic alcohol **370** was synthesized in 59% yield by monobromination and hydrolysis.[150] *Ortho*-directed bromination of **370**, followed by Swern oxidation delivered bromoaldehyde **367** in 80% yield (Scheme 78).



Scheme 78 Synthesis of Bromoaldehyde **367**

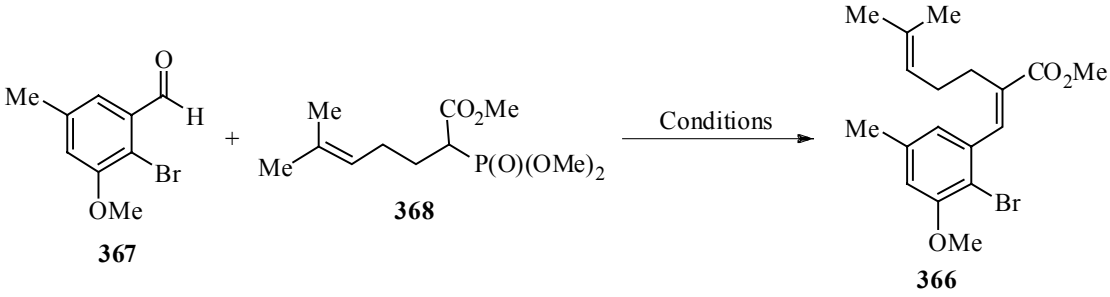
Another starting material, phosphonate **368**, was synthesized from cyclopropyl methyl ketone **371**. Addition of Grignard reagent gave tertiary alcohol, which further underwent acid-catalyzed carbonium rearrangement to give a 5-iodo-2-methylpent-2-ene **372**.[151] Compound **368** was generated in 83% yield together with 6% of dialkylated phosphonate (not shown) upon treatment of iodide **372** with phosphonoacetate anion (Scheme 79).[152]



Scheme 79 Synthesis of Phosphate **368**

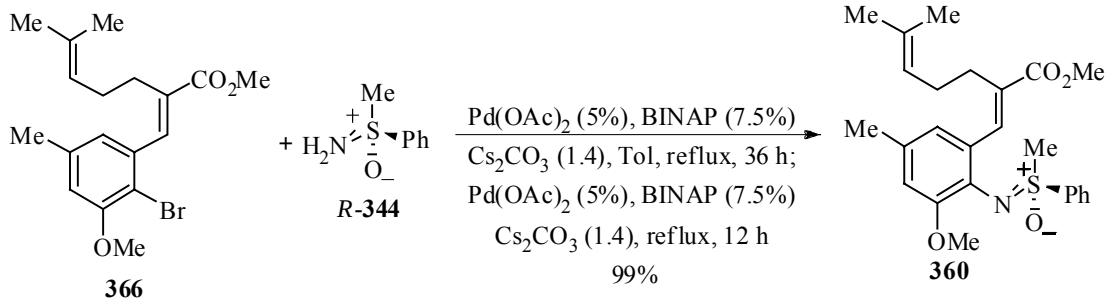
Several reaction conditions were investigated to achieve good *E* selectivity for olefination reaction (Table 10). Under standard conditions for the Horner-Wadsworth-Emmons reaction (*n*-BuLi, THF, 0 ^{o}C to room temperature), ester **362** was obtained as a mixture of *E* and *Z* isomers (*E*:*Z* 5.0:1.0) (entry 1). When the same reaction was conducted using the Roush's modified conditions[153], the *E/Z* ratio increased to 10:1.0 and the *E* isomer was isolated in 83% yield (entry 2).

Table 10 Synthesis of *E*-trisubstituted α, β-unsaturated Ester **366**



entry	Conditions	Yield (%)	*E*: *Z*
1	**368** (1.1), BuLi (1.1) THF, 0 ^{o}C, 15 mins, rt, 12 h	NA	5.0: 1.0
2	**368** (1.2), LiCl (1.2), DBU (1.0) MeCN, RT, 4 h	83% E + 10% Z	10: 1.0

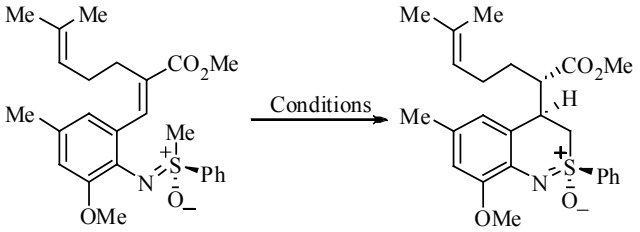
With ester **366** in hand, coupling with enantiomerically pure *R*-sulfoximine (**344**) in the presence of 5% $Pd(OAc)_2$, 7.5% racemic BINAP and 1.4 eq of Cs_2CO_3 afforded **360**. The conversion of the starting material largely relied on the efficiency of the catalyst system. In our hands, the conversion varied from 30% to 80%. However, complete conversion was achieved when additional catalyst ($Pd(OAc)_2$ and BINAP) was added after 36 h (Scheme 80).



Scheme 80 Synthesis of Benzothiazine Ester **360**

With **360** in hand, we started to explore the intramolecular Michael reaction, one of the key steps in this total synthesis (Table 11). Initial attempts using previously reported procedures afforded the desired product in good yield. But neither LDA nor LiHMDS produced acceptable diastereoselectivity (entries 1 and 2). This poor selectivity could result from the rapid epimerization at C-11 position during the protonation of enolate. When using LDA as a base, cold HCl in methanol as a proton donor increased the diastereomeric ratio from 3.8: 1.0 to 5.8: 1.0 (entry 3). A diastereomeric ratio of 9.2: 1.0 was obtained when the reaction was quenched by cold 1N HCl in methanol using LiHMDS as a base (entry 4). A weaker but sterically hindered proton donor (diisopropyl amine HCl salt) afforded a moderate diastereoselectivity (entries 5 and 6). Gerenally, LiHMDS gave better results compared with LDA, which might suggest the role of free amines (HMDS and DIPA) in the reaction mixture should not be overlooked.

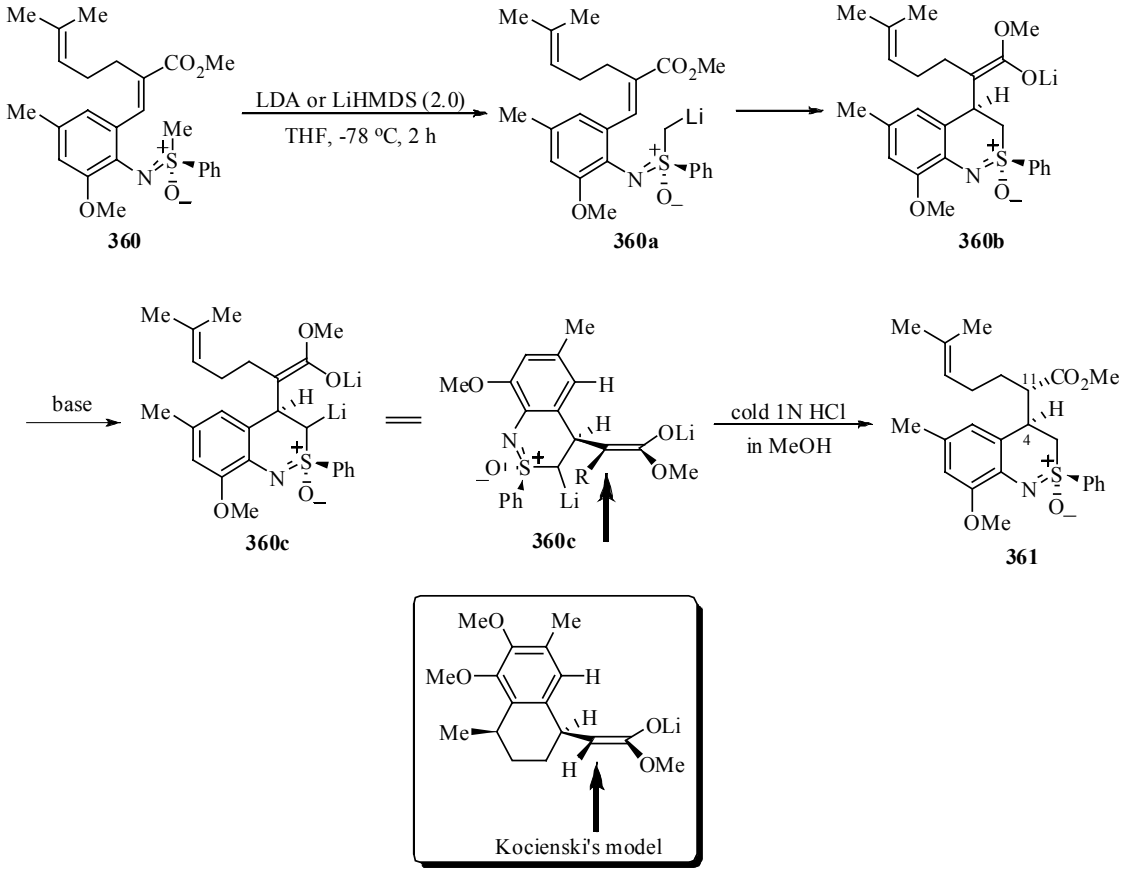
Table 11 Optimization of Intramolecular Michael Reaction



360 **361**

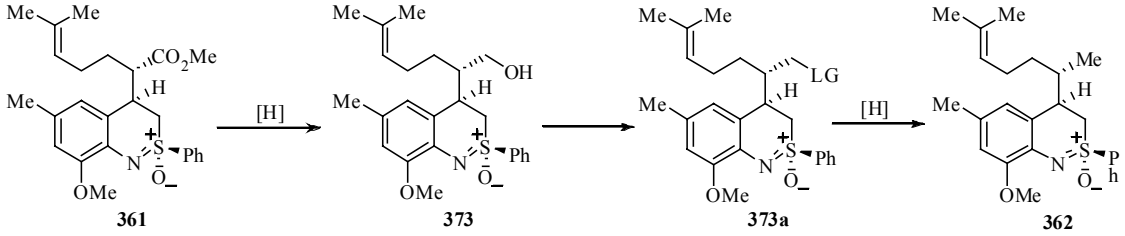
entry	Base (2.0)	quenched by electrophile	*d. r.*	Yield (%)
1	LDA	Cold MeOH	3.8: 1.0	85
2	LiHMDS	Cold MeOH	4.6 :1.0	95
3	LDA	Cold 1N HCl in MeOH	5.8: 1.0	NA
4	LiHMDS	Cold 1NHCl in MeOH	9.2 : 1.0	99
5	LDA	Cold DIPA·HCl in MeOH	4.4: 1.0	98
6	LiHMDS	Cold DIPA·HCl in MeOH	5.6:1.0	80

The rationale for the stereochemical ourcome of the process is shown in Scheme 80. Deprotonation by LDA or LiHMDS gave carbanion **360a**, which could undergo intramolecular Michael reaction to afford enolate intermediate **360b** with high stereoselectivity aided by the sulfoximine auxiliary moiety (as shown in Figure 16). Dianion **360c** might be formed in the presence of excess base. Based on the Kocienski's model[137], an electrophile would prefer to come in from *Re* face of enolate **360c** to avoid the interaction with the hydrogen atom on the benzene ring to give the kinetic products **361**.



Scheme 81 Rationlization of Stereochemical Outcome

After the successful assembly of the stereocenters at the C-4 and C-11 positions, we set out to reduce the ester group to methyl group in a few steps. The strategy is quite straightforward. Reduction of ester would afford alcohol **369**. The hydroxy group could be first converted to a good leaving group (sulfonate ester or iodide), and then further reduced to methyl group (Scheme 82).



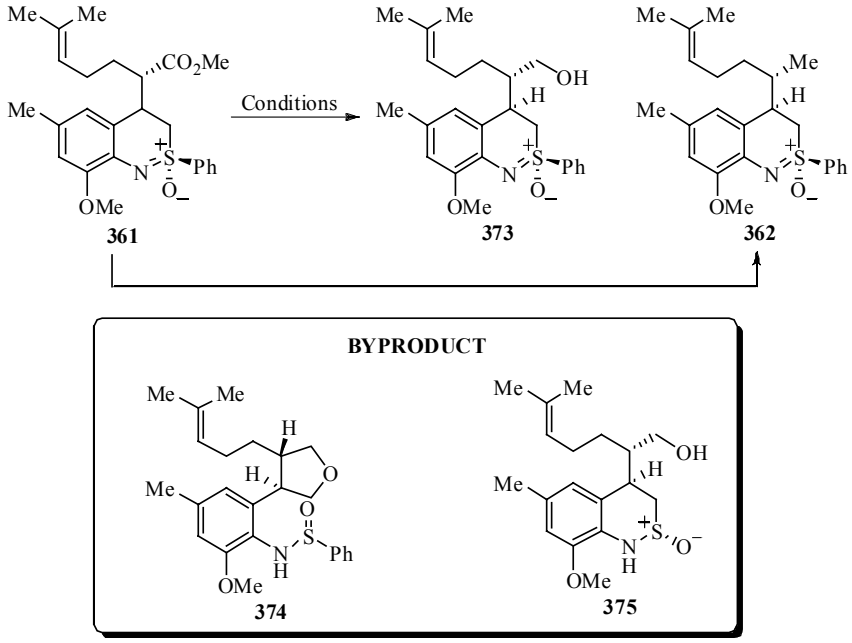
Scheme 82 Proposed Route **358**

However, real life was not as straightforward as we anticipated. The simple reduction of the ester turned out to cause a lot of problems (Table 12). LAH reduction of the ester gave only moderate yields of alcohol varying from 43 to 57% after silica gel column chromatography, despite the fact that relatively clean conversion was achieved up to a 200 mg scale. The low yield of this reaction might be attributed to the lability of alcohol **373**. Compound **373** was prone to rearrangement to give significant mass amount of byproducts under the reaction conditions and during silica gel column chromatography. Two such byproducts were assigned as **374** and **375** based on the spectroscopic data, whose structures were further confirmed by the X-ray data of their analogs. The detailed mechanisms leading to **374** and **375** will be discussed in the following section (entry 1).

Red Al reacted sluggishly with **361** to give a complicated mixture and some starting material (entry 2). Stereo hindered reducing agent DIBAL-H afforded moderate yield of

alcohol **373** (entry 3). Ionic reduction of ester to methyl group using TES and PMHS was carried out in the presence of catalytic and stoichiometric amount of $B(C_6F_5)_3$ (entry 4, 5). [154] Only clean starting material was recovered in both cases. Presumable the sulfoximine group bounded to Lewis acid and deactivated it. Finally, we found that $LiEt_3BH$ is the reagent of choice to give quantitative yield of alcohol **373**, which was immediately used for further steps without any purification (entry 6).

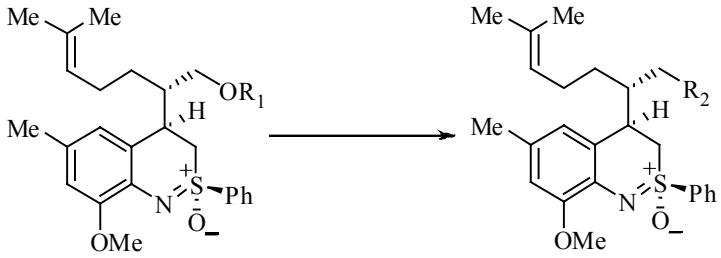
Table 12 Reduction of Ester **361**



entry	Conditions	Yield (%)
1	LAH (1.5), THF, 0 ^{o}C, 0.5 h	43-57
2	Red Al (3.0), 0 ^{o}C, 2 h, rt, 5 h	decomposed
3	DIBAL (2.5), 0 ^{o}C, 1.5 h, rt	46
4	$B(C_6F_5)_3$ 5%, TES or PMHS(5.0), rt, 12 h	Clean SM
5	$B(C_6F_5)_3$ (1.1), PMHS (5.0), rt, 12 h	Clean SM
6	$LiEt_3BH$ (3.0), THF, 0 ^{o}C, 0.5 h	Quant.

To fully explore the reductive cleavage of C-X bond, a series of substrates, including mesylate **376**, tosylate **377** and isopropylsulfonate **378** were prepared from alcohol **373**. Iodide **378** was also prepared from mesylate **376** and tosylate **377** in good yield (Table 13).

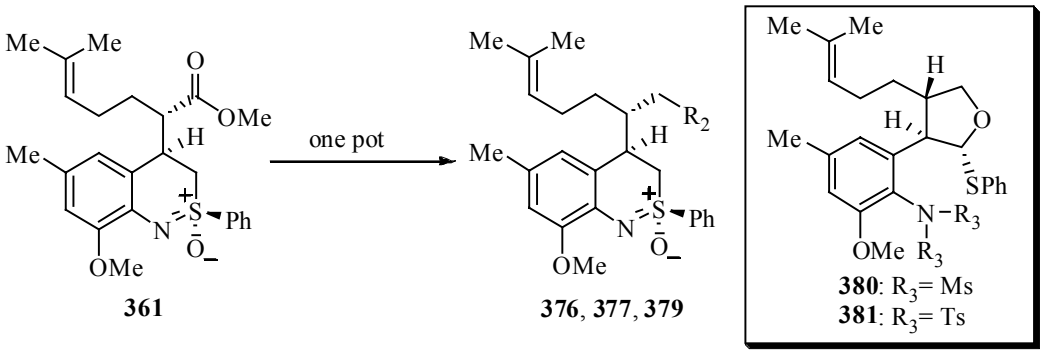
Table 13 Preparation of Sulfonate Esters and Iodide



Entry	R_1	R_2	Compound	Yield (%)
1	H	$-OSO_2Me$	**376**	87
2	H	$-OSO_2Tol$	**377**	87
3	H	$-OSO_2iPr$	**378**	95
4	OTs	-I	**379**	85
5	OMs	-I	**379**	86

Before we found the best reducing reagent ($LiEt_3BH$) for our system, we also carried out the two-step sequence of LAH-reduction and sulfonation to avoid the rapid decomposition of alcohol **373** during the column chromatography. The results are shown in Table 14, together with $LiEt_3BH$-reduction and sulfonation.

Table 14 Preparation of Sulfonate Esters and Iodide from Ester **361** in One-pot



361 **376**, **377**, **379**

Entry	Conditions	R_2	Yield (%) 2 steps	Yield (%) **380** or **381**
1	LAH, THF; TsCl, DMAP, TEA	-OTs	39	18 (**380**)
2	LAH, THF; MsCl, DMAP, TEA	-OMs	45	11 (**381**)
3	LAH, THF; I_2, PPh_3, imid.	-I	86[a], 53[b]	na
4[c]	$LiEt_3BH$, THF; I_2, PPh_3, imid.	-I	80-89	na

[a] 170 mg scale. [b] 400 mg scale. [c] 25 mg- 4.0 g scale.

The crude reaction mixture from LAH reduction, obtained by simple workup with Glauber's salt ($Na_2SO_4 \cdot 10H_2O$) and filteration, was subjected to the sulfonation reaction conditions. The desired sulfonates **376** and **377** were obtained in frustrating yields. However, to our surprise, tetrahydrofuran byproducts **380** and **381** were formed in significant amounts (18% and 11% yield, respectively, Table 14, entries 1 and 2). These structures were assigned based on the extensive NMR studies. For example, The reduction of sulfoximine moiety to –SPh group in **381** was indicated by the higher field of phenyl group as comparison with **376**. The incorporation of two -OTs groups was clearly shown in the proton NMR. The presence of a distinct siglet (: 5.59 ppm) and

unusual low field carbons at 94.9 ppm and 72.3 ppm suggested a tetrahydrofuran moiety in **381**. Finally, the structure of **381** was confirmed by X-ray crystallography (Figure 17).

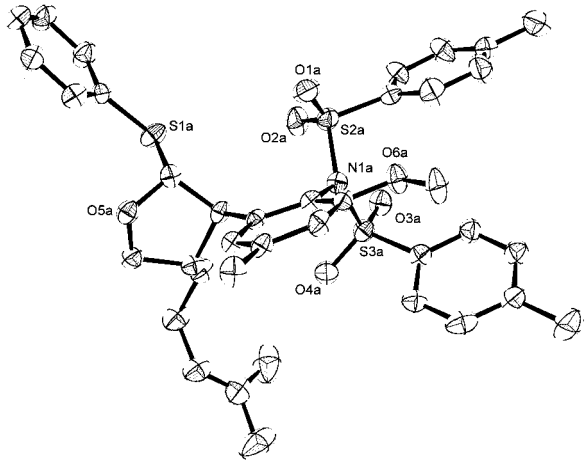
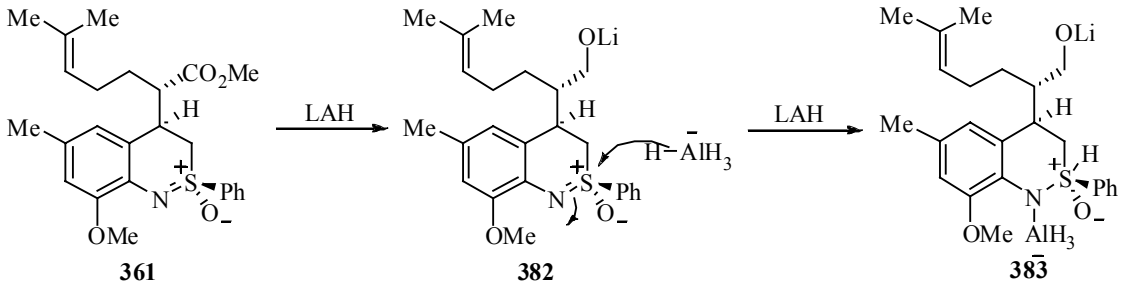
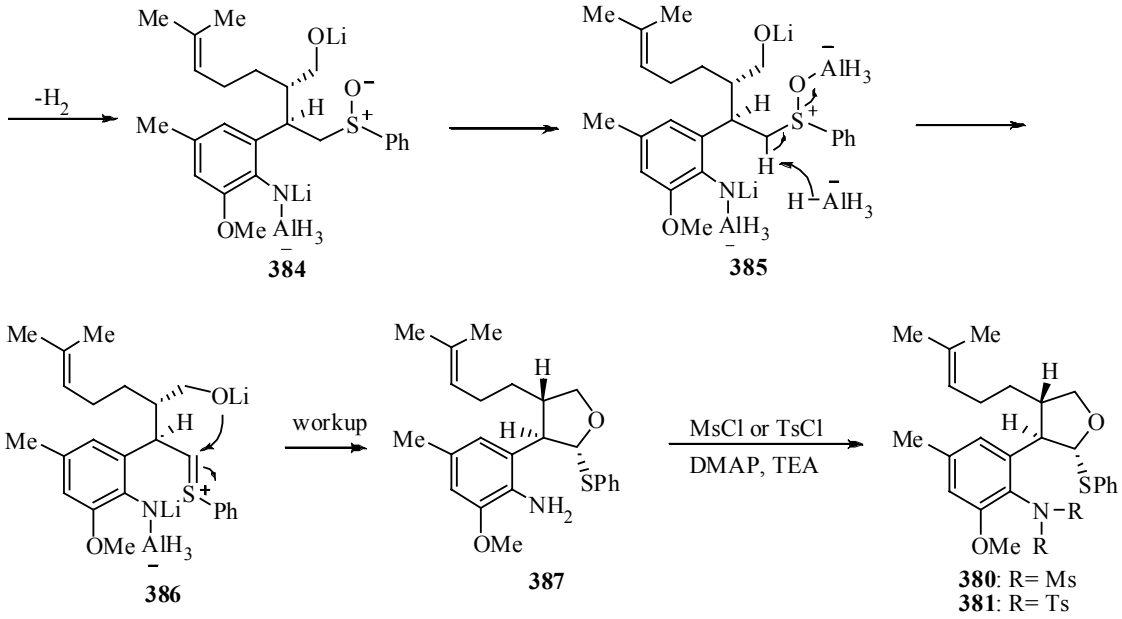


Figure 17 X-ray Structure of **381**

A possible mechanism for the formation of **380** and **381** is proposed in Scheme 82 based on the mechanisms for the LAH reduction of sulfones and sulfoxides. Reduction of ester **361** could give alcohol **382**. S-N bond might be cleaved to afford **384**, which might undergo Pummer rearrangement to give sulfonium intermediate **386**. Subsequent ring closure and Sulfonate ester formation could deliver tetrahydrofuran **380** and **381**,



361 **382** **383**



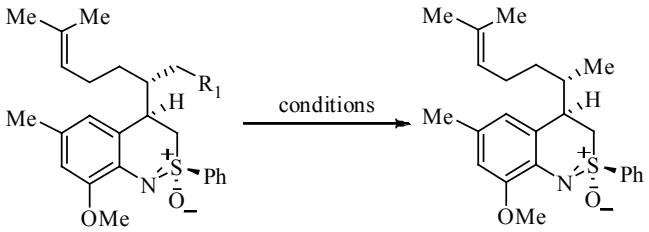
Scheme 83 Proposed Mechanism for the Formation of **380** and **381**

The sequence of LAH-reduction and iodination was also carried out in both small and large scales. As shown before, iodide **379** was obtained in 86% yield for two steps on a scale of 170 mg, but only 53% yield on a 400 mg scale. The LAH reduction of ester didn't give us any consistent results for the different scale reactions. This might have been caused by the increasing heat produced when adding relatively large amounts of LAH (Table 14, entry 3).

A switch to $LiEt_3BH$ did give us a clean conversion of ester to alcohol. The crude alcohol was treated with iodine in the presence of triphenyl phosphine to give iodide **379** in 80-89% yield on a reaction scales from 25 mg to 2.0 g (Table 14, entry 4).

With a reliable procedure to access alcohol derivatives in hand, we set out to explore the reductive cleavage of C-X bond to access key intermediate **362**.

Table 15 Reductive Cleavage Approach to **362**



376-379 **362**

entry	SM	Conditions	Yield (%) **362**	Yield (%) Byproduct
1	**376**	LAH(3.0), Et_2O, -25 ^oC, 12 h	45 (60[a])	15 (**388**)
2	**376**	$LiEt_3BH$ (3.0), THF, 0 ^oC, 12 h	[b]	na
3	**376**	$LiAlH(OMe)_3$, CuI, THF, 0 ^oC, 12 h	[b]	na
4	**376**	LiH_3BNMe_2, Et_3B,THF, 65 ^oC, 12 h	[c]	na
5	**376**	$NaBH_4$, DMSO, 50 ^oC, 24 h	71, <40[d]	na
6	**377**	LAH(3.0), Et_2O, 0 ^oC, 1 h; rt, 1 h	[e]	na
7	**377**	$LiEt_3BH$ (3.0), THF, rt, 12 h	[e]	na
8	**378**	LAH(3.0), Et_2O, 0 ^oC, 3 h	50	24 (**388**), 4 (**389**)
9	**378**	LAH(3.0), Et_2O, -25 ^oC, 12 h	53	Na
10	**378**	LAH (1.2), Et_2O, 0 ^oC, 12 h	35 (62[a])	5 (**388**), 2 (**389**)
11	**378**	$LiEt_3BH$ (3.0), THF, rt, 24 h	23[e]	na
12	**379**	H_2, 5% Pd/C (20%), EtOAc, 12 h	[f]	na
13	**379**	$NaBH_4$, DMSO, 50^oC, 24 h	[e]	na
14	**379**	$LiEt_3BH$ (3.0), THF, 0 ^oC, 2 h	80-91	5-12 (**390**)

[a]: Yield was calculated based on recovered starting material. [b]: Clean starting material was recovered. [c] Complex mixture. [d]: Lage scale (900 mg). [e]: Decomposition of starting material was observed. [f]: **379**: **362** = 1.6: 1.0.

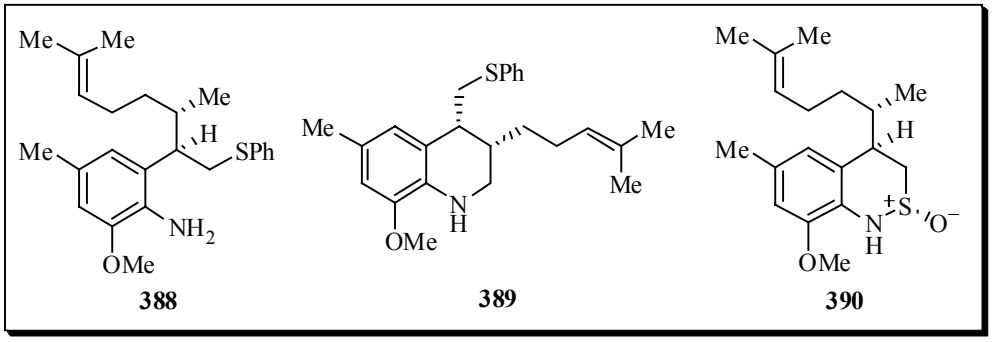


Figure 18 Byproducts in the Reductive Cleavage of C-X

Substrates **376-379** were subjected to the different conditions of reductive cleavage of C-X bond (Table 15). When **376** was first exposed to 3.0 equivalents of LAH at –25 ^{o}C, the desired compound **362** was obtained in 45% yield (60% based on recovered starting material). A 15% yield of over-reduction product **388** was isolated (entry 1). Compound **376** reacted very slowly upon treatment with $LiEt_3BH$ or $LiAlH(OMe)_3$ combined with CuI[155] (entry 2 and 3). An unidentified complex mixture was obtained when **376** was exposed to a system using lithium aminoborohydride and 20% Et_3B[156] (entry 4). $NaBH_4$ with enhanced reactivity (dissolved in DMSO solution) [157] was also applied to the deoxygenation of **376**. A 71% yield of **362** was harvested for the small-scale test reaction but failed on a relative large scale (900 mg).

The 2-propanesulfonate group[158] was found to be unsuitable as a leaving group. Only decomposition of starting material was observed either with LAH or $LiEt_2BH$ (entry 6 and 7).

Tosylate **378** was also subjected to the reductive cleavage reaction. Over-reduction products **388** and **389** were separated when **378** was stirring with LAH at 0 ^{o}C (entry 8). A lower temperature (-25 ^{o}C) and lower loading of LAH could suppress the side reaction

(entry 9, 10), but the yield of **362** was still not satisfied. Significant decomposition of **378** was observed when reacted with $LiEt_3BH$ (entry 11).

Alkyl iodide **379** was first subjected to catalytic hydrogenolysis.[159] Only 38% conversion was observed by ^{1}H-NMR analysis of the crude reaction mixture (entry 12). Heating in the presence of $NaBH_4$ in DMSO resulted in the decomposition of starting material (entry 13). Finally, using 3.0 equivalents of $LiEt_3BH$ at 0 ^oC for 2 hours was found to offer the best results so far. Compound **362** was obtained in up to 91% yield together with 5-12% of sulfinamide **390**. This reaction was generally very clean and could be scaled up. Furthermore, to our surprise, byproduct **390** was formed as a single diastereomer with retention of all of the stereochemistry. The details of this side reaction will be discussed in the next chapter.

The structures of **388** and **389** were established by the spectroscopic data. The presence of $-NH_2$ group was indicated by a doublet (3444.2 cm^{-1} and 3366.6 cm^{-1}) in IR. From ^{1}H-NMR, a distinct doublet peak at 1.03 ppm (Me group) with coupling constant of 6.5 Hz clearly indicated the tosylate group was cleaved. Furthermore, a lower chemical shift for the *S*-phenyl group (7.15-7.32 ppm in **388**, as compared 7.52-8.12 ppm in **362**) suggested the more shielding from sulfur atom and low valent sulfur in the molecule, which was later confirmed to be thiophenyl ether by the high resolution mass spectrometry. Thus, the structure of **388** was assigned.

As for **389**, the sulfoximine moiety was reduced as clearly indicated by the lower chemical shift of *S*-phenyl group. The absence of the tosylate group and a distinct doublet around 1.00 ppm (methyl group), together with evidence of a free NH group, suggested the presence of tetrahydroquinoline moiety in the molecule. Attempts to extract the

coupling constants of H_7 in the ^{1}H-NMR failed because signal for H_7 overlapped with the for H_{10a} and the spectrum turned into second-order spectrum ($\Delta\delta/J$:1.9). Thus, the stereochemistry of H_7 and H_8 were assigned based on the stereoinformation in the starting material. The structural assignment was also supported by NOESY experiment, as shown in Figure 19 and Figure 20.

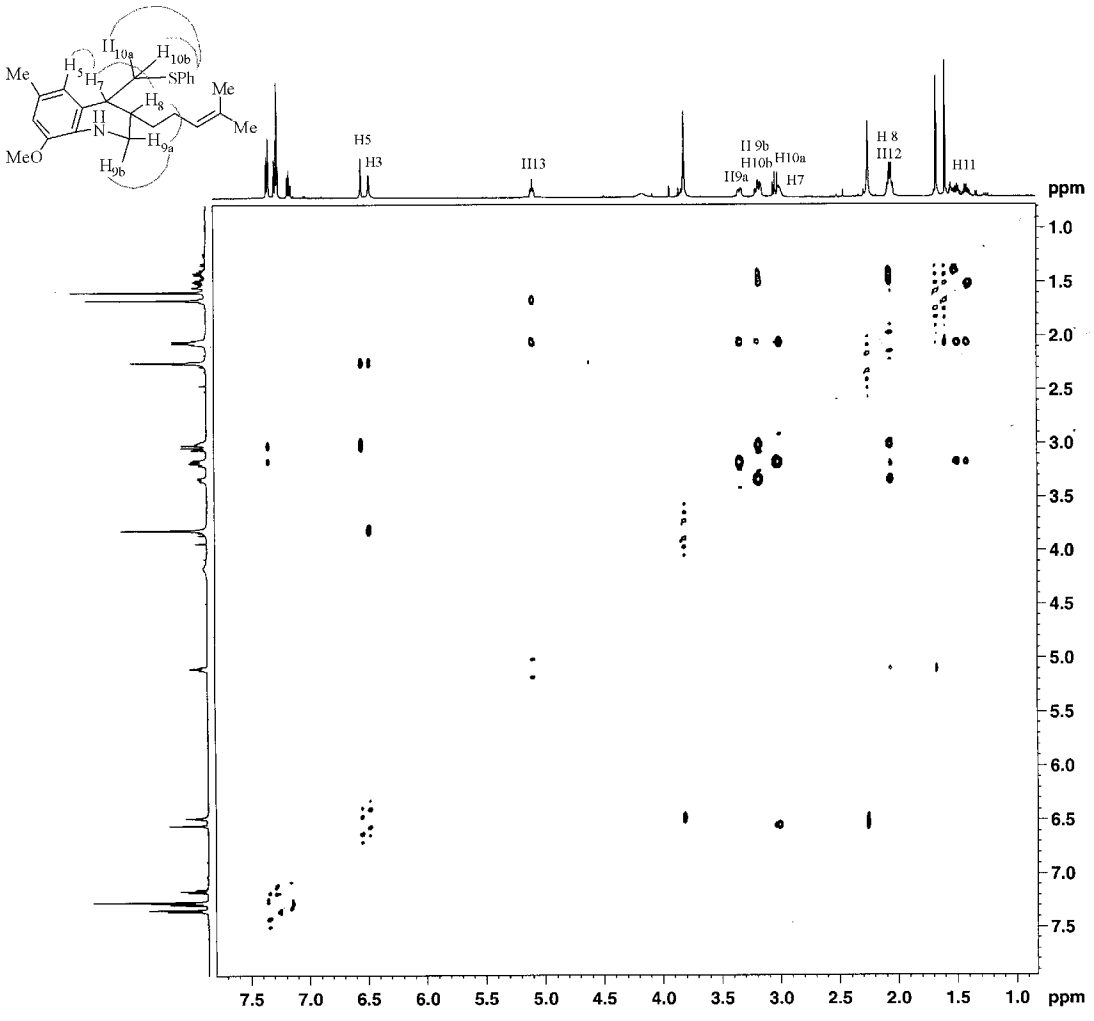


Figure 19 NOE Spectrum of **389**

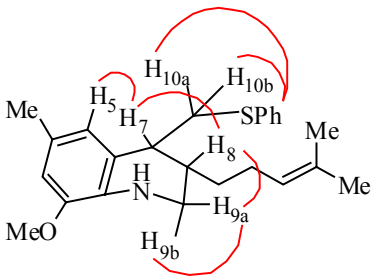
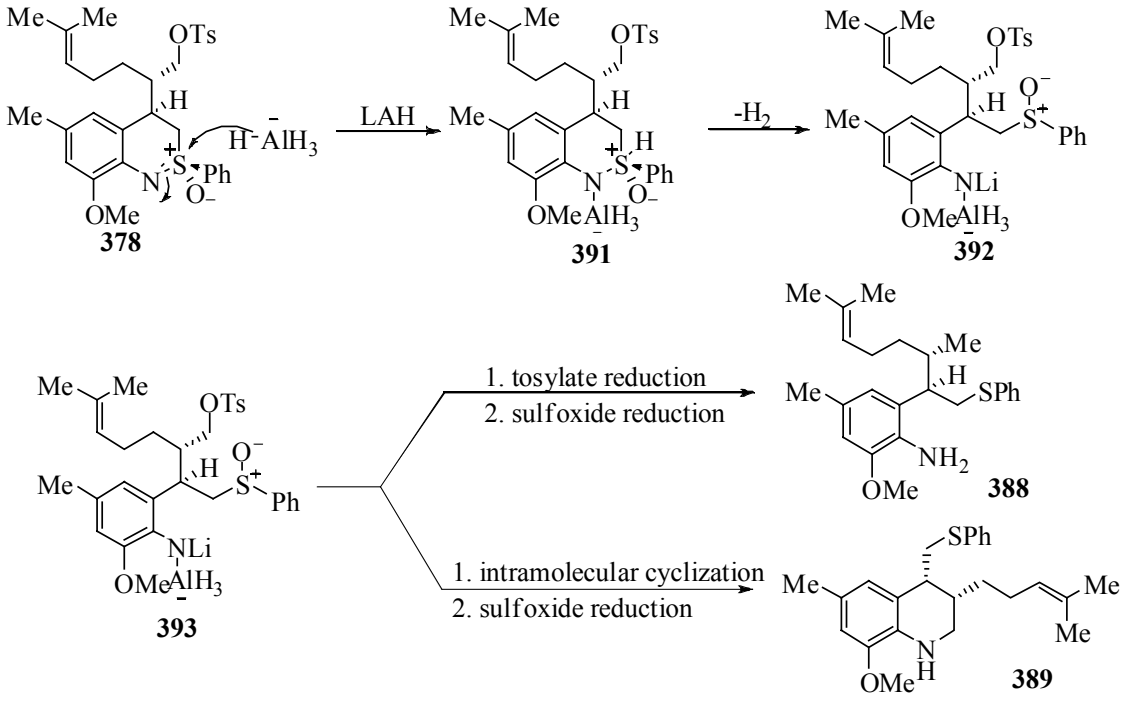


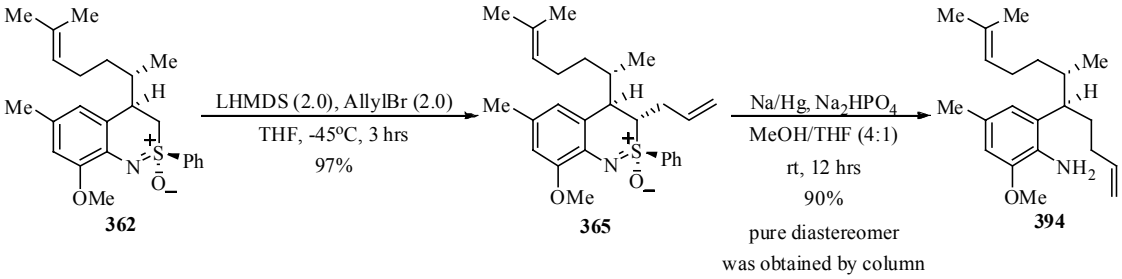
Figure 20 Key NOE correlation of **389**

A possible mechanism was proposed for the formation of byproducts **388** and **389** (Scheme 84). LAH-assisted reductive cleavage of C-N bond could deliver **378** to **392**. Sequential tosylate reduction and sulfoxide reduction could give **388**. Alternatively, a competitive intramolecular cyclization followed by sulfoxide reduction might afford tetrahydroquinoline **389**.



Scheme 84 Proposed Mechanism for the Formation of **388** and **389**

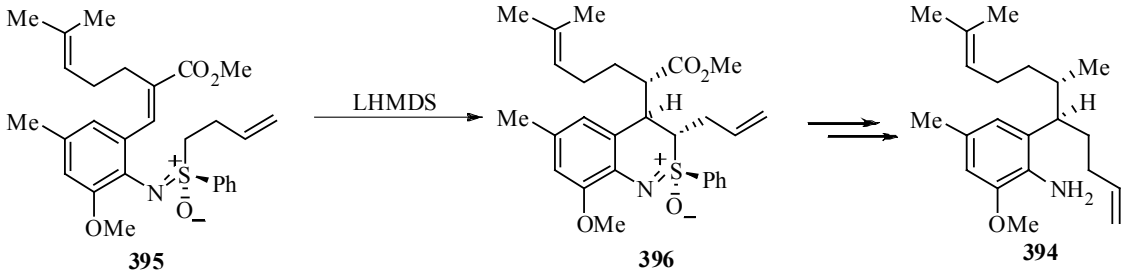
With an established methodology to access methyl benzothiazine **362** in hand, allylation was studied and occurred smoothly to give allylic benzothiazine **365** in 97% yield. Reductive cleavage of the sulfoximine moiety produced aniline **394** in 90% yield. Fortunately, the desired diastereomer was obtained in a pure form after silica gel column chromatography (Scheme 84).



Scheme 85 Preparation of Aniline **394**

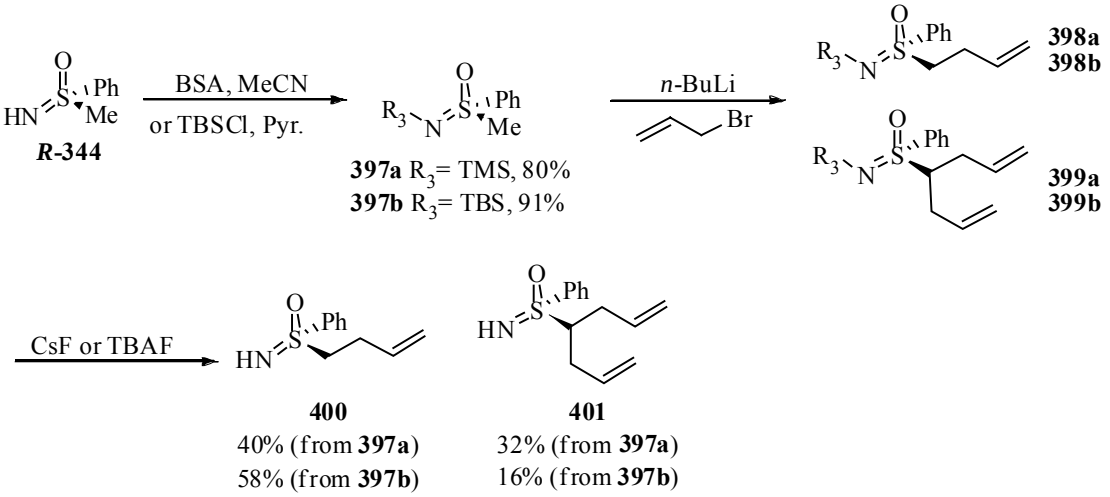
2.2.2 Second Approach to Introduce the Stereochemistry at C-4 and C-11 Position

Another approach to access aniline **394** was also investigated based on the idea that sufoximine **395** would be constructed and undergo intramolecular Michael reaction to set up all stereocenters in one step. Functional group interconversions would then deliver the aniline **394** (Scheme 86).



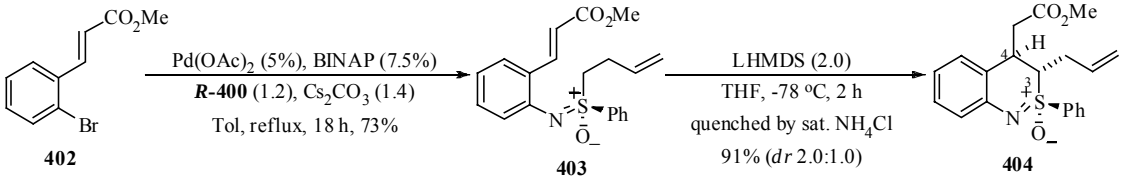
Scheme 86 Second Approach to Aniline **394**

The required building block, allyl sulfoximine **400** was prepared from ***R*-344**. Protection of the nitrogen with TMS or TBS group yielded **397a** and **397b**, which were respectively further allylated and deprotected to afford **400**[160] in 40% and 58% yield, accompanied by diallylated product **401** in 32% and 16% yield (Scheme 87).



Scheme 87 Preparation of Allylic Sulfoximine **400**

A model study was first carried out to explore the effect of the allyl substituent in the intramolecular Michael reaction. Compound **402** was coupled with *R*-**400** to yield **403** in moderate yield. Intramolecular Michael reaction took place smoothly. Benzothiazine **404** was produced in 91% yield as a 2:1 mixture of diastereomers (Scheme 88). The major isomer was assigned as *trans* based on the axial-equatorial coupling (C_4-H: *J* value of 9.5 Hz). This stereoselectivity might be explained by the gauche interaction of α-hydrogen with allyl group (Figure 21).



Scheme 88 Model Studies to Access Allylic Benzothiazine **404**

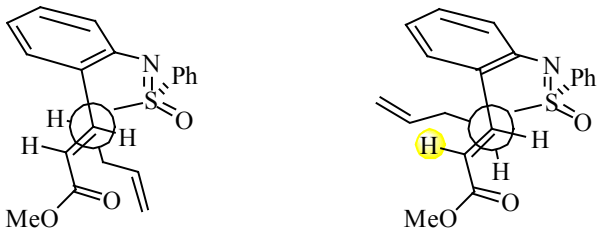
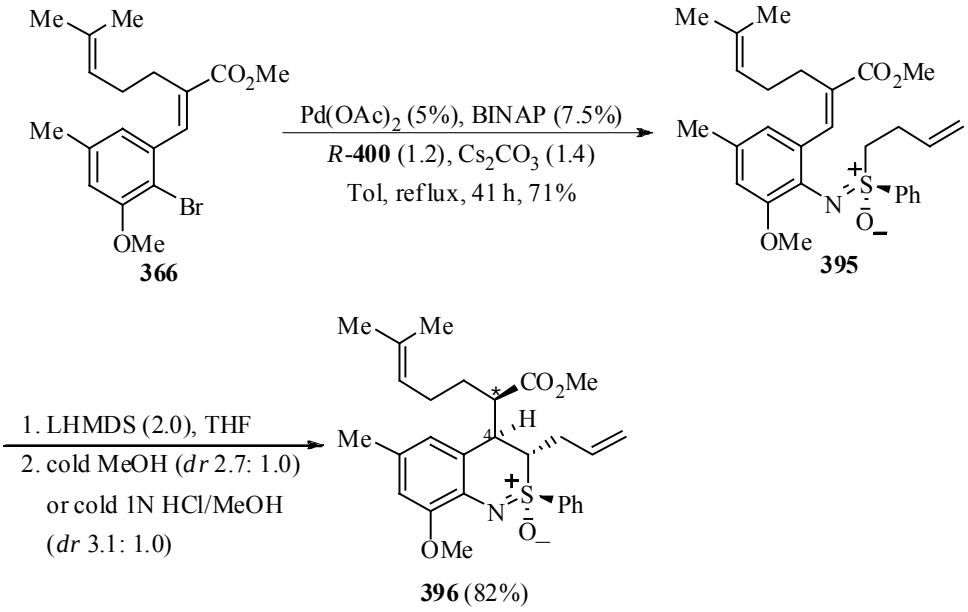


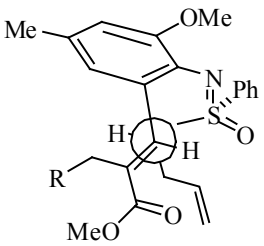
Figure 21 Conformational Analysis of **403**

Encouraged by the excellent yield of **404**, we carried out the synthesis of allylic benzothiazine **396**. Compound **366** was coupled with allyl sulfoximine **400** to give **395** under our standard conditions. Cyclization was carried out to deliver benzothiazine **396** in 82% yield. The major isomer was assigned as **396**, which was proved at a later stage (Scheme 89). To our delight, only two diastereomers were formed in a moderate yield no matter how the reaction was quenched. The facts that both isomers possess a doublet of doublets with coupling constants of 10.9 and 4.3 Hz suggested that the C-3 allyl group and C-4 side chain are *trans* to each other in both isomers.

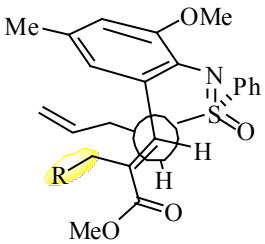


Scheme 89 Synthesis of Allylic Benzothiazine **396**

The stereochemical outcome might be involved a transition state like **395a** (less congested), which would result in *trans* configuration at the C-3 and C-4 positions in the Michael addition products (Figure 22). The stereochemistry at C-11 was established at the protonation stage. The C-11 stereocenter of major isomer was assigned as *R* based on the Koscienski's model, which suggests that the allyl group might block the incoming proton (Figure 23).



395a (Favored)
R= prenyl



395b

Figure 22 Conformational Analysis of **395**

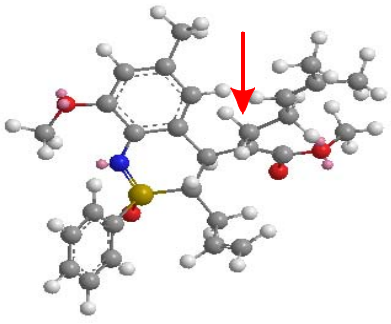
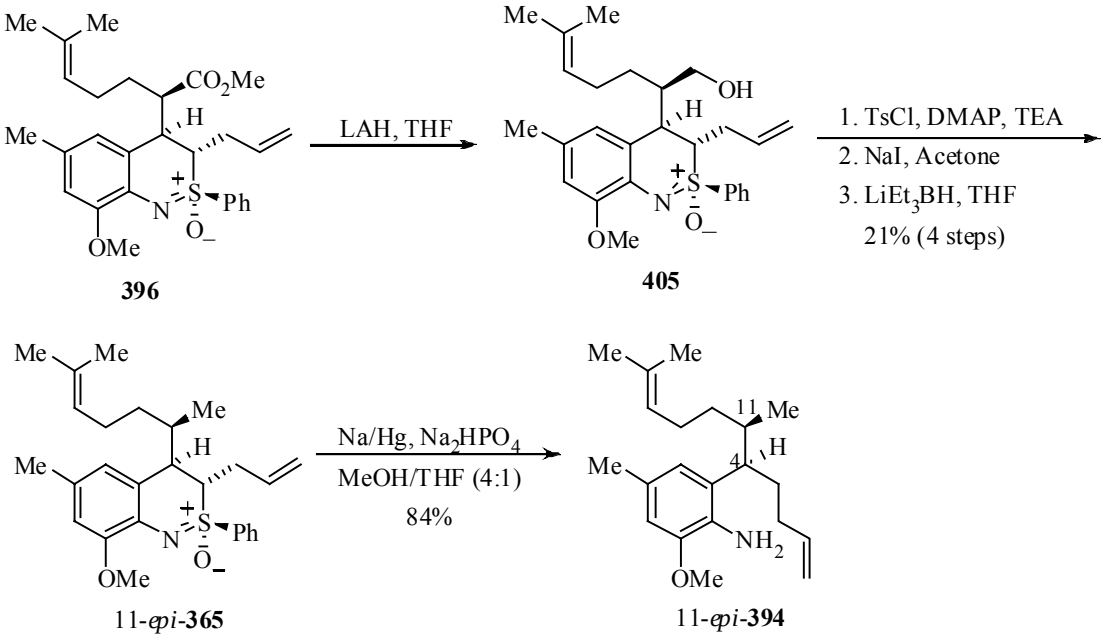


Figure 23 Model for Protonation

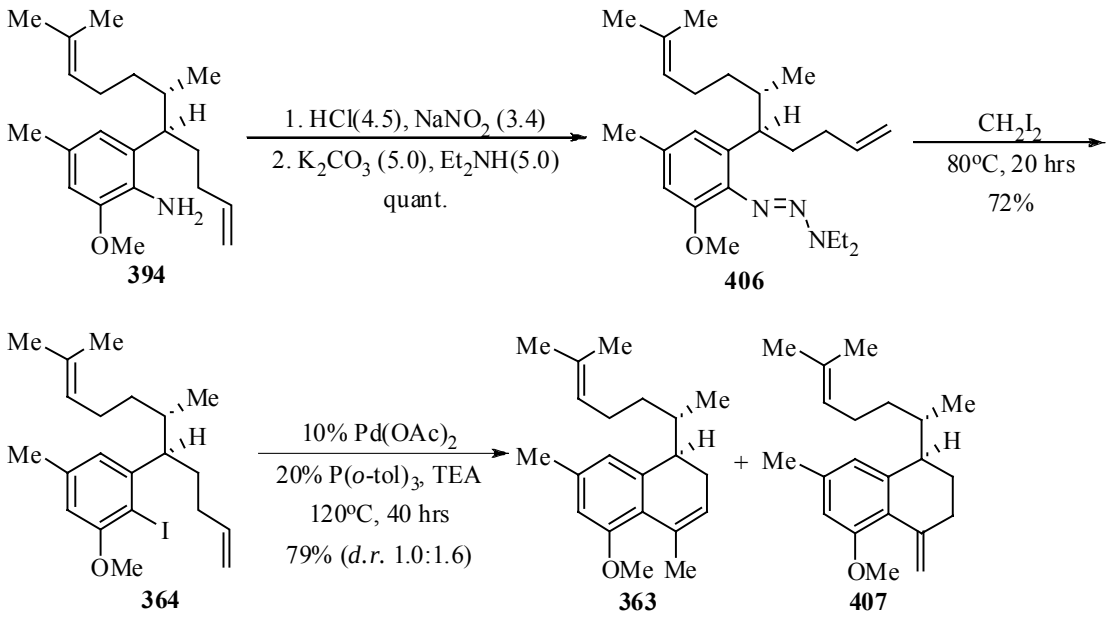
Reduction and tosylation of **396** yielded tosylate **397** in 52% yield. Iodination and reduction using super hydride afforded 11-*epi*-**365**, which was later converted to aniline *epi*-**394**. After the comparison of the ^{1}H-NMR of *epi*-**365** and *epi*-**394** with the previous compounds, we found that both are completely identical with the minor isomers **365** and **394** (Scheme 90).



Scheme 90 Another Approach to Aniline **394**

2.2.3 Finish the Total Synthesis of 1-*epi*-*seco*-Pseudopteroxazole

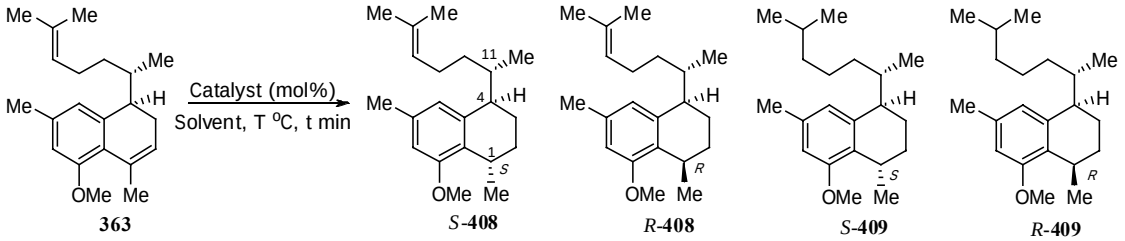
Pure **394** was converted to triazine **406** in quantitative yield. This was subsequently converted to iodide **364** in 72% yield.[149,161] Intramolecular Heck coupling utilizing the catalytic system of $Pd(OAc)_2$, $P(o\text{-}Tol)_3$ and triethylamine yielded a mixture of alkene **363** and terminal alkene **407** in 79% yield (ratio: 1.0: 1.6). Pure **363** and **407** were obtained using preparative TLC (Scheme 91).



Scheme 91 Preparation of Heck Precursor **363**

With **363** in hand, we set out to explore the reduction reaction to form C-1 stereocenter (Table 16). When **363** was exposed to 10% Pd/C under 40 psi of hydrogen, over-hydrogenated product *R*-**401** was found to predominate in the mixture. The stereoselectivity (*S*/*R*) was 1.0:9.7, which indicates the hydrogen primarily attacked from the less hindered *Re* face of benzylic alkene, as expected based on substrate control of stereochemistry. Furthermore, the regioselectivity between selective hydrogenation and over hydrogenation was 1.0: 35 (entry 1).

Table 16 Asymmetric Reduction of **363**



#	Catalyst (mol%) Solvent, T °C, t min	*S*-**408**: *R*-**408**: *S*-**409**: *R*-**409** [a]	*S*: *R*	Regioselectivity **408**: **409**
1	Pd/C (10%), 40 psi H_2, 3 hr	0: 1.0: 3.4: 32	1.0: 9.7	1.0: 35
2	Pfaltz's **357**., 60 psi H_2, 1 hr	3.8: 1.3: 3.5: 1.0 [b]	3.2: 1.0	1.1: 1.0
3	Li, NH_3, -78 °C, 15 min	1.0: 8.2: 0: 0 [c]	1.0: 8.2	100: 0

[a]: Stereochemistry assignment of **408** and **409** was based on the following research; the ratio was determined by GC-MS analysis of crude mixture. [b]: The ratio of *S*-**408**: *R*-**408**: *S*-**409**: *R*-**409**: **363** is 3.8: 1.3: 3.5: 1.0: 1.8. [c]: The crude NMR ratio is 1.0: 4.6.

Not surprisingly, no selective hydrogenation was observed under the hydrogenation with Pd/C. We turned to Pfaltz's chiral catalyst **357**, which was successfully applied to the total synthesis of pseudopteroxazole.[149] The reaction turned out to produce all of possible hydrogenation products and the ratio of *S*-**408**: *R*-**408**: *S*-**409**: *R*-**409**: **363** is 3.8: 1.3: 3.5: 1.0: 1.8. It is noteworthy that the catalyst control prevailed in the process and the *S*/*R* selectivity for C-1 stereochemistry was 3.2: 1.0 (entry 2). The *S*/*R* ratio of **409** (3.5:1.0) were consistent with that of **408** (2.9: 1.0). Thus, the configuration of major isomer of **409** was assigned as *S*.

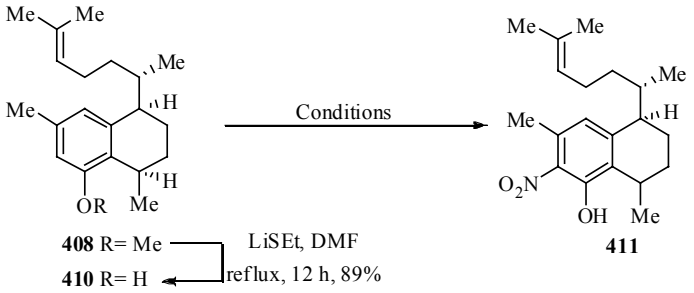
Dissolving metal reduction was also applied to the substrate **363**. When **363** was treated with 10 equivalents of lithium in the liquid ammonium, inherent substrate control gave a *S*/*R* ratio of 1.0: 8.2 at C-1 position based on GC-MS analysis. A more accurate ratio (*S*/*R*: 1.0: 4.6) was measured by NMR analysis. Only the benzylic double bond was

reduced under these conditions. The configuration (C-1) of major isomer of **408** was assigned as *R*.

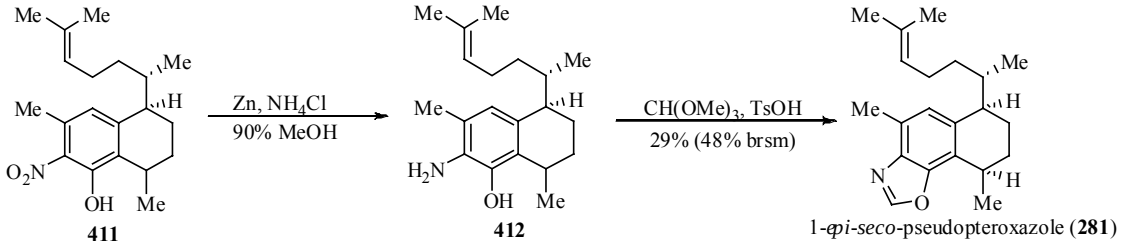
To confirm the stereochemistry at C-1 position and further explore the proposed route to *seco*-pseudopteroxazole, compound **408** (*d. r.*: 1.0: 4.6), obtained from dissolving metal reduction, was carried forward. LiSEt-mediated deprotection to the phenol was carried out to yield **410** in 89% yield.

Selective *ortho* nitration of phenol **410** turned out problematic (Table 17). Only 23% of the desired *ortho* nitrophenol **411** was isolated when **410** was treated with 70% HNO_3 for 70 seconds (entry 1). Significant loss of mass was observed in the reaction. Neither acetyl nitrate[162] nor cerium(IV) ammonium nitrate[163] afforded **411**. The total synthesis was accomplished utilizing the known two-step sequence of reduction and condensation (Scheme 92).

Table 17 *ortho*-Nitration of Phenol **410**



Entry	Conditions	Yield of **411** (%)
1	HNO_3 (70%), Hexanes, rt, 70 s	23
2	$AgNO_3$, AcCl, $CHCl_3$ -20 ^oC, 1.5 h	mess
3	CAN, $NaHCO_3$, MeCN, rt, 1 h	mess



Scheme 92 Completion of the Total Synthesis of 1-*epi*-*seco*-pseudopteroxazole **281**

The comparison of proton NMR of natural product and synthetic product **281** is shown in Table 17.

Table 18 ^{1}H-NMR Comparison of Natural Product and Synthetic Product **281**

Atom	Natural product	Synthetic product
	δ_H, mult (*J* in Hz)	δ_H, mult (*J* in Hz)
1	3.22, m	3.31, m
4	2.87, m	2.89, m
5	7.03, s	7.06, s
14	5.16, m	5.17, m
16	1.72, s	1.72, s
17	1.64, s	1.64, s
18	0.68, d (6.9)	0,68, d (7.0)
19	2.57, s	2.57, s
20	1.38, d (6.9)	Major:1.35, d (7.0) Minor: 1.38, d (6.9)
21	8.02, s	8.01, s

We found that all peaks match very well, except C-1H and C-20H. Moreover, the doublet peak at 1.38 ppm in the minor isomer was identical to that in the ^{1}H-NMR reported for the natural product. So we concluded that we have accomplished the total synthesis of 1-*epi*-*seco*-pseudopteroxazole (**281**).

3 Summary

We have accomplished the total synthesis of 1-*epi*-*seco*-pseudopteroxazole **281** in 17 steps. Our synthesis featured the Buchwald-Hartwig coupling, stereoselective intramolecular Michael reaction, Heck coupling and asymmetric reduction. Total synthesis of "natural" *seco*-pseudopteroxazole is still in progress in our lab.

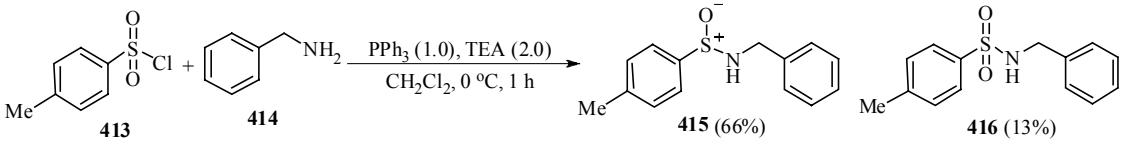
Chapter IV

A Novel Approach to Chiral Cyclic Sulfinamide

1 Introduction

1.1 Approaches to Acyclic Sulfinamides

Since the early 1920s,[164,165] the chemistry of sulfinamides has been of particular interest in modern organic chemistry.[166-168] A number of methods have been developed for the synthesis of sulfinamides from sulfinic acids,[169] sulfonyl chloride,[1,170] *N*-sulfinylamines,[171] sulfinates,[172] sulfenamides[173] and thiosulfinates[174]. However, two or more steps are usually required. Very recently, our group developed a one-step process to prepare sulfinamides by reductive amidation of sulfonyl chlorides.[175] For example, commercially available sulfonyl chloride **413** was coupled with benzylamine **414** under the reductive conditions and sulfinamide **415** was formed in 66% yield, accompanied with 13% of sulfonamide **416**. The reaction presumably proceeded via the sulfinyl chloride intermediate, which is formed *in situ* (Scheme 93).

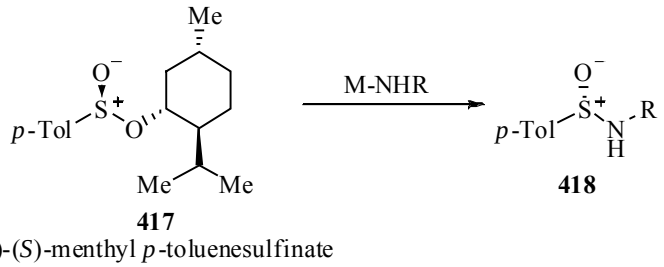


Scheme 93 Harmata's Synthesis of Sulfinamide **415**

1.1.1 Chirality Transfer from Sulfinic Acid Derivatives

The synthesis of enantiopure substances is at the center of modern organic chemistry. One of the most popular methods to access chiral sulfinamides is chirality transfer from optically pure menthyl *p*-toluenesulfinate[172,176] (Scheme 94).

Enantiomerically pure menthyl *p*-toluenesulfinate was treated with LiHMDS or other amides to afford sulfinamides **418** with complete inversion at configuration at the sulfur atom.

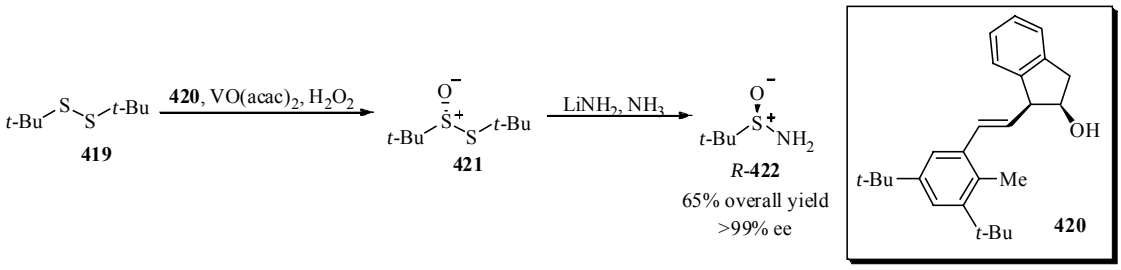


417
(-)-(*S*)-menthyl *p*-toluenesulfinate

418

Scheme 94 Asymmetric Synthesis of Chiral Sulfinamides from Chiral Sulfinates

Ellman and coworkers[174] reported a more inexpensive route to an enantiomerically pure sulfinamide (Scheme 95). The synthesis started from the readily available starting material *t*-butyl disulfide. Asymmetric oxidation of disulfide **419** was carried out in the presence of 0.5 mol% of $VO(acac)_2$ and chiral ligand **420**. Addition of lithium amide delivered *t*-butyl sulfinamide *R*-**422** in 65% overall yield from disulfide.



419

421

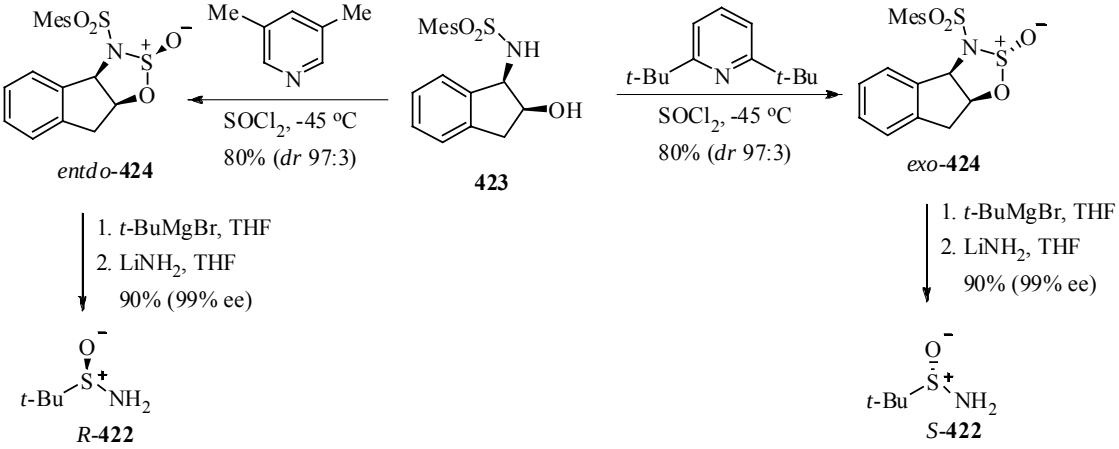
R-**422**
65% overall yield
>99% ee

420

Scheme 95 Ellman's Asymmetric Synthesis of **422**

In 2002, Senanayake and coworkers[177,178] developed a stereospecific double inversion nucleophilic displacement route to chiral sulfinamides (Scheme 96). The process started with readily available enantiopure *N*-sulfonyl aminoindanol **423**.

Compound **423** was converted to **424** with excellent diastereoselectivity (*endo*: *exo* 97: 3) in the presence of 3,5-lutidine. In contrast, stereohindered base (2,6-di-*t*-butyl pyridine) drove the reaction to high *exo* selectivity (*endo: exo*: 3: 97). Both isomers were highly crystalline and were isolated in 80% yield after recrystalization. Double S_N2 reaction with *t*-butyl magnesium bromide and lithium amide produced both *R* and *S* isomers of *t*-butylsulfinamide **422** in 90% yield with up to 99% *ee*. It is worth pointing out that this methodology has been applied to the synthesis of a number of tertiary alkyl sulfinamides and aryl sulfinamides using appropriate Grignard reagents.

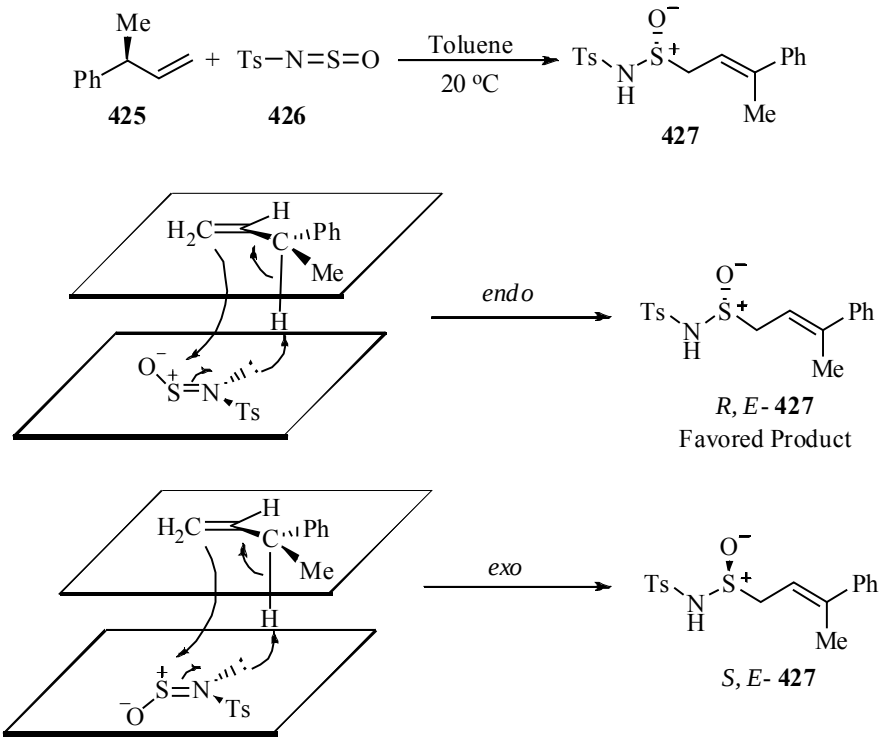


Scheme 96 Senanayake's Synhesis of *ent*-**422**

1.1.2 Ene Approach to Access the Chiral Sulfinamides

Kresze[179] has applied an ene approach to the synthesis of chiral sulfinamides. Compound **427** was formed as a single isomer when *S*-**425** was treated with *N*-sulfinylamine in toluene solution at ambient temperature (Scheme 97). The stereochemistry was rationalized as shown in scheme 97. A lone pair of electrons on the nitrogen atom could coordinate to the allylic hydrogen to form a "pseudopericyclic"

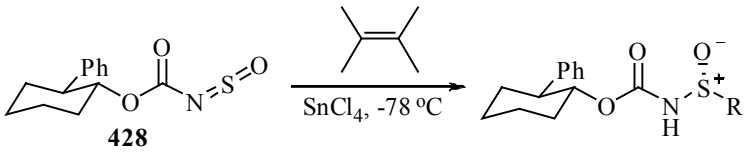
transition state. The reaction proceeded through a *endo* transition state to deliver the observed isomer *R, E*-**427**.



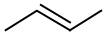
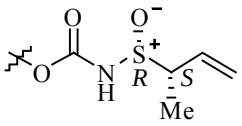
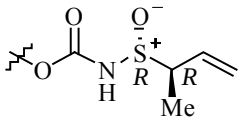
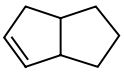
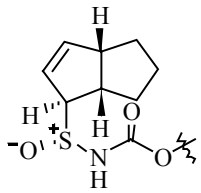
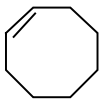
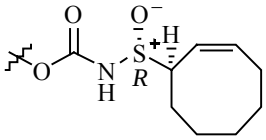
Scheme 97 Ene Approach to Chiral Sulfinamide **427**

Whitesell and coworkers[180] demonstrated a similar reaction but with the stereocontrol from chiral *N*-sulfinylamine **428**. Starting from *trans*-2-butene a single diastereomer **433** was obtained, whereas with *cis*-2-butene the product was **434**. Cyclic alkenes **431** and **432** were also converted to sulfinamides with high stereoselectivity. The stereoselectivity of this intermolecular ene reaction might be rationalized by a 6-membered chair transition state, in which the alkene approached from the bottom face of sulfinylamine (Table 19).

Table 19 Whitesell's synthesis of sulfinamides

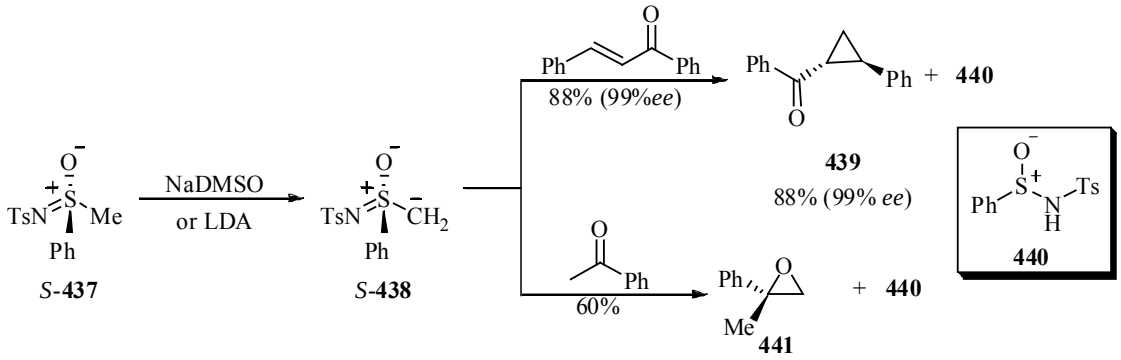


428

	**429** 	**433** (84%)
	**430** 	**434** (62%)
	**431** 	**435** (86%)
	**432** 	**436** (81%)

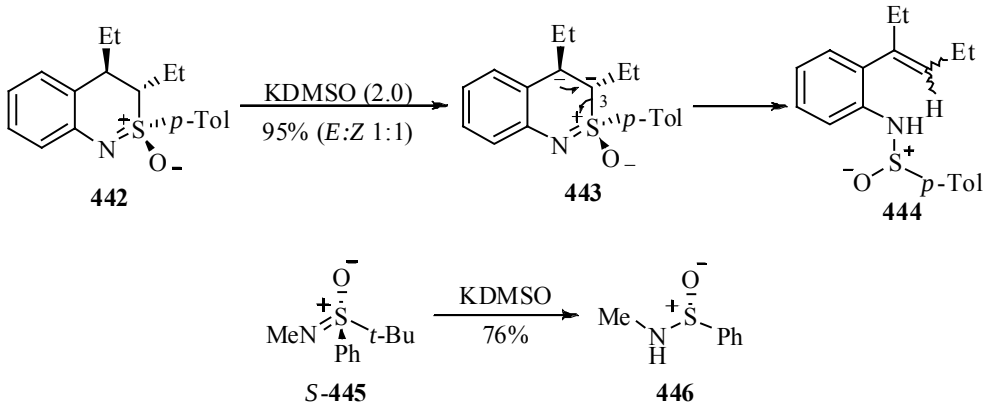
1.1.3 Sulfinamides Generated from Sulfoximine Derivatives

Besides the above approaches to access the sulfinamides, sulfinamides have been reported as side products during the reduction of sulfoximine derivatives, for example the stereoselective epoxidation[181] and cyclopropanation[182] (Scheme 98).



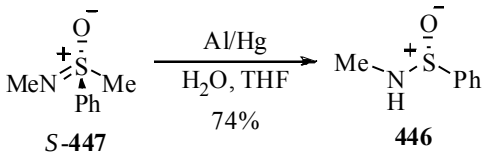
Scheme 98 Epoxidation and Cyclopropanation Using Sulfoximine as Reagent

Harmata and coworkers[183] reported the base-induced conversion of benzothiazine **442** into **444**, a precursor to 2-alkenyl aniline. Dianion intermediate **443** would undergo elimination reaction to generate **444** (Scheme 99). The lack of stereoselectivity of the double bond might be attributed to the epimerization of C-3 position under the reaction conditions. Regardless of the low stereoselectivity, the reaction opened up a new general route to 2-alkenyl anilines with high regioselectivity. A similar approach was utilized to convert **446** from *S*-**445**.[184]



Scheme 99 Synthesis of Sulfinamide from Benzothiazine or Sulfoximine

Johnson and Schroeck[185] reported a reductive approach to convert sulfoximine to sulfinamide. Compound **446** was obtained by the aluminum amalgam reduction of readily available enantiomerically pure *N*-methyl sulfoximine **447** (Scheme 100). The reaction generally proceeded with the retention of configuration at the stereogenic sulfur atom.

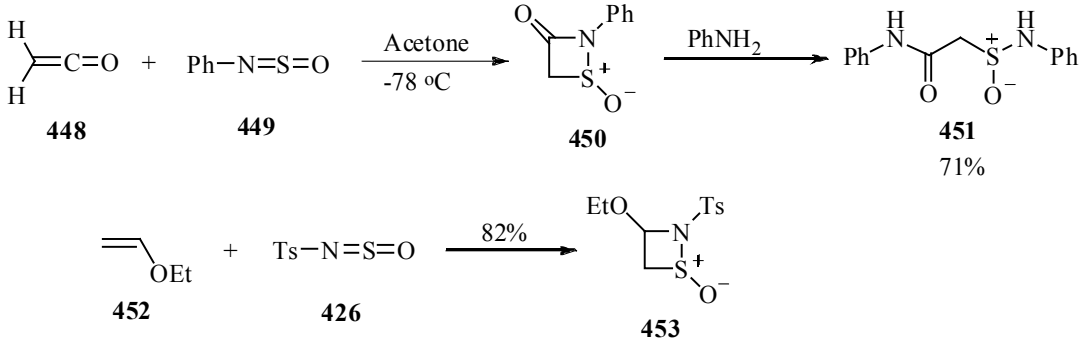


Scheme 100 Asymmetric Synthesis of Sulfinamide **446**

1.2 Approach to Cyclic Sulfinamides

1.2.1 Access 4-Membered Cyclic Sulfinamides

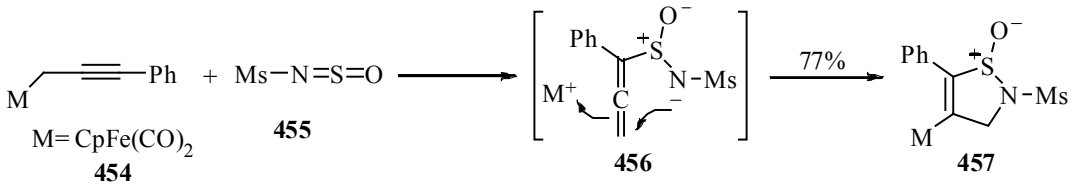
Joullié and coworkers[186,187] developed a [2+2] cycloaddition to access 4-membered cyclic sulfinamide **450**. **450** was generated by the treatment of ketene **448** and *N*-sulfinylamine **449** at low temperature. Compound **450** was unstable and underwent facile cleavage with aniline to afford sulfinamide **451** in 71% yield over the two steps. In addition, electron- deficient *N*-sulfinylamine **426** can also react with enol ether **452** to provide the [2+2] adduct **454** in 82% yield (Scheme 101).[188]



Scheme 101 [2+2] Cycloaddition Spproach

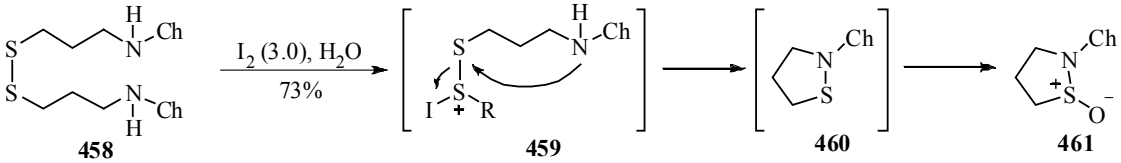
1.2.2 Access 5-membered cyclic sulfinamides

Iron-propargyl complex **454** was documented to react via [3+2] cycloaddition with electron deficient sulfinamine **455**. The reaction presumably involved allene intermediate **456**, which was formed by the nucleophilic addition of metal complex to sulfinylamine (Scheme 102).[189]



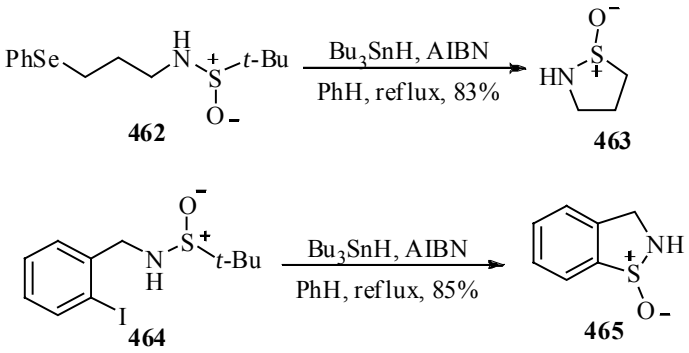
Scheme 102 [3+2] Cycloaddition Approach

Doi and coworkers[190] reported the synthesis of the simple 5-membered cyclic sulfinamide **461** from disulfide **458**. This approach presumably proceeded via iodosulfonium intermediate **459** and isothiazolidine **460** (Scheme 103).



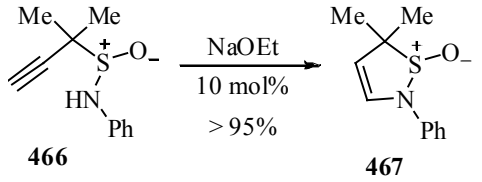
Scheme 103 Doi's synthesis of 5-membered Sulfinamides

Recently, Malacria and coworkers[191] discovered a general approach to a series of cyclic sulfinamides featuring an intramolecular radical cyclization. This methodology has been applied to the synthesis of simple sulfinamide **463** and benzosulfinamide **465** and also extended to the synthesis of cyclic sulfinates (Scheme 104).



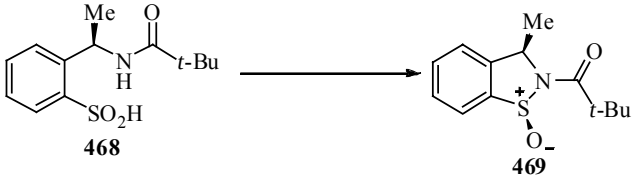
Scheme 104 Radical Cyclization

Intramolecular nucleophilic attack of the triple bond by the sulfinamide nitrogen atom to triple bond produced the desired product **467** in excellent yield (Scheme 105).[192]



Scheme 105 Nucleophilic Addition of Triple Bond

The asymmetric synthesis of 5-membered sulfinamide **469** was explored by Wills and coworkers[193]. They found that the diastereoselective cyclization step turned out to be very sensitive to different bases. After some exploration, DMAP was found to give the best result. Pure *cis*-**469** was obtained in 67% yield. In contrast, pyridine gave **469** as a mixture of *cis/trans* (60:40) (Scheme 106).

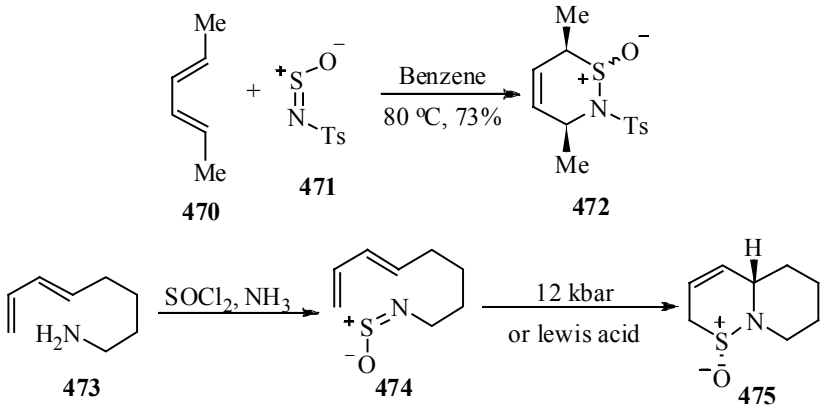


Conditions	Yield	*cis*: *trans*
$SOCl_2$, DMAP	67%	100: 0
$SOCl_2$, Pyridine	---	60: 40

Scheme 106 Synthesis of *N*-carboxy Cyclic Sulfinamide **469**

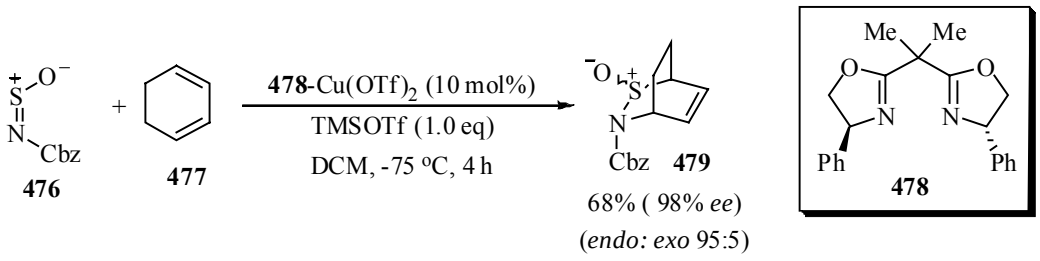
1.2.3 Access 6-membered cyclic sulfinamides

Hetero Diels-Alder reactions provided a unique way to access 6-membered cyclic sulfinamide.[194-196] Electron poor sulfinyl amines **471**, which were freshly prepared by the condensation of amines with thionyl chloride, reacted with 2,4-hexadiene to yield cyclic sulfinamides **472**.[197] An intramolecular version of the Diels-Alder reaction also successfully afforded the unusual bicyclic sulfinamide **475** under extremely high pressure or Lewis acid-catalyzed conditions.[198] In general, the reaction was highly regio- and stereoselective and occured at or below room temperature. The stereochemistry at the sulphur atom was variable (Scheme 107).



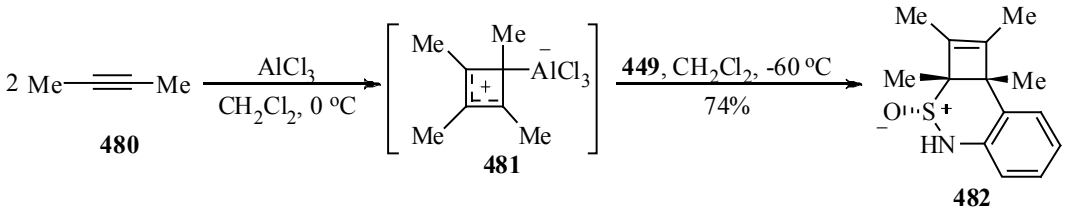
Scheme 107 Diels-Alder Approach to Cyclic Sulfinamides

An asymmetric version of hetero Diels-Alder reactions was also explored by Gautun and coworkers.[199] Bis(oxazoline) **478** –copper (II) triflate was found to give the desired endo cycloadduct **479** with excellent enantioselectivity (98% *ee*) (Scheme 108).

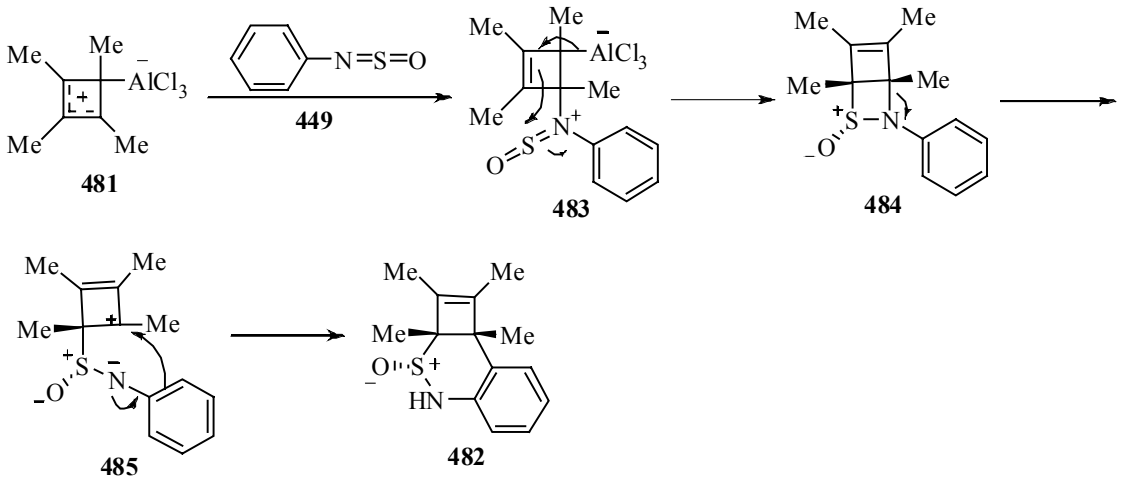


Scheme 108 Asymmetric Diels-Alder Reaction

Hogeveen and coworker[200] found that tricyclic sulfinamide **482** was synthesized from the aluminum halide σ complex of cyclobutadiene **481**. When freshly prepared **481** was treated with *N*-sulfinylaniline **449** at –60 °C, tricyclic sulfinamide **482** was isolated in 74% yield as a single diastereomer, whose structure was elucidated by X-ray analysis. A stepwise mechanism was proposed based on the mechanistic studies (scheme 109). Nucleophilic attack of sulfinylaniline would afford **483**, followed by a subsequent ring closure of **483** to give bicyclic sulfinamide **484**. Heterolytic cleavage of the C-N bond might yield the intermediate **485**, which could be further converted to **482**via an intramolecular Friedel-Crafts reaction and subsequent hydrogen shift (Scheme 110).[201]



Scheme 109 Synthesis of Rricyclic Sulfinamide **482**

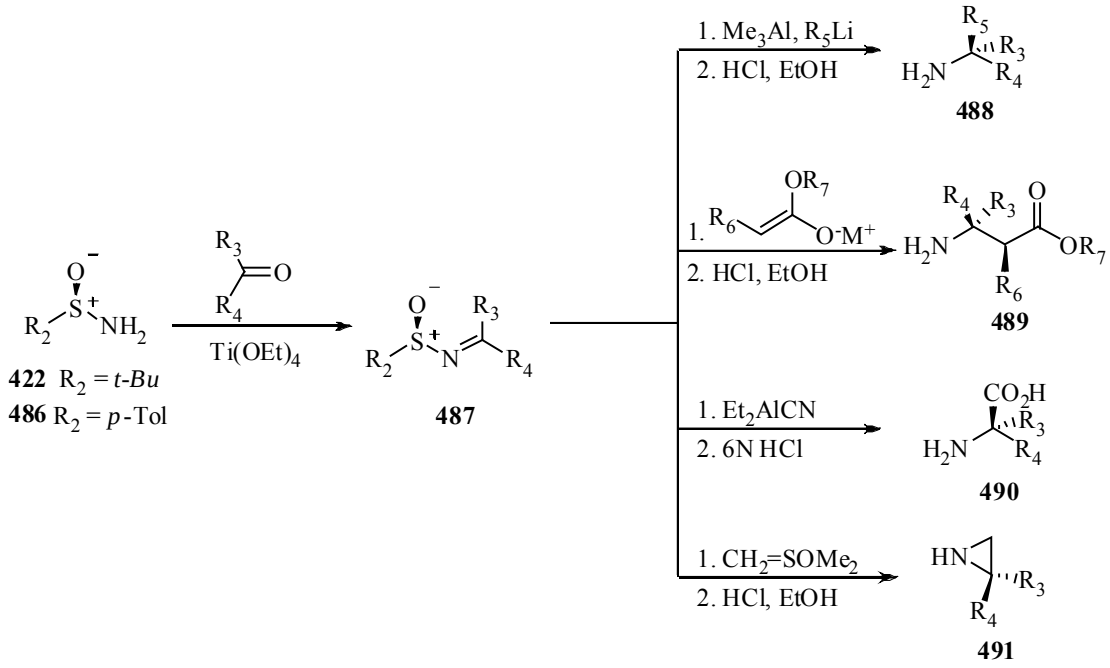


Scheme 110 Mechanism of Formation of **482**

1.3 Applications in Organic Synthesis

1.3.1 Acyclic Sulfinamides in Organic Synthesis

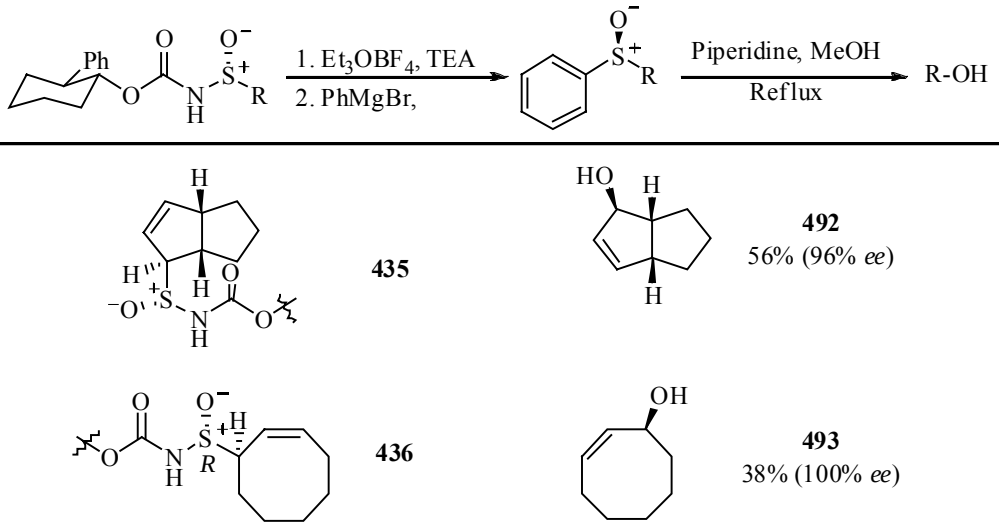
Simple sulfinamides are valuable precursors to sulfinimines, with the latter being proven to be versatile building blocks in organic synthesis by independent studies from Davis[202] and Ellman[203]. For example, sulfinamides were condensed with aldehydes or ketones to afford sulfinimines **487** using $Ti(OEt)_4$ as a Lewis acid[172,204]. Diastereoselective nucleophilic additions converted the sulfinimines to amines **488**,[205] β-amino acids **489**,[206] α-amino acids **490**,[207] and aziridines **491**[208](Scheme 111).



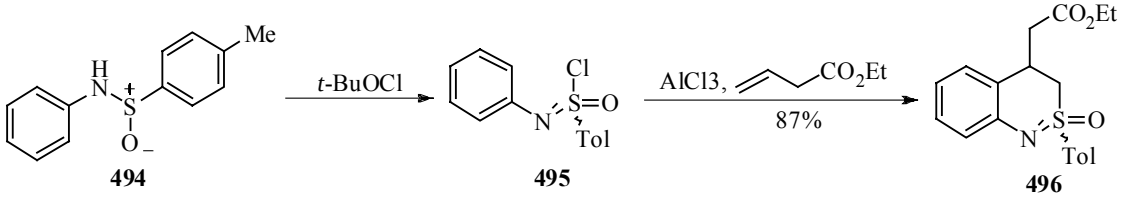
Scheme 111 Sulfinimine Chemistry

Furthermore, Whitesell and Carpenter[180] demonstrated the synthesis of chiral alcohols from sulfinamides. Ethylation of sulfinamides, followed by treatment with Grignard reagent (PhMgBr) provided allylic sulfoxides that readily underwent sequential [2,3]-sigmatropic rearrangement with high retention of stereochemistry. Upon methanolysis, **492** and **493** were formed in 56% and 38% yields, respectively, with excellent stereoselectivity (Table 20).

Table 20 Synthesis of Chiral Alcohol



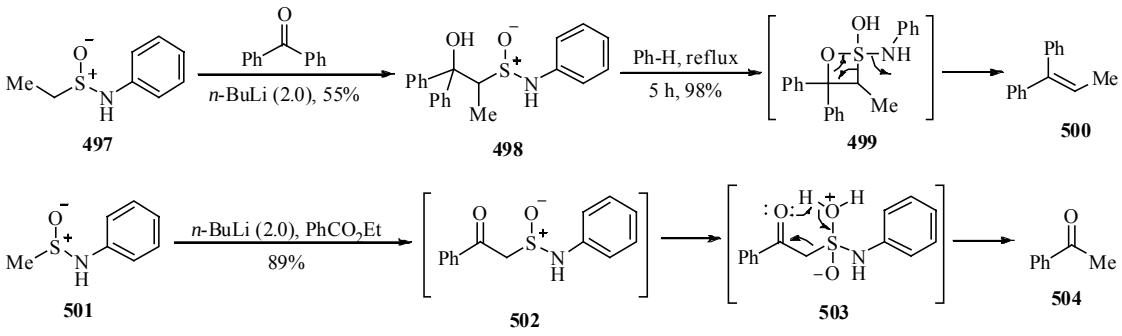
Harmata and coworkers[209-211] have shown that sulfinamides are valuable precursors for the formation of benzothiazines. Compound **494** was converted to **496** in 87% yield as a single regioisomer. It was assumed that **494** was first oxidized to sulfonimidoyl chloride **495** by *t*-butylhypochlorite, followed by stepwise cyclization to yield **496** (Scheme 112).



Scheme 112 Harmata's Synthesis of Benzothiazine **496**

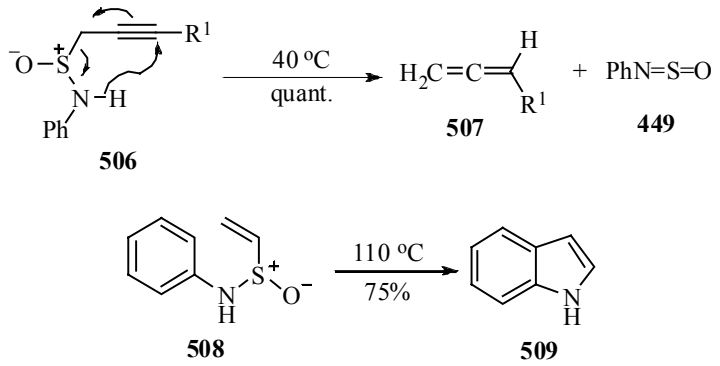
Corey and coworkers[212] found that when β-hydroxy sulfinamide **498** was refluxing in the benzene solution, 1,1-diphenyl propene **500** was formed in excellent yield, which would presumably proceed through a four-membered ring intermediate **499**. It was also

found out that the ratio of *E/Z* isomers in 1-phenyl propene was moderate with 1.6:1.0 when benzaldehyde was engaged in the reaction. On the other hand, β-keto sulfinamide **502**, prepared *in situ*, underwent facile decomposition to afford acetophenone **504** in 89% yield (Scheme 113).



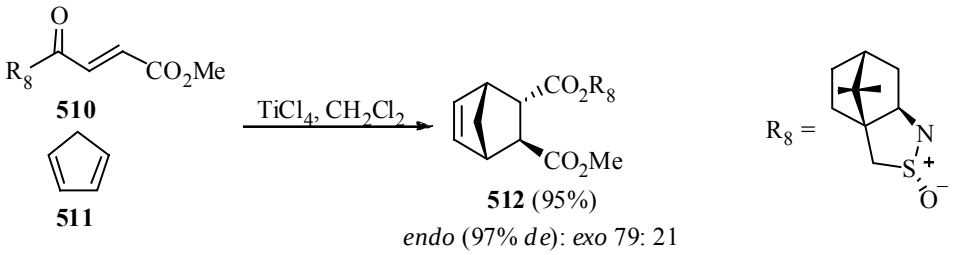
Scheme 113 Synthesis of Olefin and Ketone

Propargyl and vinyl sulfinamides can also participate in sigmatropic rearrangements. For example, **506** underwent a retro-ene reaction in aprotic solvents to form allenes **507** and *N*-sulfinylamine under very mild conditions (quantitative conversion within 30 min at 40 °C).[192] In addition, indole **509** was formed in 75% yield from *N*-phenyl-1-vinylsulfinamide **508** via a [3.3] sigmatropic rearrangement (Scheme 114).[171]



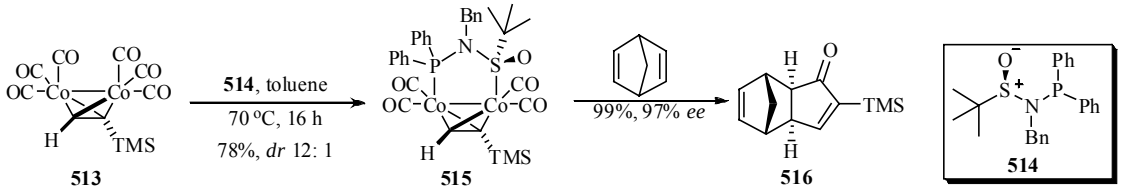
Scheme 114 Sigmatropic Rearrangement

Besides being valuable precursors to a variety of building blocks, sulfinamides have also been utilized as chiral auxiliary groups in asymmetric synthesis. In 2001, Chapuis and coworkers[213] reported the asymmetric Diels-Alder reaction using a chiral cyclic sulfinamide as an auxiliary group. Diels-Alder adduct **512** was obtained in 95% yield with an *endo/exo* ratio of 79: 21, the *endo* isomer (as shown) being formed with 97% *de* (Scheme 115).



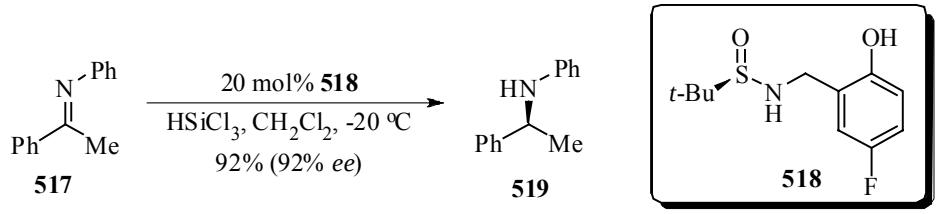
Scheme 115 Sulfinamide as Chiral Auxiliary in Diels-Alder Reaction

Sulfinamides were also incorporated into *N*-phosphinosulfinamide (PNS=O) ligands in the early 1970s.[214] Recently, the first application of this type of PNS=O ligands was reported by Verdaguer[215]. Several novel PNSO ligands were synthesized and applied in the intramolecular Pauson-Khand reaction. For example, heating the ligand **514** with dicobalthexacarbonyl complex **513** provided **515** in 78% yield with good diastereoselectivity. The major isomer was obtained by crystallization. A Pauson-Khand reaction was carried out with norbornadiene to give compound **516** in nearly quantitative yield with 97% *ee* (Scheme 116).



Scheme 116 PNS=O Ligand in the Asymmetric Pauson-Khand Reaction

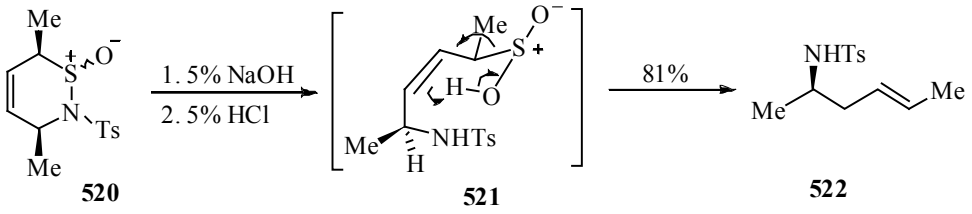
Chiral sulfinamides can serve as organocatalysts in organic synthesis. Sun and coworkers[216] reported the first example of chiral sulfinamide **518** being employed as an enantioselective organocatalyst. Ketimine **517** was converted to amine **519** in 92% yield with 92% *ee* (scheme 117). The reaction was found to be applicable to a broad range of *N*-aryl ketimines giving amines in high yield and enantioselectivity.



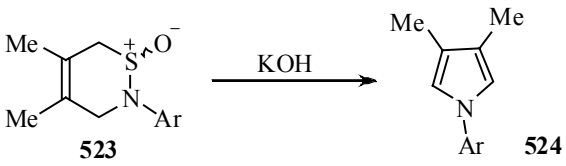
Scheme 117 Enantioselective Reduction of Ketimine **517**

1.3.2 Cyclic Sulfinamides in Organic Synthesis

Cyclic sulfinamides, particularly Diels-Alder adducts of *N*-substituted sulfinamine, have been widely applied in organic synthesis.[167,196] For example, hydrolysis of **520** under basic and acidic conditions produced amine **522** in 81% yield, which apparently involved a retro-ene reaction (Scheme 118).[217] Treatment of **523** with potassium hydroxide delivered pyrrole **524** with the loss of sulfur oxide (Scheme 119).

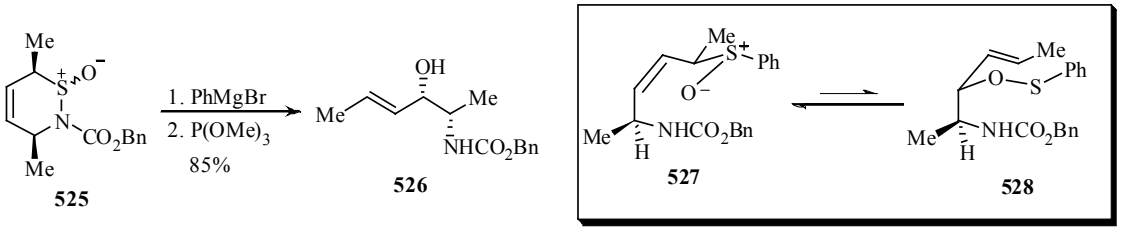


Scheme 118 Hydrolysis of **520** in the Basic Medium



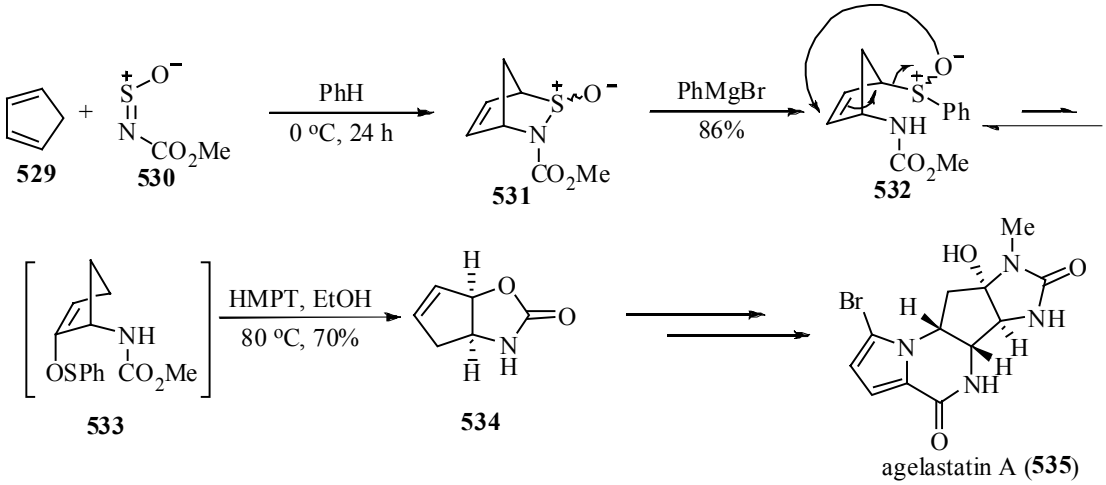
Scheme 119 Ring Contraction of **523**

More importantly, these Diels-Alder adducts have been applied to the diastereoselective synthesis of unsaturated vicinal amino alcohols.[196] Employing the sequential treatment with phenylmagnesium bromide and trimethyl phosphite, **525** was converted to (*E*)-*threo*-hydroxy carbamate **526** in 85% yield as a single diastereomer. Two intermediates allylic sulfoxide **527** and sulfenate ester **528** were presumably in equilibrium. In the presence of phosphite, the reduction of **528** occurred to give sulfenate ester **526** (Scheme 120).[218]



Scheme 120 Synthesis of *E-threo*-hydroxy Carbamate **526**

The Diels-Alder reaction/[2.3] rearrangement sequence has been beautifully applied in the total synthesis of agelastatin A (**535**) by the Weinreb group in 1999. A Diels-Alder reaction was carried out smoothly at 0 ^{o}C to provide adduct **531**, which was immediately treated upon formation with Grignard reagent and furnished sulfoxide **532**. HMPT-induced a [2,3]-sigmatropic rearrangement converted **532** to sulfenate ester **533**. Subsequent ring closure afforded **534**, a key intermediate in the total synthesis of agelastatin A (Scheme 121).

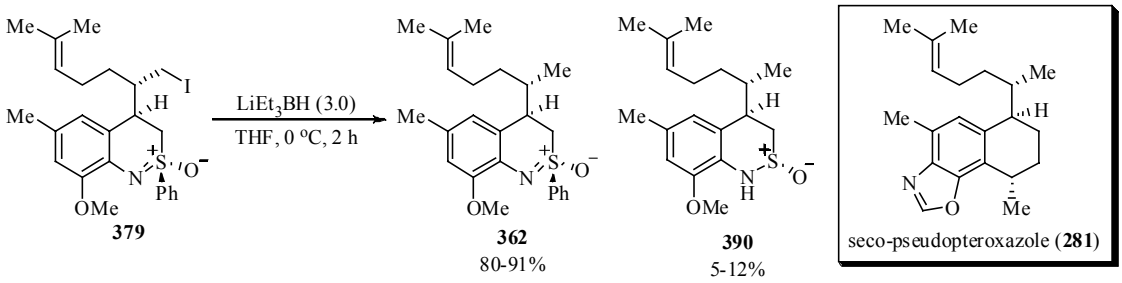


Scheme 121 Weinreb's Synthesis of Agelastatin A

Other than the extensive studies of Diels-Alder adducts of sulfinylamine, the chemistry of other cyclic sulfinamides remains less developed. For example, chiral cyclic sulfinamides are seldomly envisaged as chiral templates for organic molecules or as chiral ligands in asymmetric synthesis. This is probably due to the lack of a general approach to accessing chiral cyclic sulfinamides.

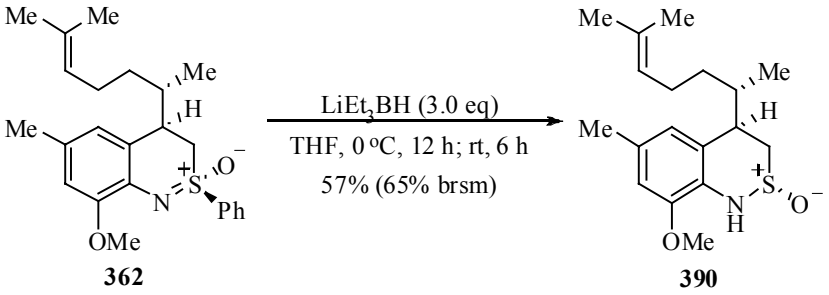
2 Results and Discussion

In the course of the total synthesis of *seco*-pseudopteroxazole **281**, some synthetic efforts were made to convert **379** to **362**, which was expected to be a key intermediate in the synthesis of **281**. After extensive exploration, conditions utilizing 3.0 equivalents of lithium triethylborohydride were adopted to afford 80-91% yield of **362** (Scheme 122). Despite the excellent yield of **362**, we did notice that a small amount of byproduct **390** was isolated in yields of 5-12%. NMR spectra of byproduct **390** showed the absence of *S*-phenyl group. The distinct deuterium exchangeable peak at 6.86 ppm, combined with IR data (3252, 1082, 878, 829 cm^{-1}) suggested the presence of the sulfinamide functional group in the molecule. Thus the structure was assigned as **390**.



Scheme 122 Reductive Cleavage of C-I Bond

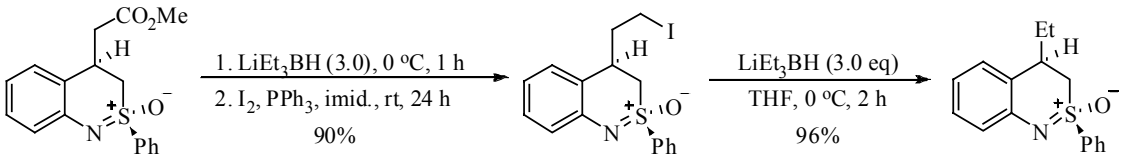
To confirm the intermediacy of **362** during the dephenylation reaction[219], **362** was treated with 3.0 equivalents of $LiEt_3BH$. After being stirred for 12 hours at 0 °C and 6 hours at room temperature, sulfinamide **390** was isolated in 57% yield, accompanied by 12% of recovered starting material (Scheme 123).



362 390

Scheme 123 Dephenylation of **362**

Excited by these results, we set out to synthesize enantiomerically pure **538** and optimized the conditions of dephenylation reaction. Enantiomerically pure Harmata benzothiazine ester **536** was synthesized from methyl 2-bromocinnamate employing our benzothiazine chemistry.[220] Compound **536** was reduced with lithium triethylborohydride, followed by iodination. Iodide **537** was formed in 90% yield. Reductive cleavage of C-I bond delivered **538** in 96% yield (Scheme 122).



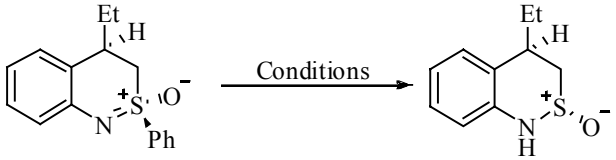
536 537 538

Scheme 124 Preparation of Benzothiazine **538**

Various reaction conditions were explored and the results are summarized in Table 21. A mixture containing **538** and **539** (0.46:1.0) was obtained after 24 hours at room temperature when **538** was treated with 3.0 equivalents of lithium triethylborohydride (entry 1). When the reaction was refluxed for 6 hours, **539** was obtained in 71% yield as a single diastereomer, whose structure was securely confirmed by X-ray analysis (Figure 24). No reaction was observed in the presence of dry cerium chloride[221]. Compound **538**

was found to slowly decompose to a complicated mixture when stired with lithium aluminohydride. In addition, **538** remained intact after prolonged treatment with 3.0 equivalents of diborane in THF solution.

Table 21 Optimization of Dephenylation of **538**



538 **539**

entry	Conditions	Yield (%)
1	$LiEt_3BH$ (3.0), THF, rt, 24 h	[a]
2	$LiEt_3BH$ (3.0), THF, reflux, 6 h	71
2	$LiEt_3BH$ (3.0), $CeCl_3$ (3.0), THF, reflux, overnight	0 [b]
3	$LiAlH_4$ (3.0), THF, rt, 60 h	0 [c]
4	BH_3 (3.0), THF, rt, 60 h	0 [b]

[a] The ratio **538**: **539** (0.46: 1.0) was determined by NMR analysis of crude mixture.

[b] Only clean starting material was recovered. [c] Complicated mixture.

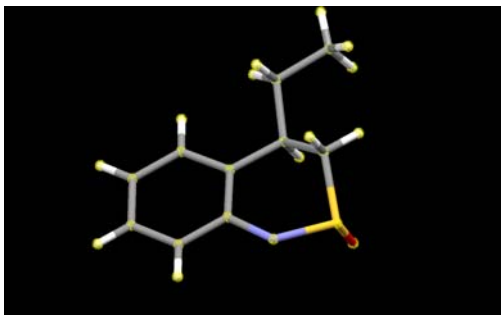


Figure 24 X-ray Structure of **539**

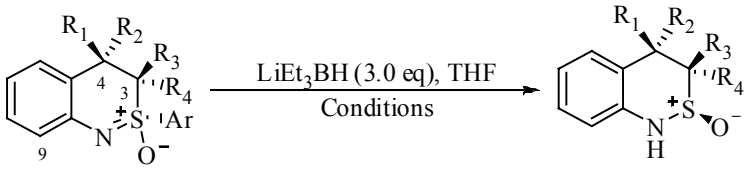
To examine the generality of this dephenylation reaction, we applied the best conditions to a series of Harmata type benzothiazines (Table 22). When compound **540**

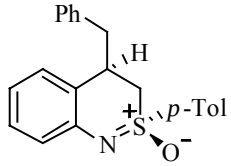
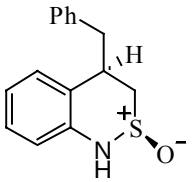
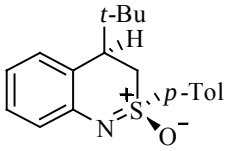
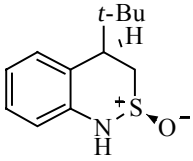
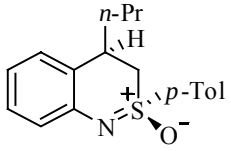
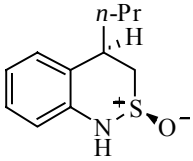
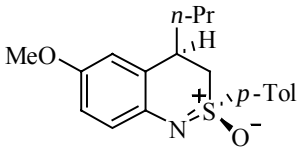
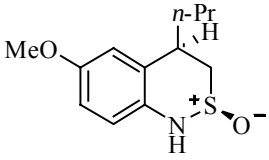
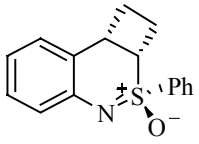
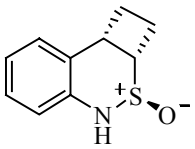
was refluxed with 3.0 equivalents of lithium triethylborohydride, a nearly quantitative yield of **541** was obtained as a single diastereomer after column chromatography (entry 1). A similar result was obtained for *t*-butyl substrate (entry 2). The reaction worked well for *n*-propyl substrate (entry 3, 4). In general, the substituent at C-4 position plays little role in the dephenylation of benzothiazine.

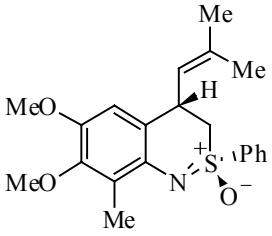
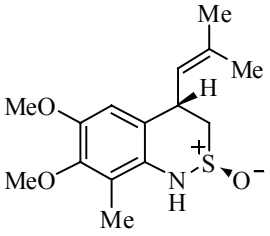
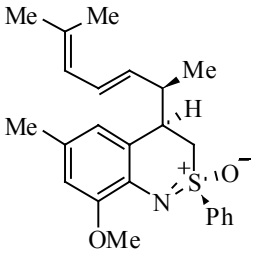
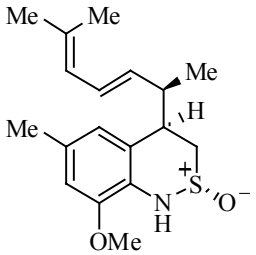
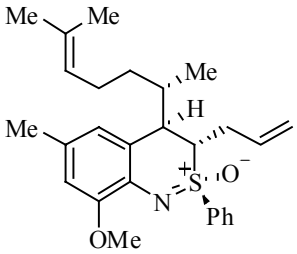
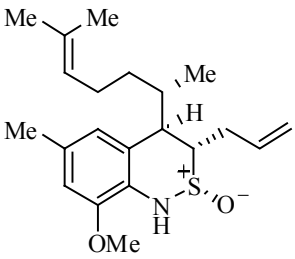
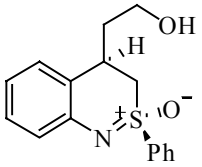
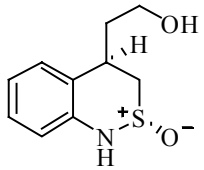
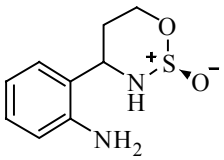
To our surprise, the cyclobutane ring in **548** remained untouched in the presence of the strongly nucleophilic reducing reagent lithium triethylborohydride. The desired sulfinamide **549** was isolated in 59% yield in addition to 17% recovered starting material (entry 5). Interestingly, benzothiazine **550** with an electron rich *N*-phenyl ring reacted surprisingly fast to afford **551** in excellent yield (entry 6). The labile diene moiety and allyl group stayed intact during the reaction (entry 7, 8). Steric hindrance at C-3 position was tolerated in the dephenylation and epimerization at C-3 was not observed (entry 8). The structure of **555** was firmly established by X-ray analysis (Figure 25). Alcohol **556** was also refluxed with 4.0 equivalents of lithium triethylborohydride, the desired sulfinamide **557** was isolated in 70% yield. A 14% yield of sulfinate **558** was also separated, due to the most likely S_N2 substitution on sulfur atom (entry 9).

In conclusion, electron rich substituents on the *S*-phenyl ring tend to decrease the reactivity in the dephenylation reaction and result in longer reaction time. In contrast, an increase of electron density on the *N*-phenyl ring seems to accelerate the reaction. The reaction seems unaffected by the steric hindrance at C-3 or C-4 position.

Table 22 Dephenylation of a Series of Harmata Benzothiazines



entry	Benzothiazine[a,h]		Sulfinamide[h], Yield (%)[b]
1		**540**	 **541** (99)[c]
2		**542**	 **543** (96)[c]
3		**544**	 **545** (90)[c]
4		**546**	 **547** (70)[c]
5		**548**	 **549** (59)[d] (73 brsm)

6		**550**		**551** (90)[e]
7		**552**		**553** (84)[f]
8		**554**		**555** (89)[g]
9		**556**		**557** (70)[d]
				**558** (14)[d]

[a]Compound **540**, **542**, **544** and **546** were racemic. [b]Yields are for chromatographically purified materials. [c]Refluxed for 24 h. [d]Refluxed for 12 h. [e]Refluxed for 3 h. [f]Refluxed for 8 h. [g]12 h at rt. [h]Diastereomeric ratios determined by ^{1}H-NMR of crude reaction mixtures: **544**, 1.6:1.0; **545**, 1.7:1.0; **546**, 1.3:1.0; **547**, 1.3:1.0; **554**, 8.1:1.0; **555**, 8.2:1.0. [i]4.0 equivalents of lithium triethylborohydride was utilized.

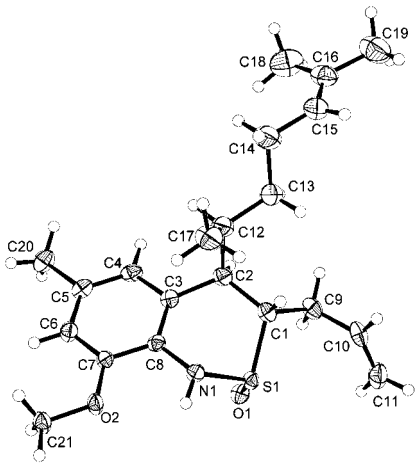
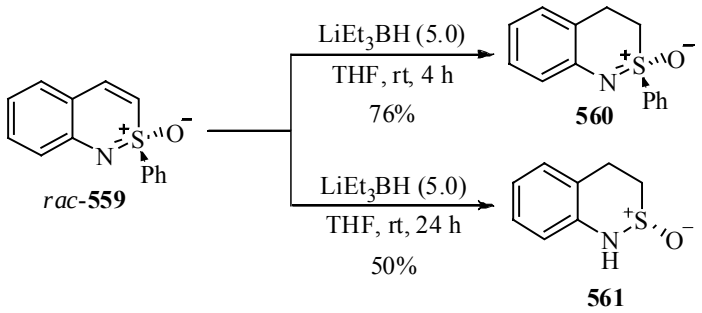


Figure 25 X-ray Structure of **555**

The readily available benzothiazine **559** was also treated with lithium triethylborohydride (Scheme 125). The double bond was easily reduced to give **560** in 76% yield. The reaction was found to undergo further reductive dephenylation when the reaction mixture was stirred for 24 hours at room temperature. The reaction proceeded smoothly to give simple cyclic sulfinamide **561** in ca. 50% yield. The structure of **561** was also confirmed by X-ray analysis (Figure 26).



Scheme 125 Reduction of *rac*-**559**

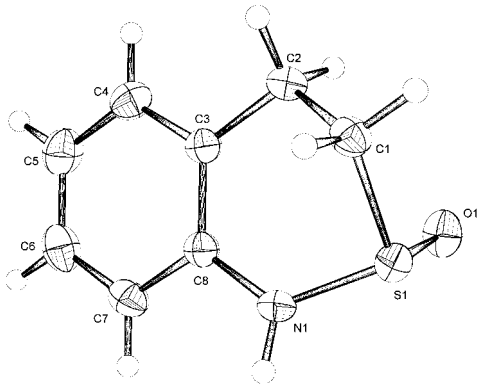
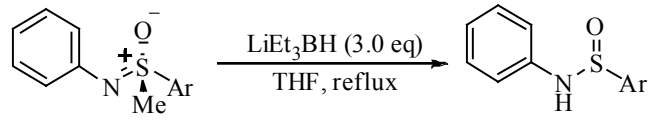


Figure 26 X-ray Structure of **561**

With excellent results obtained from Harmata benzothiazines, we turned our attention to acyclic sulfoximines. *Rac*-*S*-phenyl sulfoximine **562** was subjected to the standard dephenylation conditions, sulfinamide **564** was isolated in 57% yield. Similarly, *rac*-*S*-tolyl sulfoximine **563** was converted to **565** in 60% yield. Apparently acyclic sulfoximines proceeded through a different mechanism to that of cyclic Harmata benzothiazines (Scheme 126).



rac-**562** Ar= Ph
rac-**563** Ar= Tol

564 Ar= Ph (57%)
565 Ar= Tol (60%)

Scheme 126 Reduction of Acyclic Sulfoximines

Some preliminary mechanistic studies were carried out on the substrate **529** to determine the existence of volatile products employing quantitative GC analysis with *n*-decane as internal standard. The GC yield was calculated using the following equations. The response factor of compound A was calculated as the ratio of peak area of compound

A and a standard compound (*n*-decane) (Figure 27). The GC yield of compound A was calculated using the equation in Figure 28.

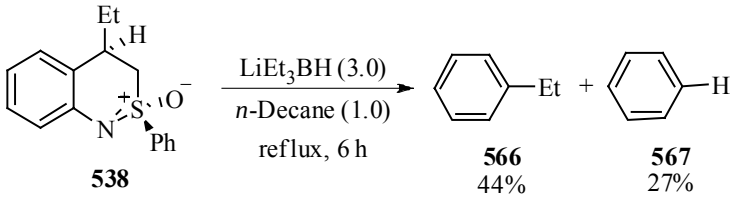
$$Rf_A = \frac{S_A / n_A}{S_{std} / n_{std}} = \frac{S_A}{S_{std}}$$

Figure 27 Calculation of Responding Factor for Equimolar of Compound A Relative to Standard Compound

$$A\% = \frac{n'_A}{n'_{std}} \times 100\% = \frac{S'_A}{S'_{std}} \times \frac{1}{Rf_A}$$

Figure 28 Calculation of GC Yield of Compound A

Compound **538** was refluxed with 3.0 equivalents of lithium triethylborohydride in the presence of 1.0 equivalent of *n*-decane. The excess borohydride was quenched by the sequential addition of methanol, sodium hydroxide solution and hydrogen peroxide. Ethyl benzene was obtained in 44% yield, accompanied by 27% of benzene, which provided valuable information for this dephenylation reaction (Scheme 127).

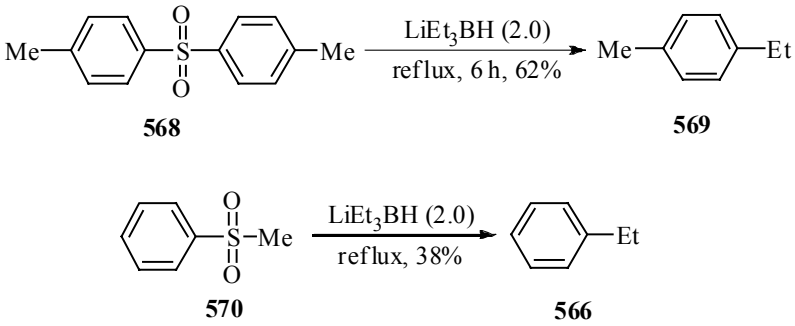


538 **566** 44% **567** 27%

Scheme 127 Quantitative GC Studies of Dephenylation of **538**

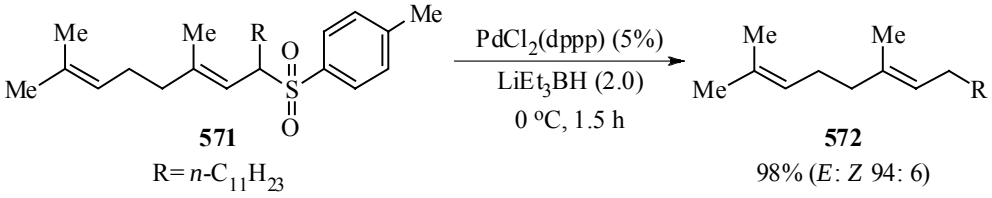
The similar observation in the sulfone system was also made in 1983 by Brown and coworkers (Scheme 128).[219] They shown that ditolylsulfone **568** was converted into *p*-ethyltoluene **569** in 62% yield when refluxing with 2.0 equivalents of lithium

triethylborohydride. This reaction didn't work well for alkyl sulfone system such as **570**. Only a 38% yield of ethyl benzene **566** was formed by GC (Scheme 128).



Scheme 128 Reaction of Sulfones with $LiEt_3BH$

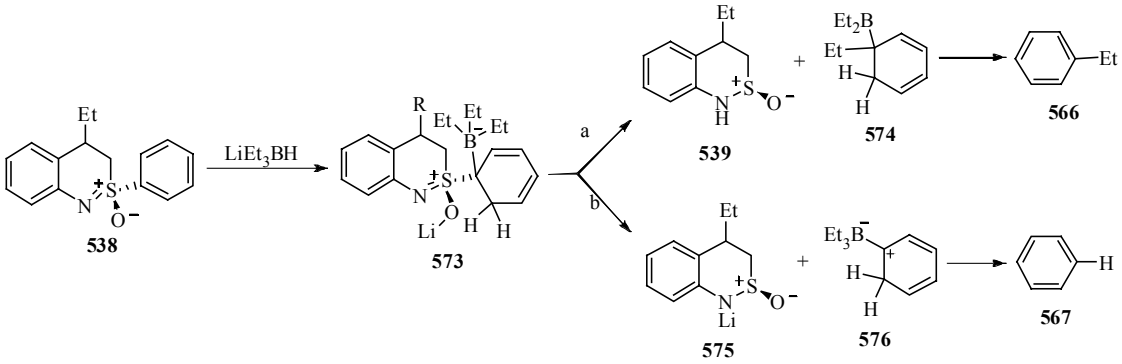
Another $LiEt_3BH$-mediated desulfonation was first reported by Hutchins[222] and was further developed into a synthetically useful methodology by Inomata[223] in 1985. When allylic tolyl sulfone **571** was treated with 2.0 equivalents of lithium triethylborohydride in the presence of 5% $PdCl_2$(dppp), an alkene was formed in 98% yield with high stereo retention of the *E*-alkene. Migration of the double bond was also observed in this reaction (Scheme 129).



Scheme 129 Pd-catalyzed Desulfonation Reaction

Based on our experimental results and literature information, we proposed a mechanism for the dephenylation reaction as shown in Scheme 130. Addition of $LiEt_3BH$ to the electron deficient phenyl ring could yield tetrahedron intermediate **573**. Compound

573 could further undergo 1,2-migration of the ethyl group to another tetrahedron intermediate **574**, and the sulfoximine moiety would be reduced to give sulfinamide **539**. Aromatization of intermediate **574** might generate ethyl benzene **566** (path a). On the other hand, **573** might also eliminate lithium sulfinamide **575** to form intermediate **576**, which was protonated to generate benzene **567**.



Scheme 130 Proposed Mechanism for the Dephenylation **538**

3 Summary

We have discovered the first approach towards chiral cyclic sulfinamides from readily available enantiomerically pure Harmata benzothiazines. This methodology features mild reaction conditions and complete stereocontrol. Preliminary mechanistic studies were carried out and a plausible mechanism was proposed based on our experimental results. Further application of this reaction is under way in our lab and results will be reported in due course.

Chapter V

Experiments

1 General information

All reactions were carried out under an atmosphere of nitrogen or argon in flamed-dried glassware. Et_2O, THF and toluene were distilled over sodium-benzophenone before use. Triethylamine, dichloromethane and acetonitrile were distilled over cacium hydride. Trifluoroethanol was distilled from $CaSO_4$. All commercial grade reagents and solvents were used, unless otherwise noted.

Chromatographic separations were carried out using Silicycle ultra pure silica gel (230-400 mesh). Analytical thin chromatography was performed on EM reagent 0.25 nm silica gel 60-F plates with F-254 indicator. Melting points were measured with a Fisher-Johns melting point apparatus. Infrared spectra were recorded on a Thermo Nicolet NEXUS 670 FT-IR spectrometer. Optical rotations were measured on a Jasco DIP-370 digital polarimeter with a sodium lamp and are reported as follows: $[\alpha]^{25}_{D}$ (*c* g/100 mL, solvent). HRMS was carried out using Bruker 12 Tesla FRICR-MS with an Apollo II ion source in Old Dominion University and Ohio State University. Elemental analysis were performed by the MHW laboratories, Phoenix, AZ.

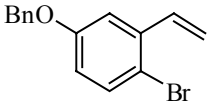
GC-MS analysis was performed on an Agilent 5973N Massive Selective Detector interfaced to an Agilent 6890 GC System equipped with an HP capillary column (HP-624, 27.8m X 0.25 mm). *n*-Decane was utilized as internal standard. GC conditions were as followed: flow rate: 1ml/min; 70 ^{o}C, 5 min, 10 ^{o}C/min, 200 ^{o}C, 1 min.

^{1}H-NMR were recorded on a Bruker ARX-250 (250 MHz), DRX-300 (300 MHz), DRX-500 (500 MHz) spectrometer and are reported in ppm (δ) from tetramethylsilane (TMS: δ 0.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, ddd = doublet of doublet of doublet), coupling constants (Hz) and integration. ^{13}C-NMR spectra were recorded on a Bruker ARX-250 (62.5 MHz), DRX-300 (75 MHz), DRX-500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with solvent resonance as the internal standard ($CDCl_3$: δ 77.0 ppm).

2 Deantiaromatization as a Driving Force in an Electrocyclic Reaction

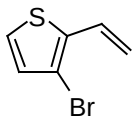
Typical procedure for synthesizing bromoalkenes

The methyltriphenylphosphonium iodide (2.81 g, 6.96 mmol) in THF (25 mL) solution under nitrogen at room temperature was added *n*-BuLi (2.3 M in hexanes, 3.0 ml, 6.9 mmol) dropwise. Stiring was continued for another 1.0 hr. Bromoaldehyde (6.63 mmol) in THF (5 ml) solution was then added to the above mixture. The reaction was monitored with TLC. After all of the bromoaldehyde was consumed, the reaction mixture was poured into 200 ml ice water, extracted with 100 ml x3 hexane and washed with saturated NaCl solution. The organic extract was dried over $MgSO_4$ and the solvent was removed by rotavap. Column chromatography (pure hexane) provided the desired bromoalkene.



4-Benzyloxy-1-bromo-2-vinylbenzene: colorless liquid, 64% yield; IR: ν 1585.0, 1560.5, 1462.4 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.32 – 7.46 (m, 6H), 7.18 (d, *J*= 3.0 Hz, 1H), 7.02 (dd, *J*= 17.4, 10.9 Hz, 1H), 6.78 (dd,

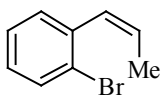
J= 8.8, 3.0 Hz, 1H), 5.67 (dd, *J*= 17.3, 0.9 Hz, 1H), 5.37 (dd, *J*= 10.9, 0.9 Hz, 1H), 5.08 (s, 2H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 158.1, 138.2, 136.5, 135.8, 128.6, 128.1, 127.4, 116.7, 116.0, 114.5, 113.0, 70.2; Anal. calcd for $C_{15}H_{13}BrO$: C, 62.30, H, 4.53, found C, 62.21, H, 4.45.



3-Bromo-4-vinylthiophene: colorless liquid, 69% yield; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.15 (d, *J* = 5.2 Hz, 1H), 6.95 (d, *J* = 5.3 Hz, 1H), 6.89 (ddd, *J* =17.4, 11.0, 0.7 Hz, 1H), 5.65 (d, *J* = 17.4 Hz, 1H), 5.27 (d, *J* = 11.0 Hz, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 137.1, 130.5, 128.2, 124.0, 115.3, 110.4; HRMS caclcd for C_6H_5BrS M^+ 187.9289, found 187.9278.

Preparation of (*Z*)-1-bromo-(2-prop-1-enyl)benzene

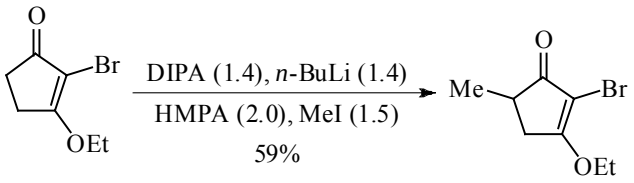
A solution of nickelous acetate tetrahydrate (67.8 mg, 0.272 mmol) in EtOH (48 ml) under H_2 was treated with a 1 M solution of $NaBH_4$ (272 μl, 0.272 mmol, EtOH). To this black solution was added a solution of 1-bromo-2-(prop-1-ynyl)benzene (208.5 mg, 1.06 mmol) and ethylenediamine (18.2 μl, 0.272 mmol) in EtOH (10 ml). The reaction was monitored by TLC (ca 1hr). The reaction mixture was evaporated. The residue was dissolved in ether, sequentially washed with 0.5 N HCl (x 1), with H_2O (x 2) and brine (x 1). The organic extract was dried over $MgSO_4$ and the solvent was evaporated. Column chromatography (pentane) would give (*Z*)-1-bromo-(2-prop-1-enyl)benzene (135.1 mg, 66% yield).



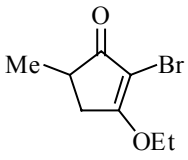
(*Z*)-1-bromo-(2-prop-1-enyl)benzene: Colorless liquid, 66% yield; IR: ν 3084.6, 1621.7, 1437.9, 1348.0, 972.0, 910.7, 869.9, 718.7, 677.8 cm^{-1};

^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.60 (d, *J*= 7.9 Hz, 1H), 7.25-7.31 (m, 2H), 7.07-7.14 (m, 1H), 6.46-6.52 (m, 1H), 5.90 (dt, *J*= 11.4, 7.1 Hz, 1H), 1.79 (dd, *J*= 7.1, 1.7 Hz, 3H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 137.2, 132.5, 130.6, 129.3, 128.1, 128.0, 126.7, 123.9, 14.3; HRMS caclcd for C_9H_9Br M^+ 195.9882, found 195.9891.

Preparation of 2-bromo-3-ethoxy-5-methylcyclopent-2-enone



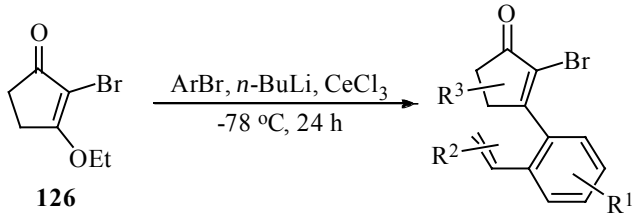
To a solution of diisopropylamine (380 μL, 2.73 mmol) in THF (2.0 mL) at –20 ^{o}C under N_2 atmosphere, was added *n*-BuLi (2.0 M, 1.3 mL, 2.73 mmol) dropwise. The resulting mixture was stirred for 30 mins before it was brought to 0 ^{o}C for another 10 mins. The resulting mixture was cooled to –78 ^{o}C and was added a solution of 2-bromo-3-ethoxycyclopentenone (400 mg, 1.95 mmol) in THF (1.5 mL) solution. After 45 mins at –78 ^{o}C, a mixture of MeI (180 μL, 2.93 mmol) and HMPA (680 μL, 3.90 mmol) in THF (1.0 mL) solution was added dropwise. The stirring was continued for another 2.5 hrs before it was quenched by the addition of sat. NH_4Cl solution. Dilute with water, extract with CH_2Cl_2 (x 3) and sequentially wash with H_2O, brine. The organic extract was dried over $MgSO_4$ and the solvent was evaporated. Column chromatography (30% EtOAc) gave the title compound 252 mg (59% yield).



Colorless oil, 59% yield; IR: ν 2974.3, 1691.2, 1593.1 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 4.37 (q, *J* = 7.0 Hz, 2H), 3.01 (dd, *J* = 17.3, 7.0 Hz, 1H), 2.64 (qdd, *J* = 7.4, 7.3, 2.3 Hz, 1H), 2.33 (dd, *J*= 17.3, 2.3 Hz,

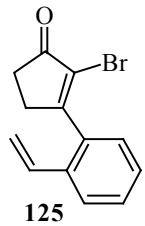
1H), 1.46 (t, J = 7.0 Hz, 3H), 1.25 (t, J = 7.4 Hz, 3H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 200.7, 182.5, 97.2, 66.7, 38.4, 34.8, 16.9, 15.1; HRMS caclcd for $C_8H_{11}BrO_2$ M^+ 217.9936, found 217.9945.

Typical procedure for synthesizing 2-bromo-3-styrenyl-cyclopentenones



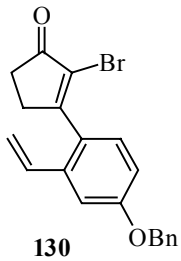
126 **130-140**

$CeCl_3$ was dried using Bunnelle's method[71]. A Schlenk flask was charged with $CeCl_3 \cdot 7H_2O$ (558 mg, 1.5 mmol), which was immersed in oil bath under full vacuum. The flask was heated slowly to 150 ^oC. After the flask was slowly stirred for 2 hrs at 150 ^oC, it was cooled to RT and vented to dry N_2. THF (3.4 ml) was added with good stirring. The white suspension was stirred overnight at RT. The above slurry at -78 ^oC was treated dropwise with 2-lithio-styrene[224], which was prepared in situ by dropwise addition of *n*-BuLi (2.3 M in hexanes, 650 µl, 1.5 mmol) to 2-bromostyrene (188 µl, 1.5 mmol) in a mixture of THF (13 ml) and Et_2O (3.0 ml) and stirring for 15 mins at this termperature. Stirring was continued for an additional 1.0 hr. At this stage, 2-bromo-3-ethoxy-cyclopent-2-en-1-one (205 mg, 1.0 mmol) in THF (2.0 ml) solution was added slowly. The resulting slurry mixture was stirred for 24 hrs at –78^oC before it was quenched by addition of saturated NH_4Cl solution. Extract the mixture with Et_2O and dry over $MgSO_4$. Column chromatography (20% EtOAc in hexane) provided 2-bromo-3-(2-vinylphenyl) cyclopent-2-en-1-one (71% yield based on recovered starting material).



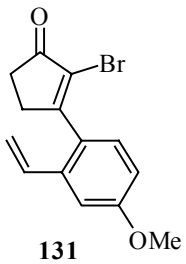
125

2-Bromo-3-(2-vinylphenyl) cyclopent-2-en-1-one (125): pale yellow solid 61% yield (71% yield b.r.s.m.), m.p.: 101-2 ^{o}C; IR: ν 1707.6, 1613.6 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.64-7.67 (m, 1H), 7.34-7.45 (m,2H), 7.17 (dd, *J*= 7.5, 1.4 Hz, 1H), 6.60 (dd, *J*= 17.4, 11.0 Hz, 1H), 5.74 (dd, *J*= 17.4, 0.6 Hz, 1H), 5.33 (dd, *J*= 11.0, 0.6 Hz, 1H), 2.93-2.96 (m, 2H), 2.71-2.74 (m, 2H); ^{13}C-NMR (75.0 MHz, $CDCl_3$): δ 201.1, 172.6, 134.4, 134.3, 133.8, 129.3, 127.7, 126.6, 125.8, 125.0, 116.7, 33.3, 33.1; HRMS caclcd for $C_{13}H_{11}BrO$ M^+ 261.9987, found 261.9977.



130

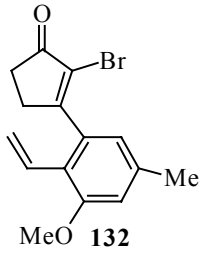
3-(4-(benzyloxy)-2-vinylphenyl)2-bromocyclopent-2-enone (130): pale brown solid, 51% yield; m.p.: 127-8 ^{o}C; IR: ν 2921.2, 1707.6, 1621.8, 1593.2, 1486.9 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.34-7.49 (m, 5H), 7.24 (d, *J* = 2.5 Hz, 1H), 7.14 (d, *J* = 8.5 Hz, 1H), 7.00 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.58 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.71 (dd, *J* = 17.3, 0.7 Hz, 1H), 5.33 (dd, *J* = 10.9, 0.7 Hz, 1H), 5.13 (s, 2H), 2.91-2.95 (m, 2H), 2.69-2.73 (m, 2H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 201.3, 172.5, 159.6, 136.5, 136.4, 134.1, 128.6, 128.3, 128.1, 127.5, 127.1, 125.0, 116.9, 114.3, 112.1, 70.1, 33.4, 33.3; HRMS caclcd for $C_{20}H_{17}BrO_2Na$ $[M+Na]^+$ 391.0304, found 391.0322.



131

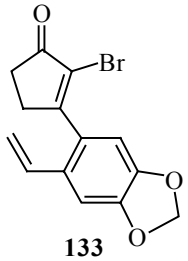
2-Bromo-3-(4-methoxy-2-vinylphenyl)cyclopent-2-enone(131): Brown solid, 46% yield; m.p.: 112-3 ^{o}C; IR: ν 1723.9, 1691.2, 1556.4 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.12-7.15 (m, 2H), 6.91 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.58 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.71 (d, *J*

= 17.2 Hz, 1H), 5.32 (d, *J* = 11.2 Hz, 1H), 3.86 (s, 3H), 2.91-2.94 (m, 2H), 2.67-2.71 (m, 2H); ^{13}C-NMR (75.0 MHz, $CDCl_3$): δ 201.3, 172.5, 160.3, 136.2, 134.1, 128.2, 126.8, 124.8, 116.7, 113.6, 110.9, 55.2, 33.3, 33.2; HRMS caclcd for $C_{14}H_{13}BrO_2Na$ $[M+Na]^+$ 314.9991, found 314.9993.



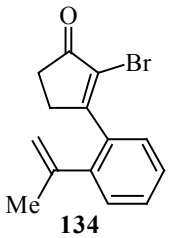
132

2-Bromo-3-(3-methoxy-5-methyl-2-vinylphenyl)cyclopent-2-enone (132): Yellow solid, 71% yield (b.r.s.m.); m.p.: 67-8 ^{o}C; IR ν 1715.7, 1617.7, 1593.1 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 6.76 (s, 1H), 6.69 (dd, *J* = 17.7, 11.5 Hz, 1H), 6.59 (s, 1H), 5.46 (dd, *J* =17.7, 1.8 Hz, 1H), 5.31 (dd, *J* = 11.5, 1.8Hz, 1H), 3.87 (s, 3H), 2.89-2.93 (m, 2H), 2.63-2.67 (m, 2H), 2.38 (s, 3H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 201.4, 174.3, 157.6, 138.7, 135.6, 130.7, 124.5, 121.6, 119.5, 119.1, 112.1, 55.5, 33.4, 32.4, 21.5; HRMS caclcd for $C_{15}H_{15}BrO_2Na$ $[M+Na]^+$ 329.0147, found 329.0141.



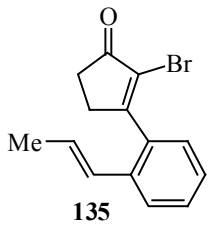
133

2-Bromo-3-(6-vinylbenzo[d][1,3]dioxol-5-yl)cyclopent-2-enone (133): Pale brown solid, 56% yield; m.p.: 145-6 ^{o}C; IR ν 1707.6, 1589.1, 1486.9cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.12 (s, 1H), 6.63 (s, 1H), 6.47 (dd, *J* = 17.3, 10.9 Hz), 6.03 (s, 2H), 5.60 (d, *J* = 17. Hz, 1H), 5.22 (d, *J* = 10.9 Hz, 1H), 2.88-2.92 (m, 2H), 2.69-2.72 (m, 2H); ^{13}C-NMR (75.0 MHz, $CDCl_3$): δ 201.2, 172.2, 148.9, 147.5, 133.4, 129.1, 128.1, 125.4, 114.9, 106.5, 105.5, 101.6, 33.4, 33.3; HRMS caclcd for $C_{14}H_{11}BrO_3$ M^+ 305.9886, found 305.9900.



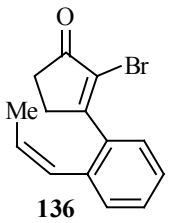
134

2-Bromo-3-(2-(prop-1-en-2-yl)phenyl)cyclopent-2-enone (134): Pale yellow solid, 32% yield; m.p.: 58-9 ^{o}C; IR ν 1715.7, 1613.6, 1433.8 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ7.31-7.44 (m, 3H), 7.22-7.27 (m, 1H), 5.12 (t, *J* = 1.5 Hz, 1H), 4.88 (d, *J* = 0.5 Hz, 1H), 2.90-2.93 (m, 2H), 2.63-2.67 (m, 2H), 2.09 (s, 3H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 201.4, 174.3, 143.7, 141.5, 133.5, 129.2, 128.2, 127.7, 127.1, 124.2, 116.5, 33.4, 32.1, 23.6; HRMS caclcd for $C_{14}H_{13}BrO$ M^+ 197.0960, found 197.0969.



135

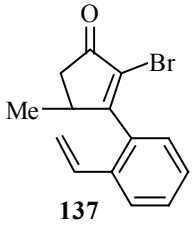
(*E*)-2-bromo-3-(2-(prop-1-enyl)phenyl)cyclopent -2-enone (135): Pale yellow solid, 85% yield, m.p.: 92-3 ^{o}C; IR: ν 2908.9, 1707.6, 1613.6, 1433.8, 1184.5 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J*= 7.5 HZ, 1H), 7.37 (td, *J*= 7.5, 1.0 Hz, 1H), 7.30 (td, *J*= 7.5, 1.0 Hz, 1H), 7.14 (dd, *J*= 7.5, 1.0 Hz, 1H), 6.19-6.27 (m, 2H), 2.93-2.95 (m, 2H), 2.71-2.73 (m, 2H), 1.87 (d, *J*= 5.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 202.2, 174.0, 135.6,134.4, 130.1, 129.7, 128.8, 127.6, 127.4, 126.8, 125.7, 34.2, 33.9, 19.5; HRMS caclcd for $C_{14}H_{13}BrO$ M^+ 276.0144, found 276.0137.



136

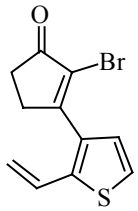
(*Z*)-2-bromo-3-(2-(prop-1-enyl)phenyl)cyclopent -2-enone (136): pale brown solid, 16% yield (78% b.r.s.m.). m.p.: 64-5 ^{o}C; IR: ν 3015.2, 1715.8, 1613.6 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.24-7.45 (m, 4H), 6.33 (d, *J*= 11.4, 1H), 5.83 (dt, *J*= 11.4, 7.0 Hz, 1H), 2.93-2.96 (m, 2H),

2.67-2.70 (m, 2H), 1.75 (dd, *J*= 7.0, 1.7 Hz, 3H); ^{13}C-NMR (75.0 MHz, $CDCl_3$): δ 201.5, 173.3, 134.9, 134.6, 129.8, 129.0, 128.8, 127.5, 126.8, 126.7, 124.3, 33.2, 32.3, 14.4; HRMS caclcd for $C_{14}H_{13}BrO$ M^+ 276.0144, found 276.0137.



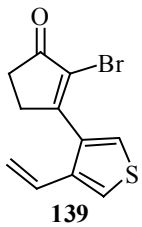
137

2-Bromo-4-methyl-3-(2-vinylphenyl)cyclopent-2-enone (137): Semi-solid, 33% yield; IR ν 2958.0, 1719.8, 1605.4 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.67 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.39 (tdd, *J* = 7.4, 7.4, 1.5 Hz, 2H), 7.09-7.13 (m, 1H), 6.60 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.75 (dd, *J* = 17.4, 0.8 Hz, 1H), 5.31 (dd, *J* = 10.9, 0.9 Hz, 1H), 3.30 (qdd, *J* = 7.2, 6.8, 2.0 Hz, 1H), 2.96 (dd, *J* = 18.8, 6.5 Hz, 1H), 2.31 (dd, *J* = 18.8, 2.0 Hz, 1H), 1.09 (d, *J* = 7.2 Hz, 3H); HRMS caclcd for $C_{14}H_{13}BrO$ M^+ 276.0144, found 276.0186.



138

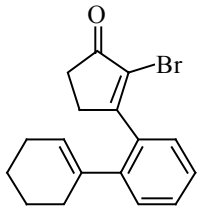
2-Bromo-3-(2-vinylthiophen-3-yl)cyclopent-2-enone (138): Yellow solid, 57% yield; m.p.: 93-4 ^oC; IR ν 1711.6, 1601.3 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.26 (d, *J* = 5.2 Hz, 1H), 7.09 (d, *J* = 5.2 Hz, 1H), 6.72 (dd, *J* = 17.2, 10.9Hz, 1H), 5.67 (d, *J* = 17.2 Hz, 1H), 5.28 (d, *J* = 10.9 Hz, 1H), 2.97-2.99 (m, 2H), 2.68-2.70 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 202.0, 167.5, 142.1, 133.6, 129.7, 127.9, 125.3, 124.8, 116.8, 33.9, 33.3; HRMS caclcd for $C_{11}H_9BrOSNa$ $[M+Na]^+$ 290.9449, found 290.9445.



139

2-Bromo-3-(4-vinylthiophen-3-yl)cyclopent-2-enone 139: Yellow solid, 34% yield; m.p.: 88-89 ^oC; IR ν 1703.5, 1609.5 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.56 (d, *J*= 3.2 Hz, 1H), 7.40 (d, *J*= 3.2 Hz, 1H), 6.60 (dd, *J*=

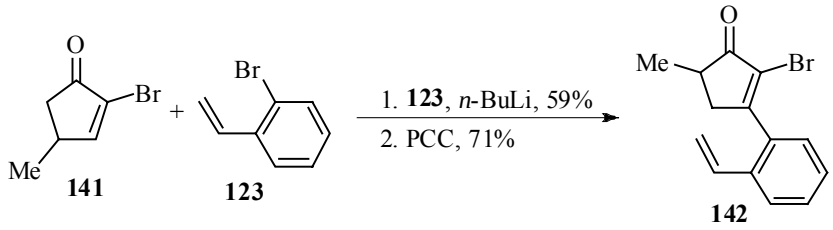
17.5, 10.8 Hz, 1H), 5.67 (dd, *J*= 17.4, 1.1 Hz, 1H), 5.28 (dd, *J*= 10.9, 1.1 Hz, 1H), 2.96-3.00 (m, 2H), 2.66-2.70 (m, 2H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 201.1, 167.0, 138.5, 134.7, 130.1, 126.3, 123.8, 122.7, 116.3, 33.1, 32.5; HRMS caclcd for $C_{11}H_9BrOS$ M^+ 267.9551, found 267.9490.



140

2-Bromo-3-(2-cyclohexenylphenyl)cyclopent-2-enone (140): Pale yellow solid, 12% yield (48% yield b.r.s.m.); m.p.: 76-7 ^{o}C; IR: ν 2921.2, 1711.7 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.40 (t, *J* = 7.46 Hz, 1H), 7.31-7.35 (m, 2H), 7.26 (d, *J* = 7.5 Hz, 1H), 5.60 (s, 1H), 2.92-2.94 (m, 2H), 2.65-2.67 (m, 2H), 2.30-2.31 (m, 2H), 2.08-2.11 (m, 2H), 1.72-1.77 (m, 2H), 1.62-1.67 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 201.6, 174.7, 142.5, 137.0, 133.5, 129.2, 128.3, 127.8, 126.5, 123.8, 33.3, 32.0, 29.4, 25.6, 23.0, 21.7; HRMS caclcd for $C_{17}H_{17}BrONa$ $[M+Na]^+$ 339.0354, found 339.0349.

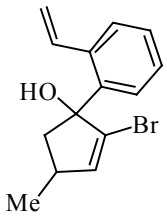
Preparation of 2-bromo-5-methyl-3-(*o*-vinylphenyl)cyclopent-2-en-1-one



141 **123** **142**

$CeCl_3 \cdot 7H_2O$ (558 mg, 1.5 mmol) was dried as before. To the dry $CeCl_3$ under dry N_2 was added THF (3.4 ml) with good stirring. The white suspension was stirred overnight at room temperature. To the above slurry at -78 ^{o}C, was treated dropwise with 2-lithio-styrene, which was prepared in situ by dropwise addition of *n*-BuLi (2.3 M in hexanes, 650 µl, 1.5 mmol) to 2-bromostyrene (188 µl, 1.5 mmol) in a mixture of THF

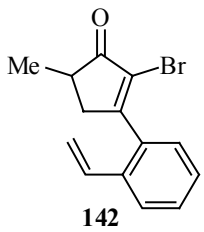
(13 ml) and Et_2O (3.0 ml) and stirring for 15 mins at this termperature. The slurry was stirred for additional 1.0 hr. At this stage, 4-methyl-2-bromocyclopent-2-en-1-one[6] (175 mg, 1.0 mmol) in THF (2.0 ml) solution was added slowly. The resulting slurry mixture was stirred for 24 hrs at –78°C before it was quenched by addition of saturated NH_4Cl solution. Extract the mixture with Et_2O, and dry over $MgSO_4$. Column chromatography (4% EtOAc in hexane) gave 2-bromo-4-methyl-1-(2-vinylphenyl) cyclopent-2-en-1-ol 96.2 mg as white solid (35% yield, 60% based on recovered starting material) and starting material 74.4 mg (43%).



2-Bromo-4-methyl-1-(2-vinylphenyl) cyclopent-2-en-1-ol: (35% yield, 60% b.r.s.m.). m.p.: 42-3 °C; IR: ν 3305.4, 2985.1 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.58 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.47 (dd, *J* = 17.3, 10.9 Hz, 1H), 7.21-7.36 (m, 3H), 6.20 (d, *J* = 1.9 Hz, 1H), 5.60 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.29 (dd, *J* = 10.9, 1.5 Hz, 1H), 2.76(dd, *J* = 12.6, 7.2 Hz, 1H), 2.60-2.70 (m, 1H), 2.58 (s, 1H), 2.00 (dd, *J* = 12.6, 6.4 Hz, 1H), 1.17 (d, *J* = 6.8 Hz, 3H); ^{13}C-NMR (75.0 MHz, $CDCl_3$): δ 140.3, 139.8, 137.1, 136.6, 128.2, 127.9, 127.9, 127.1, 126.1, 115.1, 87.6, 48.2, 37.4, 20.3; HRMS caclcd for $C_{14}H_{15}BrO$ M^+ 278.0300, found 278.0299.

To 2-bromo-4-methyl-1-(2-vinylphenyl) cyclopent-2-enol (90.3 mg, 0.323 mmol) in CH_2Cl_2 (5 ml) solution, was added pyridinium chlorochromate (105 mg, 0.485 mmol). The reaction mixture was stirred overnight at room temperature. Filter through a pad of celite, remove solvent using rotavap. The crude product was purified by column

chromatography (10% EtOAc) to give 2-bromo-5-methyl-3-(2-vinylphenyl)cyclopent-2-en-1-one 63.7 mg. 71% yield, white solid.

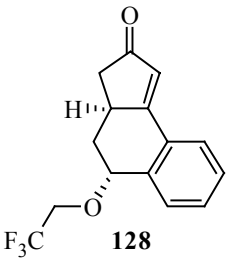


142

2-Bromo-5-methyl-3-(2-vinylphenyl)cyclopent-2-en-1-one (142): 71% yield; m.p.: 103-4 ^{o}C; IR: ν 2966.1, 2917.1, 1711.6, 1613.6, 1417.4 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.64 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.42 (td, *J* = 7.5 Hz, 1.5 Hz, 1H); 7.36 (td, *J*= 7.4, 1.5 Hz), 7.15-7.18 (m, 1H), 6.59 (dd, *J*= 17.4, 10.9 Hz, 1H), 5.73 (dd, *J*= 17.4, 0.9 Hz, 1H), 5.32 (dd, *J*= 10.9, 0.9 Hz, 1H), 3.16 (dd, *J*= 18.5, 6.6 Hz, 1H), 2.73 (qdd, *J*= 7.4, 6.6, 2.3 Hz, 1H), 2.54 (dd, *J*= 18.5, 2.3 Hz, 1H), 1.33 (d, *J*= 7.4 Hz, 3H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 203.9, 171.1, 134.5, 134.3, 133.8, 129.3, 127.7, 126.6, 125.9, 124.0, 116.7, 41.9, 39.2, 16.5; HRMS caclcd for $C_{14}H_{13}BrO$ M^+: 276.0144, found 276.0159.

Typical procedure for electrocyclization

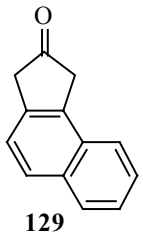
To a trifluoroethanol solution of 2-bromo-3-(2-vinylphenyl)cyclopent-2-enone was added triethylamine (3.0 eq). The resulting mixture was heated under certain conditions (**method A**: 50 ^{o}C, 7 days; **method B**: 70 ^{o}C, 2 days). The reaction was monitored by TLC. After the completion of reaction, trifluoroethanol was removed and the residue was dissolve in CH_2Cl_2 and washed with 1N HCl, saturated $NaHCO_3$, H_2O and brine. The extract was dried over $MgSO_4$ and the solvent was removed by rotavap. Column chromatography (30% EtOAc) would give the desired product.



128

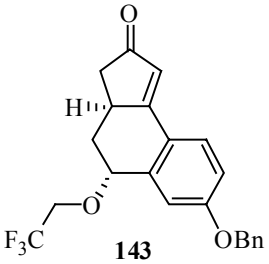
(3a*S*, 5*R*)-5-(2, 2, 2- Trifluoro-ethoxy)- 3, 3a, 4, 5-tetrahydrocyclopenta[*a*] naphthalene-2-one (128): method A: 56% yield; method B: 69% yield.

Purple solid, m.p.: 73-4 ^{o}C; IR: ν 2925.3, 1695.3, 1601.3, 1282.6, 1172.3, 1098.7 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.72-7.75 (m, 1H), 7.39-7.52 (m, 3H), 6.45 (d, *J*= 2.0 Hz, 1H), 4.69 (t, *J*= 2.6 Hz, 1H), 3.85-4.06 (m, 2H), 3.54-3.64 (m, 1H), 2.83 (dd, *J*= 18.3, 6.6 Hz, 1H), 2.57 (ddd, *J*= 13.7, 3.6, 2.8 Hz, 1H), 2.23 (dd, *J*= 18.3, 3.7 Hz, 1H), 1.81 (dt, *J*= 13.5, 3.0 Hz, 1H); ^{13}C-NMR (75.0 MHz, $CDCl_3$): δ 207.3, 73.4, 134.9, 131.2, 130.9, 130.0, 129.4, 127.1, 125.7, 124.8, 122.0, 76.5, 66.1 (q, $J_{C\text{-}F}$= 34.1 Hz), 42.0, 34.2, 33.9; HRMS caclcd for $C_{15}H_{13}F_3O_2Na$ $[M+Na]^+$ 305.0759, found 305.0761.



129

1*H*-cyclopenta[*a*]naphthalene-2(3*H*)-one 129: ^{1}H-NMR and ^{13}C-NMR were consistent with literature reported[225]. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.90 (d, *J*= 7.6 Hz, 1H), 7.81 (d, *J*= 8.3 Hz, 1H), 7.71 (d, *J*= 8.0 Hz, 1H), 7.49-7.59 (m, 2H), 7.44 (d, *J*= 8.3 Hz, 1H), 3.86 (s, 2H), 3.75 (s, 2H); ^{13}C-NMR (75.0MHz, $CDCl_3$): δ 214.7, 134.9, 133.8, 132.6, 129.9, 128.7, 127.8, 126.7, 125.6, 124.1, 122.7, 45.0, 42.5; HRMS caclcd for $C_{13}H_{10}O$ M^+ 182.0726, found 182.0738.

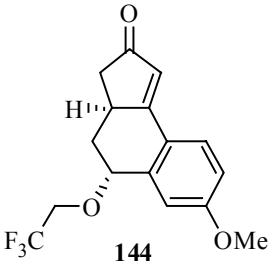


143

(3a*S*, 5*R*)-7-Benzyloxy-5-(2, 2, 2-trifluoro-ethoxy)-3, 3a, 4, 5-tetrahydrocyclopenta[*a*] naphthalene-2-one 143: method A: 64% yield; method B: 61% yield.

Pale brown solid, m.p.: 165-6 ^{o}C; IR: ν 1683.0, 1589.1, 1495.1,

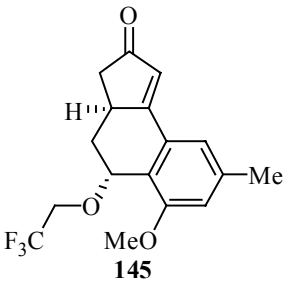
1282.6 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.67 (d, *J*= 8.7 Hz, 1H), 7.35-7.46 (m, 5H), 7.06 (dd, *J*= 8.7, 2.6 Hz, 1H), 6.93 (d, *J*= 2.6 Hz, 1H), 6.32 (d, *J*= 1.8 Hz, 1H), 5.16 (s, 2H), 4.60 (t, *J*= 2.6 Hz, 1H), 3.77-4.00 (m, 2H), 3.48-3.60 (m, 1H), 2.78 (dd, *J*= 18.2, 6.6 Hz, 1H), 2.48-2.56 (m, 1H), 2.21 (dd, *J*= 18.2, 3.8 Hz, 1H), 1.78 (td, *J*=13.5, 3.0 Hz, 1H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 207.3, 173.3, 160.9, 136.8. 136.0, 129.1, 128.7, 128.3, 127.4, 123.2, 123.0, 121.7, 116.7, 116.4, 76.8, 70.2, 66.2 (q, J_{C-F}= 34.2 Hz), 42.0, 34.2, 34.0; HRMS caclcd for $C_{22}H_{19}F_3O_3Na$ $[M + Na]^+$: 411.1178 found 411.1173.



144

(3a*S*, 5*R*)-7-Methoxy-5-(2, 2, 2-trifluoroethoxy)-3, 3a, 4, 5-tetrahydrocyclopenta[*a*] naphthalene-2-one 144: method A: 54% yield (72% yield b.r.s.m.); method B: 64% yield.

Brown crystal, m.p.: 124-5 ^oC; IR: ν 2917.1, 1691.2, 1593.1, 1486.9, 1274.4 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.67 (d, *J*=8.6 Hz, 1H), 6.98 (dd, *J*= 8.6, 2.6 Hz, 1H), 6.88 (d, *J*= 2.6 Hz, 1H), 6.31 (d, *J*= 2.0 Hz, 1H), 4.63 (t, *J*= 2.6 Hz, 1H), 3.87-4.03 (m, 2H), 3.88 (s, 3H), 3.48-3.60 (m, 1H), 2.78 (dd, *J*= 18.2, 6.6 Hz, 1H), 2.48-2.57 (m, 1H), 2.21 (dd, *J*= 18.2, 3.8 Hz, 1H), 1.78 (td, *J*= 13.5, 3.0 Hz, 1H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 207.3, 173,4, 161.9, 136.9, 129.1, 123.0, 122.9, 115.8, 115.4, 76.9, 66.3 (q, J_{C-F}= 34.1 Hz), 55.5, 41.9, 34.1, 34.0; HRMS caclcd for $C_{16}H_{15}F_3O_3Na$ $[M + Na]^+$: 335.0865, found 335.0851.

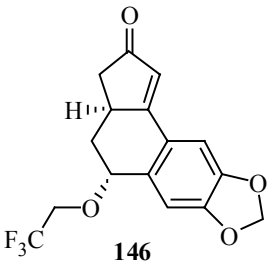


145

(3a*S*, 5*R*)-6-methoxy-8-methyl-5-(2, 2, 2-trifluoroethoxy)-3, 3a, 4, 5-tetrahydrocyclo- penta[*a*]naphthalene-2-one 145: method A: 39% yield (58% yield b.r.s.m.); method B: 61% yield

(72% yield b.r.s.m.).

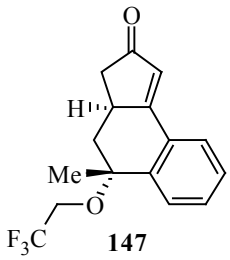
Pale purple solid, m.p.: 124-5 ^{o}C; IR: ν 2949.8, 1699.4, 1601.3, 1568.6, 1266.2 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.13 (s, 1H), 6.85 (s, 1H), 6.42 (d, *J*= 1.9 Hz, 1H), 5.00 (t, *J*= 2.7 Hz, 1H), 4.08-4.14 (m, 1H), 3.94-4.04 (m, 1H), 3.91 (s, 3H), 3.53-3.59 (m, 1H), 2.82 (dd, *J*= 18.3, 6.6 Hz, 1H), 2.51-2.55 (m, 1H), 2.42 (s, 3H), 2.22 (dd, *J*= 18.3, 3.5 Hz, 1H), 1.69 (td, *J*= 13.4, 3.0 Hz, 1H); ^{13}C-NMR (125.0MHz, $CDCl_3$): δ 208.6, 175.1, 158.7, 141.1, 131.6, 125.9, 123,7, 122.7, 120.1, 115.2, 114.9, 71.6, 68.2 (q, J_{C-F} = 34.1 Hz), 56.4, 43.0, 35.6, 34.7, 22.4; HRMS caclcd for $C_{17}H_{17}F_3O_3Na$ $[M+Na]^+$: 349.1021, found 349.1008.



146

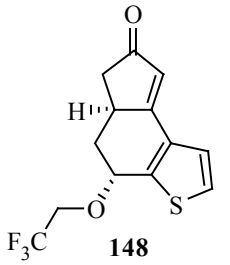
(3a*S*, 5*R*)-5-(2, 2, 2-trifluoroethoxy)-3, 3a, 4, 5-tetrahydrocyclopenta[*a*]naphthalene-[1, 3]dioxol-2-one 146: method A: 71% yield; method B: 78% yield.

Pale purple solid, m.p.: 139-40 ^{o}C; IR: ν 1691.2, 1478.7 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.04-7.14 (m,1H), 6.83(s, 1H), 6.26 (d, *J*= 1.8 Hz, 1H), 6.05 (s, 2H),4.59 (s, 1H), 3.88-4.03 (m, 2H), 3.46-3.53 (m, 1H), 2.77 (dd, *J*= 18.2, 6.6 Hz, 1H), 2.46-2.53 (m, 1H), 2.20 (dd, *J*= 18.2, 3.8 Hz, 1H), 1.75 (td, *J*= 13.5, 2.9 Hz, 1H); ^{13}C-NMR (75.0 MHz, $CDCl_3$): δ 207.0, 173.2, 150.3, 148.6, 130.6, 124.5, 123.4, 110.3, 105.9, 101.8, 76.8, 66.2 (q, J_{C-F}= 34.1 Hz), 41.8, 33.8, 33.6; HRMS caclcd for $C_{16}H_{13}F_3O_4Na$ $[M+Na]^+$: 349.0658, found 349.0657.



147

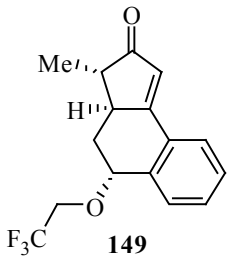
(3a*S*, 5*R*)-5-methyl-5-(2, 2, 2-trifluoroethoxy)-3, 3a, 4, 5-tetrahydrocyclopenta[*a*] naphthalene-2-one 147: method A: 27% yield (48% yield b.r.s.m.); method B: 50% yield (71% yield b.r.s.m.). m.p.: 91-2 ^{o}C; IR: ν 2917.1, 1703.5, 1593.1, 1274.4, 1155.9 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.76 (dd, *J*= 7.7, 1.1 Hz, 1H), 7.58 (dd, *J*= 7.8, 1.1 Hz, 1H), 7.54 (td, *J*= 7.3, 1.3 Hz, 1H), 7.47 (td, *J*= 7.6, 1.3 Hz, 1H), 6.45 (d, *J*= 1.8 Hz, 1H), 3.78-3.86 (m, 1H), 3.54-3.62 (m, 2H), 2.84 (dd, *J*= 18.3, 6.5 Hz, 1H), 2.53 (dd, *J*= 13.6, 4.3 Hz, 1H), 2.22 (dd, *J*= 18.3, 3.5 Hz, 1H), 1.82 (t, *J*= 13.5 Hz), 1.68 (s, 3H); ^{13}C-NMR (125.0MHz, $CDCl_3$): δ 208.4, 175.2, 138.3, 132.0, 130.9, 129.9, 128.4, 128.3, 125.6, 123.6, 76.1, 62.1 (q, $J_{C\text{-}F}$ = 34.4 Hz), 43.6, 42.9, 35.8, 25.7; HRMS caclcd for $C_{16}H_{15}F_3O_2Na$ $[M+Na]^+$: 319.0916, found 319.0909.



148

(4*R*, 5a*S*)-4-(2, 2, 2-trifluoroethoxy)-4, 5, 5a, 6-tetrahydroindeno[5, 4- *b*]thiophen-7-one 148: method A: 84% yield (*d.r.*: 10: 1); method B: 86% yield (*d.r.*: 5.4: 1).

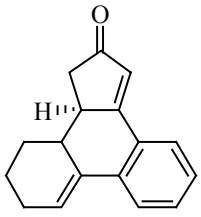
Light brown solid, m.p.: 122-3 ^{o}C; IR: ν 1691.2, 1609.5, 1278.5, 1151.8 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.42 (d, *J*= 5.2 Hz, 1H), 7.29 (d, *J*= 5.4 Hz, 1H), 6.20 (dd, *J*= 2.0, 0.7 Hz, 1H), 4.85 (t, *J*= 2.7 Hz, 1H), 3.98-4.05 (m, 2H), 3.53-3.59 (m, 1H), 2.78 (dd, *J*= 8.0, 6.7 Hz, 1H), 2.58-2.62 (m, 1H), 2.21 (dd, *J*= 18.1, 4.1 Hz, 1H), 1.89 (td, *J*= 13.4, 3.3 Hz, 1H); ^{13}C-NMR (125.0MHz, $CDCl_3$): δ 208.2, 169.1, 141.4, 134.5, 128.1, 127.9, 125.7, 125.6, 124.1, 123.4, 72.8, 67.2 (q, $J_{C\text{-}F}$ = 34.1 Hz), 42.0, 36.6, 34.7; HRMS caclcd for $C_{13}H_{11}F_3O_4SNa$ $[M+Na+O_2]^+$: 343.0222, found 343.0224.



149

(3*S*, 3a*S*, 5*R*)-3-methyl-5-(2, 2, 2-trifluoroethoxy)-3, 3a, 4, 5-tetrahydrocyclopenta [*a*]naphthalene-2-one 149: method A: 24% yield (44% yield b.r.s.m., *d. r.*: 5.5: 1); method B: 33% yield (67% yield b.r.s.m., *d.r.*: 4.5: 1).

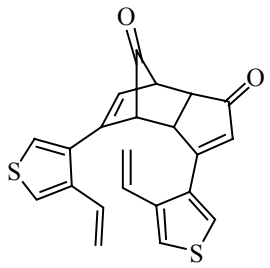
Pale yellow solid, m.p.: 79-80 ^{o}C; IR: ν 1695.3, 1597.2 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.73-7.78 (m, 1H), 7.46-7.52 (m, 2H), 7.38-7.44 (m, 1H), 6.46 (d, *J*= 1.9 Hz, 1H), 6.44 (d, *J*= 2.2 Hz, 1H), 4.73 (t, *J*= 2.6 Hz, 1H), 4.71 (t, *J*= 2.5 Hz, 1H), 3.86-4.06 (m, 2H), 3.10-3.18 (m, 1H), 2.57-2.64 (m, 1H), 2.26 (qd, *J*= 7.2, 3.9 Hz, 1H), 1.79 (td, *J*= 13.4, 2.9 Hz, 1H), 1.31 (d, *J*= 7.3 Hz, 3H), 1.17 (d, *J*= 7.7 Hz, 3H); ^{13}C-NMR (75.0MHz, $CDCl_3$): δ 211.6, 209.6, 172.3, 170.6, 135.0, 131.3, 131.2, 131.0, 130.9, 130.0, 129.8, 129.5, 127.3, 127.1, 125.7, 123.6, 123.0, 122.0, 77.1, 76.5, 66.0 (q, J_{C-F} = 34.2 Hz), 48.2, 43.5, 42.1, 37.1, 33.1, 29.5, 13.4, 12.8; HRMS caclcd for $C_{16}H_{15}F_3O_2Na$ $[M+Na]^+$: 319.0916, found 319.0935.



150

(3a*R*)-3, 3a, 3b, 4, 5, 6-hexahydrocyclopenta[*l*]phenanthren-2-one 150: method A: 23% yield.

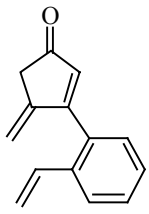
Solid, m.p.: 99-100^{o}C; IR: ν 2921.2, 1695.3, 1593.1 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.70 (d, *J*= 8.1 Hz, 1H), 7.67 (d, *J*= 7.8 Hz, 1H), 7.42 (td, *J*= 7.6 Hz, 1.2 Hz, 1H), 7.31 (t, *J*= 7.2 Hz, 1H), 6.63 (m, 1H), 6.43 (d, *J*= 0.7 Hz, 1H), 2.74-2.83 (m, 2H), 2.28-2.35 (m, 4H), 2.14-2.17 (m, 1H), 1.90-1.9 (m, 1H), 1.51-1.56 (m, 1H), 1.39-1.44 (m, 1H); ^{13}C-NMR (125.0MHz, $CDCl_3$): δ 207.8, 174.4, 137.0, 134.5, 131.4, 128.2, 127.3, 127.0, 126.4, 124.5, 123.5, 45.9, 41.3, 41.2, 29.6, 26.7, 20.9; HRMS caclcd for $C_{17}H_{16}O$ M^+: 236.1195, found 236.1188.



151

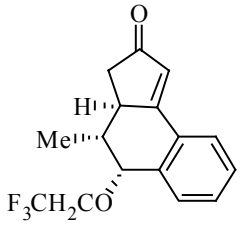
3,5-Bis(4-vinylthiophenyl)-3a*R, 4*S**, 7a*S**, 7a*S**-tetrahydro-4,7-methano-1*H*-indene-1, 8-dione 151**: method A: 79% yield (single regioisomer).

Semi solid; IR: ν 1768.9, 1679.0, 1581.0 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.65 (d, *J*= 3.1 Hz, 1H), 7.24 (dd, *J*= 3.1, 0.8 Hz, 1H), 7.10 (dd, *J*= 3.2, 0.7 Hz, 1H), 6.65 (ddd, *J*= 17.3, 10.7, 0.7 Hz, 1H), 6.41-6.43 (m, 1H), 6.38 (d, *J*= 0.9 Hz, 1H), 6.23 (d, *J*= 3.2 Hz, 1H), 6.11 (ddd, *J*= 17.2, 10.7, 0.7 Hz, 1H), 5.48 (dd, *J*= 17.3, 1.6 Hz, 1H), 5.42 (dd, *J*= 17.3, 1.5 Hz, 1H), 5.22 (dd, *J*= 10.8, 1.6 Hz, 1H), 5.13 (dd, *J*= 10.7, 1.5 Hz, 1H), 4.07-4.12 (m, 1H), 3.8-362 (m, 2H), 3.18 (dd, *J*= 6.4, 4.9 Hz, 1H); ^{13}C-NMR (75.0MHz, $CDCl_3$): δ 205.9, 198.3, 165.4, 140.3, 139.0, 136.0, 135.0, 134.4, 133.5, 131.1, 130.2, 127.4, 124.2, 123.5, 122.8, 122.5, 117.5, 116.6, 53.1, 50.3, 45.3, 42.8; HRMS caclcd for $C_{22}H_{16}O_2S_2Na$ $[M+Na]^+$ 399.0484, found 399.0496.



152

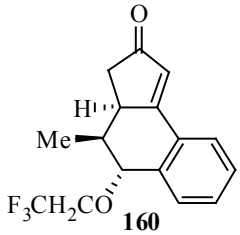
4-Methylene-3-(2-vinylphenyl)cyclopent-2-enone 152: Semisolid; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.68 (d, *J* = 7.7 Hz, 1H), 7.43 (td, *J* = 7.2, 0.8 Hz, 1H), 7.37 (td, *J* = 7.5, 1.2 Hz, 1H), 7.22 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.66 (dd, *J* = 17.4, 10.9 Hz, 1H), 6.29 (d, *J* ＝ 1.5 Hz, 1H), 5.73 (d, *J* = 17.4 Hz, 1H), 5.38 (d, *J* = 1.2 Hz, 1H), 5.26 (d, *J* = 11.0 Hz, 1H), 5.14 (s, 1H), 3.21 (s, 2H); ^{13}C-NMR (75.0MHz, $CDCl_3$): δ 204.3, 170.3, 144.5, 135.6, 135.2, 134.2, 131.8, 129.1, 128.4, 127.4, 125.4, 115.8, 114.1, 40.2; HRMS caclcd for $C_{14}H_{12}O$ M^+ 196.0882, found 196.0884.



158

(4*R*, 5*R*)-4-methyl-5-(2, 2, 2-trifluoroethoxy)-3, 3*a*, 4, 5-tetrahydrocyclopenta [*a*]naphthalene-2-one (158): method A: 43% yield (64%, b.r.s.m.); method B: 39 % yield (53%, b.r.s.m.).

Colorless crystal, m.p.: 132-3 ^{o}C; IR: ν 2917.1, 1687.1, 1670.8, 1593.1, 1270.3, 1151.8, 1115.1 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.78-7.81 (m, 1H), 7.44-7.51 (m, 2H), 7.29-7.33 (m, 1H), 6.44 (d, *J*= 2.2 Hz, 1H), 4.39 (d, *J*= 2.4 Hz, 1H), 3.78-3.94 (m, 2H), 3.44-3.54 (m, 1H), 2.75 (dd, *J*= 18.0, 6.4 Hz, 1H), 2.25 (dd, *J*= 18.0, 4.1 Hz, 1H), 1.95-2.08 (m, 1H), 1.29 (d, *J*= 6.8 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 207.3, 173.6, 135.8, 131.0, 130.3, 130.0, 129.7, 127.8, 125.1, 123.6, 81.8, 66.2 (q, $J_{C\text{-}F}$= 34.1 Hz), 41.1, 40.5, 40.4, 29.7, 15.6; HRMS caclcd for $C_{16}H_{15}F_3O_2Na$ $[M+Na]^+$ 319.0916, found 319.0902.



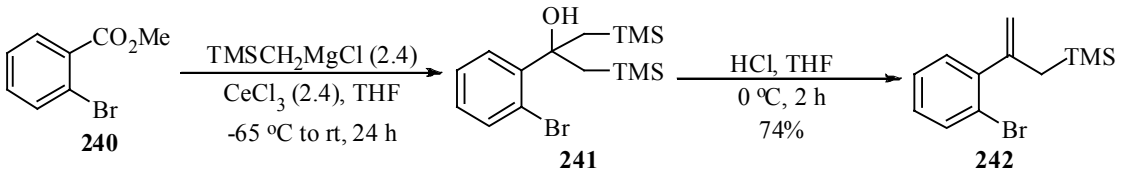
160

(4*S*, 5*R*)-4-methyl-5-(2, 2, 2-trifluoroethoxy)-3, 3*a*, 4, 5-tetrahydrocyclopenta [*a*]naphthalene-2-one (160): method A: 56% yield (77% , b.r.s.m.).

Purple solid, m.p.: 55-6 ^{o}C; IR: ν 2966.1, 2925.3, 1699.4, 1597.2, 1278.5, 1151.8, 1102.8 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.74-7.77 (m, 1H), 7.37-7.53 (m, 3H), 6.52 (d, *J*= 1.5 Hz, 1H), 4.41 (d, *J*= 2.2 Hz, 1H), 3.80-4.06 (m, 3H), 2.67 (dd, *J*= 18.6, 6.8 Hz, 1H), 2.53-2.59 (m, 1H), 2.35 (dd, *J*= 18.6, 3.5 Hz, 1H), 0.73 (d, *J*= 7.1 Hz, 3H); ^{13}C-NMR (75.0 MHz, $CDCl_3$): δ 208.0, 171.6, 133.2, 131.9, 131.6, 129.9, 129.4, 127.1, 126.4, 125.8, 122.1, 82.6, 66.2 (q, $J_{C\text{-}F}$= 34.1 Hz), 38.4, 37.9, 34.8, 10.3; HRMS caclcd for $C_{16}H_{15}F_3O_2Na$ $[M+Na]^+$ 319.0916, found 319.0923.

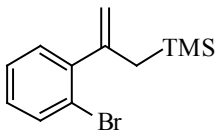
3 An Unusual Observation During a Lithium-bromine Exchange Reaction

Preparation of (2-(2-bromophenyl)allyl)alkylsilane



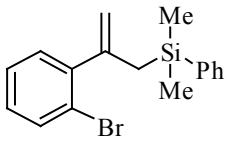
(2-(2-Bromophenyl)allyl)trimethylsilane **242** was prepared using Bunnelle's protocol.[104] A round bottom flask charged with $CeCl_3 \cdot 7H_2O$ (6.3 g, 16.9 mmol, 2.4 eq) was immersed into an oil bath under full pump. The solid was agitated by stirring as the flask was heated to 150°C for 2 hr, cool to RT and vent to dry N_2 for 2 min. THF (36 ml) was introduced with good stirring. The white suspension was stirred for overnight at room termperature. This resulting suspension was cooled to -65 °C before it was added trimethylsilyl methyl magnesium chloride (1.0 M, Et_2O, 16.9 ml, 16.9 mmol, 2.4 eq) dropwise. After 15 min, methyl bromobenzoate (1.0ml, 6.98 mmol, 1.0 eq) was added dropwise and stirring was continued, as the flask is allowed to warm slowly to room temperature and stirred for 24 hr. The reaction was quenched by the portionwise addition of 1N HCl. Extract with Ethyl ether and dry over $MgSO_4$ to give crude compound 2.89 g, which is 2-(2-bromo-phenyl)-1,3-bis(trimethylsilanyl)-propan-2-ol.

To the mixture of crude alcohol in THF (25 ml) solution at 0 °C, was added 2.4N HCl (THF solution, 16.2 ml, 39 mmol) or *p*-TsOH (5.0 eq, THF solution) dropwise. Stirring was continued for 2hr at 0 °C. Extract with ethyl ether and dry over $MgSO_4$. Evaporate the solvent to give crude product. Purification was carried out by Kugelrohr distillation (full pump, 60 °C) to give desired product 74% (> 96% GC pure).



242

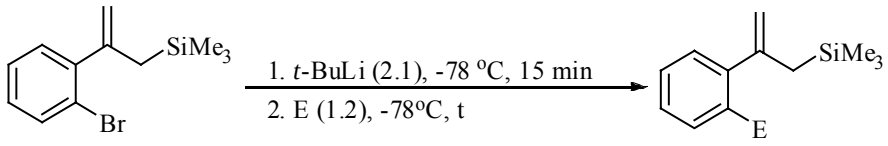
(2-(2-Bromophenyl)allyl)trimethylsilane 242: colorless liquid, distilled at full pump, 60 °C, 74% yield; IR: ν 3080.6, 2953.9, 2892.6, 1621.7, 1462.4, 1421.5, 130.0, 1245.8, 1164.1, 1021.1, 845.4, 759.6 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ7.55 (d, *J*= 7.90 Hz, 1H), 7.20-7.28 (m, 2H), 7.07-7.13 (m, 1H), 5.07 (d, *J*= 1.2 Hz, 1H), 4.89 (d, *J*= 1.7 Hz), 2.06 (s, 2H), 0.06 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 147.5, 145.0, 132.8, 130.2, 128.1, 126.9, 121.6, 113.7, 28.0, -1.4.



270

(2-(2-Bromophenyl)allyl)dimethyl(phenyl)silane 270: colorless liquid, distilled at full pump, 120 °C, 50% yield; IR: ν 3068.3, 2949.8, 1621.7, 1585.0, 1466.5, 1421.5, 1249.9, 1115.1, 1021.1, 833.1 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.43-7.53 (m, 3H), 7.28-7.36 (m, 3H), 7.02-7.19 (m, 3H), 5.05 (d, *J*= 1.3 Hz, 1H), 4.88 (d, *J*= 1.6 Hz, 1H), 2.06 (d, *J*= 0.6 Hz, 2H), 0.21 (s, 6H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 146.9, 144.8, 138.6, 133.5, 132.8, 130.3, 128.8, 128.2, 127.6, 126.9, 121.6, 114.6, 26.9, -2.8.

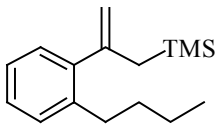
Typical procedure coupling reaction



243 **244-250**

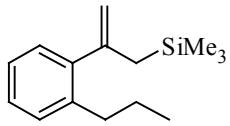
A flame-dried 25ml round bottom flask, was charged with bromoalkene **243** (400 mg, 1.48 mmol) in 7.5ml THF. The solution was brought to –78 °C before it was added *t*-BuLi (1.06M, 2.9 ml, 2.1 eq) dropwise. After this organge clean solution was stirred for 15 min at –78 °C, the reaction was quenched by slow addition of *n*-BuBr (190 μL, 1.2

eq). The reaction was monitored by GC-MS. After being stirred for 30 min, it was diluted with diethyl ether, washed with water and dried over $MgSO_4$. Remove the solvent by rotavap to give crude product 342 mg. GC-MS analysis of crude product showed that coupling product **244** was more than 98% pure. NMR analysis of crude product showed clean product. For some other cases, analytical sample was obtained by careful column chromatography using silica gel.



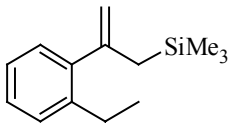
244

(2-(2-Butylphenyl)allyl)trimethylsilane 244: colorless liquid, 94% NMR yiled; IR: ν 2953.9, 2925.3, 1462.4, 1245.8, 1115.1, 898.5, 837.2, 726.9 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.58, (dd, *J*= 7.1, 1.4 Hz, 1H); 7.26-7.35 (m, 2H), 7.14 (dd, *J*= 7.5, 1.0Hz), 5.16 (q, *J*= 1.7 Hz, 1H), 4.93 (m, 1H), 2.34 (t, *J*= 7.9 Hz, 2H), 1.55-1.58 (m, 2H), 1.36-1.40 (m, 4H), 0.93-0.96 (m, 3 H), 0.31 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 152.1, 150.8, 137.1, 134.8, 128.3, 127.9, 125.8, 113.3, 38.7, 31.7, 27.0, 22.5, 14.0. 0.9.



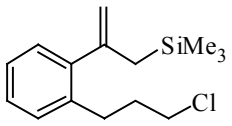
245

(2-(2-Propylphenyl)allyl)trimethylsilane 245: colorless liquid, 83% NMR yield; IR: ν 3051.9, 2958.0, 1634.0, 1466.5, 1241.7, 1119.1, 833.1cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.54 (dd, *J*= 7.5, 1.0 Hz, 1H), 7.30 (td, *J*= 7.5, 1.5 Hz, 1H), 7.25 (td, *J*= 7.5, 1.5 Hz, 1H), 7.10 (dd, *J*= 7.75, 1.0 Hz, 1H), 5.12 (d, *J*= 1.5 Hz), 4.89-4.90 (m, 1H), 2.32 (t, *J*=7.5 Hz), 1.49-1.54 (m, 2H), 1.39 (dq, *J*= 15.1, 7.25 Hz, 2H), 0.93 (t, *J*= 7.5 Hz, 3H), 0.28 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 152.1, 150.8, 137.1, 134.8, 128.3, 127.9, 12.58, 113.3, 38.4, 29.5, 22.6, 14.0, 0.92.



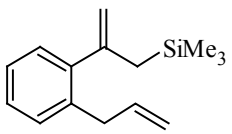
246

(2-(2-Ethylphenyl)allyl)trimethylsilane 246: colorless liquid, 89% NMR yield; IR: ν 3047.9,2953.9, 1638.1, 1458.3, 1245.8, 1115.1, 829.0 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.56 (dd, *J*= 7.30, 1.26 Hz, 1H), 7.30 (td, *J*= 7.57, 1.58 Hz, 1H), 7.25 (td, *J*= 7.57, 1.58 Hz, 1H), 7.11 (dd, *J*= 7.57, 1.0 Hz, 1H), 5.12 (q, *J*=1.89 Hz, 1H), 4.91 (m, 1H), 2.30 (t, *J*= 8.0 Hz, 2H), 1.53-1.58 (m, 2H), 0.98 (t, *J*= 7.5 Hz, 3H), 0.29 (m, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 151.9, 150.6, 137.1, 134.7, 128.2, 127.8, 125.8, 113.4, 40.8, 20.5, 13.9, 0.85.



247

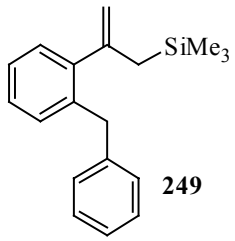
(2-(2-Chloropropylphenyl)allyl)trimethylsilane 247: colorless liquid, 58% NMR yield; IR: ν 3047.9, 2953.9, 1634.0, 1466.5, 1421.5, 1245.8, 1106.9, 837.2 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.54-7.57 (m, 1H), 7.22-7.35 (m, 2H), 7.07-7.11 (m, 1H), 5.14 (q, *J*= 1.6 Hz, 1H), 4.94-4.95 (m, 1H), 3.57 (t, *J*= 6.6 Hz, 2H), 2.35 (t, *J*= 7.7, 2H), 1.81-1.92 (m, 2H), 1.62-1.74 (m, 2H), 0.28 (s, 9H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 151.2, 150.2, 137.1, 134.8, 128.3, 127.8, 125.9, 113.8, 44.7, 37.8, 32.3, 24.6, 0.86; HRMS caclcd for $C_{15}H_{23}ClSi^{+}$ M^{+} 266.12520, found 266.12579.



248

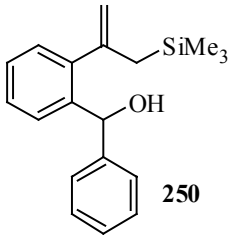
(2-(2-Allylphenyl)allyl)trimethylsilane 248: colorless liquid, 74% NMR yield; IR: ν 3068.3, 2945.7, 1634.0, 1425.6, 1249.9, 837.2 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.54 (d, *J*= 7.0 Hz, 1H), 7.24-7.30 (m, 2H), 7.10 (d, *J*= 7.5 Hz, 1H), 5.83-5.91 (m, 1H), 5.14 (d, *J*= 1.5 Hz, 1H), 5.06 (dd, *J*= 17.0, 1.5 Hz, 1H), 4.98 (dd, *J*= 10.0, 0.75 Hz, 1H), 4.92 (d, *J*= 0.5 Hz, 1H), 2.39-2.43 (m,

2H), 2.27-2.28 (m, 2H), 0.28 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 151.2, 150.3, 138.1, 137.2, 134.8, 128.3, 127.9, 126.0, 114.7, 113.9, 37.8, 31.5, 0.92.



249

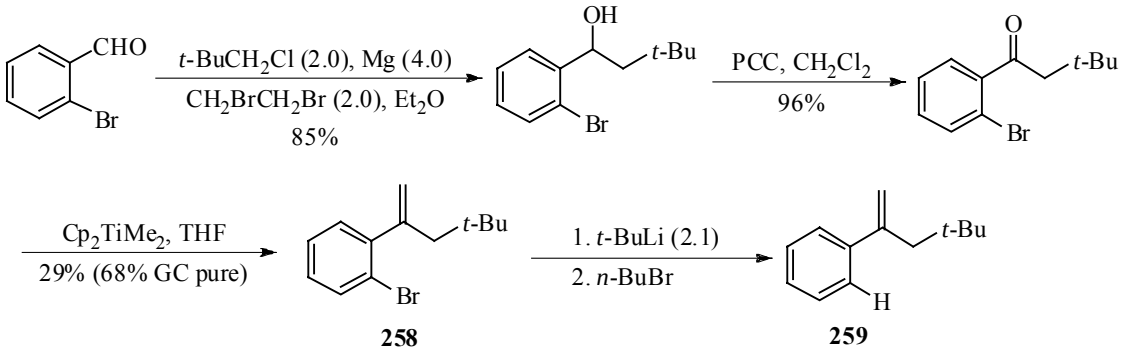
(2-(2-Benzylphenyl)allyl)trimethylsilane 249: colorless liquid, 94% NMR yield; IR: ν 30.23.3, 2945.7, 2888.5, 1454.2, 1241.7, 833.1, 726.9 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.57-7.61 (m, 1H), 7.14-7.34 (m, 8H), 5.25 (d, *J*= 1.6 Hz, 1H), 5.01 (s, 1H), 2.85-2.91 (m, 2H), 2.63-2.70 (m, 2H), 0.33 (s, 9H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 151.4, 150.2, 141.8, 137.2, 134.8, 128.3, 128.3, 128.2, 127.8, 126.0, 125.8, 113.8, 40.4, 33.8, 0.93; HRMS caclcd for $C_{19}H_{24}SiNa$ M^+ 303.153948, found 303.15425.



250

Phenyl(2-(3-(trimethylsilyl)prop-1-en-2-yl)phenyl)methanol 250: colorless liquid, 68% yield; column chromatography (10% EtOAc); IR: ν 3399.3, 3047.9, 2953.9, 2892.6, 1629.9, 1450.1, 1249.9, 833.1 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.60 (dd, *J*= 7.2, 1.5 Hz, 1H), 7.26-7.39 (m, 7H), 7.18 (dd, *J*= 7.5, 1.5 Hz, 1H), 5.37 (s, 1H), 5.14 (d, *J*= 1.5 Hz, 1H), 4.84 (td, *J*= 6.6, 2.1 Hz, 1H), 2.76 (d, *J*= 6.9 Hz, 2H), 2.21 (d, *J*= 2.4, 1H), 0.31 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 148.9, 148.7, 143.9,137.3, 135.0, 128.5, 128.4, 128.3, 127.5, 126.3, 125.8, 117.5, 71.3, 49.4, 0.91; HRMS caclcd for $C_{19}H_{24}OSiNa$ M^+ 319.148863, found 319.148142.

Preparation of 1-bromo-2-(4,4-dimethylpent-1-en-2-yl)benzene 258



258 **259**

A 25 mL round bottomed flask was charged 1-chloro-2,2-dimethylpropane (540 µL, 4.38 mmol) and Et_2O (5.4 mL). Mg turnings (233 mg, 8.76 mmol) and 1,2-dibromoethane (377 µL, 4.38 mmol) in Et_2O (2.0 mL) was added sequentially. The resulting mixture was refluxed for 28 hours before it was cooled to 0 ^oC and neat bromobenzaldehyde (256 µL, 2.19 mmol) was added dropwise. The resulting mixture was stirred for 4.0 hours at 0 ^oC before it was quenched by sat. NH_4Cl. Extract with Et_2O and dry over $MgSO_4$. The solvent was removed *in vacuo*. Column chromatography (5% EtOAc) gave the alcohol 478 mg (85% yield). IR: ν 3325.7, 2945.7, 1462.4, 1074.2 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.56 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.50 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.32 (td, *J* = 7.5, 1.1 Hz, 1H), 7.09 (td, *J* = 7.7, 1.7 Hz, 1H), 5.24 (dt, *J* = 7.3, 3.9 Hz, 1H), 2.03-2.05 (m, 1H), 1.57-1.60 (m, 2H), 1.07 (s, 9H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 145.2, 132.5, 128.5, 127.6, 127.4, 121.3, 71.1, 51.3, 30.8, 30.2.

To alcohol (434 mg, 1.68 mmol) in 17 mL of CH_2Cl_2 solution, was added PCC (545 mg, 2.53 mmol) slowly. The resulting mixture was stirred for 3 hours at room temperature before it was filtered through a pad of celite. Column chromatography (5% EtOAc) gave the ketone (413 mg, 96% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.8 Hz, 1H),

7.25-7.36 (m, 3H), 2.85 (s, 2H), 1.07 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 204.1, 143.1, 133.6, 131.1, 128.2, 127.2, 118.5, 54.8, 31.7, 29.8.

To a 10 mL round bottomed flask, was charged with bromoketone (100 mg, 0.39 mmol), Cp_2TiMe_2 (20wt% in toluene, 1.2 g, 1.17 mmol) and titanocene dichloride (5.8 mg, 0.023 mmol). The orange mixture was heated to 80 ^{o}C and was aged in the dark for 8 hours. After the reaction mixture was then cooled to room temperature, $NaHCO_3$ (51 mg), MeOH (0.8 mL) and H_2O (0.03 mL) was added and the mixture was heated to 40 ^{o}C for 14 hour. Cool to room temperature and filter through a pad of celite. Solvent was removed by rotavap. Purification was carried out using chromatron (pentane) to give 45 mg a mixture of **258** and the debrominated product **259** (1.9:1.0) with 68% GC pure (29% yield).). **258**: ^{1}H-NMR (250 MHz, $CDCl_3$): 7.55 (d, *J* = 7.9 Hz, 1H), 7.06-7.40 (m, 3H), 5.25 (d, *J* = 2.0 Hz, 1H), 5.13 (d, *J* = 2.0 Hz, 1H), 2.50 (s, 2H), 0.84 (s, 9H).

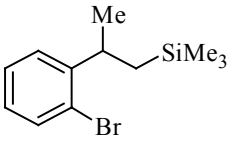
(4,4-Dimethylpent-1-en-2-yl)benzene 259

258 was subjected to the standard coupling reaction condition. **259** was obtained with 90% NMR pure (76% GC pure).). **259**: ^{1}H-NMR (300 MHz, $CDCl_3$): 7.18-7.43 (m, 5H), 5.28 (d, *J* = 2.1 Hz, 1H), 5.05 (d, *J* = 1.0 Hz, 1H), 2.50 (s, 2H), 0.84 (s, 9H).

Preparation of (2-(2-bromophenyl)propyl)trimethylsilane 262

To a 50-mL round bottomed flask, was added **241** (500 mg, 1.86 mmol), THF (18 mL), and H_2O (18 mL). NaOAc (3.05 g, 37.2 mmol) and tosyl hydrazine (3.46 g, 18.6 mmol) was added successively. The resulting mixture was heated to reflux for 7 days and

monitored by GC-MS. The reaction mixture was cooled to room temperature and diluted with Et_2O. Extract with Et_2O (X 3) and the organic extract was dried over $MgSO_4$ and concentrated in *vacuo* to afford crude product (**241**: **262** 7.86: 1.00) in ca. 500 mg.

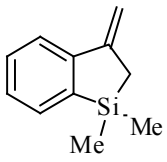


262

(2-(2-Bromophenyl)propyl)trimethylsilane (262): Colorless liquid, 89% NMR yield, pure sample was obtained by careful distillation at full pump and 60 ^oC; IR: ν 2962.0, 1466.5, 1249.9, 1025.2, 837.2 cm^{-1}; ^1H-NMR (500 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.32 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.04 (td, *J* = 7.5, 1.5 Hz, 1H), 3.45 (qt, *J* = 7.2, 7.2 Hz, 1H), 1.27 (d, *J* = 7.0 Hz, 3H), 1.05 (dd, *J* = 15.0, 7.0 Hz, 1H), 0.87 (dd, *J* = 14.5, 7.0 Hz, 1H), 0.02 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 148.3, 132.6, 127.4, 127.3, 127.0, 123.7, 34.4, 25.9, 24.7, -0.94.

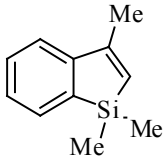
Lithium-bromo exchange reaction with (2-(2-Bromophenyl)allyl)dimethyl(phenyl) silane 270

A flame-dried 10 mL round bottom flask, was charged with bromoalkene **270** (50 mg, 0.15 mmol) in 3.0 mL THF. The solution was brought to –78 ^oC before it was added *t*-BuLi (1.4 M, 230 μL, 0.315 mmol) dropwise. After this organge clean solution was stirred for 15 min at –78 ^oC, the reaction was warmed up to room temperature and stirred at ambient temperature for 20 hours. The reaction mixture was cooled to 0 ^oC before it was quenched by slow addition of saturated aqueous NH_4Cl. Dilute with diethyl ether and water and extract with Et_2O (X 3). The organic extract was washed with water, brine and dried over $MgSO_4$. Remove the solvent by rotavap to give crude product. GC-MS analysis of crude product showed that 15% of **272**, 10% of **273**, and 44% of **274**.



273

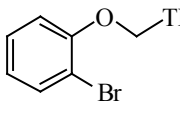
1,1-Dimethyl-3-methylene-2,3-dihydro-1*H*-benzo[*b*]silole 273: colorless liquid, analytical sample was obtained by the careful column chromatography (SiO_2, Hexanes); IR: ν 3060.1, 2945.7, 1617.7, 1433.8, 1241.7, 1131.4, 845.4, 812.7, 731.0 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J*= 7.8 Hz, 1H), 7.54 (d, *J*= 7.2 Hz, 1H), 7.35 (dt, *J*= 1.2, 6.9 Hz, 1H), 7.26 (t, *J*= 7.2 Hz, 1H), 5.53 (d, *J*= 1.2 Hz, 1H), 5.10 (d, *J*= 1.2 Hz, 1H), 1.89 (t, *J*= 1.8 Hz, 2H), 0.30 (s, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 149.5, 148.5, 141.5, 132.0, 129.5, 127.4, 121.8, 107.7, 21.7, -2.1.



274

1,1,3-trimethyl-1*H*-benzo[*b*]silole 274: colorless liquid, obtained as a mixture (2.85: 1.00) with **273**; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.54 (d, *J*= 6.6 Hz, 1H), 7.25-7.38 (m, 3H), 5.94 (s, 1H), 2.24 (d, *J*= 1.2 Hz, 3H), 0.30 (s, 6H); ^{13}C-NMR (75.0 MHz, $CDCl_3$): δ 156.2, 149.9, 139.8, 131.2, 129.4, 127.8, 126.5, 121.2, 19.5, -3.7.

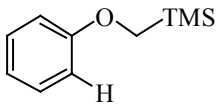
Preparation of ((2-bromophenoxy)methyl)trimethylsilane 277



277

After sodium hydride (60%, 462 mg, 11.5 mmol) was washed with Et_2O, dry DMSO (12 mL) was added. To the sodium hydride in DMSO solution was added bromophenol (2.0 g, 11.5 mmol) in dry DMSO (12 mL) dropwise. The mixture was stirred at rt for 8 hours before chloromethyl trimethylsilane (1.42 g, 11.5 mmol) was introduced. The stirring was continued for additional 8 hours. At the end of reaction, DI water was added to quench the reaction. Extract with Et_2O, dry with $MgSO_4$ and concentrate *in vacuo*. Distillation (full pump, 120-140 ^oC) afforded the

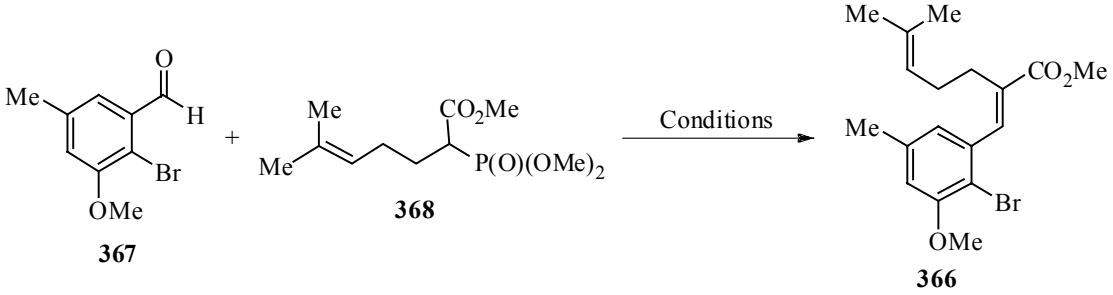
title compound 1.95 g (66% yield). IR: ν 2958.0, 2892.6, 1580.9, 1474.6, 1245.8, 861.7 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.52 (dd, *J*= 7.8, 1.5 Hz, 1H), 7.27 (td, *J* = 7.8, 1.8 Hz, 1H), 7.00 (dd, *J* = 8.1, 0.9 Hz, 1H), 6.80 (td, *J* = 7.5, 1.2 Hz, 1H), 3.64 (s, 2H), 0.21 (s, 9H); ^{13}C-NMR (75.0 MHz, $CDCl_3$): δ 157.6, 133.0, 128.2, 121.2, 112.3, 112.2, 62.0, -3.90.



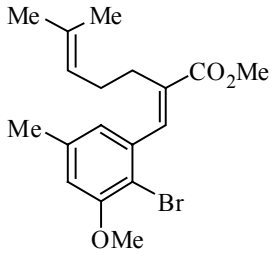
Trimethyl(phenoxymethyl)silane: IR: ν 2953.9, 2880.3, 1597.2, 1495.1, 1249.9, 865.8, 755.5 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.25-7.32 (m, 2H), 6.92-6.99 (m, 3H), 3.59 (s, 2H), 0.16 (s, 9H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 161.5, 129.1, 120.1, 114.0, 60.8, -3.20.

4 Total synthesis of 1-epi-*seco*-pseudopteroxazole

Preparation of bromoester 366



To a stirred suspension of LiCl in dry acetonitrile under N_2 atmosphere at room temperature, was added phosphonate **368**, DBU and finally aldehyde **367**. The resulting mixture was stirred for overnight (12 hrs) before it was diluted with diethyl ether. Wash with water and dried over $MgSO_4$. Removal of solvent gave the crude product. NMR analysis of crude reaction mixture showed the ratio of *E*: Z isomer is 10: 1.0. Silica gel column chromatography (5% EtOAc) gave 83% *E* and ~10% *E*/*Z* mixture.

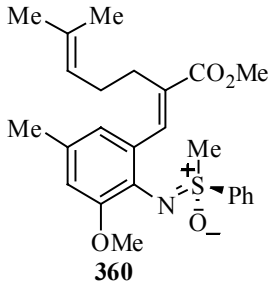


366

366: Yellow liquid; IR: ν 2945.7, 2851.7, 1715.7, 1572.7, 1425.6, 1323.5, 1258.1, 1090.5, 1029.2, 833.1 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.60 (s, 1H), 6.68 (s, 1H), 6.64 (s, 1H), 5.03 (t, *J* = 7.5 Hz, 1H), 3.84 (d, *J* = 1.9 Hz, 3H), 3.79 (d, *J* = 1.6 Hz, 3H), 2.32-2.39 (m, 2H), 2.29 (s, 3H), 2.10-2.16 (m, 2H), 1.61 (s, 3H), 1.15 (s, 3H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 168.1, 155.7, 139.0, 137.7, 137.5, 134.0, 132.1, 123.4, 122.4, 112.0, 109.6, 56.1, 51.8, 27.7, 27.4, 25.5, 21.3, 17.4; HRMS caclcd for $C_{18}H_{23}BrO_3Na^+$ $[M+ Na]^+$ 389.07227, found 389.07160.

Procedure for Buchwald-Hartwig coupling reaction

To a 500 mL round bottomed flask equipped with a reflux condenser was sequentially added bromoester **366** (10 g, 27.2 mmol), *R*-sulfoximine (5.0 g, 32.6 mmol), $Pd(OAc)_2$ (312 mg, 1.36 mmol), *rac*-BINAP (1.31 g, 2.04 mmol), Cs_2CO_3 (12.4 g, 38.0 mmol) and then 270 mL toluene. The reaction mixture was heated in an oil bath at 110-115 ^oC for 36 hr. Additional $Pd(OAc)_2$ (312 mg, 1.36 mmol), *rac*-BINAP (1.31 g, 2.04 mmol), Cs_2CO_3 (12.4 g, 38.0 mmol) were refilled. And the resulting mixture was refluxed for additional 12 hours. The solution was cooled to room temperature and diluted with dichloromethane, filtered through a pad of Celite and concentranted in vacuo, to give brown oil. Purification of the product was carried out by flash chromatography (30% EtOAc/hexane) afforded a pale yellow semisolid 12.0 g (100%).

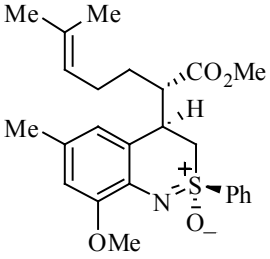


360

360: Pale yellow semisolid (foam); IR: ν 2929.4, 1703.5, 1462.4, 1335.7, 1258.1, 1204.9, 1160.0, 1090.5, 739.1 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 8.06 (s, 1H), 8.00-8.04 (m, 2H), 7.47-7.57 (m, 3H), 6.77 (s, 1H), 6.60 (d, *J* = 1.3 Hz, 1H), 5.17 (tt, *J* = 7.3, 1.3 Hz, 1H), 3.82 (s, 3H), 3.58 (s, 3H), 3.12 (s, 3H), 2.46-2.52 (m, 2H), 2.28 (s, 3H), 2.22-2.25 (m, 2H), 1.68 (s, 3H), 1.62 (s, 3H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 169.0, 151.9, 142.6, 139.1, 132.3, 131.9, 131.8, 131.5, 130.0, 128.8, 127.4, 123.8, 122.0, 112.9, 55.4, 51.6, 46.0, 28.0, 27.8, 25.6, 21.2, 17.6; HRMS caclcd for $C25H31NO_4SNa^+$ $[M+ Na]^+$ 464.18498, found 464.18498; $[\alpha]^{25}_D$ = +15.66 (c 1.66, acetone).

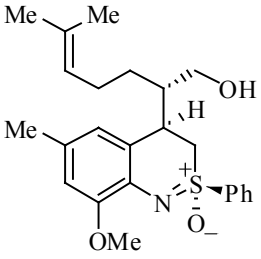
Procedure for the intramolecular Michale reaction

To a 1 L round bottom flask was discharged **360** (9.6 g, 21.7 mmol) and 430 mL THF. The mixture was cooled to –78 ^{o}C before it was added dropwise LiHMDS (1.0 M in THF, 43.4 mmol). The stirring was continued for 1 hr. The mixture was vigorously stirring with rapid addition of a cold 1N HCl in methanol solution (-78 ^{o}C). The resulting mixture was warmed to room temperature, diluted with EtOAc and H_2O, extracted with EtOAc, washed with brine and dried over $MgSO_4$. The solvent was removed by rotavap. NMR analysis of the crude mixture showed a ratio of 9.2: 1.0 of diastereomeric ratio. Purification was carried out using column chromatography (30% EtOAc/hexane) to afford 9.5 g of **361** (> 99%).



361

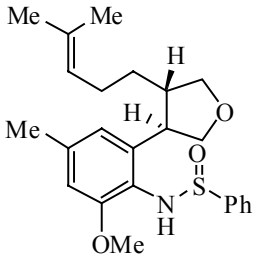
361: Yellow foam; IR: ν 2929.4, 1732.1, 1458.3, 1254.0, 1155.9, 1012.9, 747.3 cm^{-1}; major isomer: ^{1}H-NMR (250 MHz, $CDCl_3$): δ 8.11 (d, *J* = 7.8 Hz, 2H), 7.50-7.65 (m, 3H), 6.68 (s, 1H), 6.60 (s, 1H), 4.96 (t, *J* = 7.0 Hz, 1H), 3.86 (s, 3H), 3.52-3.58 (m, 2H), 3.37 (s, 3H), 3.29-3.37 (m, 1H), 3.11-3.20 (m, 1H), 2.30 (s, 3H), 1.85-1.91 (m, 2H), 1.65 (s, 3H), 1.56-1.62 (m, 1H), 1.52 (s, 3H), 1.45-1.52 (m, 1H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 174.9, 152.7, 139.5, 133.3, 132.6, 131.4, 130.2, 129.1, 129.0, 125.3, 122.7, 120.1, 111.9, 55.9, 52.4, 51.2, 44.3, 38.5, 31.4, 25.6, 21.3, 17.5; HRMS caclcd for $C_{25}H_{31}NO_4SNa^+$ $[M+ Na]^+$ 464.18660, found 464.18531.



373

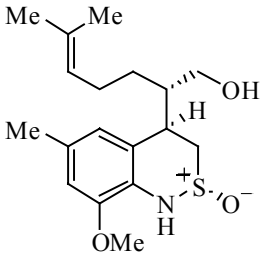
373: In a 300-mL flask was placed **361** (3.6 g, 8.15 mmol) in 160 mL of THF. The flask was cooled to –20 ^oC before $LiEt_3BH$ (1.0 M in THF, 24.4. mL, 24.4 mmol) was added using syringe pump in 50 mins with vigorous stirring. The stirring was continued for an additional 30 mins. The reaction was quenched by sequential addition of MeOH, 1 N NaOH and 30% H_2O_2. Extract the mixture with CH_2Cl_2, wash with H_2O and brine. Dry over $MgSO_4$ and evaporate by rotavap to afford crude **373** (> 99% yield), whose spectrum was good enough to carry out further reaction. **373**: Yellow semi-solid; IR: ν 3440.1, 2925.3, 1470.6, 1249.9 cm^{-1}; major isomer: ^{1}H-NMR (250 MHz, $CDCl_3$): δ 8.01 (d, *J* =7.2 Hz, 2H), 7.43-7.59 (m, 3H), 6.64 (s, 1H), 6.59 (s, 1H), 5.03 (t, *J* = 7.1 Hz), 3.82 (s, 3H), 3.48-3.54 (m, 1H), 3.30-3.43 (m, 3H), 3.15-3.21 (m, 1H), 2.28 (s, 3H), 2.24-2.33 (m, 2H), 1.94-2.03 (m, 2H), 1.66 (s, 3H), 1.54 (s, 3H), 1.24-

1.36 (m, 2H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 152.3, 139.1, 133.4, 132.1, 131.9, 129.6, 129.0, 129.0, 126.1, 123.8, 118.9, 111.1, 61.4, 55.8, 49.9, 38.4, 29.3, 25.6, 21.4, 17.6; HRMS caclcd for $C_{24}H_{32}NO_3S^+$ M^+ 414.20974, found 414.20978.



374

374: Yellow oil; IR: ν 3342.1, 2921.2, 2847.6, 1585.0, 1474.6, 1450.1, 1290.8, 1135.5, 1066.0, 735.0, 680.0 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.35-7.37 (m, 2H), 7.27-7.31 (m, 2H), 7.17 (tt, *J* = 7.0, 1.0 Hz, 1H), 6.72 (s, 1H), 6.48 (d, *J* = 1.0 Hz, 1H), 5.54 (s, 1H), 5.00 (tt, *J* = 7.0, 1.0 Hz, 1H), 4.15 (q, *J* = 7.8 Hz, 2H), 3.72 (s, 3H), 3.65 (t, *J* = 7.5 Hz, 1H), 3.59 (q, *J* = 7.5 Hz, 1H), 3.37 (t, *J* = 8.0 Hz, 1H), 2.30 (s, 3H), 2.27-2.34 (m, 1H), 1.83-1.90 (m, 2H), 1.60-1.71 (m, 1H), 1.66 (s, 3H), 1.53 (s, 3H), 1.44-1.48 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 151.9, 140.7, 136.7, 133.9, 132.7, 131.4, 128.9, 128.4 (CH), 126.3 (CH), 124.2 (CH), 120.3 (CH), 109.0 (CH), 75.6 (CH_2), 74.2 (CH_2), 55.5 (CH_3), 47.7 (CH), 45.2 (CH), 32.6 (CH_2), 26.8 (CH_2), 25.6 (CH_3), 21.5 (CH_3), 17.5 (CH_3).



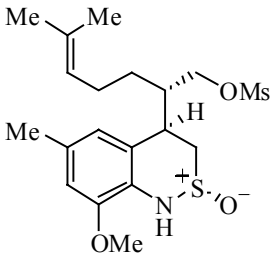
375

375: Semi-solid; IR: ν 23395.2, 2917.4, 1589.1, 1462.4, 1053.8 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.87 (s, 1H), 6.74 (s, 1H), 6.56 (s, 1H), 5.16 (t, *J* = 6.9 Hz, 1H), 3.82 (s, 3H), 3.62-3.72 (m, 2H), 3.49-3.56 (m, 1H), 2.96 (ddd, *J* = 12.9, 4.8, 2.4 Hz, 1H), 2.80 (t, *J* = 12.9 Hz, 1H), 2.56-2.58 (m, 1H), 2.30 (s, 3H), 2.11-2.18 (m,

2H), 1.72 (s, 3H), 1.63 (s, 3H), 1.56 (t, J = 5.1 Hz, 1H), 1.38-1.45 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 147.7, 132.3, 131.0, 125.4, 123.8, 122.6, 118.7, 109.4, 63.0, 55.6, 45.6, 40.1, 29.3, 27.9, 25.8, 25.7, 21.5.

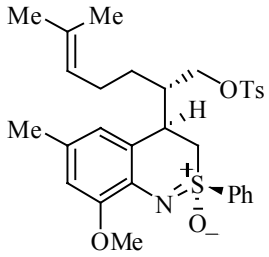
Procedure for the preparation of sulfonate ester

To the dichloromethane solution (17 mL) of alcohol **373** (360 mg, 0.87 mmol), was successively added sulfonyl chloride (1.30 mmol), DMAP (10.6 mg, 0.09 mmol) and TEA (365 μL, 2.60 mmol). The resulting mixture was stirred at room temperature for a few hours before it was diluted with water. The organic layer was washed with brine and dried over $MgSO_4$. Flash chromatography (50% EtOAc/hexane) provided the desired sulfonate ester.



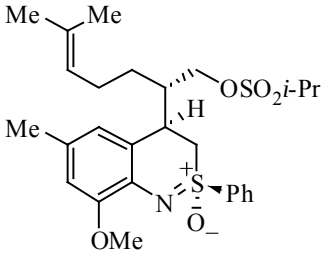
376

376: Yellow oil, 87% yield; IR: ν 2929.4, 1462.4, 1254.0, 1168.2 cm^{-1}; major isomer: ^{1}H-NMR (250 MHz, $CDCl_3$): δ 8.11 (d, J = 8.0 Hz, 2H), 7.53-7.69 (m, 3H), 6.70 (s, 1H), 6.59 (s, 1H), 5.04 (t, J = 6.5 Hz, 1H), 4.17-4.21 (m, 1H), 3.85-3.93 (m, 1H), 3.88 (s, 3H), 3.42-3.46 (m, 2H), 3.14 (dd, J = 13.7, 9.5 Hz, 1H), 2.87 (s, 3H), 2.65-2.67 (m, 1H), 2.33 (s, 3H), 2.03-2.10 (2H), 1.70 (s, 3H), 1.44-1.70 (m, 2H), 1.59 (s, 3H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 152.7, 138.8, 133.8, 132.8, 132.0, 130.1, 129.3, 129.1, 124.7, 122.8, 118.7, 111.5, 68.7, 55.9, 49.4, 37.0, 36.4, 36.1, 29.1, 25.6, 25.2, 21.4, 17.7; HRMS caclcd for $C_{25}H_{33}NO_5S_2Na^+$ $[M+Na]^+$ 514.1692, found 514.1695.



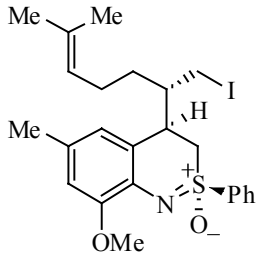
377

377: Yellow foam, 87% yield. IR: ν 2913.0, 1450.1, 1168.2, 1086.4cm^{-1}; major isomer: ^{1}H-NMR (250 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.4 Hz, 2H), 7.48-7.65 (m, 5H), 7.24 (d, *J* = 8.1 Hz), 6.65 (s, 1H), 6.46 (s, 1H), 4.91 (t, *J* = 6.7 Hz, 1H), 3.90 (dd, *J* = 10.3, 3.0 Hz, 1H), 3.85 (s, 3H), 3.63 (dd, *J* = 10.0, 4.3 Hz, 1H), 3.28-3.38 (m, 2H), 2.99-3.09 (m, 1H), 2.42-2.50 (m, 1H), 2.39 (s, 3H), 2.26 (s, 3H), 1.83-1.89 (m, 2H), 1.64 (s, 3H), 1.47 (s, 3H), 1.22-1.55 (m, 2H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 152.6, 144.9, 138.9, 133.7, 132.5, 132.2, 131.8, 130.1, 129.8, 129.2, 129.0, 127.6, 124.9, 122.9, 119.0, 111.5, 69.0, 55.9, 49.8, 36.5, 36.0, 28.9, 25.6, 25.1, 21.5, 21.3, 17.6.



378

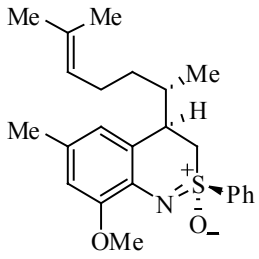
378: Yellow solid, 95% yield, m.p. 103-4 ^{o}C; IR: ν 2929.4, 1462.4 1331.6, 1254.0, 1151.8 cm^{-1}; major isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.08-8.11 (m, 2H), 7.54-7.66 (m, 3H), 6.70 (d, *J* = 1.2 Hz, 1H), 6.59 (s, 1H), 5.04 (td, *J* = 7.0, 1.5 Hz, 1H), 4.14-4.19 (m, 1H), 3.89-3.92 (m, 1H), 3.89 (s, 3H), 3.41-3.47 (m, 2H), 3.12-3.21 (m, 2H), 2.60-2.70 (m, 1H), 2.33 (s, 3H), 2.02-2.15 (m, 2H), ^{13}C-NMR (75 MHz, $CDCl_3$): δ 152.7, 138.9, 133.8, 132.8, 132.0, 130.1, 129.3, 129.0, 124.9, 122.9, 118.8, 111.5, 67.7, 56.0, 52.0, 49.5, 36.4, 36.2, 29.3, 25.7, 25.3, 21.4, 17.7, 16.5, 16.4; HRMS caclcd for $C_{27}H_{37}NO_5S_2Na^+$ $[M+Na]^+$ 542.2005, found 524.2004.



379

379: To a stirred, cooled (0 ^{o}C) acetonitrile (30 mL) and ether (30 mL) mixture was successively added **373** (3.30 g, 8.15 mmol), triphenyl phosphine (4.27 g, 16.3 mmol) and imidazole (1.11 g, 16.3

mmol). Iodine (4.10 g, 16.3 mmol) was slowly added. After the resulting pale yellow suspension was stirred for 5 hr (monitored by TLC), the reaction mixture was diluted with ether and sequentially washed with saturated aqueous $Na_2S_2O_3$, saturated aqueous $CuSO_4$ and water. The organic layer was dried over $MgSO_4$ and concentrated to afford crude iodide. Flash chromatography (30% EtOAc/hexanes) gave desired iodide 3.79 g (89% over the two steps). Yellow seimi-solid; IR: ν 2921.2, 1462.4, 1254.0, 1151.8, 1017.0, 747.3 cm^{-1}; major isomer: ^{1}H-NMR (250 MHz, $CDCl_3$): δ 8.12 (d, *J* = 7.9 Hz, 2H), 7.51-7.67 (m, 3H), 6.70 (s, 1H), 6.55 (s, 1H), 4.97 (t, *J* = 7.0 Hz, 1H), 3.88 (s, 3H), 3.42 (d, *J* = 5.3 Hz, 2H), 3.09-3.14 (m, 2H), 2.51 (dd, *J* = 10.4, 5.7 Hz, 1H), 2.33 (s, 3H), 1.80-1.96 (m, 3H), 1.68 (s, 3H), 1.55 (s, 3H), 1.23-1.52 (m, 2H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 152.9, 139.4, 133.7, 132.4, 131.6, 130.5, 129.3, 129.0, 125.7, 123.0, 120.3, 111.7, 56.0, 50.7, 40.6, 36.5, 31.8, 25.7, 25.1, 21.3, 17.7, 11.1; HRMS caclcd for $C_{24}H_{31}INO_2S^+$ M^+ 524.11146, found 524.11092.

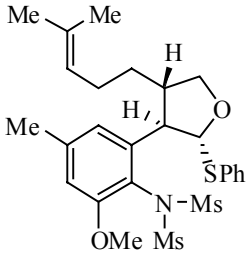


362

362: In a 300-mL flask was placed **379** (4.62 g, 8.82 mmol) in 175 mL of THF. The flask was immersed into an ice bath. $LiEt_3BH$ (1.0 M in THF, 26.3 mL, 26.3 mmol) was added dropwise using syringe pump (0.49 mL/min) with vigorous stirring. The stirring was continued for an additional 1 hour. The reaction was quenched by sequential addition of MeOH, 1 N NaOH and 30% H_2O_2. Extract the mixture with CH_2Cl_2, wash with H_2O and brine. The combined organic layer was dried over $MgSO_4$ and the solvents were removed by rotavap to afford crude **362**. Flash chromatography

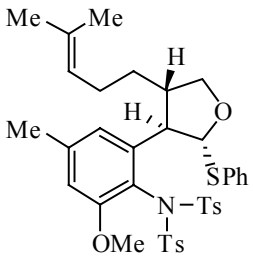
(30% EtOAc/Hexane) afforded 3.19 g of **362** (91% yield) and 260 mg of the mixture of **362** and **390** (ca. 10% yield).

362: Yellow semi-solid; IR: ν 2913.0, 1458.3, 1241.7, 1012.9 cm^{-1}; major isomer: ^{1}H-NMR (250 MHz, $CDCl_3$): δ 8.08-8.12 (m, 2H), 7.52-7.67 (m, 3H), 6.68 (s, 2H), 5.12 (tt, *J* = 7.1, 1.3 Hz, 1H), 3.89 (s, 3H), 3.30-3.44 (m, 2H), 2.85 (t, *J* = 12.0 Hz, 1H), 2.49-2.56 (m, 1H), 2.34 (s, 3H), 2.03-2.09 (m, 2H), 1.71 (s, 3H), 1.62 (s, 3H), 1.27-1.51 (m, 2H), 0.80 (d, *J* = 6.7 Hz, 3H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 152.2, 139.2, 133.5, 132.3, 131.9, 129.4, 129.1, 125.7, 123.8, 118.3, 110.9, 55.9, 47.9, 40.2, 38.0, 35.2, 31.4, 25.8, 25.6, 21.4, 17.6, 14.7; HRMS caclcd for $C_{24}H_{31}NO_2SNa^+$ $[M+Na]^+$ 420.19677, found 420.19584.



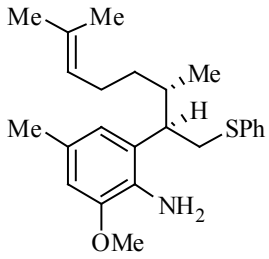
380

380: Yellow semi-solid; IR: ν 2921.2, 1605.4, 1589.1, 1343.9, 1160.0, 1066.0, 963.9, 878.0, 739.1 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.0 Hz, 2H), 7.23-7.31 (m, 3H), 6.87 (s, 1H), 6.71 (s, 1H), 5.44 (s, 1H), 5.12 (t, *J* = 7.0 Hz, 1H), 4.43 (t, *J* = 8.5 Hz, 1H), 4.14 (t, *J* = 8.5 Hz, 1H), 3.91 (s, 3H), 3.71 (s, 3H), 3.47 (s, 3H), 3.43 (d, *J* = 2.5 Hz, 1H), 2.39-2.43 (m, 1H), 2.37 (s, 3H), 2.09-2.14 (m, 1H), 1.96-2.00 (m, 2H), 1.70-1.75 (m, 1H), 1.72 (s, 3H), 1.62 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 156.4, 148.0, 142.6, 134.8, 131.8, 131.5, 128.8, 127.2, 123.7, 120.7, 118.5, 111.2, 95.2, 72.4, 56.0, 53.4, 48.6, 43.9, 43.2, 34.2, 27.0, 25.6, 22.0, 17.6; HRMS caclcd for $C_{26}H_{35}NO_6S_3Na^+$ $[M+Na]^+$ 576.1518, found 576.1520.



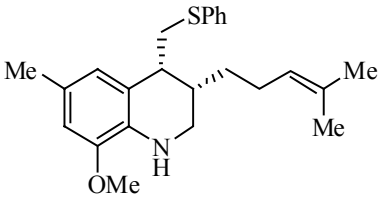
381

381: Colorless crystal; m.p. 142-3 ^{o}C; IR: ν 2970.2, 2925.3, 1597.2, 1589.0, 1372.5, 1180.4 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.51-7.58 (m, 2H), 7.17-7.31 (m, 7H), 6.92 (d, *J* = 1.1 Hz, 1H), 6.39 (d, *J* = 1.3 Hz, 1H), 5.59 (s, 1H), 5.13 (t, *J* = 6.9 Hz, 1H), 4.38 (t, *J* = 8.6 Hz, 1H), 4.16 (t, *J* = 8.2 Hz, 1H), 3.63 (d, *J* = 1.8 Hz, 1H), 3.07 (s, 3H), 2.47 (s, 3H), 2.42 (s, 3H), 2.33 (s, 3H), 1.89-2.05 (m, 3H), 1.67-1.72 (m, 1H), 1.67 (s, 3H), 1.58 (s, 3H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 155.8, 149.8, 144.4, 144.3, 142.3, 136.8, 136.5, 136.0, 132.0, 131.3, 129.8, 129.3, 128.8, 128.7, 128.6, 126.6, 124.1, 120.5, 118.3, 109.9, 94.9, 72.3, 54.0, 53.2, 48.4, 34.7, 27.2, 25.6, 22.0, 21.5, 17.6; HRMS caclcd for $C_{38}H_{43}NO_6S_3Na^+$ $[M+Na]^+$ 728.2144, found 728.2161.



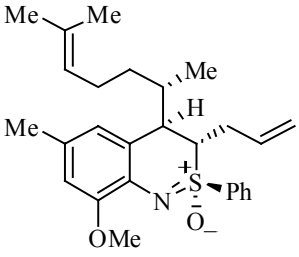
388

388: Red liquid; *d.r.*: 3.3: 1.0; IR: ν 3444.2, 3366.6, 2913.0, 1585.0, 1486.9, 1290.8, 1160.0, 735.0 cm^{-1}; major isomer: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.25-7.32 (m, 4H), 7.16 (t, *J* = 7.0 Hz, 1H), 6.53 (s, 2H), 5.02 (t, *J* = 6.8 Hz, 1H), 3.86 (s, 3H), 3.64 (s, 2H, NH_2), 3.43 (dd, *J* = 12.5, 4.5 Hz, 1H), 3.20 (dd, *J* = 12.5, 10.0 Hz, 1H), 2.86-2.90 (m, 1H), 2.29 (s, 3H), 1.85-2.0 (m, 5H), 1.68 (s, 3H), 1.56 (s, 3H), 1.38-1.40 (m, 1H), 1.13-1.17 (m, 1H), 1.03 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 147.4, 137.4, 132.0, 131.4, 128.8, 128.7, 127.9, 127.0, 125.5, 124.5, 119.6, 109.0, 55.3, 43.5, 36.5, 36.4, 34.3, 25.6, 25.4, 21.3, 17.5, 16.8; HRMS caclcd for $C_{24}H_{33}NOSNa^+$ $[M+Na]^+$ 406.2175, found 406.2165.



389

389: Red liquid; single diastereomer; IR: 3423.8, 2908.9, 1585.0, 1507.3, 1262.2, 1102.8, 833.1, 735.0, 690.1 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.13-7.37 (m, 5H), 6.55 (s, 1H), 6.49 (d, *J* = 1.4 Hz, 1H), 5.10 (td, *J* = 7.0, 1.3 Hz, 1H), 4.17 (s, 1H), 3.81 (s, 3H), 3.35 (dd, *J* = 11.5, 4.5 Hz, 1H), 3.13-3.23 (m, 2H), 2.96-3.08 (m, 2H), 2.25 (s, 3H), 2.02-2.10 (m, 3H), 1.67 (s, 3H), 1.60 (s, 3H), 1.25-1.55 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 145.9, 137.3, 131.8, 130.6, 129.0, 128.7, 125.6, 124.2, 124.0, 123.2, 121.6, 109.1, 55.3, 42.9, 39.4, 35.3, 34.9, 29.5, 25.7, 25.6, 20.9, 17.6; HRMS caclcd for $C_{24}H_{31}NOSNa^{+}$ $[M+Na]^{+}$ 404.2018, found 404.2014.

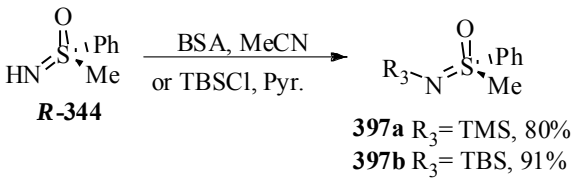


365

365: To a 500 mL round-bottomed flask was charged **362** (4.53 g, 11.4 mmol) and 215 mL THF. After the mixture was stirring at –45 ^{o}C for 10 mins, lithium triethylborohydride (1.0 M, 34.2 mL, 34.2 mmol) was added dropwise. After a hour, then allyl bromide (2.96 mL, 34.2 mmol) was added dropwise to the reaction mixture at –45 ^{o}C. The stirring was continued for another 1.0 hour, before it was quenched by addition of methanol. The reaction was diluted with water and extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$ and the solvent was removed by rotovap. The crude product was purified by flash chromatography (30% EtOAc/Hexanes) to afford 4.80 g of **365** (97% yield). Yellow semisolid; IR: ν 2917.1, 1572.7, 1482.8, 1254.0, 1151.8, 1017.0, 743.2 cm^{-1}; major isomer: ^{1}H-NMR (250 MHz, $CDCl_3$): δ 8.12-8.17 (m, 2H), 7.50-7.65 (m, 3H), 6.66 (d, *J* = 1.3 Hz, 1H), 6.39 (s, 1H), 5.62-5.79 (m, 1H), 5.13 (d, *J* = 9.4 Hz, 1H), 5.07 (dd, *J* = 16.7, 1.0 Hz, 1H), 4.88 (t, *J* =

7.0 Hz, 1H), 3.87 (s, 3H), 3.72 (ddd, *J* = 10.6, 4.2, 1.3 Hz, 1H), 2.89-2.98 (m, 1H), 2.30 (s, 3H), 2.11-2.24 (m, 1H), 1.85-1.96 (m, 2H), 1.65 (s, 3H), 1.50 (s, 3H), 1.23-1.37 (m, 1H), 0.83-1.01 (m, 1H), 0.49 (d, *J* = 6.6 Hz, 3H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 153.1, 141.1, 134.3, 133.0, 131.1, 130.4, 128.9, 128.9, 125.9, 124.3, 123.9, 118.6, 111.5, 60.8, 55.9, 49.8, 34.8, 33.1, 25.6, 25.1, 21.2, 17.5, 16.6; HRMS caclcd for $C_{27}H_{35}NO_2SNa^+$ $[M+Na]^+$ 460.22807, found 460.22823.

Preparation of *N*-protected sulfoximines



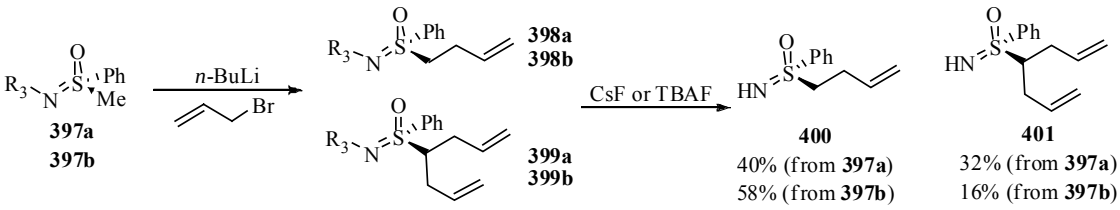
***R*-344**

397a R_3= TMS, 80%
397b R_3= TBS, 91%

397a: Following the literature reported procedure,[226] **397a** was obtained as colorless liquid in 80% yield. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.95-7.98 (m, 2H), 7.51-7.60 (m, 3H), 3.03 (s, 3H), 0.12 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 144.8, 132.2, 128.8, 126.9, 49.2, 2.26; $[\alpha]^{25}_D$ = -90.9 (c 1.10, acetone).

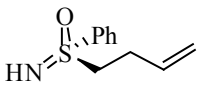
397b: Following the literature reported procedure,[227] **397b** was obtained as colorless liquid in 91% yield. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 7.5, 1.2 Hz, 2H), 7.51-7.55 (m, 3H), 3.00 (s, 3H), 0.93 (s, 9H), 0.06 (s, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 145.0, 132.1, 128.8, 126.9, 49.5, 25.9, 17.9, -2.51; $[\alpha]^{25}_D$ = -0.82 (c 1.04, acetone).

Preparation of *N*-allylsulfoximine 392



To a flame dried 50 mL round bottomed flask, was charged with **397a** (2.87 g, 12.6 mmol) and THF (12 mL). The reaction mixture was cooled to –78 ^{o}C and was added dropwise *n*-BuLi (2.2 M, 6.5 mL, 13.9 mmol). After the addition was complete, the reaction mixture was warmed up to –20 ^{o}C for 10 mins and 0 ^{o}C for additional 20 mins. The resulting mixture was cooled to –78 ^{o}C before it was added dropwise allylic bromide (1.20 mL, 13.9 mmol). After 2.0 hours at –78 ^{o}C, the reaction was quenched by the addition of saturated aqueous NH_4Cl. Dilute with water, extract with CH_2Cl_2. The organic extract was washed with H_2O, brine, dried over $MgSO_4$ and concentrated to afforded crude product (**398a**: **399a** 3:2), which was subjected to deprotection without further purification.

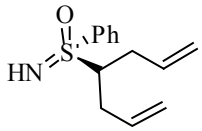
To the crude product in the solution of MeOH-H_2O (10:1, 6.0 mL) was added CsF (136 mg, 0.1 eq). The resulting mixture was stirred for 1 hour at room temperature and 10 mins at 50 ^{o}C. After the reaction was cooled to room temperature, it was diluted with CH_2Cl_2, extracted with CH_2Cl_2, and washed with H_2O and brine. The organic extract was dried over $MgSO_4$ and concentrated in *vacuo* to afford crude product. Flash column chromatography (20% EtOAc, then 50% EtOAc) afforded 955 mg of **400** (32%) and 971 mg of **401** (40%).



400

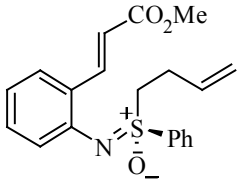
Colorless liquid, 40% yield, whose ^{1}H-NMR and ^{13}C-NMR are identical with literature reported.[228] ^{1}H-NMR (250 MHz, $CDCl_3$): δ

7.98 (dt, *J* = 6.8, 1.5 Hz, 2H), 7.52-7.63 (m, 3H), 5.72 (ddt, *J* = 17.2, 10.3, 6.7 Hz, 1H), 5.00-5.08 (m, 2H), 3.18-3.25 (m, 2H), 2.52 (s, 1H), 2.45-2.51 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 141.8, 133.9, 133.0, 129.1, 128.3, 116.9, 56.5, 27.2.



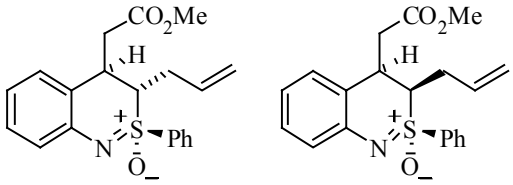
401

Colorless liquid, 32%. IR: ν 3268.5, 3072.4, 1646.3, 1442.0, 1229.5, 996.5, 914.8 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.51-7.65 (m, 3H), 5.65-5.82 (m, 2H), 5.00-5.09 (m, 4H), 3.06-3.14 (m, 1H), 2.57-2.73 (m, 3H), 2.34-2.50 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 140.3, 133.7, 133.6, 133.0, 129.1, 129.0, 118.1, 64.6, 32.3, 32.2; HRMS caclcd for $C_{13}H_{17}NOSNa^+$ $[M+Na]^+$ 258.0927, found 258.0923.



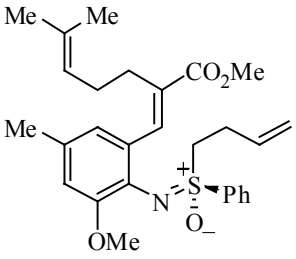
403

403: Following the procedure for preparing **361**, the reaction was complete after 18 hours at 110-115 ^{o}C. **403** was obtained in 73% yield after flash chromatography (25% EtOAc/hexanes). Yellow foam; IR: ν 2945.7, 1711.6, 1621.7, 1478.7, 1315.3, 1274.4, 1164.1 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 8.42 (d, *J* = 16.2 Hz, 1H), 7.86-7.90 (m, 2H), 7.49-7.60 (m, 4H), 7.01-7.04 (m, 2H), 6.82-6.88 (m, 1H), 6.52 (d, *J* = 16.2, Hz, 1H), 5.75 (ddt, *J* = 17.0, 10.3, 6.5 Hz, 1H), 5.10 (dd, *J* = 11.7, 1.5 Hz, 1H), 5.04-5.06 (m, 1H), 3.83 (s, 3H), 3.38-3.49 (m, 2H), 2.52-2.61 (m, 2H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ168.0, 144.9, 142.5, 137.5, 133.5, 133.3, 130.7, 129.5, 129.0, 128.0, 127.4, 122.3, 121.4, 117.3, 116.7, 57.0, 51.4, 27.0; HRMS caclcd for $C_{20}H_{21}NO_3SNa^+$ $[M+Na]^+$ 378.1134, found 378.1132; $[\alpha]^{25}_D$ = +330.0 (c 1.42, acetone).



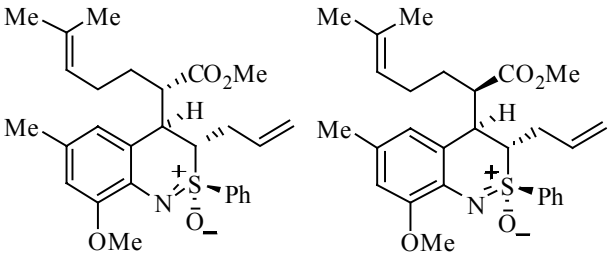
404 (*d.r.* 2.0: 1.0)

404: To a 10 mL round bottomed flask was discharged **403** (48.7 mg, 0.13 mmol) and 2.7 mL THF. The mixture was cooled to –78 ^{o}C before it was added dropwise LiHMDS (1.0 M in THF, 270 μL, 0.27 mmol). The stirring was continued for 2 hr. The reaction was quenched by the addition of MeOH. The resulting mixture was warmed to room temperature, diluted with EtOAc and H_2O, extracted with EtOAc, washed with brine and dried over $MgSO_4$. The solvent was removed by rotavap. NMR analysis of the crude mixture showed a ratio of 2.0: 1.0 of diastereomeric ratio. Purification was carried out using column chromatography (30% EtOAc/hexane) to afford 44.3 mg of **404** (91%, *d.r.* 2.0: 1.0) as yellow liquid. Major isomer: ^{1}H-NMR (250 MHz, $CDCl_3$): δ 8.05 (d, *J* = 6.9 Hz, 2H), 7.54-7.69 (m, 3H), 7.22 (td, *J* = 7.5, 1.5 Hz, 1H), 7.13 (td, *J* = 7.1, 1.2 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.87-6.95 (m, 1H), 5.70-5.86 (m, 1H), 5.14 (d, *J* = 9.2 Hz, 1H), 5.09 (dd, *J* = 16.8, 1.3 Hz, 1H), 3.78 (dt, *J* = 9.5, 4.4 Hz, 1H), 3.57-3.65 (m, 1H), 3.47 (s, 3H). 2.90-3.00 (m, 1H), 2.49-2.60 (m, 2H), 2.27 (dt, *J* = 9.5, 4.2 Hz, 1H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): 171.4, 144.2, 140.4, 133.5, 133.2, 130.6, 129.4, 129.1, 128.4, 128.3, 124.3, 121.4, 119.0, 59.0, 51.5, 37.7, 37.2, 32.0.Minor isomer: ^{1}H-NMR (250 MHz, $CDCl_3$): δ 8.13 (d, *J* = 7.2 Hz, 2H), 7.54-7.69 (m, 3H), 7.22-7.27 (m, 1H), 7.13-7.20 (m, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.87-6.95 (m, 1H), 5.24-5.35 (m, 1H), 4.83 (d, *J* = 10.0 Hz, 1H), 4.71 (d, *J* = 17.0 Hz, 1H), 4.05-4.15 (m, 1H), 3.70 (s, 3H), 3.50-3.54 (m, 1H), 2.90-3.10 (m, 1H), 2.49-2.66 (m, 1H), 1.90-2.10 (m, 2H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): 171.6, 144.3, 135.2, 134.0, 132.8, 128.7, 128.6, 123.7, 123.2, 121.0, 118.0, 51.9, 33.9; HRMS caclcd for $C_{20}H_{21}NO_3SH^+$ $[M+H]^+$ 356.1314, found 356.1313.



395

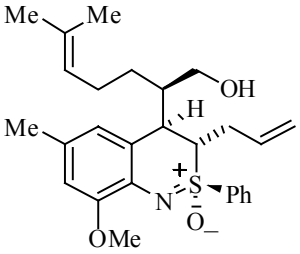
395: Following the procedure for preparing **361**, the reaction was complete after 41 hours at 110-115 °C. **395** was obtained in 71% yield after flash chromatography (20% EtOAc/hexanes). Yellow foam; IR: ν 2917.1, 1703.5, 1454.2, 1335.7, 1241.7, 1090.5, 1012.9 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.87-7.91 (m, 2H), 7.45-7.55 (m, 3H), 6.76 (s, 1H), 6.53 (d, *J* = 1.5 Hz, 1H), 5.71 (ddt, *J* = 17.0, 10.2, 6.5 Hz, 1H), 5.18 (tt, *J* = 7.3, 1.2 Hz, 1H), 4.97-5.07 (m, 2H), 3.81 (s, 3H), 3.41 (s, 3H), 3.14-3.38 (m, 2H), 2.44-2.59 (m, 4H), 2.26 (s, 3H), 2.20-2.29 (m, 2H), 1.69 (s, 3H), 1.63 (s, 3H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): 169.0, 151.4, 141.7, 139.2, 134.3, 132.1, 131.8, 131.5, 131.3, 131.0, 130.0, 128.7, 127.7, 123.9, 121.9, 116.6, 112.8, 57.7, 55.1, 51.6, 28.0, 27.9, 27.4, 25.6, 21.1, 17.6; HRMS caclcd for $C_{28}H_{35}NO_4SNa^+$ $[M+Na]^+$ 504.2179, found 504.2165; $[\alpha]^{25}_D$ = +27.3 (c 2.00, acetone).



396 (*d.r.* 2.7: 1.0)

396: Following the procedure for preparing **363**, **396** was obtained in 82% (*d.r.* 2.7: 1.0) as yellow semi-solid. IR: ν 2937.5, 1732.1, 1462.4, 722.8 cm^{-1}; major isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.19 (d, *J* = 7.2 Hz, 2H), 7.54-7.68 (m, 3H), 6.66 (d, *J* = 1.2 Hz, 1H), 6.33 (s, 1H), 5.67-5.76 (m, 1H), 5.17 (d, *J* = 9.9 Hz, 1H), 5.10 (d, *J* = 17.1 Hz, 1H), 4.66 (t, *J* = 7.2 Hz, 1H), 3.88 (s, 3H), 3.71 (dd, *J* = 10.9, 4.3 Hz, 1H), 3.37 (s, 3H), 3.12 (d, *J* = 11.1 Hz, 1H), 2.93-3.02 (m, 1H), 2.83 (td, *J* = 11.1, 3.5 Hz, 1H), 2.26 (s, 3H), 2.13-2.22 (m, 1H), 1.60 (s, 3H), 1.39 (s, 3H), 1.24-1.73 (m, 2H), 0.81-0.89 (m, 1H); ^{13}C-

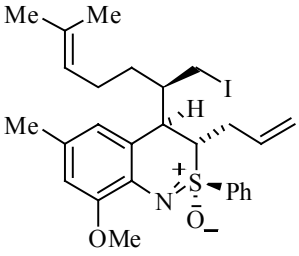
NMR (75 MHz, $CDCl_3$): 174.6, 152.8, 141.3, 133.6, 133.0, 132.2, 131.0, 129.2, 129.0, 128.7, 123.7, 122.7, 122.3, 119.3, 112.1, 59.1, 55.9, 51.1, 47.6, 45.6, 32.5, 29.6, 25.6, 21.1, 17.5; minor isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): 8.13-8.17 (m, 2H), 7.54-7.68 (m, 3H), 6.70 (s, 1H), 6.45 (s, 1H), 5.67-5.76 (m, 1H), 5.17 (d, *J* = 9.9 Hz, 1H), 5.10 (d, *J* = 17.1 Hz, 1H), 4.85 (t, *J* = 7.0 Hz, 1H), 3.89 (s, 3H), 3.51 (dd, *J* = 10.9, 4.3 Hz, 1H), 3.26 (s, 3H), 3.10-3.14 (m, 1H), 2.90-3.02 (m, 1H), 2.79-2.88 (m, 1H), 2.32 (s, 3H), 2.13-2.22 (m, 1H), 1.64 (s, 3H), 1.47 (s, 3H), 1.24-1.73 (m, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): 175.2, 153.3, 133.8, 133.0, 131.1, 130.1, 129.0, 128.9, 123.9, 123.2, 118.7, 112.2, 62.7, 55.9, 51.1, 46.1, 45.3, 32.9, 31.8, 25.6, 21.3, 17.5; HRMS caclcd for $C_{28}H_{35}NO_4SNa^+$ $[M+Na]^+$ 504.2179, found 504.2161.



405

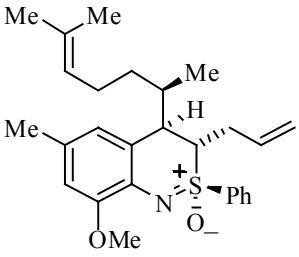
Semi-solid; major isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.14-8.18 (m, 2H), 7.53-7.64 (m, 3H), 6.69 (d, *J* = 1.4 Hz, 1H), 6.52 (s, 1H), 5.66-5.74 (m, 1H), 5.15 (d, *J* = 8.3 Hz, 1H), 5.10 (d, *J* = 15.8 Hz, 1H), 3.88 (s, 3H), 3.76 (ddd, *J* = 9.3, 4.2, 1.4 Hz, 1H), 3.35-3.41 (m, 2H), 2.96-3.00 (m, 1H), 2.94 (dd, *J* = 10.2, 1.1 Hz, 1H), 2.34 (s, 3H), 2.14-2.31 (m, 1H), 1.84-1.95 (m, 2H), 1.59 (s, 3H), 1.45 (s, 3H), 0.88-1.14 (m, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): 153.3, 141.1, 134.0, 133.2, 131.7, 131.3, 130.3, 129.2, 128.8, 125.4, 123.7, 122.8, 119.0, 111.9, 62.0, 60.8, 55.9, 44.9, 40.5, 33.1, 28.3, 25.6, 24.9, 21.3, 17.6; minor isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): 8.05-8.17 (m, 2H), 7.51-7.64 (m, 3H), 6.66 (s, 1H), 6.52 (s, 1H), 5.66-5.74 (m, 1H), 5.07-5.29 (m, 2H), 4.85 (t, *J* = 7.0 Hz, 1H), 3.87-3.93 (m, 4H), 3.35-3.41 (m, 1H), 3.05-3.10 (m, 1H), 2.39-2.45 (m, 1H), 2.28 (s, 3H), 1.70 (s, 3H), 1.44 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$):

153.2, 141.0, 134.2, 133.2, 131.6, 130.8, 130.7, 130.3, 129.9, 129.7, 129.0, 128.9, 125.6, 124.1, 123.8, 118.5, 111.7, 61.6, 61.1, 55.9, 44.7, 40.0, 33.4, 29.3, 25.6, 25.5; HRMS caclcd for $C_{27}H_{35}NO_3SNa^+$ $[M+Na]^+$ 476.2229, found 476.2210.



405a

Yellow semi-solid; major isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.13-8.18 (m, 2H), 7.54-7.69 (m, 3H), 6.76 (s, 1H), 6.71 (s, 1H), 5.68-5.77 (m, 1H), 5.19 (d, *J* = 9.6 Hz, 1H), 5.12 (dd, *J* = 17.1, 1.0 Hz, 1H), 4.60 (t, *J* = 7.2 Hz, 1H), 3.89 (s, 3H), 3.80 (dd, *J* =10.8, 4.2 Hz, 1H), 3.20 (dd, *J* = 10.2, 3.3 Hz, 1H), 2.92-3.00 (m, 2H), 2.83 (d, *J* = 10.5 Hz, 1H), 2.34 (s, 3H), 2.14-2.25 (m, 1H), 1.78-1.90 (m, 1H), 1.61 (s, 3H), 1.48 (s, 3H), 1.26-1.46 (m, 2H), 0.75-0.90 (m, 2H).



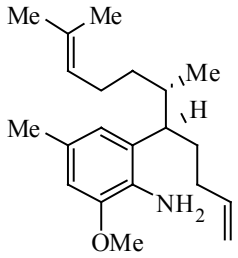
11-*epi*-**365**

Yellow foam; major isomer: ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.16 (dd, *J* = 7.0, 2.2 Hz, 2H), 7.27-7.65 (m, 3H), 6.67 (s, 1H), 6.39 (s, 1H), 5.60-5.80 (m, 1H), 5.13 (d, *J* = 10.2 Hz, 1H), 5.09 (d, *J* = 17.7 Hz, 1H), 4.70 (t, *J* = 7.0 Hz, 1H), 3.88 (s, 3H), 3.78 (dd, *J* = 10.8, 4.2 Hz, 1H), 2.95 (dt, *J* = 14.4, 5.1 Hz, 1H), 2.53 (d, *J* = 10.2 Hz, 1H), 2.31 (s, 3H), 2.13-2.24 (m, 1H), 1.80-1.95 (m, 2H), 1.60 (s, 3H), 1.45 (s, 3H), 0.97-1.00 (m, 1H), 0.68-0.77 (m, 1H), 0.69 (d, *J* = 6.6 Hz, 3H).

2-((5R,6S)-6,10-dimethylundeca-1,9-dien-5-yl)-6-methoxy-4-methylaniline (386)

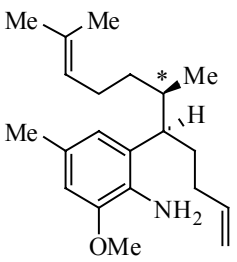
To a 200 mL round-bottomed flask under N_2 atmosphere was sequentially added with 5% sodium amalgam (17.1 g, 37.2 mmol), dry methanol (60 mL) and solid

Na_2HPO_4 (5.28 g, 37.2 mmol). The mixture was stirred at room temperature for 10 minutes. A 15 mL THF solution of **365** (1.63 g, 3.72 mmol) was added into the well-stirred dispersion of buffered sodium amalgam. The reaction mixture was stirred at room temperature overnight. The mixture was filtered through a pad of Celite and concentrated *in vacuo*, to afford crude product. Purification of the product was made by flash column chromatography (5% EtOAc) to give 1.05 g of a diastereomerically mixture of aniline **394** (90% yield). Enantiomerically pure **394** was obtained by careful chromatography using chromatron or long column (1% EtOAc).



394

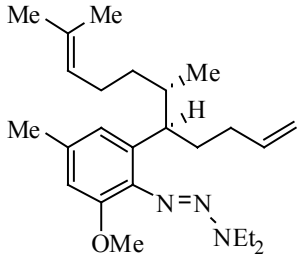
Colorless liquid; IR: ν 3464.7, 3378.8, 2925.3, 1585.0, 1486.9, 1458.3, 1290.8, 1155.9, 1061.9, 906.7, 829.0 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.50 (s, 1H), 6.49 (s, 1H), 5.77-5.82 (m, 1H), 5.04 (td, *J* =7.0, 1.5 Hz, 1H), 4.95 (dd, *J* = 15.5, 2.0 Hz, 1H), 4.92 (d, *J* = 7.5 Hz, 1H), 3.84 (s, 3H), 3.66 (s, 2H), 2.52-2.54 (m, 1H), 2.27 (s, 3H), 1.90-2.04 (m, 3H), 1.70-1.83 (m, 4H), 1.66 (s, 3H), 1.57 (s, 3H), 1.36-1.38 (m, 1H), 1.13-1.16 (m, 1H); 0.92 (d, *J* = 6.6 Hz, 3H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 147.3, 139.2, 131.8, 131.2, 129.0, 126.6, 124.8, 119.8, 114.2, 108.4, 55.3, 42.8, 36.5, 34.8, 31.6, 29.2, 25.7, 25.6, 21.3, 17.5, 16.5; HRMS caclcd for $C_{21}H_{33}NONa^+$ $[M+Na]^+$ 338.2454, found 338.2445; $[\alpha]^{25}_D$ = -0.55 (c 1.46, $CHCl_3$).



11-*epi*-**394**

Colorless liquid; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 6.49 (s, 2H), 5.73-5.80 (m, 1H), 5.11 (tt, *J* = 7.0, 1.2 Hz, 1H), 4.90-4.98 (m, 2H), 3.84 (s, 3H), 3.64 (s, 2H), 2.45-2.48 (m, 1H), 2.30 (s, 3H), 1.56-1.96 (m, 8H), 1.75 (s, 3H), 1.61 (s, 3H), 1.14-1.17 (m, 1H), 0.79 (d, *J* = 6.7 Hz, 3H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 147.3, 139.2, 132.0, 131.0, 129.2, 126.8, 124.8, 119.9, 114.2, 108.3, 55.3, 37.6, 34.2, 31.7, 31.3, 25.6, 25.5, 21.2, 17.6, 17.3; HRMS caclcd for $C_{21}H_{33}NONa^{+}$ $[M+Na]^{+}$ 338.2454, found 338.2449; $[\alpha]^{25}_{D}$ = 3.87 (*c* 2.58, MeOH).

(*E*)-1-(2-((5*R*,6*S*)-6,10-dimethylundeca-1,9-dien-5-yl)-6-methoxy-4-methylphenyl)-3,3-diethyltriaz-1-ene (406)



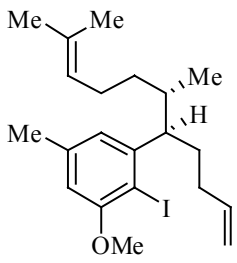
406

To 100 mL round-bottomed flask was charged with enantiomerically pure aniline **394** (682 mg, 2.16 mmol), 4.5 M aq. HCl (2.2 mL) and a mixture of Et_2O/THF/CH_3CN (7:6:1, 30 mL). The reaction mixture was immersed into the ice bath. A solution of $NaNO_2$ (507 mg, 7.35 mmol) in a mixture of CH_3CN/H_2O (2:3, 15 mL) was added and the reaction mixture was stirred at 0 ^{o}C for 1 h. A second 100 mL round bottomed flask was charged with diethyl amine (1.2 mL, 10.8 mmol), K_2CO_3 (1.49 g, 10.8 mmol), and a mixture of CH_3CN/H_2O (2:1, 30 mL). The reaction was cooled to 0 ^{o}C and was introduced the solution of diazonium solution over 15 minutes and stirred for additional 1 hour at 0 ^{o}C. The solution was extracted with Et_2O. The combined organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to

afford brown oil. Flash chromatography (basic aluminum oxide, 5% Et_2O/Pentanes) provided a colorless oil 837 mg (97%) and was immediately carried out further step.

406: Colorless liquid; IR: ν 2925.3, 1580.9, 1462.4, 1082.4, 906.7 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.60 (s, 1H), 6.59 (s, 1H), 5.74-5.83 (m, 1H), 5.00 (t, *J* =7.0 Hz, 1H), 4.91 (dd, *J* = 18.5 Hz, 1.5 Hz, 1H), 4.86 (dd, *J* = 12.3, 1.6 Hz, 1H), 3.73 (s, 3H), 3.74 (q, *J* = 7.2 Hz, 4H), 2.75-2.81 (m, 1H), 2.32 (s, 3H), 1.61-2.02 (m, 7H), 1.61 (s, 3H), 1.54 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 6 H), 1.26-1.32 (m, 1H), 0.99-1.07 (m, 1H), 0.88 (d, *J* = 6.6 Hz, 3H); ^{13}C-NMR (72.5 MHz, $CDCl_3$): δ 151.2, 139.6, 138.5, 138.3, 134.1, 130.5, 125.2, 120.0, 113.6, 110.3, 55.9, 37.3, 35.1, 31.8, 30.5, 25.8, 25.6, 21.7, 17.5, 16.3, 13.0; $[\alpha]^{25}_D$ = -20.28 (c 2.12, $CHCl_3$).

1-((5R,6S)-6,10-dimethylundeca-1,9-dien-5-yl)-2-iodo-3-methoxy -5-methylbenzene



364

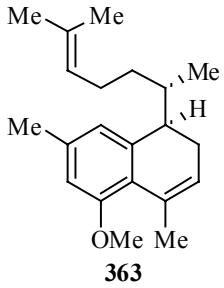
A 75 mL sealed tube under Argon atmosphere was charged with triazene **406** (837 mg) in diiodomethane (38 mL). The solution was degassed with Argon for several times and stirred at 80-1 ^oC for 20 hours. The diiodomethane was distilled under reduced pressure and the red residue was dissolved in Et_2O (180 mL) and washed with saturated $Na_2S_2O_3$ solution, water and dried over $MgSO_4$. The solvent was removed by *in vacuo* to give crude product, which was purified by flash chromatography (2% Et_2O/Pentanes) afforded 654 mg of a colorless liquid **364** (71% yield).

364: Colorless liquid; IR: ν 2921.2, 1572.7, 1450.1, 1298.9, 1004.7 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.57 (s, 1H), 6.51 (s, 1H), 5.73-5.80 (m, 1H), 5.01 (tt, *J* = 7.0, 1.0 Hz, 1H), 4.94 (dd, *J* = 16.5, 1.0 Hz, 1H), 4.91 (dd, *J* = 9.0, 1.0 Hz, 1H), 3.87 (s, 3H), 3.07-

3.11 (m, 1H), 2.34 (s, 3H), 1.98-2.01 (m, 1H), 1.78-1.93 (m, 4H), 1.61-1.69 (m, 2H), 1.65 (s, 3H), 1.55 (s, 3H), 1.26-1.33 (m, 1H), 1.11-1.18 (m, 1H), 0.93 (d, J = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 157.6, 148.6, 139.1, 138.5, 131.1, 124.8, 121.0, 114.1, 109.6, 93.0, 56.3, 53.2, 37.7, 34.9, 31.3, 30.8, 25.8, 25.6, 21.5, 17.6, 15.9; HRMS caclcd for $C_{21}H_{31}IONa^+$ $[M+Na]^+$ 449.1311, found 449.1307; $[\alpha]^{25}_D$ = 1.43 (c 5.30, acetone).

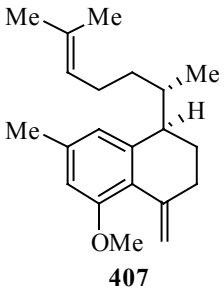
(R)-5-methoxy-4,7-dimethyl-1-((S)-6-methylhept-5-en-2-yl)-1,2-dihydronaphthalene (363)

To a 75 mL sealed tube under argon atmosphere was sequentially added iodide **360** (190 mg, 0.44 mmol), $Pd(OAc)_2$ (5.0 mg, 0.022 mmol), tri-*o*-tolylphosphine (13.4 mg, 0.044 mmol) and triethylamine (13 mL). The reaction mixture was degassed by argon several times before it was heated at 120 ^oC for 45 hours. The reaction mixture was cooled to room temperature and diluted with 12 mL of 6 N sodium hydroxide and 12 mL of ether. The etherate layer was separated and the aqueous layer was extracted with ether twice. The combined etherate extracts was washed with water, brine, dried over $MgSO_4$ and concentrated to give crude product (*d.r.* 1.0:1.6 **363:407**). Tri-*o*-tolylphosphine was removed as following method: To a 10 mL dichloromethane of crude product at 0 ^oC was added 30% H_2O_2 solution dropwise. The stirring was continued for 2 hours and then was diluted with H_2O. Extract with dichloromethane, dry over $MgSO_4$ and concentrate *in vacuo*. The crude product was purified using flash chromatography (hexanes) to afforded 86.2 mg of a mixture of **363:407** (7.4:1.0, 65% yield).



363

363: Colorless oil; IR: ν 2921.2, 1605.4, 1462.4, 1098.7 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.60 (s, 2H), 5.63 (s, 1H), 5.05 (tt, *J* = 7.0, 1.5 Hz, 1H), 3.78 (s, 3H), 2.38 (q, *J*= 6.0 Hz, 1H), 2.33 (s, *J* = s, 3H), 2.19-2.21 (m, 2H), 2.18 (d, *J* = 1.0 Hz, 3H), 1.98-2.05 (m, 1H), 1.79-1.84 (m, 1H), 1.74 (s, 3H), 1.59 (s, 3H), 1.36-1.39 (m, 1H), 1.15-1.18 (m, 1H), 0.87 (d, *J* = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 156.5, 142.4, 136.5, 132.2, 130.9, 124.9, 124.0, 122.2, 121.9, 111.0, 55.4, 43.6, 35.1, 34.1, 25.9, 25.6, 24.5, 23.0, 21.5, 17.6, 17.1; HRMS caclcd for $C_{21}H_{30}ONa^+$ $[M+Na]^+$ 321.2188, found 321.2183.



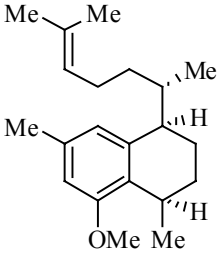
407

407: Colorless oil; IR: ν 2921.2, 1506.4, 1458.3, 1098.7 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.65 (s, 1H), 6.58 (s, 1H), 5.71 (s, 1H), 5.23 (s, 1H), 5.11 (td, *J* = 7.0, 1.0 Hz, 1H), 3.83 (s, 3H), 2.79 (q, *J* = 6.5 Hz, 1H), 2.52 (dt, *J* = 14.0, 6.5 Hz, 1H), 2.35-2.41 (m, 1H), 2.33 (s, 3H), 1.93-2.07 (m, 2H), 1.80-1.84 (m, 1H), 1.70 (s, 3H), 1.61 (s, 3H), 1.36-1.42 (m, 1H), 1.20-1.27 (m, 1H), 0.73 (d, *J* = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 157.0, 143.2, 140.0, 137.0, 131.1, 124.8, 122.8, 121.3, 113.0, 109.3, 55.3, 43.3, 35.9, 35.1, 32.9, 26.0, 25.7, 23.7, 21.6, 17.6, 15.1; HRMS caclcd for $C_{21}H_{30}NONa^+$ $[M+Na]^+$ 321.2118, found 321.2187.

(1R,4R)-5-methoxy-4,7-dimethyl-1-((S)-6-methylhept-5-en-2-yl)-1,2,3,4-tetrahydro naphthalene (400)

NH_3 (l) (ca. 20 mL) was condensed in 50 mL round-bottomed flask at –78 ^oC, was added lithium (98%, 6.3 mg, 0.88 mmol) wire in small pieces. The solution was stirred

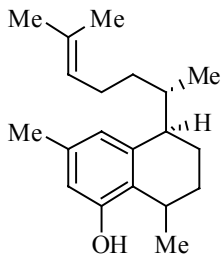
vigorously (5 mins) until the solution turned into deep blue solution. A solution of **363** (26.5 mg, 0.088 mmol) in THF (2.0 mL) was added dropwise. The resulting reaction mixture was stirred for additional 15 mins before it was quenched by the slow addition of solid NH_4Cl. The reaction mixture was slowly warm up to room temperature with the evaporation of ammonium. The mixture was diluted with H_2O and extracted with ether (3 times). The combined organic layer was dried over Mg_2SO_4 and concentrated in *vacuo* to give crude product, which was further purified by column chromatography (hexanes) to afford 24.6 mg of **408** (*d.r.* 4.6: 1.0, 93% yield).



408

Pale yellow oil; major isomer 1-*R*-**408**: IR: ν 2925.3, 1585.0, 1454.2, 1270.3, 1094.6, 833.1 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 6.72 (s, 1H), 6.49 (s, 1H), 5.19 (tt, *J* = 7.0, 1.3 Hz, 1H), 3.81 (s, 3H), 3.13-3.16 (m, 1H), 2.82-2.84 (m, 1H), 2.31 (s, 3H), 2.02-2.28 (m, 4H), 1.32-1.73 (m, 5H), 1.73 (s, 3H), 1.65 (s, 3H), 1.16 (d, *J* = 6.9 Hz, 3H), 0.65 (d, *J* = 6.8 Hz, 3H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 156.8, 140.5, 135.3, 131.1, 129.3, 124.8, 119.8, 107.7, 55.0, 41.0, 35.7, 35.1, 30.2, 29.6, 28.9, 26.2, 25.6, 21.5, 20.2, 17.6, 16.5, 14.1.

(5R)-3,8-dimethyl-5-((S)-6-methylhept-5-en-2-yl)-5,6,7,8-tetrahydronaphthalen-1-ol (410)

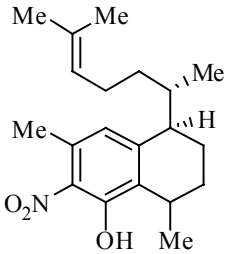


410

To a 10 mL round-bottomed flask was chaged EtSH (200 μL, 2.66 mmol) and 3 mL THF. The resulting mixture was cooled to 0 ^oC before it was added *n*-BuLi (2.3 M, 580 μL, 1.33 mmol) dropwise. After the stirring was continued for 15 mins, all volatile solvents was slowly

removed in *vacuo* to leave solid powder, which was dissolved in DMF (2.0 mL). A solution of **408** (20 mg, 0.067 mmol) in 1.0 mL DMF solution was added to the LiSEt DMF solution. After the resulting mixture was refluxed for overnight, it was brought to room temperature and diluted with water, neutralized with concentrated HCl, extracted with Et_2O (four times). The combined organic layer was dried over $MgSO_4$ and concentrated in *vacuo* to give crude product. Flash chromatography (5% Et_2O/Hexanes) afforded 12.1 mg of **410** (89% yield, *d.r.* 5.3: 1.0). Colorless oil; IR: ν 3489.2, 2921.2, 1576.8, 1450.1, 1372.5 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.70 (s, 1H), 6.41 (s, 1H), 5.17 (t, *J* = 7.0 Hz, 1H), 4.54 –4.56 (m, 1H), 3.05-3.08 (m, 1H), 2.79-2.83 (m, 1H), 2.28 (s, 3H), 2.05-2.11 (m, 2H), 1.73 (s, 3H), 1.65 (s, 3H), 1.12-1.73 (m, 4H), 1.21 (d, *J* =7.0 Hz, 3H), 1.20 (minor, d, *J* = 6.9 Hz, 3H), 0.84-0.89 (m, 3H), 0.73 (minor, d, *J* = 6.9 Hz, 3H), 0.66 (d, *J* = 6.8 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 152.7, 141.0, 135.7, 131.2, 126.9, 124.7, 120.3, 112.5, 41.0, 35.7, 35.1, 28.9, 26.3, 26.2, 25.7, 21.1, 20.1, 17.6, 16.5.

(5R)-3,8-dimethyl-5-((S)-6-methylhept-5-en-2-yl)-2-nitro-5,6,7,8-tetrahydronaph-thalen-1-ol (411)

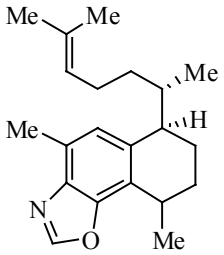


411

To a stirred solution of phenol **410** (13.5 mg, 0.024 mmol) in hexanes (1.8 mL) at room temperature was added 70% HNO_3 (18 drops). The reaction was stirred for 1 mins 10 secs and then quenched by saturated $NaHCO_3$. The reaction mixture was extracted with ether (4 times). The combined organic layer was dried over $MgSO_4$ and concentrated in *vacuo* to give crude product. Preparative TLC (5% Et_2O/Hexanes) afforded a yellow oil 1.8 mg of **411** (23% yield, *d.r.* 5.1: 1.0). ^{1}H-NMR

(500 MHz, $CDCl_3$): δ 11.2 (s, 1H), 6.72 (s, 1H), 5.16 (t, *J* = 7.0 Hz, 1H), 3.22-3.27 (m, 1H), 2.80-2.84 (m,1H), 2.57 (s, 3H), 2.21-2.27 (m, 1H), 2.03-2.10 (m, 2H), 1.64-1.77 (m, 4H), 1.72 (s, 3H), 1.64 (s, 3H), 1.34-1.50 (m, 2H), 1.22 (d, *J* = 7.0 Hz, 3H), 1.18 (minor, d, *J* = 7.0 Hz, 3H), 0.71 (minor, d, *J* = 7.0 Hz, 3H), 0.63 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 153.9, 149.2, 132.8, 132.2, 132.1, 131.6, 124.4, 122.6, 41.5, 35.5, 34.9, 28.5, 26.6, 26.1, 25.7, 22.9, 19.3, 17.7, 16.1, 14.2.

1-*epi*-*seco*-pseudopteroxazole (281)



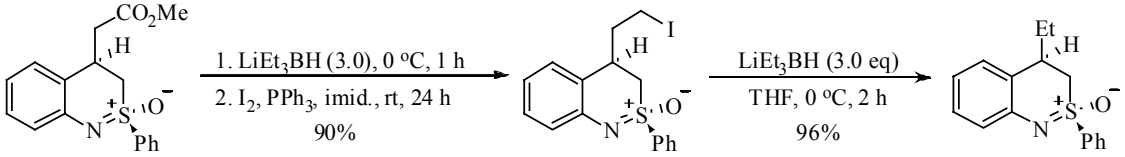
To a stirred solution of **411** (1.8 mg, 0.005 mmol) in 90% MeOH (0.8 mL) at room temperature, was added solid ammonium chloride (1.0 mg, 0.015 mmol), followed by zinc dust (3.6 mg, 0.05 mmol). The resulting mixture was stirred for 1 hour at room temperature. The mixture was filtered through Celite, rinsing with MeOH. The solution was concentrated in *vacuo*. The residue was diluted with water and extracted with Et_2O (3 times). The combined organic extract was dried over $MgSO_4$ and concentrated in *vacuo* to yield the crude amine, which was used in the next step without any further purification.

The crude amine was dissolved in trimethyl orthoformate (0.3 mL) and cat. TsOH. The resulting mixture was stirred at room temperature for 1 hour. The volatile solvents were removed in *vacuo* and trace water was removed by azeotropeic distillation with the addition benzene. The crude product was subjected to preparative TLC (15% EtOAc/Hexanes) to afford **281** (0.4 mg, 29% yield, 48% b.r.s.m.) and **411** (0.7 mg, 39% r.s.m.). Major isomer: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.06 (s, 1H), 5.17 (m,

1H), 3.31 (m, 1H), 2.89 (m, 1H), 2.57 (s, 3H), 1.72 (s, 3H), 1.64 (s, 3H), 1.34 (d, *J* = 7.0 Hz, 3H), 0.68 (d, *J* = 7.0 Hz, 3H).

5 A Novel Approach to Chiral Cyclic Sulfinamide

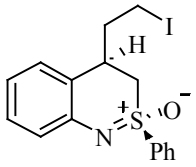
Preparation of 4-ethyl-2,1-benzothiazine 538



536 **537** **538**

526 (1.2g, 4.0 mmol) was dissolved in 70 mL THF. The solution was cooled to 0 °C before it was dropwisely added lithium triethylborohydride (1.0 M in THF solution, 12 ml, 12 mmol). After the addition, the stirring was continued for another 1 hour. The reaction was quenched by sequential addition of methanol, 1N NaOH solution and hydrogen peroxide solution. Extract the reaction mixture with CH_2Cl_2 (3 times) and dry over $MgSO_4$. After the removal of solvent by rotary evaporization, crude product was obtained in 1.17g, which was used for next step without further purification.

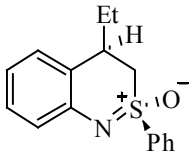
To a cold solution of crude alcohol (662 mg), triphenylphospine (1.2 g, 4.6 mmol) and imidazole (312 mg, 4.6 mmol) in acetonitrile (5.0 mL) and ether (20 mL), was slowly added iodine (1.16 g, 4.6 mmol) resulting in a pale yellow suspension. After being stirred for overnight, the reaction mixture was diluted with ether and sequentially washed with saturated aqueous $Na_2S_2O_3$, saturated $CuSO_4$ and water. The organic layer was dried briefly over $MgSO_4$, filtered and concentrated to give crude product. Silica gel column chromatography (30% EtOAc/Hexanes) gave 820 mg of pure iodide **537** (90% yield).



528

537: Pale yellow solid, mp: 103-4 ^{o}C; IR: ν 2929.4, 1482.8, 1442.0, 1017.0, 747.3 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.5 Hz, 2H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 2H), 7.23-7.27 (m, 1H), 7.17 (d, *J* = 7.0 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.95 (t, *J* = 7.2 Hz, 1H), 3.52 (dd, *J* =8.5, 13.0 Hz, 1H), 3.47-3.49 (m, 1H), 3.23 (dd, *J* = 5.0, 13.5 Hz, 1H), 3.03-3.14 (m, 2H), 2.47-2.54 (m, 1H), 2.08-2.14 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 144.7, 139.3, 133.8, 129.5, 128.7, 126.2, 124.5, 124.1, 121.1, 52.5, 36.0, 35.7, 1.96; HRMS caclcd for $C_{16}H_{16}INOSNa^+$ $[M+Na]^+$ 419.9889, found 419.9886; $[\alpha]^{25}_D$ = -7.83 (*c* 2.92, $CHCl_3$).

To the THF (40 mL) solution of iodide **537** (820 mg) at 0 ^{o}C, was dropwisely added lithium triethylborohydride (1.0M in THF solution, 6.2 mL, 6.2 mmol). The stirring was continued for another 2.0 h before it was quenched by the sequential addition of methanol, 1N NaOH and hydrogen peroxide solution. The reaction mixture was extracted with CH_2Cl_2 (3 times) and dry over $MgSO_4$. After the removal of solvent by rotary evaporation, crude product was subjected to silica gel column chromatography (30% EtOAc in hexanes). Compound **538** was isolated in 540 mg (96% yield).



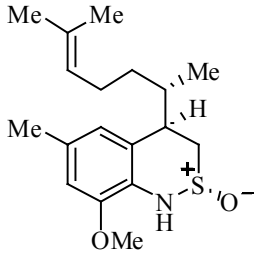
538

Yellow solid, 96% yield, mp: 102-3 ^{o}C; IR: ν 2966.1, 1597.2, 1474.6, 1442.0, 1270.3, 1204.9, 1111.0, 1012.9, 747.3 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 8.06-8.11 (m, 2H), 7.54-7.70 (m, 3H), 7.23 (t, *J* = 7.2 Hz, 2H), 7.12-7.16 (m, 1H), 6.94 (td, *J* = 7.4, 1.5 Hz, 1H), 3.37-3.51 (m, 2H), 2.92 (t, *J* = 11.5 Hz, 1H), 2.09-2.21 (m, 1H), 1.84 (td, *J* = 14.2, 7.1 Hz, 1H), 0.98 (t, *J* = 7.4 Hz, 3H);

^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 145.2, 139.1, 133.7, 129.3, 128.8, 128.1, 125.6, 125.4, 123.7, 120.5, 51.3, 34.6, 24.2, 10.5; HRMS caclcd for $C_{16}H_{17}NOSNa^+$ $[M+Na]^+$ 294.0923, found 294.0919; $[\alpha]^{25}_D$ = +3.13 (*c* 0.83, $CHCl_3$).

Typical Procedure of Dephenylation Reaction

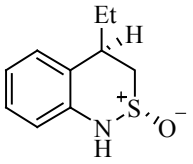
To the THF (6.0 mL) solution of **4** (0.3 mmol) at 0 ^oC, was dropwisely added lithium triethylborohydride (1.0M in THF solution, 0.9 mL, 0.9 mmol). The resulting mixture was refluxed for certain hours. The reaction was monitored by TLC analysis. When the reaction was complete, the mixture was cooled to room temperature and quenched by the sequential addition of methanol, 1N NaOH and hydrogen peroxide solution. The reaction mixture was extracted with CH_2Cl_2 (3 times) and dry over $MgSO_4$. After the removal of solvent by rotary evaporation, crude product was subjected to purify by silica gel column chromatography.



390

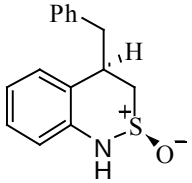
390: yellow liquid, 57% yield (65% yield based on recovered starting material), silica gel column chromatography (30% EtOAc/Hexanes); IR: ν 3252.2, 2917.1, 1585..0, 1482.8, 1458.3, 1082.4, 878.0, 829.0 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.86 (s, 1H), 6.74 (s, 1H), 6.56, (s, 1H), 5.16 (td, *J* = 7.2, 1.2 Hz, 1H), 3.83 (s, 3H), 3.63 (dt, *J* = 13.0, 4.0 Hz,, 1H), 2.90 (ddd, *J* = 12.8, 4.7, 2.4 Hz, 1H), 2.60 (t, *J* = 13.0 Hz, 1H), 2.56-2.60 (m, 1H), 2.31 (s, 3H), 2.05-2.13 (m, 2H), 1.72 (s, 3H), 1.64 (s, 3H), 1.36-1.48 (m, 2H), 0.82 (d, *J* = 6.8 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 147.4,

131.9, 130.8, 125.4, 123.9, 122.6, 118.8, 109.1, 55.6, 44.2, 35.0, 32.5, 29.7, 26.0, 25.7, 21.5, 17.7, 14.6; HRMS caclcd for $C_{18}H_{27}NO_2SNa^+$ $[M+ Na]^+$ 344.1654, found 344.1647.



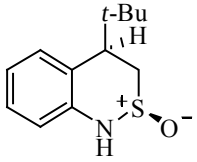
539

539: Colorless crystal (recrystallized from Hexane-EtOAc), 71% yield, silica gel column chromatography (50% EtOAc/Hexanes); mp: 112-3 ^oC; IR: ν 3170.4, 1470.6, 1037.4, 898.5, 747.3 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.31 (d, *J* = 7.5 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.95 (td, *J* = 7.5, 1.0 Hz, 1H), 6.80 (s, 1H), 6.58 (td, *J* = 8.0, 1.0 Hz, 1H), 3.59-3.65 (m, 1H), 3.01 (ddd, *J* = 13.0, 4.0, 2.0 Hz, 1H), 2.64 (t, *J* ═ 13.0 Hz, 1H), 2.11-2.17 (m, 1H), 1.99 (td, *J* = 15.0, 7.5 Hz, 1H), 1.00 (t, *J* = 7.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 135.4, 127.4, 126.6, 125.3, 121.9, 117.4, 48.5, 26.4, 24.2, 10.0; HRMS caclcd for $C_{10}H_{13}NOSNa^+$ $[M+ Na]^+$ 218.0610, found 218.0606; $[\alpha]^{25}_D$ = -61.2 (*c* 0.84, $CHCl_3$).



541

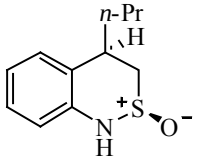
541: Off-white solid, 99% yield, silica gel column chromatography (50% EtOAc/Hexanes); mp: 153-4 ^oC; IR: ν 3190.9, 1462.4, 1049.7, 743.2 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.46 (s, 1H), 7.26-7.38 (m, 5H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.14 (td, *J* = 7.5, 1.4 Hz, 1H), 7.00 (td, *J* = 7.4, 1.2 Hz, 1H), 6.78 (dd, *J* = 7.8, 1.1 Hz, 1H), 3.63 (dd, *J* = 12.6, 10.7 Hz, 1H), 3.30-3.40 (m, 1H), 3.24 (dd, *J* = 12.6, 5.2 Hz, 1H), 3.04 (ddd, *J* = 13.7. 3.4, 1.8 Hz, 1H), 2.77 (dd, *J* = 13.7, 6.0 Hz, 1H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 139.5, 134.6, 129.6, 129.3, 128.5, 127.9, 126.3, 125.7, 122.1, 118.2, 46.5, 41.5, 35.9; HRMS caclcd for $C_{15}H_{15}NOSNa^+$ $[M+ Na]^+$ 280.0766, found 280.0760.



543

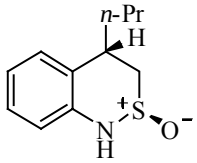
543: White solid, 96% yield, silica gel column chromatography (50% EtOAc/Hexanes); mp: 179-80 ^{o}C; IR: ν 3182.7, 2958.0, 1474.6, 1061.9, 890.3, 751.4 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.30 (d, *J* = 7.5 Hz, 1H), 7.19 (td, *J* = 7.5, 1.0 Hz, 1H), 7.00 (td, *J* = 7.5, 1,0 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 3.21 (dd, *J* = 14.3, 5.3 Hz, 1H), 3.06 (dd, *J* = 14.2, 6.4 Hz, 1H), 2.90 (t, *J* = 5.8 Hz, 1H), 1.19 (s, 9H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 137.5, 129.5, 127.6, 126.3, 121.9, 118.2, 51.8, 45.7, 34.1, 28.7; HRMS caclcd for $C_{12}H_{17}NOSNa^{+}$ $[M+ Na]^{+}$ 246.0923, found 246.0916.

545: 90% yield, a mixture of *cis* and *trans* isomers (*d.r.*: 1.7: 1.0), which were partially separated by silica gel column chromatography (50% EtOAc/Hexanes).



cis-**545**

1st fraction, major isomer *cis*-**545**: off-white solid, mp: 159-60 ^{o}C; IR: ν 3166.4, 2958.0, 1462.4, 1041.5, 902.6, 739.1 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.18 (d, *J* = 6.6 Hz, 1H), 7.12 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.00 (td, *J* = 7.4, 1,2 Hz, 1H), 6.92 (s, 1H), 6.75 (dd, *J* = 7.8, 1.1 Hz, 1H), 2.96-3.16 (m, 3H), 2.11-2.18 (m, 1H), 1.91-1.98 (m, 1H), 1.42-1.62 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 134.8, 128.3, 127.7, 127.6, 122.3, 118.2, 50.3, 36.4, 33.8, 20.9, 13.8; HRMS caclcd for $C_{11}H_{15}NOSNa^{+}$ $[M+ Na]^{+}$ 232.0766, found 232.0764.

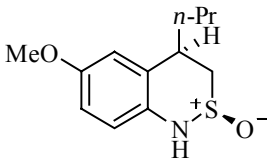


trans-**545**

2nd fraction, minor isomer *trans*-**545**: white solid, mp: 105-6 ^{o}C; IR: ν 3154.1, 2945.7, 1470.6, 1041.5, 910.7, 747.3 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.31 (d, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.02 (s, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 3.60-3.66 (m, 1H), 3.01 (ddd, *J* = 13.0,

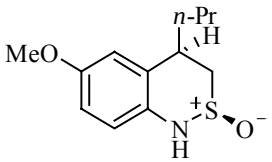
4.0, 2.0 Hz, 1H), 2.61 (t, *J* = 13.0 Hz, 1H), 2.03-2.11 (m, 1H), 1.83-1.91 (m, 1H), 1.45-1.52 (m, 1H), 1.32-1.39 (m, 1H), 1.01 (t, *J* = 7.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 135.4, 127.3, 126.5, 125.8, 121.9, 117.4, 48.9, 33.8, 25.3, 19.1, 14.2; HRMS caclcd for $C_{11}H_{15}NOSNa^+$ $[M+ Na]^+$ 232.0766, found 232.0764.

547: 70%% yield, a mixture of *cis* and *trans* isomers (***d.r.*** 1.3: 1.0), which were partially separated by silica gel column chromatography (50% EtOAc/Hexanes).



cis-**547**

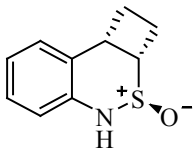
1st fraction, major isomer *cis*-**547**: pale yellow solid, mp: 170-1 ^{o}C; IR: ν 3154.1, 2949.8, 1033.3, 808.6 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): 6.78 (s, 1H), 6.74 (s, 1H), 6.73 (s, 1H), 6.50 (s, 1H), 3.79 (s, 3H), 3.29 (dd, *J* = 13.5, 5.5 Hz, 1H), 2.91-2.94 (m, 1H), 2.77 (ddd, *J* = 14.0, 7.5, 1.5 Hz, 1H), 2.02-2.05 (m, 1H), 1.91-1.95 (m, 1H), 1.59-1.61 (m, 1H), 1.46-1.48 (m, 1H), 1.00 (t, *J* = 7.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 155.5, 130.3, 128.3, 119.7, 113.6, 112.5, 52.5, 52.6, 35.5, 33.9, 20.7, 13.9; HRMS caclcd for $C_{12}H_{17}NO_2SNa^+$ $[M+Na]^+$ 262.0872, found 262.0868.



trans-**547**

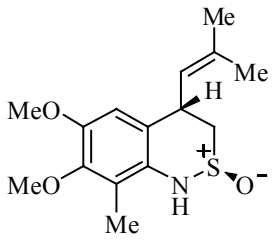
2nd fraction, minor isomer *trans*-**547**: white solid, mp:110-1 ^{o}C; IR: ν 3170.4, 2837.5, 1466.5, 1217.2, 1045.6, 816.8 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): 6.88 (d, *J* = 2.5 Hz, 1H), 6.68 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.59 (d, *J* = 8.5 Hz, 1H), 6.47 (s, 1H), 3.77 (s, 3H), 3.58-3.62 (m, 1H), 3.02 (ddd, *J* = 12.5, 4.0, 2.0 Hz, 1H), 2.67 (t, *J* = 13.0 Hz, 1H), 2.01-2.06 (m, 1H), 1.82-1.84 (m, 1H), 1.45-1.49 (m, 1H), 1.34-1.38 (m, 1H), 1.02 (t, *J* = 7.5 Hz, 3H); ^{13}C-NMR

(125 MHz, $CDCl_3$): δ 154.9, 128.7, 127.4, 118.4, 112.9, 112.5, 55.6, 49.4, 34.1, 26.2, 19.1, 14.2; HRMS caclcd for $C_{12}H_{17}NO_2SNa^+$ $[M+Na]^+$ 262.0872, found 262.0868.



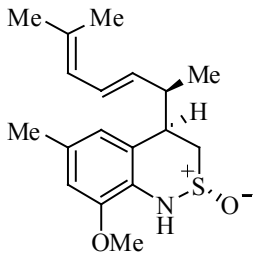
549

549: white solid, 59% yield (73% yield based on recovered starting material), silica gel column chromatography (50% EtOAc/Hexanes); mp: 220 ^oC (decomposed); IR: ν 3252.2, 1462.4, 1049.7, 747.3 cm^{-1}; ^1H-NMR (250 MHz, $CDCl_3$): 7.13-7.19 (m, 1H), 6.99-7.08 (m, 2H), 6.79 (d, *J* = 7.4 Hz, 1H), 6.65 (s, 1H), 4.00-4.09 (m, 1H), 3.86-3.97 (m, 1H), 2.59-2.74 (m, 1H), 2.33-2.48 (m, 1H), 2.10-2.25 (m, 1H), 1.93-2.06 (m, 1H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 132.8, 129.7, 128.6, 127.8, 123.8, 120.6, 57.7, 34.2, 28.8, 20.2; HRMS caclcd for $C_{10}H_{11}NOSNa^+$ $[M+Na]^+$ 216.0453, found 216.0450; $[\alpha]^{25}_D$ = -262.1 (*c* 0.47, MeOH).



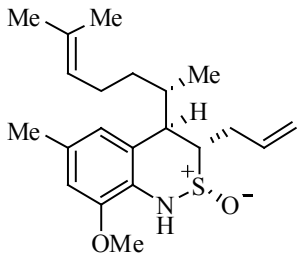
551

.**551**: pale yellow liquid, 90% yield, silica gel column chromatography (50% EtOAc/Hexanes); IR: ν 3264.4, 2929.4, 1437.9, 1086.4, 874.0 cm^{-1}; ^1H-NMR (500 MHz, $CDCl_3$): 6.64 (s, 1H), 6.30 (s, 1H), 5.22 (dt, *J* = 9.5, 1.0 Hz, 1H), 4.48 (ddd, *J* = 13.5, 9.5, 4.0 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 2.89 (ddd, *J* = 12.5, 4.5, 2.0 Hz, 1H), 2.62 (t, *J* = 13.0 Hz, 3H), 2.10 (s, 3H), 1.86 (d, *J* = 1.0 Hz, 3H), 1.81 (d, *J* = 1.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 147.5, 146.6, 136.2, 127.1, 123.7, 120.2, 118.4, 110.6, 60.5, 56.2, 48.5, 25.9, 25.8, 18.1, 9.5; HRMS caclcd for $C_{15}H_{21}NO_3SNa^+$ $[M+Na]^+$ 318.1134, found 318.1129; $[\alpha]^{25}_D$ = +136.9 (*c* 1.83, $CHCl_3$).



553

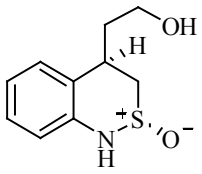
553: pale brown needle, 84% yield, silica gel column chromatography (50% EtOAc/Hexanes); mp: 118-9 ^{o}C; IR: ν 3244.0, 2966.1, 2913.0, 1593.1, 1482.8, 1454.2, 1074.2 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): 6.82 (s, 1H), 6.81 (s, 1H), 6.57 (s, 1H), 6.26 (ddd, *J* = 15.5, 11.0, 1.5 Hz, 1H), 5.71 (d, *J* = 10.5 Hz, 1H), 5.43 (dd, *J* = 15.0, 5.5 Hz, 1H), 3.83 (s, 3H), 3.50 (dt, *J* = 12.0, 5.0 Hz, 1H), 3.37 (q, *J* = 5.5 Hz, 1H), 2.91 (ddd, *J* = 13.0, 5.0, 2.5 Hz, 1H), 2.71 (t, *J* = 12.5 Hz, 1H), 1.73 (s, 3H), 1.72 (s, 3H), 1.21 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 147.7, 134.1, 131.6, 130.9, 127.4, 125.2, 124.9, 122.4, 119.5, 109.4, 55.6, 46.5, 35.9, 32.7, 25.8, 21.5, 18.2, 17.5; HRMS caclcd for $C_{18}H_{25}NO_2SNa^+$ $[M+Na]^+$ 342.1498, found 342.1497; $[\alpha]^{25}_D$ = +162.8 (*c* 1.82, $CHCl_3$).



555

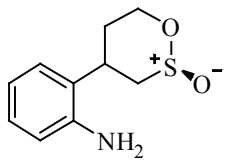
555: off-white needle, 89% yield (*d.r.* 8.2: 1.0), silica gel column chromatography (40% EtOAc/Hexanes); mp: 85-6 ^{o}C; IR: ν 3231.7, 2913.0, 1597.2, 1486.9, 1450.1, 1074.2, 833.1, 726.9 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): 6.68 (s, 1H), 6.55 (s, 1H), 6.54 (s, 1H), 5.88-5.94 (m, 1H), 5.24 (dd, *J* = 17.0, 1.0 Hz, 1H), 5.19 (d, *J* = 10.0 Hz, 1H), 5.03 (t, *J* = 7.0 Hz, 1H), 3.81 (s, 3H), 2.93 (dt, *J* = 9.5, 5.5 Hz, 1H), 2.83 (dd, *J* = 6.0, 3.5 Hz, 1H), 2.71 (dt, *J* = 15.0, 8.0 Hz, 1H), 2.34 (td, *J* = 15.0, 5.5 Hz, 1H), 2.28 (s, 3H), 2.00-2.04 (m, 1H), 1.84-1.92 (m, 2H), 1.68 (s, 3H), 1.58 (s, 3H), 1.37-1.40 (m, 1H), 0.99-1.04 (m, 1H), 0.92 (d, *J* = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 149.1, 134.1, 132.0, 131.6, 128.4, 124.1, 121.9, 120.8, 118.5, 109.5,

60.7, 55.5, 44.3, 38.8, 35.3, 33.6, 25.9, 25.6, 21.4, 17.6, 16.7; HRMS caclcd for $C_{21}H_{31}NO_2SNa^+$ $[M+Na]^+$ 384.1967, found 384.1955.



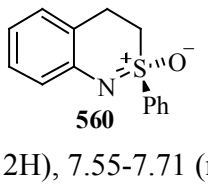
557

557: brown liquid, 70% yield, silica gel column chromatography (MeOH); IR: ν 3317.5, 1560.5, 1462.4, 1405.2, 1045.6, 898.5, 751.4 cm^{-1}; ^{1}H-NMR (500 MHz, d_4-MeOD): 7.36 (d, *J* = 7.5 Hz, 1H), 7.13 (dd, *J* = 7.5, 0.5 Hz, 1H), 6.96 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.78 (dd, *J* = 8.0, 1.5 Hz, 1H), 3.61-3.75 (m, 3H), 3.30-3.31 (m, 1H), 3.13 (dd, *J* = 13.0, 4.5 Hz, 1H), 2.73 (t, *J* = 13.0 Hz, 1H), 2.39-2.45 (m, 1H), 1.98-2.04 (m, 1H); ^{13}C-NMR (125 MHz, d_4-MeOD): δ 136.9, 128.5, 127.6, 126.8, 122.9, 118.5, 60.1, 49.6, 35.6, 24.8; HRMS caclcd for $C_{10}H_{13}NO_2SNa^+$ $[M+Na]^+$ 234.0559, found 234.0559.



558

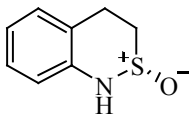
558: brown liquid, 14% yield, silica gel column chromatography (EtOAc); IR: ν 3436.1, 1572.7, 1139.6 cm^{-1}; ^{1}H-NMR (500 MHz, d_6-acetone): 7.36 (d, *J* = 8.0 Hz, 1H), 7.17-7.20 (m, 1H), 7.04 (td, *J* = 7.5, 1.0 Hz, 1H), 6.89 (dd, *J* = 8.0, 1.5 Hz, 1H), 3.69-3.75 (m, 3H), 3.50 (dd, *J* = 13.5, 6.0 Hz, 1H), 3.36 (dd, *J* = 13.5, 8.0 Hz, 1H), 2.85 (s, 2H), 2.22-2.28 (m, 1H), 2.15-2.19 (m, 1H); ^{13}C-NMR (125 MHz, d_6-acetone): δ 138.1, 128.5, 127.4, 125.9, 122.7, 118.6, 58.5, 49.3, 36.5, 35.4; HRMS caclcd for $C_{10}H_{13}NO_2SNa^+$ $[M+Na]^+$ 234.0559, found 234.0549.



560

Semi-solid, 76% yield; IR: ν 3060.1, 1597.2, 1478.7, 1446.0, 1266.2, 1111.0, 1012.9, 743.2 cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): 8.05-8.10 (m, 2H), 7.55-7.71 (m, 3H), 7.22 (td, *J* = 7.8, 1.5 Hz, 1H), 7.08 (td, *J* = 7.7, 1.0 Hz, 2H), 6.89

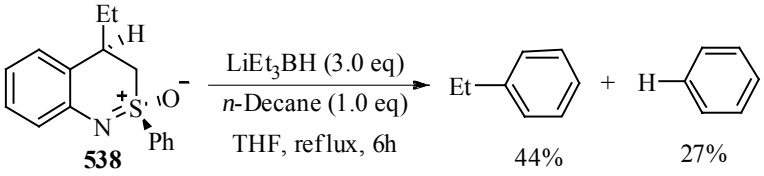
(td, J = 7.3, 1.2 Hz, 1H), 3.36-3.50 (m, 2H), 3.03-3.22 (m, 2H); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 145.0, 138.5, 133.8, 129.3, 128.9, 128.5, 128.3, 123.4, 120.8, 120.4, 47.1, 24.6; HRMS caclcd for $C_{14}H_{13}NOSNa^+$ [M+ Na]$^+$ 266.0610, found 266.0604.



561

Colorless crystal; ^{1}H-NMR (500 MHz, $CDCl_3$, d_4-MeOH): 6.99-7.03 (m, 2H), 6.80 (t, J = 7.5 Hz, 1H), 6.62 (d, J = 7.5 Hz, 1H), 3.46 (dt, J = 15.8, 4.5 Hz, 1H), 2.92 (ddd, J = 12.5, 4.5, 3.0 Hz, 1H), 2.83 (dt, J = 17.0, 3.5 Hz, 1H), 2.62 (ddd, J = 15.0, 13.0, 4.5 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$, d_4-MeOH): δ 135.0, 129.3, 127.6, 121.4, 120.9, 116.7, 42.7, 16.6;

Quantitative GC Experiment



To the THF solution of **538** and *n*-decane at 0 ^{o}C, was dropwisely added lithium triethylborohydride (1.0M in THF solution). The resulting mixture was refluxed for 6.0 h. The reaction mixture was cooled to room temperature and quenched by the sequential addition of methanol, 1N NaOH and hydrogen peroxide solution. The reaction mixture was extracted with CH_2Cl_2 (3 times) and dry over $MgSO_4$. The crude mixture was subjected to GC-MS analysis. GC conditions were as followed: flow rate: 1ml/min; 70 ^{o}C, 5 min, 10 ^{o}C/min, 200 ^{o}C, 1 min. Ethyl benzene was obtained in 44% yield and benzene was obtained in 27% yield.

APPENDIX I

List of Abbreviations

ACN – Acetonitrile

Boc – *t*-butoxycarbonyl

BOM – Benzyloxymethyl

BSA – N, O-Bis(trimethylsilyl) acetamide

dba – Dibenzylideneacetone

DCM – Dichloromethane

DBU – 1,8-diazabicyclo-[5.4.0]undec-7-ene

DIPEA – diisopropylethyl amine

HFIP — Hexafluoroisopropanol

HMPP – 1, 3, 4, 6, 7, 8-hexahrdro-1-methyl-2H-pyrimido[1, 2-a]pyrimidine

Lawesson's reagent – 2,4-bis-(4-methoxyphenyl)-[1,2,3,4] dithiadiphosphetane 2,4-dithion)

PMHS – Polymethylhydrosiloxane

p-TsOH – *p*-Tolyl sulfonic acid

TEA – Triethylamine

TEEDA – tetraethylethylendiamine

TES – Triethylsilane

TFAA – Trifluoroacetic anhydride

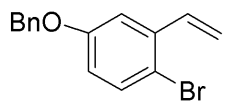
TFE – 2,2,2-trifluoroethanol

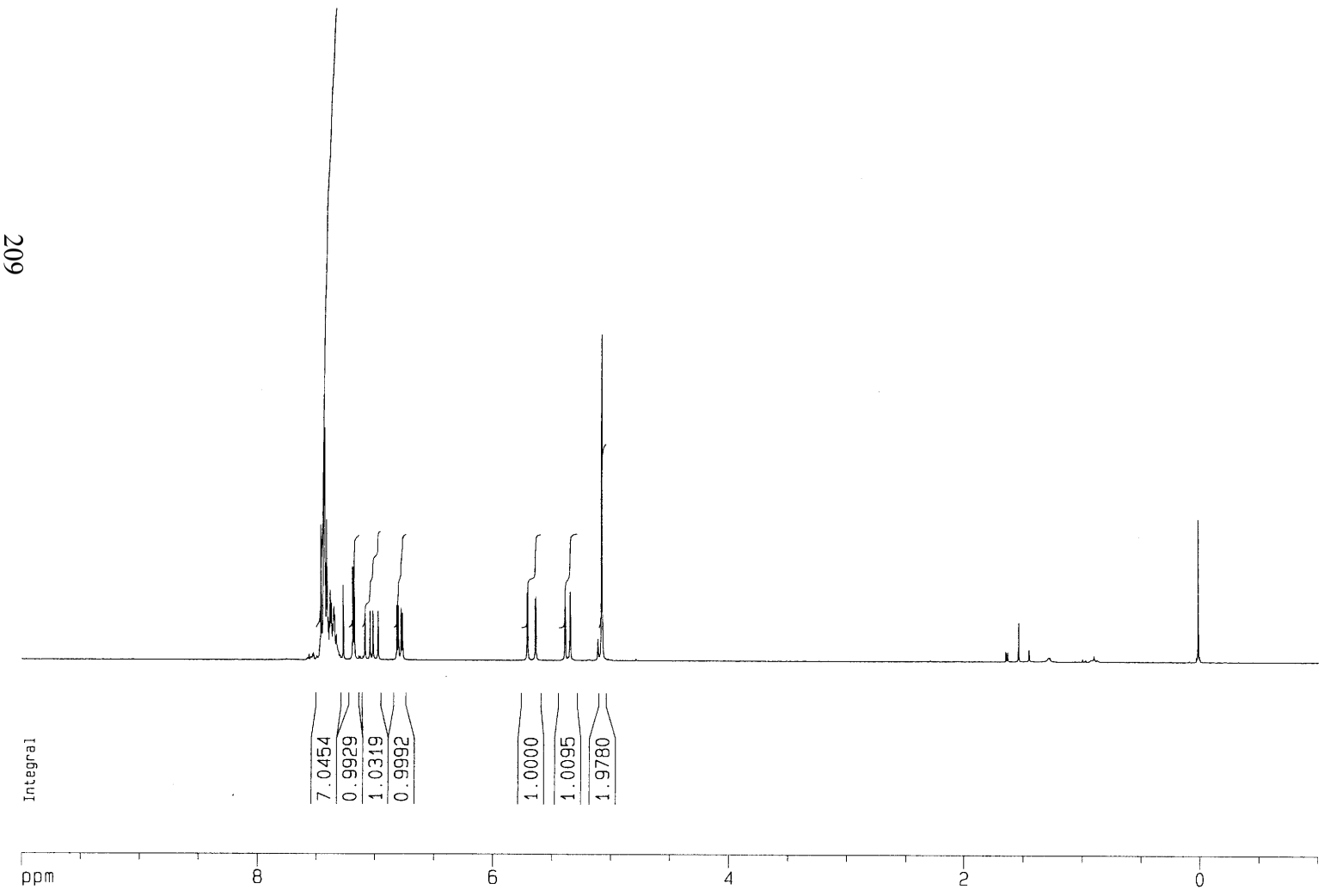
APPENDIX II

^{1}H-NMR and ^{13}C-NMR Spectra

1H NMR

PZ-III-149-A1





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PROCNO	1

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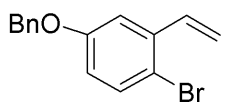
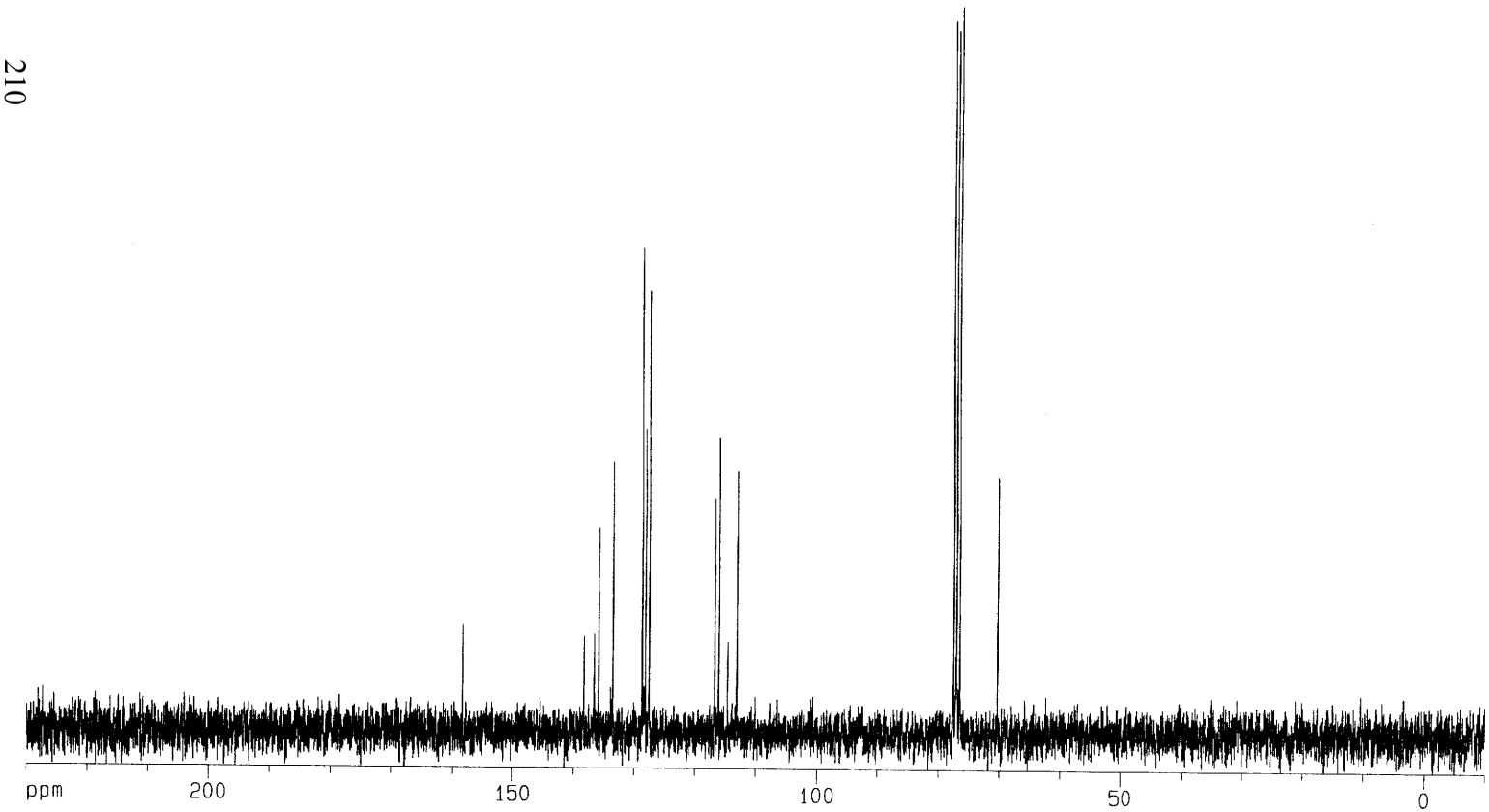
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	1430
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	8.70 use
SFO1	250.1315321 MHz
NUCLEUS	1H

F2 - Processing parameters	
SI	16384
SF	250.1300051 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters	
CX	20.00 cm
CY	5.00 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57150 Hz/

13C NMR
PZ-III-149-A1





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PROCNO	1

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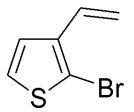
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	208
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	1.00000000 sec
P1	6.00 use
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

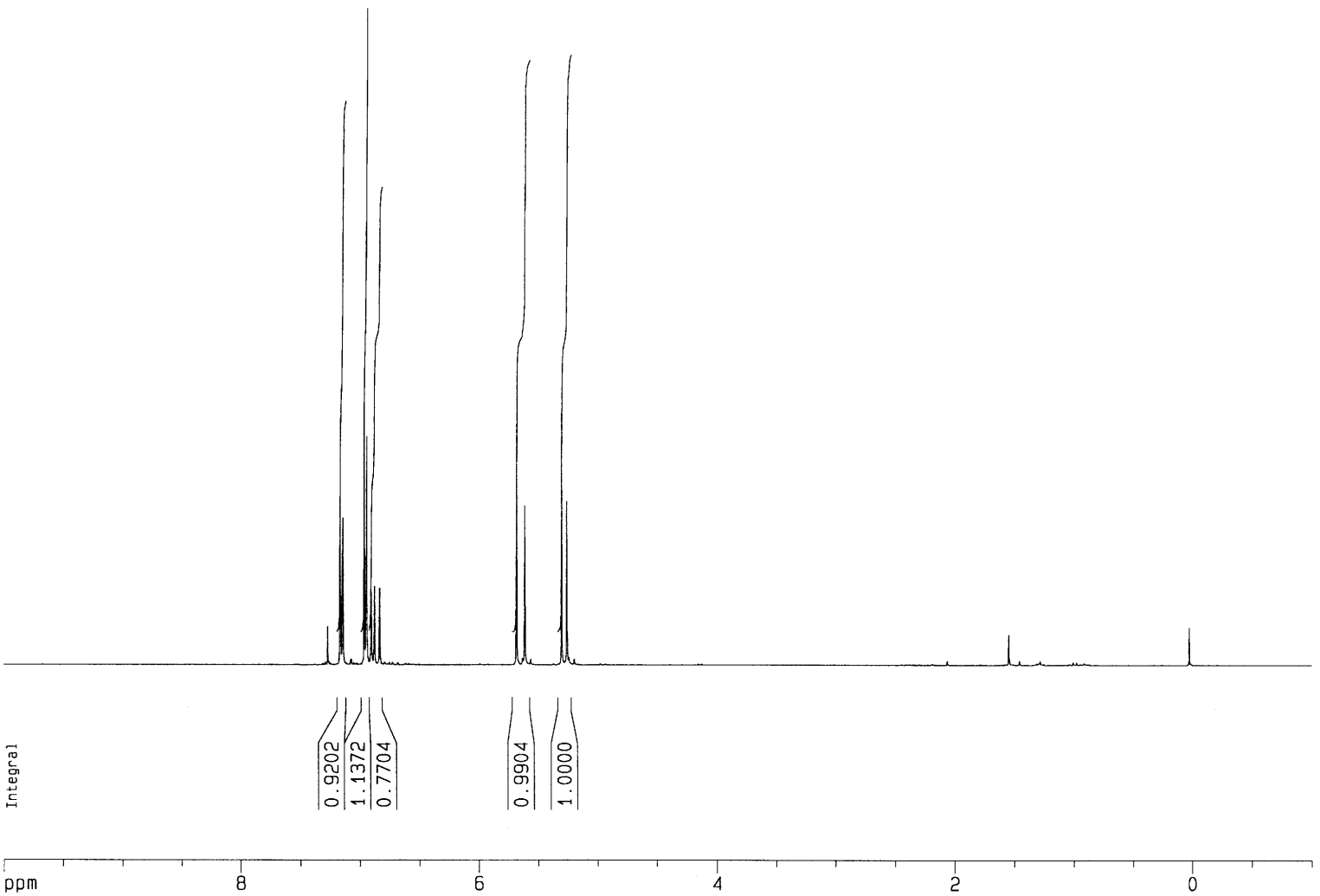
F2 - Processing parameters	
SI	32768
SF	62.8952413 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters	
CX	20.00 cm
CY	10.00 cm
F1P	230.000 ppm
F1	14465.90 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	12.00000 ppm
HZCM	754.74292 Hz/

1H NMR

PZ-IV-66-A1





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PROCNO	1

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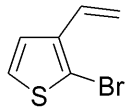
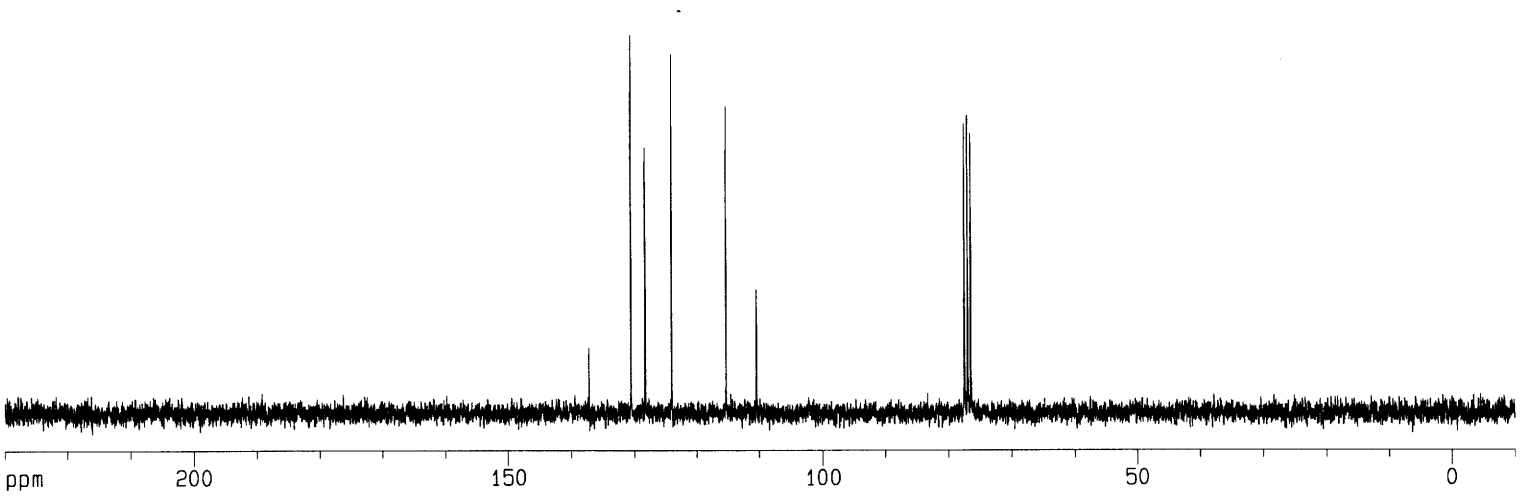
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	1024
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	8.70 use
SFO1	250.1315321 MHz
NUCLEUS	1H

F2 - Processing parameters	
SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters	
CX	20.00 cm
CY	4.00 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57150 Hz/

13C NMR
PZ-IV-66-A1





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PROCNO	1

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PROBHD	5 mm GNP 1H	
PULPROG	zgdc30	
TD	36864	
SOLVENT	CDCl3	
NS	158	
DS	4	
SWH	17241.379	Hz
FIDRES	0.467702	Hz
AQ	1.0691060	sec
RG	22800	
DW	29.000	use
DE	41.43	use
TE	300.0	K
D12	0.00002000	sec
DL5	23.00	dB
CPDPRG	waltz16	
P31	103.00	use
D1	1.00000000	sec
P1	6.00	use
SFO1	62.9023694	MHz
NUCLEUS	13C	
D11	0.03000000	sec

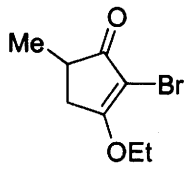
F2 - Processing parameters		
SI	32768	
SF	62.8952440	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

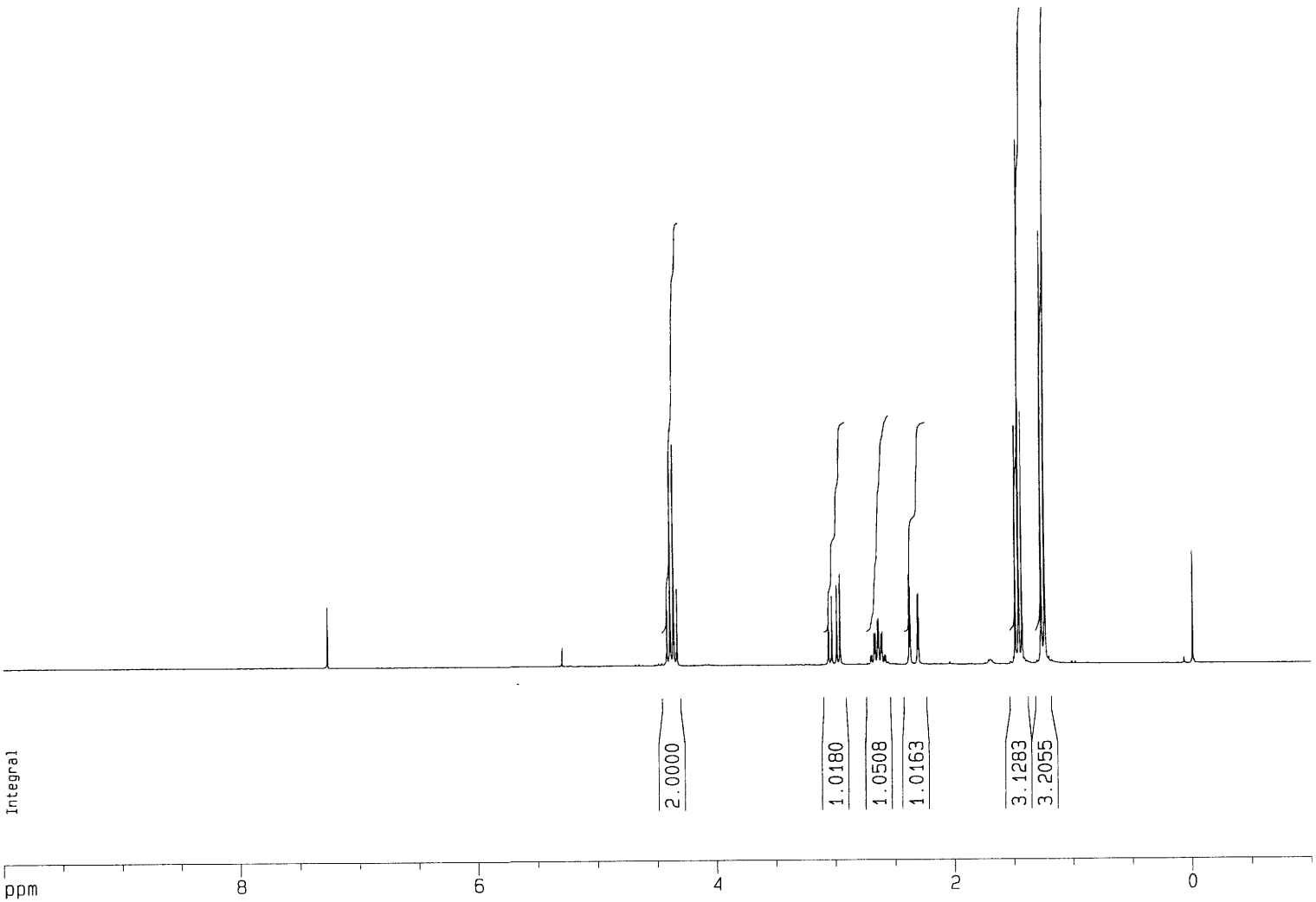
1D NMR plot parameters		
CX	20.00	cm
CY	5.00	cm
F1P	230.000	ppm
F1	14465.91	Hz
F2P	-10.000	ppm
F2	-628.95	Hz
PPMCM	12.00000	ppm
HZCM	754.74292	Hz/

1H NMR

PZ-III-145-A1

1.4eq LDA, 1.5eq MeI, 2.0eq HMPA





Current Data Parameters

NAME	PZ-III-145-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

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PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	1024
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	8.70 use
SFO1	250.1315321 MHz
NUCLEUS	1H

F2 - Processing parameters

SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

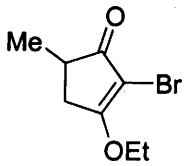
1D NMR plot parameters

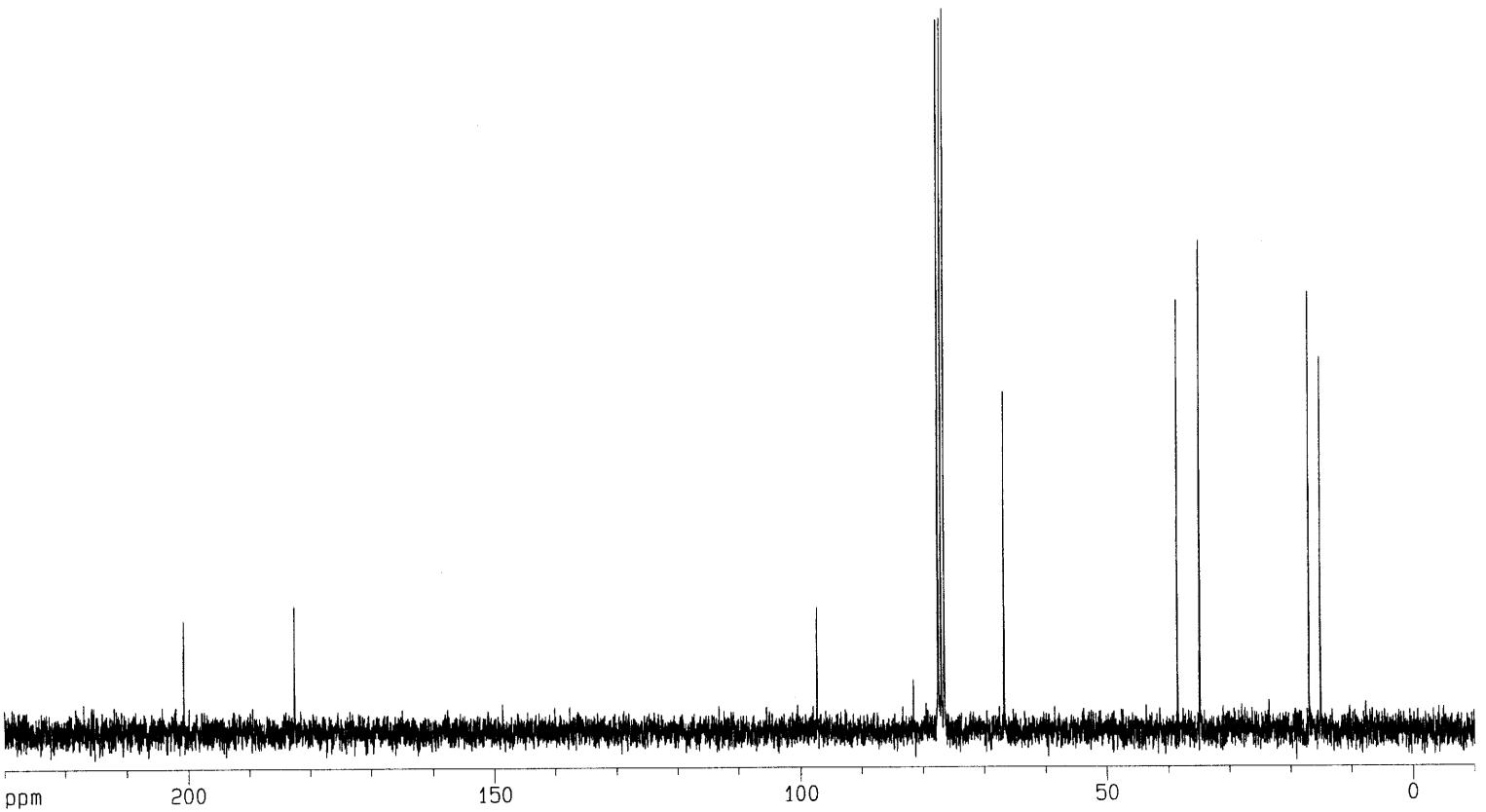
CX	20.00 cm
CY	8.00 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57150 Hz/

13C NMR

PZ-III-145-A1

1.4eq LDA, 1.5eq MeI, 2.0eq HMPA





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PROCNO	1

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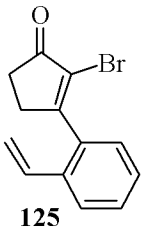
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	493
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	1.00000000 sec
P1	6.00 use
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

F2 - Processing parameters	
SI	32768
SF	62.8952419 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters	
CX	20.00 cm
CY	10.00 cm
F1P	230.000 ppm
F1	14465.90 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	12.00000 ppm
HZCM	754.74292 Hz/

1H NMR
PZ-II-019-A1



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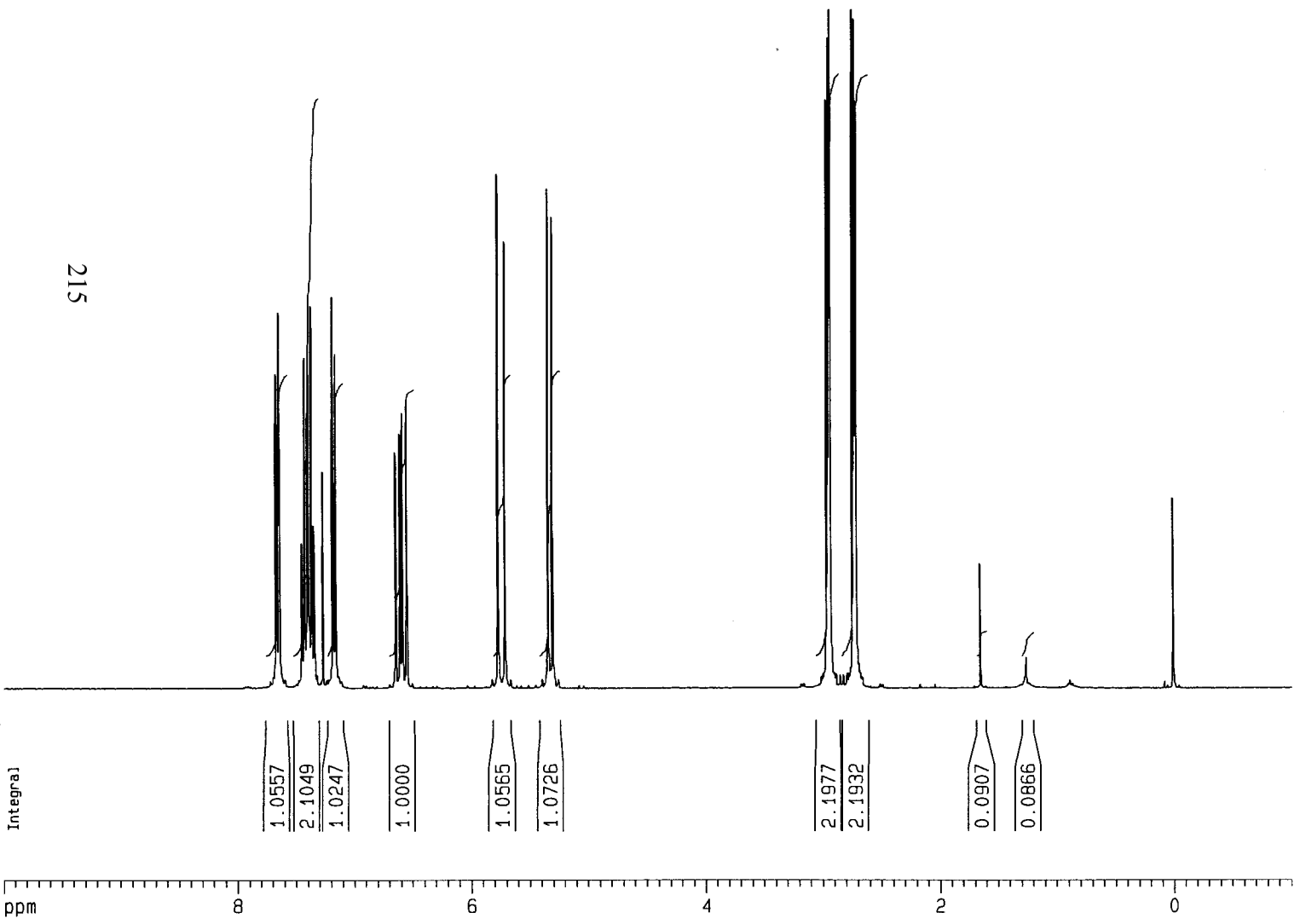

Current Data Parameters

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EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

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TD	32768
SOLVENT	CDCl3
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DS	2
SWH	6172.839 Hz
FIDRES	0.188380 Hz
AQ	2.6542580 sec
RG	228.1
DW	81.000 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
D31	0.00000000 sec

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

NUC1	1H
P1	7.05 usec
PL1	0.00 dB
SFO1	300.1318534 MHz

F2 - Processing parameters

SI	32768
SF	300.1300022 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.30

1D NMR plot parameters

CX	20.00 cm
CY	12.50 cm
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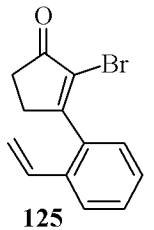
F1	3001.30 Hz
F2P	-1.000 ppm
F2	-300.13 Hz
PPMCM	0.55000 ppm/cm
HZCM	165.07150 Hz/cm

13C NMR
PZ-II-019-A1



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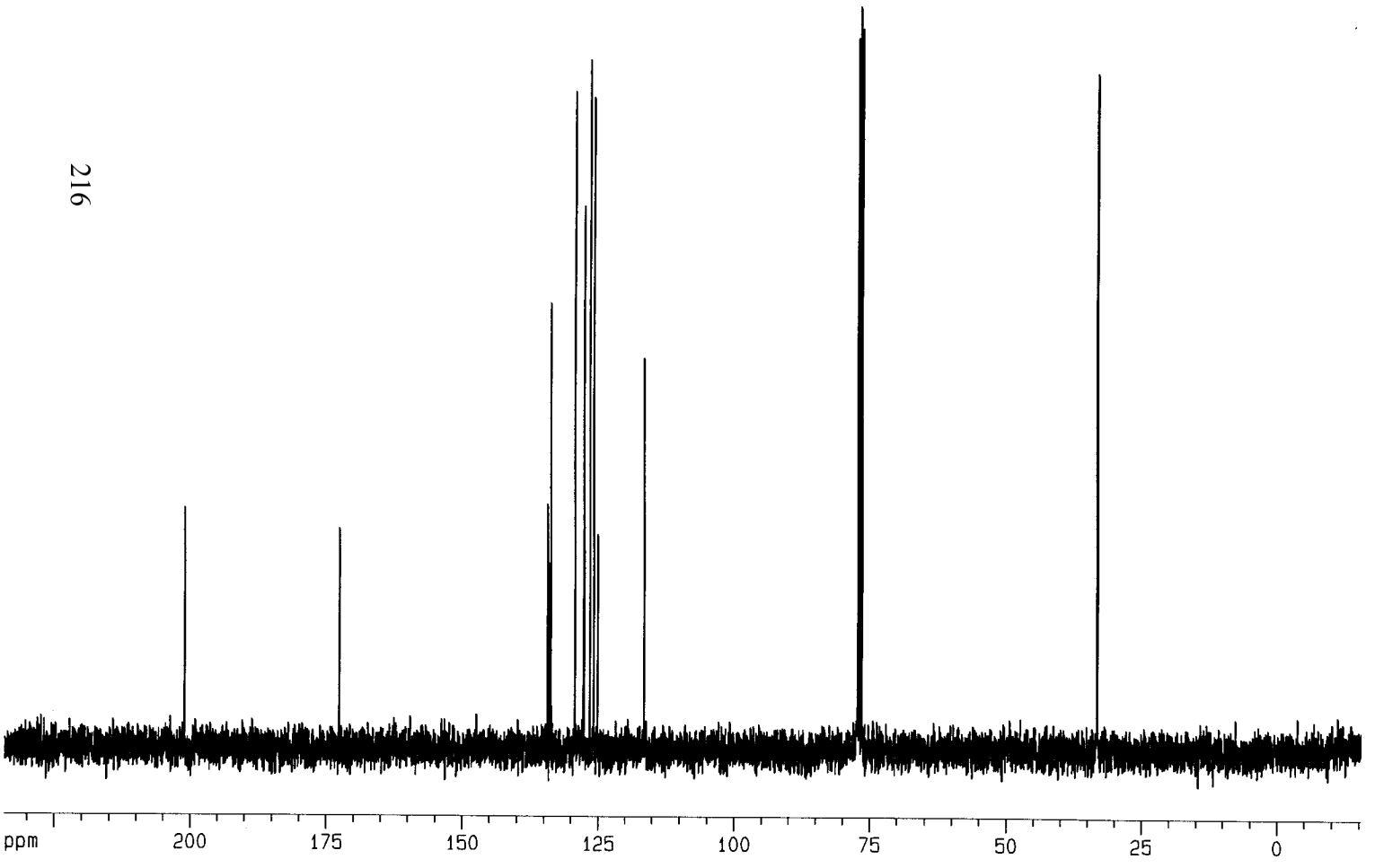


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PROCNO                 1

F2 - Acquisition Parameters
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PULPROG           zgdc30
TD                65536
SOLVENT           CDCl3
NS                   99
DS                    4
SWH           18832.393 Hz
FIDRES         0.287360 Hz
AQ             1.7400308 sec
RG                22528
DW               26.550 usec
DE                6.00 usec
TE               300.0 K
D1             1.29999995 sec
d11            0.03000000 sec
D31            0.00000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 8.00 usec
PL1                6.00 dB
SFO1         75.4760107 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2               120.00 dB
PL12               25.60 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
SF           75.4677571 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMA plot parameters
CX                20.00 cm
CY                11.00 cm
F1P              234.137 ppm
F1             17669.80 Hz
F2P             -15.405 ppm
F2             -1162.59 Hz
PPMCM          12.47711 ppm/cm
HZCM          941.61969 Hz/cm
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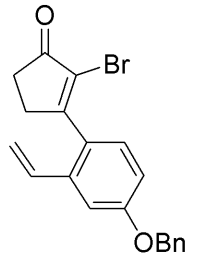
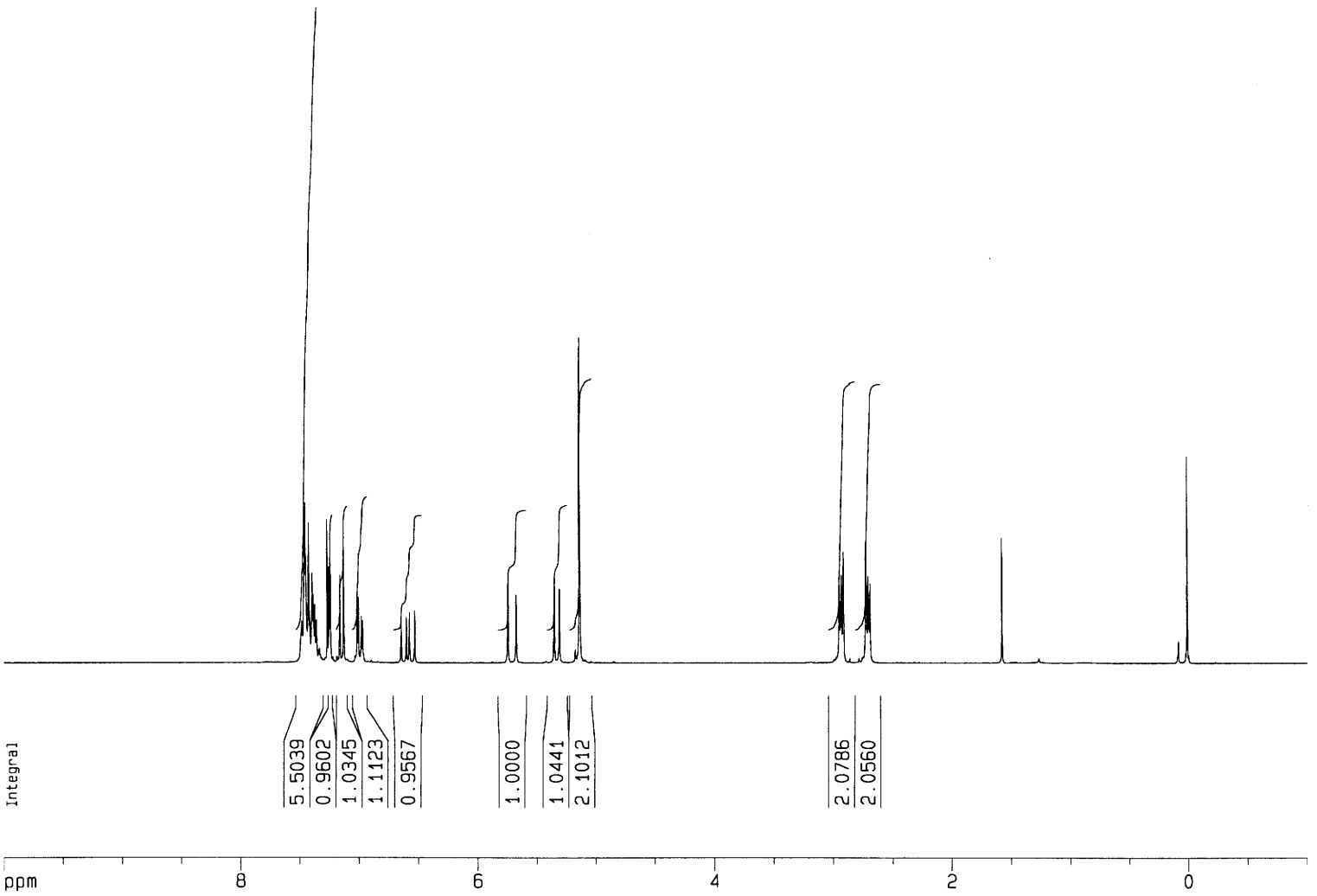
1H NMR
PZ-IV-04-A2





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PROCNO	1

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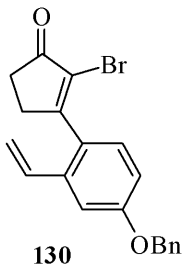
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	2048
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	8.70 use
SFO1	250.1315321 MHz
NUCLEUS	1H

F2 - Processing parameters	
SI	16384
SF	250.1300051 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters	
CX	20.00 cm
CY	5.00 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57150 Hz/

13C NMR
PZ-IV-04-A2



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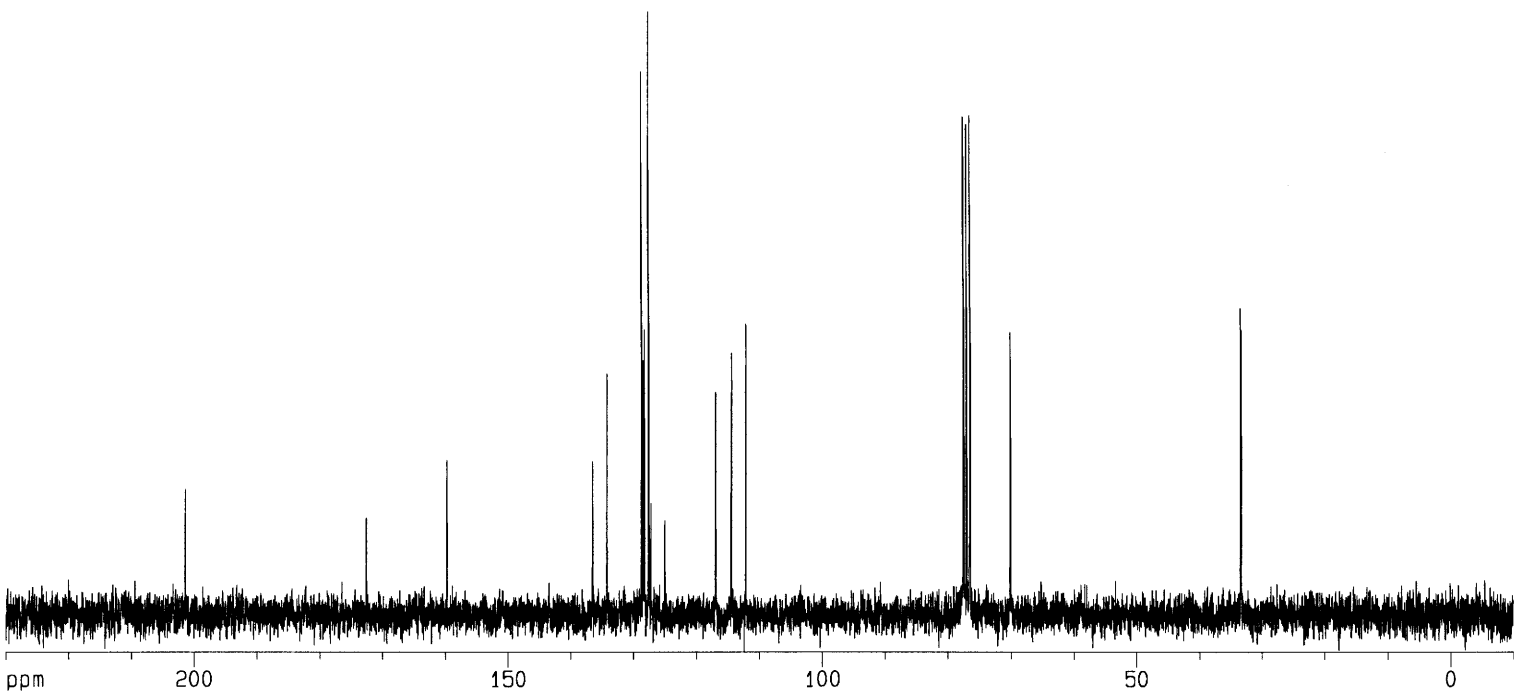


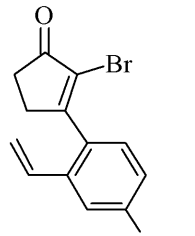
Current Data Parameters	
NAME	PZ-IV-04-A2
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters	
Date_	20041116
Time	12.52
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	315
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	1.00000000 sec
P1	6.00 use
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

F2 - Processing parameters	
SI	32768
SF	62.8952424 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters	
CX	20.00 cm
CY	8.00 cm
F1P	230.000 ppm
F1	14465.90 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	12.00000 ppm
HZCM	754.74292 Hz/

1H NMR
PZ-IV-28-A1



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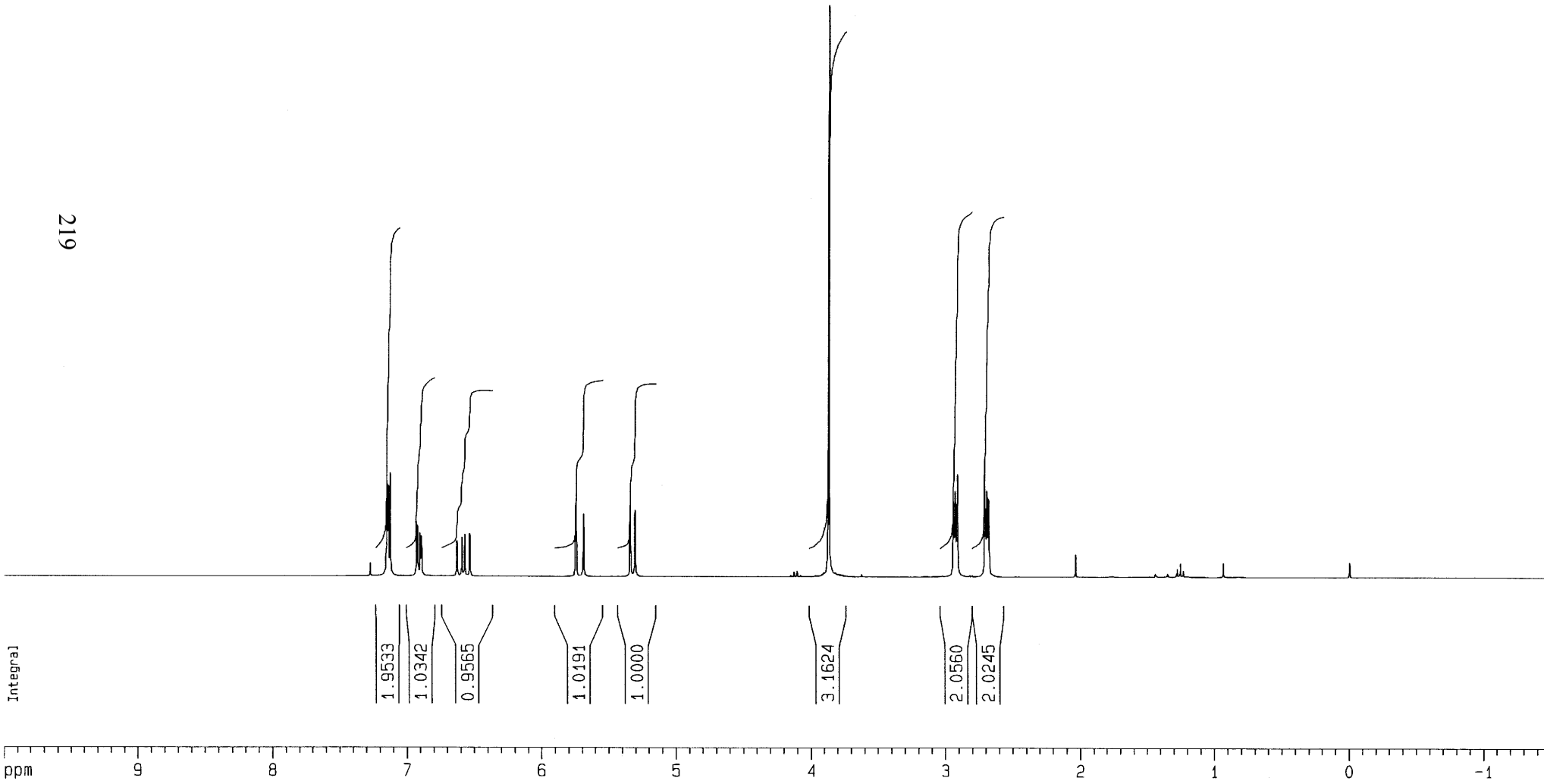
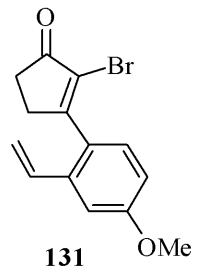


13C NMR

PZ-IV-25-A1



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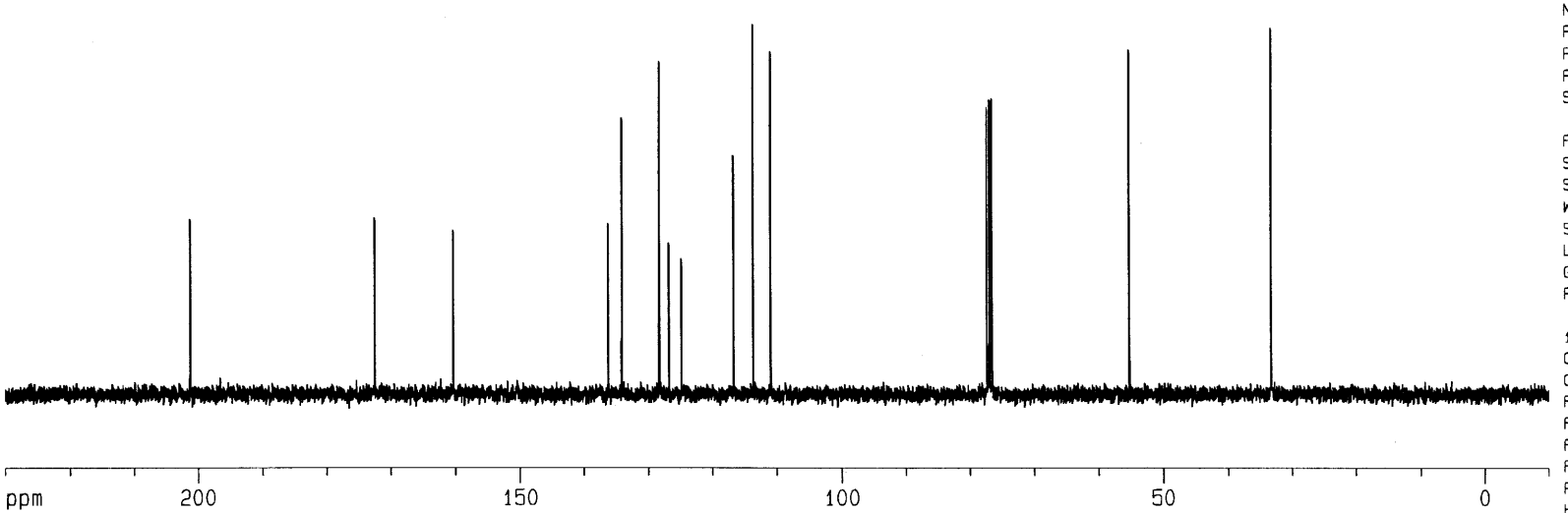


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Current Data Parameters
NAME         PZ-IV-25-A1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20041217
Time               16.31
INSTRUM          drx300
PROBHD   5 mm Multinucl
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                   99
DS                    4
SWH           18832.393 Hz
FIDRES        0.287360 Hz
AQ            1.7400308 sec
RG                22528
DW               26.550 usec
DE                6.00 usec
TE               297.1 K
D1            1.29999995 sec
d11           0.03000000 sec
D31           0.00000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 8.50 usec
PL1                5.00 dB
SFO1         75.4760107 MHz

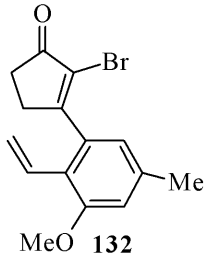
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2              120.00 dB
PL12              25.60 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
SF           75.4677571 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.80 cm
CY                 5.00 cm
F1P              230.000 ppm
F1             17357.58 Hz
F2P              -10.000 ppm
F2               -754.68 Hz
PPMCM          11.54113 ppm/cm
HZCM          870.98346 Hz/cm
```

1H NMR

PZ-IV-55-A1



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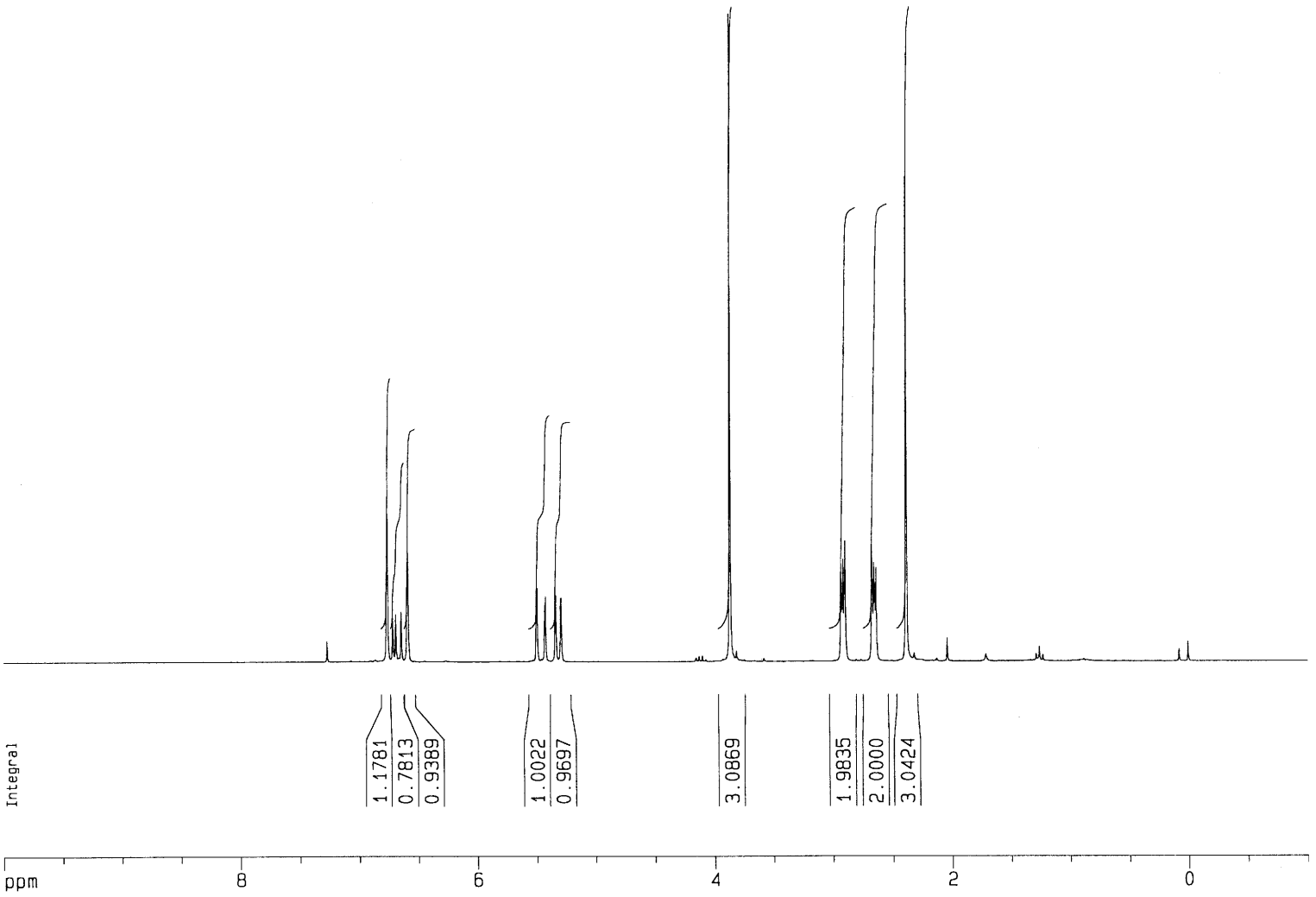


Current Data Parameters

NAME	PZ-IV-55-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050118
Time	11.32
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	715
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	8.70 use
SFO1	250.1315321 MHz
NUCLEUS	1H

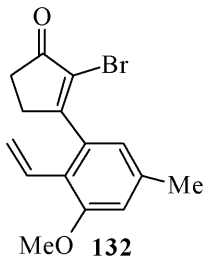
F2 - Processing parameters

SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	10.00 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57150 Hz/

13C NMR
PZ-IV-55-A1



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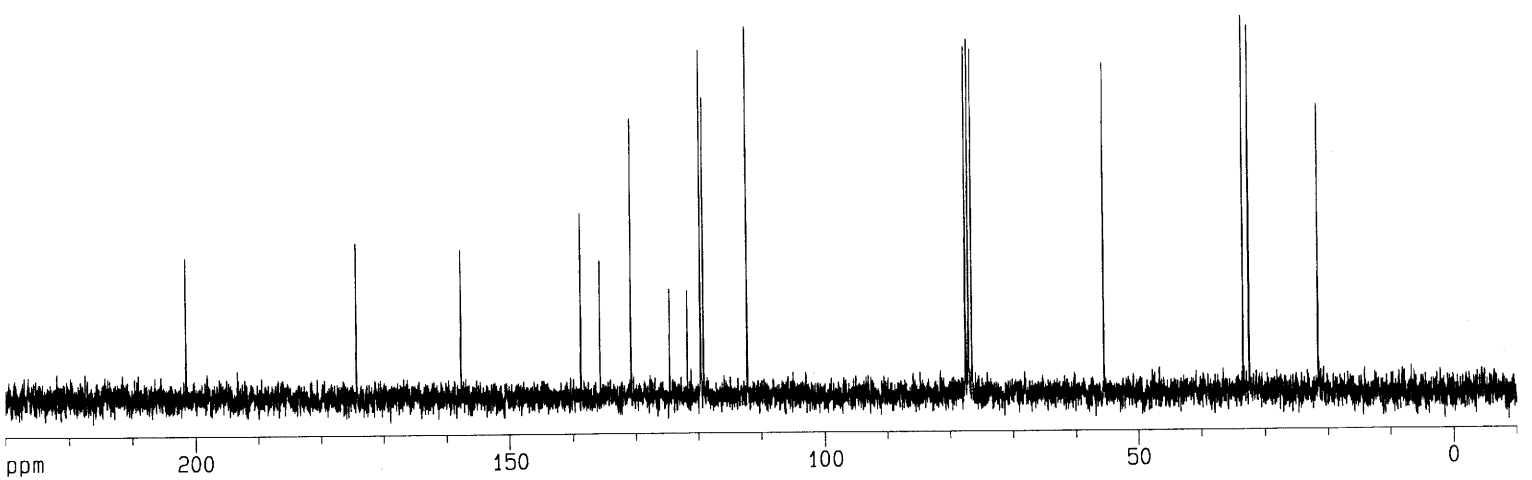


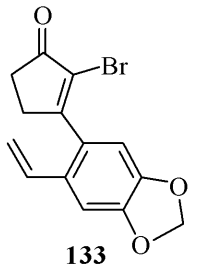
Current Data Parameters	
NAME	PZ-IV-55-A1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters	
Date_	20050118
Time	11.34
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	110
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	1.00000000 sec
P1	6.00 use
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

F2 - Processing parameters	
SI	32768
SF	62.8952440 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters	
CX	20.00 cm
CY	5.00 cm
F1P	230.000 ppm
F1	14465.91 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	12.00000 ppm
HZCM	754.74292 Hz/

1H NMR
PZ-IV-36-A1



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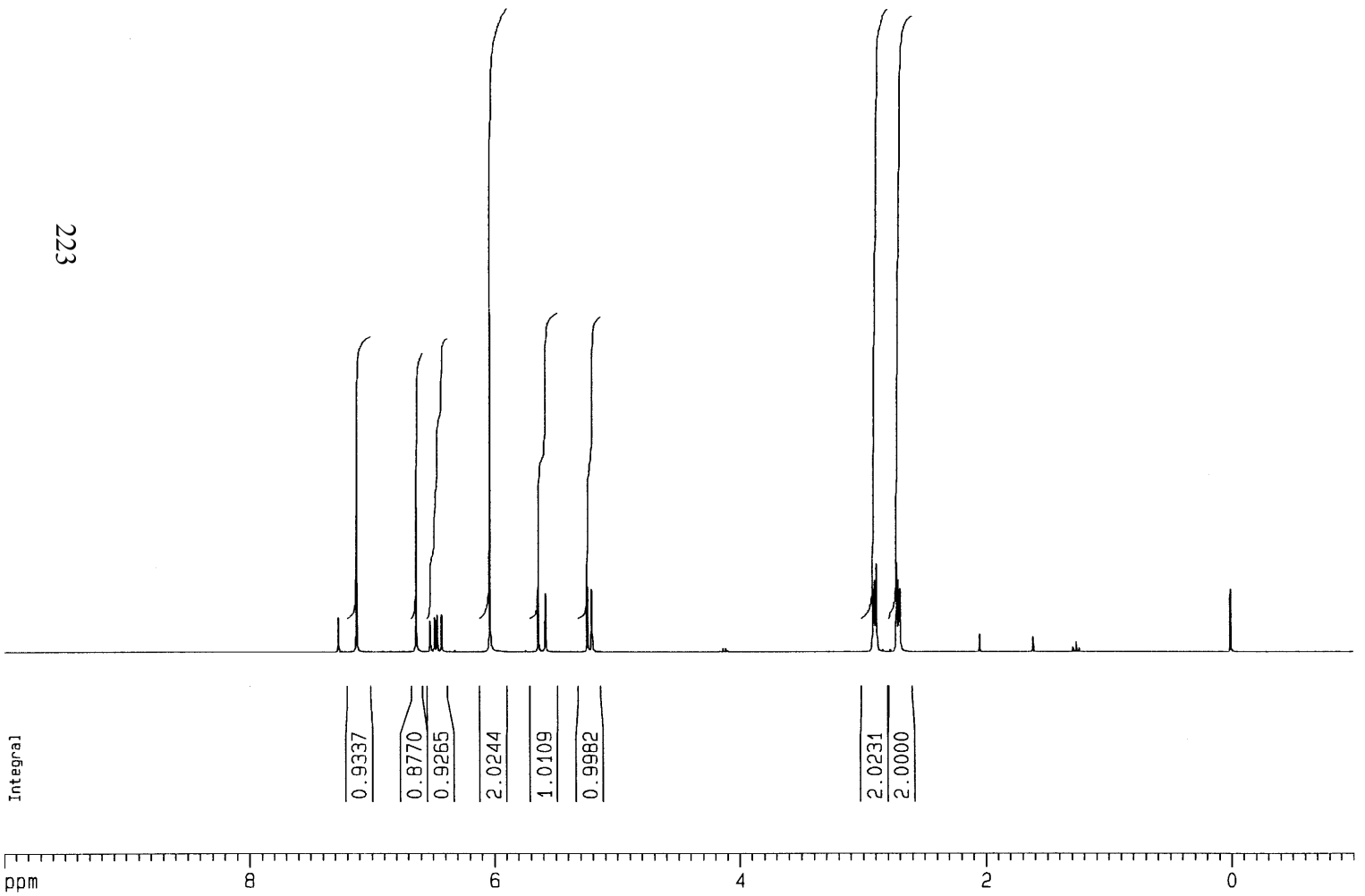


Current Data Parameters	
NAME	PZ-IV-36-A1
EXPNO	1
PROCNO	1

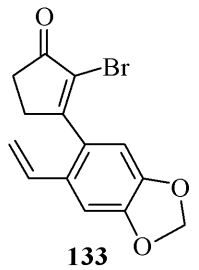
F2 - Acquisition Parameters	
Date_	20041229
Time	10.56
INSTRUM	drx300
PROBHD	5 mm Multinucl
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6172.839 Hz
FIDRES	0.188380 Hz
AQ	2.6542580 sec
RG	406.4
DW	81.000 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
D31	0.00000000 sec

======== CHANNEL f1 ========	
NUC1	1H
P1	7.05 usec
PL1	0.00 dB
SFO1	300.1318534 MHz

F2 - Processing parameters	
SI	32768
SF	300.1300034 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.30

1D NMR plot parameters	
CX	20.00 cm
CY	5.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-1.000 ppm
F2	-300.13 Hz
PPMCM	0.55000 ppm/cm
HZCM	165.07150 Hz/cm

13C NMR
PZ-IV-36-A1



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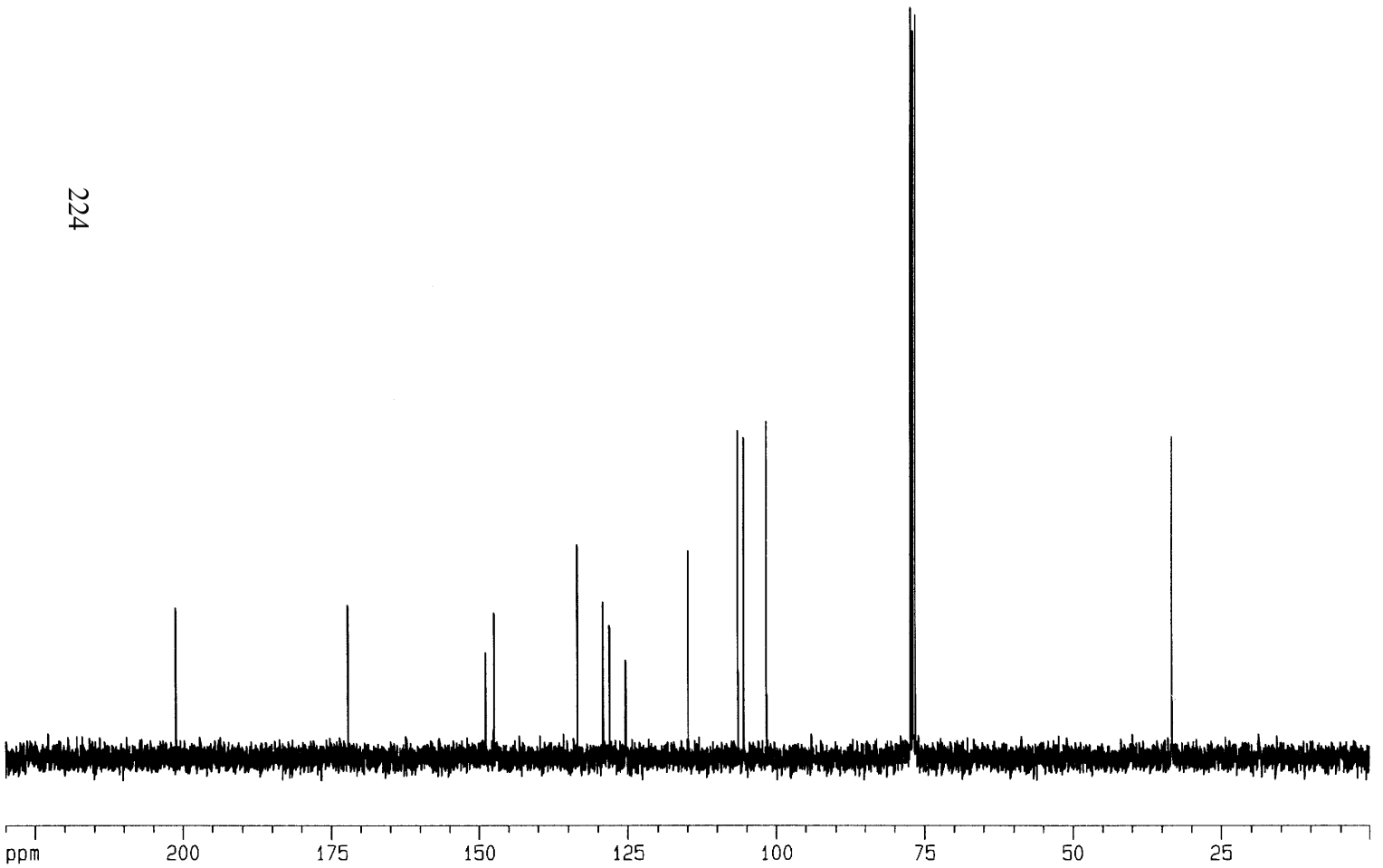


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Current Data Parameters
NAME         PZ-IV-36-A1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20041229
Time               10.58
INSTRUM          drx300
PROBHD   5 mm Multinucl
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                  229
DS                    4
SWH           18832.393 Hz
FIDRES        0.287360 Hz
AQ            1.7400308 sec
RG                22528
DW               26.550 usec
DE                6.00 usec
TE               297.1 K
D1           1.29999995 sec
d11          0.03000000 sec
D31          0.00000000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 8.50 usec
PL1                5.00 dB
SFO1         75.4760107 MHz

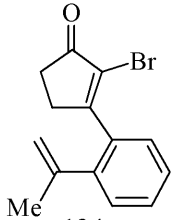
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            100.00 usec
PL2              120.00 dB
PL12              25.60 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677520 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40

1D NMR plot parameters
CX                20.00 cm
CY                11.00 cm
F1P             230.000 ppm
F1              17357.58 Hz
F2P               0.000 ppm
F2                0.00 Hz
PPMCM          11.50000 ppm/cm
HZCM          867.87909 Hz/cm
```

1H NMR

PZ-IV-60-A1



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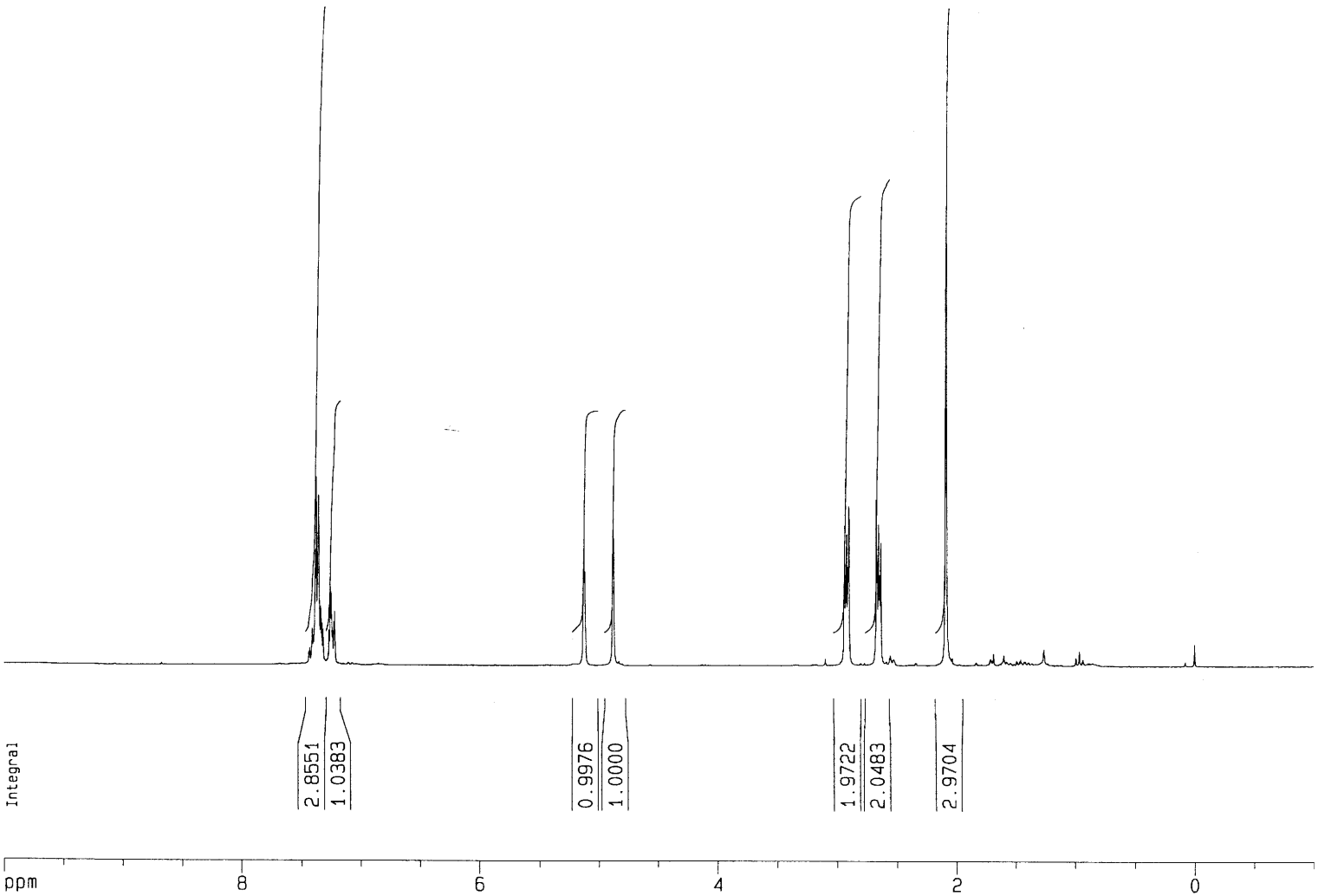


Current Data Parameters

NAME	PZ-IV-60-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050122
Time	22.11
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	715
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	8.70 use
SFO1	250.1315321 MHz
NUCLEUS	1H

F2 - Processing parameters

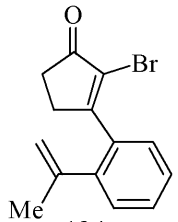
SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	7.00 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57150 Hz/

13C NMR

PZ-IV-60-A1



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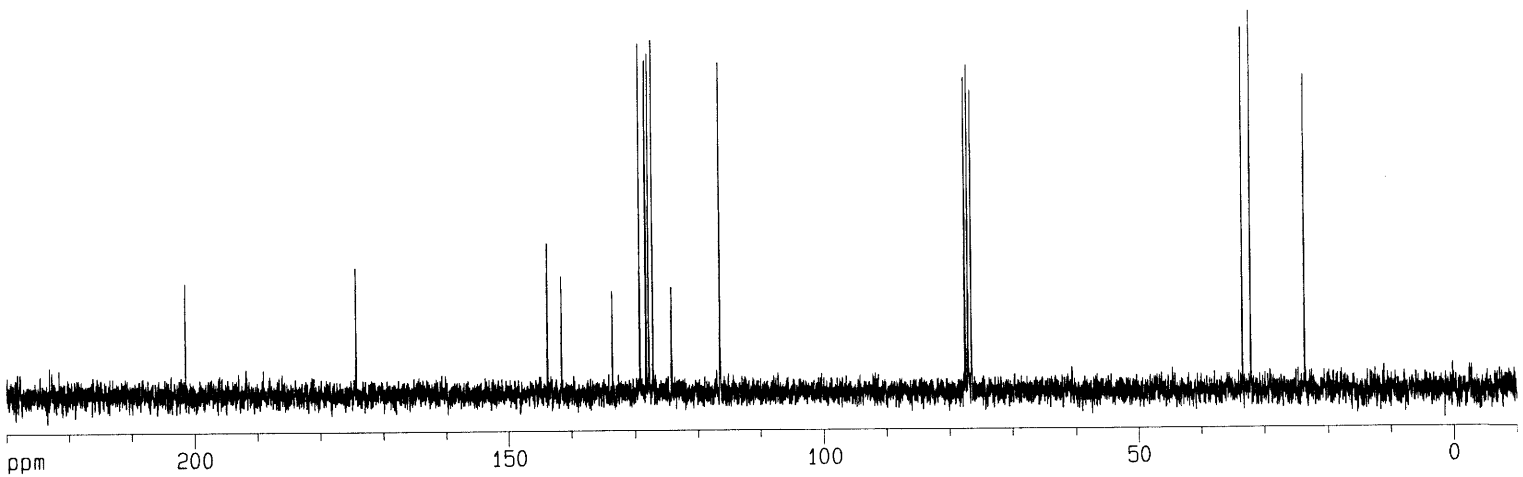


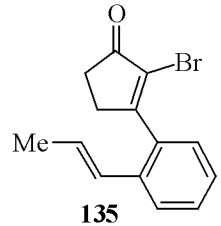
Current Data Parameters	
NAME	PZ-IV-60-A1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters	
Date_	20050122
Time	22.12
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	129
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	1.00000000 sec
P1	6.00 use
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

F2 - Processing parameters	
SI	32768
SF	62.8952440 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters	
CX	20.00 cm
CY	5.00 cm
F1P	230.000 ppm
F1	14465.91 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	12.00000 ppm
HZCM	754.74292 Hz/

1H-NMR
PZ-IV-54-A1



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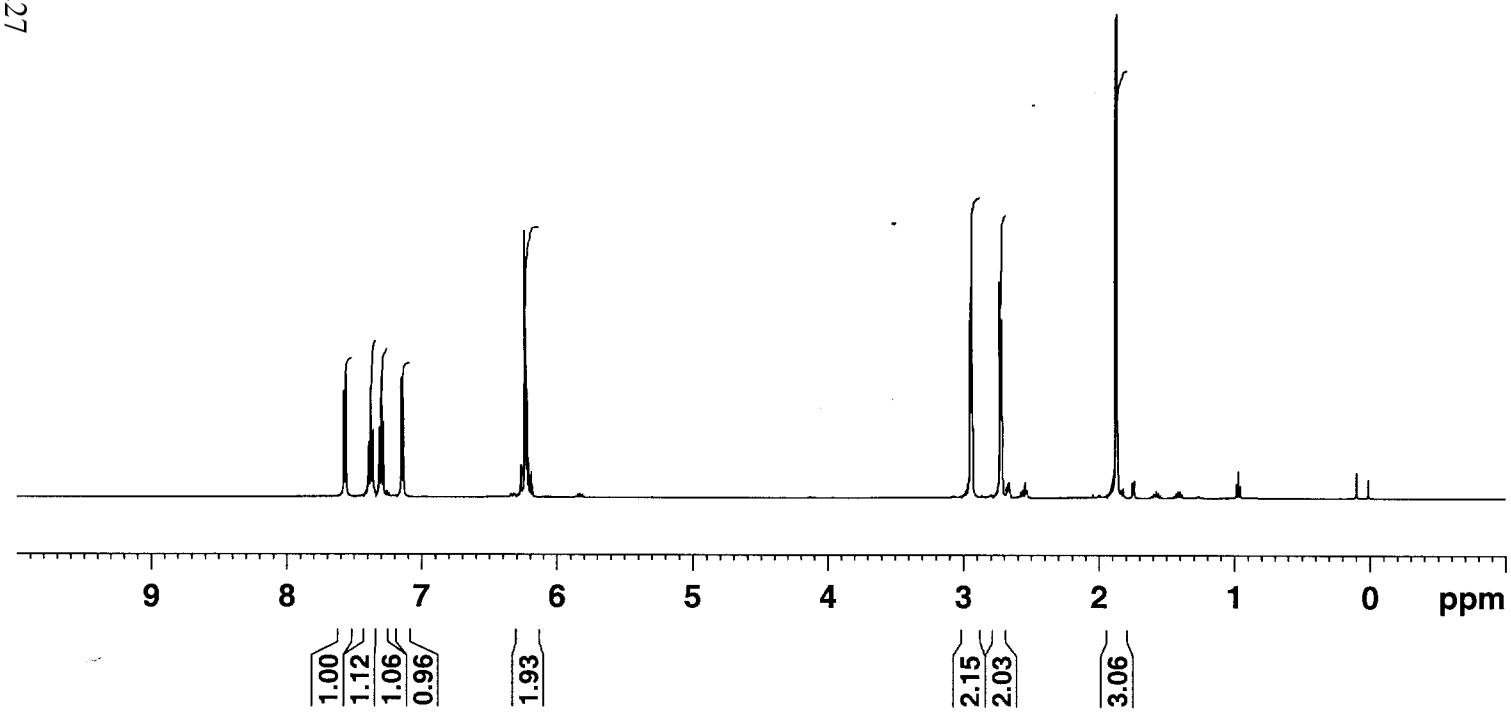


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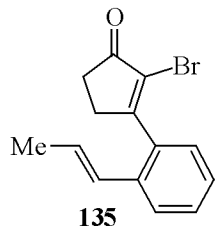
Current Data Parameters
NAME          PZ-IV-54-A1
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20050117
Time                16.22
INSTRUM           DRX500
PROBHD   5 mm Multinucl
PULPROG              zg30
TD                  57344
SOLVENT             CDCl3
NS                     16
DS                      2
SWH           10330.578 Hz
FIDRES         0.180151 Hz
AQ            2.7754996 sec
RG                     64
DW                48.400 use
DE                 6.00 use
TE                296.7 K
D1           1.00000000 sec

======== CHANNEL f1 =======
NUC1                   1H
P1                 13.25 use
PL1                -3.00 dB
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                  32768
SF          500.1300000 MHz
WDW                    EM
SSB                     0
LB                 0.20 Hz
GB                      0
PC                 1.40
```

13C-NMR
PZ-IV-54-A1



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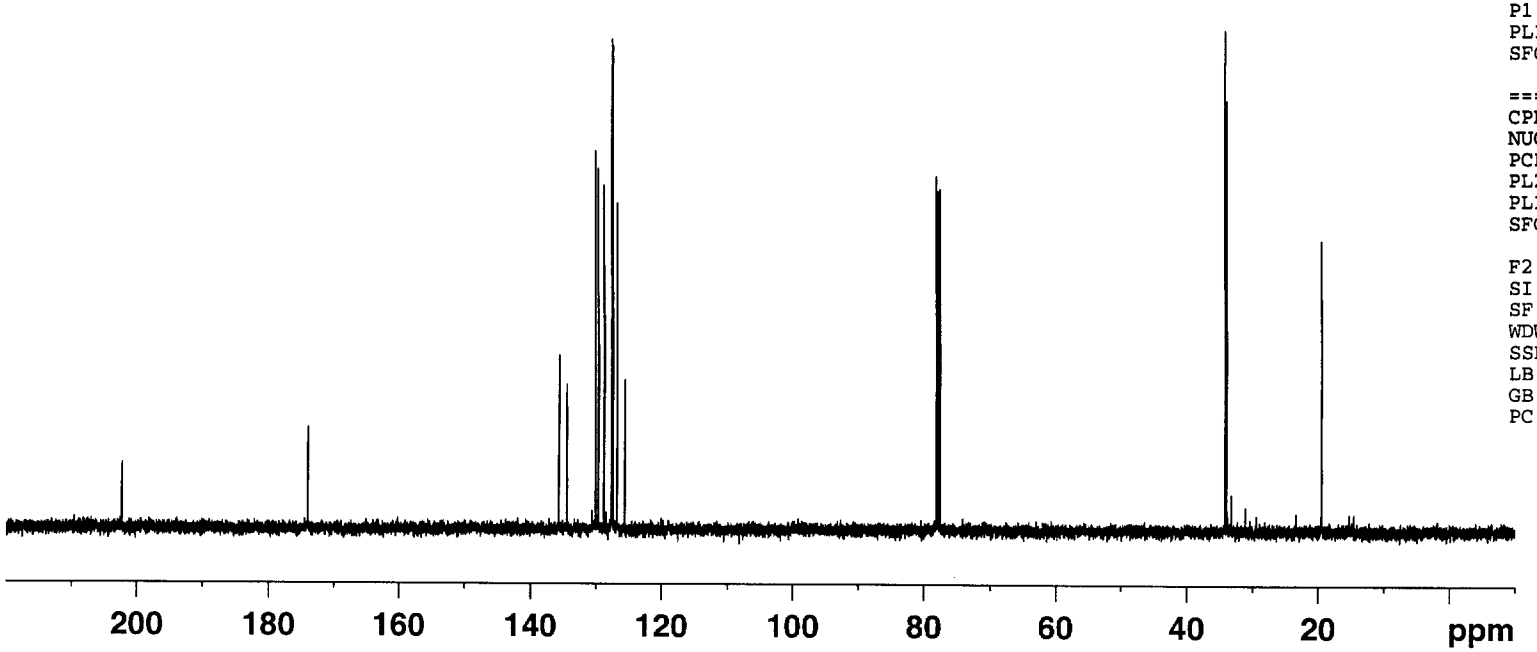



```
Current Data Parameters
NAME          PZ-IV-54-A1
EXPNO                   2
PROCNO                  1

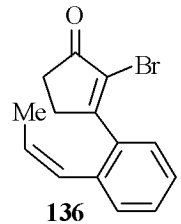
F2 - Acquisition Parameters
Date_            20050117
Time                16.23
INSTRUM           DRX500
PROBHD   5 mm Multinucl
PULPROG           zgdc30
TD                 65536
SOLVENT              MeOH
NS                     29
DS                      4
SWH             39681.812 Hz
FIDRES           0.605496 Hz
AQ               0.8258188 sec
RG                  16384
DW                 12.600 usec
DE                  6.00 usec
TE                 298.0 K
D1            2.00000000 sec
d11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                  8.10 usec
PL1                 3.00 dB
SFO1         125.7713108 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              88.00 usec
PL2                 0.00 dB
PL12               21.00 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7576929 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

1H NMR
PZ-IV-108-B1



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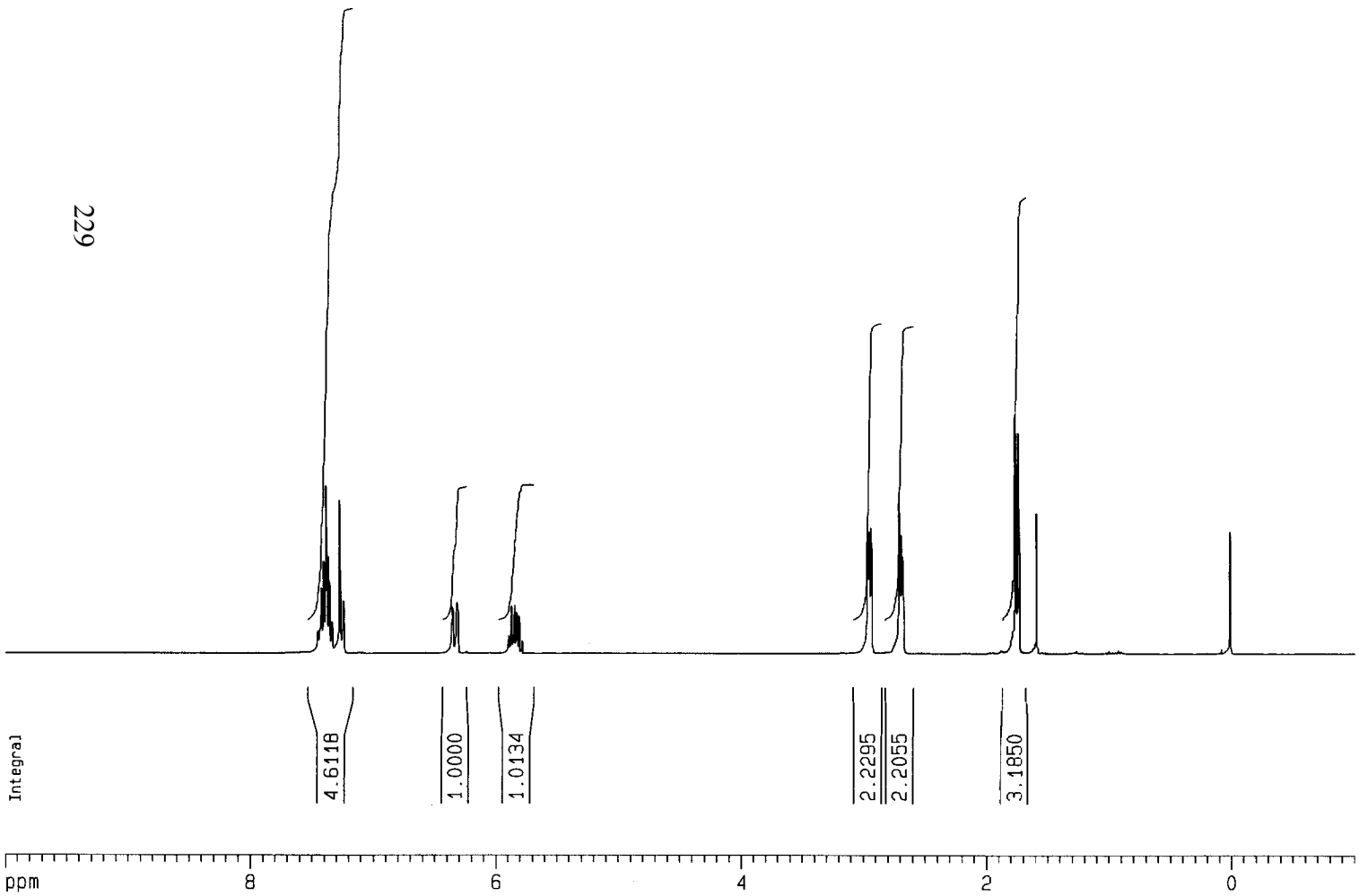


Current Data Parameters

NAME	PZ-IV-108-B1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050405
Time	17.21
INSTRUM	drx300
PROBHD	5 mm Multinucl
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6172.839 Hz
FIDRES	0.188380 Hz
AQ	2.6542580 sec
RG	574.7
DW	81.000 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
D31	0.00000000 sec

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

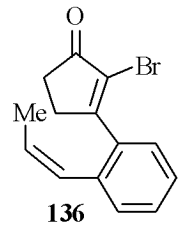
NUC1	1H
P1	7.05 usec
PL1	0.00 dB
SFO1	300.1318534 MHz

F2 - Processing parameters

SI	32768
SF	300.1300022 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.30

1D NMR plot parameters

CX	20.00 cm
CY	3.50 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-1.000 ppm
F2	-300.13 Hz
PPMCM	0.55000 ppm/cm
HZCM	165.07150 Hz/cm



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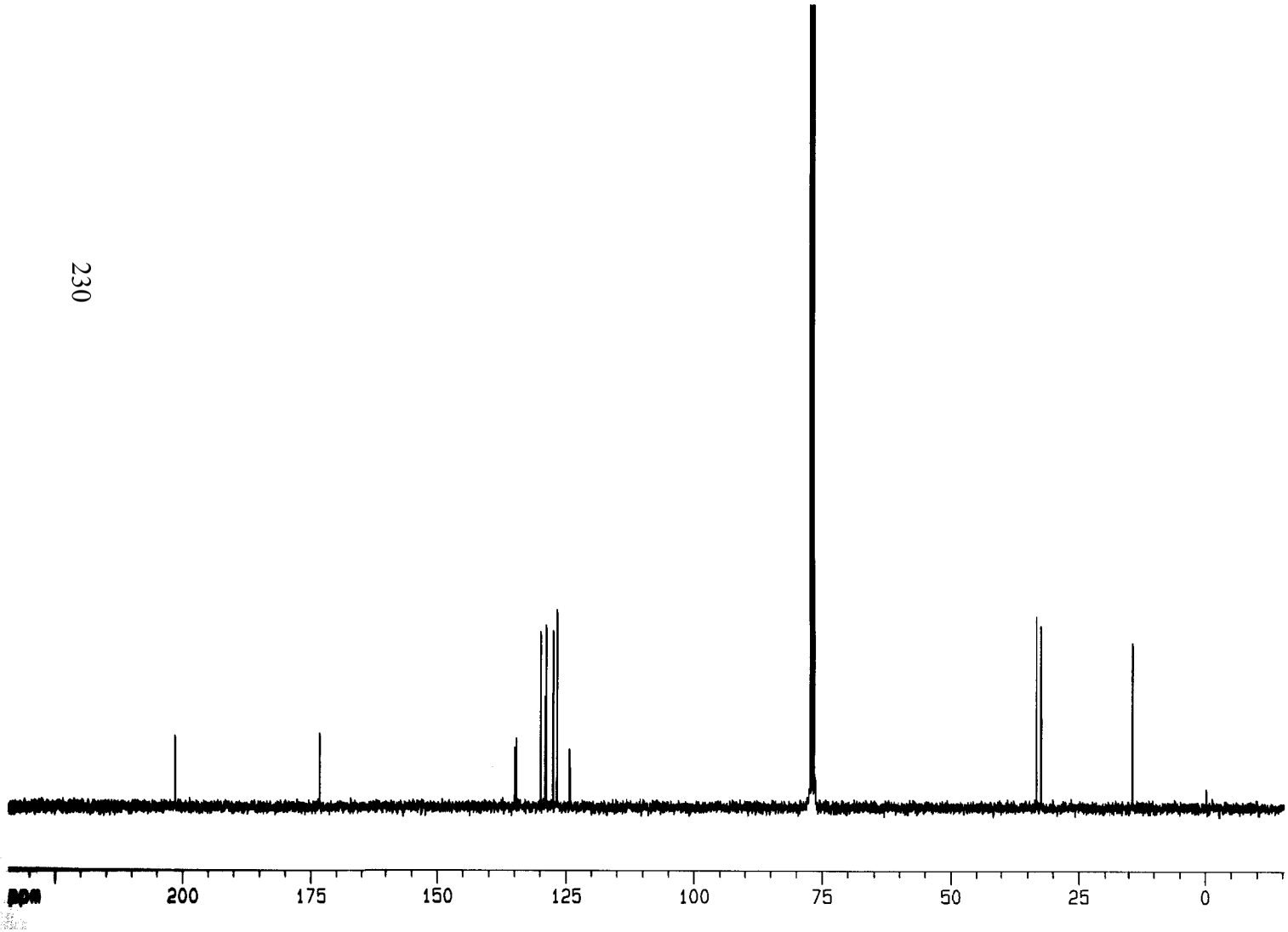


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Current Data Parameters
NAME        PZ-IV-108-B1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050405
Time               17.24
INSTRUM          drx300
PROBHD   5 mm Multinucl
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                 1667
DS                    4
SWH           18832.393 Hz
FIDRES        0.287360 Hz
AQ            1.7400308 sec
RG               1625.5
DW               26.550 usec
DE                6.00 usec
TE               297.1 K
D1            1.79999995 sec
d11           0.03000000 sec
D31           0.00000000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 8.50 usec
PL1                5.00 dB
SFO1         75.4760107 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            100.00 usec
PL2              120.00 dB
PL12              25.60 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677571 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                20.00 cm
CY                15.00 cm
F1P              234.138 ppm
F1             17669.89 Hz
F2P               -15.406 ppm
F2             -1162.69 Hz
PPMCM            12.47723 ppm/cm
HZCM           941.62885 Hz/cm
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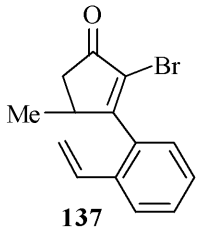
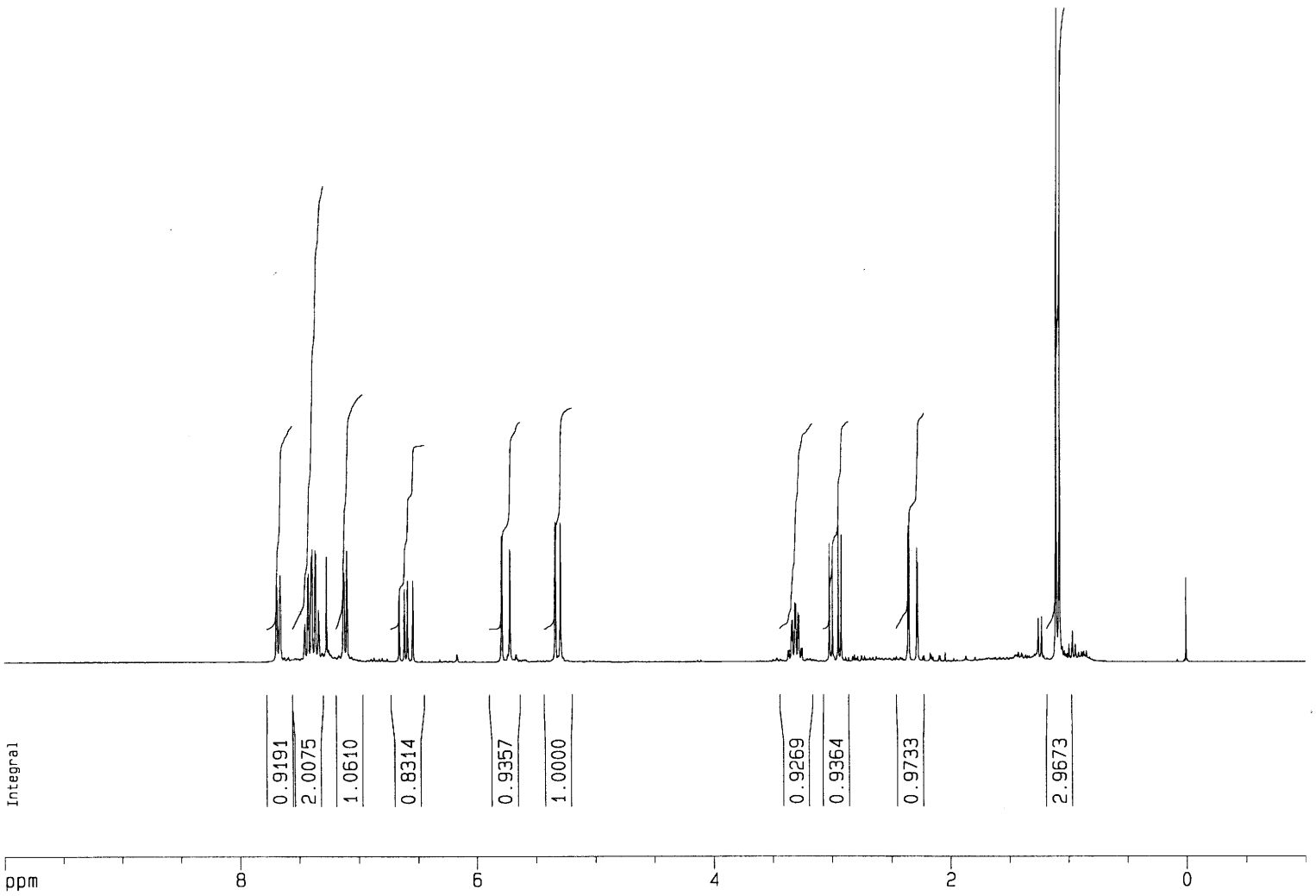
1H NMR
PZ-IV-22-A2
6-8th tube



137



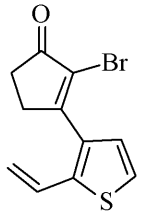
Current Data Parameters
NAME PZ-IV-22-A2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20041213
Time 23.17
INSTRUM arx250
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 5208.333 Hz
FIDRES 0.158946 Hz
AQ 3.1457779 sec
RG 1024
DW 96.000 use
DE 137.14 use
TE 300.0 K
D1 1.00000000 sec
P1 8.70 use
SFO1 250.1315321 MHz
NUCLEUS 1H

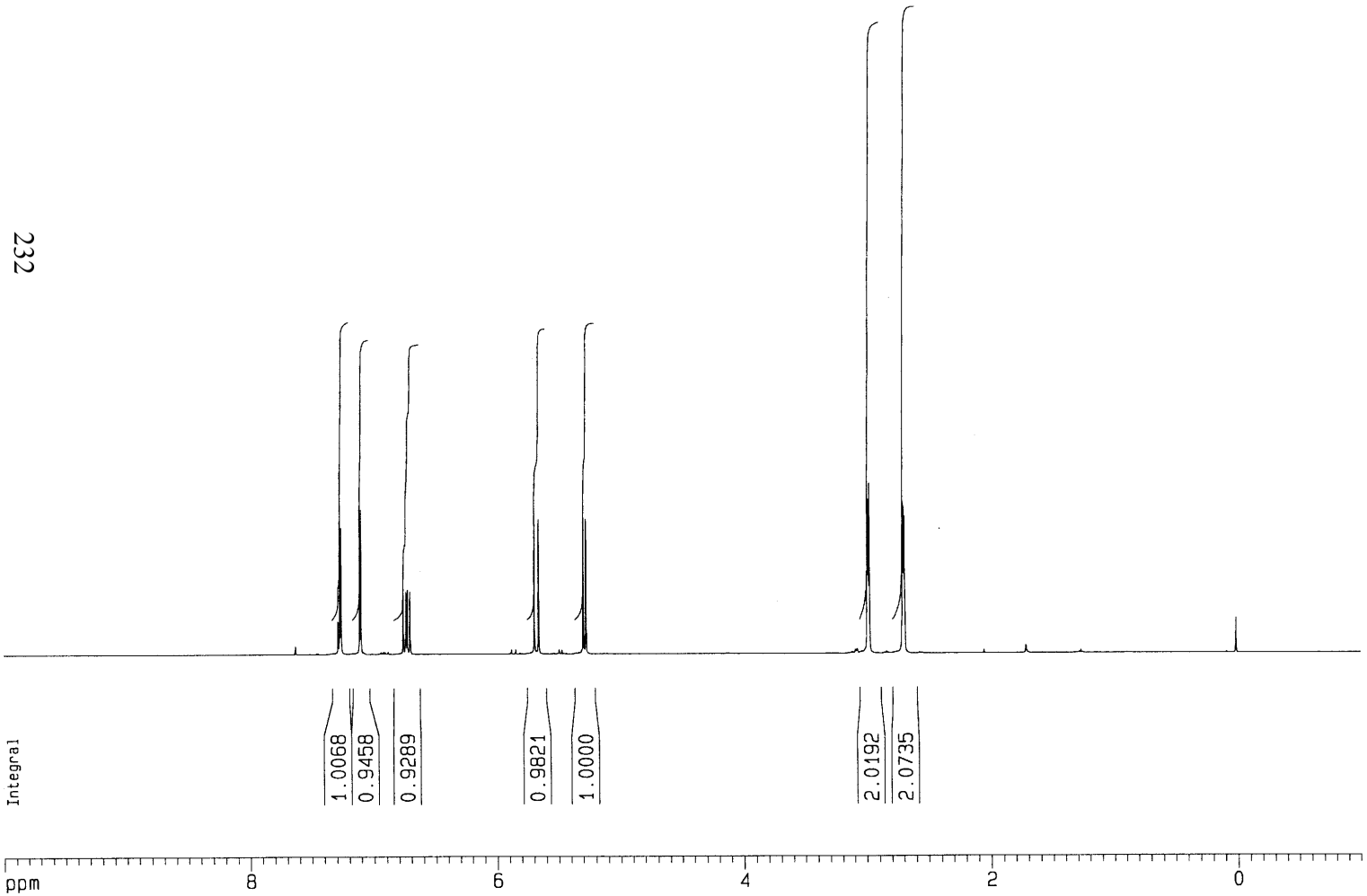
F2 - Processing parameters
SI 16384
SF 250.1300049 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.50

1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 10.000 ppm
F1 2501.30 Hz
F2P -1.000 ppm
F2 -250.13 Hz
PPMCM 0.55000 ppm
HZCM 137.57150 Hz/

1H-NMR
PZ-IV-67-A1



138



Current Data Parameters

NAME	PZ-IV-67-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050130
Time	16.17
INSTRUM	DRX500
PROBHD	5 mm Multinucl
PULPROG	zg30
TD	57344
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.180151 Hz
AQ	2.7754996 sec
RG	90.5
DW	48.400 usec
DE	6.00 usec
TE	296.7 K
D1	1.00000000 sec

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

NUC1	1H
P1	13.25 usec
PL1	-3.00 dB
SFO1	500.1330885 MHz

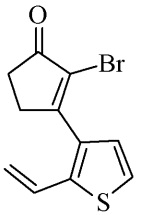
F2 - Processing parameters

SI	32768
SF	500.1300000 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	2.50 cm
F1P	10.000 ppm
F1	5001.30 Hz
F2P	-1.000 ppm
F2	-500.13 Hz
PPMCM	0.55000 ppm/cr
HZCM	275.07150 Hz/cm

13C-NMR
PZ-IV-67-A1



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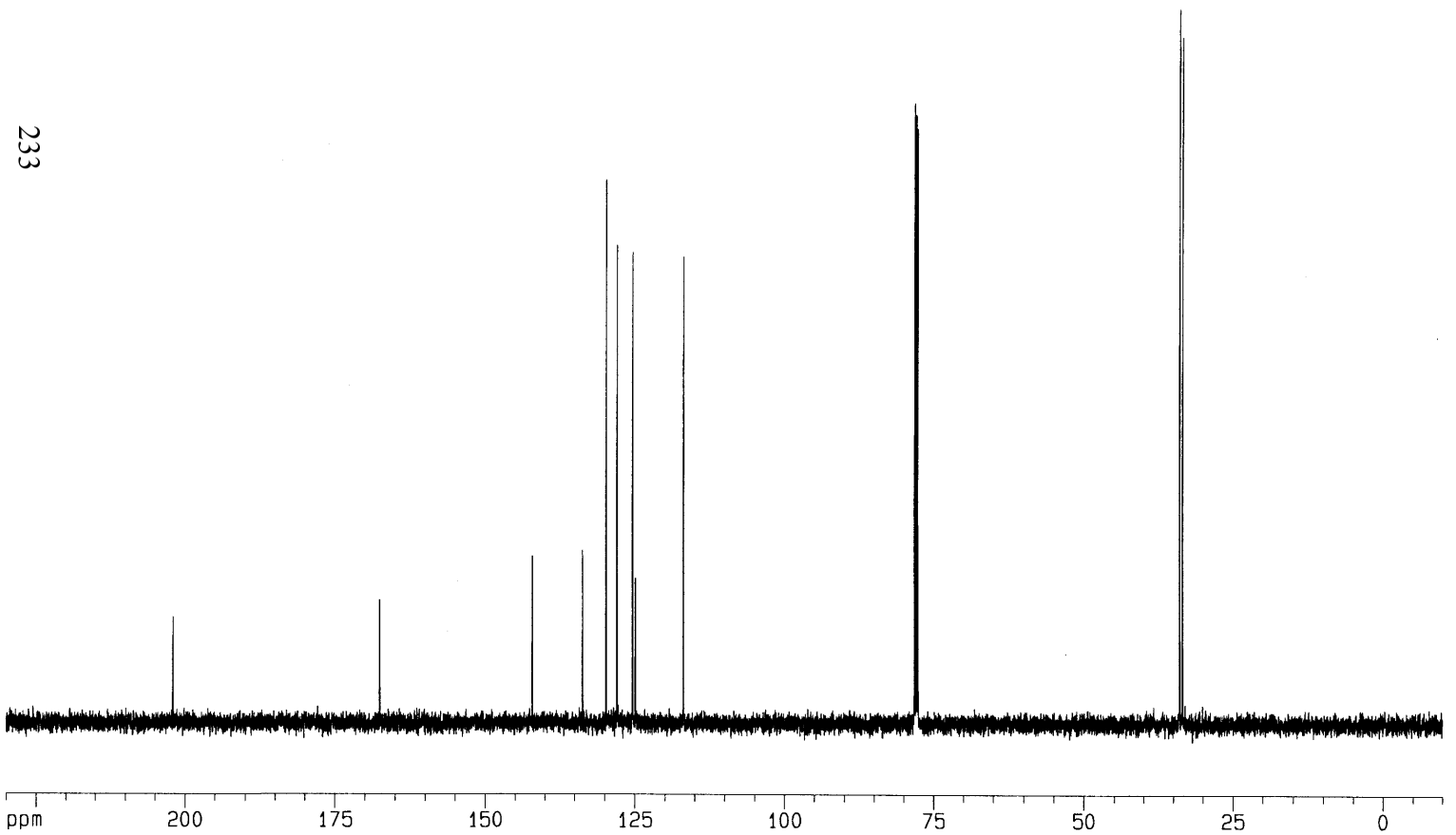
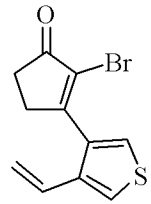


Current Data Parameters	
NAME	PZ-IV-67-A1
EXPNO	2
PROCNO	1
F2 - Acquisition Parameters	
Date_	20050130
Time	16.20
INSTRUM	DRX500
PROBHD	5 mm Multinucl
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	80
DS	4
SWH	39681.812 Hz
FIDRES	0.605496 Hz
AQ	0.8258188 sec
RG	16384
DW	12.600 usec
DE	6.00 usec
TE	298.0 K
D1	2.00000000 sec
d11	0.03000000 sec
======== CHANNEL f1 ========	
NUC1	13C
P1	8.10 usec
PL1	3.00 dB
SFO1	125.7713108 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	88.00 usec
PL2	0.00 dB
PL12	21.00 dB
SFO2	500.1320005 MHz
F2 - Processing parameters	
SI	32768
SF	125.7576929 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40
1D NMR plot parameters	
CX	20.00 cm
CY	10.00 cm
F1P	230.000 ppm
F1	28924.27 Hz
F2P	-10.000 ppm
F2	-1257.58 Hz
PPMCM	12.00000 ppm/cm
HZCM	1509.09229 Hz/cm

1H NMR

PZ-IV-98-A1



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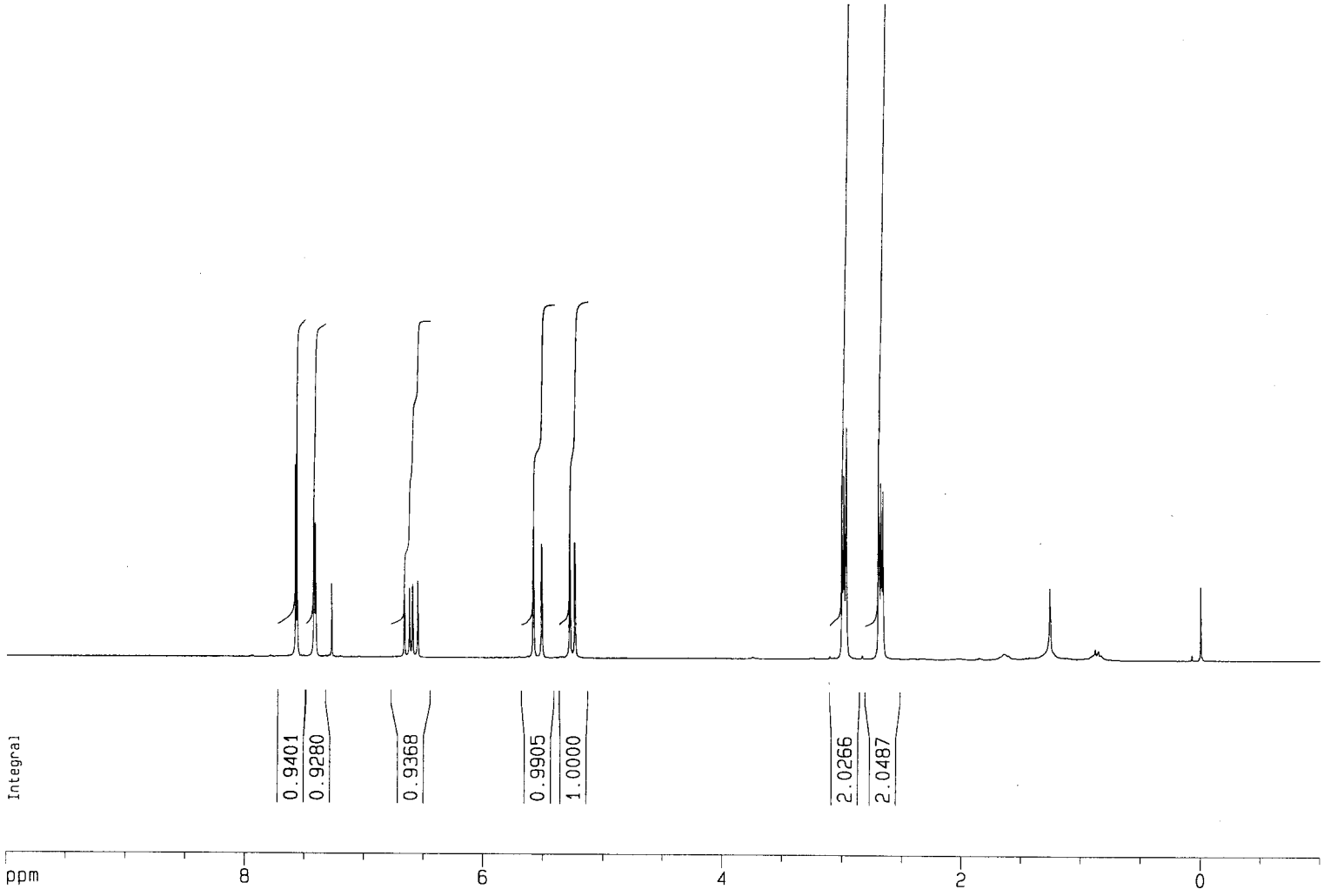


Current Data Parameters

NAME	PZ-IV-98-A1-1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050306
Time	17.35
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	1430
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	8.70 use
SFO1	250.1315321 MHz
NUCLEUS	1H

F2 - Processing parameters

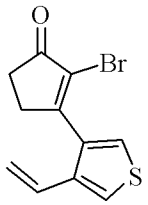
SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	3.50 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57150 Hz/

13C NMR

PZ-IV-98-A1



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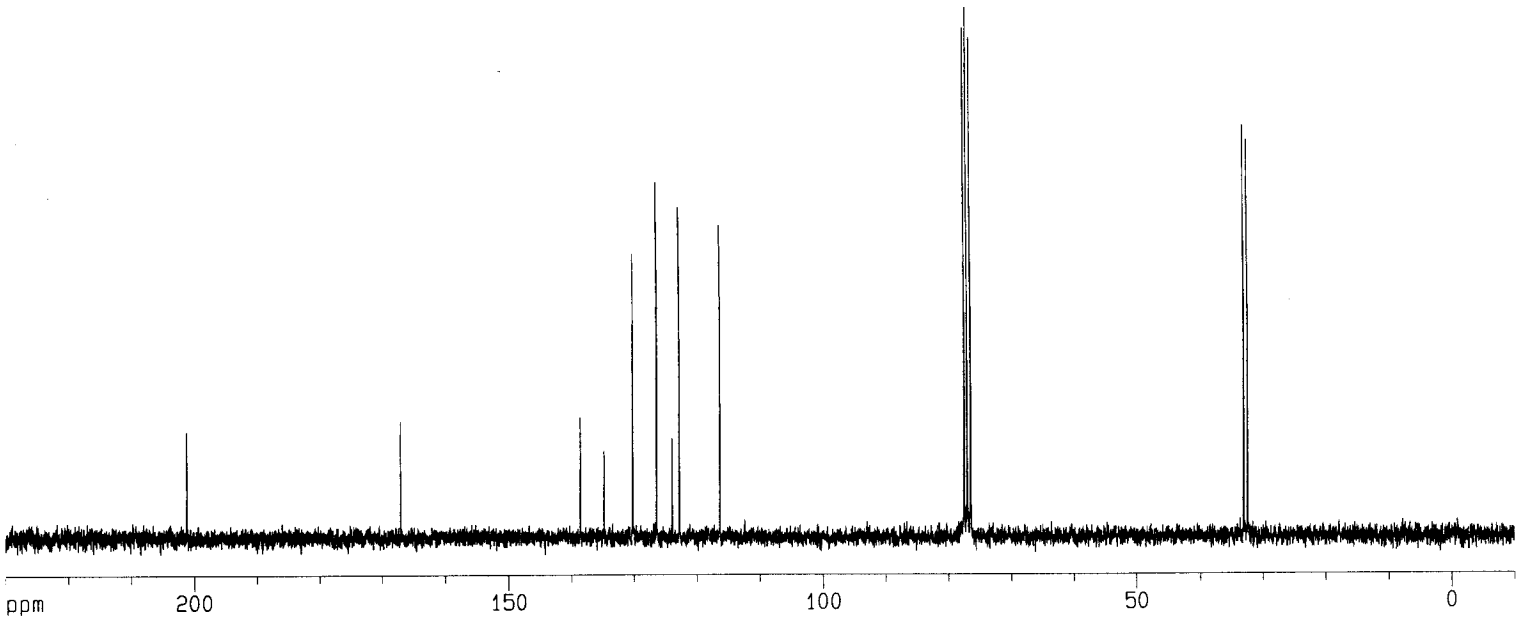


Current Data Parameters	
NAME	PZ-IV-98-A1-1
EXPNO	2
PROCNO	1

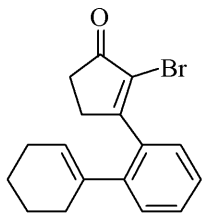
F2 - Acquisition Parameters	
Date_	20050306
Time	17.38
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	877
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	1.00000000 sec
P1	6.00 use
SF01	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

F2 - Processing parameters	
SI	32768
SF	62.8952440 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.70

1D NMR plot parameters	
CX	20.00 cm
CY	7.00 cm
F1P	230.000 ppm
F1	14465.91 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	12.00000 ppm
HZCM	754.74292 Hz/

1H-NMR

PZ-IV-112-A4



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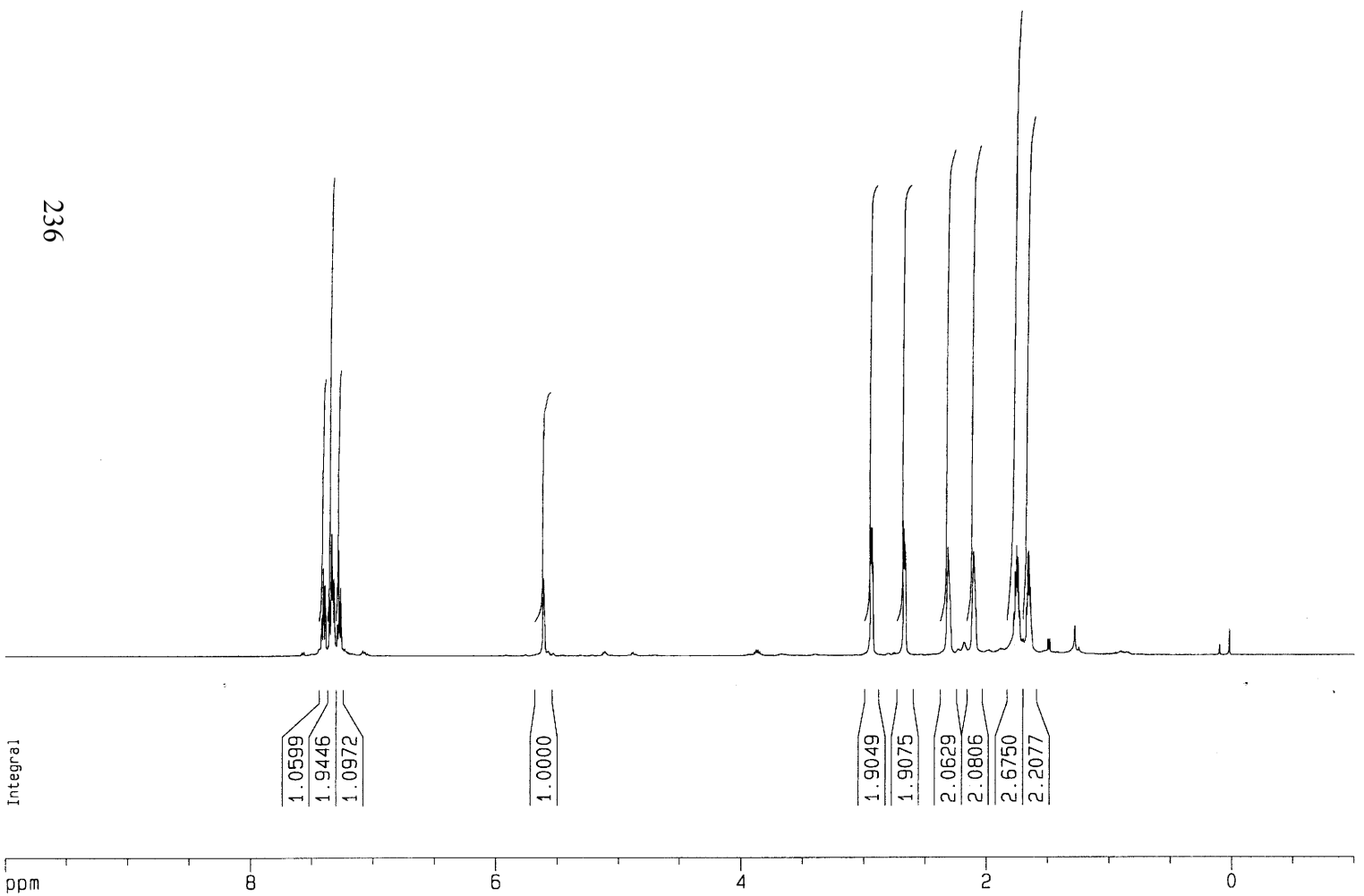


Current Data Parameters

NAME	PZ-IV-112-A4
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050321
Time	16.55
INSTRUM	DRX500
PROBHD	5 mm Multinucl
PULPROG	zg30
TD	57344
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.180151 Hz
AQ	2.7754996 sec
RG	64
DW	48.400 usec
DE	6.00 usec
TE	296.7 K
D1	1.00000000 sec

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

NUC1	1H
P1	13.25 usec
PL1	-3.00 dB
SFO1	500.1330885 MHz

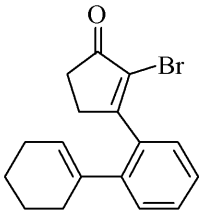
F2 - Processing parameters

SI	32768
SF	500.1300000 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	2.00 cm
F1P	10.000 ppm
F1	5001.30 Hz
F2P	-1.000 ppm
F2	-500.13 Hz
PPMCM	0.55000 ppm/cr
HZCM	275.07150 Hz/cm

13C-NMR
PZ-IV-112-A4



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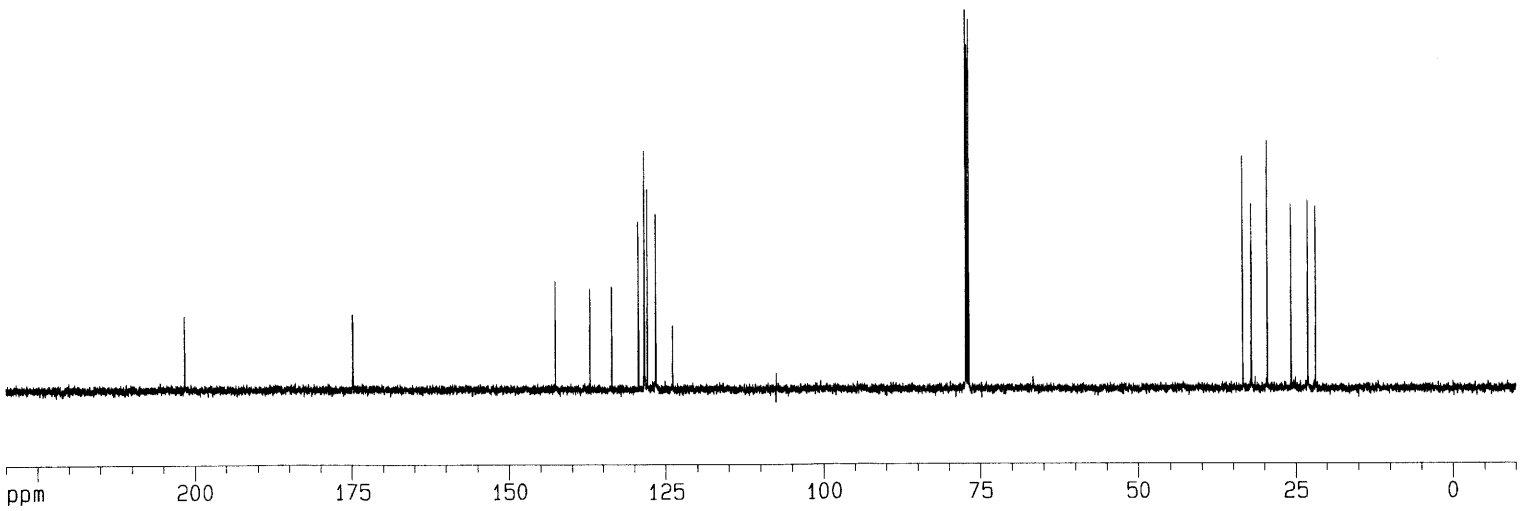


Current Data Parameters	
NAME	PZ-IV-112-A4
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters	
Date_	20050321
Time	16.57
INSTRUM	DRX500
PROBHD	5 mm Multinucl
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	113
DS	4
SWH	39681.812 Hz
FIDRES	0.605496 Hz
AQ	0.8258188 sec
RG	2580.3
DW	12.600 usec
DE	6.00 usec
TE	298.0 K
D1	2.00000000 sec
d11	0.03000000 sec

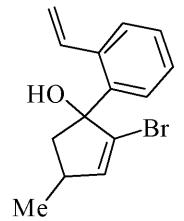
======== CHANNEL f1 ========	
NUC1	13C
P1	8.10 usec
PL1	3.00 dB
SFO1	125.7713108 MHz

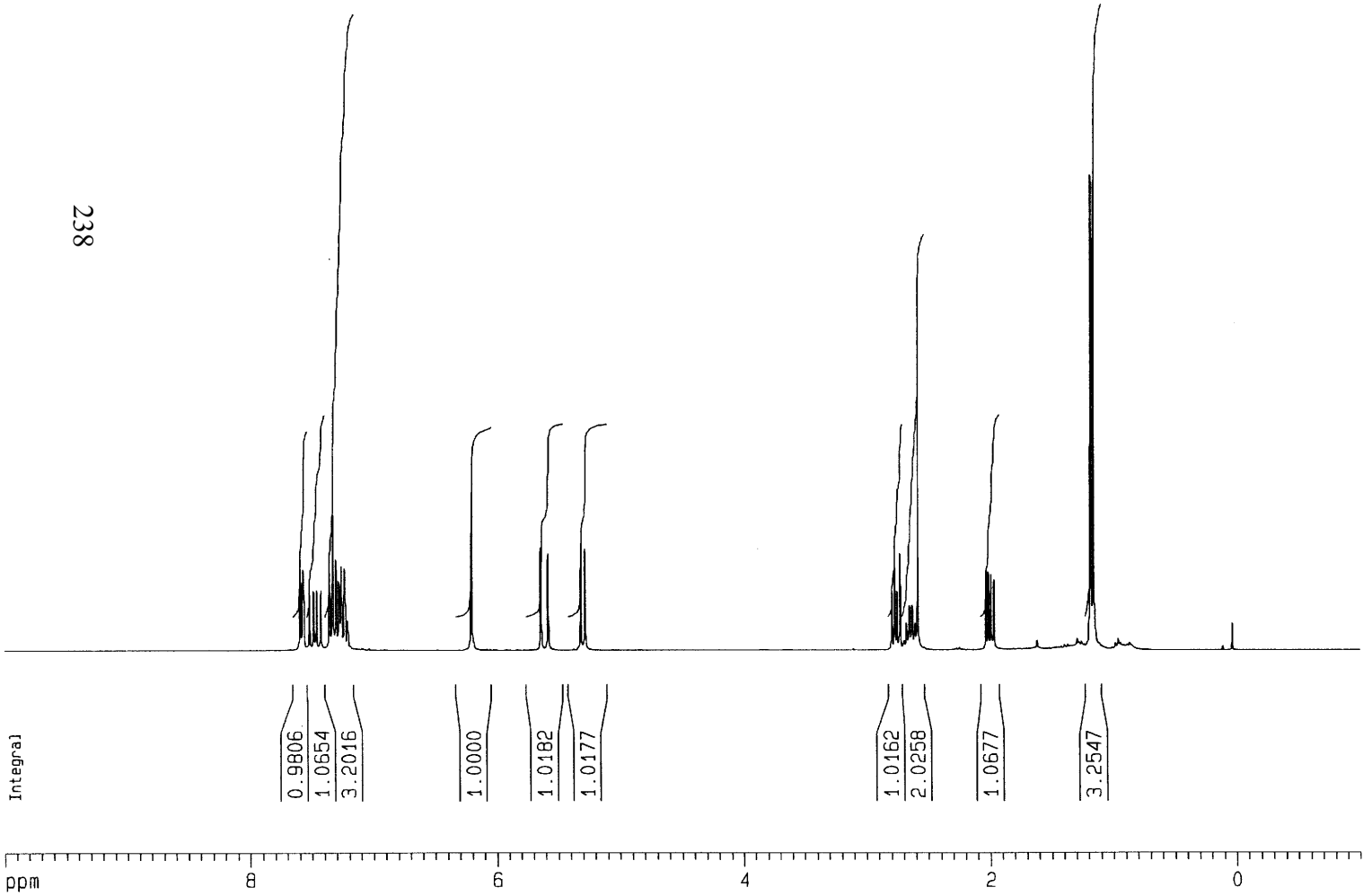
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	88.00 usec
PL2	0.00 dB
PL12	21.00 dB
SFO2	500.1320005 MHz

F2 - Processing parameters	
SI	32768
SF	125.7578019 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	2.20

1D NMR plot parameters	
CX	20.00 cm
CY	5.00 cm
F1P	230.000 ppm
F1	28924.29 Hz
F2P	-10.000 ppm
F2	-1257.58 Hz
PPMCM	12.00000 ppm/cm
HZCM	1509.09363 Hz/cm

1H NMR
PZ-IV-30-A1





Current Data Parameters
NAME PZ-IV-30-A1-1
EXPNO 1
PROCNO 1

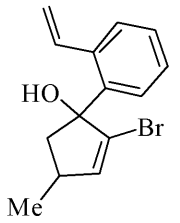
F2 - Acquisition Parameters
Date_ 20041222
Time 15.13
INSTRUM drx300
PROBHD 5 mm Multinucl
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 114
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
D31 0.00000000 sec

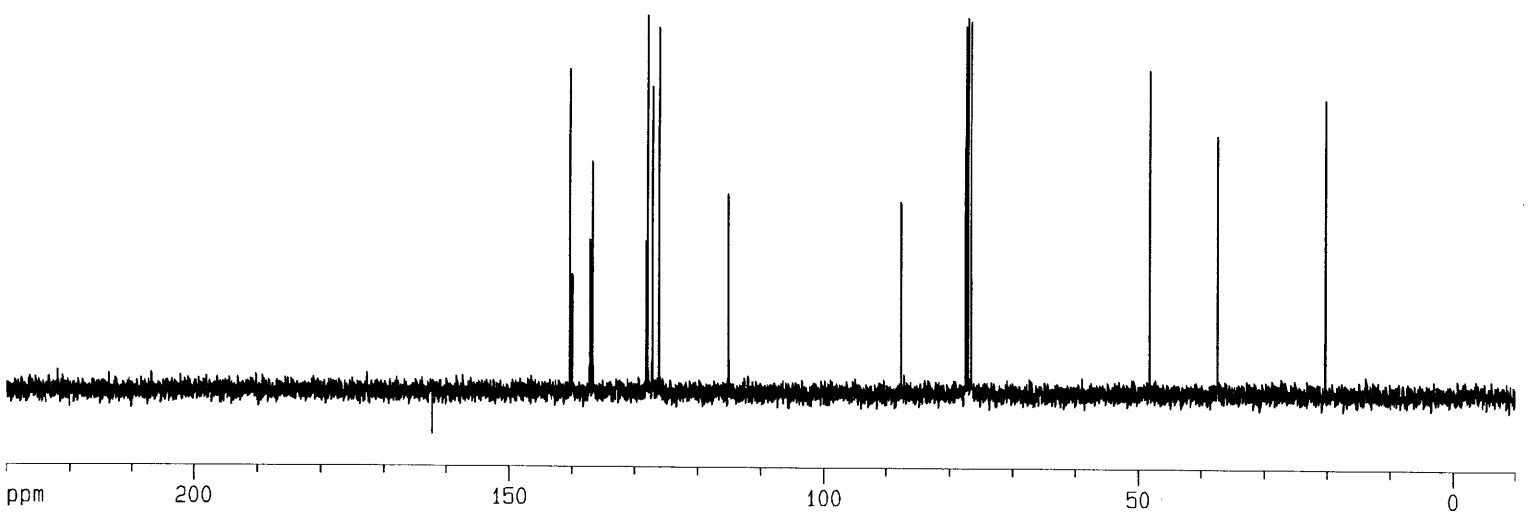
======== CHANNEL f1 ========
NUC1 1H
P1 7.05 usec
PL1 0.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300022 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.30

1D NMR plot parameters
CX 20.00 cm
CY 7.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -1.000 ppm
F2 -300.13 Hz
PPMCM 0.55000 ppm/cm
HZCM 165.07150 Hz/cm

13C NMR
PZ-IV-30-A1






```
Current Data Parameters
NAME       PZ-IV-30-A1-1
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20041222
Time              15.15
INSTRUM         drx300
PROBHD   5 mm Multinucl
PULPROG         zgdc30
TD               65536
SOLVENT          CDCl3
NS                  76
DS                   4
SWH          18832.393 Hz
FIDRES        0.287360 Hz
AQ            1.7400308 sec
RG                22528
DW               26.550 usec
DE                6.00 usec
TE               297.1 K
D1           1.29999995 sec
d11          0.03000000 sec
D31          0.00000000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 8.50 usec
PL1                5.00 dB
SFO1         75.4760107 MHz

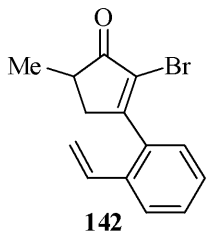
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2          100.00 usec
PL2            120.00 dB
PL12            25.60 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677542 MHz
WDW                EM
SSB                 0
LB                1.00 Hz
GB                  0
PC                1.40

1D NMR plot parameters
CX                20.00 cm
CY                 5.00 cm
F1P              230.000 ppm
F1             17357.58 Hz
F2P              -10.000 ppm
F2               -754.68 Hz
PPMCM           12.00000 ppm/cm
HZCM           905.61298 Hz/cm
```

1H NMR

PZ-IV-34-A1



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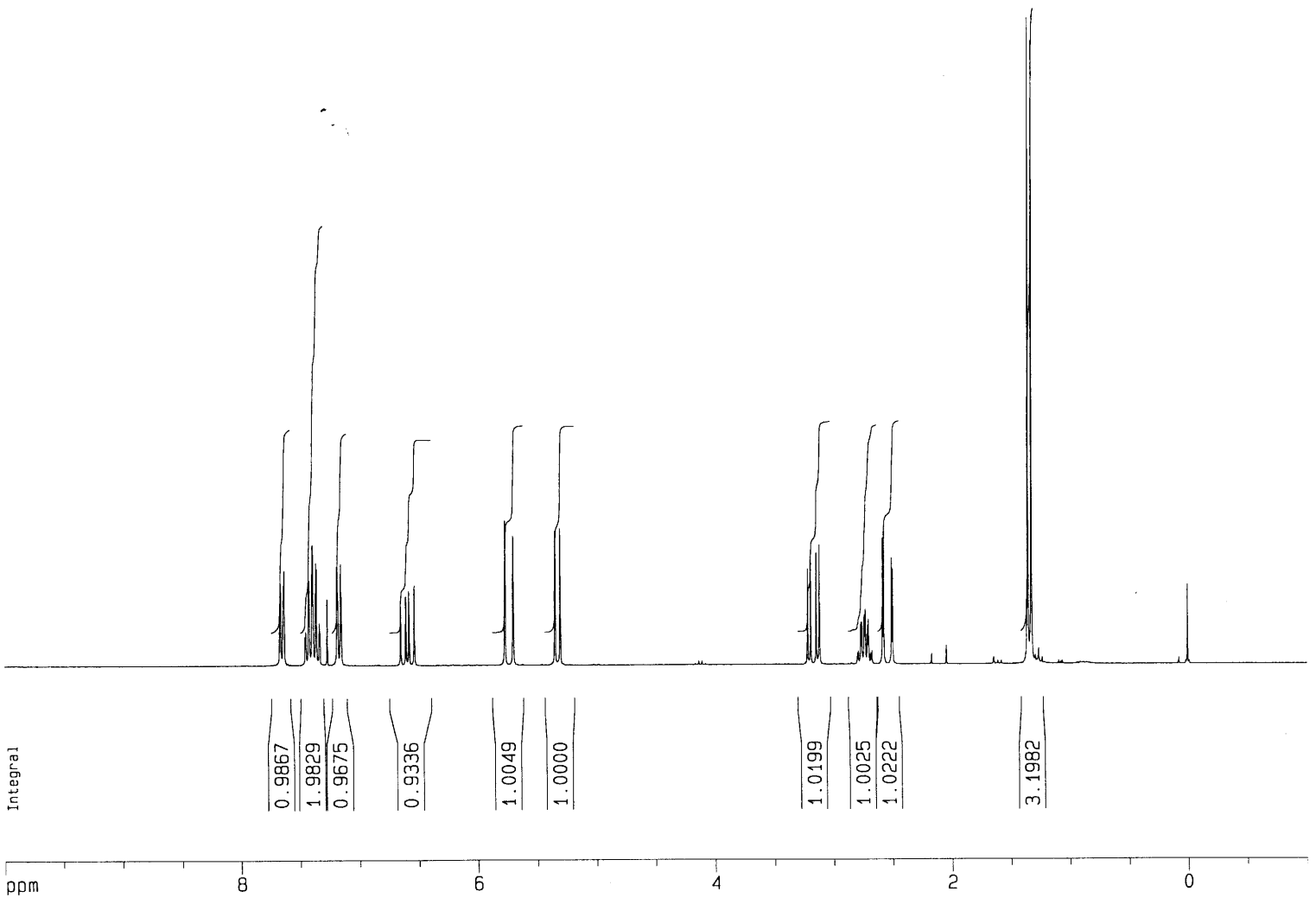


Current Data Parameters

NAME	PZ-IV-34-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20041224
Time	0.21
INSTRUM	arx250
PROBHD	5 mm GNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	1024
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	8.70 use
SFO1	250.1315321 MHz
NUCLEUS	1H

F2 - Processing parameters

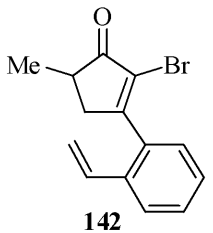
SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	10.00 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57150 Hz/

13C NMR

PZ-IV-34-A1



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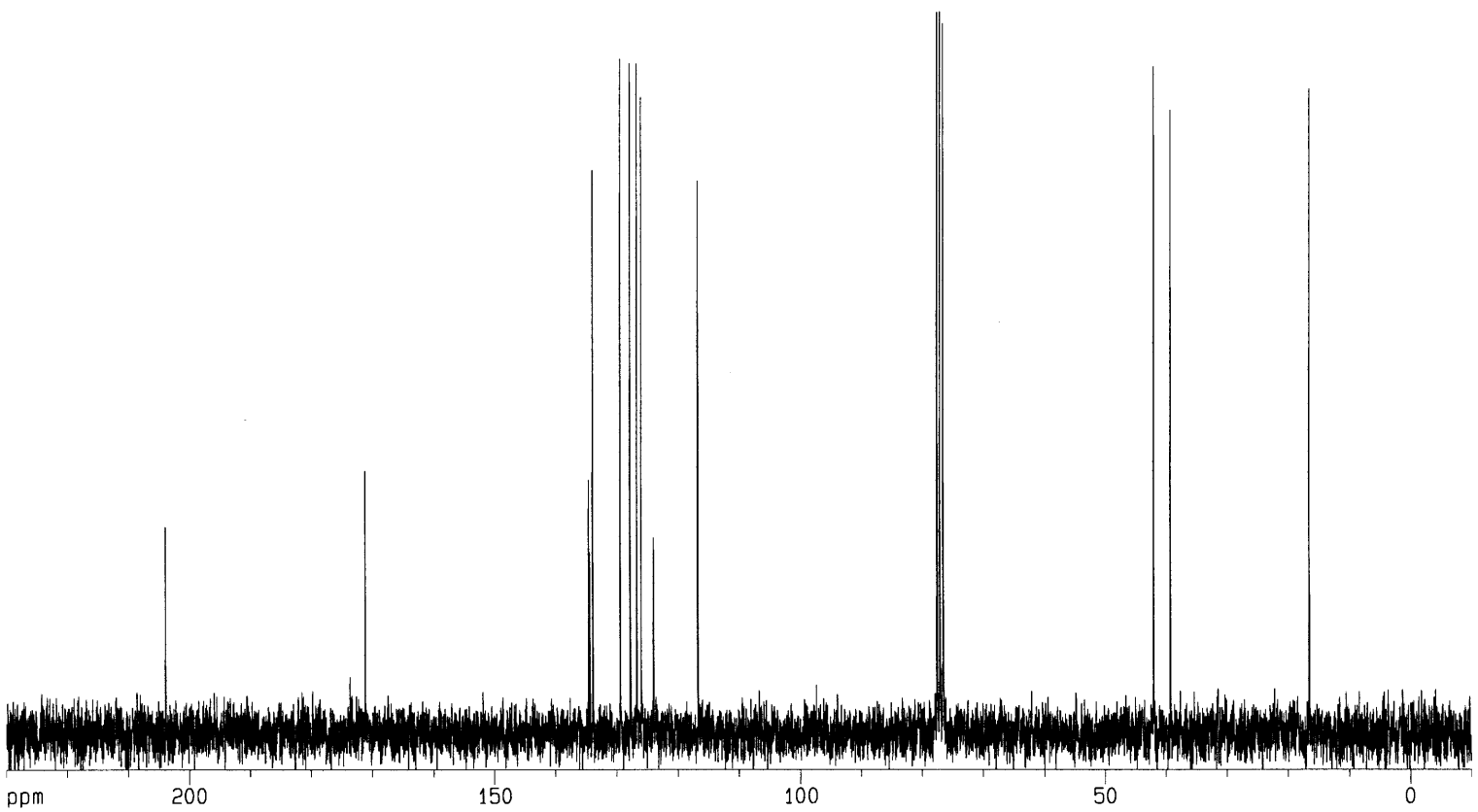


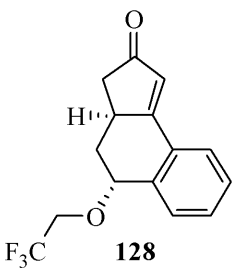
Current Data Parameters	
NAME	PZ-IV-34-A1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters	
Date_	20041224
Time	0.25
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	183
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	1.00000000 sec
P1	6.00 use
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

F2 - Processing parameters	
SI	32768
SF	62.8952440 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters	
CX	20.00 cm
CY	10.00 cm
F1P	230.000 ppm
F1	14465.91 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	12.00000 ppm
HZCM	754.74292 Hz/

1H NMR
PZ-IV-81-A2



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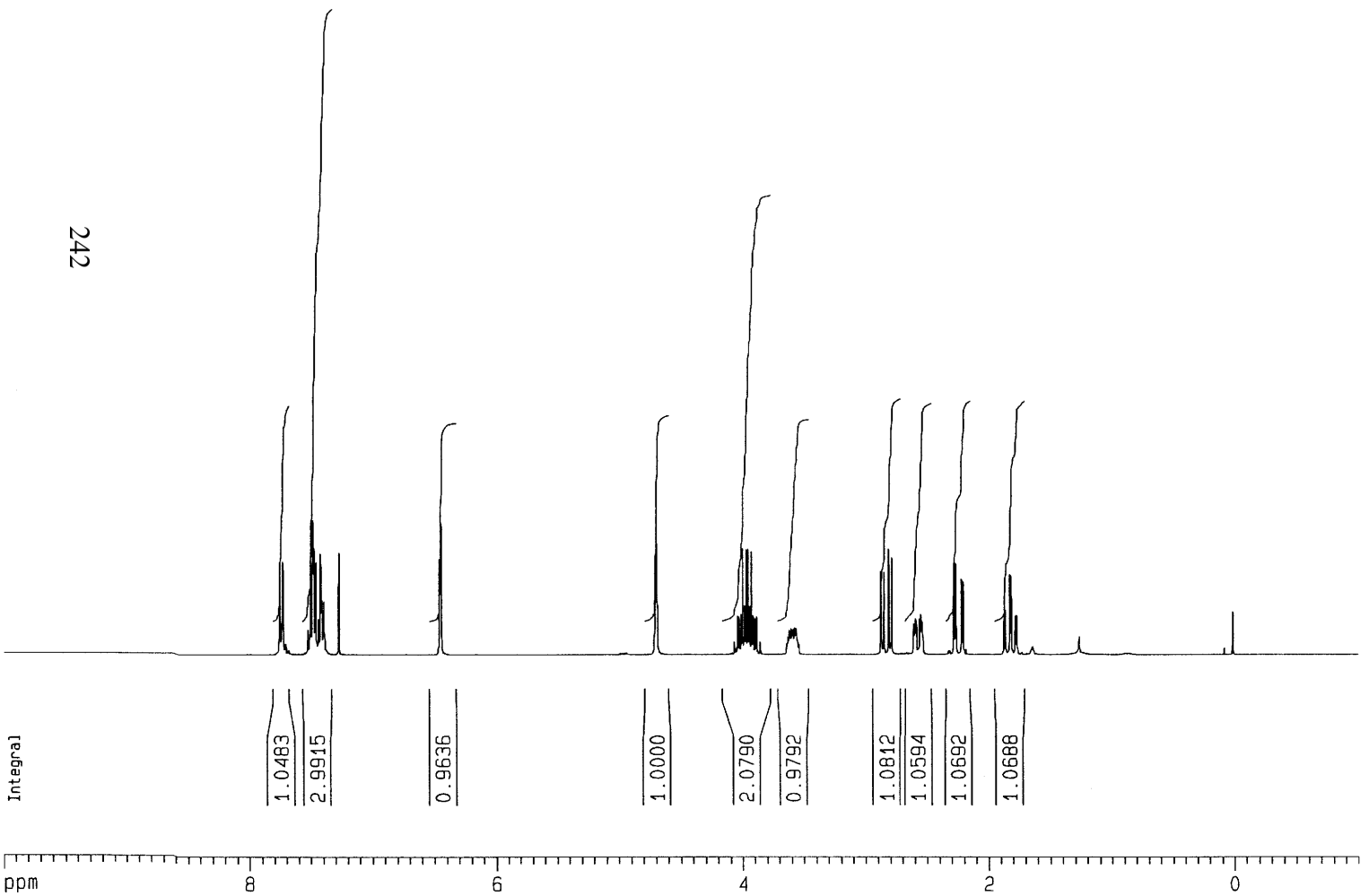


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Current Data Parameters
NAME         PZ-IV-81-A2
EXPNO                  1
PROCNO                 1

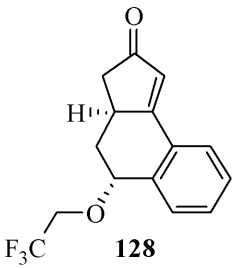
F2 - Acquisition Parameters
Date_          20050221
Time              14.42
INSTRUM          drx300
PROBHD   5 mm Multinucl
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6172.839 Hz
FIDRES         0.188380 Hz
AQ             2.6542580 sec
RG                456.1
DW               81.000 usec
DE                6.00 usec
TE               300.0 K
D1             1.00000000 sec
D31            0.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 7.05 usec
PL1                0.00 dB
SFO1         300.1318534 MHz

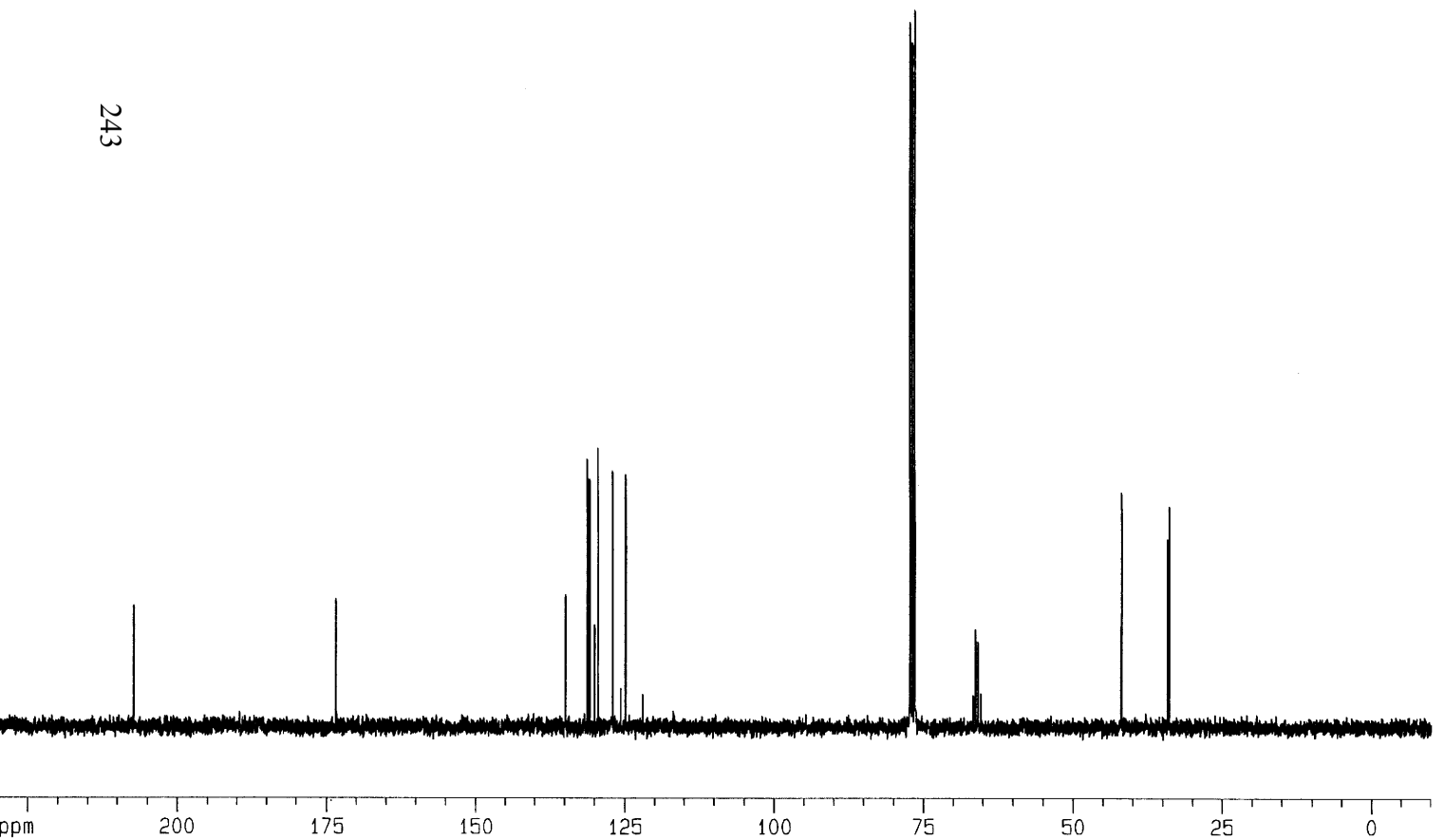
F2 - Processing parameters
SI                32768
SF         300.1300022 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.30

1D NMR plot parameters
CX                20.00 cm
CY                 2.00 cm
F1P               10.000 ppm
F1              3001.30 Hz
F2P               -1.000 ppm
F2              -300.13 Hz
PPMCM             0.55000 ppm/cm
HZCM            165.07150 Hz/cm
```

13C NMR
PZ-IV-81-A2



128

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Current Data Parameters
NAME        PZ-IV-81-A2
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20050221
Time              14.44
INSTRUM          drx300
PROBHD   5 mm Multinucl
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                  843
DS                    4
SWH           18832.393 Hz
FIDRES        0.287360 Hz
AQ            1.7400308 sec
RG                22528
DW               26.550 usec
DE                6.00 usec
TE               297.1 K
D1            1.29999995 sec
d11           0.03000000 sec
D31           0.00000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.50 usec
PL1                 5.00 dB
SFO1         75.4760107 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             100.00 usec
PL2               120.00 dB
PL12               25.60 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
SF           75.4677571 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
CY                10.00 cm
F1P              230.000 ppm
F1             17357.58 Hz
F2P              -10.000 ppm
F2              -754.68 Hz
PPMCM          12.00000 ppm/cm
HZCM          905.61310 Hz/cm
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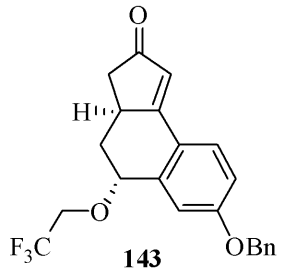
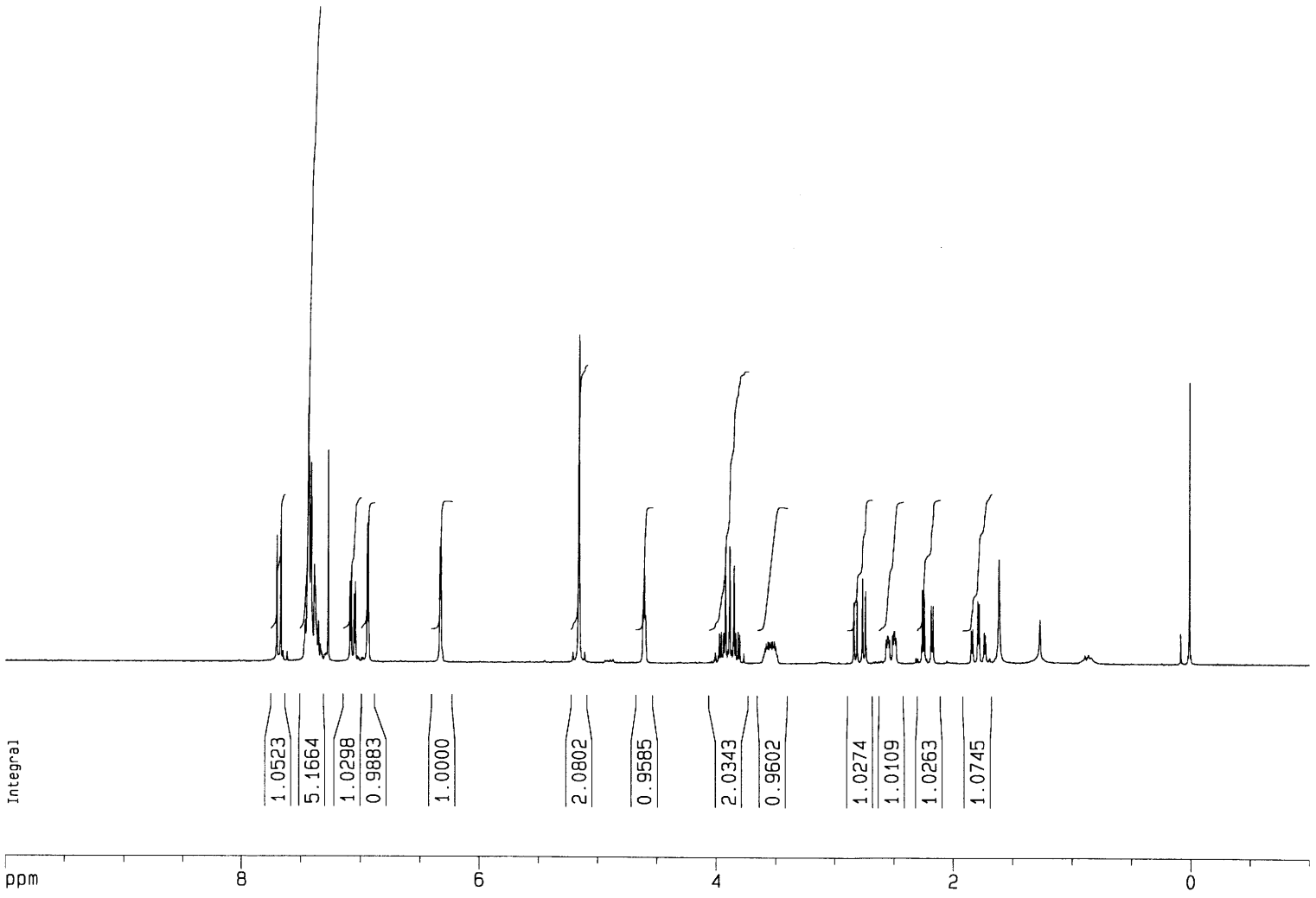
1H NMR
PZ-IV-05-A2
3.0eq TEA, 50C, 7days



143



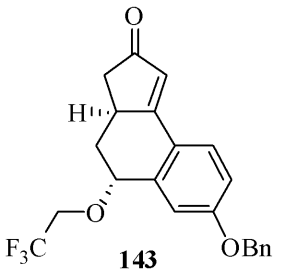
Current Data Parameters
NAME PZ-IV-05-A2-2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20041123
Time 20.23
INSTRUM arx250
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 5208.333 Hz
FIDRES 0.158946 Hz
AQ 3.1457779 sec
RG 2048
DW 96.000 use
DE 137.14 use
TE 300.0 K
D1 1.00000000 sec
P1 8.70 use
SFO1 250.1315321 MHz
NUCLEUS 1H

F2 - Processing parameters
SI 16384
SF 250.1300049 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.50

1D NMR plot parameters
CX 20.00 cm
CY 5.00 cm
F1P 10.000 ppm
F1 2501.30 Hz
F2P -1.000 ppm
F2 -250.13 Hz
PPMCM 0.55000 ppm
HZCM 137.57150 Hz/

13C NMR
PZ-IV-05-A2-2
3.0eq TEA, 50C, 7days



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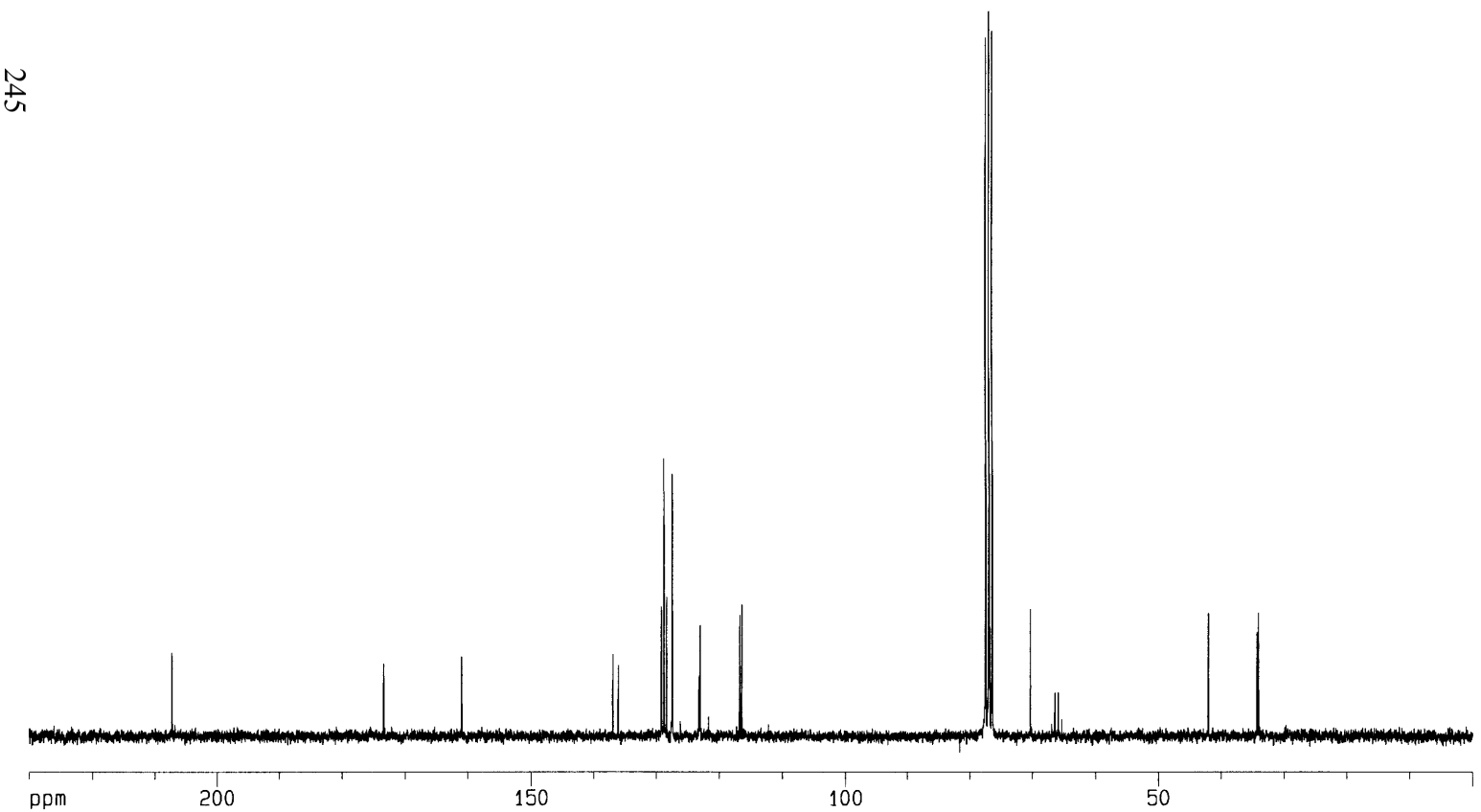
Current Data Parameters	
NAME	PZ-IV-05-A2-2
EXPNO	2
PROCNO	1

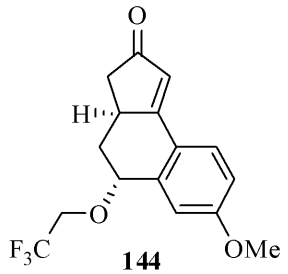
F2 - Acquisition Parameters	
Date_	20041123
Time	20.24
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	3732
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	1.00000000 sec
P1	6.00 use
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

F2 - Processing parameters	
SI	32768
SF	62.8952408 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters	
CX	20.00 cm
CY	10.00 cm
F1P	230.000 ppm
F1	14465.91 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	11.50000 ppm
HZCM	723.29529 Hz/



1H NMR
PZ-IV-28-A2



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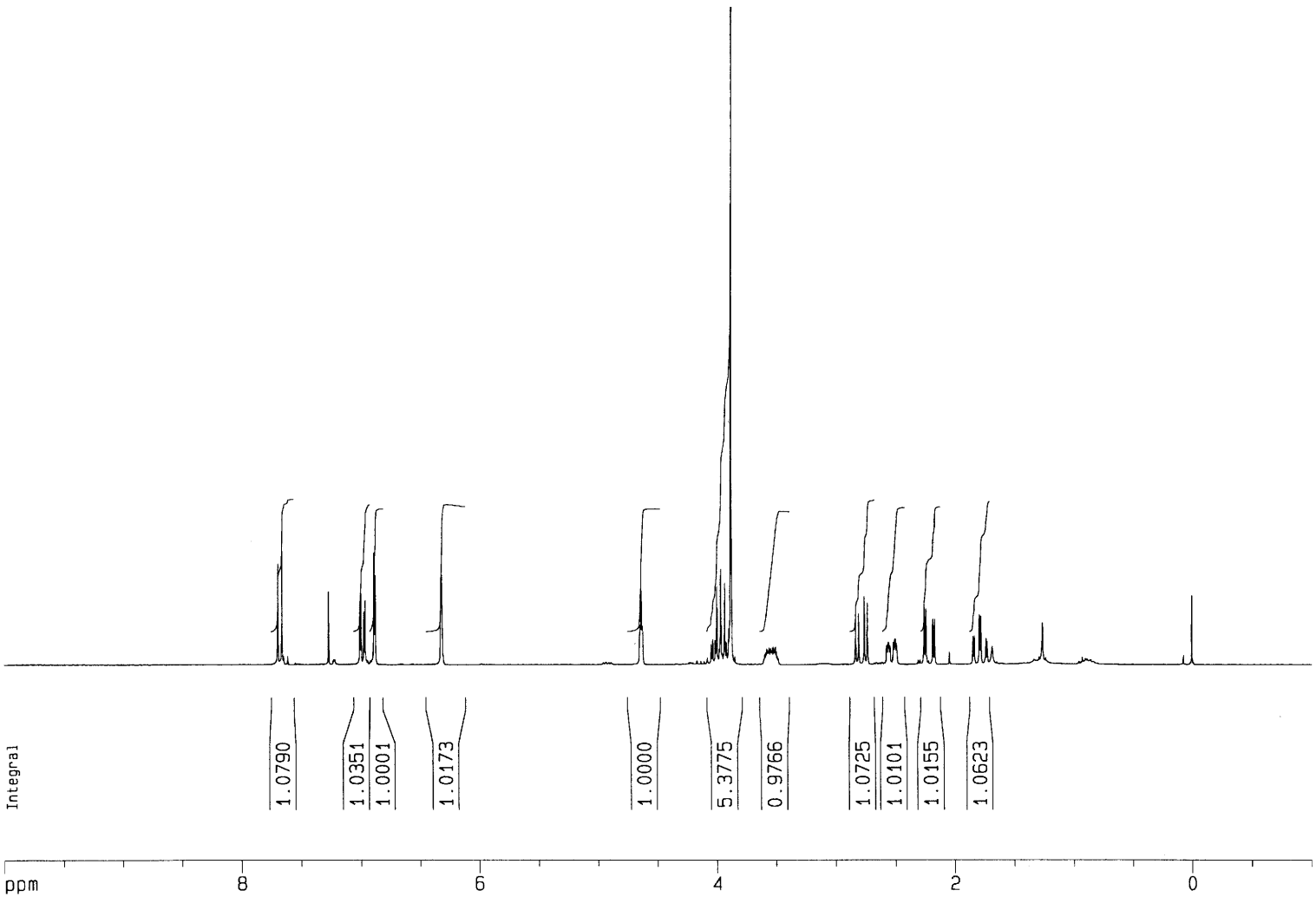


Current Data Parameters

NAME	PZ-IV-28-A2
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20041227
Time	11.38
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	1430
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	8.70 use
SFO1	250.1315321 MHz
NUCLEUS	1H

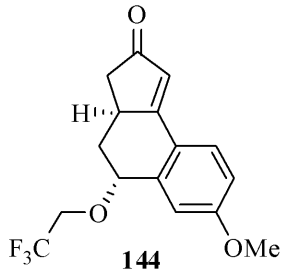
F2 - Processing parameters

SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	12.00 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57150 Hz/

13C NMR
PZ-IV-28-A2



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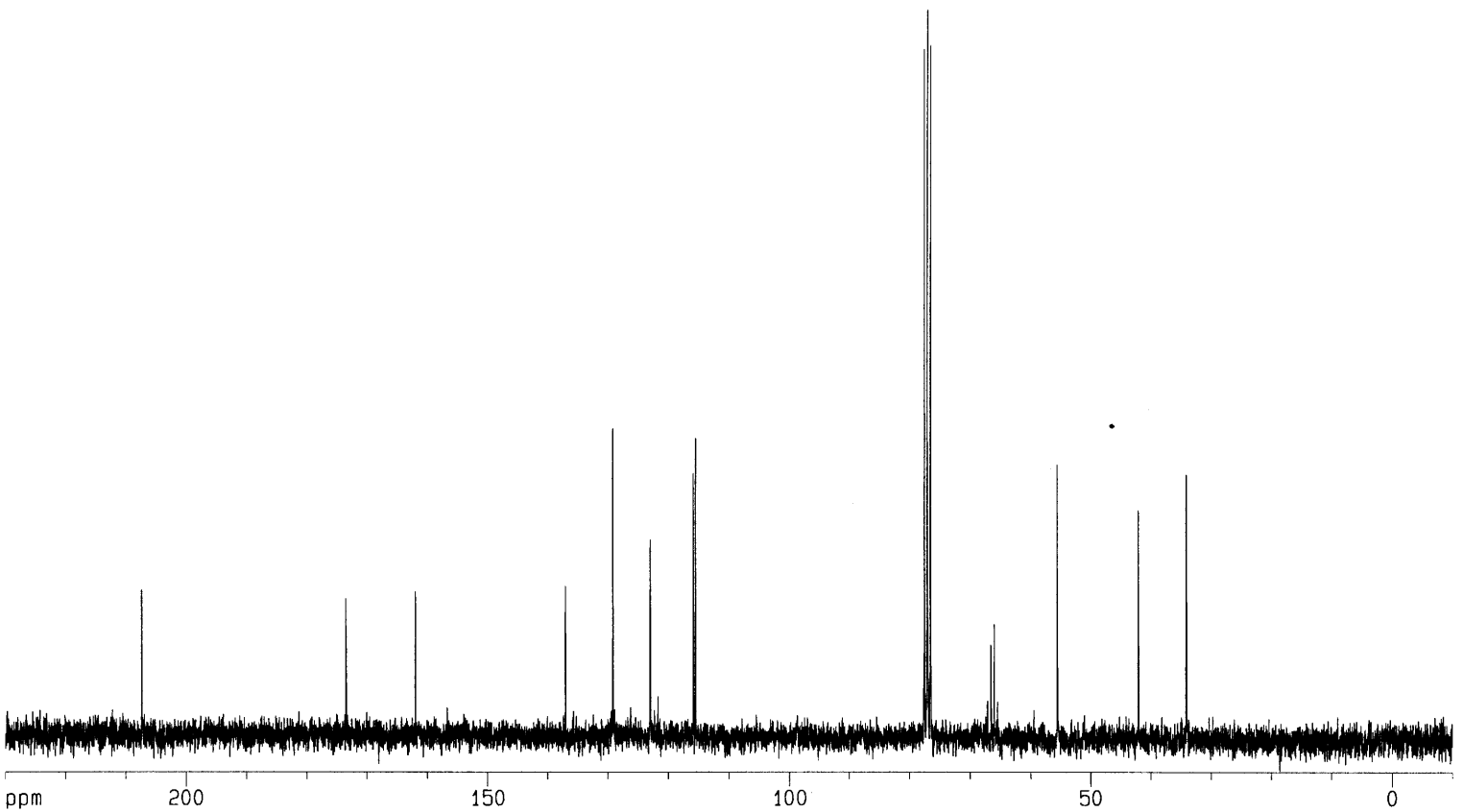


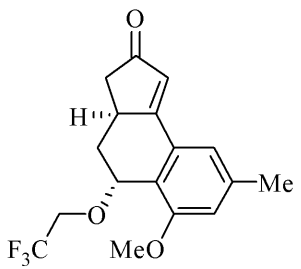
Current Data Parameters	
NAME	PZ-IV-28-A2
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters	
Date_	20041227
Time	11.46
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	523
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	1.00000000 sec
P1	6.00 use
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

F2 - Processing parameters	
SI	32768
SF	62.8952413 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters	
CX	20.00 cm
CY	10.00 cm
F1P	230.000 ppm
F1	14465.90 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	12.00000 ppm
HZCM	754.74292 Hz/

1H-NMR
PZ-IV-59-A2



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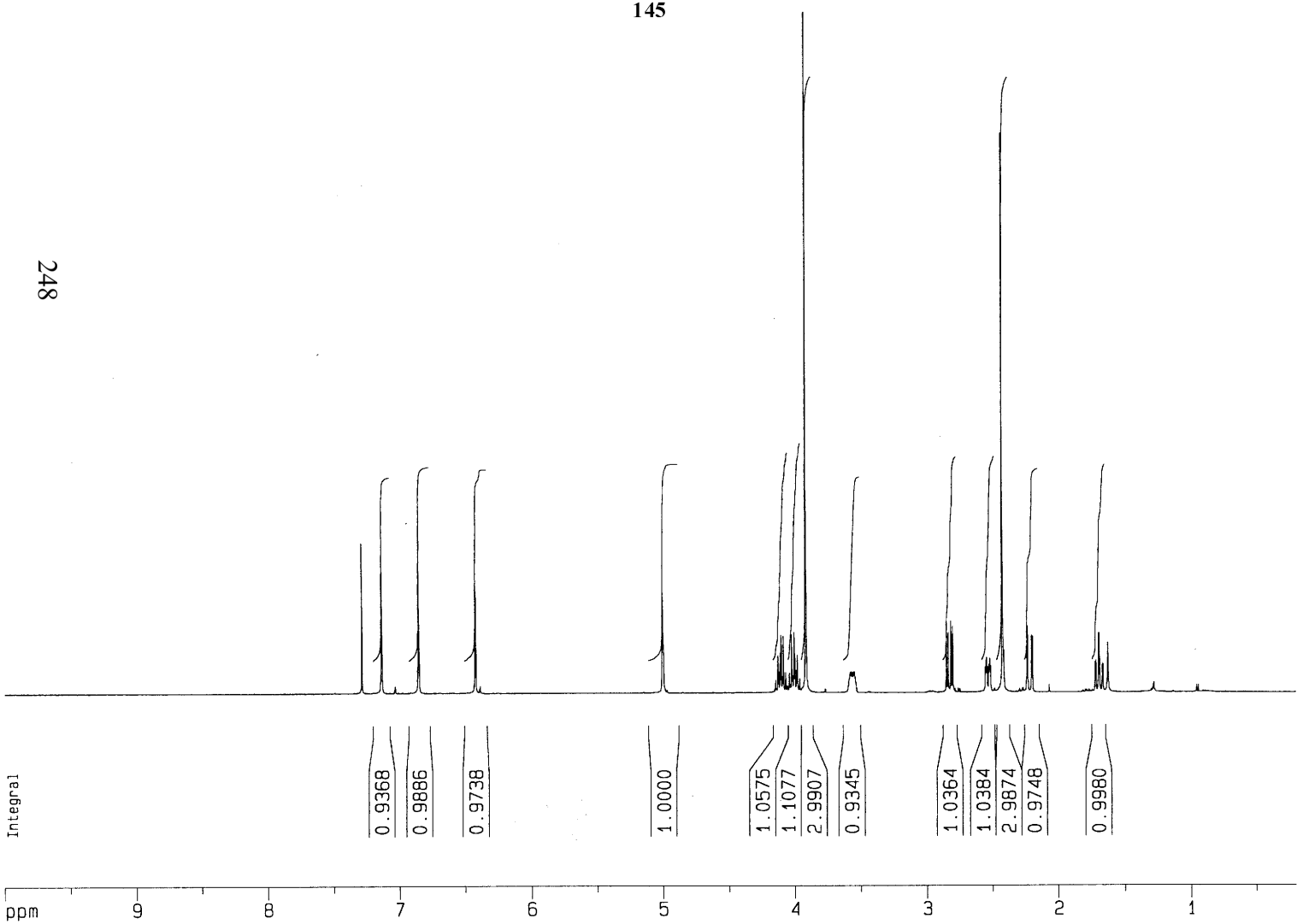


Current Data Parameters

NAME	PZ-IV-59-A2
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050130
Time	15.19
INSTRUM	DRX500
PROBHD	5 mm Multinucl
PULPROG	zg30
TD	57344
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.180151 Hz
AQ	2.7754996 sec
RG	128
DW	48.400 usec
DE	6.00 usec
TE	296.7 K
D1	1.00000000 sec

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

NUC1	1H
P1	13.25 usec
PL1	-3.00 dB
SFO1	500.1330885 MHz

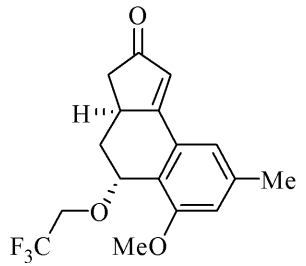
F2 - Processing parameters

SI	32768
SF	500.1300000 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	12.00 cm
F1P	10.000 ppm
F1	5001.30 Hz
F2P	0.200 ppm
F2	100.03 Hz
PPMCM	0.49000 ppm/cr
HZCM	245.06371 Hz/cm

13C-NMR
PZ-IV-59-A2



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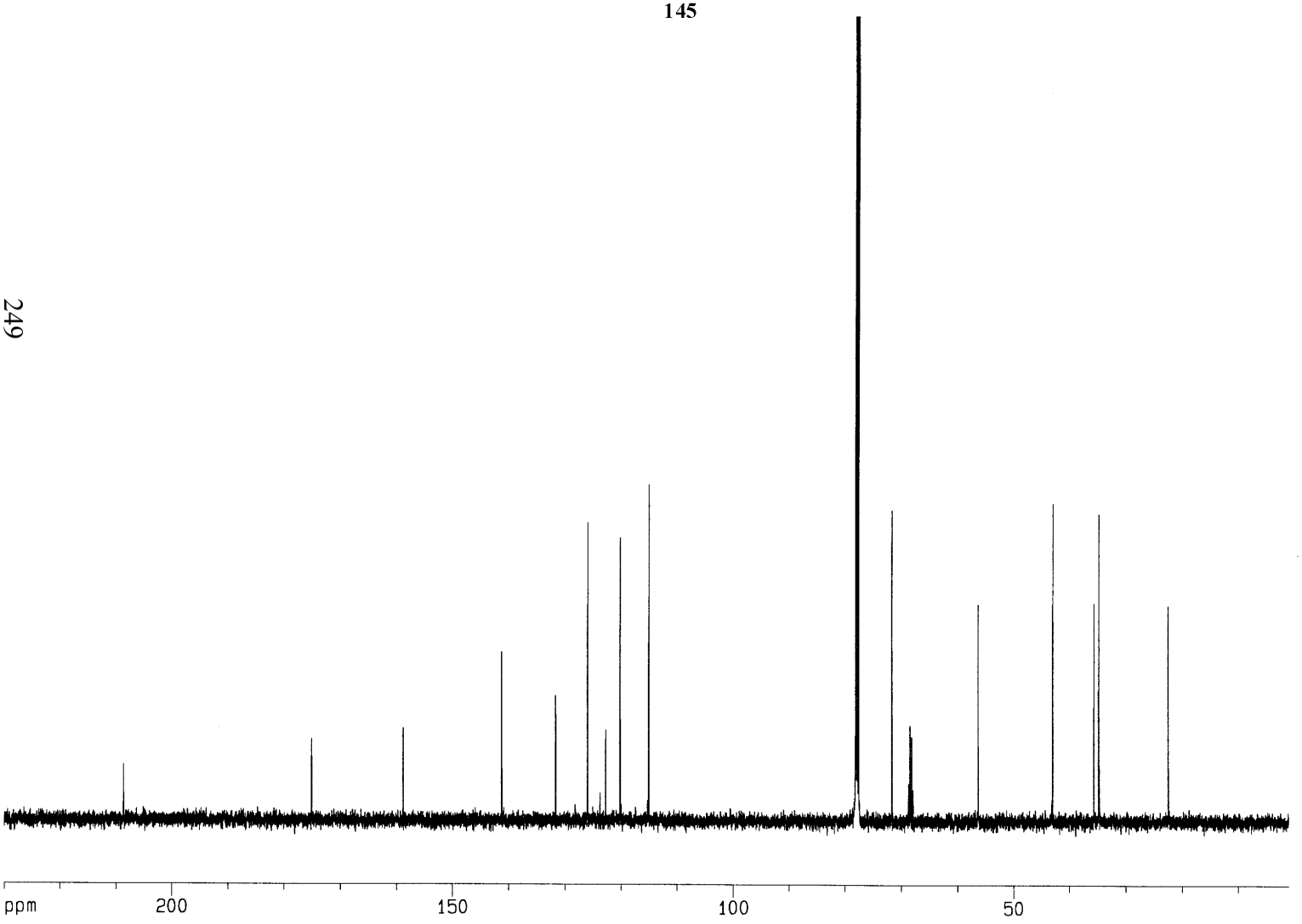


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Current Data Parameters
NAME          PZ-IV-59-A2
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_          20050130
Time              15.28
INSTRUM          DRX500
PROBHD   5 mm Multinucl
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                 1032
DS                    4
SWH           39681.812 Hz
FIDRES        0.605496 Hz
AQ            0.8258188 sec
RG                16384
DW               12.600 usec
DE                6.00 usec
TE                298.0 K
D1           2.00000000 sec
d11          0.03000000 sec

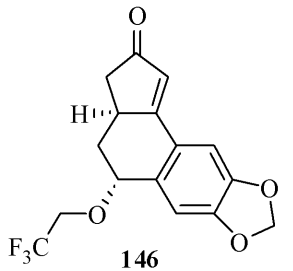
======== CHANNEL f1 ========
NUC1                13C
P1                8.10 usec
PL1               3.00 dB
SFO1        125.7713108 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            88.00 usec
PL2               0.00 dB
PL12              21.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                32768
SF          125.7576929 MHz
WDW                EM
SSB                 0
LB                1.00 Hz
GB                  0
PC                1.40

1D NMR plot parameters
CX               20.00 cm
CY               30.00 cm
F1P             230.000 ppm
F1             28924.27 Hz
F2P              1.000 ppm
F2              125.76 Hz
PPMCM         11.45000 ppm/cm
HZCM        1439.92554 Hz/cm
```

1H NMR
PZ-IV-38-A2



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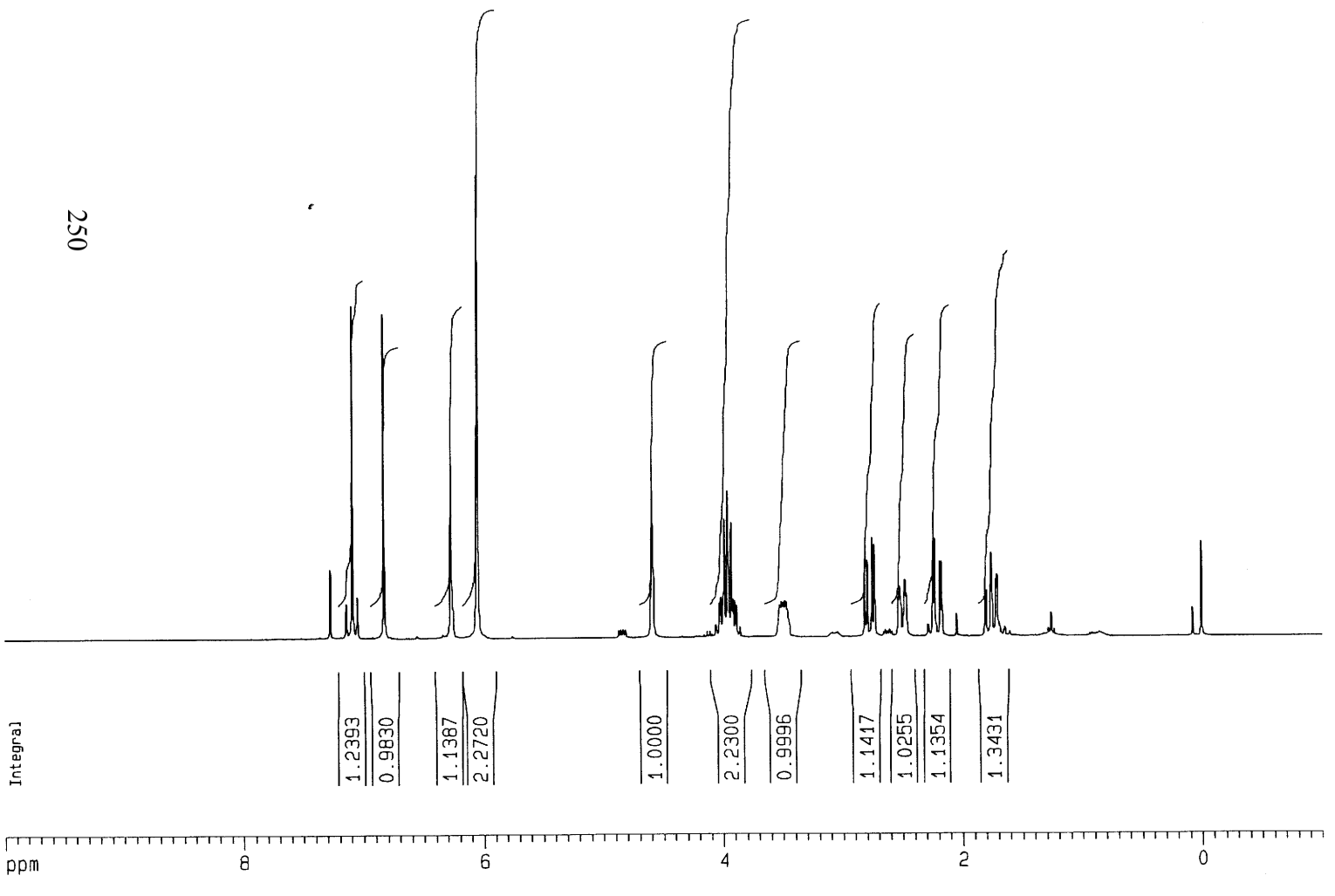


Current Data Parameters

NAME	PZ-IV-38-A2
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050109	
Time	23.24	
INSTRUM	drx300	
PROBHD	5 mm Multinucl	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	6172.839	Hz
FIDRES	0.188380	Hz
AQ	2.6542580	sec
RG	287.4	
DW	81.000	usec
DE	6.00	usec
TE	300.0	K
D1	1.00000000	sec
D31	0.00000000	sec

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

NUC1	1H	
P1	7.05	usec
PL1	0.00	dB
SFO1	300.1318534	MHz

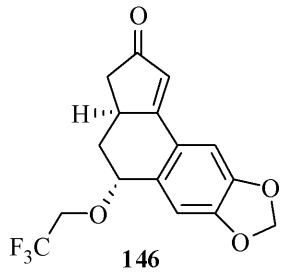
F2 - Processing parameters

SI	32768	
SF	300.1300022	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.30	

1D NMR plot parameters

CX	20.00	cm
CY	7.00	cm
F1P	10.000	ppm
F1	3001.30	Hz
F2P	-1.000	ppm
F2	-300.13	Hz
PPMCM	0.55000	ppm/cm
HZCM	165.07150	Hz/cm

13C NMR
PZ-IV-38-A2



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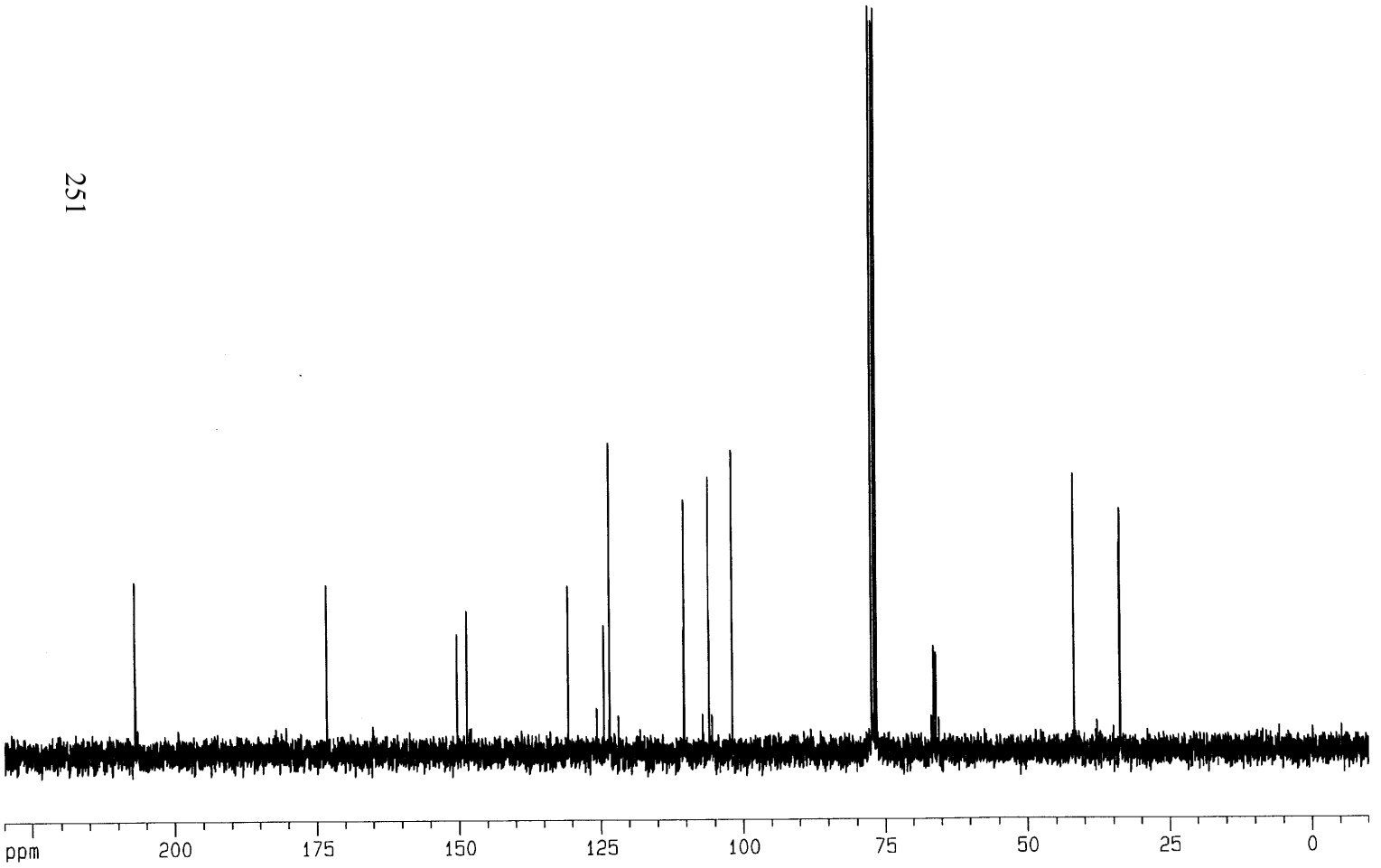


Current Data Parameters	
NAME	PZ-IV-38-A2
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters	
Date_	20050109
Time	23.27
INSTRUM	drx300
PROBHD	5 mm Multinucl
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	160
DS	4
SWH	18832.393 Hz
FIDRES	0.287360 Hz
AQ	1.7400308 sec
RG	22528
DW	26.550 usec
DE	6.00 usec
TE	297.1 K
D1	1.29999995 sec
d11	0.03000000 sec
D31	0.00000000 sec

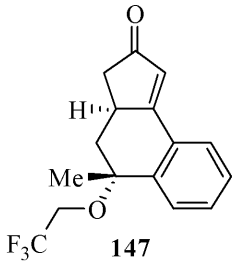
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	5.00 dB
SFO1	75.4760107 MHz

======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	120.00 dB
PL12	25.60 dB
SFO2	300.1312005 MHz

F2 - Processing parameters	
SI	32768
SF	75.4677571 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters	
CX	20.00 cm
CY	11.00 cm
F1P	230.000 ppm
F1	17357.58 Hz
F2P	-10.000 ppm
F2	-754.68 Hz
PPMCM	12.00000 ppm/cm
HZCM	905.61310 Hz/cm

1H-NMR
PZ-IV-63-A4



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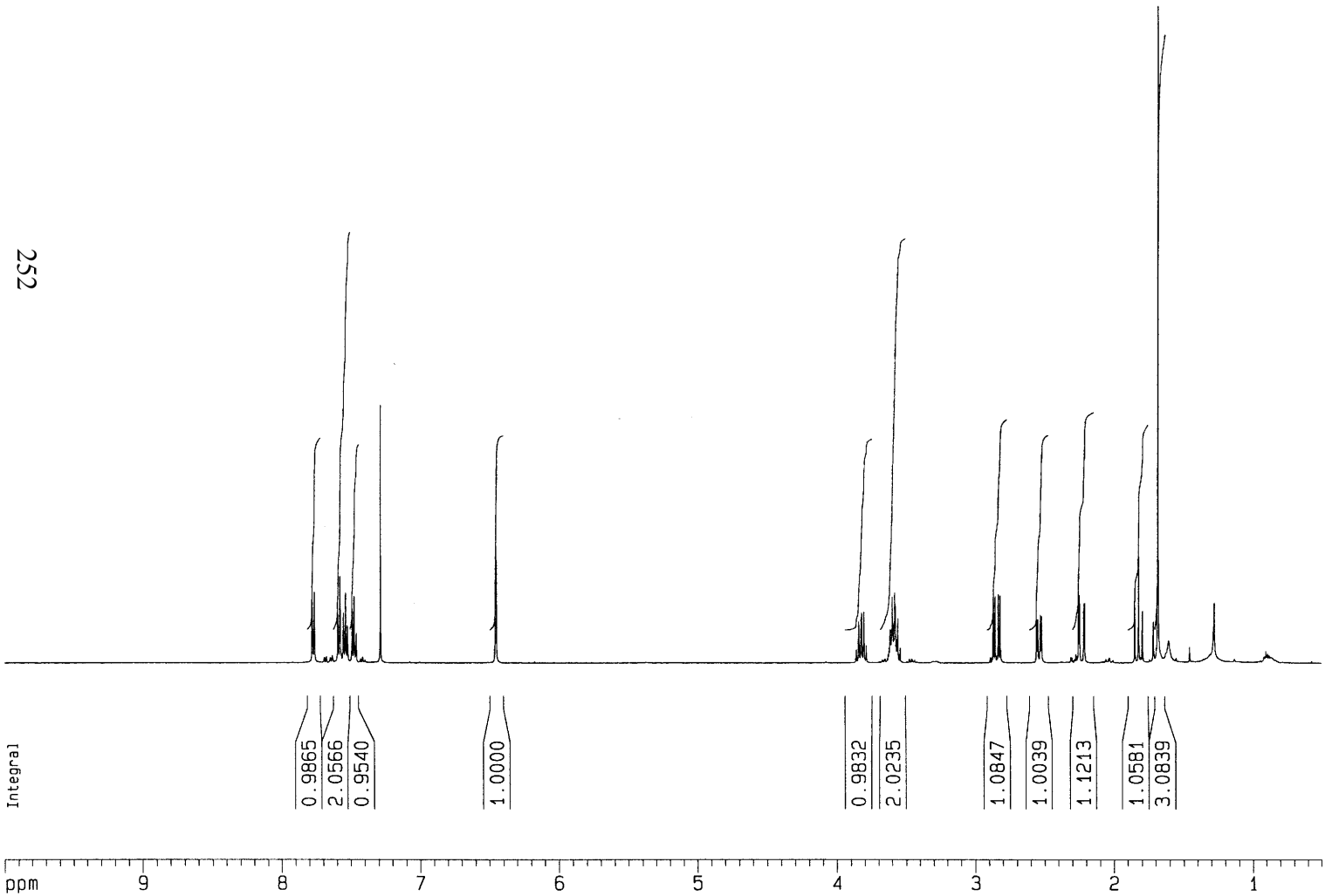


Current Data Parameters

NAME	PZ-IV-63-A4
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050201
Time	15.29
INSTRUM	DRX500
PROBHD	5 mm Multinucl
PULPROG	zg30
TD	57344
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.180151 Hz
AQ	2.7754996 sec
RG	143.7
DW	48.400 usec
DE	6.00 usec
TE	296.7 K
D1	1.00000000 sec

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

NUC1	1H
P1	13.25 usec
PL1	-3.00 dB
SFO1	500.1330885 MHz

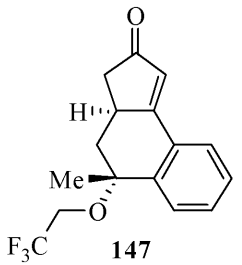
F2 - Processing parameters

SI	32768
SF	500.1300000 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	10.00 cm
F1P	10.000 ppm
F1	5001.30 Hz
F2P	0.500 ppm
F2	250.07 Hz
PPMCM	0.47500 ppm/cr
HZCM	237.56175 Hz/cm

13C-NMR
PZ-IV-63-A4



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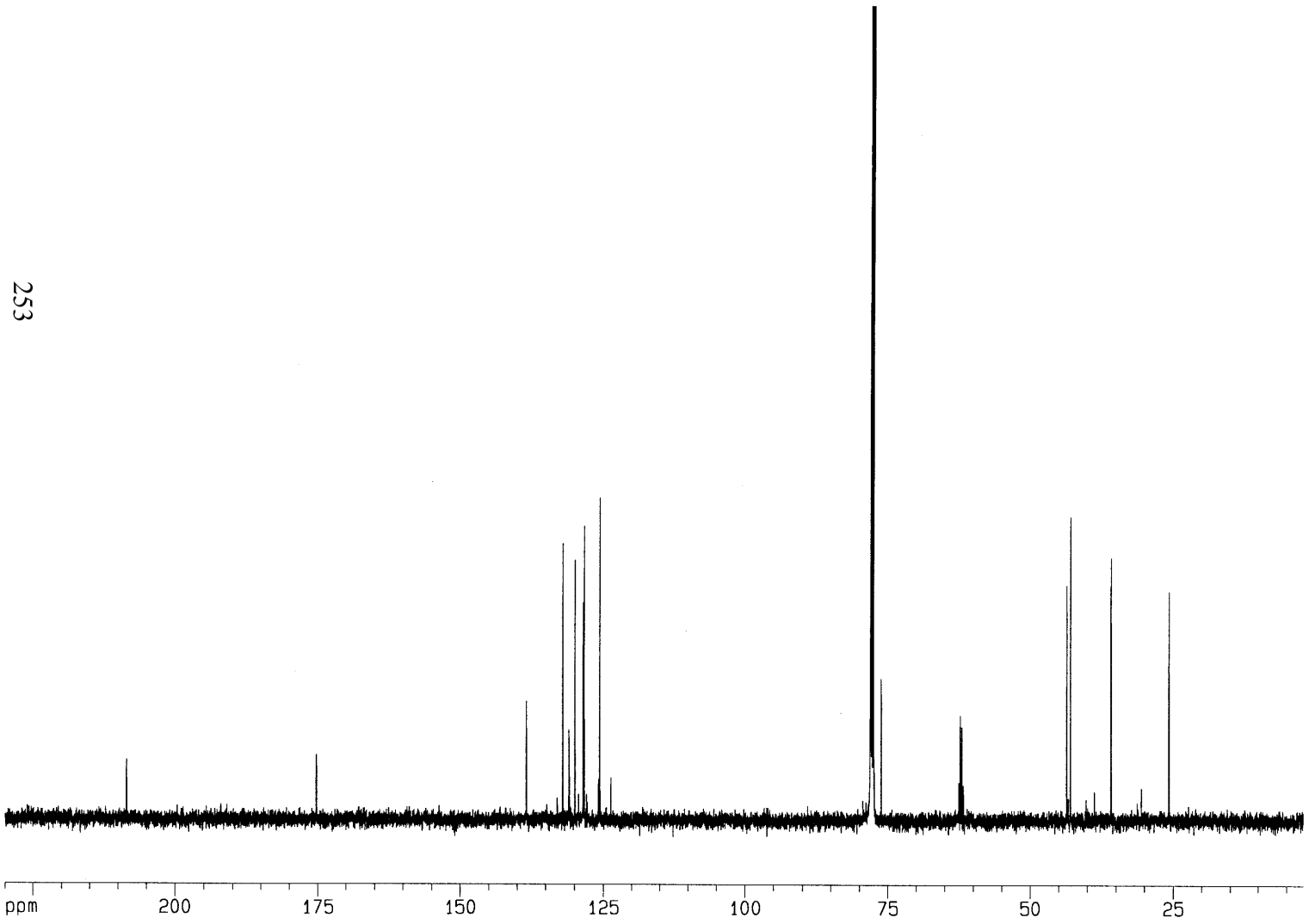
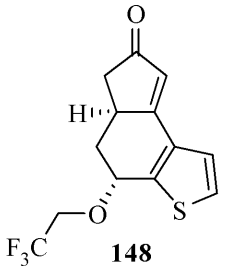


Current Data Parameters	
NAME	PZ-IV-63-A4
EXPNO	2
PROCNO	1
F2 - Acquisition Parameters	
Date_	20050201
Time	15.34
INSTRUM	DRX500
PROBHD	5 mm Multinucl
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	2366
DS	4
SWH	39681.812 Hz
FIDRES	0.605496 Hz
AQ	0.8258188 sec
RG	16384
DW	12.600 usec
DE	6.00 usec
TE	298.0 K
D1	2.00000000 sec
d11	0.03000000 sec
======== CHANNEL f1 ========	
NUC1	13C
P1	8.10 usec
PL1	3.00 dB
SFO1	125.7713108 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	88.00 usec
PL2	0.00 dB
PL12	21.00 dB
SFO2	500.1320005 MHz
F2 - Processing parameters	
SI	32768
SF	125.7576929 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40
1D NMR plot parameters	
CX	20.00 cm
CY	50.00 cm
F1P	230.000 ppm
F1	28924.27 Hz
F2P	2.000 ppm
F2	251.51 Hz
PPMCM	11.40000 ppm/cm
HZCM	1433.63770 Hz/cm

1H-NMR
PZ-IV-69-A1



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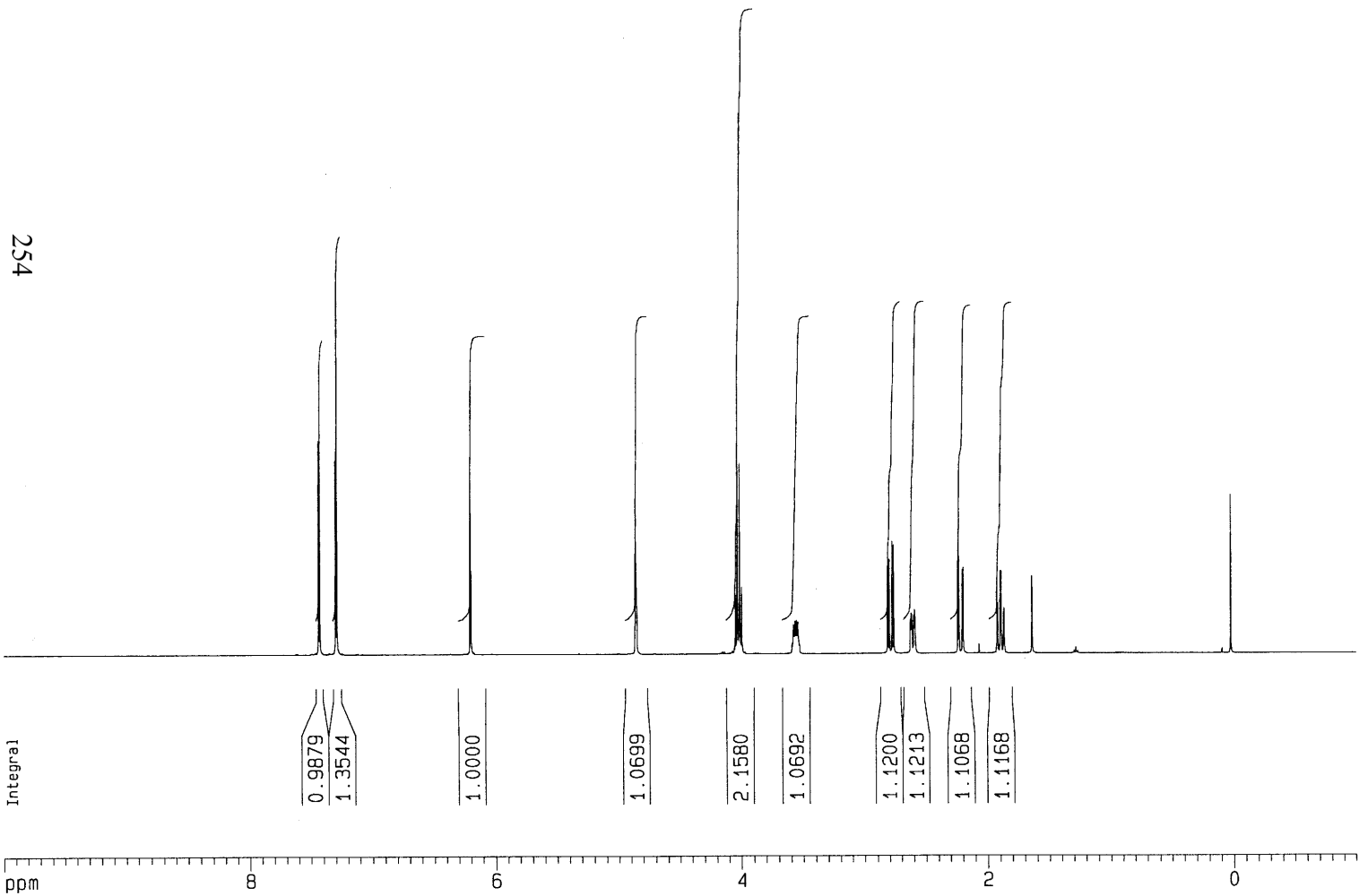


Current Data Parameters

NAME	PZ-IV-69-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050208
Time	16.06
INSTRUM	DRX500
PROBHD	5 mm Multinucl
PULPROG	zg30
TD	57344
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.180151 Hz
AQ	2.7754996 sec
RG	143.7
DW	48.400 usec
DE	6.00 usec
TE	296.7 K
D1	1.00000000 sec

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

NUC1	1H
P1	13.25 usec
PL1	-3.00 dB
SFO1	500.1330885 MHz

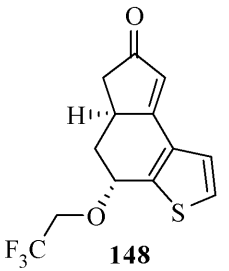
F2 - Processing parameters

SI	32768
SF	500.1300000 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	5.00 cm
F1P	10.000 ppm
F1	5001.30 Hz
F2P	-1.000 ppm
F2	-500.13 Hz
PPMCM	0.55000 ppm/cr
HZCM	275.07150 Hz/cm

13C-NMR
PZ-IV-69-A1



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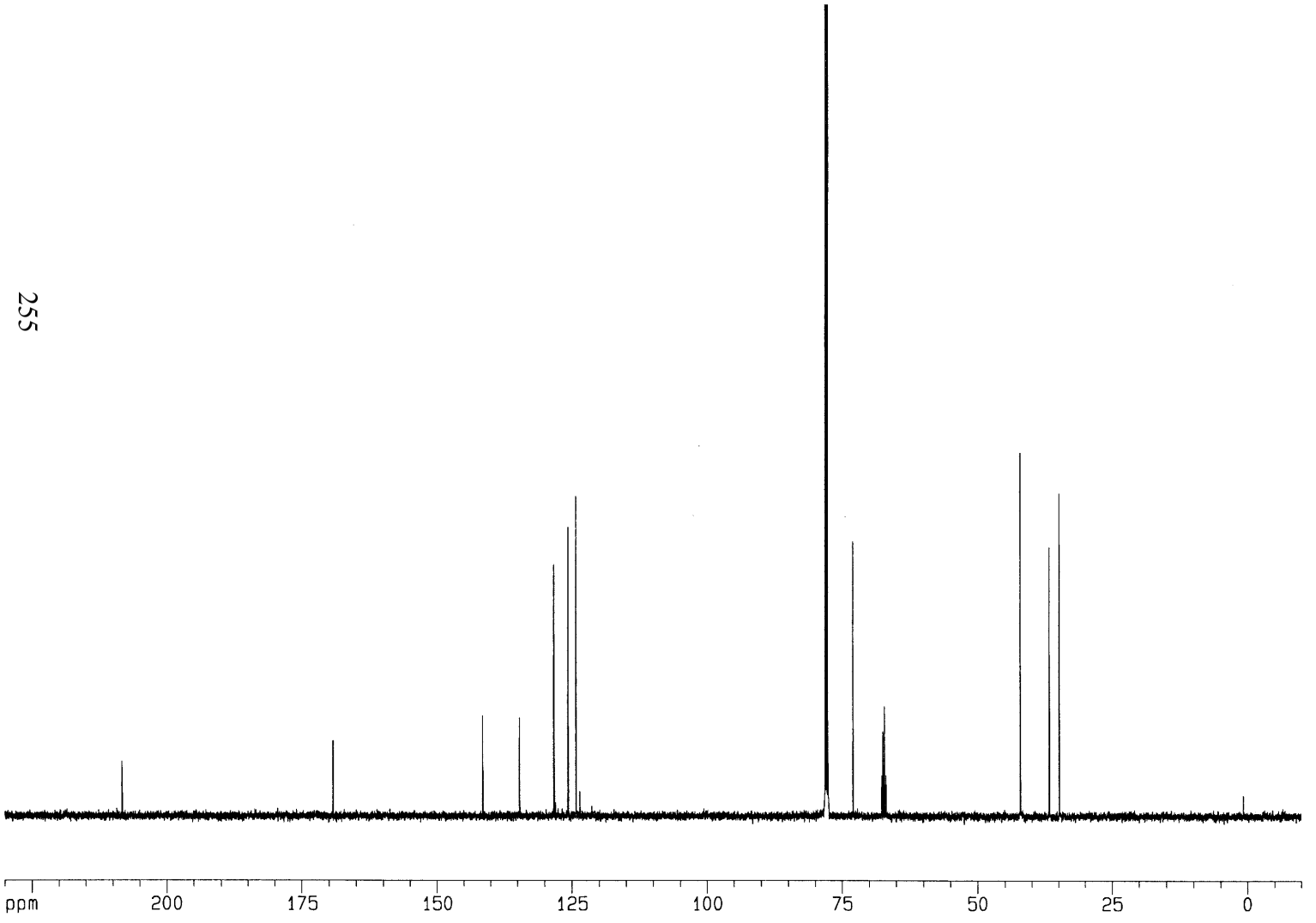


Current Data Parameters

NAME	PZ-IV-69-A1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20050208
Time	16.10
INSTRUM	DRX500
PROBHD	5 mm Multinucl
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	1574
DS	4
SWH	39681.812 Hz
FIDRES	0.605496 Hz
AQ	0.8258188 sec
RG	16384
DW	12.600 usec
DE	6.00 usec
TE	298.0 K
D1	2.00000000 sec
d11	0.03000000 sec

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

NUC1	13C
P1	8.10 usec
PL1	3.00 dB
SFO1	125.7713108 MHz

======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	88.00 usec
PL2	0.00 dB
PL12	21.00 dB
SFO2	500.1320005 MHz

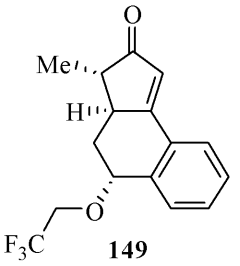
F2 - Processing parameters

SI	32768
SF	125.7576929 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	20.00 cm
F1P	230.000 ppm
F1	28924.27 Hz
F2P	-10.000 ppm
F2	-1257.58 Hz
PPMCM	12.00000 ppm/cm
HZCM	1509.09229 Hz/cm

1H NMR
PZ-IV-35-A2-2



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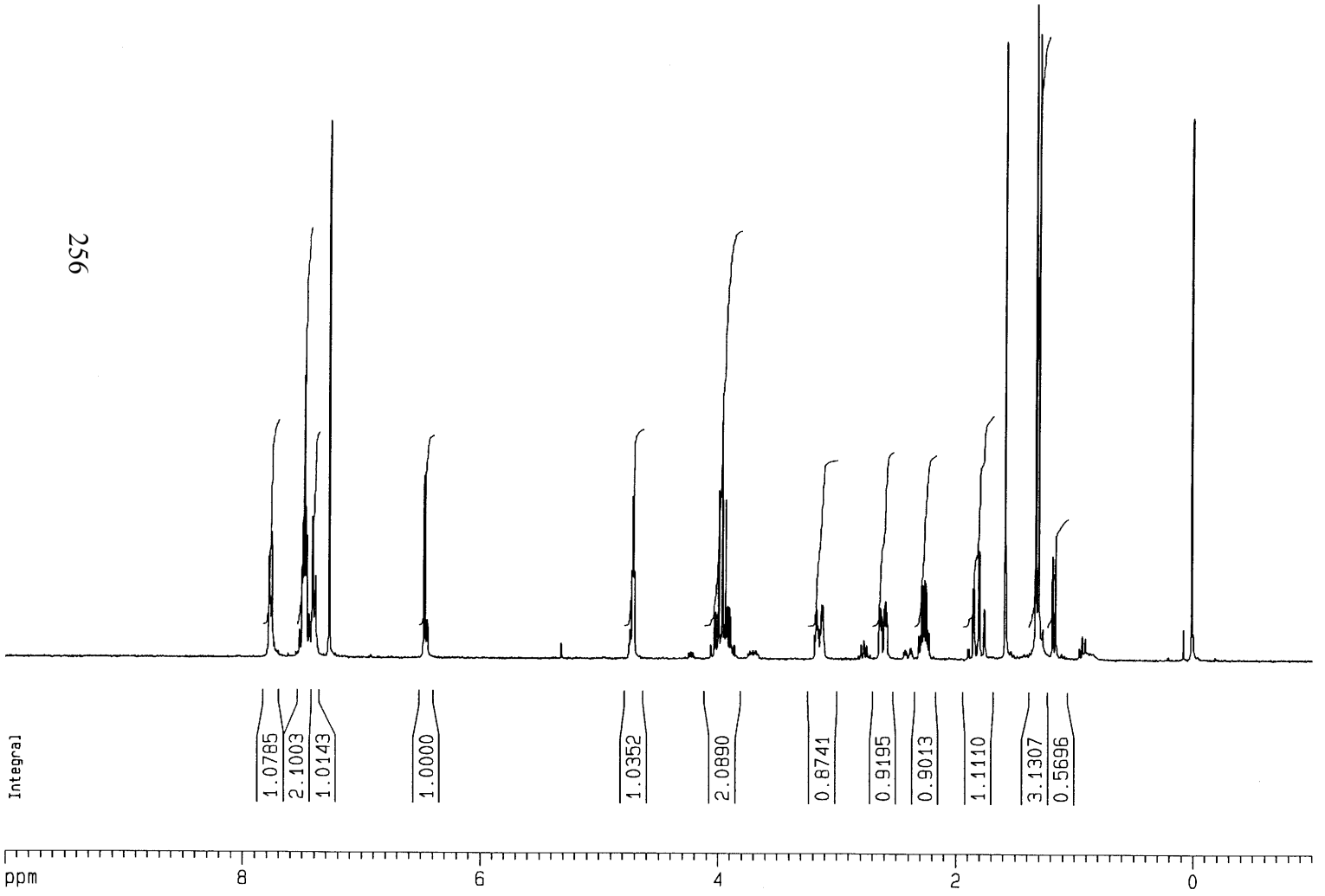


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Current Data Parameters
NAME       PZ-IV-35-A2-2
EXPNO                  1
PROCNO                 1

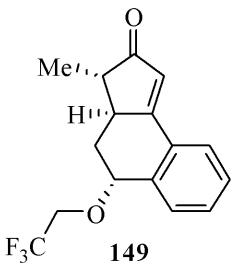
F2 - Acquisition Parameters
Date_           20050104
Time               21.23
INSTRUM          drx300
PROBHD   5 mm Multinucl
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           6172.839 Hz
FIDRES        0.188380 Hz
AQ            2.6542580 sec
RG                 1024
DW               81.000 usec
DE                6.00 usec
TE               300.0 K
D1            1.00000000 sec
D31           0.00000000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                7.05 usec
PL1               0.00 dB
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                32768
SF          300.1300022 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.30

1D NMR plot parameters
CX                20.00 cm
CY                10.00 cm
F1P               10.000 ppm
F1              3001.30 Hz
F2P              -1.000 ppm
F2             -300.13 Hz
PPMCM          0.55000 ppm/cm
HZCM          165.07150 Hz/cm
```

13C NMR
PZ-IV-35-A2-2



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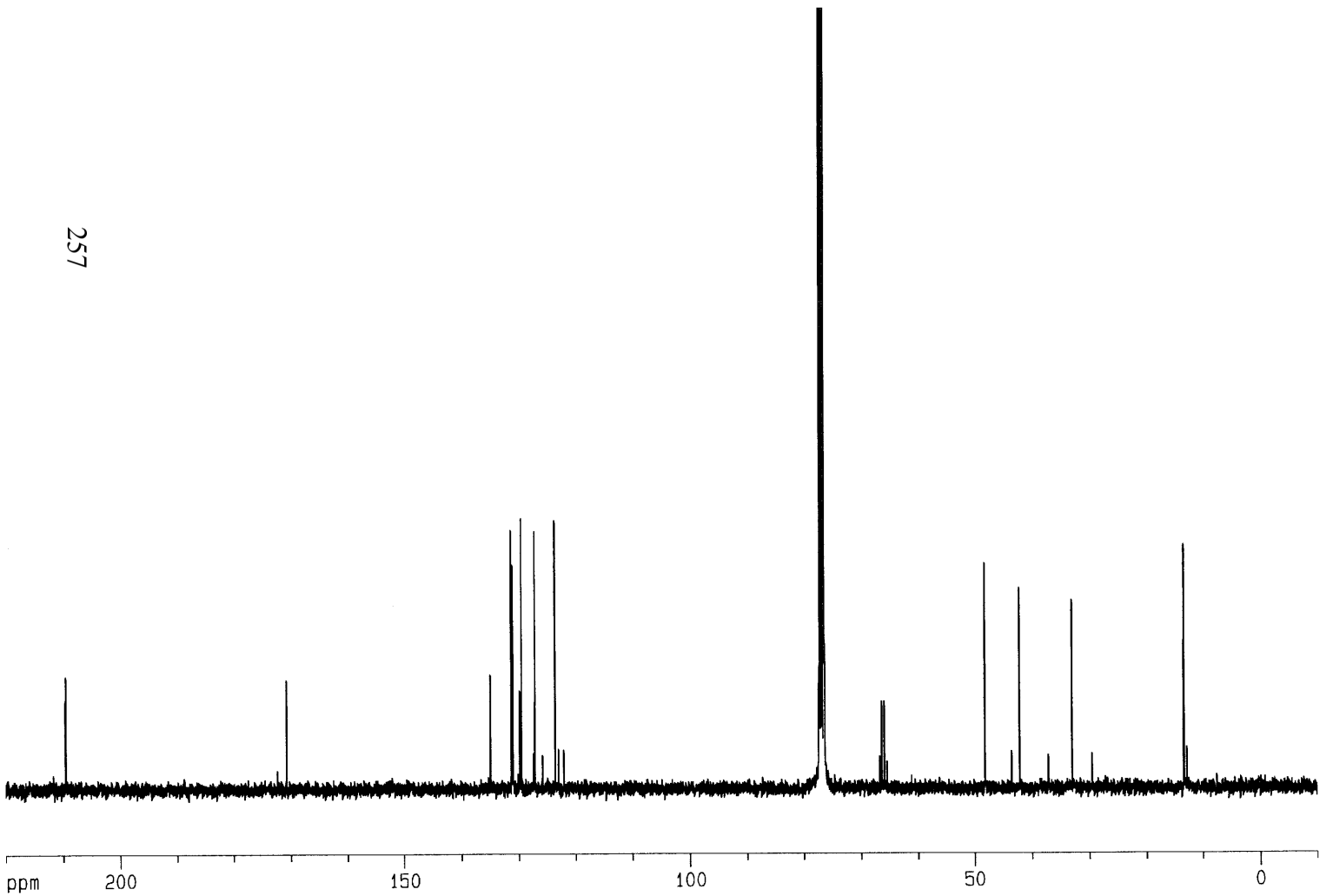


Current Data Parameters

NAME	PZ-IV-35-A2-2
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20050104
Time	21.25
INSTRUM	drx300
PROBHD	5 mm Multinucl
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	13972
DS	4
SWH	18832.393 Hz
FIDRES	0.287360 Hz
AQ	1.7400308 sec
RG	22528
DW	26.550 usec
DE	6.00 usec
TE	297.1 K
D1	1.29999995 sec
d11	0.03000000 sec
D31	0.00000000 sec

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

NUC1	13C
P1	8.50 usec
PL1	5.00 dB
SFO1	75.4760107 MHz

======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	120.00 dB
PL12	25.60 dB
SFO2	300.1312005 MHz

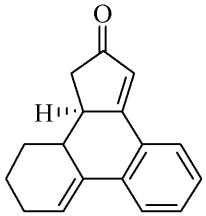
F2 - Processing parameters

SI	32768
SF	75.4677571 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
CY	50.00 cm
F1P	220.000 ppm
F1	16602.91 Hz
F2P	-10.000 ppm
F2	-754.68 Hz
PPMCM	11.50000 ppm/cm
HZCM	867.87921 Hz/cm

1H-NMR
PZ-IV-116-B2



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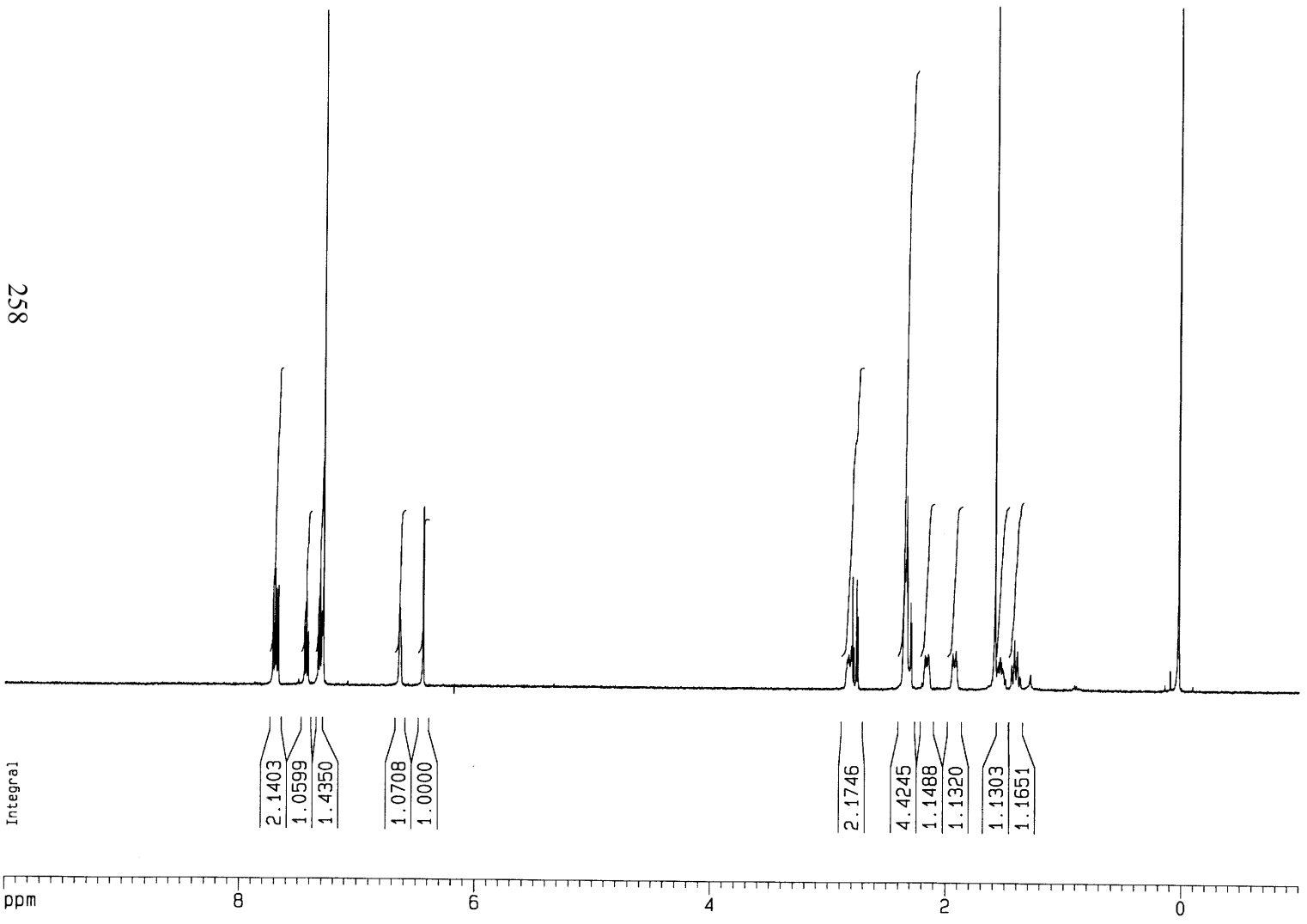


Current Data Parameters	
NAME	PZ-IV-116-B2
EXPNO	1
PROCNO	1

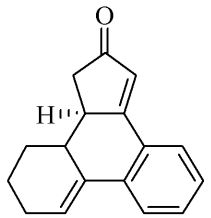
F2 - Acquisition Parameters	
Date_	20050330
Time	16.26
INSTRUM	DRX500
PROBHD	5 mm Multinucl
PULPROG	zg30
TD	57344
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.180151 Hz
AQ	2.7754996 sec
RG	161.3
DW	48.400 usec
DE	6.00 usec
TE	296.7 K
D1	1.00000000 sec

======== CHANNEL f1 ========	
NUC1	1H
P1	13.25 usec
PL1	-3.00 dB
SFO1	500.1330885 MHz

F2 - Processing parameters	
SI	32768
SF	500.1300000 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.40

1D NMR plot parameters	
CX	20.00 cm
CY	20.00 cm
F1P	10.000 ppm
F1	5001.30 Hz
F2P	-1.000 ppm
F2	-500.13 Hz
PPMCM	0.55000 ppm/cr
HZCM	275.07150 Hz/cm

13C-NMR
PZ-IV-116-B2



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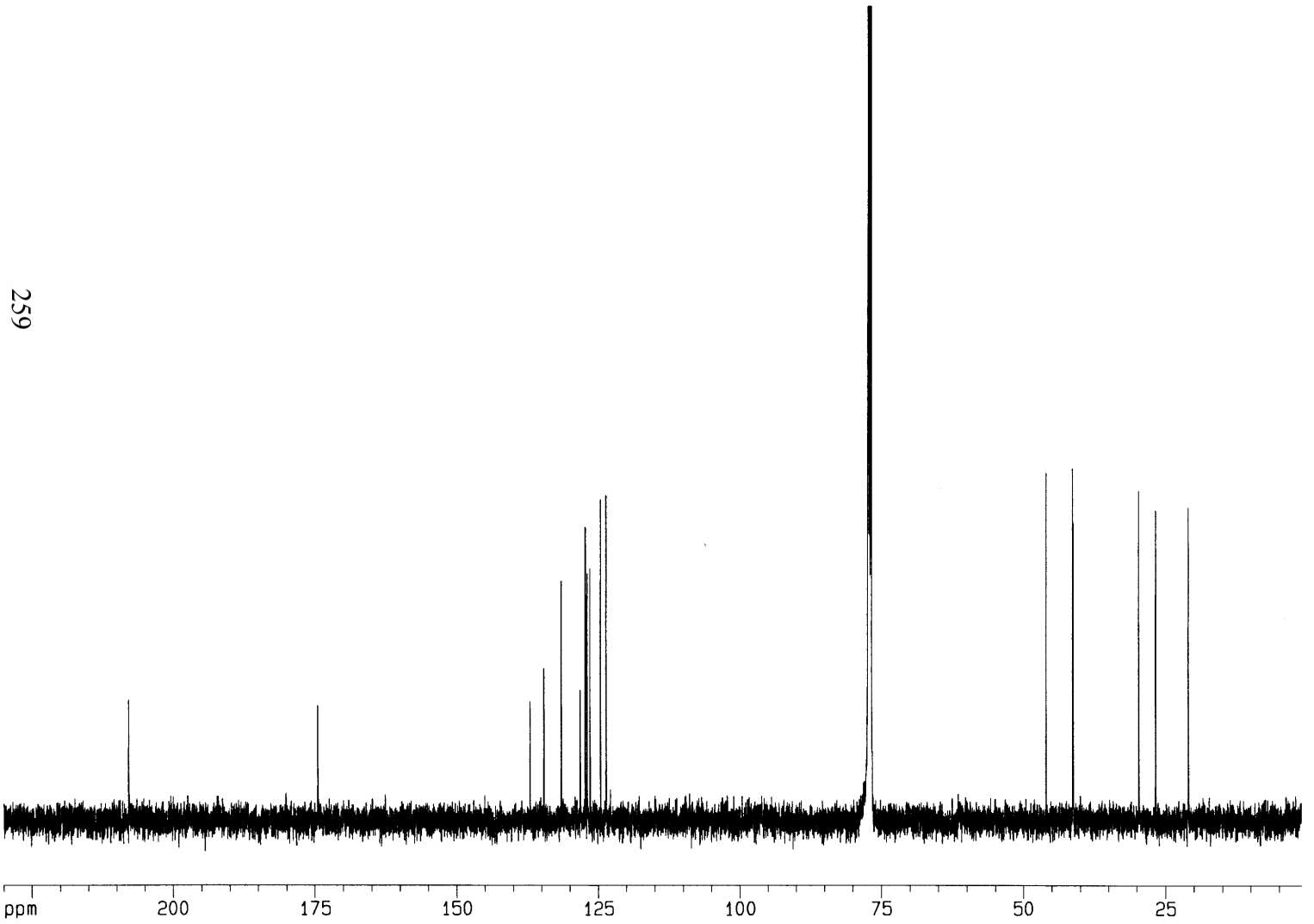


Current Data Parameters
NAME PZ-IV-116-B2-1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050330
Time 22.45
INSTRUM DRX500
PROBHD 5 mm Multinucl
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 12174
DS 4
SWH 39681.812 Hz
FIDRES 0.605496 Hz
AQ 0.8258188 sec
RG 9195.2
DW 12.600 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec

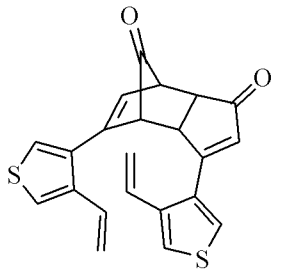
======== CHANNEL f1 ========
NUC1 13C
P1 8.10 usec
PL1 3.00 dB
SFO1 125.7713108 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 88.00 usec
PL2 0.00 dB
PL12 21.00 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 32768
SF 125.7577910 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 200.00 cm
F1P 230.000 ppm
F1 28924.29 Hz
F2P 1.000 ppm
F2 125.76 Hz
PPMCM 11.45000 ppm/cm
HZCM 1439.92664 Hz/cm

1H NMR
PZ-IV-101-A2



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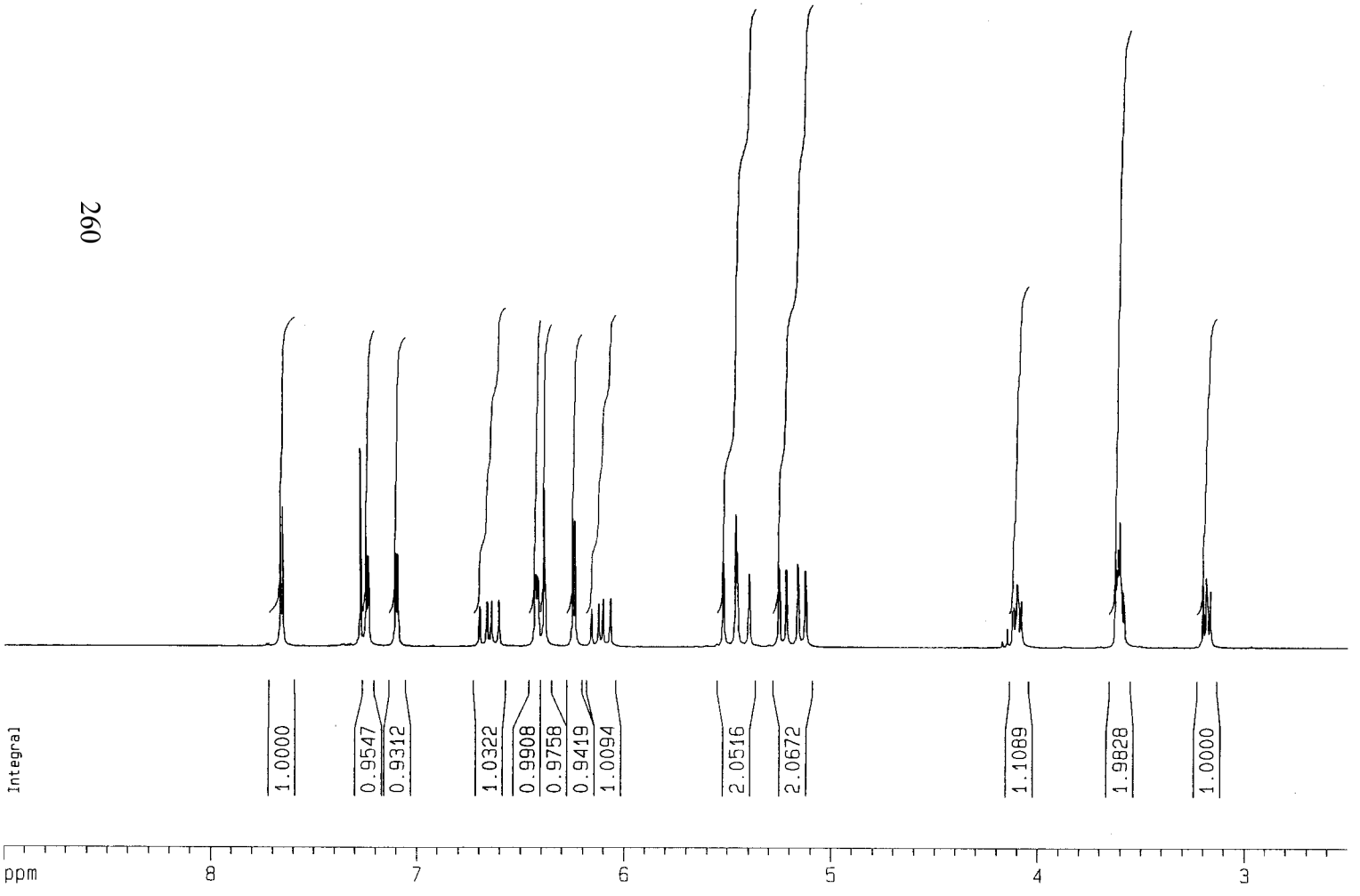



```
Current Data Parameters
NAME        PZ-IV-101-A2
EXPNO                  1
PROCNO                 1

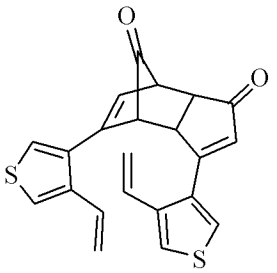
F2 - Acquisition Parameters
Date_           20050314
Time               10.53
INSTRUM          drx300
PROBHD   5 mm Multinucl
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           6172.839 Hz
FIDRES        0.188380 Hz
AQ            2.6542580 sec
RG                724.1
DW               81.000 usec
DE                6.00 usec
TE               300.0 K
D1            1.00000000 sec
D31           0.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 7.05 usec
PL1                0.00 dB
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300022 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.30

1D NMR plot parameters
CX                20.00 cm
CY                 3.00 cm
F1P               9.000 ppm
F1              2701.17 Hz
F2P               2.500 ppm
F2              750.33 Hz
PPMCM          0.32500 ppm/cm
HZCM          97.54225 Hz/cm
```

13C NMR
PZ-IV-101-A2



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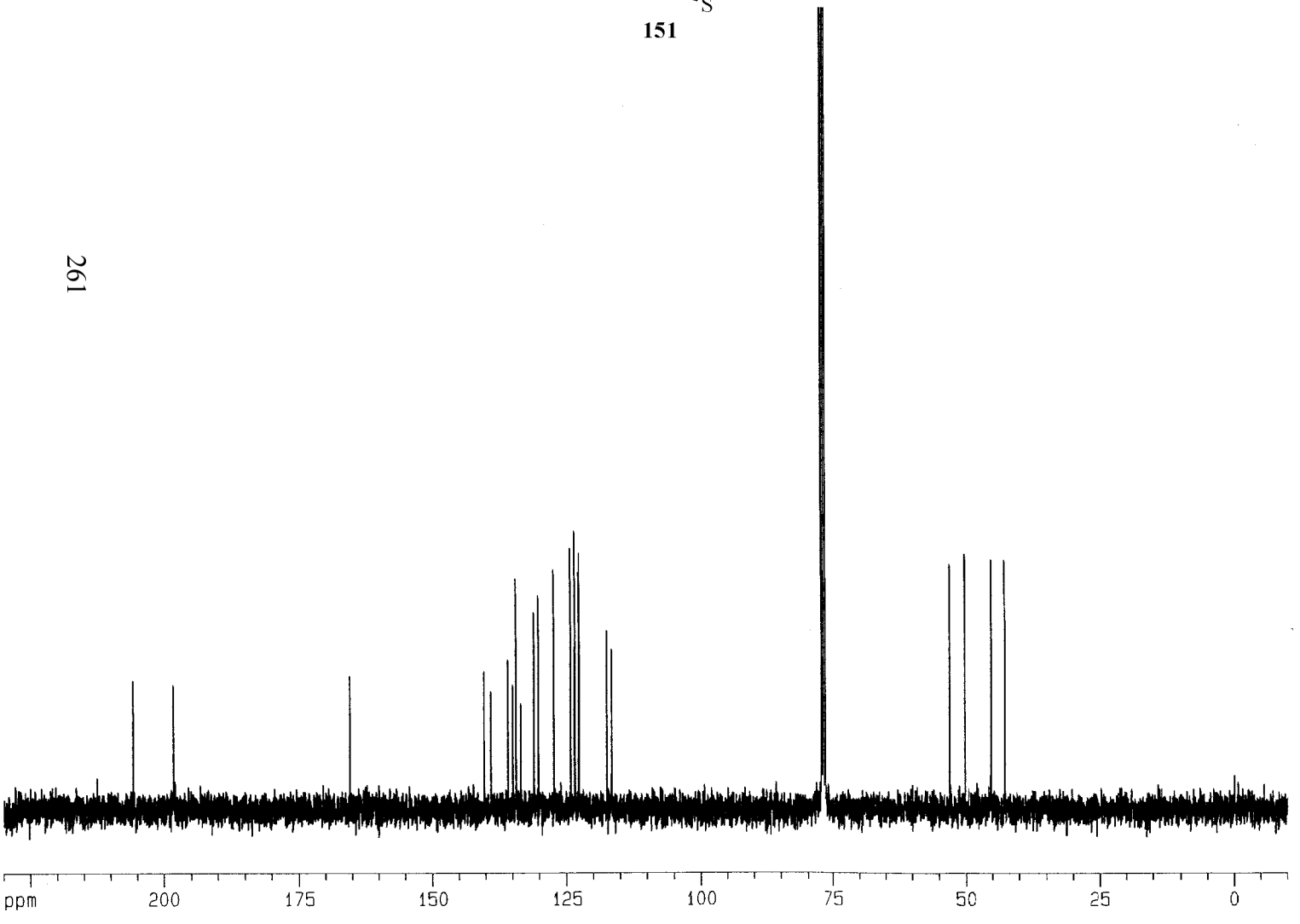


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Current Data Parameters
NAME        PZ-IV-101-A2
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050314
Time                11.00
INSTRUM           drx300
PROBHD   5 mm Multinucl
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                  1049
DS                     4
SWH           18832.393 Hz
FIDRES         0.287360 Hz
AQ             1.7400308 sec
RG                 22528
DW                26.550 usec
DE                 6.00 usec
TE                297.1 K
D1            1.29999995 sec
d11           0.03000000 sec
D31           0.00000000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 8.50 usec
PL1                5.00 dB
SFO1          75.4760107 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2             100.00 usec
PL2               120.00 dB
PL12               25.60 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677502 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
CY                 30.00 cm
F1P              230.000 ppm
F1               17357.58 Hz
F2P              -10.000 ppm
F2               -754.68 Hz
PPMCM            12.00000 ppm/cm
HZCM            905.61298 Hz/cm
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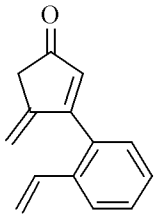

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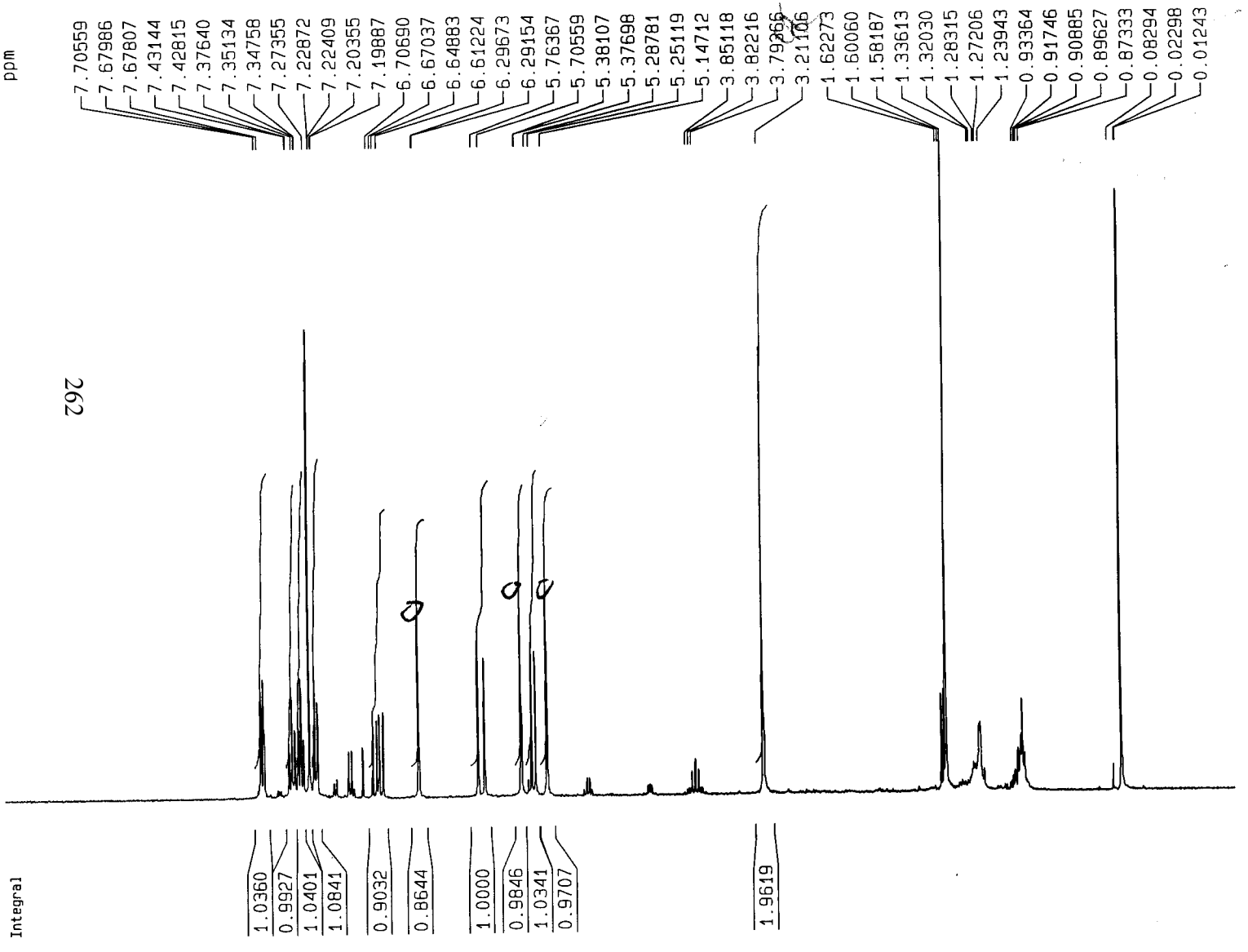


Current Data Parameters

NAME	PZ-IV-31-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20041231
Time	14.10
INSTRUM	drx300
PROBHD	5 mm Multinucl
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6172.839 Hz
FIDRES	0.188380 Hz
AQ	2.6542580 sec
RG	1024
DW	81.000 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
D31	0.00000000 sec

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

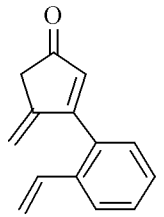
NUC1	1H
P1	7.05 usec
PL1	0.00 dB
SFO1	300.1318534 MHz

F2 - Processing parameters

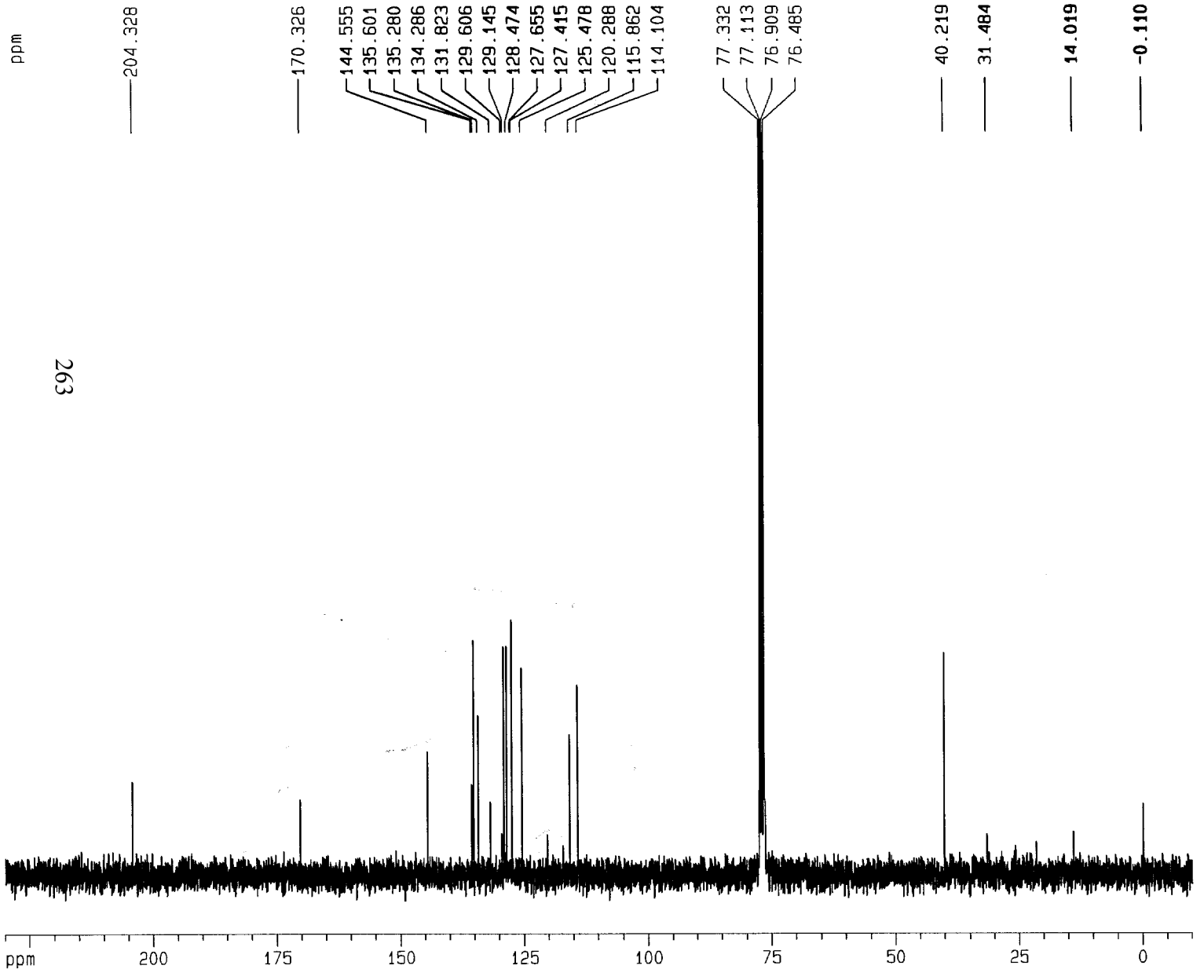
SI	32768
SF	300.1300022 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.30

1D NMR plot parameters

CX	20.00 cm
CY	12.50 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-1.000 ppm
F2	-300.13 Hz
PPMCM	0.55000 ppm/cm
HZCM	165.07150 Hz/cm



152



Current Data Parameters
NAME PZ-IV-31-A1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20041231
Time 14.41
INSTRUM drx300
PROBHD 5 mm Multinucl
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 2490
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 22528
DW 26.550 usec
DE 6.00 usec
TE 297.1 K
D1 1.29999995 sec
d11 0.03000000 sec
D31 0.00000000 sec

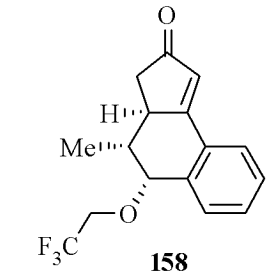
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 5.00 dB
SFO1 75.4760107 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 25.60 dB
SFO2 300.1312005 MHz

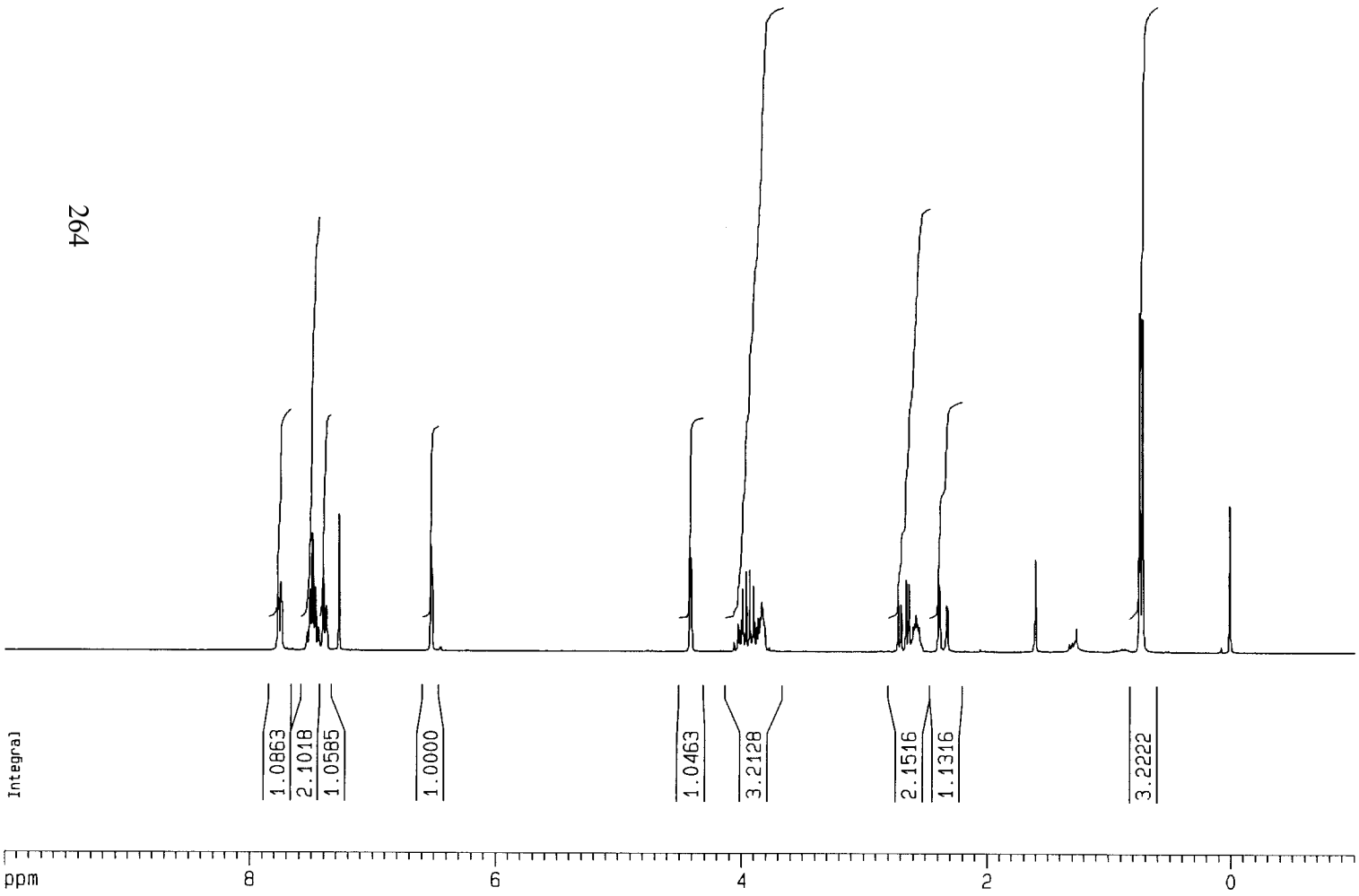
F2 - Processing parameters
SI 32768
SF 75.4677571 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 50.00 cm
F1P 230.000 ppm
F1 17357.58 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 12.00000 ppm/cm
HZCM 905.61310 Hz/cm

1H NMR
PZ-V-19-A2



158



Current Data Parameters
NAME PZ-V-19-A2
EXPNO 1
PROCNO 1

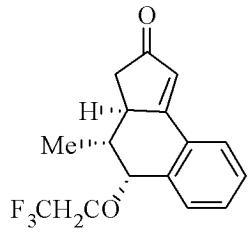
F2 - Acquisition Parameters
Date_ 20050414
Time 15.59
INSTRUM drx300
PROBHD 5 mm Multinucl
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 645.1
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
D31 0.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 7.05 usec
PL1 0.00 dB
SFO1 300.1318534 MHz

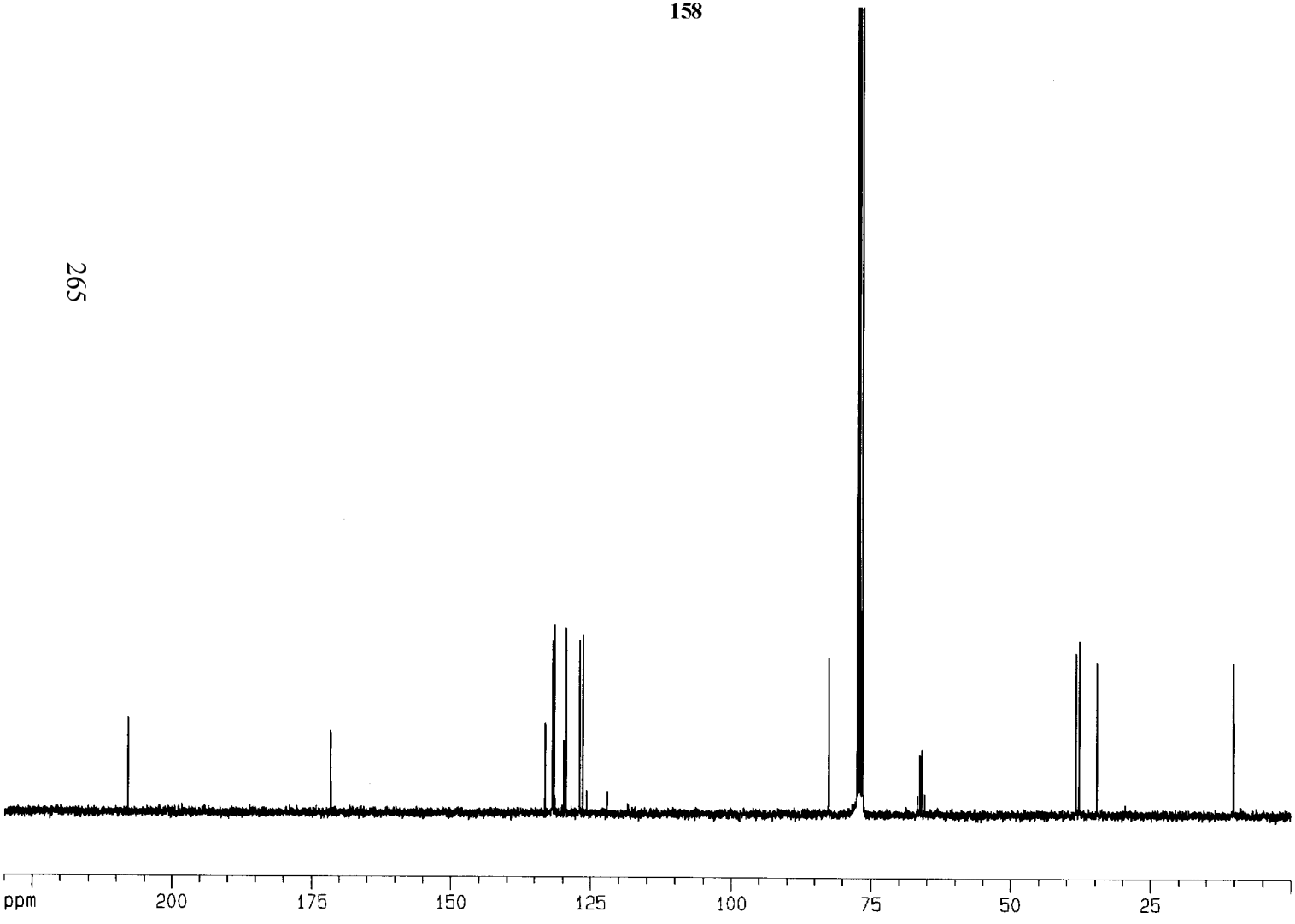
F2 - Processing parameters
SI 32768
SF 300.1300022 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.30

1D NMR plot parameters
CX 20.00 cm
CY 5.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -1.000 ppm
F2 -300.13 Hz
PPMCM 0.55000 ppm/cm
HZCM 165.07150 Hz/cm

13C NMR
PZ-V-19-A2



158



Current Data Parameters

NAME	PZ-V-19-A2
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20050414
Time	20.05
INSTRUM	drx300
PROBHD	5 mm Multinucl
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	4133
DS	4
SWH	18832.393 Hz
FIDRES	0.287360 Hz
AQ	1.7400308 sec
RG	1290.2
DW	26.550 usec
DE	6.00 usec
TE	297.1 K
D1	1.79999995 sec
d11	0.03000000 sec
D31	0.00000000 sec

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

NUC1	13C
P1	8.50 usec
PL1	5.00 dB
SFO1	75.4760107 MHz

======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	120.00 dB
PL12	25.60 dB
SFO2	300.1312005 MHz

F2 - Processing parameters

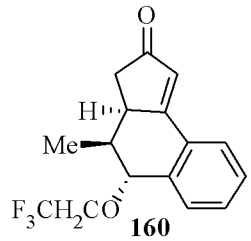
SI	32768
SF	75.4677571 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

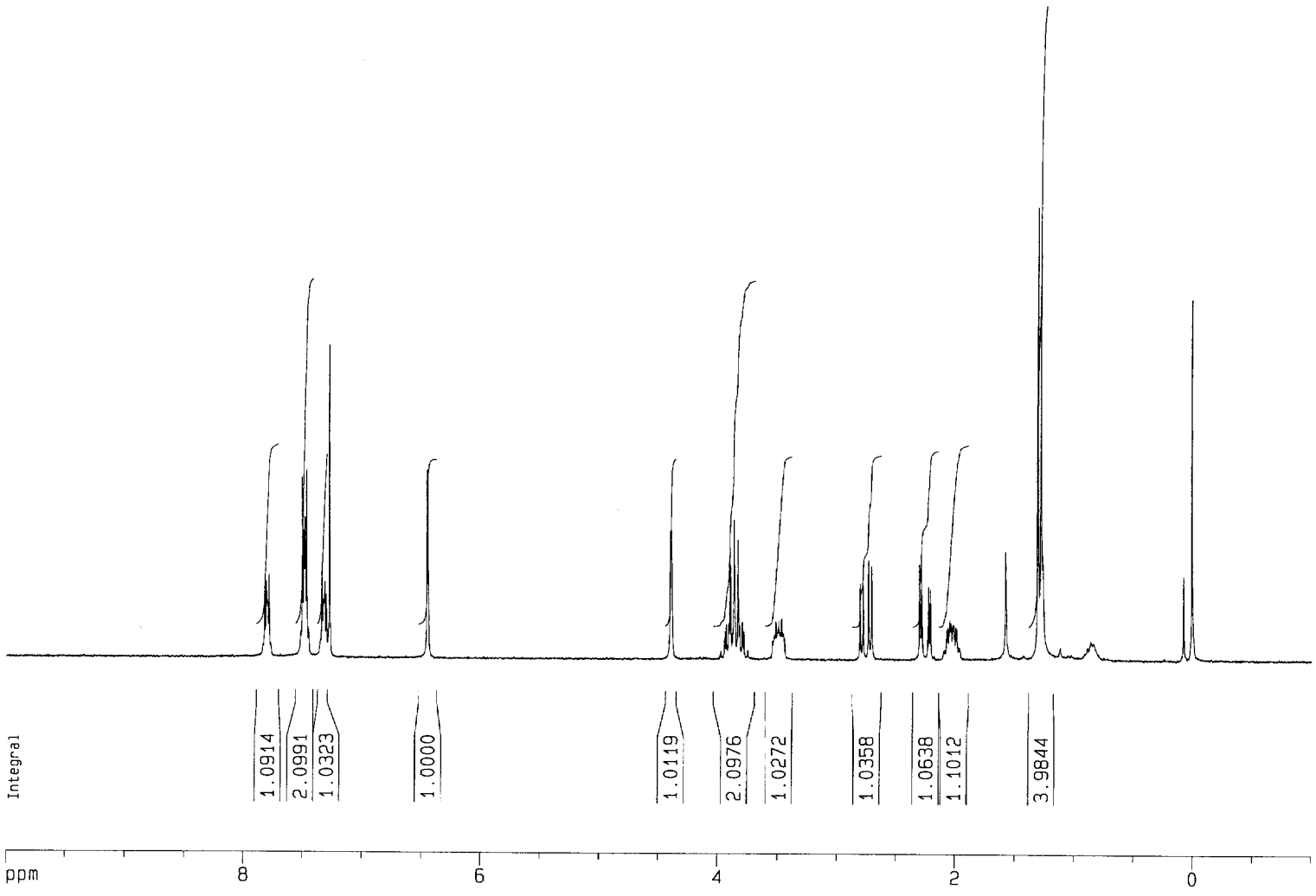
CX	20.00 cm
CY	20.00 cm
F1P	230.000 ppm
F1	17357.58 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	11.50000 ppm/cm
HZCM	867.87921 Hz/cm

1H NMR

PZ-IV-58-A1



160



Current Data Parameters

NAME	PZ-IV-58-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050127
Time	20.43
INSTRUM	arx250
PROBHD	5 mm GNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	2860
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	8.70 use
SFO1	250.1315321 MHz
NUCLEUS	1H

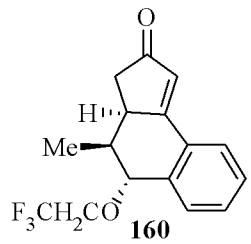
F2 - Processing parameters

SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

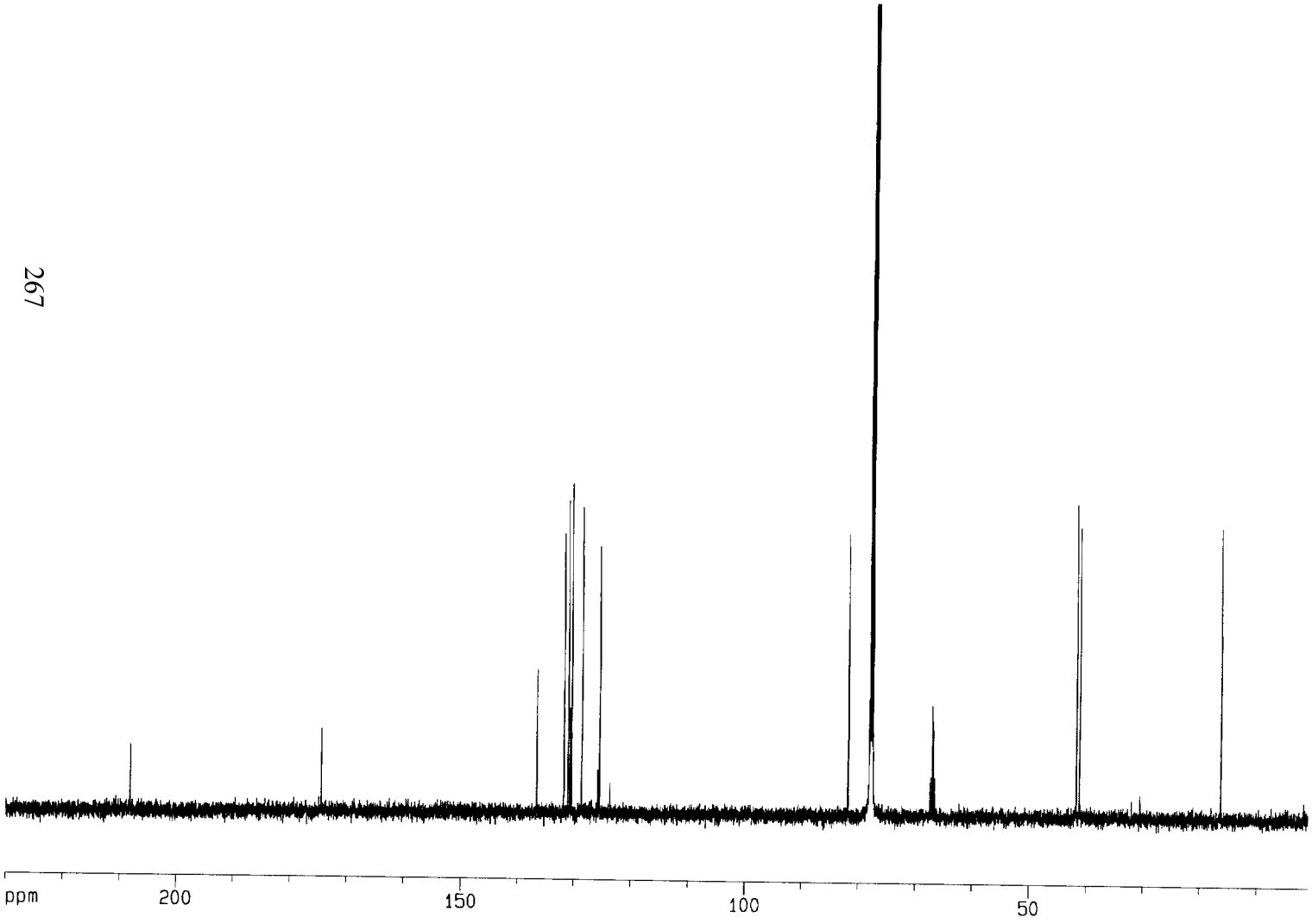
1D NMR plot parameters

CX	20.00 cm
CY	7.00 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57150 Hz/

13C-NMR
PZ-IV-58-A1



160



Current Data Parameters	
NAME	PZ-IV-58-A1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters	
Date_	20050127
Time	20.40
INSTRUM	DRX500
PROBHD	5 mm Multinucl
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	2822
DS	4
SWH	39681.812 Hz
FIDRES	0.605496 Hz
AQ	0.8258188 sec
RG	16384
DW	12.600 usec
DE	6.00 usec
TE	298.0 K
D1	2.00000000 sec
d11	0.03000000 sec

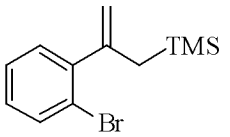
======== CHANNEL f1 ========	
NUC1	13C
P1	8.10 usec
PL1	3.00 dB
SF01	125.7713108 MHz

======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	88.00 usec
PL2	0.00 dB
PL12	21.00 dB
SF02	500.1320005 MHz

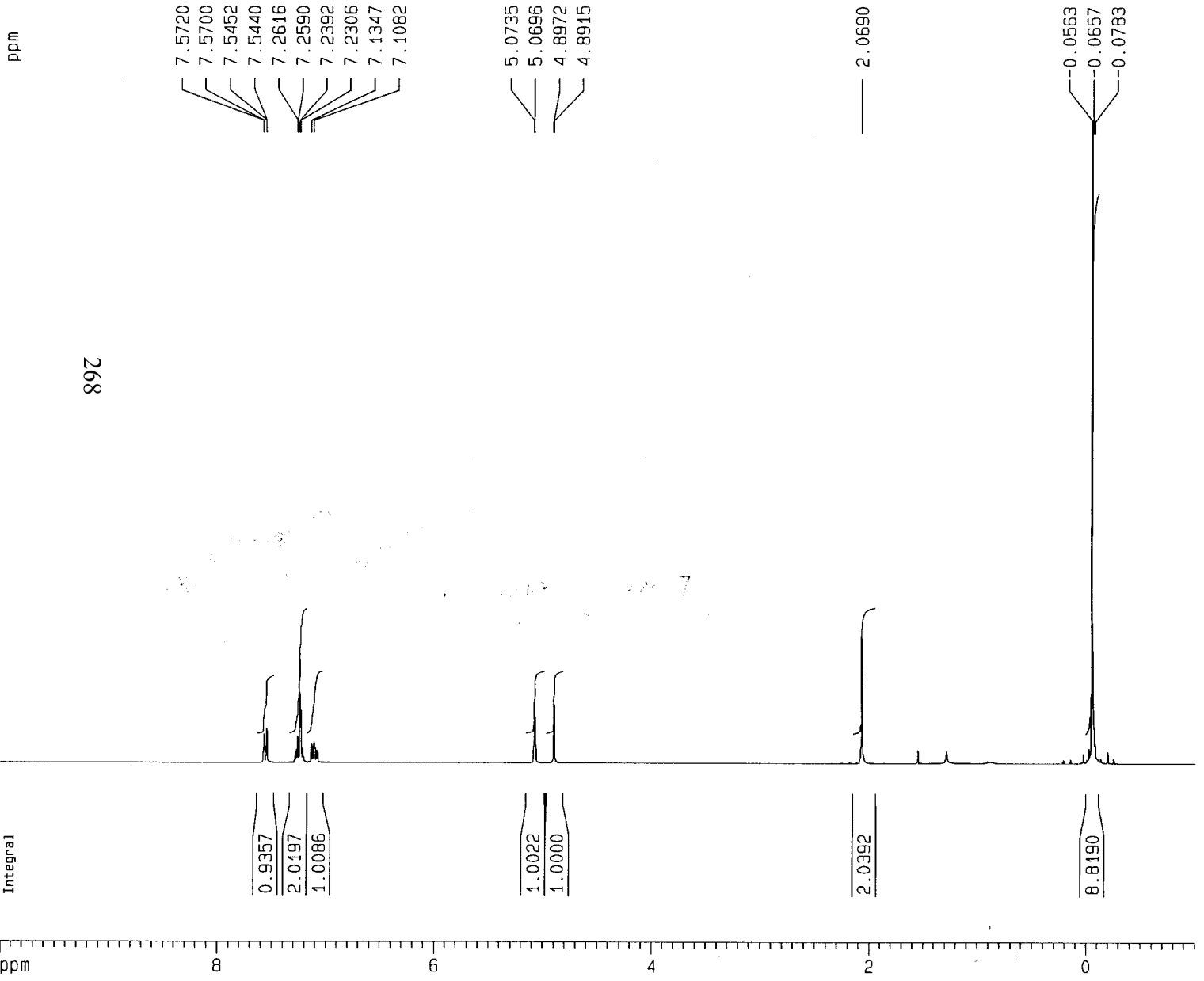
F2 - Processing parameters	
SI	32768
SF	125.7576929 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters	
CX	20.00 cm
CY	50.00 cm
F1P	230.000 ppm
F1	28924.27 Hz
F2P	1.000 ppm
F2	125.76 Hz
PPMCM	11.45000 ppm/cm
HZCM	1439.92554 Hz/cm

1H NMR
PZ-V-50-A1



242



Current Data Parameters

NAME	PZ-V-50-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050518
Time	11.33
INSTRUM	drx300
PROBHD	5 mm Multinucl
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6172.839 Hz
FIDRES	0.188380 Hz
AQ	2.6542580 sec
RG	128
DW	81.000 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
D31	0.00000000 sec

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

NUC1	1H
P1	7.05 usec
PL1	0.00 dB
SFO1	300.1318534 MHz

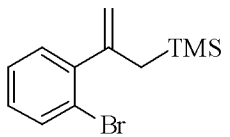
F2 - Processing parameters

SI	32768
SF	300.1300022 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.30

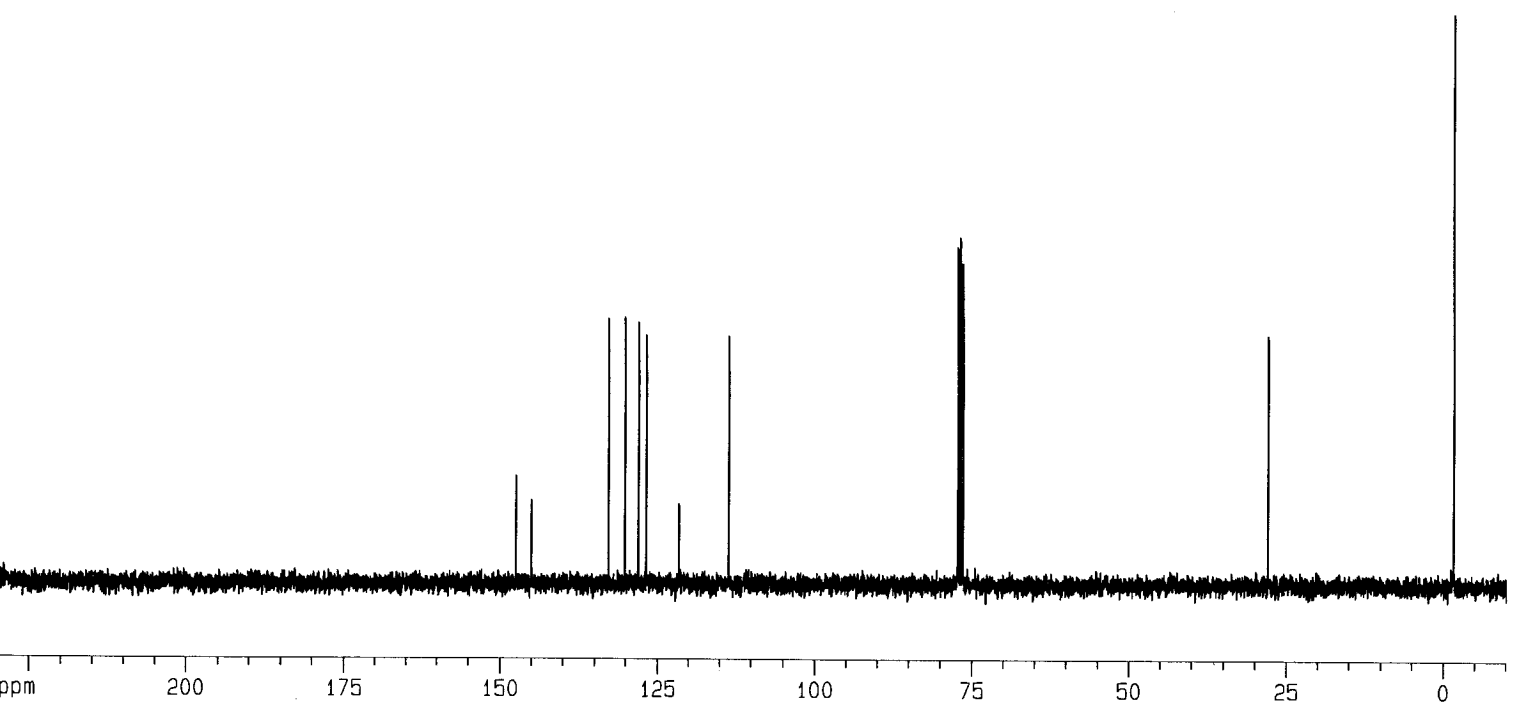
1D NMR plot parameters

CX	20.00 cm
CY	15.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-1.000 ppm
F2	-300.13 Hz
PPMCM	0.55000 ppm/cm
HZCM	165.07150 Hz/cm

13C NMR
PZ-V-50-A1



242



Current Data Parameters

NAME	PZ-V-50-A1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20050518
Time	11.35
INSTRUM	drx300
PROBHD	5 mm Multinucl
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	57
DS	4
SWH	18832.393 Hz
FIDRES	0.287360 Hz
AQ	1.7400308 sec
RG	2580.3
DW	26.550 usec
DE	6.00 usec
TE	297.1 K
D1	1.79999995 sec
d11	0.03000000 sec
D31	0.00000000 sec

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

NUC1	13C
P1	8.50 usec
PL1	5.00 dB
SFO1	75.4760107 MHz

======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	120.00 dB
PL12	25.60 dB
SFO2	300.1312005 MHz

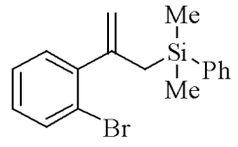
F2 - Processing parameters

SI	32768
SF	75.4677571 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

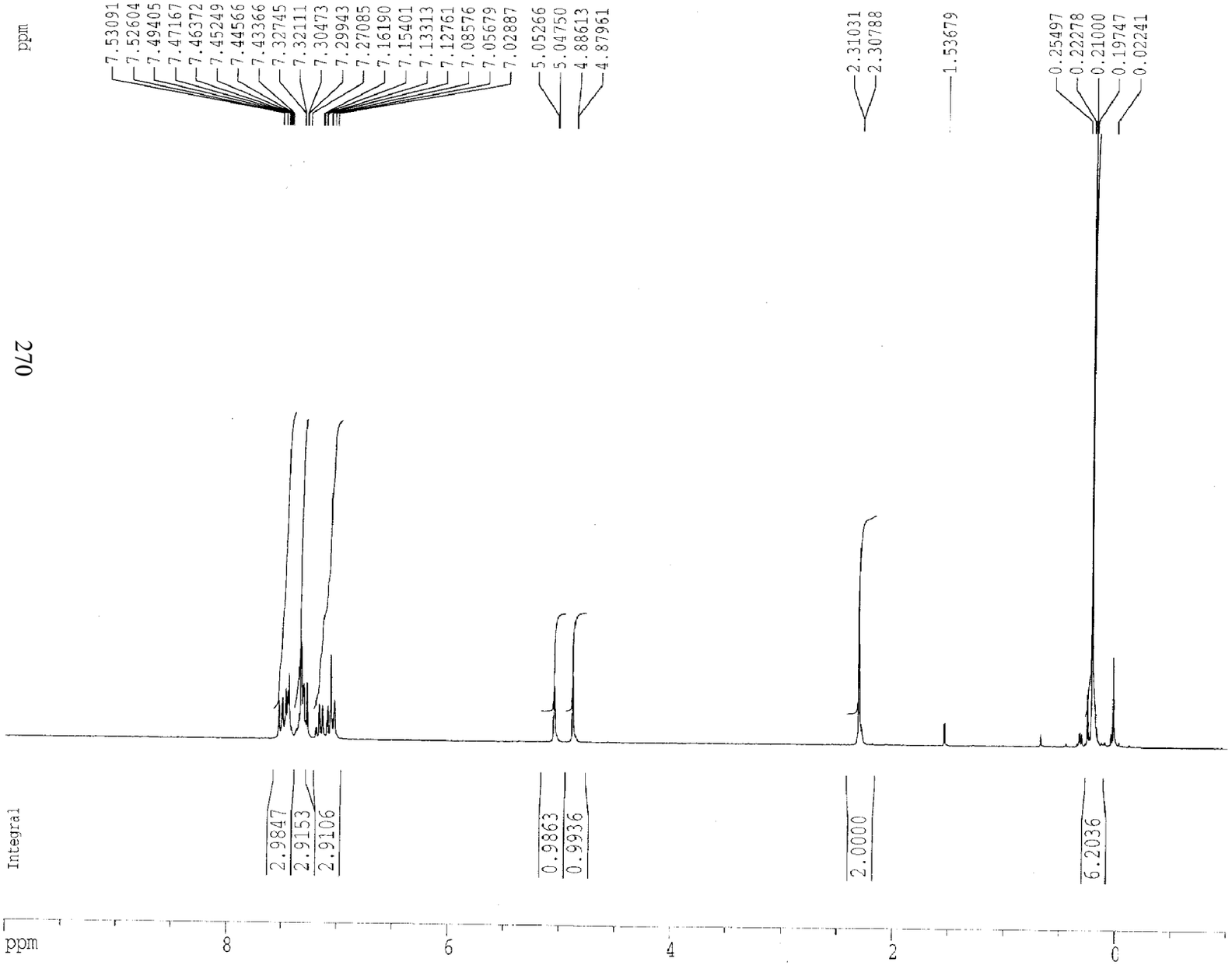
1D NMR plot parameters

CX	20.00 cm
CY	8.00 cm
F1P	230.000 ppm
F1	17357.58 Hz
F2P	-10.000 ppm
F2	-754.68 Hz
PPMCM	12.00000 ppm/cm
HZCM	905.61310 Hz/cm

1H NMR
PZ-VII-78-D3
distillate residue



270



Current Data Parameters

NAME	PZ-VII-78-D3
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20060914
Time	18.06
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	1430
DW	96.000 usec
DE	137.14 usec
TE	300.0 K
D1	1.00000000 sec
P1	9.50 usec
SFO1	250.1315321 MHz
NUCLEUS	1H

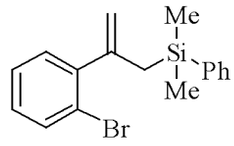
F2 - Processing parameters

SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	12.50 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm/cm
HZCM	137.57150 Hz/cm

13C NMR
PZ-VII-78-D3



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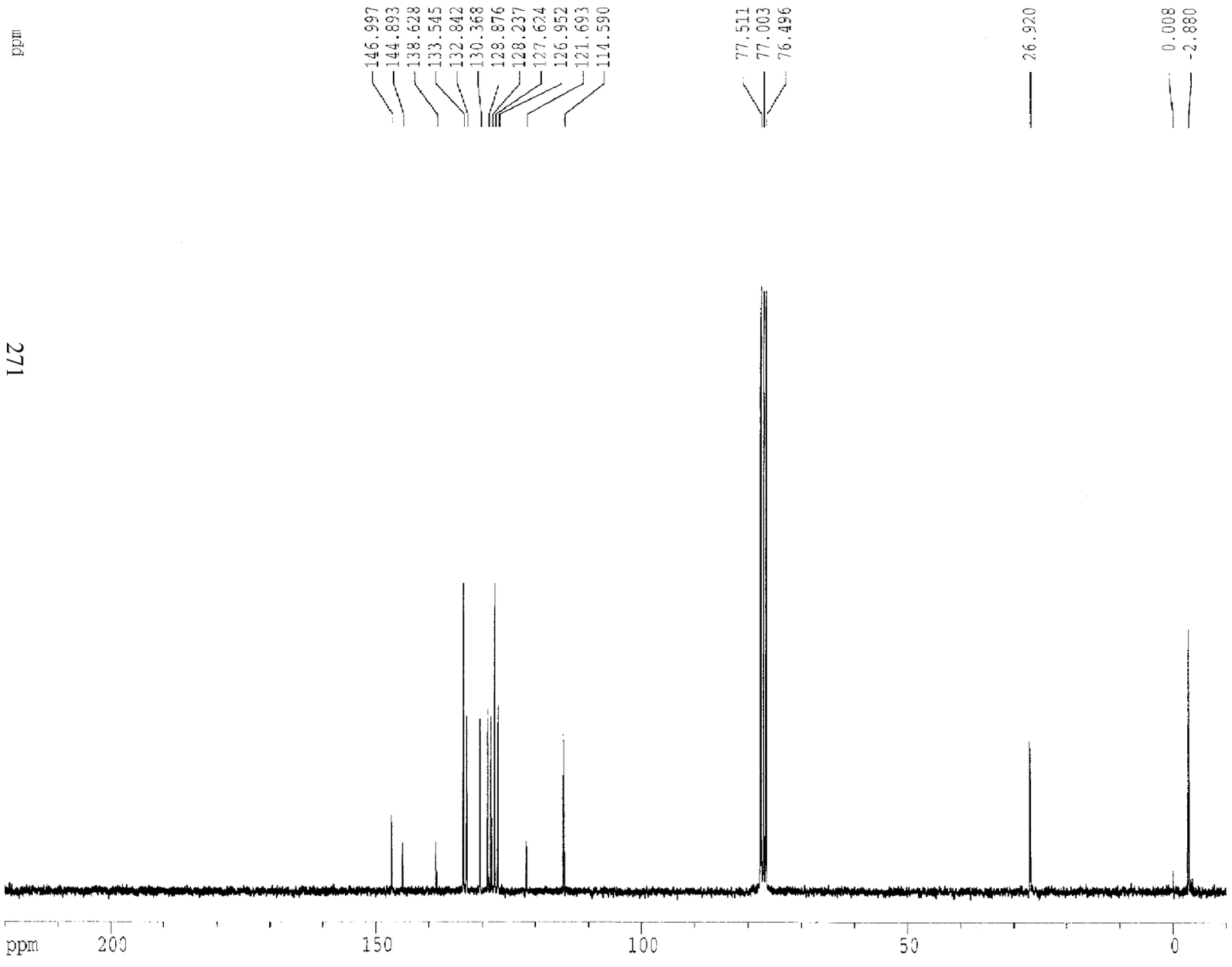

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Current Data Parameters

NAME	PZ-VII-78-D3
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20060914
Time	22.09
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	4531
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 usec
DE	41.43 usec
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 usec
D1	2.00000000 sec
P1	8.00 usec
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

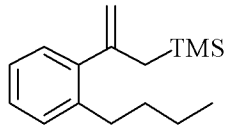
F2 - Processing parameters

SI	32768
SF	62.8952403 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

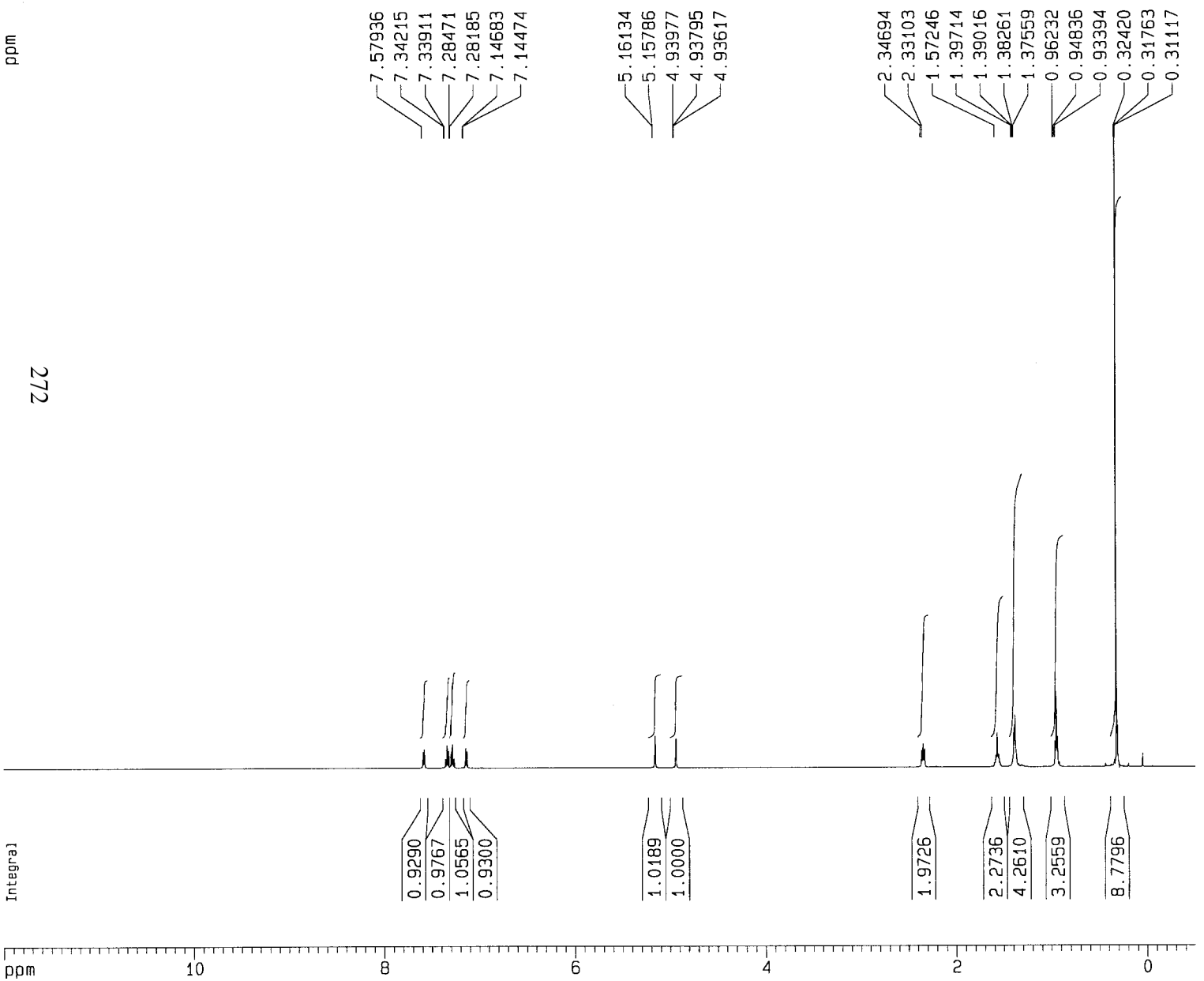
1D NMR plot parameters

CX	20.00 cm
CY	10.00 cm
F1P	220.000 ppm
F1	13836.95 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	11.50000 ppm/cm
HZCM	723.29529 Hz/cm

1H-NMR
PZ-V-63-1-A1
RLi quenched by H20, purified by pentane
8th-10th tube



244



272

Current Data Parameters

NAME	PZ-V-63-2-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050610
Time	14.11
INSTRUM	DRX500
PROBHD	5 mm Multinucl
PULPROG	zg30
TD	57344
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.180151 Hz
AQ	2.7754996 sec
RG	64
DW	48.400 usec
DE	6.00 usec
TE	296.7 K
D1	1.00000000 sec

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

NUC1	1H
P1	13.25 usec
PL1	-3.00 dB
SFO1	500.1330885 MHz

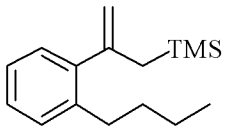
F2 - Processing parameters

SI	32768
SF	500.1300000 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.40

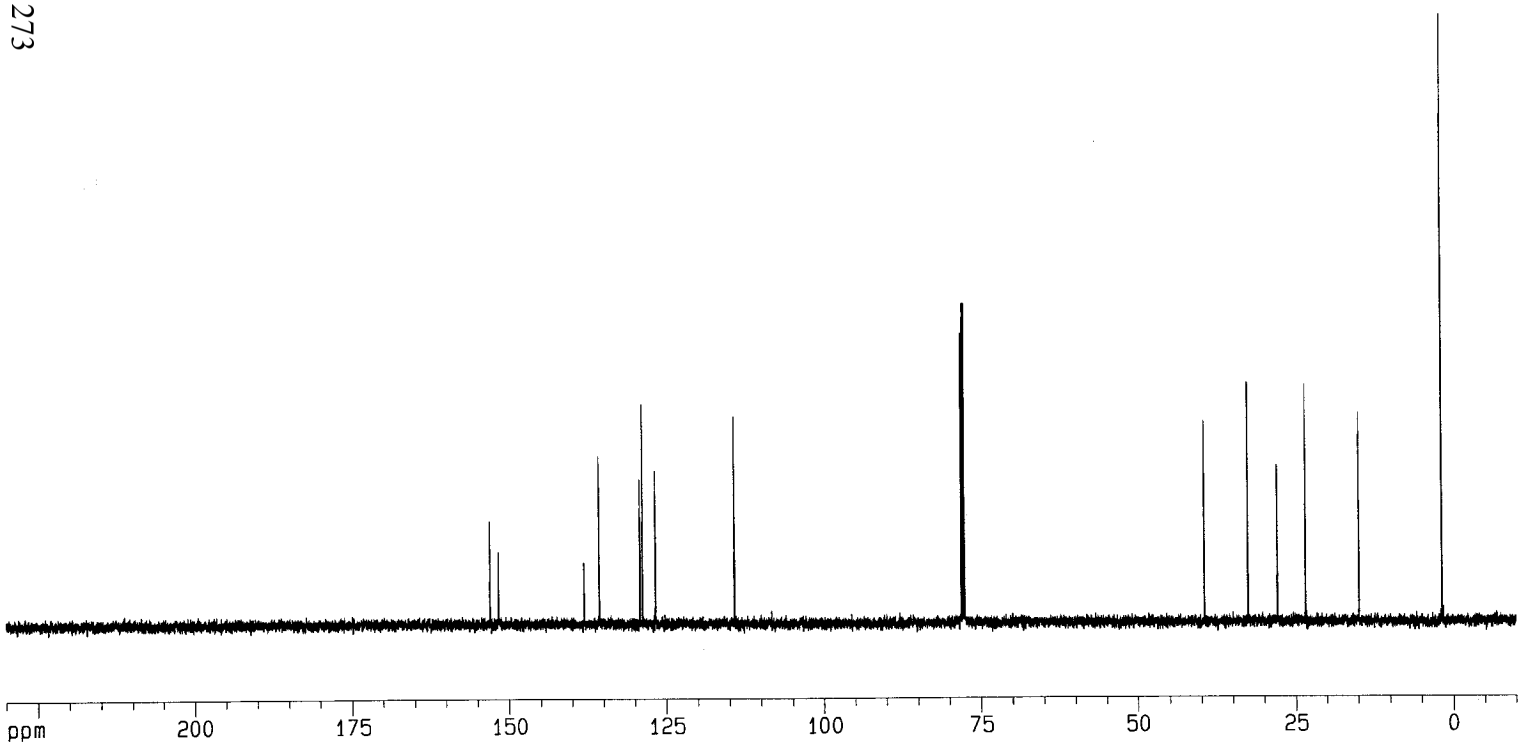
1D NMR plot parameters

CX	20.00 cm
CY	12.50 cm
F1P	12.000 ppm
F1	6001.56 Hz
F2P	-0.500 ppm
F2	-250.07 Hz
PPMCM	0.62500 ppm/cr
HZCM	312.58124 Hz/cm

13C-NMR
PZ-V-63-1-A1
RLi quenched by H20, Column purified by Pentane
8th-10th tube



244



Current Data Parameters

NAME	PZ-V-63-2-A1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20050610
Time	14.13
INSTRUM	DRX500
PROBHD	5 mm Multinucl
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	47
DS	4
SWH	39681.812 Hz
FIDRES	0.605496 Hz
AQ	0.8258188 sec
RG	7298.2
DW	12.600 usec
DE	6.00 usec
TE	298.0 K
D1	2.00000000 sec
d11	0.03000000 sec

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

NUC1	13C
P1	8.10 usec
PL1	3.00 dB
SFO1	125.7713108 MHz

======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	88.00 usec
PL2	0.00 dB
PL12	21.00 dB
SFO2	500.1320005 MHz

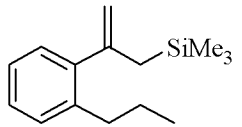
F2 - Processing parameters

SI	32768
SF	125.7576929 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	2.00

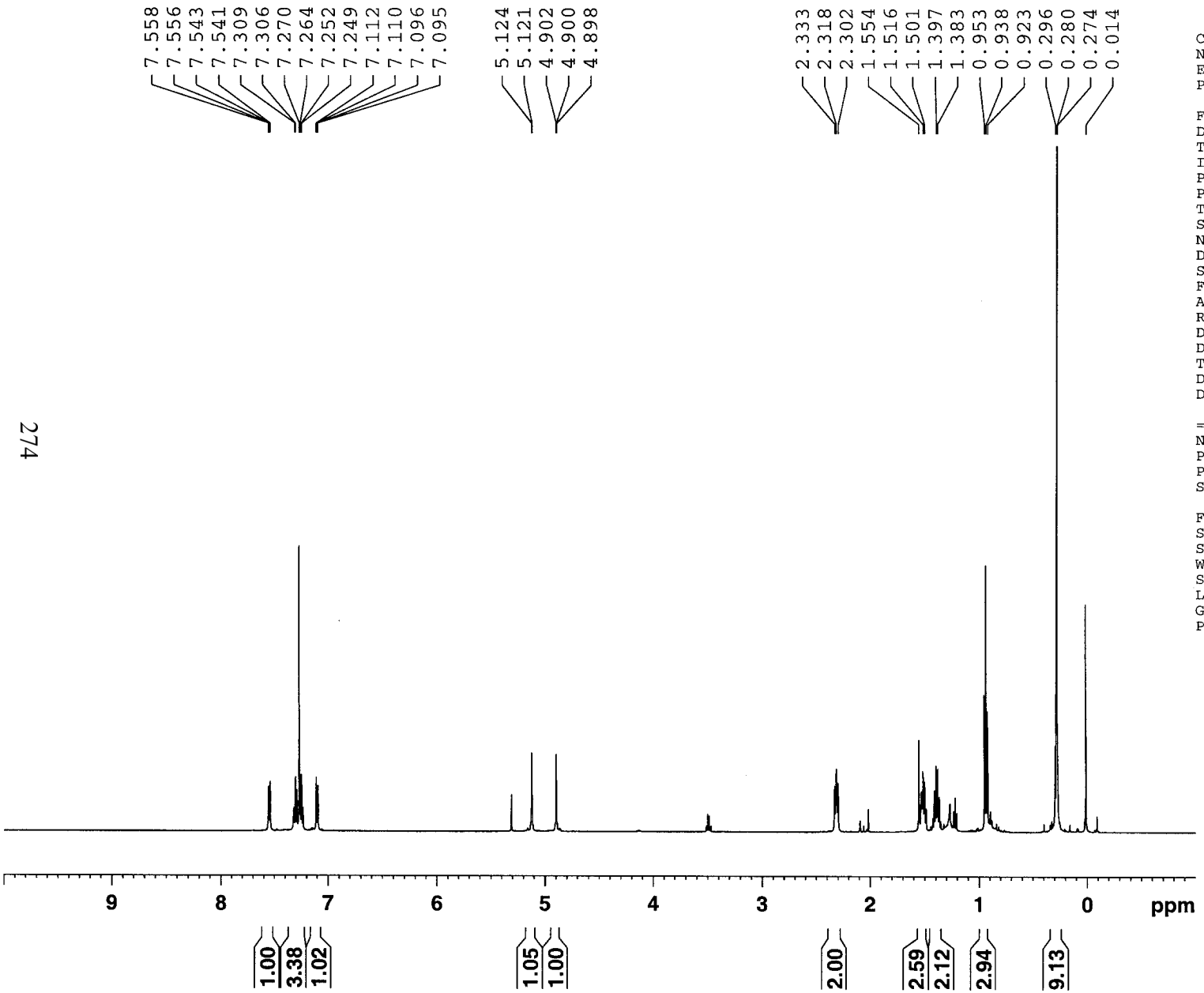
1D NMR plot parameters

CX	20.00 cm
CY	8.00 cm
F1P	230.000 ppm
F1	28924.27 Hz
F2P	-10.000 ppm
F2	-1257.58 Hz
PPMCM	12.00000 ppm/cm
HZCM	1509.09229 Hz/cm

1H NMR
PZ-V-124-A1



245



274

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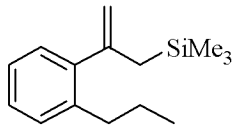
Current Data Parameters
NAME                 PZ-V-124-A1
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20060510
Time                       15.50
INSTRUM                   DRX500
PROBHD    5 mm Multinucl
PULPROG                  zg30pad
TD                         65536
SOLVENT                    CDCl3
NS                            16
DS                             2
SWH                   10330.578 Hz
FIDRES                 0.157632 Hz
AQ                    3.1719923 sec
RG                         161.3
DW                        48.400 usec
DE                         6.00 usec
TE                        300.0 K
D1                    1.00000000 sec
D31                   0.00000000 sec

======== CHANNEL f1 ========
NUC1                          1H
P1                        11.50 usec
PL1                        0.00 dB
SFO1                500.1330885 MHz

F2 - Processing parameters
SI                         32768
SF                  500.1300087 MHz
WDW                           EM
SSB                            0
LB                         0.30 Hz
GB                             0
PC                          1.40
```

13C NMR
PZ-V-124-A1



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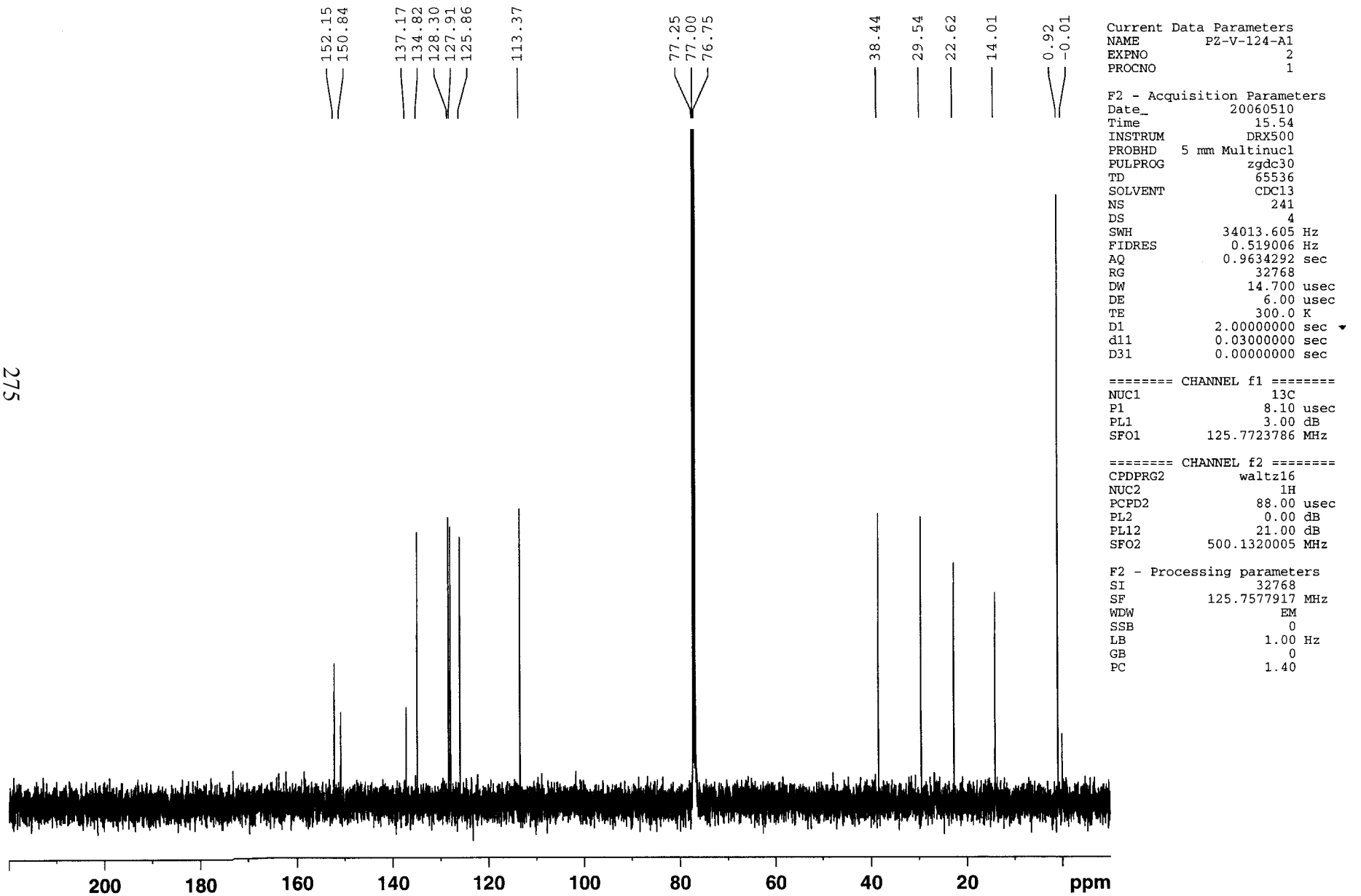


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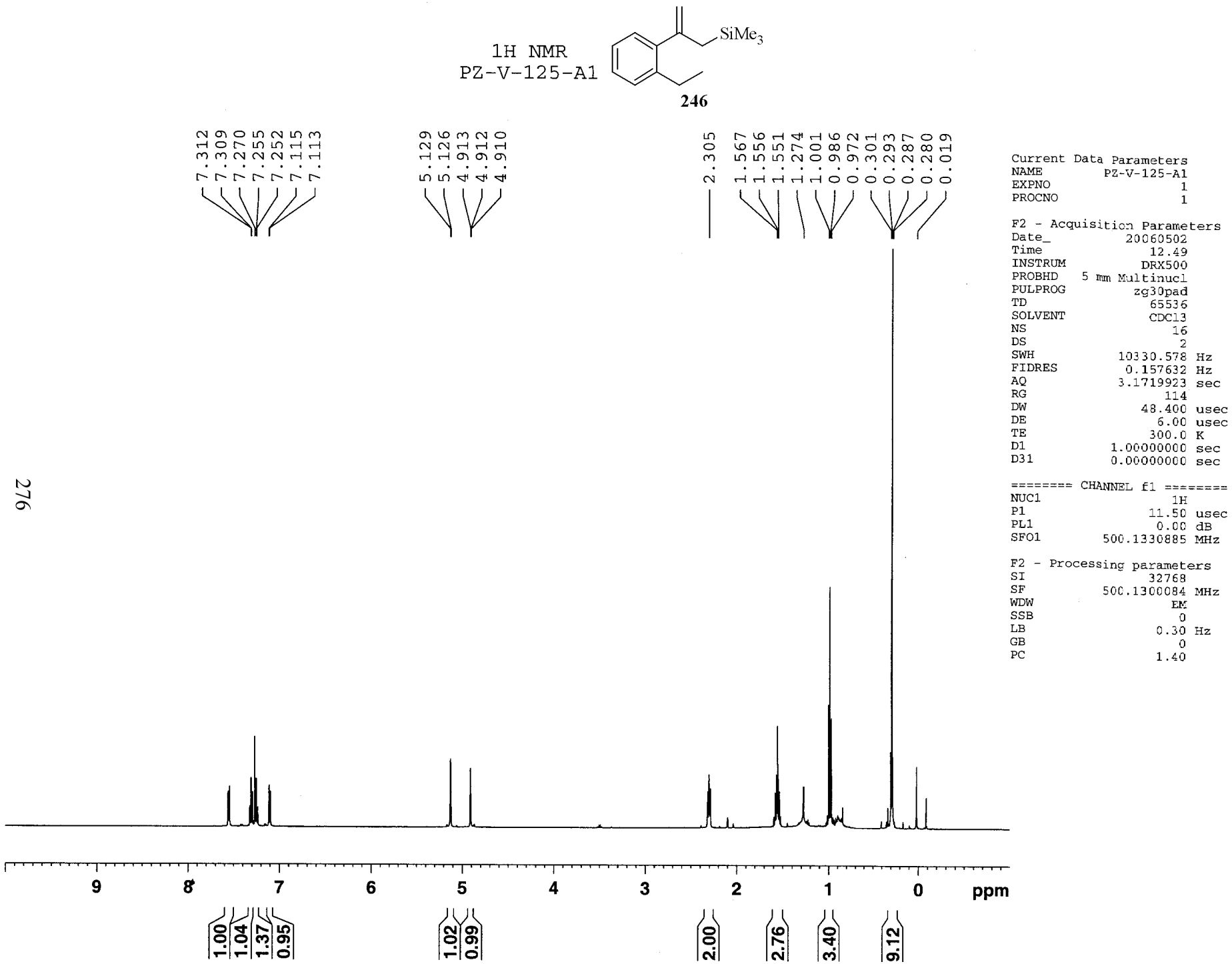
Current Data Parameters
NAME          PZ-V-124-A1
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20060510
Time               15.54
INSTRUM          DRX500
PROBHD   5 mm Multinucl
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                  241
DS                    4
SWH           34013.605 Hz
FIDRES         0.519006 Hz
AQ             0.9634292 sec
RG                32768
DW               14.700 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
D31           0.00000000 sec

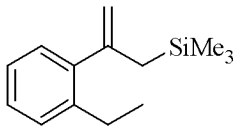
======== CHANNEL f1 ========
NUC1                13C
P1                8.10 usec
PL1               3.00 dB
SFO1        125.7723786 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            88.00 usec
PL2               0.00 dB
PL12             21.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                32768
SF          125.7577917 MHz
WDW                EM
SSB                 0
LB              1.00 Hz
GB                  0
PC               1.40
```


1H NMR
PZ-V-125-A1
SiMe3
246
7.312
7.309
7.270
7.255
7.252
7.115
7.113
5.129
5.126
4.913
4.912
4.910
2.305
1.567
1.556
1.551
1.274
1.001
0.986
0.972
0.301
0.293
0.287
0.280
0.019
Current Data Parameters
NAME PZ-V-125-A1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060502
Time 12.49
INSTRUM DRX500
PROBHD 5 mm Multinucl
PULPROG zg30pad
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 114
DW 48.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
D31 0.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 11.50 usec
PL1 0.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300084 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.04
1.37
0.95
1.02
0.99
2.00
2.76
3.40
9.12

13C NMR
PZ-V-125-A1



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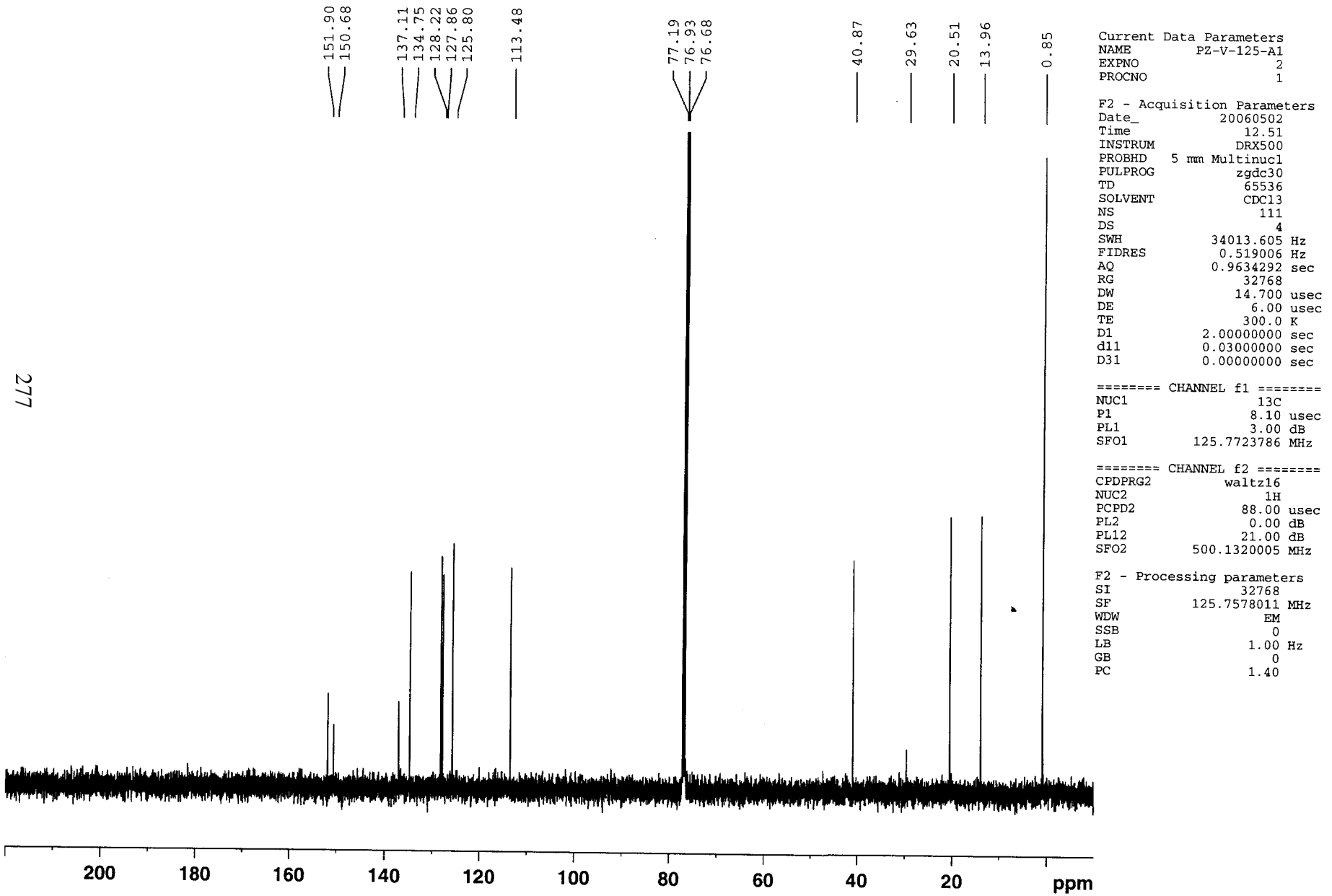

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Current Data Parameters
NAME PZ-V-125-A1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060502
Time 12.51
INSTRUM DRX500
PROBHD 5 mm Multinucl
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 111
DS 4
SWH 34013.605 Hz
FIDRES 0.519006 Hz
AQ 0.9634292 sec
RG 32768
DW 14.700 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
D31 0.00000000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 8.10 usec
PL1 3.00 dB
SFO1 125.7723786 MHz

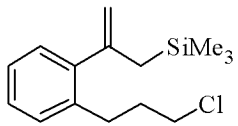
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 88.00 usec
PL2 0.00 dB
PL12 21.00 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 32768
SF 125.7578011 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1H NMR

PZ-V-126-A2

Chromatron, pentane, 16th tube



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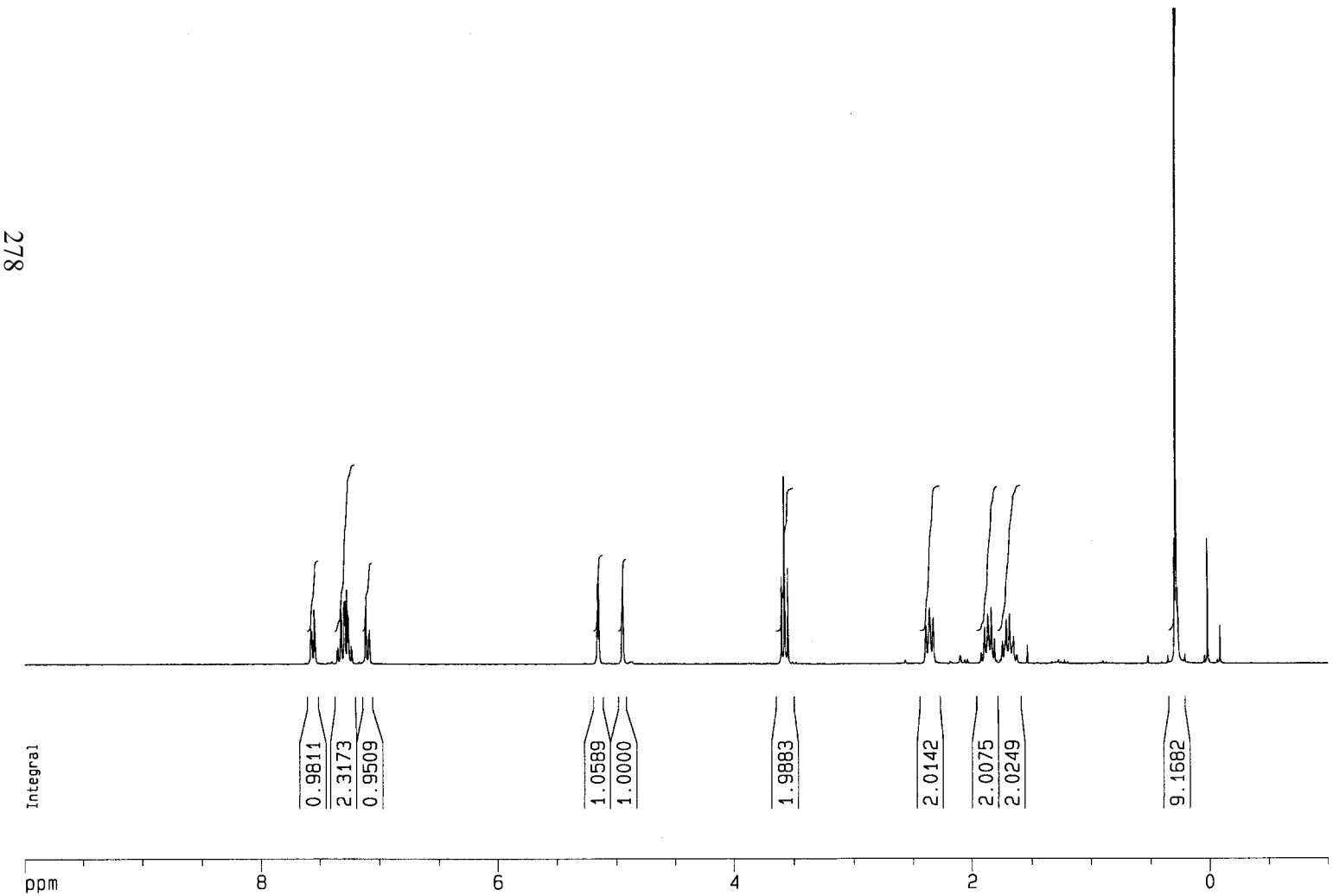


Current Data Parameters

NAME	PZ-V-126-A2
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20050815
Time	23.42
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	1024
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	8.70 use
SFO1	250.1315321 MHz
NUCLEUS	1H

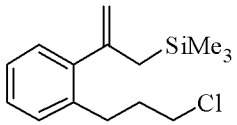
F2 - Processing parameters

SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

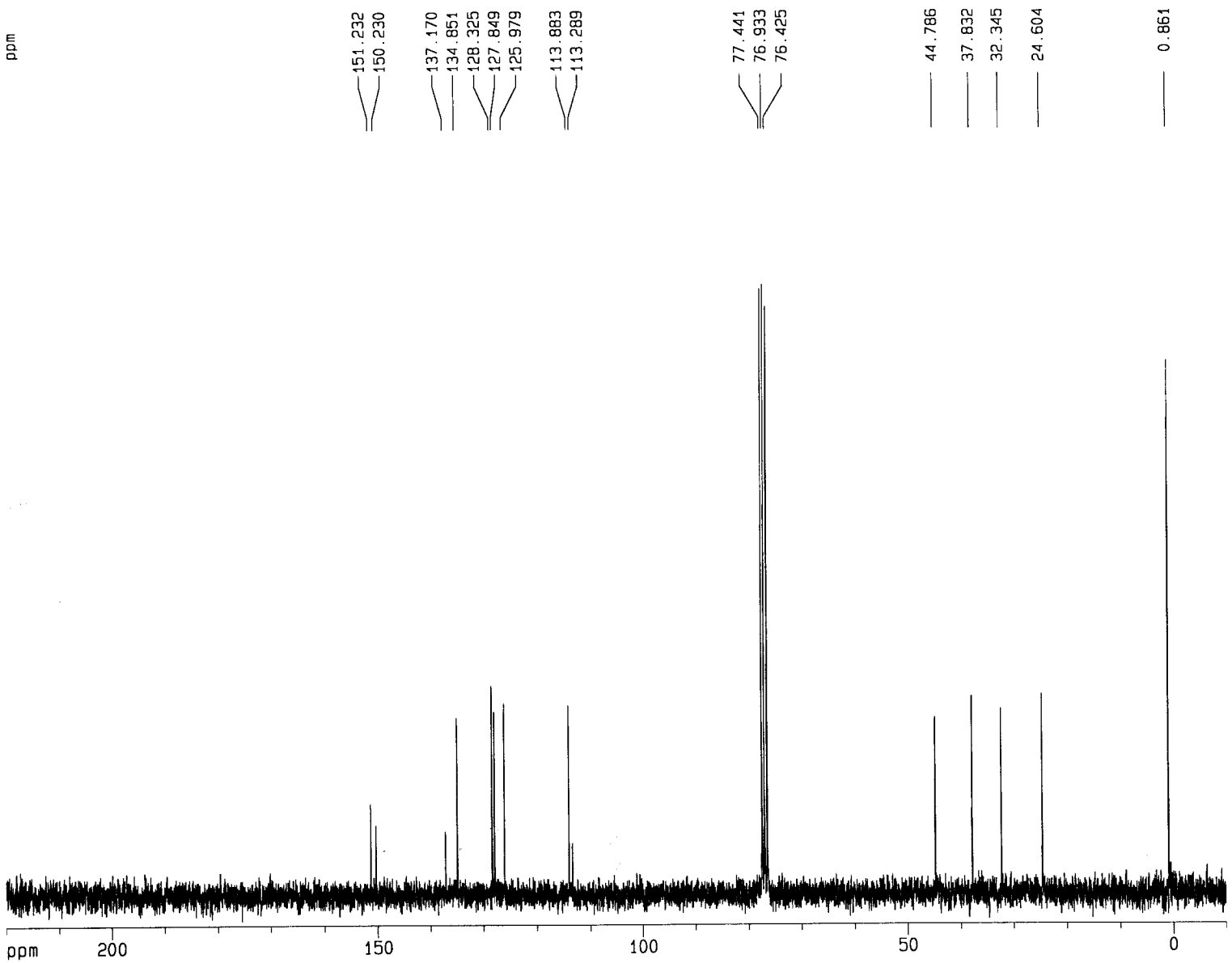
1D NMR plot parameters

CX	20.00 cm
CY	30.00 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57150 Hz/

13C NMR
PZ-V-126-A2



247



Current Data Parameters

NAME	PZ-V-126-A2
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

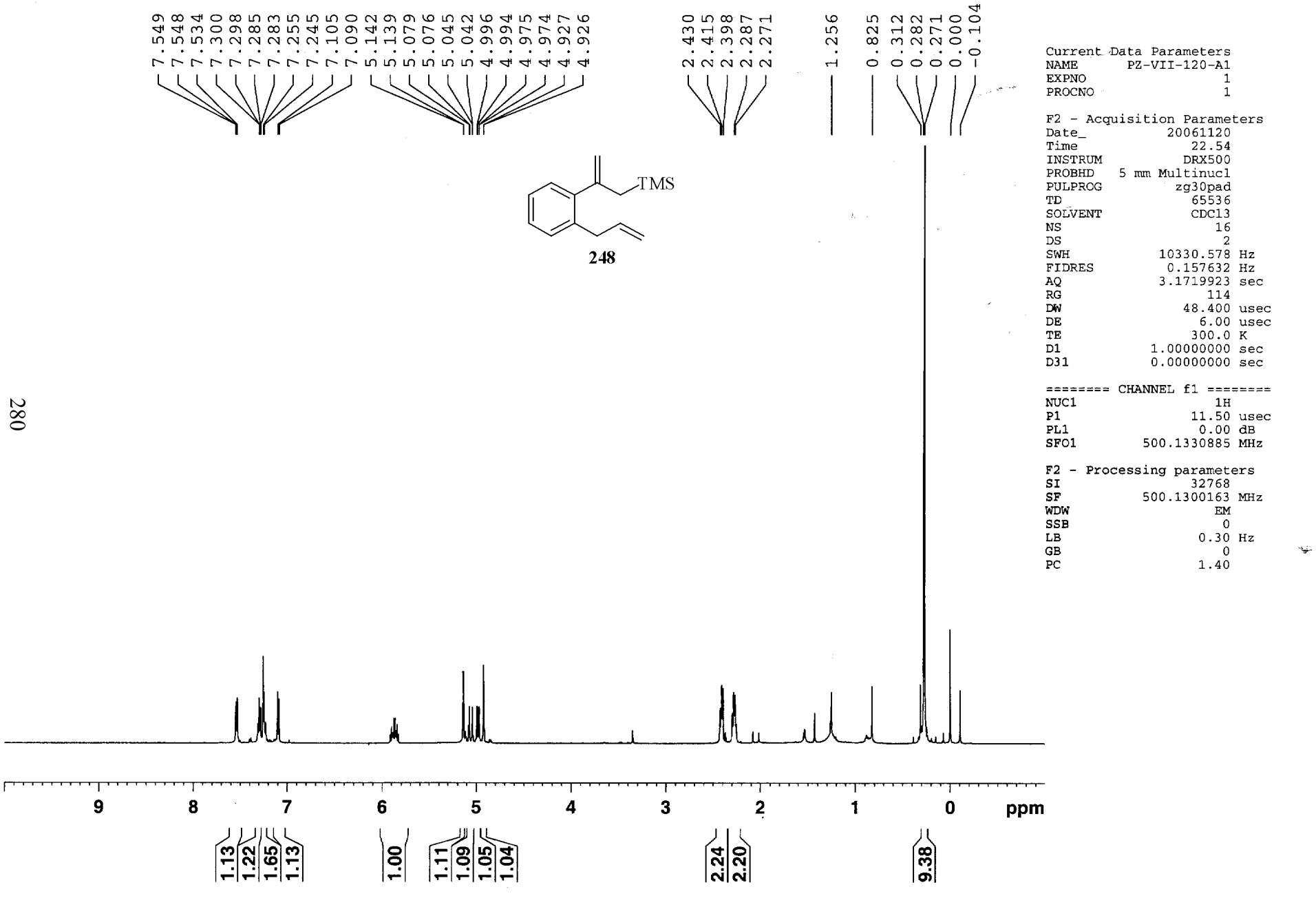
Date_	20050815
Time	23.46
INSTRUM	arx250
PROBHD	5 mm GNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	474
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	2.00000000 sec
P1	6.00 use
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

F2 - Processing parameters

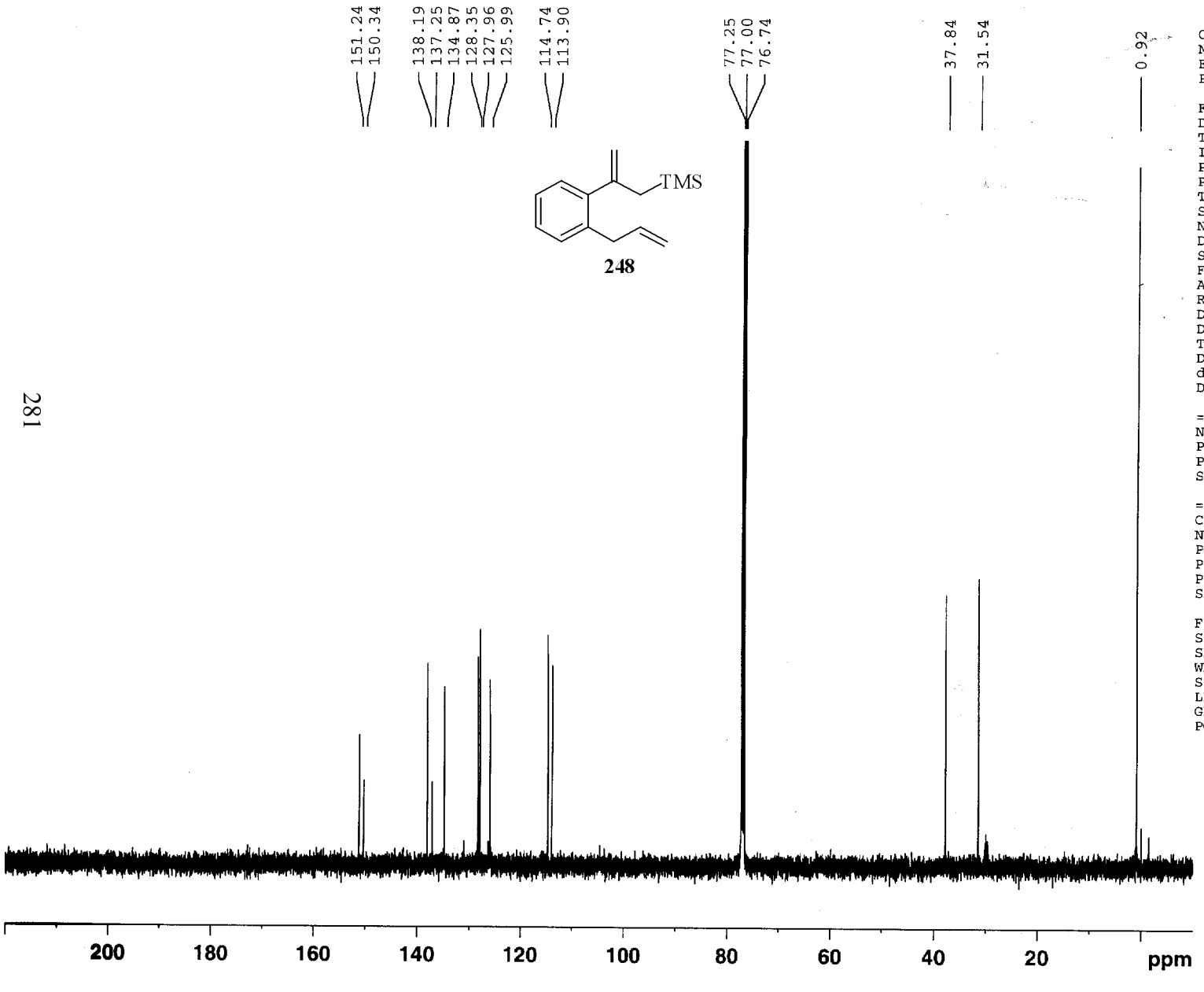
SI	32768
SF	62.8952440 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	10.00 cm
F1P	220.000 ppm
F1	13836.95 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	11.50000 ppm
HZCM	723.29529 Hz/


7.549
7.548
7.534
7.300
7.298
7.285
7.283
7.255
7.245
7.105
7.090
5.142
5.139
5.079
5.076
5.045
5.042
4.996
4.994
4.975
4.974
4.927
4.926
2.430
2.415
2.398
2.287
2.271
1.256
0.825
0.312
0.282
0.271
0.000
-0.104
TMS
248
Current Data Parameters
NAME PZ-VII-120-A1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20061120
Time 22.54
INSTRUM DRX500
PROBHD 5 mm Multinucl
PULPROG zg30pad
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 114
DW 48.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
D31 0.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 11.50 usec
PL1 0.00 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300163 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
9
8
7
6
5
4
3
2
1
0
ppm
1.13
1.22
1.65
1.13
1.00
1.11
1.09
1.05
1.04
2.24
2.20
9.38

13C NMR
PZ-VII-120-A1



248

Current Data Parameters
NAME PZ-VII-120-A1
EXPNO 2
PROCNO 1

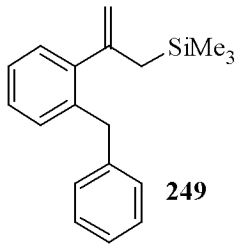
F2 - Acquisition Parameters
Date_ 20061120
Time 23.00
INSTRUM DRX500
PROBHD 5 mm Multinucl
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 524
DS 4
SWH 34013.605 Hz
FIDRES 0.519006 Hz
AQ 0.9634292 sec
RG 32768
DW 14.700 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
D31 0.00000000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 8.10 usec
PL1 3.00 dB
SFO1 125.7723786 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 88.00 usec
PL2 0.00 dB
PL12 21.00 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 32768
SF 125.7577928 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1H NMR
PZ-V-131-A1



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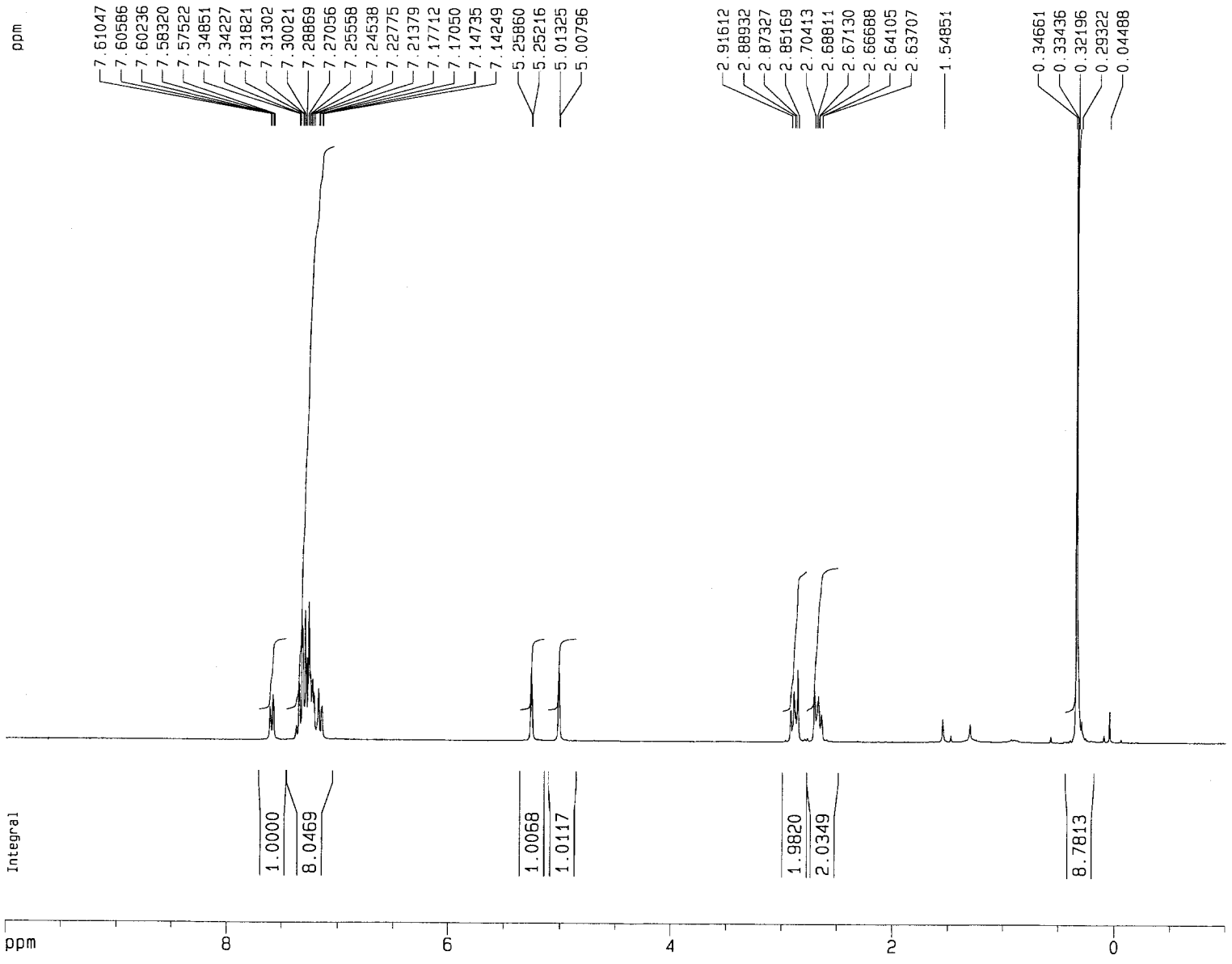


Current Data Parameters

NAME	PZ-V-131-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20060517
Time	15.14
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	715
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	9.50 use
SFO1	250.1315321 MHz
NUCLEUS	1H

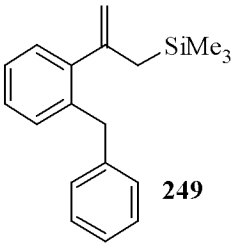
F2 - Processing parameters

SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	25.00 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57150 Hz/

13C NMR
PZ-V-131-A1



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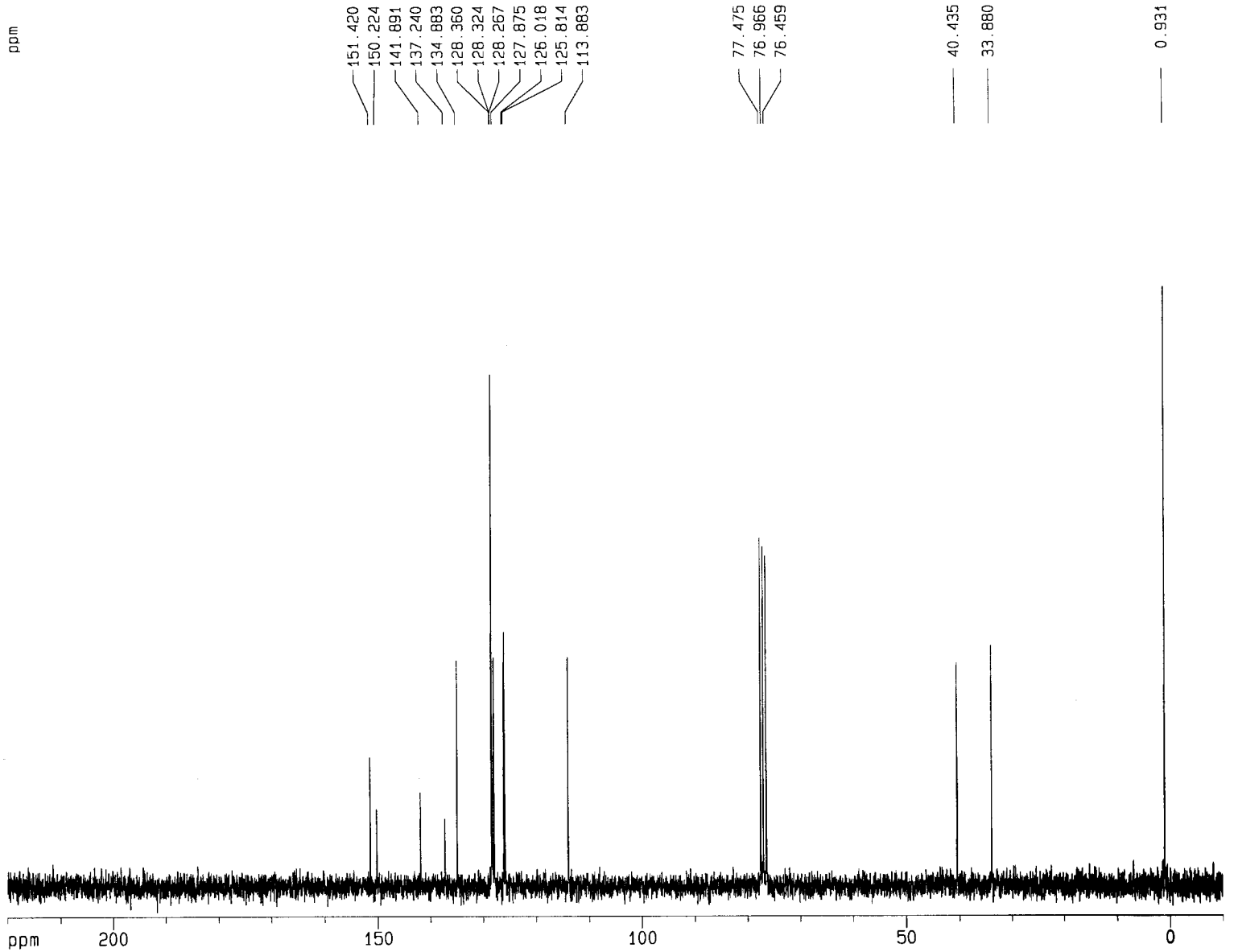


Current Data Parameters

NAME	PZ-V-131-A1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20060517
Time	15.17
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	180
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	2.00000000 sec
P1	8.00 use
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

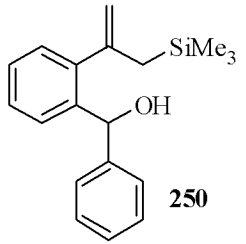
F2 - Processing parameters

SI	32768
SF	62.8952440 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	10.00 cm
F1P	220.000 ppm
F1	13836.95 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	11.50000 ppm
HZCM	723.29529 Hz/

1H-NMR
PZ-V-132-A3



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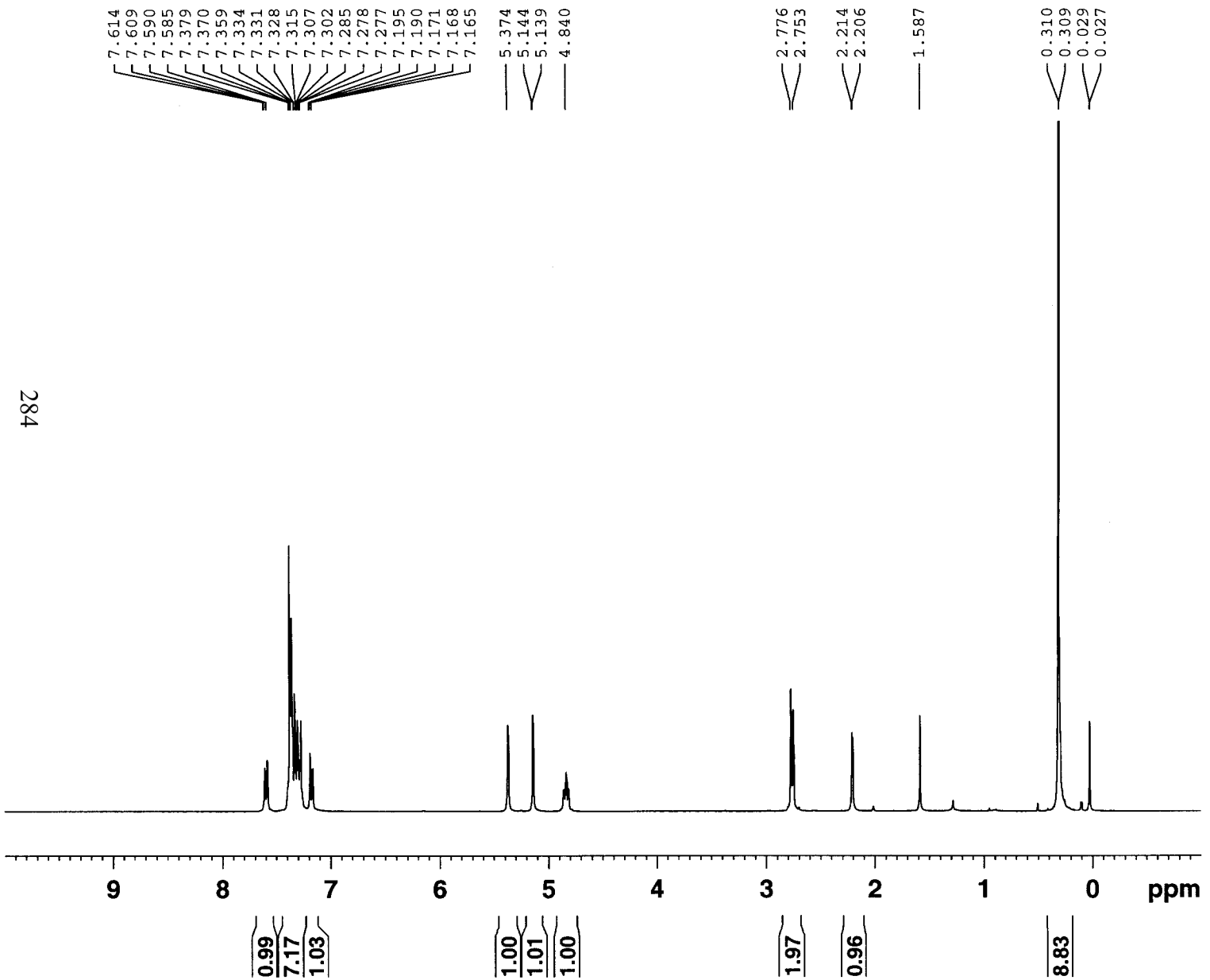

284

```
Current Data Parameters
NAME                  PZ-V-132-A3
EXPNO                           1
PROCNO                          1

F2 - Acquisition Parameters
Date_                    20050823
Time                        14.07
INSTRUM                    DRX300
PROBHD    5 mm Multinucl
PULPROG                   zg30pad
TD                          32768
SOLVENT                     CDCl3
NS                             16
DS                              2
SWH                      6172.839 Hz
FIDRES                   0.188380 Hz
AQ                       2.6542580 sec
RG                          322.5
DW                         81.000 use
DE                          6.00 use
TE                         300.0 K
D1                    1.00000000 sec
D31                   0.00000000 sec

======== CHANNEL f1 =======
NUC1                           1H
P1                          7.05 use
PL1                         0.00 dB
SFO1                300.1318534 MHz

F2 - Processing parameters
SI                          32768
SF                300.1300022 MHz
WDW                            EM
SSB                             0
LB                          0.30 Hz
GB                              0
PC                          1.30
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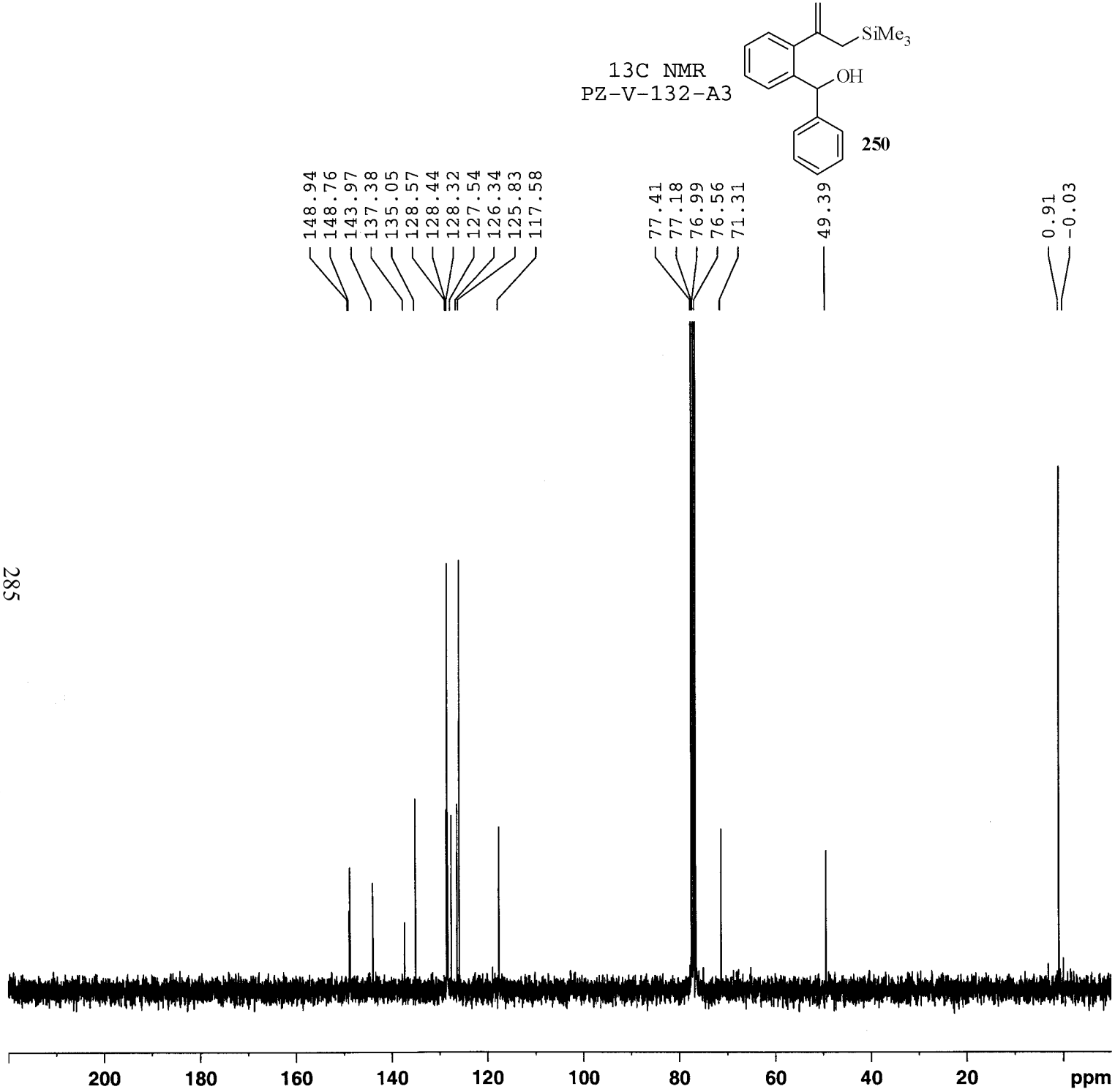


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Current Data Parameters
NAME                 PZ-V-132-A3
EXPNO                          2
PROCNO                         1

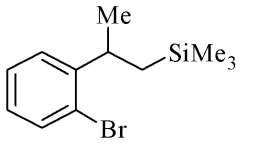
F2 - Acquisition Parameters
Date_                   20050823
Time                       14.13
INSTRUM                   DRX300
PROBHD   5 mm Multinucl
PULPROG                zgdc30pad
TD                         65536
SOLVENT                    CDCl3
NS                           201
DS                             4
SWH                    18832.393 Hz
FIDRES                 0.287360 Hz
AQ                     1.7400308 sec
RG                        2580.3
DW                        26.550 usec
DE                         6.00 usec
TE                        300.0 K
D1                    2.00000000 sec
D11                   0.03000000 sec
D31                   0.00000000 sec

======== CHANNEL f1 ========
NUC1                         13C
P1                         9.00 usec
PL1                        5.00 dB
SFO1                 75.4760107 MHz

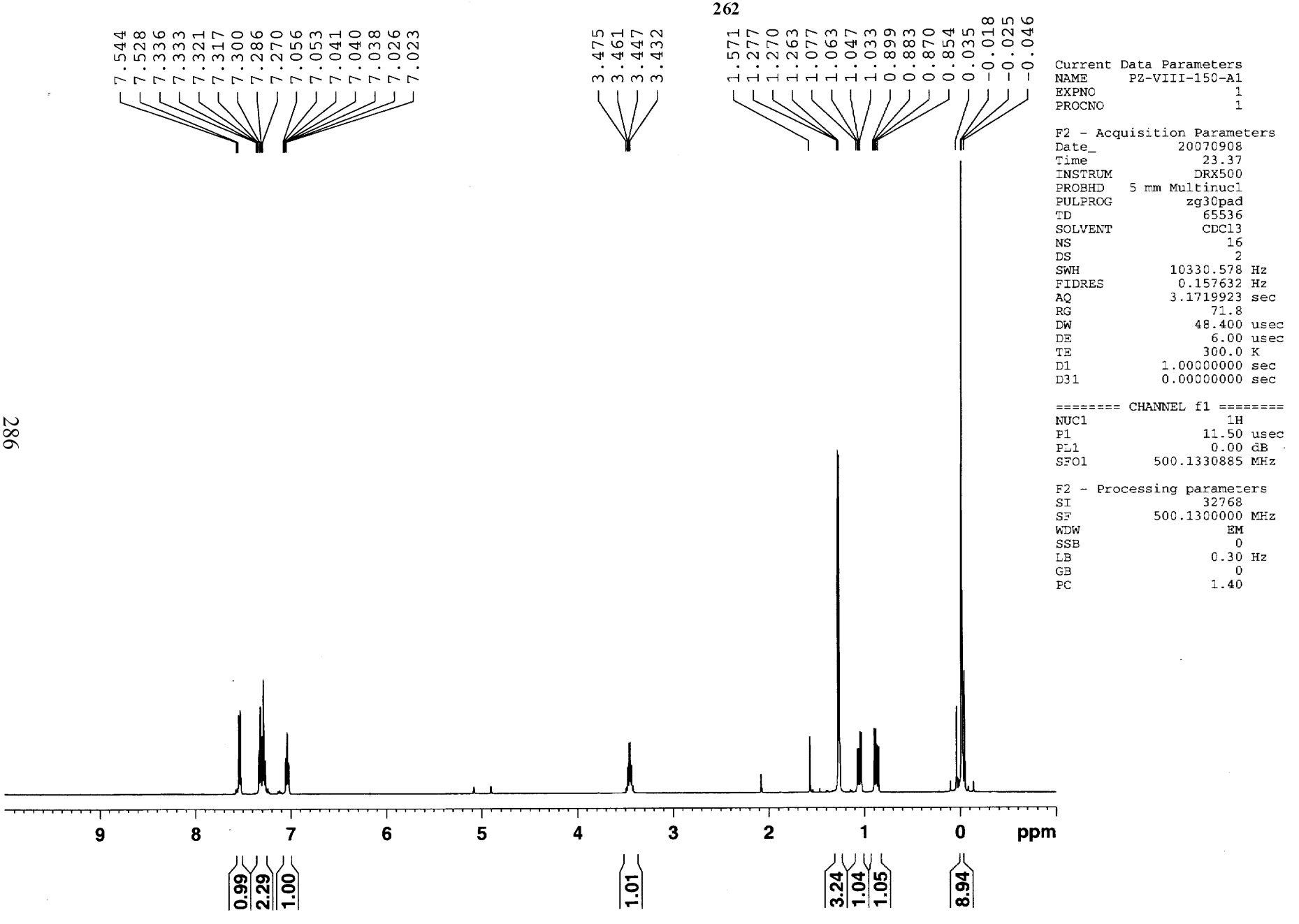
======== CHANNEL f2 ========
CPDPRG2                  waltz16
NUC2                         1H
PCPD2                    100.00 usec
PL2                      120.00 dB
PL12                      25.60 dB
SFO2                 300.1312005 MHz

F2 - Processing parameters
SI                         32768
SF                   75.4677525 MHz
WDW                           EM
SSB                            0
LB                         1.00 Hz
GB                             0
PC                          1.40
```

1H NMR
PZ-IX-150-A1



262

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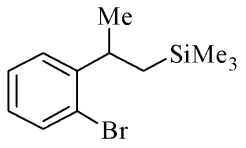
Current Data Parameters
NAME      PZ-VIII-150-A1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070908
Time               23.37
INSTRUM          DRX500
PROBHD   5 mm Multinucl
PULPROG          zg30pad
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719923 sec
RG                 71.8
DW               48.400 usec
DE                6.00 usec
TE               300.0 K
D1           1.00000000 sec
D31          0.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                11.50 usec
PL1                0.00 dB
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                 32768
SF          500.1300000 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                 1.40
```

13C NMR
PZ-VIII-150-A2



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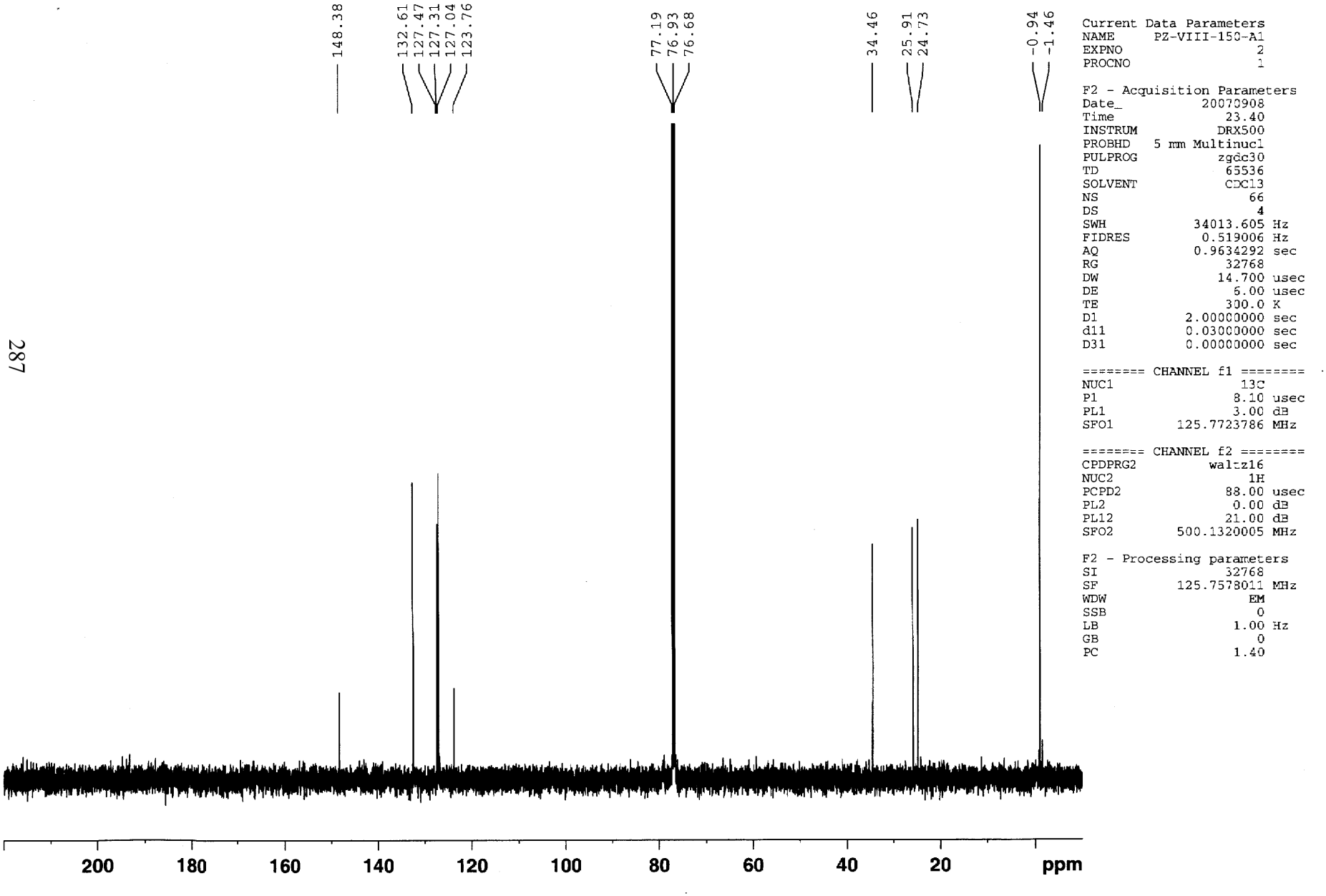


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Current Data Parameters
NAME      PZ-VIII-150-A1
EXPNO                  2
PROCNO                 1

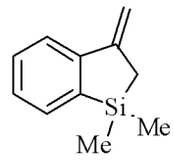
F2 - Acquisition Parameters
Date_           20070908
Time               23.40
INSTRUM           DRX500
PROBHD   5 mm Multinucl
PULPROG           zgdc30
TD                65536
SOLVENT           CDCl3
NS                   66
DS                    4
SWH           34013.605 Hz
FIDRES         0.519006 Hz
AQ             0.9634292 sec
RG                32768
DW               14.700 usec
DE                5.00 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
D31          0.00000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.10 usec
PL1                 3.00 dB
SFO1        125.7723786 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              88.00 usec
PL2                 0.00 dB
PL12               21.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                32768
SF          125.7578011 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

1H NMR
PZ-VII-103-A1



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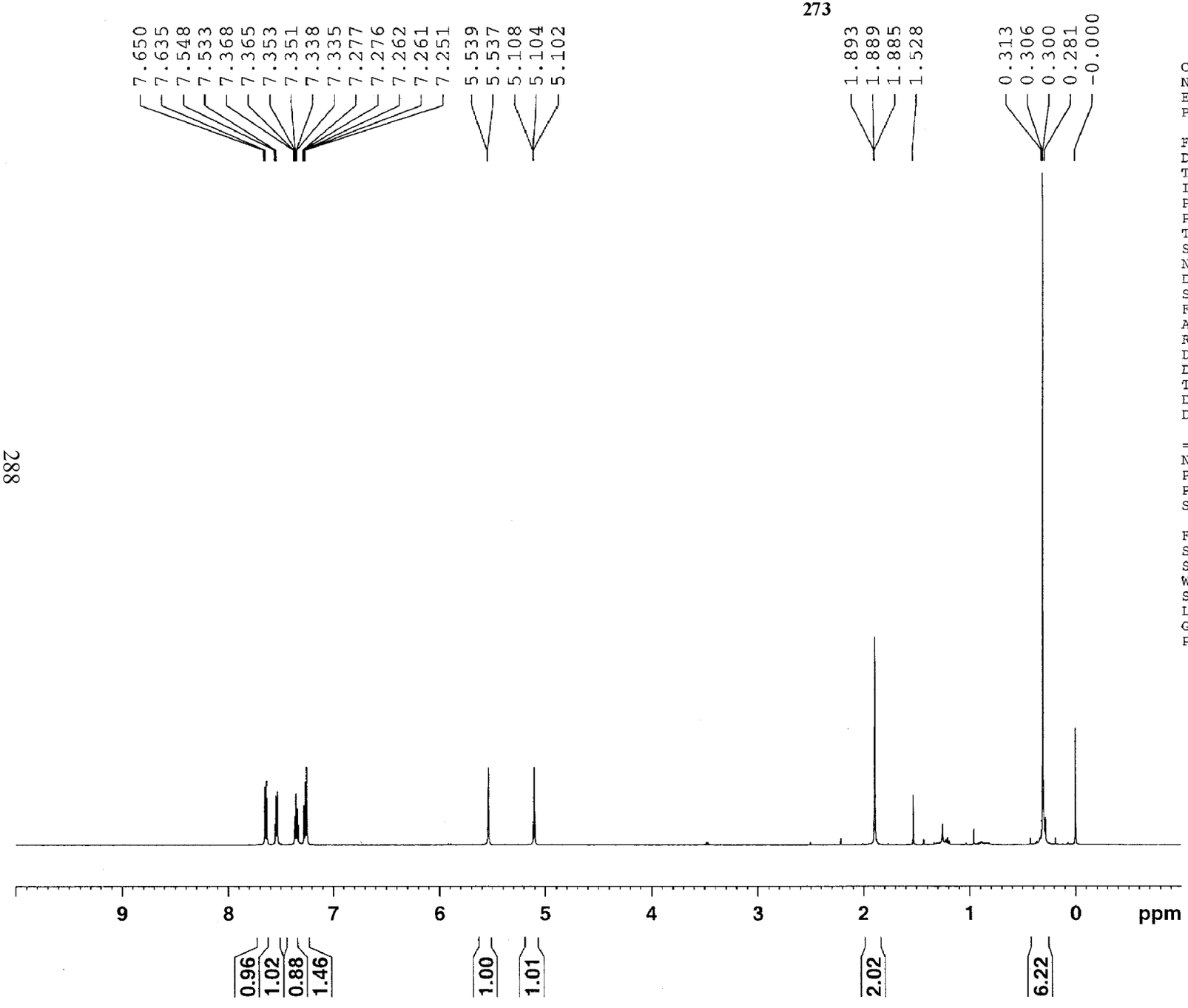

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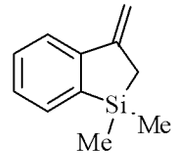
Current Data Parameters
NAME PZ-VII-103-A1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061007
Time 19.16
INSTRUM DRX500
PROBHD 5 mm Multinucl
PULPROG zg30pad
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 181
DW 48.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
D31 0.00000000 sec

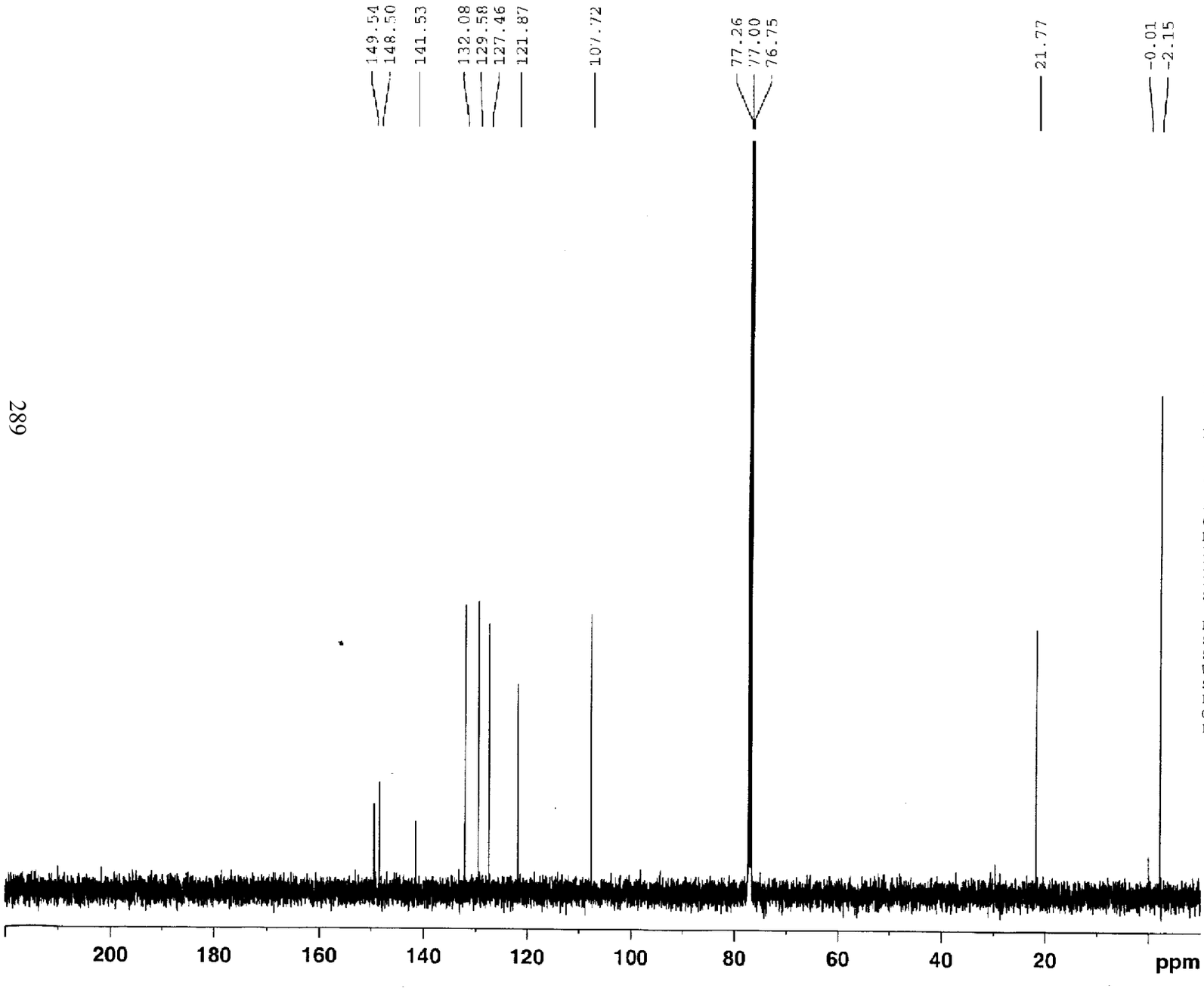
======== CHANNEL f1 ========
NUC1 1H
P1 11.50 usec
PL1 0.00 dB
SFO1 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300181 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40

13C NMR
PZ-VII-103-A1



273




```
Current Data Parameters
NAME       PZ-VII-103-A1
EXPNO                 2
PROCNO                1

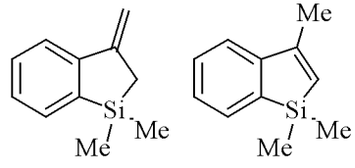
F2 - Acquisition Parameters
Date_          20061007
Time               19.21
INSTRUM          DRX500
PROBHD   5 mm Multinucl
PULPROG         zgdc30
TD               65536
SOLVENT          CDCl3
NS                 133
DS                   4
SWH          34013.605 Hz
FIDRES        0.519006 Hz
AQ            0.9634292 sec
RG               32768
DW              14.700 usec
DE               6.00 usec
TE              300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
D31          0.00000000 sec

======== CHANNEL f1 ========
NUC1               13C
P1              8.10 usec
PL1             3.00 dB
SFO1       125.7723786 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2               1H
PCPD2          88.00 usec
PL2             0.00 dB
PL12           21.00 dB
SFO2       500.1320005 MHz

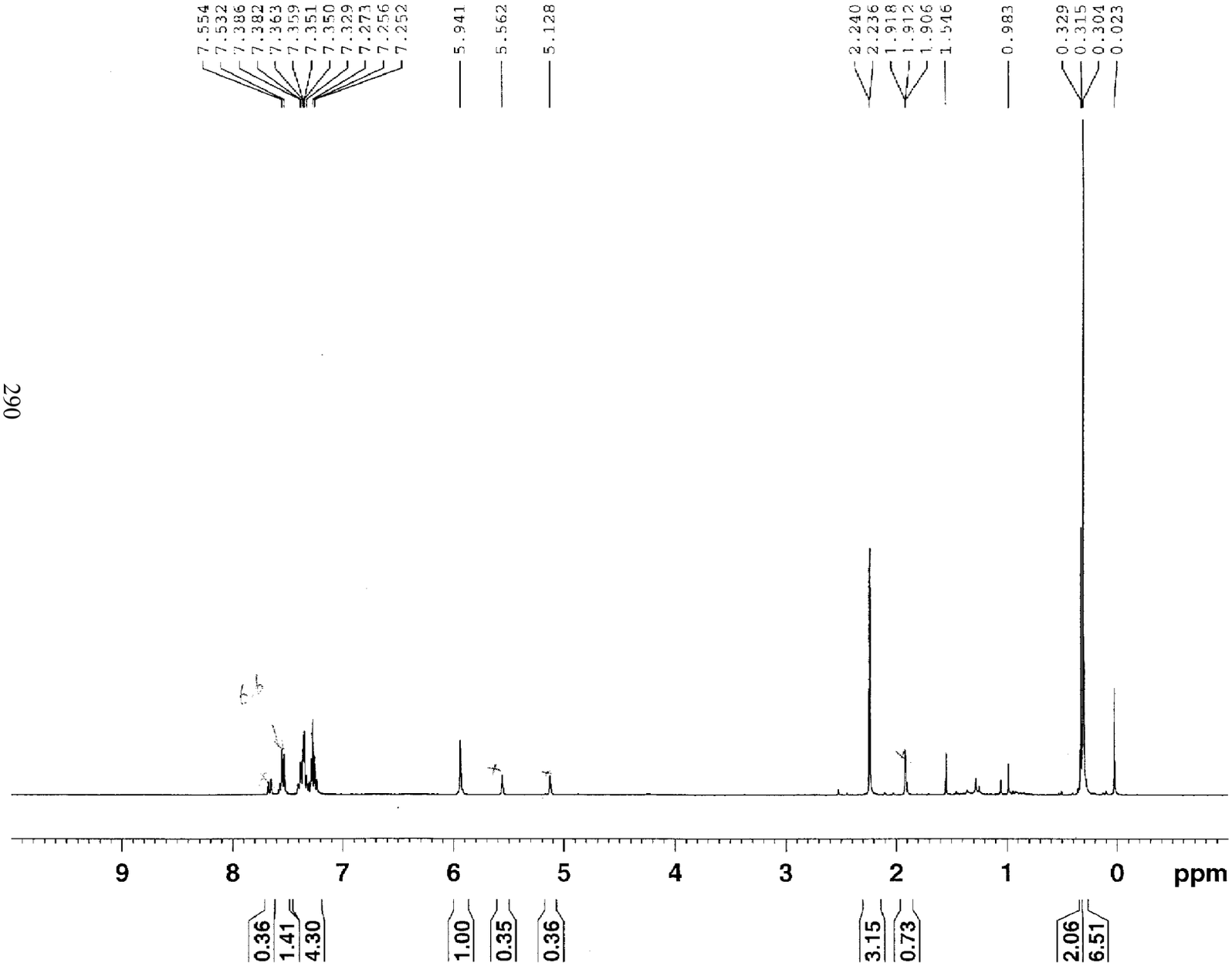
F2 - Processing parameters
SI               32768
SF         125.7577928 MHz
WDW                EM
SSB                 0
LB              1.00 Hz
GB                  0
PC              1.40
```

1H-NMR
PZ-VII-98-A1



273 **274**

2.85 : 1.00



Current Data Parameters

NAME	PZ-VII-98-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20061007
Time	10.59
INSTRUM	DRX300
PROBHD	5 mm Multinucl
PULPROG	zg30pad
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6172.839 Hz
FIDRES	0.188380 Hz
AQ	2.6542580 sec
RG	456.1
DW	81.000 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
D31	0.00000000 sec

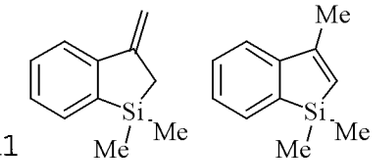
======== CHANNEL f1 ========

NUC1	1H
P1	7.05 usec
PL1	0.00 dB
SFO1	300.1318534 MHz

F2 - Processing parameters

SI	32768
SF	300.1300022 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.30

13C NMR
PZ-VII-98-A1



273 **274**

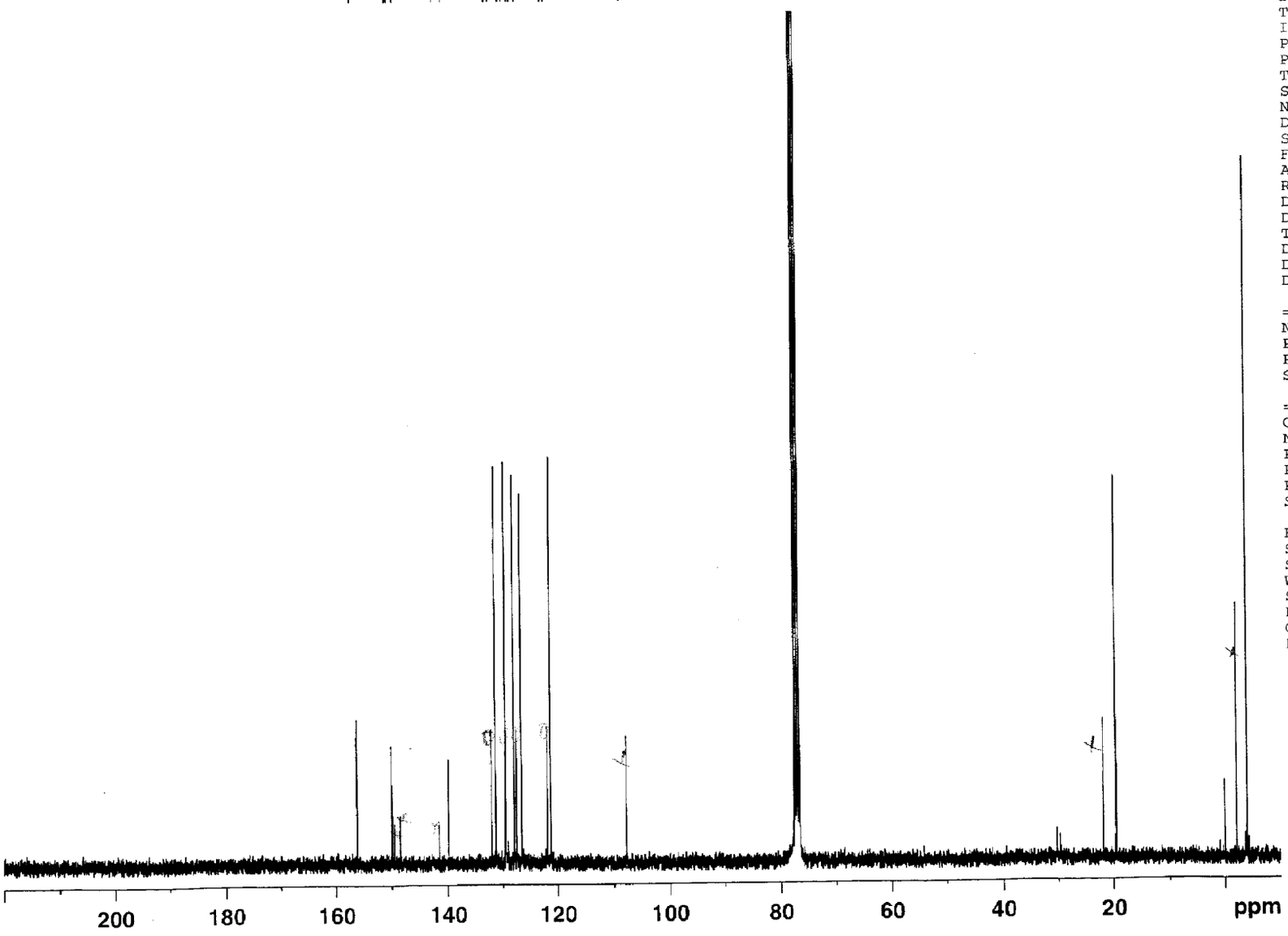
2.85 : 1.00

156.22
149.98
149.55
148.51
141.53
139.85
132.08
131.27
129.58
129.44
129.04
127.86
127.46
126.51
121.87
121.22
107.72

77.43
77.20
77.00
76.58

30.27
29.71
21.78
19.57

-0.01
-2.15
-3.69

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Current Data Parameters
NAME                  PZ-VII-98-A1
EXPNO                            2
PROCNO                           1

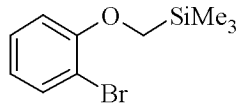
F2 - Acquisition Parameters
Date_                     20061007
Time                         11.10
INSTRUM                     DRX300
PROBHD    5 mm Multinucl
PULPROG                 zgdc30pad
TD                           65536
SOLVENT                      CDCl3
NS                            6012
DS                               4
SWH                   18832.393 Hz
FIDRES                 0.287360 Hz
AQ                    1.7400308 sec
RG                           22528
DW                      26.550 usec
DE                       6.00 usec
TE                       300.0 K
D1                    2.00000000 sec
D11                   0.03000000 sec
D31                   0.00000000 sec

======== CHANNEL f1 ========
NUC1                          13C
P1                       9.00 usec
PL1                      5.00 dB
SFO1                 75.4760107 MHz

======== CHANNEL f2 ========
CPDPRG2                  waltz16
NUC2                          1H
PCPD2                  100.00 usec
PL2                    120.00 dB
PL12                    25.60 dB
SFO2                300.1312005 MHz

F2 - Processing parameters
SI                           32768
SF                   75.4677502 MHz
WDW                             EM
SSB                              0
LB                       1.00 Hz
GB                               0
PC                            1.40
```

1H-NMR
PZ-IX-61-A2



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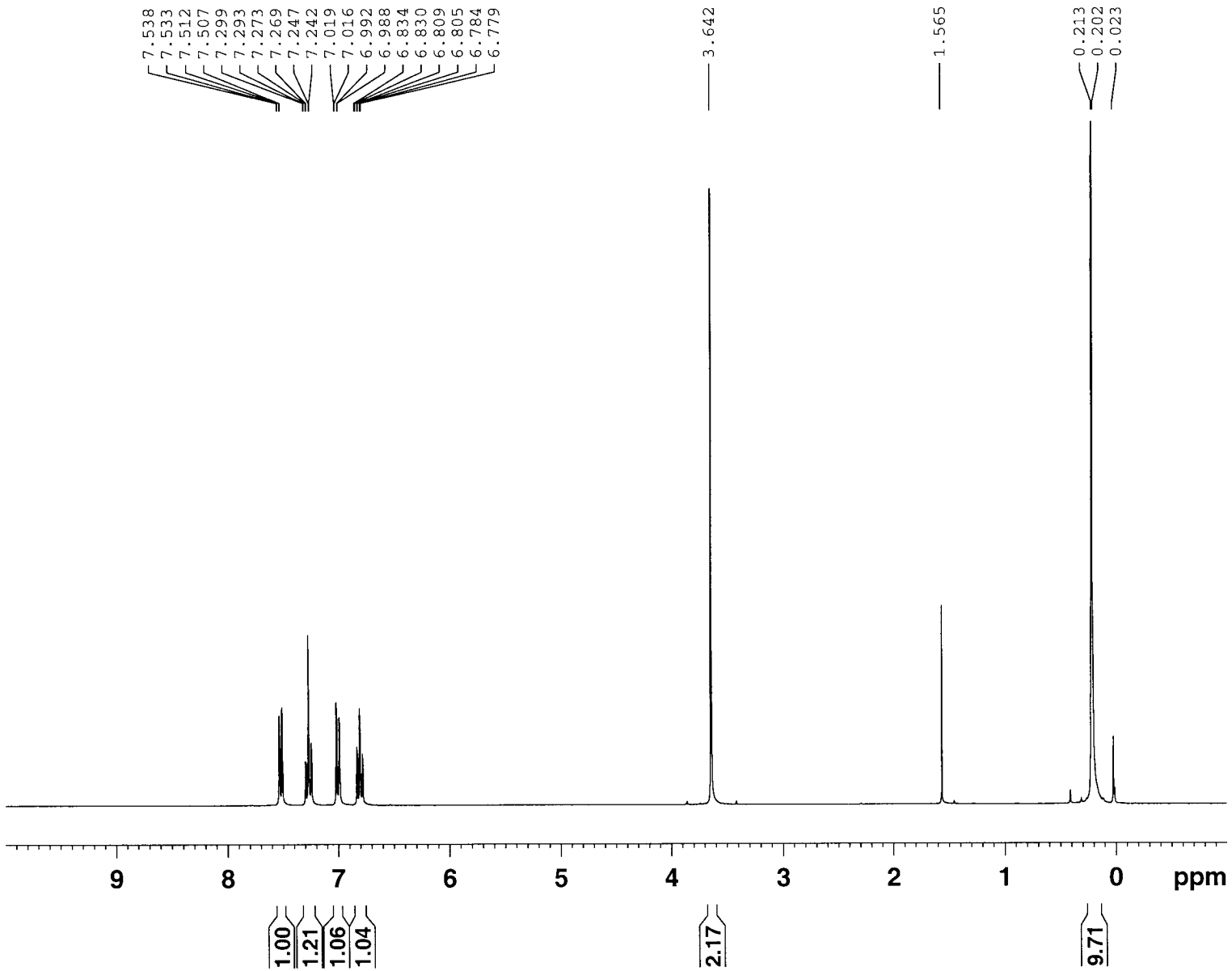


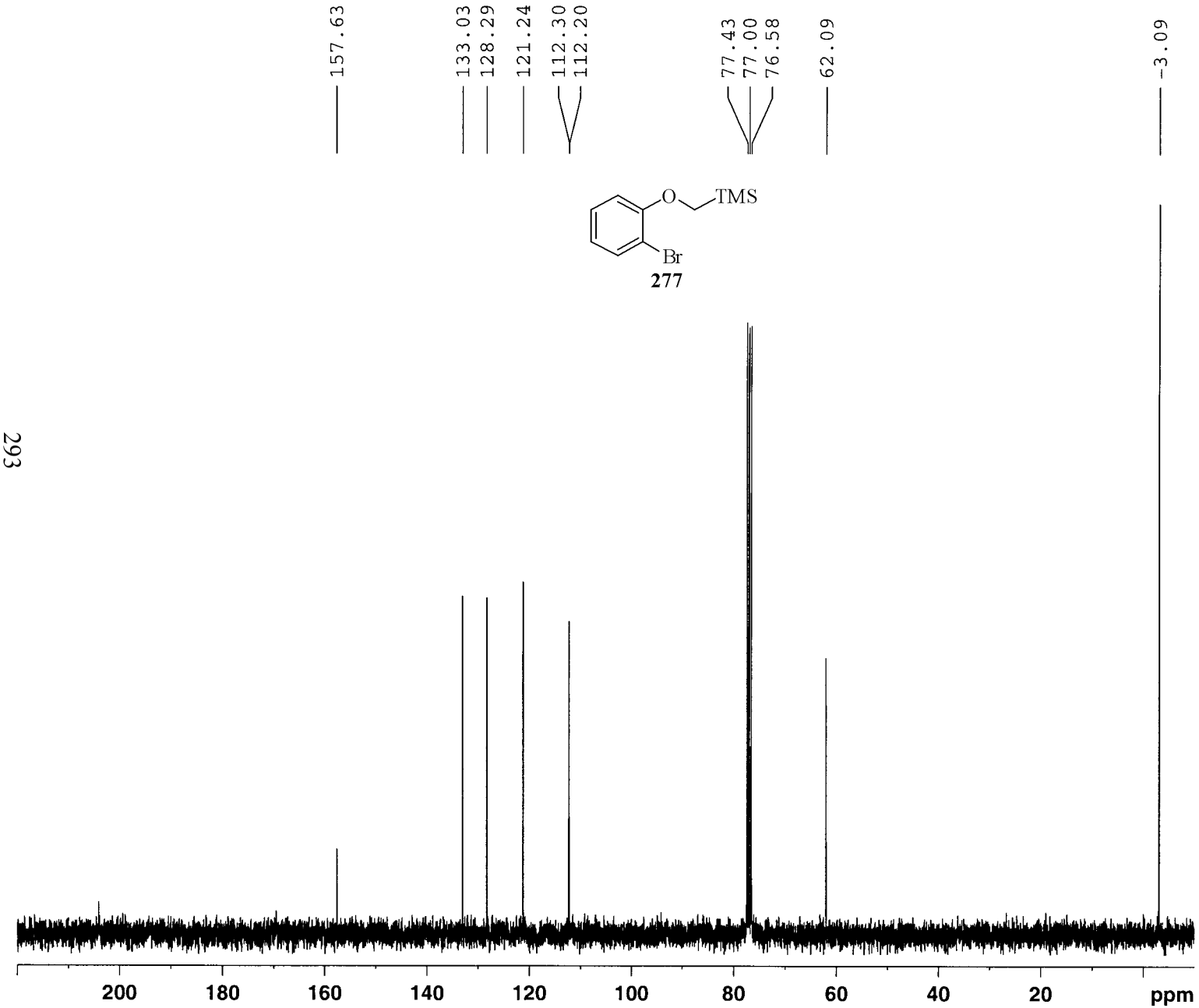

```
Current Data Parameters
NAME                  PZ-IX-61-A2
EXPNO                           1
PROCNO                          1

F2 - Acquisition Parameters
Date_                    20070717
Time                        15.35
INSTRUM                    DRX300
PROBHD   5 mm Multinucl
PULPROG                   zg30pad
TD                          32768
SOLVENT                     CDC13
NS                             16
DS                              2
SWH                     6172.839 Hz
FIDRES                  0.188380 Hz
AQ                      2.6542580 sec
RG                          228.1
DW                         81.000 usec
DE                          6.00 usec
TE                         300.0 K
D1                    1.00000000 sec
D31                   0.00000000 sec

======== CHANNEL f1 ========
NUC1                           1H
P1                          7.05 usec
PL1                         0.00 dB
SFO1                300.1318534 MHz

F2 - Processing parameters
SI                          32768
SF                300.1300022 MHz
WDW                            EM
SSB                             0
LB                          0.30 Hz
GB                              0
PC                           1.30
```

13C NMR
PZ-IX-61-A2

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Current Data Parameters
NAME          PZ-IX-61-A2
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070717
Time                15.38
INSTRUM           DRX300
PROBHD   5 mm Multinucl
PULPROG        zgdc30pad
TD                  65536
SOLVENT             CDCl3
NS                    104
DS                      4
SWH           18832.393 Hz
FIDRES         0.287360 Hz
AQ             1.7400308 sec
RG                  22528
DW                 26.550 usec
DE                  6.00 usec
TE                 300.0 K
D1             2.00000000 sec
D11            0.03000000 sec
D31            0.00000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.00 usec
PL1                  5.00 dB
SFO1          75.4760107 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                120.00 dB
PL12                21.41 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF            75.4677508 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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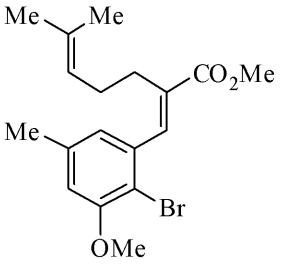

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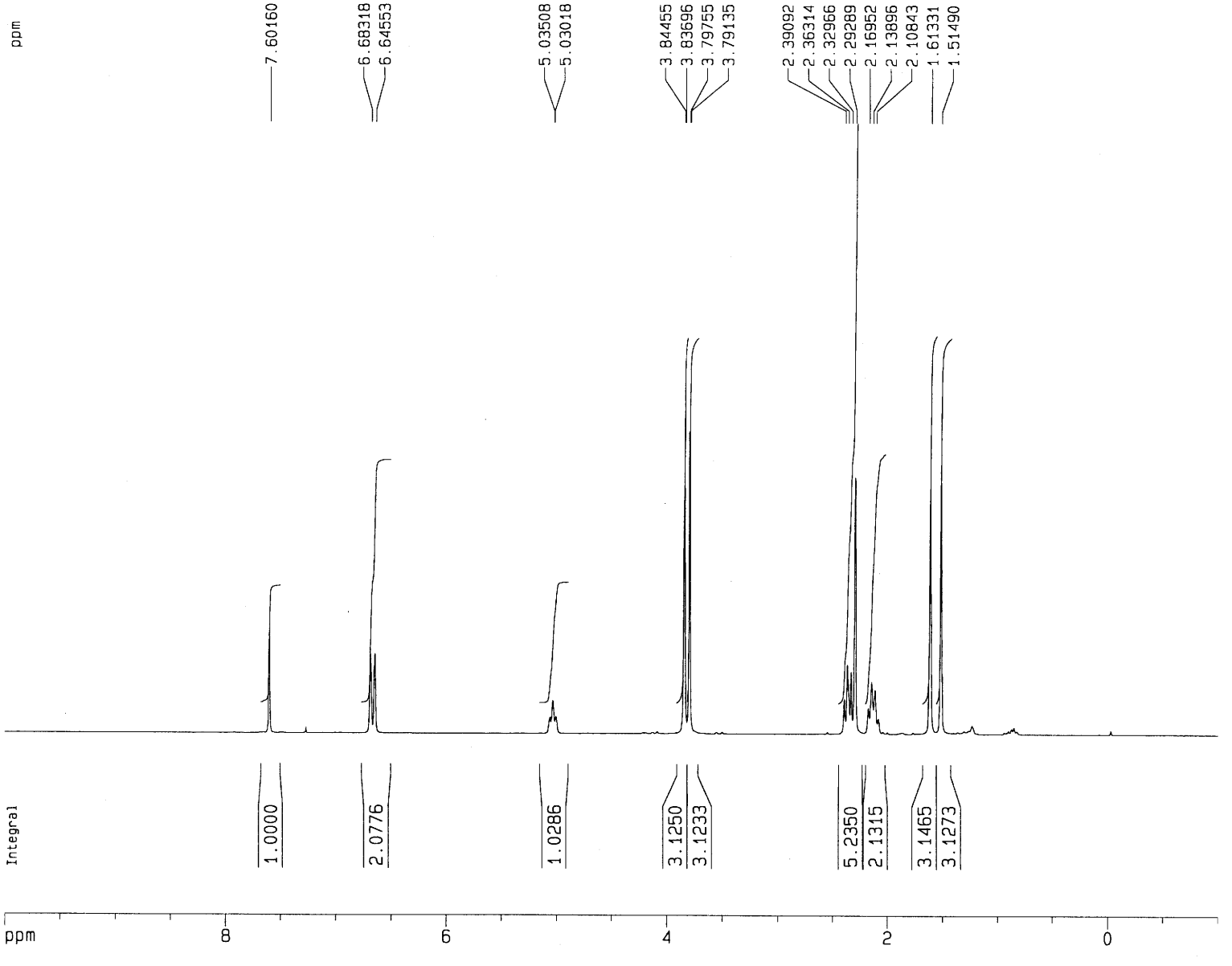


Current Data Parameters

NAME	PZ-VI-64-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

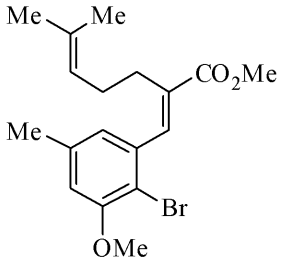
Date_	20051201
Time	12.09
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	128
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	9.50 use
SFO1	250.1315321 MHz
NUCLEUS	1H

F2 - Processing parameters

SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	5.00 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57150 Hz/



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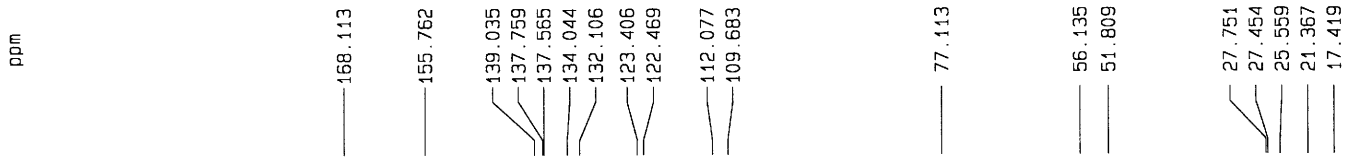
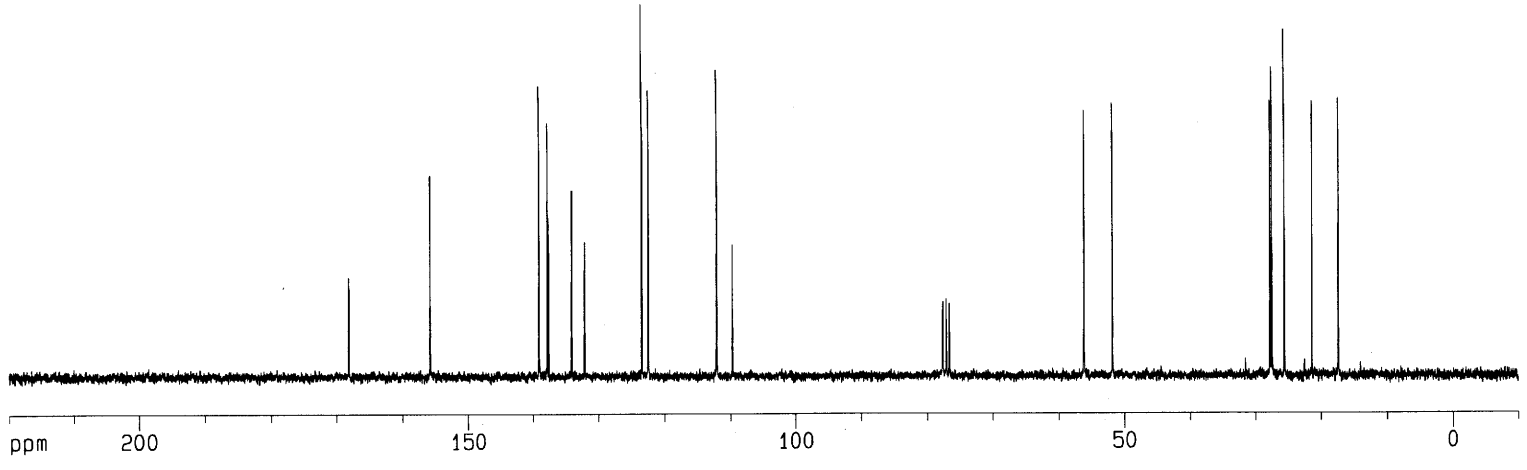




Current Data Parameters

NAME	PZ-VI-64-A1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

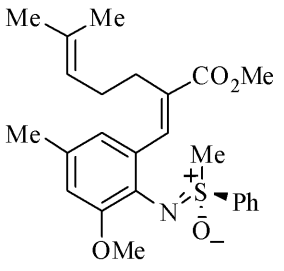
Date_	20051201
Time	12.10
INSTRUM	arx250
PROBHD	5 mm GNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	72
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	2.00000000 sec
P1	8.00 use
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

F2 - Processing parameters

SI	32768
SF	62.8952440 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	5.00 cm
F1P	220.000 ppm
F1	13836.95 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	11.50000 ppm
HZCM	723.29529 Hz/



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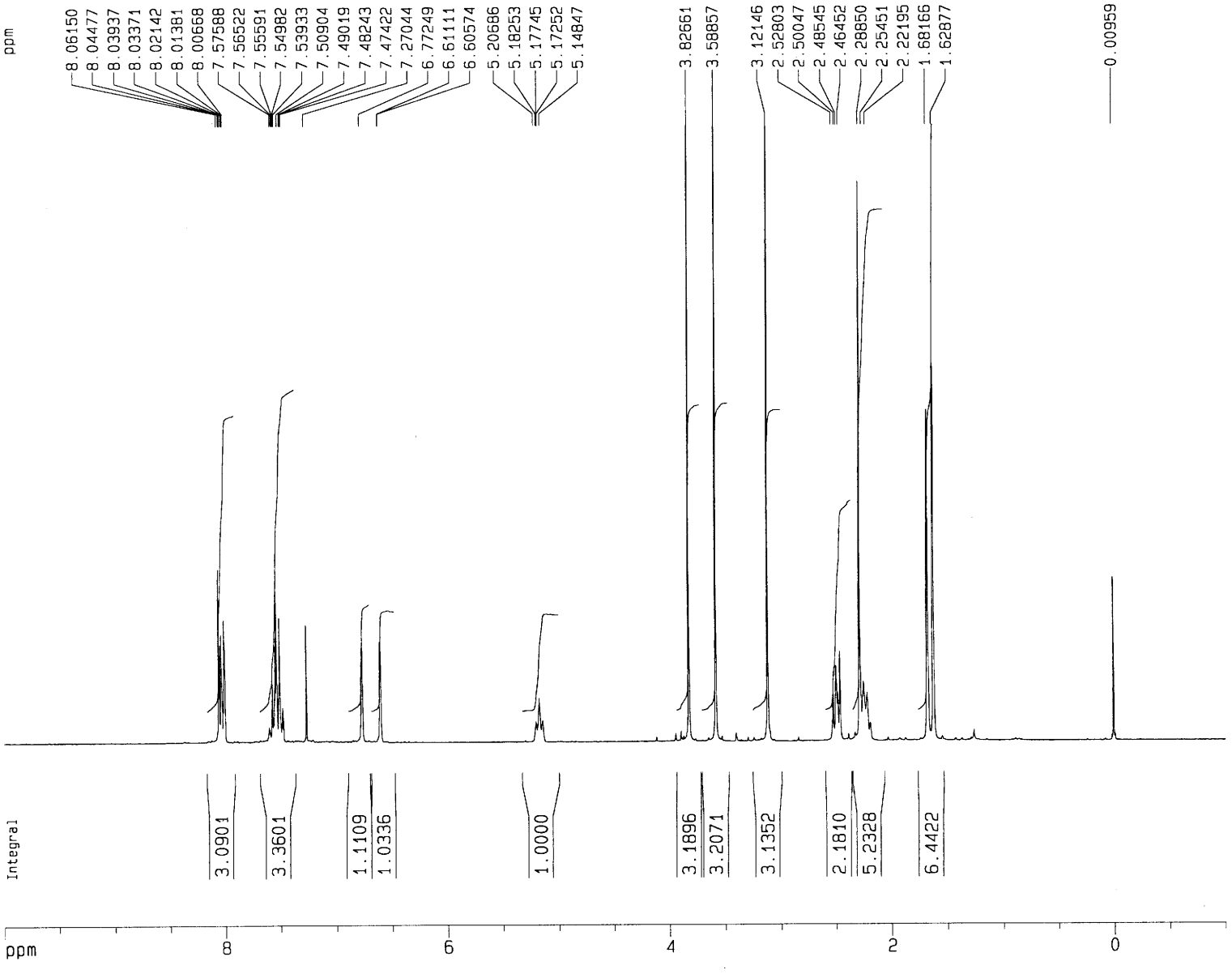


Current Data Parameters

NAME	PZ-VI-76-A3
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

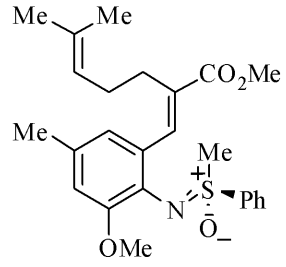
Date_	20060206
Time	23.06
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	1024
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	9.50 use
SFO1	250.1315321 MHz
NUCLEUS	1H

F2 - Processing parameters

SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	12.50 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57150 Hz/



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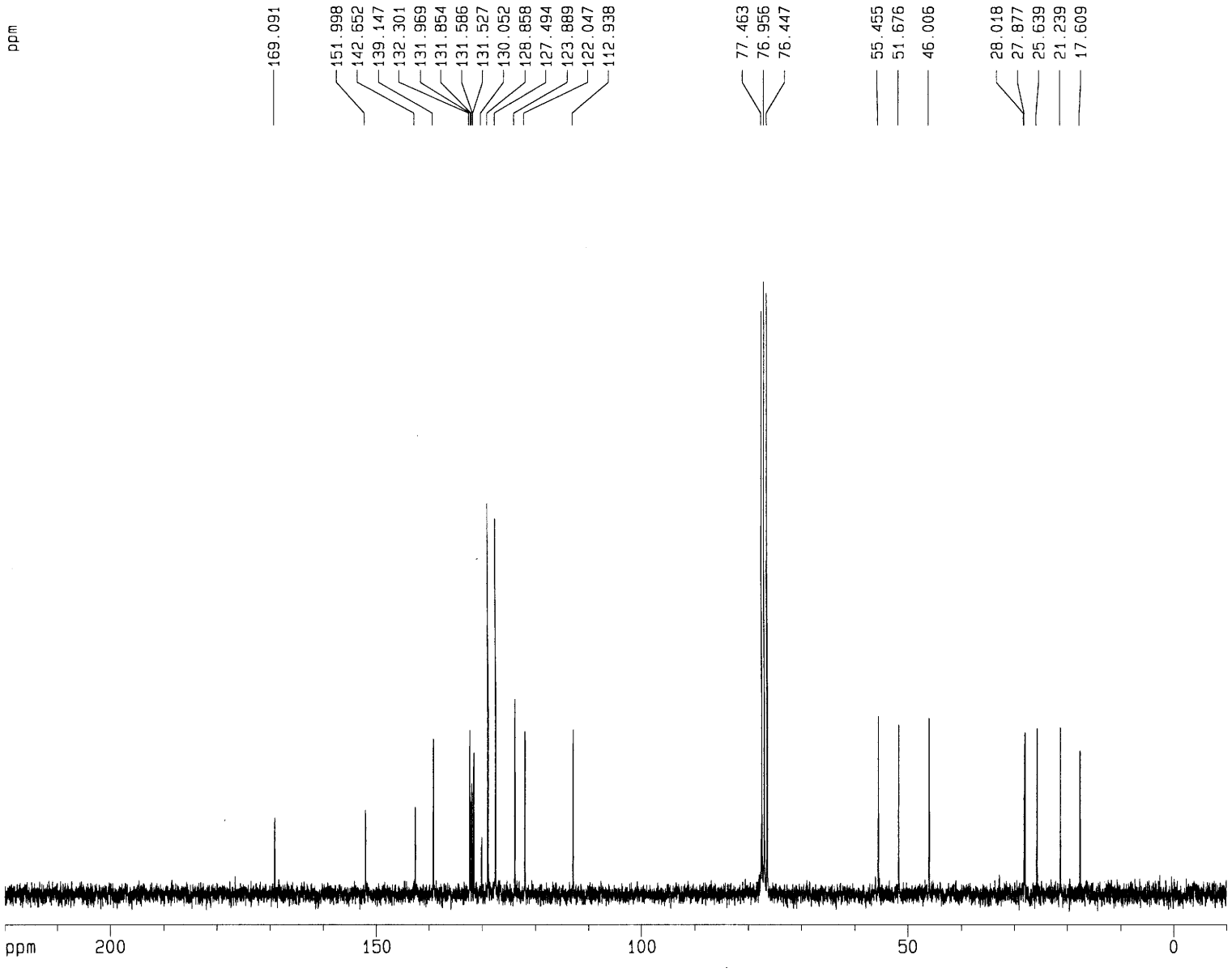


Current Data Parameters

NAME	PZ-VI-76-A3
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

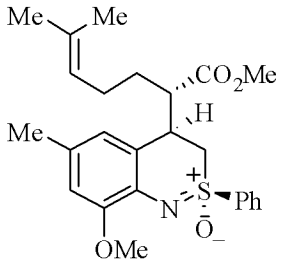
Date_	20060206
Time	23.09
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	784
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	2.00000000 sec
P1	8.00 use
SF01	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

F2 - Processing parameters

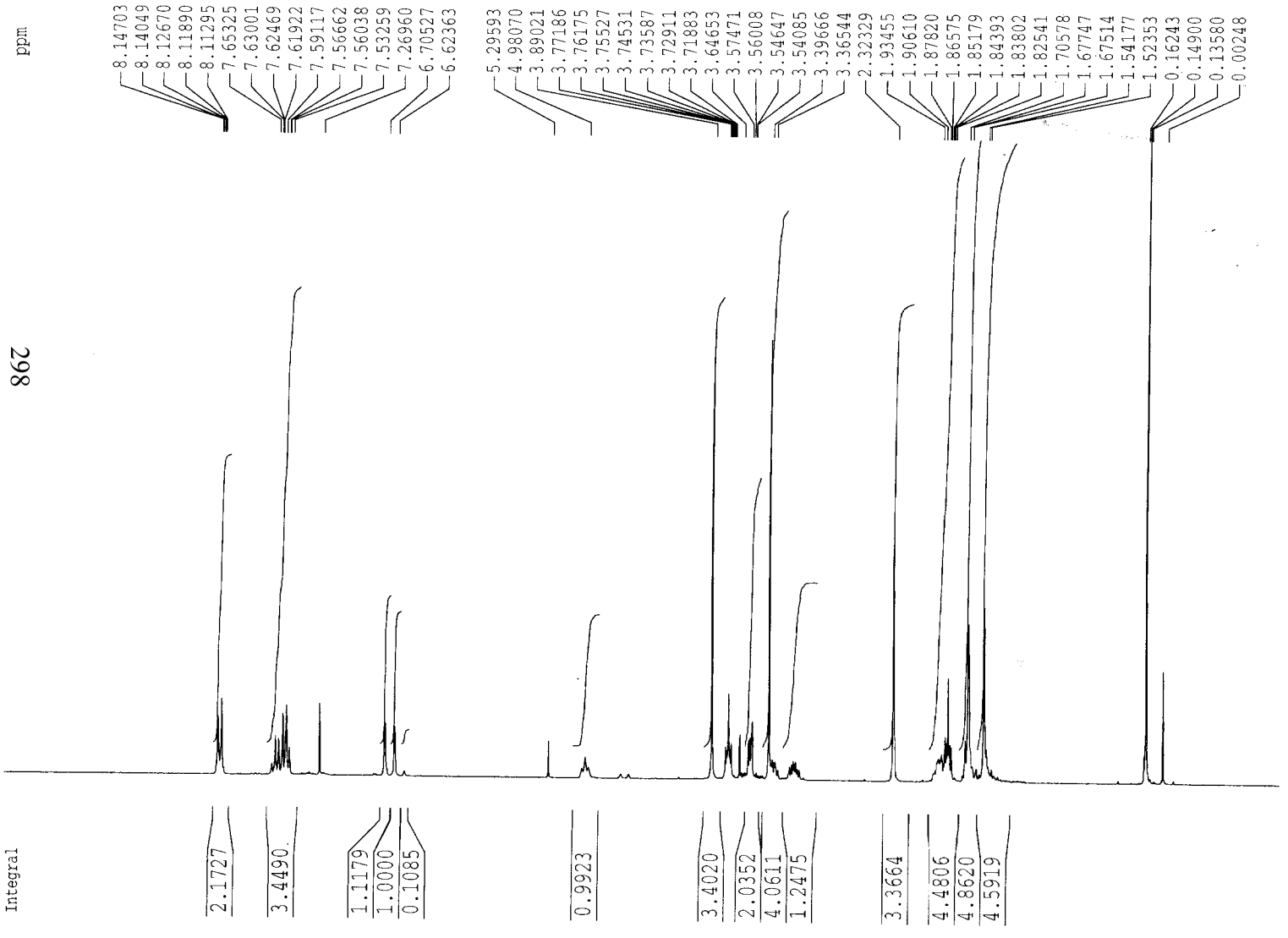
SI	32768
SF	62.8952440 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	10.00 cm
F1P	220.000 ppm
F1	13836.95 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	11.50000 ppm
HZCM	723.29529 Hz/



361 (*d.r.* 9.2:1.0)



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Current Data Parameters
NAME      PZ-VIII-61-1-c
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070127
Time               19.40
INSTRUM          arx250
PROBHD     5 mm QNP  1E
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           5208.333 Hz
FIDRES        0.158946 Hz
AQ           3.1457779 sec
RG                  715
DW             96.000 usec
DE             137.14 usec
TE              300.0 K
D1          1.00000000 sec
P1             9.50 usec
SFO1       250.1315321 MHz
NUCLEUS            1H

F2 - Processing parameters
SI                16384
SF        250.1300049 MHz
WDW                  EM
SSB                   0
LB               0.20 Hz
GB                    0
PC                 1.50

1D NMR plot parameters
CX               20.00 cm
CY               12.50 cm
F1P              10.000 ppm
F1             2501.30 Hz
F2P              -1.000 ppm
F2             -250.13 Hz
PPMCM          0.55000 ppm/cm
HZCM         137.57150 Hz/cm
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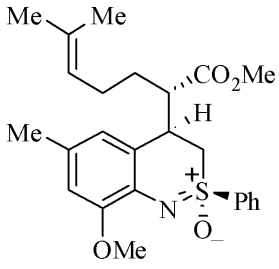

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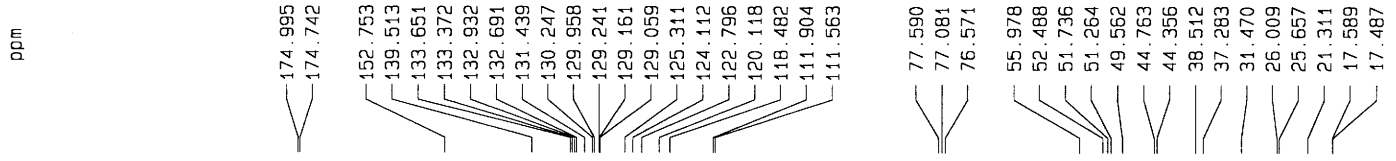
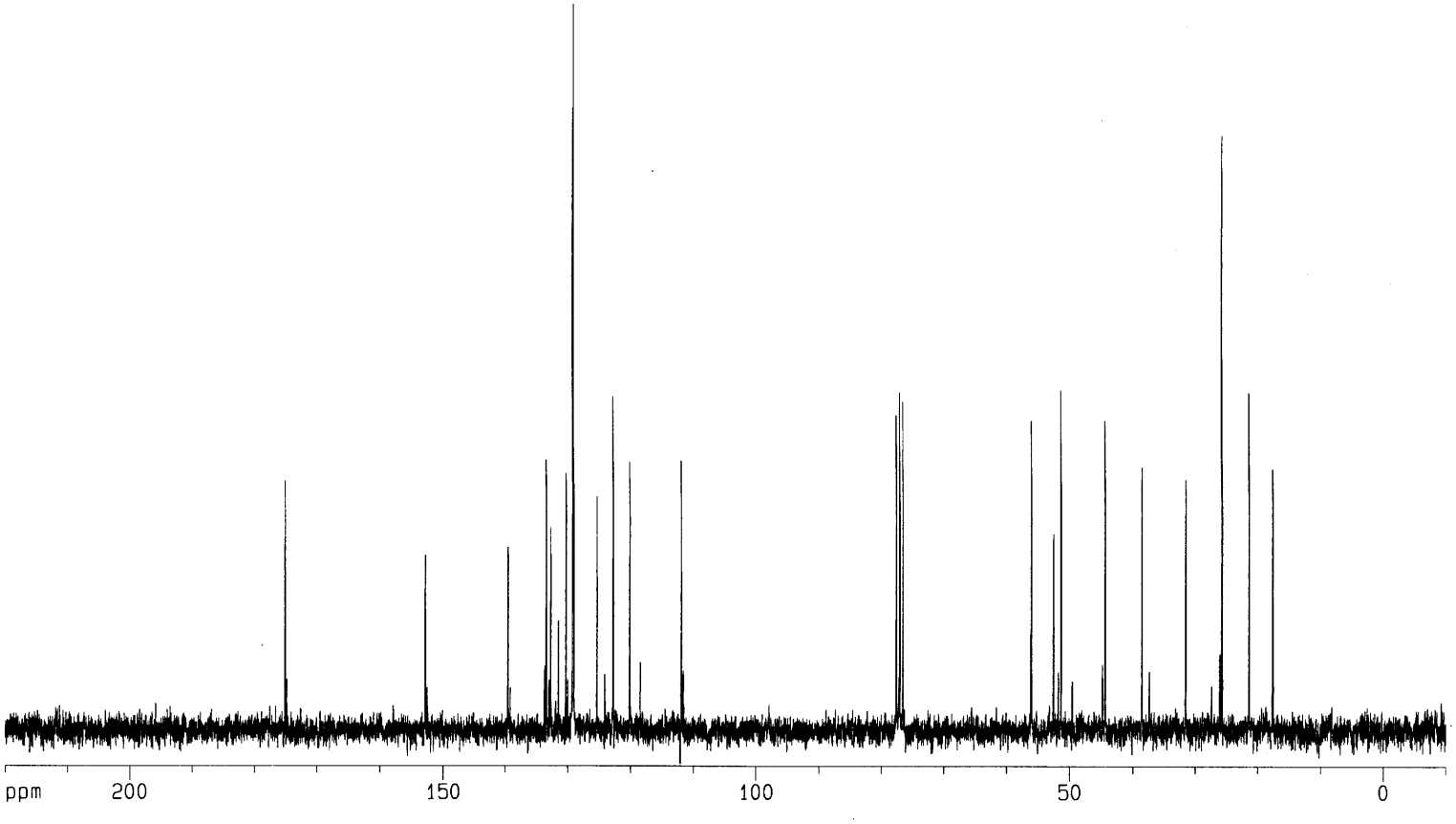




Current Data Parameters

NAME	PZ-VI-78-A1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

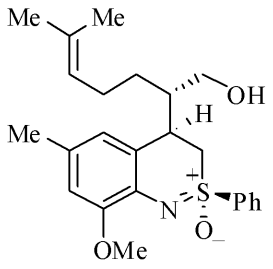
Date_	20060207
Time	23.16
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	83
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	2.00000000 sec
P1	8.00 use
SF01	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

F2 - Processing parameters

SI	32768
SF	62.8952440 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	10.00 cm
F1P	220.000 ppm
F1	13836.95 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	11.50000 ppm
HZCM	723.29529 Hz/



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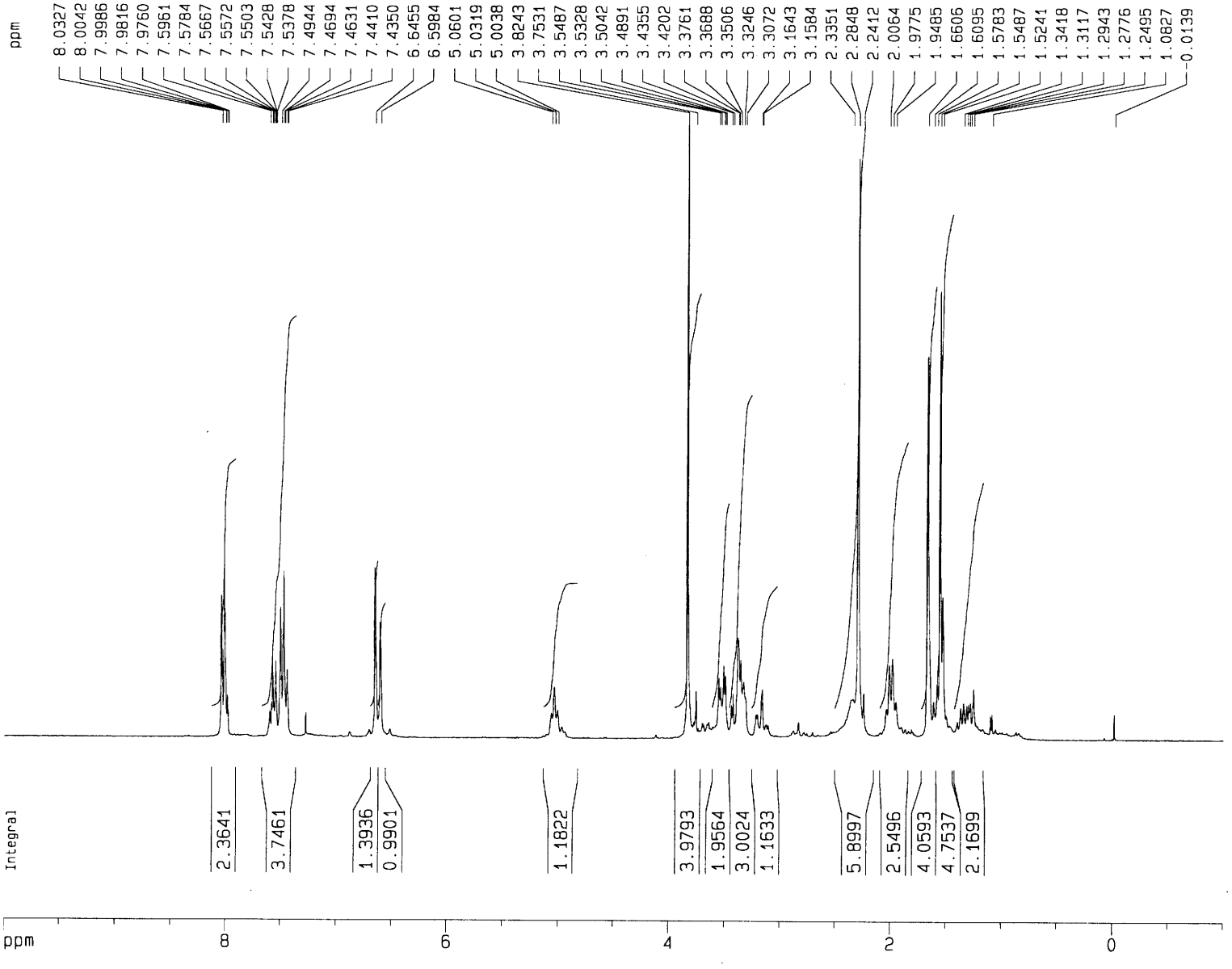


Current Data Parameters

NAME	PZ-VI-81-CRDE
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

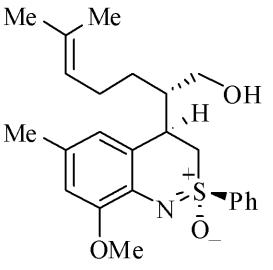
Date_	20060209
Time	16.36
INSTRUM	arx250
PROBHD	5 mm GNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	128
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	9.50 use
SFO1	250.1315321 MHz
NUCLEUS	1H

F2 - Processing parameters

SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	12.50 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57150 Hz/



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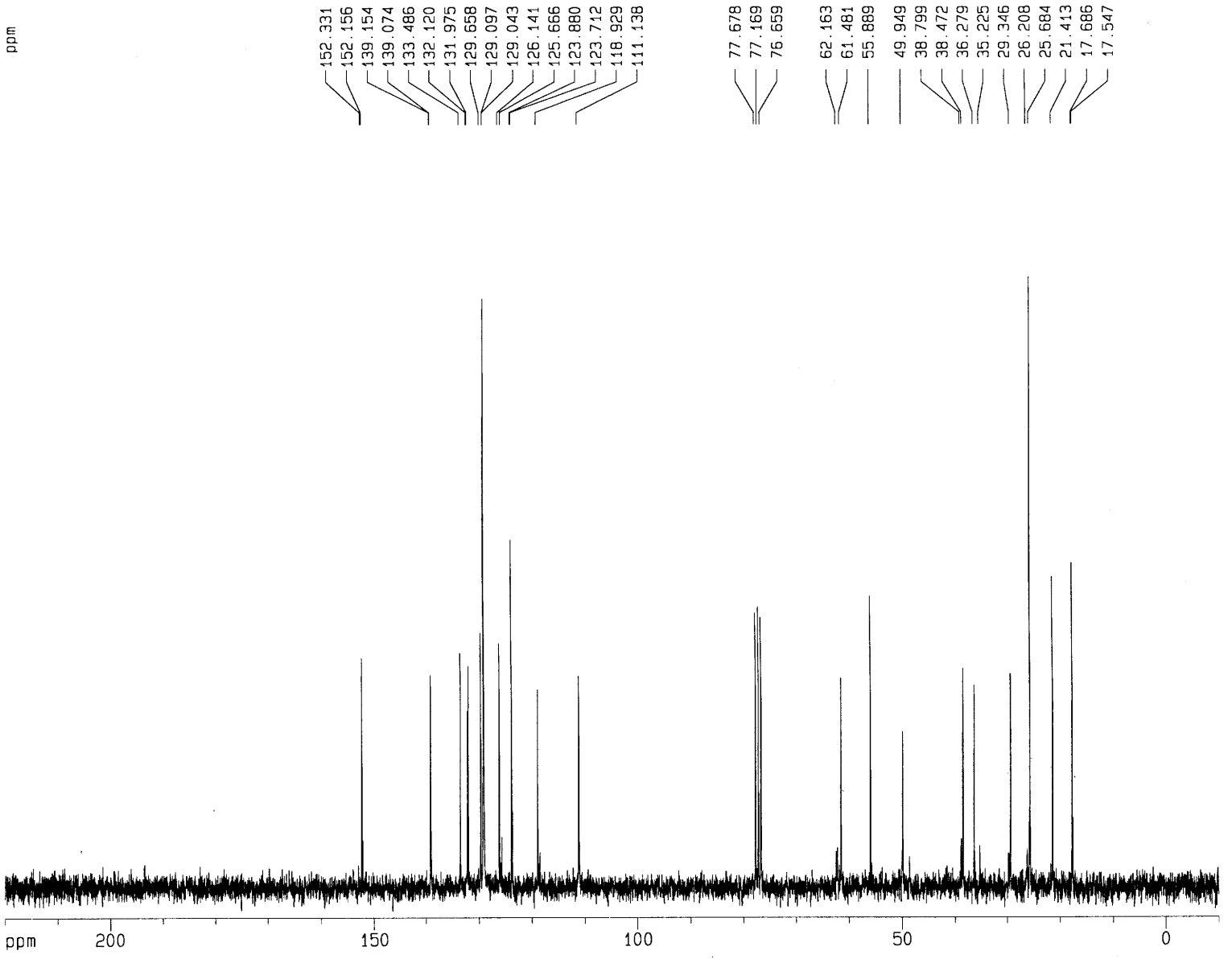


Current Data Parameters

NAME	PZ-VI-81-CRDE
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20060209
Time	16.37
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	60
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	2.00000000 sec
P1	8.00 use
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

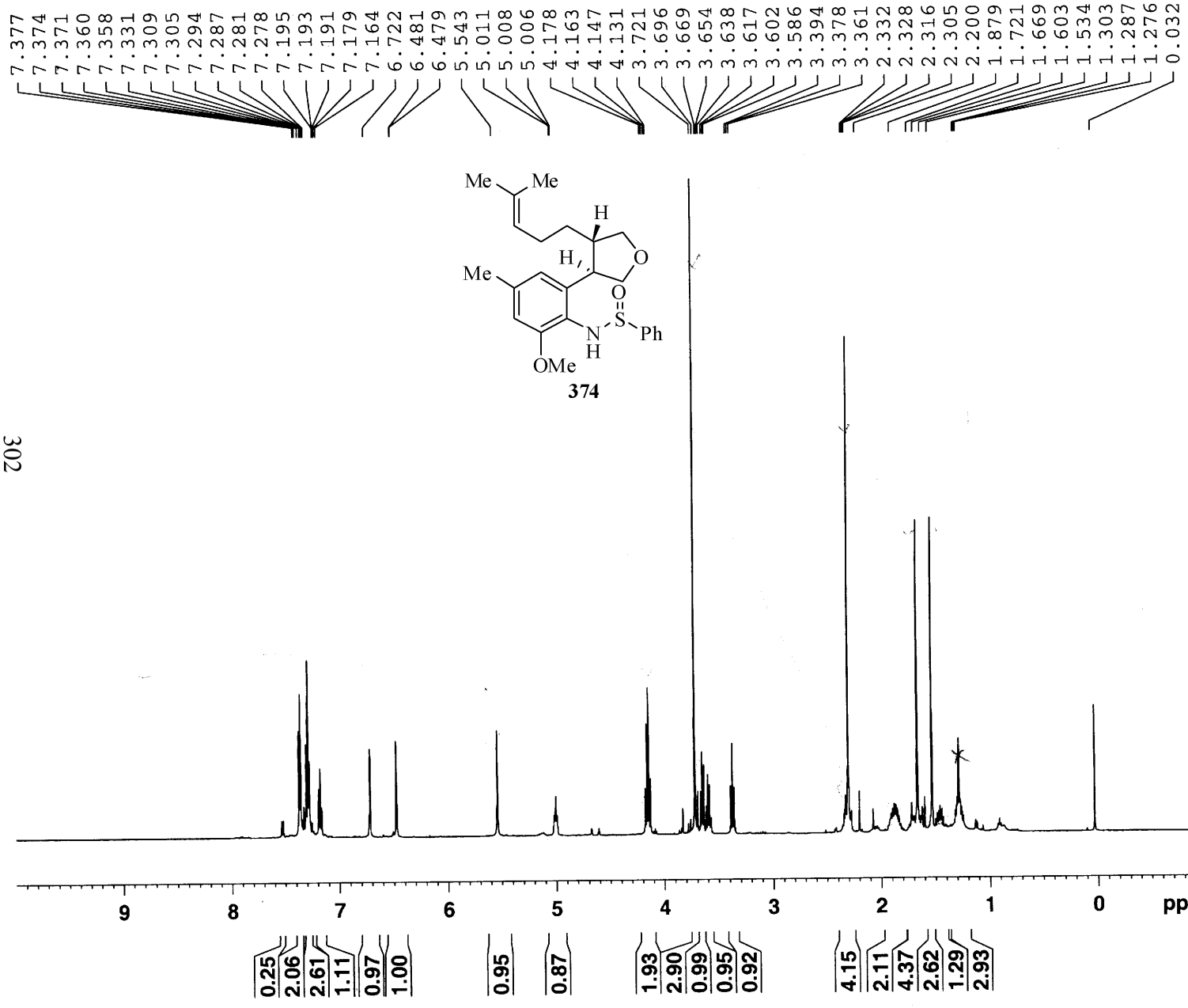
F2 - Processing parameters

SI	32768
SF	62.8952440 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	10.00 cm
F1P	220.000 ppm
F1	13836.95 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	11.50000 ppm
HZCM	723.29529 Hz/

1H NMR
PZ-VIII-83-A1

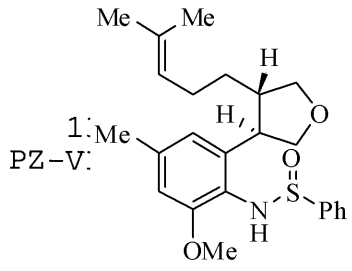


Current Data Parameters
NAME PZ-VIII-83-A1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070215
Time 18.40
INSTRUM DRX500
PROBHD 5 mm Multinucl
PULPROG zg30pad
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 101.6
DW 48.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
D31 0.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 11.50 usec
PL1 0.00 dB
SFO1 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40



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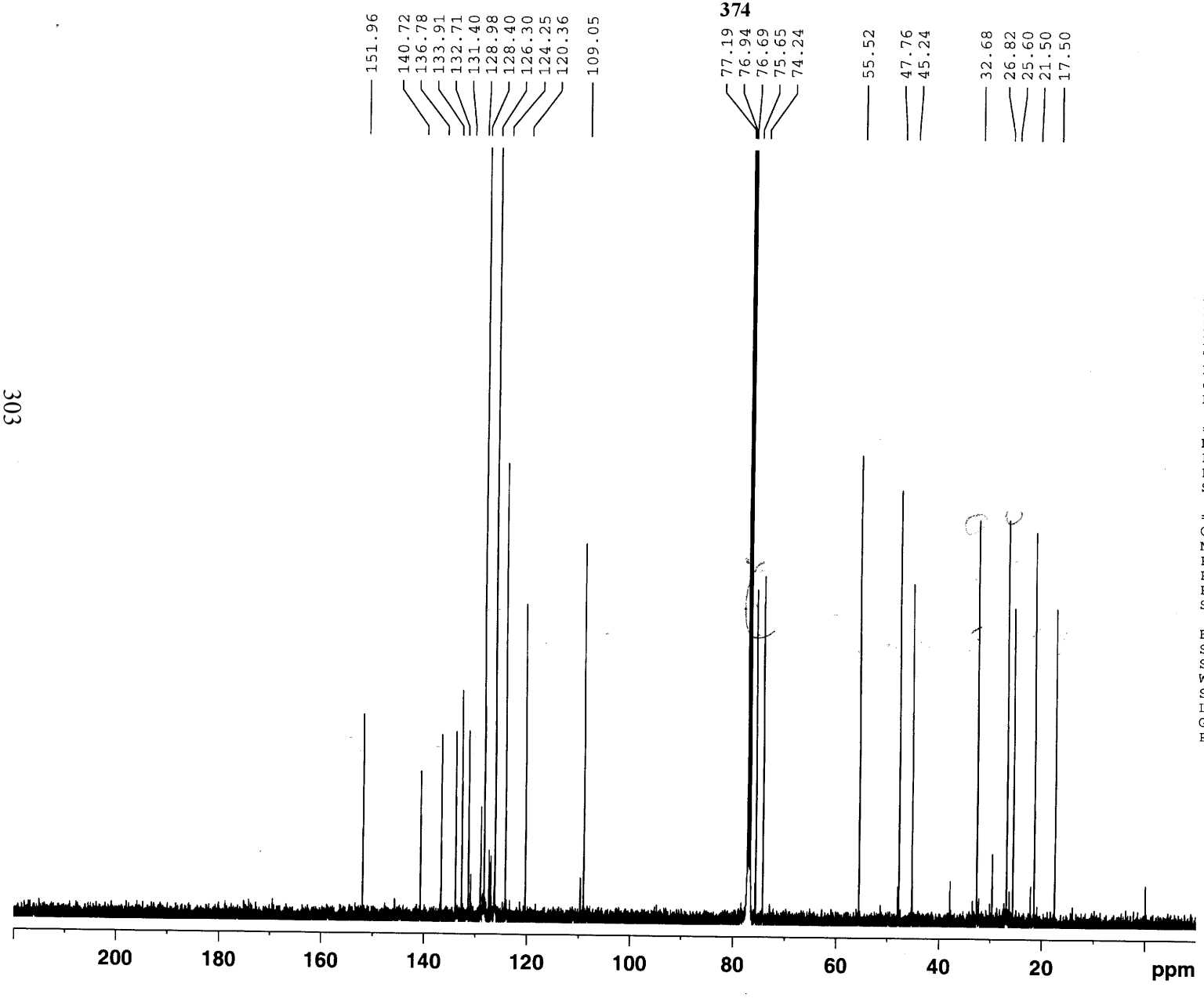


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Current Data Parameters
NAME        PZ-VIII-83-A1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070215
Time               19.05
INSTRUM          DRX500
PROBHD   5 mm Multinucl
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                 1693
DS                    4
SWH          34013.605 Hz
FIDRES        0.519006 Hz
AQ           0.9634292 sec
RG                32768
DW             14.700 usec
DE              6.00 usec
TE              300.0 K
D1          2.00000000 sec
d11         0.03000000 sec
D31         0.00000000 sec

======== CHANNEL f1 ========
NUC1               13C
P1              8.10 usec
PL1             3.00 dB
SFO1       125.7723786 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2          88.00 usec
PL2             0.00 dB
PL12           21.00 dB
SFO2       500.1320005 MHz

F2 - Processing parameters
SI                32768
SF         125.7578011 MHz
WDW                EM
SSB                 0
LB              1.00 Hz
GB                  0
PC               1.40
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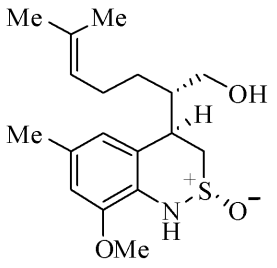
1H-NMR
PZ-VII-119-A2



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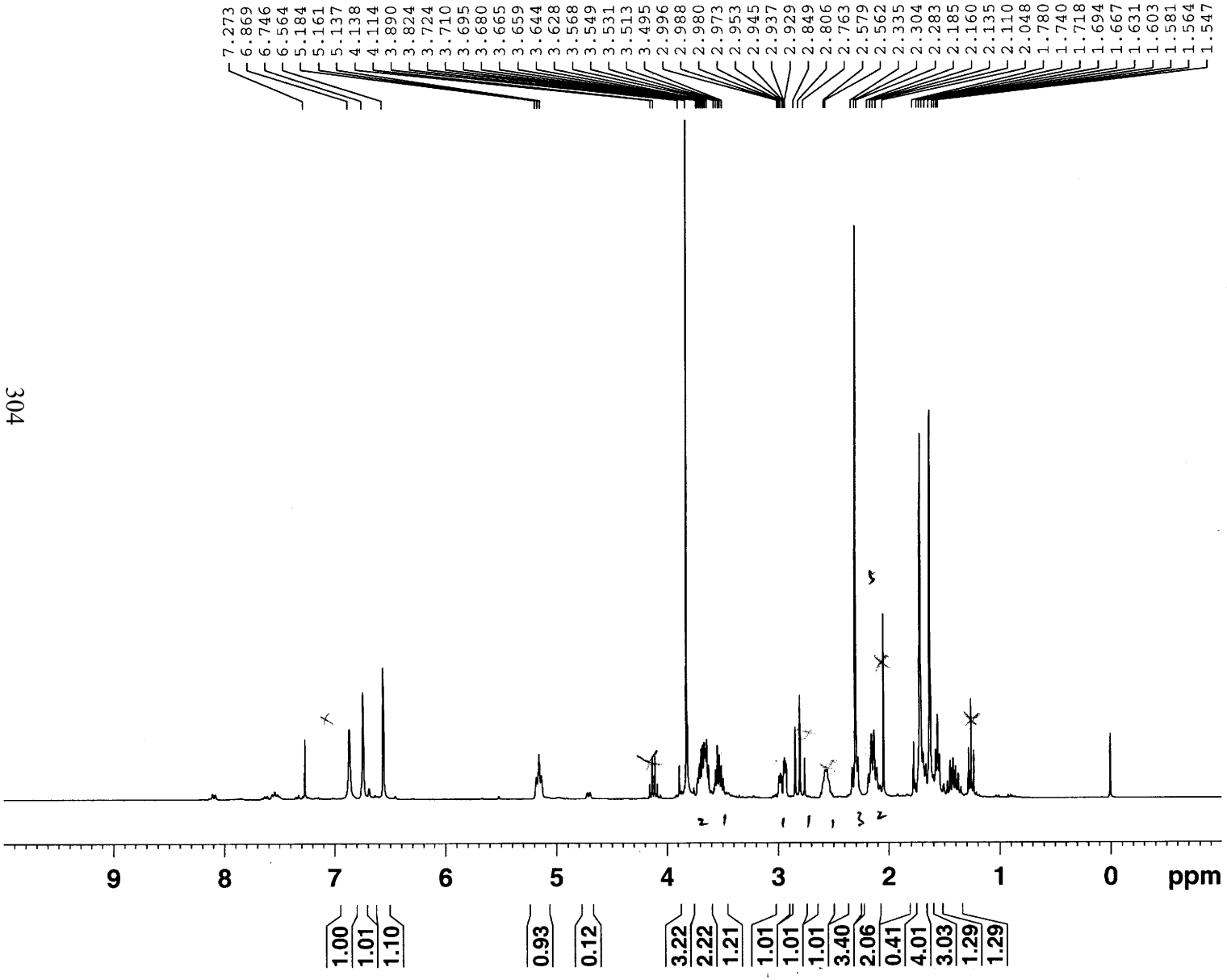


Current Data Parameters
NAME PZ-VII-119-A2
EXPNO 1
PROCNO 1

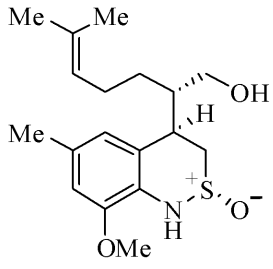
F2 - Acquisition Parameters
Date_ 20061105
Time 10.46
INSTRUM DRX300
PROBHD 5 mm Multinucl
PULPROG zg30pad
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 143.7
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
D31 0.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 7.05 usec
PL1 0.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300022 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.30

13C NMR
PZ-VII-119-A2

147.72
132.31
131.06
125.40
123.82
122.66
118.72
109.43
77.44
77.01
76.59
63.00
60.36
55.67
45.69
40.17
29.38
27.98
25.85
25.71
21.54
21.00
17.79
14.15



375

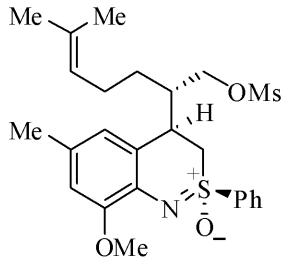
Current Data Parameters
NAME PZ-VII-119-A2
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061105
Time 10.51
INSTRUM DRX300
PROBHD 5 mm Multinucl
PULPROG zgdc30pad
TD 65536
SOLVENT CDCl3
NS 154
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 4096
DW 26.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D31 0.00000000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 5.00 dB
SFO1 75.4760107 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 21.41 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677525 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.30



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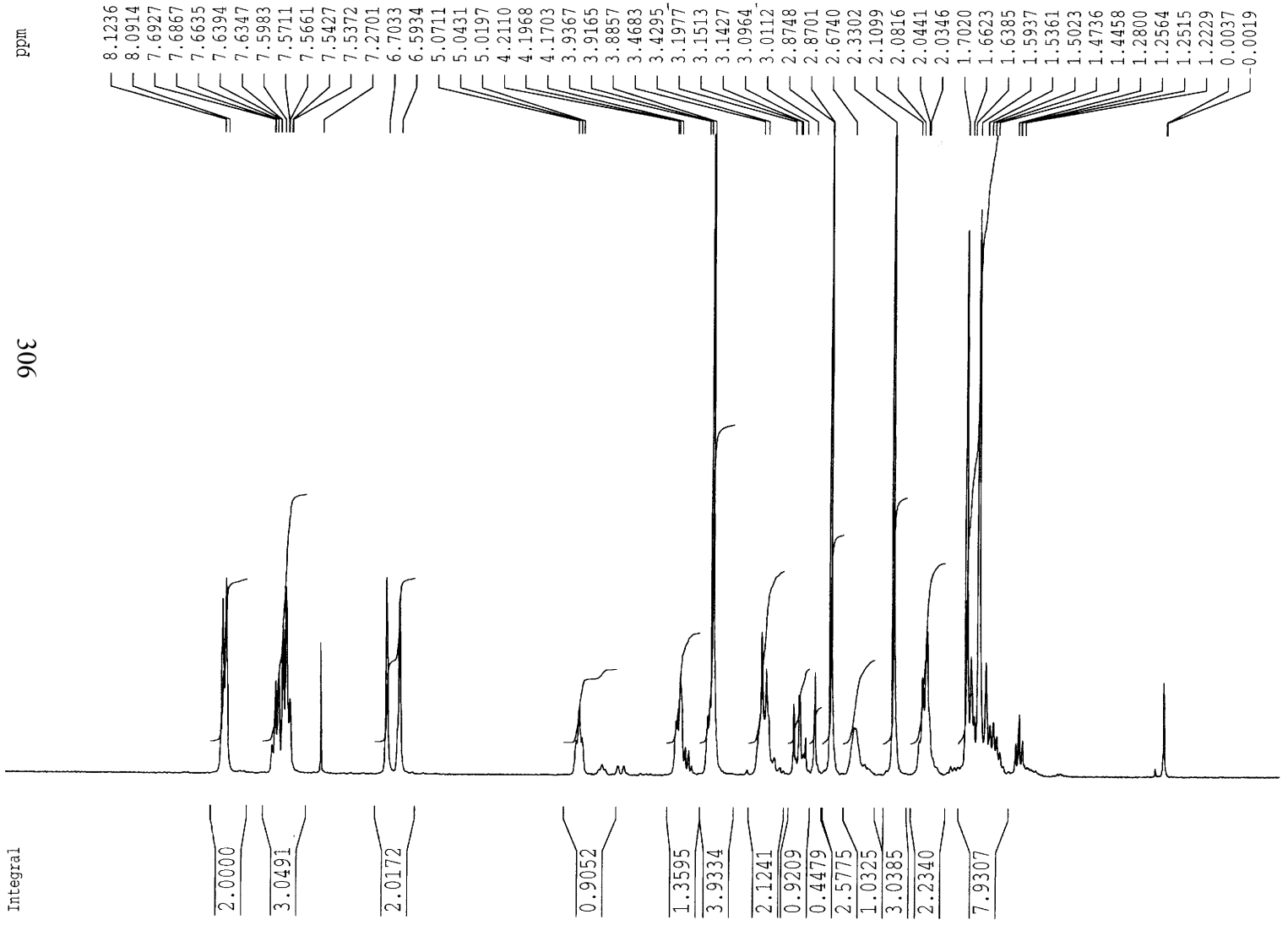


Current Data Parameters

NAME	PZ-VII-124-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

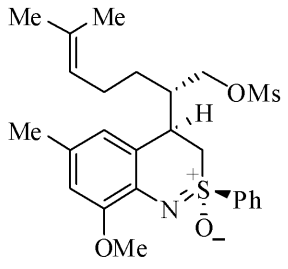
Date_	20061108
Time	19.32
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	512
DW	96.000 usec
DE	137.14 usec
TE	300.0 K
D1	1.00000000 sec
P1	9.50 usec
SFO1	250.1315321 MHz
NUCLEUS	1H

F2 - Processing parameters

SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	12.50 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm/cm
HZCM	137.57150 Hz/cm



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ppm

152.759 139.326 138.814 133.811 133.701 132.856 132.040 131.678 130.424 130.188 129.334 129.117 128.975 125.079 124.715 122.895 122.698 119.377 118.744 111.732 111.562 77.501 76.992 76.484 68.771 55.998 50.271 49.430 37.446 37.243 37.074 36.951 36.406 36.178 29.171 28.796 26.549 25.678 25.299 25.174 21.401 20.966 17.713 17.587 14.127 -0.074

307

ppm 200 150 100 50 0

Current Data Parameters

NAME	PZ-VII-124-A1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

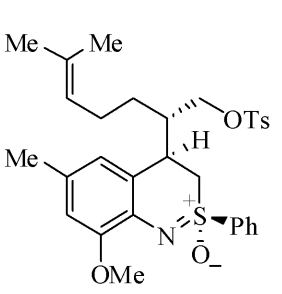
Date_	20061108
Time	23.04
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	4140
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 usec
DE	41.43 usec
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 usec
D1	2.00000000 sec
P1	8.00 usec
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

F2 - Processing parameters

SI	32768
SF	62.8952440 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	10.00 cm
F1P	220.000 ppm
F1	13836.95 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	11.50000 ppm/cm
HZCM	723.29529 Hz/cm



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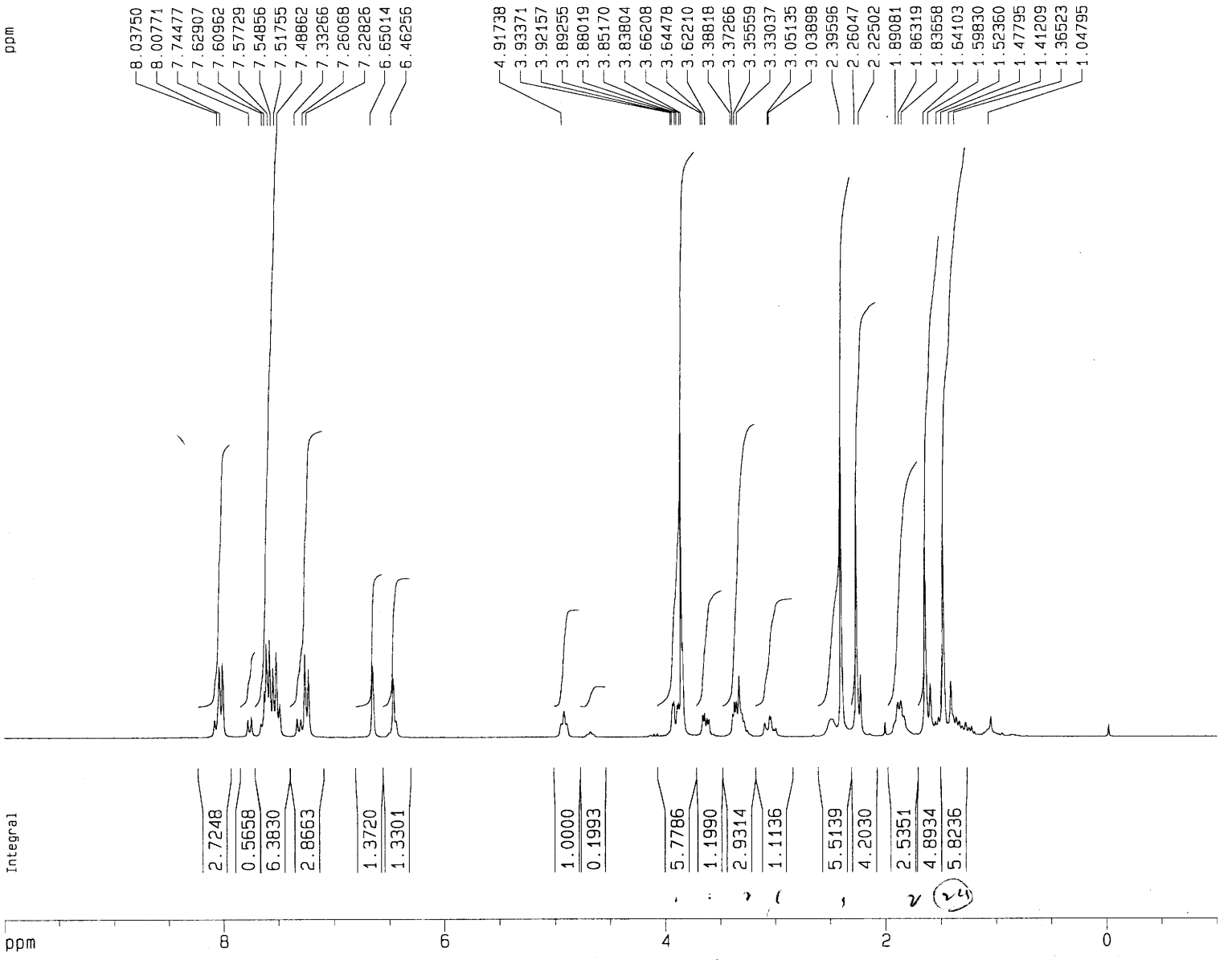


Current Data Parameters

NAME	PZ-VI-83-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

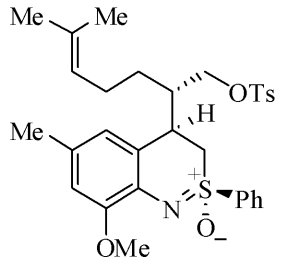
Date_	20060213
Time	13.24
INSTRUM	arx250
PROBHD	5 mm GNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	256
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	9.50 use
SFO1	250.1315321 MHz
NUCLEUS	1H

F2 - Processing parameters

SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	5.00 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57150 Hz/



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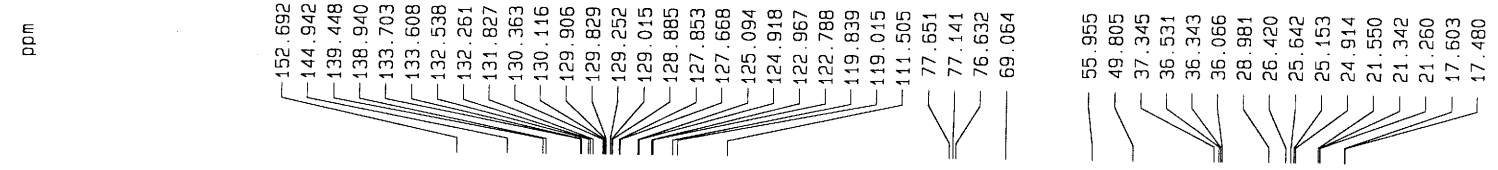
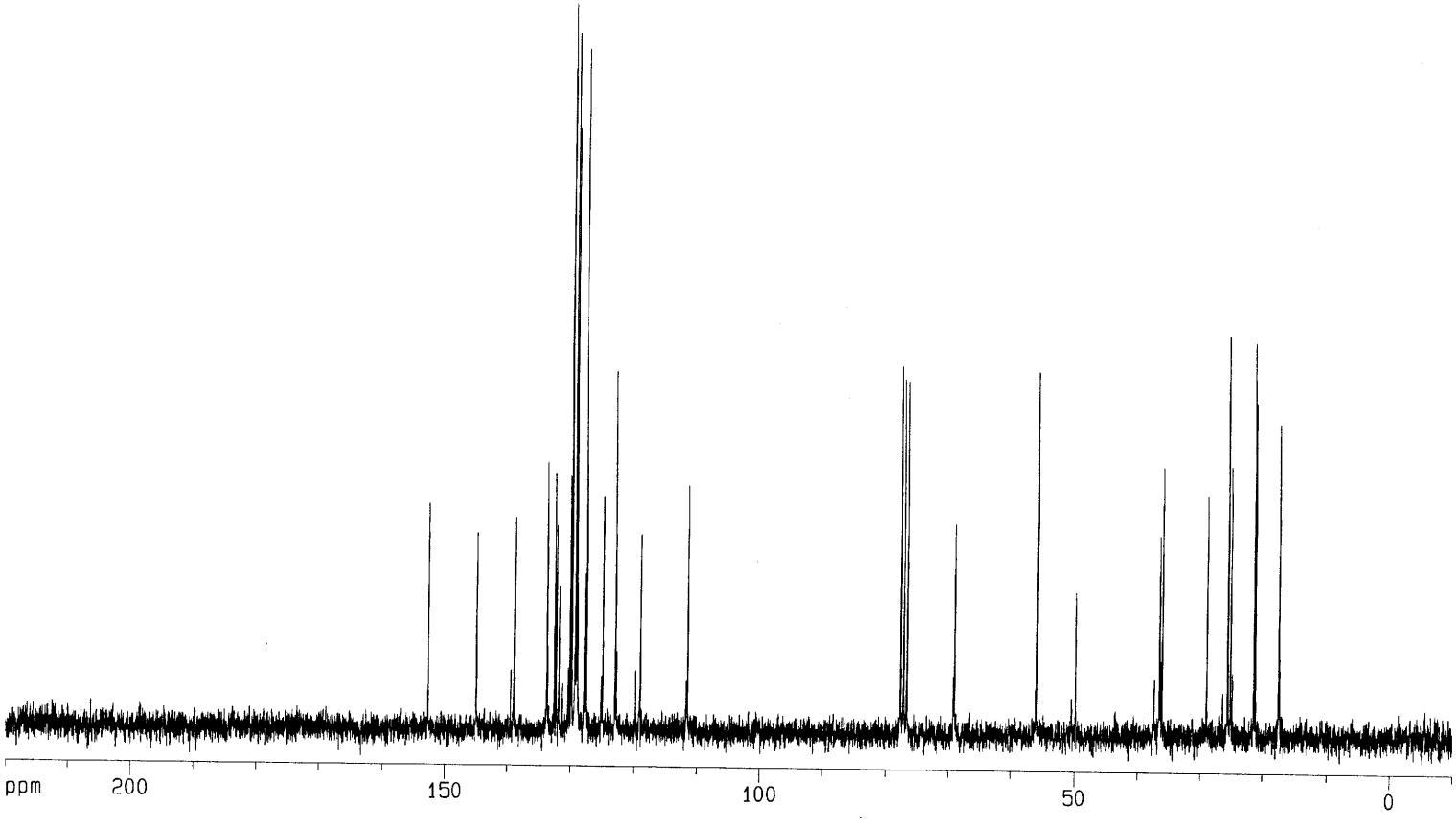




Current Data Parameters

NAME	PZ-VI-83-A1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

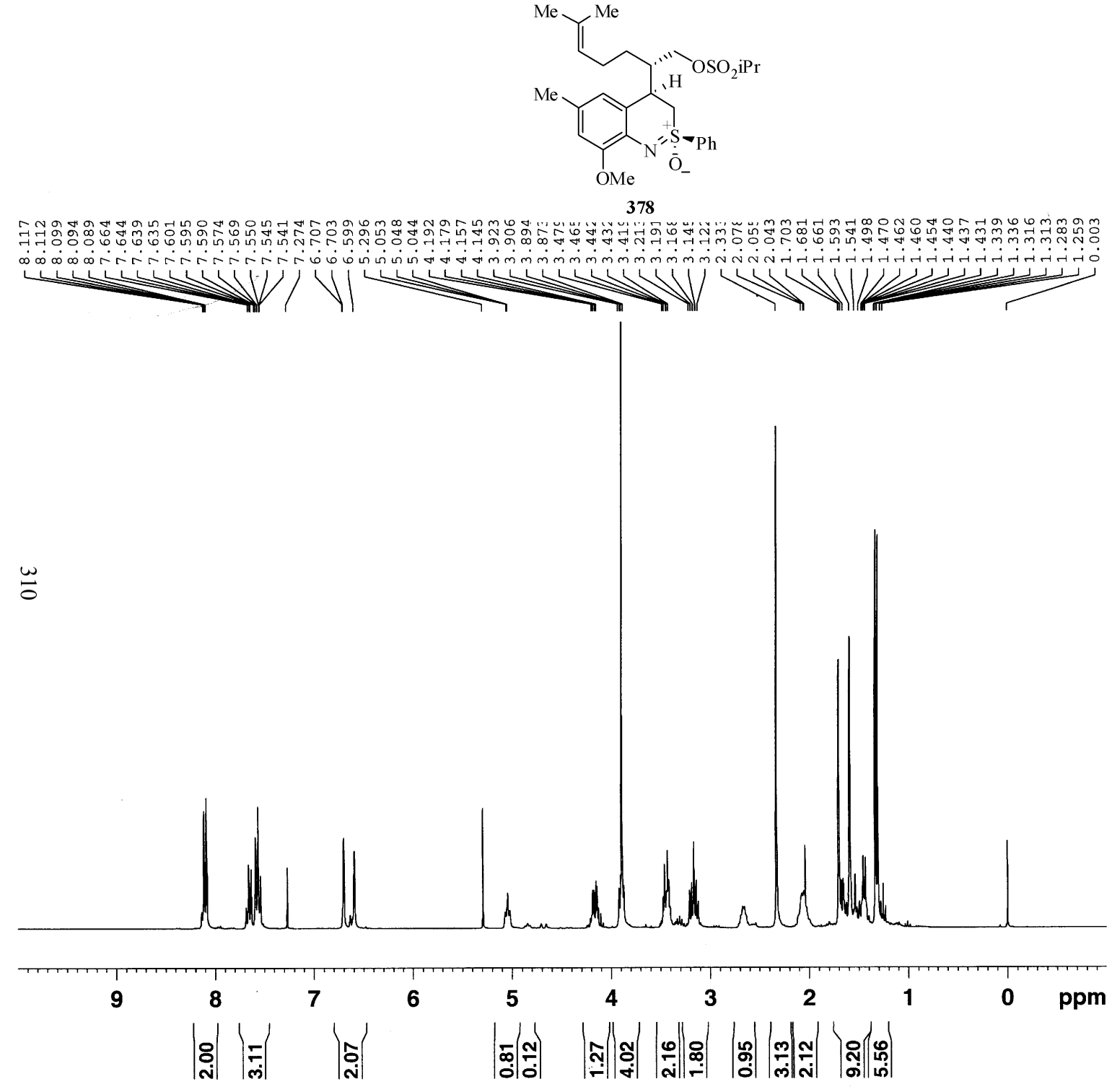
Date_	20060213
Time	13.27
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	104
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	2.00000000 sec
P1	8.00 use
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

F2 - Processing parameters

SI	32768
SF	62.8952440 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	10.00 cm
F1P	220.000 ppm
F1	13836.95 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	11.50000 ppm
HZCM	723.29529 Hz/

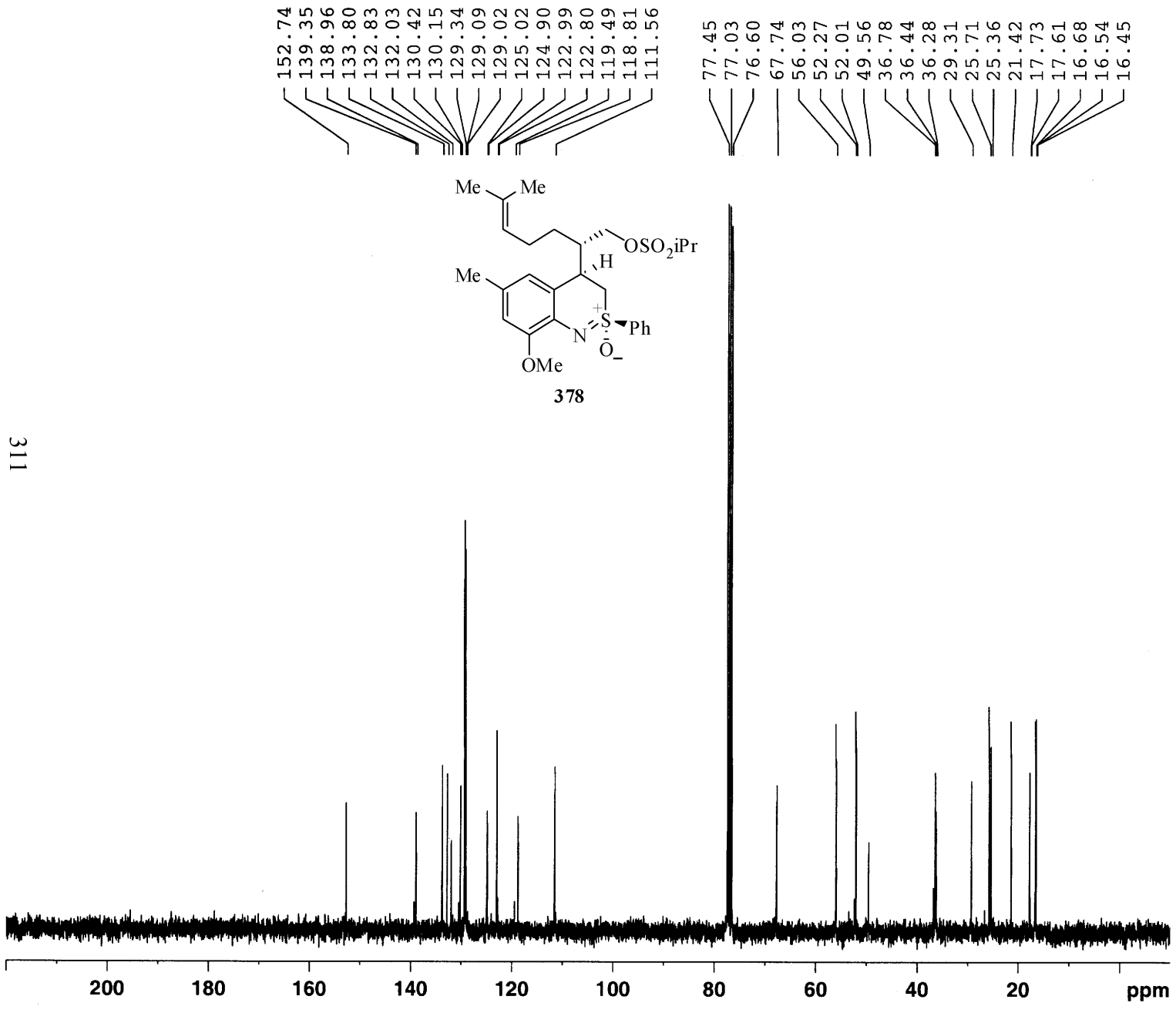


Current Data Parameters
NAME PZ-VII-125-A1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061107
Time 9.05
INSTRUM DRX300
PROBHD 5 mm Multinucl
PULPROG zg30pad
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 128
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
D31 0.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 7.05 usec
PL1 0.00 dB
SFO1 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300022 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.30



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Current Data Parameters
NAME       PZ-VII-125-A1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20061107
Time                9.07
INSTRUM           DRX300
PROBHD   5 mm Multinucl
PULPROG        zgdc30pad
TD                 65536
SOLVENT            CDCl3
NS                   253
DS                     4
SWH          18832.393 Hz
FIDRES        0.287360 Hz
AQ            1.7400308 sec
RG                 22528
DW                26.550 usec
DE                 6.00 usec
TE                300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
D31          0.00000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.00 usec
PL1                5.00 dB
SFO1         75.4760107 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                120.00 dB
PL12                21.41 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677525 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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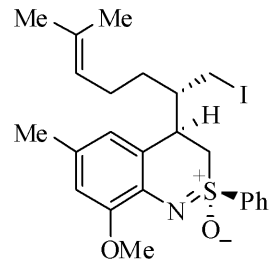

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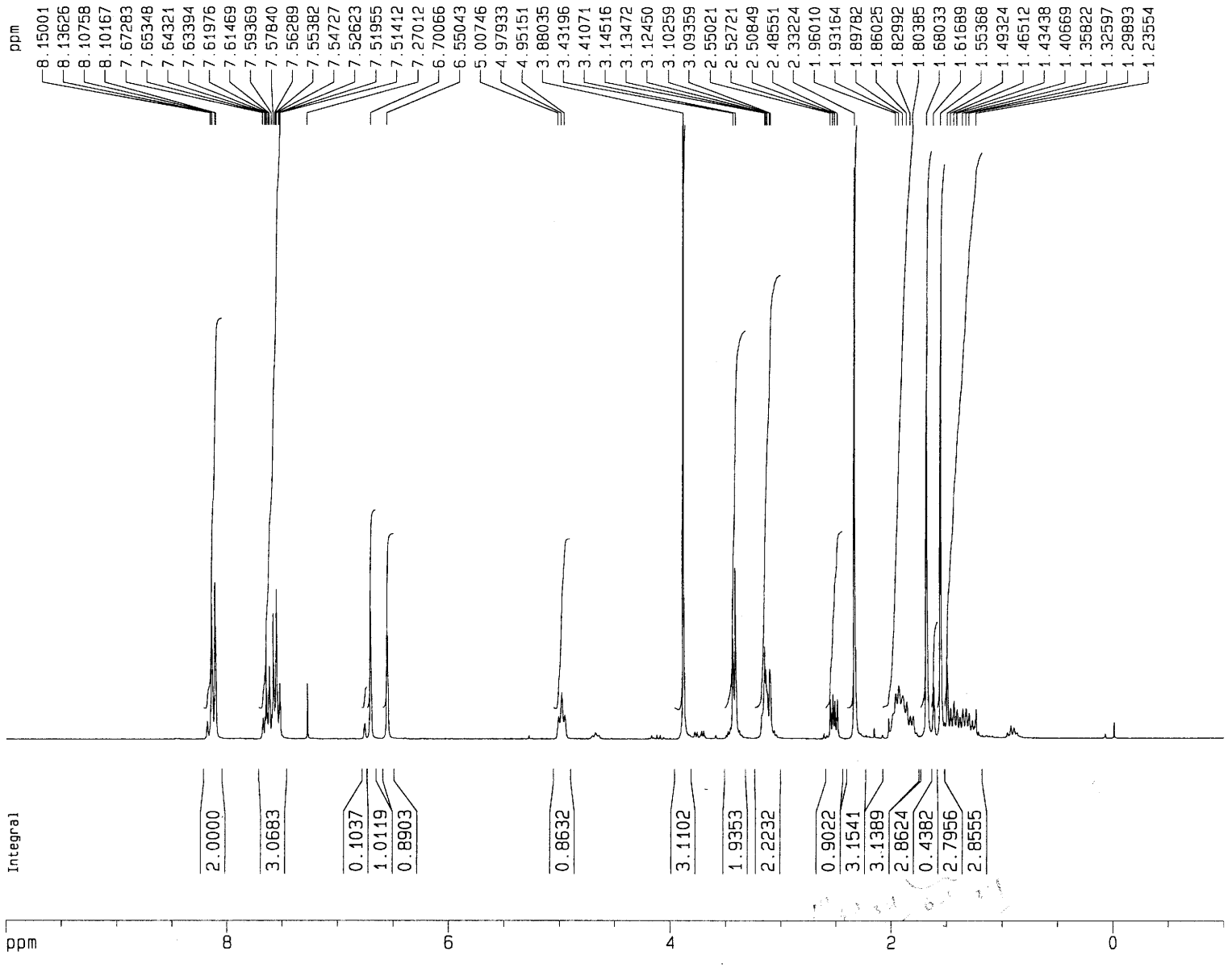


Current Data Parameters

NAME	PZ-VI-140-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

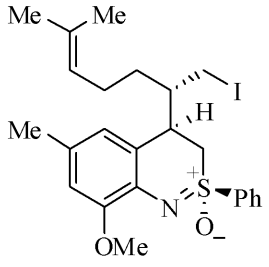
Date_	20060519
Time	14.40
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	256
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	9.50 use
SFO1	250.1315321 MHz
NUCLEUS	1H

F2 - Processing parameters

SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	12.50 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57150 Hz/



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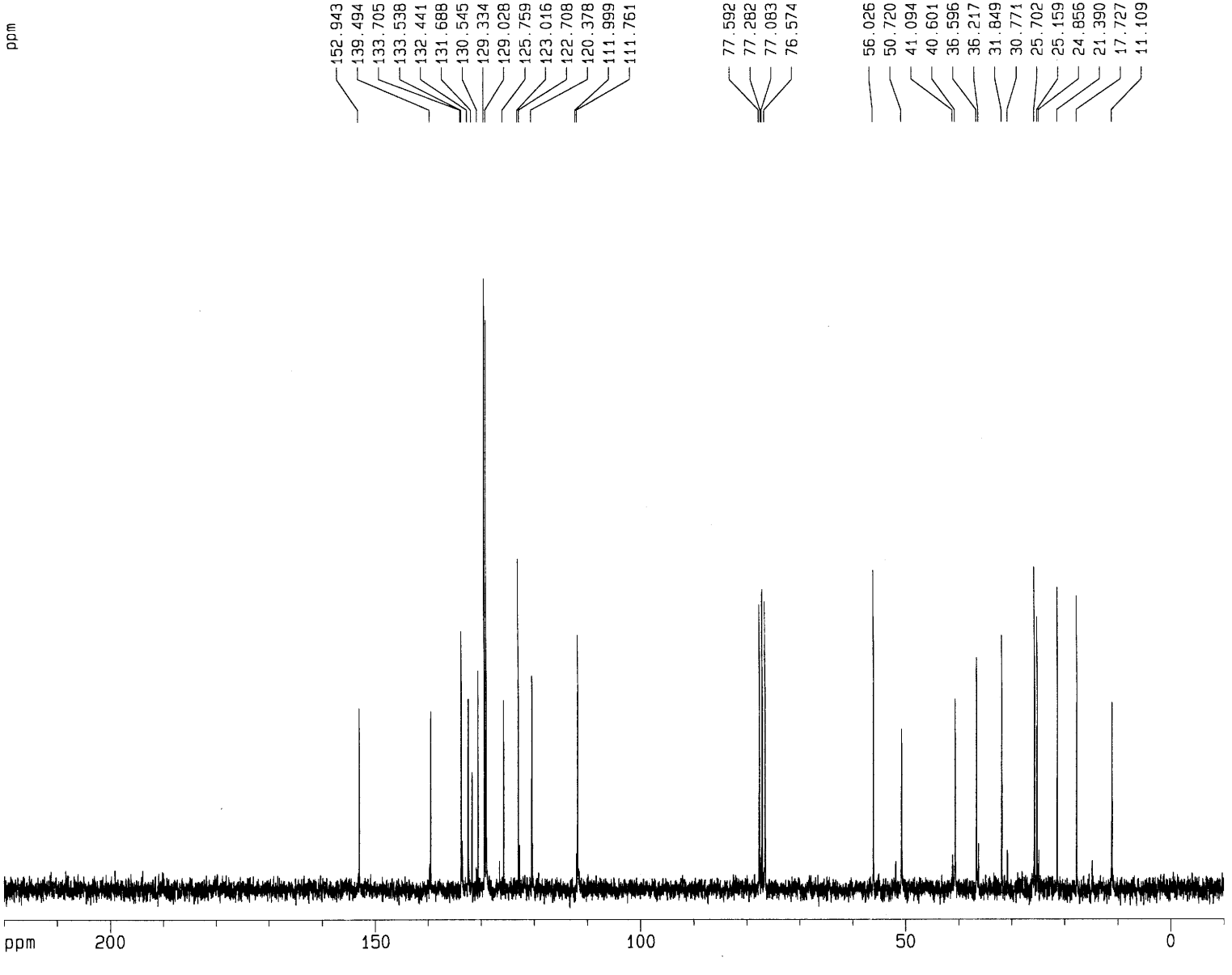


Current Data Parameters

NAME	PZ-VI-140-A1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20060519
Time	14.44
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	135
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	2.00000000 sec
P1	8.00 use
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

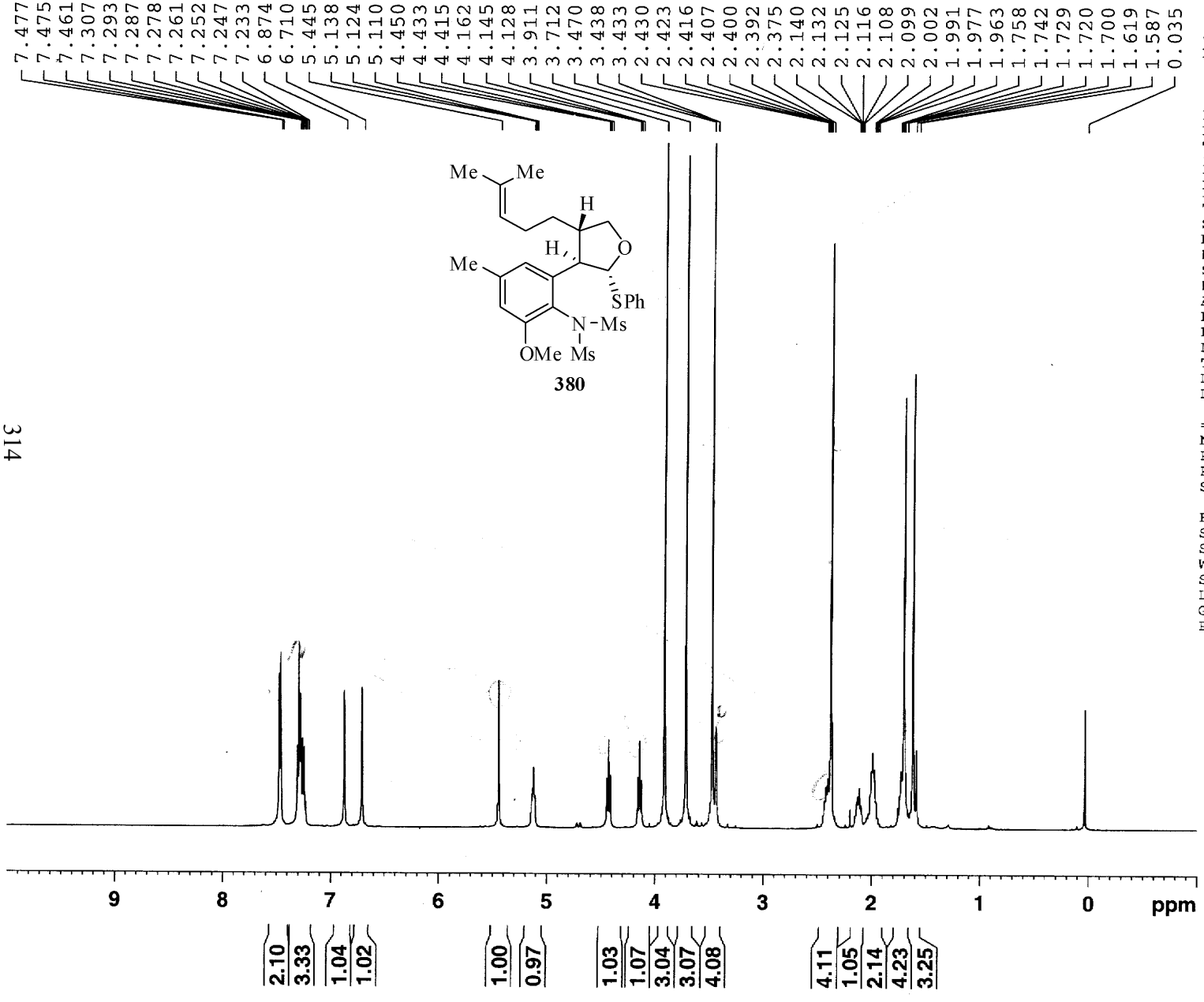
F2 - Processing parameters

SI	32768
SF	62.8952440 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	10.00 cm
F1P	220.000 ppm
F1	13836.95 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	11.50000 ppm
HZCM	723.29529 Hz/

1H NMR
PZ-VIII-20-B1
Recrystln Acetone/MeOH



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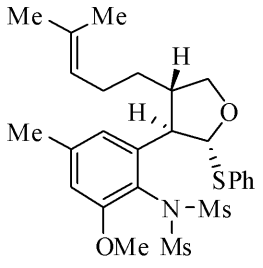
Current Data Parameters
NAME PZ-VIII-20-B1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061214
Time 16.33
INSTRUM DRX500
PROBHD 5 mm Multinucl
PULPROG zg30pad
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 161.3
DW 48.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
D31 0.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 11.50 usec
PL1 0.00 dB
SFO1 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40



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156.46
148.01
142.68
134.89
131.84
131.56
128.83
127.23
123.74
120.71
118.58
111.26
95.24
77.21
76.96
76.70
72.40
56.01
53.46
48.65
43.97
43.21
34.27
27.01
25.64
22.02
17.60

200 180 160 140 120 100 80 60 40 20 ppm

```
Current Data Parameters
NAME        PZ-VIII-20-B1
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20061214
Time                16.34
INSTRUM           DRX500
PROBHD   5 mm Multinucl
PULPROG           zgdc30
TD                65536
SOLVENT           CDCl3
NS                  149
DS                    4
SWH          34013.605 Hz
FIDRES        0.519006 Hz
AQ           0.9634292 sec
RG                32768
DW               14.700 usec
DE                6.00 usec
TE               300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
D31          0.00000000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                8.10 usec
PL1               3.00 dB
SFO1       125.7723786 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            88.00 usec
PL2               0.00 dB
PL12             21.00 dB
SFO2       500.1320005 MHz

F2 - Processing parameters
SI                32768
SF         125.7578011 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
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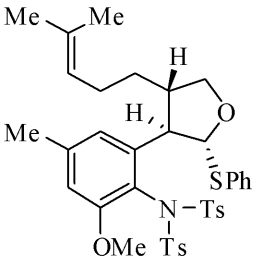

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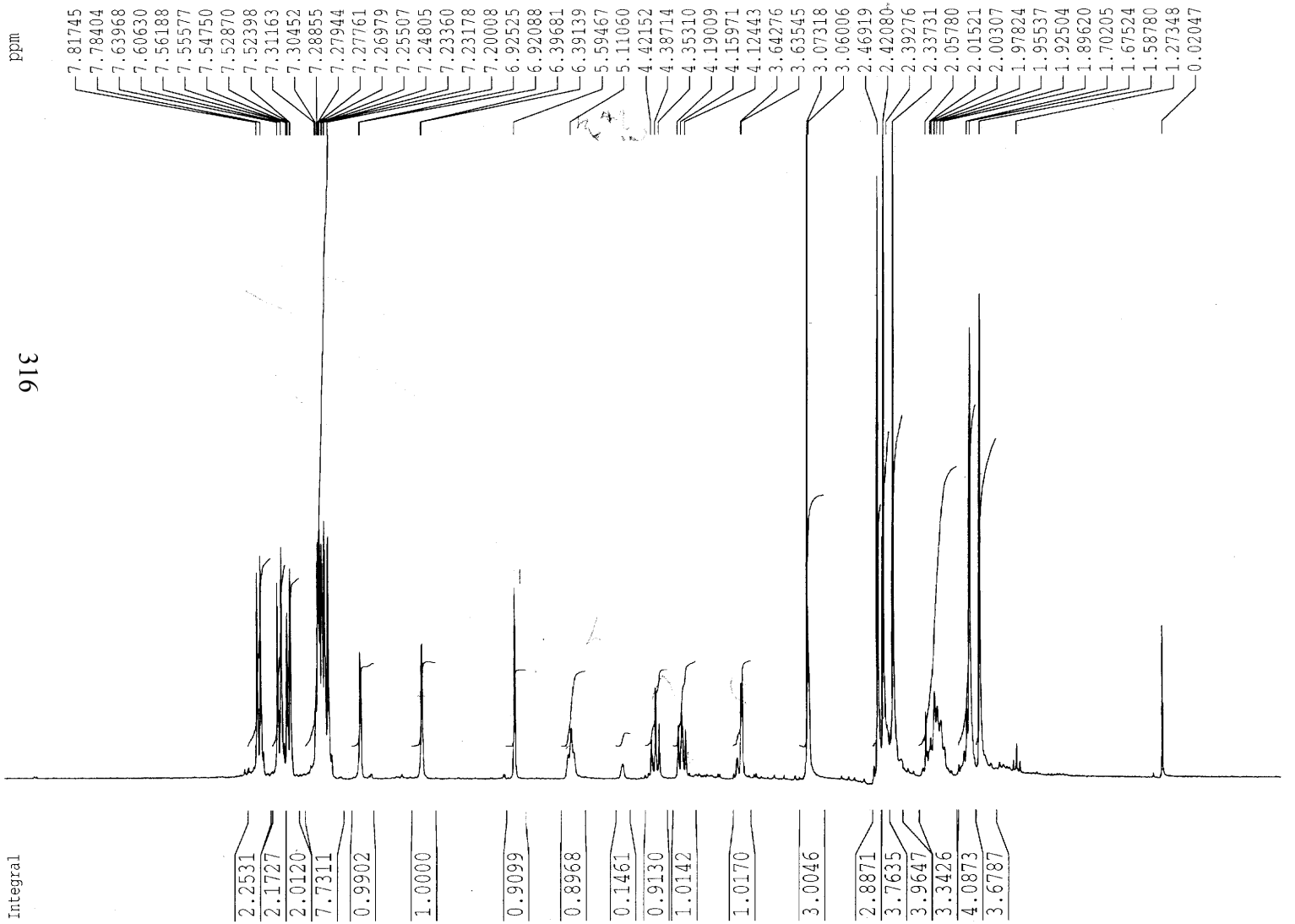


Current Data Parameters

NAME	PZ-VIII-73-A01
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

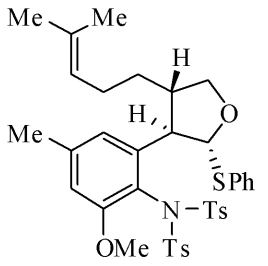
Date_	20070209
Time	23.19
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	715
DW	96.000 usec
DE	137.14 usec
TE	300.0 K
D1	1.00000000 sec
P1	9.50 usec
SFO1	250.1315321 MHz
NUCLEUS	1H

F2 - Processing parameters

SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	12.50 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm/cm
HZCM	137.57150 Hz/cm



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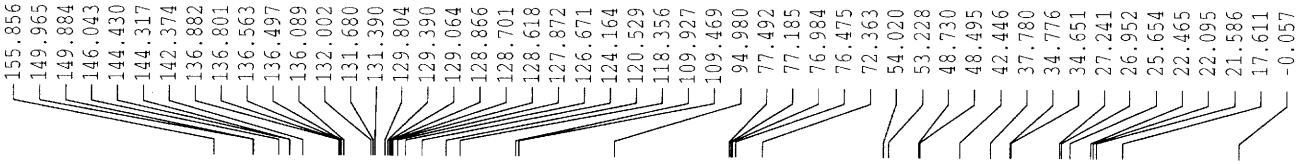
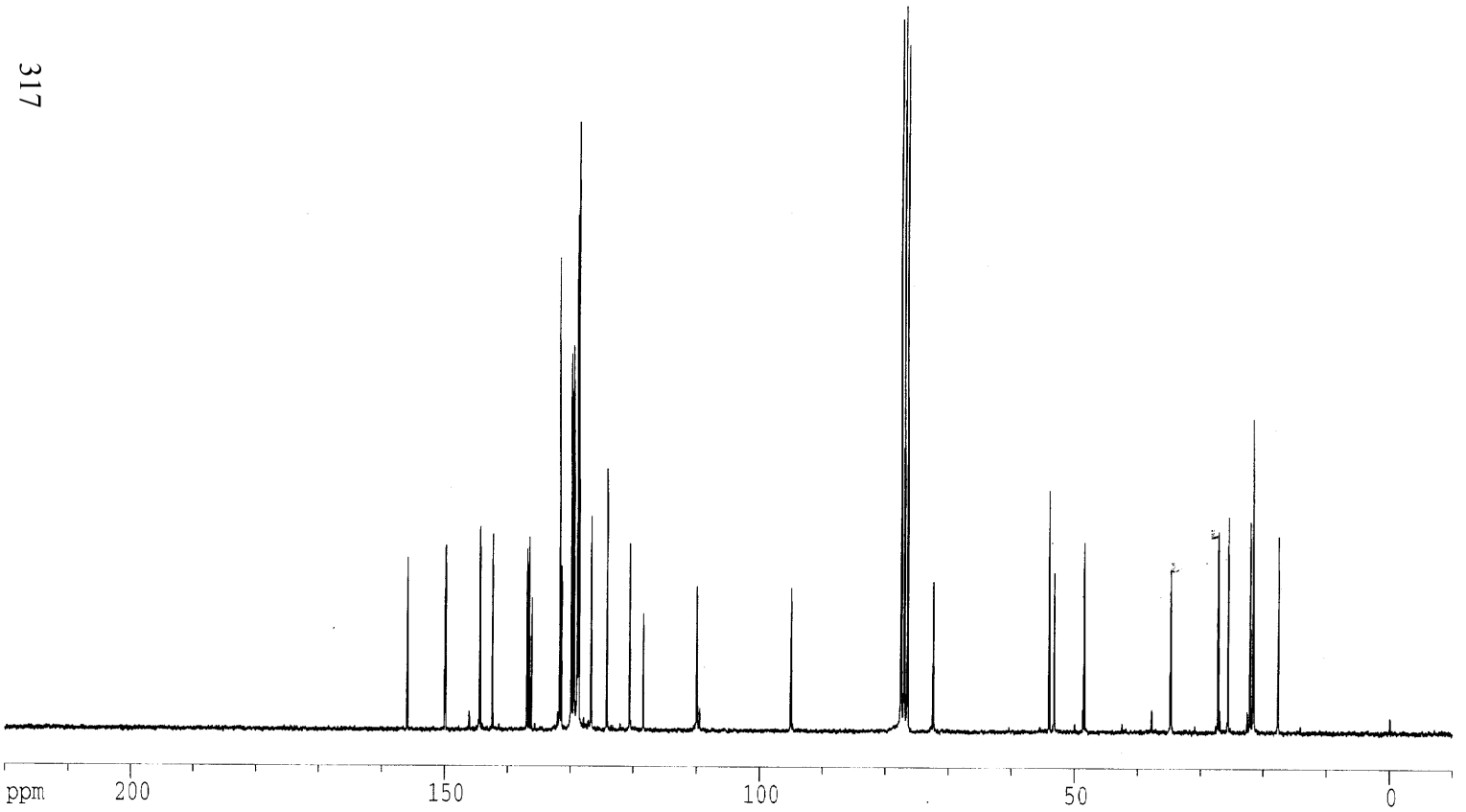




Current Data Parameters

NAME	PZ-VIII-73-A01
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

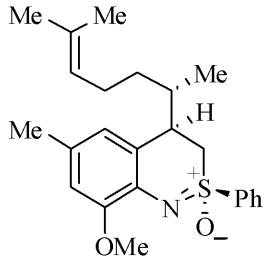
Date_	20070210
Time	19.14
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	21751
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 usec
DE	41.43 usec
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 usec
D1	2.00000000 sec
P1	8.00 usec
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

F2 - Processing parameters

SI	32768
SF	62.8952440 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	10.00 cm
F1P	220.000 ppm
F1	13836.95 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	11.50000 ppm/cm
HZCM	723.29529 Hz/cm



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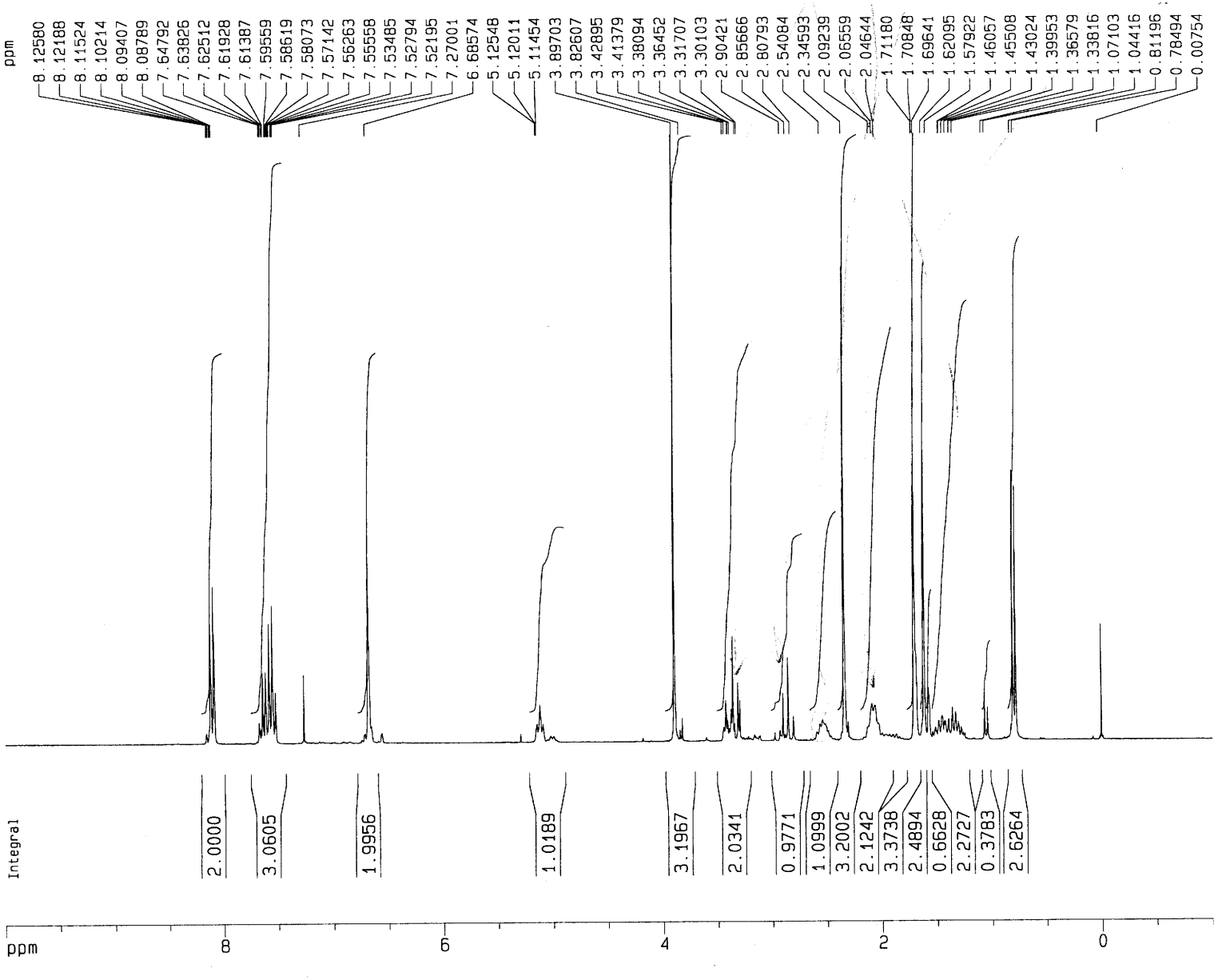


Current Data Parameters

NAME	PZ-VI-142-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

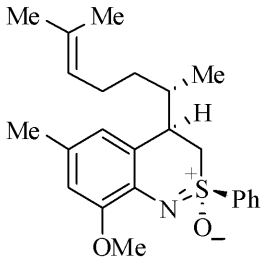
Date_	20060522
Time	23.48
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	715
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	9.50 use
SFO1	250.1315321 MHz
NUCLEUS	1H

F2 - Processing parameters

SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	12.50 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57150 Hz/



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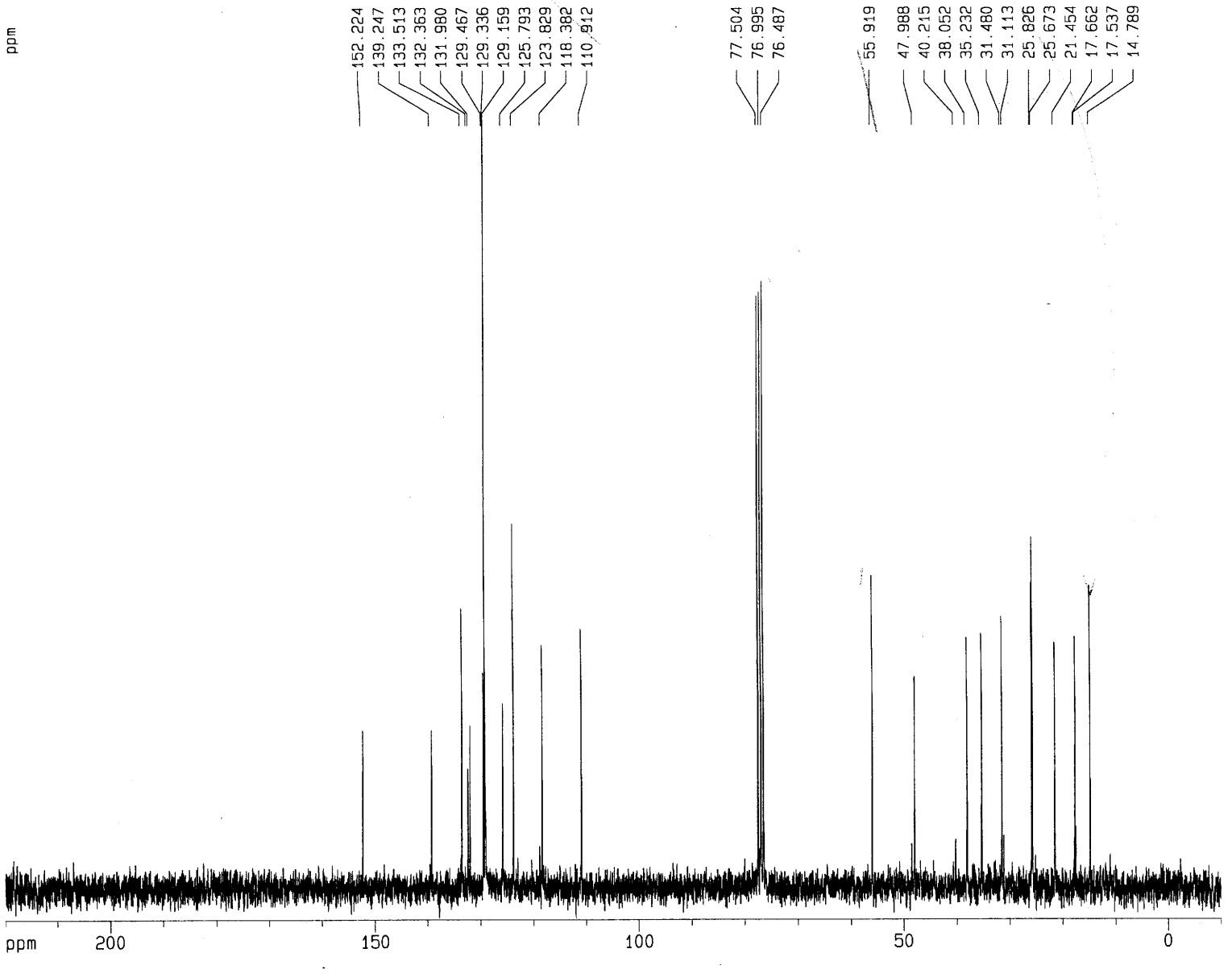


Current Data Parameters

NAME	PZ-VI-142-A1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

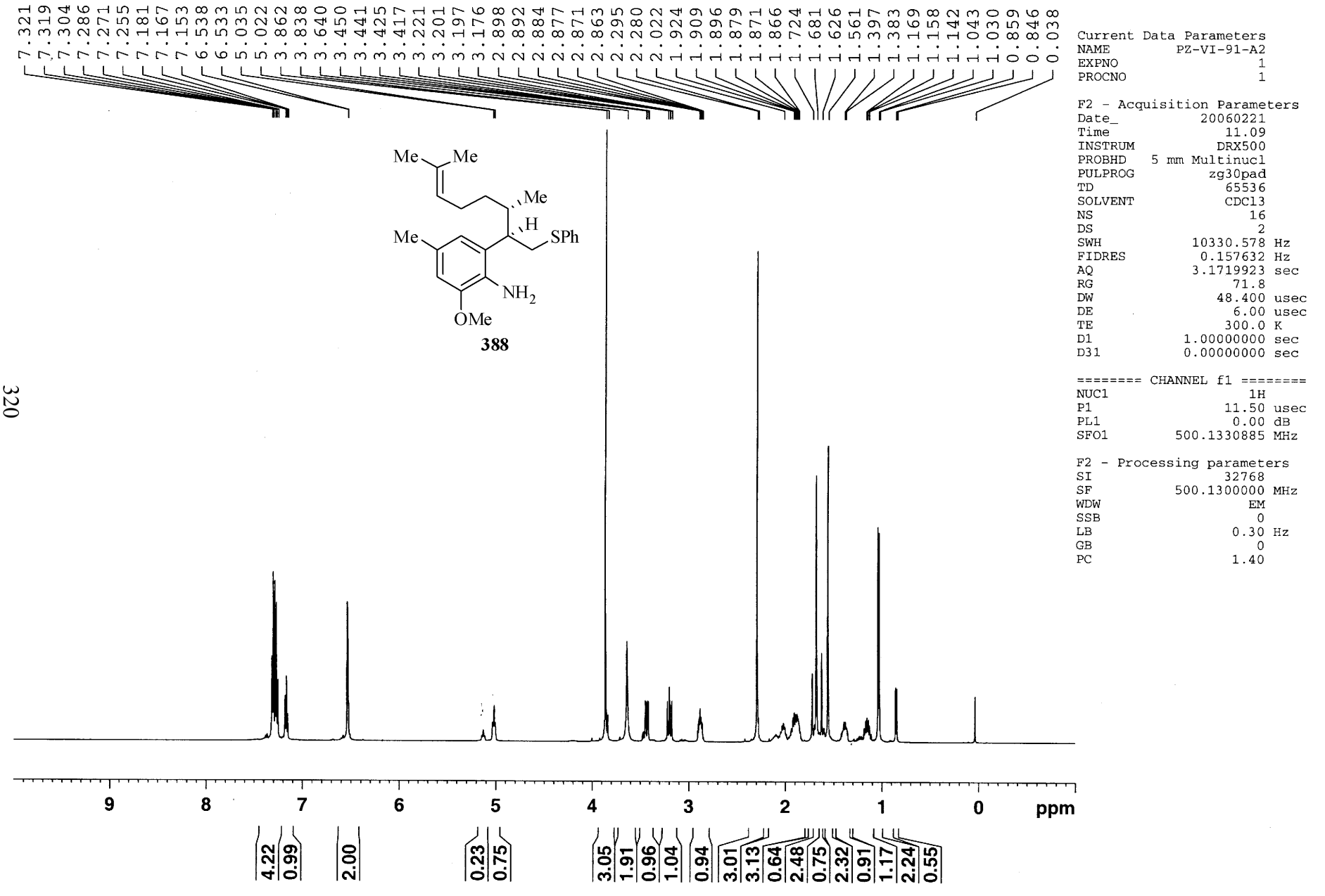
Date_	20060522
Time	23.50
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	278
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	2.00000000 sec
P1	8.00 use
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

F2 - Processing parameters

SI	32768
SF	62.8952440 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	20.00 cm
F1P	220.000 ppm
F1	13836.95 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	11.50000 ppm
HZCM	723.29529 Hz/



Current Data Parameters

NAME	PZ-VI-91-A2
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

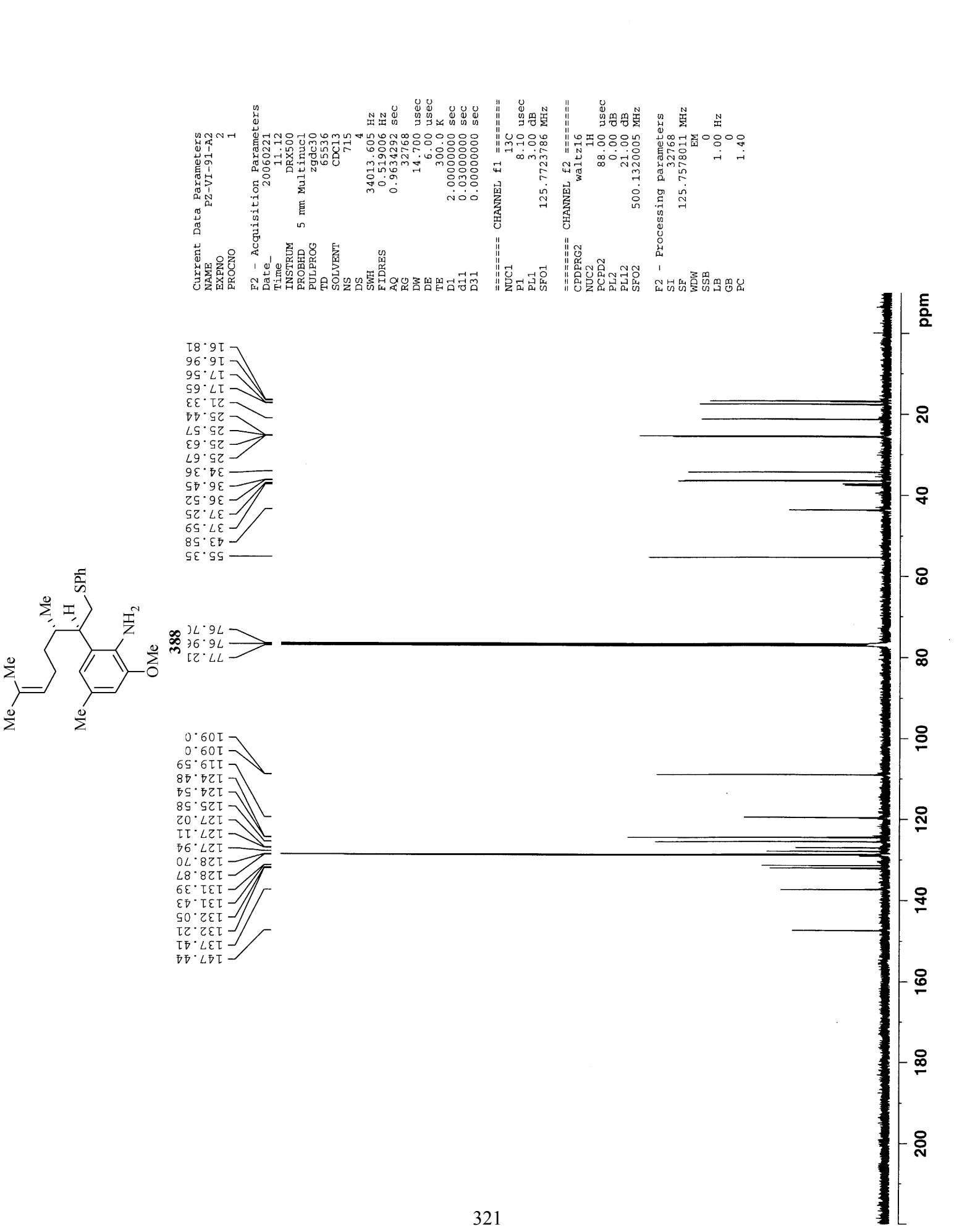
Date_	20060221
Time	11.09
INSTRUM	DRX500
PROBHD	5 mm Multinucl
PULPROG	zg30pad
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1719923 sec
RG	71.8
DW	48.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
D31	0.00000000 sec

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

NUC1	1H
P1	11.50 usec
PL1	0.00 dB
SFO1	500.1330885 MHz

F2 - Processing parameters

SI	32768
SF	500.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.40


Me
Me
Me
H
SPh
NH2
OMe
Me
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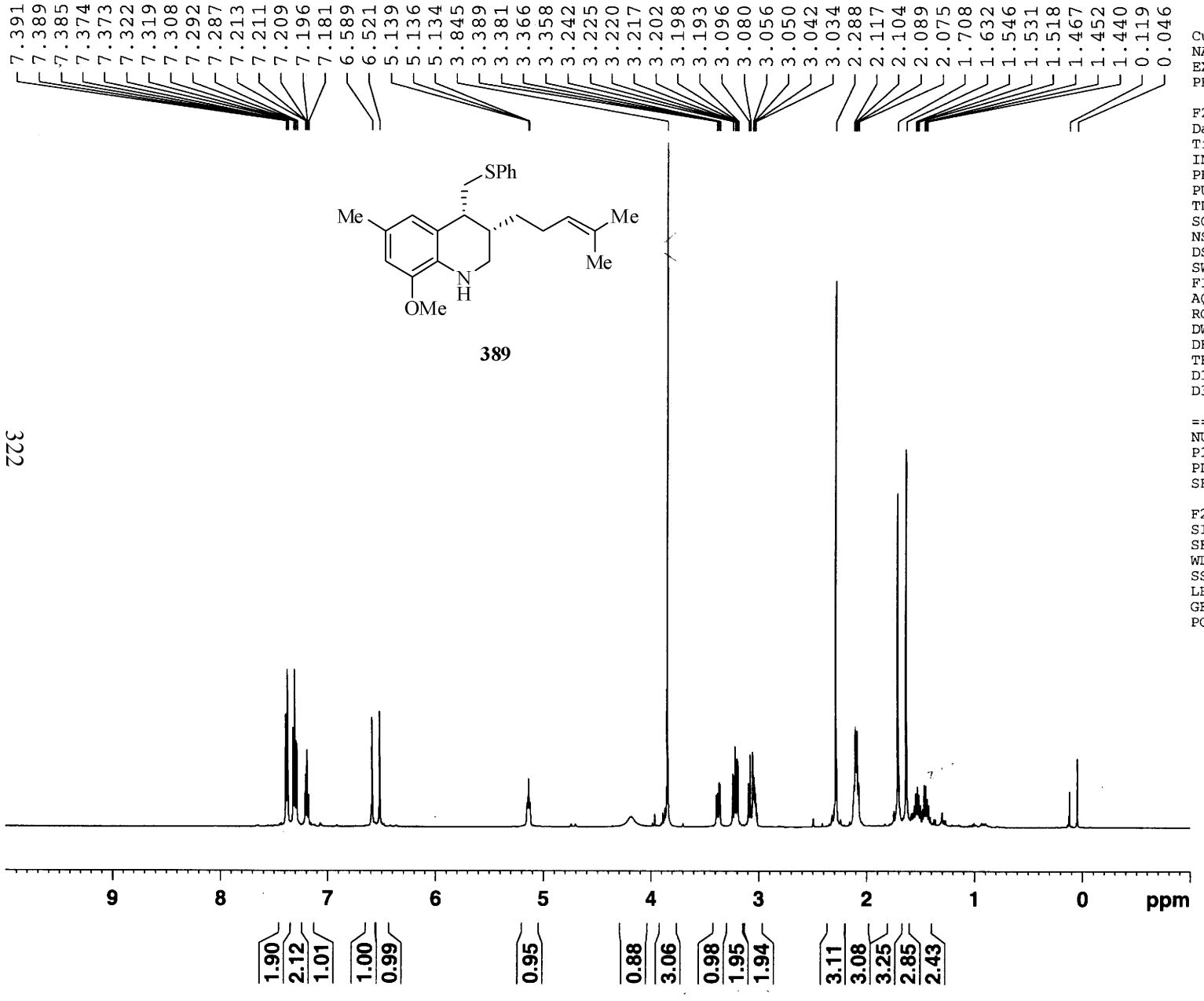
Current Data Parameters
NAME P2-VI-91-A2
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060221
Time 11.12
INSTRUM DRX500
PROBHD 5 mm Multinucl
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 715
DS 4
SWH 34013.605 Hz
FIDRES 0.519006 Hz
AQ 0.9634292 sec
RG 32768
DW 14.700 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
D31 0.00000000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.10 usec
PL1 3.00 dB
SFO1 125.7723786 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 88.00 usec
PL2 0.00 dB
PL12 21.00 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7578011 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
147.44
137.41
132.21
132.05
131.43
131.39
128.87
128.70
127.94
127.11
127.02
125.58
124.54
124.48
119.59
109.0
109.0
109.0
77.21
76.96
76.70
55.35
43.58
37.59
37.25
36.52
36.45
34.36
25.67
25.63
25.57
25.44
21.33
17.65
17.56
16.96
16.81
200
180
160
140
120
100
80
60
40
20
ppm



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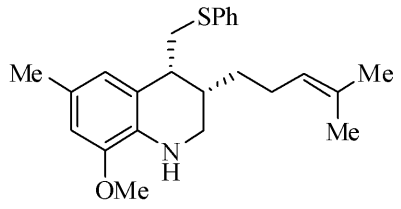
Current Data Parameters
NAME       PZ-VIII-56-A1
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20070121
Time              16.07
INSTRUM          DRX500
PROBHD   5 mm Multinucl
PULPROG        zg30pad
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH          10330.578 Hz
FIDRES        0.157632 Hz
AQ           3.1719923 sec
RG                71.8
DW              48.400 usec
DE               6.00 usec
TE              300.0 K
D1           1.00000000 sec
D31          0.00000000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1               11.50 usec
PL1               0.00 dB
SFO1       500.1330885 MHz

F2 - Processing parameters
SI                32768
SF        500.1300000 MHz
WDW                  EM
SSB                   0
LB                0.30 Hz
GB                    0
PC                1.40
```



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145.77
137.41
131.83
130.63
129.04
128.73
125.65
124.16
124.06
123.14
121.71
109.19
77.22
76.96
76.71
55.31
42.99
39.44
35.41
34.92
29.56
25.74
25.66
21.01
17.69

200 180 160 140 120 100 80 60 40 20 ppm

```
Current Data Parameters
NAME       PZ-VIII-56-A1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070121
Time               16.09
INSTRUM           DRX500
PROBHD   5 mm Multinucl
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                   53
DS                    4
SWH           34013.605 Hz
FIDRES         0.519006 Hz
AQ             0.9634292 sec
RG                32768
DW               14.700 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
D31           0.00000000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 8.10 usec
PL1                3.00 dB
SFO1        125.7723786 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2             88.00 usec
PL2                0.00 dB
PL12              21.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                32768
SF          125.7578011 MHz
WDW                EM
SSB                 0
LB              1.00 Hz
GB                  0
PC               1.40
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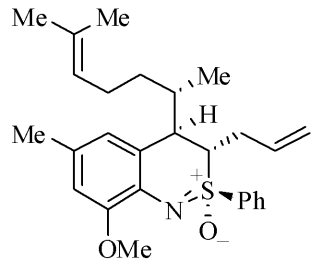


365

ppm 8.1407 8.1343 8.1259 8.1205 8.1129 8.1068 7.6057 7.5830 7.5774 7.5721 7.5613 7.5507 7.5283 7.5201 7.4927 7.4863 7.2710 6.6492 6.6437 6.3793 5.1308 5.0925 5.0904 5.0260 5.0224 4.8655 3.8569 3.7475 3.7421 3.7309 3.7253 3.7051 3.6996 3.6879 3.6830 2.5595 2.5548 2.5185 2.5137 2.2872 2.0199 1.8937 1.8766 1.8657 1.8521 1.8390 1.6344 1.5748 1.4874 1.4252 1.2627 1.2341 0.9097 0.6865 0.6601 0.4863 0.4600

Integral 2.0000 3.0020 0.9956 0.9902 0.9715 1.9982 0.8735 0.1055 3.0622 0.9382 0.9890 1.0110 2.9470 1.0727 2.1823 3.9734 2.6415 0.4419 1.1183 1.0416 0.4132 2.6501

ppm 8 6 4 2 0

Current Data Parameters

NAME	PZ-VII-12-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

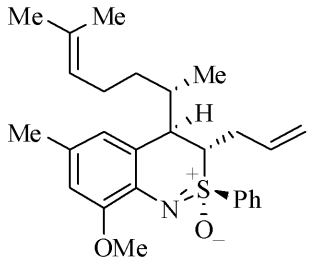
Date_	20060612
Time	12.58
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	256
DW	96.000 usec
DE	137.14 usec
TE	300.0 K
D1	1.00000000 sec
P1	9.50 usec
SFO1	250.1315321 MHz
NUCLEUS	1H

F2 - Processing parameters

SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	12.50 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm/cm
HZCM	137.57150 Hz/cm



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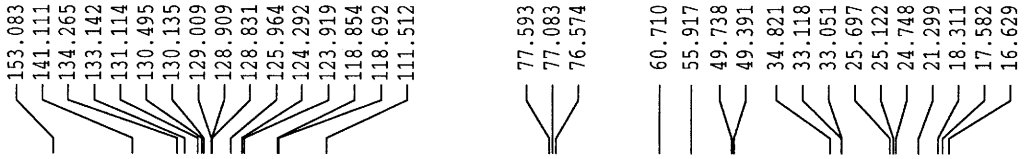
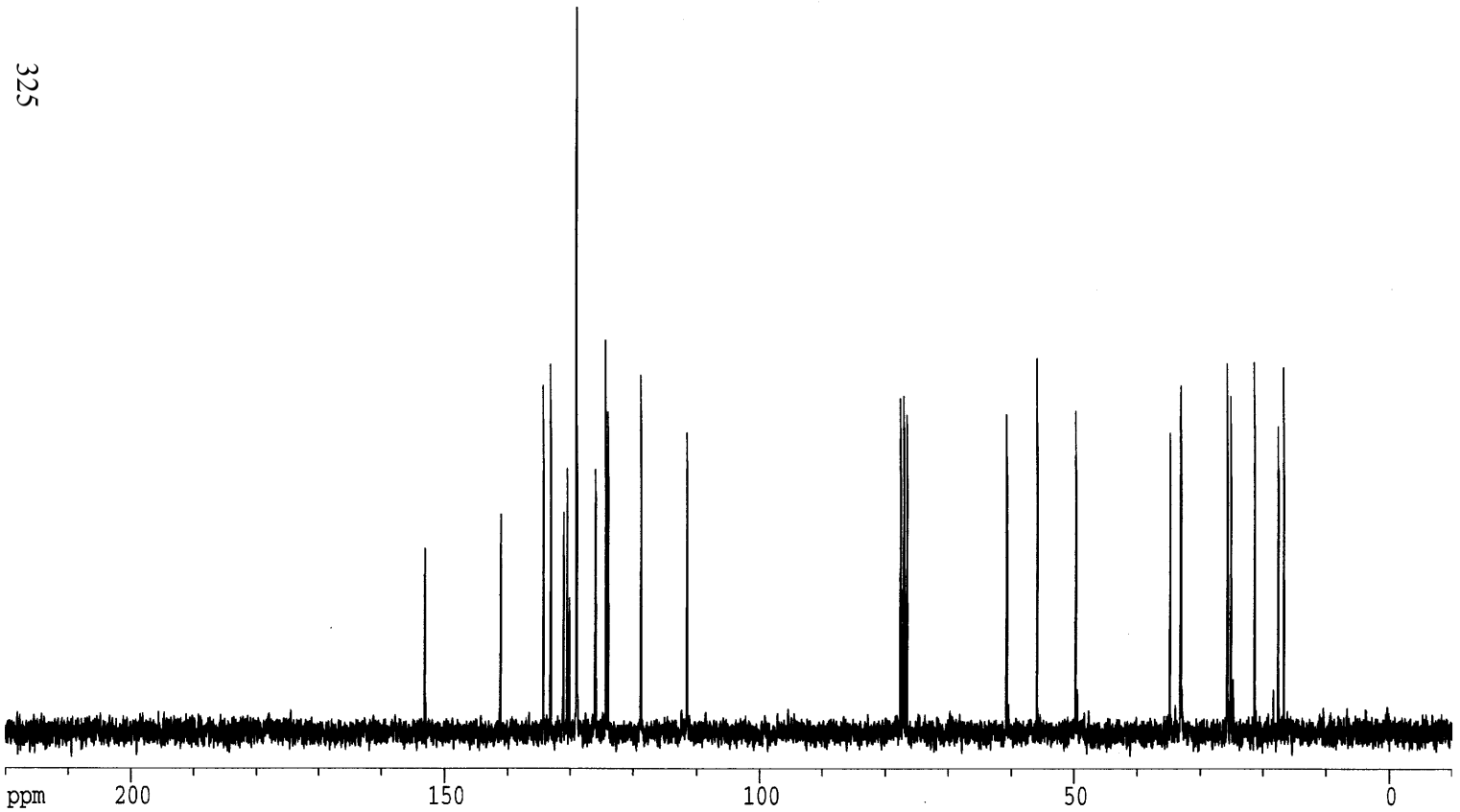


ppm

325



Current Data Parameters

NAME	PZ-VII-12-A1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20060612
Time	13.01
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	85
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 usec
DE	41.43 usec
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 usec
D1	2.00000000 sec
P1	8.00 usec
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

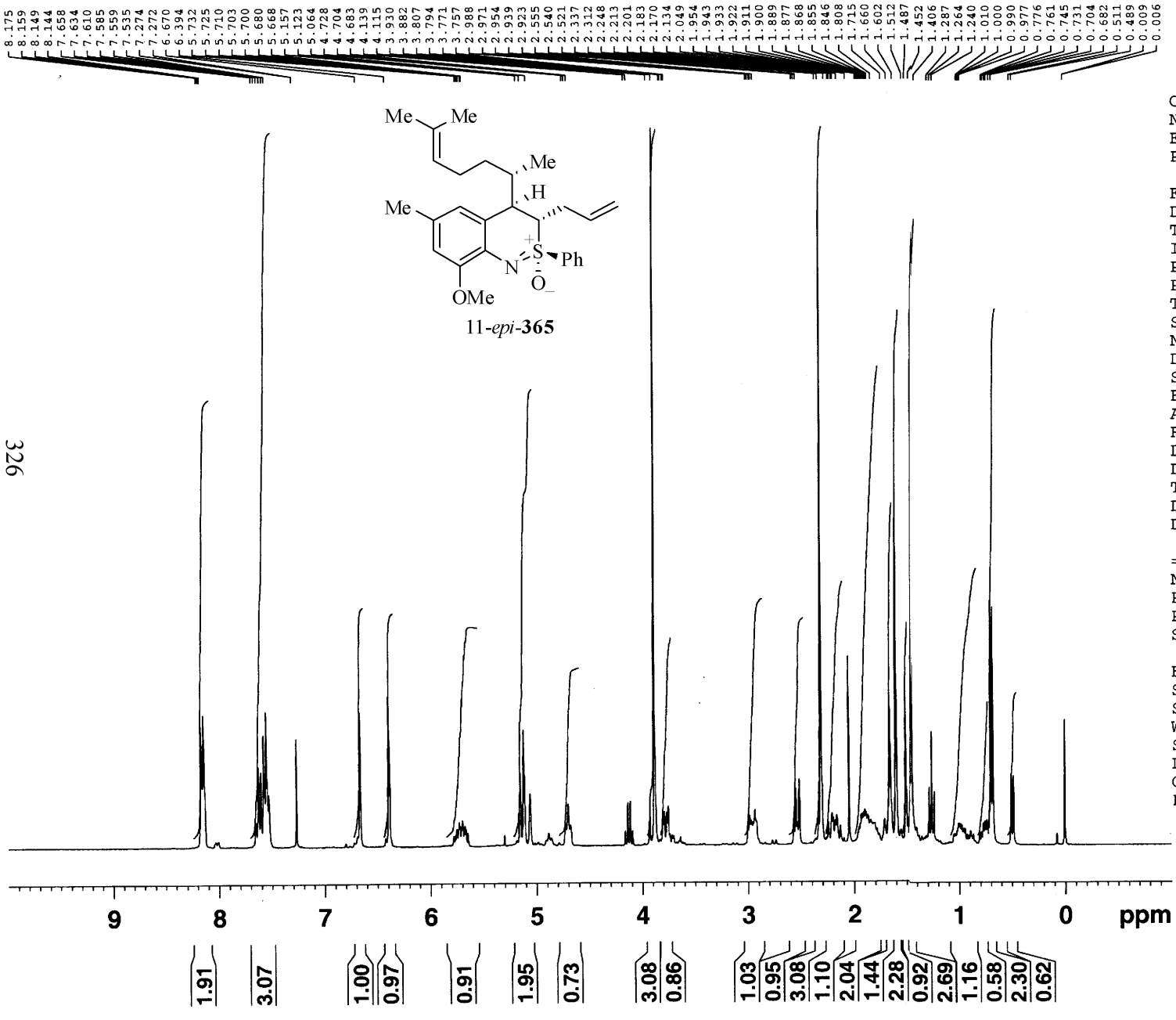
F2 - Processing parameters

SI	32768
SF	62.8952440 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	10.00 cm
F1P	220.000 ppm
F1	13836.95 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	11.50000 ppm/cm
HZCM	723.29529 Hz/cm

1H-NMR
PZ-VIII-111-A1



11-*epi*-**365**

Current Data Parameters

NAME	PZ-VIII-111-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20070317
Time	23.42
INSTRUM	DRX300
PROBHD	5 mm Multinucl
PULPROG	zg30pad
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6172.839 Hz
FIDRES	0.188380 Hz
AQ	2.6542580 sec
RG	181
DW	81.000 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
D31	0.00000000 sec

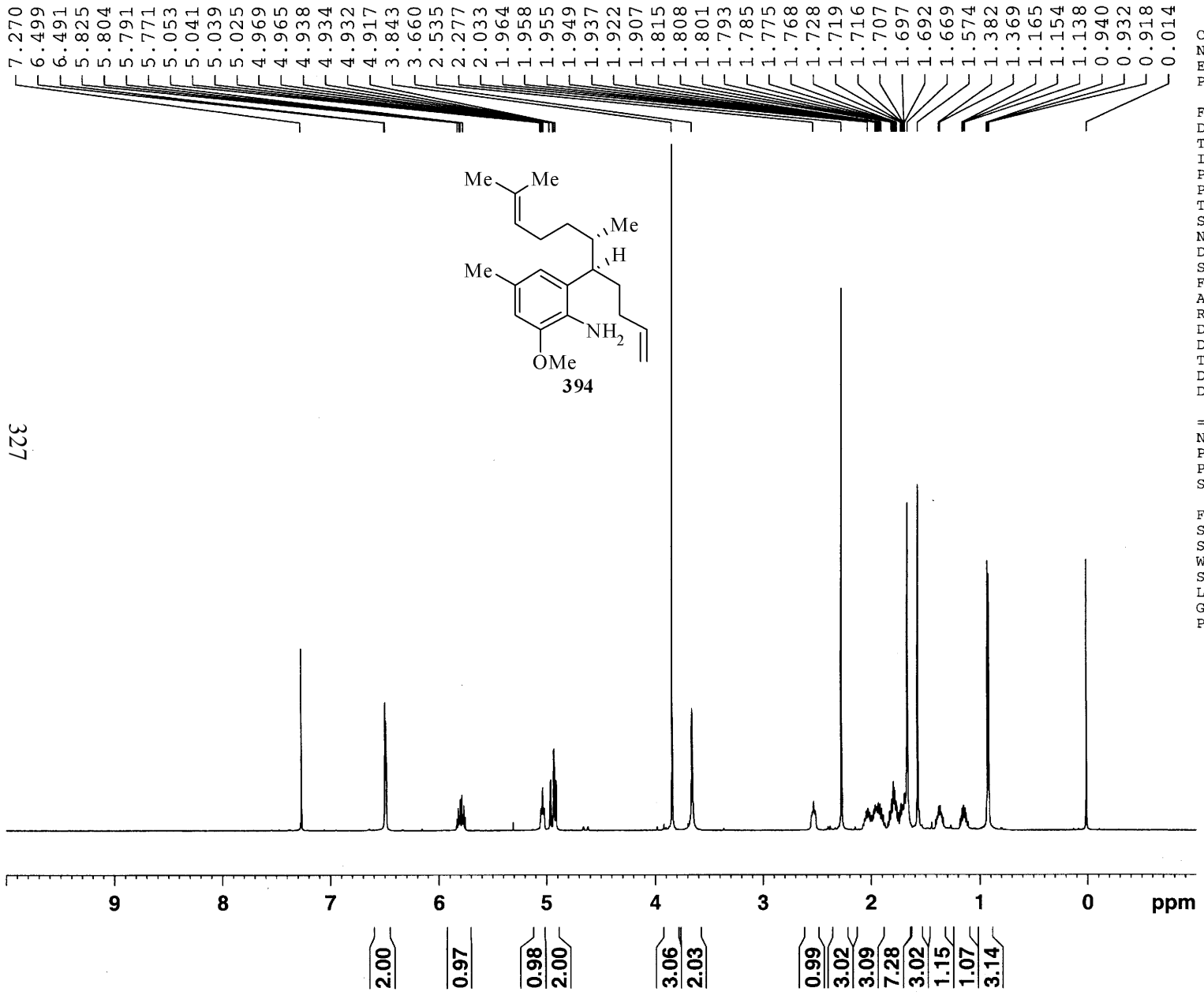
======== CHANNEL f1 ========

NUC1	1H
P1	7.05 usec
PL1	0.00 dB
SFO1	300.1318534 MHz

F2 - Processing parameters

SI	32768
SF	300.1300022 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.30

1H NMR
PZ-VIII-69-SM
aniline



Current Data Parameters

NAME	PZ-VIII-69-SM
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20070202
Time	15.10
INSTRUM	DRX500
PROBHD	5 mm Multinucl
PULPROG	zg30pad
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1719923 sec
RG	114
DW	48.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
D31	0.00000000 sec

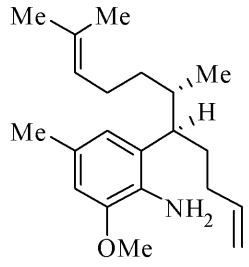
======== CHANNEL f1 ========

NUC1	1H
P1	11.50 usec
PL1	0.00 dB
SFO1	500.1330885 MHz

F2 - Processing parameters

SI	32768
SF	500.1300084 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.40

13C NMR
PZ-VII-115-C3



394

147.307
139.278
131.819
131.257
129.026
126.611
124.877
119.888
114.230
108.420
77.476
76.968
76.460
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42.855
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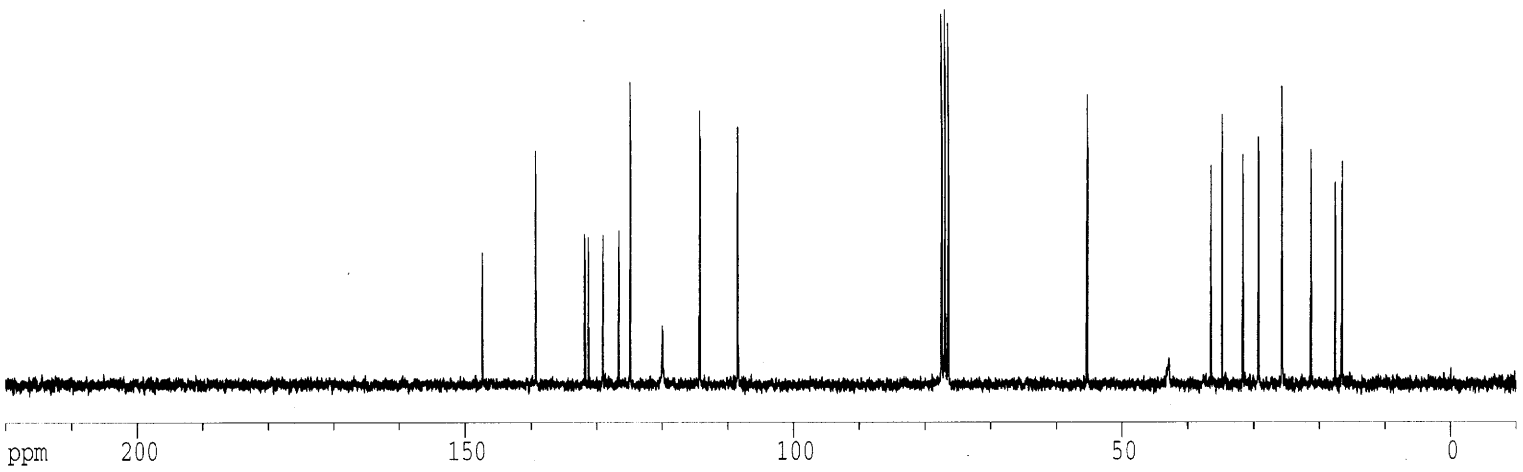
34.812
31.656
29.268
25.692
25.638
21.310
17.582
16.515



Current Data Parameters

NAME	PZ-VII-115-C3
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20061208
Time	14.40
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	702
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 usec
DE	41.43 usec
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 usec
D1	2.00000000 sec
P1	8.00 usec
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

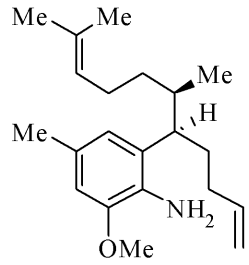
F2 - Processing parameters

SI	32768
SF	62.8952440 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	5.00 cm
F1P	220.000 ppm
F1	13836.95 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	11.50000 ppm/cm
HZCM	723.29529 Hz/cm

1H NMR
PZ-VIII-58-B3



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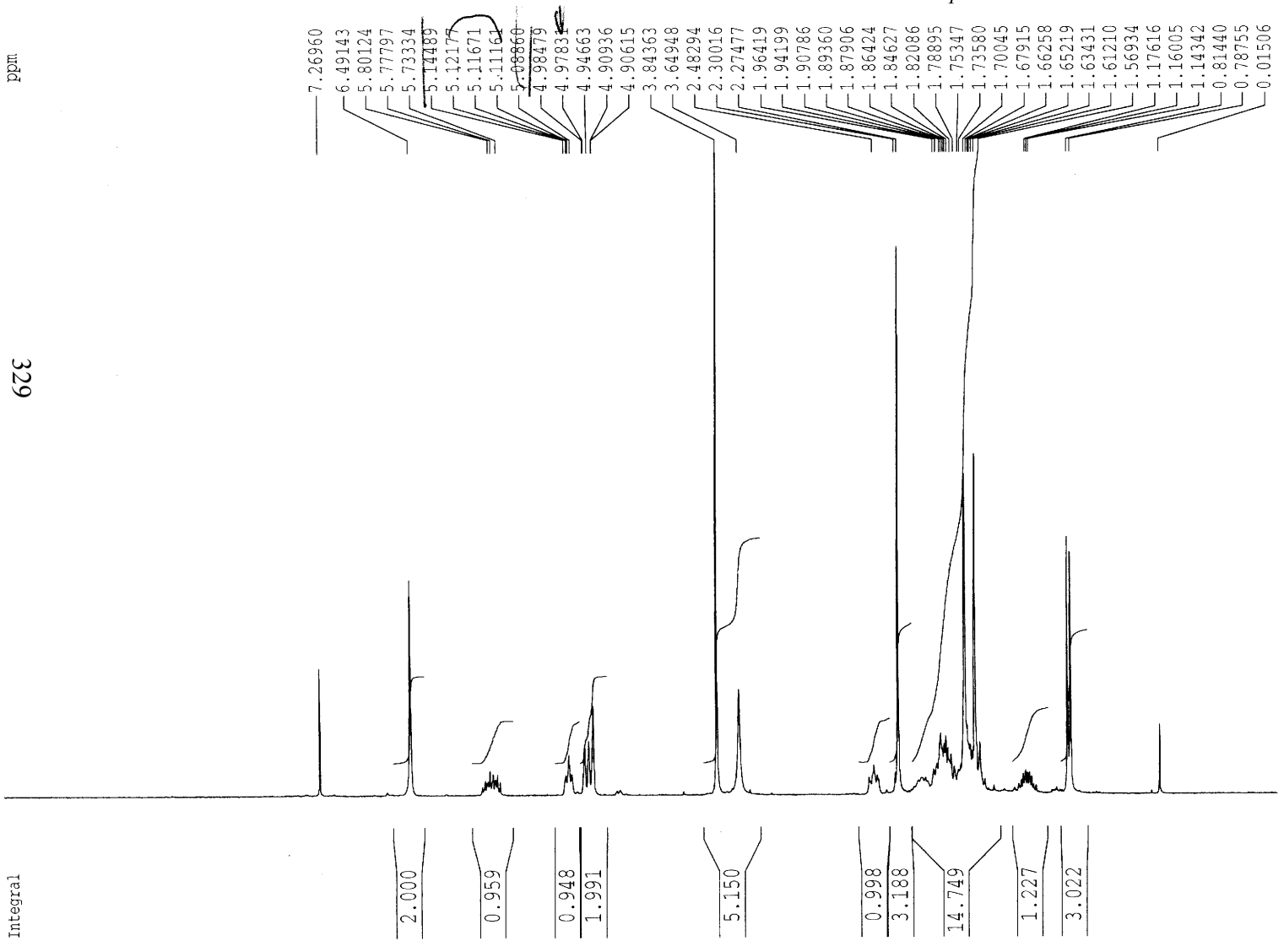


Current Data Parameters

NAME	PZ-VIII-58-B3
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20070127
Time	19.26
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	715
DW	96.000 usec
DE	137.14 usec
TE	300.0 K
D1	1.00000000 sec
P1	9.50 usec
SFO1	250.1315321 MHz
NUCLEUS	1H

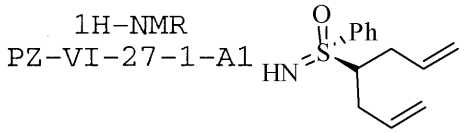
F2 - Processing parameters

SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

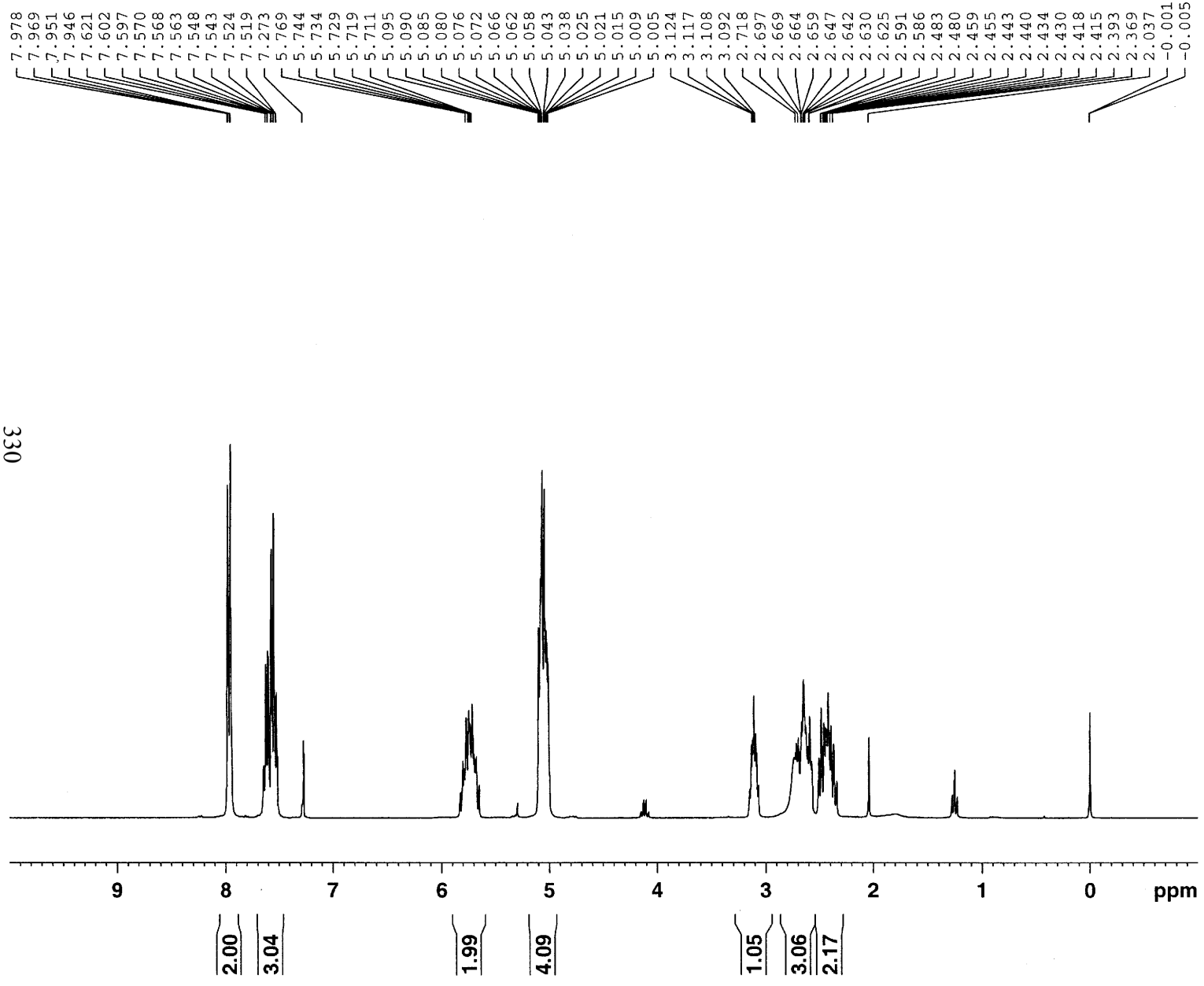
1D NMR plot parameters

CX	20.00 cm
CY	12.50 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm/cm
HZCM	137.57150 Hz/cm

1H-NMR
PZ-VI-27-1-A1



401



Current Data Parameters

NAME	PZ-VI-27-1-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20051011
Time	20.48
INSTRUM	DRX300
PROBHD	5 mm Multinucl
PULPROG	zg30pad
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6172.839 Hz
FIDRES	0.188380 Hz
AQ	2.6542580 sec
RG	161.3
DW	81.000 use
DE	6.00 use
TE	300.0 K
D1	1.00000000 sec
D31	0.00000000 sec

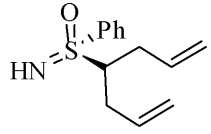
======== CHANNEL f1 =======

NUC1	1H
P1	7.05 use
PL1	0.00 dB
SFO1	300.1318534 MHz

F2 - Processing parameters

SI	32768
SF	300.1300022 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.30

13C NMR
PZ-VI-27-1-A1



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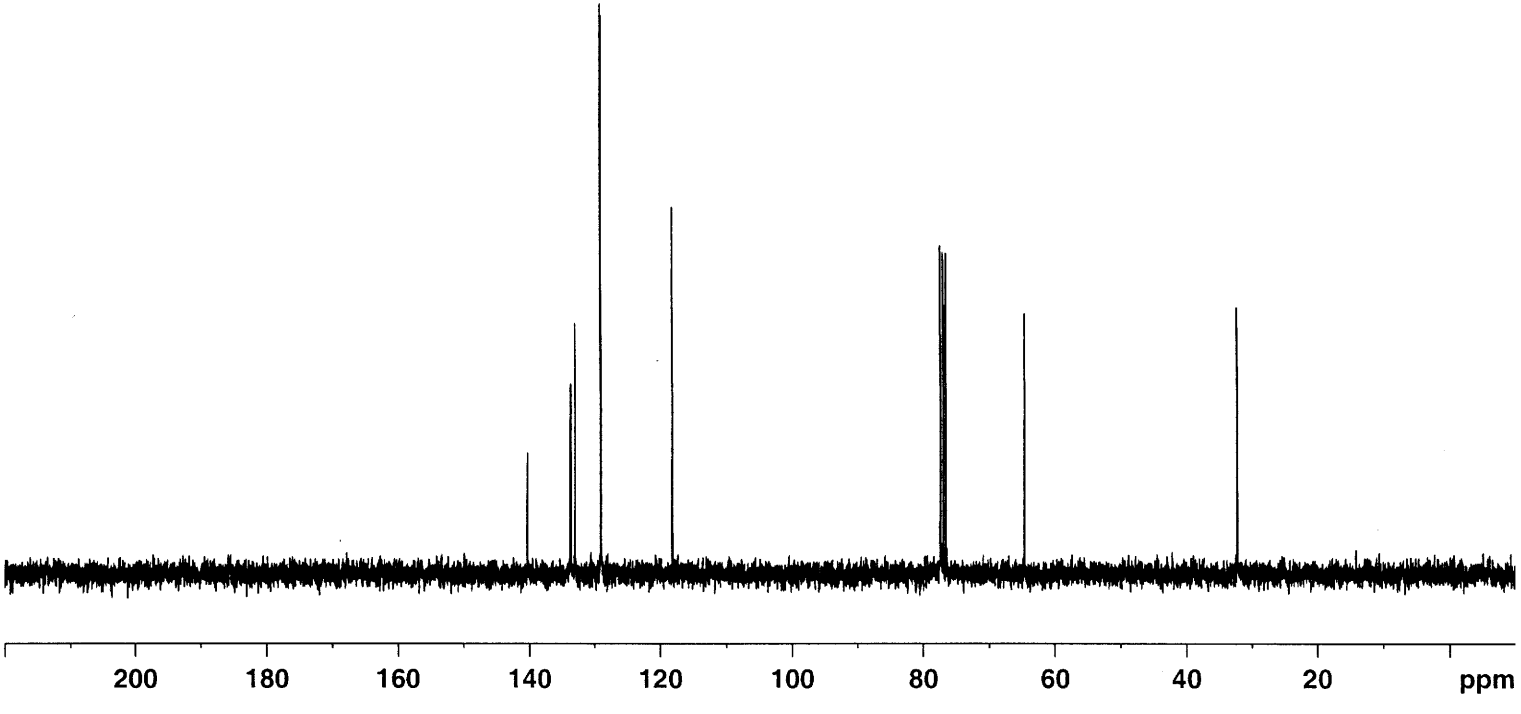


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Current Data Parameters
NAME       PZ-VI-27-1-A1
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20051011
Time              20.51
INSTRUM          DRX300
PROBHD   5 mm Multinucl
PULPROG       zgdc30pad
TD                65536
SOLVENT           CDCl3
NS                   55
DS                    4
SWH           18832.393 Hz
FIDRES         0.287360 Hz
AQ             1.7400308 sec
RG                2298.8
DW                26.550 usec
DE                 6.00 usec
TE                300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
D31           0.00000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.00 usec
PL1                 5.00 dB
SFO1          75.4760107 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             100.00 usec
PL2               120.00 dB
PL12               25.60 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677525 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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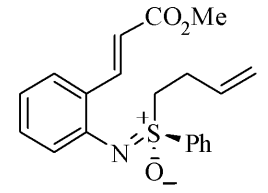

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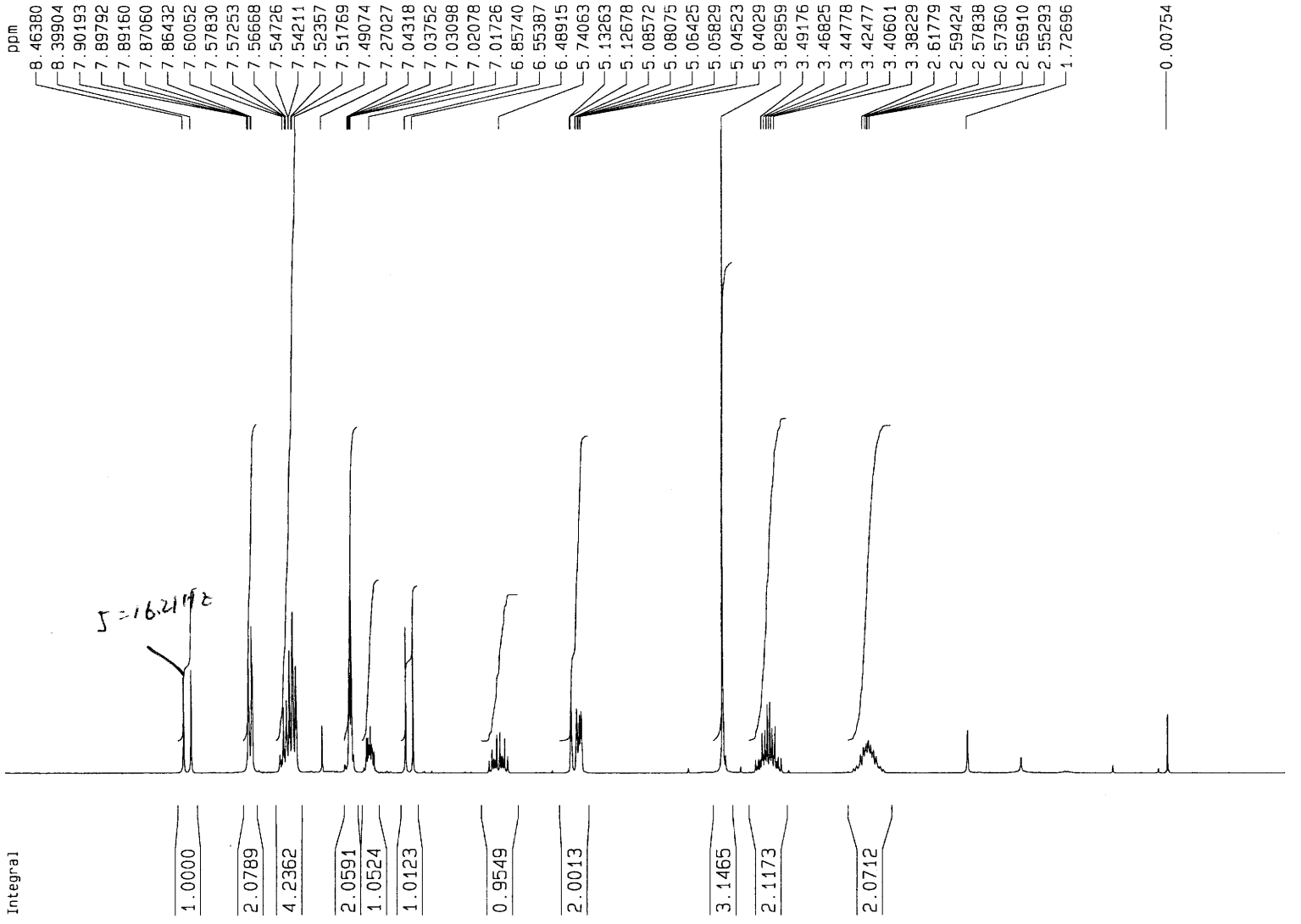


Current Data Parameters

NAME	PZ-VI-30-A2
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20051018
Time	13.28
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	715
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	9.50 use
SFO1	250.1315321 MHz
NUCLEUS	1H

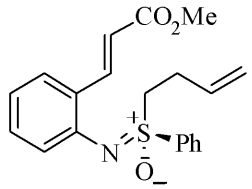
F2 - Processing parameters

SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	12.50 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57150 Hz/

13C NMR
PZ-VI-30-A2



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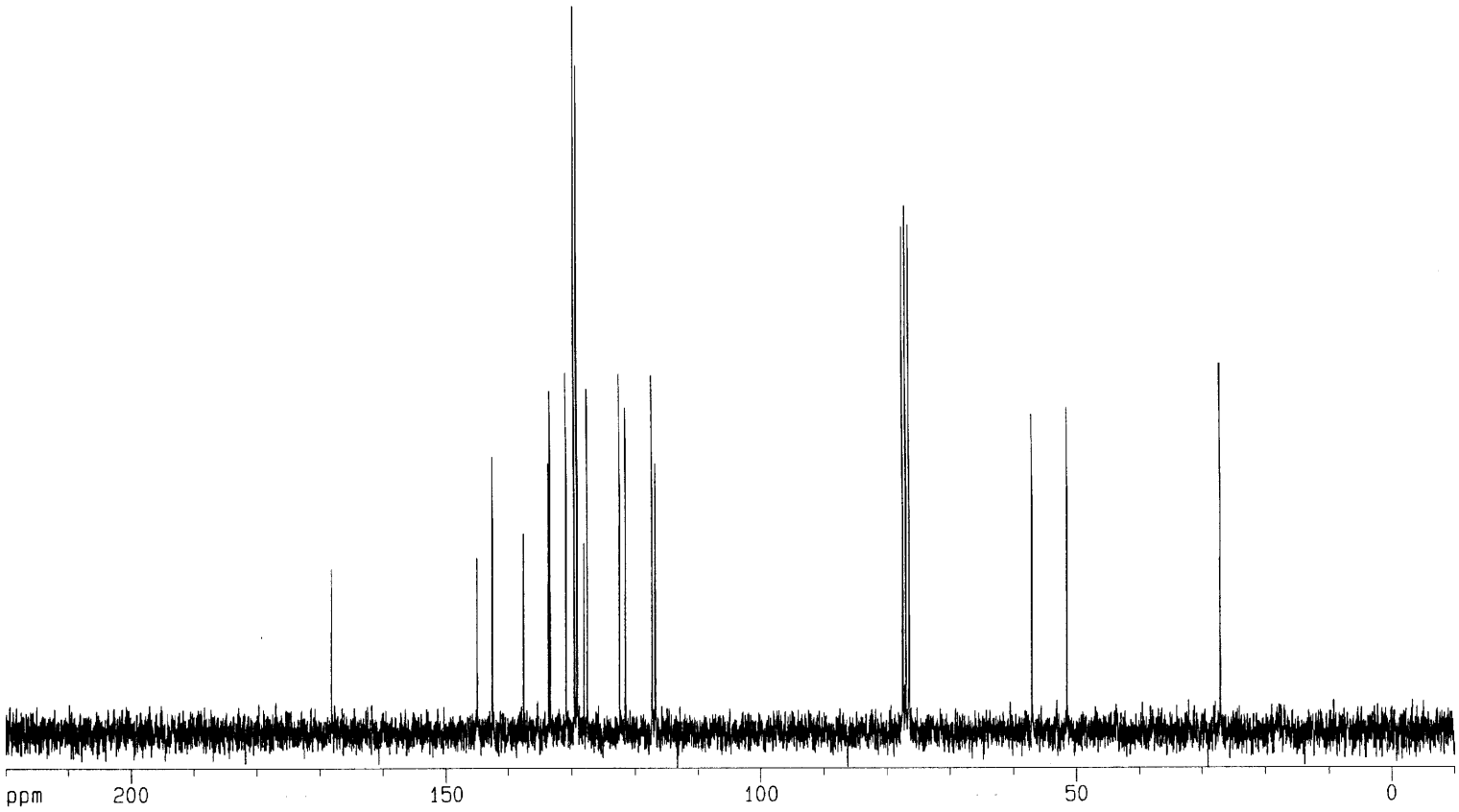
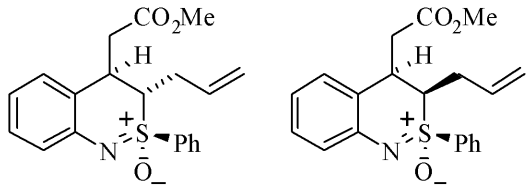


Current Data Parameters	
NAME	PZ-VI-30-A2
EXPNO	2
PROCNO	1

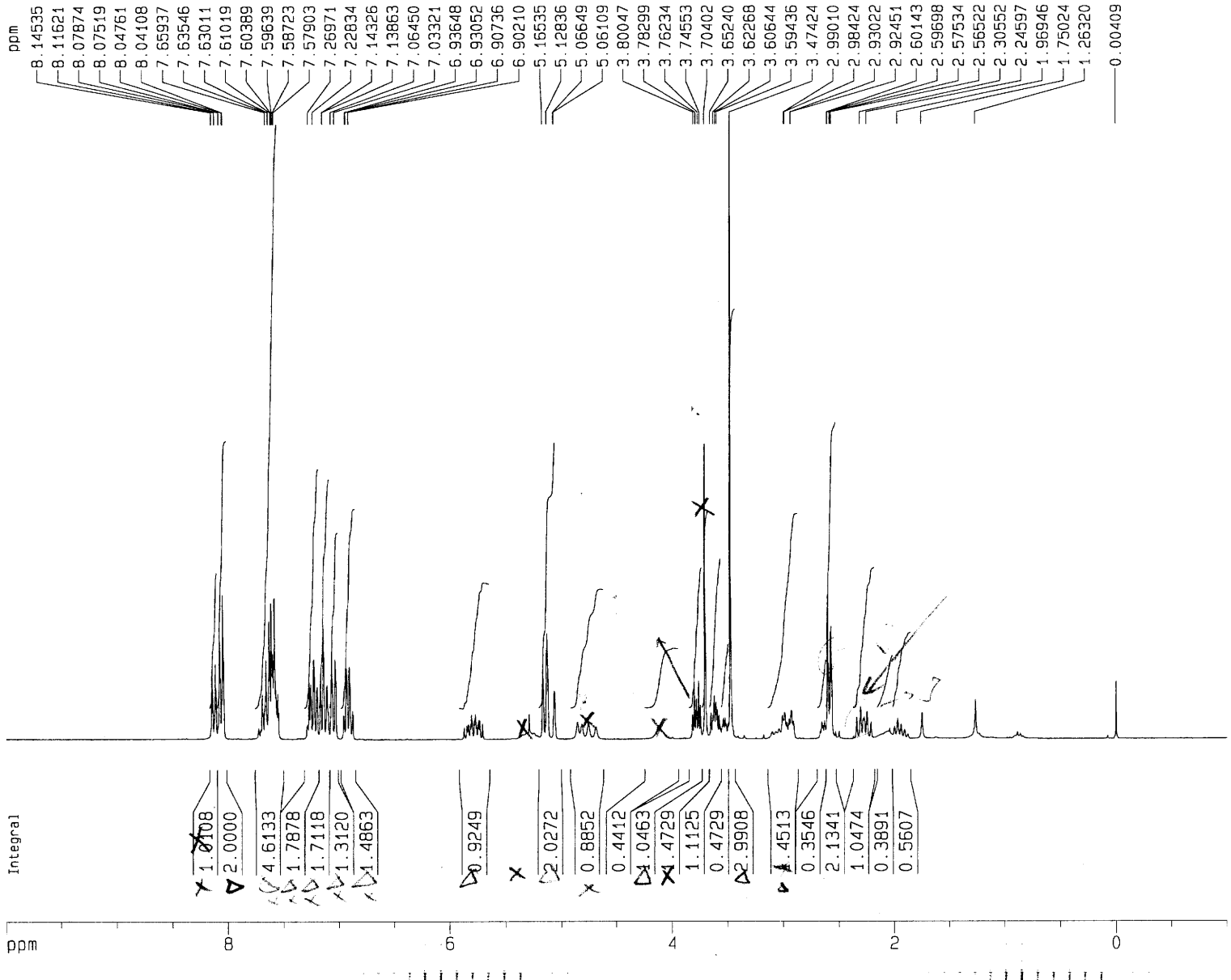
F2 - Acquisition Parameters	
Date_	20051018
Time	13.30
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	153
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	2.00000000 sec
P1	8.00 use
SF01	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

F2 - Processing parameters	
SI	32768
SF	62.8952440 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters	
CX	20.00 cm
CY	10.00 cm
F1P	220.000 ppm
F1	13836.95 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	11.50000 ppm
HZCM	723.29529 Hz/



404 (*d.r.* 2.0:1.0)



Current Data Parameters

NAME	PZ-VI-31-A1-0
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

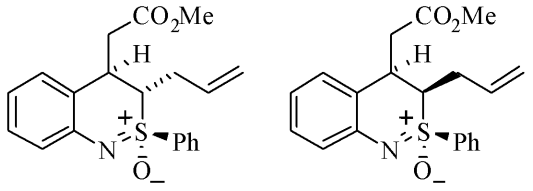
Date_	20051018
Time	13.42
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	512
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	9.50 use
SFO1	250.1315321 MHz
NUCLEUS	1H

F2 - Processing parameters

SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	12.50 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57152 Hz/



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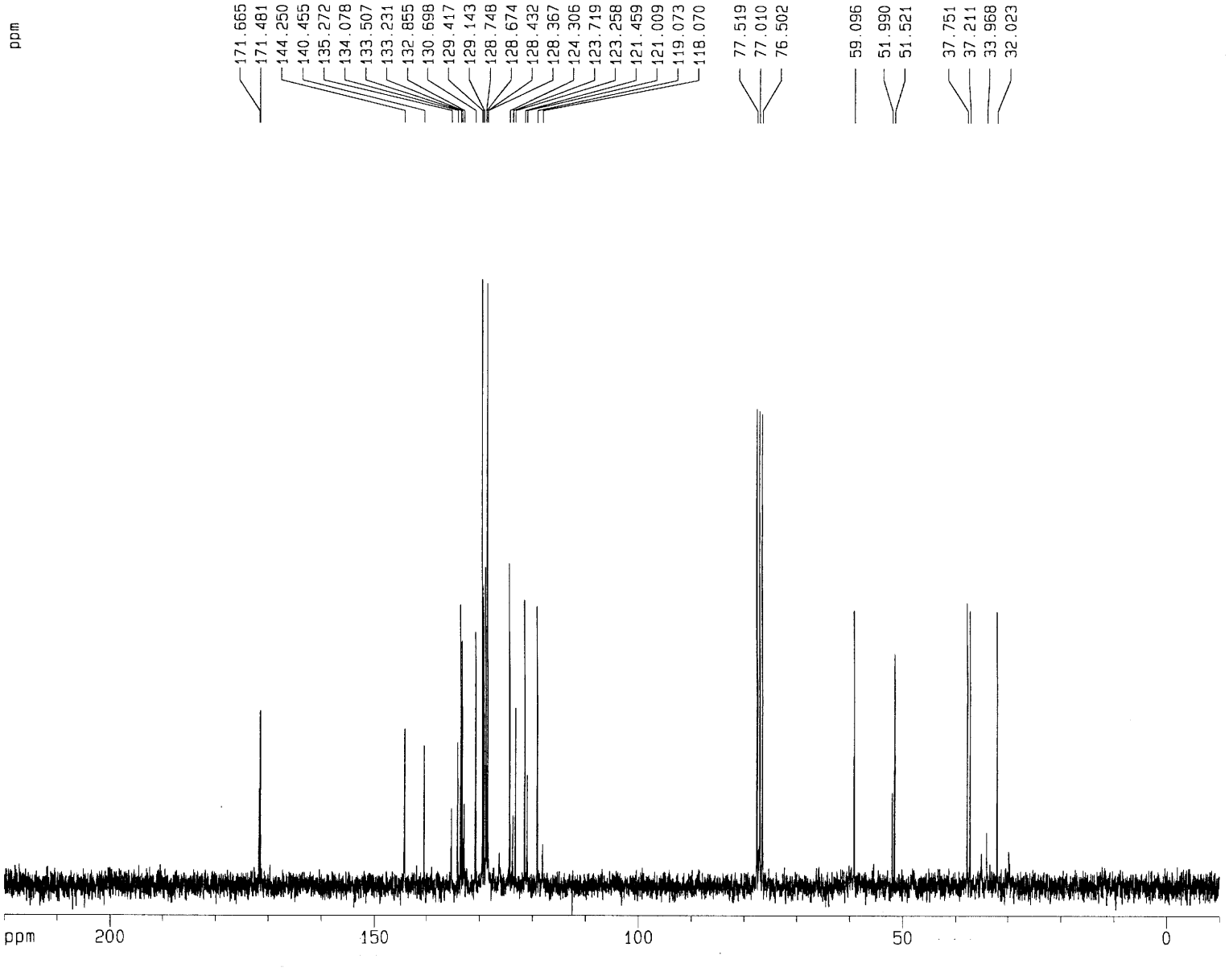


Current Data Parameters

NAME	PZ-VI-31-A1-0
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

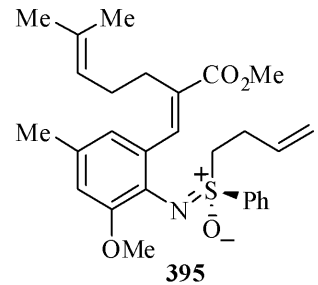
Date_	20051018
Time	13.47
INSTRUM	arx250
PROBHD	5 mm GNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	274
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	2.00000000 sec
P1	8.00 use
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

F2 - Processing parameters

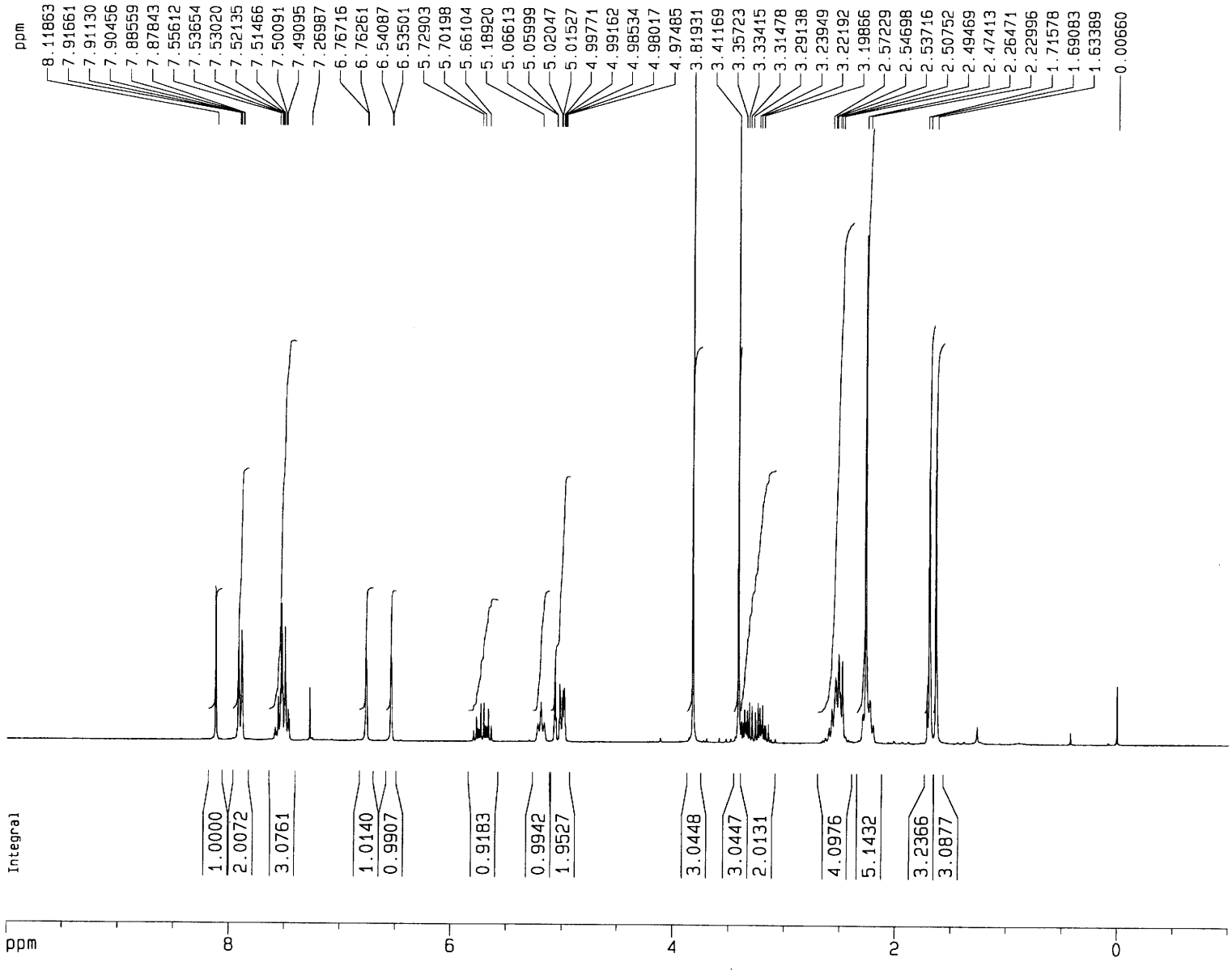
SI	32768
SF	62.8952440 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	10.00 cm
F1P	220.000 ppm
F1	13836.95 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	11.50000 ppm
HZCM	723.29529 Hz/



395



Current Data Parameters

NAME	PZ-VI-52-A3
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

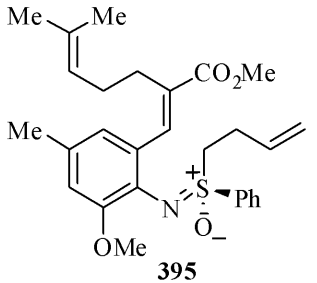
Date_	20051111
Time	11.35
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	512
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	9.50 use
SFO1	250.1315321 MHz
NUCLEUS	1H

F2 - Processing parameters

SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	12.50 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57150 Hz/



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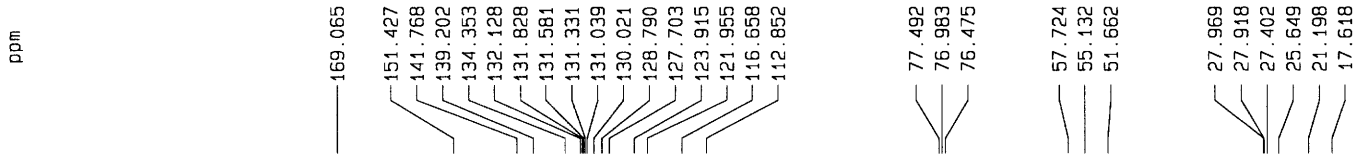
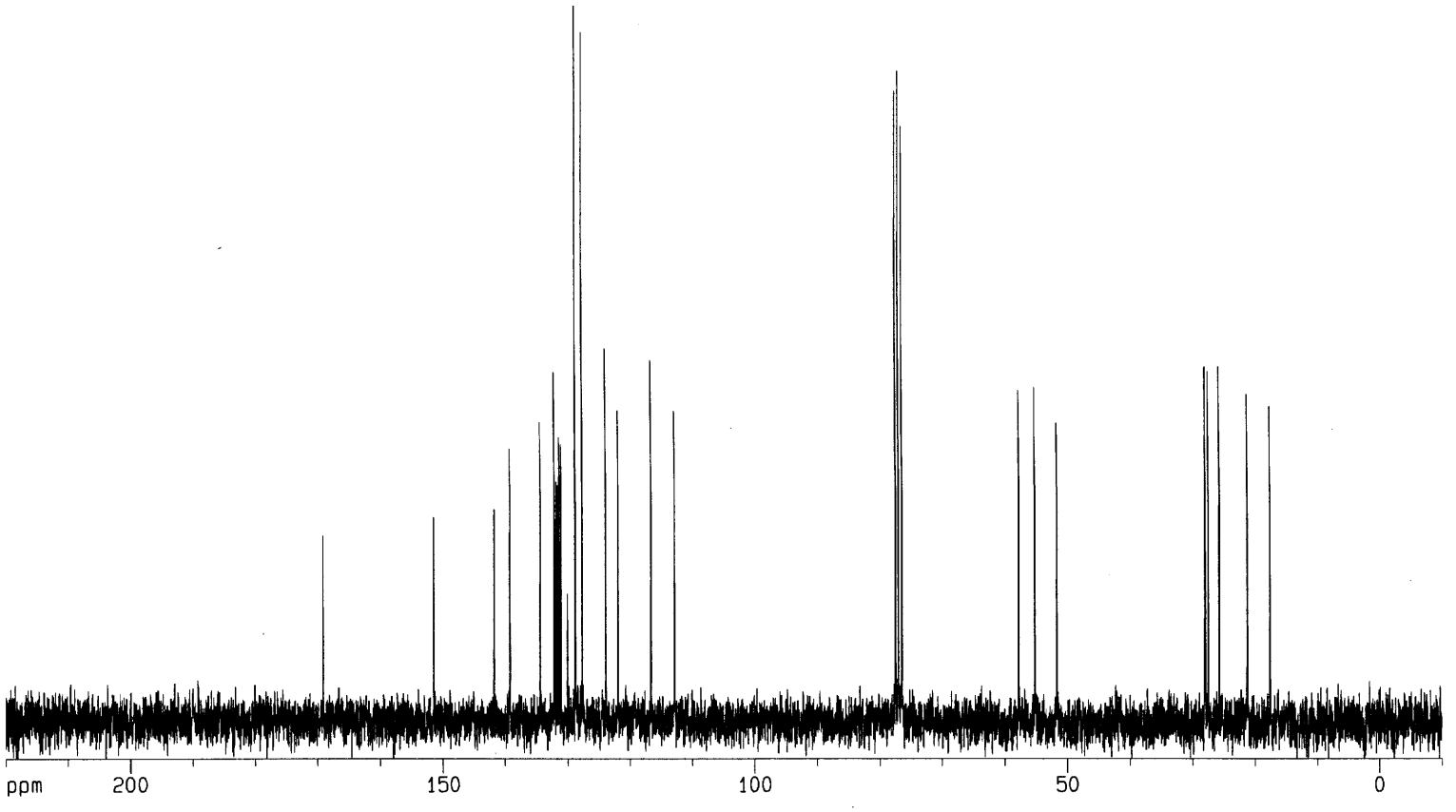


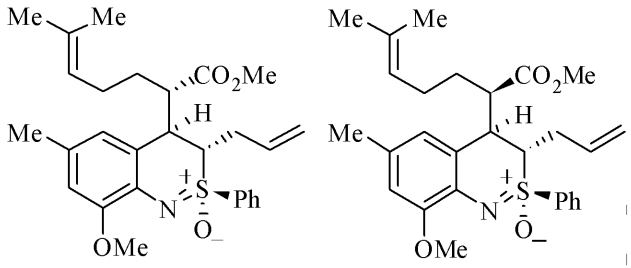


Current Data Parameters	
NAME	PZ-VI-52-A3
EXPNO	2
PROCNO	1

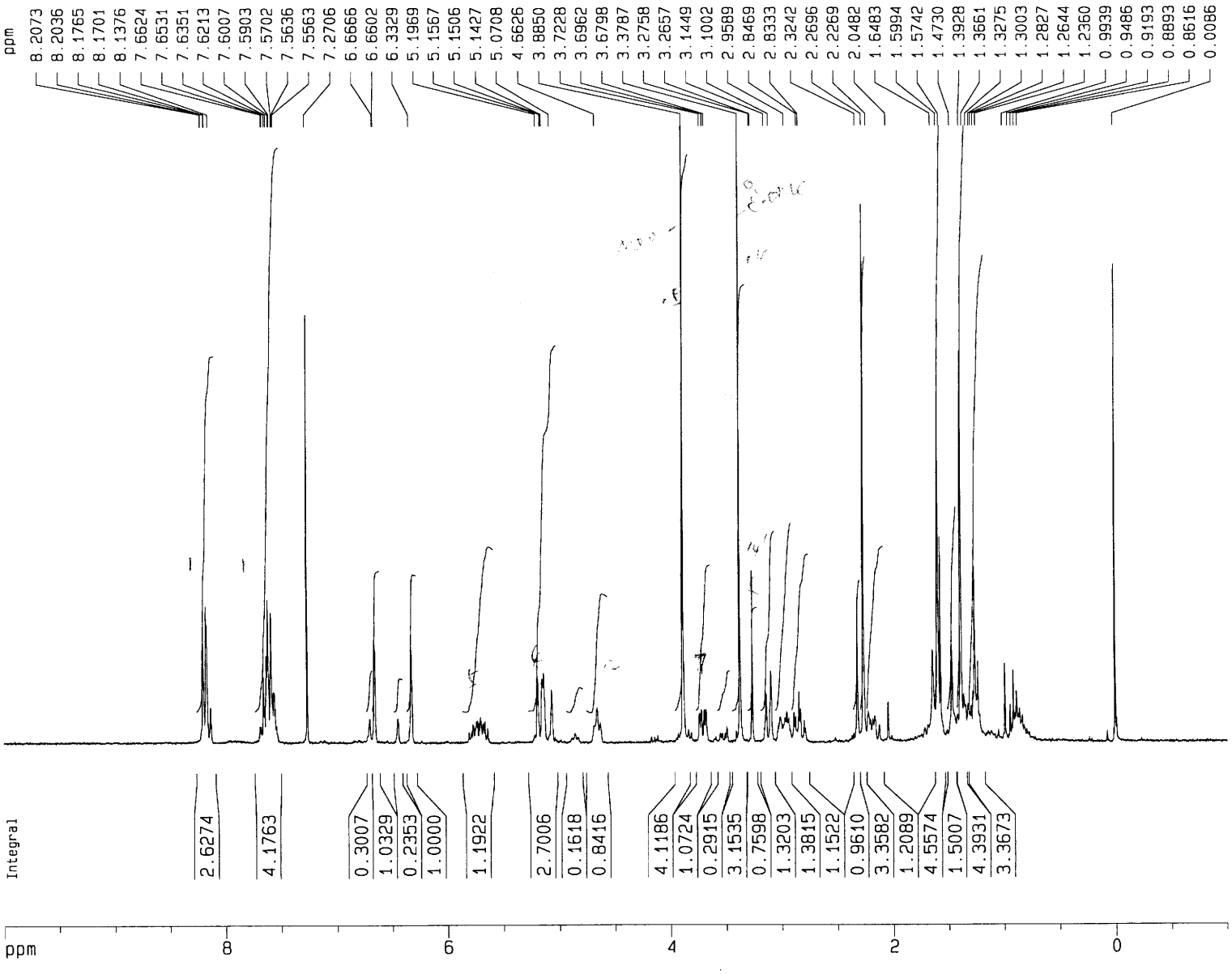
F2 - Acquisition Parameters	
Date_	20051111
Time	11.38
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	126
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	2.00000000 sec
P1	8.00 use
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

F2 - Processing parameters	
SI	32768
SF	62.8952440 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters	
CX	20.00 cm
CY	10.00 cm
F1P	220.000 ppm
F1	13836.95 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	11.50000 ppm
HZCM	723.29529 Hz/



396 (*d.r.* 3.1:1.0)



ent Data Parameters
PZ-VI-57-A1
D 1
NO 1

F2 - Acquisition Parameters

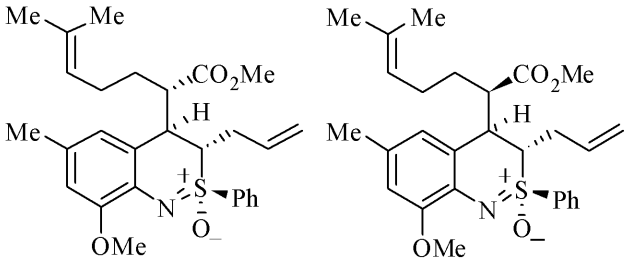
Date_	20051116
Time	22.41
INSTRUM	arx250
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	2048
DW	96.000 use
DE	137.14 use
TE	300.0 K
D1	1.00000000 sec
P1	9.50 use
SFO1	250.1315321 MHz
NUCLEUS	1H

F2 - Processing parameters

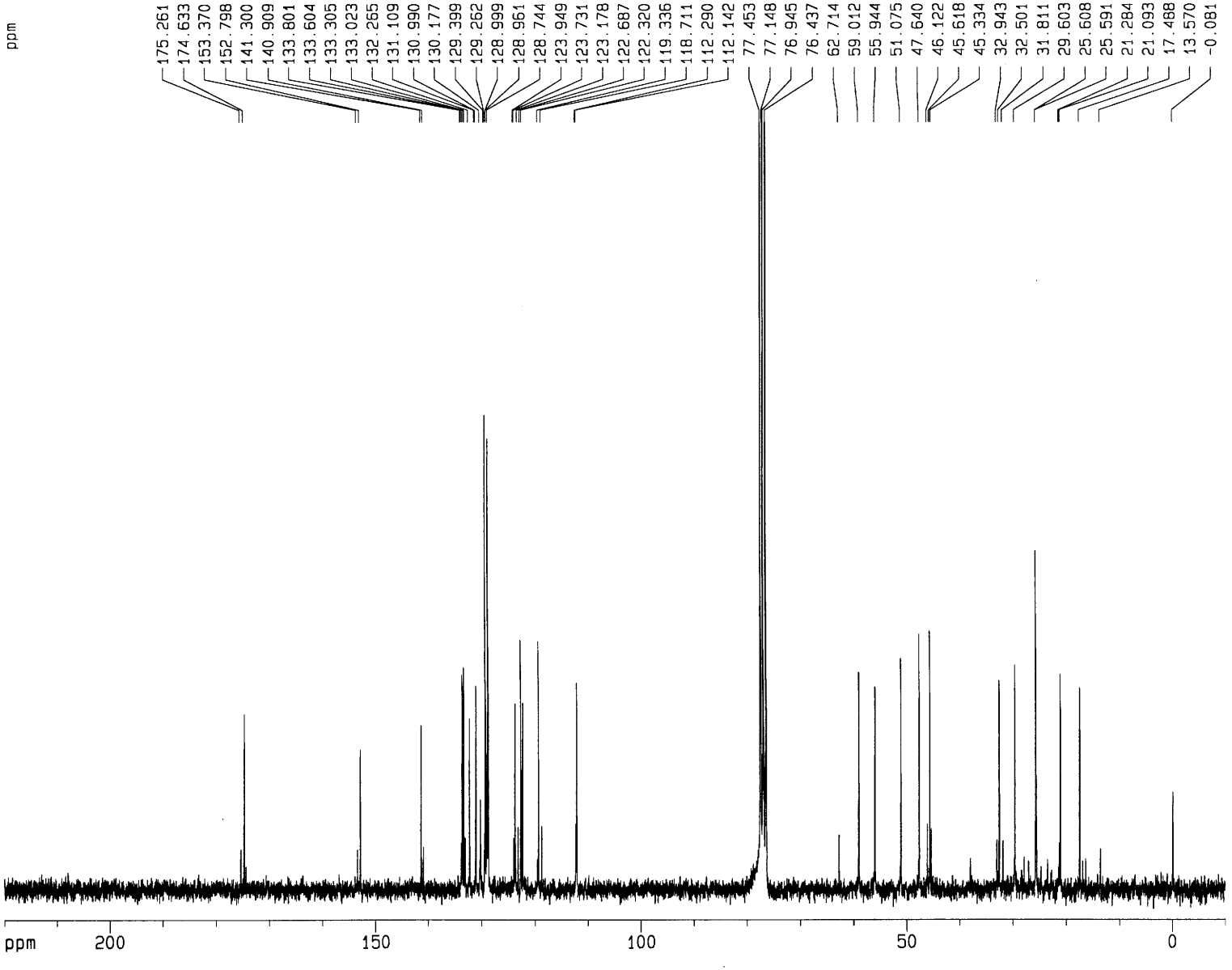
SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	12.50 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm
HZCM	137.57150 Hz/



396 (*d.r.* 3.1:1.0)



Current Data Parameters

NAME	PZ-VI-57-A1-1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20051117
Time	19.45
INSTRUM	arx250
PROBHD	5 mm GNP 1H
PULPROG	zgdc30
TD	36864
SOLVENT	CDCl3
NS	18925
DS	4
SWH	17241.379 Hz
FIDRES	0.467702 Hz
AQ	1.0691060 sec
RG	22800
DW	29.000 use
DE	41.43 use
TE	300.0 K
D12	0.00002000 sec
DL5	23.00 dB
CPDPRG	waltz16
P31	103.00 use
D1	2.00000000 sec
P1	8.00 use
SFO1	62.9023694 MHz
NUCLEUS	13C
D11	0.03000000 sec

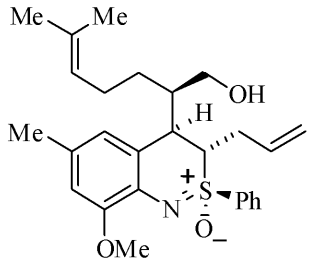
F2 - Processing parameters

SI	32768
SF	62.8952440 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	50.00 cm
F1P	220.000 ppm
F1	13836.95 Hz
F2P	-10.000 ppm
F2	-628.95 Hz
PPMCM	11.50000 ppm
HZCM	723.29529 Hz/

153.30 153.22 141.10 141.00 134.28 134.02 133.29 133.21 131.70 131.66 131.35 130.86 130.77 130.34 129.77 129.20 129.05 128.98 128.85 125.65 125.43 124.11 123.85 123.71 122.81 119.06 118.58 111.97 111.73 77.44 77.22 77.02 76.60 62.06 61.61 61.11 60.89 55.98 55.95 44.96 44.73 40.52 40.03 33.42 33.12 29.32 28.37 25.69 25.60 25.54 24.95 21.32 17.62



405


```
Current Data Parameters
NAME          PZ-VI-96-A1
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20070909
Time               20.59
INSTRUM          DRX300
PROBHD   5 mm Multinucl
PULPROG       zgdc30pad
TD                65536
SOLVENT           CDCl3
NS                 1583
DS                    4
SWH          18832.393 Hz
FIDRES        0.287360 Hz
AQ            1.7400308 sec
RG                22528
DW               26.550 usec
DE                6.00 usec
TE               300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
D31          0.00000000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 9.00 usec
PL1                5.00 dB
SFO1         75.4760107 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            100.00 usec
PL2              120.00 dB
PL12              21.41 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
SF         75.4677525 MHz
WDW                EM
SSB                 0
LB                1.00 Hz
GB                  0
PC                1.40
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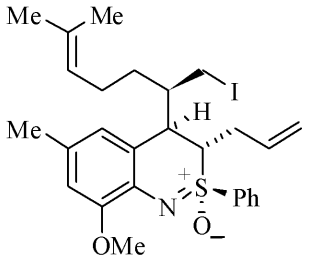
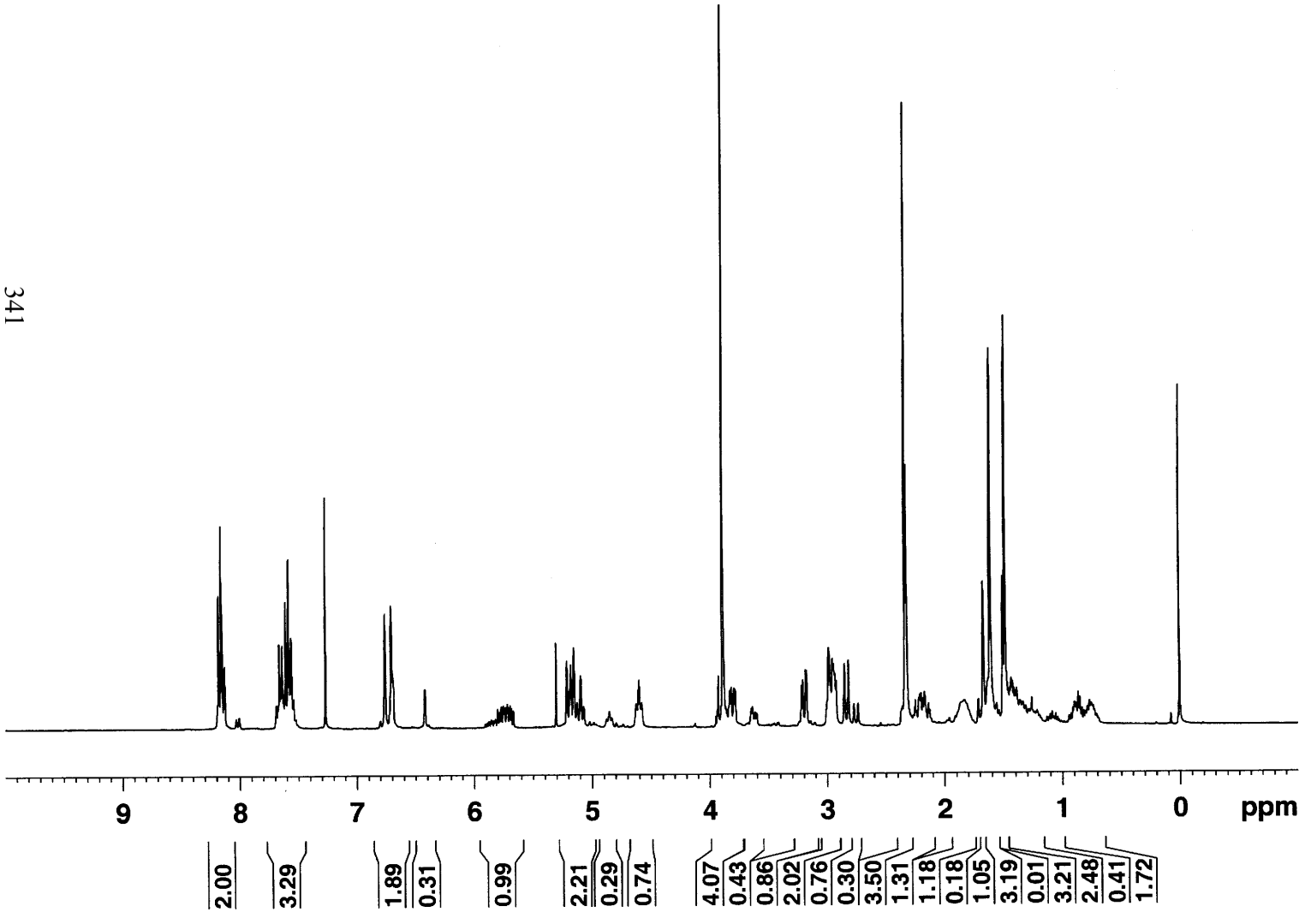


405a

8.187 8.182 8.163 8.159 8.137 8.132 7.671 7.658 7.652 7.647 7.643 7.634 7.615 7.595 7.590 7.569 7.567 7.562 7.274 6.765 6.714 6.710 6.700 6.695 6.427 6.425 5.308 5.216 5.184 5.158 5.155 5.101 5.098 4.607 3.932 3.891 3.833 3.819 3.797 3.786 3.223 3.212 3.189 3.178 2.991 2.973 2.959 2.946 2.940 2.927 2.856 2.821 2.340 2.326 2.176 1.674 1.614 1.508 1.489 1.461 1.450 1.439 1.427 1.416 1.405 1.393 0.009

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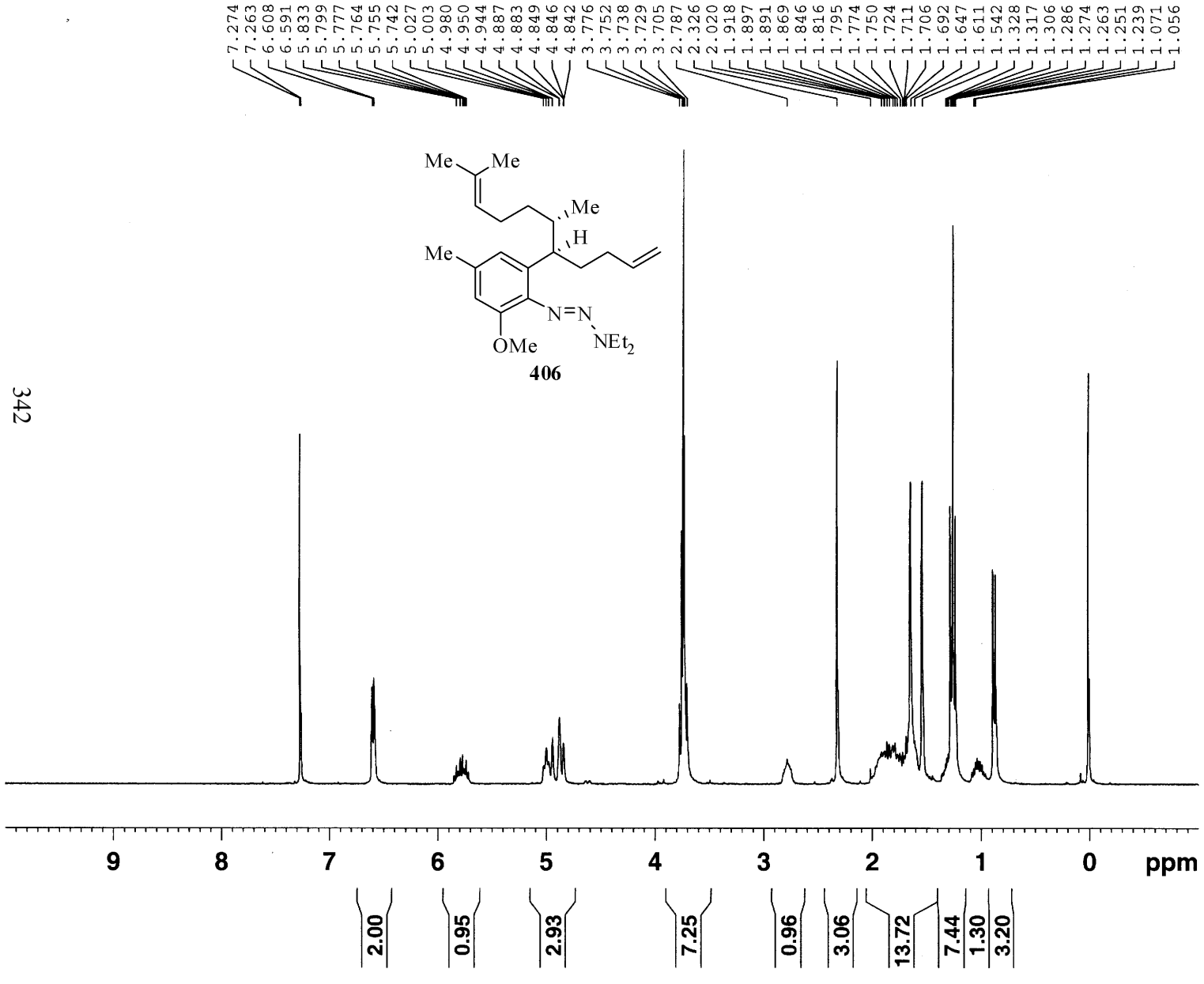
Current Data Parameters
NAME          PZ-VI-145-A1
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20060525
Time                 14.21
INSTRUM             DRX300
PROBHD   5 mm Multinucl
PULPROG           zg30pad
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6172.839 Hz
FIDRES            0.188380 Hz
AQ                2.6542580 sec
RG                     256
DW                  81.000 usec
DE                   6.00 usec
TE                  300.0 K
D1                1.00000000 sec
D31               0.00000000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   7.05 usec
PL1                  0.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                   32768
SF            300.1300022 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.30
```

1H-NMR
PZ-VIII-69



Current Data Parameters

NAME	PZ-VIII-69
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20070203
Time	0.53
INSTRUM	DRX300
PROBHD	5 mm Multinucl
PULPROG	zg30pad
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6172.839 Hz
FIDRES	0.188380 Hz
AQ	2.6542580 sec
RG	574.7
DW	81.000 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
D31	0.00000000 sec

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

NUC1	1H
P1	7.05 usec
PL1	0.00 dB
SFO1	300.1318534 MHz

F2 - Processing parameters

SI	32768
SF	300.1300022 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.30

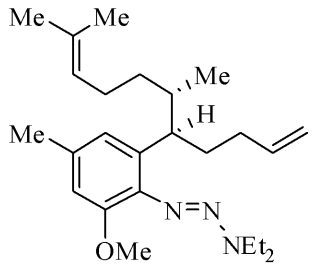
13C NMR
PZ-VIII-22-CRUDE

151.21 139.64 138.50 138.35 134.12 130.58 125.20 120.04 113.60 110.39

77.42 77.00 76.58

55.92

37.35 35.16 31.86 30.51 25.81 25.65 21.73 17.51 16.37 13.06



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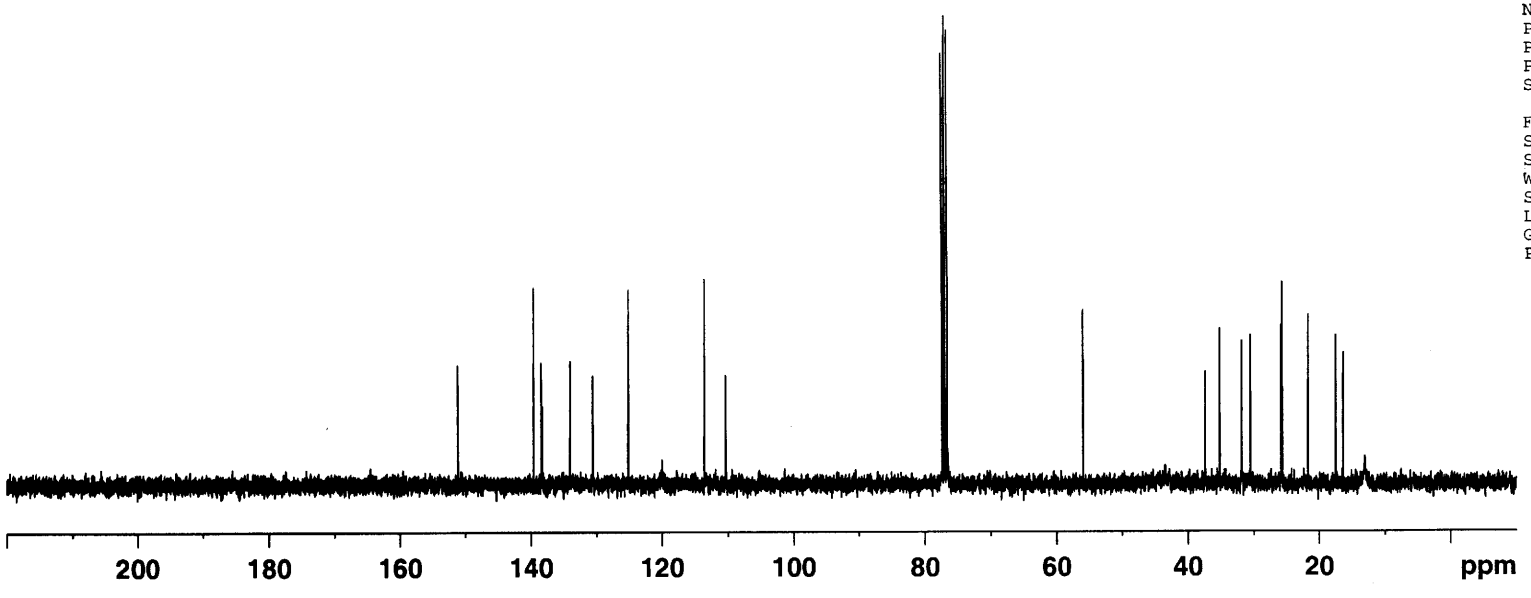


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Current Data Parameters
NAME      PZ-VIII-22-CRUDE
EXPNO                    2
PROCNO                   1

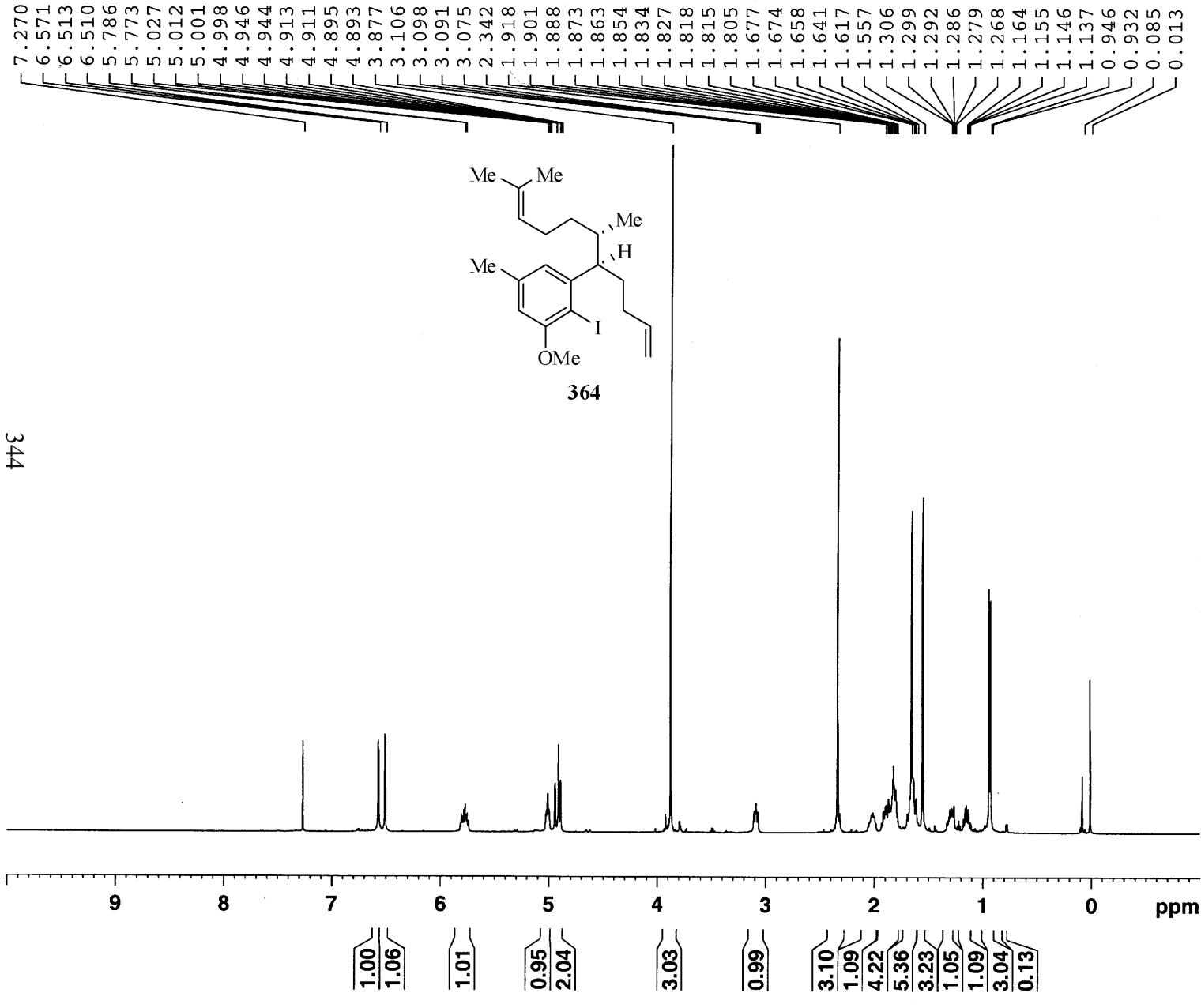
F2 - Acquisition Parameters
Date_             20061210
Time                 19.30
INSTRUM              DRX300
PROBHD   5 mm Multinucl
PULPROG          zgdc30pad
TD                   65536
SOLVENT              CDCl3
NS                     107
DS                       4
SWH              18832.393 Hz
FIDRES           0.287360 Hz
AQ               1.7400308 sec
RG                   22528
DW                26.550 usec
DE                 6.00 usec
TE                 300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
D31           0.00000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                 9.00 usec
PL1                5.00 dB
SFO1          75.4760107 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2              120.00 dB
PL12              21.41 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                   32768
SF            75.4677525 MHz
WDW                     EM
SSB                      0
LB                 1.00 Hz
GB                       0
PC                    1.30
```

1H NMR
PZ-VIII-23-A1



Current Data Parameters

NAME	PZ-VIII-23-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20061212
Time	16.27
INSTRUM	DRX500
PROBHD	5 mm Multinucl
PULPROG	zg30pad
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1719923 sec
RG	128
DW	48.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
D31	0.00000000 sec

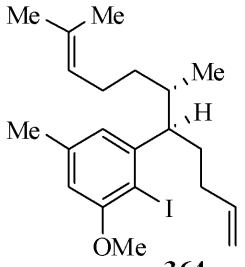
======== CHANNEL f1 ========

NUC1	1H
P1	11.50 usec
PL1	0.00 dB
SFO1	500.1330885 MHz

F2 - Processing parameters

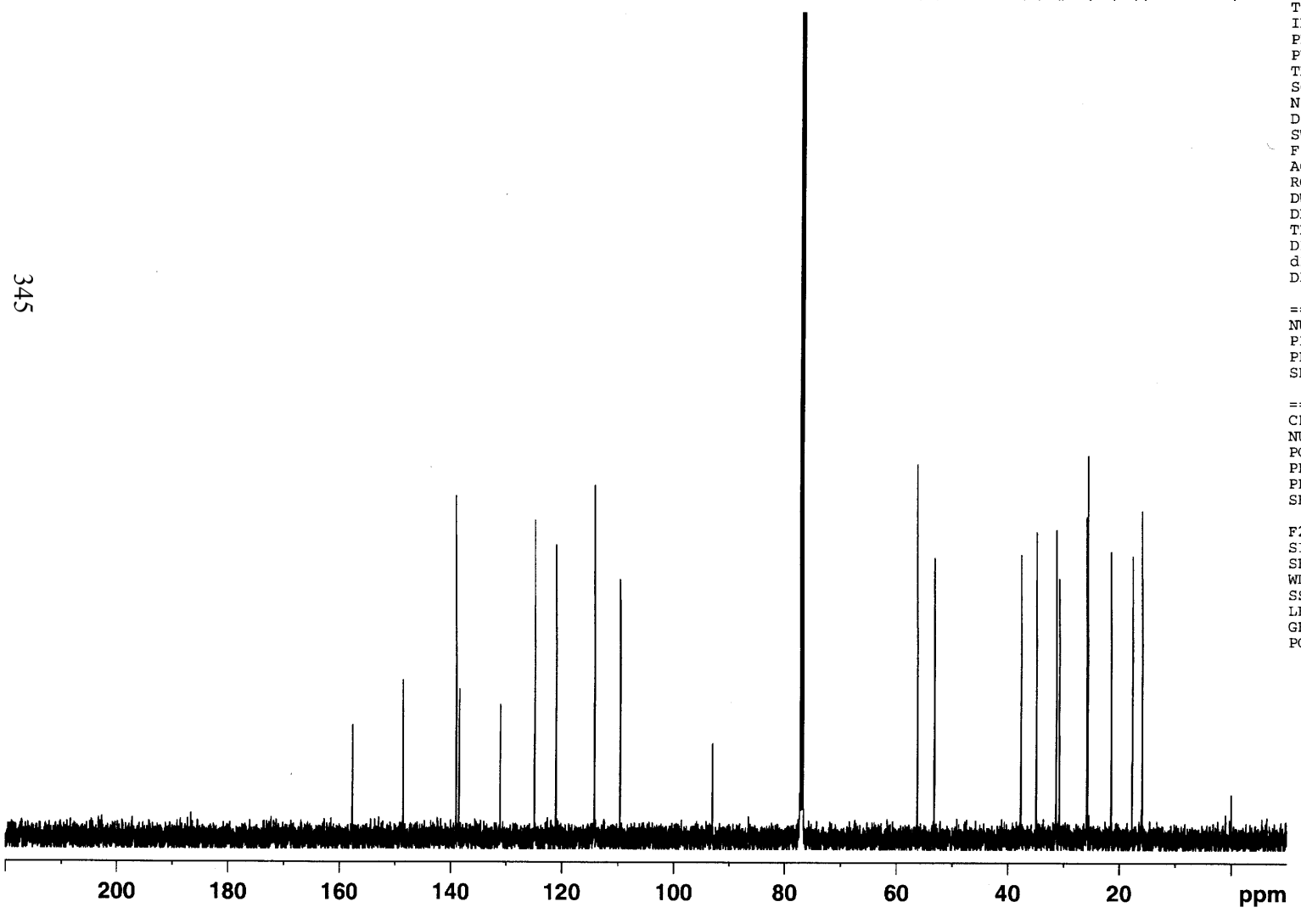
SI	32768
SF	500.1300087 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.40

13C NMR
PZ-VIII-23-A1



364

157.65
148.60
139.10
138.52
131.10
124.88
121.03
114.17
109.63
93.05
77.25
77.0
76.7
56.3
53.2
37.71
34.95
31.36
30.86
25.88
25.68
21.52
17.63
15.92
-0.02



Current Data Parameters
NAME PZ-VIII-23-A1
EXPNO 2
PROCNO 1

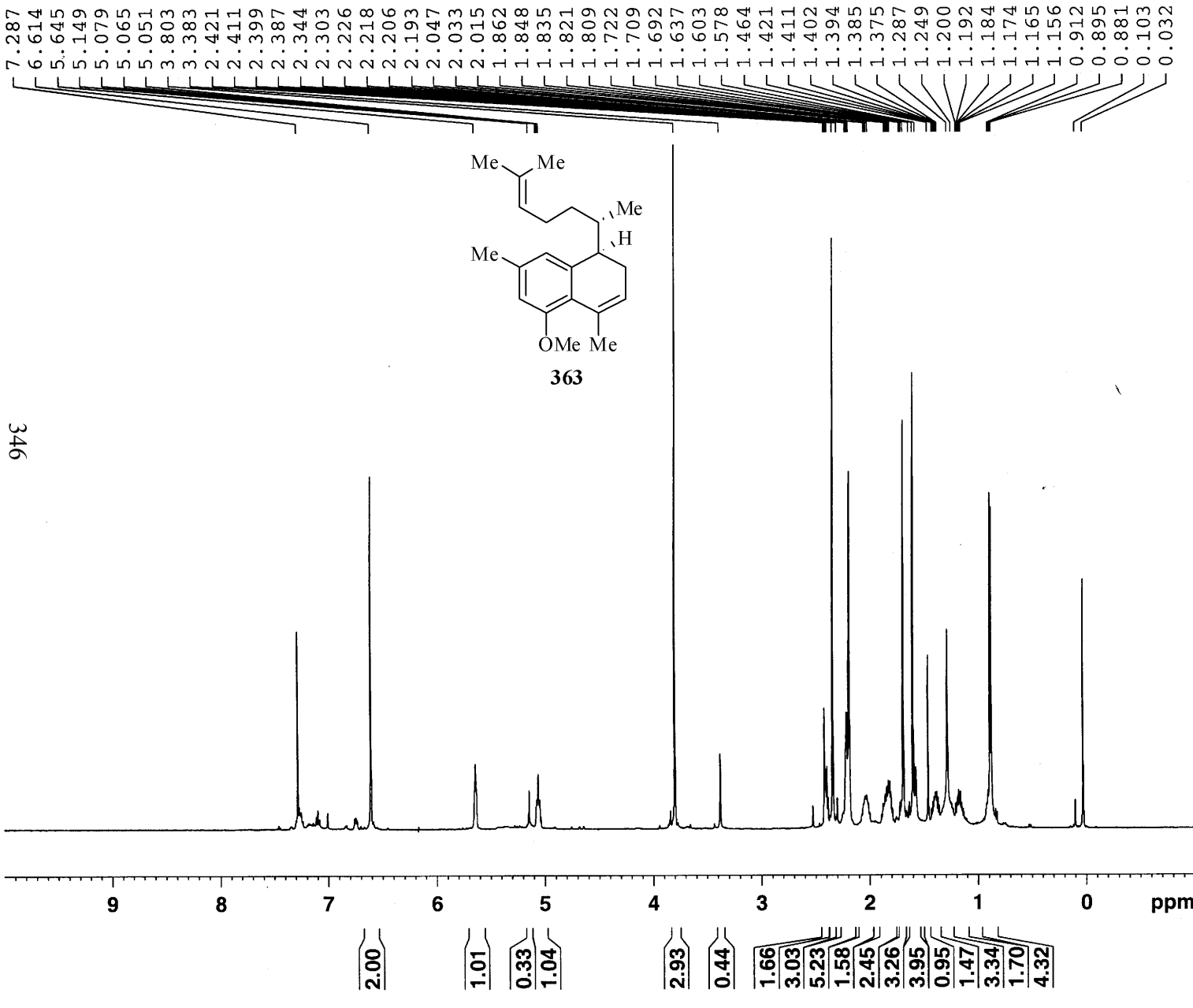
F2 - Acquisition Parameters
Date_ 20061212
Time 16.33
INSTRUM DRX500
PROBHD 5 mm Multinucl
PULPROG zgdc30
TD 65536
SOLVENT CDC13
NS 221
DS 4
SWH 34013.605 Hz
FIDRES 0.519006 Hz
AQ 0.9634292 sec
RG 32768
DW 14.700 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
D31 0.00000000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 8.10 usec
PL1 3.00 dB
SFO1 125.7723786 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 88.00 usec
PL2 0.00 dB
PL12 21.00 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 32768
SF 125.7577938 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1H NMR
PZ-VIII-24-A2

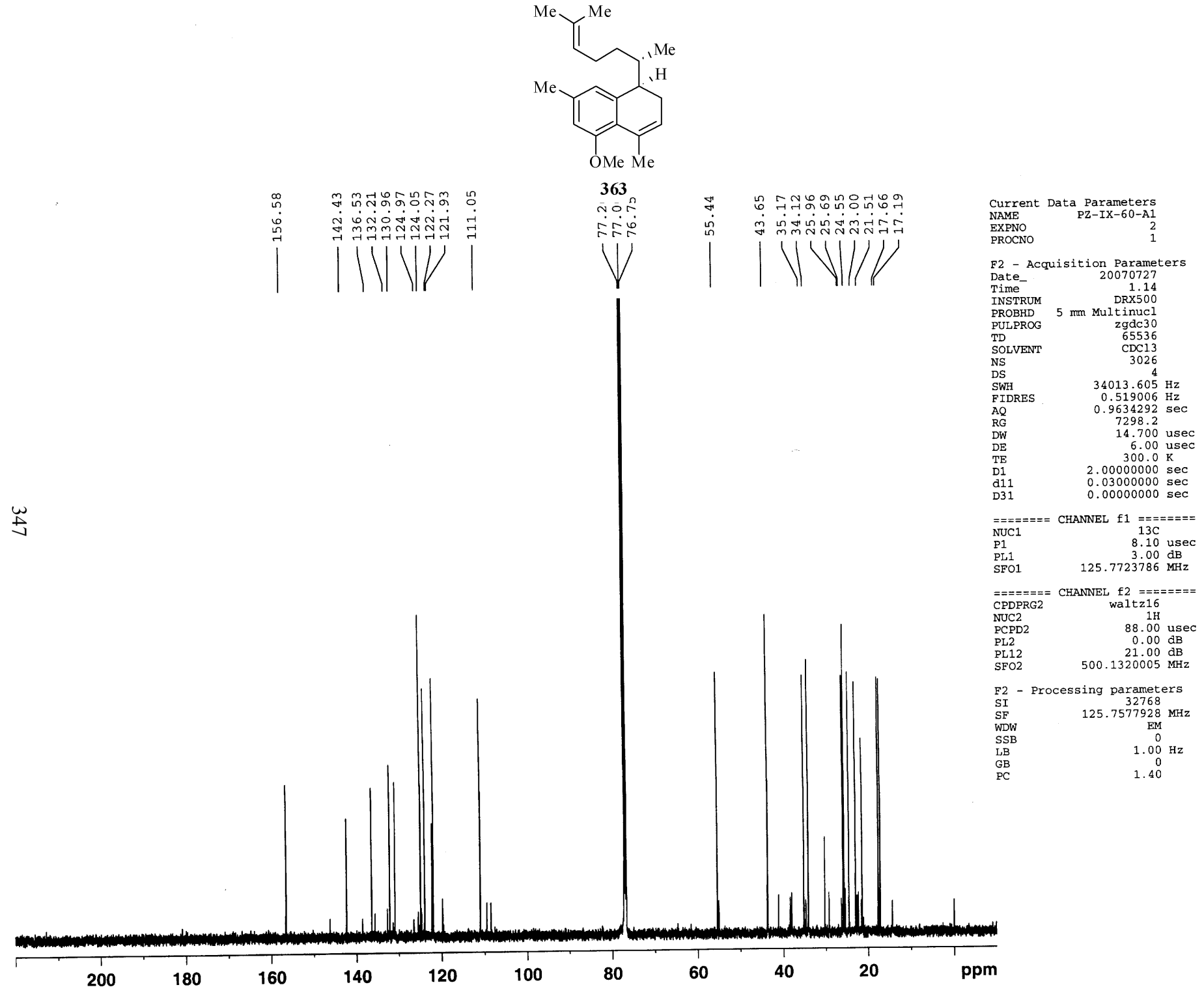


Current Data Parameters
NAME PZ-VIII-24-A2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061217
Time 23.39
INSTRUM DRX500
PROBHD 5 mm Multinucl
PULPROG zg30pad
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 181
DW 48.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
D31 0.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 11.50 usec
PL1 0.00 dB
SFO1 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40



Current Data Parameters
NAME PZ-IX-60-A1
EXPNO 2
PROCNO 1

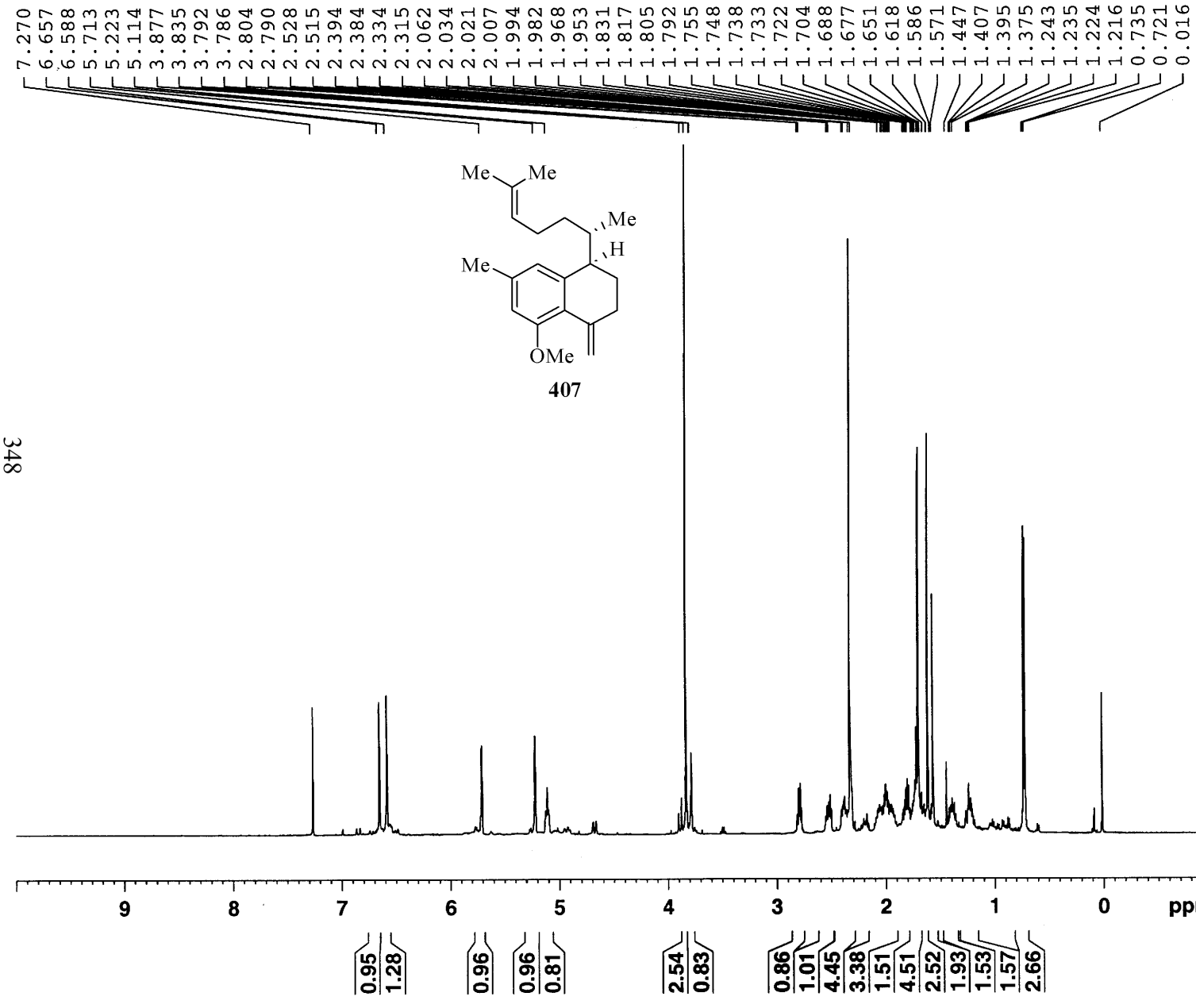
F2 - Acquisition Parameters
Date_ 20070727
Time 1.14
INSTRUM DRX500
PROBHD 5 mm Multinucl
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 3026
DS 4
SWH 34013.605 Hz
FIDRES 0.519006 Hz
AQ 0.9634292 sec
RG 7298.2
DW 14.700 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
D31 0.00000000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 8.10 usec
PL1 3.00 dB
SFO1 125.7723786 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 88.00 usec
PL2 0.00 dB
PL12 21.00 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 32768
SF 125.7577928 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1H NMR
PZ-IX-60-A2



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Current Data Parameters

NAME	PZ-IX-60-A2
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20070726
Time	21.19
INSTRUM	DRX500
PROBHD	5 mm Multinucl
PULPROG	zg30pad
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1719923 sec
RG	101.6
DW	48.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
D31	0.00000000 sec

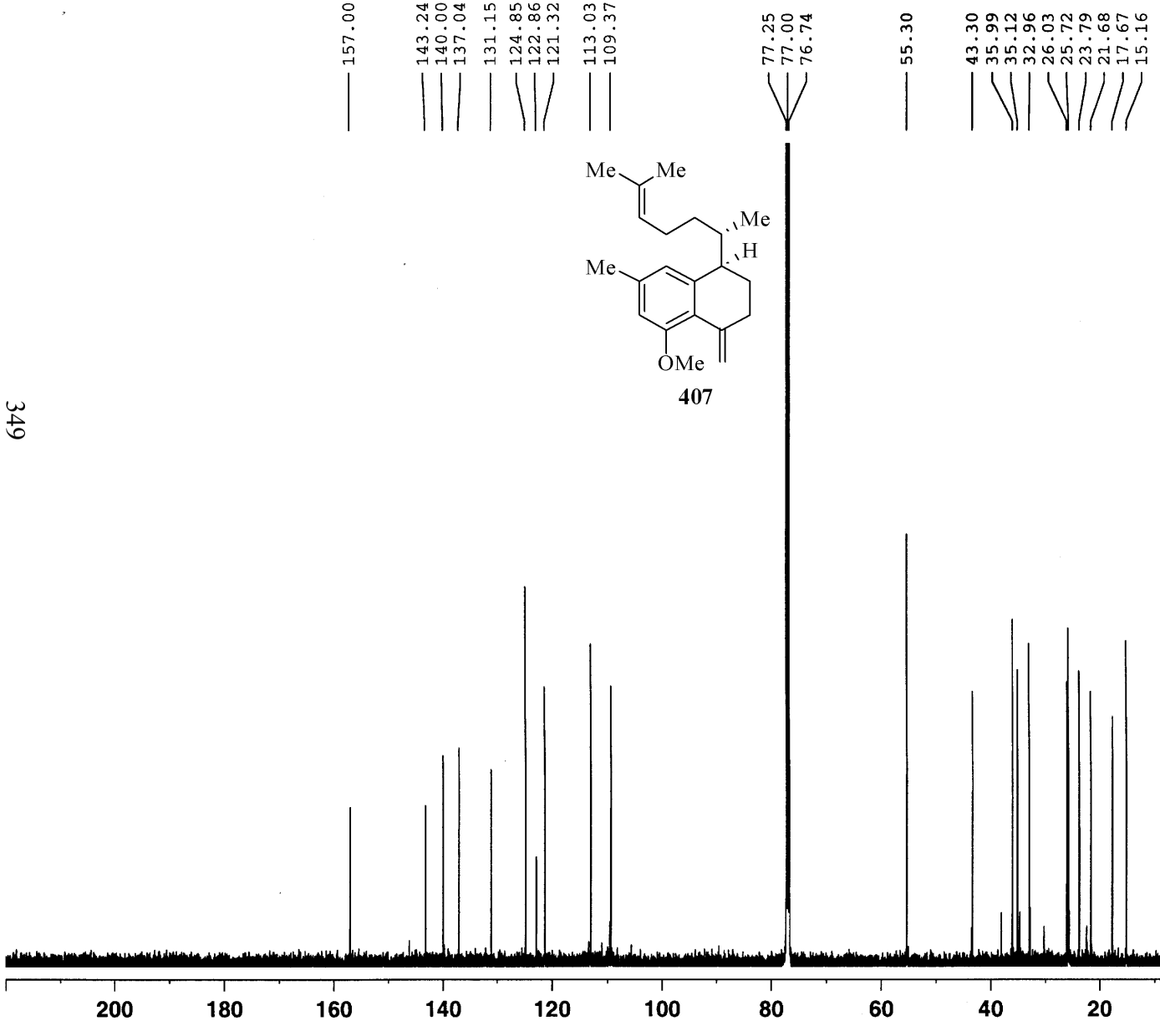
======== CHANNEL f1 ========

NUC1	1H
P1	11.50 usec
PL1	0.00 dB
SFO1	500.1330885 MHz

F2 - Processing parameters

SI	32768
SF	500.1300087 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.40

13C NMR
PZ-IX-60-A2



407

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Current Data Parameters
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EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
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PROBHD   5 mm Multinucl
PULPROG          zgdc30
TD               65536
SOLVENT          CDCl3
NS               1482
DS                  4
SWH          34013.605 Hz
FIDRES        0.519006 Hz
AQ            0.9634292 sec
RG               13004
DW              14.700 usec
DE               6.00 usec
TE              300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
D31          0.00000000 sec

======== CHANNEL f1 ========
NUC1                13C
P1               8.10 usec
PL1              3.00 dB
SFO1       125.7723786 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2           88.00 usec
PL2              0.00 dB
PL12             21.00 dB
SFO2       500.1320005 MHz

F2 - Processing parameters
SI                32768
SF         125.7577938 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
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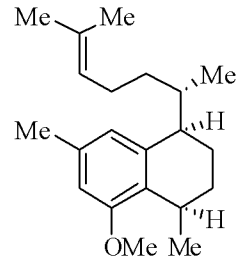
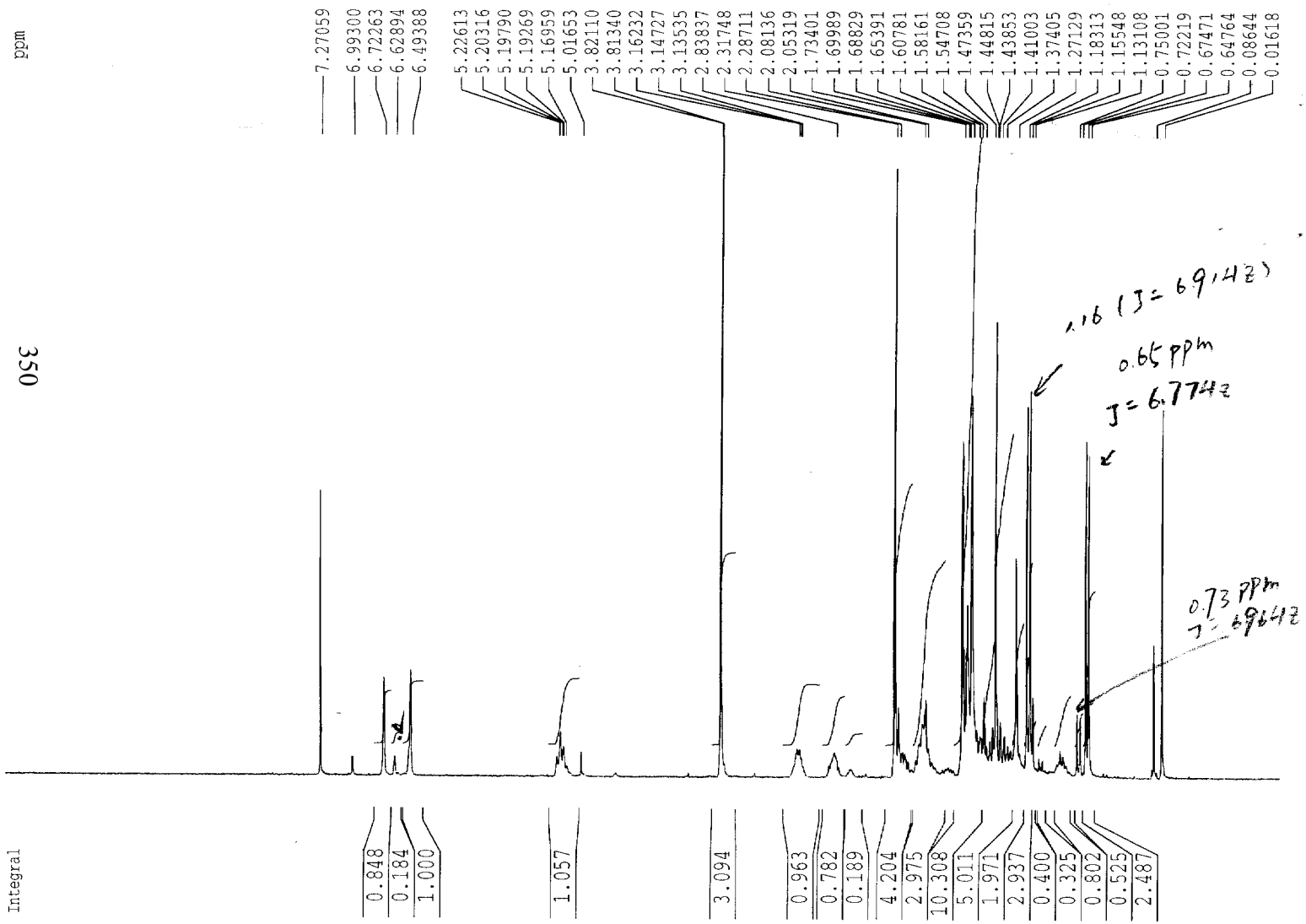


408 (*d.r.*4.6:1.0)



Current Data Parameters

NAME	PZ-VIII-44-CRU
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

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Time	23.35
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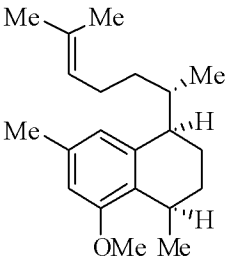
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	5208.333 Hz
FIDRES	0.158946 Hz
AQ	3.1457779 sec
RG	1430
DW	96.000 usec
DE	137.14 usec
TE	300.0 K
D1	1.00000000 sec
P1	9.50 usec
SFO1	250.1315321 MHz
NUCLEUS	1H

F2 - Processing parameters

SI	16384
SF	250.1300049 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.50

1D NMR plot parameters

CX	20.00 cm
CY	12.50 cm
F1P	10.000 ppm
F1	2501.30 Hz
F2P	-1.000 ppm
F2	-250.13 Hz
PPMCM	0.55000 ppm/cm
HZCM	137.57150 Hz/cm



408 (*d.r.*4.6:1.0)

156.870
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135.325
131.191
129.371
125.452
124.836
121.484
119.849
108.190
107.771
77.444
77.139
76.936
76.428
55.062
41.066
39.726
38.668
35.722
35.135
30.256
29.632
28.986
27.939
26.298
25.691
21.652
21.567
21.176
20.248
18.313
17.644
16.597
16.440
14.108
-0.079

ppm

200 150 100 50 0

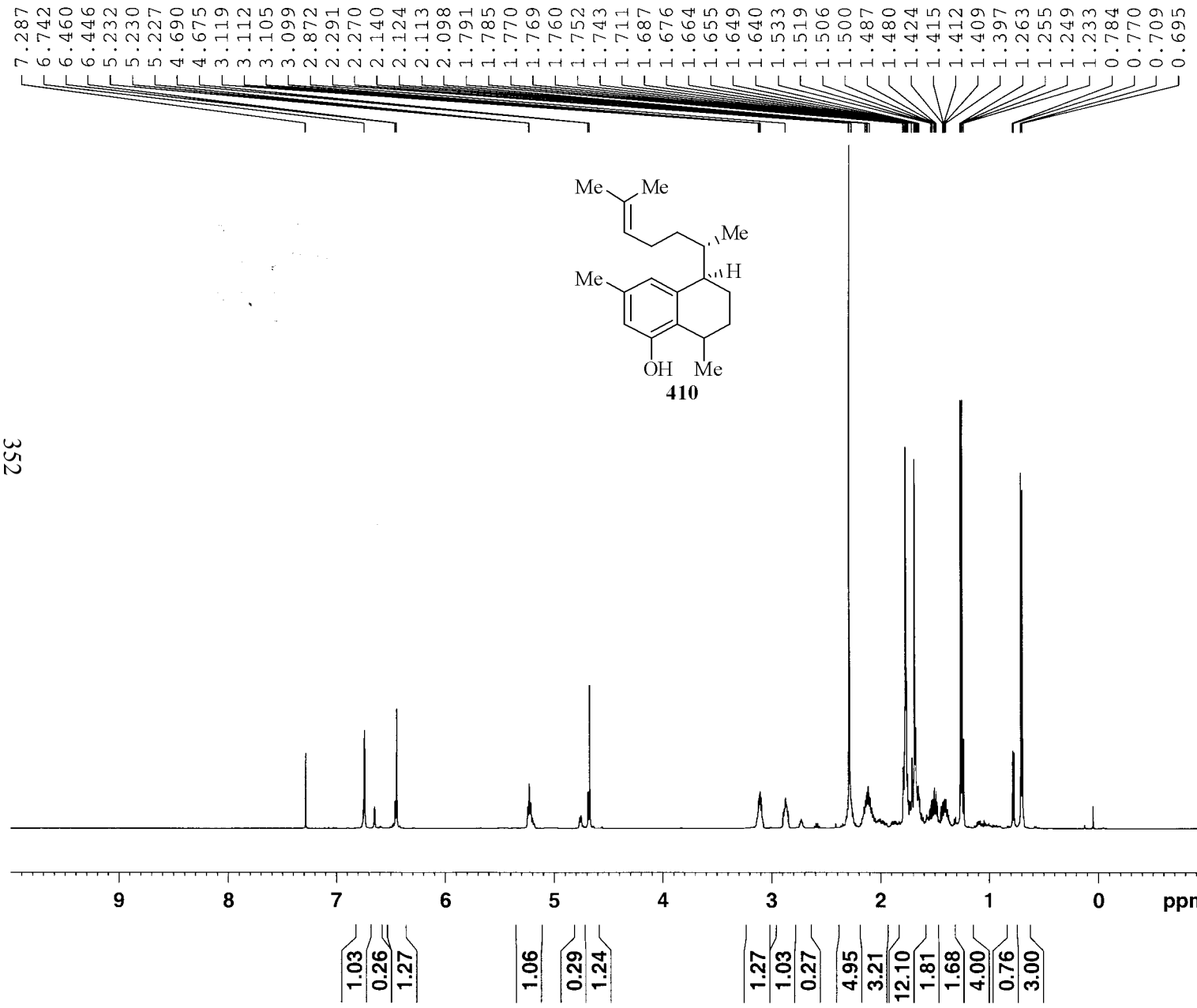
Current Data Parameters
NAME PZ-VIII-44-CRU
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070102
Time 23.43
INSTRUM arx250
PROBHD 5 mm QNP 1H
PULPROG zgdc30
TD 36864
SOLVENT CDCl3
NS 12299
DS 4
SWH 17241.379 Hz
FIDRES 0.467702 Hz
AQ 1.0691060 sec
RG 22800
DW 29.000 usec
DE 41.43 usec
TE 300.0 K
D12 0.00002000 sec
DL5 23.00 dB
CPDPRG waltz16
P31 103.00 usec
D1 2.00000000 sec
P1 8.00 usec
SFO1 62.9023694 MHz
NUCLEUS 13C
D11 0.03000000 sec

F2 - Processing parameters
SI 32768
SF 62.8952440 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 30.00 cm
F1P 220.000 ppm
F1 13836.95 Hz
F2P -10.000 ppm
F2 -628.95 Hz
PPMCM 11.50000 ppm/cm
HZCM 723.29529 Hz/cm

1H NMR
PZ-IX-99-A2



Current Data Parameters
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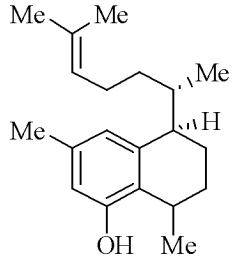
EXPNO 1
PROCNO 1

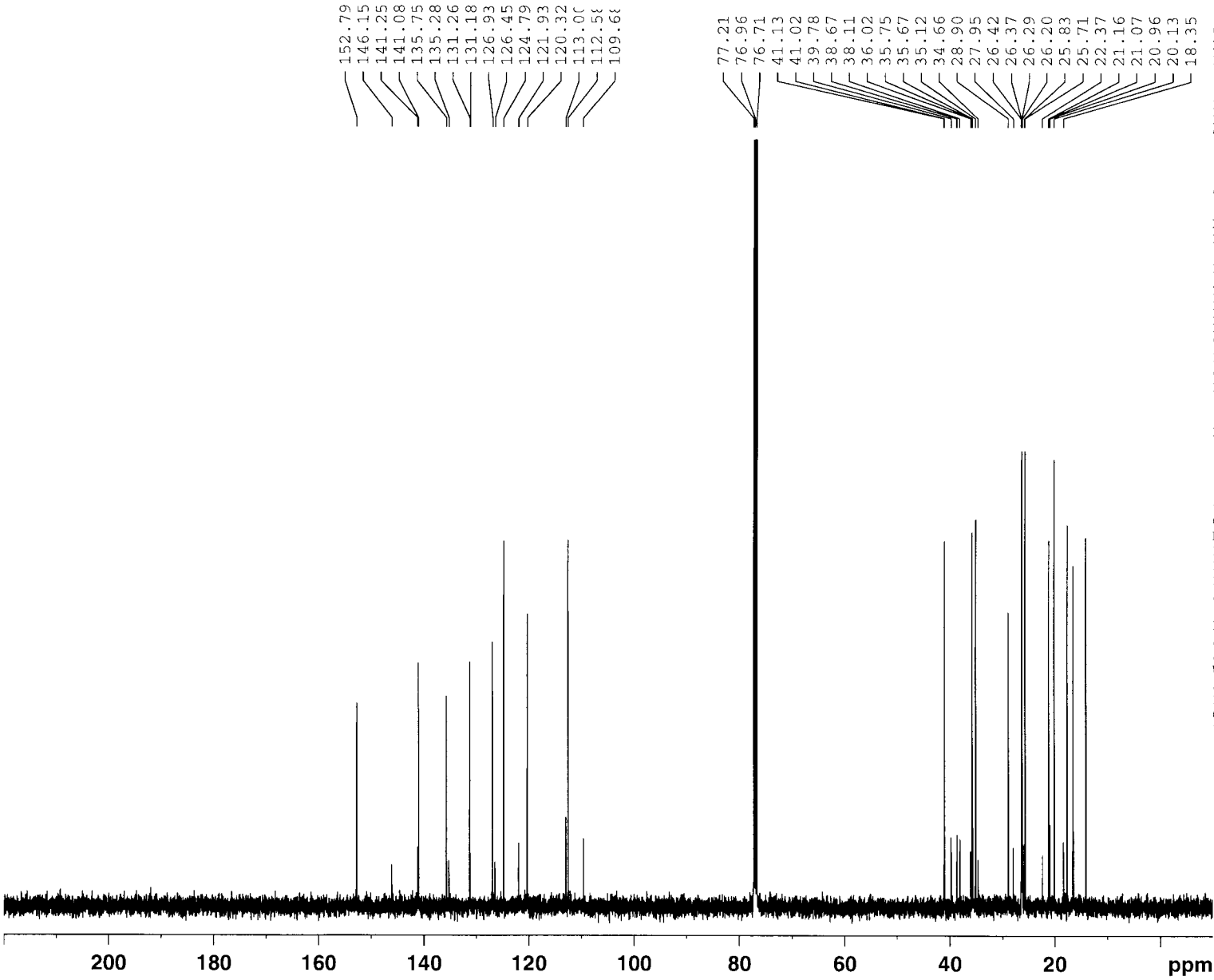
F2 - Acquisition Parameters
Date_ 20071012
Time 0.01
INSTRUM DRX500
PROBHD 5 mm Multinucl
PULPROG zg30pad
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 71.8
DW 48.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
D31 0.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 11.50 usec
PL1 0.00 dB
SFO1 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40



410

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Current Data Parameters
NAME          PZ-IX-99-A2
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20071012
Time                 0.13
INSTRUM            DRX500
PROBHD   5 mm Multinucl
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   327
DS                     4
SWH           34013.605 Hz
FIDRES         0.519006 Hz
AQ            0.9634292 sec
RG                  8192
DW                14.700 usec
DE                 6.00 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
D31          0.00000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.10 usec
PL1                 3.00 dB
SFO1         125.7723786 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              88.00 usec
PL2                 0.00 dB
PL12               21.00 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                  32768
SF           125.7578011 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                   1.40
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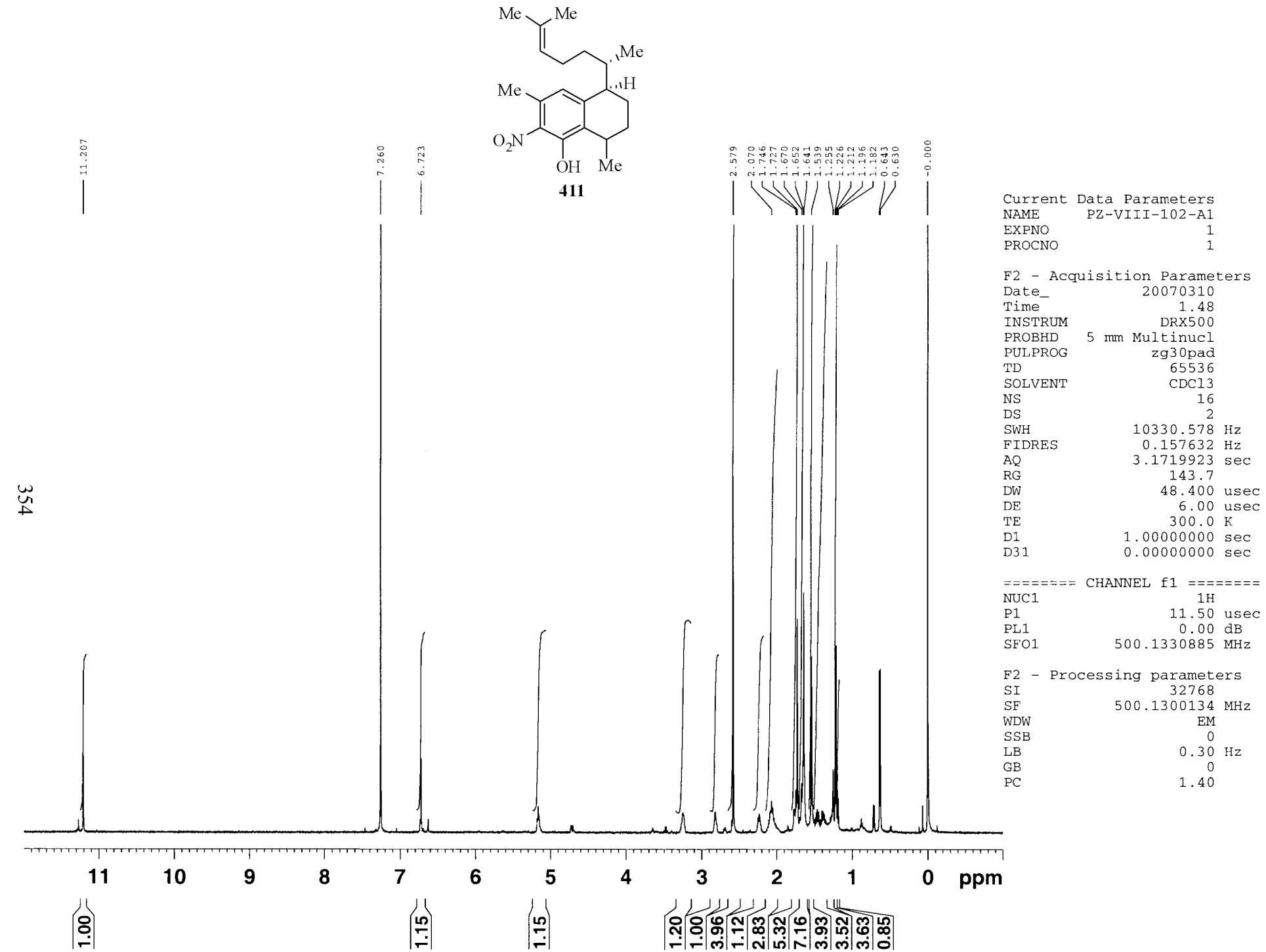

Current Data Parameters
NAME PZ-VIII-102-A1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
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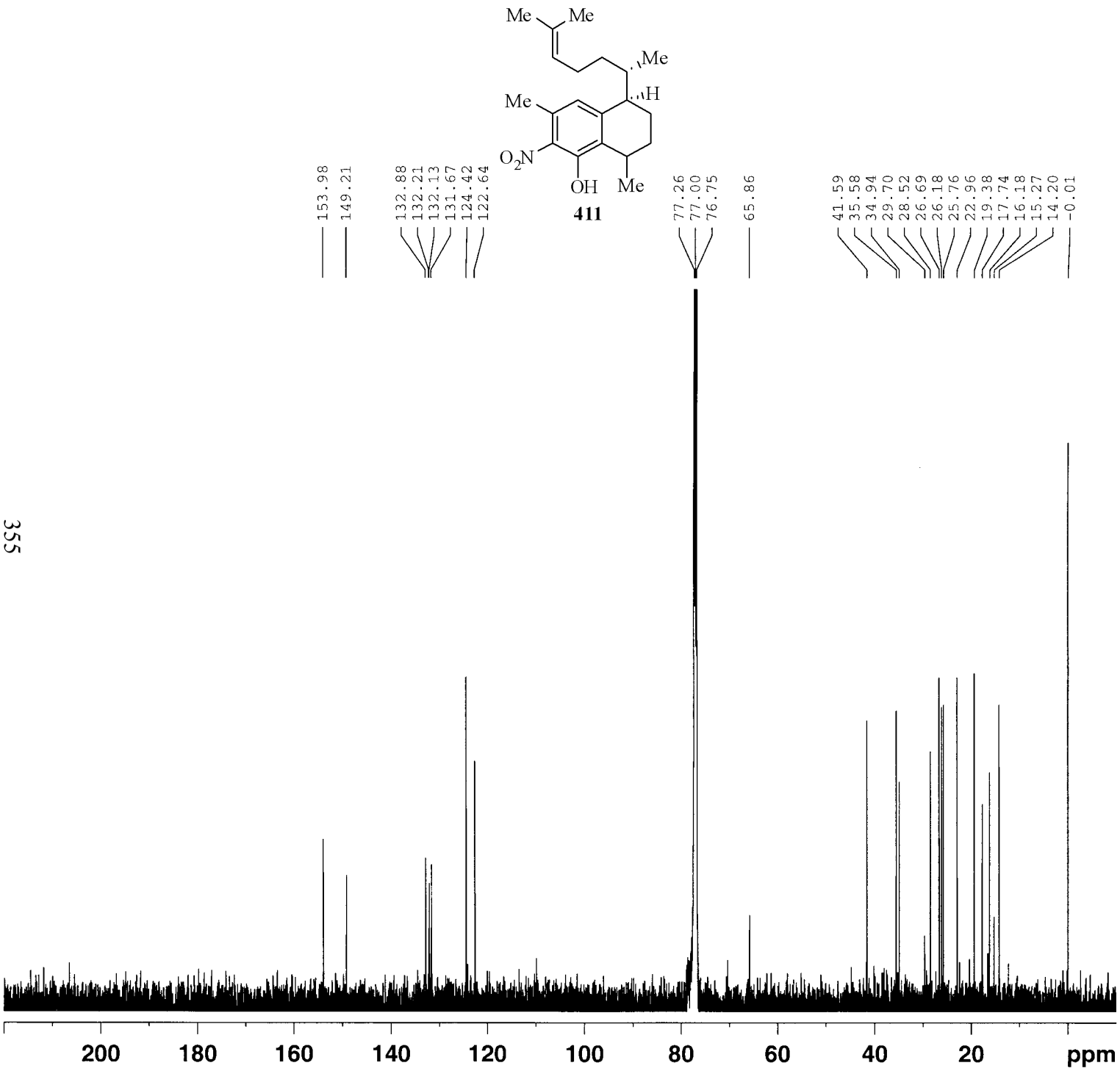
Time 1.48
INSTRUM DRX500
PROBHD 5 mm Multinucl
PULPROG zg30pad
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 143.7
DW 48.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
D31 0.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 11.50 usec
PL1 0.00 dB
SFO1 500.1330885 MHz

F2 - Processing parameters
SI 32768
SF 500.1300134 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40

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Current Data Parameters
NAME      PZ-VIII-102-A1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070312
Time                9.03
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PROBHD   5 mm Multinucl
PULPROG          zgdc30
TD                65536
SOLVENT           CDC13
NS                10952
DS                    4
SWH           34013.605 Hz
FIDRES         0.519006 Hz
AQ             0.9634292 sec
RG                32768
DW               14.700 usec
DE                6.00 usec
TE               300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
D31          0.00000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 8.10 usec
PL1                3.00 dB
SFO1        125.7723786 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             88.00 usec
PL2                0.00 dB
PL12              21.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                32768
SF          125.7577917 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
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