THE UNIVERSITY OF CHICAGO

METAL-CATALYZED ASYMMETRIC EPOXIDATION AND ITS RELATED REACTIONS

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Chapter 1. Iron-Catalyst and Asymmetric Epoxidation of Electron-Deficient Olefins

1.1 Introduction

The oxidation reaction is one of the most powerful and fundamental transformations. The asymmetric epoxidation of olefins, in particular, yields chiral epoxides that can be further functionalized and utilized in the construction of more complex chiral molecules. Therefore, numerous efforts have been dedicated to achieving higher efficiency with cleaner, cheaper, safer, and more sustainable catalysts and oxidants, as well as its applicability to a broader scope of substrates.

In our search of a greener alternative for oxidation, we are particularly interested in iron as a catalyst, since iron is most abundant metal in Earth's crust (~4.7 wt %) after aluminum. Iron is also believed to be the main component of the Earth's core, and is also widely present in soil, plants and hemoglobin (0.34 % Fe). In terms of chemistry, iron exists in variable oxidation states from -2 to +6 (+2 and +3 are most common), and is amenable to nitrogen-, oxygen-, or phosphorus-based ligands. Many iron salts and complexes are commercially available or easily synthesized and their function as good lewis acid renders them versatile in catalysis.[1]

Inspired by the many iron-containing enzymes, mainly oxidases such as cytochrome P-450, nitrogenase and methane monooxygenase, Collman *et al.* first reported the biomimetic asymmetric epoxidation of styrene derivatives with iron porphyrin complexes.[2][3] However, due to the difficulties associated with synthesizing chiral porphyrin ligands, non-heme iron complexes are explored for their catalytic capabilities.

1.2 Non-Heme Iron-Complexes for Enantioselective Epoxidation

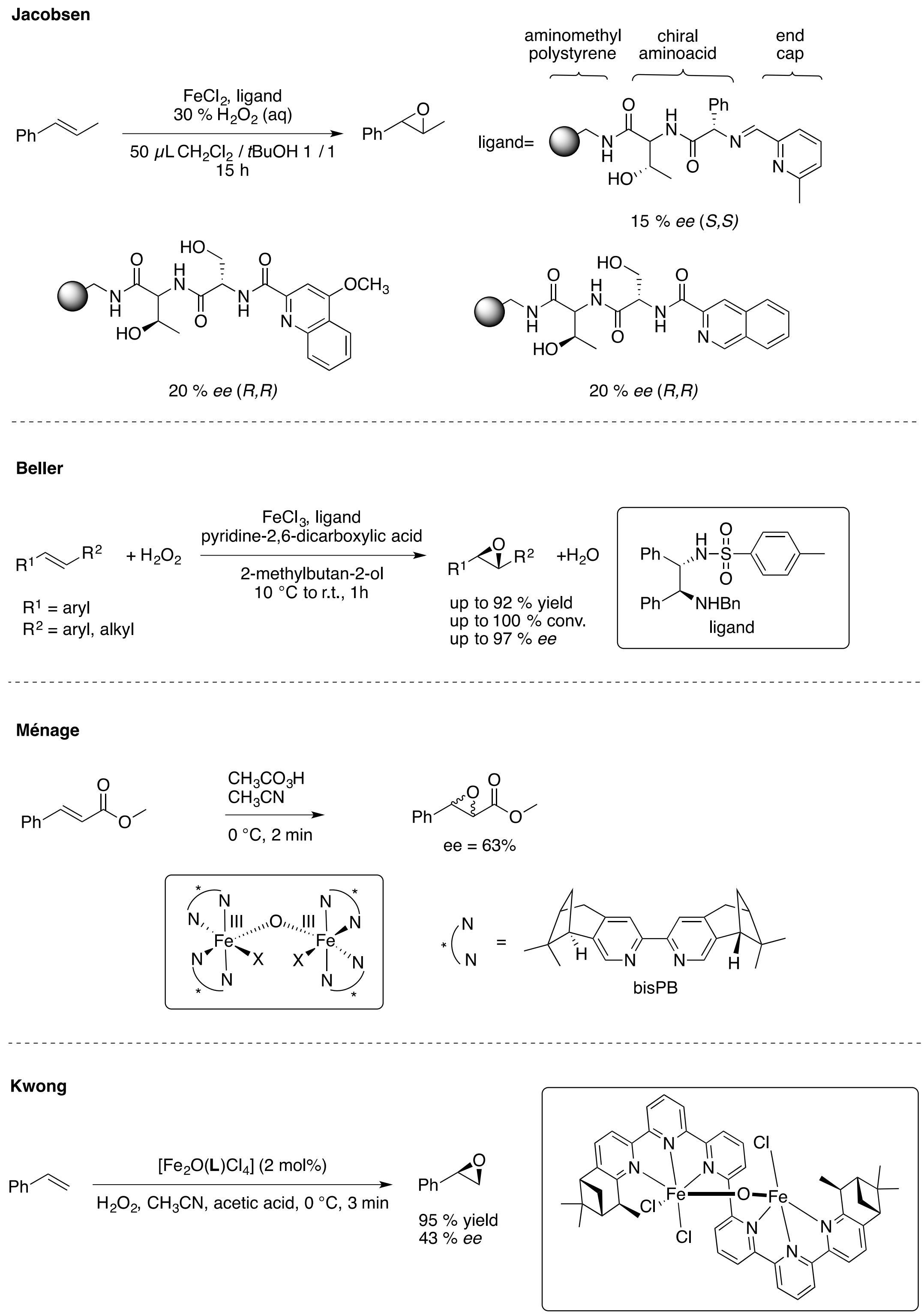
Since the heme-based iron-catalyzed oxidation has been well studied, more works on non-heme iron complexes have emerged over the years in the development for new highly reactive and enantioselective catalyst. In fact, non-heme ligands are more easily tunable for variable steric and electronic properties.

Jacobsen and co-workers utilized combinatorial chemistry as a powerful tool in the discovery of epoxidation catalysts from a library of 5760 metal-ligand complexes.[4] This non-traditional approach allows more metal-ligand combinations to be screened and with a greater number of variations in condition. Three novel and highly efficient catalysts have been discovered for the epoxidation of trans-β-methylstyrene with H_2O_2 as the terminal oxidant. These ligands consist of chiral amino acids and a variety of donor side chains. While one end of the amino acid is coupled to aminomethyl polystyrene, the other end is linked to a capping unit containing a heterocycle. Parallel optimization screening of the library was used to determine enantioselectivity-inducing features of the ligand and to identify enantioselective variants.

Beller and co-workers reported a Fe(III)-catalyzed asymmetric epoxidation of aromatic alkenes by using hydrogen peroxide and a chiral *N*-arenesulfonyl-*N′*-benzyl-substituted ethylenediamine ligand.[5]

Ménage and co-workers developed a dinuclear chiral complex $Fe_2O(bisPB)_4(X)_2(ClO_4)_4$ (X = H_2O or CH_3CN) which catalyzes the epoxidation of electron deficient alkenes 0 °C by a peracid, at with high efficiency (up to 850 TON) and moderate enantioselectivity (63%).[6]

Scheme 1. Previous non-Heme Iron-Catalyzed Asymmetric Epoxidation



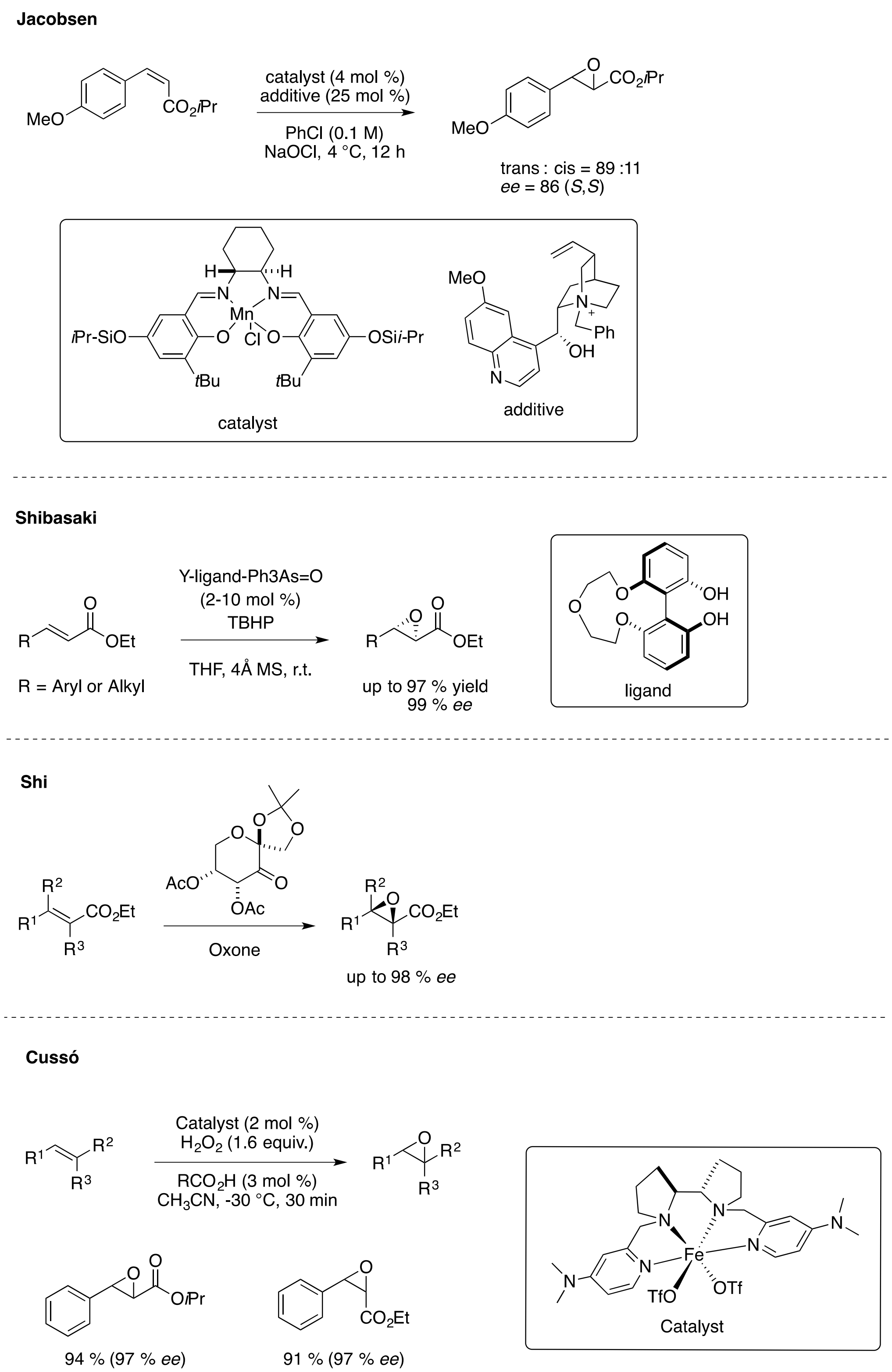
Kwong and co-workers also reported a binuclear chiral iron-sexipyridine complex that is highly efficient for styrene epoxidation with excellent reactivity (3 min, 95 % yield) and chemoselectivity (98 %), but with moderate enantioselectivity (43 % ee).[7]

1.3 Asymmetric Epoxidation of α,β-Unsaturated Esters

In addition to discovering greener alternatives for asymmetric epoxidation, the extension of accessible substrates classes for oxidation is also of great significance. Electron-deficient olefins, which are less reactive to electrophilic oxidants, represent one such difficult class of substrates.

Approaches to these targets are typically nucleophilic and generally execute through a Weitz–Scheffer-type mechanism. Representative methods include a Zinc-mediated system developed by Enders and co-workers that uses a stoichiometric amount of diethylzinc, a chiral alcohol and oxygen.[8] On the other hand, Shibasaki *et al.* used catalytic Lanthanide-BINOL complex and peroxide as an epoxidation tool for α,β-unsaturated ketones.[9] Phase-transfer catalysis using a optically active quaternary ammonium salt was studied by Corey *et al.* using stoichiometric potassium hypochlorite as oxidant at a reaction temperature of −40 °C.[10] Juliá also employs chiral polypeptides as epoxidation catalysts, where the reaction of chalcone with H_2O_2/NaOH in the three-phase system toluene-water-poly[(S)-alanine] reported an enantioselectivity of 90 %.[11]

Scheme 2. Previous Asymmetric Epoxidation of α,β-Unsaturated Esters



Previous examples of systems that target α,β-unsaturated esters are also depicted above. Jacobsen and co-workers reported on the epoxidation of cis-olefins using a Manganese-salen catalyst, a chiral quaternary salt as additive and NaOCl as oxidant. There is only one isolated example on α,β-unsaturated ester and moderate dr (*trans* : *cis* = 89 : 11) and enantioselectivity (86 % *ee*).[12]

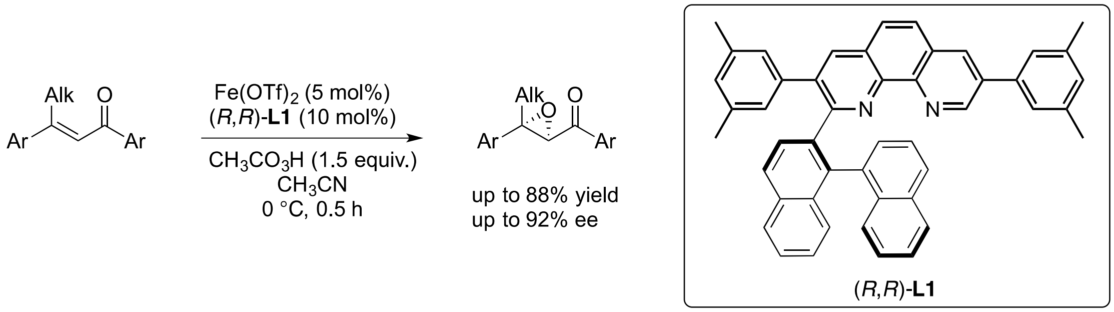
Shibasaki and co-workers demonstrated a yttrium-chiral biphenyldiol complex that is capable of epoxidizing α,β-unsaturated esters via conjugate addition of the oxidant *tert*-butyl hydrogenperoxide, with up to 97 % yield and 99 % ee.[13]

Shi and co-workers developed a system using fructose-derived ketone as catalyst and oxone as oxidant. Chiral dioxiranes are generated *in situ* from the chiral ketone and showed high enantioselectivities for the α,β-unsaturated esters.[14] However, only a few examples are trisubstituted.

More recently, Cussó and co-workers reported a chiral Fe–bipyrrolidine catalyst that was used to access a wide range of electron-deficient olefins, including α,β-unsaturated esters.[15]

1.4 Development of Chiral Iron-Phenanthroline Catalyst

Scheme 3. Iron-Catalyzed Asymmetric Epoxidation of β,β-Disubstituted Enones.

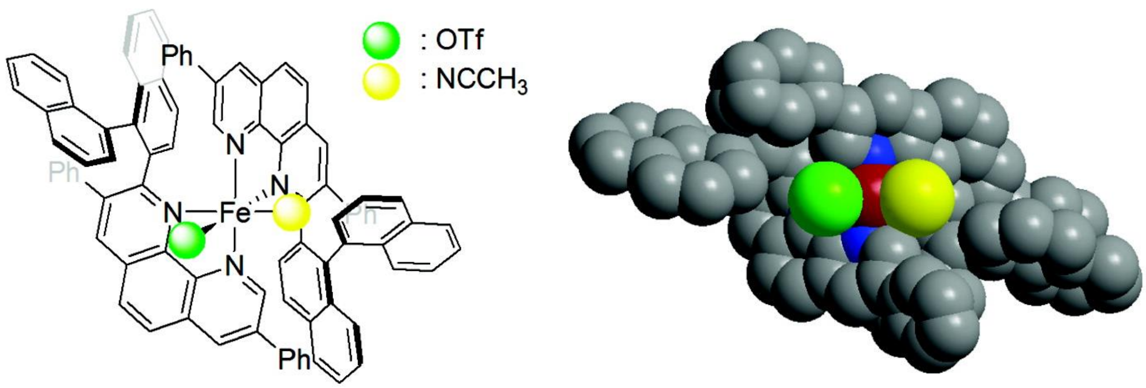


In 2011, Yamamoto and co-workers reported an iron (II)-catalyzed asymmetric epoxidation of *β,β*-disubstituted enones, with up to 88% yield and 92% enantioselectivity.[16] This work features an olefin class that was previously inaccessible to chemists. The only example was by Adam *et al.*, who reports a yield of 88% and enantioselectivity of 72% when Ar=Ph and Alk=Me.[17] This is probably because stereocongestion at the *β* carbon is deleterious for the Weitz-Scheffer-type epoxidation.

Considering the difficult synthesis of chiral porphyrin ligands, the more easily prepared non-heme iron catalyst was pursued. Inspired by nature's non-heme iron-centered enzymes such as methane monooxidase (MMO) and Rieske dioxygenase, previous work on iron catalysts, and iron's high affinity for nitrogen-based ligand, a phenanthroline-derived ligand was approached.

Optimization of the catalyst revealed $Fe(OTf)_2$ as superior to $FeCl_2$ in terms of reactivity and enantioselectivity. For iron complexes where Fe:**L1** is 1:1, introduction of a methyl group at the 2′-position in binaphthyl group is detrimental while attaching phenyl groups at the 3,8-positions on the phenanthroline is desirable. Enantioselectivity is boosted to 91 % when metal-ligand ratio is 1:2. X-ray crystallography also revealed a pseudo-C_2-symmetric iron-ligand complex.[16] The phenyl groups at the 3,8-positions on the phenanthroline are believed to restrict the bond rotation between the binaphthyl group and the phenanthroline moiety. The π-π interaction locks the catalyst in a rigid structure that results in significant increase in enantioselectivity. A preliminary screening of the reaction conditions found that peracetic acid is crucial in producing the epoxide.

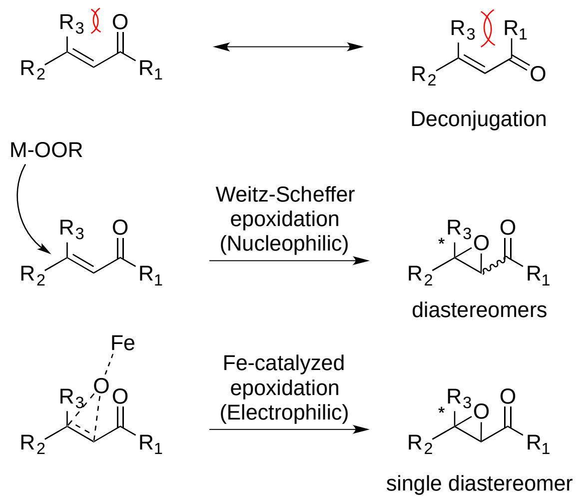
Figure 1. X-ray structure and CPK model of [Fe(L1)2(CH3CN)(OTf)](OTf).



Hydrogens and noncoordinating molecules have been omitted.

Considering the stereocongestion at the β carbon of such acyclic β,β-disubstituted substrate, where R_3 (Fig.3) creates steric repulsion between the β carbon and the nucleophile, the more commonly used nucleophilic approach is less favorable in attacking the olefin. In addition, the steric repulsion between R_3 and R_1 would force the substrate to break its conjugation and is thus more electron–rich than those in cyclic or non-β-substituted enones. As a result, the substrate is more favorable towards electrophilic epoxidation. In fact, this was supported by a competitive experiment using electron-rich and electron-deficient olefins, in which the former results in higher yield.

Figure 2. Nucleophilic vs. Electrophilic Epoxidation



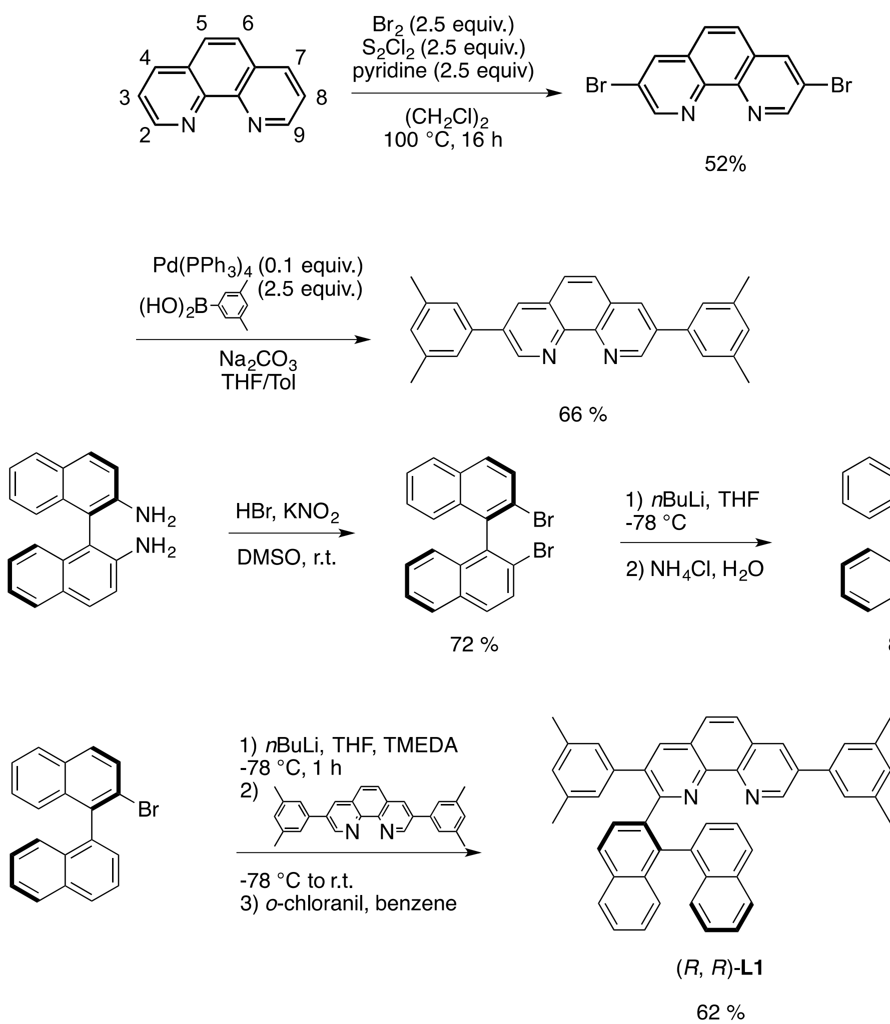
The epoxidation is believed to proceed via a concerted and electrophilic pathway since only a single diastereomer was obtained in the reaction even when (Z)-dypnone was used. This is mechanistically different from past asymmetric epoxidation methods for this class of substrates, which generally operate via a Weitz-Scheffer[18–22] type mechanism where a nucleophilic oxidant is involved. However, the interaction between the iron complex, the substrate and the oxidant in the reaction medium is unknown.

This chiral phenanthroline ligand[16] was synthesized from commercially available 1, 10-phenanthroline, bromination took place regioselectively at the 3 and 8 positions of the phenanthroline. The symmetric 3, 8-disubstituted phenanthroline then undergoes Suzuki coupling to yield the desired diarylphenanthroline.

In synthesizing the monobromo binaphthyl moiety, the starting aromatic amine undergoes nitrosation with nitrous acid (generated *in situ* from HBr and KNO_2) to form the relative diazonium salt. Subsequent displacement of the diazonium salt with Br ion leads to the dibrominated binaphthyl compound, with retention of configuration. The reasoning behind could be an ion-pair mechanism, which the carbocation can hold the configuration and Br^- is the counterion.[23] A collapse of the carbocation and Br^- on the front of the cation gives the product with retained stereochemistry. Then via quantitative lithium-halogen exchange, followed by quenching with water, the monobromo binaphthyl compound was formed with high yield.

In the synthesis of the final chiral ligand **L1**, lithium-halogen exchange, followed by aryl-lithium addition at the 2-position of the phenanthroline and reoxidation with *o*-Chloranil yield the mono-substituted ligand.

Scheme 4: Synthesis of Chiral Phenanthroline Ligand (*R*,*R*)-L1 for Iron-Catalyzed Epoxidation



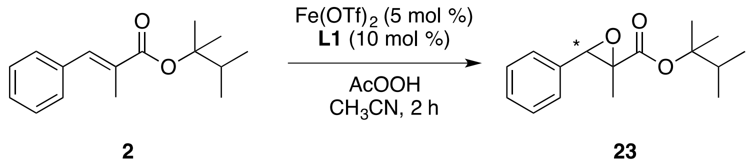
Chapter 2. Iron(II)-Catalyzed Asymmetric Epoxidation of Trisubstituted α, β-Unsaturated Esters

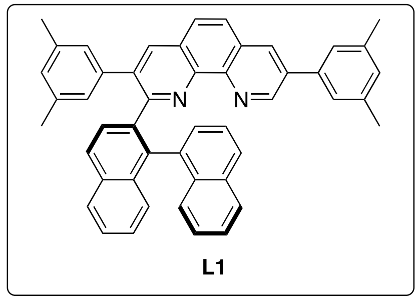
2.1 Optimization of Reaction Condition and Alkoxy Groups for Asymmetric Epoxidation

Unlike the majority of epoxidations of α,β-unsaturated esters, which generally employ disubstituted *trans*-alkenes, we were more interested in the less reported trisubstituted (*E*)-alkene.

An initial trial with the –$C(CH_3)_2$(*i*Pr) ester (Table **1**) by using conditions similar to those reported in preceding work gave valuable results. Upon brief optimization of the reaction conditions, we found performing the reaction at –20 °C significantly deteriorated the yield and enantioselectivity (Table **1**, entry 4), whereas raising the temperature to 20 °C produced a lower yield but similar selectivity. Two equivalents of peracetic acid were also observed to be the most desirable conditions (Table **1**, entry 2). In addition, stirring the complex formation and epoxidation reactions at 1200 rpm was important to provide ideal results in terms of yields and enantioselectivities. Prompt addition of the oxidant was also desirable, presumably owing to the short lifetime of the iron–oxo species.

Table 1. Optimization of Reaction Conditions for the Epoxidation.



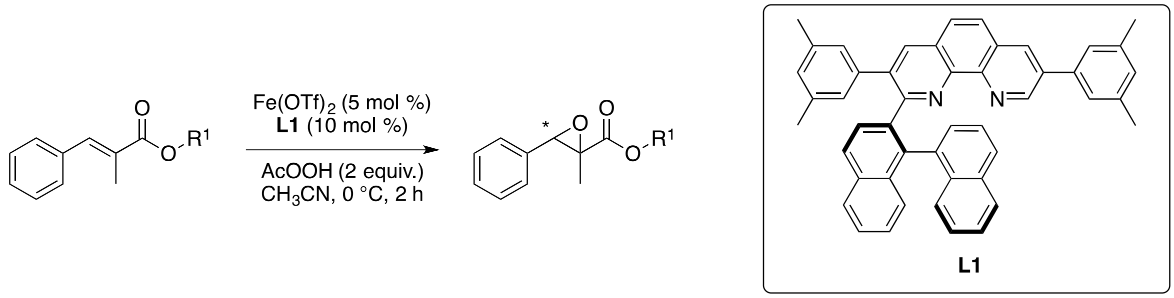


Entry	AcOOH (equiv.)	Temperature (° C)	Yield (%)[d]	ee (%)[e]
1	1.8	0	42	92
2	**2**	**0**	**58**	**94**
3	2.2	0	51	86
4	2	-20	32	66
5	2	20	38	92
6[b]	2	0	43	78
7[c]	2	0	57	86

[a] Unless otherwise stated, reactions are performed in 0.6 ml CH_3CN and stirred at 1200 revolutions per minute (rpm). [b] Reaction performed in 0.3 mL CH_3CN. [c] Reaction performed in 1.2 mL CH_3CN. [d] Isolated yields. [e] Determined by HPLC on a chiral stationary phase.

Realizing that the -C(CH_3)$_2$(*i*Pr) ester generates better results than *t*-butyl ester (Table **2**, entries 1 and 2), we further screened a variety of alkoxy moieties on the ester, which could serve as an auxiliary group for improving stereochemical induction. Subsequent screening of different esters revealed the importance of the alkoxy group on the enantioselectivity of the reaction. As a general trend, tertiary alcohol based esters (entries 1, 2, 3 and 5) perform better than secondary alcohol based esters (entries 4, 6 and 7), due to higher steric hindrance. Among them, –$C(CH_2)_2$(*t*Bu) ester (entry 3) provided optimum result with respect to both yield and ee.

Table 2. Optimization of Alkoxy Groups for Asymmetric Epoxidation

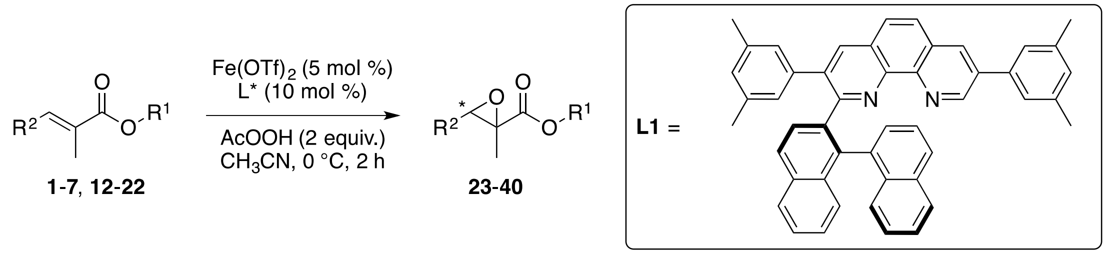


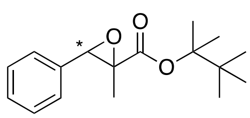
Entry[a]	R_1	Yield (%) [b]	ee (%) [c]
1	*t*Bu	49	90
2	**$C(CH_3)_2$(*i*Pr)**	**58**	**94**
3	**$C(CH_3)_2$(*t*Bu)**	**69**	**95**
4	*i*Pr	30	70
5	$C(Et)_3$	43	90
6	CH(*t*Bu)$_2$	26	76
7	cyclododecanyl	18	63

a] All reactions were carried out on a 0.15 mmol scale of using $Fe(OTf)_2$ (5 mol %), ligand (10 mol %), peracetic acid (32 wt. %, 2 equiv.) in CH_3CN (0.6 mL) at 0 °C and quenched after 2 hours. [b] Isolated yields. [c] Determined by HPLC on a chiral stationary phase.

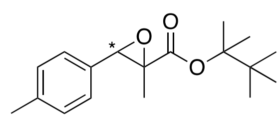
2.2 Substrate Scope of Epoxidation

Figure 3. Substrate Scope of Epoxidation.

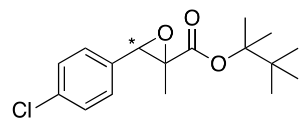




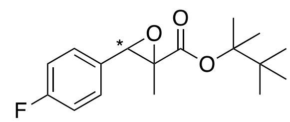
25
69 %
95 % ee



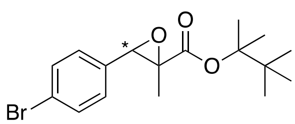
30
65 %
93 % ee



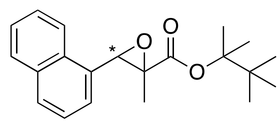
31
48 %
96 % ee



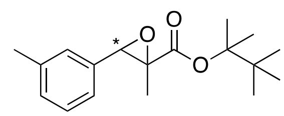
32
30 %
95 % ee



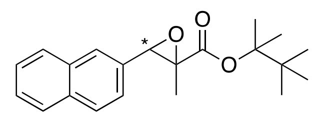
33
34 %
95 % ee



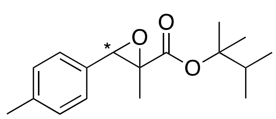
34
61 %
98 % ee



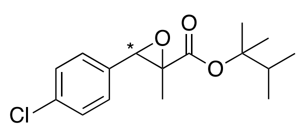
35
24 %
94 % ee



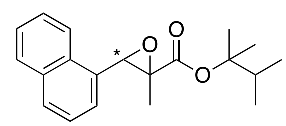
36
38 %
99 % ee



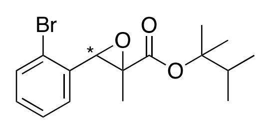
37
46 %
93 % ee



38
64 %
94 % ee



39
62 %
98 % ee



40
16 %
93 % ee

[a] All reactions were carried out on a 0.15 mmol scale using $Fe(OTf)_2$ (5 mol %), **L1** (10 mol %), substrate (0.15 mmol), peracetic acid (32 wt. %, 2 equiv.) in CH_3CN (0.6 mL) at 0 °C and quenched after 2 hours. [b] Isolated yields. [c] Determined by HPLC on a chiral stationary phase.

Our exploration of the substrate scope revealed that either -$C(CH_2)_2$(tBu) or –$C(CH_2)_2$(iPr) esters could be used to induce high enantioselectivity. While in some cases –$C(CH_2)_2$(tBu) ester gave higher yield and ee (Figure **3**, **25** and **30**), it would generate lower yield than its –$C(CH_2)_2(i\text{Pr})$ analogue (**31** and **34**) if the starting ester had lower solubility in acetonitrile. Nevertheless, high ee's were still maintained even in such cases. Enantioselectivities are remarkably high for substrates with a large naphthyl group at the β-position (**34**, **36** and **39**). In terms of reactivity, the epoxidation of *para*-substituted phenyl olefins gave a higher yield of the epoxide product than *meta*- and *ortho*-substituted ones. Although this catalytic system works well for phenyl and naphthyl system, it is not applicable to substrates bearing an alkyl, furyl, thienyl group at the β position of the ester.

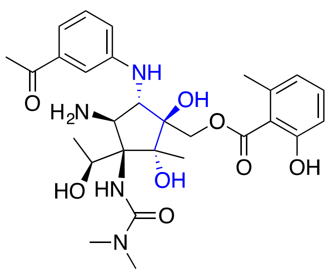
In summary, this is a highly enantioselective epoxidation of trisubstituted α,β-unsaturated esters catalyzed by a chiral iron-phenanthroline complex using peracetic acid as oxidant. The oxidation can enantioselectively target trans-α-methylcinnamic acid esters, of which –$C(CH_2)_2(t\text{Bu})$ and –$C(CH_2)_2(i\text{Pr})$ esters gave ideal results. The enantioselectivity was remarkably high for substrates bearing a large group at the β-position and was maintained even in cases of lower yields.

Chapter 3. Asymmetric Epoxidation and Enantioselective Aminolysis

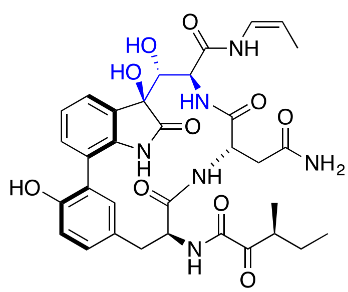
3.1 Introduction: Sequential Epoxidation and Aminolysis

Synthesizing compounds with complete enantiopurity has been a paramount challenge in organic chemistry, especially with pharmaceutical drugs or biologically important molecules. Generally highly enantioenriched chiral products can be obtained by using a combination of two moderately selective catalysts.[24–29]

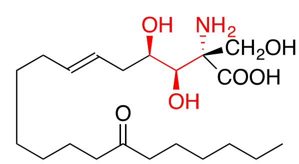
Figure 4. Potential Application of Double-Kinetic Resolution Strategy



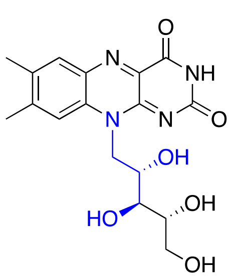
Pactamycin
(Antitumor)



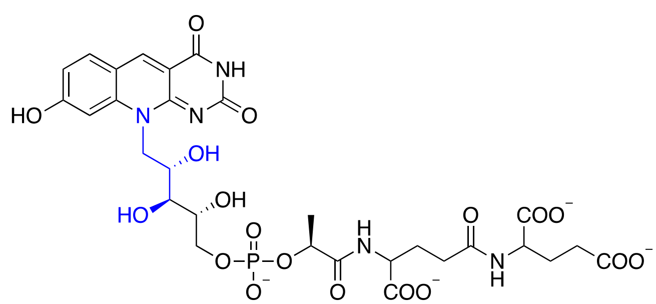
TMC-95A
(Proteasome Inhibitor)



Myriocin
(Antibiotic)



Riboflavin



Coenzyme F420

Asymmetric epoxidation of allylic alcohols yield highly enantioenriched 2,3-epoxy-alcohols.[30,31] Subsequent regioselective and stereospecific ring-opening of these epoxides with various nucleophiles provides direct access to versatile chiral building blocks for the synthesis of complex molecules.[32–44] Employing amine as nucleophiles in the ring-opening step would yield 3-amino-1,2-diols, which are vastly present in the backbone of many natural products and biologically important molecules, including the antitumor aminocyclopentitol pactamycin[45], proteasome inhibitor TMC-95A[46,47], immunosuppressant antibiotic myriocin, riboflavin (vitamin B2) and hydrogenase coenzyme F420 (**Figure 4**). The aminodiol moieties in these compounds have generally been accessed by dihydroxylation or epoxidation followed by nucleophilic ring-opening.

Although the kinetic resolution of secondary allylic alcohols has been extensively studied since the emergence of Sharpless epoxidation, there is no efficient system for the kinetic resolution of substituted 2,3-epoxy alcohols. Despite our group's recent developments that provided a catalytic regio- and enantioselective aminolysis of 2,3-epoxy alcohols using a tungsten/bis(hydroxamic acid) system,[48] only primary alcohols have been demonstrated as substrates. Developing a two-step combined epoxidation/ring-opening methodology starting with a secondary allylic alcohol would be needed to access more complex molecules. This reaction sequence was shown to generate virtually enantiopure functionalized 3-amino-1,2-diols with three stereogenic centers, an important step forward from the two stereogenic centers in the previous paper.

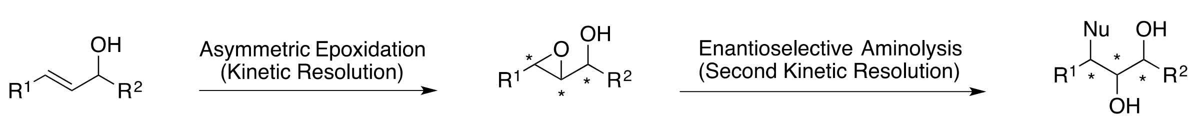
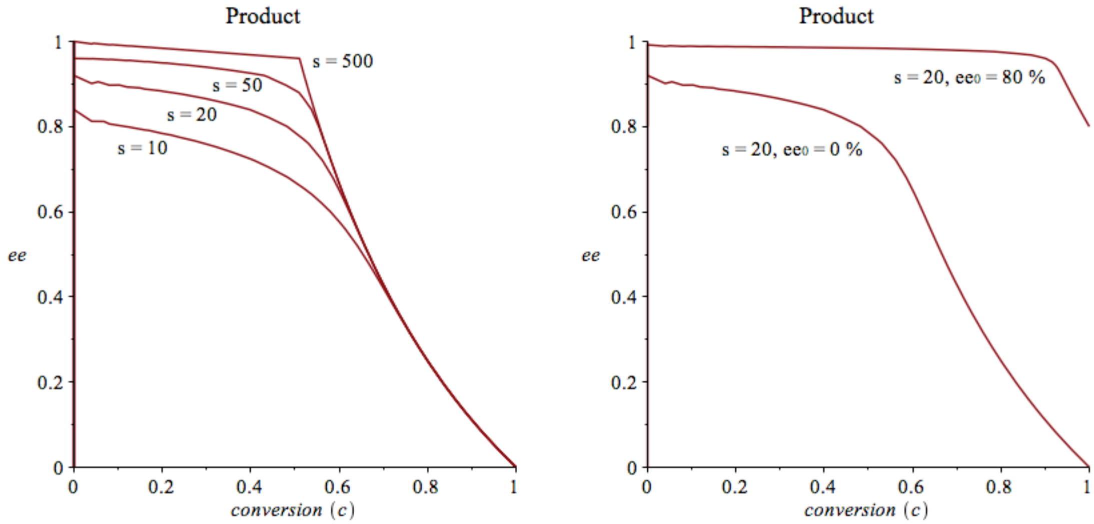


Figure 5. Enantiomeric Excess of Product Vs. Conversion for Various Selectivity

$$seletivity = k_{rel} = \frac{\ln\left[\frac{(R_o + S_o)(1 + c - ee \cdot c) + (R_o - S_o)}{2R_o}\right]}{\ln\left[\frac{(R_o + S_o)(1 + ee \cdot c - c) - (R_o - S_o)}{2S_o}\right]}$$



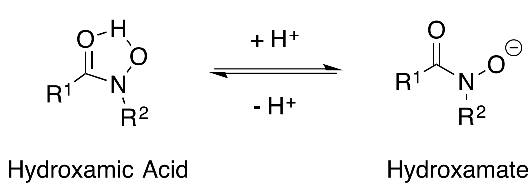
Top: Equation of k_{rel} (selectivity) as a function of *ee* and conversion (*c*), with known values of R_0, and S_0. (Refer to SI for derivation of equation) Bottom left: Plots of ee (product) vs. conversion when ee_0 = 0 % (racemic mixture), with varying selectivity (500, 50, 20 and 10). Bottom right: Plot of ee (product) vs. conversion when ee_0 = 0 % (racemic mixture) and 80 % (non-racemic), both with a selectivity of 20.

Distinct advantages are associated with a two-step kinetic resolution strategy. In the usual kinetic resolution of a racemic mixture, enantioselectivity erodes with reaction progression and plunges after about 50% conversion. (Figure **5**, left) Thus, kinetic resolution is perceived as inefficient in comparison with a normal asymmetric reaction of a prochiral substrate, which exhibits a constant enantioselectivity. However, in a two-step system, the second kinetic resolution starts with a non-racemic mixture. And if the two resolution steps have matched stereoselectivity (*i.e.* the more abundant product of the first step is also the kinetically favored substrate in the second step), the product can maintain exceptional enantiopurity up to high conversion (Figure **5**, right), since the favored substrate's higher concentration and greater rate constant act in synergy. The enhanced enantioselectivity (often more than 99.9%) would be extremely valuable to the pharmaceutical industry.

With respect to catalysis in our particular reaction, the hydroxyl group in the secondary allylic alcohol can serve as the directing group for both asymmetric epoxidation and aminolysis, alleviating the complexity of pre-functionalization and post-treatment. Our combination of two kinetic resolutions for constructing three adjacent stereogenic centers in the molecules is unprecedented to the best of our knowledge.

3.2 Metal-BHA Catalyzed Asymmetric Epoxidation

Hydroxamic acid has a formula of RC(O)N(OH)R' and a structure that resembles that of amides RC(O)NHR', wherein the nitrogen has an OH substitution. Hydroxamate, which is the deprotonated form of hydroxamic acid, can act as a good chelator for metals by binding to them in a bidentate fashion.



Due to its high affinity, nature has evolved hydroxamic acids as carriers for insoluble metal compounds, such as siderophores in bacteria that transport ferric complexes into cells for iron extraction and metabolism.[49] They are also used for rare metal extraction in ores and as histone deacetylase (HDAC) inhibitors with anti-tumor properties.

Sharpless *et al.* first revealed hydroxamic acid as chiral ligands for asymmetric induction in 1977, when he published the chiral vanadium-hydroxamic-acid-catalyzed, enantioselective epoxidation of allylic alcohols.[50] This was even before the discovery of his prominent titanium-tartrate catalyzed epoxidation system, known as Sharpless Asymmetric Epoxidation (SAE). However, few examples of hydroxamic acid in asymmetric catalysis were reported since then.

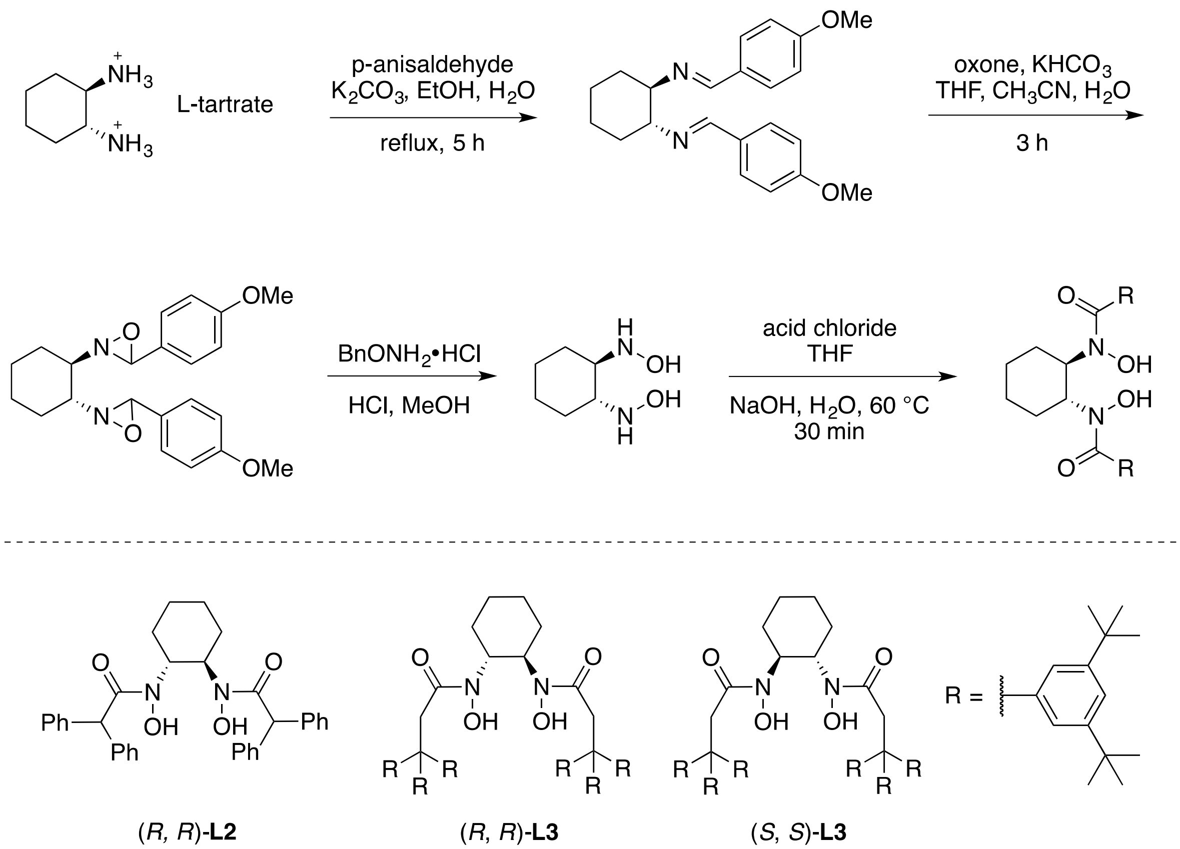
Recognizing chirality can be introduced into R^1 and R^2 groups, our group designed a series of bishydroxamic acid (BHA) ligands with a chiral cyclohexyl core. These metal-BHA systems were shown over the years to serve as "privileged chiral catalysts"[51], creating a cross-linked network instead of a specific metal-ligand combination.

As for the synthesis of bishydroxamic acid ligands, the main strategy is coupling and oxidation.[52] In forming the N-R^2 bond, coupling of hydroxylamine (protected or unprotected) and carboxylic acid derivatives (acid halides, anhydrides and esters) is often mediated by base or peptide coupling reagents such as HATU and HBTU. For converting N-H into N-OH, direct oxidation can be done using oxidants such as Oxone or stoichiometric Molybdenum[53], though methods are highly dependent on the steric and electronic properties of the substituents on the amine.[52]

This C_2-symmetric bishydroxamic acid ligand was first synthesized by Zhang *et al.*, and later modified multiple times for better compatibility with the substrate and the metal core. The synthesis of BHA ligands, as they proposed, was short and straightforward. First, the amine reacts with *p*-anisaldehyde to form the imine, then epoxidation of the imine to oxaziridine.

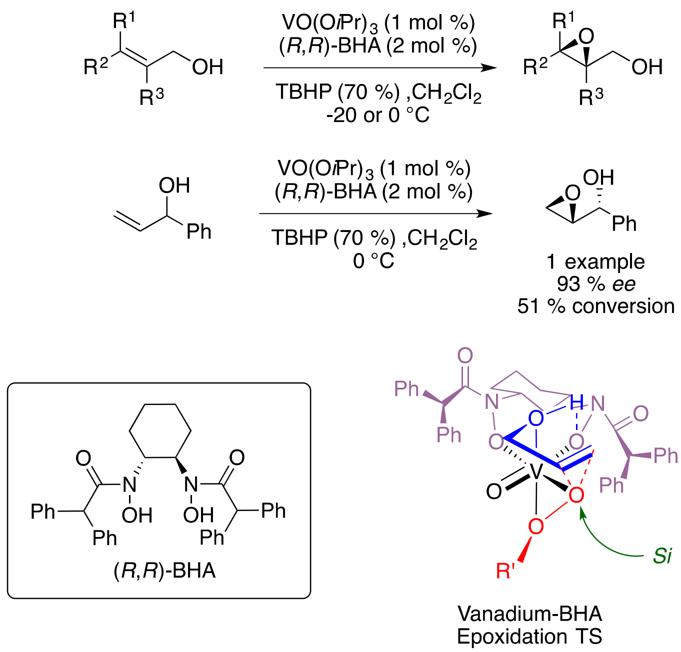
Treatment of the oxaziridine intermediate with hydroxylamine hydrochloride gives the hydroxylamine, which then couples with acid chloride to generate the final hydroxamic acid.

Scheme 5. Synthesis of Bis-Hydroxamic Acid Ligands



In Zhang's work, vanadium-BHA exhibited excellent selectivity and activity towards allylic alcohols with a variety of substitution patterns.[54] The asymmetric epoxidation of allylic alcohols are attained with up to 91 % yield and 97 % ee, with a low catalyst loading of 1 mol % (can be as low as 0.2 mol%) and reactions were performed under air in the presence of aqueous TBHP.

Scheme 6. Vanadium-BHA Catalyzed Asymmetric Epoxidation

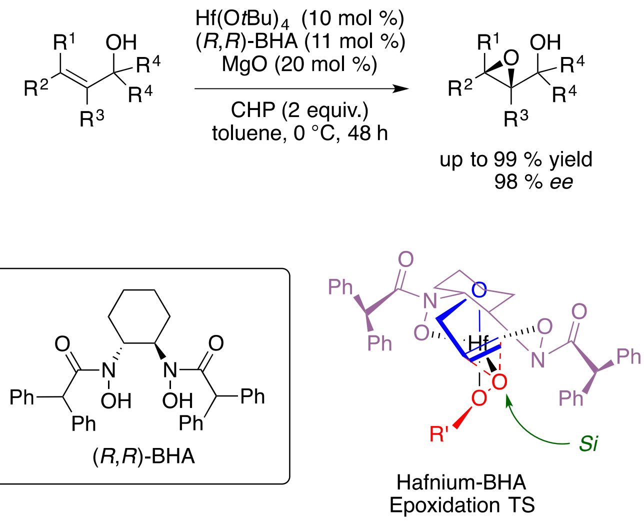


By careful tuning the ligand structure and terminal oxidant, the vanadium-BHA catalyst was also applicable to small allylic alcohols and homoallylic alcohols, which represents a challenging class of substrates. This was accomplished with BHA ligand with more bulky acyl groups and cumene hydrogenperoxide (CHP) as oxidant.

This catalyst was also utilized for the kinetic resolution of terminal secondary allylic alcohol (1 example), and desymmetrization of *meso*-secondary allylic and homoallylic alcohols.[55] In the stereochemical model, the second and fourth quadrant of the chiral space are occupied by the catalyst, the oxygen from the peroxide is spiro overlapped with the olefin, resulting in the epoxide in the observed stereochemistry in the scheme.

In the effort to expand the substrate scope and discover new metal chemistry, zirconium- and hafnium-BHA systems were discovered as better catalysts for homoallylic and the previously underexplored bishomoallylic alcohols.[56] The hafnium-BHA epoxidation conditions are also effective for tertiary allylic alcohols.[57]

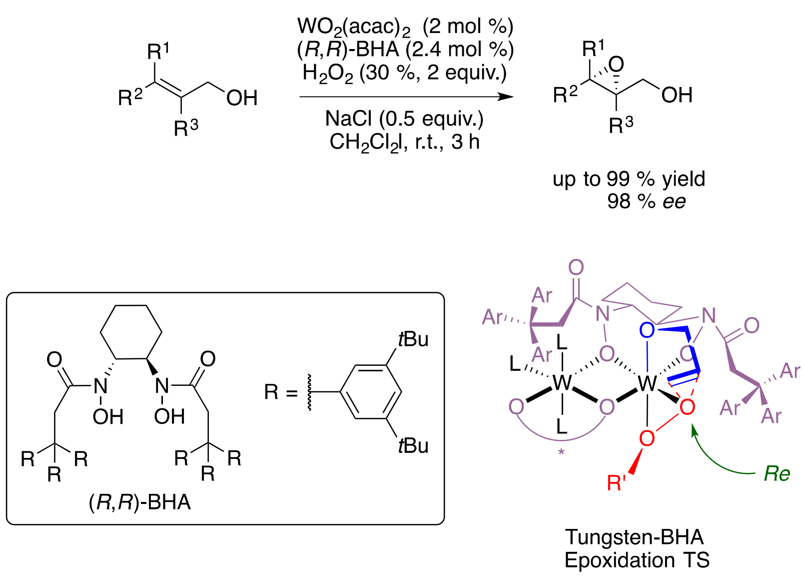
Scheme 7. Hafnium-BHA Catalyzed Asymmetric Epoxidation of Tertiary Allylic Alcohols



There are a few distinct differences between Zr/Hf- and other systems.[52] First, the active species in Zr/Hf-catalyzed epoxidation is a monomeric complex. Additives such as DMPU and MgO were believed to stabilize the metal center by coordination and regenerate active monomeric complex from polymeric form. Therefore, metal:BHA = 1:1 works better for zirconium and hafnium, whereas metal:BHA = 1:2 is usual for vanadium catalyst. The postulated stereochemical model for asymmetric induction was also different in the following ways: 1) ionic radii for Zr^{4+} (0.72 Å) and Hf^{4+} (0.71 Å) are significantly larger than Ti^{4+} (0.61 Å) and V^{5+} (0.54 Å);[37] 2) The transition states for Zr- and Hf-catalyzed epoxidation are pentacoordinate, while V-catalyzed one is hexacoordinate. These will contribute to a larger space around the metal center in the cases of zirconium- and hafnium-catalyzed epoxidation, which alleviate the steric interaction between tertiary alcohols and the complex.

The most recent reported system with bis-hydroxamic acid ligand was a tungsten-catalyzed epoxidation of allylic alcohols.[58] This highly enantioselective oxidation was achieved with mild oxidant hydrogen peroxide and air-stable tungsten catalyst. The reaction was proposed to go through a dinuclear peroxotungsten transition state. The use of sodium chloride prevents ring-opening of the epoxides with H_2O_2 as nucleophile, a property later taken advantage of for the tungsten-catalyzed aminolysis. The epoxidation was also shown to be effective for homoallylic and tertiary allylic alcohols.

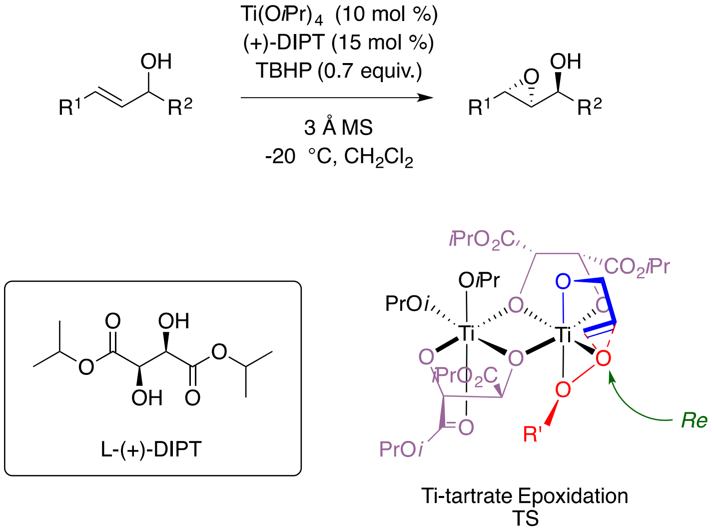
Scheme 8. Tungsten-BHA Catalyzed Asymmetric Epoxidation of Allylic Alcohols



3.3 Sharpless Asymmetric Epoxidation of Secondary Allylic Alcohols

Sharpless Asymmetric Epoxidation (SAE), which was first reported in 1980, is an enantioselective epoxidation of the primary and secondary allylic alcohols to form 2,3-epoxyalcohols with Ti(O*i*Pr)$_4$/chiral tartrate diester as catalyst and anhydrous TBHP as oxidant. The use of molecular sieves (3Å MS) is necessary for the reaction. [59,60]

Scheme 9. Titanium-tartrate Sharpless Kinetic Resolution of Secondary Allylic Alcohols



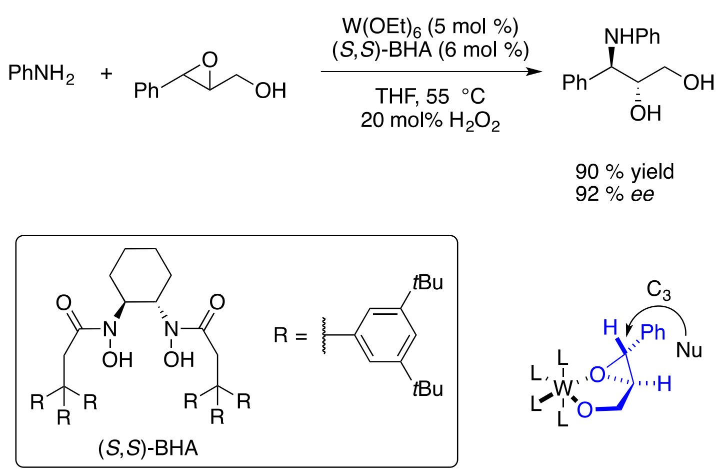
3.4 Tungsten-BHA-Catalyzed Enantioselective Aminolysis

Asymmetric epoxidation has been extensively studied since the emergence of Sharpless epoxidation, granting access to a diversity of enantioenriched epoxides. Regioselective and stereoselective ring-opening of these optically active epoxides can afford chiral building blocks for the synthesis of pharmaceutical or biologically interesting molecules.[61] However, regioselective the ring-opening of epoxides are dependent on the electronic property and steric hindrance of oxirane substituents. Thus, high regioselectivity are usually obtained for terminal or aromatic epoxides. By using directing groups that coordinate to a metal complex, the ring-opening can be regiocontrolled or even stereocontrolled by the orientation of the catalyst. Pioneering work by Sharpless and Caron in 1988 reported a Ti-mediated regioselective ring-opening of 2,3-epoxy alcohols.[62]

However, no catalytic version of the conversion was available until the work by Wang and Yamamoto in 2014, when a catalytic, highly regioselective and stereosepecific ring-opening of 2,3-epoxy alcohols and 2,3-epoxy sulfonamides has been accomplished using W-salts.[63] Complete regioselectivities were achieved for terminal, aromatic, aliphatic ß,ß-disubstituted and cyclic 2,3-epoxy alcohols. As for reactivity, substrates are arranged in descending order: terminal epoxides ≈ aromatic epoxides > aliphatic *trans*-disubstituted epoxides > aliphatic *cis*-disubstituted epoxides > aliphatic trisubstituted epoxides.

An enantioselective version of the ring-opening by amine nucleophile was also developed using tungsten-BHA catalyst.[48] Previous efforts on enantioselective ring-opening of epoxides are limited to unfunctionalized terminal or *meso* epoxides.

Scheme 10. Tungsten-BHA Catalyzed Enantioselective Aminolysis



Chapter 4. Synthesis of Virtually Enantiopure Aminodiols with Three Adjacent Stereogenic Centers by Epoxidation and Ring-Opening

4.1 Exploration of Compatible Catalyst Systems

We started by examining our two-step methodology on a few model substrates (compounds **1-5** in Scheme 1) for optimization. Screening of previously established systems $WO_2(acac)_2$/(*R*,*R*)-**L3**[58], $VO(iPr)_3$/(*R*,*R*)-**L2**[64], $Hf(OtBu)_4$/(*R*,*R*)-**L2**[57] and $Ti(OiPr)_4$/(+)-DIPT[60] was performed on the epoxidation of these secondary allylic alcohols. We began with the recent developed $WO_2(acac)_2$/(*R*,*R*)-**L3** on substrates **41** and **42**; the reaction of **41** gave substantial amount of the ketone whereas **42** gave exclusively the double-bond rearranged products. $VO(iPr)_3$/(*R*,*R*)-**L1** catalyst system was attempted subsequently, as well as Sharpless epoxidation with $Ti(OiPr)_4$/(+)-DIPT[60] (entry 2); the latter exhibit a much better efficiency with 50% yield, 99.8:0.2 diastereoselectivity, and 92 % enantioselectivity. This system also works well for substrates **41** (entry 1), **43** (entry 5), **44** (entry 9) and **45** (entry 11). $Hf(OtBu)_4$/(*R*,*R*)-**L2**, on the other hand gave the *syn*-epoxy alcohol for **44** as the major diastereomer, which differs from all the other systems. (entry 10)

In the subsequent enantioselective aminolysis of 2,3-epoxy alcohols, only the $W(OEt)_6$/**L3** approach[48] was attempted, given the scarcity of existing methods. Since all of the known tungsten-catalyzed epoxide-opening reactions proceeded with complete C3 regioselectivity via S_N2 mechanism[48,63], the theoretical outcome of the combined sequence is four product stereoisomers. Remarkably, when the racemic epoxide of **42** was exposed to asymmetric ring- opening conditions with aniline, a high selectivity for one out of the four was observed with 96% ee and >95:5 dr. (entry 4) In tandem with the stereoselective epoxidation, the enantiopurity of final product **66** was boosted to 99.9 % ee and 99.9:0.1 dr (entry 2), and its absolute configuration was determined by X-ray crystallography as (1*S*,2*R*,3*R*)-1-phenyl-3-(phenyl-amino)hexane-1,2-diol. A comparison between $W(OEt)_6$/(*S*,*S*)-**L3** (entry 5, where ee was enhanced) and $W(OEt)_6$/(*R*,*R*)-**L3** (entry 6, where ee dropped) suggested that the former matches in enantioselectivity, while diastereoselectivity remained unperturbed.

Interestingly, an unusual stereochemical outcome of the reaction sequence was observed for substrates **44** and **45**. When W- and Ti-catalyzed epoxidation was combined with W-catalyzed aminolysis, a mismatch in diastereoselectivity was observed. Two experiments (entries 7 and 8), each with only one asymmetric step revealed that W-catalyzed epoxidation gave the *anti*-epoxy alcohol while W-catalyzed aminolysis preferred the *syn*-epoxy alcohol. Hf-catalyzed epoxidation, surprisingly, showed a preference for *syn*-epoxy alcohol, and provided access to 1,2,3-*syn*, *anti*-amino diols (entry 10), which was unusual in the literature.

Scheme 11. Sequential Asymmetric Epoxidation and Enantioselective Aminolysis

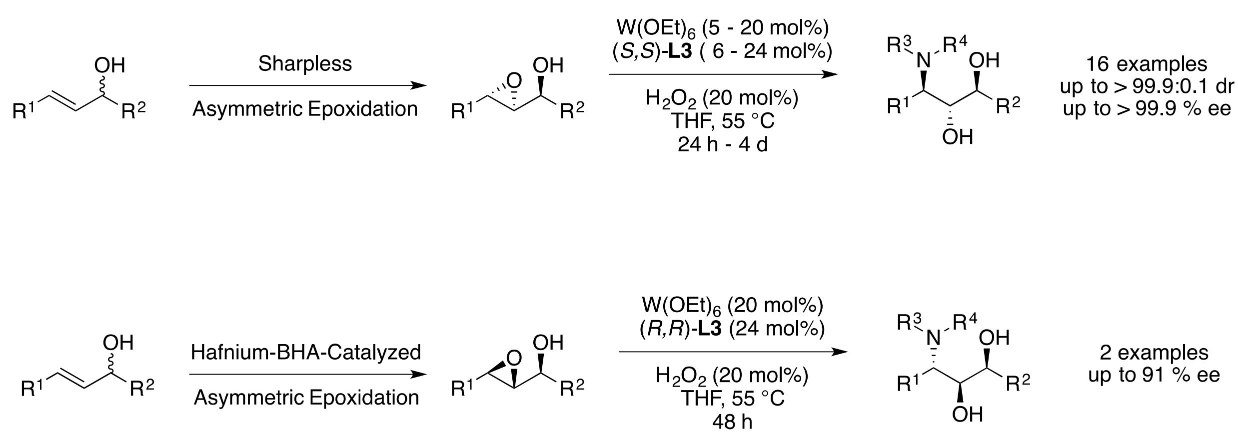


Table 3. Reaction Screening of Substrates and Catalyst Systems

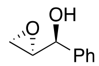
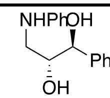
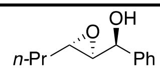
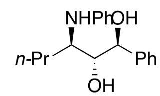
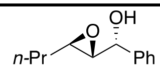
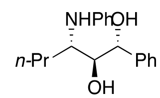
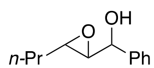
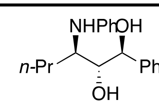
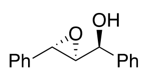
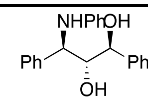
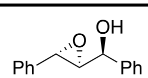
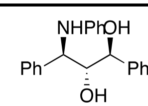
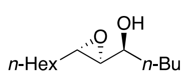
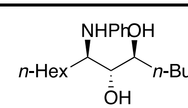
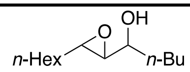
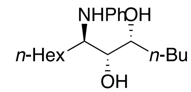
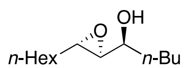
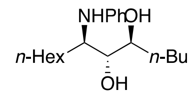
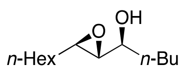
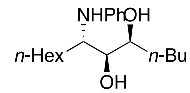
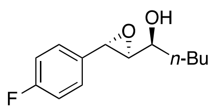
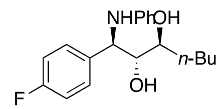
Entry	Sub.	Epoxide	Epox. Method	Time	Results[i]	Aminodiol	Aminolysis Method	Time	Results[j]
1	**41**		a[a]	15 h	48 % yield 98:2 dr 98 % ee		e[e]	24 h	69 % yield 99.5:0.5 dr 99.6 % ee
2	**42**		a[a]	2 h	50 % yield > 99.8:0.2 dr 92 % ee		e[e]	48 h	94 % yield 99.9:0.1 dr 99.9 % ee
3	**42**		b[b]	2 h	50 % yield dr and ee n.d.		f[f]	48 h	86 % yield > 99.9 : 0.1 dr > 99.9 % ee
4	**42**		*m*CPBA	overnight	56 % yield		e[e]	24 h	44 % yield > 95:5 dr 96 % ee
5	**43**		a[a]	3 h	39 % yield 17:1 dr 96 % ee		e[e]	20 h	81 % yield > 99.5:0.5 dr 98.8 % ee
6	**43**		a[a]	3 h	39 % yield 17:1 dr 96 % ee		f[f]	20 h	41 % yield > 99:1 dr 94.8 % ee
7	**44**		c[c]	20 h	35 % yield dr and ee n.d.		$W(OEt)_6$ (racemic)	24 h	81:19 dr 93 % ee

Table 3, continued

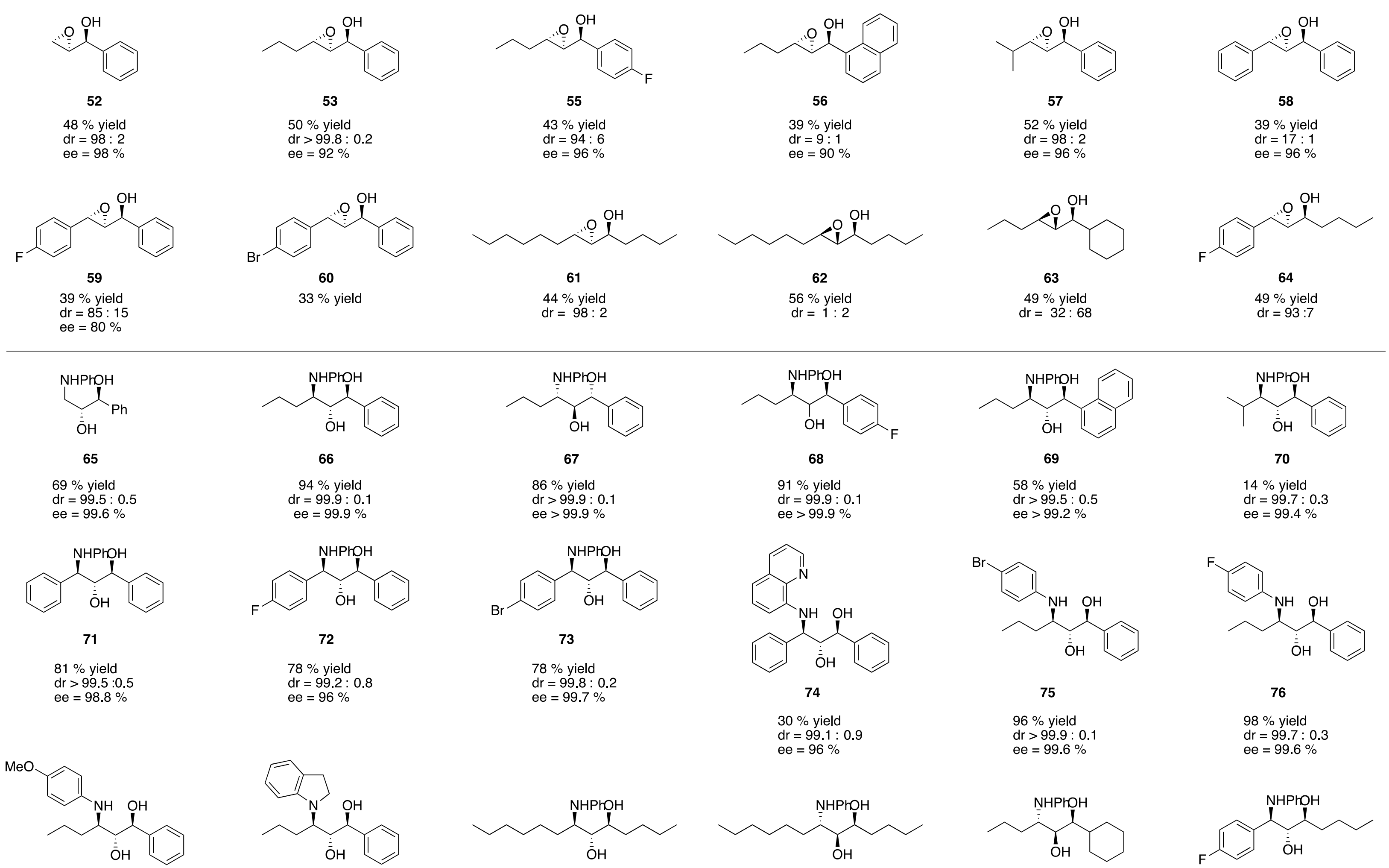
8	**44**		*m*CPBA	overnight	69 % yield		e[e]	24 h	16 % yield 6:94 dr 58 % ee
9	**44**		a[a][g]	25 min	44 % yield 98:2 dr		e[e]	4 d	33 % yield >99.9 % ee
10	**44**		d[d][g]	15 h(0°C) +3 h(r.t.)	56 % yield 1:2 dr		f[f][h]	48 h	52 % yield 91 % ee
11	**45**		a[a][g]	3 h	49 % yield 93:7 dr		e[e]	4 d	38 % yield 91 % ee

Asymmetric epoxidation methods: [a] $Ti(OiPr)_4$/(+)-DIPT/TBHP/substrate = 0.1/0.12/0.7/1, 3Å MS (30 wt %), -20 °C in CH_2Cl_2. [b] $Ti(OiPr)_4$/(-)-DIPT/TBHP/substrate = 0.1/0.12/0.7/1, 3Å MS (30 wt %), -20 °C in CH_2Cl_2. [c] $WO_2(acac)_2$/(*R*,*R*)-**L3**/NaCl/H_2O_2/substrate = 0.025/0.03/0.5/1.5/1, r.t. in CH_2Cl_2. [d] $Hf(OtBu)_4$/(*R*,*R*)-**L2**/MgO/CHP/substrate = 0.05/0.055/0.2/1/1, 0 °C in toluene. Enantioselective aminolysis methods: [e] $W(OEt)_6$/(*S*,*S*)-**L3**/H_2O_2/aniline/substrate = 0.05-0.2/0.06-0.24/0.2/1/1.5, 55 °C in THF. [f] $W(OEt)_6$/(*R*,*R*)-**L3**/H_2O_2/aniline/substrate = 0.05-0.2/0.06-0.24/0.2/1/1.5, 55 °C in THF. [g] major diastereomer isolated for ring-opening step. [h] aniline/substrate = 0.5 :1 [i] dr in anti : syn. [j] dr in anti, anti : syn, anti

4.2 Substrate Scope of Sequential Kinetic Resolutions

To explore the substrate scope of our system, different substrates and amine nucleophiles were evaluated and excellent stereochemical outcomes were obtained for most of them (Figure 4). Generally, reactions with these substrates proceed with 69 % to 98 % yield, 98.8-99.9 % ee and 99.5:0.5-99.9:0.1 dr. Starting from the model substrate **42**, we varied the structure of R_1 (**70**) and R_2 (**68** and **69**), and all gave remarkable stereoselectivity, though low yield was obtained from the more hindered compound **70** bearing an isopropyl group. Derivatives from substrate **43** gave high yields (**72** and **73**), but **72** gave relatively lower enantioselectivity of 96 %. Variations on the nucleophilic amine, such as substituted aniline (**75**, **76** and **77**) and secondary amine (**78**) all proceeded smoothly with exceptionally high yield and stereoselectivity, while heterocyclic amine (**74**) encountered lower reactivity and selectivity. Reversing the enantiomeric identity of both catalysts to $Ti(OiPr)_4$/(-)-DIPT and $W(OEt)_6$/(*R*,*R*)-**L3** provided the anticipated product **67**, the enantiomer of **66**. The aminolysis with epoxides **61** and **64** were much slower as anticipated due to a mismatch in diastereoselectivity, nevertheless products were generated with good enantioselectivity.

Figure 6. Substrate Scope of the Combined System of Epoxidation and Aminolysis



52 48 % yield, dr = 98 : 2, ee = 98 %

53 50 % yield, dr > 99.8 : 0.2, ee = 92 %

55 43 % yield, dr = 94 : 6, ee = 96 %

56 39 % yield, dr = 9 : 1, ee = 90 %

57 52 % yield, dr = 98 : 2, ee = 96 %

58 39 % yield, dr = 17 : 1, ee = 96 %

59 39 % yield, dr = 85 : 15, ee = 80 %

60 33 % yield

61 44 % yield, dr = 98 : 2

62 56 % yield, dr = 1 : 2

63 49 % yield, dr = 32 : 68

64 49 % yield, dr = 93 :7

65 69 % yield, dr = 99.5 : 0.5, ee = 99.6 %

66 94 % yield, dr = 99.9 : 0.1, ee = 99.9 %

67 86 % yield, dr > 99.9 : 0.1, ee > 99.9 %

68 91 % yield, dr = 99.9 : 0.1, ee > 99.9 %

69 58 % yield, dr > 99.5 : 0.5, ee > 99.2 %

70 14 % yield, dr = 99.7 : 0.3, ee = 99.4 %

71 81 % yield, dr > 99.5 :0.5, ee = 98.8 %

72 78 % yield, dr = 99.2 : 0.8, ee = 96 %

73 78 % yield, dr = 99.8 : 0.2, ee = 99.7 %

74 30 % yield, dr = 99.1 : 0.9, ee = 96 %

75 96 % yield, dr > 99.9 : 0.1, ee = 99.6 %

76 98 % yield, dr = 99.7 : 0.3, ee = 99.6 %

77 98 % yield, dr > 99.9 : 0.1, ee > 99.9 %

78 98 % yield, dr > 99.9 : 0.1, ee > 99.9 %

79 33 % yield, ee > 99.9 %

80 52 % yield, ee = 91 %

81 35 % yield, ee = 68 %

82 38 % yield, ee = 91 %

These remarkable results presented a route to virtually enantiopure 3-amino-1,2-diols by cascade of an asymmetric epoxidation with a tungsten-catalyzed aminolysis. The products synthesized in this paper (up to >99.9% ee and >99.9:0.1 dr) are significant since this level of enantiopurity (>99.9 % ee) is rare in the literature but are of great importance to the pharmaceutics given the ubiquity of the aminodiol motif in many drug candidates.

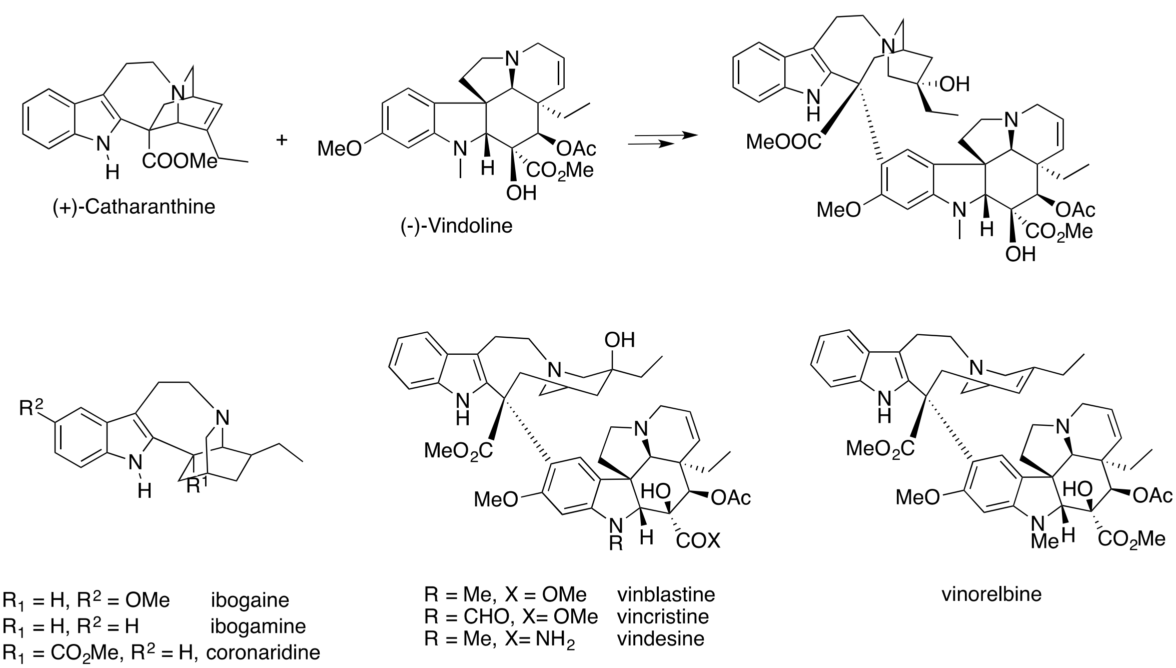
In summary, a highly enantioselective synthesis of aminodiols with three stereocenters has been accomplished by combining a $Ti(OiPr)_4$/(+)-DIPT or $Hf(OtBu)_4$/(*R*,*R*)-**L2** catalyzed asymmetric epoxidation with a subsequent enantioselective aminolysis using $W(OEt)_6$ /(*S*,*S*)-**L3**, with up to > 99.9 % ee and > 99.9:0.1 dr. This sequential approach, which tolerates a broad substrate scope and various amines, provides access to pharmaceutical or biological significant molecules.

Chapter 5. Enantioselective Synthesis of (+)-Catharanthine

5.1 Structure and Therapeutic Significance of (+)-Catharanthine

(+)-Catharanthine, a terpene indole alkaloid, is an important member of the Iboga family, and is isolated from the medicinal plant *Catharanthus roseus* (L.) G. Don.[65] Catharanthine is considered as a very important alkaloid since catharanthine and vindoline are the chemical precursors of the antitumor binary alkaloids vinblastine and vincristine. Vinblastine[66] and vincristine[67–69] are two venerable yet effective anticancer agents used in the treatment of a number of human cancers, such as leukemia and Hodgkin's disease. Their biological properties were among the first to be shown to inhibit microtubule formation and mitosis.[70] Their analogs, vindesine [71] and vinorelbine[72,73] were also used in clinical treatment.

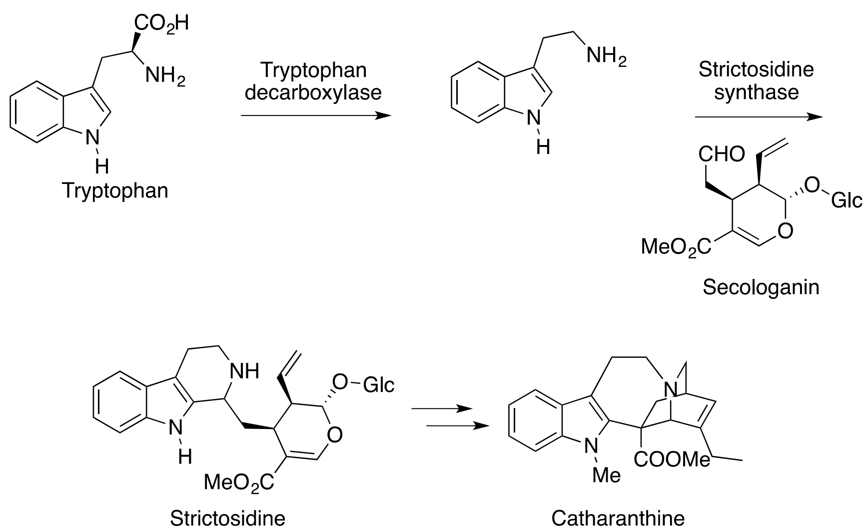
Figure 7. Therapeutic Significance of Catharanthine



5.2 Biosynthesis of Catharanthine

The biosynthesis of catharanthine is believed to begin with the decarboxylation of tryptophan to tryptamine by tryptophan decarboxylase. It then reacts with which reacts with iridoid terpene secologanin to form strictosidine. Rearrangements of this intermediate afford a variety of monoterpene indole alkaloids, such as 19,20-dihydroakuammicine, ajmalicine, tabersonine and catharanthine.[74]

Figure 8. Biosynthesis of Catharanthine



5.2 Previous Approaches to Catharanthine and Ibogamine

There have been less than ten reported total synthesis of catharanthine, of which most are racemic syntheses. Out of the three non-racemic syntheses, one was achieved with the resolution of a key intermediate[75], while the other two involves the use of chiral starting materials[76,77]. Boger and co-workers also studied the medicinal chemistry of modified vinca alkaloid, by coupling vindoline with a modified catharanthine at C10[78] or C16[79]. However, the modifications were performed directly from catharanthine, which can be restricted to the overall skeleton of the molecule and limited to selective functionalization. Our goal of the project, on the other hand is to develop an efficient enantioselective route to catharanthine, which can be used to access a highly diverse library of vinblastine and vincristine analogs for SAR evaluation.

The major challenges in the enantioselective synthesis are to construct the quaternary sp3 carbon at the 2-position of the tryptamine fragment and the enantioselective synthesis of the isoquinuclidine(azabicyclo[2.2.2]octane) unit. A selected list on the synthesis of catharanthine or ibogamine was depicted below, when cyclization of the 7-membered ring was emphasized.

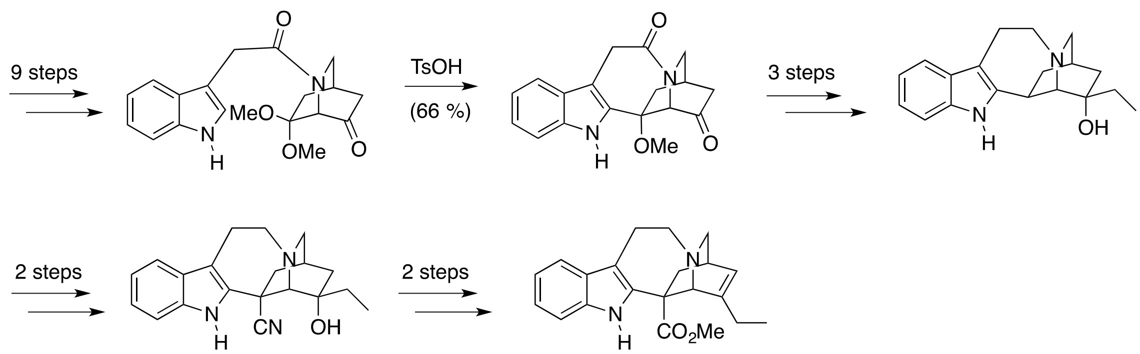
Büchi and co-workers reported the first racemic synthesis of catharanthine.[80] Their main strategy is to couple Diels-Alder adduct with indoleactate, followed by and ring-closure to form the pentacyclic skeleton. The key cyclization of the amide was accomplished by treatment with *p*-toluenesulfonic in hot benzene. The nitrile group was installed via 3-chloroindolenien intermediate formed by reaction with *t*-butylhypochlorite and KCN.

Trost *et al.* also showed a synthesis of 16-decarbomethoxy-20-hydroxydihydro-catharanthine using organopalladium chemistry.[81] The cyclization was achieved with bis(acetonitrile)palladium chloride assisted by silver ion, followed by treatment with $NaBH_4$.[82] The use of palladium trifluoroacetate in acetonitrile as an alternative also seemed promising.

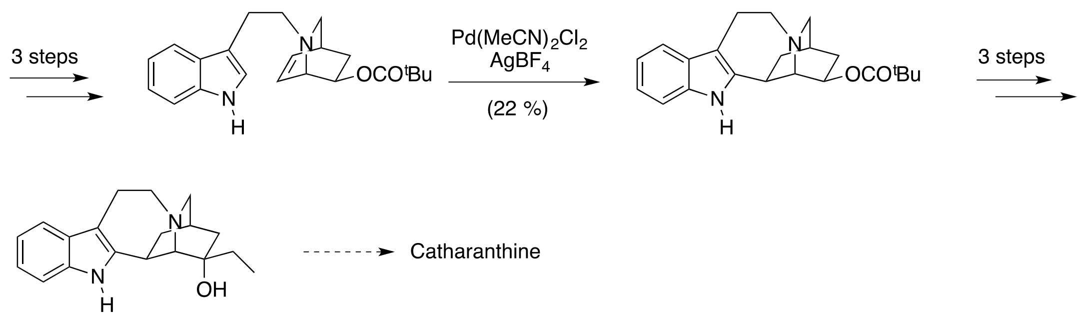
Szántay *et al.* reported in 1983 both a racemic and non-racemic synthesis of catharanthine, where the nonracemic approach was done by resolution of the isoquinuclidine intermediate.[75][83] The ring-closure was achieved by photocyclization in methanol-water. The other paper reported using a small amount of tributyl tinhydride. However, yields were not high in both cases.

Scheme 12. Previous Attempts on the Synthesis of Catharanthine

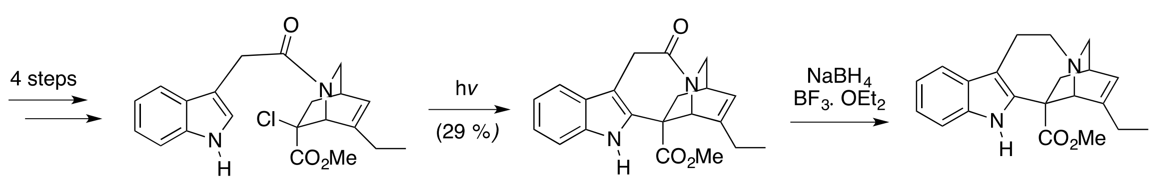
Büchi's Synthesis of (±)_Catharanthine



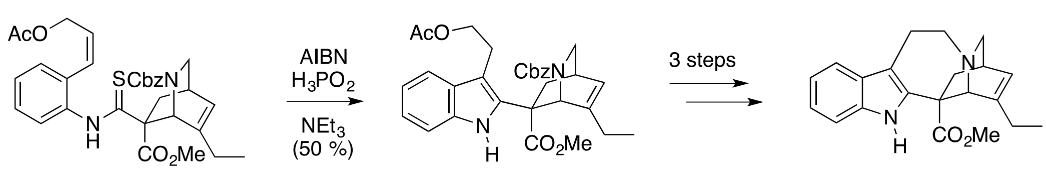
Trost's Formal Synthesis of (±)_Catharanthine



Szántay's Synthesis of (+)-Catharanthine via Resolution



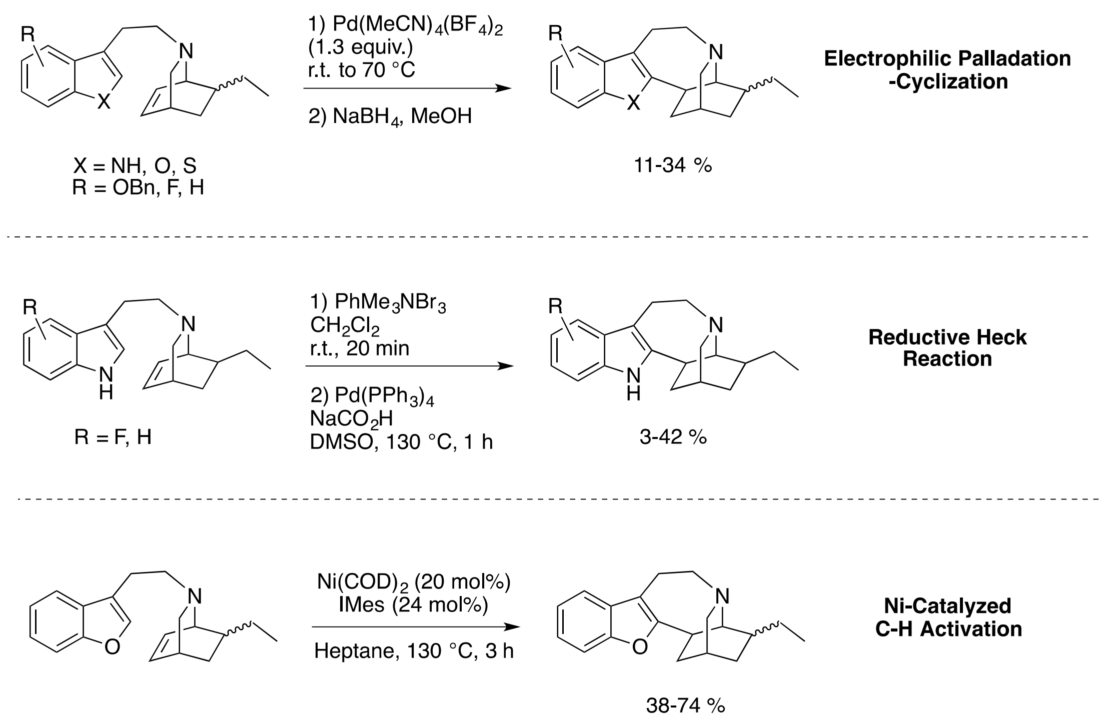
Fukuyama's Synthesis of Catharanthine



Raucher *et al.* also reported a synthesis of catharanthine, where a similar approach was taken.[84] The photocyclization, however, was performed on the thioamide instead of the amide.

In 1999, Fukuyama and co-workers a radical mediated synthesis of (±)-catharanthine, which involved the construction of the indolyl fragment.[85] The key step is a stoichiometric AIBN initiated radical cyclization of 2-alkenylthioanilide in the presence of hypophosphorous acid and triethylamine, which furnished the product in 40-50 % yield. Earlier work using tributyltin hydride and triethylborane afford low and variable results (12-22%).

Scheme 13. Sames' Cyclization to Ibogamine and Its Analogues

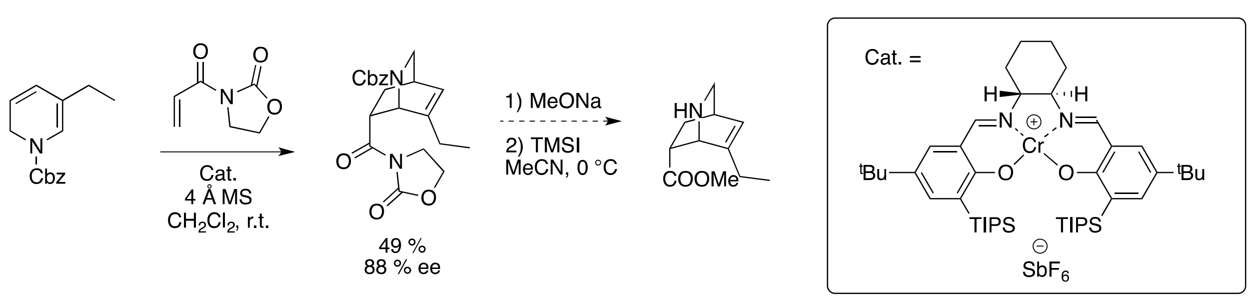


Recently, Sames and co-workers reported their effort on the cyclization of diverse *N*-(2-arylethyl)isoquinuclidine compounds to give ibogamine analogues.[86] Initially, reactions were tried with the procedure Trost [81]reported, but resulted in low and inconsistent yields. A slight modification of to $Pd(MeCN)_2(BF_4)_2$ was used in place of the $Pd(MeCN)_2Cl_2$ / $AgBF_4$ mixture.

Similar yield obtained with $Pd(MeCN)_2(BF_4)_2$ / $AgBF_4$ suggested silver acted as simple chloride scavenger to generate a more cationic palladium species. However, stoichiometric palladium is needed for this reaction. Then a reductive Heck coupling was pursued on the precursor to ibogamine, by 2-bromination of the indole with trimethylphenylammonium tribromide followed by $Pd(PPh_3)_4$ catalyzed Heck coupling. Although 42 % yield was achieved for the ibogamine, poor results were obtained for the other analogues, where electron-poor indole is detrimental to the cyclization and electron-rich substrates promote bromination at the 4-position. Finally, a intramolecular Ni(0)-catalyzed C-H activation strategy was attempted. It was envisioned that C-H insertion of the metal into the heteroaryl C-H bond would generate a metal hydride species that adds to the olefin. However, cyclization only occurred when X = O, in both cases of *exo*-(74 %) and *endo*-ethyl substrate (38 %).

5.3 Enantioselective Diels-Alder Reaction with 1,2-Dihydropyridine

Scheme 14. Cr-Catalyzed Enantioselective Diels-Alder Cycloaddition



Enantioselective Diels-Alder cycloaddition of 1,2-dihydropydine and acryloyl-oxazolidinone has been accomplished by previous members of the Rawal group.[1] The reaction

[1] Tin Yiu Lam's lab notebook I

involves the use of a Cr(III) catalyst with TIP-salen ligand and generate high distereo- and enantioselectivities.

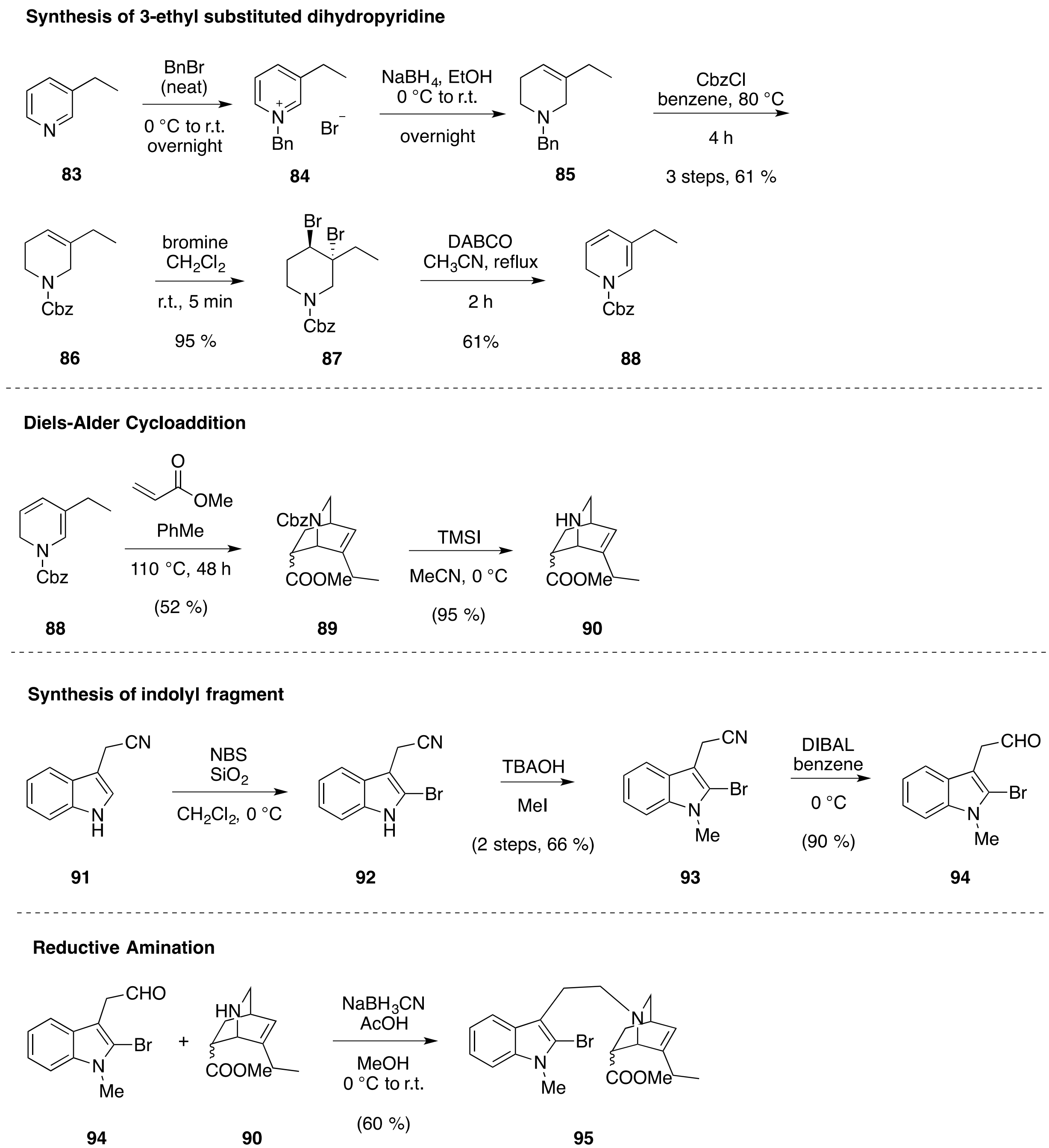
5.4 Synthetic Studies Towards the Total Synthesis of (+)-Catharanthine

Prior to this synthetic study, Dr. Norito Takenaka has laid the foundation for constructing compound **95**, which is the precursor to catharanthine.[2] However, cyclization to furnish the core seven-membered ring was unsuccessful, leading to the major hydrodehalogenation side product. We envisioned by screening a variety of Pd-catalyzed α-arylation conditions employing bulky phosphine ligands, the cyclization could be achieved with acceptable yield, and provide a practical route to diverse catharanthine analogues.

The synthesis of 3-ethyldihydropyridine was prepared according to previous literature.[85] 3-Ethylpyridine was treated with BnBr to afford the corresponding pyridinium bromide in quantitative yield. The pyridinium salt was then reduced with sodium borohydride in EtOH to give the tetrahydropyridine. The benzyl group was switched for a benzylcarbamate in 51% yield. The olefin was brominated to give the *trans*-dibromide, which was treated with DABCO to yield the target dihydropyridine in 61% purified yield. The product at this stage is unstable and subject to the next step immediately. A racemic cycloaddition was performed as a test of concept. Heat promoted Diels-Alder reaction of the 1,2-dihydropyridine and methyl acylate gave the cycloadduct in 52 % yield as a mixture of *endo*/*exo* isomers (3:1 ratio by NMR) Subsequent Cbz-deprotection with TMSI gave the amine in 95 % purified yield.

[2] Dr. Norito Takenaka's Ph.D. dissertation, 2002

Scheme 15. Synthesis of the precursor to Catharanthine

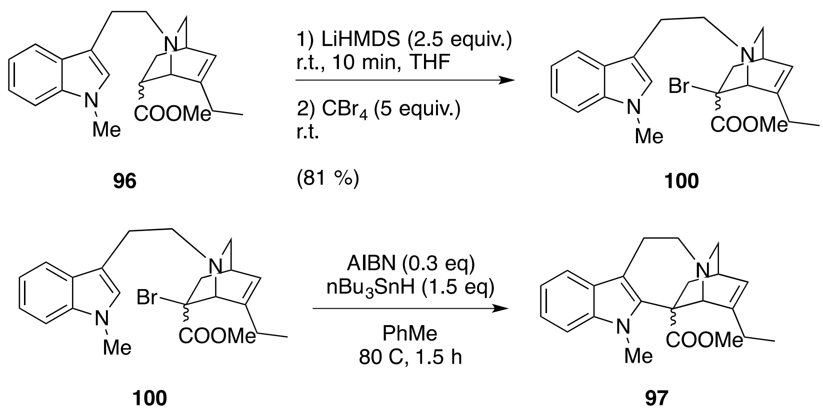


In the synthesis of the indolyl fragment, the indole was brominated regioselectively at the 2-position with NBS and silica. Treatment with tetrabutylammonium hydroxide and methyl iodide gave the N-methylindole in 66% over two steps. Reduction of the nitrile group with DIBAL yield the indoleacetaldehyde in 90%, which was used immediately in the subsequent reaction without purification.

Reductive amination of the amine and aldehyde was done with sodium cyanoborohydride to furnish the precursor to N-methyl catharanthine. Reaction with sodium triacetoxyborohydride gave inferior results.

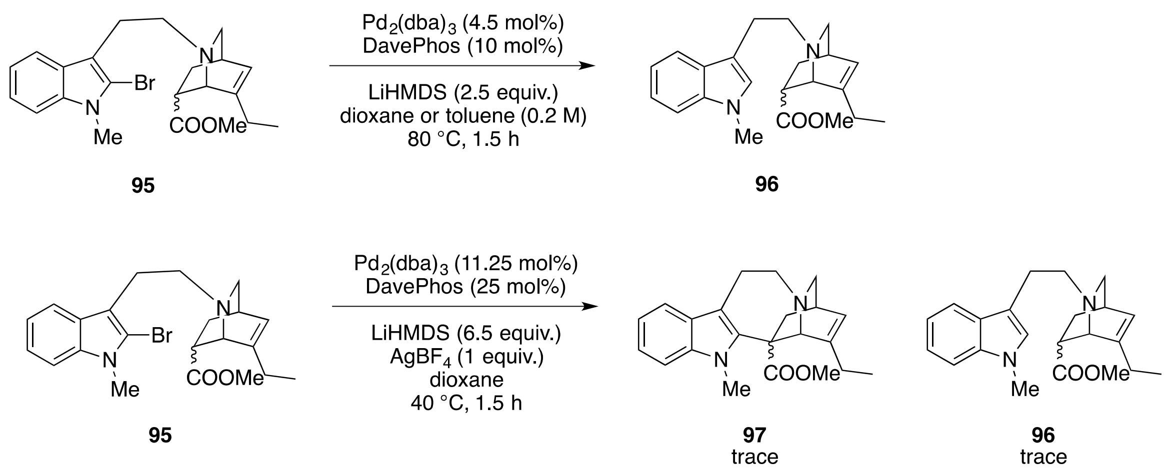
For the cyclization of **95** to form the quaternary center, Pd(II) and Pd(0) catalyzed alpha-arylation were tried using Buchwald conditions[87,88]. Various bases such as LiO*t*Bu, KO*t*Bu, NaO*t*Bu, LiHMDS was used, and LiHMDS gave full deprotonation to form the enolate, confirmed by deuteration experiment.

Scheme 16. α-Bromination of **96** and Radical Cyclization



Reaction of the enolate of **96** with carbon tetrabromide gives the α-brominated compound **100**. Radical cyclization using tin-hydride and AIBN on precursor **100** gave the cyclized **97** in trace amount.

Scheme 17. Pd(0)-Catalyzed α-Arylation



Buchwald-type α-arylation conditions of $Pd_2(dba)_3$, DavePhos and LiHMDS with precursor **95** only gave the undesired hydrodehalogenation product **96**. This side product presumably stemmed from β-hydrogen elimination, which competes with the desired reductive elimination.[89,90] However, the source of hydrogen was unknown. A palladium (II) source $Pd(OAc)_2$ was also tried, but outcome was similar with that of Pd(0). The cyclized product **97** was only observed in trace amount when stoichiometric $AgBF_4$ was added. However, attempts to improve the yield using electrophilic palladium such as $Pd(MeCN)_2(BF_4)_2$ and $Pd(TFA)_2$ did not give any desired product.

Other regioselective 2-alkylation of indole procedures were also attempted. One involved the use of norbornene and was proposed to go through a N-nonbornene type palladacycle.[91] However, no reaction was observed with N-deprotected **100**. The other procedure[92] that used $Ni(COD)_2$/dppp was also tried with substrate **100**, but did not result in the desired product.

Oxidative coupling[93] on precursor **96** was also tried using several metal oxidant such as Cu(II) 2-ethylhexanoate, $Fe(acac)_3$ and $Fe(OTf)_3$, but did not result in any reaction, which might be due to strain of the bicyclic isoquinuclidine.[86]

In conclusion, the cyclization of **95** was unexpectedly difficult, which might be due to several considerations: 1) the tertiary amine on the isoquinuclidine might have complex with Pd(0) and deactivated the metal catalyst; 2) indole metalation was hindered by the steric congestion of the molecule; 3) the use of bulky ligand to accelerate reductive elimination generate more steric interaction at the reaction site.

Chapter 6. Experimental Section

6.1 General Experimental and Synthetic Methods

All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware and were stirred using a magnetic stir plate. All reactions were carried out using anhydrous solvent unless otherwise noted. Anhydrous solvents CH_3CN, CH_2Cl_2, THF, THF (stabilized with BHT), Et_2O and toluene were purchased from J. T. Baker, and purified by M. BRAUN solvent purification system (A2 alumina). Yields refer to chromatographically and spectroscopically (1H NMR) homogenous materials unless noted otherwise.

Chemical reagents and starting materials, unless otherwise noted, were purchased from commercial vendors and used without further purification. Iron(II) trifluoromethanesulfonate was obtained from STREM. Hafnium(IV) tert-butoxide and Zirconium(IV) tert-butoxide were purchased from Alfa Aesar. Titanium(IV) isopropoxide and Vanadium(V) oxytriisopropoxide were from Sigma-Aldrich. All metal catalysts were stored in glove box, except $W(OEt)_6$ and $WO_2(acac)_2$.

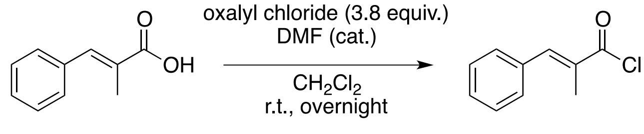
All reactions were monitored by thin layer chromatography (TLC) on Whatman Partisil ® K6F TLC plates (silica gel 60 Å, 0.25 mm thickness) or Macherey-Nagel pre-coated silica gel glass plates (0.25 mm, UV_{254} + UV_{366} indicator) and visualized using a UV lamp (366 or 254 nm) or by use of one of the following visualization reagents: PMA: 10 g phosphomolybdic acid/ 100 mL ethanol; KMnO4: 0.75 g potassium permanganate, 5 g K_2CO_3, / 100mL water; Cerium-ammonium-molybdate: from Alfa Aesar. Products were isolated by flash chromatography (Zeochem® Zeoprep 60 Eco® silica gel 40-63 μm) or by automated flash chromatography using a Biotage® Isolera One® system (UV detector), using SNAP® cartridges.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DMX 500 spectrometer. Chemical shift values (δ) are reported in ppm and calibrated to the residual solvent peak $CDCl_3$ δ = 7.26 ppm, for 1H, δ = 77.16 for 13C, or calibrated to tetramethylsilane (δ = 0.00). The proton spectra are reported as follows: δ (multiplicity, coupling constant J, number of protons). Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). High-performance liquid chromatography was performed on a Varian ProStar Series equipped with a variable wavelength detector using chiral stationary phases (Chirapak AD-H, AS-H, IB, IC, ID; 0.46 cm × 25 cm) from Daicel. Infrared spectra were recorded as thin films on sodium chloride plates using a Nicolet 20 SXB FTIR spectrometer. High-resolution mass spectra were acquired from an Agilent 6224 Tof-MS with 1290 UHPLC. The X-ray diffraction data were collected at 100 K on a Bruker D8 VENTURE with PHOTON 100 CMOS detector system equipped with a Cu-target X-ray tube (λ = 1.54178 Å).

6.2 Synthetic Procedures and Data Associated with Chapter 2

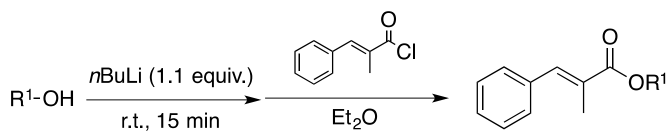
6.2.1 Synthetic Procedures and Data for Compounds **1-7**, **12-22**

Synthesis of α,β-unsaturated esters **1-5**

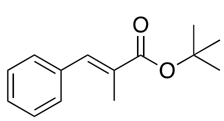


To a dry 500 ml round-bottom flask of α-methylcinnamic acid (24.8 mmol, 4g) in CH_2Cl_2 (20 ml) was slowly added oxalyl chloride (94.2 mmol, 8 ml) at room temperature. *N*,*N*-

Dimethylformamide (5 drops, catalytic) was added dropwise, at which effervescence was observed. The reaction was stirred at this temperature overnight, resulting in a light yellow solution. The solvent was removed under reduced pressure. CH_2Cl_2 was added and removed several times (under vacuum, 50 °C) until α-methylcinnamic acid chloride was collected as a light yellow solid (4.4g, 98%). α-Phenylcinnamic acid chloride (99% yield) was synthesized according to the method for α-methylcinnamic acid chloride. The product was used in the next step without further purification.

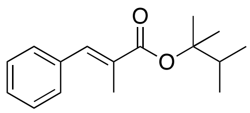


The alcohol (4.5 mmol) in ether was added to a dry round bottom flask. *n*BuLi (4.95 mmol, 1.6 M in hexane, 3.1 ml) was added dropwise to the solution at room temperature and stirred for 15 min. α-Methylcinnamic acid chloride (3 mmol, 542 mg) in ether was slowly added to the reaction and stirred overnight. Saturated aqueous ammonium chloride solution was added and the mixture was extracted with CH_2Cl_2. The organics was dried over sodium sulfate and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (hexane/CH_2Cl_2 = 1:1).



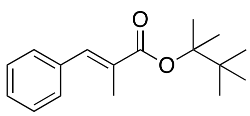
1

1 (563 mg, 86 % yield): colorless oil. IR (film): 2977, 2931, 1704, 1635, 1492, 1479, 1449, 1391, 1367, 1294, 1272, 1255, 1208, 1171, 1119, 1003, 992, 929, 852, 771, 758, 738, 702, 512 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.60 (s, 1 H), 7.37 (d, *J*=4.27 Hz, 4 H), 7.27 - 7.31 (m, 1 H), 2.07 (s, 3 H), 1.54 (s, 9 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 167.9, 137.8, 136.3, 130.2, 129.6 (2 C), 128.3 (2 C), 128.0, 80.5, 28.2 (3 C), 14.1 ppm. HRMS (ESI): calcd. for $C_{14}H_{18}NaO_2$ $[M+Na]^+$: 241.1199 found: 241.1200.



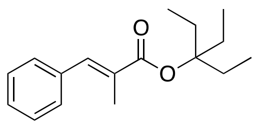
2

2 (480 mg, 65 % yield): colorless oil. IR (film): 2976, 2879, 1702, 1635, 1491, 1448, 1392, 1379, 1369, 1353, 1316, 1268, 1230, 1205, 1164, 1144, 1119,1097, 1073, 1003, 992, 928, 898, 812, 767, 743, 698, 512 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.61 (s, 1 H), 7.37 (d, *J*=4.58 Hz, 4 H), 7.26 - 7.31 (m, 1 H), 2.26 (sep, *J*=6.85 Hz, 1 H), 2.07 (s, 3 H), 1.51 (s, 6 H), 0.97 (d, *J*=7.02 Hz, 6 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 167.8, 137.7, 136.3, 130.4, 129.6 (2 C), 128.3 (2 C), 128.0, 85.6, 36.8, 22.9 (2 C), 17.4 (2 C), 14.1 ppm. HRMS (ESI): calcd. for $C_{16}H_{22}NaO_2$ $[M+Na]^+$: 269.1512 found: 269.1518.



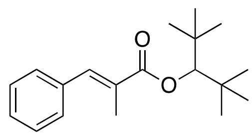
3

3 (508 mg, 65 % yield): colorless oil. IR (film): 2978, 2896, 1703, 1635, 1465, 1449, 1399, 1378, 1369, 1352, 1270, 1203, 1178, 1136, 1118, 1076, 1002, 992, 939, 849, 792, 766, 740, 713, 695, 510 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.62 (s, 1 H), 7.36 - 7.40 (m, 4 H), 7.28 - 7.31 (m, 1 H), 2.08 (s, 3 H), 1.59 (s, 6 H), 1.05 (s, 9 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 167.8, 137.7, 136.3, 130.7, 129.6 (2 C), 128.3 (2 C), 128.0, 87.4, 38.8, 25.4 (3 C), 20.6 (2 C), 14.2 ppm. HRMS (ESI): calcd. for $C_{17}H_{24}NaO_2$ $[M+Na]^+$: 283.1669 found: 283.1674.



4

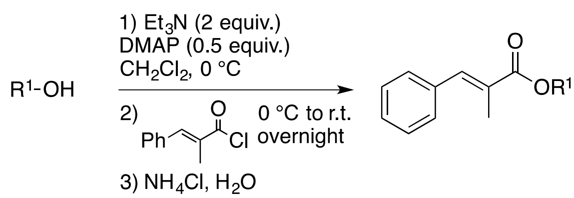
4 (672 mg, 86 % yield): colorless oil. IR (film): 2971, 2942, 2882, 1701, 1635, 1491, 1456, 1384, 1353, 1259, 1203, 1141, 1118, 1077, 1003, 993, 931, 901, 860 766, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.61 (s, 1 H), 7.37 - 7.38 (m, 4 H), 7.28 - 7.32 (m, 1 H), 2.08 (s, 3 H), 1.92 (q, *J*=7.32 Hz, 6 H), 0.87 (t, *J*=7.48 Hz, 9 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 167.6, 137.6, 136.3, 130.1, 129.6 (2 C), 128.3 (2 C), 128.0, 88.5, 27.0 (3 C), 14.1, 7.8 (3 C) ppm. HRMS (ESI): calcd. for $C_{17}H_{24}NaO_2$ $[M+Na]^+$: 283.1669 found: 283.1670.



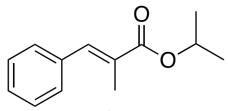
5

5 (771mg, 88 % yield): colorless oil. IR (film): 2961, 2874, 1706, 1636, 1479, 1449, 1398, 1368, 1334, 1293, 1254, 1200, 1165, 1116, 1039, 1003, 995, 939, 771, 757, 734, 700, 512 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.75 (s, 1 H), 7.35 - 7.41 (m, 4 H), 7.27 - 7.30 (m, 1 H), 4.76 (s, 1 H), 2.17 (s, 3 H), 1.07 (s, 18 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 168.2, 138.7, 136.1, 129.7 (2 C), 128.9, 128.4 (2 C), 128.2, 86.2, 37.4 (2 C), 28.9 (6 C), 14.2 ppm. HRMS (ESI): calcd. for $C_{19}H_{28}NaO_2$ $[M+Na]^+$: 311.1982 found: 311.1983.

Synthesis of α,β-unsaturated esters **6-7**

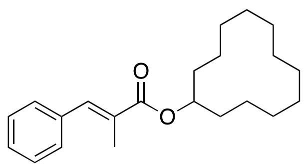


To a solution of alcohol (4.5 mmol) and DMAP (1.5 mmol, 183 mg) in CH_2Cl_2 (5 ml) was slowly added Et_3N (6 mmol, 0.84 ml) in an ice bath. α-Methylcinnamic acid chloride (3 mmol, 542 mg) in CH_2Cl_2 (5 ml) was then added dropwise to the stirring solution at 0 °C. The ice bath was then removed and the reaction was stirred overnight at room temperature. Saturated aqueous NH_4Cl solution was added to quench the reaction and the mixture was extracted with CH_2Cl_2, sodium sulfate and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (hexane/CH_2Cl_2 = 1:1).



6

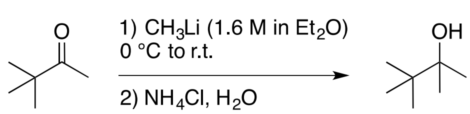
6 (499 mg, 81 % yield): colorless oil. IR (film): 2980, 2936, 1707, 1636, 1492, 1468, 1448, 1387, 1373, 1359, 1334, 1293, 1256, 1203, 1180, 1145, 1106, 1003, 994, 929, 870, 766, 740, 703, 693, 512 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.67 (d, *J*=1.50 Hz, 1 H), 7.38 - 7.39 (m, 4 H), 7.29 - 7.32 (m, 1 H), 5.10 - 5.17 (m, 1 H), 2.10 (d, *J*=1.53 Hz, 3 H), 1.32 (d, *J*=6.41 Hz, 6 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 168.2, 138.4, 136.1, 129.6 (2 C), 129.1, 128.3 (2 C), 128.2, 68.1, 21.9 (2 C), 14.0 ppm. HRMS (ESI): calcd. for $C_{13}H_{16}NaO_2$ $[M+Na]^+$: 227.1043 found: 227.1044.



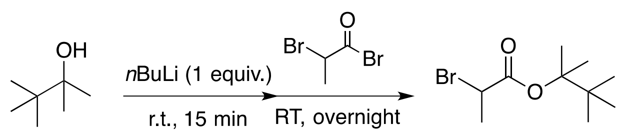
7

7 (895 mg, 91 % yield): colorless oil. IR (film): 2927, 2862, 1704, 1635, 1470, 1446, 1356, 1326, 1293, 1255, 1202, 1156, 1117, 1076, 1046, 1003, 982, 960, 931, 766, 738, 703, 694 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.67 (d, *J*=1.50 Hz, 1 H), 7.37 - 7.39 (m, 4 H), 7.29 - 7.32 (m, 1 H), 5.12-5.17 (m, 1 H), 2.11 (d, *J*=1.53 Hz, 3 H), 1.75-1.82 (m, 2 H), 1.57 - 1.63 (m, 2 H), 1.33 - 1.48 (m, 18 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 168.3, 138.3, 136.1, 129.6 (2 C), 129.1, 128.3 (2 C), 128.2, 72.8, 29.2 (2 C), 24.3 (2 C), 24.0, 23.4 (2 C), 23.2 (2 C), 20.9 (2 C), 14.1 ppm. HRMS (ESI): calcd. for $C_{22}H_{32}NaO_2$ $[M+Na]^+$: 351.2295 found: 351.2294.

Synthesis of α,β-unsaturated esters **12-22**

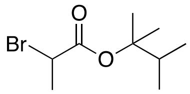


To a dry 250 ml round-bottom flask loaded with anhydrous ether (25 ml) was slowly added methyl lithium (48 mmol, 30 ml, 1.6 M in diethyl ether) at 0 °C. Pinacolone (48 mmol, 6ml) in ether (25 ml) was slowly added to the flask and stirred for 1 hour at 0 °C. The ice bath was removed and the reaction was slowly warmed up to room temperature and stirred for an additional 30 minutes. Saturated aqueous ammonium chloride solution was added at 0 °C. The organics was extracted with ether, dried over sodium sulfate and concentrated in vacuo. Flash chromatography (hexane/CH_2Cl_2 = 1:1) gave the alcohol in 46% yield (2.57g).

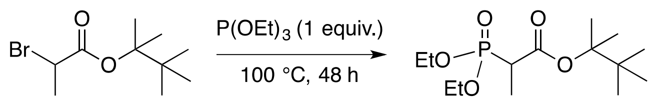


8

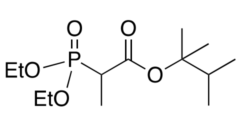
To a dry 250 ml round bottom flask was added **5** (30.4 mmol, 3.53g) and dissolved in ether (30 ml). The flask was maintained at room temperature in a water bath and *n*BuLi (30.4 mmol, 19 ml, 1.6 M in THF) was added dropwise into the solution and stirred for 15 minutes. 2-Bromopropanoyl bromide (36.5 mmol, 3.82 ml) in ether (30 ml) was added slowly to the reaction and it was stirred overnight. Saturated aqueous ammonium chloride solution was added and the mixture was extracted with CH_2Cl_2. The organics was dried over sodium sulfate and concentrated in vacuo. Flash chromatography on silica gel (hexane/CH_2Cl_2 = 1:1) gave the product **8** in 78% yield as yellow oil. IR (film): 2977, 2878, 1732, 1467, 1446, 1401, 1380, 1371, 1341, 1289, 1240, 1169, 1130, 1057, 985, 940, 847, 787 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.30 (q, *J*=6.90 Hz, 1H), 1.79 (d, *J*=6.90 Hz, 3 H), 1.52 (s, 6 H), 1.00 (s, 9 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 169.0, 89.0, 42.5, 38.5, 25.1 (3 C), 21.8, 20.3, 20.1 ppm. HRMS (ESI): calcd. for $C_{10}H_{19}BrNaO_2$ $[M+Na]^+$: 273.0461 found: 273.0461.


9

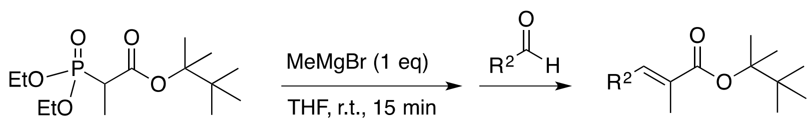
9 was synthesized according to the method for **8**. The product was purified as a yellow oil (78 % yield). IR (film): 2978, 2880, 1734, 1464, 1447, 1394, 1380, 1371, 1342, 1284, 1231, 1206, 1175, 1135, 1098, 1070, 986, 943, 903, 889, 824, 806, 765, 529 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.29 (q, *J*=6.95 Hz, 1H), 2.20 (sep, *J*=6.85 Hz, 1 H), 1.78 (d, *J*=6.95 Hz, 3 H) 1.44 (s, 6 H), 0.94 (d, *J*=6.95 Hz, 3 H), 0.93 (d, *J*=6.90 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 168.9, 87.3, 42.1, 36.4, 22.5, 22.3, 21.7, 17.2 (2 C) ppm. HRMS (ESI): calcd. for $C_9H_{17}BrKO_2$ $[M+K]^+$: 275.0044 found: 275.0063.



To a dry 100 ml round bottom flask was added 2,3,3-trimethylbutan-2-yl 2-bromopropanoate (30 mmol, 7.53g) and triethyl phosphite (30 mmol, 5.15 ml) and heated with stirring at 100 °C for 48 hours. Flash chromatography on silica gel (hexane/CH_2Cl_2 = 1:1) gave the product **10** in 64% yield (5.92g) as a yellow oil. IR (film): 2982, 2880, 1728, 1458, 1380, 1370, 1317, 1258, 1179, 1134, 1027, 966, 903, 849, 820, 782, 559, 511 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.12 - 4.17 (m, 4 H), 2.90 - 2.99 (m, 1 H), 1.51 (s, 6 H), 1.42 (dd, *J*=18.4, 7.30 Hz, 3 H), 1.32 – 1.35 (m, 6 H), 1.00 (s, 9 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 168.4 (d, *J*=5.1 Hz), 88.3, 62.4 (d, *J*=6.92 Hz), 62.3 (d, *J*=6.55 Hz), 40.8 (d, *J*=133 Hz), 38.3, 25.0 (3 C), 20.2, 20.1, 16.4 (d, *J*=2.83 Hz), 16.3 (d, *J*=2.88 Hz), 11.8 (d, *J*=6.04 Hz) ppm. HRMS (ESI): calcd. for $C_{14}H_{29}NaO_5P$ $[M+Na]^+$: 331.1645 found: 331.1649.

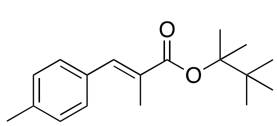

11

11 was synthesized according to the method for **10**. The product was isolated as a yellow oil (74 %). IR (film): 2982, 2942, 2909, 2882, 1728, 1458, 1393, 1380, 1370, 1319, 1257, 1190, 1161, 1139, 1098, 1027, 965, 907, 788 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.12 - 4.20 (m, 4 H), 2.90 - 2.99 (m, 1 H), 2.19 (sep, *J*=6.88 Hz, 1 H), 1.44 (s, 3 H), 1.32 (s, 3 H), 1.37 (dd, *J*=18.7, 7.30 Hz, 3 H), 1.32 - 1.36 (m, 9 H), 0.94 (d, *J*=6.90 Hz, 3 H), 0.93 (d, *J*=6.90 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 168.5 (d, *J*=4.85 Hz), 86.8, 62.3 (d, *J*=6.88 Hz), 40.4 (d, *J*=133 Hz), 36.4, 22.5, 22.4, 17.1 (2 C), 16.3 (d, *J*=1.91 Hz), 16.2 (d, *J*=1.99 Hz), 11.7 (d, *J*=6.11 Hz) ppm; HRMS (ESI): calcd. for $C_{13}H_{27}NaO_5P$ $[M+Na]^+$: 317.1488 found: 317.1490.



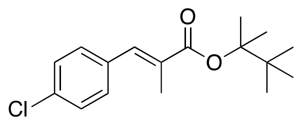
10

To a dry 100 ml round bottom flask was added **10** (2 mmol, 0.617g) and THF (10 ml). MeMgBr (2 mmol, 2 ml, 1M in THF) was added dropwise and stirred for 15 min at room temperature, at which the solution turned yellowish. The aldehyde (2.2 mmol) dissolved in ether was added and stirred overnight. The reaction was quenched with H_2O and extracted with CH_2Cl_2, dried over sodium sulfate and concentrated under reduced pressure. The crude product was purified by prep TLC (hexane/EtOAc = 10:1). The method was modified from reported precedures.


12

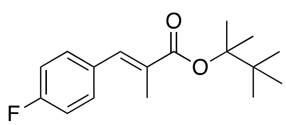
12 (376 mg, 68 % yield): colorless oil. IR (film): 2978, 2920, 2876, 1701, 1635, 1612, 1512, 1465, 1399, 1378, 1369, 1351, 1316, 1270, 1201, 1182, 1136, 1119, 995, 940, 849, 812, 793, 747, 516 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.59 (s, 1 H), 7.28 (d, *J*=7.95 Hz, 2 H), 7.19 (d, *J*=7.85 Hz, 2 H), 2.37 (s, 3 H), 2.08 (s, 3 H), 1.58 (s, 6 H), 1.05 (s, 9 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 168.0, 138.1, 137.8, 133.4, 129.9, 129.6

(2 C), 129.1 (2 C), 87.2, 38.8, 25.4 (3 C), 21.3, 20.6 (2 C), 14.3 ppm. HRMS (ESI): calcd. for $C_{18}H_{26}NaO_2$ $[M+Na]^+$: 297.1825 found: 297.1822.



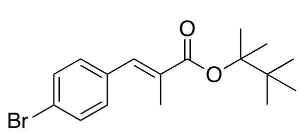
13

13 (357 mg, 61 %): white solid. IR (film): 2978, 2876, 1704, 1636, 1491, 1465, 1400, 1378, 1369, 1351, 1306, 1270, 1201, 1178, 1135, 1120, 1092, 1014, 994, 847, 811, 748, 518 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.54 (s, 1 H), 7.36 (d, J=8.45 Hz, 2 H), 7.30 (d, J=8.50 Hz, 2 H), 2.06 (s, 3 H), 1.58 (s, 6 H), 1.05 (s, 9 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 167.6, 136.4, 134.7, 133.9, 131.4, 130.8 (2 C), 128.6 (2 C), 87.6, 38.8, 25.4 (3 C), 20.5 (2 C), 14.2 ppm. HRMS (ESI): calcd. for $C_{17}H_{23}ClNaO_2$ $[M+Na]^+$: 317.1279 found: 317.1274.



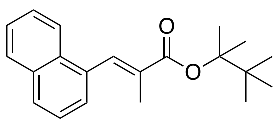
14

14 (236 mg, 42 % yield): white solid. IR (film): 2979, 2877, 1704, 1639, 1602, 1509, 1466, 1400, 1378, 1369, 1351, 1306, 1272, 1228, 1201, 1178, 1160, 1135, 1119, 995, 940, 849, 833, 780, 748, 535, 522 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.57 (s, 1 H), 7.34 - 7.36 (m, 2 H), 7.05 - 7.09 (m, 2 H), 2.06 (d, J=1.53 Hz, 3 H), 1.58 (s, 6 H), 1.05 (s, 9 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 167.7, 162.3 (d, J=249 Hz, 1 C), 136.6, 132.3, 131.3 (d, J=7.55 Hz, 2 C), 130.6, 115.4 (d, J=21.4 Hz, 2 C), 87.5, 38.8, 25.4 (3 C), 20.5 (2 C), 14.2 ppm. HRMS (ESI): calcd. for $C_{17}H_{23}FNaO_2$ $[M+Na]^+$: 301.1574 found: 301.1571.



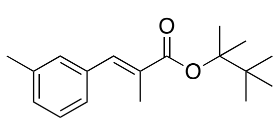
15

15 (241 mg, 36 % yield): white solid. IR (film): 2977, 2876, 1703, 1633, 1586, 1487, 1465, 1399, 1378, 1369, 1351, 1306, 1271, 1200, 1178, 1135, 1120, 1073, 1010, 994, 848, 808, 748, 514 cm^{-1};^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.52 (s, 1 H), 7.49-7.51 (m, 2 H), 7.23 (d, *J*=8.40 Hz, 2 H), 2.05 (d, *J*=1.53 Hz, 3 H), 1.58 (s, 6 H), 1.04 (s, 9 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 167.5, 136.4, 135.1, 131.5 (3 C), 131.1 (2 C), 122.1, 87.6, 38.8, 25.4 (3 C), 20.5 (2 C), 14.3 ppm. HRMS (ESI): calcd. for $C_{17}H_{23}BrNaO_2$ $[M+Na]^+$: 361.0774 found: 361.0780.



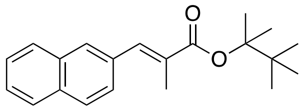
16

16 (415 mg, 67 % yield): white solid. IR (film): 2977, 2876, 1704, 1638, 1508, 1465, 1398, 1378, 1369, 1339, 1278, 1255, 1238, 1215, 1170, 1120, 1083, 986, 940, 850, 804, 783, 747, 731 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.13 (s, 1 H), 7.92 - 7.93 (m, 1 H), 7.86 - 7.88 (m, 1 H), 7.82 (d, *J*=8.24 Hz, 1 H), 7.46 - 7.53 (m, 3 H), 7.38 (d, *J*=7.02 Hz, 1 H), 1.96 (d, *J*=1.22 Hz, 3 H), 1.64 (s, 6 H), 1.07 (s, 9 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 167.5, 136.2, 133.5 (2 C), 132.8, 131.7, 128.6, 128.4, 126.6, 126.3, 126.1, 125.2, 124.7, 87.5, 38.8, 25.4 (3 C), 20.6 (2 C), 14.6 ppm. HRMS (ESI): calcd. for $C_{21}H_{26}NaO_2$ $[M+Na]^+$: 333.1825 found: 333.1828.



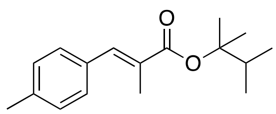
17

17 (388 mg, 71 % yield): colorless oil. IR (film): 2978, 2920, 2876, 1705, 1482, 1459, 1399, 1378, 1369, 1349, 1289, 1268, 1218, 1179, 1122, 994, 849, 793, 758, 741 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.69 (s, 1 H), 7.20 (s, 4 H), 2.28 (s, 3 H), 1.94 (d, *J*=1.22 Hz, 3 H), 1.60 (s, 6 H), 1.05 (s, 9 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 167.6, 137.0, 136.8, 135.5, 131.1, 130.0, 128.8, 128.0, 125.5, 87.2, 38.7, 25.4 (3 C), 20.6 (2 C), 19.9, 14.1 ppm. HRMS (ESI): calcd. for $C_{18}H_{26}NaO_2$ $[M+Na]^+$: 297.1825 found: 297.1829.



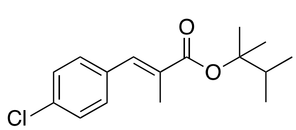
18

18 (441 mg, 71 % yield): white solid. IR (film): 2978, 2876, 1701, 1635, 1465, 1399, 1378, 1369, 1344, 1219, 1202, 1176, 1135, 1116, 998, 940, 851, 818, 793, 739, 477 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.82 - 7.85 (m, 4 H), 7.77 (s, 1 H), 7.48 - 7.50 (m, 3 H), 2.17 (d, *J*=1.53 Hz, 3 H), 1.61 (s, 6 H), 1.07 (s, 9 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 167.9, 137.8, 133.8, 133.2, 132.8, 131.1, 129.1, 128.2, 127.9, 127.7, 127.2, 126.5, 126.4, 87.5, 38.8, 25.4 (3 C), 20.6 (2 C), 14.4 ppm. HRMS (ESI): calcd. for $C_{21}H_{26}NaO_2$ $[M+Na]^+$: 333.1825 found: 333.1826.



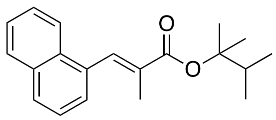
19

19 (251 mg, 48 % yield): colorless oil. IR (film): 2976, 2879, 1702, 1634, 1512, 1462, 1392, 1379, 1369, 1317, 1268, 1229, 1203, 1184, 1164, 1144, 1119, 1097, 995, 898, 839, 813, 748, 517 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.58 (s, 1 H), 7.28 (m, *J*=7.93 Hz, 2 H), 7.18 (m, *J*=7.93 Hz, 2 H), 2.36 (s, 3 H), 2.26 (sep, *J*= 6.85 Hz, 1 H), 2.07 (d, *J*=1.53 Hz, 3 H), 1.50 (s, 6 H), 0.97 (d, *J*=7.02 Hz, 6 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 167.9, 138.1, 137.7, 133.4, 129.6 (2 C), 129.5, 129.0 (2 C), 85.5, 36.8, 22.9 (2 C), 21.3, 17.4 (2 C), 14.1 ppm. HRMS (ESI): calcd. for $C_{17}H_{24}NaO_2$ $[M+Na]^+$: 283.1669 found: 283.1675.



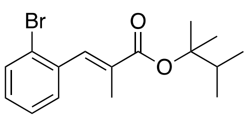
20

20 (269 mg, 48 % yield): white solid. IR (film): 2976, 2879, 1705, 1637, 1592, 1491, 1464, 1392, 1379, 1369, 1352, 1307, 1269, 1230, 1203, 1163, 1144, 1121, 1093, 1014, 995, 898, 839, 813, 749, 517 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.53 (s, 1 H), 7.34 - 7.36 (m, 2 H), 7.29 - 7.31 (m, 2 H), 2.26 (sep, *J*= 6.88 Hz, 1 H), 2.05 (d, *J*=1.53 Hz, 3 H), 1.50 (s, 6 H), 0.97 (d, *J*=6.71 Hz, 6 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 167.5, 136. 3, 134.7, 133.9, 131.0, 130.8 (2 C), 128.6 (2 C), 85.9, 36.7, 22.8 (2 C), 17.4 (2 C), 14.1 ppm. HRMS (ESI): calcd. for $C_{16}H_{21}ClNaO_2$ $[M+Na]^+$: 303.1122 found: 303.1121.



21

21 (405 mg, 68 % yield): colorless oil. IR (film): 2976, 2878, 1704, 1638, 1464, 1392, 1369, 1379, 1340, 1277, 1252, 1228, 1163, 1144, 1120, 1097, 986, 898, 805, 783, 748, 732 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.12 (s, 1 H), 7.91-7.93 (m, 1 H), 7.84 - 7.86 (m, 1 H), 7.80 (d, *J*=7.93 Hz, 1 H), 7.45 - 7.51 (m, 3 H), 7.37 (d, *J*=7.00 Hz, 1 H), 2.27 (sep, *J*=6.85, 1 H), 1.95 (d, *J*=1.83 Hz, 3 H), 1.56 (s, 6 H), 1.00 (d, *J*=7.02 Hz, 6 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 167.5, 136.2, 133.6, 133.5, 132.5, 131.6, 128.5, 126.6, 126.3, 126.1, 125.2, 124.8, 85.7, 36.9, 23.0, 17.5, 14.4 ppm. HRMS (ESI): calcd. for $C_{20}H_{24}NaO_2$ $[M+Na]^+$: 319.1669 found: 319.1676.

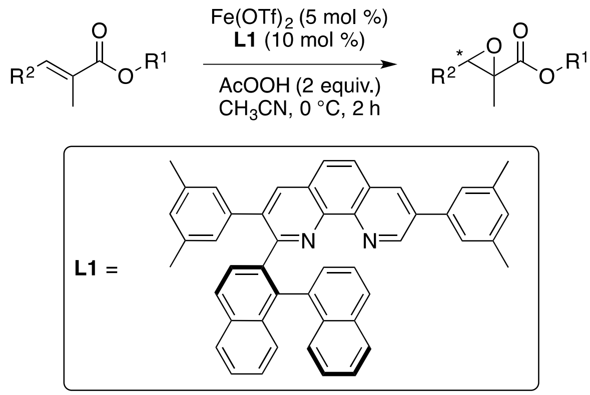


22

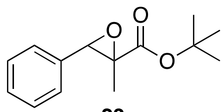
22 (472 mg, 73 % yield): colorless oil. IR (film): 2976, 2879, 1705, 1640, 1587, 1562, 1466, 1450, 1434, 1392, 1379, 1369, 1283, 1254, 1229, 1205, 1164, 1145, 1124, 1097, 1072, 1047, 1026, 993, 945, 898, 812, 762, 742, 663 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.65 (d, *J*=1.53 Hz, 1 H), 7.58-7.60 (m, 1 H), 7.28 - 7.31 (m, 2 H), 7.13 - 7.18 (m, 1 H), 2.21 (sep, *J*=6.80 Hz, 1 H), 1.95 (d, *J*=1.53 Hz, 3 H), 1.52 (s, 6 H), 0.99 (d, *J*=6.90 Hz, 6 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 167.1, 137.0, 136.5, 132.7, 131.8, 130.5, 129.3, 127.0, 124.4, 85.7, 37.0, 22.9 (2 C), 17.4 (2 C), 14.0 ppm. HRMS (ESI): calcd. for $C_{16}H_{21}BrNaO_2$ $[M+Na]^+$: 347.0617 found: 347.0625.

6.2.2 Synthetic Procedures and Data for Compounds **23-40**

General Procedure for the Asymmetric Epoxidation of Unsaturated Esters

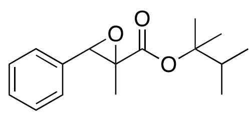


To a flame-dried test tube charged with ligand **L1** (10.3 mg, 0.016 mmol) and stir-bar under nitrogen was added a solution of $Fe(OTf)_2$ (0.32 ml, 0.008 mmol, 0.025 M in CH_3CN) followed by CH_3CN (0.32 ml), resulting in a light yellow solution. The complex was stirred vigorously (1200 rpm) for 2-3 hours at room temperature. Another dry test tube was charged with the substrate (0.15 mmol) and flushed with nitrogen. The iron complex (0.6 ml, 0.0075 mmol) in CH_3CN from the first test tube was added via syringe and the vessel was cooled to 0 °C for 10 min with vigorous stirring (1200 rpm) Peracetic acid (63 μl, 32 wt. %, 0.3 mmol) was added to the reaction via microsyringe at once, yielding a near black solution. The reaction was stirred at this temperature for 2 h and quenched with 10% $Na_2S_2O_3$ in 1:1 saturated $NaHCO_3$: H_2O (3 ml). The mixture was extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by flash chromatography (hexane/CH_2Cl_2 = 1:1) to furnish the epoxide. The column was flushed with ethyl acetate (100%) to elute the ligand.



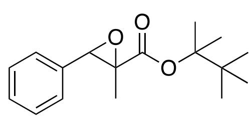
23

23 was isolated as a colorless oil (17 mg, 49 %). IR (film): 2979, 2936, 1726, 1452, 1393, 1369, 1320, 1296, 1258, 1153, 1081, 849, 766, 728, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.30 - 7.38 (m, 5 H), 4.26 (s, 1 H), 1.53 (s, 9 H), 1.27 (s, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 169.8, 134.3, 128.2 (2 C), 128.1, 126.7 (2 C), 82.3, 62.1, 60.4, 28.0 (3 C), 12.7 ppm. HRMS (ESI): calcd. for $C_{14}H_{18}NaO_3$ $[M+Na]^+$: 257.1148 found: 257.1151.



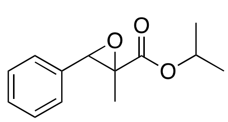
24

24 was isolated as a colorless oil (23 mg, 58 %). IR (film): 2977, 2940, 1725, 1452, 1393, 1381, 1370, 1317, 1293, 1180, 1155, 1137, 1079, 857, 806, 765, 728, 700, 608 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.30 - 7.39 (m, 5 H), 4.27 (s, 1 H), 2.20 - 2.27 (m, 1 H), 1.49 (s, 6 H), 1.27 (s, 3 H), 0.95 (d, J=7.02 Hz, 6 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 169.6, 134.3, 128.2 (2 C), 128.1, 126.7 (2 C), 87.4, 62.1, 60.5, 36.5, 22.7 (2 C), 17.3 (2 C), 12.8 ppm. HRMS (ESI): calcd. for $C_{16}H_{22}NaO_3$ $[M+Na]^+$: 285.1461 found: 285.1464.



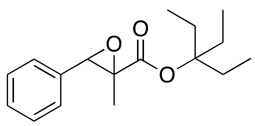
25

25 was isolated as a colorless oil (29 mg, 69 %). IR (film): 2978, 2877, 1725, 1451, 1400, 138, 1370, 1317, 1293, 1171, 1132, 1079, 1002, 940, 848, 797, 764, 727, 700, 600 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.30 -7.39 (m, 5 H), 4.28 (s, 1 H), 1.57 (s, 3 H), 1.56 (s, 3 H), 1.28 (s, 3 H), 1.01 (s, 9 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 169.7, 134.3, 128.2 (2 C), 128.1, 126.7 (2 C), 89.1, 62.0, 60.7, 38.6, 25.2 (3 C), 20.5, 20.4, 13.0 ppm. HRMS (ESI): calcd. for $C_{17}H_{24}NaO_3$ $[M+Na]^+$: 299.1618 found: 299.1619.



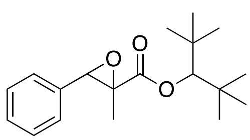
26

26 was isolated as a colorless oil (10 mg, 30 %).IR (film): 2982, 2938, 1729, 1452, 1387, 1375, 1278, 1171, 1108, 1080, 1002, 927, 886, 857, 828, 765, 728, 700, 603 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.30 - 7.39 (m, 5 H), 5.09 - 5.16 (m, 1 H), 4.29 (s, 1 H), 1.318 (d, *J*=6.30, 3 H), 1.316 (d, *J*=6.30 Hz, 3 H), 1.30 (s, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.3, 134.0, 128.3 (2 C), 128.2, 126.7 (2 C), 69.5, 62.3, 60.0, 21.8. 21.7, 12.7 ppm. HRMS (ESI): calcd. for $C_{13}H_{16}NaO_3$ $[M+Na]^+$: 243.0992 found: 243.0992.



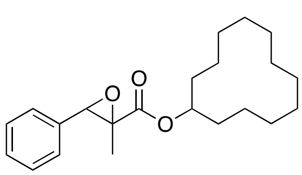
27

27 was isolated as a colorless oil (18 mg, 43 %). IR (film): 2973, 2942, 2883, 1724, 1456, 1384, 1339, 1290, 1175, 1134, 1076, 911, 870, 765, 727, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.29 - 7.38 (m, 5 H), 4.26 (s, 1 H), 1.90 (q, *J*=7.55 Hz, 3 H), 1.89 (q, *J*=7.45 Hz, 3 H), 1.28 (s, 3 H), 0.86 (t, *J*=7.48 Hz, 9 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 169.4, 134.3, 128.2 (2 C), 128.1, 126.6 (2 C), 90.3, 62.2, 60.3, 26.8 (3 C), 12.9, 7.7 (3 C) ppm. HRMS (ESI): calcd. for $C_{17}H_{24}NaO_3$ $[M+Na]^+$: 299.1618 found: 299.1615.



28

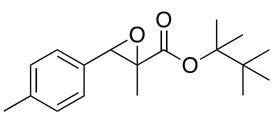
28 was isolated as a colorless oil (12 mg, 26 %). IR (film): 2963, 1730, 1475, 1452, 1398, 1369, 1339, 1275, 1164, 1079, 1039, 935, 857, 763, 725, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.30 - 7.40 (m, 5 H), 4.71 (s, 1 H), 4.34 (s, 1 H), 1.35 (s, 3 H), 1.06 (s, 9 H), 1.05 (s, 9 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.3, 134.1, 128.3 (2 C), 128.2, 126.6 (2 C), 87.6, 62.3, 60.1, 37.4, 37.2, 28.8 (3 C), 28.7 (3 C), 13.0 ppm. HRMS (ESI): calcd. for $C_{19}H_{28}NaO_3$ $[M+Na]^+$: 327.1931 found: 327.1934.



29

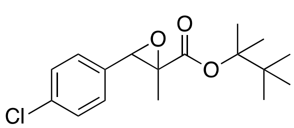
29 was isolated as a colorless oil (9 mg, 18 %). IR (film): 2935, 2863, 1727, 1471, 1448, 1277, 1169, 1152, 1079, 856, 764, 727, 700 cm^{-1}; ^1H

NMR (500 MHz, $CDCl_3$) δ = 7.30 - 7.38 (m, 5 H), 5.11 (m, 1 H), 4.29 (s, 1 H), 1.76 - 1.81 (m, 2 H), 1.56 - 1.61 (m, 2 H), 1.32 - 1.42 (m, 18 H), 1.30 (s, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.5, 134.1, 128.2 (3 C), 126.7 (2 C), 74.2, 62.3, 60.0, 29.0, 28.9, 24.2 (2 C), 24.0, 23.3 (2 C), 23.2, 23.1, 20.8 (2 C), 12.7 ppm. HRMS (ESI): calcd. for $C_{22}H_{32}NaO_3$ $[M+Na]^+$: 367.2244 found: 367.2242.



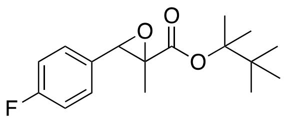
30

30 was isolated as a colorless oil (29 mg, 65 %). IR (film): 2977, 2925, 2876, 1725, 1517, 1466, 1370, 1380, 1319, 1291, 1171, 1132, 1083, 940, 861, 847, 815, 796, 780, 734, 565, 516 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.16 - 7.20 (m, 4 H), 4.24 (s, 1 H), 2.36 (s, 3 H), 1.57 (s, 3 H), 1.56 (s, 3 H), 1.28 (s, 3 H), 1.00 (s, 9 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 169.8, 137.9, 131.3, 128.9 (2 C), 126.6 (2 C), 89.0, 62.1, 60.6, 38.6, 25.2 (3 C), 21.2, 20.5, 20.4, 12.9 ppm. HRMS (ESI): calcd. for $C_{18}H_{26}NaO_3$ $[M+Na]^+$: 313.1774 found: 313.1766.



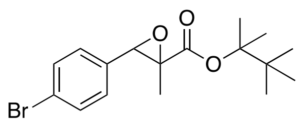
31

31 was isolated as a colorless solid (23 mg, 48 %). IR (film): 2977, 2899, 1726, 1494, 1466, 1400, 1380, 1371, 1319, 1297, 1171, 1131, 1090, 1015, 1001, 940, 848, 819, 796, 746, 536, 501 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.35 (d, *J*=8.55 Hz, 2 H), 7.25 (d, *J*=8.24 Hz, 2 H), 4.24 (s, 1 H), 1.57 (s, 3 H), 1.56 (s, 3 H), 1.26 (s, 3 H), 1.00 (s, 9 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 169.4, 134.1, 132.9, 128.5 (2 C), 128.1 (2 C), 89.3, 61.4, 60.7, 38.6, 25.2 (3 C), 20.5, 20.4, 12.9ppm. HRMS (ESI): calcd. for $C_{17}H_{23}ClNaO_3$ $[M+Na]^+$: 333.1228 found: 333.1235.



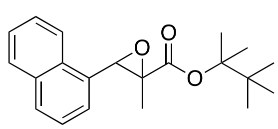
32

32 was isolated as a colorless oil (13 mg, 30 %). IR (film): 2977, 1726, 1609, 1513, 1467, 1380, 1371, 1320, 1295, 1226, 1172, 1131, 1082, 1000, 940, 905, 866, 847, 832, 796, 738, 702, 564, 520 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.27 - 7.30 (m, 2 H), 7.05 - 7.08 (m, 2 H), 4.25 (s, 1 H), 1.57 (s, 3 H), 1.56 (s, 3 H), 1.26 (s, 3 H), 1.00 (s, 9 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 169.5, 162.6 (d, *J*=243 Hz, 1 C), 130.1, 128.4 (d, *J*=8.80 Hz, 2 C), 115.3 (d, *J*=22.6 Hz, 2 C), 89.2, 61.5, 38.6, 25.2 (3 C), 20.5, 20.4, 12.9 ppm. HRMS (ESI): calcd. for $C_{17}H_{23}FNaO_3$ $[M+Na]^+$: 317.1523 found: 317.1527.



33

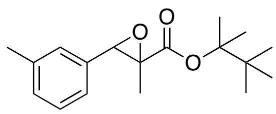
33 was isolated as a white solid (18 mg, 34 %). IR (film): 2961, 2925, 2854, 1727, 1489, 1465, 1400, 1370, 1319, 1297, 1171, 1131, 1071, 1012, 1001, 848, 817, 796, 742 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.50 (d, *J*=8.54 Hz, 2 H), 7.19 (d, *J*=8.24 Hz, 2 H), 4.22 (s, 1 H), 1.564 (s, 3 H), 1.557 (s, 3 H), 1.26 (s, 3 H), 1.00 (s, 9 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 169.3, 133.4, 131.5 (2 C), 128.4 (2 C), 122.2, 89.3, 61.5, 60.7, 38.6, 25.2 (3 C), 20.5, 20.4, 12.9 ppm. HRMS (ESI): calcd. for $C_{17}H_{23}BrNaO_3$ $[M+Na]^+$: 377.0723 found: 377.0727.



34

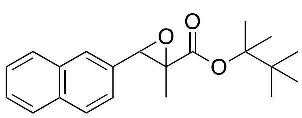
34 was isolated as a colorless oil (30 mg, 61 %). IR (film): 2977, 2876, 1726, 1510, 1466, 1400, 1380, 1371, 1319, 1295, 1263, 1176, 1131, 1091, 1045, 984, 939, 906, 848, 796, 776, 720, 668, 621, 503 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.90 - 7.92 (m, 1 H), 7.86 - 7.88 (m, 1 H), 7.82 - 7.84 (m, 1 H), 7.51 - 7.55 (m, 2 H), 7.47 - 7.51 (m, 2 H), 4.68 (s, 1 H), 1.65 (s, 3 H), 1.64 (s, 3 H), 1.21 (s, 3 H), 1.05 (s, 9 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 169.8, 133.2, 130.1, 130.5, 128.8, 128.4, 126.6, 126.0, 125.3, 124.5, 122.7, 89.3, 61.0, 60.8, 38.6, 25.2 (3 C), 20.7, 20.6, 13.4 ppm. HRMS

(ESI): calcd. for $C_{21}H_{26}NaO_3$ $[M+Na]^+$: 349.1774 found: 349.1781.



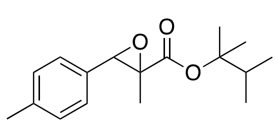
35

35 was isolated as a colorless oil (11 mg, 24 %). IR (film): 2975, 1725, 1458, 1400, 1380, 1370, 1287, 1173, 1131, 1085, 848, 790, 763, 737 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.16 - 7.27 (m, 4 H), 4.21 (s, 1 H), 2.29 (s, 3 H), 1.58 (s, 3 H), 1.57 (s, 3 H), 1.21 (s, 3 H), 1.01 (s, 9 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 169.8, 135.7, 132.9, 129.7, 127.9, 127.9, 126.3, 125.8, 89.1, 61.3, 60.2, 25.2 (3 C), 20.6, 20.5, 18.5, 13.3 ppm. HRMS (ESI): calcd. for $C_{18}H_{26}NaO_3$ $[M+Na]^+$: 313.1774 found: 313.1746.



36

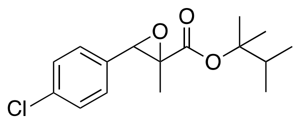
36 was isolated as a colorless oil (19 mg, 38 %). IR (film): 2976, 1724, 1466, 1400, 1380, 1370, 1319, 1289, 1170, 1131, 1081, 847, 820, 797, 749, 718 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.84 - 7.86 (m, 3 H), 7.78 (s, 1 H), 7.49 - 7.51 (m, 2 H), 7.41-7.43 (m, 1 H), 4.44 (s, 1 H), 1.593 (s, 3 H), 1.587 (s, 3 H), 1.31 (s, 3 H), 1.02 (s, 9 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 169.7, 133.2, 133.0, 131.9, 128.0, 127.9, 127.8, 126.4, 126.2, 125.9, 124.2, 89.2, 62.2, 60.9, 38.6, 25.2 (3 C), 20.6, 20.4, 13.0 ppm. HRMS (ESI): calcd. for $C_{21}H_{26}NaO_3$ $[M+Na]^+$: 349.1774 found: 349.1780.



37

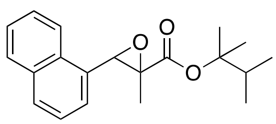
37 was isolated as a colorless oil (19 mg, 46 %). IR (film): 2973, 2927, 1725, 1517, 1462, 1381, 1370, 1319, 1290, 1179, 1156, 1137, 1084, 861, 814, 779, 734, 566 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.16 - 7.20 (m, 4 H), 4.23 (s, 1 H), 2.36 (s, 3 H), 2.20 - 2.25 (m, 1 H), 1.48 (s, 6 H), 1.27 (s, 3 H), 0.94 (d, *J*=7.02 Hz, 6 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 169.8, 138.9, 131.3, 128.9 (2 C), 126.6 (2 C), 87.4, 62.1, 60.4, 36.5, 22.7, 22.6, 21.2, 17.3 (2 C), 12.8 ppm. HRMS (ESI): calcd. for $C_{17}H_{24}NaO_3$ $[M+Na]^+$:

299.1618 found: 299.1619.



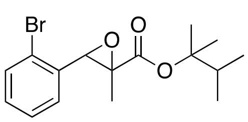
38

38 was isolated as a colorless oil (29 mg, 64 %). IR (film): 2975, 2936, 1727, 1494, 1457, 1381, 1370, 1320, 1296, 1180, 1155, 1137, 1090, 1015, 856, 820, 746, 668, 501 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.35 (d, *J*=8.54 Hz, 2 H), 7.24 (d, *J*=8.24 Hz, 2 H), 4.23 (s, 1 H), 2.19 - 2.25 (m, 1 H), 1.48 (s, 6 H), 1.25 (s, 3 H), 0.94 (d, *J*=7.02 Hz, 6 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 169.3, 134.1, 132.9, 128.5 (2 C), 128.1 (2 C), 87.7, 61.5, 60.5, 36.5, 22.7, 22.6, 17.3 (2 C), 12.8 ppm. HRMS (ESI): calcd. for $C_{16}H_{21}ClNaO_3$ $[M+Na]^+$: 319.1071 found: 319.1075.



39

39 was isolated as a colorless oil (29 mg, 62 %). IR (film): 2975, 2934, 1725, 1462, 1452, 1381, 1370, 1319, 1294, 1184, 1156, 1137, 1090, 983, 876, 845, 793, 776, 720, 624, 503 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.86 - 7.91 (m, 2 H), 7.82 - 7.84 (m, 1 H), 7.51 - 7.55 (m, 2 H), 7.46 - 7.50 (m, 2 H), 4.70 (s, 1 H), 2.26 - 2.33 (m, 1 H), 1.56 (s, 3 H), 1.55 (s, 3 H), 1.20 (s, 3 H), 1.00 (d, *J*=6.85 Hz, 3 H), 0.99 (d, *J*=6.85 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 169.8, 133.2, 131.0, 130.5, 128.8, 128.4, 126.6, 126.0, 125.3, 124.5, 122.7, 87.6, 61.1, 60.7, 36.5, 22.9, 22.8, 17.3 (2 C), 13.2 ppm. HRMS (ESI): calcd. for $C_{20}H_{24}NaO_3$ $[M+Na]^+$: 335.1618 found: 335.1620.



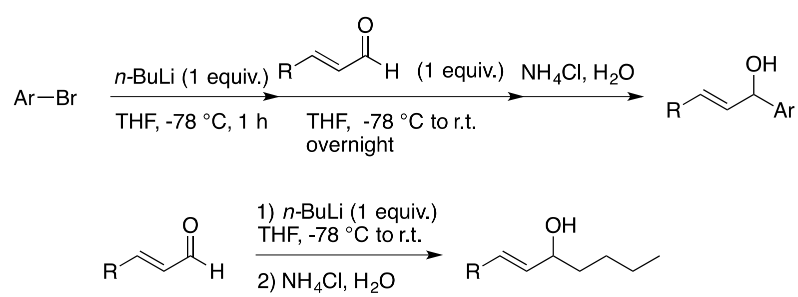
40

40 was isolated as a colorless oil (8 mg, 16 %). IR (film): 2967, 2926, 1728, 1468, 1440, 1393, 1381, 1370, 1321, 1292, 1180, 1155, 1137, 1098, 1077, 1027, 1001, 860, 807, 761, 743, 668, 611 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.53 - 7.58 (m, 1 H), 7.28 - 7.36 (m, 2 H), 7.18 - 7.25 (m, 1 H), 4.29 (s, 1 H), 2.20 - 2.30 (m, 1 H), 1.50 (s, 3 H), 1.49 (s, 3 H), 1.21 (s, 3 H), 0.96 (d, J=6.71 Hz, 6 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 169.2, 134.5, 132.1, 129.5, 128.5, 127.3, 122.3, 87.6, 62.9, 60.2, 36.4, 22.8 (2 C), 17.3 (2 C), 13.1 ppm. HRMS (ESI): calcd. for $C_{16}H_{21}BrNaO_3$ $[M+Na]^+$: 363.0566 found: 363.0565.

6.3 Synthetic Procedures and Data Associated with Chapter 4

6.3.1 Synthetic Procedures and Data for Compounds **42-51**

Preparation and Characterization of Secondary Allylic Alcohols

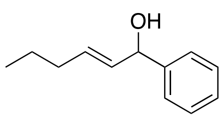


Synthesis of substrates **42-43** and **46-50**

To a 100 ml flame-dried round-bottom flask of aryl bromide (20 mmol) in THF (20 ml) was purged with nitrogen and cooled to -78 °C in an acetone/dry ice bath. *n*-BuLi (1.6 M in THF, 20 mmol) was added dropwise to the solution and stirred at -78 °C for 1 hour. Aldehyde (20 mmol) in THF (20 ml) was then added and the reaction was slowly warmed up to room temperature and stirred overnight. The mixture was quenched with saturated NH_4Cl solution, extracted with diethyl ether and dried over sodium sulfate. The solvent was removed under reduced pressure to yield the crude product, which was purified using flash column chromatography (Hex:EtOAc=10 :1).

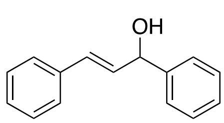
Synthesis of substrates **44** and **45**

To a 100 ml flame-dried round-bottom flask of aldehyde (20 mmol) in THF (20 ml) at -78 °C was slowly added *n*-BuLi (1.6 M in THF, 20 mmol) and maintained at this temperature for 1 h. The reaction was then warmed up to room temperature overnight and quenched with saturated NH_4Cl solution, extracted with diethyl ether and dried over sodium sulfate. The solvent was removed under reduced pressure, and the crude mixture was purified by flash column chromatography (Hex:EtOAc=10 :1).



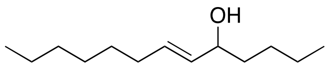
42

42: colorless oil. IR (film): 3345, 3085, 3062, 3029, 2958, 2929, 2872, 1493, 1453, 1379, 1338, 1193, 1192, 1072, 1030, 1005, 966, 914, 843, 757, 699, 634, 550 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.30-7.37 (m, 4 H), 7.22-7.26 (m, 1 H), 5.70-5.75 (m, 1 H), 5.61-5.66 (m, 1 H), 5.12 (d, *J*=6.65 Hz, 1 H), 2.23 (s, 1 H), 2.02 (q, *J*=7.08 Hz, 2 H), 1.40 (sext, *J*=7.37 Hz, 2 H), 0.89 (t, *J*=7.37 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 143.6, 132.6, 132.6, 128.5 (2 C), 127.5, 126.3 (2 C), 75.2, 34.3, 22.3, 13.8 ppm. HRMS (ESI): calcd. for $C_{12}H_{15}$ $[M+H-H_2O]^+$: 159.1168 found: 159.1173.



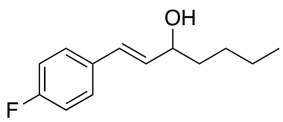
43

43: white solid. IR (film): 3340, 3059, 3082, 3027, 1600, 1494, 1449, 1391, 1300, 1191, 1092, 1067, 1009, 966, 915, 796, 745, 695, 638, 604, 544 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.21-7.42 (m, 10 H), 6.66-6.69 (m, 1 H), 6.35-6.40 (m, 1 H), 5.37 (d, *J*=5.90 Hz, 1 H), 2.10 (s, 1 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 142.9, 136.7, 131.7, 130.7, 128.8 (2 C), 128.7 (2 C), 127.9, 126.7 (2 C), 126.5 (2 C), 75.3 ppm. HRMS (ESI): calcd. for $C_{15}H_{13}$ $[M+H-H_2O]^+$: 193.1012 found: 193.1008.



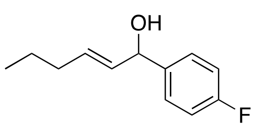
44

44: colorless oil. IR (film): 3341, 2957, 2927, 2857, 1467, 1378, 1005, 1025, 967, 727 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.59-5.65 (m, 1 H), 5.42-5.47 (m, 1 H), 4.02 (q, *J*=6.71 Hz, 1 H), 2.02 (q, *J*=7.08 Hz, 2 H), 1.70 (s, 1 H), 1.23-1.59 (m, 15 H), 0.89 (q, *J*=7.28 Hz, 6 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 133.2, 132.2, 73.3, 37.2, 32.3, 31.8, 29.3, 28.9, 28.9, 27.8, 22.7, 22.7, 14.2 ppm. HRMS (ESI): calcd. for $C_{13}H_{25}$ $[M+H-H_2O]^+$: 181.1951 found: 181.1943.



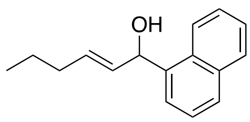
45

45: yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.28-7.31 (m, 2 H), 6.95-6.98 (m, 2 H), 6.49 (d, *J*=15.90 Hz, 1 H), 6.11 (dd, *J*=15.90, 6.80 Hz, 1 H), 4.21-4.25 (m, 1 H), 3.05 (s, 1H), 1.55-1.66 (m, 2 H), 1.30-1.38 (m, 4 H), 0.89 (t, *J*=7.00 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ =162.3 (d, *J*=247 Hz, 1 C), 133.0, 132.5, 128.9, 128.0, 128.0 (d, *J*=7.97 Hz, 2 C), 115.4 (d, *J*=21.6 Hz, 2 C), 73.0, 37.1, 27.7, 22.7, 14.0 ppm.



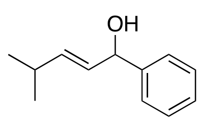
46

46: colorless oil. IR (film): 2243, 2960, 2930, 2873, 1604, 1509, 1464, 1412, 1379, 1223, 1156, 1086, 1042, 1013, 968, 866, 836, 586, 549 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.29-7.32 (m, 2 H), 6.98-7.02 (m, 2 H), 5.68-5.74 (m, 1 H), 5.57-5.62 (m, 1 H), 5.10 (d, *J*=6.80 Hz, 1 H), 2.33 (s, 1 H), 2.02 (q, *J*=7.15 Hz, 2 H), 1.40 (sext, *J*=7.38 Hz, 2 H), 0.89 (t, *J*=7.37 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 162.2 (d, *J*=245 Hz, 1 C), 139.3 (d, *J*=3.08 Hz, 1 C), 132.8, 132.5, 127.9 (d, *J*=8.07 Hz, 2 C), 115.2 (d, *J*=21.3 Hz, 2 C), 74.6, 34.3, 22.3, 13.8 ppm. HRMS (ESI): calcd. for $C_{12}H_{14}F[M+H-H_2O]^+$: 177.1074 found: 177.1083.



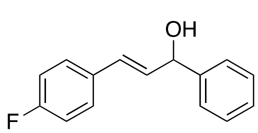
47

47: yellow oil. IR (film): 3335, 3049, 2957, 2928, 2871, 1597, 1510, 1456, 1436, 1395, 1378, 1260, 1228, 1165, 1092, 1074, 1049, 968, 798, 777, 734, 634, 570 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.10-8.12 (m, 1 H), 7.81-7.83 (m, 1 H),7.73-7.75 (m, 1 H), 7.58-7.60 (m, 1 H), 7.40-7.48 (m, 3 H), 5.77-5.82 (m, 3 H), 2.26 (s, 1 H), 1.97-2.01 (m, 2 H), 1.36 (sext, *J*=7.37 Hz, 2 H), 0.85 (t, *J*=7.37 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 139.0, 134.0, 133.1, 131.9, 130.7, 128.8, 128.3, 126.0, 125.6, 125.5, 124.0, 123.6 ppm. HRMS (ESI): calcd. for $C_{16}H_{17}$ $[M+H-H_2O]^+$: 209.1325 found: 209.1333.



48

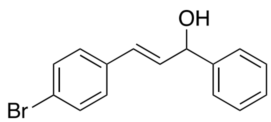
48: colorless oil. IR (film): 3351, 3062, 3029, 2959, 2929, 2869, 1666, 1493, 1465, 1451, 1383, 1364, 1305, 1221, 1193, 1102, 1059, 1007, 969, 915, 760, 699, 634, 547 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.22-7.35 (m, 5 H), 5.68-5.72 (m, 1 H), 5.55-5.60 (m, 1 H), 5.10 (d, *J*=6.80 Hz, 1 H), 2.45 (s, 1 H), 2.29 (oct, *J*=6.58 Hz, 1 H), 0.99 (d, *J*=6.75 Hz, 3 H), 0.98 (d, *J*=6.75 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 143.5, 139.5, 129.5, 128.5 (2 C), 127.4, 126.3 (2 C), 75.2, 30.7, 22.3, 22.2 ppm. HRMS (ESI): calcd. for $C_{12}H_{15}$ $[M+H-H_2O]^+$: 159.1168 found: 159.1172.



49

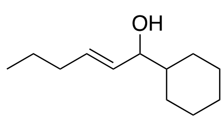
49: yellow oil. IR (film): 3335, 3030, 1601, 1559, 1540, 1508, 1455, 1418, 1228, 1158, 1070, 1013, 967, 857, 834, 763, 700, 668, 513 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.26- 7.41 (m, 7 H), 6.95-6.98 (m, 2 H), 6.58-6.62 (m, 1 H), 6.24-6.29 (m, 1 H), 5.32 (d, *J*=6.45 Hz, 1 H), 2.36 (s, 1 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 162.4 (d, *J*=247 Hz, 1 C), 142.8, 132.8, 131.4, 129.3, 128.6 (2 C), 128.2 (d, *J*=8.02

Hz, 2 C), 127.8, 126.4 (2 C), 115.5 (d, *J*=21.6 Hz, 2 C), 74.9 ppm. HRMS (ESI): calcd. for $C_{15}H_{12}F$ [M+H-H_2O]$^+$: 211.0918 found: 211.0927.



50

50: white solid. IR (film): 3334, 3061, 3028, 1653, 1559, 1487, 1453, 1419, 1400, 1298, 1190, 1071, 1008, 967, 850, 818, 790, 762, 699, 658, 634, 559 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.23-7.43 (m, 9 H), 6.61-6.64 (m, 1 H), 6.35-6.39 (m, 1 H), 5.37 (d, *J*=5.90 Hz, 1 H), 2.06 (s, 1 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 142.7, 135.6, 132.4, 131.8 (2 C), 129.4, 128.8 (2 C), 128.3 (2 C), 128.1, 126.5 (2 C), 121.7, 75.1 ppm. HRMS (ESI): calcd. for $C_{15}H_{12}Br$ [M+H-H_2O]$^+$: 271.0117 found: 271.0121.



51

51: colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.55-.61 (m, 1 H), 5.42-5.47 (m, 1 H), 3.75 (t, *J*=7.00 Hz, 1 H), 2.18 (s, 1 H), 1.99-2.04 (m, 2 H), 1.84-1.88 (m, 1 H), 1.70-1.75 (m, 2 H), 1.64-1.68 (m, 2 H), 1.35-1.42 (m, 3 H), 1.16-1.25 (m, 2 H), 0.94-1.00 (m, 2 H), 0.90 (t, *J*=7.37 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 132.5, 131.8, 77.6, 43.7, 34.4, 28.8, 28.8, 26.6, 26.2, 22.4, 13.6 ppm.

6.3.2 Synthetic Procedures and Data for Compounds **52-64**

General Procedure for the Enantioselective Epoxidation of Secondary Allylic Alcohols

Method a: Titanium-Tartrate Catalyzed Enantioselective Epoxidation

To a room temperature solution of substrate (1 mmol) and L-(+)-DIPT (28 mg, 0.12 mmol) in CH_2Cl_2 (4 ml) was added activated 3 Å molecular sieves (30 wt % of substrate) and cooled to -

20 °C for 10 min. $Ti(OiPr)_4$ (30 μl, 0.1 mmol) was added and stirred at -20 °C for 20-30 min. *tert*-Butyl hydroperoxide (127 μl, 0.7 mmol, ~5.5 M in decane) was added dropwise until 50 % conversion indicated by TLC analysis. The reaction was quenched with 6 ml of an aqueous solution (50 ml) of ammonia iron sulfate heptahydrate (16.5 g) and L-tartaric acid (5 g) at room temperature, and stirred vigorously until phase separation. The organic layer was dried over sodium sulfate and concentrated *in vacuo*. The product was purified by preparatory TLC (Hexane:EtOAc = 10:1). Procedure was similar to previous literature.[60]

Method b: Titanium-Tartrate Catalyzed Enantioselective Epoxidation

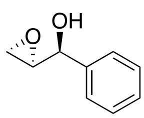
Similar to method A, except D-(-)-DIPT was used.

Method c: Tungsten-BHA Catalyzed Asymmetric Epoxidation

To a test tube was added substrate (0.4 mmol), (*R*, *R*)-**L3** (17 mg, 0.012 mmol), $WO_2(acac)_2$ (4.1 mg, 0.01 mmol), NaCl (12 mg, 0.2 mmol) and CH_2Cl_2 (4 ml). H_2O_2 (30 wt %, 0.8 mmol) was added (solution turned from murky yellow to clear light yellow color after 10 min) and the reaction was stirred at room temperature for 24 hours. The mixture was diluted with CH_2Cl_2, dried over sodium sulfate and concentrated *in vacuo*. The crude product was purified using flash chromatography (Hexane:EtOAc = 10:1). The procedure was same as previous literature.[58]

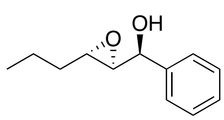
Method d: Hafnium-BHA Catalyzed Asymmetric Epoxidation

To a flame-dried test tube was added (*R*, *R*)-**L2** (0.055 mmol, 29.4 mg) and MgO (0.2 mmol, 8 mg). $Hf(OtBu)_4$ (0.05 mmol, 20.2 μl, fresh out of the glove box) was dissolved in toluene (2.5 ml) and added to the test tube with **L2**, and stirred at room temperature for 2 h. Substrate (1 mmol) in toluene (2.5 ml) was added to complex at room temperature and cooled to 0 °C, cumene peroxide (80 %, 1 mmol, 184 µl) was added at once and stirred at 0 °C until approximately 50 % conversion. The mixture was quenched with methanol, filtered over a plug of silica, and concentrated *in vacuo*. The residue was purified by flash chromatography (100 % CH_2Cl_2) to furnish the epoxide. The procedure was similar to previous literature.[57]



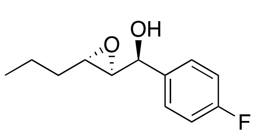
52

Asymmetric epoxidation, method a, 15 h. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.33-7.41 (m, 5 H), 4.94 (d, *J*=2.75 Hz, 1 H), 3.23-3.25 (m, 1 H), 2.96-2.98 (m, 1 H), 2.76-2.77 (m, 1 H), 2.30 (s, 1 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 139.5, 128.8 (2 C), 128.4, 126.5 (2 C), 70.8, 55.2, 43.6 ppm. HRMS (ESI): calcd. for C_9H_9O $[M+H]^+$ [-H_2O]: 133.0648 found: 133.0649.



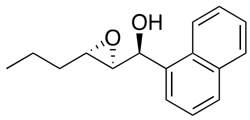
53

Asymmetric epoxidation: method a, 2 h, 50 % yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.31-7.38 (m, 5 H), 4.86 (d, *J*=3.05 Hz, 1 H), 3.16-3.18 (m, 1 H), 2.96-2.97 (m, 1 H), 2.46 (s, 1 H), 1.35-1.55 (m, 4 H), 0.87 (t, *J*=7.25 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 139.8, 128.7 (2 C), 128.3, 126.5 (2 C), 71.1, 61.4, 55.2, 33.6, 19.4, 13.9 ppm. HRMS (ESI): calcd. for $C_{12}H_{16}$ Na O_2 $[M+Na]^+$: 215.1043 found: 215.1007.



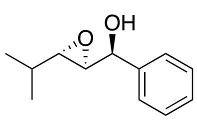
55

Asymmetric epoxidation: method a, 1 h, 43 % yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.34-7.37 (m, 2 H), 7.04-7.07 (m, 2 H), 4.84 (d, *J*=2.95 Hz, 1 H), 3.13-3.16 (m, 1 H), 2.93-2.94 (m, 1 H), 2.54 (s, 1 H), 1.36-1.57 (m, 4 H), 0.88 (t, *J*=7.22 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 162.7 (d, *J*=246 Hz, 1 C), 135.6, 128.2 (d, *J*=8.16 Hz, 2 C), 115.6 (d, *J*=21.5 Hz, 2 C) 70.6, 61.3, 55.2, 33.6, 19.4, 13.9 ppm. HRMS (ESI): calcd. for $C_{15}H_{18}NO_2$ $[M+H]^+[-H_2O]$: 193.1023 found: 193.1017.



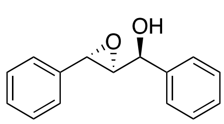
56

Asymmetric epoxidation: method a, 1 h, 39 % yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.09 (d, *J*=8.40 Hz, 1 H), 7.87 (d, *J*=7.85 Hz, 1 H), 7.81 (d, *J*=8.25 Hz, 1 H), 7.64 (d, *J*=7.10 Hz, 1 H), 7.46-7.54 (m, 3 H), 5.67 (d, *J*=2.50 Hz, 1 H), 3.18-3.22 (m, 2 H), 2.68 (s, 1 H), 1.34-1.1.50 (m, 4 H), 0.82 (t, *J*=7.27 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 135.6, 133.9, 130.9, 129.0, 128.7, 126.4, 125.8, 125.6, 123.8, 123.1, 67.6, 60.9, 55.5, 33.6, 19.3, 13.8 ppm. HRMS (ESI): calcd. for $C_{16}H_{19}O_2$ $[M+H]^+$: 243.1380 found: 243.1381.



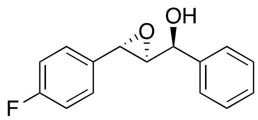
57

Asymmetric epoxidation: method a, 80 min, 52 % yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.29-7.39 (m, 5 H), 4.85 (d, *J*=2.45 Hz, 1 H), 2.97-2.99 (m, 2 H), 2.53 (s, 1 H), 1.49-1.54 (m, 1 H), 0.99 (t, *J*=6.70 Hz, 3 H), 0.85 (t, *J*=6.90 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 139.9, 128.7 (2 C), 128.3, 126.6 (2 C), 71.1, 60.6, 60.5, 30.1, 19.1, 18.4 ppm. HRMS (ESI): calcd. for $C_{12}H_{17}O_2$ $[M+H]^+$: 193.1223 found: 193.1201.



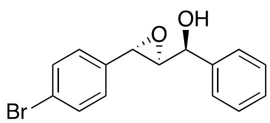
58

Asymmetric epoxidation: method a, 3 h, 48 % yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.24-7.38 (m, 10 H), 4.99 (s, 1 H), 4.14 (d, *J*=1.95 Hz, 1 H), 3.28-3.29 (m, 1 H), 2.55 (d, *J*=2.05 Hz, 1 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 139.3, 136.6, 128.8 (2 C), 128.6 (2 C), 128.5, 128.4, 126.7 (2 C), 125.9 (2 C), 71.3, 65.1, 55.1 ppm. HRMS (ESI): calcd. for $C_{15}H_{14}NaO_2$ $[M+Na]^+$: 249.0886 found: 249.0881.



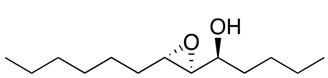
59

Asymmetric epoxidation: method a, 80 min, 39 % yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.99-7.41 (m, 9 H), 5.00 (d, *J*=2.75 Hz, 1 H), 4.12 (d, *J*=1.80 Hz, 1 H), 3.25-3.26 (m, 1 H), 2.45 (s, 1 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 162.9 (d, *J*=247 Hz, 1 C), 139.3, 132.4, 128.9 (2 C), 128.6, 127.6 (d, *J*=8.31 Hz, 2 C), 126.7 (2 C), 115.7 (d, *J*=21.7 Hz, 2 C), 71.3, 65.1, 54.6 ppm. HRMS (ESI): calcd. for $C_{15}H_{13}FNaO_2$ $[M+Na]^+$: 267.0792 found: 267.0806.



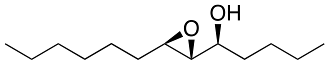
60

Asymmetric epoxidation: method a, 1 h, 33 % yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.30-7.41 (m, 7 H), 7.11 (d, *J*=8.40 Hz, 2 H), 5.00 (s, 1 H), 4.09 (d, *J*=1.85 Hz, 1 H), 3.22-3.23 (m, 1 H), 2.51 (s, 1 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 139.2, 135.8, 131.8 (2 C), 128.9 (2 C), 128.6, 127.5 (2 C), 126.6 (2 C), 122.3, 71.3, 65.2, 54.6 ppm. HRMS (ESI): calcd. for $C_{15}H_{13}BrNaO_2$ $[M+Na]^+$: 326.9991 found: 327.0046.



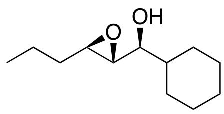
61

Asymmetric epoxidation: method a, 25 min, 44 % yield, 98:2 dr, major diastereomer *anti*-epoxy alcohol isolated for aminolysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.78-3.79 (m, 1 H), 2.98-3.01 (m, 1 H), 2.76-.2.77 (m, 1 H), 2.00-2.01 (m, 1 H), 1.30-1.59 (m, 16 H), 0.87-0.94 (m, 6 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 68.6, 61.2, 55.1, 33.4, 31.9, 31.7, 29.2, 27.6, 26.1, 22.9, 22.7, 14.2, 14.1 ppm. HRMS (ESI): calcd. for $C_{13}H_{27}O_2$ $[M+H]^+$: 215.2006 found: 215.1987.



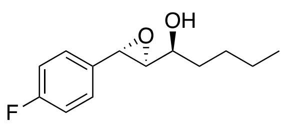
62

Asymmetric epoxidation: method d, 15 h (0 °C) + 3 h (r.t.), 56 % yield, 1:2 dr, major diastereomer *syn*-epoxy alcohol isolated for aminolysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.44-3.45 (m, 1 H), 2.91-2.92 (m, 1 H), 2.72-2.74 (m, 1 H), 1.95 (m, 1 H), 1.55-1.58 (m, 4 H), 1.27-1.46 (m, 12 H), 0.87-0.93 (m, 6 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 71.6, 62.0, 57.2, 34.2, 31.9, 31.8, 29.2, 27.6, 26.1, 22.8, 22.7, 14.2, 14.1ppm.



63

Asymmetric epoxidation: method d, 24 h (r.t.), 49 % yield, 32:68 dr, major diastereomer *syn*-epoxy alcohol was isolated for aminolysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.59 (s, 1 H), 3.01-3.01 (m, 1 H), 2.82-2.83 (m, 1 H), 1.89 (s, 1 H), 1.14-1.76 (m, 14 H), 0.98 (t, *J*=7.17 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 72.5, 59.7, 55.0, 41.8, 33.8, 29.0, 28.4, 26.6, 26.3, 19.5, 14.1 ppm. HRMS (ESI): calcd. for $C_{12}H_{23}O_2$ $[M+H]^+$: 199.1693 found: 199.1675.



64

Asymmetric epoxidation method a, 3 h, 49 % yield, 93:7 dr, major diastereomer *anti*-epoxy alcohol was isolated for aminolysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.23-7.26 (m, 2 H), 7.02-7.05 (m, 2 H), 3.93-3.95 (m, 1 H), 3.03-3.04 (m, 1 H), 2.12 (s, 1 H), 1.33-1.64 (m, 6 H), 0.91 (t, *J*=7.22 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 162.9 (d, *J*=247 Hz, 1 C), 132.9, 127.5 (d, *J*=8.27 Hz, 2 C), 115.6 (d, *J*=21.8 Hz, 2 C), 68.6, 65.1, 54.2, 33.2, 27.5, 22.8, 14.1 ppm. HRMS (ESI): calcd. for $C_{13}H_{18}FO_2$ $[M+H]^+$: 225.1285 found: 225.1252.

6.3.2 Synthetic Procedures and Data for Compounds **65-83**

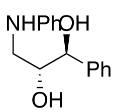
General Procedure for the Kinetic Resolution of Secondary Epoxy-Alcohols By Tungsten-Catalyzed Asymmetric Ring-Opening

Method e: Tungsten-Catalyzed Kinetic Resolution of Secondary Epoxy-Alcohols

To a THF (2 ml) solution of substrate (0.15 mmol for all, except 0.2 mmol for **62** and **63**), $W(OEt)_6$ (4.5 mg, 0.01 mmol) and (*S*, *S*)-**L3** was added H_2O_2 (2.2 µl, 0.02 mmol, 30 wt %) at stirred at 55 °C for 1.5 h. Amine (0.1 mmol) was added to reaction and it was stirred at 55 °C until completion. The product was purified using preparatory TLC (Hexane:EtOAc = 4:1). Procedure was similar to previous literature.[48]

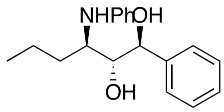
Method f: Tungsten-Catalyzed Kinetic Resolution of Secondary Epoxy-Alcohols

Similar to method e, except (*R*, *R*)-**L3** was used.



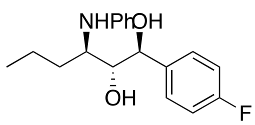
65

Enantioselective aminolysis: method e, 24 h, **65** was isolated as a yellow oil (34 mg, 69 %). IR (film): 3391, 3054, 2922, 1603, 1502, 1452, 1432, 1320, 1257, 1061, 751, 694, 509 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.31-7.38 (m, 5 H), 7.13-7.16 (m, 2 H), 6.71-6.74 (m, 1 H), 6.57-6.59 (m, 2 H), 4.85 (d, *J*=5.10 Hz, 1 H), 3.97-4.01 (m, 1 H), 3.96 (s, 1 H), 3.22-3.93 (m, 1 H), 3.14-3.18 (m, 1 H), 2.81 (s, 1 H), 2.51(s, 1 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 148.2, 140.3, 129.4 (2 C), 128.8 (2 C), 128.3, 126.5 (2 C), 118.4, 113.8 (2 C), 76.0, 73.4, 45.5 ppm. HRMS (ESI): calcd. for $C_{15}H_{18}NO_2$ [M+H]$^+$: 244.1332 found: 244.1332.



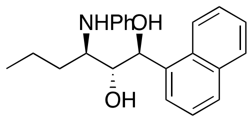
66

Enantioselective aminolysis: method e, 48 h, **66** was isolated as a white solid (27.3 mg, 94 %). IR (film): 3402, 3054, 3029, 2957, 2930, 2871, 1601, 1504, 1453, 1431, 1379, 1318, 1260, 1181, 1154, 1102, 1035, 910, 749, 694, 624, 508 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.31-7.39 (m, 5 H), 7.13-7.16 (m, 2 H), 6.69-6.72 (m, 1 H), 6.58-6.60 (m, 2 H), 4.71 (d, *J*=7.30 Hz, 1 H), 3.81-3.83 (m, 1 H), 3.67-3.69 (m, 1 H), 3.57 (s, 1 H), 2.88 (s, 1 H), 1.82 (s, 1 H), 1.76-1.77 (m, 1 H), 1.47-1.51 (m, 2 H), 1.32-1.33 (m, 1 H), 0.90 (t, *J*=7.27 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 147.7, 141.3, 129.5 (2 C), 128.8 (2 C), 128.5, 127.2 (2 C), 117.9, 114.0 (2 C), 76.0, 75.5, 55.0, 32.3, 19.3, 14.4 ppm. HRMS (ESI): calcd. for $C_{18}H_{24}NO_2$ $[M+H]^+$: 286.1802 found: 286.1797.



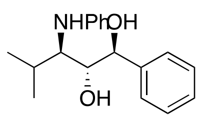
68

Enantioselective aminolysis: method e, 24 h, **68** was isolated as a yellow oil (27.4 mg, 91 %). IR (film): 3400. 2958, 2931, 2871, 1602, 1509, 1467, 1431, 1380, 1317, 1224, 1156, 1035, 837, 786, 751, 693, 573 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.33-7.36 (m, 2 H), 7.14-7.17 (m, 2 H), 7.02-7.05 (m, 2 H), 6.70-6.73 (m, 1 H), 6.58-6.60 (m, 2 H), 4.72 (d, *J*=7.20 Hz, 1 H), 3.76-3.78 (m, 1 H), 3.62 (m, 1 H), 3.56 (s, 1 H), 2.99 (s, 1 H), 1.87 (s, 1 H), 1.74-1.77 (m, 1 H), 1.45-1.52 (m, 2 H), 1.30-1.32 (m, 1 H), 0.89 (t, *J*=7.27 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 162.8 (d, *J*=246 Hz, 1 C), 147.5, 137.1, 129.5 (2 C), 129.0 (d, *J*=8.07 Hz, 2 C), 118.2 (2 C), 115.6 (d, *J*=21.4 Hz, 2 C), 114.1 (2 C), 75.6, 75.4, 55.2, 32.5, 19.2, 14.3 ppm. HRMS (ESI): calcd. for $C_{18}H_{23}FNO_2$ $[M+H]^+$: 304.1707 found: 304.1711.



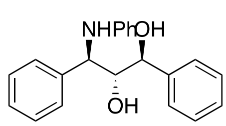
69

Enantioselective aminolysis: method e, 44 h, **69** was isolated as an orange oil (19.6 mg, 58 %). IR (film): 3402, 3051, 2957, 2929, 2870, 1601, 1503, 1462, 1431, 1319, 1260, 1180, 1154, 1036, 992, 909, 801, 780, 749, 693 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.18-8.20 (m, 1 H), 7.86-7.88 (m, 1 H), 7.81 (d, *J*=8.25 Hz, 1 H), 7.69 (d, *J*=7.10 Hz, 1 H), 7.45-7.50 (m, 3 H), 7.08 (t, *J*=7.90 Hz, 2 H), 6.66 (t, *J*=7.32 Hz, 1 H), 6.51 (d, *J*=7.75 Hz, 2 H), 5.52 (d, *J*=7.65 Hz, 1 H), 4.14-4.17 (m, 1 H), 3.73-3.75 (m, 1 H), 1.84-1.90 (m, 1 H), 1.47-1.58 (m, 2 H), 1.29-1.38 (m, 1 H), 0.90 (t, *J*=7.25 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 147.7, 137.2, 134.0, 131.4, 129.4 (2 C), 129.0, 128.9, 126.4, 125.9, 125.6, 124.8, 123.8, 117.8, 113.9 (2 C), 75.2, 73.3, 55.1, 31.9, 19.5, 14.3 ppm. HRMS (ESI): calcd. for $C_{22}H_{26}NO_2$ $[M+H]^+$: 336.1958 found: 336.1948.



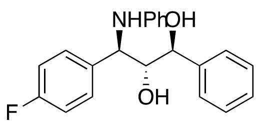
70

Enantioselective aminolysis: method e, 48 h, **70** was isolated as a yellow oil (4 mg, 14 %). IR (film): 3400, 3056, 3028, 2958, 2926, 2871, 1600, 1511, 1496, 1462, 1452, 1384, 1300, 1253, 1065, 1037, 748, 693 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.36-7.42 (m, 5 H), 7.16-7.20 (m, 2 H), 6.74-6.77 (m, 1 H), 6.65-6.67 (m, 2 H), 4.86 (d, *J*=6.25 Hz, 1 H), 3.84-3.86 (m, 1 H), 3.47-3.49 (m, 1 H), 2.24-2.29 (m, 1 H), 0.99 (d, *J*=6.85 Hz, 1 H), 0.94 (d, *J*=6.95 Hz, 1 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ =148.4, 140.8, 129.5 (2 C), 128.8 (2 C), 128.5, 127.8 (2 C), 118.4, 114.5 (2 C), 76.8, 75.2, 61.6, 30.1, 20.8, 17.1 ppm. HRMS (ESI): calcd. for $C_{18}H_{24}NO_2$ $[M+H]^+$: 286.1802 found: 286.1794.



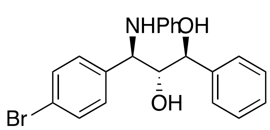
71

Enantioselective aminolysis: method e, 24 h, **71** was isolated as a yellow oil (32.7 mg, 81 %). IR (film): 3541, 3412, 3058, 3029, 2922, 1601, 1503, 1453, 1431, 1391, 1315, 1250, 1180, 1078, 1036, 910, 751, 733, 701, 668, 606, 648, 578 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.42-7.44 (m, 2 H), 7.31-7.34 (m, 7 H), 7.24-7.27 (m, 1 H), 7.06-7.09 (m, 2 H), 6.63-6.66 (m, 1 H), 6.53-6.55 (m, 2 H), 4.80 (d, *J*=4.80 Hz, 1 H), 4.37 (d, *J*=7.75 Hz, 1 H), 4.09 (dd, *J*=7.72, 4.77 Hz, 1 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 146.7, 141.0, 139.1, 129.2 (2 C), 128.8 (2 C), 128.6 (2 C), 128.6, 128.3 (4 C), 127.8, 127.4 (2 C), 118.0, 114.2, 77.0, 75.4, 59.2 ppm. HRMS (ESI): calcd. for $C_{21}H_{22}NO_2$ $[M+H]^+$: 320.1645 found: 320.1634.



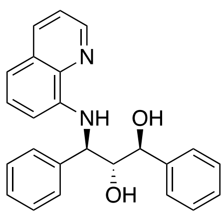
72

Enantioselective aminolysis: method e, 24 h, **72** was isolated as a yellow oil (26.2 mg, 78 %). IR (film): 3400, 3053, 2922, 1601, 1509, 1503, 1452, 1432, 1315, 1222, 1157, 1089, 832, 750, 693 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.31-7.45 (m, 8 H), 7.00-7.10 (m, 4 H), 6.64-6.67 (m, 1 H), 6.53-6.55 (m, 2 H), 4.83 (dd, *J*=7.92, 4.42 Hz, 1 H), 4.68 (d, *J*=8.05 Hz, 1 H), 4.30 (dd, *J*=8.05, 2.70 Hz, 1 H), 4.09 (dt, *J*=9.12, 4.09 Hz, 1 H), 2.28 (d, *J*=3.05 Hz, 1 H), 1.53 (d, *J*=4.80 Hz, 1 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 162.4 (d, *J*=246 Hz, 1 C), 146.6, 140.9, 134.7, 130.0 (d, *J*=8.01 Hz, 2 C), 129.3 (2 C), 129.0 (2 C), 128.8, 127.4 (2 C), 118.1, 115.4 (d, *J*=21.3 Hz, 2 C), 114.1 (2 C), 77.0, 75.4, 58.3 ppm. HRMS (ESI): calcd. for $C_{21}H_{21}FNO_2$ $[M+H]^+$: 338.1551 found: 338.1545.



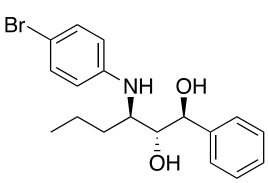
73

Enantioselective aminolysis: method e, 24 h, **73** was isolated as a white solid (31 mg, 78 %). IR (film): 3540, 3413, 3031, 2912, 1601, 1502, 1486, 1453, 1433, 1408, 1391, 1315, 1250, 1207, 1180, 1155, 1072, 1011, 909, 872, 847, 823, 793, 749, 734, 694, 613, 576 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.43-7.44 (m, 2 H), 7.29-7.34 (m, 7 H), 7.06-7.09 (m, 2 H), 6.64-6.67 (m, 1 H), 6.50-6.52 (m, 2 H), 4.80 (d, *J*=3.45 Hz, 1 H), 4.69 (s, 1 H), 4.25 (d, *J*=8.10 Hz, 1 H), 4.07 (dd, *J*=8.07, 4.07 Hz, 1 H), 2.30 (s, 1 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 146.4, 140.8, 138.1, 131.6 (2 C), 130.3 (2 C), 129.3 (2 C), 129.0 (2 C), 128.8, 127.4 (2 C), 121.6, 118.1, 114.0 (2 C), 76.9, 75.3, 58.3 ppm. HRMS (ESI): calcd. for $C_{21}H_{21}BrNO_2$ $[M+H]^+$: 398.0750 found: 398.0707.



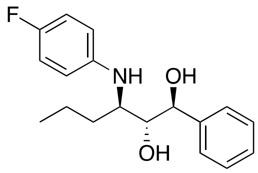
74

Enantioselective aminolysis: method e, 65 h, **74** was isolated as a yellow oil (11 mg, 30 %). IR (film): 3396, 2923, 1653, 1576, 1540, 1519, 1479, 1456, 1379, 818, 790, 736, 702, 589 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.71 (dd, *J*=4.17, 1.52 Hz, 1 H), 8.03 (dd, *J*=8.25, 1.55 Hz, 1 H), 7.53 (d, *J*=7.30 Hz, 2 H), 7.21-7.39 (m, 10 H), 7.01 (d, *J*=7.90 Hz, 1 H), 6.53 (d, *J*=7.45 Hz, 1 H), 4.88 (m, 1H), 4.63 (d, *J*=7.25 Hz, 1 H), 4.34 (dd, *J*=7.20, 5.40 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 147.2, 143.2, 140.9, 139.9, 139.2, 138.7, 136.1, 128.7 (2 C), 128.6 (2 C), 128.5, 128.4 (2 C), 127.8, 127.7, 127.5 (2 C), 121.5, 114.7, 106.8, 77.3, 75.3, 58.8 ppm. HRMS (ESI): calcd. for $C_{24}H_{23}N_2O_2$ $[M+H]^+$: 371.1754 found: 371.1726.



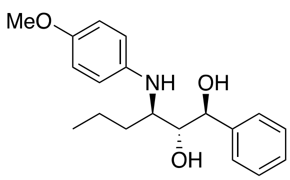
75

Enantioselective aminolysis: method e, 48 h, **75** was isolated as a white solid (34.9 mg, 96 %). I13.0813R (film): 3407, 2957, 2928, 2871, 1594, 1495, 1454, 1400, 1318, 1294, 1257, 1179, 1097, 1074, 1035, 908, 813, 767, 733, 702, 556 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.33-7.38 (m, 5 H), 7.20-7.22 (m, 2 H), 6.44-6.46 (m, 2 H), 4.71 (d, *J*=7.35 Hz, 1 H), 3.81-3.82 (m, 1 H), 3.65 (m, 1 H), 2.47 (s, 1 H), 1.76-1.80 (m, 1 H), 1.46-1.53 (m, 2 H), 1.30-1.37 (m, 1 H), 0.91 (t, *J*=7.27 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 146.7, 141.1, 132.0 (2 C), 128.8 (2 C), 128.5, 127.0 (2 C), 115.2 (2 C), 109.0, 75.6, 75.5, 54.4, 31.9, 19.3, 14.2 ppm. HRMS (ESI): calcd. for $C_{18}H_{23}BrNO_2$ $[M+H]^+$ 364.0907 found: 364.0916.



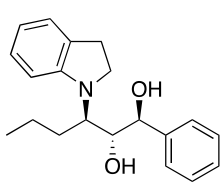
76

Enantioselective aminolysis: method e, 48 h, **76** was isolated as a white solid (29.7 mg, 98 %). IR (film): 3400, 2958, 2931, 2871, 1510, 1453, 1316, 1220, 1155, 1035, 821, 766, 702, 509 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.32-7.38 (m, 5 H), 6.84-6.87 (m, 2 H), 6.51-6.53 (m, 2 H), 4.70 (d, *J*=7.35 Hz, 1 H), 3.77 (dd, *J*=7.07, 4.52 Hz, 1 H), 3.57-3.59 (m, 1 H), 1.74-1.76 (m, 1 H), 1.46-1.51 (m, 2 H), 1.30-1.33 (m, 1 H), 0.90 (t, *J*=7.27 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 156.1 (d, *J*=236 Hz, 1 C), 144.0, 141.3, 128.8 (2 C), 128.5, 127.2 (2 C), 115.9 (d, *J*=22.2 Hz, 2 C), 115.0 (d, *J*=7.38 Hz, 2 C), 76.1, 75.4, 56.0, 32.3, 19.3, 14.3 ppm. HRMS (ESI): calcd. for $C_{18}H_{23}FNO_2$ $[M+H]^+$: 304.1707 found: 304.1656.



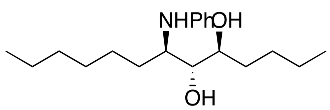
77

Enantioselective aminolysis: method e, 48 h, **77** was isolated as a colorless oil (31 mg, 98 %). IR (film): 3405, 2956, 2871, 2833, 1512, 1453, 1409, 1238, 1180, 1149, 1100, 1038, 910, 821, 765, 734, 702, 518 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.30-7.40 (m, 5 H), 6.75-6.76 (m, 2 H), 6.58-6.60 (m, 2H), 4.71 (d, *J*=7.30 Hz, 1 H), 3.74-3.76 (m, 4 H), 3.54 (s, 1 H), 3.47 (m, 1 H), 3.30-3.31 (m, 1 H), 1.84 (d, *J*=4.35 Hz, 1 H), 1.71-1.77 (m, 1 H), 1.43-1.52 (m, 2 H), 1.26-1.35 (m, 1 H), 0.88 (t, *J*=7.25 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 152.8, 141.5, 141.4, 128.7 (2 C), 128.4, 127.3 (2 C), 116.0 (2 C), 115.1 (2 C), 76.6, 75.3, 57.2, 55.9, 32.7, 19.1, 14.4 ppm. HRMS (ESI): calcd. for $C_{19}H_{26}NO_3$ $[M+H]^+$: 316.1907 found: 316.1890.



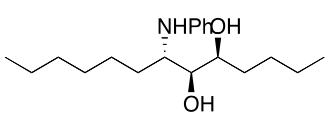
78

Enantioselective aminolysis: method e, 48 h, **78** was isolated as a colorless oil (30.5 mg, 98 %). IR (film): 3410, 2956, 2929, 2870, 1606, 1490, 1475, 1461, 1454, 1402, 1329, 1263, 1193, 1024, 742, 702, 585, 543, 513 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.30-7.34 (m, 5 H), 7.04 (d, *J*=7.10 Hz, 1 H), 6.98 (t, *J*=7.67 Hz, 1 H), 6.59 (t, *J*=7.30 Hz, 1 H), 6.23 (d, *J*=7.90 Hz, 1 H), 4.77 (dd, *J*=5.75, 2.95 Hz, 1 H), 3.95 (q, *J*=5.78 Hz, 1 H), 3.48-3.54 (m, 2 H), 3.43 (q, *J*=9.10 Hz, 1 H), 3.05 (s, 1 H), 2.88-3.01 (m, 2 H), 1.80 (s, 1 H), 1.67-1.77 (m, 2 H), 1.15-1.31 (m, 2 H), 0.83 (t, *J*=7.35 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 151.4, 140.4, 129.3, 128.6 (2 C), 128.4, 127.6 (2 C), 127.3, 124.6, 117.1, 107.1, 76.7, 76.1, 56.5, 47.3, 29.9, 28.5, 20.5, 14.4 ppm. HRMS (ESI): calcd. for $C_{20}H_{26}NO_2$ $[M+H]^+$: 312.1958 found: 312.1948.



79

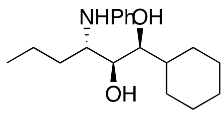
Enantioselective aminolysis: method e, 4 d. **79** was isolated as a colorless solid (10 mg, 33 % yield) IR (film): 3383, 2956, 2927, 2855, 1601, 1510, 1466, 1432, 1378, 1324, 1262, 1130, 1073, 992 747, 692 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.15-7.18 (m, 2 H), 6.69-6.72 (m, 1 H), 6.64-6.66 (m, 2 H), 3.65-3.72 (m, 2 H), 3.607-3.613 (m, 1 H), 2.02 (s, 1 H), 1.69-1.79 (m, 2 H), 1.58 (s, 1 H), 1.21-1.50 (m, 14 H), 0.91 (t, *J*=7.10 Hz, 3 H), 0.85 (t, *J*=6.82 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 147.9, 129.6 (2 C), 117.9, 113.8 (2 C), 75.3, 73.1, 55.4, 33.3, 31.9, 30.1, 29.6, 27.9, 26.2, 22.9, 22.7, 14.2, 14.2 ppm. HRMS (ESI): calcd. for $C_{19}H_{34}NO_2$ $[M+H]^+$: 308.2584 found: 308.2596.



80

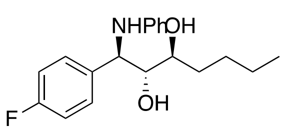
Enantioselective aminolysis: method f (W(OEt)$_6$/(*R*,*R*)-**L3** / H_2O_2 / aniline / substrate = 0.2/0.24/0.2/1/2), 48 h. **80** was isolated as a yellow oil (16 mg, 52 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.15-7.18 (m, 2 H), 6.67-6.73 (m, 3 H), 3.75-3.78 (m, 1 H), 3.56-3.60 (m, 1 H), 3.49-3.50 (m, 1

H), 2.60 (s, 1 H), 1.21-1.60 (m, 17 H), 0.92 (t, *J*=7.05 Hz, 3 H), 0.85 (t, *J*=6.95 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 148.4, 129.5 (2 C), 118.0, 113.9 (2 C), 74.1, 71.3, 57.0, 34.1, 31.8, 31.8, 29.5, 28.0, 26.3, 22.8, 22.7, 14.2, 14.2 ppm.



81

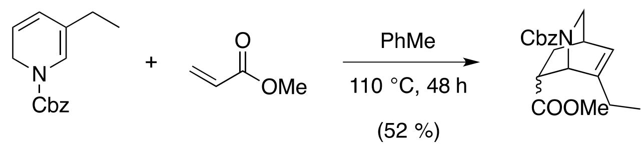
Enantioselective aminolysis: method f (W(OEt)$_6$/(*R*,*R*)-**L3** / H_2O_2 / aniline / substrate = 0.2/0.24/0.2/1/2), 48 h. **81** was isolated as a yellow oil (10 mg, 35%). IR (film): 3393, 2922, 2851, 1601, 1501, 1450, 1033, 791, 745, 692 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ =7.15-7.18 (m, 2 H), 6.68-6.73 (m, 3 H), 3.69 (m, 1 H), 3.59-3.63 (m, 1 H), 3.45-3.47 (m, 1 H), 2.63 (s, 1 H), 2.62 (s, 1 H), 1.00-1.93 (m, 14 H), 0.91 (t, *J*=7.30 Hz, 1 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ =148.6, 129.5 (2 C), 118.0, 114.0 (2 C), 75.2, 71.1, 57.4, 40.9, 34.5, 29.6, 28.9, 26.5, 26.2, 26.1, 19.6, 14.3 ppm. HRMS (ESI): calcd. for $C_{18}H_{30}NO_2$ [M+H]$^+$: 292.2271 found: 292.2270.



82

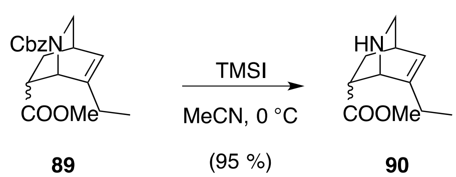
Enantioselective aminolysis: method e, 4 d. **82** was isolated as a yellow oil (12 mg, 38 %). IR (film): 3399, 2927, 2858, 1603, 1507, 1432, 1315, 1223, 1157, 1049, 840, 750, 693 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ =7.40-7.43 (m, 2 H), 7.08-7.11 (m, 2 H), 7.01-7.04 (m, 2 H), 6.65-6.68 (m, 1 H), 6.55-6.56 (m, 2 H), 4.77 (d, *J*=4.45 Hz, 1 H), 3.79 (m, 1 H), 3.35-3.38 (m, 1 H), 1.66 (s, 1 H), 1.56 (s, 1H), 1.42-1.48 (m, 2 H), 1.27-1.34 (m, 4 H), 0.89 (t, *J*=7.12 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ =162.5 (d, *J*=246 Hz, 1 C), 146.6, 134.8, 129.7 (d, *J*=7.99 Hz, 2 C), 129.3 (2 C), 118.1, 115.8 (d, *J*=21.3 Hz, 2 C), 114.0 (2 C), 77.0, 73.1, 58.8, 33.4, 27.6, 22.9, 14.1 ppm. HRMS (ESI): calcd. for $C_{19}H_{25}FNO_2$ [M+H]$^+$: 318.1864 found: 318.1854.

6.4 Synthetic Procedures and Data Associated with Chapter 5



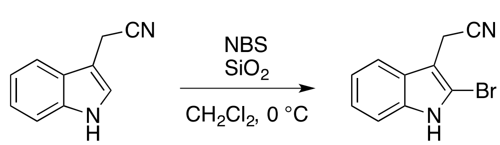
88 **89**

To a solution of **88** (24.5 mmol, 5.95 g) in anhydrous toluene (0.4 M, 61 ml) was added methyl acrylate (490 mmol, 44.1 ml) at room temperature. The solution was degassed three times and purged with nitrogen. The reaction mixture was heated to reflux for 48 h when it turned yellow, cooled to room temperature and filtered through a pad of silica. The crude mixture was concentrated *in vacuo* and purified by flash chromatography (Hex:EtOAc = 10 : 1) to give **89** (4.19 g, 52 %) as a faint yellowish oil.



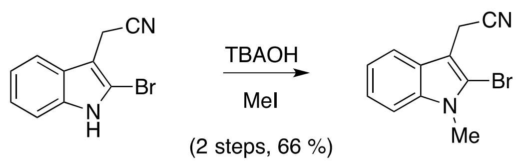
89 **90**

A solution of **89** (2 mmol, 659 mg) in acetonitrile (0.04 M, 50 ml) was cooled down to 0 °C for 5 min. TMSI (7 mmol, 0.996 ml) was added dropwise, as the solution slowly changed from clear to orange. The reaction was further stirred at 0 °C for 40 min until TLC indicates full consumption of starting material. The reaction mixture was loaded directly onto silica for flash chromatography (Hex:EtOAc = 1: 1) to affort the title compound **90** as a red oil (371 mg, 95 %)



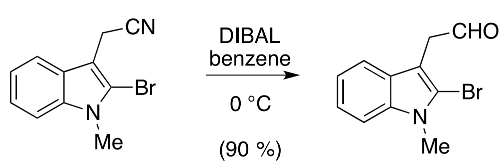
91 **92**

A solution of 3-indoleacetonitrile **91** (21.34 mmol, 3.333 g) and SiO_2 (3.333 g) in CH_2Cl_2 (50 ml) was cooled to 0 °C. N-Bromosuccinimide (21.34 mmol, 3.841 g) was added portion wise over 1 h at 0 °C and stirred at 0 °C for another 30 min before warming to room temperature for 15 min. The mixture was filtered through SiO_2 plug, washed with CH_2Cl_2 and concentrated *in vacuo*. The crude mixture is used for the next step without purification.



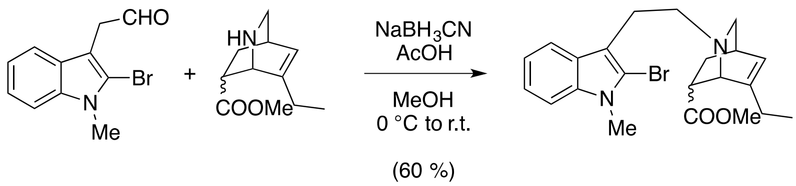
92 **93**

A solution of **92** (19.9 mmol, 4.68 g) and methyl iodide (35.2 mmol, 2.19 ml) in benzene (250 ml) was cooled to 0 °C and stirred vigorously. Tetrabutylammonium hydroxide (40 wt % aqueous, 34.4 mmol, 25.6 ml) was added portion by portion over 30 min. The reaction mixture was stirred overnight and gradually warmed up to room temperature. It was then quenched with NH_4Cl, and extracted with ether : Hex = 1 : 1. The organics were washed with brine, dried over Na_2SO_4, and concentrated. The crude mixture was purified with flash chromatography (Hex : EtOAc = 2 : 1) to yield **93** in 66 %.



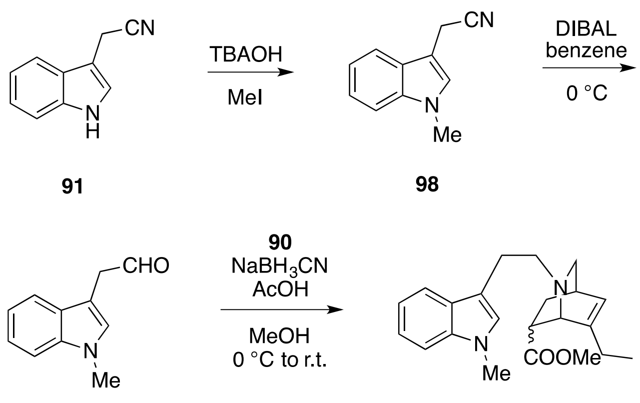
93 **94**

A solution of **93** (0.6 mmol, 149.5 mg) in benzene (20 ml) was cooled to 0 °C. DIBAL-H (0.72 mmol, 1 M, 0.72 ml) was added slowly and stirred at this temperature for 20 min, when TLC indicated full conversion. The reaction was quenched with saturated aqueous L-(+)-tartaric acid solution (10 ml) and extracted with CH_2Cl_2, washed with H2O, brine, dried over Na_2SO_4, concentrated into a brown solid. The crude product **94** was immediately carried on to the next step with purification.

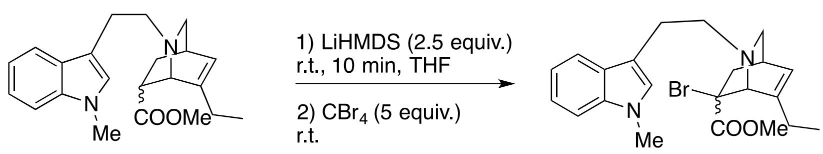


94 90 91

A solution of **90** (0.56 mmol, 109 mg) and **94** (0.84, 212 mg) in MeOH (5 ml) was cooled to 0 °C. Glacial acetic acid (1.12 mmol, 0.064 ml) and Na_2BH_3CN was added and the reaction vessel was purged with nitrogen. The reaction was stirred for 12 h and slowly warmed up to room temperature overnight. The mixture was quenched with aqueous $NaHCO_3$, extracted with ethyl acetate, dried over Na_2SO_4 and concentrated. The crude mixture was purified by flash chromatography (Hex : EtOAc = 1 : 1) as a red oil **91** in 60 %.

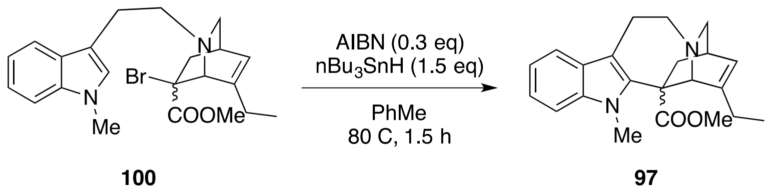


Compound **96** was synthesized using similar procedures. It was isolated as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ =7.57 (d, *J*=7.85 Hz, 1 H), 7.29 (d, *J*=8.20 Hz, 1 H), 7.22 (t, *J*=7.55 Hz, 1 H), 7.11 (t, *J*=7.42 Hz, 1 H), 6.90 (s, 1 H), 6.06 (d, *J*=6.40 Hz, 1 H), 3.85 (s, 1 H), 3.74 (s, 3 H), 3.64 (s, 3 H), 3.31 (s, 1 H), 3.13-3.15 (m, 1 H), 2.94-3.04 (m, 2 H), 2.87-2.92 (m, 1 H), 2.66-2.67 (m, 1 H), 2.57-2.62 (m, 1 H), 2.04-2.11 (m, 3 H), 1.76-1.85 (m, 1 H), 1.73-1.76 (m, 1 H), 0.98 (t, *J*=7.40 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 173.7, 142.8, 137.1, 127.9, 126.8, 125.5, 121.8, 119.0, 119.0, 112.0, 109.4, 59.1, 58.9, 54.7, 51.9, 42.9, 32.7, 30.3, 28.0, 26.4, 23.8, 11.2 ppm. HRMS (ESI): calcd. for $C_{22}H_{29}N_2O_2$ $[M+H]^+$: 353.2224 found: 353.2223.

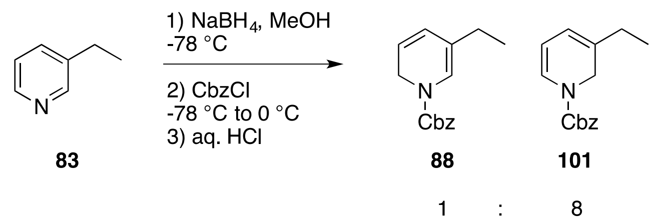


96 **100**

A solution of **96** (0.04 mmol, 14 mg) in THF (2 ml) was added LiHMDS (1 M in toluene, 0.1 mmol, 0.1 ml) and stirred at room temperature for 10 min, when solution turned yellow. Tetrabromomethane (0.2 mmol, 66 mg) in THF (2 ml) was added to the mixture slowly and stirred at room temperature for 14 h. A color change to orange was observed. The mixture was concentrated to 1 ml and loaded directly onto preparatory TLC for separation (Hex : EtOAc = 1 : 1 to CH_2Cl_2 : MeOH = 10 : 1). Workup or concentration to dryness lead to decomposition of the product. Compound **100** was isolated as an orange oil in 81 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ =7.58 (d, *J*=7.90 Hz, 1 H), 7.29 (d, *J*=8.20 Hz, 1 H), 7.23 (t, *J*=7.55 Hz, 1 H), 7.11 (t, *J*=7.42 Hz, 1 H), 6.93 (s, 1 H), 6.13 (d, *J*=6.00 Hz, 1 H), 4.05 (s, 1 H), 3.74 (s, 3 H), 3.65 (s, 3 H), 3.35 (s, 1 H), 3.17-3.21 (m, 1 H), 3.10 (m, 1 H), 2.96-3.01 (m, 1 H), 2.71-2.75 (m, 2 H), 2.08-2.17 (m, 3 H), 1.90-1.95 (m, 1 H), 1.73-1.78 (m, 1 H), 0.99 (t, *J*=7.37 Hz, 3 H) ppm. HRMS (ESI): calcd. for $C_{22}H_{27}BrN_2NaO_2$ $[M+Na]^+$: 453.1148 found: 454.1111.



A solution of 100 (0.06 mmol, 26 mg) in toluene (0.5 ml) was purged three times with argon. Tributyl tin-hydride (0.09 mmol, 0.024 ml) and AIBN (0.018 mmol, 3 mg) in toluene (0.5 ml) was added dropwise over 30 min to the mixture at 80 °C, the reaction was stirred for another hour. Trace of **97** was detected by ESI-MS.



A solution of 3-ethylpyridine (1.5 mmol, 0.173 ml) in methanol (5 ml) was cooled to -78 °C. Sodium borohydride (1.8 mmol, 68 mg) was added as a powder at this temperature and the flask was purged with nitrogen. Benzyl chloroformate (1.5 mmol, 0.214 ml) was added over a period of 5 min and the reaction vessel was slowly warmed up to 0 °C, when effervescence was observed. Aqueous HCl (1M, 5 ml) was added to quench the solution after 5 min. The mixture was concentrated to half of the volume, and extracted with ethyl acetate, washed with aqueous $NaHCO_3$, brine and dried over Na_2SO_4. The ratio of isomer was determined by NMR analysis.

6.5 Derivation of the Kinetic Resolution Equation for Non-Racemic Mixture

$$R_0 + S_0 \longrightarrow R + R_p + S + S_p$$

Assume reaction starts with a known $\frac{R_o}{S_o}$, where $R_o > S_o$, thus

$$ee_o = \frac{(R_o - S_o)}{(R_o + S_o)}$$

$$conversion(c) = \frac{total\ product}{total\ starting\ material} = \frac{(R_o - R) + (S_o - S)}{(R_o + S_o)}$$

$$ee = \frac{product\ diff.}{total\ product} = \frac{(R_p - S_p)}{(R_p + S_p)} = \frac{(R_o - R) + (S_o - S)}{(R_o - R) + (S_o - S)}$$

S and R are expressed as a function of ee, c, R_0 and S_0, and

$$R = \frac{(R_o + S_o)(1 + c - ee \cdot c) + (R_o - S_o)}{2}$$

$$S = \frac{(R_o + S_o)(1 + ee \cdot c - c) - (R_o - S_o)}{2}$$

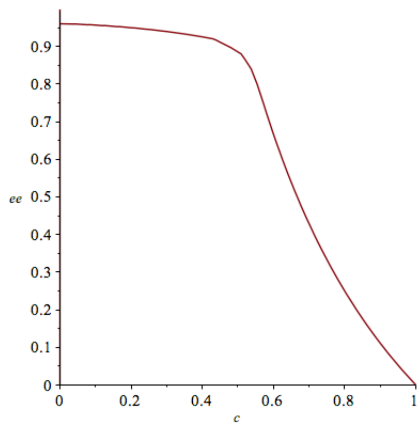
$$seletivity = \frac{\ln(\frac{R}{R_o})}{\ln(\frac{S}{S_o})}$$

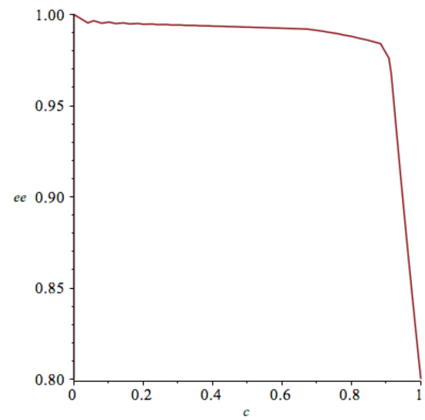
$$0 < c < 1$$

A plot of *ee* vs *c* is generated using Maplesoft, given the values of constants R_0 and S_0, and *selectivity*.

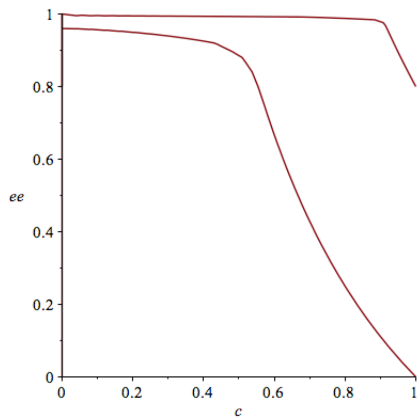
When R_0 = 0.5, S_0 = 0.5 and *selectivity* = 50, ee_0 = 0. This is the standard scenario of a kinetic resolution of a racemic mixture, and the plot of *ee* vs *c* is shown. (Below, left)

When R_0 = 0.9, S_0 = 0.1 and *selectivity* = 50, ee_0 = 0.8. This is the case when reaction proceeds with an unequal mixture of R_0 and S_0. (Below, right)

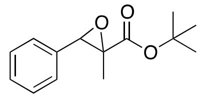
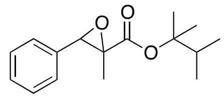
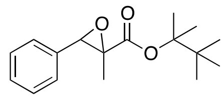
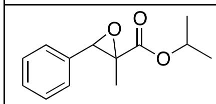
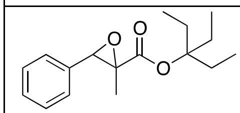
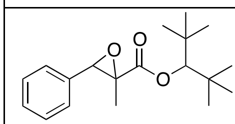
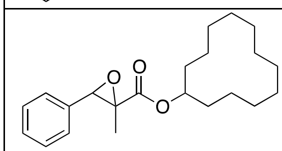
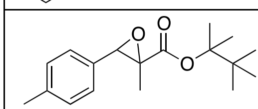
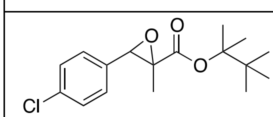
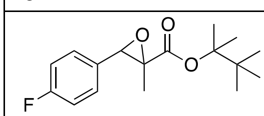
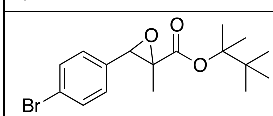
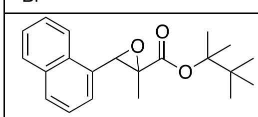
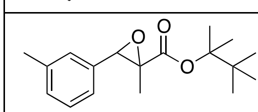


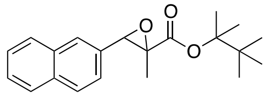
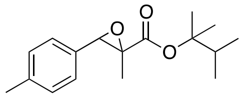
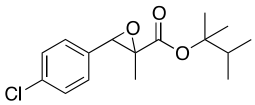
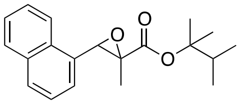
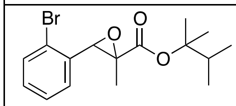


Intergrating the two plots above, one could see the advantage of running a kinetic resolution of non-racemic mixture.

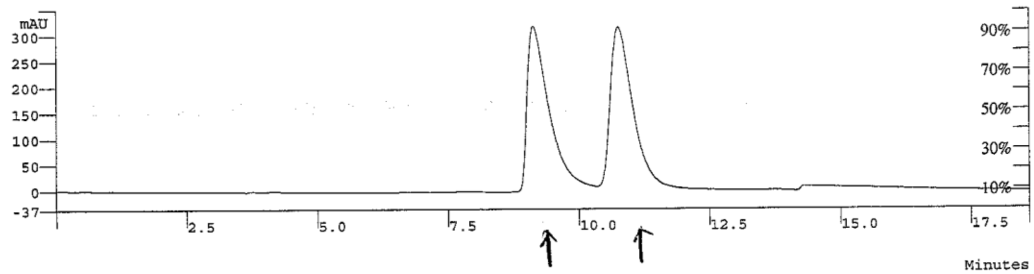


6.6 HPLC Data for Compounds **23-40**

Product		Conditions
	**23**	HPLC (Chiralcel OB-H): Condition: Hex, flow rate = 1.0 mL/min; result: 9.0 min (major), 11.0 (minor)
	**24**	HPLC (Chiralcel OJ-H): Condition: 1:99 Hexane/Isopropanol, flow rate = 0.5 mL/min; result: 11.4 min (minor), 13.1 (major)
	**25**	HPLC (Chiralcel OJ-H): Condition: 1:99 Hexane/Isopropanol, flow rate = 0.5 mL/min; result: 10.7 min (minor), 12.7 (major)
	**26**	HPLC (Chiralcel OB-H): Condition: 1:99 Hexane/Isopropanol, flow rate = 1.0 mL/min; result: 10.1 min (minor), 11.5 (major)
	**27**	HPLC (Chiralcel OJ-H): Condition: 1:99 Hexane/Isopropanol, flow rate = 0.5 mL/min; result: 11.8 min (minor), 13.2 (major)
	**28**	HPLC (Chiralcel IB): Condition: 1:99 Hexane/Isopropanol, flow rate = 0.5 mL/min; result: 10.0 min (minor), 10.7 (major)
	**29**	HPLC (Chiralcel OJ-H): Condition: 1:99 Hexane/Isopropanol, flow rate = 0.5 mL/min; result: 12.2 min (minor), 15.9 (major)
	**30**	HPLC (Chiralcel OJ-H): Condition: 1:99 Hexane/Isopropanol, flow rate = 0.5 mL/min; result: 9.8 min (minor), 12.8 (major)
	**31**	HPLC (Chiralcel OJ-H): Condition: 1:99 Hexane/Isopropanol, flow rate = 0.5 mL/min; result: 10.9 min (minor), 14.1 (major)
	**32**	HPLC (Chiralcel OJ-H): Condition: 1:99 Hexane/Isopropanol, flow rate = 0.5 mL/min; result: 10.9 min (minor), 12.8 (major)
	**33**	HPLC (Chiralcel OJ-H): Condition: 1:99 Hexane/Isopropanol, flow rate = 0.5 mL/min; result: min 11.5 (minor), 15.8 (major)
	**34**	HPLC (Chiralcel OJ-H): Condition: 1:99 Hexane/Isopropanol, flow rate = 0.5 mL/min; result: 11.8 min (minor), 14.1 (major)
	**35**	HPLC (Chiralcel OJ-H): Condition: 1:99 Hexane/Isopropanol, flow rate = 0.5 mL/min; result: 11.0 min (minor), 14.4 (major)

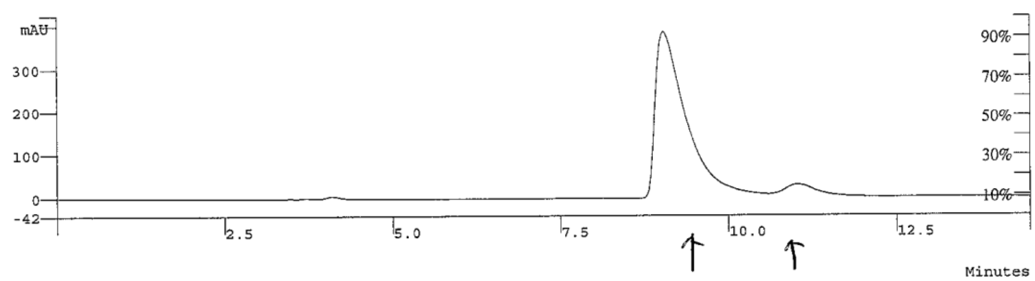
	**36**	HPLC (Chiralcel OJ-H): Condition: 1:99 Hexane/Isopropanol, flow rate = 0.5 mL/min; result: 15.6 min (minor), 23.1 (major)
	**37**	HPLC (Chiralcel OJ-H): Condition: 1:99 Hexane/Isopropanol, flow rate = 0.5 mL/min; result: 10.7 min (minor), 13.4 (major)
	**38**	HPLC (Chiralcel OJ-H): Condition: 1:99 Hexane/Isopropanol, flow rate = 0.5 mL/min; result: 12.3 min (minor), 16.7 (major)
	**39**	HPLC (Chiralcel OJ-H): Condition: 1:99 Hexane/Isopropanol, flow rate = 0.5 mL/min; result: 14.5 min (minor), 18.6 (major)
	**40**	HPLC (Chiralcel OJ-H): Condition: 1:99 Hexane/Isopropanol, flow rate = 0.5 mL/min; result: 10.1 min (minor), 13.5 (major)

Data File:	c:\star\5-31-13 5;11;46 pm -1.run	Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS	Calc Date:	05/31/13 05:33:05 PM
Sample ID:	B2043-rac	Times Calculated:	1
Operator (Inj):	OB-H, Hex=100%, FR=1	Calculation Method:	c:\windows\temp\~5-31-13 5;11;46 pm
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 0%.mth	Run Mode:	Analysis
Run Time (min):	18.640	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

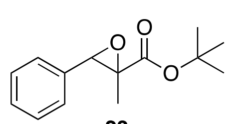


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		49.9739	9.133	0.000	46898876	0.00	BB	25.7		0
2		50.0261	10.760	0.000	46947808	0.00	BB	26.6		0
	Totals	**100.0000**		**0.000**	**93846688**					

Data File:	c:\star\5-31-13 5;32;18 pm -1.run	Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS	Calc Date:	05/31/13 05:47:38 PM
Sample ID:	B2043-L*	Times Calculated:	1
Operator (Inj):	OB-H, Hex=100%, FR=1	Calculation Method:	c:\windows\temp\~5-31-13 5;32;18 pm
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 0%.mth	Run Mode:	Analysis
Run Time (min):	14.507	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

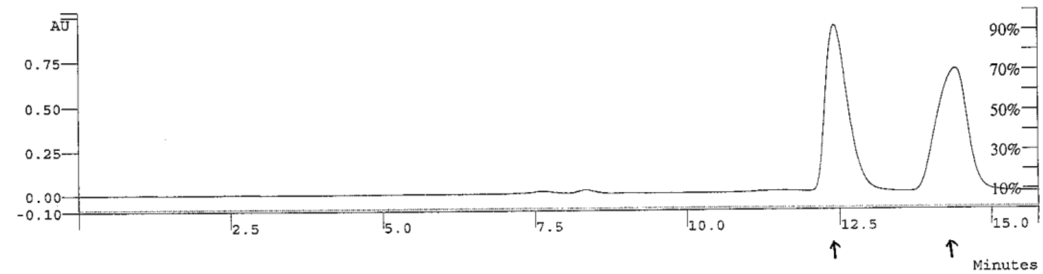


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		94.8887	9.027	0.000	62161884	0.00	BB	27.6		0
2		5.1113	11.027	0.000	3348395	0.00	BB	25.2		0
	Totals	**100.0000**		**0.000**	**65510280**					



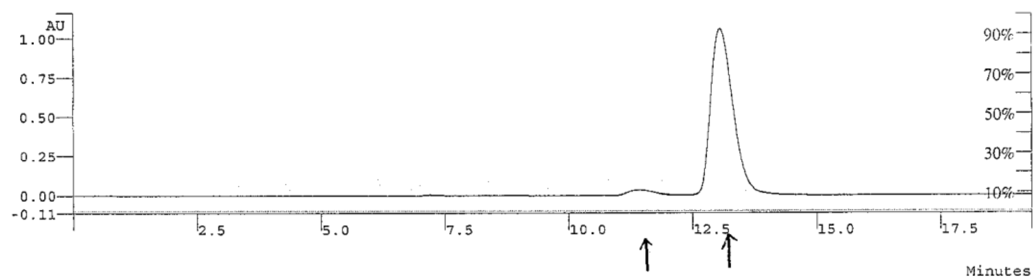
23

Data File:	c:\star\3-31-14 4;47;41 pm -1.run	Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS	Calc Date:	03/31/14 05:06:32 PM
Sample ID:	B3065-rac	Times Calculated:	1
Operator (Inj):	OJ-H, iPrOH/Hex = 1:99, FR=0.5	Calculation Method:	c:\windows\temp\~3-31-14 4;47;41 pm
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
Run Time (min):	15.787	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		49.6283	12.413	0.000	120562616	0.00	BB	23.7		0
2		50.3717	14.413	0.000	122368648	0.00	BB	34.1		0
	Totals	**100.0000**		**0.000**	**242931264**					

Data File:	c:\star\11-25-13 10;29;46 am -1.run	Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS	Calc Date:	11/25/13 11:23:26 AM
Sample ID:	B3065-L*	Times Calculated:	1
Operator (Inj):	OJ-H, iPrOH/Hex=1:99, FR=0.5	Calculation Method:	c:\windows\temp\~11-25-13 10;29;46
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
Run Time (min):	19.360	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		2.7636	11.427	0.000	4760573	0.00	BB	29.7		0
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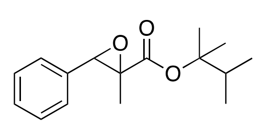

24

Data File:	c:\star\1-8-14 3;14;00 pm -1.run		Operator (Calc):	
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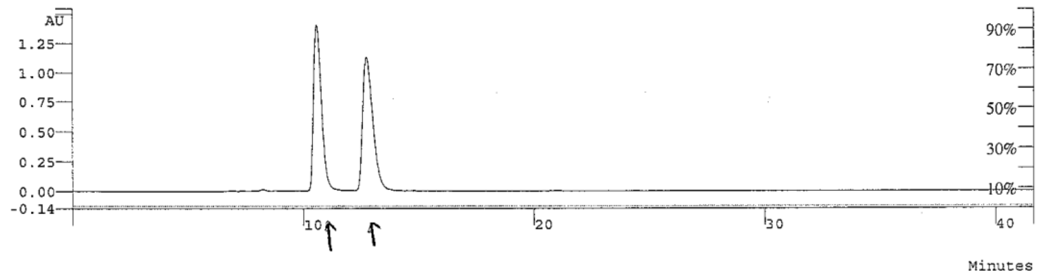
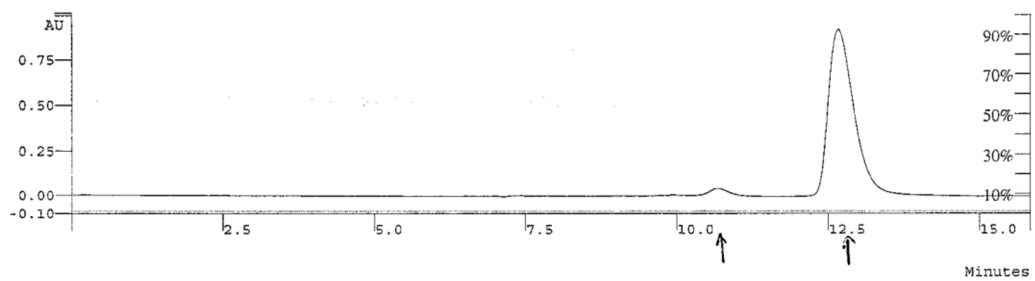
Sample ID:	B3103-rac		Times Calculated:	4
Operator (Inj):	OJ-H, iPrOH/Hex=1:99, FR=0.5		Calculation Method:	c:\windows\temp\~1-8-14 3;14;00 pm
Injection Date:			Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 1%.mth		Run Mode:	Analysis
Run Time (min):	41.680		Peak Measurement:	Peak Area
Workstation:			Calculation Type:	Percent
Instrument (Inj):	Varian Star #1		Calibration Level:	N/A
			Verification Tolerance:	N/A

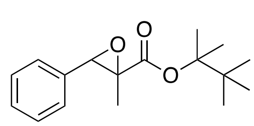


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		49.6881	10.573	0.000	172283264	0.00	BB	22.2		0
2		50.3119	12.733	0.000	174446272	0.00	BB	28.3		0
	Totals	100.0000		0.000	346729536					

Data File:	c:\star\1-8-14 2;40;18 pm -1.run		Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS		Calc Date:	01/08/14 02:58:41 PM
Sample ID:	B3103-L*		Times Calculated:	1
Operator (Inj):	OJ-H, iPrOH/Hex=1:99, FR=0.5		Calculation Method:	c:\windows\temp\~1-8-14 2;40;18 pm
Injection Date:			Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 1%.mth		Run Mode:	Analysis
Run Time (min):	15.867		Peak Measurement:	Peak Area
Workstation:			Calculation Type:	Percent
Instrument (Inj):	Varian Star #1		Calibration Level:	N/A
			Verification Tolerance:	N/A



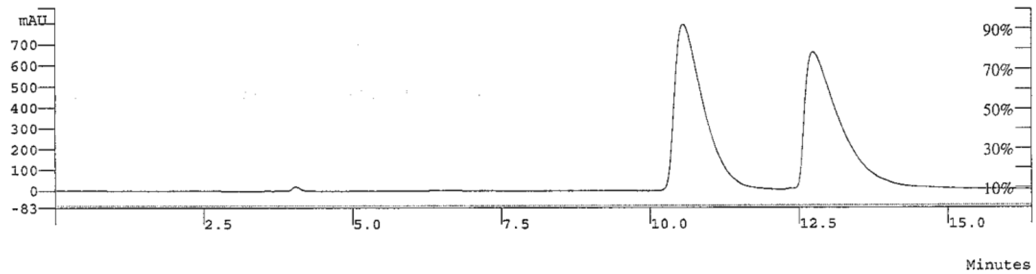
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		2.5166	10.680	0.000	3626571	0.00	BB	17.6		0
2		97.4834	12.653	0.000	140479488	0.00	BB	26.8		0
	Totals	100.0000		0.000	144106064					



25

Data File: c:\star\3-17-13 2;04;45 pm -1.run
Channel: 2 = 225.00 nm RESULTS
Sample ID: B1241-rac
Operator (Inj): OB-H, iPrOH/Hex = 1:99, FR=1
Injection Date:
Injection Method: c:\star\lan\standard 1%.mth
Run Time (min): 16.427
Workstation:
Instrument (Inj): Varian Star #1

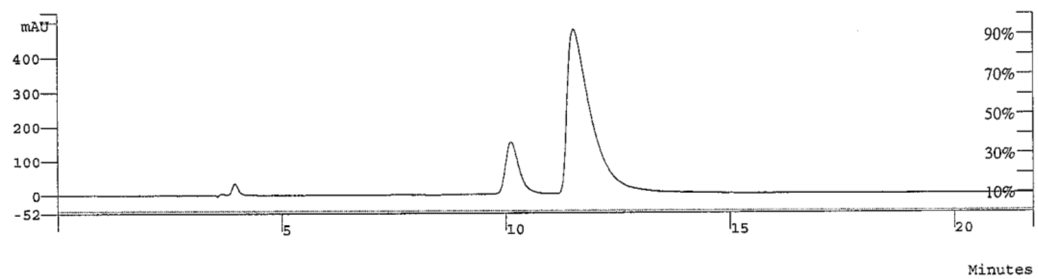
Operator (Calc):
Calc Date: 03/17/13 02:23:29 PM
Times Calculated: 1
Calculation Method: c:\windows\temp\~3-17-13 2;04;45 pm
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



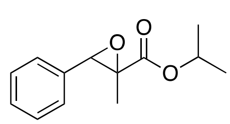
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		49.7441	10.547	0.000	136652736	0.00	BB	30.6		0
2		50.2559	12.733	0.000	138058848	0.00	BB	35.8		0
	Totals	**100.0000**		**0.000**	**274711584**					

Data File: c:\star\3-17-13 2;26;35 pm -1.run
Channel: 2 = 225.00 nm RESULTS
Sample ID: B1241-L*
Operator (Inj): OB-H, iPrOH/Hex = 1:99, FR=1
Injection Date:
Injection Method: c:\star\lan\standard 1%.mth
Run Time (min): 21.787
Workstation:
Instrument (Inj): Varian Star #1

Operator (Calc):
Calc Date: 03/17/13 02:50:33 PM
Times Calculated: 1
Calculation Method: c:\windows\temp\~3-17-13 2;26;35 pm
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



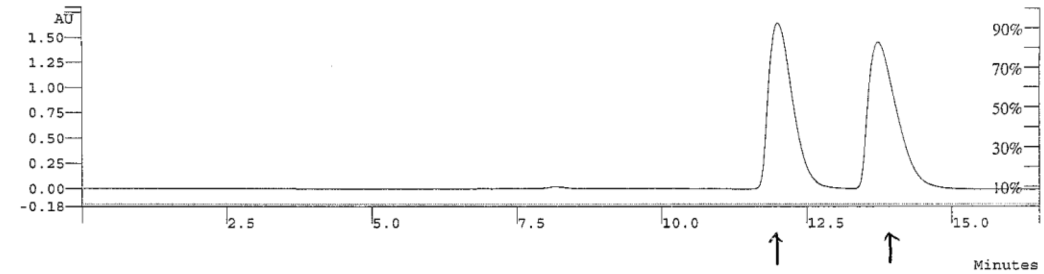
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		14.8209	10.120	0.000	15861016	0.00	BB	18.7		0
2		85.1791	11.507	0.000	91156696	0.00	BB	31.9		0
	Totals	**100.0000**		**0.000**	**107017712**					



26

Data File: c:\star\1-10-14 3;32;59 pm -1.run
Channel: 2 = 225.00 nm RESULTS
Sample ID: B3113-rac
Operator (Inj): OJ-H, iPrOH/Hex=1:99, FR=0.5
Injection Date:
jection Method: c:\star\lan\standard 1%.mth
Run Time (min): 16.533
Workstation:
Instrument (Inj): Varian Star #1

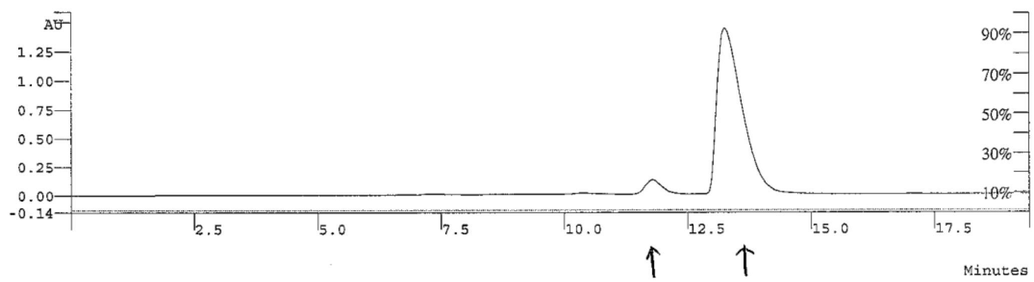
Operator (Calc):
Calc Date: 01/10/14 03:53:05 PM
Times Calculated: 2
Calculation Method: c:\windows\temp\~1-10-14 3;32;59 pm
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



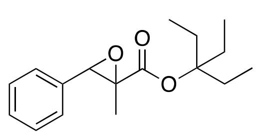
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		49.3217	11.987	0.000	243173600	0.00	BB	27.2		0
2		50.6783	13.720	0.000	249861888	0.00	BB	31.7		0
Totals		**100.0000**		**0.000**	**493035488**					

Data File: c:\star\1-10-14 3;51;16 pm -1.run
Channel: 2 = 225.00 nm RESULTS
Sample ID: B3113-L*
Operator (Inj): OJ-H, iPrOH/Hex=1:99, FR=0.5
Injection Date:
jection Method: c:\star\lan\standard 1%.mth
Run Time (min): 19.440
Workstation:
Instrument (Inj): Varian Star #1

Operator (Calc):
Calc Date: 01/10/14 04:13:39 PM
Times Calculated: 1
Calculation Method: c:\windows\temp\~1-10-14 3;51;16 pm
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		5.0180	11.773	0.000	13800778	0.00	BB	21.3		0
2		94.9820	13.240	0.000	261222176	0.00	BB	33.2		0
Totals		**100.0000**		**0.000**	**275022944**					



27

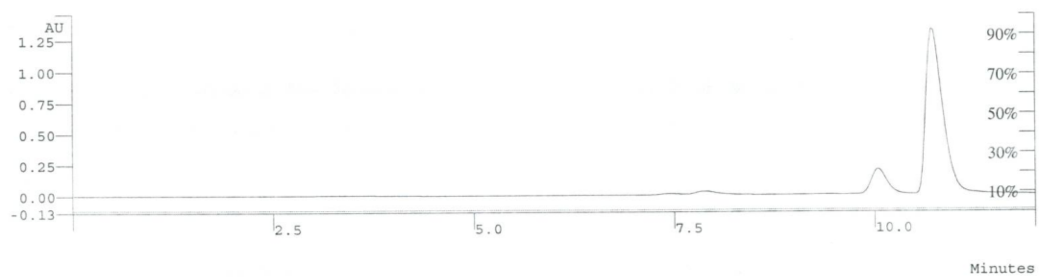
Data File: c:\star\6-13-14 5;42;20 pm -1.run
Channel: 2 = 225.00 nm RESULTS
Sample ID: B2011-rac
Operator (Inj): IB, iPrOH/Hex=1:99, FR=0.5
Injection Date:
Injection Method: c:\star\lan\standard 1%_0.5ml.mth
Run Time (min): 11.813
Workstation:
Instrument (Inj): Varian Star #1

Operator (Calc):
Calc Date: 06/13/14 05:57:54 PM
Times Calculated: 2
Calculation Method: c:\windows\temp\~6-13-14 5;42;20 pm
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A

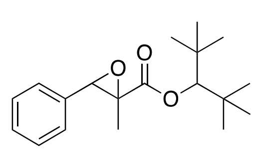
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.1569	9.667	0.000	53792972	0.00	BB	11.6		0
2		49.8431	10.253	0.000	53456400	0.00	BB	11.4		0
	Totals	**100.0000**		**0.000**	**107249376**					

Data File: c:\star\6-13-14 6;15;35 pm -1.run
Channel: 2 = 225.00 nm RESULTS
Sample ID: B2011-L*
Operator (Inj): IB. iPrOH/Hex=1:99, FR=0.5
Injection Date:
Injection Method: c:\star\lan\standard 1%_0.5ml.mth
Run Time (min): 12.027
Workstation:
Instrument (Inj): Varian Star #1

Operator (Calc):
Calc Date: 06/13/14 06:28:25 PM
Times Calculated: 1
Calculation Method: c:\windows\temp\~6-13-14 6;15;35 pm
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



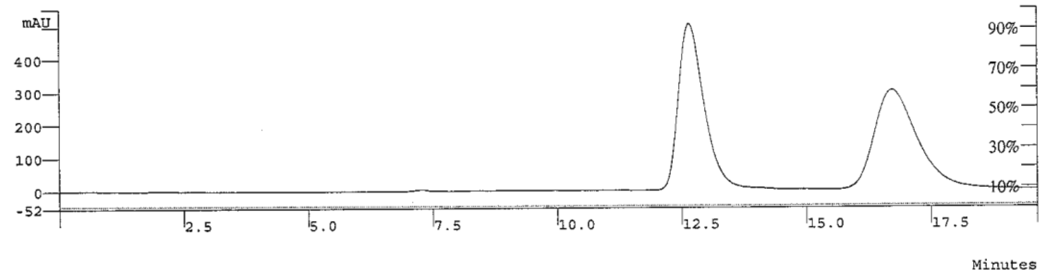
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		12.1989	10.040	0.000	13779410	0.00	BB	12.4		0
2		87.8011	10.707	0.000	99176512	0.00	BB	13.5		0
	Totals	**100.0000**		**0.000**	**112955920**					



28

Data File: c:\star\3-31-14 5;05;12 pm -1.run
Channel: 2 = 225.00 nm RESULTS
Sample ID: B1273-rac
Operator (Inj): OJ-H, iPrOH/Hex=1:99, FR=0.5
Injection Date:
jection Method: c:\star\lan\standard 1%.mth
Run Time (min): 19.653
Workstation:
Instrument (Inj): Varian Star #1

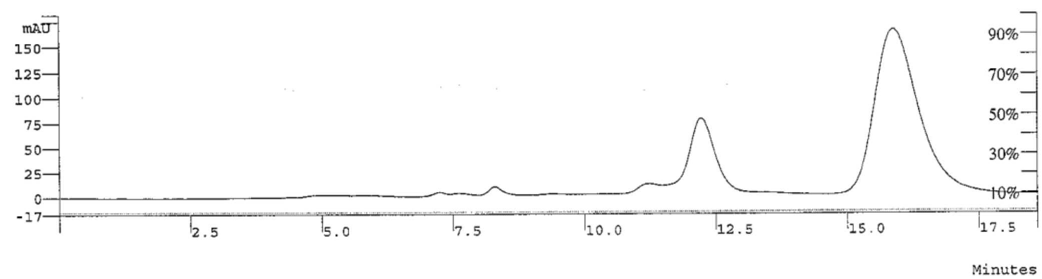
Operator (Calc):
Calc Date: 03/31/14 05:27:21 PM
Times Calculated: 1
Calculation Method: c:\windows\temp\~3-31-14 5;05;12 pm
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



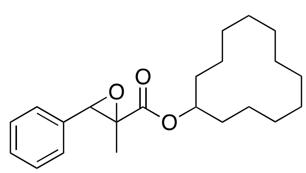
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.1950	12.653	0.000	92983448	0.00	BB	32.7		0
2		49.8050	16.707	0.000	92260832	0.00	BB	54.0		0
	Totals	**100.0000**		**0.000**	**185244288**					

Data File: c:\star\3-31-14 5;26;34 pm -1.run
Channel: 2 = 225.00 nm RESULTS
Sample ID: B1273-L*
Operator (Inj): OJ-H, iPrOH/Hex=1:99, FR=0.5
Injection Date:
jection Method: c:\star\lan\standard 1%.mth
Run Time (min): 18.640
Workstation:
Instrument (Inj): Varian Star #1

Operator (Calc):
Calc Date: 03/31/14 05:47:41 PM
Times Calculated: 1
Calculation Method: c:\windows\temp\~3-31-14 5;26;34 pm
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		18.3755	12.227	0.000	11111682	0.00	BB	28.3		0
2		81.6245	15.880	0.000	49358576	0.00	BB	53.2		0
	Totals	**100.0000**		**0.000**	**60470256**					



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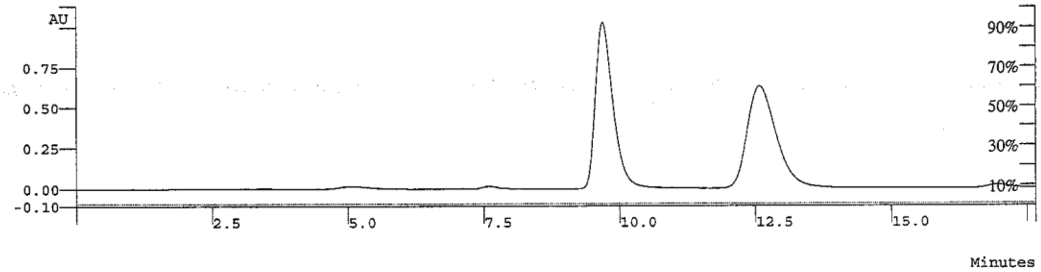
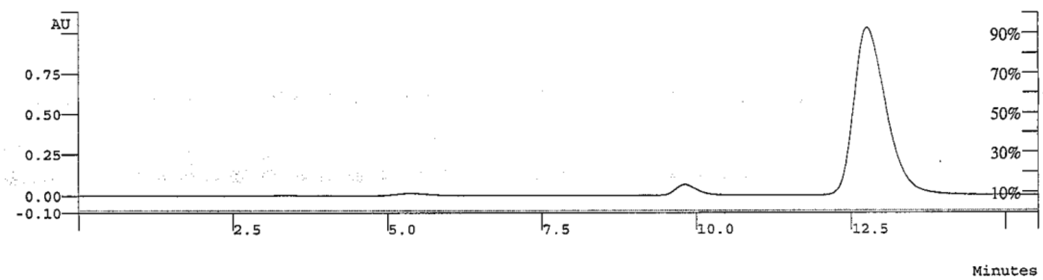
Data File:	c:\star\3-16-14 3;43;20 pm -1.run	Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS	Calc Date:	03/16/14 04:03:36 PM
Sample ID:	B3245-rac	Times Calculated:	1
Operator (Inj):	OJ-H, iPrOH/Hex=1:99, FR=0.5	Calculation Method:	c:\windows\temp\~3-16-14 3;43;20 pm
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
Run Time (min):	17.680	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

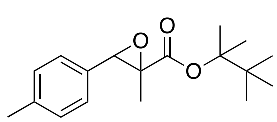


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		49.8955	9.693	0.000	117905496	0.00	BB	20.2		0
2		50.1045	12.573	0.000	118399520	0.00	BB	33.7		0
	Totals	**100.0000**		**0.000**	**236305024**					

Data File:	c:\star\3-16-14 4;02;45 pm -1.run	Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS	Calc Date:	03/16/14 04:20:47 PM
Sample ID:	B3245-L*	Times Calculated:	1
Operator (Inj):	OJ-H, iPrOH/Hex=1:99, FR=0.5	Calculation Method:	c:\windows\temp\~3-16-14 4;02;45 pm
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
Run Time (min):	15.547	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		3.6362	9.800	0.000	7181815	0.00	BB	21.2		0
2		96.3638	12.760	0.000	190326384	0.00	BB	33.2		0
	Totals	**100.0000**		**0.000**	**197508192**					



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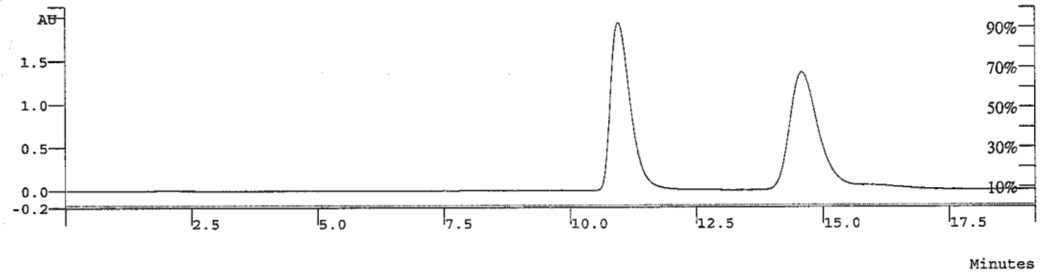
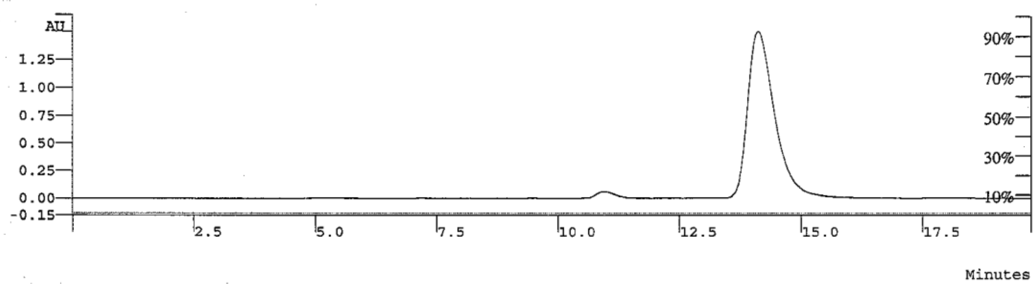
Data File:	c:\star\3-16-14 5;02;52 pm -1.run	Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS	Calc Date:	03/16/14 05:24:55 PM
Sample ID:	B3247-rac	Times Calculated:	3
Operator (Inj):	OJ-H, iPrOH/Hex=1:99, FR=0.5	Calculation Method:	c:\windows\temp\~3-16-14 5;02;52 pm
Injection Date:		Instrument (Calc):	Varian Star #1
Injection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
Run Time (min):	19.227	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

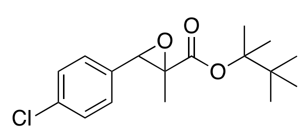


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.2059	10.947	0.000	271010720	0.00	BB	25.1		0
2		49.7941	14.573	0.000	268787424	0.00	BB	35.8		0
Totals		**100.0000**		**0.000**	**539798144**					

Data File:	c:\star\3-16-14 4;41;23 pm -1.run	Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS	Calc Date:	03/16/14 05:11:04 PM
Sample ID:	B3247-L*	Times Calculated:	2
Operator (Inj):	OJ-H, iPrOH/Hex=1:99, FR=0.5	Calculation Method:	c:\windows\temp\~3-16-14 4;41;23 pm
Injection Date:		Instrument (Calc):	Varian Star #1
Injection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
Run Time (min):	19.760	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		2.1111	10.947	0.000	6366485	0.00	BB	22.3		0
2		97.8889	14.120	0.000	295206720	0.00	BB	34.6		0
Totals		**100.0000**		**0.000**	**301573216**					



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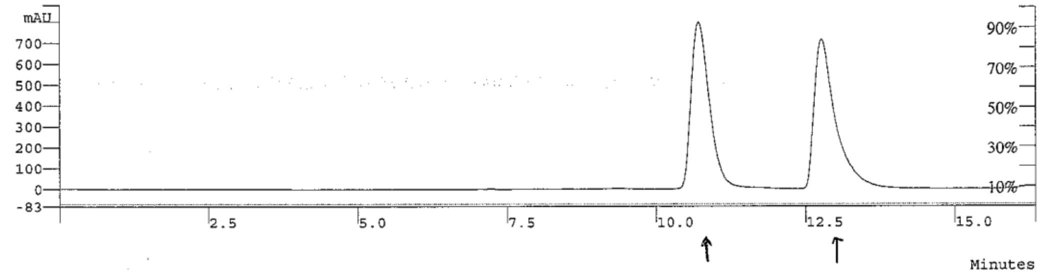
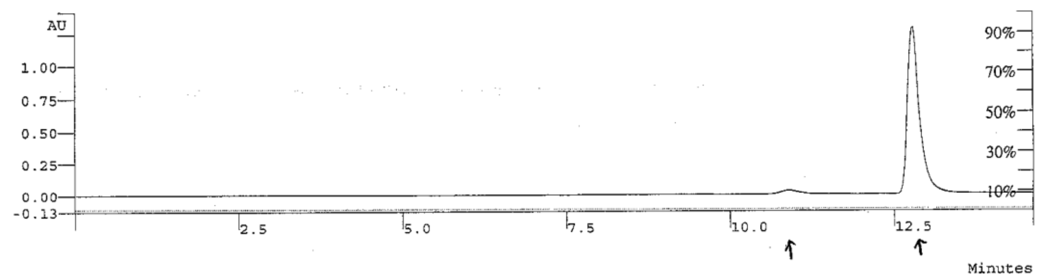
Data File:	c:\star\4-21-14 2;21;09 pm -1.run	Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS	Calc Date:	04/21/14 02:41:17 PM
Sample ID:	B3293-rac	Times Calculated:	2
Operator (Inj):	OJ-H, iPrOH/Hex=1:99, FR=0.5	Calculation Method:	c:\windows\temp\~4-21-14 2;21;09 pm
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
~κun Time (min):	16.373	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

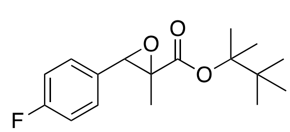


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		49.5958	10.707	0.000	87856920	0.00	BB	19.6		0
2		50.4042	12.760	0.000	89288896	0.00	BB	20.9		0
Totals		**100.0000**		**0.000**	**177145824**					

Data File:	c:\star\4-21-14 3;21;12 pm -1.run	Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS	Calc Date:	04/21/14 03:38:31 PM
Sample ID:	B3293-L*	Times Calculated:	1
Operator (Inj):	OJ-H, iPrOH/Hex=1:99, FR=0.5	Calculation Method:	c:\windows\temp\~4-21-14 3;21;12 pm
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
~κun Time (min):	14.640	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		2.5526	10.893	0.000	2249279	0.00	BB	16.5		0
2		97.4474	12.787	0.000	85866496	0.00	BB	11.1		0
Totals		**100.0000**		**0.000**	**88115776**					



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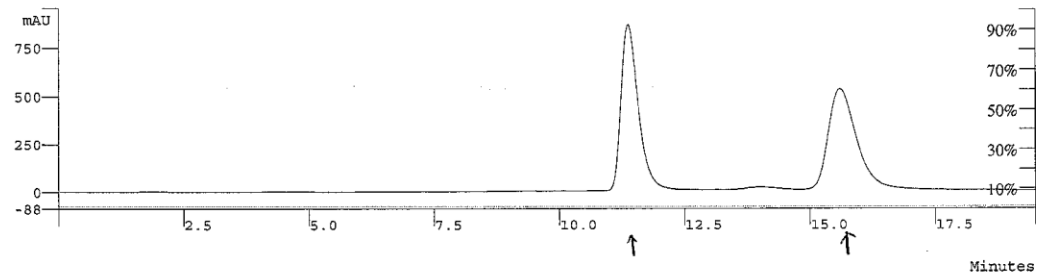
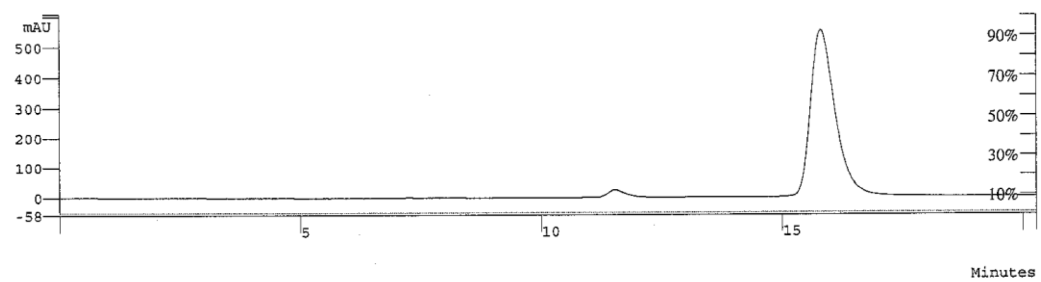
Data File:	c:\star\4-21-14 3;37;34 pm -1.run	Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS	Calc Date:	04/21/14 03:59:52 PM
Sample ID:	B3295-rac	Times Calculated:	1
Operator (Inj):	OJ-H, iPrOH/Hex=1:99, FR=0.5	Calculation Method:	c:\windows\temp\~4-21-14 3;37;34 pm
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
Run Time (min):	19.520	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

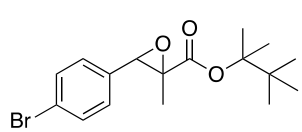


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.4868	11.373	0.000	106435448	0.00	BB	21.9		0
2		49.5131	15.587	0.000	104382720	0.00	BB	35.1		0
Totals		**99.9999**		**0.000**	**210818176**					

Data File:	c:\star\4-21-14 3;59;02 pm -1.run	Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS	Calc Date:	04/21/14 04:20:45 PM
Sample ID:	B3295-L*	Times Calculated:	1
Operator (Inj):	OJ-H, iPrOH/Hex=1:99, FR=0.5	Calculation Method:	c:\windows\temp\~4-21-14 3;59;02 pm
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
Run Time (min):	20.293	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		2.7222	11.533	0.000	2809447	0.00	BB	21.4		0
2		97.2778	15.800	0.000	100394864	0.00	BB	32.0		0
Totals		**100.0000**		**0.000**	**103204312**					



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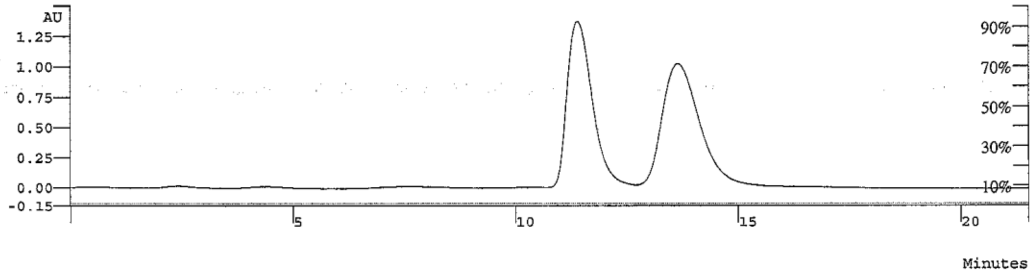
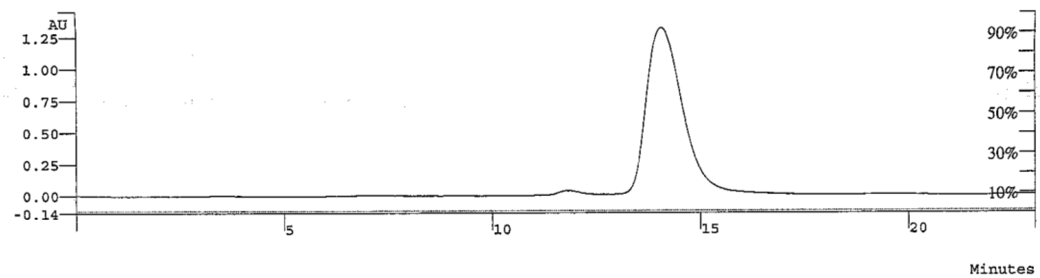
Data File:	c:\star\3-22-14 6;16;11 pm -1.run	Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS	Calc Date:	03/22/14 06:42:24 PM
Sample ID:	B3253-rac	Times Calculated:	3
Operator (Inj):	OJ-H, iPrOH/Hex=1:99, FR=0.5	Calculation Method:	c:\windows\temp\~3-22-14 6;16;11 pm
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
Run Time (min):	21.547	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

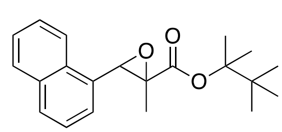


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		49.4752	11.373	0.000	263362288	0.00	BB	36.2		0
2		50.5248	13.640	0.000	268949952	0.00	BB	51.6		0
Totals		**100.0000**		**0.000**	**532312256**					

Data File:	c:\star\3-22-14 6;39;26 pm -1.run	Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS	Calc Date:	03/22/14 07:05:10 PM
Sample ID:	B3253-L*	Times Calculated:	1
Operator (Inj):	OJ-H, iPrOH/Hex=1:99, FR=0.5	Calculation Method:	c:\windows\temp\~3-22-14 6;39;26 pm
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
Run Time (min):	23.067	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		0.9857	11.827	0.000	4032378	0.00	BB	27.3		0
2		99.0144	14.067	0.000	405075904	0.00	BB	55.6		0
Totals		**100.0001**		**0.000**	**409108288**					



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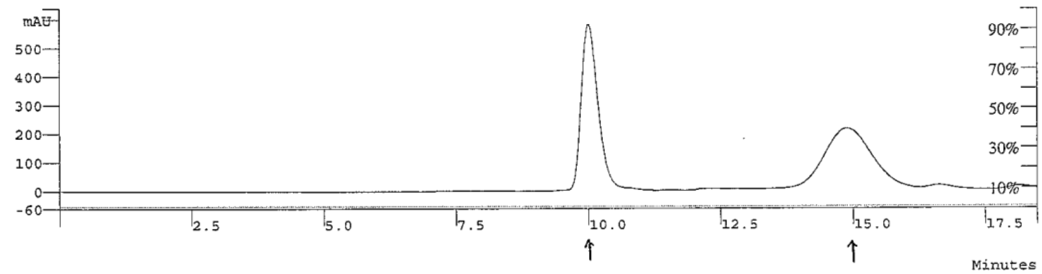
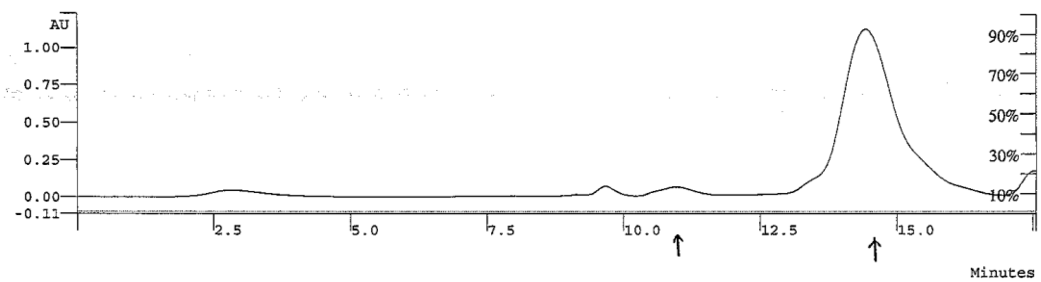
Data File:	c:\star\3-31-14 3;23;44 pm -1.run	Operator (Calc):	
Channel:	3 = 210.00 nm RESULTS	Calc Date:	03/31/14 03:44:48 PM
Sample ID:	B3265-rac	Times Calculated:	1
Operator (Inj):	OJ-H, iPrOH/Hex = 1:99, FR=0.5	Calculation Method:	c:\windows\temp\~3-31-14 3;23;44 pm
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
Run Time (min):	18.507	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

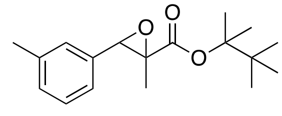


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		49.9178	10.013	0.000	64408224	0.00	BB	20.1		0
2		50.0822	14.893	0.000	64620424	0.00	BB	58.1		0
	Totals	**100.0000**		**0.000**	**129028648**					

Data File:	c:\star\3-22-14 7;24;46 pm -1.run	Operator (Calc):	
Channel:	3 = 210.00 nm RESULTS	Calc Date:	03/22/14 07:43:23 PM
Sample ID:	B3265-L*	Times Calculated:	1
Operator (Inj):	OJ-H, iPrOH/Hex=1:99, FR=0.5	Calculation Method:	c:\windows\temp\~3-22-14 7;24;46 pm
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
un Time (min):	17.573	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		2.8239	10.973	0.000	11804418	0.00	BB	42.5		0
2		97.1761	14.413	0.000	406218400	0.00	BB	59.8		0
	Totals	**100.0000**		**0.000**	**418022816**					



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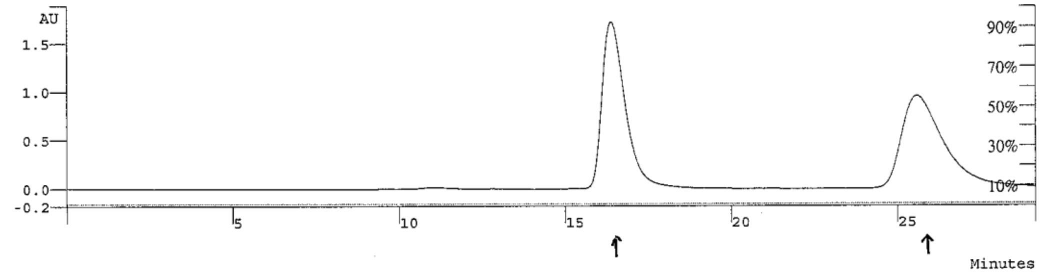
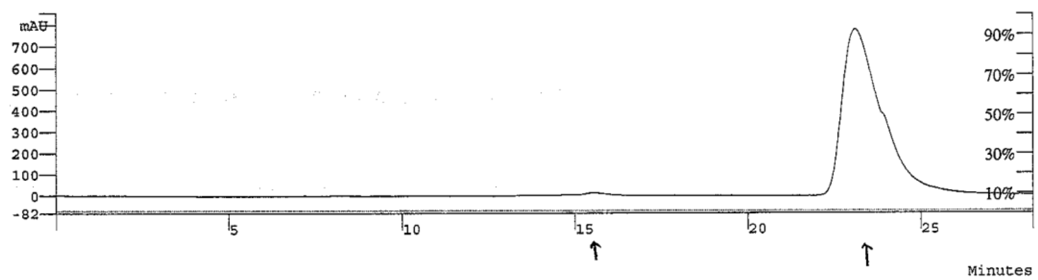
Data File:	c:\star\3-31-14 4;16;03 pm -1.run	Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS	Calc Date:	03/31/14 04:46:05 PM
Sample ID:	B3267-rac	Times Calculated:	1
Operator (Inj):	OJ-H, iPrOH/Hex = 1:99, FR=0.5	Calculation Method:	c:\windows\temp\~3-31-14 4;16;03 pm
Injection Date:		Instrument (Calc):	Varian Star #1
ection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
Run Time (min):	29.173	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

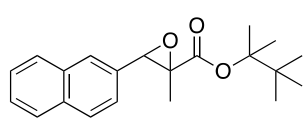


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.0061	16.387	0.000	423843648	0.00	BB	43.3		0
2		49.9939	25.560	0.000	423740608	0.00	BB	78.0		0
Totals		**100.0000**		**0.000**	**847584256**					

Data File:	c:\star\3-22-14 8;15;09 pm -1.run	Operator (Calc):	
Channel:	3 = 210.00 nm RESULTS	Calc Date:	03/22/14 08:44:32 PM
Sample ID:	B3267-L*	Times Calculated:	1
Operator (Inj):	OJ-H, iPrOH/Hex=1:99, FR=0.5	Calculation Method:	c:\windows\temp\~3-22-14 8;15;09 pm
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
Run Time (min):	28.267	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		0.6084	15.560	0.000	1967648	0.00	BB	32.3		0
2		99.3916	23.107	0.000	321460480	0.00	BB	71.5		0
Totals		**100.0000**		**0.000**	**323428128**					



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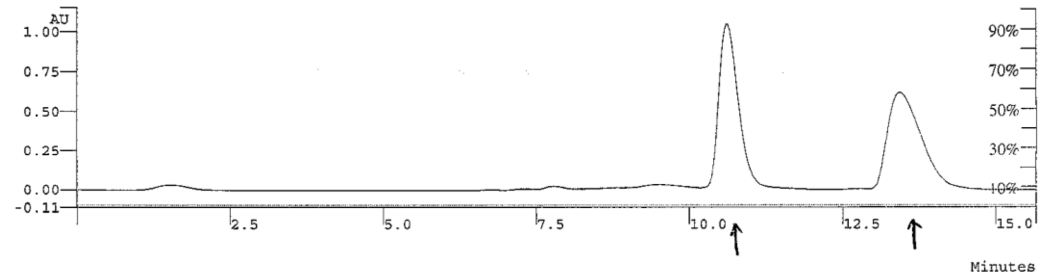
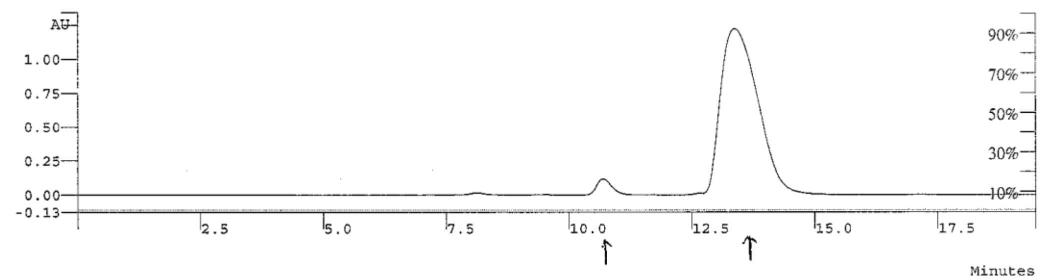
Data File:	c:\star\12-11-13 5;39;06 pm -1.run	Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS	Calc Date:	12/11/13 05:56:44 PM
Sample ID:	B3079-rac	Times Calculated:	2
Operator (Inj):	OJ-H, iPrOH/Hex=1:99, FR=0.5	Calculation Method:	c:\windows\temp\~12-11-13 5;39;06
Injection Date:		Instrument (Calc):	Varian Star #1
Injection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
ın Time (min):	15.680	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

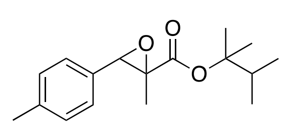


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		49.8809	10.600	0.000	117847672	0.00	BB	20.4		0
2		50.1191	13.427	0.000	118410512	0.00	BB	35.9		0
	Totals	100.0000		0.000	236258176					

Data File:	c:\star\12-11-13 4;13;32 pm -1.run	Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS	Calc Date:	12/11/13 04:37:41 PM
Sample ID:	B3079-L*	Times Calculated:	2
Operator (Inj):	OJ-H, iPrOH/Hex=1:99, FR=0.5	Calculation Method:	c:\windows\temp\~12-11-13 4;13;32
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
Run Time (min):	19.520	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		3.5252	10.680	0.000	12022462	0.00	BB	19.2		0
2		96.4748	13.373	0.000	329024544	0.00	BB	51.2		0
	Totals	100.0000		0.000	341047008					



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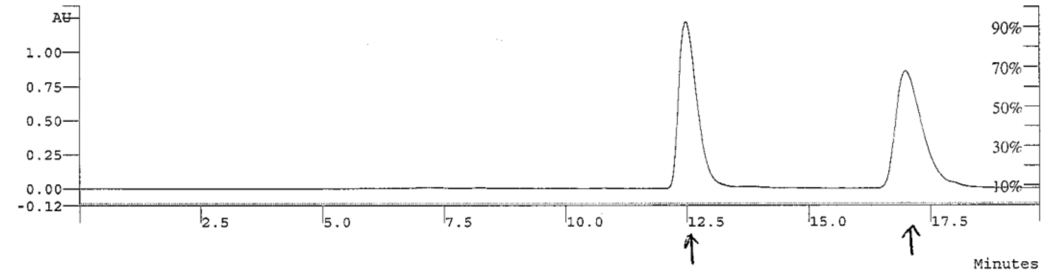
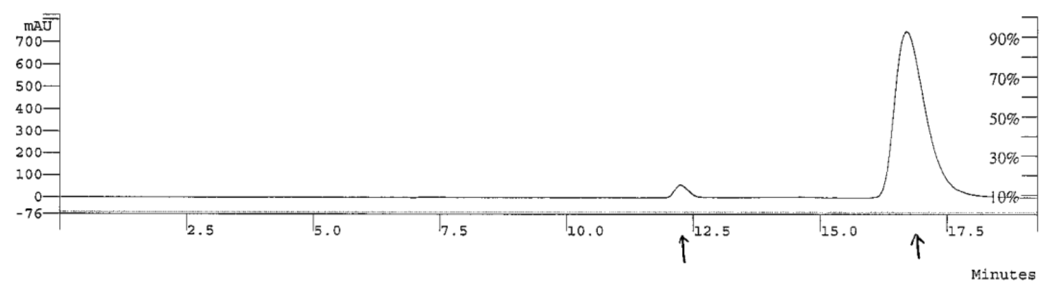
Data File:	c:\star\12-11-13 5;57;06 pm -1.run	Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS	Calc Date:	12/11/13 06:19:20 PM
Sample ID:	B3081-rac	Times Calculated:	3
Operator (Inj):	OJ-H, iPrOH/Hex=1:99, FR=0.5	Calculation Method:	c:\windows\temp\~12-11-13 5;57;06
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
Run Time (min):	19.760	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

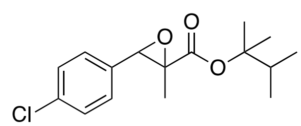


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		49.8363	12.467	0.000	164969536	0.00	BB	24.3		0
2		50.1637	16.973	0.000	166053072	0.00	BB	34.8		0
Totals		**100.0000**		**0.000**	**331022592**					

Data File:	c:\star\12-11-13 4;55;33 pm -1.run	Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS	Calc Date:	12/11/13 05:16:03 PM
Sample ID:	B3081-L*	Times Calculated:	1
Operator (Inj):	OJ-H, iPrOH/Hex=1:99, FR=0.5	Calculation Method:	c:\windows\temp\~12-11-13 4;55;33
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
Run Time (min):	19.307	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		2.8695	12.253	0.000	4856539	0.00	BB	17.0		0
2		97.1305	16.707	0.000	164390544	0.00	BB	39.2		0
Totals		**100.0000**		**0.000**	**169247088**					



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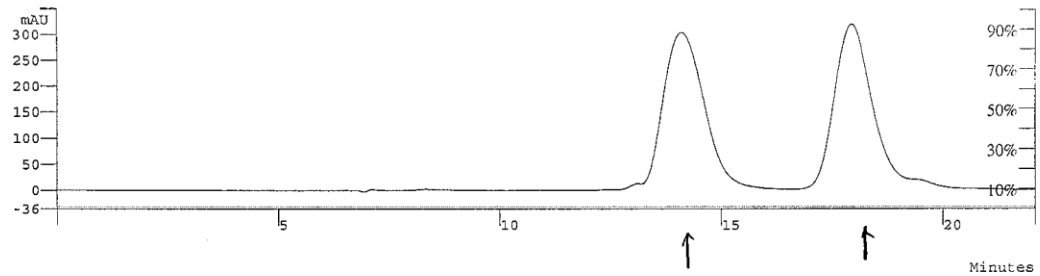
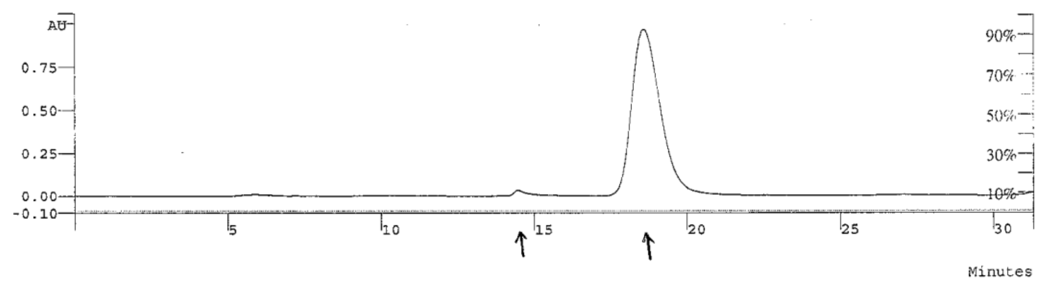
Data File:	c:\star\11-13-13 1;28;07 pm -1.run	Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS	Calc Date:	11/13/13 01:53:19 PM
Sample ID:	B3043-rac	Times Calculated:	1
Operator (Inj):	OJ-H, iPrOH/Hex=1:99, FR=0.5	Calculation Method:	c:\windows\temp\~11-13-13 1;28;07
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
Run Time (min):	22.107	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

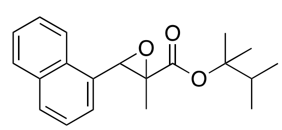


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.0535	14.093	0.000	99332464	0.00	BB	60.4		0
2		49.9465	17.933	0.000	99119984	0.00	BB	54.4		0
Totals		**100.0000**		**0.000**	**198452448**					

Data File:	c:\star\11-13-13 3;09;00 pm -1.run	Operator (Calc):	
Channel:	2 = 225.00 nm RESULTS	Calc Date:	11/13/13 03:42:29 PM
Sample ID:	B3043-L*	Times Calculated:	1
Operator (Inj):	OJ-H, iPrOH/Hex = 1:99, FR=0.5	Calculation Method:	c:\windows\temp\~11-13-13 3;09;00
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 1%.mth	Run Mode:	Analysis
Run Time (min):	31.333	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		1.0019	14.467	0.000	3272965	0.00	BB	18.1		0
2		98.9981	18.573	0.000	323410208	0.00	BB	60.5		0
Totals		**100.0000**		**0.000**	**326683168**					



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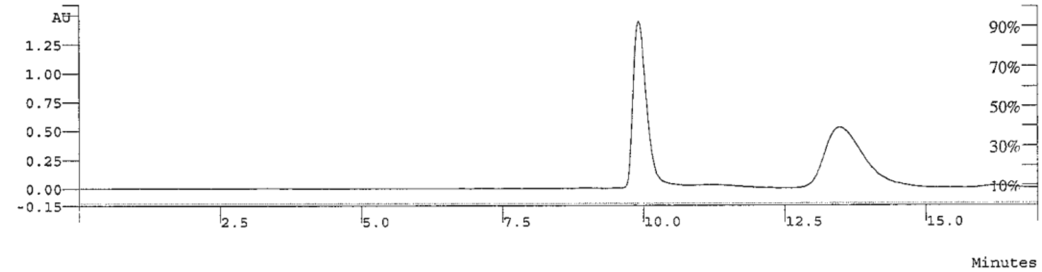
Data File: c:\star\12-18-13 10;45;17 am -1.run
Channel: 2 = 225.00 nm RESULTS
Sample ID: B3095-rac
Operator (Inj): OJ-H, iPrOH/Hex=1:99, FR=0.5
Injection Date:
jection Method: c:\star\lan\standard 1%.mth
Run Time (min): 16.987
Workstation:
Instrument (Inj): Varian Star #1

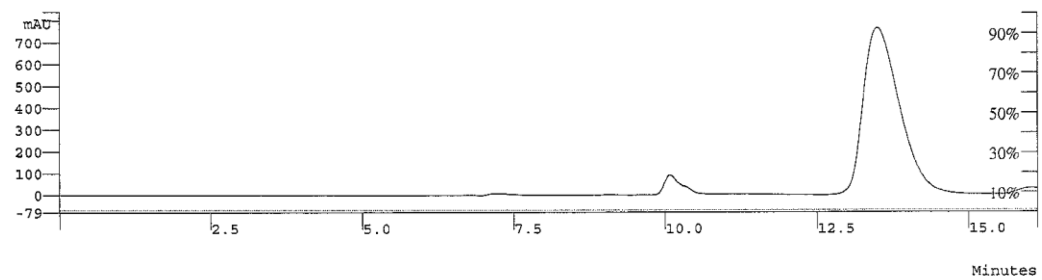
Operator (Calc):
Calc Date: 12/18/13 11:06:05 AM
Times Calculated: 5
Calculation Method: c:\windows\temp\~12-18-13 10;45;17
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



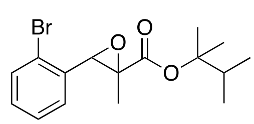
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		49.7787	9.907	0.000	123523392	0.00	BB	15.4		0
2		50.2213	13.480	0.000	124621584	0.00	BB	43.8		0
Totals		100.0000		0.000	248144976					

Data File: c:\star\12-18-13 11;11;21 am -1.run
Channel: 2 = 225.00 nm RESULTS
Sample ID: B3095-L*
Operator (Inj): OJ-H, iPrOH/Hex=1:99, FR=0.5
Injection Date:
jection Method: c:\star\lan\standard 1%.mth
Run Time (min): 16.160
Workstation:
Instrument (Inj): Varian Star #1

Operator (Calc):
Calc Date: 12/18/13 11:28:48 AM
Times Calculated: 1
Calculation Method: c:\windows\temp\~12-18-13 11;11;21
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A

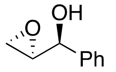
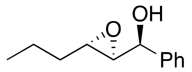
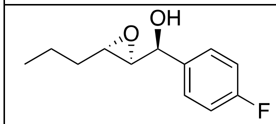
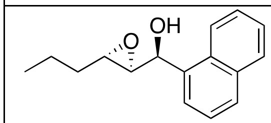
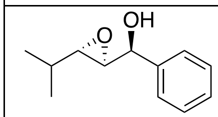
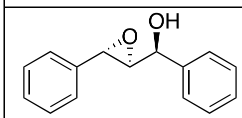
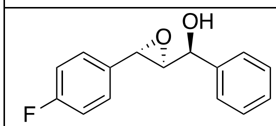


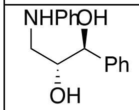
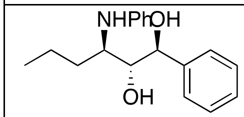
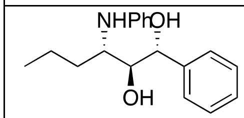
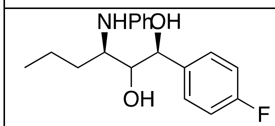
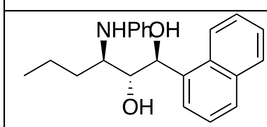
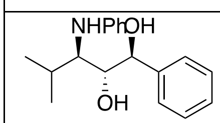
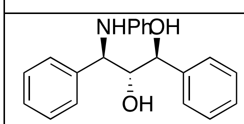
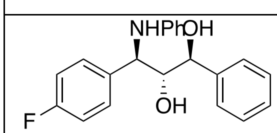
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		3.5411	10.067	0.000	5973274	0.00	BB	13.2		0
2		96.4589	13.507	0.000	162709312	0.00	BB	38.8		0
Totals		100.0000		0.000	168682592					

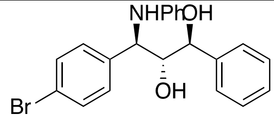
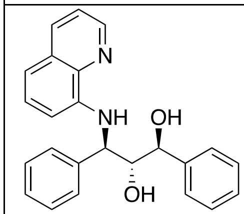
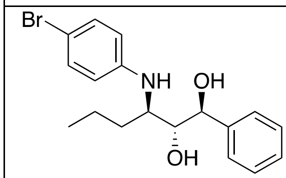
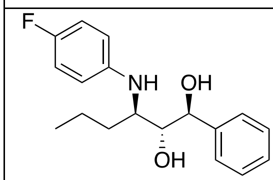
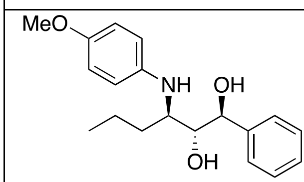
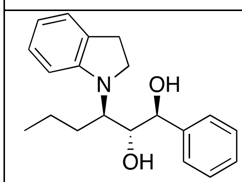
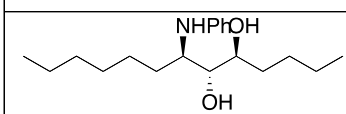
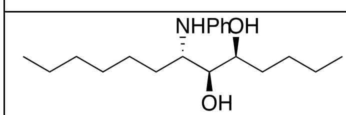


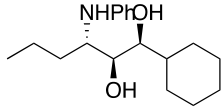
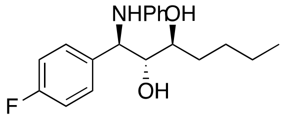
40

6.7 HPLC Data for Compounds **52-82**

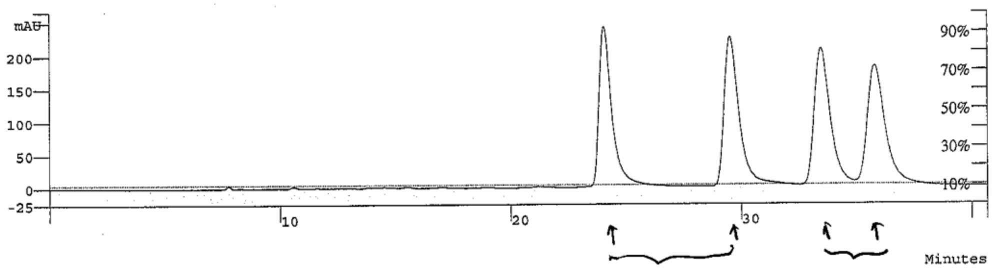
Epoxides		Conditions
	**52**	HPLC (Chiralpak IC): Condition: Isopropanol/Hexane = 5:95, flow rate = 0.75 mL/min; result: 18.9 min (major diastereomer, minor enantiomer), 25.0 min (major diastereomer, major enantiomer), 31.9 min (minor diastereomer)
	**53**	HPLC (Chiralpak IB): Condition: Isopropanol/Hexane = 5:95, flow rate = 0.75 mL/min; result: 11.6 min (major diastereomer, major enantiomer), 12.9 min (major diastereomer, minor enantiomer), 14.0 and 16.3 min (minor diastereomer)
	**55**	HPLC (Chiralpak IC): Condition: Isopropanol/Hexane = 5:95, flow rate = 0.75 mL/min; result: 10.9 min (major diastereomer, minor enantiomer), 13.0 min (major diastereomer, major enantiomer), 18.0 and 24.0 min (minor diastereomer)
	**56**	HPLC (Chiralpak AS-H): Condition: Isopropanol/Hexane = 10:90, flow rate = 0.75 mL/min; result: 12.6 min (major diastereomer, minor enantiomer), 16.5 min (major diastereomer, major enantiomer), 18.8 min (minor diastereomer)
	**57**	HPLC (Chiralpak IC): Condition: Isopropanol/Hexane = 5:95, flow rate = 0.75 mL/min; result: 1.31 min (major diastereomer, minor enantiomer), 19.0 min (major diastereomer, major enantiomer), 22.4 min (minor diastereomer)
	**58**	HPLC (Chiralpak AD-H): Condition: Isopropanol/Hexane = 10:90, flow rate = 0.75 mL/min; result: 15.7 min (major diastereomer, minor enantiomer), 19.6 min (major diastereomer, major enantiomer), 21.1 and 22.2 min (minor diastereomer)
	**59**	HPLC (Chiralpak IC): Condition: Isopropanol/Hexane = 5:95, flow rate = 0.75 mL/min; result: 15.5 min (major diastereomer, minor enantiomer), 21.7 min (major diastereomer, major enantiomer), 25.3 and 34.3 min (minor diastereomer)

Aminodiols		Conditions
	**65**	HPLC (Chiralpak IC): Condition: Hexane/Isopropanol = 10:90, flow rate = 0.5 mL/min; result: 24.5 and 30.1 min (minor diastereomer), 32.6 min (major diastereomer, minor enantiomer), 35.8 min (major diastereomer, major enantiomer)
	**66**	HPLC (Chiralpak IC): Condition: Isopropanol/Hexane = 5:95, flow rate = 0.75 mL/min; result: 17.2 min (major diastereomer, minor enantiomer), 18.3 min (major diastereomer, major enantiomer), 23.3 min (minor diastereomer)
	**67**	HPLC (Chiralpak IC): Condition: Isopropanol/Hexane = 5:95, flow rate = 0.75 mL/min; result: 17.1 min (major diastereomer, major enantiomer), 18.7 min (major diastereomer, minor enantiomer), 23.4 min (minor diastereomer)
	**68**	HPLC (Chiralpak ID): Condition: Isopropanol/Hexane = 5:95, flow rate = 0.75 mL/min; result: 24.9 min (major diastereomer, minor enantiomer), 26.1 min (minor diastereomer), 32.8 (major diastereomer, major enantiomer)
	**69**	HPLC (Chiralpak AD-H): Condition: Isopropanol/Hexane = 2:8, flow rate = 0.75 mL/min; result: 16.1 min (major diastereomer, minor enantiomer), 26.1 min (minor diastereomer), 32.8 (major diastereomer, major enantiomer)
	**70**	HPLC (Chiralpak IC): Condition: Isopropanol/Hexane = 5:95, flow rate = 0.75 mL/min; result: 16.7 min (major diastereomer, minor enantiomer), 18.5 min (minor diastereomer), 30.1 min (major diastereomer, major enantiomer)
	**71**	HPLC (Chiralpak AD-H): Condition: Isopropanol/Hexane = 2:8, flow rate = 0.75 mL/min; result: 14.5 min (major diastereomer, minor enantiomer), 16.3 and 25.3 min (minor diastereomer), 30.9 min (major diastereomer, major enantiomer)
	**72**	HPLC (Chiralpak AS-H): Condition: Isopropanol/Hexane = 2:8, flow rate = 0.5 mL/min; result: 16.3 min (major diastereomer, major enantiomer), 20.6 min (major diastereomer, minor enantiomer), 23.8 and 30.0 min (minor diastereomer)

	**73**	HPLC (Chiralpak IC): Condition: Isopropanol/Hexane = 5:95, flow rate = 0.75 mL/min; result: 15.6 min (major diastereomer, minor enantiomer), 19.7 min (major diastereomer, major enantiomer), 22.5 and 25.4 min (minor diastereomer)
	**74**	HPLC (Chiralpak IC): Condition: Isopropanol/Hexane = 3:7, flow rate = 0.5 mL/min; result: 12.2 min (major diastereomer, minor enantiomer), 14.5 min (major diastereomer, major enantiomer), 15.7 and 26.1 min (minor diastereomer)
	**75**	HPLC (Chiralpak IB): Condition: Isopropanol/Hexane = 1:9, flow rate = 0.5 mL/min; result: 20.6 (major diastereomer, minor enantiomer), 21.4 (minor diastereomer), 22.8 (major diastereomer, major enantiomer), 27.5 (minor diastereomer)
	**76**	HPLC (Chiralpak IC): Condition: Isopropanol/Hexane = 5:95, flow rate = 0.75 mL/min; result: 13.5 min (major diastereomer, minor enantiomer), 14.7 min (major diastereomer, major enantiomer), 17.4 and 20.1 min (minor diastereomer)
	**77**	HPLC (Chiralpak AD-H): Condition: Isopropanol/Hexane = 2:8, flow rate = 0.5 mL/min; result: 20.3 min (major diastereomer, major enantiomer), 22.3 (major diastereomer, minor enantiomer), 24.0 and 37.5 (minor diastereomer)
	**78**	HPLC (Chiralpak AD-H): Condition: Isopropanol/Hexane = 1:9, flow rate = 0.75 mL/min; result: 13.3 min (major diastereomer, major enantiomer), 14.5 (major diastereomer, minor enantiomer), 15.3 and 18.6 (minor diastereomer)
	**79**	HPLC (Chiralpak AS-H): Condition: Isopropanol/Hexane = 6:94, flow rate = 0.4 mL/min; result: 16.0 min (major enantiomer), 19.6 min (minor enantiomer)
	**80**	HPLC (Chiralpak AS-H): Condition: Isopropanol/Hexane = 6:94, flow rate = 0.4 mL/min; result: 21.3 min (major enantiomer), 23.1 min (minor enantiomer)

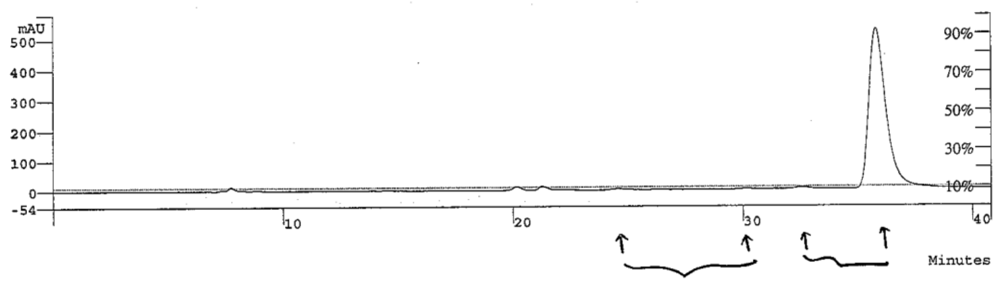
	**81**	HPLC (Chiralpak AD-H): Condition: Isopropanol/Hexane = 1:9, flow rate = 0.5 mL/min; result: 22.4 min (major enantiomer), 24.3 min (minor enantiomer)
	**82**	HPLC (Chiralpak IC): Condition: Isopropanol/Hexane = 5:95, flow rate = 0.75 mL/min; result: 10.3 min (minor enantiomer), 12.5 min (major enantiomer)

Data File:	c:\star\1-16-15 3;32;38 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	01/16/15 04:16:52 PM
Sample ID:	B5207_rac+rac	Times Calculated:	2
Operator (Inj):	IC, iPrOH/Hex=1:9, FR=0.5	Calculation Method:	c:\windows\temp\~1-16-15 3;32;38 pm
Injection Date:		Instrument (Calc):	Varian Star #1
ection Method:	c:\star\lan\standard 10%_0.5ml.mth	Run Mode:	Analysis
Run Time (min):	40.693	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

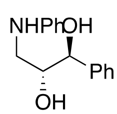


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		25.0983	24.040	0.000	48623556	0.00	BB	33.7		0
2		25.5755	29.507	0.000	49547992	0.00	BB	39.3		0
3		24.8864	33.427	0.000	48212876	0.00	BB	43.4		0
4		24.4398	35.773	0.000	47347740	0.00	BB	46.5		0
	Totals	**100.0000**		**0.000**	**193732176**					

Data File:	c:\star\1-16-15 4;17;30 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	01/16/15 05:02:02 PM
Sample ID:	B6039_Ti(L)+W(S)	Times Calculated:	4
Operator (Inj):	IC, iPrOH/Hex=1:9, FR=0.5	Calculation Method:	c:\windows\temp\~1-16-15 4;17;30 pm
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 10%_0.5ml.mth	Run Mode:	Analysis
Run Time (min):	40.827	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

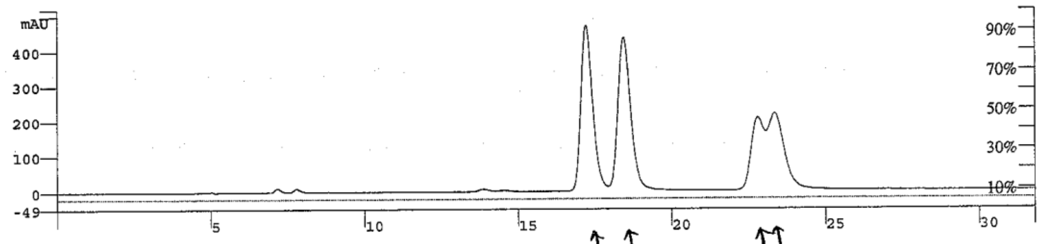


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		0.2800	24.547	0.000	398810	0.00	BB	28.9		0
2		0.1862	30.147	0.000	265262	0.00	BB	32.3		0
3		0.2359	32.573	0.000	336013	0.00	BB	21.7		0
4		99.2978	35.773	0.000	141428528	0.00	BB	46.4		0
	Totals	**99.9999**		**0.000**	**142428608**					



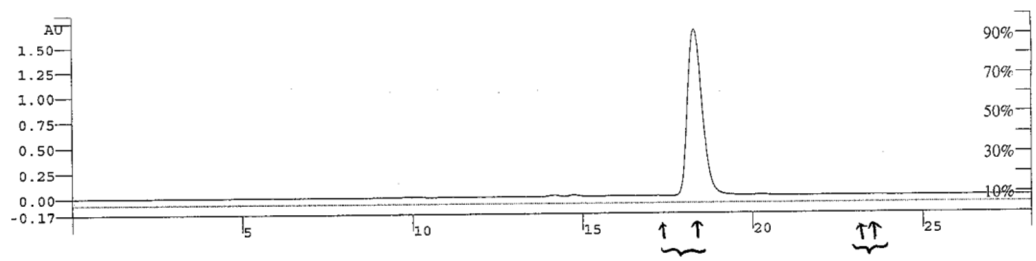
65

Data File:	c:\star\1-28-15 5;59;17 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	01/28/15 06:32:24 PM
Sample ID:	B6079_rac+rac	Times Calculated:	1
Operator (Inj):	IC, iPrOH/Hex=5:95, FR=0.75	Calculation Method:	c:\windows\temp\~1-28-15 5;59;17 pm
Injection Date:		Instrument (Calc):	Varian Star #1
Injection Method:	c:\star\lan\standard 5%_0.75ml.mth	Run Mode:	Analysis
Run Time (min):	31.840	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

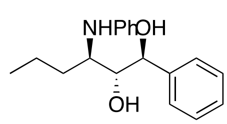


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		31.9587	17.213	0.000	61281116	0.00	BB	24.3		0
2		30.9963	18.440	0.000	59435848	0.00	BB	25.5		0
3		37.0450	23.347	0.000	71034160	0.00	BB	65.9		0
	Totals	**100.0000**		**0.000**	**191751120**					

Data File:	c:\star\1-31-15 4;08;31 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	01/31/15 04:40:22 PM
Sample ID:	B6081_Ti(L)+W(S,S)	Times Calculated:	1
Operator (Inj):	IC, iPrOH/Hex=5:95, FR=0.75	Calculation Method:	c:\windows\temp\~1-31-15 4;08;31 pm
Injection Date:		Instrument (Calc):	Varian Star #1
Injection Method:	c:\star\lan\standard 5%_0.75ml.mth	Run Mode:	Analysis
Run Time (min):	28.213	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

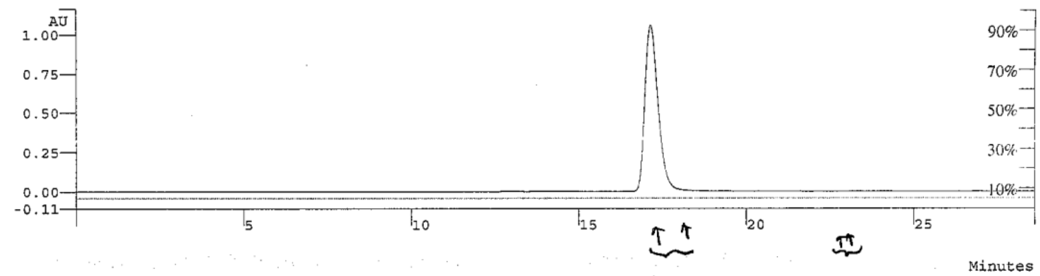


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		0.0483	17.160	0.000	122217	0.00	BB	13.5		0
2		99.8829	18.280	0.000	252486272	0.00	BB	27.7		0
3		0.0687	23.320	0.000	173717	0.00	BB	24.7		0
	Totals	**99.9999**		**0.000**	**252782208**					

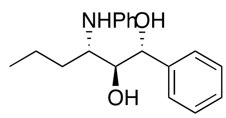


66

Data File:	c:\star\1-31-15 4;38;25 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	01/31/15 05:15:15 PM
Sample ID:	B6101_Ti(D)+W(R,R)	Times Calculated:	16
Operator (Inj):	IC, iPrOH/Hex=5:95, FR=0.75	Calculation Method:	c:\windows\temp\~1-31-15 4;38;25 pm
Injection Date:		Instrument (Calc):	Varian Star #1
Injection Method:	c:\star\lan\standard 5%_0.75ml.mth	Run Mode:	Analysis
Run Time (min):	28.640	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

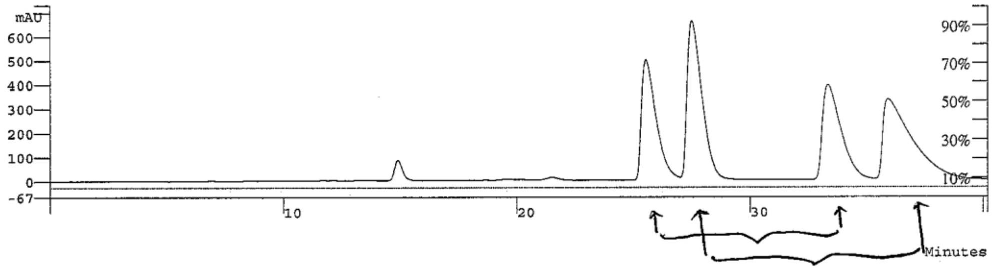


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		99.9243	17.133	0.000	148680608	0.00	BB	25.4		0
2		0.0171	18.733	0.000	25398	0.00	BB	0.0		0
3		0.0587	23.427	0.000	87304	0.00	BB	21.7		0
	Totals	**100.0001**		**0.000**	**148793312**					



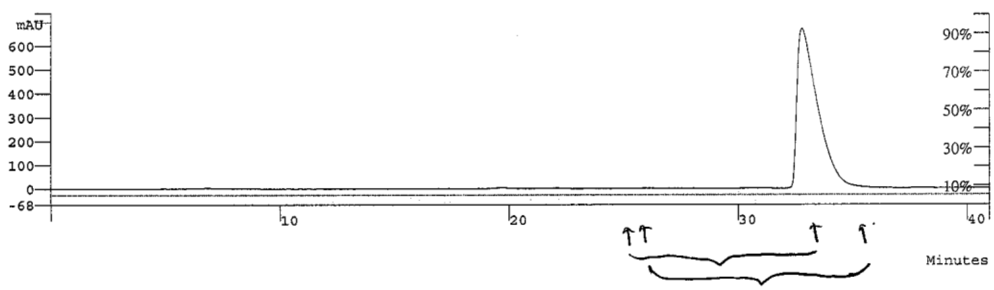
67

Data File:	c:\star\1-29-15 5;57;06 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	01/29/15 06:39:22 PM
Sample ID:	B6073_rac+rac	Times Calculated:	1
Operator (Inj):	ID, iPrOH/Hex=5:95, FR=0.75	Calculation Method:	c:\windows\temp\~1-29-15 5;57;06 pm
Injection Date:		Instrument (Calc):	Varian Star #1
ection Method:	c:\star\lan\standard 5%_0.75ml.mth	Run Mode:	Analysis
Run Time (min):	40.213	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

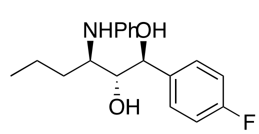


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		21.4068	25.533	0.000	107920968	0.00	BB	39.8		0
2		28.0996	27.480	0.000	141662352	0.00	BB	40.0		0
3		21.5864	33.320	0.000	108826552	0.00	BB	50.9		0
4		28.9073	35.907	0.000	145734528	0.00	BB	77.0		0
	Totals	**100.0001**		**0.000**	**504144416**					

Data File:	c:\star\1-29-15 6;41;29 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	01/29/15 07:30:04 PM
Sample ID:	B6097_Ti(L)+W(S,S)	Times Calculated:	5
Operator (Inj):	ID, iPrOH/Hex=5:95, FR=0.75	Calculation Method:	c:\windows\temp\~1-29-15 6;41;29 pm
Injection Date:		Instrument (Calc):	Varian Star #1
ection Method:	c:\star\lan\standard 5%_0.75ml.mth	Run Mode:	Analysis
Run Time (min):	40.987	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		0.0184	24.920	0.000	39843	0.00	BB	25.6		0
2		0.0766	26.067	0.000	166012	0.00	BB	33.0		0
3		99.9050	32.760	0.000	216518832	0.00	BB	57.0		0
	Totals	**100.0000**		**0.000**	**216724688**					



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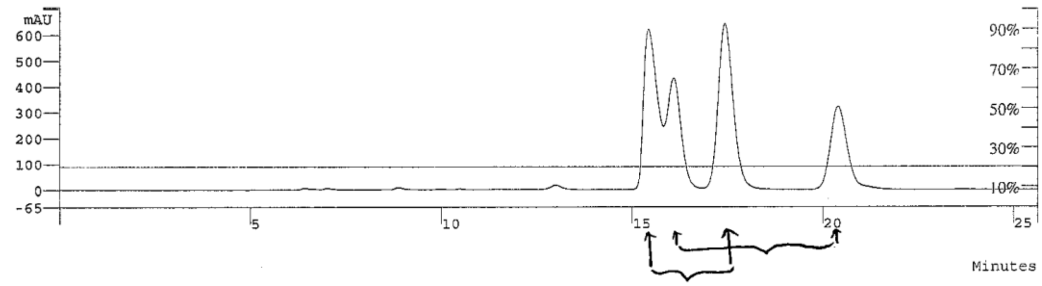
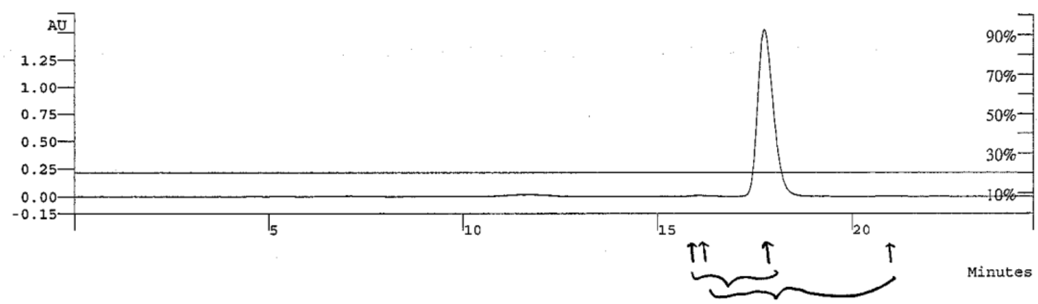
Data File:	c:\star\1-31-15 8;50;44 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	02/02/15 07:03:18 PM
Sample ID:	B6075_rac+rac	Times Calculated:	2
Operator (Inj):	AD-H, iPrOH/Hex=2:8, FR=0.75	Calculation Method:	c:\windows\temp\~2-2-15 6;18;25 pm
Injection Date:		Instrument (Calc):	Varian Star #1
;ection Method:	c:\star\lan\standard 20%_0.75ml.mth	Run Mode:	Analysis
~.un Time (min):	25.653	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

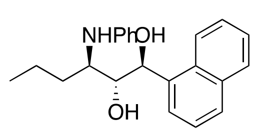


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		49.8843	15.427	0.000	135710368	0.00	BB	25.5		0
2		31.9281	17.427	0.000	86860528	0.00	BB	24.8		0
3		18.1875	20.387	0.000	49479132	0.00	BB	27.5		0
	Totals	**99.9999**		**0.000**	**272050016**					

Data File:	c:\star\2-2-15 7;21;39 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	02/02/15 07:49:50 PM
Sample ID:	B6099_Ti(L)+W(S,S)	Times Calculated:	2
Operator (Inj):	AD-H, iPrOH/Hex=2:8, FR=0.75	Calculation Method:	c:\windows\temp\~2-2-15 7;21;39 pm
Injection Date:		Instrument (Calc):	Varian Star #1
;ection Method:	c:\star\lan\standard 20%_0.75ml.mth	Run Mode:	Analysis
~.un Time (min):	24.693	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		0.3196	16.067	0.000	701760	0.00	BB	21.1		0
2		99.4820	17.747	0.000	218422640	0.00	BB	25.8		0
3		0.1984	21.000	0.000	435562	0.00	BB	25.0		0
	Totals	**100.0000**		**0.000**	**219559968**					



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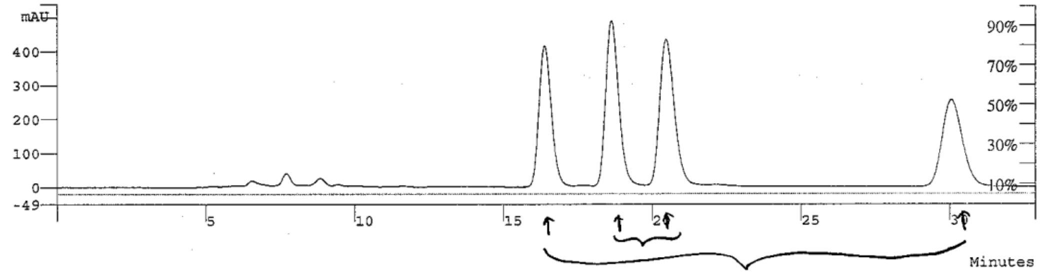
Data File: c:\star\2-16-15 3;55;26 pm -1.run
Channel: 1 = 254.00 nm RESULTS
Sample ID: B6135_rac+rac
Operator (Inj): IC, iPrOH/Hex=5:95, FR=0.75
Injection Date:
ection Method: c:\star\lan\standard 5%_0.75ml.mth
.un Time (min): 32.907
Workstation:
Instrument (Inj): Varian Star #1

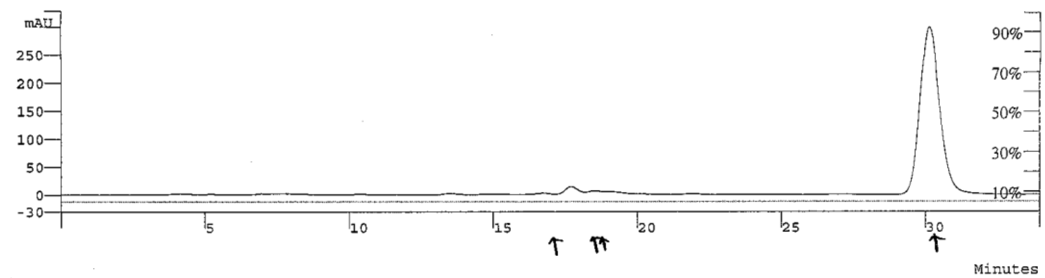
Operator (Calc):
Calc Date: 02/16/15 04:30:06 PM
Times Calculated: 1
Calculation Method: c:\windows\temp\~2-16-15 3;55;26 pm
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



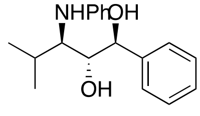
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		22.4219	16.387	0.000	61268648	0.00	BB	27.1		0
2		27.5499	18.627	0.000	75280960	0.00	BB	28.1		0
3		27.3876	20.467	0.000	74837592	0.00	BB	31.7		0
4		22.6406	30.040	0.000	61866192	0.00	BB	44.2		0
Totals		**100.0000**		**0.000**	**273253376**					

Data File: c:\star\2-16-15 4;30;36 pm -1.run
Channel: 1 = 254.00 nm RESULTS
Sample ID: B6143_Ti(L)+W(S,S)
Operator (Inj): IC, iPrOH/Hex=5:95, FR=0.75
Injection Date:
ection Method: c:\star\lan\standard 5%_0.75ml.mth
.un Time (min): 34.000
Workstation:
Instrument (Inj): Varian Star #1

Operator (Calc):
Calc Date: 02/16/15 05:07:57 PM
Times Calculated: 3
Calculation Method: c:\windows\temp\~2-16-15 4;30;36 pm
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		0.3140	16.733	0.000	229130	0.00	BB	24.8		0
2		0.2794	18.520	0.000	203884	0.00	BB	21.4		0
3		99.4065	30.120	0.000	72528952	0.00	BB	43.6		0
Totals		**99.9999**		**0.000**	**72961968**					



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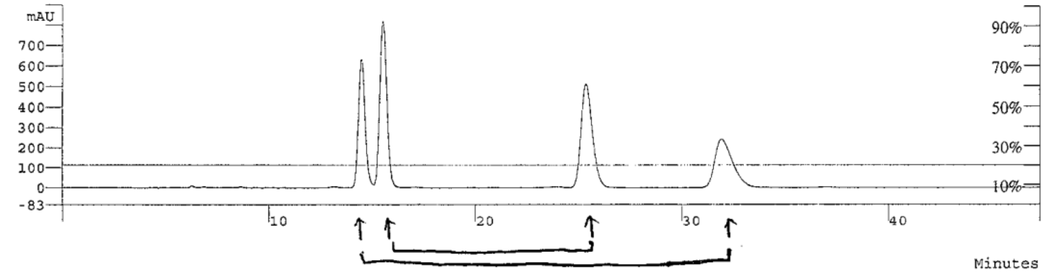
Data File: c:\star\11-20-14 1;37;34 pm -1.run
Channel: 1 = 254.00 nm RESULTS
Sample ID: B5233_rac
Operator (Inj): AD-H, iPrOH/Hex=2:8, FR=0.75
Injection Date:
Injection Method: c:\star\lan\standard 20%_0.75ml.mth
Run Time (min): 47.360
Workstation:
Instrument (Inj): Varian Star #1

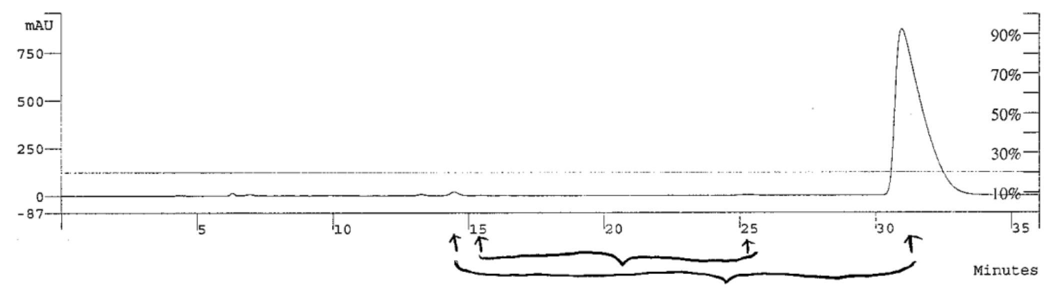
Operator (Calc):
Calc Date: 11/20/14 04:14:06 PM
Times Calculated: 1
Calculation Method: c:\windows\temp\~11-20-14 3;17;30
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



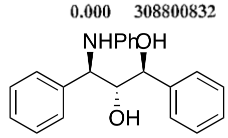
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		20.9943	14.467	0.000	71008656	0.00	BB	20.9		0
2		28.0079	15.507	0.000	94730736	0.00	BB	21.8		0
3		29.7512	25.347	0.000	100627064	0.00	BB	36.0		0
4		21.2467	31.907	0.000	71862464	0.00	BB	54.7		0
	Totals	**100.0001**		**0.000**	**338228928**					

Data File: c:\star\11-20-14 3;17;30 pm -1.run
Channel: 1 = 254.00 nm RESULTS
Sample ID: B5247_Ti(L)+W(S,S)
Operator (Inj): AD-H, iPrOH/Hex=2:8, FR=0.75
Injection Date:
Injection Method: c:\star\lan\standard 20%_0.75ml.mth
Run Time (min): 36.053
Workstation:
Instrument (Inj): Varian Star #1

Operator (Calc):
Calc Date: 11/20/14 04:22:01 PM
Times Calculated: 1
Calculation Method: c:\windows\temp\~11-20-14 3;17;30
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		0.5991	14.467	0.000	1850051	0.00	BB	18.6		0
2		0.0589	16.280	0.000	181911	0.00	BB	19.2		0
3		0.2228	25.267	0.000	688066	0.00	BB	33.0		0
4		99.1192	30.947	0.000	306080800	0.00	BB	63.1		0
	Totals	**100.0000**		**0.000**	**308800832**					



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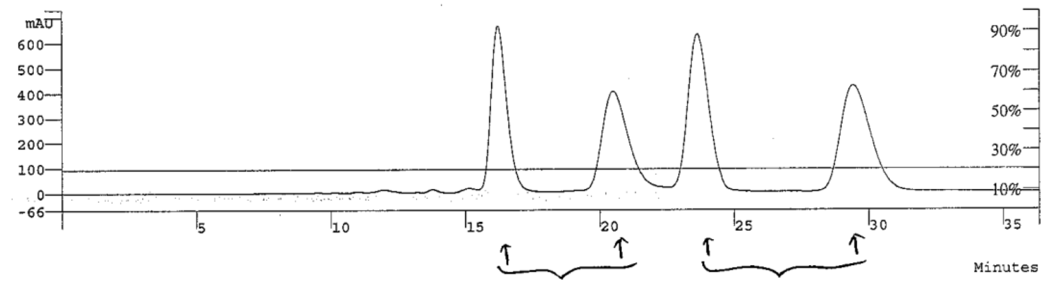
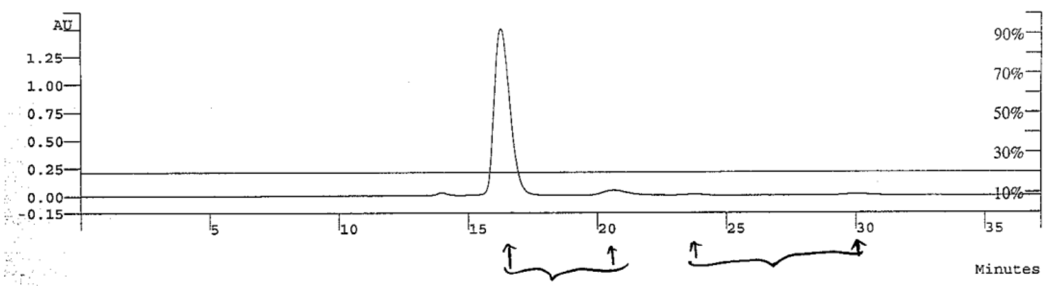
Data File:	c:\star\2-17-15 1;23;22 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	02/17/15 02:01:02 PM
Sample ID:	B6115_rac+rac	Times Calculated:	1
Operator (Inj):	AS-H, iPrOH/Hex=2:8, FR=0.5	Calculation Method:	c:\windows\temp\~2-17-15 1;23;22 pm
Injection Date:		Instrument (Calc):	Varian Star #1
ection Method:	c:\star\lan\standard 20%_0.5ml.mth	Run Mode:	Analysis
Run Time (min):	36.373	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

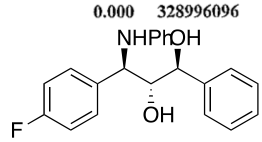


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		22.2775	16.200	0.000	134810880	0.00	BB	37.5		0
2		21.8296	20.493	0.000	132100840	0.00	BB	62.2		0
3		27.9268	23.640	0.000	168997456	0.00	BB	50.3		0
4		27.9662	29.400	0.000	169235792	0.00	BB	73.3		0
Totals		**100.0001**		**0.000**	**605144960**					

Data File:	c:\star\2-17-15 2;01;21 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	02/17/15 02:40:04 PM
Sample ID:	B6145_Ti(L)+W(S,S)	Times Calculated:	1
Operator (Inj):	AS-H, iPrOH/Hex=2:8, FR=0.5	Calculation Method:	c:\windows\temp\~2-17-15 2;01;21 pm
Injection Date:		Instrument (Calc):	Varian Star #1
ection Method:	c:\star\lan\standard 20%_0.5ml.mth	Run Mode:	Analysis
Run Time (min):	37.200	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		97.2227	16.253	0.000	319858848	0.00	BB	39.2		0
2		1.9307	20.627	0.000	6351976	0.00	BB	39.8		0
3		0.3440	23.773	0.000	1131722	0.00	BB	31.0		0
4		0.5026	30.013	0.000	1653584	0.00	BB	41.5		0
Totals		**100.0000**		**0.000**	**328996096**					



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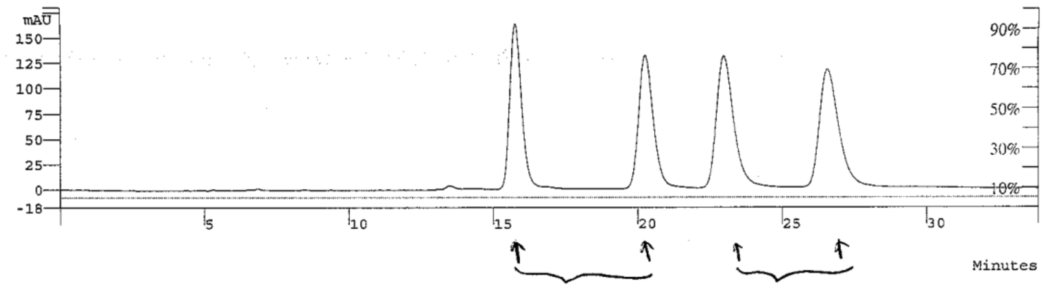
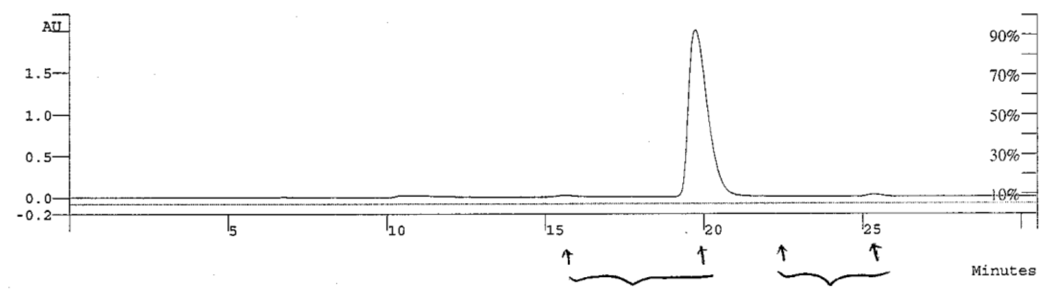
Data File:	c:\star\3-5-15 4;01;34 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	03/05/15 04:38:40 PM
Sample ID:	B6179_rac+rac	Times Calculated:	1
Operator (Inj):	IC, iPrOH/Hex=5:95, FR=0.75	Calculation Method:	c:\windows\temp\~3-5-15 4;01;34 pm
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 5%_0.75ml.mth	Run Mode:	Analysis
un Time (min):	33.893	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

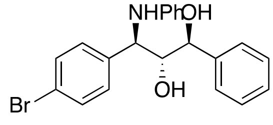


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		23.1161	15.747	0.000	23471788	0.00	BB	26.2		0
2		23.1387	20.253	0.000	23494790	0.00	BB	32.7		0
3		26.7864	22.973	0.000	27198646	0.00	BB	37.6		0
4		26.9588	26.547	0.000	27373626	0.00	BB	42.2		0
	Totals	**100.0000**		**0.000**	**101538848**					

Data File:	c:\star\3-9-15 2;11;48 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	03/09/15 02:47:02 PM
Sample ID:	B6195_Ti(L)+W(S,S)	Times Calculated:	4
Operator (Inj):	IC, iPrOH/Hex=5:95, FR=0.75	Calculation Method:	c:\windows\temp\~3-9-15 2;11;48 pm
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 5%_0.75ml.mth	Run Mode:	Analysis
un Time (min):	30.533	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		0.1669	15.613	0.000	709598	0.00	BB	15.8		0
2		99.6454	19.720	0.000	423536480	0.00	BB	38.5		0
3		0.0046	22.520	0.000	19410	0.00	BB	7.3		0
4		0.1830	25.373	0.000	778024	0.00	BB	12.5		0
	Totals	**99.9999**		**0.000**	**425043520**					



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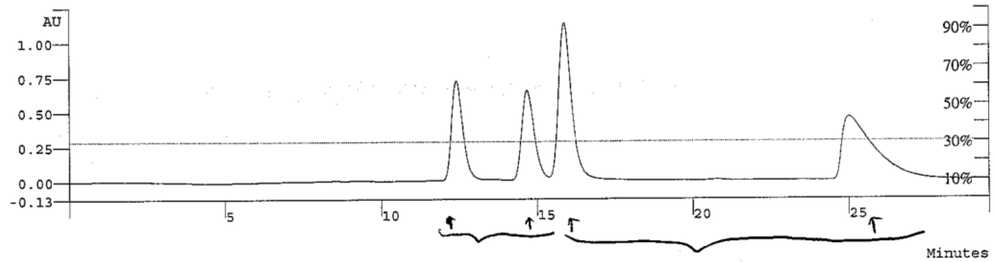
Data File: c:\star\4-27-15 4;59;29 pm -1.run
Channel: 2 = 225.00 nm RESULTS
Sample ID: B6257_rac+rac
Operator (Inj): IC, iPrOH/Hex=3:7, FR=0.5
Injection Date:
Injection Method: c:\star\lan\standard 30%_0.5ml.mth
Run Time (min): 29.520
Workstation:
Instrument (Inj): Varian Star #1

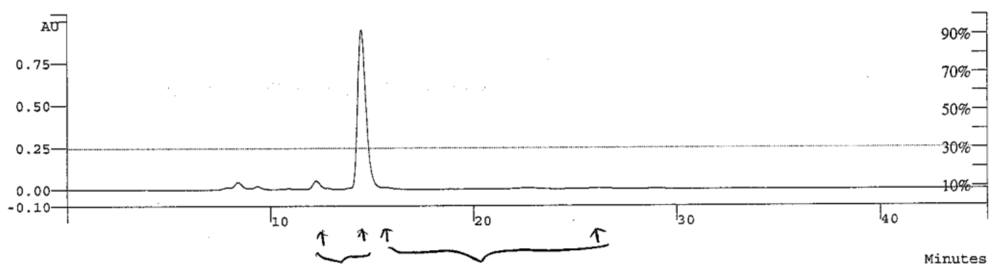
Operator (Calc):
Calc Date: 04/27/15 05:31:54 PM
Times Calculated: 3
Calculation Method: c:\windows\temp\~4-27-15 4;59;29 pm
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



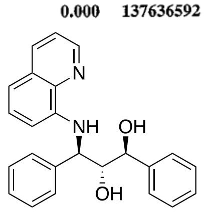
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		17.8667	12.413	0.000	88310664	0.00	BB	23.0		0
2		17.8553	14.680	0.000	88254688	0.00	BB	25.7		0
3		32.3890	15.880	0.000	160091216	0.00	BB	25.9		0
4		31.8890	25.000	0.000	157619840	0.00	BB	64.2		0
	Totals	**100.0000**		**0.000**	**494276416**					

Data File: c:\star\4-27-15 5;32;29 pm -1.run
Channel: 2 = 225.00 nm RESULTS
Sample ID: B6265_Ti(L)+W(S)
Operator (Inj): IC, iPrOH/Hex=3:7, FR=0.5
Injection Date:
Injection Method: c:\star\lan\standard 30%_0.5ml.mth
Run Time (min): 45.307
Workstation:
Instrument (Inj): Varian Star #1

Operator (Calc):
Calc Date: 04/27/15 06:22:48 PM
Times Calculated: 4
Calculation Method: c:\windows\temp\~4-27-15 5;32;29 pm
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		1.8313	12.227	0.000	2520500	0.00	BB	14.3		0
2		97.2593	14.467	0.000	133864400	0.00	BB	25.9		0
3		0.1447	15.667	0.000	199182	0.00	BB	2.9		0
4		0.7647	26.093	0.000	1052506	0.00	BB	43.1		0
	Totals	**100.0000**		**0.000**	**137636592**					



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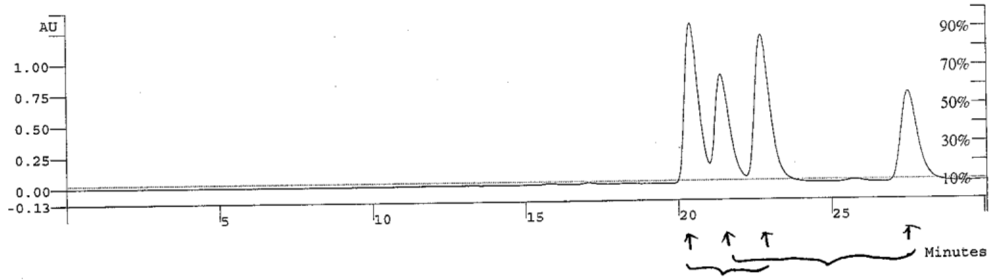
Data File: c:\star\2-20-15 4;58;45 pm -1.run
Channel: 1 = 254.00 nm RESULTS
Sample ID: B6147_rac+rac
Operator (Inj): IB
Injection Date:
Injection Method: c:\star\lan\standard 10%_0.5ml.mth
Run Time (min): 30.107
Workstation:
Instrument (Inj): Varian Star #1

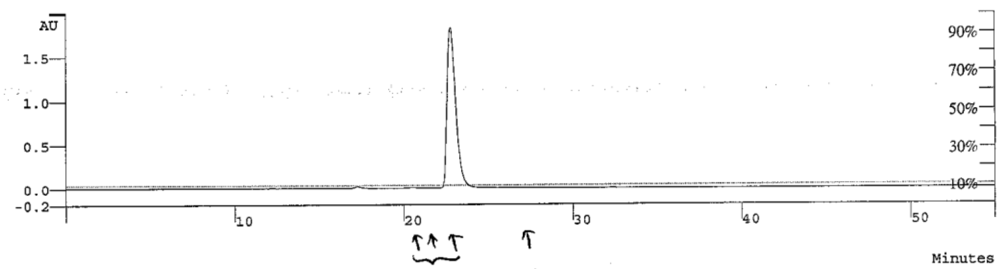
Operator (Calc):
Calc Date: 02/20/15 05:30:03 PM
Times Calculated: 1
Calculation Method: c:\windows\temp\~2-20-15 4;58;45 pm
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



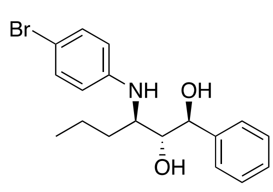
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		29.1302	20.387	0.000	172309296	0.00	BB	29.1		0
2		14.1574	21.373	0.000	83742992	0.00	BB	23.4		0
3		32.7919	22.680	0.000	193968800	0.00	BB	30.6		0
4		23.9206	27.507	0.000	141494080	0.00	BB	35.1		0
	Totals	100.0001		0.000	591515136					

Data File: c:\star\2-25-15 4;33;01 pm -1.run
Channel: 1 = 254.00 nm RESULTS
Sample ID: B6153_Ti(L)+W(S,S)
Operator (Inj): IB, iPrOH/Hex=1:9, FR=0.5
Injection Date:
Injection Method: c:\star\lan\standard 10%_0.5ml.mth
Run Time (min): 55.013
Workstation:
Instrument (Inj): Varian Star #1

Operator (Calc):
Calc Date: 02/25/15 05:32:10 PM
Times Calculated: 2
Calculation Method: c:\windows\temp\~2-25-15 4;33;01 pm
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		0.1768	20.573	0.000	592482	0.00	BB	25.0		0
2		99.8232	22.760	0.000	334603168	0.00	BB	32.8		0
	Totals	100.0000		0.000	335195648					



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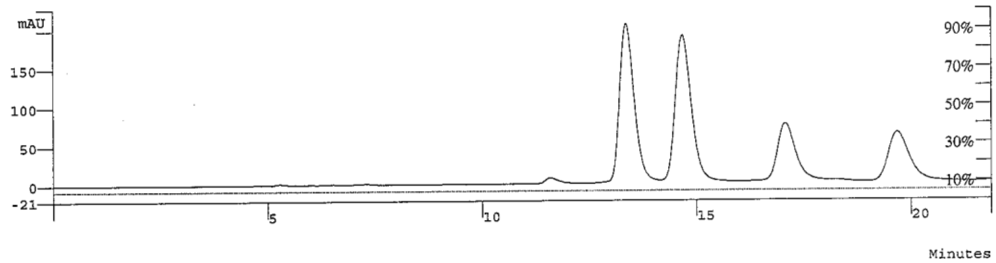
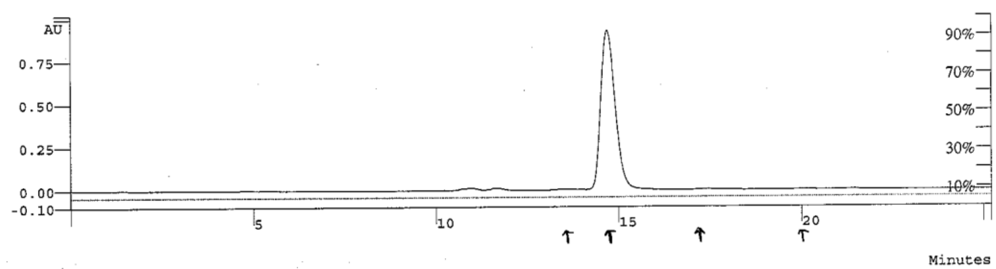
Data File:	c:\star\2-17-15 12;37;13 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	02/17/15 01:02:12 PM
Sample ID:	B6149_rac+rac	Times Calculated:	1
Operator (Inj):	IC, iPrOH/Hex=5:95, FR=0.75	Calculation Method:	c:\windows\temp\~2-17-15 12;37;13
Injection Date:		Instrument (Calc):	Varian Star #1
ection Method:	c:\star\lan\standard 5%_0.75ml.mth	Run Mode:	Analysis
ın Time (min):	21.893	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

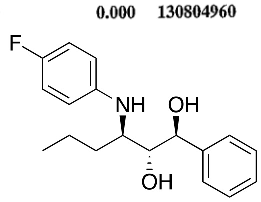


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		34.7445	13.373	0.000	24434754	0.00	BB	21.8		0
2		34.9763	14.680	0.000	24597800	0.00	BB	23.6		0
3		14.9323	17.053	0.000	10501462	0.00	BB	26.0		0
4		15.3469	19.667	0.000	10792987	0.00	BB	30.9		0
	Totals	**100.0000**		**0.000**	**70327000**					

Data File:	c:\star\2-20-15 2;42;17 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	02/20/15 03:11:03 PM
Sample ID:	B6155_Ti(L)+W(S,S)	Times Calculated:	3
Operator (Inj):	IC, iPrIH/Hex=5:95, FR=0.75	Calculation Method:	c:\windows\temp\~2-20-15 2;42;17 pm
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 5%_0.75ml.mth	Run Mode:	Analysis
ın Time (min):	25.227	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		0.2336	13.533	0.000	305566	0.00	BB	21.6		0
2		99.4988	14.680	0.000	130149392	0.00	BB	25.6		0
3		0.1784	17.400	0.000	233421	0.00	BB	23.4		0
4		0.0891	20.147	0.000	116577	0.00	BB	22.0		0
	Totals	**99.9999**		**0.000**	**130804960**					



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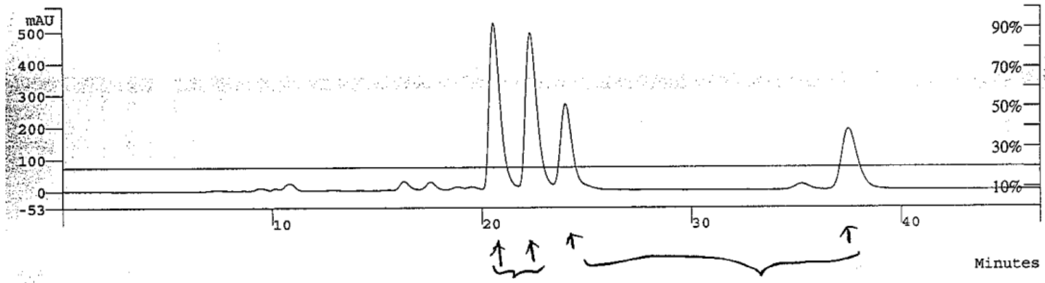
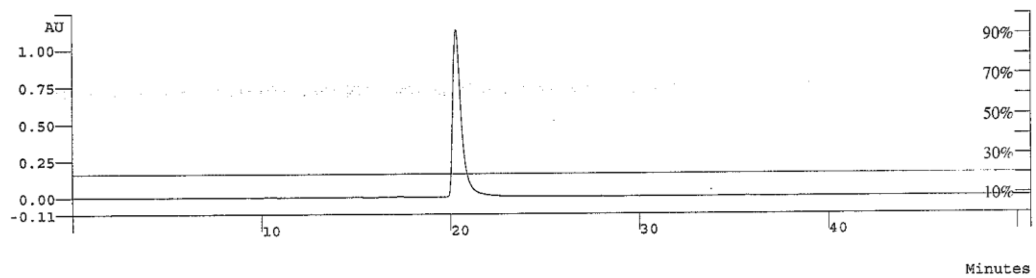
Data File:	c:\star\2-25-15 6;58;54 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	02/25/15 07:50:21 PM
Sample ID:	B6157_rac+rac	Times Calculated:	6
Operator (Inj):	AD-H, iPrOH/Hex=2:8, FR=0.5	Calculation Method:	c:\windows\temp\~2-25-15 6;58;54 pm
Injection Date:		Instrument (Calc):	Varian Star #1
ection Method:	c:\star\lan\standard 20%_0.5ml.mth	Run Mode:	Analysis
un Time (min):	46.667	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

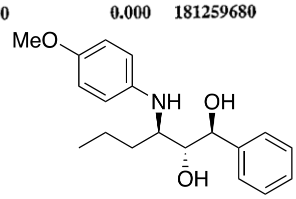


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		37.2175	20.547	0.000	90539472	0.00	BB	32.8		0
2		35.0896	22.280	0.000	85362936	0.00	BB	34.2		0
3		14.5842	23.987	0.000	35479124	0.00	BB	30.8		0
4		13.1087	37.480	0.000	31889580	0.00	BB	38.8		0
	Totals	**100.0000**		**0.000**	**243271104**					

Data File:	c:\star\2-26-15 4;38;54 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	02/26/15 05:36:30 PM
Sample ID:	B6161_Ti(L)+W(S,S)	Times Calculated:	10
Operator (Inj):	AD-H, iPrOH/Hex=2:8, FR=0.5	Calculation Method:	c:\windows\temp\~2-26-15 4;38;54 pm
Injection Date:		Instrument (Calc):	Varian Star #1
jection Method:	c:\star\lan\standard 20%_0.5ml.mth	Run Mode:	Analysis
un Time (min):	50.747	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		100.0000	20.280	0.000	181259680	0.00	BB	27.2		0
	Totals	**100.0000**		**0.000**	**181259680**					



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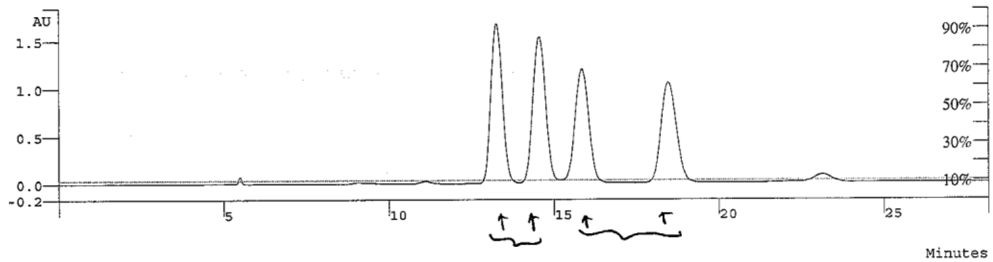
Data File: c:\star\2-24-15 3;22;07 pm -1.run
Channel: 1 = 254.00 nm RESULTS
Sample ID: B6159_rac+rac
Operator (Inj): AD-H, iPrOH/Hex=1:9, FR=0.75
Injection Date:
jection Method: c:\star\chuan\standard 10% 0.75 ml.mth
un Time (min): 28.187
Workstation:
Instrument (Inj): Varian Star #1

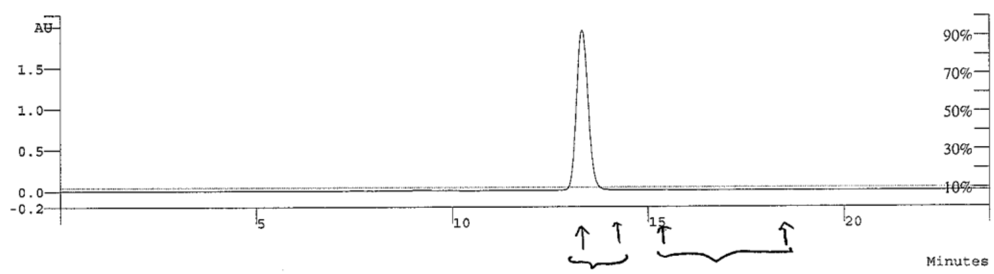
Operator (Calc):
Calc Date: 02/24/15 03:51:33 PM
Times Calculated: 1
Calculation Method: c:\windows\temp\~2-24-15 3;22;07 pm
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



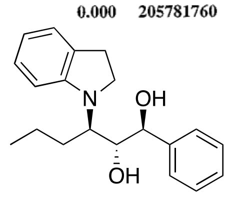
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		27.2154	13.240	0.000	206342352	0.00	BB	23.1		0
2		27.2808	14.547	0.000	206838272	0.00	BB	25.6		0
3		22.7360	15.827	0.000	172379792	0.00	BB	27.1		0
4		22.7678	18.467	0.000	172621136	0.00	BB	30.6		0
Totals		**100.0000**		**0.000**	**758181504**					

Data File: c:\star\2-24-15 4;48;54 pm -1.run
Channel: 1 = 254.00 nm RESULTS
Sample ID: B6163_Ti(L)+W(S,S)
Operator (Inj): AD-H, iPrOH/Hex=1:9, FR=0.75
Injection Date:
'ection Method: c:\star\chuan\standard 10% 0.75 ml.mth
un Time (min): 23.733
Workstation:
Instrument (Inj): Varian Star #1

Operator (Calc):
Calc Date: 02/24/15 05:38:00 PM
Times Calculated: 4
Calculation Method: c:\windows\temp\~2-24-15 4;48;54 pm
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		99.8897	13.320	0.000	205554688	0.00	BB	19.3		0
2		0.0060	14.547	0.000	12435	0.00	BB	4.0		0
3		0.0559	15.320	0.000	115011	0.00	BB	12.0		0
4		0.0484	18.627	0.000	99629	0.00	BB	19.3		0
Totals		**100.0000**		**0.000**	**205781760**					



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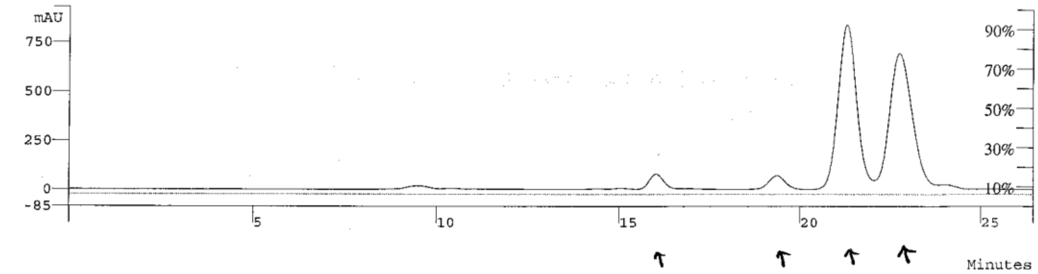
Data File: c:\star\7-20-15 1;56;28 pm -1.run
Channel: 1 = 254.00 nm RESULTS
Sample ID: B5251_rac+rac
Operator (Inj): AS-H, iPrOH/Hex=6:94, FR=0.4
Injection Date:
Injection Method: c:\star\lan\standard 6%_0.4ml.mth
Run Time (min): 26.427
Workstation:
Instrument (Inj): Varian Star #1

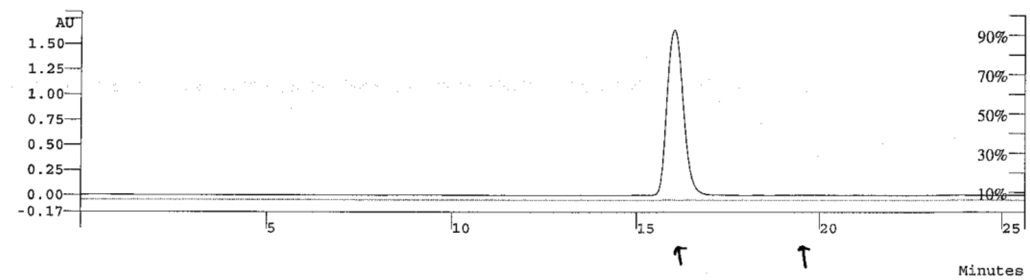
Operator (Calc):
Calc Date: 07/20/15 03:11:39 PM
Times Calculated: 2
Calculation Method: c:\windows\temp\~7-20-15 1;56;28 pm
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



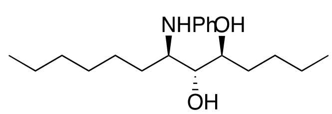
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		3.4601	16.013	0.000	10582829	0.00	BB	26.0		0
2		3.5673	19.347	0.000	10910850	0.00	BB	28.7		0
3		46.8159	21.267	0.000	143189152	0.00	BB	32.8		0
4		46.1567	22.707	0.000	141172944	0.00	BB	38.6		0
Totals		100.0000		0.000	305855776					

Data File: c:\star\7-20-15 5;17;27 pm -1.run
Channel: 1 = 254.00 nm RESULTS
Sample ID: B6269_Ti(L)+W(S,S)
Operator (Inj): AS-H, iPrOH/Hex=6:94, FR=0.4
Injection Date:
Injection Method: c:\star\lan\standard 6%_0.4ml.mth
Run Time (min): 25.627
Workstation:
Instrument (Inj): Varian Star #1

Operator (Calc):
Calc Date: 07/20/15 05:46:44 PM
Times Calculated: 3
Calculation Method: c:\windows\temp\~7-20-15 5;17;27 pm
Instrument (Calc): Varian Star #1
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
Calibration Level: N/A
Verification Tolerance: N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		99.9822	16.040	0.000	262232432	0.00	BB	29.0		0
2		0.0178	19.613	0.000	46643	0.00	BB	21.1		0
Totals		100.0000		0.000	262279072					



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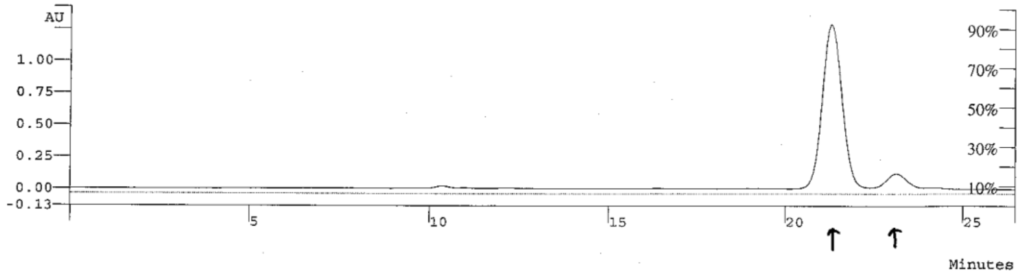
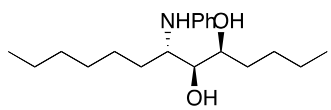
Data File:	c:\star\7-20-15 4;25;37 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	07/20/15 04:55:59 PM
Sample ID:	B6303_Hf(R,R)+W(R,R	Times Calculated:	1
Operator (Inj):	AS-H, iPrOH/Hex=6:94, FR=0.4	Calculation Method:	c:\windows\temp\~7-20-15 4;25;37 pm
Injection Date:		Instrument (Calc):	Varian Star #1
Injection Method:	c:\star\lan\standard 6%_0.4ml.mth	Run Mode:	Analysis
Run Time (min):	26.453	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		95.6432	21.267	0.000	249218080	0.00	BB	35.5		0
2		4.3568	23.080	0.000	11352630	0.00	BB	25.6		0
	Totals	100.0000		0.000	260570704					



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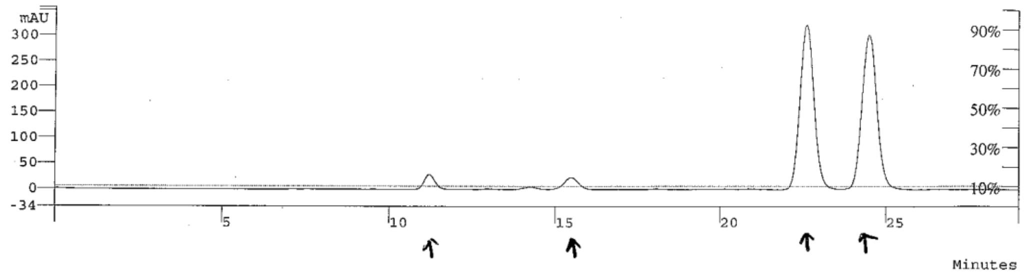
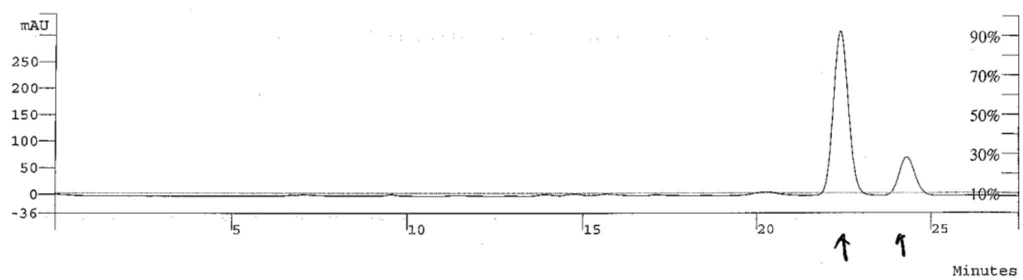
Data File:	c:\star\7-16-15 7;24;00 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	07/16/15 07:54:17 PM
Sample ID:	B6181_rac+rac	Times Calculated:	1
Operator (Inj):	AD-H, iPrOH/Hex=1:9 ,FR=0.5	Calculation Method:	c:\windows\temp\~7-16-15 7;24;00 pm
Injection Date:		Instrument (Calc):	Varian Star #1
Injection Method:	c:\star\lan\standard 10%_0.5ml.mth	Run Mode:	Analysis
Run Time (min):	29.040	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

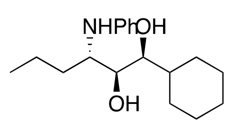


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		2.9095	11.187	0.000	2995055	0.00	BB	19.8		0
2		3.0884	15.480	0.000	3179250	0.00	BB	26.1		0
3		47.0541	22.600	0.000	48438364	0.00	BB	27.2		0
4		46.9481	24.467	0.000	48329244	0.00	BB	28.8		0
	Totals	**100.0001**		**0.000**	**102941912**					

Data File:	c:\star\7-16-15 5;11;46 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	07/16/15 05:41:55 PM
Sample ID:	B8009_Hf(R,R)+W(R,R	Times Calculated:	1
Operator (Inj):	AD-H, iPrOH/Hex=1:9, FR=0.5	Calculation Method:	c:\windows\temp\~7-16-15 5;11;46 pm
Injection Date:		Instrument (Calc):	Varian Star #1
Injection Method:	c:\star\lan\standard 10%_0.5ml.mth	Run Mode:	Analysis
Run Time (min):	27.520	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		83.9265	22.387	0.000	47328368	0.00	BB	27.9		0
2		16.0735	24.280	0.000	9064257	0.00	BB	25.7		0
	Totals	**100.0000**		**0.000**	**56392624**					



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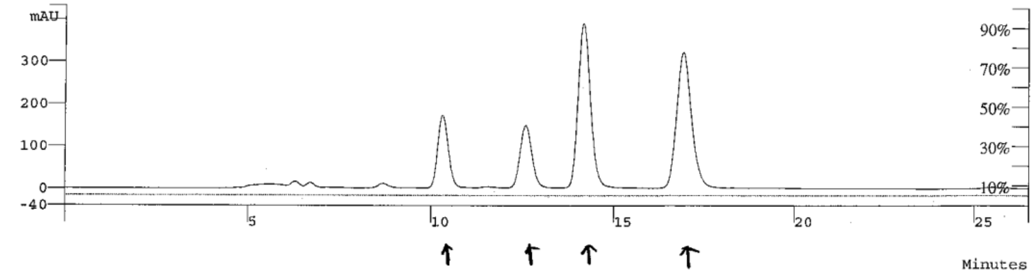
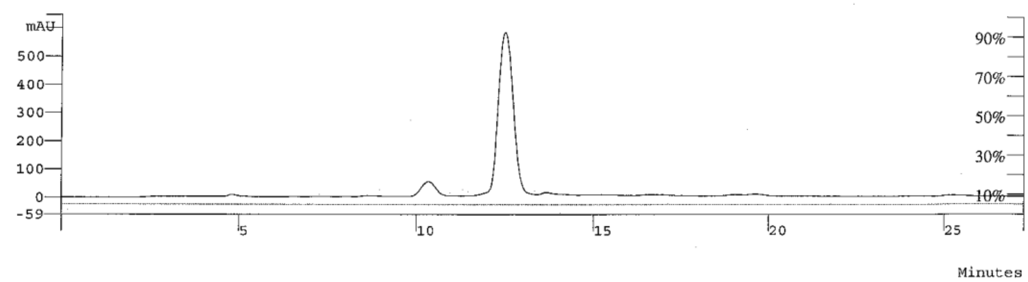
Data File:	c:\star\7-16-15 6;33;29 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	07/16/15 07:01:40 PM
Sample ID:	B6113_rac+rac	Times Calculated:	1
Operator (Inj):	IC, iPrOH/Hex=5:95, FR=0.75	Calculation Method:	c:\windows\temp\~7-16-15 6;33;29 pm
Injection Date:		Instrument (Calc):	Varian Star #1
Injection Method:	c:\star\lan\standard 5%_0.75ml.mth	Run Mode:	Analysis
Run Time (min):	26.480	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A

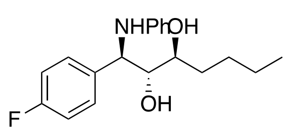


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		13.2683	10.307	0.000	16791260	0.00	BB	18.5		0
2		12.5839	12.573	0.000	15925203	0.00	BB	20.4		0
3		37.0870	14.173	0.000	46934392	0.00	BB	21.8		0
4		37.0608	16.947	0.000	46901292	0.00	BB	26.6		0
	Totals	**100.0000**		**0.000**	**126552144**					

Data File:	c:\star\7-16-15 5;58;31 pm -1.run	Operator (Calc):	
Channel:	1 = 254.00 nm RESULTS	Calc Date:	07/16/15 06:27:58 PM
Sample ID:	B8007_Ti(L)+W(S,S)	Times Calculated:	3
Operator (Inj):	IC, iPrOH/Hex=5:95, FR=0.75	Calculation Method:	c:\windows\temp\~7-16-15 5;58;31 pm
Injection Date:		Instrument (Calc):	Varian Star #1
Injection Method:	c:\star\lan\standard 5%_0.75ml.mth	Run Mode:	Analysis
Run Time (min):	27.280	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		4.3719	10.333	0.000	3875561	0.00	BB	20.9		0
2		95.6281	12.493	0.000	84771648	0.00	BB	27.9		0
	Totals	**100.0000**		**0.000**	**88647208**					



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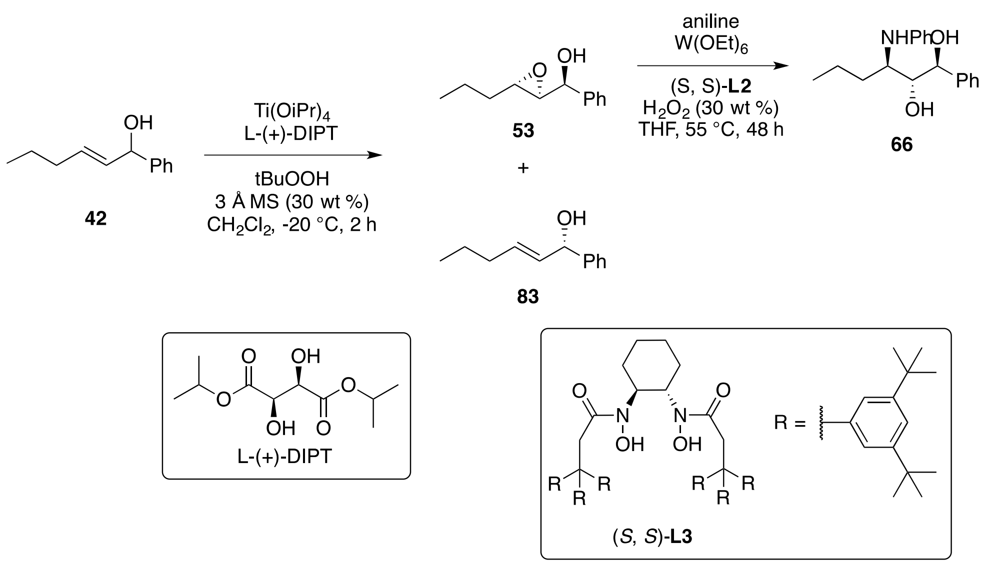
6.8 Single Crystal X-Ray Diffraction Data for Compound **66**

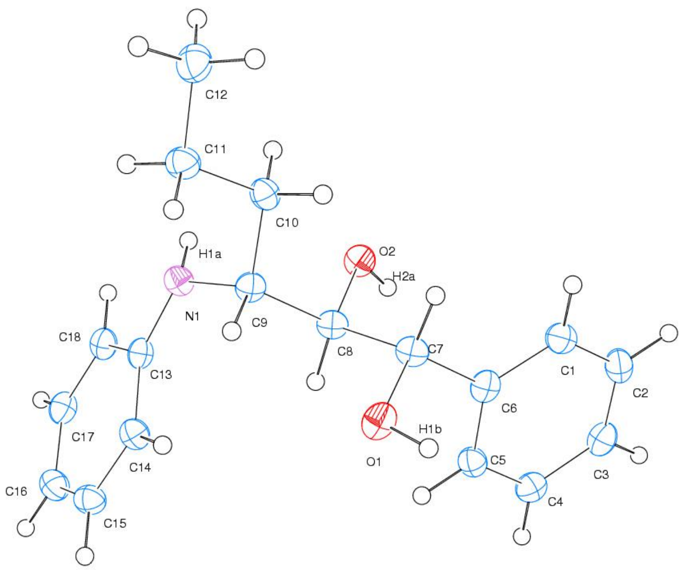
Crystal growth of $C_{18}H_{23}NO_2$: Lan Luo (Prof. Yamamoto's group).
Data collected: Alexander S. Filatov, 02/11/2015 (X-ray Laboratory, Searle B013, Department of Chemistry, the University of Chicago, Chicago, Il).
Report prepared: Alexander S. Filatov, 02/12/2015 (X-ray Laboratory, Searle B013, Department of Chemistry, the University of Chicago, Chicago, Il).

General information: A colorless plate (0.06 x 0.18 x 0.38 mm) was mounted on a Dual-Thickness MicroMount^{tm} (MiTeGen) with 30 μm sample aperture using grease to hold the crystal. The diffraction data were measured at 100 K on a Bruker D8 VENTURE with PHOTON 100 CMOS detector system equipped with a Cu-target X-ray tube (λ = 1.54178 Å). Data reduction and integration were performed with the Bruker APEX2 software package (Bruker AXS, version 2014.9-0, 2014). Data were corrected for absorption effects using the numerical scaling as implemented in SADABS (Bruker AXS, version 2014/4, 2014, part of Bruker APEX2 software package). The structure was solved by SHELXT (Sheldrick, G. M. *Acta Cryst*. **2015**, ***A71***, 3-8) and refined by full-matrix least-squares procedure using Bruker SHELXTL (version 6.14) software package (XL refinement program version 2014/7, Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122; *Sheldrick, G. M. Acta Cryst.* **2015**, *C71*, 3-8). Crystallographic data and details of the data collection and structure refinement are listed in Table 1.

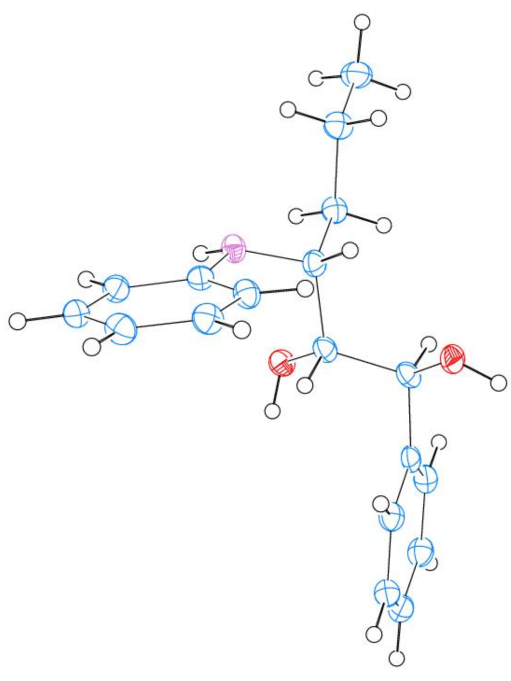
Specific details for structure refinement: All elements were refined anisotropically and hydrogen atoms were included in idealized positions for structure factor calculations except hydrogen atoms attached to O and N atoms. These H atoms were located at the difference Fourier map and their coordinates were allowed to be freely refined while their thermal parameters were constrained to be 1.2 or 1.5 times of the U_{eq} value of the N or O atoms, respectively. All structures are drawn with thermal ellipsoids at 40% probability.



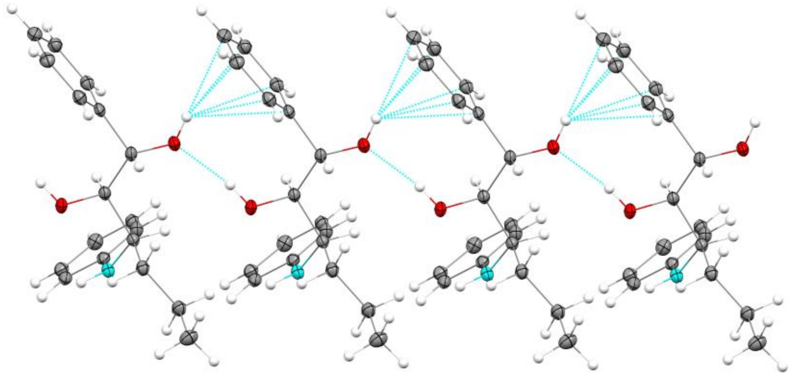
The configuration of **83** was determined by Chiral HPLC to be *S* and compared with literature value[1]. Since the configuration of this stereocenter was not changed, the absolute configuration of the compound **66** can be identified as (1*S*,2*R*,3*R*)-1-phenyl-3-(phenylamino)hexane-1,2-diol.



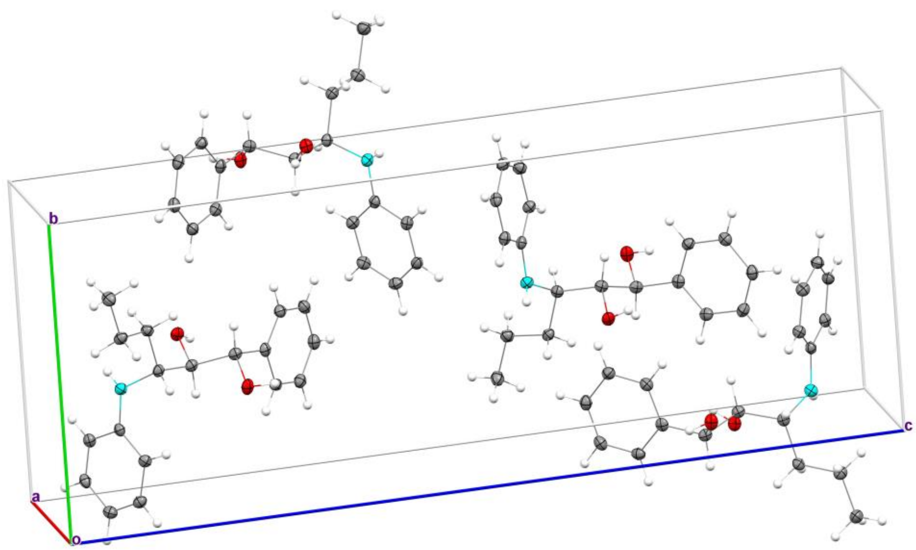
Thermal ellipsoids drawing with atoms labeling



1 *J. Am. Chem. Soc.*, **2006**, *128* (46), pp 14808–14809



1D chain along [100] direction based on O-H···O and O-H···π intermolecular binding



Packing diagram showing unit cell content

Crystal data and structure refinement for 0055_Lan.

Identification code	0055_Lan	
Empirical formula	$C_{18}H_{23}NO_2$	
Formula weight	285.37	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.2823(3) Å	α= 90°.
	b = 10.7630(7) Å	β= 90°.
	c = 27.6349(17) Å	γ = 90°.
Volume	1571.14(17) $Å^3$	
Z	4	
Density (calculated)	1.206 Mg/m^3	
Absorption coefficient	0.615 mm^{-1}	
F(000)	616	
Crystal size	0.380 x 0.180 x 0.060 mm^3	
Theta range for data collection	3.198 to 66.519°.	
Index ranges	-6<=h<=5, -12<=k<=9, -26<=l<=32	
Reflections collected	10178	
Independent reflections	2739 [R(int) = 0.0744]	
Completeness to theta = 66.519°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.753 and 0.561	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2739 / 0 / 206	
Goodness-of-fit on F^2	1.087	
Final R indices [I>2sigma(I)]	R1 = 0.0510, wR2 = 0.1063	
R indices (all data)	R1 = 0.0661, wR2 = 0.1134	
Absolute structure parameter	0.3(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.177 and -0.175 e.$Å^{-3}$	

$R_{int} = \Sigma | F_o^2 - \langle F_o^2 \rangle | / \Sigma | F_o^2|$

$R1 = \Sigma | | F_o| - | F_c|| / \Sigma| F_o|$

$wR2 = [\Sigma [w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2]]^{1/2}$

Goodness-of-fit $= [\Sigma [w (F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 0055_Lan. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1745(6)	4164(4)	7821(1)	29(1)
C(2)	9(7)	4396(4)	8187(1)	32(1)
C(3)	-625(7)	5611(4)	8299(1)	33(1)
C(4)	497(7)	6592(4)	8054(1)	30(1)
C(5)	2208(7)	6345(4)	7686(1)	28(1)
C(6)	2844(6)	5131(3)	7564(1)	26(1)
C(7)	4530(6)	4881(4)	7131(1)	26(1)
C(8)	3185(6)	5257(4)	6660(1)	25(1)
C(9)	4715(6)	5049(3)	6196(1)	25(1)
C(10)	5191(7)	3688(3)	6074(1)	27(1)
C(11)	7128(7)	3528(4)	5669(1)	31(1)
C(12)	7622(8)	2186(4)	5538(1)	37(1)
C(13)	3239(6)	6932(4)	5746(1)	25(1)
C(14)	4989(7)	7742(3)	5947(1)	27(1)
C(15)	4808(7)	9008(3)	5859(1)	30(1)
C(16)	2885(7)	9490(4)	5580(1)	31(1)
C(17)	1094(7)	8685(4)	5388(1)	30(1)
C(18)	1256(6)	7430(4)	5466(1)	28(1)
N(1)	3439(5)	5643(3)	5788(1)	26(1)
O(1)	6827(4)	5605(3)	7149(1)	32(1)
O(2)	886(4)	4567(3)	6615(1)	29(1)

Bond lengths [Å] and angles [°] for 0055_Lan.

C(1)-C(6)	1.387(5)
C(1)-C(2)	1.388(5)
C(1)-H(1)	0.9500
C(2)-C(3)	1.386(5)
C(2)-H(2)	0.9500
C(3)-C(4)	1.387(5)
C(3)-H(3)	0.9500
C(4)-C(5)	1.386(5)
C(4)-H(4)	0.9500
C(5)-C(6)	1.391(5)
C(5)-H(5)	0.9500
C(6)-C(7)	1.516(5)
C(7)-O(1)	1.443(4)
C(7)-C(8)	1.537(5)
C(7)-H(7)	1.02(4)
C(8)-O(2)	1.429(4)
C(8)-C(9)	1.533(5)
C(8)-H(8)	1.05(4)
C(9)-N(1)	1.461(4)
C(9)-C(10)	1.524(5)
C(9)-H(9)	1.0000
C(10)-C(11)	1.526(5)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-C(12)	1.512(5)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.387(5)
C(13)-N(1)	1.397(5)
C(13)-C(18)	1.407(5)
C(14)-C(15)	1.387(5)
C(14)-H(14)	0.9500
C(15)-C(16)	1.376(5)
C(15)-H(15)	0.9500
C(16)-C(17)	1.388(5)
C(16)-H(16)	0.9500
C(17)-C(18)	1.372(5)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
N(1)-H(1A)	0.89(4)
O(1)-H(1B)	0.88(4)
O(2)-H(2A)	0.87(4)
C(6)-C(1)-C(2)	121.0(4)
C(6)-C(1)-H(1)	119.5
C(2)-C(1)-H(1)	119.5
C(3)-C(2)-C(1)	119.5(4)
C(3)-C(2)-H(2)	120.3
C(1)-C(2)-H(2)	120.3
C(2)-C(3)-C(4)	120.4(4)
C(2)-C(3)-H(3)	119.8
C(4)-C(3)-H(3)	119.8
C(5)-C(4)-C(3)	119.4(4)
C(5)-C(4)-H(4)	120.3
C(3)-C(4)-H(4)	120.3
C(4)-C(5)-C(6)	121.1(4)
C(4)-C(5)-H(5)	119.5
C(6)-C(5)-H(5)	119.5
C(1)-C(6)-C(5)	118.6(3)
C(1)-C(6)-C(7)	121.1(3)
C(5)-C(6)-C(7)	120.1(3)
O(1)-C(7)-C(6)	111.7(3)
O(1)-C(7)-C(8)	106.0(3)
C(6)-C(7)-C(8)	110.5(3)
O(1)-C(7)-H(7)	111(2)
C(6)-C(7)-H(7)	109(2)
C(8)-C(7)-H(7)	109(2)
O(2)-C(8)-C(9)	107.3(3)
O(2)-C(8)-C(7)	109.3(3)
C(9)-C(8)-C(7)	115.3(3)
O(2)-C(8)-H(8)	110(2)
C(9)-C(8)-H(8)	110(2)
C(7)-C(8)-H(8)	105(2)
N(1)-C(9)-C(10)	109.1(3)
N(1)-C(9)-C(8)	109.8(3)
C(10)-C(9)-C(8)	114.3(3)
N(1)-C(9)-H(9)	107.8
C(10)-C(9)-H(9)	107.8
C(8)-C(9)-H(9)	107.8
C(9)-C(10)-C(11)	112.3(3)
C(9)-C(10)-H(10A)	109.1
C(11)-C(10)-H(10A)	109.1
C(9)-C(10)-H(10B)	109.1
C(11)-C(10)-H(10B)	109.1

H(10A)-C(10)-H(10B)	107.9
C(12)-C(11)-C(10)	113.6(3)
C(12)-C(11)-H(11A)	108.9
C(10)-C(11)-H(11A)	108.9
C(12)-C(11)-H(11B)	108.9
C(10)-C(11)-H(11B)	108.9
H(11A)-C(11)-H(11B)	107.7
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(14)-C(13)-N(1)	122.7(3)
C(14)-C(13)-C(18)	118.5(3)
N(1)-C(13)-C(18)	118.7(3)
C(15)-C(14)-C(13)	120.0(3)
C(15)-C(14)-H(14)	120.0
C(13)-C(14)-H(14)	120.0
C(16)-C(15)-C(14)	121.3(3)
C(16)-C(15)-H(15)	119.4
C(14)-C(15)-H(15)	119.4
C(15)-C(16)-C(17)	118.8(4)
C(15)-C(16)-H(16)	120.6
C(17)-C(16)-H(16)	120.6
C(18)-C(17)-C(16)	120.8(4)
C(18)-C(17)-H(17)	119.6
C(16)-C(17)-H(17)	119.6
C(17)-C(18)-C(13)	120.5(3)
C(17)-C(18)-H(18)	119.7
C(13)-C(18)-H(18)	119.7
C(13)-N(1)-C(9)	122.3(3)
C(13)-N(1)-H(1A)	112(2)
C(9)-N(1)-H(1A)	113(2)
C(7)-O(1)-H(1B)	107(3)
C(8)-O(2)-H(2A)	107(3)

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters ($Å^2$x 10^3) for 0055_Lan. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	28(2)	28(2)	31(2)	1(2)	-5(2)	1(2)
C(2)	31(2)	37(3)	29(2)	7(2)	0(2)	-3(2)
C(3)	29(2)	42(3)	26(2)	0(2)	-2(2)	2(2)
C(4)	28(2)	32(2)	30(2)	-2(2)	-3(2)	3(2)
C(5)	25(2)	29(2)	29(2)	3(2)	-2(2)	-3(2)
C(6)	17(2)	35(2)	26(2)	2(2)	-6(1)	1(2)
C(7)	18(2)	28(2)	32(2)	-1(2)	0(1)	0(2)
C(8)	19(2)	27(2)	30(2)	-2(2)	-2(2)	0(1)
C(9)	21(2)	29(2)	26(2)	0(2)	-3(1)	-1(2)
C(10)	24(2)	27(2)	29(2)	3(2)	0(2)	-2(2)
C(11)	28(2)	31(2)	34(2)	-3(2)	2(2)	-4(2)
C(12)	43(2)	35(3)	34(2)	1(2)	7(2)	8(2)
C(13)	24(2)	30(2)	22(2)	2(2)	4(2)	1(2)
C(14)	22(2)	29(2)	31(2)	2(2)	0(2)	-1(2)
C(15)	26(2)	31(2)	35(2)	-2(2)	0(2)	-4(2)
C(16)	32(2)	27(2)	35(2)	3(2)	3(2)	1(2)
C(17)	30(2)	33(3)	26(2)	2(2)	0(2)	8(2)
C(18)	23(2)	35(3)	26(2)	2(2)	1(1)	0(2)
N(1)	21(2)	28(2)	29(2)	2(1)	-2(1)	-2(1)
O(1)	19(1)	49(2)	29(1)	-2(1)	-3(1)	-3(1)
O(2)	19(1)	38(2)	31(1)	-1(1)	1(1)	-5(1)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 0055_Lan.

	x	y	z	U(eq)
H(1)	2186	3331	7745	35
H(2)	-738	3726	8360	39
H(3)	-1835	5774	8546	39
H(4)	96	7425	8138	36
H(5)	2959	7015	7515	33
H(7)	4920(70)	3960(30)	7117(13)	31
H(8)	2780(70)	6210(40)	6702(13)	30
H(9)	6397	5462	6238	31
H(10A)	3576	3296	5976	32
H(10B)	5806	3254	6368	32
H(11A)	6517	3972	5378	37
H(11B)	8742	3917	5770	37
H(12A)	8145	1728	5828	56
H(12B)	8968	2145	5295	56
H(12C)	6073	1816	5407	56
H(14)	6312	7430	6146	33
H(15)	6035	9553	5994	36
H(16)	2784	10358	5521	38
H(17)	-260	9009	5200	36
H(18)	20	6891	5330	33
H(1A)	2010(70)	5270(30)	5705(13)	31
H(1B)	7450(80)	5530(40)	7445(15)	48
H(2A)	-220(80)	4910(40)	6809(14)	44

Torsion angles [°] for 0055_Lan.

C(6)-C(1)-C(2)-C(3)	-0.3(5)
C(1)-C(2)-C(3)-C(4)	-1.2(5)
C(2)-C(3)-C(4)-C(5)	1.8(5)
C(3)-C(4)-C(5)-C(6)	-0.9(5)
C(2)-C(1)-C(6)-C(5)	1.2(5)
C(2)-C(1)-C(6)-C(7)	-173.7(3)
C(4)-C(5)-C(6)-C(1)	-0.5(5)
C(4)-C(5)-C(6)-C(7)	174.3(3)
C(1)-C(6)-C(7)-O(1)	-133.5(3)
C(5)-C(6)-C(7)-O(1)	51.7(4)
C(1)-C(6)-C(7)-C(8)	108.7(4)
C(5)-C(6)-C(7)-C(8)	-66.1(4)
O(1)-C(7)-C(8)-O(2)	179.6(3)
C(6)-C(7)-C(8)-O(2)	-59.2(4)
O(1)-C(7)-C(8)-C(9)	58.6(4)
C(6)-C(7)-C(8)-C(9)	179.9(3)
O(2)-C(8)-C(9)-N(1)	68.2(4)
C(7)-C(8)-C(9)-N(1)	-169.8(3)
O(2)-C(8)-C(9)-C(10)	-54.8(4)
C(7)-C(8)-C(9)-C(10)	67.2(4)
N(1)-C(9)-C(10)-C(11)	67.7(4)
C(8)-C(9)-C(10)-C(11)	-169.0(3)
C(9)-C(10)-C(11)-C(12)	-179.5(3)
N(1)-C(13)-C(14)-C(15)	174.6(3)
C(18)-C(13)-C(14)-C(15)	-2.0(5)
C(13)-C(14)-C(15)-C(16)	1.2(6)
C(14)-C(15)-C(16)-C(17)	0.4(5)
C(15)-C(16)-C(17)-C(18)	-1.1(5)
C(16)-C(17)-C(18)-C(13)	0.3(5)
C(14)-C(13)-C(18)-C(17)	1.2(5)
N(1)-C(13)-C(18)-C(17)	-175.5(3)
C(14)-C(13)-N(1)-C(9)	27.5(5)
C(18)-C(13)-N(1)-C(9)	-155.9(3)
C(10)-C(9)-N(1)-C(13)	-165.9(3)
C(8)-C(9)-N(1)-C(13)	68.1(4)

Symmetry transformations used to generate equivalent atoms:

Hydrogen bonds for 0055_Lan [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2A)...O(1)#1	0.87(4)	1.97(4)	2.833(3)	169(4)

Symmetry transformations used to generate equivalent atoms:
#1 x-1,y,z

References

[1] K. Gopalaiah, *Chem. Rev.* **2013**, *113*, 3248–96.

[2] J. P. Collman, Z. Wang, A. Straumanis, M. Quelquejeu, E. Rose, *J. Am. Chem. Soc.* **1999**, *121*, 460–461.

[3] E. Rose, B. Andrioletti, S. Zrig, M. Quelquejeu-Ethève, *Chem. Soc. Rev.* **2005**, *34*, 573–83.

[4] M. B. Francis, E. N. Jacobsen, *Angew. Chemie Int. Ed.* **1999**, *38*, 937–941.

[5] C. Marchi-Delapierre, A. Jorge-Robin, A. Thibon, S. Ménage, *Chem. Commun. (Camb).* **2007**, 1166–8.

[6] F. G. Gelalcha, G. Anilkumar, M. K. Tse, A. Brückner, M. Beller, *Chemistry* **2008**, *14*, 7687–98.

[7] H.-L. Yeung, K.-C. Sham, C.-S. Tsang, T.-C. Lau, H.-L. Kwong, *Chem. Commun. (Camb).* **2008**, 3801–3.

[8] D. Enders, J. Zhu, G. Raabe, *Angew. Chemie Int. Ed. English* **1996**, *35*, 1725–1728.

[9] M. Bougauchi, S. Watanabe, T. Arai, H. Sasai, M. Shibasaki, *J. Am. Chem. Soc.* **1997**, *119*, 2329–2330.

[10] E. J. Corey, F.-Y. Zhang, *Org. Lett.* **1999**, *1*, 1287–1290.

[11] S. Juliá, J. Masana, J. C. Vega, *Angew. Chemie Int. Ed. English* **1980**, *19*, 929–931.

[12] S. Chang, J. M. Galvin, E. N. Jacobsen, *J. Am. Chem. Soc.* **1994**, *116*, 6937–6938.

[13] H. Kakei, R. Tsuji, T. Ohshima, M. Shibasaki, *J. Am. Chem. Soc.* **2005**, *127*, 8962–3.

[14] X.-Y. Wu, X. She, Y. Shi, *J. Am. Chem. Soc.* **2002**, *124*, 8792–8793.

[15] O. Cussó, I. Garcia-Bosch, X. Ribas, J. Lloret-Fillol, M. Costas, *J. Am. Chem. Soc.* **2013**, *135*, 14871–8.

[16] Y. Nishikawa, H. Yamamoto, *J. Am. Chem. Soc.* **2011**, *133*, 8432–8435.

[17] W. Adam, P. B. Rao, H.-G. Degen, C. R. Saha-Möller, *European J. Org. Chem.* **2002**, *2002*, 630–639.

[18] O. Lifchits, M. Mahlau, C. M. Reisinger, A. Lee, C. Farès, I. Polyak, G. Gopakumar, W.

Thiel, B. List, *J. Am. Chem. Soc.* **2013**, *135*, 6677–93.

[19] X. Wang, C. M. Reisinger, B. List, *J. Am. Chem. Soc.* **2008**, *130*, 6070–1.

[20] E. Weitz, A. Scheffer, *Berichte der Dtsch. Chem. Gesellschaft (A B Ser.* **1921**, *54*, 2327–2344.

[21] D. R. Kelly, E. Caroff, R. W. Flood, W. Heal, S. M. Roberts, *Chem. Commun. (Camb).* **2004**, 2016–7.

[22] D. R. Kelly, S. M. Roberts, *Biopolymers* **2006**, *84*, 74–89.

[23] N. Ileby, M. Kuzma, L. R. Heggvik, K. Sørbye, A. Fiksdahl, *Tetrahedron: Asymmetry* **1997**, *8*, 2193–2198.

[24] L. Fransson, C. Moberg, *ChemCatChem* **2010**, *2*, 1523–1532.

[25] T. R. Hoye, J. C. Suhadolnik, *J. Am. Chem. Soc.* **1985**, *107*, 5312–5313.

[26] S. L. Schreiber, T. S. Schreiber, D. B. Smith, *J. Am. Chem. Soc.* **1987**, *109*, 1525–1529.

[27] W. R. Roush, J. A. Straub, M. S. VanNieuwenhze, *J. Org. Chem.* **1991**, *56*, 1636–1648.

[28] M. I. Klauck, S. G. Patel, S. L. Wiskur, *J. Org. Chem.* **2012**, *77*, 3570–5.

[29] S. Xu, C.-T. Lee, G. Wang, E. Negishi, *Chem. Asian J.* **2013**, *8*, 1829–35.

[30] T. Katsuki, V. S. Martin, *Org. React.* **1996**, *48*.

[31] E. N. Jacobsen, A. Pfaltz, H. Yamamoto, in *2*, **1999**, p. 621.

[32] R. M. Hanson, *Chem. Rev.* **1991**, *91*, 437–475.

[33] M. Caron, K. B. Sharpless, *J. Org. Chem.* **1985**, *50*, 1557–1560.

[34] C. H. Behrens, K. B. Sharpless, *J. Org. Chem.* **1985**, *50*, 5696–5704.

[35] S. Y. Ko, K. B. Sharpless, *J. Org. Chem.* **1986**, *51*, 5413–5415.

[36] M. Caron, P. R. Carlier, K. B. Sharpless, *J. Org. Chem.* **1988**, *53*, 5185–5187.

[37] M. Onaka, K. Sugita, H. Takeuchi, Y. Izumi, *J. Chem. Soc. Chem. Commun.* **1988**, 1173.

[38] T. Chakrabory, G. Reddy, *Tetrahedron Lett.* **1991**, *32*, 679–682.

[39] M. Chini, P. Crotti, L. A. Flippin, C. Gardelli, E. Giovani, F. Macchia, M. Pineschi, *J. Org. Chem.* **1993**, *58*, 1221–1227.

[40] R. Martín, G. Islas, A. Moyano, M. A. Pericàs, A. Riera, *Tetrahedron* **2001**, *57*, 6367–6374.

[41] M. Sasaki, K. Tanino, M. Miyashita, *Org. Lett.* **2001**, *3*, 1765–1767.

[42] M. Sasaki, K. Tanino, A. Hirai, M. Miyashita, *Org. Lett.* **2003**, *5*, 1789–91.

[43] M. Pastó, B. Rodríguez, A. Riera, M. A. Pericàs, *Tetrahedron Lett.* **2003**, *44*, 8369–8372.

[44] Y. Tomata, M. Sasaki, K. Tanino, M. Miyashita, *Tetrahedron Lett.* **2003**, *44*, 8975–8977.

[45] J. T. Malinowski, R. J. Sharpe, J. S. Johnson, *Science* **2013**, *340*, 180–182.

[46] M. Inoue, H. Sakazaki, H. Furuyama, M. Hirama, *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 2654–2657.

[47] B. K. Albrecht, R. M. Williams, *Proc. Natl. Acad. Sci. U. S. A.* **2004**, *101*, 11949–11954.

[48] C. Wang, H. Yamamoto, *Angew. Chem. Int. Ed. Engl.* **2014**, *53*, 13920–13923.

[49] M. J. Miller, *Chem. Rev.* **1989**, *89*, 1563–1579.

[50] A. O. Chong, K. B. Sharpless, *J. Org. Chem.* **1977**, *42*, 1587–1590.

[51] T. P. Yoon, E. N. Jacobsen, *Science* **2003**, *299*, 1691–3.

[52] Z. Li, H. Yamamoto, *Acc. Chem. Res.* **2013**, *46*, 506–18.

[53] S. A. Matlin, P. G. Sammes, R. M. Upton, *J. Chem. Soc. Perkin Trans. 1* **1979**, 2481.

[54] W. Zhang, A. Basak, Y. Kosugi, Y. Hoshino, H. Yamamoto, *Angew. Chemie Int. Ed.* **2005**, *44*, 4389–4391.

[55] Z. Li, W. Zhang, H. Yamamoto, *Angew. Chem. Int. Ed. Engl.* **2008**, *47*, 7520–2.

[56] Z. Li, H. Yamamoto, *J. Am. Chem. Soc.* **2010**, *132*, 7878–80.

[57] J. L. Olivares-Romero, Z. Li, H. Yamamoto, *J. Am. Chem. Soc.* **2013**, *135*, 3411–3.

[58] C. Wang, H. Yamamoto, *J. Am. Chem. Soc.* **2014**, *136*, 1222–1225.

[59] V. S. Martin, S. S. Woodard, T. Katsuki, Y. Yamada, M. Ikeda, K. B. Sharpless, *J. Am. Chem. Soc.* **1981**, *103*, 6237–6240.

[60] Y. Gao, J. M. Klunder, R. M. Hanson, H. Masamune, S. Y. Ko, K. B. Sharpless, *J. Am. Chem. Soc.* **1987**, *109*, 5765–5780.

[61] C. Wang, L. Luo, H. Yamamoto, *Acc. Chem. Res.* **2016**, *49*, 193–204.

[62] M. Caron, P. R. Carlier, K. B. Sharpless, *J. Org. Chem.* **1988**, *53*, 5185–5187.

[63] C. Wang, H. Yamamoto, *J. Am. Chem. Soc.* **2014**, *136*, 6888–91.

[64] W. Zhang, A. Basak, Y. Kosugi, Y. Hoshino, H. Yamamoto, *Angew. Chem. Int. Ed. Engl.* **2005**, *44*, 4389–91.

[65] R. L. NOBLE, C. T. BEER, J. H. CUTTS, *Ann. N. Y. Acad. Sci.* **1958**, *76*, 882–94.

[66] P. G. Gobbi, C. Broglia, F. Merli, M. Dell'Olio, C. Stelitano, E. Iannitto, M. Federico, R. Bertè, D. Luisi, S. Molica, et al., *Cancer* **2003**, *98*, 2393–401.

[67] M. Qweider, J. M. Gilsbach, V. Rohde, *J. Neurosurg. Spine* **2007**, *6*, 280–3.

[68] W. D. Graf, P. F. Chance, M. W. Lensch, L. J. Eng, H. P. Lipe, T. D. Bird, *Cancer* **1996**, *77*, 1356–62.

[69] I. S. JOHNSON, J. G. ARMSTRONG, M. GORMAN, J. P. BURNETT, *Cancer Res.* **1963**, *23*, 1390–427.

[70] R. J. Owellen, C. A. Hartke, R. M. Dickerson, F. O. Hains, *Cancer Res.* **1976**, *36*, 1499–502.

[71] C. J. Barnett, G. J. Cullinan, K. Gerzon, R. C. Hoying, W. E. Jones, W. M. Newlon, G. A. Poore, R. L. Robison, M. J. Sweeney, *J. Med. Chem.* **1978**, *21*, 88–96.

[72] M. Marty, P. Fumoleau, A. Adenis, Y. Rousseau, Y. Merrouche, G. Robinet, J. Senac, C. Puozzo, *Ann. Onc.* **2001**, *12*, 1643–1649.

[73] M. Casanova, A. Ferrari, F. Spreafico, M. Terenziani, M. Massimino, R. Luksch, G. Cefalo, D. Polastri, I. Marcon, F. F. Bellani, *Cancer* **2002**, *94*, 3263–8.

[74] W. Runguphan, X. Qu, S. E. O'Connor, *Nature* **2010**, *468*, 461–4.

[75] C. Szántay, H. Bölcskei, E. Gács-Baitz, *Tetrahedron* **1990**, *46*, 1711–1732.

[76] J. P. Kutney, F. Bylsma, *Helv. Chim. Acta* **1975**, *58*, 1672–89.

[77] R. Z. Andriamialisoa, N. Langlois, Y. Langlois, *Heterocycles* **1980**, *14,* 1457–1460.

[78] H. Gotoh, K. K. Duncan, W. M. Robertson, D. L. Boger, *ACS Med. Chem. Lett.* **2011**, *2*, 948–952.

[79] A. Tam, H. Gotoh, W. M. Robertson, D. L. Boger, *Bioorg. Med. Chem. Lett.* **2010**, *20*, 6408–10.

[80] G. Buechi, P. Kulsa, K. Ogasawara, R. L. Rosati, *J. Am. Chem. Soc.* **1970**, *92*, 999–1005.

[81] B. M. Trost, S. A. Godleski, J. L. Belletire, *J. Org. Chem.* **1979**, *44*, 2052–2054.

[82] B. M. Trost, S. A. Godleski, J. P. Genet, *J. Am. Chem. Soc.* **1978**, *100*, 3930–3931.

[83] L. Szabó, J. Sápi, K. Nógrádi, G. Kalaus, C. Szántay, *Tetrahedron* **1983**, *39*, 3749–3753.

[84] S. Raucher, B. L. Bray, R. F. Lawrence, *J. Am. Chem. Soc.* **1987**, *109*, 442–446.

[85] M. T. Reding, T. Fukuyama, *Org. Lett.* **1999**, *1*, 973–976.

[86] A. C. Kruegel, S. Rakshit, X. Li, D. Sames, *J. Org. Chem.* **2015**, *80*, 2062–71.

[87] W. A. Moradi, S. L. Buchwald, *J. Am. Chem. Soc.* **2001**, *123*, 7996–8002.

[88] O. Gaertzen, S. L. Buchwald, *J. Org. Chem.* **2002**, *67*, 465–475.

[89] S. Lee, J. F. Hartwig, *J. Org. Chem.* **2001**, *66*, 3402–3415.

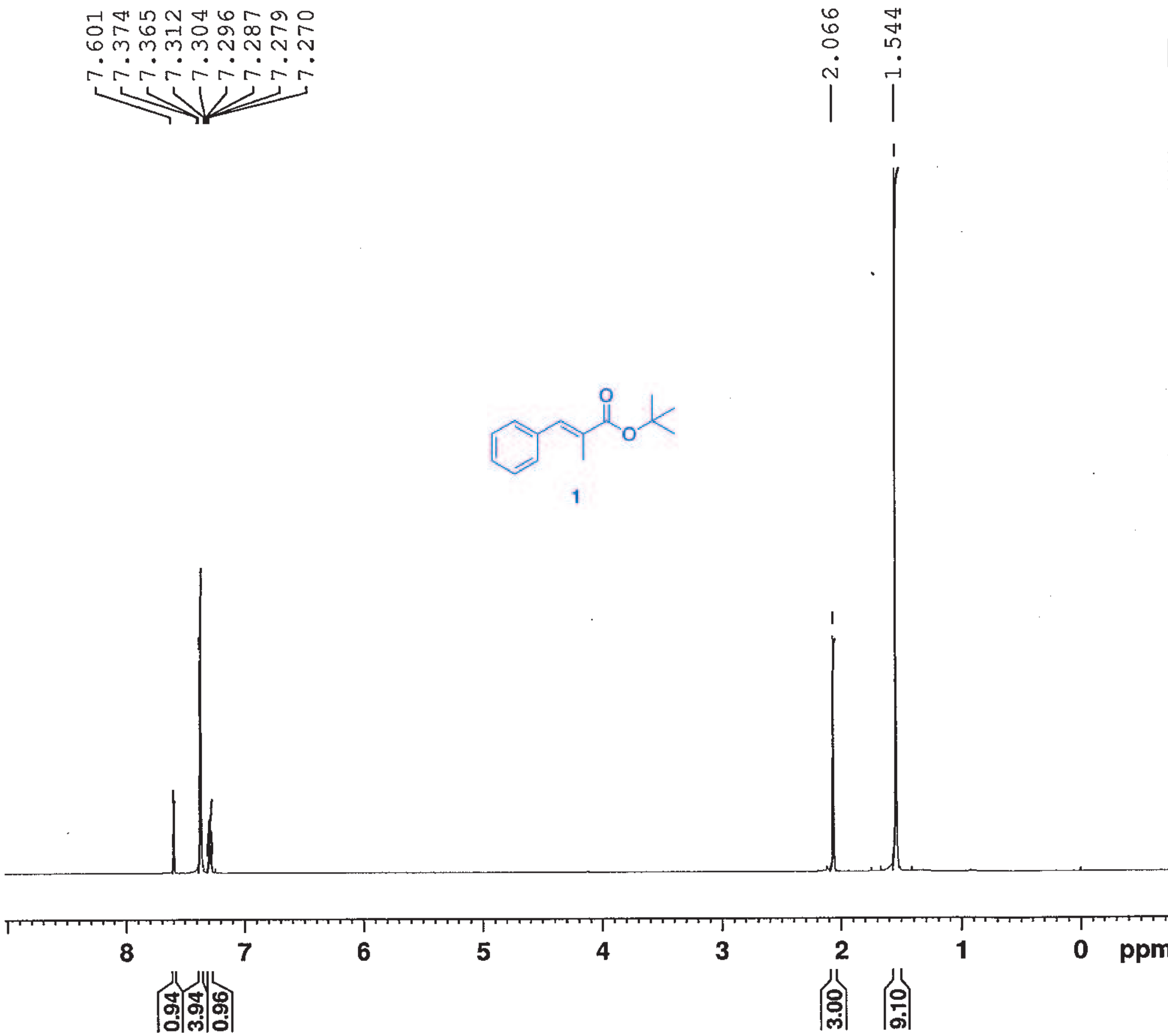
[90] N. A. Beare, J. F. Hartwig, *J. Org. Chem.* **2002**, *67*, 541–555.

[91] L. Jiao, E. Herdtweck, T. Bach, *J. Am. Chem. Soc.* **2012**, *134*, 14563–72.

[92] A. Nakatani, K. Hirano, T. Satoh, M. Miura, *Chemistry* **2013**, *19*, 7691–5.

[93] J. M. Richter, B. W. Whitefield, T. J. Maimone, D. W. Lin, M. P. Castroviejo, P. S. Baran, *J. Am. Chem. Soc.* **2007**, *129*, 12857–69.

Appendix. ^{1}H and ^{13}C NMR Spectra

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DW                   50.000 usec
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TE                    296.1 K
D1              10.00000000 sec
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P1                     8.00 usec
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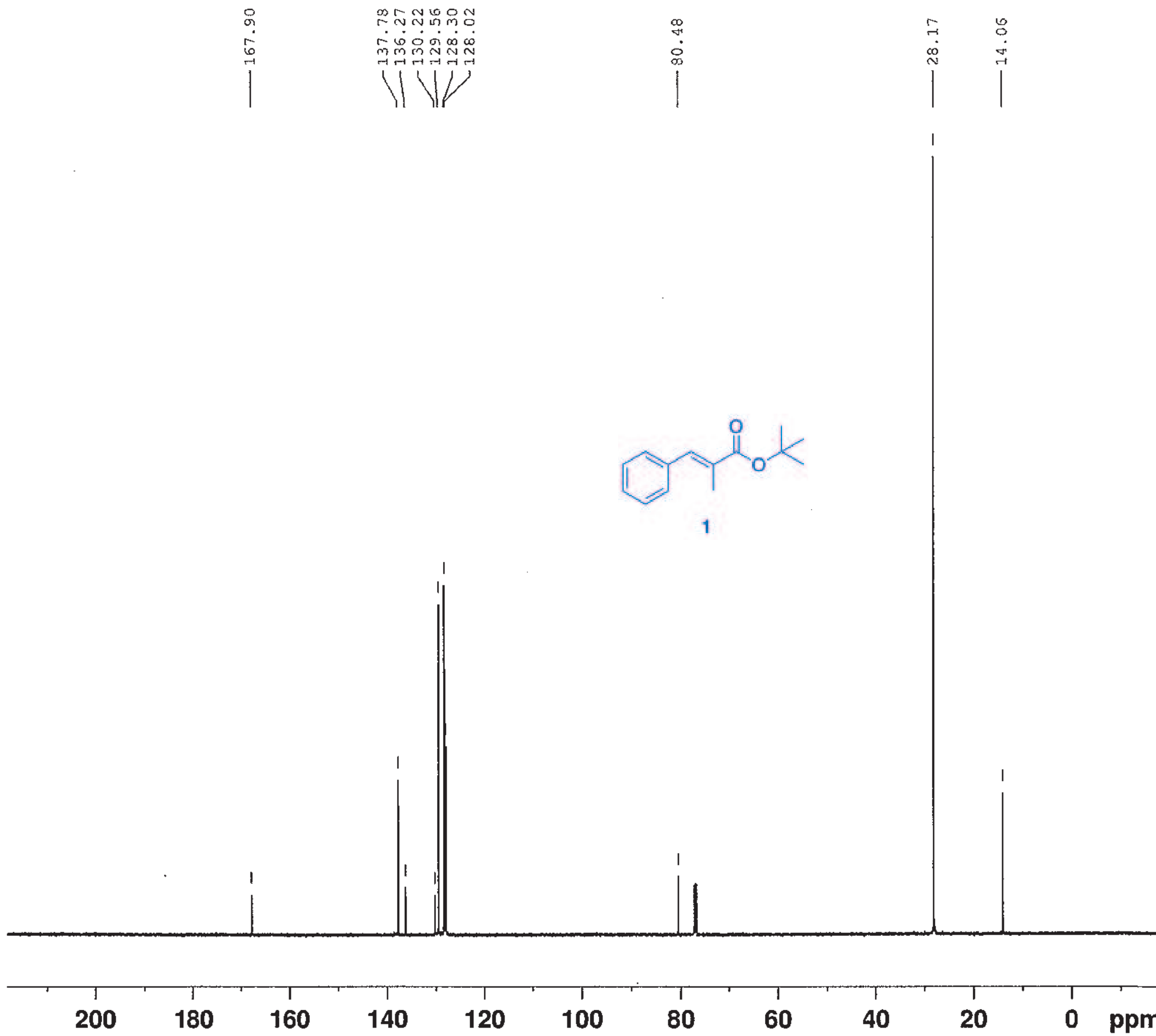

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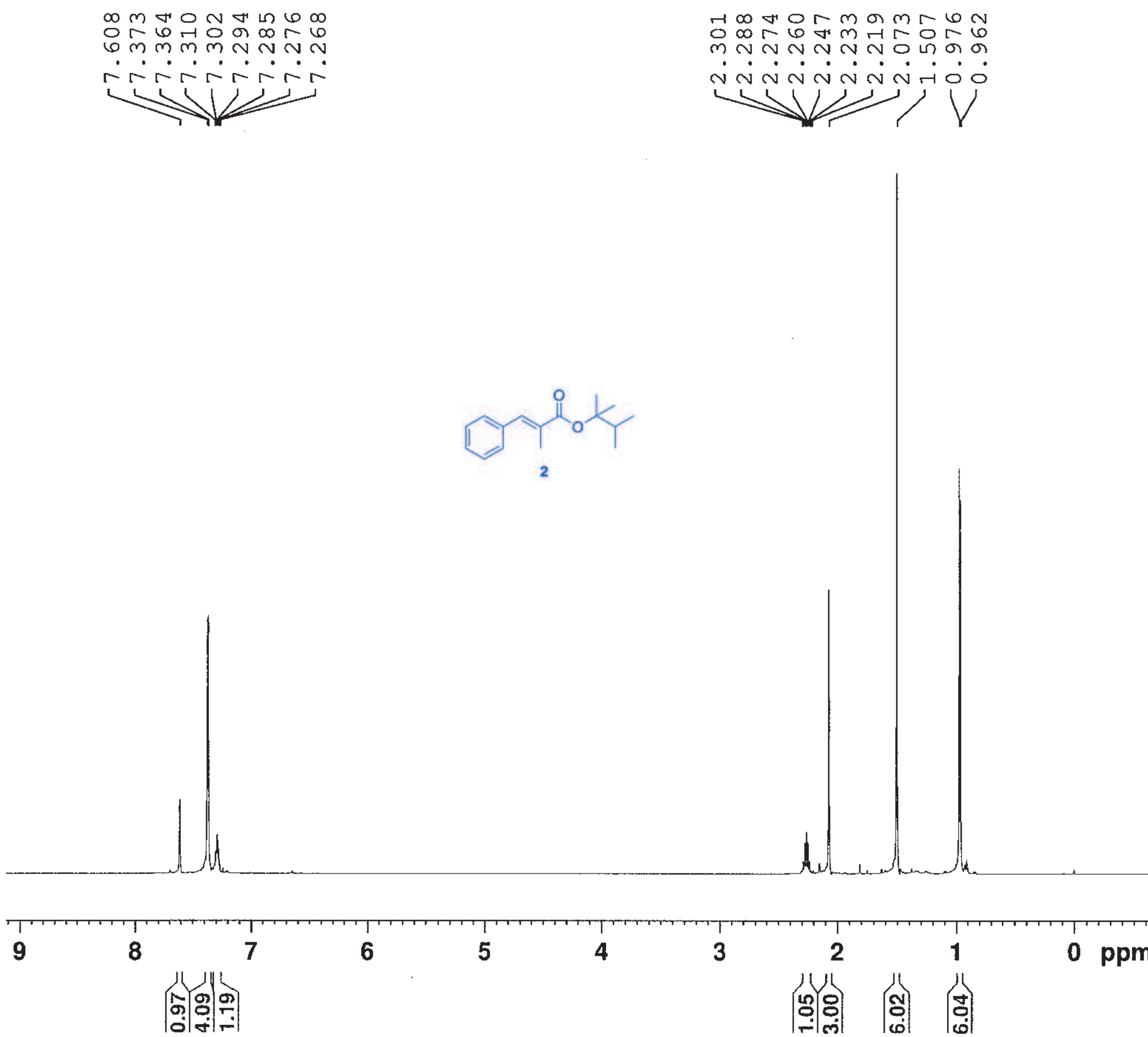

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SOLVENT                  CDCl3
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TD0                          1

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P1                   8.00 usec
PLW1           12.19999981 W

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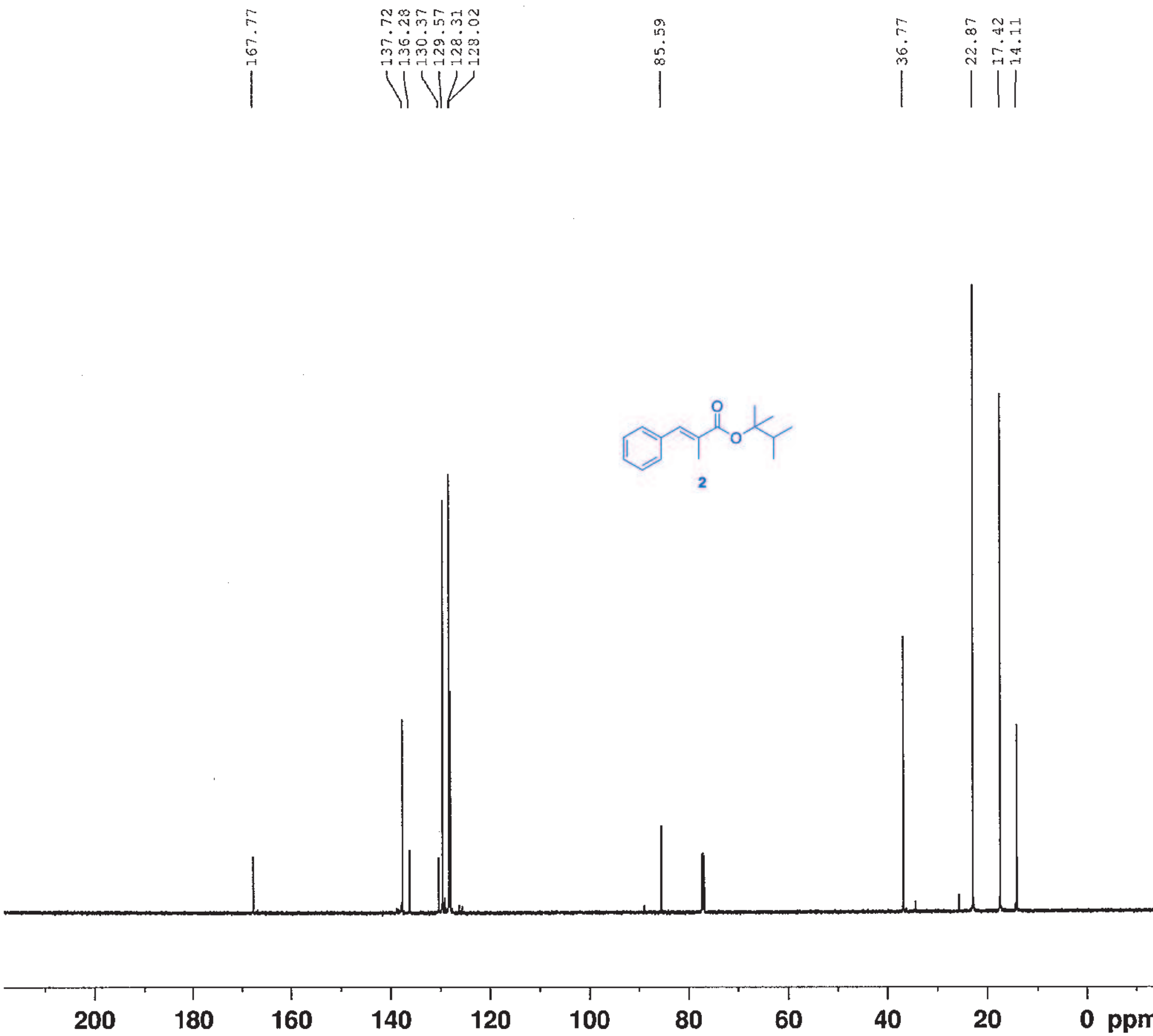

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FIDRES	0.166670 Hz
AQ	2.9999924 sec
RG	196.79
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D11	0.03000000 sec
TD0	1

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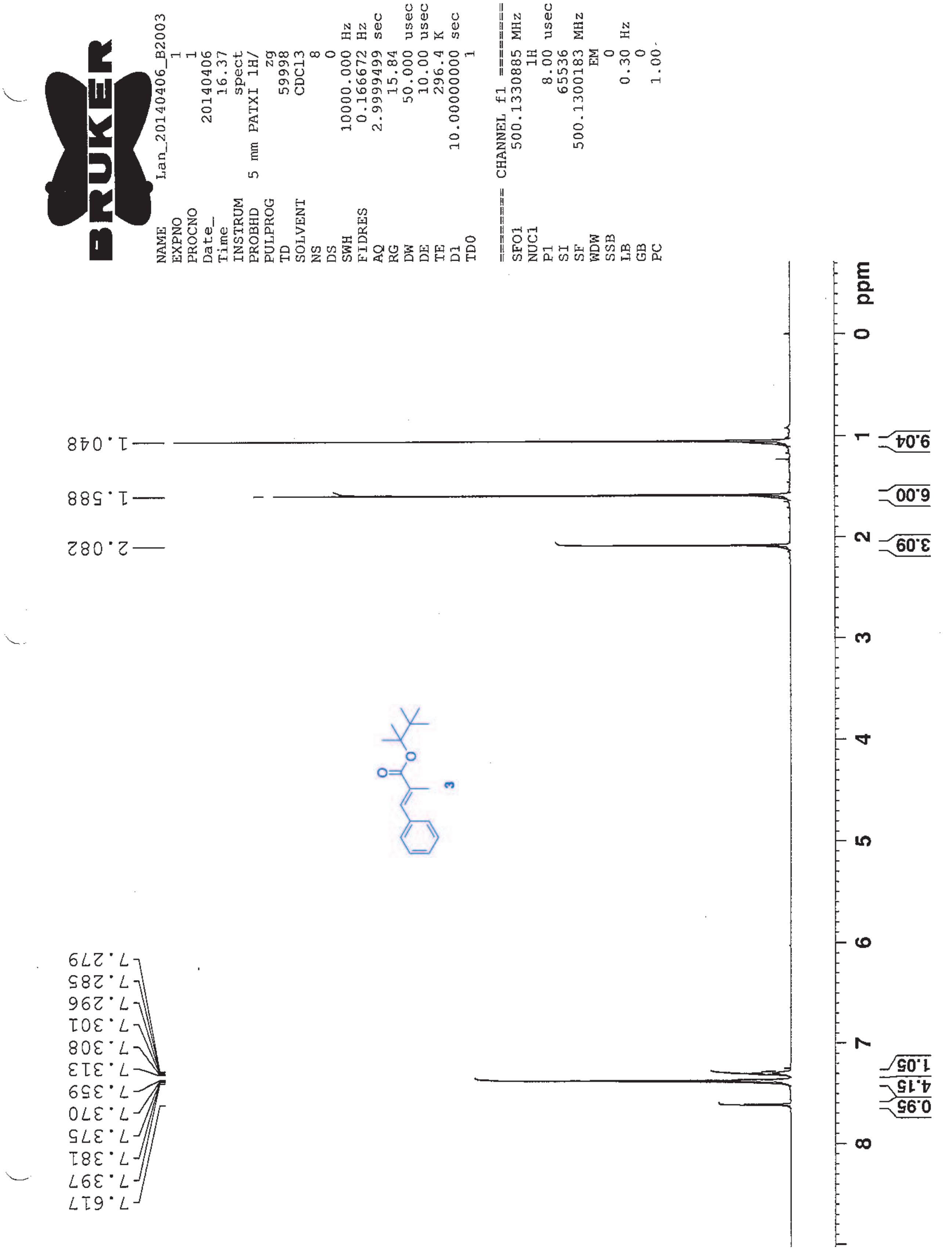
PC	1.40



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7.301
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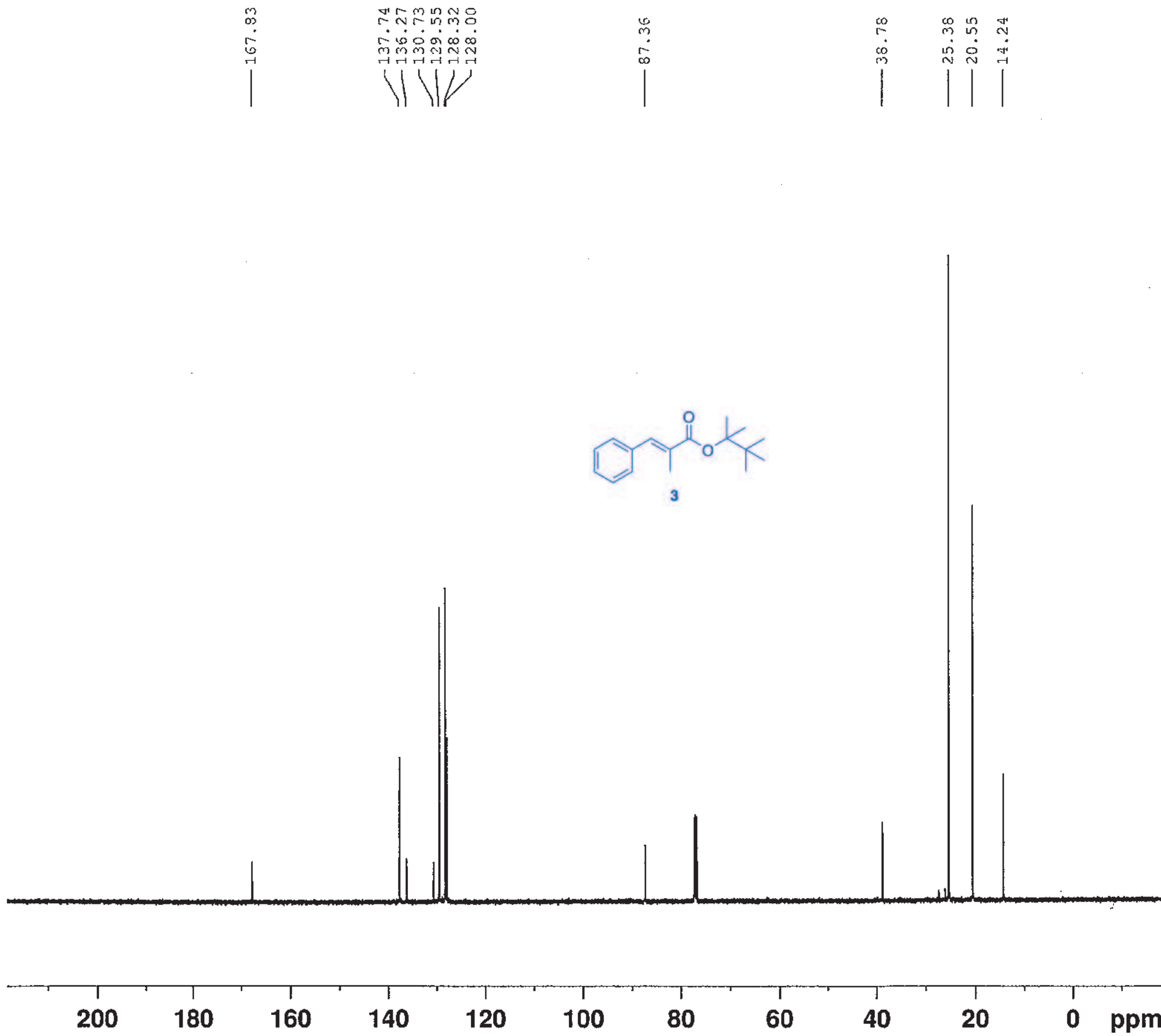

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TE	297.1 K
D1	3.00000000 sec
D11	0.03000000 sec
TD0	1

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SI	131072
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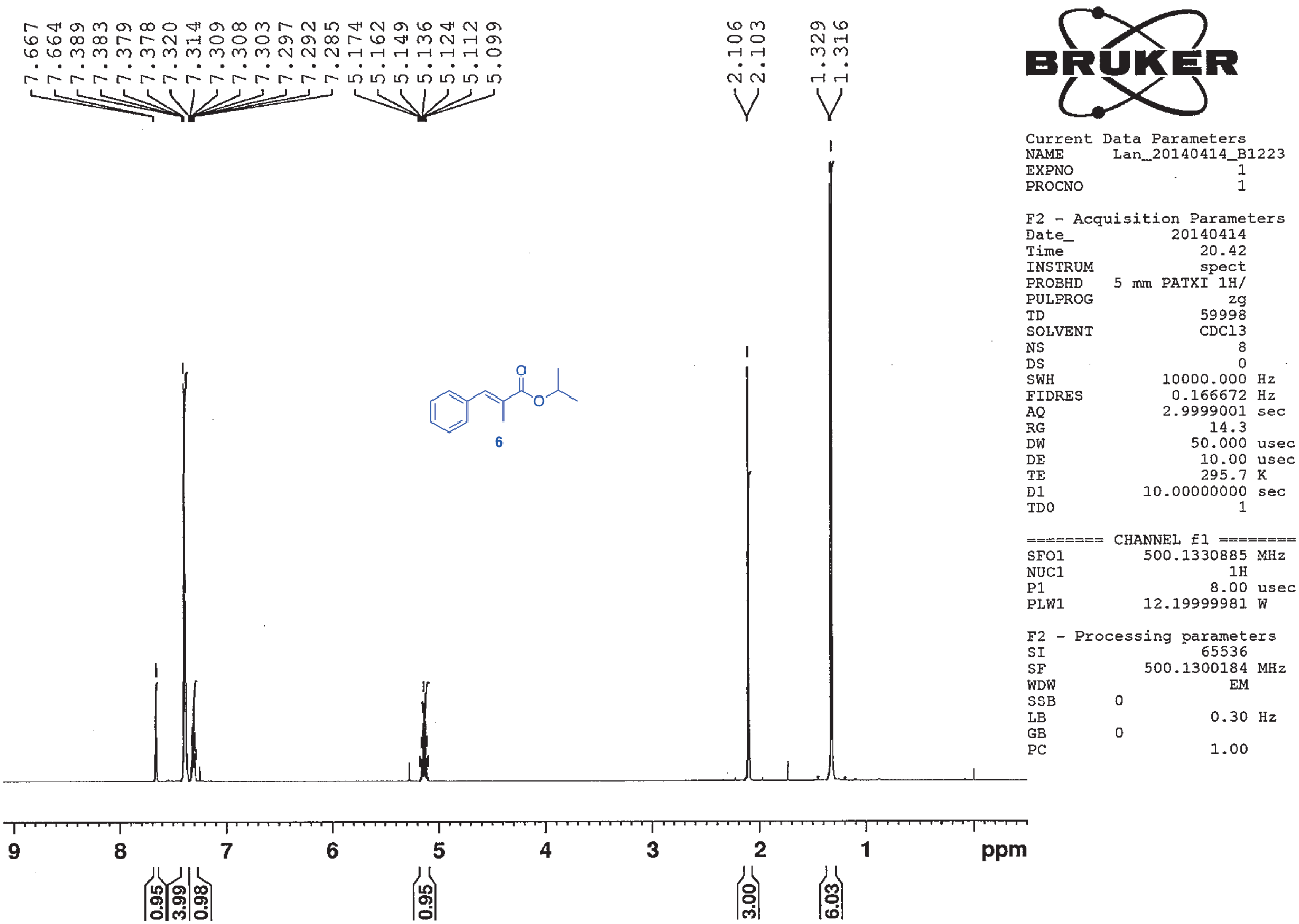
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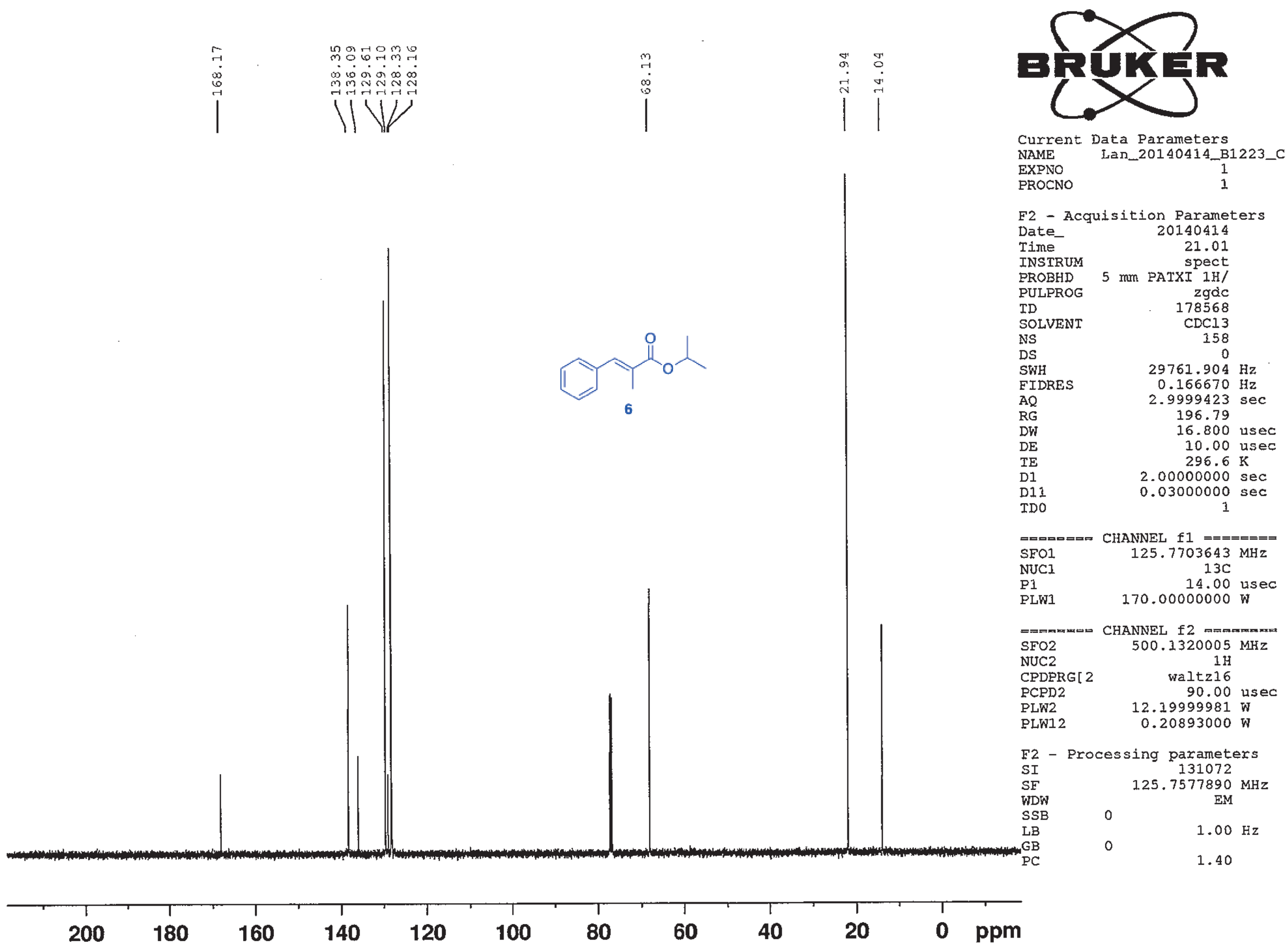
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D11 0.03000000 sec
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NUC2 1H
CPDPRG[2 waltz16
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PLW12 0.20893000 W
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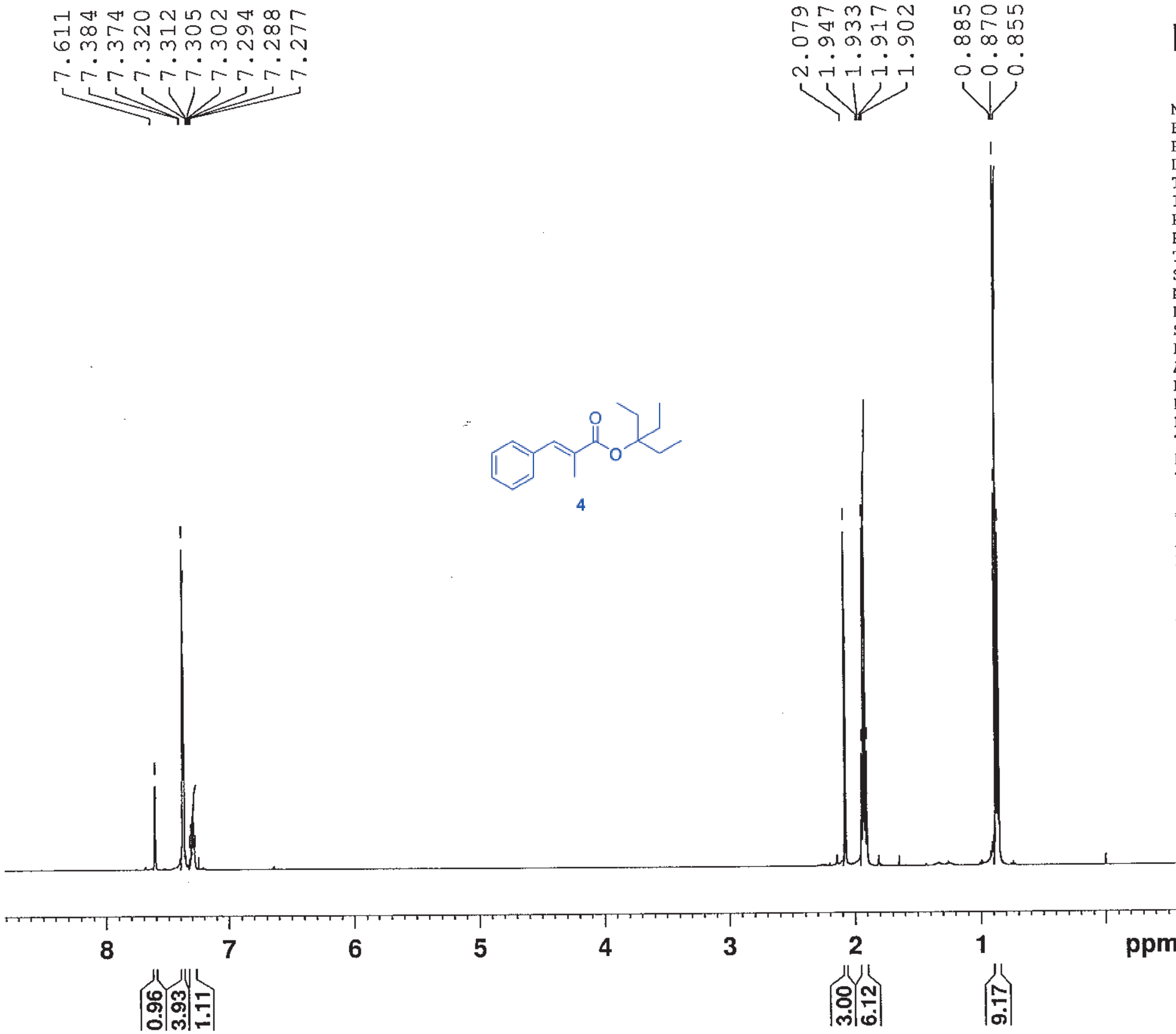
200
180
160
140
120
100
80
60
40
20
0
ppm

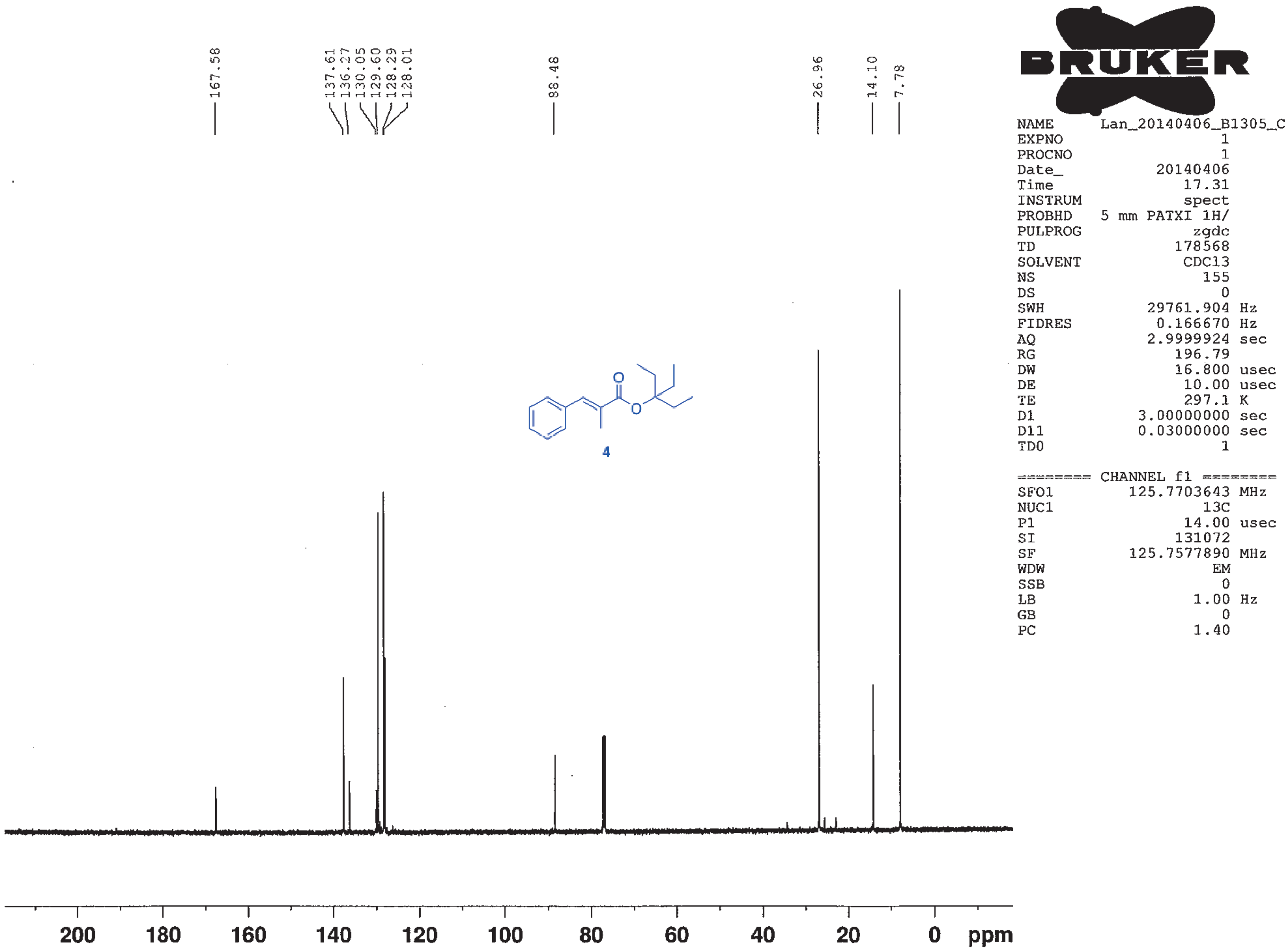


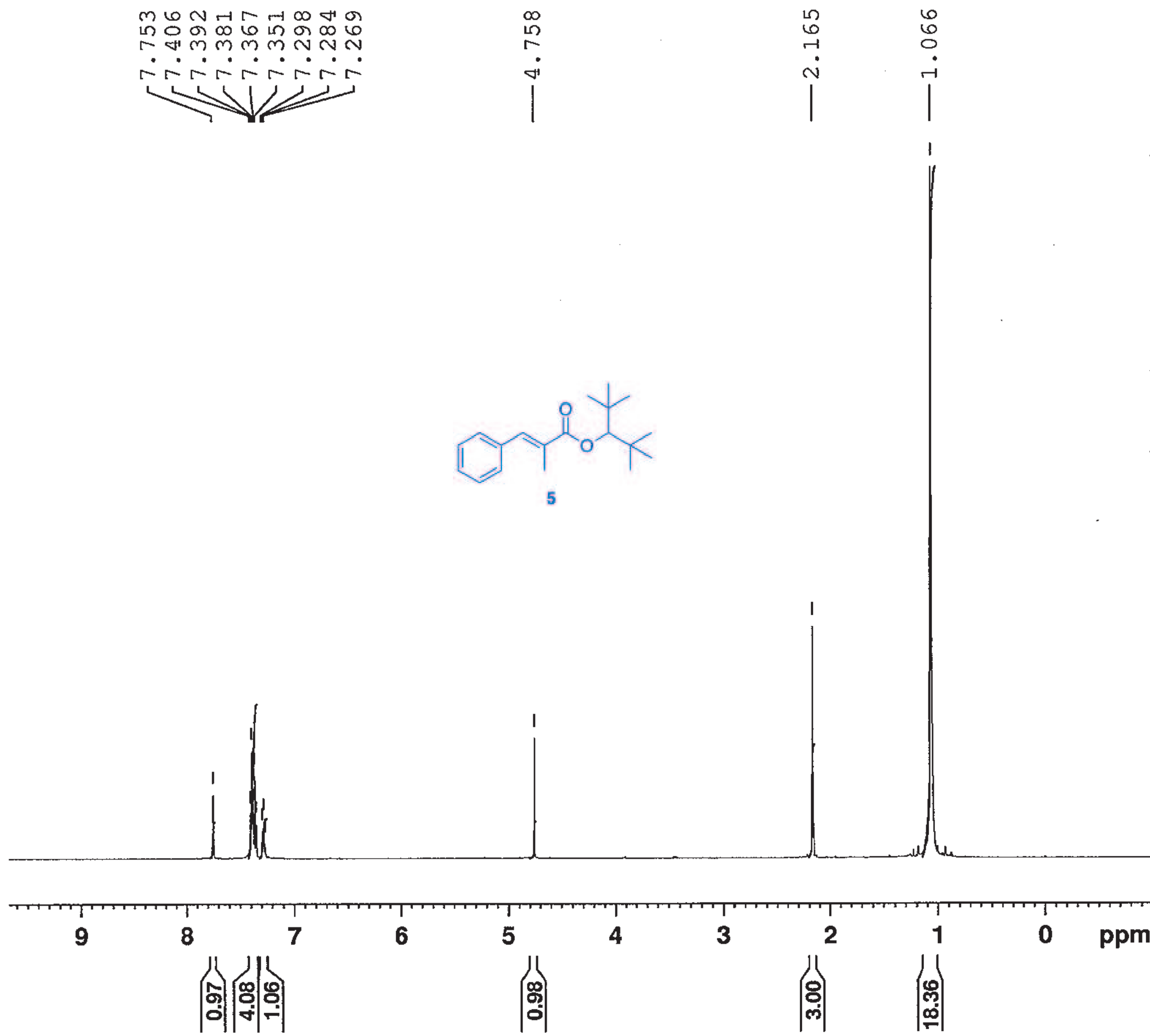
4

NAME	Lan_20140406_B1305
EXPNO	1
PROCNO	1
Date_	20140406
Time	17.09
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	8
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999499 sec
RG	15.84
DW	50.000 usec
DE	10.00 usec
TE	296.3 K
D1	10.00000000 sec
TD0	1

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

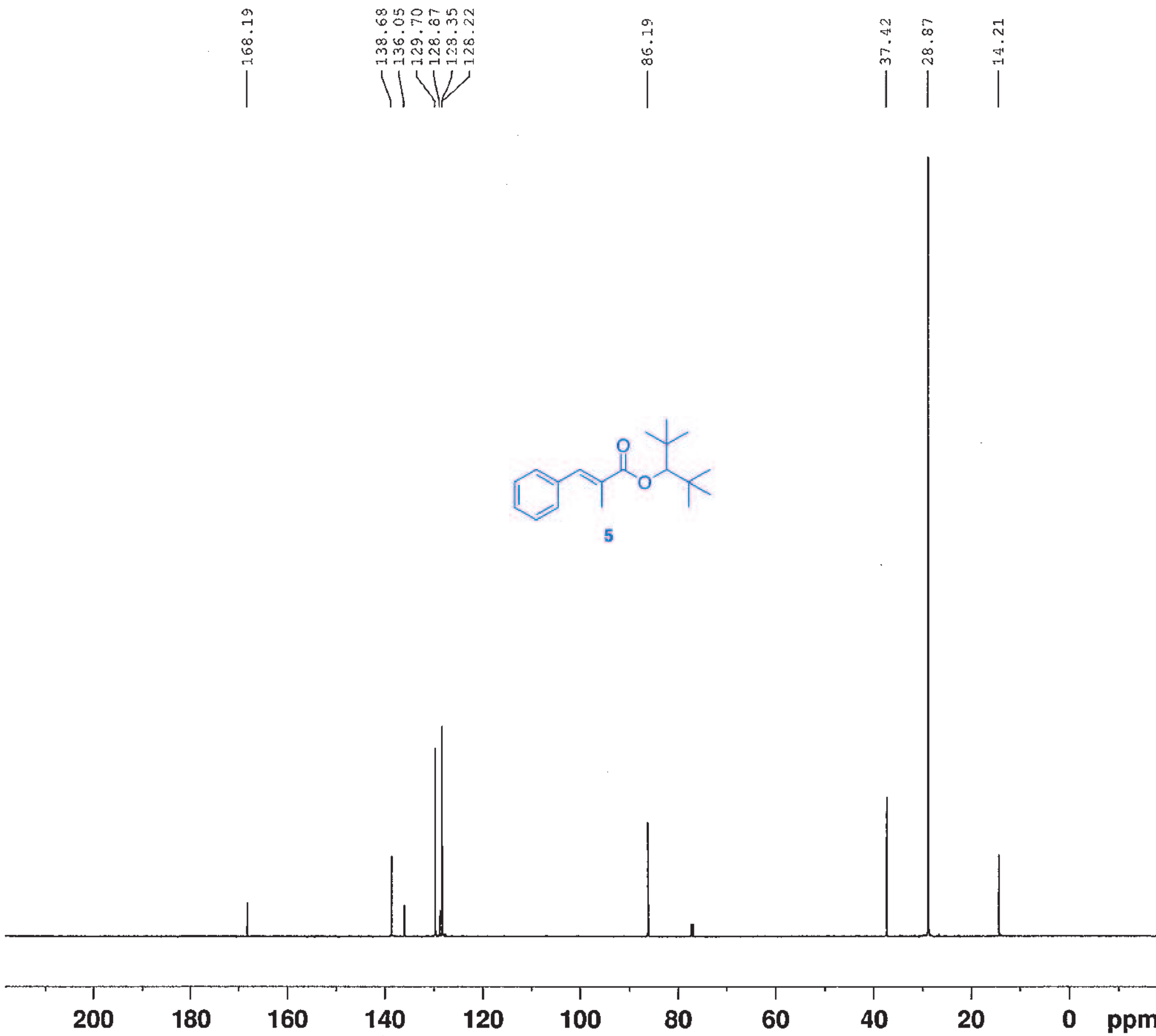
SFO1	500.1330885 MHz
NUC1	1H
P1	8.00 usec
SI	65536
SF	500.1300182 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00


167.58
137.61
136.27
130.05
129.60
128.29
128.01
88.48
26.96
14.10
7.78
4
200
180
160
140
120
100
80
60
40
20
0
ppm
BRUKER
NAME Lan_20140406_B1305_C
EXPNO 1
PROCNO 1
Date_ 20140406
Time 17.31
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgdc
TD 178568
SOLVENT CDCl3
NS 155
DS 0
SWH 29761.904 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 196.79
DW 16.800 usec
DE 10.00 usec
TE 297.1 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703643 MHz
NUC1 13C
P1 14.00 usec
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



BRUKER

Current Data Parameters	
NAME	Lan_20140406_B2009
EXPNO	1
PROCNO	1
F2 - Acquisition Parameters	
Date_	20140406
Time	17.37
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	8
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999001 sec
RG	4.63
DW	50.000 usec
DE	10.00 usec
TE	296.4 K
D1	10.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	500.1330885 MHz
NUC1	1H
P1	8.00 usec
PLW1	12.19999981 W
F2 - Processing parameters	
SI	65536
SF	500.1300218 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

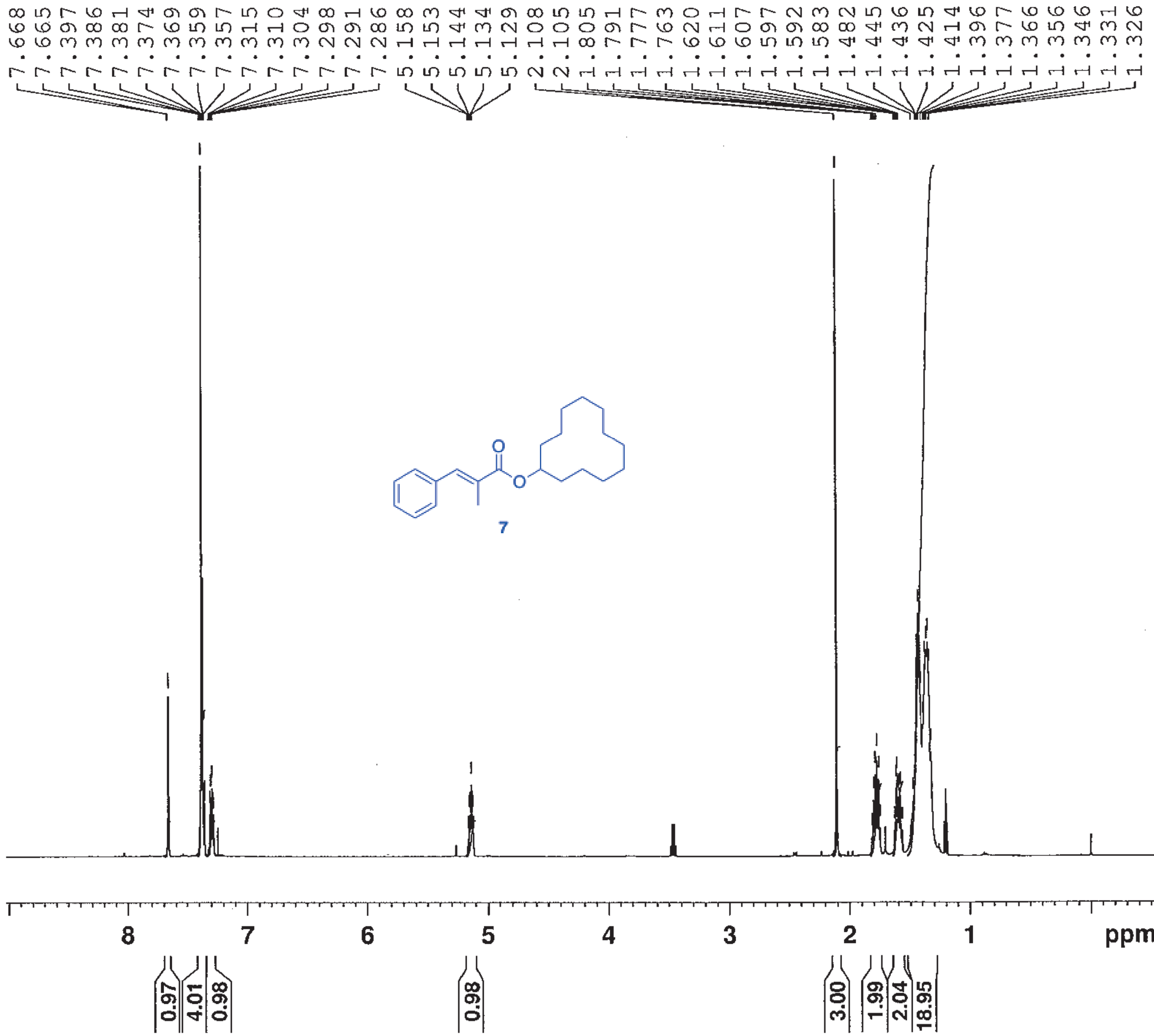


BRUKER

NAME	Lan_20140406_B2009_C
EXPNO	1
PROCNO	1
Date_	20140406
Time	17.59
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zgdc
TD	178568
SOLVENT	CDCl3
NS	117
DS	0
SWH	29761.904 Hz
FIDRES	0.166670 Hz
AQ	2.9999924 sec
RG	196.79
DW	16.800 usec
DE	10.00 usec
TE	297.0 K
D1	3.00000000 sec
D11	0.03000000 sec
TD0	1

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

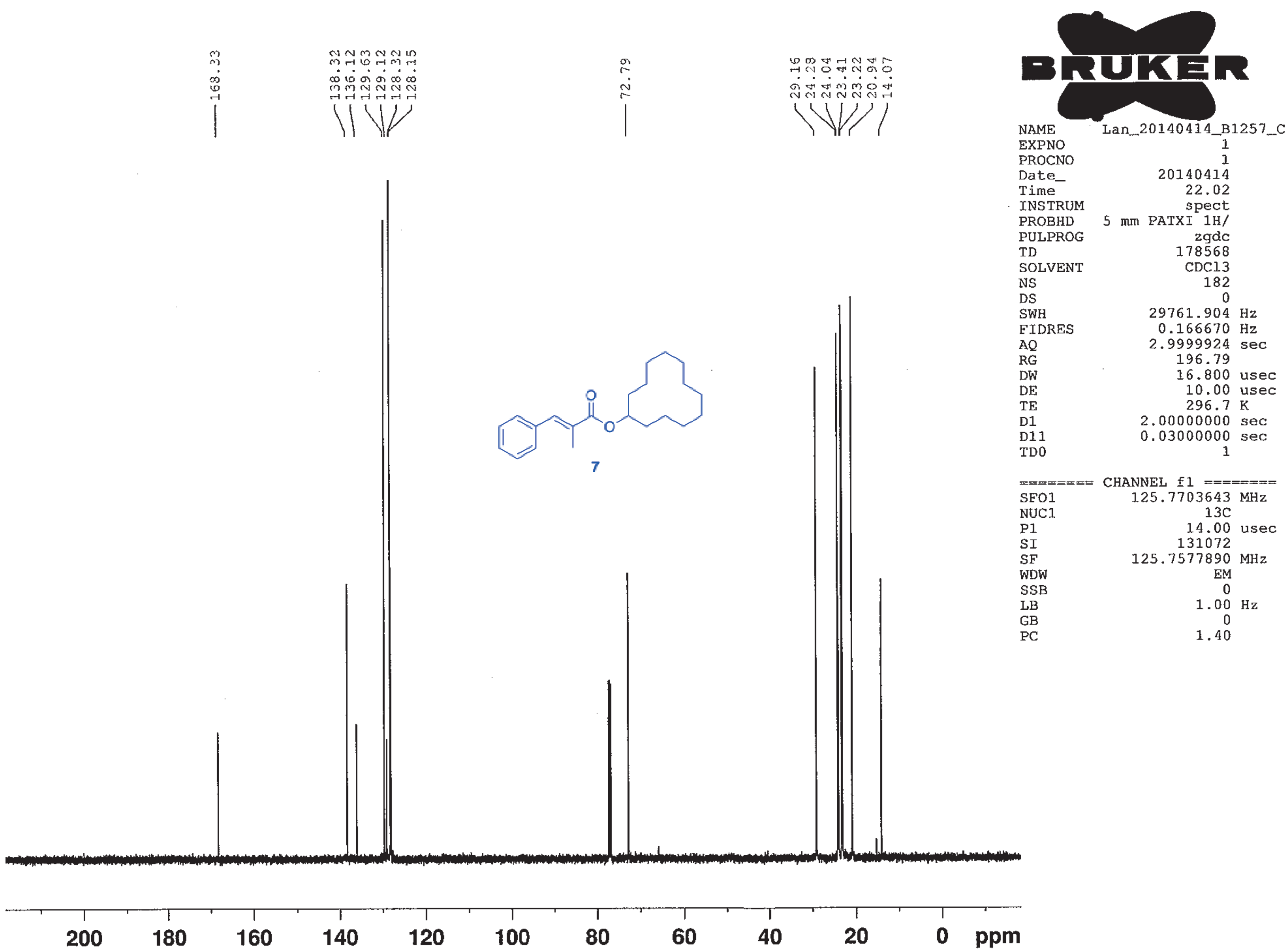
SFO1	125.7703643 MHz
NUC1	13C
P1	14.00 usec
SI	131072
SF	125.7577890 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

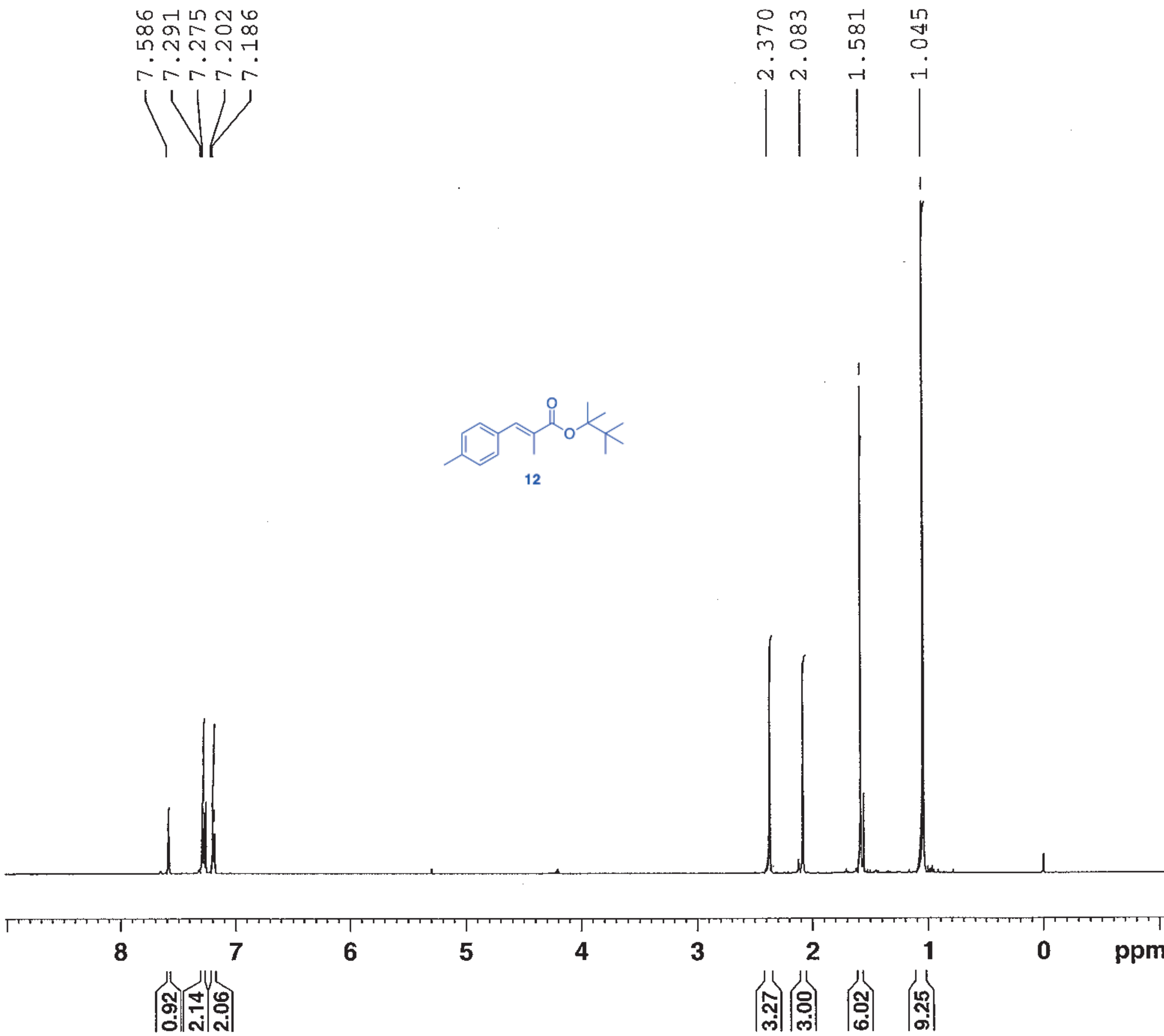


NAME	Lan_20140414_B1257
EXPNO	1
PROCNO	1
Date_	20140414
Time	21.41
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	8
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999499 sec
RG	6.92
DW	50.000 usec
DE	10.00 usec
TE	295.9 K
D1	10.00000000 sec
TD0	1

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

SFO1	500.1330885 MHz
NUC1	1H
P1	8.00 usec
SI	65536
SF	500.1300192 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00


168.33
138.32
136.12
129.63
129.12
128.32
128.15
72.79
29.16
24.28
24.04
23.41
23.22
20.94
14.07
7
200 180 160 140 120 100 80 60 40 20 0 ppm
NAME Lan_20140414_B1257_C
EXPNO 1
PROCNO 1
Date_ 20140414
Time 22.02
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgdc
TD 178568
SOLVENT CDCl3
NS 182
DS 0
SWH 29761.904 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 196.79
DW 16.800 usec
DE 10.00 usec
TE 296.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703643 MHz
NUC1 13C
P1 14.00 usec
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



BRUKER

Current Data Parameters

NAME	Lan_20140311_B3237
EXPNO	6
PROCNO	1

F2 - Acquisition Parameters

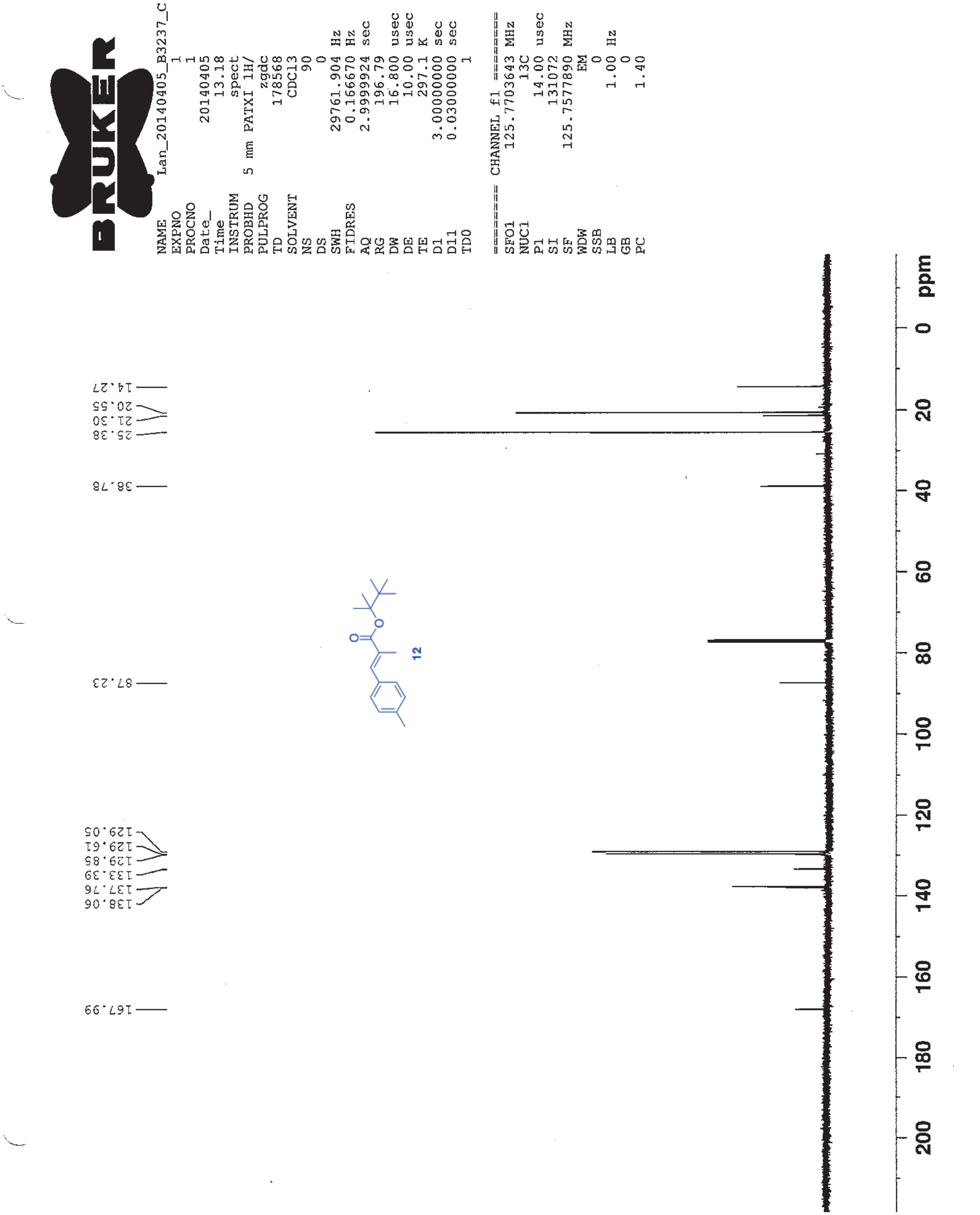
Date_	20140311
Time	16.26
INSTRUM	spect
PROBHD	5 mm QNP 1H/13
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	8
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999499 sec
RG	203.2
DW	50.000 usec
DE	7.50 usec
TE	295.0 K
D1	10.00000000 sec
TD0	1

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

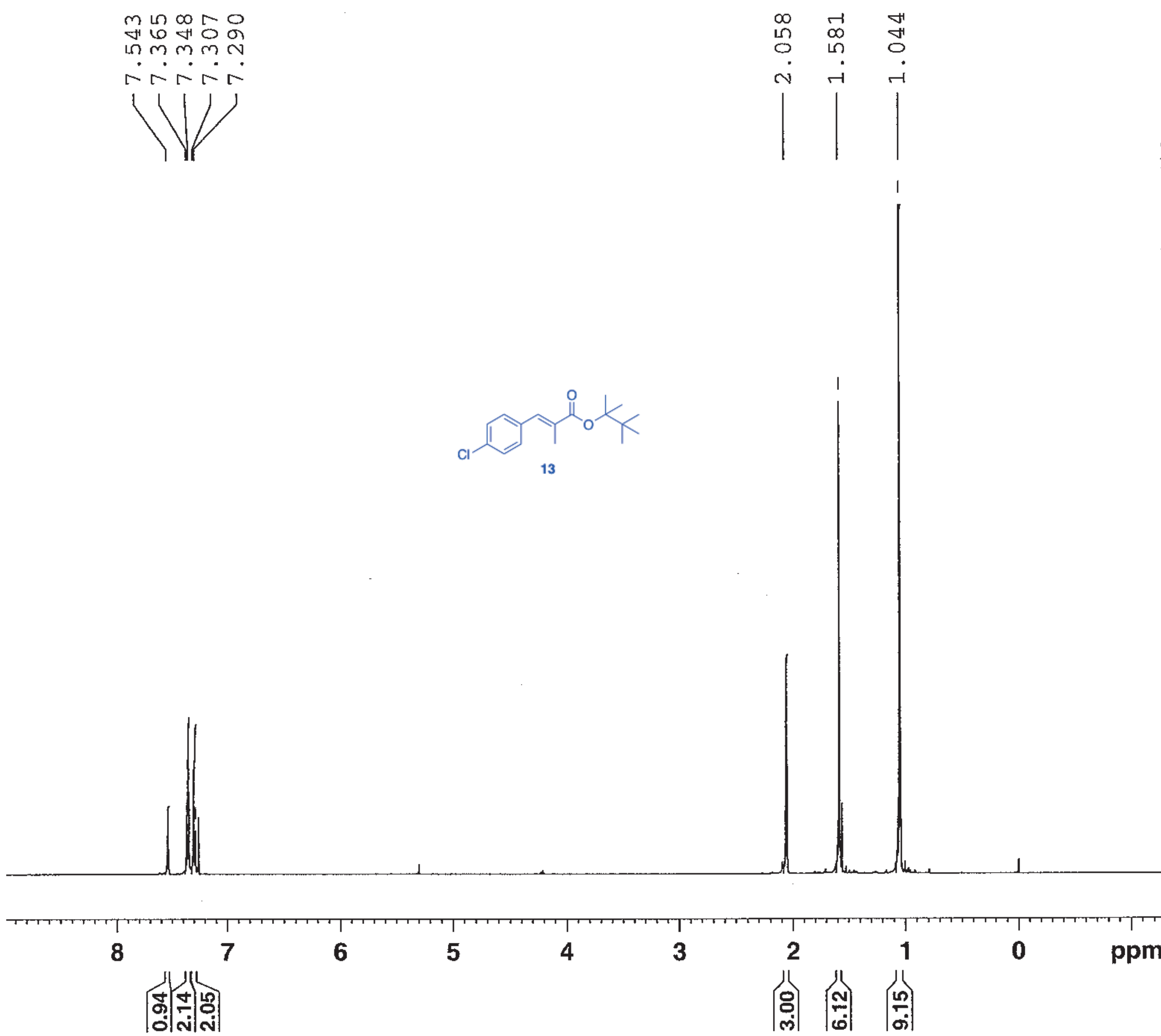
NUC1	1H
P1	10.00 usec
PL1	0.00 dB
SFO1	499.8740056 MHz

F2 - Processing parameters

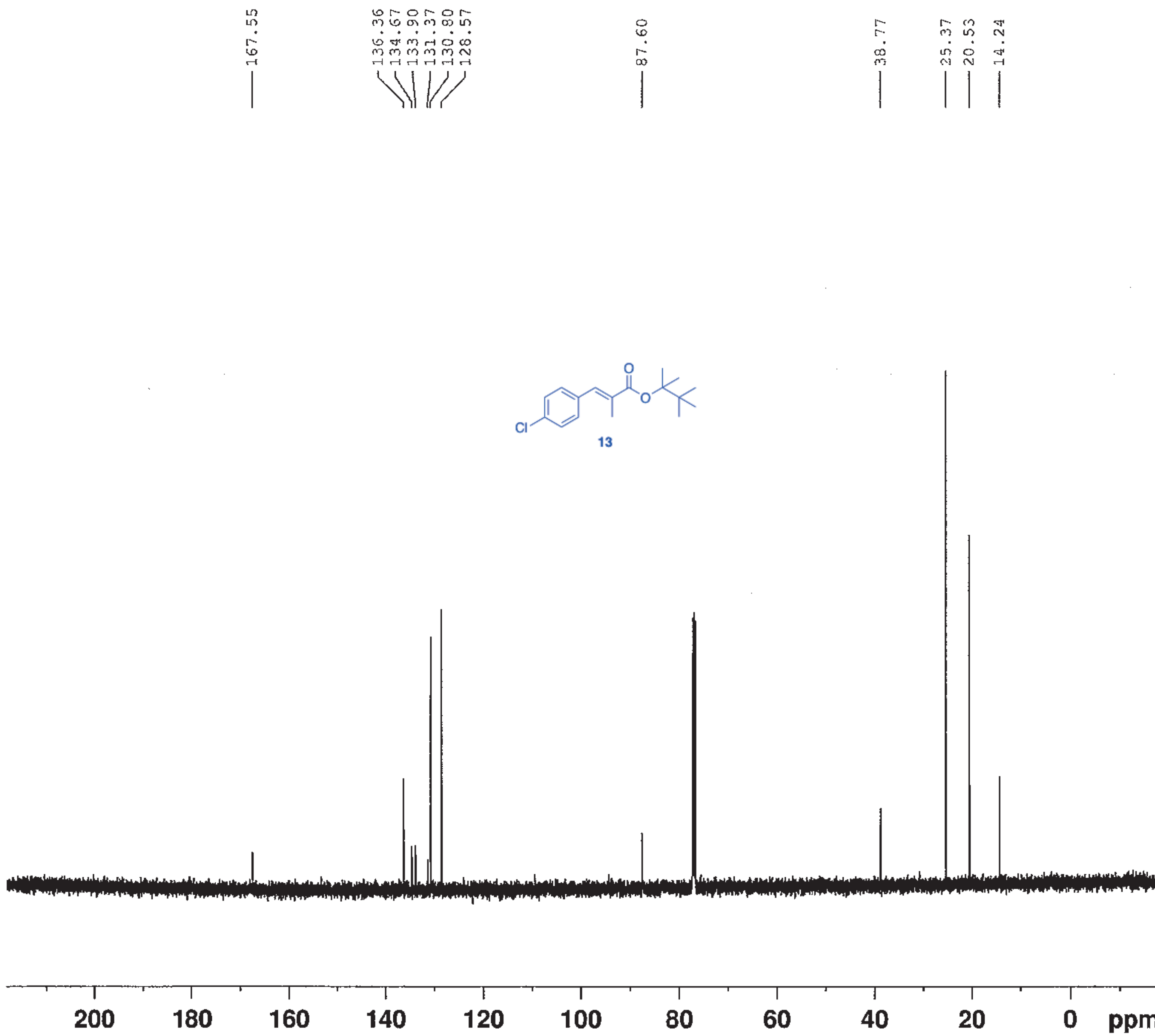
SI	32768
SF	499.8700188 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



14.27
20.55
21.30
25.38
38.78
87.23
129.05
129.61
129.85
133.39
137.76
138.06
167.99
12
NAME Lan_20140405_B3237_C
EXPNO 1
PROCNO 1
Date_ 20140405
Time 13.18
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgdc
TD 178568
SOLVENT CDCl3
NS 90
DS 0
SWH 29761.904 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 196.79
DW 16.800 usec
DE 10.00 usec
TE 297.1 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703643 MHz
NUC1 13C
P1 14.00 usec
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm



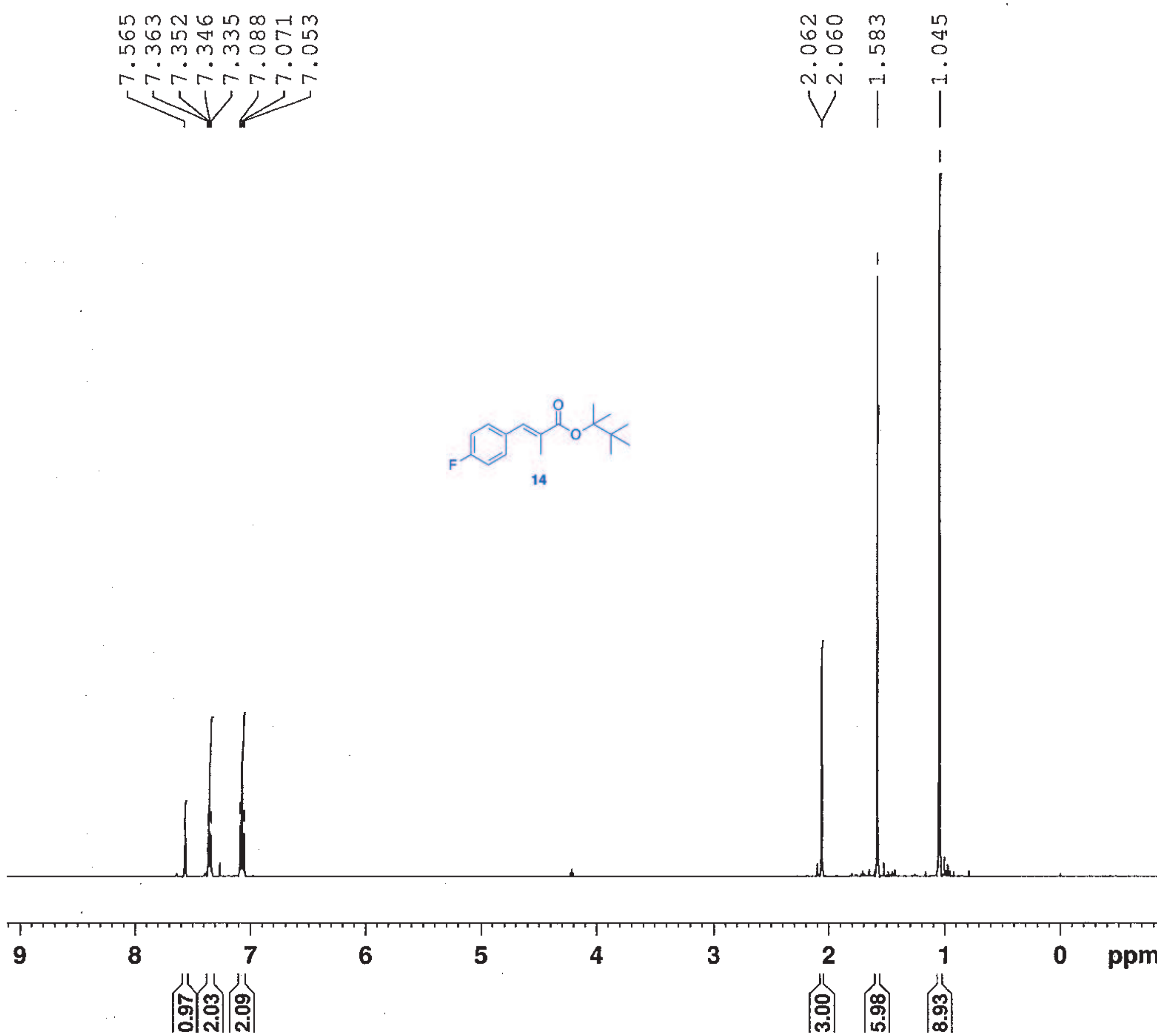

```
Current Data Parameters
NAME        Lan_20140311_B3239
EXPNO                        6
PROCNO                       1

F2 - Acquisition Parameters
Date_               20140311
Time                   16.37
INSTRUM                spect
PROBHD      5 mm QNP 1H/13
PULPROG                   zg
TD                     59998
SOLVENT                CDCl3
NS                         8
DS                         0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999499 sec
RG                       181
DW                50.000 usec
DE                  7.50 usec
TE                 294.9 K
D1           10.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                 10.00 usec
PL1                  0.00 dB
SFO1         499.8740056 MHz

F2 - Processing parameters
SI                     32768
SF           499.8700179 MHz
WDW                       EM
SSB                        0
LB                   0.30 Hz
GB                         0
PC                      1.00
```



NAME	Lan_20140405_B3239_C
EXPNO	1
PROCNO	1
Date_	20140405
Time	14.57
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zgdc
TD	178568
SOLVENT	CDCl3
NS	109
DS	0
SWH	29761.904 Hz
FIDRES	0.166670 Hz
AQ	2.9999924 sec
RG	196.79
DW	16.800 usec
DE	10.00 usec
TE	297.2 K
D1	3.00000000 sec
D11	0.03000000 sec
TD0	1

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

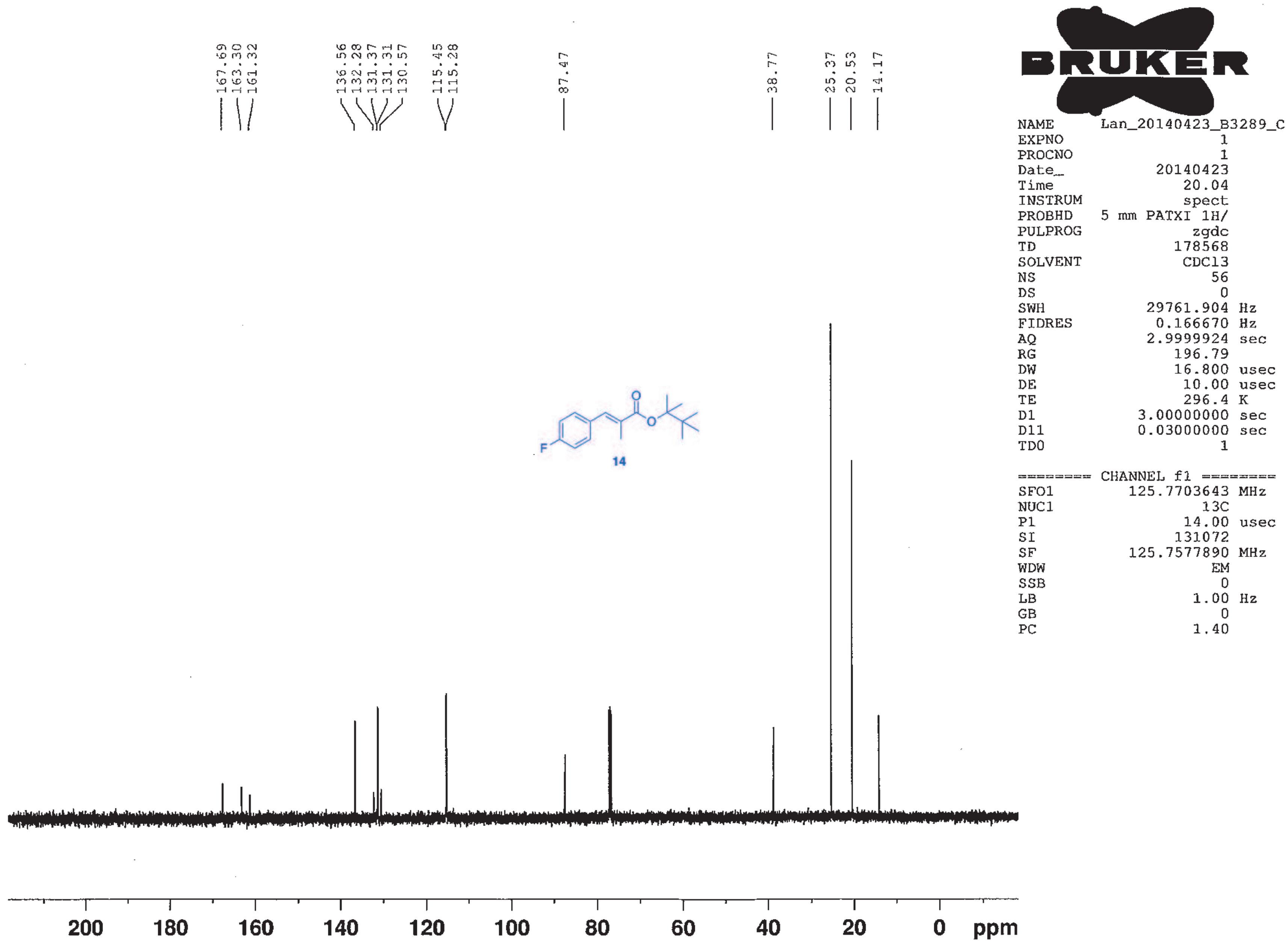
SFO1	125.7703643 MHz
NUC1	13C
P1	14.00 usec
SI	131072
SF	125.7577890 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

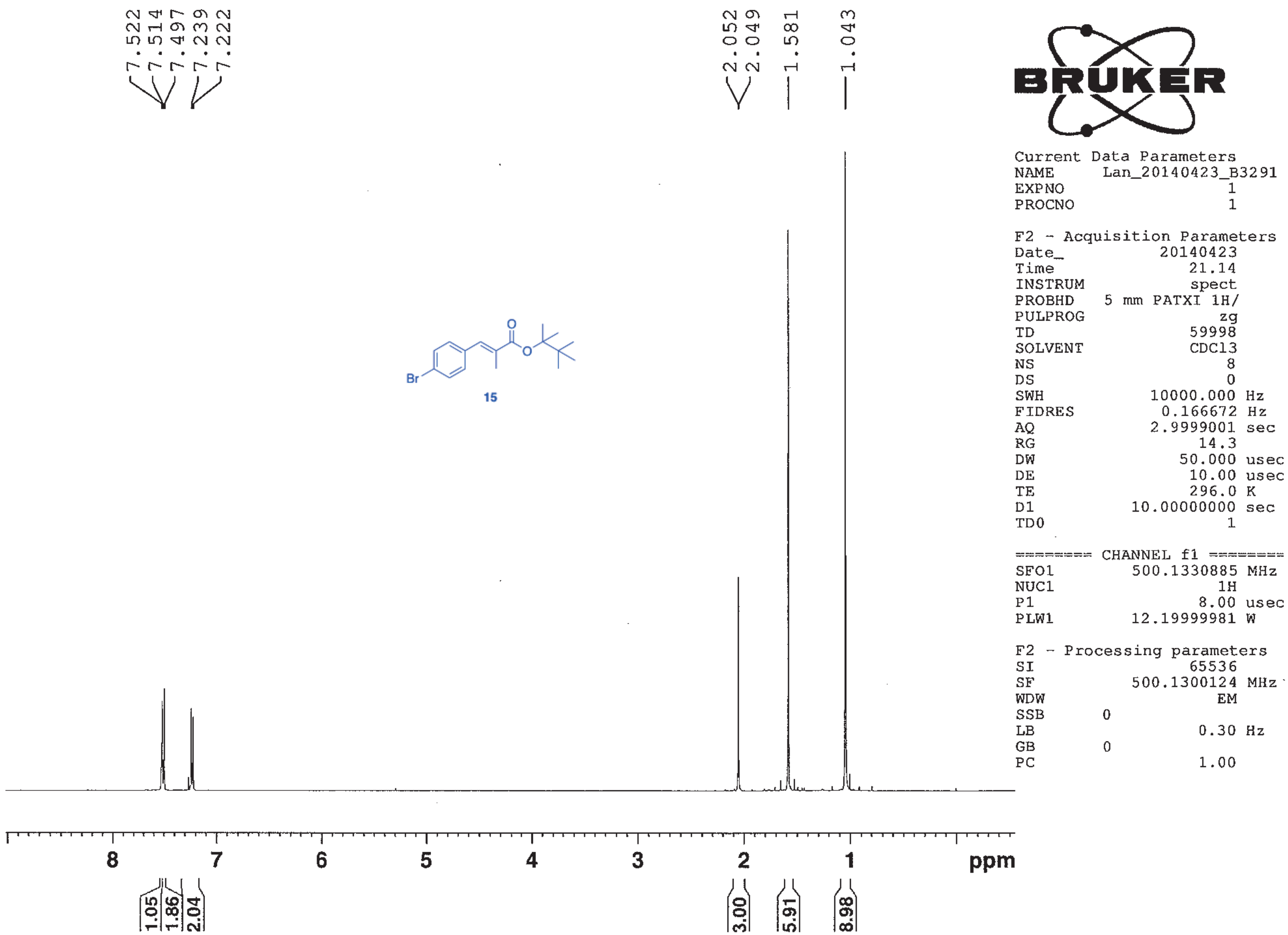


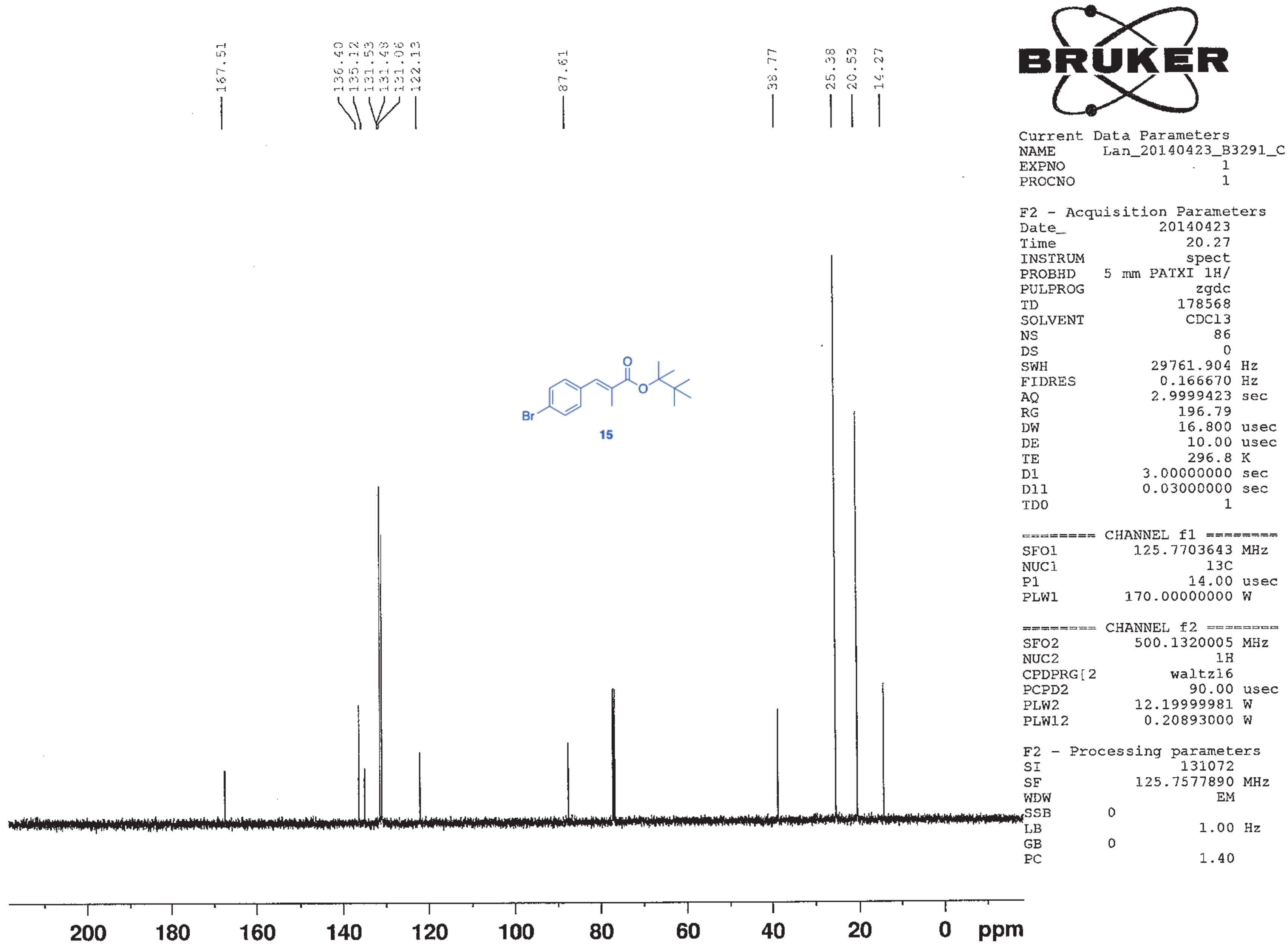
NAME	Lan_20140423_B3289
EXPNO	1
PROCNO	1
Date_	20140423
Time	19.58
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	8
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999499 sec
RG	15.84
DW	50.000 usec
DE	10.00 usec
TE	295.8 K
D1	10.00000000 sec
TD0	1

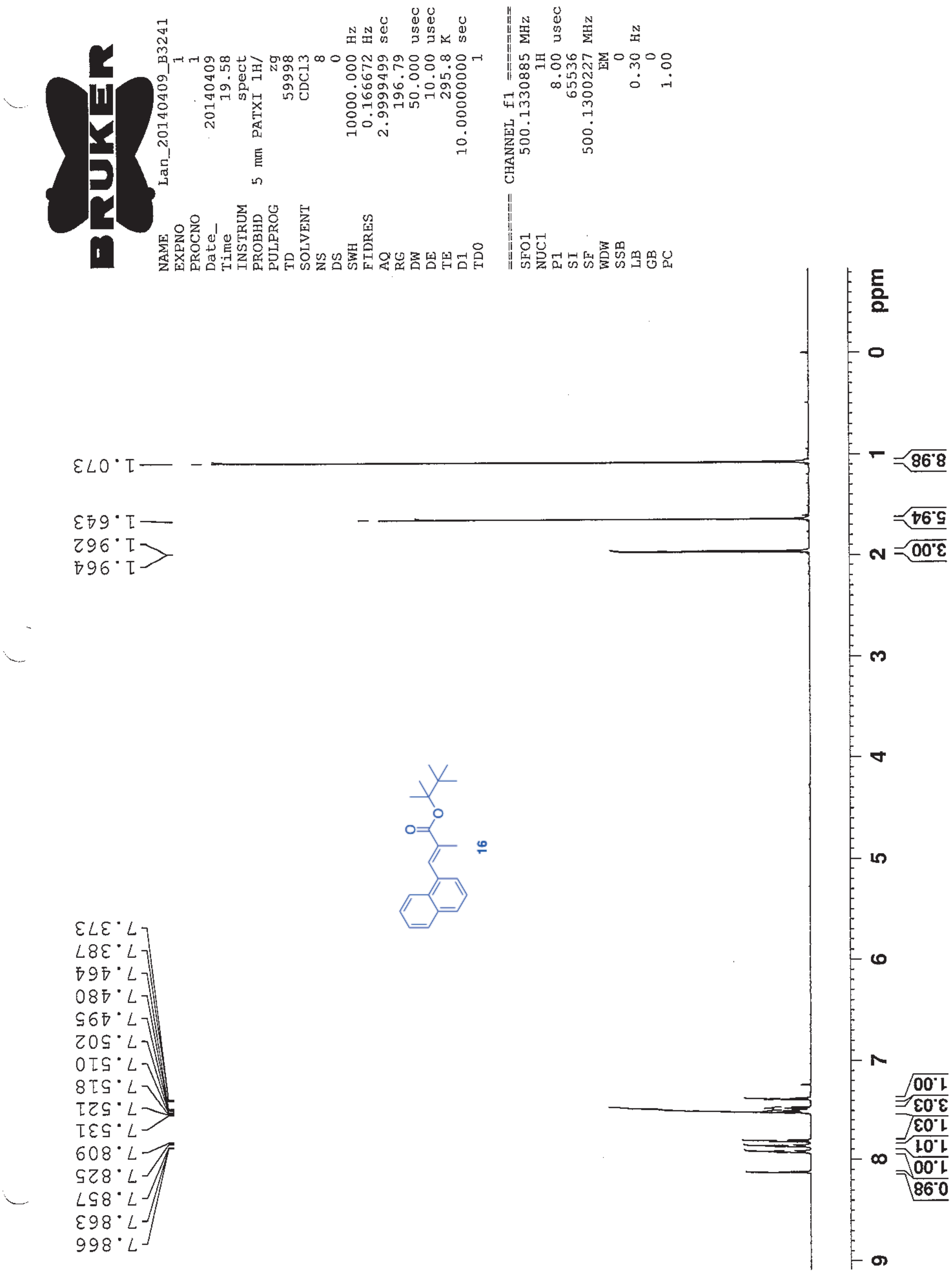
======== CHANNEL f1 ========

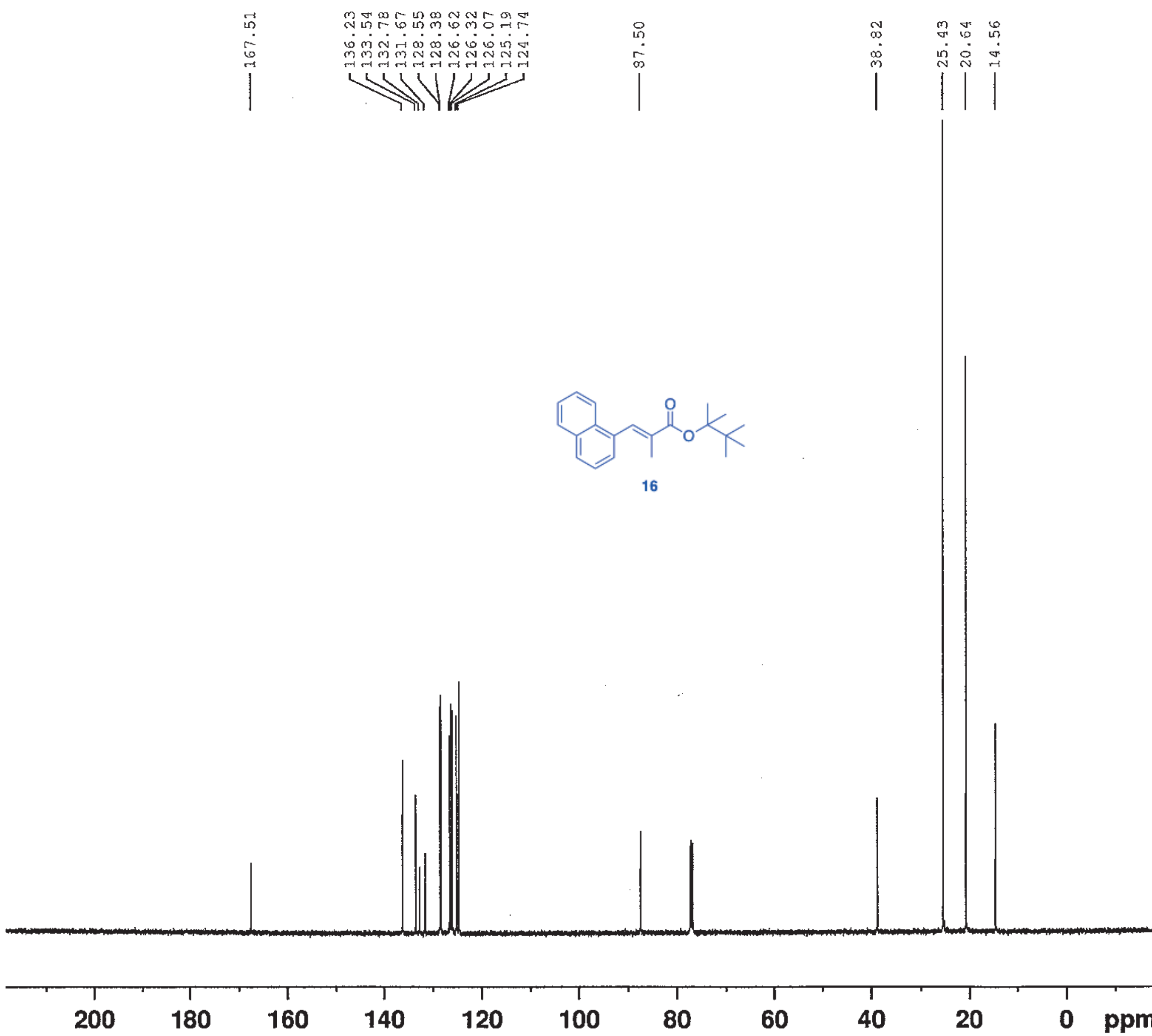
SFO1	500.1330885 MHz
NUC1	1H
P1	8.00 usec
SI	65536
SF	500.1300128 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00


167.69
163.30
161.32
136.56
132.28
131.37
131.31
130.57
115.45
115.28
87.47
38.77
25.37
20.53
14.17
F
O
O
14
NAME Lan_20140423_B3289_C
EXPNO 1
PROCNO 1
Date_ 20140423
Time 20.04
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgdc
TD 178568
SOLVENT CDCl3
NS 56
DS 0
SWH 29761.904 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 196.79
DW 16.800 usec
DE 10.00 usec
TE 296.4 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703643 MHz
NUC1 13C
P1 14.00 usec
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm


7.522
7.514
7.497
7.239
7.222
2.052
2.049
1.581
1.043
Br
15
8
7
6
5
4
3
2
1
ppm
1.05
1.86
2.04
3.00
5.91
8.98
Current Data Parameters
NAME Lan_20140423_B3291
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140423
Time 21.14
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 14.3
DW 50.000 usec
DE 10.00 usec
TE 296.0 K
D1 10.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 8.00 usec
PLW1 12.19999981 W
F2 - Processing parameters
SI 65536
SF 500.1300124 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


167.51
136.40
135.12
131.53
131.48
131.06
122.13
87.61
38.77
25.38
20.53
14.27
Br
15
O
O
200
180
160
140
120
100
80
60
40
20
0
ppm
BRUKER
Current Data Parameters
NAME Lan_20140423_B3291_C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140423
Time 20.27
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgdc
TD 178568
SOLVENT CDCl3
NS 86
DS 0
SWH 29761.904 Hz
FIDRES 0.166670 Hz
AQ 2.9999423 sec
RG 196.79
DW 16.800 usec
DE 10.00 usec
TE 296.8 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703643 MHz
NUC1 13C
P1 14.00 usec
PLW1 170.00000000 W
======== CHANNEL f2 ========
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 12.19999981 W
PLW12 0.20893000 W
F2 - Processing parameters
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


BRUKER
NAME Lan_20140409_B3241
EXPNO 1
PROCNO 1
Date_ 20140409
Time 19.58
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999499 sec
RG 196.79
DW 50.000 usec
DE 10.00 usec
TE 295.8 K
D1 10.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 8.00 usec
SI 65536
SF 500.1300227 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.073
1.643
1.962
1.964
7.373
7.387
7.464
7.480
7.495
7.502
7.510
7.518
7.521
7.531
7.809
7.825
7.857
7.863
7.866
16
8.98
5.94
3.00
1.00
3.03
1.03
1.01
1.00
0.98
ppm
0
1
2
3
4
5
6
7
8
9



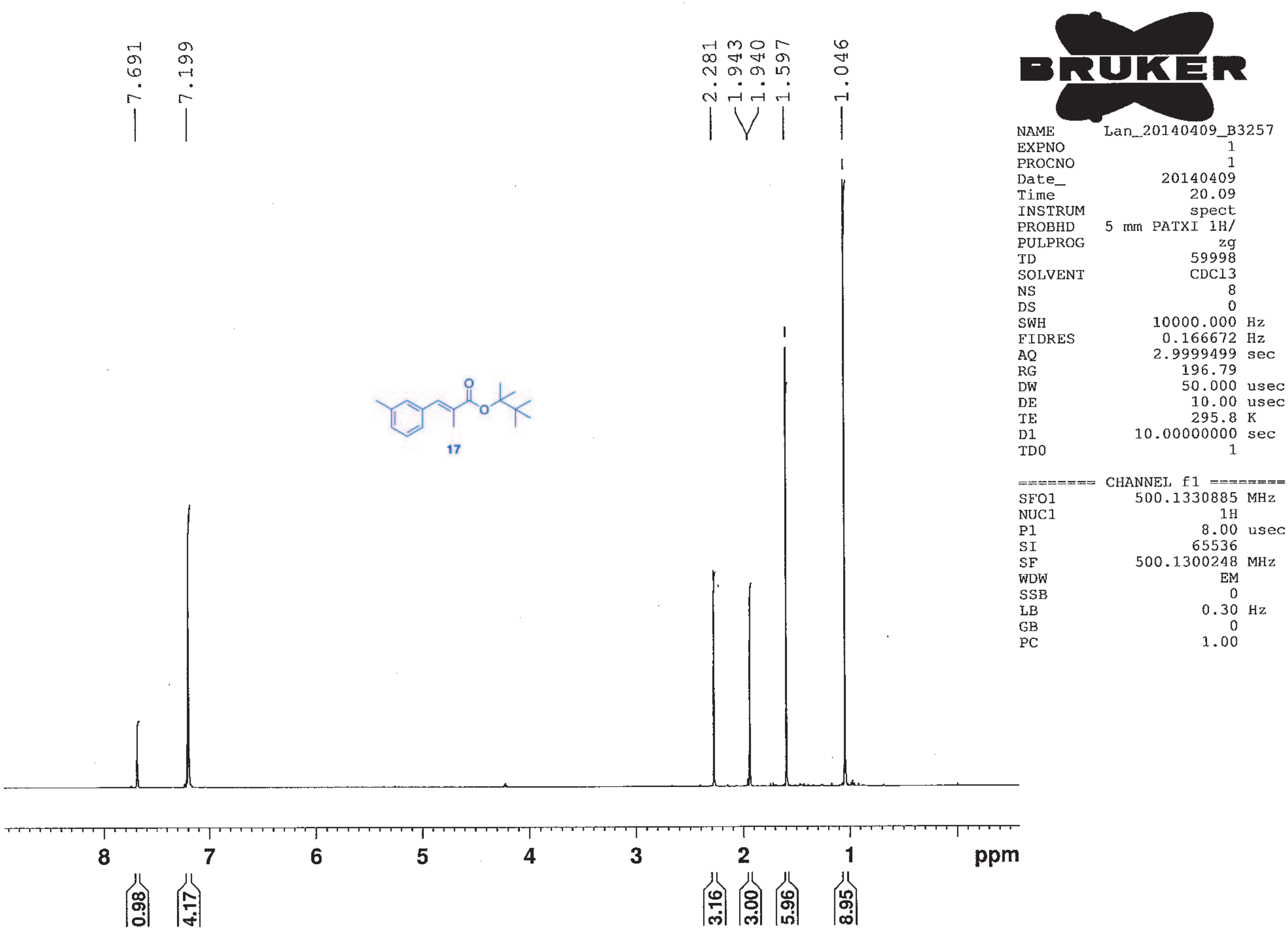
Current Data Parameters
NAME Lan_20140405_B3241_C
EXPNO 1
PROCNO 1

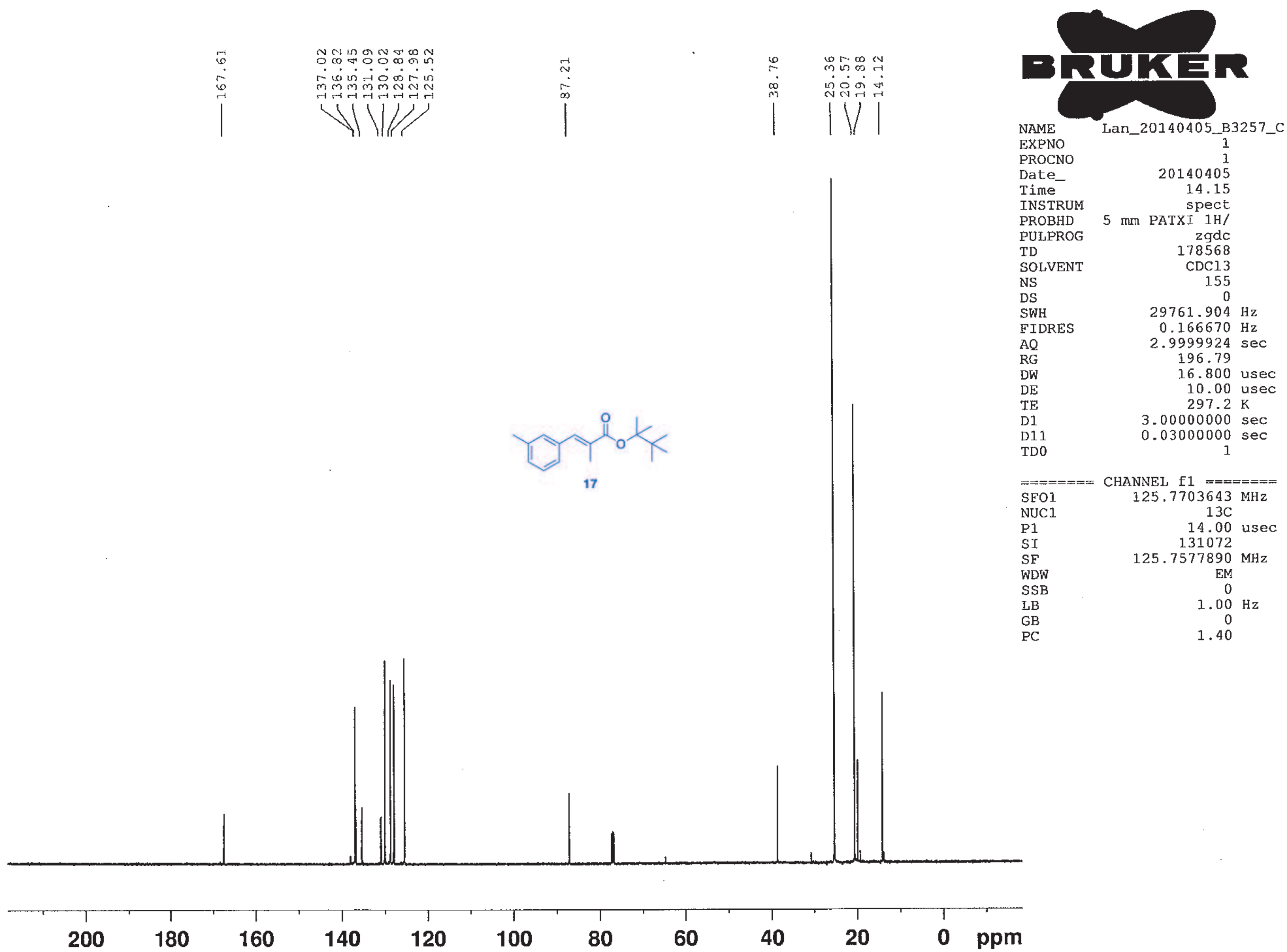
F2 - Acquisition Parameters
Date_ 20140405
Time 13.53
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgdc
TD 178568
SOLVENT CDCl3
NS 130
DS 0
SWH 29761.904 Hz
FIDRES 0.166670 Hz
AQ 2.9999423 sec
RG 196.79
DW 16.800 usec
DE 10.00 usec
TE 297.2 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1

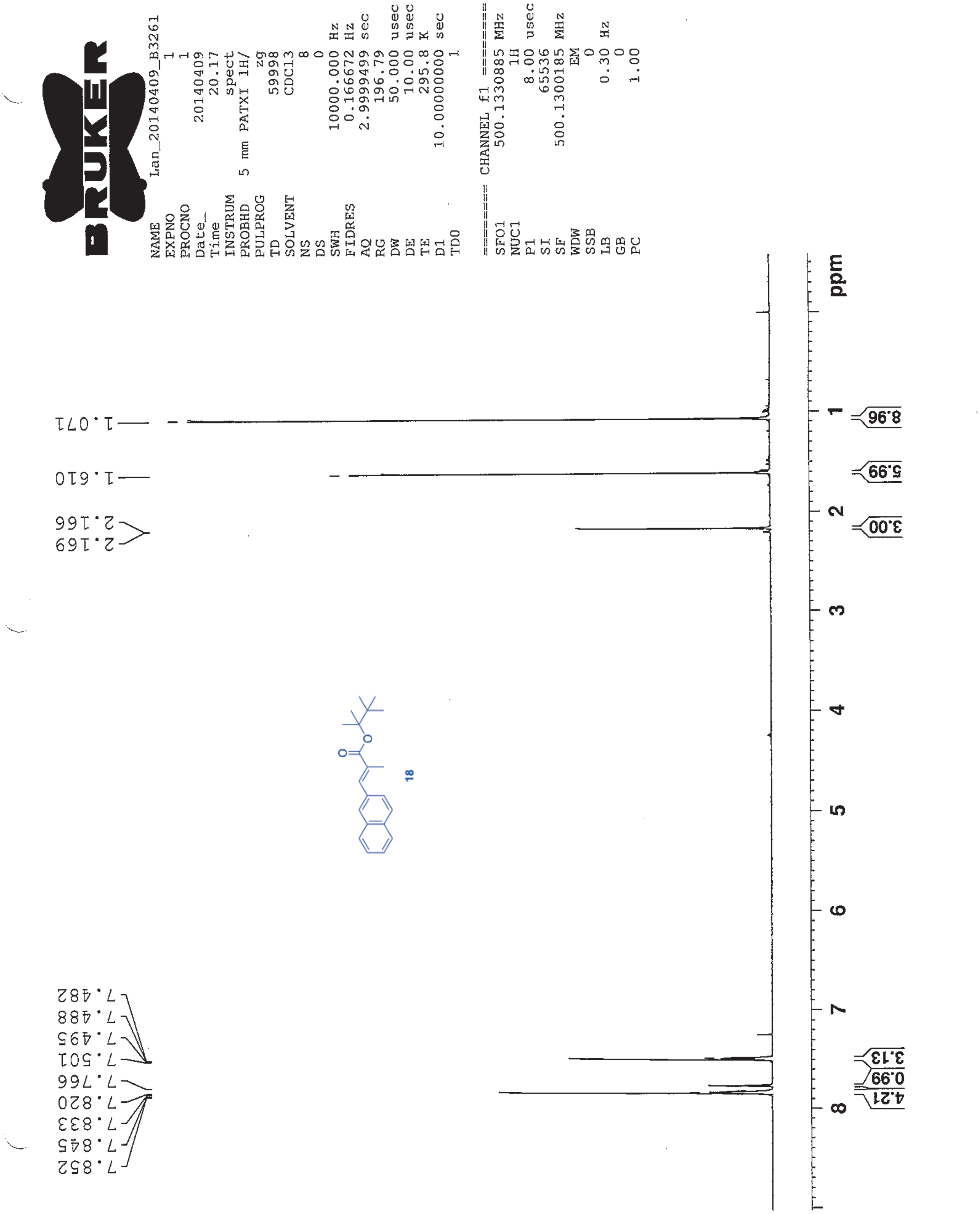
======== CHANNEL f1 ========
SFO1 125.7703643 MHz
NUC1 13C
P1 14.00 usec
PLW1 170.00000000 W

======== CHANNEL f2 ========
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 12.19999981 W
PLW12 0.20893000 W

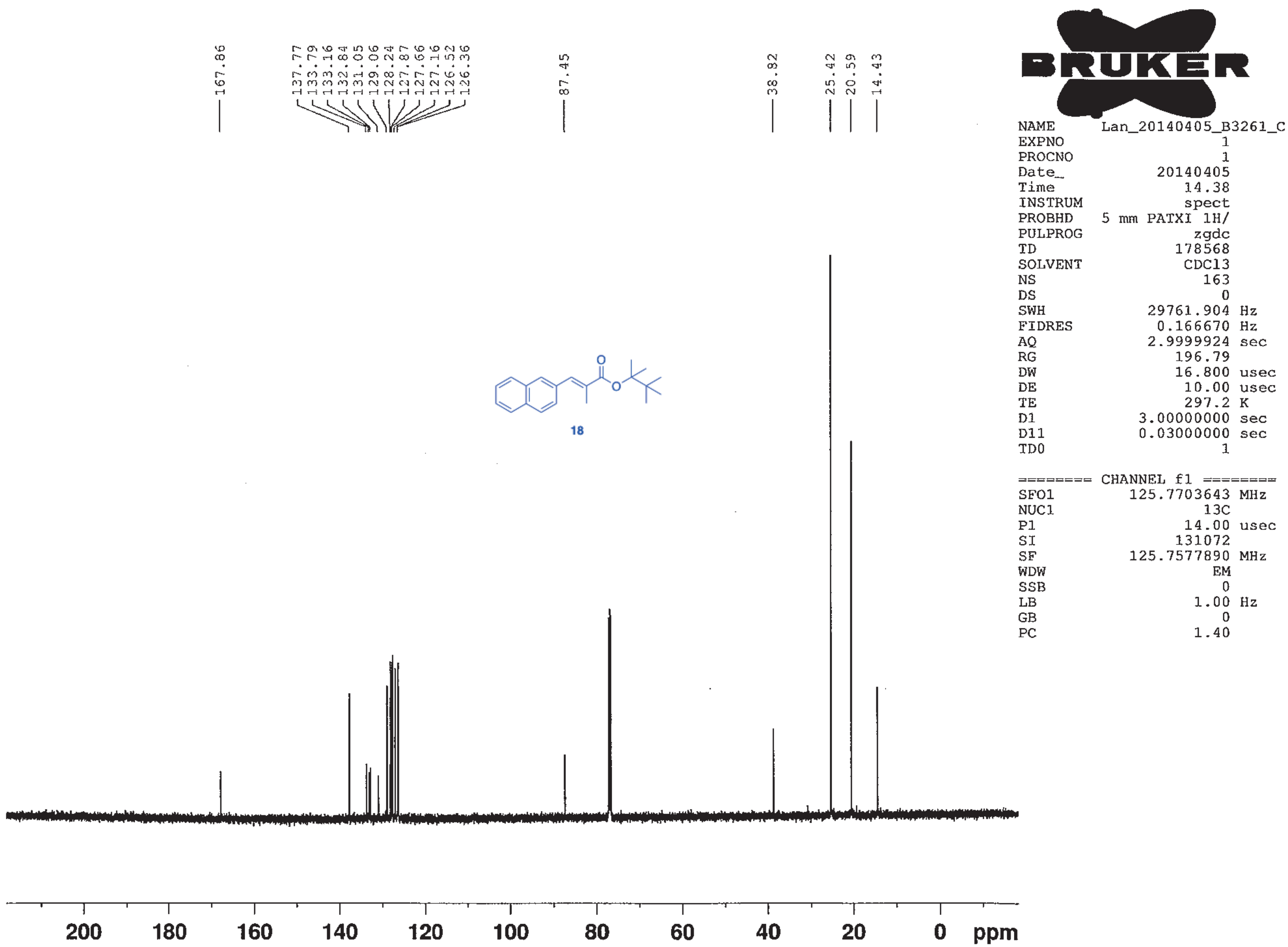
F2 - Processing parameters
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

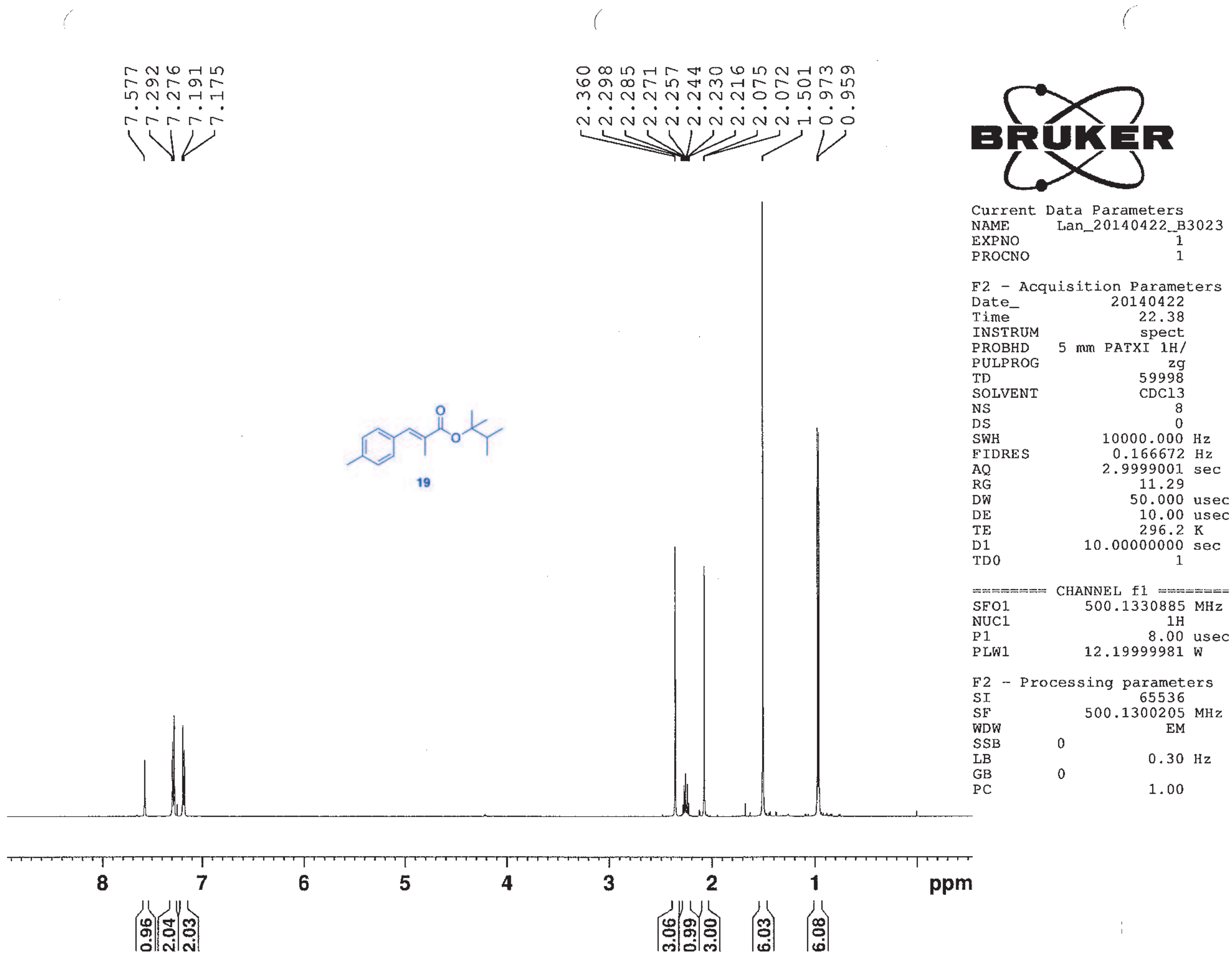

7.691
7.199
2.281
1.943
1.940
1.597
1.046
17
NAME Lan_20140409_B3257
EXPNO 1
PROCNO 1
Date_ 20140409
Time 20.09
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999499 sec
RG 196.79
DW 50.000 usec
DE 10.00 usec
TE 295.8 K
D1 10.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 8.00 usec
SI 65536
SF 500.1300248 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
ppm
0.98
4.17
3.16
3.00
5.96
8.95

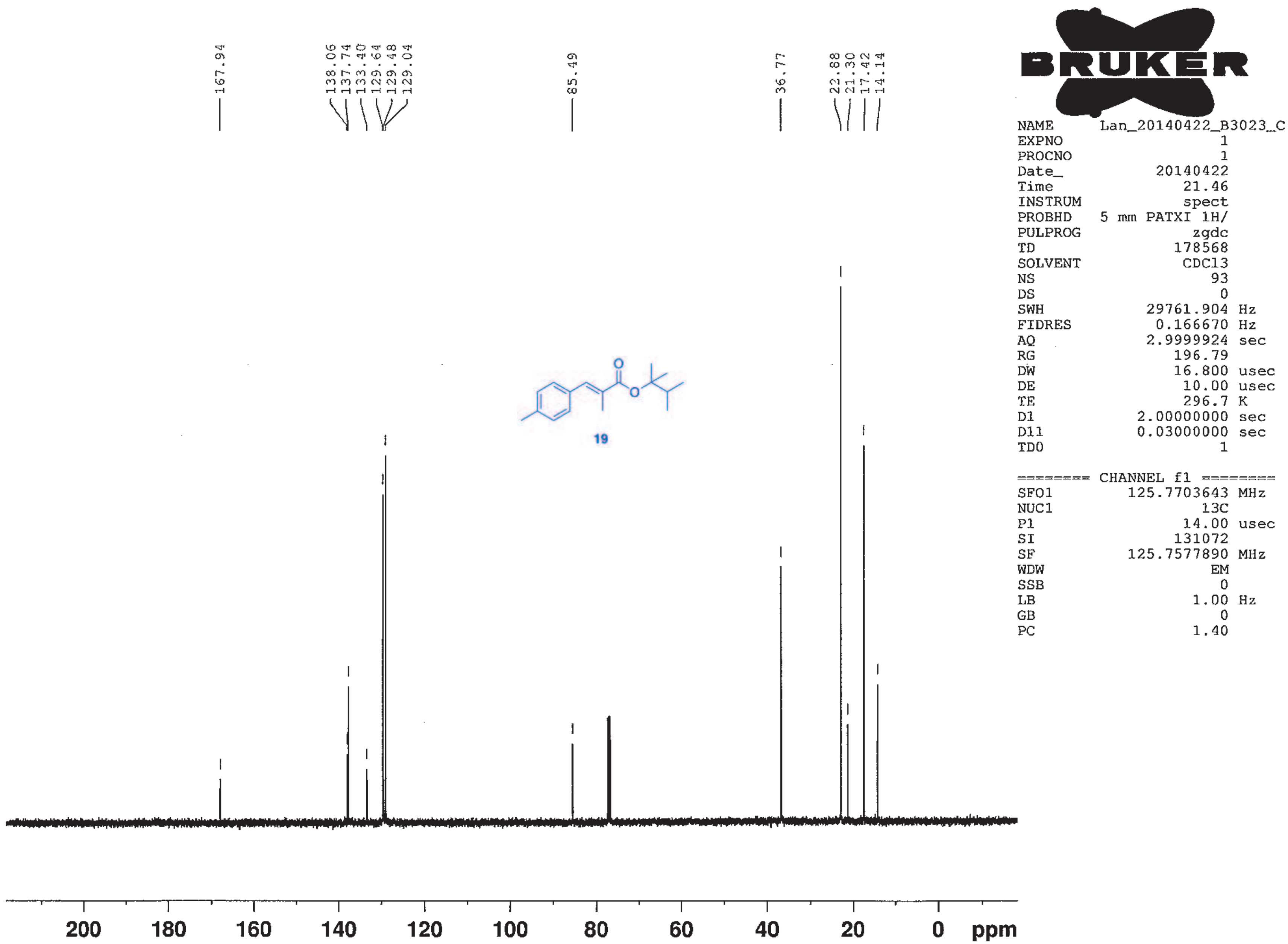

167.61
137.02
136.82
135.45
131.09
130.02
128.84
127.98
125.52
87.21
38.76
25.36
20.57
19.88
14.12
17
200 180 160 140 120 100 80 60 40 20 0 ppm
BRUKER
NAME Lan_20140405_B3257_C
EXPNO 1
PROCNO 1
Date_ 20140405
Time 14.15
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgdc
TD 178568
SOLVENT CDCl3
NS 155
DS 0
SWH 29761.904 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 196.79
DW 16.800 usec
DE 10.00 usec
TE 297.2 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703643 MHz
NUC1 13C
P1 14.00 usec
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

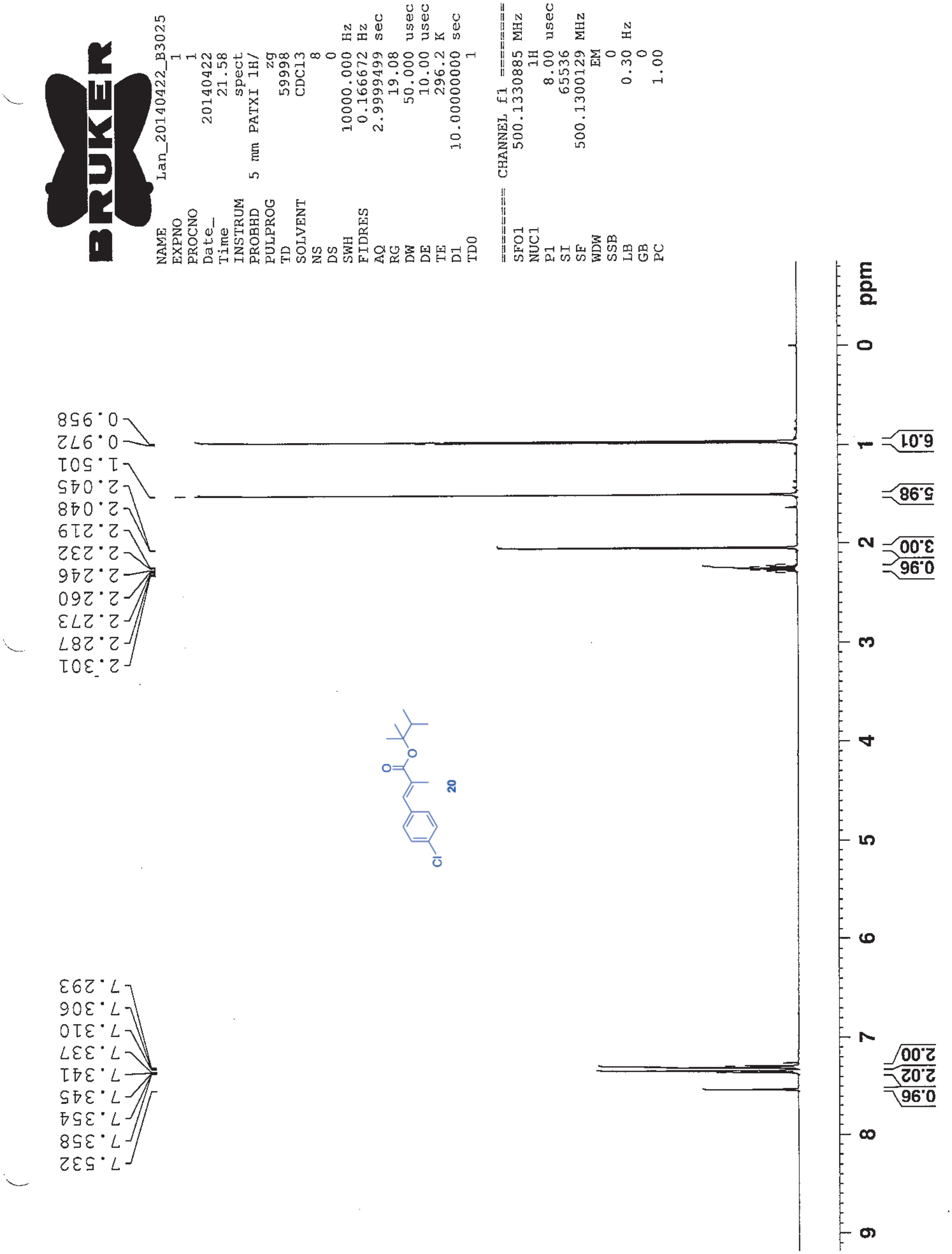


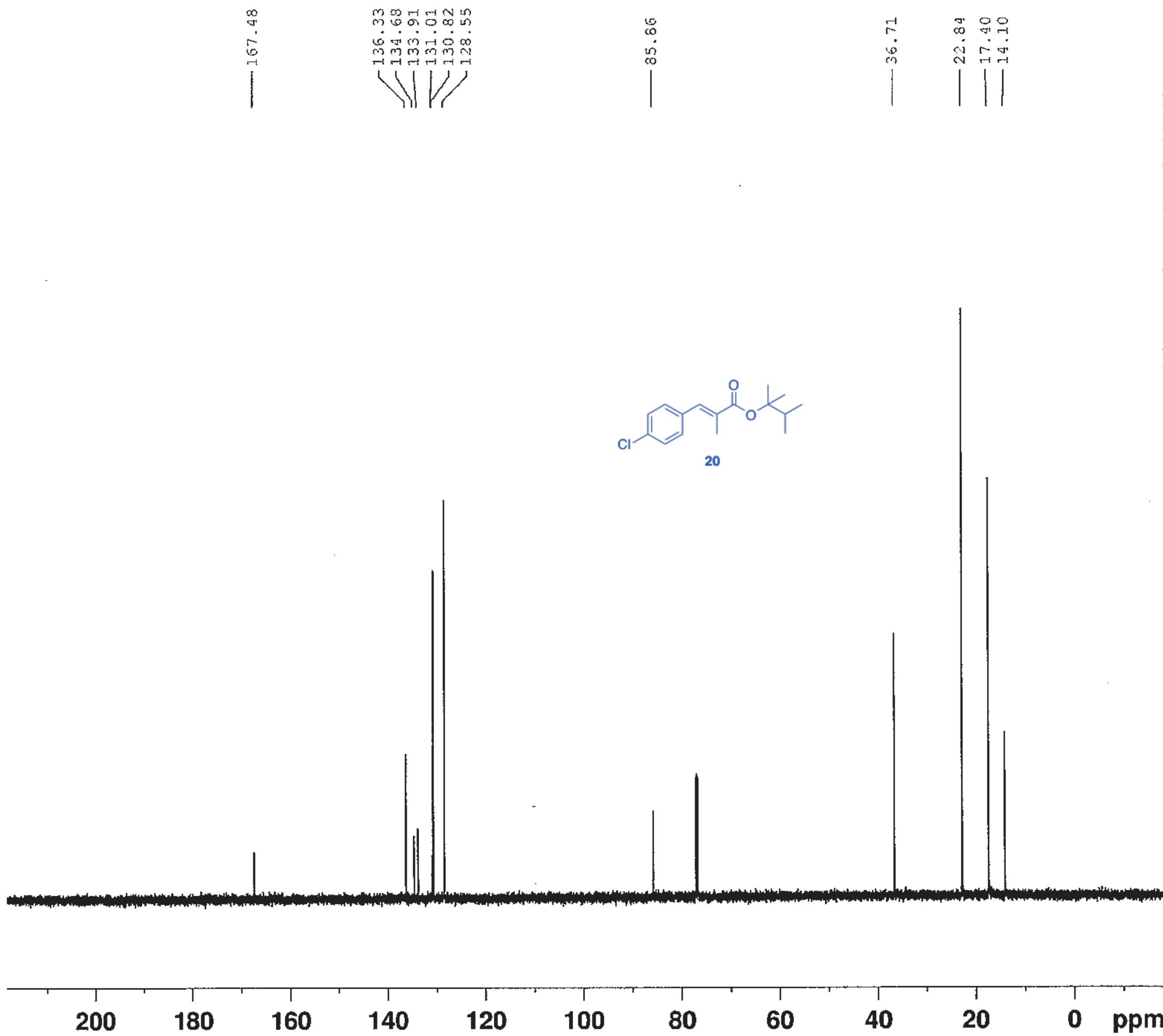
1.071
1.610
2.166
2.169
7.482
7.488
7.495
7.501
7.766
7.820
7.833
7.845
7.852
18
8.96
5.99
3.00
3.13
0.99
4.21
1
2
3
4
5
6
7
8
ppm
BRUKER
NAME Lan_20140409_B3261
EXPNO 1
PROCNO 1
Date_ 20140409
Time 20.17
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999499 sec
RG 196.79
DW 50.000 usec
DE 10.00 usec
TE 295.8 K
D1 10.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 8.00 usec
SI 65536
SF 500.1300185 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


167.86
137.77
133.79
133.16
132.84
131.05
129.06
128.24
127.87
127.66
127.16
126.52
126.36
87.45
38.82
25.42
20.59
14.43
18
NAME Lan_20140405_B3261_C
EXPNO 1
PROCNO 1
Date_ 20140405
Time 14.38
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgdc
TD 178568
SOLVENT CDCl3
NS 163
DS 0
SWH 29761.904 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 196.79
DW 16.800 usec
DE 10.00 usec
TE 297.2 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703643 MHz
NUC1 13C
P1 14.00 usec
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm


7.577
7.292
7.276
7.191
7.175
2.360
2.298
2.285
2.271
2.257
2.244
2.230
2.216
2.075
2.072
1.501
0.973
0.959
19
BRUKER
Current Data Parameters
NAME Lan_20140422_B3023
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140422
Time 22.38
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 11.29
DW 50.000 usec
DE 10.00 usec
TE 296.2 K
D1 10.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 8.00 usec
PLW1 12.19999981 W
F2 - Processing parameters
SI 65536
SF 500.1300205 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
ppm
0.96
2.04
2.03
3.06
0.99
3.00
6.03
6.08


167.94
138.06
137.74
133.40
129.64
129.48
129.04
85.49
36.77
22.88
21.30
17.42
14.14
19
200
180
160
140
120
100
80
60
40
20
0
ppm
BRUKER
NAME Lan_20140422_B3023_C
EXPNO 1
PROCNO 1
Date_ 20140422
Time 21.46
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgdc
TD 178568
SOLVENT CDCl3
NS 93
DS 0
SWH 29761.904 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 196.79
DW 16.800 usec
DE 10.00 usec
TE 296.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703643 MHz
NUC1 13C
P1 14.00 usec
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

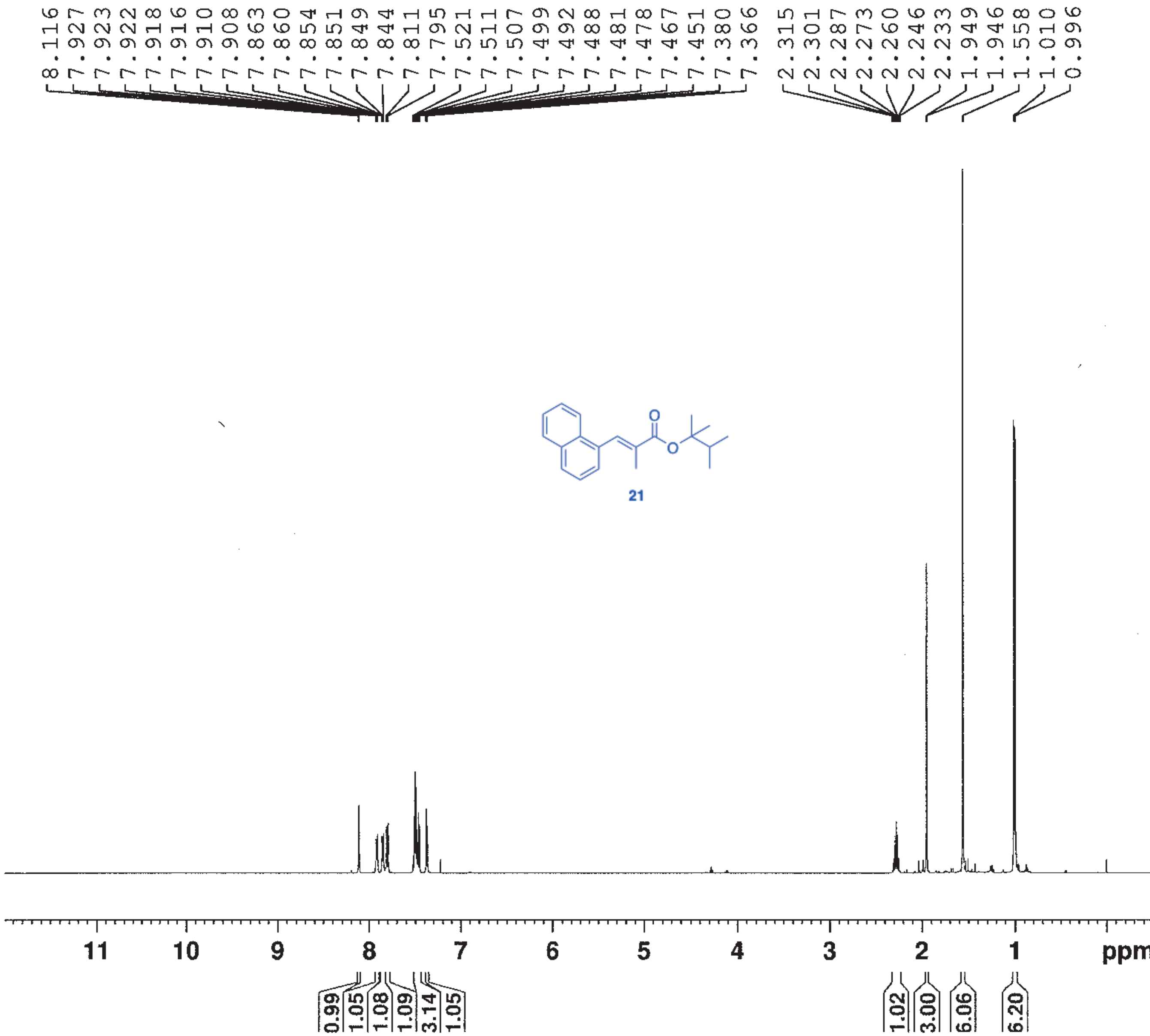

BRUKER
NAME Lan_20140422_B3025
EXPNO 1
PROCNO 1
Date_ 20140422
Time 21.58
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999499 sec
RG 19.08
DW 50.000 usec
DE 10.00 usec
TE 296.2 K
D1 10.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 8.00 usec
SI 65536
SF 500.1300129 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.958
0.972
1.501
2.045
2.048
2.219
2.232
2.246
2.260
2.273
2.287
2.301
7.293
7.306
7.310
7.337
7.341
7.345
7.354
7.358
7.532
20
Cl
O
6.01
5.98
3.00
0.96
2.00
2.02
0.96
ppm



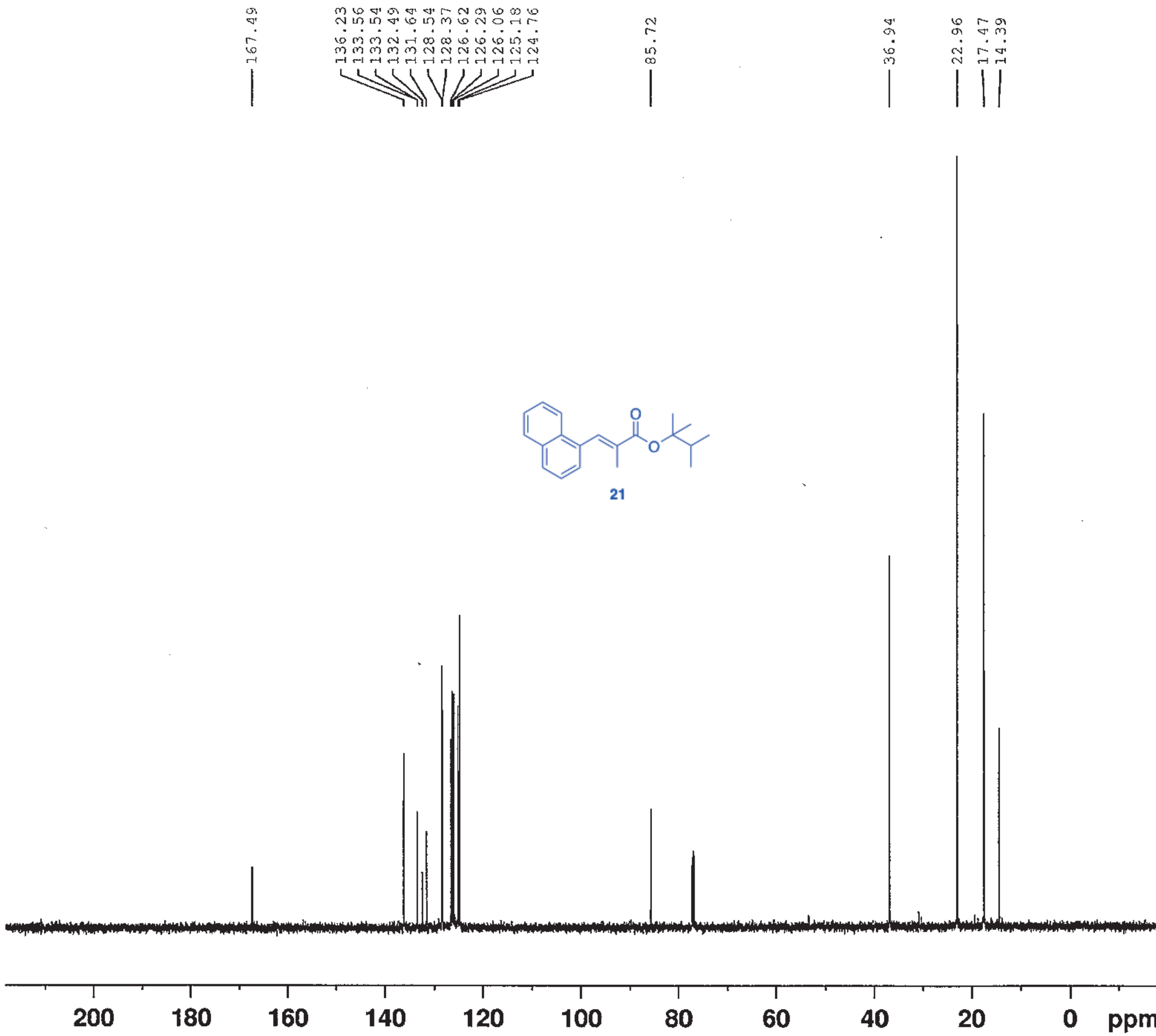
BRUKER

NAME Lan_20140422_B3025_C
EXPNO 1
PROCNO 1
Date_ 20140422
Time 22.07
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgdc
TD 178568
SOLVENT CDCl3
NS 111
DS 0
SWH 29761.904 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 196.79
DW 16.800 usec
DE 10.00 usec
TE 296.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

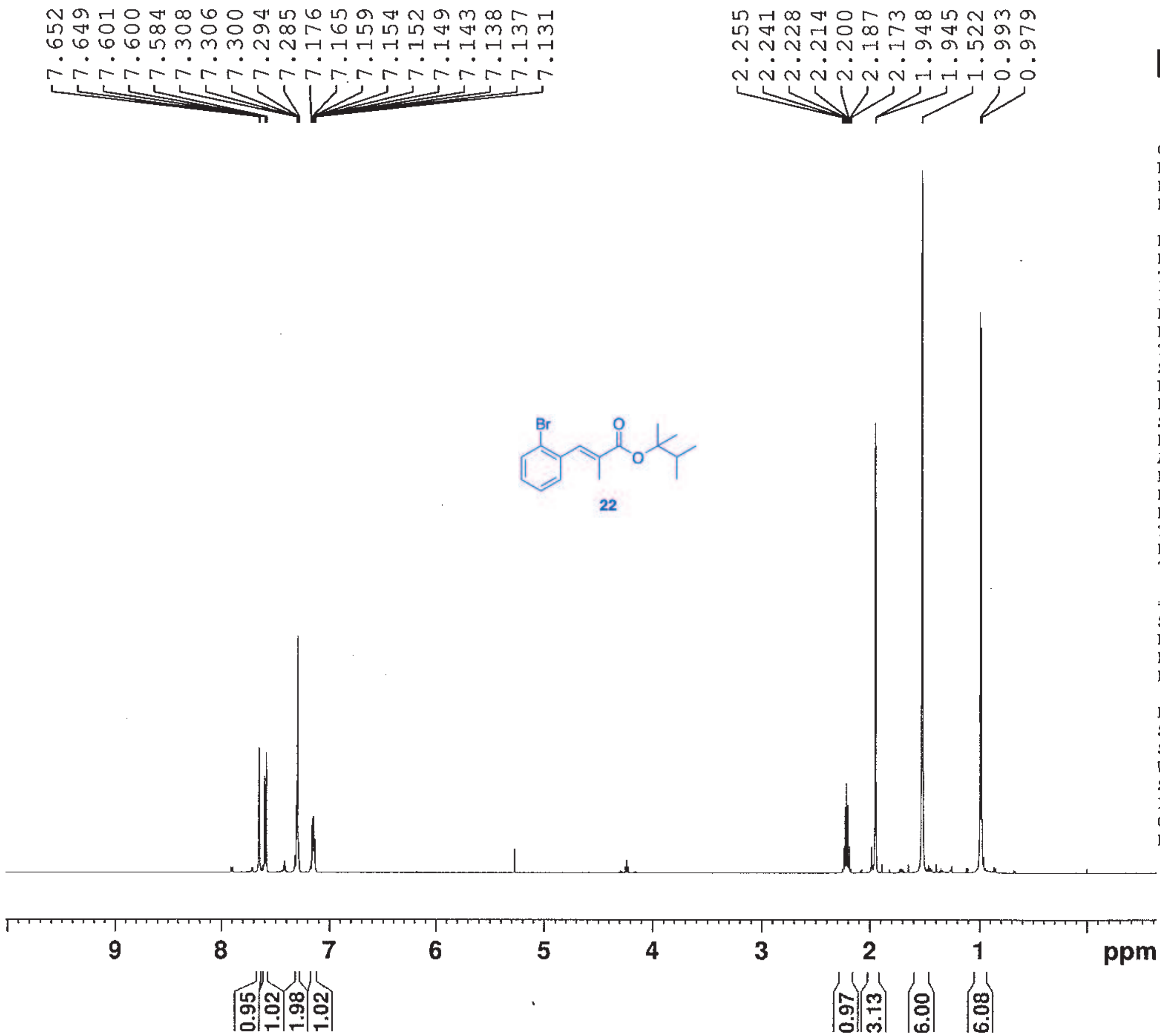
======== CHANNEL f1 ========
SFO1 125.7703643 MHz
NUC1 13C
P1 14.00 usec
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



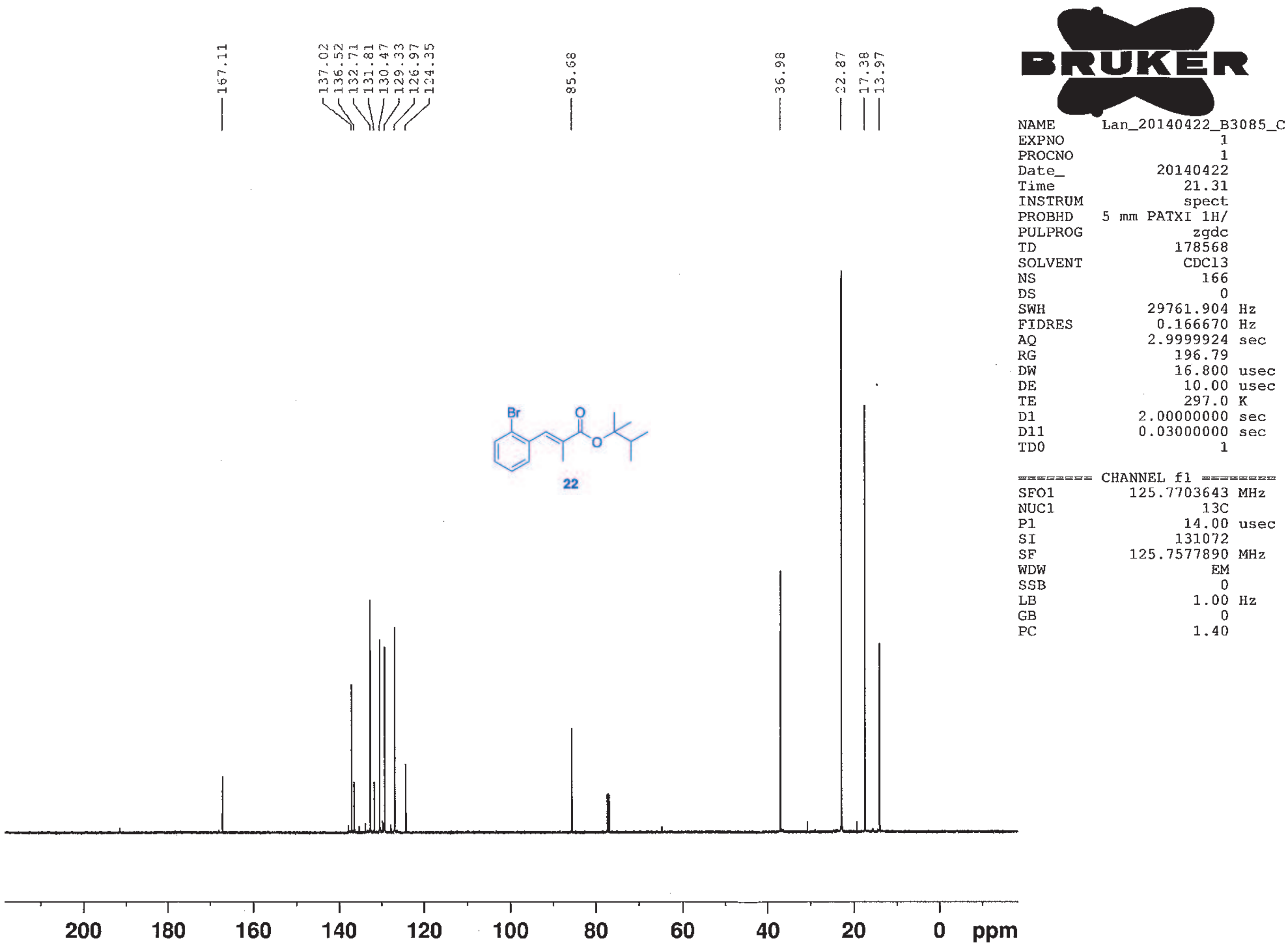

```
Current Data Parameters
NAME      Lan_20140430_B2265
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_             20140430
Time                 20.43
INSTRUM              spect
PROBHD   5 mm PATXI 1H/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                       8
DS                       0
SWH          10000.000 Hz
FIDRES        0.166672 Hz
AQ           2.9999001 sec
RG                   11.29
DW              50.000 usec
DE              10.00 usec
TE                295.9 K
D1         10.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1       500.1330885 MHz
NUC1                    1H
P1                8.00 usec
PLW1        12.19999981 W

F2 - Processing parameters
SI                   65536
SF         500.1300320 MHz
WDW                     EM
SSB      0
LB                 0.30 Hz
GB       0
PC                    1.00
```

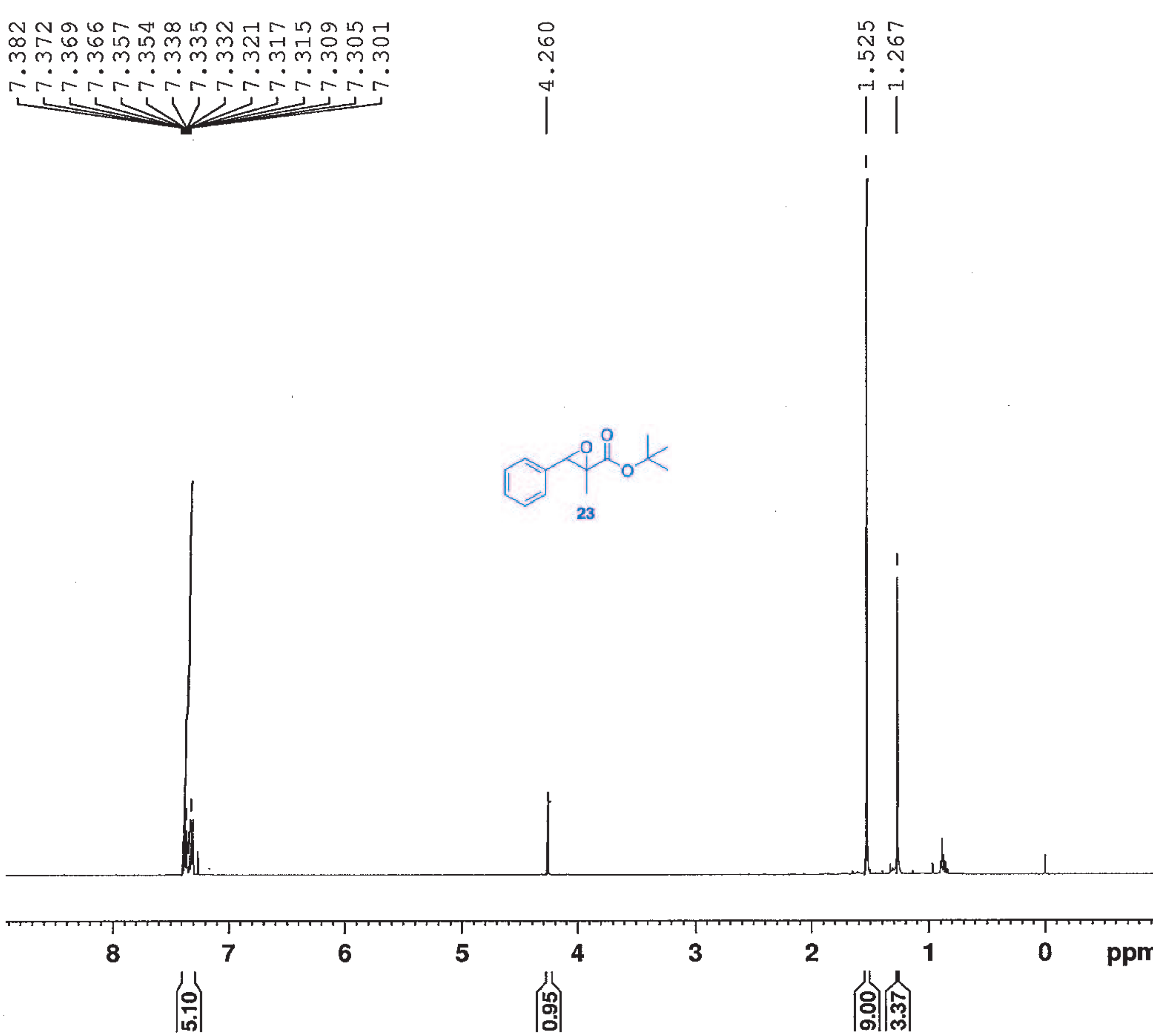



```
Current Data Parameters
NAME     Lan_20140422_B2265_C
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20140422
Time                  22.28
INSTRUM               spect
PROBHD   5 mm PATXI 1H/
PULPROG                zgdc
TD                   178568
SOLVENT               CDCl3
NS                       76
DS                        0
SWH               29761.904 Hz
FIDRES             0.166670 Hz
AQ                2.9999423 sec
RG                   196.79
DW                   16.800 usec
DE                    10.00 usec
TE                    296.7 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            125.7703643 MHz
NUC1                    13C
P1                    14.00 usec
PLW1           170.00000000 W

======== CHANNEL f2 ========
SFO2            500.1320005 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 90.00 usec
PLW2            12.19999981 W
PLW12            0.20893000 W

F2 - Processing parameters
SI                   131072
SF              125.7577890 MHz
WDW                      EM
SSB      0
LB                     1.00 Hz
GB       0
PC                     1.40
```

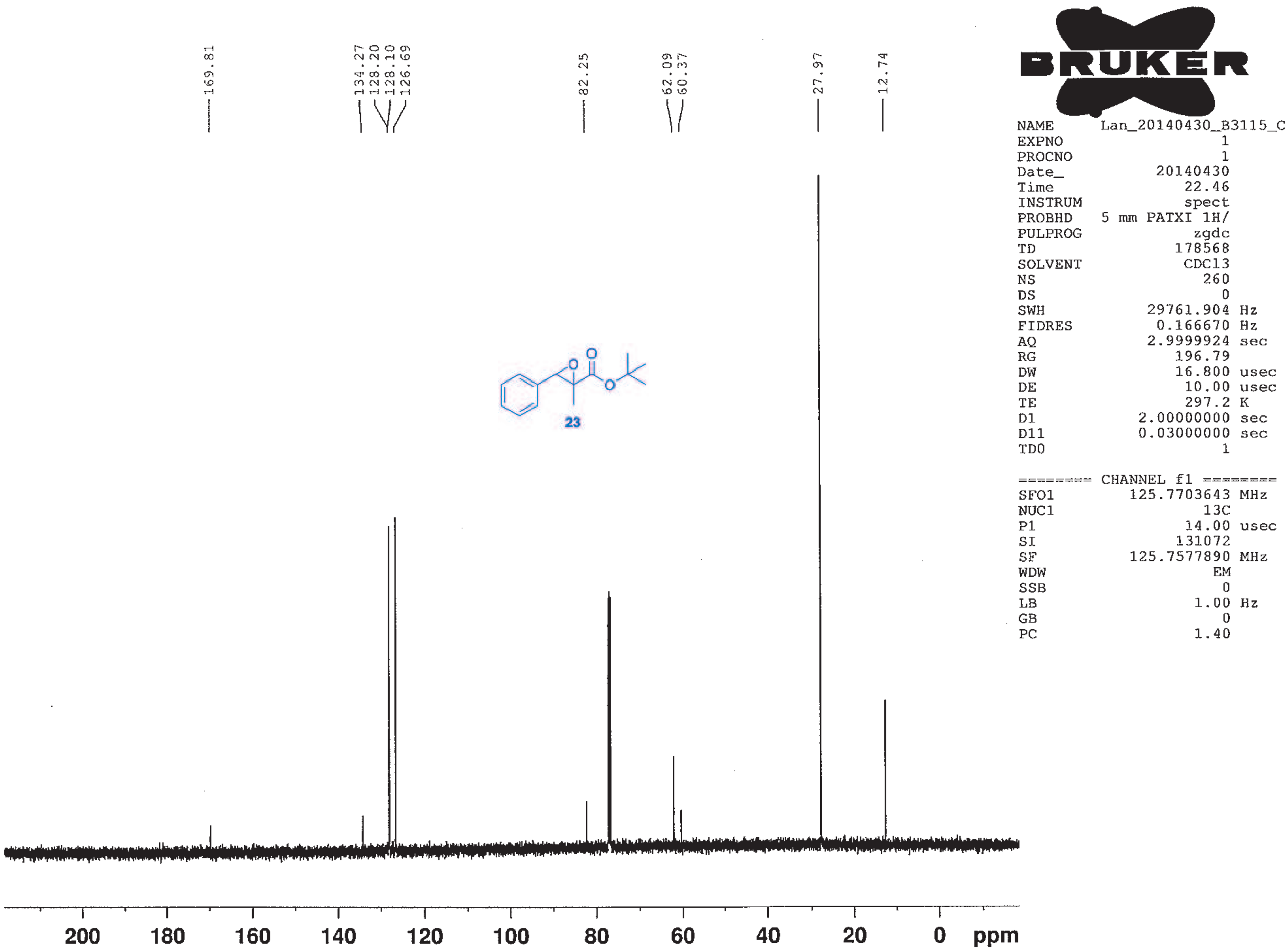


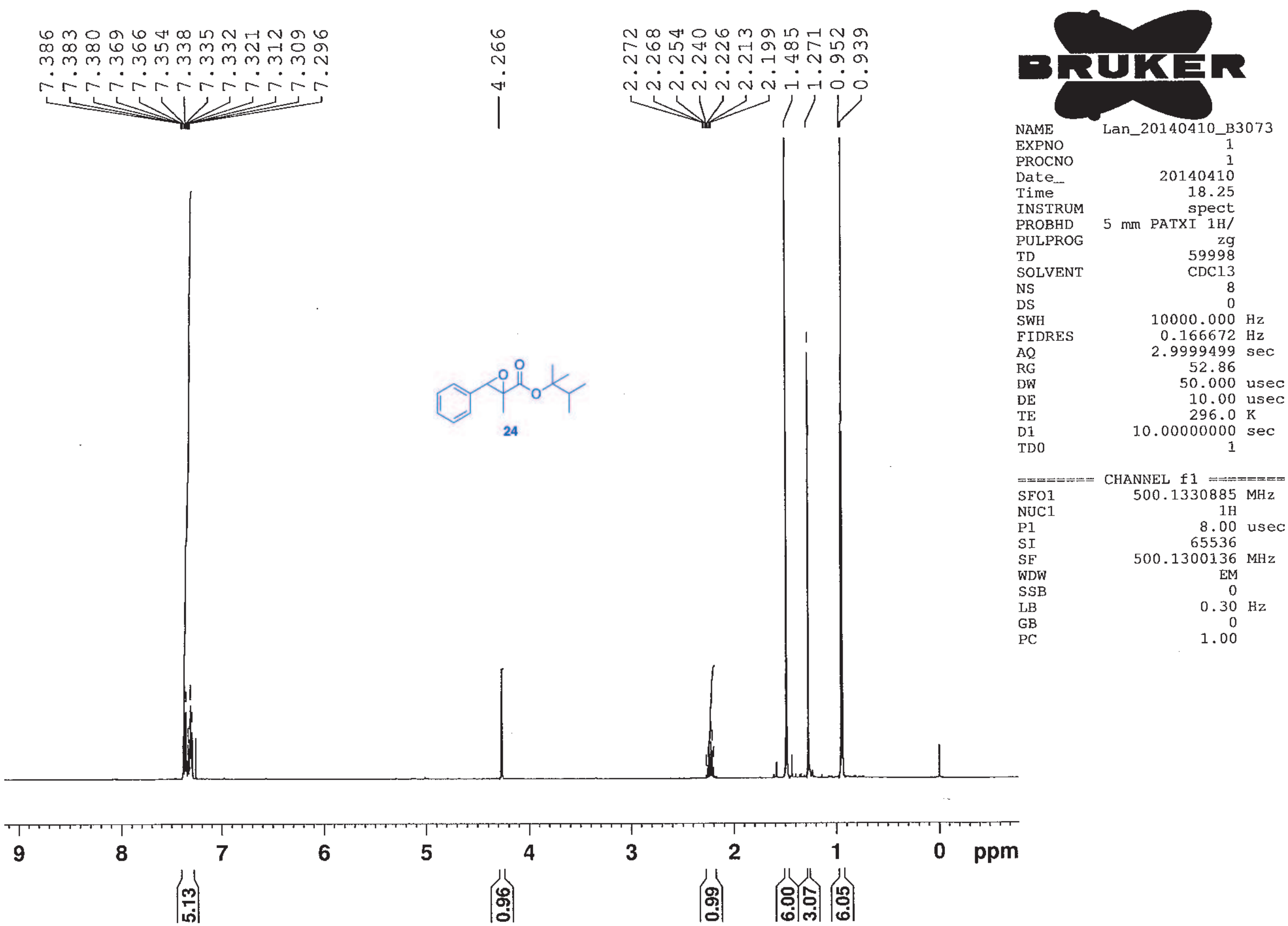

```
Current Data Parameters
NAME        Lan_20140422_B3085
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_               20140422
Time                   22.12
INSTRUM                spect
PROBHD     5 mm PATXI 1H/
PULPROG                   zg
TD                     59998
SOLVENT                CDCl3
NS                         8
DS                         0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                      5.58
DW                 50.000 usec
DE                  10.00 usec
TE                  296.0 K
D1            10.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                      1H
P1                   8.00 usec
PLW1          12.19999981 W

F2 - Processing parameters
SI                     65536
SF            500.1300069 MHz
WDW                       EM
SSB         0
LB                   0.30 Hz
GB          0
PC                      1.00
```


167.11
137.02
136.52
132.71
131.81
130.47
129.33
126.97
124.35
85.68
36.98
22.87
17.38
13.97
Br
O
O
22
BRUKER
NAME Lan_20140422_B3085_C
EXPNO 1
PROCNO 1
Date_ 20140422
Time 21.31
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgdc
TD 178568
SOLVENT CDCl3
NS 166
DS 0
SWH 29761.904 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 196.79
DW 16.800 usec
DE 10.00 usec
TE 297.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703643 MHz
NUC1 13C
P1 14.00 usec
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm

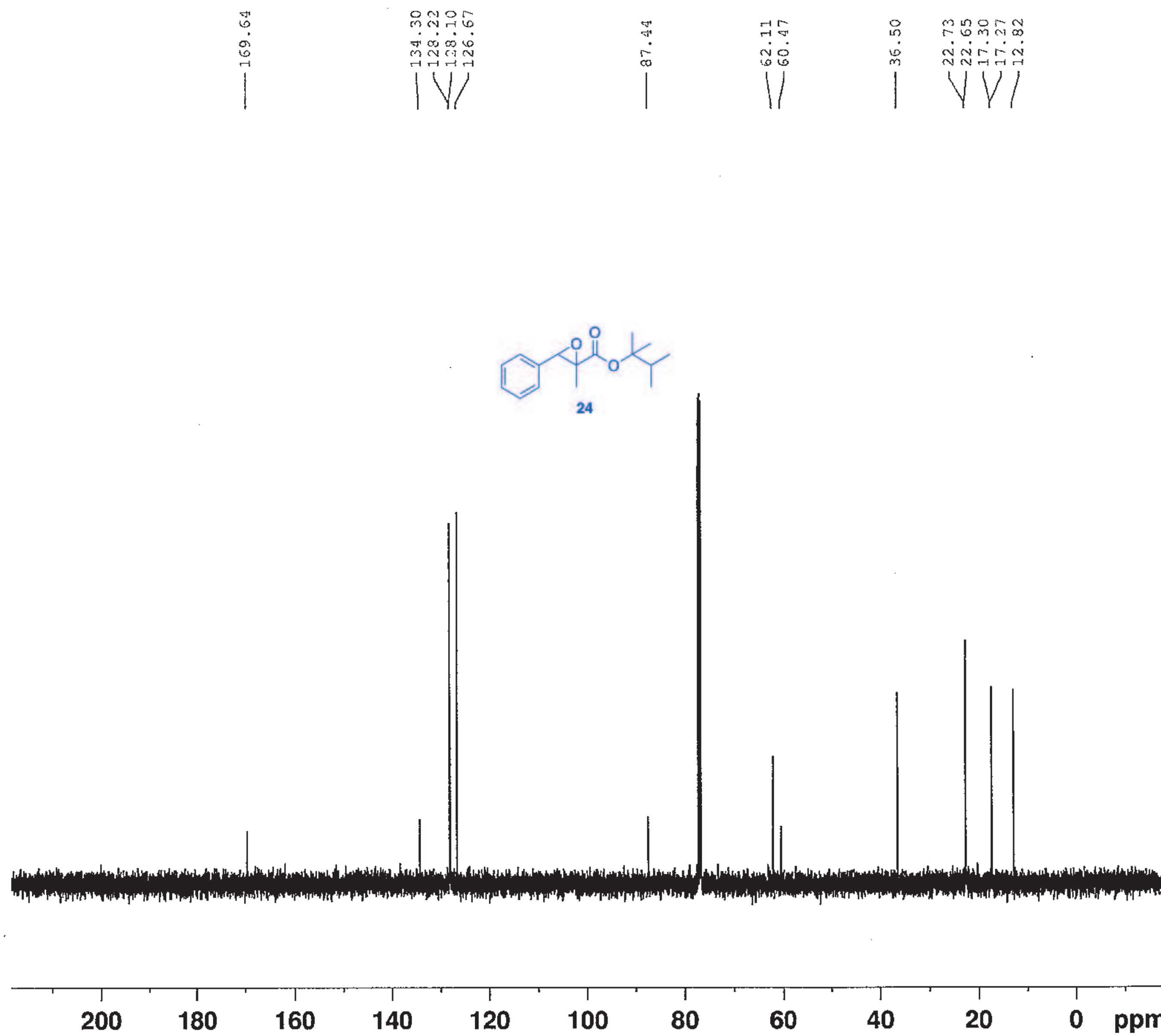



```
Current Data Parameters
NAME     Lan_20140410_B3115
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20140410
Time                  17.39
INSTRUM               spect
PROBHD    5 mm PATXI 1H/
PULPROG                  zg
TD                    59998
SOLVENT               CDCl3
NS                        8
DS                        0
SWH           10000.000 Hz
FIDRES         0.166672 Hz
AQ            2.9999001 sec
RG                    31.72
DW               50.000 usec
DE                10.00 usec
TE                  295.9 K
D1          10.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1        500.1330885 MHz
NUC1                     1H
P1                 8.00 usec
PLW1        12.19999981 W

F2 - Processing parameters
SI                    65536
SF          500.1300133 MHz
WDW                      EM
SSB        0
LB                  0.30 Hz
GB         0
PC                     1.00
```


169.81
134.27
128.20
128.10
126.69
82.25
62.09
60.37
27.97
12.74
BRUKER
NAME Lan_20140430_B3115_C
EXPNO 1
PROCNO 1
Date_ 20140430
Time 22.46
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgdc
TD 178568
SOLVENT CDCl3
NS 260
DS 0
SWH 29761.904 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 196.79
DW 16.800 usec
DE 10.00 usec
TE 297.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703643 MHz
NUC1 13C
P1 14.00 usec
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
23
200
180
160
140
120
100
80
60
40
20
0
ppm



7.386
7.383
7.380
7.369
7.366
7.354
7.338
7.335
7.332
7.321
7.312
7.309
7.296
4.266
2.272
2.268
2.254
2.240
2.226
2.213
2.199
1.485
1.271
0.952
0.939
24
NAME Lan_20140410_B3073
EXPNO 1
PROCNO 1
Date_ 20140410
Time 18.25
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999499 sec
RG 52.86
DW 50.000 usec
DE 10.00 usec
TE 296.0 K
D1 10.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 8.00 usec
SI 65536
SF 500.1300136 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
0
ppm
5.13
0.96
0.99
6.00
3.07
6.05

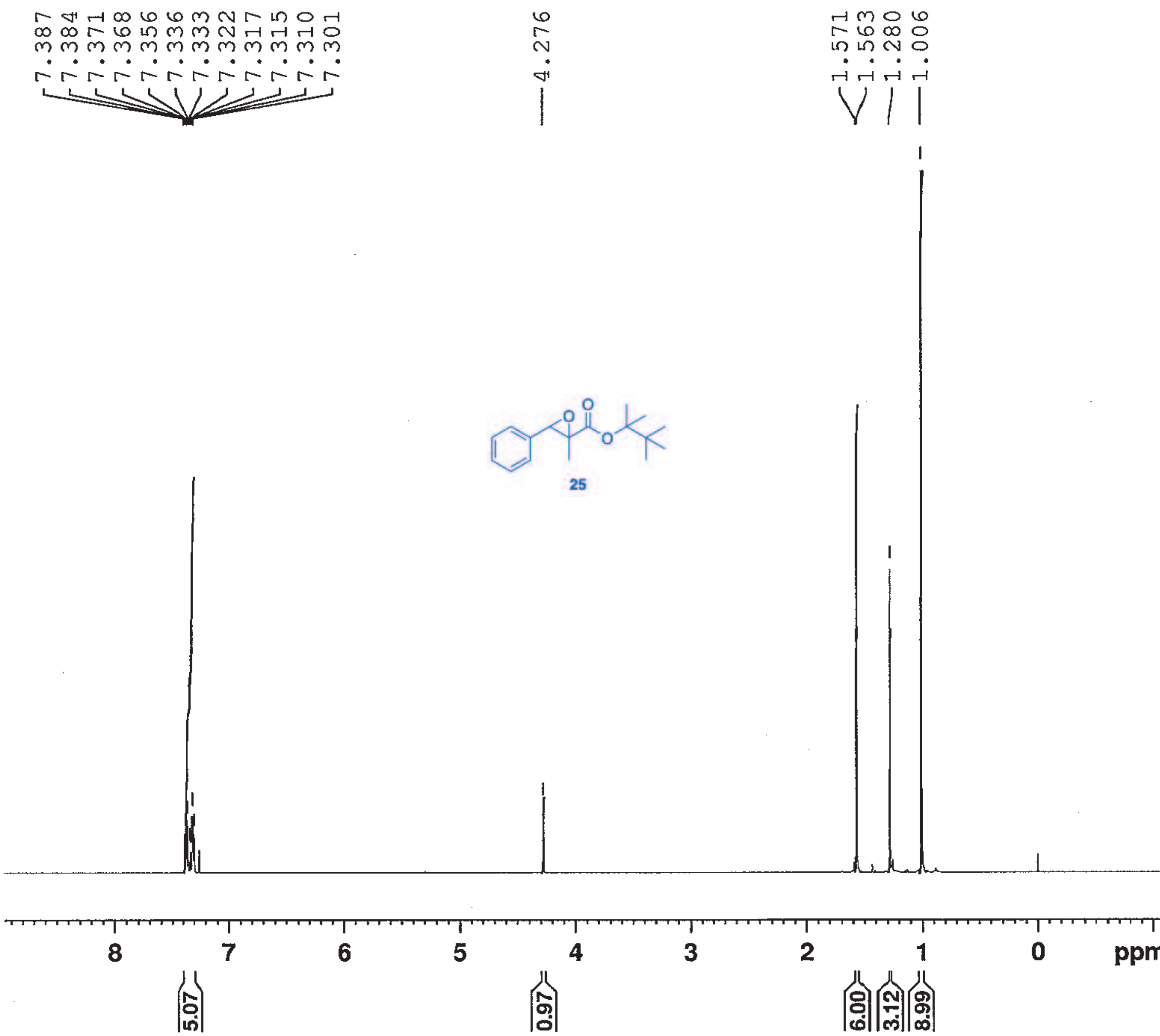


BRUKER

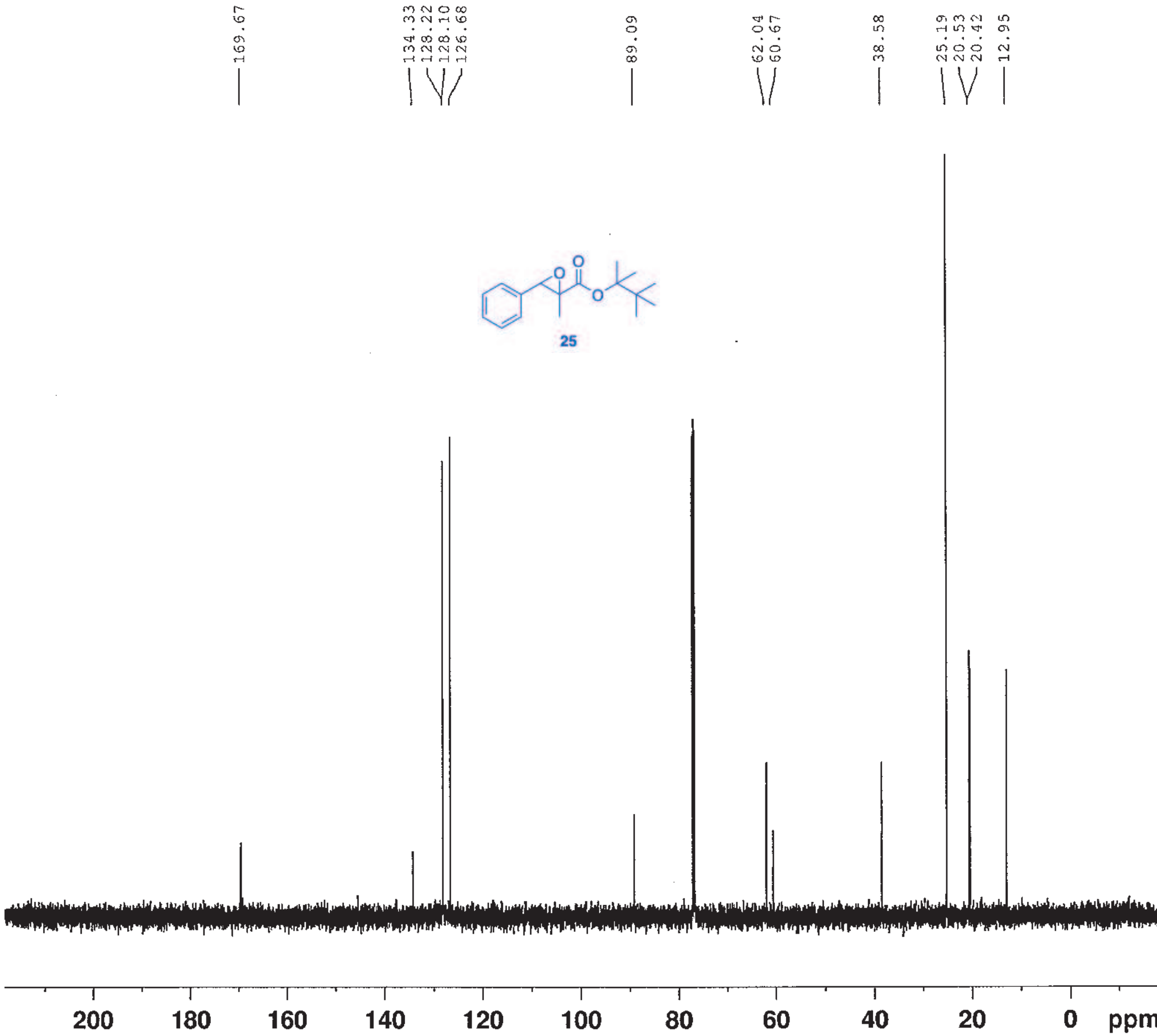
NAME	Lan_20140410_B3073_C
EXPNO	1
PROCNO	1
Date_	20140410
Time	18.44
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zgdc
TD	178568
SOLVENT	CDCl3
NS	153
DS	0
SWH	29761.904 Hz
FIDRES	0.166670 Hz
AQ	2.9999924 sec
RG	196.79
DW	16.800 usec
DE	10.00 usec
TE	296.9 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

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

SFO1	125.7703643 MHz
NUC1	13C
P1	14.00 usec
SI	131072
SF	125.7577890 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



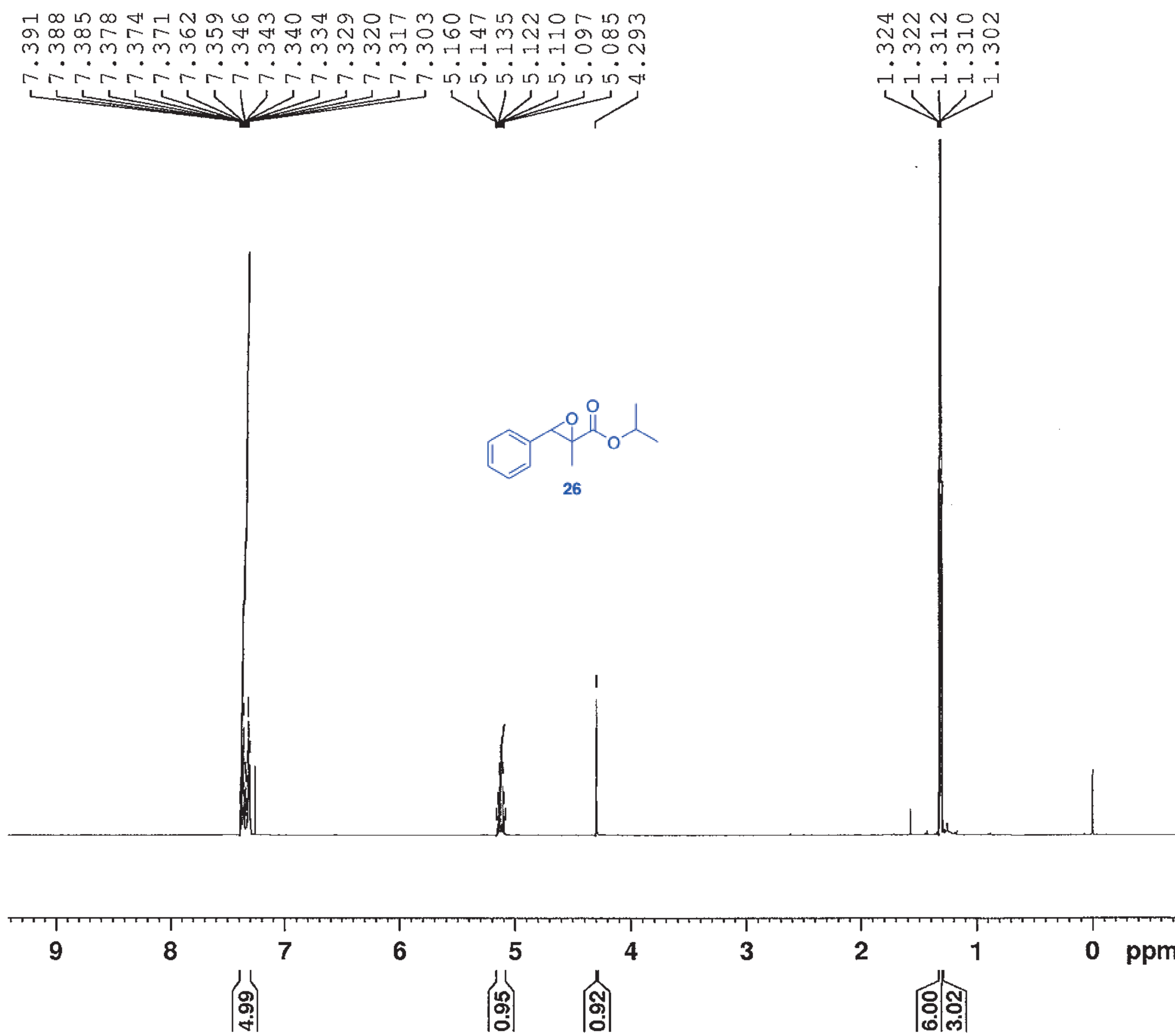

```
Current Data Parameters
NAME      Lan_20140410_B3103
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20140410
Time                  18.53
INSTRUM               spect
PROBHD    5 mm PATXI 1H/
PULPROG                  zg
TD                    59998
SOLVENT               CDCl3
NS                        8
DS                        0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                    30.11
DW                   50.000 usec
DE                    10.00 usec
TE                    296.2 K
D1              10.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                     1H
P1                     8.00 usec
PLW1            12.19999981 W

F2 - Processing parameters
SI                    65536
SF            500.1300137 MHz
WDW                      EM
SSB        0
LB                     0.30 Hz
GB         0
PC                     1.00
```



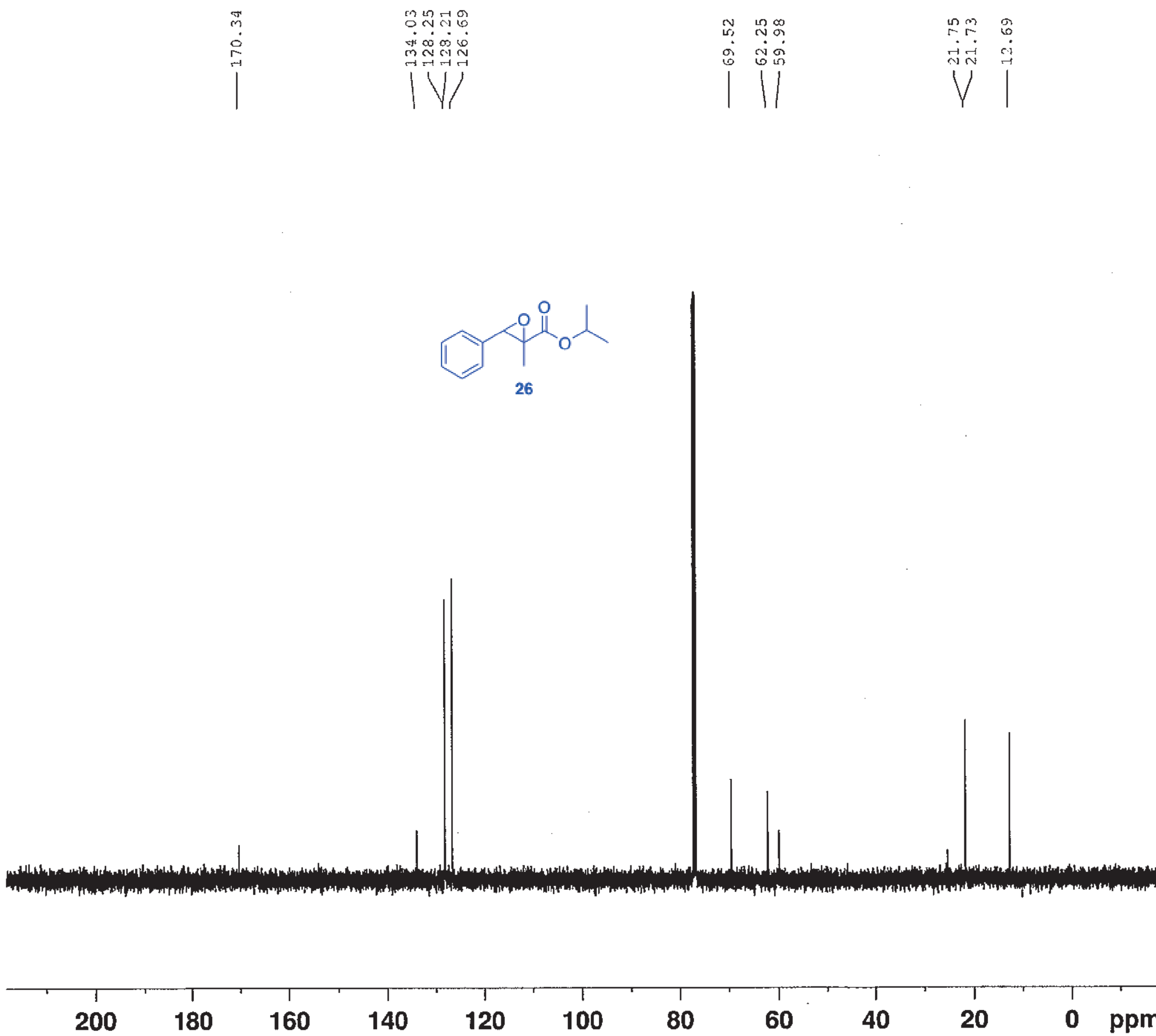
NAME	Lan_20140410_B3103_C
EXPNO	1
PROCNO	1
Date_	20140410
Time	19.15
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zgdc
TD	178568
SOLVENT	CDCl3
NS	172
DS	0
SWH	29761.904 Hz
FIDRES	0.166670 Hz
AQ	2.9999924 sec
RG	196.79
DW	16.800 usec
DE	10.00 usec
TE	297.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

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

SFO1	125.7703643 MHz
NUC1	13C
P1	14.00 usec
SI	131072
SF	125.7577890 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40




```
Current Data Parameters
NAME      Lan_20140430_B1241
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20140430
Time                 19.16
INSTRUM              spect
PROBHD    5 mm PATXI 1H/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                       8
DS                       0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                   79.04
DW                  50.000 usec
DE                   10.00 usec
TE                   295.9 K
D1             10.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                    1H
P1                    8.00 usec
PLW1           12.19999981 W

F2 - Processing parameters
SI                   65536
SF            500.1300135 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

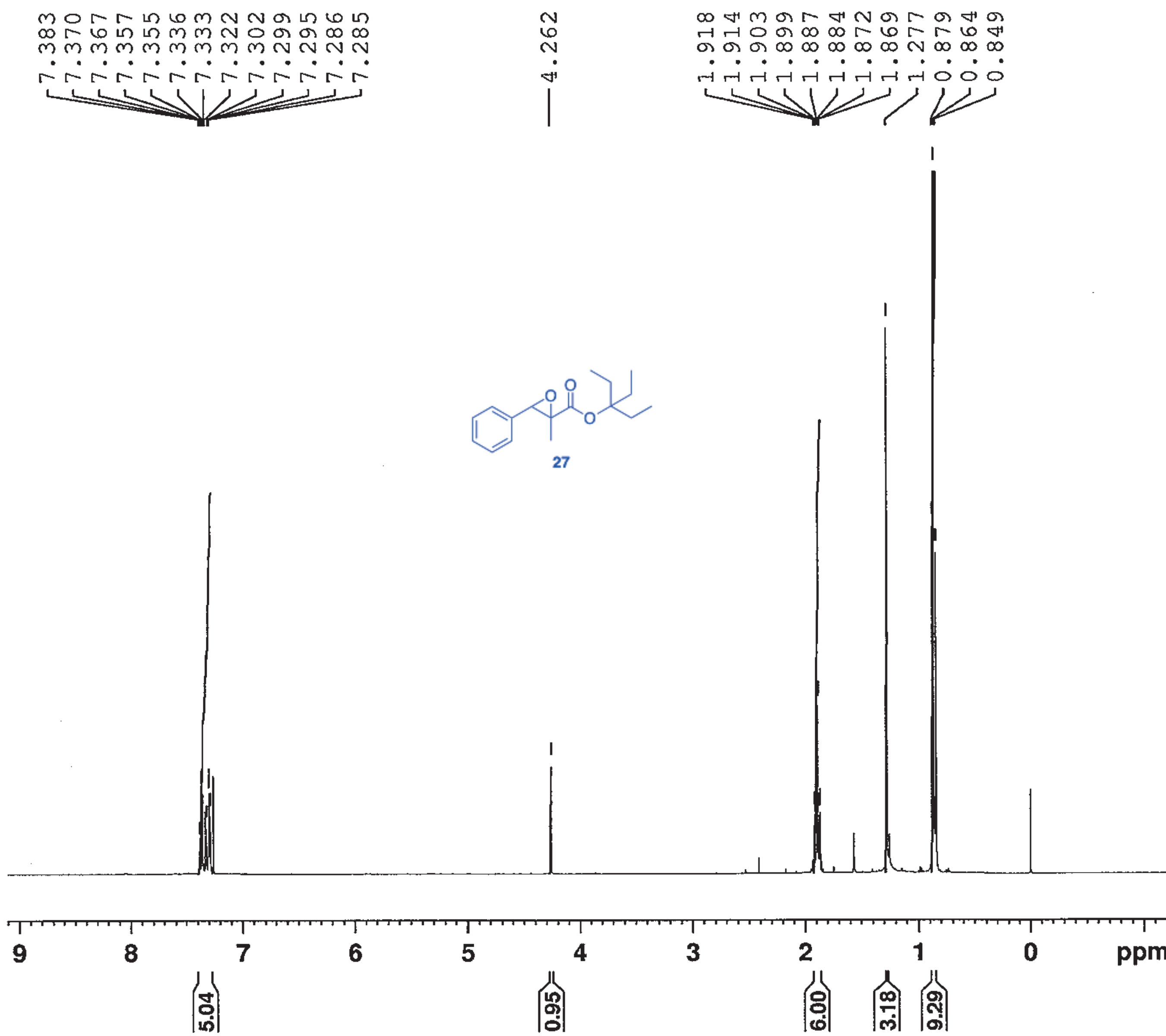


26

NAME	Lan_20140410_B1241_C
EXPNO	1
PROCNO	1
Date_	20140410
Time	19.56
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zgdc
TD	178568
SOLVENT	CDCl3
NS	151
DS	0
SWH	29761.904 Hz
FIDRES	0.166670 Hz
AQ	2.9999924 sec
RG	196.79
DW	16.800 usec
DE	10.00 usec
TE	296.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

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

SFO1	125.7703643 MHz
NUC1	13C
P1	14.00 usec
SI	131072
SF	125.7577890 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

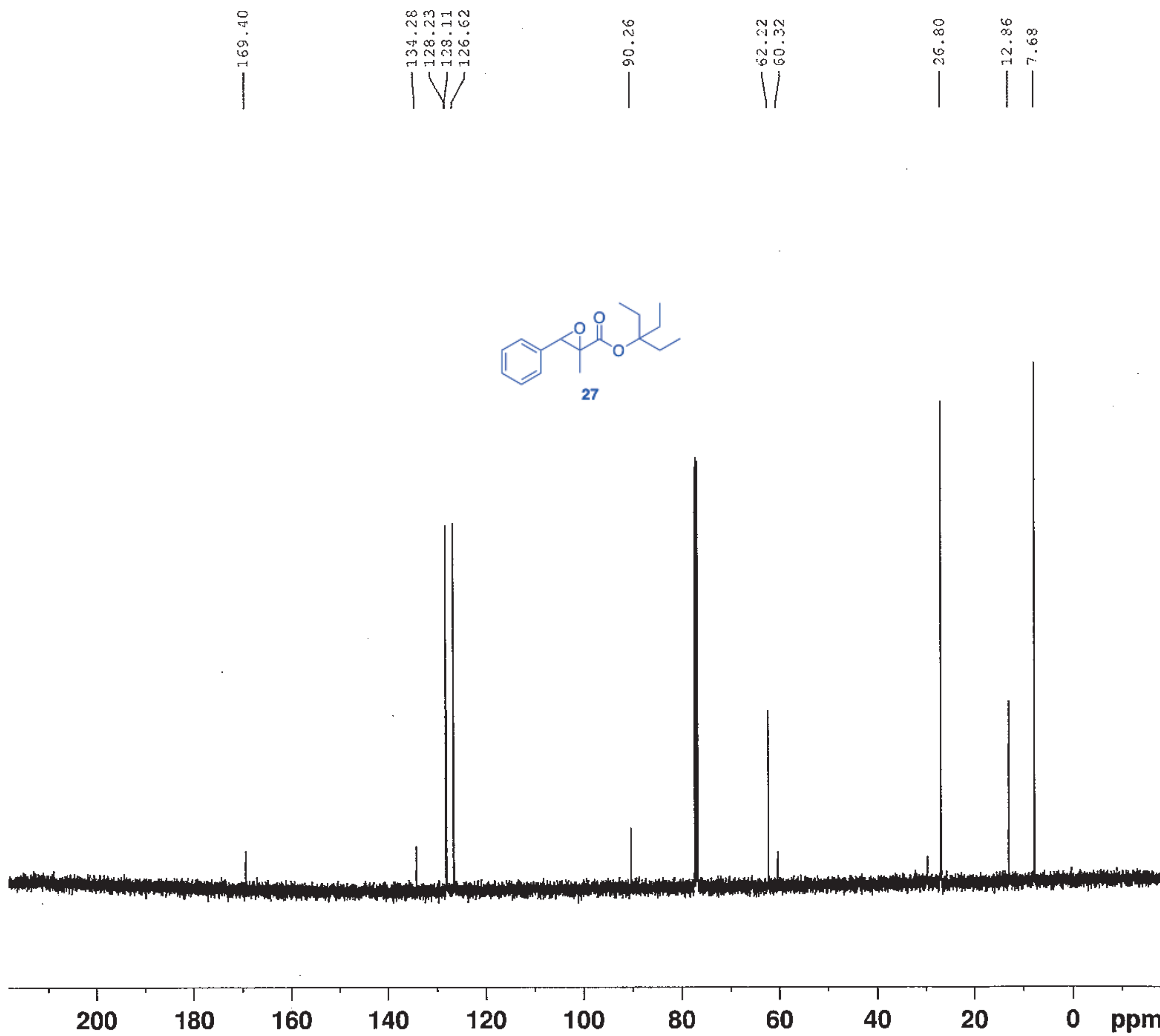


Current Data Parameters
NAME Lan_20140410_B3113
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140410
Time 20.15
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 71.78
DW 50.000 usec
DE 10.00 usec
TE 296.1 K
D1 10.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 8.00 usec
PLW1 12.19999981 W

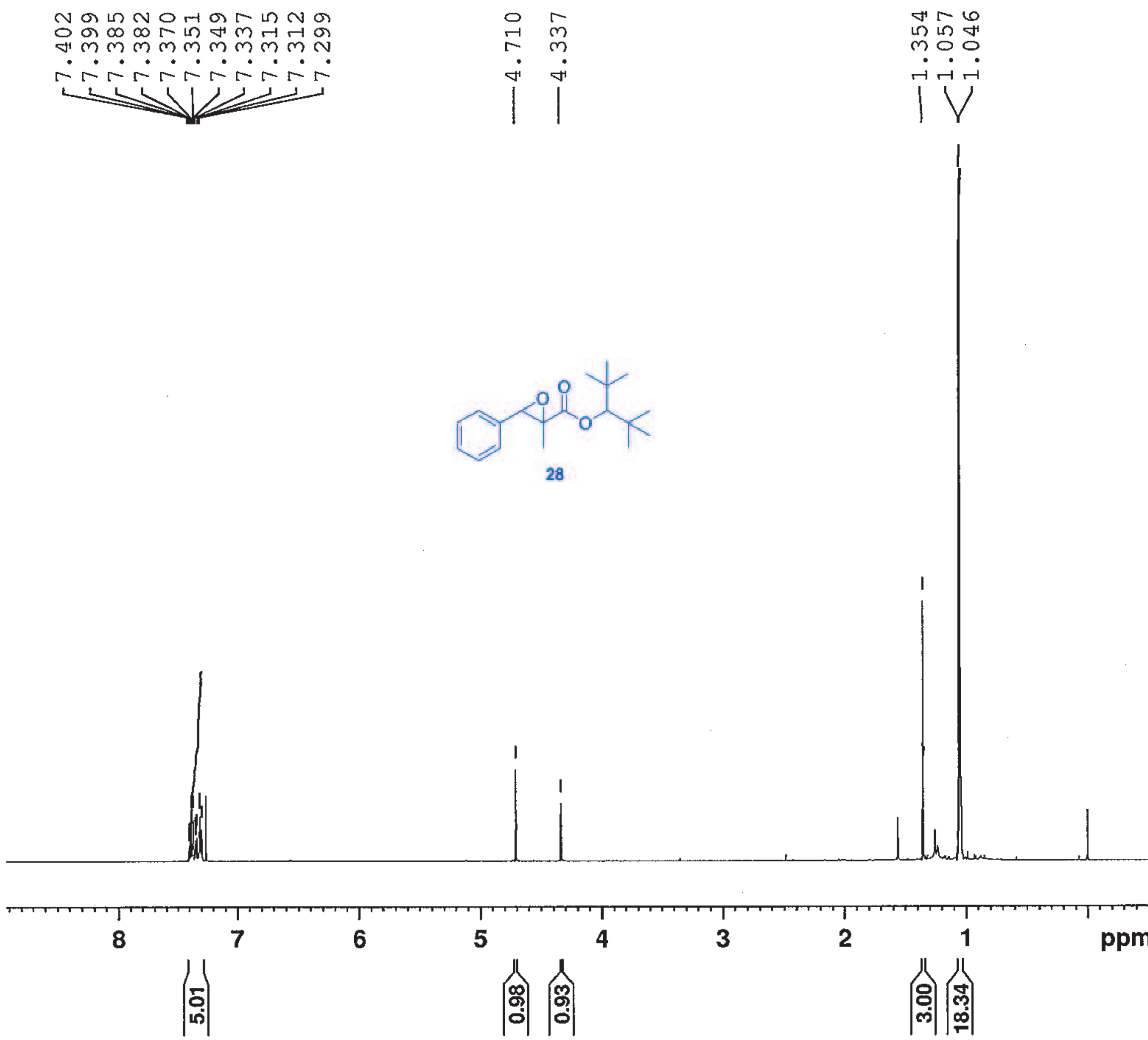
F2 - Processing parameters
SI 65536
SF 500.1300136 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



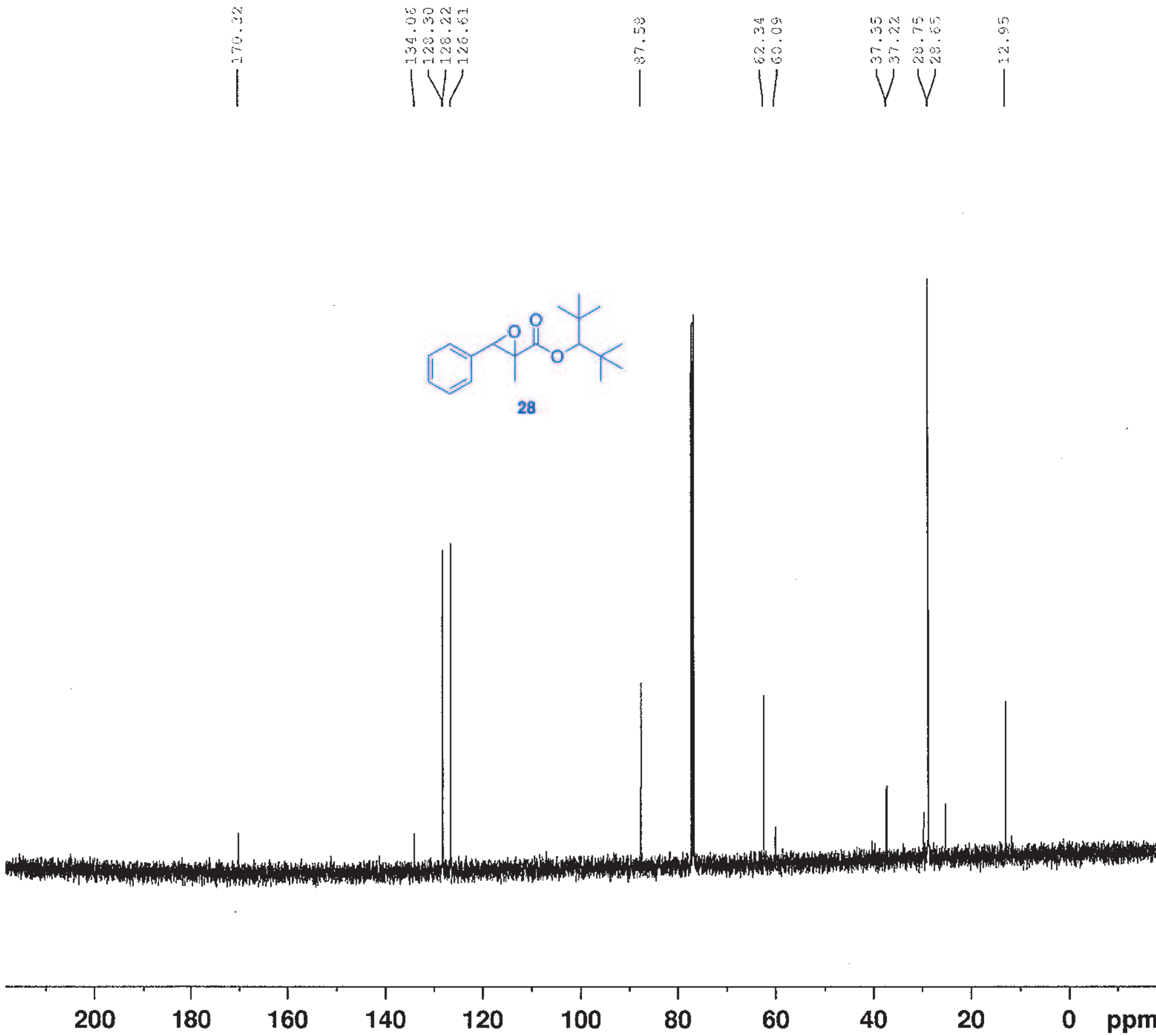
NAME	Lan_20140426_B3113_C	
EXPNO	1	
PROCNO	1	
Date_	20140426	
Time	13.43	
INSTRUM	spect	
PROBHD	5 mm PATXI 1H/	
PULPROG	zgdc	
TD	178568	
SOLVENT	CDCl3	
NS	399	
DS	0	
SWH	29761.904	Hz
FIDRES	0.166670	Hz
AQ	2.9999924	sec
RG	196.79	
DW	16.800	usec
DE	10.00	usec
TE	297.2	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	

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

SFO1	125.7703643	MHz
NUC1	13C	
P1	14.00	usec
SI	131072	
SF	125.7577890	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	




```
Current Data Parameters
NAME       Lan_20140414_B2011
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20140414
Time                  21.08
INSTRUM               spect
PROBHD    5 mm PATXI 1H/
PULPROG                  zg
TD                    59998
SOLVENT               CDCl3
NS                        8
DS                        0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                    87.71
DW               50.000 usec
DE                10.00 usec
TE                295.9 K
D1          10.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                     1H
P1                 8.00 usec
PLW1         12.19999981 W

F2 - Processing parameters
SI                    65536
SF           500.1300135 MHz
WDW                      EM
SSB       0
LB                  0.30 Hz
GB        0
PC                     1.00
```



BRUKER

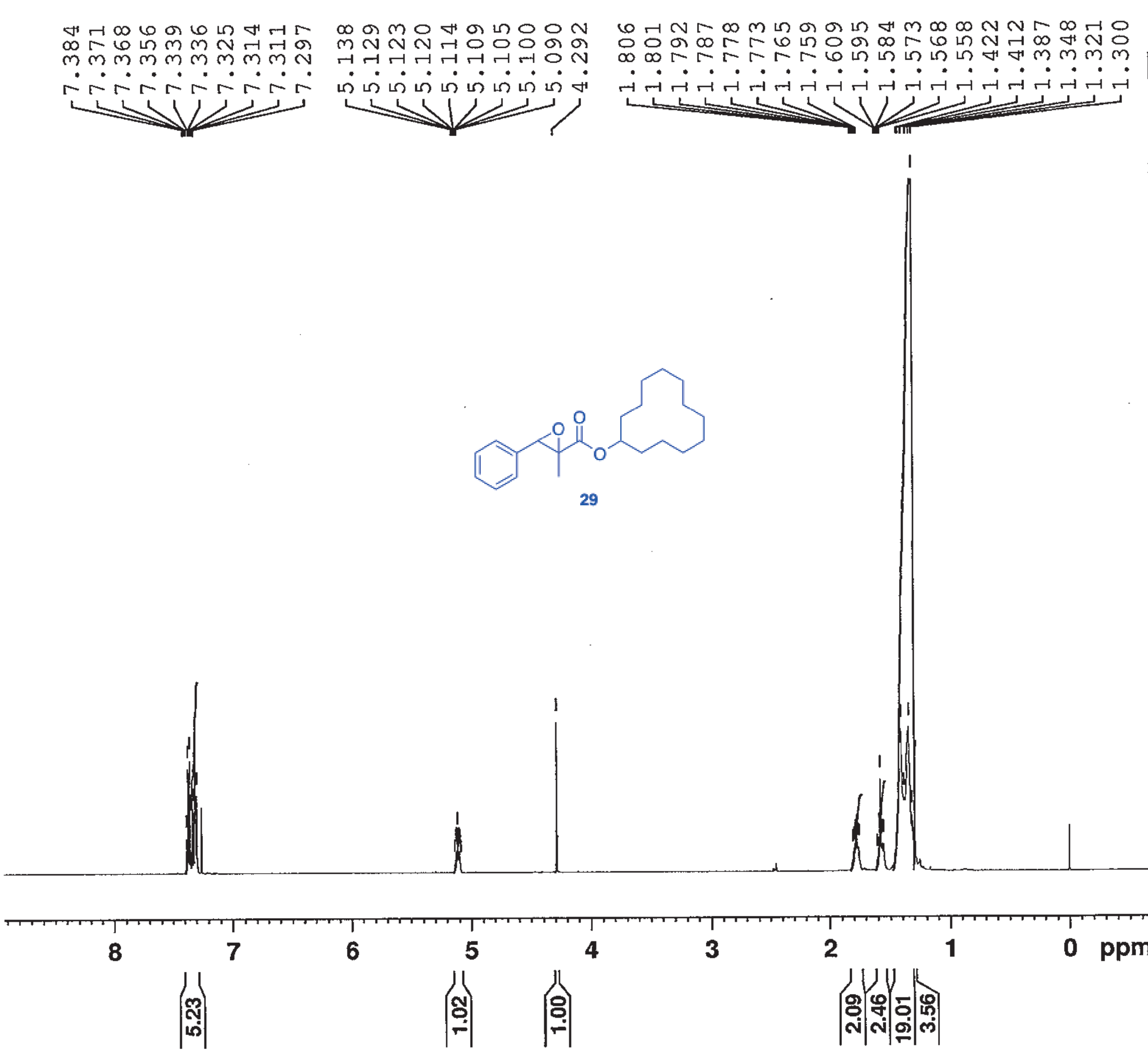
Current Data Parameters
NAME Lan_20140426_B2011_C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140426
Time 14.13
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgdc
TD 178568
SOLVENT CDCl3
NS 474
DS 0
SWH 29761.904 Hz
FIDRES 0.166670 Hz
AQ 2.9999423 sec
RG 196.79
DW 16.800 usec
DE 10.00 usec
TE 297.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

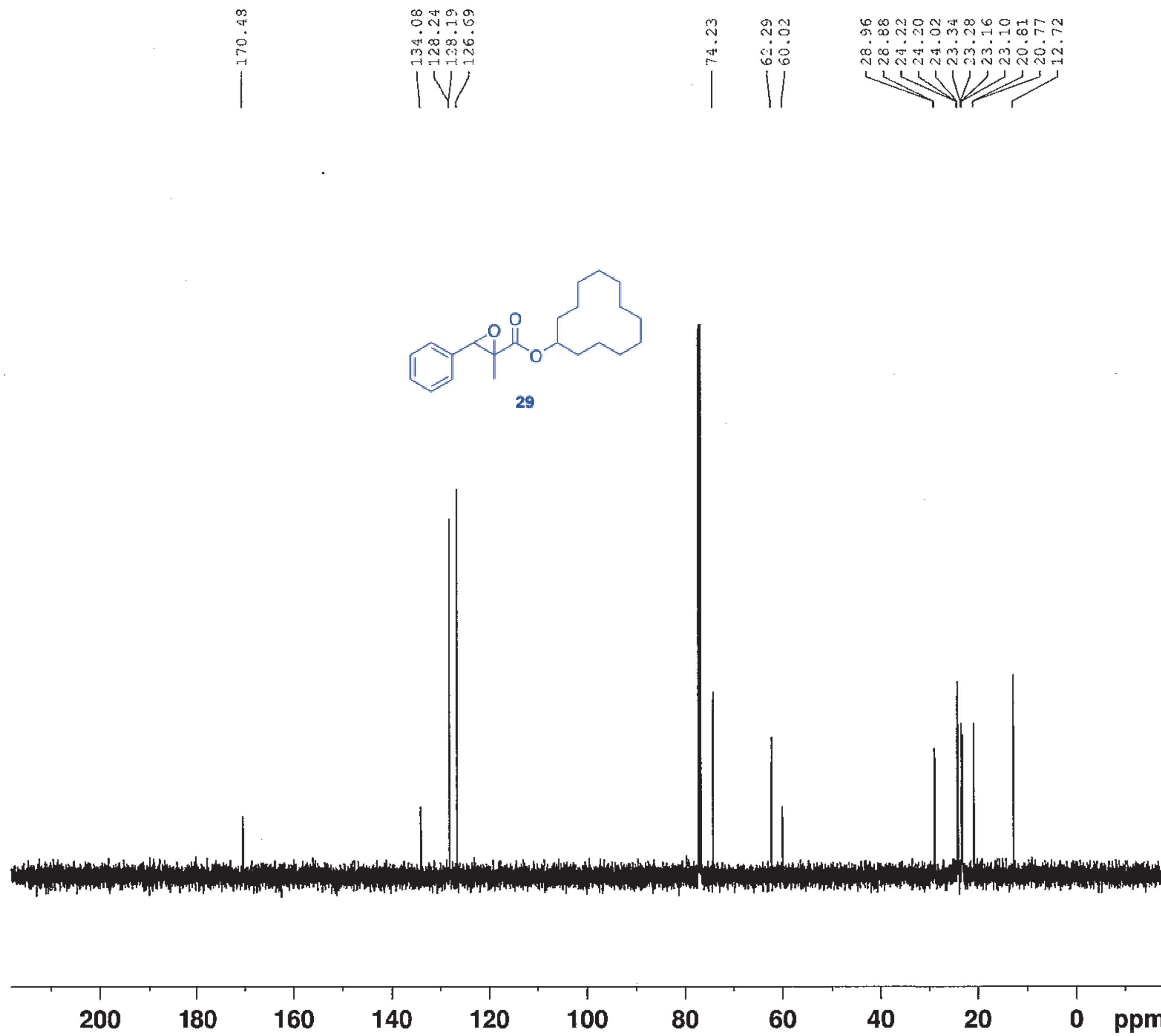
======== CHANNEL f1 ========
SFO1 125.7703643 MHz
NUC1 13C
P1 14.00 usec
PLW1 170.00000000 W

======== CHANNEL f2 ========
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 12.19999981 W
PLW12 0.20893000 W

F2 - Processing parameters
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40




```
Current Data Parameters
NAME      Lan_20140414_B1273
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_            20140414
Time                22.09
INSTRUM             spect
PROBHD    5 mm PATXI 1H/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                      8
DS                      0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                  30.11
DW                 50.000 usec
DE                  10.00 usec
TE                  295.9 K
D1            10.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                  1H
P1                  8.00 usec
PLW1         12.19999981 W

F2 - Processing parameters
SI                  65536
SF           500.1300137 MHz
WDW                    EM
SSB        0
LB                   0.30 Hz
GB         0
PC                   1.00
```

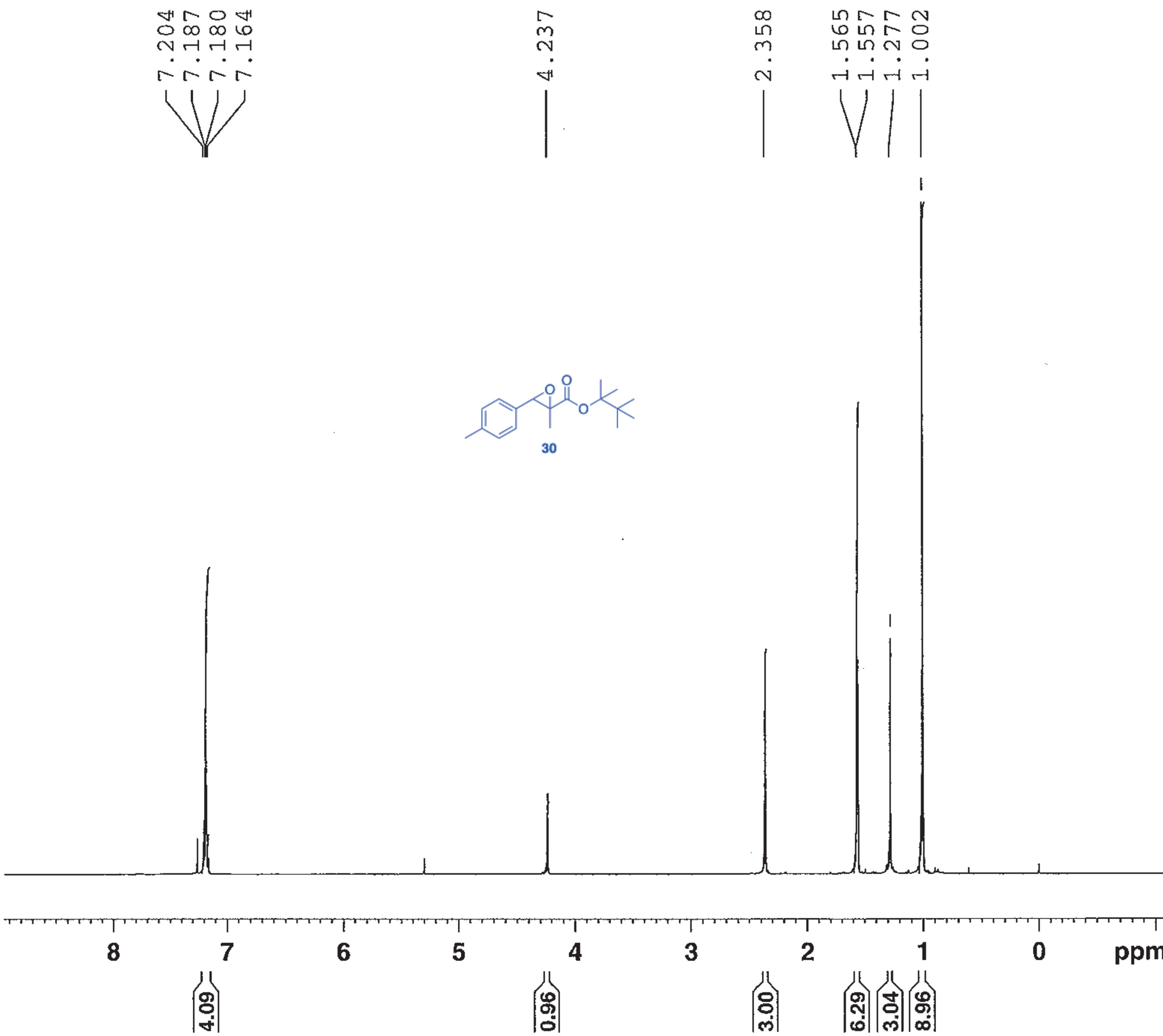


29

NAME	Lan_20140414_B1273_C
EXPNO	1
PROCNO	1
Date_	20140414
Time	22.25
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zgdc
TD	178568
SOLVENT	CDCl3
NS	119
DS	0
SWH	29761.904 Hz
FIDRES	0.166670 Hz
AQ	2.9999924 sec
RG	196.79
DW	16.800 usec
DE	10.00 usec
TE	296.6 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

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

SFO1	125.7703643 MHz
NUC1	13C
P1	14.00 usec
SI	131072
SF	125.7577890 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

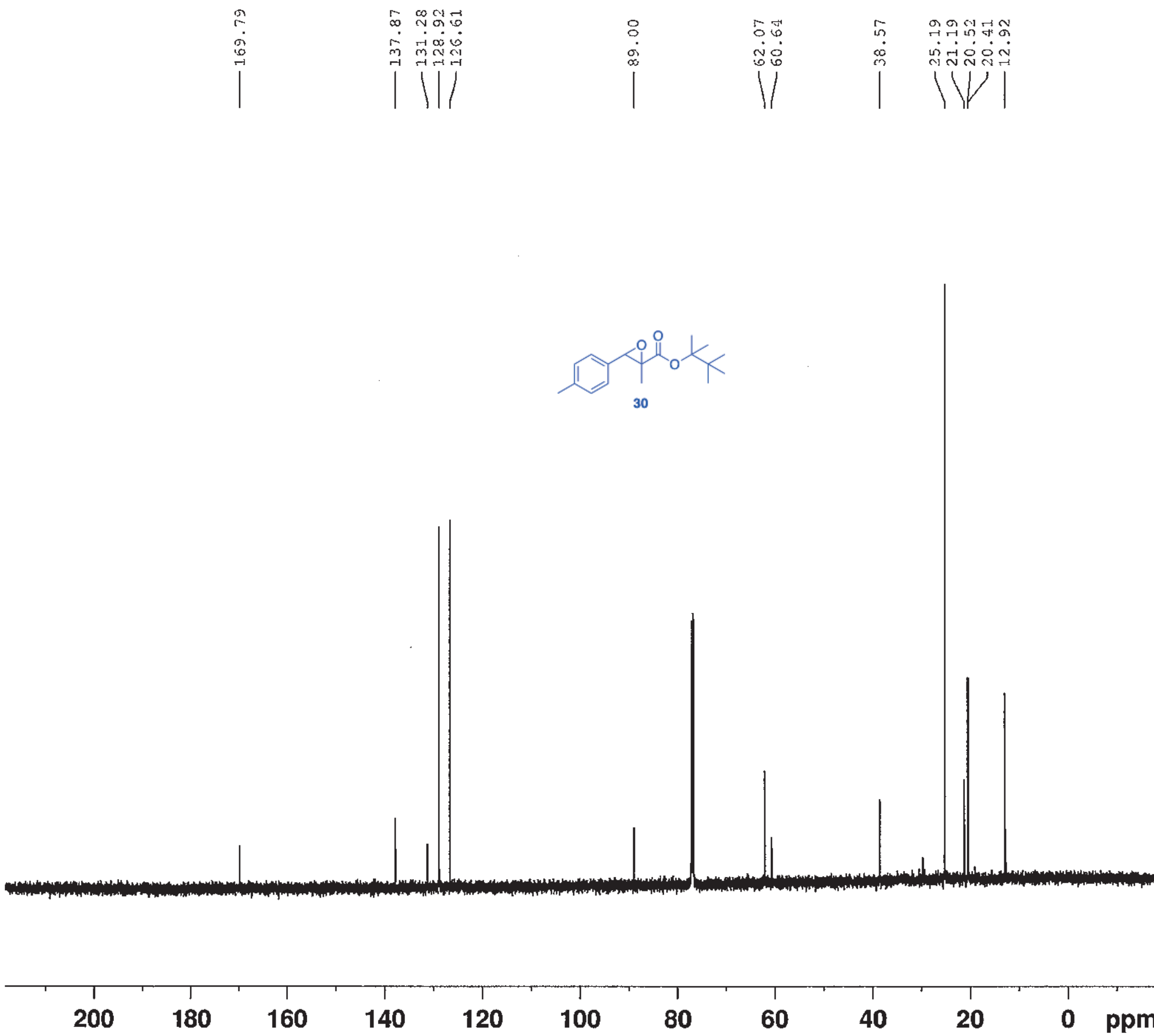


Current Data Parameters
NAME Lan_20140313_B3245
EXPNO 6
PROCNO 1

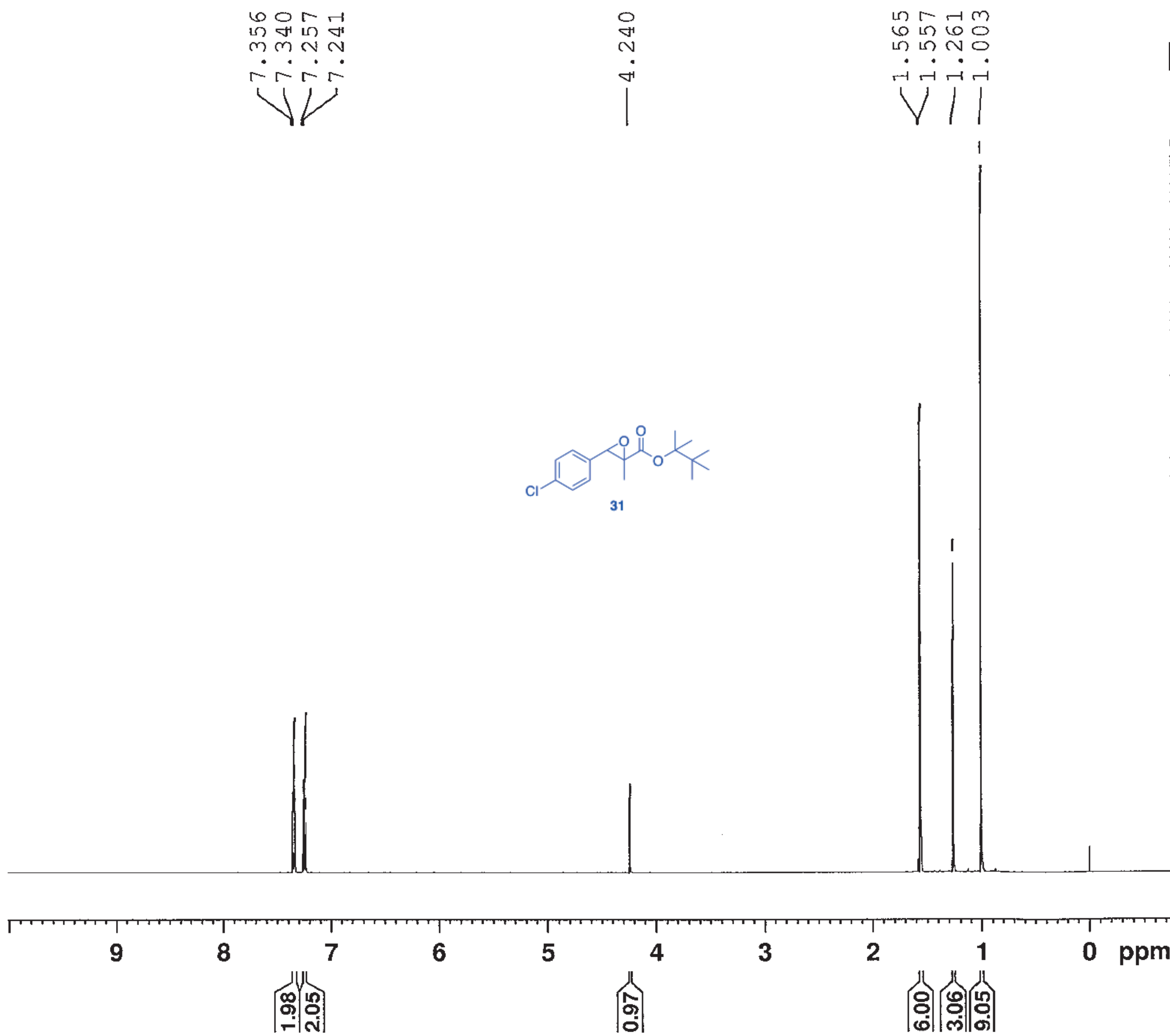
F2 - Acquisition Parameters
Date_ 20140313
Time 15.06
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg
TD 59998
SOLVENT CDC13
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999499 sec
RG 90.5
DW 50.000 usec
DE 7.50 usec
TE 295.0 K
D1 10.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 0.00 dB
SFO1 499.8740056 MHz

F2 - Processing parameters
SI 32768
SF 499.8700182 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



NAME	Lan_20140405_B3245_C
EXPNO	1
PROCNO	1
Date_	20140405
Time	17.45
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zgdc
TD	178568
SOLVENT	CDCl3
NS	203
DS	0
SWH	29761.904 Hz
FIDRES	0.166670 Hz
AQ	2.9999924 sec
RG	196.79
DW	16.800 usec
DE	10.00 usec
TE	297.1 K
D1	3.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	125.7703643 MHz
NUC1	13C
P1	14.00 usec
SI	131072
SF	125.7577890 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

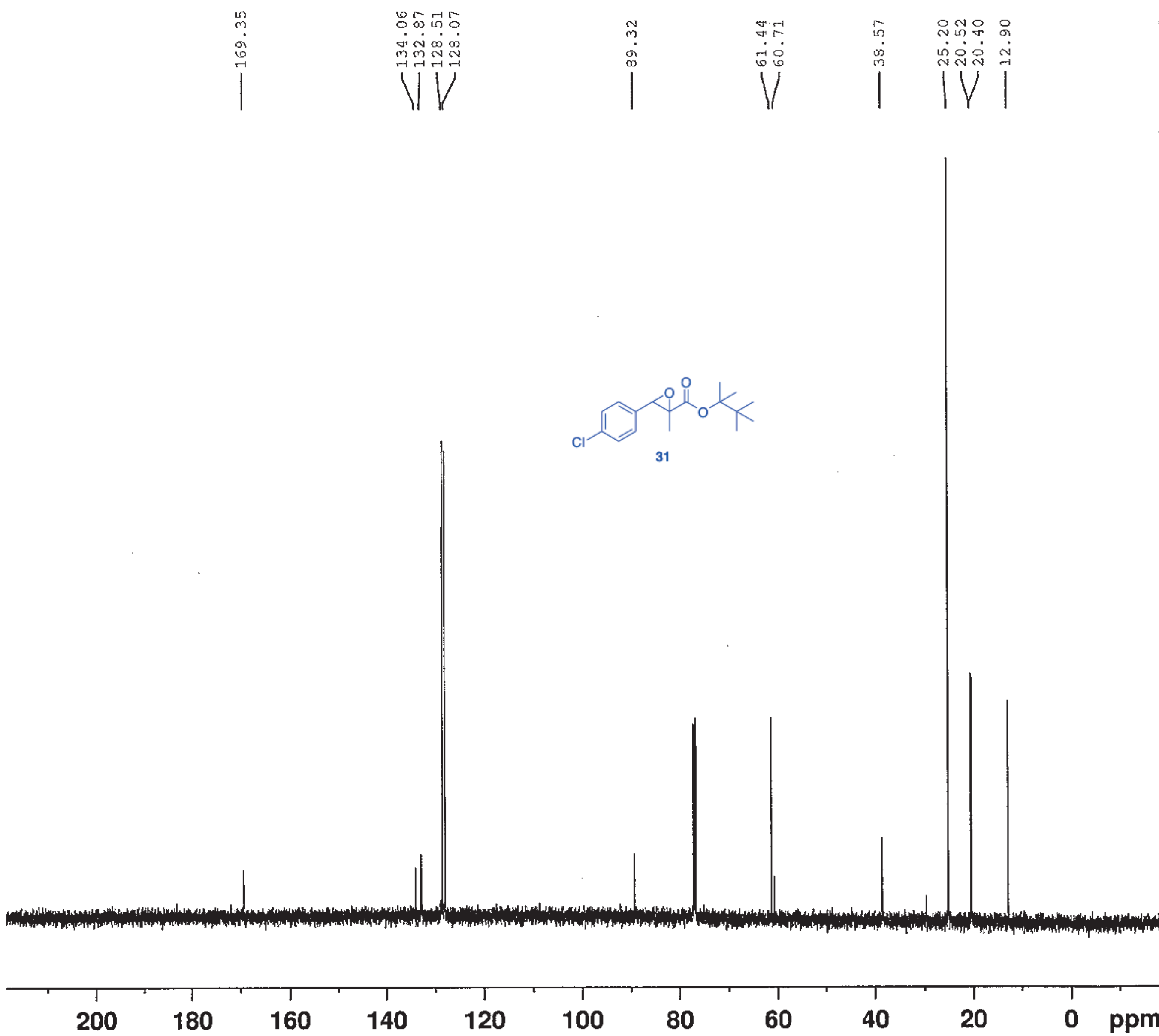


Current Data Parameters
NAME Lan_20140430_B3247
EXPNO 1
PROCNO 1

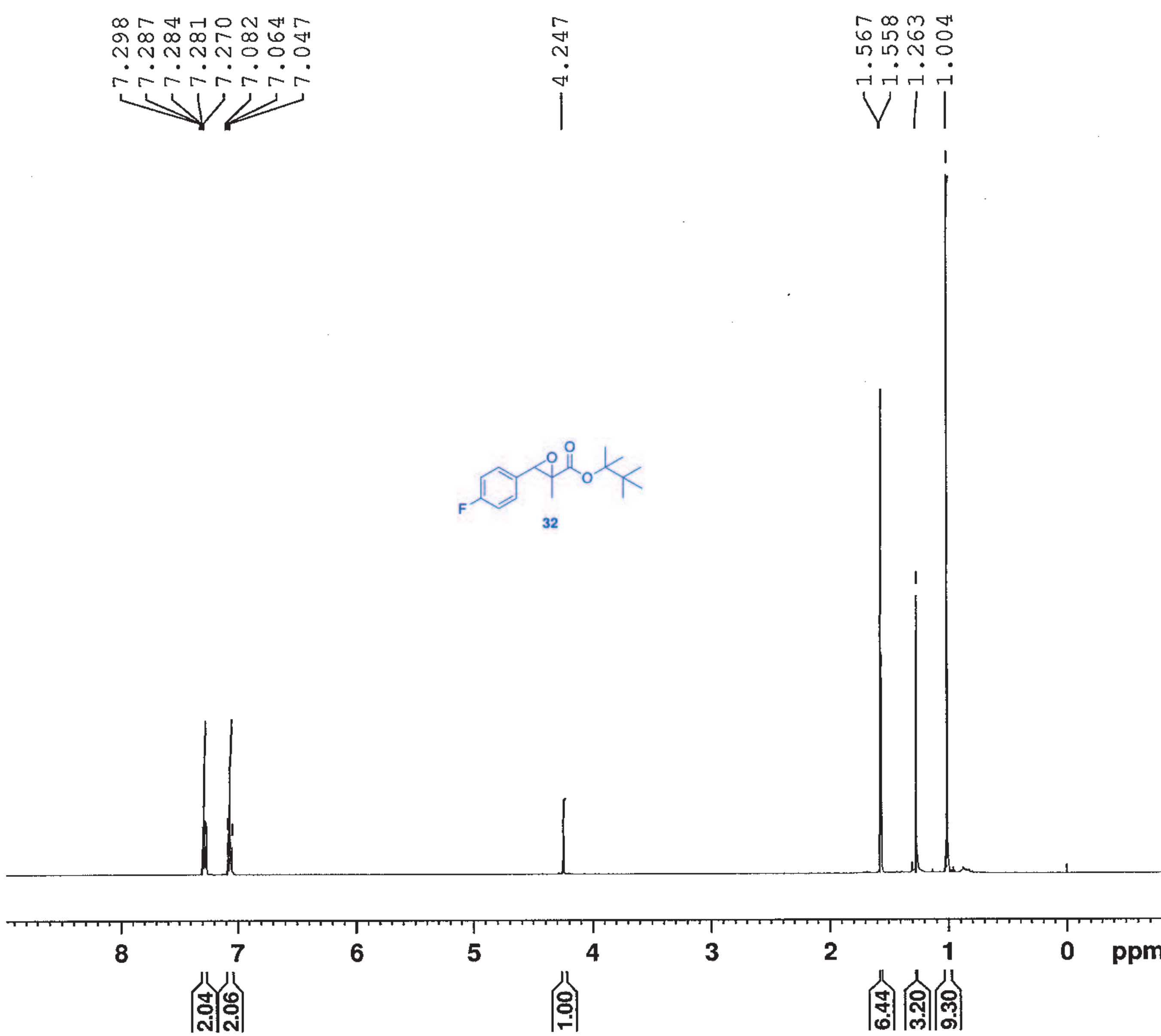
F2 - Acquisition Parameters
Date_ 20140430
Time 19.26
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 52.86
DW 50.000 usec
DE 10.00 usec
TE 295.9 K
D1 10.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 8.00 usec
PLW1 12.19999981 W

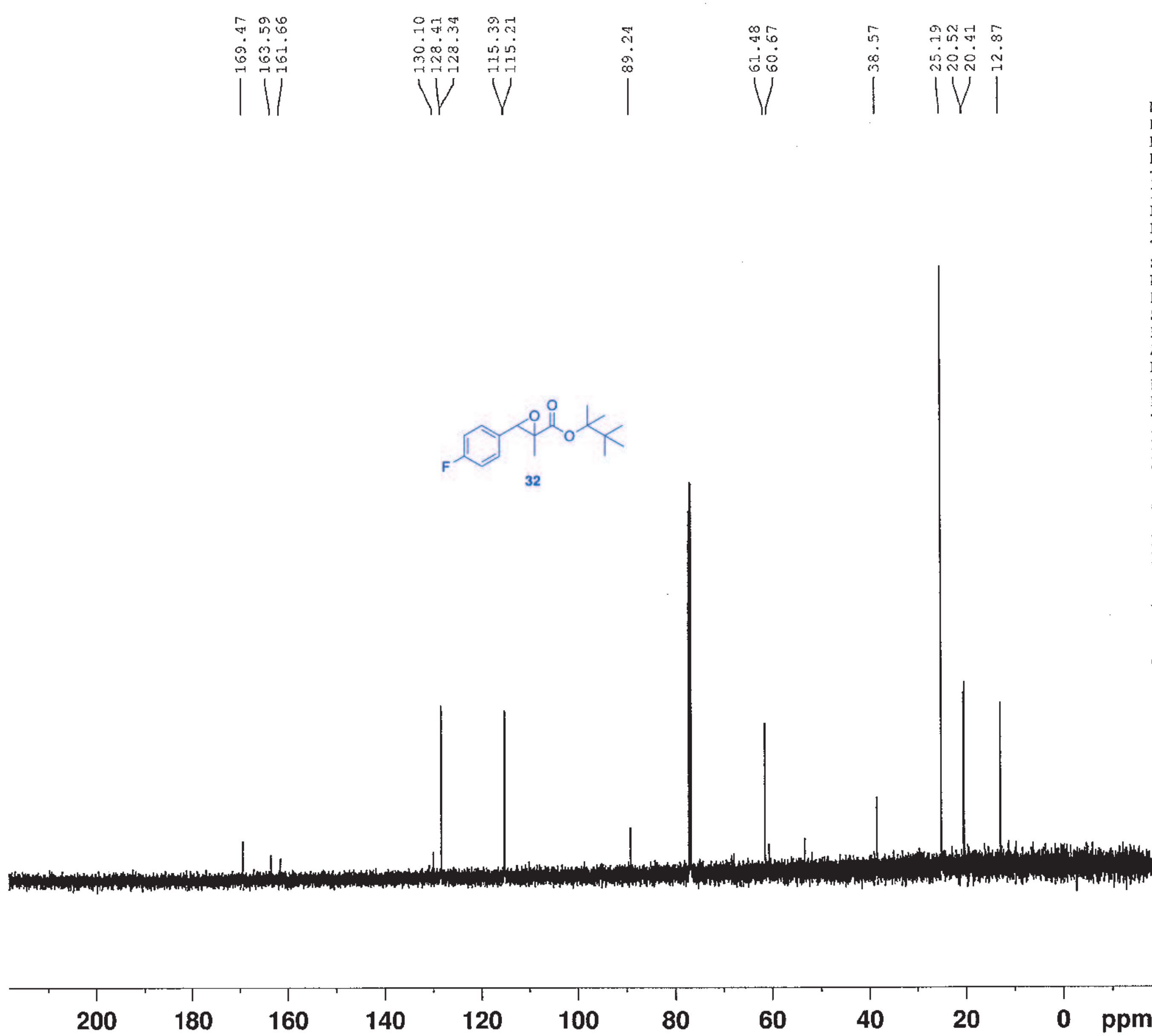
F2 - Processing parameters
SI 65536
SF 500.1300123 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00




```
Current Data Parameters
NAME      Lan_20140507_B3247_C
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20140507
Time                  16.54
INSTRUM               spect
PROBHD   5 mm PATXI 1H/
PULPROG                zgdc
TD                   178568
SOLVENT               CDCl3
NS                      172
DS                        0
SWH             29761.904 Hz
FIDRES           0.166670 Hz
AQ              2.9999423 sec
RG                 196.79
DW                 16.800 usec
DE                  10.00 usec
TE                  295.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1          125.7703643 MHz
NUC1                  13C
P1                  14.00 usec
PLW1         170.00000000 W

======== CHANNEL f2 ========
SFO2          500.1320005 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2               90.00 usec
PLW2          12.19999981 W
PLW12          0.20893000 W

F2 - Processing parameters
SI                 131072
SF            125.7577890 MHz
WDW                    EM
SSB        0
LB                   1.00 Hz
GB         0
PC                   1.40
```

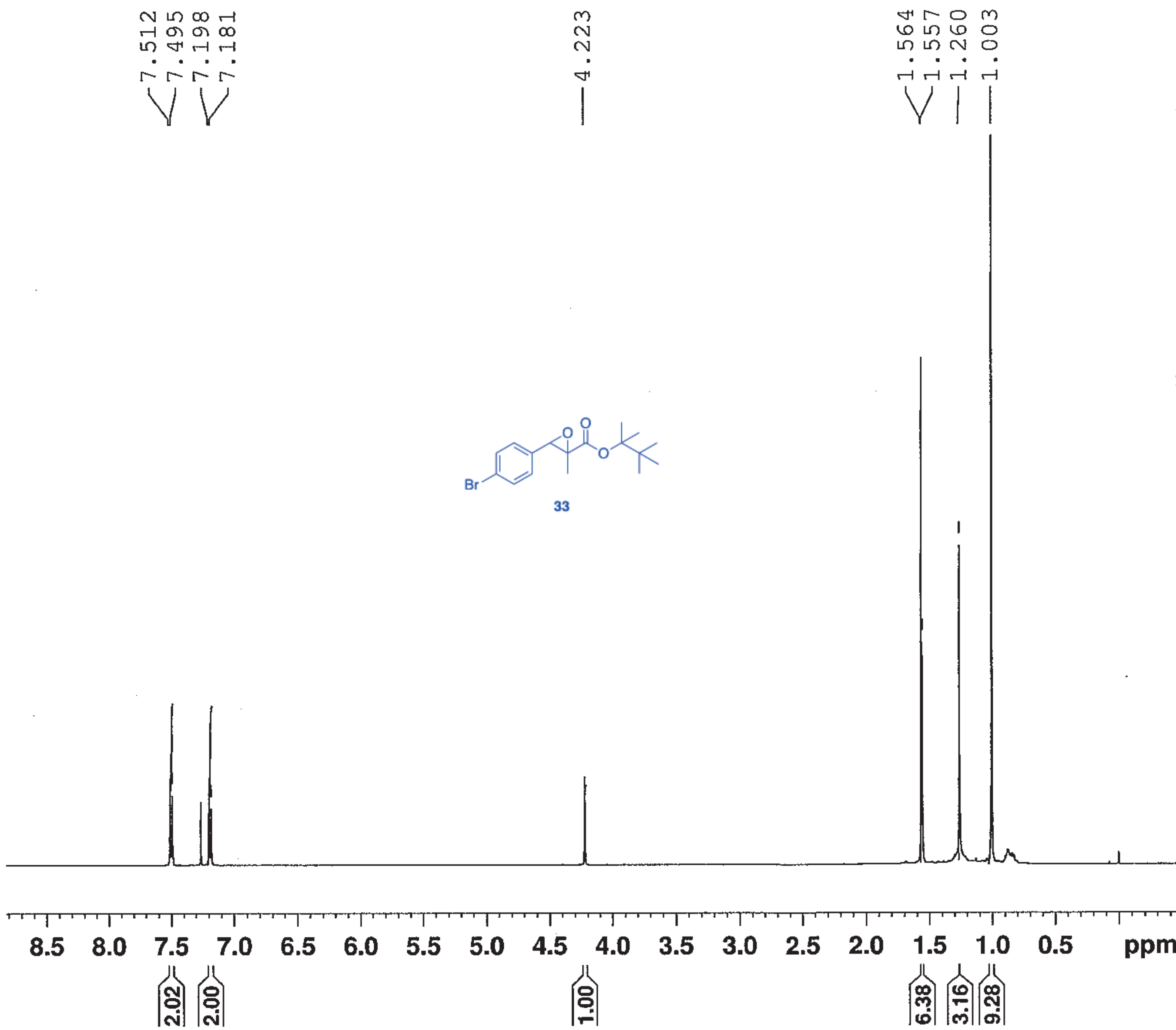



```
Current Data Parameters
NAME      Lan_20140423_B3293
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20140423
Time                   18.42
INSTRUM                spect
PROBHD    5 mm PATXI 1H/
PULPROG                   zg
TD                     59998
SOLVENT                CDCl3
NS                         8
DS                         0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                     71.78
DW                50.000 usec
DE                 10.00 usec
TE                 295.8 K
D1            10.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                      1H
P1                  8.00 usec
PLW1          12.19999981 W

F2 - Processing parameters
SI                     65536
SF           500.1300128 MHz
WDW                       EM
SSB       0
LB                   0.30 Hz
GB        0
PC                      1.00
```



32

NAME	Lan_20140426_B3293_C
EXPNO	1
PROCNO	1
Date_	20140426
Time	15.07
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zgdc
TD	178568
SOLVENT	CDCl3
NS	466
DS	0
SWH	29761.904 Hz
FIDRES	0.166670 Hz
AQ	2.9999924 sec
RG	196.79
DW	16.800 usec
DE	10.00 usec
TE	297.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	125.7703643 MHz
NUC1	13C
P1	14.00 usec
SI	131072
SF	125.7577890 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



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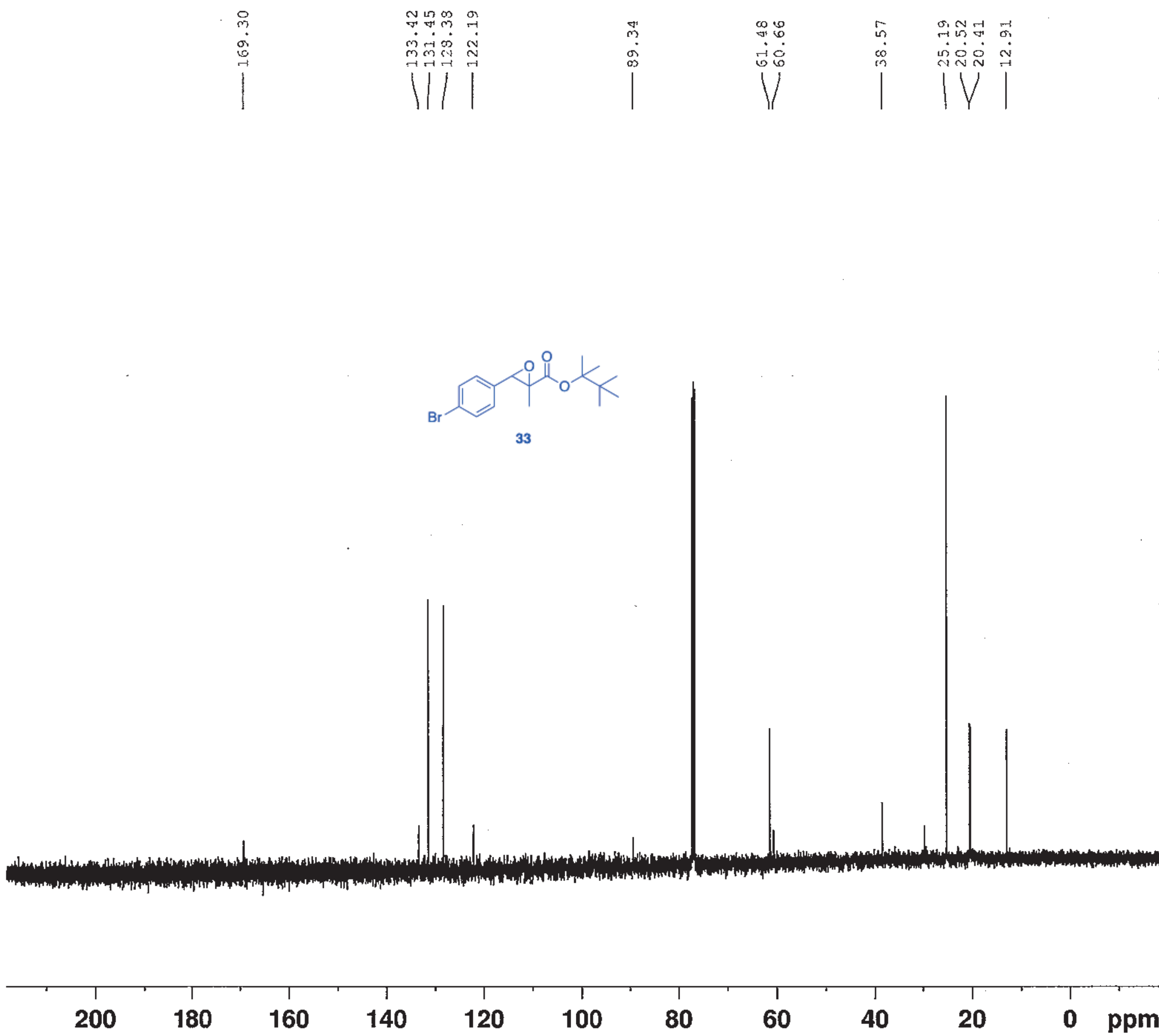
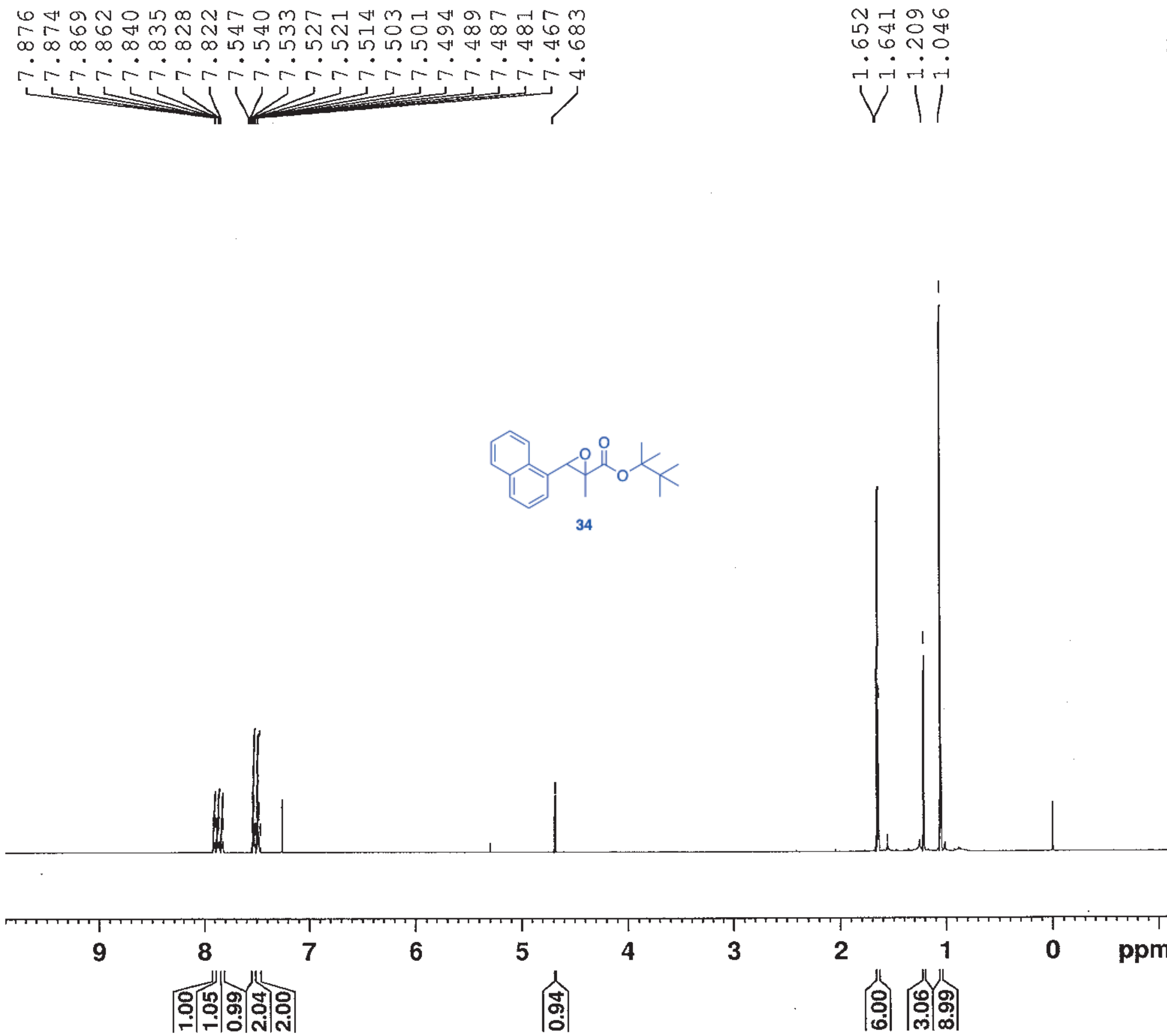
NAME	Lan_20140423_B3295
EXPNO	1
PROCNO	1
Date_	20140423
Time	19.14
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	8
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999499 sec
RG	87.71
DW	50.000 usec
DE	10.00 usec
TE	296.0 K
D1	10.00000000 sec
TD0	1

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

SFO1	500.1330885 MHz
NUC1	1H
P1	8.00 usec
SI	65536
SF	500.1300128 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

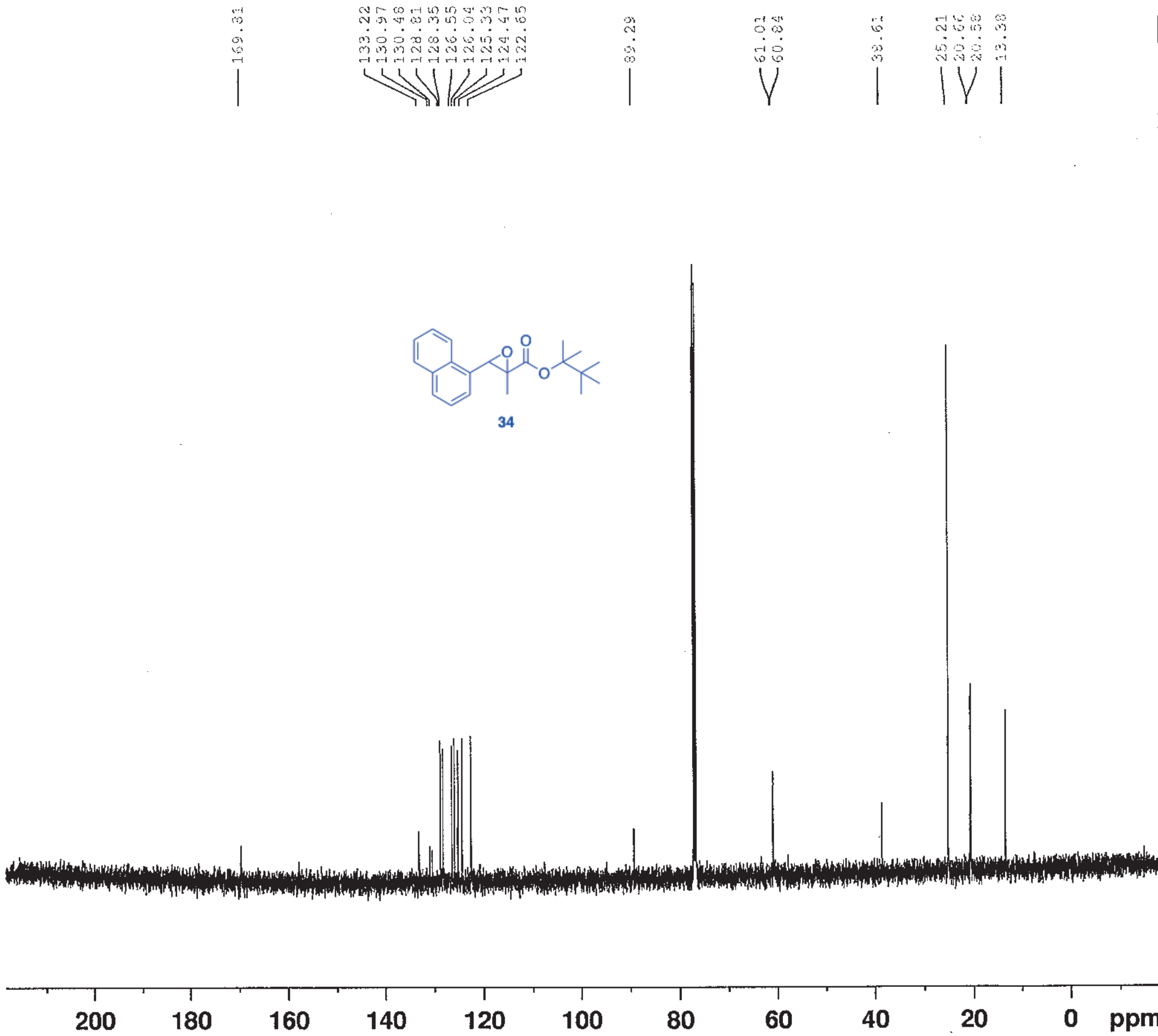


NAME	Lan_20140426_B3295_C
EXPNO	1
PROCNO	1
Date_	20140426
Time	15.51
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zgdc
TD	178568
SOLVENT	CDCl3
NS	705
DS	0
SWH	29761.904 Hz
FIDRES	0.166670 Hz
AQ	2.9999924 sec
RG	196.79
DW	16.800 usec
DE	10.00 usec
TE	297.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	125.7703643 MHz
NUC1	13C
P1	14.00 usec
SI	131072
SF	125.7577890 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

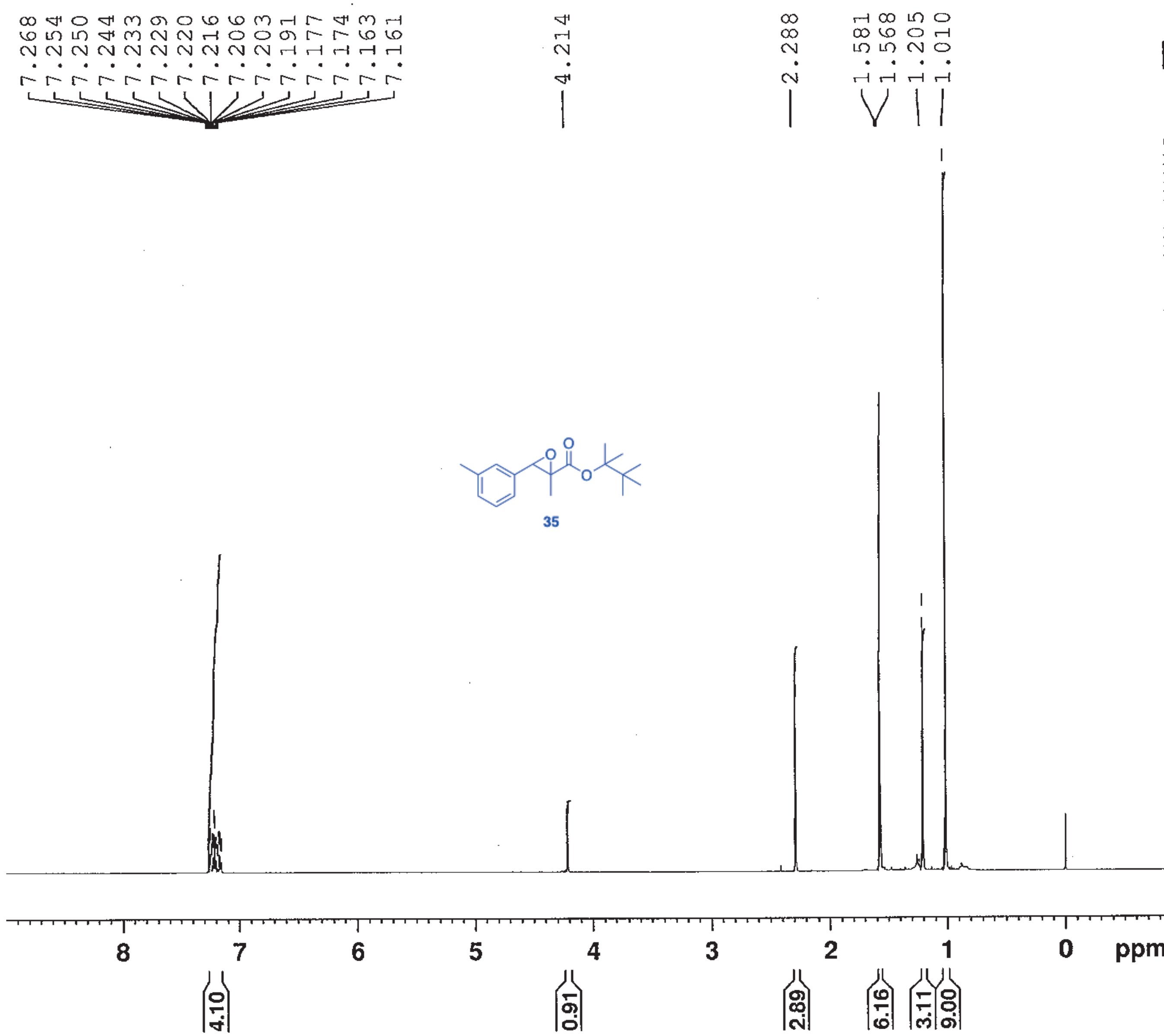


BRUKER

```
Current Data Parameters
NAME      Lan_20140430_B3253
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20140430
Time                   19.34
INSTRUM                spect
PROBHD     5 mm PATXI 1H/
PULPROG                   zg
TD                     59998
SOLVENT                CDCl3
NS                         8
DS                         0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                     97.37
DW                50.000 usec
DE                 10.00 usec
TE                 296.0 K
D1           10.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                      1H
P1                  8.00 usec
PLW1         12.19999981 W

F2 - Processing parameters
SI                     65536
SF           500.1300152 MHz
WDW                       EM
SSB      0
LB                   0.30 Hz
GB       0
PC                      1.00
```

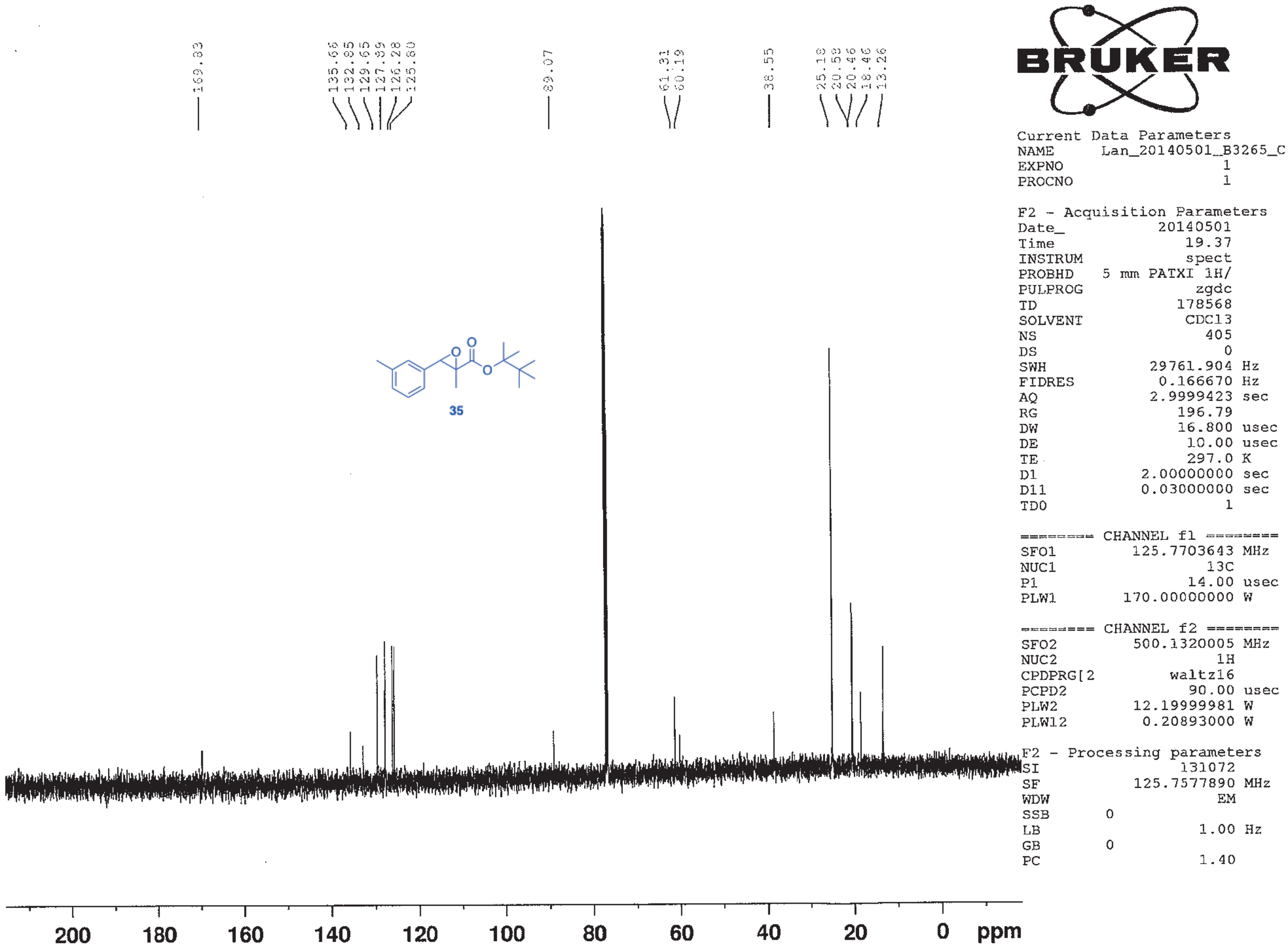


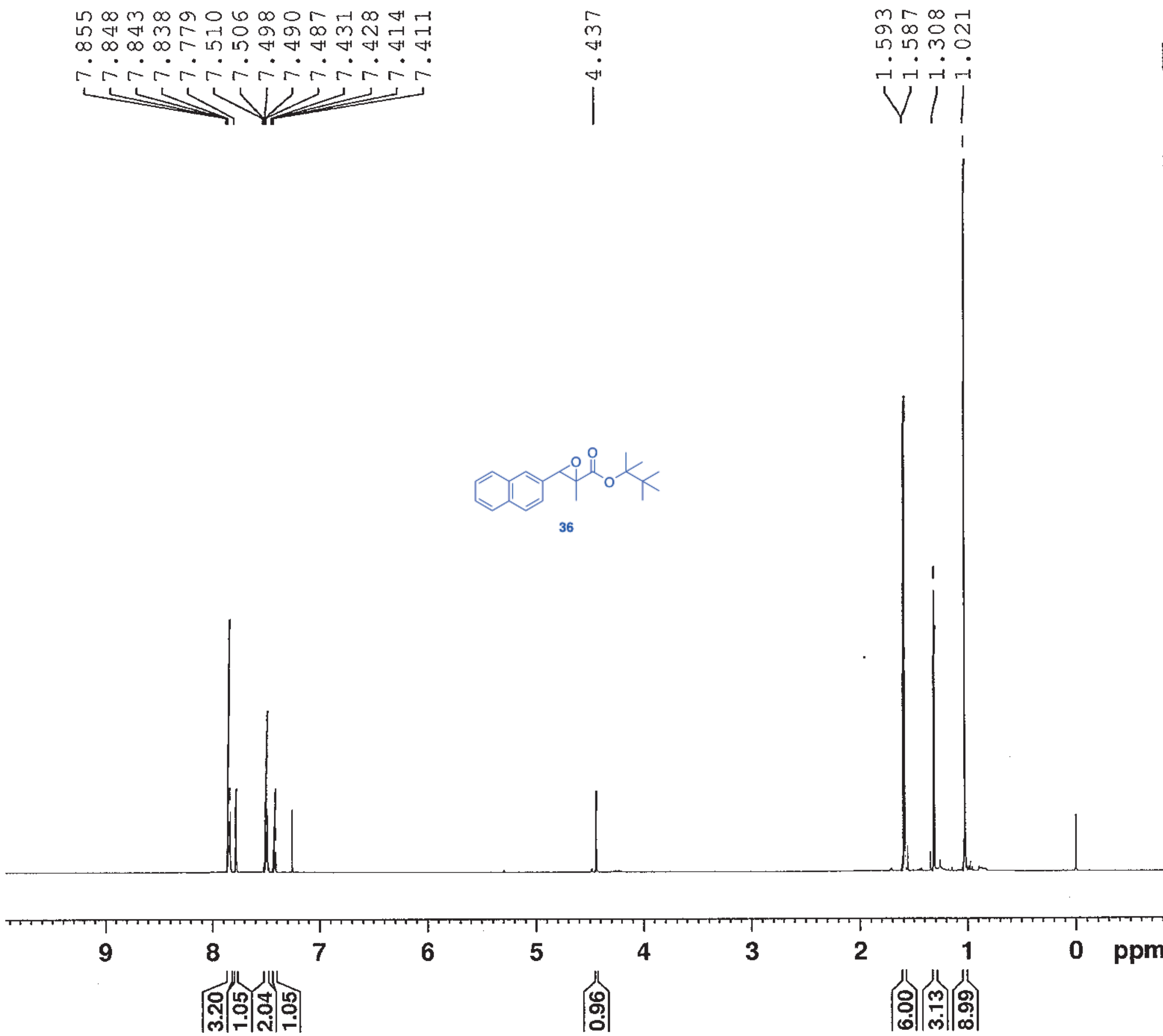

```
Current Data Parameters
NAME       Lan_20140405_B3253_C
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20140405
Time                  16.08
INSTRUM               spect
PROBHD     5 mm PATXI 1H/
PULPROG                zgdc
TD                   178568
SOLVENT               CDCl3
NS                      163
DS                        0
SWH               29761.904 Hz
FIDRES             0.166670 Hz
AQ                2.9999423 sec
RG                   196.79
DW                   16.800 usec
DE                    10.00 usec
TE                    297.0 K
D1               3.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            125.7703643 MHz
NUC1                    13C
P1                    14.00 usec
PLW1           170.00000000 W

======== CHANNEL f2 ========
SFO2            500.1320005 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 90.00 usec
PLW2            12.19999981 W
PLW12            0.20893000 W

F2 - Processing parameters
SI                   131072
SF              125.7577890 MHz
WDW                      EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.40
```



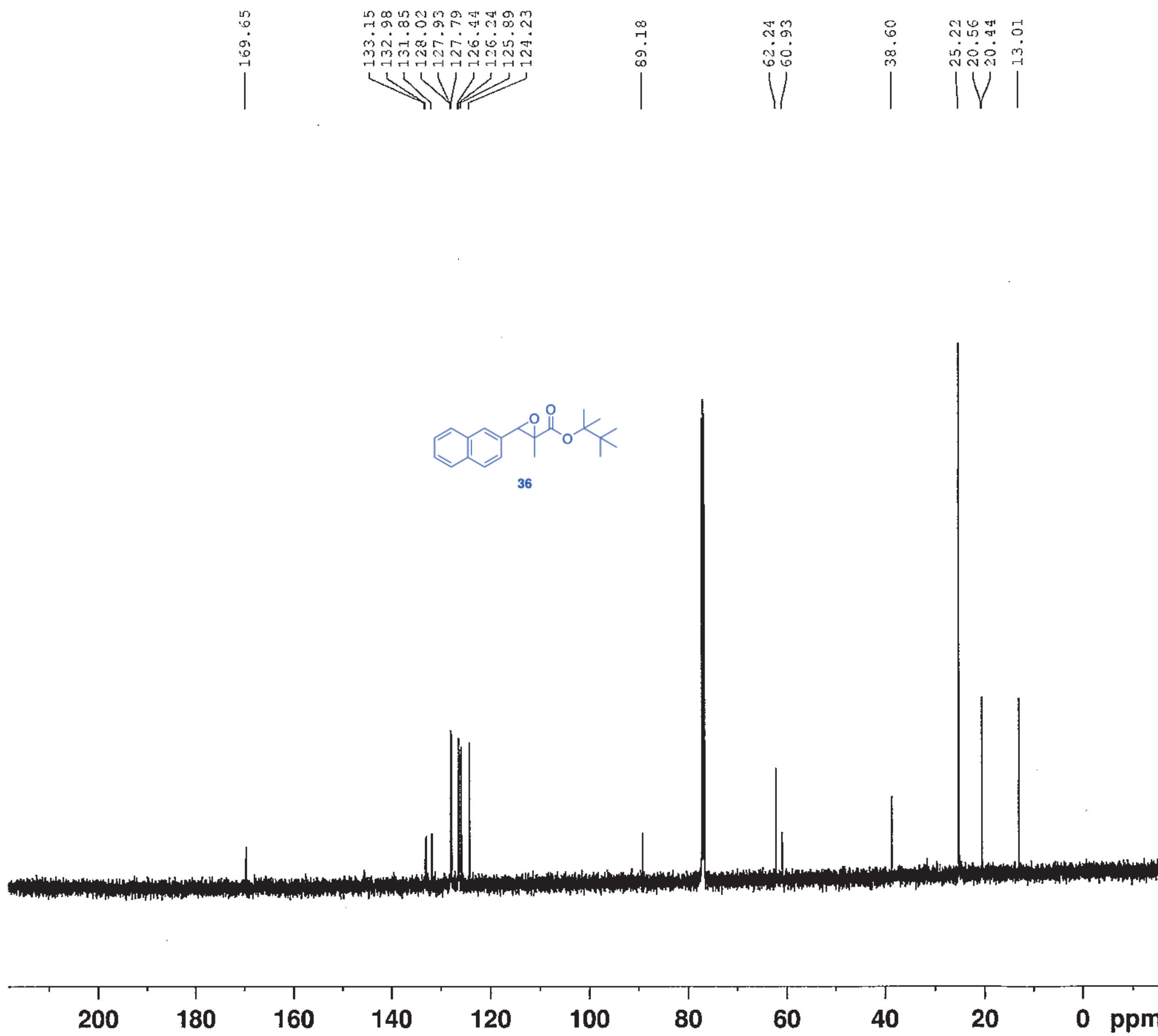
BRUKER

```
Current Data Parameters
NAME        Lan_20140501_B3265
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20140501
Time                  19.09
INSTRUM               spect
PROBHD     5 mm PATXI 1H/
PULPROG                  zg
TD                    59998
SOLVENT               CDCl3
NS                        8
DS                        0
SWH               10000.000 Hz
FIDRES             0.166672 Hz
AQ                2.9999001 sec
RG                    87.71
DW                   50.000 usec
DE                    10.00 usec
TE                    295.8 K
D1              10.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            500.1330885 MHz
NUC1                     1H
P1                     8.00 usec
PLW1            12.19999981 W

F2 - Processing parameters
SI                    65536
SF              500.1300136 MHz
WDW                      EM
SSB       0
LB                     0.30 Hz
GB        0
PC                     1.00
```


169.83
135.66
132.85
129.65
127.89
126.28
125.80
89.07
61.31
60.19
38.55
25.18
20.58
20.46
18.46
13.26
BRUKER
Current Data Parameters
NAME Lan_20140501_B3265_C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140501
Time 19.37
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgdc
TD 178568
SOLVENT CDCl3
NS 405
DS 0
SWH 29761.904 Hz
FIDRES 0.166670 Hz
AQ 2.9999423 sec
RG 196.79
DW 16.800 usec
DE 10.00 usec
TE 297.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703643 MHz
NUC1 13C
P1 14.00 usec
PLW1 170.00000000 W
======== CHANNEL f2 ========
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 12.19999981 W
PLW12 0.20893000 W
F2 - Processing parameters
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
35
200
180
160
140
120
100
80
60
40
20
0
ppm



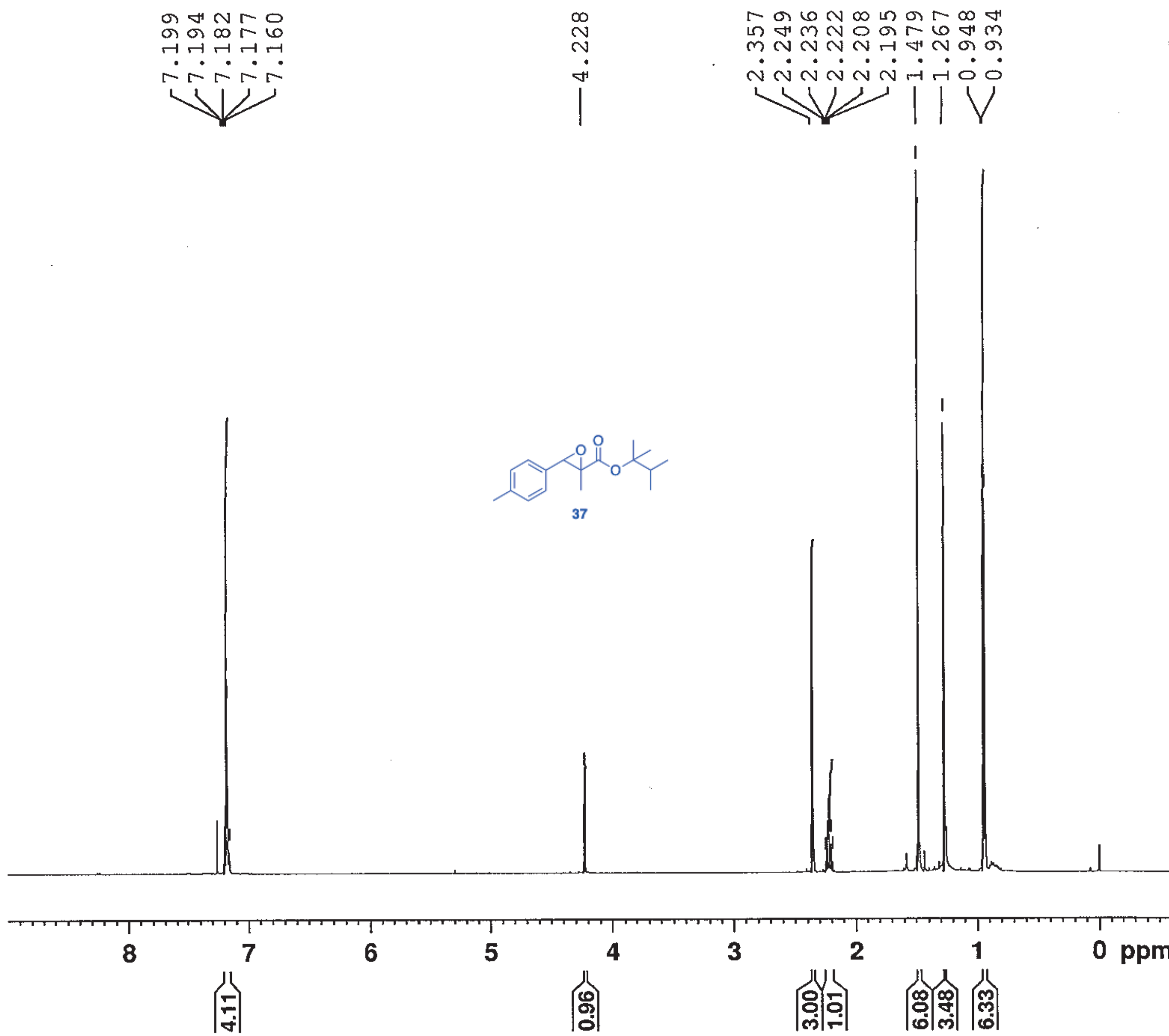

```
Current Data Parameters
NAME      Lan_20140430_B3267
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20140430
Time                  21.31
INSTRUM               spect
PROBHD    5 mm PATXI 1H/
PULPROG                  zg
TD                    59998
SOLVENT               CDC13
NS                        8
DS                        0
SWH           10000.000 Hz
FIDRES         0.166672 Hz
AQ            2.9999001 sec
RG                    87.71
DW               50.000 usec
DE                10.00 usec
TE                296.3 K
D1          10.00000000 sec
TDO                       1

======== CHANNEL f1 ========
SFO1        500.1330885 MHz
NUC1                     1H
P1                 8.00 usec
PLW1        12.19999981 W

F2 - Processing parameters
SI                    65536
SF          500.1300156 MHz
WDW                      EM
SSB       0
LB                  0.30 Hz
GB        0
PC                     1.00
```



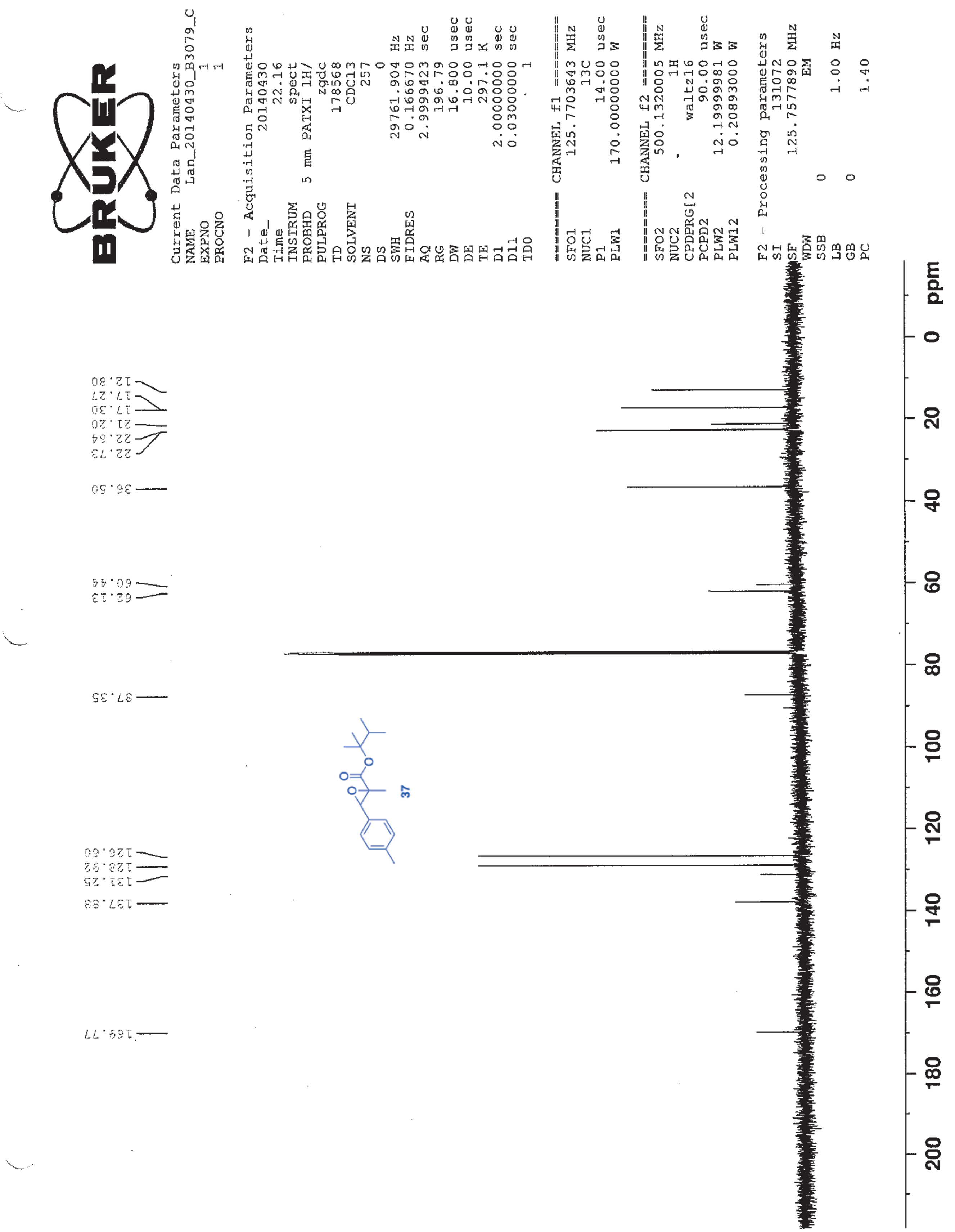
NAME	Lan_20140405_B3267_C	
EXPNO	1	
PROCNO	1	
Date_	20140405	
Time	17.20	
INSTRUM	spect	
PROBHD	5 mm PATXI 1H/	
PULPROG	zgdc	
TD	178568	
SOLVENT	CDCl3	
NS	232	
DS	0	
SWH	29761.904	Hz
FIDRES	0.166670	Hz
AQ	2.9999924	sec
RG	196.79	
DW	16.800	usec
DE	10.00	usec
TE	297.1	K
D1	3.00000000	sec
D11	0.03000000	sec
TD0	1	

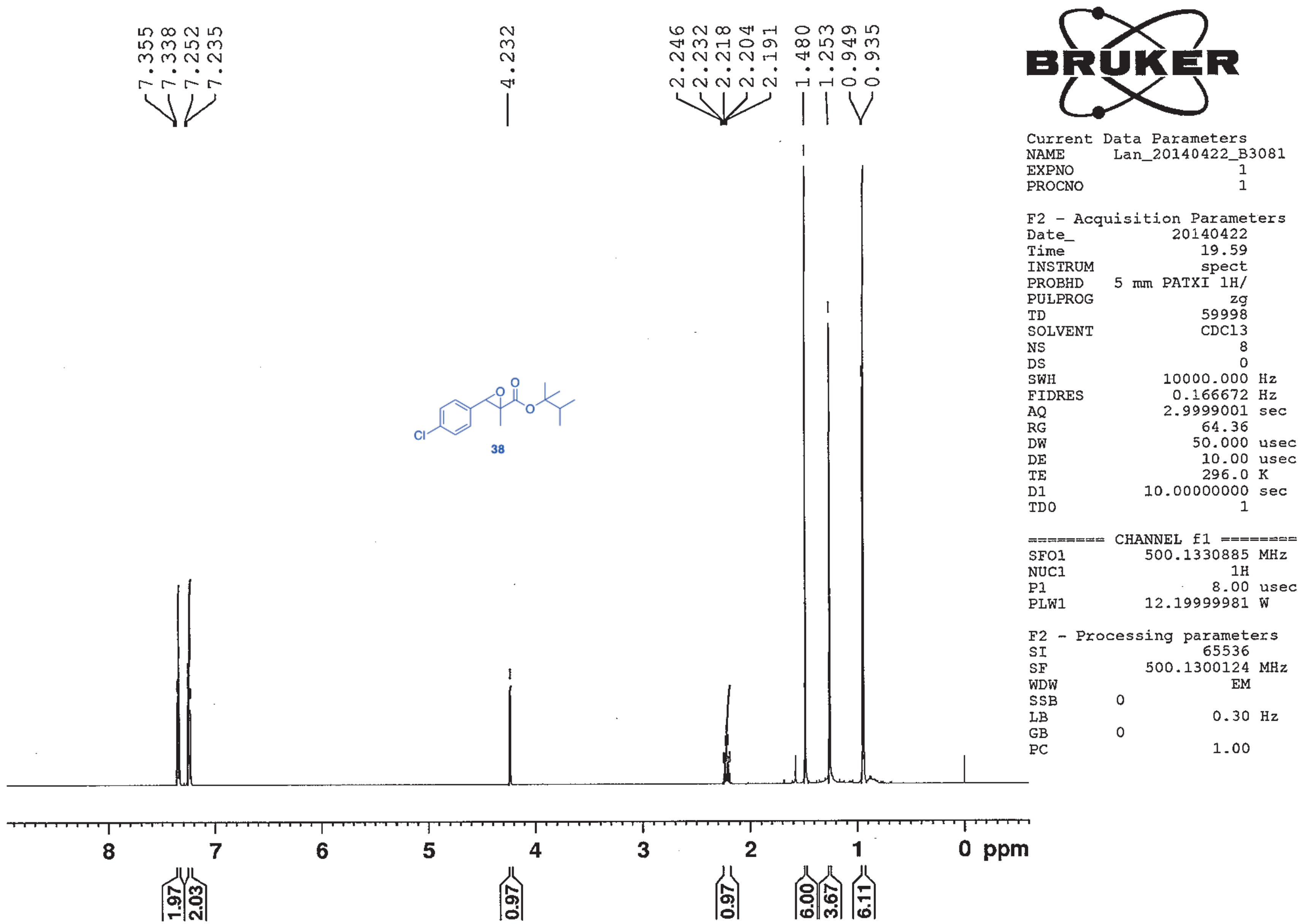
======== CHANNEL f1 ========

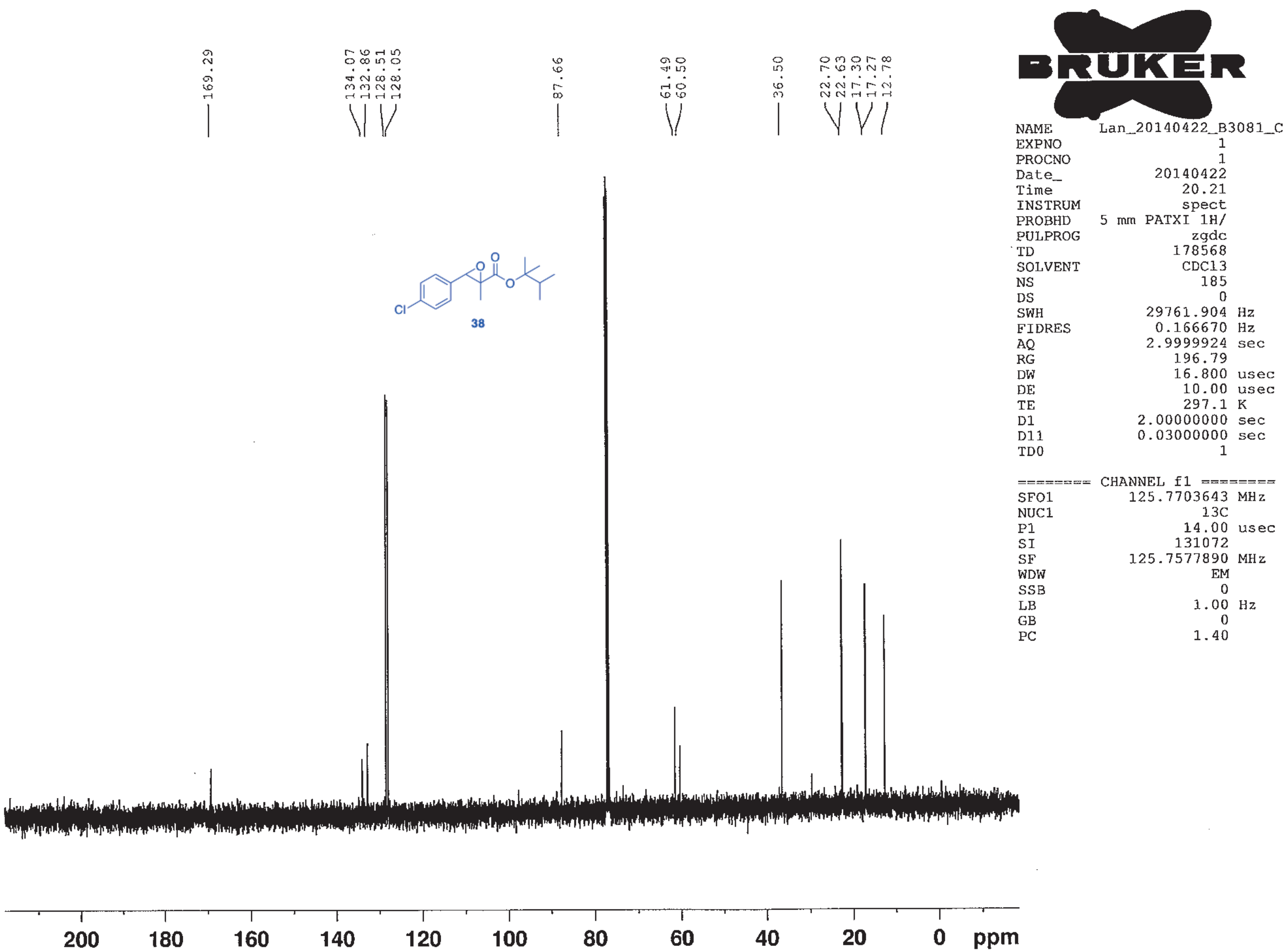
SFO1	125.7703643	MHz
NUC1	13C	
P1	14.00	usec
SI	131072	
SF	125.7577890	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

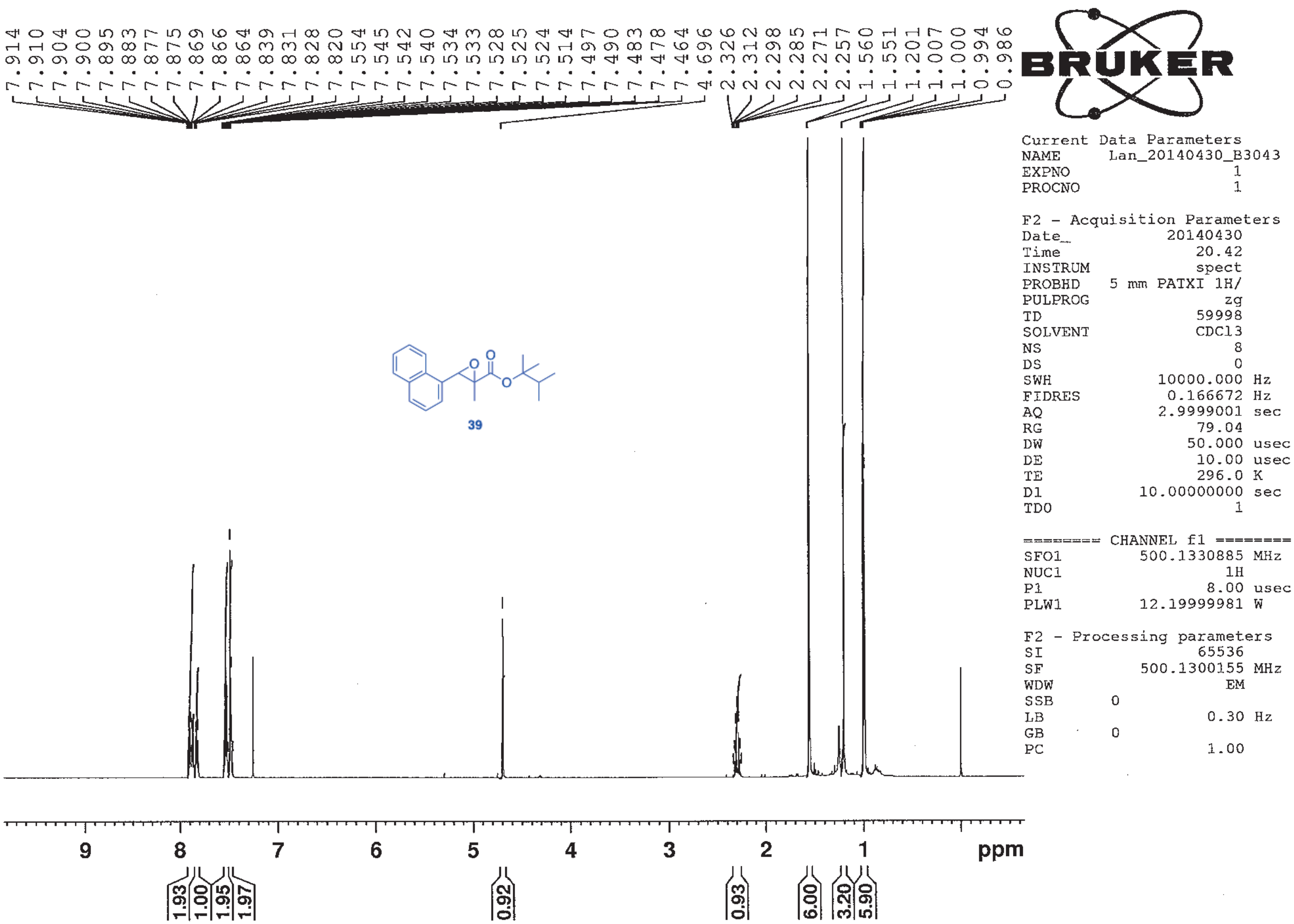


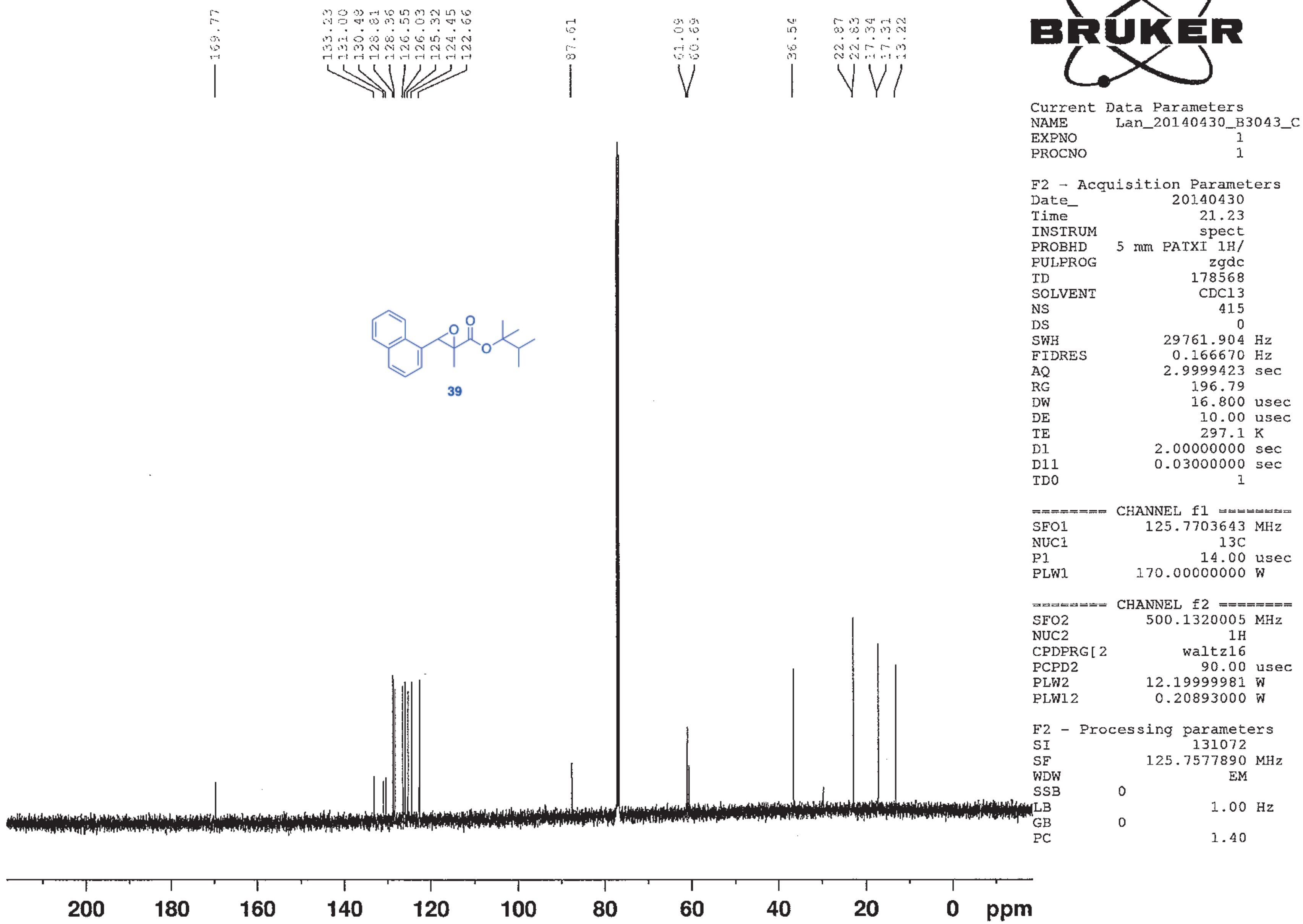

```
Current Data Parameters
NAME      Lan_20140422_B3079
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20140422
Time                 19.16
INSTRUM              spect
PROBHD    5 mm PATXI 1H/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                       8
DS                       0
SWH          10000.000 Hz
FIDRES        0.166672 Hz
AQ           2.9999001 sec
RG                   52.86
DW              50.000 usec
DE               10.00 usec
TE                296.2 K
D1         10.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1       500.1330885 MHz
NUC1                    1H
P1                8.00 usec
PLW1       12.19999981 W

F2 - Processing parameters
SI                   65536
SF         500.1300138 MHz
WDW                     EM
SSB      0
LB                 0.30 Hz
GB       0
PC                    1.00
```


BRUKER
Current Data Parameters
NAME Lan_20140430_B3079_C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140430
Time 22.16
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgdc
TD 178568
SOLVENT CDCl3
NS 257
DS 0
SWH 29761.904 Hz
FIDRES 0.166670 Hz
AQ 2.9999423 sec
RG 196.79
DW 16.800 usec
DE 10.00 usec
TE 297.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703643 MHz
NUC1 13C
P1 14.00 usec
PLW1 170.00000000 W
======== CHANNEL f2 ========
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 12.19999981 W
PLW12 0.20893000 W
F2 - Processing parameters
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
12.80
17.27
17.30
21.20
22.64
22.73
36.50
60.44
62.13
87.35
126.60
128.92
131.25
137.88
169.77
37
ppm
0
20
40
60
80
100
120
140
160
180
200

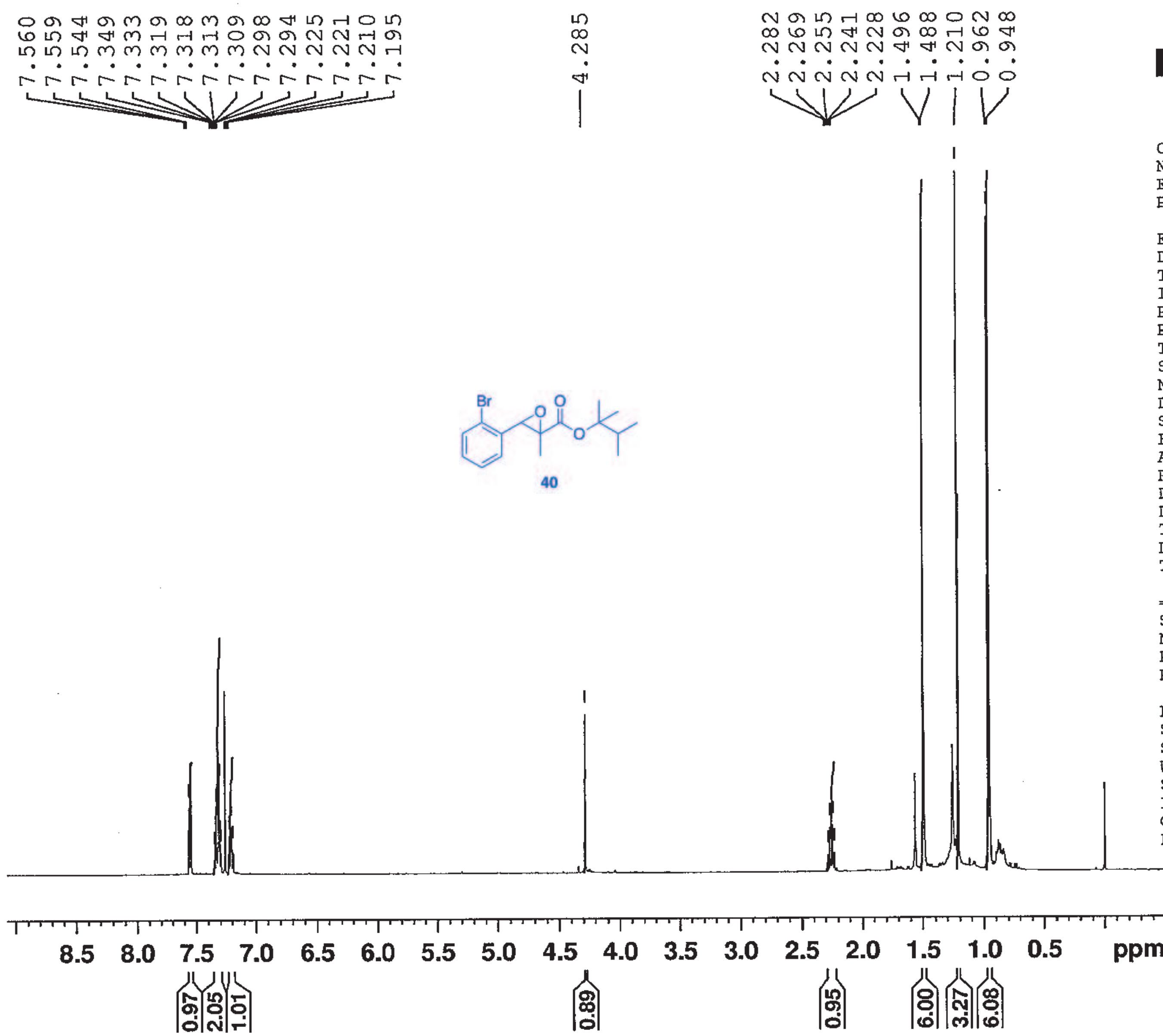

7.355
7.338
7.252
7.235
4.232
2.246
2.232
2.218
2.204
2.191
1.480
1.253
0.949
0.935
Cl
O
O
O
38
BRUKER
Current Data Parameters
NAME Lan_20140422_B3081
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140422
Time 19.59
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 64.36
DW 50.000 usec
DE 10.00 usec
TE 296.0 K
D1 10.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 8.00 usec
PLW1 12.19999981 W
F2 - Processing parameters
SI 65536
SF 500.1300124 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
0 ppm
1.97
2.03
0.97
0.97
6.00
3.67
6.11


169.29
134.07
132.86
128.51
128.05
87.66
61.49
60.50
36.50
22.70
22.63
17.30
17.27
12.78
Cl
38
NAME Lan_20140422_B3081_C
EXPNO 1
PROCNO 1
Date_ 20140422
Time 20.21
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgdc
TD 178568
SOLVENT CDCl3
NS 185
DS 0
SWH 29761.904 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 196.79
DW 16.800 usec
DE 10.00 usec
TE 297.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703643 MHz
NUC1 13C
P1 14.00 usec
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm


7.914
7.910
7.904
7.900
7.895
7.883
7.877
7.875
7.869
7.866
7.864
7.839
7.831
7.828
7.820
7.554
7.545
7.542
7.540
7.534
7.533
7.528
7.525
7.524
7.514
7.497
7.490
7.483
7.478
7.464
4.696
2.326
2.312
2.298
2.285
2.271
2.257
1.560
1.551
1.201
1.007
1.000
0.994
0.986
BRUKER
39
Current Data Parameters
NAME Lan_20140430_B3043
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140430
Time 20.42
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 79.04
DW 50.000 usec
DE 10.00 usec
TE 296.0 K
D1 10.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 8.00 usec
PLW1 12.19999981 W
F2 - Processing parameters
SI 65536
SF 500.1300155 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
1.93
1.00
1.95
1.97
0.92
0.93
6.00
3.20
5.90


169.77
133.23
131.00
130.48
128.81
128.36
126.55
126.03
125.32
124.45
122.66
87.61
61.09
60.69
36.54
22.87
22.83
17.34
17.31
13.22
O
O
O
200
180
160
140
120
100
80
60
40
20
0
ppm
Current Data Parameters
NAME Lan_20140430_B3043_C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140430
Time 21.23
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgdc
TD 178568
SOLVENT CDCl3
NS 415
DS 0
SWH 29761.904 Hz
FIDRES 0.166670 Hz
AQ 2.9999423 sec
RG 196.79
DW 16.800 usec
DE 10.00 usec
TE 297.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703643 MHz
NUC1 13C
P1 14.00 usec
PLW1 170.00000000 W
======== CHANNEL f2 ========
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 12.19999981 W
PLW12 0.20893000 W
F2 - Processing parameters
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

39

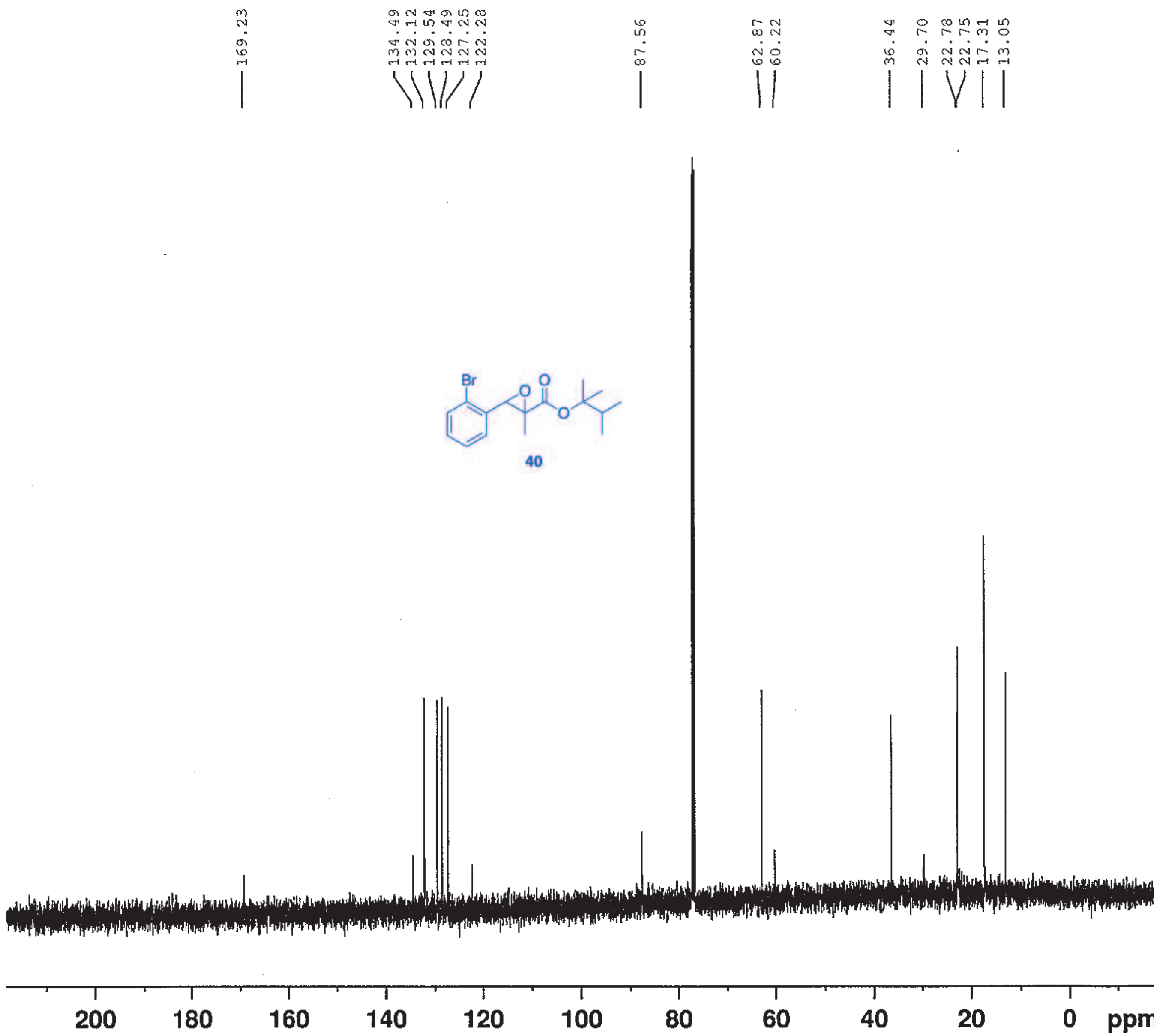


Current Data Parameters
NAME Lan_20140422_B3095
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140422
Time 18.43
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 97.37
DW 50.000 usec
DE 10.00 usec
TE 295.9 K
D1 10.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 8.00 usec
PLW1 12.19999981 W

F2 - Processing parameters
SI 65536
SF 500.1300135 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



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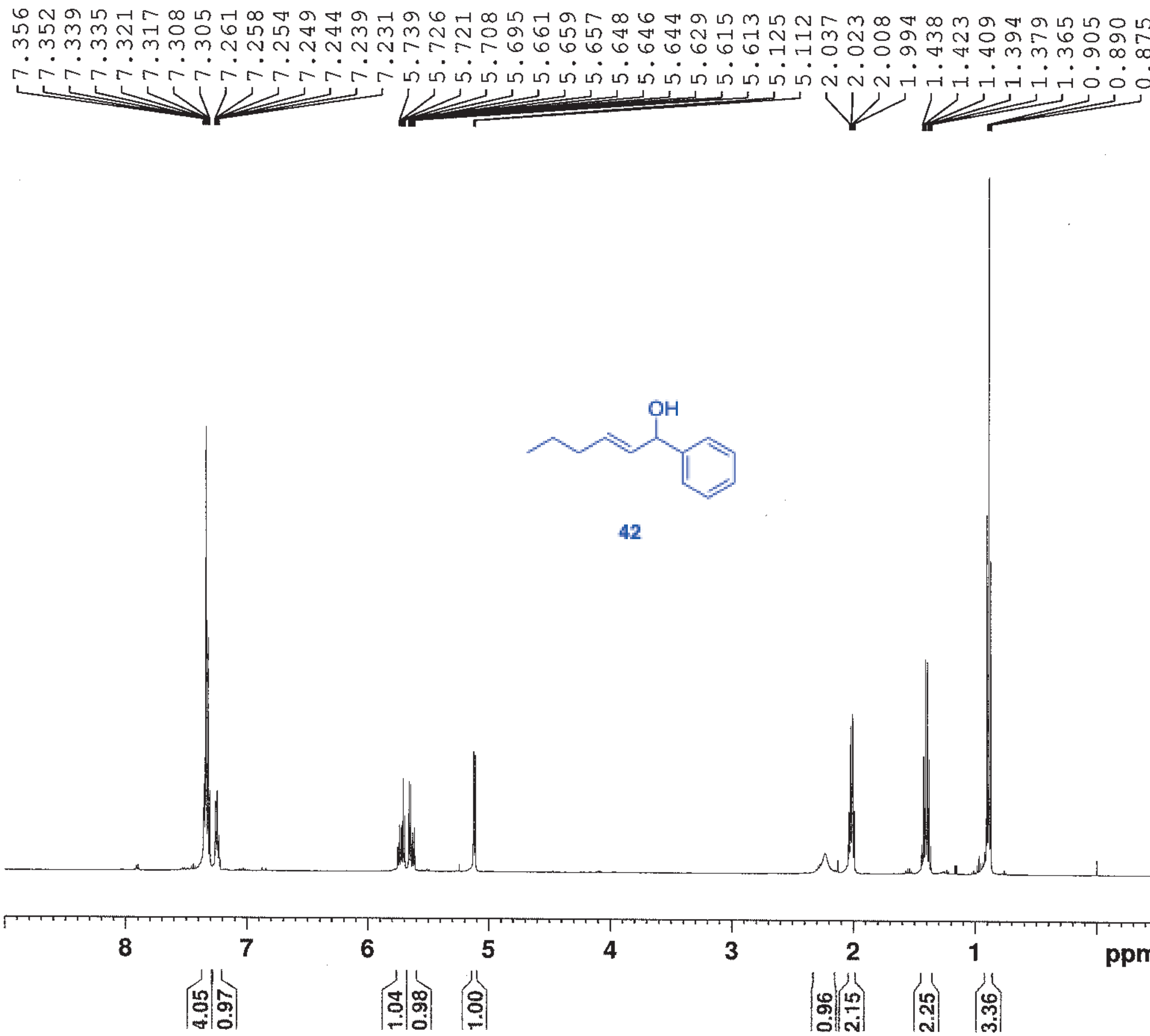
```
Current Data Parameters
NAME       Lan_20140426_B3095_C
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20140426
Time                  16.53
INSTRUM               spect
PROBHD     5 mm PATXI 1H/
PULPROG                zgdc
TD                   178568
SOLVENT               CDCl3
NS                      457
DS                        0
SWH              29761.904 Hz
FIDRES            0.166670 Hz
AQ               2.9999423 sec
RG                   196.79
DW                   16.800 usec
DE                    10.00 usec
TE                    297.0 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           125.7703643 MHz
NUC1                    13C
P1                    14.00 usec
PLW1           170.00000000 W

======== CHANNEL f2 ========
SFO2           500.1320005 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 90.00 usec
PLW2            12.19999981 W
PLW12            0.20893000 W

F2 - Processing parameters
SI                   131072
SF             125.7577890 MHz
WDW                      EM
SSB        0
LB                     1.00 Hz
GB         0
PC                     1.40
```



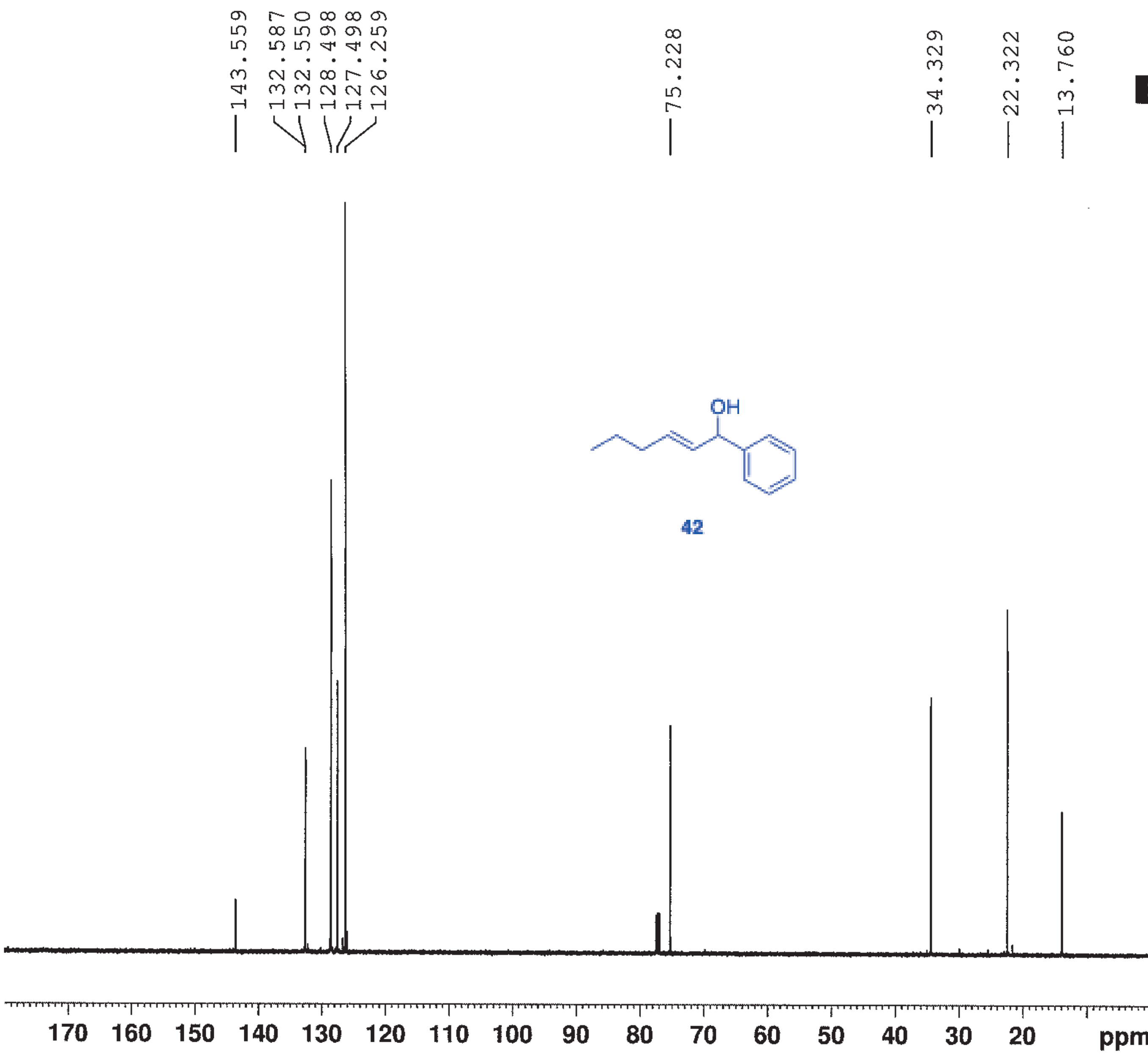
BRUKER

Current Data Parameters
NAME Lan_20150405_B6015
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150405
Time 16.51
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 6.6
DW 50.000 usec
DE 6.50 usec
TE 297.7 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 499.8730869 MHz
NUC1 1H
P1 10.75 usec
PLW1 18.25000000 W

F2 - Processing parameters
SI 65536
SF 499.8700316 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



BRUKER

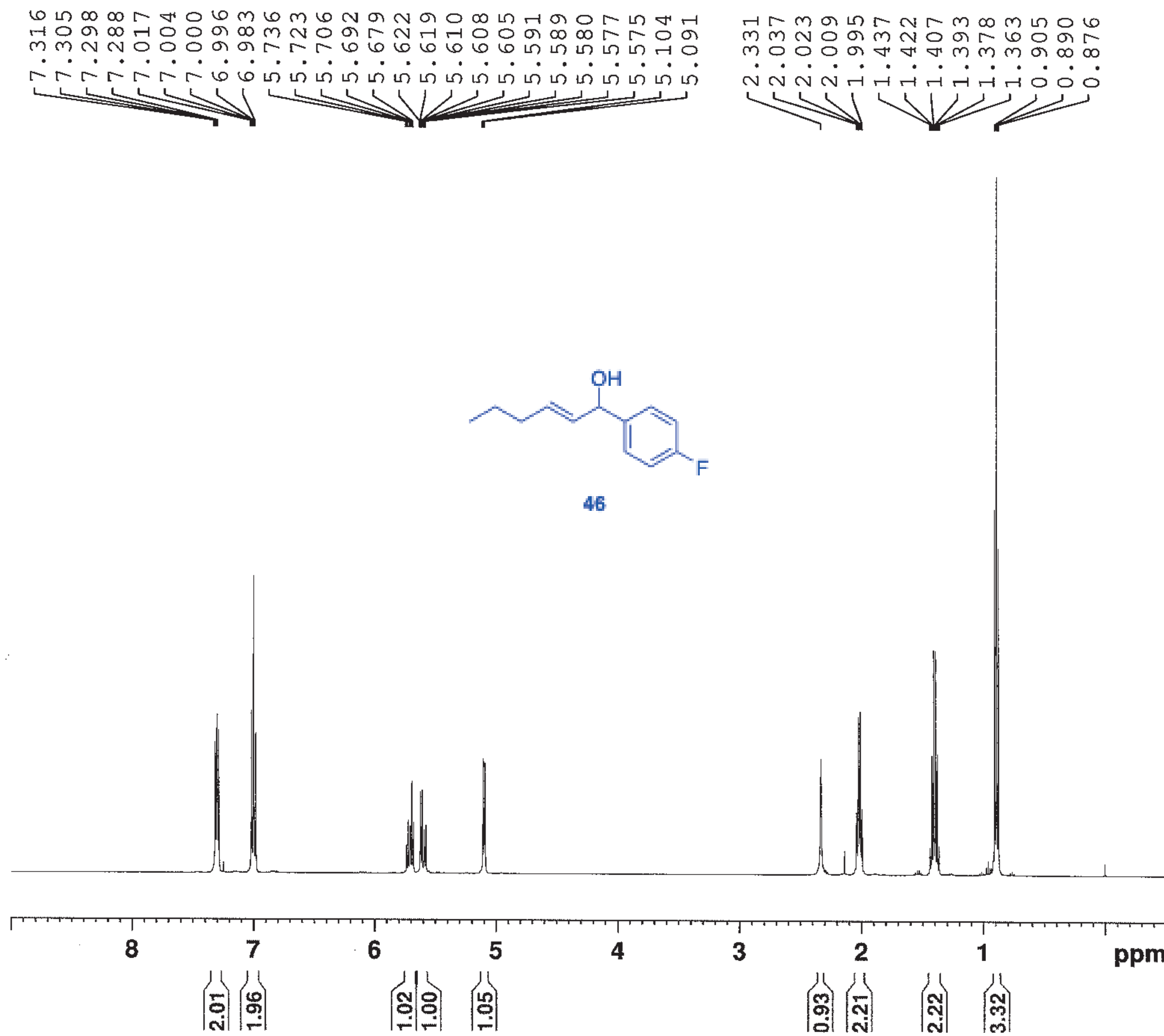
Current Data Parameters
NAME Lan_20150405_B6015_C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150405
Time 17.00
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgdc
TD 187496
SOLVENT CDCl3
NS 64
DS 0
SWH 31250.000 Hz
FIDRES 0.166670 Hz
AQ 2.9999361 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 298.2 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 125.7049802 MHz
NUC1 13C
P1 10.00 usec
PLW1 72.83999634 W

======== CHANNEL f2 ========
SFO2 499.8724993 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.29688001 W

F2 - Processing parameters
SI 1048576
SF 125.6924047 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40



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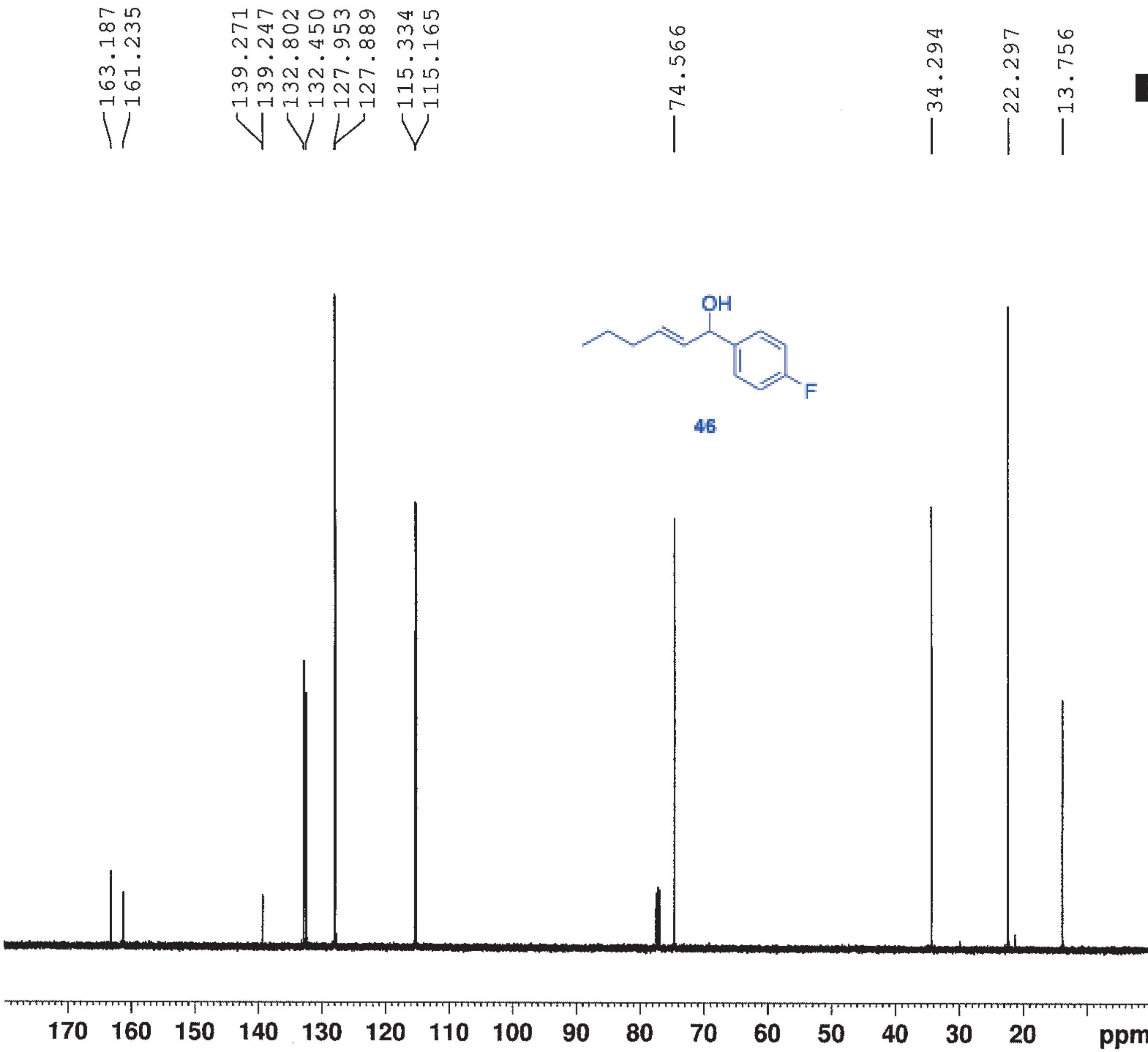
Current Data Parameters	
NAME	Lan_20150406_B6061
EXPNO	1
PROCNO	1
F2 - Acquisition Parameters	
Date_	20150406
Time	18.38
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	8
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999001 sec
RG	8.83
DW	50.000 usec
DE	6.50 usec
TE	296.9 K
D1	5.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	499.8730869 MHz
NUC1	1H
P1	10.75 usec
PLW1	18.25000000 W
F2 - Processing parameters	
SI	65536
SF	499.8700183 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



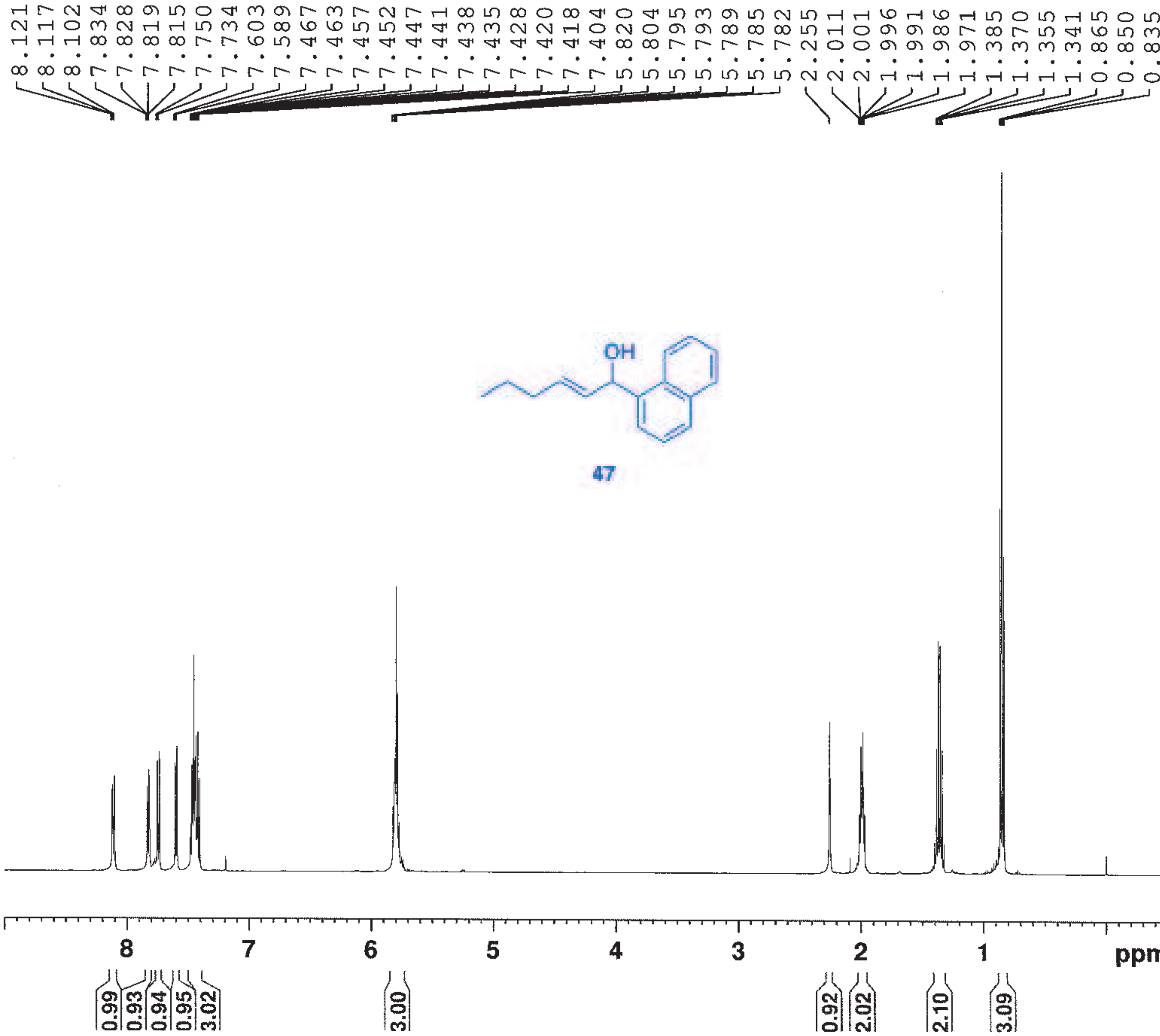

```
Current Data Parameters
NAME         Lan_20150406_B6061_C
EXPNO                           1
PROCNO                          1

F2 - Acquisition Parameters
Date_                    20150406
Time                        18.52
INSTRUM                     spect
PROBHD       5 mm PABBO BB/
PULPROG                      zgdc
TD                         187496
SOLVENT                     CDCl3
NS                             25
DS                              0
SWH                     31250.000 Hz
FIDRES                   0.166670 Hz
AQ                      2.9999361 sec
RG                           2050
DW                         16.000 usec
DE                           6.50 usec
TE                          297.5 K
D1                     3.00000000 sec
D11                    0.03000000 sec
TD0                             1

======== CHANNEL f1 ========
SFO1                  125.7049802 MHz
NUC1                          13C
P1                          10.00 usec
PLW1                  72.83999634 W

======== CHANNEL f2 ========
SFO2                  499.8724993 MHz
NUC2                           1H
CPDPRG[2                  waltz16
PCPD2                       80.00 usec
PLW2                  19.00000000 W
PLW12                  0.29688001 W

F2 - Processing parameters
SI                        1048576
SF                    125.6924019 MHz
WDW                            EM
SSB          0
LB                           0.30 Hz
GB           0
PC                           1.40
```

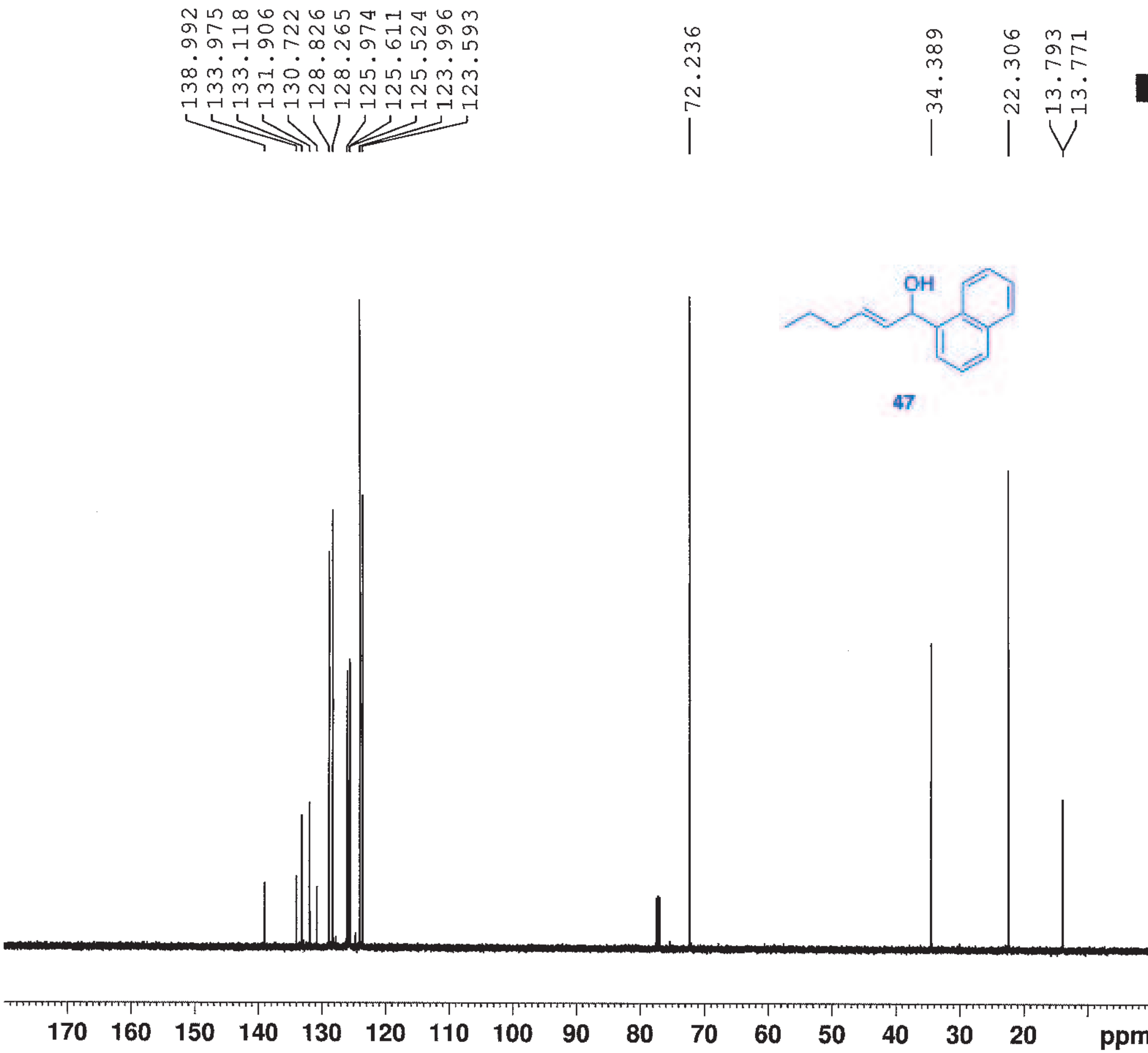



```
Current Data Parameters
NAME          Lan_20150406_B6063
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20150406
Time                       18.58
INSTRUM                    spect
PROBHD      5 mm PABBO BB/
PULPROG                       zg
TD                         59998
SOLVENT                    CDCl3
NS                             8
DS                             0
SWH                10000.000 Hz
FIDRES              0.166672 Hz
AQ                 2.9999001 sec
RG                           6.6
DW                   50.000 usec
DE                     6.50 usec
TE                     297.3 K
D1                5.00000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1          499.8730869 MHz
NUC1                       1H
P1                  10.75 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                       65536
SF             499.8700459 MHz
WDW                         EM
SSB          0
LB                     0.30 Hz
GB           0
PC                        1.00
```



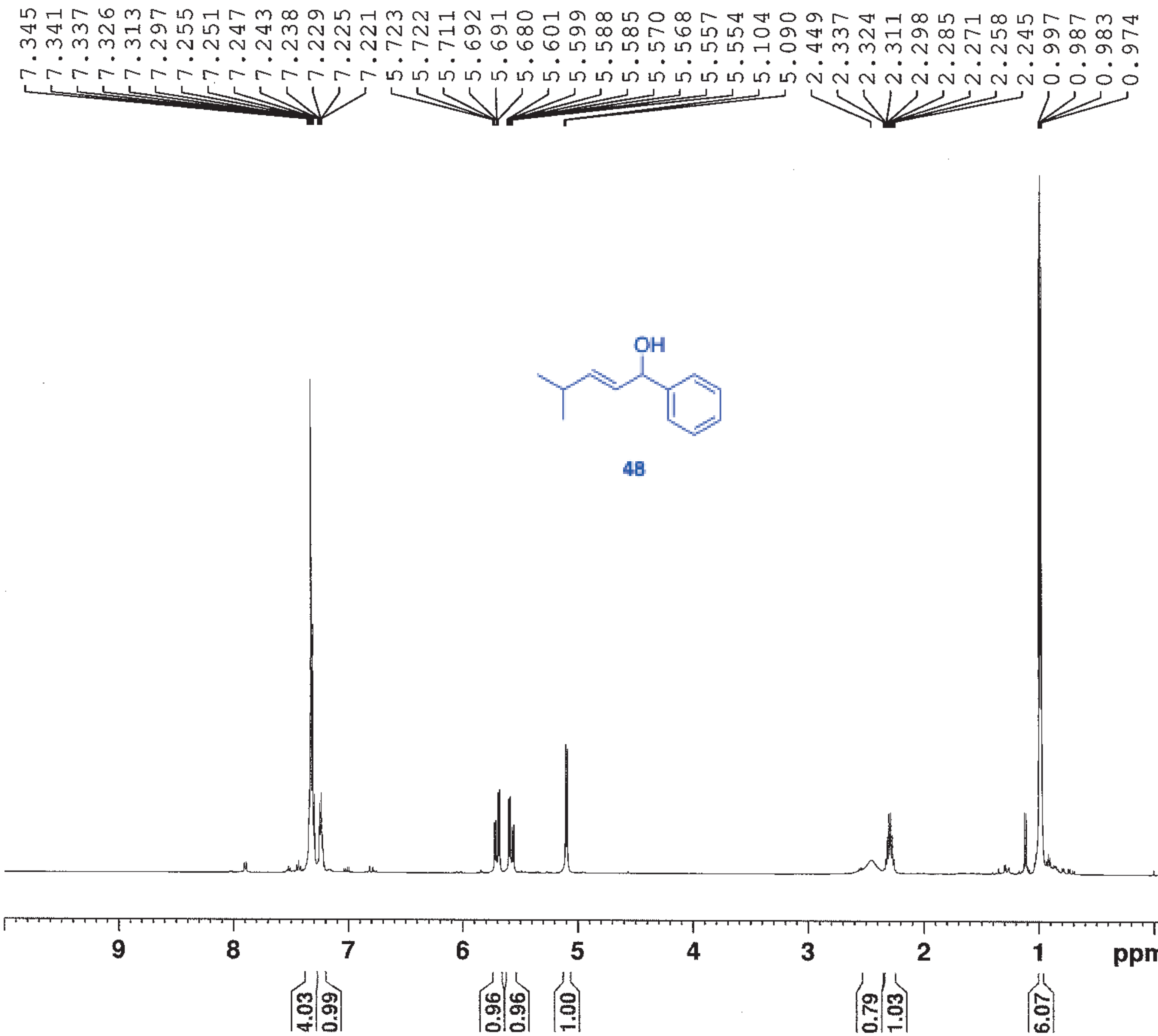

```
Current Data Parameters
NAME       Lan_20150406_B6063_C
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150406
Time                  19.04
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG                zgdc
TD                   187496
SOLVENT               CDCl3
NS                       27
DS                        0
SWH           31250.000 Hz
FIDRES         0.166670 Hz
AQ            2.9999361 sec
RG                     2050
DW              16.000 usec
DE                6.50 usec
TE                297.6 K
D1           3.00000000 sec
D11          0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1        125.7049802 MHz
NUC1                    13C
P1                10.00 usec
PLW1        72.83999634 W

======== CHANNEL f2 ========
SFO2        499.8724993 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2             80.00 usec
PLW2        19.00000000 W
PLW12        0.29688001 W

F2 - Processing parameters
SI                  1048576
SF          125.6924082 MHz
WDW                      EM
SSB       0
LB                  0.30 Hz
GB        0
PC                     1.40
```



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Current Data Parameters

NAME	Lan_20150406_B6103
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

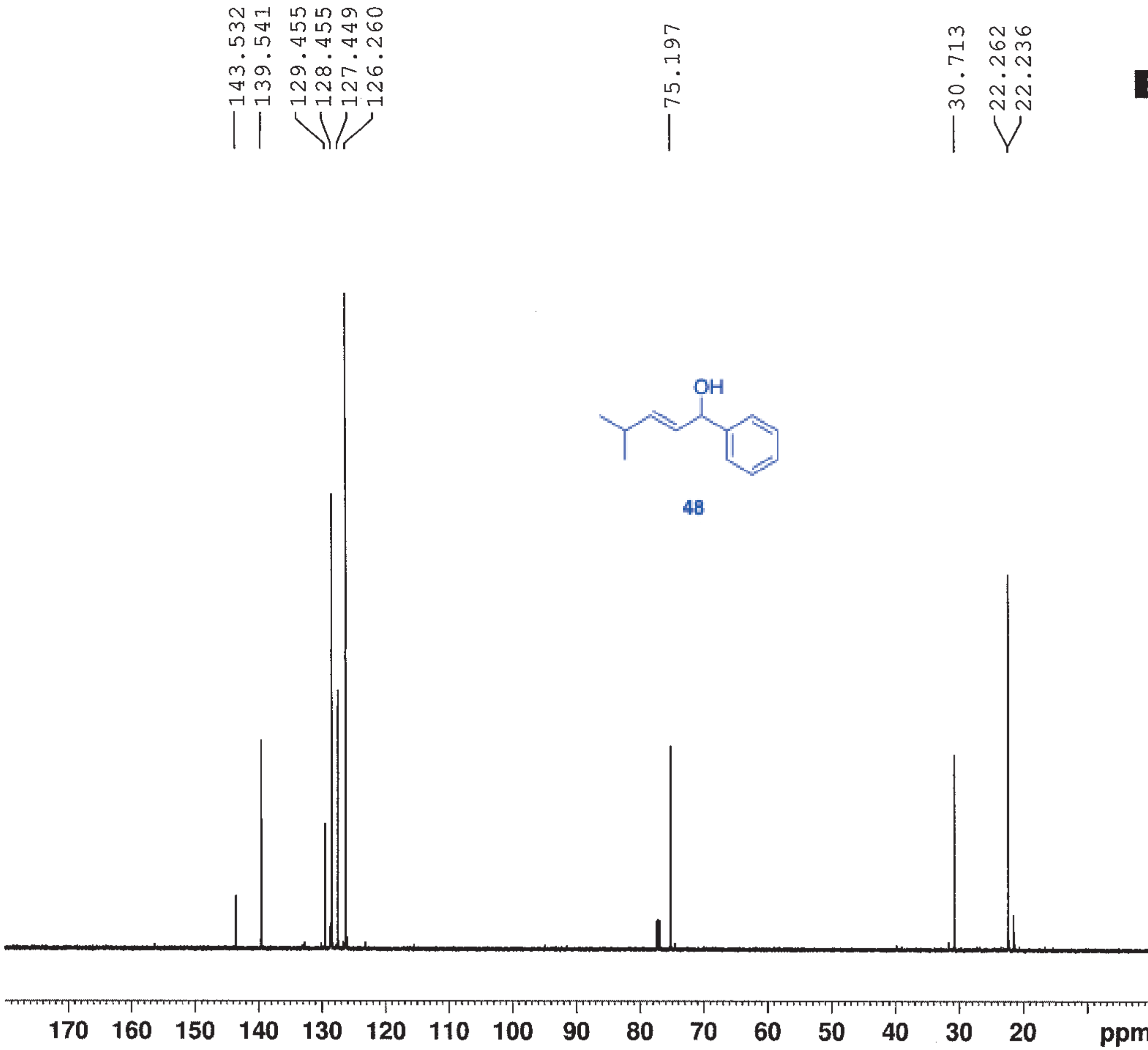
Date_	20150406
Time	16.34
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	8
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999001 sec
RG	5.21
DW	50.000 usec
DE	6.50 usec
TE	297.1 K
D1	5.00000000 sec
TD0	1

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

SFO1	499.8730869 MHz
NUC1	1H
P1	10.75 usec
PLW1	18.25000000 W

F2 - Processing parameters

SI	65536
SF	499.8700371 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



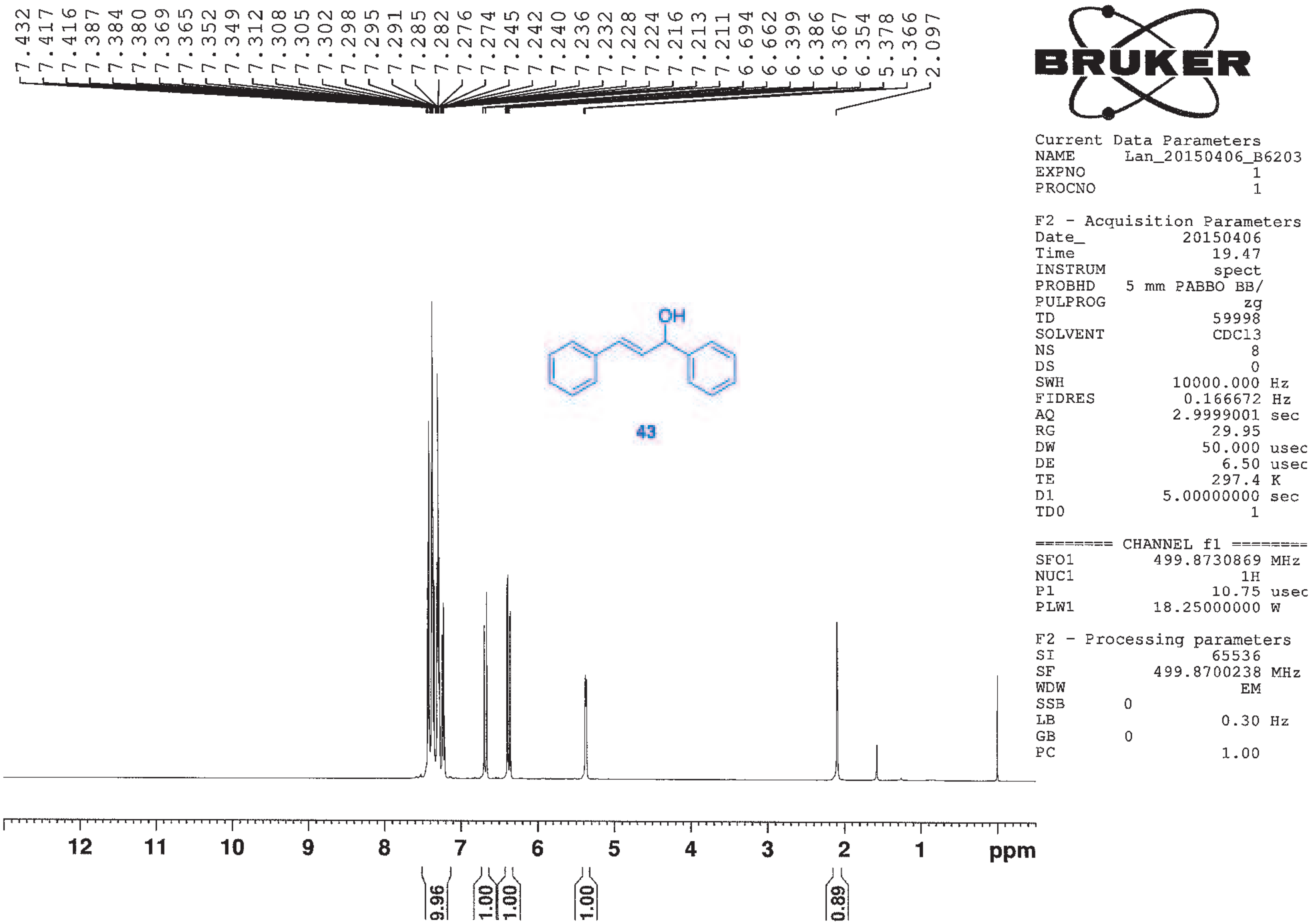

```
Current Data Parameters
NAME      Lan_20150406_B6103_C
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_             20150406
Time                 16.43
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG               zgdc
TD                  187496
SOLVENT              CDCl3
NS                      39
DS                       0
SWH              31250.000 Hz
FIDRES            0.166670 Hz
AQ               2.9999361 sec
RG                    2050
DW                  16.000 usec
DE                    6.50 usec
TE                   297.6 K
D1              3.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           125.7049802 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           72.83999634 W

======== CHANNEL f2 ========
SFO2           499.8724993 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           19.00000000 W
PLW12           0.29688001 W

F2 - Processing parameters
SI                 1048576
SF             125.6924111 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.40
```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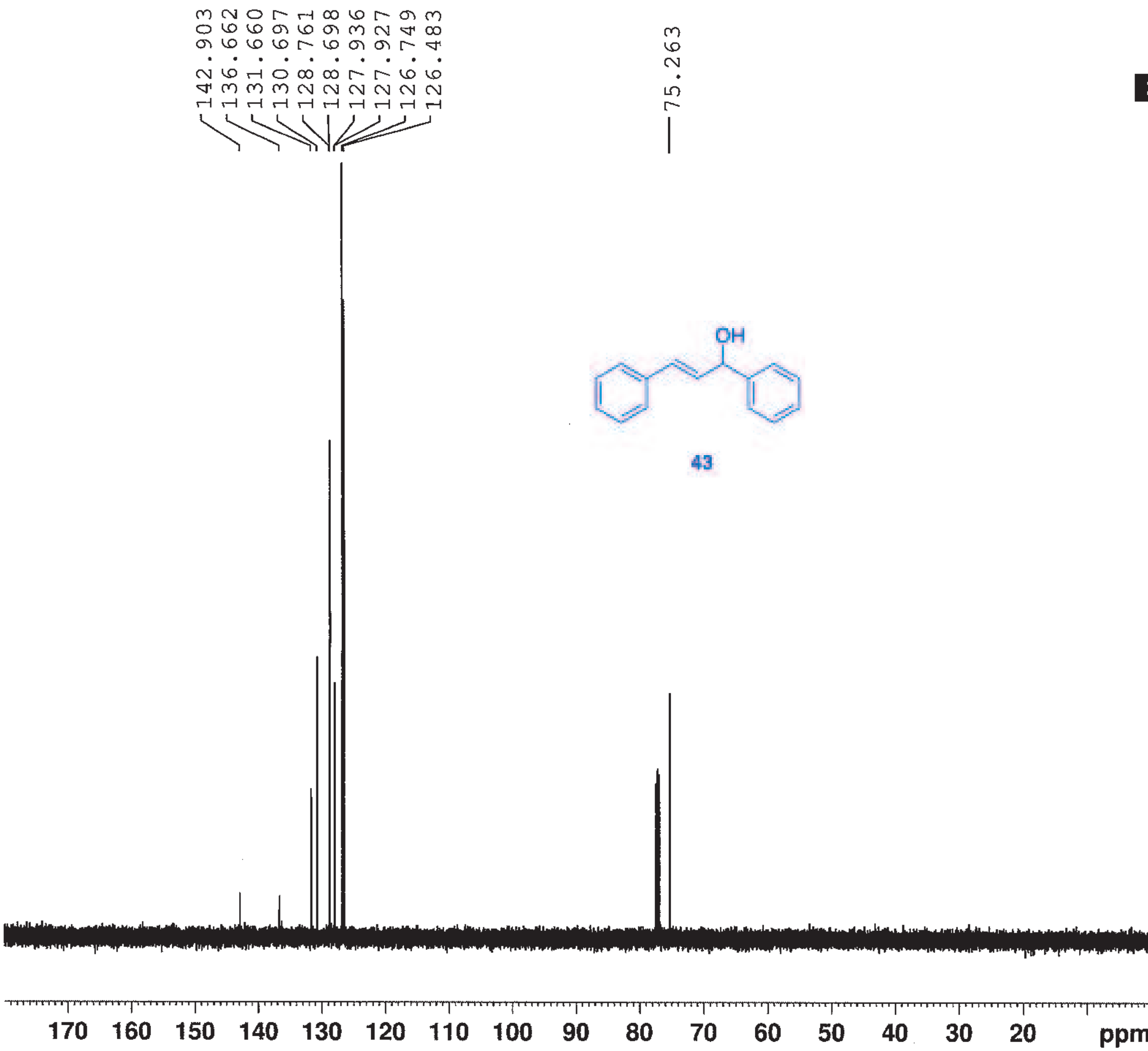
7.416
7.387
7.384
7.380
7.369
7.365
7.352
7.349
7.312
7.308
7.305
7.302
7.298
7.295
7.291
7.285
7.282
7.276
7.274
7.245
7.242
7.240
7.236
7.232
7.228
7.224
7.216
7.213
7.211
6.694
6.662
6.399
6.386
6.367
6.354
5.378
5.366
2.097
OH
43
Current Data Parameters
NAME Lan_20150406_B6203
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150406
Time 19.47
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 29.95
DW 50.000 usec
DE 6.50 usec
TE 297.4 K
D1 5.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 499.8730869 MHz
NUC1 1H
P1 10.75 usec
PLW1 18.25000000 W
F2 - Processing parameters
SI 65536
SF 499.8700238 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
12
11
10
9
8
7
6
5
4
3
2
1
ppm
9.96
1.00
1.00
1.00
0.89



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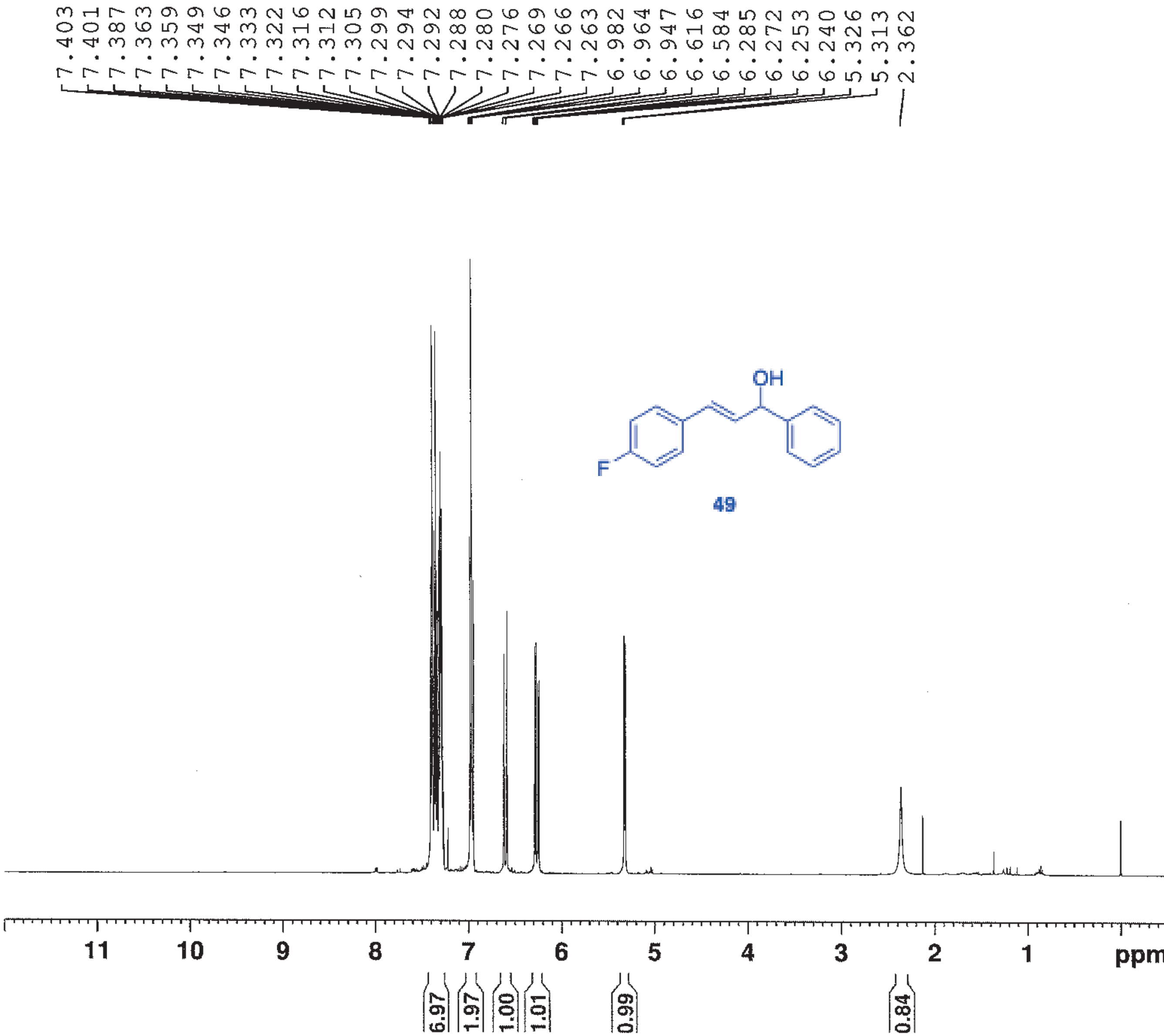
```
Current Data Parameters
NAME          Lan_20150406_B6203_C
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150406
Time                 19.53
INSTRUM              spect
PROBHD      5 mm PABBO BB/
PULPROG               zgdc
TD                  187496
SOLVENT              CDCl3
NS                      29
DS                       0
SWH              31250.000 Hz
FIDRES            0.166670 Hz
AQ               2.9999361 sec
RG                    2050
DW                  16.000 usec
DE                    6.50 usec
TE                   297.5 K
D1              3.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           125.7049802 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           72.83999634 W

======== CHANNEL f2 ========
SFO2           499.8724993 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           19.00000000 W
PLW12           0.29688001 W

F2 - Processing parameters
SI                 1048576
SF             125.6923991 MHz
WDW                     EM
SSB        0
LB                    0.30 Hz
GB         0
PC                    1.40
```

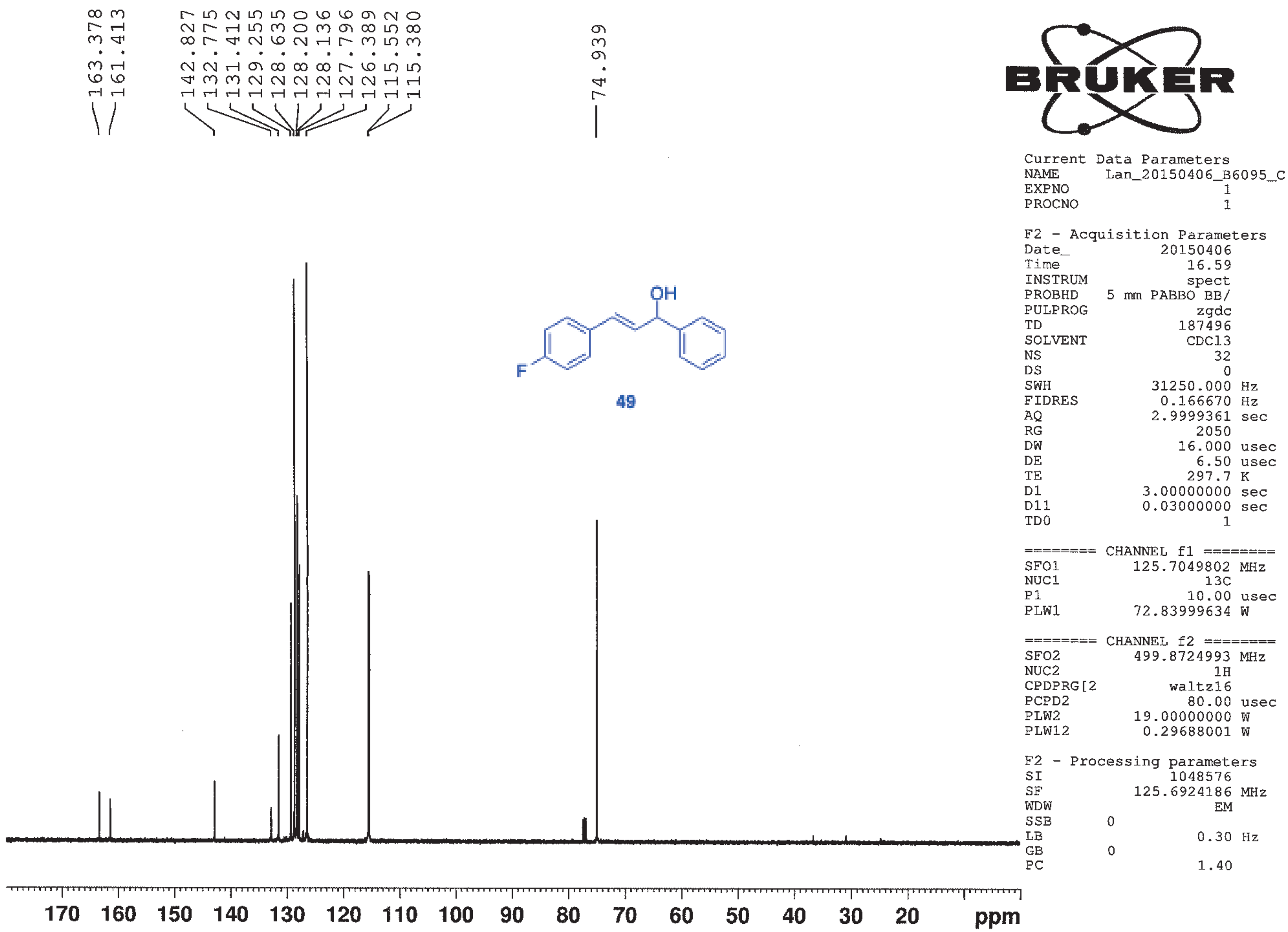


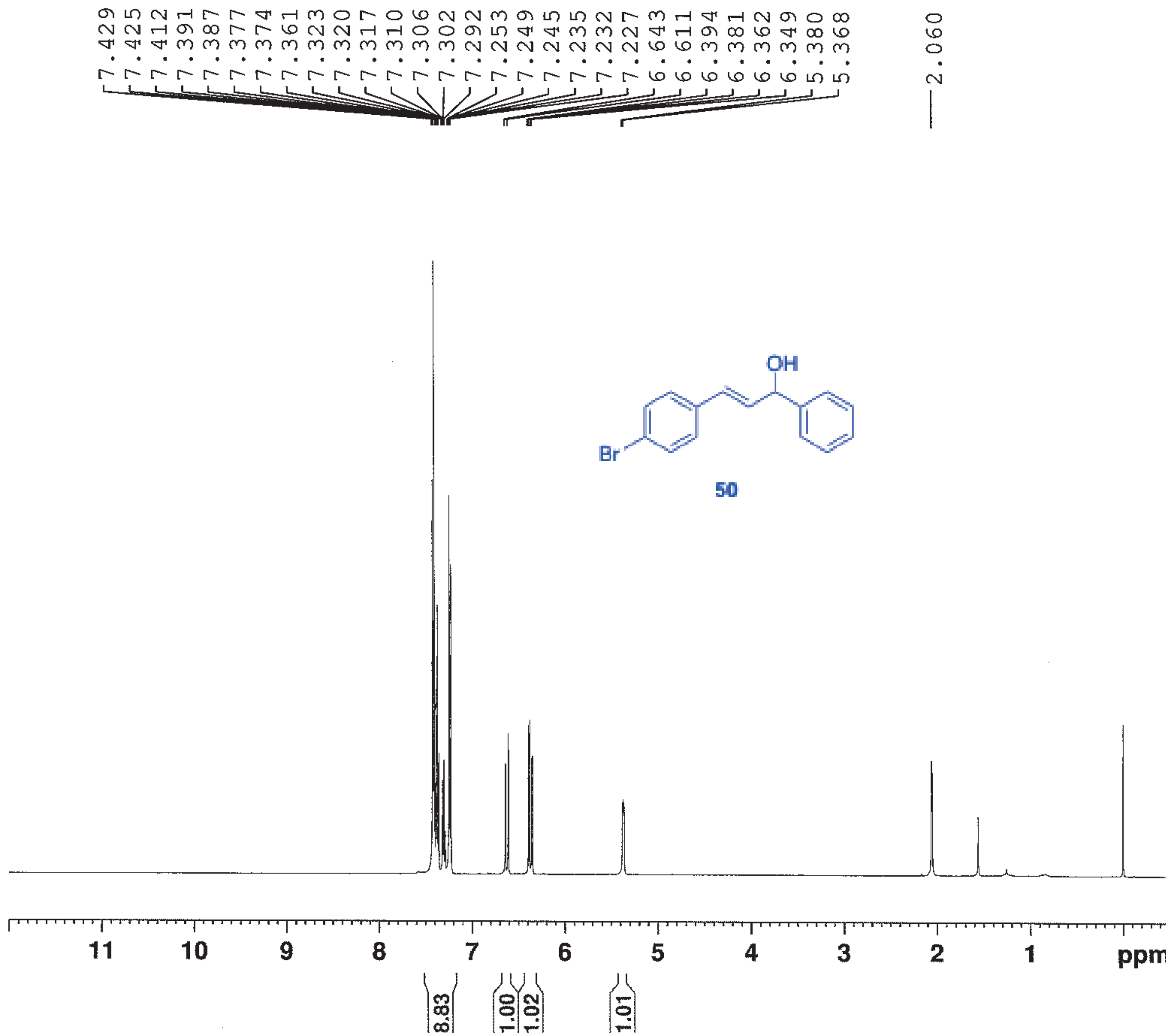
Current Data Parameters
NAME Lan_20150406_B6095
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150406
Time 18.24
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 15.35
DW 50.000 usec
DE 6.50 usec
TE 296.9 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 499.8730869 MHz
NUC1 1H
P1 10.75 usec
PLW1 18.25000000 W

F2 - Processing parameters
SI 65536
SF 499.8700325 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


163.378
161.413
142.827
132.775
131.412
129.255
128.635
128.200
128.136
127.796
126.389
115.552
115.380
74.939
OH
F
49
Current Data Parameters
NAME Lan_20150406_B6095_C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150406
Time 16.59
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgdc
TD 187496
SOLVENT CDCl3
NS 32
DS 0
SWH 31250.000 Hz
FIDRES 0.166670 Hz
AQ 2.9999361 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 297.7 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7049802 MHz
NUC1 13C
P1 10.00 usec
PLW1 72.83999634 W
======== CHANNEL f2 ========
SFO2 499.8724993 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.29688001 W
F2 - Processing parameters
SI 1048576
SF 125.6924186 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

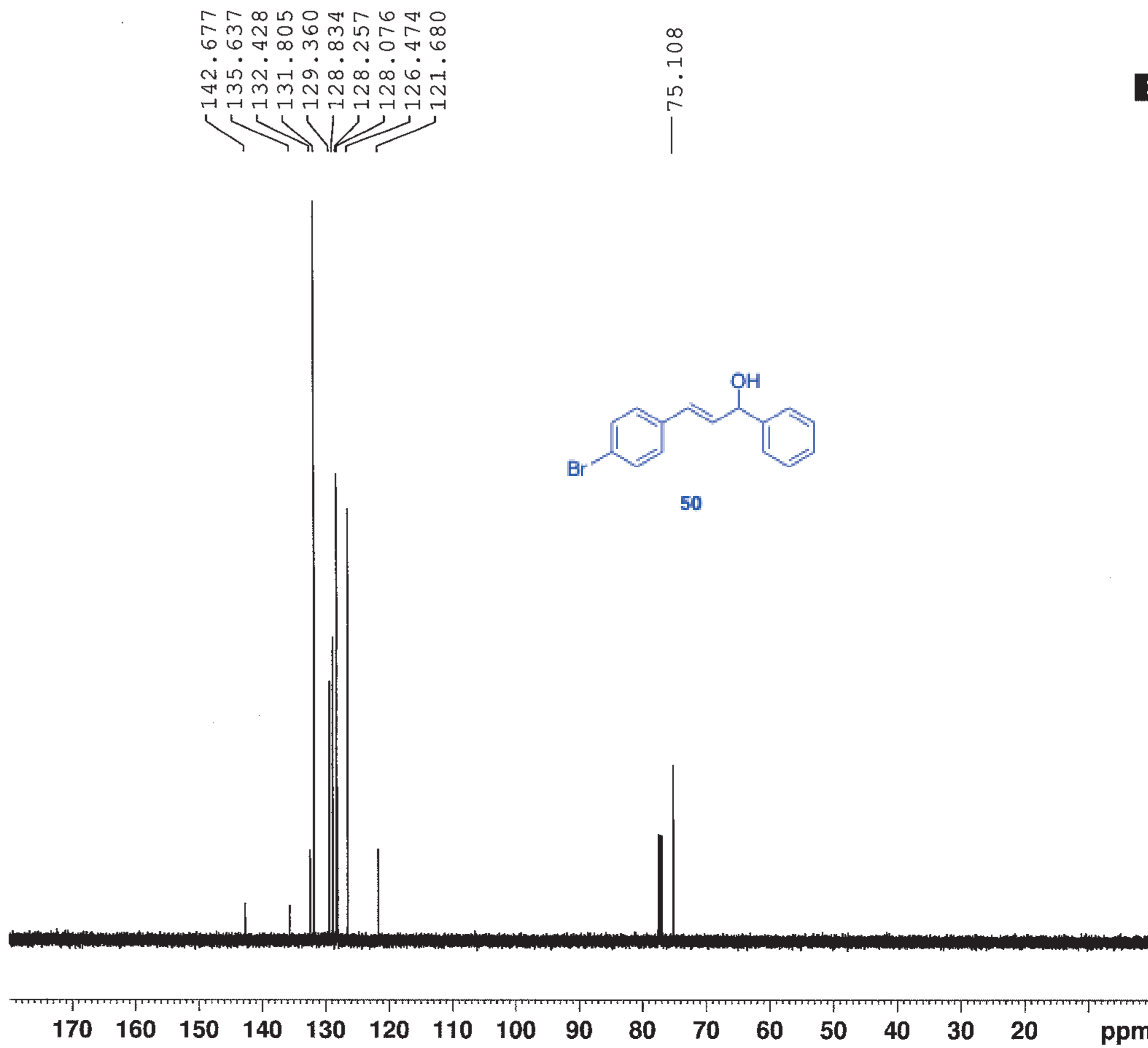



```
Current Data Parameters
NAME        Lan_20150406_B6165
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20150406
Time                  18.30
INSTRUM               spect
PROBHD     5 mm PABBO BB/
PULPROG                  zg
TD                    59998
SOLVENT               CDCl3
NS                        8
DS                        0
SWH               10000.000 Hz
FIDRES             0.166672 Hz
AQ                2.9999001 sec
RG                    44.57
DW                   50.000 usec
DE                     6.50 usec
TE                    296.9 K
D1               5.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1         499.8730869 MHz
NUC1                  1H
P1                 10.75 usec
PLW1         18.25000000 W

F2 - Processing parameters
SI                    65536
SF              499.8700155 MHz
WDW                      EM
SSB       0
LB                     0.30 Hz
GB        0
PC                     1.00
```



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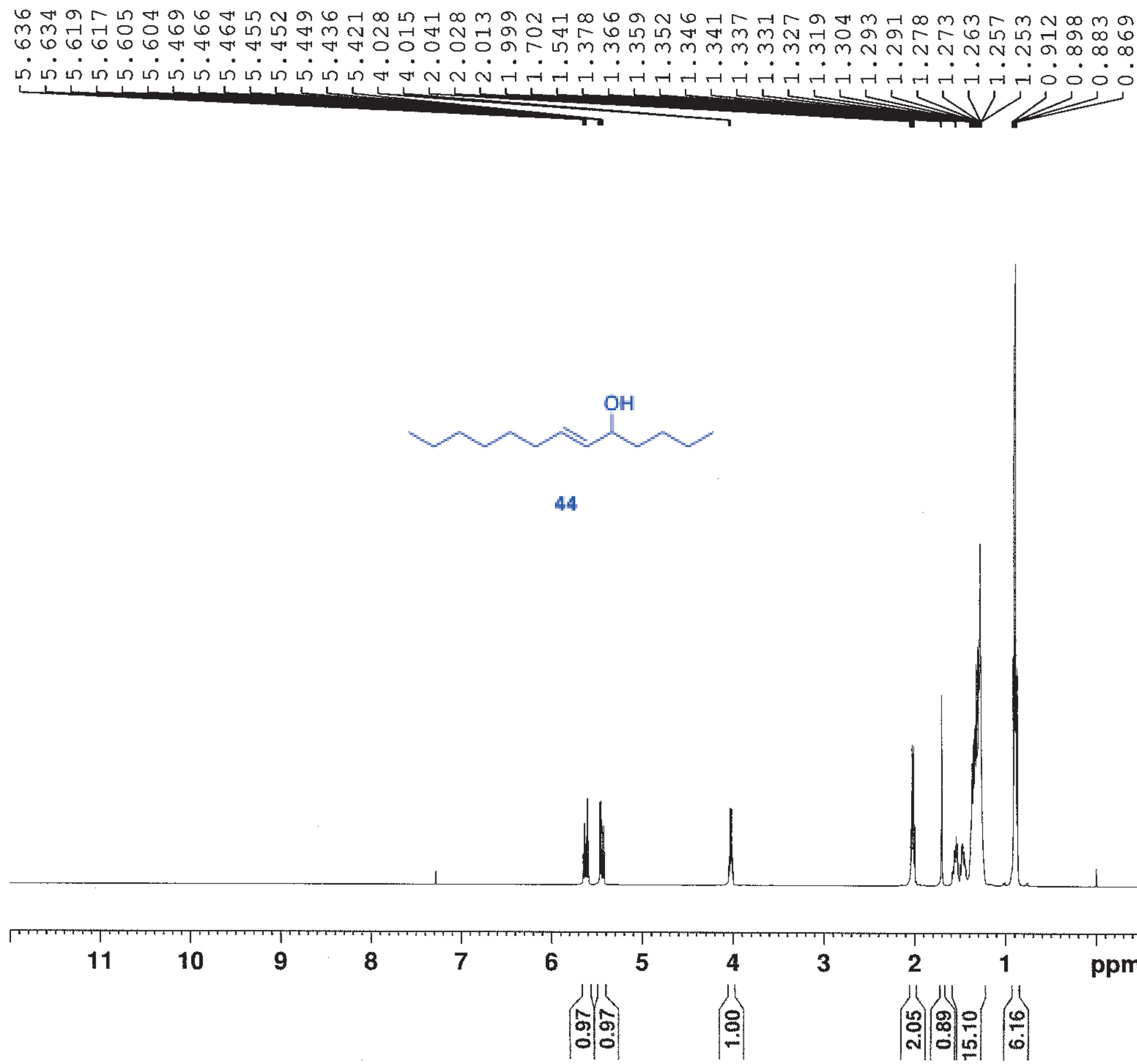
Current Data Parameters
NAME Lan_20150406_B6165_C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150406
Time 15.53
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgdc
TD 187496
SOLVENT CDCl3
NS 32
DS 0
SWH 31250.000 Hz
FIDRES 0.166670 Hz
AQ 2.9999361 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 297.7 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 125.7049802 MHz
NUC1 13C
P1 10.00 usec
PLW1 72.83999634 W

======== CHANNEL f2 ========
SFO2 499.8724993 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.29688001 W

F2 - Processing parameters
SI 1048576
SF 125.6923983 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40

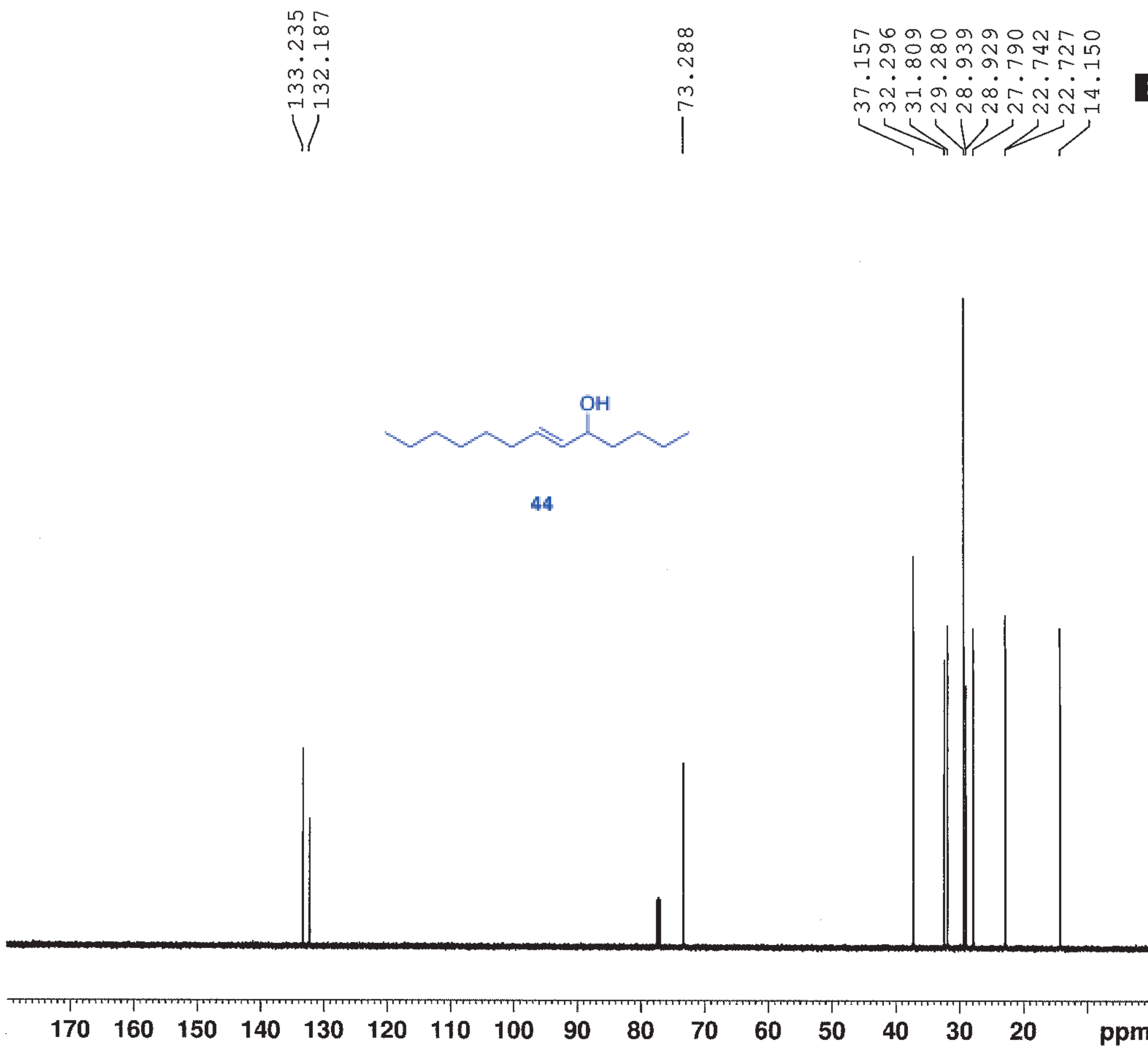



```
Current Data Parameters
NAME          Lan_20150406_B5299
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20150406
Time                       20.01
INSTRUM                    spect
PROBHD       5 mm PABBO BB/
PULPROG                       zg
TD                         59998
SOLVENT                    CDCl3
NS                             8
DS                             0
SWH                    10000.000 Hz
FIDRES                  0.166672 Hz
AQ                     2.9999001 sec
RG                          4.57
DW                        50.000 usec
DE                          6.50 usec
TE                         297.4 K
D1                    5.00000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                 499.8730869 MHz
NUC1                          1H
P1                         10.75 usec
PLW1                 18.25000000 W

F2 - Processing parameters
SI                         65536
SF                   499.8700011 MHz
WDW                           EM
SSB          0
LB                          0.30 Hz
GB           0
PC                          1.00
```



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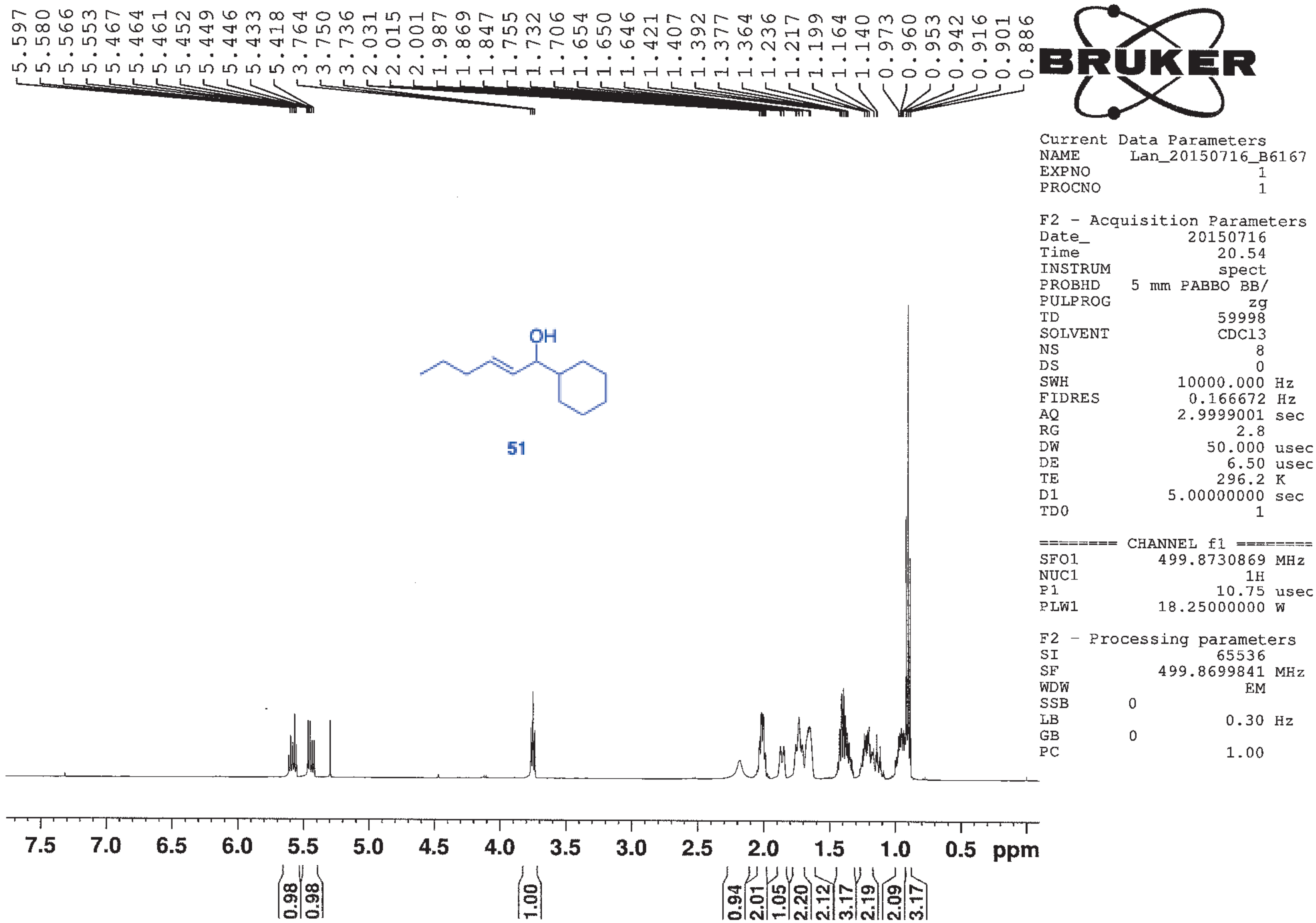
Current Data Parameters	
NAME	Lan_20150406_B5299_C
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters	
Date_	20150406
Time	20.07
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgdc
TD	187496
SOLVENT	CDCl3
NS	25
DS	0
SWH	31250.000 Hz
FIDRES	0.166670 Hz
AQ	2.9999361 sec
RG	2050
DW	16.000 usec
DE	6.50 usec
TE	297.5 K
D1	3.00000000 sec
D11	0.03000000 sec
TD0	1

======== CHANNEL f1 ========	
SFO1	125.7049802 MHz
NUC1	13C
P1	10.00 usec
PLW1	72.83999634 W

======== CHANNEL f2 ========	
SFO2	499.8724993 MHz
NUC2	1H
CPDPRG[2	waltz16
PCPD2	80.00 usec
PLW2	19.00000000 W
PLW12	0.29688001 W

F2 - Processing parameters	
SI	1048576
SF	125.6923969 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.40


5.597 5.580 5.566 5.553 5.467 5.464 5.461 5.452 5.449 5.446 5.433 5.418 3.764 3.750 3.736 2.031 2.015 2.001 1.987 1.869 1.847 1.755 1.732 1.706 1.654 1.650 1.646 1.421 1.407 1.392 1.377 1.364 1.236 1.217 1.199 1.164 1.140 0.973 0.960 0.953 0.942 0.916 0.901 0.886
BRUKER
OH
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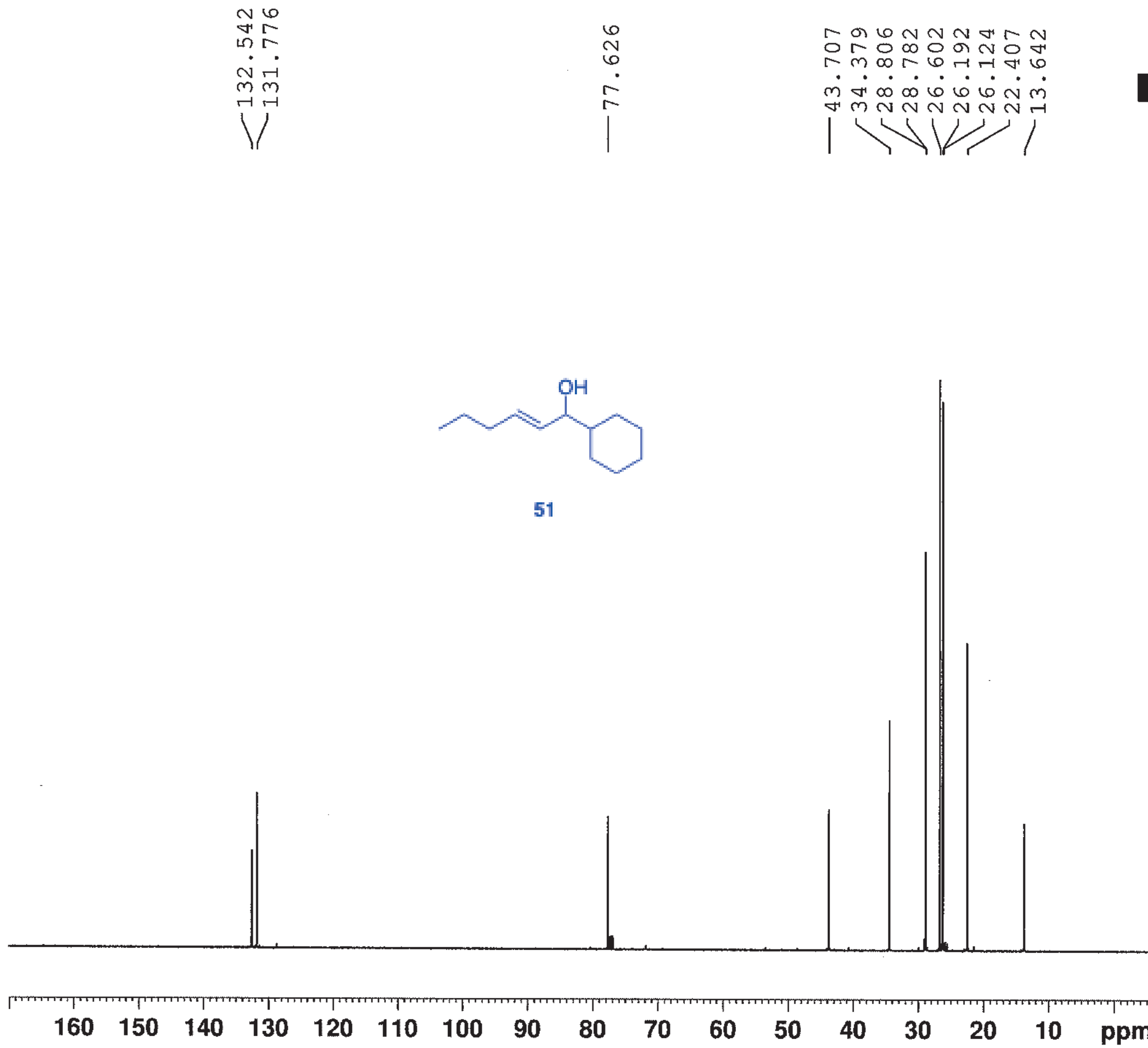
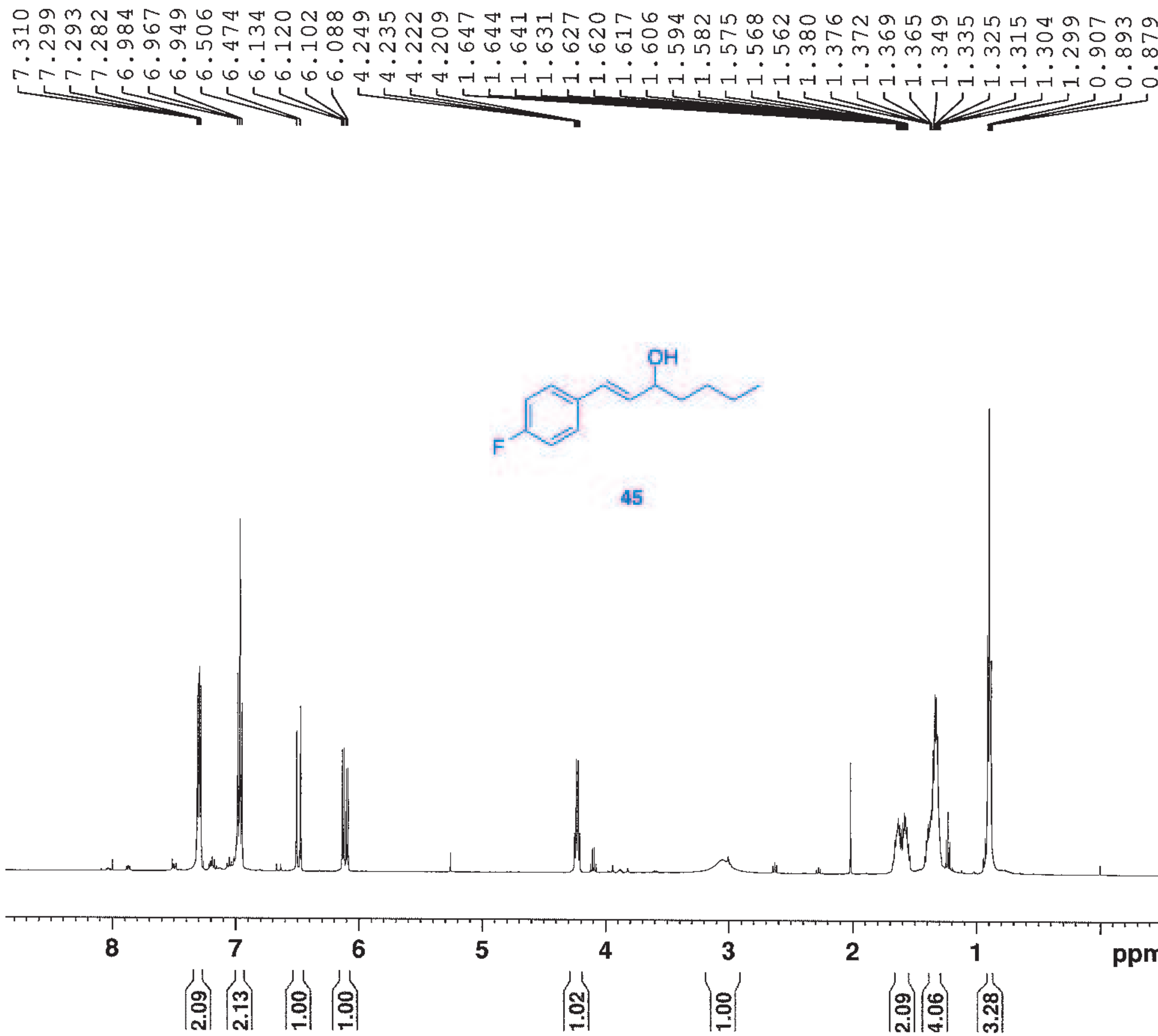
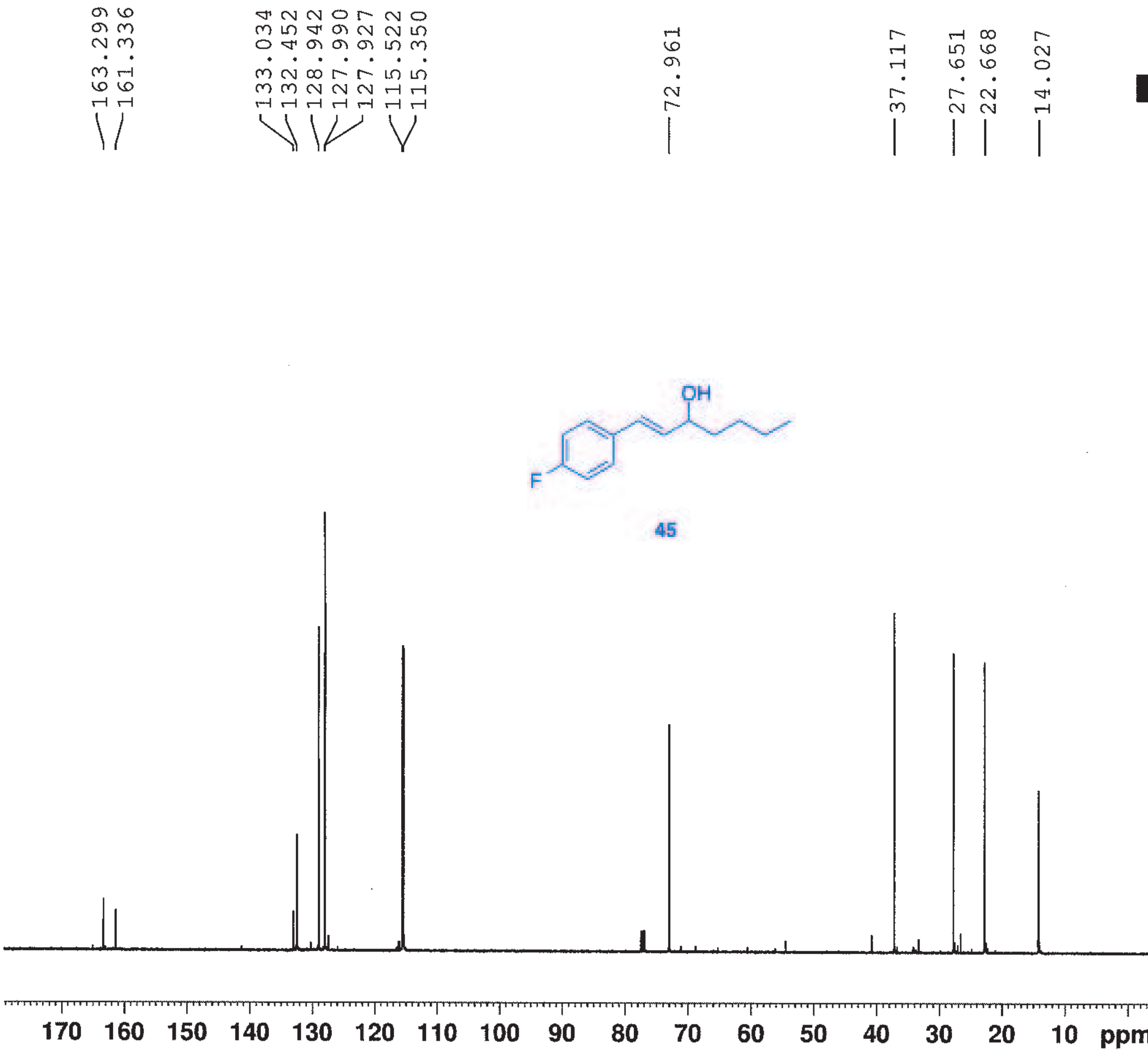
Current Data Parameters
NAME Lan_20150716_B6167
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150716
Time 20.54
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 2.8
DW 50.000 usec
DE 6.50 usec
TE 296.2 K
D1 5.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 499.8730869 MHz
NUC1 1H
P1 10.75 usec
PLW1 18.25000000 W
F2 - Processing parameters
SI 65536
SF 499.8699841 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.98 0.98 1.00 0.94 2.01 1.05 2.20 2.12 3.17 2.19 2.09 3.17




```
Current Data Parameters
NAME       Lan_20150716_B6167_C
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_              20150716
Time                  21.04
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG                zgdc
TD                   187496
SOLVENT               CDCl3
NS                       69
DS                        0
SWH            31250.000 Hz
FIDRES          0.166670 Hz
AQ             2.9999361 sec
RG                     2050
DW               16.000 usec
DE                 6.50 usec
TE                296.9 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1        125.7049802 MHz
NUC1                    13C
P1                10.00 usec
PLW1        72.83999634 W

======== CHANNEL f2 ========
SFO2        499.8724993 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2             80.00 usec
PLW2        19.00000000 W
PLW12        0.29688001 W

F2 - Processing parameters
SI                  1048576
SF          125.6924053 MHz
WDW                      EM
SSB      0
LB                  0.30 Hz
GB       0
PC                     1.40
```



Current Data Parameters	
NAME	Lan_20150716_B6093
EXPNO	1
PROCNO	1
F2 - Acquisition Parameters	
Date_	20150716
Time	20.34
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	8
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999001 sec
RG	3.89
DW	50.000 usec
DE	6.50 usec
TE	295.9 K
D1	5.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	499.8730869 MHz
NUC1	1H
P1	10.75 usec
PLW1	18.25000000 W
F2 - Processing parameters	
SI	65536
SF	499.8700113 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



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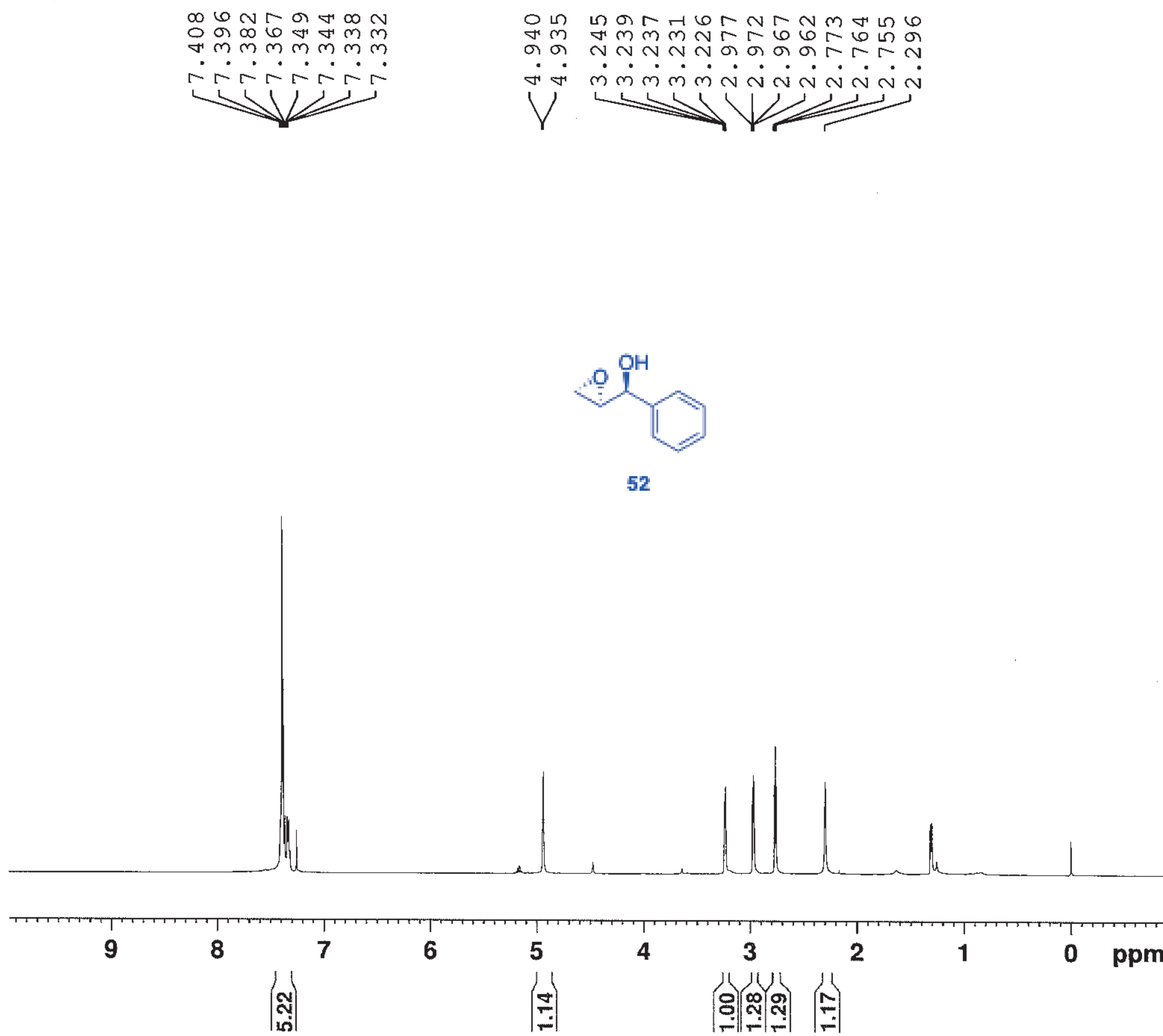
```
Current Data Parameters
NAME          Lan_20150716_B6093_C
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150716
Time                 20.44
INSTRUM              spect
PROBHD     5 mm PABBO BB/
PULPROG               zgdc
TD                  187496
SOLVENT              CDCl3
NS                      75
DS                       0
SWH              31250.000 Hz
FIDRES            0.166670 Hz
AQ               2.9999361 sec
RG                    2050
DW                  16.000 usec
DE                    6.50 usec
TE                   296.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           125.7049802 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           72.83999634 W

======== CHANNEL f2 ========
SFO2           499.8724993 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           19.00000000 W
PLW12           0.29688001 W

F2 - Processing parameters
SI                 1048576
SF             125.6924085 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.40
```



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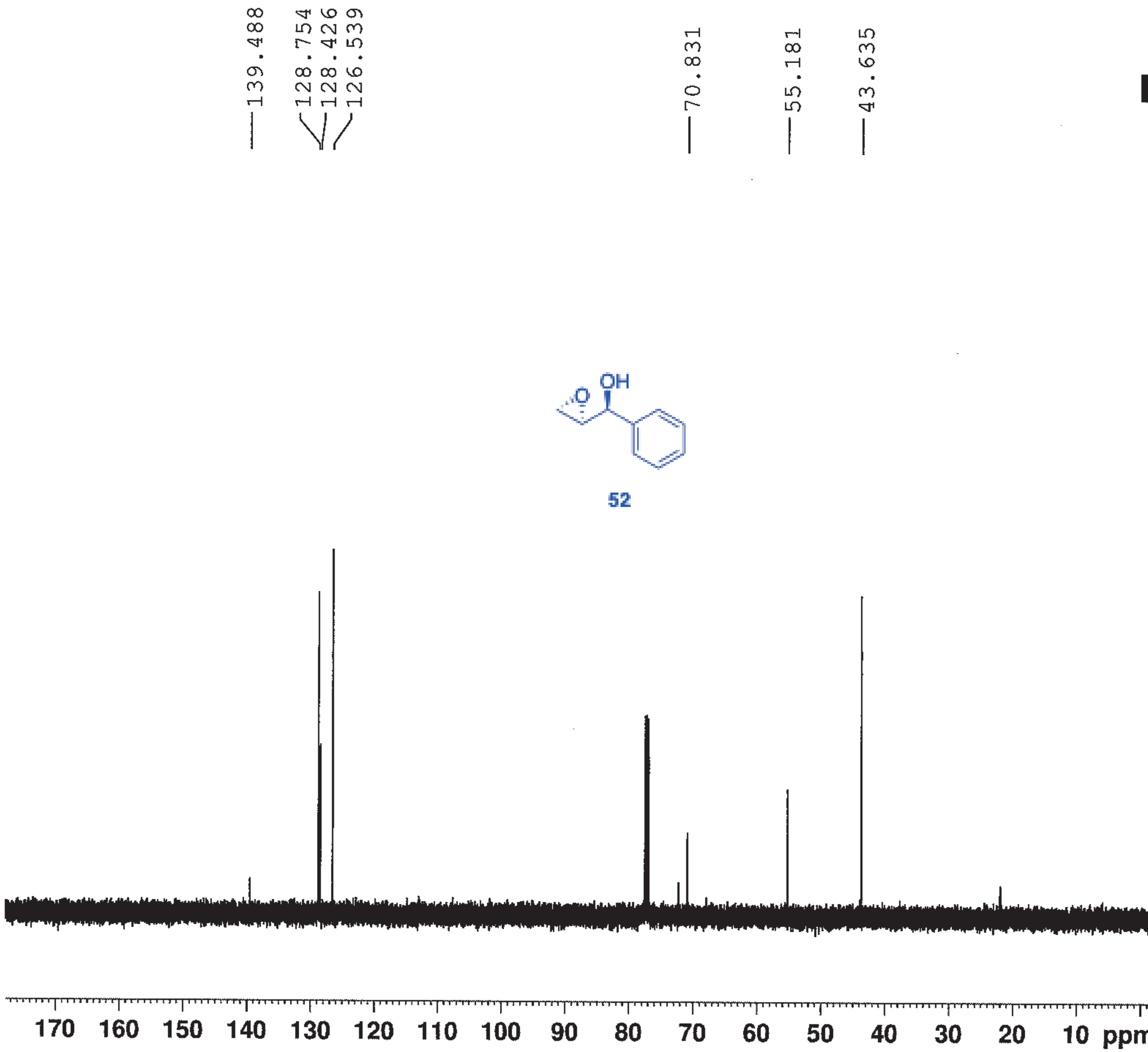
Current Data Parameters	
NAME	Lan_20150921_B6051_1
EXPNO	1
PROCNO	1
F2 - Acquisition Parameters	
Date_	20150921
Time	18.30
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	8
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999001 sec
RG	44.57
DW	50.000 usec
DE	6.50 usec
TE	297.0 K
D1	3.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	499.8730869 MHz
NUC1	1H
P1	10.75 usec
PLW1	18.25000000 W
F2 - Processing parameters	
SI	65536
SF	499.8700136 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



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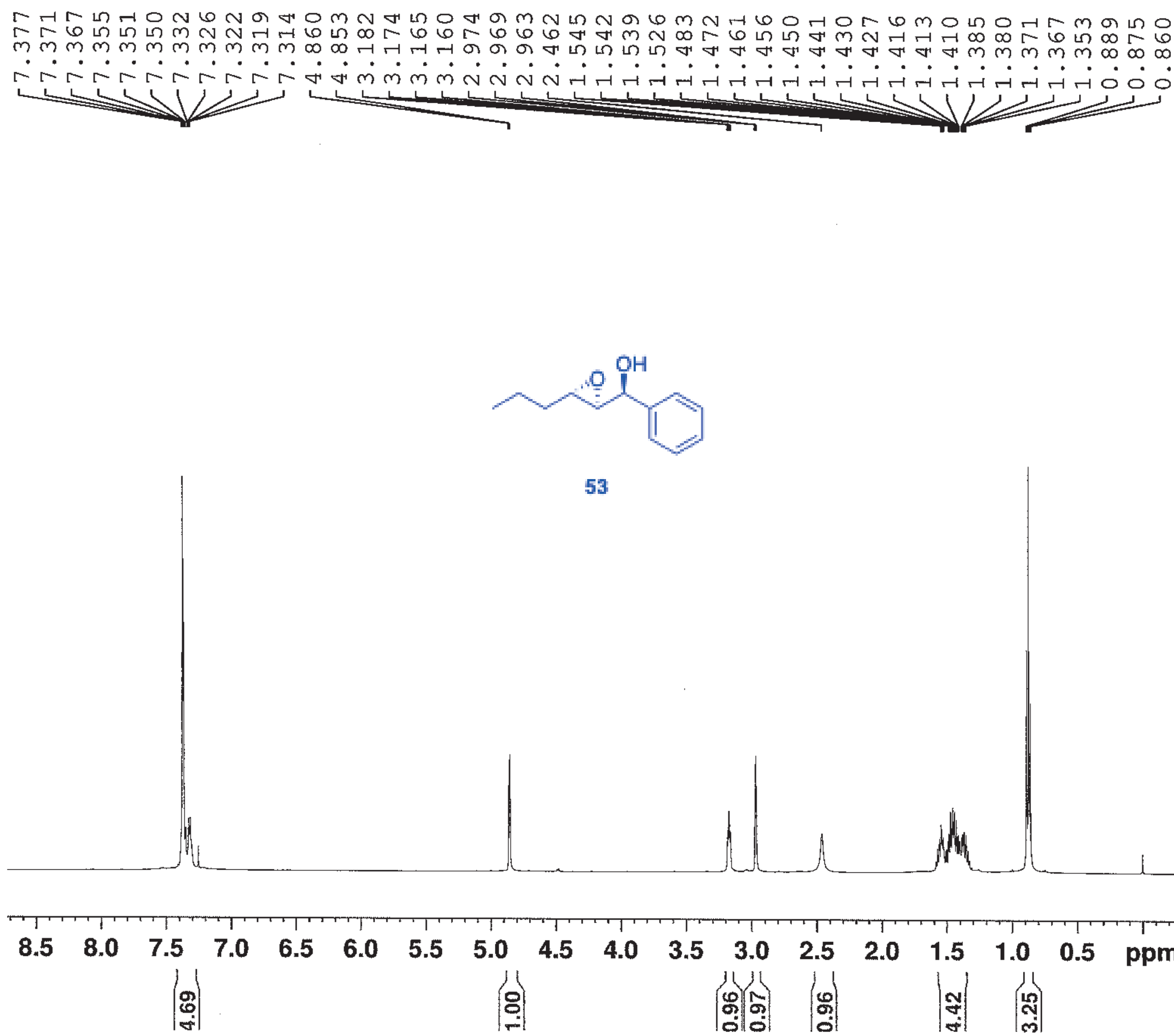
Current Data Parameters	
NAME	Lan_20150921_B6051_1_C
EXPNO	1
PROCNO	1
F2 - Acquisition Parameters	
Date_	20150921
Time	18.45
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgdc
TD	187496
SOLVENT	CDCl3
NS	16
DS	0
SWH	31250.000 Hz
FIDRES	0.166670 Hz
AQ	2.9999361 sec
RG	2050
DW	16.000 usec
DE	6.50 usec
TE	297.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	125.7049802 MHz
NUC1	13C
P1	10.00 usec
PLW1	72.83999634 W
======== CHANNEL f2 ========	
SFO2	499.8724993 MHz
NUC2	1H
CPDPRG[2	waltz16
PCPD2	80.00 usec
PLW2	19.00000000 W
PLW12	0.29688001 W
F2 - Processing parameters	
SI	1048576
SF	125.6923972 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.40

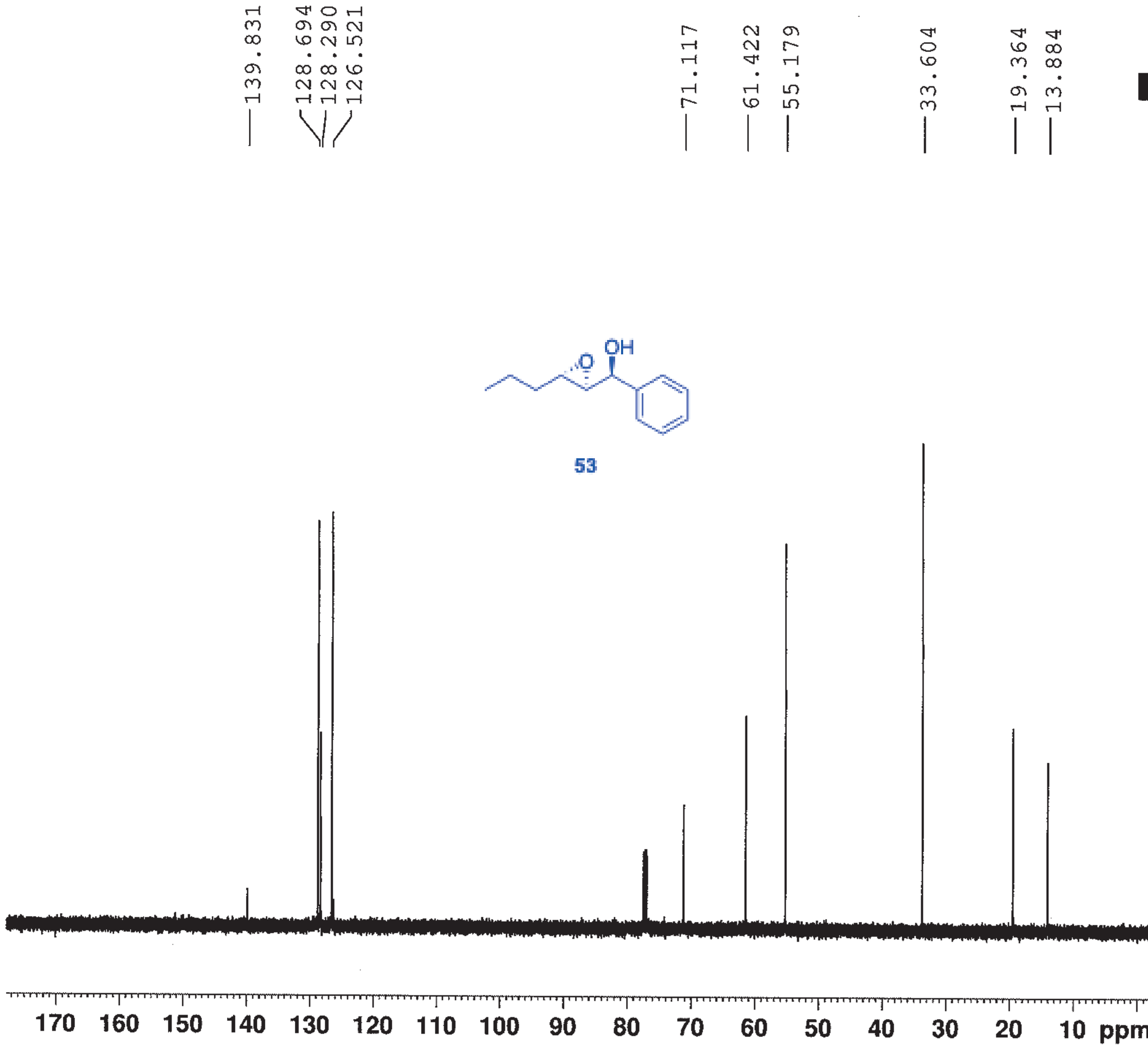



```
Current Data Parameters
NAME        Lan_20150915_B6089
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20150915
Time                     21.36
INSTRUM                  spect
PROBHD      5 mm PABBO BB/
PULPROG                     zg
TD                       59998
SOLVENT                  CDCl3
NS                           8
DS                           0
SWH                  10000.000 Hz
FIDRES                0.166672 Hz
AQ                   2.9999001 sec
RG                       22.37
DW                      50.000 usec
DE                        6.50 usec
TE                       297.2 K
D1                  5.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1              499.8730869 MHz
NUC1                        1H
P1                       10.75 usec
PLW1               18.25000000 W

F2 - Processing parameters
SI                       65536
SF                 499.8700146 MHz
WDW                         EM
SSB      0
LB                        0.30 Hz
GB       0
PC                        1.00
```



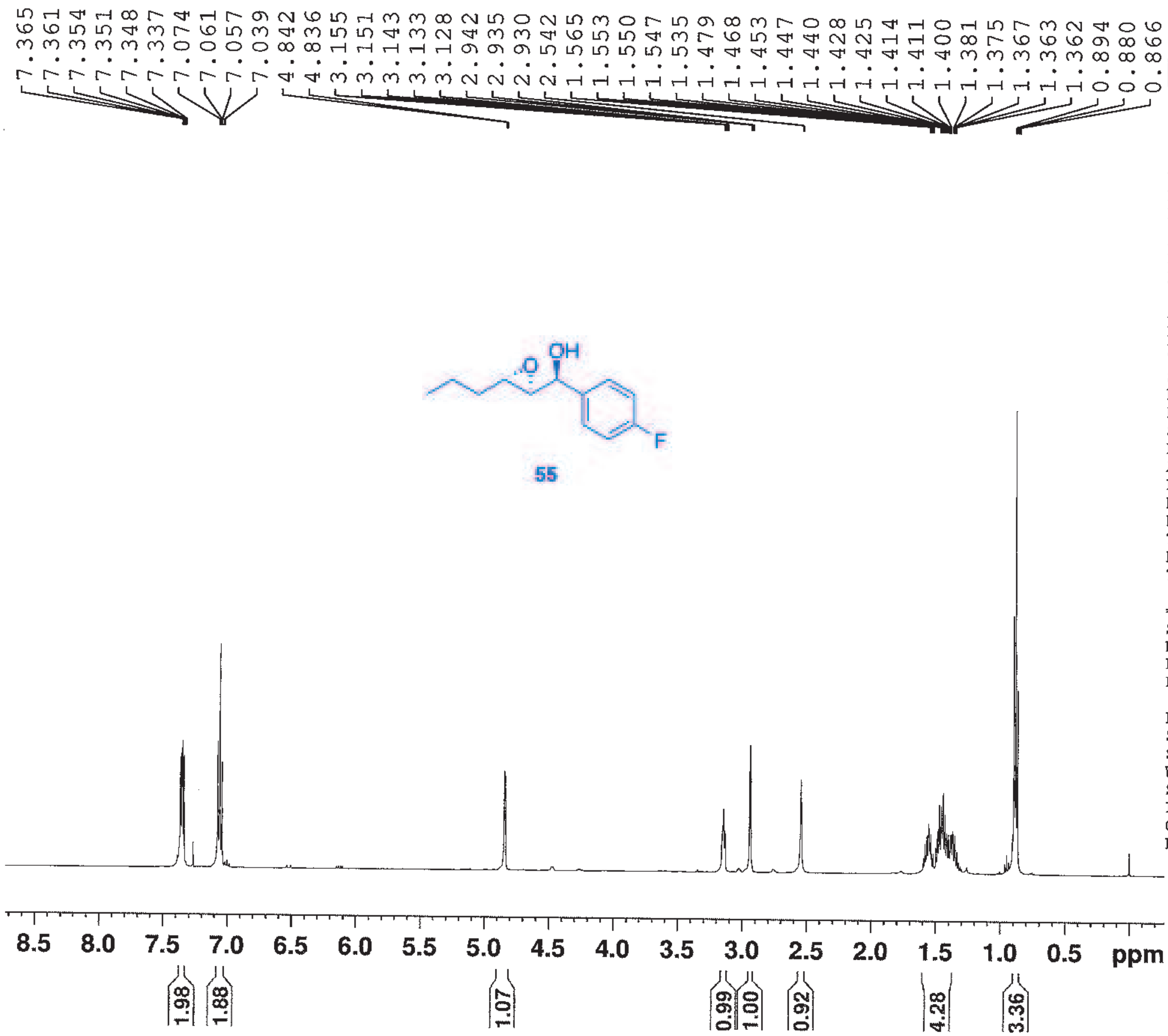
Current Data Parameters
NAME Lan_20150915_B6089_C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150915
Time 21.42
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgdc
TD 187496
SOLVENT CDCl3
NS 29
DS 0
SWH 31250.000 Hz
FIDRES 0.166670 Hz
AQ 2.9999361 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 297.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 125.7049802 MHz
NUC1 13C
P1 10.00 usec
PLW1 72.83999634 W

======== CHANNEL f2 ========
SFO2 499.8724993 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.29688001 W

F2 - Processing parameters
SI 1048576
SF 125.6923987 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40

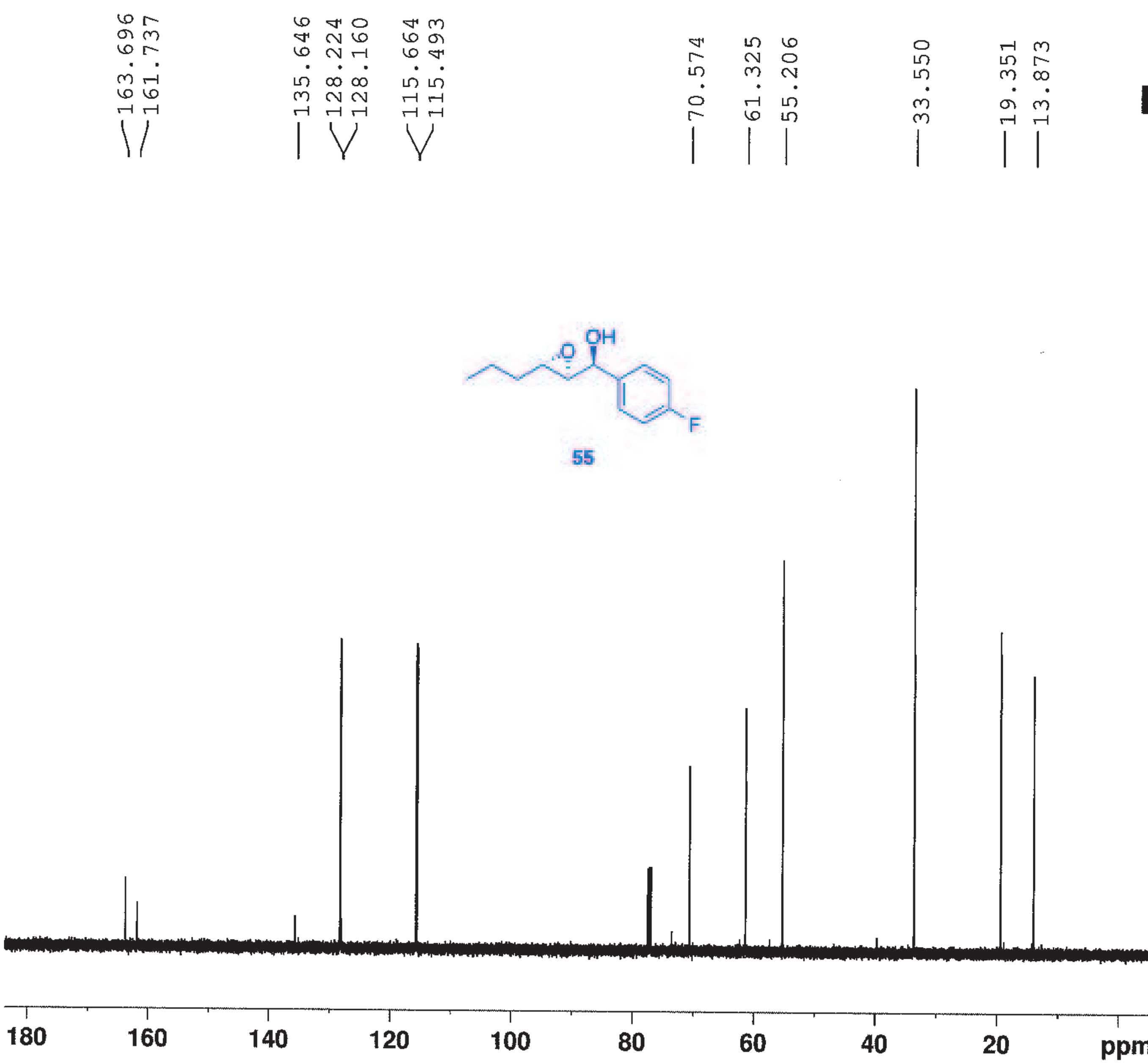



```
Current Data Parameters
NAME        Lan_20150914_B6065
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_               20150914
Time                   21.30
INSTRUM                spect
PROBHD     5 mm PABBO BB/
PULPROG                   zg
TD                     59998
SOLVENT                CDCl3
NS                         8
DS                         0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                     19.64
DW                50.000 usec
DE                  6.50 usec
TE                 295.8 K
D1            5.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1       499.8730869 MHz
NUC1                    1H
P1                10.75 usec
PLW1         18.25000000 W

F2 - Processing parameters
SI                     65536
SF           499.8700092 MHz
WDW                       EM
SSB        0
LB                   0.30 Hz
GB         0
PC                      1.00
```



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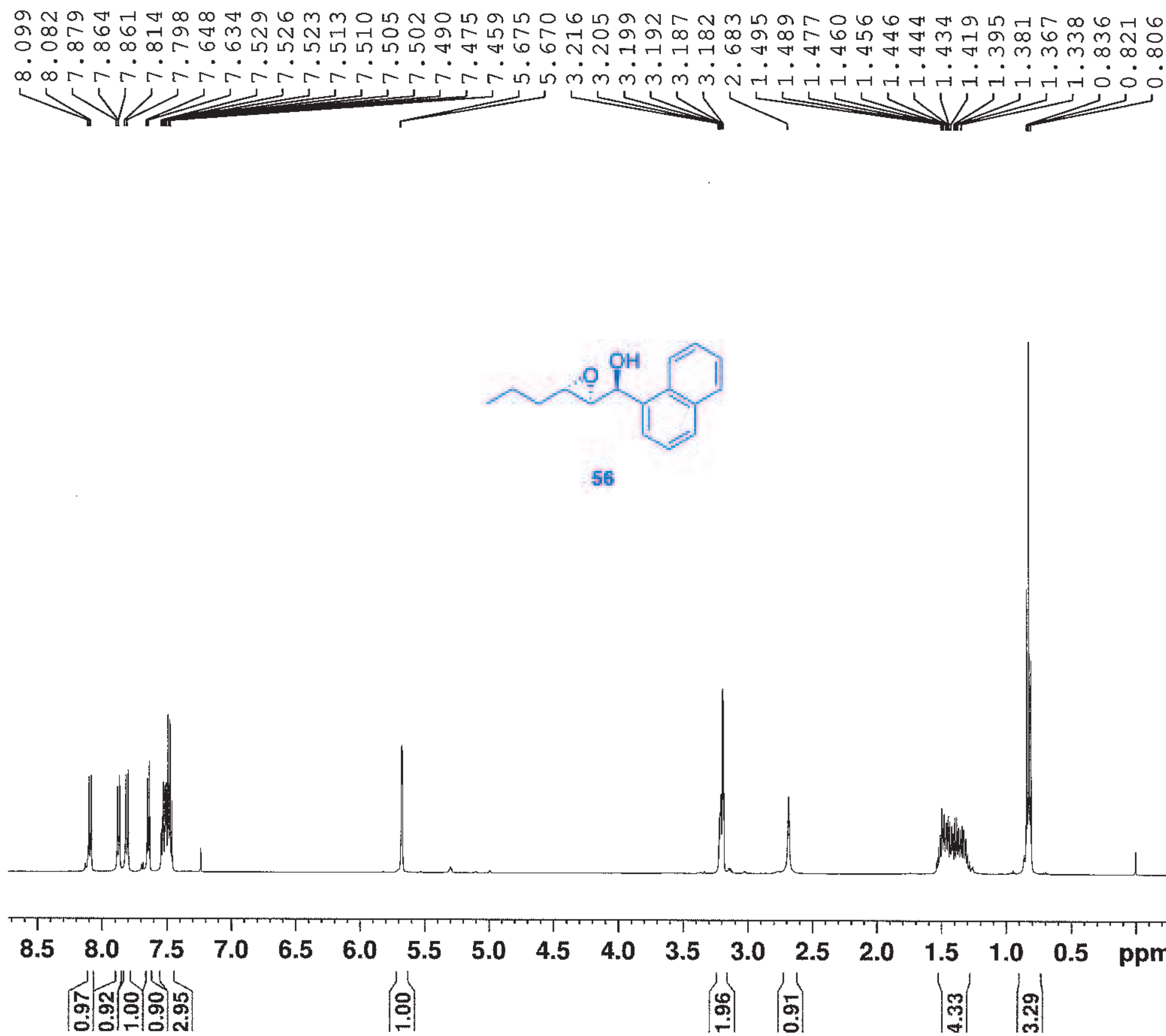
```
Current Data Parameters
NAME          Lan_20150914_B6065_C
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150914
Time                 21.43
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zgdc
TD                  187496
SOLVENT              CDCl3
NS                      35
DS                       0
SWH              31250.000 Hz
FIDRES            0.166670 Hz
AQ               2.9999361 sec
RG                    2050
DW                  16.000 usec
DE                    6.50 usec
TE                   296.4 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           125.7049802 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           72.83999634 W

======== CHANNEL f2 ========
SFO2           499.8724993 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           19.00000000 W
PLW12           0.29688001 W

F2 - Processing parameters
SI                 1048576
SF             125.6923972 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.40
```



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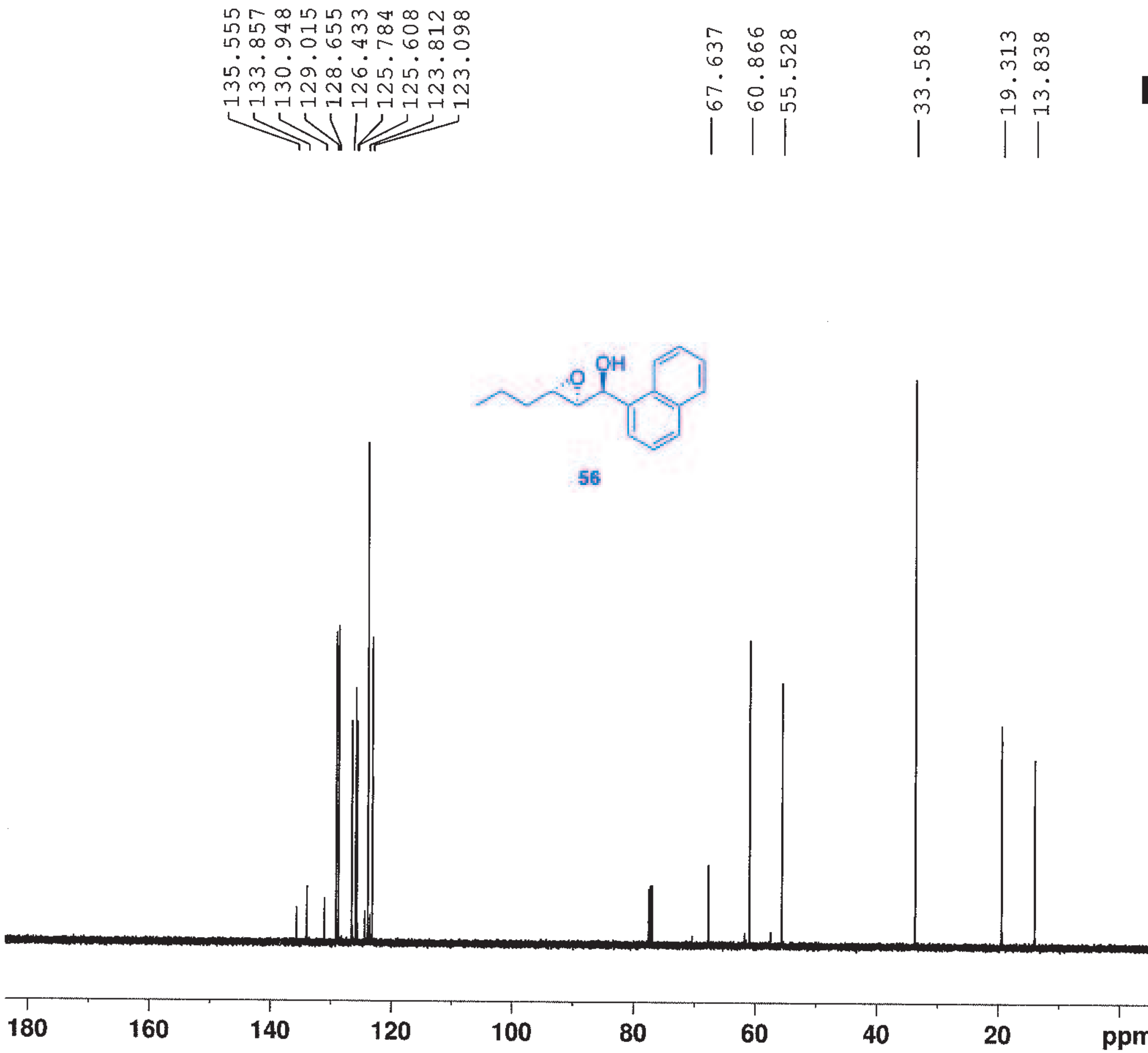
```
Current Data Parameters
NAME          Lan_20150914_B6067
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20150914
Time                       21.58
INSTRUM                    spect
PROBHD          5 mm PABBO BB/
PULPROG                       zg
TD                         59998
SOLVENT                    CDCl3
NS                             8
DS                             0
SWH               10000.000 Hz
FIDRES             0.166672 Hz
AQ                2.9999001 sec
RG                         16.71
DW                    50.000 usec
DE                      6.50 usec
TE                       296.0 K
D1               5.00000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1           499.8730869 MHz
NUC1                          1H
P1                    10.75 usec
PLW1             18.25000000 W

F2 - Processing parameters
SI                         65536
SF             499.8700240 MHz
WDW                           EM
SSB          0
LB                       0.30 Hz
GB           0
PC                          1.00
```



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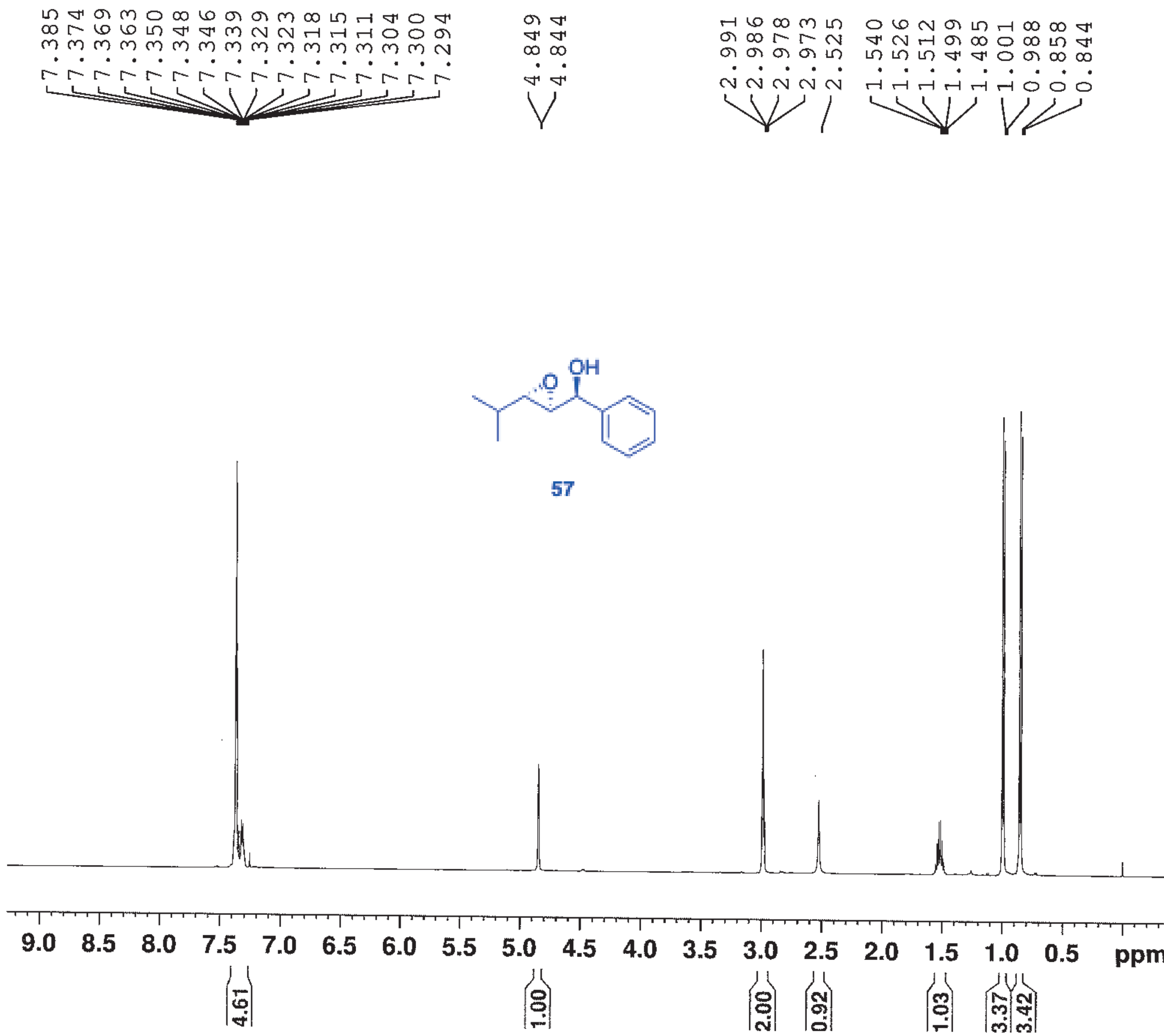
```
Current Data Parameters
NAME        Lan_20150914_B6067_C
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20150914
Time                       22.06
INSTRUM                    spect
PROBHD     5 mm PABBO BB/
PULPROG                     zgdc
TD                        187496
SOLVENT                    CDCl3
NS                            69
DS                             0
SWH                    31250.000 Hz
FIDRES                  0.166670 Hz
AQ                     2.9999361 sec
RG                          2050
DW                        16.000 usec
DE                          6.50 usec
TE                         296.6 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                 125.7049802 MHz
NUC1                         13C
P1                         10.00 usec
PLW1                 72.83999634 W

======== CHANNEL f2 ========
SFO2                 499.8724993 MHz
NUC2                          1H
CPDPRG[2                 waltz16
PCPD2                      80.00 usec
PLW2                 19.00000000 W
PLW12                 0.29688001 W

F2 - Processing parameters
SI                       1048576
SF                   125.6924021 MHz
WDW                           EM
SSB       0
LB                          0.30 Hz
GB        0
PC                          1.40
```



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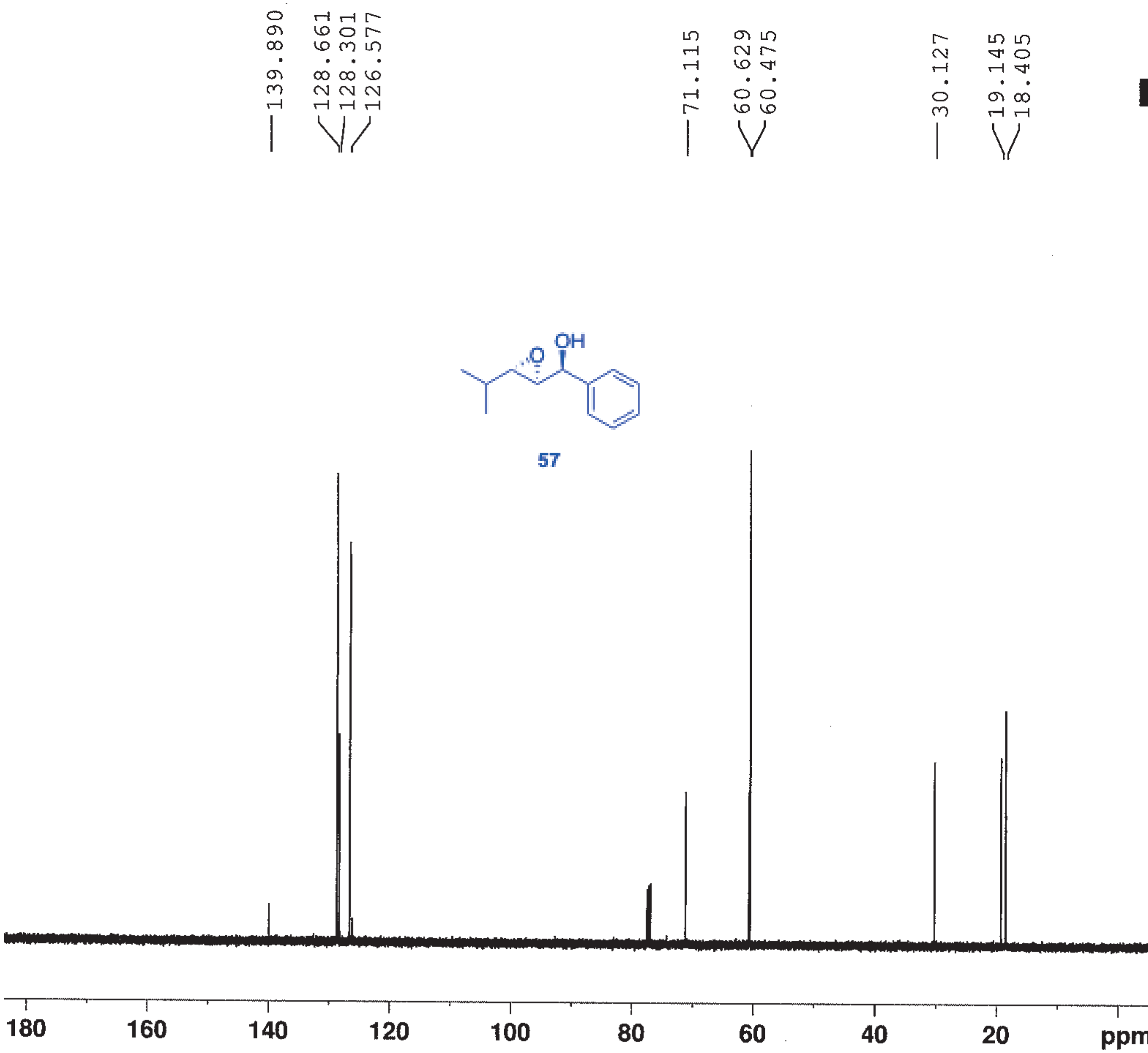
Current Data Parameters
NAME Lan_20150914_B6125
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150914
Time 22.13
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 15.35
DW 50.000 usec
DE 6.50 usec
TE 296.2 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 499.8730869 MHz
NUC1 1H
P1 10.75 usec
PLW1 18.25000000 W

F2 - Processing parameters
SI 65536
SF 499.8700147 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



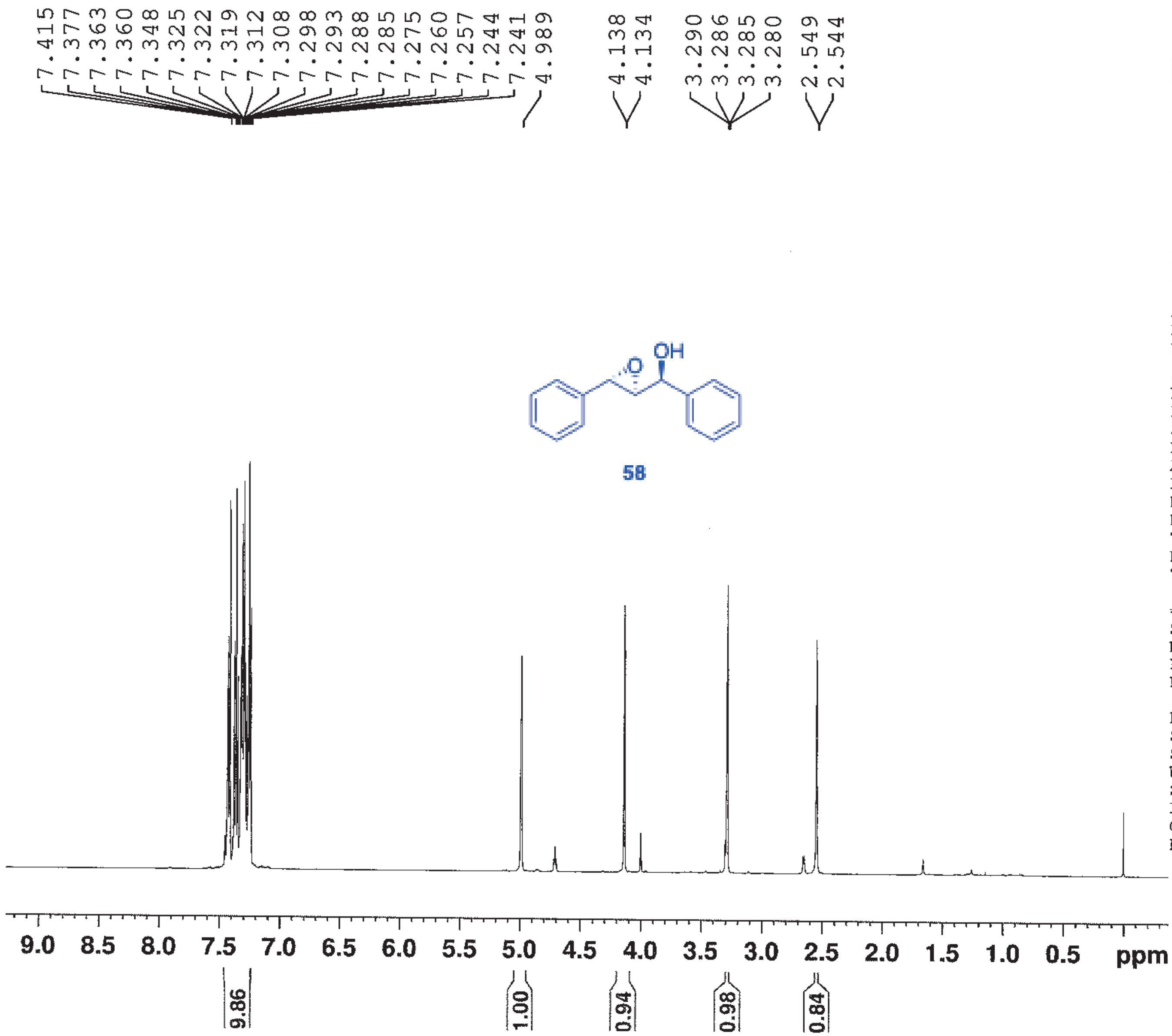
Current Data Parameters
NAME Lan_20150914_B6125_C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150914
Time 22.19
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgdc
TD 187496
SOLVENT CDCl3
NS 26
DS 0
SWH 31250.000 Hz
FIDRES 0.166670 Hz
AQ 2.9999361 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 296.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 125.7049802 MHz
NUC1 13C
P1 10.00 usec
PLW1 72.83999634 W

======== CHANNEL f2 ========
SFO2 499.8724993 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.29688001 W

F2 - Processing parameters
SI 1048576
SF 125.6924008 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40



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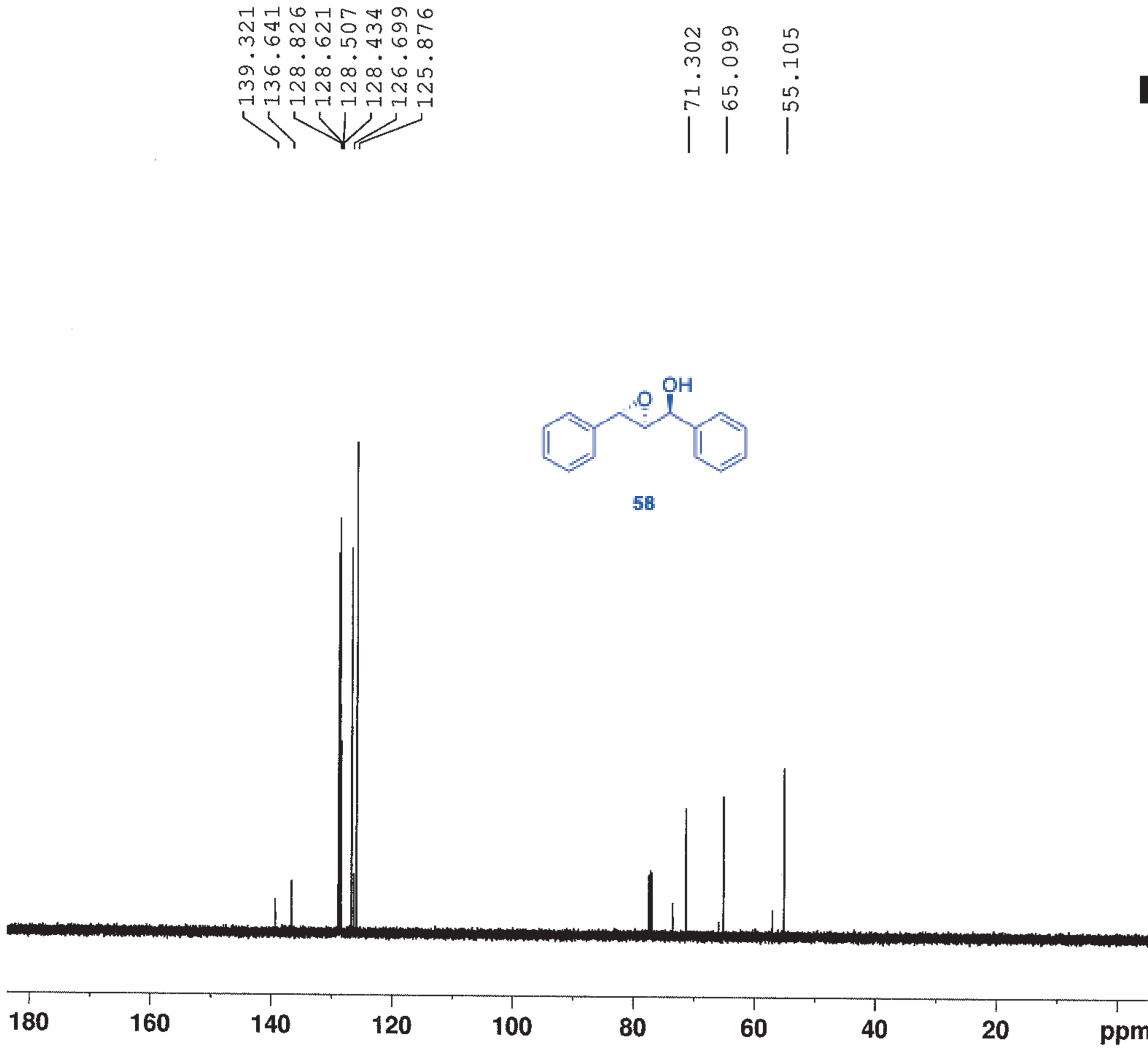
```
Current Data Parameters
NAME      Lan_20150915_B5303
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20150915
Time                   18.43
INSTRUM                spect
PROBHD     5 mm PABBO BB/
PULPROG                   zg
TD                     59998
SOLVENT                CDCl3
NS                         8
DS                         0
SWH              10000.000 Hz
FIDRES            0.166672 Hz
AQ               2.9999001 sec
RG                     28.76
DW                   50.000 usec
DE                     6.50 usec
TE                    296.1 K
D1               5.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1          499.8730869 MHz
NUC1                      1H
P1                     10.75 usec
PLW1          18.25000000 W

F2 - Processing parameters
SI                     65536
SF            499.8700242 MHz
WDW                       EM
SSB      0
LB                      0.30 Hz
GB       0
PC                      1.00
```



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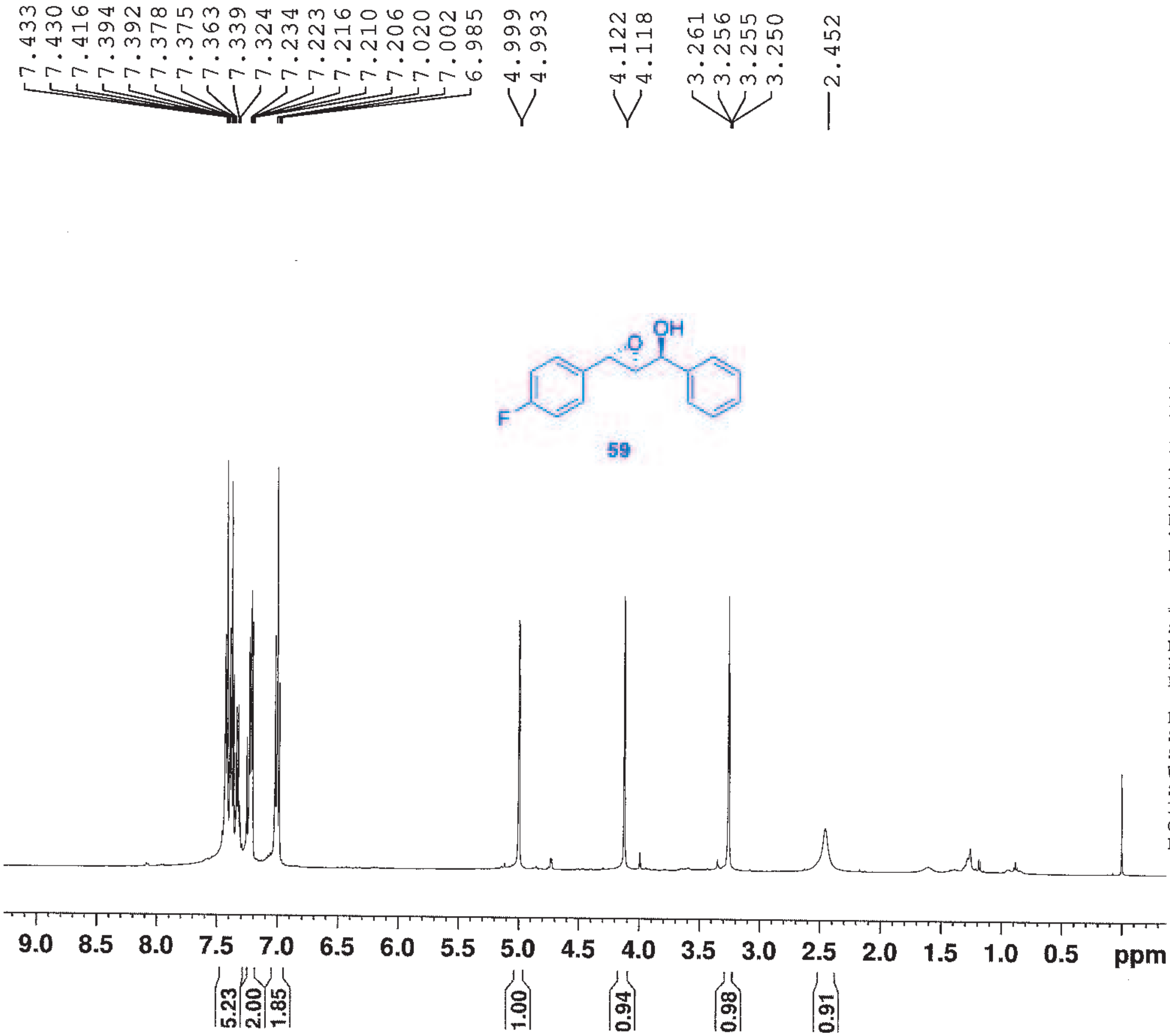
Current Data Parameters		
NAME	Lan_20150915_B5303_C	
EXPNO	1	
PROCNO	1	
F2 - Acquisition Parameters		
Date_	20150915	
Time	18.49	
INSTRUM	spect	
PROBHD	5 mm PABBO BB/	
PULPROG	zgdc	
TD	187496	
SOLVENT	CDCl3	
NS	12	
DS	0	
SWH	31250.000	Hz
FIDRES	0.166670	Hz
AQ	2.9999361	sec
RG	2050	
DW	16.000	usec
DE	6.50	usec
TE	296.2	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
SFO1	125.7049802	MHz
NUC1	13C	
P1	10.00	usec
PLW1	72.83999634	W
======== CHANNEL f2 ========		
SFO2	499.8724993	MHz
NUC2	1H	
CPDPRG[2	waltz16	
PCPD2	80.00	usec
PLW2	19.00000000	W
PLW12	0.29688001	W
F2 - Processing parameters		
SI	1048576	
SF	125.6924009	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.40	



Current Data Parameters

NAME	Lan_20150915_B6111
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

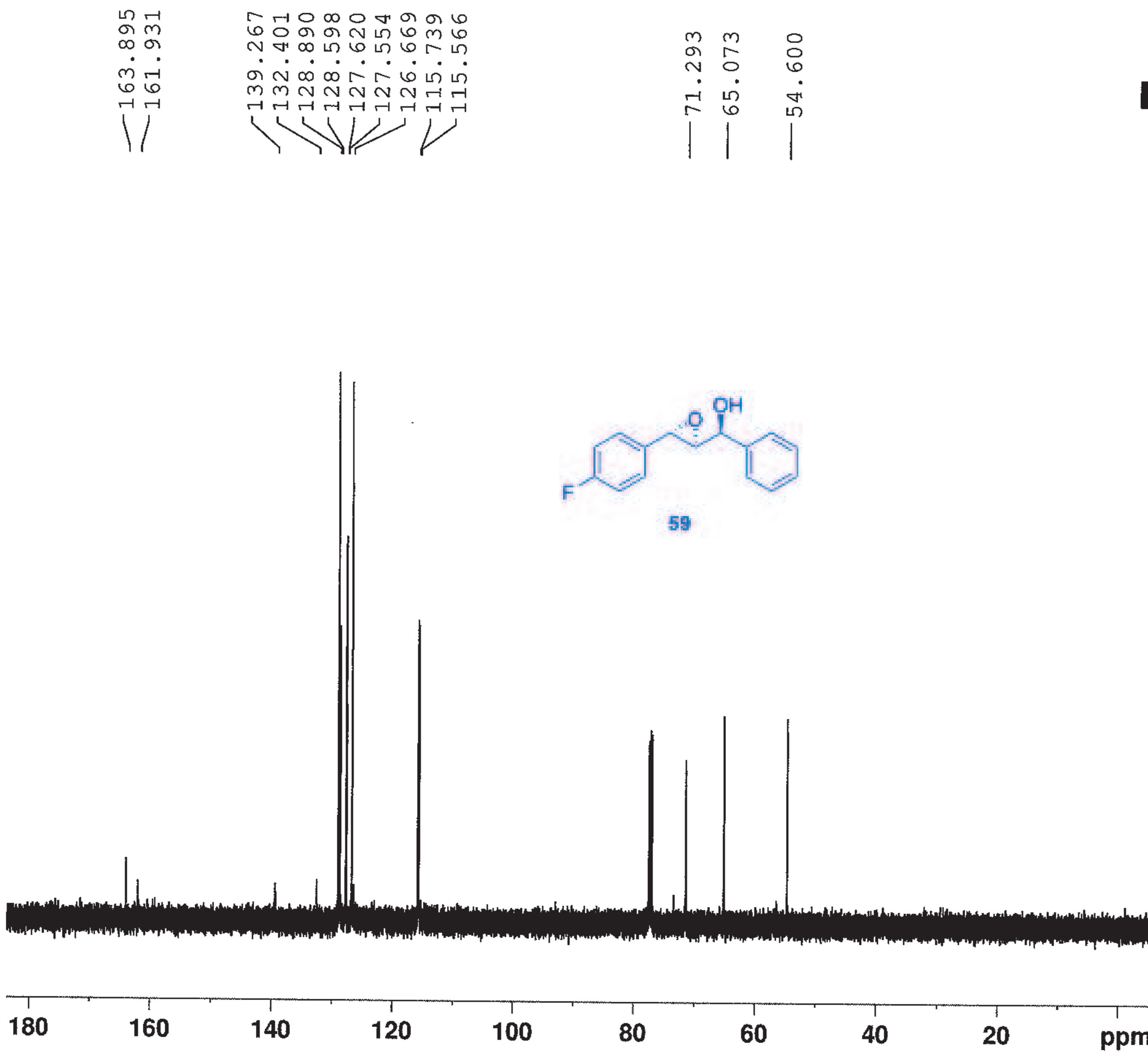
Date_	20150915
Time	21.17
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	8
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999001 sec
RG	37.92
DW	50.000 usec
DE	6.50 usec
TE	296.7 K
D1	5.00000000 sec
TD0	1

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

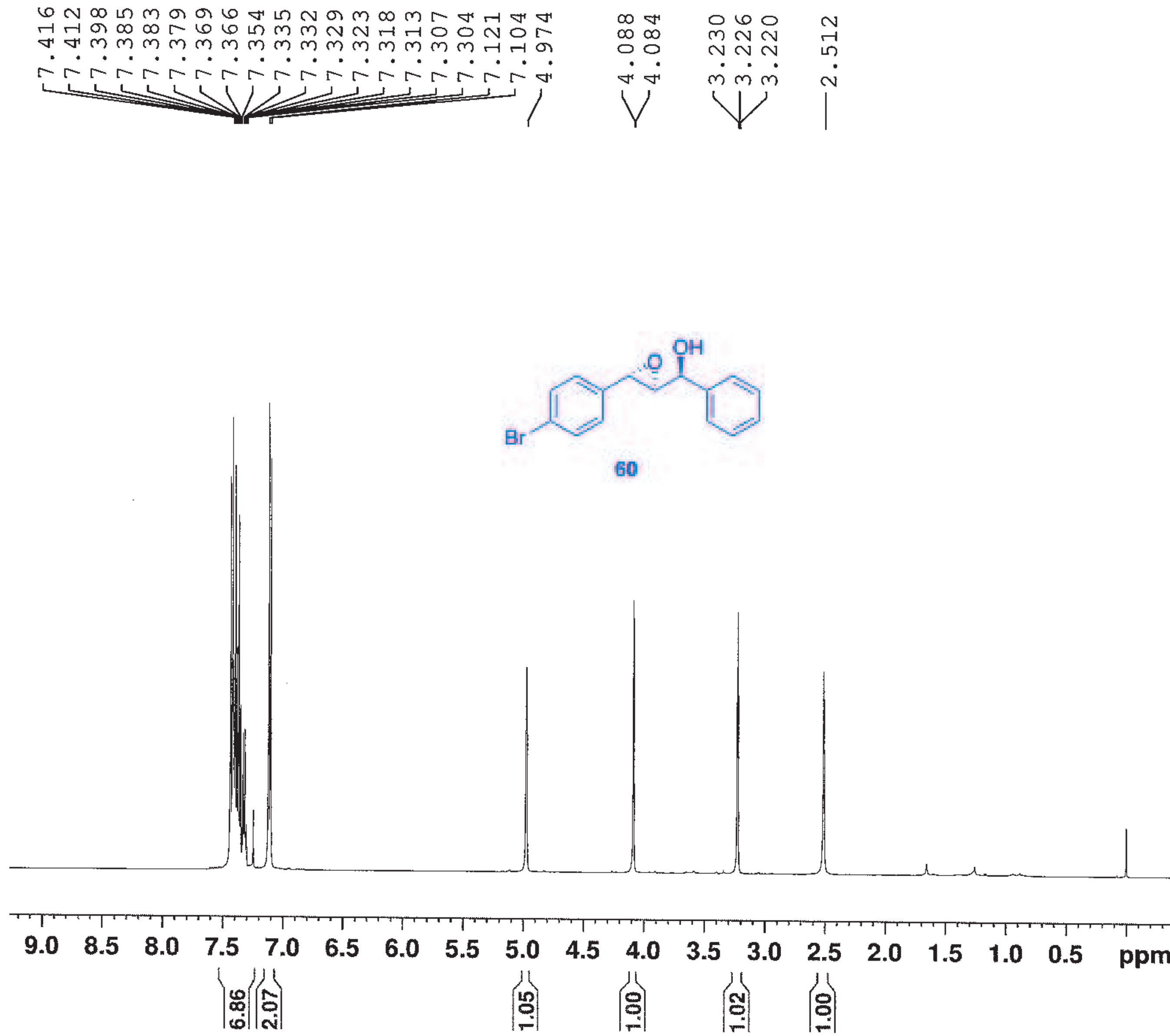
SFO1	499.8730869 MHz
NUC1	1H
P1	10.75 usec
PLW1	18.25000000 W

F2 - Processing parameters

SI	65536
SF	499.8700157 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



Current Data Parameters	
NAME	Lan_20150915_B6111_C
EXPNO	1
PROCNO	1
F2 - Acquisition Parameters	
Date_	20150915
Time	21.23
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgdc
TD	187496
SOLVENT	CDCl3
NS	91
DS	0
SWH	31250.000 Hz
FIDRES	0.166670 Hz
AQ	2.9999361 sec
RG	2050
DW	16.000 usec
DE	6.50 usec
TE	297.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	125.7049802 MHz
NUC1	13C
P1	10.00 usec
PLW1	72.83999634 W
======== CHANNEL f2 ========	
SFO2	499.8724993 MHz
NUC2	1H
CPDPRG[2	waltz16
PCPD2	80.00 usec
PLW2	19.00000000 W
PLW12	0.29688001 W
F2 - Processing parameters	
SI	1048576
SF	125.6923958 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.40



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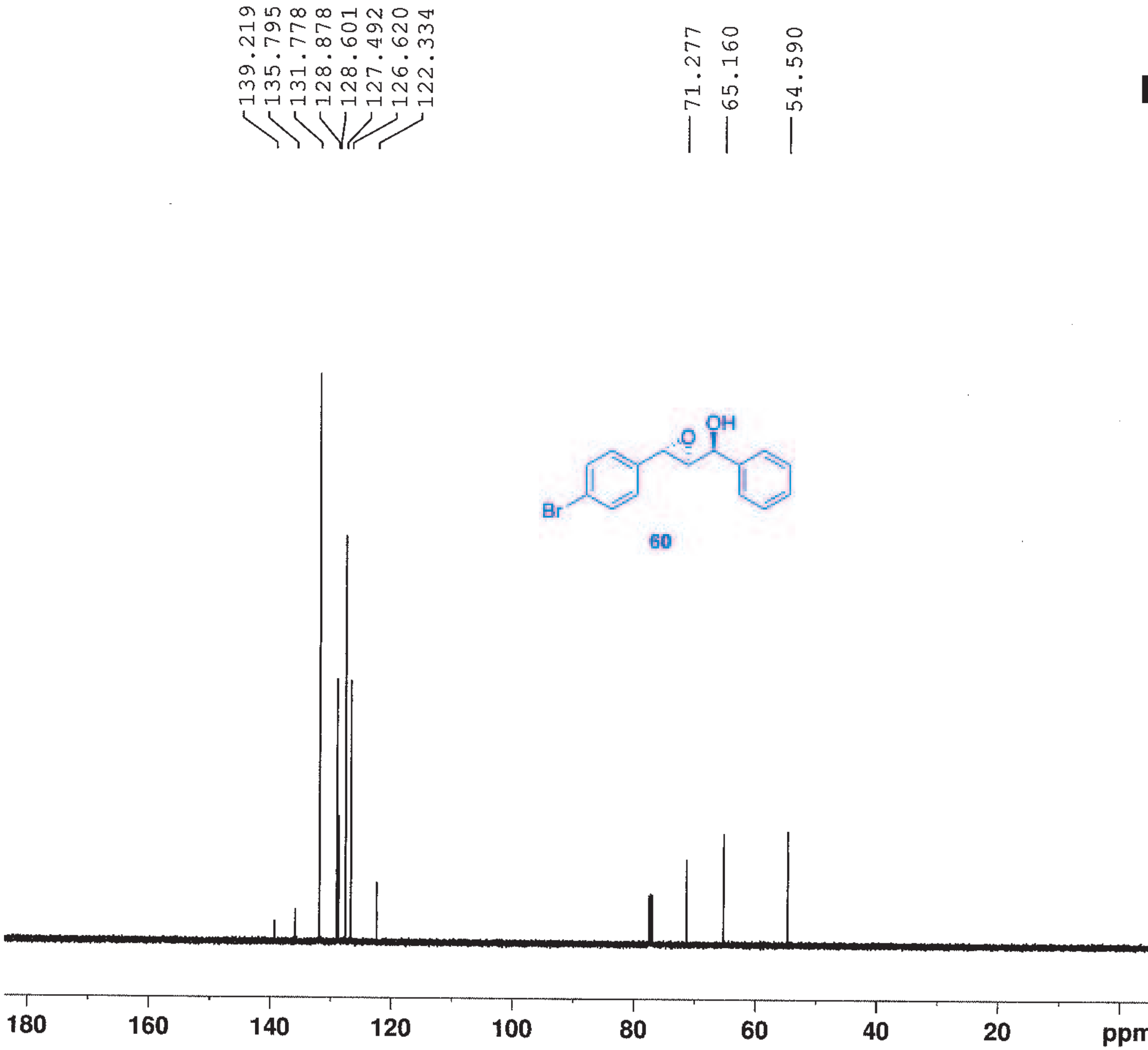
Current Data Parameters
NAME Lan_20150915_B6173
EXPNO 1
PROCNO 1

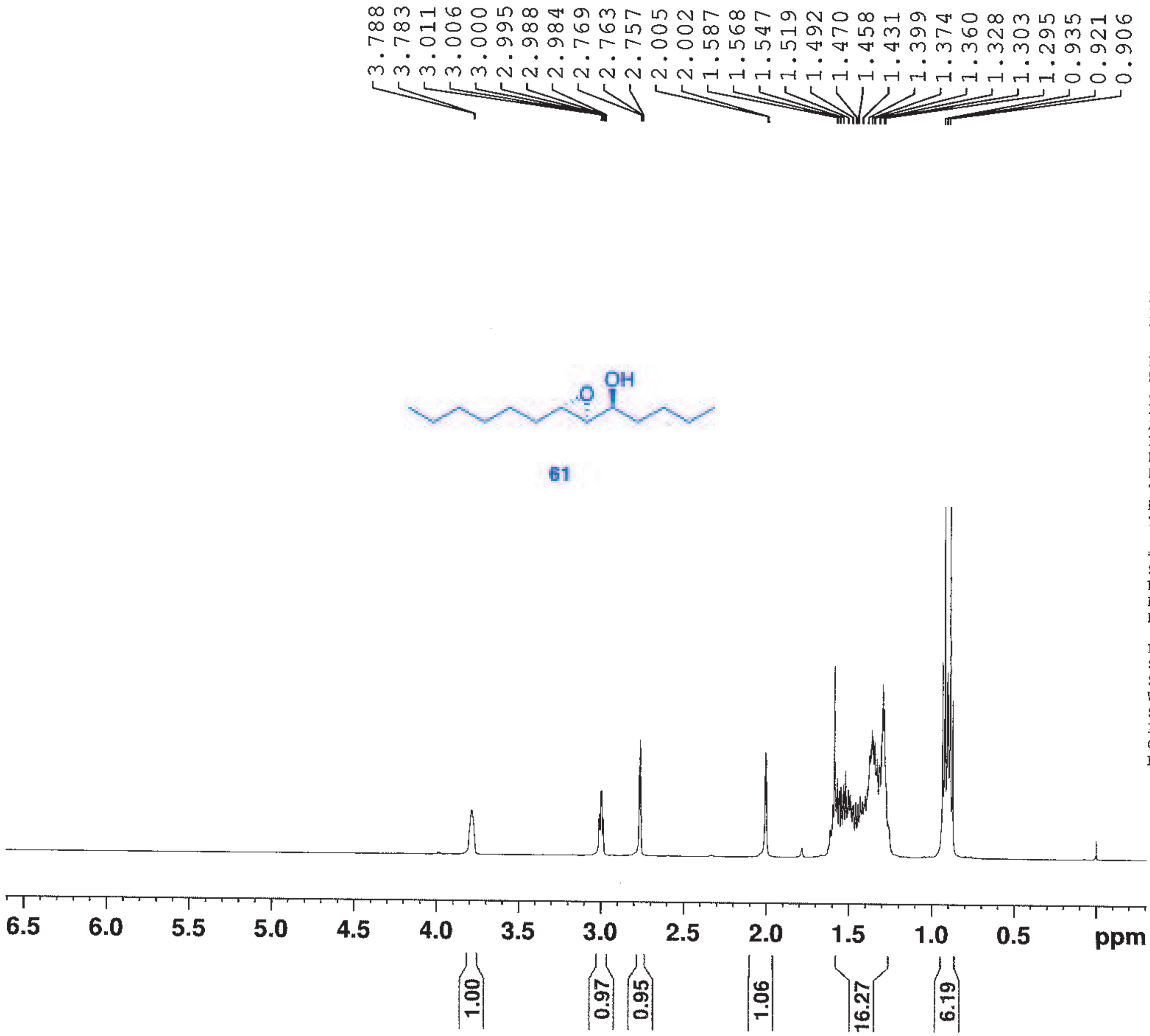
F2 - Acquisition Parameters
Date_ 20150915
Time 17.38
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 28.76
DW 50.000 usec
DE 6.50 usec
TE 295.7 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 499.8730869 MHz
NUC1 1H
P1 10.75 usec
PLW1 18.25000000 W

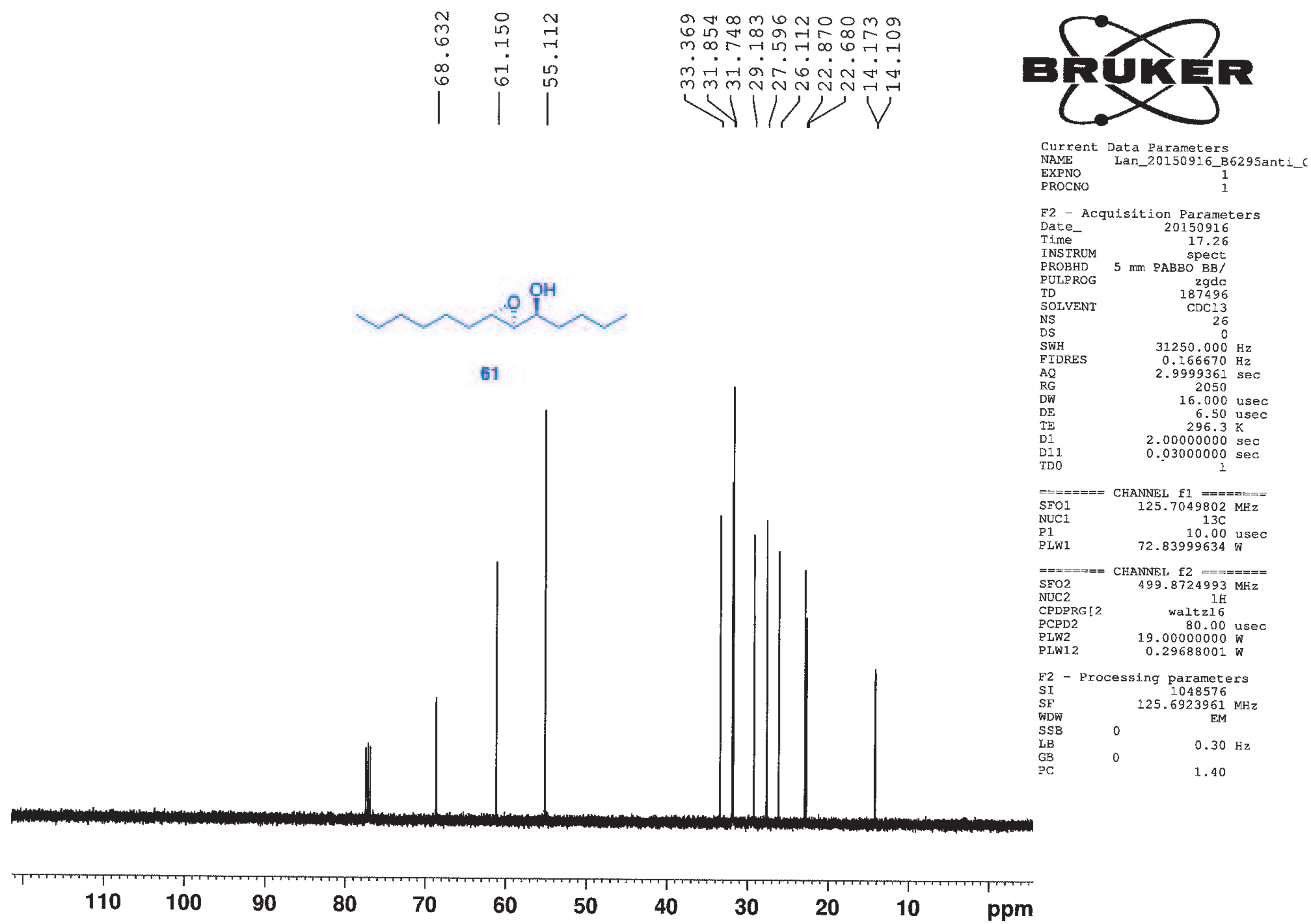
F2 - Processing parameters
SI 65536
SF 499.8700186 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



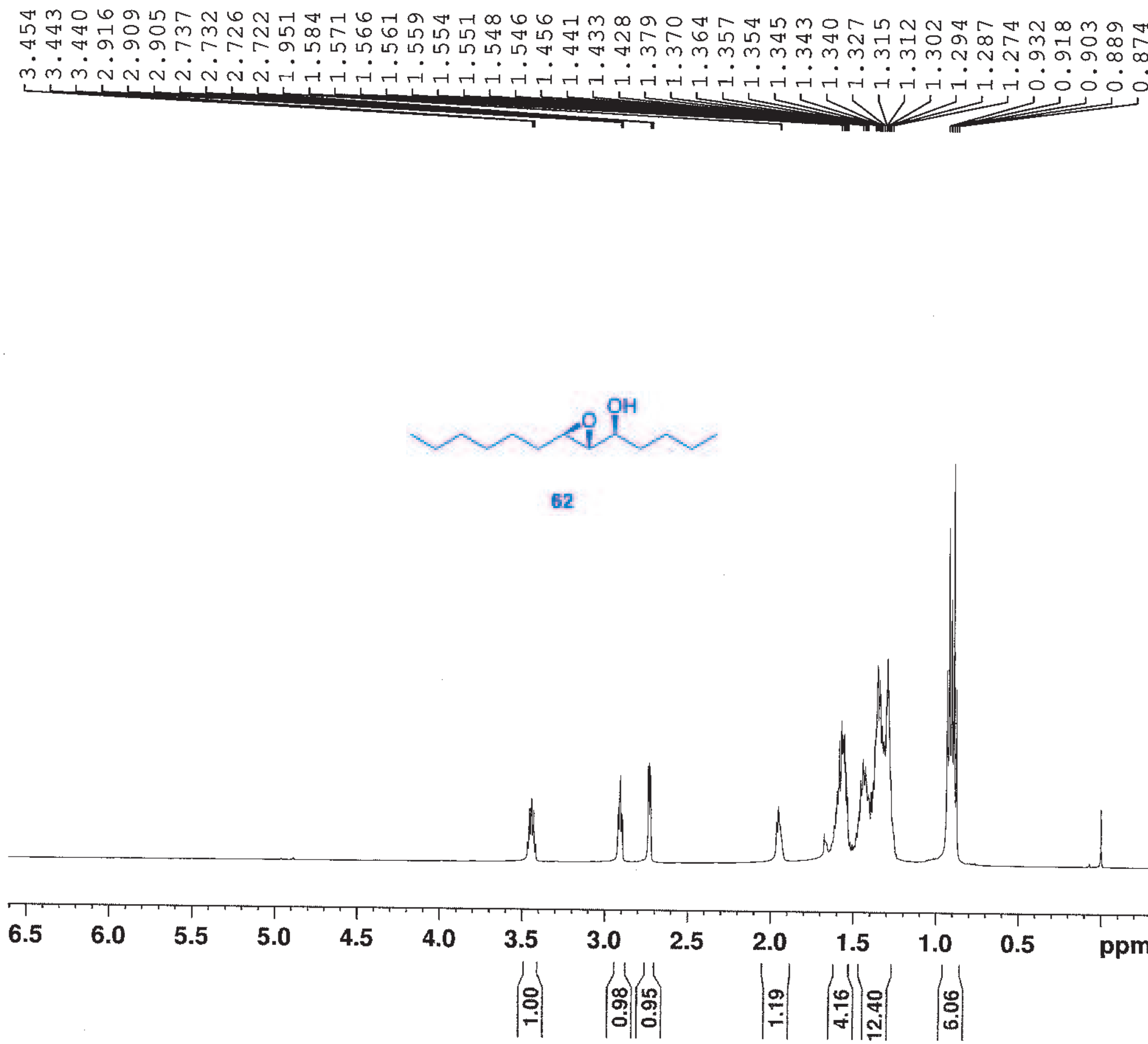
Current Data Parameters		
NAME	Lan_20150915_B6173_C	
EXPNO	1	
PROCNO	1	
F2 - Acquisition Parameters		
Date_	20150915	
Time	17.47	
INSTRUM	spect	
PROBHD	5 mm PABBO BB/	
PULPROG	zgdc	
TD	187496	
SOLVENT	CDCl3	
NS	71	
DS	0	
SWH	31250.000	Hz
FIDRES	0.166670	Hz
AQ	2.9999361	sec
RG	2050	
DW	16.000	usec
DE	6.50	usec
TE	296.5	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
SFO1	125.7049802	MHz
NUC1	13C	
P1	10.00	usec
PLW1	72.83999634	W
======== CHANNEL f2 ========		
SFO2	499.8724993	MHz
NUC2	1H	
CPDPRG[2	waltz16	
PCPD2	80.00	usec
PLW2	19.00000000	W
PLW12	0.29688001	W
F2 - Processing parameters		
SI	1048576	
SF	125.6923986	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.40	



Current Data Parameters	
NAME	Lan_20150916_B6295anti
EXPNO	1
PROCNO	1
F2 - Acquisition Parameters	
Date_	20150916
Time	17.22
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	8
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999001 sec
RG	11.05
DW	50.000 usec
DE	6.50 usec
TE	296.1 K
D1	5.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	499.8730869 MHz
NUC1	1H
P1	10.75 usec
PLW1	18.25000000 W
F2 - Processing parameters	
SI	65536
SF	499.8700042 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



68.632
61.150
55.112
33.369
31.854
31.748
29.183
27.596
26.112
22.870
22.680
14.173
14.109
OH
O
61
110
100
90
80
70
60
50
40
30
20
10
ppm
Current Data Parameters
NAME Lan_20150916_B6295anti_C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150916
Time 17.26
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgdc
TD 187496
SOLVENT CDCl3
NS 26
DS 0
SWH 31250.000 Hz
FIDRES 0.166670 Hz
AQ 2.9999361 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 296.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7049802 MHz
NUC1 13C
P1 10.00 usec
PLW1 72.83999634 W
======== CHANNEL f2 ========
SFO2 499.8724993 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.29688001 W
F2 - Processing parameters
SI 1048576
SF 125.6923961 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40



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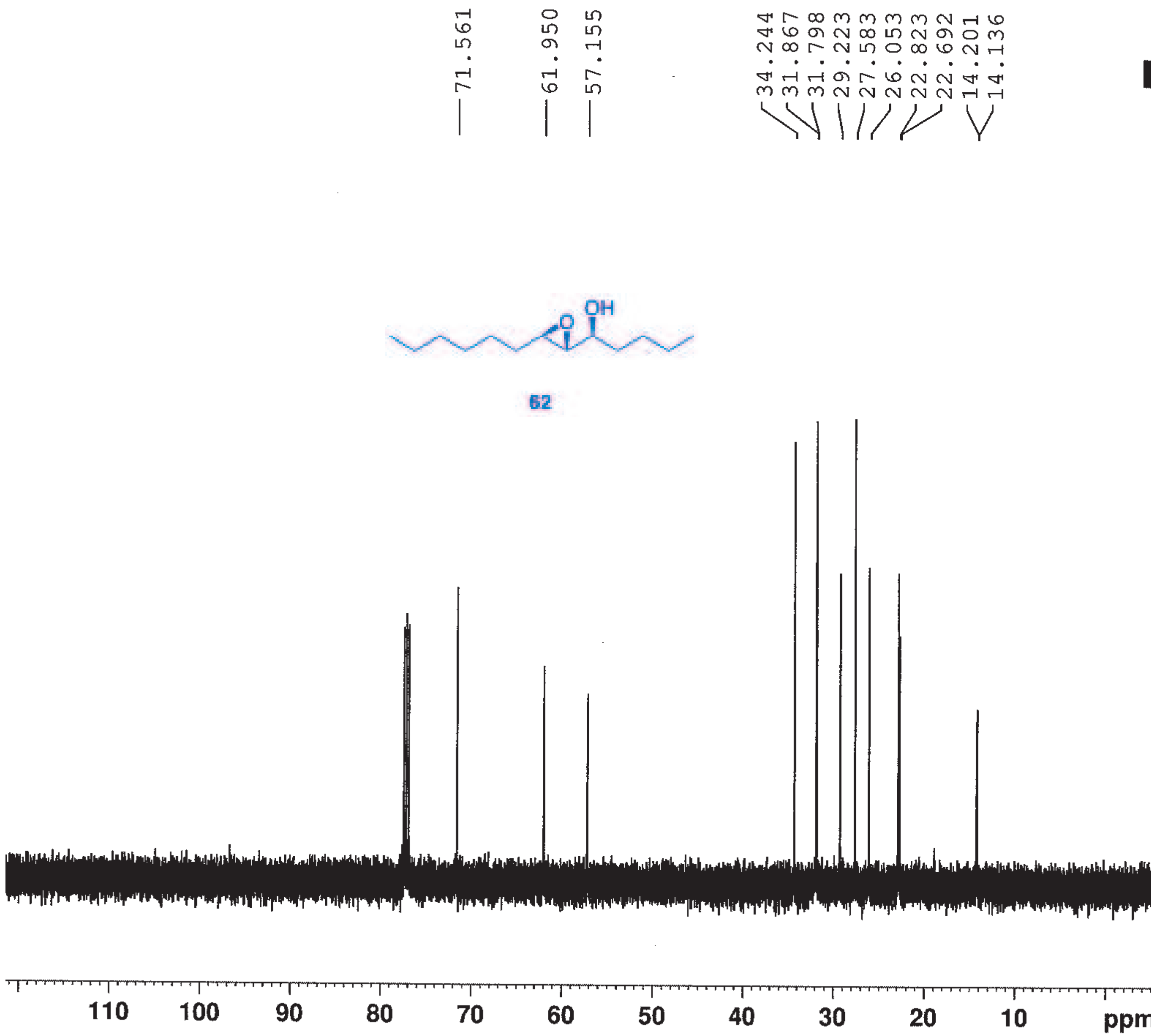
```
Current Data Parameters
NAME       Lan_20150916_B6295syn
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150916
Time                  17.07
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                  zg
TD                    59998
SOLVENT               CDCl3
NS                        8
DS                        0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                    25.24
DW                   50.000 usec
DE                     6.50 usec
TE                    295.9 K
D1               5.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1          499.8730869 MHz
NUC1                     1H
P1                    10.75 usec
PLW1            18.25000000 W

F2 - Processing parameters
SI                    65536
SF            499.8700082 MHz
WDW                      EM
SSB       0
LB                     0.30 Hz
GB        0
PC                     1.00
```



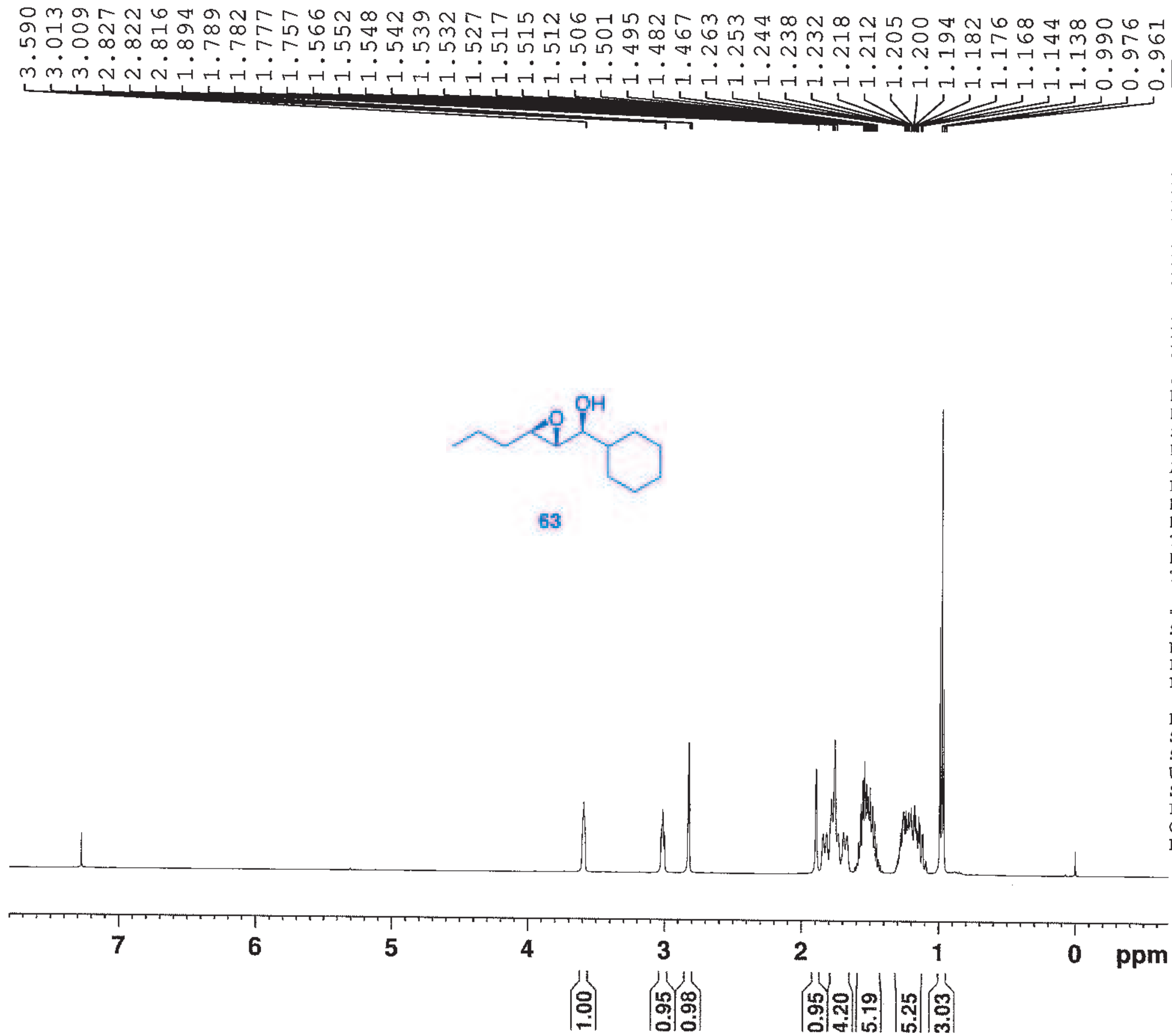

```
Current Data Parameters
NAME       Lan_20150916_B6295syn_C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_            20150916
Time                17.15
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgdc
TD                 187496
SOLVENT             CDCl3
NS                     40
DS                      0
SWH           31250.000 Hz
FIDRES         0.166670 Hz
AQ            2.9999361 sec
RG                  2050
DW               16.000 usec
DE                 6.50 usec
TE                296.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        125.7049802 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         72.83999634 W

======== CHANNEL f2 ========
SFO2        499.8724993 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2         19.00000000 W
PLW12         0.29688001 W

F2 - Processing parameters
SI                1048576
SF            125.6923948 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.40
```



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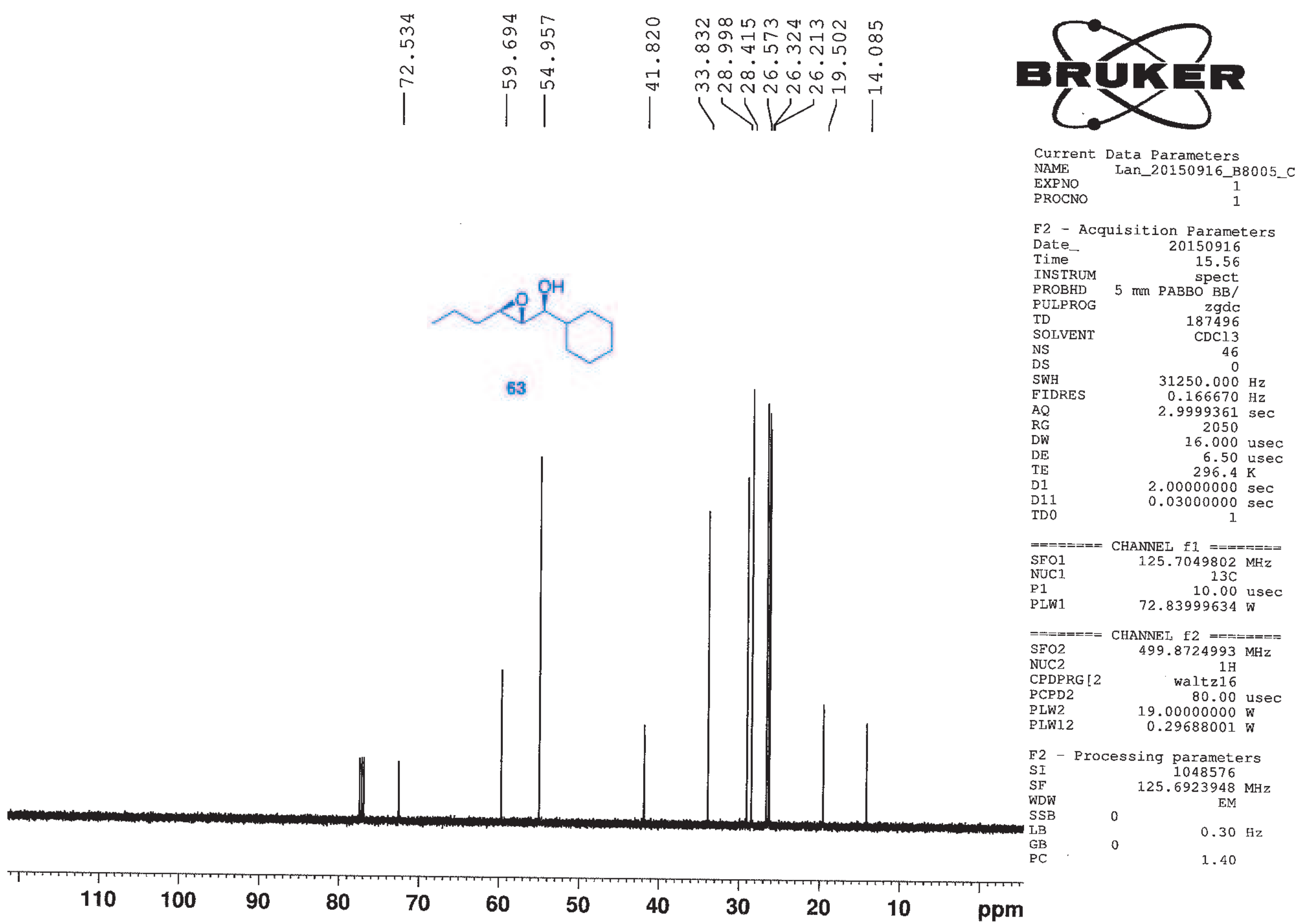
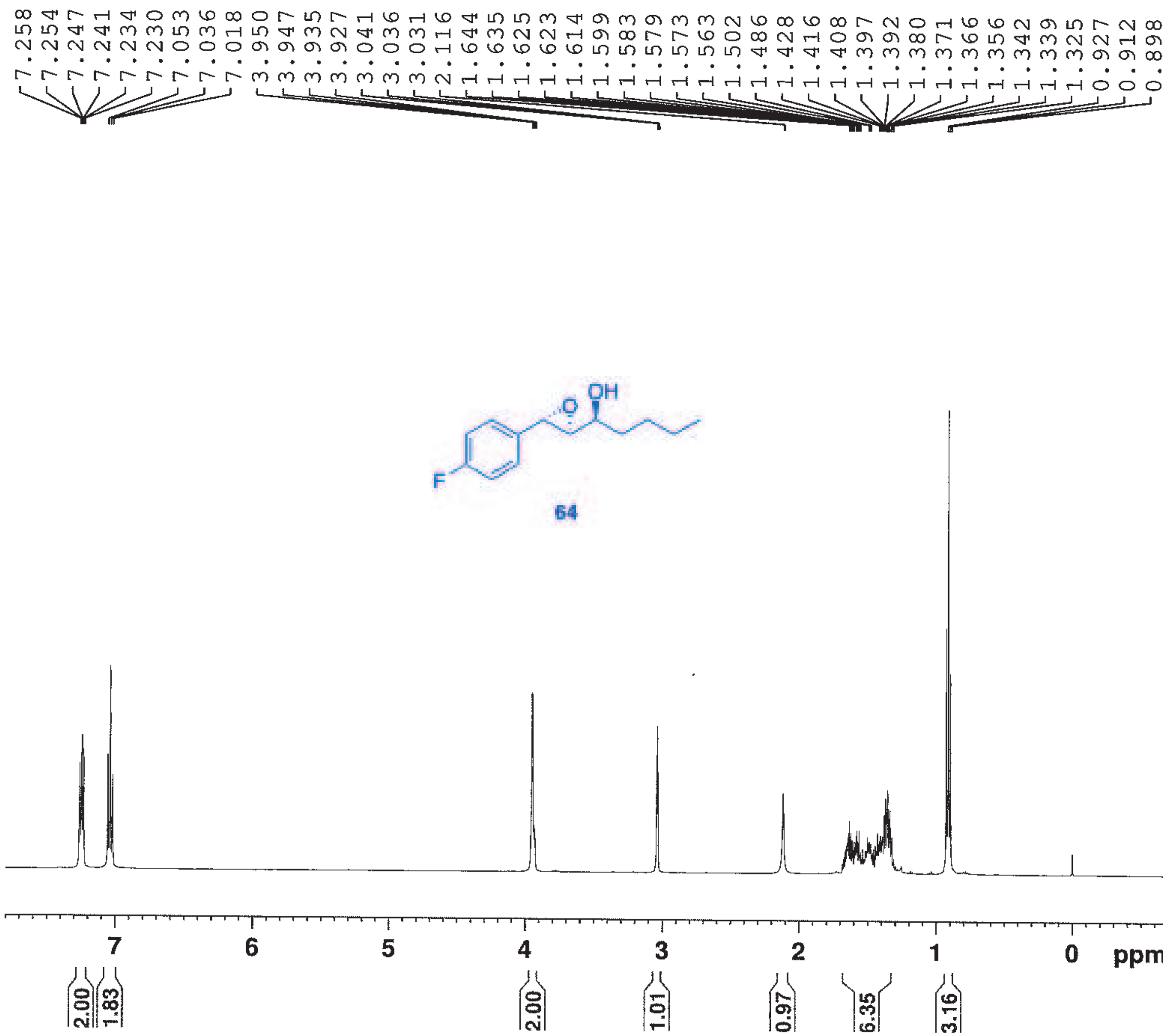
```
Current Data Parameters
NAME          Lan_20150916_B8005
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20150916
Time                       15.48
INSTRUM                    spect
PROBHD          5 mm PABBO BB/
PULPROG                       zg
TD                         59998
SOLVENT                    CDCl3
NS                             8
DS                             0
SWH                 10000.000 Hz
FIDRES               0.166672 Hz
AQ                  2.9999001 sec
RG                         19.64
DW                    50.000 usec
DE                      6.50 usec
TE                       295.9 K
D1                5.00000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1             499.8730869 MHz
NUC1                          1H
P1                     10.75 usec
PLW1               18.25000000 W

F2 - Processing parameters
SI                         65536
SF               499.8700057 MHz
WDW                           EM
SSB           0
LB                       0.30 Hz
GB            0
PC                          1.00
```


72.534
59.694
54.957
41.820
33.832
28.998
28.415
26.573
26.324
26.213
19.502
14.085
OH
O
63
BRUKER
Current Data Parameters
NAME Lan_20150916_B8005_C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150916
Time 15.56
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgdc
TD 187496
SOLVENT CDCl3
NS 46
DS 0
SWH 31250.000 Hz
FIDRES 0.166670 Hz
AQ 2.9999361 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 296.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7049802 MHz
NUC1 13C
P1 10.00 usec
PLW1 72.83999634 W
======== CHANNEL f2 ========
SFO2 499.8724993 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.29688001 W
F2 - Processing parameters
SI 1048576
SF 125.6923948 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
110
100
90
80
70
60
50
40
30
20
10
ppm

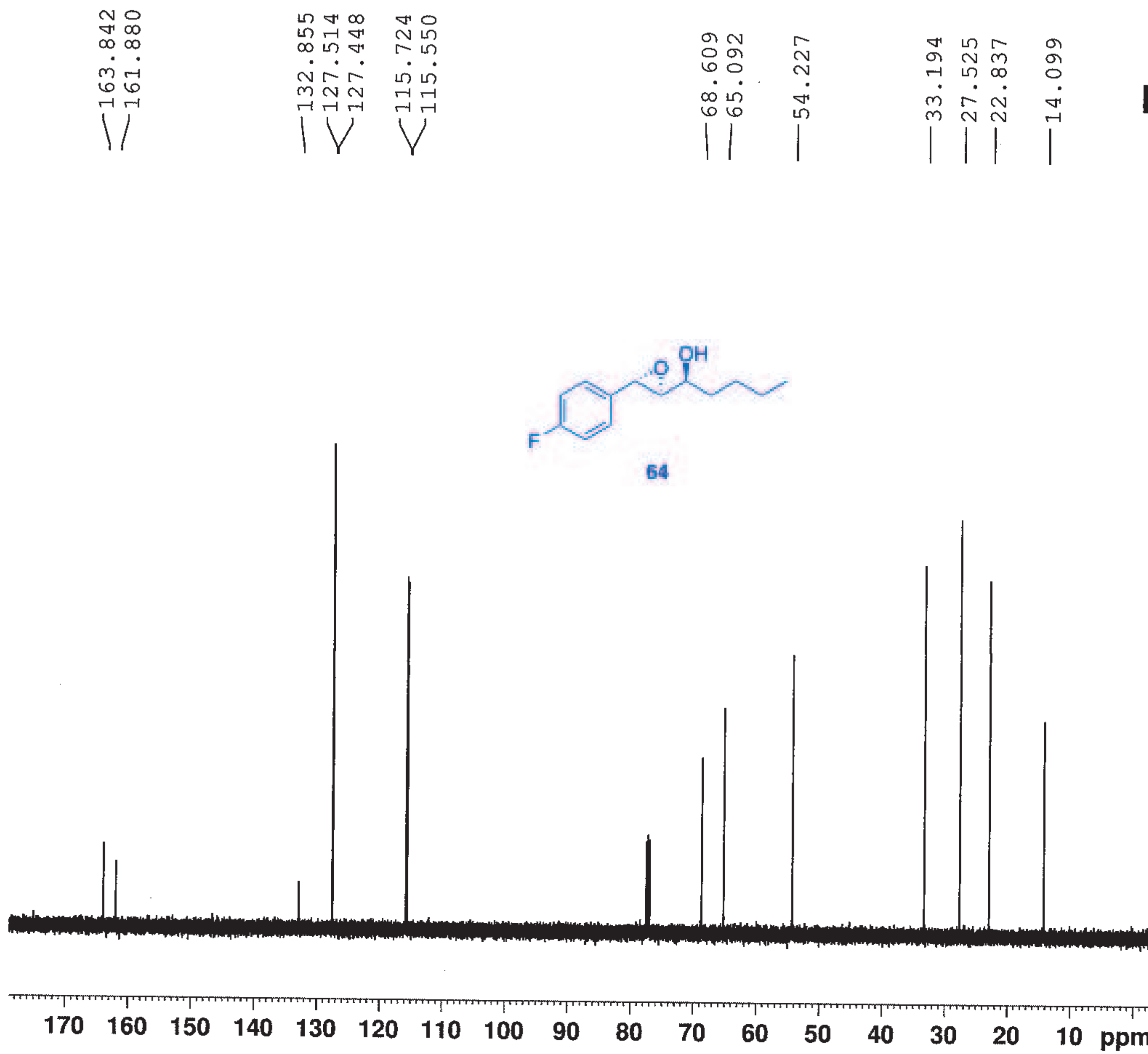



```
Current Data Parameters
NAME       Lan_20150916_B6299
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20150916
Time                  15.34
INSTRUM               spect
PROBHD      5 mm PABBO BB/
PULPROG                  zg
TD                    59998
SOLVENT               CDCl3
NS                        8
DS                        0
SWH               10000.000 Hz
FIDRES             0.166672 Hz
AQ                2.9999001 sec
RG                    19.64
DW                   50.000 usec
DE                     6.50 usec
TE                    295.9 K
D1               5.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            499.8730869 MHz
NUC1                     1H
P1                    10.75 usec
PLW1            18.25000000 W

F2 - Processing parameters
SI                    65536
SF              499.8700100 MHz
WDW                      EM
SSB      0
LB                     0.30 Hz
GB       0
PC                     1.00
```



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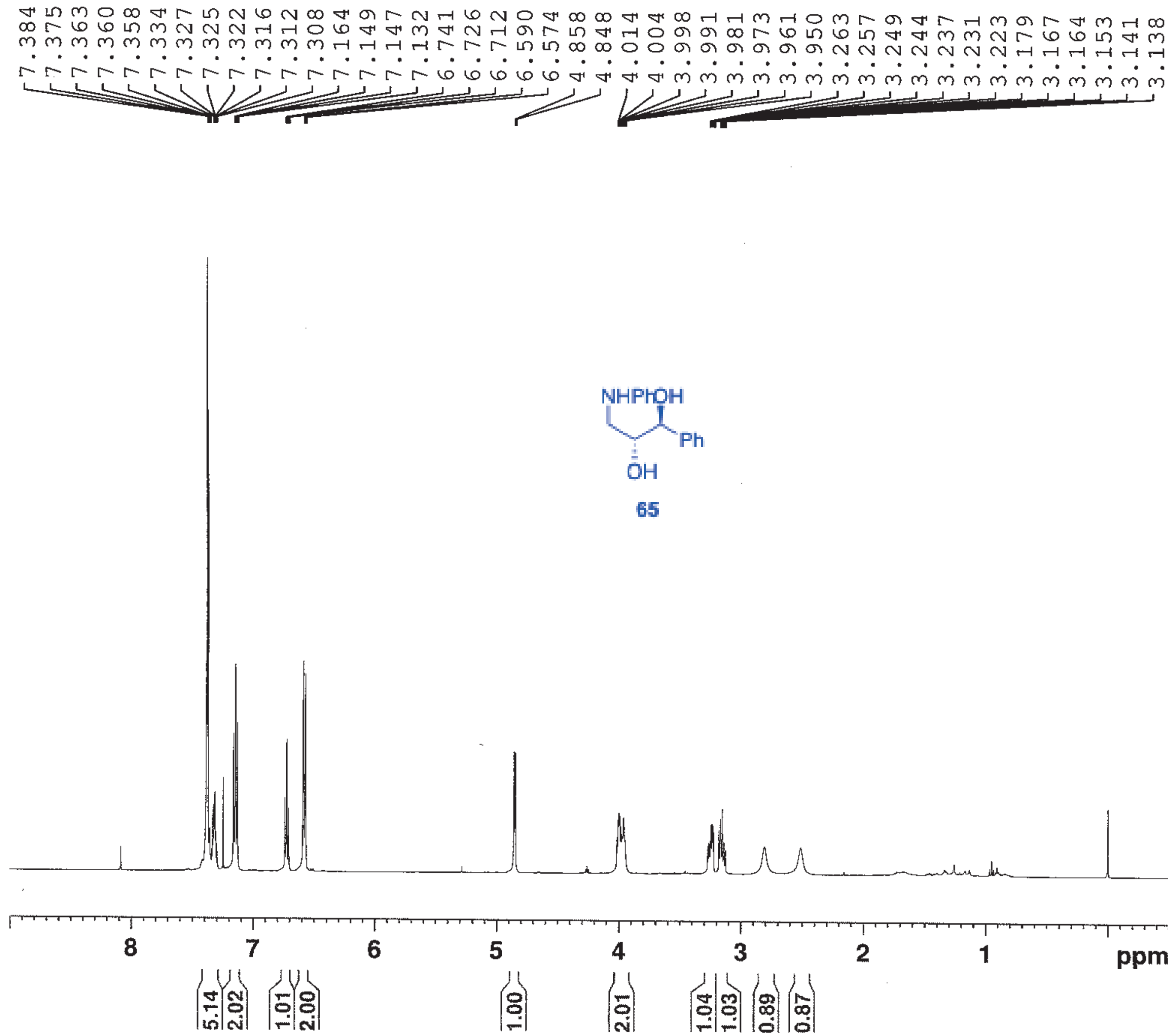
Current Data Parameters	
NAME	Lan_20150916_B6299_C
EXPNO	1
PROCNO	1
F2 - Acquisition Parameters	
Date_	20150916
Time	15.41
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgdc
TD	187496
SOLVENT	CDCl3
NS	22
DS	0
SWH	31250.000 Hz
FIDRES	0.166670 Hz
AQ	2.9999361 sec
RG	2050
DW	16.000 usec
DE	6.50 usec
TE	296.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	125.7049802 MHz
NUC1	13C
P1	10.00 usec
PLW1	72.83999634 W
======== CHANNEL f2 ========	
SFO2	499.8724993 MHz
NUC2	1H
CPDPRG[2	waltz16
PCPD2	80.00 usec
PLW2	19.00000000 W
PLW12	0.29688001 W
F2 - Processing parameters	
SI	1048576
SF	125.6923969 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.40

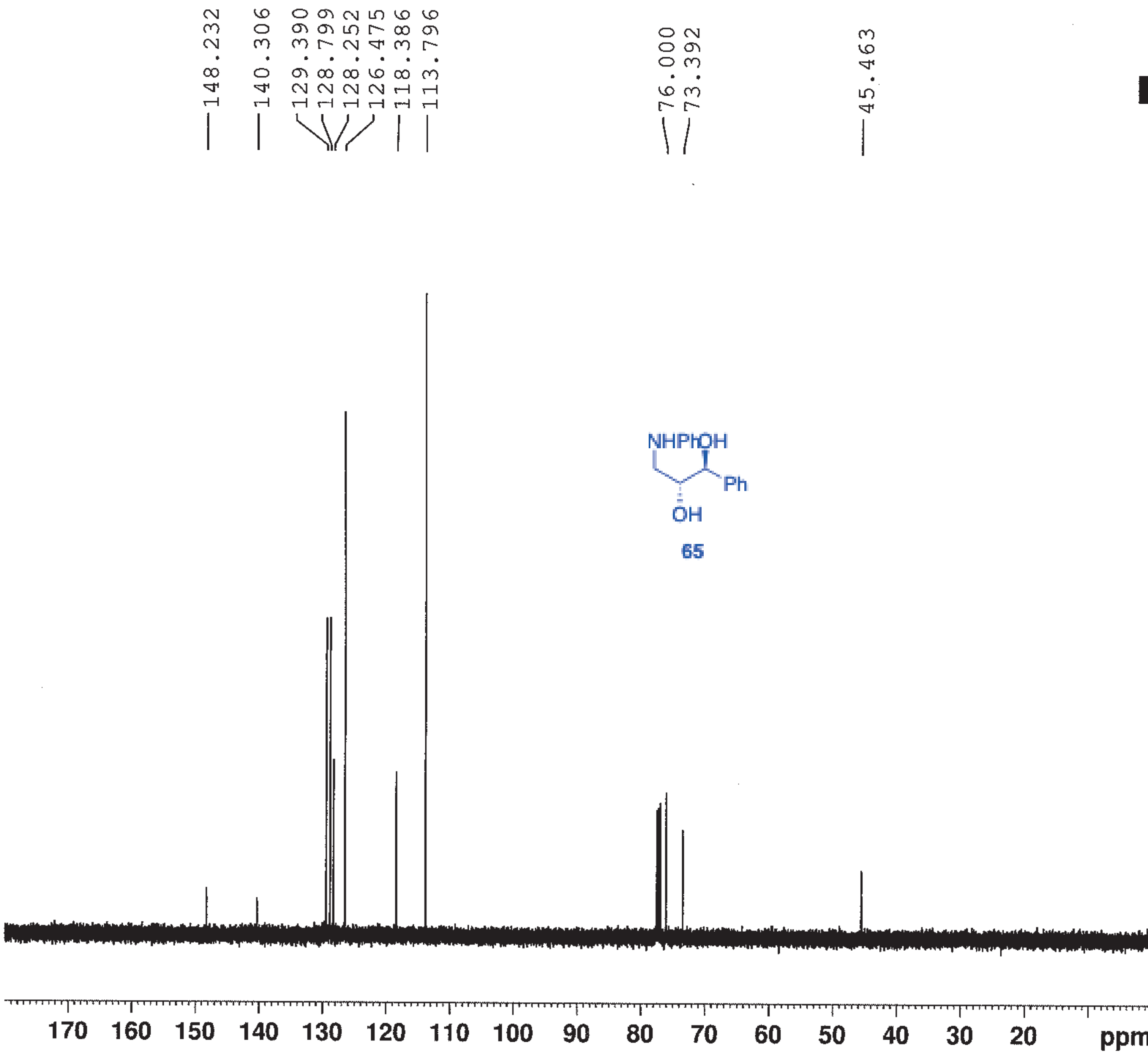



```
Current Data Parameters
NAME        Lan_20150407_B6039
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150407
Time                 21.08
INSTRUM              spect
PROBHD     5 mm PABBO BB/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                       8
DS                       0
SWH           10000.000 Hz
FIDRES         0.166672 Hz
AQ            2.9999001 sec
RG                   29.95
DW               50.000 usec
DE                 6.50 usec
TE                297.3 K
D1          10.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1        499.8730869 MHz
NUC1                    1H
P1                10.75 usec
PLW1        18.25000000 W

F2 - Processing parameters
SI                   65536
SF          499.8700179 MHz
WDW                     EM
SSB      0
LB                 0.30 Hz
GB       0
PC                    1.00
```



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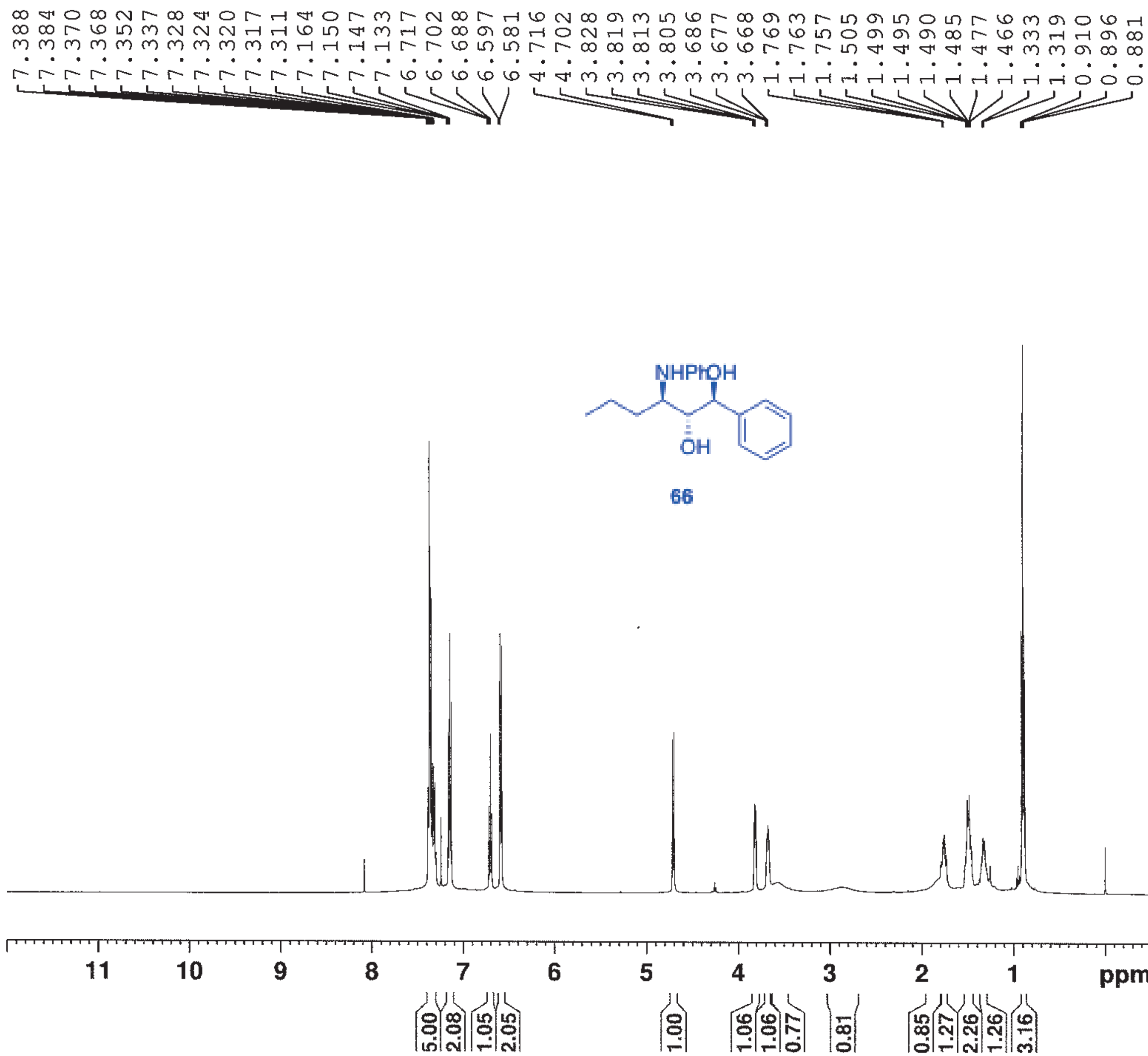
```
Current Data Parameters
NAME          Lan_20150407_B6039_C
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150407
Time                 21.20
INSTRUM              spect
PROBHD      5 mm PABBO BB/
PULPROG               zgdc
TD                  187496
SOLVENT              CDCl3
NS                      40
DS                       0
SWH              31250.000 Hz
FIDRES            0.166670 Hz
AQ               2.9999361 sec
RG                    2050
DW                  16.000 usec
DE                    6.50 usec
TE                   297.6 K
D1              3.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           125.7049802 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           72.83999634 W

======== CHANNEL f2 ========
SFO2           499.8724993 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           19.00000000 W
PLW12           0.29688001 W

F2 - Processing parameters
SI                 1048576
SF             125.6923965 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.40
```



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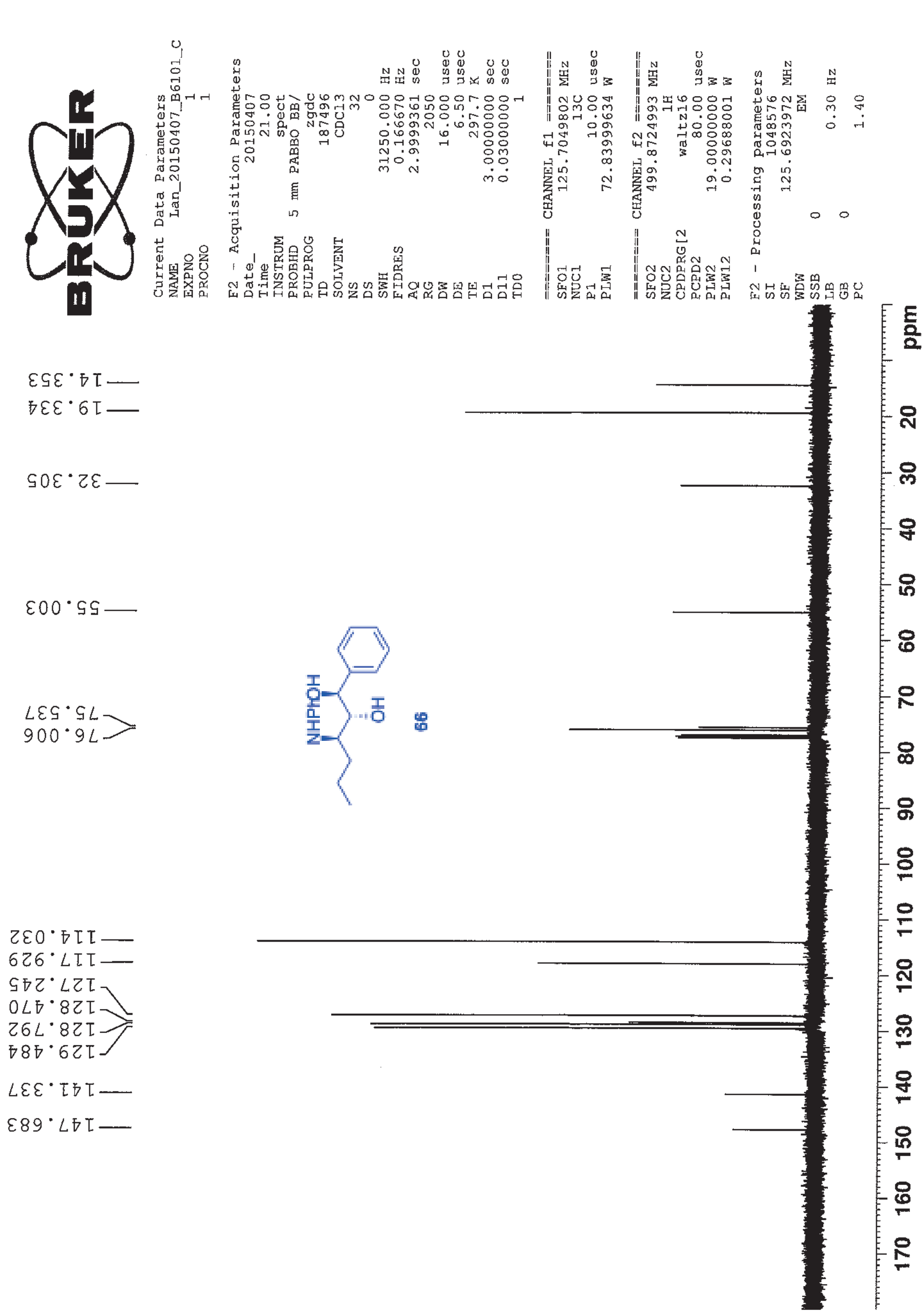
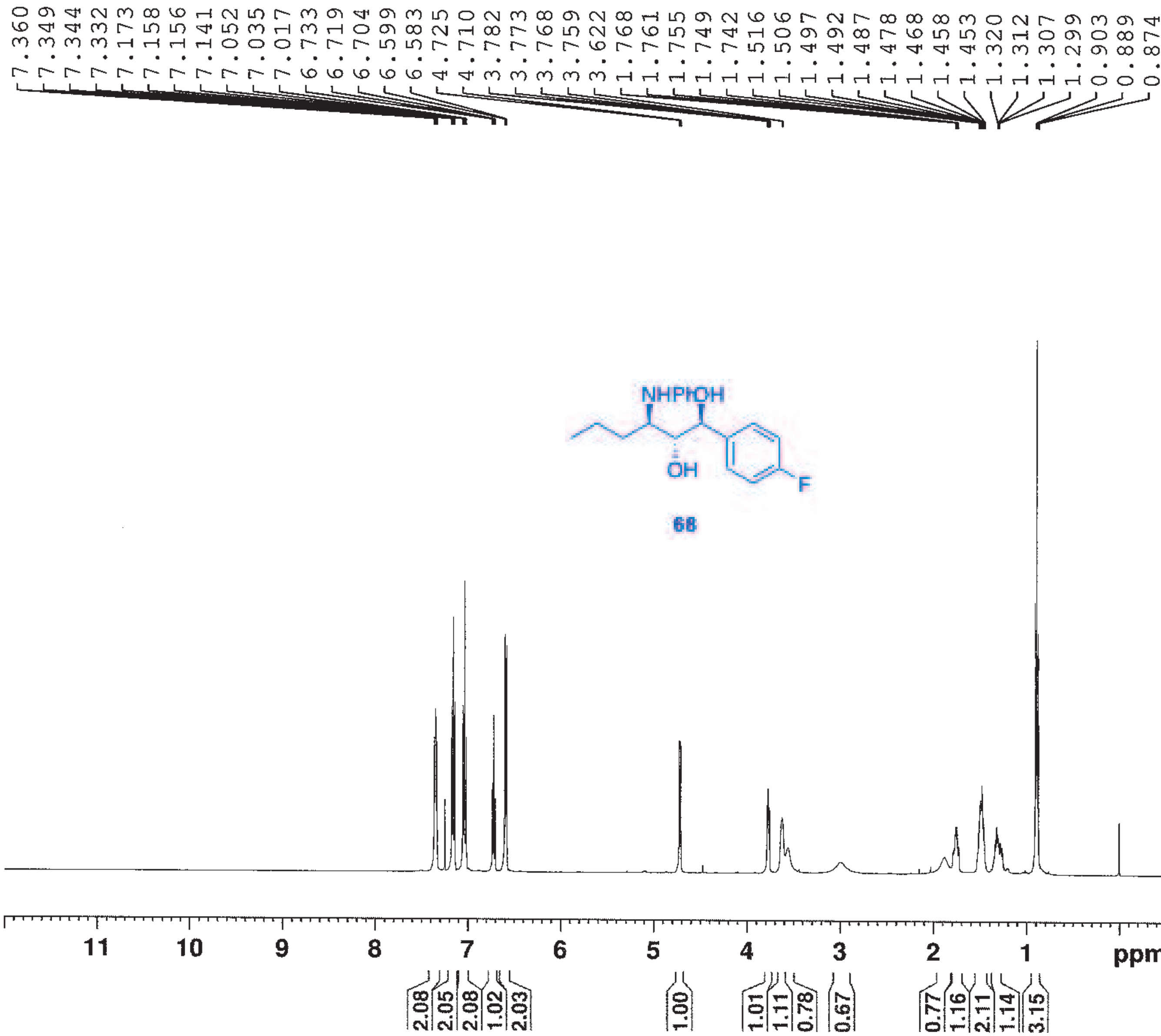
```
Current Data Parameters
NAME        Lan_20150407_B6101
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_               20150407
Time                   20.48
INSTRUM                spect
PROBHD     5 mm PABBO BB/
PULPROG                   zg
TD                     59998
SOLVENT                CDCl3
NS                         8
DS                         0
SWH              10000.000 Hz
FIDRES            0.166672 Hz
AQ               2.9999001 sec
RG                     25.24
DW                    50.000 usec
DE                      6.50 usec
TE                     297.0 K
D1               10.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1          499.8730869 MHz
NUC1                   1H
P1                   10.75 usec
PLW1           18.25000000 W

F2 - Processing parameters
SI                     65536
SF            499.8700203 MHz
WDW                       EM
SSB       0
LB                      0.30 Hz
GB        0
PC                      1.00
```


14.353
19.334
32.305
55.003
75.537
76.006
114.032
117.929
127.245
128.470
128.792
129.484
141.337
147.683
NHPhOH
OH
66
BRUKER
Current Data Parameters
NAME Lan_20150407_B6101_C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150407
Time 21.00
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgdc
TD 187496
SOLVENT CDCl3
NS 32
DS 0
SWH 31250.000 Hz
FIDRES 0.166670 Hz
AQ 2.9999361 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 297.7 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7049802 MHz
NUC1 13C
P1 10.00 usec
PLW1 72.83999634 W
======== CHANNEL f2 ========
SFO2 499.8724993 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.29688001 W
F2 - Processing parameters
SI 1048576
SF 125.6923972 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm



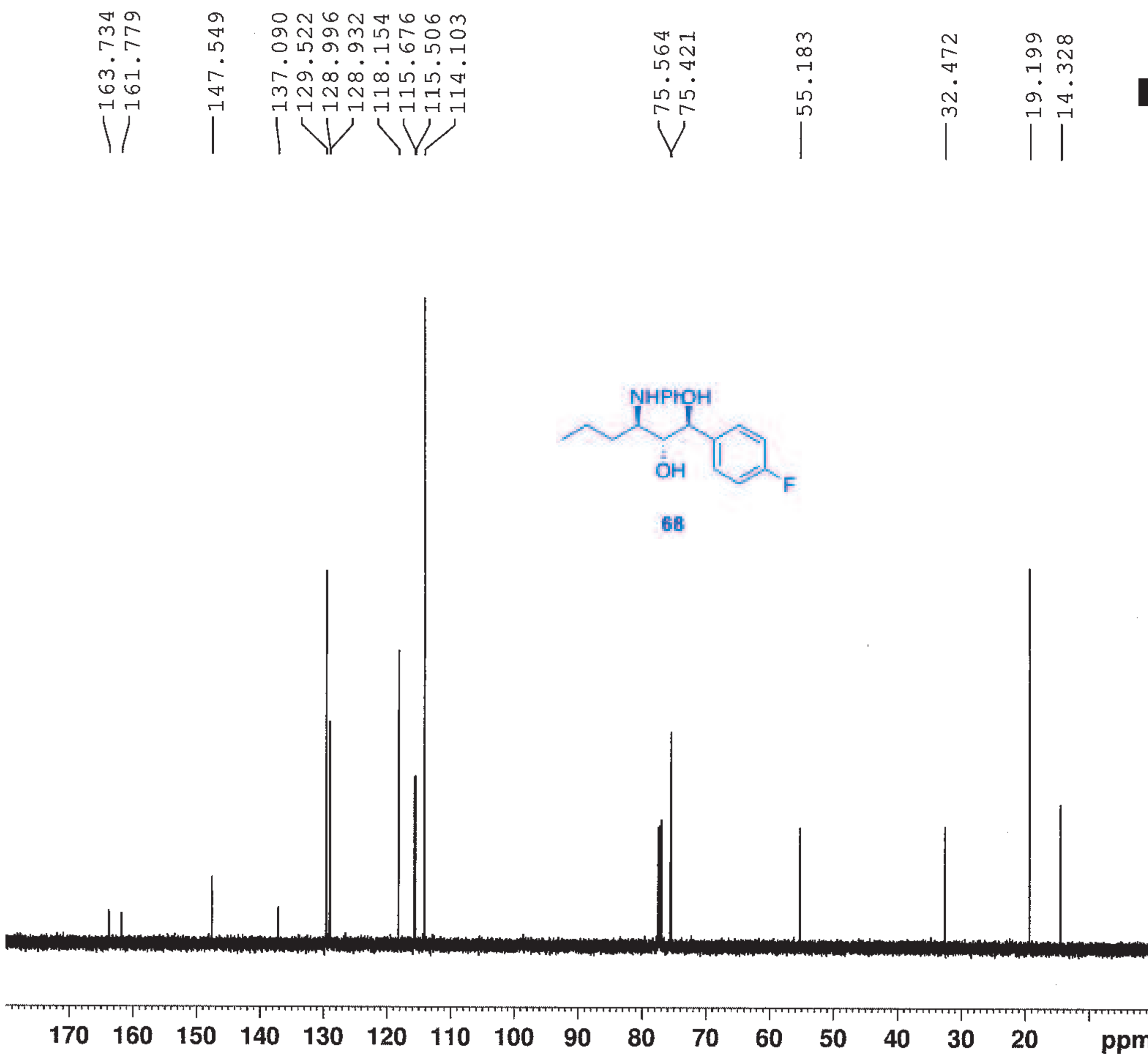
BRUKER

```
Current Data Parameters
NAME        Lan_20150408_B6097
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_               20150408
Time                   19.59
INSTRUM                spect
PROBHD     5 mm PABBO BB/
PULPROG                   zg
TD                     59998
SOLVENT                CDCl3
NS                         8
DS                         0
SWH             10000.000 Hz
FIDRES           0.166672 Hz
AQ              2.9999001 sec
RG                     25.24
DW                 50.000 usec
DE                   6.50 usec
TE                  296.9 K
D1            10.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1        499.8730869 MHz
NUC1                     1H
P1                 10.75 usec
PLW1         18.25000000 W

F2 - Processing parameters
SI                     65536
SF           499.8700178 MHz
WDW                       EM
SSB         0
LB                   0.30 Hz
GB          0
PC                      1.00
```



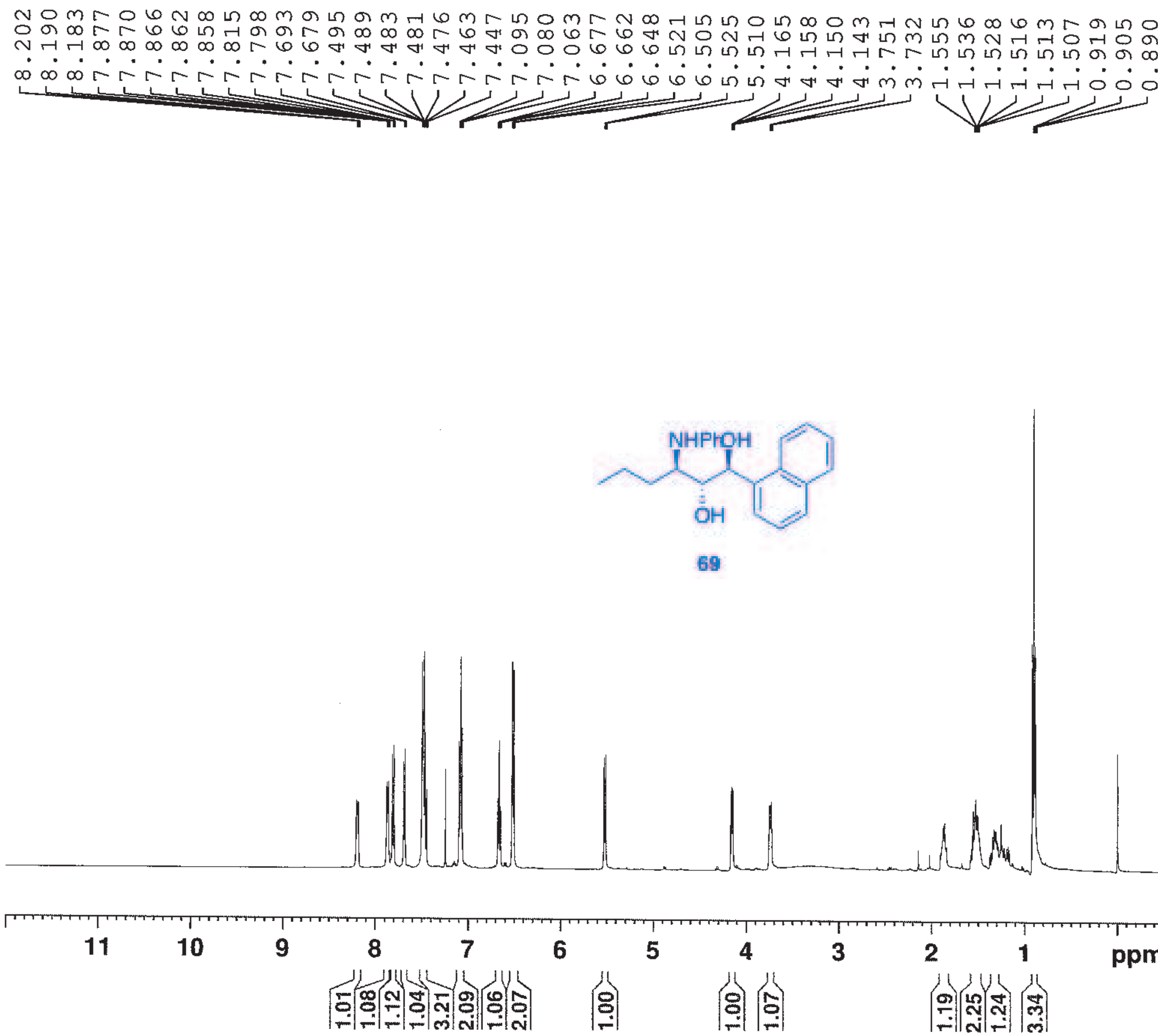
Current Data Parameters
NAME Lan_20150408_B6097_C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150408
Time 20.06
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgdc
TD 187496
SOLVENT CDCl3
NS 59
DS 0
SWH 31250.000 Hz
FIDRES 0.166670 Hz
AQ 2.9999361 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 297.5 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 125.7049802 MHz
NUC1 13C
P1 10.00 usec
PLW1 72.83999634 W

======== CHANNEL f2 ========
SFO2 499.8724993 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.29688001 W

F2 - Processing parameters
SI 1048576
SF 125.6923966 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40



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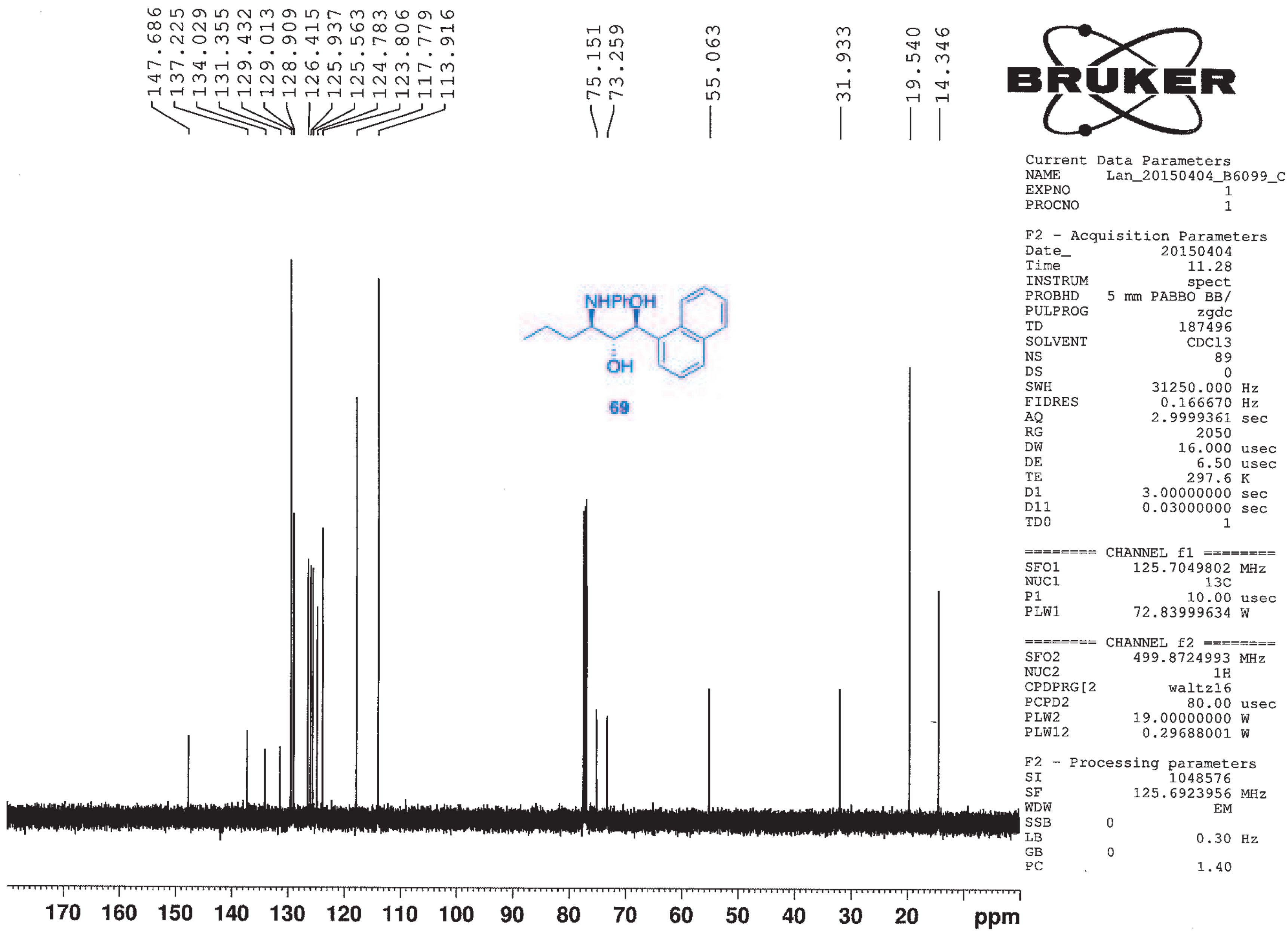
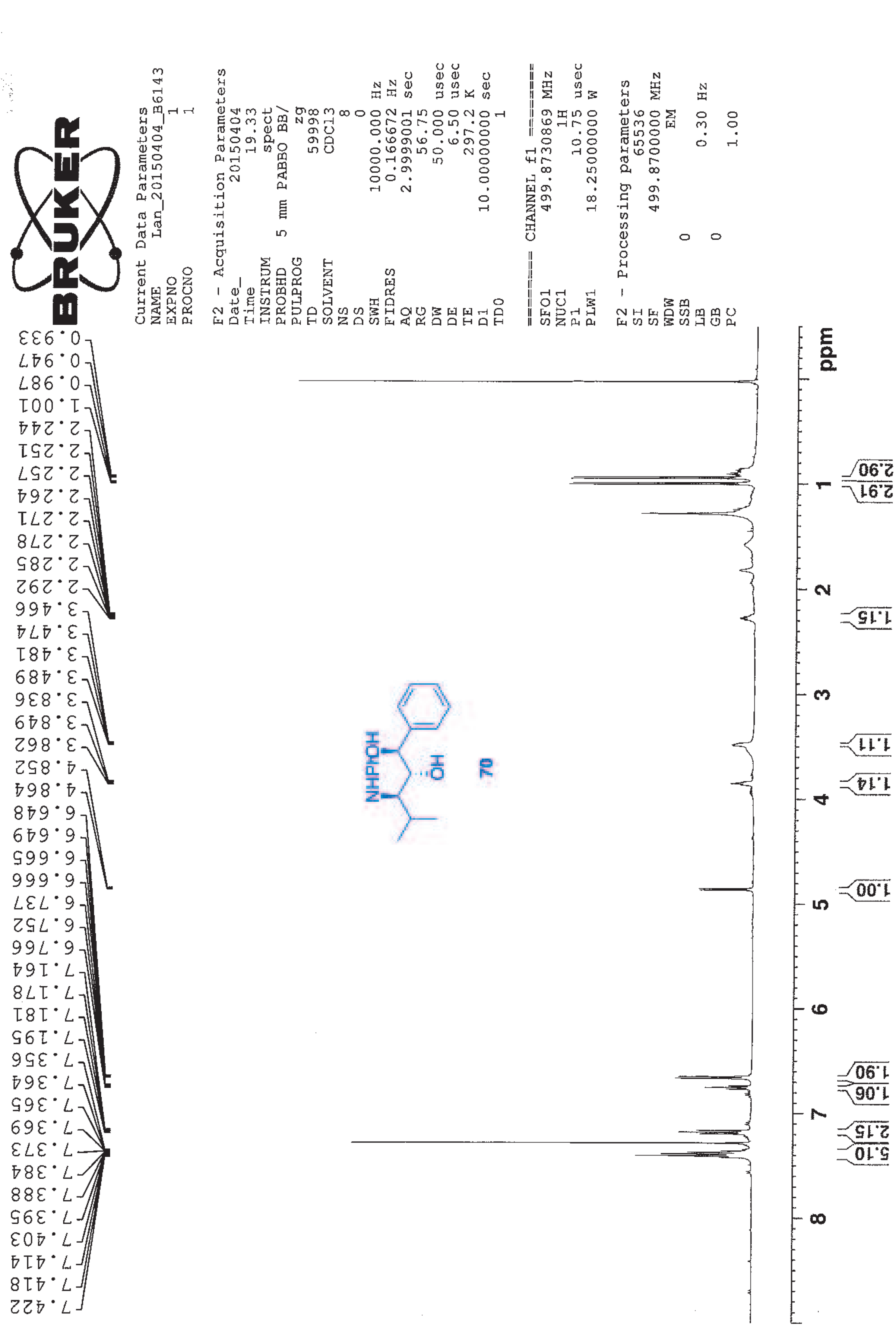
Current Data Parameters
NAME Lan_20150404_B6099
EXPNO 1
PROCNO 1

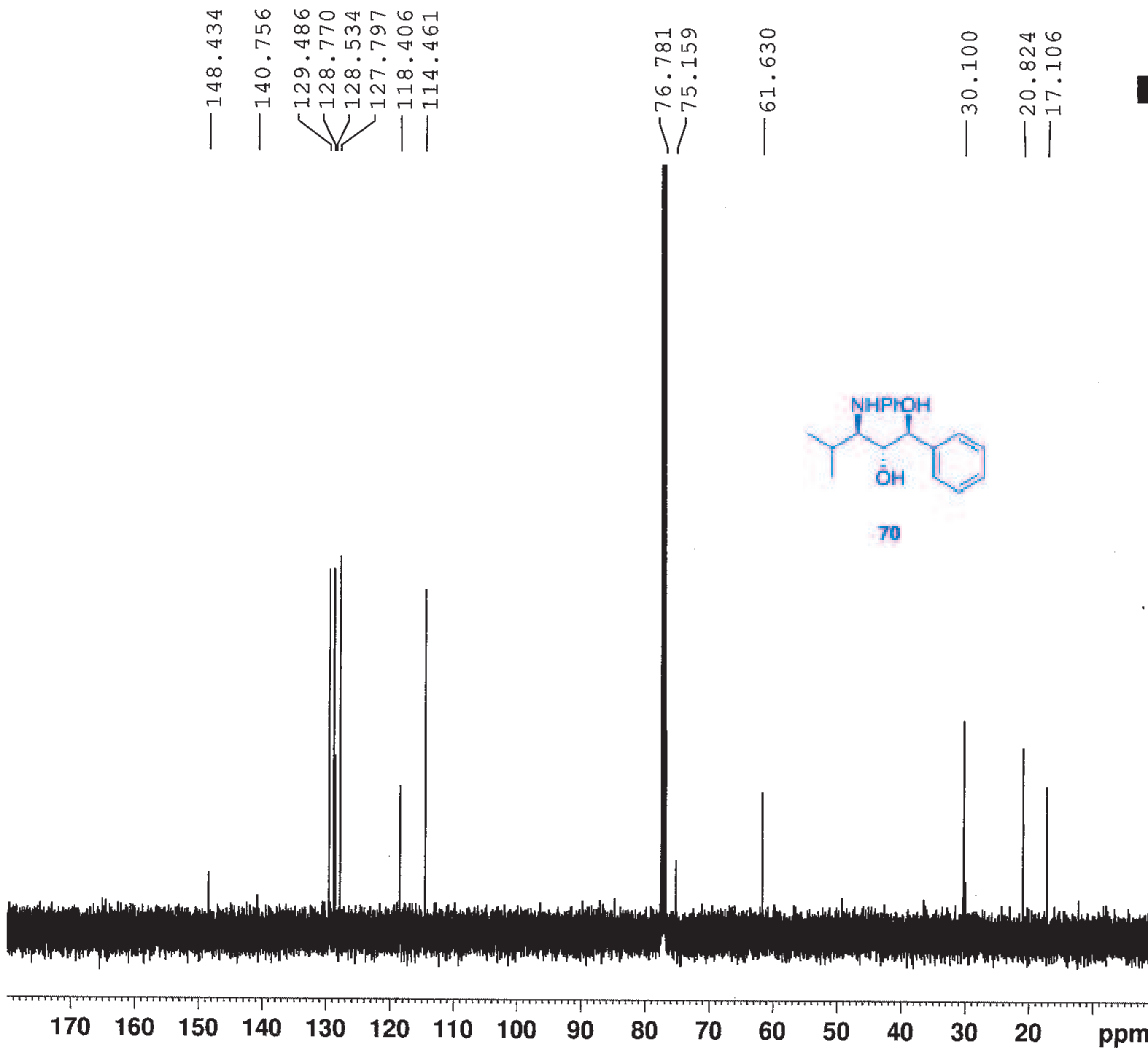
F2 - Acquisition Parameters
Date_ 20150404
Time 11.14
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 28.76
DW 50.000 usec
DE 6.50 usec
TE 297.0 K
D1 10.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 499.8730869 MHz
NUC1 1H
P1 10.75 usec
PLW1 18.25000000 W

F2 - Processing parameters
SI 65536
SF 499.8700203 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


147.686
137.225
134.029
131.355
129.432
129.013
128.909
126.415
125.937
125.563
124.783
123.806
117.779
113.916
75.151
73.259
55.063
31.933
19.540
14.346
NHPhOH
OH
69
BRUKER
Current Data Parameters
NAME Lan_20150404_B6099_C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150404
Time 11.28
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgdc
TD 187496
SOLVENT CDCl3
NS 89
DS 0
SWH 31250.000 Hz
FIDRES 0.166670 Hz
AQ 2.9999361 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 297.6 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7049802 MHz
NUC1 13C
P1 10.00 usec
PLW1 72.83999634 W
======== CHANNEL f2 ========
SFO2 499.8724993 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.29688001 W
F2 - Processing parameters
SI 1048576
SF 125.6923956 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


BRUKER
Current Data Parameters
NAME Lan_20150404_B6143
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150404
Time 19.33
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 56.75
DW 50.000 usec
DE 6.50 usec
TE 297.2 K
D1 10.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 499.8730869 MHz
NUC1 1H
P1 10.75 usec
PLW1 18.25000000 W
F2 - Processing parameters
SI 65536
SF 499.8700000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0.933
0.947
0.987
1.001
2.244
2.251
2.257
2.264
2.271
2.278
2.285
2.292
3.466
3.474
3.481
3.489
3.836
3.849
3.862
4.852
4.864
6.648
6.649
6.665
6.666
6.737
6.752
6.766
7.164
7.178
7.181
7.195
7.356
7.364
7.365
7.369
7.373
7.384
7.388
7.395
7.403
7.414
7.418
7.422
NHPhOH
OH
70
2.90
2.91
1.15
1.11
1.14
1.00
1.90
1.06
2.15
5.10
ppm
1
2
3
4
5
6
7
8



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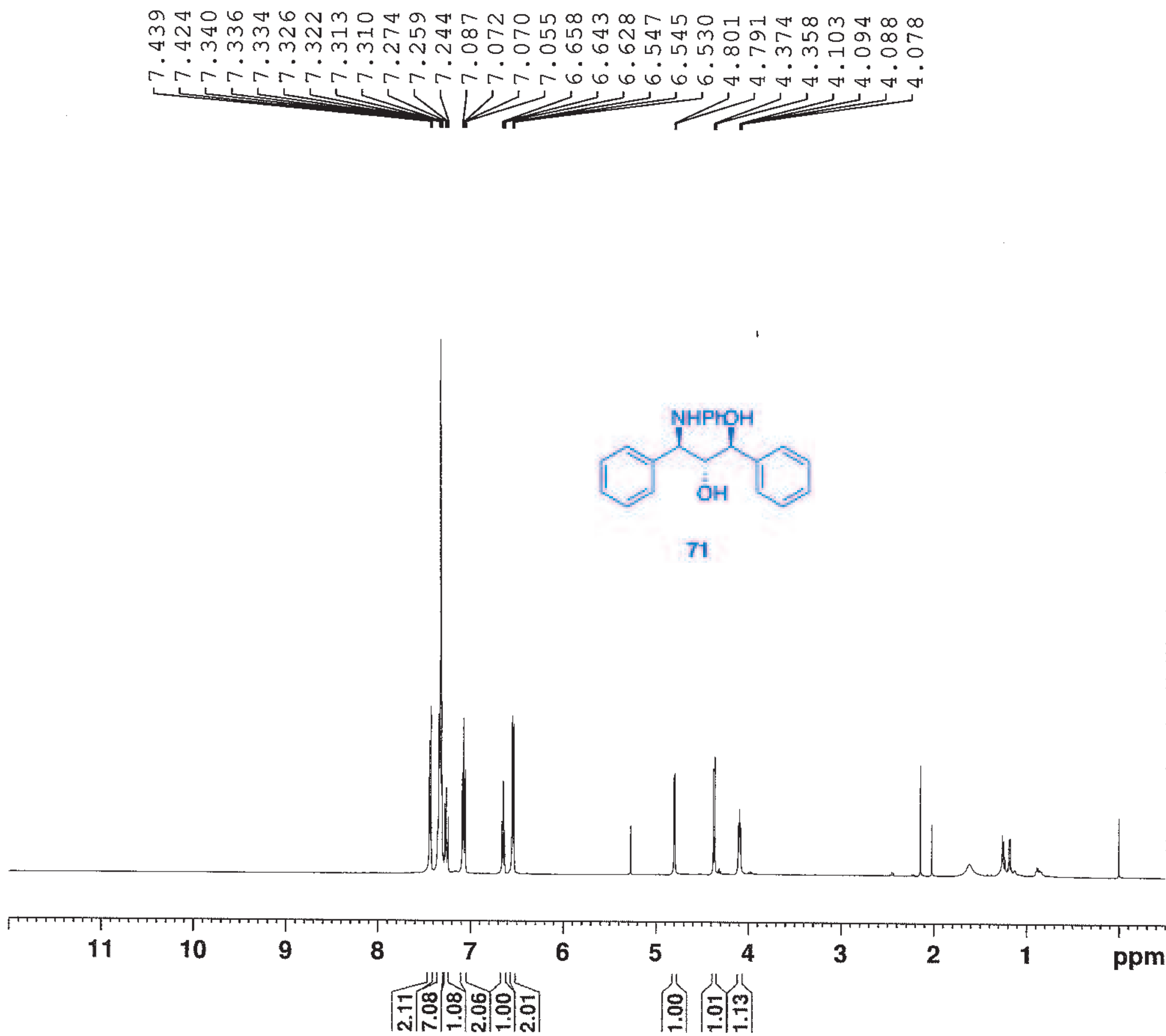
```
Current Data Parameters
NAME          Lan_20150404_B6143_C
EXPNO                            1
PROCNO                           1

F2 - Acquisition Parameters
Date_                     20150404
Time                         19.43
INSTRUM                      spect
PROBHD        5 mm PABBO BB/
PULPROG                       zgdc
TD                          187496
SOLVENT                      CDCl3
NS                             344
DS                               0
SWH                      31250.000 Hz
FIDRES                    0.166670 Hz
AQ                       2.9999361 sec
RG                            2050
DW                          16.000 usec
DE                            6.50 usec
TE                           297.6 K
D1                      3.00000000 sec
D11                     0.03000000 sec
TD0                              1

======== CHANNEL f1 ========
SFO1                   125.7049802 MHz
NUC1                           13C
P1                           10.00 usec
PLW1                   72.83999634 W

======== CHANNEL f2 ========
SFO2                   499.8724993 MHz
NUC2                            1H
CPDPRG[2                   waltz16
PCPD2                        80.00 usec
PLW2                   19.00000000 W
PLW12                   0.29688001 W

F2 - Processing parameters
SI                         1048576
SF                     125.6923910 MHz
WDW                             EM
SSB          0
LB                            0.30 Hz
GB           0
PC                            1.40
```

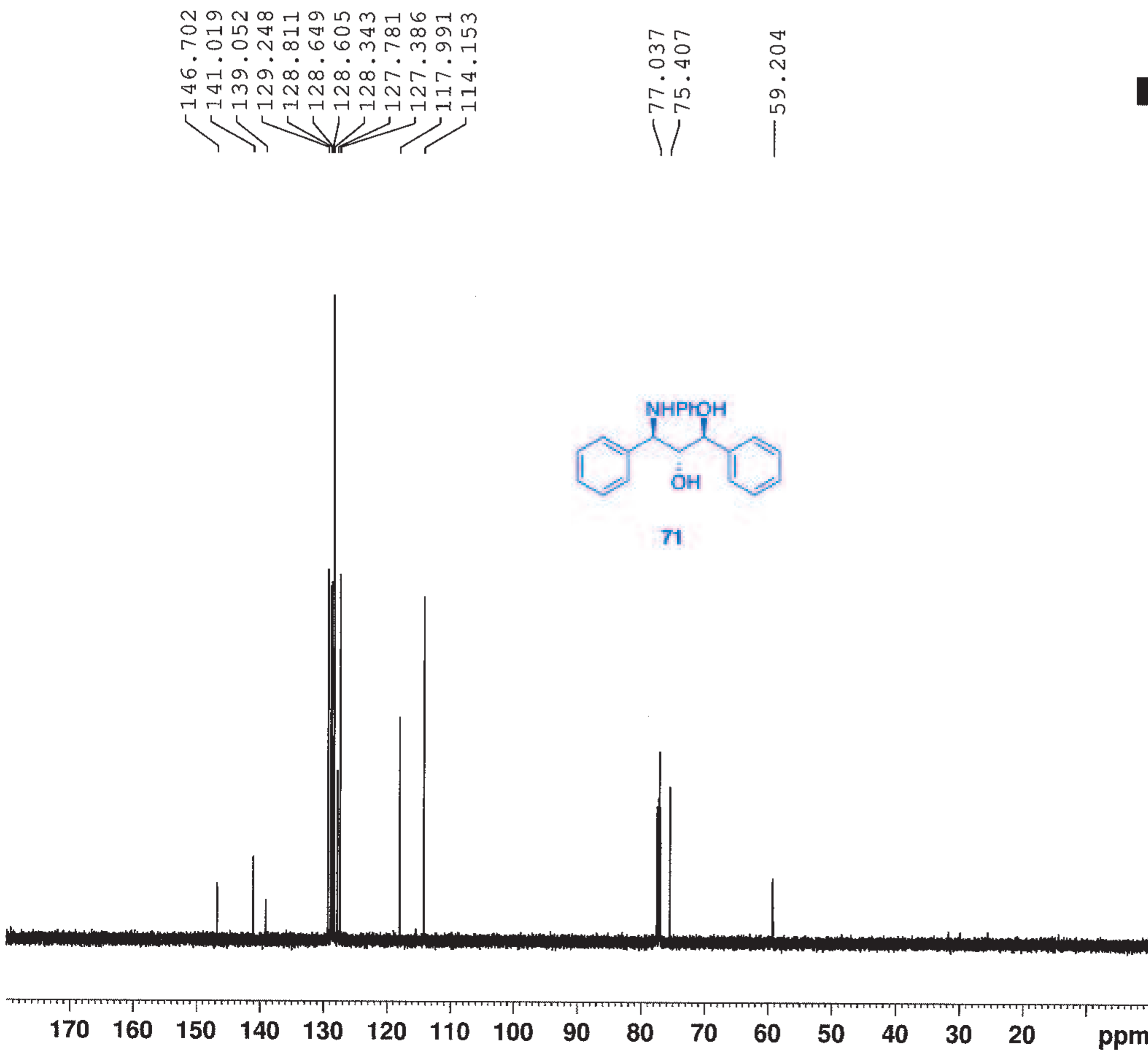



```
Current Data Parameters
NAME        Lan_20150404_B5247
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150404
Time                 20.24
INSTRUM              spect
PROBHD     5 mm PABBO BB/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                       8
DS                       0
SWH           10000.000 Hz
FIDRES         0.166672 Hz
AQ            2.9999001 sec
RG                   25.24
DW               50.000 usec
DE                 6.50 usec
TE                297.7 K
D1          10.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1        499.8730869 MHz
NUC1                    1H
P1                10.75 usec
PLW1        18.25000000 W

F2 - Processing parameters
SI                   65536
SF          499.8700233 MHz
WDW                     EM
SSB          0
LB                    0.30 Hz
GB           0
PC                    1.00
```



BRUKER

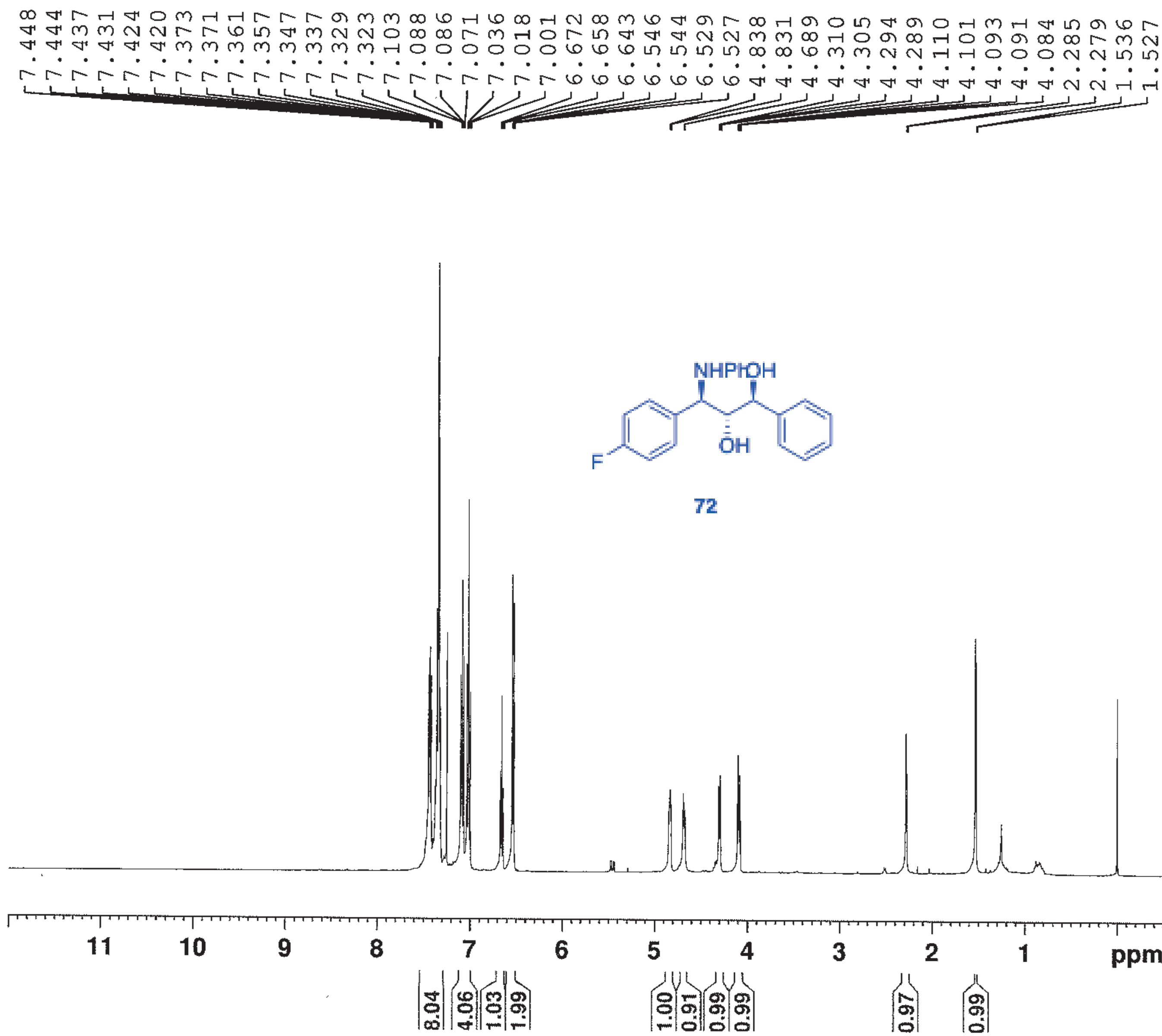
```
Current Data Parameters
NAME          Lan_20150404_B5247_C
EXPNO                            1
PROCNO                           1

F2 - Acquisition Parameters
Date_                     20150404
Time                         20.39
INSTRUM                      spect
PROBHD       5 mm PABBO BB/
PULPROG                       zgdc
TD                          187496
SOLVENT                      CDCl3
NS                              63
DS                               0
SWH                  31250.000 Hz
FIDRES                0.166670 Hz
AQ                   2.9999361 sec
RG                            2050
DW                      16.000 usec
DE                        6.50 usec
TE                       297.8 K
D1                  3.00000000 sec
D11                 0.03000000 sec
TD0                              1

======== CHANNEL f1 ========
SFO1               125.7049802 MHz
NUC1                           13C
P1                        10.00 usec
PLW1               72.83999634 W

======== CHANNEL f2 ========
SFO2               499.8724993 MHz
NUC2                            1H
CPDPRG[2                   waltz16
PCPD2                     80.00 usec
PLW2               19.00000000 W
PLW12               0.29688001 W

F2 - Processing parameters
SI                         1048576
SF                 125.6923978 MHz
WDW                             EM
SSB        0
LB                            0.30 Hz
GB         0
PC                            1.40
```

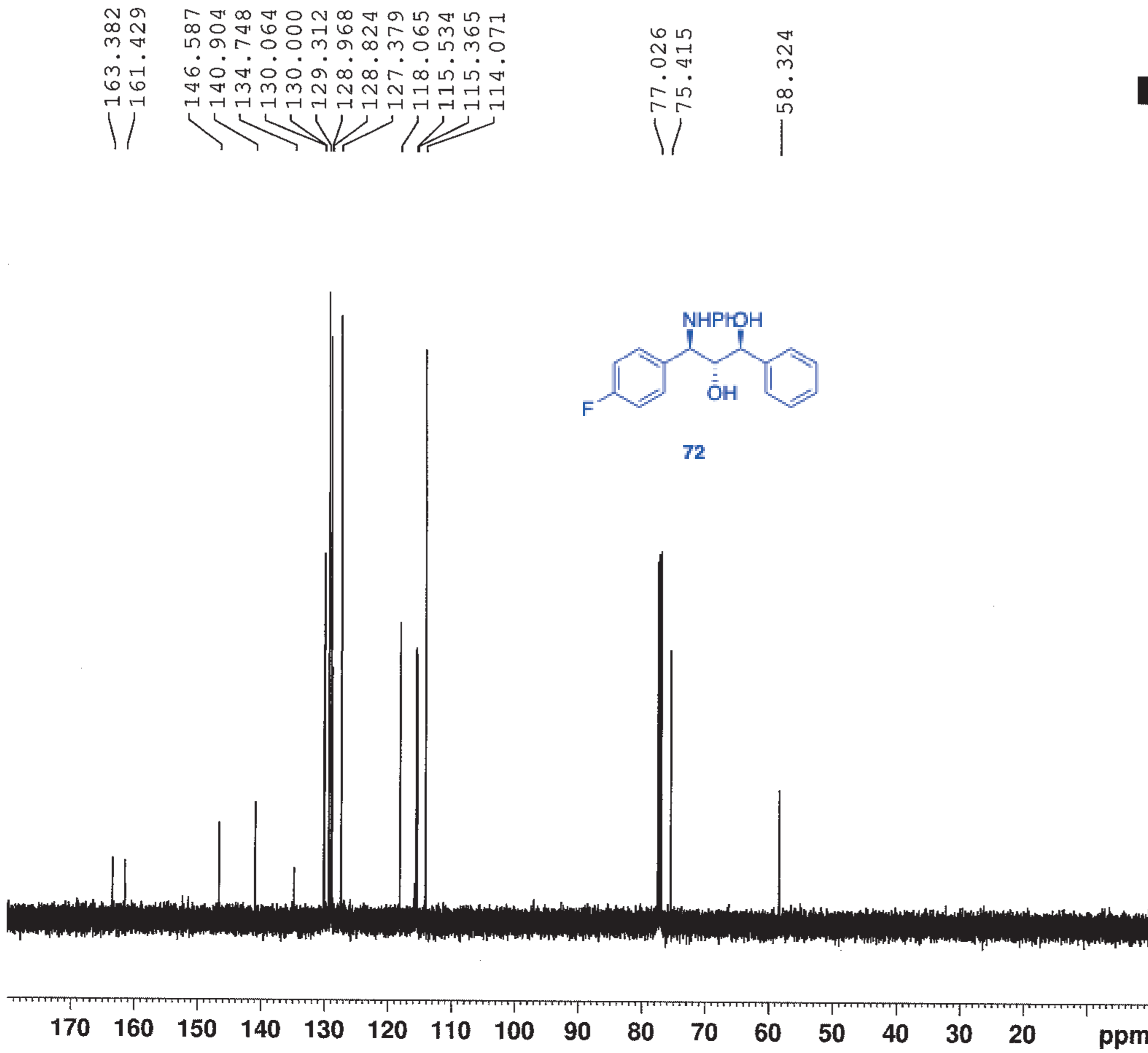



```
Current Data Parameters
NAME        Lan_20150407_B6221
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_             20150407
Time                 20.39
INSTRUM              spect
PROBHD     5 mm PABBO BB/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                       8
DS                       0
SWH           10000.000 Hz
FIDRES         0.166672 Hz
AQ            2.9999001 sec
RG                   44.57
DW               50.000 usec
DE                 6.50 usec
TE                297.0 K
D1          10.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1       499.8730869 MHz
NUC1                    1H
P1               10.75 usec
PLW1       18.25000000 W

F2 - Processing parameters
SI                   65536
SF         499.8700164 MHz
WDW                     EM
SSB      0
LB                 0.30 Hz
GB       0
PC                    1.00
```



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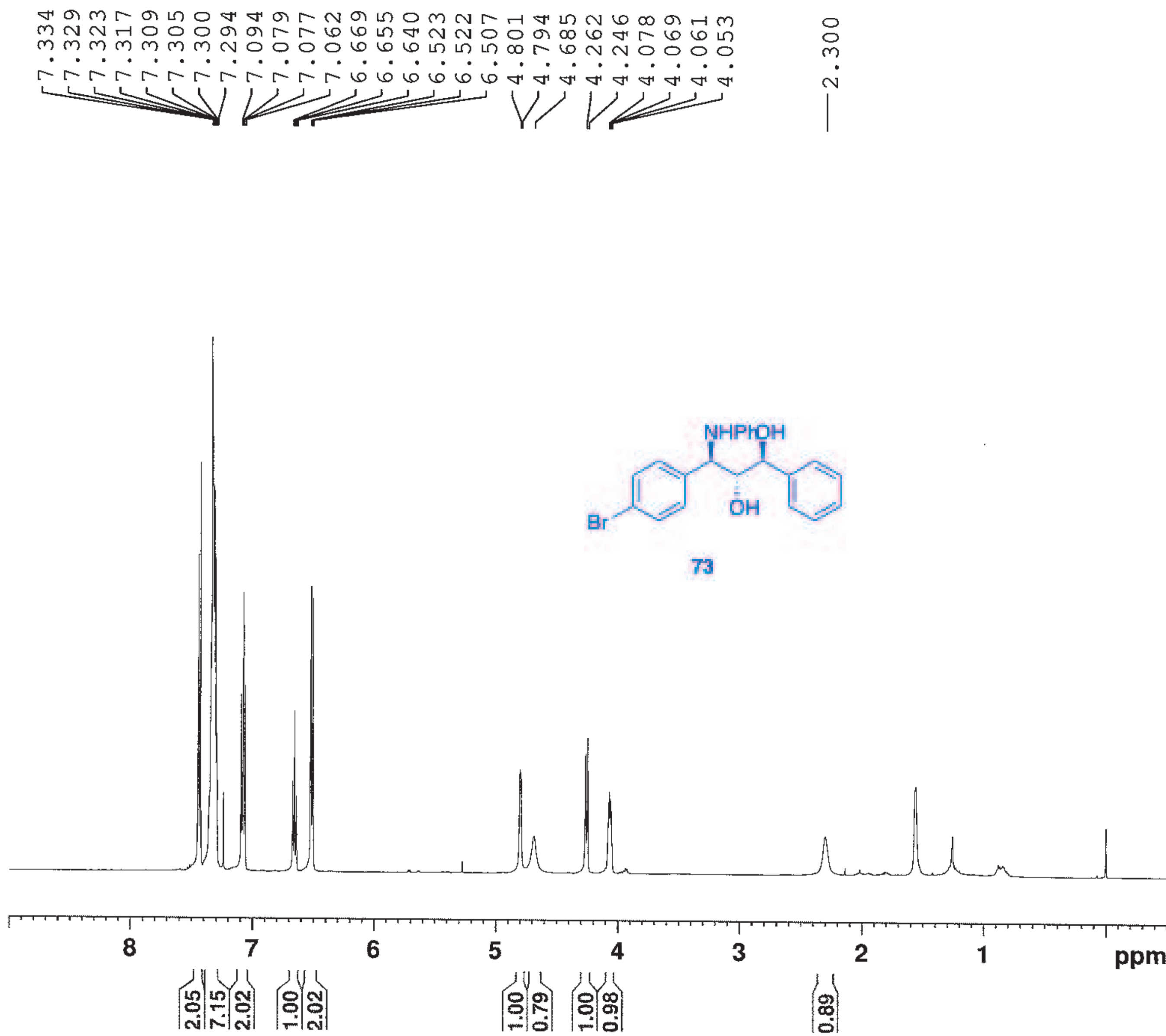
Current Data Parameters
NAME Lan_20150407_B6221_C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150407
Time 19.30
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgdc
TD 187496
SOLVENT CDCl3
NS 146
DS 0
SWH 31250.000 Hz
FIDRES 0.166670 Hz
AQ 2.9999361 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 297.4 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 125.7049802 MHz
NUC1 13C
P1 10.00 usec
PLW1 72.83999634 W

======== CHANNEL f2 ========
SFO2 499.8724993 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.29688001 W

F2 - Processing parameters
SI 1048576
SF 125.6923926 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40



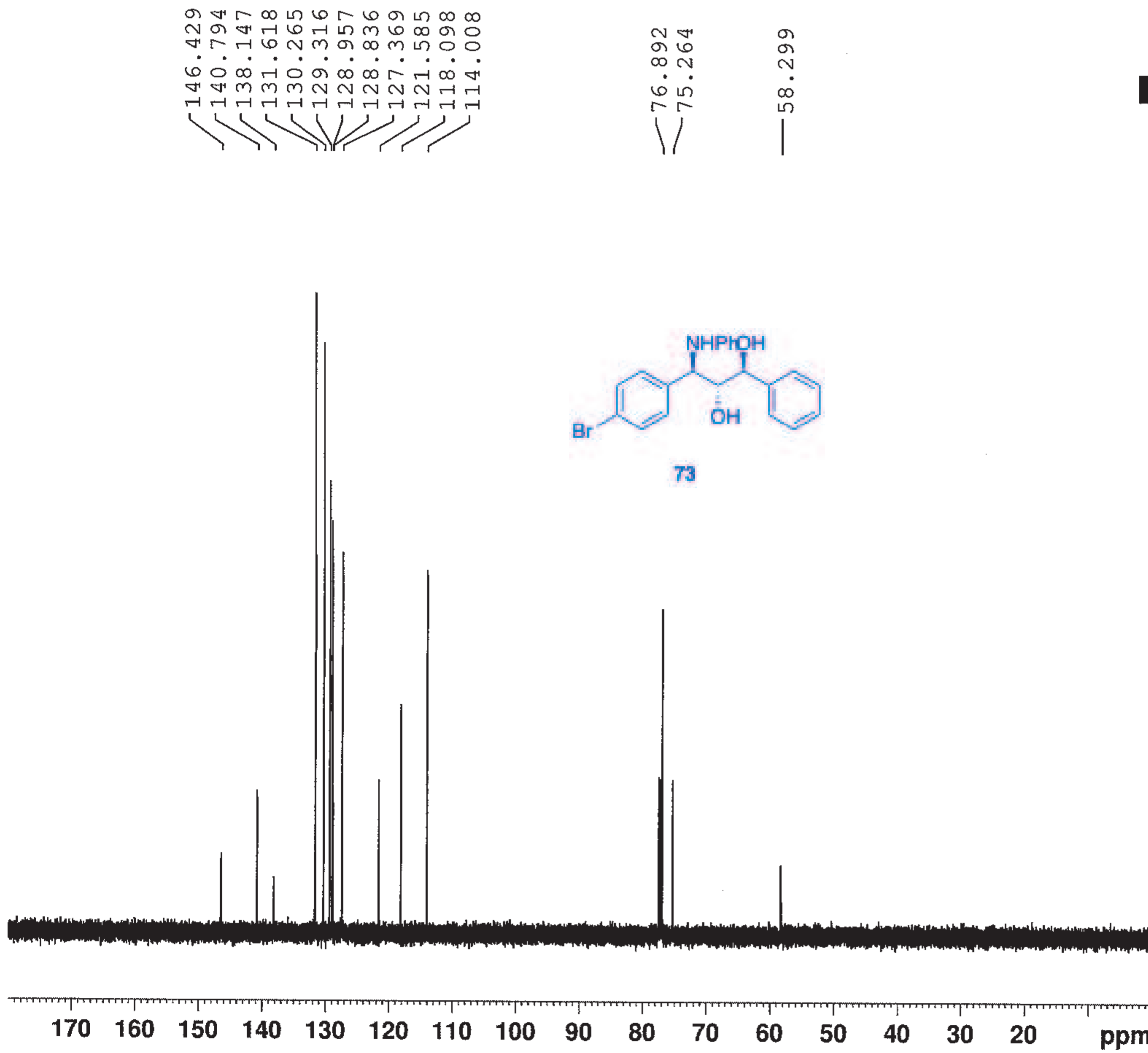
BRUKER

```
Current Data Parameters
NAME          Lan_20150407_B6195
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20150407
Time                       19.07
INSTRUM                    spect
PROBHD        5 mm PABBO BB/
PULPROG                       zg
TD                         59998
SOLVENT                    CDCl3
NS                             8
DS                             0
SWH                    10000.000 Hz
FIDRES                  0.166672 Hz
AQ                     2.9999001 sec
RG                         28.76
DW                        50.000 usec
DE                          6.50 usec
TE                         297.4 K
D1                   10.00000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                 499.8730869 MHz
NUC1                          1H
P1                         10.75 usec
PLW1                 18.25000000 W

F2 - Processing parameters
SI                         65536
SF                   499.8700227 MHz
WDW                           EM
SSB          0
LB                          0.30 Hz
GB           0
PC                          1.00
```



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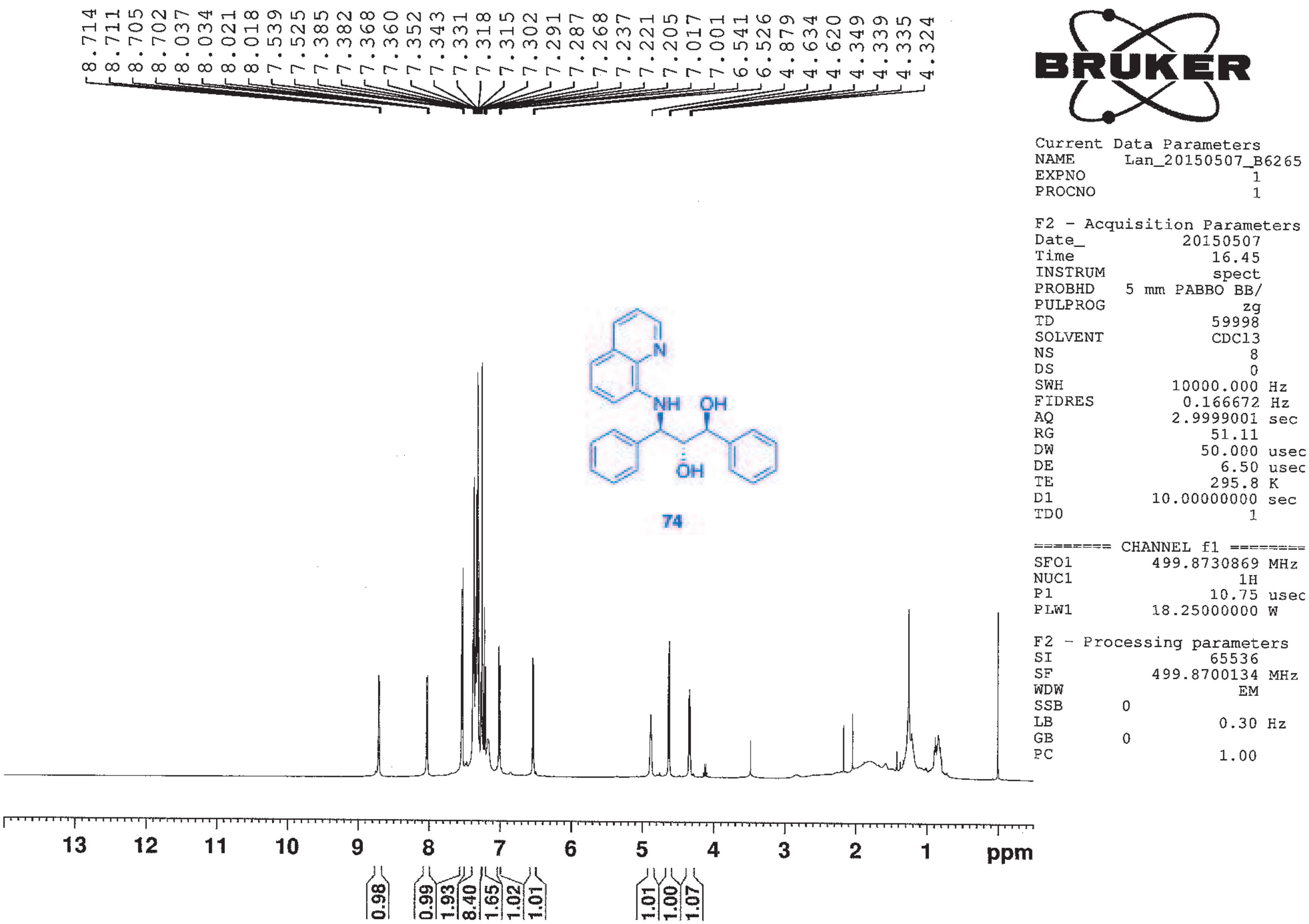
Current Data Parameters
NAME Lan_20150407_B6195_C
EXPNO 1
PROCNO 1

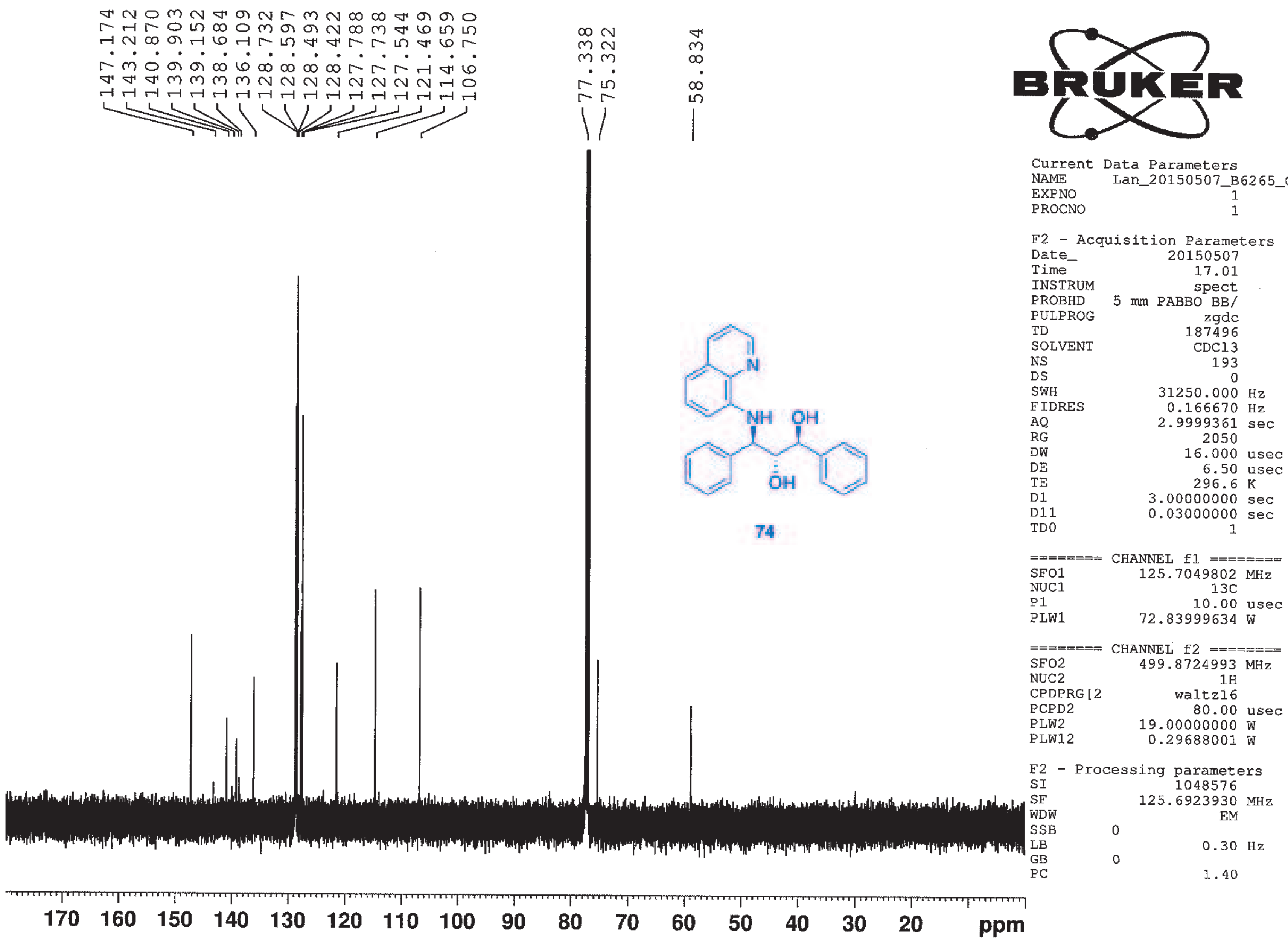
F2 - Acquisition Parameters
Date_ 20150407
Time 19.14
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgdc
TD 187496
SOLVENT CDCl3
NS 41
DS 0
SWH 31250.000 Hz
FIDRES 0.166670 Hz
AQ 2.9999361 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 297.5 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 125.7049802 MHz
NUC1 13C
P1 10.00 usec
PLW1 72.83999634 W

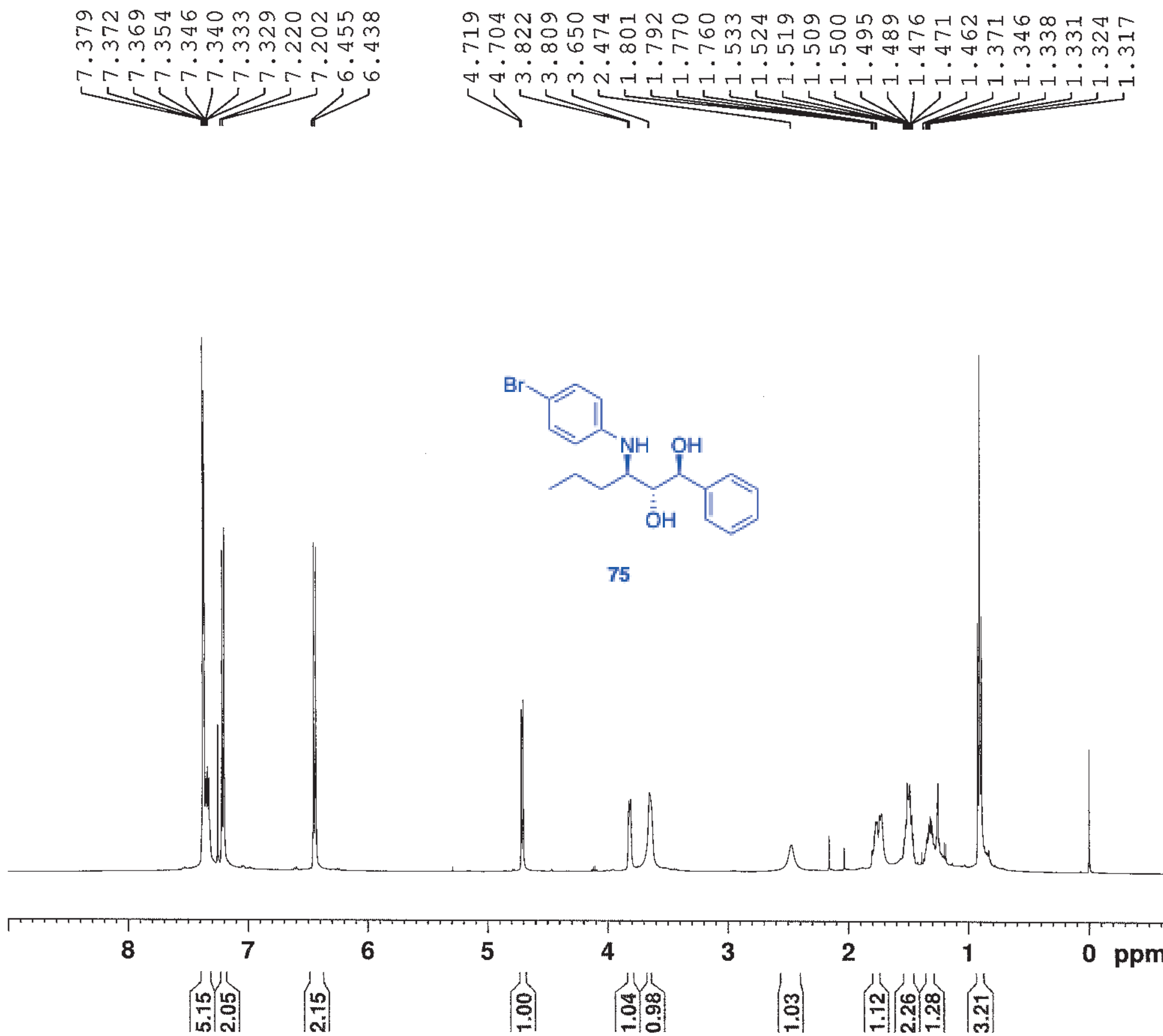
======== CHANNEL f2 ========
SFO2 499.8724993 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.29688001 W

F2 - Processing parameters
SI 1048576
SF 125.6923982 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40

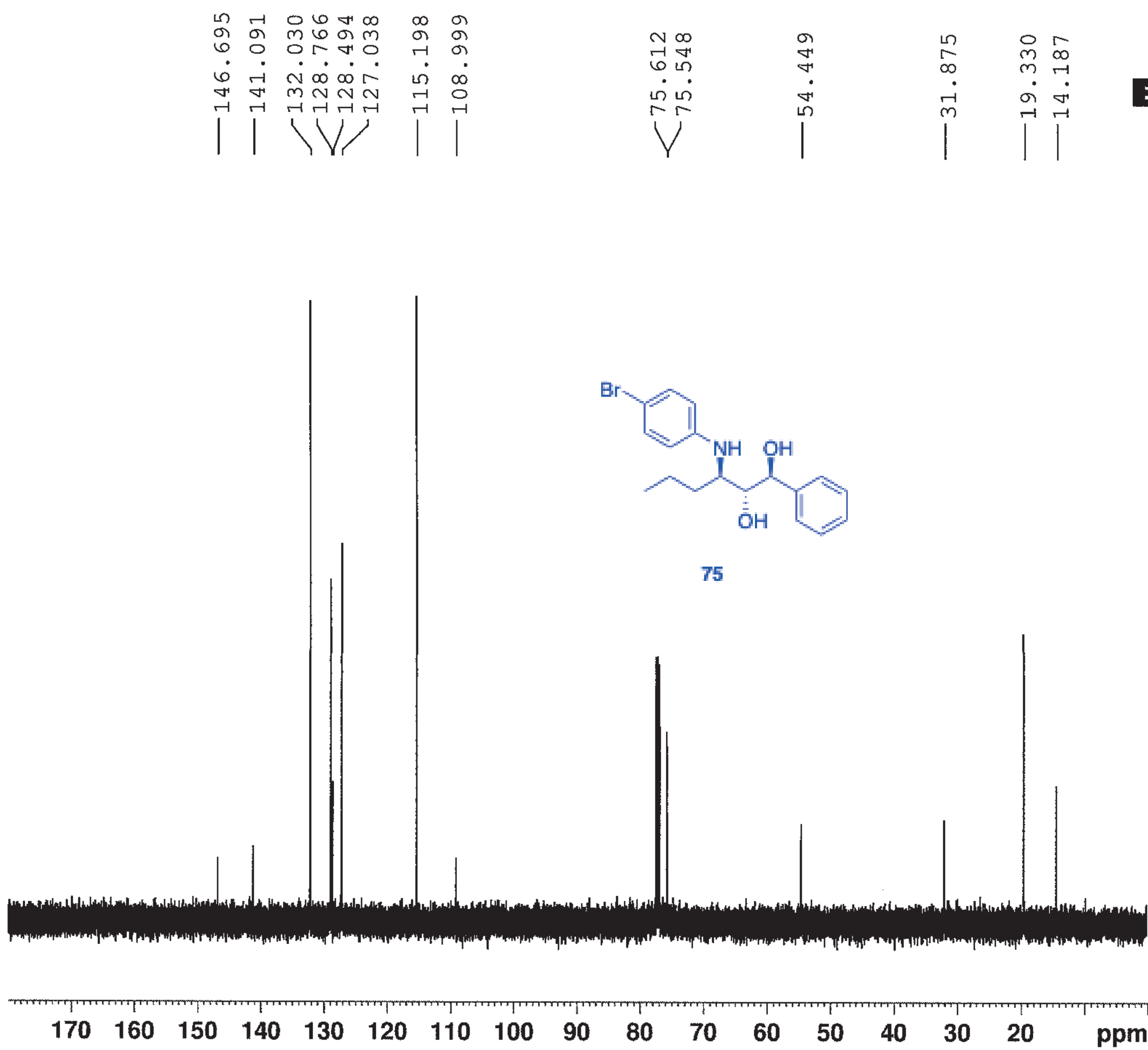

8.714 8.711 8.705 8.702 8.037 8.034 8.021 8.018 7.539 7.525 7.385 7.382 7.368 7.360 7.352 7.343 7.331 7.318 7.315 7.302 7.291 7.287 7.268 7.237 7.221 7.205 7.017 7.001 6.541 6.526 4.879 4.634 4.620 4.349 4.339 4.335 4.324
BRUKER
Current Data Parameters
NAME Lan_20150507_B6265
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150507
Time 16.45
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 51.11
DW 50.000 usec
DE 6.50 usec
TE 295.8 K
D1 10.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 499.8730869 MHz
NUC1 1H
P1 10.75 usec
PLW1 18.25000000 W
F2 - Processing parameters
SI 65536
SF 499.8700134 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
NH
OH
OH
N
74
13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.98 0.99 1.93 8.40 1.65 1.02 1.01 1.01 1.00 1.07



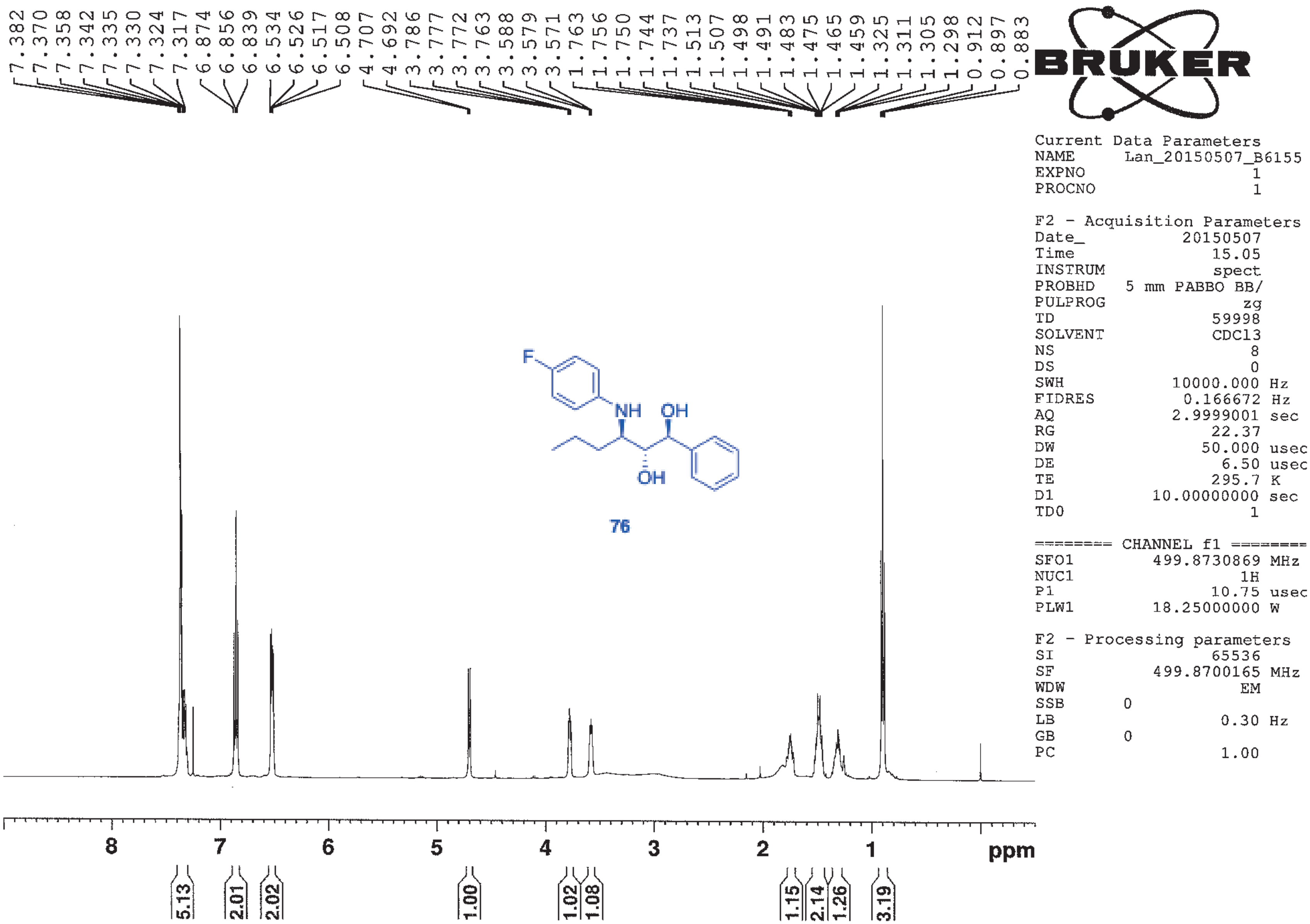
147.174
143.212
140.870
139.903
139.152
138.684
136.109
128.732
128.597
128.493
128.422
127.788
127.738
127.544
121.469
114.659
106.750
77.338
75.322
58.834
BRUKER
Current Data Parameters
NAME Lan_20150507_B6265_C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150507
Time 17.01
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgdc
TD 187496
SOLVENT CDCl3
NS 193
DS 0
SWH 31250.000 Hz
FIDRES 0.166670 Hz
AQ 2.9999361 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 296.6 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7049802 MHz
NUC1 13C
P1 10.00 usec
PLW1 72.83999634 W
======== CHANNEL f2 ========
SFO2 499.8724993 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.29688001 W
F2 - Processing parameters
SI 1048576
SF 125.6923930 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
N
NH
OH
OH
74
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

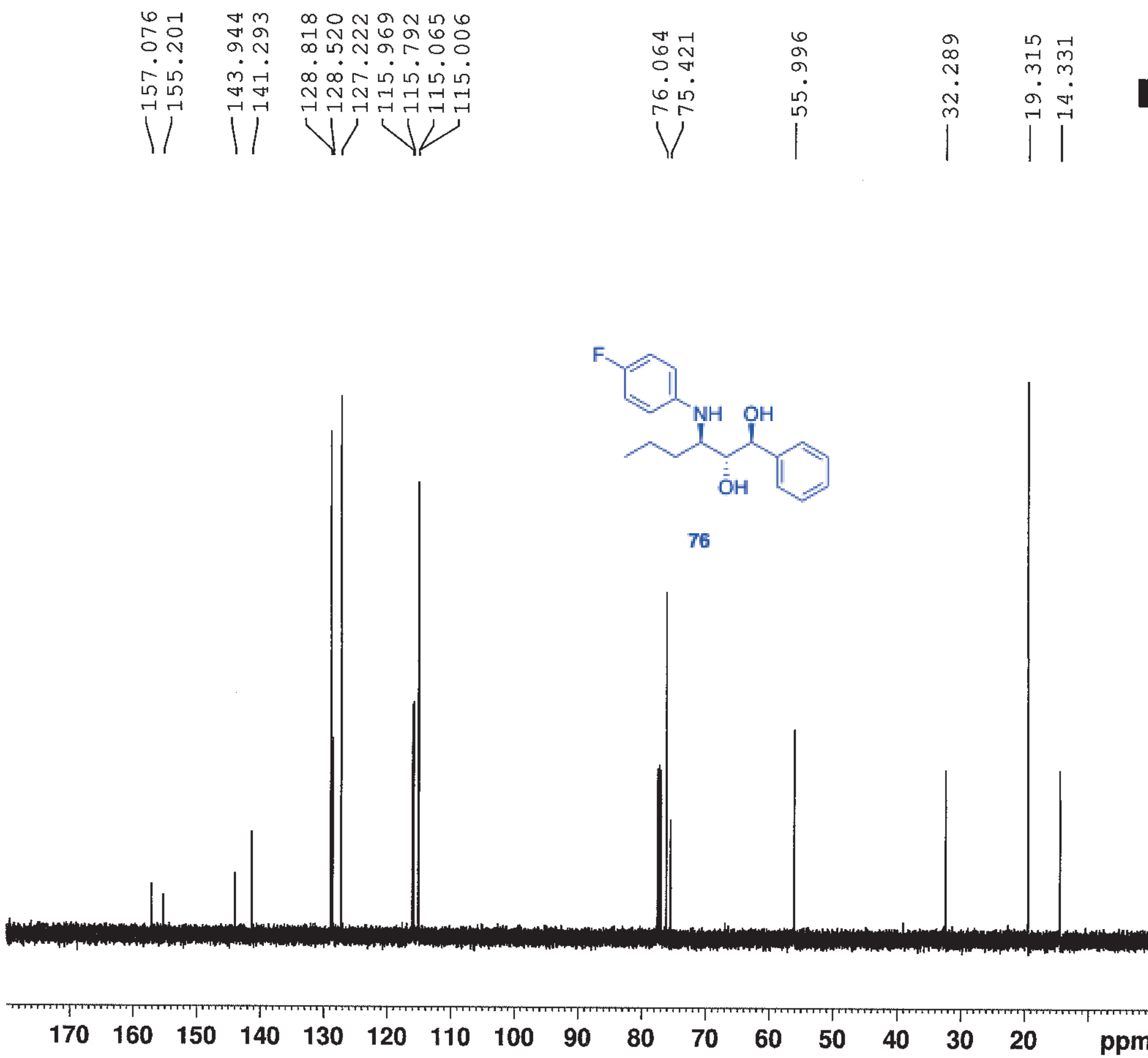



```
Current Data Parameters
NAME       Lan_20150405_B6153
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20150405
Time                  18.47
INSTRUM               spect
PROBHD     5 mm PABBO BB/
PULPROG                  zg
TD                    59998
SOLVENT               CDCl3
NS                        8
DS                        0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                    35.92
DW                50.000 usec
DE                  6.50 usec
TE                 297.5 K
D1           10.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1        499.8730869 MHz
NUC1                     1H
P1                10.75 usec
PLW1        18.25000000 W

F2 - Processing parameters
SI                    65536
SF          499.8700144 MHz
WDW                      EM
SSB       0
LB                  0.30 Hz
GB        0
PC                     1.00
```

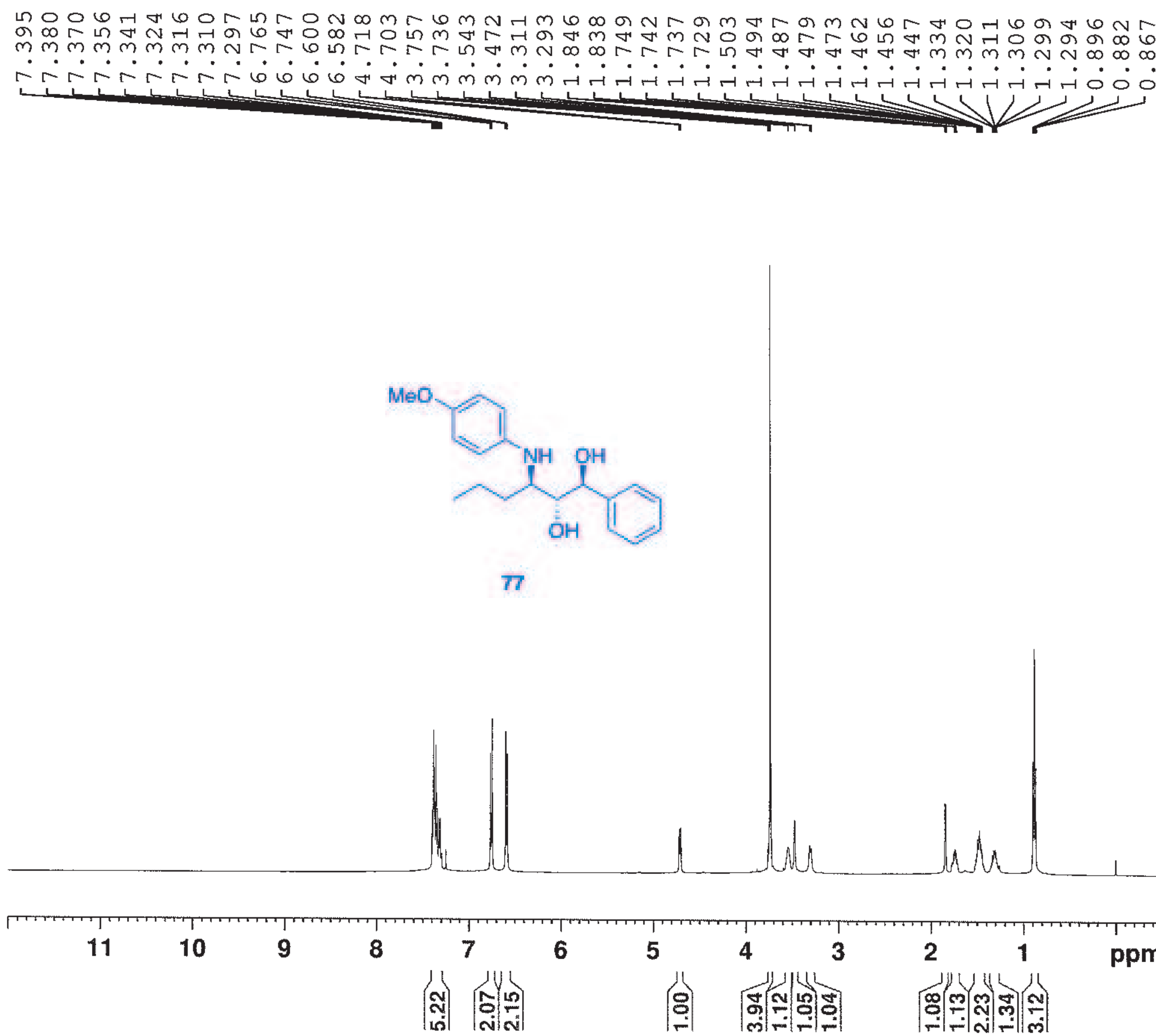



```
Current Data Parameters
NAME        Lan_20150405_B6153_C
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20150405
Time                   18.15
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                 zgdc
TD                    187496
SOLVENT                CDCl3
NS                        56
DS                         0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                      2050
DW                16.000 usec
DE                  6.50 usec
TE                 297.9 K
D1            3.00000000 sec
D11           0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                     13C
P1                  10.00 usec
PLW1          72.83999634 W

======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                      1H
CPDPRG[2             waltz16
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                   1048576
SF           125.6923937 MHz
WDW                       EM
SSB      0
LB                  0.30 Hz
GB       0
PC                      1.40
```


7.382 7.370 7.358 7.342 7.335 7.330 7.324 7.317 6.874 6.856 6.839 6.534 6.526 6.517 6.508 4.707 4.692 3.786 3.777 3.772 3.763 3.588 3.579 3.571 1.763 1.756 1.750 1.744 1.737 1.513 1.507 1.498 1.491 1.483 1.475 1.465 1.459 1.325 1.311 1.305 1.298 0.912 0.897 0.883
BRUKER
Current Data Parameters
NAME Lan_20150507_B6155
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150507
Time 15.05
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 22.37
DW 50.000 usec
DE 6.50 usec
TE 295.7 K
D1 10.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 499.8730869 MHz
NUC1 1H
P1 10.75 usec
PLW1 18.25000000 W
F2 - Processing parameters
SI 65536
SF 499.8700165 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
F
NH
OH
OH
76
8 7 6 5 4 3 2 1 ppm
5.13 2.01 2.02 1.00 1.02 1.08 1.15 2.14 1.26 3.19




```
Current Data Parameters
NAME         Lan_20150507_B6155_C
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_                20150507
Time                    15.15
INSTRUM                 spect
PROBHD      5 mm PABBO BB/
PULPROG                  zgdc
TD                     187496
SOLVENT                 CDCl3
NS                         51
DS                          0
SWH             31250.000 Hz
FIDRES           0.166670 Hz
AQ              2.9999361 sec
RG                       2050
DW                16.000 usec
DE                  6.50 usec
TE                  296.2 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1         125.7049802 MHz
NUC1                      13C
P1                 10.00 usec
PLW1           72.83999634 W

======== CHANNEL f2 ========
SFO2         499.8724993 MHz
NUC2                       1H
CPDPRG[2              waltz16
PCPD2              80.00 usec
PLW2           19.00000000 W
PLW12           0.29688001 W

F2 - Processing parameters
SI                    1048576
SF           125.6923974 MHz
WDW                        EM
SSB      0
LB                    0.30 Hz
GB       0
PC                       1.40
```



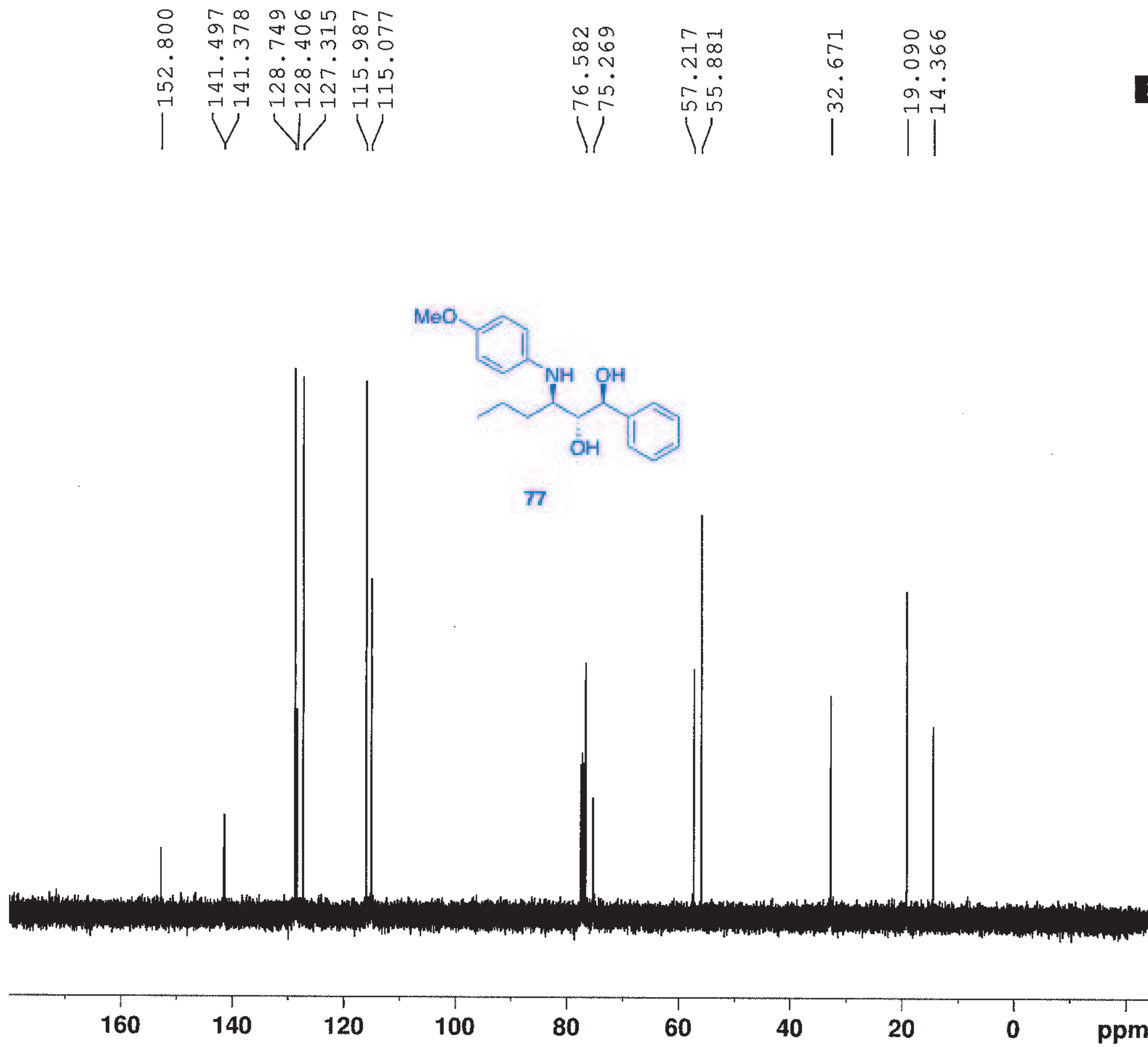
BRUKER

Current Data Parameters
NAME Lan_20150408_B6161
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150408
Time 20.18
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 22.37
DW 50.000 usec
DE 6.50 usec
TE 297.2 K
D1 10.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 499.8730869 MHz
NUC1 1H
P1 10.75 usec
PLW1 18.25000000 W

F2 - Processing parameters
SI 65536
SF 499.8700173 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



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BRUKER

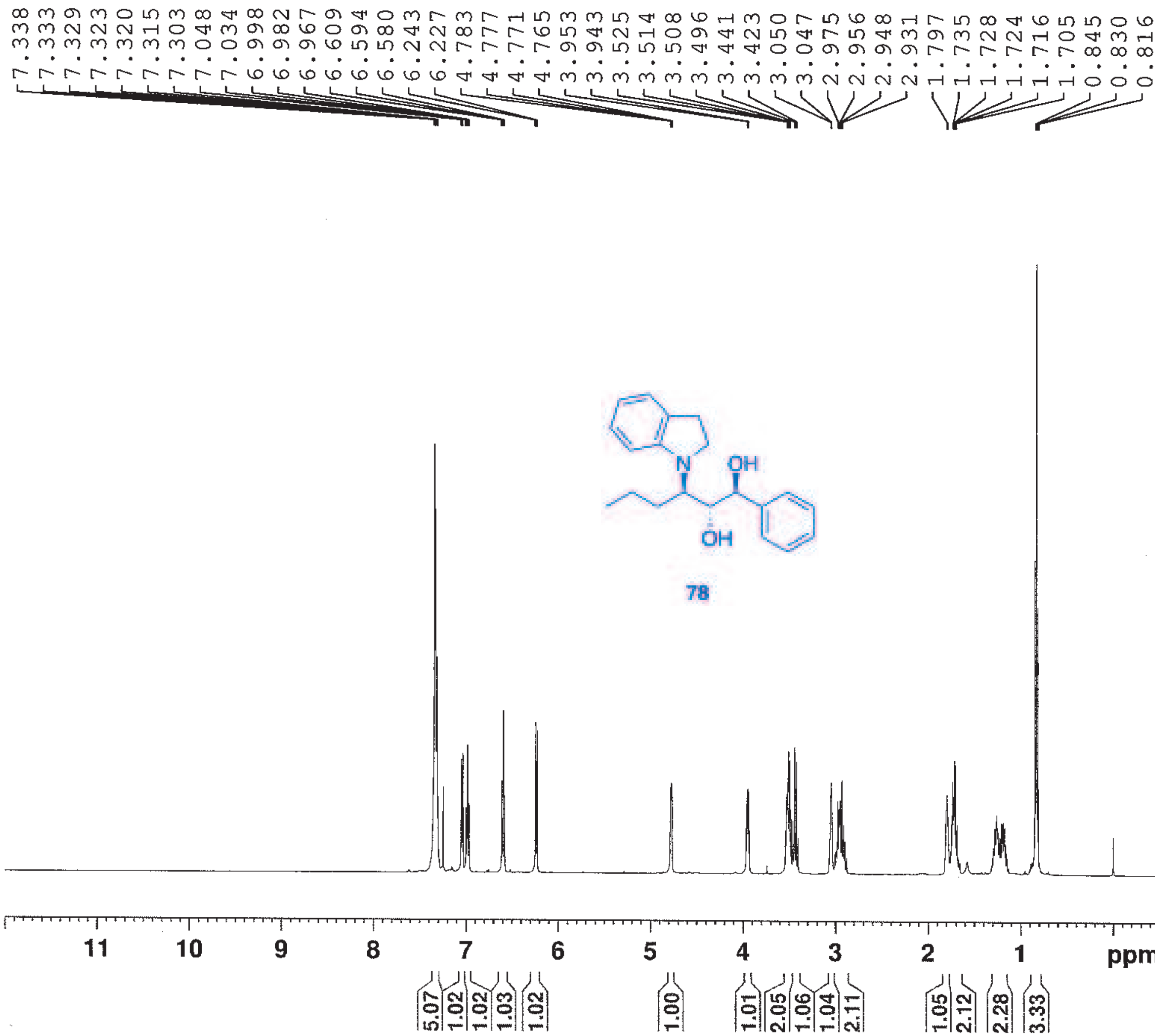
```
Current Data Parameters
NAME       Lan_20150408_B6161_C
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150408
Time                  20.30
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zgdc
TD                   187496
SOLVENT               CDCl3
NS                       33
DS                        0
SWH           31250.000 Hz
FIDRES         0.166670 Hz
AQ            2.9999361 sec
RG                     2050
DW               16.000 usec
DE                 6.50 usec
TE                297.5 K
D1           3.00000000 sec
D11          0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1       125.7049802 MHz
NUC1                    13C
P1                 10.00 usec
PLW1          72.83999634 W

======== CHANNEL f2 ========
SFO2       499.8724993 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2              80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                  1048576
SF         125.6923977 MHz
WDW                      EM
SSB        0
LB                  0.30 Hz
GB         0
PC                     1.40
```



BRUKER

Current Data Parameters

NAME	Lan_20150408_B6163
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

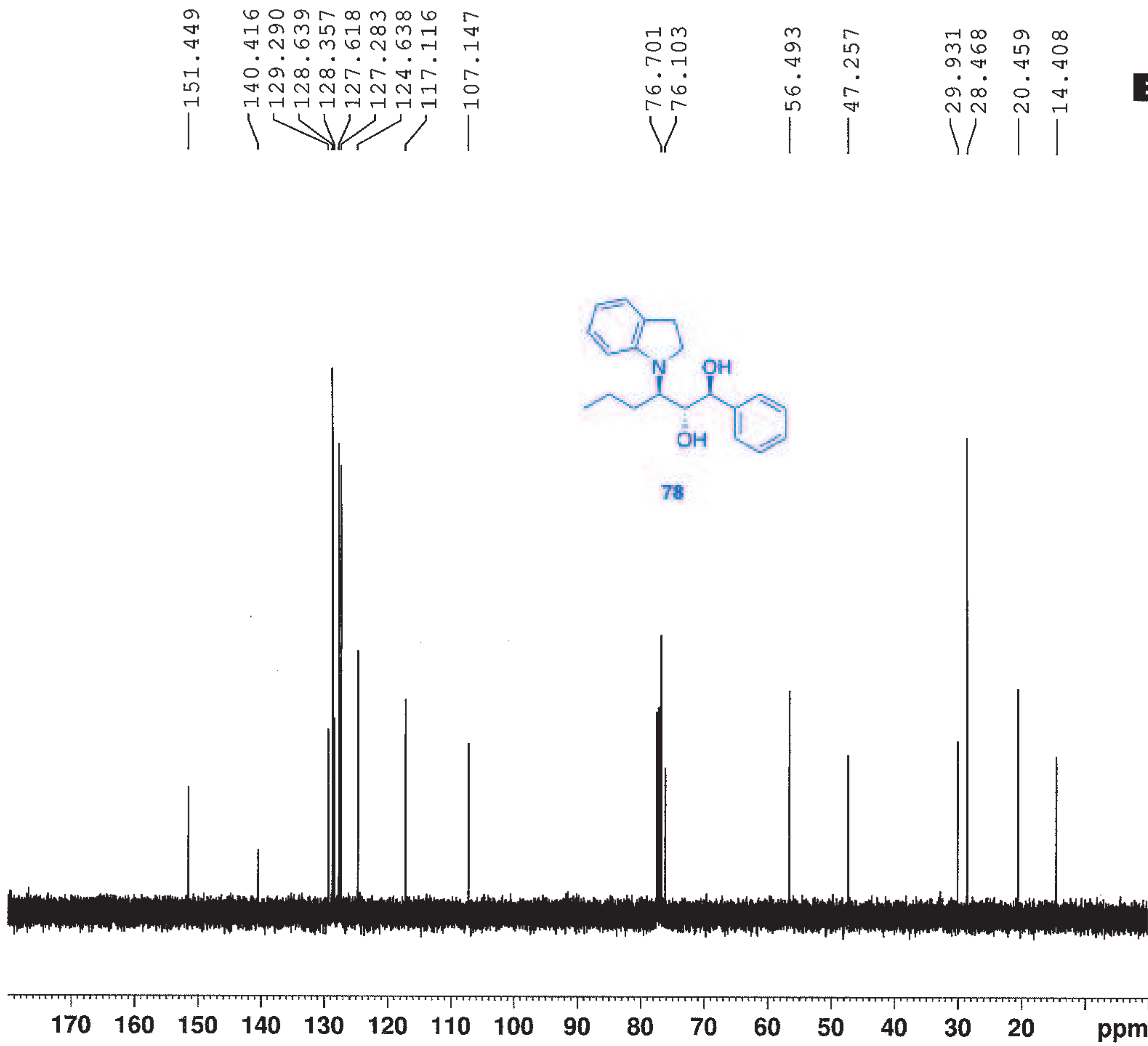
Date_	20150408
Time	20.38
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	8
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999001 sec
RG	25.24
DW	50.000 usec
DE	6.50 usec
TE	297.2 K
D1	10.00000000 sec
TD0	1

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

SFO1	499.8730869 MHz
NUC1	1H
P1	10.75 usec
PLW1	18.25000000 W

F2 - Processing parameters

SI	65536
SF	499.8700188 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



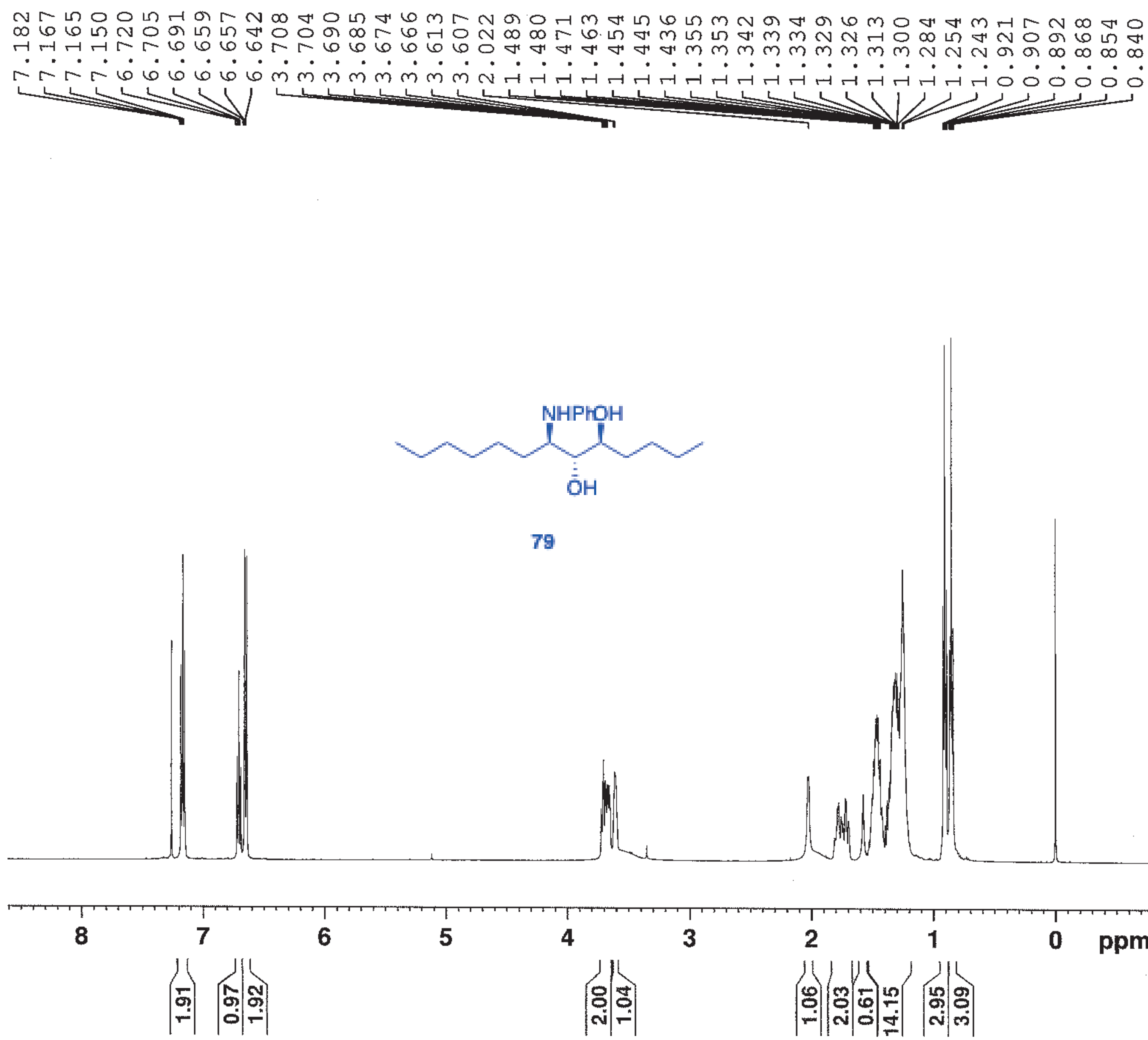

```
Current Data Parameters
NAME          Lan_20150408_B6163_C
EXPNO                            1
PROCNO                           1

F2 - Acquisition Parameters
Date_                     20150408
Time                         20.44
INSTRUM                      spect
PROBHD        5 mm PABBO BB/
PULPROG                       zgdc
TD                          187496
SOLVENT                      CDCl3
NS                              33
DS                               0
SWH                      31250.000 Hz
FIDRES                    0.166670 Hz
AQ                       2.9999361 sec
RG                            2050
DW                          16.000 usec
DE                            6.50 usec
TE                           297.4 K
D1                      3.00000000 sec
D11                     0.03000000 sec
TD0                              1

======== CHANNEL f1 ========
SFO1                   125.7049802 MHz
NUC1                           13C
P1                           10.00 usec
PLW1                   72.83999634 W

======== CHANNEL f2 ========
SFO2                   499.8724993 MHz
NUC2                            1H
CPDPRG[2                   waltz16
PCPD2                        80.00 usec
PLW2                   19.00000000 W
PLW12                   0.29688001 W

F2 - Processing parameters
SI                         1048576
SF                     125.6923975 MHz
WDW                             EM
SSB      0
LB                            0.30 Hz
GB       0
PC                            1.40
```

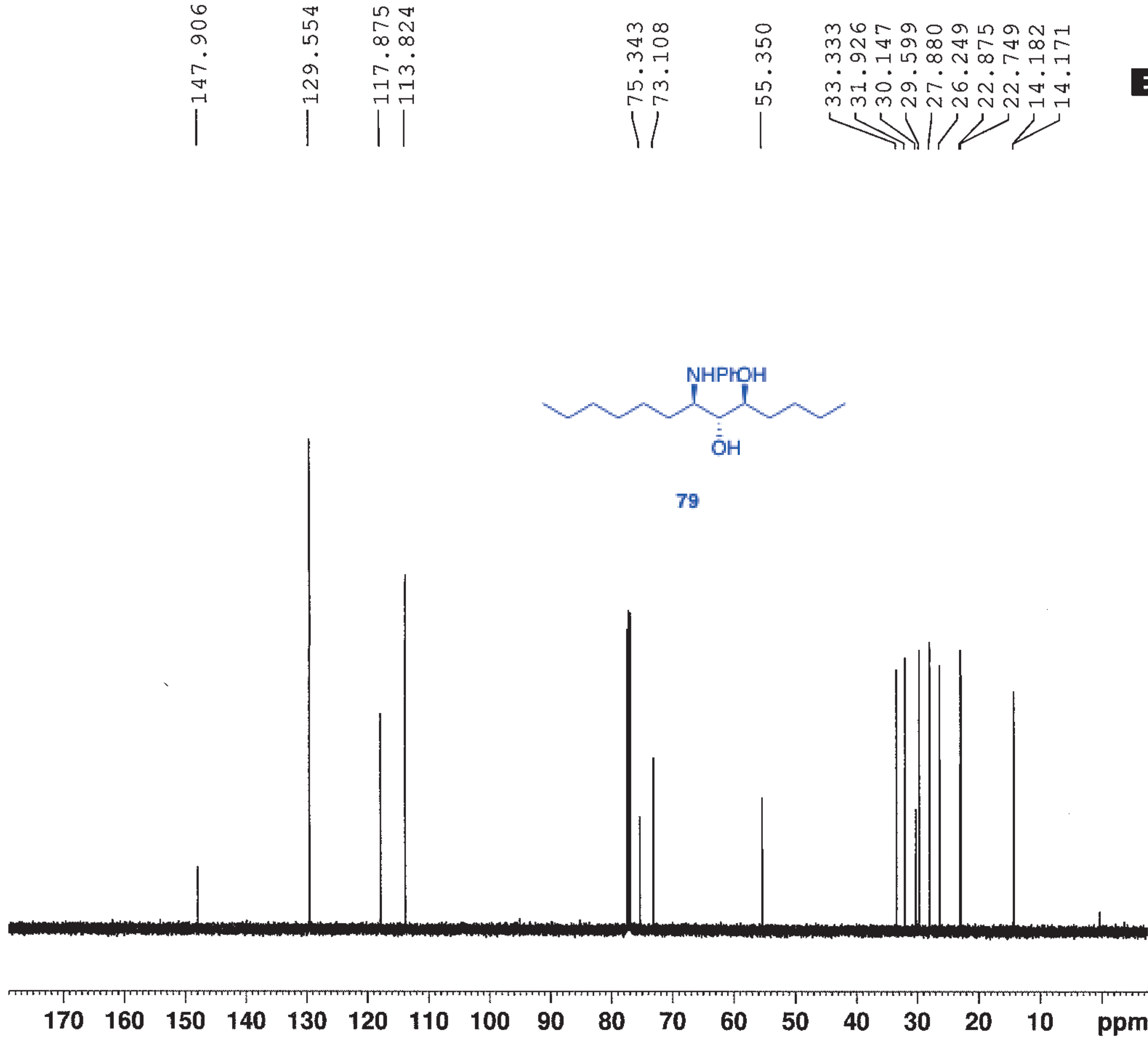



```
Current Data Parameters
NAME      Lan_20150721_B6269
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20150721
Time                   18.07
INSTRUM                spect
PROBHD     5 mm PABBO BB/
PULPROG                   zg
TD                     59998
SOLVENT                CDCl3
NS                         8
DS                         0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                     44.57
DW                50.000 usec
DE                  6.50 usec
TE                   296.0 K
D1           10.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1         499.8730869 MHz
NUC1                      1H
P1                10.75 usec
PLW1         18.25000000 W

F2 - Processing parameters
SI                     65536
SF           499.8700122 MHz
WDW                       EM
SSB      0
LB                   0.30 Hz
GB       0
PC                      1.00
```



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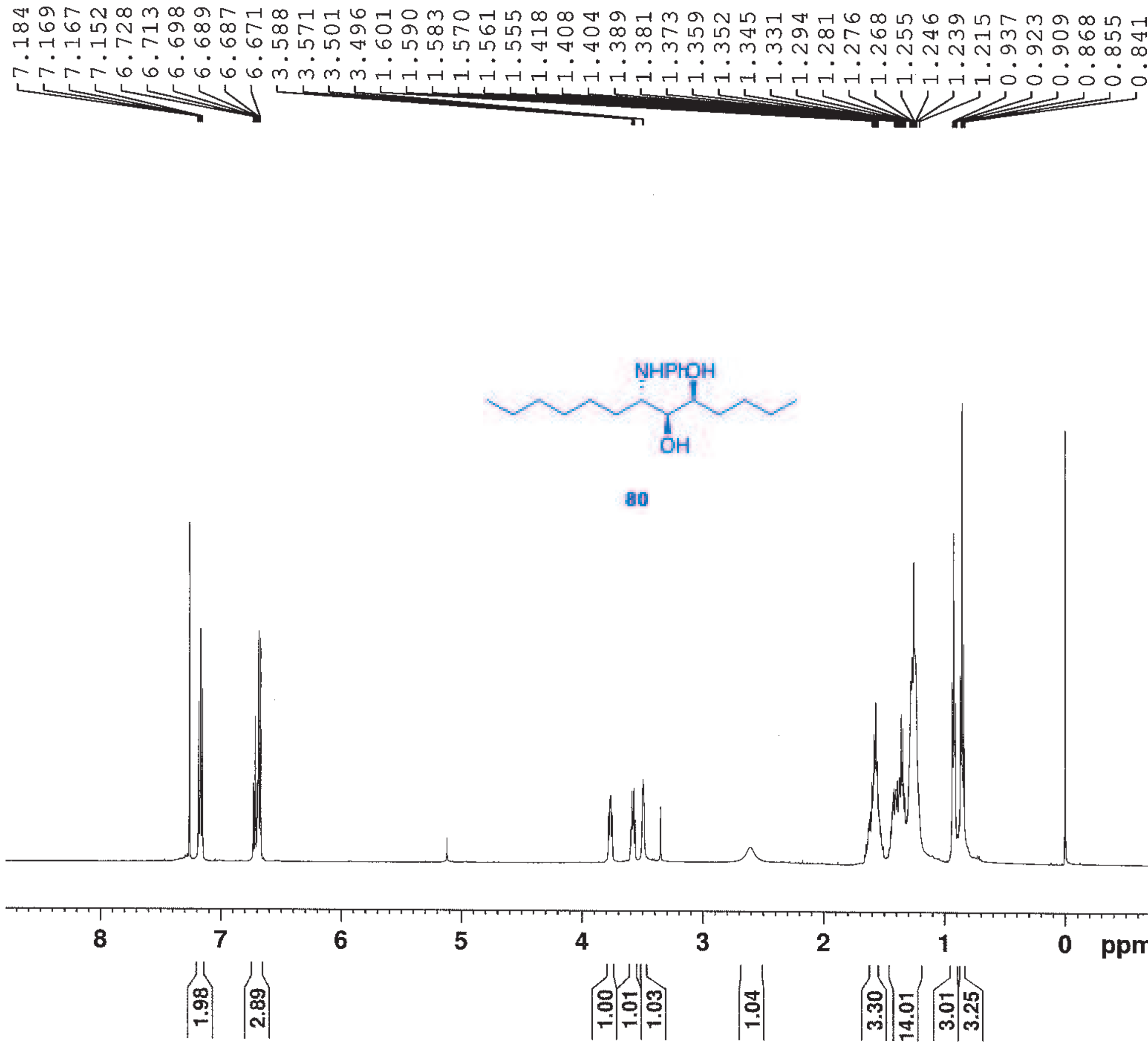
```
Current Data Parameters
NAME       Lan_20150721_B6269_C
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_             20150721
Time                 18.14
INSTRUM              spect
PROBHD     5 mm PABBO BB/
PULPROG               zgdc
TD                  187496
SOLVENT              CDCl3
NS                     523
DS                       0
SWH          31250.000 Hz
FIDRES        0.166670 Hz
AQ           2.9999361 sec
RG                    2050
DW             16.000 usec
DE               6.50 usec
TE               296.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1       125.7049802 MHz
NUC1                   13C
P1               10.00 usec
PLW1       72.83999634 W

======== CHANNEL f2 ========
SFO2       499.8724993 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2            80.00 usec
PLW2       19.00000000 W
PLW12       0.29688001 W

F2 - Processing parameters
SI                 1048576
SF         125.6923911 MHz
WDW                     EM
SSB      0
LB                 0.30 Hz
GB       0
PC                    1.40
```



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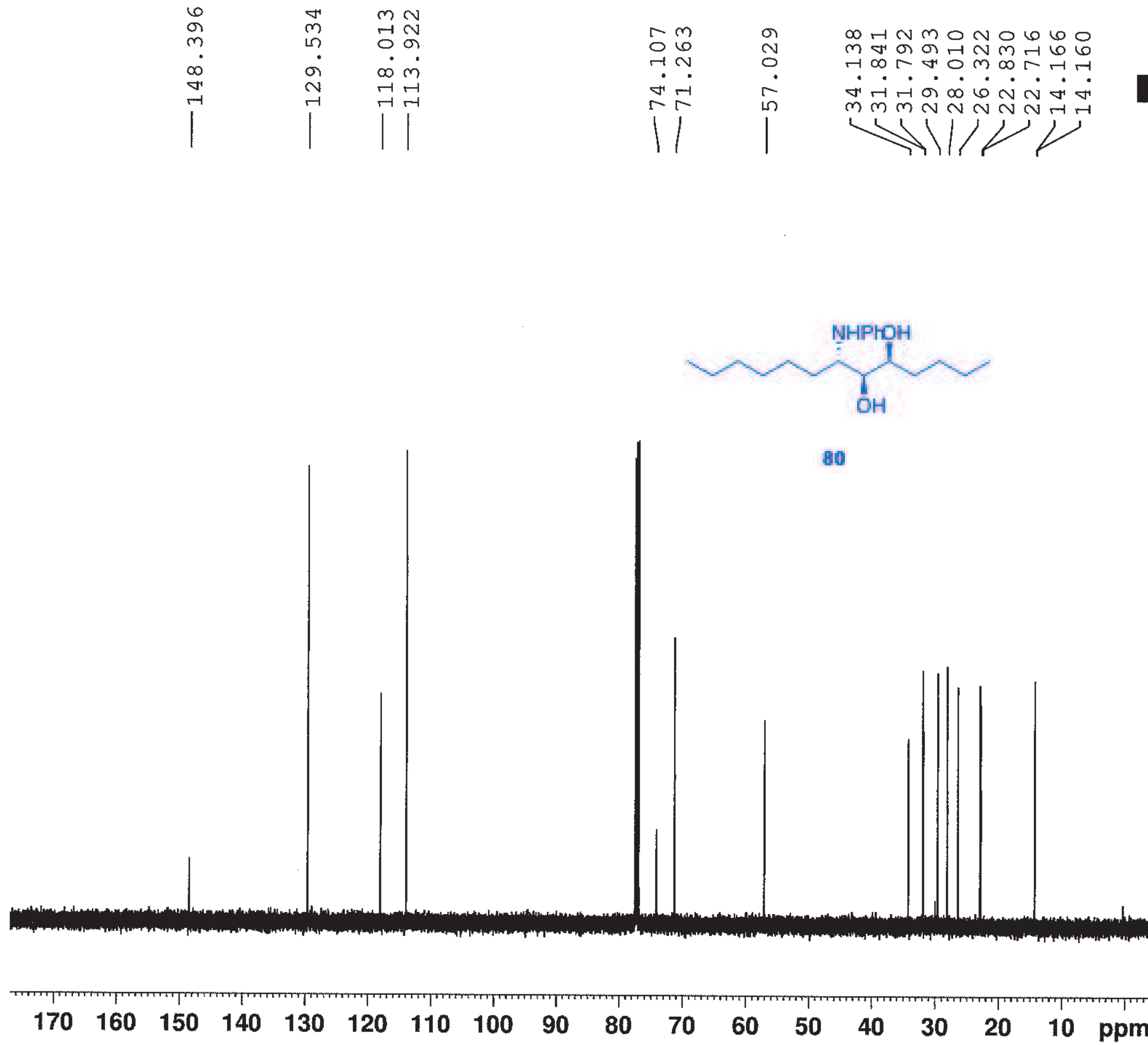
BRUKER

Current Data Parameters
NAME Lan_20150721_B6303
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150721
Time 19.23
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 59998
SOLVENT CDC13
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 44.57
DW 50.000 usec
DE 6.50 usec
TE 296.2 K
D1 10.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 499.8730869 MHz
NUC1 1H
P1 10.75 usec
PLW1 18.25000000 W

F2 - Processing parameters
SI 65536
SF 499.8700120 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



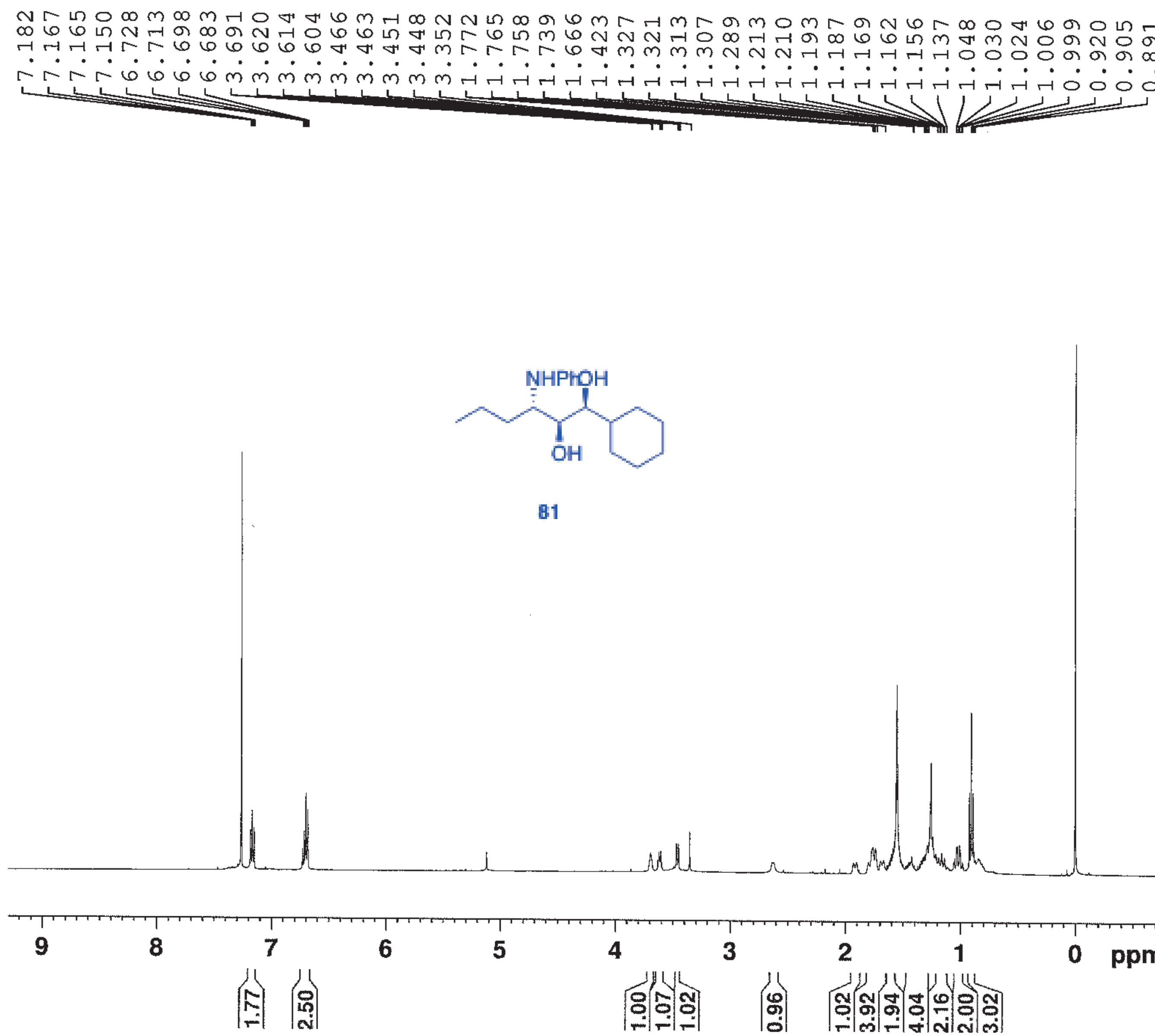

```
Current Data Parameters
NAME      Lan_20150721_B6303_C
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150721
Time                 19.34
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zgdc
TD                  187496
SOLVENT              CDCl3
NS                     344
DS                       0
SWH              31250.000 Hz
FIDRES            0.166670 Hz
AQ               2.9999361 sec
RG                    2050
DW                  16.000 usec
DE                    6.50 usec
TE                   296.9 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           125.7049802 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           72.83999634 W

======== CHANNEL f2 ========
SFO2           499.8724993 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           19.00000000 W
PLW12           0.29688001 W

F2 - Processing parameters
SI                 1048576
SF             125.6923913 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.40
```



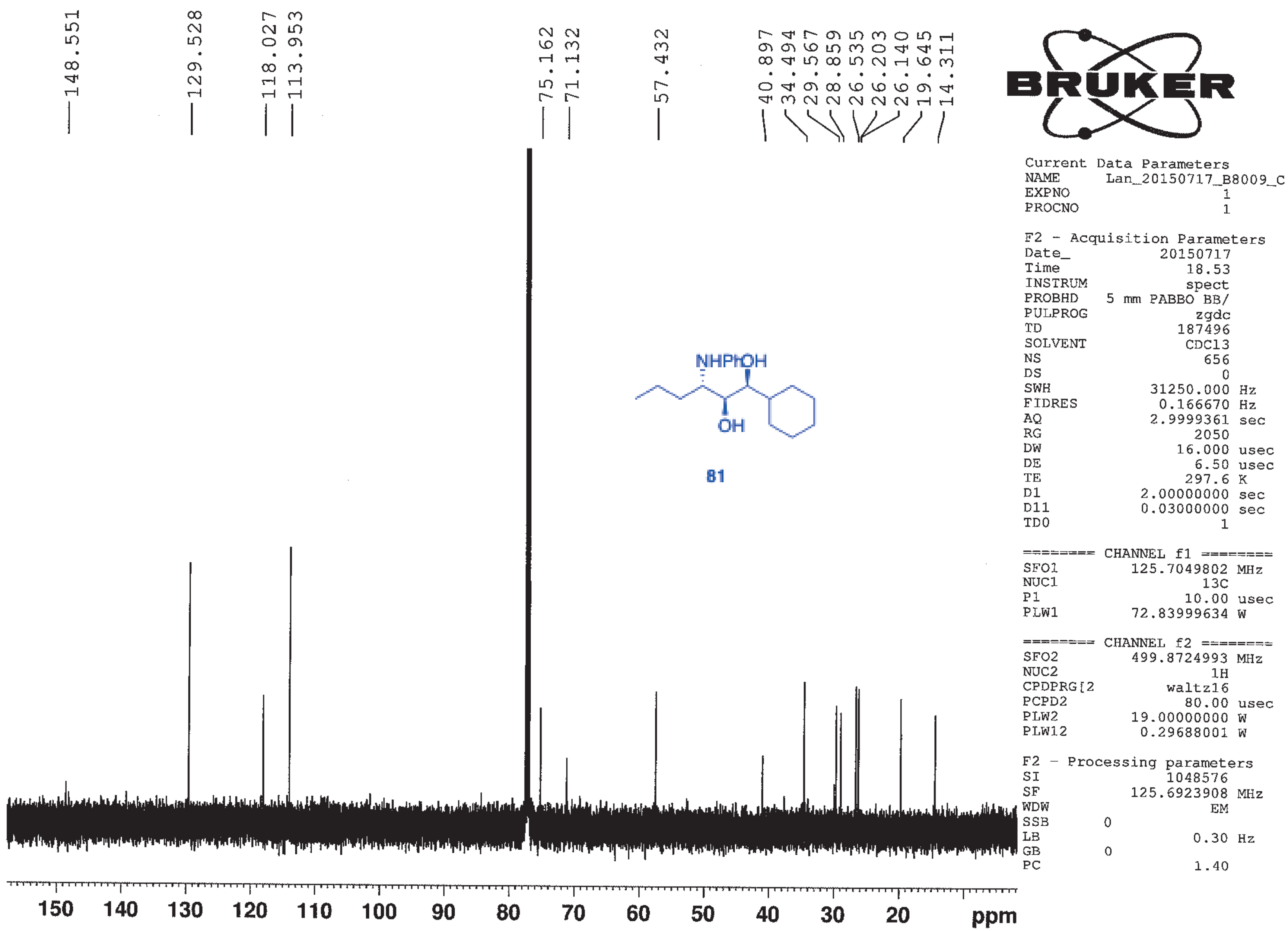
BRUKER

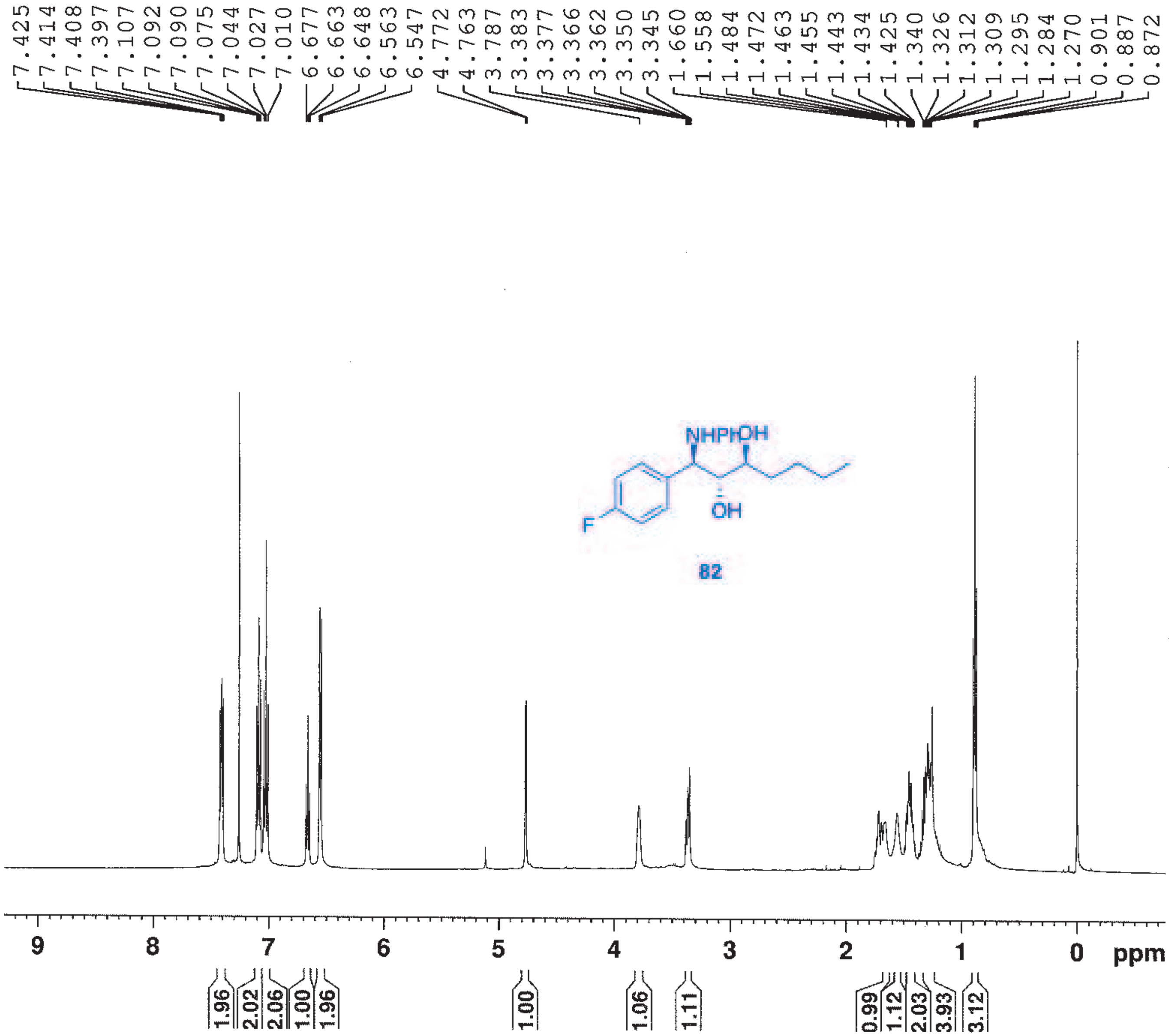
Current Data Parameters
NAME Lan_20150717_B8009
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150717
Time 18.11
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 62.78
DW 50.000 usec
DE 6.50 usec
TE 296.1 K
D1 10.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 499.8730869 MHz
NUC1 1H
P1 10.75 usec
PLW1 18.25000000 W

F2 - Processing parameters
SI 65536
SF 499.8700112 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


148.551
129.528
118.027
113.953
75.162
71.132
57.432
40.897
34.494
29.567
28.859
26.535
26.203
26.140
19.645
14.311
BRUKER
NHPh
OH
OH
81
Current Data Parameters
NAME Lan_20150717_B8009_C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150717
Time 18.53
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgdc
TD 187496
SOLVENT CDCl3
NS 656
DS 0
SWH 31250.000 Hz
FIDRES 0.166670 Hz
AQ 2.9999361 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 297.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7049802 MHz
NUC1 13C
P1 10.00 usec
PLW1 72.83999634 W
======== CHANNEL f2 ========
SFO2 499.8724993 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.29688001 W
F2 - Processing parameters
SI 1048576
SF 125.6923908 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm



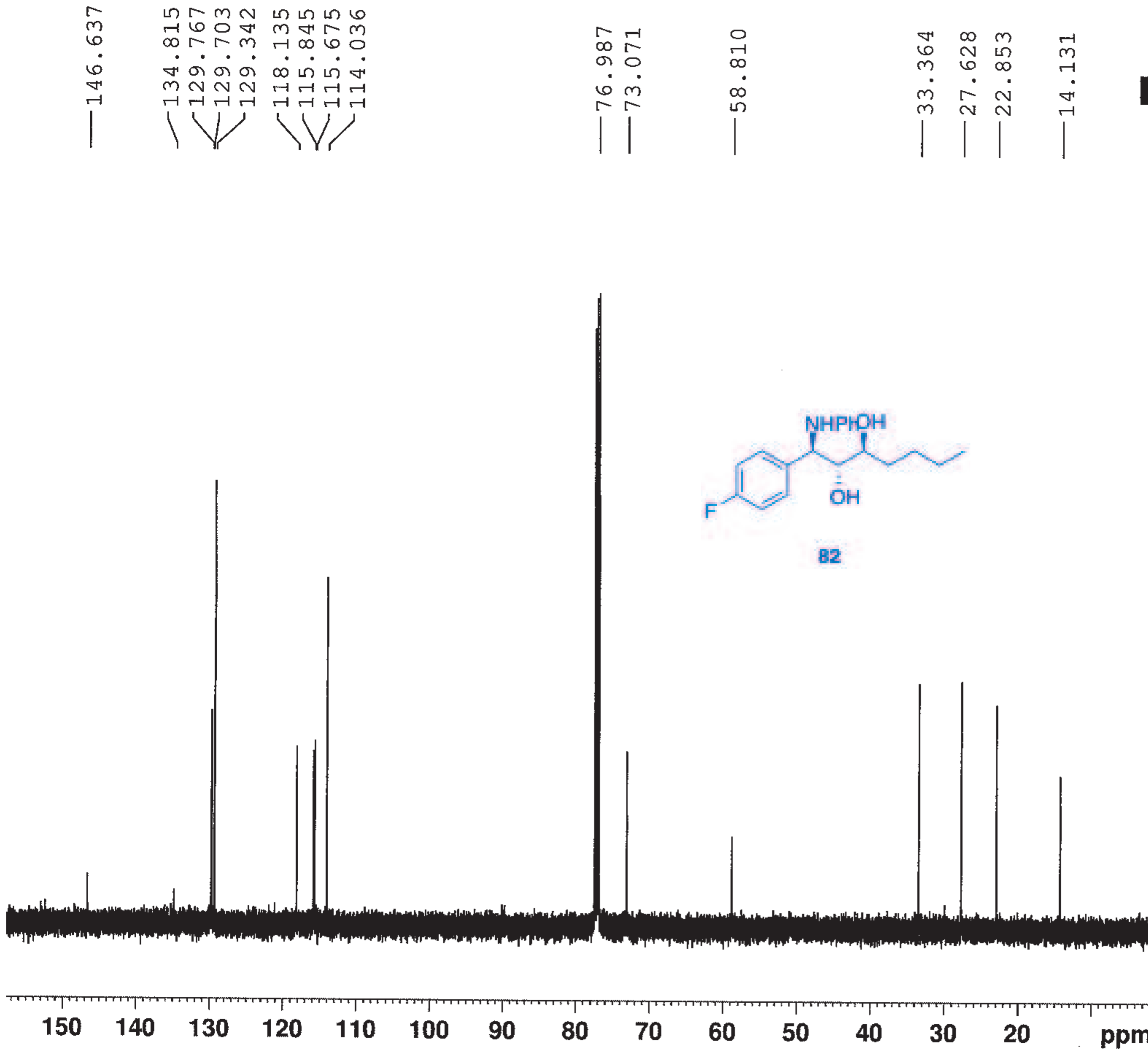
BRUKER

Current Data Parameters
NAME Lan_20150717_B8007
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150717
Time 19.25
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 62.78
DW 50.000 usec
DE 6.50 usec
TE 296.7 K
D1 10.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 499.8730869 MHz
NUC1 1H
P1 10.75 usec
PLW1 18.25000000 W

F2 - Processing parameters
SI 65536
SF 499.8700126 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



BRUKER

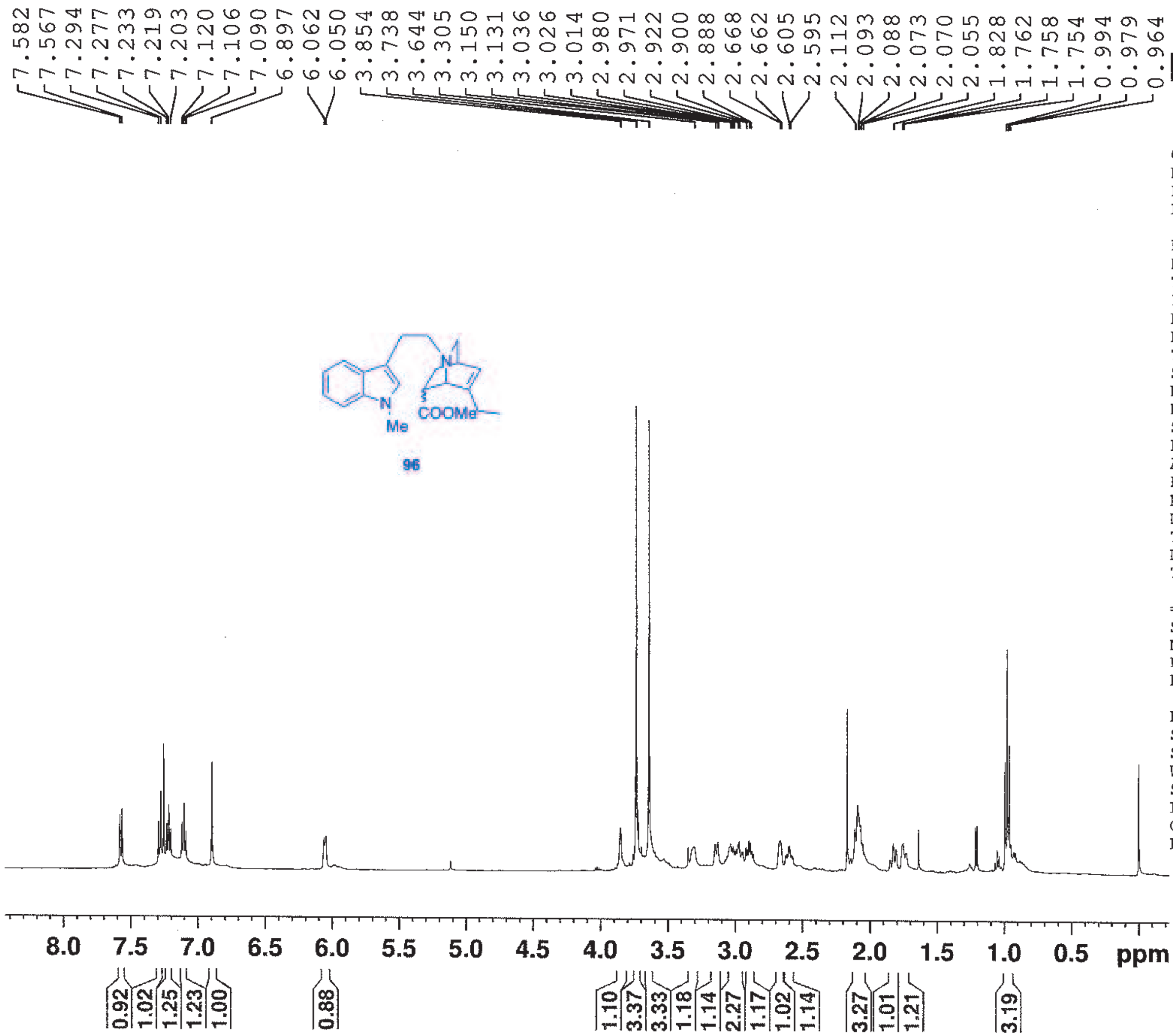
Current Data Parameters
NAME Lan_20150717_B8007_C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150717
Time 20.10
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgdc
TD 187496
SOLVENT CDCl3
NS 876
DS 0
SWH 31250.000 Hz
FIDRES 0.166670 Hz
AQ 2.9999361 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 298.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 125.7049802 MHz
NUC1 13C
P1 10.00 usec
PLW1 72.83999634 W

======== CHANNEL f2 ========
SFO2 499.8724993 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.29688001 W

F2 - Processing parameters
SI 1048576
SF 125.6923910 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40



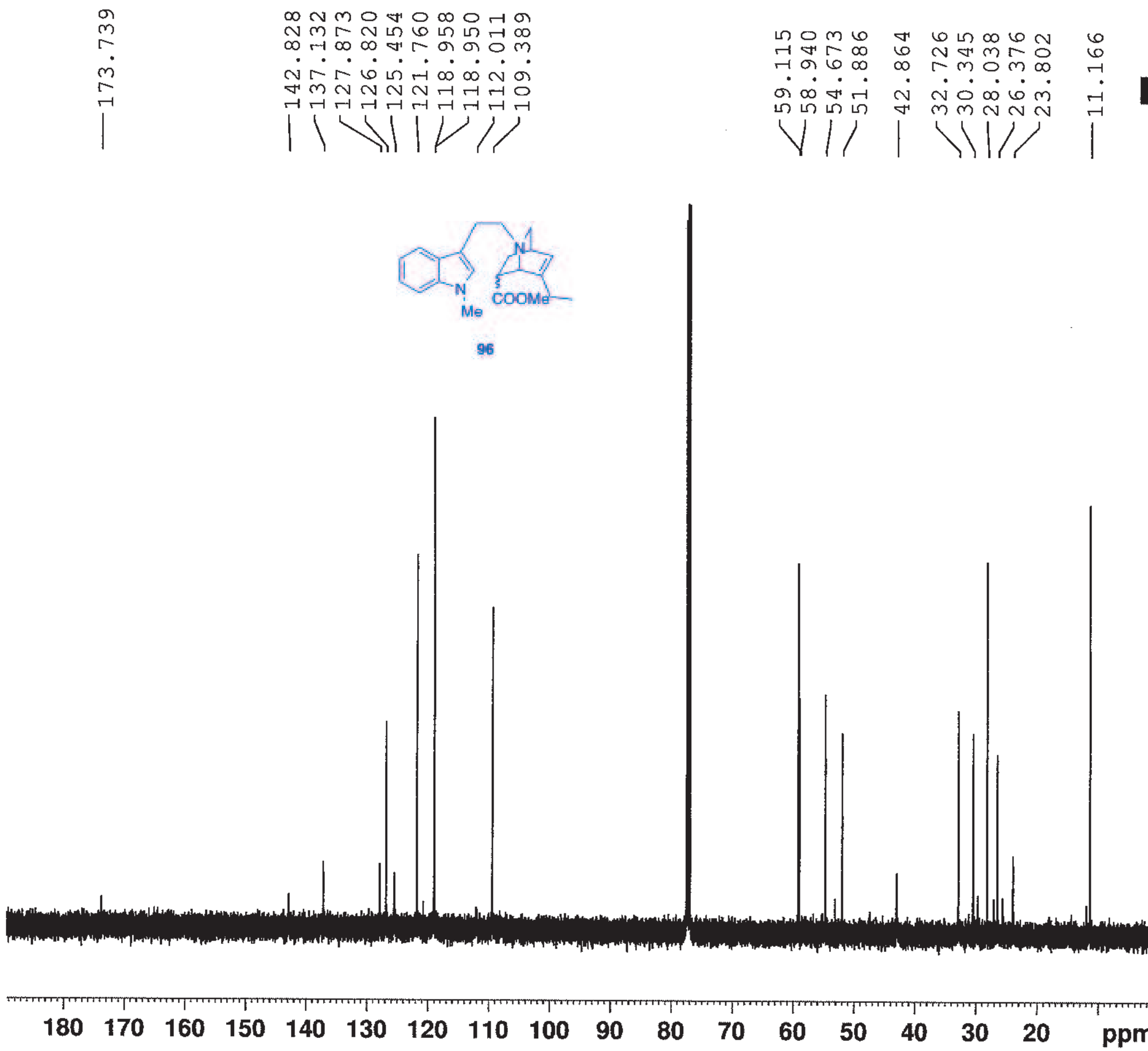
BRUKER

Current Data Parameters
NAME Lan_20160419_B9008
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160419
Time 21.02
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 37.92
DW 50.000 usec
DE 6.50 usec
TE 296.9 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 499.8730869 MHz
NUC1 1H
P1 10.75 usec
PLW1 18.25000000 W

F2 - Processing parameters
SI 65536
SF 499.8700139 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters

NAME	Lan_20160419_B9008_C	
EXPNO	1	
PROCNO	1	

F2 - Acquisition Parameters

Date_	20160419	
Time	21.17	
INSTRUM	spect	
PROBHD	5 mm PABBO BB/	
PULPROG	zgdc	
TD	187496	
SOLVENT	CDCl3	
NS	526	
DS	0	
SWH	31250.000	Hz
FIDRES	0.166670	Hz
AQ	2.9999361	sec
RG	2050	
DW	16.000	usec
DE	6.50	usec
TE	297.6	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	

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

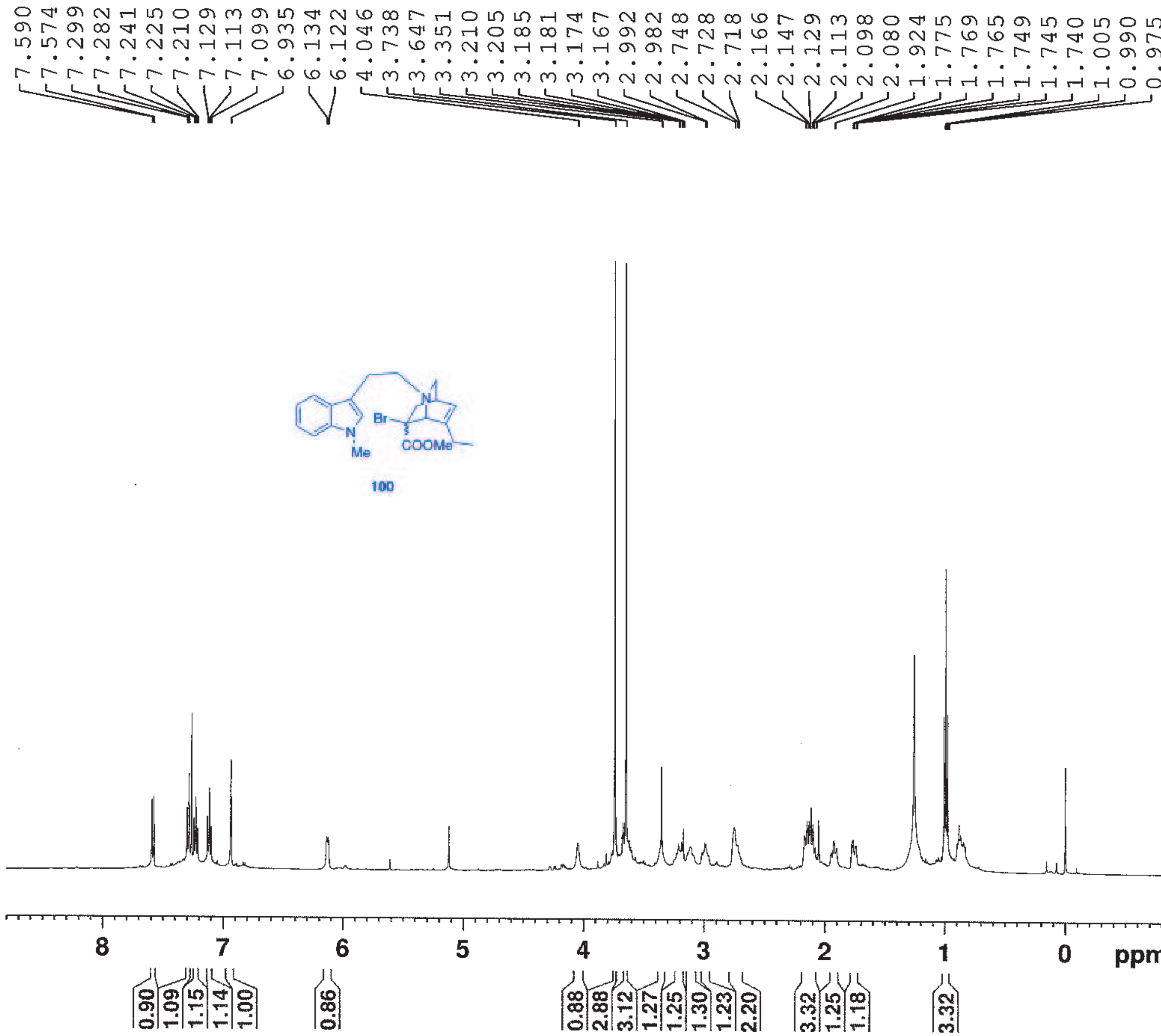
SFO1	125.7049802	MHz
NUC1	13C	
P1	10.00	usec
PLW1	72.83999634	W

======== CHANNEL f2 ========

SFO2	499.8724993	MHz
NUC2	1H	
CPDPRG[2	waltz16	
PCPD2	80.00	usec
PLW2	19.00000000	W
PLW12	0.29688001	W

F2 - Processing parameters

SI	1048576	
SF	125.6923938	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.40	



Current Data Parameters
NAME Lan_20151112_B7229
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20151112
Time 14.29
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 35.92
DW 50.000 usec
DE 6.50 usec
TE 296.8 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 499.8730869 MHz
NUC1 1H
P1 10.75 usec
PLW1 18.25000000 W

F2 - Processing parameters
SI 65536
SF 499.8700117 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00