TOTAL SYNTHESIS OF SCHULZEINES AND ANALOGUES AND SCREENING FOR ALPHA-GLUCOSIDASE INHIBITORS

By

Sunisa Akkarasamiyo

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree
MASTER OF SCIENCE
Department of Chemistry
Graduate School
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การสังเคราะห์สารผลิตภัณฑ์ธรรมชาติชุลเซอีน และอนุพันธ์ และการทดสอบความสามารถในการยับยั้งเอนไซม์อัลฟากลูโคซิเดส

โดย

นางสาวสุนิสา อัคคะรัสมิโย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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……..
(Associate Professor Sirichai Chinatangkul, Ph.D.)
Dean of Graduate School
........../.................../..........

The Thesis Advisor

Punlop Kuntiyong, Ph.D.

The Thesis Examination Committee

.... Chairman
(Supachai Supalaknari, Ph.D.)
............./......................../..............

.... Member
(Associate Professor Boonsong Kongkathip, Ph.D.)
.........../......................../.............

.... Member
(Associate Professor Surachai Nimgirawath, Ph.D.)
............/......................../..............

....Member
(Punlop Kuntiyong, Ph.D.)
............/......................../..............

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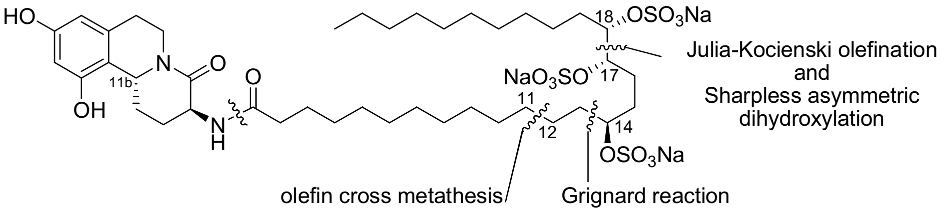

Schulzeine C
Schulzeine B = 11b-*epi*-Schulzeine C

Marine natural products schulzeines B and C, which are epimers at C11b, possess inhibitory effect toward alpha-glucosidase. Herein we report a total synthesis of these natural products. The structure of schulzeines was divided into two major subunits; the tricyclic core and C28 fatty acid side chain. The tricyclic core was synthesized from L-glutamic acid and 2-(3, 5-dihydroxyphenyl)-ethylamine featuring *N*-acyliminium ion cyclization as the key reaction. The C28 fatty acid side chain was synthesized from 10-undecenoic acid and 1-dodecene. The key reactions are Julia-Kocienski olefination, Sharpless asymmetric dihydroxylation, Grignard addition and olefin metathesis. The two subunits were united by amide formation. Subsequent removal of protecting groups, and formation of sodium sulfate functionality of the side chain then completed the total synthesis of the natural products.

Department of Chemistry Graduate School, Silpakorn University Academic Year 2008
Student's signature...
Thesis Advisor's signature......................................

49302204 : สาขาวิชาเคมีอินทรีย์

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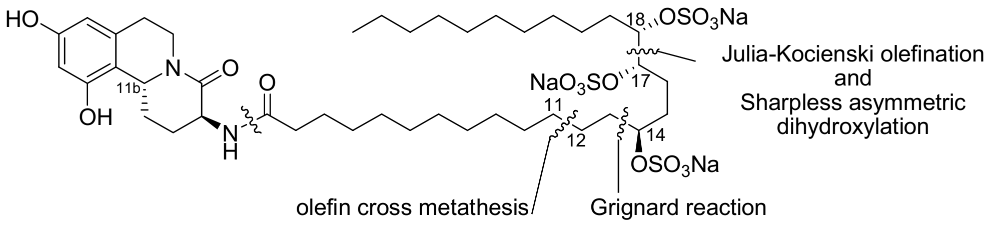

Schulzeine C
Schulzeine B = 11b-*epi*-Schulzeine C

สารผลิตภัณฑ์ธรรมชาติชุลเซอีน บี และ ซี เป็นสารที่มีฤทธิ์ยับยั้งการทำงานของเอนไซม์อัลฟากลูโคซิเดส ชุลเซอีน บี และ ซี เป็น epimer กันที่ C11b ถูกสังเคราะห์ขึ้นด้วยกระบวนการทางเคมีอินทรีย์สังเคราะห์ที่มีหลายขั้นตอนโครงสร้างของชุลเซอีนถูกแบ่งออกเป็นสองส่วนคือ ส่วนโครงหลักสามวงและส่วนสายโซ่กรดไขมันที่มี 28 คาร์บอน ส่วนโครงหลักสามวงที่ถูกสังเคราะห์ขึ้นจาก L-glutamic acid และ2-(3,5-dihydroxyphenyl)-ethylamine โดยใช้ปฏิกิริยาการปิดวงของ *N*-acyliminium ion เป็นปฏิกิริยาหลัก ส่วนสายโซ่กรดไขมันที่มี 28 คาร์บอนนั้นถูกสังเคราะห์ขึ้น ด้วยปฏิกิริยา 10 ขั้นตอน เริ่มจาก 10-undecenoic acid และ 1-dodecene ปฏิกิริยาหลักที่ใช้ในการสังเคราะห์คือ Julia-Kocienski olefination Sharpless asymmetric dihydroxylation Grignard addition และ olefin metathesis ส่วนโครงหลักสามวงและส่วนสายโซ่กรดไขมันที่มี 28 คาร์บอน ถูกนำมาเชื่อมต่อกันโดยใช้การสร้างพันธะเอไมด์ จากนั้นการกำจัดหมู่ป้องกันและการทำให้อยู่ในรูปของเกลือโซเดียมซัลเฟตก็ทำให้ได้สารผลิตภัณฑ์ธรรมชาติชุลเซอีน

ภาควิชาเคมี บัณฑิตวิทยาลัย มหาวิทยาลัยศิลปากร ปีการศึกษา 2551

ลายมือชื่อนักศึกษา..

ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์ ....

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Finally, this thesis will never be accomplished without my family’s care.

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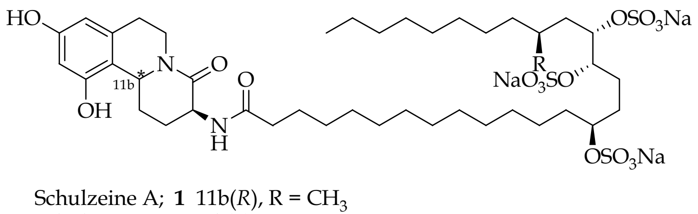
CHAPTER 1

GENERAL INTRODUCTION

Schulzeines are a new group of natural products isolated from Japanese marine sponge, *Penares schulzei.*[1] They strongly inhibit the activity of alpha-glucosidase with the IC_{50} values of 48-170 nM, making them potential candidates for development into drugs for such diseases as cancers, diabetes and viral infections. The structure of schulzeines can be divided into two major fragments; 9, 11-tetrahydroisoquinoline-delta lactam tricyclic core and C28 fatty acid side chain (Figure 1). The tricyclic core contains two stereogenic centers at C3 and C11b. Schulzeines A and C have *R* configuration at C11b whereas schulzeine B has *S* C11b. The C3 stereogenic center of the tricyclic core bearing acylamino group has *S* configuration in all members of this group. The C28 fatty acid side chain of schulzeine B and C possesses three stereogenic centers at C14, C17, and C18 in the form of sodium sulfate salts with *S,S,S* configurations, respectively. The C28 fatty acid side chain of schulzeine A has an extra stereogenic center at C20 (*S*) bearing a methyl substituent. The structural complexity and intriguing biological activity combined with scarcity of this group of natural products from their natural source necessitate the synthetic studies toward schulzeines and their non-natural analogues for further medicinal investigation.



Schulzeine A; **1** 11b(*R*), R = CH_3
Schulzeine B; **2** 11b(*S*), R = H
Schulzeine C; **3** 11b(*R*), R = H

Figure 1. Schulzeines.

ISOLATION AND STRUCTURE ELUCIDATION

Schulzeines A-C were isolated from the hydrophobic extract of Japanese marine sponge *Penares schulzei*, collected off the coast of Japan by Fusetani's group in 2004. Their structures were elucidated by spectral analysis and chemical degradations to be the isoquinoline alkaloids, encompassing two amino acids, and sulfated C28 fatty acid. Absolute stereochemistry was determined by application of the modified Mosher analysis to fragments obtained from chemical degradations.

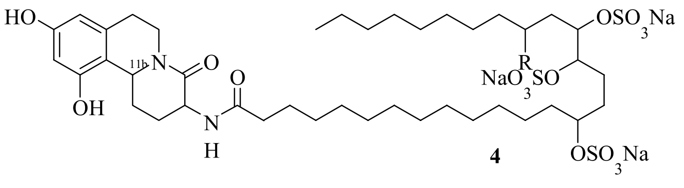
Schulzeines A-C had a molecular formular of $C_{42}H_{69}N_2O_{16}S_3Na_3$, $C_{41}H_{67}N_2O_{16}S_3Na_3$, $C_{41}H_{67}N_2O_{16}S_3Na_3$ respectively, established on the basics of NMR and HRFABMS data. The sulfate group was evident from fragment ions at m/z 97 (HSO_4^-) and 80 (SO_3^{2-}) in the negative mode FABMS, which was supported by an IR band at 1223 cm^{-1}. The analysis of NMR data found that schulzeines have two carbonyl carbons (δ_C 176.0 and 170.4), six aromatic carbons (δ_C 157.6, 156.6, 138.4, 115.8, 107.5, and 102.2) two of which were protonated (δ_H 6.17 and 6.07), a nitrogenous methylene (δ_H 4.79 and 2.62, δ_C 40.6), two nitrogenous methines (δ_H 4.77 and 4.28; δ_C 57.0 and 51.9), three oxygenated methines (δ_H 4.84, 4.70, and 4.35; δ_C 81.1, 79.8, and 77.5), a methylene envelop (δ_H 1.30 - 1.20), a terminal methyl (δ_H 0.87), an exchangeable proton (δ_H 8.21), and a secondary methyl (δ_H 0.93) for schulzeine A (Table 1.).

Table 1. ^{1}H and ^{13}C-NMR Chemical Shifts of Schulzeines A in CD_3OH and B in CD_3OD.

	Schulzeine A		**Schulzeine B**	
	^{1}H	**^{13}C**	**^{1}H**	**^{13}C**
1α	1.39[a]	29.3	1.39[c]	29.0
1β	3.06 (dq, 11.9, 3.5)		2.55 (m)	
2α	2.10 (m)	28.3	1.55 (m)	26.0
2β	1.93 (m)		2.26 (m)	
3	4.28 (dt, 11.8, 7.5)	51.9	4.63[d]	49.8
3-NH	8.21 (d, 8.1)			
4		170.4		171.8
6α	4.79[b]	40.6	4.62[d]	40.4
6β	2.62 (dt, 12.3, 2.3)		2.72 (m)	
7α	2.69 (dt, 15.4, 2.3)	30.9	2.60 (dt, 2.5, 12.3)	30.5
7β	2.52 (dt, 15.4, 2.3)		2.71 (m)	
7a		138.4		138.4
8	6.07 (d, 2.3)	107.5	6.11 (d, 2.3)	107.3
9		157.6		157.9
10	6.17 (d, 2.3)	102.2	6.18 (d, 2.3)	101.9
11		156.6		156.1
11α		115.8		115.0
11β	4.77[b]	57.0	4.84 (dd, 11.1, 3.8)	51.6
1’		176.0		176.1
2’	2.22 (dt, 4.2, 7.5)	37.0	2.27 (dt, 2.0, 7.7)	37.0
3’	1.61(m)	26.7	1.61(m)	26.8
4’-11’	1.3[a]	30[b]	1.3[c]	30[b]
12’	1.40 (m)	25.8	1.40 (m)	25.9
13’	1.71(m)	35.3	1.72(m)	35.4
	1.62 (m)		1.62 (m)	
14’	4.35 (dt, 10.8, 6.5)	81.1	4.33 (dt, 10.4, 6.2)	81.2
15’	1.95 (m)	31.6	1.95 (m)	31.7
	1.71 (m)		1.70 (m)	
16’	1.94 (m)	25.4	1.94 (m)	25.8
	1.60 (m)		1.59 (m)	
17’	4.70 (dt, 9.6, 3.4)	79.8	4.65[e]	80.0
18’	4.84 (ddd, 11.9, 3.4, 2.5)	77.5	4.64[e]	80.0
19’	1.59 m)	36.8	1.74 (m)	29.8
	1.40 (m)		1.54(m)	
20’	1.75 (m)	29.5	1.3[c]	30[b]
21’	1.16 (m)	39.0	1.3[c]	30[b]
	1.30 (m)			
22’-26’	1.3[a]	30[b]	1.3[c]	30[b]
27’	1.28 (m)	23.6	1.28 (m)	23.7
28’	0.87 (t,6.9)	14.3	0.87 (t, 7.1)	14.4
29’	0.93 (d, 6.5)	19.4		

[a-e]Signals overlapped with each other. [b,d, e] Interpretation of the co-occurring signals was conducted with the data in pyridine-d_5.

Interpretation of NMR data (^{1}H, ^{13}C, COSY, HMBC, HMQC), IR and FABMS led to the gross structure **4** shown in Figure 2.



Schulzeine A : R = CH_3

Schulzeine B-C : R = H

Figure 2. Gross structure of schulzeines.

The analysis of absolute stereochemistry employed desulfated schulzeines as substrate for methanolysis which afforded fragments **7**, **8**, **9.**

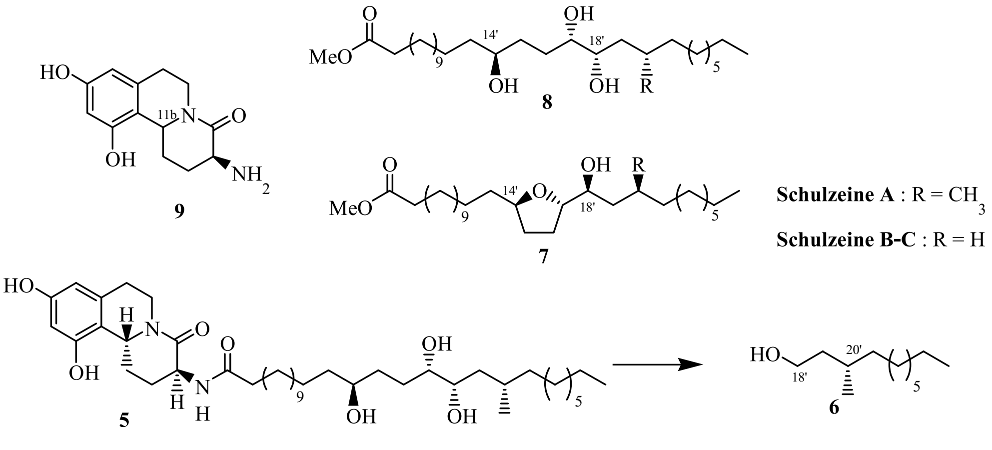


Figure 3. Determination of absolute configuration of Schulzeines.

The absolute stereochemistry at C-3 was determined by application of the Mosher analysis. The distribution of Δδ values indicated the 3*S*-configuration. The relationship of H-3 and H-11b were determined by NOE (ROESY) data and it was found that H-3 and H-11b of schulzeines A and C were on the anti face of the six membered ring whereas those of schulzeine B were on the same face. The configuration of C-14' was determined by Mosher analysis. The triol was converted to the 17', 18'-*O* isopropylidene derivative followed by MTPA esterification.

Analysis of this ester indicated the 14'*S* configuration. The *trans*-relationship for H-17' and 18' was determined by ROESY data. The C-18 stereochemistry of ether linkage was determined by Mosher analysis to be 18'S- configuration, therefore the absolute stereochemistry at C-17 was *S*. The extra stereocenter at C-20 of schulzeine A was determined by analysis of its MTPA ester which was obtained by desulfation of schulzeine A with TsOH, $NaIO_4$ oxidation, and $NaBH_4$ reduction to afford **6** which was converted to MTPA ester. The C20 stereocenter of this MTPA ester was determined to be *S* configuration.

BIOLOGICAL ACTIVITY

The IC_{50} values of schulzeines A-C against yeast alpha-glucosidase varied from 48-170 nM. Desulfated schulzeines A-B still retained activity with IC_{50} values of 2.5 and 1.1 μM, respectively. Furthermore, schulzeines were also inhibitive against viral neuraminidase with IC_{50} value of 60 μM.

Natural products from *Penares sp.* family were studied by two groups of researchers, i.e. Kobayashi et al and Fusetani et al. Since 1988 to present, they found nine compounds namely, penasterol (antileukemic),[2] penaresidines A and B (potent actomyosin ATPase activity),[3] penarolide sulfates A_1 and A_2 (alpha-glucosidase inhibitors),[4] penasulfate A (alpha-glucosidase inhibitor)[5] and schulzeines A-C from *Penares schulzei* (alpha-glucosidase inhibitors, Figure 4).

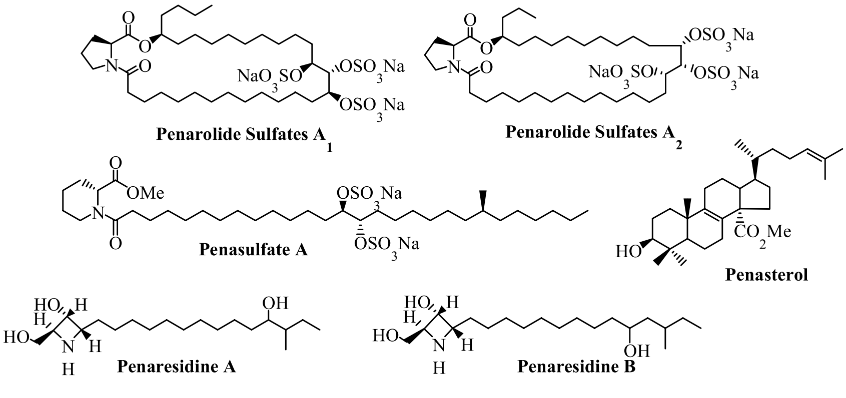


Figure 4. Natural products from marine sponges *Penarese sp.*

Many natural anti alpha-glucosidase are mono or polysaccharides. Acarbose, miglitol and *N*-butyl-1-deoxynokirimycin are commercial drugs used for the therapy of diabetes. These are glycosidic derivatives which exhibit potent anti-alpha-glucosidase activity.[6] Some examples are shown in Figure 5.

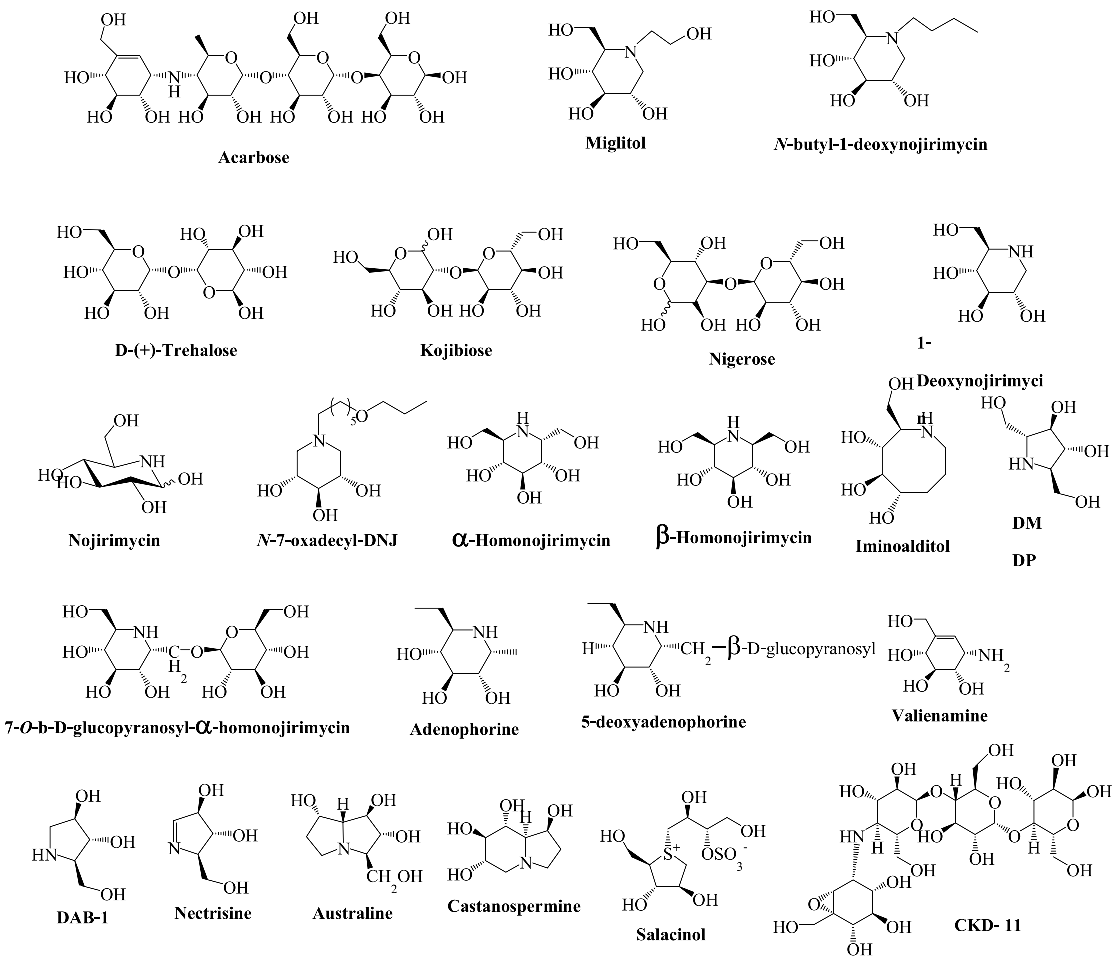


Figure 5. Natural glycosidic anti-alpha-glucosidase.

There are numerous natural products which are non-glycosidic compounds which exhibit anti-α-glucosidase, including schulzeines, penarolide and penasulfate. Other examples are dibutyl phthalate from *Streptomyces melanosporofaciens*, *N*-*p*-coumaroyl-*N'*-feruloylputrescine and *N,N'*-diferuloyputrescine from by-product of corn starch processing, callyspongynic acid from sponge *Callyspongia trancata*, corticatic acid A from *Petrosia Corticato*, petrosynol from *Petrosia sp*., and baicalein from marioram leaves of *Origanum makorana* (Figure 6).

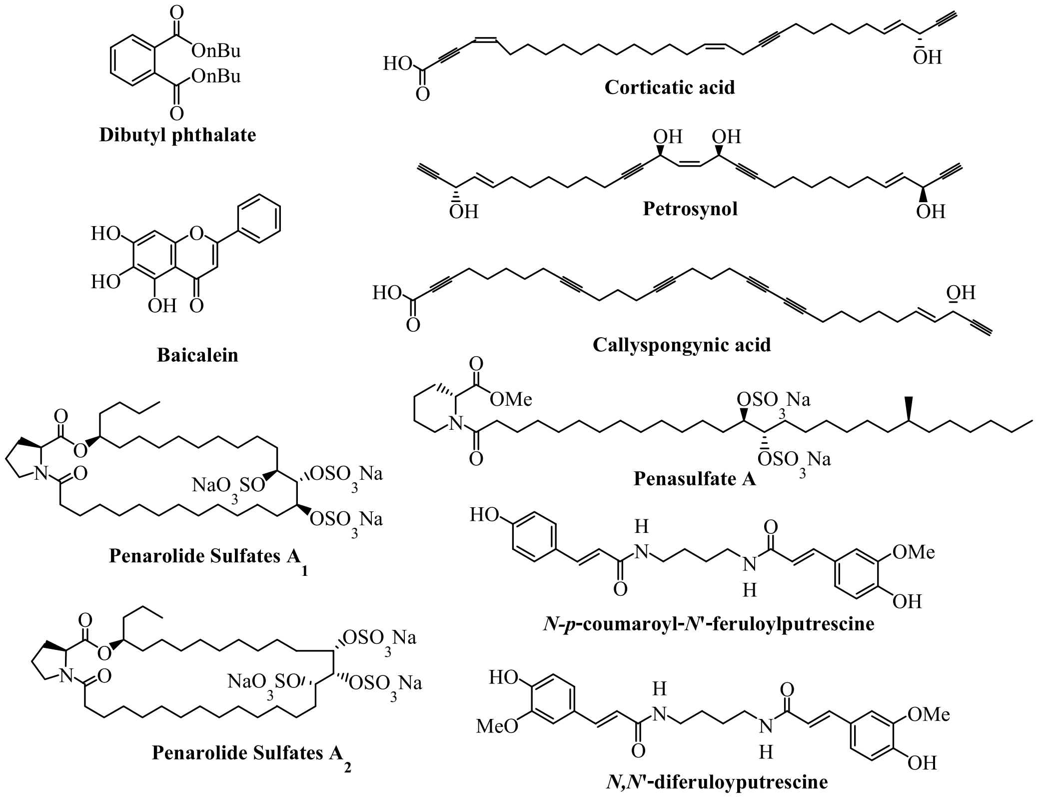
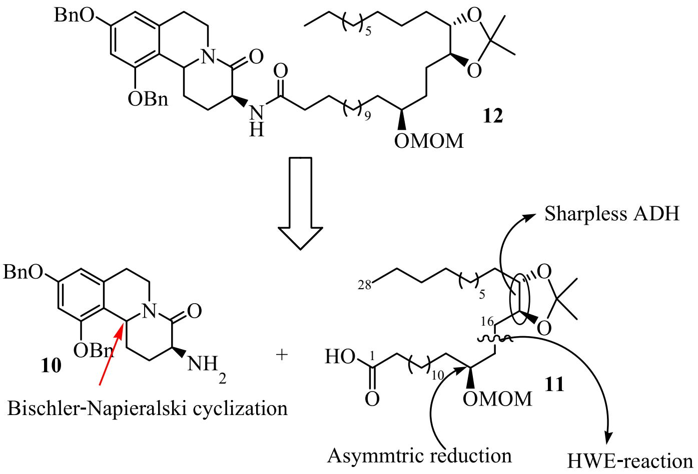


Figure 6. Natural non-glycosidic anti-alpha-glucosidase.

PREVIOUS SYNTHESIS OF SCHULZEINES

Since Fusetani reported the isolation and structure elucidation of schulzeines (A-C) in 2004, there have been two reported synthetic studies toward these compounds. We have previously reported a short synthetic route toward the tricyclic core of schulzeines using *N*-acyliminium ion cyclization in 2006.[7] Gunjar and coworkers reported the total synthesis of schulzeines B and C in 2007.[8] Their retrosynthetic analysis shown in scheme 1 divided the molecule of schulzeines into two major parts. The tetrahydroisoquinoline unit could be synthesized employing Bischler Napieralski reaction as the key reaction. The key reactions for

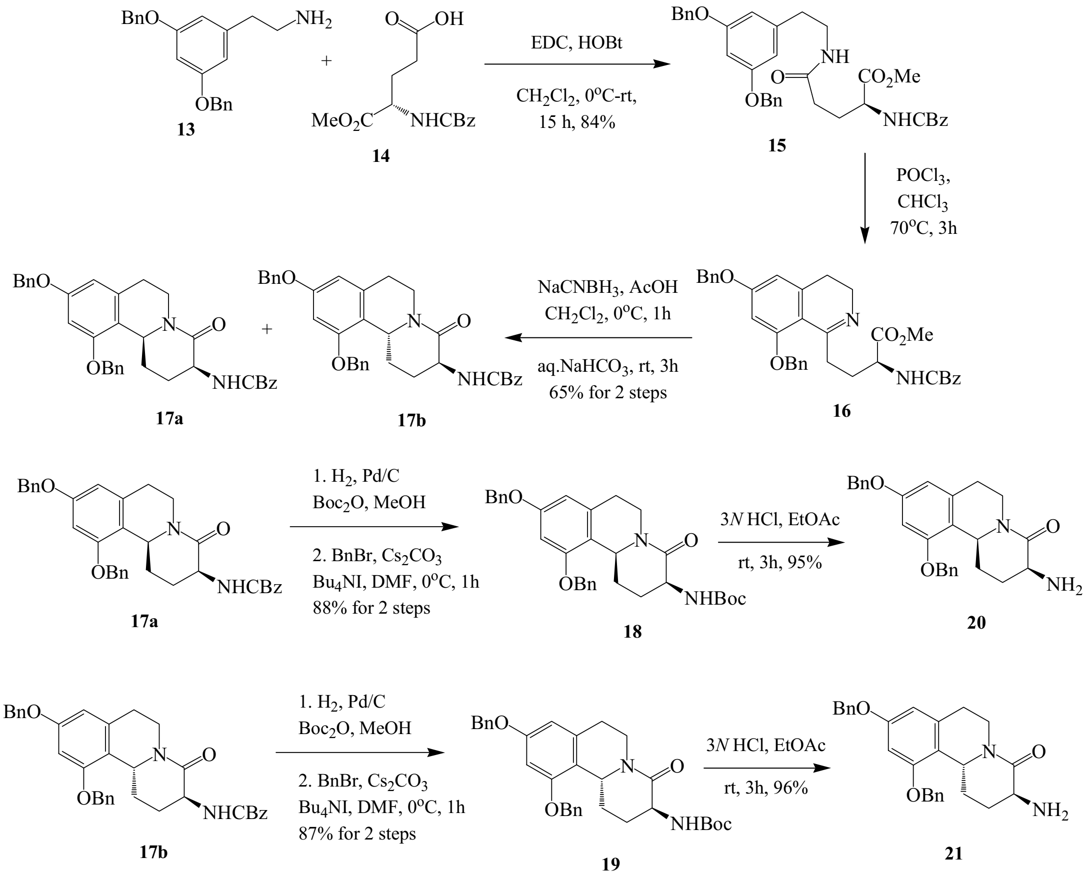
C28 fatty acid side chain were HWE reaction, Sharpless asymmetric dihydroxylation, and BINAL-H mediated asymmetric reduction (scheme1.).



Scheme 1. Gunjar's retrosynthetic analysis of schulzeines B, C.

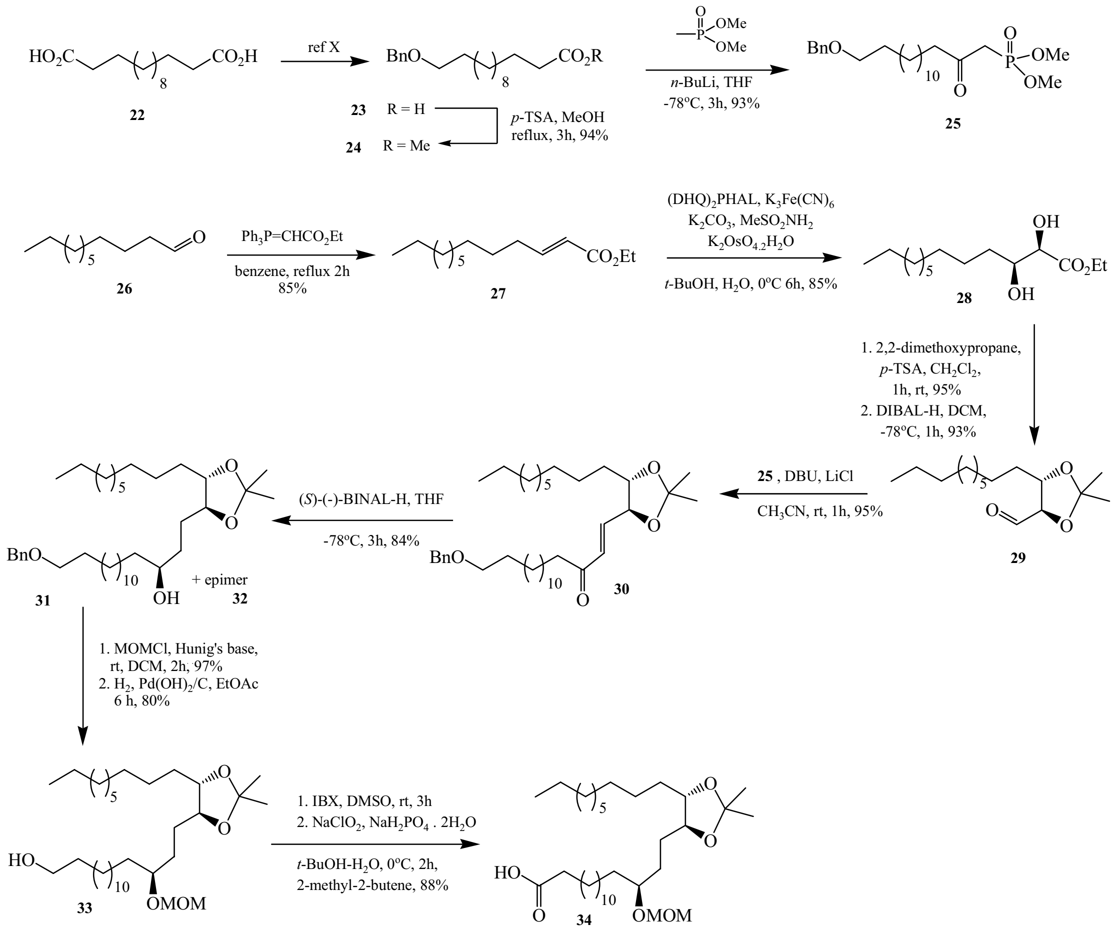
The construction of Gunjar's tetrahydroisoquinoline tricyclic core began with the amide formation between amine **13** and acid **14** to give amide **15**. This amide was treated with $POCl_3$ in Bischler Napieralski reaction to give dihydroisoquinoline **16**. Reduction of **16** with $NaCNBH_3$ gave tetrahydroisoquinoline as a mixture of two diastereomers. Treatment of this mixture with $NaHCO_3$ gave tricyclic lactam **17a** and **17b** in 2:3 ratio. The two diastereomers were separated by simple column chromatography and protection/deprotection manipulation afforded amines **20** and **21** (scheme 2.).

The synthesis of C28 fatty acid began with conversion of 1, 12-dodecanedicarboxylic acid to acid **23**, according to reported procedure, followed by acid catalyzed esterification to afford methyl ester **24**. Treatment of **24** with lithiated methyl dimethylphosphonate gave phosphonate **25**, which represents C1-C15 of the fatty acid side chain. The HWE coupling partner of phosphonate **25**, aldehyde **29**, was prepared in 4 steps from undecan-1-al. Wittig reaction of undecan-1-al with ethoxycarbonyl-methylene-triphenylphosphorane provided enoate **27** as 85:15 E/Z mixture. Sharpless asymmetric dihydroxylation of **27***E* using $(DHQ)_2$PHAL ligand at 0 °C gave diol **28** which was protected with 2,2-dimethoxypropane, and reduction with DIBAL-H gave aldehyde **29**.



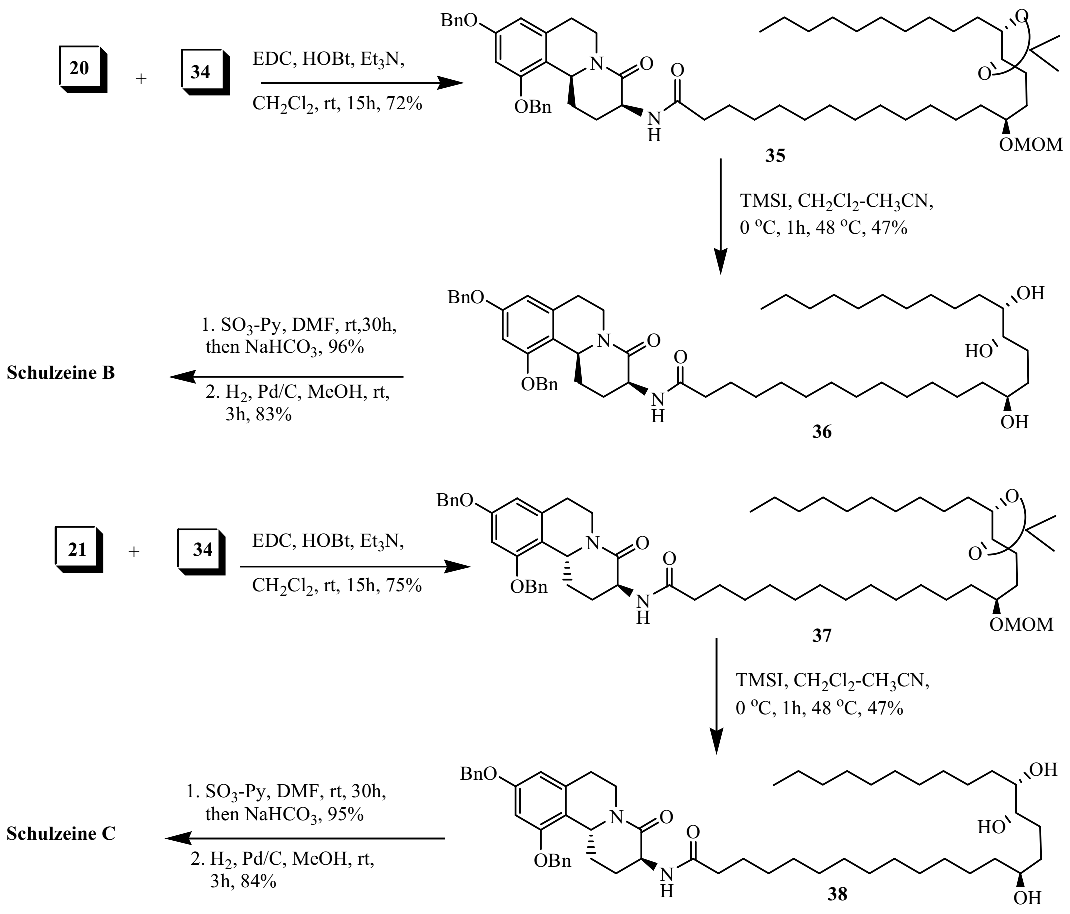
Scheme 2. Gurjar's synthesis of tricyclic core of schulzeine

HWE reaction of phosphonate **25** and aldehyde **29** yielded enone **30**. The resulting enone **30** underwent asymmetric reduction with (*S*)-BINAL-H in THF to afford alcohol **31** and its epimer **32** (11:1). The desired absolute configuration of **31** was established by Mosher method. Protection of the hydroxyl group as MOM ether followed by hydrogenation and $NaClO_2$ oxidation gave C28 fatty acid side chain (Scheme 3).



Scheme 3. Gurjar’s synthesis of C28 fatty acid side chain.

Coupling of tetrahydroidoquinoline unit with C28 fatty acid was achieved by amide formation in the presence of EDC and HOBt, and TMSI mediated deprotection of acetonide and MOM ether gave triol **36**, which was converted to sulfonate salt using SO_3-Py in DMF. Debenzylation of the sulfonate afforded schulzeines B and C (scheme 4).



Scheme 4. Gurjar's synthesis of schulzeines B and C

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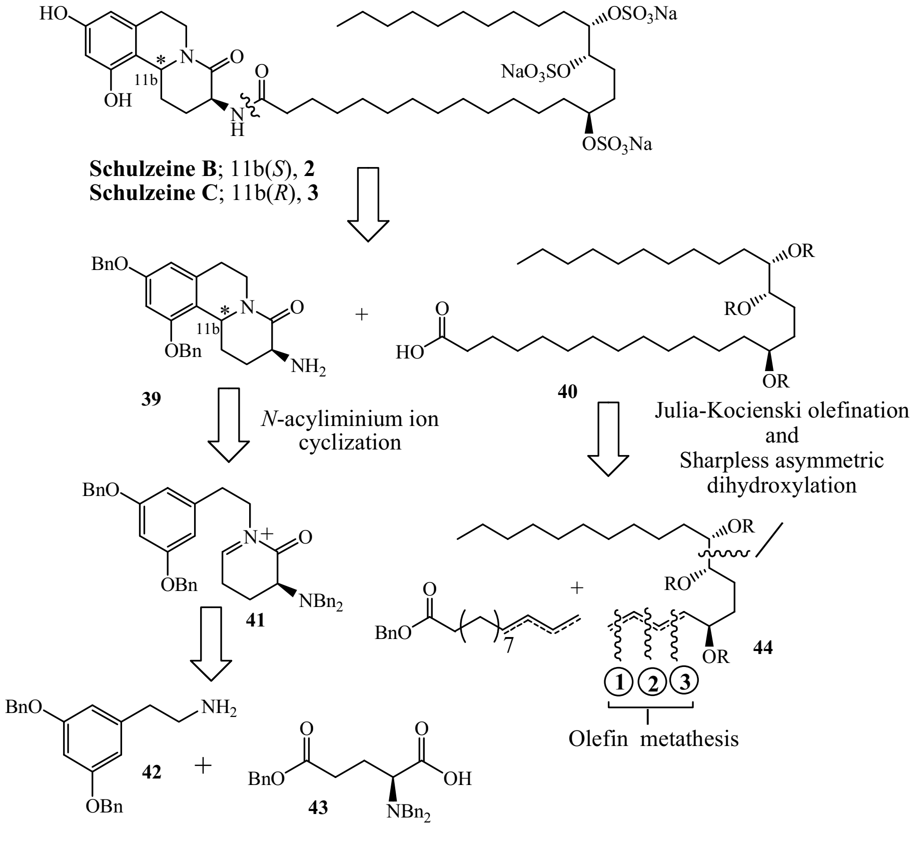
CHAPTER 2

TOTAL SYNTHESIS OF SCHULZEINES B AND C

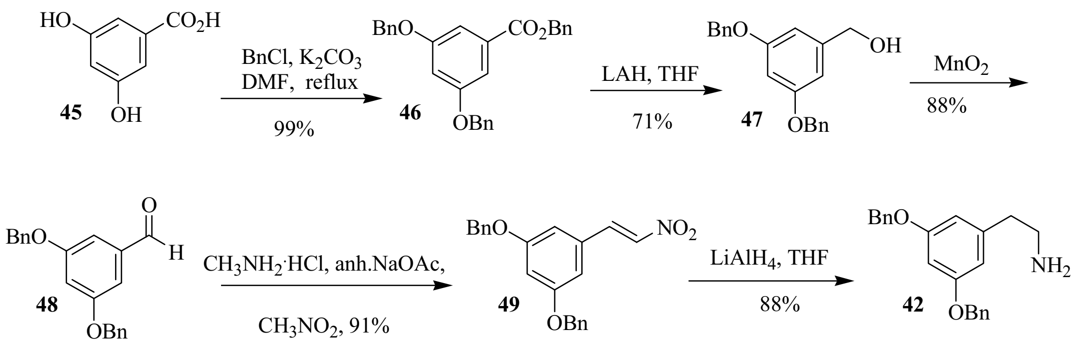
Our retrosynthetic analysis of schulzeines B and C is shown in scheme 5. The structure of schulzeines can be divided into two parts; the tricyclic core and the C28 fatty acid. The former could be synthesized with cyclization of *N*-acyliminium ion[1] which in turn could be prepared from 2-arylethylamine and L-glutamic acid derivative. The C28 fatty acid side chain would be assembled using olefin cross methathesis, Grignard reaction, CBS reduction, *E*-selective Julia-Kocienski olefination and Sharpless asymmetric dihydroxylation.



Scheme 5. Retrosynthetic analysis of schulzeines B and C

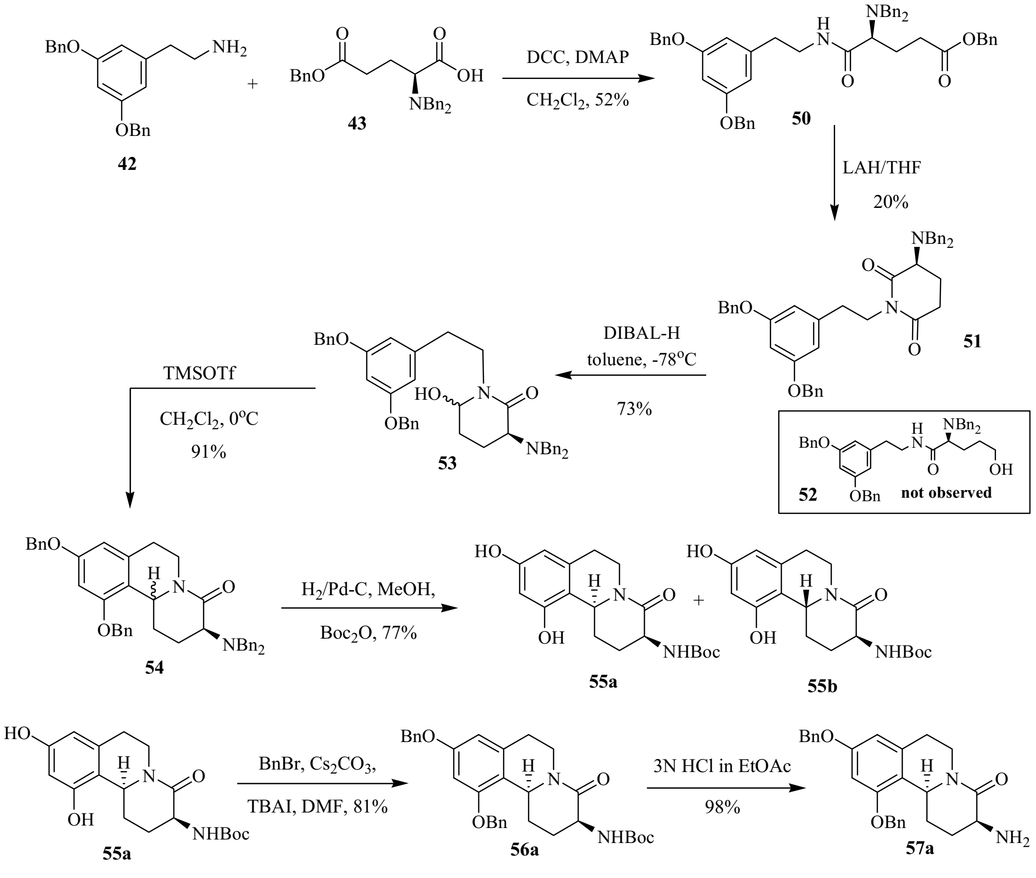
SYNTHESIS OF TRICYCLIC CORE OF SCHULZEINES

Synthesis of the tricyclic core of schulzeines began from amide bond formation between 2-(3,5-dibenzyloxyphenyl)ethylamine and L-glutamic acid derivative. 2- (3,5-dibenzyloxyphenyl) ethylamine was prepared in a straightforward fashion in 5 steps from 3,5-dihydroxybenzoic acid (scheme 6).



Scheme 6. Synthesis of 2-(3, 5-dibenzylphenyl)ethylamine

Reaction of amine **42** with glutamic acid derivative **43** in the presence of DCC gave amide-ester **50**. Initially, we planed to reduce amide-ester **50** to the primary alcohol and subsequently oxidize it to the aldehyde which would cyclize into the hydroxylactam. Treatment of this hydroxylactam with Lewis acid would give the tricyclic product. However, the reaction of **50** with lithium aluminum hydride gave imide **51** as an unexpected product. The corresponding alcohol from reduction of benzyl ester was not detected. Imide **51** was treated with DIBALH in toluene to give hydroxylactam **53**.[2] Treatment of this product with Lewis acid gave the tricyclic core as an inseparable mixture of two diastereomers at C-11b. Hydrogenolysis of the tricyclic **54** in the presence of Boc$_2$O gave the corresponding Boc carbamates which could be separated by flash chromatography. Reprotection of 9, 11-dihydroxy as benzyl ether and hydrolysis of the Boc carbamate gave amines **57a** and **57b**.



Scheme 7. Synthesis of tricyclic core of schulzeines.

Previously, We have reported a concise synthesis of the 9, 11- dimethoxytetrahydroisoquinoline tricyclic core of schulzeines featuring *N*-acyliminium ion cyclization.[3] The two diastereomers were separated by flash column chromatography as benzamide derivatives. The configuration of the *cis* diastereomer was confirmed by NOESY and X-ray crystal structure (figure 7). We found that the diastereomeric ratio depends on the nature of Lewis acid used in the reaction (scheme 8).

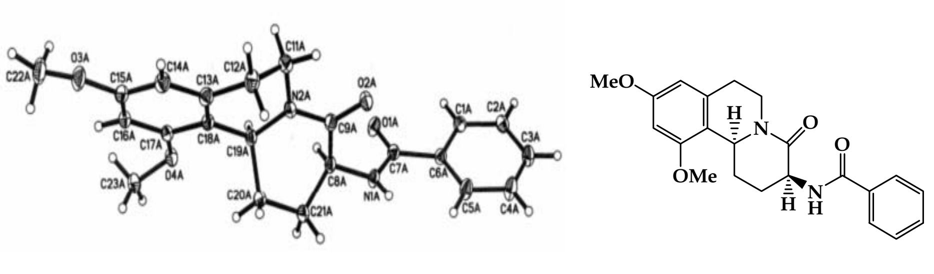
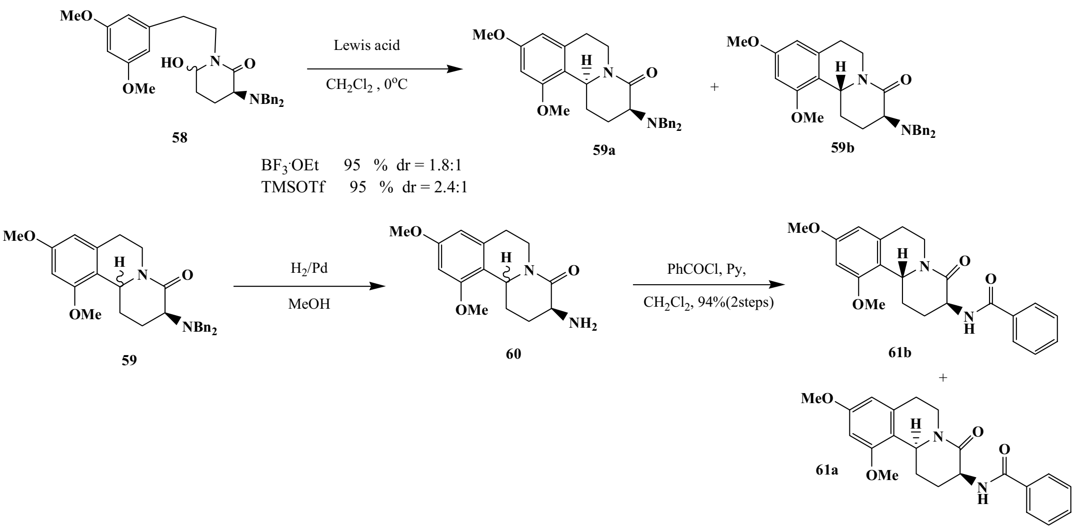


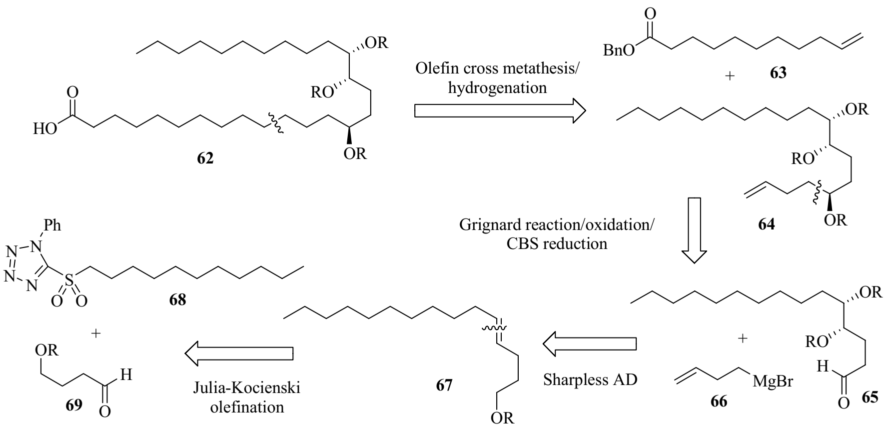
Figure 7. X-ray crystal structure of the *cis*-diastereomer of tricyclic core of schulzeine.



Scheme 8. Synthesis of 9, 11-dimethoxytetrahydroisoquinoline core of schulzeines.

SYNTHESIS OF C28 FATTY ACID SIDE CHAIN OF SCHULZEINES B AND C

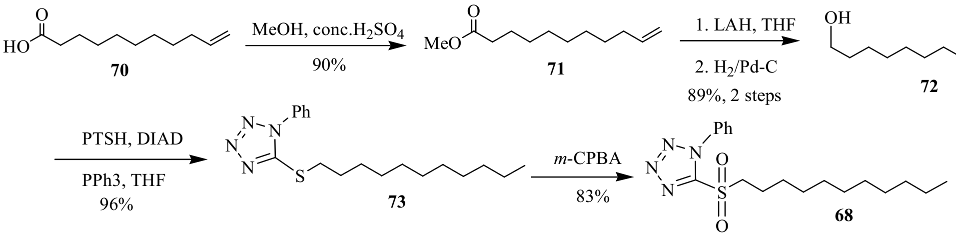
After finishing the synthesis of the tricyclic portion of the molecule, we embarked on the synthesis of the C28 fatty acid side chain of schulzeines B and C. The strategic bond formations of this portion of the molecules correspond to the stereoselective installation of the hydroxyl groups. The C1-C10 portion was installed using olefin cross metathesis of benzyl 10-undecenoate and C11-C28 terminal olefin. The C14 stereocenter would be constructed by a Grignard reaction and CBS reduction. The C17-C18 *syn* diol would be obtained using *E*-selective Julia-Kocienski reaction followed by Sharpless asymmetric dihydroxylation (scheme9).



Scheme 9. Retrosythesis of C28 fatty acid side chain of schulzeines B and C.

First generation synthesis: C28 fatty acid side chain as mixture of C14 diastereomers

The synthesis of the C28 fatty acid side chain commenced with preparations of the Julia-Kocienski coupling partners, sulfone **68** and aldehyde **74**. Sulfone **68** was prepared using standard chemistry from commercially available 10-undecenoic acid **70** (scheme10). Aldehyde **74** was obtained from 1,4-butane diol in two steps (monosilylation and Swern oxidation).

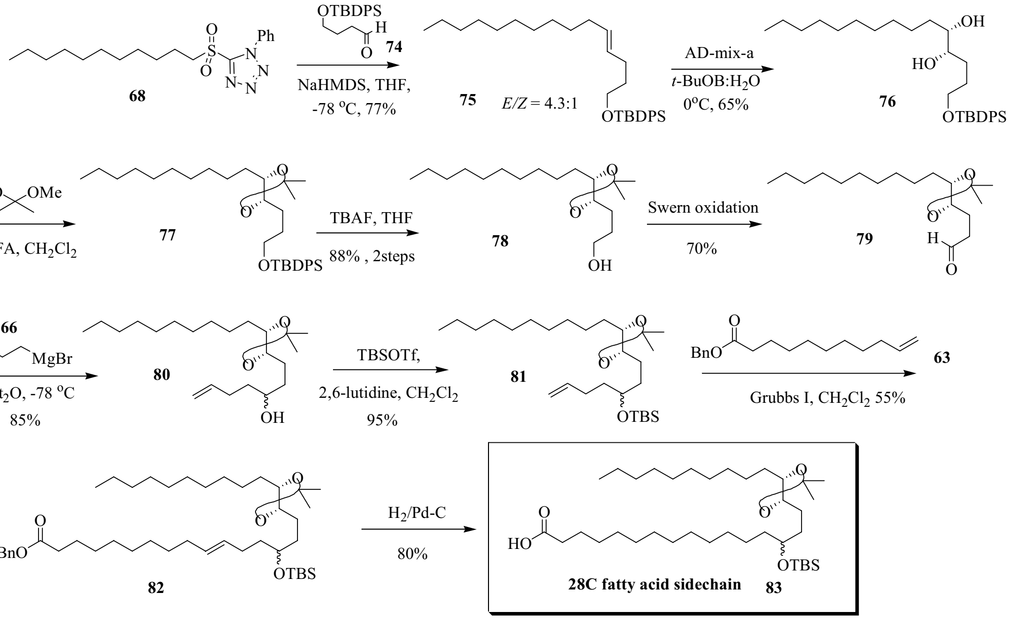


Scheme 10. Preparation of sulfone **68**.

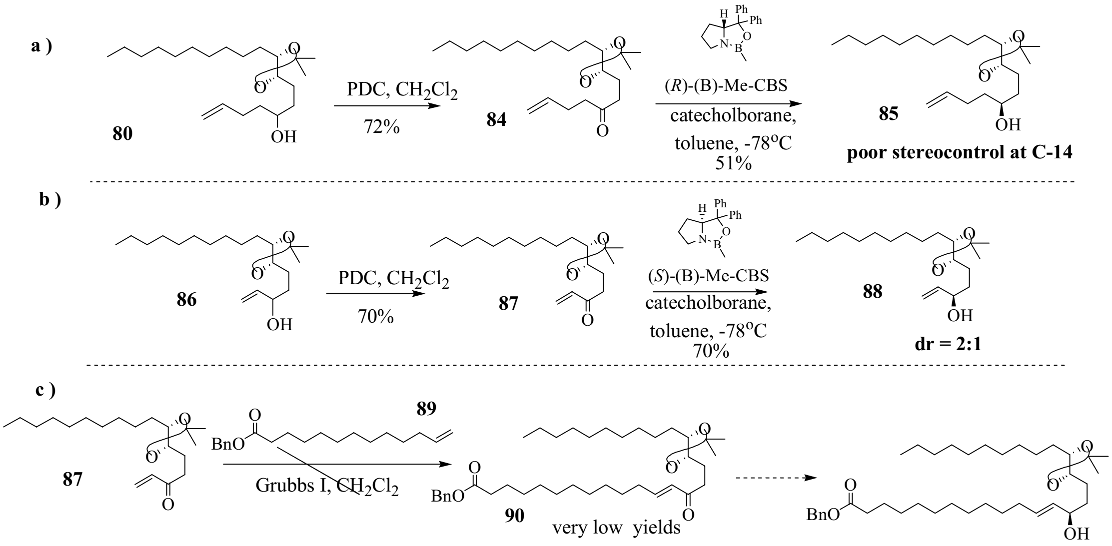
Julia-Kocienski olefination of sulfone **68** and aldehyde **74** was carried out in the presence of NaHMDS to give *E* olefin **75** predominantly (4.3:1, *E/Z*) in excellent yield.[4] The mixture of *E/Z* olefins underwent Sharpless asymmetric dihydroxylation with ADmix-α.[5] The reactive *E* olefin was converted to diol **76** whereas the unreactive *Z*-olefin was recovered intact. Diol **76** was subsequently protected as acetonide **77**. Desilylation and Swern oxidation furnished aldehyde **79** via primary alcohol **78**. The C11-C28 subunit was then obtained by addition of 3-butenyl magnesium bromide to give secondary alcohol **80** as a mixture of two diastereomers (ca. 1:1).[6] Protection of this alcohol with TBSOTf gave silyl ether **81** which was coupled with benzyl-10-undecenoate by olefin cross metathesis using Grubbs' first generation catalyst.[7] The metathesis product was hydrogenated to give C28 fatty acid side chain as inseparable diastereomers at C14 (scheme 11).

Stereoselective construction of C14 stereocenter

We planed to setup C14 stereo center with asymmetric reduction of a C14 carbonyl group using B-Me-(*S*)-CBS reagent and catecholborane. Oxidation of alcohol **80** with PDC or Swern reaction gave ketone **84**. (scheme 12a). Unfortunately, CBS reduction of this ketone had negligible stereocontrol. Literature review showed that most starting materials for the CBS reduction were α,β-unsaturated ketone[8]. Therefore we modified our synthetic route to accompany vinyl ketone **87**. This can be synthesized by addition of vinyl magnesium bromide to aldehyde **79** and subsequent oxidation to ketone **87**. However, the result was unsatisfactory because the diastereoselectivity was not sufficient (~2:1), (scheme 12b).

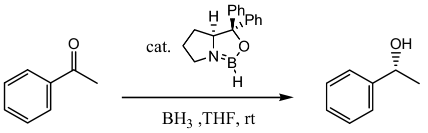


Scheme 11. Synthesis of C28 fatty acid side chain as a mixture of two diastereomers at C14.



Scheme 12. Attempts at stereoselective construction of C14 stereocenter.

We suspect that the larger C15-C28 portion and the C12-C13 vinyl substituents on the C14 carbonyl are not suitable for diastereotopic face differentiation by the CBS reagent. In general, the transition state model for CBS reduction differentiates between the R_L and R_S substituents on the carbonyl carbon. Usually R_L is alkenyl or aryl group and R_S is smaller alkyl group[9].



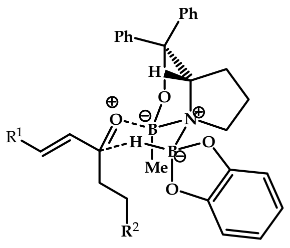
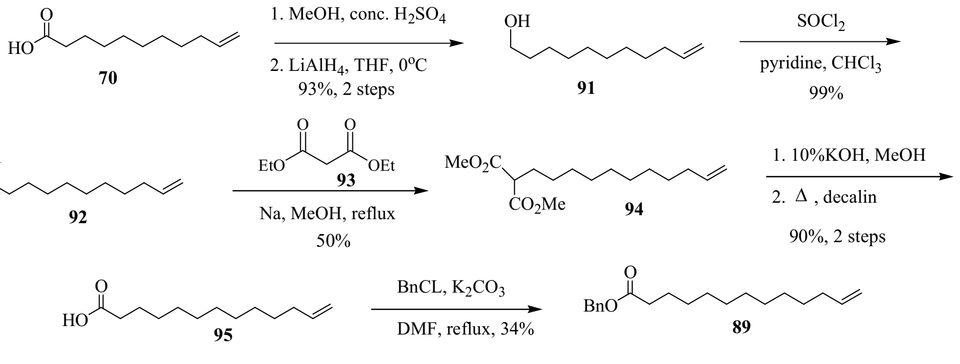


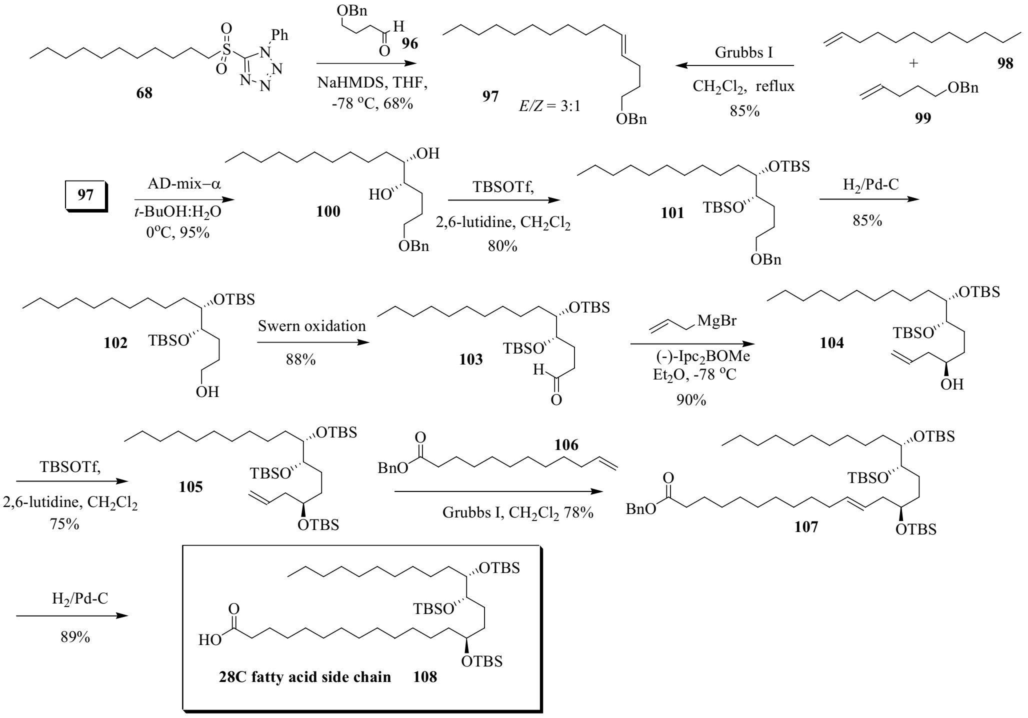
Figure 8. Transition State for CBS reduction.

For this reason, we changed the order of reaction by carrying out cross olefin metathesis between benzyl-12-tridecenoate **89** (scheme 13)[10] and vinyl ketone **87** to give α,β-unsaturated ketone **90** before performing CBS reduction. However, ketone **90** was obtained in very low yield (ca. 5%), thus this route was not further pursued (scheme 12c).

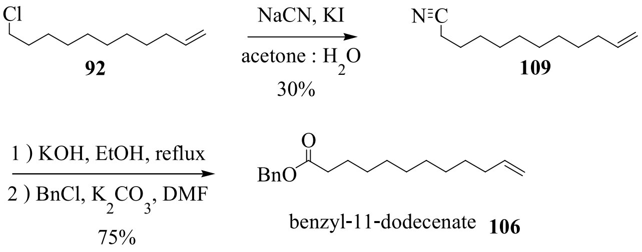


Scheme 13. Synthesis of benzyl-12-tridecenoate **89**.

Consequently, we changed the method for the installation of the C14 stereocenter to Brown's asymmetric allylboration. However, C14-aldehyde **77** did not give the desired product from asymmetric allylboration, most likely, because the acetonide protection group of C17-C18 diol did not survive the reaction condition. Therefore, we had to reconsider the protection/deprotection sequences. The C17-C18 diol would be protected as bis-TBS sillyl ether and the C14 hydroxy would initially be protected as benzyl ether. Thus, Julia-Kocienski of sulfone **68** and 4-benzyloxy-butanal **96** gave olefin **97** in a 3:1 *E/Z* ratio. In addition, alkene **97** could be synthesized by cross metathesis of bezyloxy 4-pentene **99** and 1-dodecene **98** in high yields and practically same *E/Z* ratio as *E*-selective Julia Kocienski olefination. Sharpless asymmetric dihydroxylation with ADmix-α gave diol **100** which was subsequently protected as bis-TBS silyl ether. The C14 benzyl ether underwent hydrogenolysis and the resulting primary alcohol **102** was oxidized to the corresponding aldehyde **103** by Swern oxidation. Asymmetric allylboration of this aldehyde using (-)-Ipc$_2$BOMe and allyl magnesium bromide at -78°C gave homoallylic secondary alcohol **104** as a single diastereomer.[11] The secondary alcohol was protected as tris-TBS ether **105** followed by cross metathesis with benzyl 11-dodecenoate **106** (prepared from 10-undecenoic acid in 3 steps, scheme 14) to give alkene-ester **107**. Hydrogenation of this alkene-ester gave 28 carbon fatty acid side chain of schulzeines B and C (scheme 15).



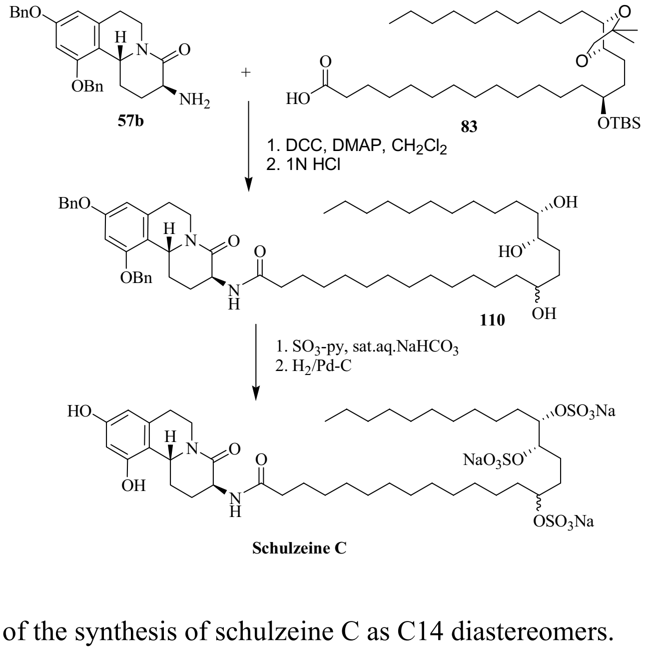
Scheme 14. Synthesis of C28 fatty acid side chain as a single diastereomer.



Scheme 15. Synthesis of benzyl-11-dodecenoate **106**.

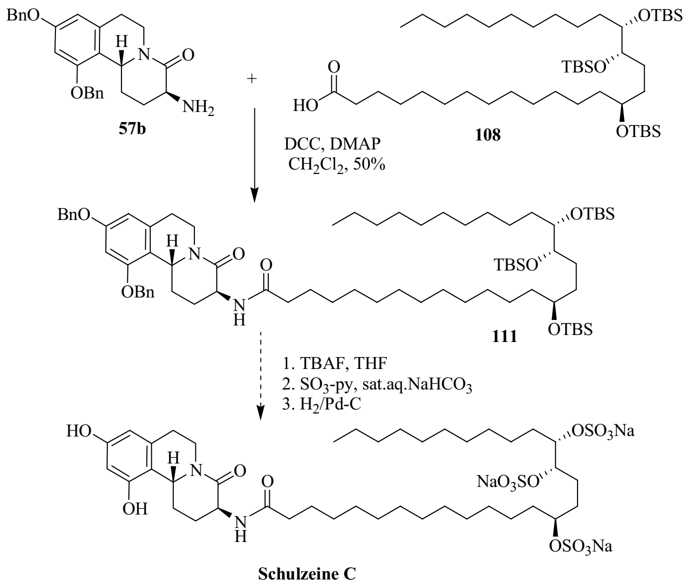
COMPLETION OF THE TOTAL SYNTHESIS

With the tricycle core and the C28 fatty acid side chain in hand, the total synthesis was completed in a few remaining straightforward steps. The key fragments were coupled via amide bond formation in the presence of DCC and DMAP. The amide product **110** representing the full carbon skeleton of schulzeines C was exhaustively deprotected with diluted HCl. The resulting triol was converted to trisulfonate salt using SO_3-Py. The total synthesis of schulzeine C was then achieved by debenzylation at C9 and C11 on the tricyclic core by hydrogenation. The synthesis of schulzeine B was realized in the same fashion starting from the C11b epimer of tricyclic core, **57a**. However, the synthetic schulzeines were obtained as mixture of diastereomers at C14.



Scheme 16. Completion of the synthesis of schulzeine C as C14 diastereomers.

Synthesis of schulzeines B and C as a single diastereomer could be achieved in the same manner, using the C28 fatty acid side chain **108** which was synthesized in a diastereoselective fashion (scheme 17). Currently the amide **111** and its C11b epimer have been synthesized separately. These compounds would be converted into schulzeines C and B, respectively, with a few remaining steps of desilylation, sulfate formation, and debenzylation.



Scheme 17. Synthesis of schulzeine C as single diastereomer.

ALPHA-GLUCOSIDASE INHIBITION ASSAY

Prodedure

The enzyme inhibition assay is based on the breakdown of substrate to produce a colored product, followed by measuring the absorbance over a period of time. In brief, alpha-glucosidase (Sigma, type V, from yeast) was dissolved in buffer A (0.1 mol/L potassium phosphate, 3.2 mmol/L-$MgCl_2$, pH6.8) (1.00 units/mL), *p*-Nitrophenyl-α-D-glucopyranoside dissolved in buffer A at 0.05 mg/mL was used as substrates. 120 μLsample solution (0.5 mg/mL in methanol), 600 μL enzyme solution and 600 μL substrate were mixed. This mixture was incubated in water-bath at 37 °C for 30 min. Enzymatic activity was quantitied by measuring the absorbance 410 nm. [12]

Results and Conclusion

The absorbance of *p*-nitrophenoxide at 410 nm decreased from 1.629 to 1.040 AU. Thus, schulzeine C as a mixture of diastereomer at C-14 still retained alpha-glucosidase inhibitor activity at 36 μM.

Table 2. Inhibition of Synthetic Schulzeine C Against Alpha- Glucosidase.

	[Sample] (μM)	Absorbance 410 nm
Control	-	1.629
Schulzeine C	36	1.040

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CHAPTER 3

GENERAL CONCLUSION

We have synthesized the natural products schulzeines B and C in 16 steps longest linear sequence (26 total steps, 0.96% overall yield). The natural products were synthesized along with their C14 epimer. The key reaction for the construction of tetrahydroisoquinoline-δ-lactam tricyclic core is *N*-acyliminium ion cyclization. The C28 fatty acid side chain was constructed in 10 steps longest linear sequence from commercially available starting materials with Julia-Kocienski reaction, Sharpless asymmetric dihydroxylation, Grignard addition, and olefin cross metathesis as key reactions. This gave the C28 fatty acid side chain as a mixture of 2 diastereomers at C14. A completely asymmetric route for the synthesis of the fatty acid was also developed by replacing Grignard addition with Brown's asymmetric allylboration. Currently we have converted the C28 fatty acid synthesized in such diastereselective fashion into the advanced intermediate of schulzeines B and C by amide formation with the tricyclic core. A few remaining steps of deprotections and sulfate formation would complete the fully asymmetric total synthesis of schulzeines B and C in a near future.

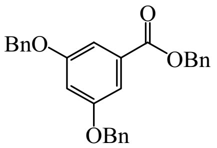
CHAPTER 4

EXPERIMENTAL PROCEDURES

General Methods.

Starting materials and reagents were obtained from commercial sources and were used without further purification. Solvents were dried by distillation from the appropriate drying reagents immediately prior to use. Tetrahydrofuran and ether were distilled from sodium and benzophenone under an argon atmosphere. Toluene, triethylamine, and dichloromethane were distilled from calcium hydride under argon. Moisture- and air-sensitive reactions were carried out under an atmosphere of argon. Reaction flasks were oven dried at 105 °C overnight. Unless otherwise stated, concentration under reduced pressure refers to a rotary evaporator at water aspirator pressure. Analytical thin-layer chromatography (TLC) was conducted using Fluka precoated TLC plates (0.2 mm layer thickness of silica gel 60 F-254). Compounds were visualized by ultraviolet light and/or by heating the plate after dipping in a 1% solution of vanillin in 0.1 M sulfuric acid in ethanol. Flash chromatography was carried out using Scharlau. silica gel (0.06-0.23 mm particle size). Optical rotations were measured with a JASCO P-1010 polarimeter. Infrared (IR) spectra were recorded on a Perkin-Elmer spectrum GX FT-IR spectrometer. Proton and carbon nuclear magnetic resonance (NMR) spectra were obtained using either a Bruker ADVANCE 300 MHz spectrometer.

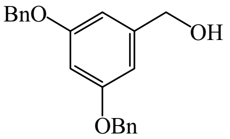
SYNTHESIS OF THE TRICYCLIC CORE



46

3,5-Bis-benzyloxybenzoic acid benzyl ester 46: To a solution of 3, 5-dihydroxybenzoic acid (1.00 g, 6.49 mmol) in DMF (30 mL) was added K_2CO_3 (3.59 g, 25.95 mmol) followed by addition of benzyl chloride (3.0 mL, 25.95 mmol). The solution was refluxed for 5 h, then K_2CO_3 was filtered. The filtrate was dissolved in water and benzyl benzoate precipitated when the solution was cooled in an ice-bath to give benzyl ester **46** (2.75 g, 99%) as a yellow solid: mp 63-65 °C.

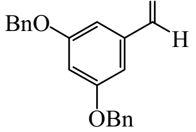
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.25 (m, 17H), 6.80 (t, 1H, *J* = 2.3 Hz), 5.31 (s, 2H), 5.0 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 159.8, 136.5, 132.1, 128.6 (2C), 128.3, 128.1, 127.6, 108.6, 107.2, 70.3, 66. 9; IR (film) 3418, 3054, 3035, 2950, 2877, 1716, 1595, 1445, 1376, 1345, 1266, 1226, 1160, 1106, 1055.



47

(3,5-Bis-benzyloxy-phenyl)methanol 47: To a solution of the benzyl ester **46** (10.00 g, 23.58 mmol) in dry THF (230 mL) at 0 °C was added lithium aluminum hydride (2.68 g, 70.74 mmol). This solution was stirred at 0 °C under argon atmosphere for 30 min. The reaction was quenched with sat. aq. $NaHCO_3$ at 0 °C and extracted with Et_2O (3x100 mL) The combined organic phase was dried with anh.Na_2SO_4, filtered and concentrated under reduced pressure and the crude product was recrystalized with hexane to give alcohol **47** (5.36 g, 71%) as a white solid: mp.78-79 °C.

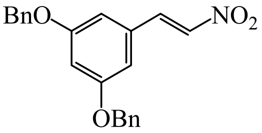
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.28 (m, 10H), 6.63 (d, 2H, *J*= 2.2 Hz), 6.55 (t, 1H, *J* = 2.2 Hz), 5.05 (s, 4H), 4.62 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2, 143.5, 136.9, 128.6, 128.0, 127.6, 105.8, 101.3, 70.1, 65.3; IR (film) 3413, 3065, 2933, 2875, 1595, 1497, 1455, 1376, 1216, 1159, 1052, 1028 cm^{-1}.



48

3,5-Bis-benzyloxybenzaldehyde 48: To a solution of alcohol **47** (8.29 g, 25.90 mmol) in $CHCl_3$ (300 mL) was added MnO_2 (13.60 g, 155.40 mmol). The reaction flask was equipped with a drying tube and the mixture was stirred overnight at room temperature. The mixture was then filtered through silica gel and eluted with $CHCl_3$. The filtrate was concentrated under reduced pressure to give aldehyde **48** (6.48 g, 79%) as a white solid : mp.80-81 °C.

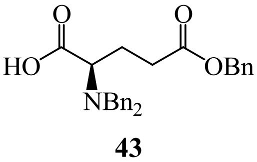
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46-7.30 (m, 10H), 7.11 (d, 2H, *J*= 2.3 Hz), 6.87 (t, 1H, *J*= 2.3 Hz), 5.10 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$,) δ 191.8, 161.3, 138.9, 136.8, 128.7, 128.2, 127.6, 108.7, 108.3, 70.4; IR (film) 3383, 1698, 1594, 1451, 1379, 1161, 1056 cm^{-1}.



49

1,3-Bis-benzyloxy-5-(2-nitro-vinyl)benzene 49 : A mixture of aldehyde **48** (13.61 g, 42.80 mmol), CH_3NH_2-HCl (0.79 g, 12.95 mmol), and anh. NaOAc (0.82 g, 1.00 mmol) in nitromethane (45 mL) was stirred overnight at room temperature under argon atmosphere. The reaction was quenched with water and extracted with CH_2Cl_2 (3x80 mL). The combined organic phase was dried with anh. Na_2SO_4, filtered, and concentrated under reduced pressure to give the nitrostyrene **49** (14.1 g, 91%) as yellow solid : mp 107-160 °C.

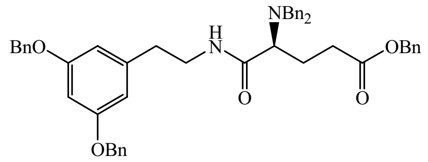
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89(d, 1H, *J*= 13.6 Hz), 7.49(d, 1H, *J*= 13.6 Hz), 7.44-7.28 (m, 10H), 6.75 (s, 3H), 5.05 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$,) δ 160.4, 139.1, 137.6, 136.2, 131.8, 128.8, 128.3, 127.5, 108.2, 104.5, 70.4; IR (film) 3411, 1441, 1339, 1265, 1164 cm^{-1}.



43

2-Dibenzylamino-pentanedioic acid 5-benzyl ester 43: To a mixture of L-glutamic acid (5.00 g, 33.98 mmol), K_2CO_3 (11.00 g, 79.60 mmol) and NaOH (3.00 g, 79.60 mmol) in 100 mL of MeOH : water (1:1) was added benzyl chloride (16.0 mL, 118.90 mmol). The reaction mixture was heated to reflux overnight and quenched with 1M HCl (50 mL). Water was added and the mixture was extracted with CH_2Cl_2 (3x100 mL). The combined organic phase was dried with anh. Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by flash column chromatography (silica gel, 2:1 hexane: ethyl acetate) to give *N*, *N*-dibenzyl-L-glutamic acid-5-benzyl ester (2.53 g, 18%) as oil, along with the corresponding dibenzyl ester.

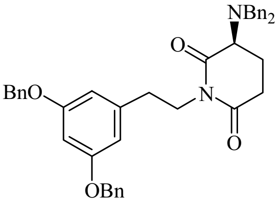
^{1}H NMR (300 MHz, CDCl$_3$) δ 7.45-7.12 (m, 15H), 5.32 (d, 1H, *J*= 12.2 Hz), 5.08 (d, 1H, *J*= 12.2 Hz), 3.90 (d, 2H, *J*= 13.6 Hz) 3.48 (d, 2H, *J*= 13.6 Hz), 3.38 (t, 1H, *J*= 6.9 Hz), 2.37 (m, 2H), 2.09 (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 178.9, 172.1, 138.9, 128.9, 128.7, 128.6 (2C), 128.4, 128.3, 127.1, 66.3, 59.8, 54.4, 30.7, 23.9; $[\alpha]_D^{25}$ -74.7 (*c*, 1.5, CHCl$_3$); IR (film) 3066, 2959, 1951, 1714, 1603, 1496, 1456, 1420, 1373, 1217, 1162 cm^{-1}.



50

4-[2-(3,5-Bis-benzyloxy-phenyl)-ethylcarbamoyl]-4-dibenzylamino-butyric acid benzyl ester 50: To a suspension of lithium aluminium hydride (0.82 g, 21.61 mmol) in dry THF (75 ml.) at 0°C was added 3, 5-dibenzyloxynitrostyrene **49** (1.95 g, 5.40 mmol). This solution was stirred at 0°C under argon atmosphere for 30 min. The reaction was quenched with sat. aq. NaHCO$_3$ and extracted with Et$_2$O (3x70 mL). The combined organic phase was dried with anh. Na$_2$SO$_{4,}$ filtered, and concentrated under reduced pressure to give 2-(3, 5-dibenzyl-phenyl)ethylamine **42** as an orange-brown oil. This amine was used immediately in the next step without further purification. A mixture of 2-(3, 5-dibenzyloxyphenyl)ethylamine (1.81 g, 5.43 mmol), *N*,*N*-dibenzyl-L-glutamic acid-5-benzyl ester (0.94 g, 2.25 mmol), DCC (1.49 g, 7.20 mmol), and DMAP (55 mg, 0.45 mmol) in CH$_2$Cl$_2$ (60 mL) was stirred at room temperature under argon atmosphere for 48 h after which the mixture was filtered. The filtrate was concentrated under reduced pressure and the crude material was purified by flash column chromatography (silica gel, 2:1 hexanes: ethyl acetate) to give amide-ester **50** (0.86 g, 52 %) as a yellow-brown oil.

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.50-7.10 (m, 25H), 6.50 (t, 1H, *J*= 2.2 Hz), 6.40 (d, 2H, *J*= 2.2 Hz), 5.18 (AB system, 2H, *J* =12.2 Hz), 5.08 (t, 1H, *J*= 5.6 Hz), 5.0(s, 4H), 4.25 (d, 1H, *J*= 7.8 Hz), 3.85 (d, 2H, *J* =13.7 Hz), 3.50 (d, 2H, *J*= 13.7 Hz), 3.44-3.10 (m, 3H), 2.60 (t, 2H, *J* = 7.0 Hz), 2.25-1.70 (m, 4H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 172.4, 172.3, 160.1, 157.1, 141.4, 139.4, 136.9, 136.0, 129.0, 128.7, 128.6 (2C), 128.4, 128.0, 127.6, 127.2, 108.0, 100.1, 70.1, 66.2, 60.3, 54.6, 49.1, 40.4, 36.7, 35.9, 34.0, 33.1, 25.7, 25.4, 25.0, 24.8, 24.0, 23.5; $[\alpha]_D^{25}$ -39.2 (*c*, 2.4, $CHCl_3$); IR (film) 3425, 3033, 2934, 2857, 1727, 1664, 1594, 1519, 1496, 1455, 1265, 1214, 1158, 1070 cm^{-1}.

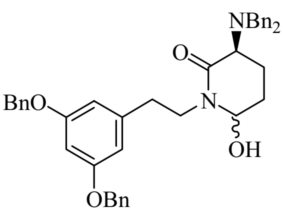


51

1-[2-(3,5-Bis-benzyloxy-phenyl)-ethyl]-3-dibenzylamino-piperidine-2,6-dione 51 :

To a solution of the amide-ester **50** (216 mg, 0.30 mmol) in THF (6 mL) was added lithium aluminium hydride (34 mg, 0.89 mmol) in one portion at 0°C. The resulting suspension was stirred at 0°C under argon atmosphere for 45 min. The reaction was quenched by dropwise addition of sat. aq. $NaHCO_3$ into the mixture until all bubbling subsided. Water (5 mL) was added and the mixture was then extracted with Et_2O (3x20 mL). The combined organic layers were dried with anh. Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by flash column chromatography (silica gel, 4:1 hexanes: ethyl acetate) to give the imide **51** (36 mg, 20%) as a colorless oil, and the unreacted amide was also recovered.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.15 (m, 20H), 6.43 (d, 2H, *J*= 2.2 Hz), 6.36 (t, 1H, *J*= 2.2 Hz), 4.88 (s, 4H), 3.87 (m, 1H), 3.82 (d, 2H, *J* = 13.9 Hz), 3.55 (d, 2H, *J* = 13.9 Hz), 3.35 (m, 1H), 2.70 (t, 2H, *J* = 7.3 Hz), 1.90 (m, 2H), 2.32 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 171.7, 159.9, 140.7, 139.6, 136.9, 128.6 (2C), 128.4, 127.9, 127.6, 127.2, 108.3, 100.2, 70.0, 59.3, 55.0, 40.5, 34.3, 32.3, 22.7; $[\alpha]_D^{25}$ -39.3 (*c*, 1.0, $CHCl_3$); IR (film) 2879, 1725, 1674, 1595, 1495, 1455, 1376, 1344, 1264, 1151, 1051, 1027 cm^{-1}.

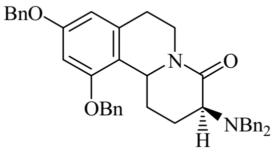


53

1-[2-(3,5-Bis-benzyloxy-phenyl)-ethyl]-3-dibenzylamino-6-hydroxy-piperidin-2-one 53:

To a solution of the imide **51** (93 mg, 0.15 mmol) in toluene (2 mL) was added diisobutyl aluminium hydride (1.0M solution in THF, 0.75 mL, 0.75 mmol) via syringe at -78°C under argon. The mixture was stirred for 1 h at -78°C then MeOH (5 mL) was added. The reaction mixture was allowed to warm to room temperature and sat. aq. $NaHCO_3$ was added. The mixture was extracted with CH_2Cl_2 (3x20 mL) and the combined organic layers were dried with anh. Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, 2:1 hexanes: ethyl acetate) to give the hydroxylactam **53** (68 mg, 73% mixture of 2 diastereomers) as a colorless oil.

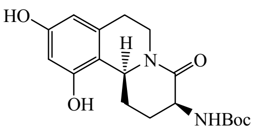
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.10 (m, 20H), 6.43 (t, 2H, *J*= 2.0 Hz), 6.37 (t, 2H, *J*= 2.0 Hz), 4.85 (s, 4H), 4.54 (t, 1H, *J*= 7.3 Hz), 3.91 (d, 2H, *J* = 14 Hz), 3.79 (m, 1H), 3.55 (d, 2H, *J* = 14 Hz), 3.22 (q, 1H, *J* = 5.8 Hz), 2.80 (m, 2H), 2.09 (m, 1H), 1.80 (m,1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.8, 159.9, 141.7, 140.4, 136.9, 128.7, 128.6 (2C), 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.5, 126.8, 108.1, 100.2, 80.4, 70.0, 69.9, 58.2, 55.2, 43.8, 34.4, 31.4, 23.2, 14.2; IR (film) 3429, 2832, 1644, 1606, 1552, 1495, 1375, 1265, 1055, 1027 cm^{-1}.



54

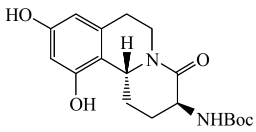
9,11-Bis-benzyloxy-3-dibenzylamino-1,2,3,6,7,11b-hexahydro-pyrido[2,1-a]isoquinolin-4-one 54: To a solution of the hydroxylactam **53** (68 mg, 0.11mmol) in CH_2Cl_2 (9 mL) was added TMSOTf (39 μL, 0.22 mmol) via syringe at 0 °C under argon atmosphere. The mixture was stirred at this temperature for 4 h and sat. aq. $NaHCO_3$ was added dropwise. The mixture was extracted with CH_2Cl_2 (3x10 mL). The combined organic layers were dried with anh. Na_2SO_4, filtered and concentrated under reduced pressure to give the tricyclic core **54** (inseparable mixture of two diastereomers) (60 mg, 91%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.20 (m, 20H), 6.47 (d, 2H, *J*= 2.0 Hz), 6.38 (d, 1H, *J* = 2.1 Hz), 6.34 (d, 1H, *J* = 2.1 Hz), 5.05-4.95 (m, 4H), 4.85 (dd, 1H, *J*= 10.3, 3.9 Hz), 4.70 (dd, 1H, *J* = 10.6, 2.1 Hz), 4.57 (dd, 1H, *J* = 10.9, 3.2 Hz), 4.26 (d, 2H, *J* = 14.6 Hz), 4.08 (d, 2H, *J* = 13.9 Hz), 3.89 (d, 2H, *J* = 14.6 Hz), 3.84 (d, 2H, *J* = 13.9 Hz), 3.55 (dd, 1H, *J* = 9.9, 9.1 Hz), 3.42 (dd, 1H, *J* = 11.1, 7.3 Hz), 2.80 (m, 2H), 2.78 (m, 1H), 2.72 (m, 2H), 2.59 (m, 1H), 2.35 (m, 1H), 2.17 (m, 1H), 2.00 (m, 2H), 1.90 (m, 1H), 1.40 (m, 1H), 1.25 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 169.1, 157.3, 157.1, 155.5, 154.9, 140.0, 139.5, 137.1, 136.7, 135.7, 135.7, 135.6, 127.7, 127.6, 127.4, 127.0, 127.0, 126.9, 126.5, 125.9, 125.7, 125.7, 125.6, 117.5, 116.8, 105.0, 104.8, 98.0, 97.9, 69.1, 69.1, 69.0, 68.8, 57.7, 57.4, 55.6, 54.4, 54.2, 24.1, 48.9, 37.5, 37.1, 29.5, 29.0, 28.4, 26.0, 22.6, 20.0, 13.2; IR (film) 2874, 2833, 2254, 1703, 1641, 1609, 1542, 1493 cm^{-1}.



55a

+



55b

(9,11-Dihydroxy-4-oxo-1,3,4,6,7,11b-hexahydro-2H-pyrido[2,1-a]isoquinolin-3-yl)-carbamic acid tert-butyl ester 55a, 55b : To a solution of the tricyclic core **54** (292 mg, 0.48 mmol) in methanol (9 mL) was added palladium on activated carbon (10%w/w, 29 mg) and the resulting suspension was stirred under hydrogen atmosphere for 3 h (a balloon of hydrogen gas was equipped to the reaction flask, ca. 1.1 atm). Then Boc_2O (210 mg, 0.96 mmol) was added to the reaction mixture and stirred for 5 h. The mixture was then filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica gel, 2:1 ethyl acetate: hexane) to give two separated diastereomers of the tricyclic core **55a** and **55b** (130 mg, 77% combined yield in c.a. 3:1 ratio in favor of **55a**) as clear oil.

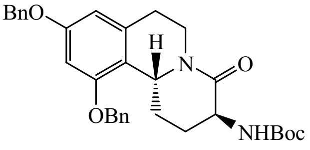
55b

^{1}H NMR (300 MHz, CD_3OD) δ 6.08 (d, 1H, *J* = 2.3 Hz), 5.99 (d, 1H, *J* = 2.3 Hz), 4.69 (dd, 1H, *J*= 3.2, 10.8 Hz), 4.63 (dd, 1H, *J* = 2.5, 11.0 Hz), 3.87 (m, 1H), 2.97 (m, 1H), 2.50 (m, 3H), 1.99 (m, 1H), 1.85 (m, 1H), 1.40 (s, 9H), 1.22 (m, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ 169.6, 156.2, 155.3, 137.3, 137.2, 114.6, 106.2, 100.7, 79.0, 55.8, 51.8, 39.4, 29.7, 29.6, 28.1, 27.4, 27.3; $[\alpha]_D^{25}$ +30.2 (*c*, 0.8, MeOH); IR (film) 3274, 2924, 2854, 1683, 1646, 1511, 1464, 1376, 1277, 1251, 1159, 1055, 947, 842 cm^{-1}.

55a

^{1}H NMR (300 MHz, CD_3OD) δ 6.11 (d, 1H, *J* = 2.3 Hz), 6.02 (d, 1H, *J* = 2.3 Hz), 4.71 (d, 1H, *J* = 3.6 Hz), 4.48 (d, 1H, *J*= 7.1 Hz), 4.23 (t, 1H, *J* = 8.9 Hz), 2.57 (m, 3H), 2.40 (m, 1H), 2.19

(m, 1H), 1.38 (s, 9H), 1.25 (m, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ 171.0, 156.7, 156.5, 154.7, 137.0, 113.7, 105.9, 100.6, 79.3, 49.7, 49.4, 39.0, 28.9, 27.8, 27.4, 24.9; $[\alpha]_D^{25}$ -76.0 (*c*, 0.9, MeOH); IR (film) 3274, 2924, 2854, 1683, 1646, 1511, 1464, 1376, 1277, 1251, 1159, 1055, 947, 842 cm^{-1}.



56b

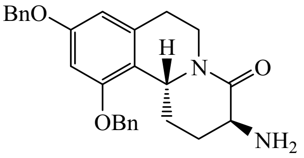
(9,11-Bis-benzyloxy-4-oxo-1,3,4,6,7,11b-hexahydro-2H-pyrido[2,1-a]isoquinolin-3-yl)-carbamic acid tert-butyl ester 56b: To a solution of the 9, 11-dihydroxytetrahydroisoquinoline -lactam **55b** (23 mg, 0.07 mmol), Cs_2CO_3 (65 mg, 0.20 mmol), and TBAI (4 mg) in DMF (1 mL) at 0 °C was added benzyl bromide (17 μL, 0.15 mmol). This solution was stirred at 0 °C under argon atmosphere for 1 h. Water was added and the mixture was extracted with ethyl acetate (3x10 mL). The combined organic phase were dried with anh. Na_2SO_4, filtered and concentrated under reduced pressure. The crude material was purified by flash column chromatography (silica gel, 2:1 hexane: ethyl acetate) to give the dibenzyl ether **56b** (20 mg, 69%) as a clear oil.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.42–7.34 (m, 10H), 6.47 (d, 1H, *J* = 2.3 Hz), 6.35 (d, 1H, *J* = 2.3 Hz), 5.33 (d, 1H, *J* = 5.0 Hz), 5.04–5.00 (m, 4H), 4.96 (m, 1H), 4.78 (dd, 1H, *J* = 11.0, 3.7 Hz), 3.99 (m, 1H), 3.10 (m, 1H), 2.81 (m, 1H), 2.63 (m, 1H), 2.45 (m, 1H), 1.77 (m, 2H), 1.50 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 156.7, 156.1, 137.8, 136.6, 136.4, 128.6, 128.5, 128.0, 127.4, 127.1, 118.3, 106.0, 99.0, 79.4, 70.1, 70.0, 56.1, 52.7, 39.4, 30.5, 29.6, 28.3, 27.9; $[\alpha]_D^{25}$ +96.9 (*c*, 2.8, $CHCl_3$); IR (film) 3413, 2983, 2931, 1710, 1655, 1609, 1497, 1432, 1367, 1162, 1060 cm^1.

56a

(9,11-Bis-benzyloxy-4-oxo-1,3,4,6,7,11b-hexahydro-2H-pyrido[2,1-a]isoquinolin-3-yl)-carbamic acid tert-butyl ester 56a: To a solution of the the 9,11-dihydroxytetrahydroisoquinoline-lactam **55a** (73 mg, 0.21 mmol), Cs_2CO_3 (205 mg, 0.63 mmol), and TBAI (12 mg) in DMF (3 mL) at 0 °C was added benzyl bromide (55 μL, 0.46 mmol). This solution was stirred at 0°C under argon atmosphere for 1 h. Water was added and the mixture was extracted with ethyl acetate (3x10 mL). The combined organic phase were dried with anh. Na_2SO_4, filtered and concentrated under reduced pressure. The crude material was purified by flash column chromatography (silica gel, 2:1 hexane: ethyl acetate) to give the dibenzyl ether **56a** (74 mg, 81%) as a clear oil.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.35 (m, 10 H), 6.45 (d, 1H, *J* = 2.2 Hz), 6.36 (d, 1H, *J* = 2.2 Hz), 5.75 (d, 1H, *J* = 5.3 Hz), 5.05 (s, 2H), 4.97 (s, 2H), 4.89 (dd, 1H, *J* = 10.3, 4.0 Hz), 4.76 (m, 1H), 4.32 (m, 1H), 2.78 (m, 3H), 2.53 (m, 2H), 1.50 (s, 9 H), 1.42 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 158.2, 155.7, 155.4, 137.0, 136.5, 136.2, 128.5, 128.3, 127.9, 127.8, 127.2, 126.8, 117.1, 105.7, 98.8, 79.0, 69.9, 69.8, 49.5, 48.5, 38.6, 29.5, 29.4, 28.3, 28.2; $[\alpha]_D^{25}$ -83.4 (*c*, 1.4, $CHCl_3$); IR (film) 3413, 2983, 2931, 1710, 1655, 1609, 1497, 1432, 1367, 1162, 1060 cm^{-1}.

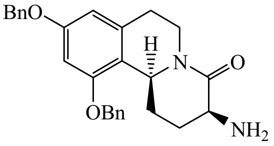


57b

3-Amino-9,11-bis-benzyloxy-1,2,3,6,7,11b-hexahydro-pyrido[2,1-a]isoquinolin-4-one 57b: A solution of the NHBoc- tricyclic core **56b** (62 mg, 0.12 mmol) was treated with 3N HCl in ethyl acetate (1.1mL) at room temperature. The solution was stirred for 3 h. Ethyl acetate was added and the solution was neutralized with sat. aq. $NaHCO_3$ and the aqueous layer was extracted with ethyl acetate (3x10 mL). The combined organic layers were dried with anh. Na_2SO_4, filtered, and concentrated under reduced pressure to give amine **57b** (44 mg, 88%) as oil.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.10 (m, 10 H), 6.50 (d, 1H, *J* = 2.2 Hz), 6.37 (d, 1H, *J* = 2.1 Hz), 5.05 (d, 2H, *J* = 3.9 Hz), 5.00 (s, 2H), 4.92 (dd, 1H, *J* = 2.5, 11.3 Hz), 4.80 (dd, 1H, *J* = 1.7, 8.3

Hz), 3.01 (m, 1H), 2.85 (m, 1H), 2.63 (m, 1H), 2.40(m, 1H), 2.22 (m, 1H), 2.22 (m, 1H), 1.65 (m, 1H), 1.42 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1, 158.2, 156.7, 138.0, 136.8, 136.6, 128.7, 128.4, 128.1, 128.1, 127.5, 127.0, 118.5, 106.2, 99.1, 70.1, 56.1, 52.5, 39.2, 33.9, 30.6, 29.7, 29.3, 28.5, 25.6, 24.9.



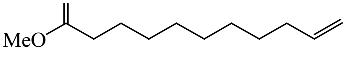
57a

3-Amino-9,11-bis-benzyloxy-1,2,3,6,7,11b-hexahydro-pyrido[2,1-a]isoquinolin-4-one 57a: A solution of the NHBoc- tricyclic core **56a** (74 mg, 0.14 mmol) was treated with 3N HCl in ethyl acetate (1.4 mL) at room temperature. The solution was stirred for 3 h. Ethyl acetate was added and the solution was neutralized with sat. aq. $NaHCO_3$ and the aqueous layer was extracted with ethyl acetate (3x10 mL). The combined organic layers were dried with anh. Na_2SO_4, filtered, and concentrated under reduced pressure to give amine **57a** (59 mg, 98%) as oil.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.35 (m, 10 H), 6.49 (d, 1H, *J* = 2.2 Hz), 6.38 (d, 1H, *J* = 2.1 Hz), 5.07 (d, 2H, *J* = 2.9 Hz), 5.00 (s, 2H), 4.85 (dd, 1H, *J* = 3.6, 11.3 Hz), 4.72 (dd, 1H, *J* = 1.8, 8.2 Hz), 3.82 (m, 1H), 2.74 (m, 3H), 2.49 (m, 2H), 1.70 (m, 1H), 1.46 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 158.5, 156.0, 137.4, 136.7, 136.5, 128.8, 128.6, 128.1, 127.5, 127.0, 117.0, 107.1, 105.7, 99.1, 70.1, 49.8, 49.2, 39.0, 29.7, 28.2, 25.1, 22.1.

SYNTHESIS OF THE C28 FATTY ACID SIDE CHAIN

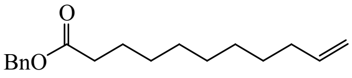
Synthesis of benzyl-11-dodecenoate (C1-C11 subunit)



71

10-Undecenoic acid methyl ester 71: To a solution of 10-undecenoic acid (20.2 mL, 100 mmol) in methanol (192 mL) was added dropwise conc. H_2SO_4 (1 mL) and the mixture was stirred under argon atmosphere for 4 h. The reaction mixture was quenched with sat. aq. $NaHCO_3$ and extracted with CH_2Cl_2 (3x100 mL). The combined organic phase was dried with anh. Na_2SO_4, filtered, and concentrated under reduced pressure to give methyl ester **71** (20.00 g, 93%) as a clear oil.

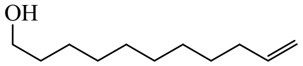
^{1}H NMR (300MHz, $CDCl_3$) δ 5.76 (m, 1H), 4.95 (m, 1H), 4.88 (m, 1H), 3.65 (s, 3H), 2.26 (t, 2H, *J*= 7.5 Hz), 2.00 (q, 2H, *J*= 6.8 Hz), 1.59 (m, 2H), 1.40-1.20 (br. s, 10H): ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9, 138.9, 114.0, 51.2, 34.1, 33.9, 33.7, 30.1, 29.2, 29.1, 29.0 (2C), 25.0, 24.8, 24.6; IR (film) 3077, 2927, 1741, 1639, 1436, 1362, 995, 910 cm^{-1}.



63

10-Undecenoic acid benzyl ester 63: To a solution of 10-undecenoic acid (1.0 mL, 4.95 mmol) in DMF (20 mL) was added K_2CO_3 (1.03 g, 7.43 mmol), followed by benzyl chloride (1.2 ml, 9.90 mmol). The solution was heated to reflux for 40 minutes, then K_2CO_3 was filtered and the filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, 10:1 hexane: ethyl acetate) to give benzyl ester **63** (1.30 g, 90%) as a clear oil.

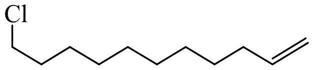
^{1}H NMR (300MHz, $CDCl_3$) δ 7.33 (m, 5H), 5.79 (m, 1H), 5.09 (s, 2H), 4.98 (m, 1H), 4.92 (m, 1H), 2.33 (t, 2H, *J*= 7.5 Hz), 2.22 (q, 2H, *J*= 7.1 Hz), 1.63 (m, 2H), 1.40-1.24 (br. s, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 139.1, 136.2, 128.5, 128.2, 114.2, 66.1, 34.3, 33.8, 29.3, 29.2, 29.1, 29.0, 28.9, 24.9; IR (film) 3455, 3068, 3034, 2927, 2856, 1736, 1498, 1456, 1381, 1352, 1164 cm^{-1}.



91

10-Undecene-1-ol 91: To a solution of methyl ester **71** (6.05 g, 30.56 mmol) in THF (200 mL) at 0°C was slowly added lithium aluminum hydride (3.48 g , 91.67 mmol). The mixture was stirred at 0°C under argon atmosphere for 30 min. The reaction was quenched with sat. $NaHCO_3$ and extracted with Et_2O (3x100 mL). The combined organic phase was dried with anh. Na_2SO_4, filtered, and concentrated under reduced pressure to give 10-undecenol **91** (4.85 g, 93.4%) as a colorless oil.

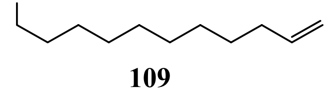
^{1}H NMR (300MHz, $CDCl_3$) δ 5.82 (m, 1H), 4.99 (m,1H), 4.93 (m, 1H), 3.64 (t, 2H, *J*= 6.6 Hz), 2.04 (q, 2H, *J*= 7.0 Hz), 1.62-1.51 (br. s, H), 1.42-1.23 (br. s, H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2, 114.1, 62.8, 33.8, 32.7, 29.5, 29.4, 29.1, 28.9, 25.7; IR (film) 3368, 3077, 1639, 1465, 1438, 1265, 1055 cm^{-1}.



92

10-Undecenyl chloride 92: To a solution of 10-undecenol **91** (5.00 g, 29.30 mmol) and pyridine (2.5 mL) in $CHCl_3$ (36 mL) at 0°C was added dropwise thionyl chloride (2.6 mL, 35.16 mmol). The mixture was stirred overnight at room temperature under argon atmosphere. The reaction was quenched with cold solution of 5N HCl (100 mL) and washed with 5N HCl (3x300 mL), water (2x200 mL), 10% Na_2CO_3 (3x300 mL), water (2x200 mL) and brine. The combined organic phase was dried over anh. Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, hexane) to give 10-undecenyl chloride **92** (5.51g, 99.5%) as a colorless oil.

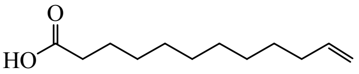
^{1}H NMR (300MHz, $CDCl_3$) δ 5.80 (m, 1H), 4.91 (m, 1H), 4.85 (m, 1H), 3.52 (t, 2H, *J*= 6.7 Hz), 2.04 (q, 2H, *J*= 7.1 Hz), 1.76 (m, 2H), 1.45-1.25(br.s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1 (2C), 139.1, 45.1, 33.8, 32.7, 29.4 (2C), 29.1, 28.9 (2C), 26.9; IR (film) 3456, 3077, 2927, 2856, 1823, 1640, 1464, 1310, 993, 910, 724, 654 cm^{-1}.



109

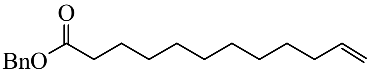
11-Dodecenenitrile 109: A mixture of 10-undecenyl chloride **92** (10.55 g, 55.9 mmol), NaCN (27.40 g, 599 mmol), and KI (4.64 g, 2.79 mmol) in acetone: water (150 mL, 3: 1) was heated to reflux for 24 h. Acetone was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (3x200 mL). The combined organic phase was dried over anh. Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, hexane and 10: 1 hexane: ethyl acetate) to give nitrile **109** (2.97 g, 30%) as a clear oil.

^{1}H NMR (300MHz, $CDCl_3$) δ 5.80 (m, 1H), 4.97 (m, 1H), 4.91 (m, 1H), 2.32 (t, 2H, *J*= 7.0 Hz), 2.04 (q, 2H, *J*= 6.7 Hz), 1.63 (m, 2H), 1.49-1.27 (br.s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9, 119.6, 114.1, 33.7, 29.3, 29.2, 29.0, 28.8, 28.7, 28.5, 25.3, 16.9; IR (film) 1639, 1426, 1328, 914, 770, 667 cm^{-1}



11-Dodecenoic acid: A mixture of nitrile **109** (2.97 g, 16.60 mmol), 10% KOH (70 mL) in ethanol (140 mL) was heated to reflux for 10 h after which ethanol was removed under reduced pressure. The residue was acidified with 1N HCl and extracted with CH_2Cl_2 (3x100 mL). The combined organic phase was dried over anh. Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, hexane and 10: 1 hexane: ethyl acetate) to give 11-dodecenoic acid (2.0 g, 61%) as a clear oil.

^{1}H NMR (300MHz, $CDCl_3$) δ 10.73 (br, 1H), 5.80 (m, 1H), 4.98 (m, 1H), 4.92 (m, 1H), 2.34 (t, 2H, *J*= 7.5 Hz), 2.04 (q, 2H, *J*= 7.1 Hz), 1.72 (m, 2H), 1.21-1.48 (br. s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.6, 139.1, 114.2, 34.2, 33.8, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 24.7; IR (film) 2928, 2856, 1713, 1639, 1464, 1415, 1287, 1218, 914 cm^{-1}.



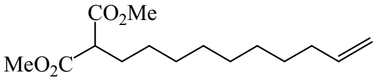
106

11-Dodecenoic acid benzyl ester 106: To a solution of 11-dodecenoic acid (1.61 g, 8.13 mmol) in DMF (33 mL) was added K_2CO_3 (5.62 g, 40.60 mmol) followed by addition of benzyl chloride (4.68 mL, 40.60 mmol). The solution was heated to reflux for 3 h, then K_2CO_3 was filtered and the filtrate was concentrated under reduce pressure. The crude product was purified by flash column chromatography (silica gel, 30:1 hexane: ethyl acetate) to give benzyl 11-dodecenoate **106** (1.97g, 84%) as a clear oil.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.33 (m, 5H), 5.81 (m, 1H), 5.12 (s, 2H), 4.99 (m, 1H), 4.93 (m, 1H), 2.35 (t, 2H, *J*= 7.5 Hz), 2.03 (q, 2H, *J*= 6.6 Hz), 1.64 (m, 2H), 1.40-1.24 (br. s, 12H); ^{13}C

NMR (75 MHz, $CDCl_3$) δ 173.7, 139.2, 136.2, 128.5, 128.2, 114.1, 66.0, 34.3, 33.8, 29.4 (2C), 29.2, 29.1, 29.0, 25.0; IR (film) 2929, 2856, 1731, 1639, 1520, 1456, 1422, 1382 cm^{-1}.

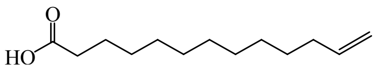
Synthesis of benzyl 12-tridecenoate (C1-C12 subunit)



94

2-Dec-9-enyl-malonic acid dimethyl ester 94: To a solution of NaOMe (3.40 g of Na, 78.2 mmol) in methanol (323 mL) was added diethyl malonate (21.5 mL, 142.50 mmol) and stirred for 30 minutes at 0°C under argon atmosphere. To this mixture was added 10-undecenyl chloride (5.39 g, 28.50 mmol). The reaction mixture was heated to reflux under argon atmosphere for 43 h. Methanol was removed under reduced pressure .The residue was acidified with 1N HCl and extracted with CH_2Cl_2 (3x100 mL). The combined organic layers were dried over anh. Na_2SO_4, filtrated, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, 10:1 hexane: ethyl acetate) to give dimethyl ester **94** (4.17g, 50%) as a clear oil.

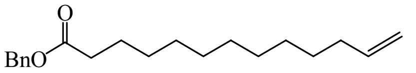
^{1}H NMR (300MHz, $CDCl_3$) δ 5.80 (m, 1H), 4.98 (m, 1H), 4.92 (m, 1H), 3.74 (s, 6H), 2.36 (dt, 1H, *J*= 1.3, 7.5 Hz), 2.04 (q, 2H, *J*= 6.6 Hz), 1.90 (m, 2H), 1.22-1.41 (br. s, 14H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.9, 139.1, 114.0, 52.3, 51.6, 33.7, 29.4, 29.3, 29.2, 29.1, 29.0, 28.8 (2C), 27.2; IR (film) 3471, 3077, 2998, 2927, 2856, 1736, 1639, 1436, 1342, 1154 cm^{-1}.



95

12-Tridecenoic acid 95: A mixture of **94** (760 mg, 2.67 mmol), 10% KOH (38 mL) in ethanol (200 mL) was heated to reflux for 10 h, then ethanol was removed under reduced pressure. The residue was acidified with 1N HCl and extracted with CH_2Cl_2 (3x50 mL). The combined organic phases were dried over anh. Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product dicarboxylic acid was decarboxylated in decalin at 180 °C until CO_2 bubbling subsided. Purification by flash column chromatography (silica gel, 4:1 hexane: ethyl acetate) gave 12-tridecenoic acid **95** (509 mg, 90%) as a clear oil.

^{1}H NMR (300MHz, $CDCl_3$) δ 5.81 (m, 1H), 4.99 (m, 1H), 4.93 (m, 1H), 2.34 (t, 2H, *J*= 7.4 Hz), 2.03 (q, 2H, *J*= 7.1 Hz), 1.64 (m, 2H), 1.40-1.22 (br. s, 14H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.9, 139.2, 114.1, 34.1, 33.8, 29.5, 29.4 (2C), 29.2, 29.1, 29.0, 28.9, 24.7; IR (film) 2928, 2856, 1713, 1639, 1464, 1415, 1287, 1218, 914 cm^{-1}.

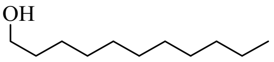


89

12-Tridecenoic acid benzyl ester 89: To a solution of 12-tridecenoic acid **95** (2.90 g, 13.70 mmol) in DMF (53 mL) was added K_2CO_3 (5.67 g, 41.0 mmol) followed by addition of benzyl chloride (4.7 mL, 40.87 mmol). The solution was heated to reflux for 12 h then K_2CO_3 was filtered and the solvent was removed under reduced pressure. Purification by flash column chromatography (silica gel, 10:1 hexane: ethyl acetate) gave benzyl 12-tridecenoate **89** (1.39 g, 34 %) as a clear oil.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.35 (m, 5H), 5.81 (m, 1H), 5.11 (s, 2H), 4.99 (m, 1H), 4.92 (m, 1H), 2.35 (t, 2H, *J*= 7.5 Hz), 2.04 (q, 2H, *J*= 7.0 Hz), 1.64 (m, 2H), 1.22-1.42 (br. s, 14H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 139.2, 136.2, 128.5, 128.2, 114.1, 66.1, 34.3, 33.8, 29.7, 29.5 (2C), 29.4, 29.2, 29.1, 28.9, 25.0; IR (film) 3444, 2928, 2855, 1736, 1639, 1498, 1420, 1352, 1167 cm^{-1}.

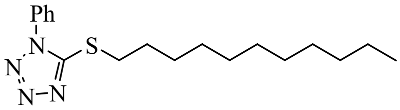
Synthesis of C11-C28 subunit



72

Undecan-1-ol 72: A solution of 10-undecenol **91** (500 mg, 2.94 mmol) in hexane (10 mL) was added palladium on activated carbon (50 mg, 10%w/w) and the resulting suspension was stirred under hydrogen atmosphere for 5 h (a balloon of hydrogen gas was equipped to the reaction flask, ca. 1.1 atm). The mixture was then filtered and the solvent was removed under reduced pressure. Purification by flash column chromatography (10:1 and 4:1, hexane: ethyl acetate) gave 1-undecanol **72** (446 mg, 86%) as a colorless oil.

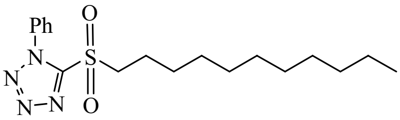
^{1}H NMR (300MHz, $CDCl_3$) δ 3.65 (t, 2H, *J*= 6.6 Hz), 1.57 (m, 2H), 1.35 (m, 16H), 0.90 (t, 3H, *J*= 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 63.1, 32.8, 31.9, 29.6, 29.4, 29.3, 29.2, 25.7, 22.7, 14.1; IR (film) 3343, 2925, 2854, 1467, 1378, 1056 cm^{-1}.



73

1-Phenyl-5-undecylsulfanyl-1H-tetrazole 73: To a solution of 1-undecanol **72** (86 mg, 0.50 mmol), PPh_3 (260 mg, 1.00 mmol), and phenyltetrazolethiol (180 mg, 1.00 mmol) in dry THF (3 mL) at 0 °C under argon atmosphere was added DIAD (0.25 mL, 1.25 mmol). The mixture was stirred at room temperature for 2 h and diluted with CH_2Cl_2. Silica gel was added, and the mixture was concentrated in vacuo. Purification by flash column chromatography (silica gel, 15:1 hexane: ethyl acetate) to give sulfide **73** (160 mg, 96.4%) as a white solid: mp. 41-42 °C.

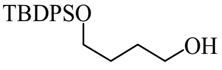
^{1}H NMR (300MHz, $CDCl_3$) δ 7.53-7.40 (m, 5H), 3.33 (t, 2H, *J*= 7.3 Hz), 1.75 (m, 2H), 1.37 (m, 2H), 1.20 (br. s, 14H), 0.81 (t, 3H, *J*= 6.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 133.8, 130.0, 129.7, 123.8, 33.4, 31.9, 29.6, 29.5, 29.4, 29.3, 29.1, 29.0, 28.6, 22.7, 14.1; IR (film) 2926, 2855, 1598, 1500, 1463, 1267, 1042, 759 cm^{-1}.



68

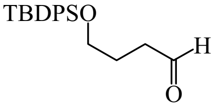
1-Phenyl-5-(undecane-1-sulfonyl)-1H-tetrazole 68: To a solution of the sulfide **73** (0.92 g, 2.76 mmol) in $CHCl_3$ (45 mL) was added *m*-CPBA (70%, 1.36 g, 11.50 mmol). This solution was stirred at room temperature for 1 h while opened to air. The mixture was applied directly to flash column chromatography (silica gel, 10:1 hexane: ethyl acetate) to give the sulfone **68** (0.84 g, 83%) as a white solid: mp. 50-51 °C.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.53-7.40 (m, 5H), 3.73 (m, 2H), 1.95 (m, 2H), 1.49 (m,2H), 1.30 (br.s, 14H), 0.89 (t, 3H, *J*= 6.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 133.1, 131.4, 129.7, 125.1, 56.0, 31.9, 29.5, 29.4, 29.3, 29.2, 28.9, 28.1, 22.7, 21.9, 14.1; IR (film) 2926, 2855, 1498, 1463, 1342, 1153, 1043 cm^{-1}.



4-(*tert*-Butyldiphenylsilanyloxy)butan-1-ol: To a solution of NaH (60% suspension in oils, 1.08 g, 27.00 mmol) in dry THF (60 mL) was added 1,4-butane diol (2.0 mL, 22.50 mmol) followed by addition of TBDPSCl (6.91 mL, 27.00 mmol). The mixture was stirred at room temperature under argon atmosphere for 3 h. The reaction was quenched with sat. $NaHCO_3$ and extracted with CH_2Cl_2 (3x60 mL). The combined organic layers were dried over anh. Na_2SO_4, filtered, and concentrated. The crude product was purified by flash column chromatography (silica gel, 4:1 hexane: ethyl acetate) to give mono-TBDPS ether, (5.11 g, 69%) as a clear oil.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.71 (m, 4H), 7.50-7.43 (m, 6H), 3.74 (t, 2H, *J*= 7.2 Hz), 3.69 (t, 2H, *J*= 6.2 Hz), 1.70 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6, 133.7, 129.7, 127.7, 64.0, 62.8, 29.8, 29.3, 26.8, 19.2; IR (film) 3350, 3071, 3050, 2932, 2858, 1589, 1472, 1389, 1361, 1111 cm^{-1}.

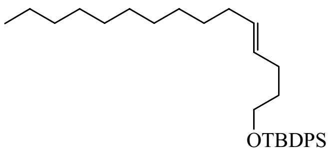


74

4-(*tert*-Butyldiphenylsilanyloxy)butyraldehyde 74: To a solution of oxalyl chloride (0.80 mL, 9.14 mmol) in dry CH_2Cl_2 (65 mL) at -78°C under argon atmosphere was added dropwise DMSO (1.30 mL, 18.30 mmol). After 30 min, the alcohol (1.00 g, 3.05 mmol) in dry CH_2Cl_2 (3 mL) was added slowly. The mixture was stirred at -78°C for 1 h. Et_3N (3.8 mL, 27.43 mmol) was added at -78°C and the mixture was allowed to warmed to room temperature over 45 minutes. The reaction was quenched with water and extracted with CH_2Cl_2 (3x70 mL). The combined organic layers were dried over anh. Na_2SO_4, filtered, and concentrated to give the aldehyde **74** (0.99 g, 99%) as a yellow oil.

PDC oxidation : A mixture of the alcohol (215 mg, 0.66 mmol) and PDC (370 mg, 0.98 mmol) in CH_2Cl_2 (21 mL) was stirred at room temperature for 6 h and filtered through a short column of silica. The filtrate was concentrated under reduced pressure and the crude material was purified by column chromatography (silica gel, 10:1 hexane: ethyl acetate) to give the aldehyde **74** (120 mg, 56%) as a clear oil.

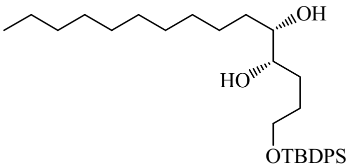
^{1}H NMR (300MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.69 (m, 4H), 7.51-7.27 (m, 6H), 3.62 (t, 2H, *J*= 6.0 Hz), 2.48 (dt, 2H, *J*= 1.6, 5.6 Hz), 1.82 (m, 2H), 0.98 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.6, 135.9, 135.5, 135.3, 135.2, 133.6, 129.7, 129.5, 129.4, 128.0, 127.7, 127.6, 62.9, 40.8, 27.0, 26.8, 25.3, 19.2; IR (film) 3426, 3071, 2959, 2859, 2728, 1709, 1473, 1428, 1390, 1265, 1111 cm^{-1}.



75

***tert*-Butylpentadec-4-enyloxydiphenylsilane 75:** To a solution of the aldehyde **74** (1.30 g, 3.99 mmol) and the sulfone (0.97 g, 2.66 mmol) in dry THF (30 mL) at -78°C was added NaHMDS (2M in THF, 2.7 mL, 5.32 mmol) dropwise. The reaction mixture was stirred at -78°C under argon atmosphere for 2 h and then allowed to warm to room temperature overnight. The reaction was quenched with sat. aq. NH_4Cl (and the aqueous layer was extracted with Et_2O (3x100 mL). The combined organic layers were washed with brine, dried over anh. Na_2SO_4, filtered, and concentrated. Purification by flash column chromatography (silica gel, hexane) gave the alkene **75** (0.95 g, 77%, *E: Z*= 4.3:1) as a clear oil.

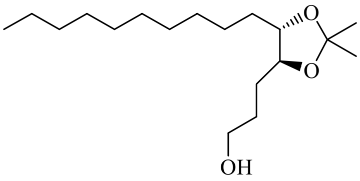
^{1}H NMR (300MHz, $CDCl_3$) δ 7.58 (m, 4H), 7.35-7.22 (m, 6H), 5.82 (m, 2H), 3.57 (m, 2H), 1.80-2.01 (m, 4H), 1.52 (m, 2H), 1.20 (br. s, 16H), 0.96 (s, 9H), 0.78 (t, 3H, *J*= 6.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.7, 135.6, 134.2, 130.9, 130.5, 129.7, 129.5, 129.2, 127.6, 63.5, 63.4, 32.8, 32.7, 32.6, 32.0, 29.9, 29.8, , 29.7 (2C), 29.6, 29.4, 29.3, 28.9, 27.3, 26.9, 23.6, 22.8, 19.3, 14.2; IR (film) 3072, 2928, 2856, 1659, 1471, 1428, 1362, 1264, 1111, 969, 740 cm^{-1}.



76

1-(*tert*-Butyldiphenylsilanyloxy)pentadecane-4,5-diol 76: To a solution of ADmix-α (3.69 g) and methansulfonamide (0.25 g) in *tert*-butanol and water (96 mL, 1:1) at 0 °C was added the alkene **75** (1.22 g, 2.63 mmol). The reaction mixture was stirred vigorously at 0 °C for 4 days and quenched with sodium sulfite (6.63 g). The ice-bath was removed and the mixture was stirred at room temperature for 45 min. The resulting mixture was extracted with ethyl acetate (3x120 mL). The combined organic layers were dried over anh. Na_2SO_4 and concentrated. Purification by flash column chromatography (silica gel, 4:1 and 2:1 hexane: ethyl acetate) to give the diol **76** (0.84 g, 65%) as a clear oil.

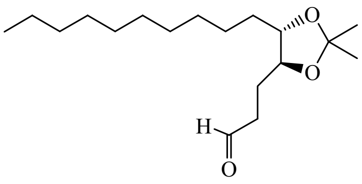
^{1}H NMR (300MHz, $CDCl_3$) δ 7.67 (m, 4H), 7.37-7.20 (m, 6H), 3.71 (t, 2H, *J*= 5.2 Hz), 3.41 (m, 2H), 3.12 (br, 1H), 1.70 (m, 2H), 1.50 (m, 2H), 1.30 (br. s, 16H), 1.07 (s, 9H), 0.88 (t, 3H, *J*= 6.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6, 133.5, 129.7, 127.7, 74.7, 74.2, 64.2, 33.6, 31.9, 30.6, 29.8, 29.6, 29.4, 28.6, 26.8, 25.7, 22.7, 19.2, 14.1; $[\alpha]_D^{25}$ -6.7 (*c*, 1.9, $CHCl_3$); IR (film) 3429, 3054, 2930, 2857, 1711, 1636, 1471, 1428, 1390, 1265, 1111 cm^{-1}.



78

3-(5-Decyl-2,2-dimethyl-[1,3]dioxolan-4-yl)propan-1-ol 78: To a solution of the diol **76** (1.18 g, 2.37 mmol) in 2,2-dimethoxy propane (66 mL) was added TFA (0.4 mL) and the mixture was stirred under argon atmosphere at room temperature for 3 h. The reaction was quenched with sat. $NaHCO_3$ and the aqueous layer was extract with dichloromethane (3x100 mL), dried over anh. Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting acetonide was used directly in the next step. Dry THF (30 mL) was added to this crude material and TBAF (1M in THF, 4.1 mL) was added to the resulting solution. The mixture was stirred under argon atmosphere for 3 h. The reaction was quenched with sat. $NaHCO_3$ and extracted with Et_2O (3x50 mL) .The combined organic layers were washed with brine, dried over anh. Na_2SO_4, filtered, and concentrated. Purification by flash column chromatography (silica gel, 4:1 hexane: ethyl acetate) gave the primary alcohol **78** (0.62 g, 88%, 2 steps) as a clear oil.

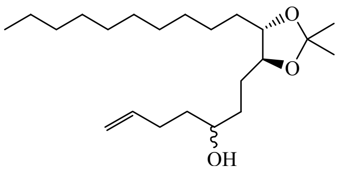
^{1}H NMR (300MHz, $CDCl_3$) δ 3.49 (t, 2H, *J*= 5.7 Hz), 3.45 (m, 2H), 2.70 (br, 1H), 1.55 (m, 2H), 1.36 (m, 4H), 1.23 (s, 6H), 1.11 (br. s, 16H), 0.72 (t, 3H, *J*= 6.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 107.9, 81.0, 80.9, 62.4, 32.7, 31.8, 29.7, 29.5 (2C), 29.4, 29.3, 27.2 (2C), 26.1, 22.6, 14.0; $[\alpha]_D^{25}$ -16.9 (*c*, 1.2, $CHCl_3$); IR (film) 3459, 2928, 2856, 1456, 1379, 1371, 1095, 1058, 1019 cm^{-1}.



79

3-(5-Decyl-2,2-dimethyl-[1,3]dioxolan-4-yl)propionaldehyde 79: To a solution of oxalyl chloride (0.9 ml, 2.61 mmol) in dry CH_2Cl_2 (18 mL) at -78°C under argon atmosphere was added DMSO (0.4 mL, 5.22 mmol) dropwise. After 30 minutes, alcohol **78** (260 mg, 0.87 mmol) in dry CH_2Cl_2 (3 mL) was added dropwise. The mixture was stirred at -78°C for 1 h. Et_3N (1.1 mL, 7.83 mmol) was added at -78°C and the mixture was allowed to warm to room temperature over 45 min. The reaction was quenched with water and extracted with CH_2Cl_2 (3x15 mL). The combined organic layers were dried over anh. Na_2SO_4, filtered, and concentrated. Purification by flash column chromatography (silica gel, 4:1 hexane: ethyl acetate) gave the aldehyde **79** (180 mg, 70%) as a clear oil.

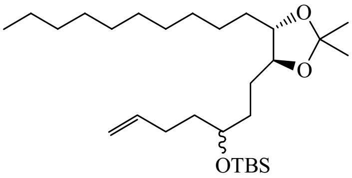
^{1}H NMR (300MHz, $CDCl_3$) δ 9.71 (s, 1H), 3.54 (m, 2H), 2.56 (q, 2H, *J*= 7.5 Hz), 1.89 (m, 1H), 1.66 (m, 1H), 1.47 (m, 4H), 1.29 (s, 6H), 1.20 (br. s, 16H), 0.81 (t, 3H, *J*= 6.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.7, 108.1, 80.8, 79.8, 40.4, 32.8, 31.9, 29.70, 3, 29.5 (2C), 29.3, 27.3, 27.1, 26.0, 25.0, 22.6, 14.1; $[\alpha]_D^{25}$ +8.7 (*c*, 1.6, $CHCl_3$); IR (film) 2930, 2856, 1723, 1456, 1380, 1371 cm^{-1}.



80

1-(5-Decyl-2,2-dimethyl-[1,3]dioxolan-4-yl)hept-6-en-3-ol 80: To a 100 ml. round-bottom flask was added magnesium (2.40 g, 2.39 mmol) under argon atmosphere. Dry Et_2O (40 mL) and 4-bromo-1-butene (2 mL, 19.73 mmol) were added to the flask. The solution boiled gently during addition and was allowed to stir at room temperature for 48 h, to give 3-butenyl magnesium bromide. This solution was added dropwise to the solution of the C14 aldehyde **79** (0.16 g, 0.54 mmol) in dry Et_2O (3 mL) at -78 °C under argon atmosphere via syringe. The mixture was stirred at -78 °C for 1 h. The reaction was quenched with sat. NH_4Cl at -78 °C and allowed to warm to room temperature. The mixture was extracted with Et_2O (3x20 mL). The combined organic layers were washed with brine, dried over anh. Na_2SO_4, filtered, and concentrated. Purification by flash column chromatography (silica gel, 4:1 hexane: ethyl acetate) gave the secondary alcohol **80** (159 mg, 85%) as a clear oil.

^1H NMR (300MHz, $CDCl_3$) δ 5.80 (m, 1H), 4.99 (m, 1H), 4.91 (m, 1H), 3.57 (m, 3H), 2.13 (m, 2H), 1.95 (br, 1H), 1.64 (m, 2H), 1.48 (m, 8H), 1.32 (s, 6H), 1.22 (br. s, 16H), 0.82 (t, 3H, *J*= 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.6 (2C), 113.7, 113.6 (2C), 107.0 (2C), 80.2, 80.1 (2C), 80.0, 70.3, 69.8, 35.7, 35.4, 33.3, 33.0, 31.8, 31.7, 30.9, 29.1, 28.8, 28.6 , 28.5 (2C), 28.3, 27.7, 26.3, 26.2 (2C), 25.1, 21.7, 13.1; IR (film) 3429, 2928, 2856, 1716, 1639, 1456, 1421, 1264, 1052 cm^{-1}.

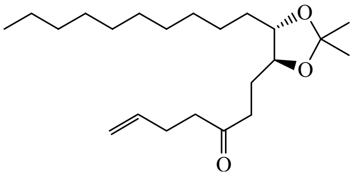


81

***tert*-Butyl-{1-[2-(5-decyl-2,2-dimethyl-[1,3]dioxolan-4-yl)-ethyl]pent-4-enyloxy}-dimethyl-silane 81:** To an ice-cold solution of the alcohol **80** (50 mg, 0.14 mmol) in dry CH_2Cl_2 (1.5 mL) under argon atmosphere was added 2, 6-lutidine (21 μL, 0.18 mmol) followed by addition of

TBSOTf (39 μL, 0.17 mmol). The mixture was stirred at room temperature for 3 h. The reaction was quenched with sat. $NaHCO_3$ and extracted with CH_2Cl_2 (3x10 mL). The combined organic layers were dried over anh. Na_2SO_4, filtered, and concentrated. Purification by flash column chromatography (silica gel, 20:1 hexane: ethyl acetate) gave TBS ether **81** (61 mg, 95%) as a clear oil.

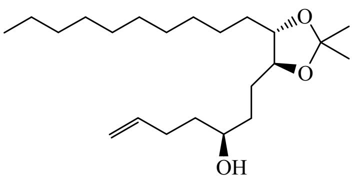
^{1}H NMR (300MHz, $CDCl_3$) δ 5.75 (m, 1H), 4.95 (m, 1H), 4.88 (m, 1H), 3.68 (m, 1H), 3.56 (m, 2H), 2.05 (m, 2H), 1.48 (m, 8H), 1.82 (s, 6H), 1.25 (br. s, 16H), 0.82 (s, 9H), 0.0 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7 (2C), 114.3 (2C), 107.7, 81.2 (2C), 81.0 (2C), 71.5, 71.3, 36.3, 36.0, 33.3, 33.1, 31.9, 29.8, 29.7, 29.6 (3C), 29.5, 29.4, 29.3, 28.7, 28.0, 27.3, 26.1, 25.9, 22.7, 18.1, 14.1, -4.43; IR (film) 3427, 2929, 2856, 1722, 1639, 1456, 1379, 1092 cm^{-1}.



84

1-(5-Decyl-2,2-dimethyl-[1,3]dioxolan-4-yl)hept-6-en-3-one 84: To a solution of oxalyl chloride (36 μL, 0.42 mmol) in dry CH_2Cl_2 (3 mL) at -78°C under argon atmosphere was added DMSO (60 μL, 0.84 mmol) dropwise. After 30 min, the alcohol **80** (50 mg, 0.14 mmol) in dry CH_2Cl_2 (0.5 mL) was added dropwise. The mixture was stirred at -78°C for 1 h. Et_3N (0.2 mL, 1.26 mmol) was added at -78°C and the mixture was allowed to warm to room temperature over 45 min. The reaction was quenched with water and extracted with CH_2Cl_2 (3x2 mL). The combined organic layers were dried over anh. Na_2SO_4, filtered, and concentrated. Purification by flash column chromatography (silica gel, 4:1 hexane: ethyl acetate) gave the ketone **84** (46 mg, 72%) as a clear oil.

^{1}H NMR (300MHz, $CDCl_3$) δ 5.74 (m, 1H), 4.96 (m, 1H), 3.51 (m, 2H), 2.65-2.42 (m, 2H), 2.28 (m, 2H), 1.85 (m, 2H), 1.61 (m, 2H), 1.54 (m, 2H), 1.10 (s, 6H), 1.20 (br. s, 16H), 0.81 (t, 3H, *J*= 6.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.6, 137.1, 115.2, 108.0, 80.9, 80.1, 41.9, 32.8, 31.9, 29.7, 29.6, 29.5, 29.3, 27.8, 27.3, 27.2, 26.6, 26.1, 22.7, 14.1.

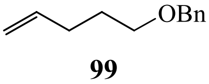


85

1-(5-Decyl-2,2-dimethyl-[1,3]dioxolan-4-yl)hept-6-en-3-ol 85: Ketone **84** (86 mg, 0.25 mmol) was dried in dry toluene (0.5 mL) over 3Å molecular sieves (86 mg) under argon atmosphere for 2 h. The solution was then transferred to a round bottom flask fitted with a septum under an argon atmosphere. A solution of (*R*)-B-Me-CBS catalyst (0.13 mL, 0.12 mmol) was added to the reaction which was then cooled to -78 °C. After 30 min, catechol borane (0.1 mL, 0.98 mmol) was added dropwise to the reaction mixture over 10 min. After the addition was complete, the reaction mixture was allowed to stir at -78 °C for 10 h. The reaction was quenched at -78 °C by the addition of Et_2O (2.0 mL) and cautious dropwise addition of NaOH (1M, 1.0 mL). The solution was allowed to warm to room temperature over 1 h with stirring. To the resulting biphasic black solution was added Et_2O. The organic layer was extracted with NaOH (5x5 mL), washed with water (2x5 mL), and brine, dried over anh. Na_2SO_4, filtered, and concentrated. Purification by flash column chromatography (silica gel, 10:1 hexane: ethyl acetate) to give secondary alcohol **84** (44 mg, 51%) as a clear oil.

^{1}H NMR (300MHz, $CDCl_3$) δ 5.85 (m, 1H), 5.05 (m, 1H), 4.97 (m, 1H), 3.60 (m, 3H), 2.20 (m, 2H), 1.69 (m, 2H), 1.53 (m, 8H), 1.40 (s, 6H), 1.28 (br. s, 16H), 0.83 (t, 3H, *J*= 6.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6 (2C), 114.7, 114.6 (2C), 108.0 (2C), 81.2, 81.1 (2C), 81.0, 71.3, 70.8, 56.7, 36.4, 34.3, 34.0, 32.8, 32.7, 31.9, 30.1, 29.8, 29.6, 29.5 (2C), 29.3, 28.7, 27.3, 27.2 (2C), 26.1, 22.7, 14.1; IR (film) 3429, 2928, 2856, 1716, 1639, 1456, 1421, 1264, 1052 cm^{-1}.

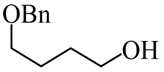
Synthesis of C12-C28 subunit



99

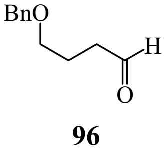
Benzyloxy-4-pentene 99: To a solution of NaH (60% suspension in oil, 1.16 g, 29.05 mmol) in dry THF (25 ml) was added pentene-1-ol (1.0 mL, 9.68 mmol), TBAI (0.72 g, 1.94mmol), and benzyl chloride(2.2 mL, 19.37 mmol). The mixture was heated to reflux under argon atmosphere for 2h. The reaction was quenched with sat. aq. $NaHCO_3$ and extracted with CH_2Cl_2 (3x100 mL). The combined organic layers were dried over anh. Na_2SO_4, filtered, and concentrated. The crude product was purified by flash column chromatography (silica gel, 40:1 hexane: ethyl acetate) to give benzyloxy-4-pentene **99** (1.42 g, 83 %) as a clear oil.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.35-7.20 (m, 5H), 5.80 (m, 1H), 5.01 (m, 1H), 4.94 (m, 1H), 4.47 (s, 2H), 3.46 (t, 3H, *J*= 6.5 Hz), 2.14 (m, 2H), 1.70 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 138.3, 128.4, 127.7, 127.5, 114.8, 72.9, 69.8, 30.4, 29.1; IR (film) 2864, 2941, 1639, 1496, 1455, 1417, 1308, 1099, 1075 cm^{-1}.



4-Benzyloxybutan-1-ol: To a solution of NaH (60% suspension in oils, 5.39 g, 0.13 mol) in dry THF (303 mL) was added 1,4-butane diol (10 mL, 0.11 mol) and benzyl bromide (16 mL, 0.13 mol). The mixture was stirred at room temperature under argon atmosphere for 3 h. The reaction was quenched with sat. $NaHCO_3$ and extracted with CH_2Cl_2 (3x150 mL). The combined organic layers were dried over anh. Na_2SO_4, filtered, and concentrated to give mono-benzyl ether (9.30 g, 53%) as a clear oil.

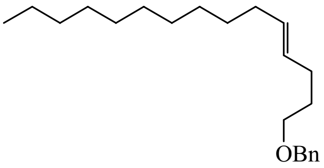
^{1}H NMR (300MHz, $CDCl_3$) δ 7.30-7.17 (m, 5H), 4.43 (s, 2H), 3.81 (br, 1H), 3.51 (t, 2H, *J*= 6.1 Hz), 3.43 (t, 2H, *J*= 6.0 Hz), 1.60 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 128.4, 127.6, 72.8, 70.3, 62.0, 29.6, 26.3; IR (film) 3406, 3010, 2943, 2971, 1713, 1279, 1098, 1071 cm^{-1}.



96

4-Benzyloxybutyraldehyde 96: To a solution of oxalyl chloride (0.3 ml, 3.20 mmol) in dry CH_2Cl_2 (23 mL) at -78°C under argon atmosphere was added DMSO (0.5 mL, 6.40 mmol) dropwise. After 30 min, the alcohol (166 mg, 1.07 mmol) in dry CH_2Cl_2 (3 mL) was added dropwise. The mixture was stirred at -78°C for 1 h. Et_3N (1.3 mL, 9.59 mmol) was added at -78°C and the mixture was allowed to warm to room temperature over 45 min. The reaction was quenched with water and extracted with CH_2Cl_2 (3x20 mL). The combined organic layers were dried over anh. Na_2SO_4, filtered, and concentrated to give the aldehyde **96** (150 mg, 92%) as a yellow oil.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.34-7.20 (m,5H), 4.43 (s, 2H), 3.44 (t, 2H, *J*= 6.1 Hz), 2.45 (dt, 2H, *J*=1.6, 7.1 Hz), 1.88 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.1, 138.3, 128.3, 127.5, 72.8, 69.1, 40.8, 22.5.

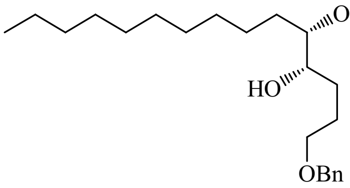


97

4-Pentadecenyloxymethylbenzene 97: To a solution of the aldehyde **96** (300 mg, 1.95 mmol) and the sulfone (354 mg, 0.97 mmol) in dry THF (12 mL) at -78°C was added NaHMDS (2M in THF, 2.0 mL, 1.95 mmol) dropwise. The mixture was stirred at -78°C under argon atmosphere for 2 h. The reaction was allowed to warm to room temperature and stirred overnight. The reaction was quenched with sat. aq. NH_4Cl and the aqueous layer was extracted with Et_2O (3x50 mL). The combined organic layers were washed with brine (sat.), dried over anh. Na_2SO_4 filtered and concentrated. Purification by flash column chromatography (silica gel, hexane) gave the alkene **97** (208 mg, 68%, *E:Z*= 3:1) as a clear oil.

Cross metathesis: To a solution of benzyloxy-4-pentene (757 mg, 4.28 mmol) and 1-dodecene (9.6 mL, 42.77 mmol) in CH_2Cl_2 (150 mL) was added Grubbs I (176 mg, 10 mol%) in CH_2Cl_2(10 mL). The reaction was refluxed under argon atmosphere for 4 h and then allowed to cooled to room temperature. Silica gel was added, and the mixture was concentrated in vacuo. Purification by flash column chromatography (silica gel, 20:1 hexane: ethyl acetate) gave the alkene **97** (1.15 g, 85%, *E:Z* = 3:1) as a clear oil.

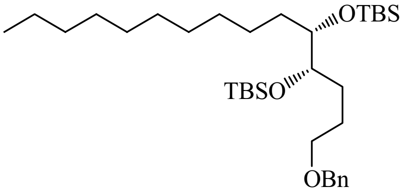
^{1}H NMR (300MHz, $CDCl_3$) δ 7.33-7.20 (m, 5H), 5.39 (m, 2H), 4.50 (s, 2H), 3.47 (t, 2H, *J*= 6.5 Hz)(*Z*-olefin), 3.45 (t, 2H, *J*= 6.5 Hz)(*E*-olefin), 2.17-1.91 (m, 4H), 1.67 (m, 2H), 1.39 (br. s, 16H), 0.88 (t, 3H, *J*= 6.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2, 131.5, 131.1, 129.9, 129.4, 128.8, 128.1, 127.9, 73.4 (2C), 70.3, 33.1, 32.4, 30.3, 30.2, 30.1 (2C), 29.9, 29.7, 29.6, 27.7, 24.3, 23.2, 14.6 ; IR (film) 2929, 2856, 1715, 1603, 1467, 1456, 1316, 1099 cm^{-1}.



100

1-Benzyloxypentadecane-4,5-diol 100: To a solution of ADmix-α (0.92 g) and methansulfonamide (60 mg) in *tert*-butanol and water (15 mL, 1:1) at 0°C was added the alkene **97** (0.21 g, 0.66 mmol). The reaction mixture was stirred vigorously at 0°C for 3 days and quenched with sodium sulfite (1.70 g). Ice bath was removed and the mixture was stirred at room temperature for 45 min. The resulting mixture was extracted with ethyl acetate (3x25 mL). The combined organic layers were dried over anh. Na_2SO_4, filtered, and concentrated. Purification by flash column chromatography (silica gel, 2:1 hexane: ethyl acetate) gave diol **100** (220 mg, 95%) as a clear oil.

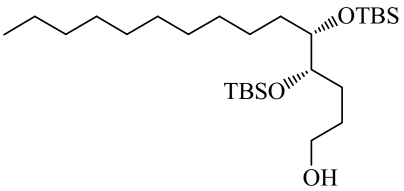
^{1}H NMR (300MHz, $CDCl_3$) δ 7.34-7.22 (m, 5H), 4.50 (s, 2H), 3.65 (br, 2H), 3.49 (t, 2H, *J*= 6.0 Hz), 3.35 (m, 2H), 1.70 (m, 2H), 1.45 (m, 4H), 1.30 (br. s, 16H), 0.88 (t, 3H, *J*= 6.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0, 128.5, 127.8, 74.6, 74.1, 73.1, 70.5, 33.6, 31.9, 31.1, 29.7, 29.6, 29.3, 26.1, 25.7, 22.7, 14.1; $[\alpha]_D^{25}$ -8.1 (*c*, 1.1, $CHCl_3$); IR (film) 3423, 2930, 2856, 1717, 1316, 1279, 1115, 1071, 1001, 892 cm^{-1}.



101

[4,5-Bis-(*tert*-butyl-dimethyl-silanyloxy)pentadecyloxymethyl]benzene 101: To an ice-cold solution of the diol **100** (690 mg, 1.79 mmol) in dry CH_2Cl_2 (21 mL) under argon atmosphere was added 2,6-lutidine (0.7 mL, 5.90 mmol) and TBSOTf (1.4 mL, 5.90 mmol.) The mixture was stirred at room temperature for 2 h. The reaction was quenched with sat. $NaHCO_3$ and extracted with CH_2Cl_2 (3x50 mL). The combined organic layers were dried over anh. Na_2SO_4, filtered, and concentrated. Purification by flash column chromatography (silica gel, 20:1 hexane: ethyl acetate) gave the bis-TBS ether **101** (853 mg, 75%) as a clear oil.

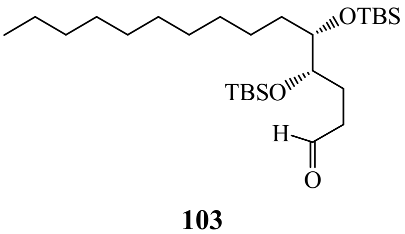
^{1}H NMR (300MHz, $CDCl_3$) δ 7.30-7.10 (m, 5H), 4.42 (s, 2H), 3.53 (m, 2H), 3.41 (t, 2H, *J*= 6.1 Hz), 1.72 (m, 2H), 1.50 (m, 2H), 1.22 (s, 18H), 0.84 (s, 22H), 0.00 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8, 128.3, 127.6, 127.3, 75.5, 75.4, 72.8, 70.8, 32.0, 30.0, 29.8 (2C), 29.7, 29.5, 27.2, 26.9, 26.7, 26.1, 26.0, 18.1, 14.2, -4.0, -4.5; $[\alpha]_D^{25}$ -22.7 (*c*, 1.9, $CHCl_3$); IR (film) 2928, 2857, 2710, 1716, 1520, 1471, 1463, 1389, 1361, 1256, 1217, 1075, 835, 773 cm^{-1}.



102

4,5-Bis-(*tert*-butyl-dimethyl-silanyloxy)pentadecan-1-ol 102: To a solution of **101** (850 mg, 1.47 mmol) in hexane (17 mL) was added palladium on activated carbon (85 mg, 10% w/w) and the resulting suspension was stirred under hydrogen atmosphere for 3 h (a balloon of hydrogen gas was equipped to the reaction flask, ca. 1.1 atm). The mixture was then filtered and the solvent was removed under reduced pressure. Purification by flash column chromatography (silica gel, 4:1 hexane: ethyl acetate) gave the primary alcohol **102** (561 mg, 78%) as a clear oil.

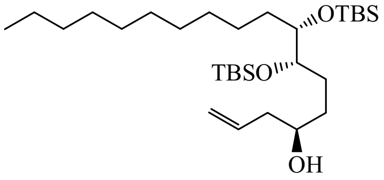
^{1}H NMR (300MHz, $CDCl_3$) δ 3.51 (m, 1H), 3.49 (m, 1H), 3.57 (t, 2H, *J*= 6.2 Hz), 2.30 (br, 1H), 1.75-1.33 (m, 6H), 1.21 (br. s, 16H), 0.84 (br. s, 21H), 0.00 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 75.4, 75.3, 63.1, 31.9, 30.1, 29.8, 29.7, 29.6, 29.5, 29.3, 26.6, 26.3, 26.0, 25.8, 22.6, 17.9, 14.1, -4.2, -4.6; $[\alpha]_D^{25}$ -17.0 (*c*, 0.6, $CHCl_3$); IR (film) 3429, 2955, 2929, 2857, 1471, 1463, 1361, 1258, 1097, 836, 759 cm^{-1}.



103

4,5-Bis-(*tert*-butyl-dimethyl-silanyloxy)pentadecanal 103: To a solution of oxalyl chloride (0.3 mL, 3.44 mmol) in dry CH_2Cl_2 (25 mL) at -78°C under argon atmosphere was added DMSO (0.5 mL, 6.88 mmol) dropwise. After 30 min, alcohol **102** (561 mg, 1.15 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise. The mixture was stirred at -78°C for 1 h. Et_3N (1.4 mL, 10.32 mmol) was added at -78°C and the reaction mixture was allowed to warm to room temperature over 45 min. The reaction was quenched with water and extracted with CH_2Cl_2 (3x50 mL). The combined organic layers were dried over anh. Na_2SO_4, filtered, and concentrated. Purification by flash column chromatography (silica gel, 10:1 hexane: ethyl acetate) gave the aldehyde **103** (550 mg, 98 %) as a clear oil.

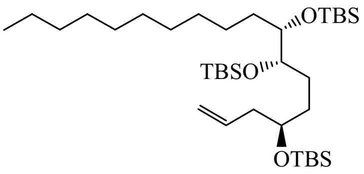
^{1}H NMR (300MHz, $CDCl_3$) δ 9.70 (s, 1H), 3.53 (m, 1H), 3.51 (m, 1H), 2.56-2.38 (m, 2H), 1.95 (m, 2H), 1.58 (m, 2H), 1.43 (m, 2H), 1.22 (br. s, 10H), 0.82 (br. s, 21H), 0.00 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.2, 75.1, 74.5, 41.1, 31.9, 29.8, 29.7, 29.6, 29.5, 29.3, 29.0, 26.6, 25.9, 25.8, 25.7, 22.8, 22.6, 17.9, 14.0, -4.2, -4.7, -5.0.



104

7,8-Bis-(tert-butyl-dimethyl-silanyloxy)octadec-1-en-4-ol 104: To a solution of (-)-methoxydiisopinocampheylborane (743 mg, 2.32 mmol) in dry Et_2O (25 mL) at 0°C was added allyl magnesium bromide solution (1M in THF, 2.4 mL, 2.09 mmol). The mixture was stirred at rt for 1 h and then cooled to -78°C. The aldehyde **103** (564 mg, 1.16 mmol) in dry Et_2O (10 mL) was added dropwise into the solution. The mixture was stirred at -78°C for 1 h. MeOH (1.3 mL) was added and the solution was allowed to warm to room temperature. 3M NaOH (11 mL), and H_2O_2 (40 mL) were added and the solution was stirred overnight. To this mixture was added brine and the layers were separated. The aqueous layer was extracted with Et_2O (3x50 mL). The combined organic layers were dried over anh. Na_2SO_4, filtered, and concentrated. Purification by flash column chromatography (silica gel, 20:1 hexane: ethyl acetate) gave the homoallylic secondary alcohol **104** (563 mg, 92%) as a clear oil.

^{1}H NMR (300MHz, $CDCl_3$) δ 5.78 (m, 1H), 5.10 (m, 1H), 5.05 (m, 1H), 3.59 (m, 1H), 3.51 (m, 1H), 3.48 (m, 1H), 2.25 (m, 2H), 2.12 (m, 2H), 1.65 (m, 4H), 1.38 (m, 2H), 1.21 (br. s, 19H), 0.82 (br. s, 18H), 0.00 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.9, 117.9, 75.7, 75.5, 75.3, 71.1, 70.8, 41.8, 41.7, 34.2, 34.0, 31.9, 29.9, 29.7, 29.6 (2C), 29.3, 26.6, 26.2, 26.0, 25.8, 22.7, 18.0, 14.1, -4.1, -4.6; $[\alpha]_D^{25}$ -27.7 (*c*, 2.2, $CHCl_3$); IR (film) 3429, 2929, 2856, 1639, 1520, 1472, 1424, 1361, 1257, 1218, 1006, 928, 771 cm^{-1}.

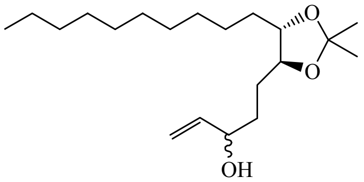


105

4,7,8-Tris-(tert-butyl-dimethyl-silanyloxy)octadec-1-ene 105: To an ice-cold solution of the secondary alcohol **104** (495 mg, 1.25 mmol) in dry CH_2Cl_2 (10 mL) under argon atmosphere was added 2,6-lutidine (0.14 mL, 1.62 mmol) and TBSOTf (0.26 mL, 1.50 mmol). The mixture was stirred at room temperature for 2 h. The reaction was quenched with sat. $NaHCO_3$ and extracted with CH_2Cl_2 (3x50 mL). The combined organic layers were dried over anh. Na_2SO_4, filtered, and concentrated. Purification by flash column chromatography (silica gel, hexane) gave the tris-TBS ether **105** (590 mg, 73%) as a clear oil.

^{1}H NMR (300MHz, $CDCl_3$) δ 5.75 (m, 1H), 4.99 (m, 1H), 4.94 (m, 1H), 3.63 (m, 1H), 3.46 (m, 2H), 2.17 (t, 2H, *J*= 6.5 Hz), 1.78-1.49 (m, 4H), 1.21 (br. s, 19H), 0.83 (br. s, 27H), 0.00 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.5, 116.5, 76.0, 75.4, 72.6, 72.4, 42.2, 41.4, 29.9 (2C), 29.7, 29.6 (2C), 29.3, 26.6, 26.3, 25.9, 25.8, 22.7, 18.0, 14.1, -4.1, -4.2, -4.5, -4.6; $[\alpha]_D^{25}$ -19.5 (*c*, 1.8, $CHCl_3$); IR (film) 2956, 2857, 1639, 1472, 1463, 1361, 1257, 1218, 1091, 1006 cm^{-1}.

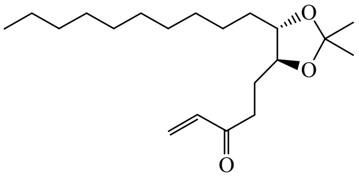
Synthesis of C13-C28 subunit



86

5-(5-Decyl-2,2-dimethyl-[1,3]dioxolan-4-yl)-1-penten-3-ol 86: To a solution of the C14 aldehyde (98 mg, 0.33 mmol) in dry THF (1.6 mL) at -78 °C under argon atmosphere was added vinyl magnesium bromide (1M in THF, 1.0 mL, 0.99 mmol). The reaction mixture was stirred at -78 °C for 1 h and then quenched with sat. NH_4Cl. The mixture was allowed to warm to room temperature and extracted with Et_2O (3x10 mL). The combined organic layers were washed with brine, dried over anh. Na_2SO_4, filtered, and concentrated. Purification by flash column chromatography (silica gel, 4:1 hexane: ethyl acetate) gave the alcohol **86**, (72 mg, 67%) as a clear oil.

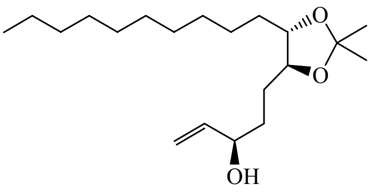
^{1}H NMR (300MHz, $CDCl_3$) δ 5.88 (m, 1H), 5.25 (m, 1H), 5.12 (m, 1H), 4.19 (m, 1H), 3.63 (m, 2H), 1.71 (m, 2H), 1.54 (m, 2H), 1.40 (s, 6H), 1.38 (m, 2H), 1.30 (br. s, 12H), 0.88 (t, 3H, *J*= 6.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.9 (2C), 114.5 (2C), 108.0 (2C), 81.0, 80.9, 72.8, 72.4, 33.9, 33.6, 32.8, 31.9, 29.8, 29.5, 29.3, 29.0, 28.4, 27.3, 27.2, 26.1, 22.7, 14.1; IR (film) 3429, 2988, 2857, 1638, 1421, 1379, 1263, 746 cm^{-1}.



87

5-(5-Decyl-2,2-dimethyl-[1,3]dioxolan-4-yl)-1-penten-3-one 87: A mixture of the allylic alcohol **86** (90 mg, 0.28 mmol) and PDC (155 mg, 0.41 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 8 h and filtered through a short column of silica. The filtrate was concentrated under reduced pressure and the crude material was purified by column chromatography (silica gel, 10:1 hexane: ethyl acetate) to give the vinyl ketone **87** (50.4 mg, 93%) as a yellow oil.

^{1}H NMR (300MHz, $CDCl_3$) δ 6.25 (m, 2H), 5.73 (dd, 1H, *J*= 1.30, 10.0 Hz), 3.56 (m,2H), 2.73 (m, 2H), 1.90 (m, 1H), 1.66 (m, 1H), 1.46 (m,2H), 1.32 (s,6H), 1.21 (br. s, 16H), 0.81 (t, 3H, *J*= 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.1, 136.5, 128.2, 108.0, 80.8, 80.1, 36.0, 32.8, 31.9, 29.8, 29.7, 29.6, 29.5, 29.3, 27.3, 27.5, 26.7, 26.1, 22.7, 14.1, 1.0; $[\alpha]_D^{25}$ -5.3 (*c*, 1.0, $CHCl_3$); IR (film) 3429, 2929, 2856, 1774, 1721, 1637, 1421, 1265, 745 cm^{-1}.

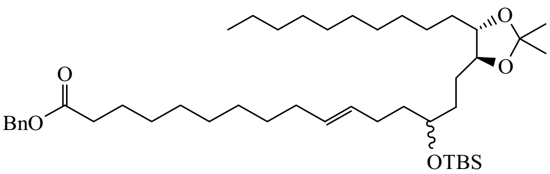


88

5-(5-Decyl-2,2-dimethyl-[1,3]dioxolan-4-yl)-1-penten-3-ol 88: The ketone **87** (71 mg, 0.22 mmol) was dried in dry toluene (1.0 mL) over 3Å molecular sieves (71 mg) under argon atmosphere for 2 hours. The solution was then transferred to a dry round bottom flask fitted with a septum under an argon atmosphere. A solution of (*S*)-B-Me-CBS catalyst (110 μL, 0.11 mmol) was added to the reaction which was then cooled to -78 °C and stirred (30 min). Catechol borane (46 μL, 0.44 mmol) was added dropwise over 10 min to the reaction. After the addition was complete, the reaction mixture was allowed to stir at -78 °C for 10 h. The reaction was quenched by addition of Et_2O (2.5 mL) and cautious dropwise addition of NaOH (1M, 1.2 mL) The solution was allowed to warm to room temperature over 1 hour with stirring. Diethyl ether was added to the resulting biphasic black solution. The organic layer was extracted with NaOH (5x2 mL), washed with water (2x3 mL), and brine, dried over anh. Na_2SO_4, filtered, and concentrated. Purification by flash column chromatography (silica gel, 10:1 hexane: ethyl acetate) gave the allylic alcohol **88** (22 mg, 31%) as a colorless oil.

^{1}H NMR (300MHz, $CDCl_3$) δ 5.88 (m, 1H), 5.25 (m, 1H), 5.12 (m, 1H), 4.19 (m, 1H), 3.63 (m, 2H), 1.71 (m, 2H), 1.54 (m, 2H), 1.40 (s, 6H), 1.38 (m, 2H), 1.30 (br. s, 12H), 0.88 (t, 3H, *J*= 6.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.9 (2C), 114.5 (2C), 108.0 (2C), 81.0 (2C), 80.9, 72.8, 72.4, 33.9, 33.6, 32.8, 31.9, 29.8, 29.5, 29.3, 29.0, 28.4, 27.3, 27.2, 26.1, 22.7, 14.1; IR (film) 3429, 2988, 2857, 1638, 1421, 1379, 1263, 746 cm^{-1}.

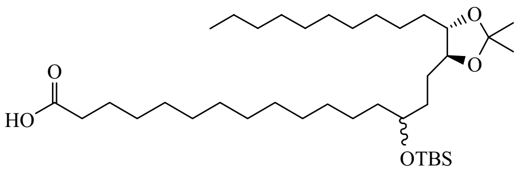
Cross olefin metathesis



82

14-(tert-Butyl-dimethyl-silanyloxy)-16-(5-decyl-2,2-dimethyl-[1,3]dioxolan-4-yl)-10-hexadecenoic acid benzyl ester 82: To a solution of the C11-C28 alkene **81** (280 mg, 0.60 mmol) and benzyl-10-undecenoate **63** (1.89 g, 6.90 mmol) in CH_2Cl_2 (20 mL) was added Grubbs I catalyst (25 mg, 5 mol%) in CH_2Cl_2 (5 mL). The reaction was refluxed under argon atmosphere for 8 h and then allowed to cool to room temperature. Silica gel was added, and the mixture was concentrated in vacuo. Purification by flash column chromatography (silica gel, 30:1 hexane: ethyl acetate) gave the internal alkene **82** (220 mg, 51%, E:Z ratio undetermined) as a clear oil.

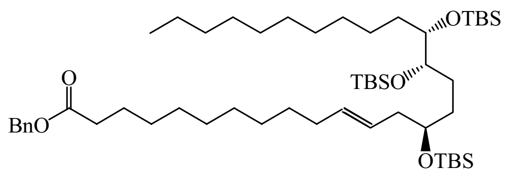
^{1}H NMR (300MHz, $CDCl_3$) δ 7.30 (m, 5H), 5.37 (m, 2H), 5.08 (s, 2H), 3.67 (m, 1H), 3.55(m, 2H), 2.31 (t, 2H, *J*= 7.5 Hz), 1.96 (m, 4H), 1.68-1.37 (m, 12H), 1.33 (s, 6H), 1.22 (br. s, 24H), 0.84 (br. s, 12H), 0.00 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 136.1, 130.5, 130.1, 130.0, 129.5, 129.4, 128.5, 128.1, 107.8, 81.3, 81.2, 81.1, 81.0, 71.8, 71.7, 71.4, 66.0, 37.2, 37.1, 37.0, 36.8, 34.3, 33.3, 33.1, 32.6, 31.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3 (2C), 29.2, 29.1, 28.9, 28.5, 28.4, 28.2, 28.1, 27.3 (2C), 27.2, 26.1, 25.9, 25.0, 23.3, 23.1, 22.7, 18.1, 14.3, -4.3, -4.4; IR (film) 3450, 3054, 2927, 1717, 1498, 1456, 1379, 1264, 1084, 836, 741 cm^{-1}.



83

14-(tert-Butyl-dimethyl-silanyloxy)-16-(5-decyl-2,2-dimethyl-[1,3]dioxolan-4-yl)-hexadecanoic acid 83: To a solution of the alkene **82** (70 mg, 0.10 mmol) in hexane (7 mL) was added palladium on activated carbon (7 mg, 10%w/w) and the resulting suspension was stirred under hydrogen atmosphere for 12 h (a balloon of hydrogen gas was equipped to the reaction flask, ca. 1.1 atm). The mixture was then filtered and the solvent was removed under reduced pressure. Purification by flash column chromatography (silica gel, 10:1 hexane: ethyl acetate) gave the C28 fatty acid **83** (36 mg, 59 %) as a clear oil.

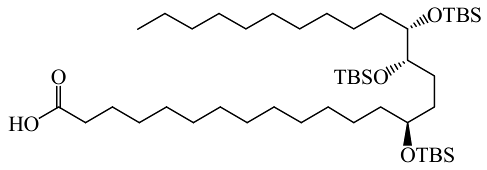
^{1}H NMR (300MHz, $CDCl_3$) δ 3.62 (m, 1H), 3.54 (m, 2H), 2.30 (t, 2H, *J*= 7.5 Hz), 1.32 (s, 6H), 1.23 (br. s, 32H), 0.83 (br. s, 12H), 0.00 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.4. 107.8, 81.3, 81.2, 81.1, 81.0, 72.2, 72.0, 37.2, 36.9, 36.6, 34.0, 33.4, 33.1, 31.9, 29.8 (2C), 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.9, 28.1, 27.3 (3C),, 26.1, 25.9, 25.4, 25.2, 24.7, 22.7, 18.1, 14.1, -4.3, -4.4; IR (film) 3416, 2929, 2856, 1709, 1607, 1552, 1421, 1379 1263, 1166, 1055, 896, 745 cm^{-1}.



107

14,17,18-Tris-(*tert*-butyl-dimethyl-silanyloxy)-11-octacosenoic acid benzyl ester 107: To a solution of C12-C28 alkene **105** (35 mg, 0.053 mmol) and benzyl-11-dodecenoate **106** (154 mg, 0.53 mmol) in CH_2Cl_2 (1.8 mL) was added Grubbs I catalyst (4.4 mg, 10 mol%) in CH_2Cl_2 (1 mL). The reaction was heated to reflux under argon atmosphere for 4 h and then allowed to cool to room temperature. Silica gel was added, and the mixture was concentrated in vacuo. Purification by flash column chromatography (silica gel, 30:1 hexane: ethyl acetate) gave the internal alkene **107** (35 mg, 73%) as a clear oil.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.33 (m, 5H), 5.37 (m, 2H), 5.08 (s, 2H), 3.57 (m, 1H), 3.47 (m, 2H), 2.32 (t, 2H, *J*= 6.4 Hz), 2.14 (m, 2H), 1.90 (m, 2H), 1.60 (m, 4H), 1.24 (br. s, 32H), 0.85 (br. s, 30H), 0.01 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 136.1, 132.7, 132.6 (2C), 131.4, 128.5, 128.1, 126.6, 125.9, 76.0, 75.8, 75.4, 73.2, 72.9, 72.8, 66.0, 41.0, 40.2, 34.4, 34.3, 32.7, 31.9, 29.9, 29.7, 29.6 (2C), 29.5, 29.4 (2C), 29.3, 29.1, 26.6, 26.4, 25.9 (2C), 25.0, 22.7, 18.1, 18.0, 18.0, 14.1, -4.1, -4.2, -4.4, -4.5 (2C), -4.6; $[\alpha]_D^{25}$ -7.0 (*c*, 1.0, $CHCl_3$); IR (film) 2929, 2856, 1732, 1602, 1520, 1471, 1463, 1434, 1361, 1257, 1218, 1093, 1006, 929, 836, 771 cm^{-1}.

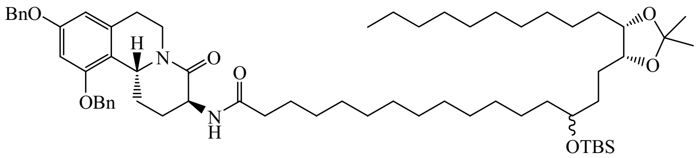


108

14,17,18-Tris-(*tert*-butyl-dimethyl-silanyloxy)octacosanoic acid 108: To a solution of the alkene **107** (130 mg, 0.14 mmol) in hexane (2.5 mL) was added palladium on activated carbon (13 mg, 10%w/w) and the resulting suspension was stirred under hydrogen atmosphere for 12 h (a balloon of hydrogen gas was equipped to the reaction flask, ca. 1.1 atm). The mixture was then filtered and the solvent was removed under reduced pressure. Purification by flash column chromatography (silica gel, 10:1 hexane: ethyl acetate) gave the C28 fatty acid **108** (81 mg, 69%) as a clear oil.

^{1}H NMR (300MHz, CDCl$_3$) δ 3.59(m, 1H), 3.48 (m, 2H), 2.30 (t, 2H, *J*= 7.5 Hz), 1.62 (m, 6), 1.40 (m, 4H), 1.25 (br. s, 34H), 0.85 (br. s, 30H), 0.00 (s, 18H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 180.2, 77.0, 76.7, 76.1, 75.9, 75.4, 72.9, 72.7, 37.3, 36.6, 34.7 (2C), 34.1, 31.9, 29.9 (2C), 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1, 26.6, 26.2, 26.1, 26.0, 28.9, 25.8, 25.3, 25.2, 24.7, 22.7, 18.2, 18.1, 18.0, 14.1, -4.0, -4.5 (2C), -4.6 (2C); $[\alpha]_D^{25}$ -16.1 (*c*, 1.7, CHCl$_3$); IR (film) 2927, 2856, 1709, 1463, 1388, 1361, 1256, 1215, 1091, 835, 774, 669 cm^{-1}.

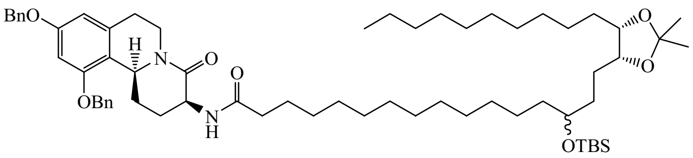
FRAGMENT COUPLING



112

14-(*tert*-Butyl-dimethyl-silanyloxy)-16-(5-decyl-2,2-dimethyl-[1,3]dioxolan-4-yl)-hexadecanoic acid (9,11-bis-benzyloxy-4-oxo-1,3,4,6,7,11b-hexahydro-2H-pyrido[2,1-a]isoquinolin-3-yl)-amide 112: A mixture of the tricyclic amine **57b** (18 mg, 0.04 mmol), C28 fatty acid side chain **83** (27 mg, 0.04 mmol), DCC (29 mg, 0.14 mmol), and DMAP (1 mg, 8.60 μmol) in CH$_2$Cl$_2$ (0.5 mL) was stirred at room temperature under argon atmosphere for 48 h and filtered. The filtrate was concentrated under reduced pressure and the crude material was purified by flash column chromatography (silica gel, 2:1 hexanes: ethyl acetate) to give the amide **112** (13 mg, 29 %) as a clear oil.

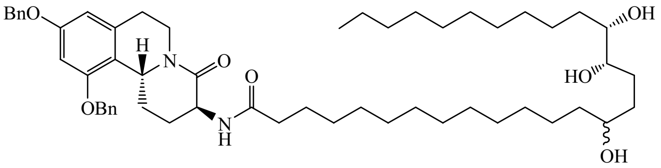
^{1}H NMR (300MHz, CDCl$_3$) δ 7.40 (m, 10 H), 6.51 (d, 1H, *J* = 2.4 Hz), 6.38 (d, 1H, *J* = 2.0 Hz), 6.31 (d, 1H, *J* = 4.7 Hz), 5.04 (d, 2H, *J*= 2.9 Hz), 5.02 (s, 2H), 4.92 (m, 1H), 4.80 (m, 1H), 4.22 (m, 1H), 4.68(m, 1H), 3.59 (m, 2H), 3.50 (m, 4H), 3.20-2.50 (m, 8H), 2.23 (t, 2H, *J*= 10.1 Hz), 1.89 (m, 10H), 1.80-1.50 (m, 10H), 1.48 (s, 6H), 1.34 (br. s, 30H), 1.20 (m, 18H), 0.90 (s, 12H), 0.0 (s, 6H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 173.7, 168.8, 158.3, 157.0, 156.8, 137.8, 136.7, 136.5, 135.9, 128.8, 128.7, 128.7, 128.1, 127.2, 127.1 (2C), 118.2, 107.7, 106.1, 99.2, 98.6, 81.3 (2C), 81.1, 81.0, 72.2, 72.0, 71.4, 71.2, 70.6, 70.2 (2C), 56.3, 56.0, 53.9, 52.149.5, 48.8, 39.6, 39.1, 37.7, 37.5, 37.3, 36.9, 36.8, 34.4, 34.1, 33.4, 33.1, 32.8, 31.9, 31.1, 30.6, 30.6, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 28.9, 28.3, 28.2, 27.9, 27.3, 27.3, 26.4, 26.1, 25.9, 25.7, 25.5, 25.4, 25.3, 25.2, 24.9, 24.3, 22.7, 14.1, -4.3, -4.4; IR (film) 3337, 2930, 2855, 1648, 1610, 1500, 1422, 1265, 1151, 1088, 1045 cm^{-1}.



113

14-(*tert*-Butyl-dimethyl-silanyloxy)-16-(5-decyl-2,2-dimethyl-[1,3]dioxolan-4-yl)-hexadeca- noic acid (9,11-bis-benzyloxy-4-oxo-1,3,4,6,7,11b-hexahydro-2H-pyrido[2,1-a]isoquinolin-3-yl)-amide 113: A mixture of tricyclic amine 57a (22 mg, 0.05 mmol), C28 fatty acid side chain **83** (16 mg, 0.03 mmol), DCC (17 mg, 0.08 mmol), and DMAP (0.6 mg, 5.2 μmol) in CH_2Cl_2 (0.5 mL) was stirred at room temperature under argon atmosphere for 48 h and filtered. The filtrate was concentrated under reduced pressure and the crude material was purified by flash column chromatography (silica gel, 2:1 hexanes: ethyl acetate) to give the amide **113** (18 mg, 33%) as a clear oil.

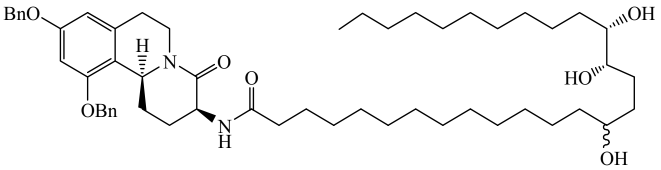
^{1}H NMR (300MHz, $CDCl_3$) δ 7.35 (m, 10 H), 6.75 (d, 1H, *J*= 2.0 Hz), 6.50 (m, 1H), 6.49 (d, 1H, *J* = 2.2 Hz), 6.38 (d, 1H, *J* = 2.1 Hz), 5.07 (s, 2H), 4.95 (s, 2H), 4.68 (m, 1H), 4.50 (m, 1H), 4.30 (m, 1H), 3.58 (m, 4H), 3.18 (m, 2H), 2.74 (m, 3H), 2.22 (t, 2H, *J*= 7.4 Hz), 1.88 (d, 2H, *J*= 9.1 Hz), 1.48-1.52 (m, 10H), 1.40 (s, 6H), 1.25 (br. s, 24H), 0.84 (s, 9H), 0.0 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.2, 170.6, 158.5, 156.0, 137.2, 136.7, 136.5, 128.8, 128.6, 128.2, 128.1, 127.5, 127.1, 117.2, 107.7, 105.9, 99.1, 81.3 (2C), 81.1, 81.0, 72.2, 72.0, 70.2, 48.8, 38.9, 37.3, 36.9, 36.8, 33.5, 33.1, 31.9, 29.9, 29.8 (2C), 29.7, 29.6, 29.5, 29.4, 29.3 (2C), 29.1, 28.9, 28.5, 28.2, 27.3, 26.1, 25.9, 25.8, 25.7, 25.3, 25.2, 24.8, 24.7, 14.1, -4.3, -4.4; IR (film) 3337, 2930, 2855, 1648, 1610, 1500, 1422, 1265, 1151, 1088, 1045 cm^{-1}.



110

14,17,18-Trihydroxy-octacosanoic acid (9,11-bis-benzyloxy-4-oxo-1,3,4,6,7,11b-hexahydro-2H-pyrido[2,1-a]isoquinolin-3-yl)-amide 110: A solution of the amide **112** (13 mg, 13 μmol) in 1N HCl in THF (0.5 mL) were stirred at room temperature for 30 min. The solution was neutralized with sat. aq. $NaHCO_3$ and the aqueous layer was extracted with ethyl acetate (3x5 mL). The combined organic layers were dried with anh. Na_2SO_4, filtered, and concentrated under reduced pressure to give the triol **110** (10 mg, 95%) as a clear oil.

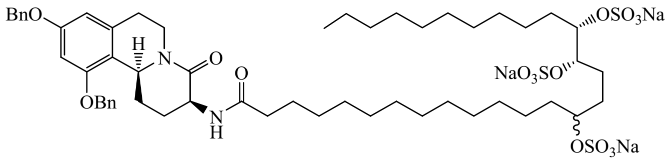
^{1}H NMR (300MHz, $CDCl_3$) δ 7.40 (m, 10 H), 6.50 (d, 1H, *J* = 2.4 Hz), 6.38 (d, 1H, *J* = 2.1 Hz), 5.04 (d, 2H, *J*= 2.9Hz), 5.02 (s, 2H), 4.92 (m, 1H), 4.80 (m, 1H), 4.22 (m, 1H), 3.62 (m, 2H), 3.49 (m, 6H), 3.20-2.50 (m, 6H), 2.23 (m, 4H), 1.95 (m, 10H), 1.75-1.40 (m, 20H), 1.35 (br. s, 40H), 1.12 (m, 12H), 0.85 (t, 3H, *J*= 6.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.8, 168.8, 168.7, 158.3, 156.8, 154.6, 153.3, 137.8, 136.7, 136.5, 136.4, 135.9, 128.8, 128.7 (2C), 128.7, 128.1, 127.5, 127.2, 127.1, 125.5, 118.2, 106.1, 99.18, 98.6, 74.8, 74.7, 74.6, 74.5, 72.3, 71.9, 71.2, 70.6, 70.2 (2C), 56.3, 56.0, 52.0 (2C), 48.2, 39.6, 39.1, 37.8, 37.5, 36.8, 34.0, 33.8, 33.7, 33.2, 31.9, 31.1, 30.6, 30.4, 30.3, 29.7, 29.6, 29.5 (2C), 29.4 (2C), 29.3 (2C), 29.2, 28.3, 27.9, 27.8, 27.3, 27.2, 25.7 (2C), 25.6, 24.9, 22.7, 14.1; IR (film) 3394, 3016, 2925, 2853, 1636, 1608, 1498, 1465, 1375, 1358, 1308, 1271, 1151, 1090, 1048 cm^{-1}.



114

14,17,18-Trihydroxy-octacosanoic acid (9,11-bis-benzyloxy-4-oxo-1,3,4,6,7,11b-hexahydro-2H-pyrido[2,1-a]isoquinolin-3-yl)-amide 114: A solution of amide **113** (18 mg, 0.08 mmol) in 1N HCl in THF (0.7 mL) were stirred at room temperature for 30 min. The solution was neutralized with sat. aq. $NaHCO_3$ and the aqueous phase was extracted with ethyl acetate (3x5 mL). The combined organic layers were dried with anh. Na_2SO_4, filtered, and concentrated under reduced pressure to give the triol **114** (12 mg, 78%) as a clear oil.

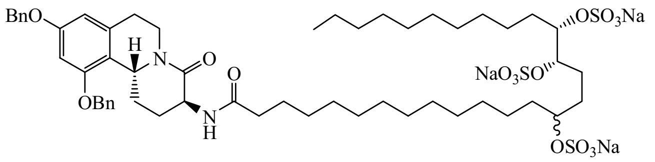
^{1}H NMR (300MHz, $CDCl_3$) δ 0.85 (t, *J*= 3.6 Hz, 3H), 1.12 (m, 54H), 1.38 (br. s, 40H), 1.40-2.00 (m, 20H), 2.43 (m, 2H), 2.65 (m, 4H), 3.43 (m, 2H), 3.55 (m, 3H), 4.45 (m, 1H), 4.66 (m, 1H), 4.85(m, 1H), 4.90 (d, *J*= 3.9Hz, 2H), 5.00 (s, 2H), 6.29 (d, *J* = 2.1 Hz, 1H), 6.38 (d, *J* = 2.4 Hz, 1H), 7.25 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ14.12, 22.68, 25.28, 25.66, 25.73, 28.58, 28.93, 29.23, 29.27, 29.33, 29.36, 29.46, 29.55, 29.61, 29.70, 30.41, 31.91, 33.11, 33.44, 33.54, 33.69, 36.78, 37.55, 37.79, 38.91, 48.82, 70.17, 71.96, 72.34 74.45, 74.61, 74.68, 74.80, 99.10, 105.86, 114.10, 117.21, 127.07, 127.52, 128.11, 128.17, 128.44, 128.65, 128.83, 132.04, 132.17, 136.70, 137.18, 155.97, 158.51, 170.59, 173.18; IR (film) 3394, 3016, 2925, 2853, 1636, 1608, 1498, 1465, 1375, 1358, 1308, 1271, 1151, 1090, 1048 cm^{-1}.



115

9, 11- dibenzylschulzeine B 115: A solution of the triol **114** (6.9 mg, 0.008 mmol) and sulfur trioxide-pyridine complex (38 mg, 0.24 mmol) in DMF (1.0 ml) was stirred at room temperature for 30 h. Then sat. aq. $NaHCO_3$ was added and the mixture was stirred for 30 min. The resulting solution was concentrated under reduced pressure. The residue was triturated with ethyl acetate and filtered. The crude material was purified by flash column chromatography (silica gel, 4:1 ethyl acetate: methanol) to give the trisulfate salt **115** (0.5 mg, 5.3 %).

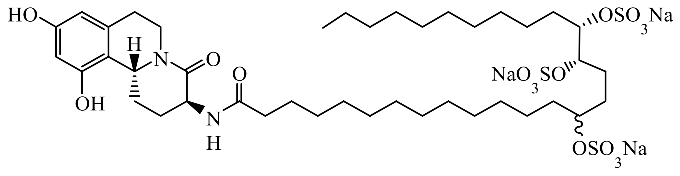
^{1}H NMR (300 MHz, MeOD) δ 7.42-7.28 (m, 10 H), 6.57 (d, 1H, *J*= 2.1 Hz), 6.45 (d, 1H, *J*= 2.1 Hz), 5.09 (d, 2H, *J*= 6.8 Hz), 5.03 (s, 2H), 4.90 (dd, 2H, *J* = 11.0, 3.8 Hz), 4.65 (m, 2H), 4.59 (dd, 1H, *J*= 9.7, 7.9 Hz), 4.36 (m, 1H), 2.78-2.69 (m, 3H), 2.50 (m, 1H), 2.50 (m, 1H), 2.26 (t, 2H, *J* = 7.4 Hz), 2.21 (m, 1H), 1.95-1.90 (m, 2H), 1.87-1.81 (m, 1H), 1.75-1.50 (m, 10H), 1.45-1.36 (m, 3H), 1.30-1.22 (m, 30H), 0.87 (t, 3H, *J* = 6.6 Hz); IR (film) 2947, 2835, 1650, 1449, 1418, 1220, 1113, 1026 cm^{-1}.



116

9, 11- dibenzylschulzeine C 116: A solution of triol **110** (10 mg, 0.012 mmol) and sulfur trioxide-pyridine complex (54 mg, 0.35 mmol) in DMF (1.5 mL) was stirred at room temperature for 30 h. Then sat. aq. $NaHCO_3$ was added and the mixture was stirred for 30 min. The resulting solution was concentrated under reduced pressure. The residue was triturated with ethyl acetate and filtered. The crude material was purified by flash column chromatography (silica gel, 4:1 ethyl acetate: methanol) to give the sulfate salt **116** (3 mg, 21%).

^{1}H NMR (300 MHz, MeOD) δ 7.42–7.29 (m, 10H), 6.58 (d, 1H, J = 2.2 Hz), 6.42 (d, 1H, J = 2.2 Hz), 5.04–5.12 (m, 4H), 4.77 (m, 2H), 4.67 (m, 2H), 4.35 (dt, 1H, J = 11.1, 5.7 Hz), 4.22 (dd, 1H, J = 11.5, 6.9 Hz), 2.77 (m, 1H), 2.95 (dq, 1H, J = 13.5, 3.2 Hz), 2.60–2.66 (m, 2H), 2.22 (dt, 2H, J = 7.4, 2.2 Hz), 2.06 (m, 1H), 1.94 (m, 1H), 1.90 (m, 1H), 1.75-1.51 (m, 10H), 1.40 (m, 4H), 1.27 (m, 30H), 0.88 (t, 3H, J = 6.7 Hz); IR (film) 2947, 2835, 1650, 1449, 1418, 1220, 1113, 1026 cm^{-1}.

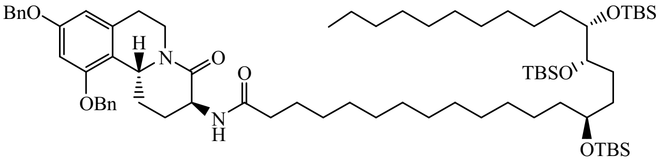


Schulzeine C

Schulzeine C: A solution of dibenzylschulzeine C **116** (3 mg, 0.003 mmol) in methanol (0.5 mL) was added palladium on activated carbon (0.3 mg, 10%w/w) and the resulting suspension was stirred under hydrogen atmosphere for 12 h (a balloon of hydrogen gas was equipped to the reaction flask, ca. 1.1 atm). The catalyst was then filtered and the solvent was removed under reduced pressure to obtain schulzeine C **110** (2.4 mg, 94%).

^{1}H NMR (300 MHz, MeOD) δ 6.19 (d, 1H, J = 2.3 Hz), 6.09 (d, 1H, J = 2.3 Hz), 4.79 (m, 2H), 4.66 (m, 2H), 4.35 (q, 1H, J = 5.6 Hz), 4.28 (dd, 1H, J = 11.8, 6.8 Hz), 3.07 (dq, 1H, J = 14.0, 3.4 Hz), 2.69 (d, 1H, J = 13.2 Hz), 2.63 (dt, 1H, J =11.7, 2.0 Hz), 2.53 (d, 1H, J = 16.6 Hz), 2.23 (dt, 2H, J = 7.4, 2.4 Hz), 2.09 (m, 1H), 1.94 (m, 2H), 1.75–1.50 (m, 10H), 1.42–1.39 (m, 4H), 1.36–

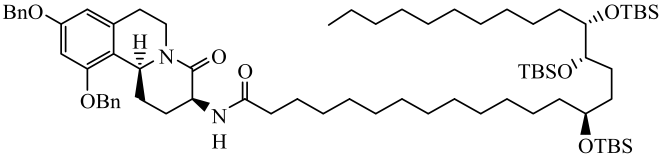
1.25 (m, 30H), 0.88 (t, 3H, *J* = 6.8 Hz); IR (film) 3341, 2923, 2853, 1603, 1462, 1376, 1253, 1220, 1150, 1063, 951 cm^{-1}.



111

14,17,18-Tris-(tert-butyl-dimethyl-silanyloxy)-octacosanoic acid (9,11-bis-benzyloxy-4-oxo-1,3,4,6,7,11b-hexahydro-2H-pyrido[2,1-a]isoquinolin-3-yl)-amide 111 : A mixture of tricyclic amine (40 mg, 0.09 mmol), C28 fatty acid side chain (152 mg, 0.19 mmol), DCC (62 mg, 0.29 mmol), and DMAP (2.5 mg, 0.02 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature under argon atmosphere for 48 h and filtered. The filtrate was concentrated under reduced pressure and the crude material was purified by flash column chromatography (silica gel, 2:1 hexanes: ethyl acetate) to give the amide**111** (105 mg, 91%) as a clear oil.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.35 (m, 10 H), 6.46 (d, 1H, *J*= 2.1 Hz), 6.38 (d, 1H, *J*= 5.1 Hz), 6.33 (d, 1H, *J* = 2.1 Hz), 5.00 (d, 2H, *J*= 6.0 Hz), 4.98 (s, 2H), 4.88 (dd, 1H, *J*= 4.1, 12 Hz), 4.77 (dd, 1H, J= 3.0, 10.5 Hz), 4.18 (m, 1H), 3.57 (m, 2H), 3.47(m, 4H), 3.04 (d, 1H, J= 11.4 Hz), 2.81(d, 1H, *J*= 12.6 Hz), 2.54 (m, 3H), 2.19 (t, 2H, *J*= 7.2 Hz), 1.89 (m, 4H), 1.63 (m, 20H), 1.30 (br. s,32H), 0.84 (s, 27H), 0.0 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9, 170.0, 158.3, 157.1, 156.8, 137.8, 136.7, 136.5, 128.7, 128.6, 128.1, 127.5, 127.2, 118.2, 106.1, 99.2, 76.64, 76.1, 75.9, 75.4, 72.9, 72.7, 70.2 (2C), 56.2, 52.0, 49.2, 40.9, 39.6, 37.3, 36.8, 36.7, 34.7, 31.9, 30.6, 29.9, 29.7, 29.6 (2C), 29.5, 29.4, 29.3 (2C), 29.2, 28.7, 28.4, 27.9, 27.6, 27.2, 26.6, 26.4, 26.2, 26.1, 26.0, 25.9, 25.7, 25.6, 25.5, 25.2, 24.9, 24.7, 20.8, 20.6, 18.2, 18.0, 17.5, 17.3, 14.6, 14.1, 14.0, 7.9, -4.1, -4.4, -4.5 (2C), -4.6; $[\alpha]_D^{25}$ +22.5 (*c*, 2.0, $CHCl_3$); IR (film) 3401, 2928, 2856, 2253, 1794, 1645, 1610, 1499, 1464, 1376, 1257, 1149, 1093, 1006 cm^{-1}.



117

14,17,18-Tris-(tert-butyl-dimethyl-silanyloxy)-octacosanoic acid (9,11-bis-benzyloxy-4-oxo-1,3,4,6,7,11b-hexahydro-2H-pyrido[2,1-a]isoquinolin-3-yl)-amide 118 : A mixture of the tricyclic amine (70 mg, 0.16 mmol), C28 fatty acid side chain (133 mg, 0.16 mmol), DCC (108 mg, 0.52 mmol), and DMAP (4 mg, 0.03 mol) in CH_2Cl_2 (2 mL) was stirred at room temperature under argon atmosphere for 48 h and filtered. The filtrate was concentrated under reduced pressure and the crude material was purified by flash column chromatography (silica gel, 2:1 hexanes: ethyl acetate) to give the amide**117** (60 mg, 30%) as a clear oil.

^{1}H NMR (300MHz, $CDCl_3$) δ 7.35 (m, 10 H), 6.79 (d, 1H, *J*= 5.4 Hz), 6.47(d, 1H, *J*= 2.7 Hz), 6.35 (d, 1H, *J* = 2.1 Hz), 5.06 (s, 2H), 4.96 (s, 2H), 4.89 (m, 1H), 4.70 (m, 1H), 4.51 (m, 1H), 3.58 (m, 2H), 3.48 (m, 3H), 2.74 (m, 4H), 2.49 (m, 1H), 2.22 (t, 2H, *J*= 7.4 Hz), 1.90 (m, 2H), 1.62 (m, 10H), 1.35 (br. s, 32H), 0.84 (s, 27H), 0.0 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.2, 170.6, 158.5, 155.9, 137.2, 136.7, 136.4, 128.8, 128.6, 128.2, 128.1, 127.5, 127.1, 117.2, 105.9, 99.1, 76.1, 75.9, 75.4, 72.9, 72.6, 70.1, 48.8, 38.9, 37.3, 36.8, 36.6, 34.7, 34.6, 33.8, 33.7, 33.5, 33.2, 32.7, 31.9, 30.8, 29.9, 29.7, 29.6 (2C), 29.4, 29.3 (2C), 29.1, 28.4, 26.6, 26.4, 26.2, 26.1, 25.9 (2C), 25.8 (2C), 25.7, 25.5, 25.3, 25.2, 25.0, 24.8, 24.7, 24.2, 23.8, 23.4, 22.7, 18.2, 18.3, 17.3, 14.1, -4.1, -4.5 (2C), -4.6; $[\alpha]_D^{25}$ -29.4 (*c*, 3.0, $CHCl_3$); IR (film) 3401, 2928, 2856, 2253, 1794, 1645, 1610, 1499, 1464, 1376, 1257, 1149, 1093, 1006 cm^{-1}.

APPENDIX

ABBREVIATIONS

Admix-α	Sharpless asymmetric dihydroxylation reagent mixture
BINAL-H	2,2'-dihydroxy -1,1'-binaphthyllithium aluminum hydride
BnCl , BnBr	benzyl chloride , benzyl bromide
Boc	*tert*-butoxycarbonyl
CBS	Corey-Bakshi-Shibata
Cbz	benzyloxycarbonyl
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCC	dicyclohexyl carbodiimide
DCM	dichloromethane
DIAD	diisopropylazodicarboxylate
DIBALH	diisobutylaluminum hydride
DMAP	4-*N*-*N*'-dimethylaminopyridine
DMF	dimethylformamide
DMSO	dimethylsulfoxide
EDC	1-ethyl-3- (3-dimethyaminopropyl) carbodiimide
HOBt	1-hydroxybenzotriazole
HWE	Horner-Wadsworth-Emmons
Ipc	isopinocampheyl
LAH	lithium aluminum hydride
m-CPBA	meta-chloroperbenzoic acid
MOM	methoxymethyl
MTPA	α- methoxy- α- trifluoromethylphenylacetic acid
NaHMDS	sodium hexamethyldisilazide, sodium bis(trimethylsilylamide)
PDC	pyridinium dichromate
p-TSA	para-toluene sulfonic acid
PTSH	1-phenyl-1H-tetrazole-5-thiol
TBAF	tetrabutylammonium fluoride

TBAI	tetrabutylammonium iodide
TBDPSCl	*tert*-butyldiphenylsilyl chloride
TBSOTf	*tert*-butyldimethylsilyl triflate
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TMSI	trimethylsilyl iodide
TMSOTf	trimethylsilyl triflate

^{1}H NMR and ^{13}C NMR Spectra of Compounds

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Compound 46	^{1}H NMR spectrum	74
	^{13}C NMR spectrum	75
Compound 47	^{1}H NMR spectrum	76
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Compound 48	^{1}H NMR spectrum	78
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Compound 49	^{1}H NMR spectrum	80
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Compound 43	^{1}H NMR spectrum	82
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Compound 50	^{1}H NMR spectrum	84
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Compound 51	^{1}H NMR spectrum	86
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^{13}C NMR spectrum………………………………………… 103

Compound 57b ^{1}H NMR spectrum………………………………………… 104

^{13}C NMR spectrum………………………………………… 105

Compound 63 ^{1}H NMR spectrum………………………………………… 106

^{13}C NMR spectrum………………………………………… 107

Compound 71 ^{1}H NMR spectrum………………………………………… 108

^{13}C NMR spectrum………………………………………… 109

Compound 91 ^{1}H NMR spectrum………………………………………… 110

^{13}C NMR spectrum………………………………………… 111

Compound 92 ^{1}H NMR spectrum………………………………………… 112

^{13}C NMR spectrum………………………………………… 113

Compound 109 ^{1}H NMR spectrum………………………………………… 114

^{13}C NMR spectrum………………………………………… 115

11-dodecenoic acid ^{1}H NMR spectrum………………………………………… 116

^{13}C NMR spectrum………………………………………… 117

Compound 106 ^{1}H NMR spectrum………………………………………… 118

^{13}C NMR spectrum………………………………………… 119

Compound 94 ^{1}H NMR spectrum………………………………………… 120

^{13}C NMR spectrum………………………………………… 121

Compound 95 ^{1}H NMR spectrum………………………………………… 122

^{13}C NMR spectrum………………………………………… 123

Compound 89 ^{1}H NMR spectrum………………………………………… 124

^{13}C NMR spectrum………………………………………… 125

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^{13}C NMR spectrum…………………………………………… 131

4-TBDPSO butanol ^{1}H NMR spectrum…………………………………………… 132
^{13}C NMR spectrum…………………………………………… 133

Compound 74 ^{1}H NMR spectrum…………………………………………… 134
^{13}C NMR spectrum…………………………………………… 135

Compound 75 ^{1}H NMR spectrum…………………………………………… 136
^{13}C NMR spectrum…………………………………………… 137

Compound 76 ^{1}H NMR spectrum…………………………………………… 138
^{13}C NMR spectrum…………………………………………… 139

Compound 78 ^{1}H NMR spectrum…………………………………………… 140
^{13}C NMR spectrum…………………………………………… 141

Compound 79 ^{1}H NMR spectrum…………………………………………… 142
^{13}C NMR spectrum…………………………………………… 143

Compound 80 ^{1}H NMR spectrum…………………………………………… 144
^{13}C NMR spectrum…………………………………………… 145

Compound 81 ^{1}H NMR spectrum…………………………………………… 146
^{13}C NMR spectrum…………………………………………… 147

Compound 82 ^{1}H NMR spectrum…………………………………………… 148
^{13}C NMR spectrum…………………………………………… 149

Compound 83 ^{1}H NMR spectrum…………………………………………… 150
^{13}C NMR spectrum…………………………………………… 151

Compound 84 ^{1}H NMR spectrum…………………………………………… 152
^{13}C NMR spectrum…………………………………………… 153

Compound 85 ^{1}H NMR spectrum…………………………………………… 154
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^{13}C NMR spectrum…………………………………………… 157

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^{13}C NMR spectrum…………………………………………… 159

Compound 88 ^{1}H NMR spectrum…………………………………………… 160
^{13}C NMR spectrum…………………………………………… 161

Compound 99 ^{1}H NMR spectrum…………………………………………… 162
^{13}C NMR spectrum…………………………………………… 163

4-benzyloxy butanol ^{1}H NMR spectrum…………………………………………… 164
^{13}C NMR spectrum…………………………………………… 165

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^{13}C NMR spectrum…………………………………………… 167

Compound 97 ^{1}H NMR spectrum…………………………………………… 168
^{13}C NMR spectrum…………………………………………… 169

Compound 100 ^{1}H NMR spectrum…………………………………………… 170
^{13}C NMR spectrum…………………………………………… 171

Compound 101 ^{1}H NMR spectrum…………………………………………… 172
^{13}C NMR spectrum…………………………………………… 173

Compound 102 ^{1}H NMR spectrum…………………………………………… 174
^{13}C NMR spectrum…………………………………………… 175

Compound 103 ^{1}H NMR spectrum…………………………………………… 176
^{13}C NMR spectrum…………………………………………… 177

Compound 104 ^{1}H NMR spectrum…………………………………………… 178
^{13}C NMR spectrum…………………………………………… 179

Compound 105 ^{1}H NMR spectrum…………………………………………… 180
^{13}C NMR spectrum…………………………………………… 181

Compound 107 ^{1}H NMR spectrum…………………………………………… 182
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Compound 113 ^{1}H NMR spectrum…………………………………………… 186
^{13}C NMR spectrum…………………………………………… 187

Compound 112 ^{1}H NMR spectrum…………………………………………… 188
^{13}C NMR spectrum…………………………………………… 189

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^{13}C NMR spectrum…………………………………………… 191

Compound 110 ^{1}H NMR spectrum…………………………………………… 192
^{13}C NMR spectrum…………………………………………… 193

Compound 115 ^{1}H NMR spectrum…………………………………………… 194

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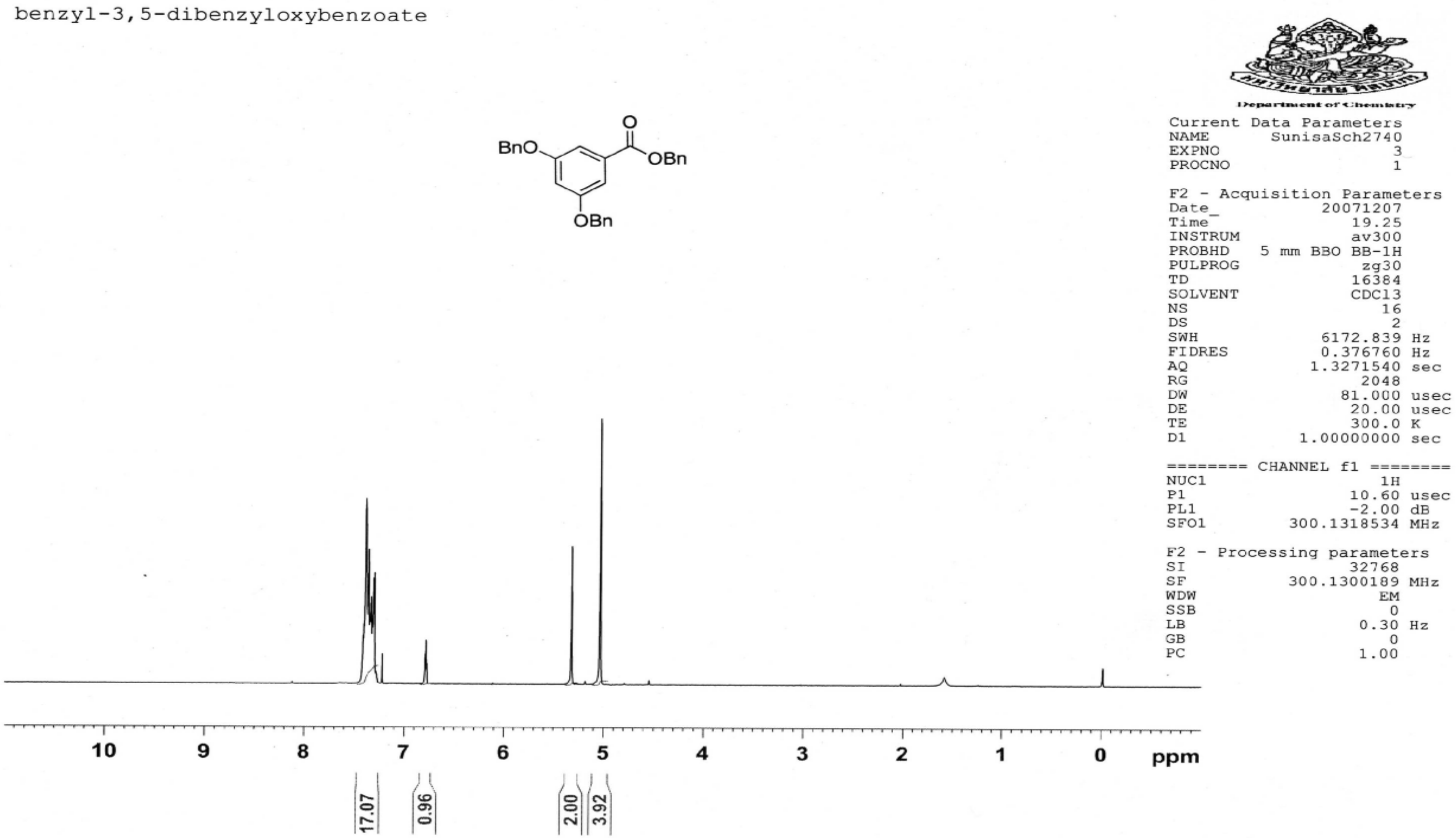
^{13}C NMR spectrum…………………………………………… 200



benzyl-3,5-dibenzyloxybenzoate

```
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NAME          SunisaSch2740
EXPNO                     3
PROCNO                    1

F2 - Acquisition Parameters
Date_              20071207
Time                  19.25
INSTRUM               av300
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                6172.839 Hz
FIDRES             0.376760 Hz
AQ                1.3271540 sec
RG                     2048
DW                   81.000 usec
DE                    20.00 usec
TE                    300.0 K
D1               1.00000000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    10.60 usec
PL1                   -2.00 dB
SFO1            300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF              300.1300189 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```
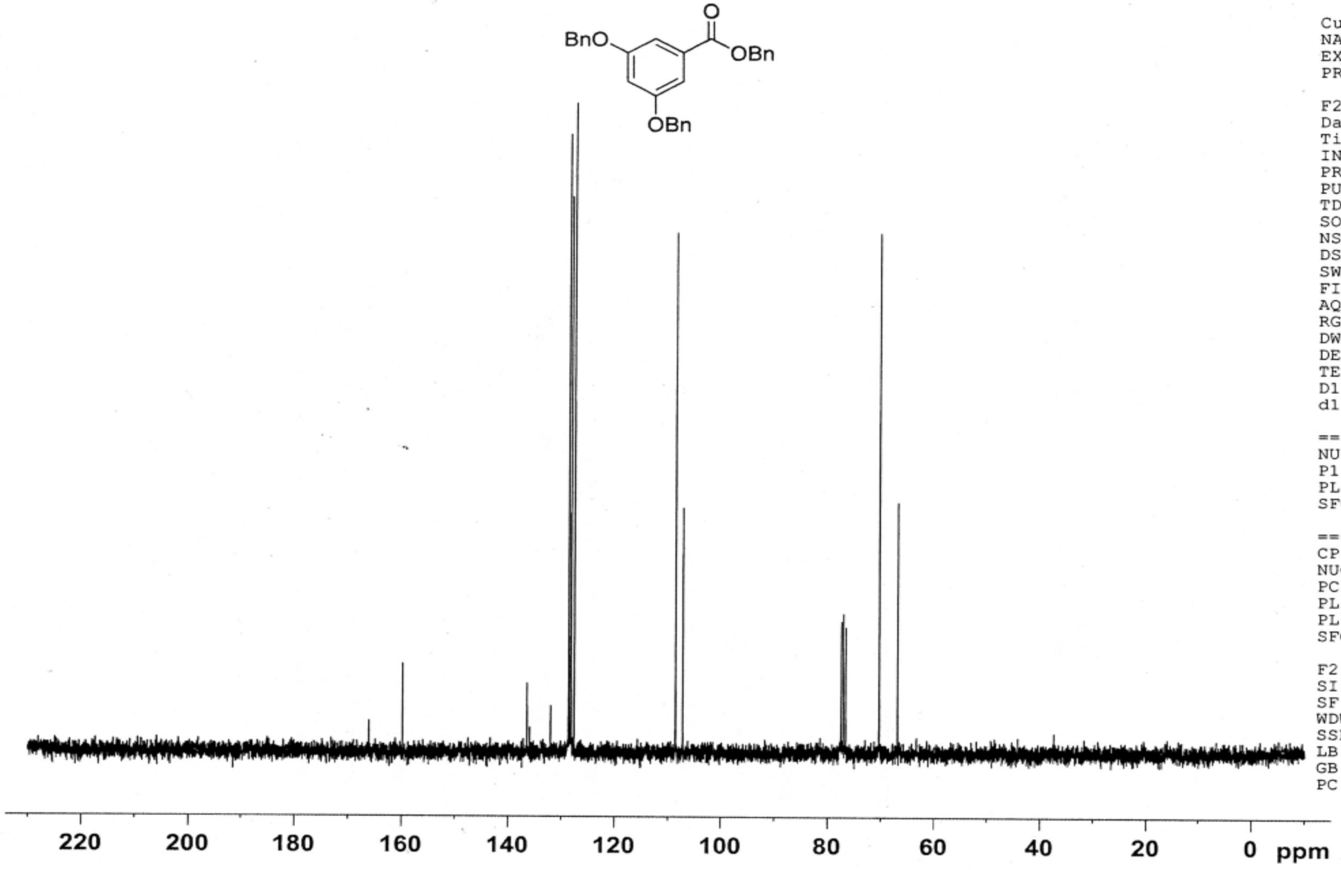

^{1}H NMR spectrum of compound **46**

13C of benzyl-3,5-dibenzyloxybenzoate



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Current Data Parameters
NAME       SunisaSch2760
EXPNO      °           3
PROCNO                 1

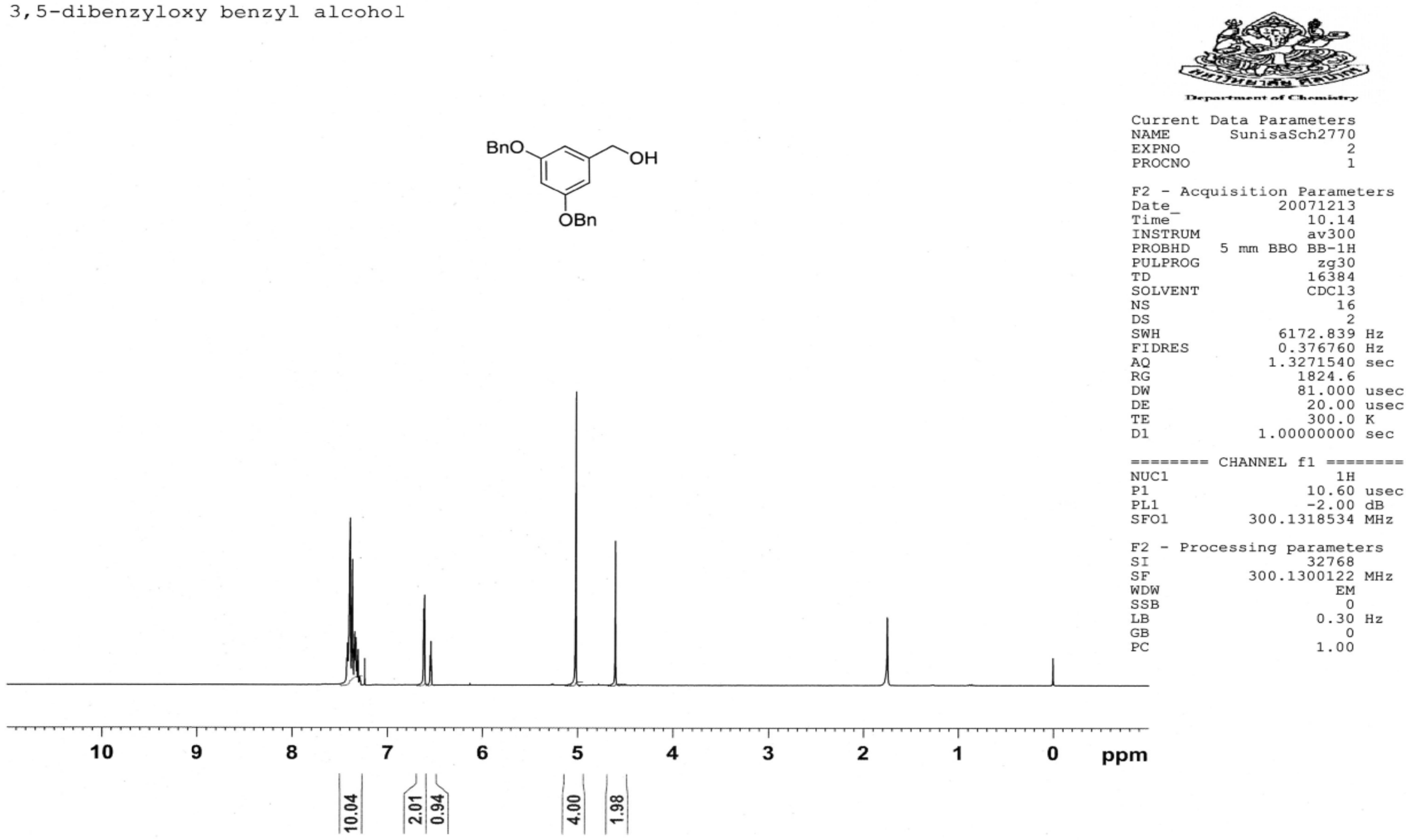
F2 - Acquisition Parameters
Date_          20071212
Time              18.04
INSTRUM           av300
PROBHD   5 mm BBO BB-1H
PULPROG            zgdc
TD                32768
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           18115.941 Hz
FIDRES         0.552855 Hz
AQ            0.9044468 sec
RG                13004
DW               27.600 usec
DE                20.00 usec
TE                300.0 K
D1           1.00000000 sec
d11          0.03000000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 5.20 usec
PL1               -3.00 dB
SFO1         75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2               -2.00 dB
PL12              -2.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
SF           75.4677490 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

^{13}C NMR spectrum of compound **46**



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Current Data Parameters
NAME       SunisaSch2770
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20071213
Time               10.14
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                1824.6
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.60 usec
PL1                -2.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300122 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```
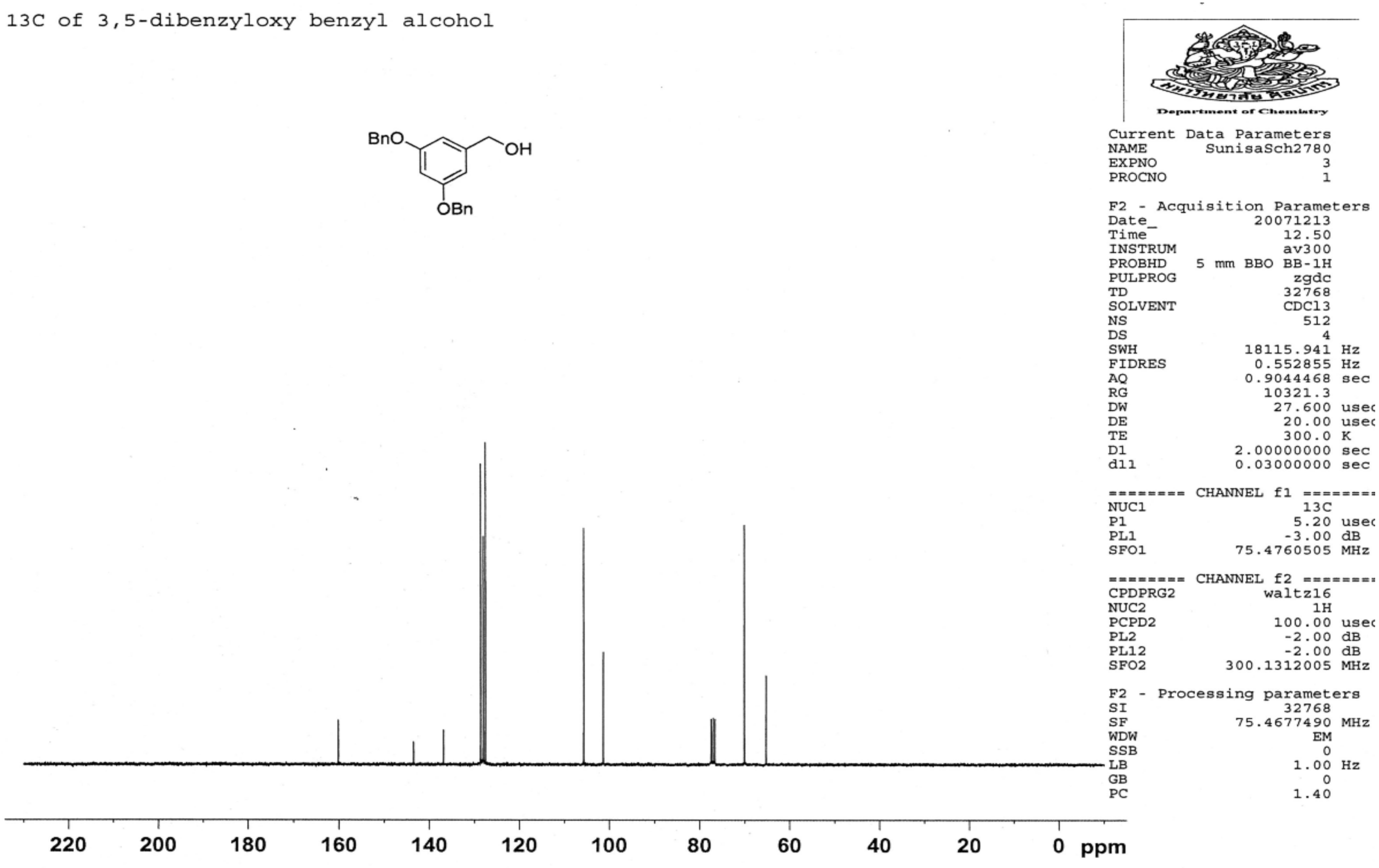
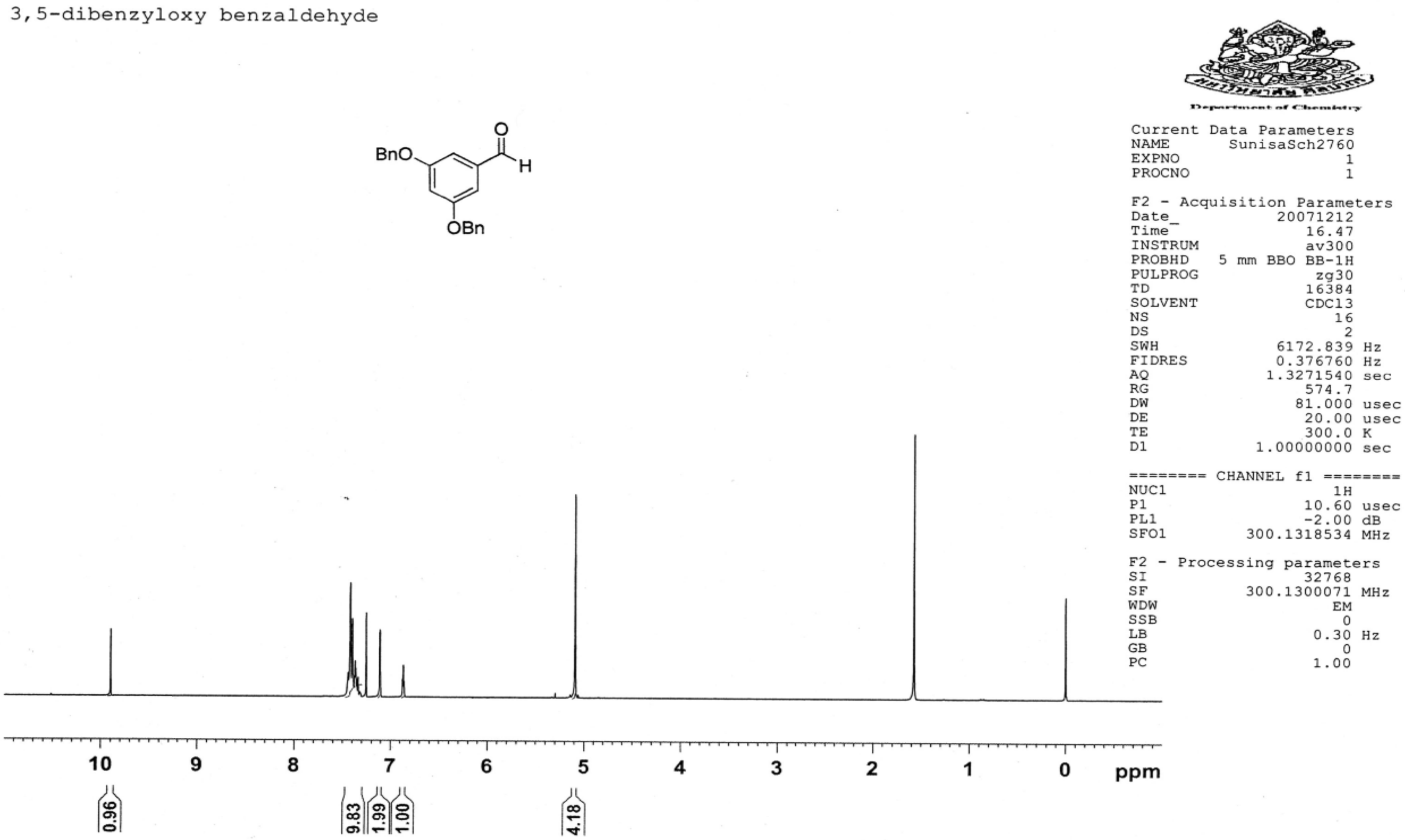

^{1}H NMR spectrum of compound **47**



13C of 3,5-dibenzyloxy benzyl alcohol

```
Current Data Parameters
NAME       SunisaSch2780
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20071213
Time               12.50
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zgdc
TD                 32768
SOLVENT            CDCl3
NS                   512
DS                     4
SWH            18115.941 Hz
FIDRES          0.552855 Hz
AQ             0.9044468 sec
RG               10321.3
DW                27.600 usec
DE                 20.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  5.20 usec
PL1                -3.00 dB
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -2.00 dB
PL12               -2.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{13}C NMR spectrum of compound **47**

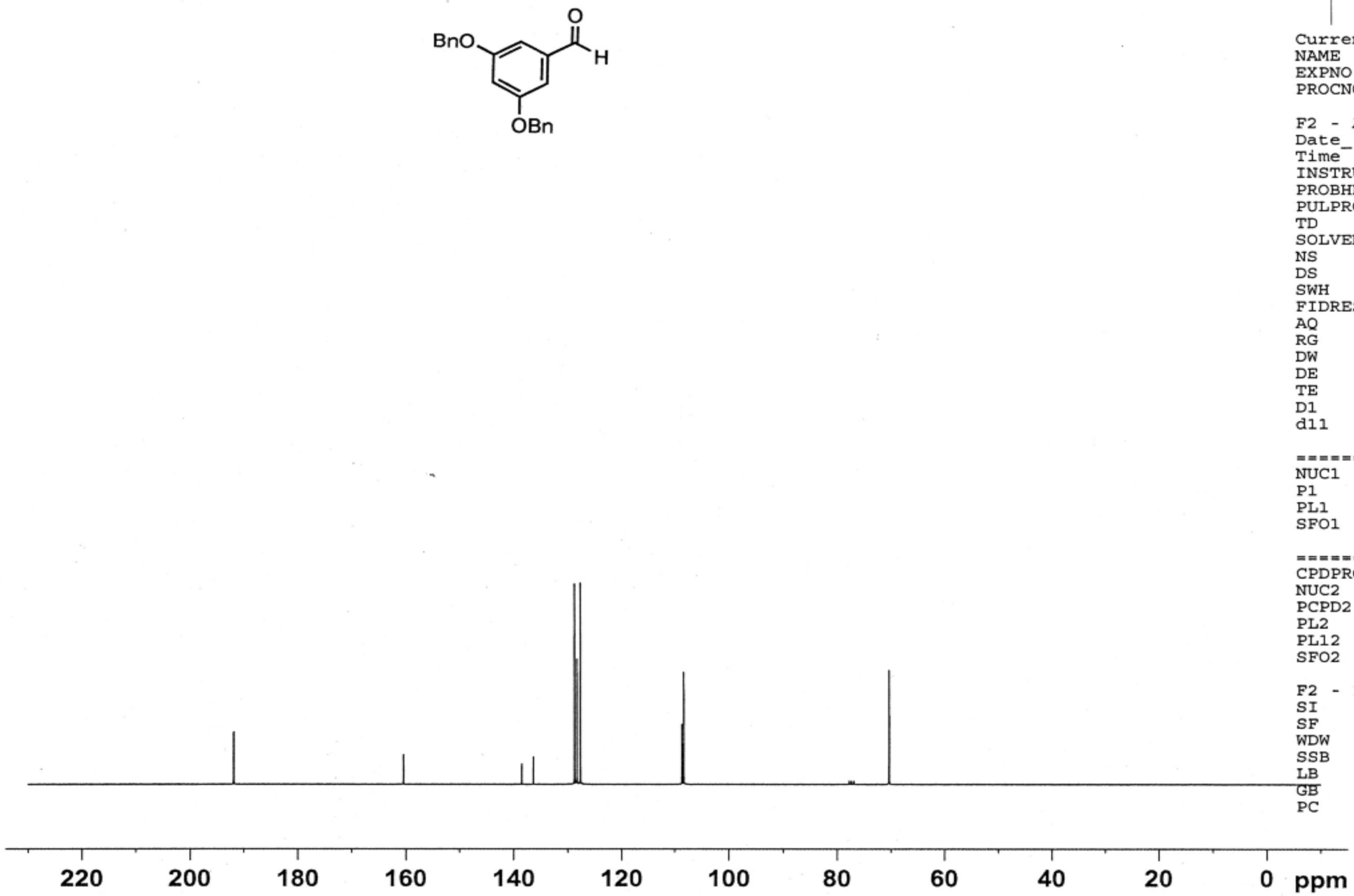


3,5-dibenzyloxy benzaldehyde

```
Current Data Parameters
NAME       SunisaSch2760
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20071212
Time               16.47
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                 574.7
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.60 usec
PL1                -2.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300071 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR spectrum of compound **48**

3,5-dibenzyloxy benzaldehyde



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Current Data Parameters
NAME        SunisaSch3068
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20081012
Time                12.47
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PROBHD   5 mm BBO BB-1H
PULPROG              zgdc
TD                  32768
SOLVENT             CDCl3
NS                    256
DS                      4
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                 9195.2
DW                 27.600 usec
DE                  20.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   5.40 usec
PL1                 -3.00 dB
SFO1           75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -1.00 dB
PL12                17.00 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF             75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

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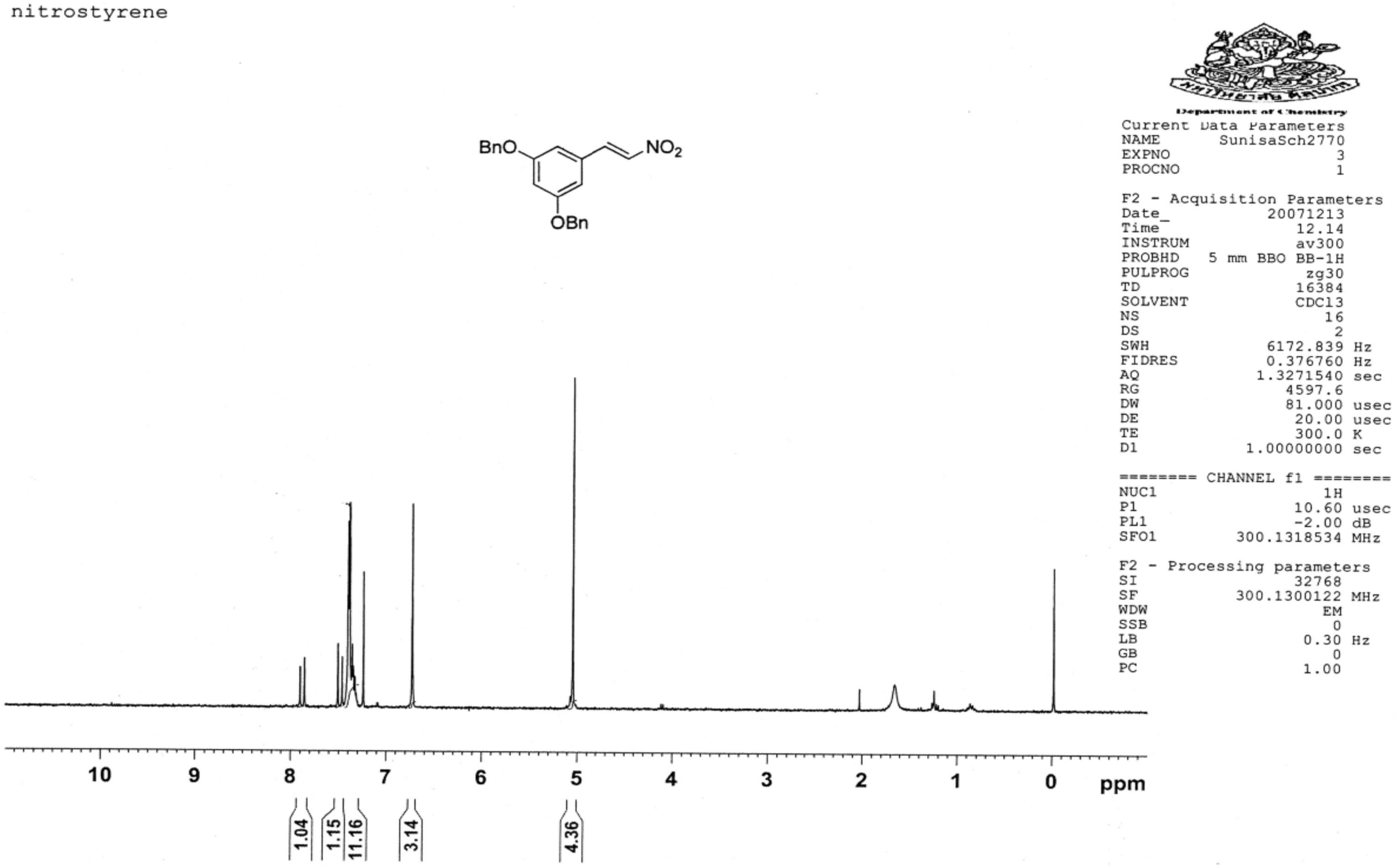
^{13}C NMR spectrum of compound **48**



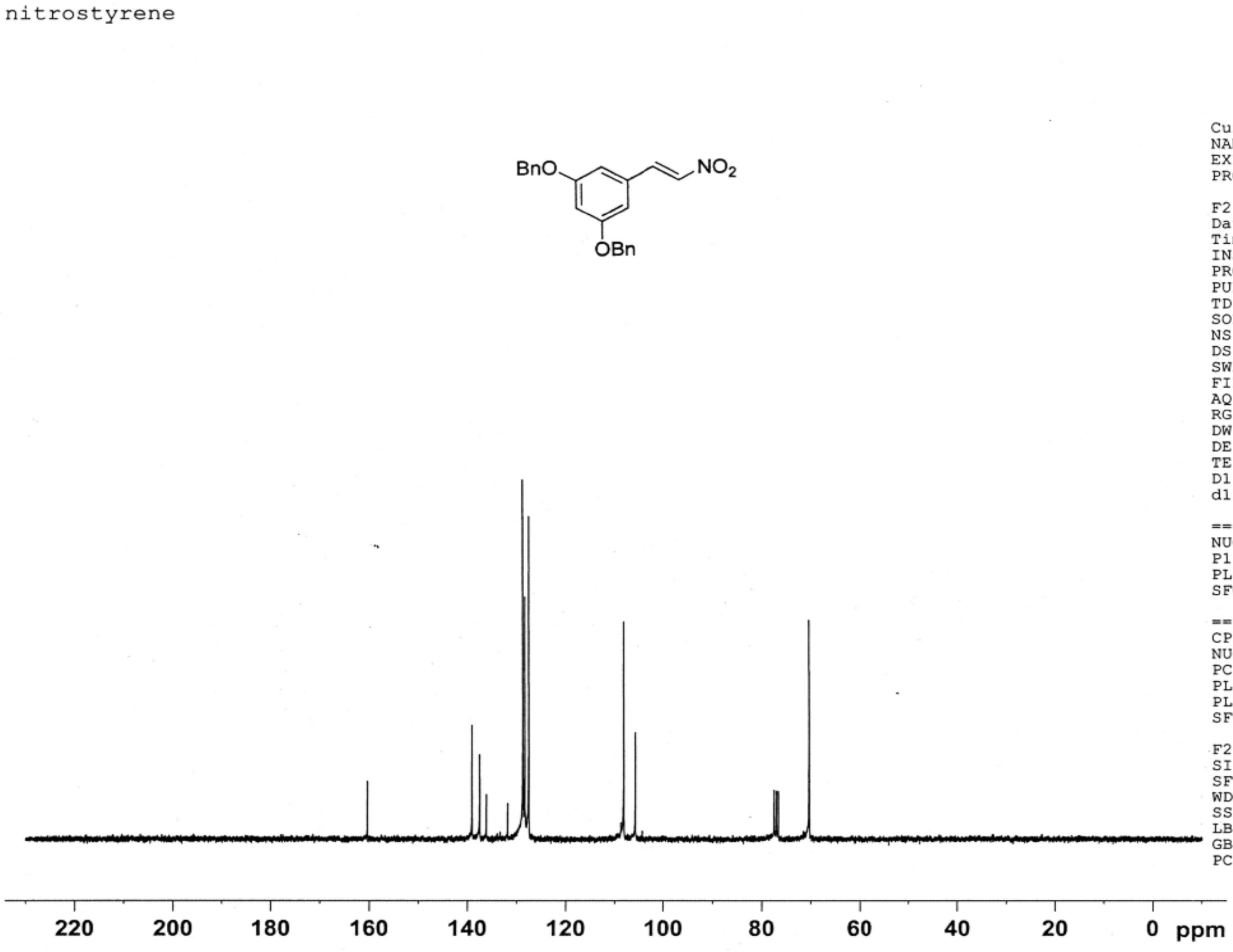
```
Current Data Parameters
NAME        SunisaSch2770
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20071213
Time                12.14
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.376760 Hz
AQ              1.3271540 sec
RG                 4597.6
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  10.60 usec
PL1                 -2.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300122 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR spectrum of compound **49**



```
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Current Data Parameters
NAME      SunisaSch2800
EXPNO                 5
PROCNO                1

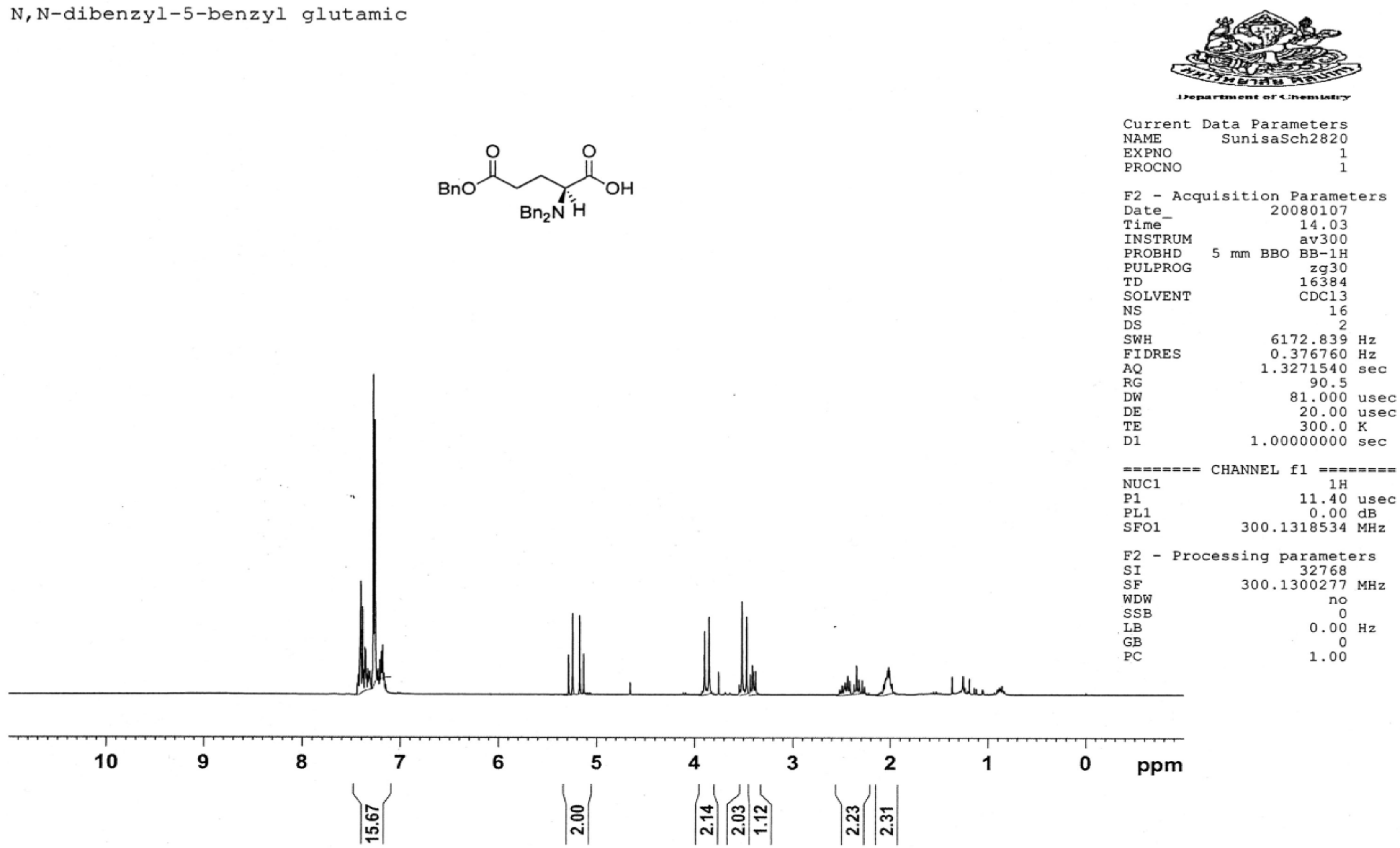
F2 - Acquisition Parameters
Date_          20071220
Time              14.39
INSTRUM           av300
PROBHD   5 mm BBO BB-1H
PULPROG            zgdc
TD                32768
SOLVENT           CDCl3
NS                  512
DS                    4
SWH           18115.941 Hz
FIDRES         0.552855 Hz
AQ            0.9044468 sec
RG              10321.3
DW               27.600 usec
DE                20.00 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 5.20 usec
PL1               -3.00 dB
SFO1         75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2               -2.00 dB
PL12              -2.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
SF           75.4677490 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.00
```

^{13}C NMR spectrum of compound **49**



N,N-dibenzyl-5-benzyl glutamic

```
Current Data Parameters
NAME      SunisaSch2820
EXPNO                 1
PROCNO                1

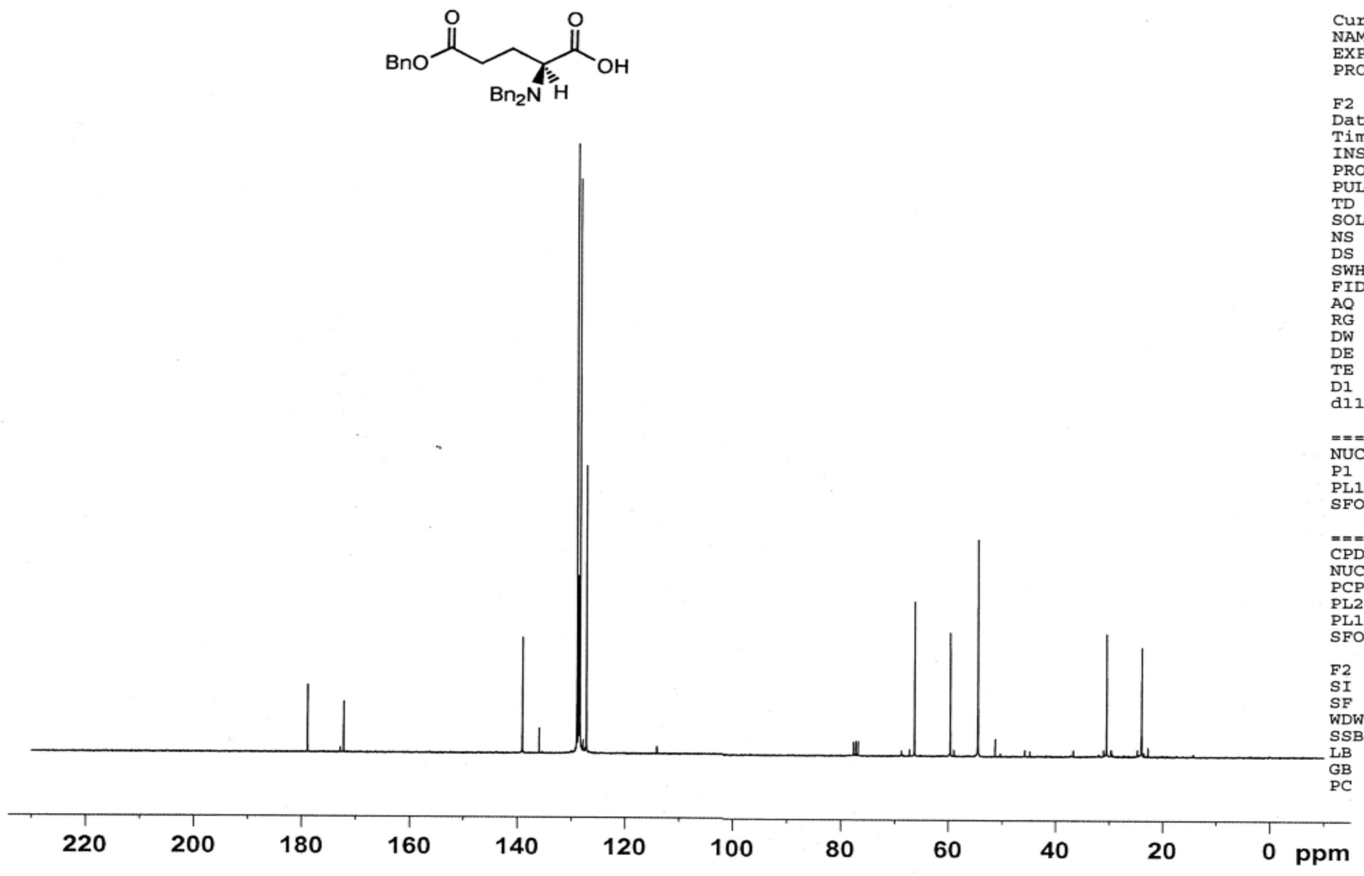
F2 - Acquisition Parameters
Date_          20080107
Time              14.03
INSTRUM           av300
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                16384
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            6172.839 Hz
FIDRES         0.376760 Hz
AQ            1.3271540 sec
RG                 90.5
DW               81.000 usec
DE                20.00 usec
TE                300.0 K
D1           1.00000000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                11.40 usec
PL1                0.00 dB
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                32768
SF          300.1300277 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```

^{1}H NMR spectrum of compound **43**

L-glutamic derivative



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```
Current Data Parameters
NAME          SunisaSch3067
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20081010
Time                  13.55
INSTRUM               av300
PROBHD    5 mm BBO BB-1H
PULPROG                zgdc
TD                    32768
SOLVENT               CDCl3
NS                      512
DS                        4
SWH               18115.941 Hz
FIDRES             0.552855 Hz
AQ                0.9044468 sec
RG                  11585.2
DW                   27.600 usec
DE                    20.00 usec
TE                    300.0 K
D1               1.00000000 sec
d11              0.03000000 sec

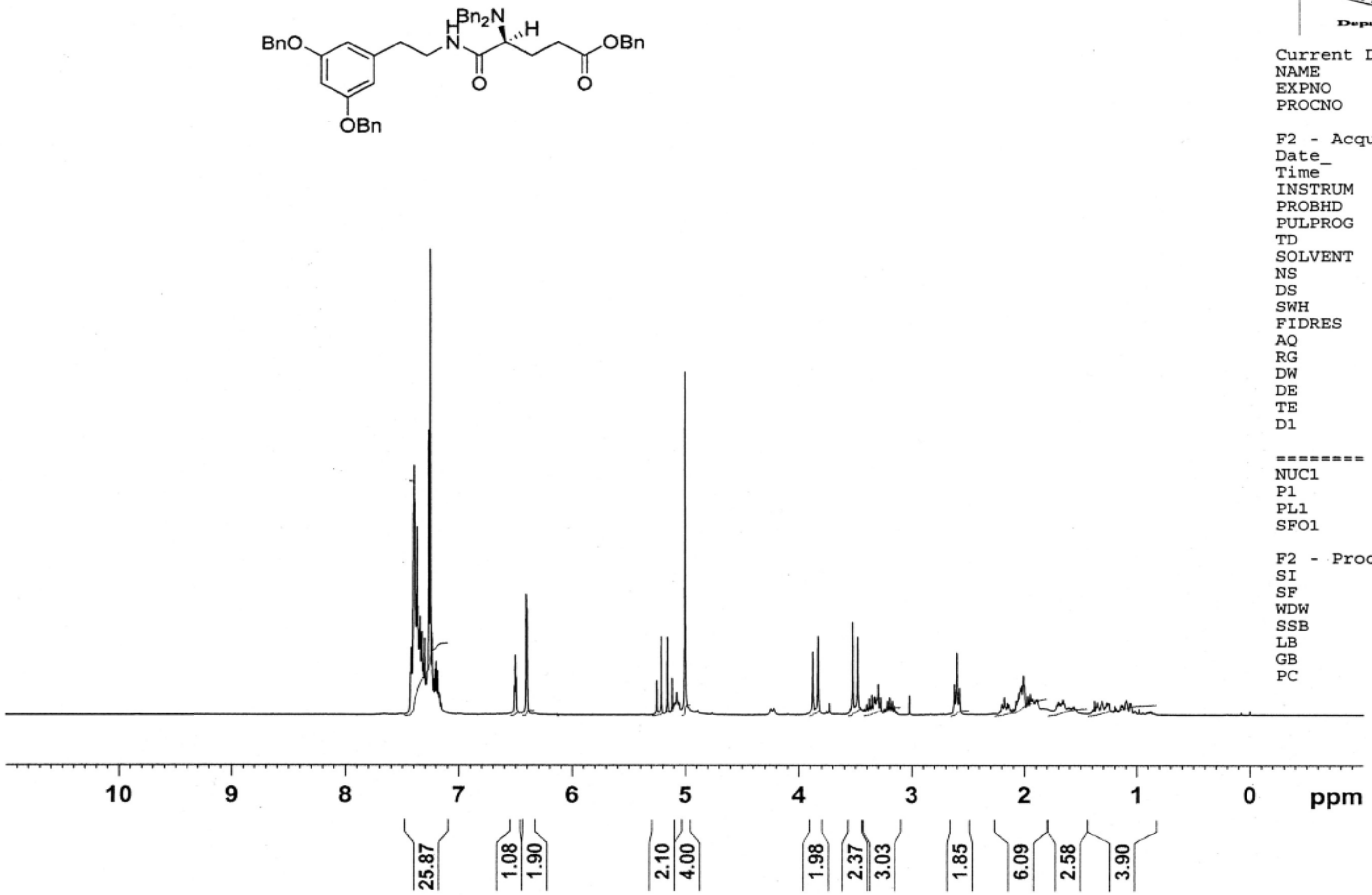
======== CHANNEL f1 ========
NUC1                    13C
P1                     5.40 usec
PL1                   -3.00 dB
SFO1            75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                   -1.00 dB
PL12                  17.00 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF               75.4677490 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.00
```

^{13}C NMR spectrum of compound **43**

amide



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```
Current Data Parameters
NAME       SunisaSch2850
EXPNO                  1
PROCNO                 1

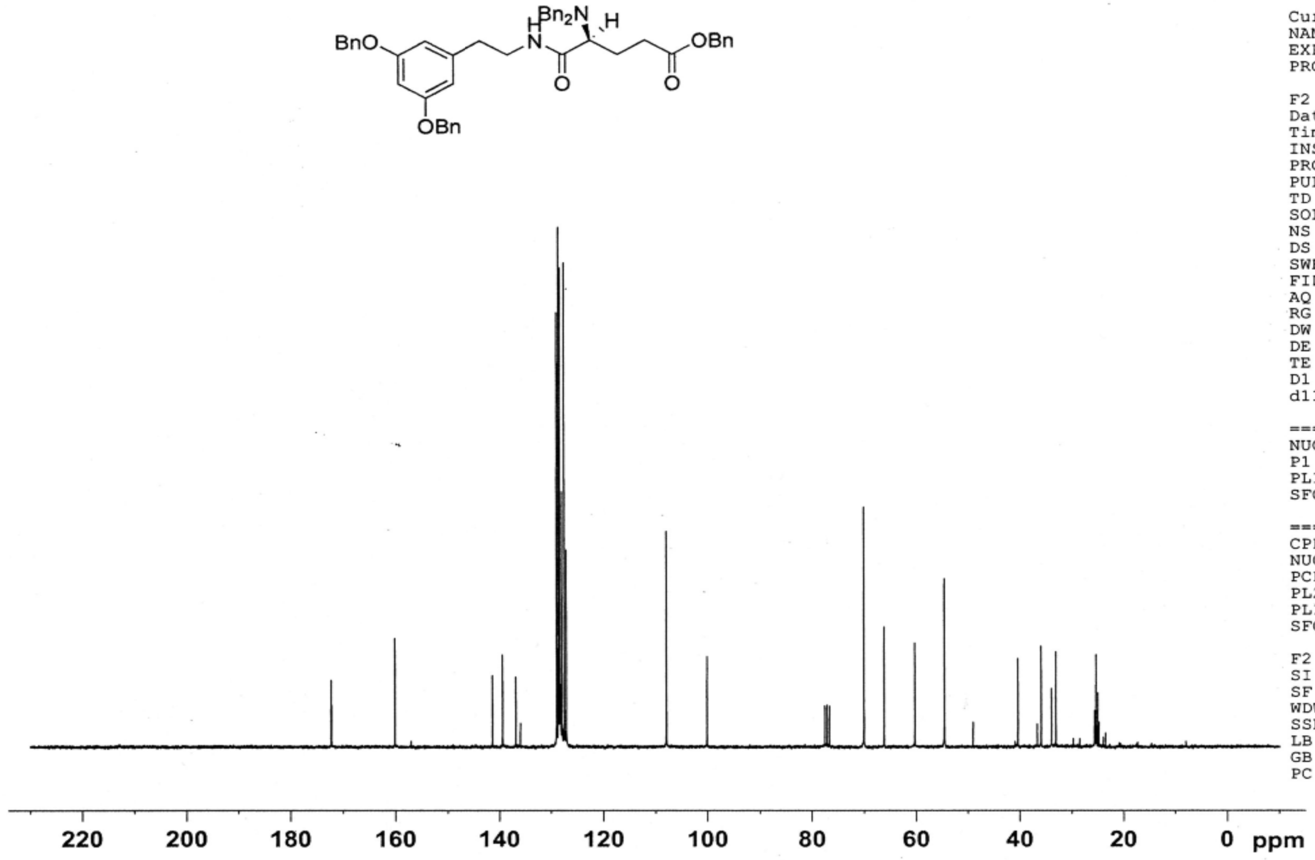
F2 - Acquisition Parameters
Date_           20080117
Time               11.30
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                   181
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.40 usec
PL1                 0.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300137 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR spectrum of compound **50**

13C of amide



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```
Current Data Parameters
NAME       SunisaSch2920
EXPNO                  4
PROCNO                 1

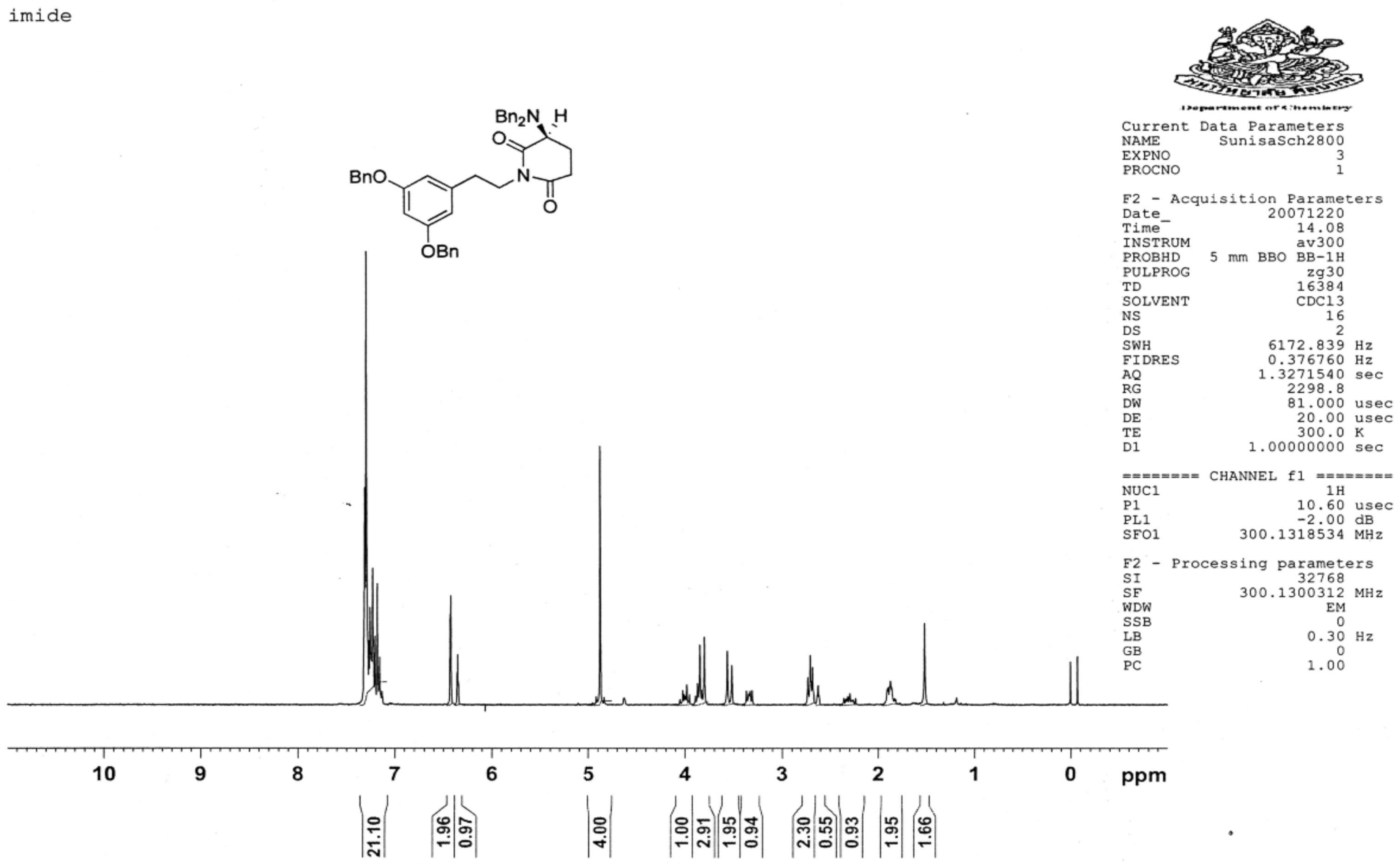
F2 - Acquisition Parameters
Date_           20080218
Time               17.15
INSTRUM            av300
PROBHD    5 mm BBO BB-1H
PULPROG             zgdc
TD                 32768
SOLVENT            CDCl3
NS                   400
DS                     4
SWH            18115.941 Hz
FIDRES          0.552855 Hz
AQ             0.9044468 sec
RG                5792.6
DW                27.600 usec
DE                 20.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  5.20 usec
PL1                -3.00 dB
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 0.00 dB
PL12               17.20 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.00
```

^{13}C NMR spectrum of compound **50**



```
Current Data Parameters
NAME       SunisaSch2800
EXPNO                  3
PROCNO                 1

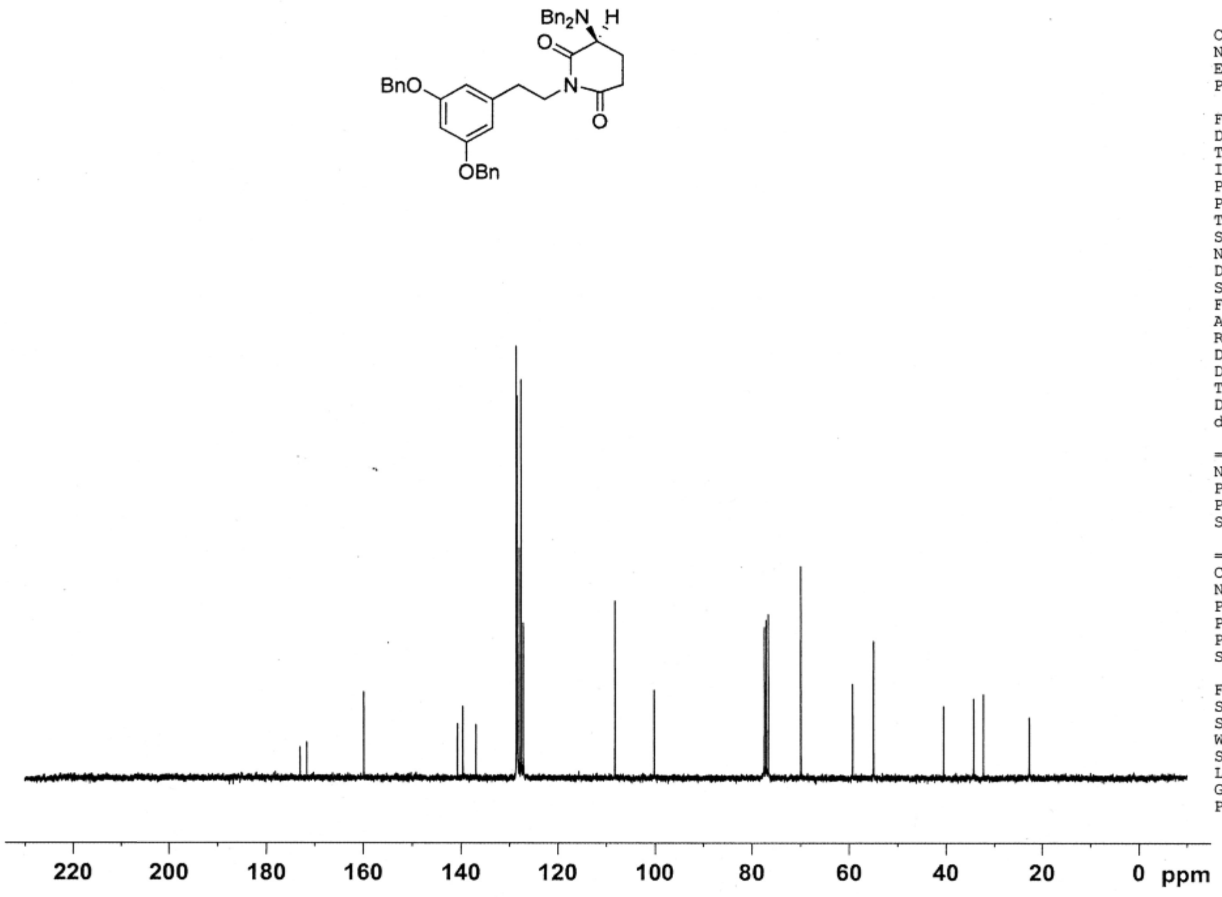
F2 - Acquisition Parameters
Date_           20071220
Time               14.08
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                2298.8
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.60 usec
PL1                -2.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300312 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR spectrum of compound **51**

13C of imide



```
Current Data Parameters
NAME        SunisaSch2800
EXPNO                   6
PROCNO                  1

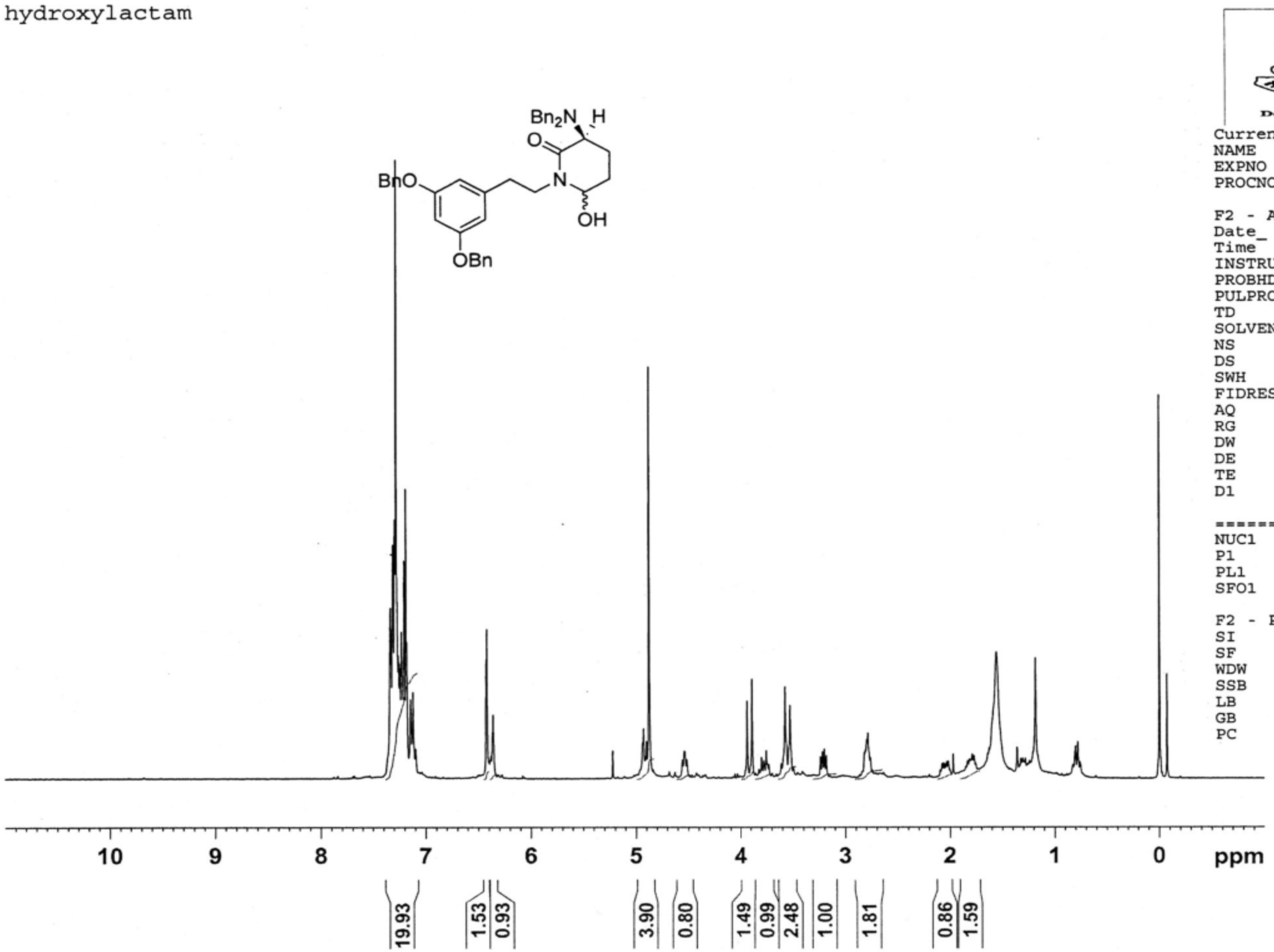
F2 - Acquisition Parameters
Date_            20071220
Time_               15.40
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zgdc
TD                  32768
SOLVENT             CDCl3
NS                    600
DS                      4
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                  13004
DW                 27.600 usec
DE                  20.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   5.20 usec
PL1                 -3.00 dB
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -2.00 dB
PL12                -2.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF             75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

^{13}C NMR spectrum of compound **51**



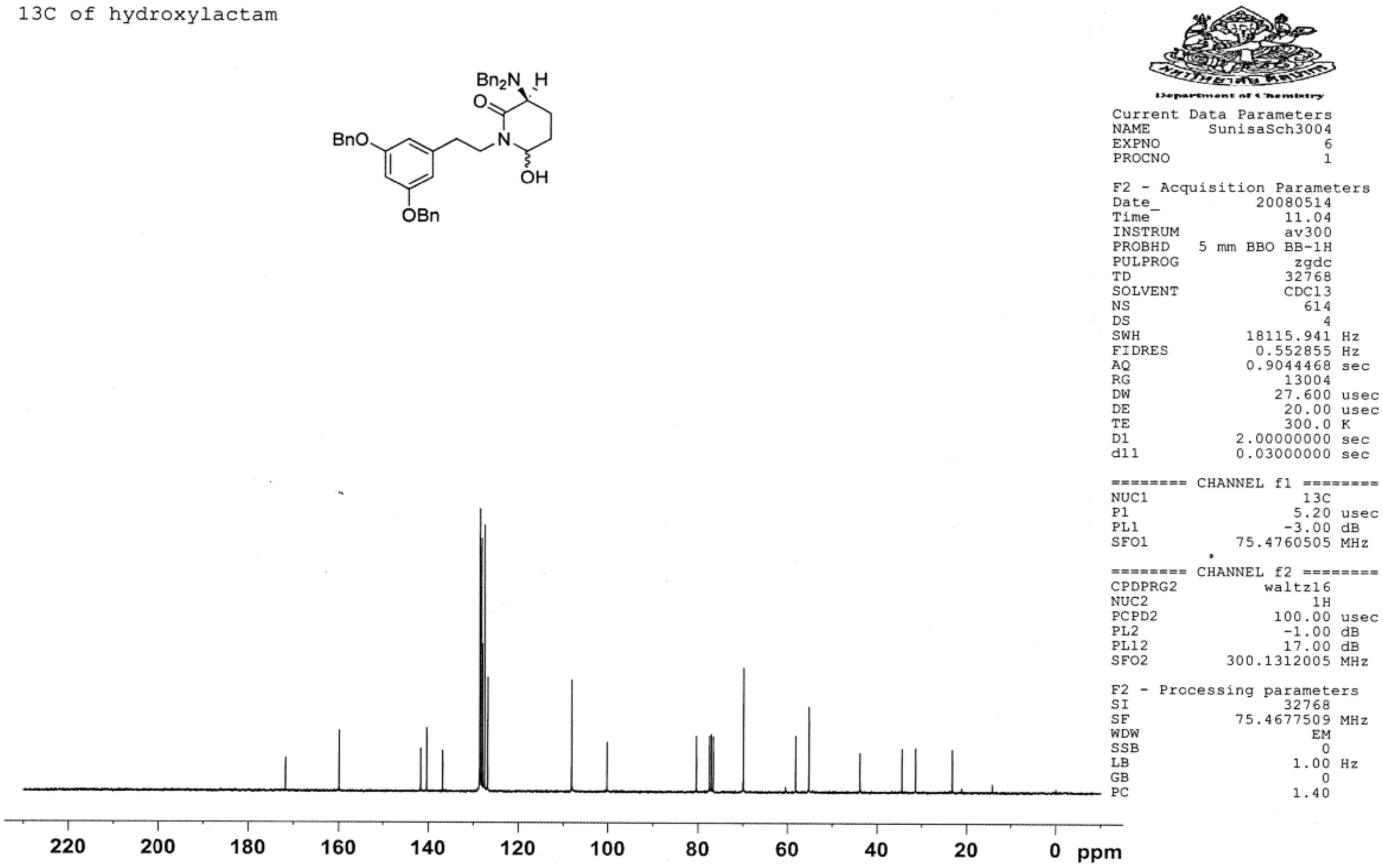
```
Current Data Parameters
NAME        SunisaSch2997
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080411
Time                10.51
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT             CDCl3
NS                     32
DS                      2
SWH              6172.839 Hz
FIDRES           0.376760 Hz
AQ              1.3271540 sec
RG                    362
DW                 81.000 use
DE                  20.00 use
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 =======
NUC1                   1H
P1                  12.80 use
PL1                  0.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300285 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR spectrum of compound **53**



```
Current Data Parameters
NAME       SunisaSch3004
EXPNO                  6
PROCNO                 1

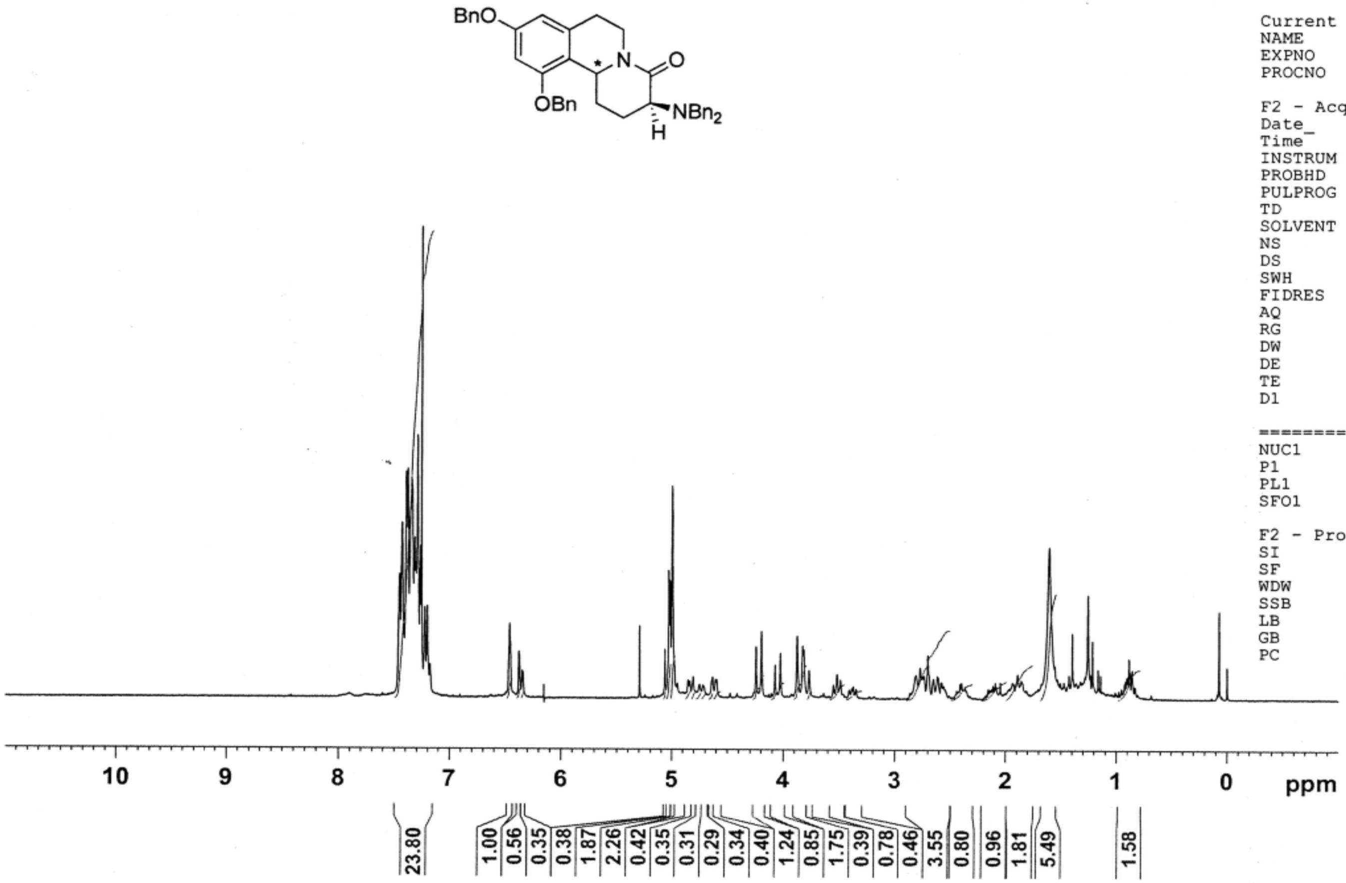
F2 - Acquisition Parameters
Date_           20080514
Time               11.04
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zgdc
TD                 32768
SOLVENT            CDCl3
NS                   614
DS                     4
SWH            18115.941 Hz
FIDRES          0.552855 Hz
AQ             0.9044468 sec
RG                 13004
DW                27.600 usec
DE                 20.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  5.20 usec
PL1                -3.00 dB
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -1.00 dB
PL12               17.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677509 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{13}C NMR spectrum of compound **53** tricyclic core NBn2



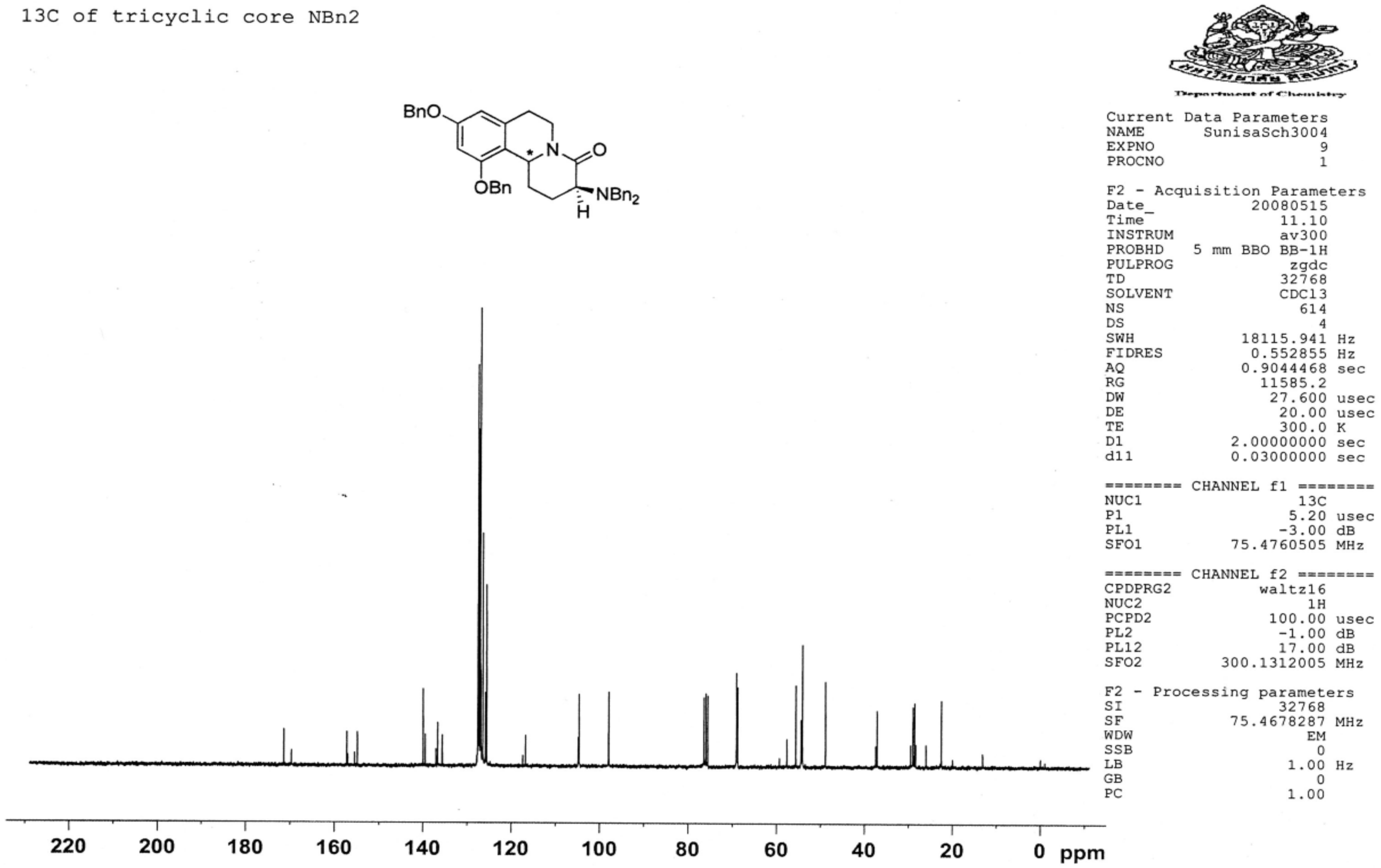
```
Current Data Parameters
NAME       SunisaSch3002
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080508
Time_              10.02
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                   362
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.80 usec
PL1                 0.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300068 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR spectrum of compound **54**



13C of tricyclic core NBn2

```
Current Data Parameters
NAME          SunisaSch3004
EXPNO                     9
PROCNO                    1

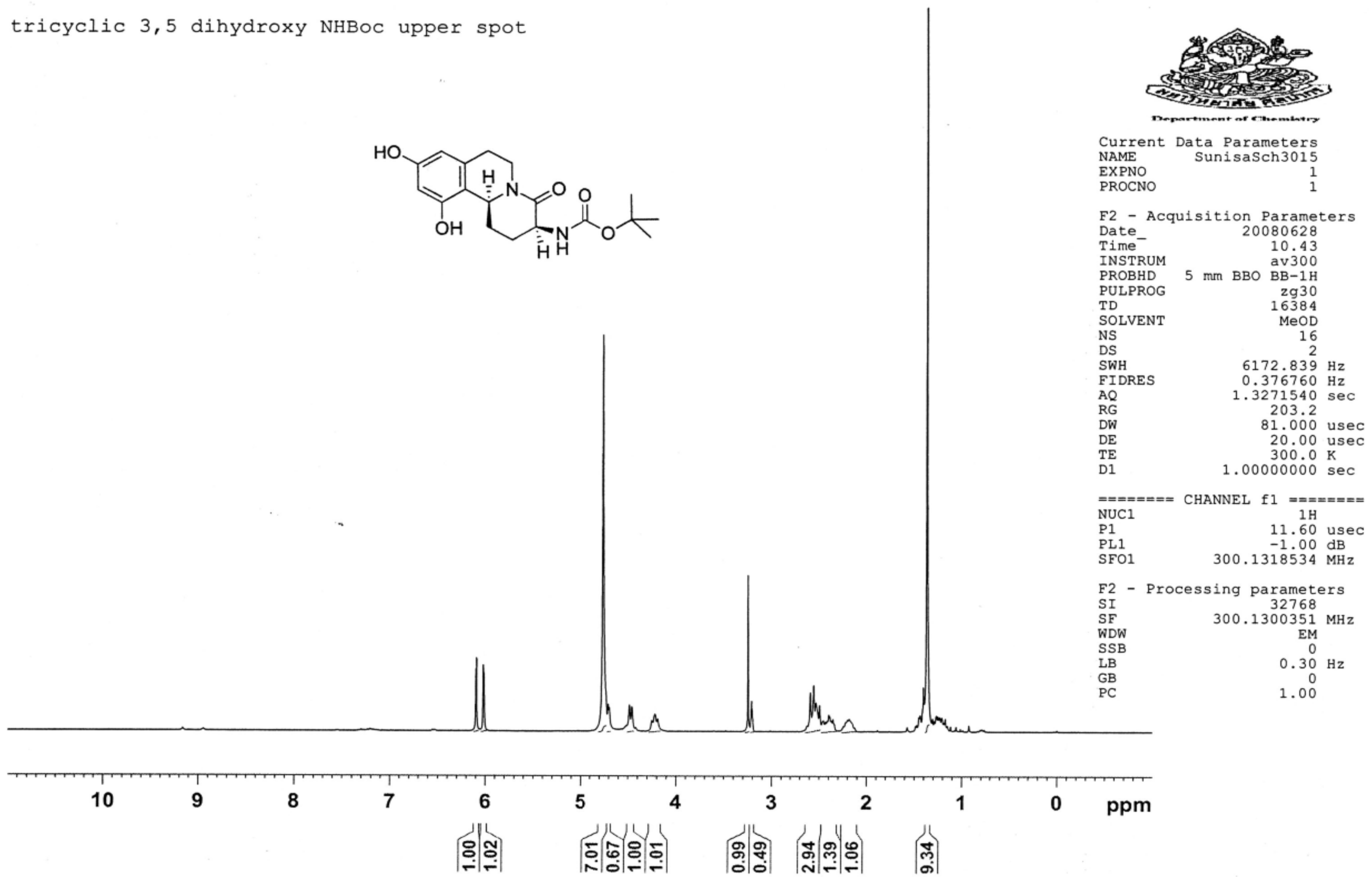
F2 - Acquisition Parameters
Date_              20080515
Time                  11.10
INSTRUM               av300
PROBHD   5 mm BBO BB-1H
PULPROG                zgdc
TD                    32768
SOLVENT               CDCl3
NS                      614
DS                        4
SWH               18115.941 Hz
FIDRES             0.552855 Hz
AQ                0.9044468 sec
RG                  11585.2
DW                   27.600 usec
DE                    20.00 usec
TE                    300.0 K
D1               2.00000000 sec
d11              0.03000000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                     5.20 usec
PL1                   -3.00 dB
SFO1            75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                   -1.00 dB
PL12                  17.00 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF               75.4678287 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.00
```

^{13}C NMR spectrum of compound **54**



tricyclic 3,5 dihydroxy NHBoc upper spot

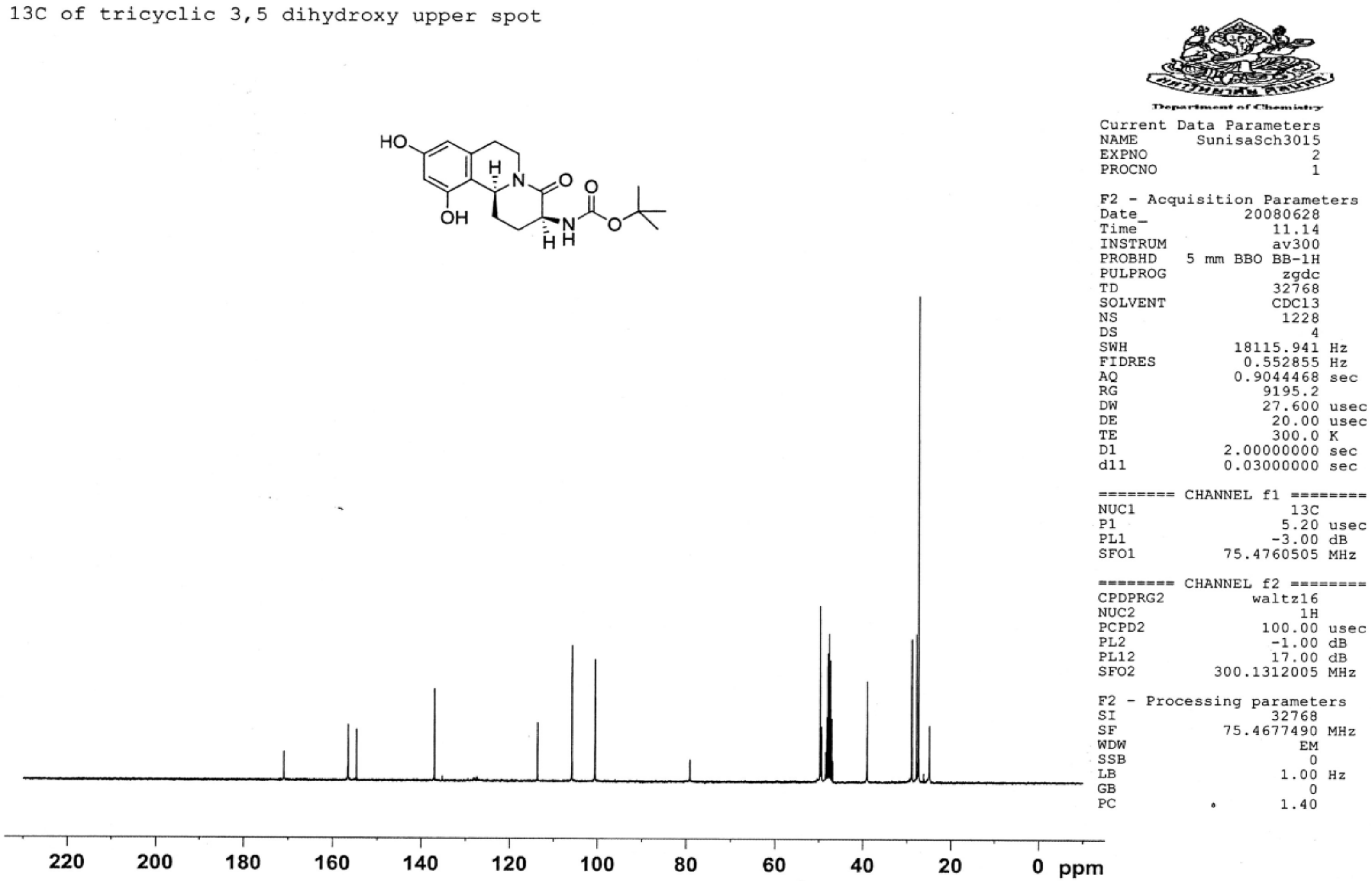
```
Current Data Parameters
NAME        SunisaSch3015
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080628
Time                10.43
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT              MeOD
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.376760 Hz
AQ              1.3271540 sec
RG                  203.2
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.60 usec
PL1                 -1.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300351 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR spectrum of compound **55a**



```
13C of tricyclic 3,5 dihydroxy upper spot
```

```
Department of Chemistry
Current Data Parameters
NAME          SunisaSch3015
EXPNO                     2
PROCNO                    1

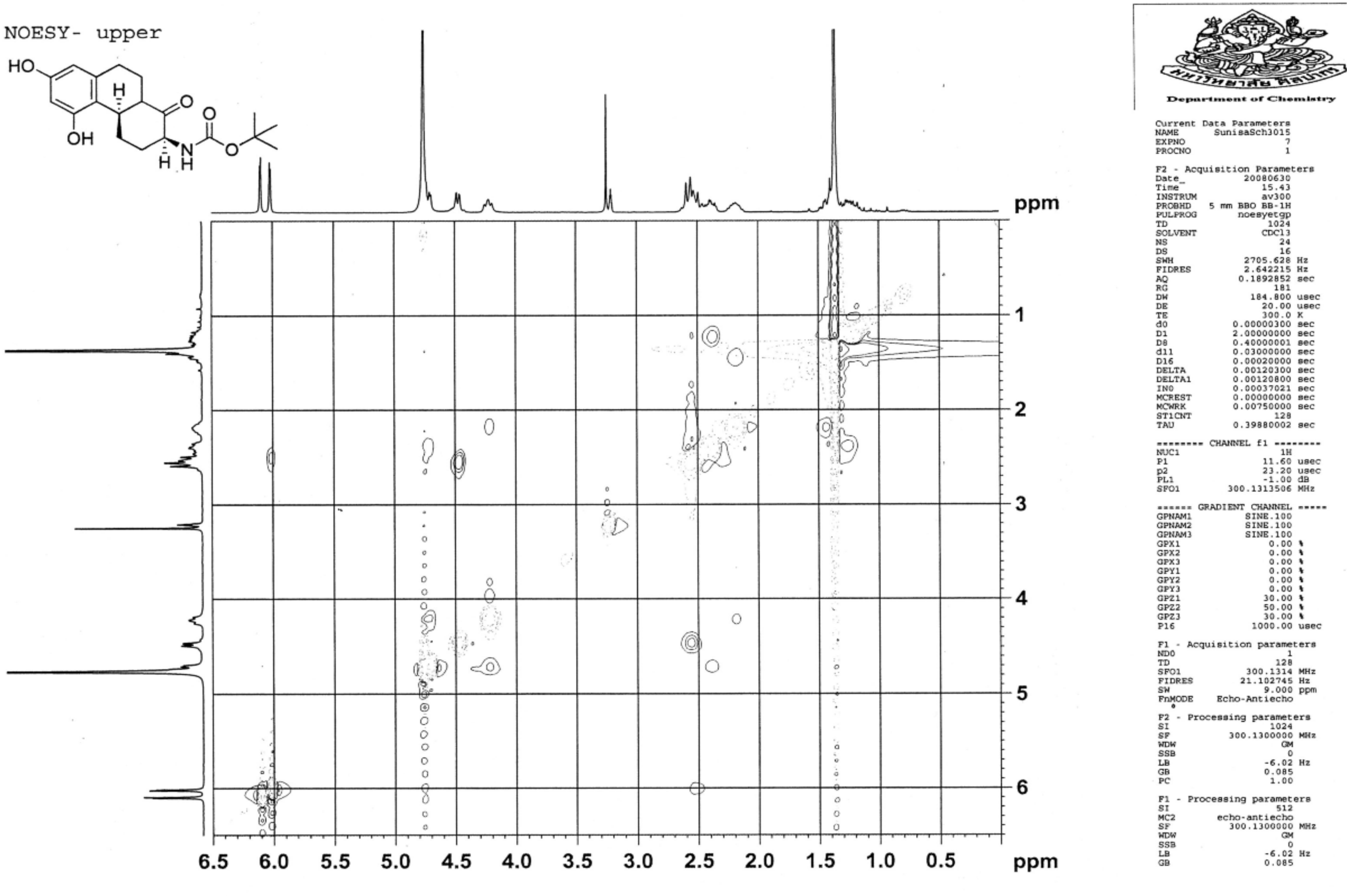
F2 - Acquisition Parameters
Date_              20080628
Time                  11.14
INSTRUM               av300
PROBHD   5 mm BBO BB-1H
PULPROG                zgdc
TD                    32768
SOLVENT               CDCl3
NS                     1228
DS                        4
SWH               18115.941 Hz
FIDRES             0.552855 Hz
AQ                0.9044468 sec
RG                   9195.2
DW                   27.600 usec
DE                    20.00 usec
TE                    300.0 K
D1               2.00000000 sec
d11              0.03000000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                     5.20 usec
PL1                   -3.00 dB
SFO1             75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                   -1.00 dB
PL12                  17.00 dB
SFO2            300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF               75.4677490 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

^{13}C NMR spectrum of compound **55a**



```
Current Data Parameters
NAME       SunisaSch3015
EXPNO                  7
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080630
Time               15.43
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG        noesyetgp
TD                  1024
SOLVENT            CDCl3
NS                    24
DS                    16
SWH             2705.628 Hz
FIDRES          2.642215 Hz
AQ             0.1892852 sec
RG                   181
DW               184.800 usec
DE                 20.00 usec
TE                 300.0 K
d0            0.00000300 sec
D1            2.00000000 sec
D8            0.40000001 sec
d11           0.03000000 sec
D16           0.00020000 sec
DELTA         0.00120300 sec
DELTA1        0.00120800 sec
IN0           0.00037021 sec
MCREST        0.00000000 sec
MCWRK         0.00750000 sec
ST1CNT               128
TAU           0.39880002 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.60 usec
p2                 23.20 usec
PL1                -1.00 dB
SFO1         300.1313506 MHz

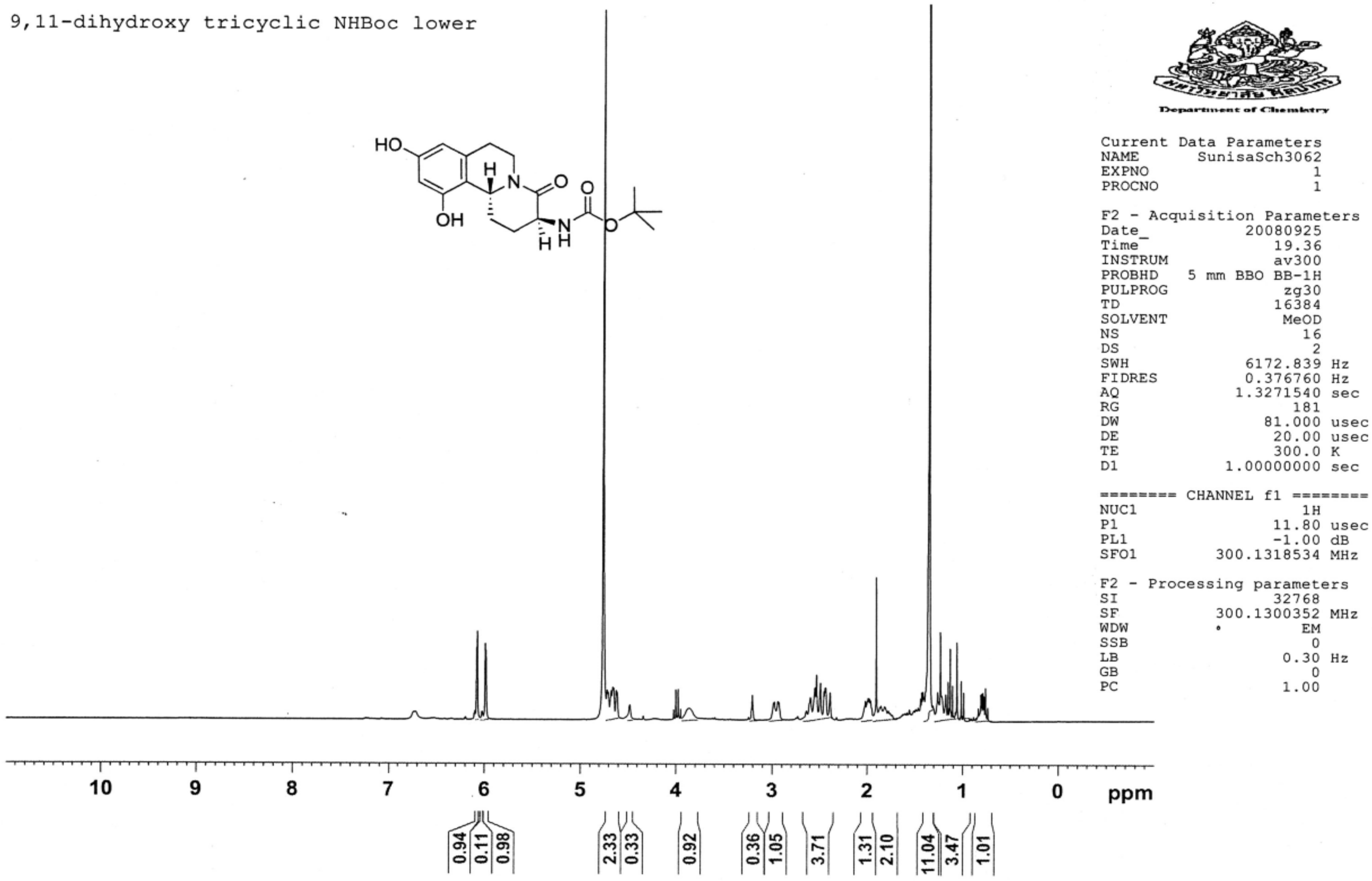
====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPNAM3          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
GPZ3               30.00 %
P16              1000.00 usec

F1 - Acquisition parameters
ND0                    1
TD                   128
SFO1            300.1314 MHz
FIDRES         21.102745 Hz
SW                 9.000 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                  1024
SF           300.1300000 MHz
WDW                   GM
SSB                    0
LB                 -6.02 Hz
GB                 0.085
PC                  1.00

F1 - Processing parameters
SI                   512
MC2       echo-antiecho
SF           300.1300000 MHz
WDW                   GM
SSB                    0
LB                 -6.02 Hz
GB                 0.085
```

NOESY spectrum of compound **55a**



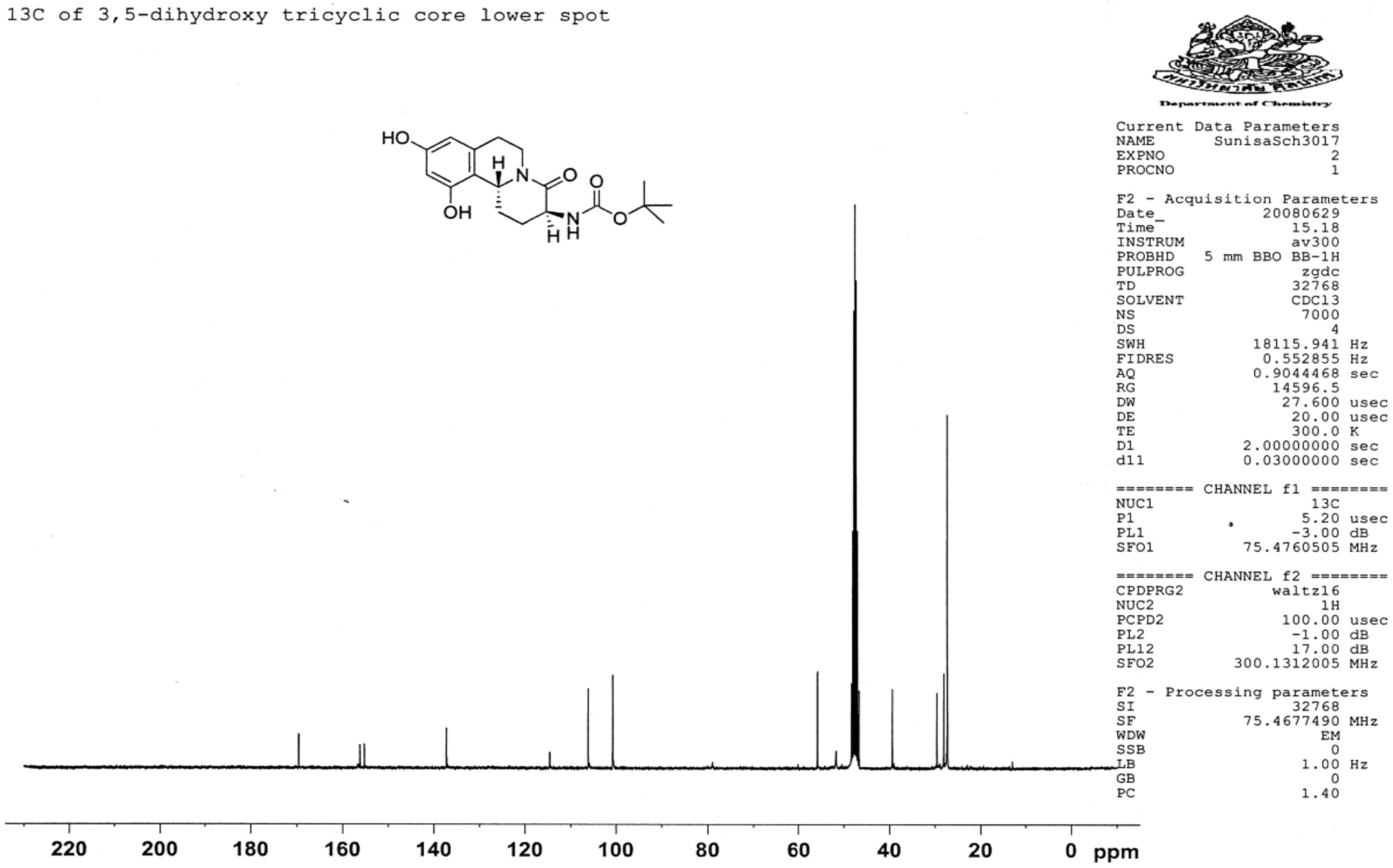
```
Current Data Parameters
NAME         SunisaSch3062
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20080925
Time                 19.36
INSTRUM              av300
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   16384
SOLVENT               MeOD
NS                      16
DS                       2
SWH            6172.839 Hz
FIDRES         0.376760 Hz
AQ            1.3271540 sec
RG                     181
DW              81.000 usec
DE               20.00 usec
TE                300.0 K
D1          1.00000000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1               11.80 usec
PL1               -1.00 dB
SFO1       300.1318534 MHz

F2 - Processing parameters
SI                   32768
SF         300.1300352 MHz
WDW         •           EM
SSB                      0
LB                 0.30 Hz
GB                       0
PC                    1.00
```

^{1}H NMR spectrum of compound **55b**



13C of 3,5-dihydroxy tricyclic core lower spot

```
Current Data Parameters
NAME       SunisaSch3017
EXPNO                  2
PROCNO                 1

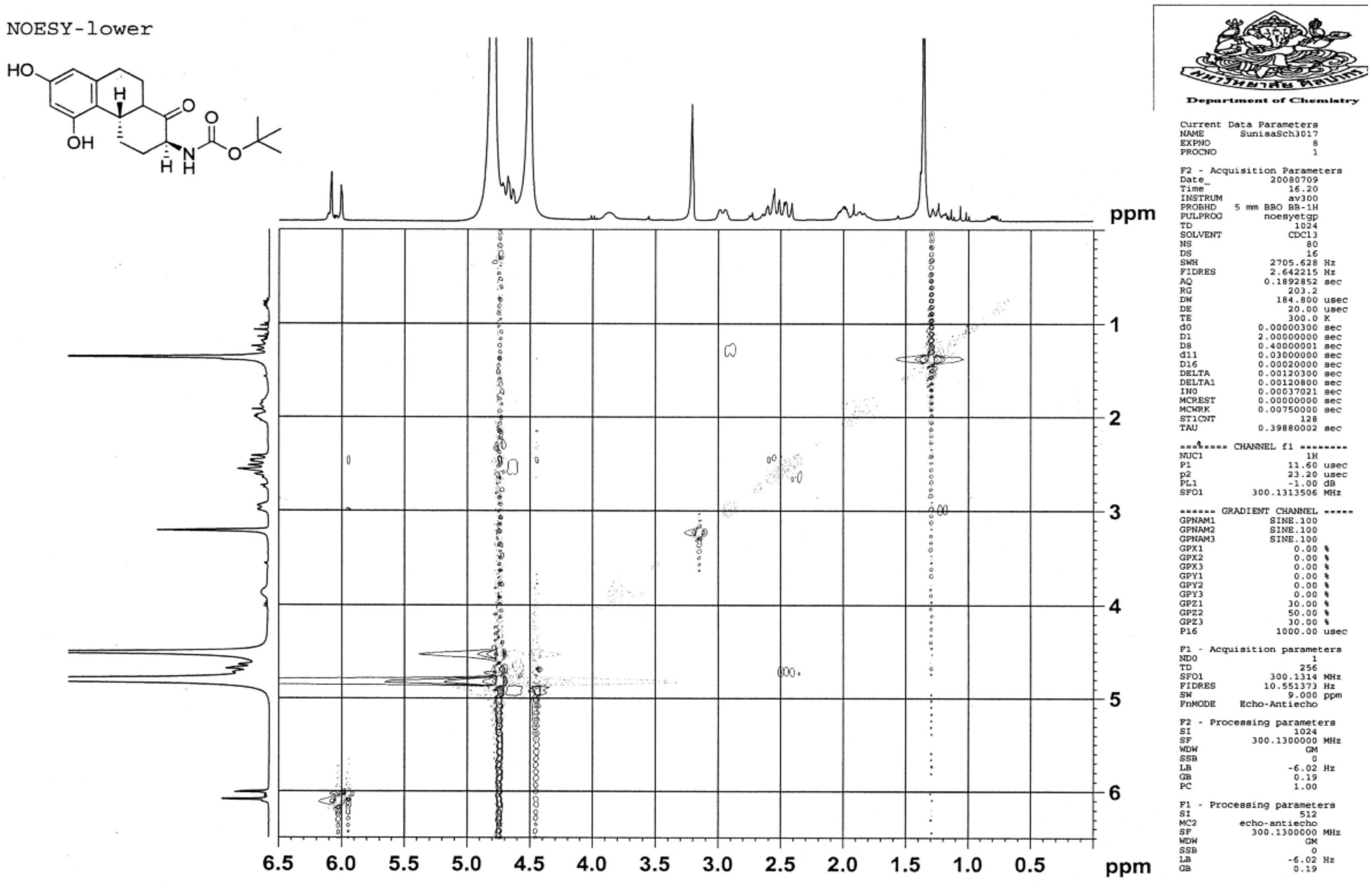
F2 - Acquisition Parameters
Date_           20080629
Time               15.18
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zgdc
TD                 32768
SOLVENT            CDC13
NS                  7000
DS                     4
SWH            18115.941 Hz
FIDRES          0.552855 Hz
AQ             0.9044468 sec
RG               14596.5
DW                27.600 usec
DE                 20.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  5.20 usec
PL1                -3.00 dB
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -1.00 dB
PL12               17.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{13}C NMR spectrum of compound **55b**



```
Current Data Parameters
NAME        SunisaSch3017
EXPNO                   8
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080709
Time                16.20
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG         noesyetgp
TD                   1024
SOLVENT             CDCl3
NS                     80
DS                     16
SWH              2705.628 Hz
FIDRES           2.642215 Hz
AQ              0.1892852 sec
RG                  203.2
DW                184.800 usec
DE                  20.00 usec
TE                  300.0 K
d0             0.00000300 sec
D1             2.00000000 sec
D8             0.40000001 sec
d11            0.03000000 sec
D16            0.00020000 sec
DELTA          0.00120300 sec
DELTA1         0.00120800 sec
IN0            0.00037021 sec
MCREST         0.00000000 sec
MCWRK          0.00750000 sec
ST1CNT                128
TAU            0.39880002 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.60 usec
p2                  23.20 usec
PL1                 -1.00 dB
SFO1          300.1313506 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPNAM3           SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPX3                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPY3                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
GPZ3                30.00 %
P16               1000.00 usec

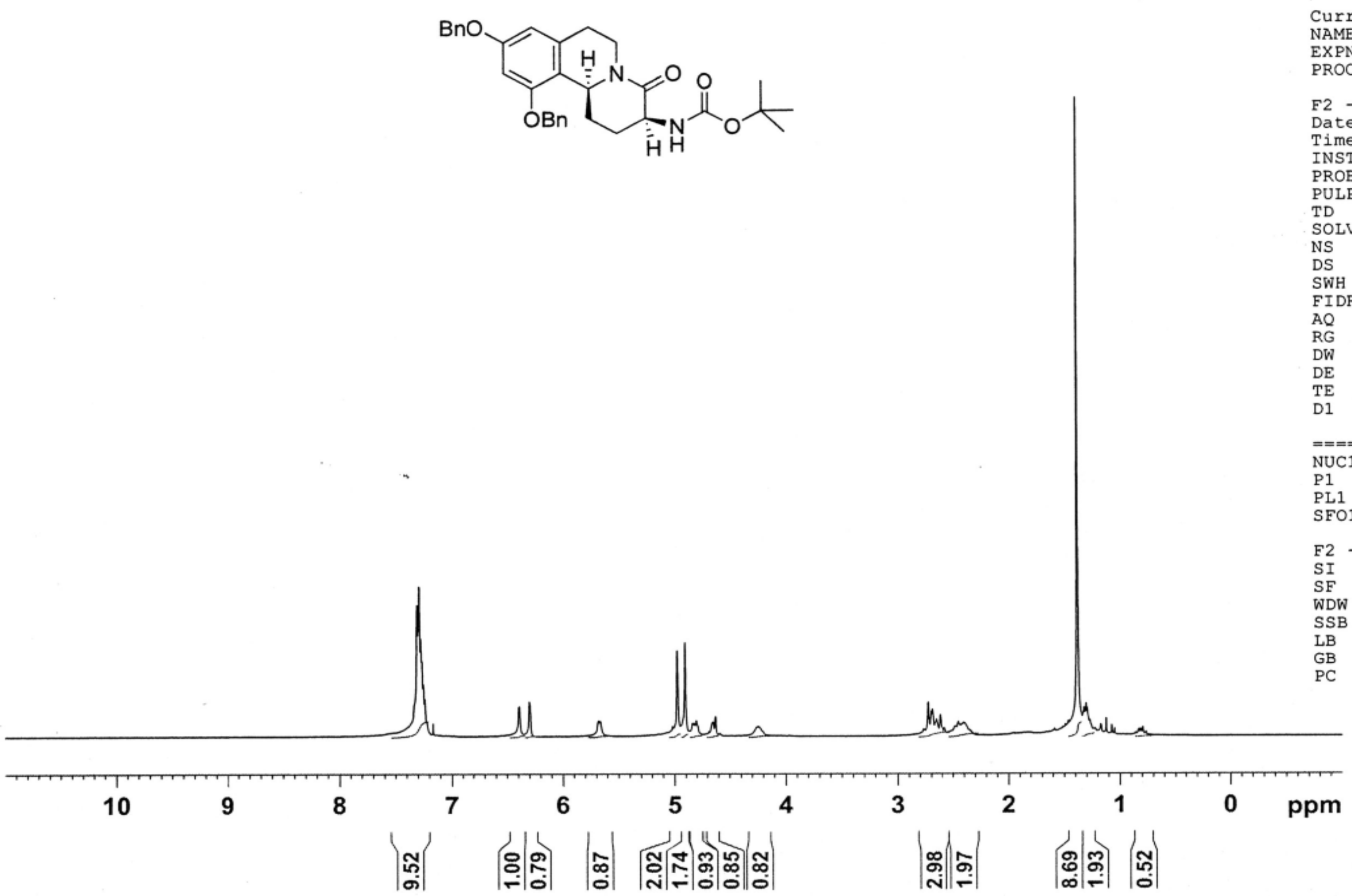
F1 - Acquisition parameters
ND0                     1
TD                    256
SFO1             300.1314 MHz
FIDRES          10.551373 Hz
SW                  9.000 ppm
FnMODE       Echo-Antiecho

F2 - Processing parameters
SI                   1024
SF            300.1300000 MHz
WDW                    GM
SSB                     0
LB                  -6.02 Hz
GB                   0.19
PC                   1.00

F1 - Processing parameters
SI                    512
MC2         echo-antiecho
SF            300.1300000 MHz
WDW                    GM
SSB                     0
LB                  -6.02 Hz
GB                   0.19
```

NOESY spectrum of compound **55b**

3,5-dibenzyloxy tricyclic core upper



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```
Current Data Parameters
NAME        SunisaSch3022
EXPNO                   1
PROCNO                  1

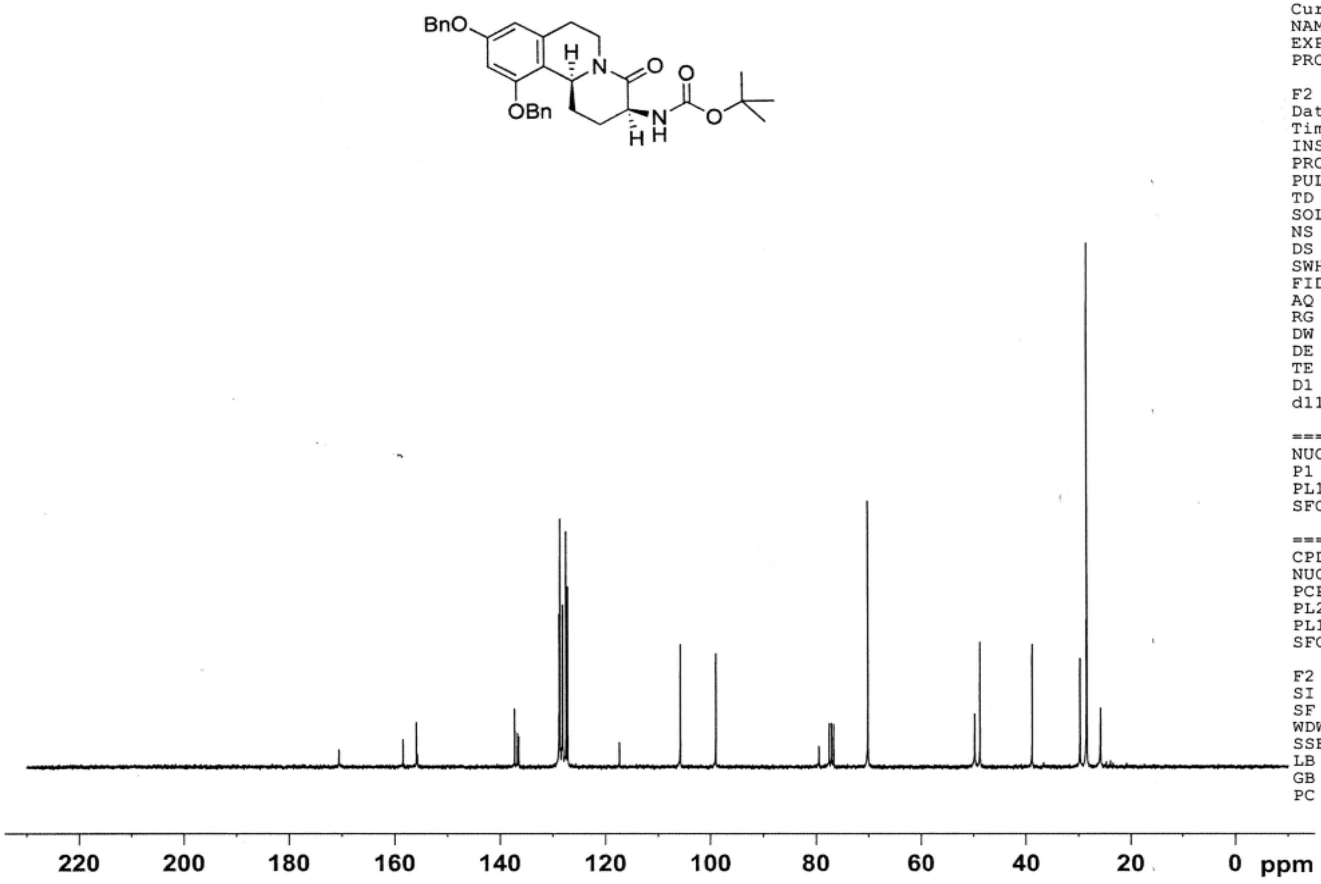
F2 - Acquisition Parameters
Date_            20080708
Time                10.07
INSTRUM             av300
PROBHD    5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT             CDC13
NS                     16
DS                      2
SWH          6172.839 Hz
FIDRES       0.376760 Hz
AQ          1.3271540 sec
RG                    128
DW             81.000 usec
DE             20.00 usec
TE              300.0 K
D1         1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1              11.60 usec
PL1             -1.00 dB
SFO1       300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF         300.1300338 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR spectrum of compound **56a**

13C of 3,5-dibenzyloxy tricyclic core upper



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```
Current Data Parameters
NAME        SunisaSch3022
EXPNO                   3
PROCNO                  1

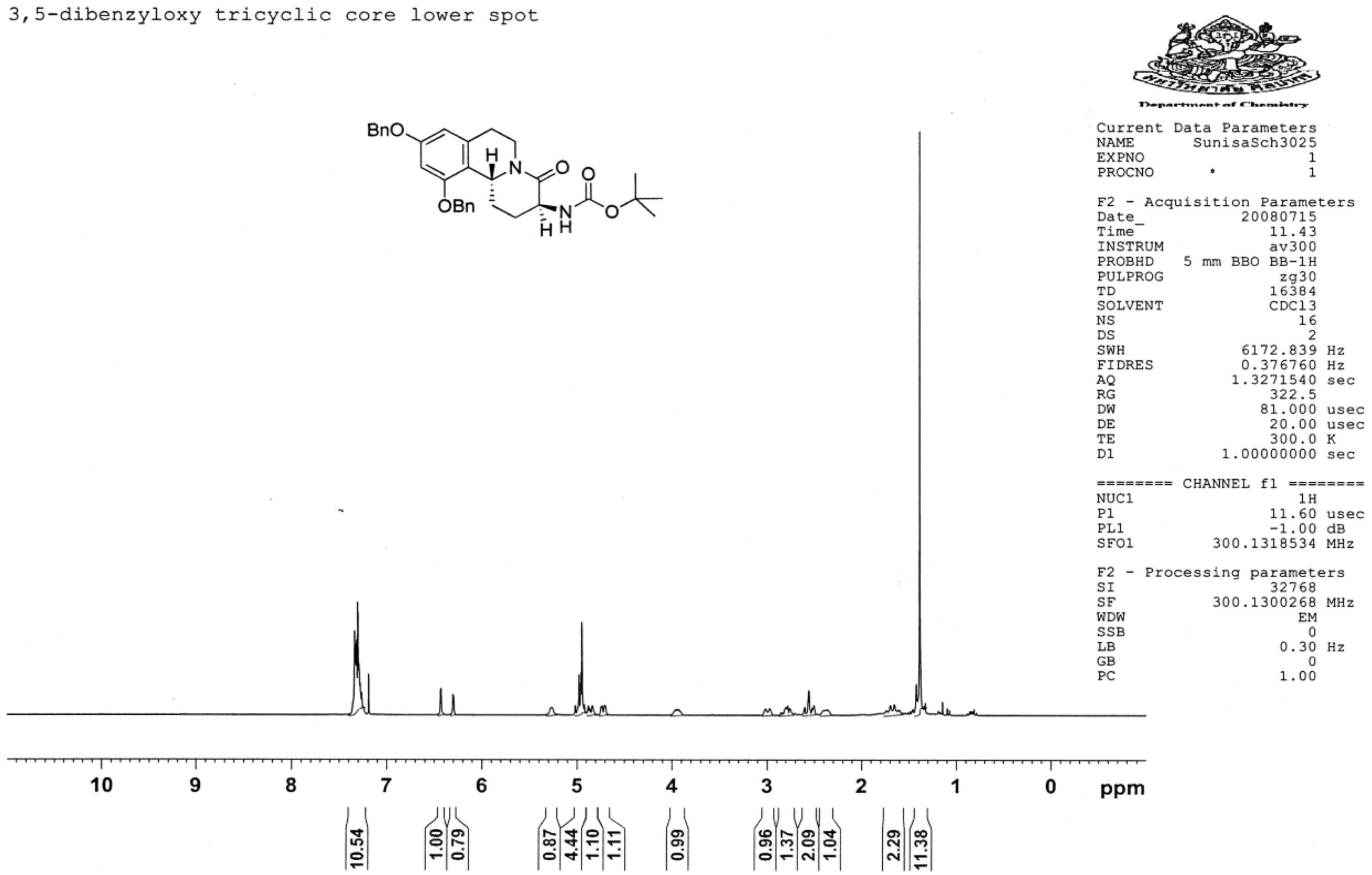
F2 - Acquisition Parameters
Date_            20080708
Time                10.31
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zgdc
TD                  32768
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                  16384
DW                 27.600 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   5.20 usec
PL1                 -3.00 dB
SFO1           75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -1.00 dB
PL12                17.00 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF             75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

^{13}C NMR spectrum of compound **56a**



3,5-dibenzyloxy tricyclic core lower spot

```
Current Data Parameters
NAME       SunisaSch3025
EXPNO                  1
PROCNO      •          1

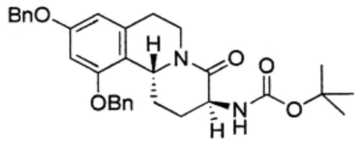
F2 - Acquisition Parameters
Date_           20080715
Time_              11.43
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                 322.5
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

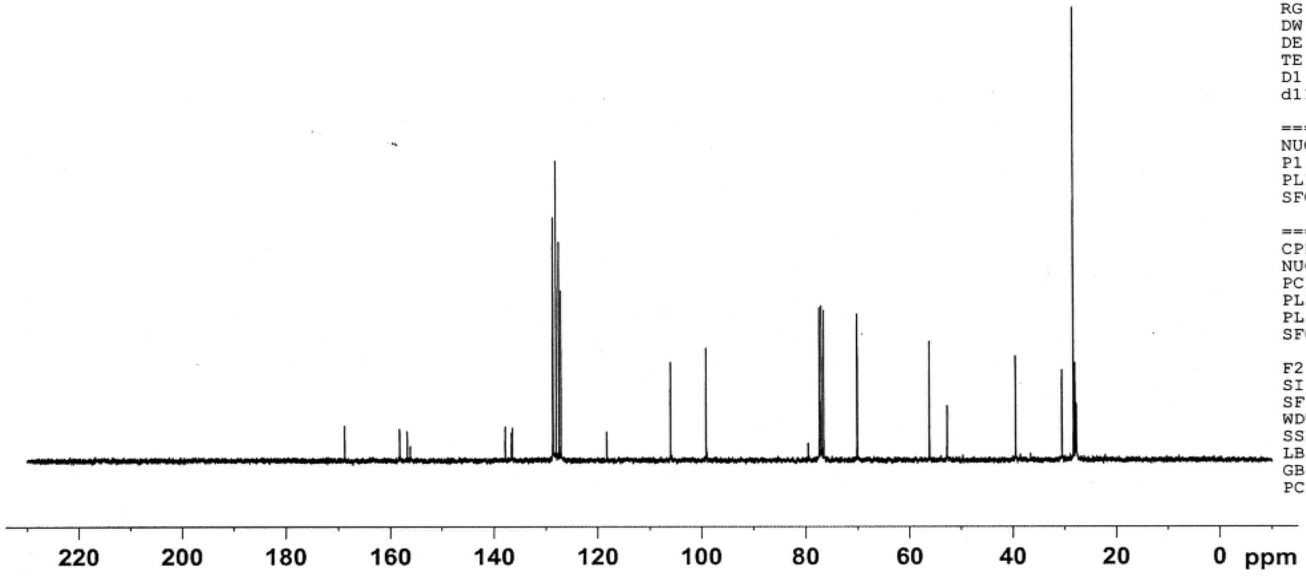
======== CHANNEL f1 ========
NUC1                  1H
P1                 11.60 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300268 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR spectrum of compound **56b**

13C of 3,5-dibenzyloxy tricyclic core lower spot





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```
Current Data Parameters
NAME      SunisaSch3025
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20080715
Time_             11.48
INSTRUM           av300
PROBHD   5 mm BBO BB-1H
PULPROG            zgdc
TD                32768
SOLVENT           CDCl3
NS                 2048
DS                    4
SWH           18115.941 Hz
FIDRES         0.552855 Hz
AQ            0.9044468 sec
RG              18390.4
DW               27.600 usec
DE                20.00 usec
TE                300.0 K
D1           1.00000000 sec
d11          0.03000000 sec

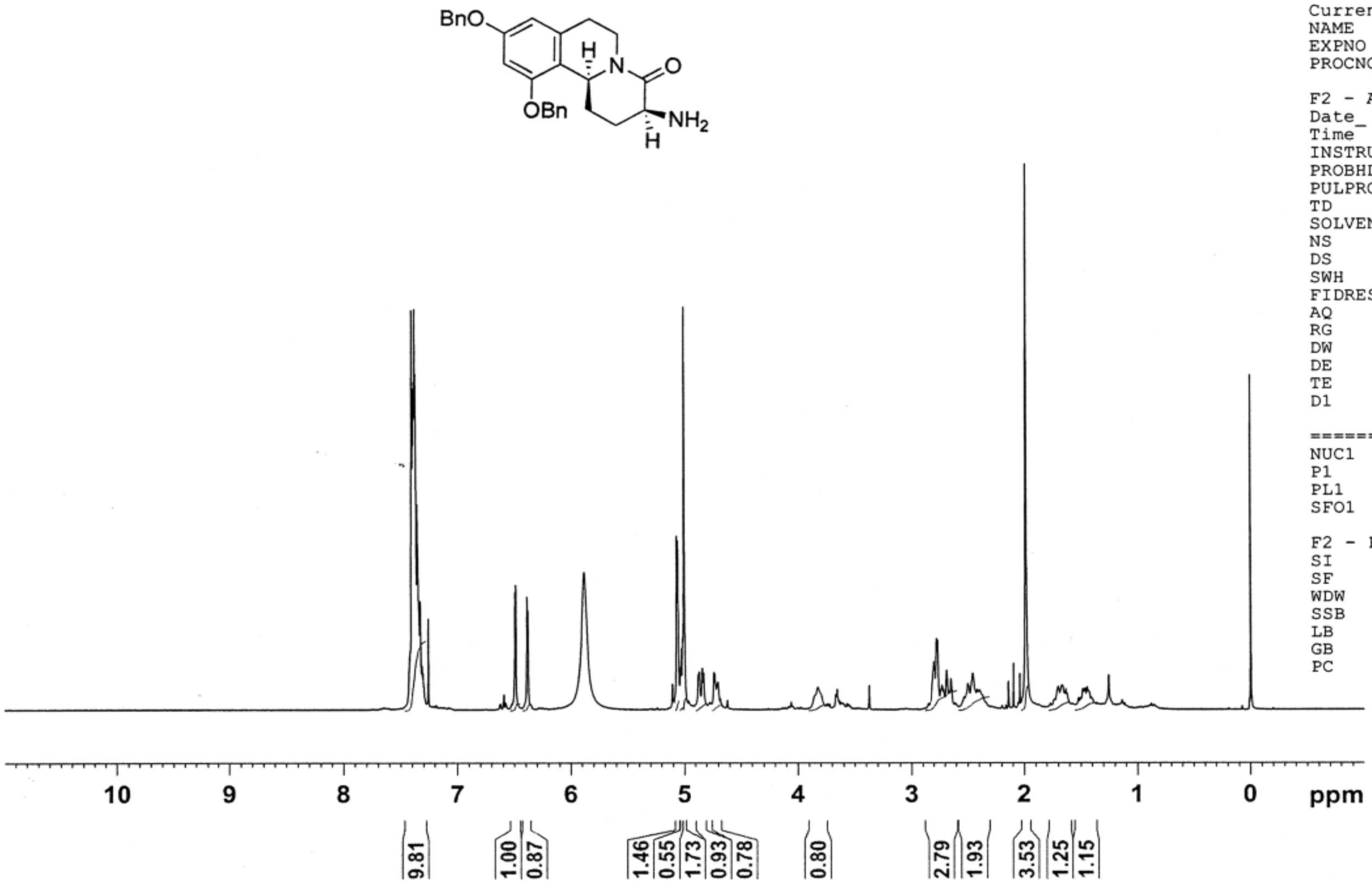
======== CHANNEL f1 ========
NUC1                13C
P1                 5.20 usec
PL1               -3.00 dB
SFO1         75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2               -1.00 dB
PL12              17.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
SF           75.4677490 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

^{13}C NMR spectrum of compound **56b**

tricyclic amine upper



```
Current Data Parameters
NAME        SunisaSch3064
EXPNO                   1
PROCNO                  1

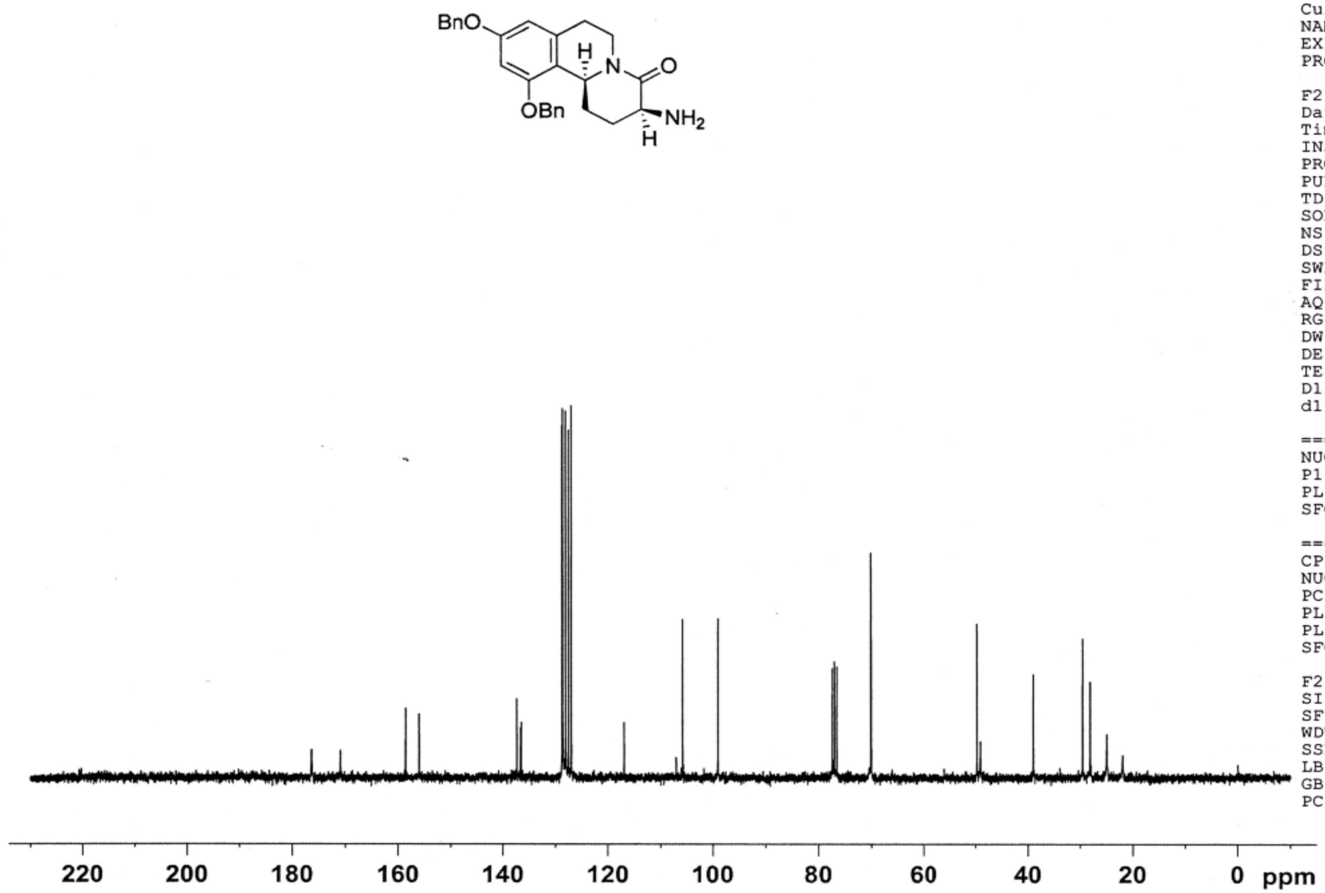
F2 - Acquisition Parameters
Date_            20080930
Time                14.53
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.376760 Hz
AQ              1.3271540 sec
RG                  203.2
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.80 usec
PL1                 -1.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300071 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR spectrum of compound **57a**

13C of tricyclic amine upper



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```
Current Data Parameters
NAME        SunisaSch3064
EXPNO                   2
PROCNO                  1

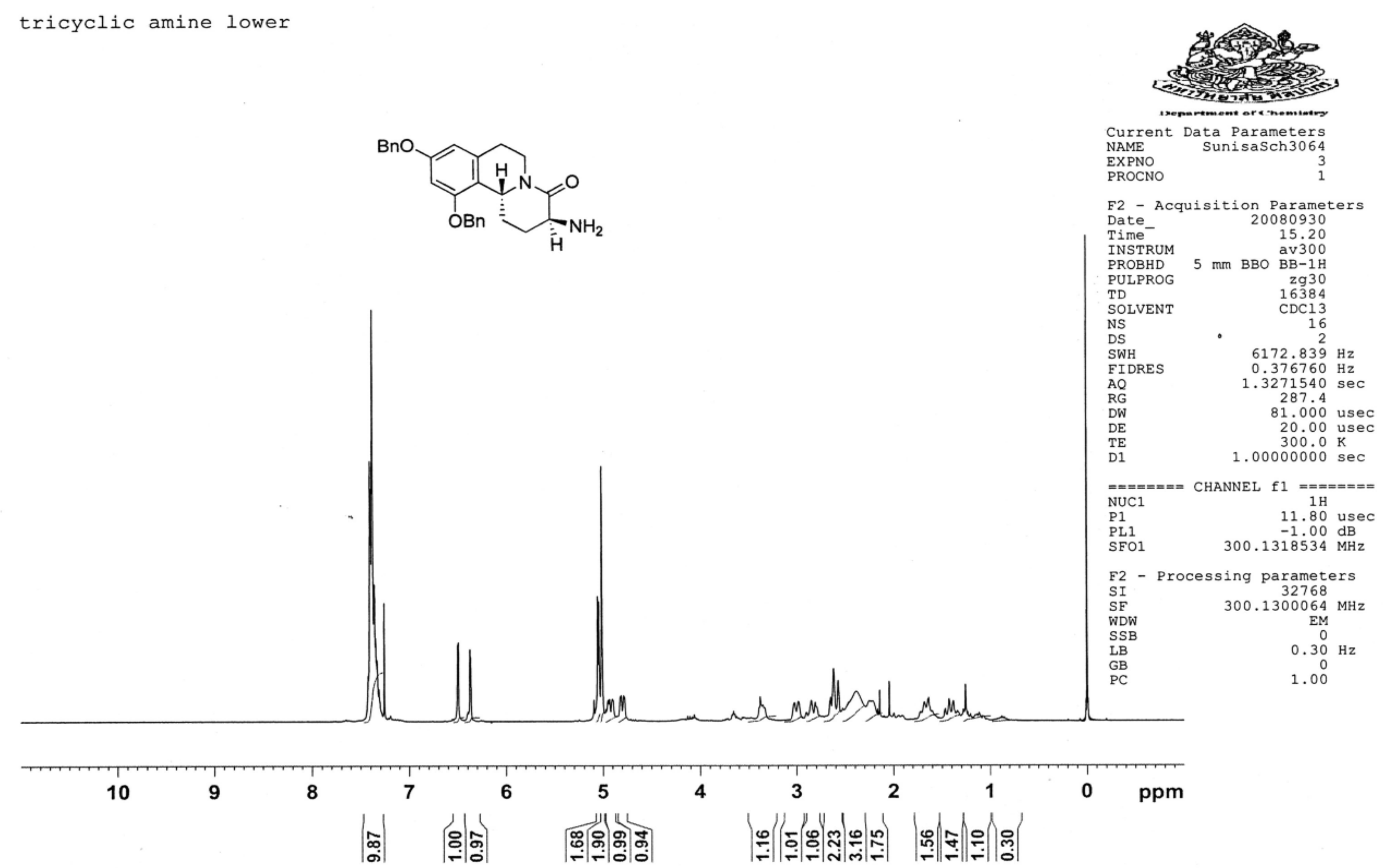
F2 - Acquisition Parameters
Date_            20080930
Time                15.05
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zgdc
TD                  32768
SOLVENT             CDCl3
NS                    512
DS                      4
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                10321.3
DW                 27.600 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   5.40 usec
PL1                 -3.00 dB
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -1.00 dB
PL12                17.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF            75.4677486 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00
```

^{13}C NMR spectrum of compound **57a**


tricyclic amine lower

```
Current Data Parameters
NAME       SunisaSch3064
EXPNO                  3
PROCNO                 1

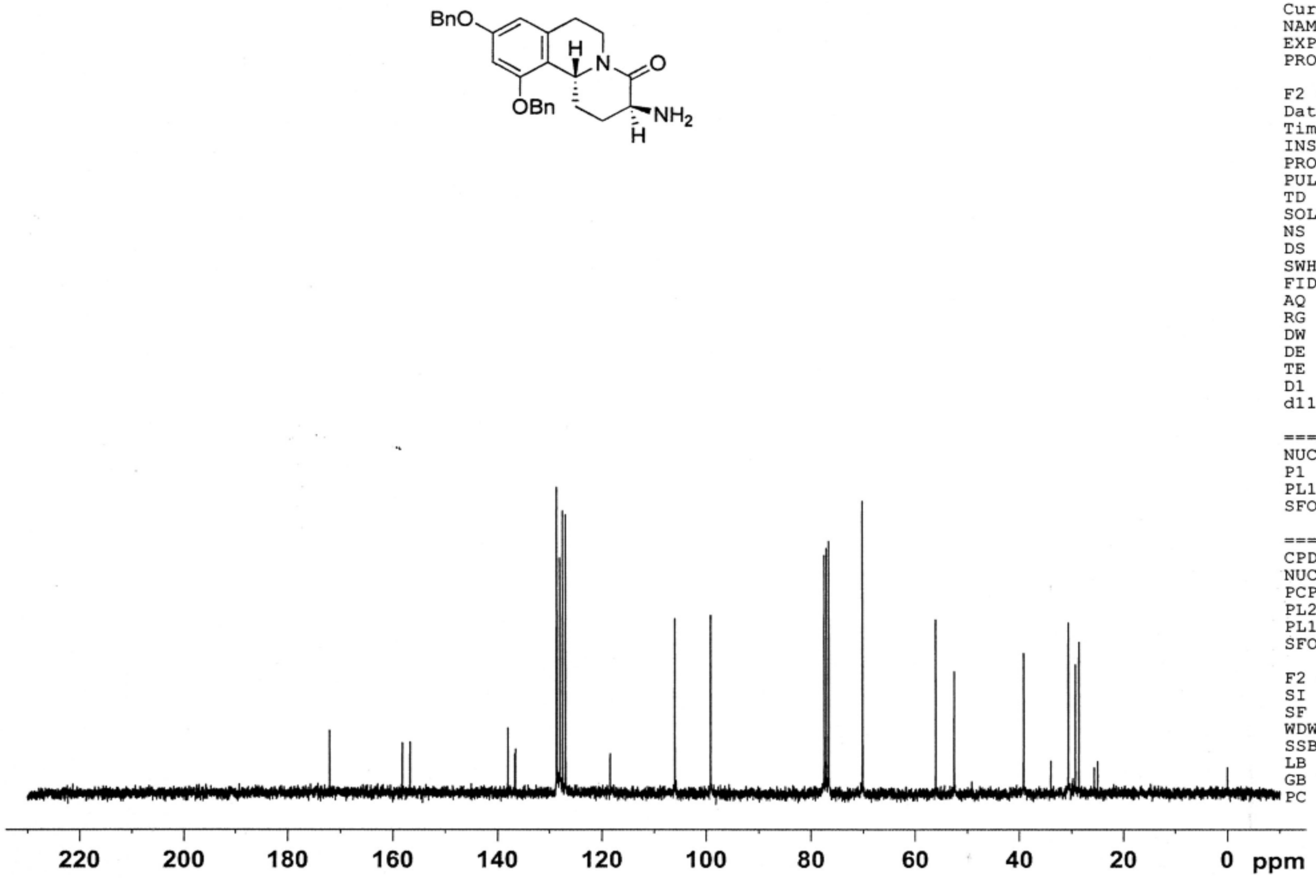
F2 - Acquisition Parameters
Date_           20080930
Time               15.20
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            6172.839 Hz
FIDRES         0.376760 Hz
AQ            1.3271540 sec
RG                 287.4
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.80 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300064 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR spectrum of compound **57b**

13C of tricyclic amine lower



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```
Current Data Parameters
NAME         SunisaSch3064
EXPNO                    4
PROCNO                   1

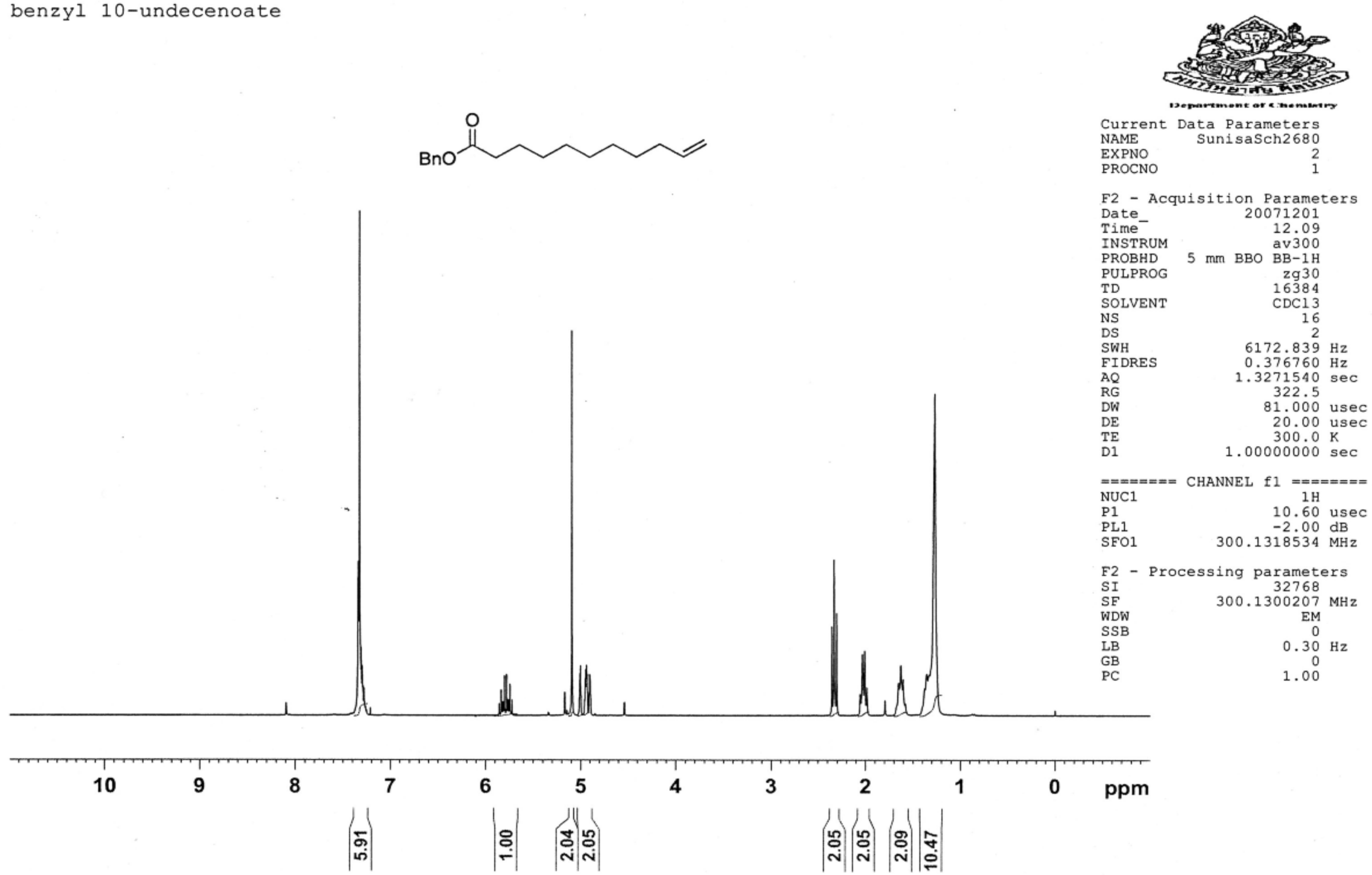
F2 - Acquisition Parameters
Date_             20080930
Time                 15.28
INSTRUM              av300
PROBHD   5 mm BBO BB-1H
PULPROG               zgdc
TD                   32768
SOLVENT              CDCl3
NS                     700
DS                       4
SWH              18115.941 Hz
FIDRES            0.552855 Hz
AQ               0.9044468 sec
RG                   16384
DW                  27.600 usec
DE                   20.00 usec
TE                   300.0 K
D1              1.00000000 sec
d11             0.03000000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    5.40 usec
PL1                  -3.00 dB
SFO1           75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                  -1.00 dB
PL12                 17.00 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                   32768
SF              75.4677490 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

^{13}C NMR spectrum of compound **57b**



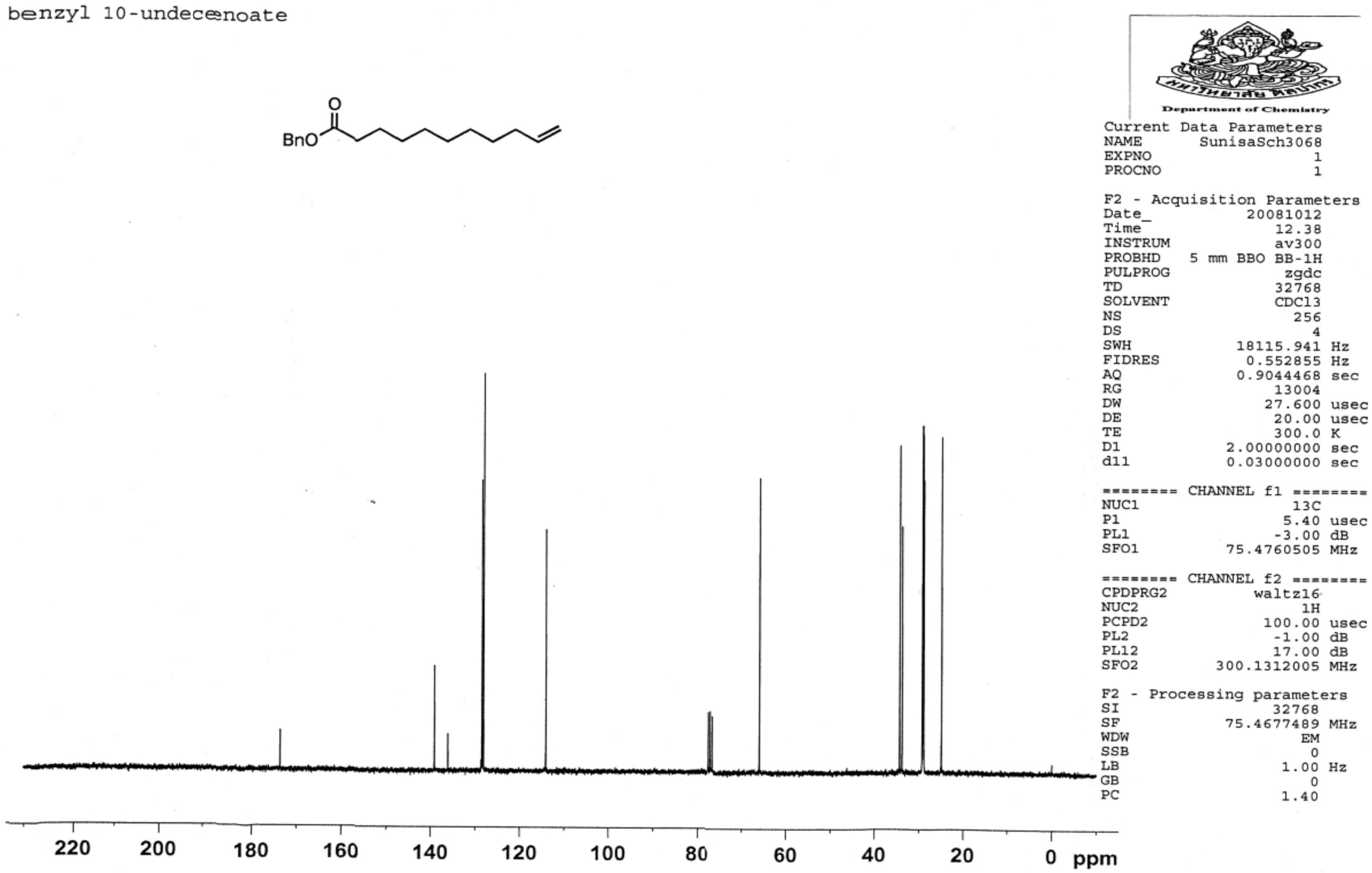
```
Current Data Parameters
NAME       SunisaSch2680
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20071201
Time               12.09
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                 322.5
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.60 usec
PL1                -2.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300207 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR spectrum of compound **63**



```
Current Data Parameters
NAME          SunisaSch3068
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20081012
Time                  12.38
INSTRUM               av300
PROBHD   5 mm BBO BB-1H
PULPROG                zgdc
TD                    32768
SOLVENT               CDCl3
NS                      256
DS                        4
SWH               18115.941 Hz
FIDRES             0.552855 Hz
AQ                0.9044468 sec
RG                    13004
DW                   27.600 usec
DE                    20.00 usec
TE                    300.0 K
D1               2.00000000 sec
d11              0.03000000 sec

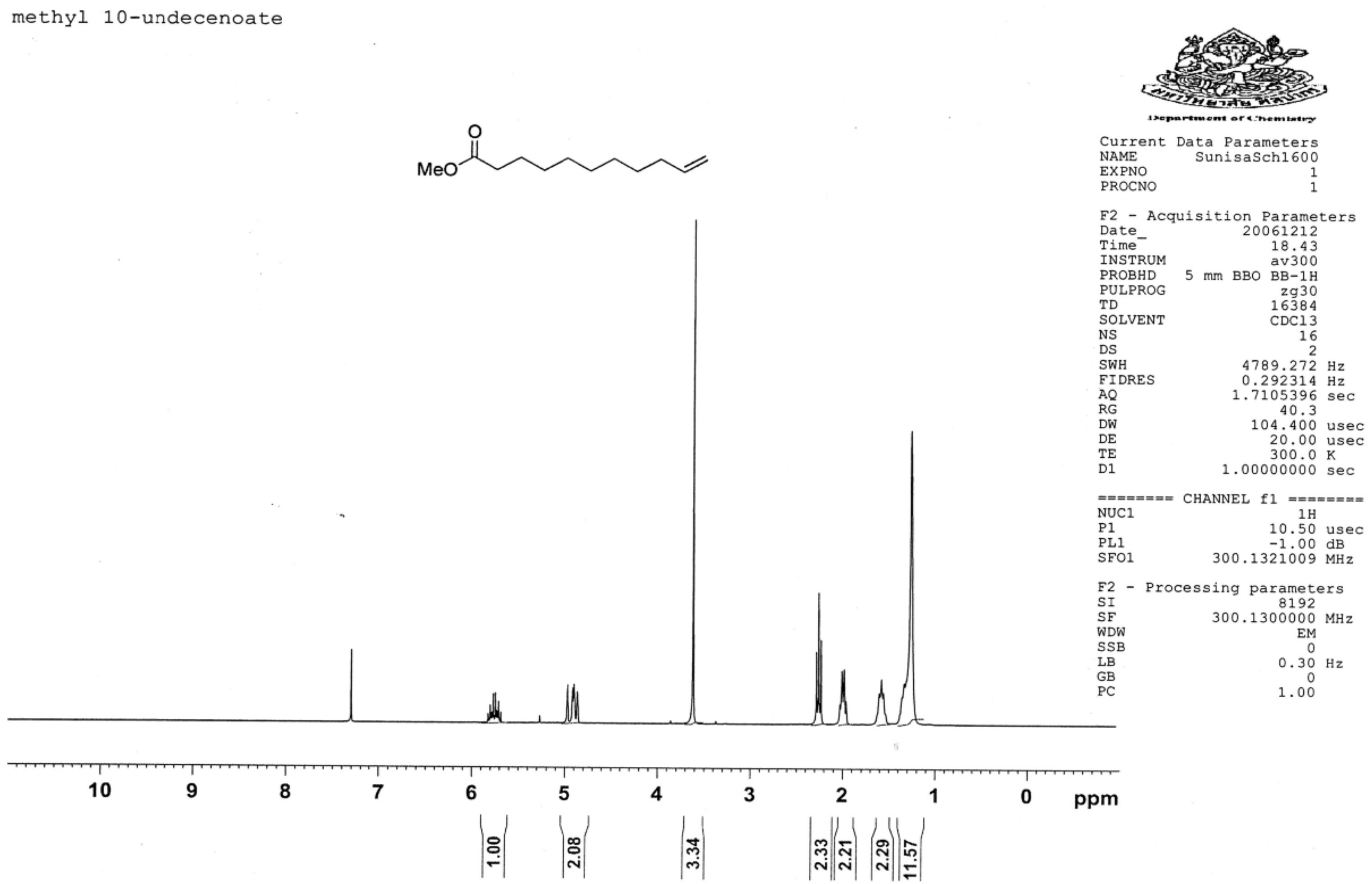
======== CHANNEL f1 ========
NUC1                    13C
P1                     5.40 usec
PL1                   -3.00 dB
SFO1            75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                   -1.00 dB
PL12                  17.00 dB
SFO2            300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF               75.4677489 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

^{13}C NMR spectrum of compound **63**

methyl 10-undecenoate



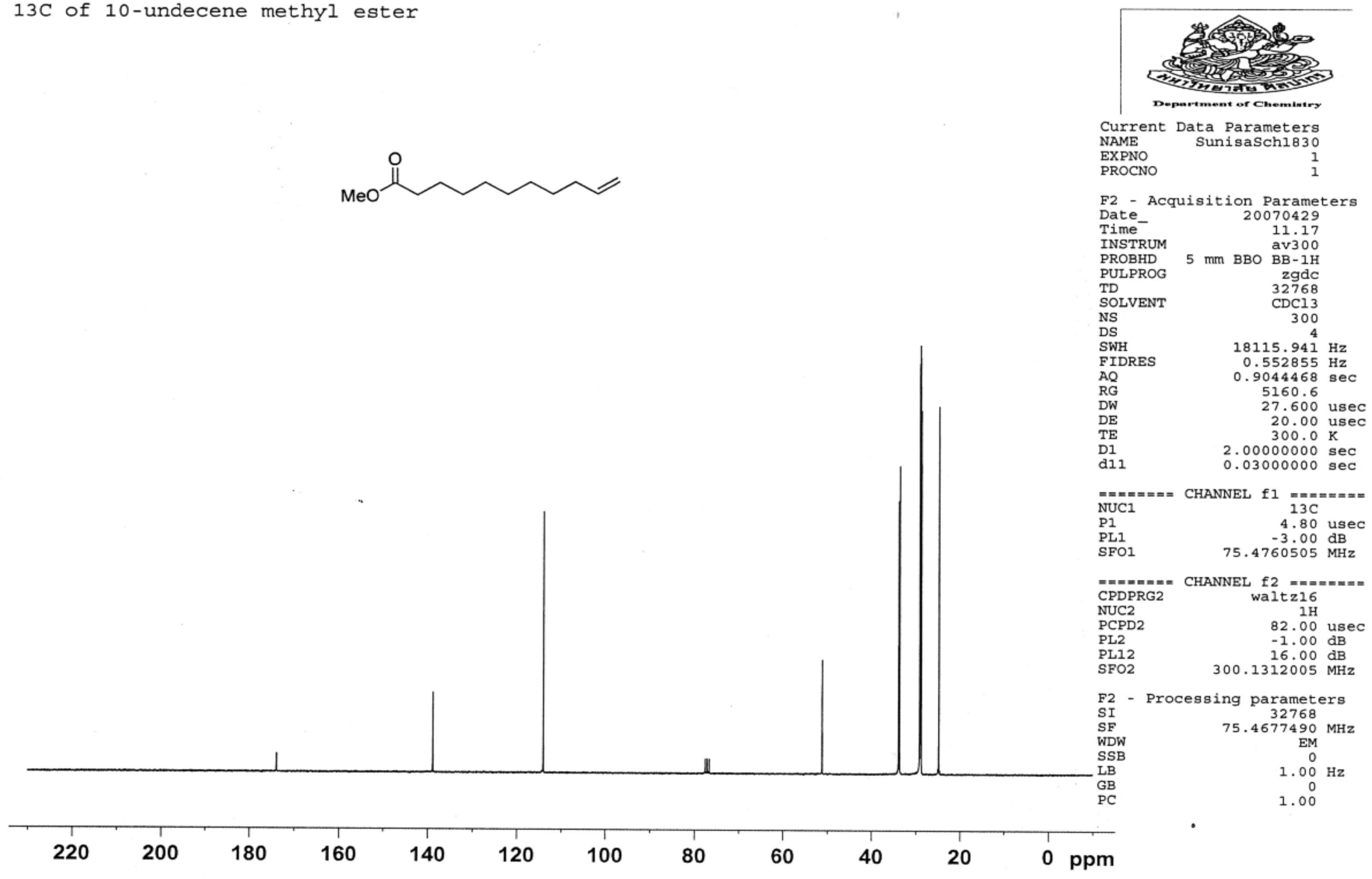
```
Current Data Parameters
NAME       SunisaSch1600
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20061212
Time               18.43
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4789.272 Hz
FIDRES          0.292314 Hz
AQ             1.7105396 sec
RG                  40.3
DW               104.400 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.50 usec
PL1                -1.00 dB
SFO1         300.1321009 MHz

F2 - Processing parameters
SI                  8192
SF           300.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR spectrum of compound **71**



13C of 10-undecene methyl ester

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```
Current Data Parameters
NAME        SunisaSch1830
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070429
Time                11.17
INSTRUM             av300
PROBHD    5 mm BBO BB-1H
PULPROG              zgdc
TD                  32768
SOLVENT             CDCl3
NS                    300
DS                      4
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                 5160.6
DW                 27.600 usec
DE                  20.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec

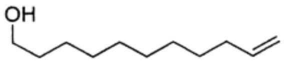
======== CHANNEL f1 ========
NUC1                  13C
P1                   4.80 usec
PL1                 -3.00 dB
SFO1           75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               82.00 usec
PL2                 -1.00 dB
PL12                16.00 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF             75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00
```

^{13}C NMR spectrum of compound **71**

10-undecenol

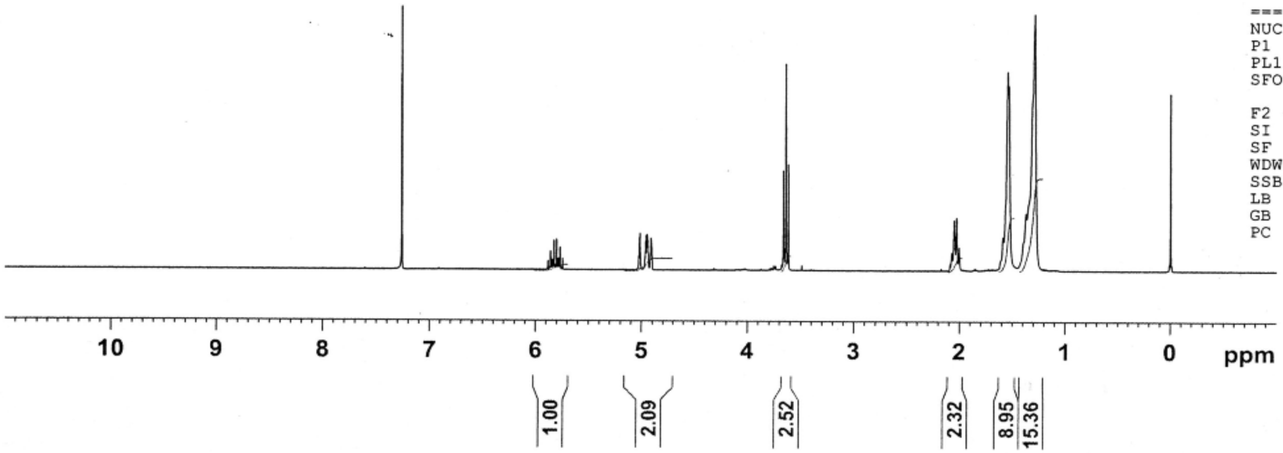


```
Current Data Parameters
NAME        SunisaSch2991
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080311
Time                18.28
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.376760 Hz
AQ              1.3271540 sec
RG                  724.1
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1            1.00000000 sec

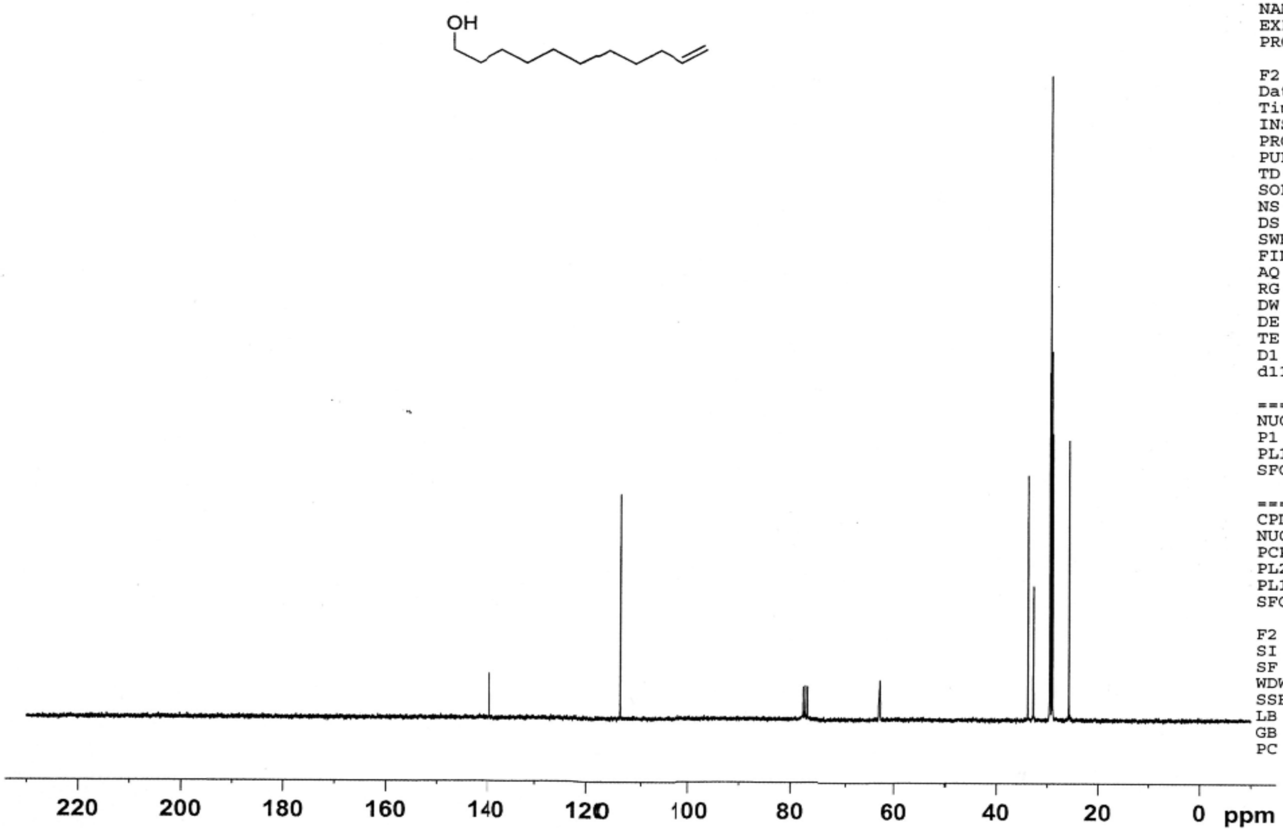
======== CHANNEL f1 ========
NUC1                   1H
P1                  12.80 usec
PL1                  0.00 dB
SFO1          300.1318534 MHz

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



^{1}H NMR spectrum of compound **91**

13C of 10-undecenol



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```
Current Data Parameters
NAME       SunisaSch1830
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070429
Time               11.45
INSTRUM            av300
PROBHD    5 mm BBO BB-1H
PULPROG             zgdc
TD                 32768
SOLVENT            CDCl3
NS                   300
DS                     4
SWH            18115.941 Hz
FIDRES          0.552855 Hz
AQ             0.9044468 sec
RG                9195.2
DW                27.600 usec
DE                 20.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec

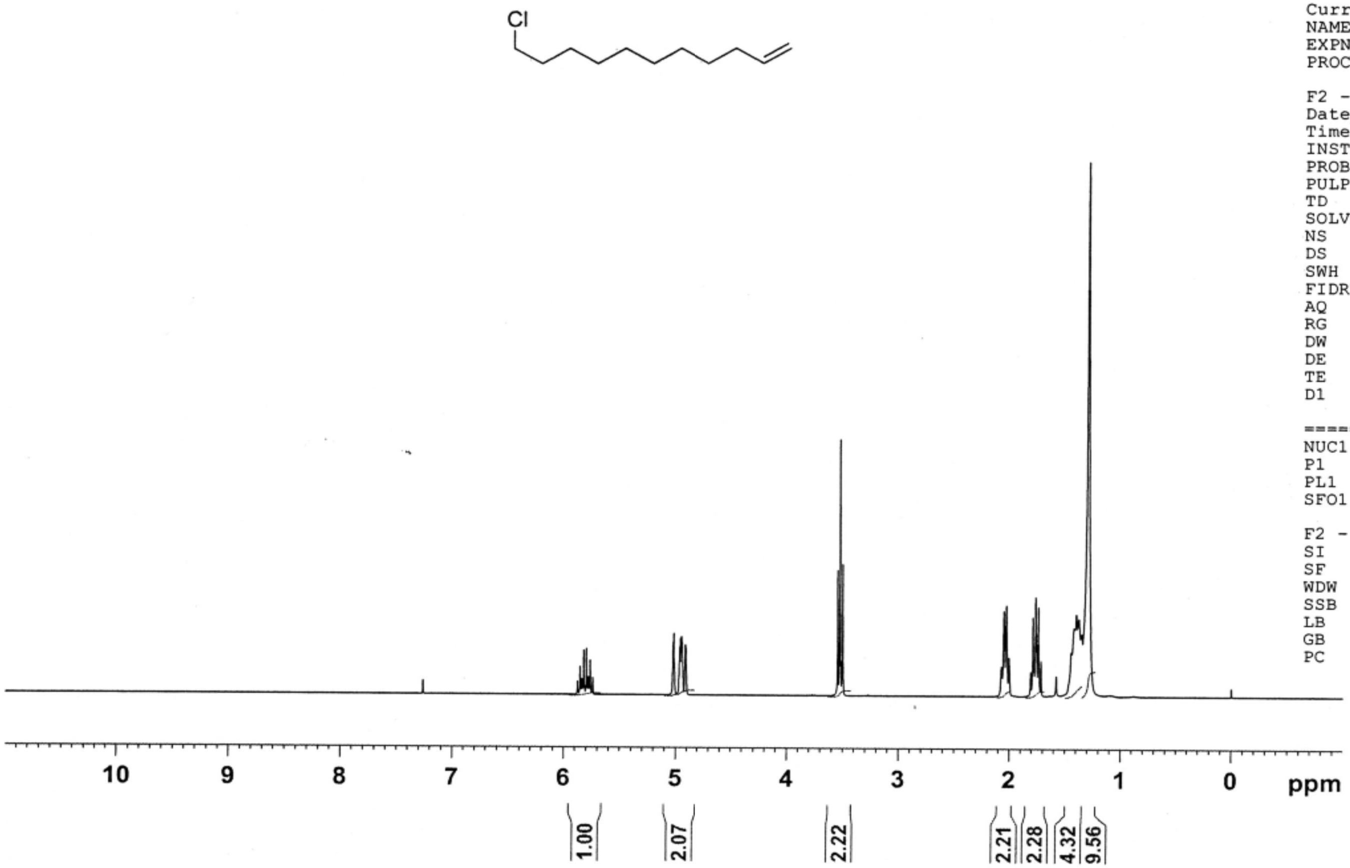
======== CHANNEL f1 ========
NUC1                 13C
P1                  4.80 usec
PL1                -3.00 dB
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              82.00 usec
PL2                -1.00 dB
PL12               16.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{13}C NMR spectrum of compound **91**

10-undecenyl chloride



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```
Current Data Parameters
NAME        SunisaSch2990
EXPNO                   8
PROCNO                  1

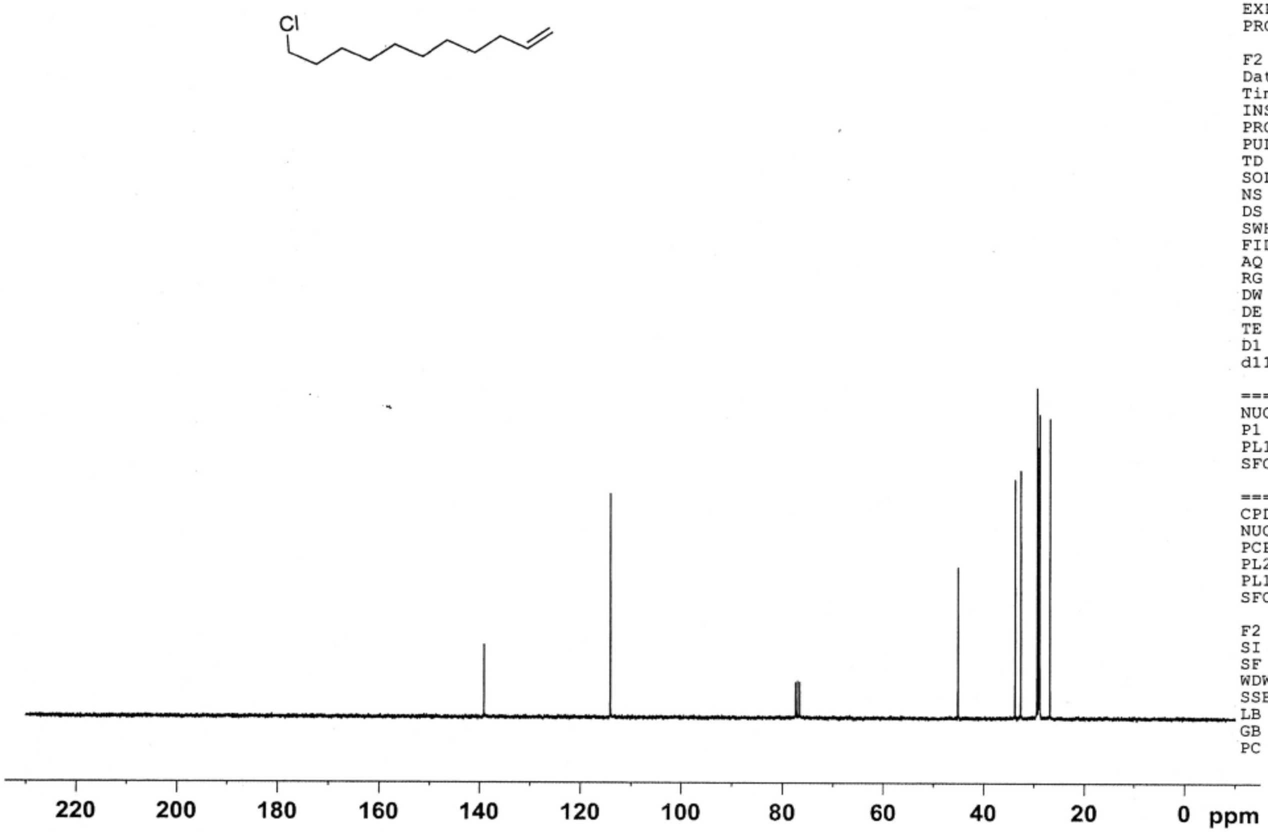
F2 - Acquisition Parameters
Date_            20080311
Time_               18.03
INSTRUM             av300
PROBHD    5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.376760 Hz
AQ              1.3271540 sec
RG                   90.5
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.80 usec
PL1                  0.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300064 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR spectrum of compound **92**

13C of 10-undecenyl chloride



```
Current Data Parameters
NAME       SunisaSch2990
EXPNO                  9
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080311
Time               18.08
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zgdc
TD                 32768
SOLVENT            CDCl3
NS                   204
DS                     4
SWH            18115.941 Hz
FIDRES          0.552855 Hz
AQ             0.9044468 sec
RG                9195.2
DW                27.600 usec
DE                 20.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec

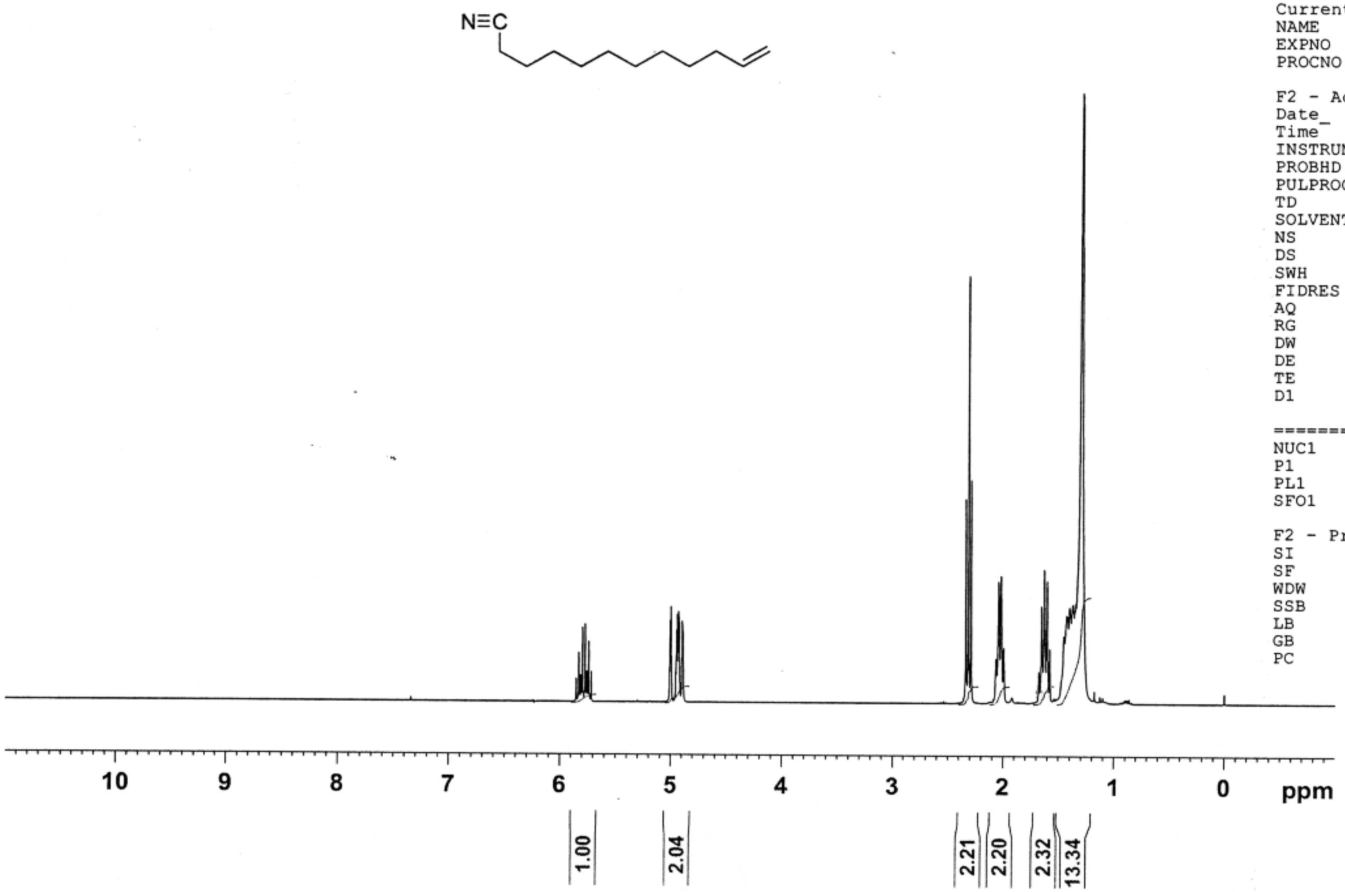
======== CHANNEL f1 ========
NUC1                 13C
P1                  5.20 usec
PL1                -3.00 dB
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 0.00 dB
PL12               17.20 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{13}C NMR spectrum of compound **92**

cyanide



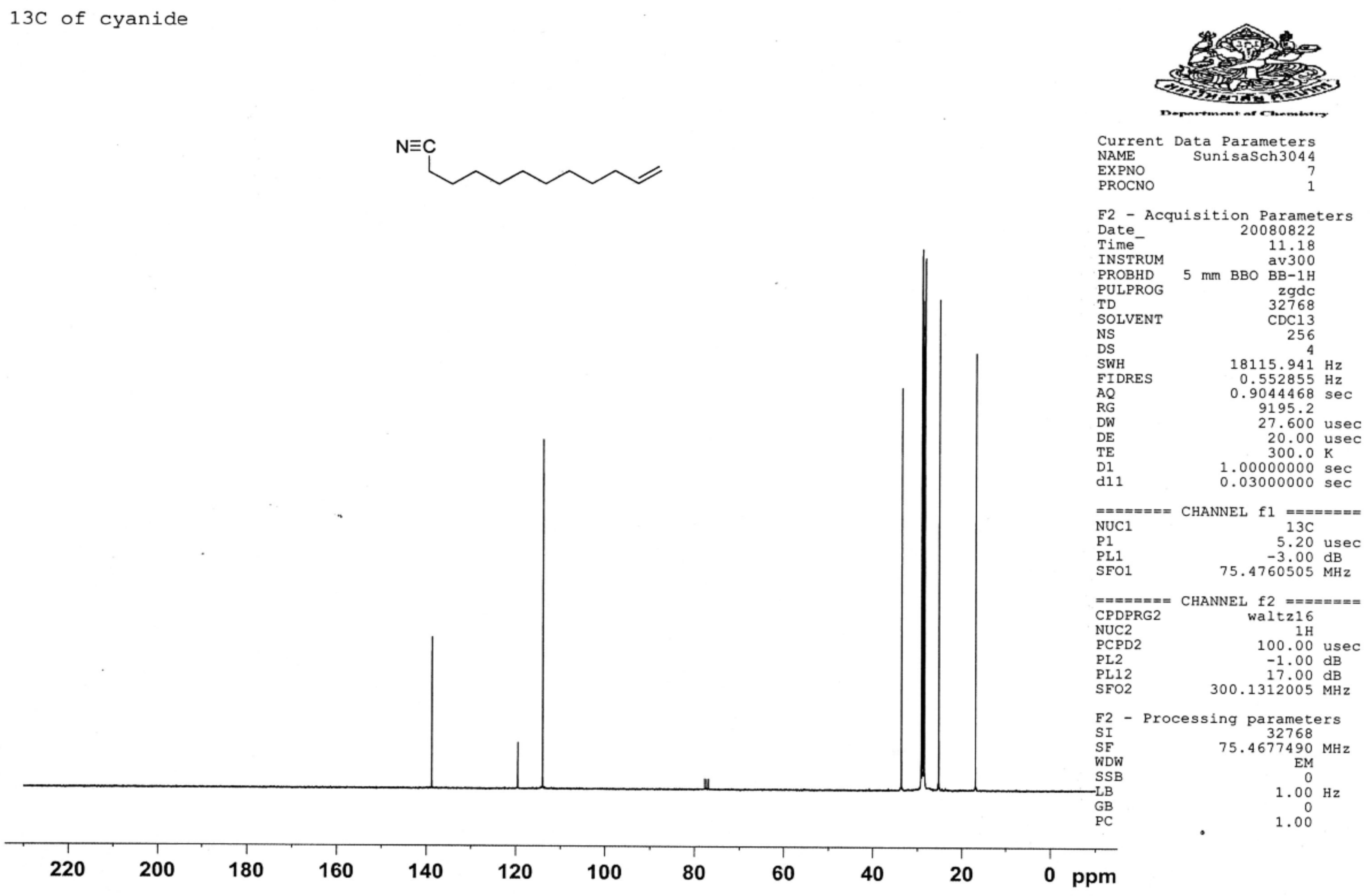
```
Current Data Parameters
NAME        SunisaSch3044
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080822
Time                11.09
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.376760 Hz
AQ              1.3271540 sec
RG                   22.6
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.60 usec
PL1                 -1.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1299814 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR spectrum of compound **109**



```
Current Data Parameters
NAME        SunisaSch3044
EXPNO                   7
PROCNO                  1

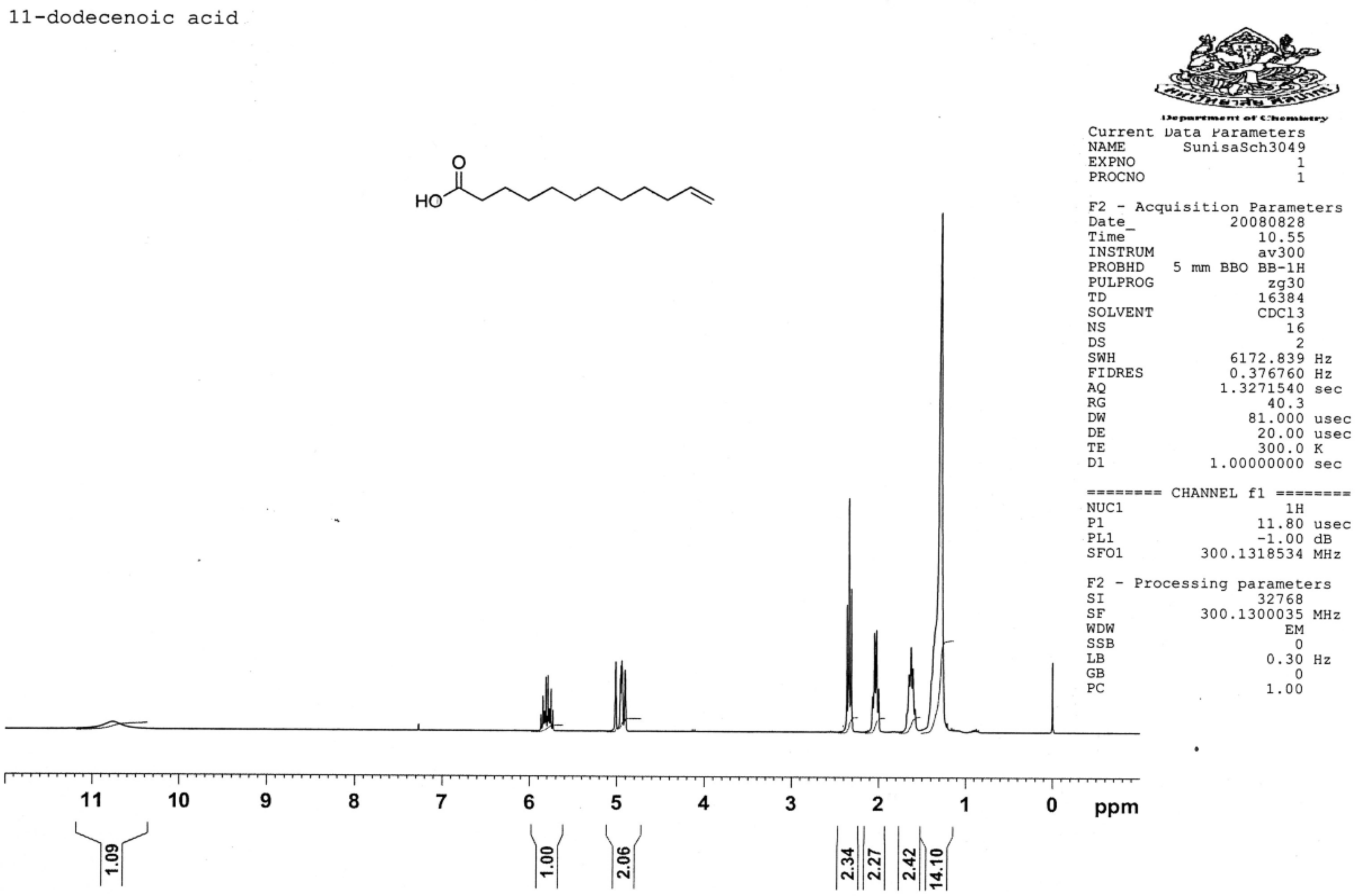
F2 - Acquisition Parameters
Date_            20080822
Time                11.18
INSTRUM             av300
PROBHD    5 mm BBO BB-1H
PULPROG              zgdc
TD                  32768
SOLVENT             CDCl3
NS                    256
DS                      4
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                 9195.2
DW                 27.600 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   5.20 usec
PL1                 -3.00 dB
SFO1           75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -1.00 dB
PL12                17.00 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF             75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00
```

^{13}C NMR spectrum of compound **109**



11-dodecenoic acid

```
Current Data Parameters
NAME        SunisaSch3049
EXPNO                   1
PROCNO                  1

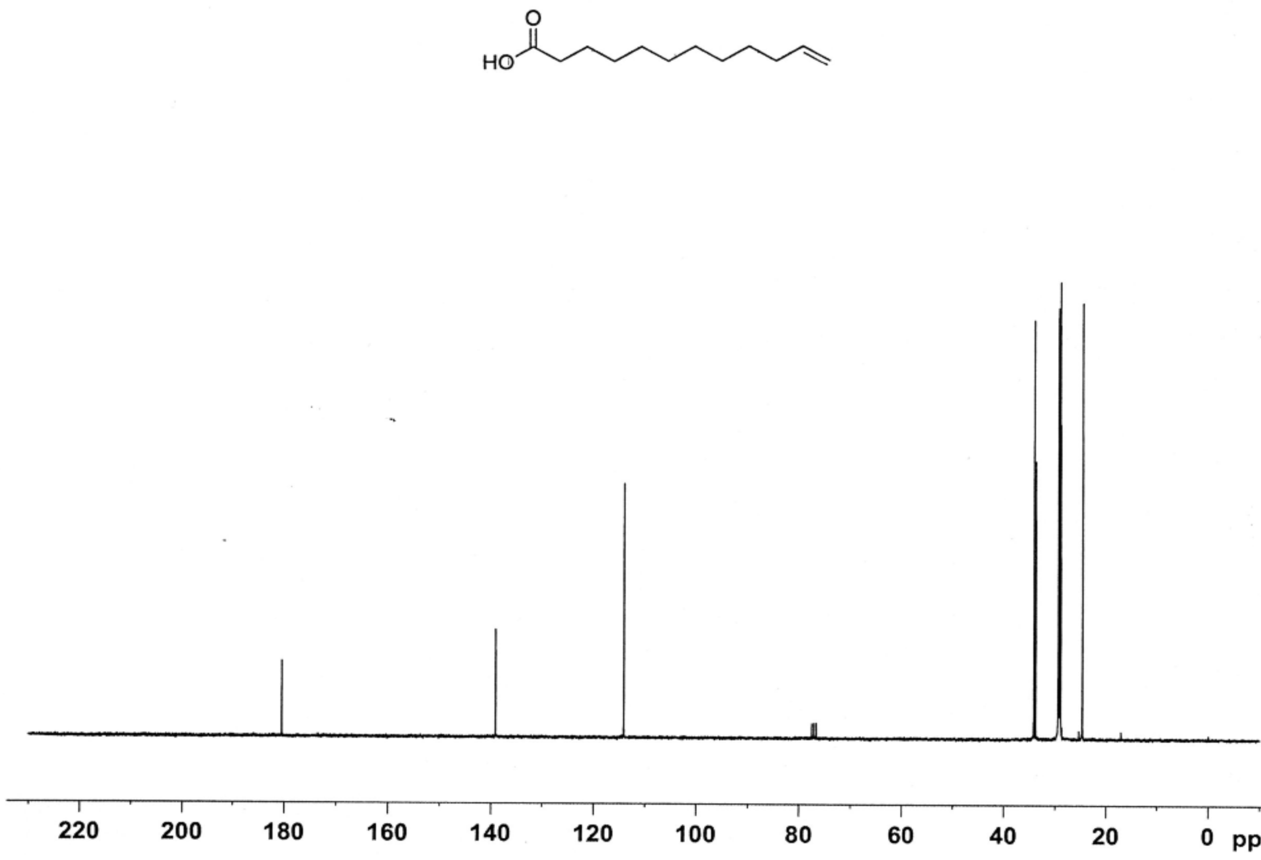
F2 - Acquisition Parameters
Date_            20080828
Time                10.55
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.376760 Hz
AQ              1.3271540 sec
RG                   40.3
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.80 usec
PL1                 -1.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300035 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR spectrum of 11-dodecenoic acid

13C of 11-dodecenoic acid



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```
Current Data Parameters
NAME          SunisaSch3049
EXPNO                     2
PROCNO                    1

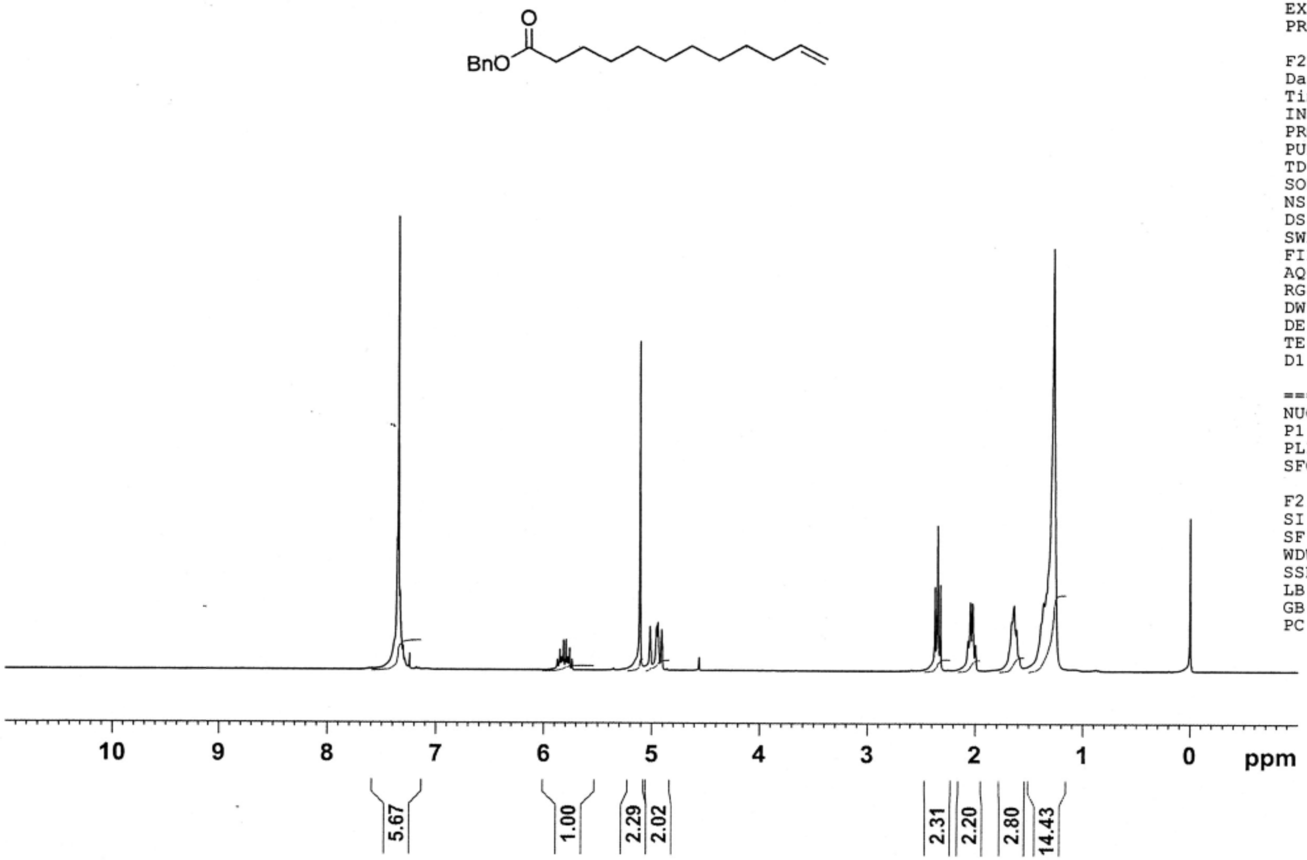
F2 - Acquisition Parameters
Date_              20080828
Time_                 11.00
INSTRUM               av300
PROBHD     5 mm BBO BB-1H
PULPROG                zgdc
TD                    32768
SOLVENT               CDCl3
NS                      128
DS                        4
SWH              18115.941 Hz
FIDRES            0.552855 Hz
AQ               0.9044468 sec
RG                  10321.3
DW                   27.600 usec
DE                    20.00 usec
TE                    300.0 K
D1               1.00000000 sec
d11              0.03000000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                     5.40 usec
PL1                   -3.00 dB
SFO1            75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                   -1.00 dB
PL12                  17.00 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF              75.4677433 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

^{13}C NMR spectrum of 11-dodecenoic acid benzyl-11-dodecenoate



```
Current Data Parameters
NAME       SunisaSch3052
EXPNO                  2
PROCNO                 1

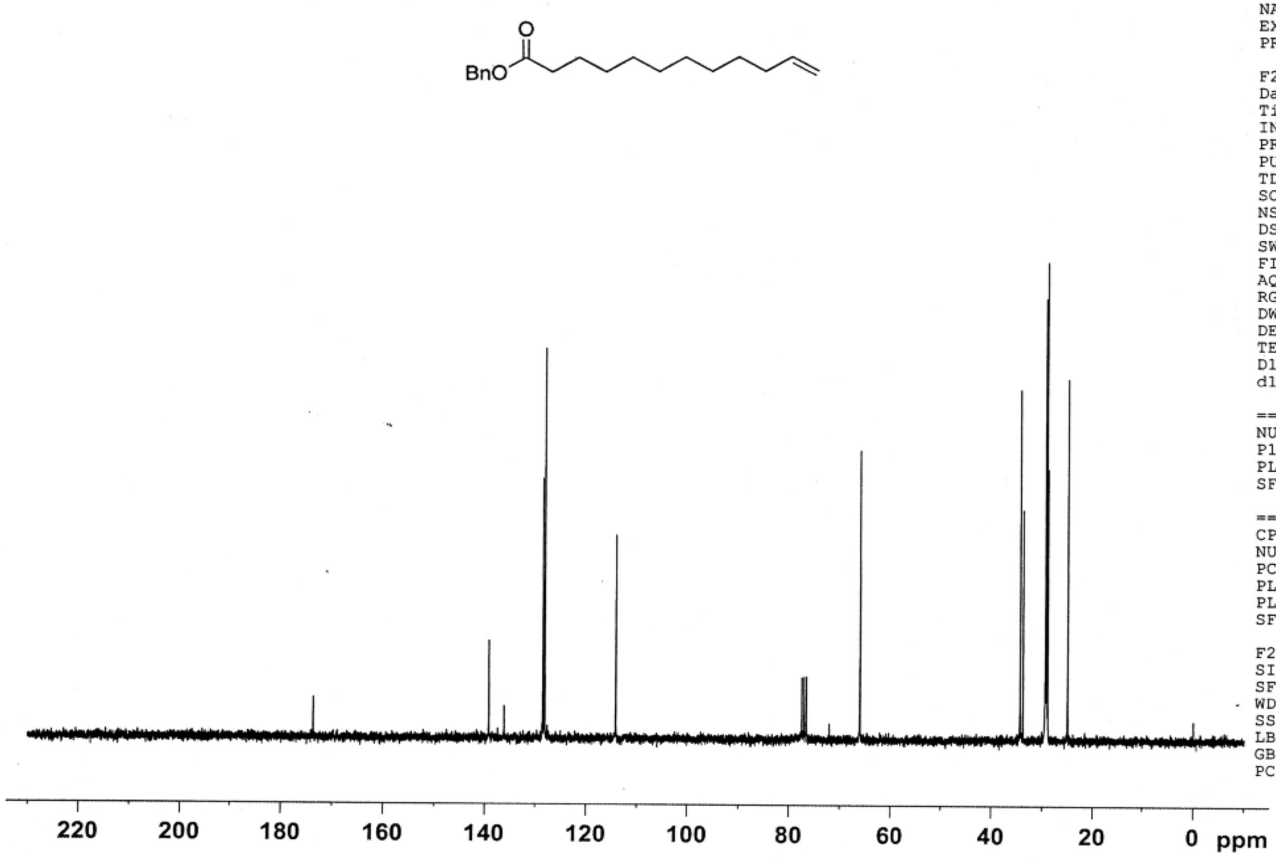
F2 - Acquisition Parameters
Date_           20080903
Time                9.45
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                   114
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.80 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300105 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR spectrum of compound **106**

13C of benzyl-11-dodecenoate



```
Current Data Parameters
NAME          SunisaSch3052
EXPNO                     3
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080903
Time                   9.55
INSTRUM               av300
PROBHD     5 mm BBO BB-1H
PULPROG                zgdc
TD                    32768
SOLVENT               CDCl3
NS                      256
DS                        4
SWH               18115.941 Hz
FIDRES             0.552855 Hz
AQ                0.9044468 sec
RG                  11585.2
DW                   27.600 usec
DE                    20.00 usec
TE                    300.0 K
D1             1.00000000 sec
d11            0.03000000 sec

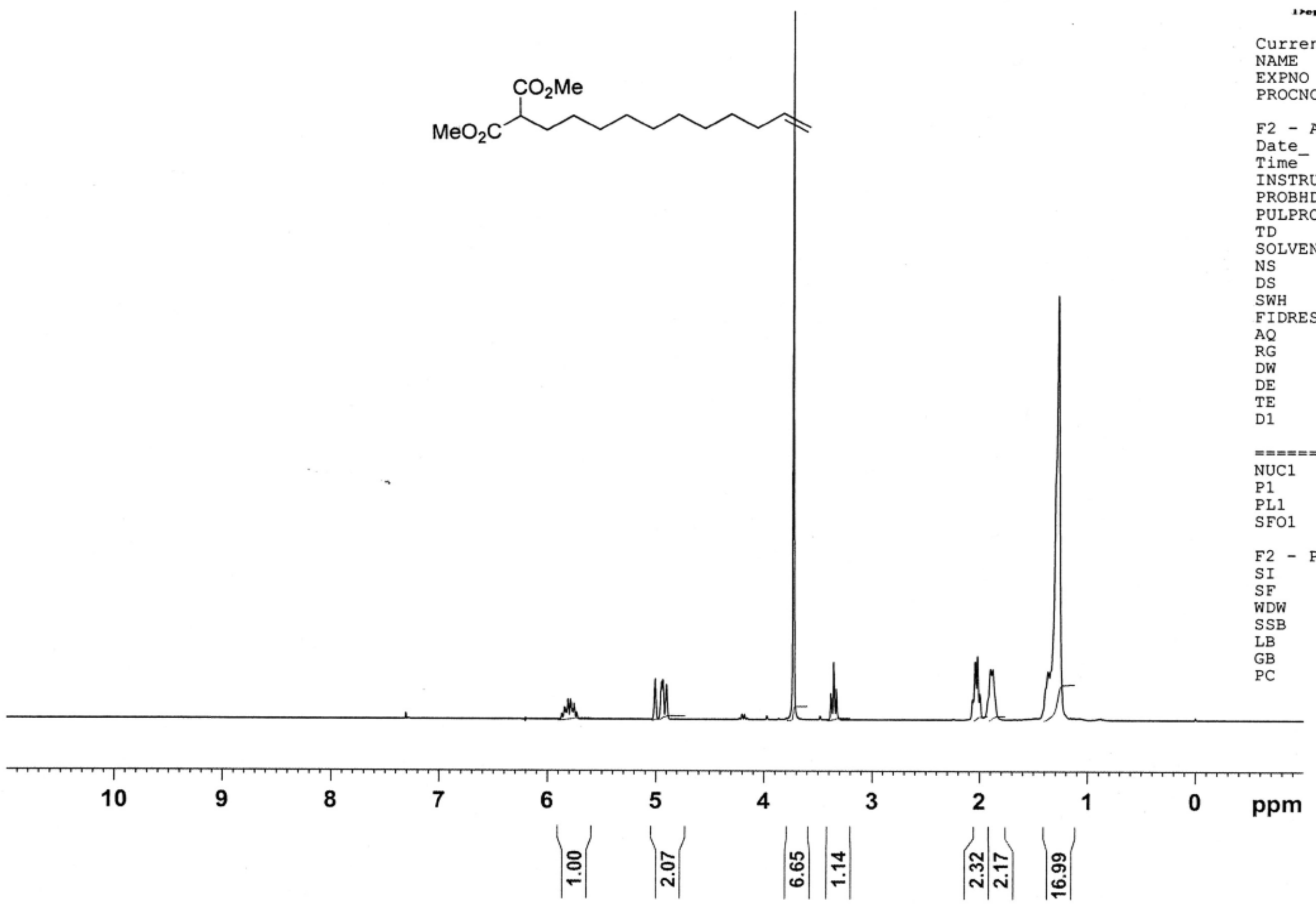
======== CHANNEL f1 ========
NUC1                    13C
P1                     5.40 usec
PL1                   -3.00 dB
SFO1            75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                   -1.00 dB
PL12                  17.00 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF               75.4677490 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

^{13}C NMR spectrum of compound **106**

alkylation of diethylmalonate



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```
Current Data Parameters
NAME       SunisaSch2990
EXPNO                  3
PROCNO                 1

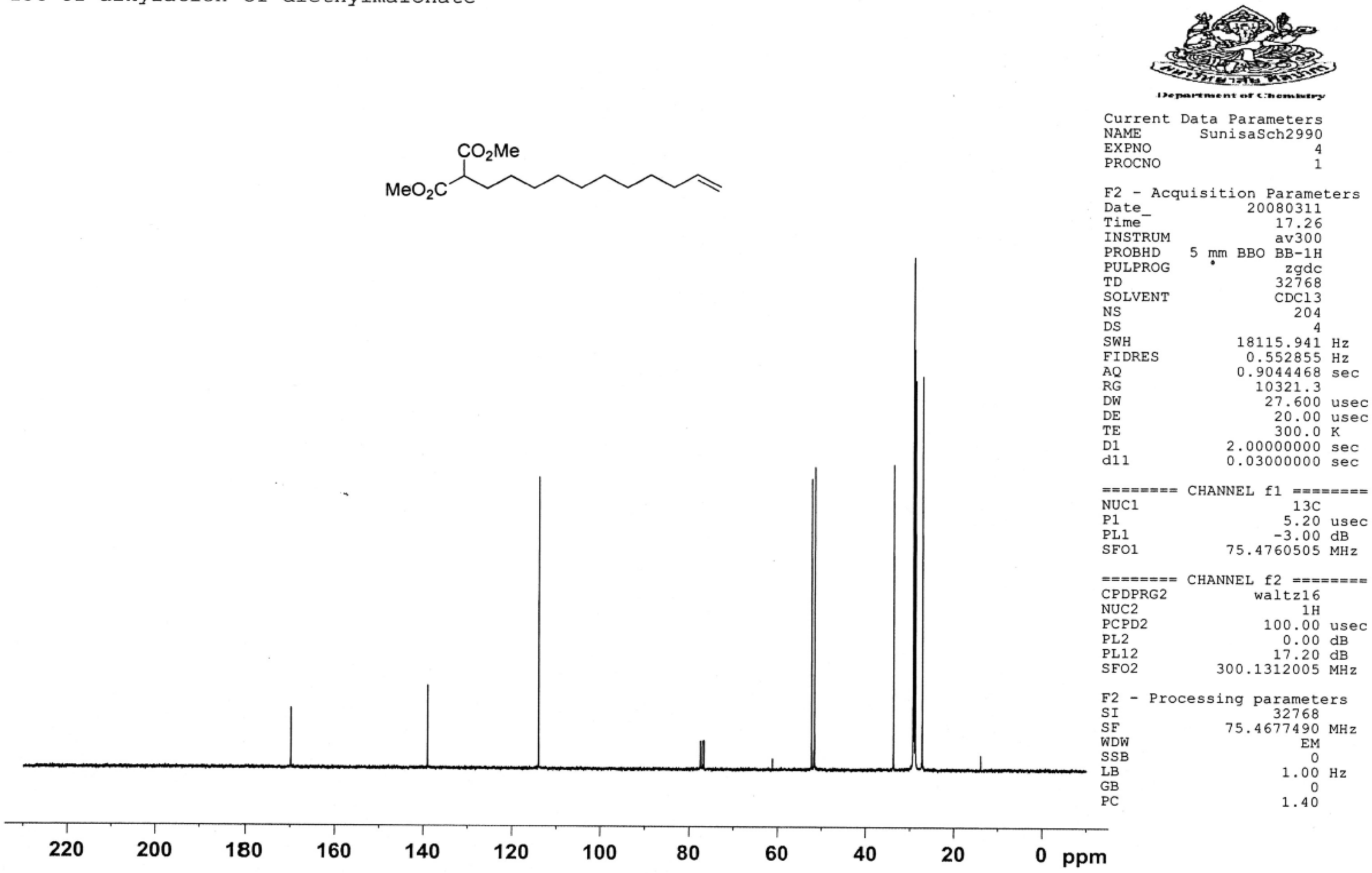
F2 - Acquisition Parameters
Date_           20080311
Time               17.15
INSTRUM            av300
PROBHD    5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES   •      0.376760 Hz
AQ             1.3271540 sec
RG                  40.3
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.80 usec
PL1                 0.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1299910 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR spectrum of compound **94**

13C of alkylation of diethylmalonate



Department of Chemistry

```
Current Data Parameters
NAME          SunisaSch2990
EXPNO                     4
PROCNO                    1

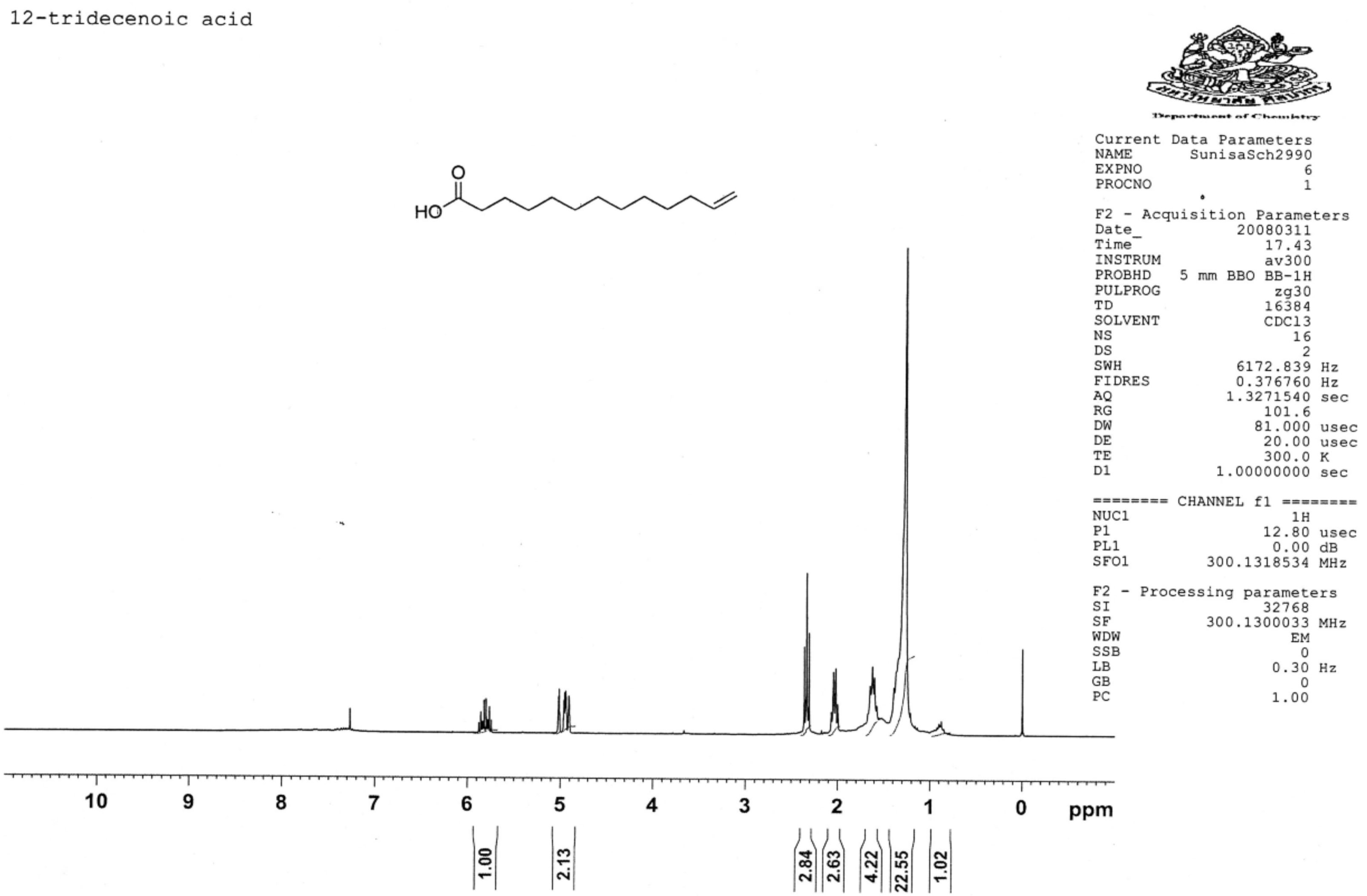
F2 - Acquisition Parameters
Date_              20080311
Time                  17.26
INSTRUM               av300
PROBHD   5 mm BBO BB-1H
PULPROG                zgdc
TD                    32768
SOLVENT               CDCl3
NS                      204
DS                        4
SWH               18115.941 Hz
FIDRES             0.552855 Hz
AQ                0.9044468 sec
RG                  10321.3
DW                   27.600 usec
DE                    20.00 usec
TE                    300.0 K
D1               2.00000000 sec
d11              0.03000000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                     5.20 usec
PL1                   -3.00 dB
SFO1             75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                    0.00 dB
PL12                  17.20 dB
SFO2            300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF               75.4677490 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

^{13}C NMR spectrum of compound **94**



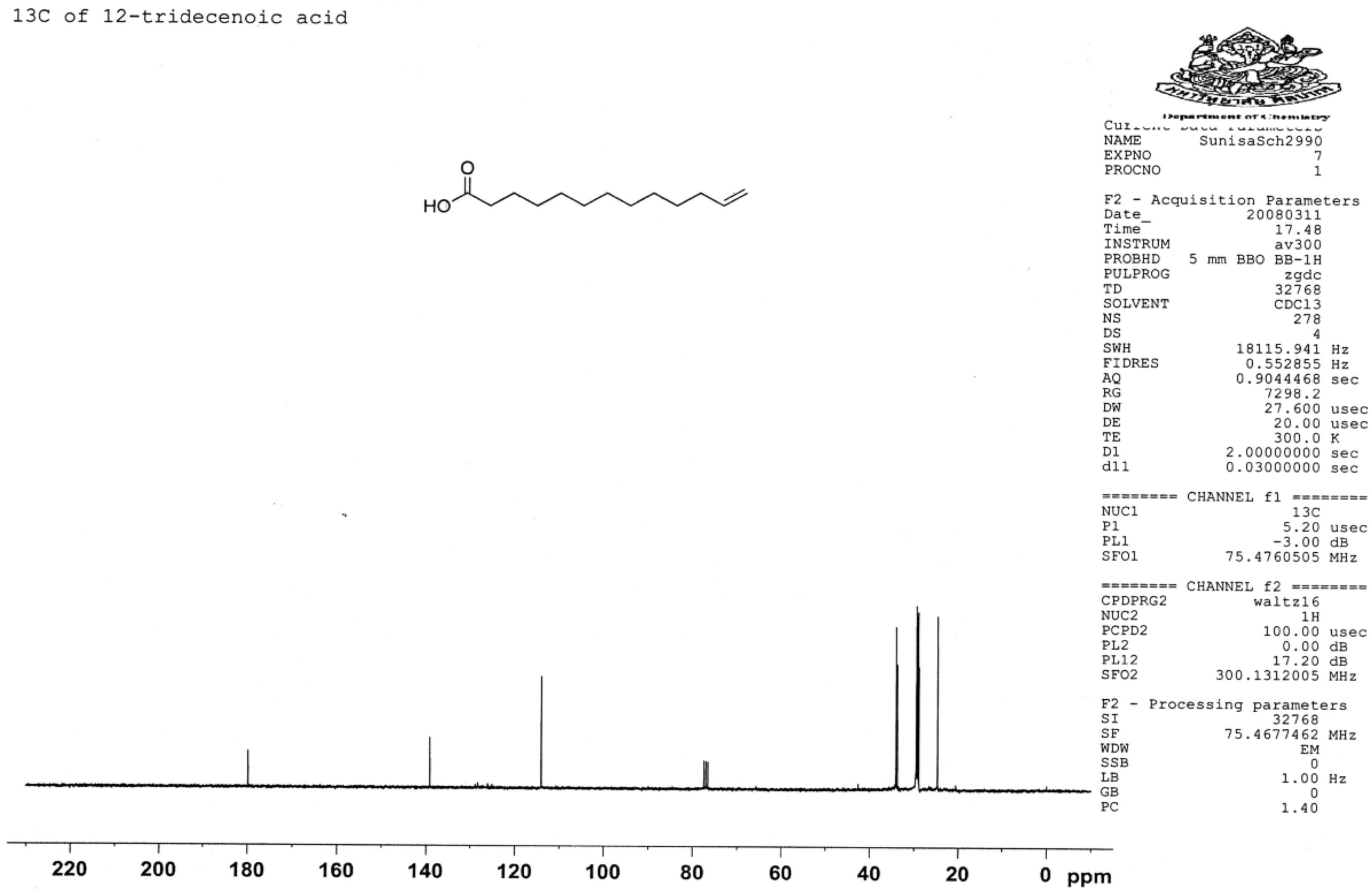
```
Current Data Parameters
NAME       SunisaSch2990
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080311
Time               17.43
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                 101.6
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.80 usec
PL1                 0.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300033 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR spectrum of compound **95**



13C of 12-tridecenoic acid

Department of Chemistry

```
Current Data Parameters
NAME       SunisaSch2990
EXPNO                  7
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080311
Time               17.48
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zgdc
TD                 32768
SOLVENT            CDCl3
NS                   278
DS                     4
SWH            18115.941 Hz
FIDRES          0.552855 Hz
AQ             0.9044468 sec
RG                7298.2
DW                27.600 usec
DE                 20.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec

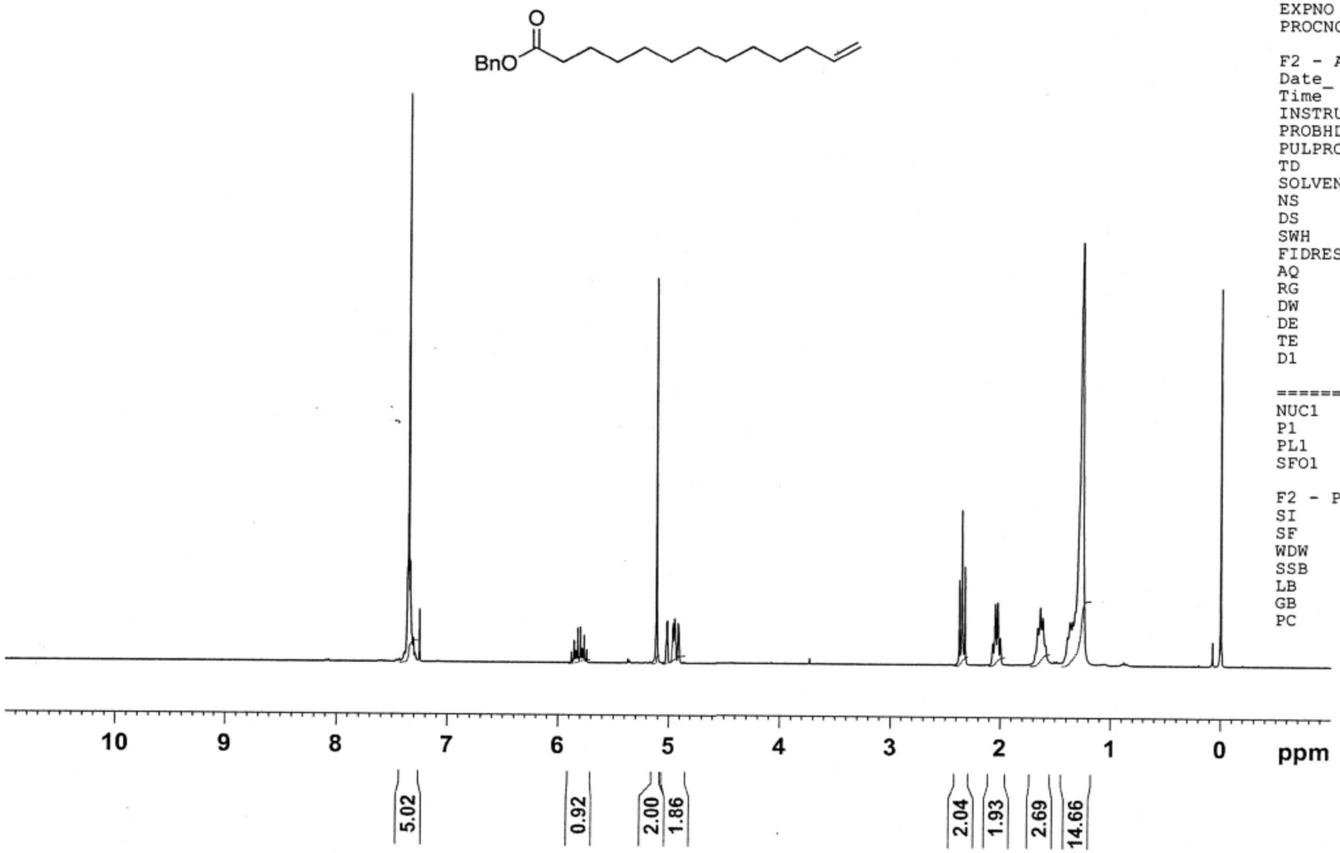
======== CHANNEL f1 ========
NUC1                 13C
P1                  5.20 usec
PL1                -3.00 dB
SFO1         75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 0.00 dB
PL12               17.20 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677462 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{13}C NMR spectrum of compound **95**

benzyl-12-tridecenoate



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Current Data Parameters
NAME        SunisaSch3060
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080920
Time                19.42
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.094190 Hz
AQ              5.3084660 sec
RG                  161.3
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.80 usec
PL1                 -1.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300079 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.40
```
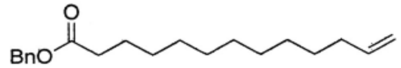

^{1}H NMR spectrum of compound **89**

benzyl-12-tridecenoate



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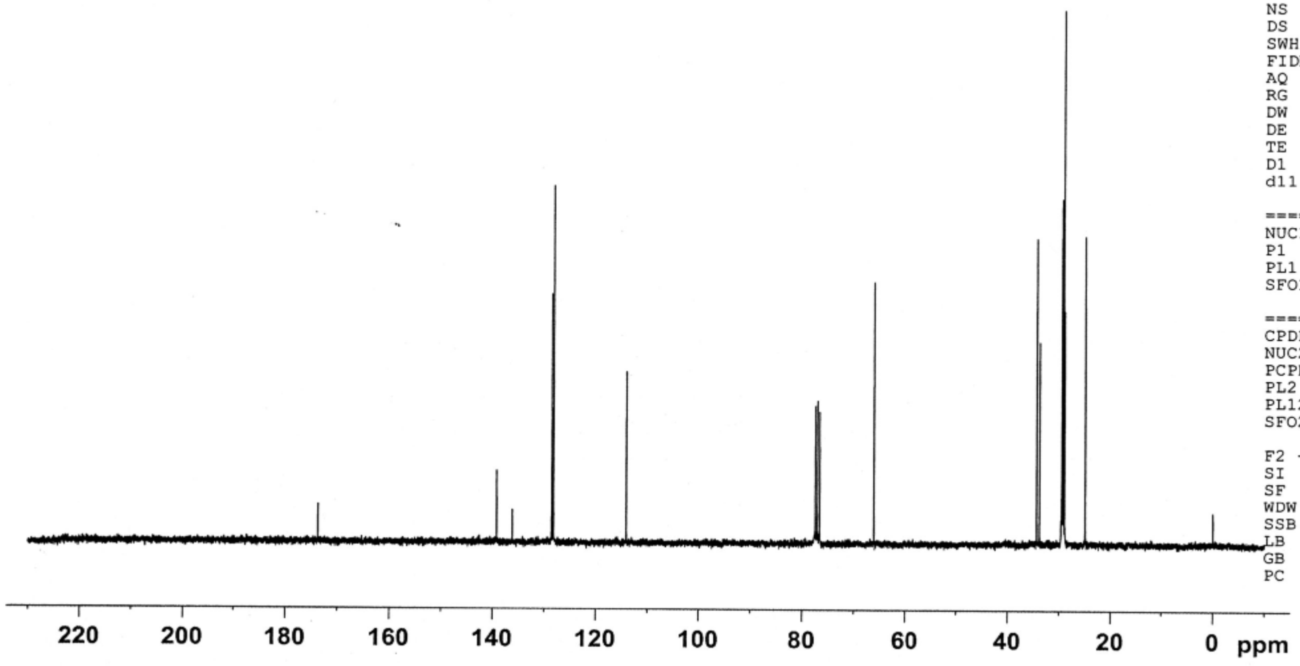
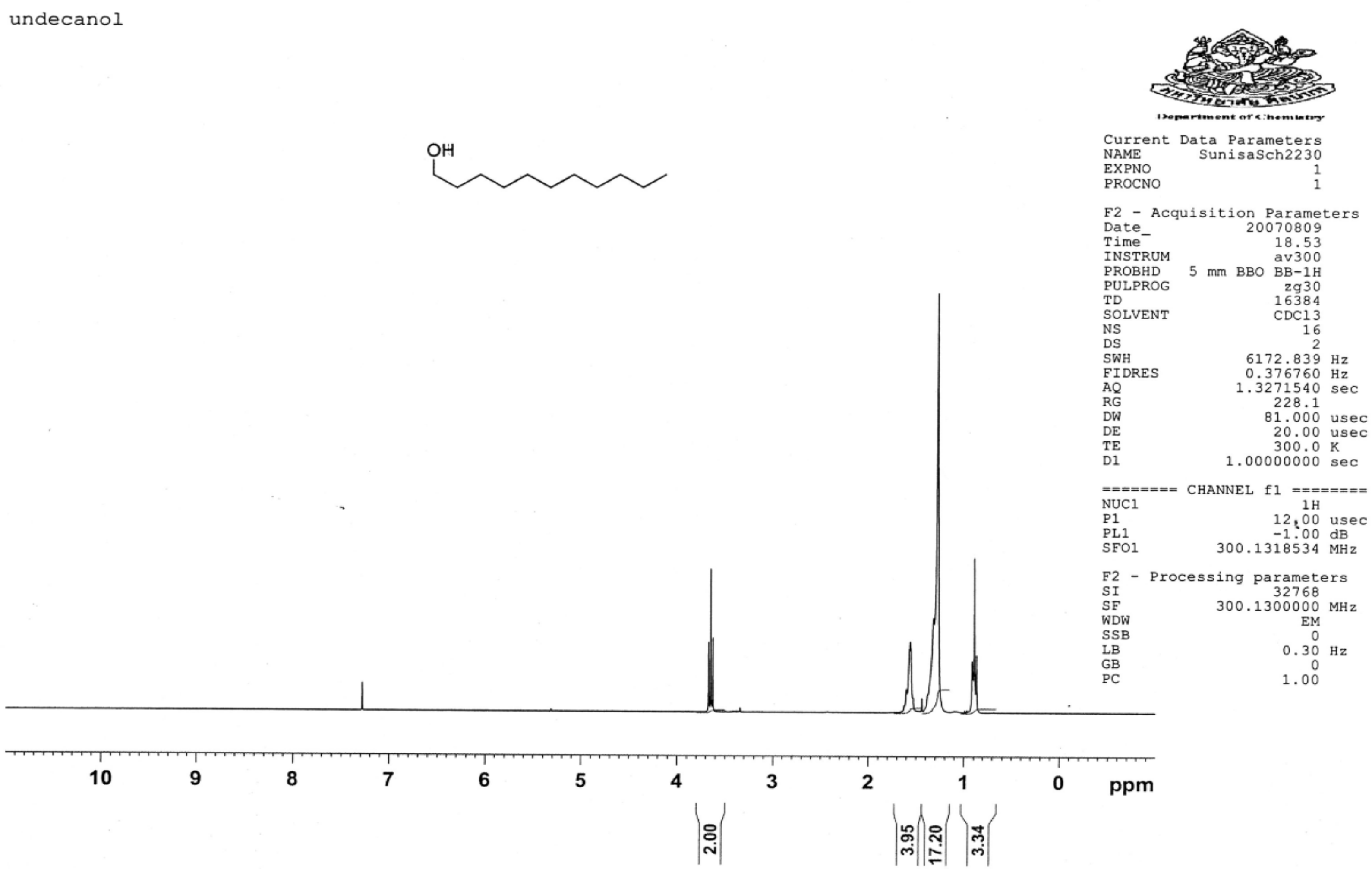
```
Current Data Parameters
NAME          SunisaSch3060
EXPNO                     6
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080920
Time                  20.16
INSTRUM               av300
PROBHD   5 mm BBO BB-1H
PULPROG                zgdc
TD                    32768
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH               18115.941 Hz
FIDRES             0.552855 Hz
AQ                0.9044468 sec
RG                  11585.2
DW                   27.600 usec
DE                    20.00 usec
TE                    300.0 K
D1               1.00000000 sec
d11              0.03000000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                     5.40 usec
PL1                   -3.00 dB
SFO1             75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                   -1.00 dB
PL12                  17.00 dB
SFO2            300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF               75.4677478 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.00
```



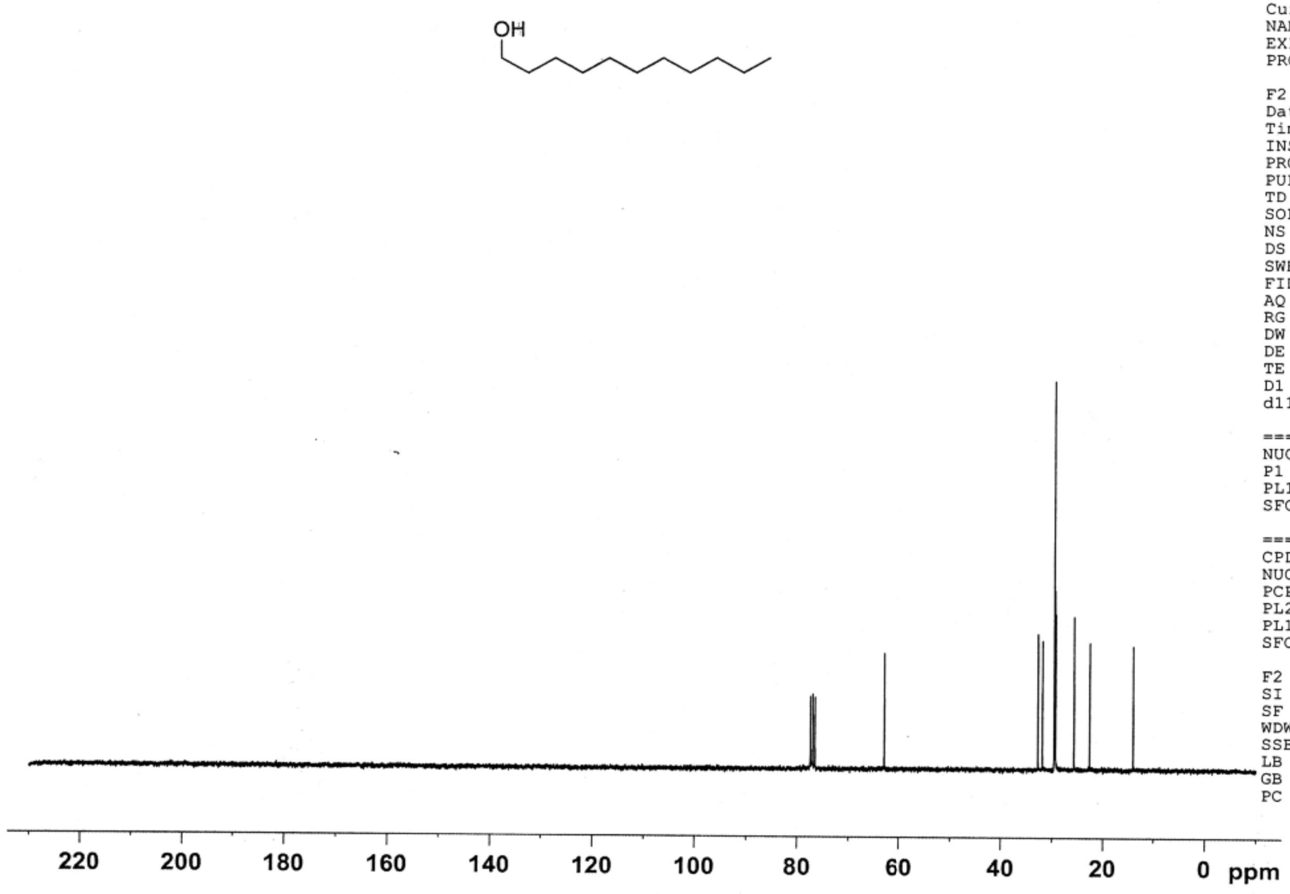
^{13}C NMR spectrum of compound **89**



```
Current Data Parameters
NAME         SunisaSch2230
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20070809
Time                 18.53
INSTRUM              av300
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   16384
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6172.839 Hz
FIDRES            0.376760 Hz
AQ               1.3271540 sec
RG                   228.1
DW                  81.000 usec
DE                   20.00 usec
TE                   300.0 K
D1              1.00000000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.00 usec
PL1                  -1.00 dB
SFO1           300.1318534 MHz

F2 - Processing parameters
SI                   32768
SF             300.1300000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

^{1}H NMR spectrum of compound **72**

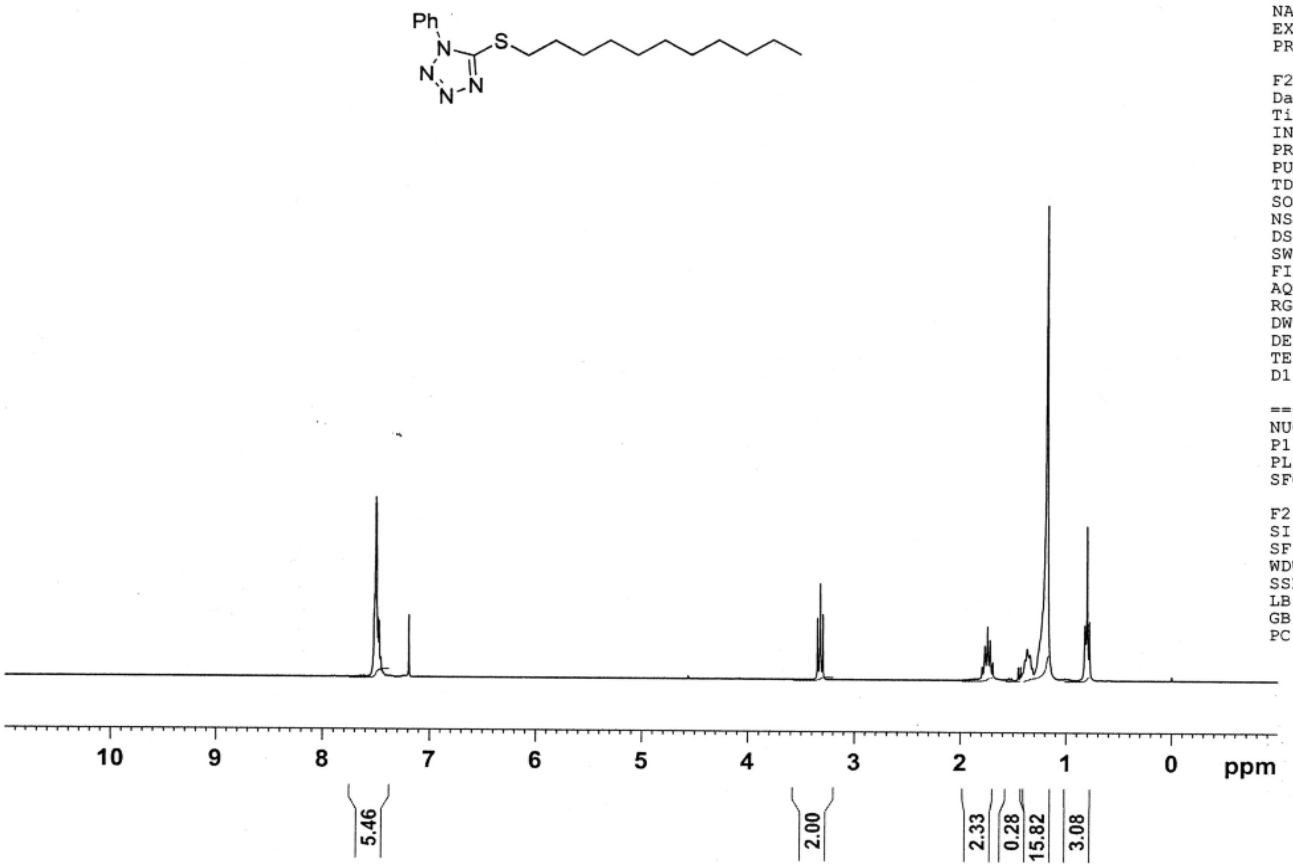
13C of undecanol



```
Current Data Parameters
NAME        SunisaSch2230
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070809
Time                18.59
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zgdc
TD                  32768
SOLVENT             CDCl3
NS                    409
DS                      4
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                 9195.2
DW                 27.600 usec
DE                  20.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   5.20 usec
PL1                 -3.00 dB
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               92.00 usec
PL2                 -1.00 dB
PL12                16.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF            75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00
```

^{13}C NMR spectrum of compound **72**

undecane sulfide



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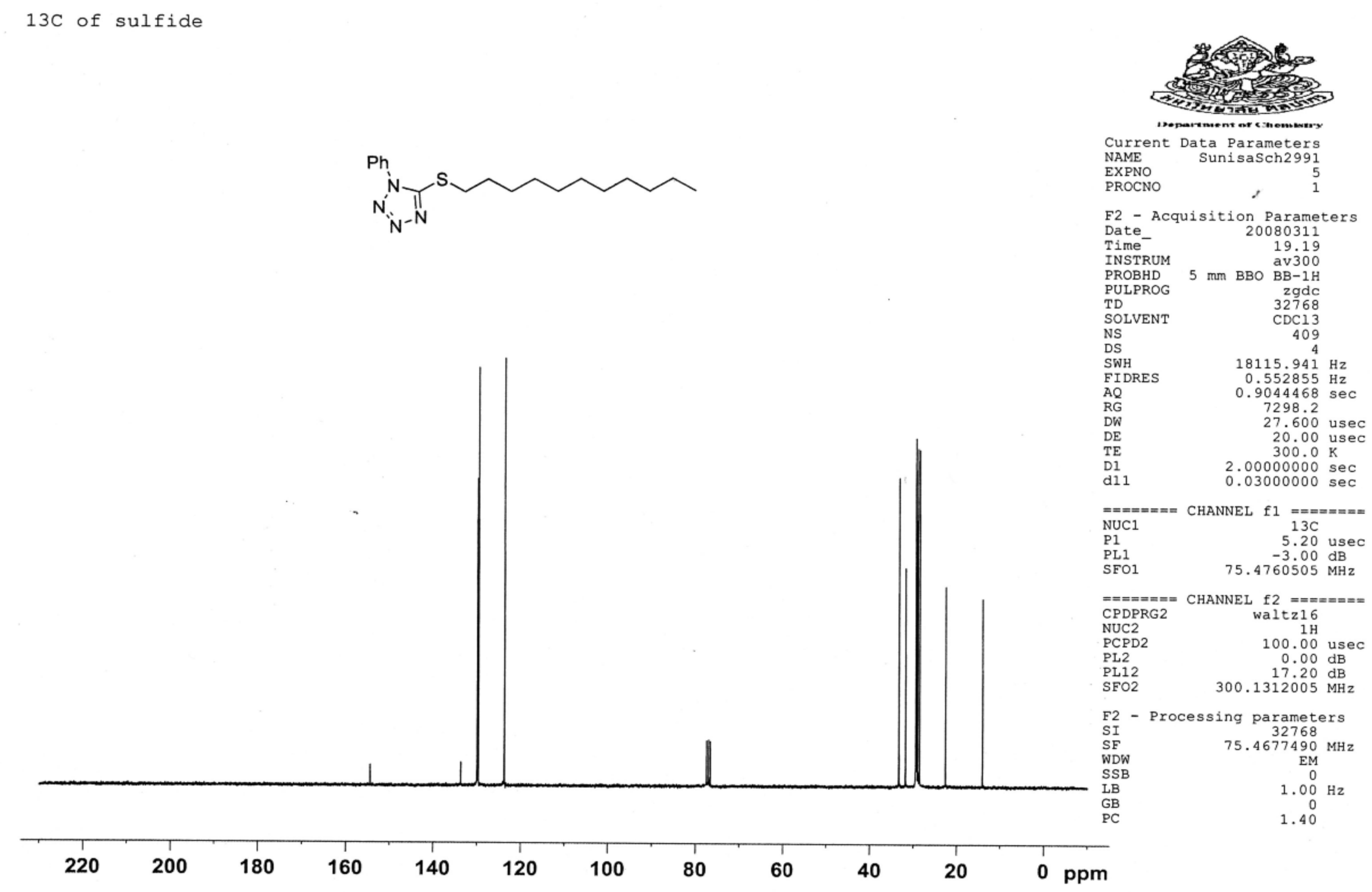
```
Current Data Parameters
NAME        SunisaSch1980
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070531
Time                10.18
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.094190 Hz
AQ              5.3084660 sec
RG                  322.5
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  10.50 usec
PL1                 -1.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

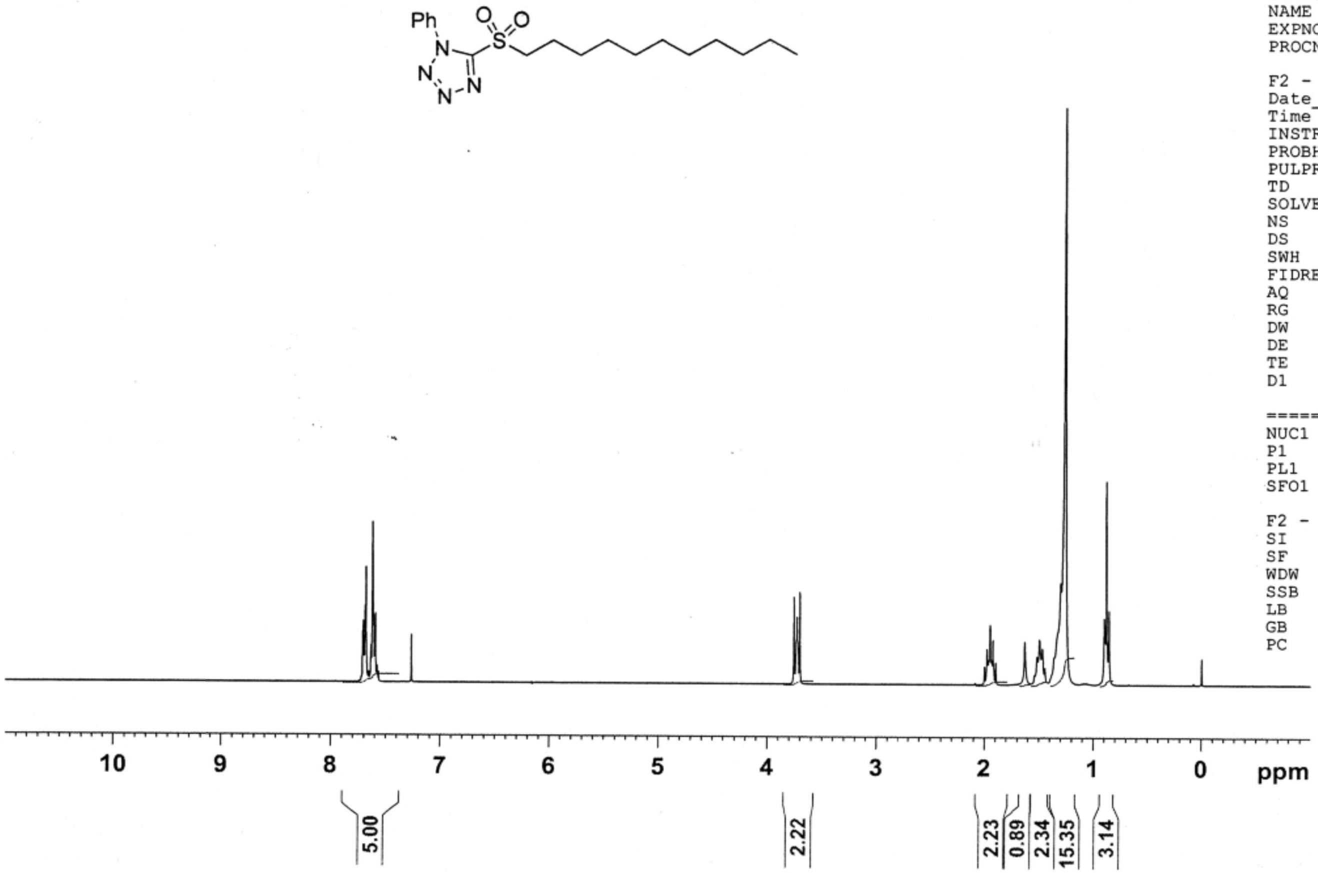
^{1}H NMR spectrum of compound **73**



```
Current Data Parameters
NAME        SunisaSch2991
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080311
Time                19.19
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zgdc
TD                  32768
SOLVENT             CDCl3
NS                    409
DS                      4
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                 7298.2
DW                 27.600 usec
DE                  20.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   5.20 usec
PL1                 -3.00 dB
SFO1           75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  0.00 dB
PL12                17.20 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF             75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

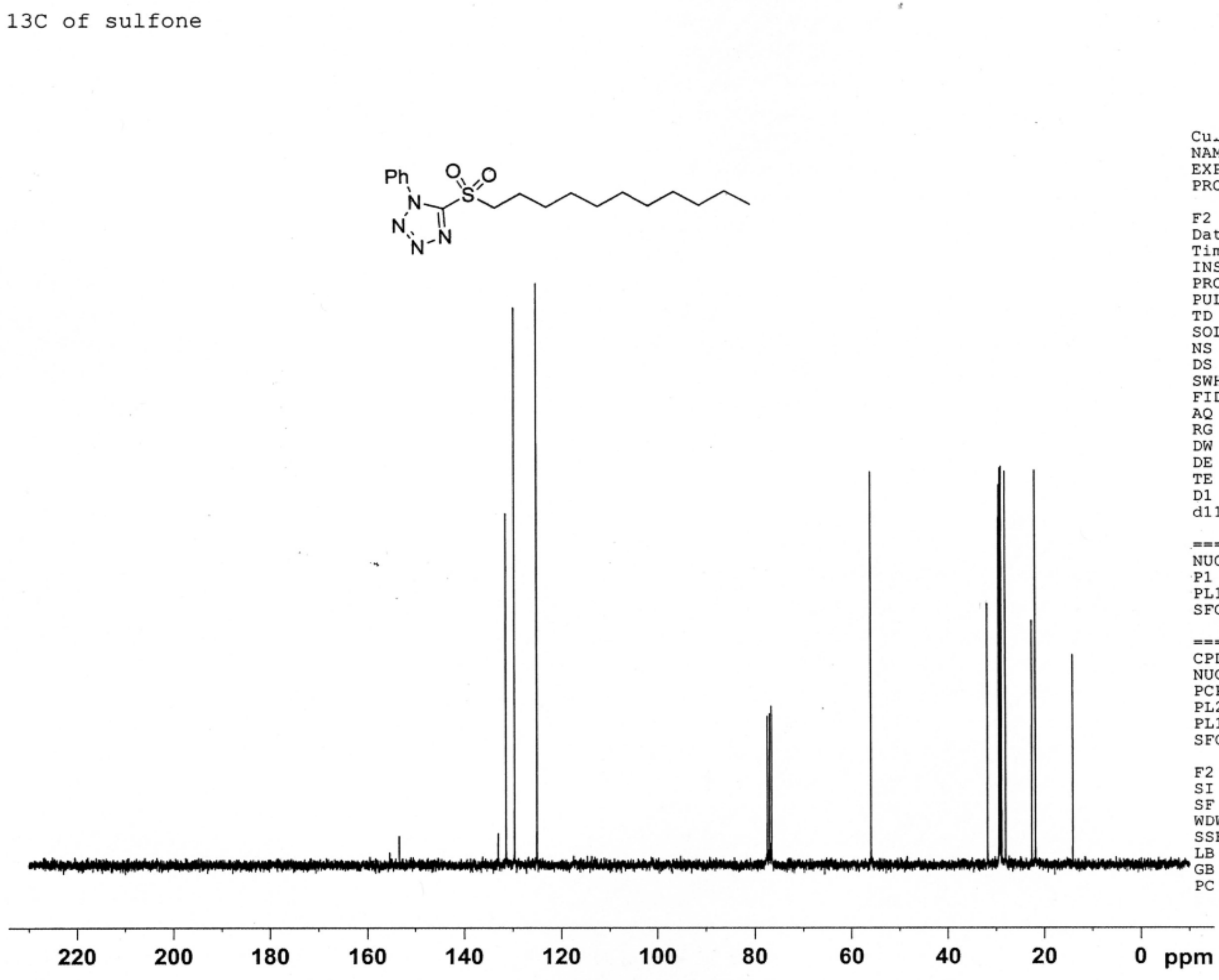
^{13}C NMR spectrum of compound **73**

sulfone



```
Current Data Parameters
NAME        SunisaSch2991
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080311
Time                18.41
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.376760 Hz
AQ              1.3271540 sec
RG                  228.1
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.80 usec
PL1                  0.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300064 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

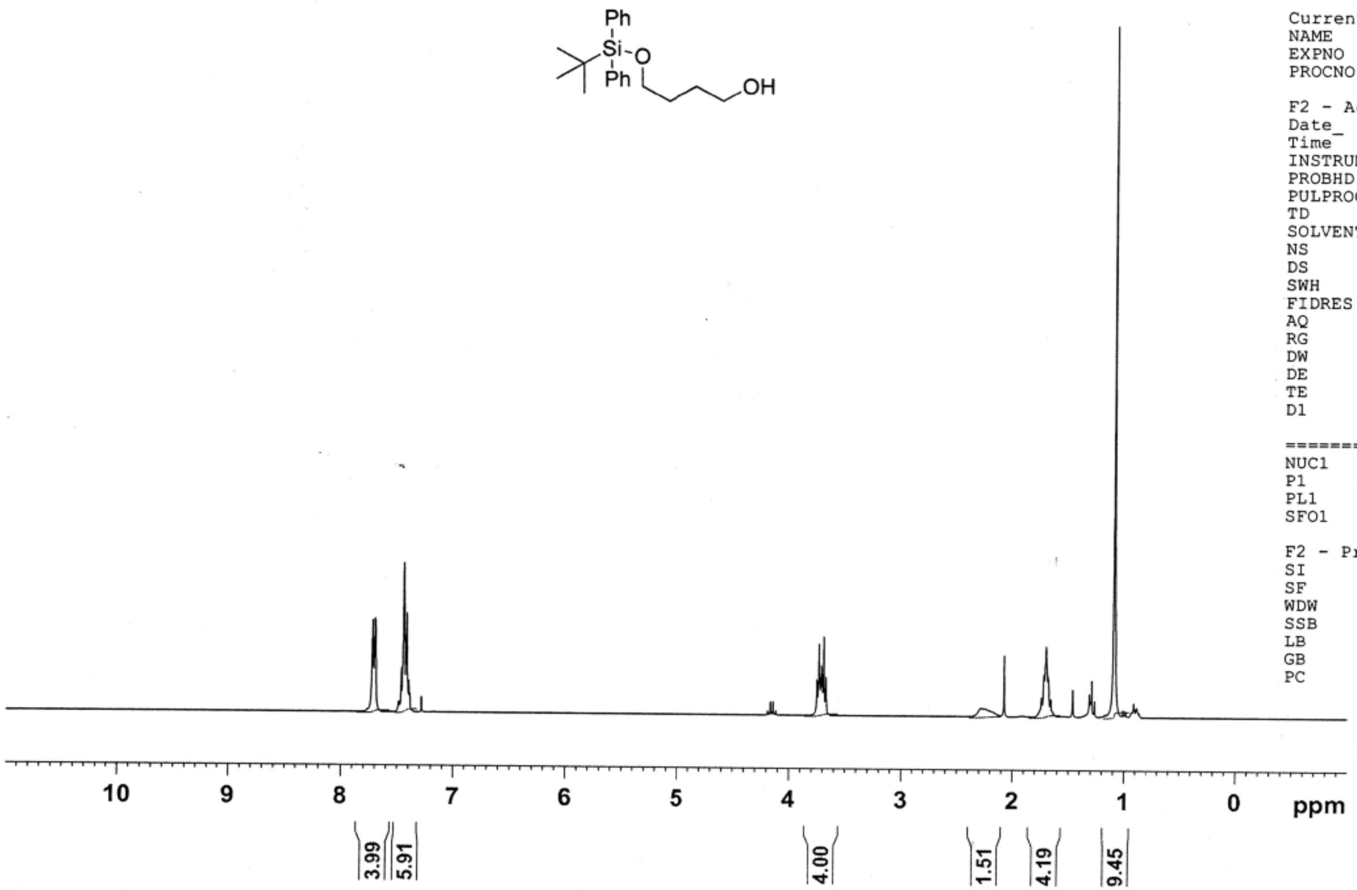
^{1}H NMR spectrum of compound **68**



```
Current Data Parameters
NAME          SunisaSch2991
EXPNO                     4
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080311
Time                  19.05
INSTRUM               av300
PROBHD    5 mm BBO BB-1H
PULPROG                zgdc
TD                    32768
SOLVENT               CDCl3
NS                      409
DS                        4
SWH              18115.941 Hz
FIDRES            0.552855 Hz
AQ               0.9044468 sec
RG                   7298.2
DW                   27.600 usec
DE                    20.00 usec
TE                    300.0 K
D1               2.00000000 sec
d11              0.03000000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                     5.20 usec
PL1                   -3.00 dB
SFO1            75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                    0.00 dB
PL12                  17.20 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF              75.4677490 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.00
```

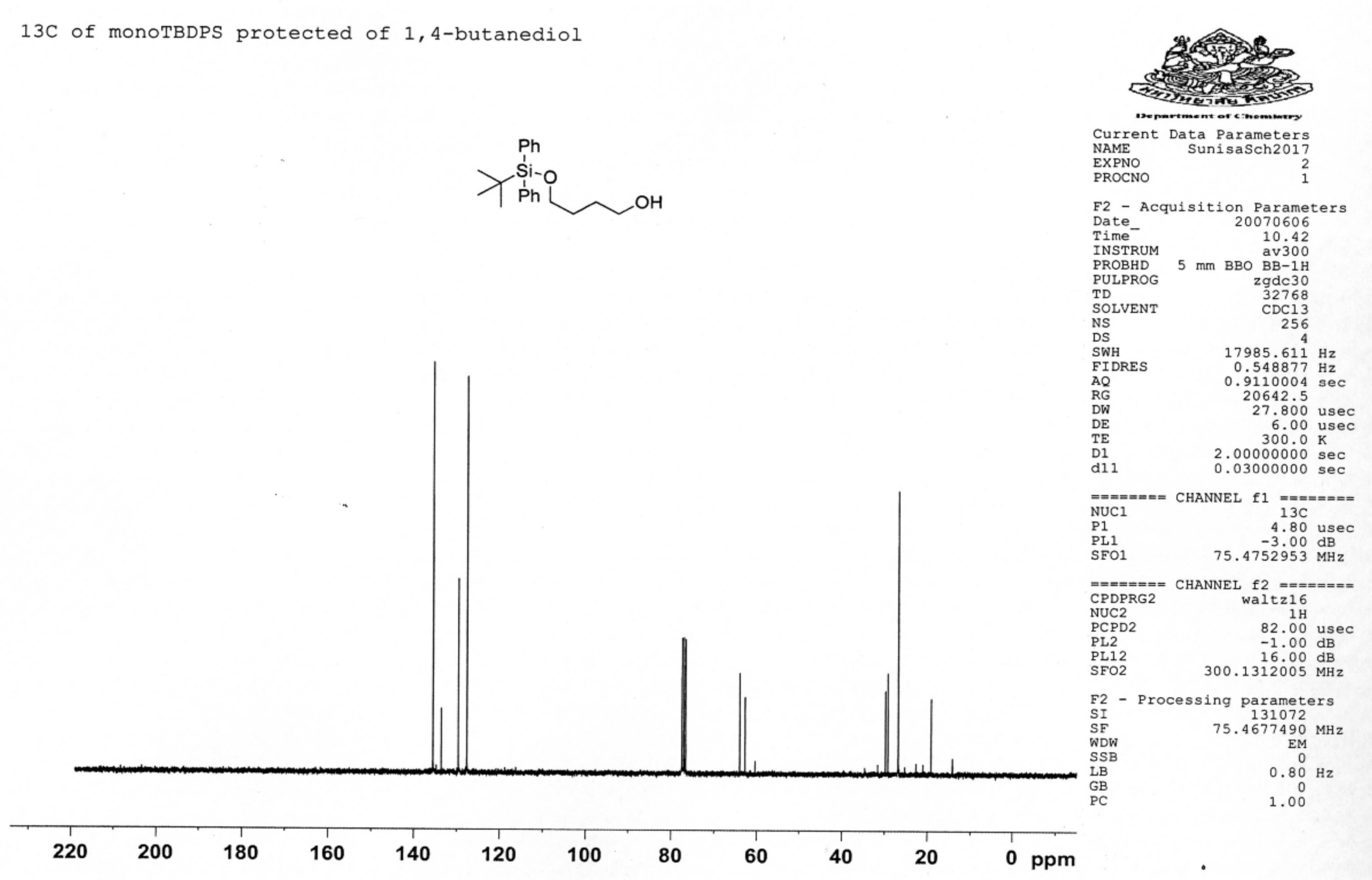
^{13}C NMR spectrum of compound **68**

monoTBDPS protected of 1,4-butanediol



```
Current Data Parameters
NAME        SunisaSch2017
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070606
Time                10.29
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  32768
SOLVENT             CDC13
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.188380 Hz
AQ              2.6542580 sec
RG                  161.3
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  10.50 usec
PL1                 -1.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR spectrum of 4-TBDPSO butanol

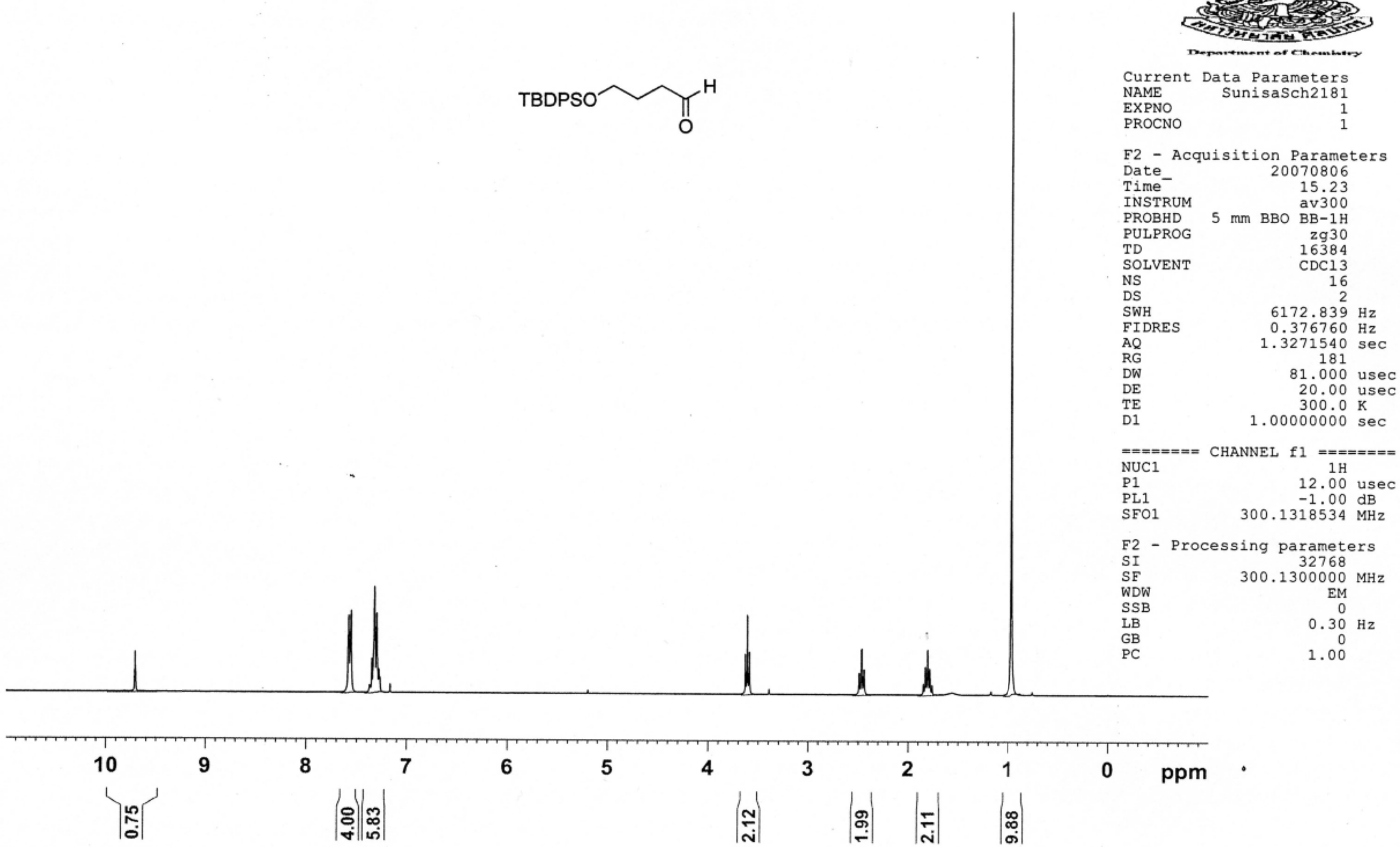


13C of monoTBDPS protected of 1,4-butanediol

```
Current Data Parameters
NAME       SunisaSch2017
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070606
Time               10.42
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG          zgdc30
TD                32768
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           17985.611 Hz
FIDRES         0.548877 Hz
AQ            0.9110004 sec
RG              20642.5
DW               27.800 usec
DE                 6.00 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  4.80 usec
PL1                -3.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              82.00 usec
PL2                -1.00 dB
PL12               16.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                131072
SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                  0.80 Hz
GB                     0
PC                  1.00
```

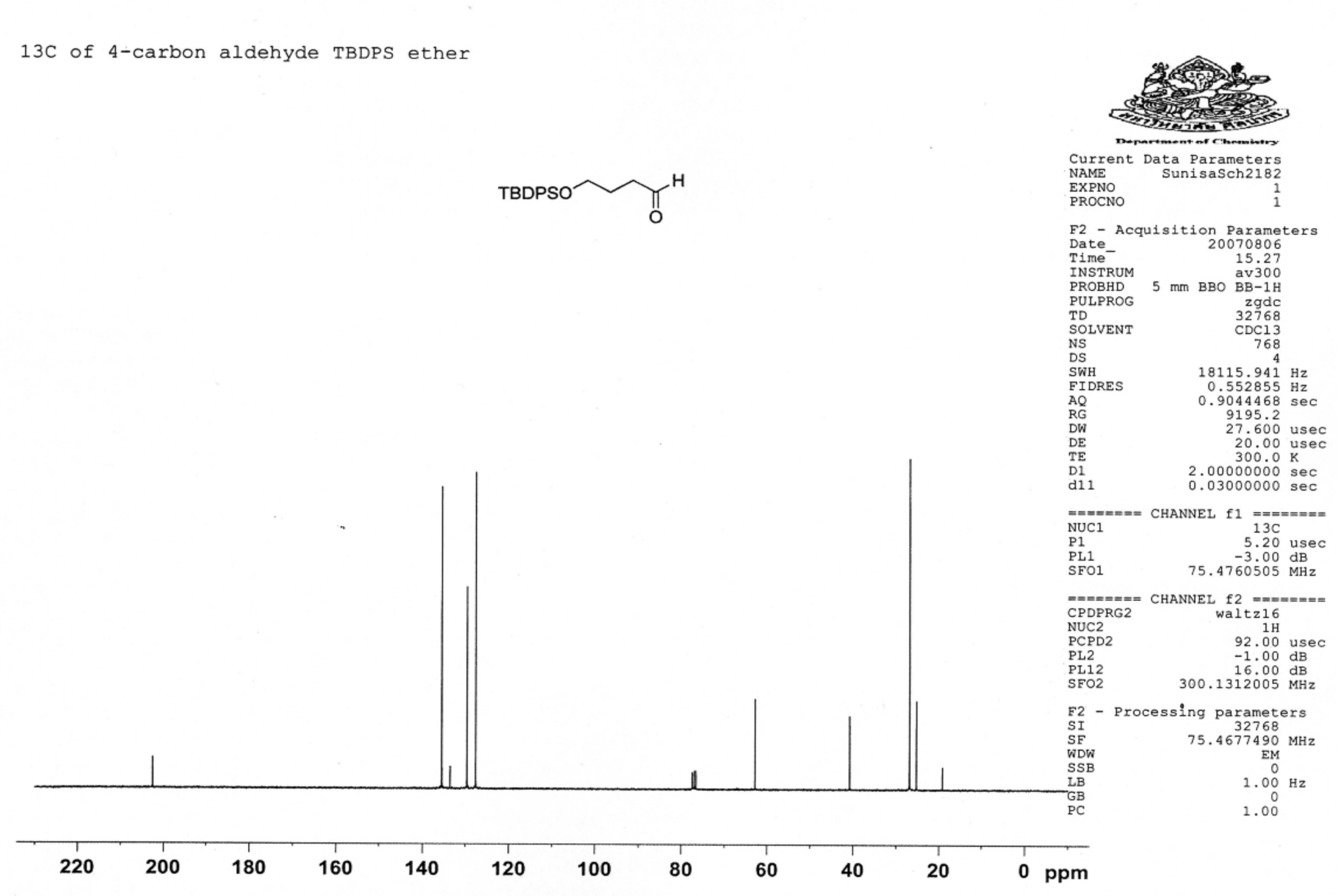
^{13}C NMR spectrum of 4-TBDPSO butanol

4C-aldehyde TBDPS ether



```
Current Data Parameters
NAME       SunisaSch2181
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070806
Time               15.23
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                   181
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

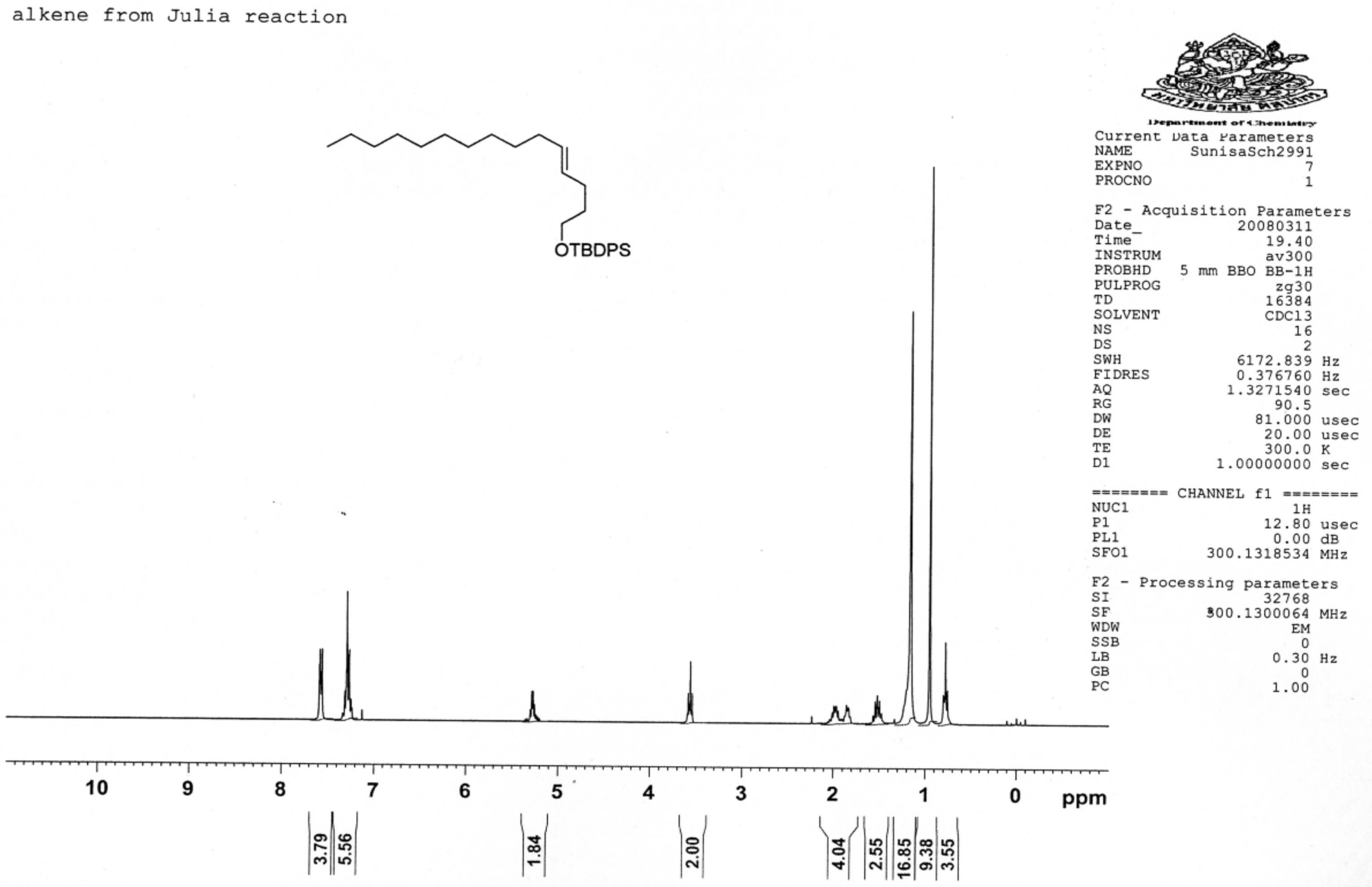
^{1}H NMR spectrum of compound **74**



13C of 4-carbon aldehyde TBDPS ether

```
Current Data Parameters
NAME        SunisaSch2182
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070806
Time                15.27
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zgdc
TD                  32768
SOLVENT             CDCl3
NS                    768
DS                      4
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                 9195.2
DW                 27.600 usec
DE                  20.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   5.20 usec
PL1                 -3.00 dB
SFO1           75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               92.00 usec
PL2                 -1.00 dB
PL12                16.00 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF             75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00
```

^{13}C NMR spectrum of compound **74**



alkene from Julia reaction

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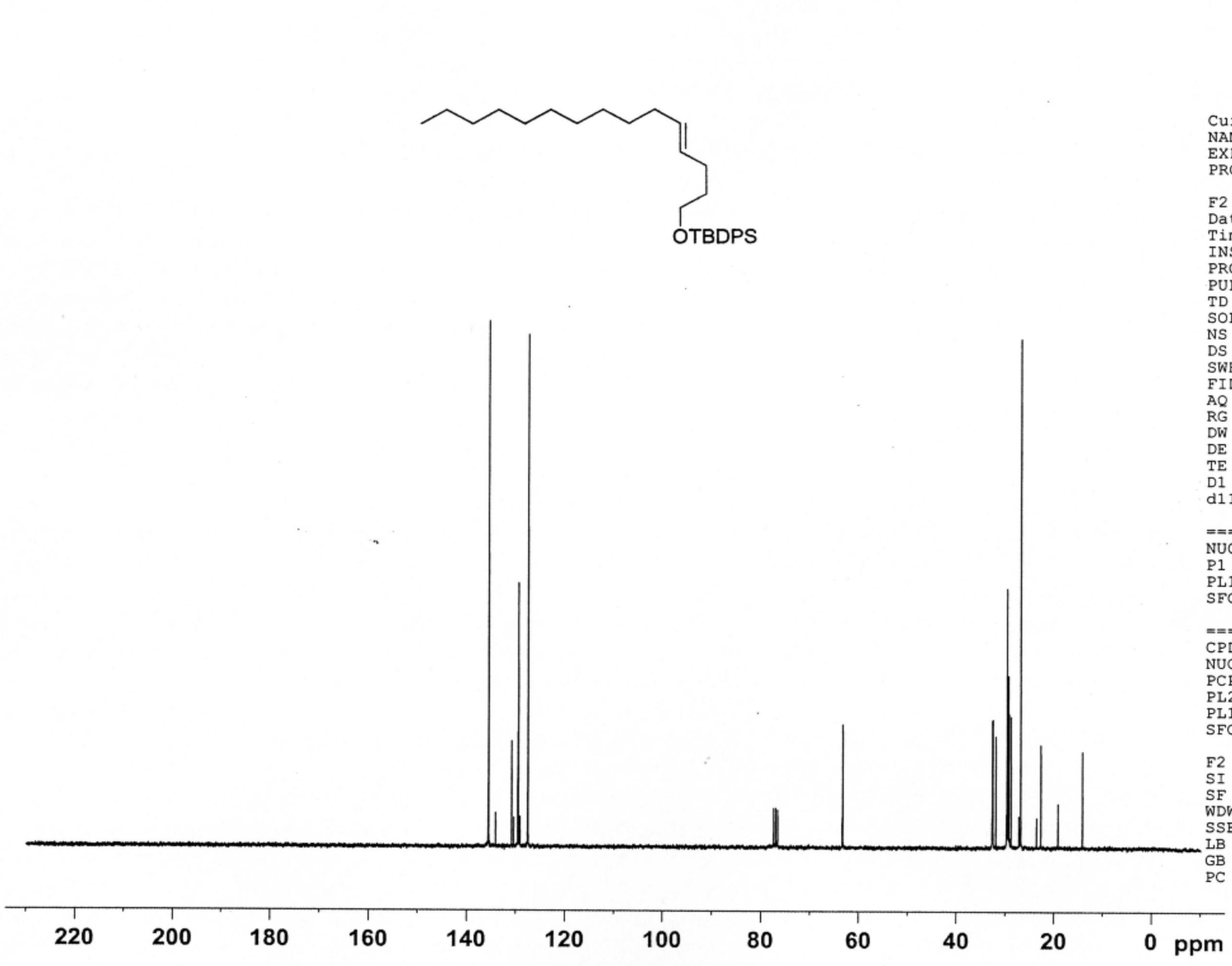
```
Current Data Parameters
NAME         SunisaSch2991
EXPNO                    7
PROCNO                   1

F2 - Acquisition Parameters
Date_             20080311
Time                 19.40
INSTRUM              av300
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   16384
SOLVENT              CDC13
NS                      16
DS                       2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                    90.5
DW                  81.000 usec
DE                   20.00 usec
TE                   300.0 K
D1              1.00000000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.80 usec
PL1                   0.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                   32768
SF            300.1300064 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

^{1}H NMR spectrum of compound **75**

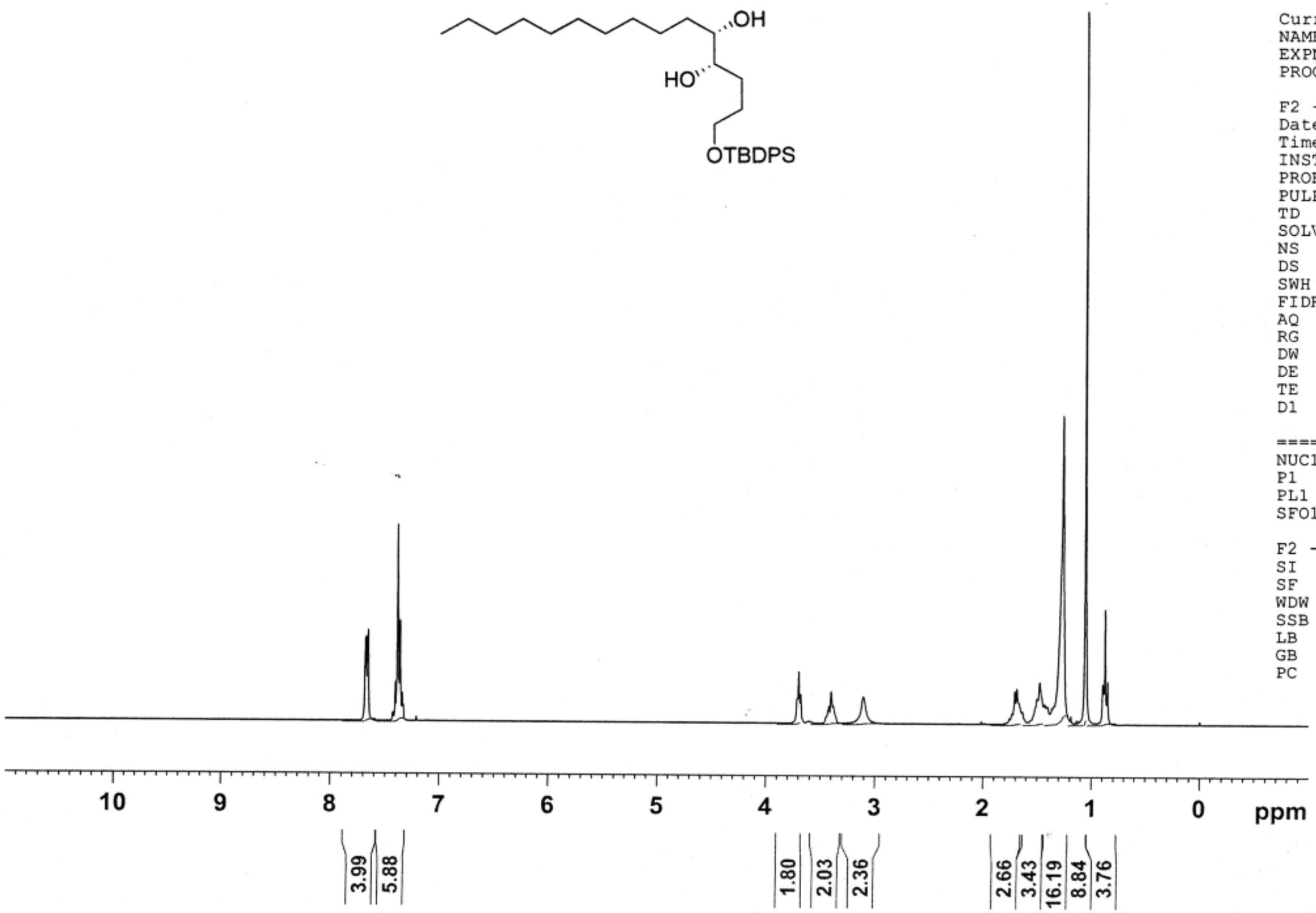
Julia reaction



```
Current Data Parameters
NAME        SunisaSch2991
EXPNO                   8
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080311
Time                19.51
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zgdc
TD                  32768
SOLVENT             CDCl3
NS                    328
DS                      4
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                 7298.2
DW                 27.600 usec
DE                  20.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   5.20 usec
PL1                 -3.00 dB
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  0.00 dB
PL12                17.20 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF             75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

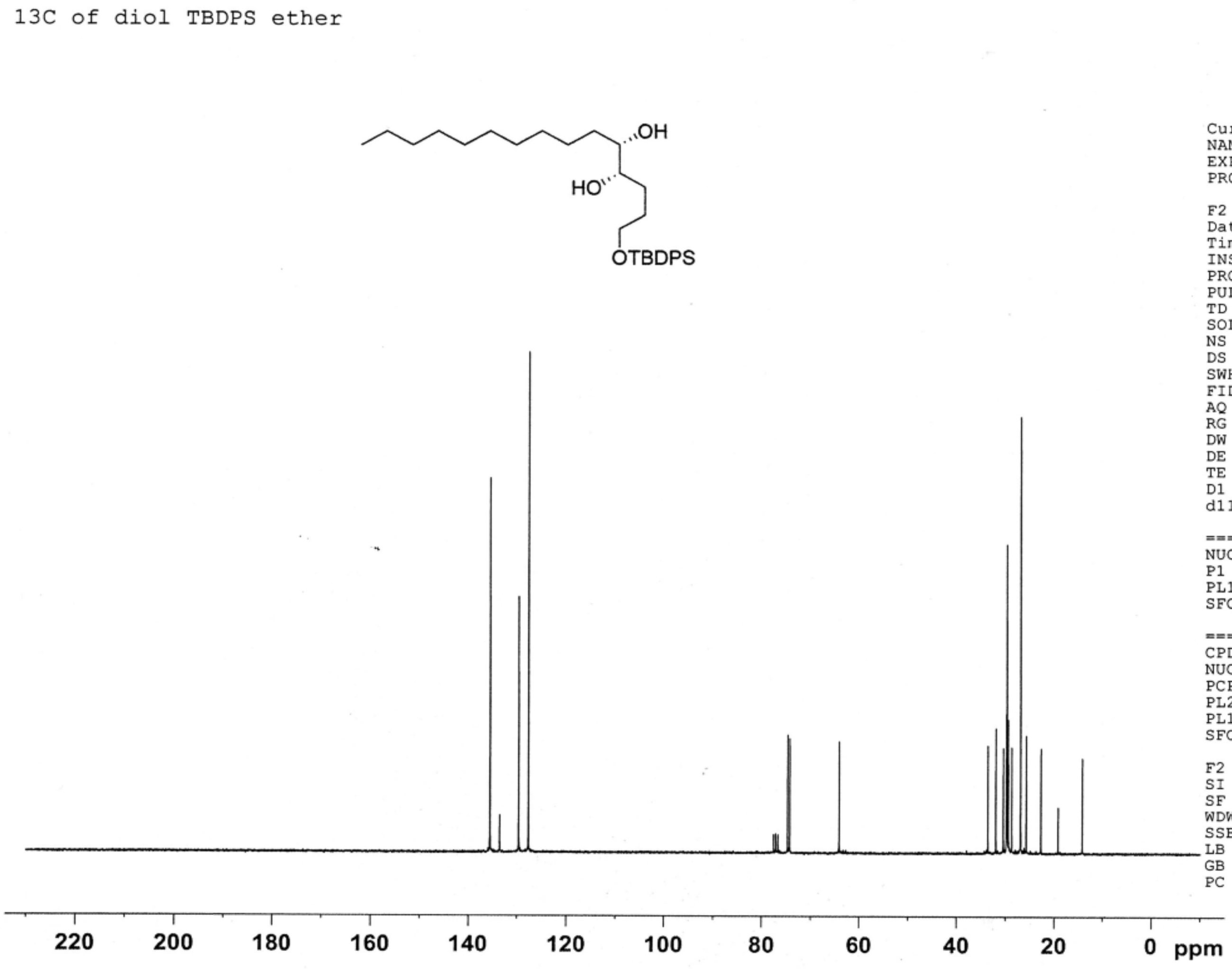
^{13}C NMR spectrum of compound **75**

Diol (TBDPS)



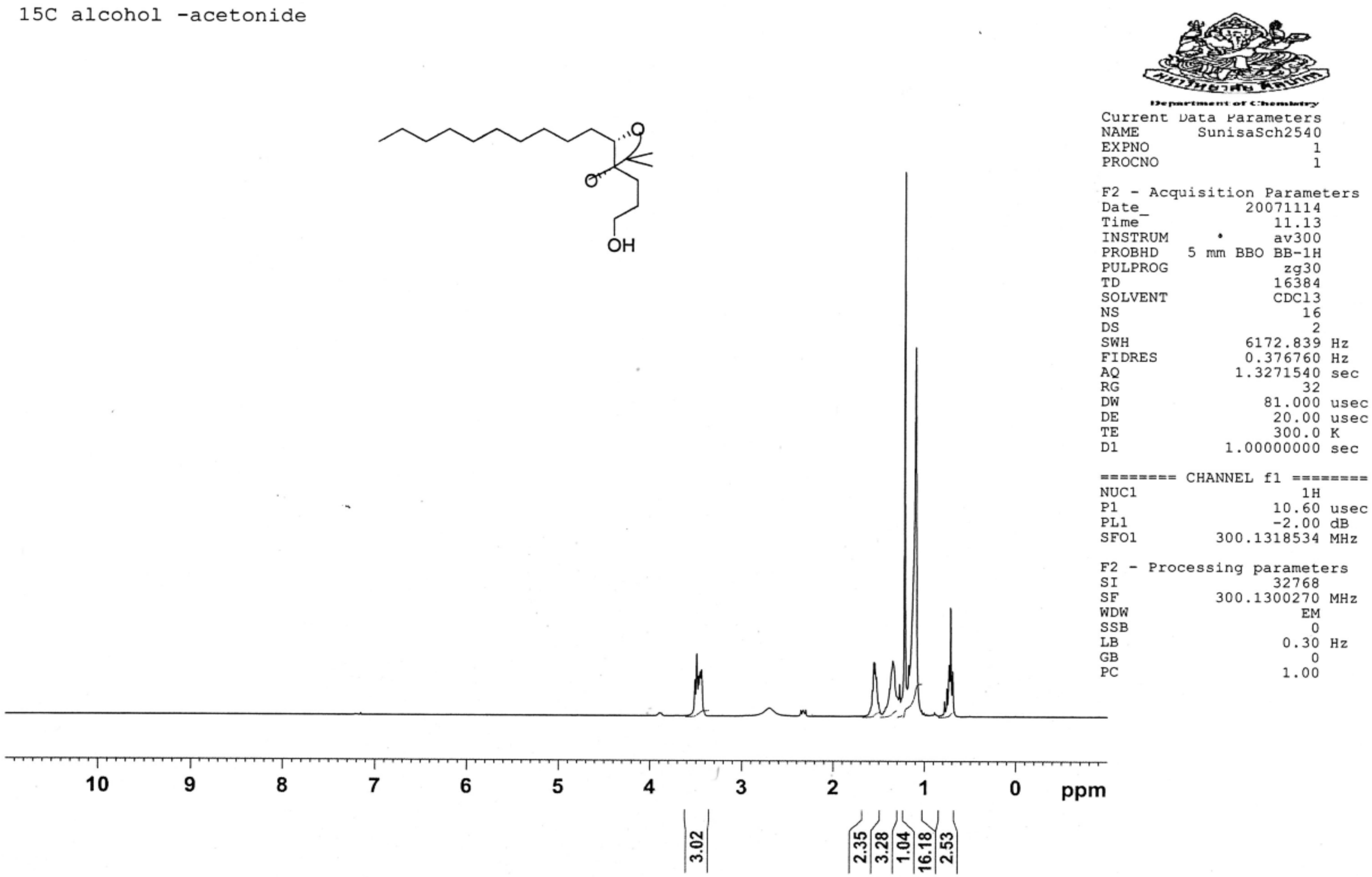
```
Current Data Parameters
NAME        SunisaSch2600
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20071121
Time                 7.56
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.376760 Hz
AQ              1.3271540 sec
RG                   40.3
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  10.60 usec
PL1                 -2.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR spectrum of compound **76**



```
Current Data Parameters
NAME        SunisaSch2995
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080326
Time                14.14
INSTRUM             av300
PROBHD    5 mm BBO BB-1H
PULPROG              zgdc
TD                  32768
SOLVENT             CDCl3
NS                    256
DS                      4
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                18390.4
DW                 27.600 usec
DE                  20.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   5.20 usec
PL1                 -3.00 dB
SFO1           75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  0.00 dB
PL12                17.20 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF             75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

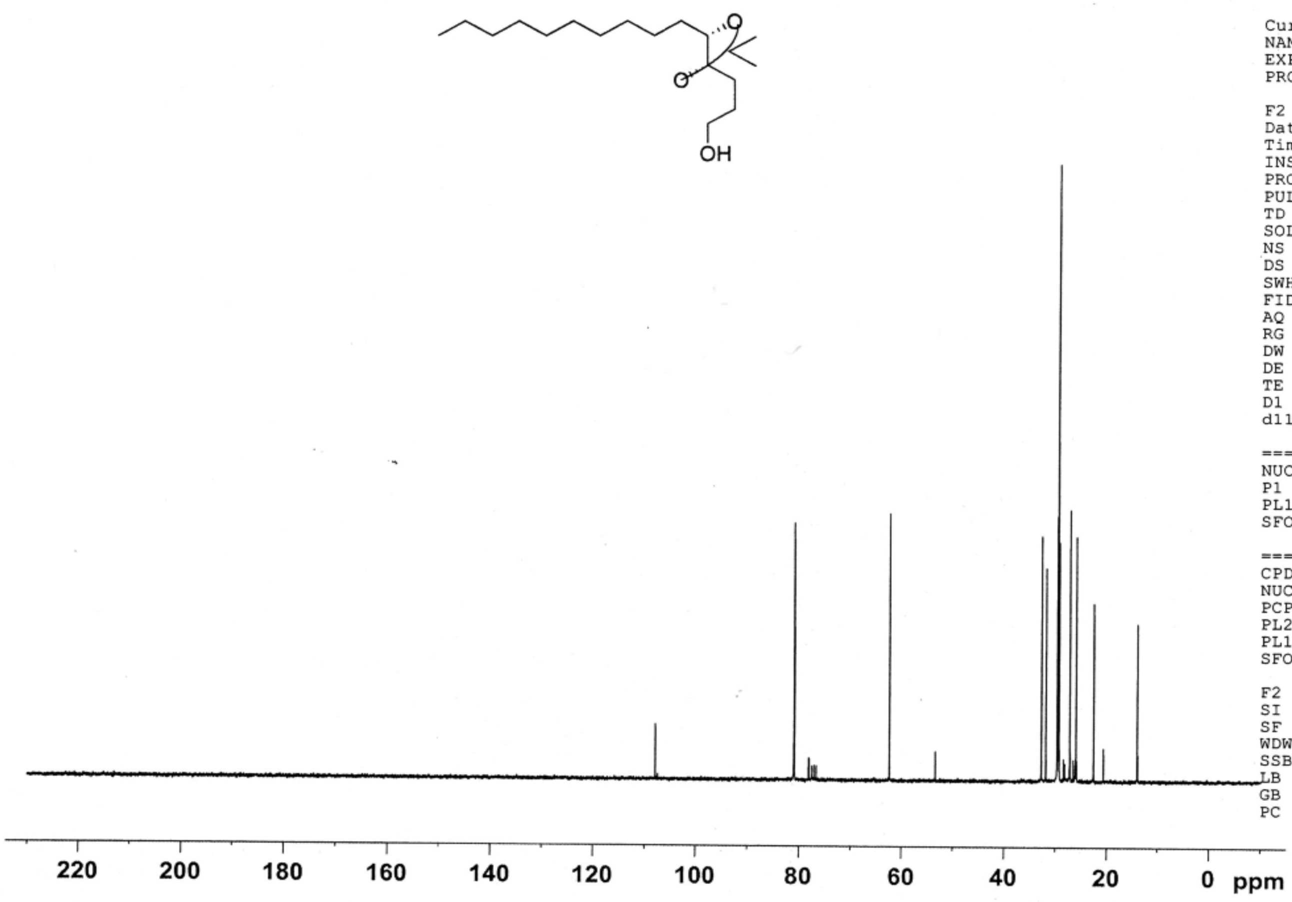
^{13}C NMR spectrum of compound **76**



```
Current Data Parameters
NAME         SunisaSch2540
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20071114
Time                 11.13
INSTRUM      •       av300
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   16384
SOLVENT              CDCl3
NS                      16
DS                       2
SWH            6172.839 Hz
FIDRES         0.376760 Hz
AQ            1.3271540 sec
RG                      32
DW               81.000 usec
DE                20.00 usec
TE                300.0 K
D1         1.00000000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                10.60 usec
PL1               -2.00 dB
SFO1       300.1318534 MHz

F2 - Processing parameters
SI                   32768
SF         300.1300270 MHz
WDW                     EM
SSB                      0
LB                 0.30 Hz
GB                       0
PC                    1.00
```

^{1}H NMR spectrum of compound **78**

13C of 15 carbon alcohol-acetonide



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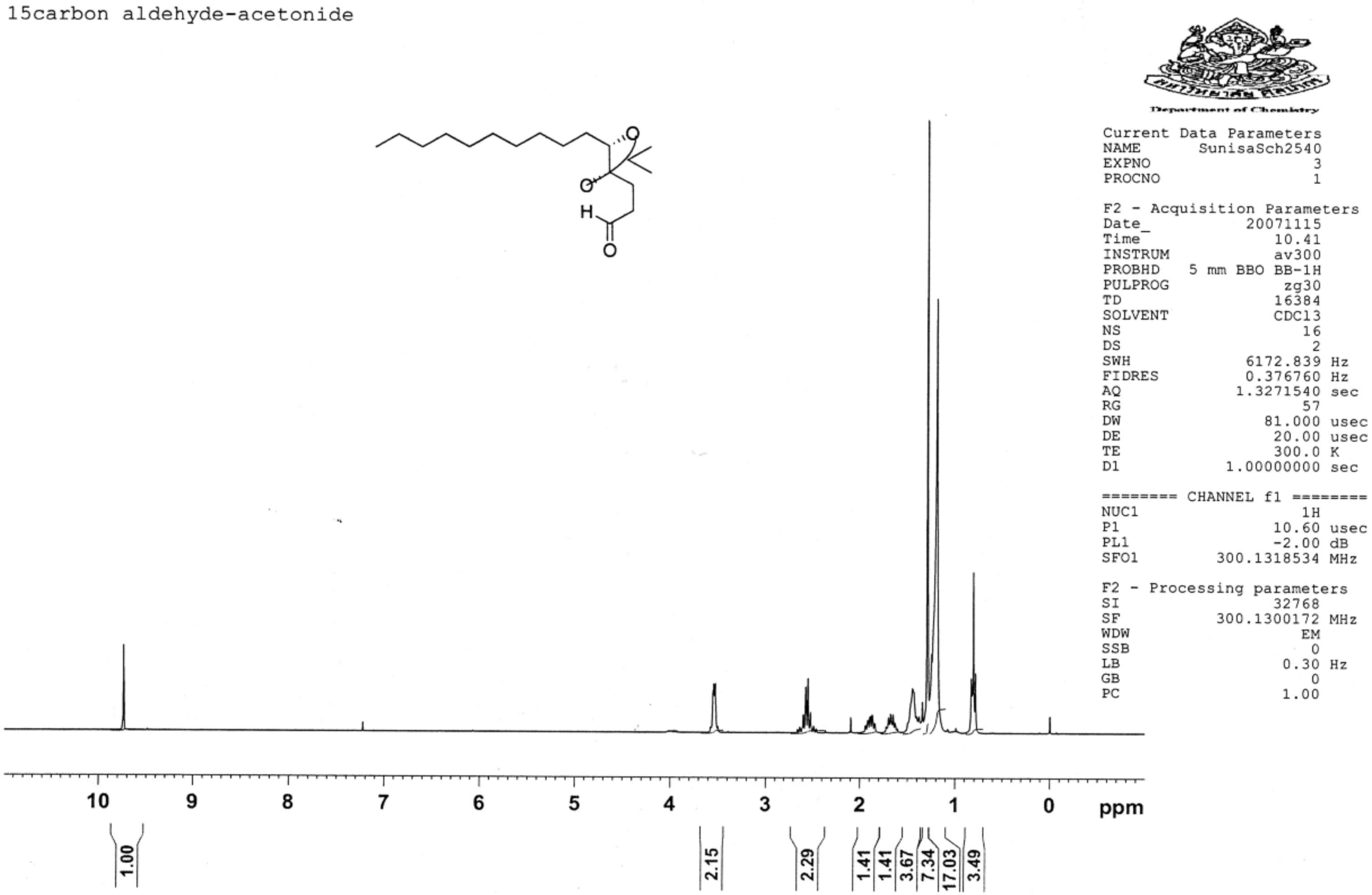
```
Current Data Parameters
NAME          SunisaSch2540
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20071114
Time                  11.20
INSTRUM               av300
PROBHD   5 mm BBO BB-1H
PULPROG                zgdc
TD                    32768
SOLVENT               CDC13
NS                      102
DS                        4
SWH               18115.941 Hz
FIDRES             0.552855 Hz
AQ                0.9044468 sec
RG                   9195.2
DW                   27.600 usec
DE                    20.00 usec
TE                    300.0 K
D1               2.00000000 sec
d11              0.03000000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                     5.20 usec
PL1                   -3.00 dB
SFO1             75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 95.00 usec
PL2                   -2.00 dB
PL12                  16.20 dB
SFO2            300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF               75.4677490 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.00
```

^{13}C NMR spectrum of compound **78**

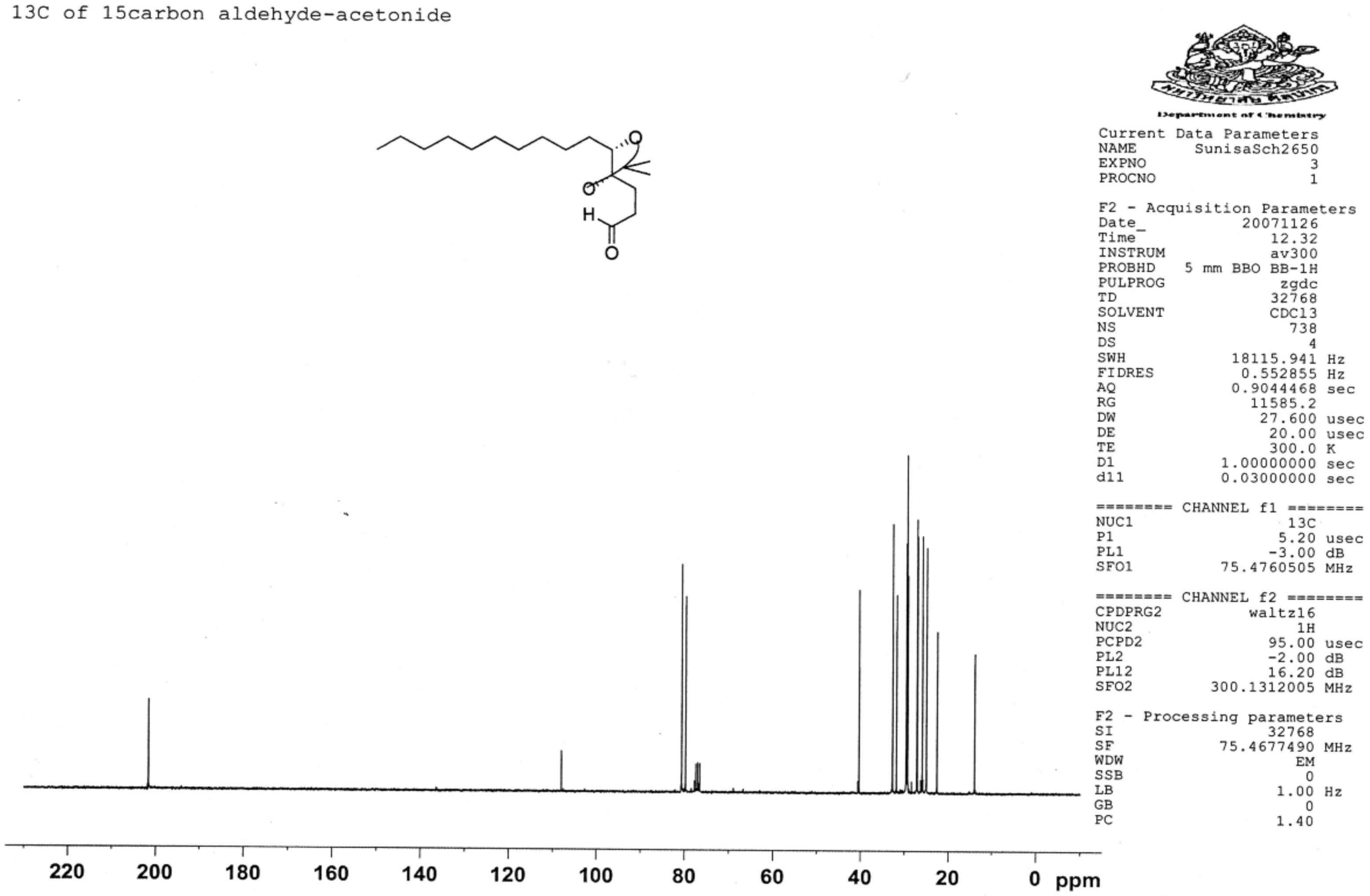


15carbon aldehyde-acetonide

```
Current Data Parameters
NAME         SunisaSch2540
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20071115
Time                 10.41
INSTRUM              av300
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   16384
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6172.839 Hz
FIDRES            0.376760 Hz
AQ               1.3271540 sec
RG                      57
DW                  81.000 usec
DE                   20.00 usec
TE                   300.0 K
D1              1.00000000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   10.60 usec
PL1                  -2.00 dB
SFO1           300.1318534 MHz

F2 - Processing parameters
SI                   32768
SF             300.1300172 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

^{1}H NMR spectrum of compound **79**

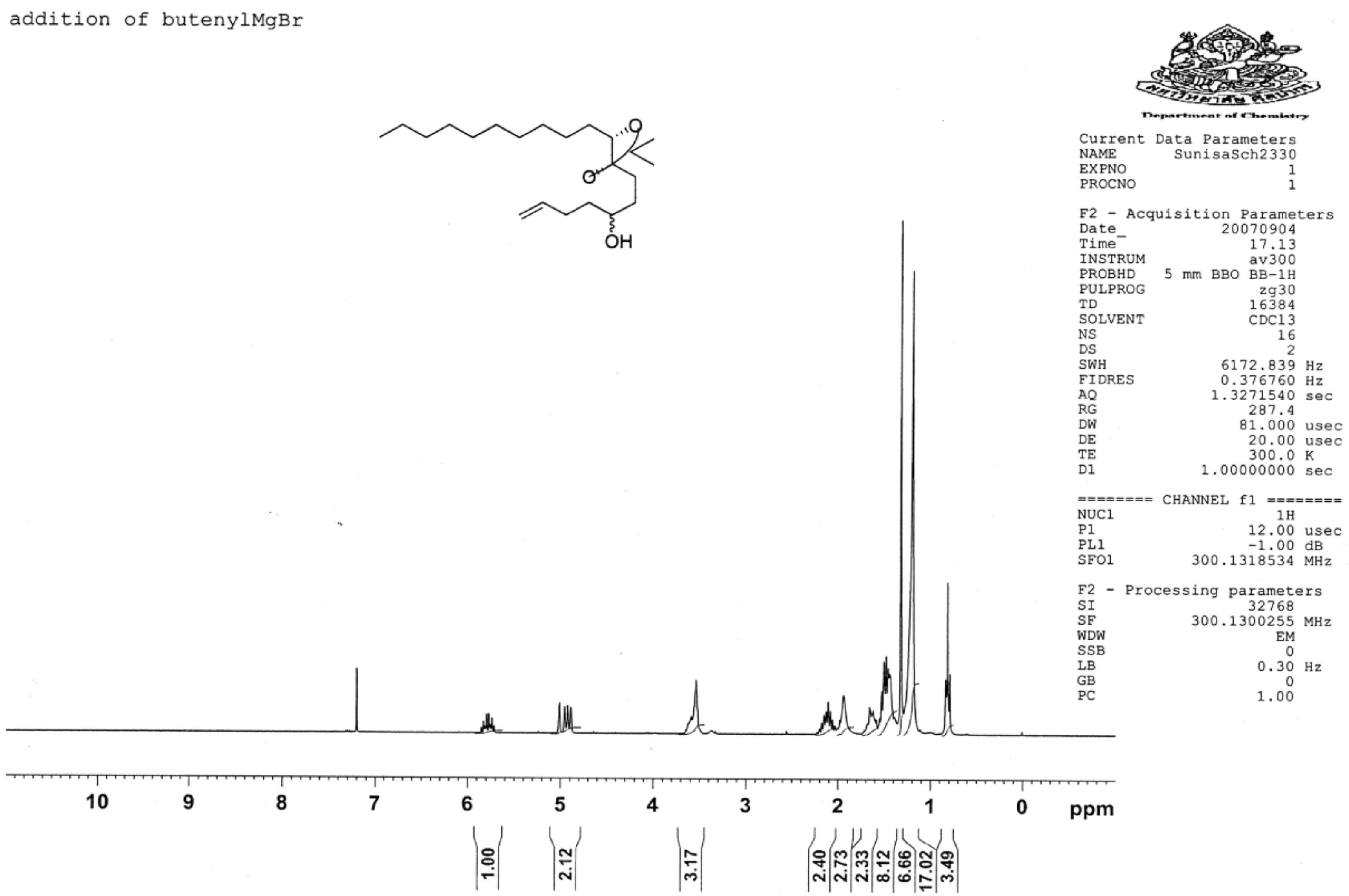
13C of 15carbon aldehyde-acetonide



```
Current Data Parameters
NAME        SunisaSch2650
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20071126
Time                12.32
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zgdc
TD                  32768
SOLVENT             CDCl3
NS                    738
DS                      4
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                11585.2
DW                 27.600 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   5.20 usec
PL1                 -3.00 dB
SFO1           75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               95.00 usec
PL2                 -2.00 dB
PL12                16.20 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF             75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

^{13}C NMR spectrum of compound **79**

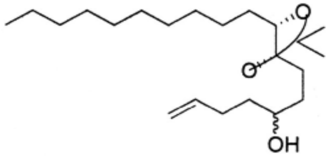
addition of butenylMgBr



```
Current Data Parameters
NAME       SunisaSch2330
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070904
Time               17.13
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                 287.4
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300255 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR spectrum of compound **80**

13C of addition of butenylMgBr



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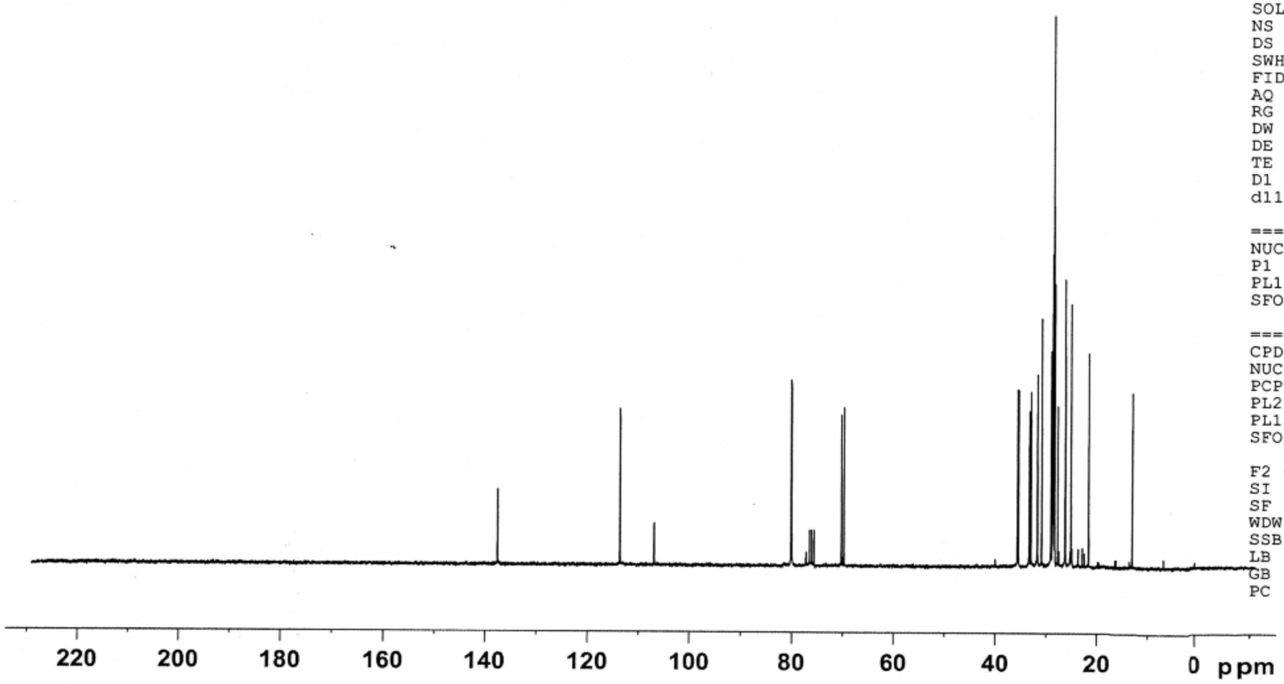
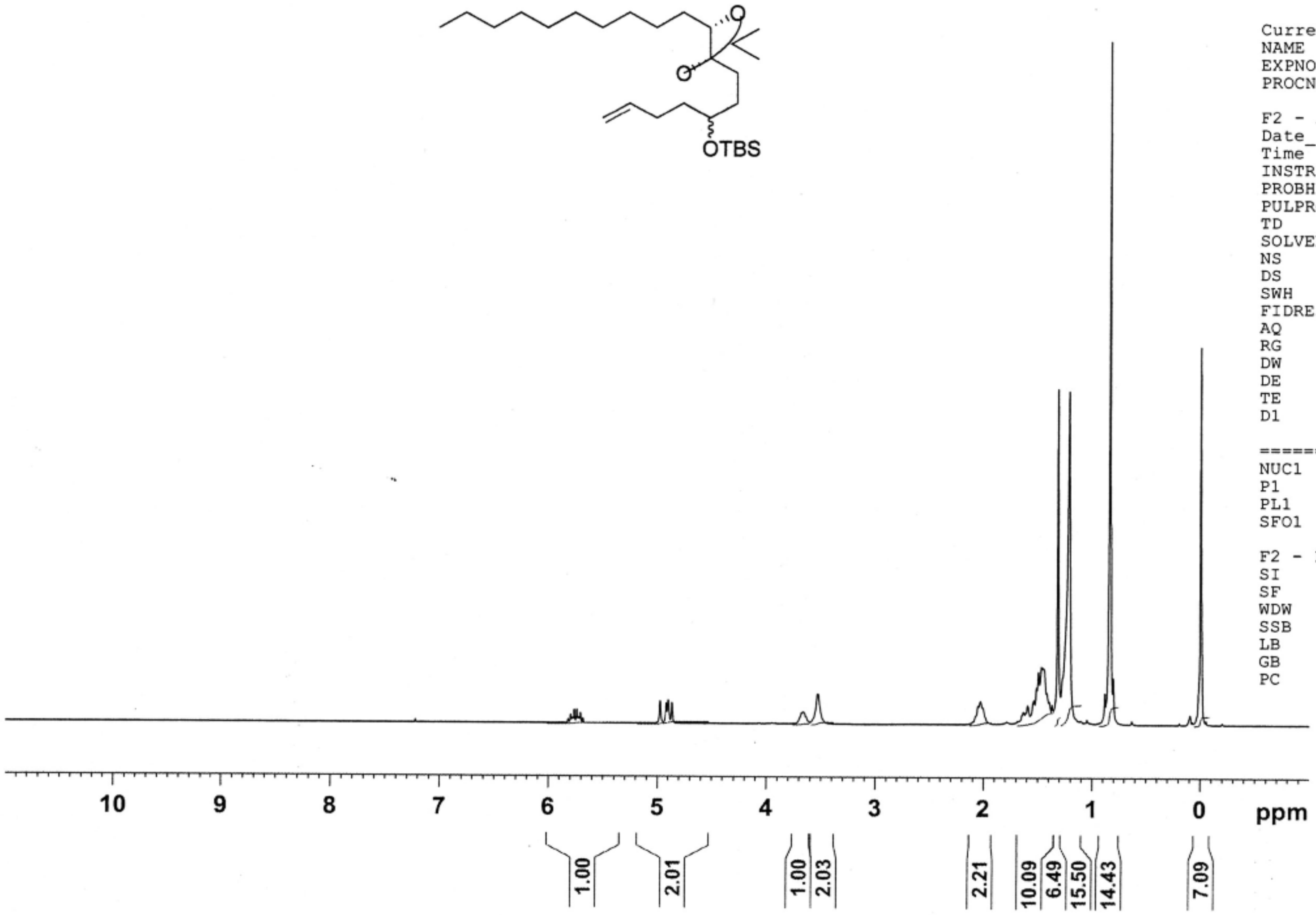
```
Current Data Parameters
NAME          SunisaSch2670
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20071128
Time                  10.08
INSTRUM               av300
PROBHD   5 mm BBO BB-1H
PULPROG                zgdc
TD                    32768
SOLVENT               CDCl3
NS                      512
DS                        4
SWH               18115.941 Hz
FIDRES             0.552855 Hz
AQ                0.9044468 sec
RG                  10321.3
DW                   27.600 usec
DE                    20.00 usec
TE                    300.0 K
D1               1.00000000 sec
d11              0.03000000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                     5.20 usec
PL1                   -3.00 dB
SFO1            75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 95.00 usec
PL2                   -2.00 dB
PL12                  16.20 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF               75.4678216 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```



^{13}C NMR spectrum of compound **80**

TBS protect 2o alcohol



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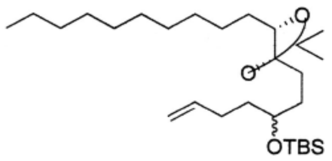
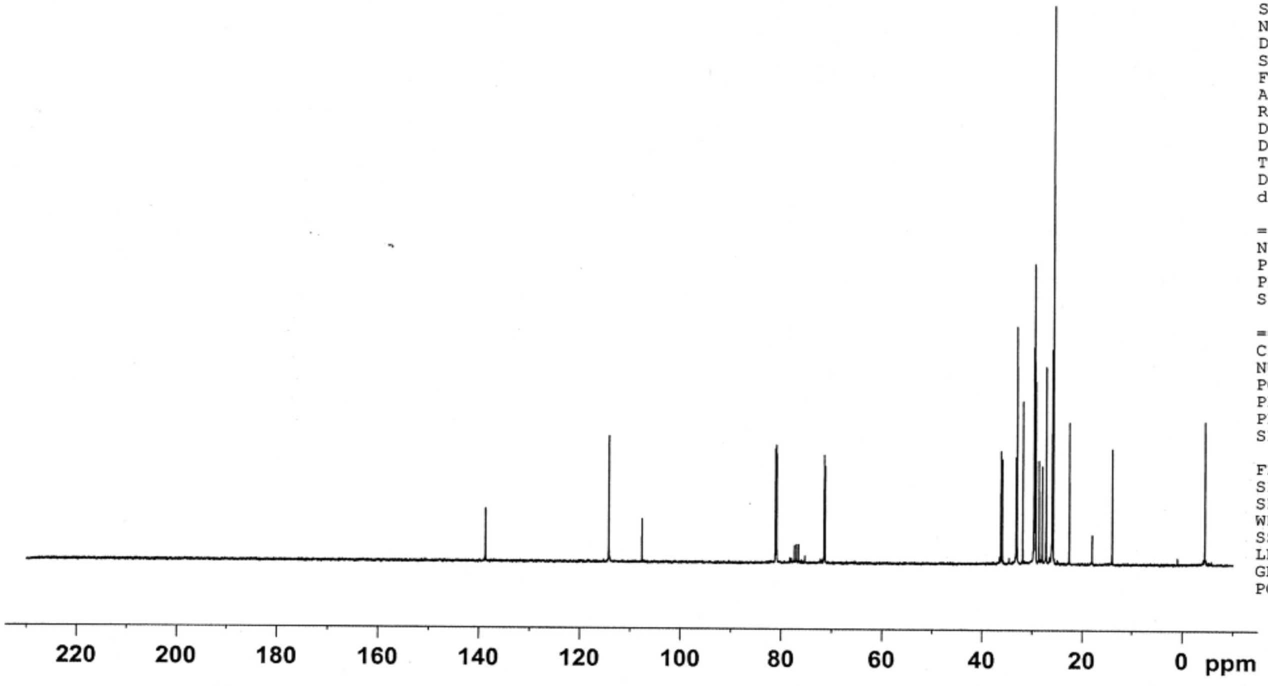
```
Current Data Parameters
NAME       SunisaSch2700
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20071201
Time               12.50
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                  28.5
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.60 usec
PL1                -2.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300189 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR spectrum of compound **81**

13C of TBS protect 2o alcohol

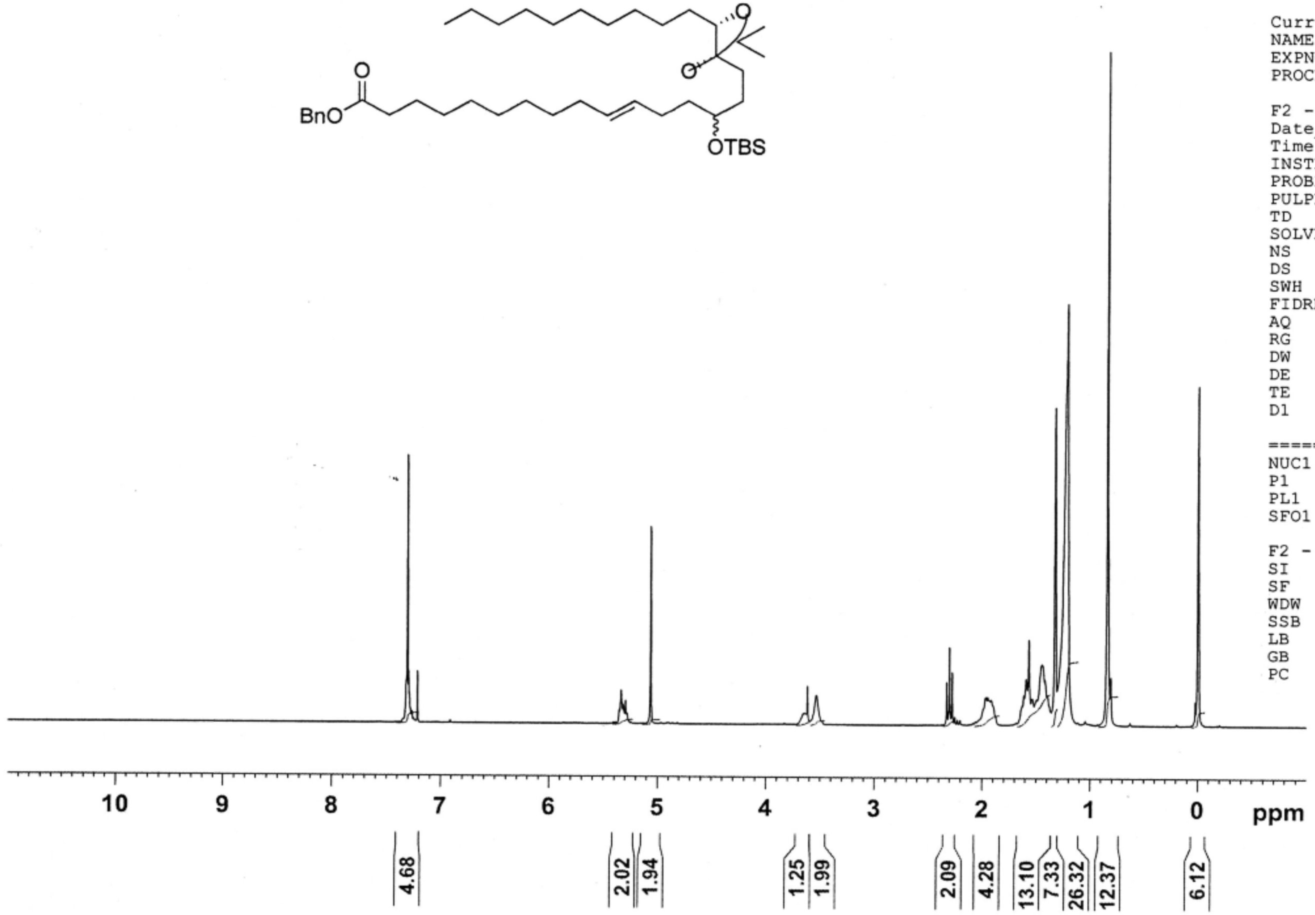




```
Department of Chemistry
Current Data Parameters
NAME          SunisaSch2700
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20071201
Time                  12.56
INSTRUM               av300
PROBHD   5 mm BBO BB-1H
PULPROG                zgdc
TD                    32768
SOLVENT               CDCl3
NS                      307
DS                        4
SWH               18115.941 Hz
FIDRES             0.552855 Hz
AQ                0.9044468 sec
RG                   9195.2
DW                   27.600 usec
DE                    20.00 usec
TE                    300.0 K
D1               1.00000000 sec
d11              0.03000000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                     5.20 usec
PL1                   -3.00 dB
SFO1             75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 95.00 usec
PL2                   -2.00 dB
PL12                  16.20 dB
SFO2            300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF               75.4677490 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

^{13}C NMR spectrum of compound **81**

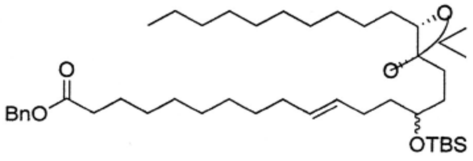
Olefin metathesis monoTBS



```
Current Data Parameters
NAME          SunisaSch2340
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20070906
Time                   8.47
INSTRUM               av300
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                    161.3
DW               81.000 usec
DE                20.00 usec
TE                  300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                12.00 usec
PL1                 -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF           300.1300198 MHz
WDW                      EM
SSB                       0
LB                  0.30 Hz
GB                        0
PC                     1.00
```

^{1}H NMR spectrum of compound **82**

13C of olefin metathesis monoTBS



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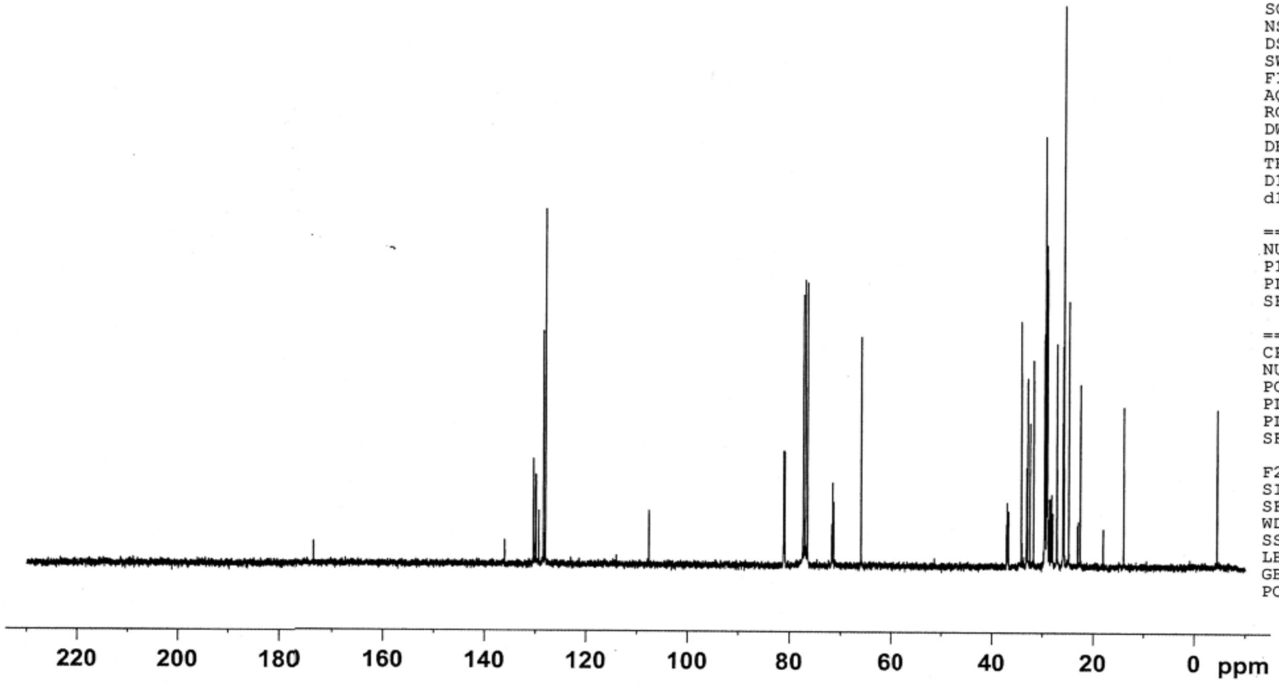
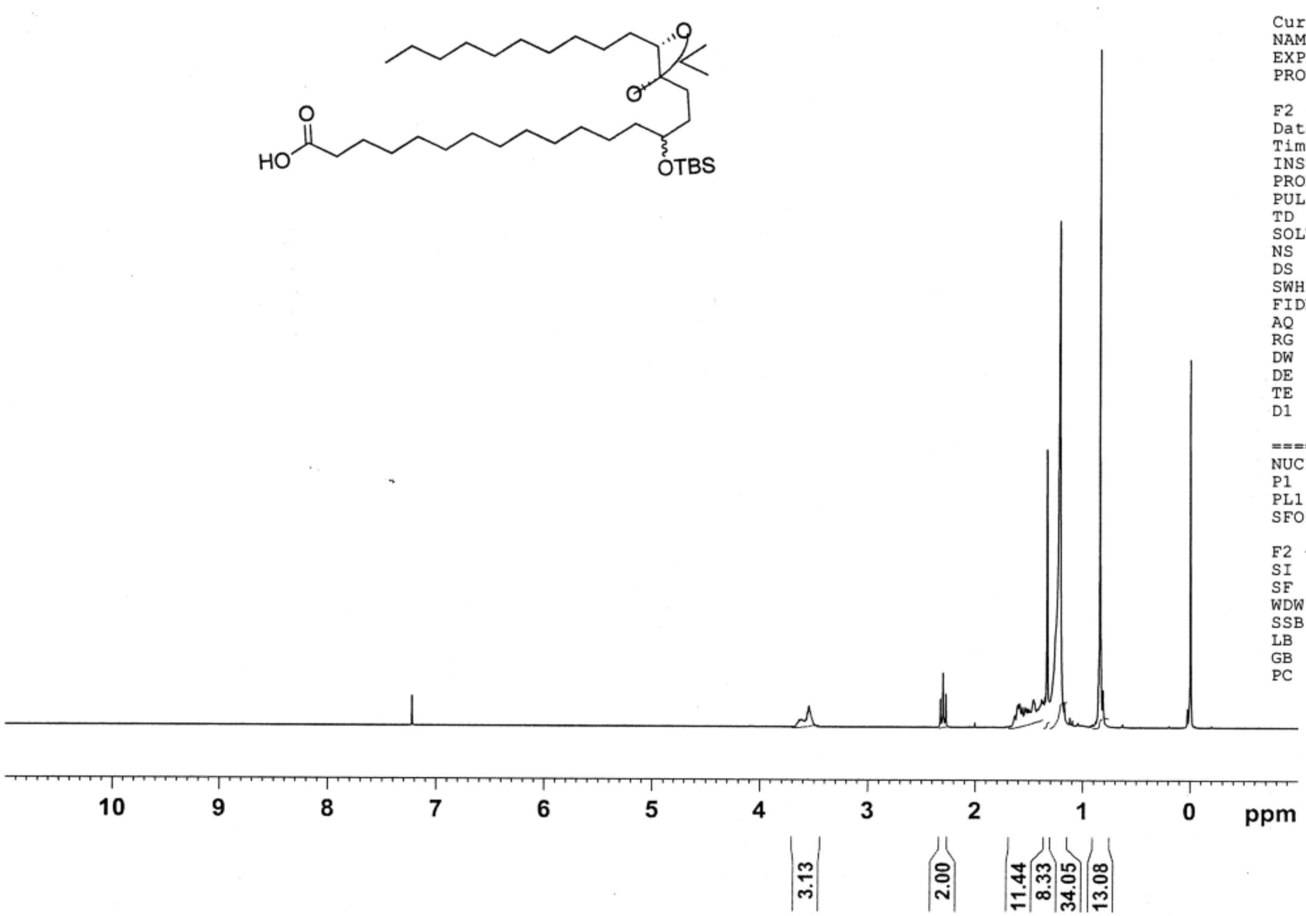
```
Current Data Parameters
NAME          SunisaSch2360
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20070906
Time                  18.55
INSTRUM               av300
PROBHD     5 mm BBO BB-1H
PULPROG                zgdc
TD                    32768
SOLVENT               CDCl3
NS                     2048
DS                        4
SWH               18115.941 Hz
FIDRES             0.552855 Hz
AQ                0.9044468 sec
RG                  11585.2
DW                   27.600 usec
DE                    20.00 usec
TE                    300.0 K
D1               2.00000000 sec
d11              0.03000000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                     5.20 usec
PL1                   -3.00 dB
SFO1             75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 92.00 usec
PL2                   -1.00 dB
PL12                  16.00 dB
SFO2            300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF               75.4677490 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```



^{13}C NMR spectrum of compound **82**

28C fatty acid side chain mixture 2 diastereomer



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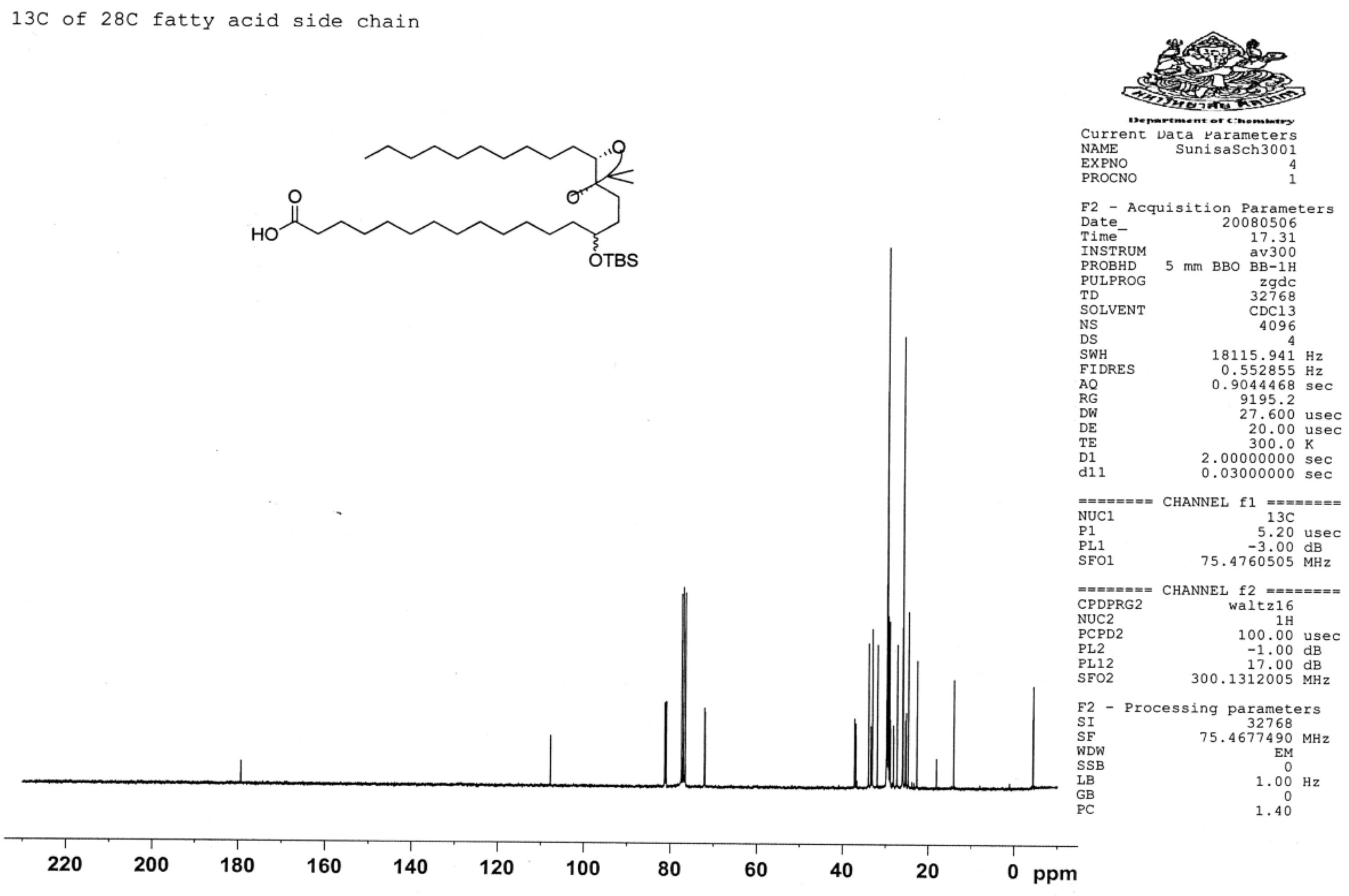
```
Current Data Parameters
NAME          SunisaSch3001
EXPNO                     3
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080506
Time                  17.16
INSTRUM               av300
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    16384
SOLVENT               CDC13
NS                       16
DS                        2
SWH               6172.839 Hz
FIDRES            0.376760 Hz
AQ               1.3271540 sec
RG                      181
DW                   81.000 usec
DE                    20.00 usec
TE                    300.0 K
D1               1.00000000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    12.80 usec
PL1                    0.00 dB
SFO1           300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF             300.1300175 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

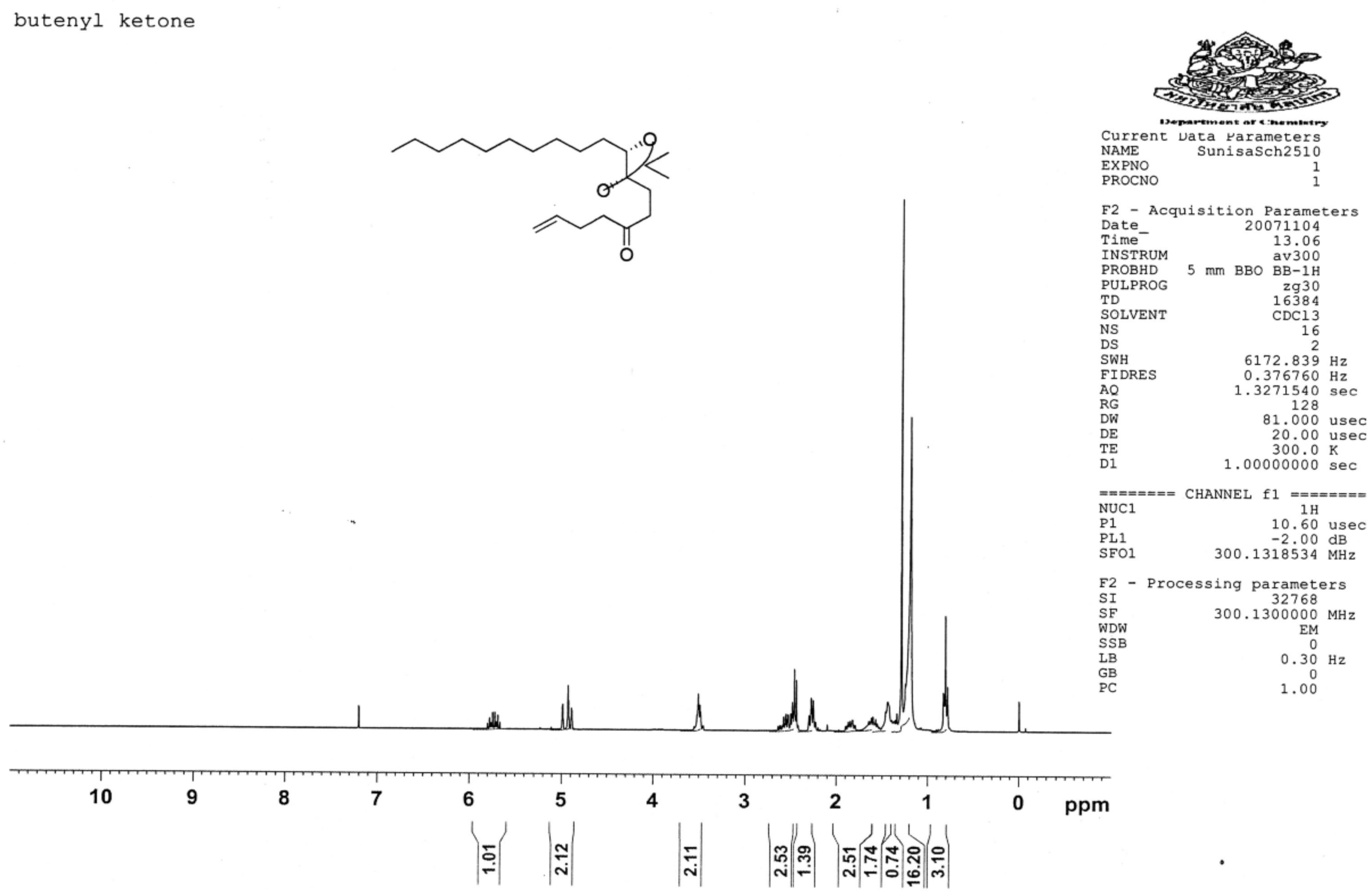
^{1}H NMR spectrum of compound **83**



13C of 28C fatty acid side chain

```
Department of Chemistry
Current Data Parameters
NAME         SunisaSch3001
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_             20080506
Time                 17.31
INSTRUM              av300
PROBHD     5 mm BBO BB-1H
PULPROG               zgdc
TD                   32768
SOLVENT              CDC13
NS                    4096
DS                       4
SWH              18115.941 Hz
FIDRES            0.552855 Hz
AQ               0.9044468 sec
RG                  9195.2
DW                  27.600 usec
DE                   20.00 usec
TE                   300.0 K
D1              2.00000000 sec
d11             0.03000000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    5.20 usec
PL1                  -3.00 dB
SFO1            75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                  -1.00 dB
PL12                 17.00 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                   32768
SF              75.4677490 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

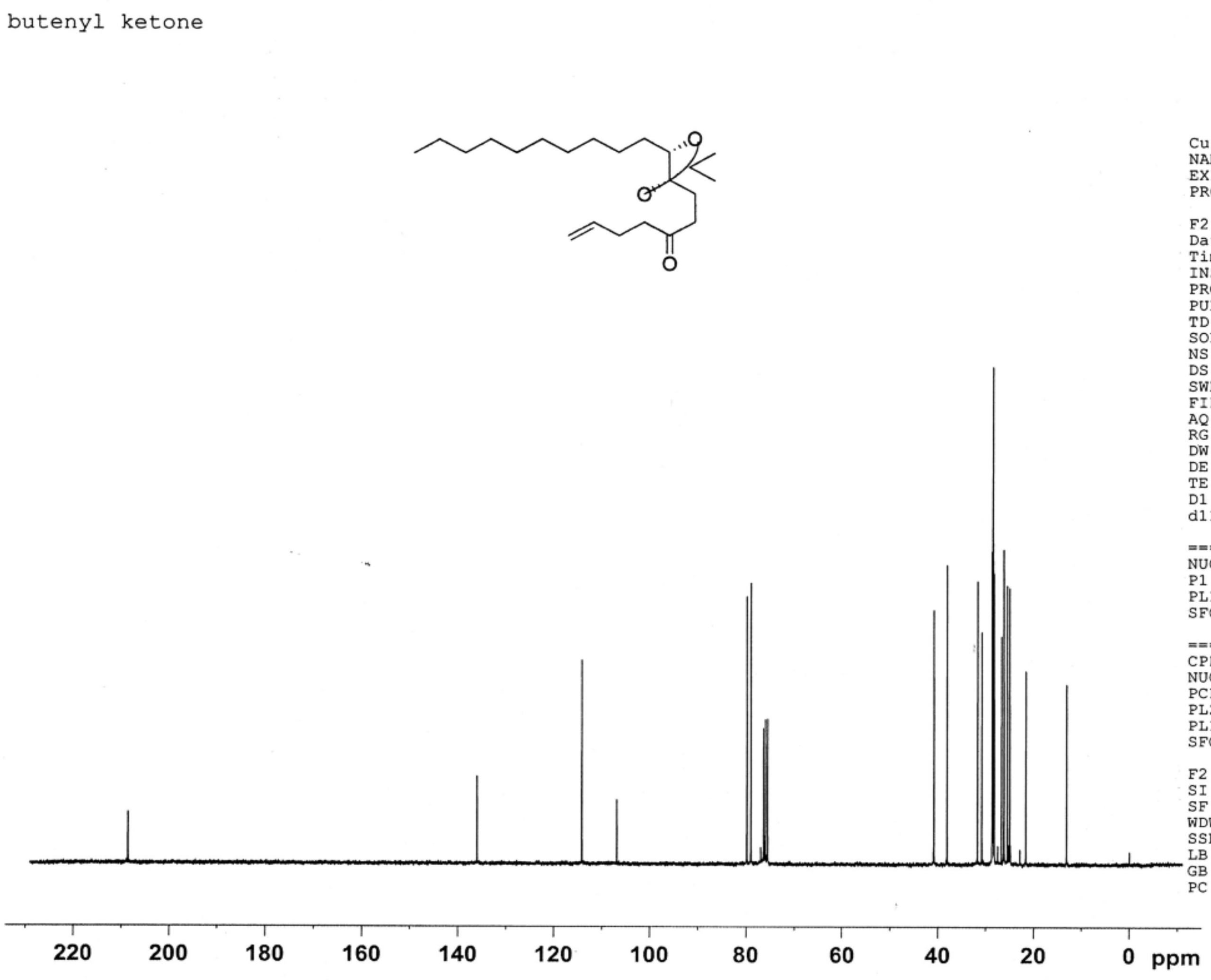
^{13}C NMR spectrum of compound **83**



butenyl ketone

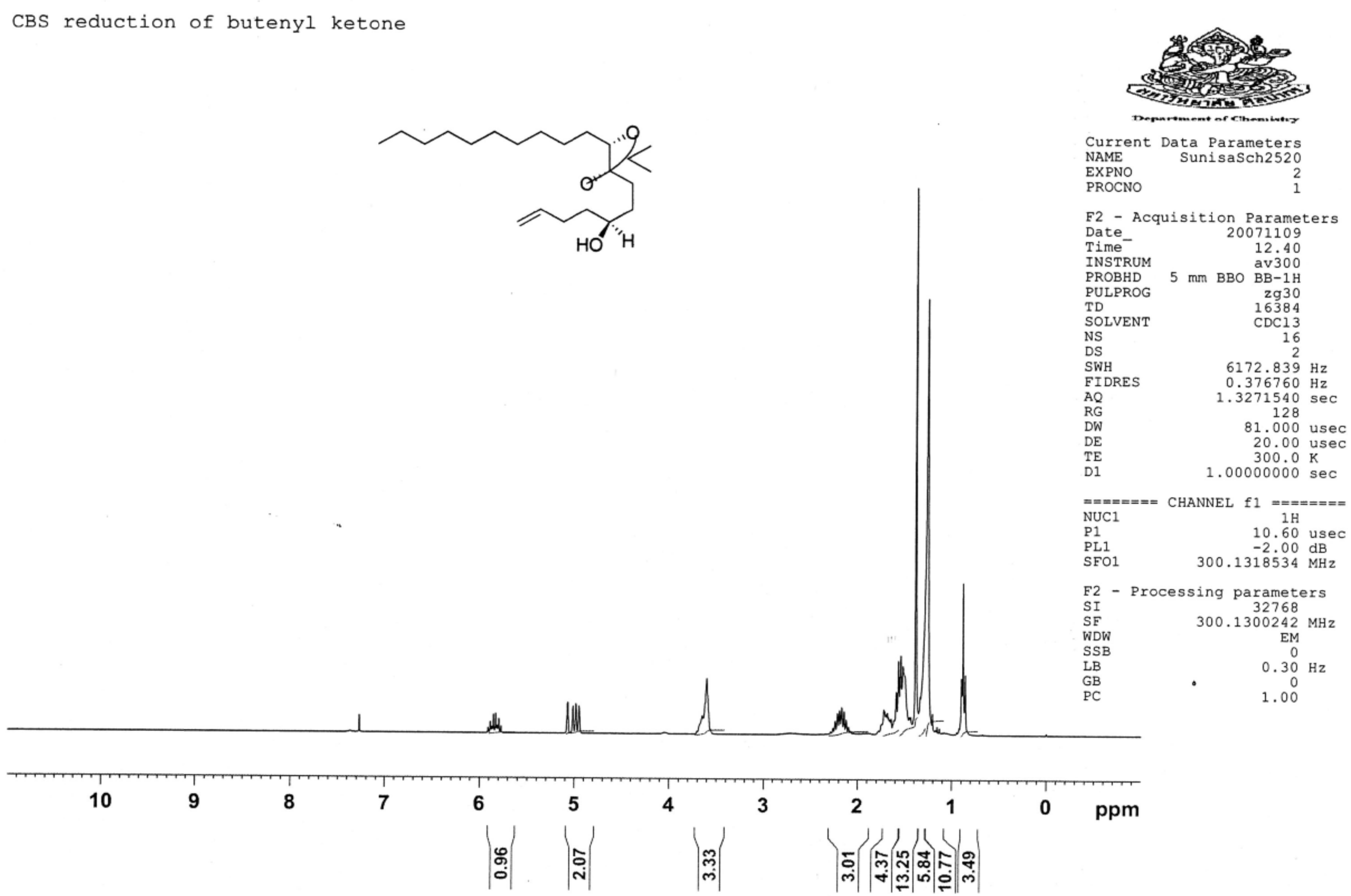
```
Current Data Parameters
NAME          SunisaSch2510
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20071104
Time_                 13.06
INSTRUM               av300
PROBHD    5 mm BBO BB-1H
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                6172.839 Hz
FIDRES             0.376760 Hz
AQ                1.3271540 sec
RG                      128
DW                   81.000 usec
DE                    20.00 usec
TE                    300.0 K
D1               1.00000000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    10.60 usec
PL1                   -2.00 dB
SFO1            300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF              300.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

^{1}H NMR spectrum of compound **84**



```
Current Data Parameters
NAME       SunisaSch2510
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20071104
Time               13.21
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zgdc
TD                 65536
SOLVENT            CDCl3
NS                  2048
DS                     2
SWH            18115.941 Hz
FIDRES          0.276427 Hz
AQ             1.8088436 sec
RG                 13004
DW                27.600 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec
d11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  5.20 usec
PL1                -3.00 dB
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              95.00 usec
PL2                -2.00 dB
PL12               16.20 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4678238 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{13}C NMR spectrum of compound **84**

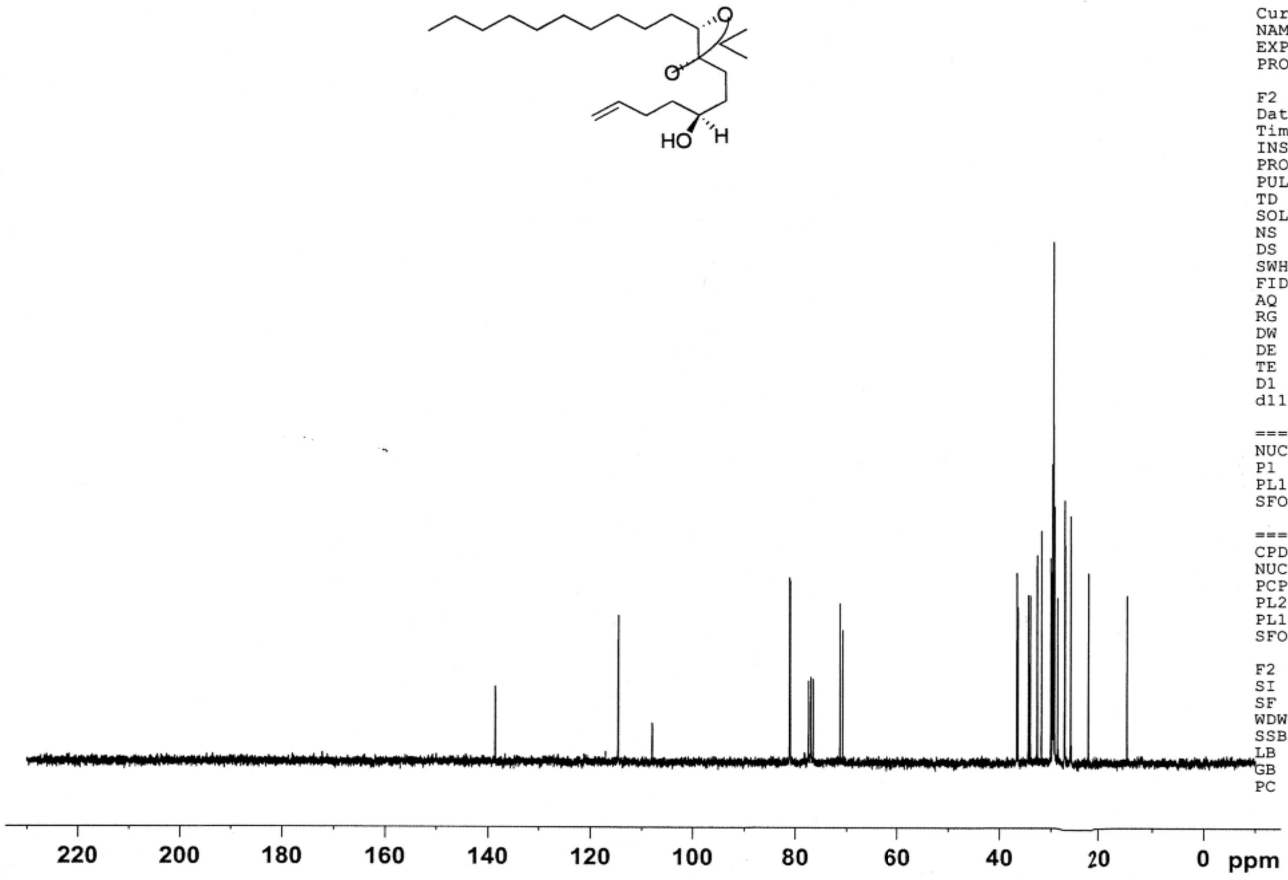


CBS reduction of butenyl ketone

```
Current Data Parameters
NAME        SunisaSch2520
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20071109
Time                12.40
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.376760 Hz
AQ              1.3271540 sec
RG                    128
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  10.60 usec
PL1                 -2.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300242 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR spectrum of compound **85**

CBS reduction of butenyl ketone



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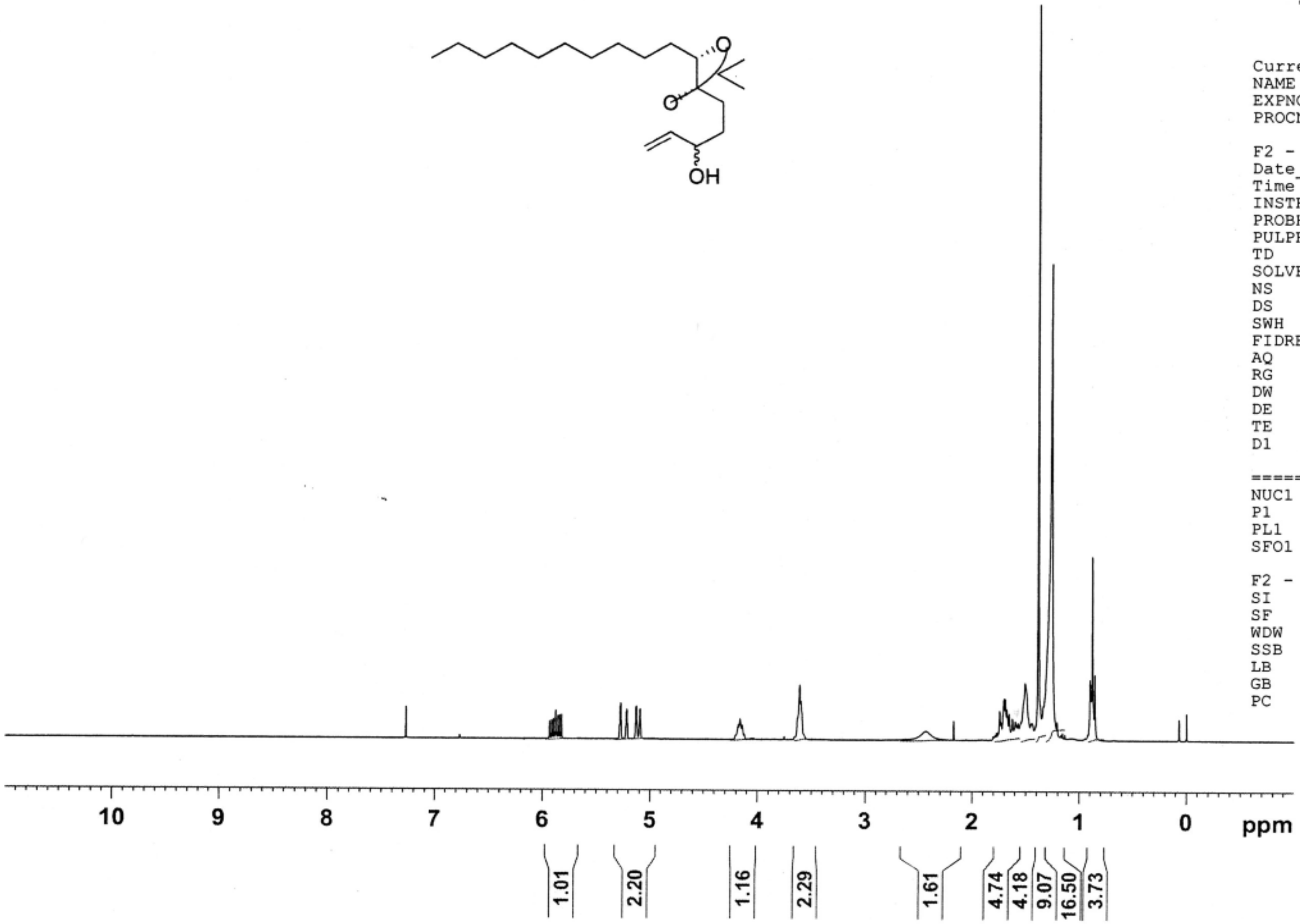
```
Current Data Parameters
NAME        SunisaSch2520
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20071109
Time_               12.44
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zgdc
TD                  32768
SOLVENT             CDCl3
NS                    204
DS                      2
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                 9195.2
DW                 27.600 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   5.20 usec
PL1                 -3.00 dB
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               95.00 usec
PL2                 -2.00 dB
PL12                16.20 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF             75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

^{13}C NMR spectrum of compound **85**

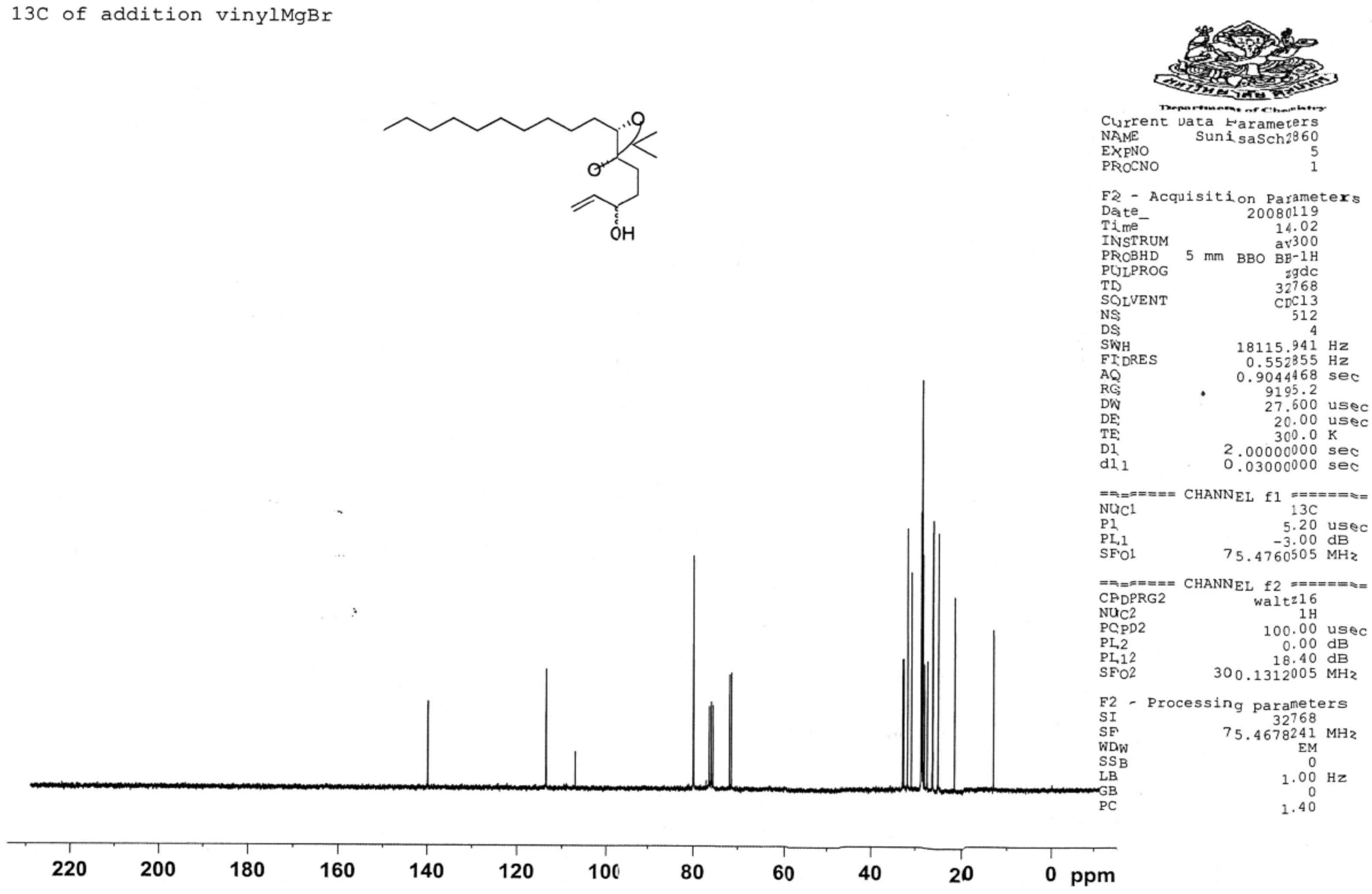
addition vinylMgBr



Department of Chemistry

```
Current Data Parameters
NAME       SunisaSch2860
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080119
Time               13.49
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                 161.3
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.40 usec
PL1                 0.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300137 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR spectrum of compound **86**

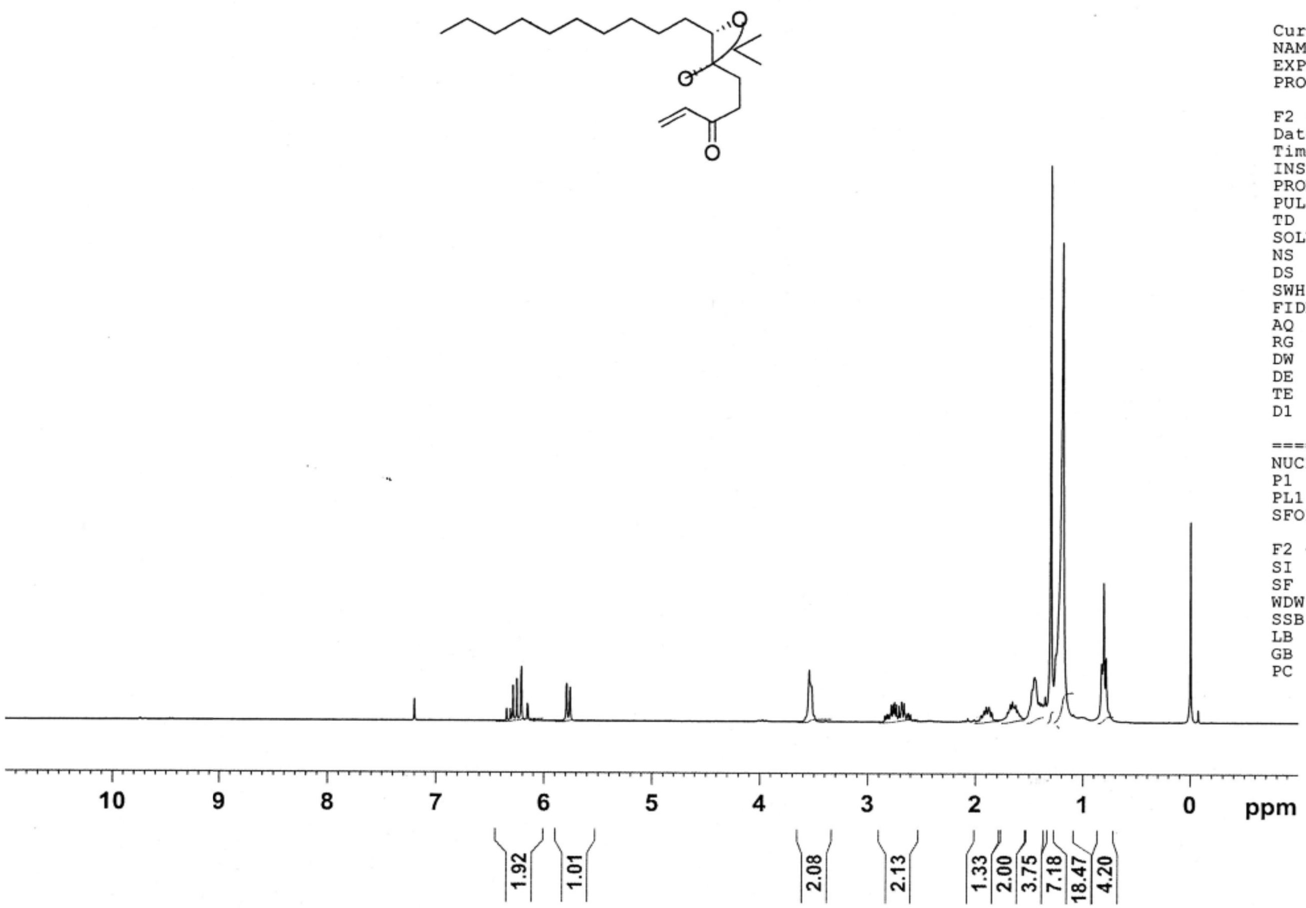


13C of addition vinylMgBr

```
Current Data Parameters
NAME          SunisaSch2860
EXPNO                     5
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080119
Time                  14.02
INSTRUM               av300
PROBHD   5 mm  BBO BB-1H
PULPROG                zgdc
TD                    32768
SOLVENT               CDCl3
NS                      512
DS                        4
SWH               18115.941 Hz
FIDRES             0.552855 Hz
AQ                0.9044468 sec
RG                   9195.2
DW                   27.600 usec
DE                    20.00 usec
TE                    300.0 K
D1               2.00000000 sec
d11              0.03000000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                     5.20 usec
PL1                   -3.00 dB
SFO1             75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                    0.00 dB
PL12                  18.40 dB
SFO2            300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF               75.4678241 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

^{13}C NMR spectrum of compound **86**

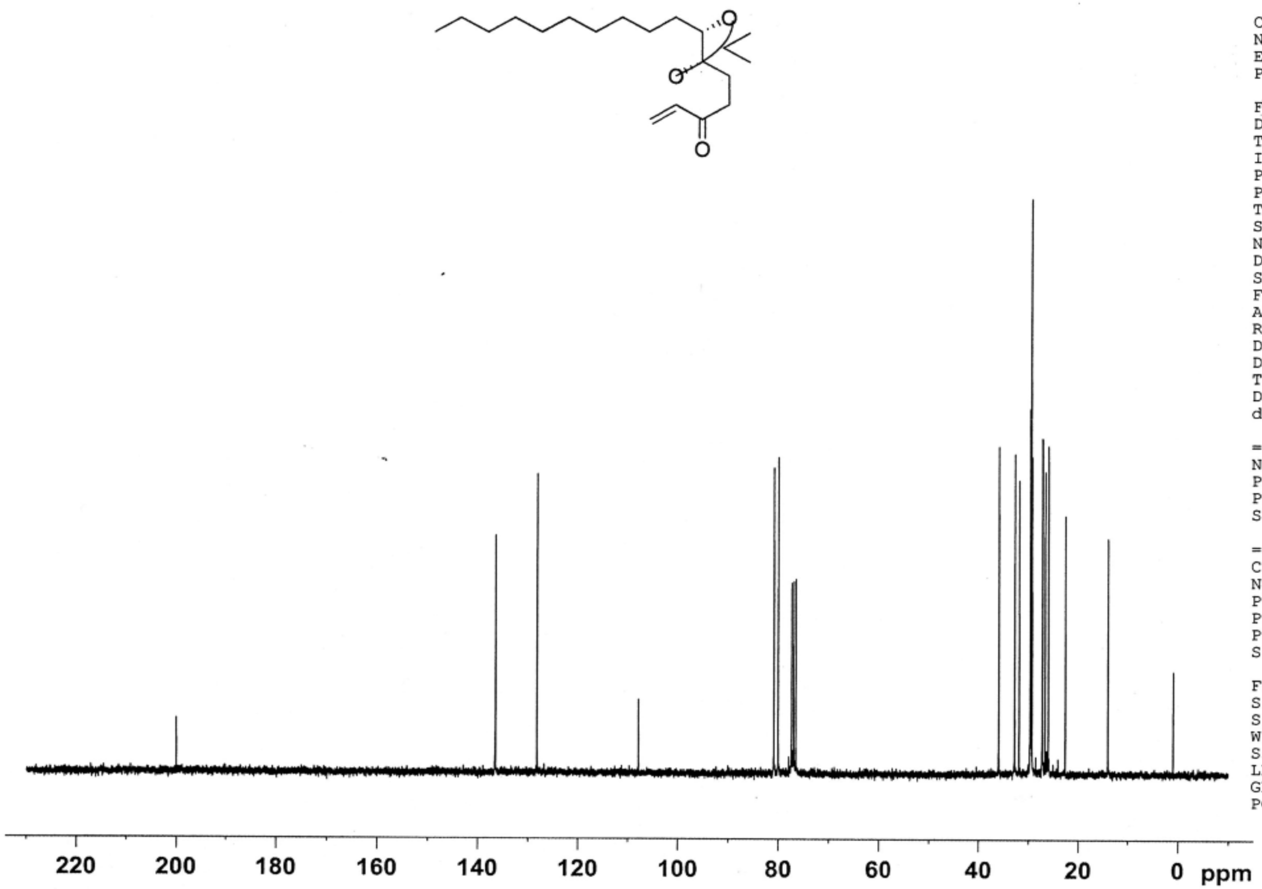
vinyl ketone



```
Current Data Parameters
NAME          SunisaSch2950
EXPNO                     4
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080228
Time                  12.46
INSTRUM               av300
PROBHD     5 mm BBO BB-1H
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH              6172.839 Hz
FIDRES           0.376760 Hz
AQ              1.3271540 sec
RG                    161.3
DW                   81.000 usec
DE                    20.00 usec
TE                    300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    12.80 usec
PL1                    0.00 dB
SFO1            300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF              300.1300238 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

^{1}H NMR spectrum of compound **87**

13C of vinylketone



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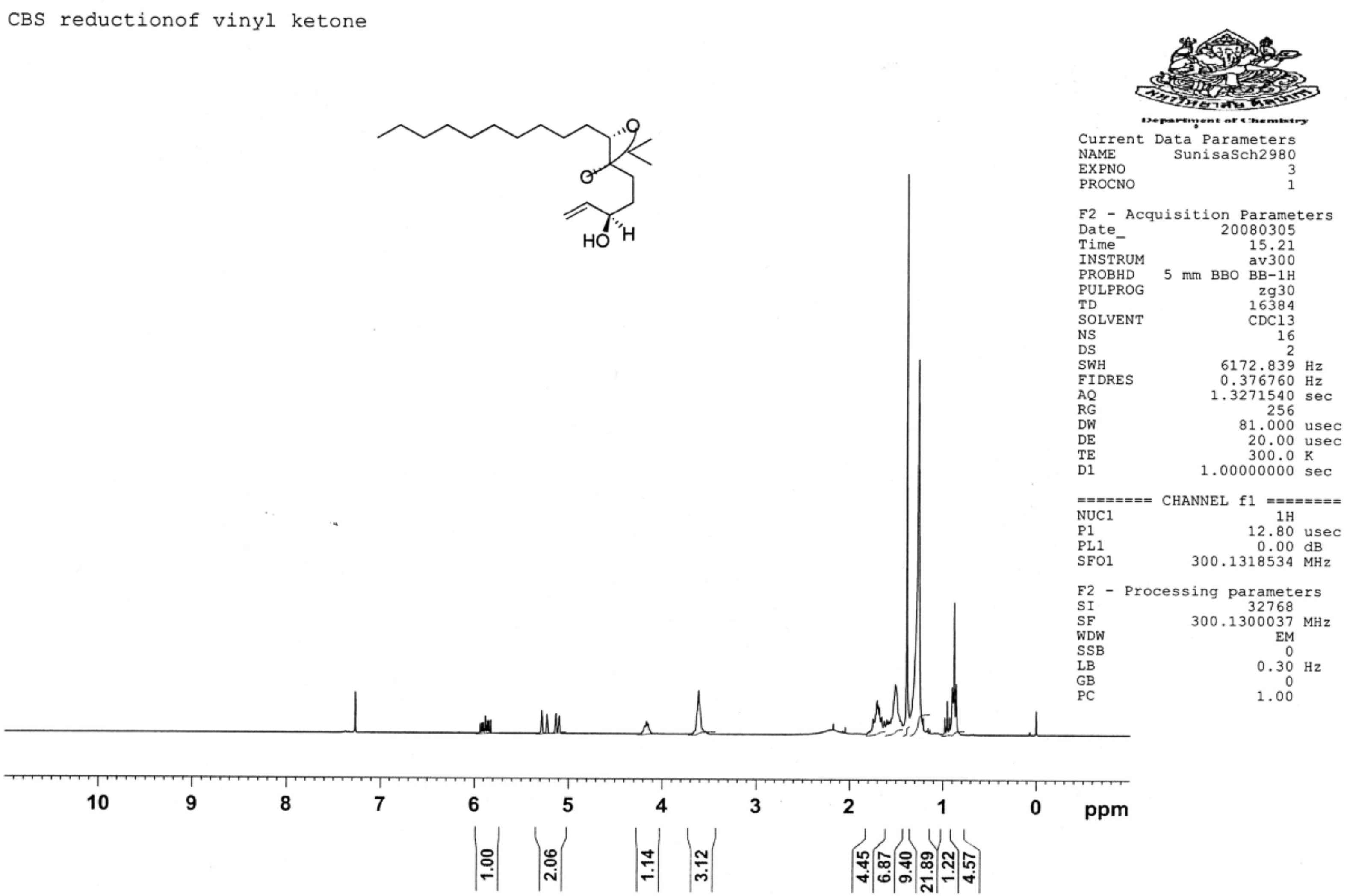
```
Current Data Parameters
NAME        SunisaSch2950
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080228
Time                12.54
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zgdc
TD                  32768
SOLVENT             CDCl3
NS                    614
DS                      4
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                 9195.2
DW                 27.600 usec
DE                  20.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   5.20 usec
PL1                 -3.00 dB
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  0.00 dB
PL12                17.20 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF            75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

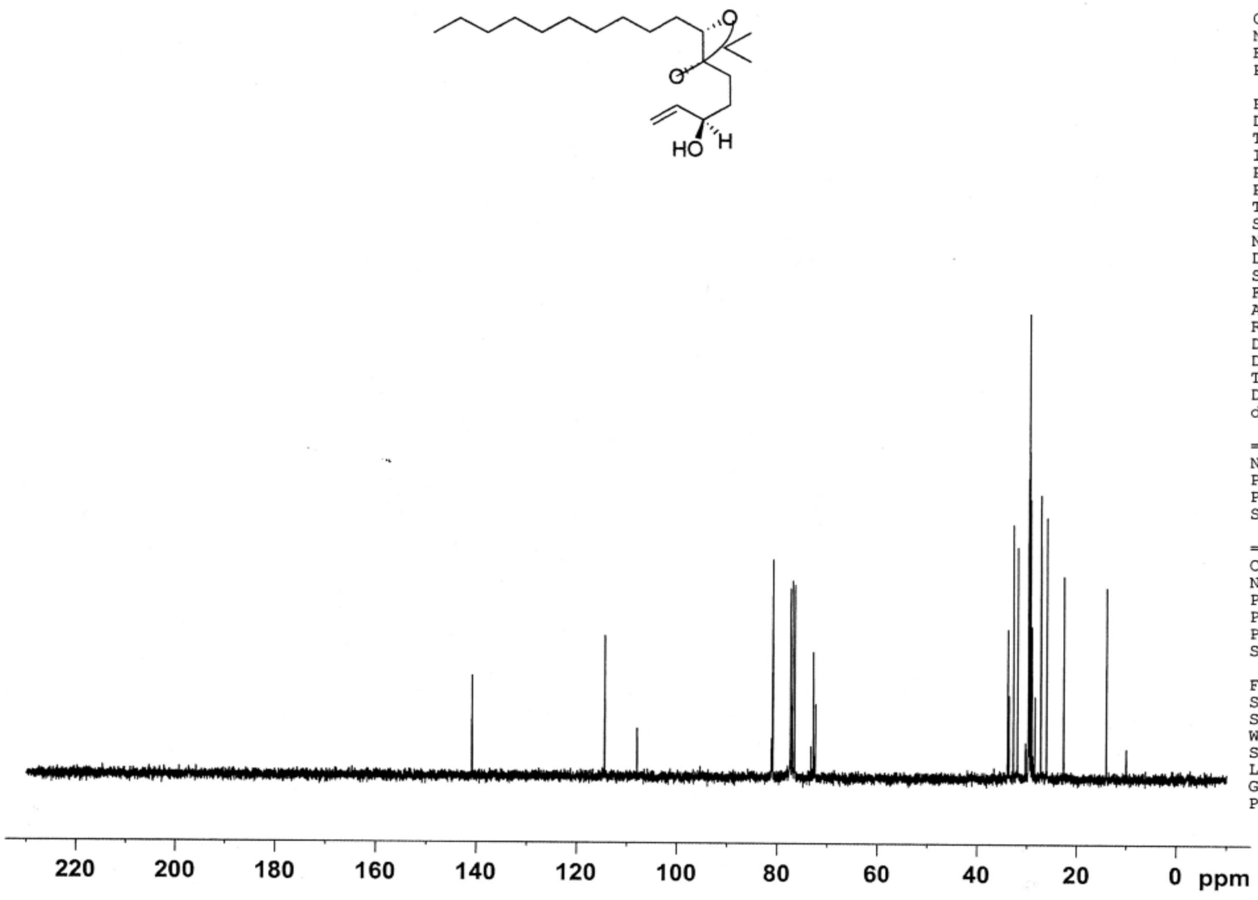
^{13}C NMR spectrum of compound **87**



```
Department of Chemistry
Current Data Parameters
NAME       SunisaSch2980
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080305
Time               15.21
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                   256
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.80 usec
PL1                 0.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300037 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR spectrum of compound **88**

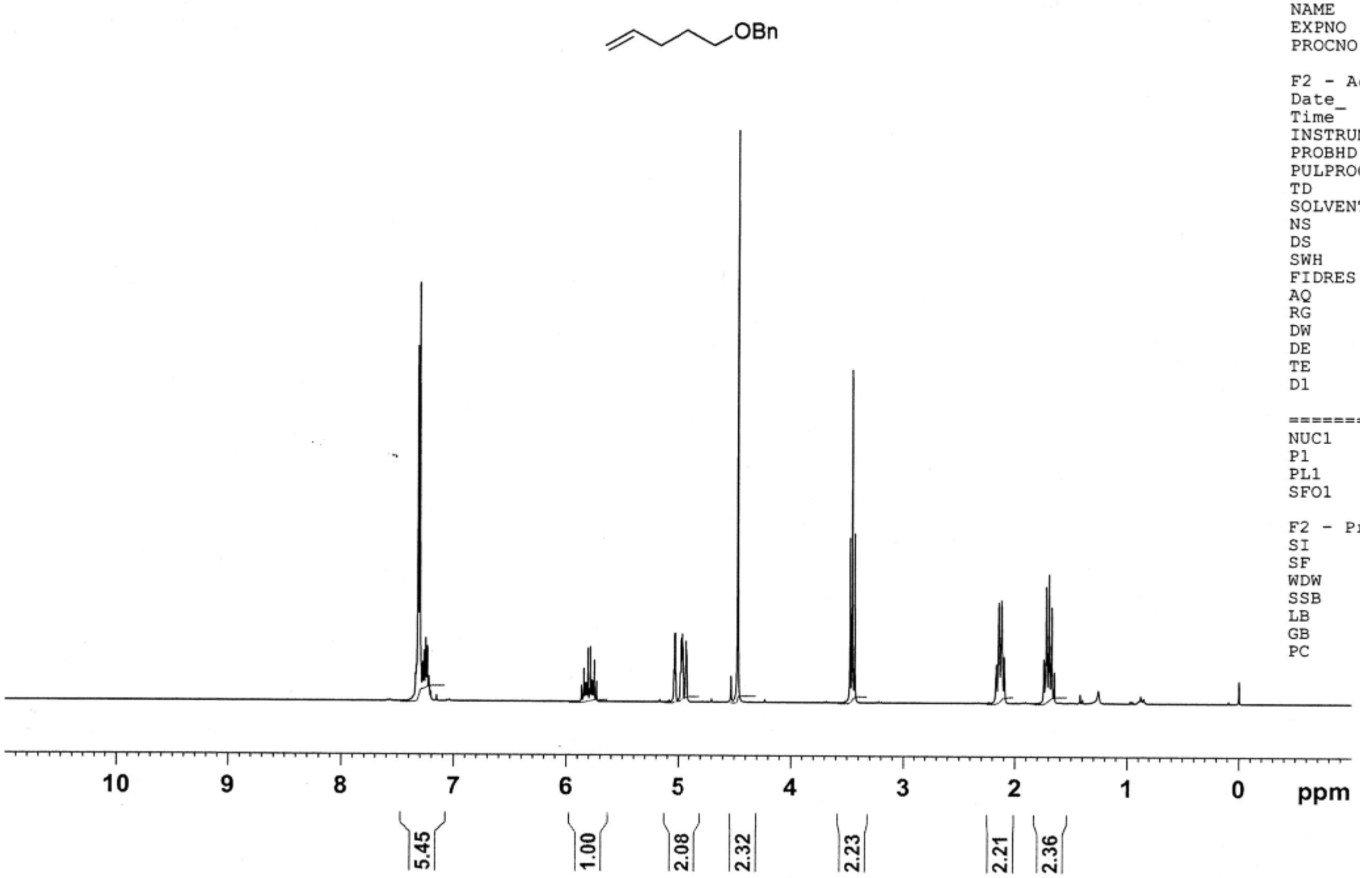
13C of CBS reaction of vinyl ketone



```
Current Data Parameters
NAME          SunisaSch2980
EXPNO                     4
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080305
Time                  15.28
INSTRUM               av300
PROBHD   5 mm BBO BB-1H
PULPROG                zgdc
TD                    32768
SOLVENT               CDCl3
NS                      512
DS                        4
SWH               18115.941 Hz
FIDRES             0.552855 Hz
AQ                0.9044468 sec
RG                  14596.5
DW                   27.600 usec
DE                    20.00 usec
TE                    300.0 K
D1               2.00000000 sec
d11              0.03000000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                     5.20 usec
PL1                   -3.00 dB
SFO1             75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                    0.00 dB
PL12                  17.20 dB
SFO2            300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF               75.4677490 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.00
```

^{13}C NMR spectrum of compound **88**

benzyloxy-4-penten



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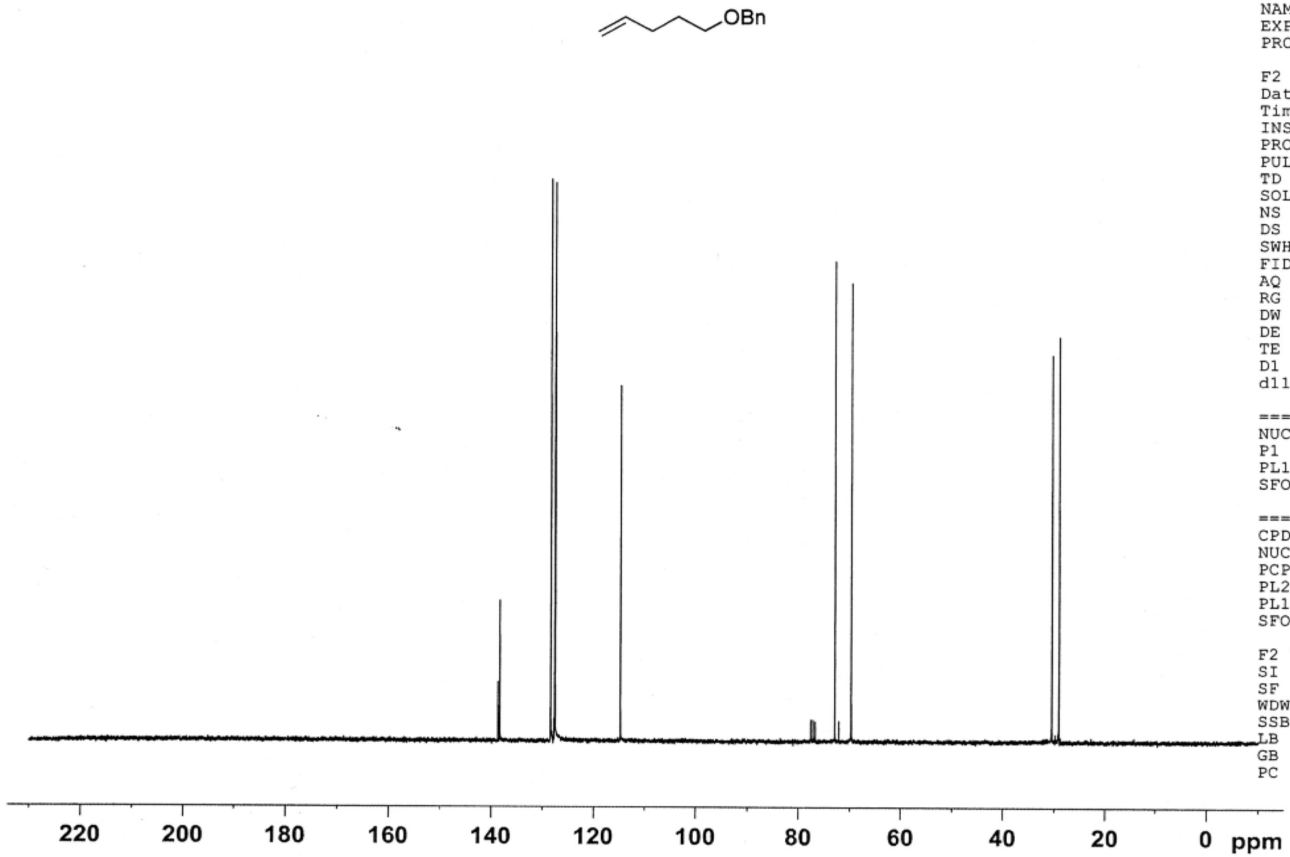
```
Current Data Parameters
NAME        SunisaSch3044
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080822
Time                10.59
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.376760 Hz
AQ              1.3271540 sec
RG                   50.8
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.60 usec
PL1                 -1.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300375 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR spectrum of compound **99**

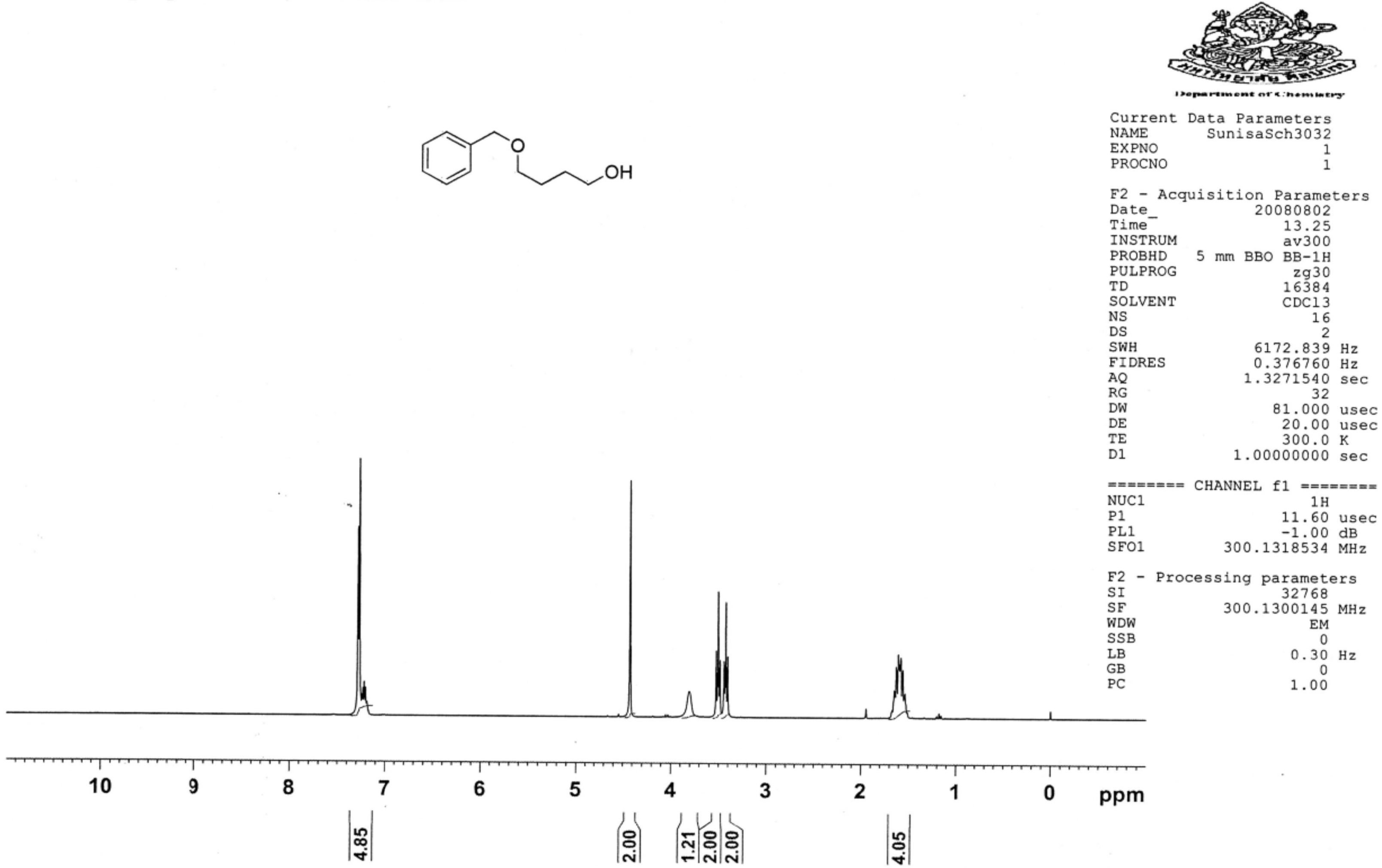
13C of benzyloxy-4-penten



```
Current Data Parameters
NAME        SunisaSch3044
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080822
Time              11.05
INSTRUM           av300
PROBHD   5 mm BBO BB-1H
PULPROG            zgdc
TD                32768
SOLVENT           CDCl3
NS                  128
DS                    4
SWH           18115.941 Hz
FIDRES         0.552855 Hz
AQ            0.9044468 sec
RG              14596.5
DW               27.600 usec
DE                20.00 usec
TE                300.0 K
D1           1.00000000 sec
d11          0.03000000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 5.20 usec
PL1               -3.00 dB
SFO1         75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2               -1.00 dB
PL12              17.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
SF           75.4677490 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.00
```

^{13}C NMR spectrum of compound **99**

mono Benzyl protect 1,4-butane diol



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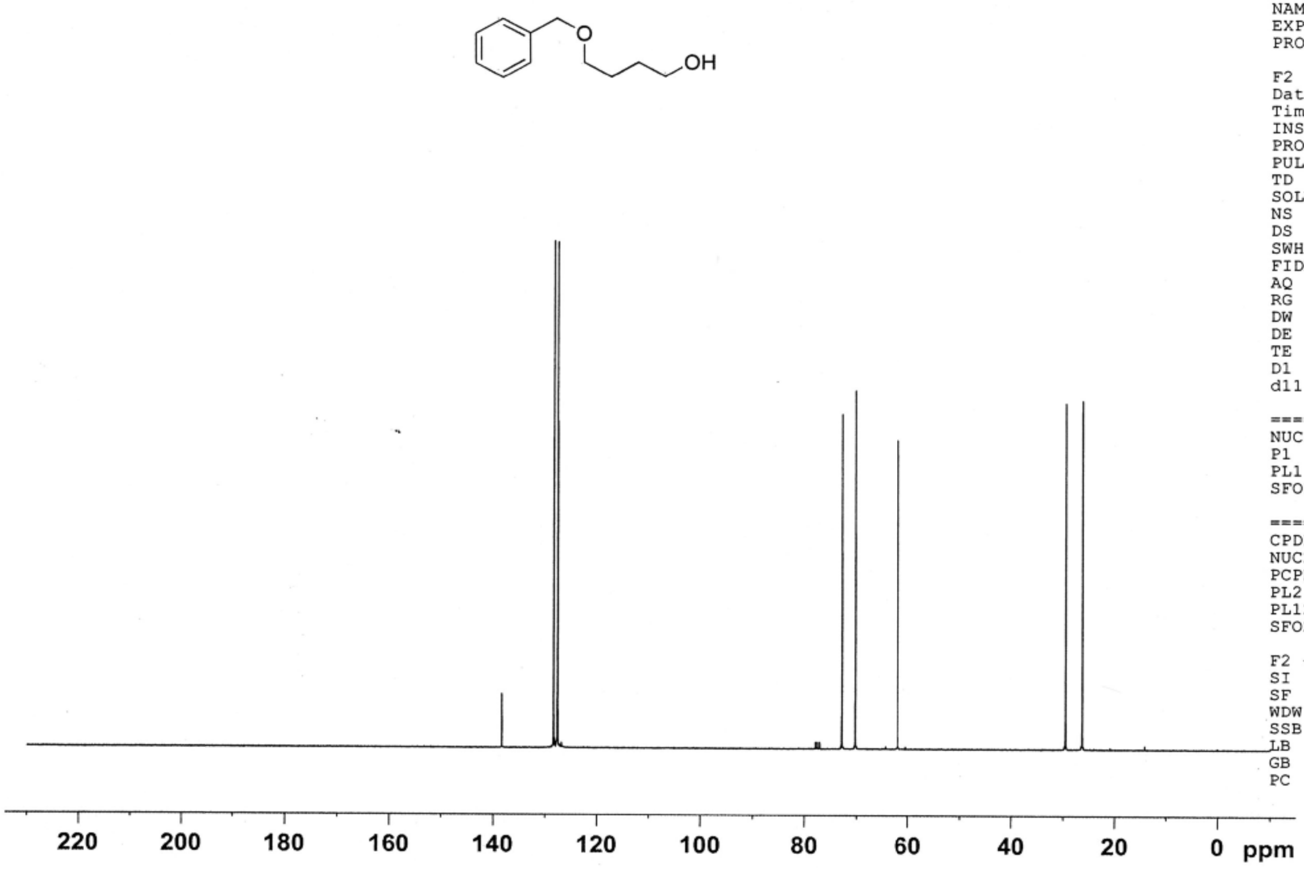
```
Current Data Parameters
NAME       SunisaSch3032
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080802
Time               13.25
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                    32
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.60 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300145 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR spectrum of 4-benzyloxy butanol

13C of mono benzyl protect 1,4 butane diol



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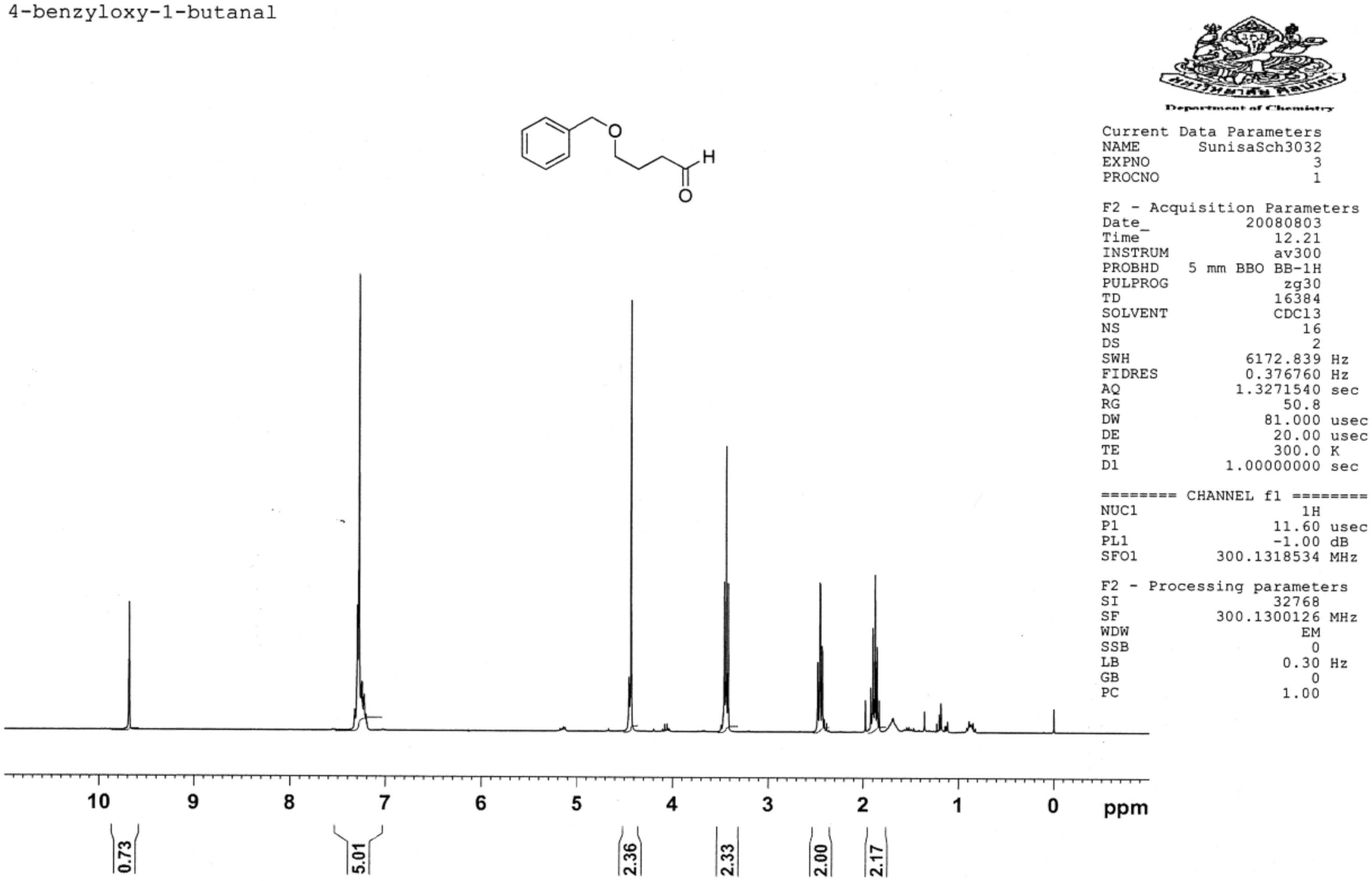
```
Current Data Parameters
NAME       SunisaSch3032
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080802
Time               13.32
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zgdc
TD                 32768
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            18115.941 Hz
FIDRES          0.552855 Hz
AQ             0.9044468 sec
RG                9195.2
DW                27.600 usec
DE                 20.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  5.20 usec
PL1                -3.00 dB
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -1.00 dB
PL12               17.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

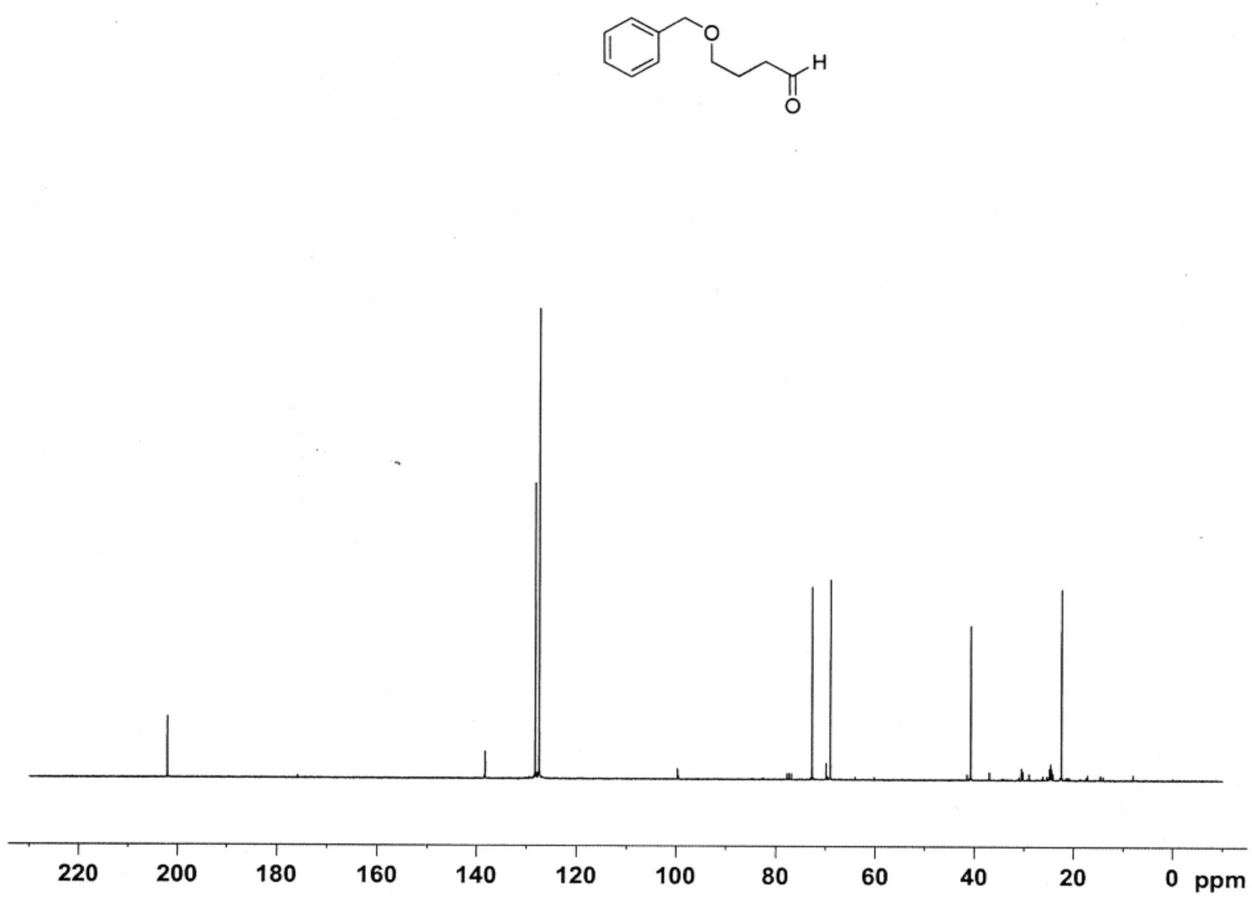
^{13}C NMR spectrum of 4-benzyloxy butanol



```
Current Data Parameters
NAME        SunisaSch3032
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080803
Time                12.21
INSTRUM             av300
PROBHD    5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.376760 Hz
AQ              1.3271540 sec
RG                   50.8
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.60 usec
PL1                 -1.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300126 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR spectrum of compound **96**

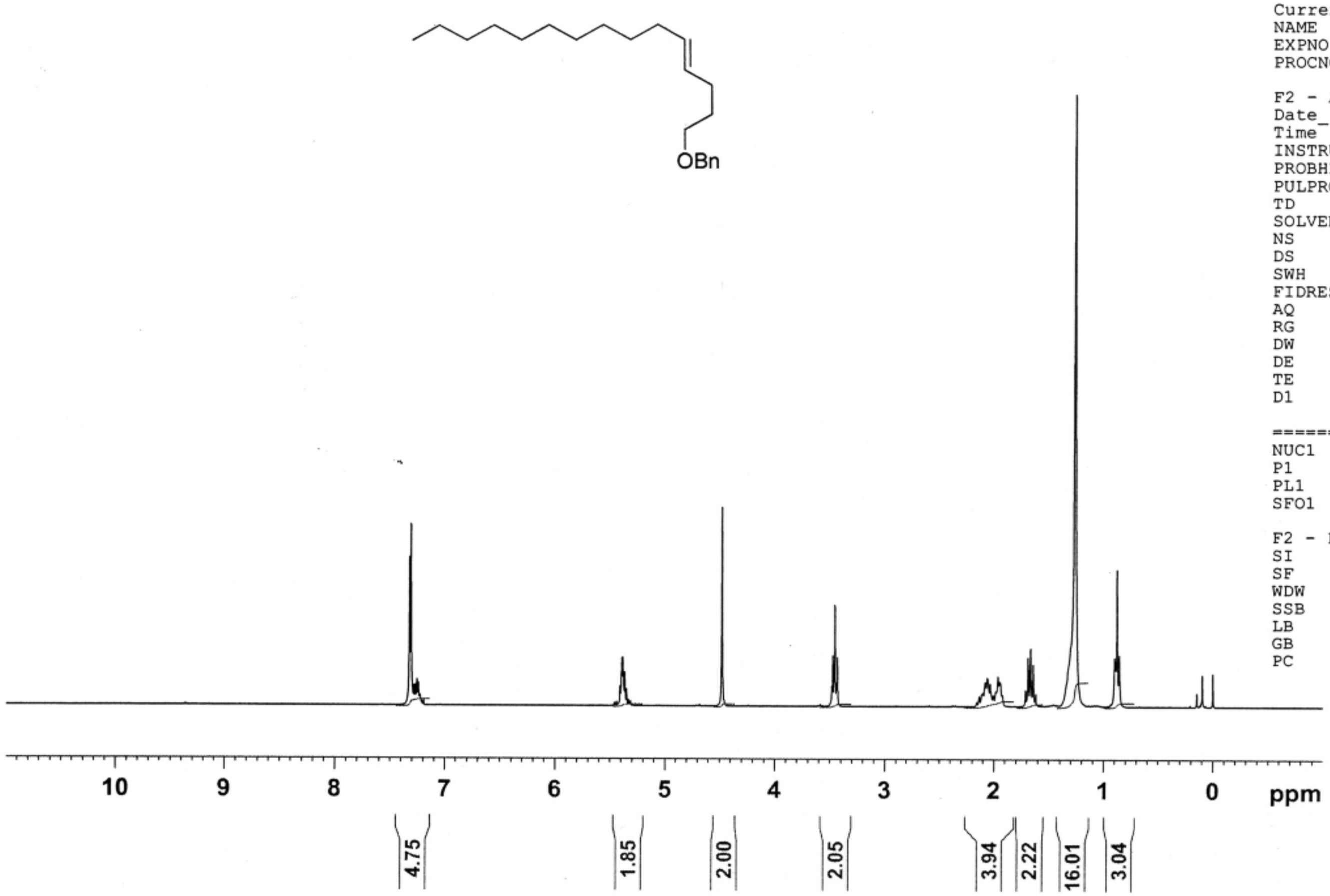
4-benzyloxy-1-butanal



```
Current Data Parameters
NAME       SunisaSch3032
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080803
Time              12.27
INSTRUM           av300
PROBHD   5 mm BBO BB-1H
PULPROG            zgdc
TD                32768
SOLVENT           CDC13
NS                  128
DS                    4
SWH           18115.941 Hz
FIDRES         0.552855 Hz
AQ            0.9044468 sec
RG               9195.2
DW               27.600 usec
DE                20.00 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 5.20 usec
PL1               -3.00 dB
SFO1         75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2               -1.00 dB
PL12              17.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
SF           75.4677523 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

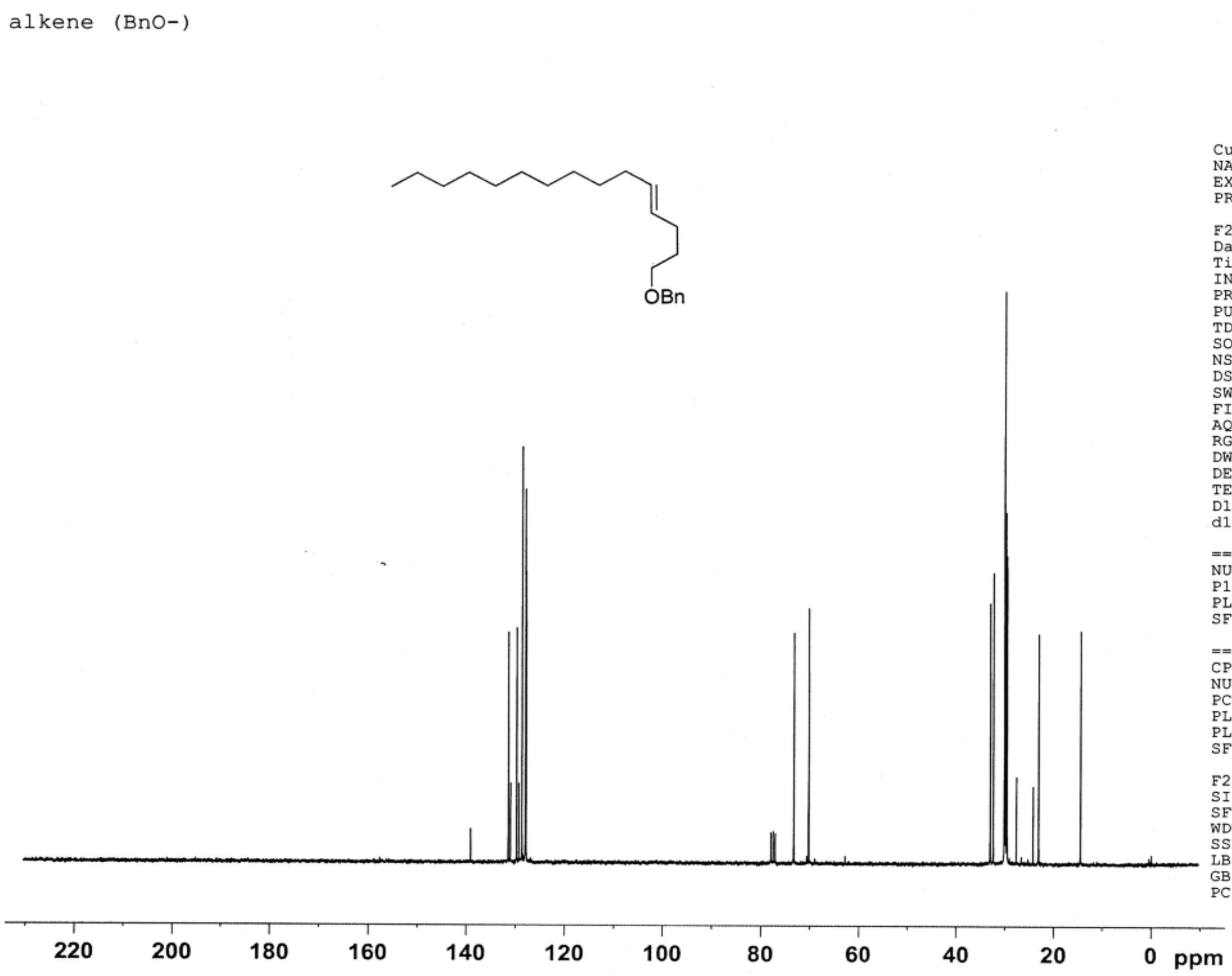
^{13}C NMR spectrum of compound **96**

alkene (BnO-)



```
Current Data Parameters
NAME          SunisaSch3034
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080804
Time                  16.24
INSTRUM               av300
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                6172.839 Hz
FIDRES             0.376760 Hz
AQ                1.3271540 sec
RG                     40.3
DW                   81.000 usec
DE                    20.00 usec
TE                    300.0 K
D1               1.00000000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    11.60 usec
PL1                   -1.00 dB
SFO1            300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF              300.1300259 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

^{1}H NMR spectrum of compound **97**



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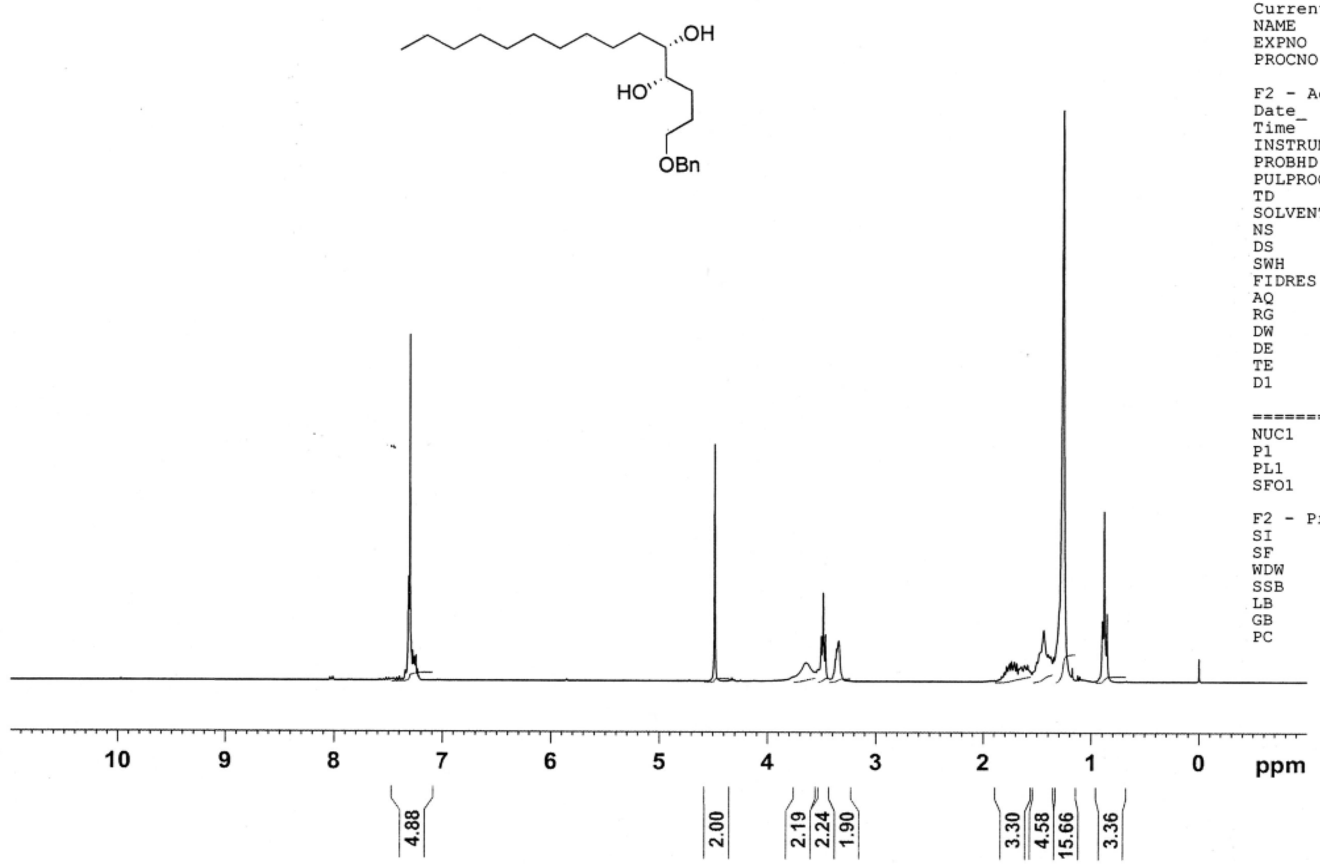
```
Current Data Parameters
NAME       SunisaSch3034
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080804
Time               16.28
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zgdc
TD                 32768
SOLVENT            CDCl3
NS                   128
DS                     4
SWH            18115.941 Hz
FIDRES          0.552855 Hz
AQ             0.9044468 sec
RG                 13004
DW                27.600 usec
DE                 20.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  5.20 usec
PL1                -3.00 dB
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -1.00 dB
PL12               17.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677146 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.00
```

^{13}C NMR spectrum of compound **97**

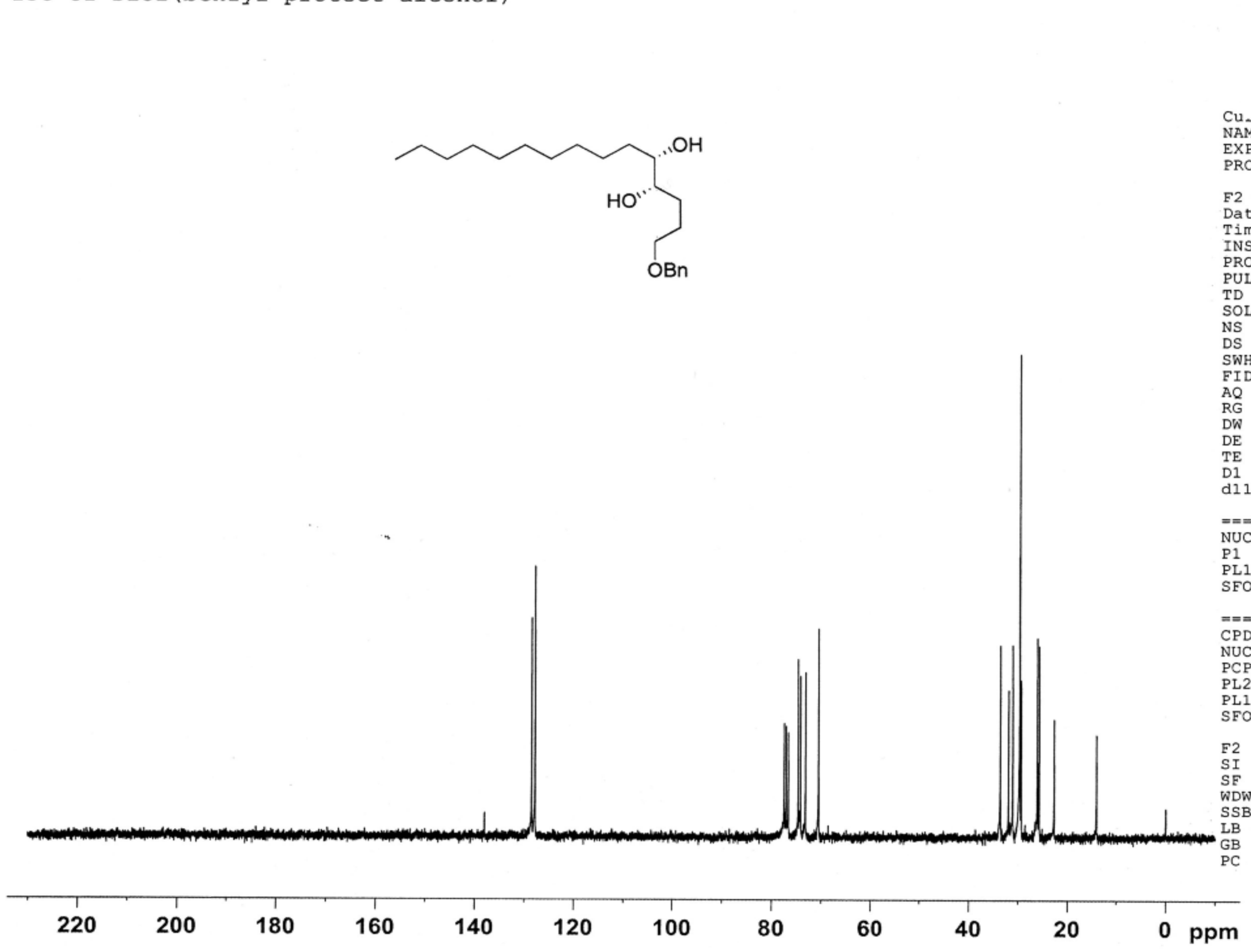
Diol (benzyl protect alcohol)



```
Current Data Parameters
NAME       SunisaSch3040
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080818
Time_              11.37
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                    32
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.60 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300093 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR spectrum of compound **100**

13C of Diol(benzyl protect alcohol)



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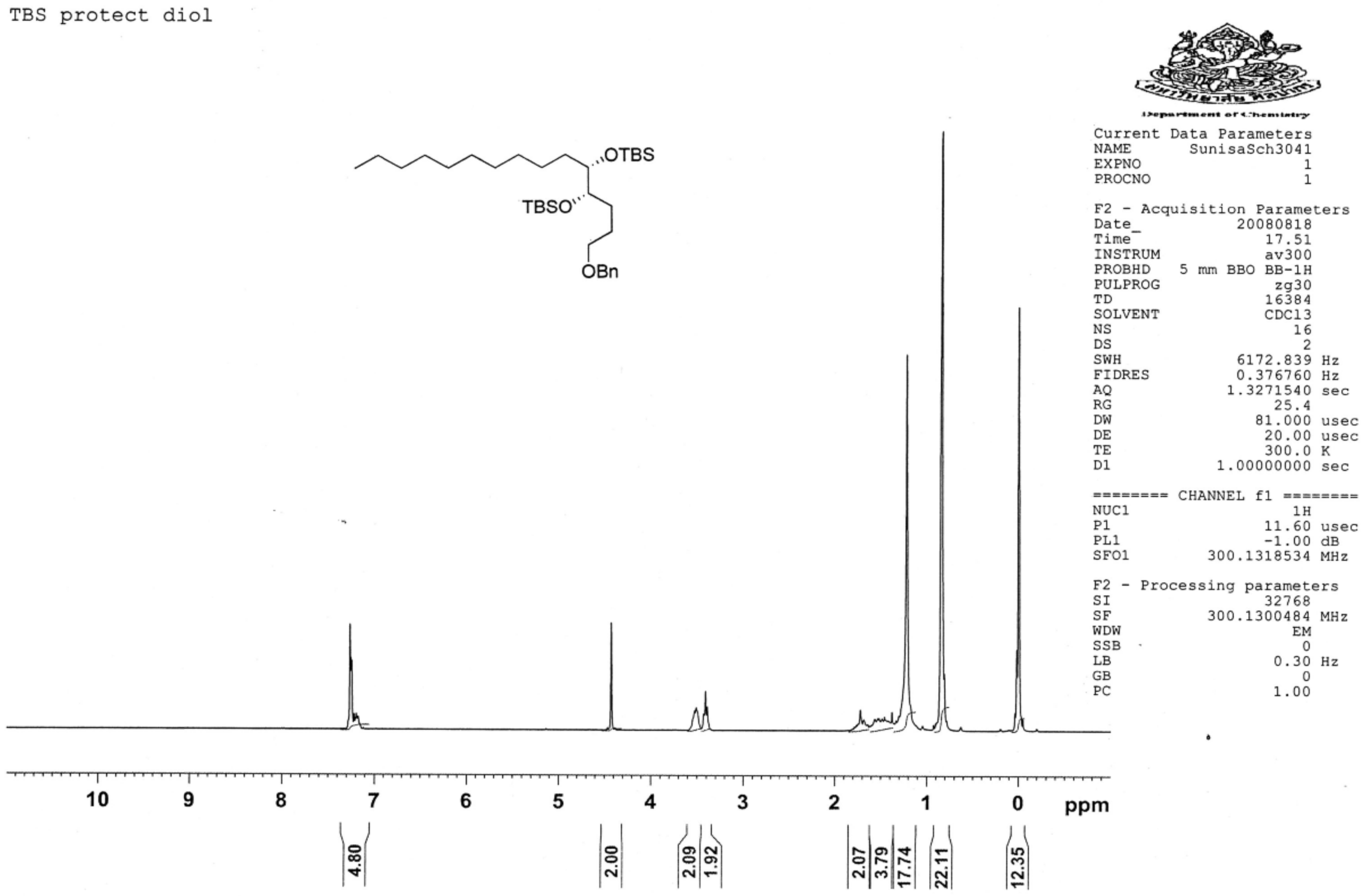
```
Current Data Parameters
NAME         SunisaSch3050
EXPNO                    6
PROCNO                   1

F2 - Acquisition Parameters
Date_             20080901
Time                 11.52
INSTRUM              av300
PROBHD   5 mm BBO BB-1H
PULPROG               zgdc
TD                   32768
SOLVENT              CDCl3
NS                    1624
DS                       4
SWH              18115.941 Hz
FIDRES            0.552855 Hz
AQ               0.9044468 sec
RG                 10321.3
DW                  27.600 usec
DE                   20.00 usec
TE                   300.0 K
D1              1.00000000 sec
d11             0.03000000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    5.40 usec
PL1                  -3.00 dB
SFO1            75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                  -1.00 dB
PL12                 17.00 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                   32768
SF              75.4677475 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

^{13}C NMR spectrum of compound **100**

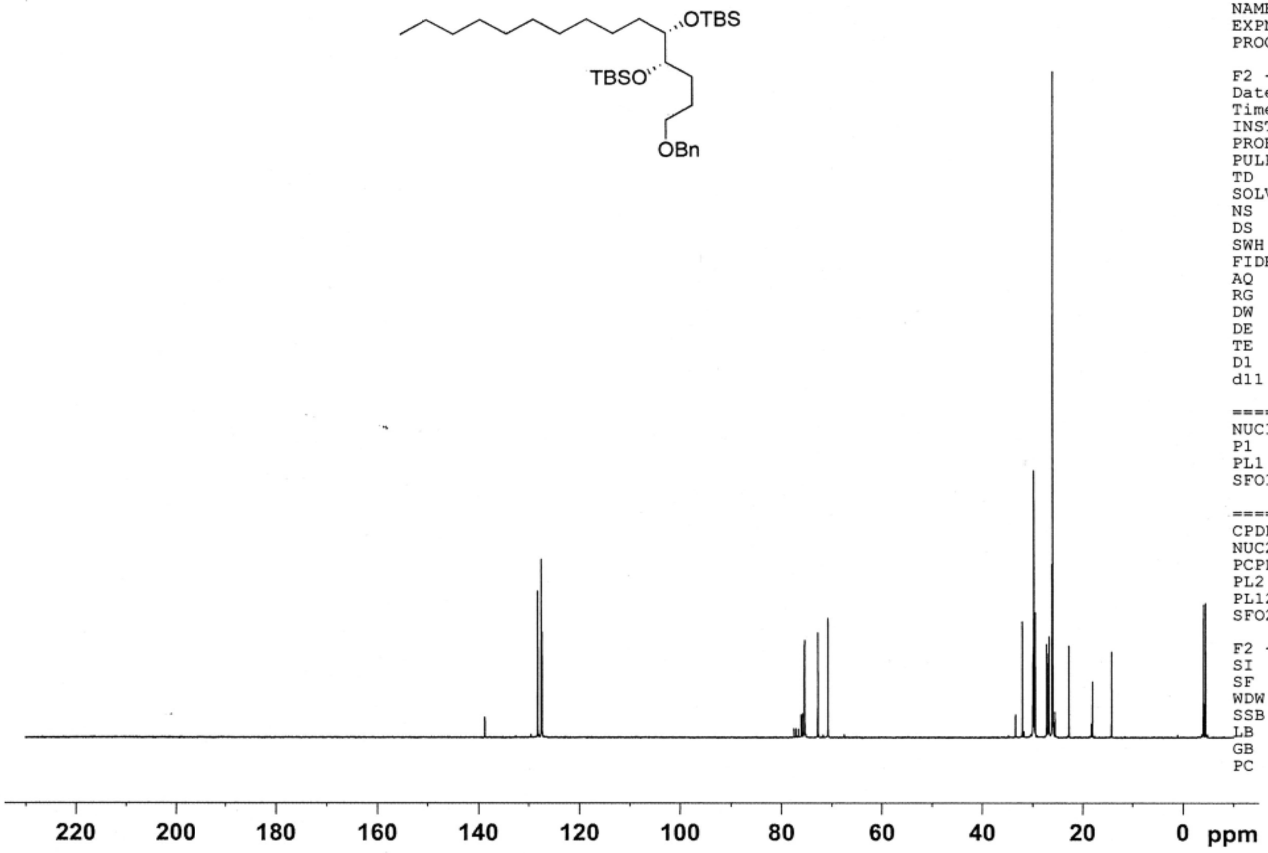


TBS protect diol

```
Current Data Parameters
NAME       SunisaSch3041
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080818
Time               17.51
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                  25.4
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.60 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300484 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR spectrum of compound **101**

TBS protect diol



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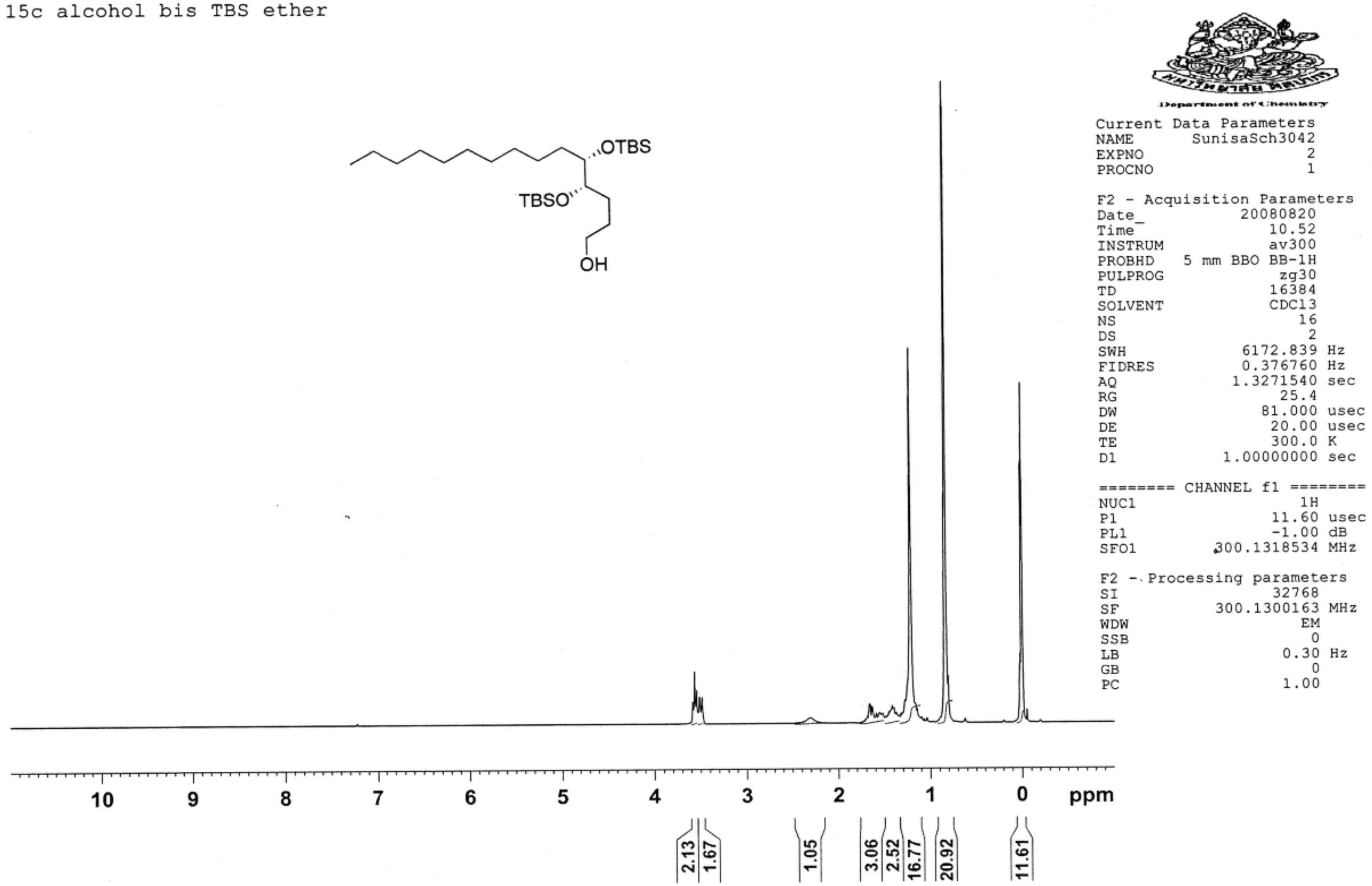
```
Current Data Parameters
NAME       SunisaSch3041
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080818
Time               17.56
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zgdc
TD                 32768
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            18115.941 Hz
FIDRES          0.552855 Hz
AQ             0.9044468 sec
RG               14596.5
DW                27.600 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec
d11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  5.20 usec
PL1                -3.00 dB
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2      •      100.00 usec
PL2                -1.00 dB
PL12               17.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677474 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{13}C NMR spectrum of compound **101**

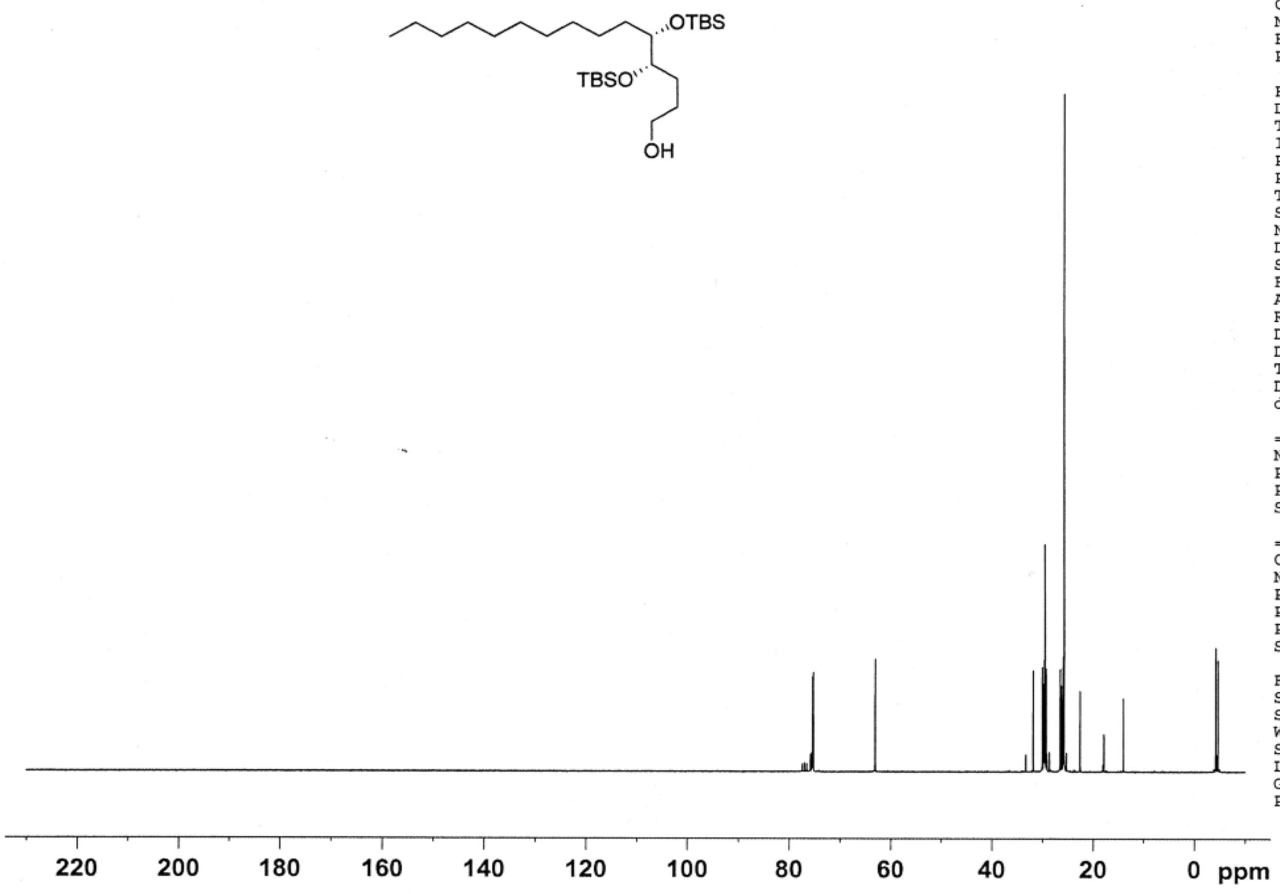
15c alcohol bis TBS ether



```
Current Data Parameters
NAME        SunisaSch3042
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080820
Time                10.52
INSTRUM             av300
PROBHD     5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.376760 Hz
AQ              1.3271540 sec
RG                   25.4
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.60 usec
PL1                 -1.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300163 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR spectrum of compound **102**

13C of 15carbon alcohol bis TBS ether



```
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Current Data Parameters
NAME       SunisaSch3042
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080820
Time               11.01
INSTRUM            av300
PROBHD    5 mm BBO BB-1H
PULPROG             zgdc
TD                 32768
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            18115.941 Hz
FIDRES          0.552855 Hz
AQ             0.9044468 sec
RG               10321.3
DW                27.600 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec
d11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  5.20 usec
PL1                -3.00 dB
SFO1         75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -1.00 dB
PL12               17.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```
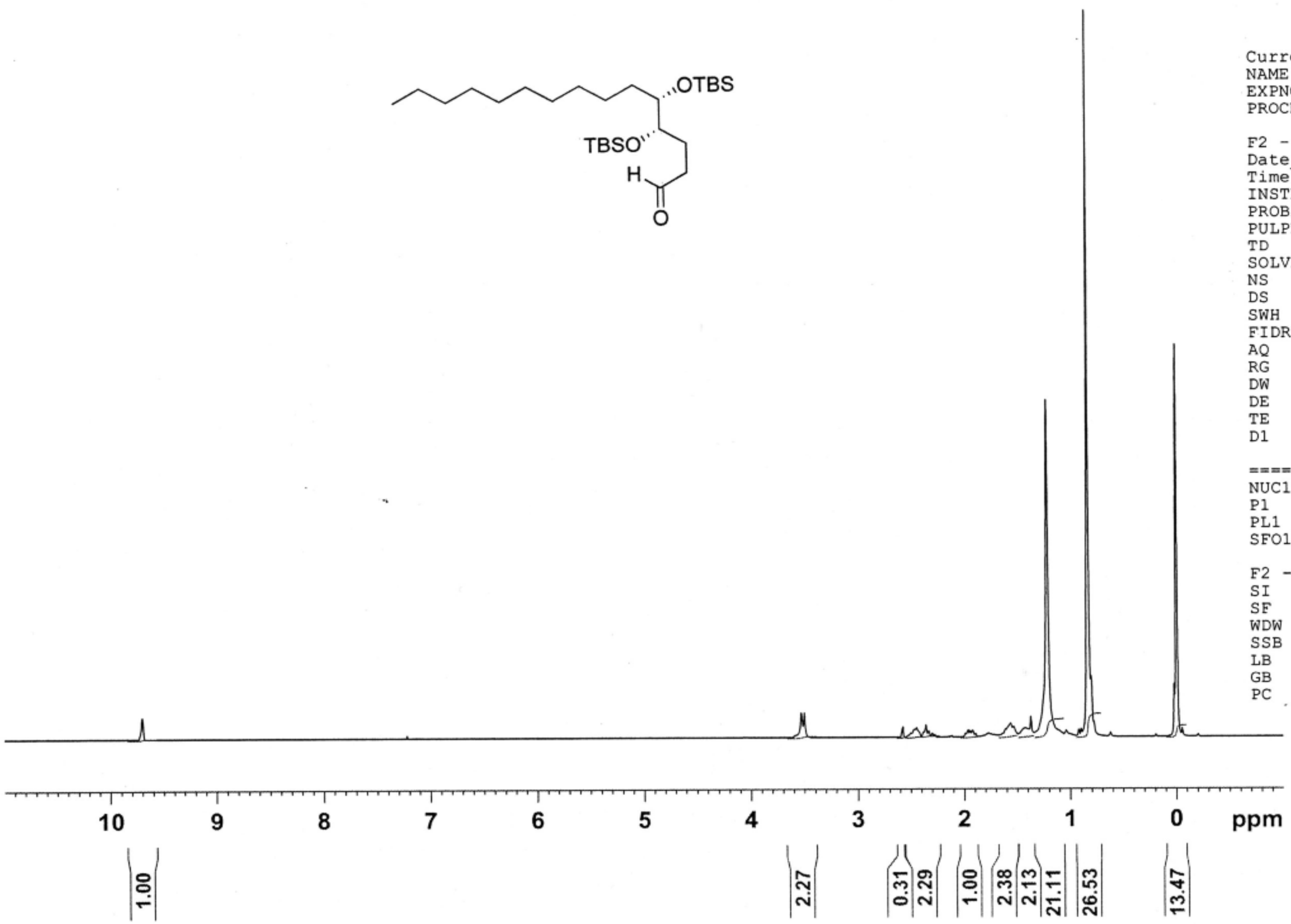

^{13}C NMR spectrum of compound **102**

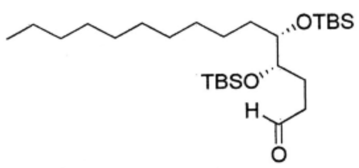
15C aldehyde bis TBS ether

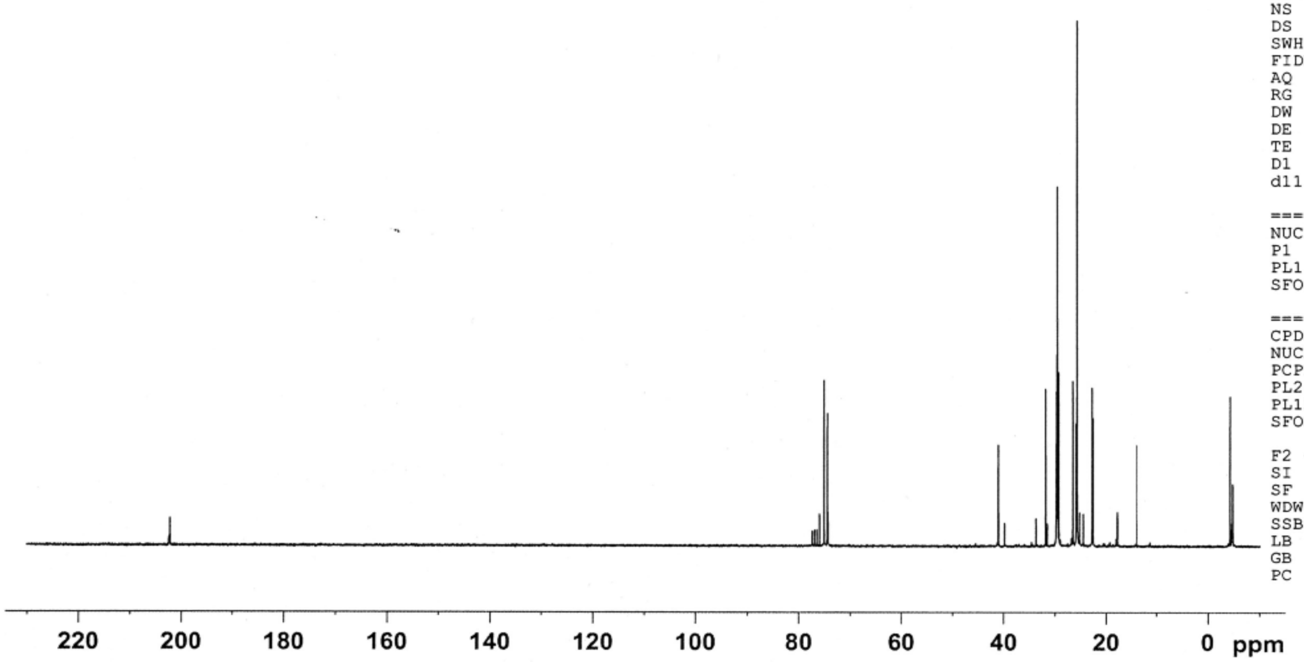


```
Current Data Parameters
NAME       SunisaSch3043
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080821
Time                9.54
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES      •   0.376760 Hz
AQ             1.3271540 sec
RG                  25.4
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.60 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300163 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR spectrum of compound **103**

13C of 15carbon aldehyde bis TBS ether





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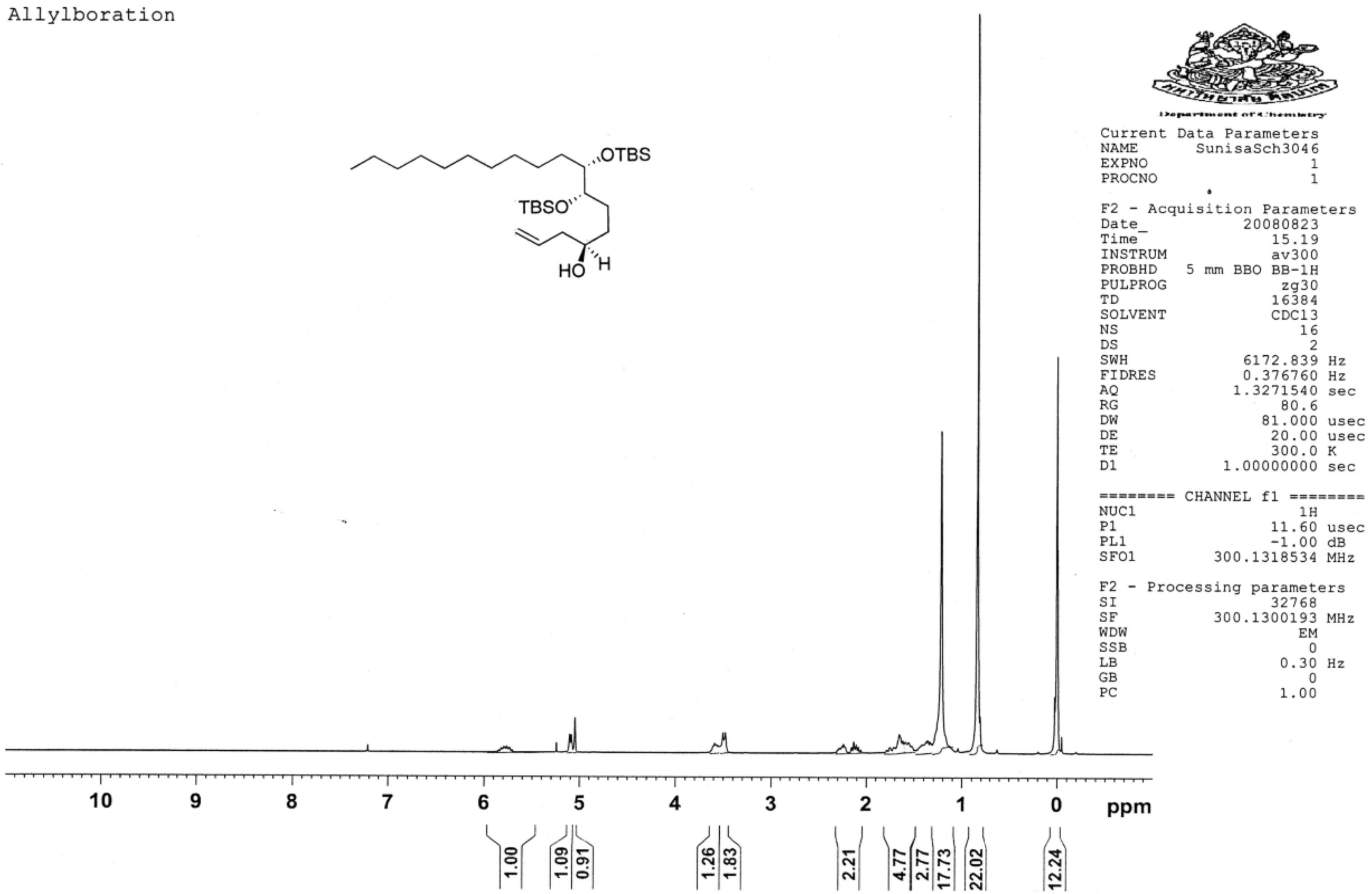
```
Current Data Parameters
NAME       SunisaSch3043
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080821
Time               10.04
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG   •         zgdc
TD                 32768
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            18115.941 Hz
FIDRES          0.552855 Hz
AQ             0.9044468 sec
RG                9195.2
DW                27.600 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec
d11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  5.20 usec
PL1                -3.00 dB
SFO1         75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -1.00 dB
PL12               17.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{13}C NMR spectrum of compound **103**

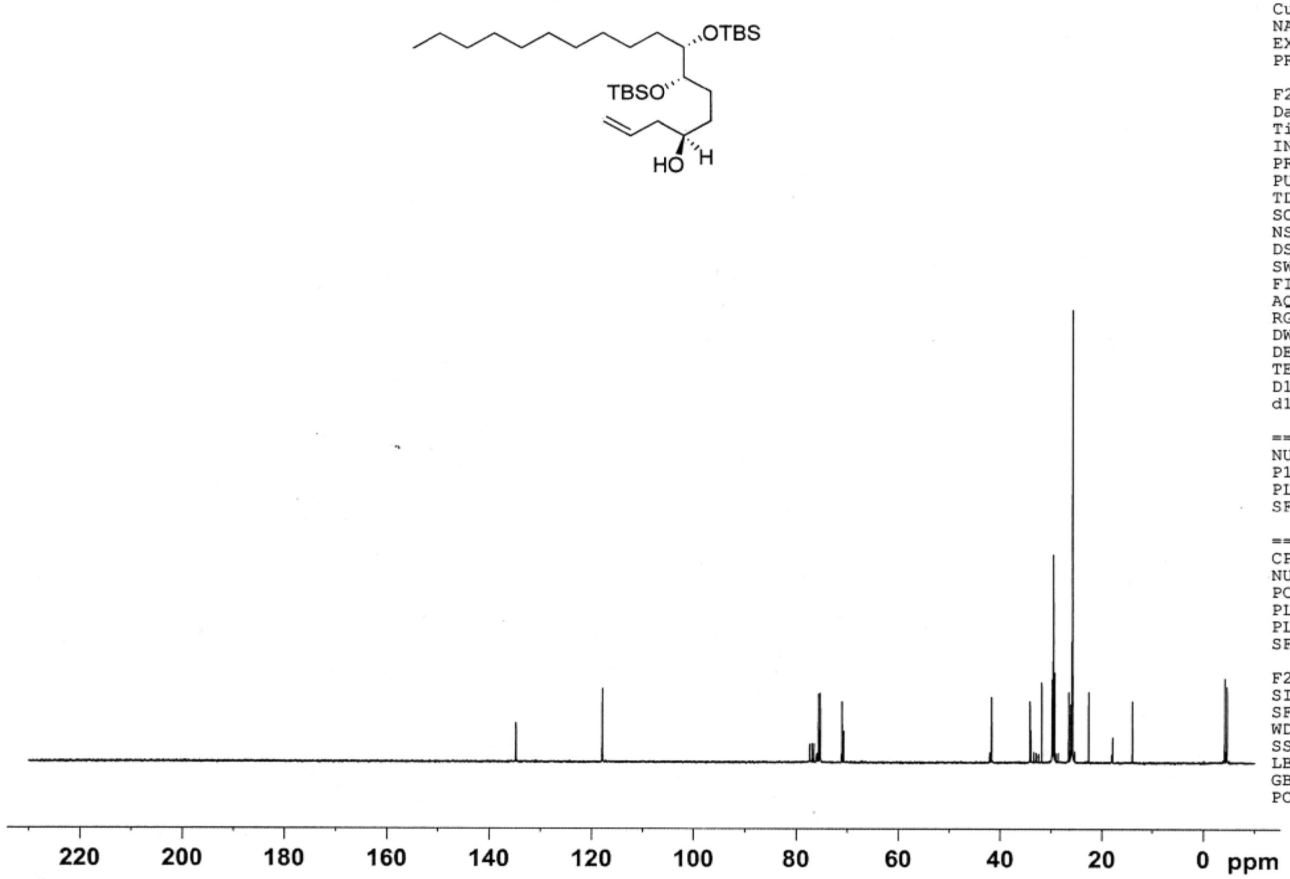
Allylboration



```
Current Data Parameters
NAME          SunisaSch3046
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080823
Time                  15.19
INSTRUM               av300
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                     80.6
DW               81.000 usec
DE                20.00 usec
TE                300.0 K
D1           1.00000000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                11.60 usec
PL1               -1.00 dB
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF          300.1300193 MHz
WDW                      EM
SSB                       0
LB                   0.30 Hz
GB                        0
PC                     1.00
```

^{1}H NMR spectrum of compound **104**

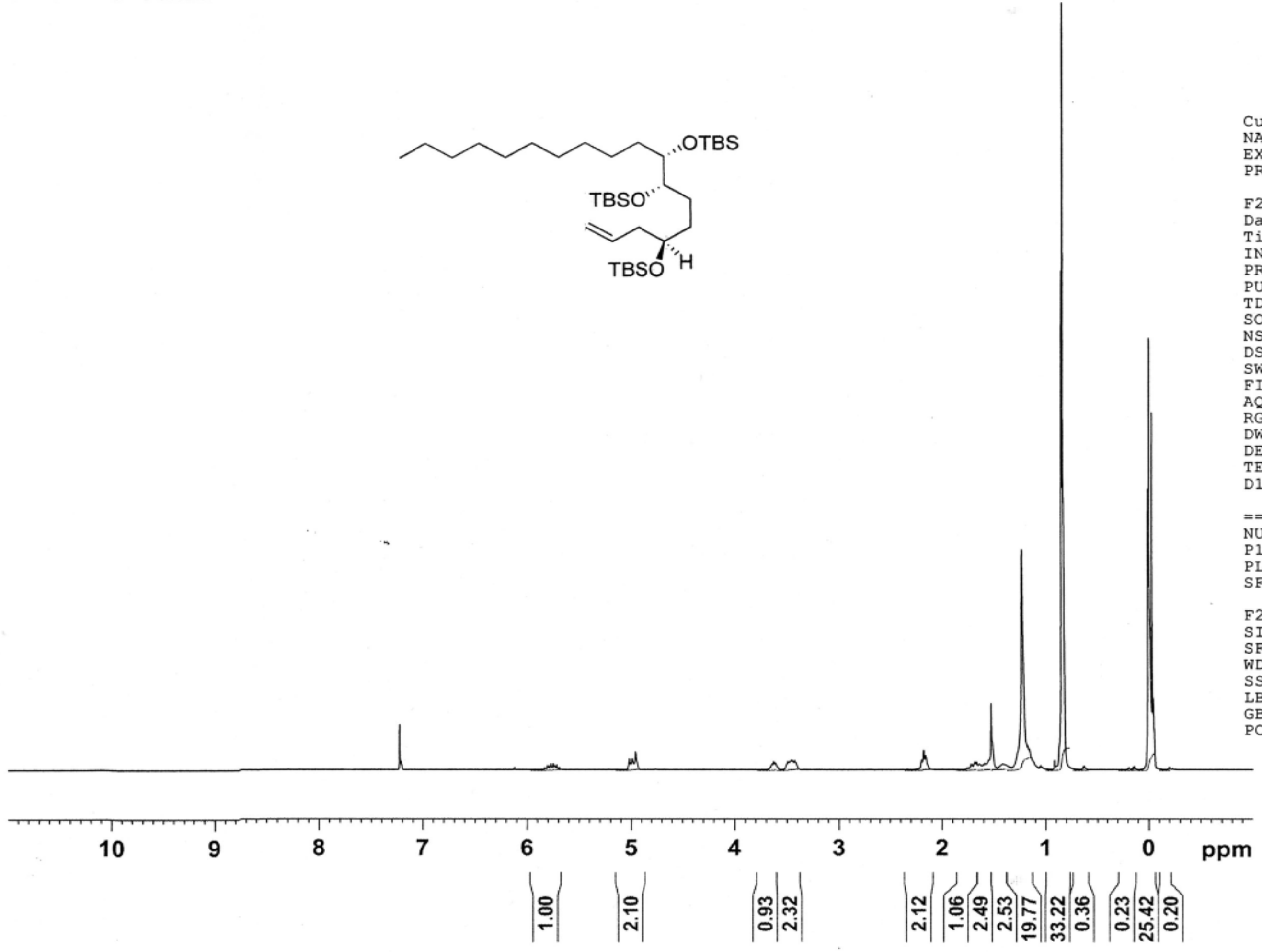
13C of Allylboration



```
Current Data Parameters
NAME          SunisaSch3046
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080823
Time                  15.24
INSTRUM               av300
PROBHD   5 mm BBO BB-1H
PULPROG                zgdc
TD                    32768
SOLVENT               CDCl3
NS                      512
DS                        4
SWH               18115.941 Hz
FIDRES             0.552855 Hz
AQ                0.9044468 sec
RG                  11585.2
DW                   27.600 usec
DE                    20.00 usec
TE                    300.0 K
D1               1.00000000 sec
d11              0.03000000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                     5.20 usec
PL1                   -3.00 dB
SFO1            75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                   -1.00 dB
PL12                  17.00 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF              75.4677490 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.00
```

^{13}C NMR spectrum of compound **104**

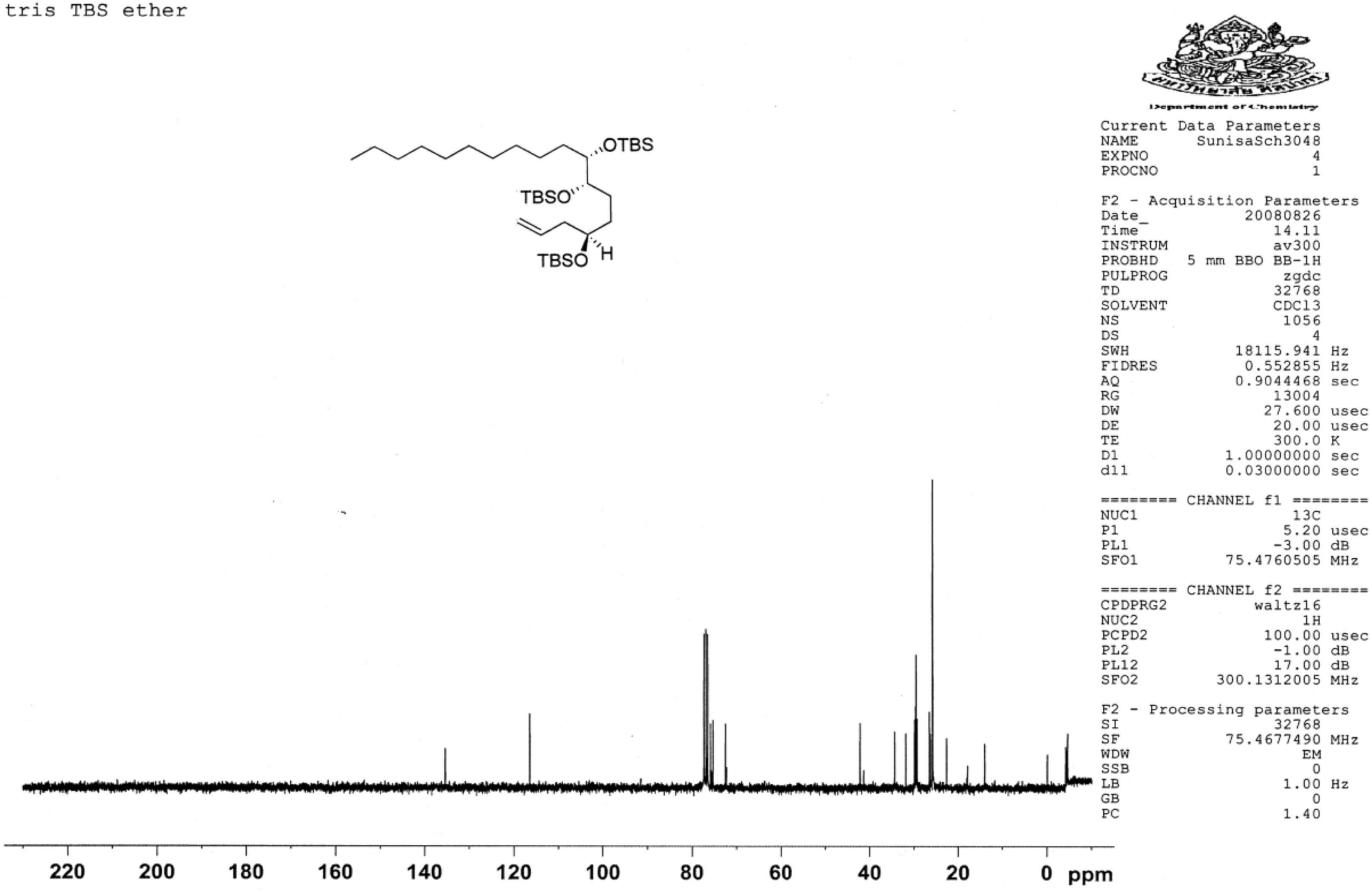
tris TBS ether



```
Current Data Parameters
NAME       SunisaSch3048
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080826
Time               13.36
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                 322.5
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.60 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.40
```

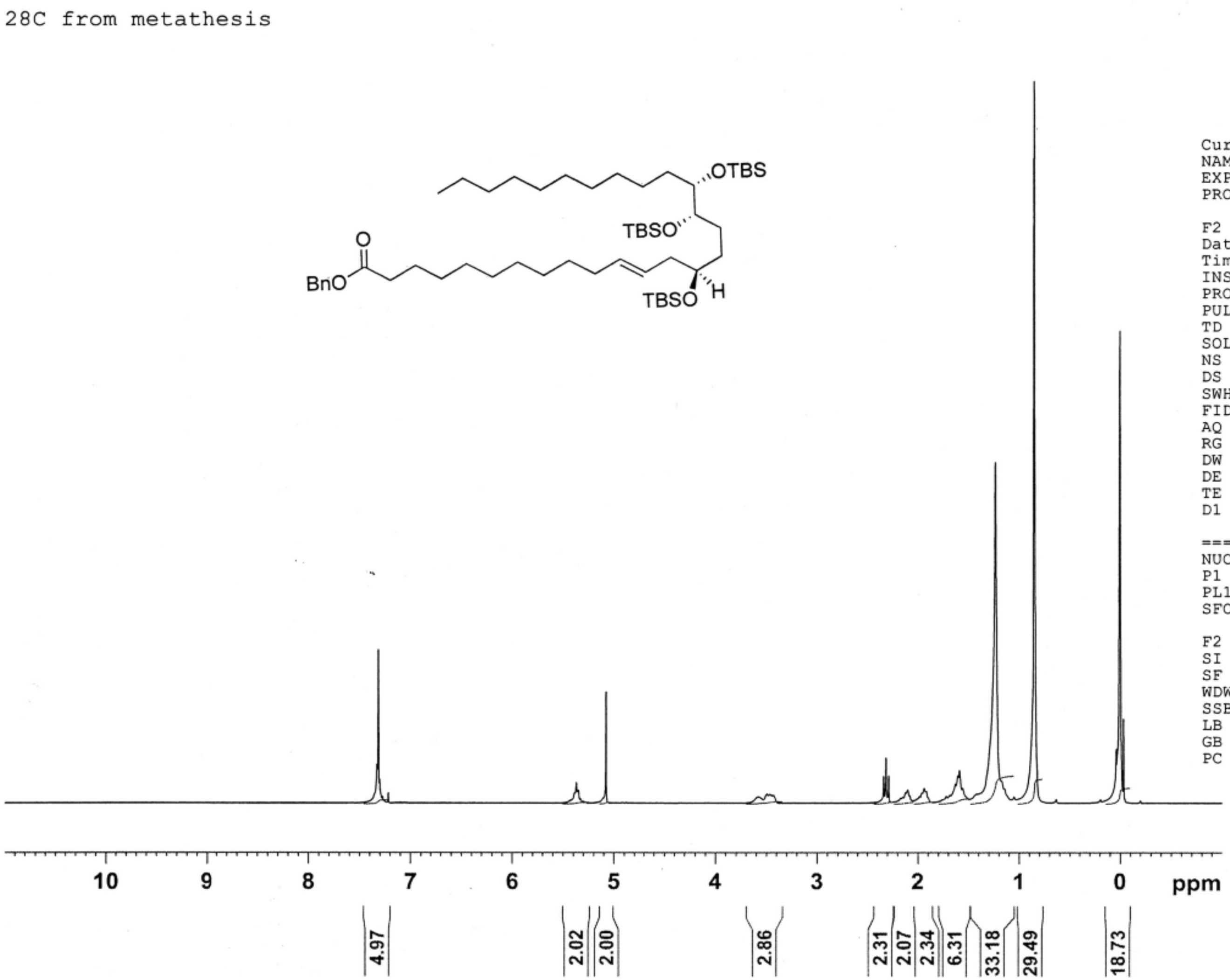
^{1}H NMR spectrum of compound **105**

tris TBS ether



```
Current Data Parameters
NAME        SunisaSch3048
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080826
Time                14.11
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zgdc
TD                  32768
SOLVENT             CDCl3
NS                   1056
DS                      4
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                  13004
DW                 27.600 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   5.20 usec
PL1                 -3.00 dB
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -1.00 dB
PL12                17.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF            75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

^{13}C NMR spectrum of compound **105**



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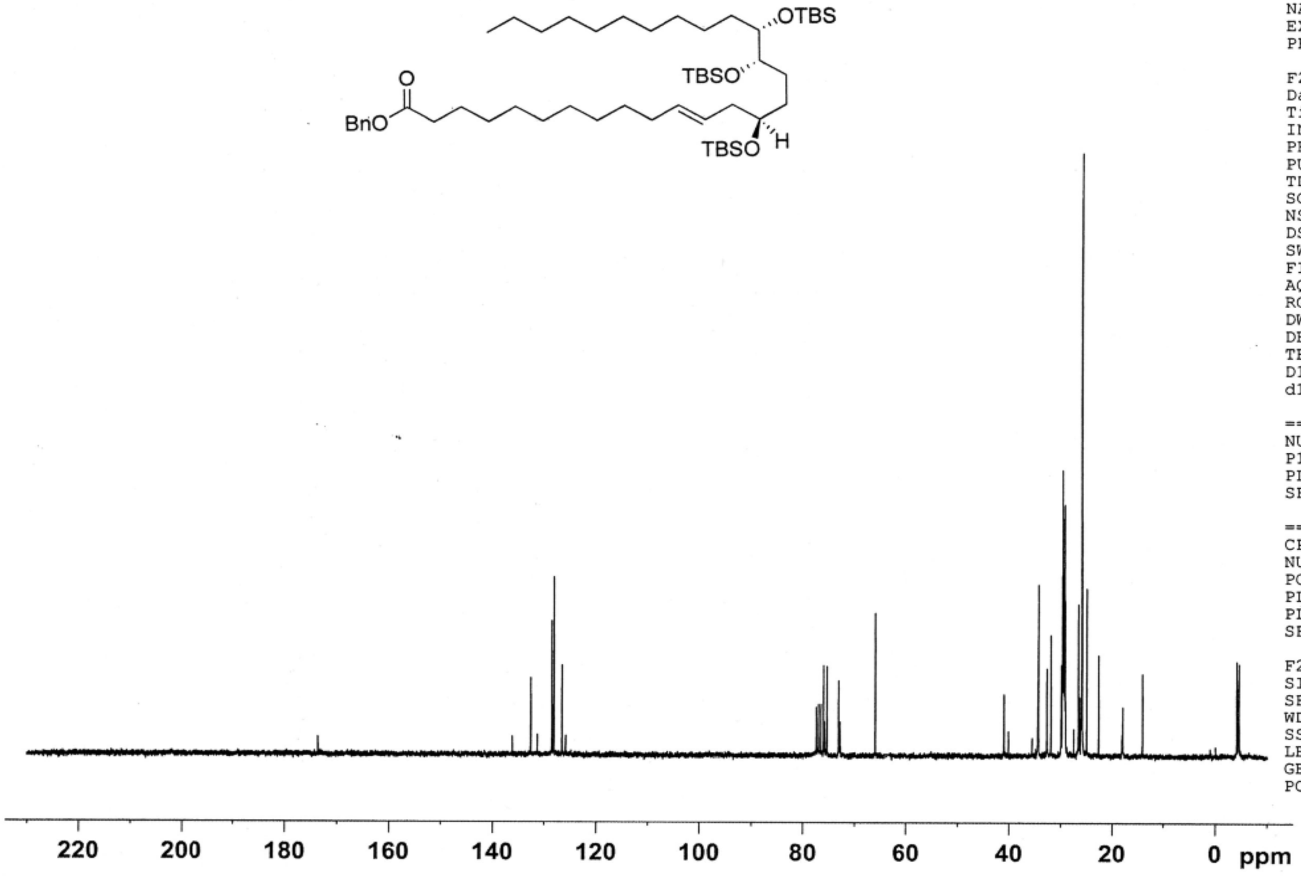
```
Current Data Parameters
NAME          SunisaSch3052
EXPNO                     4
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080903
Time_                  9.59
INSTRUM               av300
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                       64
DW               81.000 usec
DE                20.00 usec
TE                300.0 K
D1           1.00000000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                11.80 usec
PL1               -1.00 dB
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF          300.1300190 MHz
WDW                      EM
SSB                       0
LB                  0.30 Hz
GB                        0
PC                     1.00
```

^{1}H NMR spectrum of compound **107**

13C of 28C from metathsis



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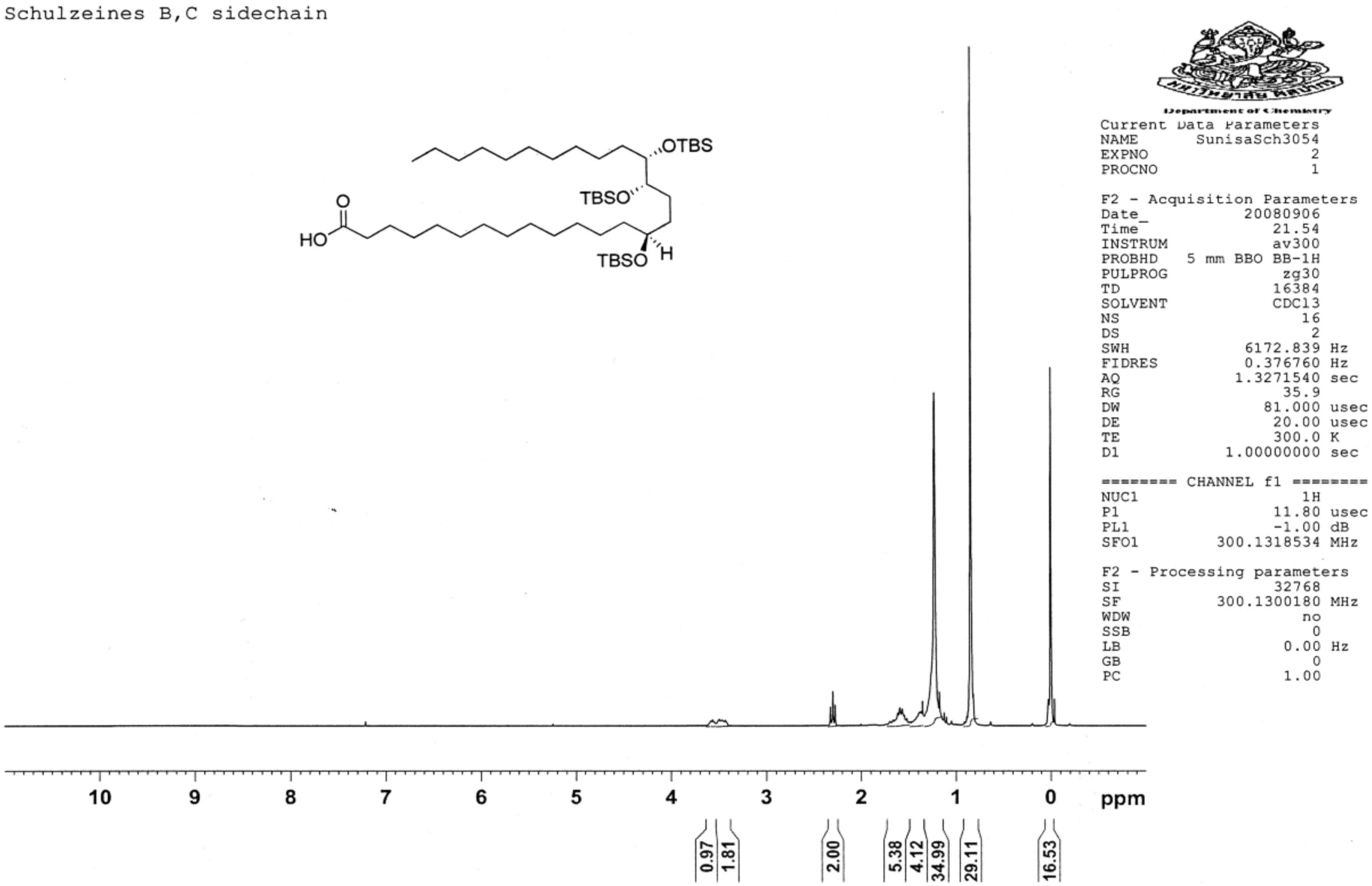
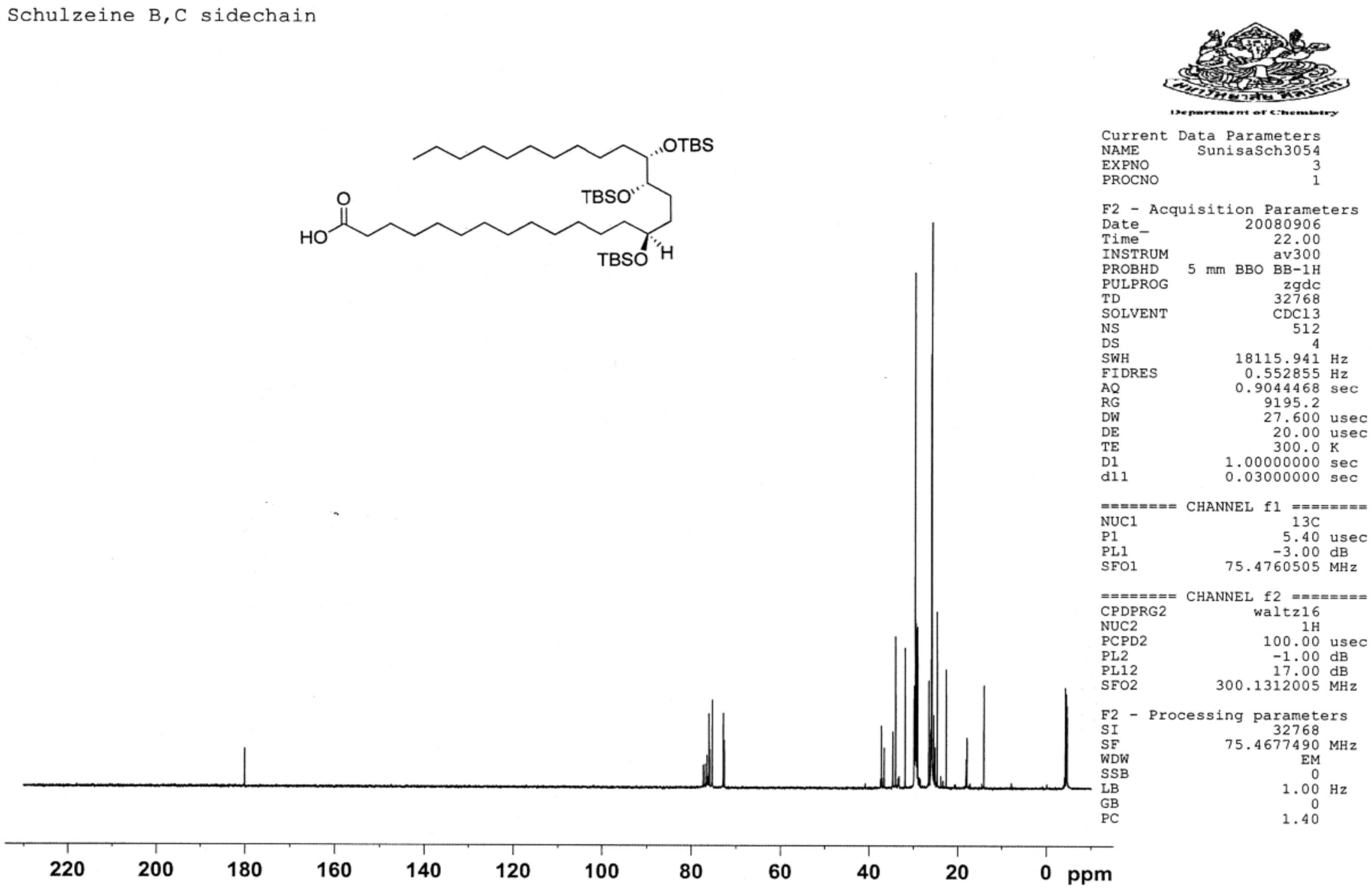
```
Current Data Parameters
NAME        SunisaSch3052
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080903
Time                10.18
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zgdc
TD                  32768
SOLVENT             CDCl3
NS                    512
DS                      4
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                10321.3
DW                 27.600 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   5.40 usec
PL1                 -3.00 dB
SFO1           75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -1.00 dB
PL12                17.00 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF             75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

^{13}C NMR spectrum of compound **107**



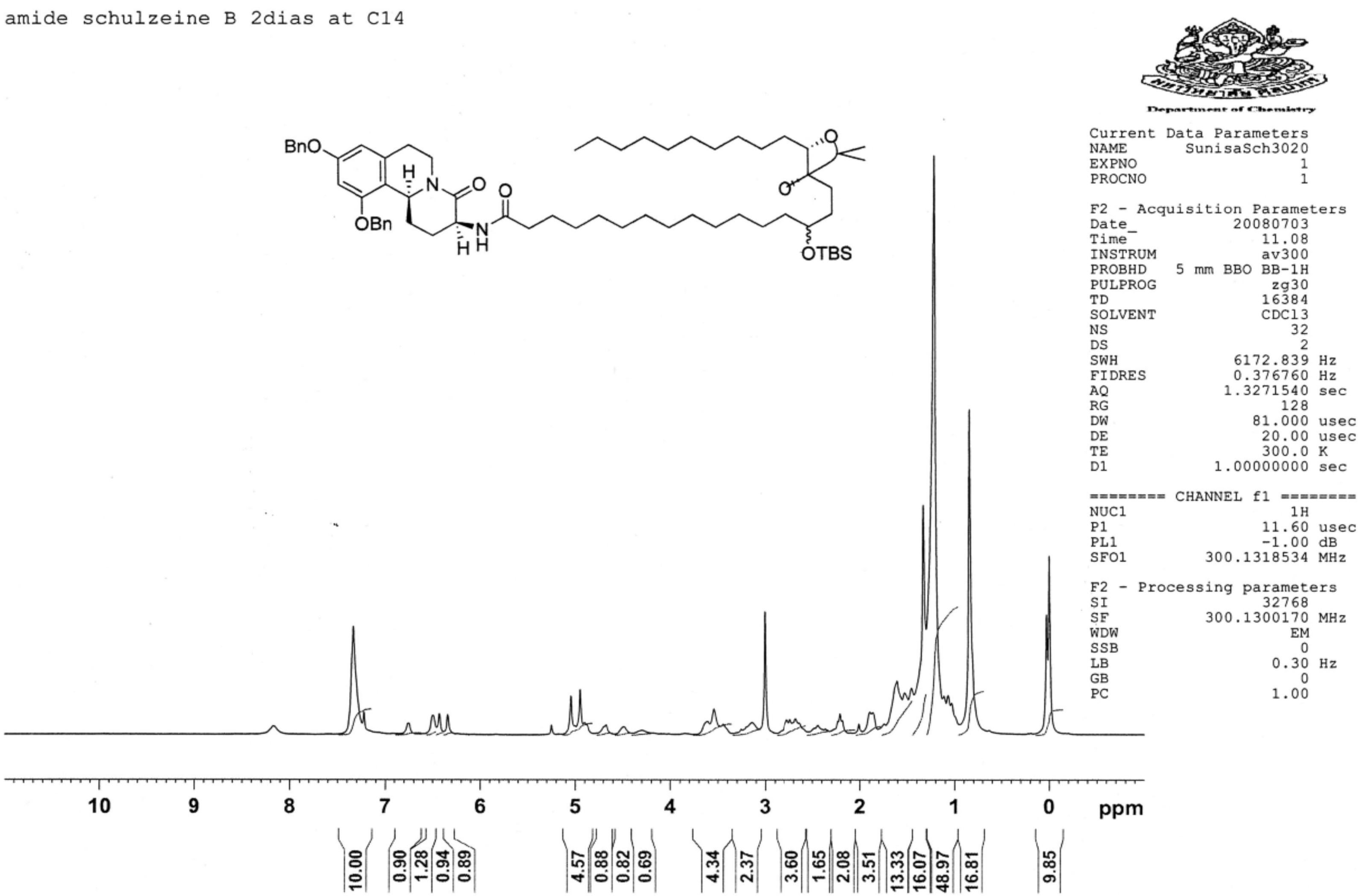
```
Current Data Parameters
NAME        SunisaSch3054
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080906
Time                21.54
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.376760 Hz
AQ              1.3271540 sec
RG                   35.9
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.80 usec
PL1                 -1.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300180 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```

^{1}H NMR spectrum of compound **108**



```
Current Data Parameters
NAME         SunisaSch3054
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20080906
Time                 22.00
INSTRUM              av300
PROBHD   5 mm BBO BB-1H
PULPROG               zgdc
TD                   32768
SOLVENT              CDCl3
NS                     512
DS                       4
SWH              18115.941 Hz
FIDRES            0.552855 Hz
AQ               0.9044468 sec
RG                  9195.2
DW                  27.600 usec
DE                   20.00 usec
TE                   300.0 K
D1              1.00000000 sec
d11             0.03000000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    5.40 usec
PL1                  -3.00 dB
SFO1            75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                  -1.00 dB
PL12                 17.00 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                   32768
SF              75.4677490 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

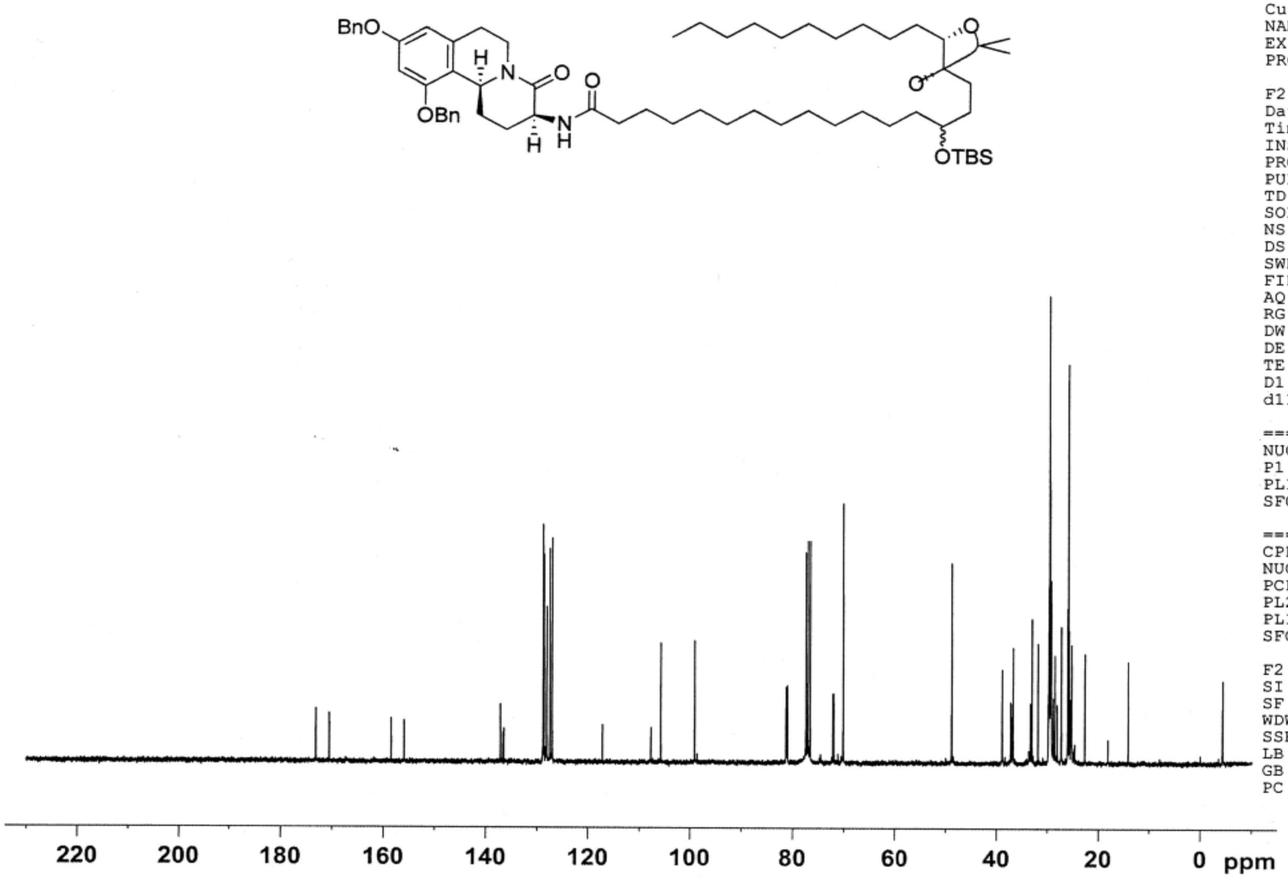
^{13}C NMR spectrum of compound **108**



```
Current Data Parameters
NAME        SunisaSch3020
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080703
Time                11.08
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT             CDC13
NS                     32
DS                      2
SWH              6172.839 Hz
FIDRES           0.376760 Hz
AQ              1.3271540 sec
RG                    128
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.60 usec
PL1                 -1.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300170 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR spectrum of compound **113**

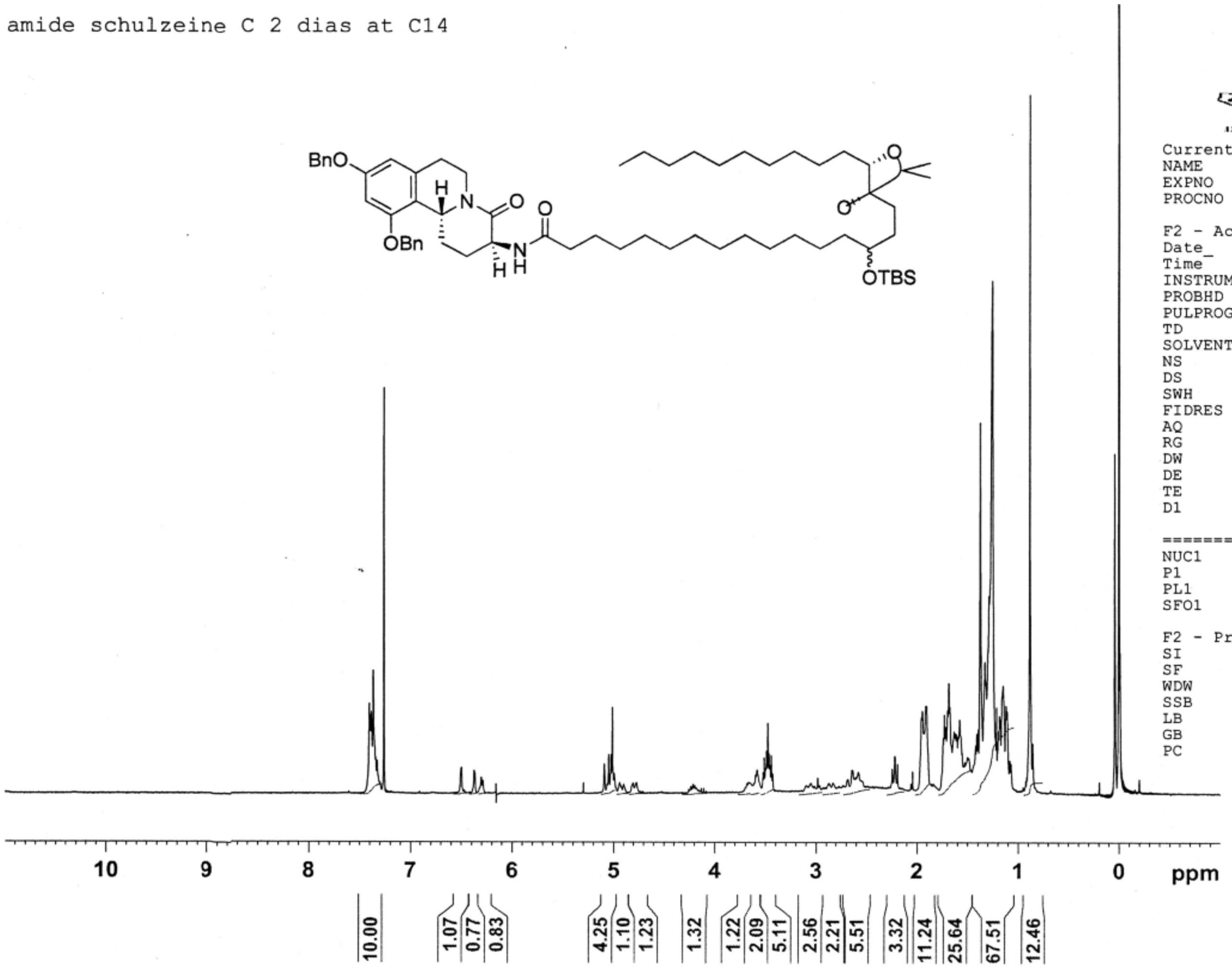
13C of amide schulzeine B 2 dias at C14



```
Current Data Parameters
NAME         SunisaSch3022
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_             20080708
Time                 16.34
INSTRUM              av300
PROBHD    5 mm BBO BB-1H
PULPROG               zgdc
TD                   32768
SOLVENT              CDCl3
NS                    6800
DS                       4
SWH              18115.941 Hz
FIDRES            0.552855 Hz
AQ               0.9044468 sec
RG                 18390.4
DW                  27.600 usec
DE                   20.00 usec
TE                   300.0 K
D1              1.00000000 sec
d11             0.03000000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    5.20 usec
PL1                  -3.00 dB
SFO1            75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                  -1.00 dB
PL12                 17.00 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                   32768
SF              75.4677490 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

^{13}C NMR spectrum of compound **113**

amide schulzeine C 2 dias at C14



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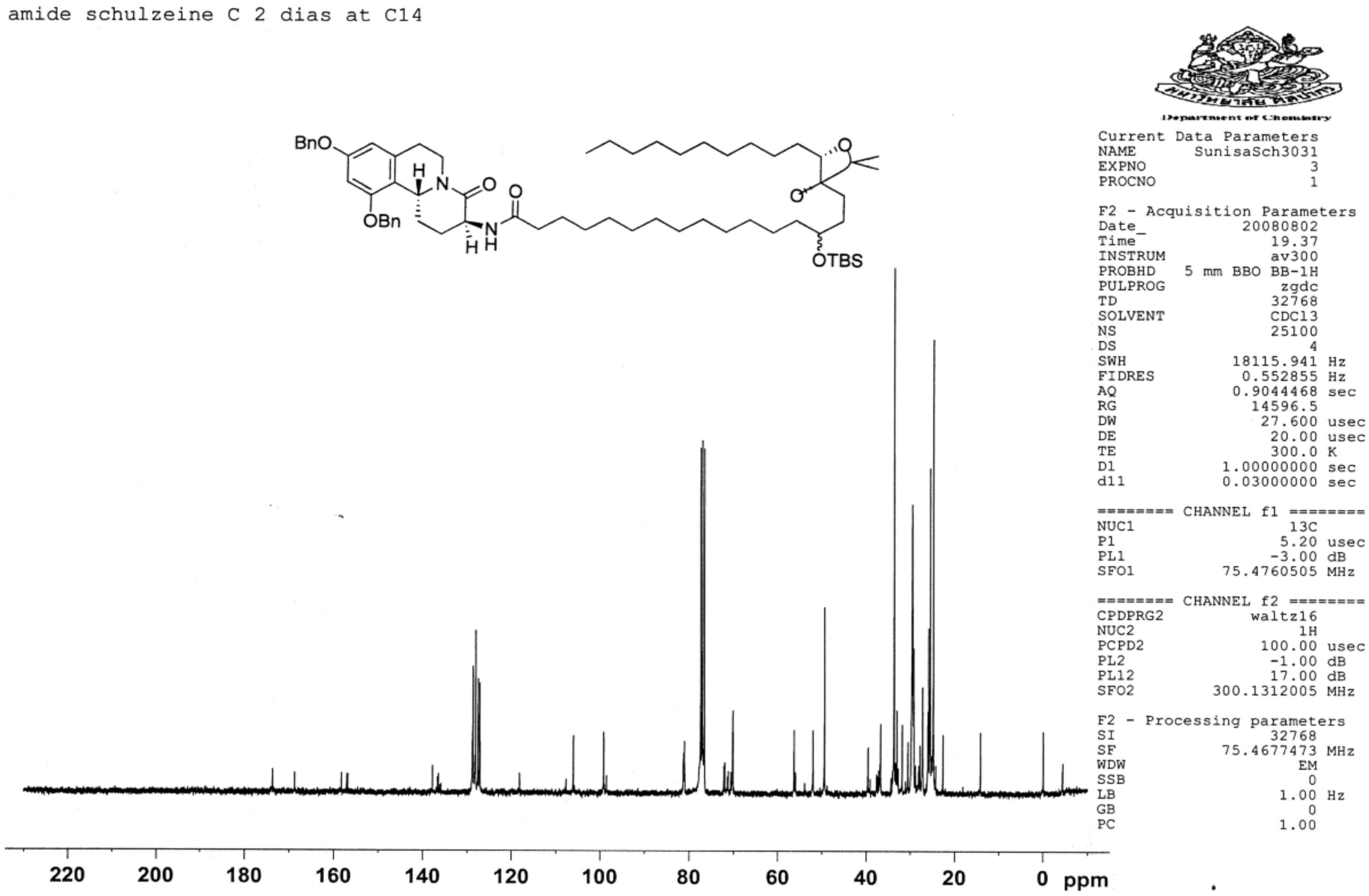
```
Current Data Parameters
NAME       SunisaSch3031
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080801
Time               15.23
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                   512
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.60 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300052 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR spectrum of compound **112**



amide schulzeine C 2 dias at C14

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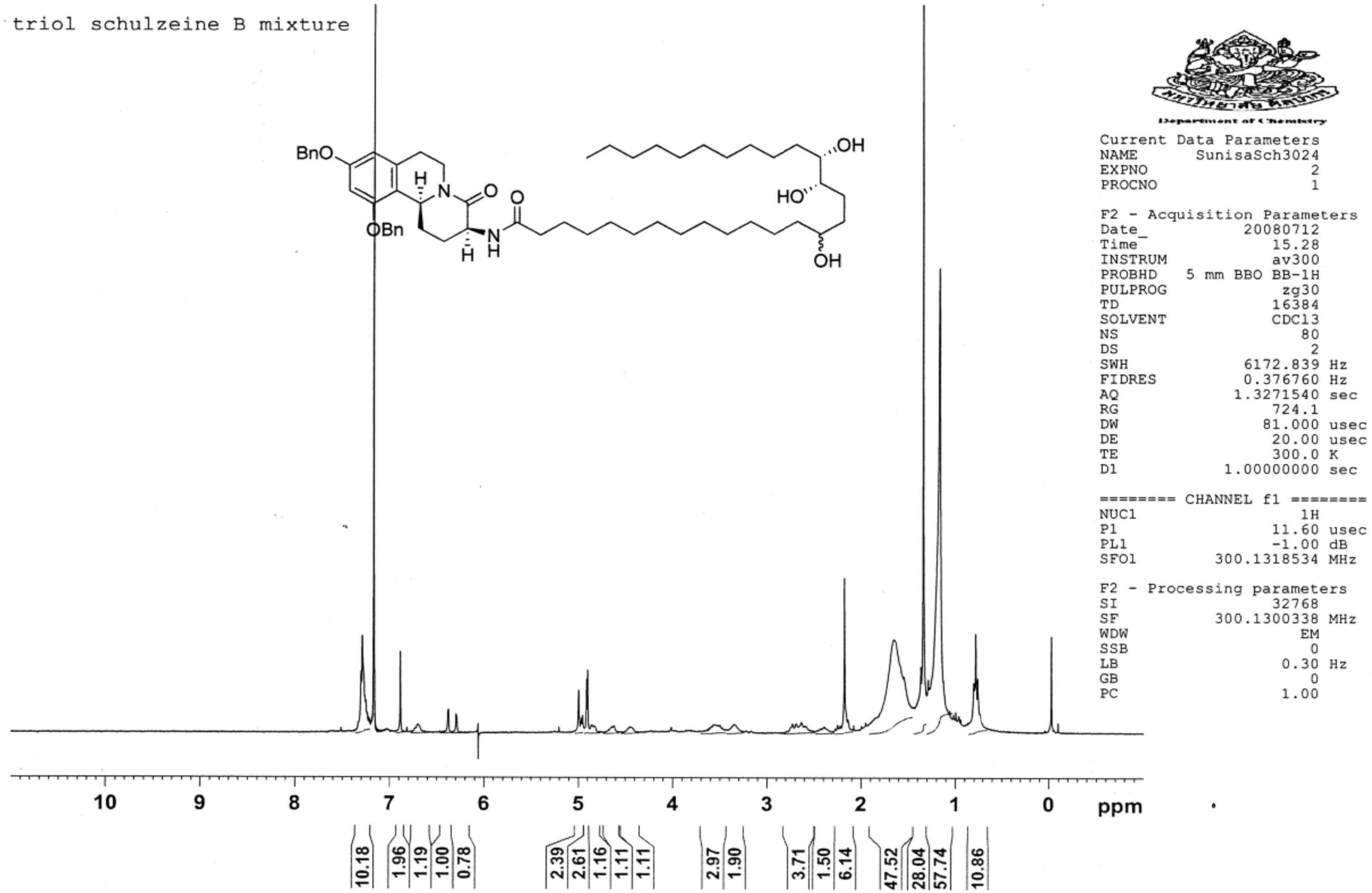
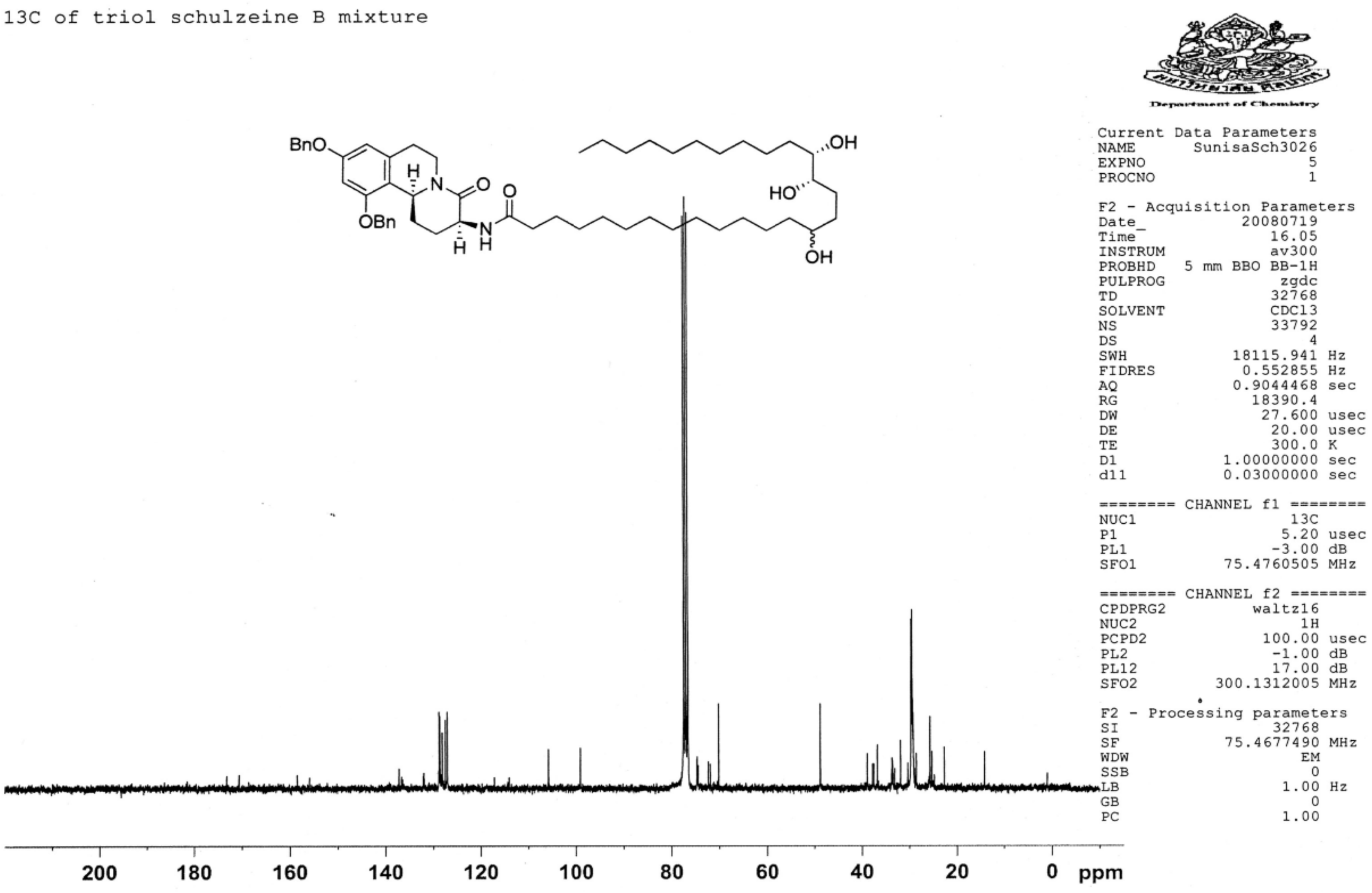
```
Current Data Parameters
NAME          SunisaSch3031
EXPNO                     3
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080802
Time                  19.37
INSTRUM               av300
PROBHD   5 mm BBO BB-1H
PULPROG                zgdc
TD                    32768
SOLVENT               CDCl3
NS                    25100
DS                        4
SWH               18115.941 Hz
FIDRES             0.552855 Hz
AQ                0.9044468 sec
RG                  14596.5
DW                   27.600 usec
DE                    20.00 usec
TE                    300.0 K
D1               1.00000000 sec
d11              0.03000000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                     5.20 usec
PL1                   -3.00 dB
SFO1            75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                   -1.00 dB
PL12                  17.00 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF              75.4677473 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.00
```

^{13}C NMR spectrum of compound **112**



```
Current Data Parameters
NAME          SunisaSch3024
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080712
Time                  15.28
INSTRUM               av300
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       80
DS                        2
SWH                6172.839 Hz
FIDRES             0.376760 Hz
AQ                1.3271540 sec
RG                    724.1
DW                   81.000 usec
DE                    20.00 usec
TE                    300.0 K
D1               1.00000000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    11.60 usec
PL1                   -1.00 dB
SFO1            300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF              300.1300338 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

^{1}H NMR spectrum of compound **114**

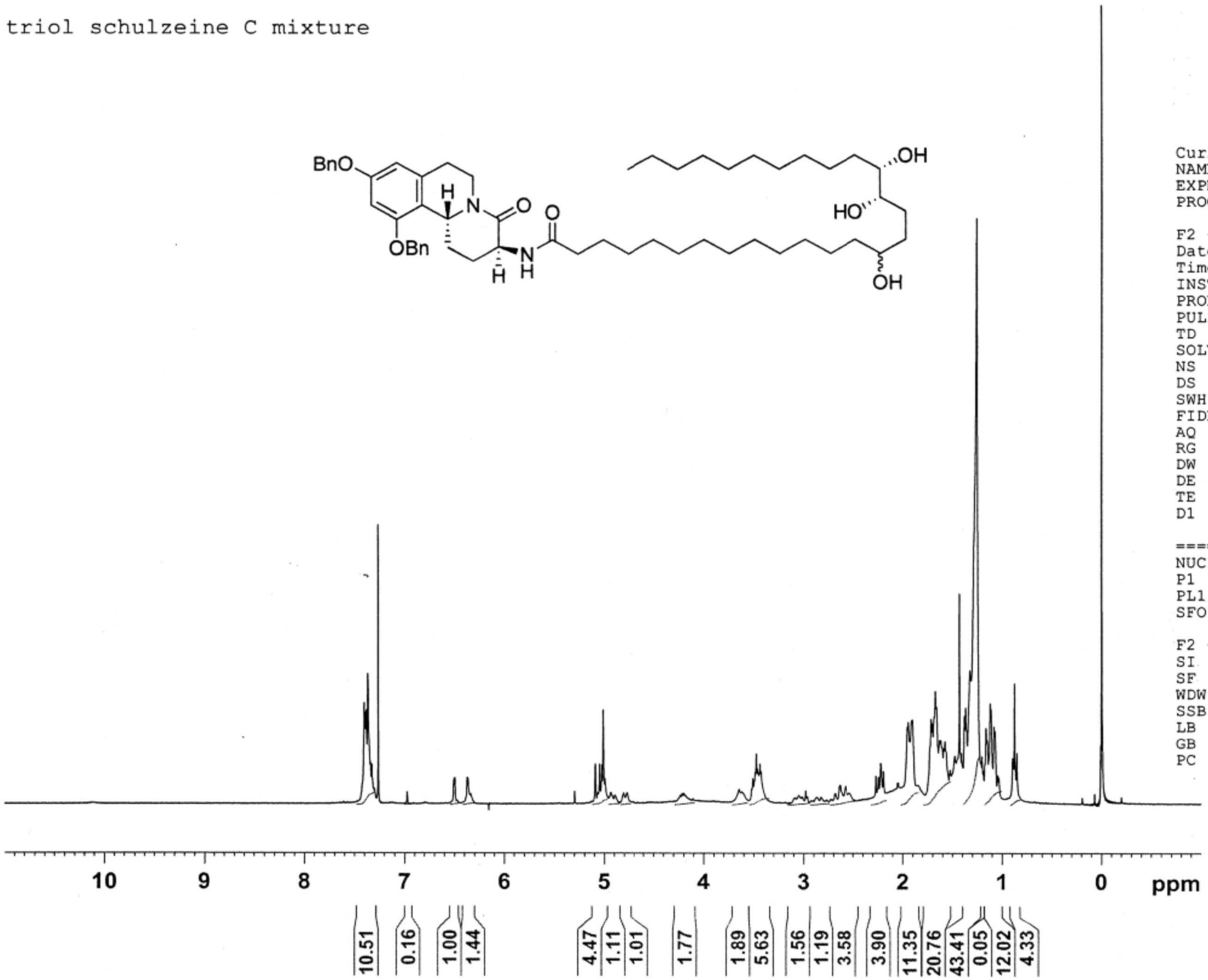


13C of triol schulzeine B mixture

Department of Chemistry

```
Current Data Parameters
NAME       SunisaSch3026
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080719
Time               16.05
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zgdc
TD                 32768
SOLVENT            CDCl3
NS                 33792
DS                     4
SWH            18115.941 Hz
FIDRES          0.552855 Hz
AQ             0.9044468 sec
RG               18390.4
DW                27.600 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec
d11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  5.20 usec
PL1                -3.00 dB
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -1.00 dB
PL12               17.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.00
```

^{13}C NMR spectrum of compound **114**

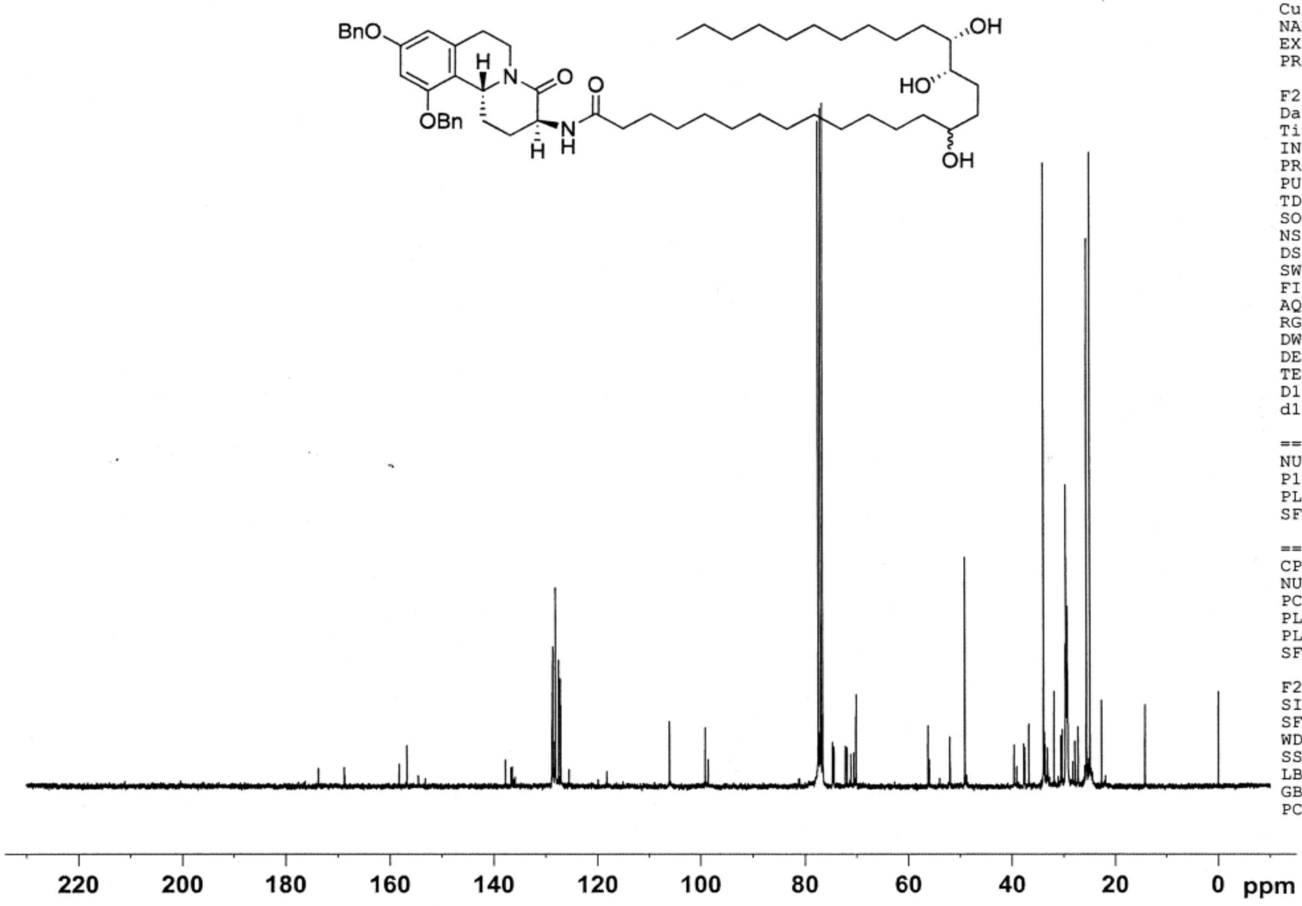


Department of Chemistry

```
Current Data Parameters
NAME        SunisaSch3033
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080804
Time                10.53
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.376760 Hz
AQ              1.3271540 sec
RG                    512
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.60 usec
PL1                 -1.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300048 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

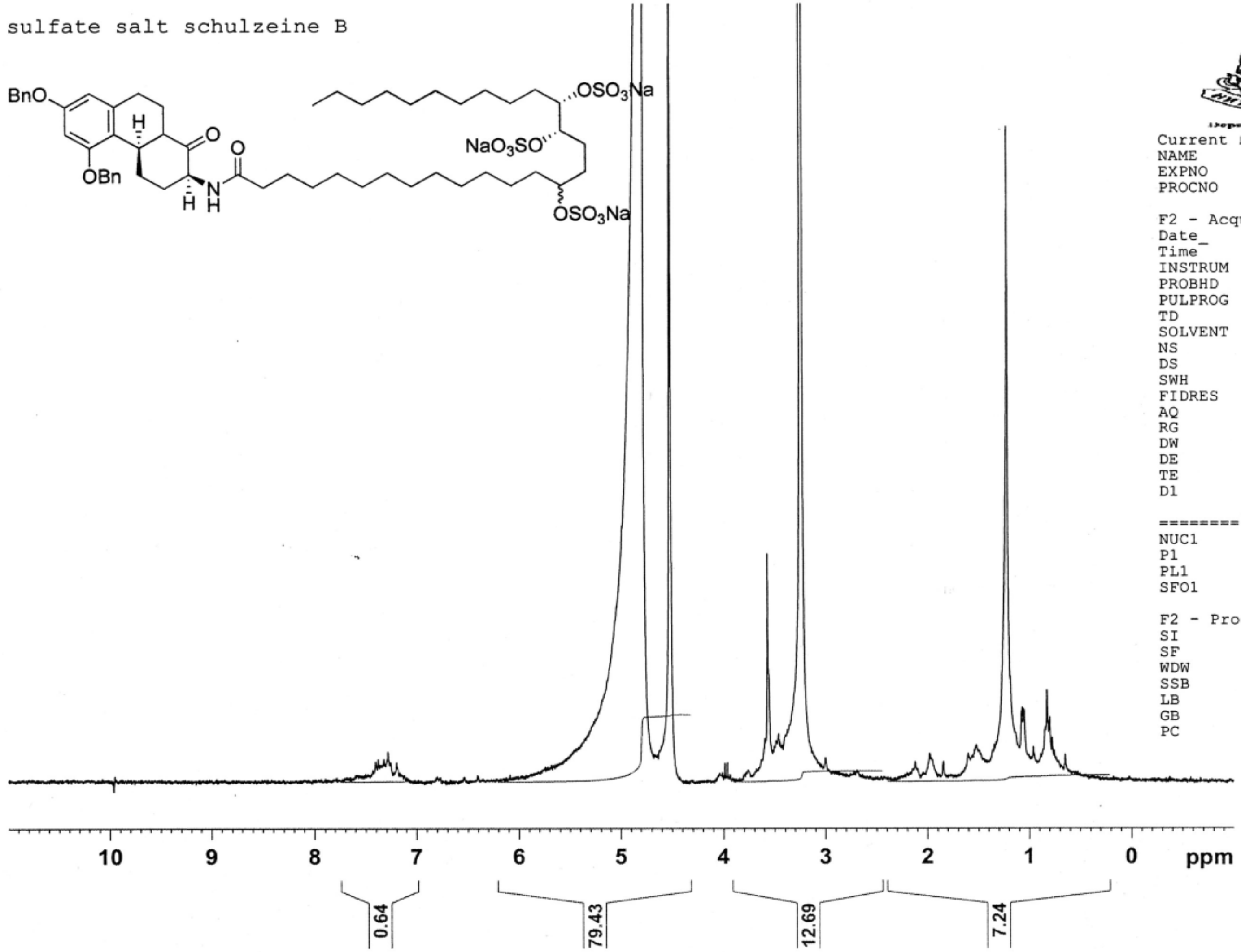
^{1}H NMR spectrum of compound **110**

triol schulzeine C mixture



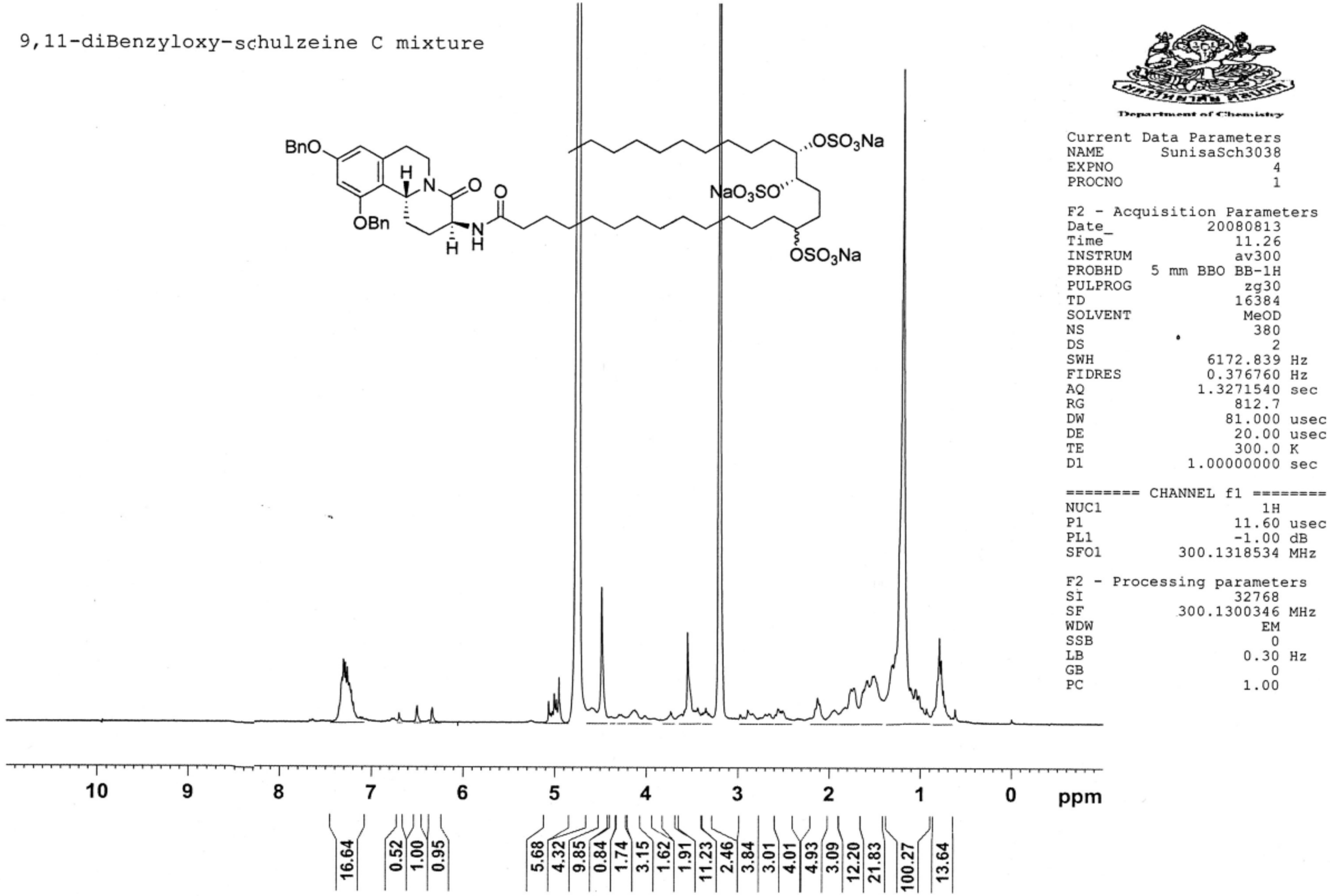
Department of Chemistry

```
Current Data Parameters
NAME        SunisaSch3033
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080804
Time_               18.01
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zgdc
TD                  32768
SOLVENT             CDCl3
NS                  27136
DS                      4
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                20642.5
DW                 27.600 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   5.20 usec
PL1                 -3.00 dB
SFO1           75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -1.00 dB
PL12                17.00 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF             75.4677473 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



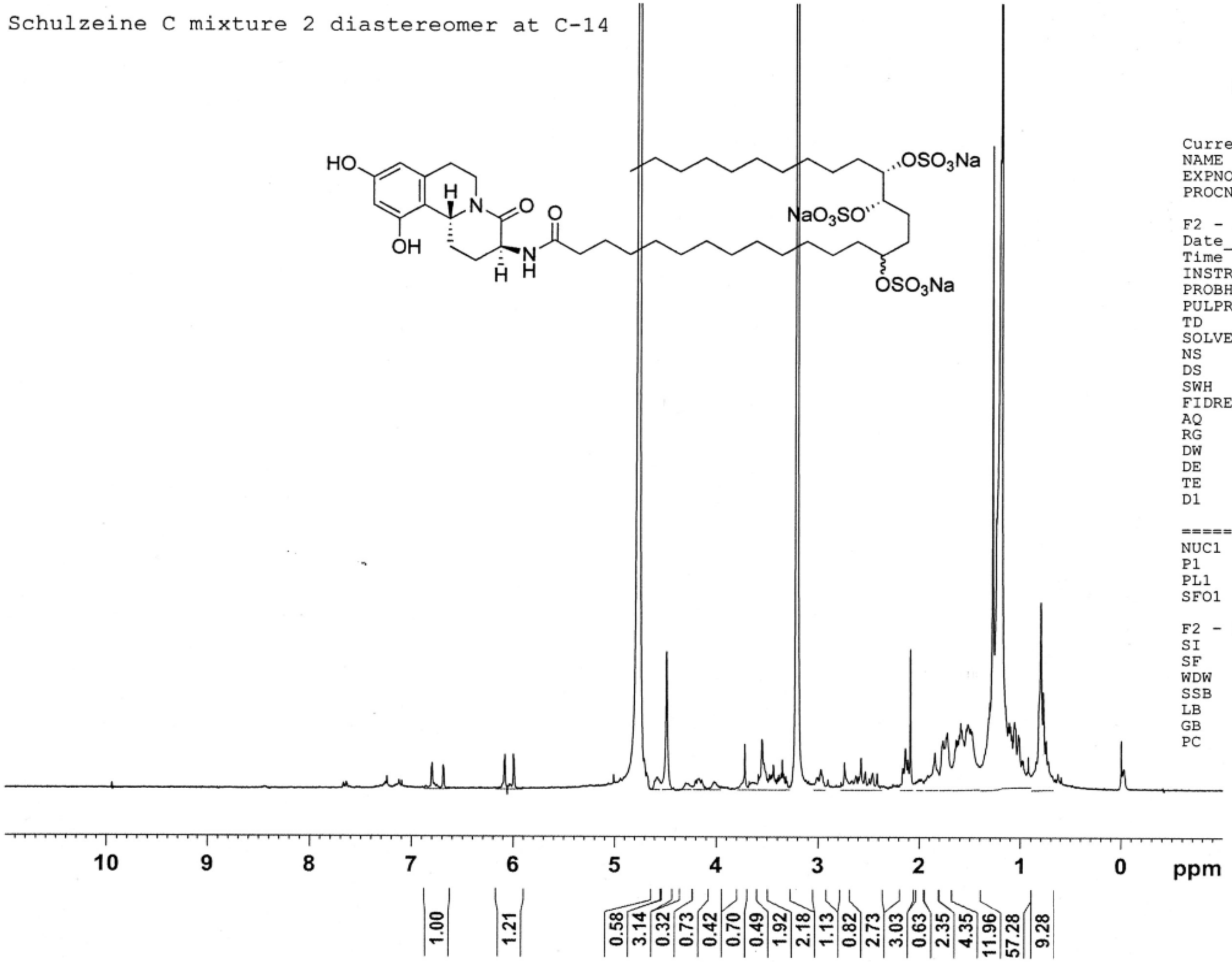
```
Current Data Parameters
NAME        SunisaSch3028
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080723
Time                 9.15
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT              MeOD
NS                    166
DS                      2
SWH              6172.839 Hz
FIDRES           0.376760 Hz
AQ              1.3271540 sec
RG                  724.1
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.60 usec
PL1                 -1.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300268 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR spectrum of compound **115**



```
Current Data Parameters
NAME       SunisaSch3038
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080813
Time               11.26
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT             MeOD
NS                   380
DS                     2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                 812.7
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.60 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300346 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

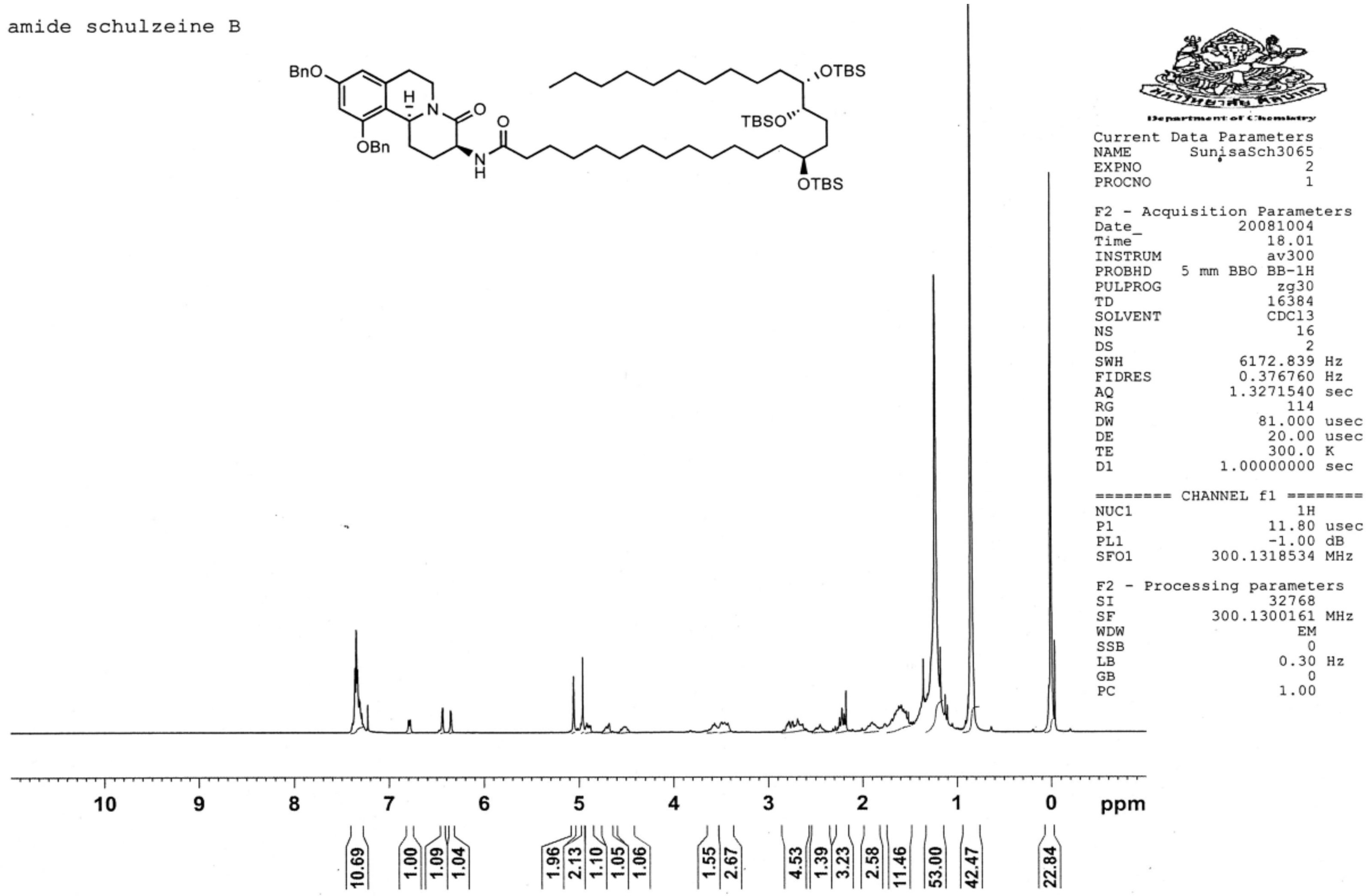
^{1}H NMR spectrum of compound **116**



Department of Chemistry

```
Current Data Parameters
NAME       SunisaSch3056
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080911
Time               16.41
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 16384
SOLVENT             MeOD
NS                   272
DS                     2
SWH             6172.839 Hz
FIDRES          0.376760 Hz
AQ             1.3271540 sec
RG                 645.1
DW                81.000 usec
DE                 20.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.80 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300346 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

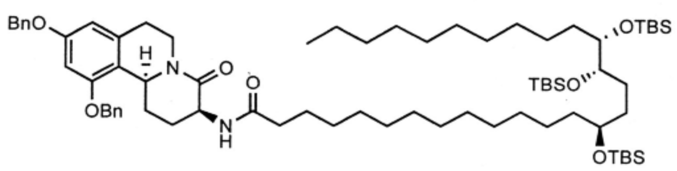
^{1}H NMR spectrum of schulzeine C



```
Current Data Parameters
NAME        SunisaSch3065
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20081004
Time                18.01
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.376760 Hz
AQ              1.3271540 sec
RG                    114
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.80 usec
PL1                 -1.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300161 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR spectrum of compound **117**

amide schulzeine B



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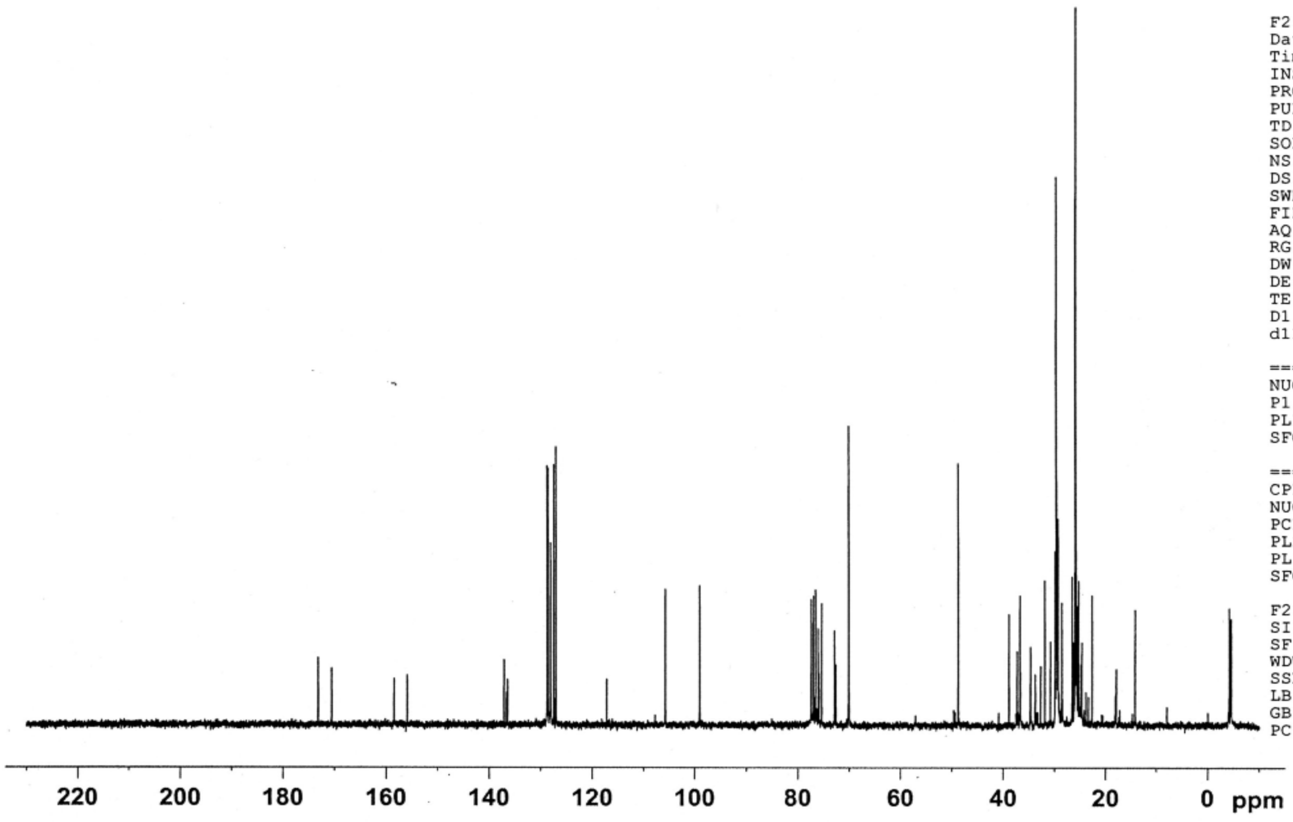
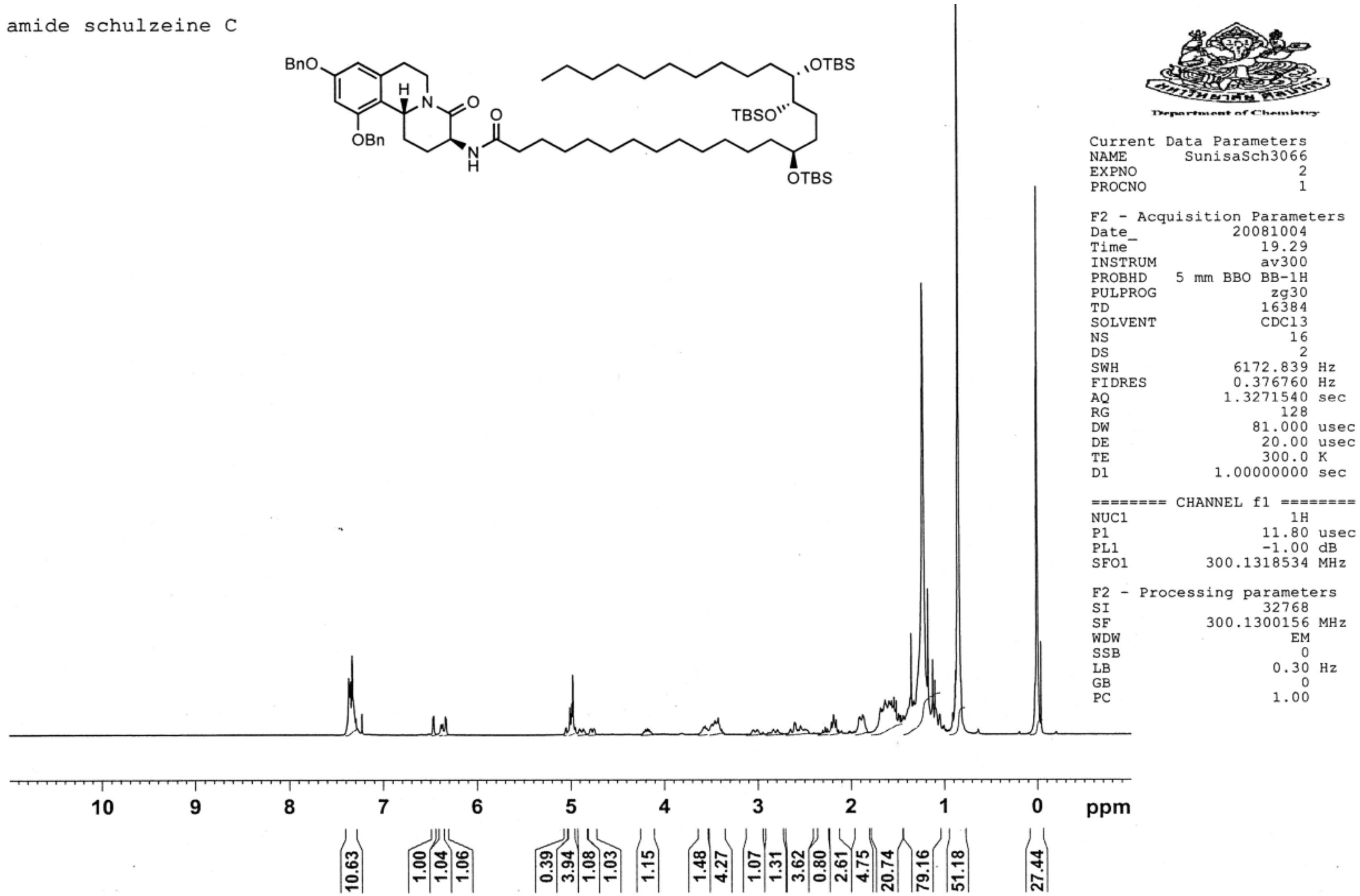
```
Current Data Parameters
NAME        SunisaSch3065
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20081004
Time                19.08
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zgdc
TD                  32768
SOLVENT             CDCl3
NS                   2048
DS                      4
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                 9195.2
DW                 27.600 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   5.40 usec
PL1                 -3.00 dB
SFO1           75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -1.00 dB
PL12                17.00 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF             75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



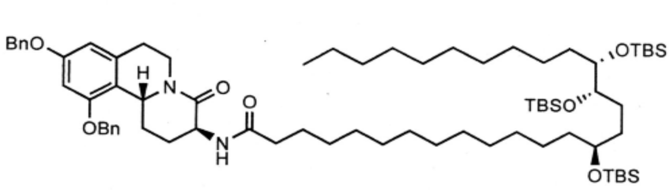
^{13}C NMR spectrum of compound **117**



```
Current Data Parameters
NAME        SunisaSch3066
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20081004
Time                19.29
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  16384
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.376760 Hz
AQ              1.3271540 sec
RG                    128
DW                 81.000 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.80 usec
PL1                 -1.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300156 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

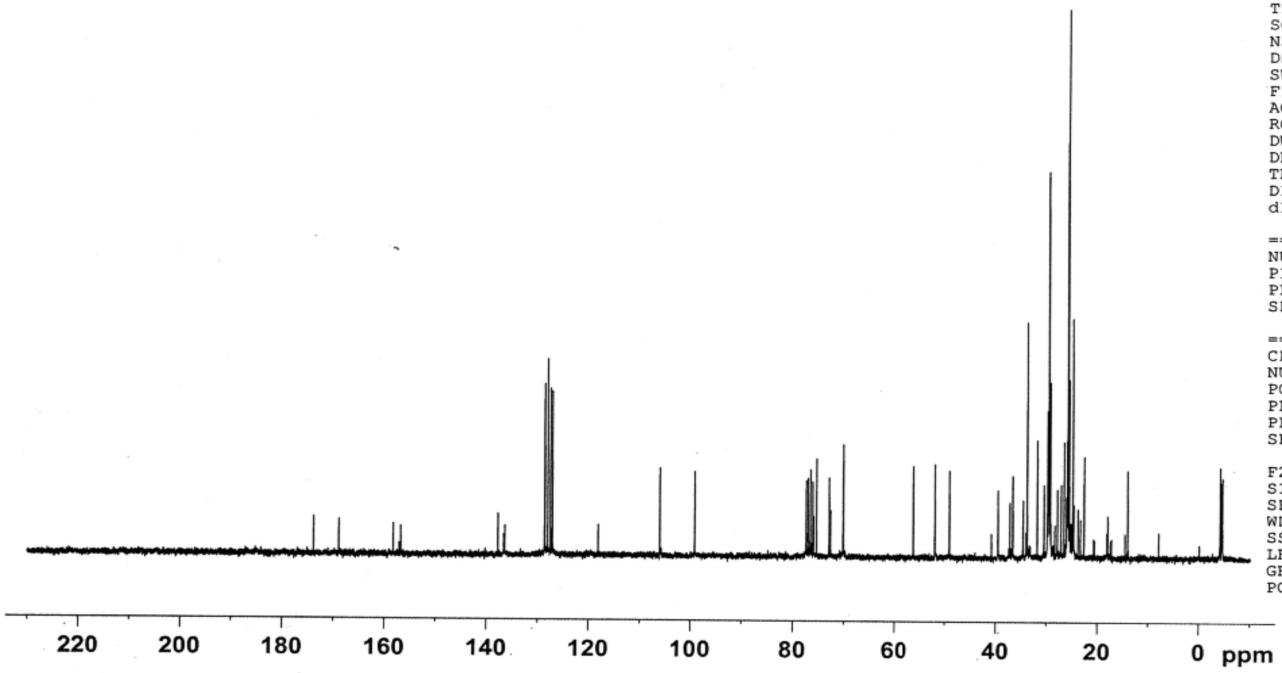
^{1}H NMR spectrum of compound **111**

amide schulzeine C



Department of Chemistry

```
Current Data Parameters
NAME        SunisaSch3066
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20081004
Time                19.41
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG              zgdc
TD                  32768
SOLVENT             CDCl3
NS                   1749
DS                      4
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                 9195.2
DW                 27.600 usec
DE                  20.00 usec
TE                  300.0 K
D1             1.00000000 sec
d11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   5.40 usec
PL1                 -3.00 dB
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -1.00 dB
PL12                17.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF             75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



^{13}C NMR spectrum of compound **111**

BIOGRAPHY

NAME	Miss Sunisa Akkarasamiyo
DATH OF BIRTH	May 4, 1983
PLACE OF BIRTH	Ratchaburi
EDUCATION	
2002 – 2006	Silpakorn university, Bachelor of Science (Chemistry)
2006 – 2008	Silpakorn university, Master of Science (Organic Chemistry)
PUBLICATIONS	Kuntiyong, P.; Akkarasamiyo, S.; and Eksinitkun, G. *Chem. Lett.* **2006**, *35*, 1008-1009.
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