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Palladium-catalysed reactions of aziridines and cyclopropanes

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Palladium-Catalysed Reactions of Aziridines and Cyclopropanes

Yin JieXiang
Student Number: 4360126

Supervisor:
Dr. Christopher Hyland

This thesis is presented as required for the conferral of the degree:

Doctor of Philosophy

The University of Wollongong
School of Chemistry
August 2016

Certification

I, Yin JieXiang, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Chemistry, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Yin JieXiang

August 2016

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Yin JieXiang

August 2016

Abstract

Strained-ring systems including vinylcyclopropanes, phenyl- and vinylaziridines were utilised to undergo ring-opening reactions under the catalysis of organotransition-metals in this research. Firstly, $\text{PdCl}_2(\text{MeCN})_2$ catalysed the formal [3+2] annulations of *N*-activated aziridines to construct a number of potentially bioactive pyrroloindolines in one-pot with C3-substituted indoles. Furthermore, C3-unsubstituted indoles were treated with *N*-tosyl arylaziridines in the presence of $\text{PdCl}_2(\text{MeCN})_2$ *via* a Friedel–Crafts pathway. The resulting β -substituted tryptamines then undergo the ring-closure with *N*-fluorobenzenesulfonimide to produce C3-fluorinated pyrroloindolines in moderate yields and selectivities. In chapter 2, the palladium(II)-catalysed addition of arylboronic acids to *N*-activated vinylaziridines has been developed. This reaction proceeds *via* a redox-neutral insertion/ring-opening process to provide unusual (*Z*)-allylsulfonamides preferentially. Finally, a highly efficient ring-opening reaction of vinylcyclopropanes by boronic acids was reported in the chapter 3, using palladium nanoparticles formed from $\text{Pd}(\text{OAc})_2$ and boronic acids in neat water. Linear and branched regioselectivities were obtained using vinylcyclopropanes and aryl-substituted vinylcyclopropanes respectively under these ligandless conditions.

Abbreviations	
Ac	acetate
Ar	aromatic ring
9-BBN	9-borabicyclo(3.3.1)nonane
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
Bn	benzyl
BQ	1,4-benzoquinone
BPO	benzoyl peroxide
Bz	benzoyl
¹³ C NMR	carbon nuclear magnetic resonance spectroscopy
COD	1,5-cyclooctadiene
DABCO	1,4-diazabicyclo[2.2.2]octane
dba	dibenzylideneacetone
DCE	1,2-dichloroethane
DCM	dichloromethane
DMA	dimethylacetamide
DMAP	4-dimethylaminopyridine
DMB	dimethoxybenzene
DMF	dimethylformamide
DMSO	dimethylsulfoxide
Dpp	diphenylphosphine oxide
¹ H NMR	proton nuclear magnetic resonance spectroscopy
hfacac	hexafluoroacetylacetone
LA	Lewis acid
LAH	lithium aluminium hydride
LDA	lithium diisopropylamide
Mes	methanesulfonyl
MS	mass spectrometry
NFSI	N-fluorobenzenesulfonimide

NOESY	nuclear overhauser enhancement spectroscopy
Ns	4-nitrobenzenesulfonyl
NMO	<i>N</i> -Methylmorpholine- <i>N</i> -Oxide
OBoc	<i>tert</i> -butyl carbonate
Phen	1,10-phenanthroline
PMB	<i>p</i> -methoxybenzyl
PTAB	phenyltrimethylammonium perbromide
TBAB	tetrabutylammonium bromide
TBS	<i>tert</i> -butyldimethylsilyl
TFA	trifluoroacetic acid
Tf	trifluoromethanesulfonate
THF	tetrahydrofuran
TMS	trimethylsilyl
Ts	<i>p</i> -toluenesulfonyl
η^n	(ligand) coordinated through <i>n</i> adjacent atoms

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Chapter 1. The Reactivity and Synthesis of Indoles, Tryptamines and Pyrroloindolines

Introduction

The transition-metal-catalysed synthesis of two nitrogen-containing heterocyclic classes: pyrroloindolines and tryptamines were developed in this chapter. These two indole-derived compounds have been frequently investigated due to their biological activities in the pharmacological area. For example, sumatriptan **1** is used for migraine treatment¹, and melatonin **5** has shown promising bioactivity in treating insomnia in older adults (Figure 1a).² In addition, it has been found that pyrroloindolines such as physostigmine **2** and its analogues **3** and **4** have promising bioactivities in the treatment of Alzheimer's disease and function as anticholinesterase and insecticidal agents (Figure 1b).³⁴⁵

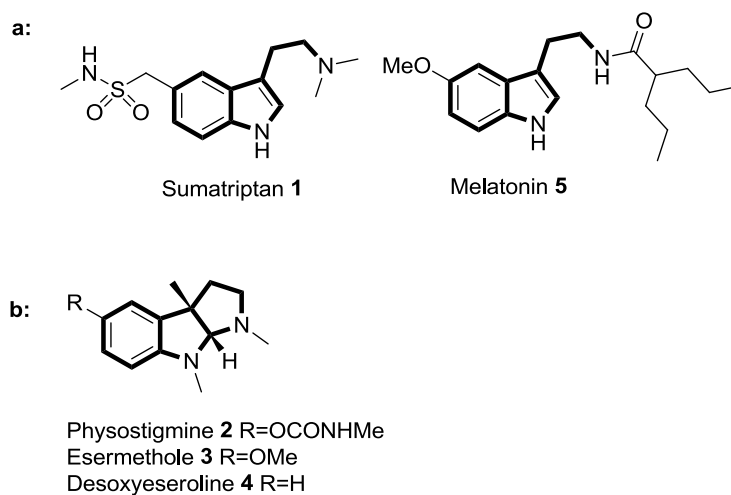
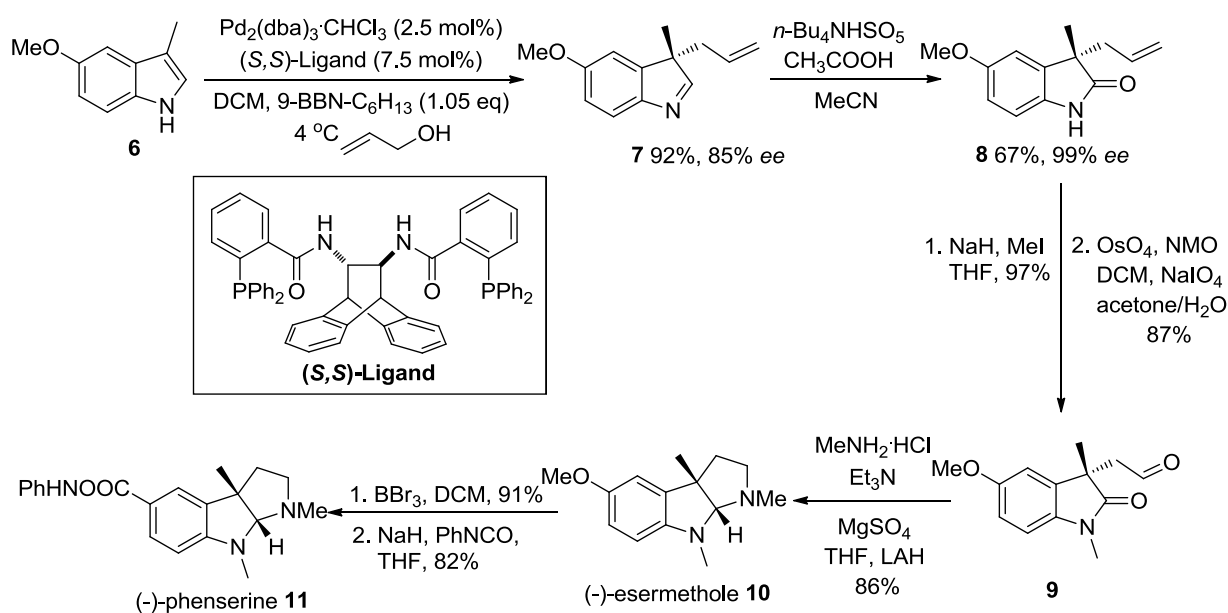


Figure 1: a) Medicinally valuable indole-fused molecules b) Bioactive pyrroloindolines

Synthesis of Pyrroloindolines *via* the Lewis Acid-Catalysed [3+2] Cycloaddition of C3-Substituted Indoles with Aziridines

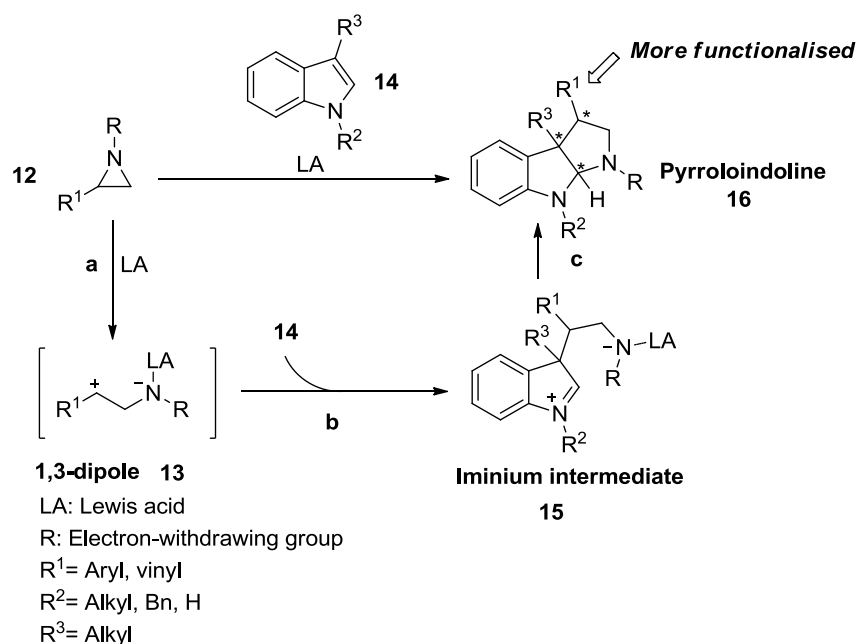
It has been known that the synthesis of pyrroloindolines previously required multiple-step methods, for example, a 3,3'-disubstituted indolenine **7**, synthesised *via* the enantioselective Pd-catalysed

C3-allylation of C3-substituted indole **6**, was treated with tetrabutylammonium oxone and acetic acid to give enantiopure oxindole **8** in a good yield (Scheme 1). Subsequently, after sequential methylation and oxidative cleavage of oxindole **8**, a reductive amination-cyclisation process occurred to convert previously generated aldehyde **9** to (–)-esermethole **10**, which was then subjected to the synthesis of (–)-phenserine **11** for treatment of Alzheimer’s disease.



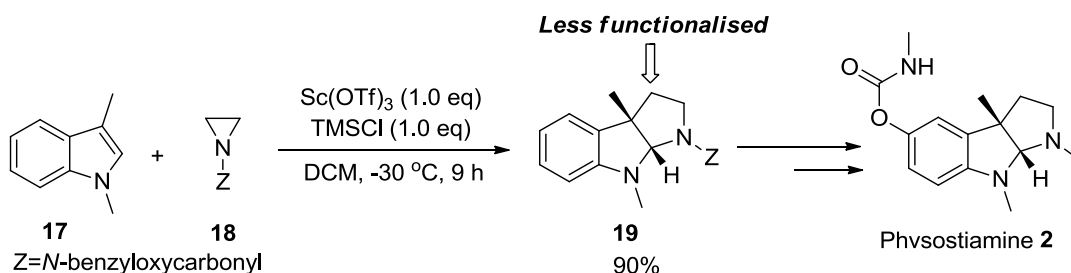
Scheme 1: Synthesis of (–)-Phenserine **11**

In this project, a more efficient method to synthesise the pyrroloindoline was developed using a formal [3+2] cycloaddition of aziridines to indoles (Scheme 2). In the presence of Lewis acids, a zwitterionic 1,3-dipole **13** could be given *via* the C-N bond cleavage of the aziridine **12** to undergo nucleophilic attack of the indole **14** to give an iminium **15**. As the indole **14** is C3-substituted by an electron-donating group such as methyl, the anionic amide branch of the iminium intermediate **15** could intramolecularly attack the C2-position to achieve the ring-closure. Finally, the pyrroloindoline skeleton **16** bearing three contiguous stereogenic centers is released. It is worth noting that an electron-withdrawing *N*-protecting group such as tosyl is generally required to facilitate the C-N bond breaking of **12** (Scheme 2a).⁶ Furthermore, a cation-stabilising R₁ group of the aziridine **12** is introduced to the final product **16** in the reaction, making the pyrroloindoline products **16** highly functionalised.



Scheme 2: Lewis acid-catalysed synthesis of the pyrroloindoline **16** via the 1,3-dipole **13**

This formal [3+2] dearomative cycloaddition of indole derivative has not been developed as a general method for pyrroloindoline synthesis (Scheme 2),⁷ with only a single report by the Nakagawa group using a stoichiometric amount of Sc(OTf)₃ and TMSCl as a cocatalyst system to synthesise the pyrroloindoline skeleton **19** via the C-N bond cleavage of *N*-benzyloxycarbonyl (*Z*)-aziridine **18** (Scheme 3). This is an efficient synthetic route to the insecticidal compound—physostigmine **2**, where the key step is alkylative cyclisation of 1,3-dimethylindole **17** with the aziridine **18** mediated by Sc(OTf)₃ and TMSCl to give the cycloadduct **19** in a 90% yield.⁸ However, although **19** was directly prepared by this versatile methodology, a stoichiometric amount of Lewis acid and flammable TMSCl are required, severely limiting its application. In addition, no substrate scope for this reaction was explored. Arylaziridines, which stabilise the carbonium ion in **13**, should facilitate this process and increase the functionality of the targeted pyrroloindoline skeleton. Reactivity of various arylaziridines in the presence of different metal-catalysts will therefore be examined in this reaction.

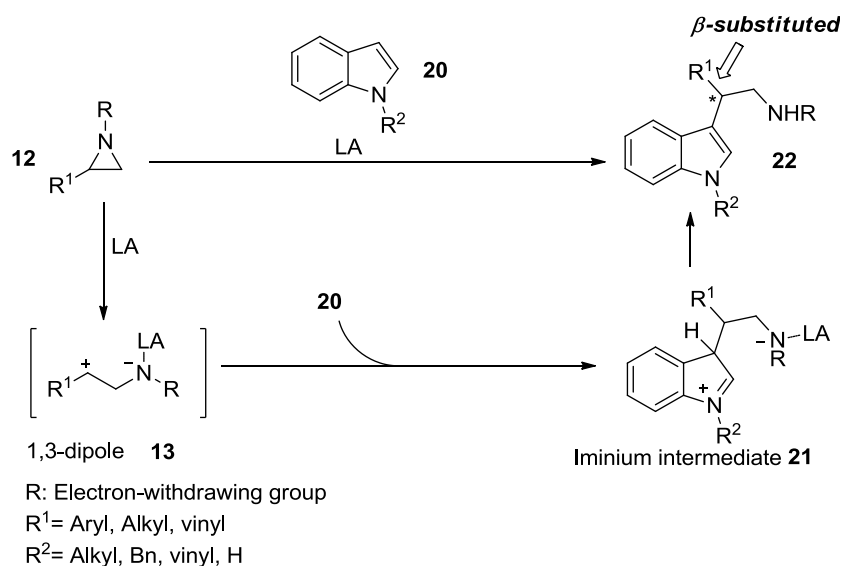


Scheme 3: A concise synthesis of physostigmine **15** from skatole **17** and activated aziridine **18** via formal [3+2] cycloaddition

In conclusion, a catalytic process to construct the highly functionalised pyrroloindoline skeleton first diastereoselectively and then enantioselectively with arylaziridines in the presence of Lewis acids under the mild conditions is the goal of the project (Scheme 2).

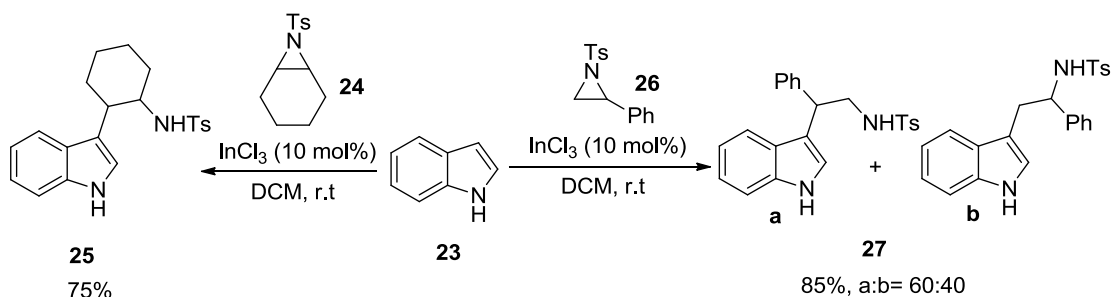
Lewis Acid-Catalysed Synthesis of Tryptamines by C3-Unsubstituted Indoles and Aziridines

The proposal in Scheme 2 demonstrates the potential application of C3-substituted indoles in the synthesis of pyrroloindolines. In addition, it was envisioned that skeletons of indole-derived bioactive tryptamines such as sumatriptan (Figure 1) could be synthesised *via* the substitution of C3-unsubstituted indoles with 1,3-dipole **13** (Scheme 4). This Friedel–Crafts process would involve the generation of 1,3-dipole **13** under Lewis acid conditions and subsequent iminium intermediate **21** resulting from the C3-substitution of **20** with **13**. Finally, elimination releases the re-aromatised β -substituted tryptamines **22** in contrast to the formal [3+2] cycloaddition (Scheme 2).



Scheme 4: Lewis acid-catalysed synthesis of tryptamines **22**

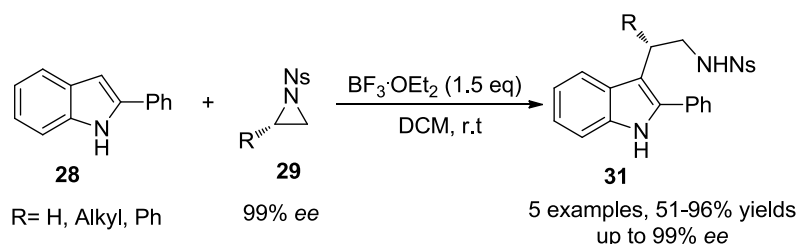
However, as a molecule that is frequently present in biologically active compounds,⁹ it is surprising to find only limited examples reported for use of indole and its derivatives **20** in the ring-opening reaction of the *N*-activated aziridines **12** (Scheme 4). For example, the Yadav group utilised InCl₃ as a mild Lewis acid to catalyse ring-opening of aziridines with 1*H*-indole **23** (Scheme 5).¹⁰ The ring-opening of less reactive symmetric alkylaziridine **24** was successful to give the product **25** in a good yield under the conditions. However, a mixture of regioisomers **27a** and **27b** were given in an excellent combined yield with the low regioselectivity with unsymmetric arylaziridine **26**. To develop a regioselective reaction with **26**, appropriate conditions will be identified in the project.



Scheme 5: InCl₃-catalysed opening of aziridines with 1*H*-indole **23**

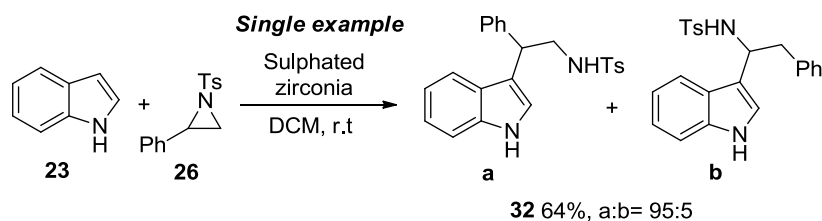
In 2003, Farr demonstrated that *N*-nosyl aziridines **29** react with *N*-H 2-phenylindole **28** to

afford β -substituted tryptamines **31** in moderate to excellent yields with high enantioselectivities and regioselectivities (Scheme 6).¹¹ Different enantiopure *N*-nosyl alkyl/phenylaziridines **29** were selected as substrates for the reaction in the presence of a stoichiometric quantity of $\text{BF}_3 \cdot \text{OEt}_2$. Furthermore, it is worth indicating that this non-catalytic reaction provides a method to synthesise Gonanotropin releasing hormone (GnRH), which could be used for suppressing gonadal steroid hormones to castrate levels. However, in addition to being a stoichiometric process, substrate scope investigated is limited to C2 substituted indoles.



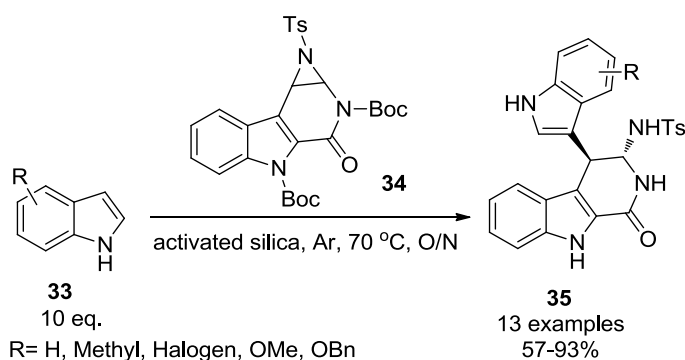
Scheme 6: Ring-opening of 2-alkyl nosylaziridines **29** by indoles **28** mediated by boron trifluoride

More Lewis acids were developed for the ring-opening reaction of aziridines with indoles. For instance, sulphated zirconia, made by acidifying zirconium isopropoxide with sulfuric acid in deionised water, could also be used as a Lewis acid to perform the ring-opening reaction of aziridines with indoles. The Castillon group reported a single example of the ring-opening of phenylaziridine **26** with 1*H*-indole **23** to give a mixture of two regioisomers **32a** and **32b** of β -phenyl tryptamine in a good yield. The nucleophilic attack preferentially occurs at the benzylic position of **26**, but the by-product generated from the C2-N bond breaking of **26** was still observed in the reaction (Scheme 7).¹² The heterogeneous sulphated zirconia demonstrated excellent catalytic efficiency for various acid-sensitive and slightly basic nucleophiles. Moreover, it can be reused for several times with no loss of activity although the relatively harsh conditions are required for the preparation of the catalyst (calcinations at 700 °C).



Scheme 7: Ring-opening of phenylaziridine **26** with 1H-indole **23**

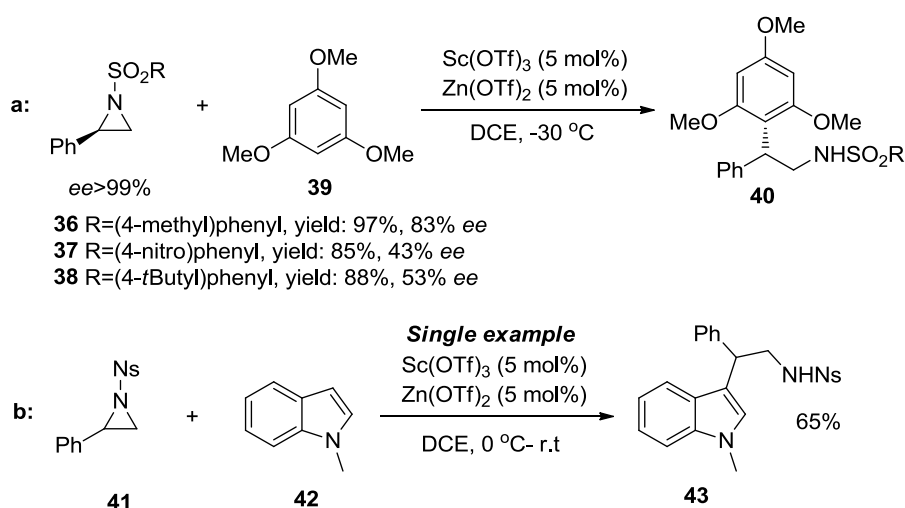
Another early example for the ring-opening of aziridines with indole derivatives was reported by the Tse group.¹³ They demonstrated a nucleophilic ring-opening reaction of a racemic *N*-activated aziridine **34** with various electron-rich indoles **33** in the presence of activated silica gel (Scheme 8). In this reaction, indoles **33** were utilised as the *C*-nucleophile to form bisindoles **35**, which could be kinase inhibitors, in excellent yields through an electrophilic aromatic substitution pathway. Notably, the two *N*-protecting *tert*-butoxycarbonyl groups of starting aziridine **34** could be easily removed under the reaction conditions. Furthermore, this reaction proceeded with excellent regioselectivity at the C3-position of the indoles and the benzylic position of aziridines. However, a large amount of the indole **33** (up to 10 equiv.) is required to ensure complete conversion of the aziridine **34** due to the sublimation of **33**, and only one *N*-tosyl aziridine **34** was utilised as a substrate.



Scheme 8: Ring-opening reaction of aziridine **34** with indoles **33** on activated silica

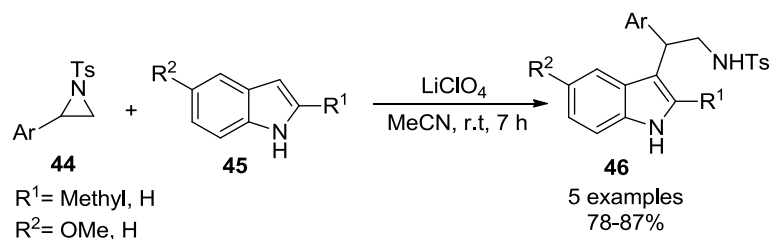
Subsequently, a diastereo- and enantioselective synthesis of 2-arylethylamines **40** was developed by Ghorai and co-workers. This route has a single example that was achieved *via* intermolecular ring opening of substituted *N*-activated aziridines with electron-rich arenes and heteroarenes such as the indole **42** in the presence of a dual catalysts system consisting of Sc(OTf)₃ and Zn(OTf)₂ (Scheme 9b).¹⁴ The nucleophilic attack occurs at the benzylic position of aziridines, which was found to be electrophilic in the previous research, but only a single example of **42** was demonstrated in this

research and some uncharacterised by-products were also produced. Moreover, other enantiopure aziridines such as **37** and **38** gave significantly reduced enantiomeric excess of the resulting products compared to **36** (Scheme 9a). To explore the reason behind obtaining reduced enantiomeric excess of the products a time dependent study of reaction of enantiopure aziridine with the arene was carried out, and it was observed that the enantiopurity of both aziridine and product decreased over time. Therefore, the racemisation of aziridine and product by the Lewis acid may be the reason why the reduced enantiopurity was observed. Furthermore, the authors found the product has a faster racemisation rate than that of the aziridine.



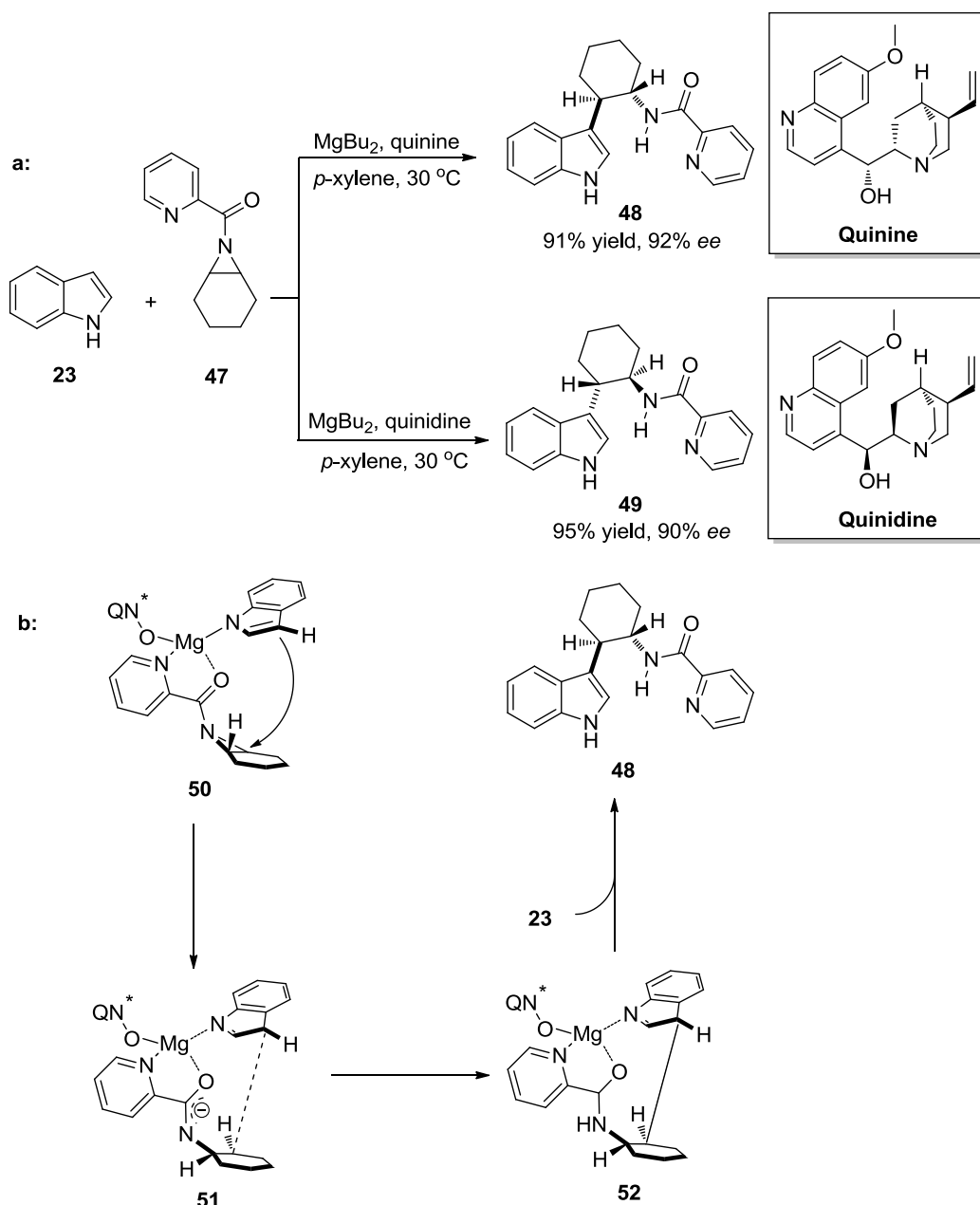
Scheme 9: Dual Lewis acid catalysed S_N2 -type ring opening of *N*-activated aziridine **41** with electron-rich arenes

Yadav and co-workers also provided some scattered examples for ring-opening of *N*-tosyl arylaziridine **44** with indole **45**. The reaction was carried out in the presence of 5M lithium perchlorate in diethyl ether at room temperature to give a 3-alkylated indole **46** in high yields with high C3-selectivities (Scheme 10).¹⁵ Nevertheless, although a number of examples were provided in the reaction, LiClO₄ is potentially explosive. Therefore, a bench stable catalyst is needed for synthesis of β -branched tryptamines.



Scheme 10: LiClO_4 -catalysed C-alkylation of indole **45** with arylaziridine **44**

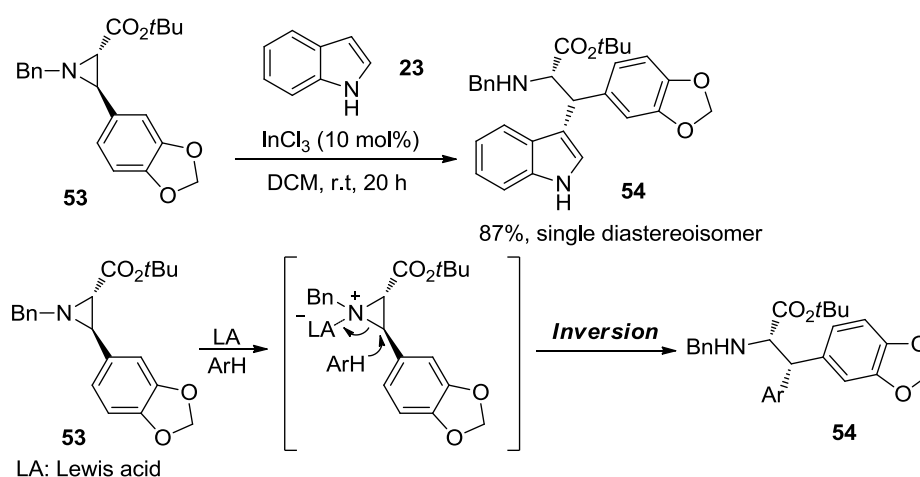
In conclusion, only a number of examples for the Friedel–Crafts ring-opening of *N*-activated aziridines with indoles could be found in the literature. Only a non-catalytic reaction resulted in enantioretention (Scheme 6), but others such as that in Scheme 9a demonstrated the significant erosion in the enantiopurity of the ring-opened product as a result of the racemisation caused by relatively strong Lewis acidity of $\text{Sc}(\text{OTf})_3$ and $\text{Zn}(\text{OTf})_2$ system. Although the stereospecific ring-opening reaction of aziridines is synthetically useful, it has relatively limited application due to the difficulty in preparing a wide range of these systems in an enantioenriched form. It is more important that no kinetic resolution (dynamic or non-dynamic) has been carried out for this type of reaction. Nevertheless, after this investigation has been started, Wang and co-workers reported a kinetic resolution for the first magnesium-catalysed asymmetric desymmetrisation of a *meso* aziridine **47** with 1-*H* indole **23** (Scheme 11).¹⁶ Both of enantiomers of the ring-opening products were synthesised with commercially available chiral ligands such as quinine and quinidine respectively.



Scheme 11: Highly enantioselective ring-opening reactions of aziridine **47** with indole **23**

A catalytic process was proposed for explanation of generation of the product **48** and stereochemistry. After the pre-catalyst was generated from the deprotonation of indole by MgBu_2 and quinine, an intermediate **50** is given from the coordination of the aziridine **47** to the magnesium center from a less sterically hindered direction that is possibly determined by the effects of pre-catalyst. Subsequently, the activated indole attacks the aziridine **47** via the 2nd transition state **51** accompanied by the ring-opening reaction to give **52**. The indole molecule **23** enters into the process to donate a proton for releasing the final compound **48** and recovering the pre-catalyst (Scheme 11b).

It can be seen from previous examples that a strong electron-withdrawing *N*-protecting group such as tosyl or nosyl was required to facilitate C-N bond breaking of aziridines in the presence of Lewis acids.¹⁷ Nevertheless, Lewis acid catalysis was also proved to be effective in the ring-opening of the less activated aziridines such as *N*-benzylaziridine. For example, in 2007, Ishikawa and co-workers reported an InCl₃-catalysed ring-opening reaction of 2,3-disubstituted *N*-benzylaziridine **53** with 1*H*-indole **23** (Scheme 12).¹⁸ The less activated aziridine **53** took part in the reaction and was activated by InCl₃ to accept nucleophilic attack in an S_N2 manner from the indole nucleophile. Notably, the corresponding product **54** was produced in an excellent yield with an absolute diastereoselectivity. Furthermore, the X-ray crystallographic analysis showed that inversion of configuration at C3 of the aziridine ring happened during the ring-opening reaction by the aromatic carbon-based nucleophile.



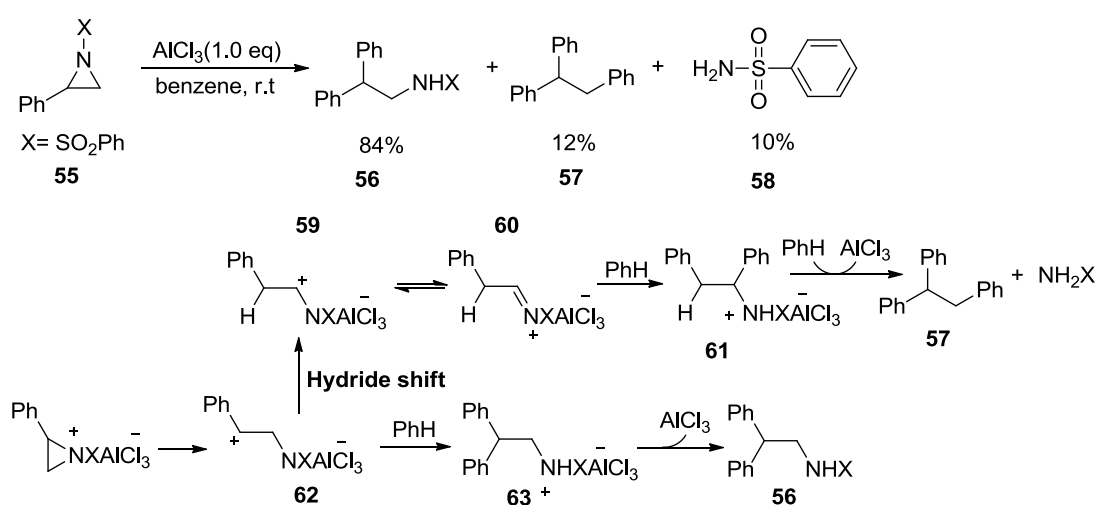
Scheme 12: Ring-opening reaction of *trans*-(1,3-benzodioxol-5-yl)aziridine-2-carboxylate **53** with indole **23**

In summary, the limited examples above demonstrate that the Lewis-catalysed synthesis of tryptamines is still under investigated, especially with regard to the dynamic kinetic resolution. Therefore, a comprehensive study for the catalytic synthesis of β -branched tryptamines *via* the ring-opening of *N*-activated arylaziridines in the presence of Lewis acids and then chiral ligands was to be performed as one of the goals in the project (Scheme 4).

C3 Ring-Opening of Aziridines with Electron-Rich Arenes

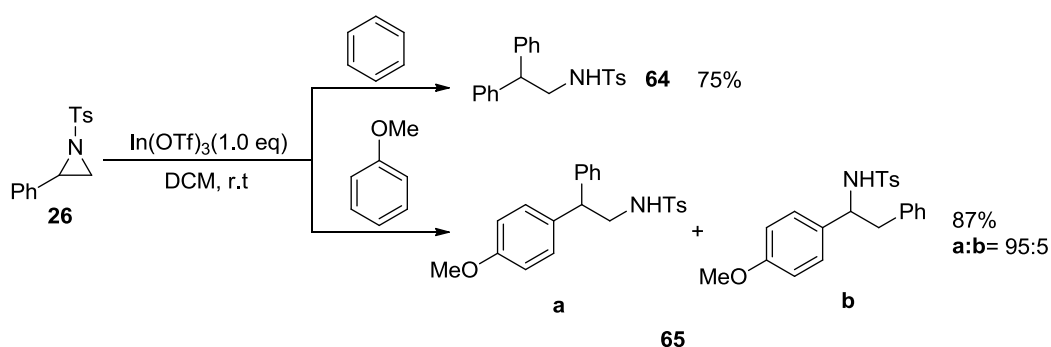
Although the Lewis acid-catalysed ring-opening of aziridines with indoles have only limited examples, a large number of electron-rich arenes have been utilised as C-based nucleophiles to open the aziridine ring for synthesis of nitrogen-containing compounds.¹⁹ To obtain a comprehensive understanding of Lewis acid-catalysed ring-opening process of aziridines, it is necessary to review those reactions.

The Stamm group provided one early example in 1989, demonstrating an efficient AlCl_3 -promoted reaction of the *N*-sulfonylaziridine **55** with benzene. The reaction proceeds rapidly at room temperature to yield the desired *N*-sulfonyl(arylethyl)amine **56** in a good yield, though significant amounts of two side-products were also given. One (**57**) resulted from 2,3-diarylation, and the other is benzenesulfonamide **58**, which is generated by decomposition of **55** (Scheme 13).²⁰ The first event in this ring-opening reaction is the coordination of AlCl_3 to the aziridine nitrogen atom or sulfonyl oxygen, forming a 1,3-dipole **62**. A Friedel-Crafts process then occurs to generate an intermediate **63** with benzene. Accompanied with the leaving of AlCl_3 , the final ring-opened compound **56** is yielded. The 1,3-dipole **62** may also undergo hydride shift to give the intermediate **59**. Benzene then adds to the intermediate **60**, which is the resonance-related structure of **59**. The subsequent intermediate **61** is therefore generated in the reaction. Subsequently, the addition of the second benzene to the intermediate **61** causes the departure of NH_2X and biarene **57** as the by-product.



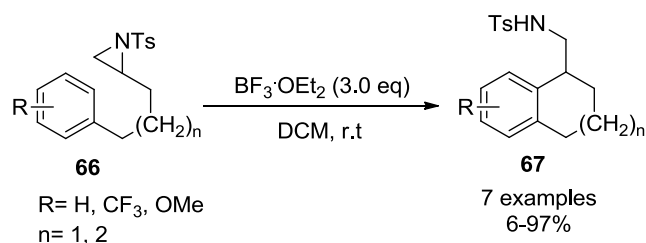
Scheme 13: Friedel–Crafts reactions with *N*-sulfonylated aziridines

The Yadav group then reported an example of C-arylation of *N*-tosyl phenylaziridine **26** via an In(OTf)₃-promoted Friedel–Crafts reaction. The reaction resulted in an exclusive regioselectivity and a good yield in the ring-opening of phenylaziridine **26** with benzene in the presence of stoichiometric amount of In(OTf)₃, and substituted arenes such as anisole also gave excellent yield and high C2-selectivity (Scheme 14).²¹



Scheme 14: First example of C-arylation of aziridine **26** promoted by indium triflate

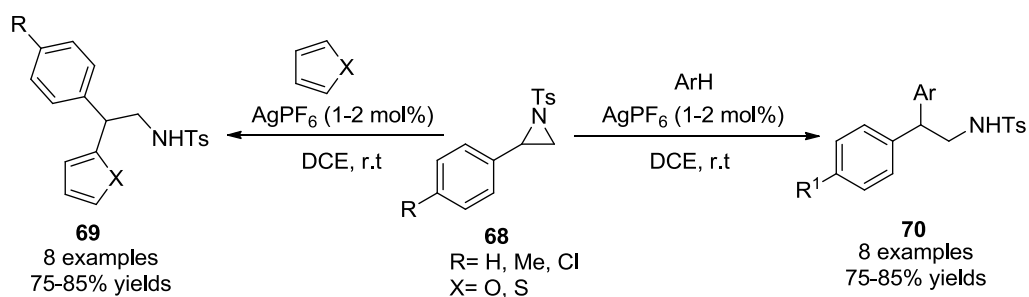
Almost all examples shown above are intermolecular reactions, but in 2004, a facile intramolecular cyclisation was uncovered by the Bergmeier group (Scheme 15).²² The substrates **66** combine an aziridine ring and a π -nucleophile in one molecule. With promotion of a stoichiometric amount of BF₃·OEt₂, intramolecular cyclisation reaction of **66** occurred to produce a nitrogen-containing core structure **67** that could be found in a variety of biologically active molecules.



Scheme 15: Intramolecular cyclisation reaction of aziridines **66** with π -nucleophiles

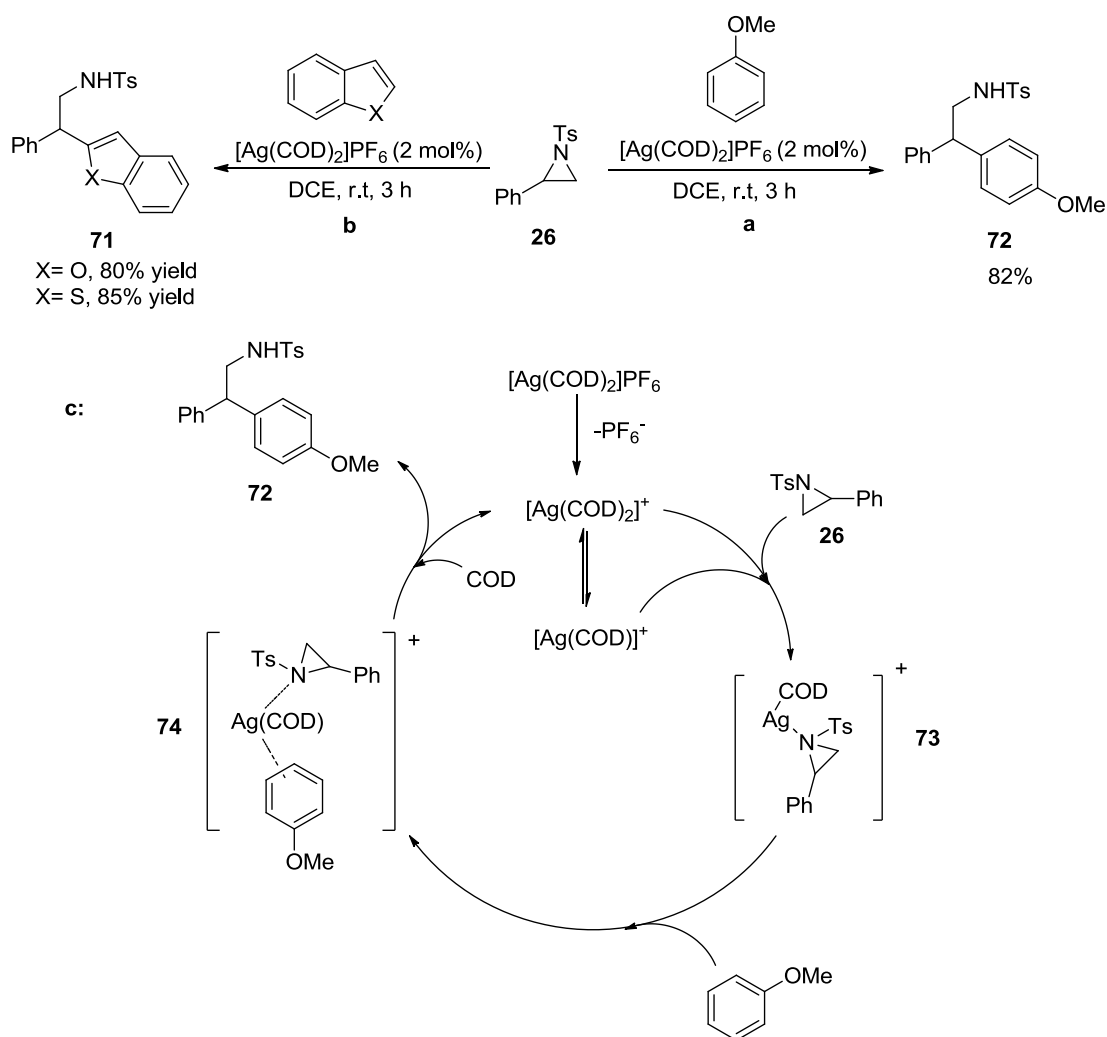
More efforts were contributed to the selection of efficient Lewis acid to open the aziridine ring catalytically. The Roy group developed the synthesis of β -aryl amine derivatives **69** and **70** from

N-tosyl aziridines **68** and a variety of arenes and heteroarenes *via* a Friedel–Crafts reaction pathway in the presence of 1-2 mol% of silver hexafluorophosphate at room temperature (Scheme 16).²³ With the catalysis of silver hexafluorophosphate, exclusive regioselectivity for attack at the benzylic position of the aziridine was observed. Moreover, the conditions proved to be efficient with heteroarenes, such as furan and thiophene, and in all cases, the substitution occurred exclusively at the C2-position of these heteroarenes. Furthermore, it was also found that electron-rich arylaziridines are more reactive towards arenes, but the aziridine bearing an alkyl C2-substituent did not give any visible reaction.



Scheme 16: AgPF_6 catalysed regioselective ring opening of *N*-tosyl aziridines **68** with arenes and heteroarenes

Roy and co-workers also developed an efficient arylation of *N*-tosylaziridine **26** with arenes and non-indole heteroarenes under the mild conditions to give the corresponding β -aryl amine derivatives **72** with excellent regioselectivity in the presence of $[\text{Ag}(\text{COD})_2]\text{PF}_6$.²⁴ For ring-activated arenes such as anisole (Scheme 17a), the benzylic position of the *N*-tosylaziridine **26** was attacked to afford the product in an excellent yield. In addition, heteroarenes such as benzofuran and benzothiophene are also able to participate in the reaction with exclusive C2 regioselectivity (Scheme 17b). However, benzene and ring-deactivated arenes proved to be inactive substrates, and reactions of alkylaziridines such as *N*-tosyl-2-hexylaziridine and *N*-benzyl-2-phenylaziridine failed.



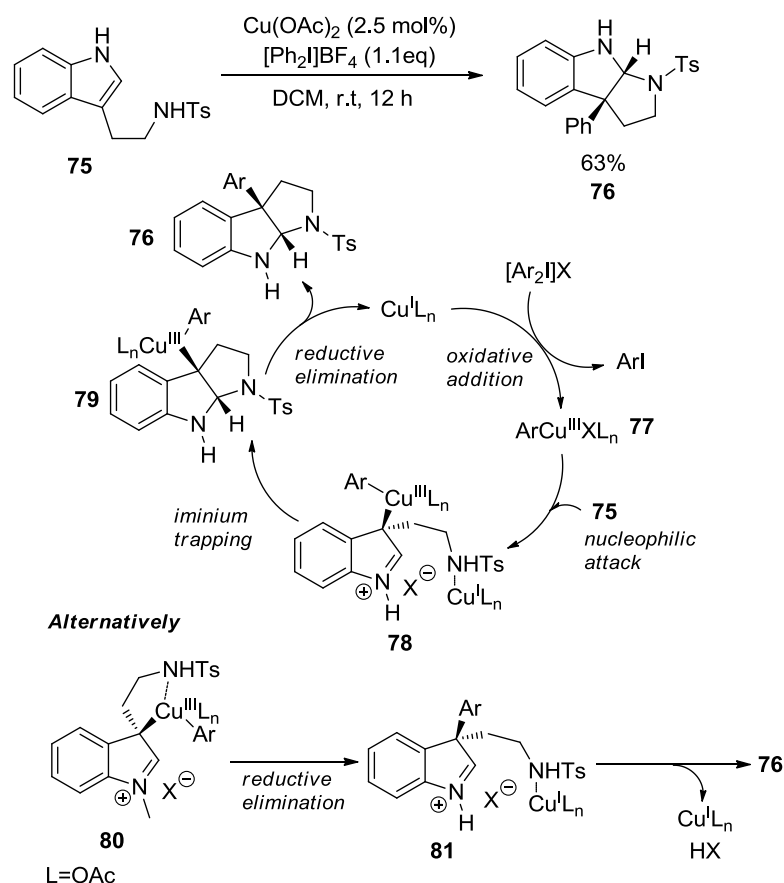
Scheme 17: Silver(I)-diene complexes as versatile catalysts for the C-arylation of N-tosylaziridines (COD = cyclooctadiene)

The authors proposed a catalytic cycle for the Ag(I)-catalysed arylation reaction of aziridines (Scheme 17c). First of all, the catalytically active species $[\text{Ag}(\text{COD})]^+$ is formed *via* dissociation of the PF_6^- and one COD ligand. The active Ag(I) species, which has coordinative unsaturation, is able to accept the first coordination from the aziridine **26**. It worth noting that this reaction is different from the cases catalysed by strong Lewis acids because the distinct free benzyl cation does not form in the resulting transition state **73**. Subsequently, additional coordination to the arene gives intermediate **74**. The coupling then occurs between two organic substrates facilitated by their close proximity in an Ag-centered activated complex intermediate **74** to release the final product **72**. A COD molecule then enters into the cycle to regenerate the active species $[\text{Ag}(\text{COD})]^+$.

Synthesis of Pyrroloindolines by the Ring-Closure of Tryptamine Derivatives

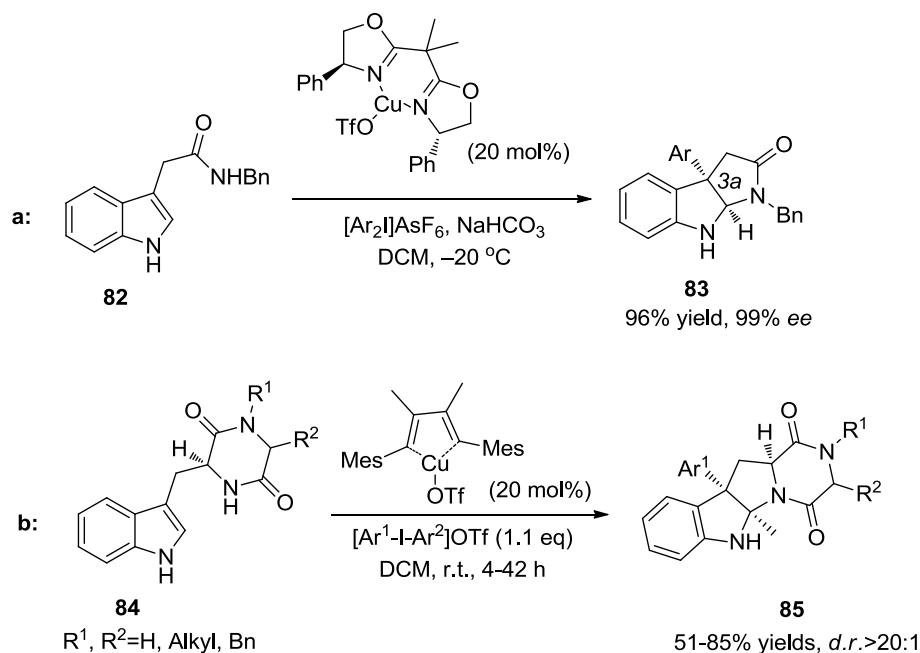
It has been shown in Scheme 2 that a dearomative Lewis acid-catalysed [3+2] cycloaddition of C3-substituted indoles with *N*-activated aziridines has been proposed for synthesis of pyrroloindolines. However, this method is limited to C3-substituted indoles **14**, otherwise, the tryptamines **22** could be generated *via* the substitution of C3-unsubstituted indoles **20** in the presence of Lewis acids (Scheme 4).

Several groups have developed methods where pyrroloindolines can be formed by the C3 arylation of tryptamine derivatives and subsequent cycloaddition, realising the synthesis of the bioactive pyrroindolines from the tryptamines. For example, the Reisman group explored a reaction utilising hypervalent iodine species that aimed to construct the pyrroloindoline **76** by using the tryptamine **75** (Scheme 18).²⁵ A Cu(I)-Cu(III) catalytic cycle was proposed for the reaction of this type based on the C3-arylation of unsubstituted indoles developed by Gaunt and co-workers.²⁶ First, an *in situ*-generated Cu(I) species is considered to be the catalytically active intermediate. A highly electrophilic Cu(III)-aryl complex **77** is generated *via* the oxidative addition of the arylodonium to the Cu(I) species. Nucleophilic attack of **75** to the electrophilic complex **77** then occurs to give the complex **78**, followed by iminium ion trapping to give the complex **79**. Subsequently, reductive elimination occurs to release an arylated pyrroloindoline **76** as the final product. An alternative mechanism was also proposed, where the sulfonamide functions as a ligand so that the nucleophilic attack is promoted by indole at the Cu(I)-aryl complex to give a spiro-metallacycle **80**. Furthermore, the rate of formation of the sp^3 - sp^2 C-C bond is faster than the rate of copper migration due to the acceleration effect caused by this ligand coordination. Finally, the active Cu(I) species is regenerated with reductive elimination, and cyclisation of the resulting **81** would afford arylated pyrroloindoline **76**.



Scheme 18: A copper-catalysed arylation of the tryptamine **75**

The Reisman and MacMillan groups further investigated the asymmetric synthesis of pyrroloindolines (Scheme 19).²⁷ MacMillan and his co-worker prepared a series of arylated 2-oxopyrroloindolines **83** by the catalytic asymmetric arylation of indole-3-carboxamides **82** in the presence of a phenyl-substituted bisoxazoline-bound Cu(I) complex in high yields and enantioselectivities (Scheme 19a). The Reisman group also developed a diastereoselective arylation of tryptophan derivatives *via* cyclisation of enantioenriched **84** *via* a similar mechanism of the reaction demonstrated in Scheme 18 (Scheme 19b). Furthermore, the appropriate carboxylate functionalities incorporated in the molecules **84** allow a direct elaboration to the natural products (+)-naseesazine A and B, which both display antibacterial activity (Figure 2).²⁸



Scheme 19: Two examples of Cu-catalysed C3-arylation-cyclisation towards pyrroloindolines

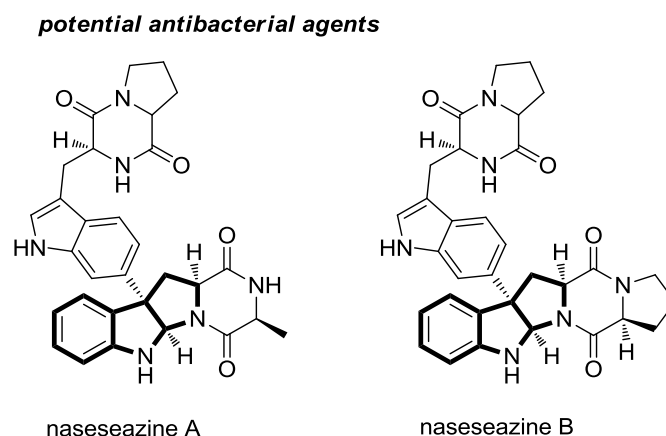
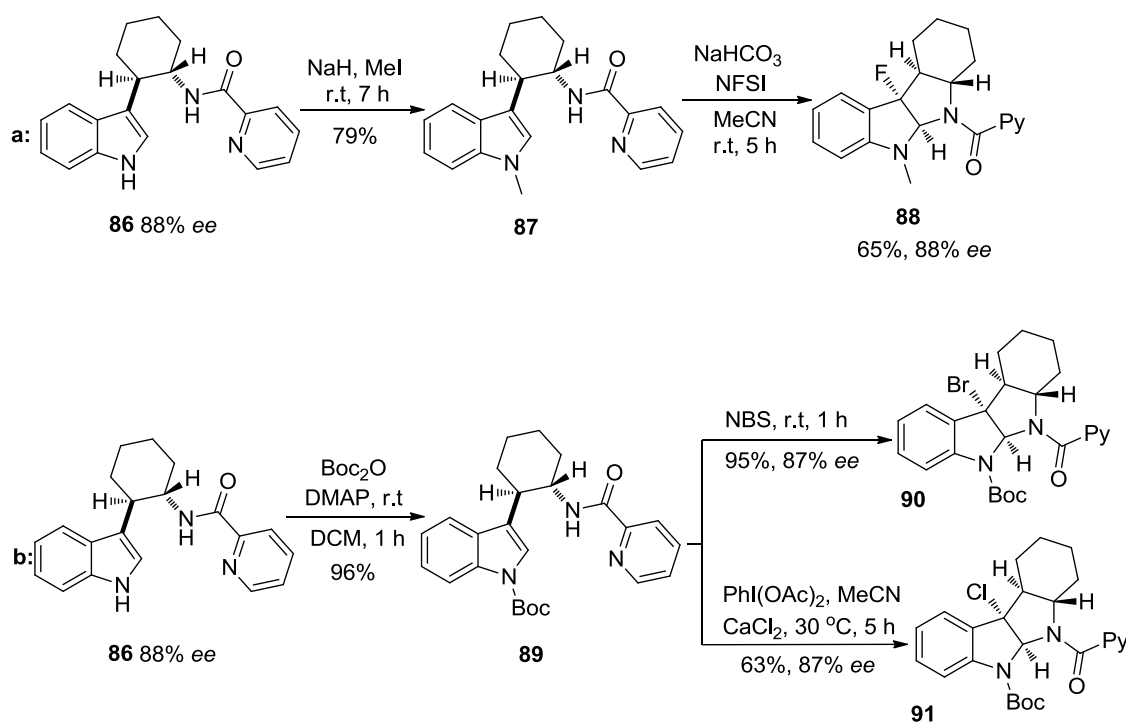


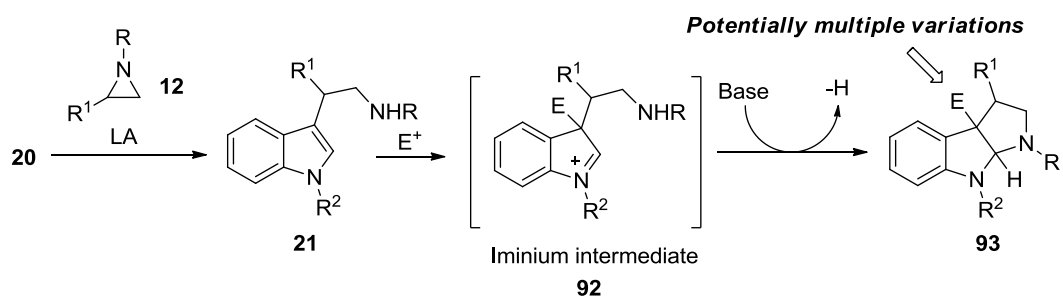
Figure 2: Natural products synthesised through the methodology from the Scheme 19b

It can be seen that all pyrroloindolines synthesised in the above examples only have aryl groups at the C3a-position. Recently, pyrroloindolines halogenated at the C3a-position have found increasing importance in synthetic and medicinal chemistry and so methods for their synthesis have been investigated.²⁹ For example, the Wang group constructed various C3a-halogenated pyrroloindolines by using electrophilic halogenating agents (Scheme 20).⁶⁴ This strategy utilised the enantioenriched *N*-H tryptamine **86** as the starting material to synthesise the corresponding C3-halogenated pyrroloindolines **88**, **90** and **91** with the retention of enantiopurity. The enantioenriched starting materials were prepared by desymmetrisation of a *meso* aziridine as shown previously in Scheme 11.



Scheme 20: Applications of the ring-opening reaction towards C3-halogenated pyrroloindolines

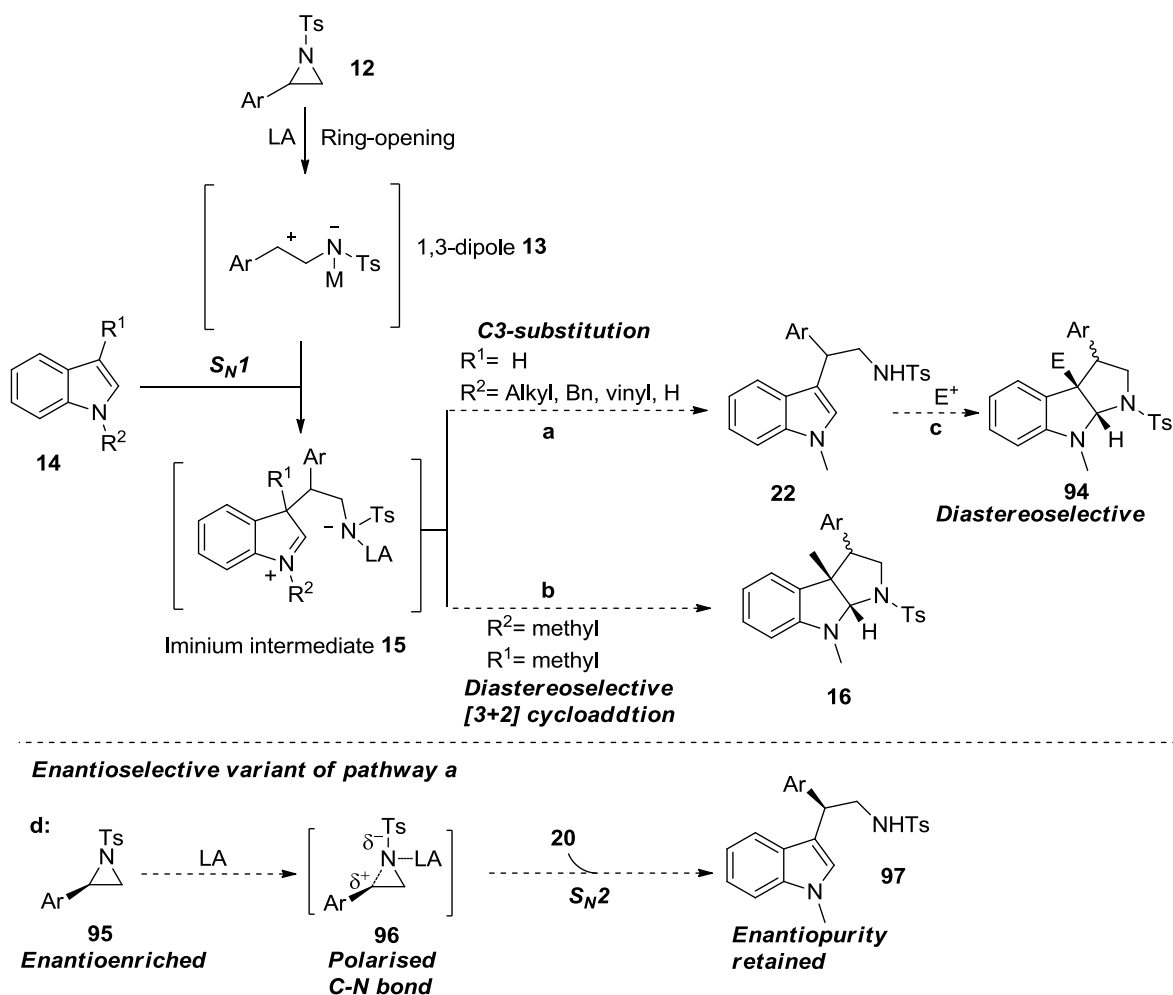
Therefore, inspired by the example carried out by the Reisman and MacMillan groups (Schemes 18-19), a proposal was designed (Scheme 21) for the synthesis of the C3-substituted pyrroloindolines from the β -substituted tryptamines **21**. The tryptamine **21** that would be prepared from C2-substituted aziridines and indoles in the presence of Lewis acids (Scheme 4) could trap an appropriate electrophile, followed by an intramolecular cycloaddition of the resultant iminium intermediate **92** to give the skeletons of the pyrroloindolines **93**. Furthermore, not only does this strategy allow the C3-position to be substituted, but the strategy also potentially provides different C3a groups by varying the external electrophiles. Such substitution patterns had not been reported, so this synthetic route could provide new pyrroloindolines that may potentially have useful bioactivities.



Scheme 21: Electrophilic cycloaddition to synthesise highly substituted pyrroloindolines **93**

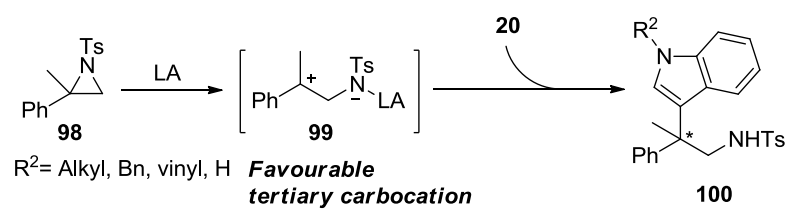
Research Plan

The overall research plan combining the reactivities of indoles and arylaziridines is summarised in Scheme 22. Firstly, a catalytic Lewis acid will be identified for achieving the C-N bond cleavage of *N*-tosyl arylaziridine **12** to form a zwitterionic 1,3-dipole **13** or an activated aziridine complex, followed by the S_N1 or S_N2 nucleophilic substitution respectively of indoles **14** to give an iminium intermediate **15**. Subsequently, an intramolecular ring-closure then occurs to diastereoselectively synthesise the biologically relevant pyrroloindoline skeleton **16** with a C3-substituted indole (Pathway **b**, Scheme 22b). Alternatively, the β-branched tryptamine **22** could be produced *via* the intramolecular protonation of **15** when R¹ is a proton (Pathway **a**, Scheme 22). In addition, to show the synthetic value of tryptamines **22** (Pathway **c**, Scheme 22), an electrophilic ring closure to prepare C3, C3a-disubstituted pyrroloindolines **94** was planned to be carried out and its diastereoselectivity studied (Pathway **c**, Scheme 22). To determine whether an S_N1 or S_N2 mechanism is operating enantioenriched aziridines **95** will be used as starting materials (Scheme 22d). In this case an S_N2 mechanism is operating, formally charged intermediate **96** may be generated by the C-N bond polarisation of an enantioenriched arylaziridine **95**, which does not enable the complete C-N cleavage of **95**. Therefore, the enantiopurity could be retained in the tryptamine **97**, which is resulted from the nucleophilic attack of **20** to the intermediate **96** *via* a S_N2 pathway with inversion of configuration. If an S_N1 mechanism is operating then it may be possible to develop catalytic asymmetric processes - here a chiral Lewis acid converts racemic aryl aziridines **12** into the zwitterionic dipole **13** and may then control the facial selectivity of attack of the indole so that the stereogenic centre in **15** is formed in an enantioselective fashion.



Scheme 22: Overall research plan for the synthesis of tryptamines and pyrroloindolines

Furthermore, the efficient formation of all-carbon quaternary all-carbon centres remains particularly challenging in intermolecular reactions because the increased steric repulsion between the carbon substituents of the resulting product.³⁰ Interestingly, as shown in the survey above, there have been no examples of the use of 2,2'-disubstituted aziridines in cycloaddition or Friedel–Crafts reactions. On the basis of Scheme 22a, it is envisioned that an all-carbon quaternary centre could be created in the tryptamine **100** via the Lewis acid-catalysed C–N bond cleavage of the 2,2'-disubstituted aziridine **98** with the C3-unsubstituted indole **20** (Scheme 23). The formation of the reactive tertiary carbocation **99** is highly likely, as it has delocalised positive charge that is stabilised by the surrounding substituents, leads to this favoured S_N1 process to give **100**. As such it may be possible to develop a catalytic enantioselective ring-opening process with a chiral Lewis acid. However, Lewis acid-catalysed $E1$ reaction of **98** may be a competing side reaction.

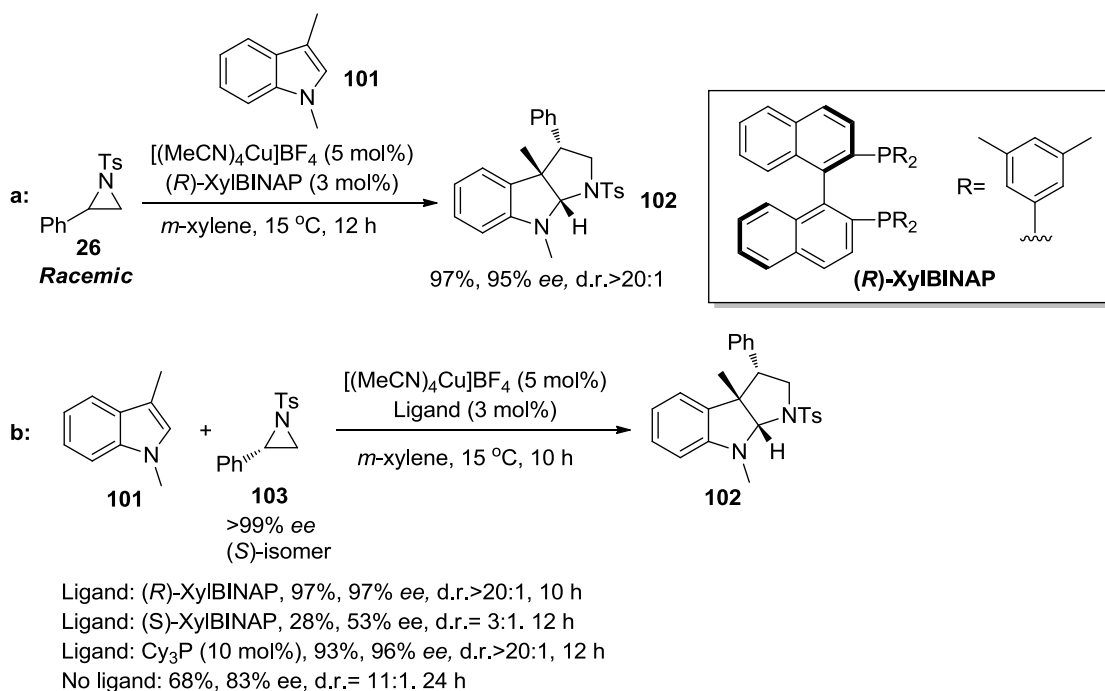


Scheme 23: Proposed synthetic pathways of the tryptamine **100** bearing an all-carbon quaternary centre

Recent Complementary Reactions

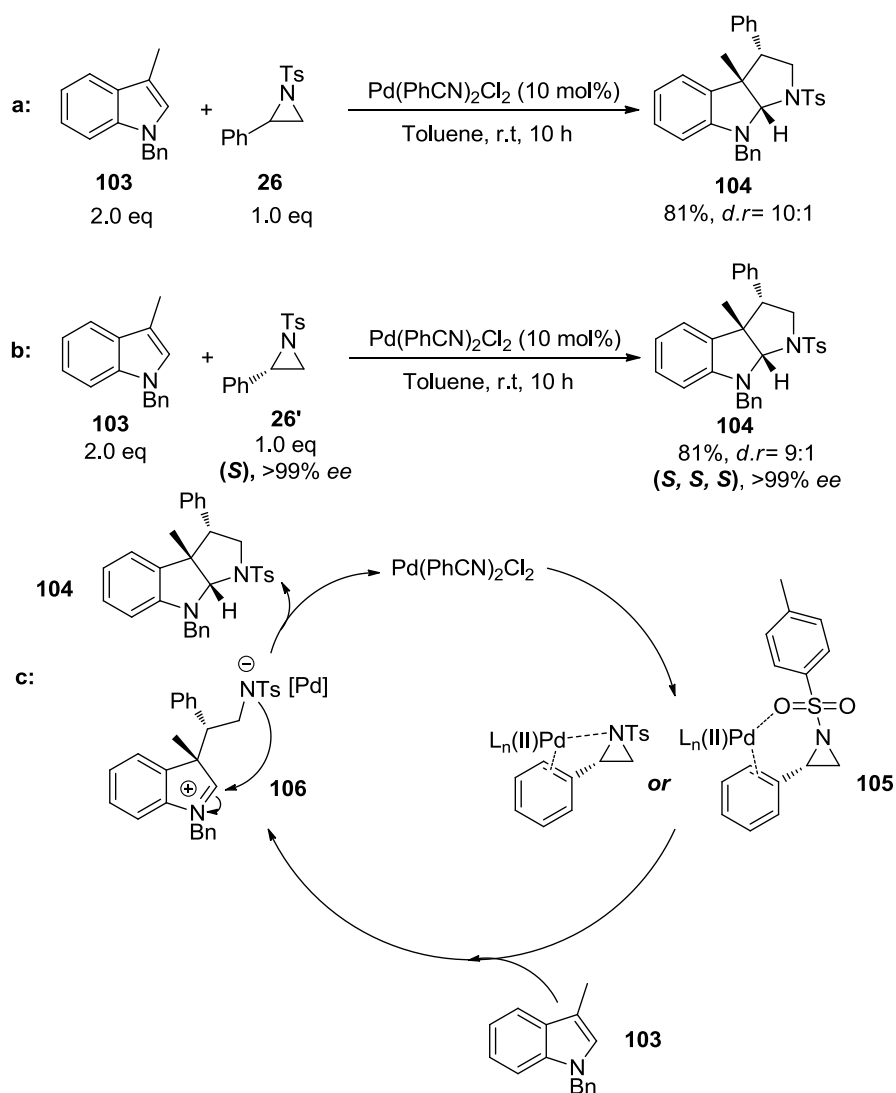
As discussed above there was only an isolated example using an unsubstituted aziridine with the stoichiometric amount of Lewis acid in [3+2] cycloaddition reactions to indoles when this project was started (Scheme 1). Nevertheless, towards the end of this project, it was found that other groups have concurrently studied this topic. Therefore, it is important to introduce those recent reports about the Lewis-catalysed [3+2] annulation of indoles and aziridines even though they had no influence on the current study. Firstly, the Chai group realised the first Lewis acid catalysed [3+2] annulation of the indole **101** and 2-phenyl-*N*-tosylaziridines **26** in the presence of copper(I)/chiral diphosphine complexes in a similar manner proposed in Scheme 2 (Scheme 24).³¹ A multi-functionalised chiral pyrroloindoline **102** bearing multiple contiguous stereogenic centers were prepared in a high yield with excellent enantio- and diastereoselectivity under mild conditions.

Excess racemic aziridine **26** (2.2 equiv) was required in the reaction to diastereo- and enantioselectively give the pyrroloindolines and recover enantiopure unreacted aziridine, indicating a kinetic resolution process occurs. To probe the stereochemical process of this reaction, a few control reactions were carried out with enantiopure (*S*)-aziridine **103** (Scheme 24b). It was then found that the pyrroloindoline **102** could be synthesised in a comparably excellent yield and a stereoselectivity with use of either (*R*)-XylBINAP or racemic Cy₃P as the ligand, however, a considerable drop in both yield and enantioselectivity was observed when (*S*)-XylBINAP was employed as the ligand. Moreover, the absolute stereochemistry of the resultant major pyrroloindoline isomer **102** was found to be determined by the structure of the aziridine. It is therefore concluded that the C2-position of the aziridine is attacked by the nucleophilic indole **101** via an S_N2 pathway with a stereoinvertive manner. Furthermore, the racemic aziridine **26** should undergo a kinetic resolution process in this asymmetric catalytic reaction to ensure the high enantiopurity in the product **102** (Scheme 24a). In addition, a significant decrease in the enantiopurity of product was found when the reaction was completed without any ligand, suggesting a slight racemisation of the aziridine (Scheme 24b).



Scheme 24: Copper(I)-catalysed kinetic resolution of *N*-sulfonylaziridines with indoles

The [3+2] cycloaddition reaction to construct C3-substituted pyrroloindoline skeletons using achiral or chiral 2-arylaziridines was also developed by the Zhao group (Scheme 25).^{32a} After carrying out an Lewis acid catalyst screening at room temperature, Pd(PhCN)₂Cl₂ and toluene were selected as the optimum Lewis acid and solvent respectively, since they were found to give the best yield and diastereoselectivity (up to 81% and 10:1 for *trans*:*cis*) (Scheme 25a). However, the reaction did not occur when 2-benzylaziridine and Pd(0)-catalysts such as Pd(PPh₃)₄ and Pd₂(dba)₃ were subjected to the reaction, verifying the C-N bond cleavage is likely being promoted by a Lewis acid pathway. In addition, the enantioenriched (*S*)-aziridine **26'** was employed as the substrate, affording the corresponding pyrroloindoline **104** in the enantiopure form in a high yield and a good diastereoselectivity (Scheme 25b). Moreover, the single crystal X-ray analysis clearly indicated the absolute configuration of the product is (*S*, *S*, *S*), confirming the aforementioned stereoinversion at the C2-position of aziridine **26**. Mechanistically, aziridine **26'** initially coordinates to the Pd(II)-centre with either nitrogen atom or sulfonyl oxygen atom, giving a reactive complex **105** as the intermediate, which then accepts S_N2 nucleophilic attack from **103** to generate a stereoinverted iminium ion **106**. Subsequently, the ring closure occurs to release the targeted product **104** (Scheme 25c).



Scheme 25: Palladium(II)-catalysed formal [3+2] cycloaddition of aziridines with 3-substituted indoles

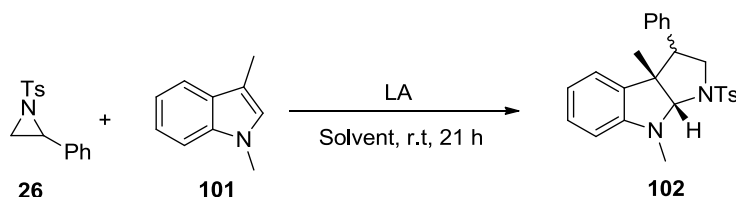
Results and Discussion

Synthesis of Pyrroloindolines *via* the Lewis Acid-Catalysed [3+2] Cycloaddition of C3-Substituted Indoles with Aziridines

At the beginning of the project, the catalytic efficiency of various Lewis acids in the [3+2] cyclisation of *N*-tosyl phenylaziridine **26** with 1,3-dimethylindole **101** under the different conditions was examined (Table 1). The aziridines **26** can be obtained by aziridination of the corresponding alkene and this will be discussed in detail in the next section. Cu(OTf)₂ was first identified as an effective Lewis acid to promote the formation of pyrroloindole **102**, however, only DCE and DCM gave moderate yields with relatively low *trans*-selectivities when **101** was limiting agent (entries 1-5). This successful [3+2] cyclisation reaction was evidenced by a singlet associated with C8a proton at 5.37 ppm and a triplet corresponding to C3 proton at 3.39 ppm (major product). Additionally, C3a methyl of **102** at 1.27 ppm is upfield in comparison to C3 methyl of **101** at 2.36 ppm. Six aliphatic carbon signals of major product were found in the ¹³C NMR of **102**, suggesting the coupling reaction between **101** and **26** has successfully occurred. High-resolution mass spectrometry indicated the molecular weight of isolated product is 441.1620 g mol⁻¹, which is agreement with the molecular weight of expected cycloadduct **102**. Furthermore, the 1D-NOESY indicates the major diastereoisomer of the resulting pyrroloindoline **102** was *trans*, which is in accordance with the subsequent result of the Chai group.³³ Therefore, 1.0 equivalent of **26** and 1.5 equivalents of **101** were then added in the presence of Cu(OTf)₂, and the reaction gave **102** in a moderate yield (47%) with significantly increased *trans*-selectivity (entry 6). Next, 3.0 equivalents of **26** was added to the reaction to enhance the yield and *trans*-selectivity (entry 7). Other Lewis acids such as Sc(OTf)₃ and Ni(acac)₂ were also evaluated but no improved results were obtained (entries 8-9), while addition of PdCl₂(MeCN)₂ considerably increased both yield (82%) and diastereoselectivity (entry 10). Reducing the catalyst loading and equivalents of **101** were detrimental since **102** was isolated in depressed yield with a drop in the *trans*-selectivity (entries 11-12). It has been proposed that the π -acidity of the Pd(II)-centre could be enhanced by the coordination of benzoquinone (BQ) as a π -accepting ligand.³⁴ BQ was therefore added to the PdCl₂(MeCN)₂-catalysed reaction (10 mol%) but the depression in both yield and diastereoselectivity were observed (entry 13). Moreover, no reactions were observed

with addition of nitrogen-based ligands such as phenanthroline, neocuproine and 2,2'-bipyridine (bpy), which are known to stabilise the Pd(II)-centre (entries 14-16).³⁵ This is likely due to them causing a reduction in Lewis acidity of the Pd(II) centre. Subsequently, MeCN was utilised as solvent but it only lead to significantly reduced conversion and decomposition of **101** (entry 17). In addition, **101** was added to the reaction in 2 portions (each 1.5 eq); however, this did not give improved results (entry 18).

Table 1: Optimisation of The [3+2] cyclisation of *N*-tosyl phenylaziridine **26** with 1,3-dimethylindole **101**



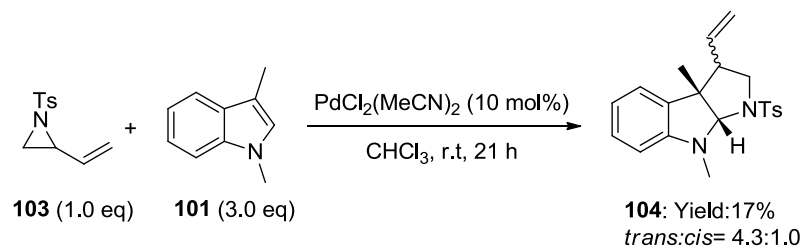
Entry	26:101	Lewis acid (mol%)	Additive (mol%)	Yield	<i>Trans:cis</i>	Solvent
1	2.0:1.0	Cu(OTf) ₂ (10)	-	50	1.8:1.0	DCE
2	2.0:1.0	Cu(OTf) ₂ (10)	-	trace	N/A	THF
3	2.0:1.0	Cu(OTf) ₂ (10)	-	trace	N/A	MeOH ^a
4	2.0:1.0	Cu(OTf) ₂ (10)	-	trace	N/A	MeCN
5	2.0:1.0	Cu(OTf) ₂ (10)	-	41	1.8:1.0	DCM
6	1.0:1.5	Cu(OTf) ₂ (10)	-	47	3.2:1.0	DCE
7	1.0:3.0	Cu(OTf) ₂ (10)	-	53	3.7:1.0 ^d	CHCl ₃
8	1.0:3.0	Sc(OTf) ₃ (10)	-	48	2.9:1.0 ^d	CHCl ₃
9	1.0:3.0	Ni(acac) ₂ (10)	-	NR	N/A	CHCl ₃
10	1.0:3.0	PdCl₂(MeCN)₂ (10)	-	82	6.5:1	CHCl₃
11	1.0:3.0	PdCl ₂ (MeCN) ₂ (5)	-	58	5.3:1.0	CHCl ₃
12	1.0:1.5	PdCl ₂ (MeCN) ₂ (10)	-	38	6.3:1.0	CHCl ₃
13	1.0:3.0	PdCl ₂ (MeCN) ₂	BQ (30)	65	6.2:1.0	CHCl ₃

		(10)				
14	1.0:3.0	PdCl ₂ (MeCN) ₂ (10)	Phen	-	N/A	CHCl ₃
15	1.0:3.0	PdCl ₂ (MeCN) ₂ (10)	Neocuproine	-	N/A	CHCl ₃
16	1.0:3.0	PdCl ₂ (MeCN) ₂ (10)	Bpy	-	N/A	CHCl ₃
17	1.0:3.0	PdCl ₂ (MeCN) ₂ (10)	-	22 ^b	N/A	MeCN
18	1.0:3.0 ^c	PdCl ₂ (MeCN) ₂ (10)	-	53	6.3:1.0	CHCl ₃

^a Methoxylation of **26** observed. ^b Conversion. ^c **101** was added in 2 portions ^d hydrolysis of **26** observed.

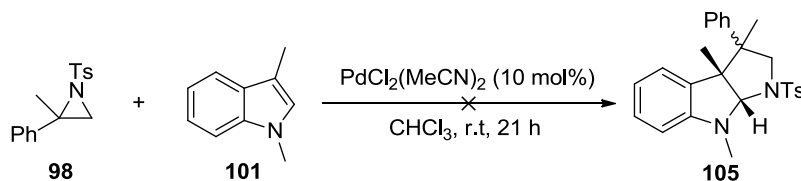
Two similar reports concurrently have been published for the pyrroloindoline synthesis using this approach: Cu(I)/chiral diphosphine catalyst system developed by the Chai group (Scheme 24) and Pd(PhCN)₂Cl₂ system used by Zhao and co-workers (Scheme 25). Therefore, instead of pursuing substrate scope for the reaction uncovered above attention was turned to a new and more versatile substrate, vinylaziridine **103**. The aziridines **103** can be obtained by aziridination of 1,3-butadiene and this will be discussed in detail in the next section. This substrate was subjected to the [3+2] cycloaddition to give a promising result: the C3-vinyl pyrroloindoline derivative **104** was given in a moderate purified ratio of *trans*:*cis* isomers (4.3:1.0), albeit with a low yield (17%) (Scheme 26). The formation of **104** was evidenced by a triplet at 2.80 ppm corresponding to the C3-H of *trans*-**104** in the ¹H NMR. In addition, a singlet associated with C8a-H of *trans*-**104** was found at 5.18 ppm, further supporting occurrence of the cycloaddition of **103**. The conservation of C3-vinyl group in **104** was confirmed by its characteristic signals on the purified ¹H NMR of **104**, including a multiplet (5.54-5.42 ppm) and two doublets (5.04 ppm and 4.90 ppm, respectively). Moreover, the C2 proton of **101** (6.85 ppm) disappeared in ¹H NMR of **104**. In addition, ¹³C NMR of **104** demonstrates seven aliphatic carbon signals, and this result matches the expected structure of **104**. The molecular weight that was given from High-resolution mass spectrometry is also in line with the structure of **104** (369.1640 g mol⁻¹). In conclusion, the expected cycloadduct **104** has been synthesised in this

reaction.



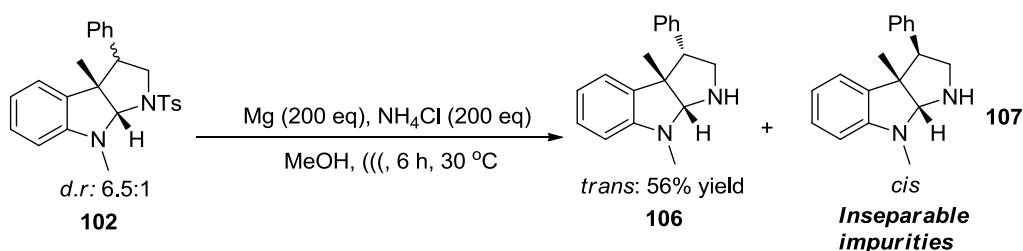
Scheme 26: Cycloaddition of vinylaziridine **103** to 1,3-dimethylindole **101**

After obtaining initial success in the [3+2] cycloaddition of mono-substituted aziridines to indole **101**, attention was switched to the 2,2'-disubstituted aziridine **98** as an electrophile. Thus, the condition shown in Scheme 26 was applied to **98**, however, this only resulted in a complicated mixture of unidentified products (Scheme 27). The synthesis of **98** will be discussed in the next section.



Scheme 27: Attempted cycloaddition of aziridine **98**

In order for the product to find general utility in synthetic projects, the tosyl unit would have to be removed. It was therefore found that the diastomeric mixture of **102** could be readily detosylated with Mg/NH₄Cl under ultrasound conditions to give the pure *trans*-**106**, highlighting the utility of the method developed (Scheme 28). The successful detosylation was evidenced by the absence of tosyl methyl in the ¹H NMR of *trans*-**106**, and a broad singlet at 2.44 ppm associated with the N1 amine proton resulted from the detosylation was also observed. In comparison with **102**, only six aliphatic carbon signals were found in the ¹³C NMR of *trans*-**106**, suggesting the tosyl group has been removed in the reaction. The molecular weight of isolated product is 265.1714 g mol⁻¹, which is approximate to the calculated molecular weight of *trans*-**106** (265.1705 g mol⁻¹). This result further proved that the tosyl group was successfully removed from **102** in this reaction. The *cis*-diastereoisomer **107** could only be isolated with many inseparable impurities.

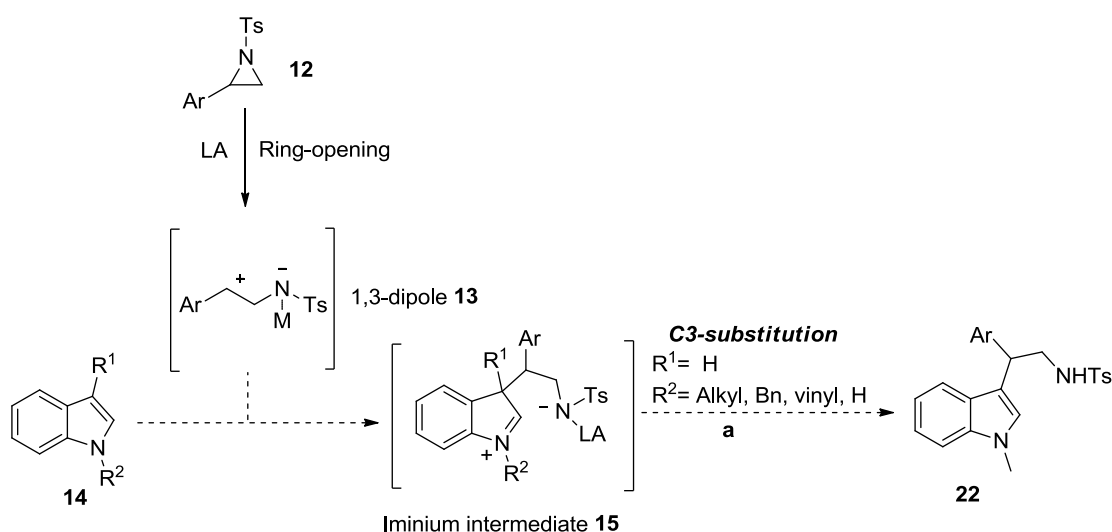


Scheme 28: Detosylation of **102**

In conclusion, a $\text{PdCl}_2(\text{MeCN})_2$ -catalysed formal [3+2] cycloaddition of phenylaziridine **26** with 1,3-dimethylindole **101** was performed to give a C3-phenyl pyrroloindoline skeleton **102** in an excellent yield (82%) with a good diastereoselectivity (6.5:1.0). Fortunately, the pure *trans*-diastereoisomer of detosylated **102** was isolated in a moderate yield (56%) by column chromatography. In addition, a C3-vinyl pyrroloindoline skeleton **104** was also synthesised from the vinylaziridine **103** with a promising diastereoselectivity (4.3:1.0) under the same conditions, albeit with a low yield (17%). Due to concurrent reports of very similar methods additional substrate was not investigated and attention turned to the synthesis of tryptamine derivatives.

Lewis Acid-Catalysed Synthesis of Tryptamines by C3-Unsubstituted Indoles and Aziridines

A synthetic pathway for β -branched tryptamines has been proposed in Scheme 22a. The Lewis acid catalyses the generation of 1,3-dipole **13**, which is then attacked by the indole **14** to give the iminium intermediate **15**. The β -branched tryptamine **22** therefore can form by rearomatisation of **15** if R_1 is a proton.

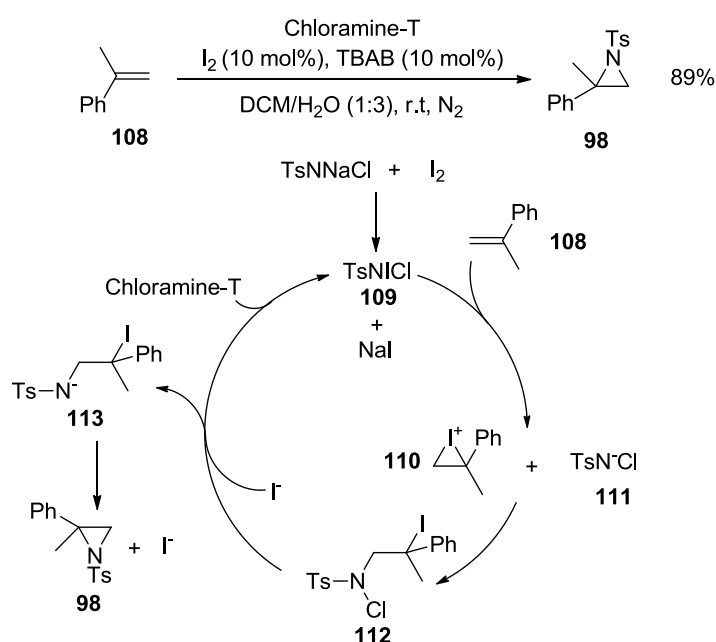


Scheme 22a: The proposed synthetic pathway for β -branched tryptamine

The above process could be facilitated with a more reactive 1,3-dipole **99** resulting from Lewis acid-catalysed ring-opening of the disubstituted aziridine **98** (Scheme 23). Therefore, the 2-methyl-2-phenyl-1-tosylaziridine **98** was first utilised in the project to synthesise the corresponding β -branched tryptamines containing an all-carbon quaternary centre with a variety of indoles.

It has been reported that aziridine **98** could be readily accessed by the aziridination of α -methylstyrene **108** using the method developed by the Morgan group (Scheme 29).³⁶ The process was promoted by a catalytic amount of I_2 in the presence of tetrabutylammonium bromide (TBAB) as a phase transfer catalyst to give the desired aziridine **98** in an excellent yield (89%). Mechanistically,³⁷ chloramine-T reacts with iodine to give iodo-chloramine-T intermediate **109**, and then an iodonium **110** and anionic intermediate **111** are yielded by the trapping of **109** with α -methylstyrene **108**. The iodoaminated intermediate **112** is subsequently formed by the attack of the anionic nitrogen atom of **111**. Next, iodide attacks the N-Cl group of intermediate **112** to generate the

anion **113** and ICl which enables TsNICl to be regenerated to initiate the next catalytic cycle. Finally, the aziridine **98** is yielded by the expulsion of iodide from the ring-closure of anion **113**. The generation of **98** was evidenced by a pair of symmetric singlets corresponding to the CH₂ (2.99 ppm and 2.55 ppm, respectively) and one singlet at 2.07 ppm associated with C2 methyl group of **98**. In addition, four aliphatic carbon signals were observed in the ¹³C NMR of **98**, suggesting NTs group has been coupled with **108**. The structure of **98** was confirmed by comparing with the literature.³⁸



Scheme 29: Preparation of aziridine **98**

The project commenced with the reaction of aziridine **98** with 1.5 equivalents of *N*-methylindole **114** to produce a β -branched tryptamine **115** containing an all-carbon quaternary stereogenic centre (Table 2). The Lewis acids Cu(OTf)₂, Sc(OTf)₃ and AgSbF₆ were quickly identified as effective catalysts for this reaction (Table 2, entries 1-3), albeit with moderate conversions and yields. The C-C bond formation in these reactions was exclusively achieved between C3-position of **114** and C2-position of **98**. Evidence for this substitution partially came from the multiplet (4.05-4.03 ppm) associated with the amine proton of side chain of **115**, which is produced by the protonation after the C-N bond of aziridine **98** is cleaved. Moreover, the disappearance of C3-H of indole **114** (doublet at 6.45 ppm) on the ¹H NMR of the crude reaction mixture also indicates the C3-position of **114** has been substituted. In addition, five signals for aliphatic carbon were observed on the ¹³C NMR of **115**,

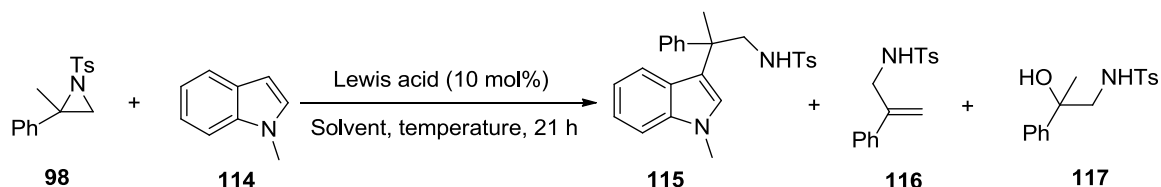
suggesting the coupling reaction of **98** with **114** has been achieved. The molecular weight of the isolated product ($441.1620 \text{ g mol}^{-1}$) is in accordance with the expected structure of **115**, further supporting the occurrence of C3-substitution of **114** with **98**. Nevertheless, the impurities **116** and **117**, resulting from aziridine decomposition, were found in all these three crude reaction mixtures (Scheme 32).

To increase conversion of the reaction, 1.0 equivalent of *N*-methyldole **114** was then used as the limiting reagent in the presence of $\text{Cu}(\text{OTf})_2$ in the reaction with dropwise addition of 3.0 equivalents of aziridine **98** at room temperature. This resulted in a complete conversion of **114**; however, the aziridine-derived ring-opened by-products **116** and **117** were still generated (entry 4). The tertiary alcohol **117** likely resulted from introduction of moisture in the reaction workup (Scheme 23). However, TLC analysis demonstrated the polarity of **116** is very similar to the targeted compound **115**, greatly enhancing the difficulty in purification of **115** using column chromatography. In order to avoid **116**, a reaction using **98** as the sole substrate in the presence of catalyst $\text{Cu}(\text{OTf})_2$ in dichloroethane under the air at room temperature was carried out (Scheme 30a). This test reaction then gave a mixture of **116** and **117** in 100% conversion with a ratio of 47:53. In addition, 2 portions of **98** were stored at different temperatures for 3 days. One portion of **98** stored at room temperature gradually completely converted into **116** and **117** in a ratio of 44:56. However, **98**, which was stored the 0°C , remained unreacted (Scheme 30b). It was therefore concluded that a low reaction temperature may deter the generation of **116**.

With these results in hand (Scheme 30), a reaction was carried out at 0°C under the conditions used in entry 4. To our delight, performing the reaction at low temperature (0°C) significantly decreased the quantity of **116**, and the desired tryptamine derivative **115** was isolated in an increased yield of 94% (entry 5); furthermore, the ^1H NMR of the isolated **115** showed only a trace amount of **89**. It can therefore be seen that the purity of the isolated **115** could be enhanced if the amount of **116** is diminished by carrying out the reaction at low temperature. Nevertheless, it was found that reducing the temperature to -20°C did not improve the isolated yield (entry 6). In addition, compared with the yield (94%) in the entry 5, the reduced loading of aziridine **98** (2.0 eq) gave an adverse effect to the reaction as the yield was diminished to 81%, and the impurity **116** was produced in this reaction with a largely increased amount and was significantly present in the isolated **115** due to the aforementioned isolation difficulties (entry 7). Different solvents were then screened in the following

three reactions (entries 8-10), but none of them was able to give a satisfactory result. Subsequently, the catalytic activities of different Lewis acids were also examined under the conditions (entries 11-14). Pleasingly, in contrast to other Lewis acids, the use of $\text{PdCl}_2(\text{MeCN})_2$ further depressed the amount of **116** with no significant loss of yield for the desired product **115**. Also, the cleanness of the crude reaction mixture was decreased, and the isolated yield of **115** was therefore reduced to 75% when 30 mol% benzoquinone (BQ) was present in the reaction despite favourable reduction in by-products (entry 15). In addition to DCE, one reaction was carried out in CHCl_3 , however, **116** was observed in the ^1H NMR of the crude reaction mixture in a significantly enhanced amount, and the isolated yield of **115** was reduced to 71% (entry 16). It was found that reducing catalyst loading (5 mol%) led to less reaction efficiency since the conversion was only 83% in this case (entry 17). Additionally, 2.0 equivalents of **98** were used in the Pd-catalysed reaction, but the yield was significantly decreased to 71% with a dramatically enhanced amount of **116** but with a reduced amount of **117** (entry 18).

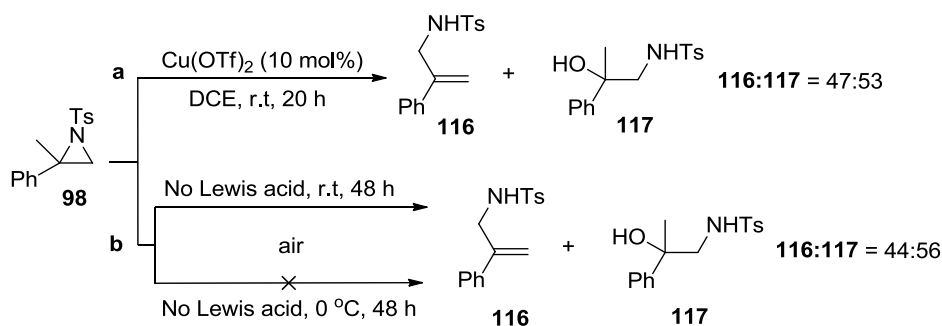
Table 2. Optimisation of C3-substitution of *N*-methylindole **114** with 2-methyl-2-phenyl-1-tosylaziridine **98**



Entry	2a:1a	Lewis acid	Solvent	T °C	115:89:90	Conversion (yield%) ^b
1	1.0:1.5	$\text{Cu}(\text{OTf})_2$	DCE	r.t	64:15:21	60(55)
2	1.0:1.5	$\text{Sc}(\text{OTf})_3$	DCE	r.t	49:29:22	63(48)
3	1.0:1.5	AgSbF_6	DCE	r.t	37:4:59	62(30)
4	3.0:1.0	$\text{Cu}(\text{OTf})_2$	DCE	r.t	33:16:51	100(59)
5	3.0:1.0	$\text{Cu}(\text{OTf})_2$	DCE	0	31:5:64	100(94)
6	3.0:1.0	$\text{Cu}(\text{OTf})_2$	DCE	-20	36:6:58	100(90)
7	2.0:1.0	$\text{Cu}(\text{OTf})_2$	DCE	0	53:19:29	100(81)
8	3.0:1.0	$\text{Cu}(\text{OTf})_2$	THF	0	0:70:30	100(N/A)
9	3.0:1.0	$\text{Cu}(\text{OTf})_2$	Diethyl ether	0	30:20:50	80 ^e
10	3.0:1.0	$\text{Cu}(\text{OTf})_2$	CHCl_3	0	33:7:60	77 ^e

11	3.0:1.0	AgSbF ₆	DCE	0	25:5:70	100(30)
12	3.0:1.0	Sc(OTf) ₃	DCE	0	49:29:22	100(63)
13	3.0:1.0	Ni(ClO ₄) ₂ ·6H ₂ O	DCE	0	20:3:77	73(N/A)
14	3.0:1.0	PdCl₂(MeCN)₂	DCE	0	62:5:33	100(93)
15	3.0:1.0	PdCl ₂ (MeCN) ₂ ^c	DCE	0	84:3:13	100(75)
16	3.0:1.0	PdCl ₂ (MeCN) ₂	CHCl ₃	0	67:40:0	100(71)
17	3.0:1.0	PdCl ₂ (MeCN) ₂ ^d	DCE	0	61:6:33	83(69)
18	2.0:1.0	PdCl ₂ (MeCN) ₂	DCE	0	67:30:2	90(66)

^a Entries 4-5: dropwise addition of **98** over 4 h. entries 6-13: dropwise addition of **98** over 6 h. ^b Isolated yield of **115**. ^c 30 mol% BQ was added. ^d 5 mol% PdCl₂(MeCN)₂. ^e Conversion



Scheme 30: Generation of allylic sulfonamide **116** and hydrolysed aziridine **117** under different conditions

With optimised conditions in hand, the reaction scope and functional-group tolerance were evaluated with various indoles (Table 3). Products **119** and **120** were successfully synthesised in good yields from *N*-benzyl and *N*-allyl indole respectively because the characteristic signals were found in the ¹H NMR of **119** (doublet for benzyl-CH₂ at 5.32 ppm) and **120** (multiplet for allyl's olefin-CH at 6.06-6.00 ppm, two doublets for allyl's olefin-CH₂ at 5.25 ppm and 5.14 ppm respectively). In addition, indoles bearing a halogen atom at C5 position were also subjected to the reaction conditions, providing the corresponding products in moderate to excellent yields (products **121-123**). Also, it needs to be indicated that a relatively low yield of product **122** was obtained although 100% conversion was found from the clean ¹H NMR of the crude reaction mixture, therefore, it is reasonable to propose the low

Table 3: Substrate scope for the ring-opening of 2,2'-disubstituted aziridine **98** with indoles

PhC1(C)N(Ts)C1 (**98**) + Indole(R^1 , R^2) $\xrightarrow[\text{DCE, 0 } ^\circ\text{C, 21 h}]{\text{PdCl}_2(\text{MeCN})_2 \text{ (10 mol\%)}}$ Product

<p>118: 93%</p>	<p>119: 81%^b</p>
<p>120: 73%</p>	<p>121: 91%</p>
<p>122: 44%</p>	<p>123: 70%</p>
<p>124: 85%</p>	<p>125: 56%</p>

^a Reaction conditions: aziridine **98** (3.0 equiv), *N*-methylindoles (1.0 equiv), 21 h. ^b 8% of an unidentified, inseparable compound was also produced.

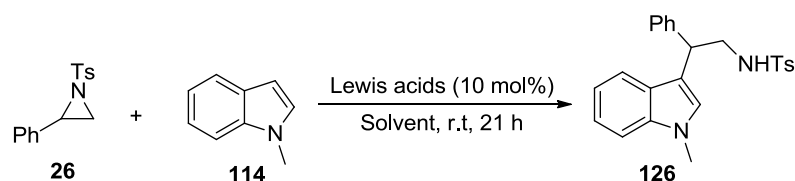
yield of **122** resulted from its instability towards purification on silica gel. Importantly, the molecular complexity of such halogen-containing products could potentially be further increased using cross-coupling reactions. Furthermore, a C5 methoxy group was found to be beneficial to the reaction yield (product **124**), and a characteristic singlet at 3.42 ppm corresponding to the methoxy group in the ¹H NMR of **124** suggests the coupling reaction between **98** and indole. The chemoselectivity of the reaction was then examined with 1*H*-indole (product **125**), and the C3-alkylated product was observed in a moderate yield of 56% with no *N*-substitution occurring. This exclusive chemoselectivity was evidenced by the observation on the broad singlet associated with N1 proton of indole moiety (8.19 ppm) in the ¹H NMR of the product.

Subsequently, the ring-opening of the less reactive 2-aryl-*N*-tosylaziridines with various indoles was explored (Table 4). Initially 1.0 equivalent of *N*-tosylaziridine **26** was utilised to react with 1.5 equivalents of *N*-methyl indole **114** in the presence of Cu(OTf)₂ and the targeted compound **126** was obtained in a good yield (73%), but with significant inseparable impurity (Table 4, entry 1). It needs to be pointed out no aziridine decomposition products were observed for **26** in the presence of Lewis acids. The ring-opening reaction successfully occurred as the ¹H NMR shown a broad triplet (4.38 ppm) for amine proton of side chain. Furthermore, it can be seen from the ¹H NMR of **126** that disappearance of the doublet (6.94 ppm) associated with the C3-H of **114** and presence of the singlet at 6.78 ppm corresponding to the C2-H of **126** suggest the C3-H of **114** has been substituted. In addition, further evidence for the C-C bond formation came from the triplet at 4.31 ppm for the side chain CH of **126**, and two symmetric multiplets (3.67-3.63 ppm and 3.57-3.53 ppm respectively) for the CH₂ adjacent to the chiral centre of **126** also suggest **126** contains a side chain resulting from the ring-opening of **26**. Additionally, five signals for aliphatic carbons of **126** were observed in the its ¹³C NMR, suggesting **26** has successfully coupled with **126**. High-resolution mass spectrometry found the molecular weight of the isolated compound is 427.1469 g mol⁻¹, matching the expected structure of **126**. This result also support **126** was given *via* the C3-substitution reaction of **114** with **26**.

Other Lewis acids such as Ni(ClO₄)₂·6H₂O and Sc(OTf)₃ also behaved in an unsatisfactory manner, due to the incomplete conversion and the production of an inseparable and unidentified impurity (entries 2 and 3). Fortunately, a yield of 42% for the production of clean targeted compound was obtained from the reaction catalysed by PdCl₂(MeCN)₂, which had been effective for the aziridine **98** (entry 4). Next, to increase the conversion, ligands were then added to stabilise the Pd(II)-centre, however, 1,10-phenanthroline (phen) largely depressed the conversion to 16% due to the low solubility of Pd(II)-phen complex that *in situ*-formed as a yellow precipitate (entry 5). In contrast, the addition of 1,4-benzoquinone (BQ) increased the conversion to 73%, albeit with a moderate yield (59%) (entry 6). More BQ, up to 0.3 equivalents, gave an increase in the isolated yield to 61% (entry 7). The solvent effect was also investigated (entries 8-10). However, tetrahydrofuran (THF) and ether proved less efficient solvents giving a relatively messy ¹H NMR of the crude reaction mixture and low conversion respectively (entries 9 and 10). Finally, chloroform was selected as the optimum solvent as it gave the highest conversion and yield (entry 8). Interestingly, the dropwise addition of

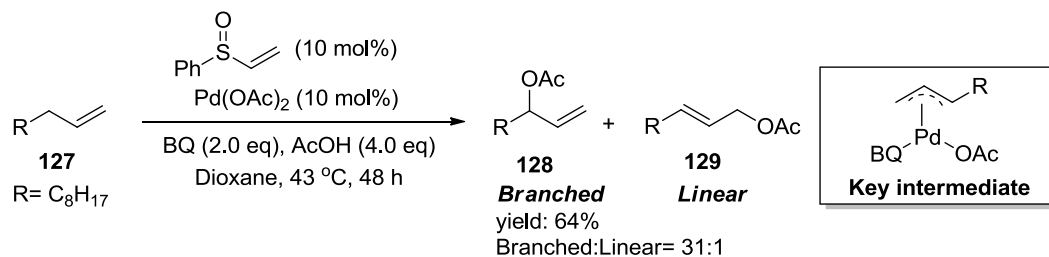
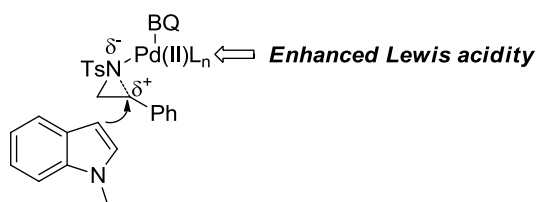
115 over 6 h, which was utilised in the table 2, significantly diminished the yield (entry 11). According to the promoting effect of BQ in the enantioselective allylic C-H oxidation of **127** found by the White group (Scheme 31),³⁹ the coordination of Lewis acids such as PdCl₂(MeCN)₂ to the carbonyl group of BQ could enhance the π acidity of the Pd(II)-centre,⁴⁰ thus accelerating the C-C bond formation when the S_N2 nucleophilic attack of indole towards benzylic position of aziridine possessing enhanced electronegativity.

Table 4. C3-substitution of *N*-methyldole **114** with 2-phenyl-1-tosylaziridine **26**



Entry	26:114	Lewis acid	Solvent	Ligand (mol%)	Conv.(Yield)%
1	1.0:1.5	Cu(OTf) ₂ ^c	DCE	N/A	100(73)
2	1.0:1.5	Ni(ClO ₄) ₂ .6H ₂ O ^c	DCE	N/A	28 ^b
3	1.0:1.5	Sc(OTf) ₃ ^c	DCE	N/A	100(40)
4	1.0:1.5	PdCl ₂ (MeCN) ₂	DCE	N/A	63(42)
5	1.0:1.5	PdCl ₂ (MeCN) ₂	DCE	Phen (12)	16 ^b
6	1.0:1.5	PdCl ₂ (MeCN) ₂	DCE	BQ (12)	73(59)
7	1.0:1.5	PdCl ₂ (MeCN) ₂	DCE	BQ (30)	75(61)
8	1.0:1.5	PdCl₂(MeCN)₂	CHCl₃	BQ(30)	99(77)
9	1.0:1.5	PdCl ₂ (MeCN) ₂	THF	BQ(30)	78 ^b
10	1.0:1.5	PdCl ₂ (MeCN) ₂	ether	BQ(30)	62 ^b
11^a	1.0:1.5	PdCl ₂ (MeCN) ₂	CHCl ₃	BQ(30)	90(63)

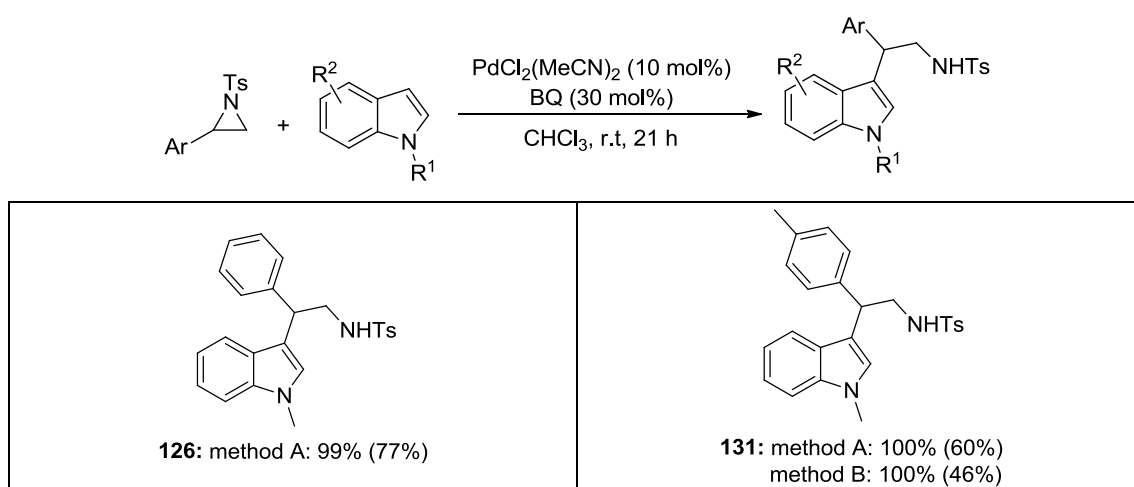
^a **26** was added dropwise over 6 h. ^b Conversion. ^c Inseparable impurities.

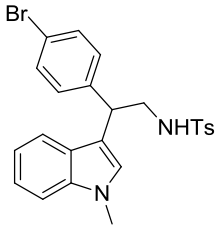
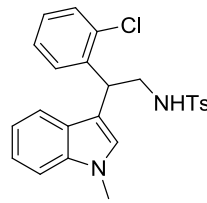
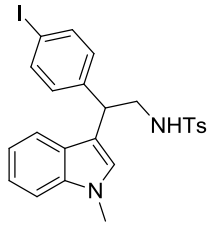
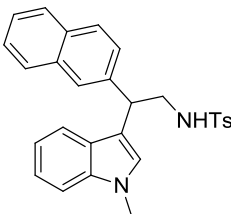
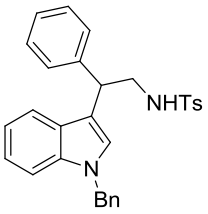
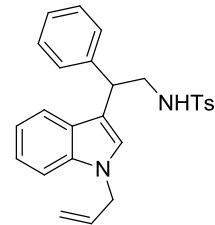
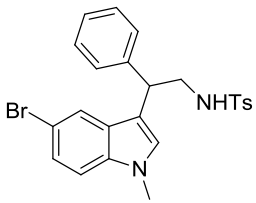
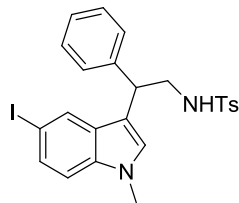
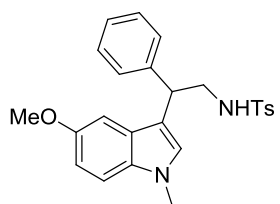
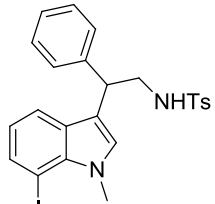
White's work**This work****Scheme 31:** Effect of benzoquinone (BQ) on Pd(II) catalytic intermediates

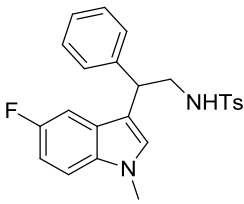
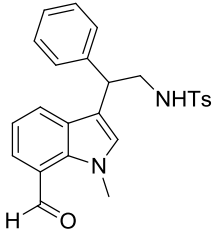
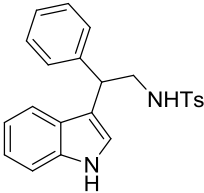
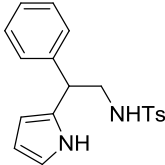
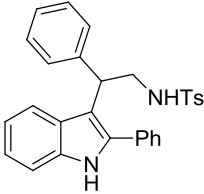
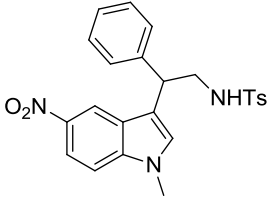
Using the optimum conditions, a variety of mono-substituted β -branched tryptamines were synthesised, demonstrating excellent functional group tolerance of the reaction conditions (method A, Table 5). All 2-aryl-*N*-tosylaziridines were synthesised by the method shown in Scheme 29. The aziridines bearing halogen atom on the *ortho*, *meta* and *para* positions of 2-aryl ring were first examined under the conditions, affording the corresponding products in moderate to good yields (product **132-134**). Moreover, alkyl and aryl groups such as methyl and naphthalene on the aziridine were also subjected to the reaction to furnish the corresponding β -branched tryptamines in good yields (products **131** and **135**). Different electron-rich indole derivatives were then examined. Thus, C-C bond formation was achieved with *N*-benzyl indole and *N*-allyl indole, and the corresponding compounds were synthesised in 60% and 86% yields respectively (products **136** and **137**). C5-substituted indoles, including those bearing a halogen atom or methoxy group at C5 position, gave the corresponding tryptamines in moderate to good yields under the conditions (products **138-140** and **142**). Indoles bearing a substituent at C7 position were also utilised under the conditions. Gratifyingly, the targeted compound was given in a good yield (76%) when 7-iodo-1-methyl indole was employed (product **141**). However, as a result of the reduced nucleophilicity caused by a C7 electron-withdrawing formyl group, a decreased yield (43%) was obtained for the desired product (product **143**). Furthermore, 1*H*-indole, which has been previously utilised as *N*-based nucleophile to synthesise *N*-alkylated indole derivatives with complete N1-chemoselectivity,⁴¹ reacted with

aziridine **26** to give a good yield (76%) of the C3-substituted product **144**. Absolute C3-selectivity was observed since the broad singlet (8.06 ppm) on the ^1H NMR of the crude reaction mixture demonstrates the conservation of N1 proton of **144** in the reaction, moreover, the presence of the singlet (6.97 ppm) for C2-H of indole moiety of the product **144** provides further evidence for the exclusive C3-substitution. Nevertheless, a much lower yield (15%) was observed with the expected C2-selectivity when 1*H*-pyrrole was used in the reaction as the conversion of phenylaziridine **26** was only 20%, and the rest of **26** and pyrrole remained unreacted (product **145**).⁴² Pleasingly, 1*H*-2-phenylindole then proved to be an effective substrate as the corresponding β -branched tryptamine **146** was given in a good yield (63%). Furthermore, as expected, exclusive C3-selectivity was obtained again since the broad singlet (8.31 ppm) associated with N1 proton of indole moiety on the ^1H NMR of the crude reaction mixture was conserved in the reaction (product **146**). No reaction observed with *N*-methyl-5-nitroindole, likely because its electron-deficiency causes low nucleophilicity. In addition, a variety of $\text{PdCl}_2(\text{MeCN})_2$ -catalysed reactions to synthesise tryptamines shown in Table 5 in the absence of BQ (method B) were carried out. In contrast to the BQ-involved reactions, conversions of almost all arylaziridines were considerably reduced without BQ, except for tolylaziridine **517**. Nevertheless, more significant hydrolysis of tolylaziridine **517** occurred without BQ, leading to a sharp drop in the yield of product **131**. These results highlight the promoting effect of BQ for this reaction.

Table 5. Substrate scope for the ring-opening of 2-aryl-*N*-tosylaziridines with indoles



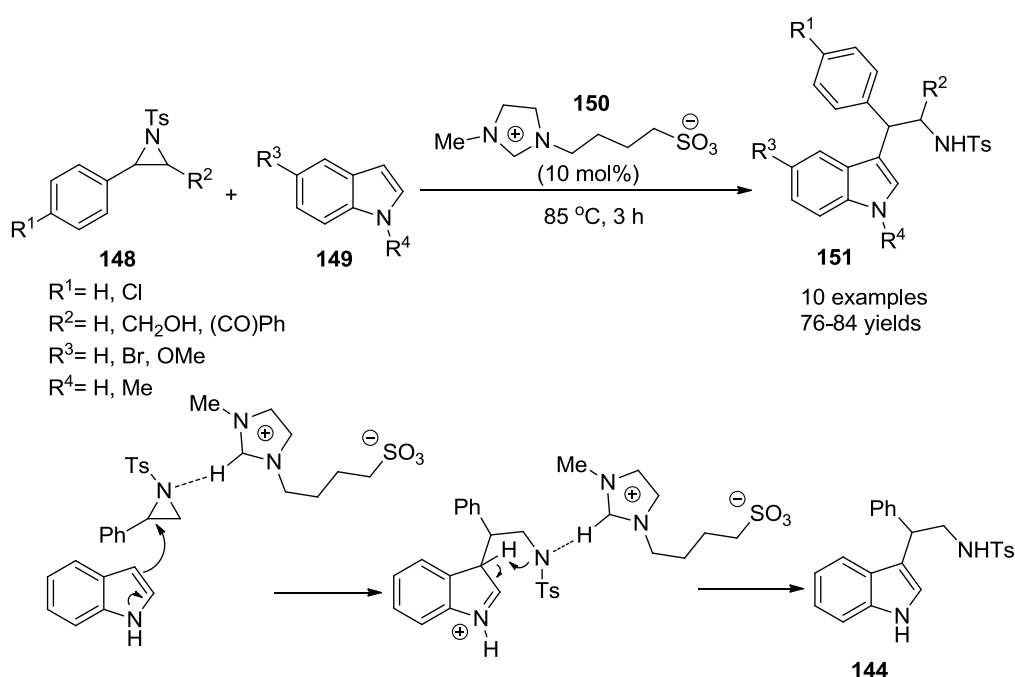
 <p>132: method A: 82% (63%) method B: 32%</p>	 <p>133: method A: 65% (57%) method B: 24%</p>
 <p>134: method A: 60% (59%) method B: 35%</p>	 <p>135: method A: 87% (78%) method B: 51%</p>
 <p>136: method A: 78% (60%) method B: 50%</p>	 <p>137: method A: 96% (86%)^a method B: 56%</p>
 <p>138: method A: 100% (86%) method B: 28%</p>	 <p>139: method A: 74% (72%) method B: 28%</p>
 <p>140: method A: 75% (50%) method B: 22%</p>	 <p>141: method A: 100% (76%) method B: 41%</p>

 <p>142: method A: 100% (60%) method B: 75%</p>	 <p>143: method A: 60% (43%)^b method B: 35%</p>
 <p>144: method A: 100% (76%) method B: 66%</p>	 <p>145: method A: 25% (15%) method B: 10%</p>
 <p>146: method A: 80% (63%) method B: 51%</p>	 <p>147: N.R.</p>

^a the reaction was carried out in DCM. ^b 17% inseparable *p*-benzoquinone accompanied product. ^c Method A: PdCl₂(MeCN)₂ (10 mol%), BQ (30 mol%), CHCl₃ (0.1M), 21 h, r.t. Method B: PdCl₂(MeCN)₂ (10 mol%), CHCl₃ (0.1M), 21 h, r.t. ^d Method A/B: conversion (isolated yield).

The examples listed in the introduction demonstrate that the aziridine is highly versatile building block in organic synthesis due to their susceptibility to nucleophilic attack after C-N bond cleavage. The ring-opening of *N*-activated aziridines with electron-rich heteroarenes such as indole keeps drawing attention amongst synthetic chemists, moreover, the corresponding products resulting from these reactions, such as tryptamine derivatives are synthetically important in pharmacological chemistry.⁴³ Under this context, it is not surprising to find one paper published for exploring a general and economic method to regioselectively open the aziridine ring by indole derivatives under the mild conditions when the manuscript associated with the work in this thesis was under review. Majee and co-workers developed a metal-free regioselective ring-opening of aziridines **148** with various indoles **149** in the presence of a non-volatile and generally nonhazardous zwitterionic-type

salt **150** under the solvent-free conditions. The author considered that the C-N bond of aziridine moiety is activated through hydrogen bond formed between C2-H of the imidazolium cation and the nitrogen atom of the aziridine, and all β -substituted typtamines **151** were synthesised in good to excellent yields with exclusive C3-regioselectivities (Scheme 32).⁴⁴ However, no reactions were observed when alkylaziridines involved in the reaction. Mechanistically, the aziridine **26** is activated by H-bonding between the C2-H of the imidazolium cation and the nitrogen atom of the aziridine, and indole then acts as a nucleophile to attack the aziridine's benzylic position with an S_N2 manner to give the ring-opening final compound **144**.

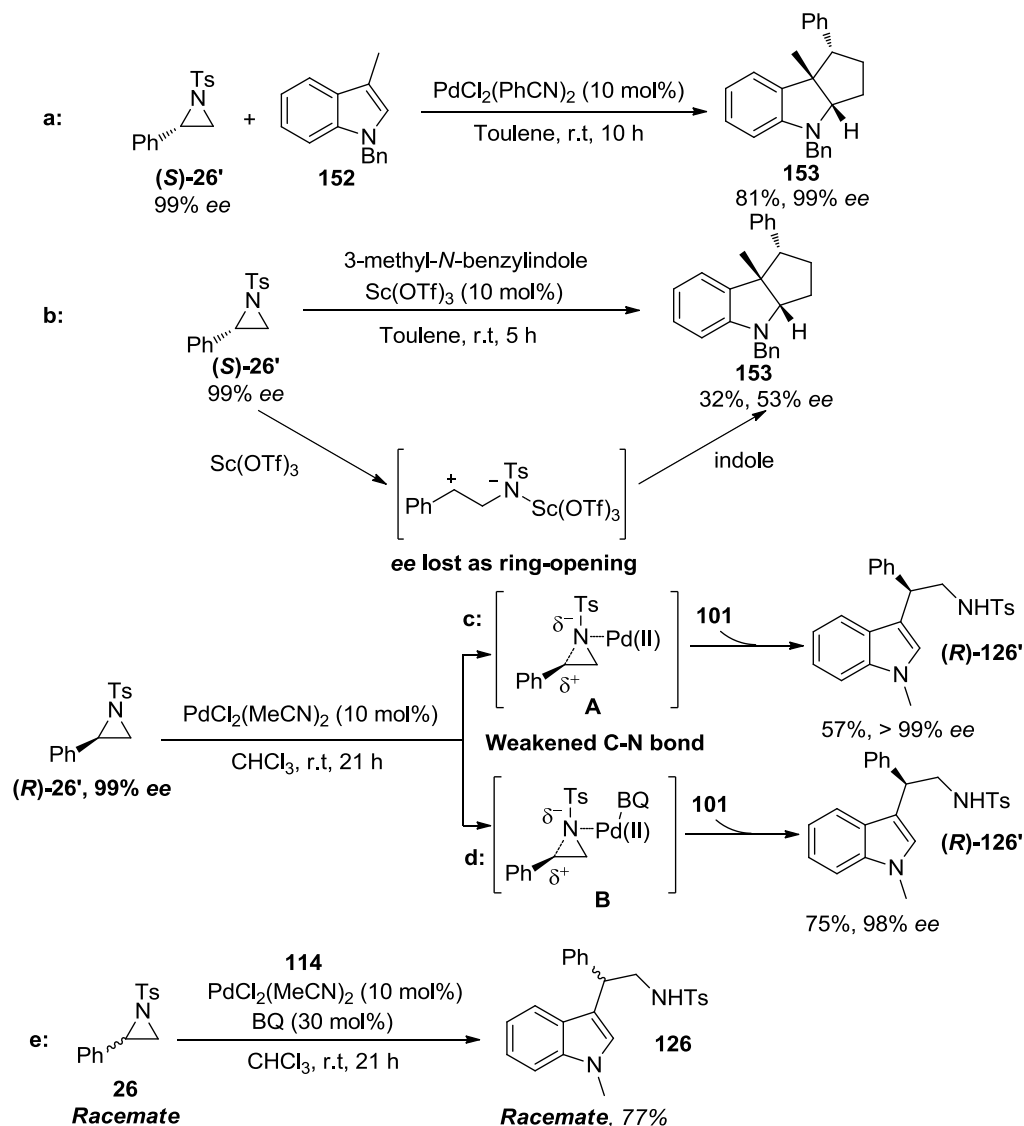


Scheme 32: Organocatalysis by an aprotic imidazolium zwitterion: regioselective ring-opening of aziridines **148**

With regard to the mechanism of the reaction demonstrated in the table 4, it was proposed that the aziridine is first activated by coordination of the Lewis acidic Pd(II)-catalyst. The Zhao group (Scheme 25) provided the results in support of this proposal.⁴⁵ The Sc(OTf)₃-catalysed [3+2] cycloaddition of *N*-benzyl-3-methylindole **152** with the enantioenriched aziridine (*S*)-**26'** only provided a considerably reduced enantiopurity of the product in contrast to a well-retained enantiopurity of the pyrroloindoline **153** produced with PdCl₂(PhCN)₂, implying the C-N bond may be partially cleaved with relatively strong Lewis acid-Sc(OTf)₃ to cause the racemisation of (*S*)-**26'** by producing zwitterionic 1,3-dipole, but the C-N bond of (*S*)-**26'** can only be polarised with PdCl₂(PhCN)₂ as it possesses a lower Lewis acidity (Scheme 32a and b). The resultant polarised C-N

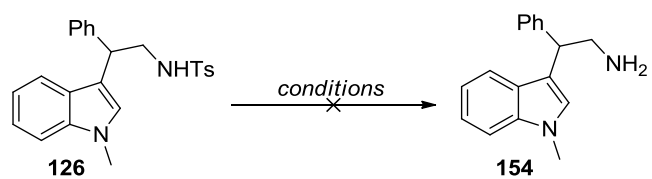
bond therefore undergoes S_N2 nucleophilic attack of indole **92** to the more-substituted position, ensuring the conservation of enantiopurity of the starting phenylaziridine (**S**)-**26'**. To study the stereochemical course of the reaction developed in this project, enantiopure phenylaziridine (**R**)-**26'**, was synthesised from commercially available (*R*)-2-phenyl glycinol (*R*, 99% *ee*).⁴⁶ This enantiopure aziridine was treated with indole **114** in the presence of $\text{PdCl}_2(\text{MeCN})_2$ with and without BQ respectively. The enantioselective HPLC analysis then indicated both reactions gave the corresponding products (**R**)-**126'** with an excellent retention of enantiopurity (99% and 98% *ee* respectively). A standard reaction was then performed with racemic **26**. Chiral HPLC analysis indicated a racemate of **126** was produced in the reaction (Scheme 32e).

Thus, it is reasonable to conclude that while BQ may increase the Lewis-acidity of the Pd(II)-centre, it is likely that its presence does not change the mechanism to a ring-opening process. Based on these reports and results, the key intermediates for both reactions were proposed (Scheme 32c and d). In the case of BQ-free reaction, as suggested by the Zhao group (Scheme 25), the NTs group first coordinates to the Pd(II)-centre, where the resulting intermediate **A** only has the polarised C-N bond (Scheme 32c). The enantiopurity is therefore retained as the polarised C-N bond in the intermediate **A** induces an S_N2 -type nucleophilic attack of indole **152** at the more substituted position of the aziridine. In addition, in the case of the BQ-involved reaction (Scheme 32d), as stated above in Scheme 47, the coordination of BQ to the Pd(II)-centre weakens the partially cleaved C-N bond of aziridine (**R**)-**26'** by acting as a π -acidic ligand to increase the overall Lewis-acidity of the Pd(II)-centre, causing enhanced susceptibility of the intermediate **B** towards the S_N2 nucleophilic attack of indole **98** hence the BQ-involved reaction leads to a higher yield. Furthermore, as the further weakened C-N bond of aziridine (**R**)-**26'** is still not completely broken with the enhanced Lewis-acidity of the BQ-Pd(II)-catalyst, therefore, the excellent enantiopurity introduced from (**R**)-**26'** is well-retained in the product (**R**)-**126'** for the same reason stated in Scheme 32a and b. This also suggests that BQ could be potentially used as an additive for improving other enantioselective Lewis acids-catalysed reactions by its coordinating effect. Another possibility to explain the beneficial effect of the BQ additive is that the Pd(II)-catalyst is undergoing deactivation by reduction under the reaction conditions to Pd(0) and aggregation to Pd-black, which is observed in reactions where the BQ is absent. The BQ then may act as a ligand to stabilise Pd(0) so that it can be reoxidised before forming Pd black.



Scheme 32: The Zhao group's enantiopurity study **a** and **b** and the corresponding enantiopurity retention study for our reaction

Next, the detosylation of the products was investigated. The detosylation of **126** under the different conditions that have been successfully applied to detosylate pyrroloindolines and various tosylamines was performed (Scheme 33),⁴⁷ however, only **126** was recovered from all crude reaction mixtures even if 100 equivalents of Mg was added in the presence of NH_4Cl under sonication (Scheme 33c). Additionally, **126** was also inert to the cleavage conditions using sodium naphthalene anion radical in THF solution (Scheme 3d).⁴⁸



a: SmI_2 (0.04 M in THF), THF, 0 °C, o/n, N_2

b: Mg (10.0 eq), MeOH, air,), 3 h

c: Mg (100 eq), NH_4Cl (100 eq), MeOH, air,), 4 h

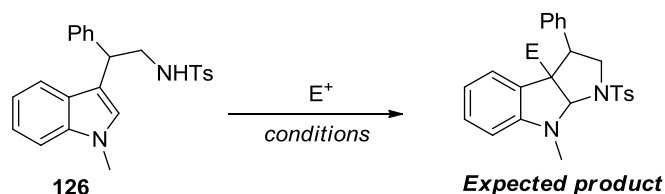
d: Na (1.0 eq), Naphthalene (1.1 eq), THF, N_2 , -78 °C, 30 mins

Scheme 33: Attempts to detosylate the **126**

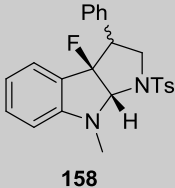
Synthesis of Pyrroloindolines by the Ring-Closure of Tryptamine Derivatives

The ring-closure of β -substituted tryptamines in order to obtain C3-functionalised pyrroloindolines (Table 6) was the aim in the next stage of research. Inspired by the Reisman group's work (Scheme 18), Cu(II)-catalyst systems were first used to couple with diaryliodonium salt (entries 2 and 3), however, no reaction occurred with either $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ or $\text{Cu}(\text{OTf})_2$. It can be rationalised on the basis of mechanism proposed by Reisman and co-workers (Figure 3). The expected key intermediate **109** resulting from the nucleophilic attack of indole may not be favoured due to the great steric hindrance between Cu(III) centre and β -phenyl group.

Table 6: Attempted ring-closure reactions of β -substituted tryptamine **126**



Entry	Conditions	Expected product	Yield
1	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (10 mol%), 4Å MS, DCM, r.t $[\text{Mes-I-Ph}]^+\text{BF}_4^-$	 155	N/R
2	$\text{Cu}(\text{OTf})_2$ (10 mol%), 4Å MS, DCM, r.t $[\text{Mes-I-Ph}]^+\text{BF}_4^-$	 156	N/R
3	cyanuric chloride (10 mol%), benzaldehyde, DMSO, 100 °C	 157	N/R
4	$\text{BF}_3 \cdot \text{OEt}_2$ (3.0 eq), MgSO_4 , benzaldehyde, DCE,	 157	Trace conversion

	60 °C		
5	NaHCO₃ (1.5 eq), NFSI, MeCN, r.t	 158	43% (<i>trans</i>:<i>cis</i>= 2.5:1)

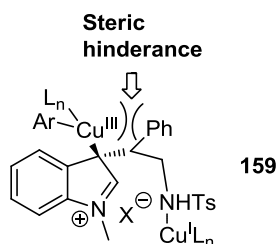


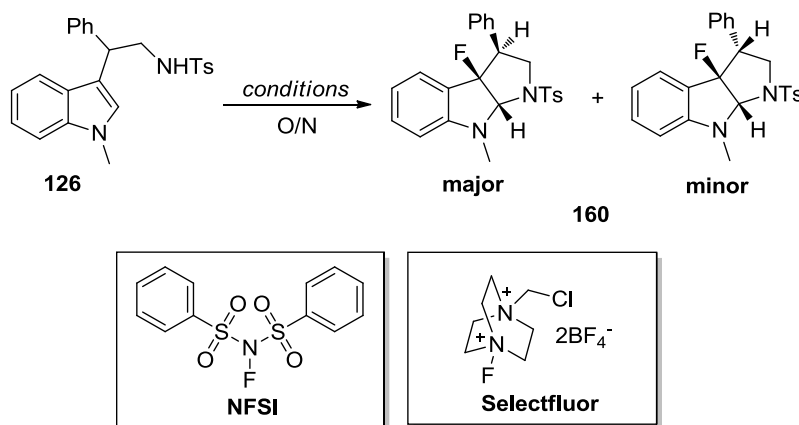
Figure 3: Key intermediate **159** of expected Cu(II)-catalysed ring-closure reaction

The formation of 6-membered ring system **157** using the Pictet–Spengler reaction was attempted (entries 3 and 4).⁴⁹ Cyanuric chloride was previously utilised as an acid source,⁵⁰ so it was envisioned that this reagent could promote the coupling between **126** and benzaldehyde, however, no reaction occurred under this condition (entry 3). Subsequently, a stoichiometric amount of Lewis acid-BF₃·OEt₂ was added to the reaction but only trace conversion was observed (entry 4).

Subsequently, inspired by the halogenative ring closure reported by Wang and co-workers⁶⁴ (Scheme 20), *N*-fluorobenzenesulfonimide (NFSI) was utilised as the fluorinating agent to construct the pyrroloindoline using β -substituted tryptamine **126** in the presence of NaHCO₃. Fortunately, although the reaction gave a relative messy ¹H NMR of the crude reaction mixture, a C3a-fluorinated pyrroloindoline **160** was isolated in a moderate yield (43%) with a moderate diastereomeric ratio of 2.5:1. The assigned product was evidenced by the absence of singlet (6.76 ppm) corresponding to the C2 proton of **126** in the ¹H NMR of the reaction mixture, moreover, the apparent triplet (4.38 ppm) associated with the amine proton of **126** cannot be observed, suggesting the occurrence of ring-closure. Furthermore, the ring-closure reaction of **126** with F⁺ can also be evidenced by a new doublet at 5.65 ppm (major isomer) corresponding to the C2a proton of the C3-fluorinated pyrroloindoline **160**. The ¹³C NMR of **160** shows six aliphatic carbon signals, and this is in line with the number of aliphatic carbons in the expected structure of **160**. Moreover, the signal of C8a proton was found at 89.1 ppm as a doublet in ¹³C NMR due to fluorine-carbon coupling. In addition, the molecular weight (445.1363 g mol⁻¹) that was given by high-resolution mass spectrometry also

supports the NMR-determined structure of **160**. Subsequently, attempts to optimise the reaction conditions were carried out (Table 7).

Table 7: Optimisation on synthesis of C3-fluorinated pyrroloindoline **160**

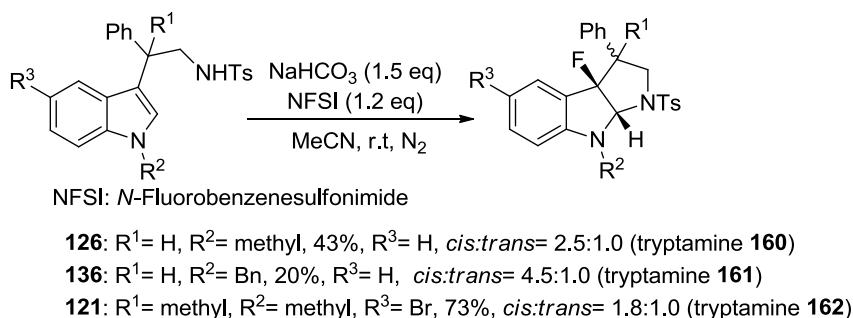


Entry	Base	Solvent	Temperature	F ⁺ source	Yield (%)	Ratio of diastereoisomers (Major:Minor)
1	NaHCO ₃	MeCN	r.t	NFSI	43	2.5:1.0
2	NaHCO ₃	MeCN ^a	r.t	NFSI	45	2.3:1.0
3	NaHCO ₃	CHCl ₃	r.t	NFSI	27	2.2:1.0
4	NaHCO ₃	DCE	r.t	NFSI	37	2.1:1.0
5	NaHCO ₃	ether	r.t	NFSI	28	2.0:1.0
6	NaHCO ₃	DCM	r.t	NFSI	27	2.1:1.0
7	NaHCO ₃	PhCN	r.t	NFSI	34	2.1:1.0
8	K ₂ HPO ₄	MeCN	r.t	NFSI	36	2.0:1.0
9	NaHCO ₃	MeCN	-20 °C	NFSI	39	2.5:1.0
10^b	NaHCO ₃	MeCN	r.t	Selectfluor	48	2.1:1.0

^a Anhydrous MeCN and 3Å MS ^b The reaction was completed after 3 h.

Performing the reaction in anhydrous MeCN was found to only give slightly increased yield with a reduced *trans*-selectivity (entry 2). Other solvents were then screened, however, none of them gave a significantly improved result (entries 3-7). K₂HPO₄ was also used as a different base, nevertheless, a reduced yield plus a diminished selectivity were observed after the reaction was completed (entry 8).

The next reaction was carried out at $-20\text{ }^{\circ}\text{C}$, but it was found to give a slightly decreased yield although the ratio of major:minor diastereoisomer remained unchanged (entry 9). In addition, a new fluorinating agent, selectfluor, was able to give a faster reaction rate as **126** was completely consumed after the reaction mixture was stirred for only 3 h at ambient temperature, and this reaction gave a moderate yield (48%) with a ratio of 2.3:1.0 (major: minor isomer) (entry 10).



Scheme 35: C3-fluorination of β -substituted tryptamines

Therefore, the conditions consisting of NaHCO_3 (1.5 eq), NFSI (1.2 eq) in MeCN at room temperature were the best obtained within the time constraints. Two different β -substituted tryptamines were then subject to the reaction (Scheme 35). *N*-Benzyl- β -phenyl tryptamine **136** gave a good selectivity, albeit with a very messy crude reaction mixture and relatively low yield (product **161**). The diastereoselectivity of entire reaction was then tentatively assigned as *cis* (*cis:trans* = 2.5:1.0, Scheme 35) since both NOESY-1D and NOESY-2D spectra of major isomer of **161** did not demonstrate the through-space correlation between H_a and H_b (Figure 4 and Appendix). Subsequently, a good yield (73%) was obtained with *N*-methyl- β -phenyl tryptamine **121**, simultaneously, but a relatively low ratio of *cis:trans* isomer was observed (product **162**).

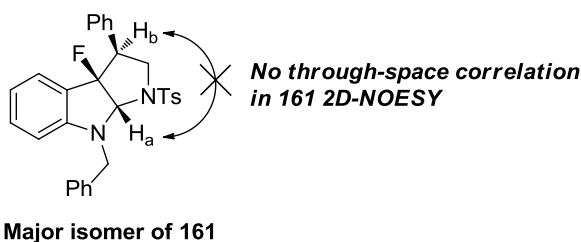
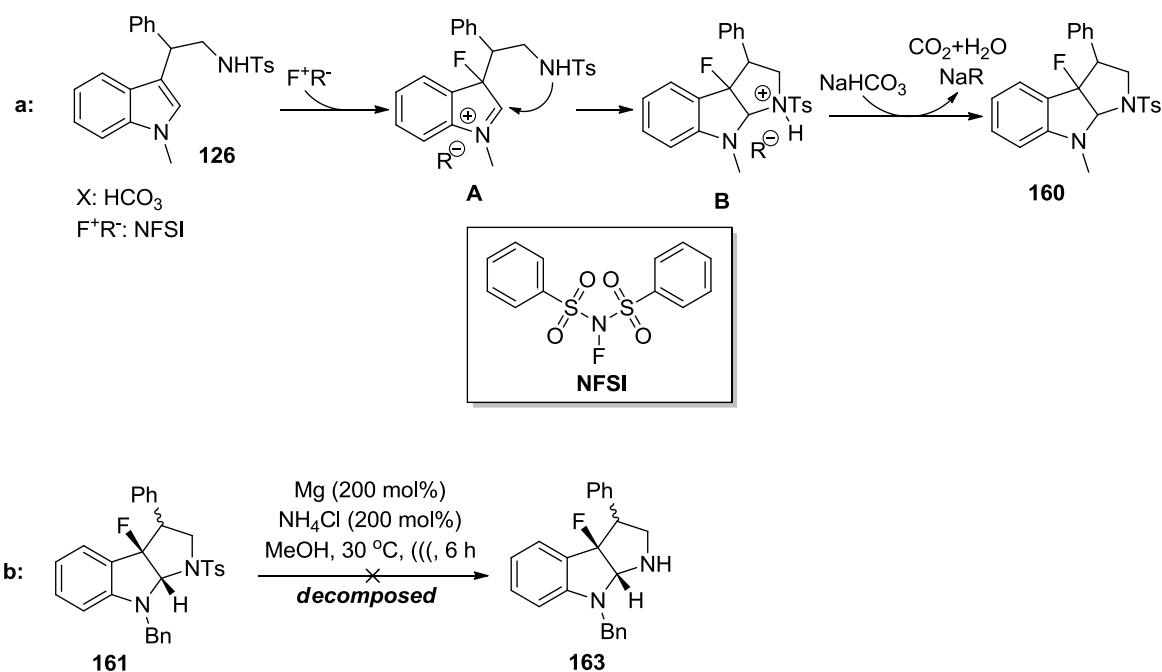


Figure 4: NOESY-1D and NOESY-2D results of major isomer of **161**

A plausible mechanism was then proposed for the metal-free synthesis of C3a-fluorinated

pyrroloindoline (Scheme 36a). Initially, the indole moiety acts as the nucleophile to trap electrophilic F^+ from the fluorinating agent (NFSI). The resulting iminium intermediate **A** undergoes the ring-closure to give the aminium intermediate **B**, which is then deprotonated by $NaHCO_3$ to yield the final product **160**.

Finally, the C3a-fluorinated pyrroloindoline **161** was subjected to the conditions that were successfully applied to detosylate the C3-methyl pyrroloindoline **102** (Scheme 28). Unfortunately, only decomposition of **161** was observed after the reaction mixture was sonicated for 6 h (Scheme 36b).



Scheme 36: Proposed mechanism for synthesis of C3-fluorinated pyrroloindoline **160** and the detosylation of

161

Summary

In summary, a $\text{PdCl}_2(\text{MeCN})_2$ -catalysed C3-selective Friedel–Crafts reaction of indole derivatives with aziridines has been developed. A series of β -substituted tryptamine derivatives were prepared in moderate to high yields, especially some products containing an all-carbon quaternary centre were synthesised from the disubstituted aziridine **98**. Furthermore, it was found that addition of 1,4-benzoquinone (BQ) is beneficial to the reaction with the less reactive 2-aryl-*N*-Ts aziridines. According to BQ chemistry proposed by the White group (Scheme 31), BQ may act as a π -acid, increasing the Lewis acidity of the Pd(II)-centre to further weaken the C-N bond of 2-aryl-*N*-Ts aziridines. Alternatively, it could play a role in preventing catalyst deactivation through the formation of Pd-black. Importantly, the chiral HPLC analysis indicated the addition of BQ did not significantly diminish the enantiopurity of the product **126** obtained from the enantiopure phenylaziridine (**R**)-**26'**, highlighting the stereospecificity of this reaction. This also suggests that BQ could also be potentially used as an additive for improving other Lewis acid-catalysed reactions by its coordinating effect, without degrading the enantiopurity of products (Scheme 32). In addition to the C3-substitution, a Pd(II)-catalysed formal [3+2] annulations of the *N*-activated aziridine **26** with 1,3-dimethylindole **101**. The *trans* domain C3-phenyl pyrroloindoline **102** was synthesised from *N*-tosyl phenylaziridine **26** in a good yield with a relatively high diastereoselectivity in the presence of bench stable $\text{PdCl}_2(\text{MeCN})_2$. Moreover, a more versatile vinyl moiety was introduced to the resulting pyrroloindoline with excellent *trans*-selectivity, albeit with a relatively low yield. Furthermore, the ring-closure of the corresponding β -substituted tryptamines with *N*-fluorobenzenesulfonimide (NFSI) to construct a number of C3a-fluorinated pyrroloindolines under metal-free conditions was also preliminarily investigated, and three different C3a-fluorinated pyrroloindolines were synthesised in synthetically acceptable to good yields with moderate *trans*-selectivities.

Future Plans

Ir-Catalysed Intramolecular Allylation of Tryptamine Derivatives

As well as further investigating the electrophilic ring-closure of β -branched tryptamines to optimized yield and diastereoselectivity, other methods to utilise these structures can be envisaged. The natural products incorporating the spiroindoline or spiroindolenine unit has drawn increasing attention in pharmacological area. For example, koumine, which was a monomer of gelsemium alkaloids, has been investigated due to its capacity to relieve neuropathic pain (Figure 5).⁵¹ Many efficient synthetic protocols have been developed for the construction of this key structure.

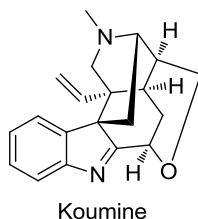
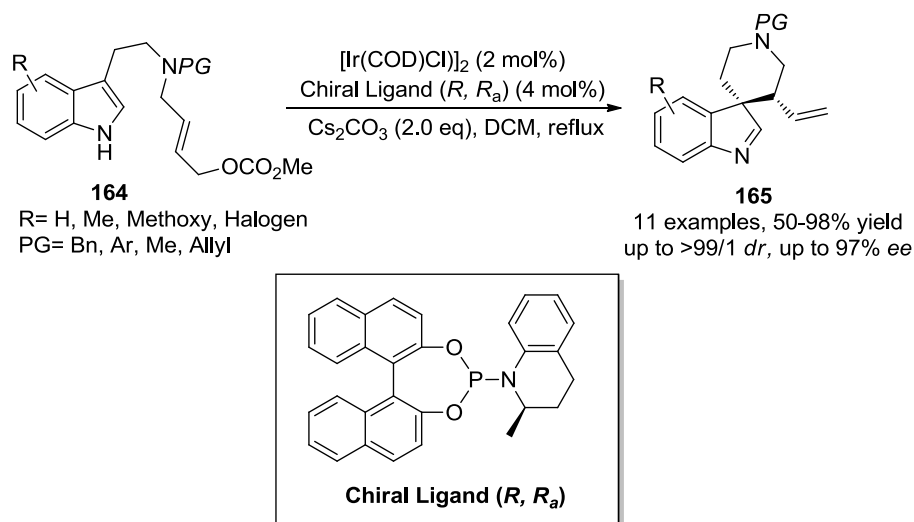


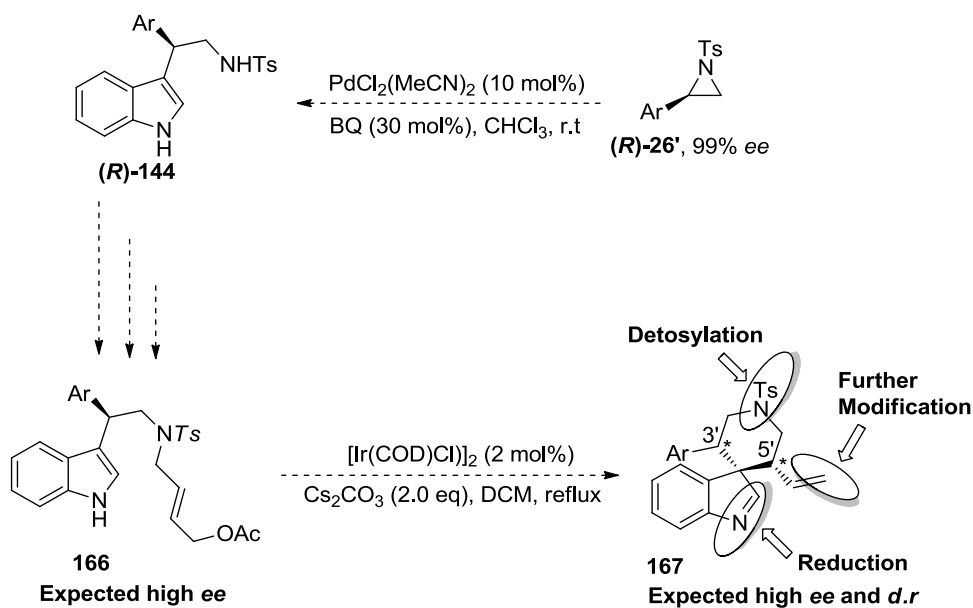
Figure 5: Koumine

A typical example for the Ir-catalysed enantioselective construction of spiroindolenines **165** is provided by the You group in 2010 (Scheme 37).⁵² This reaction was carried out in the presence of 2-methyl-1,2,3,4-tetrahydroquinoline-derived phosphoramidite ligand, and the spiroindolenine derivatives **165** were provided in excellent yields with up to >99/1 *d.r* and 97% *ee* via the Ir-catalysed intramolecular C3 allylic alkylation of tryptamine derivatives **164** using chiral phosphoramidite ligand.



Scheme 37: Enantioselective construction of spiroindolenines **165** by Ir-Catalysed allylic alkylation reactions

The analogue synthesis of the spiroindolenine **167** could be developed using the substrate **166** via an stereospecific dearomatisation/migration process based on Scheme 37. It can be seen from the expected compound **167** that the complexity of the molecule is ramped up as an extra phenyl group is introduced at C3a-position (Scheme 37). By utilising the enantiopure starting material **166**, an enantio-enriched compound **167** possessing two stereogenic centres could potentially be synthesised in a high diastereoselectivity without the need for a chiral ligand (Scheme 38). Moreover, the expected compound **167** could be divergently manipulated, such as detosylation on *N*-tosyl group, reduction of the imine moiety and modifications on the versatile vinyl group, providing multiple accesses to some potentially bioactive highly functionalised products. A compound **168** possessing a similar structure of **167** has been identified as a neuropeptide Y receptor (Figure 6).⁵³ Therefore, **167** with substituents at positions 3' and 5' would potentially be useful for analogue synthesis of **168**.



Scheme 38: Expected reaction with new substrate 166

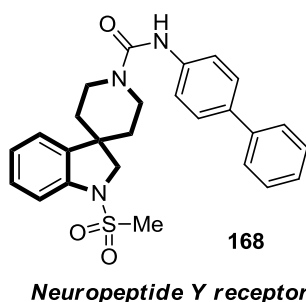


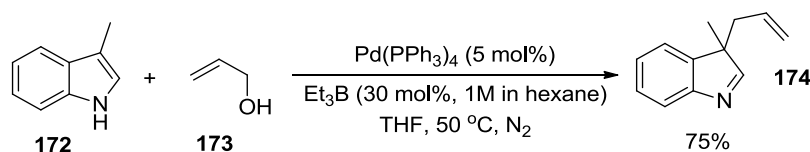
Figure 6: Example for potential medicinal application of 167 in Scheme 38

Enantiomerically pure allylic carbonate **166** containing an extra phenyl group at the β position could be synthesised from the enantiopure *N*-tosyl phenylaziridine **(R)-26'** and **171** (Scheme 39). This is a sequential strategy, including the reduction of ester **169** to alcohol **170** using DIBAL-H, acetylation of **170** and the S_N2 nucleophilic attack of enantioenriched **144** to **171**.

The [3+2] Annulations of Vinylaziridines with Electron-Rich Indoles

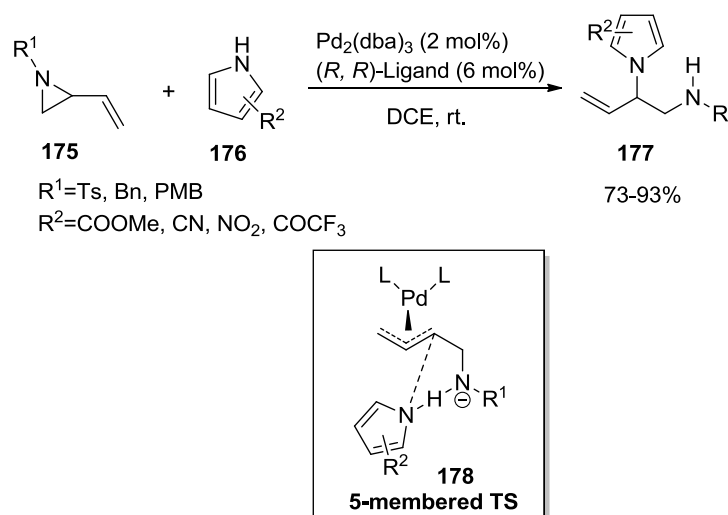
The Wang group and the Chai group demonstrated the Lewis acid-catalysed [3+2] cycloaddition of *N*-activated phenylaziridine (Schemes 24-25). It was found that the reaction scope included in their works were limited to arylaziridines. The yield was degraded considerably in our reaction when the more versatile vinylaziridine **103** was utilised in the [3+2] cycloaddition reaction developed in Scheme 26. Hence, it is beneficial to develop a new route to obtain pyrroloindolines containing a vinyl group at C3-position in an elevated yield with a high diastereoselectivity.

It was first noticed that the Tamaru group found the Pd-Et₃B system works efficiently for the C3 selective allylation of indoles and provides 3-allylindoles in excellent yields. Et₃B smoothly promotes the formation of electrophilic η^3 allyl-Pd(II) complex, which then accepts the subsequent nucleophilic attack from indole **172** to produce 3-butyl-3-methyl-3*H*-indole **174** in an excellent yield with an exclusive C3-selectivity (Scheme 40).⁵⁴



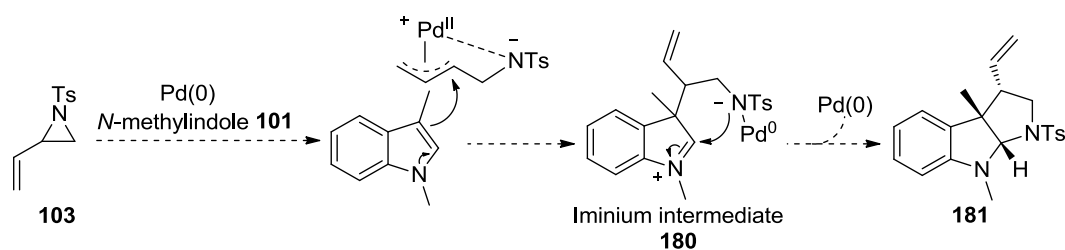
Scheme 40: C3-allylation of indole

In addition, the Trost group indicated that vinylaziridines **175** could be considered as an analogue of allyl acetate to accept *N*-nucleophile (Scheme 41). In this reaction, a 5-membered transition state **178** caused by the allyl-Pd(II) complex and electronic abstraction between pyrrole *N*-*H* **176** and *in situ*-generated amide is proposed as the key intermediate for the synthesis of diamine compounds **177**. This example demonstrates the formation of allyl-Pd(II) complex could be achieved by the oxidative addition of vinylaziridines **175** to the Pd(0)-catalyst system.



Scheme 41: *N*-based allylation with vinyl aziridine and catalysis of Pd(0)

Thus, inspired by these two examples, it was envisioned that [3+2] annulations of vinylaziridine **103** could be realised *via* an electrophilic allyl-Pd(II) complex. A plausible pathway was proposed for the designed reaction (Scheme 42). The electrophilic stabilised the allyl-Pd(II) complex initially formed from vinylaziridine **103** and the Pd(0) systems such as $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$, and then 1,3-dimethylindole **101** could act as a nucleophile to attack the sterically hindered position of the allyl-Pd(II) complex. The resultant iminium intermediate **180**, which has structural similarity with the product demonstrated in Scheme 40, subsequently undergoes ring-closure to release the pyrroloindoline **181** and regenerate the Pd(0)-catalyst.



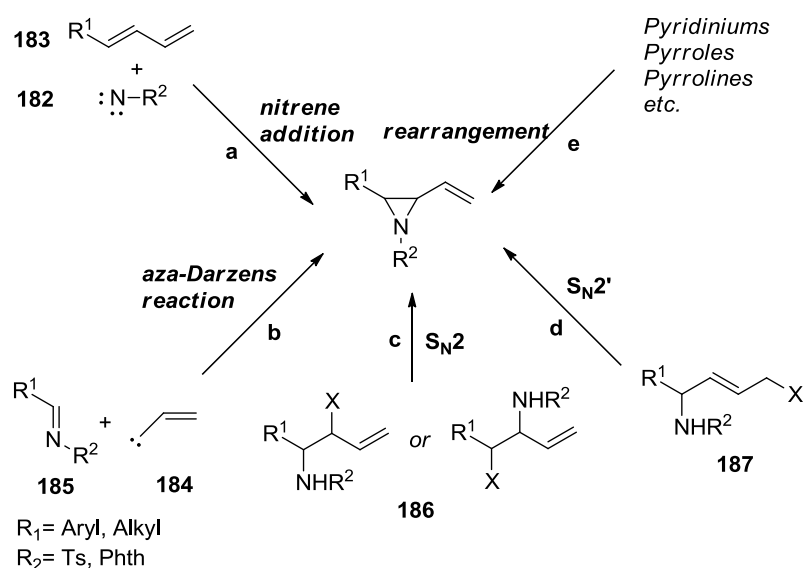
Scheme 42: *Designed reaction pathway for [3+2] annulations of vinylaziridine 103*

Chapter 2. Unusual (Z)-Selective Palladium(II)-Catalysed Addition of Aryl Boronic Acids to Vinylaziridines

Introduction

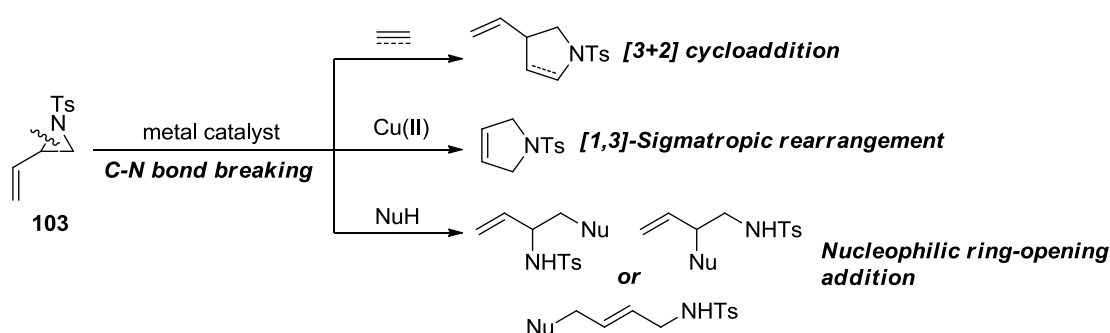
The reactivity of three-membered strained-ring systems, specifically *N*-tosyl aziridines, has been discussed in the chapter 1. As a versatile functional group that can be found in many drug molecules,⁵⁵ the vinyl group has exhibited its broad application in the oxidative cleavage,⁵⁶ olefin metathesis⁵⁷ and addition reactions⁵⁸. Therefore, the palladium-catalysed reactivity of vinyl aziridines, a particularly interesting sub-class of aziridine, was investigated in this chapter.⁵⁹

Generally, vinylaziridines can be synthesised by the following methods (Scheme 43),⁶⁰ including (1) reaction of a nitrene **182** with a conjugated diene **183** (path a);⁶¹ (2) reaction of an allylic carbene **184** with iminiums **185** via aza-Darzens-type reactions (path b);⁶² (3) Intramolecular S_N2 displacement of vinylated 1,2-amino alcohol derivatives **186** (path c);⁶³ (4) Intramolecular S_N2' reaction of 4-aminobut-2-en-1-ol derivatives **187** (path d) and;⁶⁴ (5) rearrangement reactions of pyridinium salts, pyrroles, and pyrrolines (path e).⁶⁵ The 1,2-addition of a nitrene equivalent to a conjugated diene was utilised in this research to synthesise the vinylaziridine **103** (details in Results and Discussion).



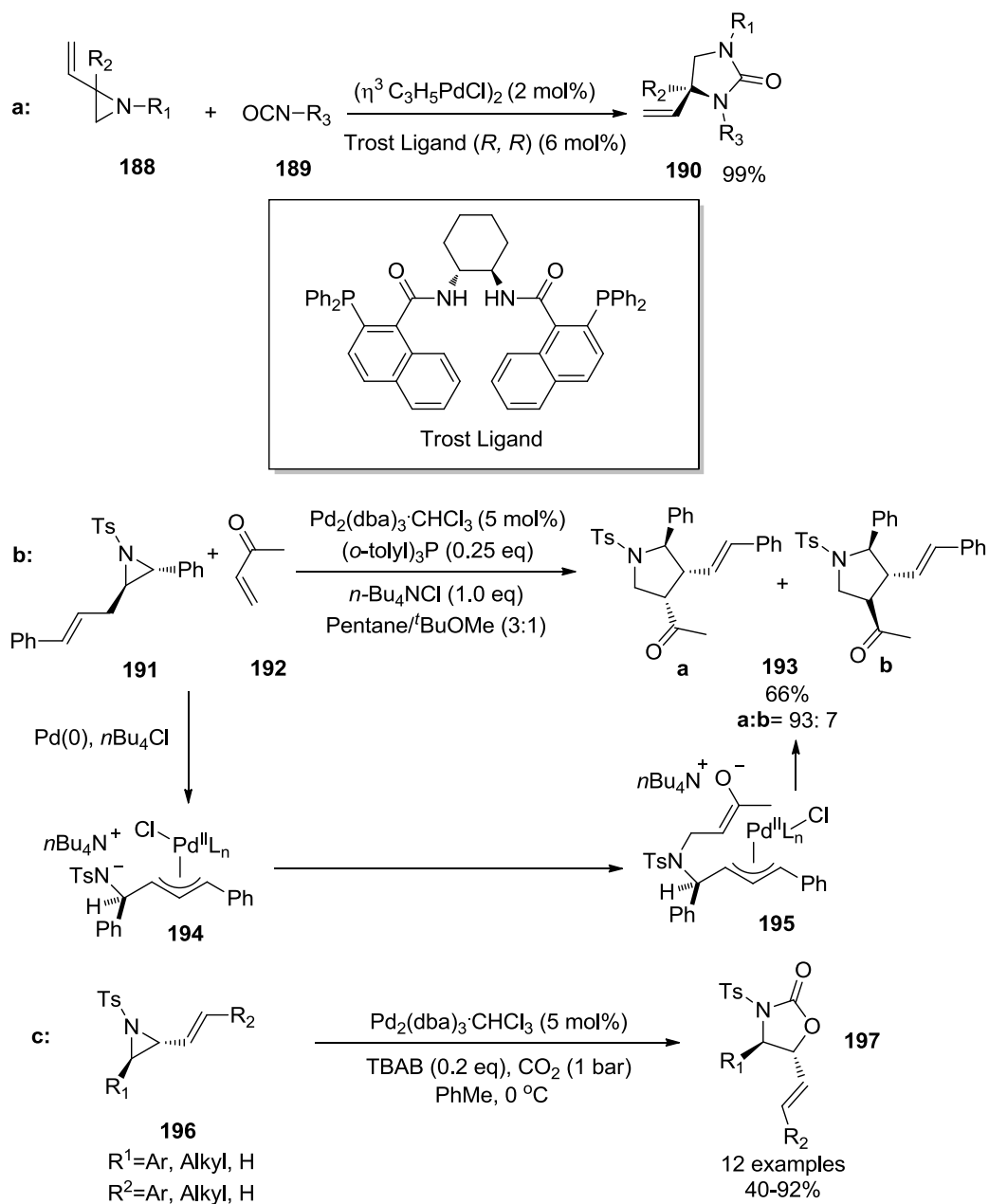
Scheme 43: General synthetic routes to vinylaziridines

Vinylaziridines are bifunctional heterocycles that undergo a range of metal-catalysed synthetic transformations by releasing its ring strain to achieve a ring-opening reaction, such as ring-opening additions/cyclisations and rearrangements *via* the C-N bond breaking with a broad range of substrates to afford heterocyclic or acyclic compounds (Scheme 44).⁶⁶ For example, a [3+2] annulation of vinylaziridine **103** with 1,3-dimethylindole **101** has been successfully demonstrated in chapter 1, and the ring-opening addition of vinylaziridine **103** was studied in this chapter.



Scheme 44: General reactivities of vinylaziridine **103**

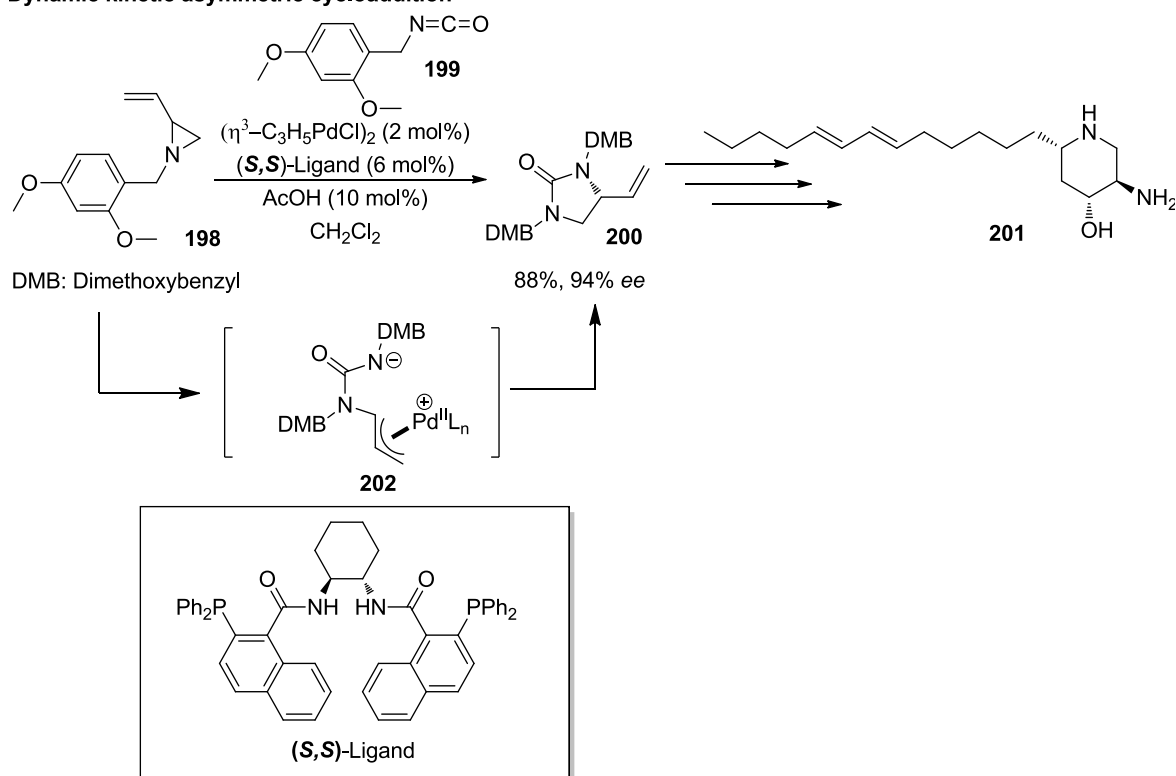
The Trost group developed a dynamic kinetic asymmetric cycloaddition of isocyanates **189** to vinylaziridines **188** (Scheme 45a).⁶⁷ Also, a diastereoselective palladium-mediated annulation of vinylaziridines **191** with Michael-acceptors **192** was reported in 2011 by the Aggarwal (Scheme 45b).⁶⁸ The additive *n*Bu₄Cl was required to form an ion pair with the amide anion of allyl-Pd(II) intermediate **194**, enhancing the nucleophilicity of the amide anion of **194** to capture the Michael-acceptors **192**. The Aggarwal group also reported a mild palladium-catalysed regioselective and diastereoselective ring-opening cyclisation of vinylaziridines **196** under an atmosphere of carbon dioxide to give a series of 5-vinyloxazolidinones **197**. The beneficial effect of TBAB in promoting the carboxylation was also observed in this reaction (Scheme 45c).⁶⁹ It is worth noting that all of these [3+2] cycloaddition reactions proceed *via* allyl-Pd(II) complexes.⁷⁰



Scheme 45: The cycloaddition of *N*-protected aziridines

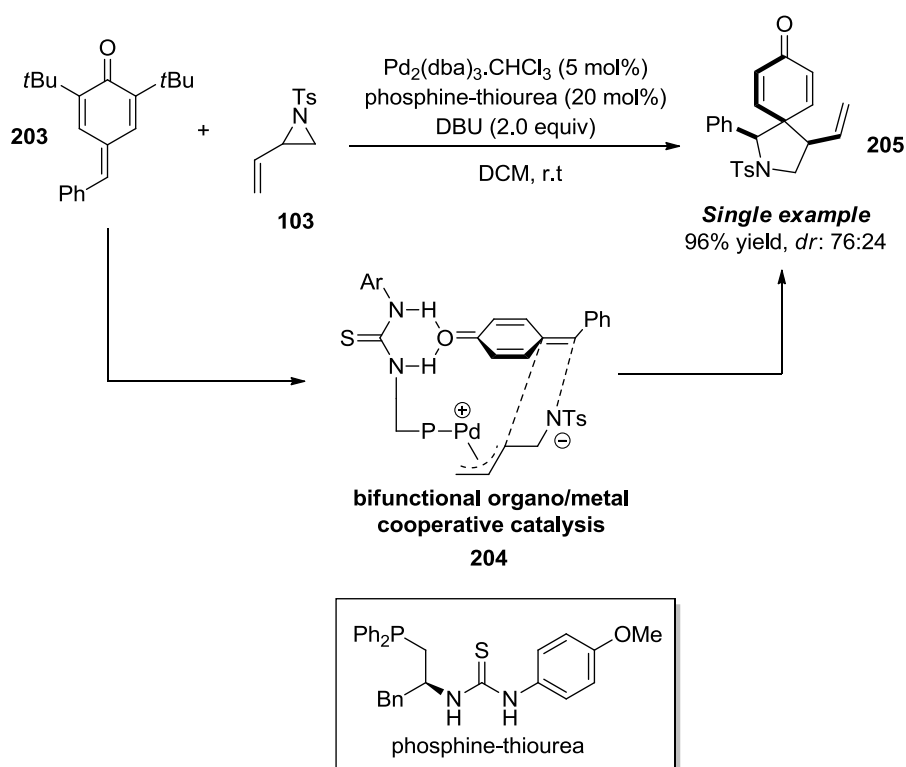
Utilising this methodology, vinylaziridines could be directly utilised as the building block in the preparation of bioactive natural products. For example, the total synthesis of (+)-pseudodistomin D **201** via dynamic kinetic asymmetric transformation (DYKAT) of vinyl aziridines **198** involving η^3 - η^1 - η^3 interconversion was developed by Trost and Frandrick (Scheme 46).⁷¹ The key intermediate, DMB-protected vinyl imidazolidinone **200**, was obtained in a high yield with an excellent enantioselectivity in the presence of the chiral ligand via a [3+2] cycloaddition proceeding with a similar mechanism involving the η^3 Pd(II)-allyl complex **202** (Scheme 45b).

Dynamic kinetic asymmetric cycloaddition



Scheme 46: Total synthesis of (+)-pseudodistomin D

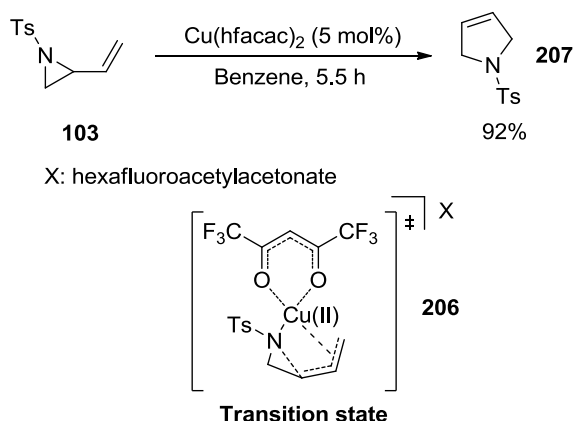
Recently, a single example for the [3 + 2] annulation between *para*-quinone methide **203** and vinylaziridine **103** for the synthesis of spiro[4.5]deca-6,9-diene-8-one **205** has been described by Yuan and co-workers (Scheme 47).⁷² A high yields and moderate diastereoselectivity were given *via* a palladium and phosphine–thiourea cooperative catalysis system **204** involving the η^3 allyl-Pd(II) intermediate.



Scheme 47: Bifunctional organo/metal cooperatively catalysed [3+2] annulation of **203** with vinylaziridine

103

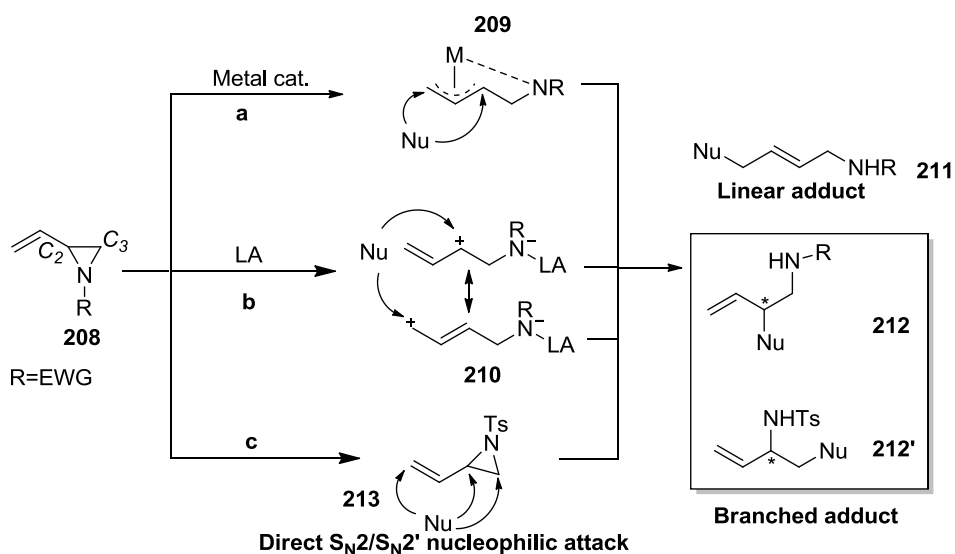
Rearrangement is also an important reaction of vinylaziridines, and this type of reaction can be exemplified by a Cu-catalysed ring expansion of *N*-tosyl vinylaziridine **103** to synthesise 3-pyrrolines **207** (Scheme 48).⁷³ The author proposed that the copper centre chelates to the nearby olefin moiety of aziridine **103** in the reaction to generate a transition state **206** containing an incompletely cleaved C-N bond. The rearrangement then occurs to produce the 3-pyrrolines **207**, which are common structural moieties in natural products and pharmaceutical agents. They have also been utilised as building blocks for other biologically important pyrroles or pyrrolidines.⁷⁴⁻⁷⁵



Scheme 48: The synthesis of 3-pyrroline **207** via intramolecular rearrangement of vinyl aziridine **103**

Generally, by controlling the conditions such as different nucleophiles and catalysts (Scheme 49),⁷⁶⁻⁷⁷ C2, C3 or the terminus of the vinyl group could be potential sites for nucleophilic attack *via* different mechanisms. The cleavage of the aziridine C-N bond could be controlled under two different conditions. Firstly, with the additional reactivity introduced by vinyl group in the presence of metal-catalysts such as Pd(0), the key allyl-metal intermediate enables a nucleophile to attack either the terminal or the C3-position of vinylaziridine **103**. Therefore, the linear adduct **211** or the branched adduct **212** containing a stereogenic centre could be yielded, respectively (Scheme 49a). Alternatively, as demonstrated in the chapter 1, the C-N bond could also be cleaved by Lewis acid activation. In this case, the generation of a resonance-stabilised dipole **210** (or activated aziridine-Lewis acid complex) is also able to give the same linear or branched products (Scheme 49b). In addition, a direct S_N2/S_N2' nucleophilic attack may occur with organometallic reagents such as cuprate to give **211**, **212** or the C3 opening product **212'**, respectively (Scheme 49c).

The presence of the double bond in the allylic amine products, resulting from reactions of vinyl aziridines, provides a versatile point for further synthetic manipulations, making them powerful organic building blocks.⁷⁸ Specific examples of these different nucleophilic ring-opening modes of vinylaziridines are now given in the next section.

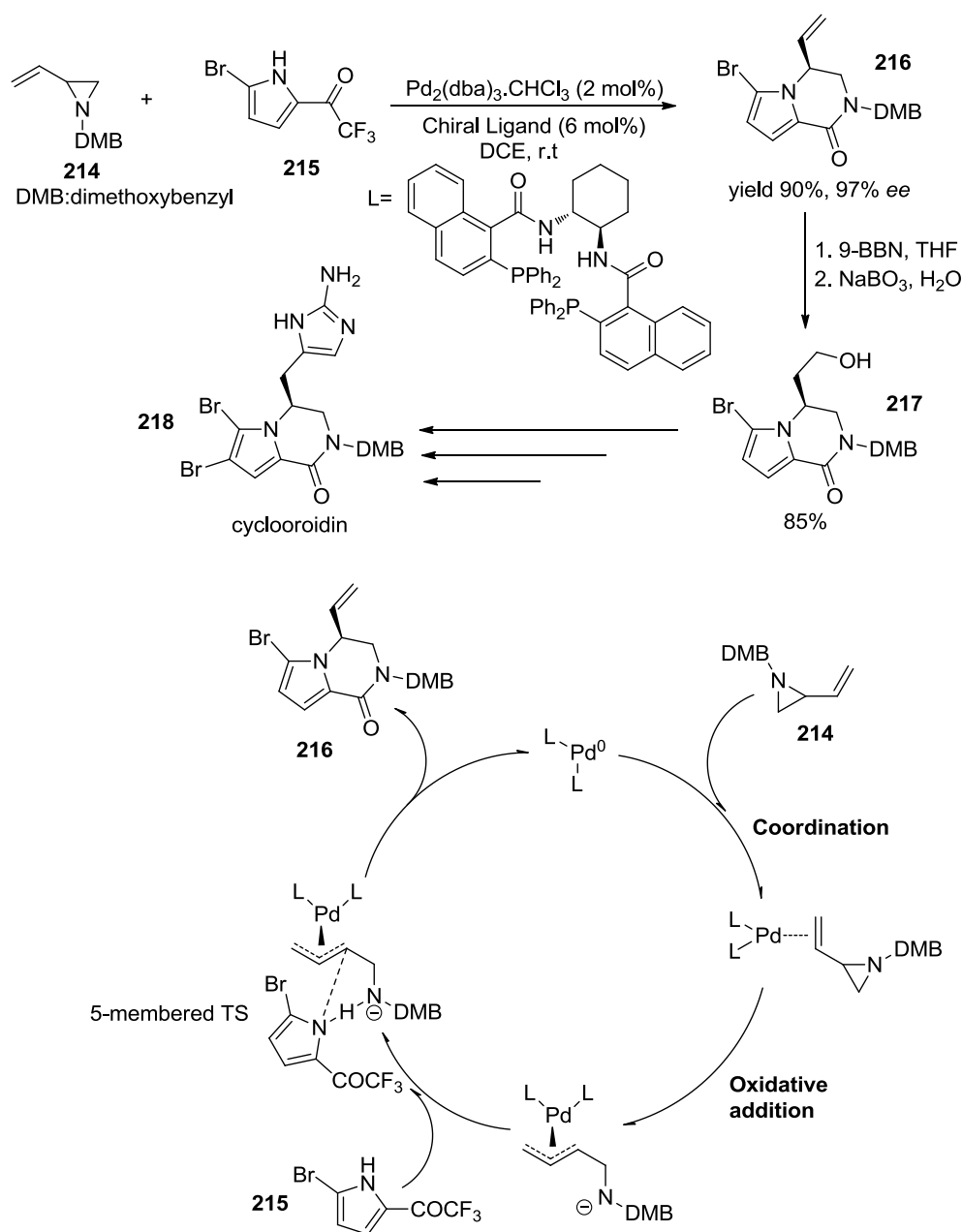


Scheme 49: Different ring-opening pathways of vinylaziridine 103

Transition Metal-Catalysed Ring-Opening Addition of Vinylaziridines with Various Nucleophiles

Several examples of the [3+2] cycloadditions intermediated by allyl-Pd(II) complexes generated from vinylaziridines were shown in Scheme 45. In addition, the use of allyl-Pd(II) complexes to give branched ring-opened adducts has been shown by the Trost group. They have developed a Pd-catalysed allylation reaction of pyrroles using vinylaziridines (Scheme 50).⁷⁹ The synthetic value of this reaction was demonstrated by applying this method to the preparation of several bioactive compounds. For example, cyclosporidine **218**, an antibiotic and cytotoxic agent, can be synthesised from **217**, which was previously prepared *via* hydroboration of **216** – this synthesis demonstrates utility of double bond.

The achiral and linear product is typically obtained in the Pd-catalysed allylic alkylation of monosubstituted π -allyl-Pd intermediates. However, in Trost's reaction, a branched product forms due to a favourable 5-membered transition state that forms after ring-opening of vinylaziridine **214**. In this transition state, the *N*-based pyrrole nucleophile **215** is directed by the amide anion of the vinylaziridine **214** by a hydrogen bond with the pyrrole N-*H*. The final ring closure occurs to release **216** by loss of CF₃ group.

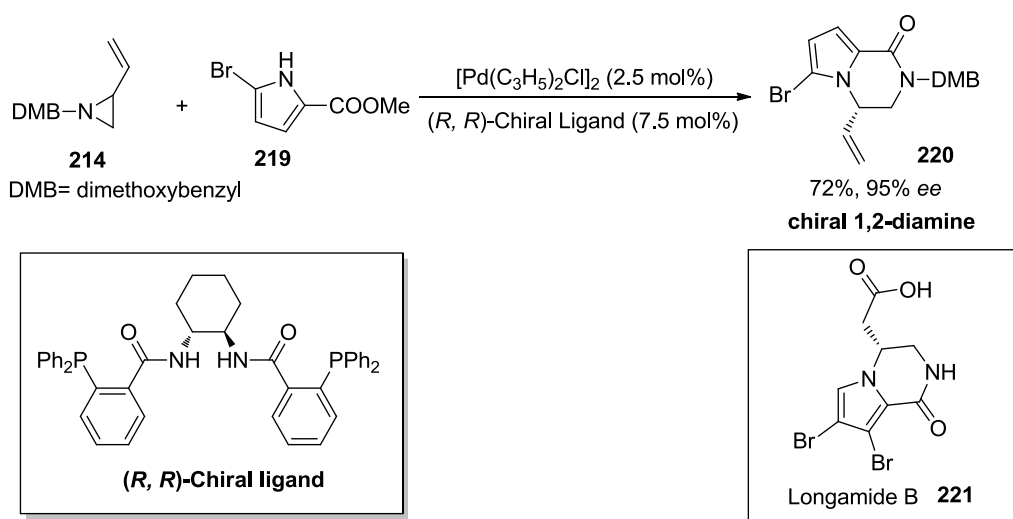


Scheme 50: The palladium catalysed asymmetric allylation of vinylaziridines **214** with nitrogen heterocycles

215

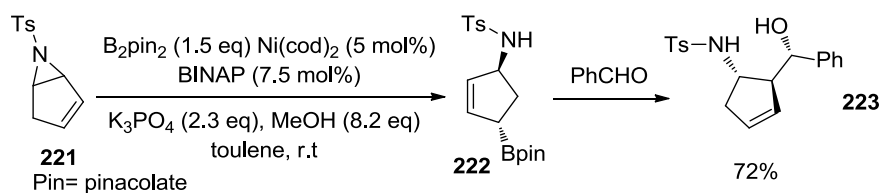
It can be seen from the mechanism above that vinylaziridine **214** has been successfully utilised as a nitrogen analogue of traditional allylating agents such as allylic ester derivatives in the palladium-catalysed ring-opening addition reaction to give chiral 1,2-diamines **216** with a versatile double bond. It is worth drawing attention to the fact that the chiral 1,2-diamine moiety is frequently found in natural products. Also, Trost's group employed 5-bromopyrrole-2-carboxylate esters **219** and vinylaziridine **214** to synthesise additional chiral 1,2-diamines **220** via the palladium-catalysed

ring-opening addition reaction of vinylaziridine **214**. The chiral 1,2-diamines **220** synthesised in this reaction can be further modified to the natural product (–)-longamide B **221** (Scheme 51).⁸⁰ Longamide B **221**, which had only be previously isolated from *agelasdispar* as a racemate in small quantities, has proved to be an antibiotic agent against several strains of Gram-positive bacteria. Therefore, three reactions shown in Schemes 46, 50 and 51 developed by the Trost group demonstrate the synthetic importance of vinylaziridines in natural products synthesis area. Moreover, they were performed with Pd(0) catalysts to construct bioactive molecules, highlighting the utility of the vinylaziridine-derived η^3 allyl-Pd(II) complexes in synthesis.



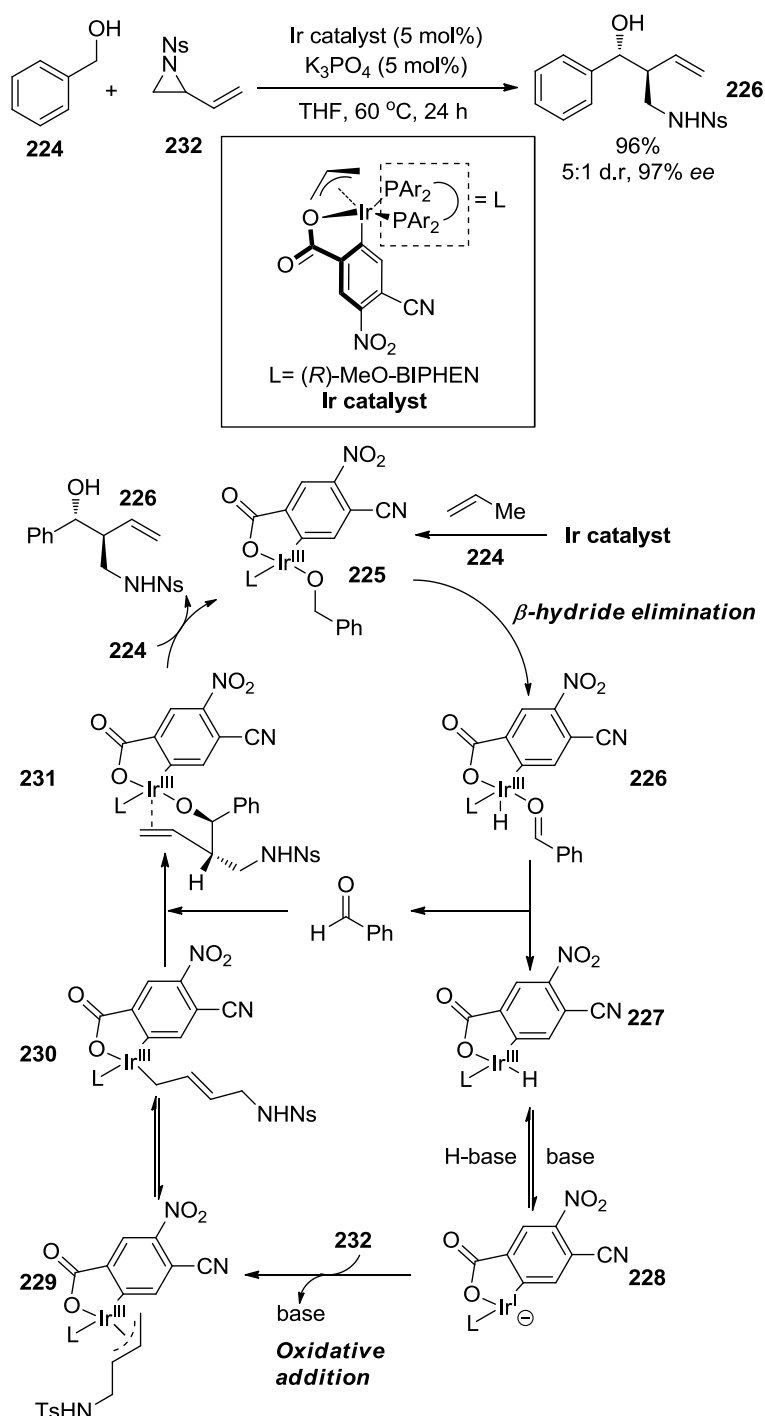
Scheme 51: Concise enantioselective syntheses of pyrrole alkaloid natural products

Alternatively, some research with respect to the ring-opening addition of vinylaziridines with heteroatoms has involved other transition metal catalysts. For example, a Ni(0)-BINAP-catalysed ring-opening addition reaction of the bicyclic vinylaziridine **221** with $\text{B}_2(\text{Pin})_2$ was explored. An electrophilic π -allyl-nickel complex was proposed as the key intermediate to give a functionalised allylic boron derivative **222** *via* transmetallation.⁸¹ After the ring-opening reaction occurred, a 1,3-amino alcohol **223** was synthesised by employing **168** to react with an aldehyde (Scheme 52).⁸²



Scheme 52: The Ni-catalysed ring-opening reactions of vinylaziridine **221**

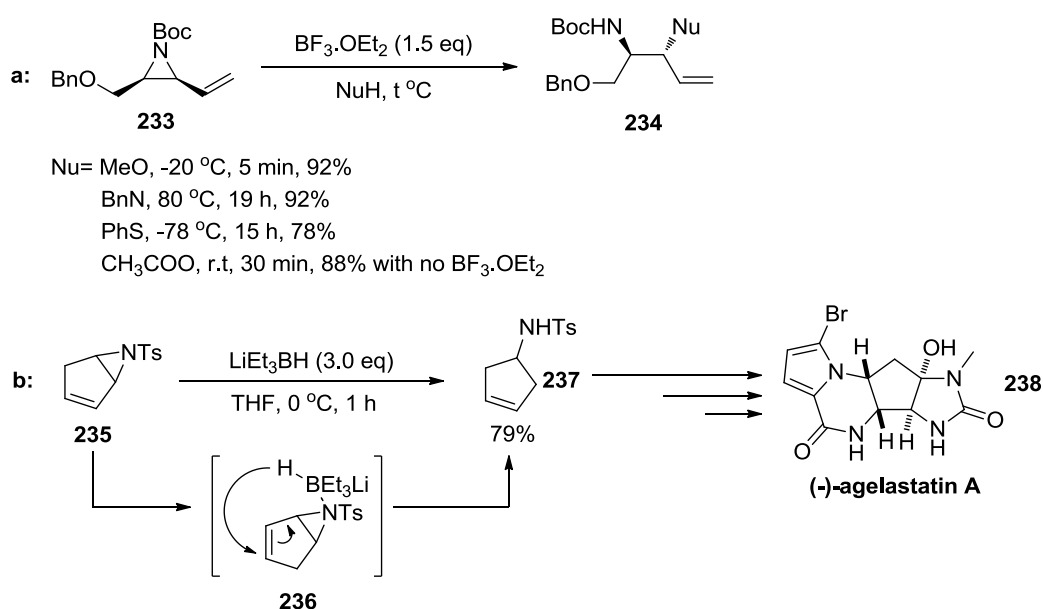
Very recently, in working towards the utility of nucleophilic allyl-metal complexes, the Krische group reported a $\text{Csp}^3\text{-Csp}^3$ coupling reaction of *N*-nosyl vinylaziridine **232** with benzyl alcohol **225** to afford an enantiopure branched adduct **226** with a moderate diastereoselectivity in the presence of cyclometalated π -allyliridium *ortho*-C,O-benzoate complex (Scheme 53).⁸³ Mechanistically, this redox process initiates with dissociation of the propene from the original Ir catalyst. The catalytically active species **225** was generated by the coordination of deprotonated benzyl alcohol **224**. Subsequently, β -hydride elimination occurs to form hydride complex **226** coordinated to benzaldehyde. The following step allows the dissociation of benzaldehyde from the complex **226**, to give the H-Ir(III) complex **227**, which is then deprotonated by the base to produce the anionic complex **228**. The oxidative addition of **228** to aziridine **232** and the protonation by H-base lead to the formation of the allylic Ir(III) complex **229**. The complex η^3 **229**, equilibrates with η^1 complex **230**, allowing sequential Ir-C cleavage and $\text{Csp}^3\text{-Csp}^3$ bond formation with previously released benzaldehyde to give complex **231**. Finally, one molecule of benzyl alcohol **224** enters into the catalytic cycle to cause the release of the desired product **226** and regenerate complex **225**. Importantly, vinylaziridine **232** is converted into a nucleophilic organometallic intermediate in the reaction, and this is reverse from above examples (Schemes 50-52), where vinylaziridines were converted to electrophilic species, making this a particular important contribution to the field.



Scheme 53: Redox-triggered C–C coupling of vinylaziridine **232** with benzyl alcohol **224**

The Lewis acid-catalysed ring-opening addition reaction of vinylaziridines has also been explored (Scheme 49b), and various nucleophiles such as nitrogen, oxygen, sulfur and boron were selected to open the aziridine ring. For example, the Kang group developed a nucleophilic ring-opening reaction of *cis*-3-substituted-2-vinylaziridine **233** by various heteroatom nucleophiles in the presence of $BF_3 \cdot OEt_2$ (Scheme 54a).⁸⁴ The reaction occurs exclusively to give the branched products **234** as a

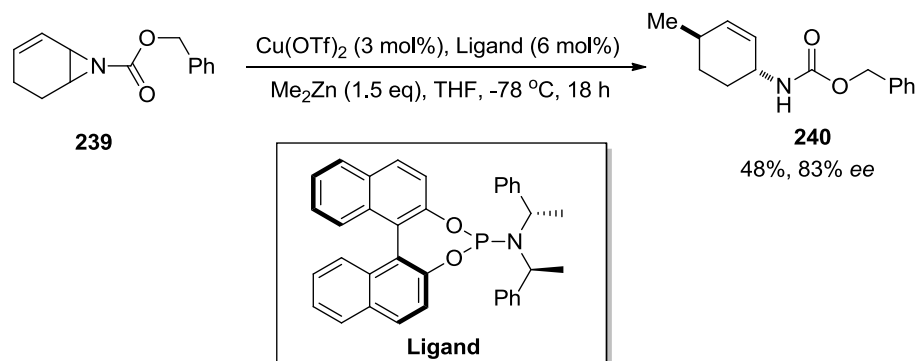
result of the favourable nucleophilic attack at the C2-position for stereoelectronic reasons.⁸⁵ In addition, lithium triethylborohydride has been shown to act as a hydride source to open the ring of vinylaziridine **235**. Baron and co-workers utilised this reaction to prepare the aminocyclopentene **237** as a precursor for synthesis of agelastatin A **238**, a novel inhibitor of osteopontin (OPN)-mediated neoplastic transformation and metastasis.⁸⁶ In this reaction, the cyclopentadiene monoaziridine **235** was treated with lithium tetraethylborohydride to give aminocyclopentene **237** in a relatively high yield (79%) at 0 °C in THF (Scheme 54b).⁸⁷ A reduction of cyclopentadiene monoaziridine **235** through the action of LiEt_3BH , either *via* a $\text{S}_{\text{N}}2'$ nucleophilic or a radical reaction, was proposed.⁸⁸



Scheme 54: The ring-opening reactions of vinylaziridines with heteroatoms and hydride

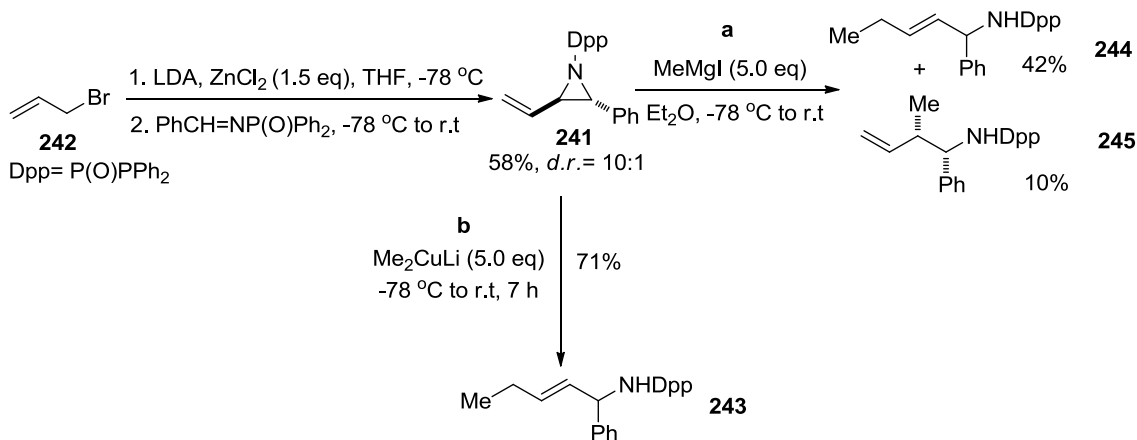
To achieve C-C bond formation in the ring-opening of vinylaziridine, stoichiometric organometallics such as Grignard reagents, cuprates and organozinc reagents have all been utilised. For instance, the Pineschi group successfully developed an addition of dimethylzinc to the vinylaziridine **239** in the presence of $\text{Cu}(\text{OTf})_2$ and a chiral phosphoramidite ligand. The corresponding ring-opening product **240** was given in a moderate yield with high enantioselectivity (Scheme 55). An increased *anti*-stereoselectivity was observed with the addition of dimethylzinc due to the presence of *in situ*-generated copper complexes and phosphoramidites. Furthermore, the major product, cyclic primary allylic amine, is a valuable building block in organic synthesis.⁸⁹ Nevertheless, the substrate scope of the reaction is limited to the cyclic vinylaziridine and alkylzinc

reagents. Thus, the relatively less investigated acyclic vinylaziridine and sp^2 carbon-based nucleophiles such as arylboronic acids are chosen as the coupling partners in the proposed project.



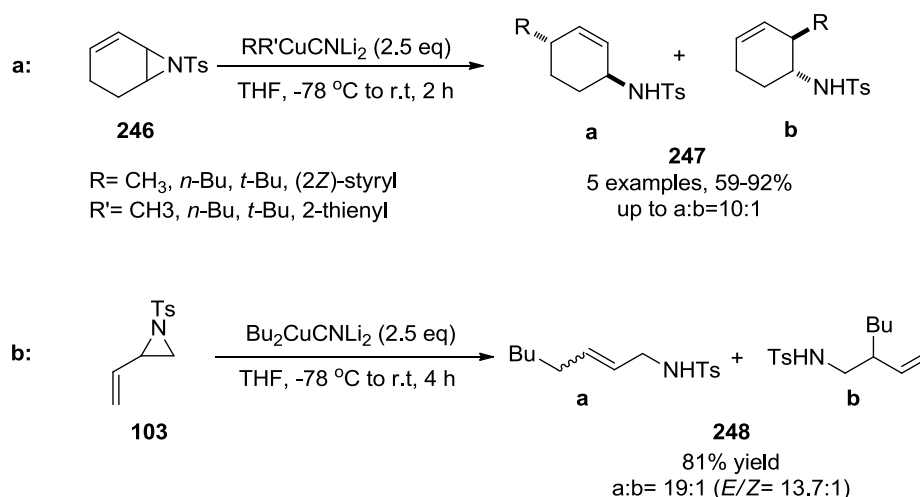
Scheme 55: The Cu(II)-catalysed addition of alkylzinc reagent to cyclovinylaziridine **239**

A di-substituted vinylaziridine **241**, which is given in moderate yield with good diastereoselectivity from the reaction of α -lithio allyl bromide **242** with an *N*-Dpp imine, undergoes a ring-opening reaction with a Grignard reagent to afford the major linear allylic amine **244** in a moderate yield. However, 10 % of a branched isomer **245** was observed as a by-product (Scheme 56a).⁹⁰ The authors also provided the first method to prepare absolute linear 1,3-disubstituted allylic amine with use of lower-order organocuprate in favour of an S_N2' pathway. In this reaction, *N*-Dpp vinylaziridine **241** reacted with lithium dimethylcuprate to give 1,3-disubstituted *N*-Dpp allylic amine **243** in a good yield with absolute regioselectivity and a *trans*-selectivity (Scheme 56b).⁸⁹



Scheme 56: Ring-opening of *N*-Dpp vinylaziridine **241** by Grignard reagent

The Comasseto group found that the Lipshutz lithium cuprate, generated from a stoichiometric amount of organolithium reagent and a Cu(I) species, is able to promote the ring-opening reaction of the vinylaziridine **246**. The reaction proceeded preferentially *via* an S_N2' pathway, giving *trans* 3,6-disubstituted cyclohexenes **247a** as the major product in moderate to excellent yields with good regioselectivities. Nevertheless, by-products **247b** from the S_N2 route were also produced in the reactions (Scheme 57a).⁹¹ Also, an acyclic vinylaziridine **103** was subjected to the conditions and gave the linear product **248a** resulting from an S_N2' pathway in a good yield with an excellent regioselectivity and a *trans*-selectivity (Scheme 57b), and this emphasises the utility of acyclic vinylaziridine **103** in the ring-opening reaction to regioselectively yield the *trans*-linear product (Scheme 49a).



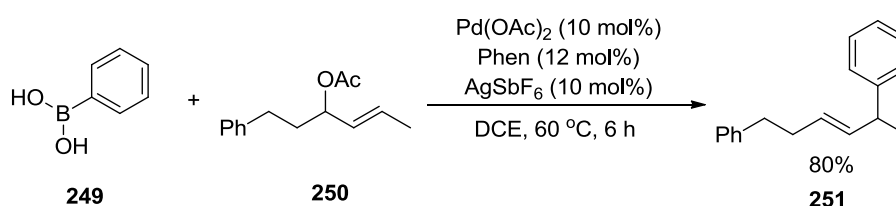
Scheme 57: The ring opening reaction of 2-vinylaziridines by carbon nucleophiles from lithium cuprates

It can be seen that C-C bond formation in the ring-opening reaction of vinylaziridines under catalytic conditions is significantly less investigated. Although above methods allow C-C bond formation *via* the ring-opening addition of aziridine, the reactions must be carried out under the air-free and anhydrous conditions, and expensive and less functional-group-tolerant stoichiometric organometallic reagents are generally required (Schemes 57-58). The use of excess stoichiometric organometallic reagents usually leads to the formation of significant organometallic side-products, which is not environmentally friendly. Therefore, the development of a safe and economic method to fulfill C-C bond formation *via* the catalytic ring-opening addition reaction of vinylaziridine is a

serious need in organic synthesis. Furthermore, the C-C coupling reactions listed above mainly use heteronucleophiles, and a limited number of carbon nucleophiles to attack vinylaziridine. In this project, it was planned to achieve a new Csp³-Csp² bond formation from the Pd(II)-catalysed ring-opening reaction of vinylaziridine and various air-stable and non-toxic arylboronic acids *via* a redox neutral cycle thereby avoiding air-sensitivity.

Research Plan Based on the Reactivity of Vinylaziridine

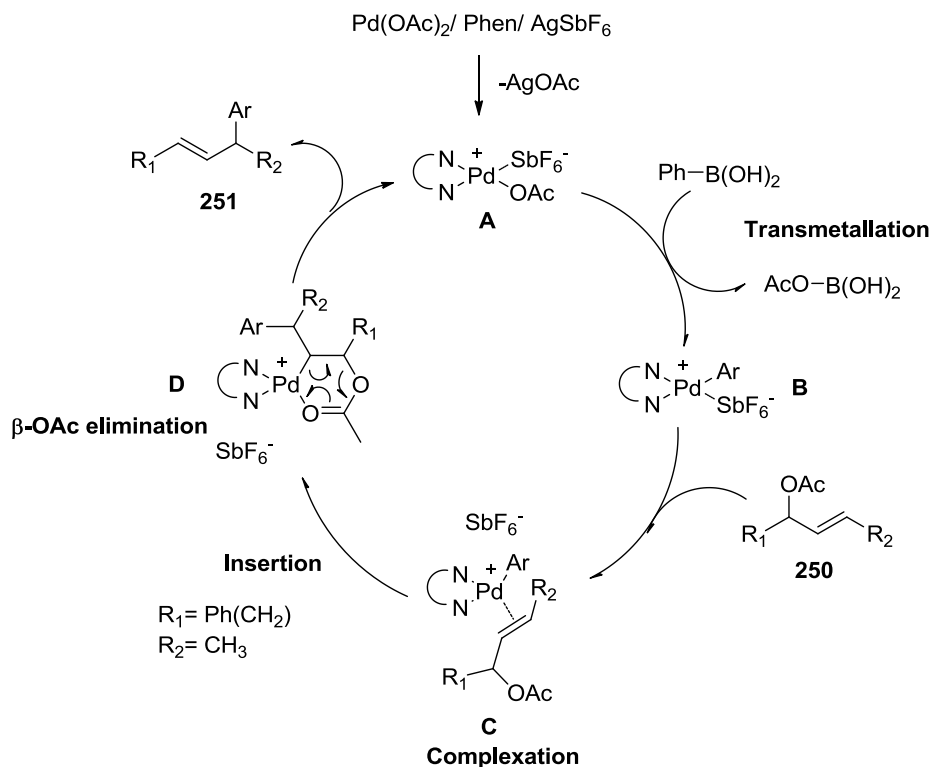
As stated above, vinylaziridines have structural similarities to allyl acetates, therefore, a Pd(II)-catalysed γ -selective and stereospecific allyl-aryl coupling between acyclic allylic esters **250** and arylboronic acids **249** developed by the Sawamura group helped guide the design of the reaction investigated here. The corresponding coupling compound **251** was produced in a good yield with an exclusive γ -selectivity in the reaction (Scheme 58).⁹²



Scheme 58: Addition of phenylboronic acid to the allylic acetate

Stoichiometric reactions of intermediary palladium complexes that were potentially relevant to the catalysis of Sawamura's reaction were performed to understand the mechanism (Scheme 60). The cationic mono(acetoxo)palladium(II) complex **253** was prepared in an excellent yield from the reaction of phenanthroline-ligated Pd(OAc)₂ complex **252** with AgSbF₆ and pyridine-*d*₅ in DCE. Complex **253** was then treated with phenylboronic acid at an elevated temperature to give a cationic (σ -phenyl)palladium(II) complex **254** in a moderate yield. Both of **253** and **254** (10 mol%) were added to the coupling reaction with **250**, and the coupling product **251** was smoothly synthesised in good yields in the two reactions with almost exclusive γ -selectivities (Scheme 59a). Moreover, the π -complex **256** was yielded as the intermediate when the [PdI(σ -Ph)(phen)] **255** reacted with 20 equivalents of allylic acetate in the presence of AgSbF₆. Subsequently, the complex **256** was

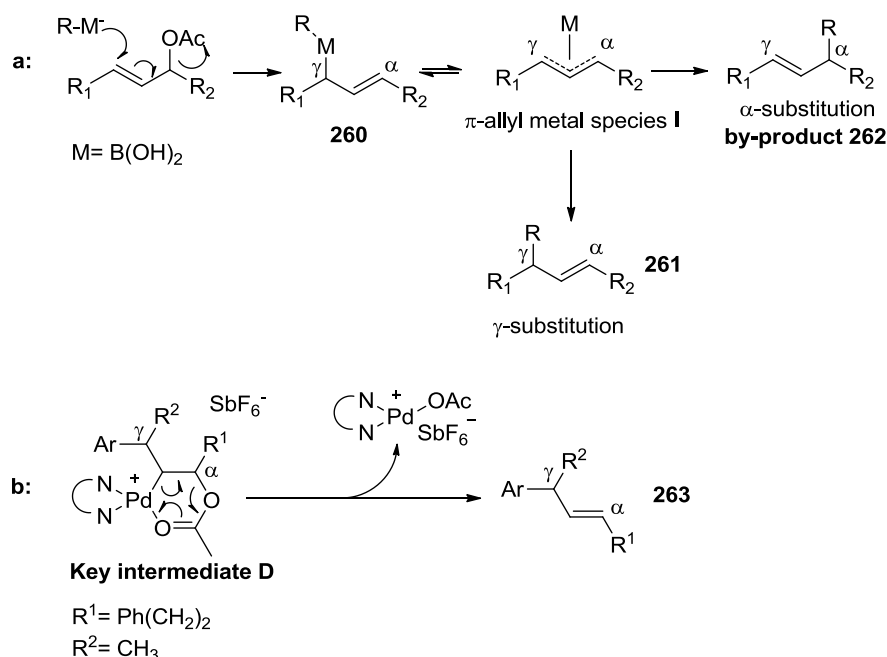
migratory insertion of the C-C double bond then gives a Pd(II) complex **D**, and following β -acetate elimination allows the generation of the final product **251** and the recovery of initial Pd(II)-catalyst. It is worth noting that the palladium catalyst remains the +2 oxidation state during the catalytic process, meaning the reaction is not sensitive to oxygen.



Scheme 60: Allyl-aryl coupling between acyclic allylic esters **250** and arylboronic acids

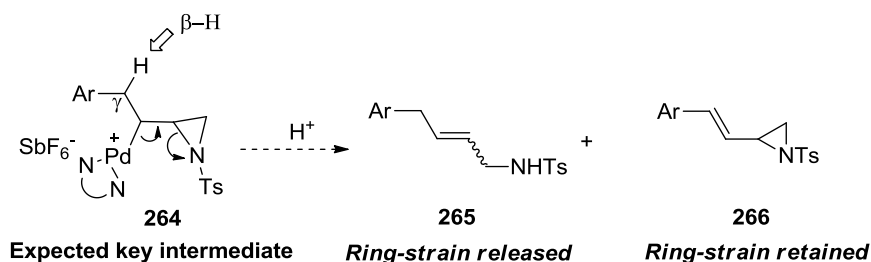
Excellent γ -regioselectivity was obtained in the allylic substitution reaction shown in Scheme 60. Generally, the model demonstrated in Scheme 61 could briefly explain the control of regioselectivity of the metal-mediated allylic substitution reaction. Firstly, an $\text{S}_{\text{N}}2'$ process occurs with an organometallic species, such as phenylboronic acid, giving a $(\pi\text{-allyl})$ metal species **I** (oxidative addition). Subsequently, reductive elimination allows a new C-C bond to form in the γ -position, generating an allylic compound **261** to predominantly create a new stereogenic centre at the γ -position by shifting the double bond.⁹³ Nevertheless, a significant side-reaction, α -substitution, may occur to give by-product **262** (Scheme 61a). In the case shown in Scheme 60, the control of γ -regioselectivity is realised by the coordination of acetate group to the cationic Pd(II)-centre in the key intermediate **D**.⁹⁴ The β -acetate elimination therefore occurs to release the coupling product **251**

with excellent γ -selectivity (Scheme 61b).



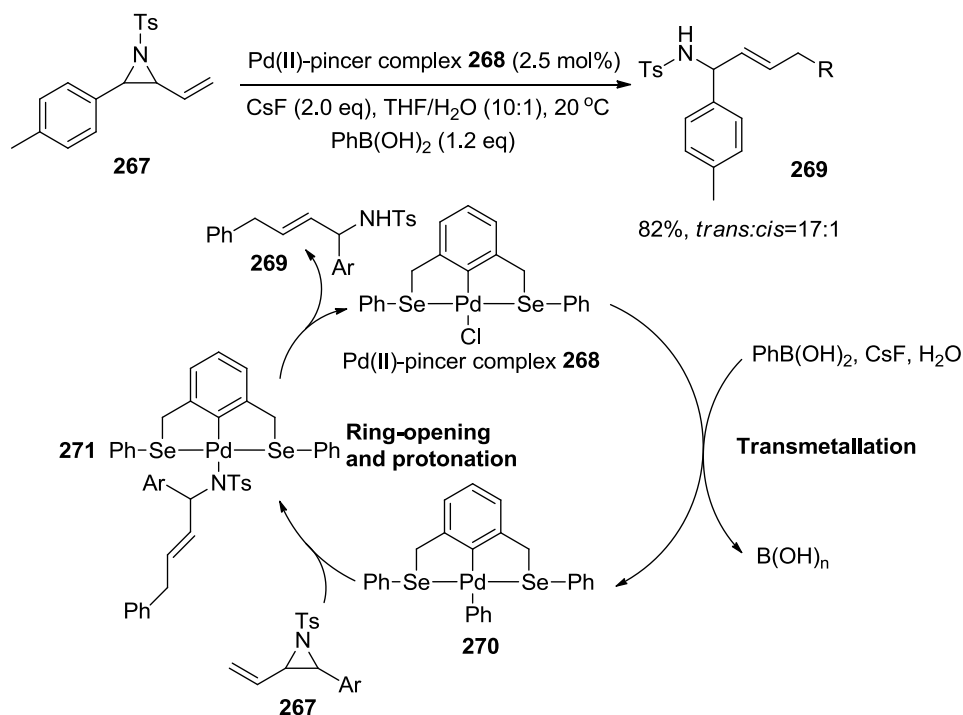
Scheme 61: Allylic substitution with hard nucleophile via a π -allyl metal intermediate

It has been mentioned that the Pd(II)-catalysed process (Scheme 60) is redox neutral as the palladium catalyst is maintained in the +2 oxidation state for the entire catalytic cycle. This is because of the dissociation of the acetate group to regenerate **A** rather than a β -hydride elimination that would subsequently be followed by reductive elimination to give Pd(0). On the basis of this and the structural similarity of vinylaziridine **103** to allylic acetates, it was envisioned that vinylaziridine **103** could be used in a similar redox neutral process to obtain γ -regioselectivity and maintain the Pd(II)-catalyst with breaking of the C-NTs bond driven by the release of ring strain. This would also keep the “leaving group” (NTs) in the product, giving a functionalised sulfonamide product. Such a process would be highly atom economical as all atoms from starting aziridine ends up in product (Scheme 62). In this proposed process, firstly, the key intermediate **264** would be generated by the regioselective migratory insertion of vinylaziridine **103**. The ring strain could then promote the formation of allylic amine **265** via the ring-opening β -nitrogen elimination. Styrenylaziridine **266** resulting from the β -hydride elimination of **264** may also be yielded as a by-product, but this should be disfavoured as it is not accompanied by the release of ring strain (Scheme 62).



Scheme 62: Proposed key intermediate directing the γ -regioselectivity

For the generation of *trans* linear allylic amine **265** (Scheme 62), the Szabo group reported a palladium pincer complex **268**-catalysed the cross coupling of *N*-tosyl-2,3-disubstituted vinylaziridine **267** with organoboronic acids (Scheme 63).⁹⁵



Scheme 63: (*E*)-allylic amine generated from Pd(II)-pincer complex-catalysed ring-opening of vinylaziridine **267** with phenylboronic acid

The proposed mechanism illustrates that transmetalation of organoboronic acids first occurred, followed by a S_N2'-type ring-opening of *N*-tosyl 2,3-disubstituted vinylaziridine (rather than by migratory insertion) **267** to release a thermodynamically favourable linear *trans* allylic amine **269** as the major product in an excellent yield with a high *E/Z*-selectivity, and the results of DFT modeling

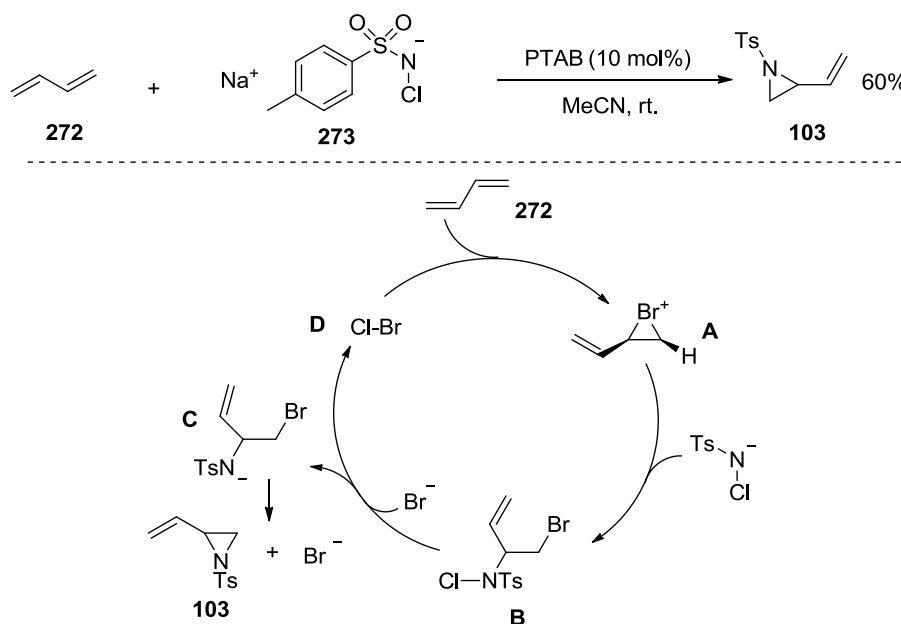
study suggested that the transmetallation probably determines the reaction rate.⁹⁶ Furthermore, the oxidation state of the palladium centre is maintained at +2 throughout the entire catalytic process. Therefore, this reaction successfully avoids oxidative side reactions that may occur in the Pd(0)-catalysed reaction (Scheme 63). However, this method requires a non-commercially available Pd-pincer catalyst **268** and a stoichiometric amount of base, limiting the application of the reaction. Moreover, only one vacant site on the Pd(II)-centre is available for external coordination as a result of the terdentate pincer ligand structure and the strong ligand-metal interaction.⁹⁷ Therefore, this Pd(II)-pincer catalyst system **268** cannot undergo the acetate or NTs-assisted stereocontrol (Schemes 60 and 62), which could potentially lead to alternate stereochemical outcomes with respect to the double bond.

Therefore, inspired by Pd(II)-catalysed reactions of allyl acetates with boronic acids (Scheme 60), it was aimed to develop an Pd(II)-catalysed addition of arylboronic acids to vinylaziridines (Scheme 62). The reaction is driven predominantly by the β -heteroatom elimination based on the propensity of 3-membered strained-ring systems to undergo ring-opening.

Results and Discussion

It has been demonstrated in Scheme 63 that Pd(II)-pincer complex **268**-catalysed ring-opening of *N*-tosyl 2,3-disubstituted vinylaziridine **267** with phenylboronic acid to give the coupling product in a good yield with an excellent *trans*-selectivity. Nevertheless, the single coordination site on the palladium pincer complex **268** compromises the coordination of vinylaziridine **103** to the transmetalated palladium complex. Therefore, a simple Pd(OAc)₂/phenanthroline/AgSbF₆ system was utilised to generate a cationic catalyst that could catalyse the reaction of vinylaziridine **103** with boronic acids and control the stereochemical outcome by the coordination of *N*-sulfonyl group of the aziridine **103**.

The aziridine **103** could be readily synthesised by aziridination of 1,3-butadiene **272** using catalytic phenyltrimethylammonium tribromide (PTAB) (Scheme 65).⁹⁸ A number of signals for vinyl group of **103** were found at 5.58-5.48 ppm (multiplet), 5.44 ppm (doublet) and 5.25 ppm (doublet) in the ¹H NMR **103**. In addition, two distinctive doublets associated with CH₂ next to the stereogenic centre of **103** (2.79 ppm and 2.21 ppm) also evidenced the successful aziridination.

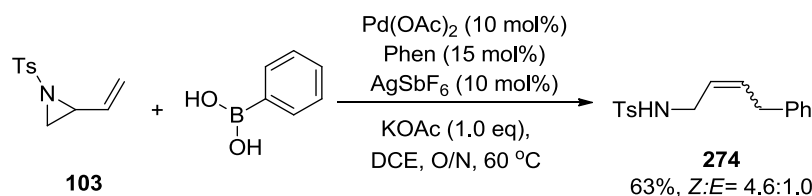


Scheme 65: Synthesis of vinylaziridine 103

The PTAB is a source of electrophilic bromine, which functions as the catalyst to initiate the reaction. It also probably behaves as a solid-liquid phase transfer agent to assist the dissolution of

chloramine-T **273** in acetonitrile.¹²¹ The bromonium ion **A** initially is formed from the addition of Br-Cl to the olefin, followed by the formation of β -bromo-*N*-chloro-*N*-toluenesulfonamide **B** by the nucleophilic attack of TsNCl. Subsequently, attack of Br⁻ (or TsNCl) on the N-Cl group of **B** releases the anion **C** and regenerated electrophilic bromine **D** as Br-Cl. The desired aziridine **103** is then given by expulsion of Br⁻ from the anion **C**.

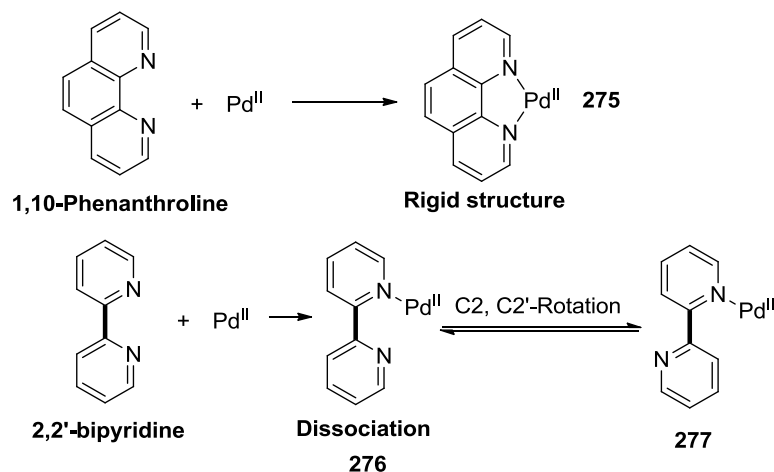
Brief preliminary research, at the end of the proceeding Masters degree project, was carried out under the conditions similar to that reported by Sawamura and co-workers (Scheme 66).⁹⁹ The product **274** was synthesised in a moderate yield with an unusual *Z*-selectivity (4.6:1 mixture of *Z*:*E* isomers), and trace styrenylaziridine was observed as the by-product in the ¹H NMR of the crude reaction mixture (Scheme 62).



Scheme 66: Preliminary result for addition of phenylboronic acid to vinylaziridine **103**

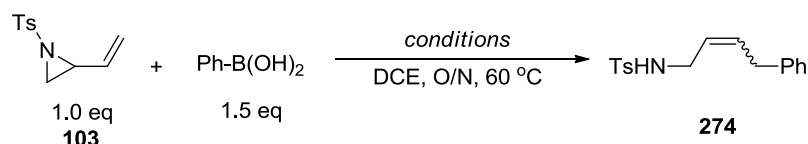
Complete optimisation of the process and substrate scope were performed during the PhD and is summarised in the table 1. Firstly, with other conditions kept the same as in Scheme 66, a reaction was carried out with 2,2'-bipyridine, which is a different *N*-based ligand (entry 1, Table 1). This only resulted in a reduced yield of 42% with a 3.5:1 ratio of *Z*/*E* isomers. The evidence for generation of the linear product **274** came from two multiplets (5.80-5.65 ppm and 5.48-5.35 ppm, respectively) associated with two olefinic protons of **274**. A broad singlet at 4.48 ppm associated with the amine proton was found in the ¹H NMR of **274**, suggesting the ring-opening of **103**. The presence of this amine proton in the structure of **274** was further evidenced by a broad frequency at 3274 cm⁻¹ in IR spectrum of **274**, and this amine proton resulted from the C-N bond cleavage of **103**. Two aliphatic CH₂ of **274** were found as a triplet at 3.70 ppm and a doublet at 3.28 ppm respectively in the ¹H NMR of **274**. In addition, the ¹³C NMR demonstrates correct number of aliphatic carbons in the expected structure of *cis*-**274**. Two olefinic carbon signals of *cis*-**274** were also observed at 132.8 ppm and 126.3 ppm. Moreover, high-resolution mass spectrometry also gave a molecular weight (302.1203 g mol⁻¹) that highly match the calculated molecular weight of **274**. In conclusion, **274** has been

successfully synthesised *via* the ring-opening of **103** with phenylboronic acid. Many by-products also appeared on the ^1H NMR of the crude reaction mixture. Perhaps as a result of the rotation of the C2-C2' bond, the 2,2'-bipyridine was apparently not able to coordinate to the Pd centre as rigidly as the 1,10-phenanthroline has in the previous reactions (Scheme 67).¹⁰⁰⁻¹⁰¹



Scheme 67: The coordination of 1,10-phenanthroline and 2,2'-bipyridine to the Pd(II)-centre

Table 1: Further optimisation for the reaction in Scheme 66

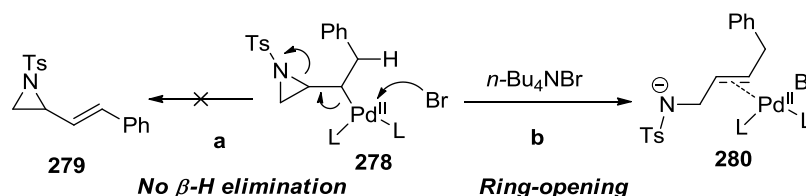


Entry	Conditions	Yield (%)	Ratio (Z/E)
1	Pd(OAc) ₂ (10 mol%) 2,2'-bipyridine (15 mol%) AgSbF ₆ (10 mol%) KOAc (1.0 eq)	42	3.5:1
2	Pd(OAc) ₂ (10 mol%) Phen (15 mol%) AgSbF ₆ (10 mol%) <i>n</i> -Bu ₄ NBr (15 mol%)	64	1.6:1
3	Pd(OAc)₂ (10 mol%) Phen (15 mol%)	79	4.2:1

	AgSbF ₆ (10 mol%)		
4	Pd(OAc) ₂ (10 mol%) Phen (15 mol%)	27 ^a	1.7:1.0

^a Conversion.

The addition of a catalytic amount of *n*-Bu₄NBr was expected to enhance the reaction in the ways shown in Scheme 68. In the pathway **a**, bromide may occupy the vacant site potentially available for the β-H elimination, preventing the formation of by-product styrenylaziridine **279** (Pathway **a**, Scheme 68). In addition, the nucleophilic attack of bromide at the Pd(II)-centre may facilitate the strain-relieving ring-opening process (pathway **b**, Scheme 68). However, the addition of *n*-Bu₄NBr only led to a sharp drop in the *Z/E* ratio with no significant change in the yield, and the trace styrenylaziridine was still present in the crude reaction mixture (entry 2, Table 1).



Scheme 68: Expected function of *n*-Bu₄NBr

The next reaction was performed with no base or additive. Surprisingly, this simplification of the conditions resulted in a very clean ¹H NMR of the crude reaction mixture. The product **274** was isolated in a high yield (79%) with a 4.2:1 mixture of *Z:E* isomers (entry 3). These results suggest that the ring-opening occurred to generate the internal alkene with no significant styrene formation due to the absence of signals range from 6.00 ppm to 7.00 ppm in ¹H NMR of the crude reaction mixture. To examine the effect of AgSbF₆ in the reaction, it was removed from the reaction mixture. As a result, the conversion was dramatically reduced to 27% with a sharp drop in the ratio of *Z:E* isomers (entry 4). This suggests the Ag maintains the Pd catalyst in a cationic state, facilitating transmetalation and coordination between Pd and NTs.

Subsequently, the reaction scope was examined with a variety of arylboronic acids (Table 2). The reactions utilising substituted arylboronic acids were found to require the addition of 0.5 equivalents

of potassium acetate (entries 2-9, Table 2). For example, the electron-rich tolylboronic acid gave the corresponding allylic sulfonamide in a 40% yield with a good *Z/E* ratio (3.5:1) in the presence of 0.5 equivalents of potassium acetate (KOAc) (entry 2). However, the reaction efficiency was considerably diminished either with no KOAc or with no AgSbF₆ (17% conversion). Furthermore, the *Z/E* ratio was significantly reduced if the silver salt was omitted but KOAc was present (entry 2). It was found that highly electron-deficient arylboronic acids were the optimum substrates for this reaction (Table 1, entries 3-6). For instance, the addition of (4-(ethoxycarbonyl)phenyl)boronic acid resulted in an excellent yield (94%) with a moderate *Z/E* ratio (2.7:1.0) in the presence of KOAc, but a slight decomposition occurred with no KOAc since an unclear ¹H NMR of the crude reaction mixture was observed (entry 3). An excellent yield (90%) was observed again with use of (4-nitrophenyl)boronic acid (entry 5), albeit with a moderate *Z/E* ratio (2.2:1.0). NOESY-1D was applied to determine the *Z/E* configuration for the product **284** as it has well-separated signals for the two aliphatic CH₂ (see Appendix). The triplet corresponding to the **a'** protons (CH₂ at 3.58 ppm, minor isomer) next to the NHTs was first selected as the reference for the NOSEY-1D, and it was found that two olefinic protons (H₁ at 5.47-5.45 ppm, H₂ at 5.73-5.71 ppm) and an amine proton (H_N at 4.67 ppm) correlated to **a'**. The other doublet corresponding to the **b'** next to the aromatic ring (CH₂ at 3.42 ppm) was absent on the NOSEY-1D spectrum (Figure 10). This result suggests **a'** has proximity in space to only H₁, H₂ and H_N. The minor isomer was therefore assigned as *trans*-olefin. In contrast, a NOSEY-1D spectrum of the major isomer shows the triplet **a** (CH₂ next to the NHTs at 3.73 ppm) correlates to only one olefinic proton H₁ (multiplet, 5.55-5.53 ppm), amine proton H_N (app. triplet, 4.73 ppm) and the doublet **b** (CH₂ next to the aromatic ring at 3.44 ppm), but the NOSEY-1D does not demonstrate the correlation between **a** and H₂, suggesting the major isomer is a *cis*-olefin (Figure 7). Therefore, the reaction exhibited an unusual *Z*-selectivity that was in stark contrast to that observed by Szabo's Pd-pincer complexes (Scheme 63).

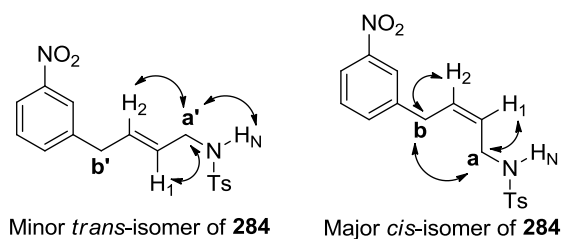
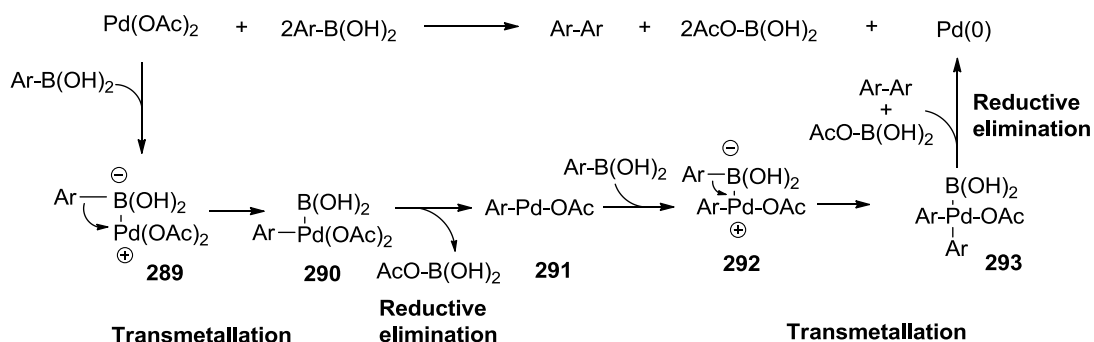


Figure 7: NOESY-1D results of **284**

Halogen-substituted arylboronic acids were investigated in the reaction scope for the potential application of the corresponding ring-opened products in coupling reactions. As expected, the more electron-deficient 4-fluorophenylboronic acid released the allylic sulfonamide in a good yield (75%) with a moderate *Z*-selectivity (entry 6). However, 4-chlorophenylboronic acid, which is less electron-deficient than 4-fluorophenylboronic acid, was able to give the targeted product in moderate yield (57%), but with a slightly increased *Z/E* ratio (2.8:1.0) compared with the result in entry 6 (entry 4). A yield (38%) and a low *Z/E* ratio (1.8:1.0) were observed with indolylboronic acid (entry 7). A moderate yield (42%) was obtained with relatively high *Z/E* ratio (4.5:1.0) when 3-methoxyphenylboronic acid participated into the reaction (entry 8). The more electron-rich (3,4-dimethoxyphenyl)boronic acid was utilised, lowering the yield to 25% with a 3.1:1.0 mixture of *Z/E* isomers (entry 9). Thus, electron-rich arylboronic acids only resulted in moderate to relatively low yields. It is worth noting that these reactions were very clean, and the low yields predominantly resulted from incomplete conversion of the starting vinylaziridine **103** (entries 2, 7 to 9). It can be tentatively proposed that the decrease in the conversion is caused by the more efficient reduction of Pd(II) catalytically active species to Pd(0) with electron-rich boronic acids (Scheme 69).¹⁰²⁻¹⁰³ Firstly, an acid-base reaction occurs between Pd(OAc)₂ and arylboronic acid to afford the intermediate **289**. The complex **290** is then generated with the transmetallation of the aryl group to the cationic palladium centre, and this Wagner Meerwein rearrangement-type process should be favoured by the electron-rich aryl group. The AcO-B(OH)₂ was released by the reductive elimination of **290**, and the resulting complex **291** repeats the process consisting of acid-base reaction, transmetallation and reductive elimination in sequence. Overall, the Pd(OAc)₂ was reduced to the Pd(0) species, and two molecules of AcO-B(OH)₂ and 1,1'-biaryl resulting from the homocoupling were yielded in the reaction.¹⁰⁴ This proposed mechanism was evidenced by the palladium black deposited on the bottom of the reaction flask after the reaction was completed, and trace 1,1'-biaryl was observed on the ¹H NMRs of the crude reaction mixtures. Furthermore, in accordance with the expectation, more significant 1,1'-biaryl was found in the crude ¹H NMR of the electron-rich compounds.



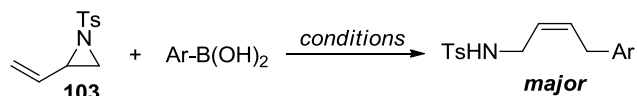
Scheme 69: Self-coupling of arylboronic acids induced by Pd(OAc)₂

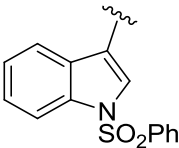
When 2-methoxyphenylboronic acid was used as a reactant no coupling reaction was observed (entry 10). Instead, undesired products were generated as a result of hydrolysis of the aziridine and ring-opening by acetate with 2-chlorophenylboronic acid (entry 11), again suggesting the reaction was sensitive to steric hindrance.

The boronic acid may be a proton source following elimination since the boronic esters exhibited a lack of reactivity in the reaction (entry 12, Table 2). Furthermore, the results in Table 2 demonstrates utilisation of electron-deficient boronic acids resulted in more efficient coupling reactions. Therefore, the reaction rate of this reaction may not be determined by the transmetallation step, because less nucleophilic electron-poor arylboronic acids generally slows transmetallation in contrast to electron-neutral arylboronic acids.¹⁰⁵⁻¹⁰⁶

In all cases shown in the table 2, trace amounts of the inseparable styrenyl system were found, as evidenced by the presence of distinctive down-field olefinic signals at the ¹H NMR of the crude reaction mixture. For example, it was found in the crude ¹H NMR for the product **282** that olefinic signals of the styrenyl by-product were present at 6.25-6.45 ppm. As proposed in Scheme 62, competing β-H elimination may cause the generation of styrenyl compounds **266** in the reactions.

Table 2: Reaction scope and optimization for the Pd(II)-catalysed addition of arylboronic acids to the vinylaziridine **103**

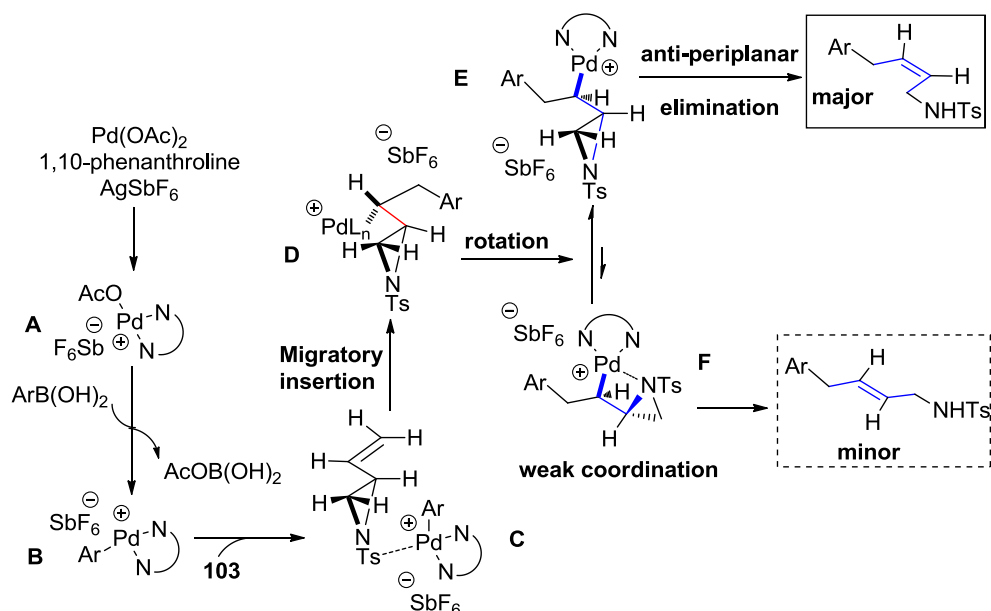


Entry	Ar	Product	Yield (%) ^b	Z:E ratio
1	C ₆ H ₅	274	79 ^c	4.2 : 1
2	4-MeC ₆ H ₄	281	17% conversion (no KOAc) ^e	
			40% (0.5 eq KOAc)	3.5 : 1
			17% conversion (0.5 eq KOAc no AgSbF ₆)	1.6:1
3	4-EtO ₂ C-C ₆ H ₄	282	Partial decomposition ^e (no KOAc)	
			94% (0.5 eq. KOAc)	2.7 : 1
4	4-ClC ₆ H ₄	283	57	2.8 : 1
5	3-NO ₂ C ₆ H ₄	284	90	2.2 : 1
6	4-FC ₆ H ₄	285	75	2.5 : 1
7		286	38	1.8 : 1
8	3-OMe-C ₆ H ₄	287	42	4.5 : 1
9	3,4-OMe-C ₆ H ₄	288	25	3.1:1
10	2-OMe-C ₆ H ₄	-	N.R.	N/A
11	2-ClC ₆ H ₄	-	Aziridine hydrolysis ^d	N/A
12	Phenylboronic ester	-	N.R.	N/A

^a Conditions: vinylaziridine (1.0 eq.), boronic acids (1.5 eq.), Pd(OAc)₂ (10 mol%), Phen (15 mol%), AgSbF₆ (10 mol%), KOAc (0.5 eq.), 70 °C, 22 h. ^b Isolated yields. ^c No addition of KOAc. ^d Product derived from attack of acetate on aziridine also observed. ^e Messy NMR of crude reaction mixture so Z/E ratio cannot be measured.

The mechanism for the reaction is tentatively proposed on the partial basis of the coupling

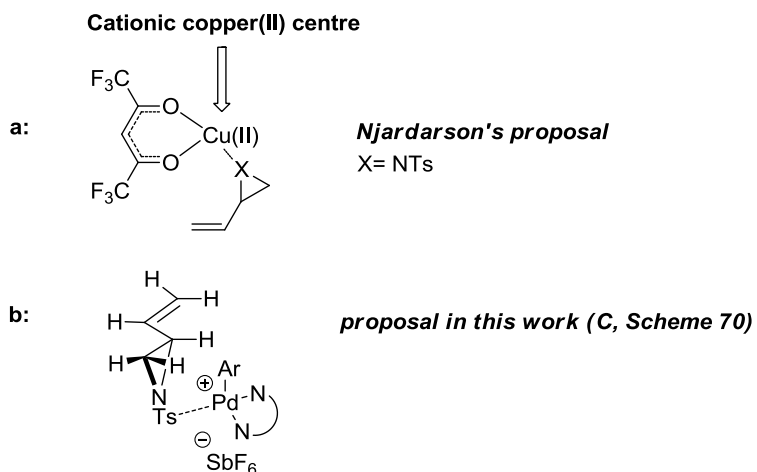
reaction between allylic esters and arylboronic acids reported by Sawamura and co-workers and the experimental results uncovered (Scheme 70).¹¹⁷



Scheme 70: Proposed model for the Z-stereoselectivity of the arylboronic acid addition to the vinylaziridine

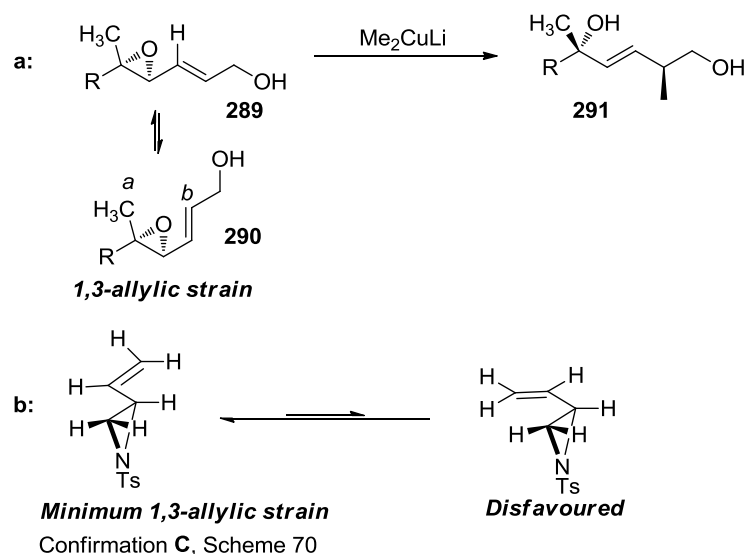
103

Firstly, a catalytically active Pd(II) species, originally generated from the reaction of the 1,10-phenanthroline, $\text{Pd}(\text{OAc})_2$ and AgSbF_6 , undergoes transmetalation with the boronic acid to release the complex **B**. According to the proposal demonstrated by the Njardarson group, the NTs group of vinylaziridine **103** has capacity of coordinating to a cationic Cu(II) centre, and this initiates a ring-opening rearrangement reaction (Scheme 71a).¹⁰⁷ Therefore, the *N*-tosyl-vinylaziridine **103** likely coordinates to the cationic Pd-aryl complex **B** (Scheme 70) through the *N*-protecting group (Scheme 71b).¹⁰⁸



Scheme 71: coordination of the vinylaziridine **103** to the cationic Pd(II)-centre

Conformation **C** is proposed since it minimises the 1,3-allylic strain (Scheme 70). In support of this, the reaction of vinyloxydes with cuprates through a confirmation **289** in which the double bond and the epoxide ring were restricted to occupy approximately perpendicular planes is demonstrated in Scheme 72a.¹⁰⁹ As a result of the significant 1,3-allylic strain between C_a and C_b, the other possible confirmation **290** is not favoured in the reaction. Similarly, the double bond and the aziridine ring of **103** need to be positioned on roughly perpendicular planes in confirmation **C** to minimise the 1,3-allylic strain (Scheme 72b).¹¹⁰ In addition, relatively high yields were observed with electron-deficient arylboronic acids, suggesting the coordination of NTs to the cationic Pd(II) complex **B** might be the rate-determining step. This is because the electron-deficient aryl group in **B** leads to low electron density of the Pd(II)-centre, enhancing the subsequent coordination between the cationic Pd(II)-centre and NTs to form **C**.



Scheme 72: Formation of the confirmation **C** in Scheme 70

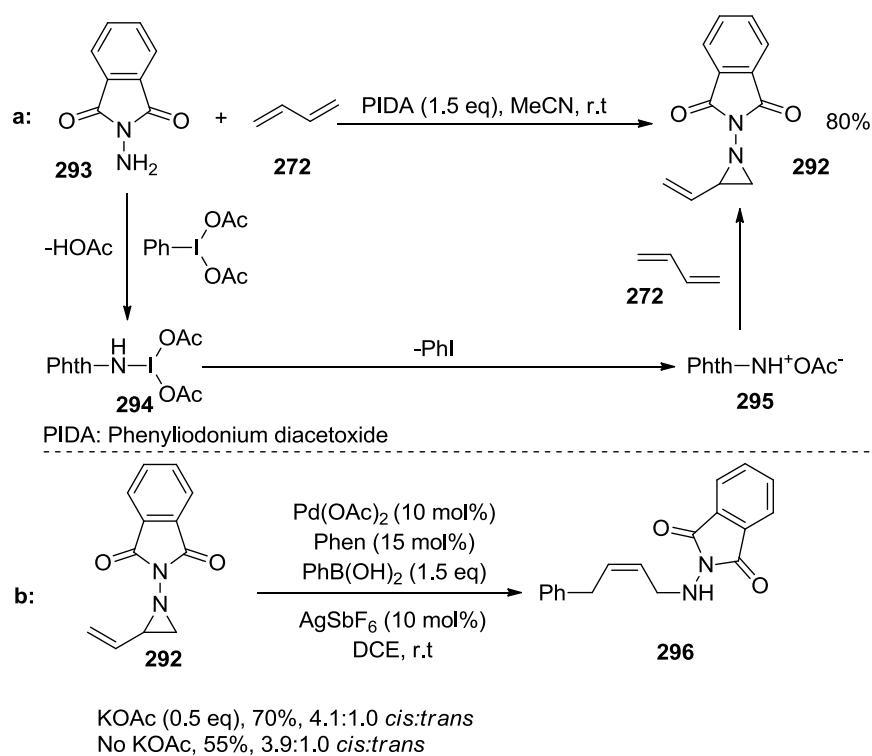
The following migratory insertion to the lower face of conformation **C** is regioselectively directed by the ancillary coordination through the *N*-tosyl group (Scheme 70), and complex **D** is therefore given in this process and favours an anti-periplanar conformation **E** for subsequent elimination to give the *cis*-allylic sulfonamide as major product. A less favoured and highly strained bicyclic intermediate **F**, would experience hampered coordination between the *N*-tosyl group of the vinylaziridine **103** and the cationic Pd(II)-centre. This less favoured intermediate causes a *syn*-elimination to yield the *trans*-allylic sulfonamide as minor side-product. In addition, in comparison with the acetate introduced by the substrate in Sawamura's work (Scheme 61), it can be proposed that the additional acetate (KOAc) may take up a vacant site on the Pd(II) centre to aid catalyst regeneration and generate AcO-B(OH)₂ through the transmetallation step.

To see if selectivity would be higher, a more coordinating electron-rich *N*-phthalimide aziridine **292** was prepared in an excellent yield (80%) using the method demonstrated in Scheme 73a.¹¹¹ The synthesis begins with oxidation of *N*-aminophthalimide **293** by PIDA to produce intermediate **294** (Scheme 73b), followed by dissociation of phenyliodide from **294** with the formation of the acetoxy nitrenium ion (*N*-acetoxyaminophthalimide **295**). *N*-acetoxyaminophthalimide **295** is the reactive intermediate that aziridinate the olefin to form the desired aziridine **292**. Simultaneously, acetic acid and iodobenzene are given as by-products. The structure of **292** contains one vinyl group because characteristic signals of vinyl group, including a multiplet (CH, 5.80-5.73 ppm) and two doublets (5.55 ppm and 5.37 ppm, respectively), were observed in ¹H NMR of **292**. Aliphatic CH₂ of **292** was

evidenced by two doublets of doublet at 2.72 ppm and 2.52 ppm. In addition, a quartet at 3.08 ppm corresponding to aliphatic CH of **292** was also observed. Two aliphatic carbon signals associated with aliphatic CH₂ and CH were observed at 38.9 ppm and 44.2 ppm respectively in the ¹³C NMR of **292**, supporting the generation of **292** in this reaction.

The relatively electron-rich *N*-phthalimide group is expected to give a more efficient reaction since its potential better coordination ability with the cationic Pd(II)-centre could favour configuration **C** (Scheme 70). Additionally, the formation of unfavoured configuration **F** (Scheme 70) from **292** could be facilitated due to the improved coordination between the electron-rich *N*-phthalimide group and the cationic Pd(II)-centre. Therefore, increased *E*-selectivity was expected in the reaction.

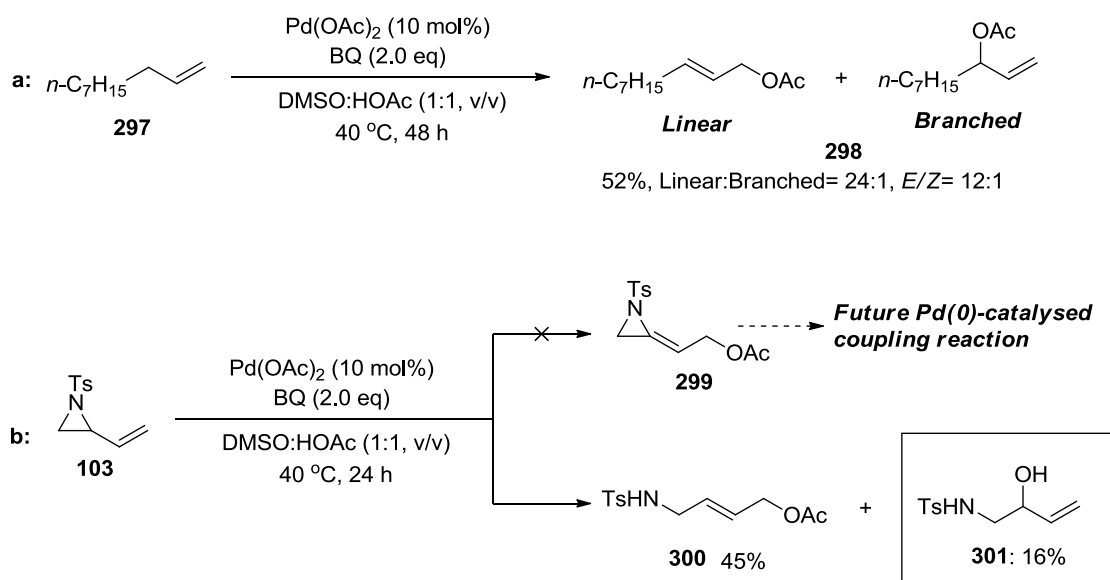
In consideration of the reduced ring-opening capacity of **292** caused by electron-rich *N*-phthalimide group, KOAc (0.5 eq) was added to the reaction to facilitate the C-N bond cleavage. **292** was completely consumed to afford the corresponding product **296** in a good yield (70%) at ambient temperature with a 4.1:1.0 *Z/E* ratio (Scheme 90b). The *Z*-selectivity was not significantly different from that of **274** (4.2:1). This may be because increased steric hindrance between the large *N*-phthalimide group and the Pd(II)-centre disfavours configuration **F** despite potentially enhanced coordination (Scheme 70). However, the yield was reduced in the absence of KOAc.



Scheme 73: Ring-opening of *N*-phthalimide vinylaziridine **292**

Hydrolysis of Vinylaziridine **103**

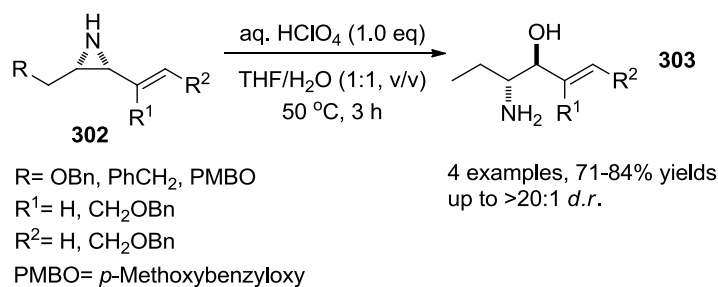
Subsequently, inspired by the Pd(II)-catalysed acetoxylation of olefin **297** developed by the White group (Scheme 74a),¹¹² a C-H oxidation of vinylaziridine **103** was attempted for synthesis of **299** as a new allylic acetate that could be utilised in the future Pd(0)-catalysed coupling reaction. However, the reaction only produced a relatively messy crude reaction mixture. Column chromatography was performed to isolate the linear acetate-substituted sulfonamide **300** in a 45% yield with many inseparable impurities. Additionally, a branched hydrolysed vinylaziridine **301** was also isolated in significant quantity (Scheme 74b). The branched-selectivity was evidenced by conservation of vinyl group in the **301**, and this regioselectivity leads to some characteristic signals in ¹H NMR of **301**, including a multiplet at 5.79-5.72 ppm (olefinic CH) and two doublets associated with terminal CH₂ of **301** (5.29 ppm and 5.17, respectively); furthermore, the aliphatic CH adjacent to OH was found at 4.22 ppm as an apparent singlet. Additionally, the ¹³C NMR shows nine carbon signals in total, which is in agreement with the number of carbons in the symmetric structure of **301**. The structure of **301** was then confirmed by compared with literature.¹¹³



Scheme 74: The acetoxylation of **103**

The branched selectivity of **301** drew our attention since vicinal amino alcohols are important structural motifs of bioactive molecules.¹¹⁴ It should be noted that the hydrolysis of vinylaziridines

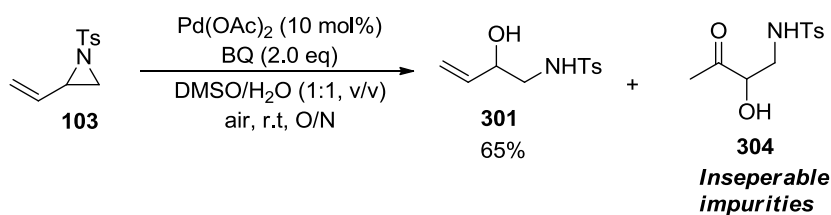
only has very limited examples. For instance, Somfai and co-workers found the complete branched selectivity of enantioenriched *vic*-amino alcohols **303** were obtained from enantiomerically pure *N*-*H* vinylaziridine **302** in the presence of HClO₄ (1.0 eq) in a co-solvent system (THF/H₂O) (Scheme 75).¹¹⁵



Scheme 75: example for the hydrolysis of vinylaziridines **302**

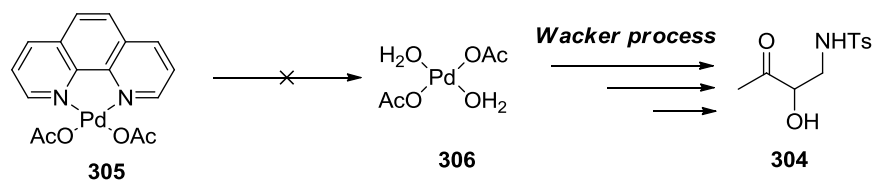
However, there is no example for the transition-metal-catalysed hydrolysis of vinylaziridines. Fortunately, this chance result provided a starting point for this topic (Scheme 74). Therefore, a palladium-catalysed hydrolysis of vinylaziridine **103** was studied as a side-project.

The first reaction was carried out in the presence of Pd(OAc)₂ (10 mol%), BQ (2.0 eq) in the co-solvent mixture (DMSO/H₂O) without acetic acid. As a result, **301** was isolated in a moderate yield (65%) at ambient temperature with no need of an inert atmosphere. However, a number of observable signals including a broad triplet (NH, 4.80 ppm), an apparent singlet (OHCHCOCH₃, 4.21 ppm), a pair of symmetric triplets (CH₂, 3.34-3.32 ppm and 3.30-3.26 ppm) and a singlet (Tosyl methyl, 2.36 ppm) in the ¹H NMR of crude reaction mixture suggest the generation of by-product **304** by the Wacker oxidation of **301**. The by-product **304** cannot be isolated without significant impurities, and it largely increased the difficulty of purifying **301** (Scheme 76).



Scheme 76: Generation of branched allylic alcohol **301**

To increase the yield of **301**, a series of reactions were performed under different conditions (Table 3). First of all, 2.0 equivalents of BQ were removed to prevent the Wacker process. Nevertheless, this only slightly increased the cleanness of the crude reaction mixture but reduced the isolated yield of **301** (56%) (entry 1, Table 3). Moreover, the observable by-product **304** was still present in the ^1H NMR of the crude reaction mixture presumably due to air oxidation. Next, it was found that the by-product **304** was largely removed when 15 mol% of phen was added as the ligand (entry 2). This may be because the bidentate 1,10-phenanthroline is a strong chelating ligand for the Pd(II) centre.¹¹⁶ The resulting complex **305** therefore has a rigid structure to inhibit the generation of the complex **306**, which is catalytically active for the Wacker process (Scheme 77).¹¹⁷ Additionally, phenanthroline-metal complexes have become attractive catalysts that can serve as a Lewis acid.¹¹⁸

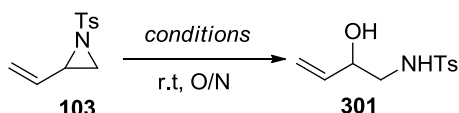


Scheme 77: The complex formed from phen and Pd(OAc)₂

Surprisingly, the yield was considerably improved to 89% when 2.0 equivalents of BQ was added to increase the acidity of Pd(II) centre in the presence of phen ligand.¹¹⁹ However, observable **304** was still present in the ^1H NMR of crude reaction mixture (entry 3). To minimise the amount of **304**, the loading of BQ decreased to 15 mol%, however, the yield was then considerably reduced to 58% (entry 4). Subsequently, PdCl₂ was used to replace Pd(OAc)₂, however, a relatively messy ^1H NMR of the crude reaction mixture was obtained if the phen was absent, and **304** was isolated in a 29% yield with some inseparable impurities but the desired product **301** was only isolated in a 15% yield (entry 5). BQ was considered as the major oxidant that participated in the Wacker process to produce **304**, therefore, BQ was removed in the next reaction. This resulted in a high yield (80%) for the desired product **301**, although the O₂-involved Wacker process still occurred to a slight extent (entry 6). Phen (15 mol%) was therefore added to inhibit the Wacker process, and the cleanness of the ^1H NMR of the crude reaction mixture was significantly improved; furthermore, **301** was isolated in an excellent yield (89%) (entry 7). The yield was only slightly increased when 15 mol% of BQ was added as an additive, but the cleanness of the crude reaction mixture decreased (entry 8). The

conditions shown in the entry 7 were considered to be promising, therefore, two reactions were performed with reduced catalyst and ligand loading based on the conditions in entry 7 (entries 9 and 10), and good yields of **301** were obtained in both reactions. Subsequently, the reaction proceeded smoothly without compromising in the cleanness of the crude reaction mixture even if the catalyst loading was reduced to 1 mol% (entry 11). A control reaction was also performed in the neat water, but only a low conversion (8%) was obtained (entry 12). The co-solvent mixture gave an increased conversion but with a 1:1 ratio of linear:branched products in the absence of the catalyst-system (entry 13). In conclusion, the catalyst loading could be reduced to 1 mol% without significant reduction in yield.

Table 3: Optimisation on hydrolysis of **103** to give branched allylic alcohol **301**



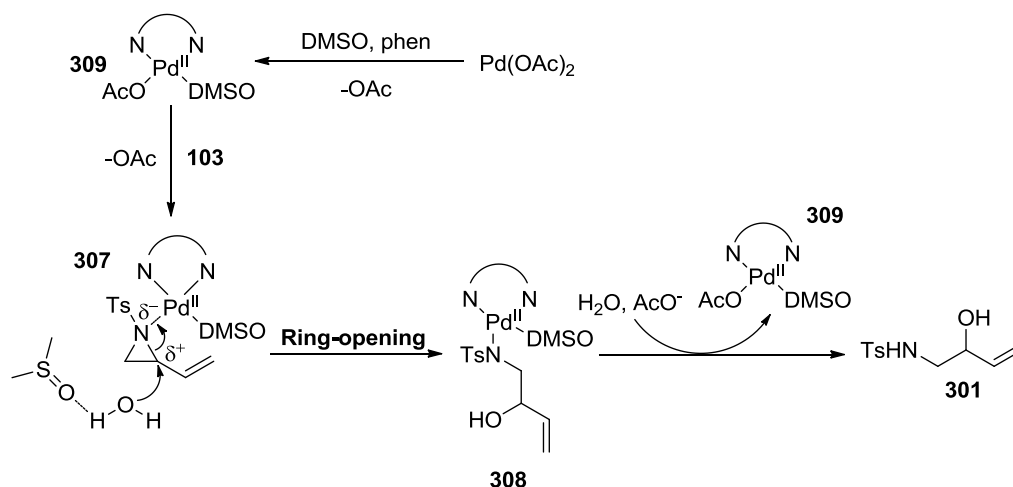
Entry	Conditions ^c	Yield (%)
1	Pd(OAc) ₂ (10 mol%), DMSO/H ₂ O (1:1, v/v)	56
2	Pd(OAc) ₂ (10 mol%), Phen (15 mol%) DMSO/H ₂ O (1:1, v/v)	62
3	Pd(OAc) ₂ (10 mol%), Phen (15 mol%), BQ (2.0 eq) DMSO/H ₂ O (1:1, v/v)	89
4	Pd(OAc) ₂ (10 mol%), Phen (15 mol%), BQ (15 mol%), DMSO/H ₂ O (1:1, v/v)	58
5	PdCl ₂ (10 mol%), BQ (2.0 eq), DMSO/H ₂ O (1:1, v/v)	15 ^d
6	PdCl ₂ (10 mol%),	80

	DMSO/H ₂ O (1:1, v/v)	
7	PdCl ₂ (10 mol%), Phen (15 mol%) DMSO/H ₂ O (1:1, v/v)	89
8	PdCl ₂ (10 mol%), Phen (15 mol%), BQ (15 mol%), DMSO/H ₂ O (1:1, v/v)	93
9	PdCl ₂ (5 mol%), Phen (7.5 mol%) DMSO/H ₂ O (1:1, v/v)	77
10	PdCl ₂ (2.5 mol%), Phen (4 mol%) DMSO/H ₂ O (1:1, v/v)	79
11	PdCl₂ (1 mol%), Phen (2 mol%) DMSO/H₂O (1:1, v/v)	88
12	H ₂ O	8 ^a
13^b	DMSO/H ₂ O (1:1, v/v)	80 ^a

^a Conversion. ^b 1:1 ratio of linear: branched products in crude reaction mixture. ^c Reactions were carried out under the air. ^d **304** was isolated in a 29% yield.

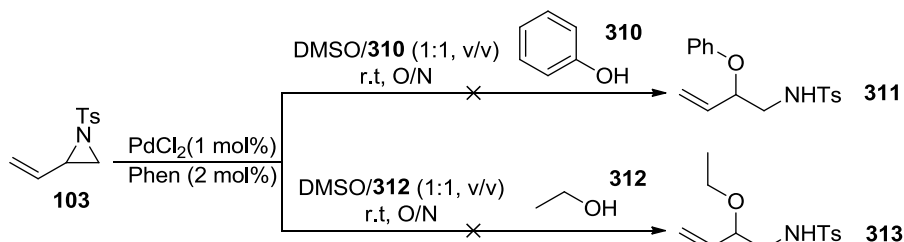
According to the experimental results (Table 3), a plausible key intermediate **307** was proposed to elucidate the branched selectivity in the hydrolysis of vinylaziridine **103**. Firstly, DMSO stabilises the cationic Pd(II)-centre by interacting with positive charges through the oxygen atom in DMSO.¹²⁰ The complex **309** is therefore formed in the presence of DMSO, phen and Pd(OAc)₂. The complex **309** then behaves as a Lewis acid and coordinates to the NTs group, polarising the C2-N bond of vinylaziridine **103** to create a partial positive charge at the C2-position. The ring-opening is then achieved with direct S_N2 nucleophilic attack of water molecule to give the complex **308**,¹²¹ followed by hydrolysis and dissociation of the desired product **301** with acetate to regenerate the

phenanthroline-Pd complex **309** (Scheme 78).



Scheme 78: The mechanism for Pd(II)-catalysed generation of **301**

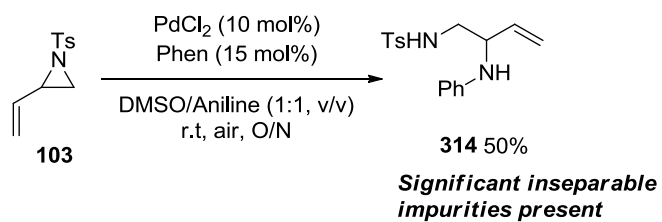
Additionally, phenol **310** and ethanol **312** were also used as the nucleophile. Unfortunately, no reactions occurred under the conditions in either case (Scheme 79).



Scheme 79: Ring-opening of vinylaziridine **103** with phenol **310** and ethanol **312**

Subsequently, aniline was utilised as an alternative *N*-based nucleophile to replace water in the reaction. The ^1H NMR of the product demonstrated a complete conversion of **103** to the branched product **314**, and the formation of **314** was evidenced by a multiplet (5.72-5.67 ppm) and two doublets (5.26 ppm and 5.19 ppm, respectively) associated with the vinyl group of **314**. In addition, a number of signals in the ^1H NMR of crude reaction mixture, including a doublet corresponding to the NH of aniline moiety in **314** (3.64 ppm), an apparent quartet associated with the aliphatic CH of **314** (3.91 ppm), a broad triplet corresponding to tosyl NH of **314** (3.55 ppm) and a pair of symmetric multiplets corresponding to the aliphatic CH_2 of **314** (3.20-3.13 ppm and 3.04-2.98 ppm, respectively), also suggest the formation of **314** in the reaction. However, **314** was isolated through

the column chromatography in only a moderate yield with significant inseparable impurities due to decomposition in the column (Scheme 80). The reaction scope was not investigated in this side-project due to time constraint although a promising result was obtained.



*Scheme 80: Ring-opening of vinylaziridine **103** by aniline*

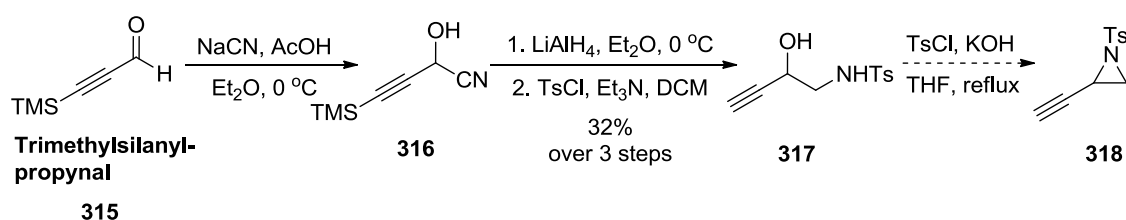
Summary

In summary, the Pd(II)-catalysed addition of arylboronic acids to *N*-tosyl-2-vinylaziridine **103** to yield a series of unusual *cis*-allylic sulfonamides as major products has been demonstrated, and the resultant allylic sulfonamides are potentially synthetically useful precursors for the synthesis of nitrogen-containing bioactive molecules.¹²² Moreover, the unusual *Z*-selectivity highlights the reaction to be an intriguing complementary strategy to the related reactions catalysed by Pd-pincer complexes (Scheme 64). Notably, the procedure does not require rigorous inert atmosphere and utilises a commercially available Pd(OAc)₂ catalyst in combination with an air stable nitrogen-containing ligand (phen), which largely increases the practicality of this reaction. In addition, a branched allylic alcohol **301** was given in an excellent yield by the hydrolysis of vinylaziridine **103** in the presence of a simple Pd(II)-catalyst system with very low loading (1 mol%). Although the aniline effectively gave a 100% conversion of **103** to the corresponding product **314** under the same conditions, **314** was isolated in only a moderate yield with significant inseparable impurities as **314** was decomposed in the column. This final result suggests the scope of ring-opening may be limited, but in future work the hydrolysis of other aziridines should be investigated.

Future Plans

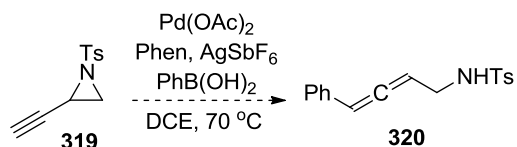
The Pd(0)/Pd(II)-catalysed ring-opening of 2-ethynyl-1-tosylaziridine

The Pd(II)-catalysed addition of boronic acids to vinylaziridines has been developed in this chapter. In the next stage, 2-ethynyl-1-tosylaziridine **318**, which has not been previously investigated for its reactivity in such ring-opening reactions, could be utilised in the future in order to obtain allenic products. Firstly, a route to synthesise this less developed substrate was proposed (Scheme 81).



*Scheme 81: Proposed synthetic route for 2-ethynyl-1-tosylaziridine **318***

According to the synthesis developed by the Padron group, amino alcohol **316** could be prepared *via* a 2-step method utilising trimethylsilanyl-propynal **315**.¹²³ It was envisioned that the subsequent ring-closure may be realised in the presence of TsCl and KOH, which has been reported by the Craig group and the Ghorai group to make enantiopure aziridines.¹²⁴

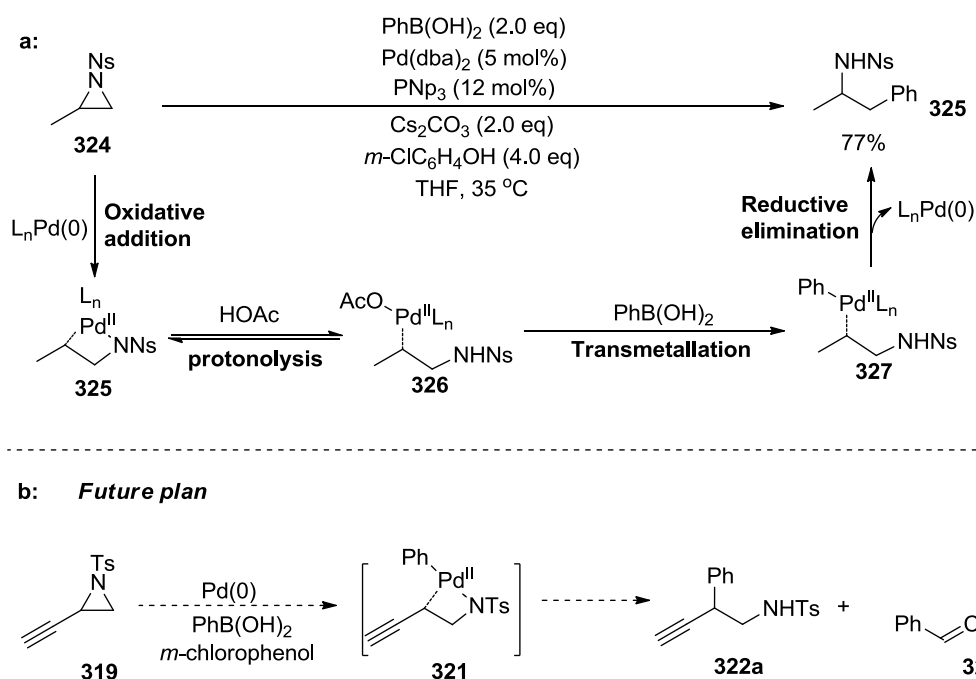


*Scheme 82: Possible reactions based on 2-ethynyl-1-tosylaziridine **319***

Two reaction pathways for the reactivity of **319** can be envisioned. Firstly, the ring-opening reaction of **319** will be performed with phenylboronic acid in the presence of the Pd(II)-system that was developed in this chapter. A sulfonamide **320** containing allene moiety is expected to be generated *via* the pathway shown in Scheme 82. In addition, Michael and co-workers developed the Pd(0)-catalysed cross-coupling of *N*-sulfonylaziridines **324** with boronic acids, and the

azametallacycle **325** was proposed as the key intermediate resulting from the oxidative addition of aziridine **324** to Pd(0) (Scheme 83a). After protonolysis of **325** with *m*-chlorophenol additive, transmetallation of the boronic acid and reductive elimination of **327** generate the product **325**. The presence of *m*-chlorophenol additive is crucial as it may minimise the lifetime of two intermediates to prevent β -H elimination by controlling the protonolytic equilibrium and the rate of transmetallation.

Thus, it is possible that the same type of intermediate **321** could be generated by oxidative addition of **319**, and **321** is able to undergo protonolysis and transmetallation, followed by the reductive elimination to release the final compound **322** in the presence of *m*-chlorophenol additive (Scheme 83b). This intriguing issue of regioselectivity would be an interesting topic of investigation that has not yet been explored in methods that involve direct oxidative addition to aziridines by low-valent transition metals and could lead to either alkyne **322a** or allene **322b**.

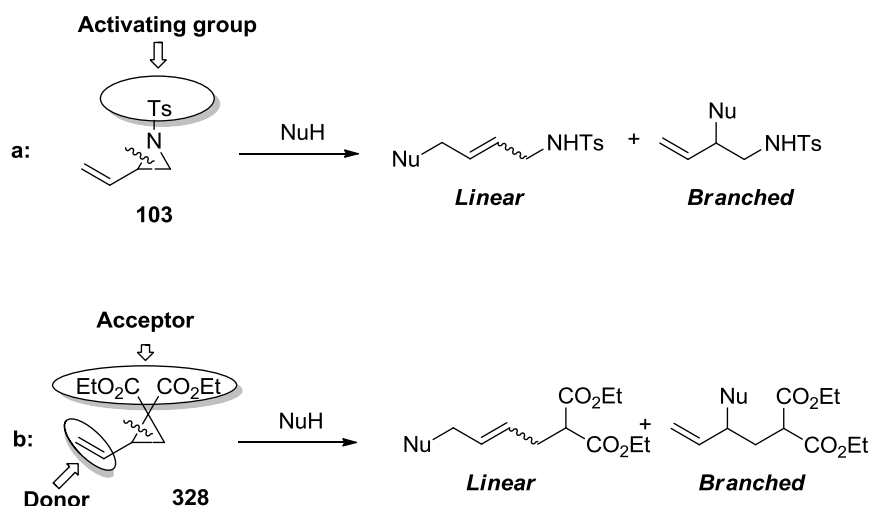


Scheme 83: Pd(0)-catalysed cross-coupling of *N*-sulfonylaziridines with boronic acids

Chapter 3. Ring-Opening of Vinylcyclopropane-1,1-dicarboxylates by Boronic Acids under Ligandless Palladium Catalysis in Neat Water

Introduction

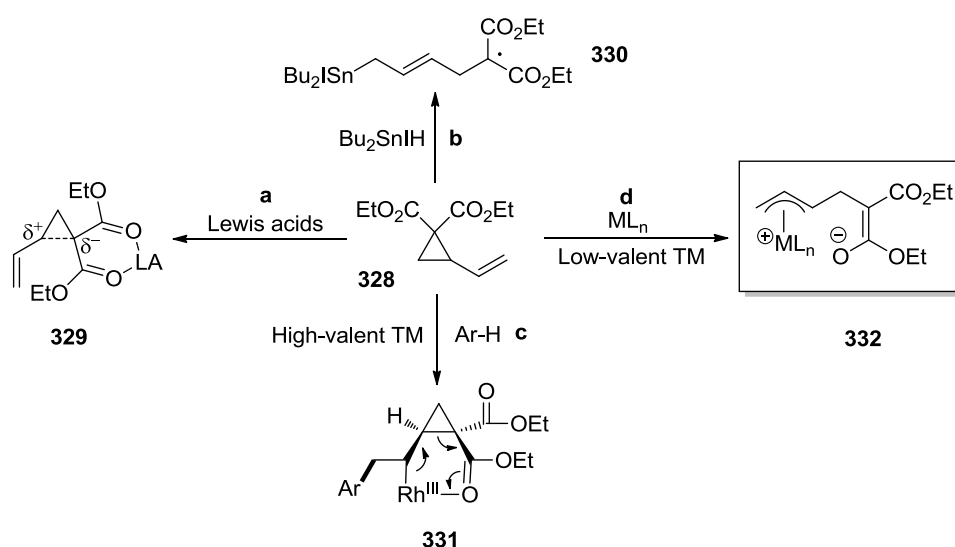
In this chapter, research focused on strained donor-acceptor vinylcyclopropane-1,1-dicarboxylates **328**, which are carbon analogues of vinylaziridine **103** investigated in chapter 2. The vicinally positioned donor vinyl group and acceptor dual CO₂Et groups are installed at the C1 and C2-positions of the 3-membered ring **328**. It has been previously mentioned in chapter 2 that C-N bond breaking of **103** could be achieved in the presence of transition metal-catalysts, and this process is facilitated by the electron-withdrawing *N*-activating groups such as tosyl (Scheme 88a). The C1-C2 bond breaking of **328** can be cleaved similarly with the facilitation of donor (vinyl) and acceptor groups (CO₂Et) (Scheme 84b).



Scheme 84: C-N bond cleavage of **103** and similar C-C bond cleavage of **328**

Generally, there are four pathways to achieve ring-opening of the donor-acceptor vinylcyclopropane **328** with activating agents (Scheme 85).¹²⁵⁻¹²⁶ They are: a) Lewis acid-catalysed C-C bond cleavage of **328**; b) radical chain pathway initiated by organotransition metal reagents such as Bu₂SnIH; c) ring-opening *via* rhodacycle **331** resulting from a high-valent Rh(III) catalyst; d) and

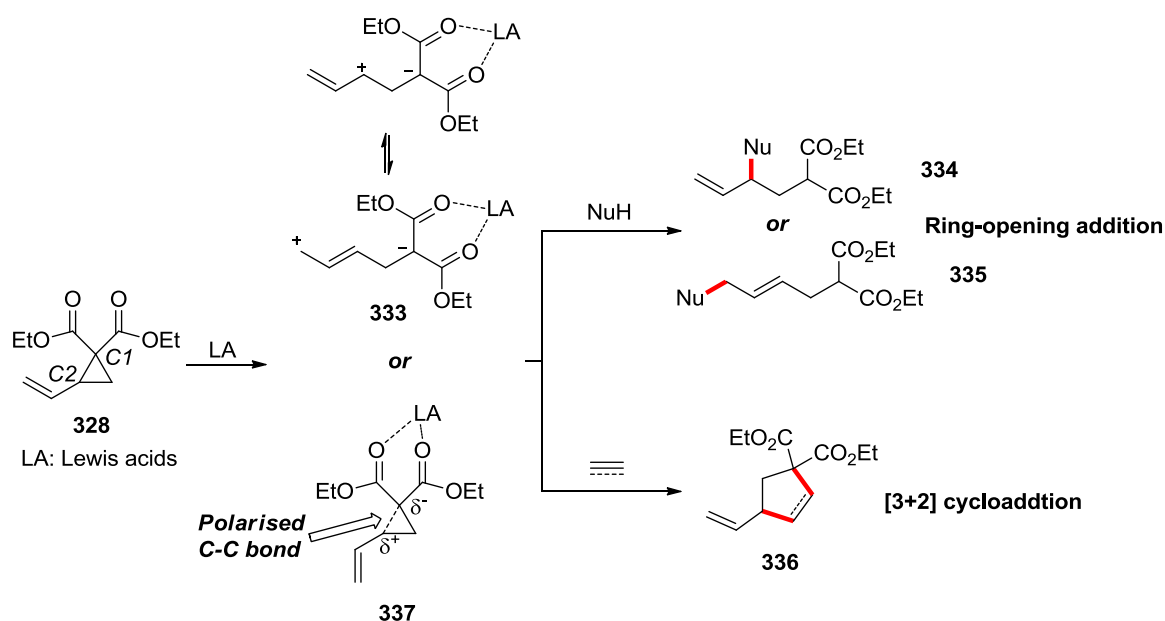
formation of the η^3 allyl-metal complex **332** as a result of low-valent transition metal catalysts. This last process is of primary interest in this chapter. Linear or branched adducts are generated *via* these pathways with various nucleophiles (Scheme 85). Each mode of activation will now be discussed in detail.



Scheme 85: C-C bond activation of vinylcyclopropane **328** in the presence of activating agents

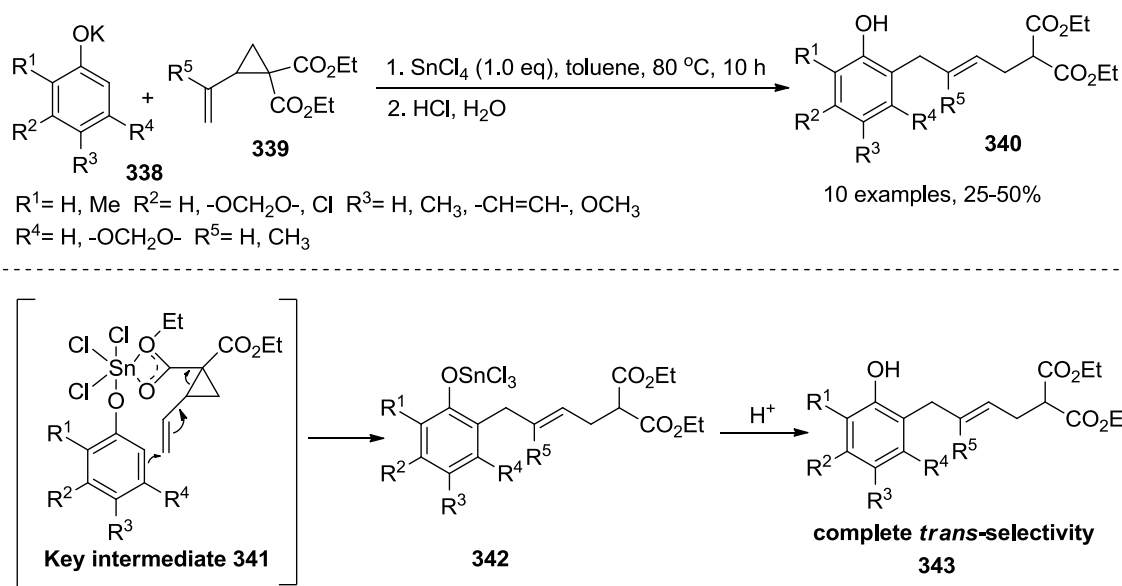
Lewis Acid-Catalysed C-C Bond Breaking of Vinylcyclopropanes

Firstly, in the Lewis acid-catalysed reactions **a**, vinylcyclopropane-1,1-dicarboxylates **328** could be activated by the Lewis acid, undergoing favourable two-point coordination to the geminal diester (Scheme 86). This activating process leads to polarisation in the vicinal $\text{C1}(\text{sp}^3)\text{-C2}(\text{sp}^3)$ bond of **328**,¹²⁷ alternatively, heterolytic ring-opening of the cyclopropane ring occurs to give a reactive 1,3-dipole **333**. Subsequently, linear **335** or branched adduct **334** can therefore be produced with a nucleophile in the presence of **333**, (Scheme 86a), or a cyclic structure **336** can be generated through a formal [3+2] cycloaddition of dipolarophiles such as alkenes or alkynes (Scheme 86b).¹²⁸



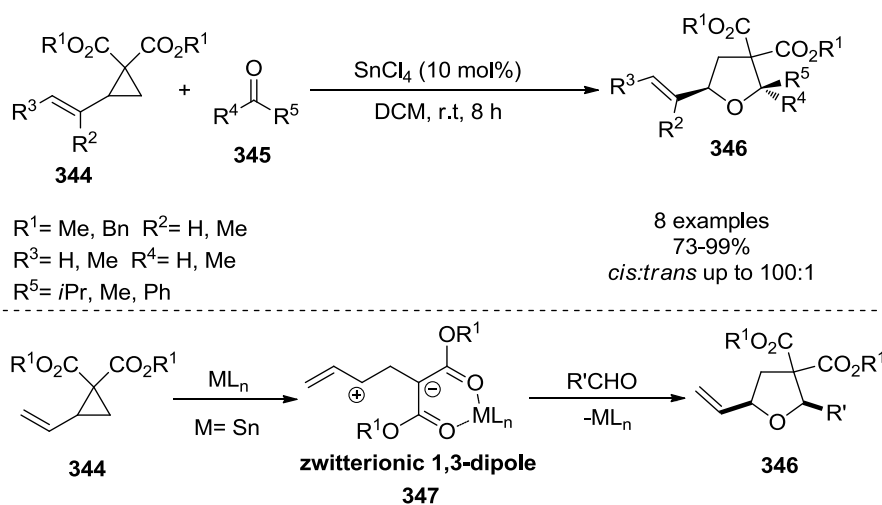
Scheme 86: Lewis acid-catalysed C-C bond breaking of vinylcyclopropanes **328**

An early example of Lewis acid-promoted ring-opening of vinylcyclopropanes **339** comes from Sartori and co-workers in 1983 who carried out a Friedel–Crafts reaction in the presence of a stoichiometric amount of SnCl_4 (Scheme 87). Potassium phenoxides were treated with vinylcyclopropanes **339** in toluene at 80°C for 10 h, yielding a series of *trans*-ethyl 6-(2-hydroxyphenyl)-2-carbethoxy-4-hexenoates **340** as major products in low to moderate yields.¹²⁹ The hexacoordinate adduct **341** resulting from coordination of the acid metal ion to oxygen atoms of both reactants directs the less-hindered terminus of the vinyl group to attack at the *ortho*-position during the C1sp^3 - C2sp^3 bond breaking of vinylcyclopropane **339**. This regioselectivity is because the terminal position of the vinyl moiety favours the attack, being held in close proximity to the *ortho*-position of phenoxide **338**.



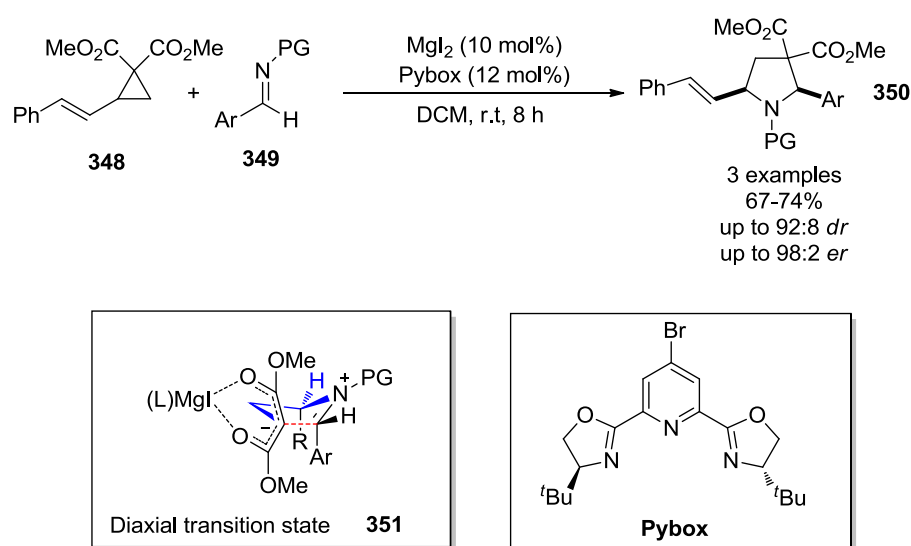
Scheme 87: SnCl_4 -catalysed reaction of potassium phenoxides with vinylcyclopropanes **339**

A major drawback of this reaction is the stoichiometric use of SnCl_4 , which is required to achieve only a relatively low yield of the products. In 2008, the Johnson group utilised catalytic amount of SnCl_4 to carry out a [3+2] cycloaddition of aldehydes/ketones **345** and donor-acceptor vinylcyclopropanes **344** (Scheme 88), affording a variety of biologically important substituted tetrahydrofurans **346**.¹³⁰ The achiral zwitterionic 1,3-dipole **347** is generated from the oxygen atoms of acceptor groups to the acidic tin centre, and the vinyl moiety serves as a donor group to stabilise the partially positive charge on the 1,3-dipole (Scheme 86).



Scheme 88: Lewis acid-catalysed cycloadditions of D-A cyclopropanes **344** with aldehydes and ketones **345**

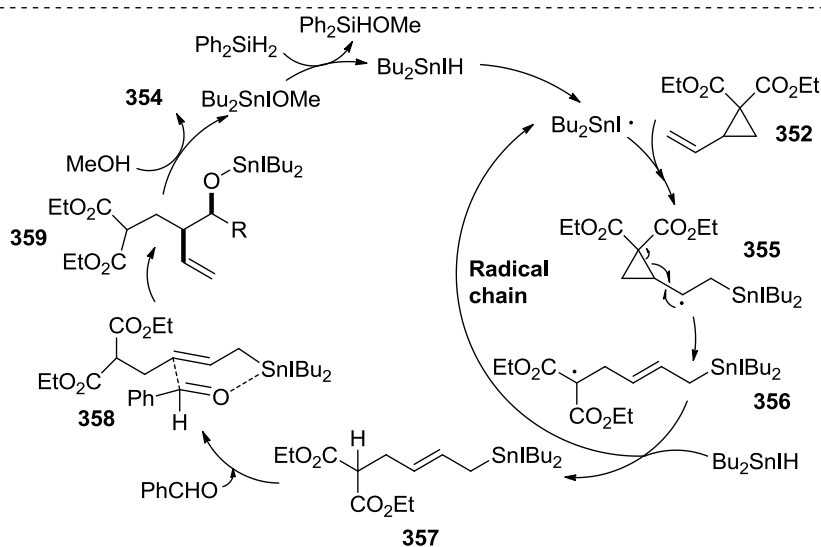
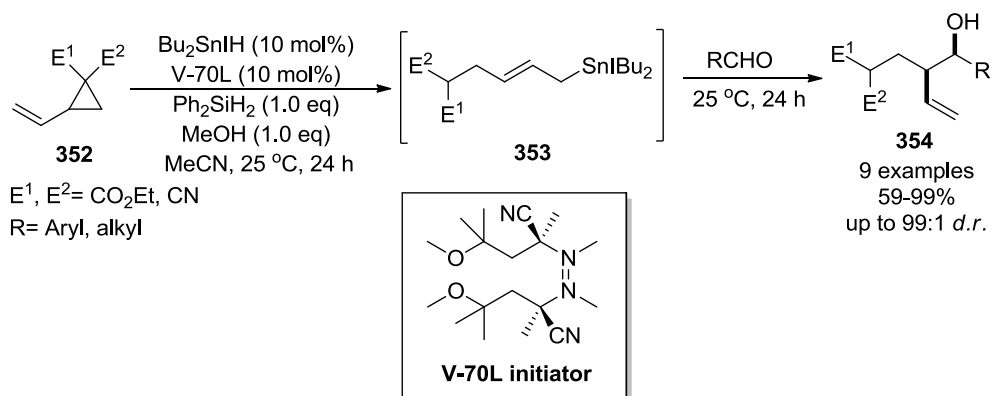
Moreover, the Johnson group provided some examples for the Lewis acid-catalysed dynamic kinetic asymmetric [3+2] cycloaddition of substituted vinylcyclopropanes **348** with aldimines **349** (Scheme 89).¹³¹ In this reaction, 2,5-*cis*-disubstituted pyrrolidines **350** were enantioselectively prepared in the presence of catalytic MgI₂ and a pybox ligand in good yields from racemic substituted vinylcyclopropanes. The least sterically hindered diaxial transition state **351** resulting from *E*-aldimine dipolarophiles was proposed to account for the *cis*-selectivity of the reaction, and an fast and competitive substrate racemisation relative to annulation was found to lead to the high enantioenrichment of the product **350**.



Scheme 89: Asymmetric [3+2] cycloaddition of substituted vinylcyclopropane **348** with aldimines **349**

C-C Bond Breaking of Vinylcyclopropanes *via* the Radical Chain Pathway

A radical chain pathway **b** has been established with radical initiators, such as Bu₂SnIH to open vinylcyclopropanes (Scheme 89b). Recently, the Shibata group reported a coupling reaction of donor-acceptor vinylcyclopropanes **352** with aldehydes catalysed by tin hydride-Bu₂SnIH (Scheme 94).¹³² The reaction shows that Bu₂SnIH is able to effectively promote the hydrostannation of vinylcyclopropanes **352**, and the resulting allylic tin compound **353** smoothly reacts with aldehydes to give a series of homoallyl alcohols **354** in excellent diastereoselectivities. The presence of radical initiator V-70L in the reaction was essential to maintain the high yields of the products, and no reaction was observed without the tin catalyst.



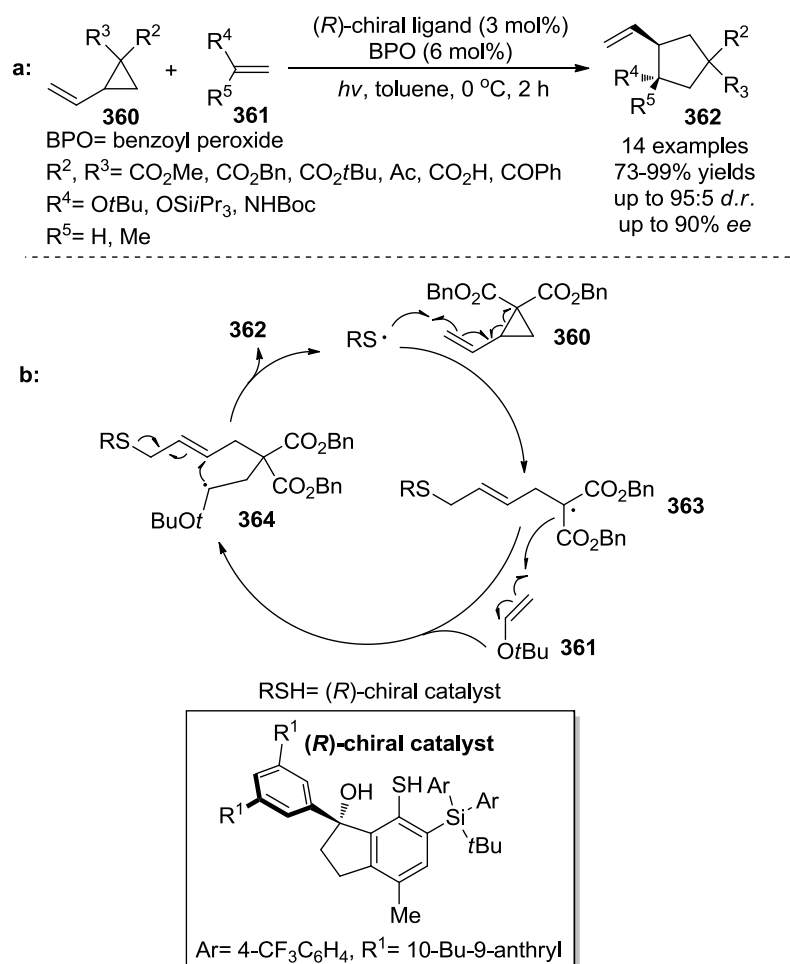
Scheme 90: Coupling reaction of vinylcyclopropanes **352** with aldehydes catalysed by tin hydride

A plausible catalytic cycle for the reaction was proposed (Scheme 90). Initially, the di-*n*-butyliodotin radical ($\text{Bu}_2\text{ISn}^\cdot$) generated *in situ* adds to the terminus of vinylcyclopropanes **352**, yielding the cyclopropylmethylene radical **355**. Next, the subsequent regioselective ring cleavage occurs from a hindered position to give a homoallyl radical **356** possessing a stable *trans*-configuration, which reacts with Bu_2SnIH to the *trans*-allylic tin **357** and regenerate the di-*n*-butyliodotin radical. The resultant *trans*-allylic tin radical **357** subsequently reacts with benzaldehyde *via* transition state **358** to afford the *threo*-homoallyl tin alkoxide **359**, followed by the rate-determining protonation with MeOH to release the product **354** and the tin methoxide. Finally, the Ph_2SiH_2 reacts with the tin methoxide to regenerate Bu_2SnIH .

Although the excellent diastereoselectivity was obtained (Scheme 90), enantiospecific coupling reactions occurring *via* a radical chain pathway still lack investigation. To address this, the Maruoka group has shown for the first time that the organic thiyl radical catalyst can promote the asymmetric

radical ring-opening process of vinylcyclopropanes **360** (Scheme 91).¹³³ A series of highly enantioenriched 5-membered ring systems **362** were synthesised in the reaction in good to excellent yields with high diastereoselectivities. This C–C bond-forming radical cyclisation was successfully developed with a chiral thiol precatalyst possessing a chiral pocket, which has a unique functionality that is capable of directly giving a radical in a vinylcyclopropane to promote the radical C–C bond formation (Scheme 85b).

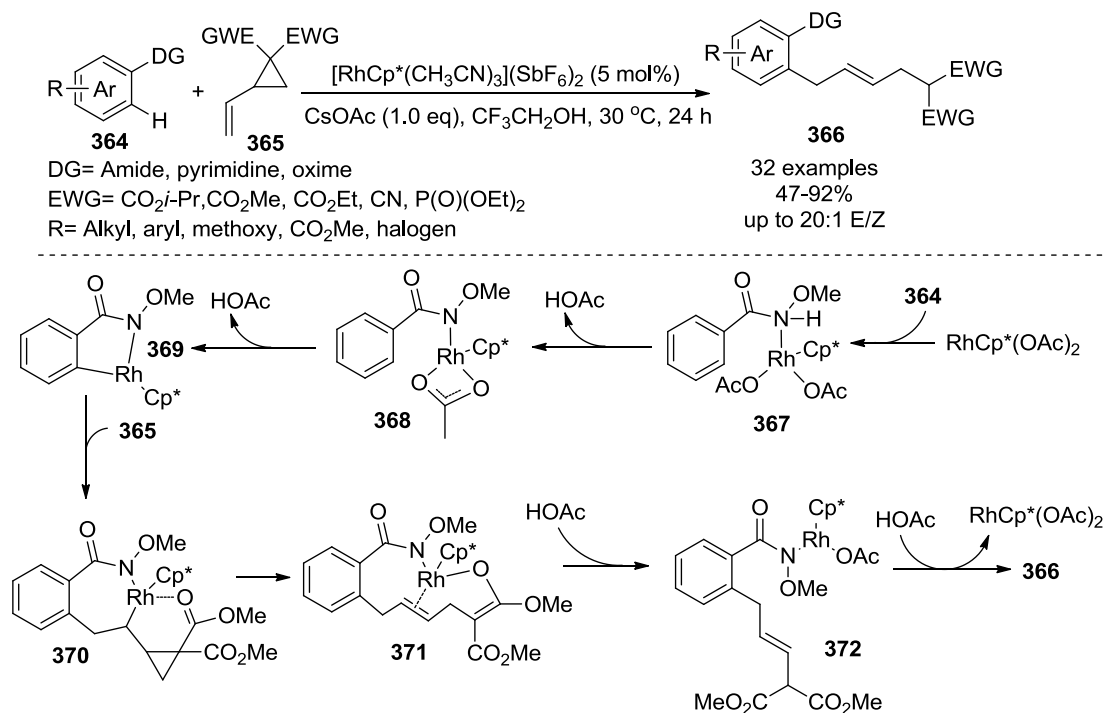
Mechanistically, it was proposed that the radical C–C bond formation initiates with photolytic generation of the thiyl radical from the corresponding sulfide. The subsequent radical transfer is believed to follow the Beckwith–Houk model^{134–135} and occurs to preferably release the favoured *trans*-isomer **362** in the presence of benzoyl peroxide (BPO) as an oxidant (Scheme 91b). Furthermore, the excellent diastereoselectivity was not diminished by a thiyl radical-mediated hydrogen abstraction after this radical cyclisation.



Scheme 91: An organic thiyl radical catalyst for enantioselective cyclisation

Ring-Opening of Vinylcyclopropanes *via* Rhodacycles

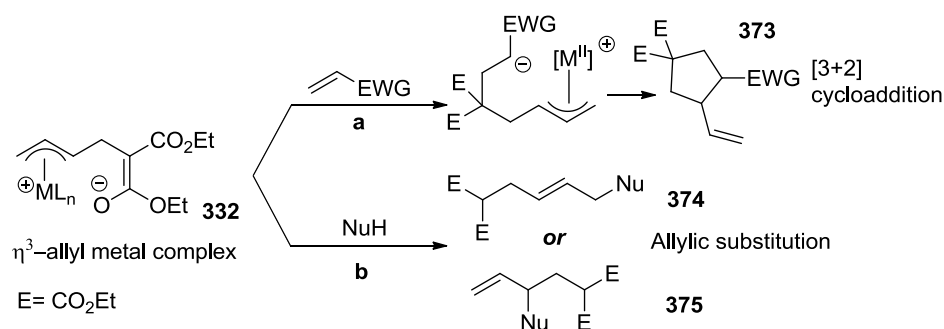
High-valent transition metals have demonstrated excellent capacity for activating C-H bond for the construction of C-C and C-heteroatom bonds.¹³⁶ This aspect has been harnessed for ring-opening of vinylcyclopropanes with C-H aryl systems. Among a variety of transition metals, a Rh(III) catalyst was selected to achieve a rhodacycle **331** due to its advantage of high catalytic efficiency, mild reaction conditions and a broad substrate scope in C-H activation of arenes (Scheme 85c).¹³⁷ Ring-opening of vinylcyclopropanes *via* rhodacycles has great potential for exploration as it is under investigated. Wang and co-workers demonstrated a sole example for the catalytic activity of Rh^{III} in a sequential C-H activation and the C-C activation reaction. Aryl systems **364** bearing a directing group, such as amide, pyrimidine and oxime reacted with various vinylcyclopropanes **365** to give a variety of *trans*-ring-opening products **366** in moderate to excellent yields with excellent diastereoselectivities. Mechanistically, after the formation of the rhodacycle **370** *via* C-H activation, the β -carbon elimination may occur to relieve the ring strain. The resulting allylated arenes **366** could be used to synthesise some valuable building blocks.¹³⁸ The alkene insertion step, followed by the β -carbon elimination, has been identified as the rate-determining step (Scheme 92).



Scheme 92: Rhodium(III)-catalysed C-H/C-C activation sequence

Ring-Opening of Vinylcyclopropanes via η^3 -Allyl Transition Metal Complexes

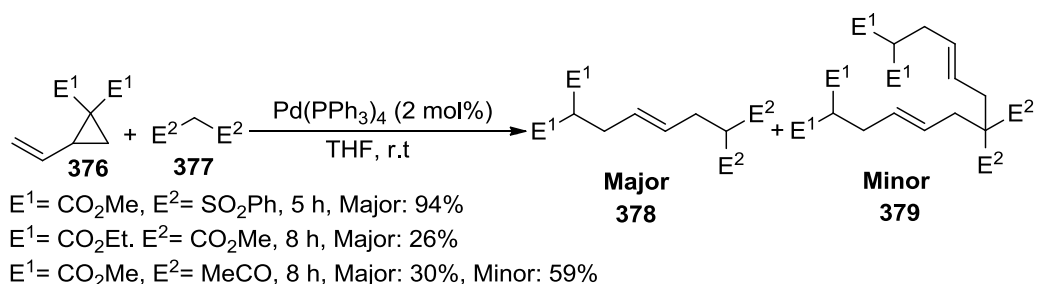
Low-valent transition metals (TM) can activate vinylcyclopropanes *via* the oxidative addition to form the electrophilic η^3 -allyl transition metal complexes **332** (Scheme 85d). This process is energetically favorable due to the formation of an allyl-metal bond in the zwitterionic π -allyl metal intermediate, and the relief of ring-strain is a partial driving force of the ring-opening process (*ca.* 28 kcal.mol⁻¹).¹³⁹ Therefore, vinylcyclopropanes have been utilised in the low-valent TM-catalysed cycloaddition reactions and allylic substitution with various nucleophiles (Scheme 93).



Scheme 93: Two pathways for ring-opening of vinylcyclopropane via the π -allyl-metal complex **332**

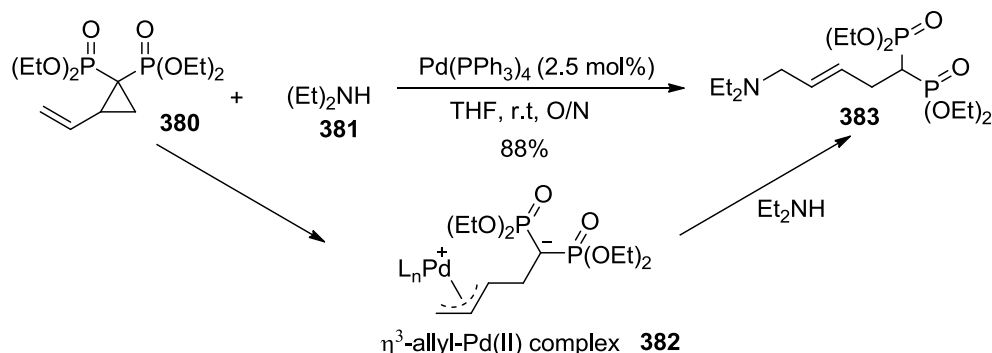
In the cycloaddition reaction (Scheme 93a), the key zwitterionic π -allyl metal intermediate **332** results in a 5-membered ring structure **373** *via* formal [3+2] cycloaddition (Scheme 93a).¹⁴⁰ In addition, a linear **374** or branched adduct **375** could be generated *via* the S_N2 or S_N2' nucleophilic attack on vinylcyclopropanes in the presence of low-valent transition metals. This reaction is generally limited to moisture sensitive organometallics and soft nucleophiles such as malonates (Scheme 93b).

The first reported nucleophilic ring-opening reaction of activated vinylcyclopropanes **376** was developed by Burgess in 1985 (Scheme 94). The zwitterionic π -allyl metal intermediate **332** was initially generated from the ring-opening of a donor-acceptor vinylcyclopropane **376** in the presence of catalytic Pd(PPh₃)₄, followed by nucleophile trapping with various active methylenes **377** such as malonates, 1,3-diketones and bis(phenylsulfonyl) methane to give a series of adducts **378**. However, in some cases, further deprotonation of the mono-alkylated product occurred to furnish the di-alkylated product **379** *via* the nucleophilic attack towards the vinylcyclopropane **376**.¹⁴¹



Scheme 94: Conjugate nucleophilic ring-opening of activated vinylcyclopropanes **376**

An increasing number of nucleophiles were utilised for ring-opening addition of vinylcyclopropanes. For example, Moreau and co-workers reported a regio- and stereoselective Pd(0)-catalysed ring-opening reaction of readily available tetraethyl 2-vinyl-1,1-cyclopropane bisphosphonate **380** with secondary amines **381** to synthesise a series of allylic amines **383** in excellent yields with complete stereoselectivities (Scheme 95).¹⁴² The reaction likely proceeds with the initial generation of an $\eta^3 \pi$ -allyl-Pd(II) complex **382** and subsequent nucleophilic attack from a secondary amine **381** to the less sterically hindered position of the intermediate. The resulting geminal bisphosphonates **383** and their derivatives display some interesting pharmacologically activities, such as binding to bone minerals and inhibiting the resorption of living bone.¹⁴³



Scheme 95: Pd(0)-catalysed synthesis of amino alkenyl geminal bisphosphonates **383**

Very recently, the scope of nitrogen-based nucleophiles in the ring-opening of donor-acceptor vinylcyclopropanes was extended to *N*-heterocycles such as purines by the Guo group.¹⁴⁴ Dual nucleophilic sites of purines (N9 and N7) allowed a diversity-oriented synthesis of acyclic nucleosides, which have attracted considerable interest as a variety of acyclic nucleosides such as acyclovir **384**, ganciclovir **385**, penciclovir **386** and famciclovir **387** have been identified as anti-HIV

agents (Figure 8).¹⁴⁵

Firstly, a series of vinylcyclopropanes **389** with different ester groups were subjected to the S_N2' -type ring-opening reaction (1,5-ring-opening) with purines **388** in the presence of catalytic $Pd_2(dba)_3 \cdot CHCl_3$ and DIOP ligand, affording N9 adducts **390** as the major products in moderate to excellent yields with exclusive *trans*-selectivity. As indicated in Scheme 85d, the electrophilic allyl-Pd(II) intermediate **C4** generated from the oxidative addition of vinylcyclopropanes **389** to $Pd_2(dba)_3 \cdot CHCl_3$ was proposed (Scheme 96a). A relatively rare 1,3-ring-opening reaction of vinylcyclopropanes **389** proceeding *via* an S_N2 pathway was observed if a stoichiometric amount of the Lewis acid ($AlCl_3$, 1.0 eq) was utilised. Therefore, a number of branched N9 adducts **391** were synthesised in low to good yields (Scheme 96b). The same 1,3-ring-opening was achieved with a catalytic amount of MgI_2 , however, N7 rather than N9 substitution regioselectively occurred in this case (Scheme 96c). It should be realised that reaction **b** and **c** are mechanistically different from reaction **a**. As a result of coordination of the bidentate vinylcyclopropane **389** and N3 in the 6-chloropurine to aluminium centre, reaction **b** proceeds with 1,3-ring-opening since the N9 position is close to the C3-position in vinylcyclopropane **389** (Scheme 96). Similarly, the coordination of the bidentate vinylcyclopropane **389** and bidentate N3, N9 in 6-chloropurine to Mg gives a complex with octahedral geometry, causing attack from the uncoordinated N7 position to C3 in the vinylcyclopropane to give the N7-adduct **392** (Scheme 96c). Both key intermediates **393** and **394** indicate that the two reactions involving $AlCl_3$ and MgI_2 respectively are catalysed by Lewis acids, and they are complementary examples that enrich the Lewis acid-catalysed ring-opening reactions of donor-acceptor vinylcyclopropanes (Scheme 85a).

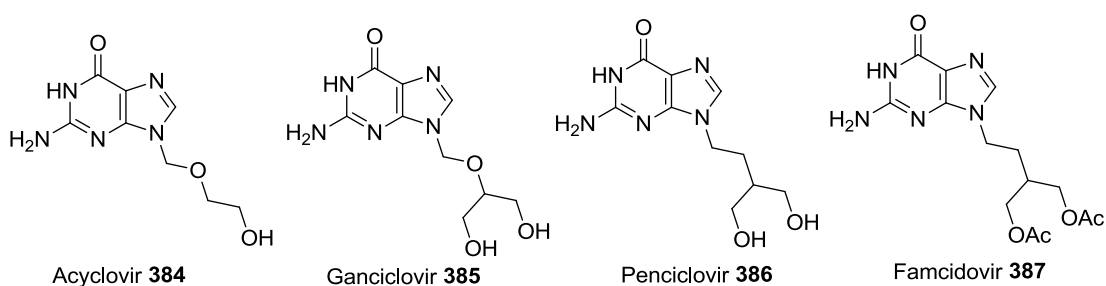
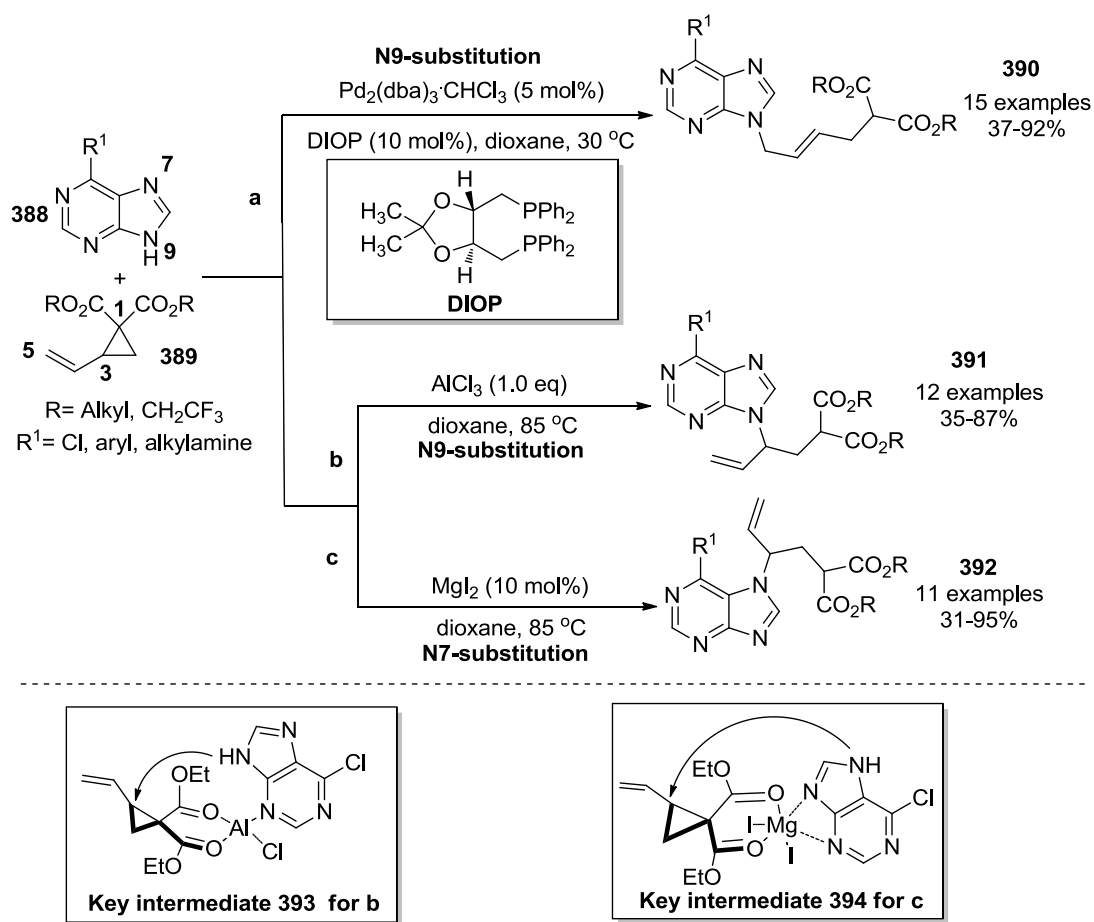
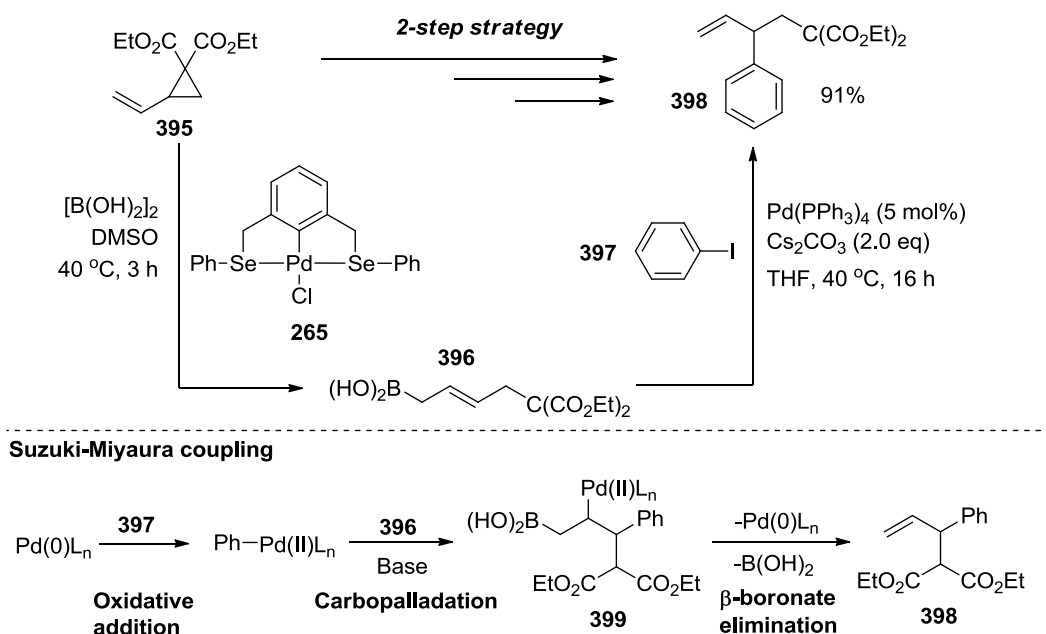


Figure 8: Representative acyclic nucleosides approved by FDA as anti-HIV agents



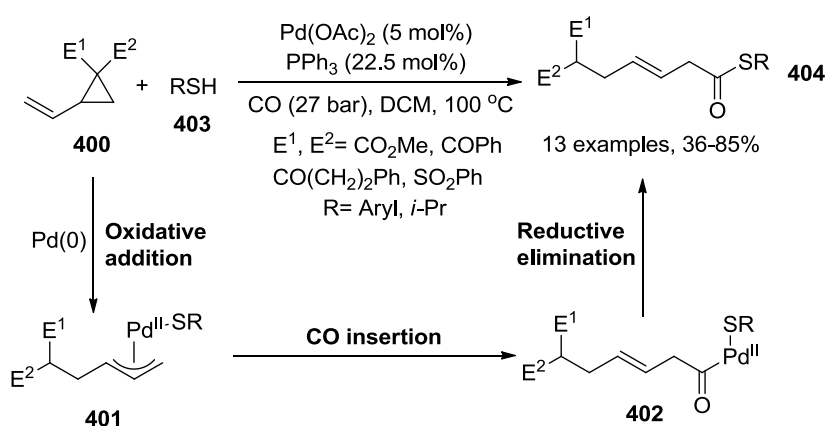
Scheme 96: Diversity-oriented synthesis of acyclic nucleosides via ring-opening of vinyl cyclopropanes with purines

All Pd-catalysed examples above produced the linear structures as the major product (Schemes 94-96), however, Szabo and co-workers synthesised branched products **398** via a 2-step strategy involving a Pd(II)-pincer complex **268** and a Pd(0) catalyst (Scheme 97).¹⁴⁶ The *trans*-allylic boronic acids **396** were first generated *and then* subjected to the conditions of the Suzuki-Miyaura coupling. This coupling reaction is initiated by oxidative addition of **397** to the Pd(0)-catalyst, followed by a highly regioselective carbopalladation process with **396** to give intermediate **399**. Subsequent elimination of the palladium boronate occurs to give a branched product **398** in an excellent yield with an almost absolute regioselectivity. It is of note that this sequence *does not* proceed via an (η^3 -allyl)palladium intermediate.



Scheme 97: Palladium-catalysed coupling of allylboronic acids **396** with iodobenzene **397**

The utility of the palladium(0)-catalysts was then further demonstrated by the synthesis of sulfur compounds **404** via the carbonylative ring-opening addition of vinylcyclopropanes **400** (Scheme 98). Alper and Xiao developed a thiocarbonylative ring-opening of donor-acceptor vinylcyclopropanes **400** with thiols **403** and carbon monoxide in the presence of $\text{Pd}(\text{OAc})_2$ and PPh_3 (Scheme 98).¹⁴⁷ The catalytically active $\text{Pd}(0)$ species is generated *in-situ* in the reaction.

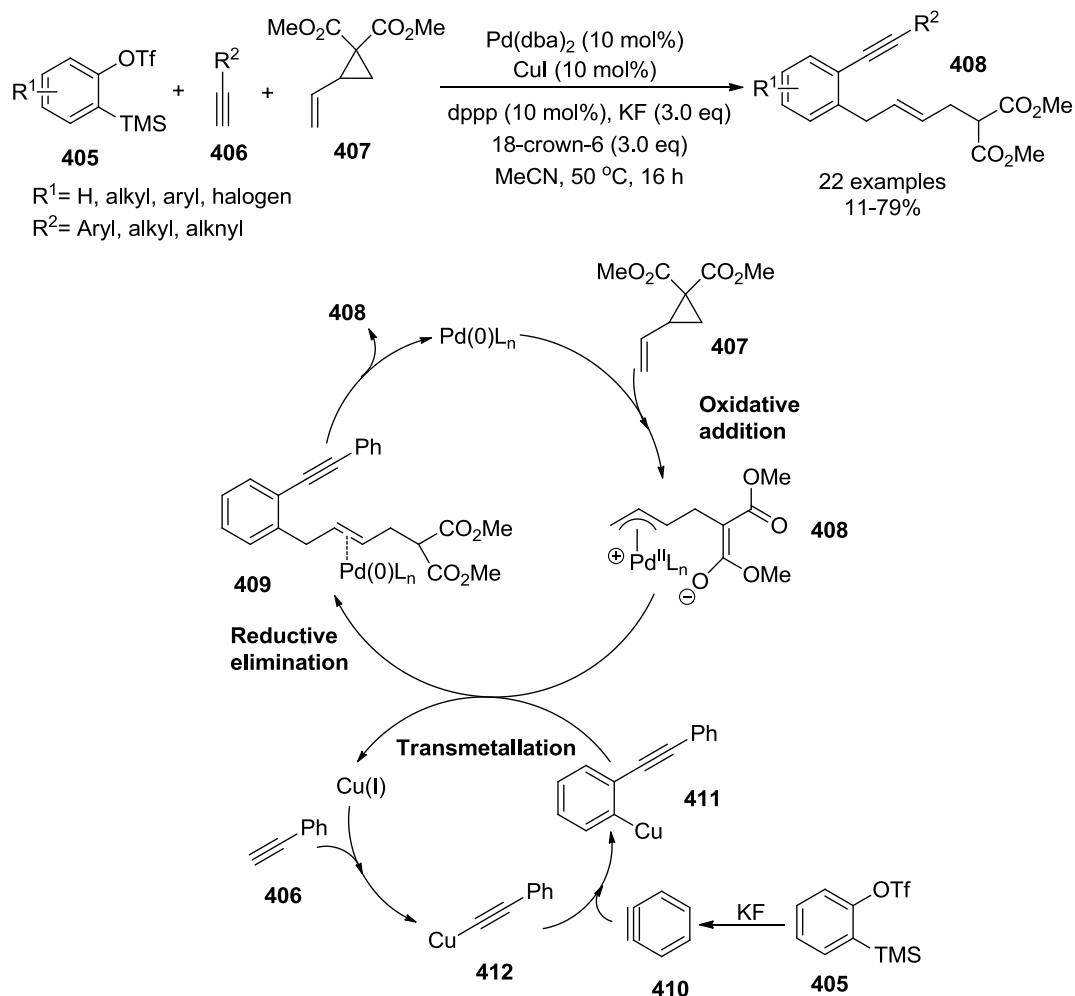


Scheme 98: Pd-catalysed thiocarbonylative ring-opening of vinylcyclopropanes **400** with thiols **403**

Mechanistically, the oxidative addition of the vinylcyclopropane to the *in situ*-generated $\text{Pd}(0)$ species gives an η^3 π -allyl- $\text{Pd}(\text{II})$ complex **401**, followed by CO insertion to give an acylpalladium

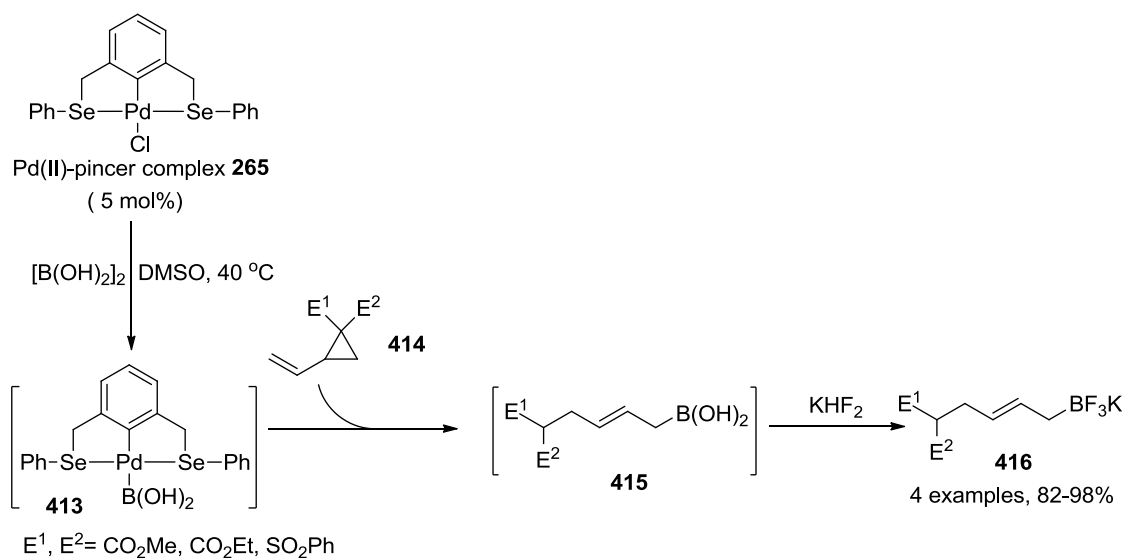
complex **402**. It should be noted that CO insertion is faster than subsequent reductive elimination. Reductive elimination then occurs to form the thioester and regenerate the Pd(0)-catalyst. The reaction has shown broad functional group tolerance as a range of aryl, heteroaryl, as well as alkyl thiols were involved into the reaction scope. However, it should be noted that isomerisation of the thiocarbonylation to the conjugated thioesters was observed to some extent in most cases.

A dual catalyst system was utilised by the Werz group for developing a Pd(0)-catalysed three-component coupling involving *in situ*-generated arynes **410**, terminal alkynes **406**, and vinylcyclopropanes **407** (Scheme 99).¹⁴⁸ The reaction starts with generation of the copper acetylide **412**, resulting from the deprotonation of a terminal alkyne **406** using a stoichiometric amount of KF and CuI. The *in situ*-generated benzyne **410**¹⁴⁹ then reacts with the nucleophilic copper acetylide **412** to afford the reactive nucleophilic aryl copper intermediate **411**. Simultaneously, the Pd(0)-catalyst participates in the reaction to activate the vinylcyclopropane **407** to form the electrophilic η^3 π -allyl-palladium complex **408**. The transmetallation subsequently occurs between the nucleophilic copper intermediate **411** and this π -allyl-palladium complex **408**, followed by reductive elimination to give the π -complex **409**. Therefore, the desired coupling product **408** is dissociated from the palladium centre to regenerate the active palladium catalyst.



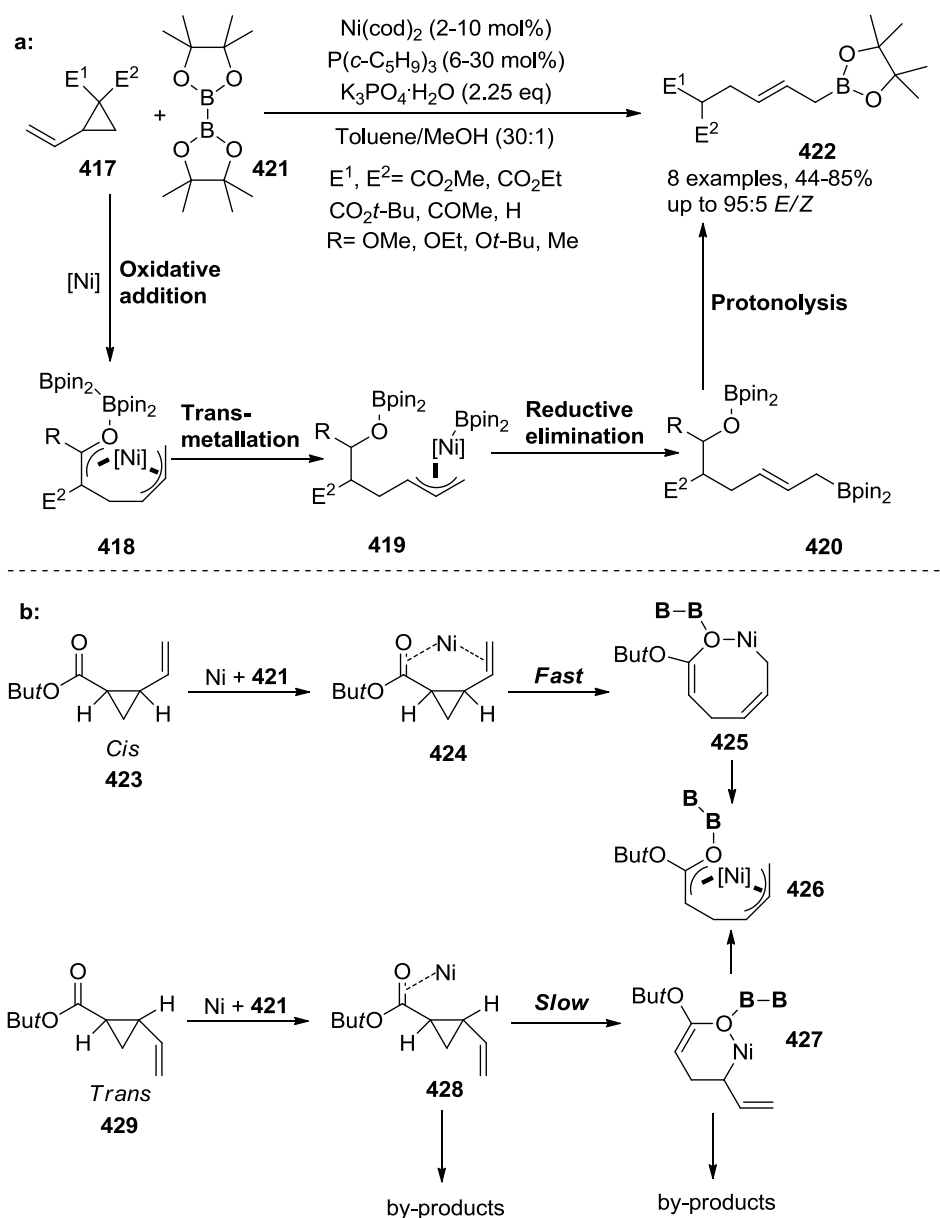
Scheme 99: Pd-Catalysed three-component coupling of terminal alkynes, arynes, and vinylcyclopropanes

As an alternative to Pd(0)-catalysed process, Pd(II)-species have been found to be effective in the ring-opening addition of vinylcyclopropanes (see also Scheme 97). For example, the palladium pincer complex **268** was again utilised by the Szabo group in a Pd(II)-catalysed ring-opening reaction to synthesise allylic boronic acid derivatives **416** from vinylcyclopropanes **414** and tetrahydroxydiboron (Scheme 100).¹⁵⁰ Transmetalation allows a B(OH)₂ group to transfer on the Pd(II)-centre, followed by a S_N2' nucleophilic attack on the vinylcyclopropanes **414** to yield the allylic boronic acids **415**. The allylic boronic acids **415** were then treated with aqueous KHF₂ to afford the more stable potassium trifluoro-(allyl)borate derivatives **416** in high yields. It is worth mentioning that allylic boronic acid derivatives are valuable precursors for synthesis of allylborane-based building blocks, such as chiral tartrate-based reagents.¹⁵¹⁻¹⁵²



Scheme 100: Pincer complex-catalysed synthesis of allylborates **416**

Apart from palladium-catalysed process, Yorimisu and Oshima further extended the catalyst scope to Ni(0) species for the borylative ring-opening reaction of donor-acceptor vinylcyclopropanes **417** (Scheme 101a).¹⁵³ Allylboronic acids, synthesised by the Szabo group (Scheme 100), can have limited application due to their instability, so they were treated with aqueous KHF_2 solution to give the stable potassium trifluoro(allyl)borates. The one-pot strategy developed by the Yorimisu group allows the direct formation of the relatively stable functionalised allylic boronates **422** in the presence of catalytic Ni(0), providing a complementary method to afford such synthetically useful substrates.

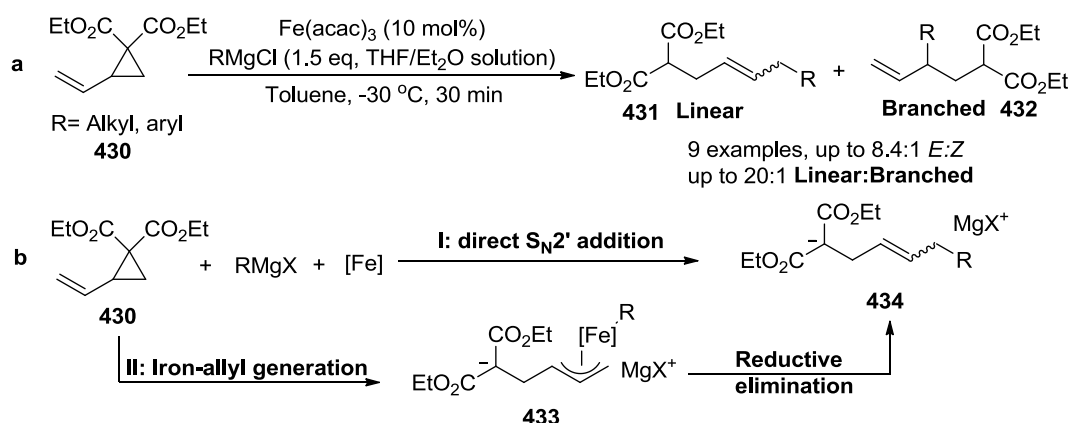


Scheme 101: Ni(0)-catalysed ring-opening of vinylcyclopropanes with $[Bpin_2]_2$

The oxidative addition of vinylcyclopropanes **417** to the Ni(0) species is likely the first step of the catalytic process, affording π -allyl(oxa- π -allyl)nickel species **418**, with bidentate coordination of the oxophilic Ni centre to the carbonyl and vinyl groups. Transmetalation then occurs to generate a π -allyl nickel complex **419**. The subsequent reductive elimination allows the generation of the boron enolate **420** and recovery of the initial Ni(0)-catalyst. Finally, protonolysis gives allylic boronates **422** in moderate to excellent yields with high *E*-selectivity. In addition, the first oxidative addition was found to be promoted by the bidentate coordinate of the Ni centre to the carbonyl and vinyl group as a reduced yield of 44% was observed for the parent *trans*-vinylcyclopropane **429** ($E_1 = H$, $E_2 =$

CO₂*t*-Bu), and this slow process may compete with side-reactions. In contrast, the reaction of a *cis*-vinylcyclopropane **423** (E₁= CO₂*t*-Bu, E₂= H) proceeded efficiently (Scheme 101b).

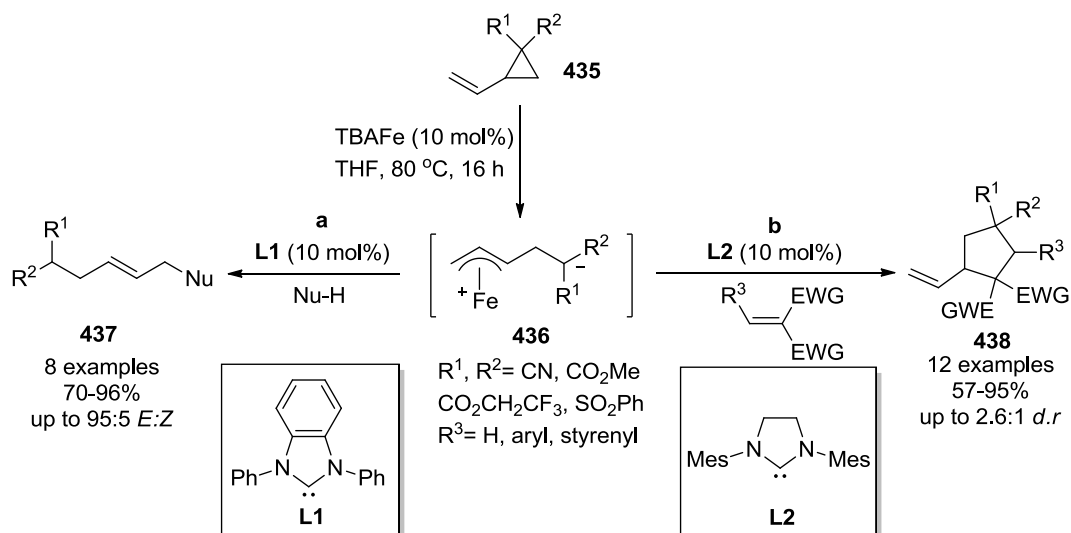
Iron catalysts have recently emerged in the activation of vinylcyclopropanes due to the economic and environmental advantages of this abundant metal.¹⁵⁴ For example, Fürstner has shown a highly regioselective iron-catalysed addition of alkyl Grignard reagents to activated vinylcyclopropanes **430** (Scheme 102a),¹⁵⁵ which is the example of the use of a hard organometallic nucleophile in catalytic ring-opening additions of vinylcyclopropanes. The reaction could either proceed *via* a direct S_N2' addition mechanism or an allyl-iron based process. The latter mechanism is possible as low-valent ferrates can be generated *in-situ* by treating Fe(acac)₃ with alkyl Grignard reagents. A number of linear ring-opened products **431** were prepared with moderate to good selectivities (Scheme 102b). In pathway **I**, an iron-ate type intermediate is proposed for this nucleophilic displacement. Additionally, the possibility of generating an iron-allyl complex **433** followed by the reductive elimination cannot be excluded (pathway **II**, Scheme 102).



Scheme 102: Iron-catalysed addition of Grignard reagents to activated vinylcyclopropanes **430**

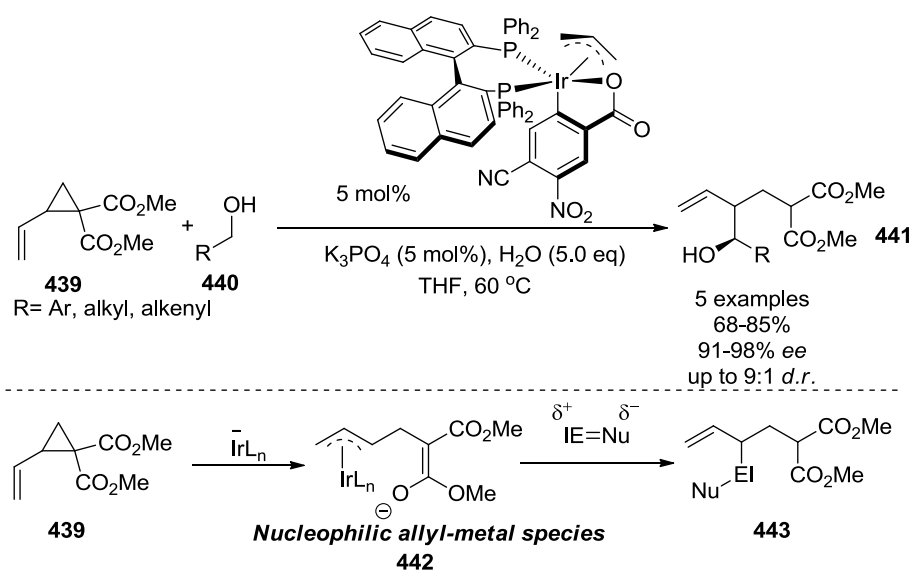
The C-C bond activation of donor-acceptor vinylcyclopropanes with iron catalysts was further investigated by Plietker and co-workers. They reported the allyl-iron intermediate could be efficiently generated from the nucleophilic ferrate Bu₄N[Fe(CO)₃(NO)] (TBAFe) to activate donor-acceptor vinylcyclopropanes **435** towards the attack of soft-nucleophiles (Scheme 103).¹⁵⁶ In this reaction, after generating the allyl-iron complex **436**, pronucleophiles such as malodinitrile, a cyanophenyl ester, cyanocyclopentanone and a phenylazlactone were deprotonated by the carbanion of the allyl-iron complex **436**, giving, after nucleophilic attack, a series of functionalised acyclic products

437 in good to excellent yields with high stereo- and regioselectivities (Scheme 107a). Interestingly, with the addition of mesityl substituted NHC-ligands, the [3+2] cycloadducts **438** were synthesised in good yields (Scheme 103b). The reactions demonstrate the synthetic versatility of the allyl-iron complex **436**, nevertheless, only relatively low to moderate diastereoselectivities were obtained (Scheme 103b).



Scheme 103: The allylic C–C-bond activation in the presence of the low-valent iron (II) complex TBAFe

All the aforementioned examples involving donor-acceptor cyclopropanes allow the nucleophilic trapping at the donor site and electrophilic trapping at the acceptor site. In contrast, a rare reaction reported by Johnson and Krische demonstrated the polarity inversion of donor-acceptor cyclopropanes **439** to give the nucleophilic allyl complexes **442** with Ir(III) catalysts (Scheme 104).¹⁵⁷ In this reaction, the key nucleophilic allyl-Ir species **442** reacts with primary alcohols or aldehydes **440** to afford enantiopure allylic alcohols **441** in high yields and with good diastereoselectivities. This special strategy could be a complementary method to the related Lewis acid-catalysed pathway (Scheme 85a) and the electrophilic allyl-metal complex pathway (Scheme 85d). The reaction proceeds in a similar manner to that discussed in Chapter 2 for the vinylaziridine system also reported by Krische and co-workers (Scheme 53).

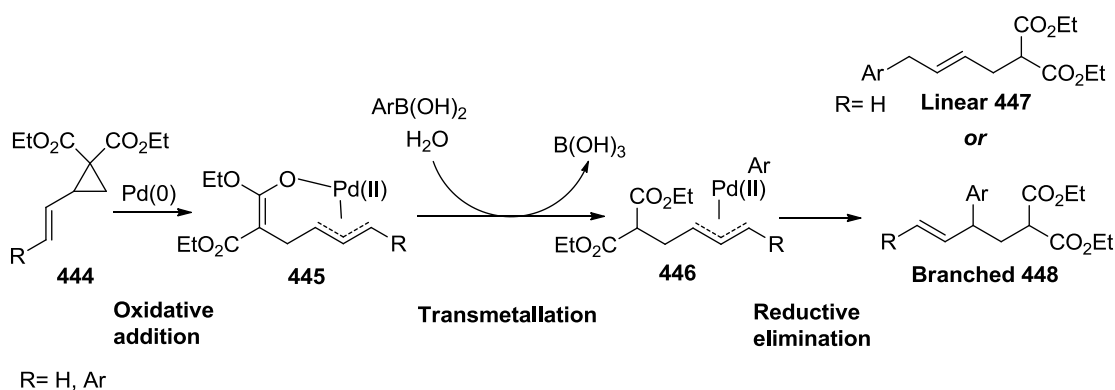


Scheme 104: Polarity Inversion of donor-acceptor cyclopropanes **439** with Ir-catalysis

Research Plan

Although the transition metal-catalysed ring-opening of vinylcyclopropanes with sp^3 carbon-based nucleophiles has been established with alkyl Grignard reagents and malonates, the substrate scope is limited due to the relatively poor functional tolerance and the high sensitivity to protic solvents of the former (Scheme 102). Therefore, the synthetic versatility of vinylcyclopropanes' nucleophilic ring-opening would be significantly increased if the scope of nucleophiles could be extended to the non-stabilised, bench-stable and economic sp^2 carbon nucleophiles such as arylboronic acids. Furthermore, the regioselective synthesis of the branched allylic product from the vinylcyclopropane-1,1-dicarboxylate **328** and boronic acids in one-pot was also important to the project. This strategy would avoid using aryl iodides, which were previously utilised by the Szabo group for synthesising the branched allylic product *via* a 2-step method (Scheme 97).

A designed catalytic cycle is illustrated in Scheme 105 to briefly describe the project. Firstly, a Pd(0)-catalyst system was chosen to form the expected η^3 -allyl Pd(II) complex **445** stabilised by the internal carboxylate oxygen atom. According to the Ikariya group's proposal, transmetallation then could occur to deliver a phenyl group on the Pd(II)-centre of **445**.¹⁵⁸ Reductive elimination from the resulting intermediate **446** is very interesting as two possible products may be finally released. This is because the reductive elimination can be governed by both sterics and electronics depending upon the nature of the R group,¹⁵⁹ in other words, there are thermodynamic and kinetic aspects to the control.



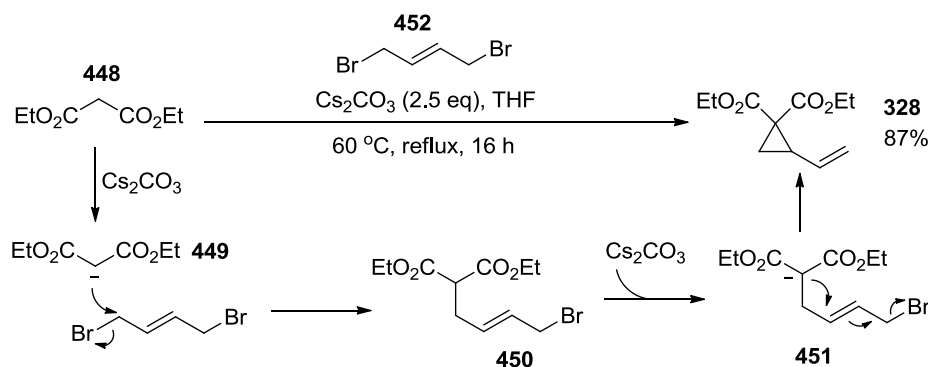
Scheme 105: Designed reaction pathway to regioselectively synthesise linear/branched products

Overall, a Pd(0)-system to achieve the coupling reaction of vinylcyclopropanes *via* the π -allyl-Pd(II) complex to regioselectively synthesise linear or branched product is the major aim of

this chapter. The project combines the synthetic versatility of vinylcyclopropanes and the high catalytic efficiency of the Pd(0)-catalyst system, furthermore, arylboronic acids will be used as a stable and hypotoxic C-based nucleophile. If successful, the reaction would extend the substrate scope for ring-opening of vinylcyclopropanes and is complementary to Plietker and Furstner's work (Schemes 102-103).

Results and Discussion

To realise the proposal in Scheme 105, studies commenced with the synthesis of 2-vinylcyclopropane-1,1-dicarboxylate **328**. This substrate was easily synthesised from (*E*)-1,4-dibromobut-2-ene **363** and diethyl malonate **362** in the presence of Cs_2CO_3 in an excellent yield (Scheme 106).¹⁶⁰ Generation of **328** was evidenced by a number of signals in ^1H NMR of the crude reaction mixture, including a multiplet (5.46-5.39 ppm) corresponding to the olefinic CH and two doublets (5.28 ppm and 5.12 ppm, respectively) associated with the olefinic CH_2 . In addition, a quartet (2.56 ppm) corresponding to the aliphatic CH and two symmetric doublets of doublet (1.67 ppm and 1.53 ppm) associated with the aliphatic CH_2 were also observed in ^1H NMR of the crude reaction mixture, suggesting the cyclopropane ring has been formed in the reaction. The formation of **328** was further evidenced by eleven carbon signals shown in the ^{13}C NMR because the structure of **328** demonstrates eleven carbons in total. In addition, it should be noted that two ester carbon signals were observed at 169.5 ppm and 167.3 ppm respectively, suggesting two ester groups that originated from **448** was incorporated into **328**.



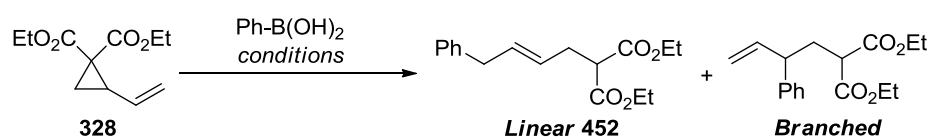
Scheme 106: Preparation of vinylcyclopropane 328

This synthesis starts with deprotonation of diethyl malonate by a stoichiometric amount of Cs_2CO_3 . The resulting anion **449** acts as nucleophile to attack 1,4-dibromobutene **452** via an $\text{S}_{\text{N}}2$ pathway, producing the allyl adduct **450**, which is then deprotonated by Cs_2CO_3 . Finally, the intramolecular $\text{S}_{\text{N}}2'$ reaction of the resultant anion **451** releases the vinylcyclopropane **328** (Scheme 105).

By employing the same conditions as the chapter 2 for the oxidative Heck reaction of vinylaziridines, the ring-opening of the vinylcyclopropane **328** was achieved (Table 1, entry 1),

though the conversion was only 48%. Unfortunately, the *E*:*Z*-selectivity (67:33) was very low, furthermore, a significant amount of an inseparable impurity was observed whenever the reaction was attempted.¹⁶¹ The coordination of carbonyls of **328** to the Pd(II)-centre leads to the remote distance between vinyl group and the Pd(II)-centre, potentially causing the low efficiency of the reaction in comparison to the aziridine **103** (Confirmation **II**, Scheme 70) (entry 1).

Table 1. Optimisation conditions for the ring-opening of **328**

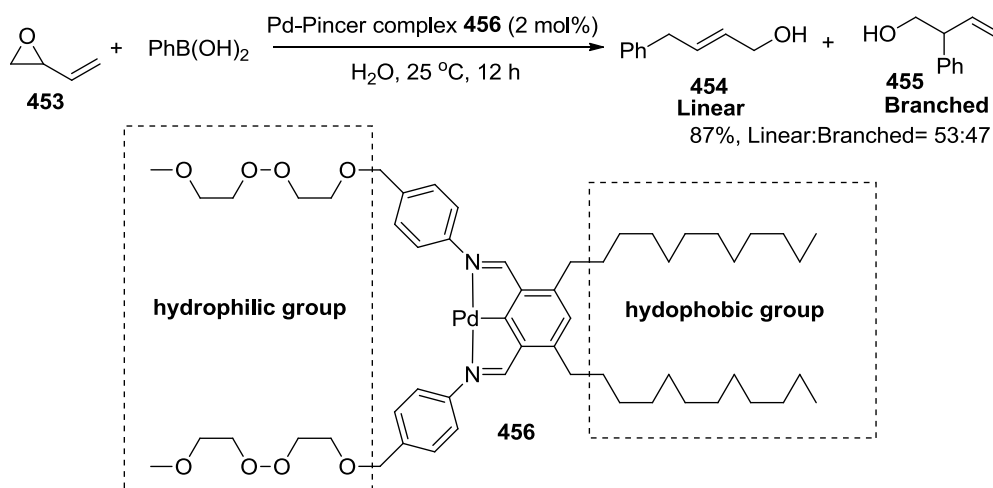


Entry	Conditions	Yield (%)	Selectivity (Linear:Branched)
1	Pd(OAc) ₂ (10 mol%) Phen (15 mol%), AgSbF ₆ (10 mol%), DCE	48% ^b	only linear (<i>E</i> / <i>Z</i> = 67:33)
2	Pd(OAc) ₂ (2 mol%) PPh ₃ (4 mol%), THF/H ₂ O	51%	8.7: 1 (<i>E</i> / <i>Z</i> = 95: 5)
3	Pd(OAc)₂ (1 mol%), H₂O	84%	11.5:1 (<i>E</i>/<i>Z</i>= 98: 2)
4	No catalyst, H ₂ O	29% ^c	1.2: 1 (only <i>E</i> observed)
5	Pd(OAc) ₂ , THF/H ₂ O ^e	26% ^c	only linear
6	Pd(OAc) ₂ , THF	trace	only linear
7	Pd(PPh ₃) ₄ , H ₂ O ^e	N.R	N/A

^a Ratios measured from the ¹H NMR of the crude reaction mixture. ^b Inseparable impurity also formed. ^c Conversion, product not isolated. ^d 5.0 equivalents of distilled water used. ^e The reaction was carried out under nitrogen.

A Pd(0)-catalyst system (entry 2) that has been shown to successfully catalyse the Suzuki-Miyaura coupling of allylic carbonates with arylboronic acids was then utilised in the reaction.¹⁶² The Pd(0)-catalyst system generated the Pd(0) species *in situ* by stirring Pd(OAc)₂ with PPh₃; this catalytic system delivered the desired product in moderate conversion and yields but with good linear:branched as well as *trans:cis* ratios.

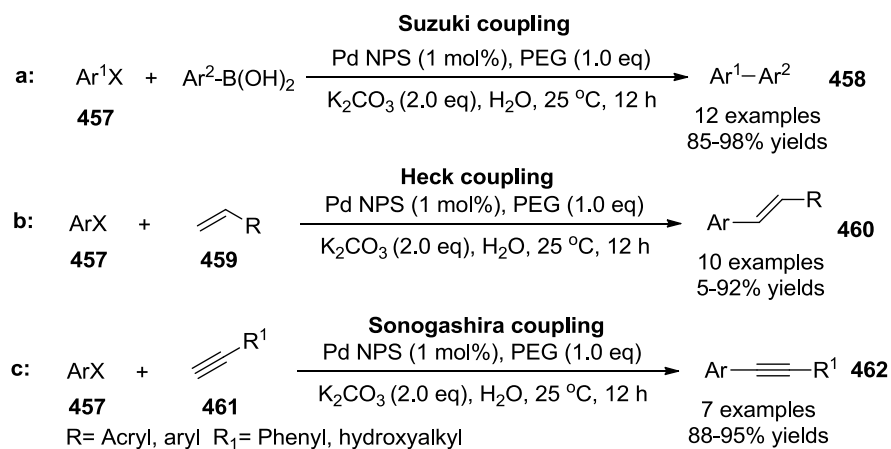
Thus, it was essential to identify an efficient Pd(0)-catalyst to further enhance the credentials of reactions involving vinylcyclopropanes **328** with boronic acids. In this regard, three reports then drew our attention. Firstly, the use of an amphiphilic Pd(II)-pincer complex **456** in water has been reported to form vesicles that catalyse the addition of boronic acids to vinylepoxy **453**, but the reaction displayed poor regioselectivity and utilised a complex catalyst consisting of both a hydrophilic group and a hydrophobic group (Scheme 107).¹⁶³



Scheme 107: Palladium-catalysed oxirane ring opening with PhB(OH)_2 in water

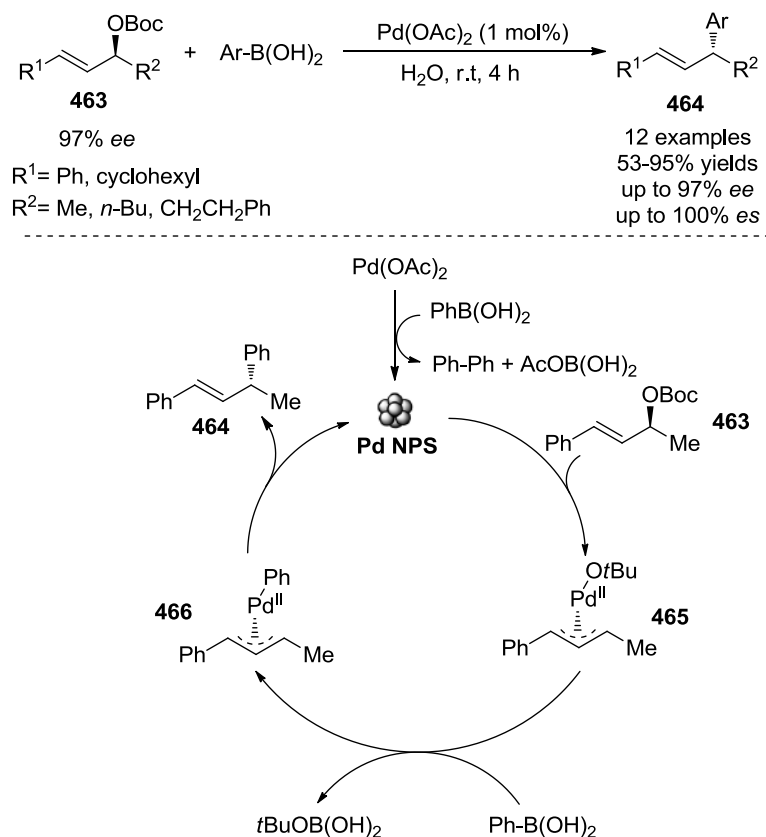
On the other hand, Pd nanoparticles (Pd NPS) have exhibited excellent catalytic activity in aryl-aryl coupling reactions in neat water under the ligand-free conditions. For example, a Pd nanoparticle solution was made by dispersing an acylmetal salt $[(\text{CO})_5\text{W}]\text{C(Me)ONeEt}_4$ into distilled water and then adding the resulting mixture into a well-mixed aqueous solution of K_2PdCl_4 and polyethylene glycol.¹⁶⁴ Sakar and co-workers successfully utilised the catalyst solution to perform a series of Heck/Suzuki/Sonogashira-type coupling using aryl halides **457** and arylboronic acids, showing the excellent versatility of Pd nanoparticles (Pd NPS) in the catalysis of coupling reactions (Scheme 108), while the presence of the stabiliser polyethylene glycol (PEG) and a stoichiometric

amount of K_2CO_3 were required.¹⁶⁵



Scheme 108: Pd nanoparticles-catalysed coupling reaction

The Zhang group subsequently demonstrated that Pd NPS can form in neat water from $Pd(OAc)_2$ and arylboronic acids without ligands and additional stabilisers (Scheme 109).¹⁶⁶ Furthermore, the *in situ*-generated Pd NPS allows the addition of arylboronic acids to enantiopure (*S*) secondary allylic carbonates **463**, producing the allyl-aryl coupling products **464** in high yields with excellent chemo-, regio- and *E/Z*-selectivities. TEM analysis showed that Pd NPS could be generated with an average size of 2.6 nm by simply stirring the mixture of $Pd(OAc)_2$ and phenylboronic acid in water for 5 mins. Therefore, a mechanism was proposed on the basis of TEM analysis and the experimental results (Scheme 109). The electrophilic π -allyl-Pd(II) complex **465** is formed by stereospecific oxidative addition of *in situ*-generated Pd NPS to the chiral allylic carbonate from the back side. Transmetallation then occurs with the active π -allyl-Pd(II) intermediate **465** and phenylboronic acid, followed by the reductive elimination, which occurs at the less sterically hindered terminus of the π -allyl-Pd(II) intermediate **466** to furnish the inversed (*R*)-allyl-aryl coupling products **464** with complete regioselectivity and retained enantiopurity. Finally, the released Pd(0) species is reaggregated to recover Pd NPS. The coupling reaction may occur at the interface of the organic substrate and water, and the stabilisation of Pd-NPS is likely achieved with the released boronic acid monobutoxide dissolved in water.



Scheme 109: Stereospecific coupling of allylic carbonates **463** with arylboronic acids catalysed by *in situ* generated Pd NPs

All these examples above show that Pd nanoparticle catalysis has demonstrated its merit in catalytic activity for organic synthesis under environmentally benign conditions that could be applied to green chemistry, as nanoparticle catalysis occurs on the broad surface of the metal. Therefore, in an attempt to identify an efficient Pd(0)-catalyst system, we turned our attention to the use of Pd(OAc)₂ and boronic acids in water (Scheme 109), a simple system which has been previously reported to produce Pd(0) nanoparticles *via* the pathway shown in Scheme 69. When these conditions were deployed, it was pleasing to find that the internal alkene **452** was smoothly produced in a high yield (84%) with excellent *E/Z*-selectivity (11.5:1) (entry 3, Table 1). The key diagnostic evidence for the formation of this product came from the ¹H NMR signals associated with ring-opening of **328**. These included two identical multiplets corresponding to two alkene protons, which were observed downfield at 5.72-5.66 ppm and 5.51-5.45 ppm respectively, suggesting the generation of an internal alkene *via* the nucleophilic attack accompanied by the shifting of the terminal double bond from the C2 carbon of the cyclopropane ring. The cleavage of the C1-C2 cyclopropane bond was evidenced by

the chemical shift of the triplet (3.40 ppm) associated with the methine proton of the malonate moiety. Further evidence of generation of **452** came from a doublet (3.31 ppm) corresponding to the CH₂ between the phenyl group and the olefinic CH, and a triplet (2.62 ppm) associated with the CH₂ between the methine and the olefinic CH also support the formation of **452** in the reaction. ¹³C NMR of the purified product demonstrates five aliphatic carbon signals, which are in line with numbers of aliphatic carbons in the symmetric structure of **452**. The molecular weight (313.1428 g mol⁻¹) of purified product that was given by high-resolution mass spectrometry matches the NMR-determined structure of **452**. In addition, the stereochemistry of the product **452** was determined by NOESY-1D (See Appendix). It was observed that the triplet **a** corresponding to the CH₂ (2.62 ppm) has proximity in space to two olefinic protons (H₁: 5.72-5.66 ppm and H₂: 5.51-5.45 ppm) and triplet **c** associated with the methine proton (3.40 ppm). However, the doublet **b** corresponding to the CH₂ adjacent to the phenyl ring does not have the NOESY-1D signal to **a**. In conclusion, the *E*-isomer is likely the major product of this reaction (Figure 9).

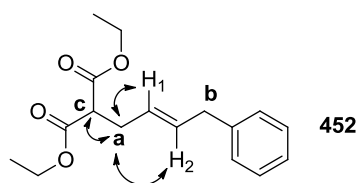


Figure 9: NOESY-1D results of the product **452**

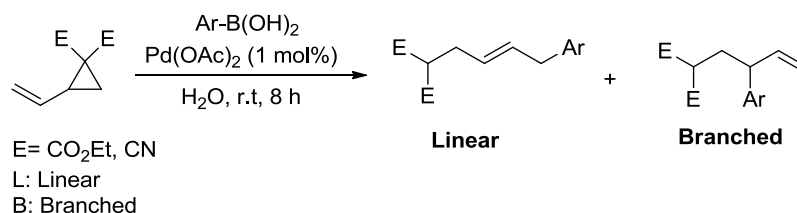
Importantly, these conditions do not require the addition of ligand, stabiliser or organic solvent, rendering the reaction synthetically practical and economical. The reaction does not require strict exclusion of air, making it operationally simple. As a control, the reaction was then carried out in the absence of catalyst, and roughly equal amount of branched:linear product in low conversion observed highlighted the importance of the catalyst (entry 4). Low conversion (26%) and dominant *E*-selectivity were given when only Pd(OAc)₂ was stirred in a mixture of THF and 5.0 equivalents of distilled water (entry 5), while only trace product was observed with the use of anhydrous THF (entry 6). Other Pd(0) species such as Pd(PPh₃)₄ were also utilised in water, however, no reaction was observed (entry 7).

With these optimised conditions in hand, the vinylcyclopropane was treated with a variety of boronic acids to give the corresponding alkenes in generally high yields and linear *trans*-selectivities

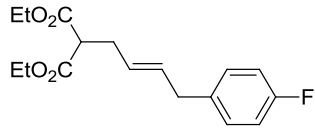
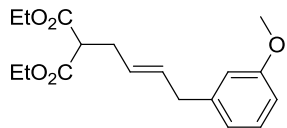
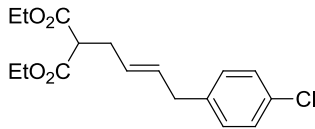
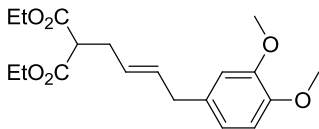
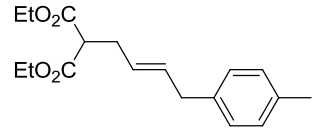
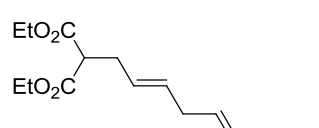
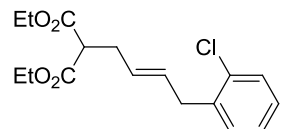
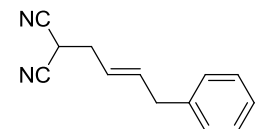
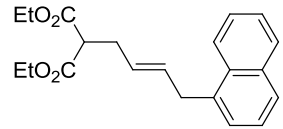
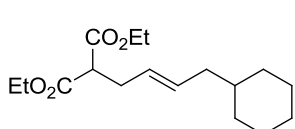
(Table 2). It was evident that electron-deficient arylboronic acids generally gave the desired product in excellent yields (products **467** to **470**). Moreover, *ortho*-substitution was tolerated and gave a good yield (product **476**), while the yield was reduced for more electron-rich systems and naphthyl-derived boronic acids (product **471**, **473**, **478** and **474**). Additionally, it needs to be noted that the relatively low yields, such as observed for products **476**, **478** and **467**, were a result of the incomplete conversion of **328** rather than production of side-products. The unreacted **328** could be therefore recovered with the column chromatography in these cases.

In addition, a cyano group could be tolerated as the electron-withdrawing donor group on the vinylcyclopropane (product **477**). The corresponding 1,1'-dicyano-2- vinylcyclopropane **530** was prepared in a moderate yield (43%) from malononitrile and (*E*)-1,4-dibromobut-2-ene **363** by the method shown in Scheme 106. An alkenyl boronic acid was an effective substrate to couple with phenylboronic acid, and the corresponding linear adduct was given in a moderate yield and with a complete linear selectivity (product **475**). Unfortunately, alkylboronic acids such as cyclohexylboronic acid gave no reaction under the conditions.

Table 2. Reaction scope for linear products with respect to boronic acids



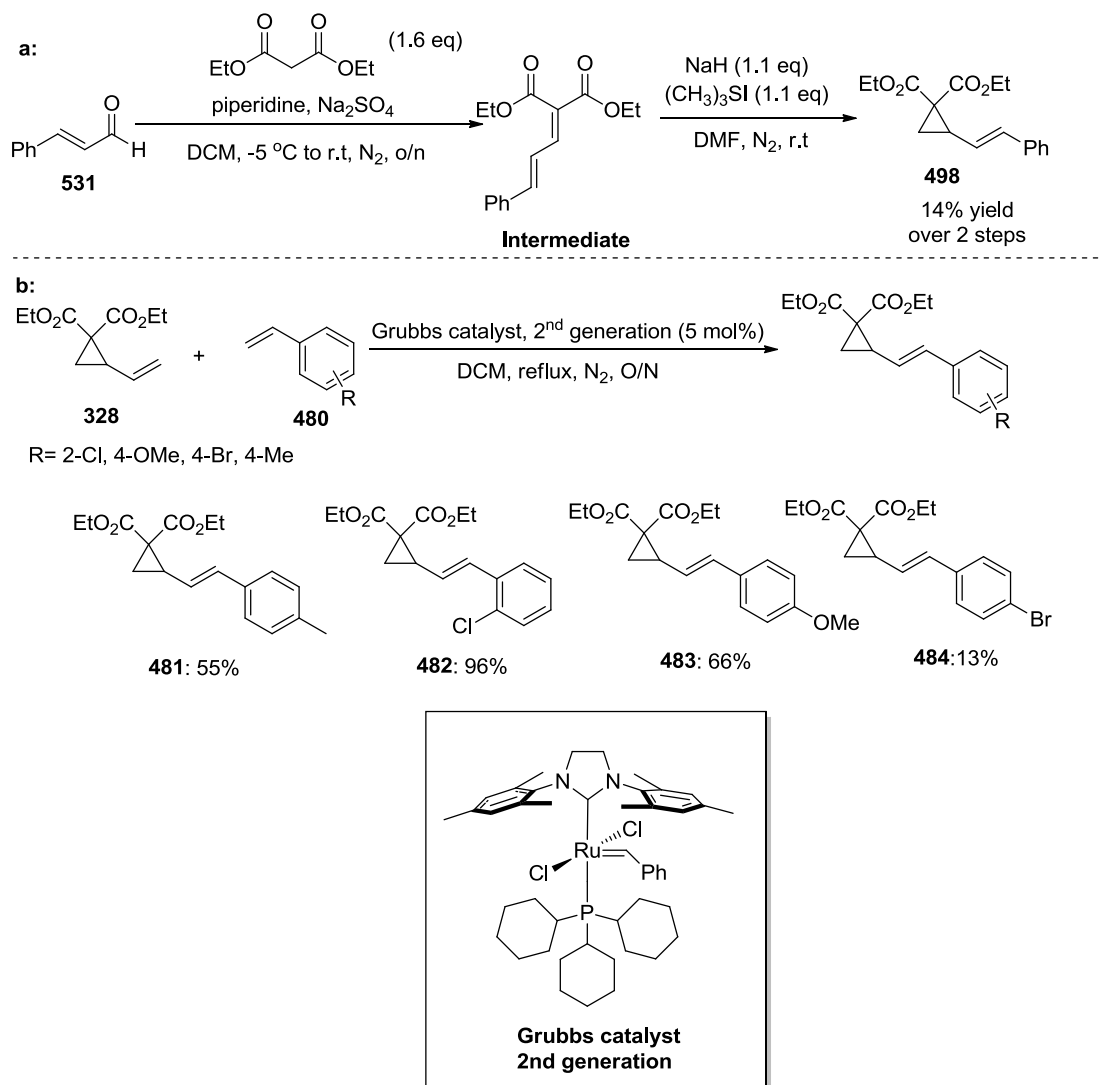
<p>452, 84%, L/B = 11.5: 1.0 E/Z = 98: 2</p>	<p>467, 61%, L/B = 18.7: 1.0 E/Z = 93: 7</p>
<p>468, 95%, L/B = 45.9: 1.0 E/Z = 94: 6</p>	<p>469, 90%, L/B = 9.7: 1.0 E/Z = 96: 4</p>

 <p>470, 86%, L/B = 25.0: 1.0 E/Z = 95:5</p>	 <p>471, 72%, L/B = 9.7: 1.0 E/Z = 96:4</p>
 <p>472, 96%, L/B = 14.9: 1.0 E/Z = 94:6</p>	 <p>473, 23%, L/B = 8.3: 1.0 E/Z = 93:7</p>
 <p>474, 48%, L/B = 20.4: 1.0 E/Z = 96: 4</p>	 <p>475, 59%, L^b E/Z = 85:15</p>
 <p>476, 65%, L/B = 7.6: 1.0 E/Z = 87:13</p>	 <p>477, 54%, L/B = 14.8: 1.0 E/Z = 73:17</p>
 <p>478, 36%, L/B = 5.3: 1.0 E/Z = 91:9</p>	 <p>479: N. R.</p>

^a ratios measured from the crude ¹H NMR ^b no branched isomer observed.

In order to see if branched ring-opened products could be obtained, attention was turned to vinylcyclopropanes substituted with an aryl group on the olefin unit (Table 3). The styrenylcyclopropane **498** was synthesised from cinnamaldehyde **531** via a 2-step strategy (Scheme 110a).¹⁶⁷ The presence of styrenyl group in **498** was evidenced by two characteristic signals, including a doublet at 6.64 ppm and a doublet of doublet at 5.83 ppm. Further evidence for formation of **498** came from a quartet associated with aliphatic CH (2.74 ppm) and two doublets of doublet at 1.82 ppm and 1.66 ppm, respectively (aliphatic CH₂). In addition, the ¹³C NMR demonstrates all fifteen carbons in the symmetric structure of **498**, supporting the synthesis of **498** was achieved in this reaction. Other *trans* β-styrenylcyclopropanes could be easily prepared by cross-metathesis using

the unsubstituted vinylcyclopropane **328** and the corresponding commercially available styrenes **480** in the presence of the Grubbs second generation catalyst (Scheme 110b).



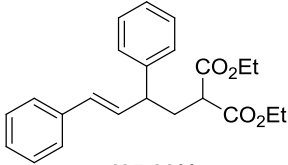
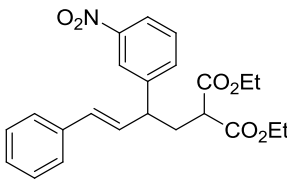
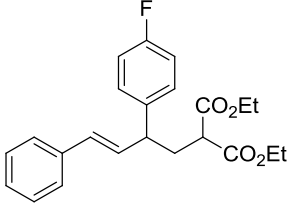
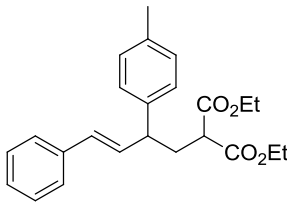
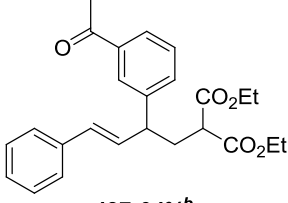
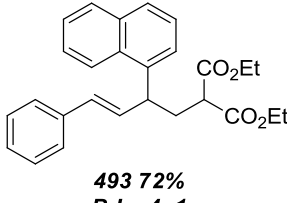
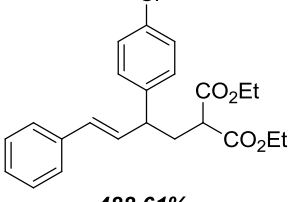
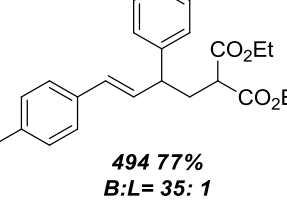
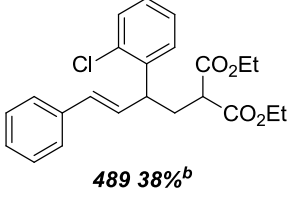
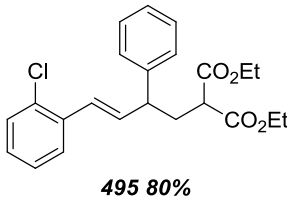
Scheme 110: The synthesis of β -styrenylcyclopropanes with Grubbs Catalyst, 2nd Generation

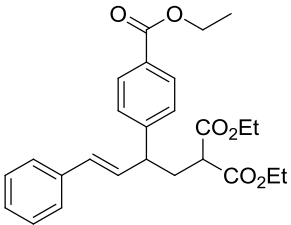
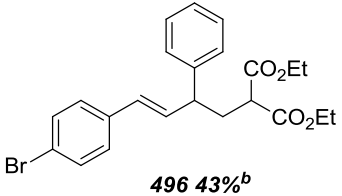
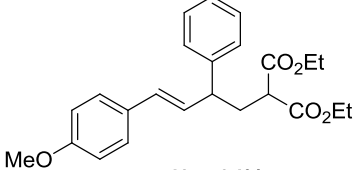
Pleasingly, using the optimised conditions (entry 1, Table 1) with substituted vinylcyclopropane **498**, the branched product **485** was generated as the major product with complete *E*-selectivity in an excellent yield (Table 3). Evidence for generation of the branched isomer came from the doublet and the doublet of doublet (6.44 and 6.29 ppm, respectively) associated with the styrenyl motif of **485** in the ¹H NMR. Furthermore, the triplet corresponding to the CH between two carboxylates group was also observed at 3.36 ppm, suggesting the ring-opening reaction has occurred (see Appendix). ¹³C NMR demonstrates six signals for aliphatic carbons, which is in accordance with the number of

aliphatic carbons in symmetric structure of **485**. It needs to be noted that two ester carbons of **485** that originated from **498** were observed at 169.5 ppm and 169.4 ppm, respectively. High-resolution mass spectrometry gave a molecular weight of 389.1745 g mol⁻¹ for the isolated product, which is in line with the calculated molecular weight of **498**. In conclusion, formation of the branched product **498** was achieved under the conditions used in Table 2.

The scope of this ring-opening was then investigated with a range of arylboronic acids, and it proved to have high functional group tolerance, providing high to exclusive branched selectivity in each case. A series of functional groups, including halides (products **486**, **488** and **489**), ester (product **490**) and ketones (product **487**), were tolerated under the conditions. It was also found that both electron-rich (product **492**) and highly electron-deficient boronic acids (product **491**) could be effective coupling partners to give corresponding products in moderate to high yields, respectively. Moreover, *ortho*-substituted boronic acids could also be used, albeit a drop in yield was observed (product **489**), however, pent-1-en-1-ylboronic acid, which previously gave a moderate yield in Table 2, now gave a complex mixture of products when reacted with the vinylcyclopropane **498**. This might result from the steric hindrance between pent-1-en-1-yl group and ester group of **498** in the proposed intermediate **446** after transmetallation (Scheme 105). Subsequently, the vinylcyclopropanes with the substituted electron-rich aromatic ring on the terminus of alkene moiety were also studied, and the corresponding products were obtained in good yields and excellent branched-selectivities (product **494** and **497**). Highly sterically hindered vinylcyclopropane **499** bearing an *ortho*-chloro group was subject to the conditions, and product **495** was then isolated in a relatively high yield with an excellent selectivity. Additionally, Suzuki coupling did not occur with *p*-bromophenyl-substituted vinylcyclopropane **500**, which produced the sole branched isomer **496** in a synthetically acceptable yield. Again, it needs to be highlighted that the moderate yields in the table 3 for some products such as **489**, **491** and **495** were a result of low conversions of the corresponding vinylcyclopropanes after the reaction completed, and the unreacted vinylcyclopropanes were recovered by the column chromatography.

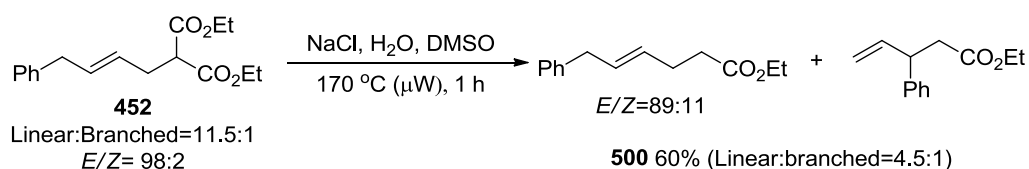
Table 3. Reaction scope with respect to boronic acid for branched systems

$ \begin{array}{c} \text{EtO}_2\text{C} \quad \text{CO}_2\text{Et} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{CH} \quad \text{Ar}' \end{array} \xrightarrow[\text{H}_2\text{O, r.t., 8 h}]{\text{Ar-B(OH)}_2, \text{Pd(OAc)}_2 (1 \text{ mol}\%)} \begin{array}{c} \text{Ar} \quad \text{CO}_2\text{Et} \\ \quad \\ \text{CH} \quad \text{CH} \\ \quad \\ \text{CH}_2 \quad \text{CH} \quad \text{CO}_2\text{Et} \end{array} + \begin{array}{c} \text{Ar} \quad \text{CO}_2\text{Et} \\ \quad \\ \text{CH} \quad \text{CH} \\ \quad \\ \text{CH}_2 \quad \text{CH} \quad \text{CO}_2\text{Et} \end{array} $	
Branched	Linear
 <p>485 82% B:L= 25:1</p>	 <p>491 37%^b</p>
 <p>486 82%^b B:L= 25:1</p>	 <p>492 84% B:L= 19: 1</p>
 <p>487 64%^b</p>	 <p>493 72% B:L= 4: 1</p>
 <p>488 61% B:L= 16:1</p>	 <p>494 77% B:L= 35: 1</p>
 <p>489 38%^b</p>	 <p>495 80% B:L= 93: 1</p>

 <p>490 62% B:L = 21:1</p>	 <p>496 43%^b</p>
	 <p>497, 64% B:L = 59:1</p>

^a ratios measured from the ¹H NMR of the crude reaction mixture, only the *E* isomer of the major product was observed ^b no linear isomer observed.

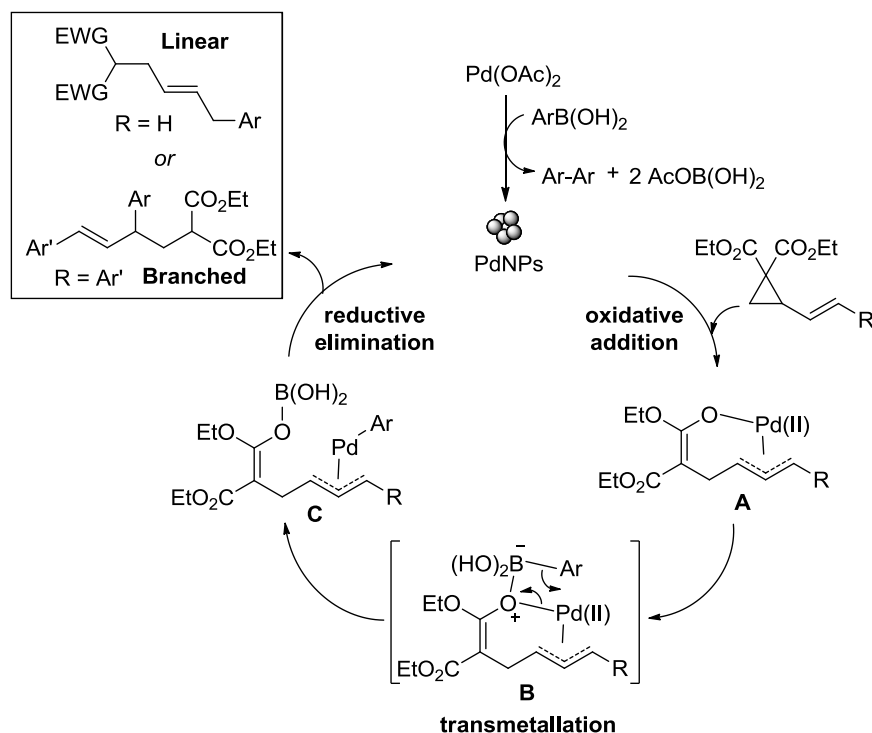
To show that these products can be manipulated in a facile manner, the product **452** was subjected to the Krapcho decarboxylation reaction to give the ester **500** in a good yield (Scheme 111). The ¹H NMR of the pure product **500** showed a multiplet with an integration of four (2.40-2.36 ppm) for two adjacent methylenes between the olefin moiety and the single carboxylate group. Further evidence for formation of **500** came from two signals in ¹H NMR, including two multiplets associated with two olefinic protons of **500** (5.66-5.57 ppm and 5.55-5.46 ppm, respectively) and a doublet at 3.33 ppm corresponding to the CH₂ next to the phenyl group of **500**. Importantly, it was found that integrations for two characteristic signals of carboxylate such as a quartet at 4.12 ppm (OCH₂CH₃) and a triplet at 1.24 ppm (OCH₂CH₃) demonstrate **500** has only one carboxylate group. In addition, high-resolution mass spectrometry (241.1208 g mol⁻¹) also confirmed the removal of one carboxylate from **452**.



Scheme 111: Decarboxylation reaction of **452**

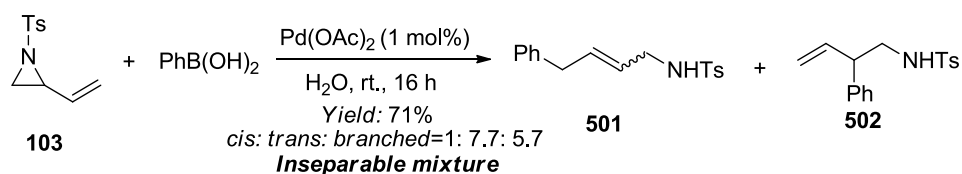
According to the designed reaction pathway (Scheme 105),¹⁶⁸ a catalytic cycle was proposed to explain the experimental results (Scheme 112). Firstly, Pd(0) nanoparticles can be generated *via*

double processes of transmetallation plus reductive elimination (Scheme 69), and Zhang and co-workers¹³⁶ have proved the reduction of Pd(II) to Pd(0) by the reaction of palladium acetate and two molar equivalents of arylboronic acid in water. The presence of trace biphenyl signals were also observed in the ¹H NMR of the crude reaction mixture, providing some evidence for this mode of activation to give Pd(0) nanoparticles. Following catalyst activation, the η^3 π -Pd-allyl complex **A** is formed *via* oxidative addition to the vinylcyclopropane **328**. Next, transmetallation may be assisted by water or internally by the ester enolate as shown in the ester enolate **B**.¹⁶⁹ In support of this, it has been postulated that transmetallation in the coupling of 1,1-diboron compounds is facilitated by the intramolecular coordination between the boron atom and an ester group.¹⁷⁰ Finally, the resultant complex **C** undergoes reductive elimination to afford the ring-opened product, and it is proposed that this is the key step that determines the regiochemical outcome of the reaction. Linear products could be furnished *via* reductive elimination at the least hindered carbon when R = H. Alternatively, when R = Ar' the reductive elimination occurs to release the branched products. The former result could be explained by the generation of thermodynamically stable internal alkene by reductive elimination to install an Ar group on the terminus of the vinyl moiety. Reductive elimination occurring on the terminal carbon also minimises the steric repulsion between the Pd-Ar complex and the vinylcyclopropane substrate. In contrast, the formation of the branched product can be explained as reductive elimination allows generation of the more stable conjugated system over the internal alkene. Additionally, the steric impulsion between two terminal aryl groups in the internal alkene may also play a role in determining the selectivity. It was therefore proposed that the transition state for the formation of the conjugated branched product is also likely to be lower in energy than that for the formation of linear product.



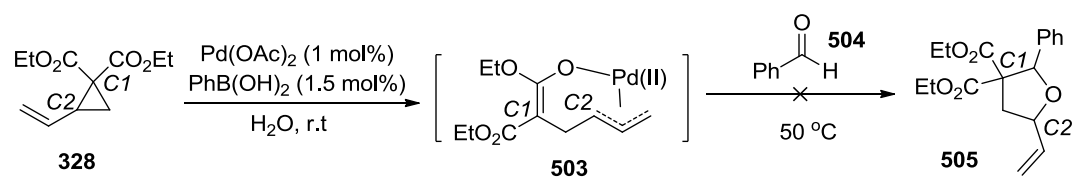
Scheme 112: Proposed mechanism for palladium-catalysed coupling of vinylcyclopropanes with boronic acids

As an analogue of vinylcyclopropane **328**, vinylaziridine **103** was also subjected to the $\text{Pd}(\text{OAc})_2/\text{H}_2\text{O}/\text{PhB}(\text{OH})_2$ conditions (Scheme 113). However, an inseparable mixture of three isomers: *cis*, *trans* and branched products were obtained in a ratio of 1.0:7.7:5.7. The formation of the branched product **502** was an interesting divergence from the vinylcyclopropane system.



Scheme 113: Palladium-catalysed coupling of vinylaziridine **103** with phenylboronic acid

In addition to the Pd NPS-catalysed addition of boronic acids to vinylcyclopropanes, it was envisioned that benzaldehyde **504** could act as a dipolarophile to cyclise with the Pd-stabilised zwitterionic dipolar intermediate **503** resulting from the oxidative addition of Pd NPS to **328**, affording a 5-membered ring system **505**, however, no reaction occurred even at an elevated temperature (50 °C) (Scheme 114).



Scheme 114: Unsuccessful cyclisation of vinylcyclopropane **328** with benzaldehyde **504** in neat water

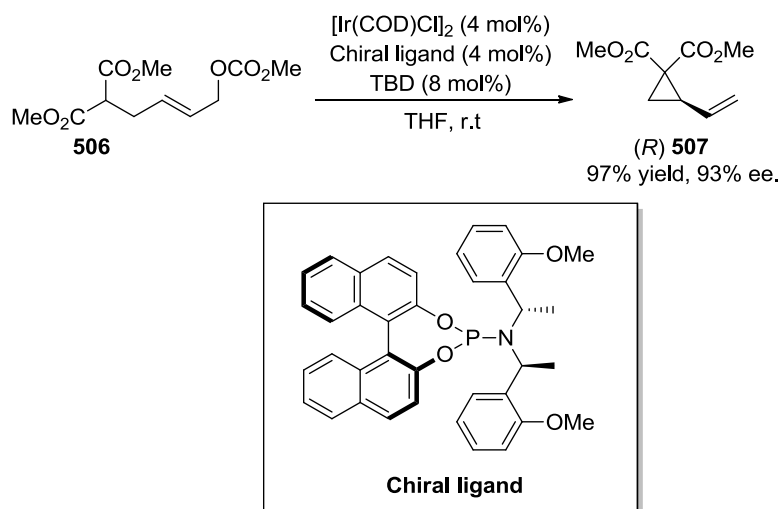
Summary

In conclusion, *in situ* generated Pd nanoparticles have been identified as a highly efficient catalyst for the ring-opening of donor-acceptor vinylcyclopropanes with boronic acids in neat water. The excellent regioselectivity is driven by the reductive elimination step of the catalytic cycle, with branched ring-opened products being synthesised for *trans* β -styrenylcyclopropanes and thermodynamically stable internal alkenes being obtained for cyclopropanes with a vinyl tether. Moreover, the reaction requires only low loading of commercially available Pd(OAc)₂ as a precatalyst with no ancillary ligands and additives, rendering it practical and economical. Unfortunately, the expected [3+2] annulations of vinylcyclopropane **328** did not occur with benzaldehyde in the presence of Pd(OAc)₂ and a catalytic amount of phenylboronic acid in water even at the elevated temperature (50 °C).

Future Plans

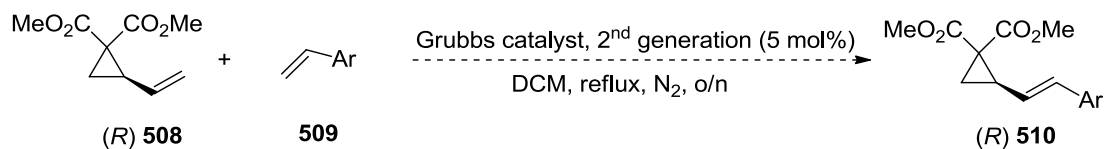
Enantioselective variant for Pd NPS-Catalysed Ring-Opening Reaction of Vinylcyclopropanes with Arylboronic acids in Neat Water

According to the Helmchen group, enantioenriched (*R*)-vinylcyclopropane **507** could be synthesised from the carbonate **506** in the presence of $[\text{Ir}(\text{COD})\text{Cl}]_2$ and phosphorus amidite (Scheme 115).¹⁷¹



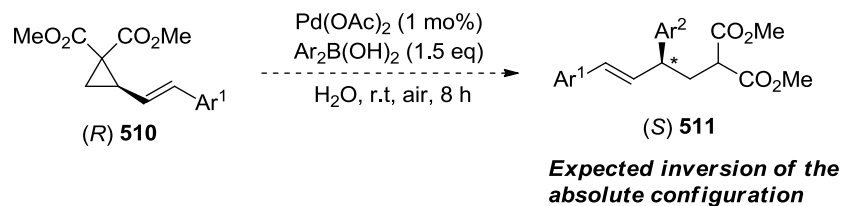
Scheme 115: Ir-catalysed cyclisations of carbonates **506**

(*R*)-vinylcyclopropanes **510** that are substituted with an aryl group on the olefin unit will be synthesised *via* the method shown in Scheme 110 (Scheme 116).



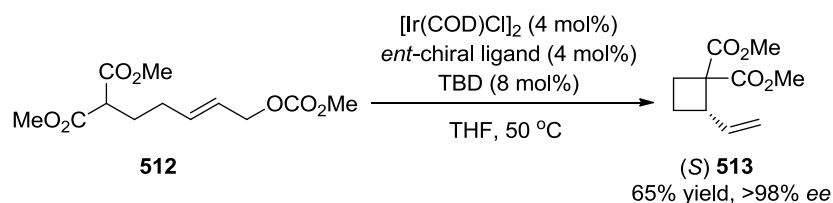
Scheme 116: Synthesis of enantioenriched substituted vinylcyclopropanes **510**

These (*R*)-vinylcyclopropanes **510** could then be utilised in Pd NPS-catalysed ring-opening reaction of vinylcyclopropanes with arylboronic acids in Neat Water. According to the Zhao group's work (Scheme 109), an enantioenriched branched product **511** may be given with complete enantiospecificity with inversion of the absolute configuration (Scheme 117).



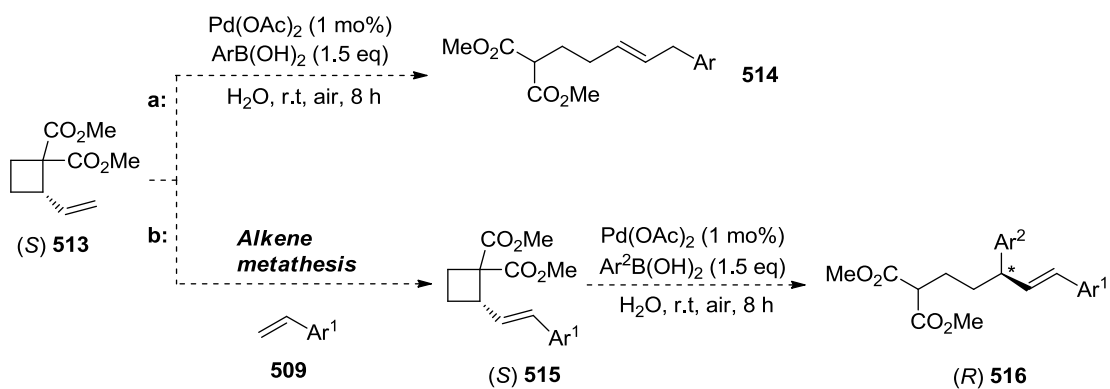
Scheme 117: Enantioselective variant for Pd NPS-catalysed ring-opening reaction of vinylcyclopropanes with arylboronic acids in Neat Water

In addition to 3-membered ring systems, 4-membered ring system is also an interesting and suitable substrates for investigation in future work. For example, Helmchen and co-workers also synthesised an enantiopure dimethyl 2-vinylcyclobutane-1,1-dicarboxylate **513** under the conditions in Scheme 115 (Scheme 118).



Scheme 118: Synthesis of entioenriched 4-membered ring system **513**

Two reaction pathways were proposed for Pd NPS-catalysed ring-opening of enantiopure **513** in neat water. Firstly, a linear product **514** is expected to be generated (Scheme 119a). Alternatively, a substituted vinylcyclobutane **515** will be prepared *via* alkene metathesis using Grubbs catalyst (Scheme 116). Subsequently, this substrate will be subjected to the conditions in Scheme 117. Similarly, this reaction may afford an entioenriched branched product **516** with complete enantiospecificity with inversion of the absolute configuration (Scheme 119b).



Scheme 119: Designed reaction pathways for 4-membered ring system **513**

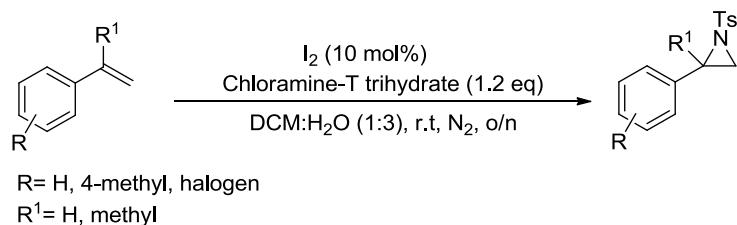
EXPERIMENTAL SECTION

General Information

All reactions were performed under atmosphere of nitrogen in oven-dried glassware. Anhydrous solvents were purified by passage through a solvent purification system (purification over activated alumina, copper catalyst, and/or molecular sieves). Flash grade silica gel was used for column chromatography, and thin layer chromatography was performed on silica gel (32-36 μm) 60 F254 aluminium backed sheets, visualized with a 254 nm UV lamp and stained with either ceric(IV) dip containing phosphomolybdic acid (37.5 g), ceric sulphate (7.5 g), sulphuric acid (37.5 ml) and water (750 mL) or potassium permanganate dip containing potassium permanganate (1.5 g), potassium carbonate (10 g) and sodium hydroxide solution (10%, 1.25 mL) and water (200 mL). ^1H NMR and ^{13}C NMR were recorded in deuterated chloroform (CDCl_3) and coupling constants are recorded in Hz and chemical shifts are recorded as δ values in ppm, referenced against residual solvent peaks (^1H NMR) or to the ^{13}C NMR resonances of the solvent. The following abbreviations are used in the assignments of ^1H NMR signals; s = singlet; d = doublet; td = doublet of triplet; tdd = triplet of doublet of doublet; m = multiplet. Other reagents and starting materials were commercially available and used without further purification. High-performance liquid chromatography (HPLC) was performed with a Waters 1525 binary pump and a WatersTM 486 tunnable absorbance detector, using Chiralpak AD (25 cm x 0.46 cm) and Chiralpak OD-H (25 cm x 0.46 cm) columns. Optical rotation was measured by JASCO P-2000 polarimeter, using a 10 mL cell with a 1 dm path length and are reported as $[\alpha]_{\text{D}}^{19}$ (c in g per 100 ml CHCl_3) at 19 °C.

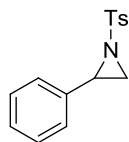
Synthesis and Characterisation of Substrates

General Procedure 1 for Synthesis of Aziridines¹



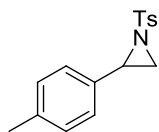
To a 0.5M solution of the corresponding styrene (1.0 eq) and chloramine-T trihydrate (1.2 eq) in 1:3 dichloromethane:distilled water was added iodine (10 mol%) and tetrabutylammonium bromide (0.1 eq) at room temperature under the nitrogen gas. The resulting mixture was stirred for overnight and subsequently passed through a pad of silica gel (1.5 cm), evaporated and first purified by the flash column chromatography with 20% ethyl acetate in hexane to afford yellow solids.

1-Tosyl-2-phenyl aziridine 26



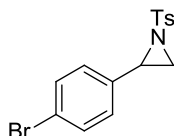
Following the general procedure 1, using 1.00 mL, 8.73 mmol of styrene. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 20:80 (v/v), white solid product (2.00 g, 83% yield) was obtained. ¹H NMR (500 MHz, CDCl₃) δ 7.87 (d, *J* = 8.5 Hz, 2H, tosyl CH_{Ar}), 7.33 (d, *J* = 8.0 Hz, 2H, tosyl CH_{Ar}), 7.31-7.26 (m, 3H, CH_{Ar}), 7.22-7.20 (m, 2H, CH_{Ar}), 3.77 (dd, *J* = 7.0, 4.5 Hz, 1H, PhCHNTs), 2.98 (d, *J* = 7.0 Hz, 1H, CHCH₂NTs), 2.43 (s, 3H, Tosyl), 2.38 (d, *J* = 4.5 Hz, 1H, CHCH₂NTs). ¹³C NMR (125 MHz, CDCl₃) δ 144.7, 135.1, 135.0, 129.8, 128.6, 128.3, 128.0, 126.6, 41.1, 36.0, 21.7. **Note** Data matched that reported previous.^{1, 25}

2-(*p*-Tolyl)-1-tosylaziridine 517



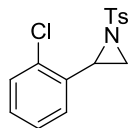
Following the general procedure **1**, using 1.00 mL, 7.59 mmol of 4-methylstyene. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 20:80 (v/v), white solid product (1.81 g, 83% yield) was obtained. ^1H NMR (300 MHz, CDCl_3): δ 7.86 (d, J = 8.1 Hz, 2H, tosyl CH_{Ar}), 7.32 (d, J = 8.1 Hz, 2H, tosyl CH_{Ar}), 7.10 (s, 4H, CH_{Ar}), 3.77 (dd, J = 7.0, 4.5 Hz, 1H, ArCHNTs), 2.97 (d, J = 6.9 Hz, 2H, CHCH_2NTs), 2.43 (s, 3H, tosyl), 2.38 (d, J = 4.8 Hz, 2H, CHCH_2NTs), 2.31 (s, 3H, tolyl). ^{13}C NMR (125 MHz, CDCl_3) δ 138.1, 132.0, 129.8, 129.3, 128.0, 127.1, 126.5, 125.8, 41.1, 35.8, 21.7, 21.2. **Note** Data matched that reported previous.^{13, 14}

2-(4-Bromophenyl)-1-tosylaziridine 518



Following the general procedure **1**, using 0.20 mL, 1.53 mmol of 4-bromostyrene. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 20:80 (v/v), white solid (286 mg, 53% yield) product was obtained. ^1H NMR (500 MHz, CDCl_3): δ 7.86 (d, J = 8.0 Hz, 2H, tosyl CH_{Ar}), 7.42 (d, J = 9.0 Hz, 2H, CH_{Ar}), 7.34 (d, J = 8.0 Hz, 2H, tosyl CH_{Ar}), 7.09 (d, J = 9.0 Hz, 2H, CH_{Ar}), 3.72 (dd, J = 7.0, 4.0 Hz, 1H, ArCHNTs), 2.99 (d, J = 7.0 Hz, 1H, CHCH_2NTs), 2.44 (s, 3H, tosyl), 2.34 (d, J = 4.5 Hz, 1H, CHCH_2NTs). ^{13}C NMR (125 MHz, CDCl_3) δ 144.9, 134.8, 134.2, 131.8, 129.9, 128.2, 128.0, 122.3, 40.4, 36.0, 21.7. **Note** Data matched that reported previous.¹⁵

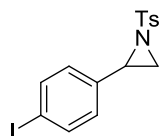
2-(2-Chlorophenyl)-1-tosylaziridine 519



Following the general procedure **1**, using 0.20 mL, 1.56 mmol of 2-chlorostyrene. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 20:80 (v/v), white solid product (235 mg, 49% yield) was obtained. ^1H NMR (500 MHz, CDCl_3): δ 7.90 (d, J = 8.0 Hz, 2H, tosyl CH_{Ar}), 7.36 (d, J = 8.0 Hz, 2H, tosyl CH_{Ar}), 7.33 (d, J = 8.0 Hz, 1H, CH_{Ar}), 7.20-7.17 (m, 3H, CH_{Ar}), 4.04

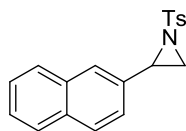
(dd, $J = 7.5, 4.5$ Hz, 1H, ArCHNTs), 3.04 (d, $J = 7.5$ Hz, 2H, CHCH₂NTs), 2.45 (s, 3H, tosyl), 2.29 (d, $J = 4.5$ Hz, 2H, CHCH₂NTs). ¹³C NMR (125 MHz, CDCl₃) δ 144.9, 134.7, 133.8, 133.1, 129.9, 129.3, 129.2, 128.1, 127.5, 127.1, 39.0, 35.7, 21.7. **Note** Data matched that reported previous.¹⁶

2-(4-Iodophenyl)-1-tosylaziridine 520



Following the general procedure **1**, using 121 mg, 0.525 mmol of 4-iodostyrene. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 20:80 (v/v), white solid product (140 mg, 67% yield) was obtained. ¹H NMR (300 MHz, CDCl₃): δ 7.85 (d, $J = 8.1$ Hz, 2H, tosyl CH_{Ar}), 7.61 (d, $J = 8.1$ Hz, 2H, CH_{Ar}), 7.33 (d, $J = 8.1$ Hz, 2H, tosyl CH_{Ar}), 6.95 (d, $J = 8.4$ Hz, 2H, CH_{Ar}), 3.70 (dd, $J = 4.2, 7.2$ Hz, 1H, ArCHNTs), 2.97 (d, $J = 6.9$ Hz, 1H, CHCH₂NTs), 2.43 (s, 3H, tosyl), 2.33 (d, $J = 4.2$ Hz, 1H, CHCH₂NTs). ¹³C NMR (125 MHz, CDCl₃) δ 144.9, 137.7, 134.9, 134.9, 129.9, 128.4, 128.0, 93.9, 40.5, 36.0, 21.7. **Note** This compound has been made according to the procedure reported by Morgan.¹

2-(Naphthalen-2-yl)-1-tosylaziridine 521



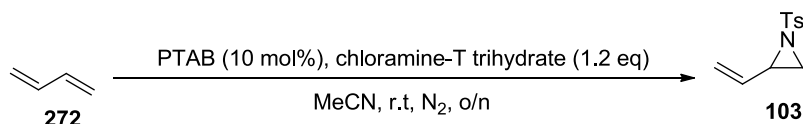
Following the general procedure **1**, using 475 mg, 3.08 mmol of 4-iodostyrene. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 20:80 (v/v), white solid product (229 mg, 23% yield) was obtained. ¹H NMR (300 MHz, CDCl₃): δ 7.90 (d, $J = 8.1$ Hz, 2H, tosyl CH_{Ar}), 7.81-7.23 (m, 4H, CH_{Ar}), 7.48-7.45 (m, 2H, CH_{Ar}), 7.33 (d, $J = 8.1$ Hz, 2H, tosyl CH_{Ar}), 7.28-7.26 (m, 1H, CH_{Ar}), 3.93 (dd, $J = 4.5, 7.2$ Hz, 1H, ArCHNTs), 3.07 (d, $J = 6.9$ Hz, 1H, CHCH₂NTs), 2.50 (d, $J = 4.2$ Hz, 1H, CHCH₂NTs), 2.42 (s, 3H, tosyl). ¹³C NMR (125 MHz, CDCl₃) δ 144.7, 135.0, 133.2, 133.1, 132.5, 129.8, 128.5, 128.0, 127.8, 127.8, 126.5, 126.3, 126.2, 123.7, 41.4, 36.0, 21.7. **Note** Data matched that reported previous.¹⁷

1-Tosyl-2-methyl-2-phenyl aziridine **98**



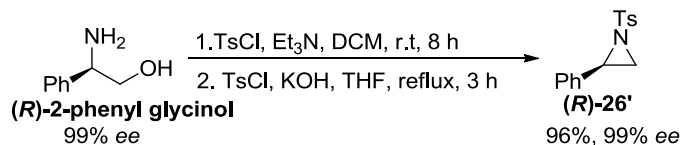
Following the general procedure **1**, using 1.00 mL, 7.70 mmol of α -methylstyrene. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 20:80 (v/v), white solid product (1.97 g, 89% yield) was obtained. ^1H NMR (500 MHz, CDCl_3): δ 7.87 (d, J = 8.3 Hz, 2H, tosyl CH_{Ar}), 7.40 – 7.36 (m, 2H, CH_{Ar}), 7.35 – 7.29 (m, 4H, tosyl CH_{Ar} & CH_{Ar} overlap), 7.29 – 7.26 (m, 1H, CH_{Ar}), 2.96 (s, 1H, CCH_2NTs), 2.52 (s, 1H, CCH_2NTs), 2.43 (s, 3H, tosyl), 2.05 (s, 3H, CH_3CPhNTs). ^{13}C NMR (CDCl_3 , 75 Hz) δ 143.9, 140.9, 137.6, 129.5, 128.3, 127.7, 127.4, 126.4, 51.7, 41.8, 21.5, 20.8. **Note** Data matched that reported previous.¹⁸

Synthesis and Characterisation of Vinylaziridine **103**²



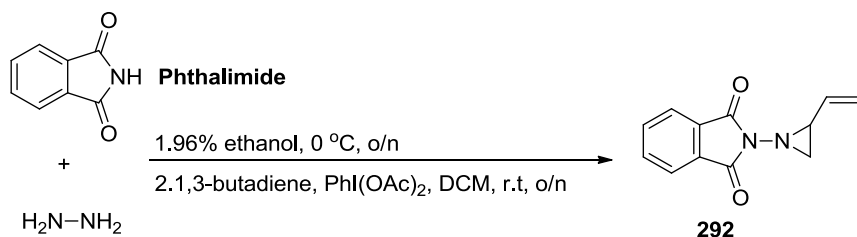
Chloramine-T trihydrate (2.57 g, 11.3 mmol) and phenyltrimethylammonium tribromide (10 mol%) were dissolved in MeCN (42 mL). With vigorous stirring, the solvent was then purged with 1,4-butadiene **272** for 30 mins and then sealed. After 24 h, the reaction mixture was passed through a pad of silica gel (5 cm), evaporated and purified by flash column chromatography (30% ethyl acetate/hexane) to give the desired product as white crystals (813 mg, 60%). ^1H NMR (300 MHz, CDCl_3) δ 7.81(d, J = 3.6 Hz, 2H, tosyl CH_{Ar}), 7.32 (d, J = 3.6 Hz, 2H, tosyl CH_{Ar}), 5.58-5.48 (m, 1H, $\text{CH}=\text{CH}_2$), 5.44 (d, J = 17.0 Hz, 1H, $\text{CH}=\text{CH}_2$), 5.25 (d, J = 10.0 Hz, 1H, $\text{CH}=\text{CH}_2$), 3.26 (m, 1H, $\text{NTsCHCH}=\text{CH}_2$), 2.79 (d, J = 7.1 Hz, 1H, CHCH_2NTs), 2.47 (s, 3H, tosyl), 2.21 (d, J = 7.1 Hz, 1H, CHCH_2NTs). ^{13}C NMR (CDCl_3 , 125 Hz) δ 144.6, 135.2, 133.0, 129.8, 127.9, 120.4, 41.0, 34.2, 21.7. **Note** Data matched that reported previous.²⁵

Synthesis and Characterisation of (*R*)-Phenylaziridine (*R*)-**26'**³



To a solution of (*R*)-2-phenyl glycinol (1.00g, 7.29 mmol, 1.0 eq, 99% *ee*) in anhydrous CH₂Cl₂ (100 ml), was added triethylamine (2.54 ml, 18.2 mmol, 2.5 equiv) followed by aryl sulfonyl chloride (1.53 g, 8.02 mmol, 1.1 equiv) in one portion. The reaction was allowed to stir at room temperature for 8 h. The reaction was quenched with water, extracted with CH₂Cl₂ and dried over anhydrous sodium sulfate. Solvent was then removed under reduced pressure to give the crude product (2.22g) for next step without purification. The crude product was then refluxed with KOH (1.28 g, 22.9 mmol, 3.0 eq) and TsCl (1.60 g, 8.38 mmol, 1.1 eq) in THF (38 mL) at 65 °C for 3 h to afford pure (*R*)-2-phenyl-*N*-sulfonylaziridine **26'** (1.91 g, 96%). The ¹H NMR of (*R*)-**26'** is in agreement with **26**.

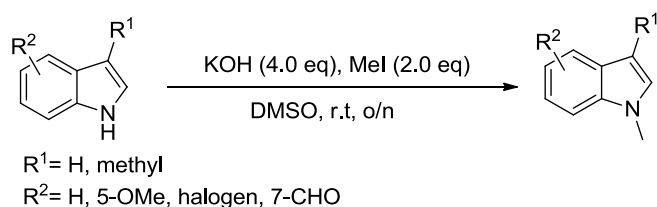
Synthesis and Characterisation of 2-(2-Vinylaziridin-1-yl)isoindoline-1,3-Dione **292**⁴



Phthalimide (1.50 g, 10.2 mmol, 1.0 eq) was dissolved in 96% ethanol (10 mL). Hydrazine (0.45 ml, 11.2 mmol, 1.1 eq, 80% water solution of N₂H₄·H₂O) was subsequently added drop-wise with stirring. The resulting solution was stirred at 0 °C for overnight, then diluted with dichloromethane (20 mL), quenched with distilled water (3×20 mL), dried over MgSO₄ and concentrated by evaporation. The crude product was recrystallised in 96% ethanol to afford white solids **206** (893 mg, 54%). ¹H NMR (500Mz, CDCl₃) δ 7.89-7.85 (m, 2H, CH_{Ar}), 7.77-7.73 (m, 2H, CH_{Ar}), 4.14 (s, 2H, NH₂). *N*-amino-phthalimide **206** (893 mg, 5.51 mmol, 1.0 eq) and PhI(OAc)₂ (1.33 g, 4.13 mmol, 0.75 eq) were dissolved in anhydrous dichloromethane (27.6 mL). The solution was bubbled with 1,3-butadiene (1 atm) at room temperature for 30 mins with stirring, then diluted with dichloromethane (30 mL), quenched with distilled water (3×30 mL), dried over MgSO₄ and concentrated by evaporation. The crude product was finally purified with 35% ethyl acetate in

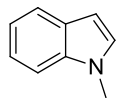
n-pentane to give yellow solids (984 mg, 83%). ¹H NMR (500MHz, CDCl₃ data for major rotamer) δ 7.78-7.77 (m, 2H, CH_{Ar}), 7.69 (m, 2H, CH_{Ar}), 5.80-5.73 (m, 1H, CHCH=CH₂), 5.55 (d, *J* = 17.0 Hz, 1H, CHCH=CH₂), 5.37 (d, *J* = 10.0 Hz, 1H, CHCH=CH₂), 3.08 (q, *J* = 7.0 Hz, 1H, CHCH=CH₂), 2.72 (dd, *J* = 2.0, 8.0 Hz, 1H, CH₂CHCH=CH₂), 2.52 (dd, *J* = 4.0, 5.5 Hz, 1H, CH₂CHCH=CH₂). ¹³C NMR (125 MHz, CDCl₃ data for major rotamer) δ 165.3, 134.4, 134.3, 130.6, 123.2, 119.9, 119.8, 44.2, 38.9. IR ν(cm⁻¹): 2364, 1715, 1464, 1378, 1184, 1064, 1053, 937, 887, 813, 706. HRMS (ES): *m/z* 215.0821 [C₁₂H₁₀N₂O₂+H]⁺, calcd. 215.0815.

General Procedure 2 for Synthesis of Indoles⁵



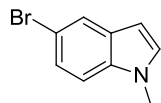
DMSO (0.2 M) was mixed with potassium hydroxide (4.0 eq) by stirring for 30 mins. The corresponding indole (1.0 eq) was then added, and the resulting solution was stirred at room temperature for 1 hr. Iodomethane (2.0 eq) was subsequently added dropwise to the reaction, stirred for 24hrs. The reaction mixture was diluted with ether (50 mL) and washed with water (3×50 mL). The organic phase dried over anhydrous MgSO₄ and concentrated. Purification by the flash column chromatography with 30% ethyl acetate in hexane gave the targeted compounds.

1-Methyl indole 114



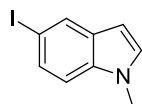
Following the general procedure 2, using 5.00 g, 38.1 mmol of 1*H*-indole. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 30:70 (v/v), brown liquid product (4.75 g, 95% yield) was obtained. ¹H NMR (500 MHz, CDCl₃): δ 7.60 (d, *J* = 7.5 Hz, 1H, CH_{Ar}), 7.25 (d, *J* = 8.0 Hz, 1H, CH_{Ar}), 7.19 (t, *J* = 7.0 Hz, 1H, CH_{Ar}), 7.08 (t, *J* = 7.0 Hz, 1H, CH_{Ar}), 6.94 (d, *J* = 3.0 Hz, 1H, NCH=CH), 6.45 (d, *J* = 3.0 Hz, 1H, NCH=CH), 3.64 (s, 1H, NCH₃). ¹³C NMR (CDCl₃, 75 Hz) δ 136.7, 128.8, 128.5, 121.5, 120.9, 119.3, 109.2, 100.9, 32.8. **Note** Data matched that reported previous.⁵

5-Bromo-1-methylindole 522



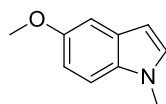
Following the general procedure **2**, using 300 mg, 1.53 mmol of 5-bromoindole. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 30:70 (v/v), yellow solid product (286 mg, 89% yield) was obtained. ^1H NMR (500 MHz, CDCl_3): δ 7.74 (s, 1H, CH_{Ar}), 7.30-7.28 (m, 1H, CH_{Ar}), 7.19 (d, $J = 8.0$ Hz, 1H, CH_{Ar}), 7.05 (d, $J = 3.0$ Hz, 1H, $\text{NCH}=\text{CH}$), 6.42 (d, $J = 3.0$ Hz, 1H, $\text{NCH}=\text{CH}$), 3.77 (s, 3H, NCH_3). ^{13}C NMR (CDCl_3 , 75 Hz) δ 135.2, 130.0, 129.9, 124.2, 123.2, 112.6, 110.6, 100.4, 32.9. **Note** Data matched that reported previous.¹⁹

5-Iodo-1-methylindole 523



Following the general procedure **2**, using 500 mg, 2.06 mmol of 5-iodoindole. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 30:70 (v/v), brown solid product (508 mg, 96% yield) was obtained. ^1H NMR (500 MHz, CDCl_3): δ 7.95 (s, 1H, CH_{Ar}), 7.46 (d, $J = 9.0$ Hz, 1H, CH_{Ar}), 7.10 (d, $J = 8.0$ Hz, 1H, CH_{Ar}), 7.00 (d, $J = 3.5$ Hz, 1H, $\text{NCH}=\text{CH}$), 6.40 (d, $J = 2.0$ Hz, 1H, $\text{NCH}=\text{CH}$), 3.77 (s, 3H, NCH_3). ^{13}C NMR (CDCl_3 , 75 Hz) δ 135.7, 130.9, 129.6, 129.6, 129.5, 111.3, 100.2, 82.9, 32.9. **Note** Data matched that reported previous.²⁰

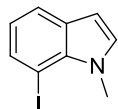
5-Methoxy-1-methylindole 524



Following the general procedure **2**, using 500 mg, 3.40 mmol of 5-methoxyindole. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 30:70 (v/v), brown solid product (510 mg, 93% yield) was obtained. ^1H NMR (500 MHz, CDCl_3): δ 7.21 (d, $J = 9.0$ Hz, 1H, CH_{Ar}), 7.09 (d, $J = 2.0$ Hz, 1H, CH_{Ar}), 7.02 (d, $J = 2.5$ Hz, 1H, $\text{NCH}=\text{CH}$), 6.89 (dd, $J = 8.5$, 2 Hz, 1H, CH_{Ar}), 6.40 (d, $J = 3.0$ Hz, 1H, $\text{NCH}=\text{CH}$), 3.85 (s, 3H, NCH_3), 3.77 (s, 3H, OCH_3). ^{13}C NMR (CDCl_3 , 75 Hz) δ 153.9, 132.0, 129.2, 128.7, 111.8, 109.8, 102.4, 100.3, 55.8, 32.8. **Note** Data matched that reported

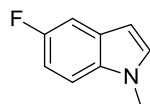
previous.²¹

7-Iodo-1-methylindole 525



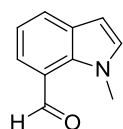
Following the general procedure **2**, using 300 mg, 1.24 mmol of 7-iodoindole. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 30:70 (v/v), brown solid product (312 mg, 98% yield) was obtained. ¹H NMR (500 MHz, CDCl₃): δ 7.66 (d, *J* = 7.5 Hz, 1H, CH_{Ar}), 7.56 (d, *J* = 7.5 Hz, 1H, CH_{Ar}), 7.00 (d, *J* = 3.0 Hz, 1H, NCH=CH), 7.76 (t, *J* = 8.0 Hz, 1H, CH_{Ar}), 6.40 (d, *J* = 3.0 Hz, 1H, NCH=CH), 4.17 (s, 3H, NCH₃). ¹³C NMR (CDCl₃, 75 Hz) δ 135.4, 133.8, 131.9, 130.8, 121.1, 120.9, 100.7, 72.8, 36.8. **Note** Data matched that reported previous.²²

7-Fluoro-1-methylindole 526



Following the general procedure **2**, using 300 mg, 2.22 mmol of 5-fluoroindole. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 30:70 (v/v), red solid product (252 mg, 76% yield) was obtained. ¹H NMR (300 MHz, CDCl₃): δ 7.28-7.19 (m, 2H, CH_{Ar}), 7.07 (d, *J* = 3.0 Hz, 1H, NCH=CH), 6.99-6.93 (m, 1H, CH_{Ar}), 6.43 (d, *J* = 2.4 Hz, 1H, NCH=CH), 3.78 (s, 3H, NCH₃). ¹³C NMR (CDCl₃, 75 Hz) δ 157.8 (*J* = 231 Hz), 133.3, 130.3, 128.5, 109.9 (*J* = 11 Hz), 109.6 (*J* = 6 Hz), 105.4 (*J* = 23 Hz), 100.7 (*J* = 6 Hz), 33.0. **Note** Data matched that reported previous.²³

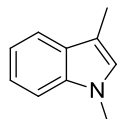
1-Methyl-1*H*-indole-7-carbaldehyde 527



Following the general procedure **2**, using 300 mg, 2.07 mmol of 1*H*-indole-7-carbaldehyde. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 30:70 (v/v), yellow solid product (158 mg, 48% yield) was obtained. ¹H NMR (500 MHz, CDCl₃): δ 10.22 (s, 1H, O=CH), 7.88 (d, *J* = 8.0 Hz, 1H, CH_{Ar}), 7.70 (d, *J* = 7.5 Hz, 1H, CH_{Ar}), 7.23 (t, *J* = 8.0 Hz, 1H, CH_{Ar}), 7.08 (d, *J* = 3.0 Hz, 1H, NCH=CH), 6.59 (d, *J* = 3.0 Hz, 1H, NCH=CH), 4.15 (s, 3H, NCH₃). ¹³C NMR (CDCl₃, 75 Hz) δ

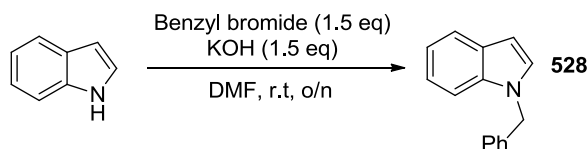
191.0, 133.6, 132.3, 131.5, 130.2, 128.0, 122.8, 118.7, 102.2, 38.9. **Note** Data matched that reported previous.²⁴

1,3-Dimethyl indole 101



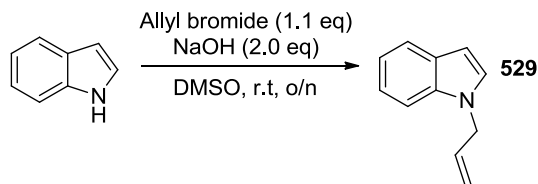
Following the general procedure **2**, using 1.00 g, 7.62 mmol of 3-methylindole. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 30:70 (v/v), yellow liquid product was obtained in quantitative yield. ¹H NMR (500 MHz, CDCl₃): δ 7.57 (d, *J* = 8.0 Hz, 1H, CH_{Ar}), 7.27 (t, *J* = 8.5 Hz, 1H, CH_{Ar}), 7.22 (t, *J* = 7.0 Hz, 1H, CH_{Ar}), 7.11 (t, *J* = 7.0 Hz, 1H, CH_{Ar}), 6.82 (s, 1H, CH₃C=CHN), 3.73 (s, 3H, NCH₃), 2.33 (s, 3H, NCH=CCH₃). ¹³C NMR (CDCl₃, 125 Hz) δ 137.1, 128.7, 126.6, 121.5, 119.0, 118.5, 110.1, 109.1, 32.5, 9.6. **Note** Data matched that reported previous.¹⁹

Synthesis and Characterisation of *N*-Benzyl Indole 528⁵



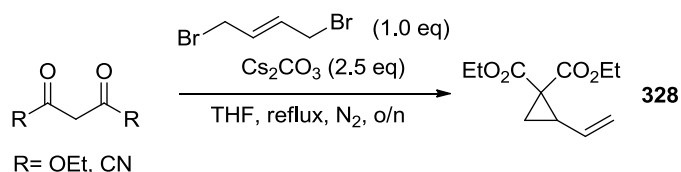
To a solution of 1H-indole (600mg, 5.12mmol, 1.0eq) and potassium hydroxide (0.431 mg, 7.68mmol, 1.5eq) in DMF (11 mL) added benzyl bromide (0.913ml, 1.31g, 7.68mmol, 1.5eq). The resultant mixture was stirred for overnight, diluted with ethyl acetate (20 mL), washed with distilled water (3×20 mL), dried over MgSO₄ and concentrated. Purification by the flash column chromatography with 30% ethyl acetate in hexane gave white solid (871g, 82%). ¹H NMR (500 MHz, CDCl₃): δ 7.65 (d, *J* = 8.0 Hz, 1H, Indole CH_{Ar}), 7.31-7.25 (m, 4H, Indole CH_{Ar}, CH_{Ar} & CH=CHNBn overlap), 7.17 (t, *J* = 7.5 Hz, 1H, Indole CH_{Ar}), 7.13-7.09 (m, 4H, Indole CH_{Ar} & CH_{Ar} overlap), 6.55 (s, 1H, BnNCH=CH), 5.33 (s, 2H, NCH₂Ph). ¹³C NMR (CDCl₃, 75 Hz) δ 137.5, 136.2, 128.7, 128.6, 128.2, 127.5, 126.7, 121.6, 120.9, 119.4, 109.6, 101.6, 50.0. **Note** Data matched that reported previous.⁵

Synthesis and Characterisation of *N*-Allyl Indole 529⁶



To a solution of 1*H*-indole (500mg, 4.27mmol, 1.0eq) and sodium hydroxide (0.342mg, 8.54mmol, 2.0eq) in DMSO (11 mL) added allyl bromide (0.410mL, 0.573g, 4.70mmol, 1.1eq). The resultant mixture was stirred for overnight, diluted with ethyl acetate (20 mL), washed with distilled water (3×20 mL), dried over MgSO₄ and concentrated. Purification by the flash column chromatography with 20% ethyl acetate in hexane gave white solids (457mg, 68%). ¹H NMR (500 MHz, CDCl₃): δ 7.64 (t, *J* = 7.0 Hz, 1H, CH_{Ar}), 7.33 (t, *J* = 7.0 Hz, 1H, CH_{Ar}), 7.25-7.18 (m, 1H, CH_{Ar}), 7.13-7.19 (m, 2H, CH_{Ar} & CH=CHN overlap), 6.52 (d, *J* = 4.0 Hz, 1H, CH=CHN), 6.04-5.97 (m, 1H, NCH₂CH=CH₂), 5.21 (dd, *J* = 4.5, 6 Hz, 1H, NCH₂CH=CH₂), 5.10 (d, *J* = 17.0 Hz, 1H, NCH₂CH=CH₂), 4.74 (d, *J* = 1.5 Hz, 2H, NCH₂CH=CH₂). ¹³C NMR (CDCl₃, 75 Hz) δ 136.1, 133.5, 128.7, 127.8, 121.5, 120.9, 119.4, 117.2, 109.6, 101.4, 48.8. **Note** Data matched that reported previous.⁶

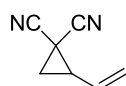
General Procedure 3 for Synthesis of Diethyl 2-Vinylcyclopropane-1, 1-Dicarboxylate 328⁷



To a solution of (*E*)-1,4-dibromobut-2-ene (3.0 g, 14.0 mmol, 1.0 eq) in anhydrous tetrahydrofuran (70 mL) was added diethyl malonate (2.14 mL, 14.0 mmol, 1.0 eq) and caesium carbonate (11.4 g, 35.1 mmol, 2.5 eq). The mixture was refluxed at 60 °C. After the reaction proceeds for 16 h, the mixture was extracted with ethyl acetate (3×50 mL) and the combined organic layer was washed with distilled water and dried over MgSO₄. After filtration, the solvent was removed *in vacuo*. The residue was purified by flash column chromatography (Ethyl acetate: Hexane, 10:90) to furnish a clear oily liquid in the yield of 87%. ¹H NMR (500 MHz, CDCl₃) δ 5.46-5.39 (m, 1H, CH=CH₂), 5.28 (d, *J* =

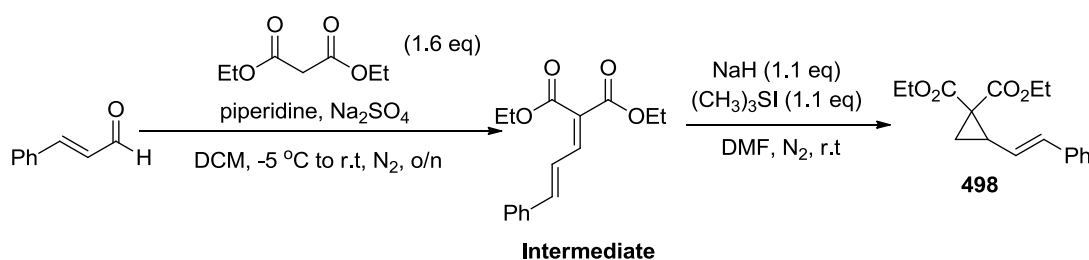
17.0 Hz, 1H, CH=CH₂), 5.12 (d, *J* = 11.5 Hz, 1H, CH=CH₂), 4.24-4.13 (m, 4H, OCH₂CH₃), 2.56 (q, *J* = 8.0 Hz, 1H, CH₂CHCH=CH₂), 1.67 (dd, *J* = 8.0, 5.0 Hz, 1H, CH₂CHCH=CH₂), 1.53 (dd, *J* = 9.5, 5.0 Hz, 1H, CH₂CHCH=CH₂), 1.52-1.24 (m, 6H, OCH₂CH₃). ¹³C NMR (CDCl₃, 75 Hz) δ 169.5, 167.3, 133.0, 118.3, 61.5, 61.3, 35.8, 30.9, 20.2, 14.0, 13.9. **Note** Data matched that reported previous.⁷

2-Vinylcyclopropane-1,1-dicarbonitrile 530⁷



This compound was synthesised in 43% yield according to the general procedure **3** using 1,4-dibromobutene (1.0 g, 4.67 mmol, 1.0 eq), malononitrile (339.7 mg, 5.14 mmol, 1.1 eq), caesium carbonate (3.81 g, 11.2 mmol, 2.5 eq) and anhydrous tetrahydrofuran (23.4 mL). Ethyl acetate cannot be completely removed due to volatility of this compound. ¹H NMR (500 MHz, CDCl₃) δ 5.65-5.59 (m, 1H, CH=CH₂), 5.54 (d, *J* = 16.0 Hz, 1H, CH=CH₂), 5.51 (d, *J* = 9.5 Hz, 1H, CH=CH₂), 2.69 (q, *J* = 8.0 Hz, 1H, CHCH=CH₂), 2.07 (dd, *J* = 8.5, 6.5 Hz, 1H, CH₂CHCH=CH₂), 1.83 (dd, *J* = 6.5, 8.5 Hz, 1H, CH₂CHCH=CH₂). ¹³C NMR (75 Hz, CDCl₃) δ 129.6, 123.0, 114.8, 113.2, 33.1, 23.2, 5.6. **Note** Data matched that reported previous, solvent signals present in the ¹H and ¹³C NMR.^{7, 26}

General Procedure 4 for Synthesis of (E)-Diethyl 2-Styrylcyclopropane-1,1-Dicarboxylate 498^{8,9}

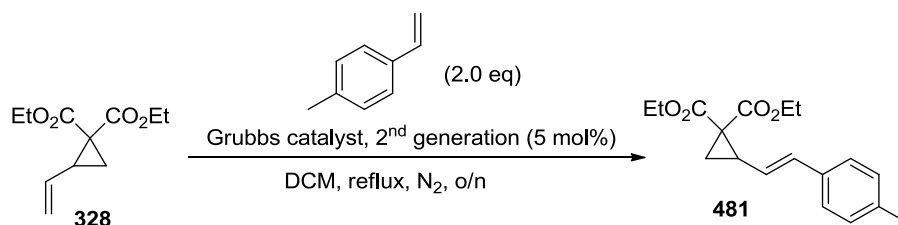


To a solution of cinnamaldehyde (3.3 g, 25.0 mmol, 1.0 eq) in anhydrous dichloromethane (40 mL), which was cooled with -5 °C ice/salt water was added diethyl malonate (6.4 g, 39.9 mmol, 1.6 eq) dropwise over 10 mins. A few drops of piperidine and sodium sulphate (10 g) were then added at room temperature. The reaction mixture was stirred for 24 hrs, diluted with ethyl acetate (50 mL), washed with distilled water (3×50 mL), and organic layer was dried over MgSO₄ and evaporated

under reduced pressure. The resulting crude product was purified with Kugelrohr distillation to give the intermediate as a dark oil. ^1H NMR (CDCl_3 , 500 MHz) δ 7.52 (d, J = 11.0 Hz, 1H, $\text{C}=\text{CHCH}=\text{CHPh}$), 7.49 (d, J = 14.0 Hz, 2H, $\text{C}=\text{CHCH}=\text{CHPh}$), 7.40-7.32 (m, 3H, CH_{Ar}), 7.26 (app t, J = 14.0 Hz, 1H, CH_{Ar}), 7.04 (d, J = 14.0 Hz, 1H, $\text{C}=\text{CHCH}=\text{CHPh}$), 4.37 (q, J = 7.0 Hz, 2H, OCH_2CH_3), 4.28 (q, J = 7.0 Hz, 2H, OCH_2CH_3), 1.38 (t, J = 7.0 Hz, 3H, OCH_2CH_3), 1.32 (t, J = 7.0 Hz, 2H, OCH_2CH_3). **Note** Data matched that reported previous.^{8,9} To a mixture of sodium hydride (0.535 g, 22.3 mmol, 1.1 eq, 60 % dispersion in mineral oil) and trimethylsulfonium iodide (4.90 g, 22.3 mmol, 1.1 eq) in anhydrous dimethylformamide (28.5 mL), which has been stirred at room temperature for 30 mins, was added a solution of the intermediate in anhydrous dimethylformamide (12.1 mL). The reaction mixture was stirred for overnight, diluted with ethyl acetate (50 mL), washed with distilled water (3×50 mL), dried over MgSO_4 , evaporated under reduced pressure and purified with 15% ethyl acetate in hexane to give yellow oil (1.00 g) as product in 14% overall yield. ^1H NMR (CDCl_3 , 500 MHz) δ 7.30-7.26 (m, 4H, CH_{Ar}), 7.23-7.20 (m, 1H, CH_{Ar}), 6.64 (d, J = 15.5 Hz, 1H, $\text{CH}=\text{CHPh}$), 5.83 (dd, J = 15.5, 8.5 Hz, 1H, $\text{CH}=\text{CHPh}$), 4.27-4.16 (m, 4H, OCH_2CH_3), 2.74 (q, J = 8.0 Hz, 1H, $\text{CHCH}=\text{CHPh}$), 1.82 (dd, J = 7.5, 5.0 Hz, 1H, $\text{CH}_2\text{CHCH}=\text{CHPh}$), 1.66 (dd, J = 7.5, 5.0 Hz, 1H, $\text{CH}_2\text{CHCH}=\text{CHPh}$), 1.27 (t, J = 7.0 Hz, 3H, OCH_2CH_3), 1.23 (t, J = 7.0 Hz, 3H, OCH_2CH_3). ^{13}C NMR (CDCl_3 , 125 Hz) δ 169.6, 167.6, 136.8, 133.6, 128.6, 127.6, 126.1, 124.8, 61.7, 61.5, 36.3, 31.2, 21.0, 14.2, 14.1. **Note** Data matched that reported previous.^{8,9}

General Procedure 5 for Synthesis of Substituted Styrenyl Cyclopropanes¹⁰

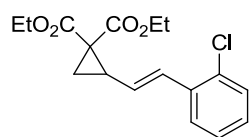
(*E*)-Diethyl 2-(4-methylstyryl)cyclopropane-1,1-dicarboxylate **481**



An oven-dried 10 mL flask was charged with Grubbs catalyst, 2nd generation (34.5 mg, 0.041 mmol, 5 mol%) under nitrogen atmosphere at room temperature. A solution of **328** (300 mg, 1.41 mmol, 1.0 eq) and 4-methylstyrene (0.21 mL, 1.63 mmol, 2.0 eq) in anhydrous dichloromethane (3.2 mL) was added to the flask. Ethyl acetate (50 mL) was added after which the reaction mixture was refluxed at

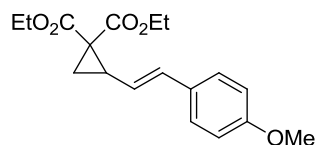
65 °C overnight, then it was washed with brine (3×30 mL) and the organic phase was dried over MgSO₄. After filtration, the solvent was removed in *vacuo*. The resulting crude product was then purified with flash column chromatography (20% ethyl acetate in hexane). The product was isolated as light green oil (134.1 mg) in 55% yield. ¹H NMR (CDCl₃, 300MHz) δ 7.19 (d, *J* = 8.1 Hz, 2H, CH_{Ar}), 7.09 (d, *J* = 7.8 Hz, 2H, CH_{Ar}), 6.60 (d, *J* = 15.6 Hz, 1H, CHCH=CHPh), 5.76 (dd, *J* = 15.9, 8.7 Hz, 1H, CHCH=CHPh), 4.27-4.14 (m, 4H, OCH₂CH₃), 2.72 (q, *J* = 8.7 Hz, 1H, CH₂CHCH=CHPh), 2.31 (s, 3H, tolyl), 1.81 (dd, *J* = 7.2, 5.1 Hz, 1H, CH₂CHCH=CHPh), 1.64 (dd, *J* = 7.2, 5.1 Hz, 1H, CH₂CHCH=CHPh), 1.28 (t, *J* = 7.2 Hz, 3H, OCH₂CH₃), 1.24 (t, *J* = 7.2 Hz, 3H, OCH₂CH₃). ¹³C NMR (75Mz, CDCl₃) δ 169.9, 167.9, 137.7, 134.2, 133.8, 129.5, 126.3, 123.9, 61.9, 61.8, 36.6, 31.6, 21.5, 21.3, 14.5, 14.4. IR ν(cm⁻¹): 2926, 2360, 2333, 1734, 1718, 1559, 1502, 1457, 1374, 1319, 1280, 1250, 1201, 1135, 1026, 964. HRMS (ESI-TOF): *m/z* 325.1403 [C₁₈H₂₂O₄ + Na]⁺, calcd. 325.1416.

(*E*)-Diethyl 2-(2-chlorostyryl)cyclopropane-1,1-dicarboxylate 482



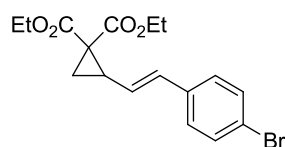
This compound was synthesised in 96% yield according to the general procedure **5** using **328** (150 mg, 0.707 mmol, 1.0 eq), 2-chlorostyrene (0.18 mL, 1.41 mmol, 2.0 eq) and Grubbs catalyst 2nd generation (30.0 mg, 0.0350 mmol, 5 mol%) in anhydrous dichloromethane (2.7 mL). ¹H NMR (CDCl₃, 300 MHz) δ 7.41-7.38 (m, 1H, CH_{Ar}), 7.34-7.31(m, 1H, CH_{Ar}), 7.20-7.12 (m, 2H, CH_{Ar}), 7.03 (d, *J* = 15.6 Hz, 1H, CHCH=CHAr), 5.82 (dd, *J* = 15.6, 9.0 Hz, 1H, CHCH=CHAr), 4.29-4.16 (m, 4H, OCH₂CH₃), 2.79 (q, *J* = 7.5 Hz, 1H, CH₂CHCH=CHAr), 1.83 (dd, *J* = 7.2, 4.8 Hz, 1H, CH₂CHCH=CHAr), 1.69 (dd, *J* = 7.2, 4.8 Hz, 1H, CH₂CHCH=CHAr), 1.29 (t, *J* = 7.2 Hz, 3H, OCH₂CH₃), 1.24 (t, *J* = 7.2 Hz, 3H, OCH₂CH₃). ¹³C NMR (75Mz, CDCl₃) δ 169.4, 167.5, 134.8, 132.7, 129.7, 129.7, 128.5, 127.8, 126.8, 126.5, 61.7, 61.6, 36.4, 31.1, 21.1, 14.2, 14.1. IR ν(cm⁻¹): 1730, 1718, 1653, 1559, 1317, 1274, 1199, 1126, 963, 749. HRMS (ESI-TOF): *m/z* 345.0886 [C₁₇H₁₉ClO₄ + Na]⁺, calcd. 345.0870.

(E)-Diethyl 2-(4-methoxystyryl)cyclopropane-1,1-dicarboxylate 483



This compound was synthesised in 66% yield according to the general procedure **5** using **328** (120 mg, 0.565 mmol, 1.0 eq), 4-methoxystyrene (0.15 mL, 1.13 mmol, 2.0 eq) and Grubbs catalyst 2nd generation (24.0 mg, 0.028 mmol, 5 mol%) in anhydrous dichloromethane (2.1 mL). **Note** compound contained 10% of homo-coupled styrene which could not be completely removed following multiple attempts at chromatography. ¹H NMR (CDCl₃, 500 MHz) δ 7.23 (d, J = 8.5 Hz, 2H, CH_{Ar}), 6.89 (d, J = 9.0 Hz, 2H, CH_{Ar}), 6.58 (d, J = 15.5 Hz, 1H, CHCH=CHAr), 5.68 (dd, J = 16.0, 8.5 Hz, 1H, CHCH=CHAr), 4.26-4.15 (m, 4H, OCH₂CH₃), 3.79 (s, 3H, OCH₃), 2.71 (q, J = 8.0 Hz, 1H, CH₂CHCH=CHAr), 1.80 (dd, J = 7.5, 4.5 Hz, 1H, CH₂CHCH=CHAr), 1.64 (dd, J = 7.5, 4.5 Hz, 1H, CH₂CHCH=CHAr), 1.28 (t, J = 7.0 Hz, 3H, OCH₂CH₃), 1.22 (t, J = 7.0 Hz, 3H, OCH₂CH₃). ¹³C NMR (125 MHz, CDCl₃) δ 169.7, 167.6, 159.2, 133.1, 129.6, 127.3, 122.4, 114.0, 61.6, 61.5, 55.3, 36.3, 31.4, 21.0, 14.3, 14.1. IR ν (cm⁻¹): 2166, 2022, 1734, 1719, 1654, 1636, 1578, 1512, 1254, 1201, 1176, 1132, 1032, 964. HRMS (ESI-TOF): m/z 341.1378 [C₁₈H₂₂O₅ + Na]⁺, calcd. 341.1365.

(E)-Diethyl 2-(4-bromostyryl)cyclopropane-1,1-dicarboxylate 484

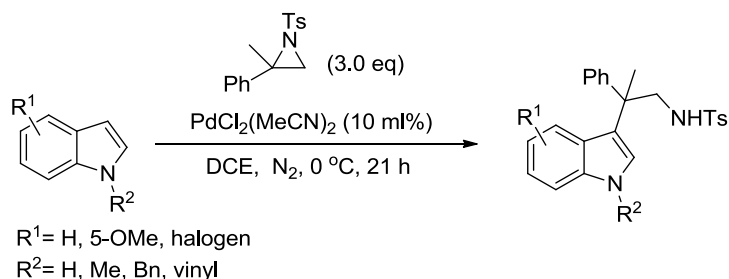


This compound was synthesised in 13% yield according to the general procedure **5** using **328** (111.5 mg, 0.5250 mmol, 1.0 eq), 4-bromostyrene (0.14 mL, 1.1 mmol, 2.0 eq) and Grubbs catalyst 2nd generation (22.3 mg, 0.0260 mmol, 5 mol%) in anhydrous dichloromethane (2.1 mL). ¹H NMR (CDCl₃, 500 MHz) δ 7.40 (d, J = 8.5 Hz, 2H, CH_{Ar}), 7.15 (d, J = 8.5 Hz, 2H, CH_{Ar}), 6.57 (d, J = 15.5 Hz, 1H, CHCH=CHAr), 5.82 (dd, J = 16.0, 9.0 Hz, 1H, CHCH=CHAr), 4.26-4.15 (m, 4H, OCH₂CH₃), 2.71 (q, J = 8.5 Hz, 1H, CH₂CHCH=CHAr), 1.81 (dd, J = 6.5, 4.5 Hz, 1H, CH₂CHCH=CHAr), 1.66 (dd, J = 6.5, 4.5 Hz, 1H, CH₂CHCH=CHAr), 1.29 (t, J = 7.5 Hz, 3H, OCH₂CH₃), 1.22 (t, J = 7.0 Hz, 3H, OCH₂CH₃). ¹³C NMR (125 MHz, CDCl₃) δ 169.5, 167.5, 135.7, 132.4, 131.7, 127.6, 125.8, 121.3, 61.7, 61.6, 36.3, 31.0, 21.0, 14.2, 14.1. IR ν (cm⁻¹): 2983, 1721,

1489, 1370, 1318, 1274, 1200, 1131, 1073, 1024, 1009, 964, 813. HRMS (ESI-TOF): m/z 389.0381 [$C_{17}H_{19}BrO_4 + Na$] $^+$, calcd. 389.0364.

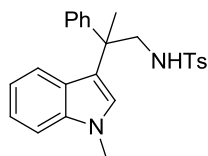
Synthesis and Characterisation of Products

General Procedure 6 for the Ring-Opening of 2,2'-Disubstituted Aziridine **98** with *N*-Methylindoles



A solution of 2-methyl-2-phenyl-1-tosyl aziridine **98** (3.0 eq) in anhydrous DCE (30 mL) was added dropwise over 6 h to a solution of *N*-methylindoles (1.0 eq) in anhydrous DCE (10 mL) in the presence of $\text{PdCl}_2(\text{MeCN})_2$ (10 mol%) at 0 °C under a N_2 atmosphere. The resultant solution was then stirred at 0 °C for overnight, diluted with ethyl acetate (20 mL), washed with distilled water (3×20 mL), and organic layer was dried over MgSO_4 and evaporated under reduced pressure. The crude product was then purified with column chromatography (ethyl acetate: hexane=40:60) to give the product as a clear oil.

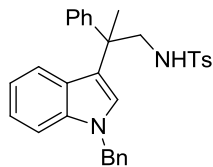
4-Methyl-*N*-(2-(1-methyl-1*H*-indol-3-yl)-2-phenylpropyl)benzenesulfonamide **118**



Following the general procedure **6**, using 100 mg, 0.348 mmol of aziridine **98** and 15.4 mg, 0.116 mmol of **114**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear oil product (45.2 mg, 93% yield) was obtained. IR (KBr): $\nu = 3337, 2978, 2922, 1647, 1560, 1540, 1473, 1452, 1374, 1317, 1155, 1085, 1045, 879, 663$. ^1H NMR (500 MHz, CDCl_3): δ 7.49 (d, $J = 8.5$ Hz, 2H, CH_{Ar}), 7.28 (d, $J = 8.5$ Hz, 1H, CH_{Ar}), 7.25-7.14 (m, 8H, CH_{Ar}), 7.01 (s, 1H, $\text{C}=\text{CHNCH}_3$), 6.76-6.72 (m, 2H, CH_{Ar}), 4.03 (m, 1H, CH_2NHTs), 3.79 (s, 3H, NCH_3), 3.65 (dd, $J = 9.0, 11.5$ Hz, 1H, CH_2NHTs), 3.53 (dd, $J = 4.5, 11.5$ Hz, 1H, CH_2NHTs), 2.39 (s, 3H, tosyl), 1.73 (s,

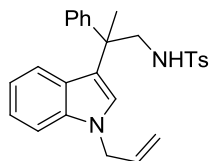
3H, PhC(CH₃)CH₂). ¹³C NMR (75 MHz, CDCl₃): δ 145.7, 143.2, 137.7, 136.1, 129.6, 128.4, 127.8, 126.9, 126.6, 126.5, 125.6, 121.7, 120.7, 118.9, 117.8, 109.4, 51.5, 43.0, 32.9, 27.3, 21.5. HRMS: *m/z*; calcd for C₂₅H₂₆N₂O₂SNa: 441.1613 [M+ Na]⁺; found: 441.1620.

***N*-(2-(1-Benzyl-1*H*-indol-3-yl)-2-phenylpropyl)-4-methylbenzenesulfonamide 119**



Following the general procedure **6**, using 90.4 mg, 0.315 mmol of aziridine **98** and 22.0 mg, 0.105 mmol of **528**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear oil product (73.5 mg, 81% yield) was obtained. 8% inseparable compound was also produced. IR (KBr): ν = 3287, 3061, 2923, 1598, 1543, 1496, 1453, 1402, 1327, 1184, 1160, 1092, 1062, 1029, 965, 909, 814, 729, 699, 665. ¹H NMR (500 MHz, CDCl₃): δ 7.48 (d, *J* = 8.5 Hz, 2H, CH_{Ar}), 7.35-7.08 (m, 15H, CH_{Ar}), 6.76 (d, *J* = 8.1 Hz, 1H, CH_{Ar}), 6.75 (s, 1H, C=CHNBN), 5.32 (d, *J* = 5 Hz, 2H, NCH₂Ph) 4.00 (dd, *J* = 4.0, 7.5 Hz, 1H, NHTs), 3.66 (dd, *J* = 8.5, 11.5 Hz, 1H, CH₂NHTs), 3.54 (dd, *J* = 4.0, 11.0 Hz, 1H, CH₂NHTs), 2.38 (s, 3H, tosyl), 1.73 (s, 3H, PhC(CH₃)CH₂). ¹³C NMR (75 MHz, CDCl₃): δ 145.5, 143.2, 137.4, 137.3, 136.1, 129.6, 128.9, 128.5, 127.7, 127.1, 127.0, 126.9, 126.6, 126.6, 125.9, 121.9, 120.9, 119.1, 118.8, 110.0, 51.5, 50.1, 43.1, 27.1, 21.5. HRMS: *m/z*; calcd for C₃₁H₃₀N₂O₂SNa: 517.1926 [M+ Na]⁺; found: 517.1951.

***N*-(2-(1-Allyl-1*H*-indol-3-yl)-2-phenylpropyl)-4-methylbenzenesulfonamide 120**

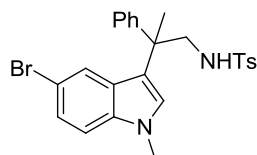


Following the general procedure **6**, using 130 mg, 0.452 mmol of aziridine **98** and 23.7 mg, 0.151 mmol of **529**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear oil product (51.0 mg, 73% yield) was obtained. IR (KBr): ν = 3299, 2360, 1635. 1539, 1466, 1399, 1328, 1186, 1161, 1093, 1061, 812, 739, 699, 663. ¹H NMR (500 MHz, CDCl₃): δ 7.50 (d, *J* = 8.0 Hz, 2H, CH_{Ar}), 7.29-7.16 (m, 8H, CH_{Ar}), 7.12 (t, *J* = 7.5 Hz, 1H, CH_{Ar}), 7.05 (s, 1H, C=CHNCH₂CH=CH₂), 6.78-6.72 (m, 2H, CH_{Ar}), 6.06-6.00 (m, 1H, NCH₂CH=CH₂), 5.25 (d, *J* = 10.0 Hz, 1H, NCH₂CH=CH₂), 5.14 (d, *J* = 17.0 Hz, 1H, NCH₂CH=CH₂), 4.50 (d, *J* = 1.5 Hz, 2H,

$\text{NCH}_2\text{CH}=\text{CH}_2$), 4.02 (dd, $J = 8.0, 4.0$ Hz, 1H, *NHTs*), 3.66 (dd, $J = 11.0, 8.0$ Hz, 1H, CH_2NHTs), 3.54 (dd, $J = 11.0, 4.0$ Hz, 1H, CH_2NHTs), 2.39 (s, 3H, tosyl), 1.73 (s, 3H, $\text{PhC}(\text{CH}_3)\text{CH}_2$). ^{13}C NMR (75 MHz, CDCl_3): δ 145.6, 143.2, 137.2, 136.2, 133.3, 129.6, 128.6, 128.5, 127.0, 126.6, 126.5, 125.9, 121.7, 120.8, 119.0, 118.4, 117.6, 109.8, 51.6, 48.9, 43.1, 27.2, 21.5. HRMS: m/z ; calcd for $\text{C}_{27}\text{H}_{28}\text{N}_2\text{O}_2\text{Na}$: 467.1769 $[\text{M}+\text{Na}]^+$; found: 467.1788.

***N*-(2-(5-Bromo-1-methyl-1*H*-indol-3-yl)-2-phenylpropyl)-4-methylbenzenesulfonamide**

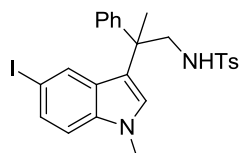
121



Following the general procedure **6**, using 101 mg, 0.352 mmol of aziridine **98** and 25.0 mg, 0.117 mmol of **522**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear oil product (53.4 mg, 91% yield) was obtained. IR (KBr): $\nu = 3289, 2916, 1705, 1653, 1573, 1488, 1420, 1317, 1161, 1093, 1060, 1029, 813, 792, 765, 700, 668$. ^1H NMR (500 MHz, CDCl_3): δ 7.47 (d, $J = 8.5$ Hz, 2H, CH_{Ar}), 7.26-7.12 (m, 9H, CH_{Ar}), 7.04 (s, 1H, $\text{C}=\text{CHNCH}_3$), 6.80 (s, 1H, CH_{Ar}), 4.01 (dd, $J = 9.0, 4.0$ Hz, 1H, *NHTs*), 3.77 (s, 3H, NCH_3), 3.65 (dd, $J = 8.5, 11.0$ Hz, 1H, CH_2NHTs), 3.41 (dd, $J = 4.0, 11.5$, 1H, CH_2NHTs), 2.41 (s, 3H, tosyl), 1.71 (s, 3H, $\text{PhC}(\text{CH}_3)\text{CH}_2$). ^{13}C NMR (75 MHz, CDCl_3): δ 145.2, 143.4, 136.4, 135.8, 129.7, 129.1, 128.6, 127.2, 126.9, 126.8, 126.5, 124.7, 122.9, 117.5, 112.4, 111.0, 51.4, 42.9, 33.1, 27.3, 21.6. HRMS: m/z ; calcd for $\text{C}_{25}\text{H}_{24}\text{BrN}_2\text{O}_2\text{S}$: 495.0742 $[\text{M}-\text{H}]^-$; found: 495.0720.

***N*-(2-(5-Iodo-1-methyl-1*H*-indol-3-yl)-2-phenylpropyl)-4-methylbenzenesulfonamide**

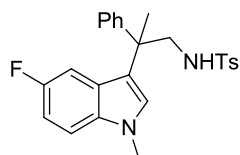
122



Following the general procedure **6**, using 83.0 mg, 0.288 mmol of aziridine **98** and 25.0 mg, 0.0961 mmol of **523**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear oil product (23.0 mg, 44% yield) was obtained. IR (KBr): $\nu = 3272, 2973, 1701, 1636, 1542, 1471, 1418, 1330, 1160, 1091, 895, 814, 766, 701, 666$. ^1H NMR (500 MHz, CDCl_3): δ 7.47 (d, $J =$

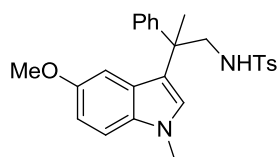
8.0 Hz, 2H, CH_{Ar}), 7.39 (d, *J* = 8.5 Hz, 1H, CH_{Ar}), 7.26-7.20 (m, 5H, CH_{Ar}), 7.12 (d, *J* = 7.5 Hz, 2H, CH_{Ar}), 7.06 (d, *J* = 8.5 Hz, 1H, CH_{Ar}), 7.02 (m, 1H, CH_{Ar}), 6.99 (s, 1H, C=CHNCH₃), 4.91-3.99 (m, 1H, NHTs), 3.77 (s, 3H, NCH₃), 3.65 (dd, *J* = 11.0, 8.5 Hz, 1H, CH₂NHTs), 3.41 (dd, *J* = 11.0, 3.5 Hz, 1H, CH₂NHTs), 2.42 (s, 3H, tosyl), 1.71 (s, 3H, PhC(CH₃)CH₂). ¹³C NMR (75 MHz, CDCl₃): δ 145.1, 143.4, 136.8, 135.8, 130.1, 129.8, 129.1, 128.7, 128.5, 128.0, 126.8, 126.7, 126.4, 117.2, 111.5, 82.7, 51.4, 42.9, 33.0, 27.3, 21.7. HRMS: *m/z*; calcd for C₂₅H₂₄IN₂O₂S: 543.0603 [M-H]⁺; found: 543.0595.

***N*-(2-(5-Fluoro-1-methyl-1*H*-indol-3-yl)-2-phenylpropyl)-4-methylbenzenesulfonamide
123**



Following the general procedure **6**, using 143 mg, 0.496 mmol of aziridine **98** and 25.0 mg, 0.165 mmol of **526**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear oil product (50.4 mg, 70% yield) was obtained. IR (KBr): ν = 3272, 2984, 1700, 1653, 1496, 1490, 1448, 1416, 1325, 1241, 1161, 1083, 1022, 886, 800, 764, 715, 665. ¹H NMR (500 MHz, CDCl₃): δ 7.47 (d, *J* = 8.0 Hz, 2H, CH_{Ar}), 7.23-7.13 (m, 8H, CH_{Ar}), 7.07 (s, 1H, C=CHNCH₃), 6.87 (dt, *J* = 8.5, 2.0 Hz, 1H, CH_{Ar}), 6.27 (dd, *J* = 10.0, 2.0 Hz, 1H, CH_{Ar}), 4.07-4.05 (m, 1H, NHTs), 3.77 (s, 3H, NCH₃), 3.65 (dd, *J* = 11.0, 8.5 Hz, 1H, CH₂NHTs), 3.43 (dd, *J* = 11.0, 3.5 Hz, 1H, CH₂NHTs), 2.39 (s, 3H, tosyl), 1.70 (s, 3H, PhC(CH₃)CH₂). ¹³C NMR (75 MHz, CDCl₃): δ 157.0 (d, *J* = 234 Hz) 145.3, 143.5, 135.8, 134.4, 129.6, 129.5, 128.5, 126.9, 126.7, 126.5, 125.7 (d, *J* = 10 Hz) 117.6 (d, *J* = 5 Hz) 110.2 (d, *J* = 9 Hz) 110.0 (d, *J* = 7 Hz) 105.5 (d, *J* = 24 Hz), 51.3, 42.9, 33.2, 27.2, 21.5. HRMS: *m/z*; calcd for C₂₅H₂₄FN₂O₂S: 435.1543 [M-H]⁺; found: 435.1559.

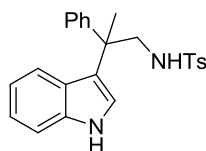
***N*-(2-(5-Methoxy-1-methyl-1*H*-indol-3-yl)-2-phenylpropyl)-4-methylbenzenesulfonamide
124**



Following the general procedure **6**, using 131 mg, 0.457 mmol of aziridine **98** and 25.0 mg, 0.152 mmol of **524**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v),

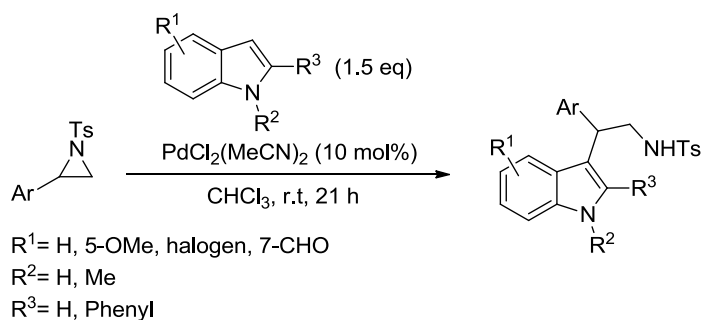
clear oil product (58.8 mg, 85% yield) was obtained. IR (KBr): ν = 3263, 2981, 1700, 1653, 1560, 1491, 1424, 1321, 1225, 1162, 1083, 1010, 814, 715, 659. ^1H NMR (300 MHz, CDCl_3): δ 7.46 (d, J = 8.0 Hz, 2H, CH_{Ar}), 7.25-7.13 (m, 8H, CH_{Ar}), 6.99 (s, 1H, $\text{C}=\text{CHNCH}_3$), 6.80 (dd, J = 8.7, 2.4 Hz, 1H, CH_{Ar}), 6.04 (d, J = 2.4 Hz, 1H, CH_{Ar}), 4.08-4.05 (m, 1H, NHTs), 3.75 (s, 3H, NCH_3), 3.63 (dd, J = 10.8, 8.4 Hz, 1H, CH_2NHTs), 3.49 (dd, J = 11.0, 3.6 Hz, 1H, CH_2NHTs), 3.42 (s, 3H, OCH_3), 2.38 (s, 3H, tosyl), 1.71 (s, 3H, $\text{PhC}(\text{CH}_3)\text{CH}_2$). ^{13}C NMR (75 MHz, CDCl_3): δ 153.2, 145.7, 143.2, 136.0, 133.1, 129.5, 128.4, 128.3, 126.9, 126.6, 126.5, 125.9, 117.1, 111.7, 110.1, 102.5, 55.3, 51.2, 42.9, 33.0, 27.2, 21.5. HRMS: m/z ; calcd for $\text{C}_{26}\text{H}_{27}\text{N}_2\text{O}_3\text{S}$: 447.1718 $[\text{M}-\text{H}]^-$; found: 447.1723.

***N*-(2-(1*H*-Indol-3-yl)-2-phenylpropyl)-4-methylbenzenesulfonamide 125**



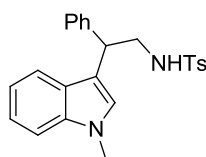
Following the general procedure **6**, using 184 mg, 0.640 mmol of aziridine **98** and 25.0 mg, 0.213 mmol of 1*H*-indole. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear oil product (48.3 mg, 56% yield) was obtained. IR (KBr): ν = 3415, 2967, 1705, 1654, 1570, 1458, 1410, 1321, 1157, 1090, 1014, 961, 813, 742, 700, 662. ^1H NMR (500 MHz, CDCl_3): δ 8.21 (broad s, 1H, $\text{C}=\text{CHNH}$), 7.48 (d, J = 8.0 Hz, 2H, CH_{Ar}), 7.34 (d, J = 8.5 Hz, 1H, CH_{Ar}), 7.22-7.16 (m, 9H, CH_{Ar} & $\text{C}=\text{CHNH}$), 7.10 (t, J = 7.5 Hz, 1H, CH_{Ar}), 6.76-6.72 (m, 1H, CH_{Ar}), 4.07-4.05 (m, 1H, NHTs), 3.67 (dd, J = 11.5, 8.5 Hz, 1H, CH_2NHTs), 3.53 (dd, J = 11.0, 4.0 Hz, 1H, CH_2NHTs), 2.38 (s, 3H, tosyl), 1.73 (s, 3H, $\text{PhC}(\text{CH}_3)\text{CH}_2$). ^{13}C NMR (75 MHz, CDCl_3): δ 145.5, 143.2, 137.0, 136.1, 129.6, 128.5, 126.9, 126.6, 126.6, 125.2, 123.0, 122.1, 120.6, 119.6, 119.3, 111.4, 51.5, 43.0, 27.1, 21.5. HRMS: m/z ; calcd for $\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_2\text{S}$: 403.1480 $[\text{M}-\text{H}]^-$; found: 403.1496.

General Procedure 7 for the Ring-Opening of 2-Aryl-*N*-Tosylaziridines with Indoles



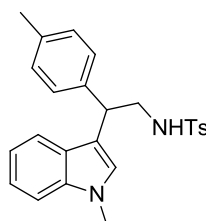
Aziridine (1.0 eq) was added to the solution of indole (1.5 eq) in the presence of $\text{PdCl}_2(\text{MeCN})_2$ (0.1 eq) and *p*-benzoquinone (0.3 eq) at room temperature under the air. The resultant solution was stirred at room temperature for 21 h, diluted with ethyl acetate (10 mL), washed with distilled water (3×10 mL), and the organic layer was dried over MgSO_4 then evaporated under reduced pressure. The crude product was then purified with column chromatography (ethyl acetate: hexane=40:60) to give the targeted products

4-Methyl-*N*-(2-(1-methyl-1H-indol-3-yl)-2-phenylethyl) benzenesulfonamide **126**



Following the general procedure **7**, using 50.0 mg, 0.183 mmol of aziridine **26**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear oily product (57.2 mg, 77% yield) was obtained. IR (KBr): $\nu = 3743, 3277, 2364, 1741, 1551, 1482, 1424, 1370, 1317, 1213, 1157, 1095, 1050, 915, 868, 809, 763, 703$. ^1H NMR (300 MHz, CDCl_3): δ 7.65 (d, $J = 8.1$ Hz, 2H, tosyl CH_{Ar}), 7.28-7.15 (m, 10H, , tosyl CH_{Ar} & CH_{Ar}), 6.98 (t, $J = 7.8$ Hz, 1H, CH_{Ar}), 6.76 (s, 1H, $\text{C}=\text{CHNCH}_3$), 4.38 (t, $J = 6.0$ Hz, 1H, *NHTs*), 4.30 (t, $J = 7.5$ Hz, 1H, $\text{CCH}(\text{Ph})\text{CH}_2\text{NHTs}$), 3.71 (s, 3H, NCH_3), 3.66-3.50 (m, 2H, CH_2NHTs), 2.42 (s, 3H, tosyl). ^{13}C NMR (125 MHz, CDCl_3): δ 143.4, 141.1, 137.2, 136.7, 129.7, 128.8, 127.9, 127.2, 127.0, 126.8, 126.7, 122.0, 119.2, 119.2, 113.9, 109.4, 47.5, 42.5, 32.8, 21.6. HRMS: m/z ; calcd for $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_2\text{SNa}$: 427.1456 $[\text{M}+\text{Na}]^+$; found: 427.1469.

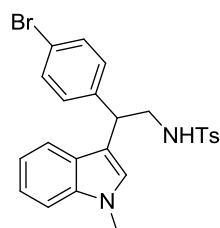
4-Methyl-*N*-(2-(1-methyl-1H-indol-3-yl)-2-(*p*-tolyl)ethyl)benzenesulfonamide **131**



Following the general procedure **7**, using 100 mg, 0.348 mmol of aziridine **517**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear oily product (87.4 mg, 60% yield) was obtained. IR (KBr): $\nu = 3323, 2949, 2835, 2367, 1650, 1512, 1449, 1410, 1326, 1157, 1094, 1018, 813, 740, 660$. ^1H NMR (300 MHz, CDCl_3): δ 7.65 (d, $J = 7.8$ Hz, 2H, tosyl CH_{Ar}),

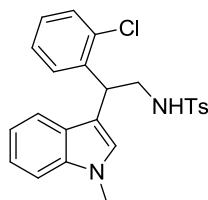
7.28-7.19 (m, 5H, tosyl CH_{Ar} & CH_{Ar}), 7.05(s, 4H, CH_{Ar}), 6.98 (t, *J* = 7.2 Hz, 1H, CH_{Ar}), 6.75 (s, 1H, C=CHNCH₃), 4.38 (t, *J* = 6.0 Hz, 1H, NHTs), 4.26 (t, *J* = 7.2 Hz, 1H, CCH(Ar)CH₂NHTs), 3.71 (s, 3H, NCH₃), 3.63-3.49 (m, 2H, CH₂NHTs), 2.43 (s, 3H, tosyl), 2.29 (s, 3H, tolyl). ¹³C NMR (75 MHz, CDCl₃): δ 143.4, 142.3, 138.0, 137.2, 136.8, 136.6, 129.7, 129.4, 127.8, 127.2, 126.7, 121.9, 119.2, 119.1, 114.1, 109.3, 47.5, 42.1, 32.8, 21.6, 21.0. HRMS: *m/z*; calcd for C₂₅H₂₆N₂O₂SNa: 441.1613 [M+Na]⁺; found: 441.1635.

***N*-(2-(4-Bromophenyl)-2-(1-methyl-1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide**
132



Following the general procedure **7**, using 100 mg, 0.284 mmol of aziridine **518**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear liquid product (86.5 mg, 63% yield) was obtained. IR (KBr): ν = 3276, 2933, 2360, 1636, 1560, 1486, 1424, 1375, 1327, 1158, 1094, 1072, 1010, 813, 738, 661. ¹H NMR (300 MHz, CDCl₃): δ 7.63 (d, *J* = 8.4 Hz, 2H, tosyl CH_{Ar}), 7.34 (d, *J* = 8.1 Hz, 2H, CH_{Ar}), 7.29-7.17(m, 4H, tosyl CH_{Ar} & CH_{Ar}), 7.06-6.96 (m, 4H, tosyl CH_{Ar} & CH_{Ar}), 6.78 (s, 1H, C=CHNCH₃), 4.55 (t, *J* = 6.0 Hz, 1H, NHTs), 4.28 (t, *J* = 7.8 Hz, 1H, CCH(Ar)CH₂NHTs), 3.72 (s, 3H, NCH₃), 3.60-3.47 (m, 2H, CH₂NHTs), 2.43 (s, 3H, tosyl). ¹³C NMR (75 MHz, CDCl₃): δ 143.5, 140.4, 137.3, 136.6, 131.7, 129.7, 129.7, 127.1, 126.7, 126.7, 122.1, 120.7, 119.3, 119.1, 113.3, 109.5, 47.3, 42.1, 32.8, 21.6. HRMS: *m/z*; calcd for C₂₄H₂₃BrN₂O₂SNa: 505.0561 [M+Na]⁺; found: 505.0591.

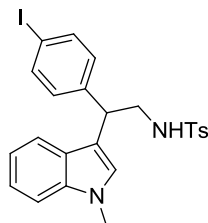
***N*-(2-(2-Chlorophenyl)-2-(1-methyl-1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide**
133



Following the general procedure **7**, using 100 mg, 0.325 mmol of aziridine **519**. Purified by

chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear liquid product (81.3 mg, 57% yield) was obtained. IR (KBr): ν = 3281, 2958, 2356, 1641, 1599, 1565, 1473, 1424, 1375, 1325, 1155, 1094, 1015, 812, 739, 706, 658. ^1H NMR (300 MHz, CDCl_3): δ 7.65 (d, J = 8.1 Hz, 2H, tosyl CH_{Ar}), 7.34-7.07 (m, 9H, tosyl CH_{Ar} & CH_{Ar}), 6.99 (t, J = 7.5 Hz, 1H, CH_{Ar}), 6.87 (s, 1H, $\text{C}=\text{CHNCH}_3$), 4.84 (t, J = 6.9 Hz, 1H, $\text{CCH}(\text{Ar})\text{CH}_2\text{NHTs}$), 4.57 (t, J = 7.0 Hz, 1H, NHTs), 3.72 (s, 3H, NCH_3), 3.57 (app. t, J = 6.6 Hz, 2H, CH_2NHTs), 2.42 (s, 3H, tosyl). ^{13}C NMR (125 MHz, CDCl_3): δ 143.4, 138.7, 137.2, 136.6, 133.8, 129.8, 129.7, 129.0, 128.1, 127.2, 127.1, 127.0, 127.0, 122.1, 119.2, 119.1, 112.8, 109.4, 46.2, 38.7, 32.8, 21.5. HRMS: m/z ; calcd for $\text{C}_{24}\text{H}_{23}\text{ClN}_2\text{O}_2\text{SNa}$: 461.1066 $[\text{M}+\text{Na}]^+$; found: 461.1073.

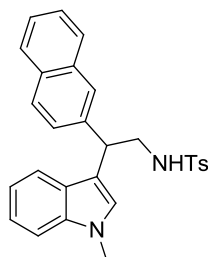
***N*-(2-(4-Iodophenyl)-2-(1-methyl-1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide 134**



Following the general procedure **7**, using 78.0 mg, 0.195 mmol of aziridine **520**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear liquid product (61.0 mg, 59% yield) was obtained. IR (KBr): ν = 3289, 2936, 1701, 1648, 1484, 1328, 1327, 1325, 1159, 1158, 1157, 1090, 1005, 900, 811, 742, 741, 672. ^1H NMR (500 MHz, CDCl_3): δ 7.62 (d, J = 8.5 Hz, 2H, tosyl CH_{Ar}), 7.53 (d, J = 8.5 Hz, 2H, CH_{Ar}), 7.26-7.17 (m, 5H, tosyl CH_{Ar} & CH_{Ar}), 6.98 (t, J = 7.5 Hz, 1H, CH_{Ar}), 6.91 (d, J = 8.5 Hz, 2H, CH_{Ar}), 6.77 (s, 1H, $\text{C}=\text{CHNCH}_3$), 4.55 (t, J = 6.0 Hz, 1H, NHTs), 4.26 (t, J = 7.5 Hz, 1H, $\text{CCH}(\text{Ar})\text{CH}_2\text{NHTs}$), 3.70 (s, 3H, NCH_3), 3.60-3.56 (m, 1H, CH_2NHTs), 3.51-3.47 (m, 1H, CH_2NHTs), 2.42 (s, 3H, tosyl). ^{13}C NMR (125 MHz, CDCl_3): δ 143.5, 141.0, 137.7, 137.3, 136.7, 130.0, 129.7, 127.1, 126.7, 126.7, 122.1, 119.3, 119.1, 113.3, 109.5, 92.3, 47.2, 42.3, 32.8, 21.6. HRMS: m/z ; calcd for $\text{C}_{24}\text{H}_{23}\text{IN}_2\text{O}_2\text{SNa}$: 553.0423 $[\text{M}+\text{Na}]^+$; found: 553.0402.

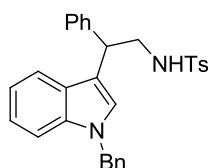
4-Methyl-*N*-(2-(1-methyl-1H-indol-3-yl)-2-(naphthalen-2-yl)ethyl)benzenesulfonamide

135



Following the general procedure **7**, using 50.0 mg, 0.155 mmol of aziridine **521**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear liquid product (55.0 mg, 78% yield) was obtained. IR (KBr): ν = 3290, 3058, 2935, 2319, 1607, 1470, 1420, 1326, 1156, 1093, 1013, 908, 858, 813, 736, 662. ^1H NMR (300 MHz, CDCl_3): δ 7.78-7.85 (m, 1H, CH_{Ar}), 7.70 (d, J = 8.4 Hz, 2H, tosyl CH_{Ar}), 7.63-7.61 (m, 3H, CH_{Ar}), 7.47-7.40 (m, 3H, CH_{Ar}), 7.30-7.15 (m, 5H, CH_{Ar} & tosyl CH_{Ar}), 6.96 (t, J = 7.2 Hz, 1H, CH_{Ar}), 6.81 (s, 1H, $\text{C}=\text{CHNCH}_3$), 4.52-4.46 (m, 2H, NHTs & $\text{CCH}(\text{Ar})\text{CH}_2\text{NHTs}$), 3.78-3.70 (m, 1H, CH_2NHTs), 3.70 (s, 3H, NCH_3), 3.66-3.57 (m, 1H, CH_2NHTs), 2.41 (s, 3H, tosyl). ^{13}C NMR (75 MHz, CDCl_3): δ 143.3, 138.6, 137.3, 136.8, 133.4, 132.5, 129.7, 128.5, 127.8, 127.6, 127.1, 126.7, 126.8, 126.4, 126.2, 125.8, 122.0, 119.2, 114.0, 109.4, 47.4, 42.7, 32.8, 21.5. HRMS: m/z ; calcd for $\text{C}_{28}\text{H}_{26}\text{N}_2\text{O}_2\text{SNa}$: 477.1613 $[\text{M}+\text{Na}]^+$; found: 477.1616.

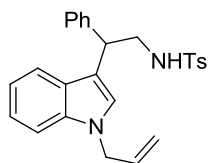
N-(2-(1-Benzyl-1H-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide **136**



Following the general procedure **7**, using 50.0 mg, 0.183 mmol of aziridine **26**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), white solid product (52.8 mg, 60% yield) was obtained. m.p. 130-135 °C; IR (KBr): ν = 3290, 3030, 2255, 1599, 1550, 1496, 1453, 1399, 1327, 1157, 1093, 1074, 1017, 908, 814, 730, 699, 662. ^1H NMR (300 MHz, CDCl_3): δ 7.64 (d, J = 7.8 Hz, 2H, tosyl CH_{Ar}), 7.34-7.06 (m, 15H, CH_{Ar} & tosyl CH_{Ar}), 6.99 (t, J = 7.8 Hz, 1H, CH_{Ar}), 6.85 (s, 1H, $\text{C}=\text{CHNCH}_3$), 5.25 (s, 2H, NCH_2Ph), 4.38 (t, J = 5.7 Hz, 1H, NHTs), 4.33 (t, J = 7.5 Hz, 1H, $\text{CCH}(\text{Ph})\text{CH}_2\text{NHTs}$), 3.70-3.48 (m, 2H, CH_2NHTs), 2.42 (s, 3H, tosyl). ^{13}C NMR (75 MHz, CDCl_3): δ 143.4, 141.0, 137.3, 136.9, 136.8, 129.7, 128.8, 128.8, 128.0, 127.7, 127.1, 127.0,

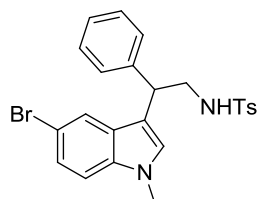
126.6, 126.0, 126.0, 122.2, 119.5, 119.4, 114.7, 109.9, 50.0, 47.5, 42.6, 21.6. HRMS: m/z ; calcd for $C_{30}H_{28}N_2O_2SNa$: 503.1769 $[M+Na]^+$; found: 503.1778.

***N*-(2-(1-Allyl-1H-indol-3-yl)-2-phenylpropyl)-4-methylbenzenesulfonamide 137**



Following the general procedure **7**, using 50.0 mg, 0.183 mmol of aziridine **26**. The reaction was carried out in DCM. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear oil product (67.9 mg, 86% yield) was obtained. IR (KBr): ν = 3300, 3033, 2926, 1598, 1546, 1494, 1466, 1452, 1405, 1325, 1184, 1156, 1093, 1074, 1016, 990, 909, 813, 735, 731, 699, 663. 1H NMR (300 MHz, $CDCl_3$): δ 7.66 (d, J = 8.4 Hz, 2H, tosyl CH_{Ar}), 7.33-7.16 (m, 10H, CH_{Ar} & tosyl CH_{Ar}), 6.99 (t, J = 7.2 Hz, 1H, CH_{Ar}), 6.82 (s, 1H, $C=CHNCH_3$), 6.01-5.92 (m, 1H, $NCH_2CH=CH_2$), 5.20 (d, J = 10.2 Hz, 1H, $NCH_2CH=CH_2$), 5.08 (d, J = 17.1 Hz, 1H, $NCH_2CH=CH_2$), 4.66 (d, J = 5.4 Hz, 2H, $NCH_2CH=CH_2$), 4.40 (t, J = 6.0 Hz, 1H, $NHTs$), 4.31 (t, J = 7.8 Hz, 1H, $CCH(Ph)CH_2NHTs$), 3.70-3.48 (m, 2H, CH_2NHTs), 2.44 (s, 3H, tosyl). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.4, 141.0, 136.8, 136.7, 133.3, 129.9, 129.7, 128.8, 127.9, 127.1, 127.1, 127.0, 125.6, 122.0, 119.3, 117.5, 114.4, 109.8, 48.8, 47.5, 42.6, 21.6. HRMS: m/z ; calcd for $C_{27}H_{28}N_2O_2SNa$: 453.1613 $[M+Na]^+$; found: 453.1593.

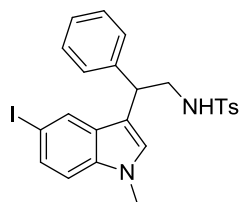
***N*-(2-(5-Bromo-1-methyl-1H-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide 138**



Following the general procedure **7**, using 50.0 mg, 0.183 mmol of aziridine **26**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear oil product (76.1 mg, 86% yield) was obtained. IR (KBr): ν = 3296, 2882, 1598, 1477, 1423, 1324, 1213, 1158, 1093, 1073, 908, 814, 793, 730, 701, 662. 1H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, J = 8.5 Hz, 2H, tosyl CH_{Ar}), 7.30-7.22 (m, 7H, CH_{Ar} & tosyl CH_{Ar}), 7.16-7.13 (m, 3H, CH_{Ar}), 6.83 (s, 1H, $C=CHNCH_3$),

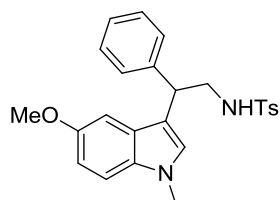
4.39 (t, $J = 6.0$ Hz, 1H, *NHTs*), 4.19 (t, $J = 7.0$ Hz, 1H, *CCH(Ph)CH₂NHTs*), 3.71 (s, 3H, *NCH₃*), 3.55 (app. q, $J = 7.5$ Hz, 2H, *CH₂NHTs*), 2.46 (s, 3H, tosyl). ¹³C NMR (75 MHz, CDCl₃): δ 143.6, 140.7, 136.7, 135.9, 129.8, 128.9, 128.5, 127.9, 127.8, 127.2, 127.1, 124.9, 121.6, 113.6, 112.6, 110.9, 47.4, 42.2, 33.0, 21.6. HRMS: m/z ; calcd for C₂₄H₂₄BrN₂O₂S : 483.0742 [M+H]⁺; found: 483.0733.

***N*-(2-(5-Iodo-1-methyl-1H-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide 139**



Following the general procedure **7**, using 50.0 mg, 0.183 mmol of aziridine **26**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear oil product (69.9 mg, 72% yield) was obtained. IR (KBr): $\nu = 3751, 3651, 3275, 2880, 2362, 1650, 1541, 1475, 1422, 1326, 1158, 1093, 909, 813, 792, 732, 665$. ¹H NMR (500 MHz, CDCl₃): δ 7.65 (d, $J = 8.0$ Hz, 2H, tosyl CH_{Ar}), 7.51 (s, 1H, CH_{Ar}), 7.42 (d, $J = 8.0$ Hz, 1H, CH_{Ar}), 7.31-7.28 (m, 2H, CH_{Ar}), 7.26 (d, $J = 8.0$ Hz, 2H, CH_{Ar}), 7.23-7.20 (m, 1H, CH_{Ar}), 7.14 (d, $J = 7.0$ Hz, 2H, tosyl CH_{Ar}), 7.03 (d, $J = 8.5$ Hz, 1H, CH_{Ar}), 6.77 (s, 1H, C=CHNCH₃), 4.42 (t, $J = 6.0$ Hz, 1H, *NHTs*), 4.18 (t, $J = 7.5$ Hz, 1H, *CCH(Ph)CH₂NHTs*), 3.69 (s, 3H, *NCH₃*), 3.53 (app. q, $J = 6.5$ Hz, 2H, *CH₂NHTs*), 2.46 (s, 3H, tosyl). ¹³C NMR (75 MHz, CDCl₃): δ 143.6, 140.7, 136.7, 136.3, 130.3, 129.9, 129.4, 128.9, 127.9, 127.8, 127.6, 127.2, 127.1, 113.4, 111.4, 82.8, 47.5, 42.2, 32.9, 21.7. HRMS: m/z ; calcd for C₂₄H₂₃IN₂O₂SNa: 553.0423 [M+Na]⁺; found: 553.0444.

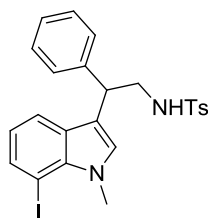
***N*-(2-(5-Methoxy-1-methyl-1H-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide 140**



Following the general procedure **7**, using 50.0 mg, 0.183 mmol of aziridine **26**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear oil product (39.8 mg, 50% yield) was obtained. IR (KBr): $\nu = 3281, 2938, 1623, 1599, 1491, 1452, 1424, 1326, 1266$,

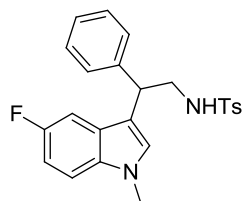
1212, 1158, 1093, 1065, 1035, 815, 794, 734, 665. ^1H NMR (500 MHz, CDCl_3): δ 7.65 (d, J = 8.0 Hz, 2H, tosyl CH_{Ar}), 7.26 (d, J = 7.5 Hz, 4H, tosyl CH_{Ar}), 7.22-7.15 (m, 4H, CH_{Ar}), 6.85 (dd, J = 2.5, 8.5 Hz, 1H, CH_{Ar}), 6.72 (s, 1H, $\text{C}=\text{CHNCH}_3$), 6.70 (d, J = 2.0 Hz, 1H, CH_{Ar}), 4.40 (t, J = 6.0 Hz, 1H, NHTs), 4.28 (t, J = 7.5 Hz, 1H, $\text{CCH}(\text{Ph})\text{CH}_2\text{NHTs}$), 3.72 (s, 3H, NCH_3), 3.69 (s, 3H, OCH_3), 3.64-3.61 (m, 1H, CH_2NHTs), 3.54-3.50 (m, 1H, CH_2NHTs), 2.43 (s, 3H, tosyl). ^{13}C NMR (75 MHz, CDCl_3): δ 153.8, 143.4, 141.0, 136.7, 132.1, 132.3, 129.7, 128.8, 127.9, 127.3, 127.1, 127.0, 113.3, 112.1, 110.1, 101.0, 55.8, 47.3, 42.6, 32.9, 21.5. HRMS: m/z ; calcd for $\text{C}_{25}\text{H}_{26}\text{N}_2\text{O}_3\text{SNa}$: 457.1567 $[\text{M}+\text{Na}]^+$; found: 457.1562.

***N*-(2-(7-Iodo-1-methyl-1H-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide 141**



Following the general procedure **7**, using 50.0 mg, 0.183 mmol of aziridine **26**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear oil product (73.8 mg, 76% yield) was obtained. IR (KBr): ν = 3292, 2919, 1599, 1550, 1482, 1451, 1405, 1324, 1303, 1156, 1089, 1065, 1028, 838, 813, 737, 699, 665. ^1H NMR (500 MHz, CDCl_3): δ 7.65 (d, J = 8.0 Hz, 2H, tosyl CH_{Ar}), 7.62 (d, J = 7.0 Hz, 1H, CH_{Ar}), 7.27-7.20 (m, 6H, CH_{Ar} & tosyl CH_{Ar}), 7.14 (d, J = 7.5 Hz, 2H, CH_{Ar}), 6.75 (s, 1H, $\text{C}=\text{CHNCH}_3$), 6.64 (t, J = 8.0 Hz, 1H, CH_{Ar}), 4.42 (t, J = 6.0 Hz, 1H, NHTs), 4.27 (t, J = 7.5 Hz, 1H, $\text{CCH}(\text{Ph})\text{CH}_2\text{NHTs}$), 4.09 (s, 3H, NCH_3), 3.63-3.57 (m, 1H, CH_2NHTs), 3.52-3.46 (m, 1H, CH_2NHTs), 2.43 (s, 3H, tosyl). ^{13}C NMR (75 MHz, CDCl_3): δ 143.5, 140.6, 136.8, 136.0, 134.4, 129.8, 129.7, 129.3, 128.8, 127.8, 127.2, 127.1, 120.9, 119.3, 113.5, 73.0, 47.4, 42.1, 36.8, 21.6. HRMS: m/z ; calcd for $\text{C}_{24}\text{H}_{23}\text{IN}_2\text{O}_2\text{SNa}$: 553.0423 $[\text{M}+\text{Na}]^+$; found: 553.0433.

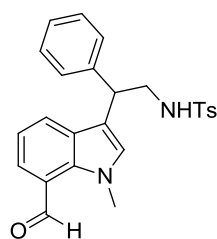
***N*-(2-(5-Fluoro-1-methyl-1H-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide 142**



Following the general procedure **7**, using 50.0 mg, 0.183 mmol of aziridine **26**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear oil product (46.4 mg, 60% yield) was obtained. IR (KBr): ν = 3283, 2933, 1598, 1490, 1452, 1424, 1325, 1158, 1093, 909, 814, 794, 730, 701, 669, 665, 659. ^1H NMR (500 MHz, CDCl_3): δ 7.65 (d, J = 8.0 Hz, 2H, tosyl CH_{Ar}), 7.29-7.14 (m, 8H, CH_{Ar} & tosyl CH_{Ar}), 6.92 (dt, J = 2.0, 9.0 Hz, 1H, CH_{Ar}), 6.86 (s, 1H, $\text{C}=\text{CHNCH}_3$), 6.79 (dd, J = 2.0, 9.5 Hz, 1H, CH_{Ar}), 4.36 (t, J = 6.0 Hz, 1H, NHTs), 4.20 (t, J = 7.5 Hz, 1H, $\text{CCH}(\text{Ph})\text{CH}_2\text{NHTs}$), 3.72 (s, 3H, NCH_3), 3.58-3.52 (m, 2H, CH_2NHTs), 2.44 (s, 3H, tosyl). ^{13}C NMR (75 MHz, CDCl_3): δ 157.5 (d, J = 234 Hz), 143.6, 140.8, 136.6, 133.9, 129.8, 128.8, 128.3, 127.8, 127.1, 127.0, 126.9, 113.7 (d, J = 4.6 Hz), 110.4 (d, J = 26.7 Hz), 110.1 (d, J = 11.5 Hz), 104.1 (d, J = 23 Hz), 47.3, 42.4, 33.1, 21.5. HRMS: m/z ; calcd for $\text{C}_{24}\text{H}_{23}\text{FN}_2\text{O}_2\text{SNa}$: 423.1543 $[\text{M}+\text{Na}]^+$; found: 423.1525.

***N*-(2-(7-Formyl-1-methyl-1H-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide**

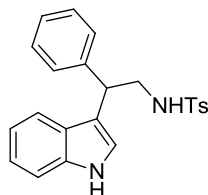
143



Following the general procedure **7**, using 50.0 mg, 0.183 mmol of aziridine **26**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear oil product (34.0 mg, 43% yield) was obtained. 17% inseparable benzoquinone was found by ^1H NMR. IR (KBr): ν = 3275, 2876, 1684, 1546, 1461, 1415, 1324, 1243, 1223, 1157, 1094, 1045, 909, 814, 729, 702, 682, 677, 670, 665, 662. ^1H NMR (500 MHz, CDCl_3): δ 10.2 (s, 1H, $\text{O}=\text{CH}$), 7.66 (d, J = 8.5 Hz, 2H, tosyl CH_{Ar}), 7.53 (d, J = 7.5 Hz, 1H, CH_{Ar}), 7.28-7.22 (m, 6H, CH_{Ar} & tosyl CH_{Ar}), 7.15 (d, J = 8.0 Hz, 2H, CH_{Ar}), 7.10 (t, J = 7.5 Hz, 1H, CH_{Ar}), 6.83 (s, 1H, $\text{C}=\text{CHNCH}_3$), 4.47 (t, J = 6.0 Hz, 1H, NHTs), 4.33 (t, J = 8.0 Hz, 1H, $\text{CCH}(\text{Ph})\text{CH}_2\text{NHTs}$), 4.04 (s, 3H, NCH_3), 3.63-3.59 (m, 1H, CH_2NHTs), 3.53-3.50 (m, 1H, CH_2NHTs), 2.43 (s, 3H, tosyl). ^{13}C NMR (125 MHz, CDCl_3): δ 190.9,

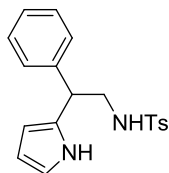
143.6, 140.6, 136.8, 134.3, 130.7, 130.1, 130.1, 129.8, 129.0, 127.9, 127.3, 127.2, 126.2, 123.0, 118.8, 115.3, 47.6, 42.3, 39.1, 21.6. HRMS: m/z ; calcd for $C_{25}H_{24}N_2O_3SNa$: 455.1405 $[M+Na]^+$; found: 455.1413.

***N*-(2-(1*H*-Indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide 144**



Following the general procedure **7**, using 50.0 mg, 0.183 mmol of aziridine **26**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear oil product (54.3 mg, 76% yield) was obtained. IR (KBr): ν = 3438, 3329, 2360, 2157, 1968, 1653, 1491, 1457, 1402, 1317, 1150, 1093, 1012, 867, 808, 755, 699, 657. 1H NMR (500 MHz, $CDCl_3$): δ 8.06 (broad s, 1H, indole *NH*), 7.66 (d, J = 8.0 Hz, 2H, tosyl CH_{Ar}), 7.35 (d, J = 7.5 Hz, 1H, CH_{Ar}), 7.28-7.25 (m, 5H, CH_{Ar} & tosyl CH_{Ar}), 7.22 (d, J = 7.0 Hz, 1H, CH_{Ar}), 7.18-7.15 (m, 3H, CH_{Ar}), 7.00 (t, J = 8 Hz, 1H, CH_{Ar}), 6.97 (s, 1H, $C=CHNCH_3$), 4.38 (t, J = 6.0 Hz, 1H, *NHTs*), 4.32 (t, J = 7.5 Hz, 1H, $CCH(Ph)CH_2NHTs$), 3.69-3.66 (m, 1H, CH_2NHTs), 3.56-3.53 (m, 1H, CH_2NHTs), 2.44 (s, 3H, tosyl). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.5, 140.9, 136.8, 136.5, 129.7, 128.8, 127.9, 127.1, 127.0, 126.4, 122.5, 121.9, 119.7, 119.2, 115.6, 111.2, 47.4, 42.6, 21.5. HRMS: m/z ; calcd for $C_{23}H_{22}N_2O_2SNa$: 413.1300 $[M+Na]^+$; found: 413.1286.

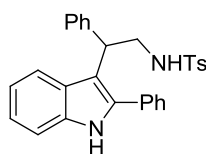
4-Methyl-*N*-(2-phenyl-2-(1*H*-pyrrol-3-yl)ethyl)benzenesulfonamide 145



Following the general procedure **7**, using 50.0 mg, 0.183 mmol of aziridine **26**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), dark oil product (9.35 mg, 15% yield) was obtained. IR (KBr): ν = 3281, 2935, 1696, 1599, 1550, 1491, 1448, 1395, 1324, 1158, 1093, 1023, 812, 700, 658. 1H NMR (300 MHz, $CDCl_3$): δ 7.81 (broad s, 1H, pyrrole *NH*), 7.62 (d, J = 8.5 Hz, 2H, tosyl CH_{Ar}), 7.24-7.16 (m, 6H, CH_{Ar} & tosyl CH_{Ar}), 7.02 (d, J = 7.0 Hz, 2H, CH_{Ar}),

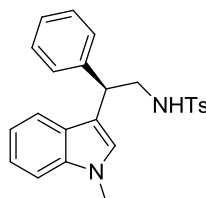
6.59 (s, 1H, pyrrole), 6.07 (d, $J = 2.5$ Hz, 1H, pyrrole), 5.88 (s, 1H, pyrrole), 4.39 (t, $J = 6.0$ Hz, 1H, *NHTs*), 4.04 (t, $J = 7.5$ Hz, 1H, *CCH(Ph)CH₂NHTs*), 3.45-3.40 (m, 1H, *CH₂NHTs*), 3.37-3.32 (m, 1H, *CH₂NHTs*), 2.37 (s, 3H, tosyl). ¹³C NMR (75 MHz, CDCl₃): δ 142.6, 138.8, 135.7, 129.6, 128.8, 128.0, 127.0, 126.5, 126.1, 116.7, 107.5, 104.7, 46.4, 43.5, 20.5. HRMS: m/z ; calcd for C₁₉H₂₀N₂O₂SNa: 363.1143 [M+ Na]⁺; found: 363.1133.

4-Methyl-*N*-(2-phenyl-2-(2-phenyl-1*H*-indol-3-yl)ethyl)benzenesulfonamide **146**



Following the general procedure **7**, using 50.0 mg, 0.183 mmol of aziridine **26**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear oil product (53.8 mg, 63% yield) was obtained. IR (KBr): $\nu = 3346, 2941, 1599, 1491, 1450, 1399, 1319, 1154, 1093, 1019, 922, 845, 813, 743, 700, 661$. ¹H NMR (500 MHz, CDCl₃): δ 8.31 (broad s, 1H, indole *NH*), 7.44 (d, $J = 8.5$ Hz, 2H, tosyl CH_{Ar}), 7.40 (d, $J = 8.0$ Hz, 1H, CH_{Ar}), 7.35 (app. s, 6H, CH_{Ar}), 7.24-7.18 (m, 6H, CH_{Ar} & tosyl CH_{Ar}), 7.09 (d, $J = 7.5$ Hz, 2H, CH_{Ar}), 6.93 (t, $J = 7.5$ Hz, 1H, CH_{Ar}), 4.44 (dd, $J = 6.0, 11.0$ Hz, 1H, *NHTs*), 4.22 (app. d, $J = 8.0$ Hz, 1H, *CCH(Ph)CH₂NHTs*), 3.76-3.72 (m, 1H, *CH₂NHTs*), 3.64 (t, $J = 11.0$ Hz, 1H, *CH₂NHTs*), 2.38 (s, 3H, tosyl). ¹³C NMR (75 MHz, CDCl₃): δ 143.1, 141.6, 137.7, 136.2, 136.2, 132.1, 129.6, 128.9, 128.7, 128.7, 128.4, 127.7, 127.0, 127.0, 126.7, 122.5, 120.2, 120.0, 111.5, 109.5, 46.7, 42.2, 21.5. HRMS: m/z ; calcd for C₂₃H₂₂N₂O₂SNa: 489.1613 [M+ Na]⁺; found: 489.1628.

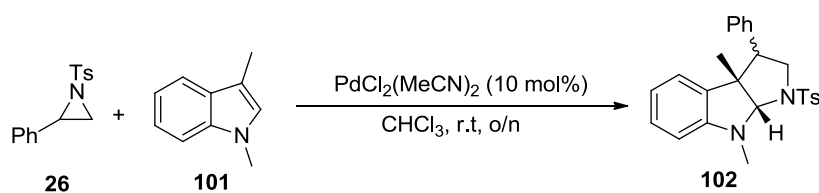
Synthesis of (*R*)-**126'**



Following the general procedure **7**, using 50.0 mg, 0.183 mmol of aziridine (*R*)-**26'**, 36.0 mg, 0.275 mmol of **114** and 5.9 mg, 0.0549 mmol of BQ. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 40:60 (v/v), clear oily product (55.5 mg, 75% yield, 98% *ee*) was obtained. Data matched **126**. $[\alpha]_D^{19} = -27.4$ ($c = 0.49$ in CHCl₃).

General Procedure 8 for the Cycloaddition of Aziridines to 1,3-Dimethylindole 101

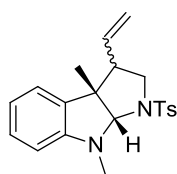
Synthesis of (3aR,8bS) -4,8b-dimethyl-1-phenyl-3-tosyl-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole 102



Aziridine **26** (114.7 mg, 0.420 mmol, 3.0 eq) was added to the solution of 1,3-dimethylindole **101** (20.6 mg, 0.140 mmol, 1.0 eq) in chloroform (1.5 ml) in the presence of $\text{PdCl}_2(\text{MeCN})_2$ (3.60 mg, 0.0140 mmol, 10 mol%) at room temperature under the air. The resultant solution was stirred at room temperature for 21 h, diluted with ethyl acetate (10 mL), washed with distilled water (3×10 mL), and the organic layer was dried over MgSO_4 then evaporated under reduced pressure. The crude product was then purified with column chromatography (ethyl acetate: hexane=20:80) to give white solid **102** (157 mg, 71%). *Trans:cis* = 6.5:1.0; m.p. 135-141°C; IR (KBr): ν = 3329, 2957, 1663, 1599, 1488, 1448, 1346, 1291, 1161, 1091, 1022, 892, 814, 753, 700, 668, 665, 613, 612. ^1H NMR (300 MHz, CDCl_3): δ = ^1H NMR (300 MHz, CDCl_3) δ 7.87(d, J = 8.0 Hz, 2H, *cis*, tosyl CH_{Ar}), 7.83(d, J = 8.0 Hz, 2H, *trans*, tosyl CH_{Ar}), 7.39(d, J = 7.5 Hz, 2H, *cis*, tosyl CH_{Ar}), 7.36(d, J = 7.0 Hz, 2H, *trans*, tosyl CH_{Ar}), 7.26-7.21(m, 6H, *trans* and *cis*, CH_{Ar}), 7.16(t, J = 8.0 Hz, 1H, *cis*, CH_{Ar}), 7.02(t, J = 8.0 Hz, *trans*, CH_{Ar}), 6.94-6.93 (m, 2H, *cis*, CH_{Ar}), 6.83(d, J = 7.5 Hz, 2H, *trans*, CH_{Ar}), 6.64 (t, J = 7.0 Hz, 1H, *trans*, CH_{Ar}), 6.53(t, J = 5.5 Hz, 2H, *trans*, CH_{Ar}), 6.36(d, J = 8.0 Hz, 1H, *ci*, CH_{Ar} s), 6.28(t, J = 7.5 Hz, 1H, *trans*, CH_{Ar}), 5.57(d, J = 7.5 Hz, 1H, *trans*, CH_{Ar}), 5.37(s, 1H, *trans*, CH_3NCHNTs), 5.07(s, 1H, *cis*, CH_3NCHNTs), 3.85-3.77(m, 3H, *trans* and *cis*, $(\text{Ph})\text{CHCH}_2\text{NTs}$), 3.62-3.58(m, 1H, *cis*, $(\text{Ph})\text{CHCH}_2\text{NTs}$), 3.41(t, J = 13.0 Hz, 1H, *trans*, $(\text{Ph})\text{CHCH}_2\text{NTs}$), 3.05(s, 3H, *trans*, NCH_3), 3.04(s, 3H, *cis*, NCH_3), 2.74-2.70(m, 1H, *trans*, $(\text{Ph})\text{CHCH}_2\text{NTs}$), 2.49(s, 3H, *trans* and *cis*, tosyl), 1.27 (s, 3H, *cis*, $(\text{CH}_3)\text{CCH}(\text{Ph})\text{CH}_2\text{NTs}$), 0.49 (s, 3H, *trans*, $(\text{CH}_3)\text{CCH}(\text{Ph})\text{CH}_2\text{NTs}$). ^{13}C NMR (75 MHz, CDCl_3): δ 150.8, 143.8, 137.1, 135.7, 132.5, 129.9, 128.8, 128.4, 127.9, 127.5, 127.3, 125.4,

116.4, 104.9, 91.1, 56.7, 54.9, 51.2, 31.2, 25.9, 21.6. ^{13}C NMR signals reported for major isomer. HRMS: m/z ; calcd for $\text{C}_{25}\text{H}_{26}\text{N}_2\text{O}_2\text{SNa}$: 441.1613 $[\text{M}+\text{Na}]^+$; found: 441.1620. Note: The pyrroloindoline and its derivatives that were discussed in this thesis are numbered according to the Hantzsch-Widman nomenclature.

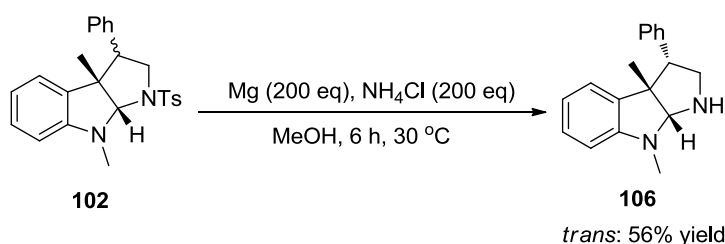
Synthesis of (3a*S*,8a*S*)-3a,8-dimethyl-1-tosyl-3-vinyl-1,2,3,3a,8,8a-hexahydro-pyrrolo[2,3-*b*]indole **104**



Vinylaziridine **103** (50.0 mg, 0.224 mmol, 1.0 eq) was added to the solution of 1,3-dimethylindole **101** (50.0 μL , 0.336 mmol, 3.0 eq) in chloroform (2.3 ml) in the presence of $\text{PdCl}_2(\text{MeCN})_2$ (5.8 mg, 0.0224 mmol, 10 mol%) at room temperature under the air. The resultant solution was stirred at room temperature for 21 h, diluted with ethyl acetate (10 ml), washed with distilled water (3×10 mL), and organic layer was dried over MgSO_4 and evaporated under reduced pressure. The crude product was then purified with column chromatography (ethyl acetate: hexane=20:80) to give white solid **104** (21.0 mg, 17%). *Trans:cis* = 4.3:1.0 (Purified); m.p. 120-125°C; IR (KBr): ν = 2954, 1701, 1648, 1604, 1491, 1347, 1302, 1241, 1160, 1090, 1001, 904, 867, 813, 745, 742, 729, 668, 662. ^1H NMR (300 MHz, CDCl_3): δ 7.72 (d, J = 8.1 Hz, 2H, *trans and cis*, tosyl CH_{Ar}), 7.27 (d, J = 7.8 Hz, 2H, *trans and cis*, tosyl CH_{Ar}), 7.07-7.00 (m, 1H, *trans and cis*, CH_{Ar}), 6.81-6.76 (m, 1H, *trans and cis*, CH_{Ar}), 6.59 (t, J = 7.5 Hz, 1H, *cis*, CH_{Ar}), 6.52 (t, J = 7.2 Hz, 1H, *trans*, CH_{Ar}), 6.40 (d, J = 8.1 Hz, 1H, *cis*, CH_{Ar}), 6.31 (d, J = 7.5 Hz, 1H, *trans*, CH_{Ar}), 5.54-5.42 (m, 1H, *trans and cis*, $\text{CH}=\text{CH}_2$), 5.18 (s, 1H, *trans and cis*, CH_3NCHNTs), 5.04 (d, J = 11.1 Hz, 1H, *trans*, $\text{CH}=\text{CH}_2$), 5.01 (d, J = 9.6 Hz, 1H, *cis*, $\text{CH}=\text{CH}_2$), 4.90 (d, J = 16.8 Hz, 1H, *trans*, $\text{CH}=\text{CH}_2$), 4.86 (d, J = 16.8, 1H, *cis*, $\text{CH}=\text{CH}_2$), 3.58-3.50 (m, 1H, *trans and cis*, CHCH_2NTs), 3.16 (t, J = 9.9 Hz, 1H, *cis*, CHCH_2NTs), 2.92 (s, 3H, *trans*, NCH_3), 2.91 (s, 3H, *cis*, NCH_3), 2.80 (t, J = 12.0 Hz, 1H, *trans*, CHCH_2NTs), 2.39 (s, 3H, *trans and cis*, tosyl), 2.05-2.00 (m, 1H, *trans and cis*, CHCH_2NTs), 1.10 (s, 3H, *cis and trans*, $(\text{CH}_3)\text{CHCH}_2\text{NTs}$). ^{13}C NMR (75 MHz, CDCl_3): δ 150.8, 143.7, 137.0, 134.2, 133.0, 129.8, 127.7, 127.2, 125.1, 118.3, 116.7, 105.3, 90.8, 55.7, 54.6, 52.2, 31.2, 25.2, 21.6. ^{13}C NMR signals reported

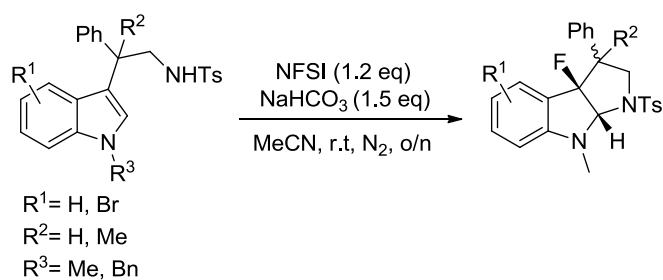
for major isomer. HRMS: m/z ; calcd for $C_{21}H_{24}N_2O_2S$ Na: 369.1637 $[M+Na]^+$; found: 369.1640.

Synthesis of **106**²⁷



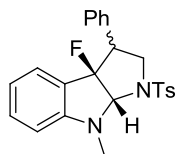
A mixture of **102** (79 mg, 0.189 mmol, 1.0 eq), magnesium (906 mg, 37.8 mmol, 200 eq) and ammonium chloride (2.02 g, 37.8 mmol, 200 eq) in anhydrous MeOH (10 mL) was sonicated for 6 h at 30 °C. The reaction mixture then passed through a short pad of silica gel (1 cm), diluted with ethyl acetate (30 mL) and washed with distilled water (3x20 mL). The organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified with column chromatography (straight ethyl acetate) to afford **106** (28 mg, 56%) as a clear oily liquid. **106**: 1H NMR ($CDCl_3$, 500 MHz) δ 7.19-7.01 (m, 3H, CH_{Ar}), 6.99 (t, $J = 7.5$ Hz, 1H, Indole CH_{Ar}), 6.89-6.87 (m, 2H, CH_{Ar}), 6.34 (d, $J = 8.0$ Hz, 1H, Indole CH_{Ar}), 6.25 (t, $J = 7.5$ Hz, 1H, Indole CH_{Ar}), 5.72 (d, $J = 7.0$ Hz, 1H, Indole CH_{Ar}), 4.70 (s, 1H, CH_3NCHNH), 3.25 (dd, $J = 10.0, 5.5$ Hz, 1H, $PhCHCH_2NH$), 3.18-2.11 (m, 2H, $PhCHCH_2NH$ & $PhCHCH_2NH$), 2.90 (s, 3H, CH_3N), 2.76 (broad s, 1H, NH). 1.50 (s, 3H, $(CH_3)C(C_6H_5)CHCH_2NH$), ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.7, 138.2, 131.1, 129.1, 127.8, 127.7, 126.7, 125.4, 116.1, 104.6, 93.2, 59.4, 56.3, 50.6, 32.4, 27.3. IR $\nu(cm^{-1})$: 2923, 1738, 1604, 1496, 1452, 1386, 1342, 1297, 1216, 1155, 1123, 1051, 1022, 984, 912, 810, 742, 699. HRMS (ESI-TOF): m/z 265.1714 $[C_{18}H_{20}N_2 + H]^+$, calcd. 265.1705.

General Procedure 9 for the Ring-Closure of β -Substituted Tryptamines



Tryptamine (1.0 eq) was dissolved into acetonitrile in the presence of NaHCO_3 (1.5 eq), and the resulting mixture was stirred at room temperature for 15 mins under the air. *N*-Fluorobenzenesulfonimide (1.2 eq) was then added to the mixture with stirring. After overnight, the reaction mixture was diluted with ethylacetate (20 mL), washed with distilled water (3×10 mL), dried over Na_2SO_4 and concentrated under the reduced pressure. The crude product was then purified with the column chromatography (ethylacetate:hexane, 15:85) to give targeted compound.

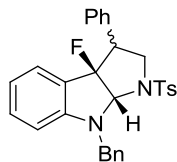
3a-Fluoro-8-methyl-3-phenyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole 160



Following the general procedure **9**, using 100 mg, 0.246 mmol of tryptamine **126**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 25:75 (v/v), clear oil product (43.5 mg, 43% yield) was obtained. **Note:** 8% Inseparable impurities present. IR (KBr): $\nu = 2922, 1705, 1612, 1493, 1472, 1454, 1431, 1346, 1317, 1306, 1265, 1236, 1159, 1107, 1092, 1020, 1013, 926, 814, 750, 735, 700, 667$. ^1H NMR (300 MHz, CDCl_3): δ 7.85 (d, $J = 8.1$ Hz, 4H, *trans* and *cis*, tosyl CH_{Ar}), 7.38 (d, $J = 8.1$ Hz, 4H, *trans* and *cis*, tosyl CH_{Ar}), 7.30-7.14 (m, 9H, *trans* and *cis*, CH_{Ar}), 7.05-7.03 (m, 2H, *cis*, , CH_{Ar}), 6.92 (d, $J = 6.6$ Hz, 2H, *trans*, CH_{Ar}), 6.70-6.62 (m, 2H, *cis*, CH_{Ar}), 6.47 (d, $J = 8.1$ Hz, 1H, *trans*, CH_{Ar}), 6.34 (t, $J = 7.8$ Hz, 1H, *trans*, CH_{Ar}), 5.85 (d, $J = 7.5$ Hz, 1H, *trans*, CH_{Ar}), 5.65 (d, $J = 19.8$ Hz, 1H, *trans*, $(\text{CH}_3)\text{NCHNTs}$), 5.36 (d, $J = 23.4$ Hz, 1H, *cis*, $(\text{CH}_3)\text{NCHNTs}$), 3.91-3.85 (m, 2H, , *trans* and *cis*, $(\text{Ph})\text{CHCH}_2\text{NTs}$), 3.75 (t, $J = 11.7$ Hz, 1H, *cis*, $(\text{Ph})\text{CHCH}_2\text{NTs}$), 3.52 (t, $J = 12.9$ Hz, 1H, *trans*, $(\text{Ph})\text{CHCH}_2\text{NTs}$), 3.46-3.38 (m, 1H, *cis*, $(\text{Ph})\text{CHCH}_2\text{NTs}$) 3.10 (s, 3H, *cis*, NCH_3), 3.07 (s, 3H, *trans*, NCH_3), 2.48 (s, 6H, *trans* and *cis*, tosyl). ^{13}C NMR (75 MHz, CDCl_3): δ 152.7, 152.5, 144.3, 144.1, 136.4, 134.1, 134.0, 131.8, 131.8, 131.1, 130.1, 129.9, 129.6, 128.4, 128.4, 128.3, 128.0, 128.0, 127.9, 127.4, 127.2, 126.8, 120.5, 118.9, 117.3, 117.2, 110.7, 108.9, 108.1, 106.7, 92.4 ($J = 24$ Hz), 89.1 ($J = 30$ Hz), 53.3 ($J = 30$ Hz), 51.7 ($J = 25$

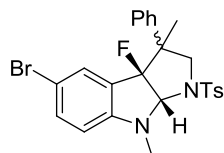
Hz), 50.3, 50.2, 33.8, 32.0, 29.7, 21.6. HRMS: m/z ; calcd for $C_{21}H_{24}N_2O_2S$ Na: 445.1362 $[M+Na]^+$; found: 445.1363.

8-Benzyl-3a-fluoro-3-phenyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole 161



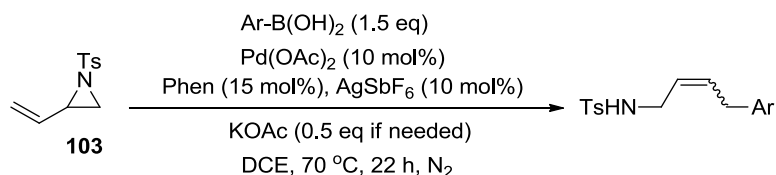
Following the general procedure **9**, using 70 mg, 0.338 mmol of tryptamine **136**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 25:75 (v/v), clear oil product (33.7 mg, 20% yield) was obtained. **Note:** 7% Inseparable impurities present. IR (KBr): ν = 3350, 1697, 1609, 1489, 1470, 1454, 1398, 1346, 1321, 1292, 1184, 1161, 1115, 1092, 1032, 1011, 924, 908, 812, 748, 731, 698, 664; m.p. 118-120°C; 1H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, J = 8.0 Hz, 2H, *trans*, tosyl CH_{Ar}), 7.68 (d, J = 7.5 Hz, 2H, *cis*, tosyl CH_{Ar}), 7.40 (m, 2H, *cis*, CH_{Ar}), 7.38-7.20 (m, 19H, *trans* and *cis*, tosyl CH_{Ar} & CH_{Ar}), 7.26 (t, J = 7.5 Hz, 1H, *cis*, CH_{Ar}), 7.14-7.03 (m, 2H, *trans*, CH_{Ar}), 6.92 (d, J = 8.0 Hz, 2H, *trans*, CH_{Ar}), 6.91-6.87 (m, 1H, *cis*, CH_{Ar}), 6.71 (d, J = 7.5 Hz, 1H, *cis*, CH_{Ar}), 6.65 (t, J = 8.0 Hz, 1H, *cis*, CH_{Ar}), 6.50 (d, J = 8.0 Hz, 1H, *cis*, CH_{Ar}), 6.41 (d, J = 8.0 Hz, 1H, *trans*, CH_{Ar}), 6.34 (t, J = 7.5 Hz, 1H, *trans*, CH_{Ar}), 5.85 (d, J = 21.0 Hz, 1H, *trans*, (Bn) $NCHNTs$), 5.67 (d, J = 23.4 Hz, 1H, *cis*, (Bn) $NCHNTs$), 5.07 (d, J = 11.7 Hz, 1H, *cis*, NCH_2Ph), 4.70 (app. q, J = 12.5 Hz, 2H, *trans*, NCH_2Ph), 4.54 (d, J = 11.7 Hz, 1H, *cis*, NCH_2Ph), 3.96-3.87 (dd, J = 3.0, 6.5 Hz, 2H, *trans*, (Ph) $CHCH_2NTs$), 3.78 (t, J = 11.5 Hz, 1H, *cis*, (Ph) $CHCH_2NTs$), 3.61 (t, J = 12.4 Hz, 1H, *trans*, (Ph) $CHCH_2NTs$), 2.43 (s, 3H, *trans*, tosyl), 2.42 (s, 3H, *cis*, tosyl). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.9, 151.9, 144.2, 143.5, 138.3, 137.8, 136.2, 134.1, 131.8, 131.8, 131.2, 130.1, 129.9, 129.8, 129.8, 129.7, 129.0, 128.9, 128.6, 128.6, 128.4, 128.4, 128.3, 128.0, 127.4, 127.4, 127.3, 127.3, 127.2, 127.1, 127.0, 126.6, 122.7 (J = 34 Hz), 120.5 (J = 14 Hz), 117.4, 110.3, 108.7, 107.1, 90.1 (J = 13 Hz), 87.7 (J = 18 Hz), 80.2, 64.5, 53.5 (J = 18 Hz), 50.3 (J = 13 Hz), 49.4, 48.6, 22.7, 21.6. HRMS: m/z ; calcd for $C_{21}H_{24}N_2O_2S$ Na: 521.1675 $[M+Na]^+$; found: 521.1666.

5-Bromo-3a-fluoro-3,8-dimethyl-3-phenyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole 162



Following the general procedure **9**, using 40 mg, 0.0804 mmol of tryptamine **121**. Purified by chromatography on silica gel, eluting with ethyl acetate/hexane 25:75 (v/v), clear oil product (30.3 mg, 73% yield) was obtained. IR (KBr): ν = 2926, 1603, 1489, 1447, 1422, 1383, 1344, 1265, 1157, 1107, 1090, 1067, 1022, 1011, 974, 941, 891, 866, 835, 812, 754, 735, 700, 664. ^1H NMR (500 MHz, CDCl_3): δ 7.83 (d, J = 8.0 Hz, 2H, *cis*, tosyl CH_{Ar}), 7.75 (d, J = 8.5 Hz, 2H, *trans*, tosyl CH_{Ar}), 7.39 (d, J = 8 Hz, 2H, *trans*, tosyl CH_{Ar}), 7.37-7.25 (m, 13H, *trans* and *cis*, tosyl CH_{Ar} & CH_{Ar}), 7.19 (d, J = 8.5 Hz, 1H, *trans*, CH_{Ar}), 7.04 (s, 1H, *cis*, CH_{Ar}), 6.50 (d, J = 8.5 Hz, 1H, *cis*, CH_{Ar}), 6.26 (d, J = 8.5 Hz, 1H, *trans*, CH_{Ar}), 5.87 (s, 1H, *cis*, CH_{Ar}), 5.53 (d, J = 16.5 Hz, 1H, *trans*, $(\text{CH}_3)\text{NCHNTs}$), 5.22 (d, J = 26.5 Hz, 1H, *cis*, $(\text{CH}_3)\text{NCHNTs}$), 4.09 (d, J = 9.5 Hz, 1H, *cis*, $\text{Ph}(\text{CH}_3)\text{CCH}_2\text{NTs}$), 3.73 (app. q, J = 6 Hz, 2H, *trans*, $\text{Ph}(\text{CH}_3)\text{CCH}_2\text{NTs}$), 3.65 (d, J = 9.5 Hz, 1H, *cis*, $\text{Ph}(\text{CH}_3)\text{CCH}_2\text{NTs}$), 3.10 (s, 3H, *cis*, NCH_3), 3.00 (s, 3H, *trans*, NCH_3), 2.47 (s, 3H, *cis*, tosyl), 2.43 (s, 3H, *trans*, tosyl), 1.54 (s, 3H, *trans*, $\text{Ph}(\text{CH}_3)\text{CCH}_2\text{NTs}$), 1.37 (s, 3H, *cis*, $\text{Ph}(\text{CH}_3)\text{CCH}_2\text{NTs}$). ^{13}C NMR (75 MHz, CDCl_3): δ 152.0, 145.2, 144.5, 143.7, 140.1, 138.0, 137.2, 134.3, 134.1, 133.2, 129.9, 129.8, 129.7, 129.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.5, 127.3, 127.1, 126.9, 126.8, 126.5, 126.5, 109.8 (J = 121 Hz), 107 (J = 61 Hz), 92.3 (J = 26 Hz), 86.8 (J = 31 Hz), 60.8, 56.4, 50.3 (J = 24 Hz), 34.4 (J = 65 Hz), 29.6, 23.8, 23.7, 23.1, 21.6, 21.5. HRMS: m/z ; calcd for $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_2\text{S Na}$: 537.0624 $[\text{M}+\text{Na}]^+$; found: 537.0650.

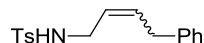
General Procedure 10 for Boronic Acids Addition to 1-Tosyl-2-Vinyl Aziridine **103**



In a typical experiment, $\text{Pd}(\text{OAc})_2$ (10 mol%), 1,10-phenanthroline (15 mol%) and AgSbF_6 (10 mol%) were dissolved in DCE (0.14 M). The resulting mixture was ultrasonically treated for 1 min, and then stirred at room temperature for 1 min. 1-tosyl-2-vinylaziridine **103** (1.0 eq), arylboronic acid (1.5 eq), KOAc (0.5 eq if needed) were then added. The mixture was then heated at 70 °C for 22 h, and then diluted with ethyl acetate, passed through a short pad of silica gel, evaporated and finally purified

with silica gel chromatography (typically 30% ethyl acetate/hexane) to give the allyl sulfonamide.

(*E/Z*)-4-Methyl-*N*-(4-phenylbut-2-enyl)benzenesulfonamide 274



Following the general procedure **10**, using 30 mg, 0.135 mmol of 1-tosyl-2-vinyl aziridine **103** and phenylboronic acid with no addition of KOAc yielded the title compound as a clear oil (32 mg, 79%). ¹H NMR (500 MHz, CDCl₃) δ 7.88-7.71 (m, 2H, *E* and *Z* isomer, tosyl) 7.31-7.19 (m, 4H, *E* and *Z* isomer, tosyl & CH_{Ar} overlap), 7.24-7.22 (m, 1H, *E* and *Z* isomer, CH_{Ar}), 7.10-7.06 (m, 2H, *E* and *Z* isomer, CH_{Ar}), 5.80-5.65 (m, 1H, *E* and *Z* isomer, CH=CHCH₂Ph), 5.48-5.35 (m, 1H, *E* and *Z* isomer, CH=CHCH₂Ph), 4.48 (s, 1H, *E* and *Z* isomer, TsNH), 3.70 (t, *J* = 7.0 Hz, 2H, *Z* isomer, CH₂CH=CHCH₂Ph), 3.54 (t, *J* = 7.0 Hz, 2H, *E* isomer, CH₂CH=CHCH₂Ph), 3.28 (d, *J* = 7.0 Hz, 2H, *Z* isomer, CH₂CH=CHCH₂Ph), 3.26 (d, *J* = 7.0 Hz, 2H, *E* isomer, CH₂CH=CHCH₂Ph), 2.43 (s, 3H, *E* and *Z* isomer, tosyl). ¹³C NMR (125 MHz, CDCl₃) δ 143.5, 143.4, 139.7, 139.6, 137.0, 133.5, 132.8, 129.7, 129.7, 128.6, 128.5, 128.2, 127.2, 126.5, 126.3, 125.9, 124.9, 45.2, 40.1, 38.5, 33.4, 21.5. IR ν(cm⁻¹): 3274, 2920, 1599, 1404, 1325, 1119, 1093. HRMS (ES): *m/z* 302.1203. [C₁₇H₁₉NO₂S + H]⁺, calcd. 302.1215.

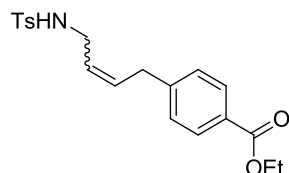
(*E/Z*)-4-Methyl-*N*-(*p*-methylphenylbut-2-enyl)benzenesulfonamide 281



Following the general procedure **10**, using 25 mg, 0.112 mmol of 1-tosyl-2-vinyl aziridine **103** with tolylboronic acid yielded the title compound as a clear oil (14.2 mg, 40%). ¹H NMR (500 MHz, CDCl₃) δ 7.75 (d, *J* = 8.5 Hz, 2H, *Z* isomer, tosyl CH_{Ar}), 7.73 (d, *J* = 9.0 Hz, 2H, *E* isomer, tosyl CH_{Ar}), 7.32-7.28 (m, 2H, *E* and *Z* isomer, tosyl CH_{Ar} & CH_{Ar}), 7.08-7.07 (m, 2H, *E* and *Z* isomer, CH_{Ar}), 6.97-6.95 (m, 2H, *E* and *Z* isomer, CH_{Ar}), 5.73-5.67 (m, 1H, *E* and *Z* isomer, CH=CHCH₂Ar), 5.44-5.39 (m, 1H, *E* and *Z* isomer, CH=CHCH₂Ar), 4.28-4.27 (m, 1H, *E* and *Z* isomer, TsNH), 3.71 (t, *J* = 6.5 Hz, 1H, *Z* isomer, CH₂CH=CHCH₂Ar) 3.55 (t, *J* = 6 Hz, *E* isomer, CH₂CH=CHCH₂Ar) 3.27-3.23 (m, 2H, *E* and *Z* isomer, CH₂CH=CHCH₂Ar) 2.43 (s, 3H, *E* and *Z* isomer, tosyl) 2.31 (s, 3H, *E* and *Z* isomer, tolyl). ¹³C NMR (125 MHz, CDCl₃) δ 143.6, 136.6, 135.8, 133.2, 129.8, 129.7, 129.3, 129.2, 128.4, 128.1, 127.2, 127.2, 124.6, 45.2, 40.3, 38.2, 32.6, 22.0, 21.7. IR ν(cm⁻¹): 3239,

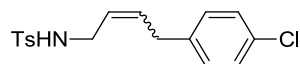
2923, 1663, 1436, 1408, 1327, 1159, 1094. HRMS (ES): m/z 338.1197 [$C_{18}H_{21}N_1O_2S_1 + Na$] $^+$, calcd. 338.1191.

(*E/Z*)-4-Methyl-*N*-(4-ethoxycarbonylphenylbut-2-enyl)benzenesulfonamide 282



Following the general procedure **10**, using 25 mg, 0.112 mmol of 1-tosyl-2-vinyl aziridine **103** and 4-(ethoxycarbonyl)phenylboronic acid yielded the title compound as a clear oil (39.3 mg, 94%). 1H NMR (500 MHz, $CDCl_3$) δ 7.77-7.71 (m, 2H, *E* and *Z* isomer, CH_{Ar}), 7.32-7.26 (m, 2H, *E* and *Z* isomer, tosyl CH_{Ar}), 7.09-7.06 (2H, m, *E* and *Z* isomer, tosyl CH_{Ar}), 6.99- 6.94 (2H, m, *E* and *Z* isomer, CH_{Ar}), 5.80-5.65 (m, 1H, *E* and *Z* isomer, $CH=CHCH_2Ar$), 5.48-5.35 (m, 1H, *E* and *Z* isomer, $CH=CHCH_2Ar$), 4.34 (m, 3H, *E* and *Z* isomer, OCH_2CH_3 & $TsNH$), 3.70 (t, $J = 7.0$ Hz, 1H, *Z* isomer, $CH_2CH=CHCH_2Ar$) 3.54 (t, $J = 7.0$ Hz, *E* isomer, $CH_2CH=CHCH_2Ar$) 3.40 (d, $J = 7.0$ Hz, *Z* isomer, $CH_2CH=CHCH_2Ar$) 3.36 (d, $J = 7.0$ Hz, *E* isomer, $CH_2CH=CHCH_2Ar$) 2.42 (s, 3H, *Z* isomer) 2.41 (s, 3H, *E* isomer) 1.42(t, $J = 7.0$ Hz, *E* and *Z* isomer, OCH_2CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 166.7, 145.1, 145.0, 143.8, 143.7, 137.2, 137.1, 132.5, 131.9, 130.1, 130.0, 129.9, 128.8, 128.7, 128.4, 127.4, 127.4, 127.0, 126.0, 61.1, 45.3, 40.3, 38.6, 33.6, 21.8, 21.7, 14.6. IR $\nu(cm^{-1})$: 3142, 2976, 2921, 2903, 1700, 1609, 1442, 1179, 1107. HRMS (ES): m/z 396.1237 [$C_{20}S_1O_4N_1H_{23} + Na$] $^+$, calcd. 396.1245.

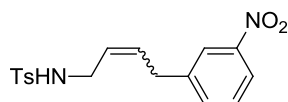
(*E/Z*)-4-Methyl-*N*-(4-chlorophenylbut-2-enyl)benzenesulfonamide 283



Following the general procedure **10**, using 25 mg, 0.112 mmol of 1-tosyl-2-vinyl aziridine **103** and 4-chlorophenylboronic acid yielded the title compound as a clear oil (21.4 mg, 57%). 1H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, $J = 8.5$ Hz, 2H, *Z* isomer, tosyl CH_{Ar}), 7.76 (d, $J = 9.0$ Hz, 2H, *E* isomer, tosyl CH_{Ar}), 7.33 (app. d, $J = 8.5$ Hz, 2H, *E* and *Z* isomer, tosyl CH_{Ar}), 7.30-7.24 (m, 2H, *E* and *Z* isomer, CH_{Ar}), 7.04 (app. d, $J = 8.5$ Hz, 2H, *E* and *Z* isomer, CH_{Ar}), 5.74- 5.61 (m, 1H, *E* and *Z* isomer, $CH=CHCH_2Ar$), 5.48-5.35 (m, 1H, *E* and *Z* isomer, $CH=CHCH_2Ar$), 4.35-4.34 (m, 1H, *E*

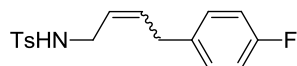
and *Z* isomer, TsNH), 3.72 (t, $J = 7.0$ Hz, 1H, *Z* isomer, $\text{CH}_2\text{CH}=\text{CHCH}_2\text{Ar}$), 3.60 (t, $J = 7.0$ Hz, 1H, *E* isomer, $\text{CH}_2\text{CH}=\text{CHCH}_2\text{Ar}$), 3.32 (d, $J = 7.5$ Hz, 2H, *Z* isomer, $\text{CH}_2\text{CH}=\text{CHCH}_2\text{Ar}$), 3.28 (d, $J = 7.0$ Hz, 2H, *E* isomer, $\text{CH}_2\text{CH}=\text{CHCH}_2\text{Ar}$), 2.42 (s, 3H, *E* and *Z* isomer, tosyl). ^{13}C NMR (125 MHz, CDCl_3) δ 143.6, 138.0, 137.9, 132.8, 132.2, 132.1, 129.9, 129.8, 129.7, 129.6, 128.7, 128.6, 127.2, 127.2, 126.4, 125.4, 45.1, 40.1, 37.8, 32.8, 21.6. IR $\nu(\text{cm}^{-1})$: 3263, 2971, 2923, 1598, 1490, 1404, 1326, 1185, 1093. HRMS (ES): m/z 358.0637 [$\text{C}_{17}\text{S}_1\text{O}_2\text{N}_1\text{Cl}_1\text{H}_{18} + \text{Na}$] $^+$, calcd. 358.0644.

(*E/Z*)-4-Methyl-*N*-(3-nitrophenylbut-2-enyl)benzenesulfonamide **284**



Following the general procedure **10**, using 25 mg, 0.112 mmol of 1-tosyl-2-vinyl aziridine **103** and 4-nitrophenylboronic acid yielded the title compound as a green oil (34.9 mg, 90%). ^1H NMR (500 MHz, CDCl_3) δ 8.10-8.08 (m, 1H, *E* and *Z* isomer, CH_{Ar}), 7.98 (app. s, 1H, *E* and *Z* isomer, CH_{Ar}), 7.81-7.76 (m, 2H, *E* and *Z* isomer, tosyl CH_{Ar}), 7.48-7.47 (2H, m, *E* and *Z* isomer, CH_{Ar}), 7.35-7.32 (m, 2H, *E* and *Z* isomer, tosyl CH_{Ar}), 5.77-5.63 (m, 1H, *E* and *Z* isomer, $\text{CH}=\text{CHCH}_2\text{Ar}$), 5.58-5.55 (m, 2H, *E* and *Z* isomer, tosyl CH_{Ar}), 5.77-5.63 (m, 1H, *E* and *Z* isomer, $\text{CH}=\text{CHCH}_2\text{Ar}$), 5.58-5.55 (m, 1H, *Z* isomer, $\text{CH}=\text{CHCH}_2\text{Ar}$), 5.54-5.47 (m, 1H, *E* isomer, $\text{CH}=\text{CHCH}_2\text{Ar}$), 4.72 (br. t, $J = 5.0$ Hz, *Z* isomer, TsNH), 4.67 (br. t, $J = 6.0$ Hz, *E* isomer, TsNH), 3.75 (t, $J = 6.5$ Hz, 1H, *Z* isomer, $\text{CH}_2\text{CH}=\text{CHCH}_2\text{Ar}$), 3.62 (t, $J = 6.5$ Hz, *E* isomer, $\text{CH}_2\text{CH}=\text{CHCH}_2\text{Ar}$), 3.49 (d, $J = 8.0$ Hz, 1H, *Z* isomer, $\text{CH}_2\text{CH}=\text{CHCH}_2\text{Ar}$), 3.42 (d, $J = 6.5$ Hz, 2H, *E* isomer, $\text{CH}_2\text{CH}=\text{CHCH}_2\text{Ar}$), 2.46 (s, 3H, *E* and *Z* isomer, tosyl). ^{13}C NMR (125 MHz, CDCl_3) δ 148.6, 144.0, 143.9, 141.9, 141.8, 137.2, 137.0, 135.0, 134.8, 131.6, 131.0, 130.4, 130.0, 129.9, 129.7, 129.6, 127.9, 127.4, 127.3, 126.8, 123.6, 123.3, 121.7, 45.2, 40.3, 38.2, 33.2, 21.8. IR $\nu(\text{cm}^{-1})$: 3410, 2921, 1591, 1383, 1044. HRMS (ES): m/z 347.1059 [$\text{C}_{17}\text{S}_1\text{O}_4\text{N}_2\text{H}_{18} + \text{H}$] $^+$, calcd. 347.1066.

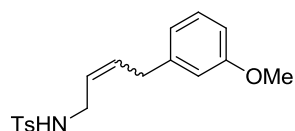
(*E/Z*)-4-Methyl-*N*-(4-fluorophenylbut-2-enyl)benzenesulfonamide **285**



Following the general procedure **10**, using 25 mg, 0.112 mmol of 1-tosyl-2-vinyl aziridine **103** and

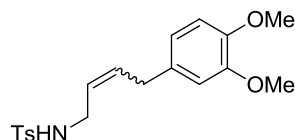
2875, 1627, 1455, 1379, 1088, 1045, 881. HRMS (ES): m/z 503.1230 [$C_{25}S_2O_4N_2H_{24} + Na$] $^+$, calcd. 503.1075.

(*E/Z*)-4-Methyl-*N*-(3-methoxyphenylbut-2-enyl)benzenesulfonamide 287



Following the general procedure **10**, using 25 mg, 0.112 mmol of 1-tosyl-2-vinylaziridine **103** and 4-methoxyphenylboronic acid yielded the title compound as a clear oil (15.6 mg, 42%). 1H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 8.5 Hz, 2H, *E* and *Z* isomer, tosyl CH_{Ar}), 7.30 (d, J = 8.5 Hz, 2H, *E* and *Z* isomer, tosyl CH_{Ar}), 7.19 (t, J = 8 Hz, 1H, *E* and *Z* isomer, CH_{Ar}), 6.75-6.73 (dd, J = 8.5, 2.0 Hz, 1H, *E* and *Z* isomer, CH_{Ar}), 6.67 (d, J = 7.5 Hz, *E* and *Z* isomer, CH_{Ar}), 6.64 (s, 1H, *E* and *Z* isomer, CH_{Ar}), 5.77-5.72 (m, 1H, *E* and *Z* isomer, $CH=CHCH_2Ar$), 5.50-5.45 (m, 1H, *E* and *Z* isomer, $CH=CHCH_2Ar$), 4.39 (br s, 1H, *E* and *Z* isomer, $TsNH$), 3.83 (s, 3H, *E* isomer, OCH_3), 3.82 (s, 3H, *Z* isomer, OCH_3), 3.74 (t, J = 7.0 Hz, 1H, *Z* isomer, $CH_2CH=CHCH_2Ar$), 3.59 (t, J = 7.0 Hz, 1H, *E* isomer, $CH_2CH=CHCH_2Ar$), 3.26 (d, J = 7.0 Hz, 2H, *Z* isomer, $CH_2CH=CHCH_2Ar$), 3.27 (d, J = 7.0 Hz, 2H, *E* isomer, $CH_2CH=CHCH_2Ar$), 2.46 (s, 3H, *E* and *Z* isomer, tosyl). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 160.0, 143.6, 143.4, 141.4, 137.2, 137.1, 130.0, 129.9, 129.8, 129.6, 127.4, 127.3, 126.2, 125.2, 121.1, 120.8, 114.5, 114.2, 111.9, 55.4, 45.2, 40.1, 38.5, 33.4, 21.5. IR $\nu(cm^{-1})$: 3257, 2919, 1600, 1490, 1454, 1325, 1259, 1159, 1094, 1045. HRMS (ES): m/z 354.1131 [$C_{18}SO_3N_1H_{21} + Na$] $^+$, calcd. 354.1140.

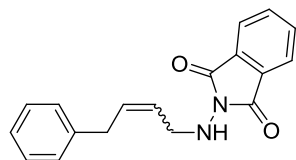
(*E/Z*)-4-Methyl-*N*-(3,4-dimethoxyphenylbut-2-enyl)benzenesulfonamide 288



Following the general procedure **10**, using 25 mg, 0.112 mmol of 1-tosyl-2-vinyl aziridine **103** and 3,4-dimethoxyphenylboronic acid yielded the title compound as a clear oil (10.1 mg, 25%). 1H NMR (500 MHz, $CDCl_3$) δ 7.78-7.72 (m, 2H, *E* and *Z* isomer, tosyl CH_{Ar}), 7.31-7.28 (m, 2H, *E* and *Z* isomer, tosyl CH_{Ar}), 6.78 (d, J = 8 Hz, 1H, *E* and *Z* isomer, CH_{Ar}), 6.64- 6.62 (m, 2H, *E* and *Z* isomer, CH_{Ar}), 5.73-5.68 (m, 1H, *E* and *Z* isomer, $CH=CHCH_2Ar$), 5.45-5.40 (m, 1H, *E* and *Z* isomer,

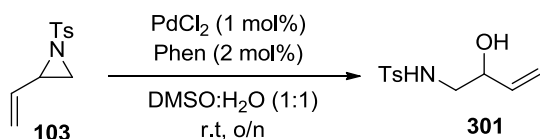
$CH=CHCH_2Ar$), 4.36 (t, $J = 5.5$ Hz, 1H, *E* and *Z* isomer, $TsNH$), 3.85 (s, 6H, *E* and *Z* isomer, OCH_3), 3.71 (t, $J = 6.5$ Hz, 2H, *Z* isomer, $CH_2CH=CHCH_2Ar$), 3.56 (t, $J = 5.5$ Hz, 1H, *E* isomer, $CH_2CH=CHCH_2Ar$), 3.27 (d, $J = 7.0$ Hz, 2H, *Z* isomer, $CH_2CH=CHCH_2Ar$), 3.23 (d, $J = 6.5$ Hz, *E* isomer, $CH_2CH=CHCH_2Ar$), 2.43 (s, 3H, *E* and *Z* isomer, tosyl). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 149.3, 147.7, 143.8, 143.7, 137.1, 137.0, 134.0, 133.2, 132.6, 132.2, 130.0, 129.9, 127.4, 127.3, 125.8, 124.9, 120.6, 120.1, 111.9, 111.8, 111.5, 111.4, 56.2, 56.1, 45.5, 40.3, 38.4, 33.0, 21.6. IR $\nu(cm^{-1})$: 3243, 2919, 1616, 1515, 1328, 1139. HRMS (ES): m/z 384.1238 [$C_{19}H_{23}NSO_4 + Na$] $^+$, calcd. 384.1245.

Synthesis of 2-((4-phenylbut-2-en-1-yl)amino)isoindoline-1,3-dione 296



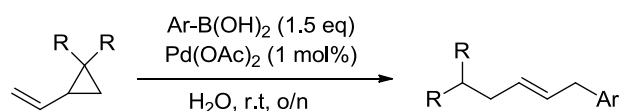
$Pd(OAc)_2$ (7.30 mg, 0.0327 mmol, 10 mol%), 1,10-phenanthroline (8.80 mg, 0.0490 mmol, 15 mol%), $AgSbF_6$ (10.9 mg, 0.0327 mmol, 10 mol%) were dissolved in anhydrous dichloroethane (2.8 mL). The resulting mixture was stirred for 30mins at room temperature. 2-(2-vinylaziridin-1-yl)isoindoline-1,3-dione (70 mg, 0.327 mmol, 1.0 eq), phenylboronic acid (59.8 mg, 0.490 mmol, 1.5 eq) and potassium acetate (11.1 mg, 0.117 mmol, 0.5 eq) were subsequently added. The mixture was then stirred at room temperature for 17hrs, and then diluted with ethyl acetate, passed through a short pad of silica gel (1 cm), evaporated and finally purified with silica gel chromatography (30% ethyl acetate/n-pentane) to give the yellow solids (67.2 mg, 70%). 1H NMR (500Mz, $CDCl_3$) δ 7.83-7.81 (m, 2H, CH_{Ar}), 7.73-7.72 (m, 2H, CH_{Ar}), 7.16-7.13 (m, 2H, CH_{Ar}), 7.10-7.08 (m, 1H, CH_{Ar}), 7.05-7.01 (m, 2H, CH_{Ar}), 5.83-5.78 (m, 1H, $PhCH_2CH=CH$), 5.74-5.68 (m, 1H, $PhCH_2CH=CH$) 3.86 (d, $J = 6.0$ Hz, 2H, $NHCH_2CH=CH$, *cis*), 3.66 (d, $J = 5.5$ Hz, 2H, $NHCH_2CH=CH$, *trans*), 3.38 (d, $J = 7.5$ Hz, 2H, $PhCH_2CH=CH$, *cis*), 3.30 (d, $J = 6.5$ Hz, 2H, $PhCH_2CH=CH$, *trans*). 2.70 (broad s, 1H, $NHCH_2CH=CH$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 166.7, 140.0, 139.7, 135.3, 135.1, 134.2, 133.7, 131.1, 130.2, 128.4, 128.4, 128.2, 128.0, 126.0, 126.0, 124.9, 124.5, 123.6, 123.5, 123.4, 53.2, 47.8, 38.8, 33.4. IR $\nu(cm^{-1})$: 2989, 2362, 1773, 1717, 1560, 1507, 1457, 1376, 1192, 1127, 1084, 883, 712. HRMS (ES): m/z 315.1109 [$C_{18}H_{16}N_2O_2 + Na$] $^+$, calcd. 315.1101.

Synthesis of *N*-(2-hydroxybut-3-en-1-yl)-4-methylbenzenesulfonamide **301**



To a mixture of PdCl₂ (0.400mg, 0.0023mmol, 1 mol%), 1,10-phenanthroline (0.80g, 0.0045mmol, 2 mol%) in DMSO/H₂O (2ml, 1:1, v/v) added vinylaziridine **103** (50mg, 0.224mmol, 1.0 eq). The resulting reaction mixture was then stirred at ambient temperature in the air for overnight, diluted with ethyl acetate (30 mL) and washed it with water (3×10 mL). The organic layer was then dried over Na₂SO₄, filtrated and concentrated under reduced pressure to give clear oily liquid (47.6mg, 88%). **Note** Data matched that reported previous.¹¹ ¹H NMR (500 MHz, CDCl₃) δ 7.72 (d, *J* = 8 Hz, 2H, tosyl CH_{Ar}), 7.51 (d, *J* = 8.0 Hz, 2H, tosyl CH_{Ar}), 5.79-5.72 (m, 1H, (OH)CHCHCH₂), 5.29 (d, *J* = 17.0 Hz, 1H, (OH)CHCHCH₂), 5.17 (d, *J* = 10.5 Hz, 1H, (OH)CHCHCH₂), 5.15 (s, 1H, *NHTs*), 4.22 (app. s, 1H, (OH)CHCHCH₂), 3.14-3.09 (m, 1H, CH₂CH(OH)), 2.89-2.83 (m, 1H, CH₂CH(OH)), 2.83 (s, 1H, OH), 2.42 (s, 1H, tosyl). ¹³C NMR (CDCl₃, 75 Hz) δ 143.5, 136.8, 136.4, 129.6, 126.9, 117.0, 71.1, 48.0, 21.4.

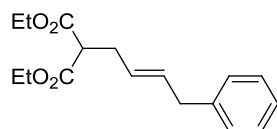
General Procedure 11 for Palladium-Catalysed Coupling of Vinylcyclopropanes with Boronic Acids in Water



R = CO₂Et, CN

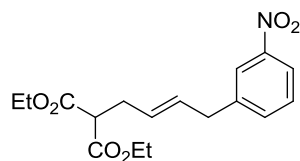
To a 10 mL Schlenk flask equipped with a stir bar, was added Pd(OAc)₂ (1 mol%), the vinylcyclopropane (1.0 eq), arylboronic acid (1.5 eq) and H₂O (0.25 M wrt to the vinylcyclopropane). The mixture was stirred at room temperature and after 8 h, it was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried over MgSO₄, filtered, and evaporated to dryness under reduced pressure. The residue was purified by flash column chromatography (typically ethyl acetate: Hexane, 20:80) or straight dichloromethane to furnish the corresponding coupling products. Data for major isomer only reported.

(*E*)-Diethyl 2-(4-phenylbut-2-en-1-yl)malonate **452**



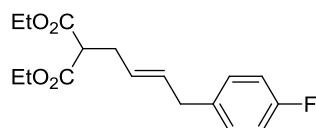
147.0 mg **452** was prepared in 84% yield *via* the general procedure **11** from **328** (127.7 mg, 0.2230 mmol, 1.0 eq), phenylboronic acid (110.2 mg, 0.3350 mmol, 1.5 eq) and palladium acetate (1.35 mg, 0.00223 mmol, 1 mol%); ^1H NMR (300 MHz, CDCl_3) δ 7.30-7.25 (m, 2H, CH_{Ar}), 7.20-7.13 (m, 3H, CH_{Ar}), 5.74-5.65 (m, 1H, $\text{CH}=\text{CHCH}_2\text{Ph}$), 5.53-5.43 (m, 1H, $\text{CH}=\text{CHCH}_2\text{Ph}$), 4.19-4.13 (m, 4H, OCH_2CH_3), 3.40 (t, $J = 7.5$ Hz, 1H, $\text{CH}(\text{CO}_2\text{Et})_2$), 3.32 (d, $J = 6.9$ Hz, 2H, $\text{CH}=\text{CHCH}_2\text{Ph}$), 2.62 (t, $J = 7.2$ Hz, 2H, $\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{Ph}$), 1.24 (t, $J = 7.2$ Hz, 6H, OCH_2CH_3). ^{13}C NMR (75 MHz, CDCl_3) δ 169.0, 140.3, 132.4, 128.5, 128.4, 127.0, 126.0, 61.4, 52.2, 39.0, 31.8, 14.1. IR $\nu(\text{cm}^{-1})$: 1729, 1516, 1262, 1233, 1152, 1140, 1026. HRMS (ESI-TOF): m/z 313.1428 [$\text{C}_{17}\text{H}_{22}\text{O}_4 + \text{Na}$] $^+$, calcd. 313.1416.

(*E*)-Diethyl 2-(4-(3-nitrophenyl)but-2-en-1-yl)malonate **468**



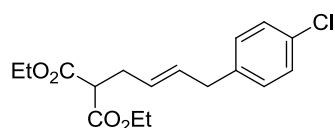
120 mg **468** was prepared in 95% yield *via* the general procedure **11** from **328** (80.0 mg, 0.377 mmol, 1.0 eq), 3-nitrophenylboronic acid (94.5 mg, 0.566 mmol, 1.5 eq) and palladium acetate (0.85 mg, 0.0038 mmol, 1 mol%); ^1H NMR (500 MHz, CDCl_3) δ 8.06 (d, $J = 7.5$ Hz, 1H, CH_{Ar}), 8.01 (s, 1H, CH_{Ar}), 7.50-7.44 (m, 2H, CH_{Ar}), 5.72-5.66 (m, 1H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 5.59-5.53 (m, 1H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 4.23-4.14 (m, 4H, OCH_2CH_3), 3.43 (d, $J = 6.5$ Hz, 2H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 3.42 (t, $J = 8.0$ Hz, 1H, $\text{CH}(\text{CO}_2\text{Et})_2$), 2.65 (t, $J = 6.5$ Hz, 2H, $\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{Ar}$), 1.25 (t, $J = 7.5$ Hz, 6H, OCH_2CH_3). ^{13}C NMR (125 MHz, CDCl_3) δ 168.8, 148.3, 142.3, 134.8, 130.6, 129.2, 128.6, 123.3, 121.3, 61.4, 51.9, 38.4, 31.6, 14.0. IR $\nu(\text{cm}^{-1})$: 1734, 1730, 1528, 1351, 1153, 1031, 971, 733. HRMS (ESI-TOF): m/z 358.1271 [$\text{C}_{17}\text{H}_{21}\text{NO}_6 + \text{Na}$] $^+$, calcd. 358.1267.

(*E*)-Diethyl 2-(4-(4-fluorophenyl)but-2-en-1-yl)malonate **470**



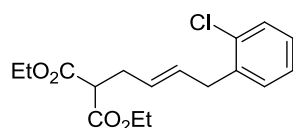
100 mg of **470** was prepared in 86% yield *via* the general procedure **11** from **328** (80.0 mg, 0.377 mmol, 1.0 eq), 4-fluorophenylboronic acid (79.2 mg, 0.566 mmol, 1.5 eq) and palladium acetate (0.85 mg, 0.0038 mmol, 1 mol%); ^1H NMR (300 MHz, CDCl_3) δ 7.11-7.07 (m, 2H, CH_{Ar}), 6.95 (t, J = 8.7 Hz, 2H, CH_{Ar}), 5.71-5.61 (m, 1H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 5.51-5.42 (m, 1H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 4.17 (q, J = 7.2 Hz, 4H, OCH_2CH_3), 3.40 (t, J = 7.2 Hz, 1H, $\text{CH}(\text{CO}_2\text{Et})_2$), 3.28 (d, J = 6.0 Hz, 2H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 2.62 (t, J = 6.9 Hz, 2H, $\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{Ar}$), 1.24 (t, J = 6.9 Hz, 6H, OCH_2CH_3). ^{13}C NMR (125 MHz, CDCl_3) δ 169.0, 161.4 (d, J = 242.2 Hz), 135.9 (d, J = 2.9 Hz), 132.2, 129.8 (d, J = 7.6 Hz), 127.1, 115.1 (d, J = 21 Hz), 61.4, 52.1, 38.1, 31.7, 14.1. IR $\nu(\text{cm}^{-1})$: 1749, 1734, 1507, 1369, 1221, 1156, 1032, 971, 734. HRMS (ESI-TOF): m/z 331.1315 [$\text{C}_{17}\text{H}_{21}\text{FO}_4 + \text{Na}$] $^+$, calcd. 331.1322.

(E)-Diethyl 2-(4-(4-chlorophenyl)but-2-en-1-yl)malonate 472



118 mg of **472** was prepared in 96% yield *via* the general procedure **11** from **328** (80.0 mg, 0.377 mmol, 1.0 eq), 4-chlorophenylboronic acid (88.5 mg, 0.566 mmol, 1.5 eq) and palladium acetate (0.85 mg, 0.0038 mmol, 1 mol%); ^1H NMR (500 MHz, CDCl_3) δ 7.23 (d, J = 8.4 Hz, 2H, CH_{Ar}), 7.07 (d, J = 7.5 Hz, 2H, CH_{Ar}), 5.67-5.60 (m, 1H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 5.52-5.45 (m, 1H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 4.17 (q, J = 7.2 Hz, 4H, OCH_2CH_3), 3.40 (t, J = 7.5 Hz, 1H, $\text{CH}(\text{CO}_2\text{Et})_2$), 3.27 (d, J = 6.3 Hz, 2H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 2.62 (t, J = 7.2 Hz, 2H, $\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{Ar}$), 1.24 (t, J = 6.9 Hz, 6H, OCH_2CH_3). ^{13}C NMR (125 MHz, CDCl_3) δ 168.9, 138.7, 131.8, 129.8, 128.8, 128.4, 127.4, 61.4, 52.0, 38.2, 31.7, 14.1. IR $\nu(\text{cm}^{-1})$: 1744, 1729, 1491, 1370, 1266, 1231, 1176, 1154, 1091, 1029, 1015, 970, 855, 810, 735, 703. HRMS (ESI-TOF): m/z 347.1017 [$\text{C}_{17}\text{H}_{21}\text{ClO}_4 + \text{Na}$] $^+$, calcd. 347.1026.

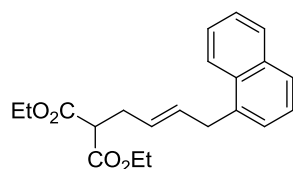
(E)-Diethyl 2-(4-(2-chlorophenyl)but-2-en-1-yl)malonate 476



79.8 mg of **476** was prepared in 65% yield (some starting material was inseparable) *via* the general procedure **11** from **328** (80.0 mg, 0.377 mmol, 1.0 eq), 2-chlorophenylboronic acid (88.5 mg, 0.566 mmol, 1.5 eq) and palladium acetate (0.85 mg, 0.0038 mmol, 1 mol%); ^1H NMR (500 MHz, CDCl_3)

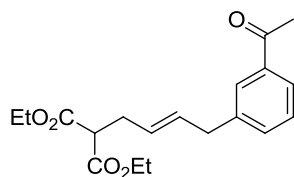
δ 7.17 (d, J = 9.0 Hz, 1H, CH_{Ar}), 7.26-7.10 (m, 3H, CH_{Ar}), 5.73-5.63 (m, 1H, CH=CHCH₂Ar), 5.51-5.42 (m, 1H, CH=CHCH₂Ar), 4.15 (q, J = 6.9 Hz, 4H, OCH₂CH₃), 3.42 (d, J = 6.6 Hz, 2H, CH=CHCH₂Ar), 3.39 (t, J = 7.8 Hz, 2H, CH(CO₂Et)₂), 2.61 (t, J = 7.8 Hz, 2H, CHCH₂CH=CHCH₂Ar), 1.23 (t, J = 6.9 Hz, 6H, OCH₂CH₃). ¹³C NMR (125 MHz, CDCl₃) δ 169.0, 138.0, 130.4, 130.3, 129.4, 127.7, 127.5, 126.8, 61.4, 52.1, 36.4, 31.8, 14.1. IR ν (cm⁻¹): 1749, 1734, 1369, 1266, 1151, 1034, 736. HRMS (ESI-TOF): m/z 347.1031 [C₁₇H₂₁ClO₄ + Na]⁺, calcd. 347.1026.

(*E*)-Diethyl 2-(4-(naphthalen-1-yl)but-2-en-1-yl)malonate 478



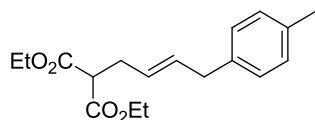
79.8 mg of **478** was prepared in 36% yield *via* the general procedure **11** from **328** (80.0 mg, 0.377 mmol, 1.0 eq), 1-naphthalenephénylboronic acid (97.4 mg, 0.566 mmol, 1.5 eq) and palladium acetate (0.85 mg, 0.0038 mmol, 1 mol%); ¹H NMR (500 MHz, CDCl₃) δ 7.98 (d, J = 8.0 Hz, 1H, naph.), 7.84 (d, J = 7.5 Hz, 1H, naph.), 7.72 (d, J = 8.0 Hz, 1H, naph.), 7.51-7.45 (m, 2H, naph.), 7.41 (t, J = 7.0 Hz, 1H, naph.), 7.29 (d, J = 7.0 Hz, 1H, naph.), 5.85-5.81 (m, 1H, CH=CHCH₂ naph.), 5.54-5.49 (m, 1H, CH=CHCH₂ naph.), 4.18-4.07 (m, 4H, OCH₂CH₃), 3.77 (d, J = 6.0 Hz, 2H, CH=CHCH₂ naph.), 3.37 (t, J = 7.0 Hz, 1H, CH(CO₂Et)₂), 2.61 (t, J = 7.0 Hz, 2H, CHCH₂CH=CHCH₂ naph.), 1.19 (t, J = 6.5 Hz, 6H, OCH₂CH₃). ¹³C NMR (125 MHz, CDCl₃) δ 168.9, 136.4, 133.9, 131.9, 131.9, 128.7, 127.3, 126.9, 126.1, 125.8, 125.6, 125.5, 124.0, 61.3, 52.1, 36.0, 31.8, 14.1. IR ν (cm⁻¹): 1744, 1734, 1506, 1369, 1150, 1030, 970, 859, 777. HRMS (ESI-TOF): m/z 363.1576 [C₂₁H₂₄O₄ + Na]⁺, calcd. 363.1572.

(*E*)-Diethyl 2-(4-(3-acetylphenyl)but-2-en-1-yl)malonate 467



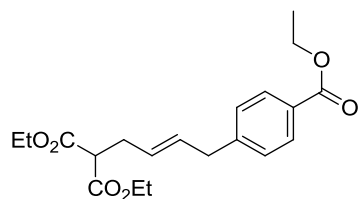
78.7 mg of **467** was prepared in 61% yield *via* the general procedure **11** from **328** (80.0 mg, 0.377 mmol, 1.0 eq), 3-acetylphenylboronic acid (92.8 mg, 0.566 mmol, 1.5 eq) and palladium acetate (0.85 mg, 0.0038 mmol, 1 mol%); ^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, J = 7.0 Hz, 1H, CH_{Ar}), 7.73 (s, 1H, CH_{Ar}), 7.38-7.33 (m, 2H, CH_{Ar}), 5.70-5.65 (m, 1H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 5.53-5.49 (m, 1H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 4.20-4.12 (m, 4H, OCH_2CH_3), 3.39 (t, J = 7.5 Hz, 1H, $\text{CH}(\text{CO}_2\text{Et})_2$), 3.37 (d, J = 7.0 Hz, 2H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 2.62 (t, J = 7.0 Hz, 2H, $\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{Ar}$), 2.59 (s, 3H, $\text{O}=\text{CCH}_3$), 1.22 (t, J = 7.5 Hz, 6H, OCH_2CH_3). ^{13}C NMR (125 MHz, CDCl_3) δ 198.3, 168.9, 140.8, 137.3, 133.3, 131.6, 128.6, 128.3, 127.6, 126.2, 61.4, 52.0, 38.7, 31.7, 26.7, 14.1. IR $\nu(\text{cm}^{-1})$: 1734, 1727, 1684, 1269, 1175, 1155, 969, 859, 797. HRMS (ESI-TOF): m/z 355.1518 [$\text{C}_{19}\text{H}_{24}\text{O}_5 + \text{Na}$] $^+$, calcd. 355.1521.

(E)- Diethyl 2-(4-(*p*-tolyl)but-2-en-1-yl)malonate 474



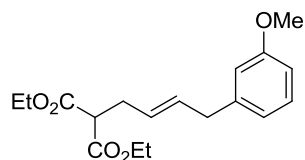
54.6 mg of **474** was prepared in 48% yield *via* the general procedure **11** from **328** (80.0 mg, 0.377 mmol, 1.0 eq), 4-methylphenylboronic acid (76.9 mg, 0.566 mmol, 1.5 eq) and palladium acetate (0.85 mg, 0.0038 mmol, 1 mol%); ^1H NMR (500 MHz, CDCl_3) δ 7.08 (d, J = 8.0 Hz, 2H, CH_{Ar}), 7.03 (d, J = 8.0 Hz, 2H, CH_{Ar}), 5.69-5.66 (m, 1H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 5.49-5.43 (m, 1H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 4.21-4.12 (m, 4H, OCH_2CH_3), 3.39 (t, J = 7.5 Hz, 1H, $\text{CH}(\text{CO}_2\text{Et})_2$), 3.28 (d, J = 7.5 Hz, 2H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 2.61 (t, J = 7.5 Hz, 2H, $\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{Ar}$), 2.31 (s, 3H, tolyl), 1.24 (t, J = 7.5 Hz, 6H, OCH_2CH_3). ^{13}C NMR (125 MHz, CDCl_3) δ 168.9, 137.2, 135.5, 132.6, 129.1, 128.4, 126.7, 61.4, 52.2, 38.5, 31.8, 21.0, 14.1. IR $\nu(\text{cm}^{-1})$: 1743, 1734, 1559, 1507, 1369, 1153, 1030, 970, 805. HRMS (ESI-TOF): m/z 327.1577 [$\text{C}_{18}\text{H}_{24}\text{O}_4 + \text{Na}$] $^+$, calcd. 327.1572.

(E)-Diethyl 2-(4-(4-(ethoxycarbonyl)phenyl)but-2-en-1-yl)malonate 469



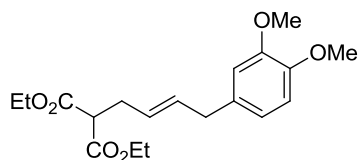
90.1 mg of **469** was prepared in 90% yield *via* the general procedure **11** from **328** (58.4 mg, 0.275 mmol, 1.0 eq), 4-ethoxycarbonylphenylboronic acid (80.1 mg, 0.413 mmol, 1.5 eq) and palladium acetate (0.62 mg, 0.0028 mmol, 1 mol%); ^1H NMR (500 MHz, CDCl_3) δ 7.95 (d, J = 8.5 Hz, 2H, CH_{Ar}), 7.21 (d, J = 8.5 Hz, 2H, CH_{Ar}), 5.71-5.65 (m, 1H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 5.53-5.48 (m, 1H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 4.36 (q, J = 7.5 Hz, 2H, (4- $\text{CO}_2\text{CH}_2\text{CH}_3$)Ph), 4.22-4.12 (m, 4H, OCH_2CH_3), 3.40 (t, J = 8.0 Hz, 1H, $\text{CH}(\text{CO}_2\text{Et})_2$), 3.37 (d, J = 6.5 Hz, 2H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 2.63 (t, J = 7.0 Hz, 2H, $\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{Ar}$), 1.39 (t, J = 7.5 Hz, 3H, (4- $\text{CO}_2\text{CH}_2\text{CH}_3$)Ph), 1.24 (t, J = 7.0 Hz, 6H, OCH_2CH_3). ^{13}C NMR (125 MHz, CDCl_3) δ 168.9, 166.6, 145.7, 131.4, 130.0, 129.7, 128.5, 127.8, 61.4, 60.8, 52.1, 38.9, 31.7, 14.4, 14.1. IR $\nu(\text{cm}^{-1})$: 1749, 1723, 1715, 1507, 1559, 1272, 1177, 1102, 1020, 857, 761, 703. HRMS (ESI-TOF): m/z 385.1622 [$\text{C}_{20}\text{H}_{26}\text{O}_6 + \text{Na}$] $^+$, calcd. 385.1627.

(E)-Diethyl 2-(4-(3-methoxyphenyl)but-2-en-1-yl)malonate 471



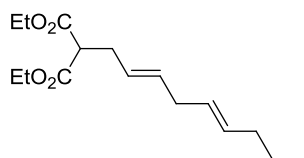
51.0 mg of **471** was prepared in 72% yield *via* the general procedure **11** from **328** (49.4 mg, 0.220 mmol, 1.0 eq), 3-methoxyphenylboronic acid (50.1 mg, 0.330 mmol, 1.5 eq) and palladium acetate (0.50 mg, 0.0022 mmol, 1 mol%); ^1H NMR (500 MHz, CDCl_3) δ 7.19 (t, J = 8.0 Hz, 1H, CH_{Ar}), 6.74-6.73 (m, 2H, CH_{Ar}), 6.69 (s, 1H, CH_{Ar}), 5.71-5.65 (m, 1H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 5.51-5.46 (m, 1H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 4.22-4.14 (m, 4H, OCH_2CH_3), 3.79 (s, 3H, OCH_3), 3.40 (t, J = 7.5 Hz, 1H, $\text{CH}(\text{CO}_2\text{Et})_2$), 3.29 (d, J = 6.5 Hz, 2H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 2.62 (t, J = 7.5 Hz, 2H, $\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{Ar}$), 1.24 (t, J = 7.0 Hz, 6H, OCH_2CH_3). ^{13}C NMR (125 MHz, CDCl_3) δ 169.0, 159.7, 141.9, 132.1, 129.3, 127.0, 120.8, 114.1, 111.3, 61.3, 55.1, 52.1, 38.9, 31.7, 14.0. IR $\nu(\text{cm}^{-1})$: 1734, 1730, 1260, 1151, 1034, 970, 858, 779. HRMS (ESI-TOF): m/z 343.1519 [$\text{C}_{18}\text{H}_{24}\text{O}_5 + \text{Na}$] $^+$, calcd. 343.1521.

(E)-Diethyl 2-(4-(3,4-dimethoxyphenyl)but-2-en-1-yl)malonate 473



18.5 mg of **473** was prepared in 23% yield *via* the general procedure **11** from **328** (48.1 mg, 0.227 mmol, 1.0 eq), 3,4-dimethoxyphenylboronic acid (62.3 mg, 0.341 mmol, 1.5 eq) and palladium acetate (0.510 mg, 0.00227 mmol, 1 mol%); ^1H NMR (500 MHz, CDCl_3) δ 6.81-6.78 (m, 1H, CH_{Ar}), 6.70-6.67 (m, 2H, CH_{Ar}), 5.70-5.63 (m, 1H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 5.51-5.45 (m, 1H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 4.21-4.14 (m, 4H, OCH_2CH_3), 3.87 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.40 (t, $J = 7.5$ Hz, 1H, $\text{CH}(\text{CO}_2\text{Et})_2$), 3.26 (d, $J = 6.5$ Hz, 2H, $\text{CH}=\text{CHCH}_2\text{Ar}$), 2.62 (t, $J = 7.0$ Hz, 2H, $\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{Ar}$), 1.24 (t, $J = 7.0$ Hz, 6H, OCH_2CH_3). ^{13}C NMR (125 MHz, CDCl_3) δ 169.0, 148.9, 147.4, 133.0, 132.6, 126.7, 120.3, 111.9, 111.3, 61.4, 56.0, 55.9, 52.2, 38.5, 31.7, 14.1. IR $\nu(\text{cm}^{-1})$: 1729, 1727, 1515, 1262, 1233, 1153, 1140, 1025. HRMS (ESI-TOF): m/z 373.1618 $[\text{C}_{19}\text{H}_{26}\text{O}_6 + \text{Na}]^+$, calcd. 373.1627.

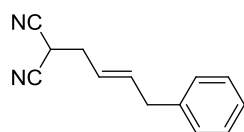
Diethyl 2-((2E,5E)-nona-2,5-dien-1-yl)malonate **475**



64.1 mg of **475** was prepared in 59% yield *via* the general procedure **11** from **328** (82.4 mg, 0.388 mmol, 1.0 eq), 1-pentenylphenylboronic acid (66.4 mg, 0.582 mmol, 1.5 eq) and palladium acetate (0.870 mg, 0.00388 mmol, 1 mol%); ^1H NMR (300 MHz, CDCl_3) δ 5.75-5.63 (m, 1H, *Branched*, $(\text{CO}_2\text{Et})_2\text{CHCH}_2\text{CH}=\text{CH}$ & $\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{CH}_3$), 5.58-5.45 (m, 1H, *Linear trans*, $(\text{CO}_2\text{Et})_2\text{CHCH}_2\text{CH}=\text{CH}$ & $\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{CH}_3$), 5.38-5.21 (m, 3H, *Linear trans*, $(\text{CO}_2\text{Et})_2\text{CHCH}_2\text{CH}=\text{CH}$ & $\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{CH}_3$), 5.05-4.99 (m, 2H, *Branched*, $(\text{CO}_2\text{Et})_2\text{CHCH}_2\text{CH}=\text{CH}$ & $\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{CH}_3$), 4.19 (q, $J = 6.9$ Hz, 4H, *Branched+Linear trans*, OCH_2CH_3), 3.38 (t, $J = 7.5$ Hz, 1H, *Branched+Linear trans*, $(\text{CO}_2\text{Et})_2\text{CH}$), 2.68-2.65 (m, 2H, *Branched+Linear trans*, $\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}$), 2.59 (t, $J = 6.9$ Hz, 2H, *Branched+Linear trans*, $(\text{CO}_2\text{Et})_2\text{CHCH}_2\text{CH}=\text{CH}$), 2.02-1.93 (m, 2H, *Branched+Linear trans*, $\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}_3$), 1.39 (m, 2H, *Branched+Linear trans*, $\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}_3$), 1.26 (t, $J = 7.2$ Hz, 6H, *Branched+Linear trans*, OCH_2CH_3), 0.88 (t, $J = 7.2$ Hz, 3H, *Branched+Linear trans*, $\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (125

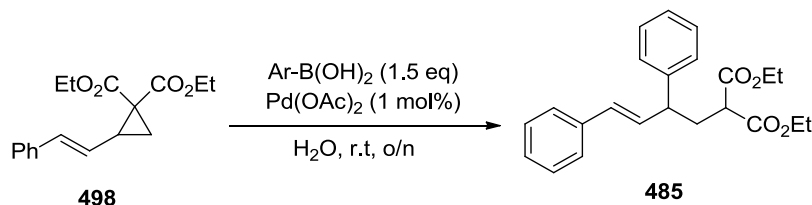
MHz, CDCl₃) δ 169.0, 132.3, 131.3, 128.0, 125.8, 61.3, 52.2, 35.5, 34.7, 31.8, 22.6, 14.1, 13.7. IR $\nu(\text{cm}^{-1})$: 1751, 1734, 1559, 1457, 1228, 1151, 1096, 1033, 968, 858. HRMS (ESI-TOF): m/z 305.1716 [C₁₆H₂₆O₄ + Na]⁺, calcd. 305.1729. **Note** Proton signals for branched isomer reported where clearly distinguished, this was not the case for the ¹³C NMR hence only the major linear *trans* product is reported.

(*E*)-2-(4-Phenylbut-2-en-1-yl)malononitrile **477**



210 mg of **477** was prepared in a yield of 54% *via* the general procedure **11** from **530** (237 mg, 2.01 mmol, 1.0 eq), phenylboronic acid (368 mg, 3.01 mmol, 1.5 eq) and palladium acetate (4.50 mg, 0.0201 mmol, 1 mol%); ¹H NMR (500 MHz, CDCl₃) δ 7.30 (t, J = 7.0 Hz, 2H, *cis*+*trans*, CHAr), 7.24-7.16 (m, 3H, *cis*+*trans*, CHAr), 6.00-5.94 (m, 1H, *cis*+*trans*, CH=CHCH₂Ph), 5.58-5.49 (m, 1H, *cis*+*trans*, CH=CHCH₂Ph), 3.69 (t, J = 6.0 Hz, 1H, *cis*+*trans*, (CN)₂CH), 3.48 (d, J = 7.0 Hz, 2H, *cis*, CH=CHCH₂Ph), 3.38 (d, J = 6.5 Hz, 2H, *trans*, CH=CHCH₂Ph), 2.86 (t, J = 7.5 Hz, 2H, *cis*, CH₂CH=CHCH₂Ph), 2.70 (t, J = 7.0 Hz, 2H, *trans*, CH₂CH=CHCH₂Ph). ¹³C NMR (125 MHz, CDCl₃) δ 139.1, 137.7, 136.0 (*cis*), 128.8 (*cis*), 128.7, 128.6, 128.4 (*cis*), 126.6 (*cis*), 126.5, 122.1, 121.1 (*cis*), 112.3, 38.8, 33.8, 33.7 (*cis*), 28.7 (*cis*), 23.4, 22.9 (*cis*). IR $\nu(\text{cm}^{-1})$: 2258, 1768, 1653, 1559, 1266, 1174, 1037, 971, 735, 699. HRMS (ESI-TOF): m/z 195.0914 [C₁₃H₁₂N₂ - H]⁺, calcd. 195.0922. **N.B.** only visible *cis* signals highlighted in ¹³C NMR.

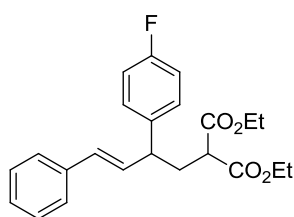
(*E*)-Diethyl 2-(2,4-diphenylbut-3-en-1-yl)malonate **485**



64.8 mg of **485** was prepared in 82% yield *via* the general procedure **11** from **498** (64.3 mg, 0.223 mmol, 1.0 eq), phenylboronic acid (40.8 mg, 0.335 mmol, 1.5 eq) and palladium(II) acetate (0.500 mg, 0.002 mmol, 1 mol%). ¹H NMR (CDCl₃, 300 MHz, CH_{Ar}) δ 7.36-7.20 (m, 10H, CH_{Ar}), 6.44 (d, J

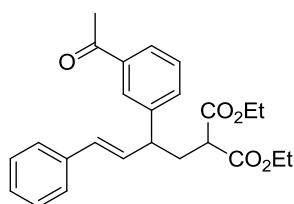
= 15.9 Hz, 1H, PhCH=CHCH(Ph)CH₂), 6.29 (dd, J = 15.9, 8.1 Hz, 1H, PhCH=CHCH(Ph)CH₂), 4.17 (q, J = 7.2 Hz, 4H, OCH₂CH₃), 3.48 (app q, J = 8.1 Hz, 1H, PhCH=CHCH(Ph)CH₂), 3.36 (t, J = 7.5 Hz, 1H, (CO₂Et)₂CH), 2.46-2.37 (m, 2H, PhCH=CHCH(Ph)CH₂), 1.25 (app q, J = 6.9 Hz, 6H, OCH₂CH₃). ¹³C NMR (CDCl₃, 75 MHz) δ 169.5, 169.4, 142.8, 137.1, 132.2, 130.6, 128.7, 128.5, 127.6, 127.4, 126.8, 126.2, 61.4, 50.2, 47.0, 34.6, 14.1, 14.0. IR ν (cm⁻¹): 1744, 1734, 1369, 1150, 1028, 966, 859, 746, 693. HRMS (ESI-TOF): m/z 389.1745 [C₂₃H₂₆O₄ + Na]⁺, calcd. 389.1729.

(*E*)-Diethyl 2-(2-(4-fluorophenyl)-4-phenylbut-3-en-1-yl)malonate **486**



69.7 mg of **486** was prepared in 82% yield *via* the general procedure **11** from **498** (64.2 mg, 0.223 mmol, 1.0 eq), 4-fluorophenylboronic acid (46.8 mg, 0.334 mmol, 1.5 eq) and palladium acetate (0.50 mg, 0.00223 mmol, 1 mol%). ¹H NMR (CDCl₃, 500 MHz) δ 7.33 (d, J = 7.5 Hz, 2H, CH_{Ar}), 7.30-7.27 (m, 3H, CH_{Ar}), 7.26-7.20 (m, 2H, CH_{Ar}), 7.01 (t, J = 8.5 Hz, 2H, CH_{Ar}), 6.41 (d, J = 16.0 Hz, 1H, PhCH=CHCH(Ar)CH₂), 6.24 (dd, J = 15.5, 7.5 Hz, 1H, PhCH=CHCH(Ar)CH₂), 4.19-4.11 (m, 4H, OCH₂CH₃), 3.47 (app q, J = 7.5 Hz, 1H, (Ar)CHCH₂CH(CO₂Et)₂), 3.33 (t, J = 7.0 Hz, 1H, CH(CO₂Et)₂), 2.43-2.34 (m, 2H, (Ar)CHCH₂CH(CO₂Et)₂), 1.25-1.21 (m, 6H, OCH₂CH₃). ¹³C NMR (CDCl₃, 125 MHz) δ 169.4, 169.3, 161.7 (d, J = 244 Hz), 138.6, 137.0, 132.0, 130.8, 129.1 (d, J = 8 Hz), 128.6, 127.5, 126.3, 115.5 (d, J = 30 Hz), 61.5, 50.2, 46.3, 34.7, 14.1, 14.1. IR ν (cm⁻¹): 1750, 1729, 1507, 1221, 1158, 1027, 967, 832, 744, 693. HRMS (ESI-TOF): m/z 407.1642 [C₂₃H₂₅FO₄ + Na]⁺, calcd. 407.1635.

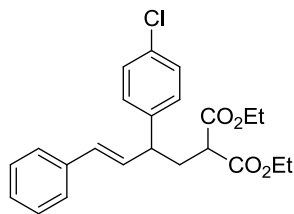
(*E*)-Diethyl 2-(2-(3-acetylphenyl)-4-phenylbut-3-en-1-yl)malonate **487**



46.1 mg of **487** was prepared in 60% yield *via* the general procedure **11** from **498** (54.9 mg, 0.191 mmol, 1.0 eq), 3-acetylphenylboronic acid (46.9 mg, 0.286 mmol, 1.5 eq) and palladium acetate

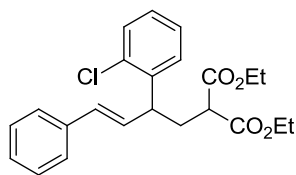
(0.430 mg, 0.00191 mmol, 1 mol%). ^1H NMR (CDCl_3 , 500 MHz) δ 7.85 (s, 1H, CH_{Ar}), 7.81 (d, $J = 7.5$ Hz, 1H, CH_{Ar}), 7.47 (d, $J = 7.5$ Hz, 1H, CH_{Ar}), 7.42 (t, $J = 8.0$ Hz, 1H, CH_{Ar}), 7.33 (d, $J = 7.5$ Hz, 2H, CH_{Ar}), 7.28 (t, $J = 7.5$ Hz, 2H, CH_{Ar}), 7.22-7.19 (m, 1H, CH_{Ar}), 6.45 (d, $J = 16.0$ Hz, 1H, $\text{PhCH=CHCH}(\text{Ar})\text{CH}_2$), 6.26 (dd, $J = 16.0, 8.5$ Hz, 1H, $\text{PhCH=CHCH}(\text{Ar})\text{CH}_2$), 4.19-4.12 (m, 4H, OCH_2CH_3), 3.56 (app q, $J = 8.0$ Hz, 1H, $(\text{Ar})\text{CHCH}_2\text{CH}(\text{CO}_2\text{Et})_2$), 3.34 (t, $J = 7.0$ Hz, 1H, $\text{CH}(\text{CO}_2\text{Et})_2$), 2.60 (s, 3H, O=CCH_3), 2.47-2.39 (m, 2H, $\text{PhCH=CHCH}(\text{Ar})\text{CH}_2$), 1.26-1.21 (m, 6H, OCH_2CH_3). ^{13}C NMR (CDCl_3 , 125 MHz) δ 198.3, 169.5, 169.4, 143.9, 137.8, 137.0, 132.3, 131.7, 131.5, 129.2, 128.8, 127.8, 127.5, 127.2, 126.5, 61.8, 61.7, 50.4, 47.3, 34.7, 27.0, 14.3, 14.2. IR $\nu(\text{cm}^{-1})$: 1749, 1734, 1727, 1684, 1559, 1507, 1369, 1267, 1151, 1027, 967, 693. HRMS (ESI-MS): m/z 431.1834 [$\text{C}_{25}\text{H}_{28}\text{O}_5 + \text{Na}$] $^+$, calcd. 431.1834.

(*E*)-Diethyl 2-(2-(4-chlorophenyl)-4-phenylbut-3-en-1-yl)malonate 488



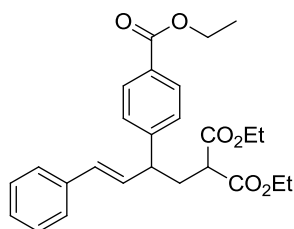
65.2 mg of **488** was prepared in 61 % yield *via* the general procedure **11** from **498** (63.9 mg, 0.222 mmol, 1.0 eq), 4-chlorophenylboronic acid (52.1 mg, 0.333 mmol, 1.5 eq) and palladium acetate (0.500 mg, 0.00222 mmol, 1 mol%). ^1H NMR (CDCl_3 , 300 MHz) δ 7.36-7.29 (m, 5H, CH_{Ar}), 7.23-7.18 (m, 4H, CH_{Ar}), 6.42 (d, $J = 15.9$ Hz, 1H, $\text{PhCH=CHCH}(\text{Ar})\text{CH}_2$), 6.23 (dd, $J = 15.6, 7.8$ Hz, 1H, $\text{PhCH=CHCH}(\text{Ar})\text{CH}_2$), 4.21-4.10 (m, 4H, OCH_2CH_3), 3.47 (app q, $J = 7.8$ Hz, 1H, $(\text{Ar})\text{CHCH}_2\text{CH}(\text{CO}_2\text{Et})_2$), 3.33 (t, $J = 7.2$ Hz, 1H, $\text{CH}(\text{CO}_2\text{Et})_2$), 2.45-2.33 (m, 2H, $\text{PhCH=CHCH}(\text{Ar})\text{CH}_2$), 1.24 (app q, $J = 7.5$ Hz, 6H, OCH_2CH_3). ^{13}C NMR (CDCl_3 , 125 MHz) δ 169.3, 169.2, 141.4, 136.9, 132.5, 131.6, 131.0, 129.0, 128.9, 128.6, 127.5, 126.3, 61.5, 50.2, 46.4, 34.5, 14.1, 14.0. IR $\nu(\text{cm}^{-1})$: 1750, 1729, 1490, 1369, 695. HRMS (ESI-TOF): m/z 423.1347 [$\text{C}_{23}\text{H}_{25}\text{ClO}_4 + \text{Na}$] $^+$, calcd. 423.1339.

(E)-Diethyl 2-(2-(2-chlorophenyl)-4-phenylbut-3-en-1-yl)malonate 489



25.3 mg of **489** was prepared in 38% yield *via* the general procedure **11** from **498** (47.8 mg, 0.166 mmol, 1.0 eq), 2-chlorophenylboronic acid (38.9 mg, 0.249 mmol, 1.5 eq) and palladium acetate (0.370 mg, 0.00166 mmol, 1 mol%). ^1H NMR (CDCl_3 , 500 MHz) δ 7.37-7.33 (m, 3H, CH_{Ar}), 7.29-7.26 (m, 4H, CH_{Ar}), 7.22-7.15 (m, 2H, CH_{Ar}), 6.47 (d, $J = 15.5$ Hz, 1H, $\text{PhCH}=\text{CHCH}(\text{Ar})\text{CH}_2$), 6.23 (dd, $J = 15.5$, 8.0 Hz, 1H, $\text{PhCH}=\text{CHCH}(\text{Ar})\text{CH}_2$), 4.17 (app q, $J = 7.0$ Hz, 4H, OCH_2CH_3), 4.11-4.06 (m, 1H, $\text{PhCH}=\text{CHCH}(\text{Ar})\text{CH}_2$), 3.37 (t, $J = 7.0$ Hz, 1H, $\text{CH}(\text{CO}_2\text{Et})_2$), 2.49-2.38 (m, 2H, $\text{PhCH}=\text{CHCH}(\text{Ar})\text{CH}_2$), 1.26 (t, $J = 7.0$ Hz, 3H, OCH_2CH_3), 1.22 (t, $J = 7.5$ Hz, 3H, OCH_2CH_3). ^{13}C NMR (CDCl_3 , 125 MHz) δ 169.3, 169.3, 140.2, 137.0, 134.0, 131.5, 130.6, 130.0, 128.5, 128.2, 127.8, 127.5, 127.3, 126.3, 61.5, 50.2, 42.7, 33.8, 14.1, 14.0. IR $\nu(\text{cm}^{-1})$: 1750, 1734, 1369, 1153, 1034, 966, 749, 697. HRMS (ESI-TOF): m/z 423.1357 [$\text{C}_{23}\text{H}_{25}\text{ClO}_4 + \text{Na}$] $^+$, calcd. 423.1339.

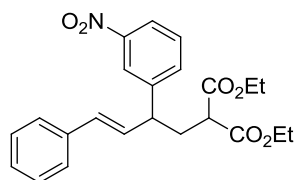
(E)-Diethyl 2-(2-(4-(ethoxycarbonyl)phenyl)-4-phenylbut-3-en-1-yl)malonate 490



84.2 mg of **490** was prepared in 62% yield *via* the general procedure **11** from **498** (89.3 mg, 0.310 mmol, 1.0 eq), 4-ethoxycarbonylphenylboronic acid (90.2 mg, 0.465 mmol, 1.5 eq) and palladium acetate (0.790 mg, 0.00310 mmol, 1 mol%). ^1H NMR (CDCl_3 , 500 MHz) δ 8.00 (d, $J = 8.5$ Hz, 2H, CH_{Ar}), 7.33 (d, $J = 8.0$ Hz, 4H, CH_{Ar}), 7.29-7.25 (m, 2H, CH_{Ar}), 7.22-7.19 (m, 1H, CH_{Ar}), 6.43 (d, $J = 15.5$ Hz, 1H, $\text{PhCH}=\text{CHCH}(\text{Ar})\text{CH}_2$), 6.25 (dd, $J = 15.5$, 8.5 Hz, 1H, $\text{PhCH}=\text{CHCH}(\text{Ar})\text{CH}_2$), 4.36 (q, $J = 7.5$ Hz, 2H, CH_{Ar} OCH_2CH_3), 4.19-4.10 (m, 4H, OCH_2CH_3), 3.55 (app q, $J = 7.5$ Hz, 1H, $\text{PhCH}=\text{CHCH}(\text{Ar})\text{CH}_2$), 3.31 (t, $J = 7.5$ Hz, 1H, $\text{CH}(\text{CO}_2\text{Et})_2$), 2.46-2.38 (m, 2H, $\text{PhCH}=\text{CHCH}(\text{Ar})\text{CH}_2$), 1.38 (t, $J = 7.5$ Hz, 3H), CH_{Ar} OCH_2CH_3 , 1.26-1.20 (m, 6H, OCH_2CH_3). ^{13}C NMR (CDCl_3 , 125 MHz) δ 169.5, 169.4, 166.6, 148.3, 137.0, 131.5, 131.5, 130.2, 129.3, 128.8, 127.8, 127.8, 126.5, 61.7, 61.1, 50.3, 47.3, 34.6, 14.6, 14.3, 14.2. IR $\nu(\text{cm}^{-1})$: 1750, 1729, 1718, 1273,

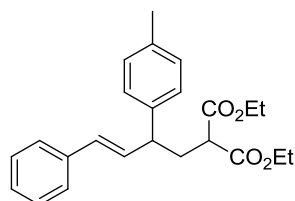
1104, 1020, 968, 855, 694. HRMS (ESI-MS): m/z 461.1942 [$C_{26}H_{30}O_6 + Na$] $^+$, calcd. 461.1940.

(E)-Diethyl 2-(2-(3-nitrophenyl)-4-phenylbut-3-en-1-yl)malonate 491



30.1 mg of **491** was prepared in 23% yield *via* the general procedure **11** from **498** (94.0 mg, 0.326 mmol, 1.0 eq), 3-nitrophenylboronic acid (81.7 mg, 0.488 mmol, 1.5 eq) and palladium acetate (0.730 mg, 0.00326 mmol, 1 mol%). 1H NMR ($CDCl_3$, 500 MHz) δ 8.14 (s, 1H, CH_{Ar}), 8.10 (d, J = 8.5 Hz, 1H, CH_{Ar}), 7.61 (d, J = 8.0 Hz, 1H, CH_{Ar}), 7.51 (t, J = 8.0 Hz, 1H, CH_{Ar}), 7.35 (d, J = 7.5 Hz, 2H, CH_{Ar}), 7.30 (t, J = 7.5 Hz, 2H, CH_{Ar}), 7.26-7.22 (m, 1H, CH_{Ar}), 6.48 (d, J = 16.0 Hz, 1H, $PhCH=CHCH(Ar)CH_2$), 6.23 (dd, J = 15.5, 8.5 Hz, 1H, $PhCH=CHCH(Ar)CH_2$), 4.21-4.11 (m, 4H, OCH_2CH_3), 3.62 (app q J = 8.0 Hz, 1H, $PhCH=CHCH(Ar)CH_2$), 3.35 (t, J = 7.5 Hz, 1H, $CH(CO_2Et)_2$), 2.47-2.42 (m, 2H, $PhCH=CHCH(Ar)CH_2$), 1.28-1.22 (m, 6H, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.1, 169.0, 148.5, 145.2, 136.4, 133.8, 132.0, 130.3, 129.7, 128.6, 127.8, 126.3, 122.5, 122.0, 61.7, 61.6, 50.0, 46.8, 34.3, 14.0, 14.0. IR $\nu(cm^{-1})$: 1744, 1734, 1719, 1528, 1349, 1152, 1027, 968, 736, 694, 690. HRMS (ESI): m/z 434.1601 [$C_{23}H_{25}NO_6 + Na$] $^+$, calcd. 434.1580.

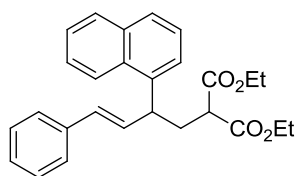
(E)-Diethyl 2-(4-phenyl-2-(p-tolyl)but-3-en-1-yl)malonate 492



61.1 mg of **492** was prepared in 84% yield *via* the general procedure **11** from **498** (55.3 mg, 0.192 mmol, 1.0 eq), 4-methylphenylboronic acid (39.2 mg, 0.288 mmol, 1.5 eq) and palladium acetate (0.440 mg, 0.00192 mmol, 1 mol%). 1H NMR ($CDCl_3$, 500 MHz) δ 7.31 (d, J = 8.5 Hz, 2H, CH_{Ar}), 7.25 (t, J = 7.5 Hz, 2H, CH_{Ar}), 7.19 (t, J = 8.0 Hz, 1H, CH_{Ar}), 7.12 (s, 4H, CH_{Ar}), 6.42 (d, J = 16.0 Hz, 1H, $PhCH=CHCH(Ar)CH_2$), 6.27 (dd, J = 16.0, 8.5 Hz, 1H, $PhCH=CHCH(Ar)CH_2$), 4.22-4.10 (m, 4H, OCH_2CH_3), 3.44 (app q, J = 8.0 Hz, 1H, $PhCH=CHCH(Ar)CH_2$), 3.34 (t, J = 8.0 Hz, 1H, $CH(CO_2Et)_2$), 2.45-2.34 (m, 2H, $PhCH=CHCH(Ar)CH_2$), 2.32 (s, 3H, tolyl), 1.28-1.20 (m, 6H, OCH_2CH_3).

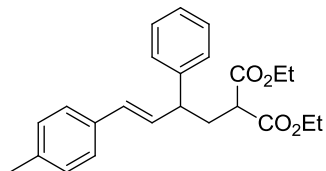
OCH₂CH₃). ¹³C NMR (CDCl₃, 125 MHz) δ 169.5, 169.4, 139.8, 137.2, 136.3, 132.6, 130.4, 129.4, 128.5, 127.5, 127.3, 126.3, 61.4, 50.3, 46.6, 34.7, 21.1, 14.1. IR ν(cm⁻¹): 1749, 1734, 1265, 1152, 1028, 967, 734, 703. HRMS (ESI-TOF): *m/z* 403.1871 [C₂₄H₂₈O₄ + Na]⁺, calcd. 403.1885.

(*E*)-Diethyl 2-(2-(naphthalen-1-yl)-4-phenylbut-3-en-1-yl)malonate 493



94.4mg of **493** was prepared in 72% yield *via* the general procedure **11** from **498** (97.8 mg, 0.340 mmol, 1.0 eq), 1-naphthalenophenylboronic acid (87.6 mg, 0.509 mmol, 1.5 eq) and palladium acetate (0.760 mg, 0.00340 mmol, 1 mol%). ¹H NMR (CDCl₃, 300 MHz) δ 8.20 (d, *J* = 8.4 Hz, 1H, CH_{Ar}), 7.86 (d, *J* = 7.8 Hz, 1H, CH_{Ar}), 7.74 (d, *J* = 7.2 Hz, 1H, CH_{Ar}), 7.55-7.14 (m, 9H, CH_{Ar}), 6.53 (d, *J* = 15.9 Hz, 1H, PhCH=CHCH(Ar)CH₂), 6.46 (dd, *J* = 15.9, 7.2 Hz, 1H, PhCH=CHCH(Ar)CH₂), 4.36 (app q, *J* = 6.9 Hz, 1H, PhCH=CHCH(Ar)CH₂), 4.20 (q, *J* = 6.9 Hz, 2H, OCH₂CH₃), 4.17-4.07 (m, 2H, OCH₂CH₃), 3.49 (t, *J* = 7.2 Hz, 1H, CH(CO₂Et)₂), 2.61-2.54 (m, 2H, PhCH=CHCH(Ar)CH₂), 1.26 (t, *J* = 7.2 Hz, 3H, OCH₂CH₃), 1.16 (t, *J* = 6.9 Hz, 3H, OCH₂CH₃). ¹³C NMR (CDCl₃, 75 MHz) δ 169.5, 169.5, 139.1, 137.0, 134.1, 131.8, 131.5, 131.3, 129.0, 128.5, 128.4, 127.4, 127.4, 126.3, 126.1, 125.6, 124.1, 123.2, 61.5, 50.3, 41.6, 34.5, 14.1, 14.0. IR ν(cm⁻¹): 1749, 1729, 1369, 1151, 1027, 969, 778, 697. HRMS (ESI-TOF): *m/z* 439.1882 [C₂₇H₂₈O₄ + Na]⁺, calcd. 439.1885.

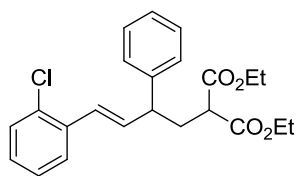
(*E*)-Diethyl 2-(2-phenyl-4-(p-tolyl)but-3-en-1-yl)malonate 494



128.7 mg of **494** was prepared in 77% yield *via* the general procedure **11** from **481** (134.1 mg, 0.4440 mmol, 1.0 eq), phenylboronic acid (81.2 mg, 0.666 mmol, 1.5 eq) and palladium acetate (0.994 mg, 0.000444 mmol, 1 mol%). ¹H NMR (CDCl₃, 500 MHz) δ 7.31 (t, *J* = 7.0 Hz, 2H, CH_{Ar}), 7.27-7.14 (m, 5H, CH_{Ar}), 7.08 (d, *J* = 8.0 Hz, 2H, CH_{Ar}), 6.40 (d, *J* = 16.0 Hz, 1H, PhCH=CHCH(Ar)CH₂), 6.22 (dd, *J* = 15.5, 8.5 Hz, 1H, PhCH=CHCH(Ar)CH₂), 4.18-4.11 (m, 4H, OCH₂CH₃), 3.46 (app q, *J*

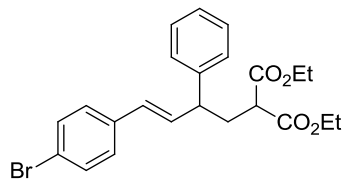
= 8.5 Hz, 1H, PhCH=CHCH(Ar)CH₂), 3.35 (t, *J* = 7.5 Hz, 1H, CH(CO₂Et)₂), 2.44-2.35 (m, 2H, PhCH=CHCH(Ar)CH₂), 2.31 (s, 3H, tolyl), 1.23 (app q, *J* = 9.0 Hz, 6H, OCH₂CH₃). ¹³C NMR (CDCl₃, 125 MHz) δ 169.5, 169.4, 143.1, 137.1, 134.3, 131.2, 130.5, 129.2, 128.7, 127.6, 126.7, 126.1, 61.4, 50.3, 47.0, 34.7, 21.1, 14.1, 14.0. IR ν(cm⁻¹): 1749, 1730, 1653, 1507, 1457, 1369, 1150, 1097, 1030, 969, 853, 807, 761, 700. HRMS (ESI-TOF): *m/z* 403.1903 [C₂₄H₂₈O₄ + Na]⁺, calcd. 403.1885.

(*E*)-Diethyl 2-(4-(2-chlorophenyl)-2-phenylbut-3-en-1-yl)malonate 495



177.1 mg of **495** was prepared in 80% yield *via* the general procedure **11** from **482** (218.1 mg, 0.6760 mmol, 1.0 eq), phenylboronic acid (123.6 mg, 1.014 mmol, 1.5 eq) and palladium acetate (1.501 mg, 0.006760 mmol, 1 mol%). ¹H NMR (CDCl₃, 500 MHz) δ 7.48 (d, *J* = 5.5 Hz, 1H, CH_{Ar}), 7.35-7.32 (m, 2H, CH_{Ar}), 7.27-7.22 (m, 3H, CH_{Ar}), 7.19-7.13 (m, 3H, CH_{Ar}), 6.83 (d, *J* = 16.0 Hz, 1H, PhCH=CHCH(Ar)CH₂), 6.26 (dd, *J* = 15.5, 8.5 Hz, 1H, PhCH=CHCH(Ar)CH₂), 4.20-4.12 (m, 4H, OCH₂CH₃), 3.54 (app q, *J* = 8.5 Hz, 1H, PhCH=CHCH(Ar)CH₂), 3.37 (t, *J* = 8.0 Hz, 1H, CH(CO₂Et)₂), 2.47-2.40 (m, 2H, PhCH=CHCH(Ar)CH₂), 1.23 (app q, *J* = 6.5 Hz, 6H, OCH₂CH₃). ¹³C NMR (CDCl₃, 125 MHz) δ 169.4, 169.3, 142.6, 135.2, 135.1, 132.9, 129.6, 128.8, 128.4, 127.6, 126.9, 126.9, 126.8, 126.8, 61.5, 50.2, 47.3, 34.5, 14.1, 14.1. IR ν(cm⁻¹): 1748, 1727, 1472, 1437, 1369, 1264, 1150, 1031, 966, 856, 750, 699. HRMS (ESI-MS): *m/z* 423.1348 [C₂₃H₂₅ClO₄ + Na]⁺, calcd. 423.1339.

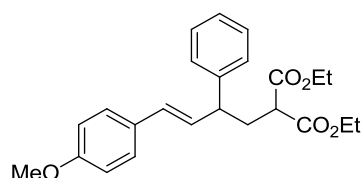
(*E*)-Diethyl 2-(4-(4-bromophenyl)-2-phenylbut-3-en-1-yl)malonate 496



13.5 mg of **496** was prepared in 43% yield *via* the general procedure **11** from **484** (25.6 mg, 0.0715 mmol, 1.0 eq), phenylboronic acid (13.1 mg, 0.107 mmol, 1.5 eq) and palladium acetate (0.160 mg,

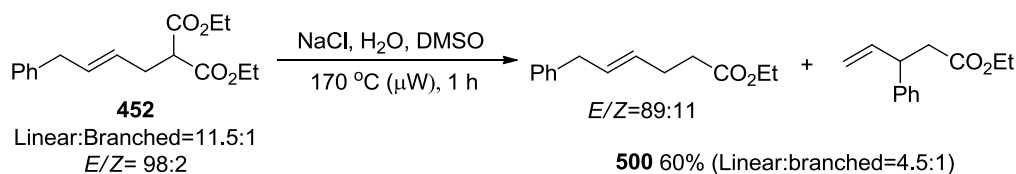
0.0000715 mmol, 1 mol%). ^1H NMR (CDCl_3 , 500 MHz) δ 7.40 (d, J = 8.5 Hz, 2H, CH_{Ar}), 7.33 (t, J = 8.0 Hz, 2H, CH_{Ar}), 7.26-7.22 (m, 3H, CH_{Ar}), 7.19 (d, J = 8.5 Hz, 2H, CH_{Ar}), 6.36 (d, J = 16.0 Hz, 1H, $\text{PhCH}=\text{CHCH}(\text{Ar})\text{CH}_2$), 6.27 (dd, J = 16.0, 7.5 Hz, 1H, $\text{PhCH}=\text{CHCH}(\text{Ar})\text{CH}_2$), 4.19-4.11 (m, 4H, OCH_2CH_3), 3.47 (app q, J = 8.0 Hz, 1H, $\text{PhCH}=\text{CHCH}(\text{Ar})\text{CH}_2$), 3.31 (t, J = 7.0 Hz, 1H, $\text{CH}(\text{CO}_2\text{Et})_2$), 2.45-2.36 (m, 2H, $\text{PhCH}=\text{CHCH}(\text{Ar})\text{CH}_2$), 1.22 (app q, J = 6.5 Hz, 6H, OCH_2CH_3). ^{13}C NMR (CDCl_3 , 125 MHz) δ 169.4, 169.3, 142.5, 136.0, 133.2, 131.6, 129.4, 128.8, 127.8, 127.6, 126.9, 121.1, 61.5, 50.2, 47.1, 34.5, 14.1. IR $\nu(\text{cm}^{-1})$: 1734, 1694, 1646, 1551, 1515, 1462, 1370, 1223, 1154, 1034, 972, 858, 804, 695. HRMS (ESI-MS): m/z 467.0856 [$\text{C}_{23}\text{H}_{25}\text{BrO}_4 + \text{Na}$] $^+$, calcd. 467.0834.

(*E*)-Diethyl 2-(4-(4-methoxyphenyl)-2-phenylbut-3-en-1-yl)malonate **497**



78.8 mg of **497** was prepared in 64% yield *via* the general procedure **11** from **483** (99.6 mg, 0.313 mmol, 1.0 eq), phenylboronic acid (57.2 mg, 0.470 mmol, 1.5 eq) and palladium acetate (0.700 mg, 0.000313 mmol, 1 mol%). ^1H NMR (CDCl_3 , 500 MHz) δ 7.31 (t, J = 8.0 Hz, 2H, CH_{Ar}), 7.26 (t, J = 8.0 Hz, 4H, CH_{Ar}), 7.21 (t, J = 7.5 Hz, 1H, CH_{Ar}), 6.82 (d, J = 8.0 Hz, 2H, CH_{Ar}), 6.37 (d, J = 16.0 Hz, 1H, $\text{PhCH}=\text{CHCH}(\text{Ar})\text{CH}_2$), 6.13 (dd, J = 16.0, 8.0 Hz, 1H, $\text{PhCH}=\text{CHCH}(\text{Ar})\text{CH}_2$), 4.18-4.10 (m, 4H, OCH_2CH_3), 3.77 (s, 3H, OCH_3), 3.45 (app q, J = 8.0 Hz, 1H, $\text{PhCH}=\text{CHCH}(\text{Ar})\text{CH}_2$), 3.35 (t, J = 7.5 Hz, 1H, $\text{CH}(\text{CO}_2\text{Et})_2$), 2.42-2.37 (m, 2H, $\text{PhCH}=\text{CHCH}(\text{Ar})\text{CH}_2$), 1.28-1.21 (m, 6H, OCH_2CH_3). ^{13}C NMR (CDCl_3 , 125 MHz) δ 169.5, 169.4, 159.0, 143.1, 130.1, 130.0, 129.9, 128.7, 127.6, 127.4, 126.7, 113.9, 61.4, 55.3, 50.3, 47.1, 34.7, 14.1. IR $\nu(\text{cm}^{-1})$: 1748, 1727, 1608, 1511, 1457, 1369, 1248, 1150, 1030, 967, 760, 700. HRMS (ESI-MS): m/z 419.1832 [$\text{C}_{24}\text{H}_{28}\text{O}_5 + \text{Na}$] $^+$, calcd. 419.1834.

General Procedure 12 for Decarboxylation of Targeted product **500**¹²



A solution of **452** (108.6 mg, 0.374 mmol, 1.0 eq) and NaCl (30.0 mg, 0.512 mmol, 1.37 eq) in DMSO (0.62 mL) and distilled water (25.4 μL) was heated at 170°C for 1 hr in a microwave. Distilled water (20 mL) was added and the mixture was extracted with ethyl acetate (3 x 20 mL). The combined organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified with column chromatography (15% ethyl acetate in hexane) to afford **500** (49 mg, 60%) as a brown oily liquid. ^1H NMR (CDCl_3 , 500 MHz) δ 7.30-7.26 (m, 2H, CH_{Ar}), 7.20-7.16 (m, 3H, CH_{Ar}), 5.66-5.57 (m, 1H, $\text{PhCH}_2\text{CH}=\text{CH}$), 5.55-5.46 (m, 1H, $\text{PhCH}_2\text{CH}=\text{CH}$), 4.12 (t, $J = 6.5$ Hz, 2H, OCH_2CH_3), 3.33 (d, $J = 6.5$ Hz, 2H, $\text{PhCH}_2\text{CH}=\text{CH}$), 2.40-2.36 (m, 4H, $\text{PhCH}_2\text{CH}=\text{CHCH}_2\text{CH}_2$), 1.25 (q, $J = 6.5$ Hz, 3H, OCH_2CH_3). ^{13}C NMR (CDCl_3 , 125 MHz) δ 173.2, 140.7, 130.2, 129.7, 128.5, 128.4, 126.0, 60.3, 49.2, 39.0, 34.3, 27.8, 14.3. IR $\nu(\text{cm}^{-1})$: 1734, 1495, 1452, 1373, 1248, 1178, 1156, 1030, 968, 745, 698. HRMS (ESI-TOF): m/z 241.1208 [$\text{C}_{14}\text{H}_{18}\text{O}_2 + \text{Na}$] $^+$, calcd. 241.1204.

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Appendix

HPLC Chromatograms for *ee* Determination

Figure 1. HPLC chromatogram for racemic 126 (AD column: 90:10 Hexane-Isopropanol; 0.5 ml·min⁻¹)

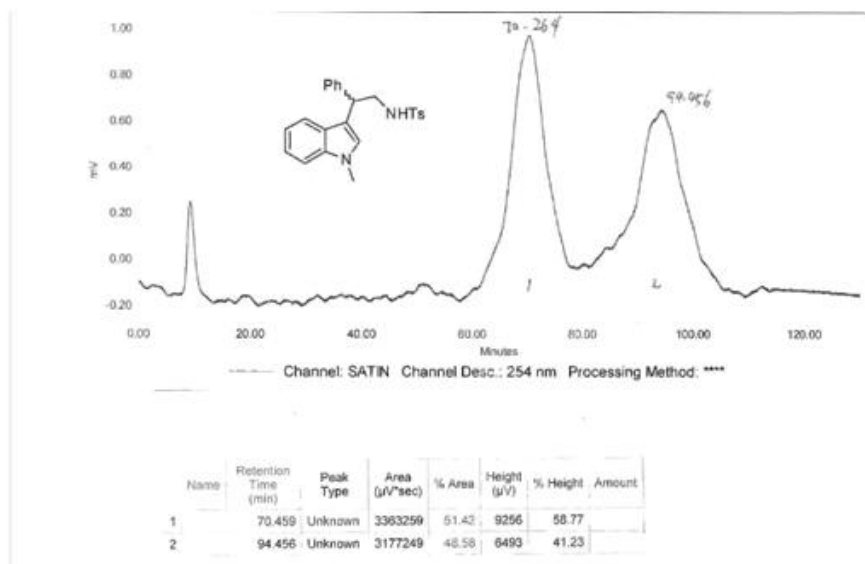


Figure 2. HPLC chromatogram for enantiopure (*R*)-126' (AD column: 90:10 Hexane-Isopropanol; 0.5 ml·min⁻¹)

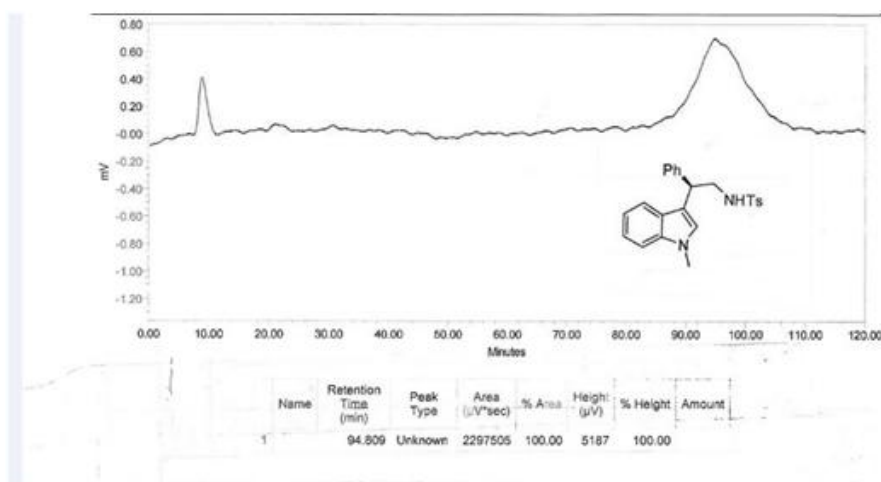
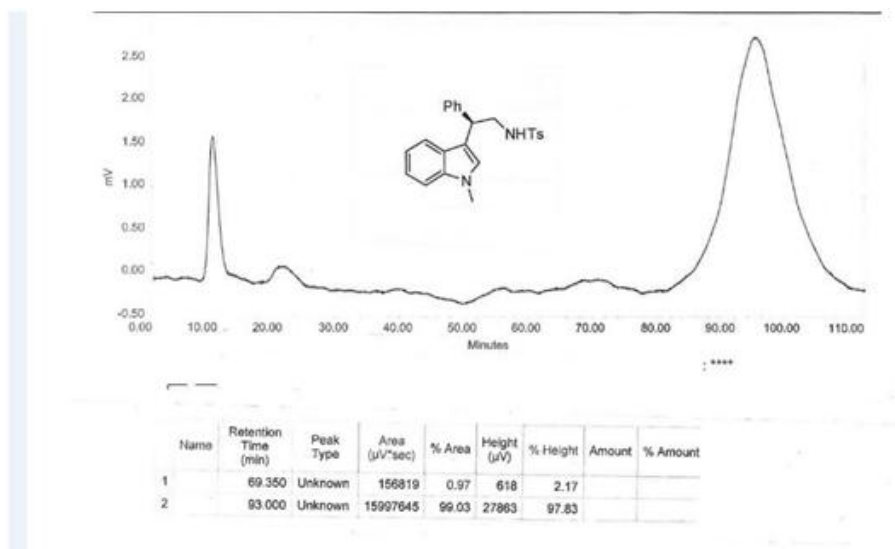


Figure 3. HPLC chromatogram for enantiopure (*R*)-126' synthesised in the presence of BQ (AD column: 90:10 Hexane-Isopropanol; 0.5 ml·min⁻¹)



jxy150812_2_vjx_phenylaziridine_1_Proton

File: Proton

Pulse Sequence: szpu1

Solvent: cdcl3

Temp: 2.0 C / 275.1 K

Operator: uowvmr2

VNMR5-500 "pyne06.domain.com"

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 2.045 sec

Width 8012.8 Hz

16 repetitions

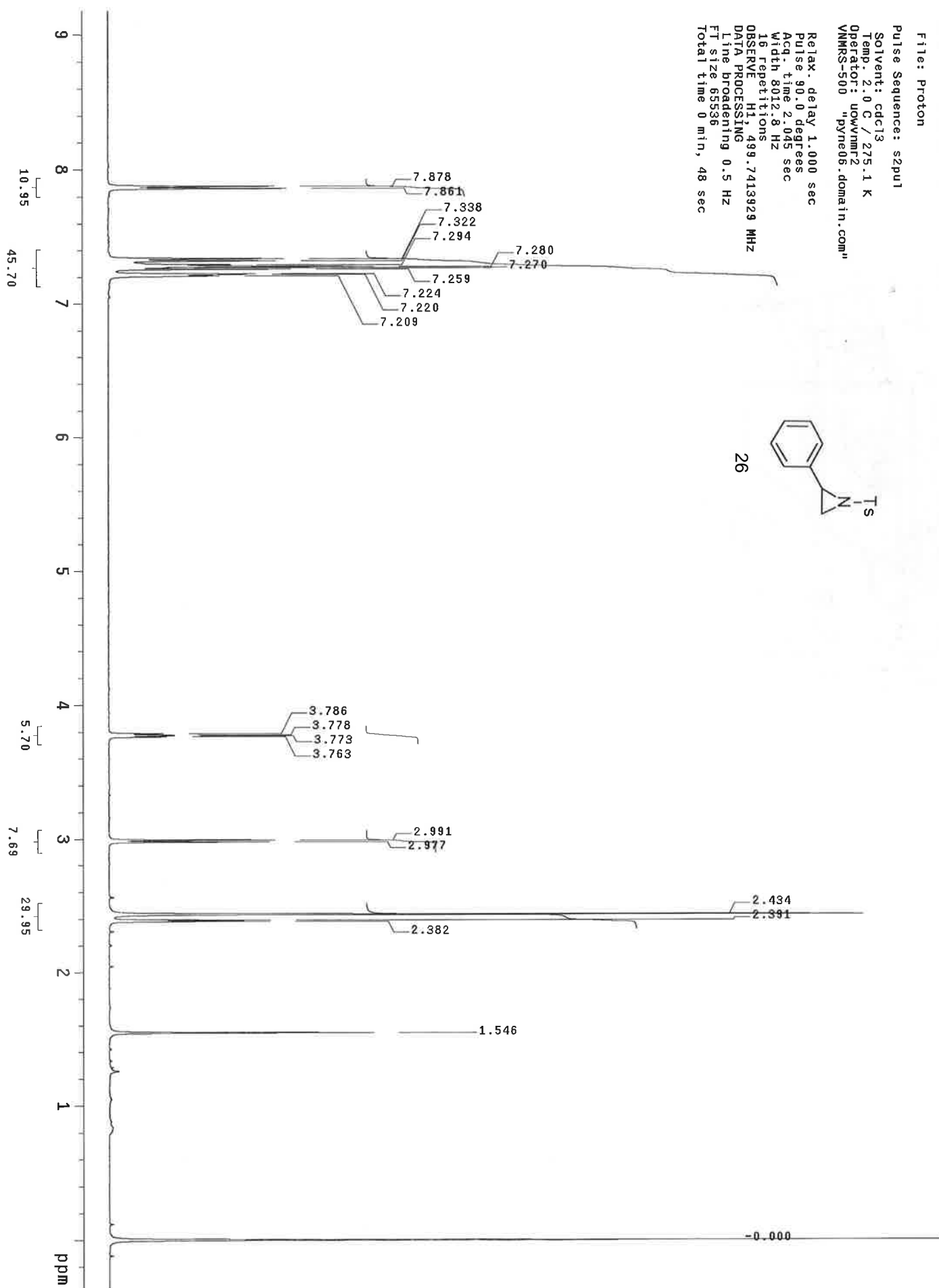
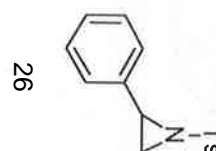
OBSERVE H1, 499.7413929 MHz

DATA PROCESSING

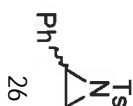
Line broadening 0.5 Hz

FT size 65536

Total time 0 min, 48 sec



jxy160114_2_yjx_pehnylaziridine_1_13c CARBON



Agilent Technologies

Sample Name:

jxy160114_2_yjx_pehnylaziridine_1_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (szpul)

Solvent: cdcl3

Data collected on: Jan 14 2016

Operator: ucwvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.521 sec

Width 31421.8 Hz

800 repetitions

OBSERVE C13, 125.7011859 MHz

DECOUPLE H1, 499.9073947 MHz

Power 42 dB

continuously on

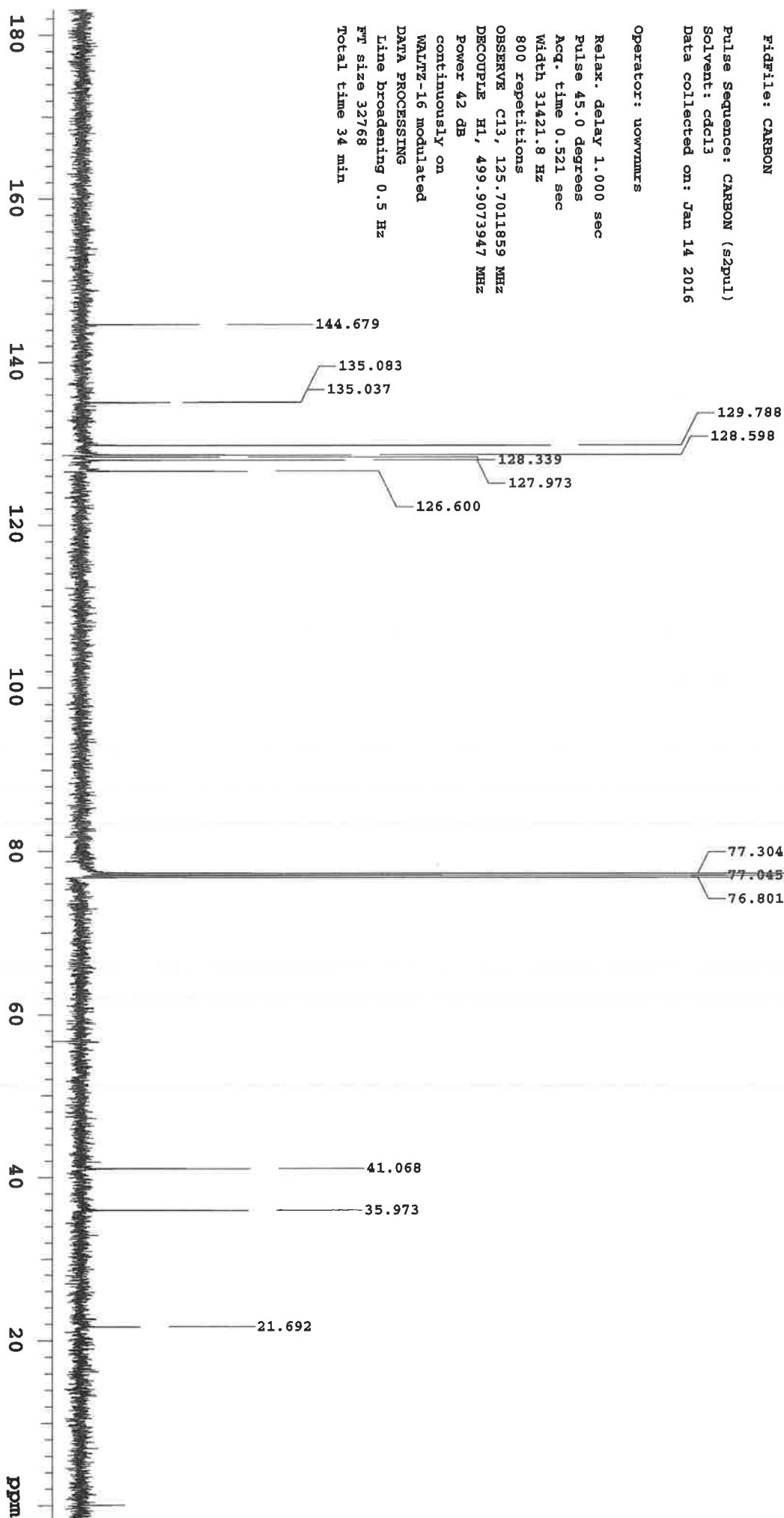
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 34 min



jxy150416_2_vjk_598_1_PROTON

Sample Name:

jxy150416_2_vjk_598_1

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (s2pul1)

Solvent: cdcl3

Data collected on: Apr 16 2015

Operator: uowmms

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 1.709 sec

Width 4793.9 Hz

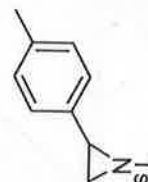
16 repetitions

OBSERVE H1, 299.9572747 MHz

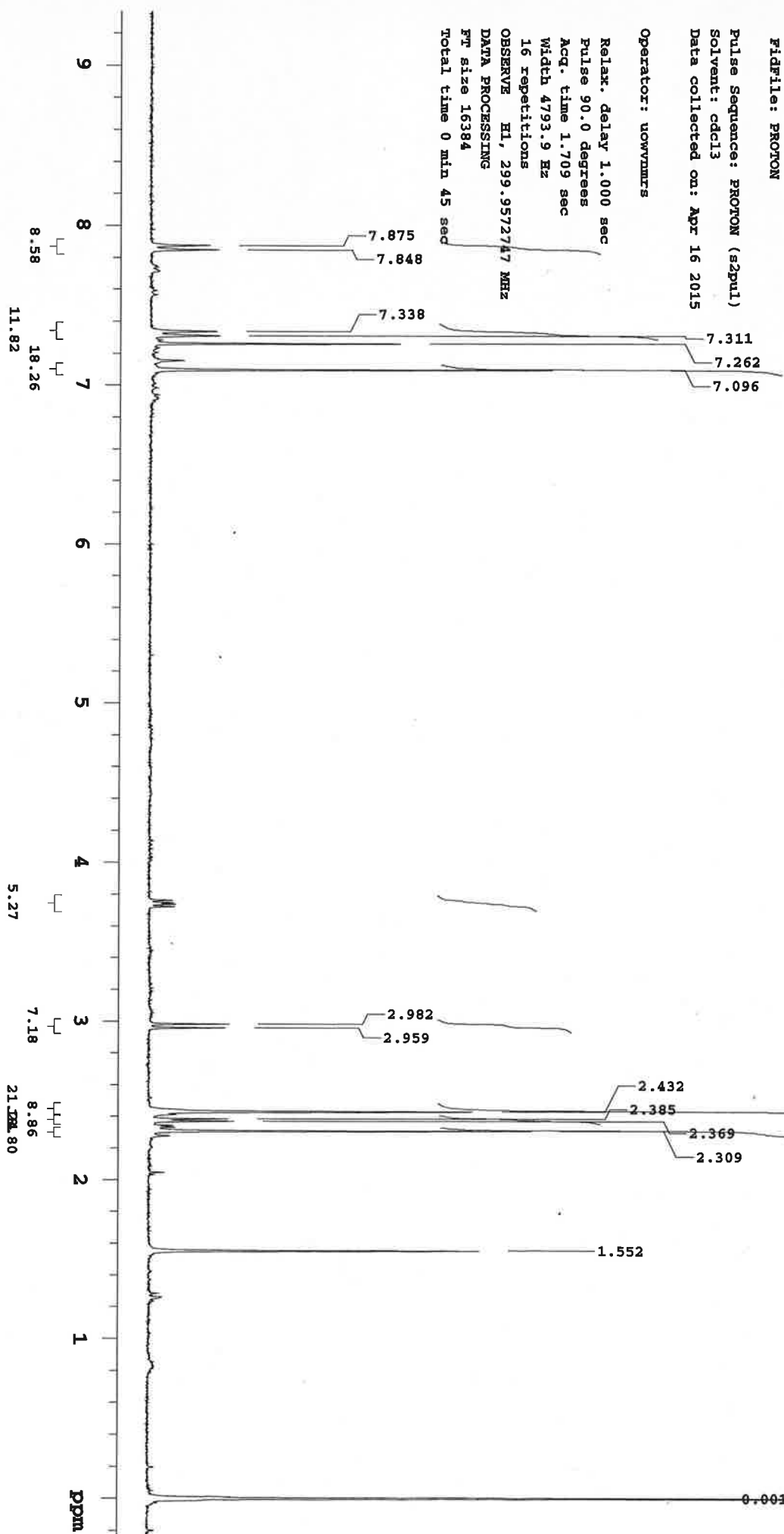
DATA PROCESSING

FT size 16384

Total time 0 min 45 sec



517



Agilent Technologies

jxy160114_2_yjx_tolylaziridine_1_13c_CARBON

Sample Name:

jxy160114_2_yjx_tolylaziridine_1_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (szpu1)

Solvent: cdcl3

Data collected on: Jan 14 2016

Operator: uowvmr

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.521 sec

Width 31421.8 Hz

896 repetitions

OBSERVE C13, 125.7011859 MHz

DECOUPLE H1, 499.9073947 MHz

Power 42 dB

continuously on

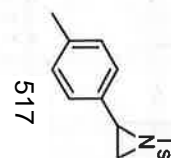
WALTZ-16 modulated

DATA PROCESSING

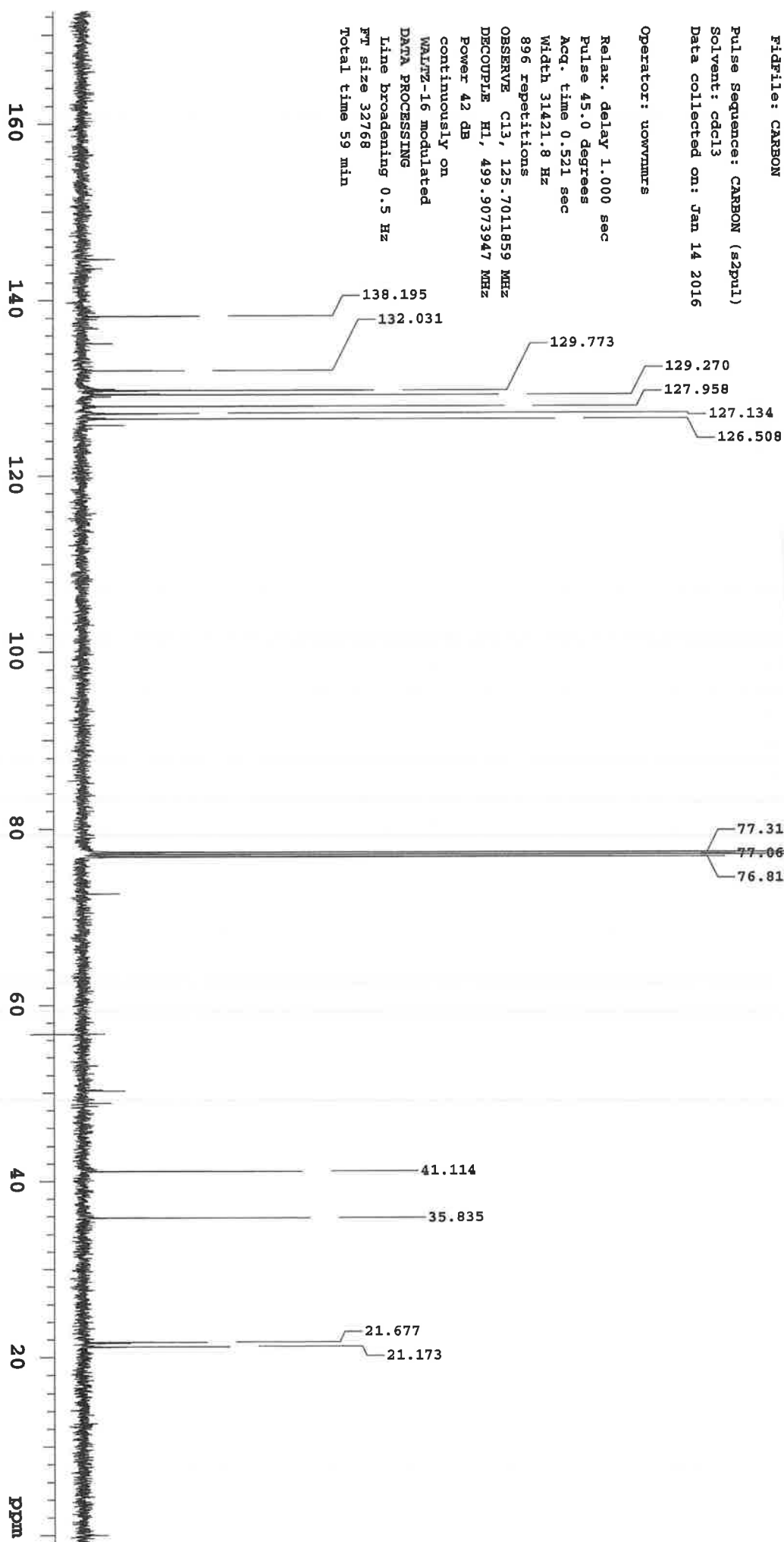
Line broadening 0.5 Hz

FT size 32768

Total time 59 min



Agilent Technologies



jxy150417_2.yjk_600_cp_PROTON

Sample Name:

jxy150417_2.yjk_600_cp

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

FidFile: PROTON

7.332

7.263

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Apr 17 2015

Operator: uowmms

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 2.048 sec

Width 7998.4 Hz

16 repetitions

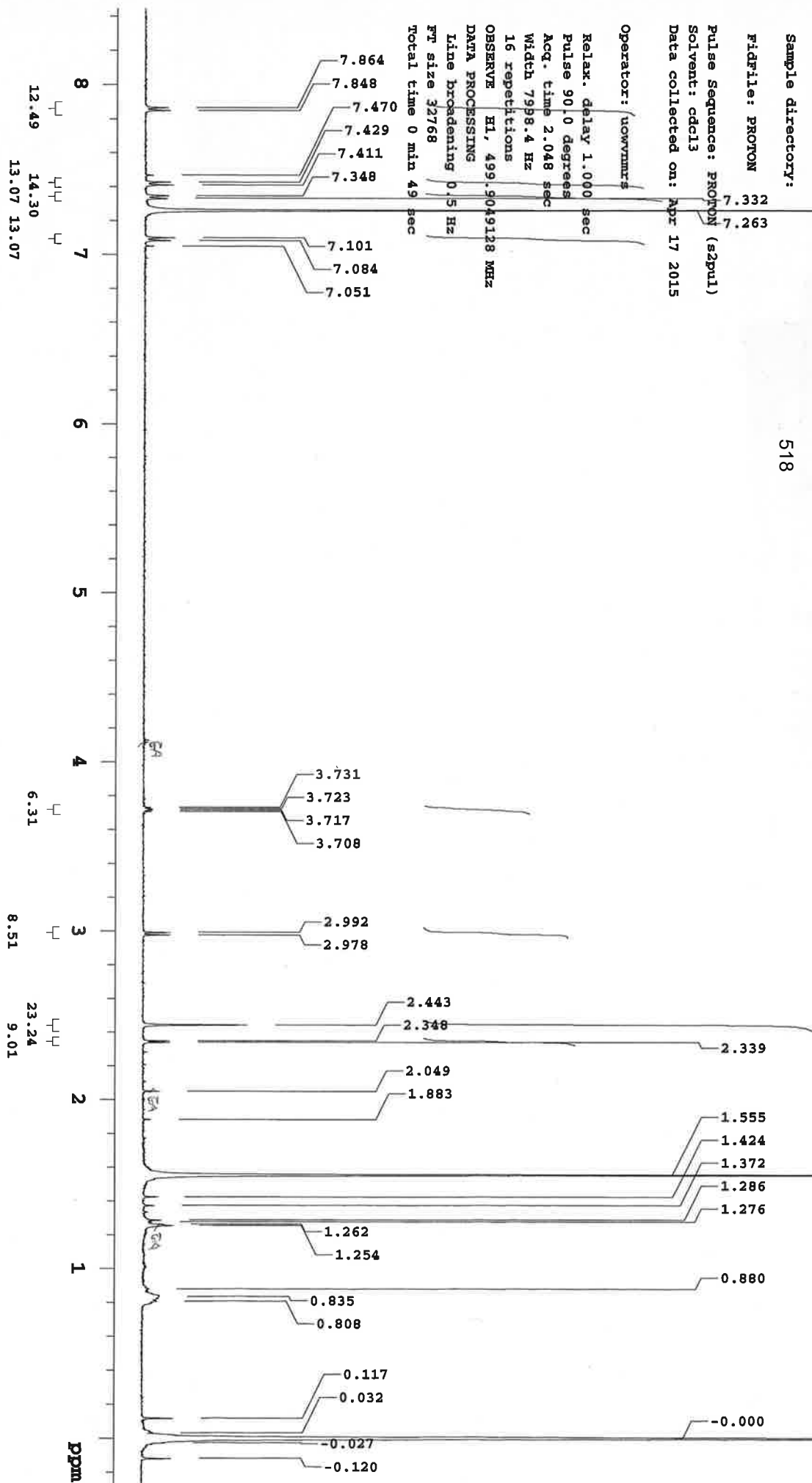
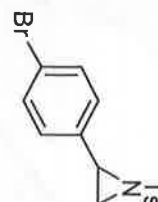
OBSERVE H1, 499.9049128 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 0 min 49 sec



jxy160114_2_yjx_4_bromophenylaziridine_1_13c CARBON

Sample Name:

jxy160114_2_yjx_4_bromophenylaziridine_1_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (szpul)

Solvent: cdcl3

Data collected on: Jan 14 2016

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.521 sec

Width 31421.8 Hz

1536 repetitions

OBSERVE C13, 125.7011859 MHz

DECOUPLE H1, 499.9073947 MHz

Power 42 dB

continuously on

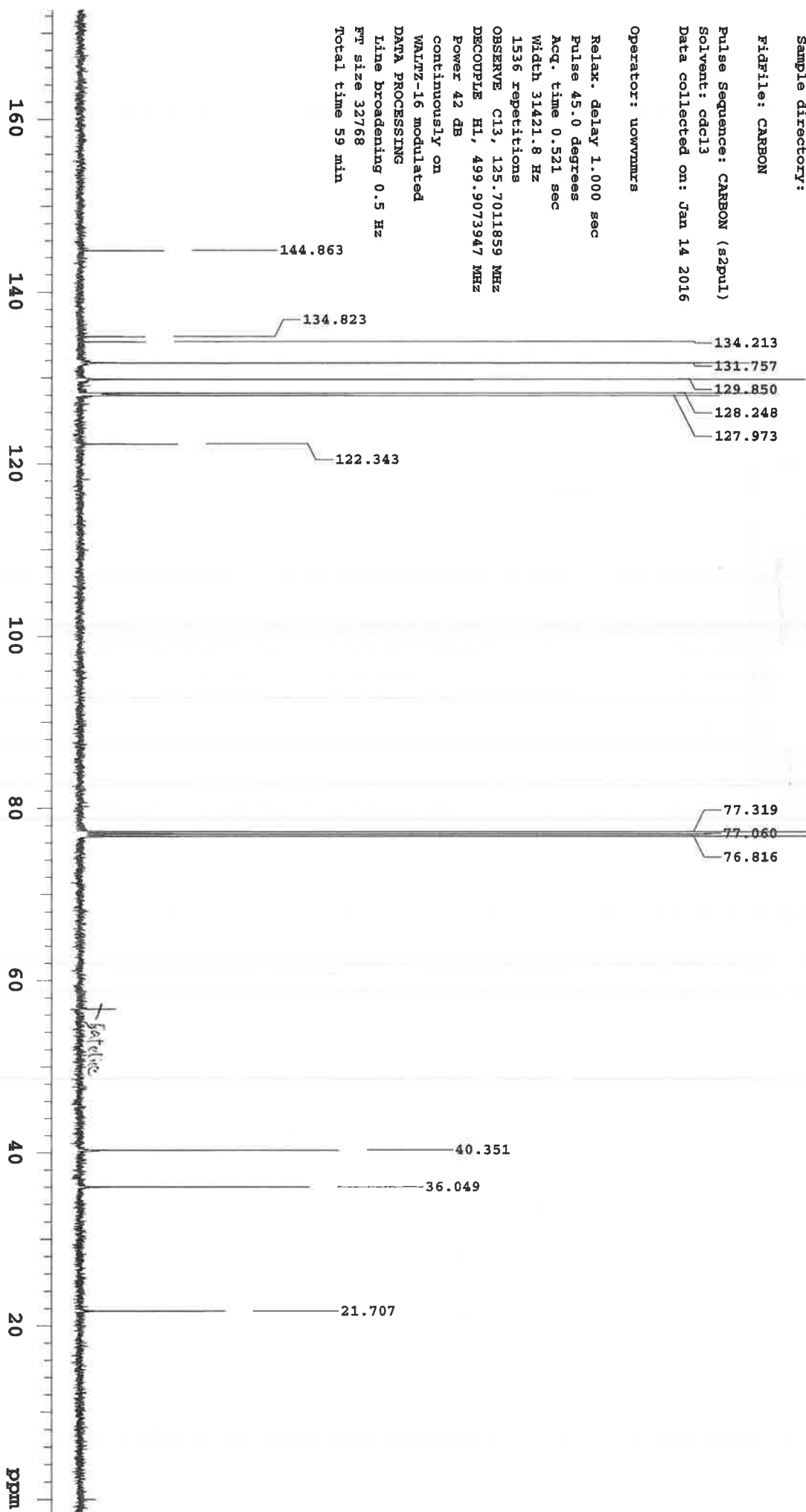
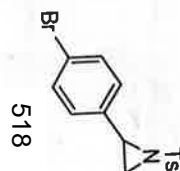
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 59 min



Agilent Technologies

jxy150417_2.yjk_601_cp_PROTON

Sample Name:
jxy150417_2.yjk_601_cp
Data Collected on:
ernst.sci.uow.edu.au-inova500
Archive directory:

Sample directory:

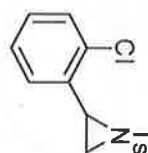
Fidfile: PROTON

Pulse Sequence: PROTON (s2pu1)
Solvent: cdcl3
Data collected on: Apr 17 2015

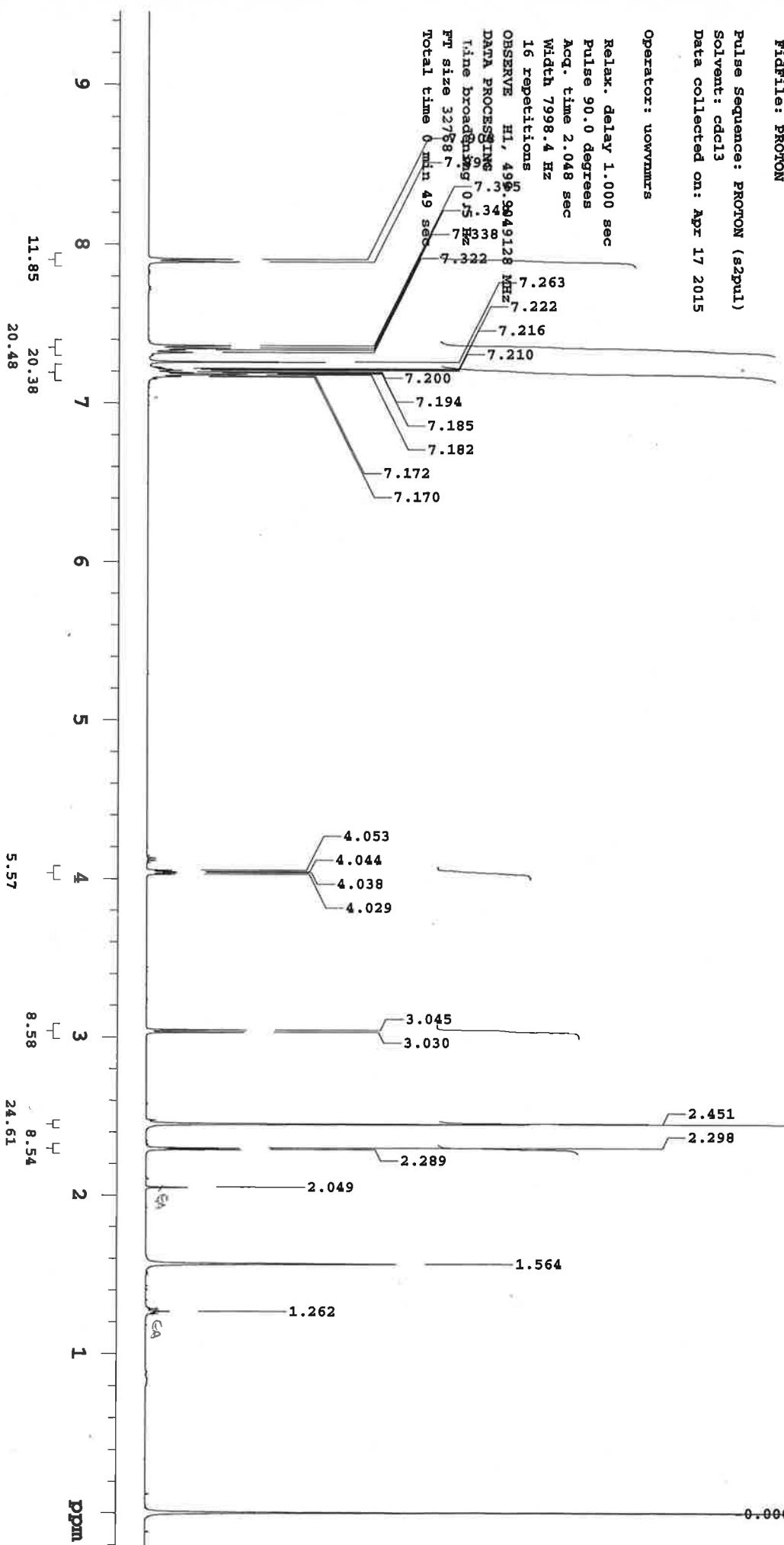
Operator: uowymms

Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 2.048 sec
Width 7998.4 Hz
16 repetitions

OBSERVE H1, 499.9649128 MHz
DATA PROCESSING
line broadening 0.5 Hz
FT size 32768
Total time 0 min 49 sec



519



jxy160114_2_yjx_2chlorophenylaziridine_13c_CARBON

Sample Name:

jxy160114_2_yjx_2chlorophenylaziridine_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: CARBON

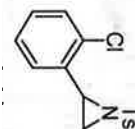
Pulse Sequence: CARBON (szpul)

Solvent: cdcl3

Data collected on: Jan 14 2016

Operator: uowvnmrs

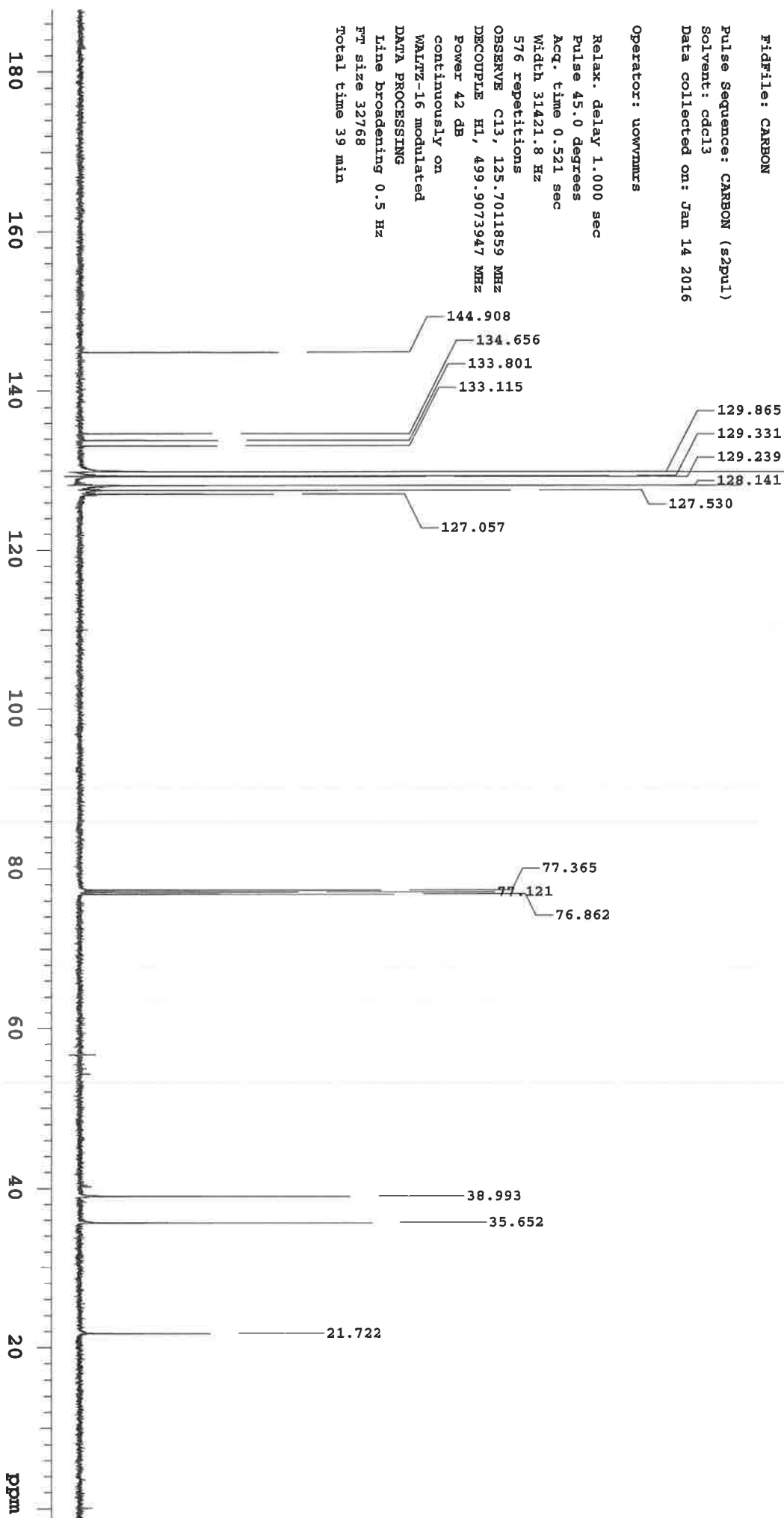
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.521 sec
Width 31421.8 Hz
576 repetitions
OBSERVE C13, 125.7011859 MHz
DECOUPLE H1, 499.9073947 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 39 min



519



Agilent Technologies



jxy150623_2.yjx_668_1_PROTON

Sample Name:

jxy150623_2.yjx_668_1

Data Collected on:

bloch.sci.nov.edu.au-mercury300

Archive directory:

/export/home/chempack/vnmrsvs/data

Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Jun 23 2015

Operator: uovnmrs

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 3.416 sec

Width 4796.2 Hz

16 repetitions

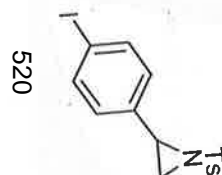
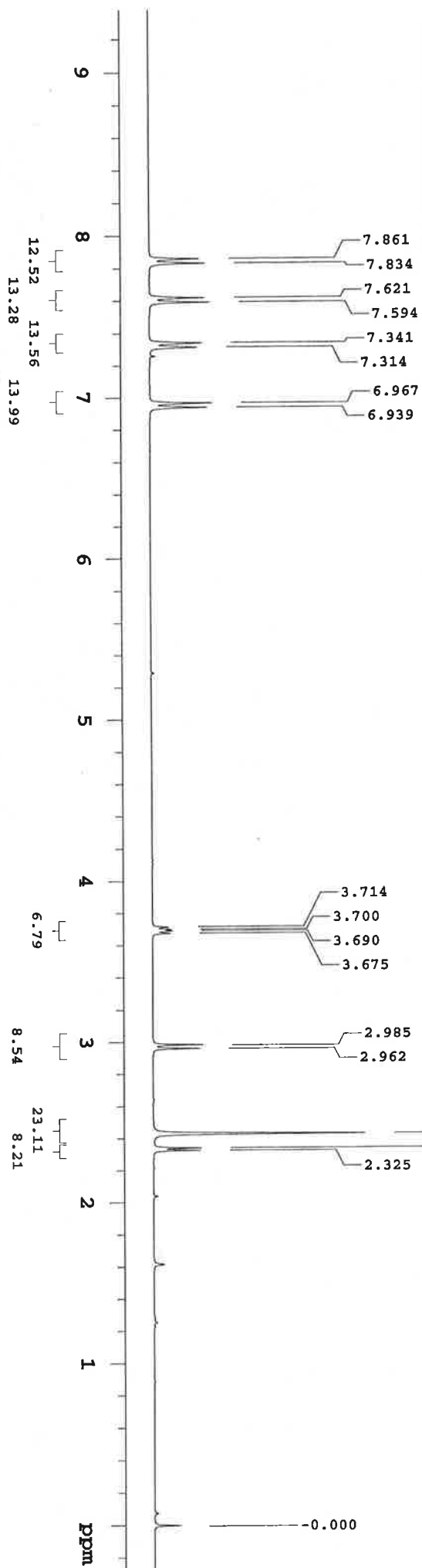
OBSERVE H1, 299.9572712 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 1 min 13 sec



Agilent Technologies

jxy160114_2_yjx_4iodophenylaziridine_13c_CARBON

Sample Name:

jxy160114_2_yjx_4iodophenylaziridine_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (szpul)

Solvent: cdcl3

Data collected on: Jan 14 2016

Operator: nowmms

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.521 sec

Width 31421.8 Hz

864 repetitions

OBSERVE C13, 125.7011859 MHz

DECOUPLE H1, 499.9073947 MHz

Power 42 dB

continuously on

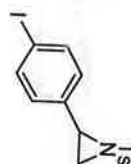
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

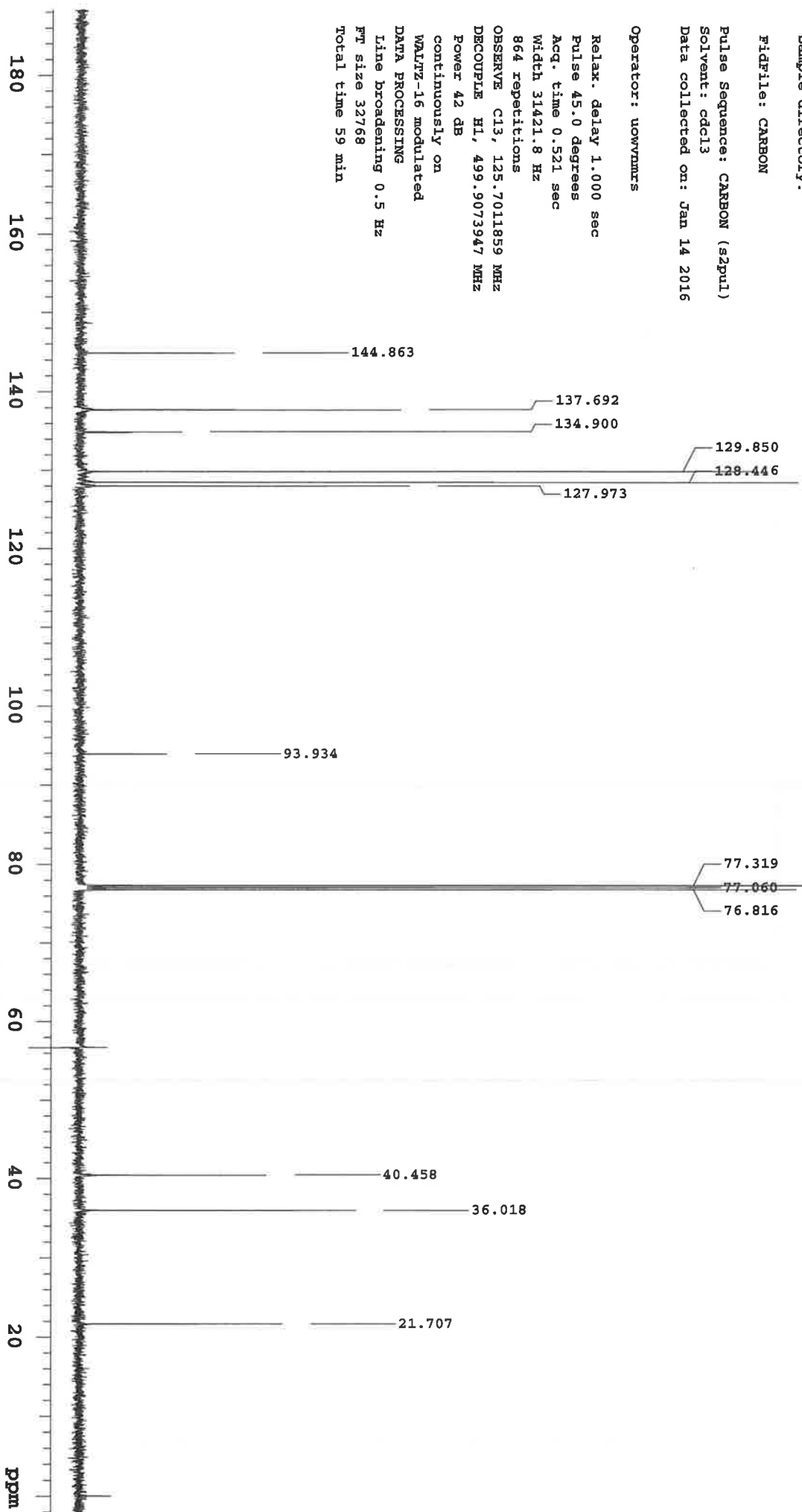
Total time 59 min



520



Agilent Technologies



jxy150621_2_yjx_667_1_PROTON

Sample Name:

jxy150621_2_yjx_667_1

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (s2pul)

Solvent: cdc13

Data collected on: Jun 21 2015

Operator: ucwvmmrs

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 3.416 sec

Width 4796.2 Hz

16 repetitions

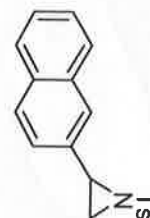
OBSERVE H1, 299.9572747 MHz

DATA PROCESSING

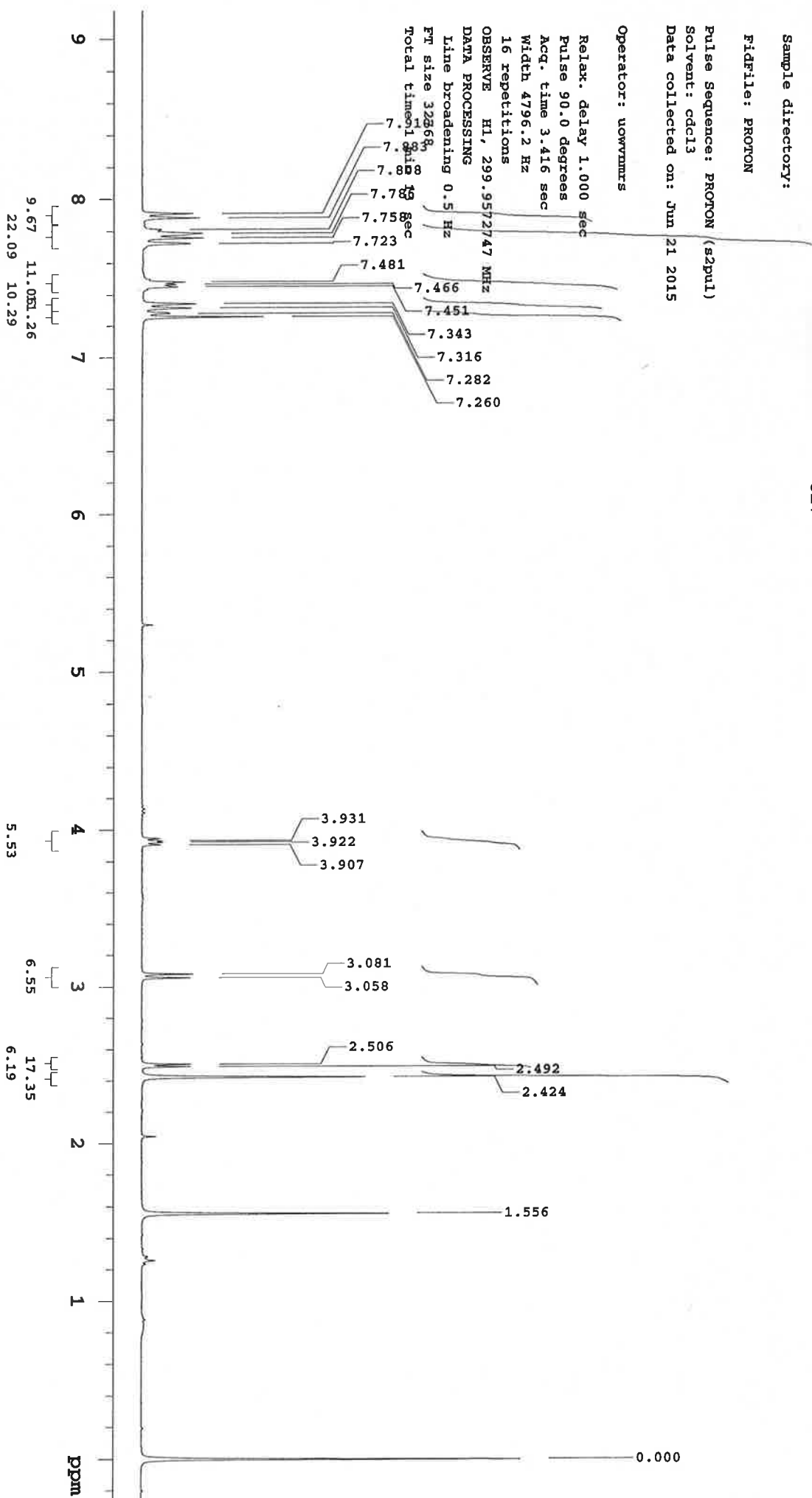
Line broadening 0.5 Hz

FT size 32368

Total time 13.118 sec



521



Agilent Technologies

jxy160114_2_yjk_naphthaleneaziridine_13c_CARBON

Sample Name:

jxy160114_2_yjk_naphthaleneaziridine_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jan 14 2016

Operator: uowymms

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.521 sec

Width 31421.8 Hz

832 repetitions

OBSERVE C13, 125.70118 Hz

DECOUPLE H1, 499.90739 Hz

Power 42 dB

continuously on

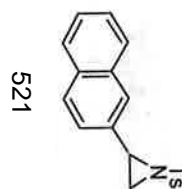
WALTZ-16 modulated

DATA PROCESSING

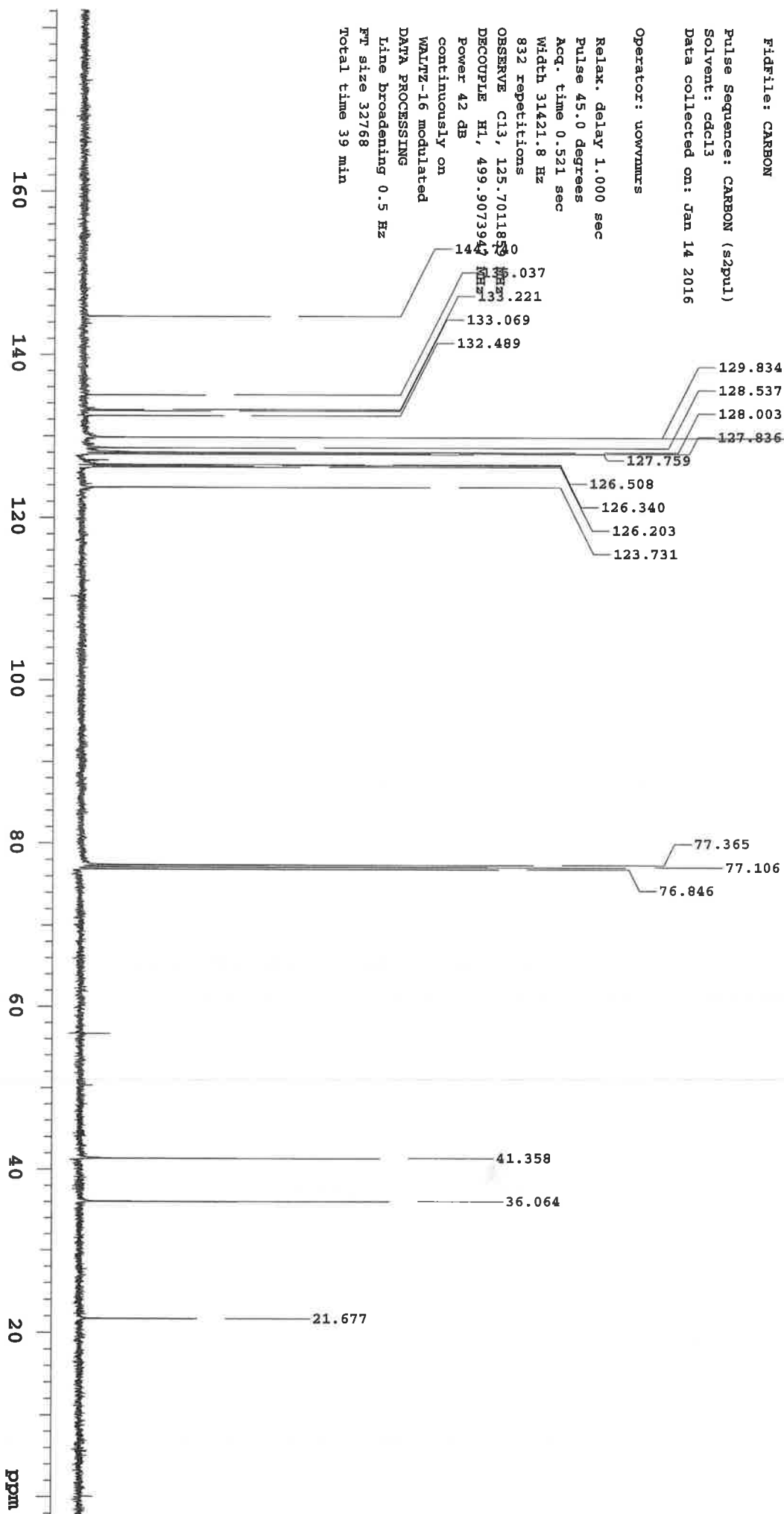
Line broadening 0.5 Hz

FT size 32768

Total time 39 min



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jxy150506_2_vjk_618_1_PROTON

Sample Name:
jxy150506_2_vjk_618_1
Data Collected on:
ernst.sci.uow.edu.au-inova500
Archive directory:

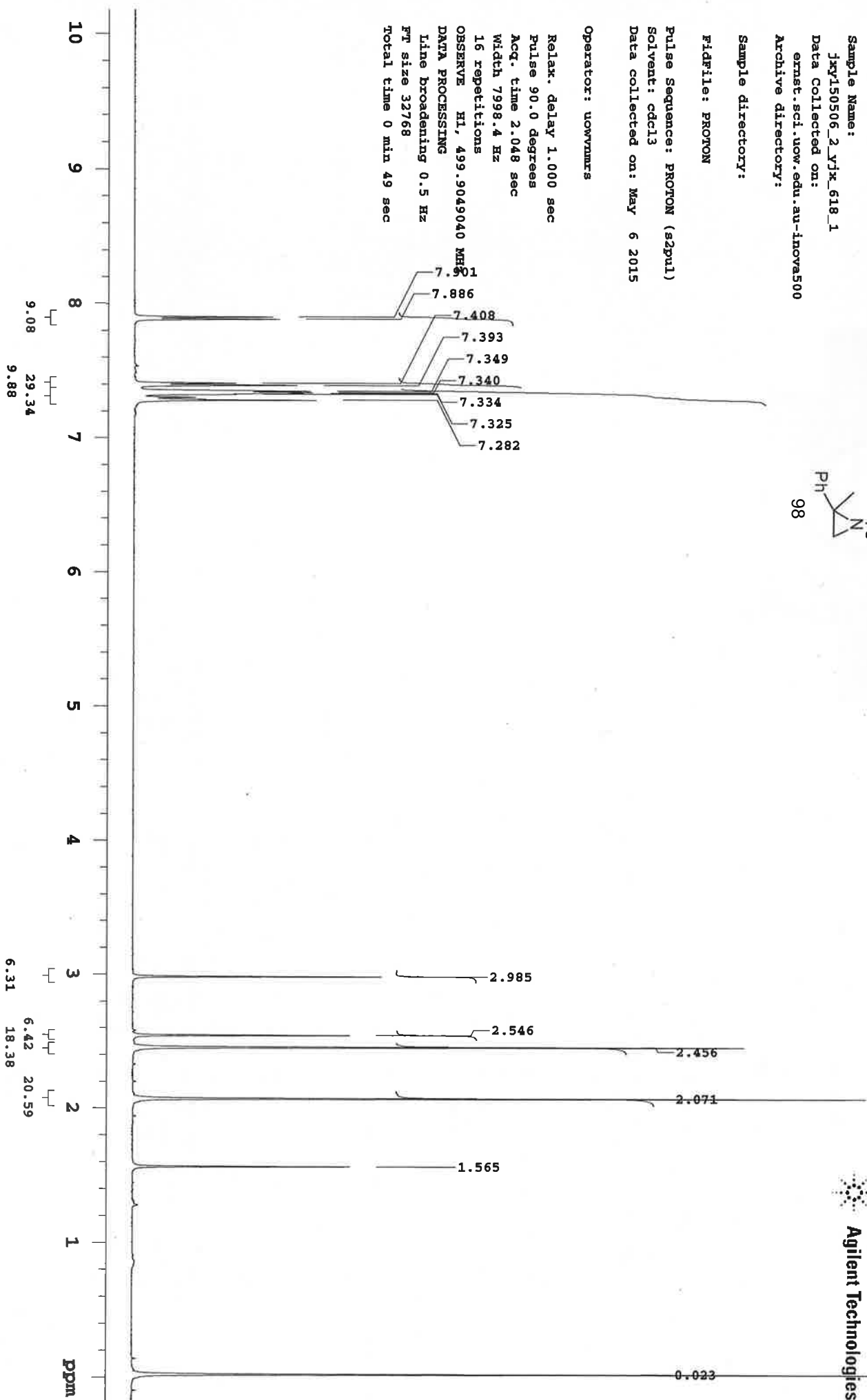
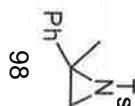
Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 6 2015

Operator: uowvnmrs

Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 2.048 sec
Width 7998.4 Hz
16 repetitions
OBSERVE H1, 499.9049040 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 0 min 49 sec



jxy160115_2_yjk_disubstitutedaziridine_13c CARBON

Sample Name:

jxy160115_2_yjk_disubstitutedaziridine_13c

Data Collected on:

bloch.sci.nov.edu.au-mercury300

Archive directory:

Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (szpu1)

Solvent: cdcl3

Data collected on: Jan 15 2016

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

768 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

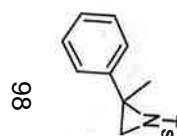
WALTZ-16 modulated

DATA PROCESSING

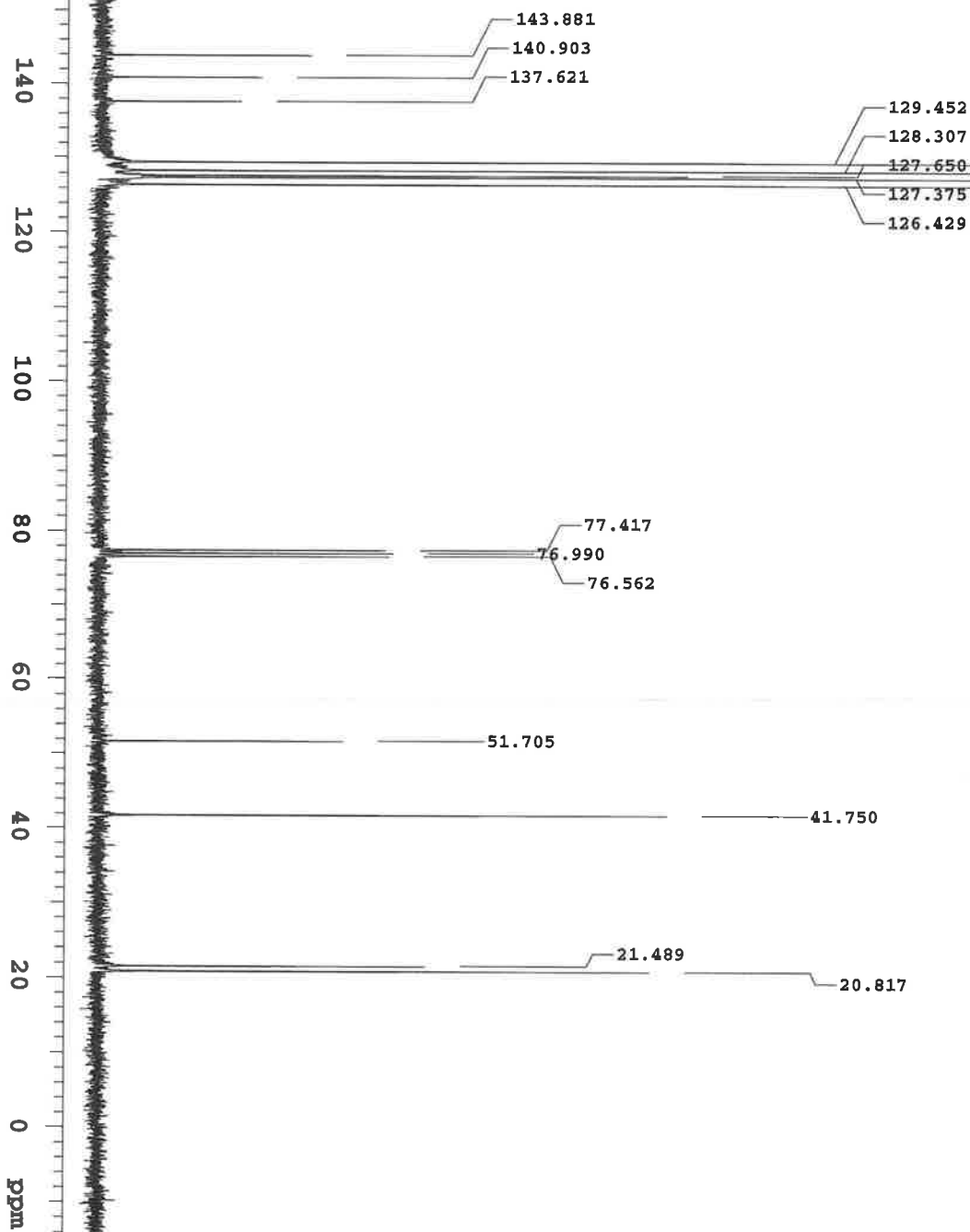
Line broadening 0.5 Hz

FT size 32768

Total time 1 hr, 1 min

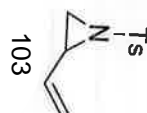


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jky140924_2_yjk_465_1_PROTON

exp1 PROTON



SAMPLE		PRESATURATION	
date	Sep 24 2014	satmode	n
solvent	cdcl3	wet	n
file	exp	SPECTAL	
ACQUISITION			
sw	5367.0	temp	not used
at	3.053	gain	40
np	32768	bst	not used
fb	3000	pw90	0.008
bs	16	alfa	11.250
dl	1.000	FLAGS	10.000
nt	16	il	n
ct	16	in	n
tn	16	dp	y
tn	16	hs	na
sfreq	499.907	PROCESSING	
tof	24.9	lb	0.50
tpwr	60	fn	not used
pw	11.250	DISPLAY	
DECOUPLER			
dn	C13	sp	-89.4
dn	0	wp	4639.4
dof	0	rfl	173.9
dm	nmn	rfd	0
dm	nmn	rfp	0
decave	W40_autocdb	ip	3.0
dpr	37	lp	-70.6
dmf	32258	PLOT	
		wc	268
		sc	0
		vs	108
		th	150
		ai	cdc
		ph	



jxy160114_2_yjk_vinylaziridine_13c CARBON

Sample Name:

jxy160114_2_yjk_vinylaziridine_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (szpul)

Solvent: cdcl3

Data collected on: Jan 14 2016

Operator: uowmms

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.521 sec

Width 31421.8 Hz

1312 repetitions

OBSERVE C13, 125.7011859 MHz

DECOUPLE H1, 499.9073947 MHz

Power 42 dB

continuously on

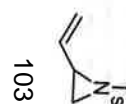
WALTZ-16 modulated

DATA PROCESSING

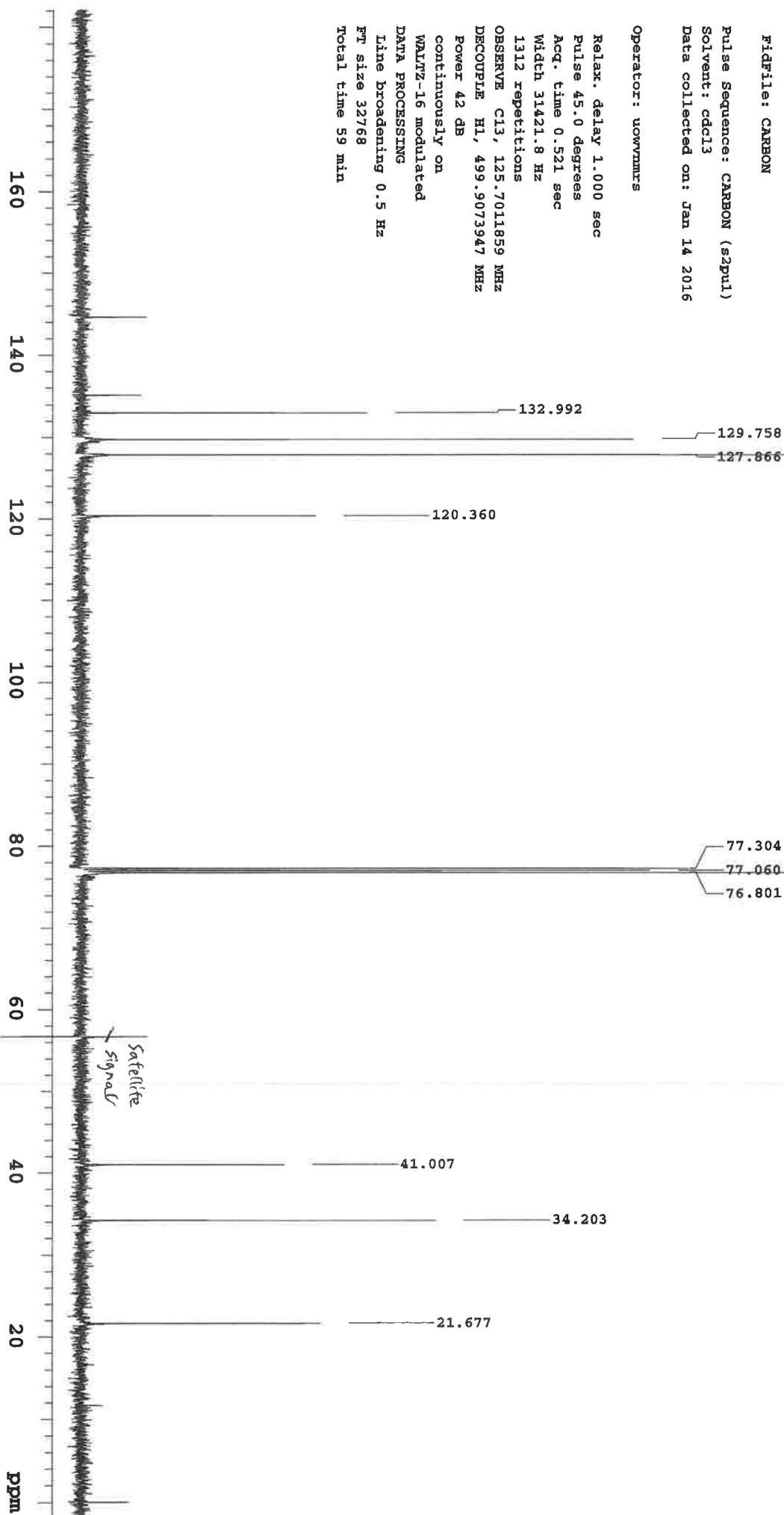
Line broadening 0.5 Hz

FT size 32768

Total time 59 min



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jxy131121_2_yjk_255_1_PROTON

Sample Name:

jxy131121_2_yjk_255_1

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

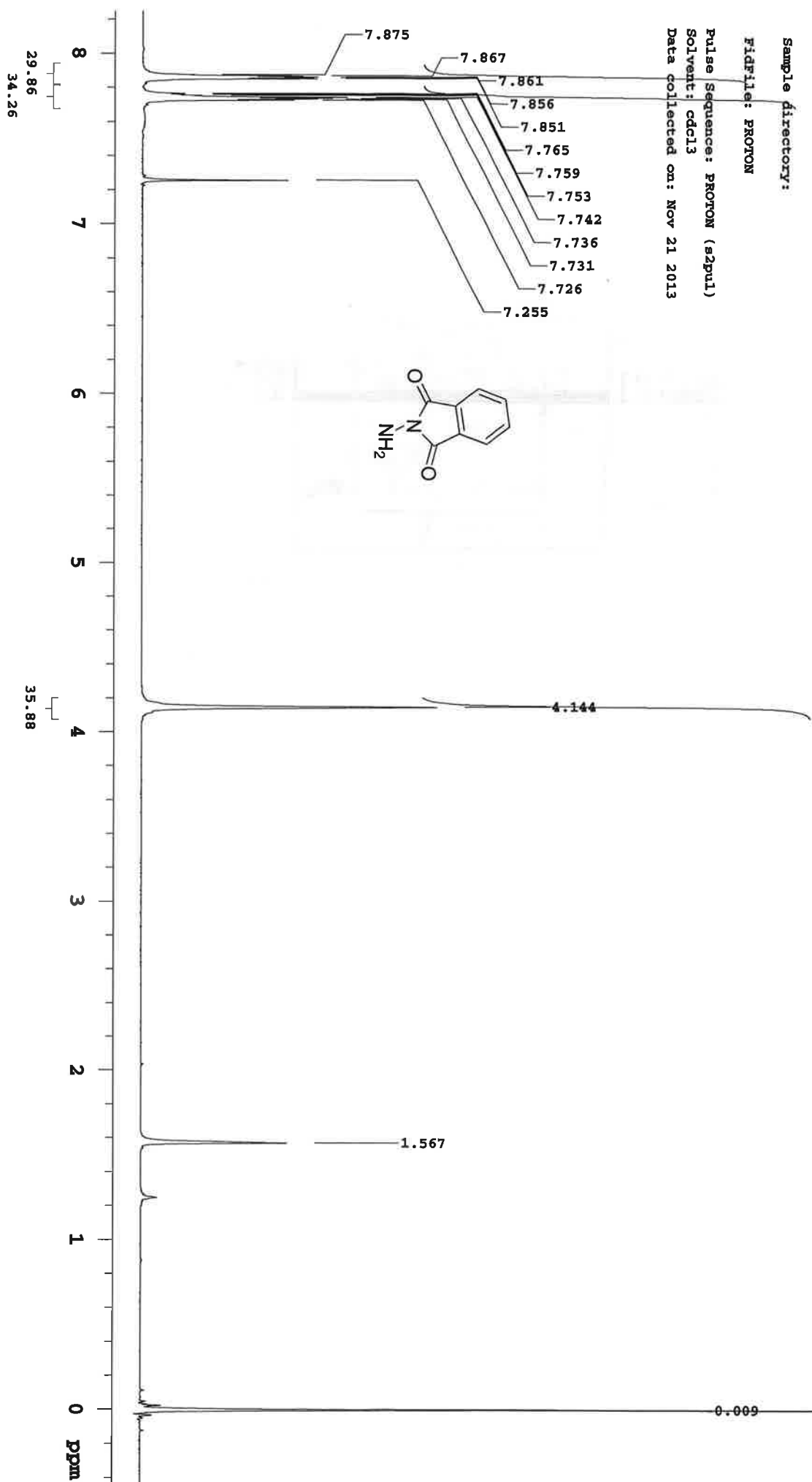
Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (s2pu1)

Solvent: cdcl3

Data collected on: Nov 21 2013

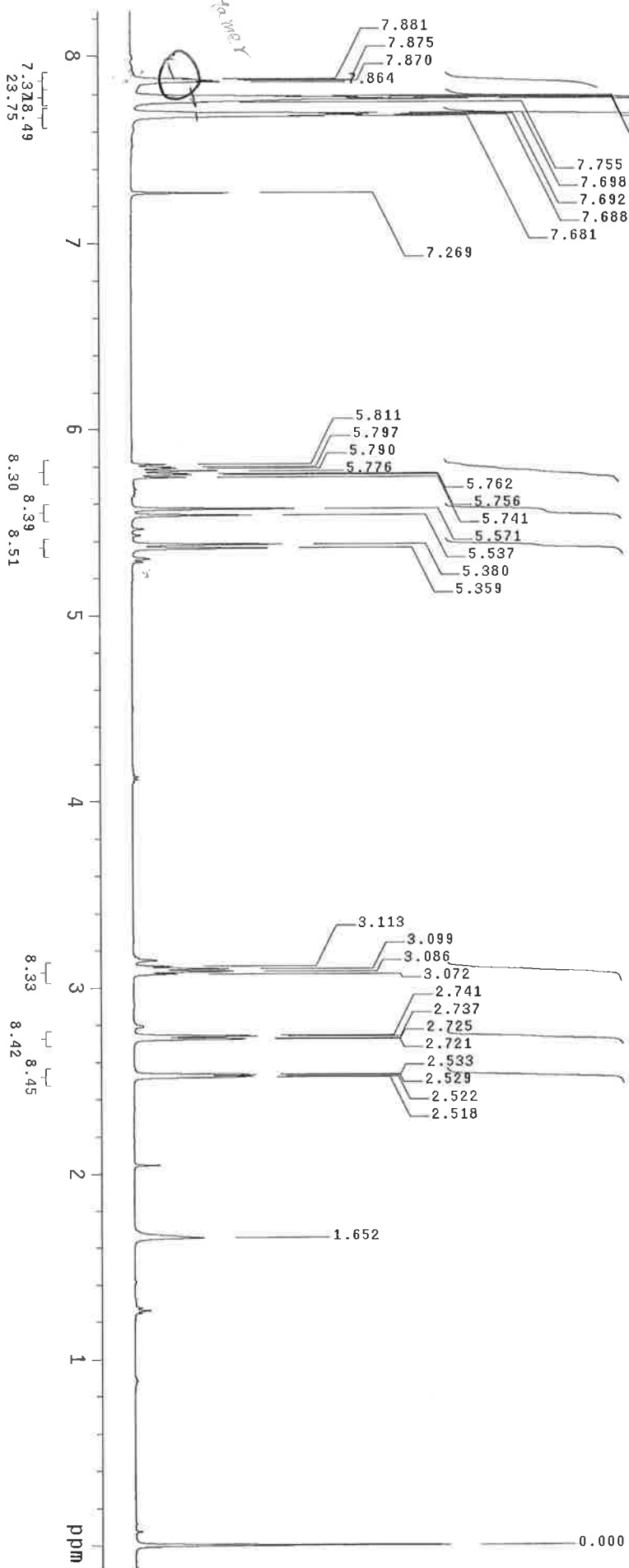
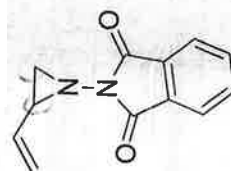


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expt1 Proton

SAMPLE		SPECIAL	
date	NOV 26 2013	temp	25.0
solvent	cdcl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	4370.6	pw90	11.100
at	3.749	ai fa	6.600
np	32768	FLAGS	
td	4000	n	n
bs	16	in	y
d1	1.000	dp	nm
nt	16	hs	nm
ct	16	PROCESSING	
TRANSMITTER		0.50	
tp	H1	fn	65536
sfreq	499.743	sp	-63.5
toF	-442.5	wp	4180.7
tpwr	62	rfl	122.2
pw	5.550	rffp	0
DECOUPLER	C13	rp	-131.1
dn	0	lp	-20.5
dof	nmn	PLOT	
dmm	C	WC	250
dpmr	47	SC	0
dmf	22200	VS	712
	ai	cdc	5
	ph		

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File: Carbon

Pulse Sequence: s2pu1

Solvent: cdcl3

Temp: 25.0 C / 298.1 K

Operator: uowvmr

VNMR5-500 "pyne06.domain.com"

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 0.537 sec

Width 30487.8 Hz

4456 Repetitions

OBSERVE C13, 125.6589960 MHz

DECOUPLE H1, 499.7437041 MHz

Power 45 dB

continuously on

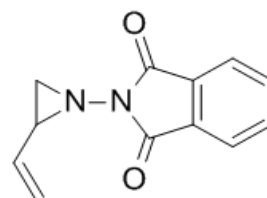
WALTZ-16 modulated

DATA PROCESSING

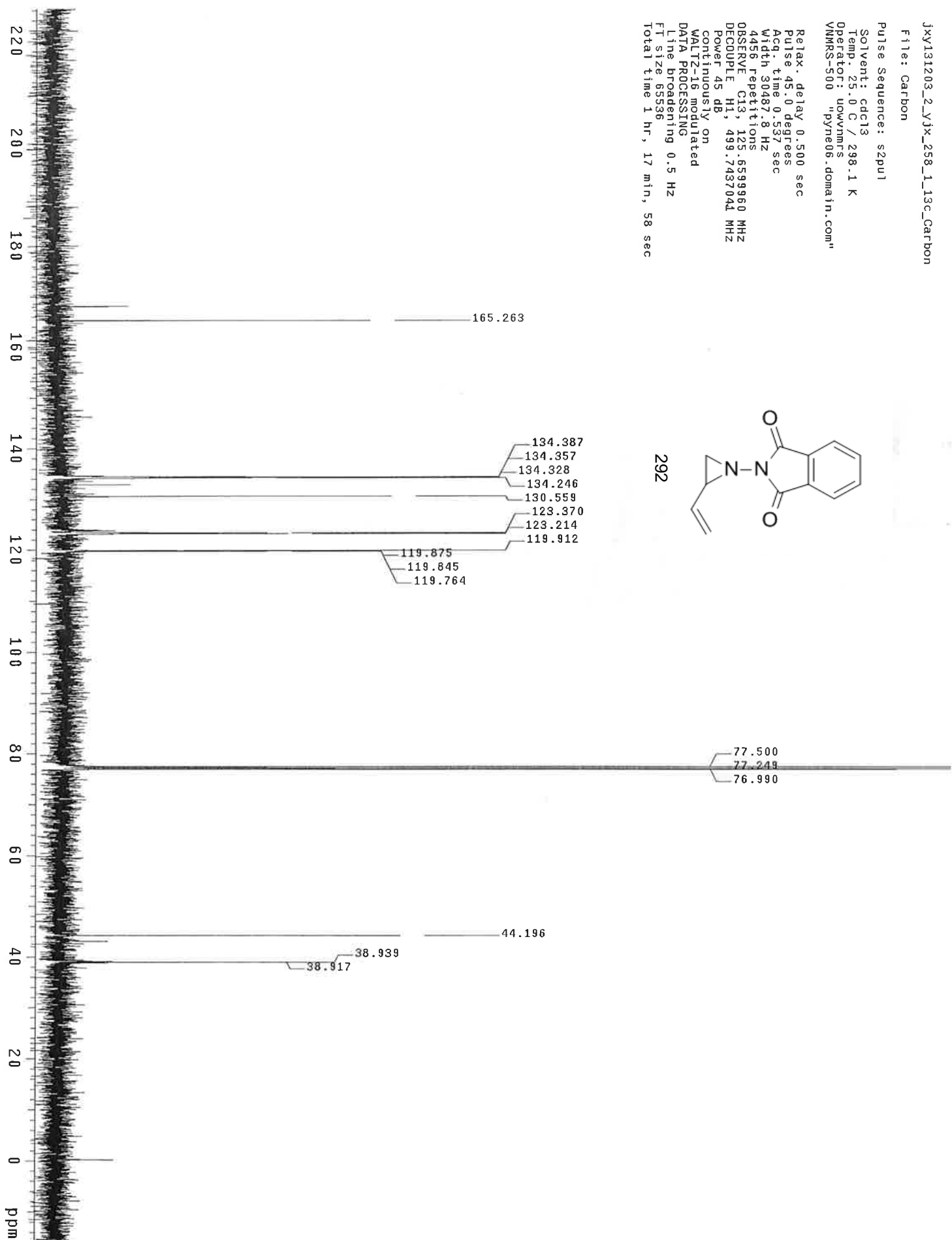
Line broadening 0.5 Hz

FT size 65536

Total time 1 hr, 17 min, 58 sec



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jxy150220_2_yjk_547_1_PROTON

Sample Name:

Data Collected on:
ernst.sci.uow.edu.au-inova500
Archive directory:

Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (szpul)
Solvent: cdcl3
Data collected on: Feb 20 2015

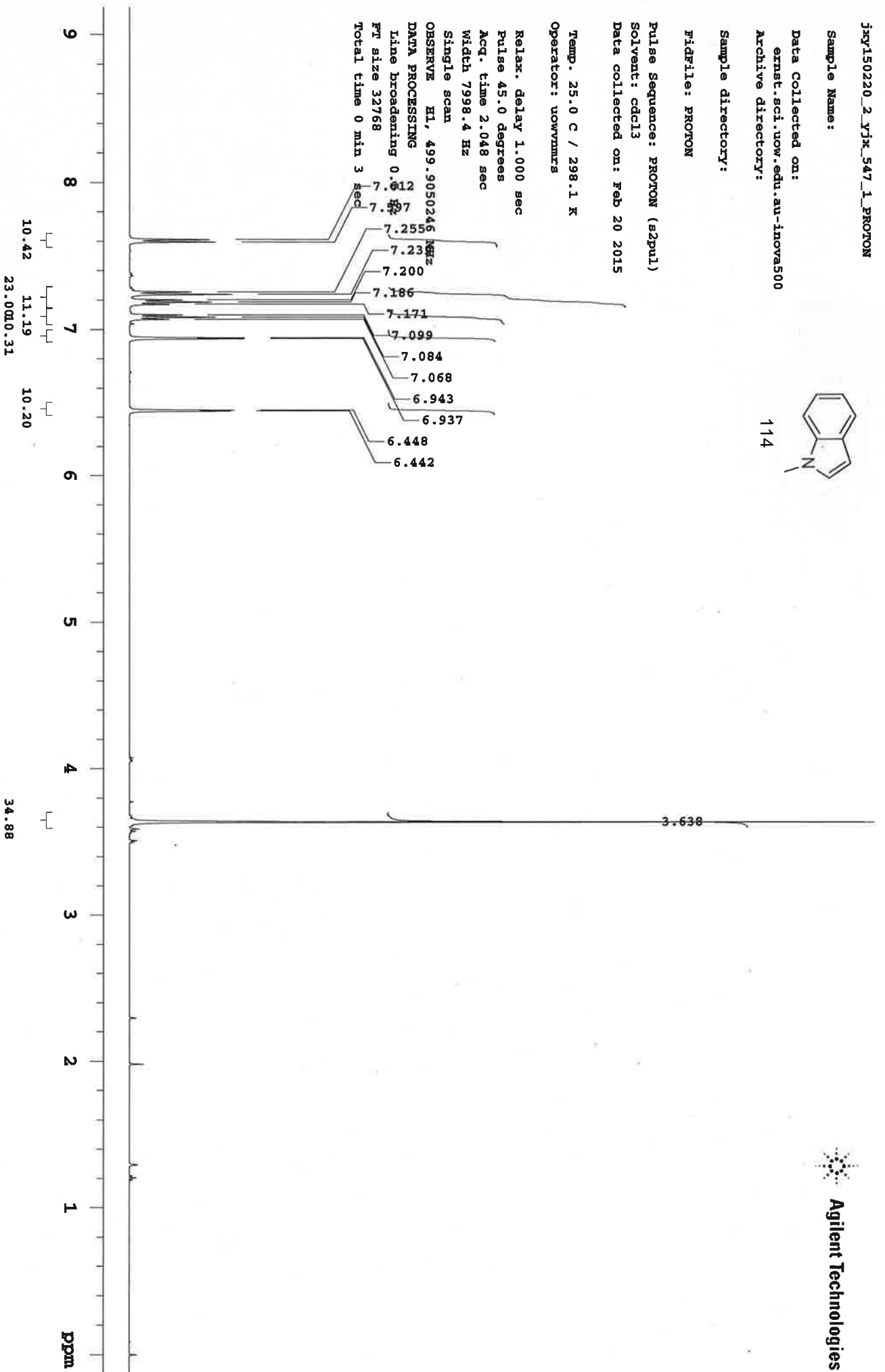
Temp. 25.0 C / 298.1 K
Operator: uowvnmrs

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 7998.4 Hz

Single scan
OBSERVE H1, 499.9050246 MHz
DATA PROCESSING
Line broadening 0.0 Hz
FT size 32768
Total time 0 min 3 sec



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jxy160114_2_yjx_methylindole_13c_CARBON

Sample Name:

jxy160114_2_yjx_methylindole_13c

Data Collected on:

bloch.sci.nsw.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (szpul)

Solvent: cdcl3

Data collected on: Jan 14 2016

Operator: uowymms

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

384 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

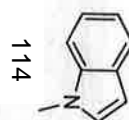
WALTZ-16 modulated

DATA PROCESSING

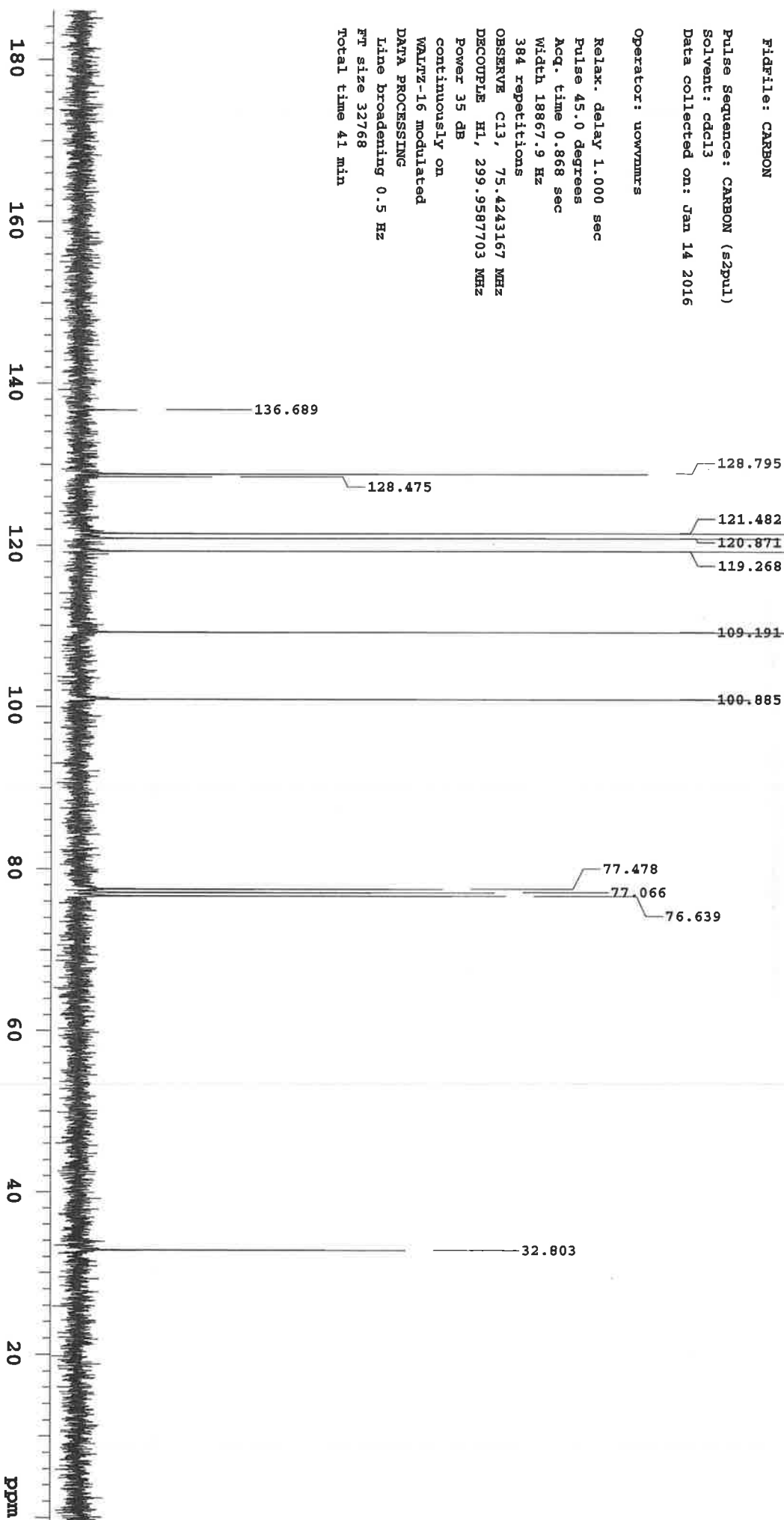
Line broadening 0.5 Hz

FT size 32768

Total time 41 min



Agilent Technologies



jxy150521_2_vjk_633_cp_PROTON

Sample Name:

jxy150521_2_vjk_633_cp

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pu1)

Solvent: cdcl3

Data collected on: May 21 2015

Temp. 25.0 C / 298.1 K

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 2.048 sec

Width 7998.4 Hz

16 repetitions

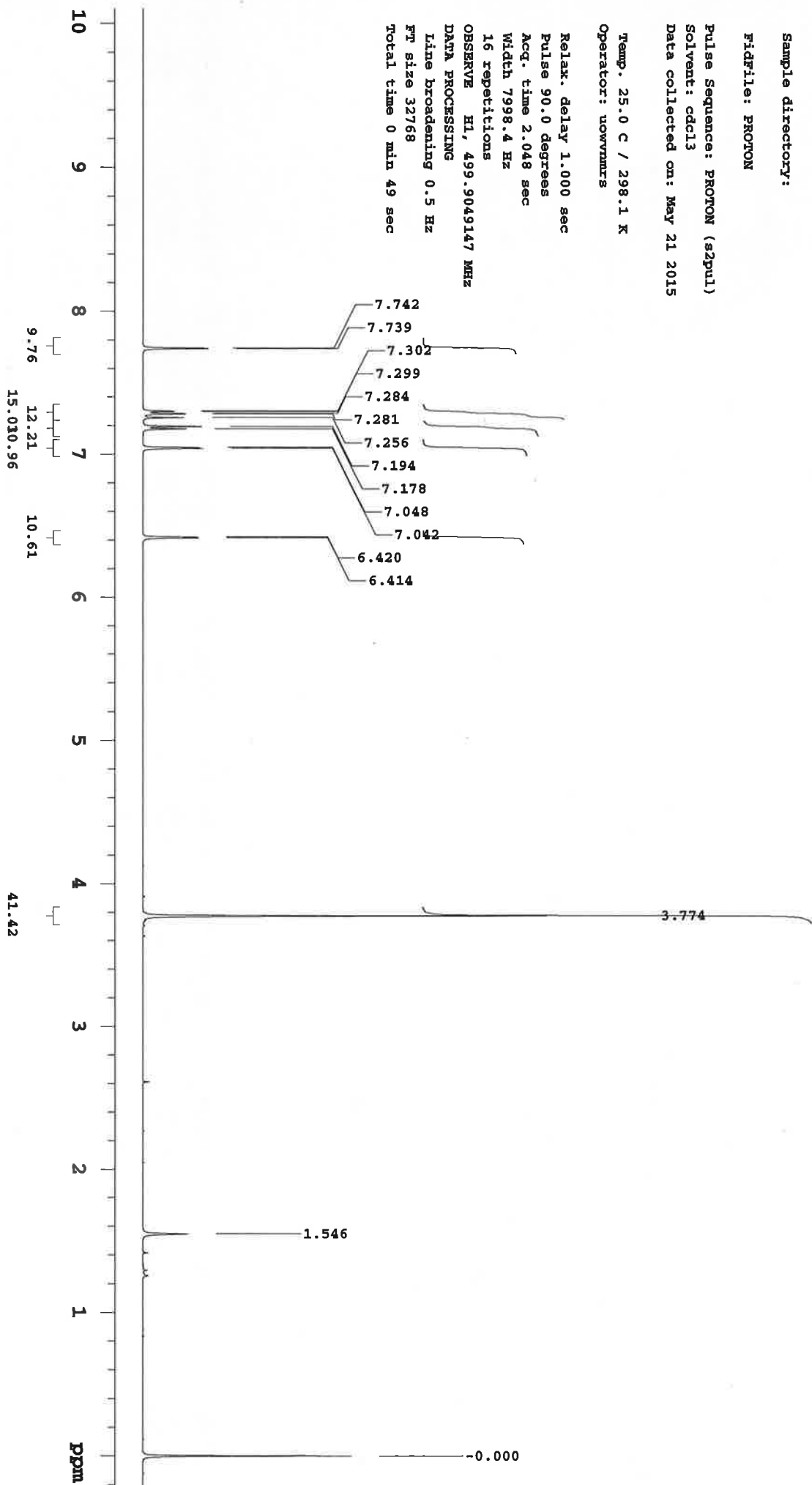
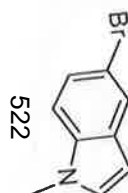
OBSERVE H1, 499.9049147 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 0 min 49 sec



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jxy160114_2_yjx_5bromomethylindole_13c_CARBON

Sample Name:

jxy160114_2_yjx_5bromomethylindole_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (szpu1)

Solvent: cdcl3

Data collected on: Jan 14 2016

Operator: uowvmms

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

22304 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

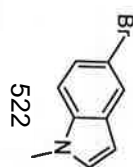
WALTZ-16 modulated

DATA PROCESSING

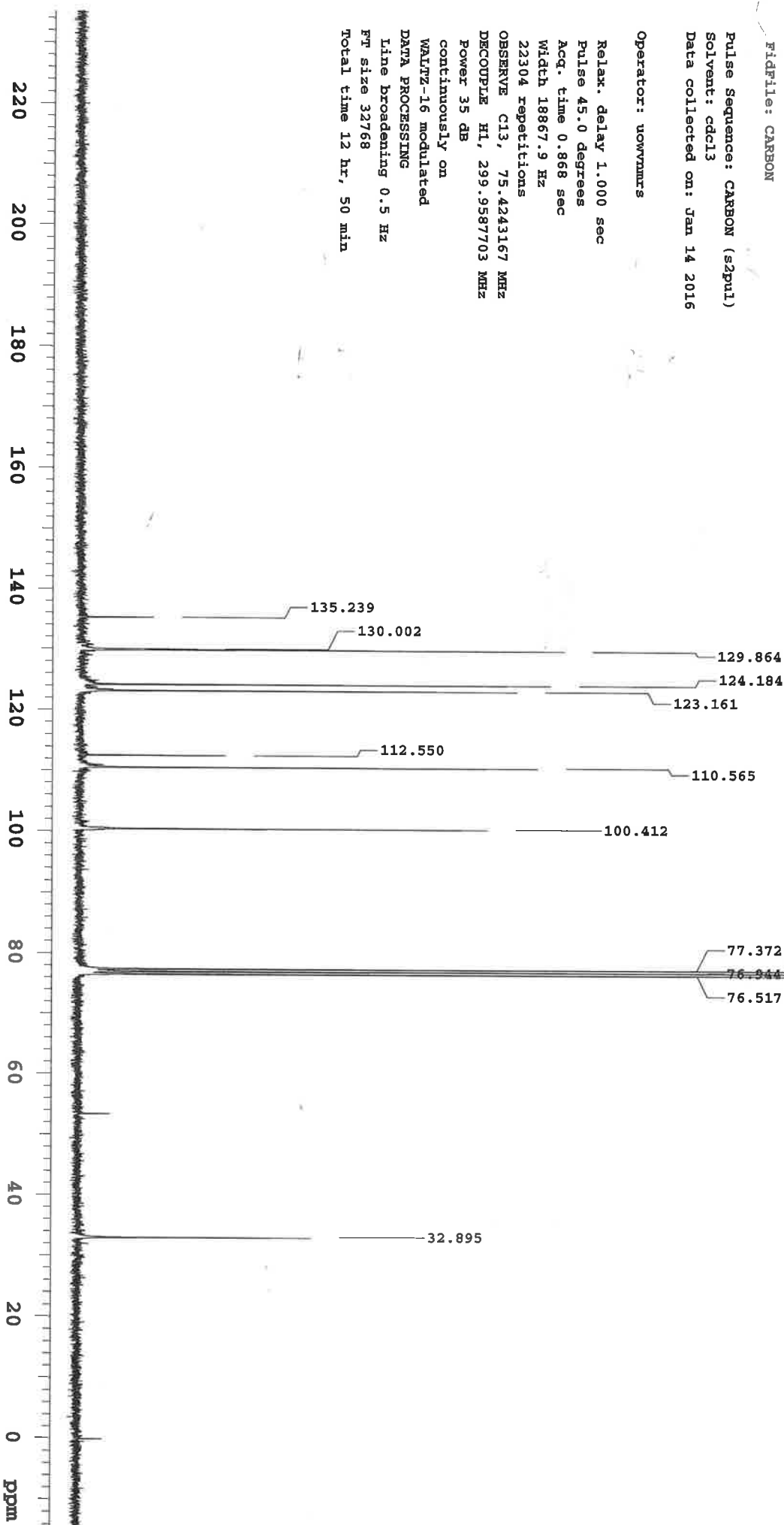
Line broadening 0.5 Hz

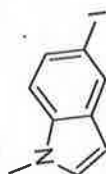
FT size 32768

Total time 12 hr, 50 min



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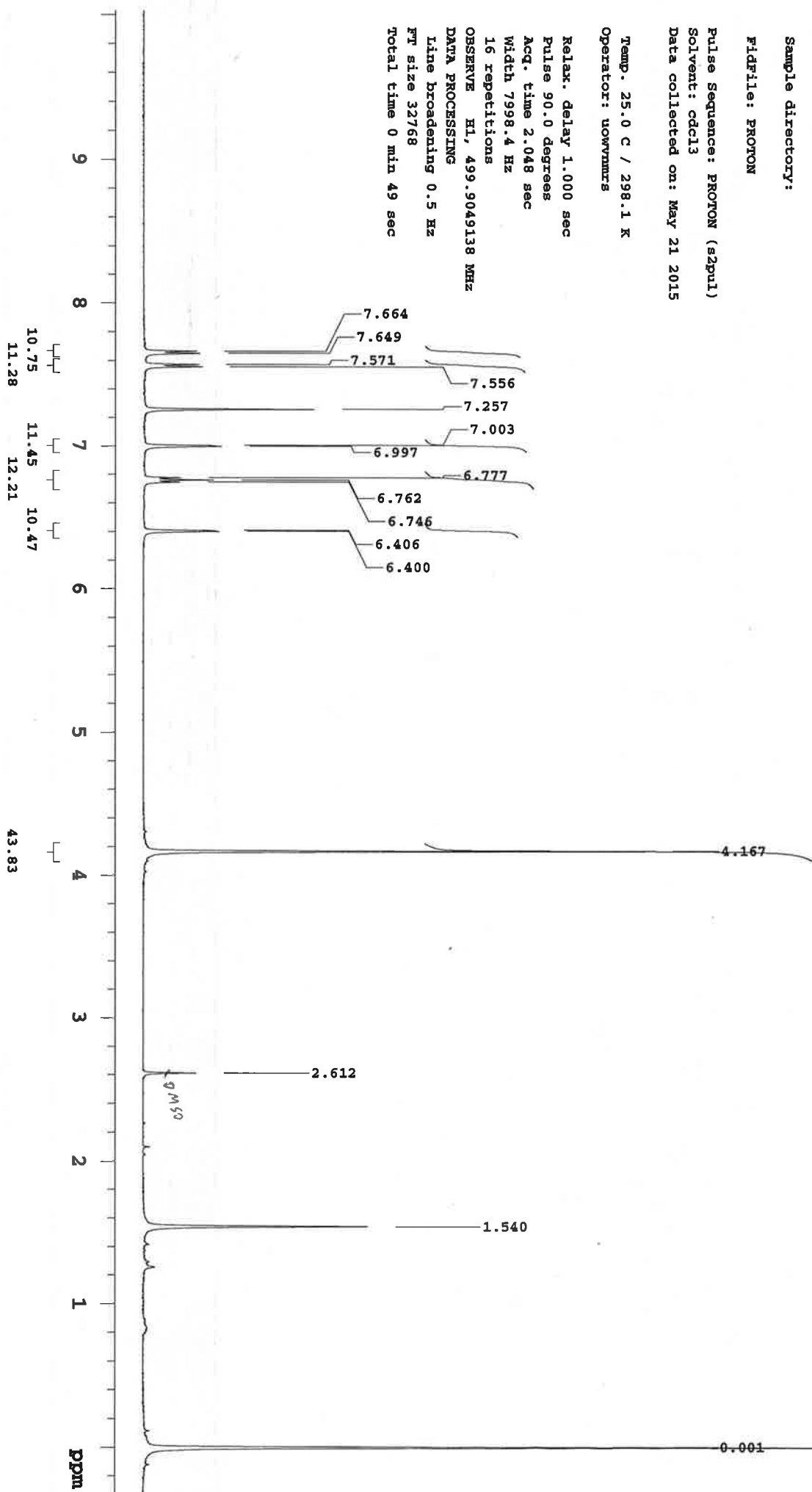
Fidfile: PROTON

Solvent: cdcl3

Data collected on: May 21 2015

Temp. 25.0 C / 298.1 K
Operator: uowvms

Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 2.048 sec
Width 7998.4 Hz
16 repetitions
OBSERVE H1, 499.9049138 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 0 min 49 sec



jxy160114_2_yjk_5iodomethylindole_13c_CARBON

Sample Name:

jxy160114_2_yjk_5iodomethylindole_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pu1)

Solvent: cdcl3

Data collected on: Jan 14 2016

Operator: uownmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

544 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

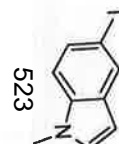
WALTZ-16 modulated

DATA PROCESSING

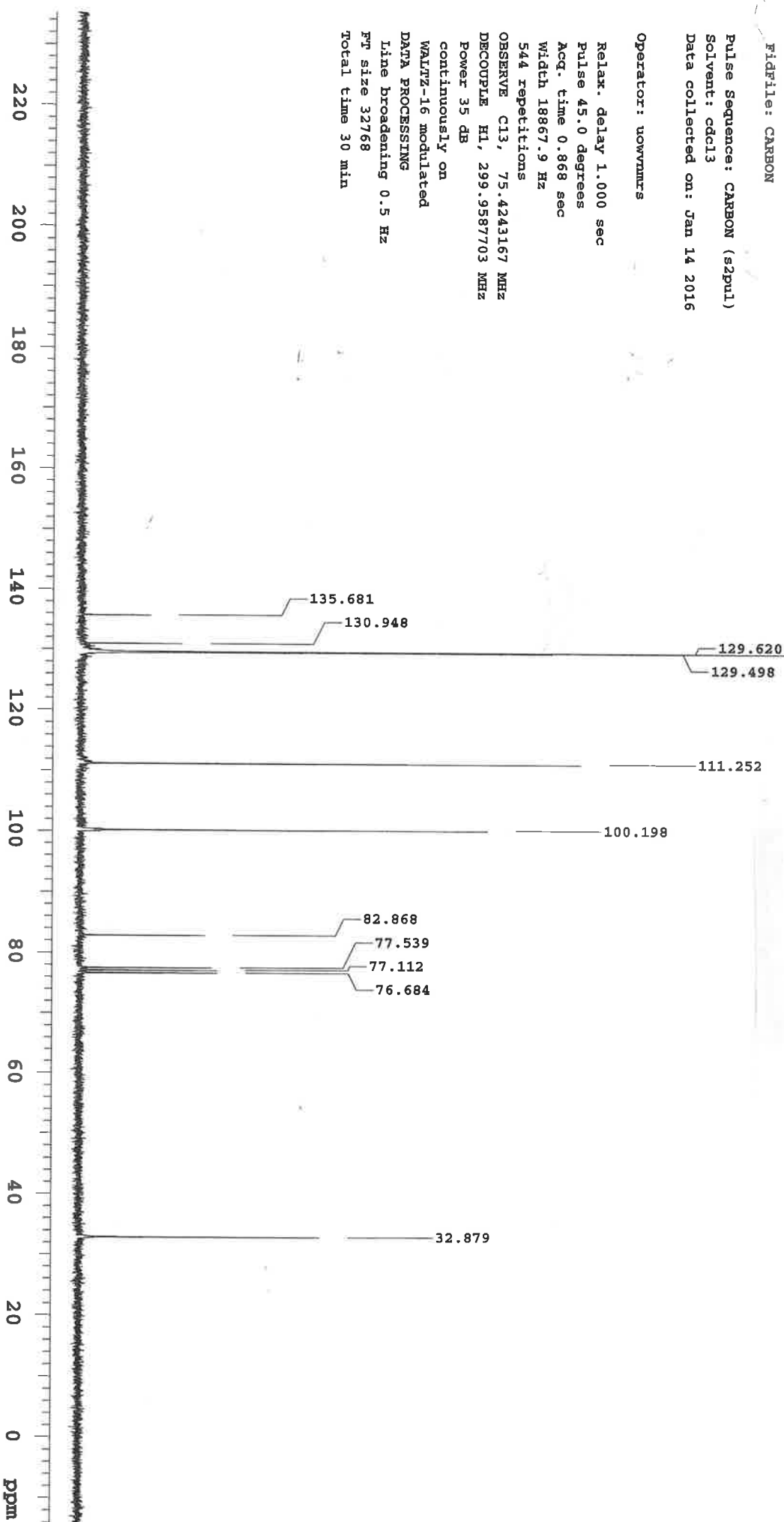
Line broadening 0.5 Hz

FT size 32768

Total time 30 min



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jxy150521_2.yjk_635_PROTON

Sample Name:
jxy150521_2.yjk_635
Data Collected on:
ernst.sci.uow.edu.au-inova500
Archive directory:

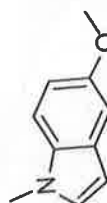
Sample directory:

Fidfile: PROTON

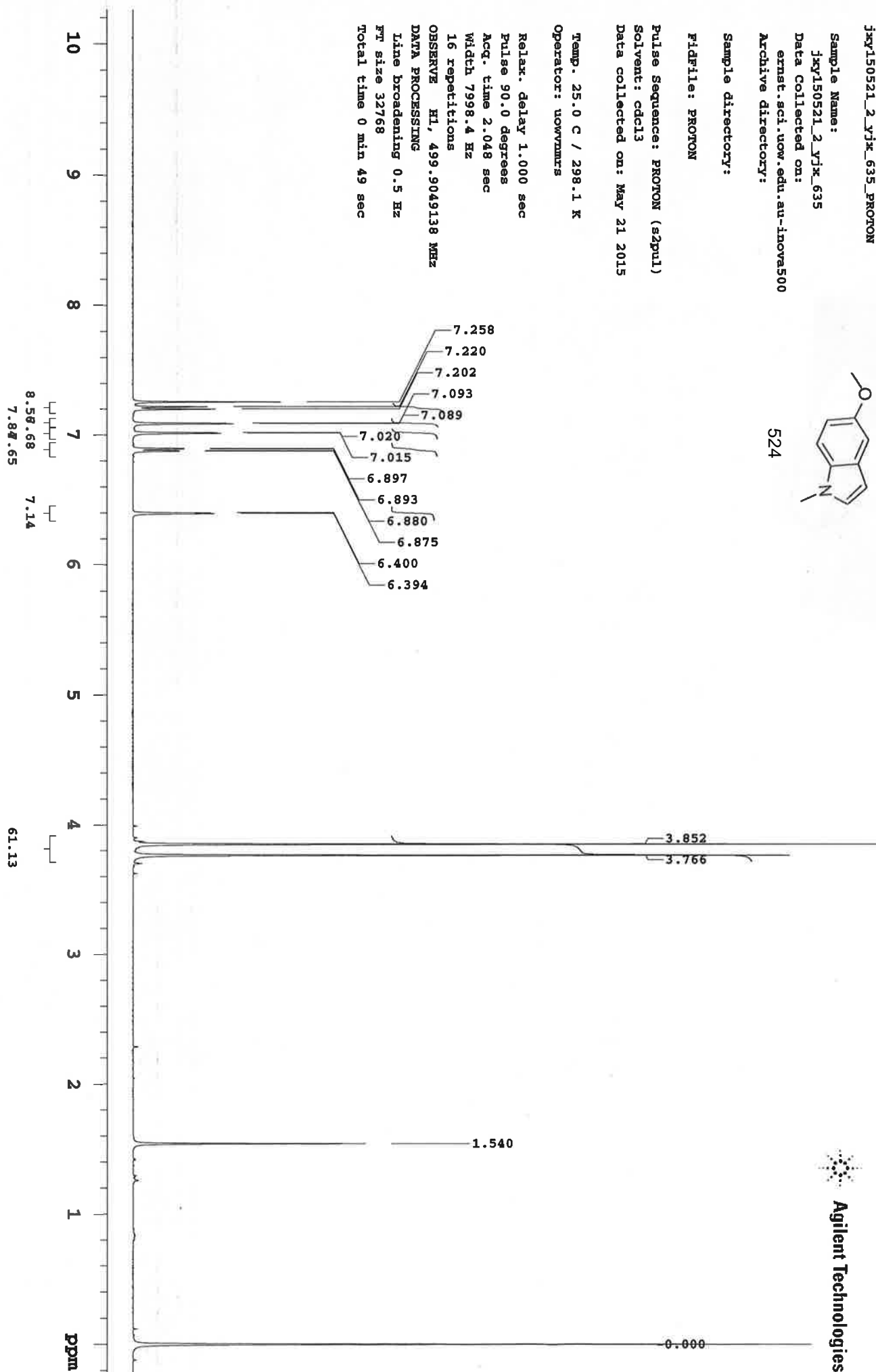
Pulse Sequence: PROTON (szpul)
Solvent: cdcl3
Data collected on: May 21 2015

Temp. 25.0 C / 298.1 K
Operator: uowmms

Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 2.048 sec
Width 7998.4 Hz
16 repetitions
OBSERVE H1, 499.9049138 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 0 min 49 sec



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jxy160114_2_yjk_5methoxymethylindole_13c CARBON

Sample Name:

jxy160114_2_yjk_5methoxymethylindole_13c

Data Collected on:

bloch.sci.nov.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jan 14 2016

Operator: uowymms

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

448 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

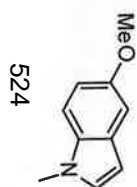
WALTZ-16 modulated

DATA PROCESSING

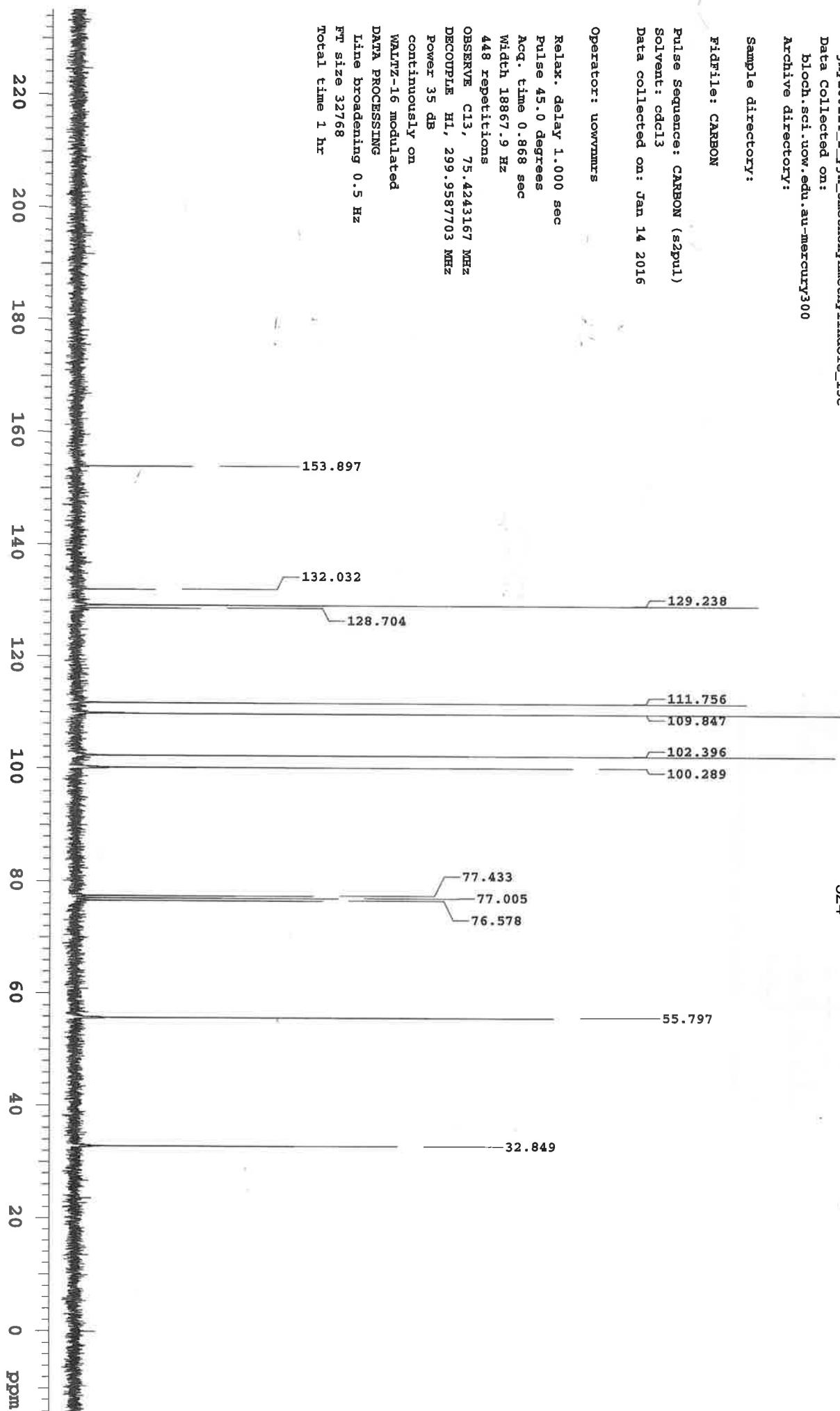
Line broadening 0.5 Hz

FT size 32768

Total time 1 hr

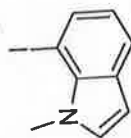


Agilent Technologies



jxy150521_2_vjk_634_cp_PROTON

Sample Name:
jxy150521_2_vjk_634_cp
Data Collected on:
ernst.sci.uow.edu.au-inova500
Archive directory:



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Agilent Technologies

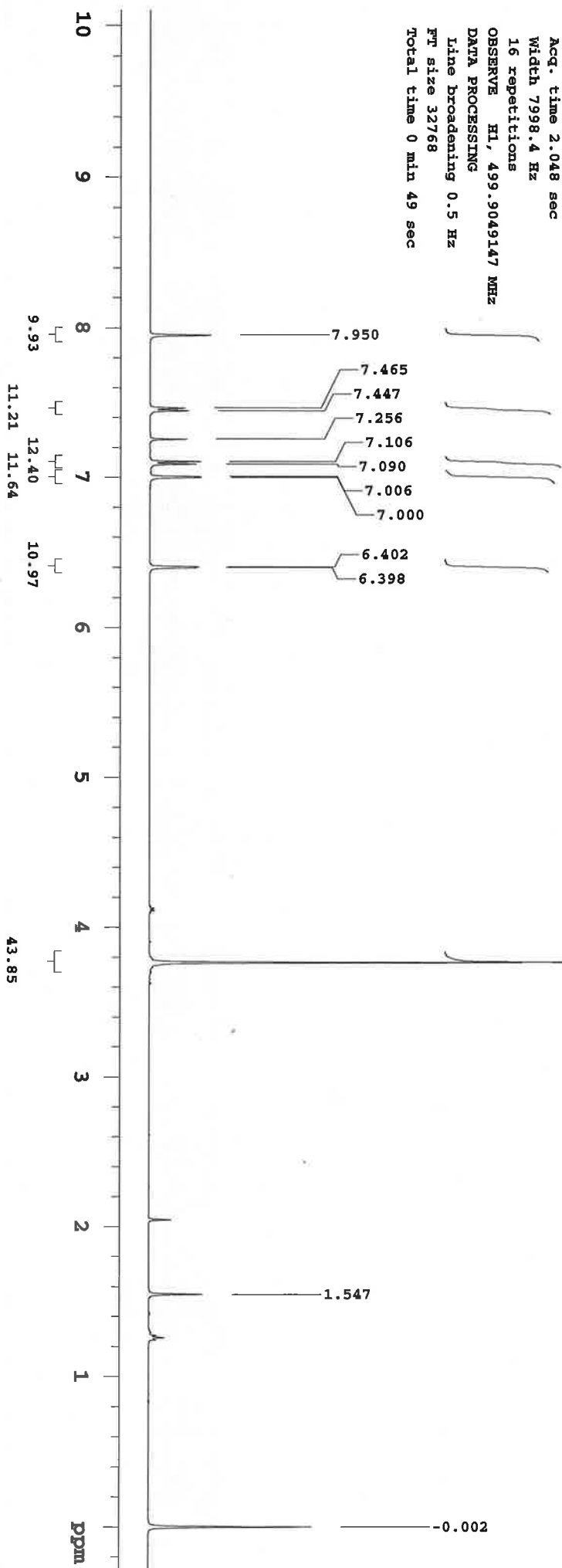
Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (szpu1)
Solvent: cdcl3
Data collected on: May 21 2015

Temp. 25.0 C / 298.1 K
Operator: uowymms

Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 2.048 sec
Width 7998.4 Hz
16 repetitions
OBSERVE H1, 499.9049147 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 0 min 49 sec



jxy160114_2_yjx_7iodomethylindole_13c_CARBON

Sample Name:
jxy160114_2_yjx_7iodomethylindole_13c
Data Collected on:
bloch.sci.uow.edu.au-mercury300
Archive directory:

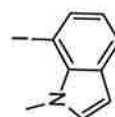
Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pu1)
Solvent: cdcl3
Data collected on: Jan 14 2016

Operator: uowymms

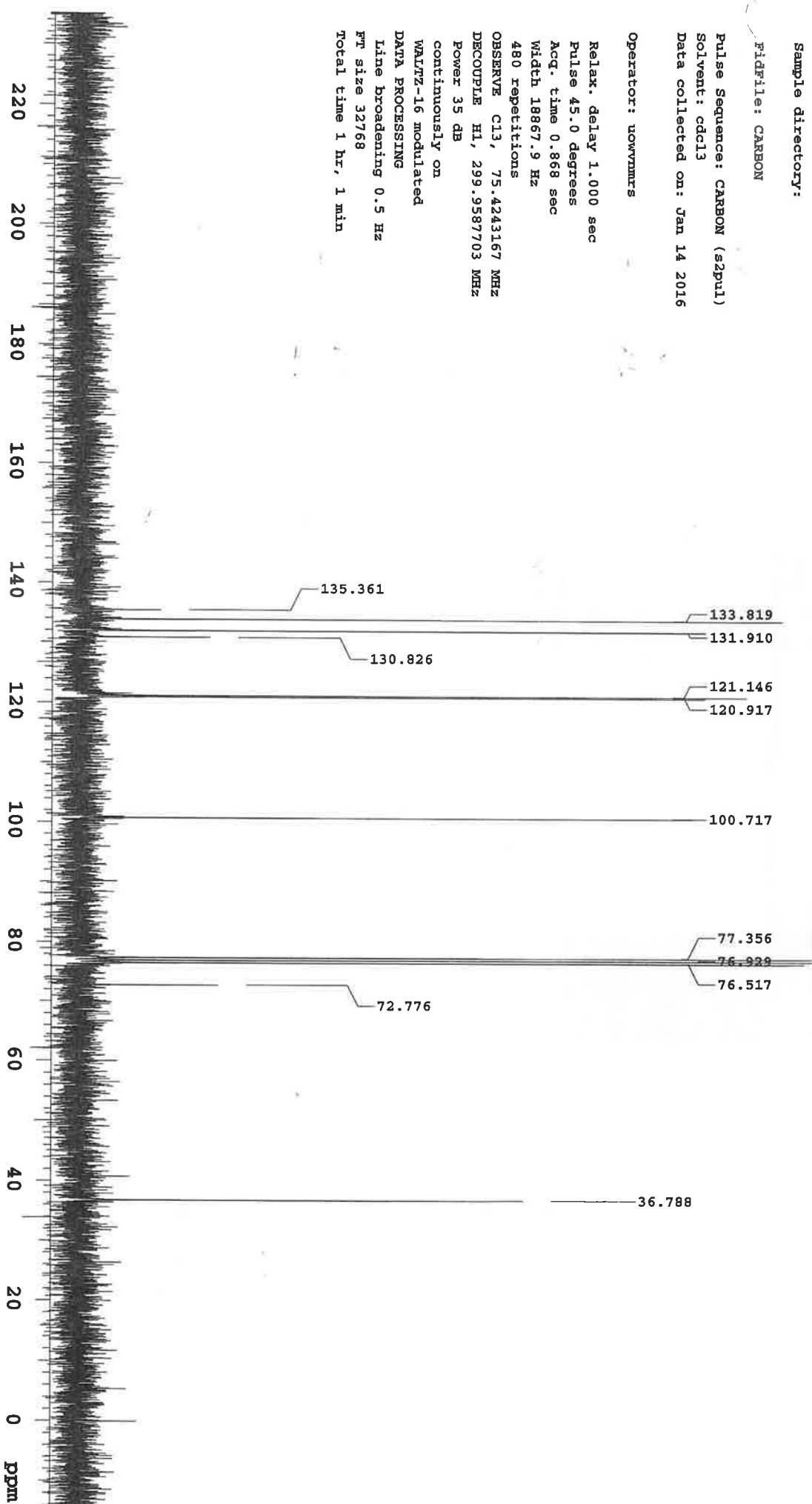
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
480 repetitions
OBSERVE C13, 75.4243167 MHz
DECOUPLE H1, 299.9587703 MHz
Power 35 dB
continously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 1 hr, 1 min



525



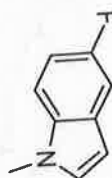
Agilent Technologies



jxy150521_2.yjk_638_cp_PROTON

Sample Name:
jxy150521_2.yjk_638_cp
Data Collected on:
bloch.sci.uow.edu.au-mercury300
Archive directory:

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Agilent Technologies

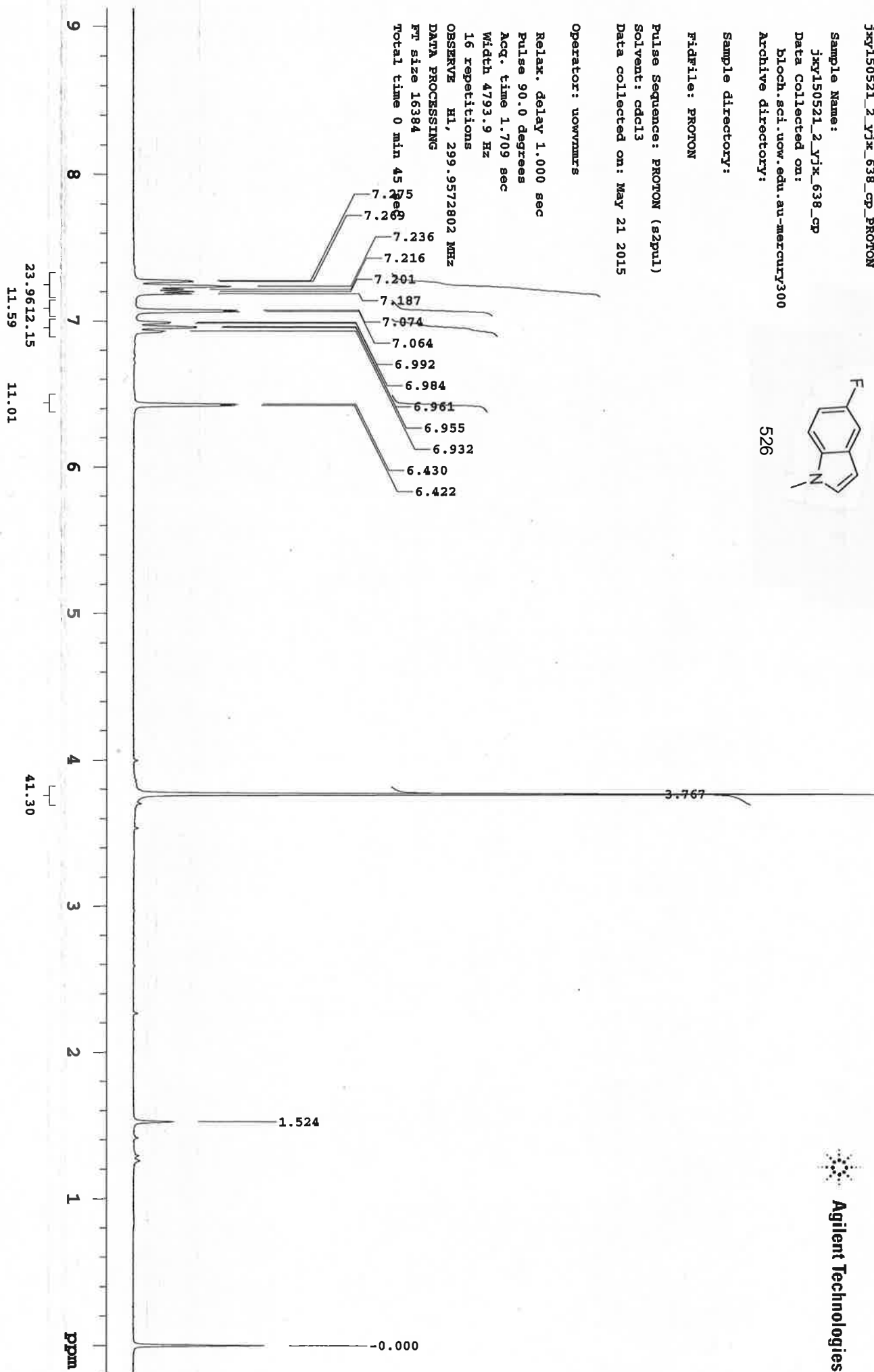
Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (szpu1)
Solvent: cdcl3
Data collected on: May 21 2015

Operator: uowvnmrs

Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 1.709 sec
Width 4793.9 Hz
16 repetitions
OBSERVE H1, 299.9572802 MHz
DATA PROCESSING
FT size 16384
Total time 0 min 45.266



jxy160114_2_yjx_5fluoromethylindole_13c_CARBON

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Agilent Technologies

Sample Name:
jxy160114_2_yjx_5fluoromethylindole_13c
Data Collected on:
bloch.sci.uow.edu.au-mercury300
Archive directory:

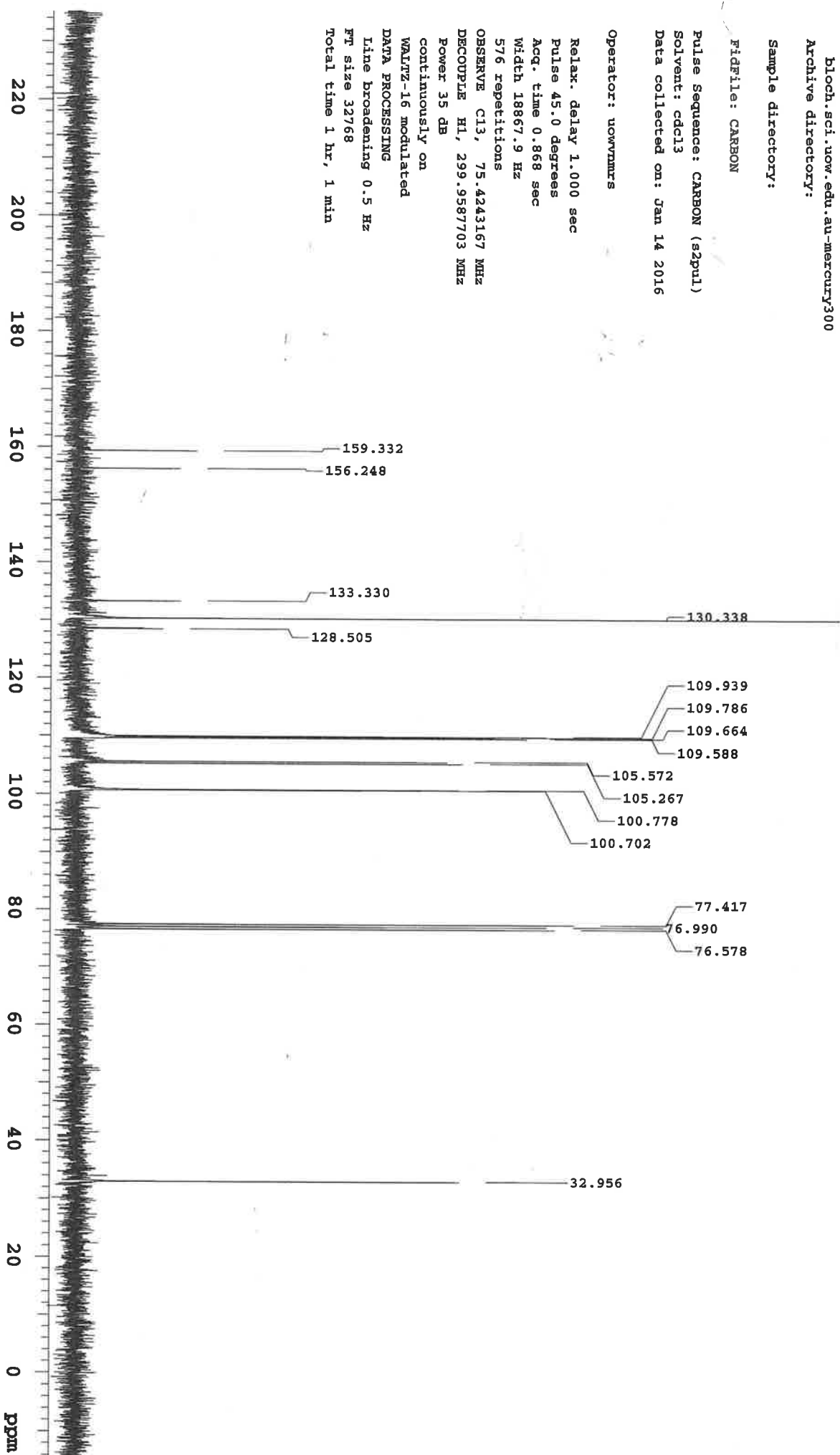
Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (szpu1)
Solvent: cdcl3
Data collected on: Jan 14 2016

Operator: uownmrs

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
576 repetitions
OBSERVE C13, 75.4243167 MHz
DECOUPLE H1, 299.9587703 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 1 hr, 1 min



jxy150527_2.yjk_639_1_PROTON

Sample Name:

jxy150527_2.yjk_639_1

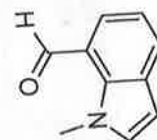
Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

527



Agilent Technologies

File: PROTON

Pulse Sequence: PROTON (szpul)

Solvent: cdcl3

Data collected on: May 27 2015

Temp. 25.0 C / 298.1 K

Operator: uowymrs

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 2.048 sec

Width 7998 Hz

16 repetitions

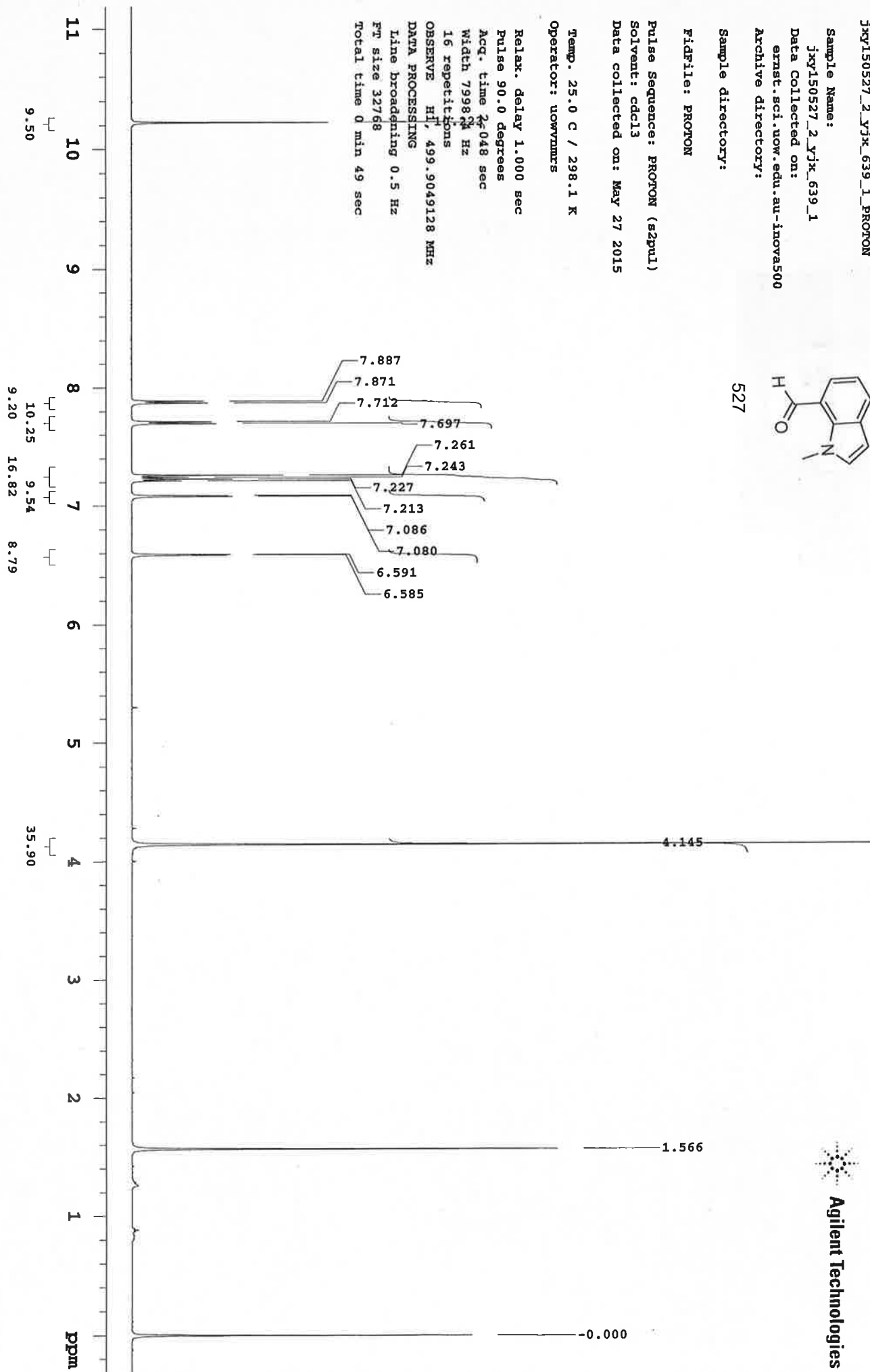
OBSERVE H1, 499.9049128 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 0 min 49 sec



jxy160114_2_yjx_7chomethylindole_13c-CARBON

Sample Name:

jxy160114_2_yjx_7chomethylindole_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2h1)

Solvent: cdcl3

Data collected on: Jan 14 2016

Operator: uownmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

480 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

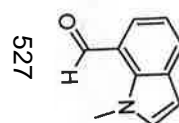
WALTZ-16 modulated

DATA PROCESSING

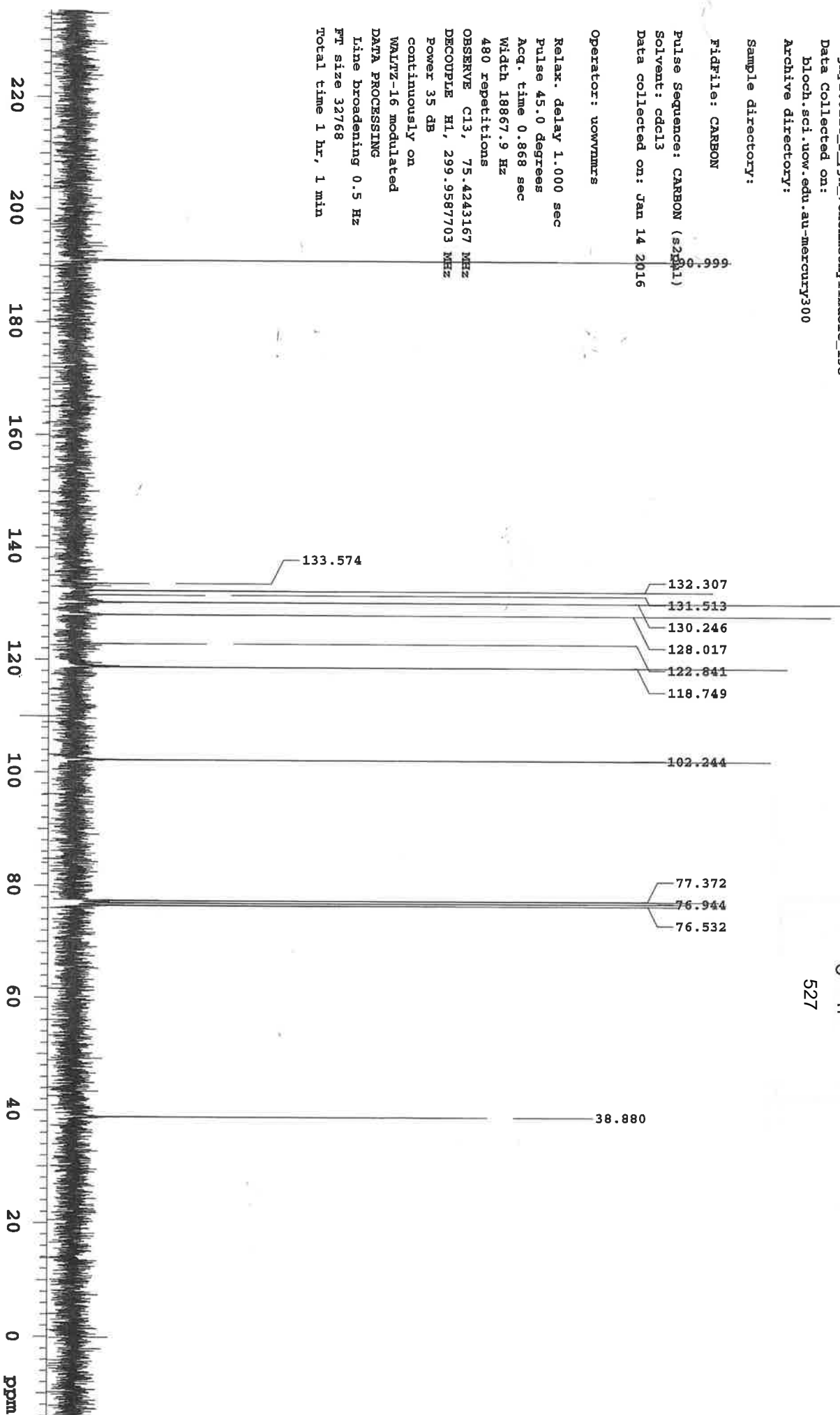
line broadening 0.5 Hz

FT size 32768

Total time 1 hr, 1 min



Agilent Technologies



jxy121219_2_yjx_64_cp_PROTON

exp1 PROTON

SAMPLE

PRESATURATION

date Dec 19 2012 satmode

n

solvent cdc13 wet

n

file exp

SPECIAL

ACQUISITION

temp 25.0

sw 7998.4

gain not used

at 2.048

spin not used

np 32768

hst 0.008

fb 4000

pw90 10.100

bs 16

alfa 10.000

dl 1.000

FLAGS

nt 16

il n

ct 16

in n

TRANSMITTER

dp y

tl 16

hs n

sfreq 499.908

PROCESSING

toe 499.9

lb 0.50

tpwr 60

fn not used

pw 10.100

DISPLAY

DECOUPLER

1 -73.7

dn 1

3975.3

doe 1

999.8

dm 1

0

decwa 1

23.0

decwa 1

-108.6

dpwr 37

lp

dcme 32258

PLOT

wc 250

sc 0

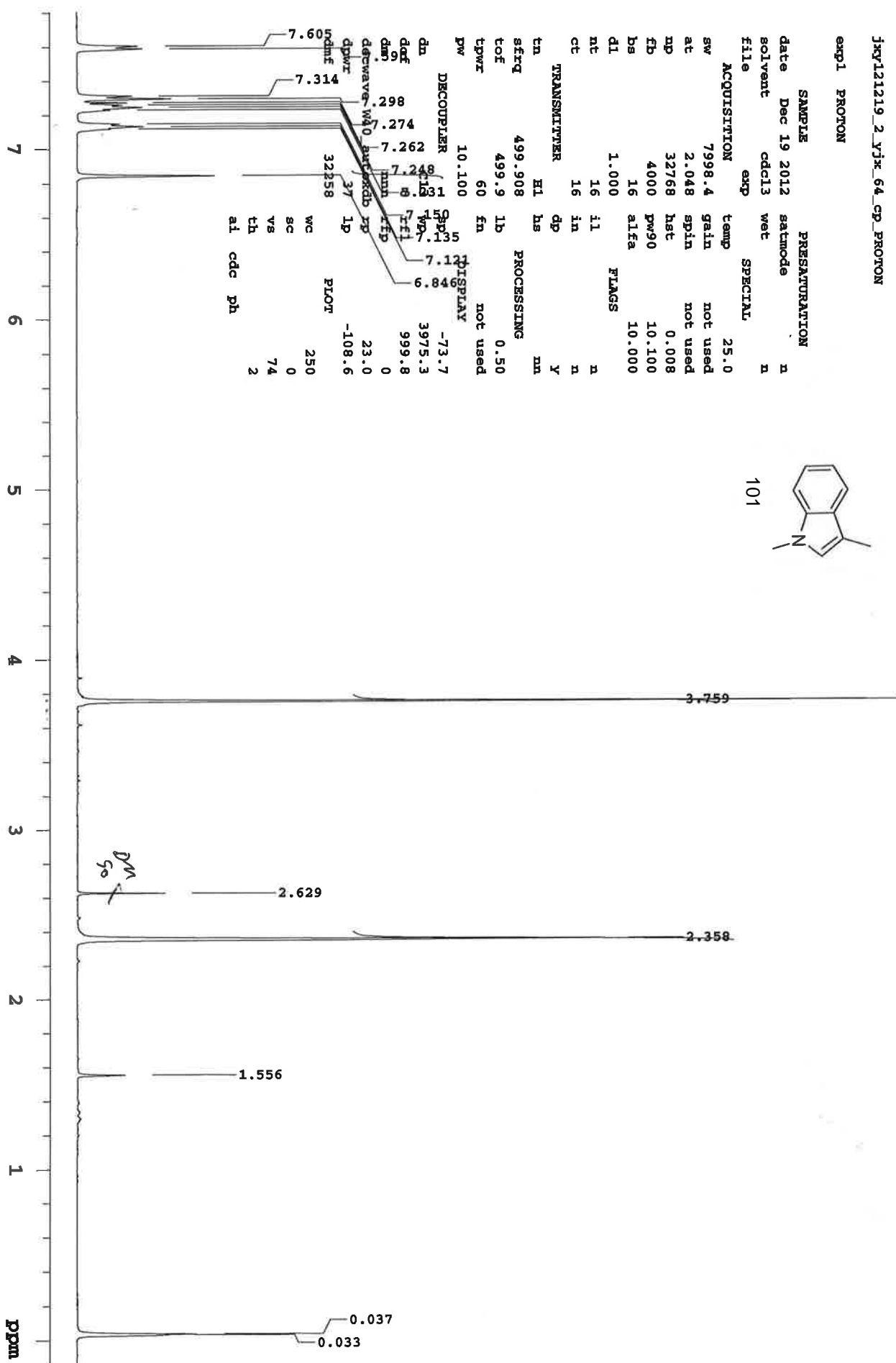
vs 74

th 2

ai cdc ph



101



jxy160114_2_vjx_dimethylindole_13c_CARBON

Sample Name:

jxy160114_2_vjx_dimethylindole_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jan 14 2016

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.521 sec

Width 31421.8 Hz

1544 repetitions

OBSERVE C13, 125.7011859 MHz

DECOUPLE H1, 499.9073947 MHz

Power 42 dB

continuously on

WALTZ-16 modulated

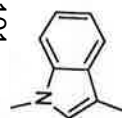
DATA PROCESSING

Line broadening 0.5 Hz

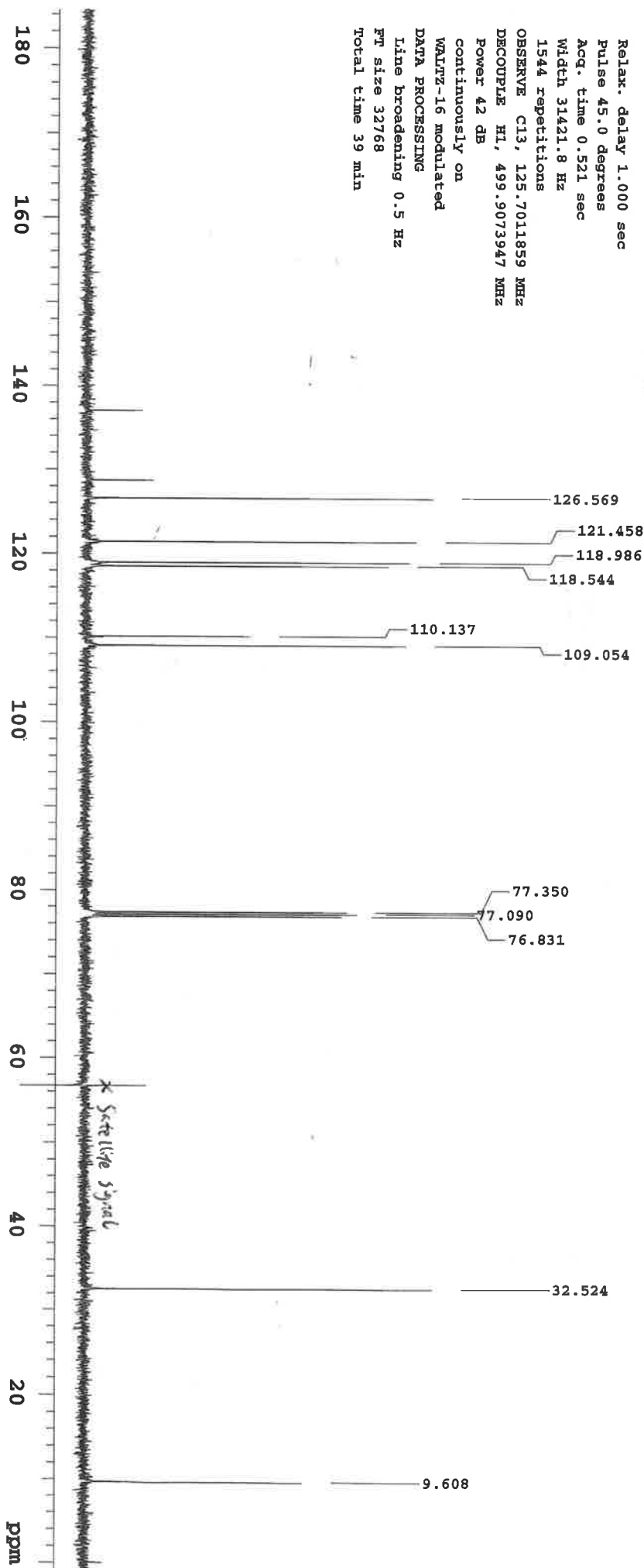
FT size 32768

Total time 39 min

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Agilent Technologies



jxy150429_2_vjx_checkpurity3_Proton

File: Proton

Pulse Sequence: s2pu1

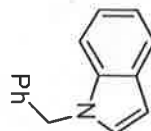
Solvent: cdc13

Temp: 2.0 C / 275.1 K

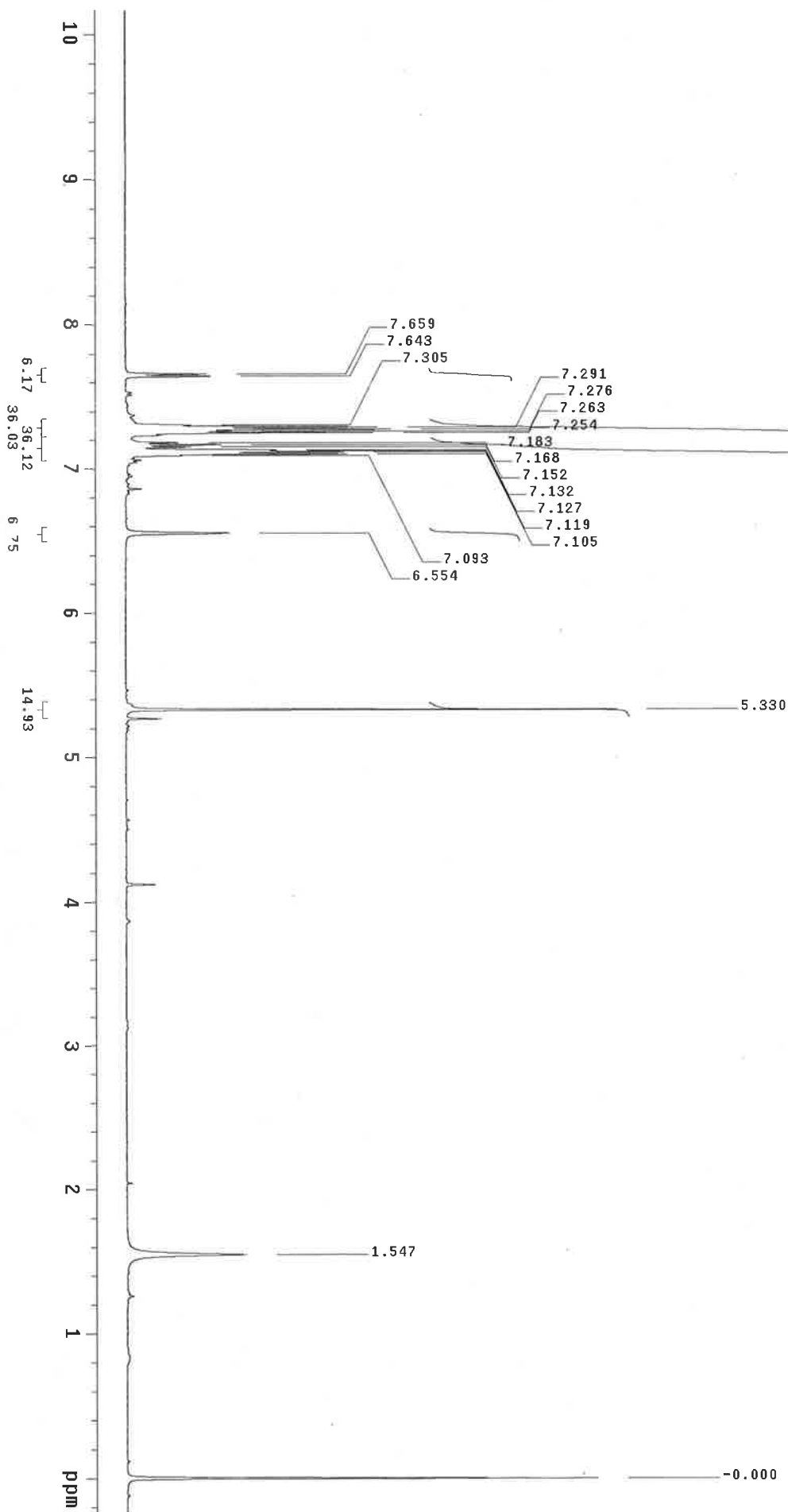
Operator: ucwvnmf2

VNMR5-500 "pyne06.domain.com"

528



Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 2.045 sec
Width 8012.8 Hz
16 repetitions
OBSERVE H1, 499.7413975 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 48 sec



jxy160114_2_yjk_nbenzylindole_13c_CARBON

Sample Name:

jxy160114_2_yjk_nbenzylindole_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jan 14 2016

Operator: uowymms

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

320 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

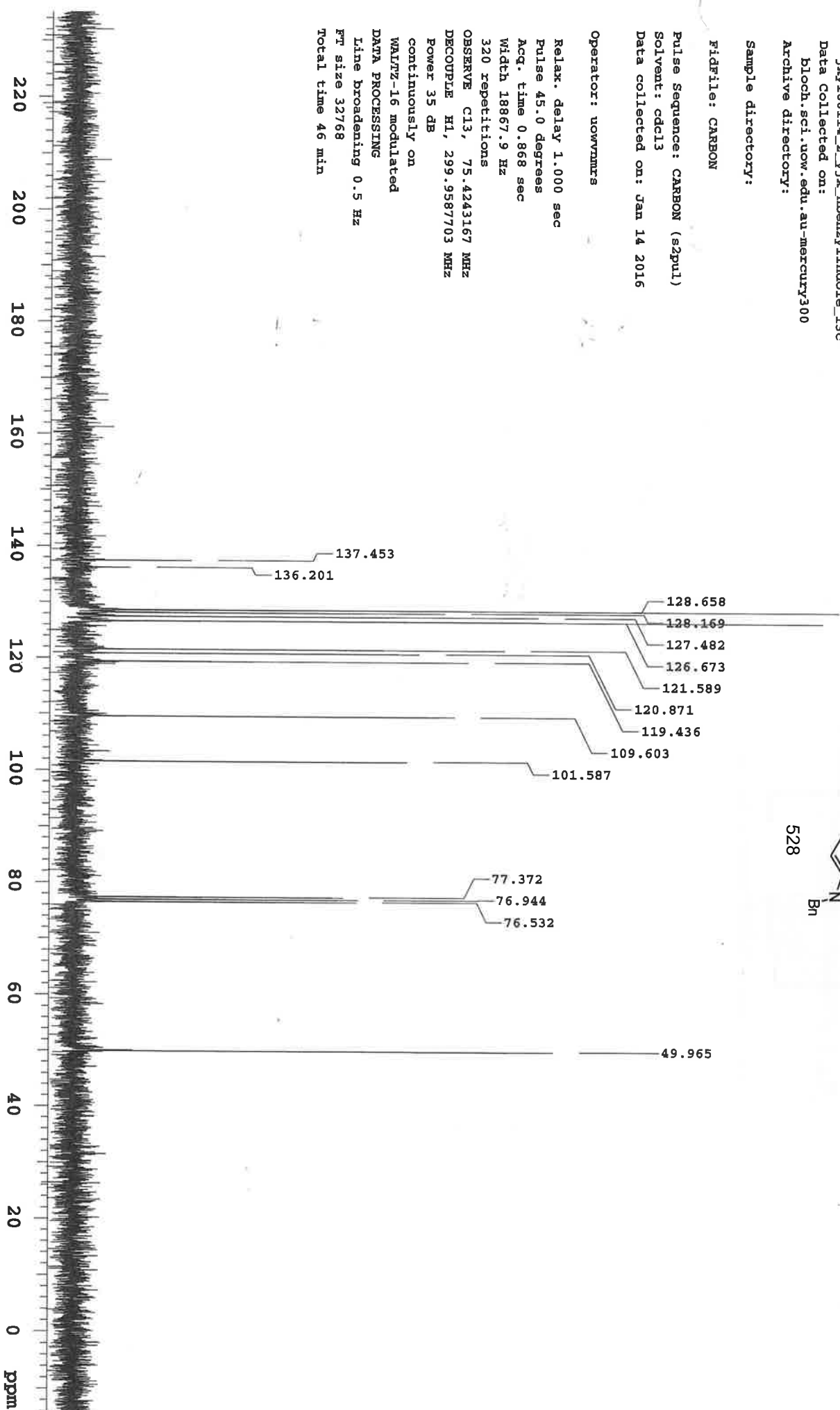
WALTZ-16 modulated

DATA PROCESSING

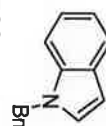
Line broadening 0.5 Hz

FT size 32768

Total time 46 min

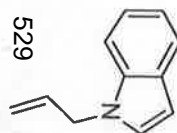


528



Agilent Technologies

Sample Name: jxy150506_2_yjk_619_1
Data Collected on: ernst.sci.uow.edu.au-inova500
Archive directory:



Agilent Technologies

Fidfile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 6 2015

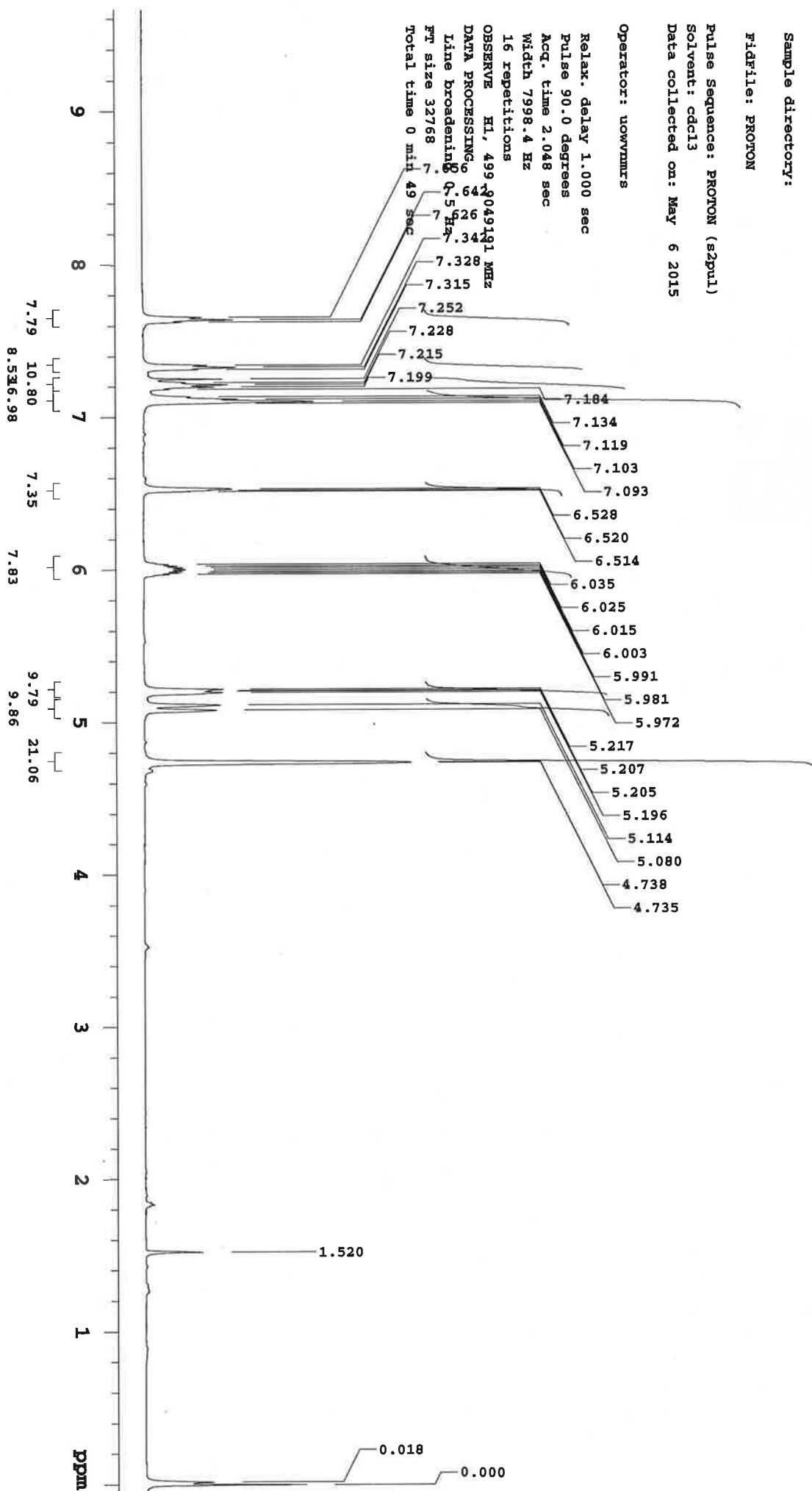
Operator: nowvmlrs

Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 2.048 sec
Width 7998.4 Hz
16 repetitions

```

OBSERVE      H1, 499      9049191 MHz
DATA PROCESSING 0.64 0.26
Line broadening 0.5 Hz 7.328
FW size 32768 7.315
Total time 0 min 49 sec

```



jxy160114_2_yjx_nallylindole_13c CARBON

Sample Name:
jxy160114_2_yjx_nallylindole_13c
Data Collected on:
bloch.sci.uow.edu.au-mercury300
Archive directory:

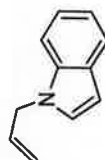
Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jan 14 2016

Operator: uowymms

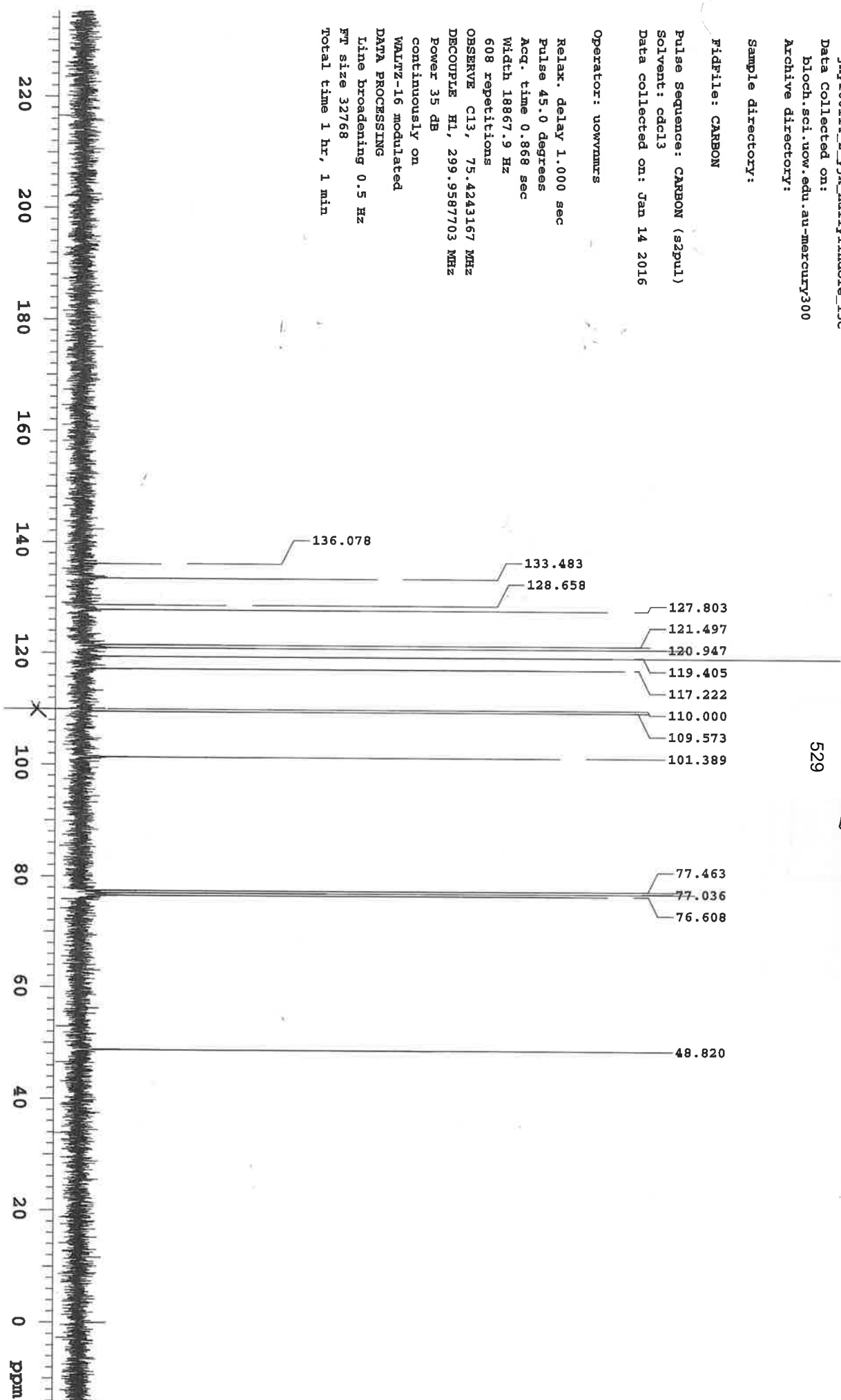
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
608 repetitions
OBSERVE C13, 75.4243167 MHz
DECOUPLE H1, 299.9587703 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
line broadening 0.5 Hz
FT size 32768
Total time 1 hr, 1 min



529



Agilent Technologies



jxy140227_2_yjk_327_1_PROTON

Sample Name:

jxy140227_2_yjk_327_1

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

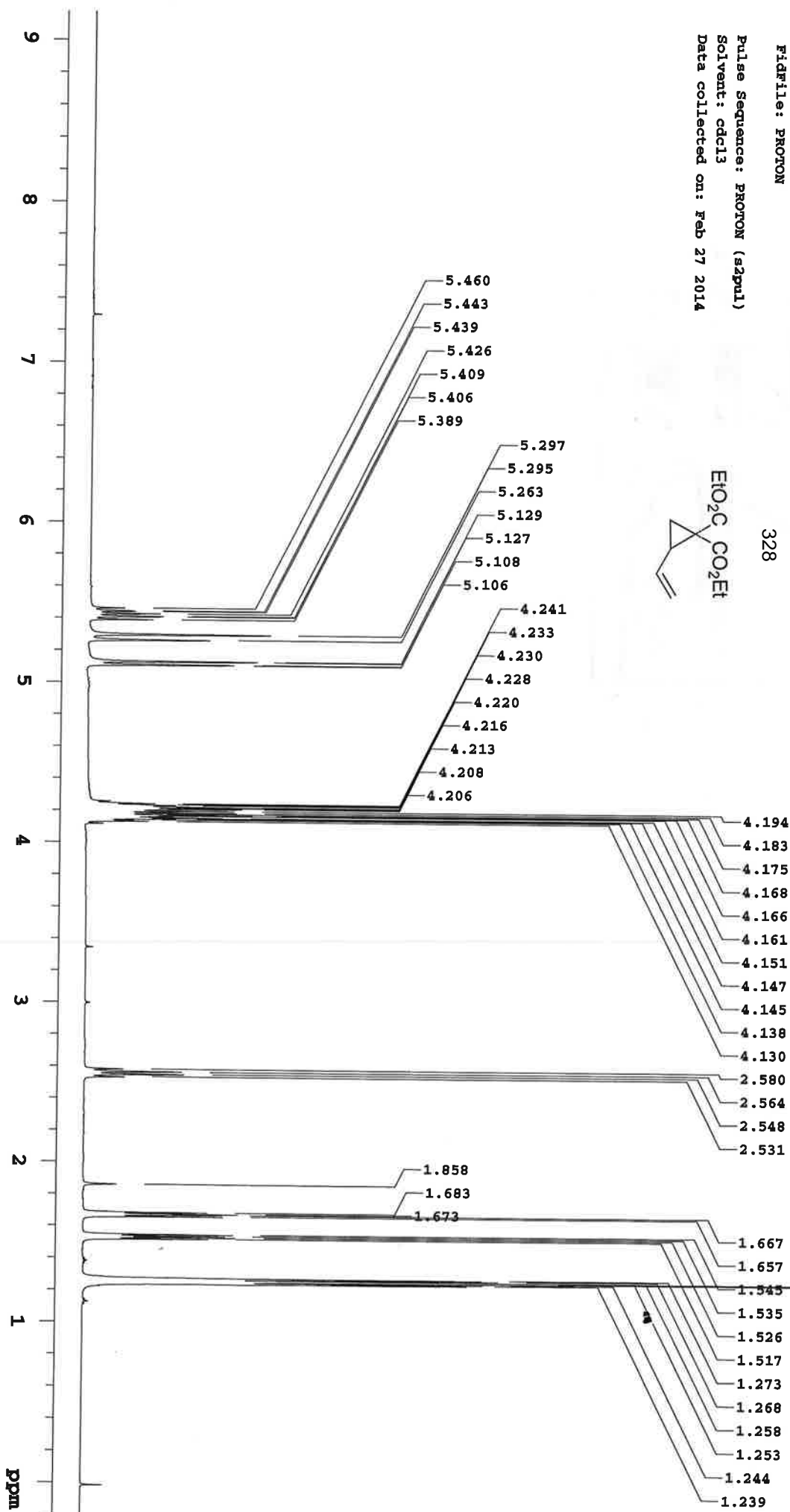
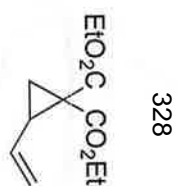
Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Feb 27 2014



jxy160114_2_yjk_vinylcyclopropane_13c-CARBON

Sample Name:

jxy160114_2_yjk_vinylcyclopropane_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jan 14 2016

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

320 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

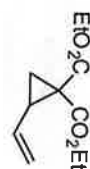
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

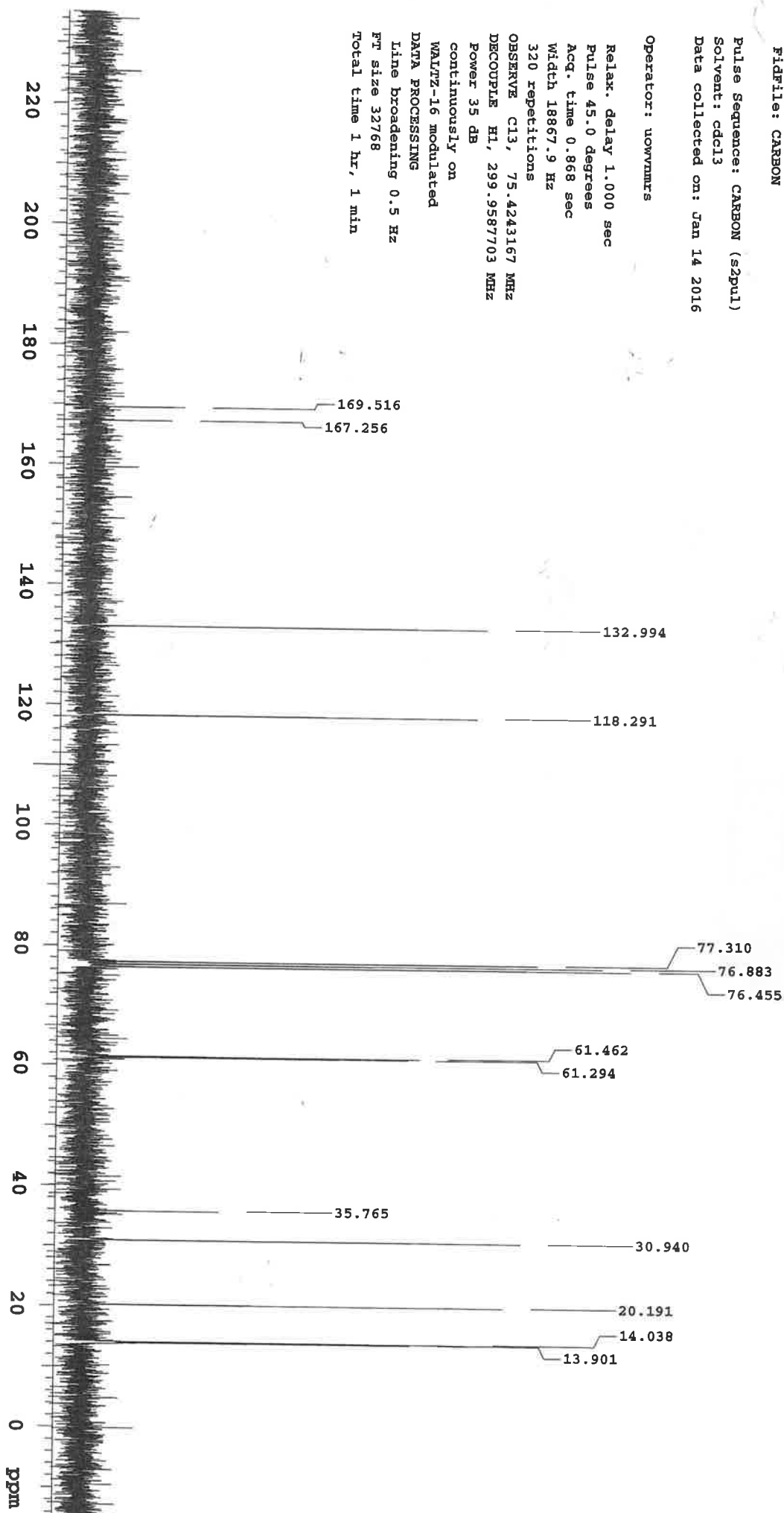
Total time 1 hr, 1 min



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Agilent Technologies



jxy140414_2_vjk_349_1_PROTON

Sample Name:

jxy140414_2_vjk_349_1

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (szpul)

Solvent: cdcl3

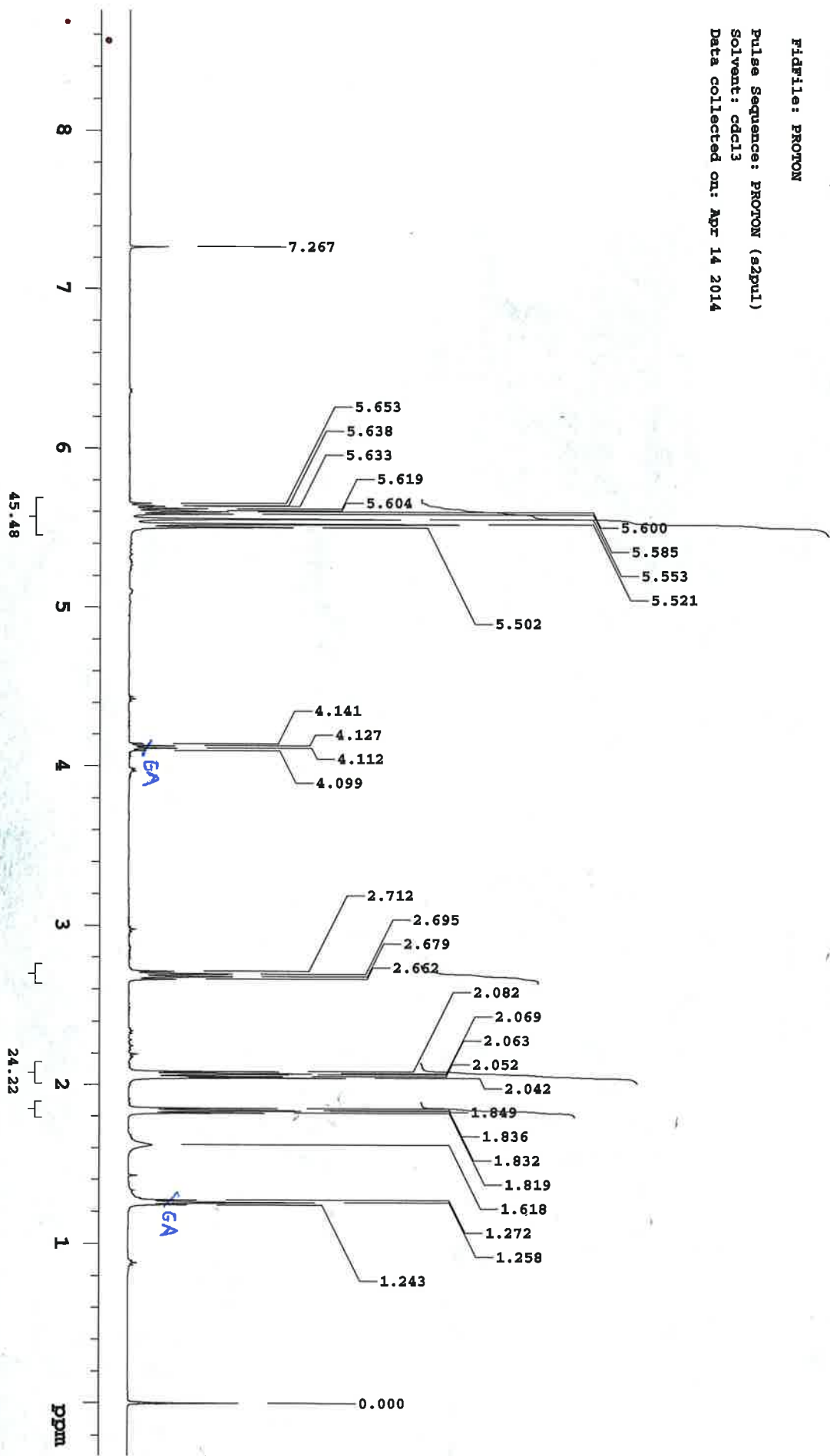
Data collected on: Apr 14 2014



530



Agilent Technologies



jxy160118_2_yjx_cyanovinylcyclopropane_1_13c CARBON

Sample Name:

jxy160118_2_yjx_cyanovinylcyclopropane_1_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (szpul)

Solvent: cdcl3

Data collected on: Jan 18 2016

Operator: nowmms

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

1056 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

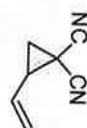
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

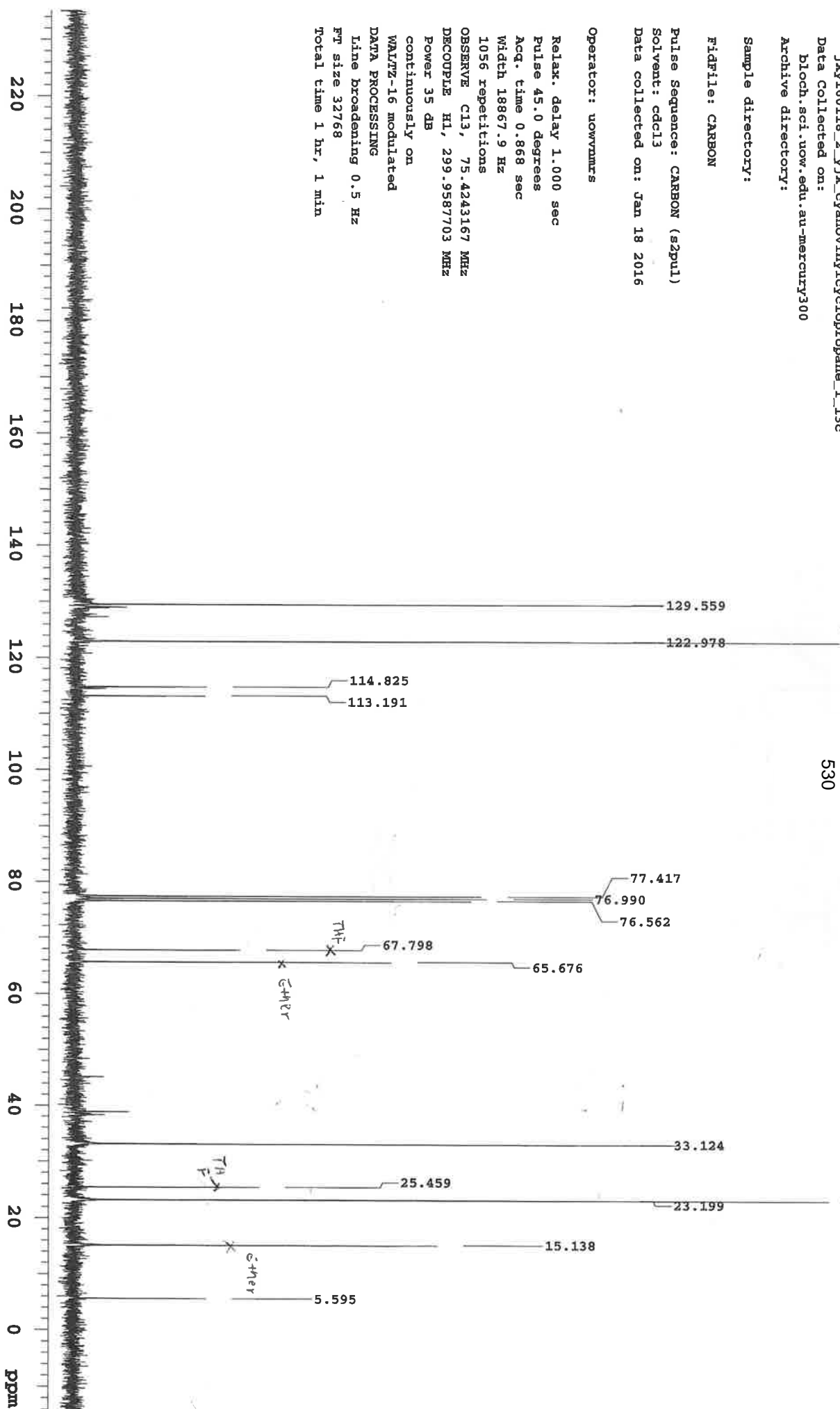
Total time 1 hr, 1 min



530



Agilent Technologies



File: Proton

Pulse Sequence: s2pu1

Solvent: cdcl3

Temp: 25.0 C / 298.1 K

Operator: uowvmrs

VNMRS-500 "pyne06.domain.com"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 2.045 sec

Width 8012.8 Hz

16 repetitions

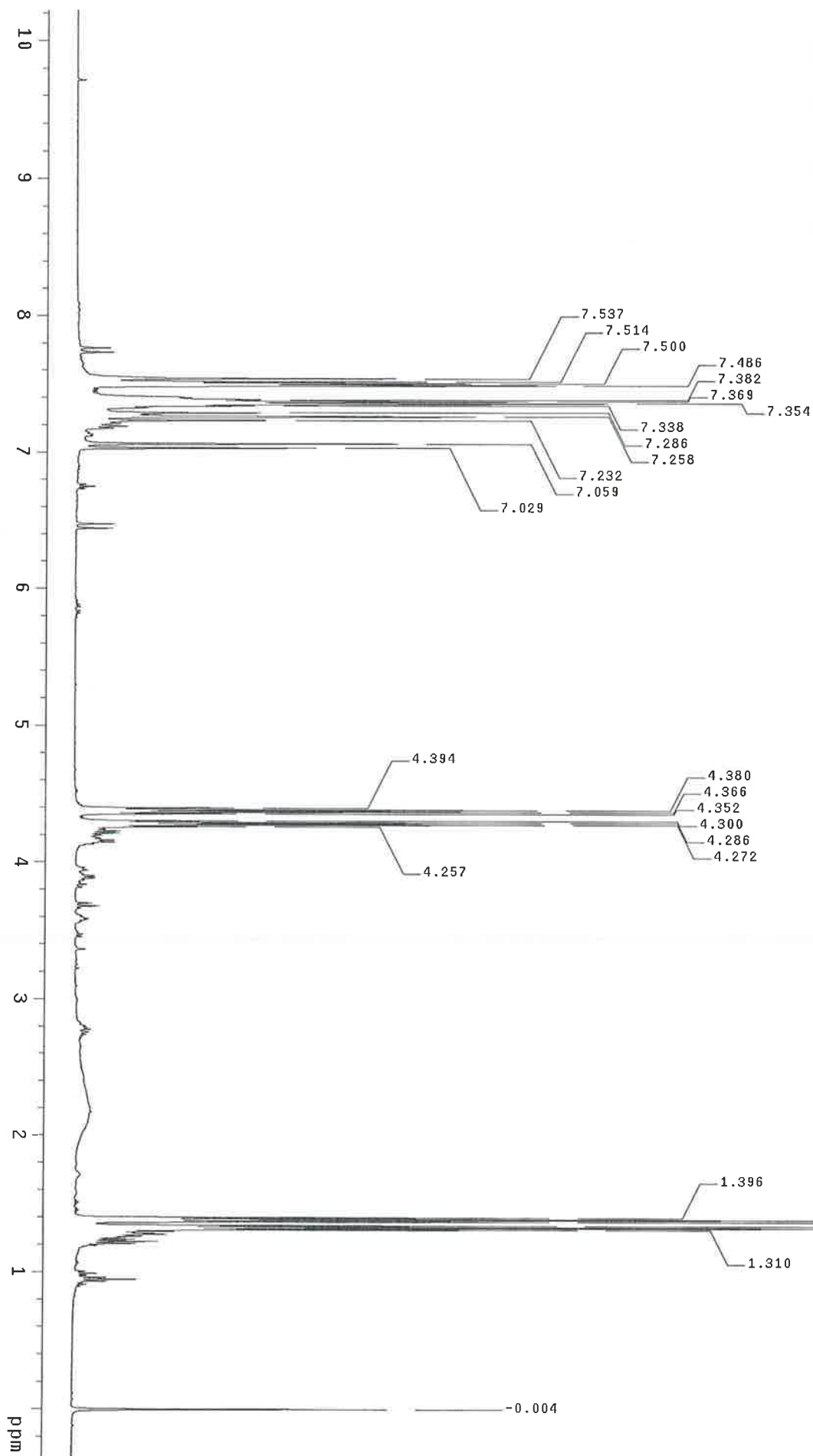
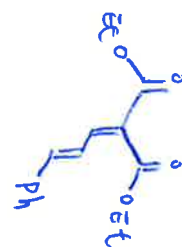
OBSERVE H1, 499.7412053 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 0 min, 48 sec



jxy140331_2.yjk_341_1_PROTON

Sample Name:

jxy140331_2.yjk_341_1

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

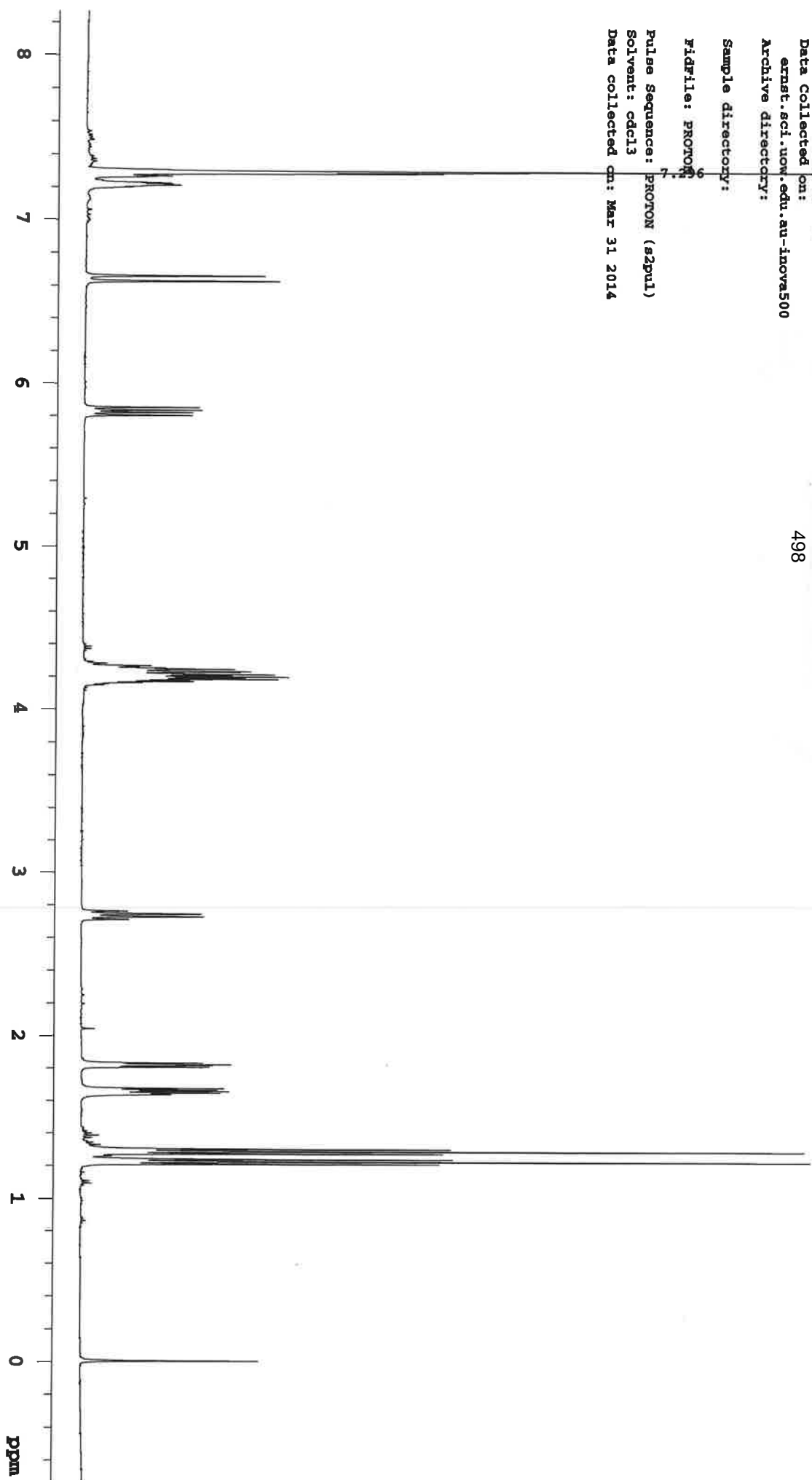
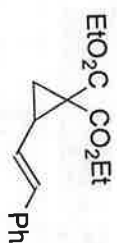
Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Mar 31 2014



jxy140331_2_yjk_341_1-CARBON

Sample Name:

jxy140331_2_yjk_341_1

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

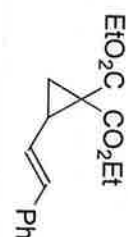
Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (szpul)

Solvent: cdcl3

Data collected on: Mar 31 2014

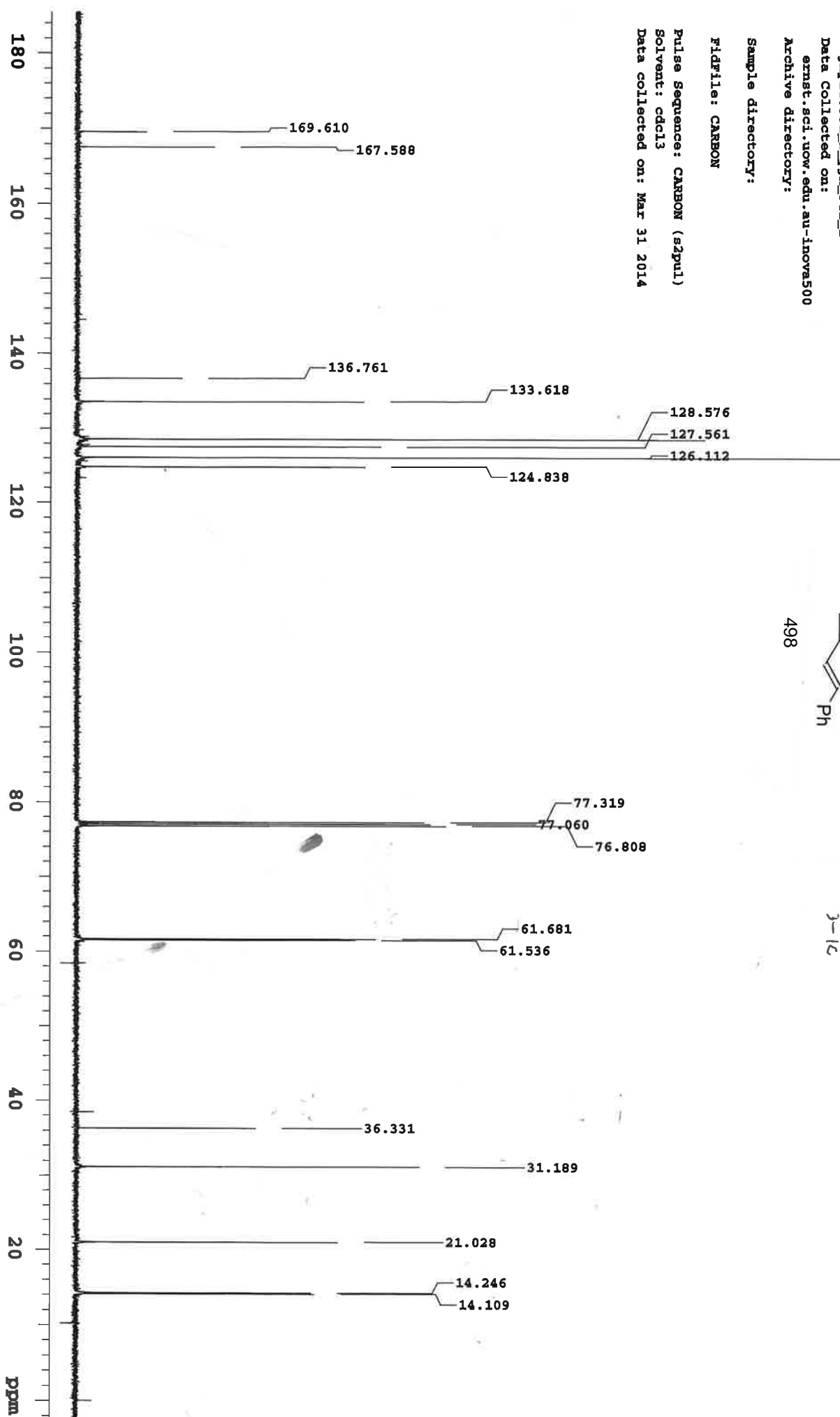


498

3-1c



Agilent Technologies



jxy140517_2.yjk_268_3_PROTON

Sample Name:

jxy140517_2.yjk_268_3

Data Collected on:

bloch.scl.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: May 17 2014

Operator: nowvnmrs

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 3.416 sec

Width 4796.2 Hz

16 repetitions

OBSERVE H1, 299.9572767 MHz

DATA PROCESSING

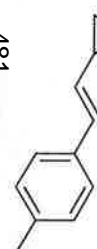
Line broadening 0.5 Hz

FT size 32768

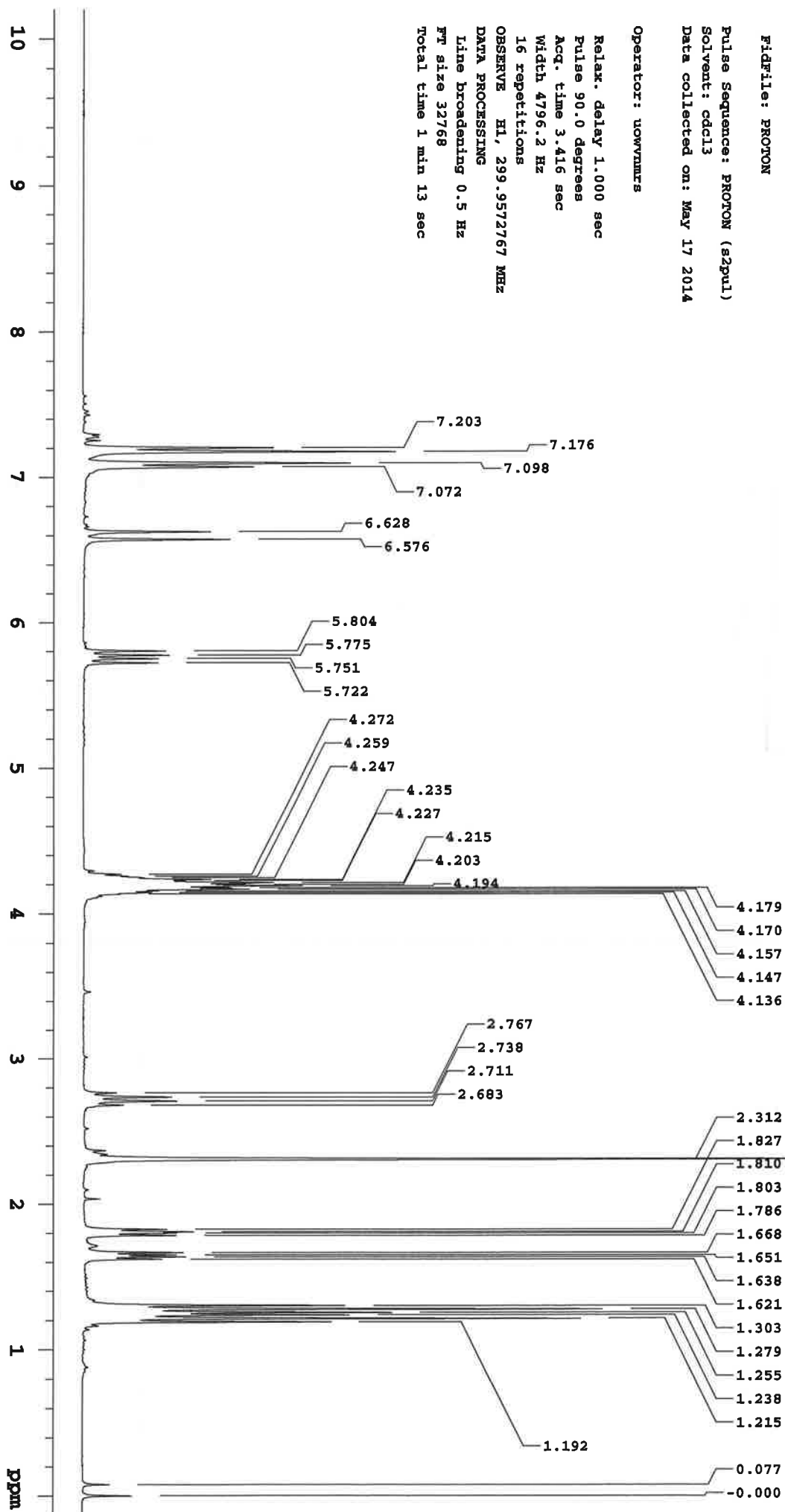
Total time 1 min 13 sec

EtO₂C CO₂Et

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Agilent Technologies



jxy140517_2_yjx_268_3_13c CARBON

Sample Name:

jxy140517_2_yjx_268_3_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: May 17 2014

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

1472 repetitions

OBSERVE C13, 75.4242951 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

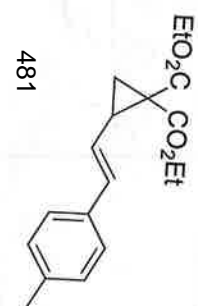
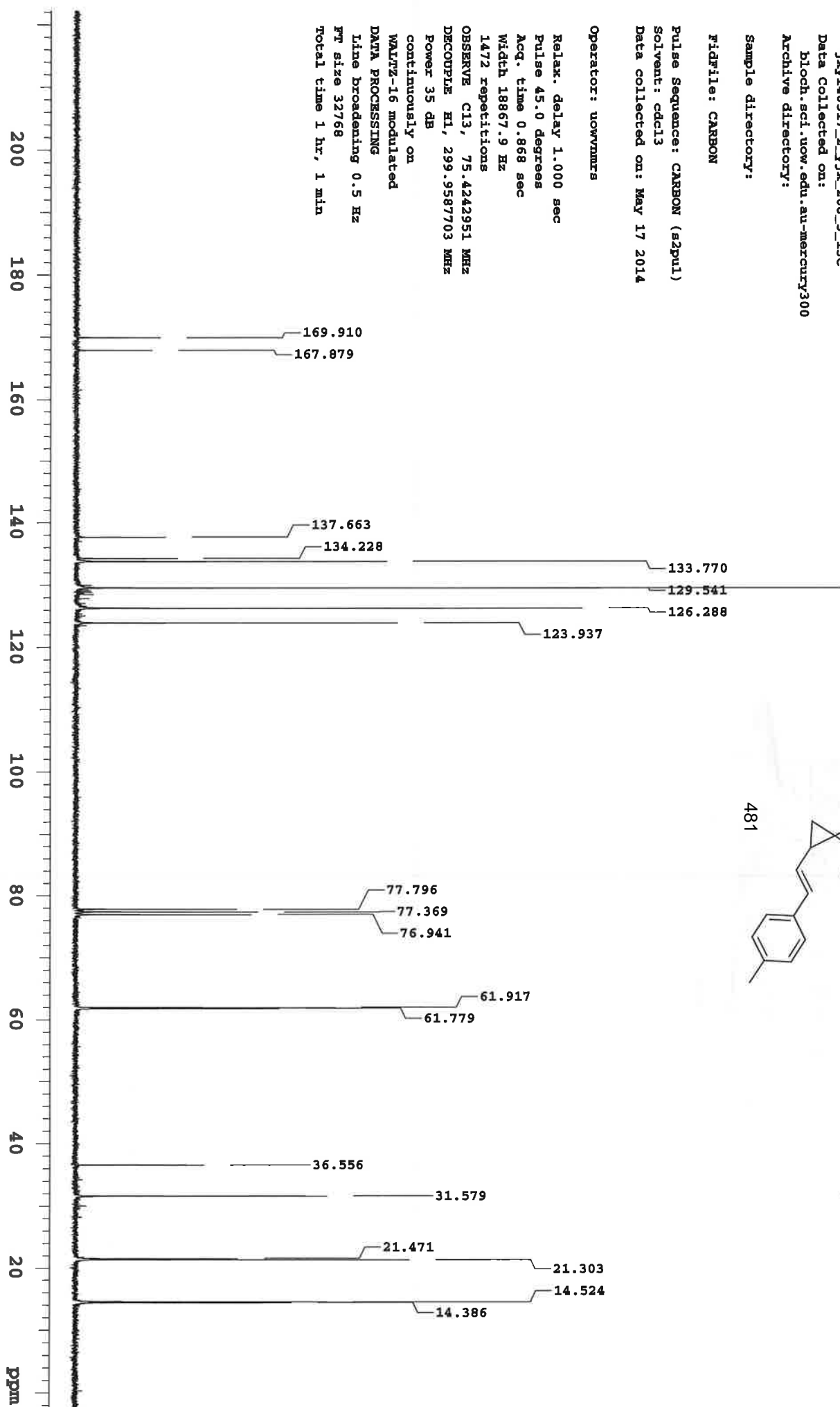
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 1 hr, 1 min



Agilent Technologies

jxy140518_2.yjk_269_1_PROTON

Sample Name:

jxy140518_2.yjk_269_1

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (szpu1)

Solvent: cdcl3

Data collected on: May 18 2014

Operator: uowmmrs

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 3.416 sec

Width 4796.2 Hz

16 repetitions

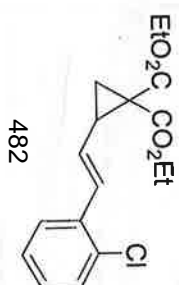
OBSERVE H1, 299.9572741 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 1 min 13 sec



jxy140518_2.yjk_269_1_13c CARBON

Sample Name:

jxy140518_2.yjk_269_1_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: May 18 2014

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

1280 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

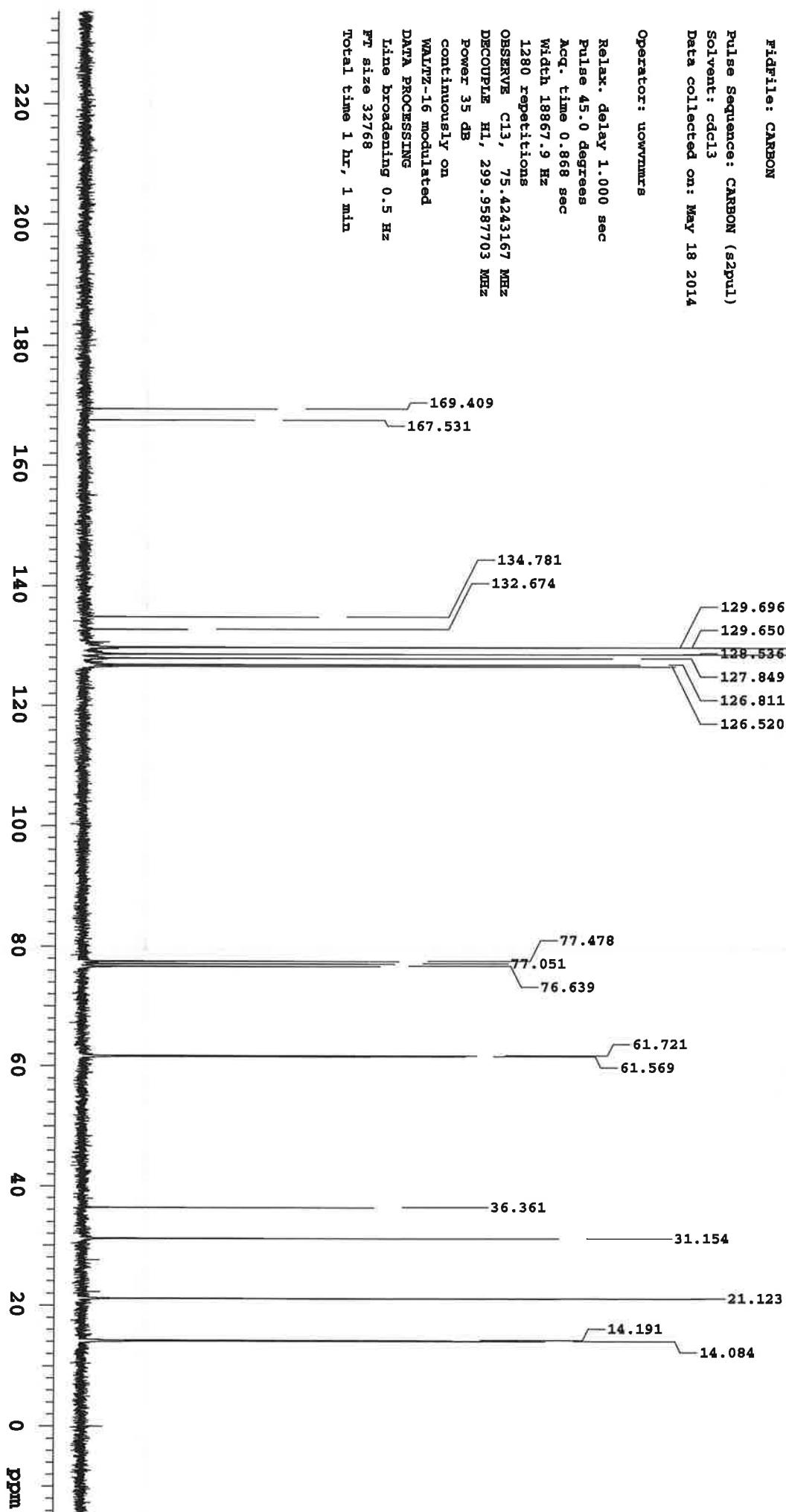
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 1 hr, 1 min



Agilent Technologies

jxy140521_2_vjk_371_2_PROTON

Sample Name:

jxy140521_2_vjk_371_2

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

File: PROTON

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: May 21 2014

Temp. 25.0 C / 298.1 K

Operator: uowmms

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 3.144 sec

Width 5211.0 Hz

16 repetitions

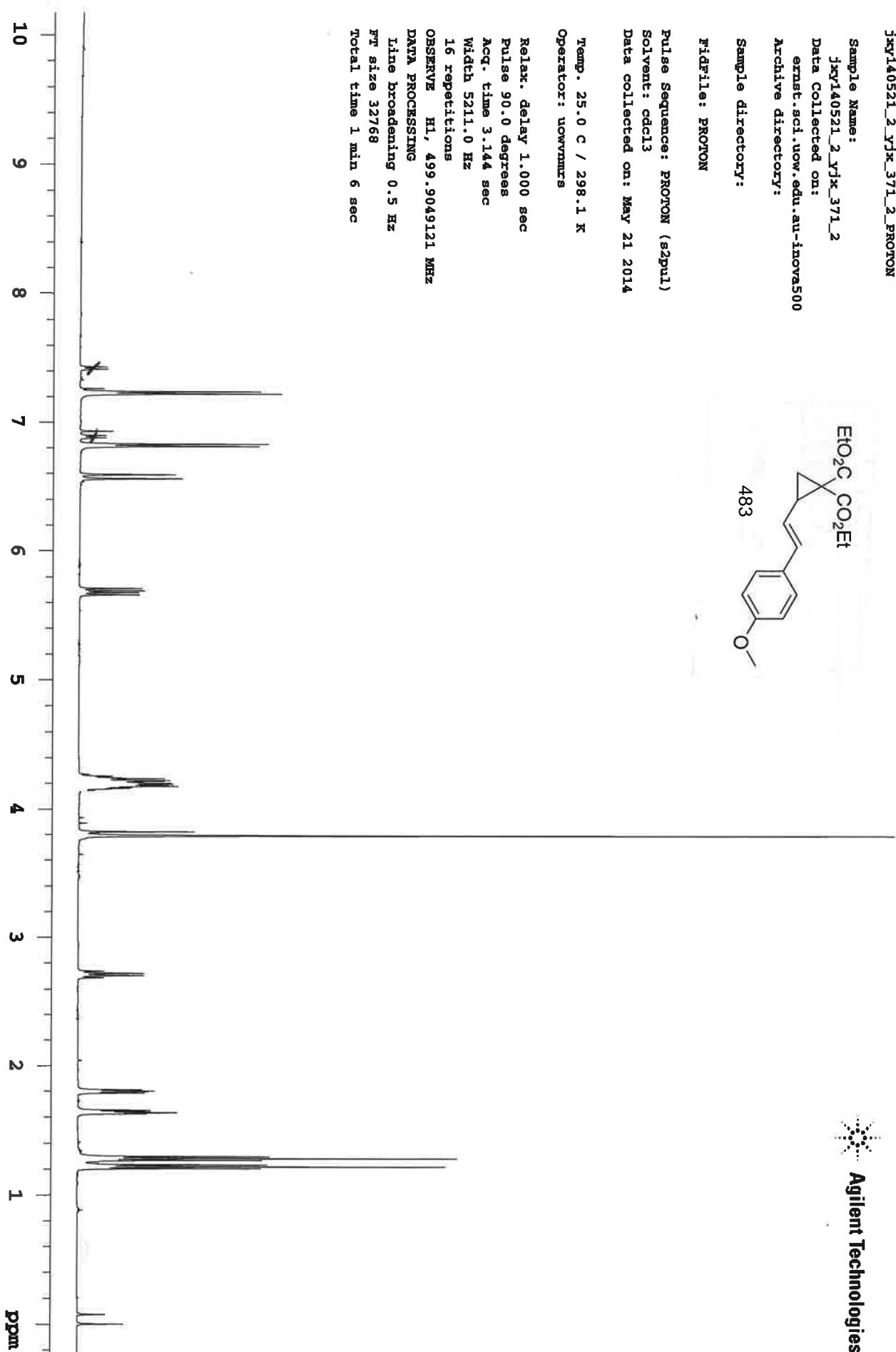
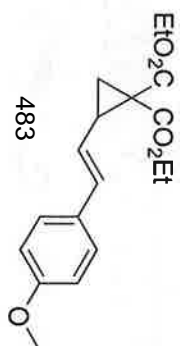
OBSERVE H1, 499.9049121 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 1 min 6 sec



jxy140521_2.yjk_371_2_13c CARBON

Sample Name:

jxy140521_2.yjk_371_2_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: jxy140521_2.yjk_371_2_13c CARBON

Pulse Sequence: CARBON (s2pul1)

Solvent: cdcl3

Data collected on: May 21 2014

Temp. 25.0 C / 298.1 K

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.521 sec

Width 31421.8 Hz

1344 repetitions

OBSERVE C13, 125.7011859 MHz

DECOUPLE H1, 499.9073947 MHz

Power 42 dB

continuously on

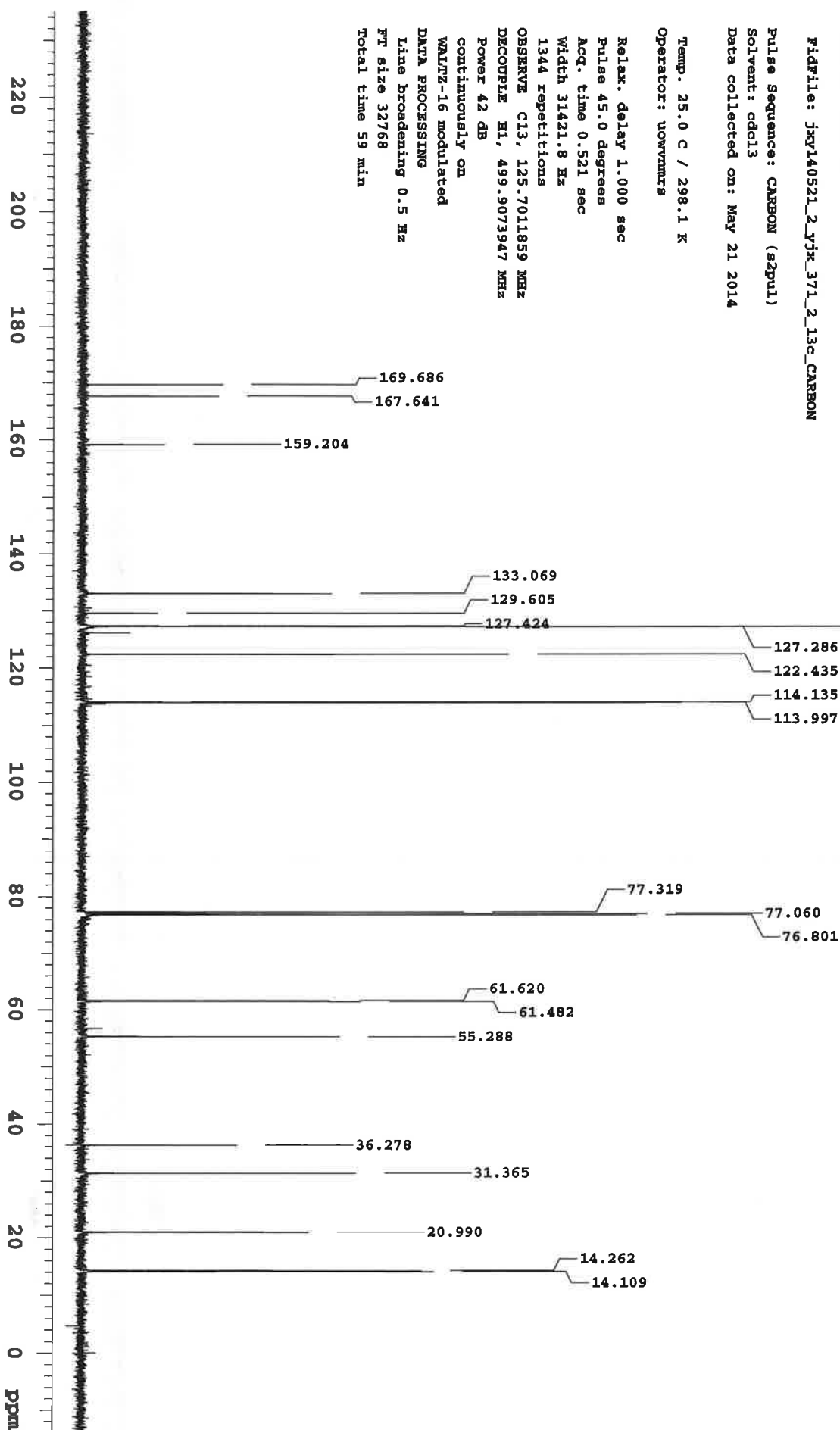
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 59 min



Agilent Technologies

jxy140524_2.yjk_372_2_PROTON

Sample Name:

jxy140524_2.yjk_372_2

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (s2pul1)

Solvent: cdcl3

Data collected on: May 24 2014

Temp. 25.0 C / 298.1 K

Operator: uownmrs

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 2.048 sec

Width 7998.4 Hz

16 repetitions

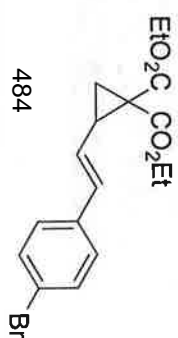
OBSERVE H1, 499.9049118 MHz

DATA PROCESSING

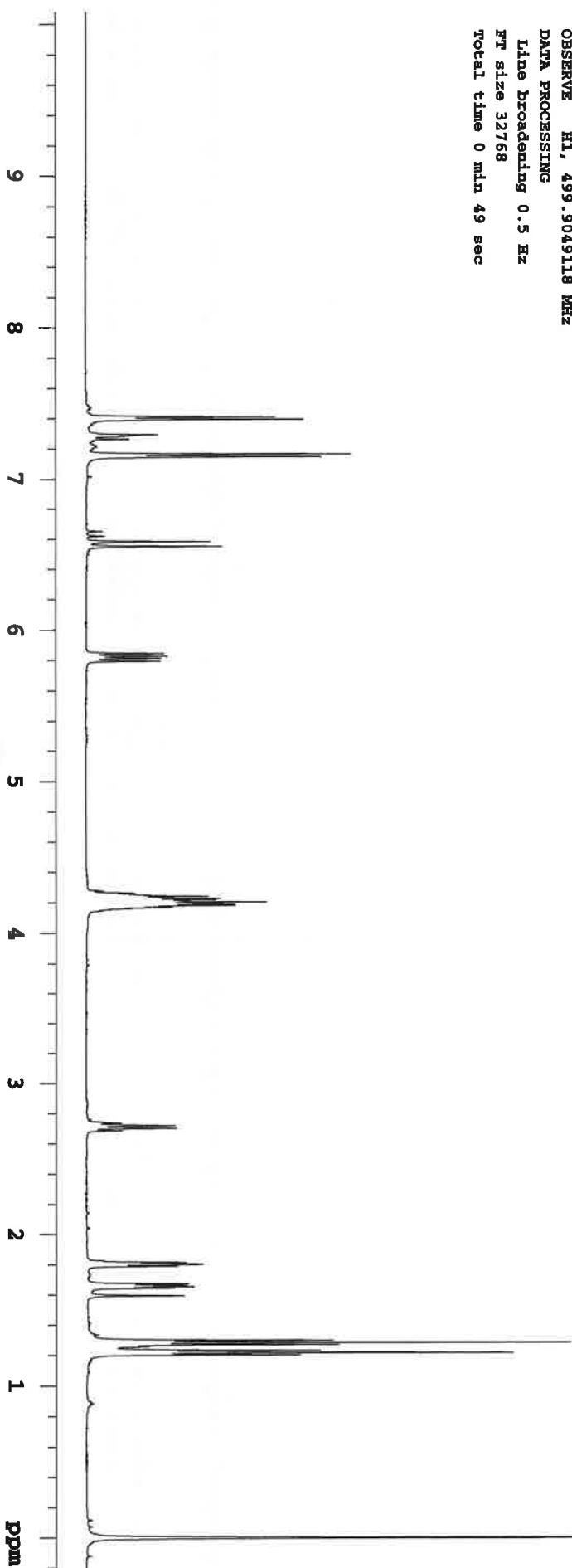
Line broadening 0.5 Hz

FT size 32768

Total time 0 min 49 sec



Agilent Technologies



jxy140524_2_yjk_372_2_13c CARBON

Sample Name:

jxy140524_2_yjk_372_2_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

FidFile: jxy140524_2_yjk_372_2_13c CARBON

Pulse Sequence: CARBON (szpul)

Solvent: cdcl3

Data collected on: May 24 2014

Temp. 25.0 C / 298.1 K

Operator: uowmms

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.521 sec

Width 31421.8 Hz

2336 repetitions

OBSERVE C13, 125.7011859 MHz

DECOUPLE H1, 499.9073947 MHz

Power 42 dB

continuously on

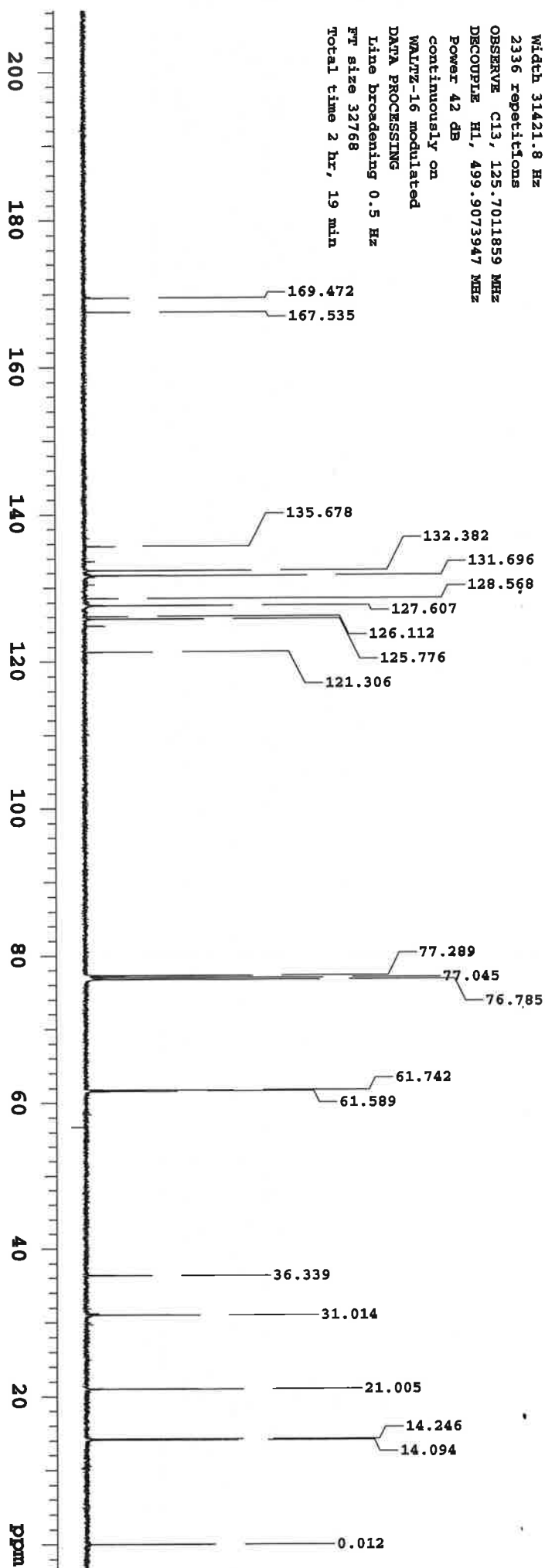
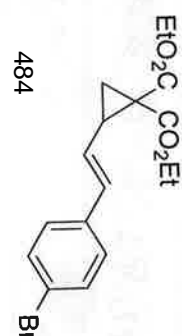
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 2 hr, 19 min



Agilent Technologies

jxy150306_2.yjk_550_3_PROTON

Sample Name:

jxy150306_2.yjk_550_3

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

FidFile: jxy150306_2.yjk_550_3_PROTON01

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Mar 6 2015

Temp. 25.0 C / 298.1 K

Operator: uowymms

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 2.048 sec

Width 7998.4 Hz

16 repetitions

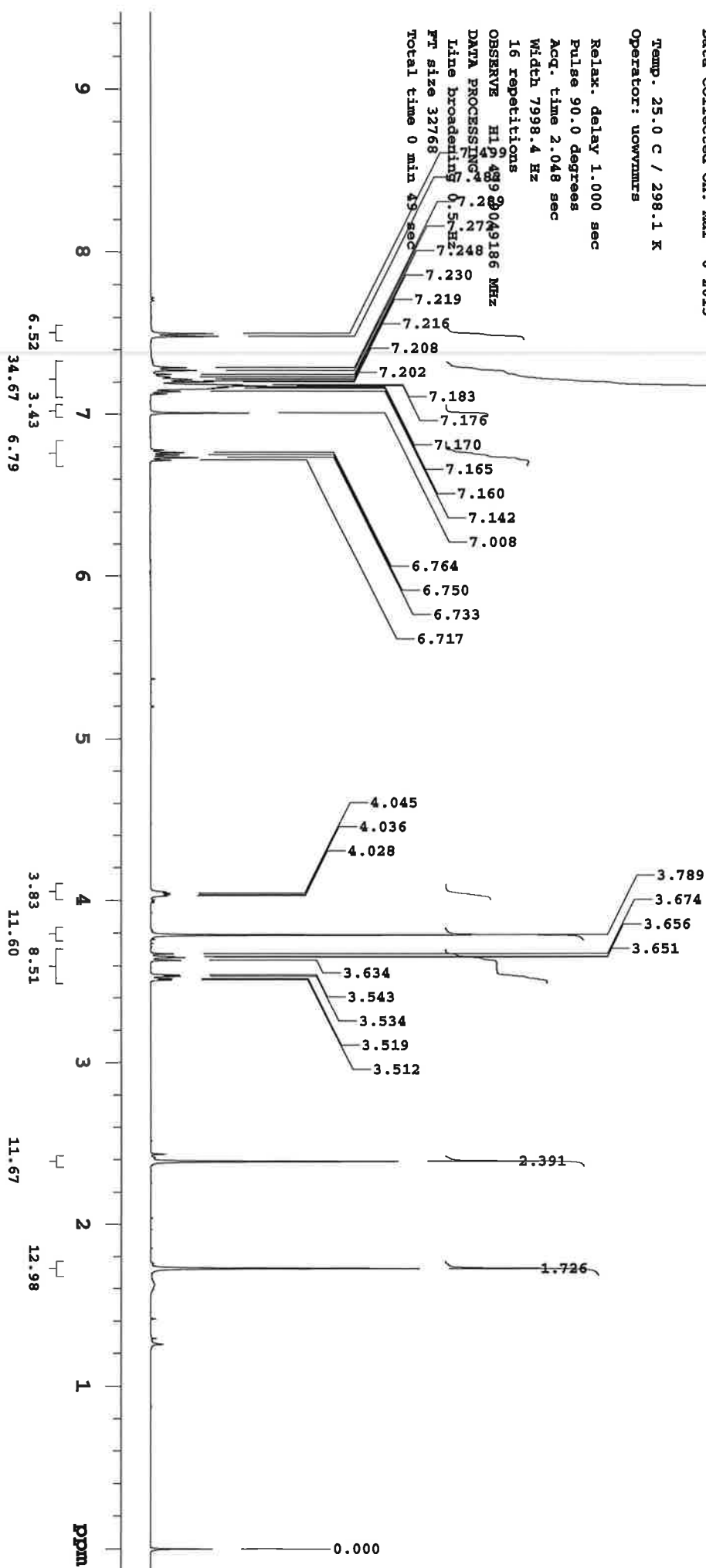
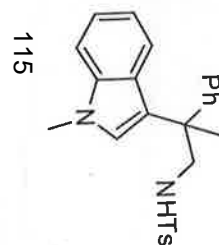
OBSERVE H1P 400.136 MHz

DATA PROCESSING:

Line broadening 0.5-Hz

FT size 32768

Total time 0 min 49 sec



jxy150306_2.yjk_550_3_13c-CARBON

Sample Name:

jxy150306_2.yjk_550_3_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

F1dFile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Mar 6 2015

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

29044 repetitions

OBSERVE C13, 75.4243172 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

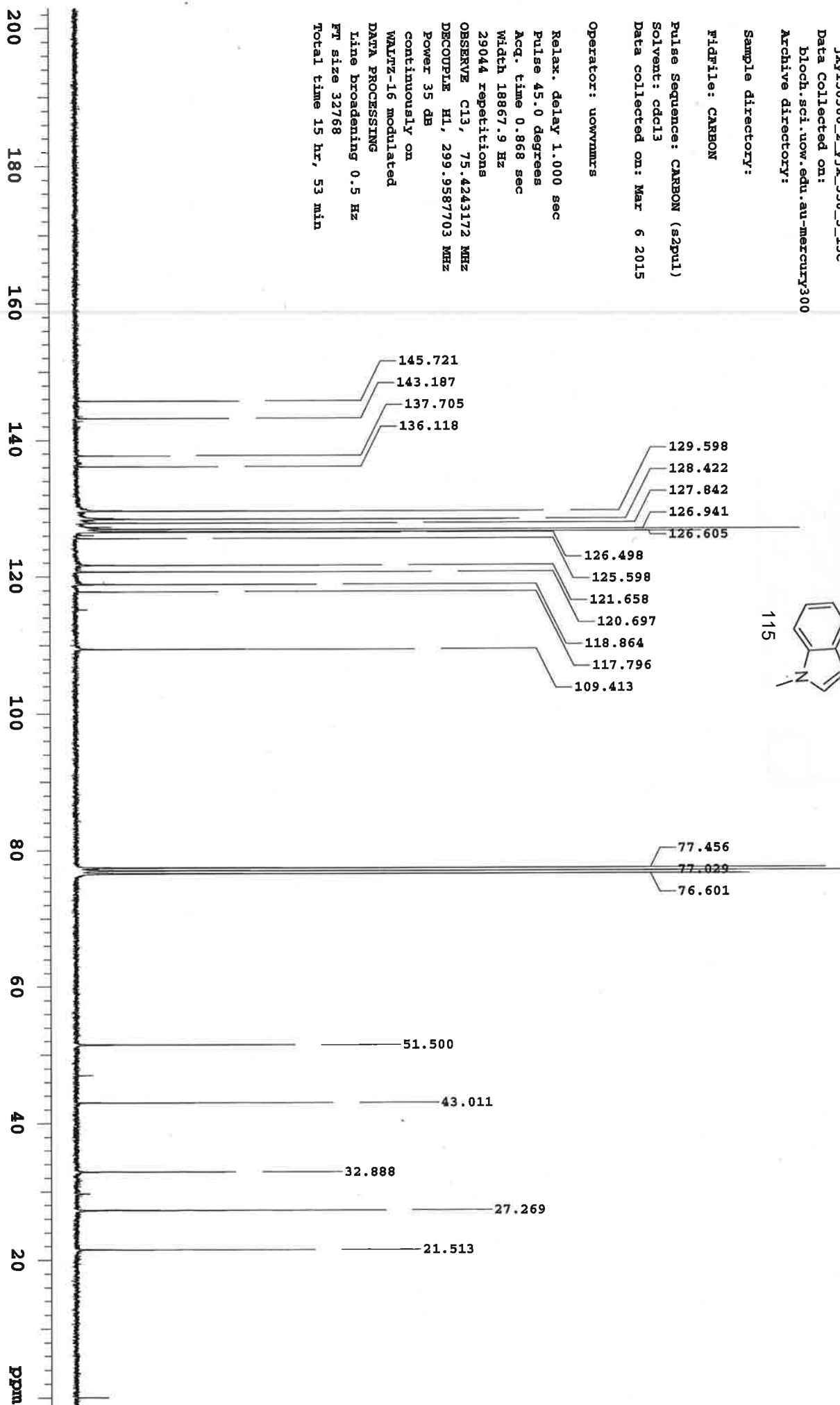
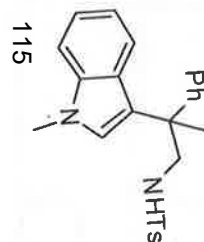
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 15 hr, 53 min



Agilent Technologies

jxy150513_2_vjx_624_1_overnightdrifed_Proton

File: Proton

Pulse Sequence: s2pul1

Solvent: cdcl3

Temp: 2.0 C / 275.1 K

Operator: uowvnmr2

VNMRS-500 "pyne06.domain.com"

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 2.045 sec

Width 8012.8 Hz

16 repetitions

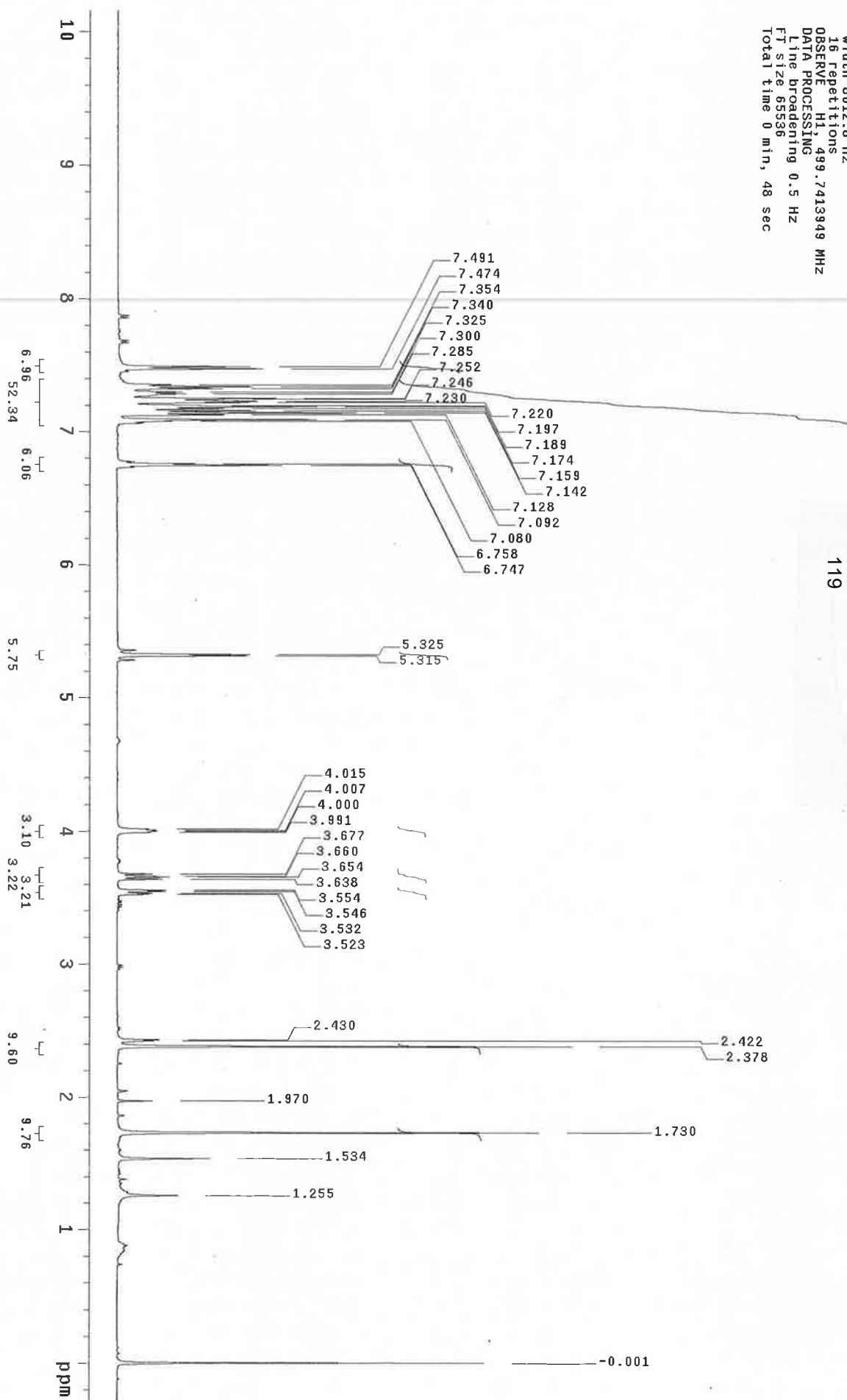
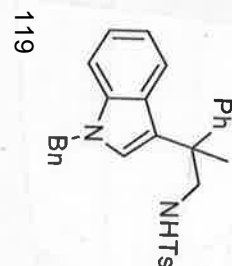
OBSERVE H1 499.7413949 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 0 min, 48 sec



jxy150513_2.yjk_624_1_13c CARBON

Sample Name:

jxy150513_2.yjk_624_1_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: jxy150513_2.yjk_624_1_13c CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: May 13 2015

Operator: uowmurs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

26880 repetitions

OBSERVE C13, 75.4243 MHz

DECOUPLE H1, 299.9587 MHz

Power 35 dB

continuously on

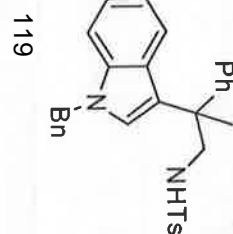
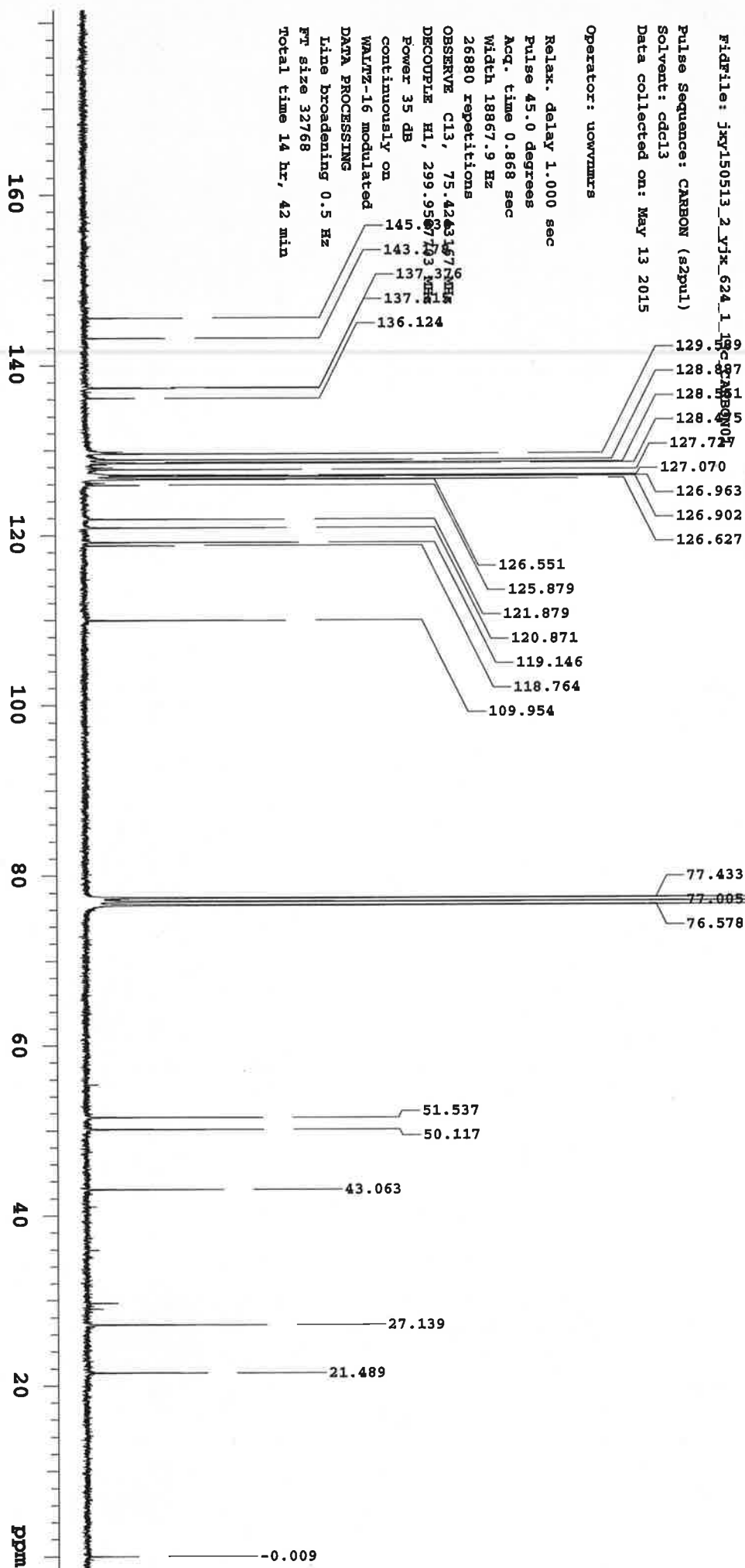
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 14 hr, 42 min



Agilent Technologies

jxy160721_2.y1x/5b_PROTON

Sample Name:
jxy160721_2.y1x_5b
Data Collected on:
ernst.sci.uow.edu.au-incova500
Archive directory:

Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (sgpul)

Solvent: cdcl3

Data collected on: Jul 21 2016

Operator: uowmurs

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 2.048 sec

Width 7998.4 Hz

Ch 600 MHz

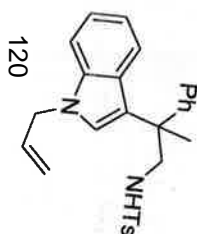
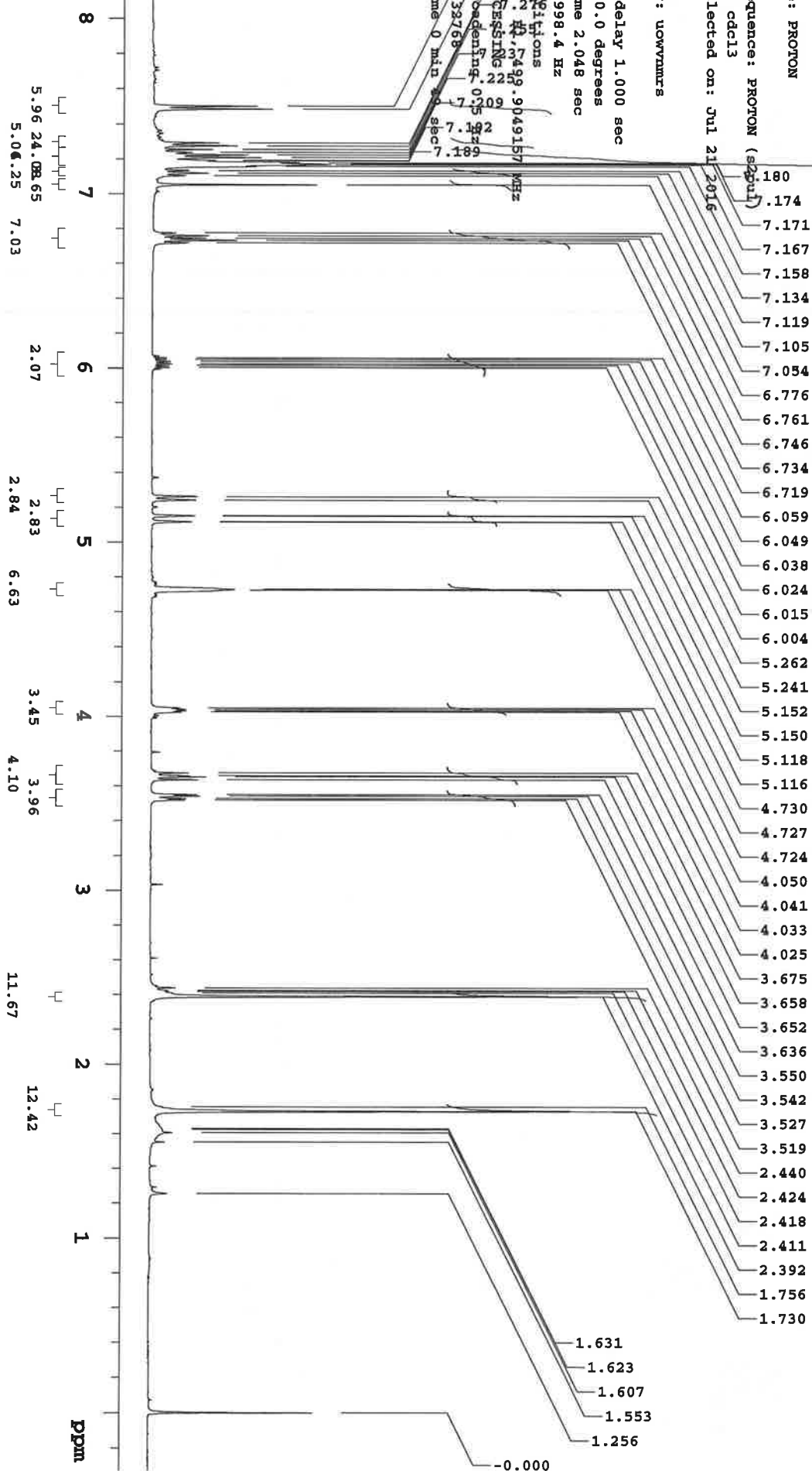
Observed N 149.9049157 MHz

DATA PROCESSING N

Line broadening 0.05 Hz

FT size 32768

Total time 0 min 40 sec



Agilent Technologies

jxy150518_2_yjk_628_3_13c_CARBON

Sample Name:
jxy150518_2_yjk_628_3_13c
Data Collected on:
bloch.sci.uow.edu.au-mercury300
Archive directory:

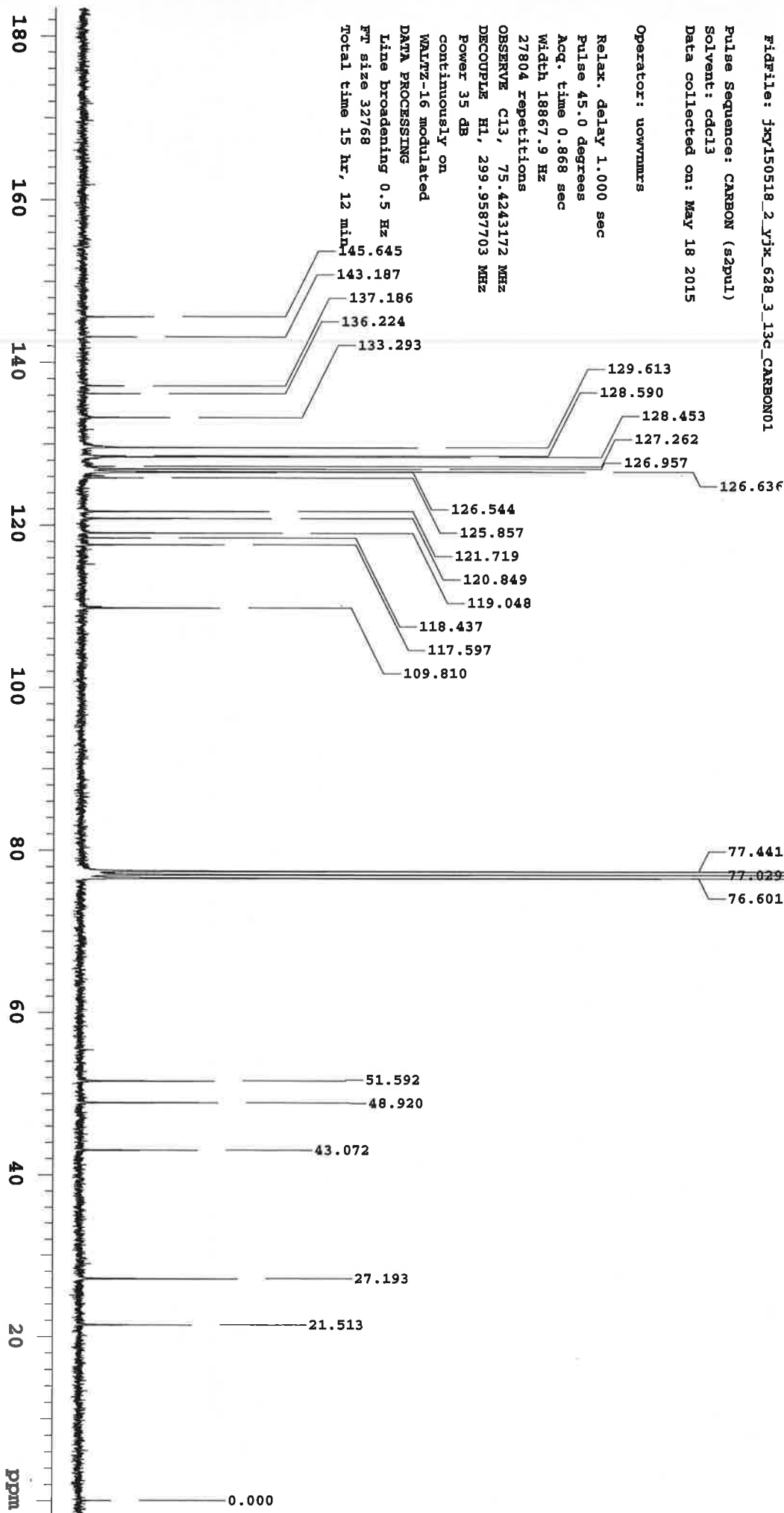
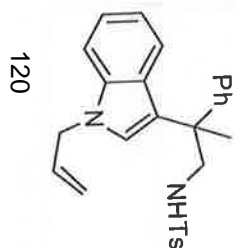
Sample directory:

Fidfile: jxy150518_2_yjk_628_3_13c_CARBON01

Pulse Sequence: CARBON (szpu1)
Solvent: cdcl3
Data collected on: May 18 2015

Operator: nowmms

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
27804 repetitions
OBSERVE C13, 75.4243172 MHz
DECOUPLE H1, 299.9587703 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 15 hr, 12 min



Agilent Technologies

jxy150628_2_yjk_674_3_PROTON

Sample Name:

jxy150628_2_yjk_674_3

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (s2pul1)

Solvent: cdcl3

Data collected on: Jun 28 2015

Operator: uowymms

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 2.048 sec

Width 7998.4 Hz

16 repetitions

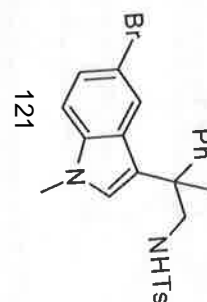
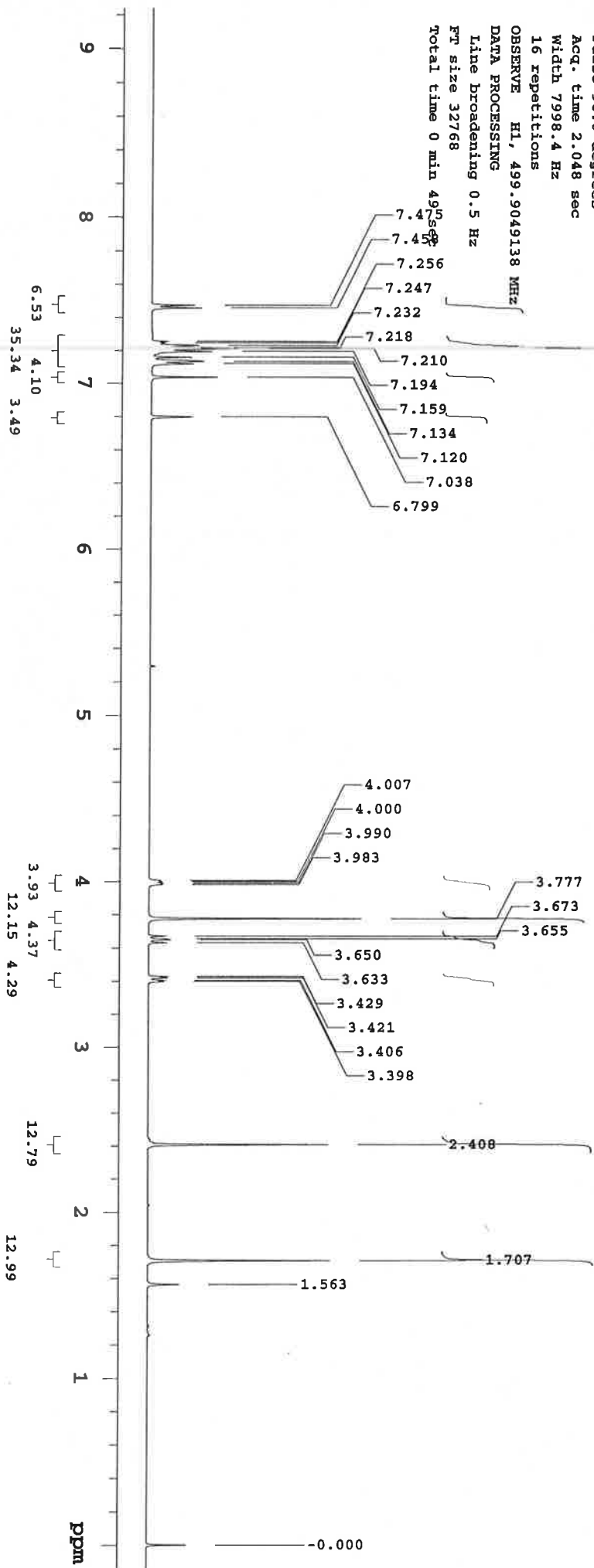
OBSERVE H1, 499.9049138 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 0 min 49s48



Agilent Technologies

jxy150626_2.yjk_674_1_13c-CARBON

Sample Name:

jxy150626_2.yjk_674_1_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

/export/home/chempack/vnmrsvs/data

Sample directory:

FidFile: CARBON

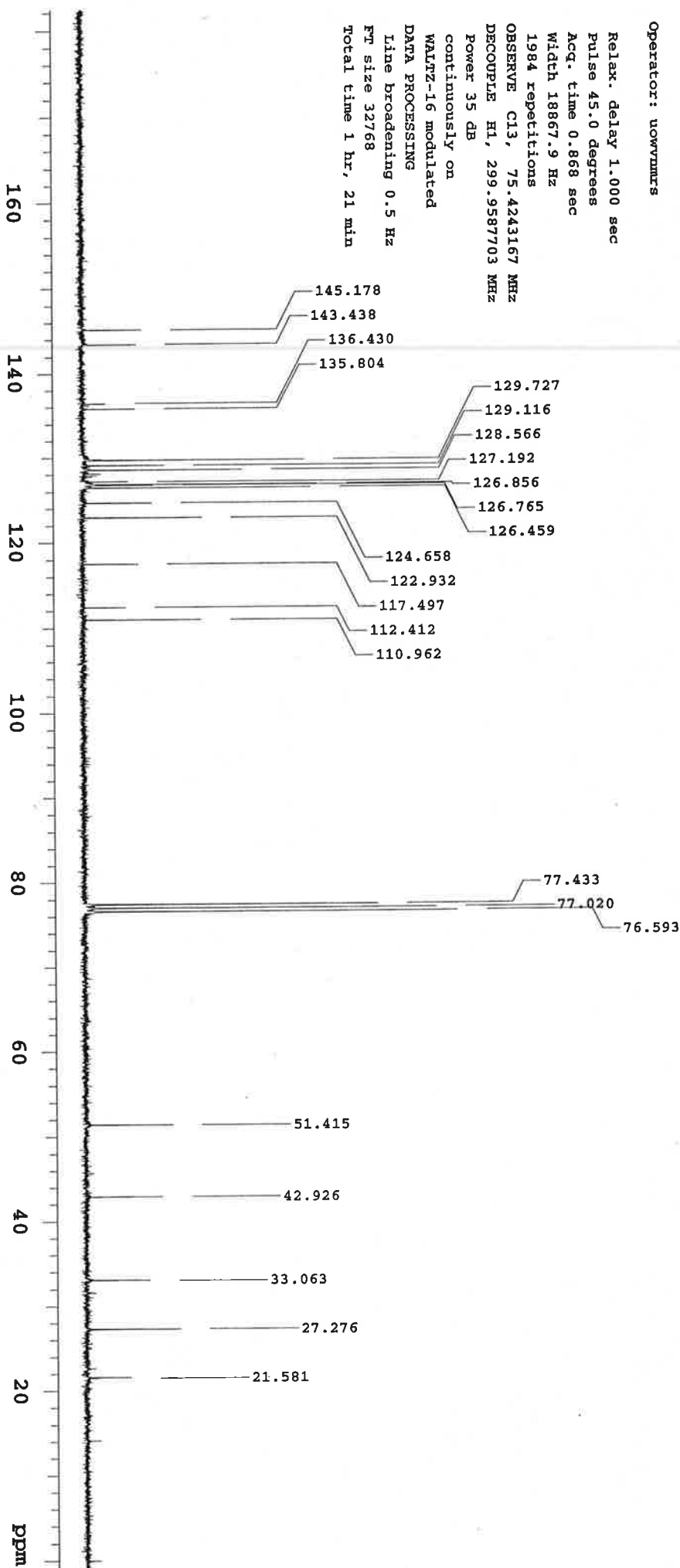
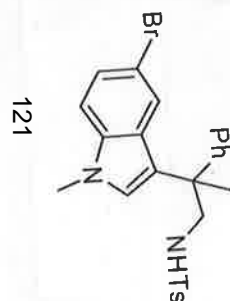
Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jun 26 2015

Operator: uowvnmrs

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
1984 repetitions
OBSERVE C13, 75.4243167 MHz
DECOUPLE H1, 299.9587703 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 1 hr, 21 min



Agilent Technologies

jxy160728_2.y1x 6d PROTON

Sample Name:

jxy160728_2.y1x_5d

Data Collected on:

ernst.sci.uow.edu.au-inoxa500

Archive directory:

Sample directory:

Fidfile: PROTON

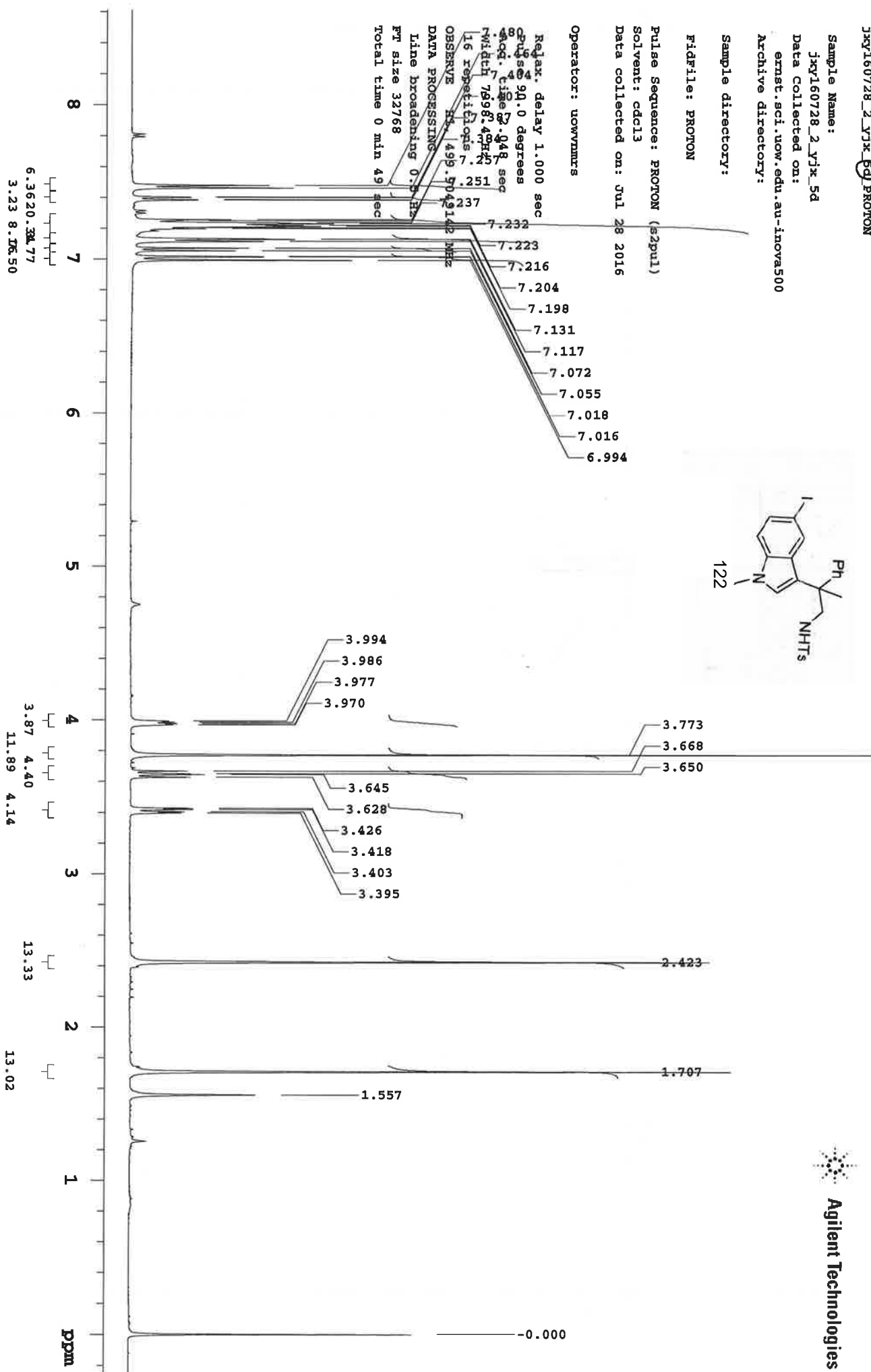
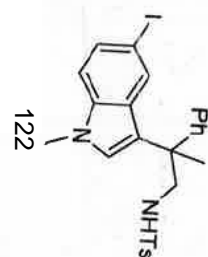
Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Jul 28 2016

Operator: uowmms

Relax. delay 1.000 sec
CPUG 90.0 degrees
Acq. time 2.948 sec
Width 7698.42 Hz
16 repetitions
OBSERVE Hz 499.9049142 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 0 min 49 sec



Agilent Technologies

jxy150702_2_yjx_678_1_13c-CARBON

Sample Name:

jxy150702_2_yjx_678_1_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jul 2 2015

Operator: uowymms

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

1856 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

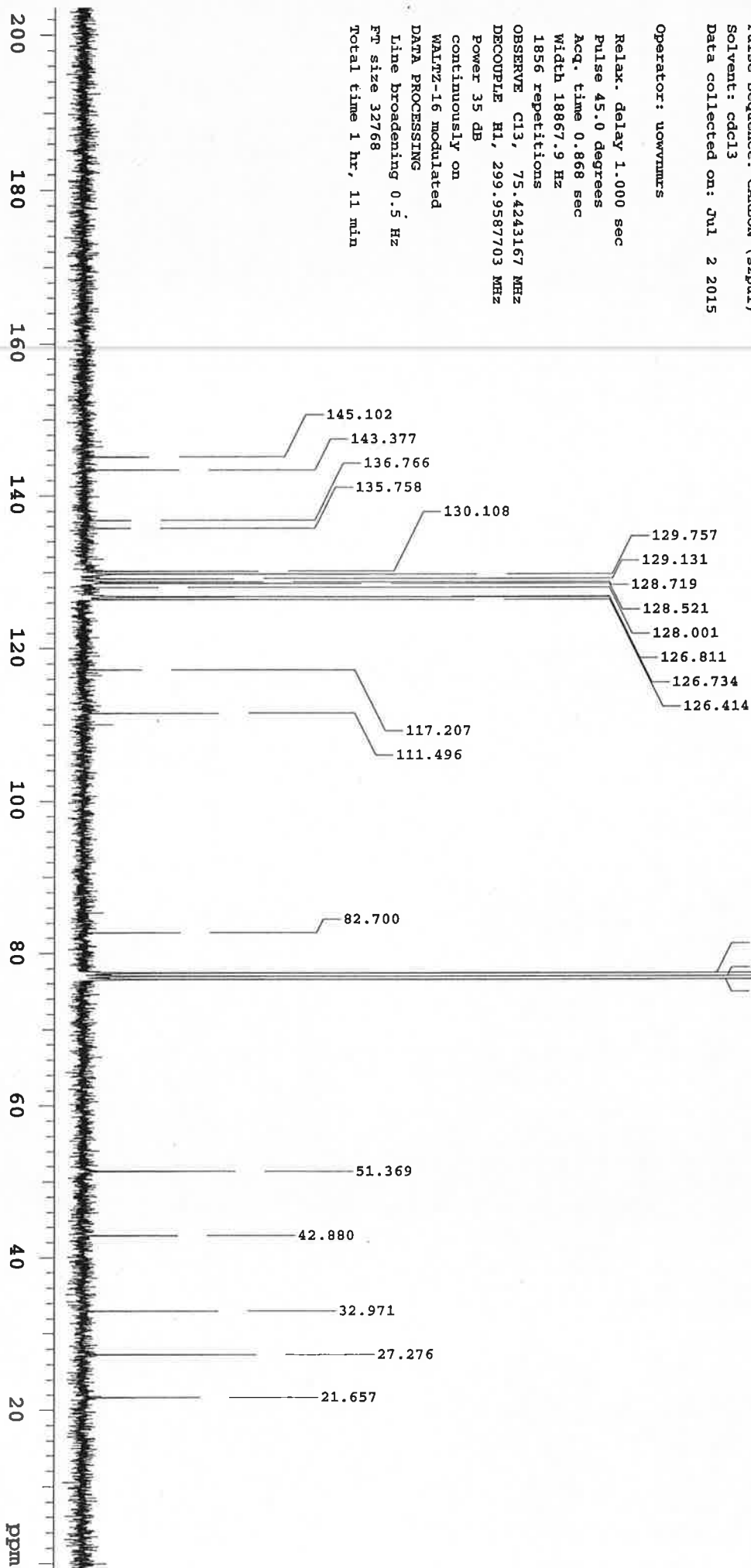
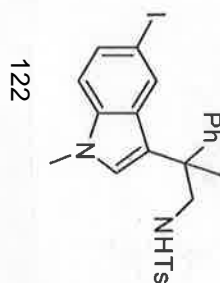
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 1 hr, 11 min



Agilent Technologies

jxy150702_2_yjx_681_1_PROTON

Sample Name:

jxy150702_2_yjx_681_1

Data Collected on:

bloch.sci.nov.edu.au-mercury300

Archive directory:

Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Jul 2 2015

Operator: novnmr

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 3.416 sec

Width 4796.2 Hz

16 repetitions

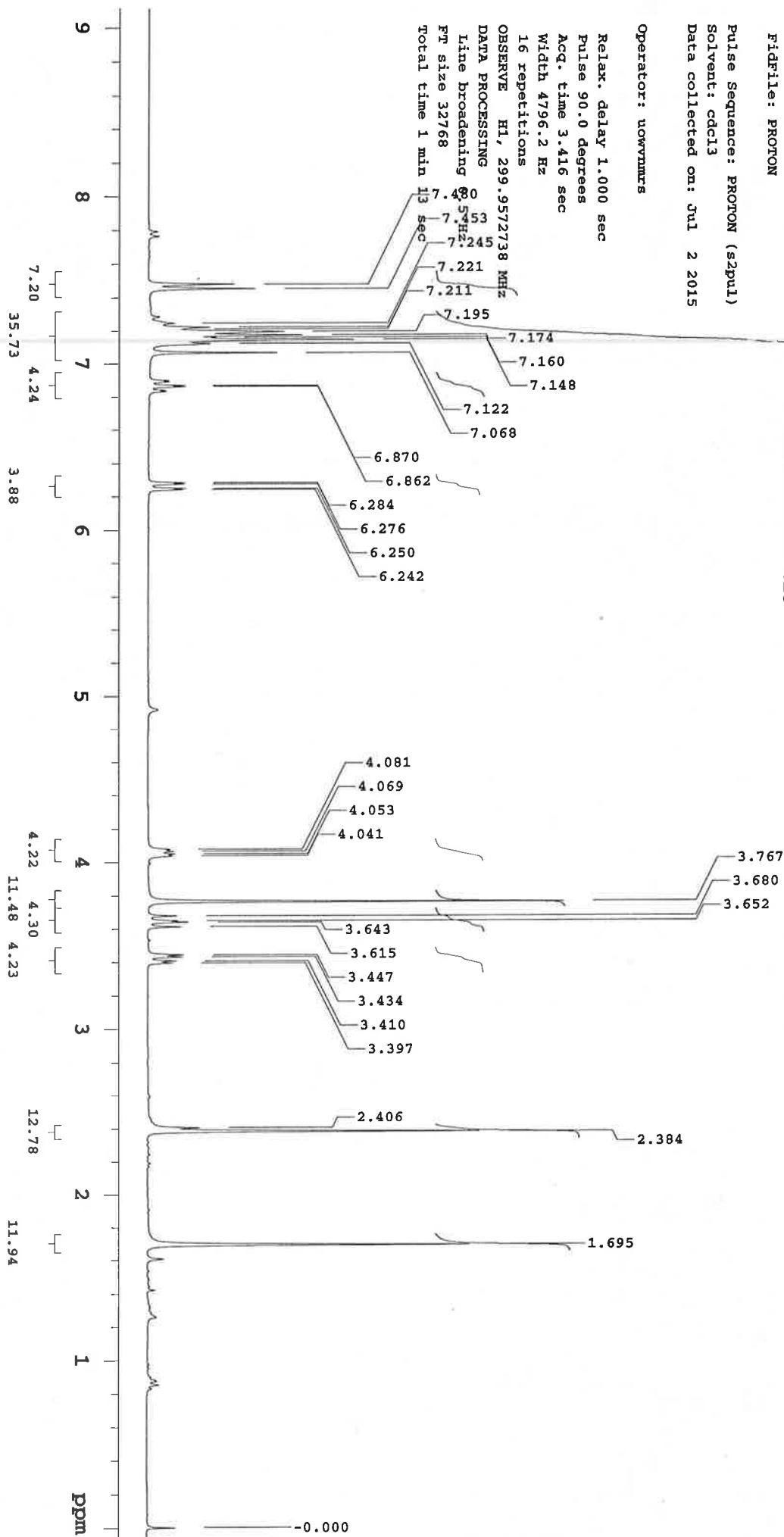
OBSERVE H1, 299.9572738 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 1 min 13 sec



Agilent Technologies

jxy150701_2_yjk_681_1_13c-CARBON

Sample Name:

jxy150701_2_yjk_681_1_13c

Data Collected on:

bloch.sci.nov.edu.au-mercury300

Archive directory:

/export/home/chempack/vnmrSYS/data

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jul 1 2015

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

1536 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

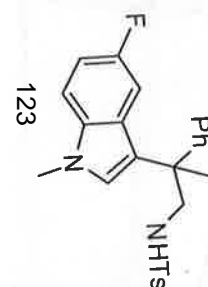
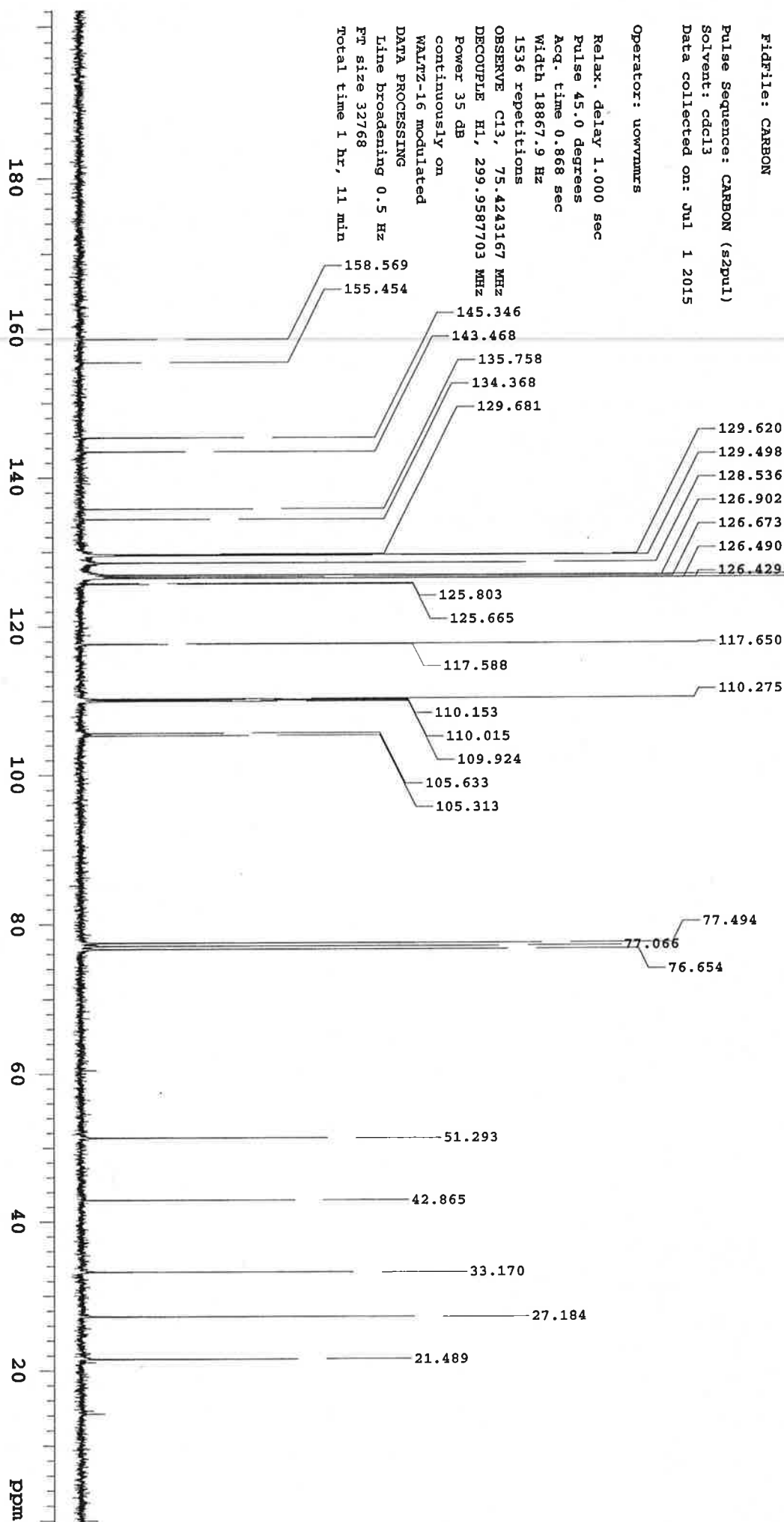
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 1 hr, 11 min



Agilent Technologies

jxy150702_2_vjk_679_1_PROTON

Sample Name:

jxy150702_2_vjk_679_1

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Jul 2 2015

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 3.416 sec

Width 4796.2 Hz

16 repetitions

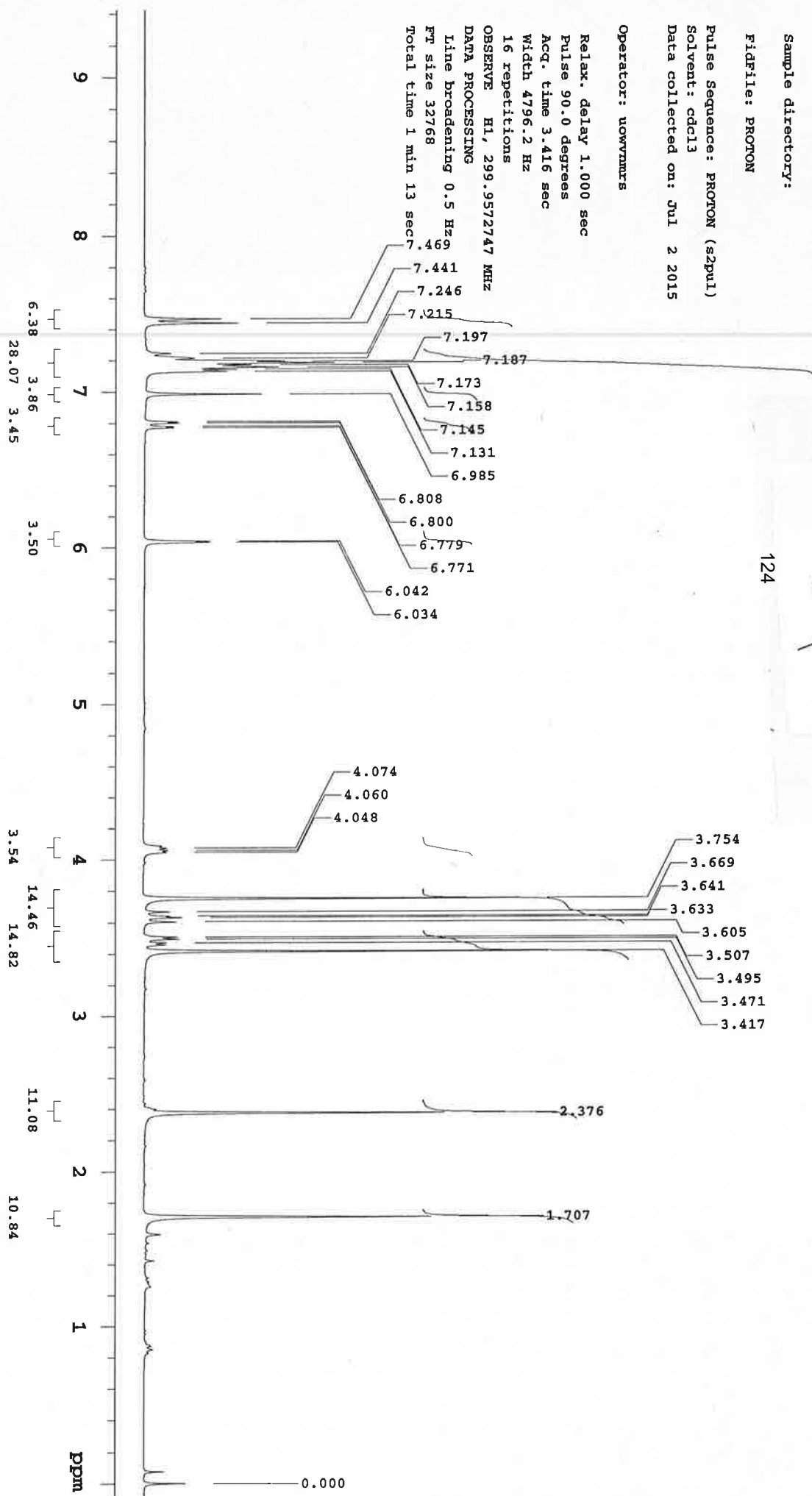
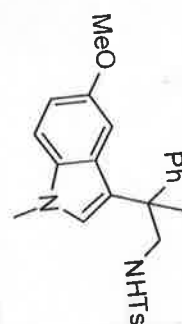
OBSERVE H1, 299.9572747 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 1 min 13 sec



Agilent Technologies

jxy150701_2_yjx_679_1_13c-CARBON

Sample Name:

jxy150701_2_yjx_679_1_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

/export/home/chempack/vnmr/s/data

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jul 1 2015

Operator: uowvnmr

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

672 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

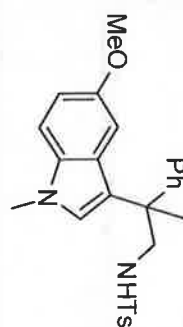
WALTZ-16 modulated

DATA PROCESSING

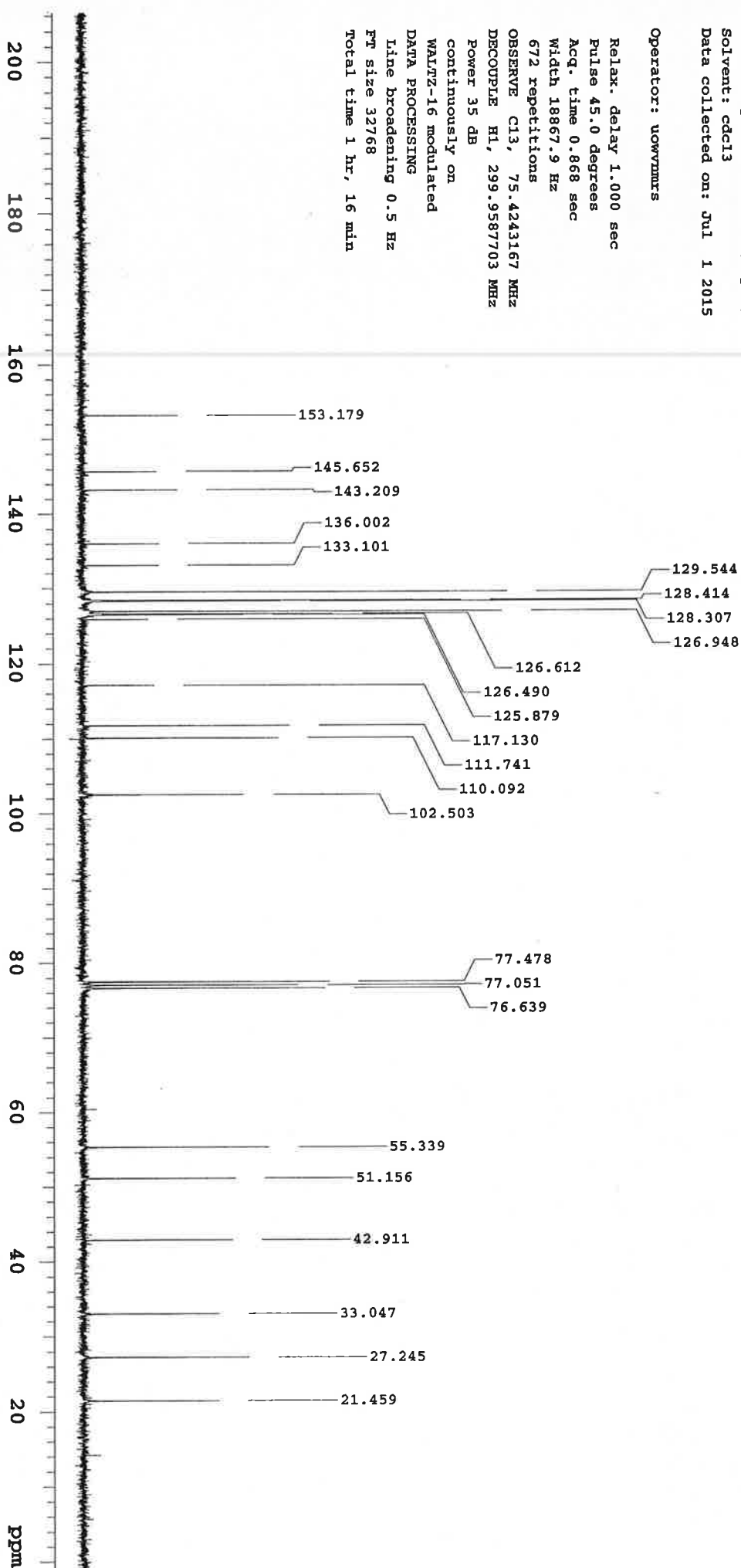
Line broadening 0.5 Hz

FT size 32768

Total time 1 hr, 16 min



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Agilent Technologies

jxy150702_2.yjk_677_1_PROTON

Sample Name:

jxy150702_2.yjk_677_1

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: jxy150702_2.yjk_677_1_PROTON01

Pulse Sequence: PROTON (szpul)

Solvent: cdc13

Data collected on: Jul 2 2015

Operator: nowvnmrs

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 5.461 sec

Width 3000.3 Hz

16 repetitions

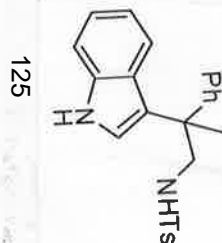
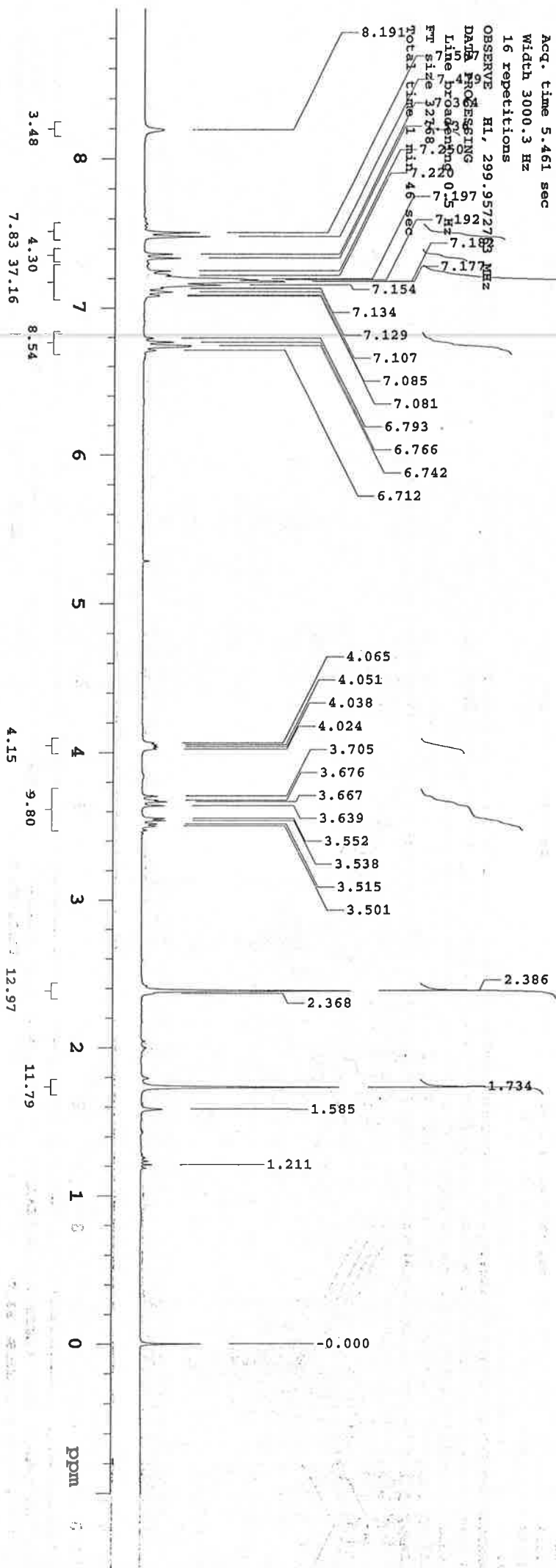
OBSERVE H1, 299.9572783 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 1 min 46 sec



Agilent Technologies

jxy150702_2_yjk_677_1_13c_CARBON

Sample Name:

jxy150702_2_yjk_677_1_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jul 2 2015

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

1312 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

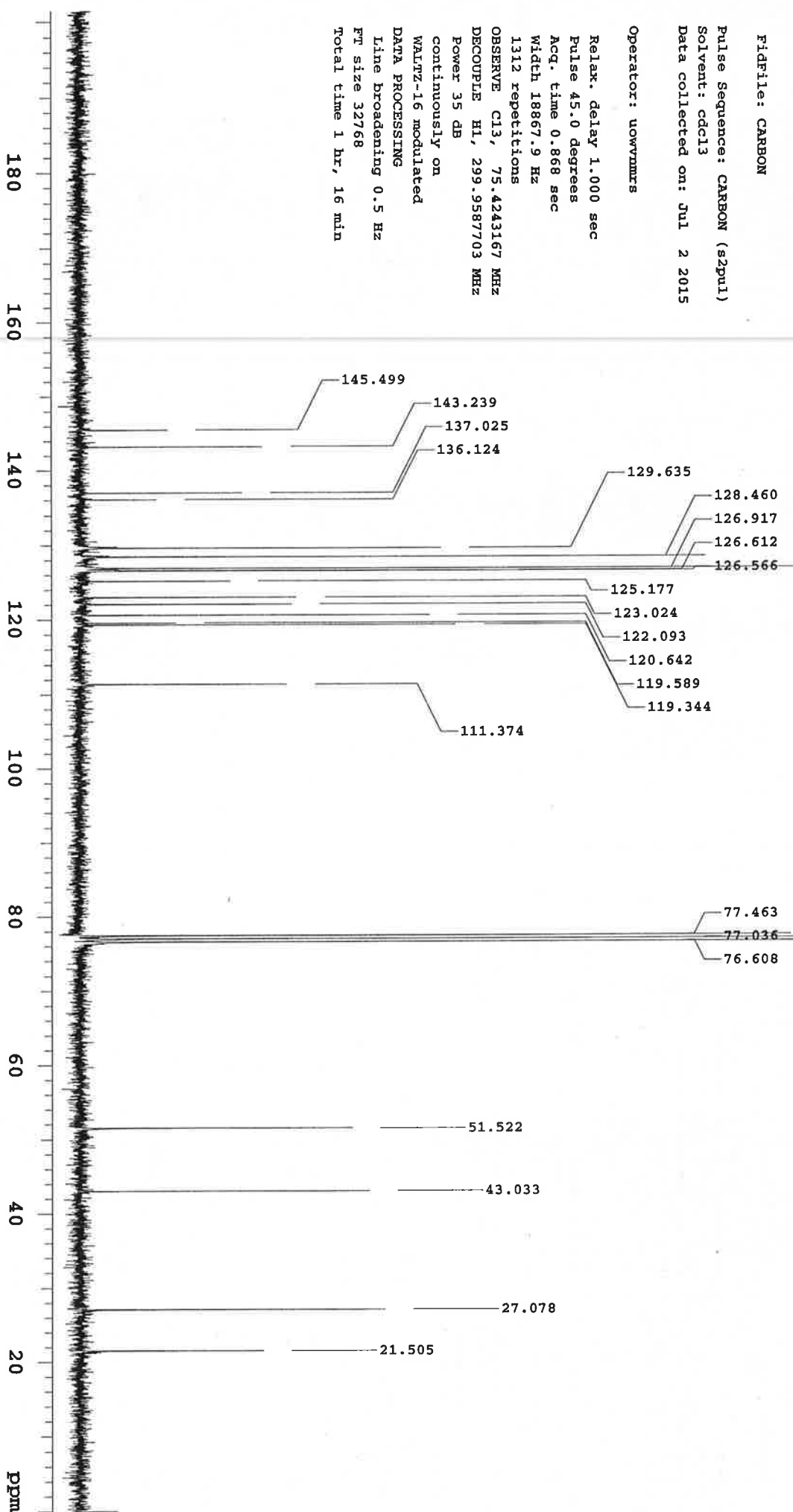
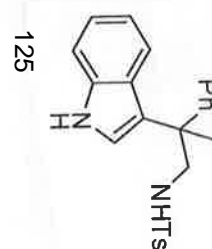
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 1 hr, 16 min



Agilent Technologies

File: Proton 1d

Pulse Sequence: s2pul

Solvent: cdcl3

Temp: 25.0 C / 298.1 K

Operator: uowvmrs

VNMR5-500 "pyne06.domain.com"

Relax. delay 0.001 sec

Pulse 45.0 degrees

Acq. time 2.045 sec

Width 8012.8 Hz

Single scan

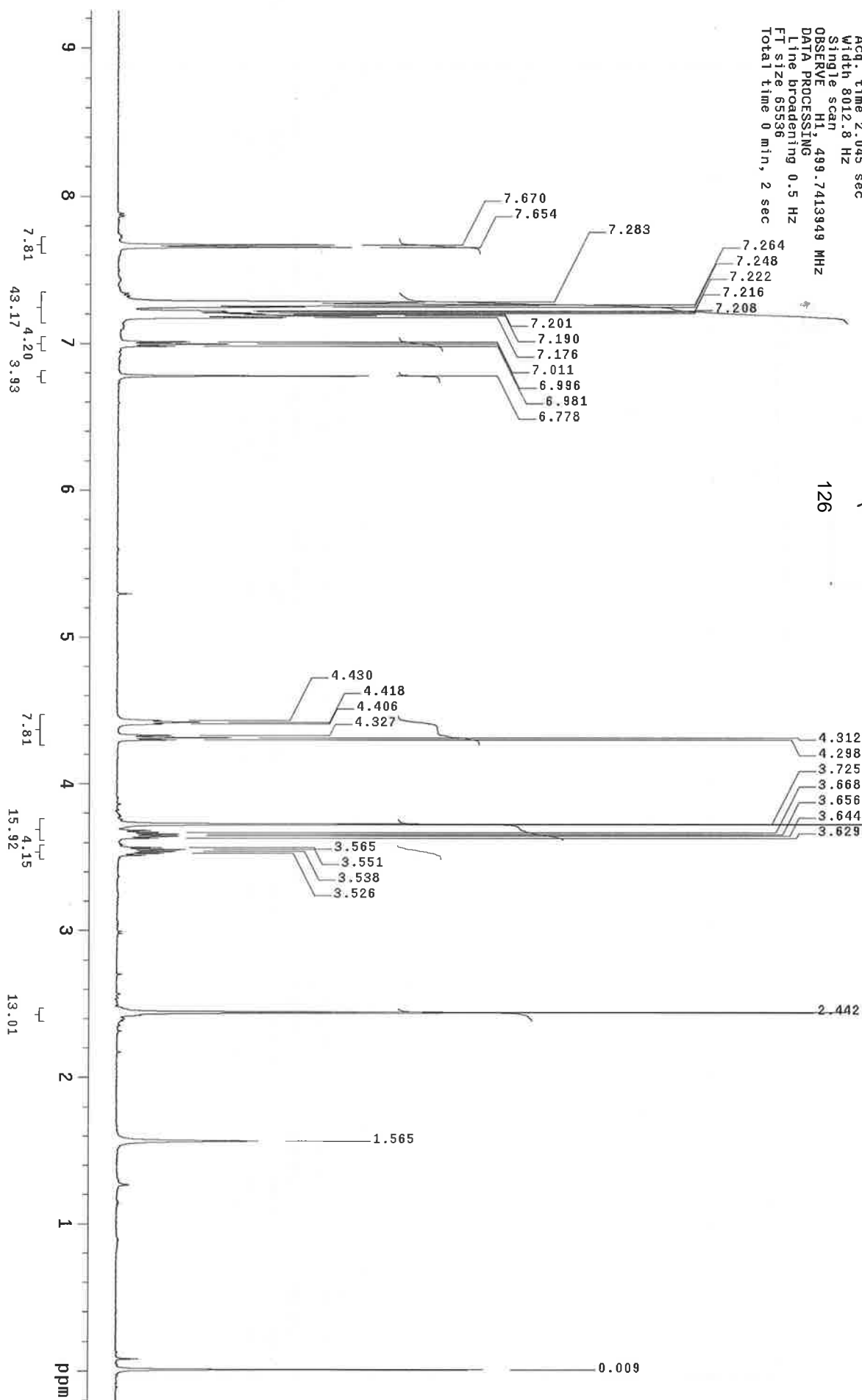
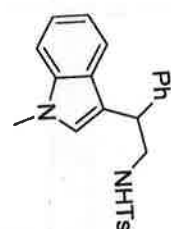
OBSERVE H1, 499.7413949 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 0 min, 2 sec



jxy150409_2_vjx_586c_1_13c_CARBON

Sample Name:

jxy150409_2_vjx_586c_1_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

/export/home/chempack/vnmrSYS/data

Sample directory:

Fidfile: jxy150409_2_vjx_586c_1_13c_CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Apr 9 2015

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.521 sec

Width 31421.8 Hz

3492 repetitions

OBSERVE C13, 125.7011911 MHz

DECOUPLE H1, 499.9073947 MHz

Power 42 dB

continuously on

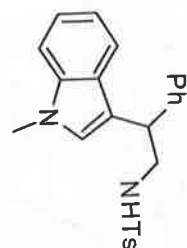
WALTZ-16 modulated

DATA PROCESSING

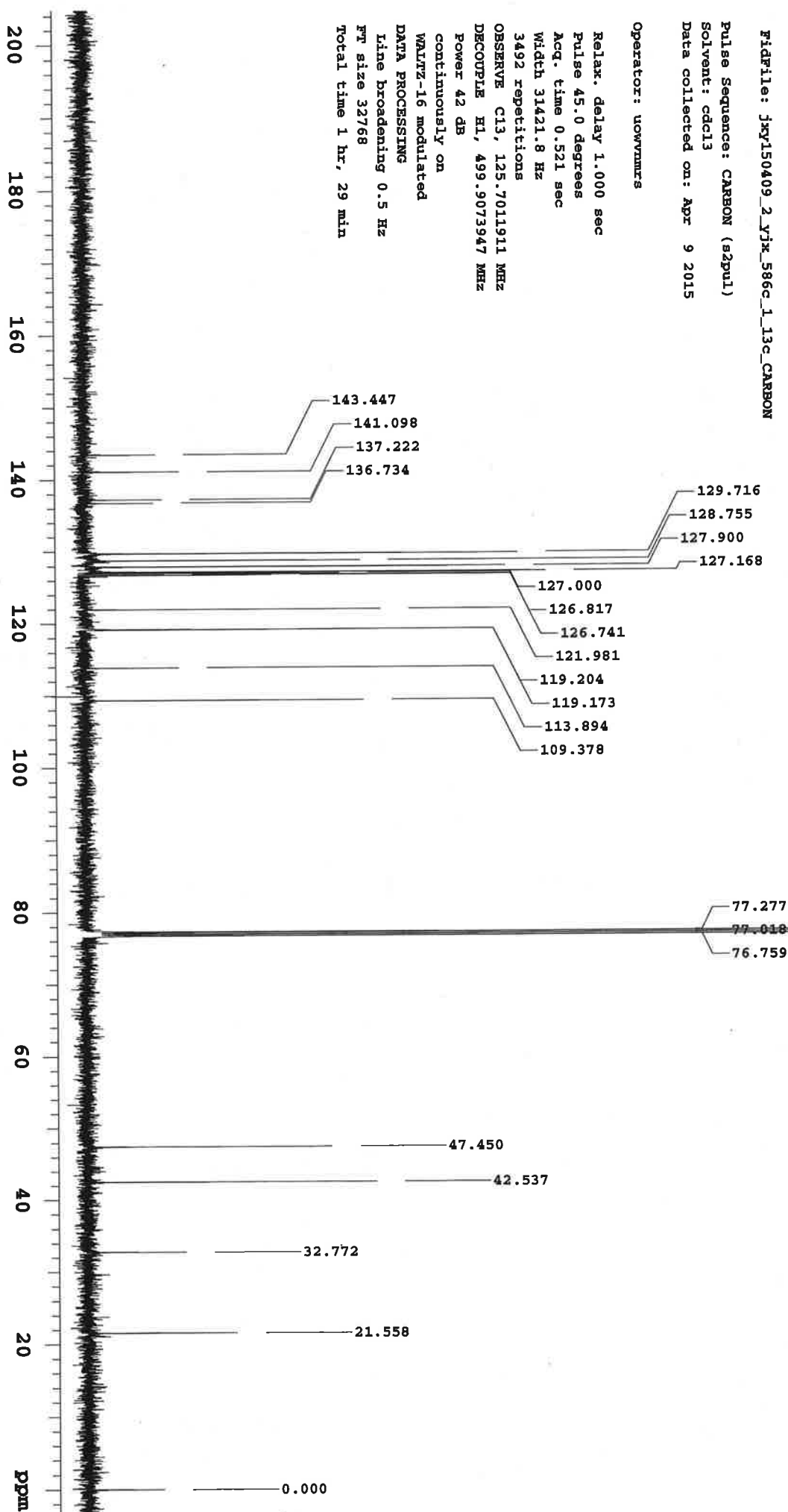
Line broadening 0.5 Hz

FT size 32768

Total time 1 hr, 29 min



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Agilent Technologies

yjx160721_3b_PROTON

3b

Sample Name:

Data Collected on:
ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: PROTON

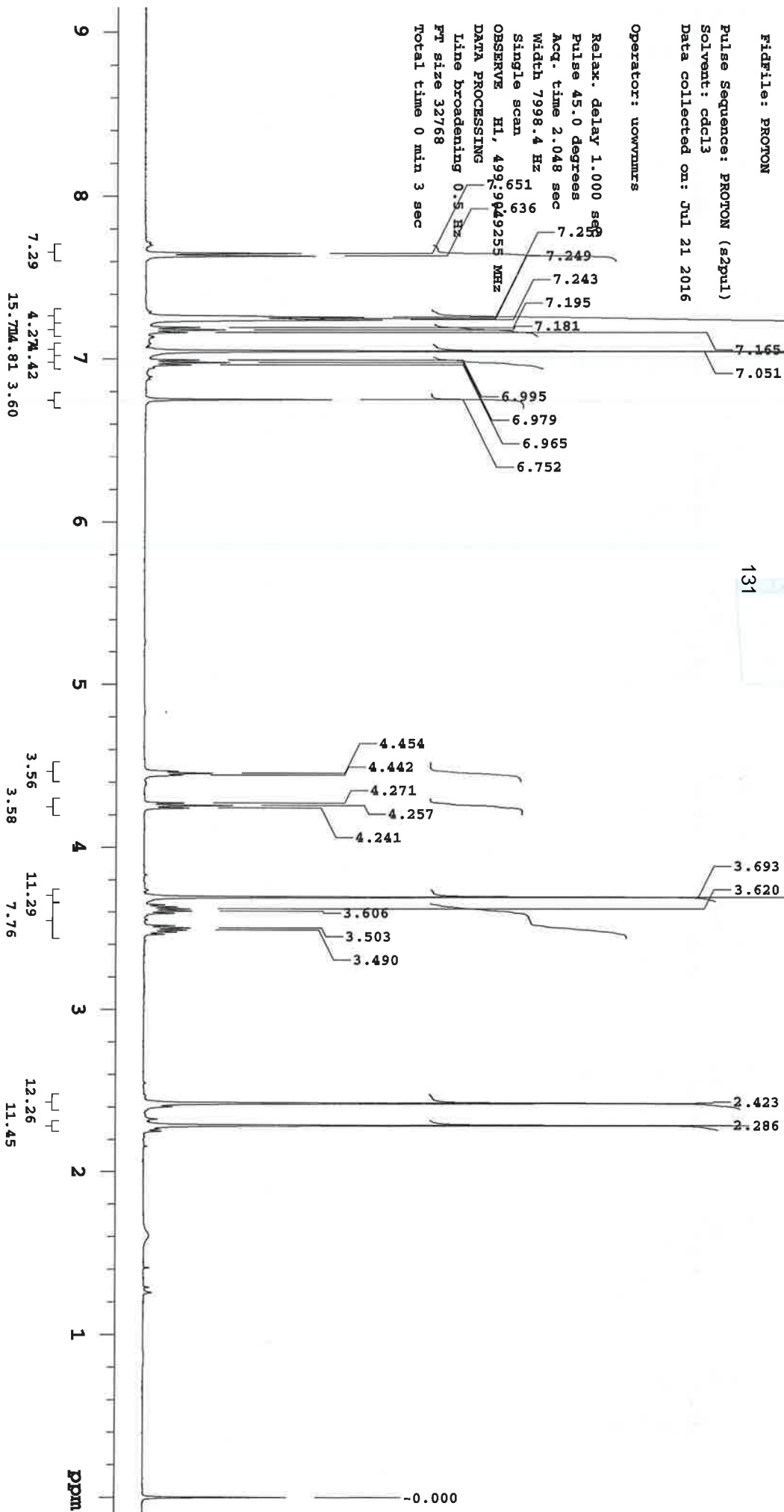
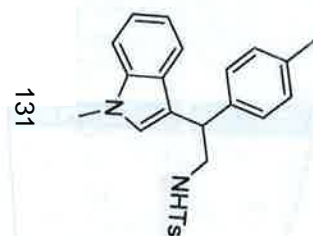
Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Jul 21 2016

Operator: uowvnmrs

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 7998.4 Hz
Single scan
OBSERVE H1, 499.9649255 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 0 min 3 sec



Agilent Technologies

jxy150421_2.yjk_602a_1_13c CARBON

Sample Name:

jxy150421_2.yjk_602a_1_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

FidFile: CARBON

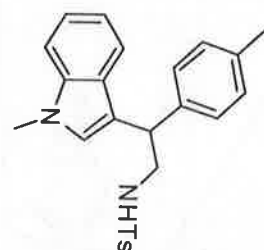
Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

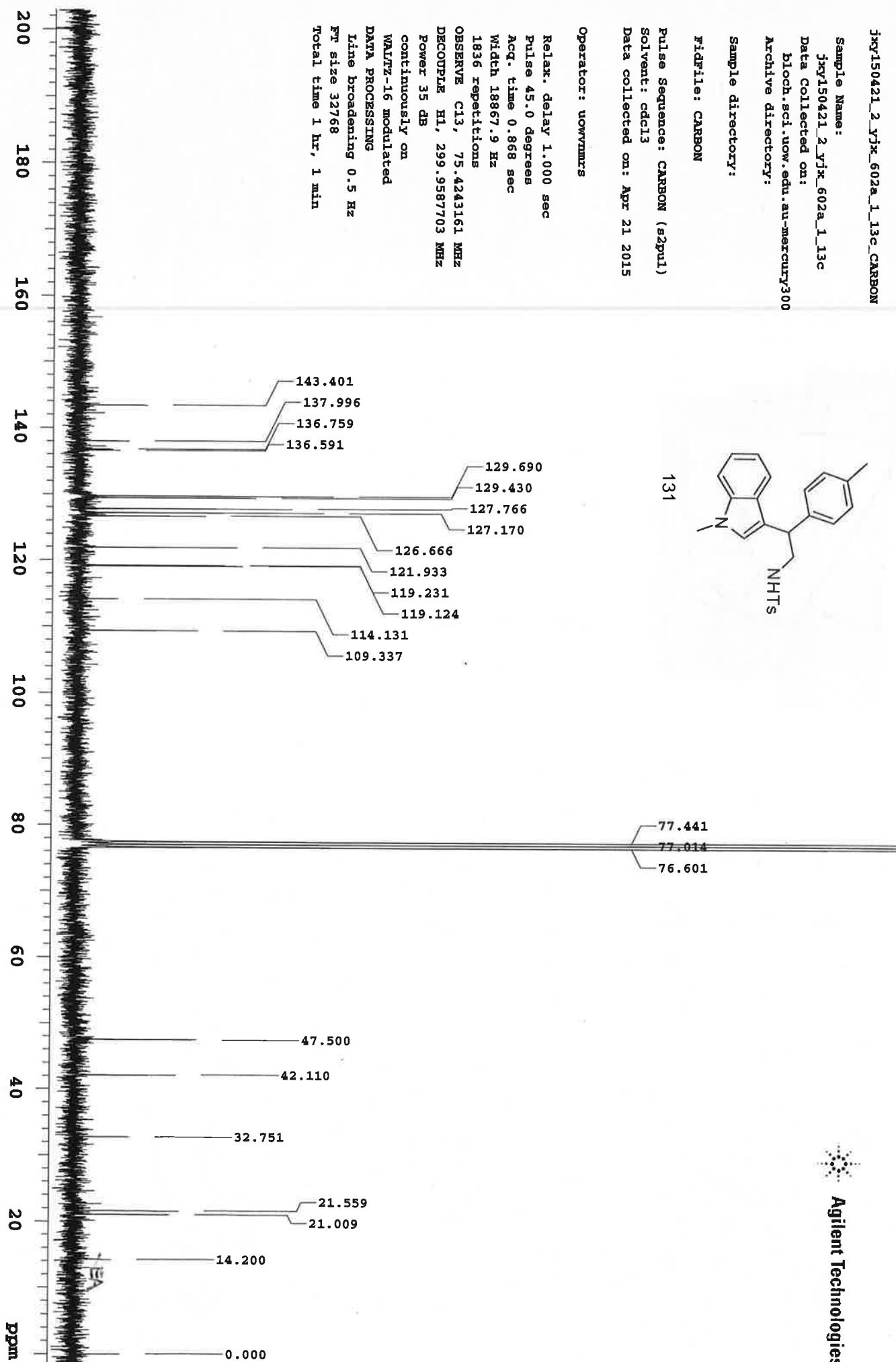
Data collected on: Apr 21 2015

Operator: uowvnmrs

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
1836 repetitions
OBSERVE C13, 75.4243161 MHz
DECOUPLE H1, 299.9587703 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
line broadening 0.5 Hz
FT size 32768
Total time 1 hr, 1 min



131



Agilent Technologies

File: Proton 3c

Pulse Sequence: szpu1

Solvent: cdcl3

Temp: 25.0 C / 298.1 K

Operator: uowvmrs

VNMR5-500 "pyre06.domain.com"

Relax. delay 0.001 sec

Pulse 45.0 degrees

Acq. time 2.045 sec

Width 8012.8 Hz

Single scan

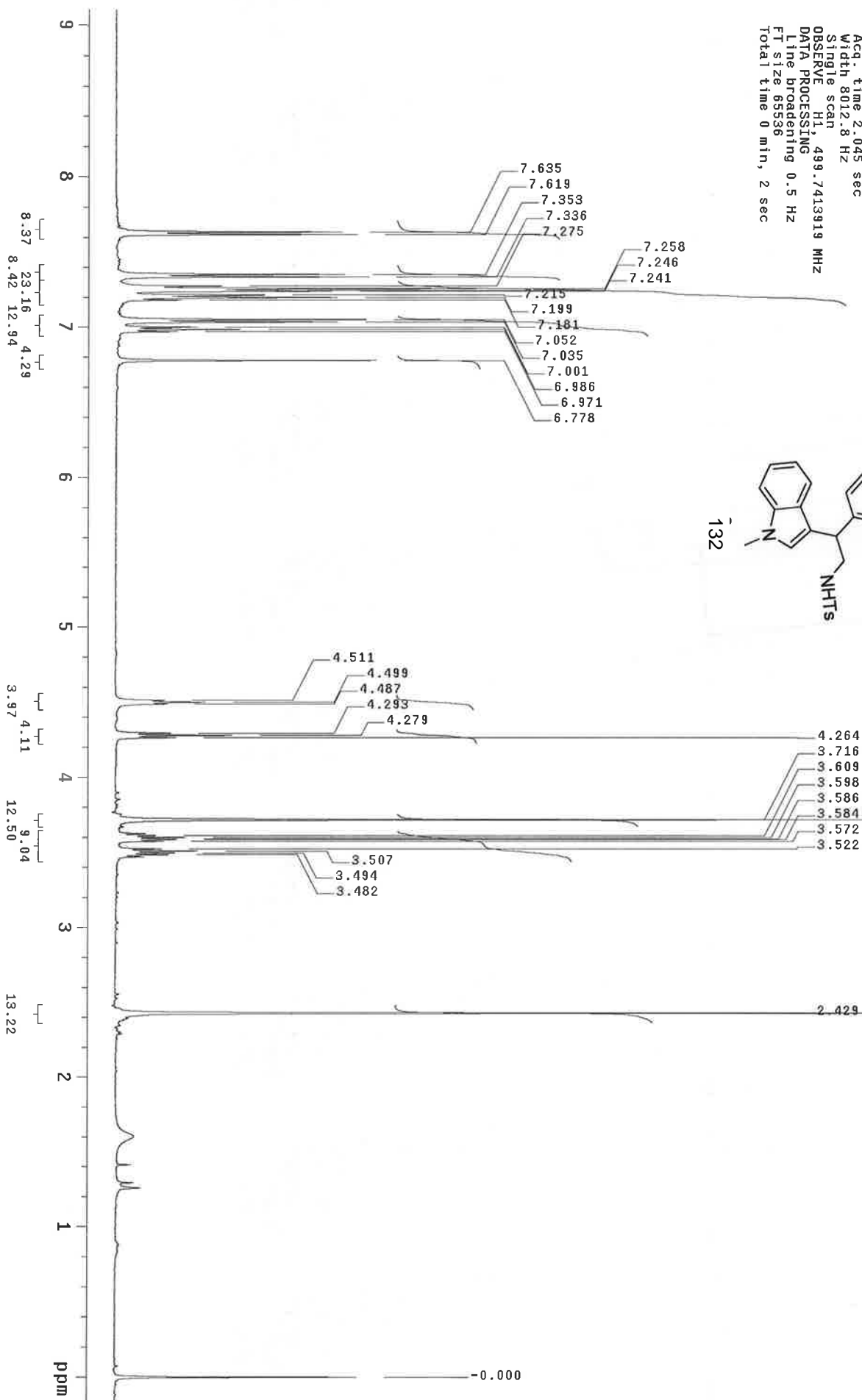
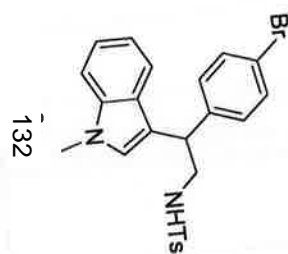
OBSERVE H1, 499.7413919 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 0 min, 2 sec



jky150421_2.yjk_602b_1_13c-CARBON

Sample Name:

jky150421_2.yjk_602b_1_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Apr 21 2015

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

672 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

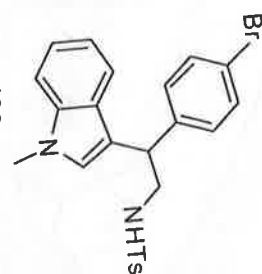
WALTZ-16 modulated

DATA PROCESSING

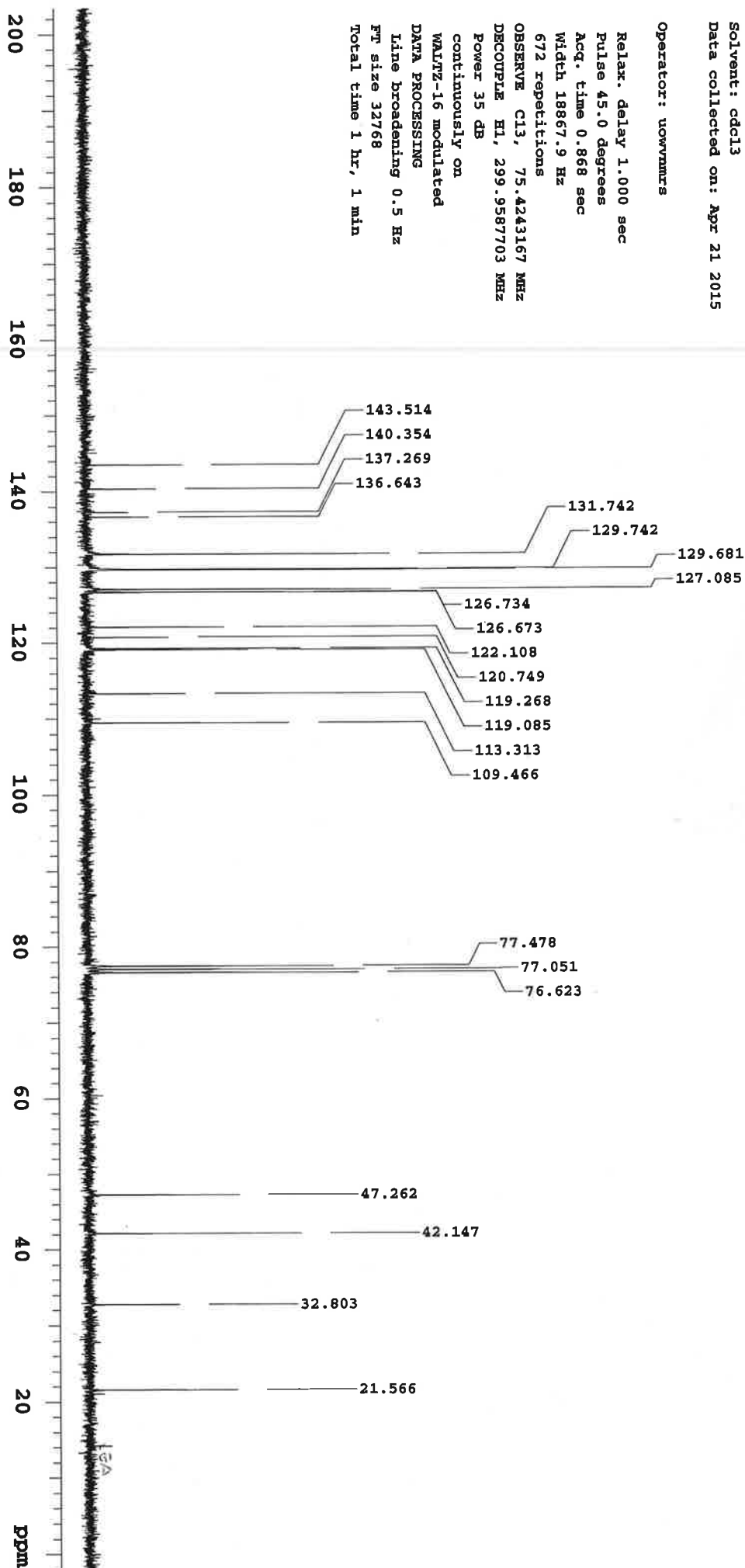
line broadening 0.5 Hz

FT size 32768

Total time 1 hr, 1 min



132



Agilent Technologies

yfx160721_34 PROTON

Sample Name:

Data Collected on:
ernst.sci.uow.edu.au-inova500
Archive directory:

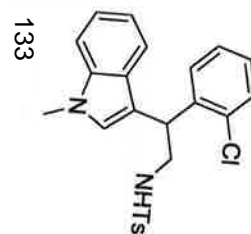
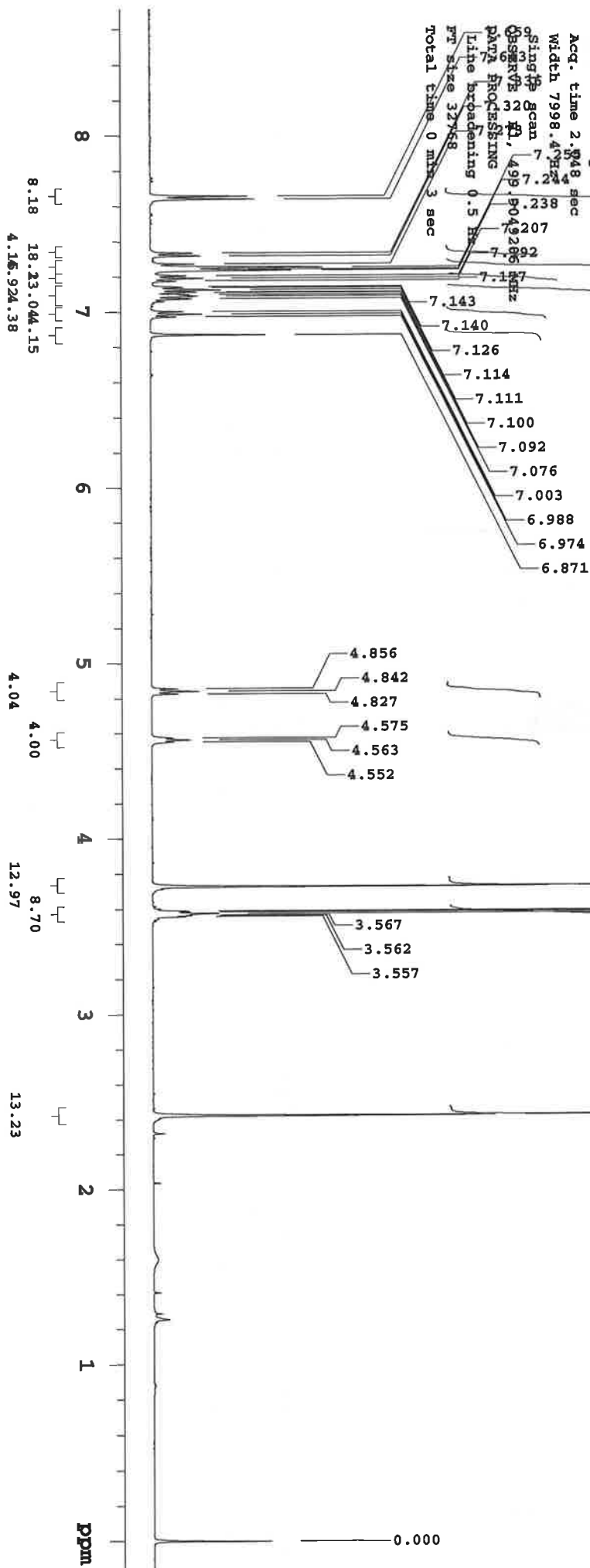
Sample directory:

File: PROTON

Pulse Sequence: PROTON (spul)
Solvent: cdcl3
Data collected on: Jul 21 2016

Operator: nowmms

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 7998.4 Hz
Sweep 1000 Hz
Observed N 1, 499 5049206 Hz
DATA PROCESSING
line broadening 0.5 Hz
FT size 32768
Total time 0 min 3 sec



Agilent Technologies

jxy150421_2_yjk_602c_1_13c CARBON

Sample Name:
jxy150421_2_yjk_602c_1_13c
Data Collected on:
bloch.sci.nov.edu.au-mercury300
Archive directory:

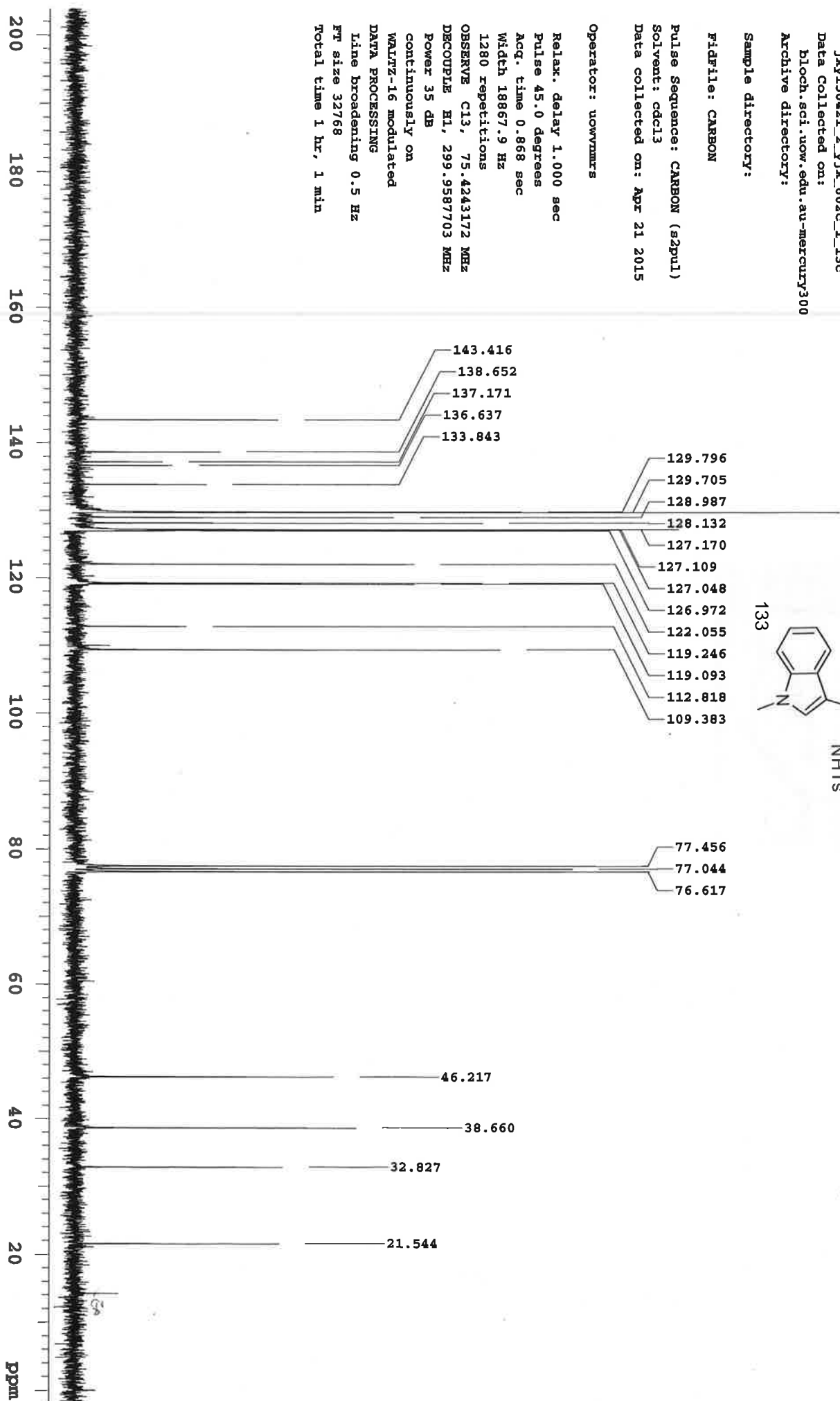
Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pu1)
Solvent: cdcl3
Data collected on: Apr 21 2015

Operator: uowvnmrs

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
1280 repetitions
OBSERVE C13, 75.4243172 MHz
DECOUPLE H1, 299.9587703 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
line broadening 0.5 Hz
FT size 32768
Total time 1 hr, 1 min



Agilent Technologies

jxy150627_2_yjx_676_1_PROTON

Sample Name:
jxy150627_2_yjx_676_1
Data Collected on:
ernst.sci.uow.edu.au-incova500
Archive directory:

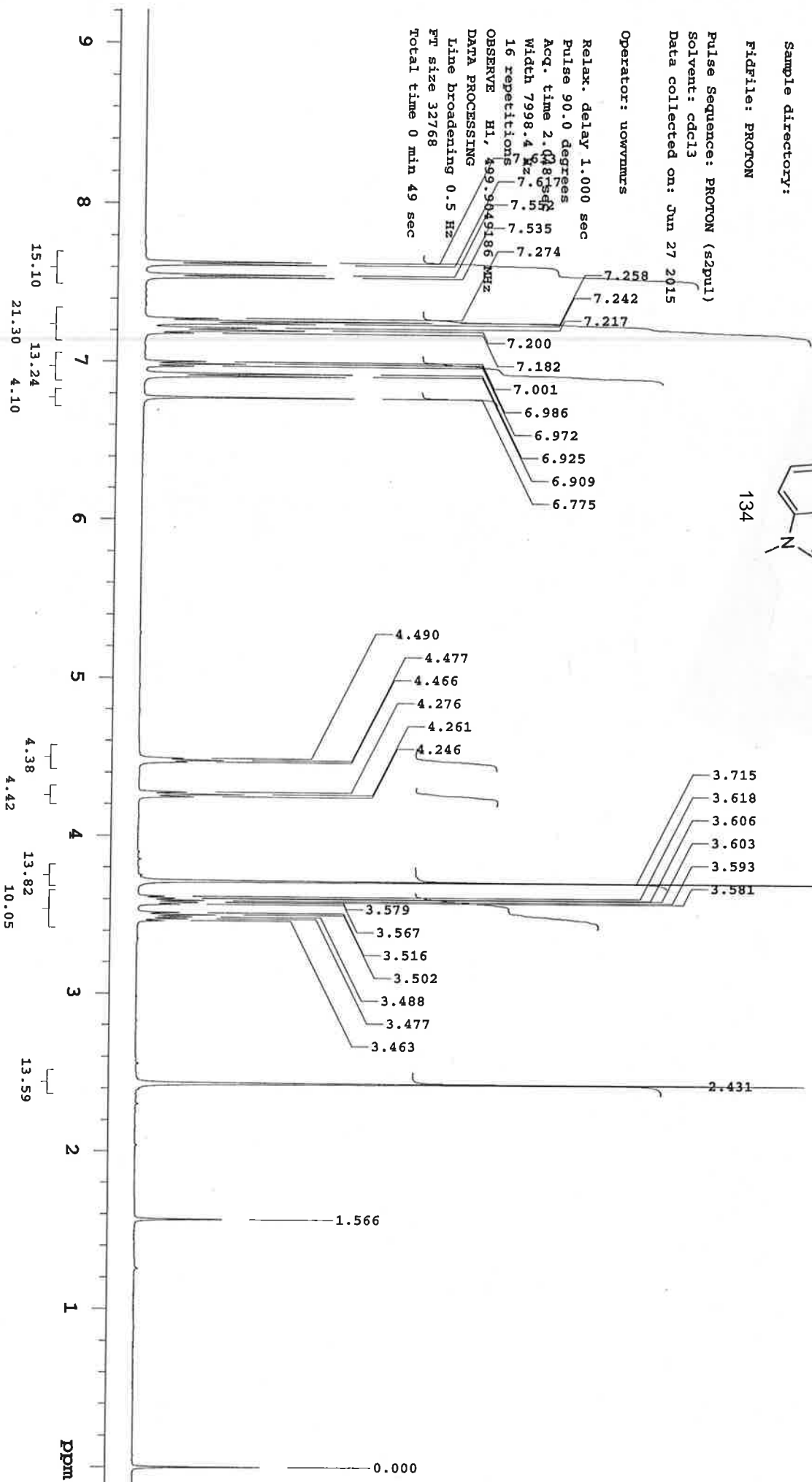
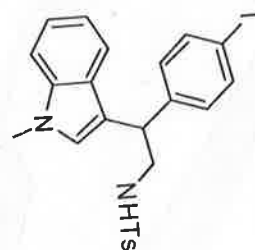
Sample directory:

FIDFile: PROTON

Pulse Sequence: PROTON (s2pul1)
Solvent: cdcl3
Data collected on: Jun 27 2015

Operator: uowvnmrs

Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 2.018 sec
Width 7998.4 Hz
16 repetitions
OBSERVE H1, 499.9049186 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 0 min 49 sec



jxy150627_2.yjx_676_1_13c_CARBON

Sample Name:

jxy150627_2.yjx_676_1_13c

Data collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

/export/home/chempack/vnmrSYS/data

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jun 27 2015

Operator: uowvnmrs

Relax. delay 1.00 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

1344 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

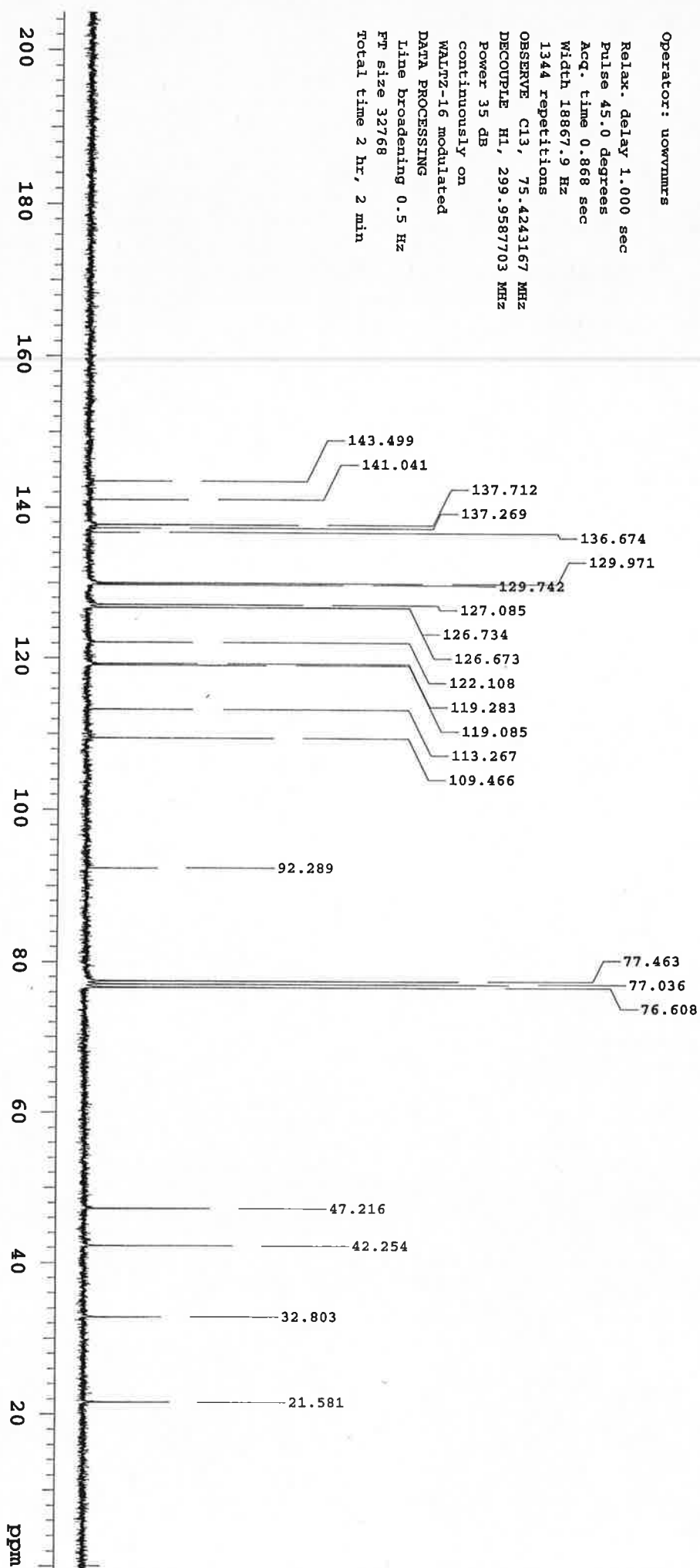
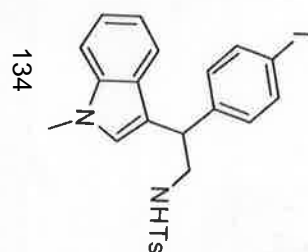
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 2 hr, 2 min



Agilent Technologies

Pulse Sequence: szpul

Solvent: cdcl3

Temp: 25.0 C / 298.1 K

Operator: uoww/mrs

VNMR5-500 "pyne06.domain.com"

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 4.000 sec

Width 8012.8 Hz

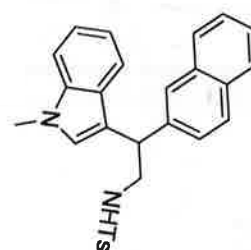
16 repetitions

OBSERVE H1, 499.7414041 MHz

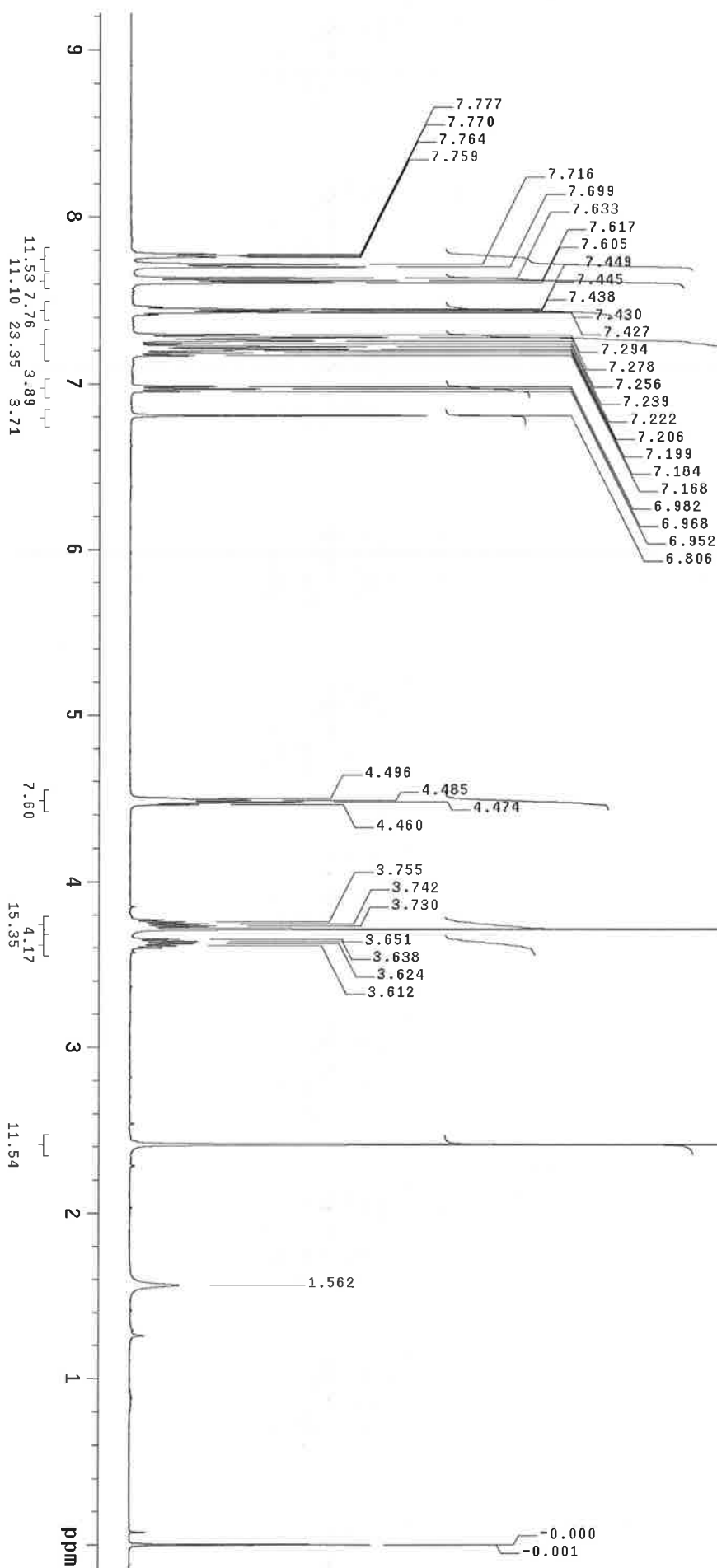
DATA PROCESSING

FT size 65536

Total time 1 min, 20 sec



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jxy150624_2_yjk_669_1_13c CARBON

Sample Name:

jxy150624_2_yjk_669_1_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

/export/home/chempack/vnmrsvs/data

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jun 24 2015

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 1867.9 Hz

2304 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

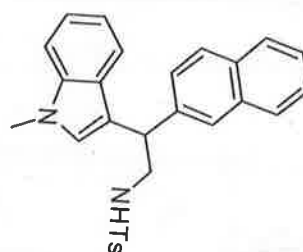
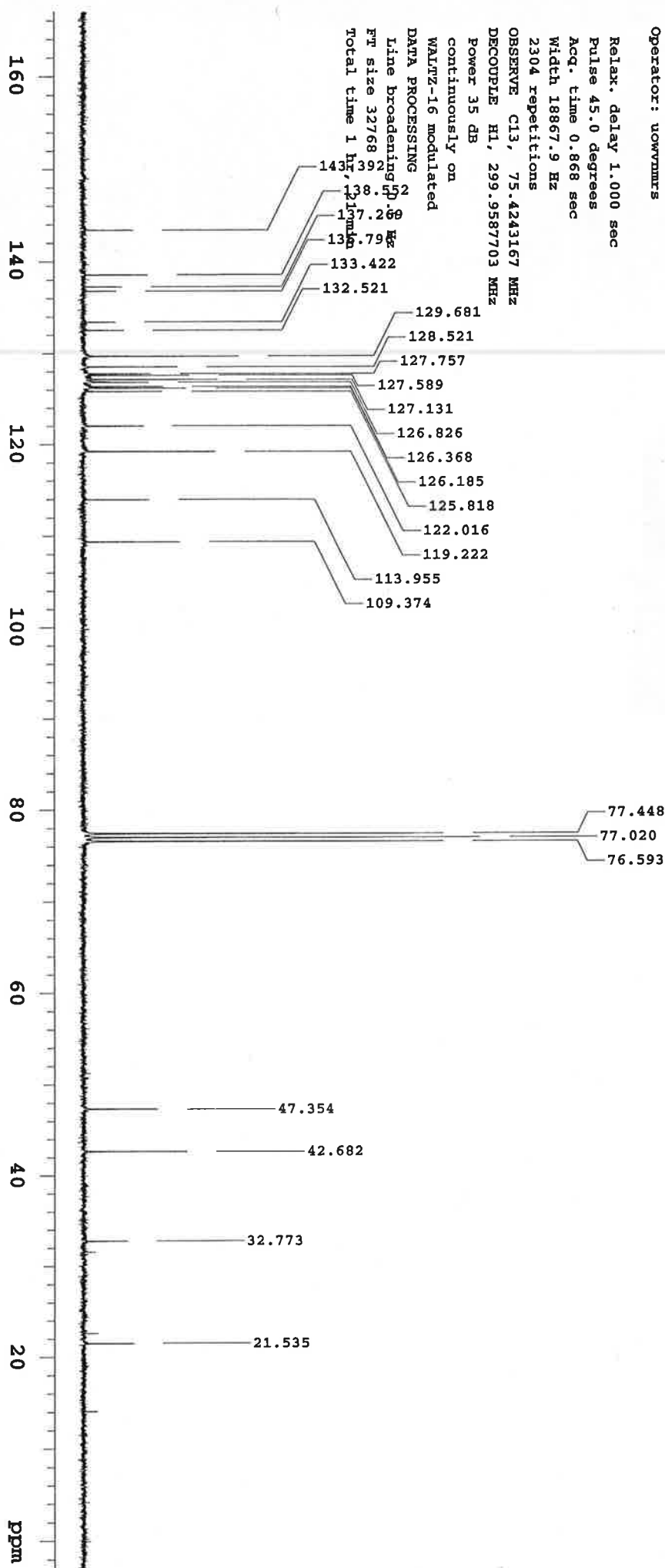
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.8 Hz

FT size 32768

Total time 1 hr, 21 min



Agilent Technologies

jxy150511_2_vjk_614_2_recristalisation_PROTON

Sample Name:

jxy150511_2_vjk_614_2_recristalisation

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: PROTON

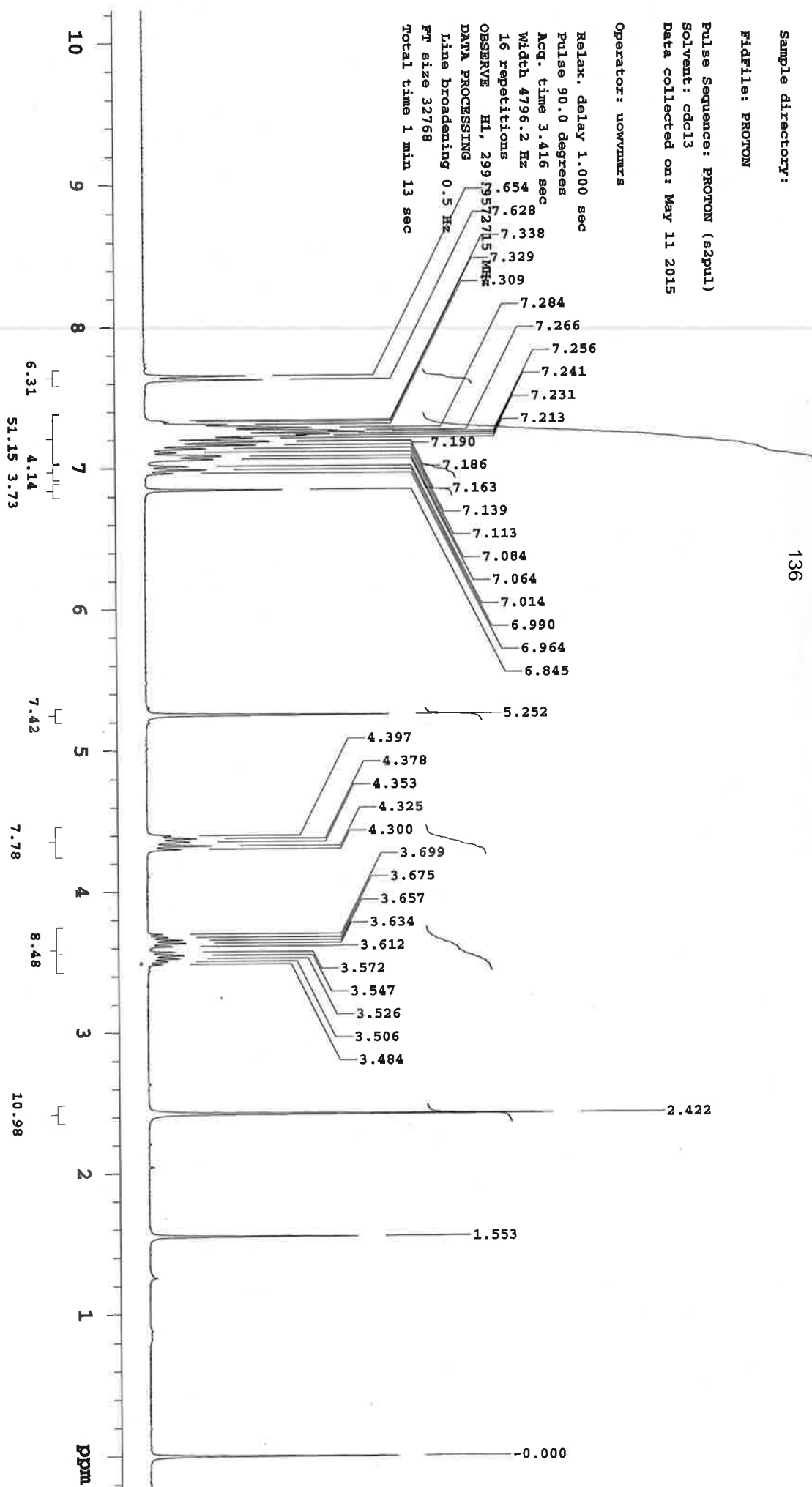
Pulse Sequence: PROTON (s2pul1)

Solvent: cdcl3

Data collected on: May 11 2015

Operator: uowvnmrs

Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 3.416 sec
Width 4796.2 Hz
16 repetitions
OBSERVE H1, 299.19572715 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 1 min 13 sec



Agilent Technologies

jxy150511_2_yjx_614_2_13c_recristalisation_CARBON

Sample Name:
jxy150511_2_yjx_614_2_13c_recristalisation
Data Collected on:
bloch.sci.uow.edu.au-mercury300
Archive directory:

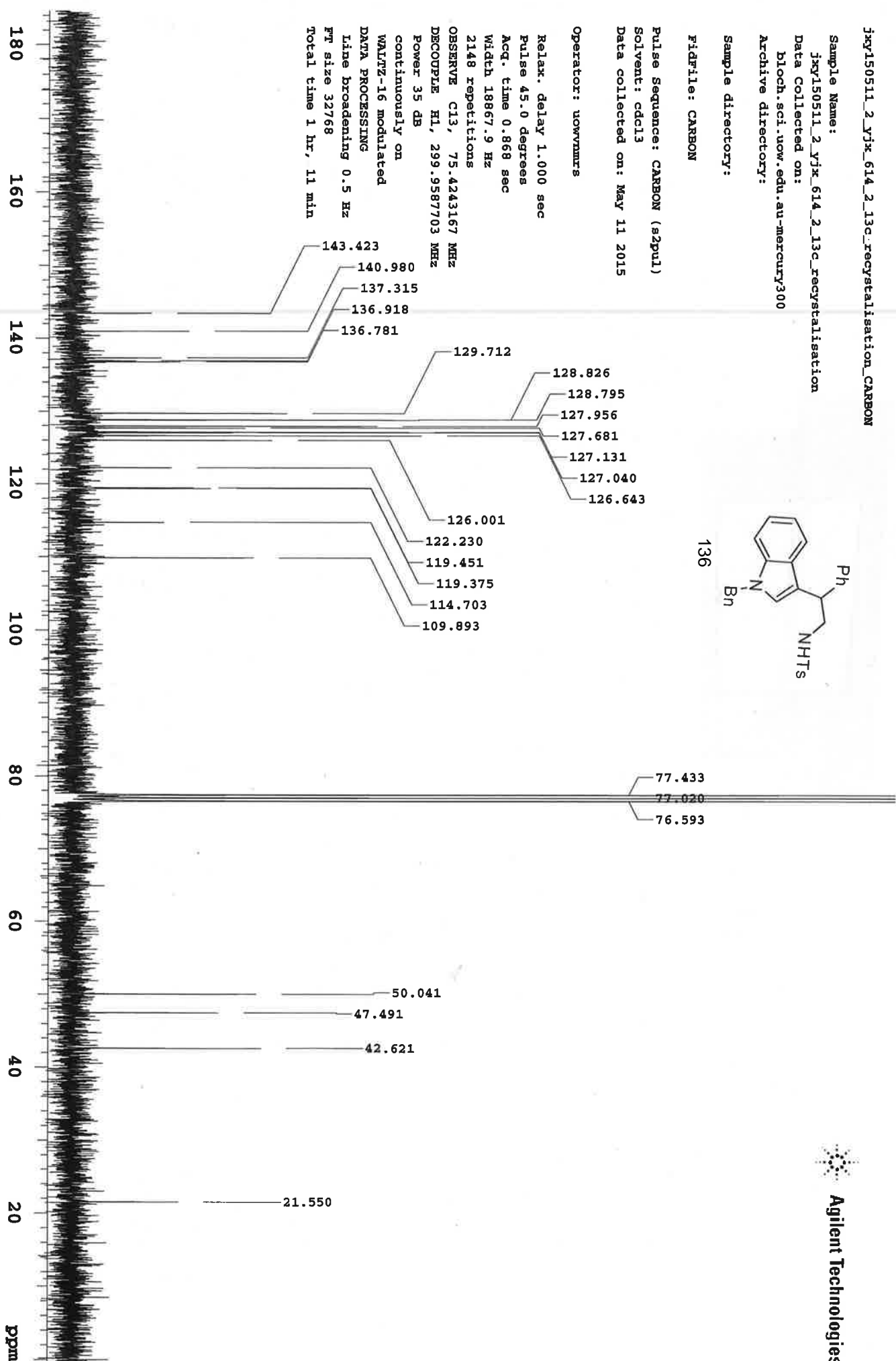
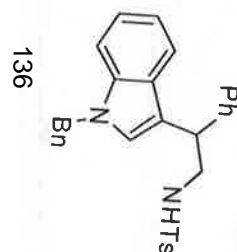
Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 11 2015

Operator: uownmrs

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
2148 repetitions
OBSERVE C13, 75.4243167 MHz
DECOUPLE H1, 299.9587703 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 1 hr, 11 min



Agilent Technologies

yjx160722_3h_PROTON

Sample Name:

yjx160722_3h

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

File: PROTON

Pulse Sequence: PROTON (zgpg30)

Solvent: cdcl3

Data collected on: Jul 22 2016

Operator: uowmms

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 2.049 sec

Width 6553.4 Hz

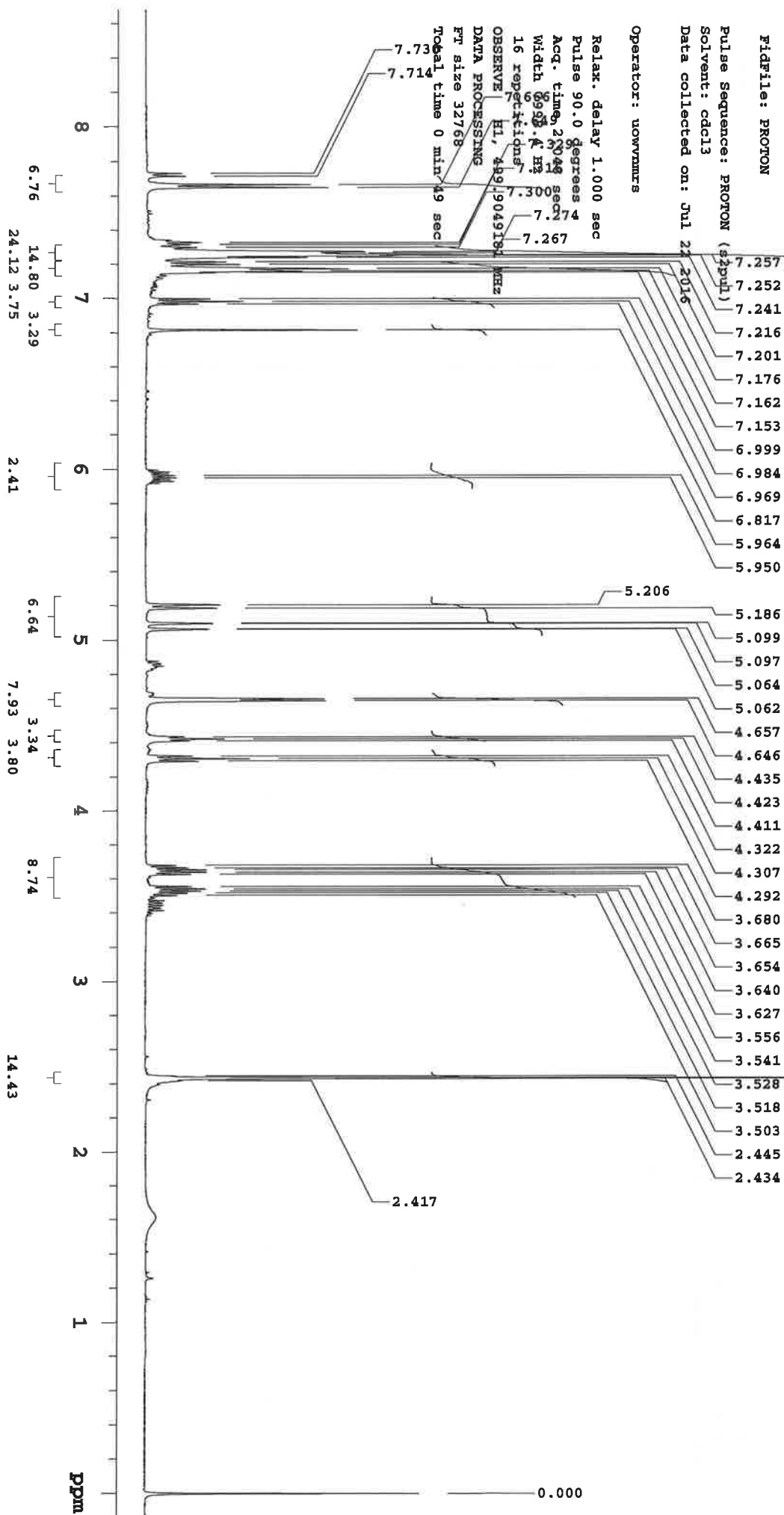
16 repetitions

OBSERVE H1, 400.19049184 MHz

DATA PROCESSING

FT size 32768

Total time 0 min 49 sec



Agilent Technologies

jxy150514_2_yjk_626_1_13c CARBON

Sample Name:

jxy150514_2_yjk_626_1_13c

Data collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: May 14 2015

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

1952 repetitions

OBSERVE C13, 75.4243172 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

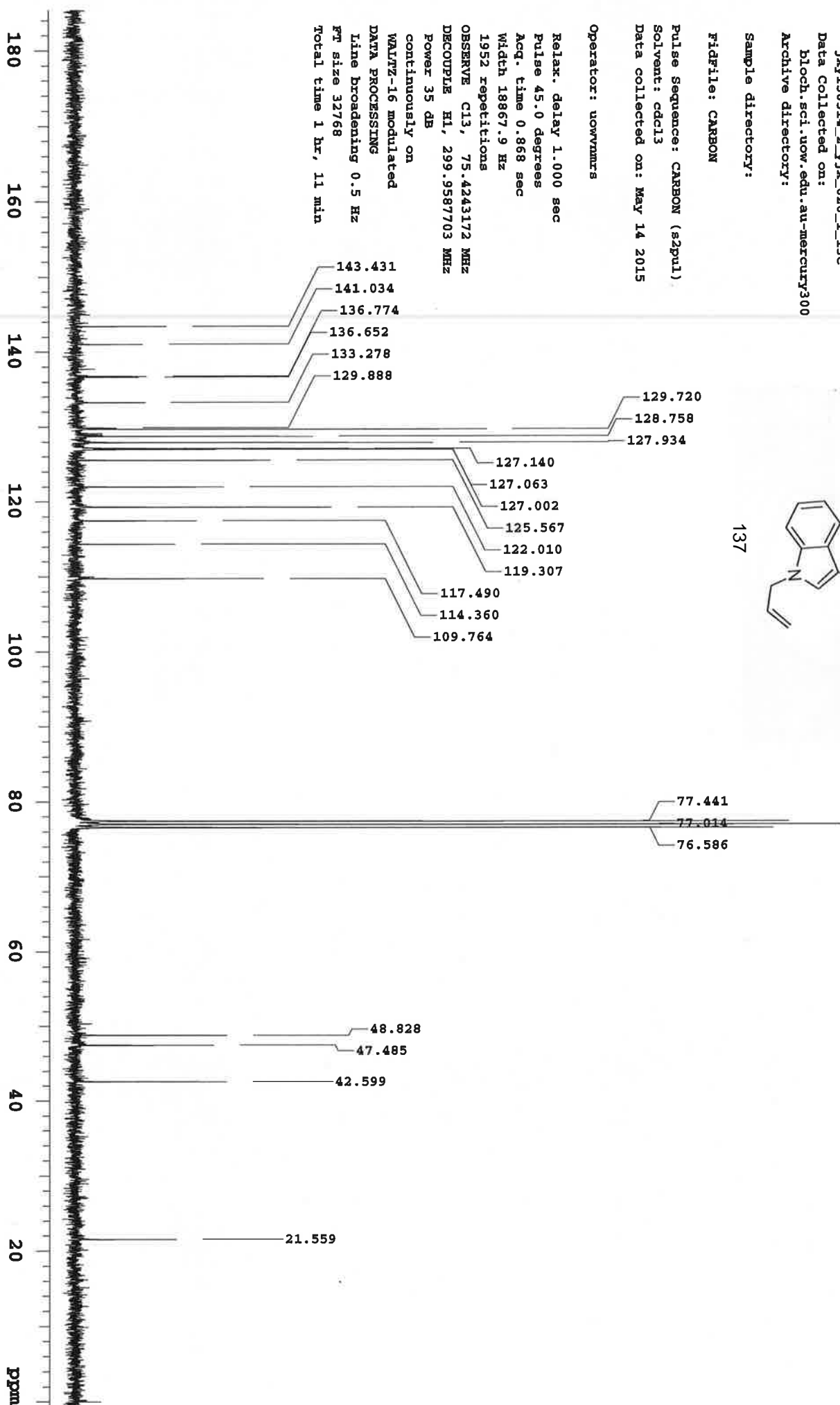
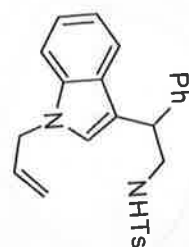
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

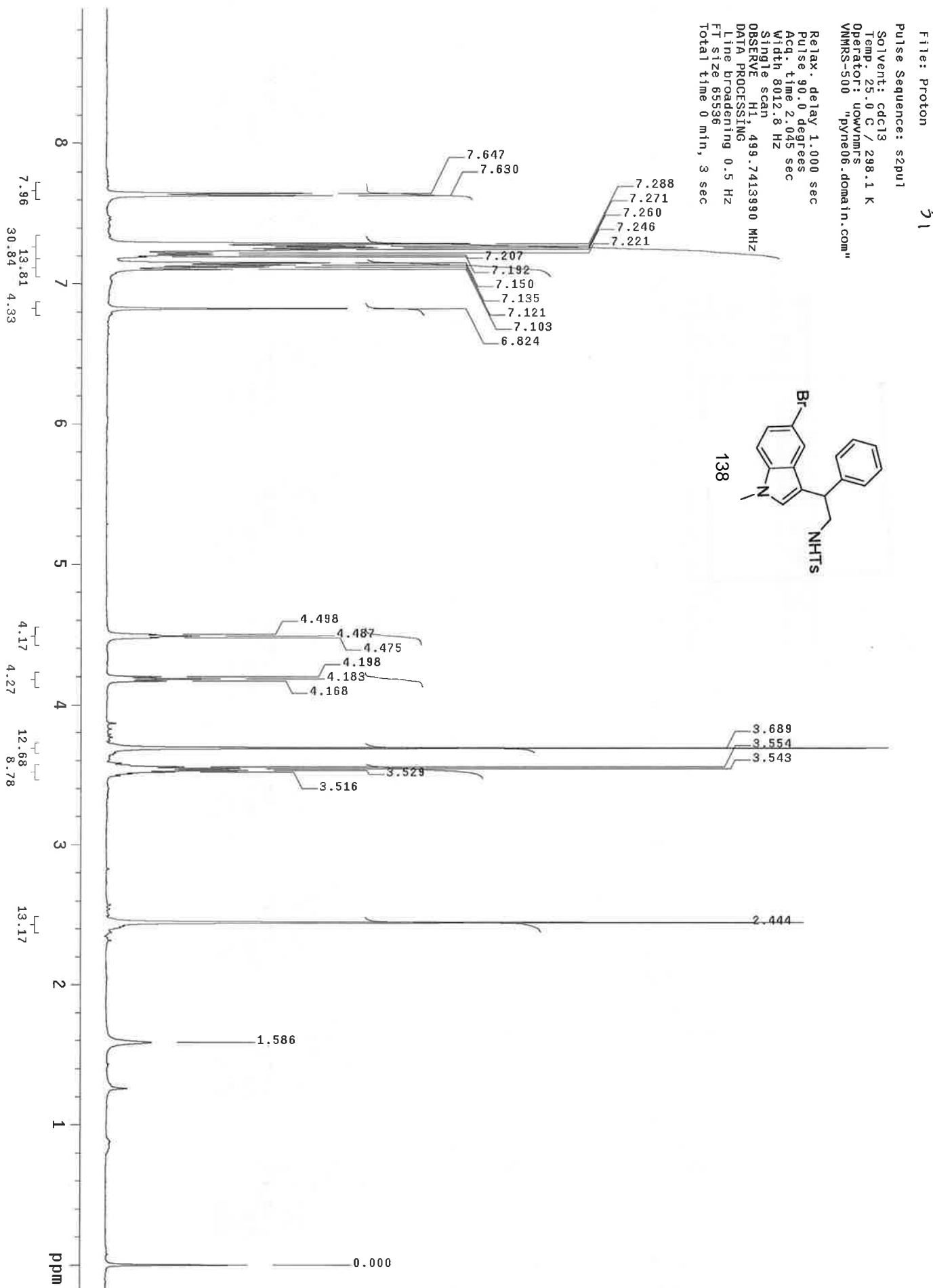
FT size 32768

Total time 1 hr, 11 min



Agilent Technologies

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jxy150531_2.yjk_642_1_13c-CARBON

Sample Name:

jxy150531_2.yjk_642_1_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdc13

Data collected on: May 31 2015

Operator: uowymms

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

3520 repetitions

OBSERVE C13, 75.4243161 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

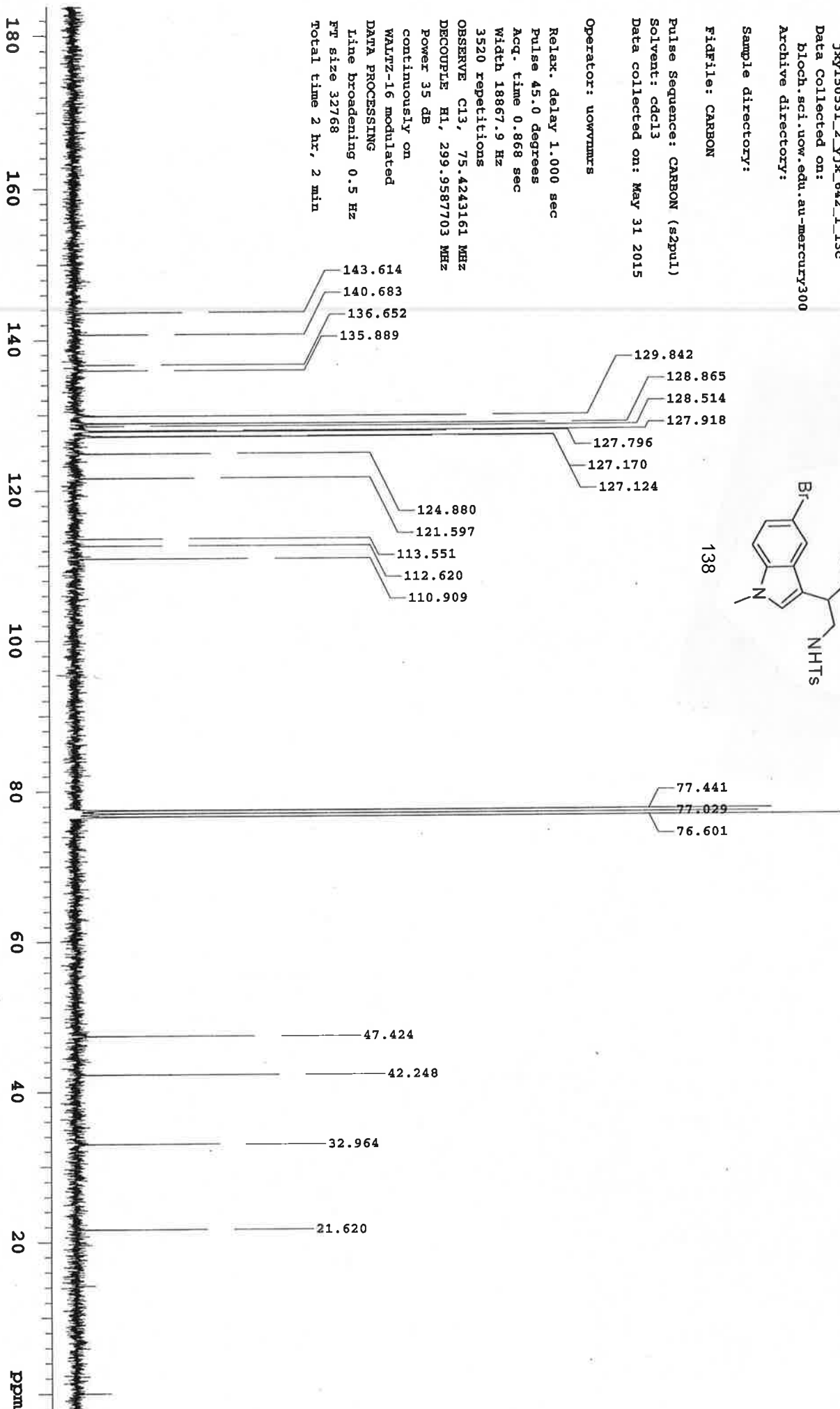
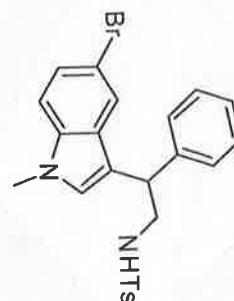
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 2 hr, 2 min



Agilent Technologies

jxy150602_2_yjx_643_1_Proton

File: Proton

Pulse Sequence: s2pu1

Solvent: cdcl3

Temp: 2.0 C / 275.1 K

Operator: uowvnmr2

VNMRK-500 "pyre06.domain.com"

Relax. delay 1.000 sec

Pulse: 90.0 degrees

Acq. time 2.045 sec

Width 8012.8 Hz

16 repetitions

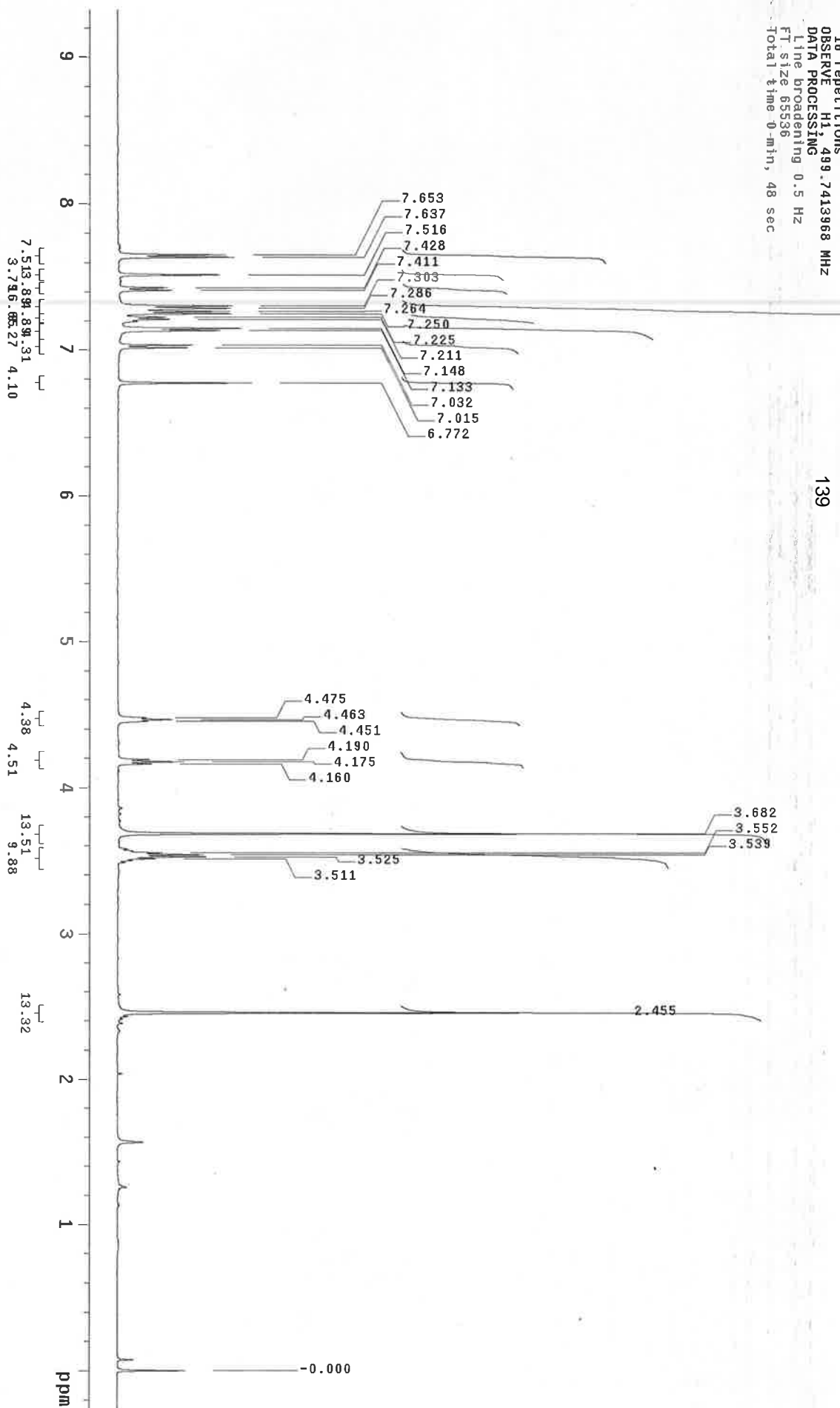
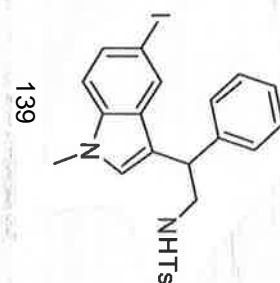
OBSERVE H1, 499.7413968 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 0-min, 48 sec



jxy150602_2_vjx_643_1_13c_Carbon

File: Carbon

Pulse Sequence: s2pul1

Solvent: cdcl3

Temp: 2.0 C / 275.1 K

Operator: ucwvnmr2

VMRS-500 "pyne06.domain.com"

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 0.537 sec

Width 30487.8 Hz

2048 repetitions

OBSERVE C13, 125.6600717 MHz

DECUPLE H1, 499.7438337 MHz

Power 45 dB

continuously on

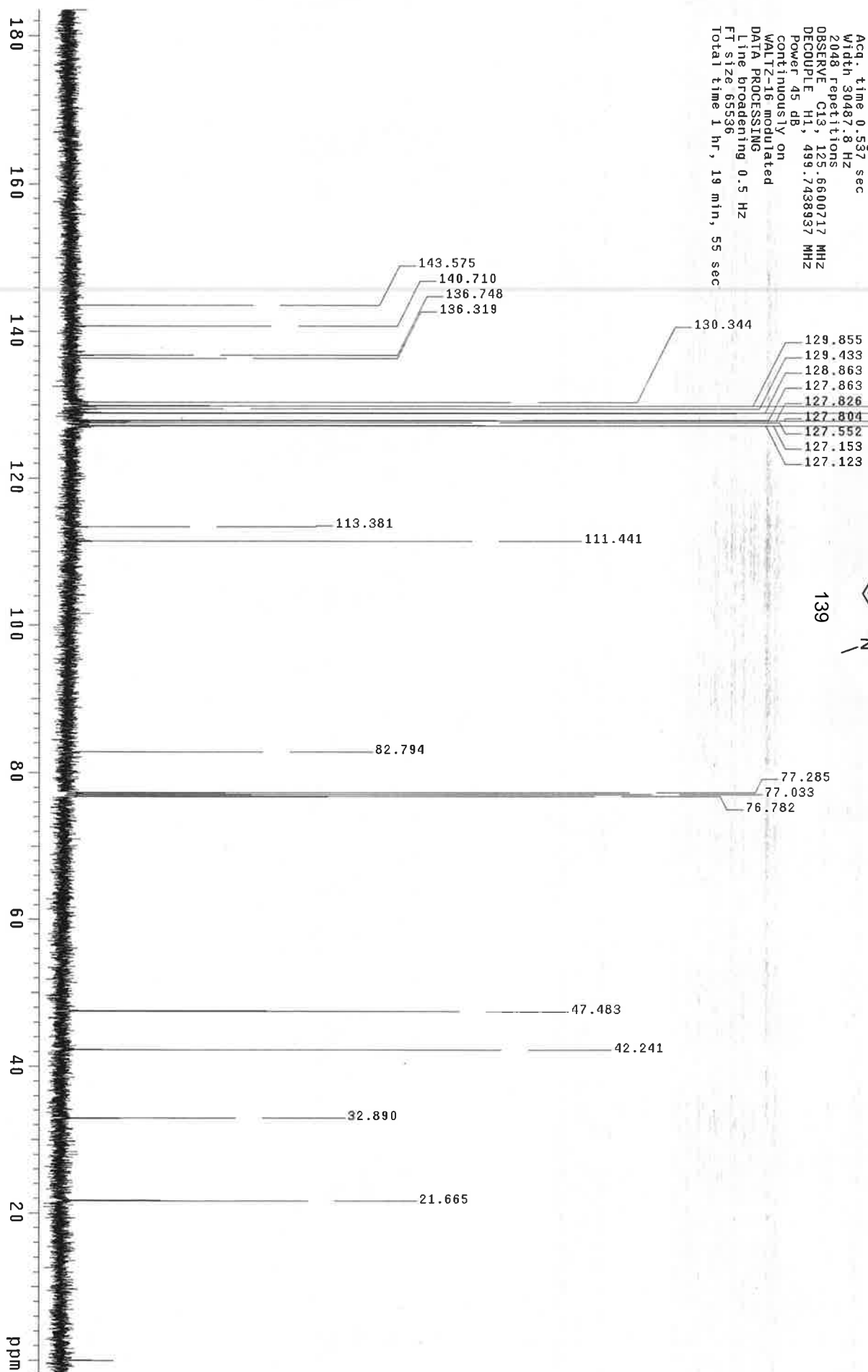
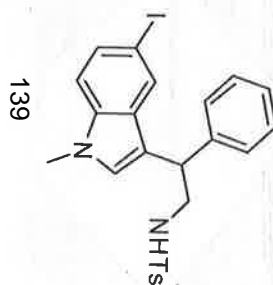
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 1 hr, 19 min, 55 sec



Sample Name:

yjk160722_3k

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (s2pul)

Solvent: cdCl_3

Data collected on: Jul 22 2016 9 m

Operator: 7
new 7
vms 2
mas 0
194
0

~~Relax. delay 2.000 sec~~

Pulse 90.0 degrees

Acq. Time 2.048 sec

91667-7998.4 Hz

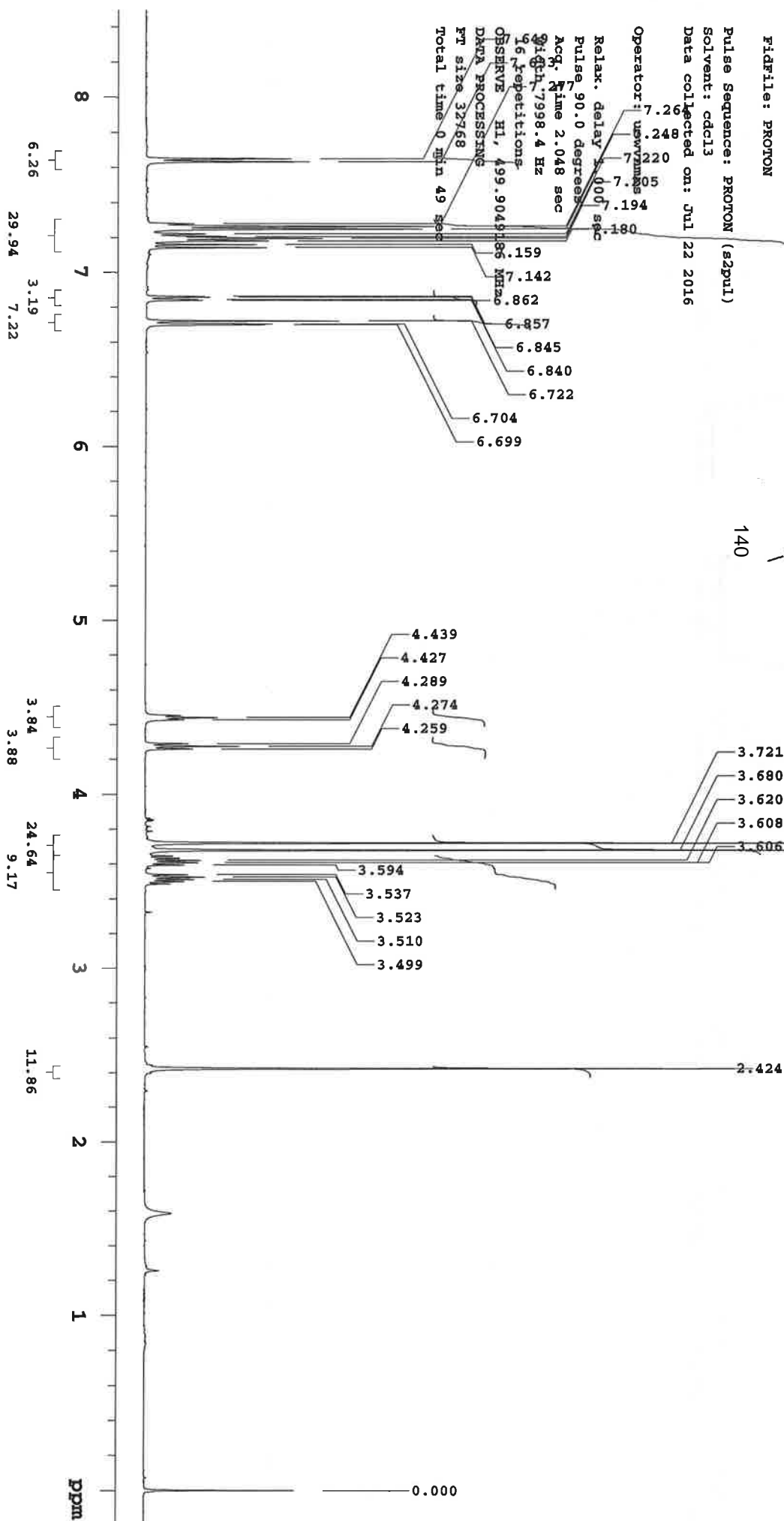
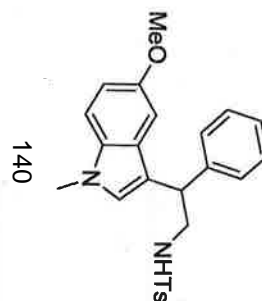
96 repetitions

OBSERVE H1, 499.90491

~~DATA PROCESSING~~

FT size	32768
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Total time 0 min 49 sec



jxy150604_2_vjk_644_1_13c CARBON

Sample Name:

jxy150604_2_vjk_644_1_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

/export/home/chempack/vnmrSYS/data

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jun 4 2015

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

2764 repetitions

OBSERVE C13, 75.4243172 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 1 hr, 31 min

160

140

120

100

80

60

40

20

ppm

153.708

141.019

136.713

132.606

129.690

128.758

127.918

127.308

127.124

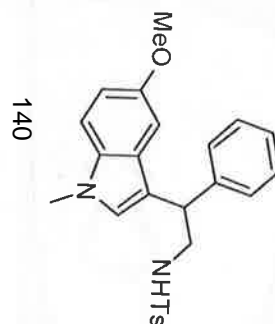
126.987

113.276

112.131

110.146

101.031



77.441

77.014

76.586

55.760

47.347

42.568

32.934

21.528



Agilent Technologies

File: Proton

36

Pulse Sequence: szpu1

Solvent: cdcl3

Temp: 25.0 C / 298.1 K

Operator: uowvmr

VNMR5-500 "pyne06.domain.com"

Relax. delay 0.001 sec

Pulse 45.0 degrees

Acq. time 2.045 sec

Width 8012.8 Hz

Single scan

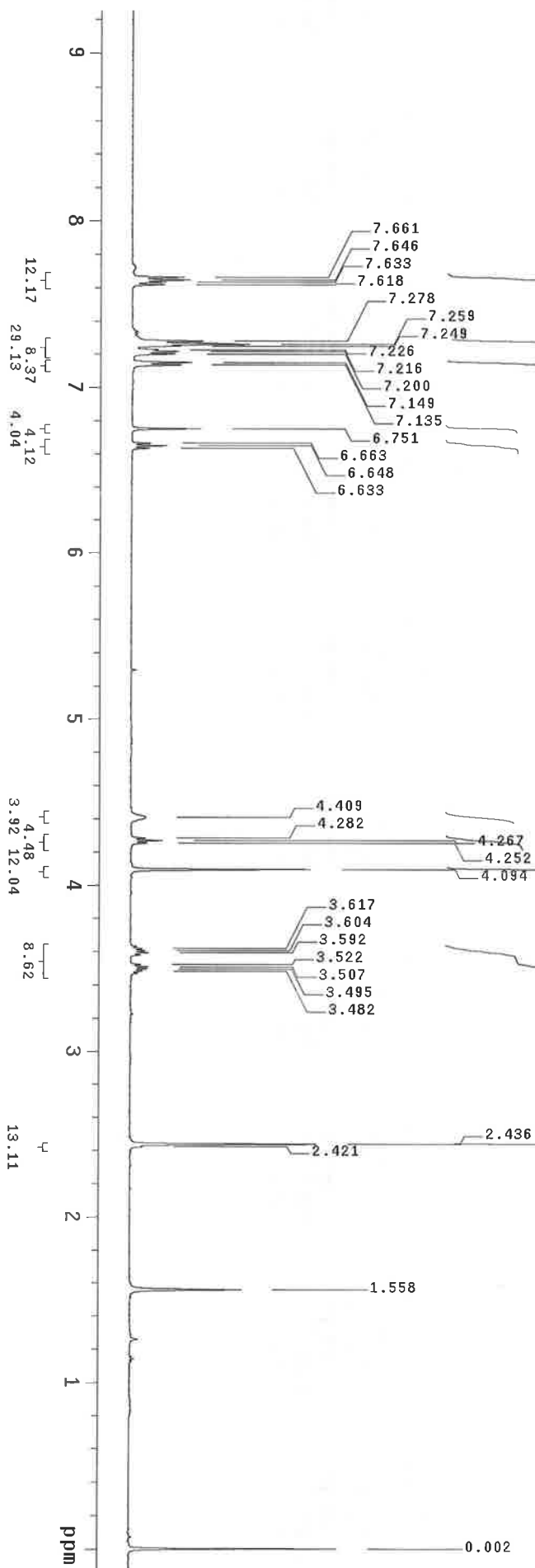
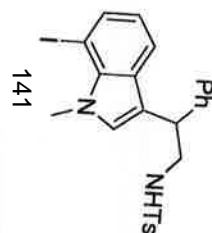
OBSERVE H1, 499.7413949 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 0 min, 2 sec



jxy150604_2.yjk_645_1_13c-CARBON

Sample Name:

jxy150604_2.yjk_645_1_13c

Data Collected on:

bloch.sci.nsw.edu.au-mercury300

Archive directory:

/export/home/chempack/vnmrSYS/data

Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdc13

Data collected on: Jun 4 2015

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

32 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 16 hr, 3 min

160

140

120

100

80

60

40

20

ppm

143.484
140.613
136.766
135.972

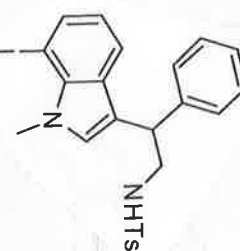
134.429
129.773

129.727
129.269
128.841
127.849
127.162
127.116

120.886
119.344

113.542

141



77.417
77.204
77.005
76.578

73.005

47.384

42.132

36.803

21.550

-0.024



Agilent Technologies

jxy150604_2.yjk_647_1_PROTON

Sample Name:

jxy150604_2.yjk_647_1

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (szpul)

Solvent: cdcl3

Data collected on: Jun 4 2015

Temp. 25.0 C / 298.1 K

Operator: ucwvmmrs

Relax. delay 1.000 sec

Pulse 80.0 degrees

Acq on time 2.048 sec

Width 7998.4 Hz

16 repetitions

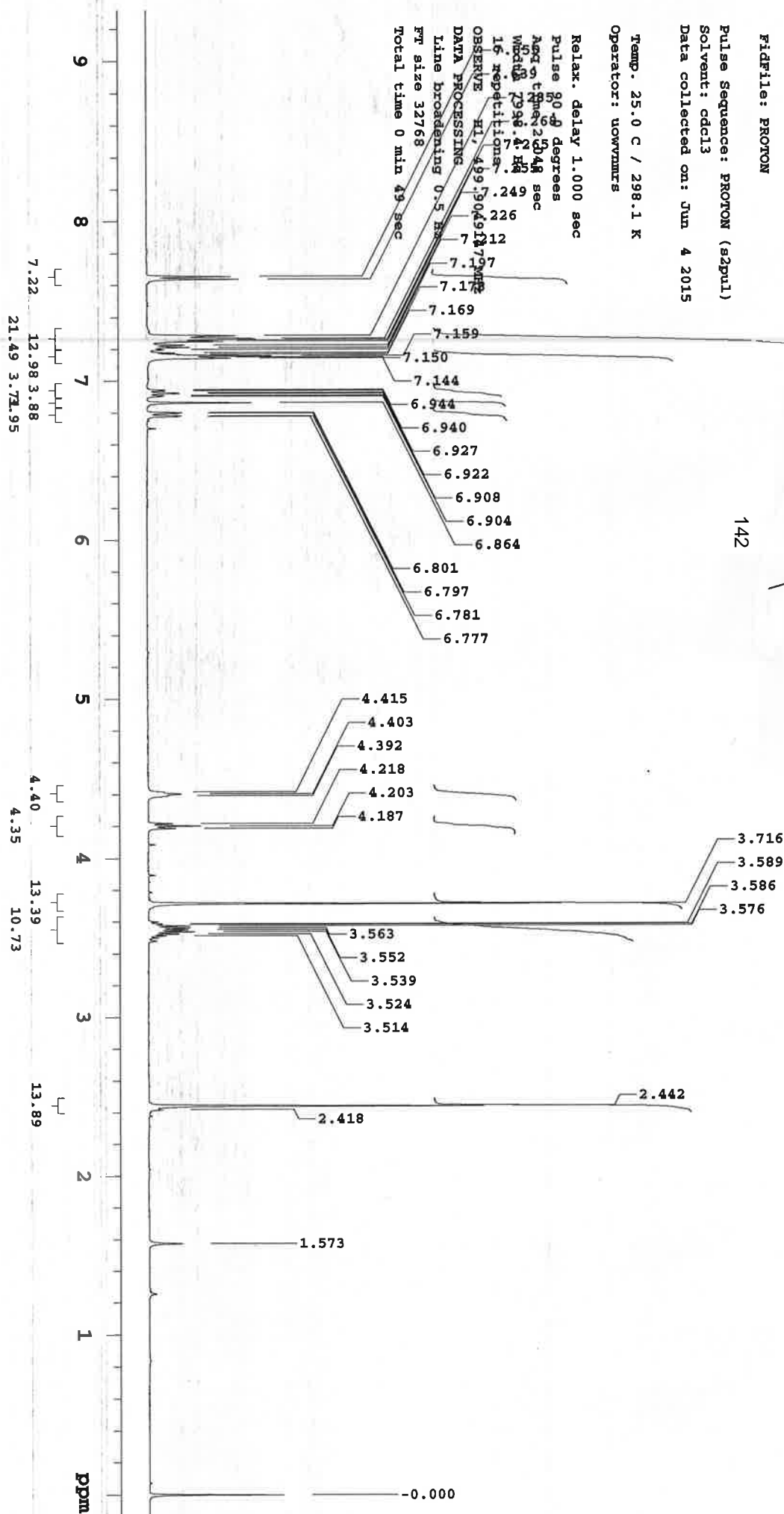
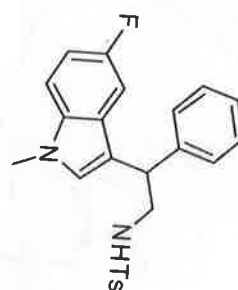
OBSERVE H1, 499.904137 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 0 min 49 sec



Agilent Technologies

jxy150604_2_vjk_647_1_13c CARBON

Sample Name:

jxy150604_2_vjk_647_1_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

/export/home/chempack/vnmr/sy/data

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pu1)

Solvent: cdcl3

Data collected on: Jun 4 2015

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

2764 repetitions

OBSERVE C13, 75.4243160 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

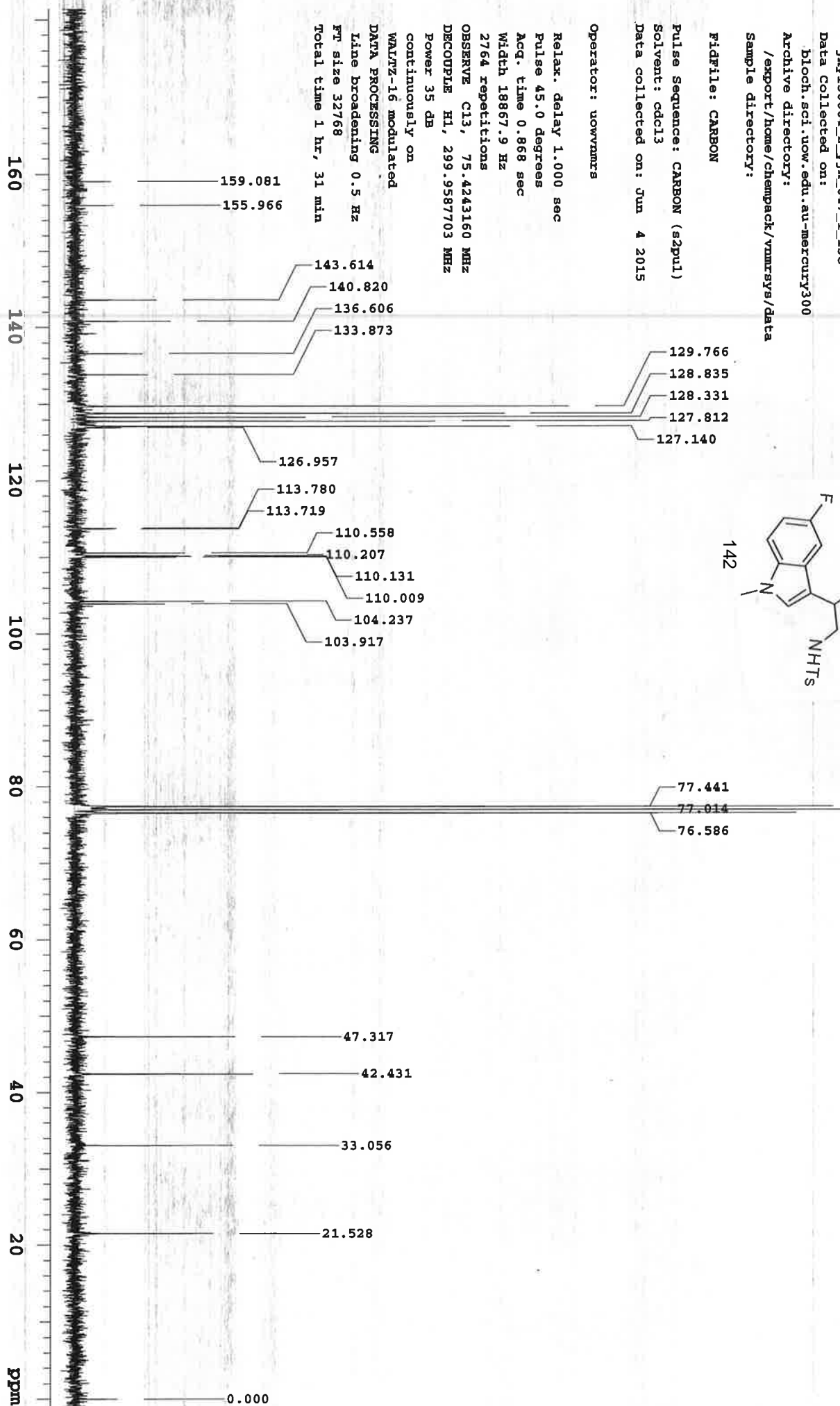
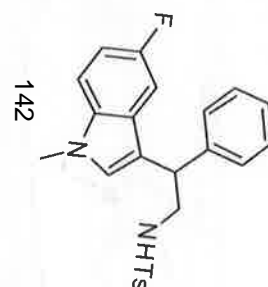
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 1 hr, 31 min



Agilent Technologies

jxy150604_2.yjk_648_1_PROTON

Sample Name:

jxy150604_2.yjk_648_1

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (s2pu1)

Solvent: cdcl3

Data collected on: Jun 4 2015

Temp. 25.0 C / 298.1 K

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 2.048 sec

Width 7998.4 Hz

16 repetitions

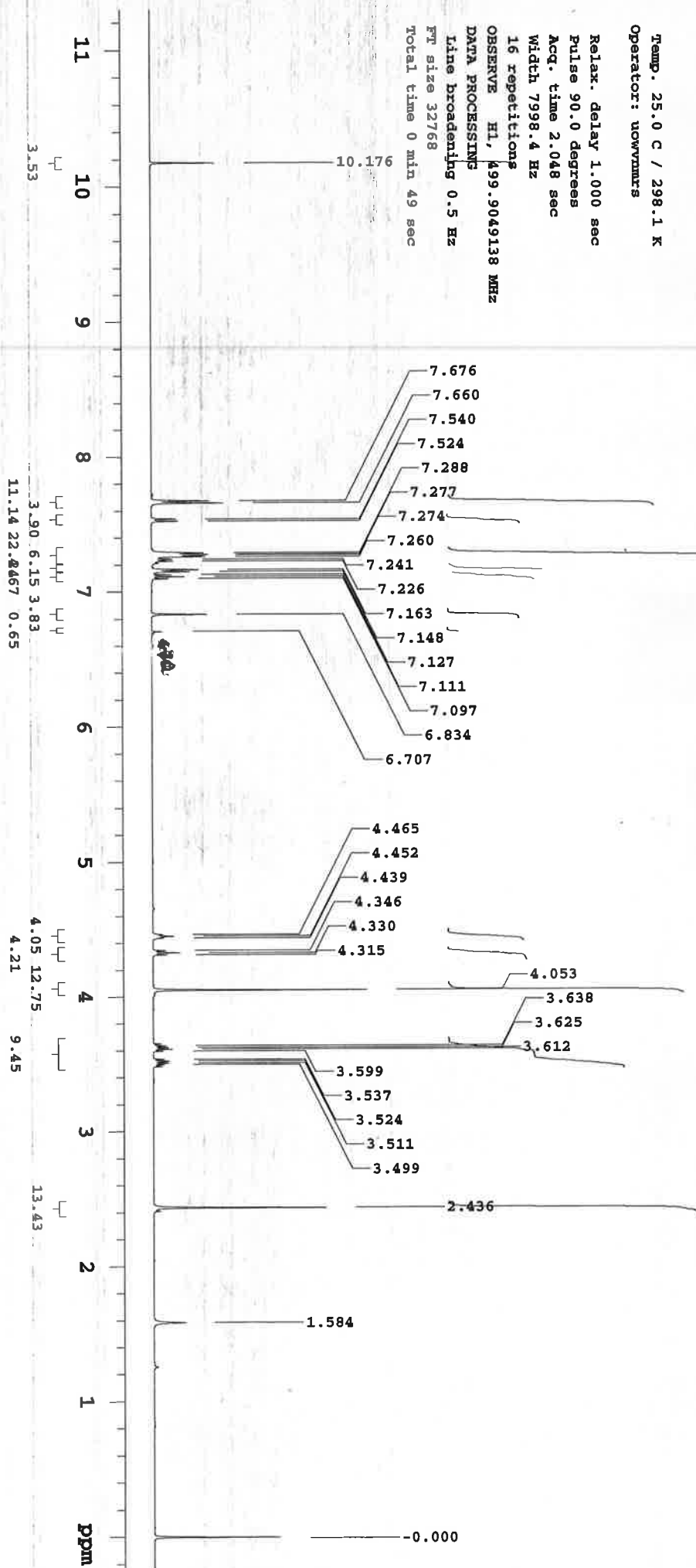
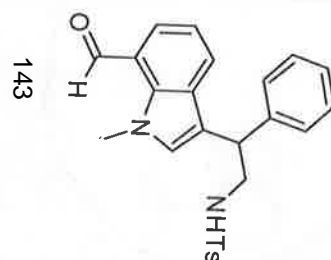
OBSERVE H1, 499.9049138 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 0 min 49 sec



Agilent Technologies

jxy150604_2_vjx_648_1_13c CARBON

Sample Name:
jxy150604_2_vjx_648_1_13c
Data Collected on:
ernst.sci.uow.edu.au-inova500
Archive directory:

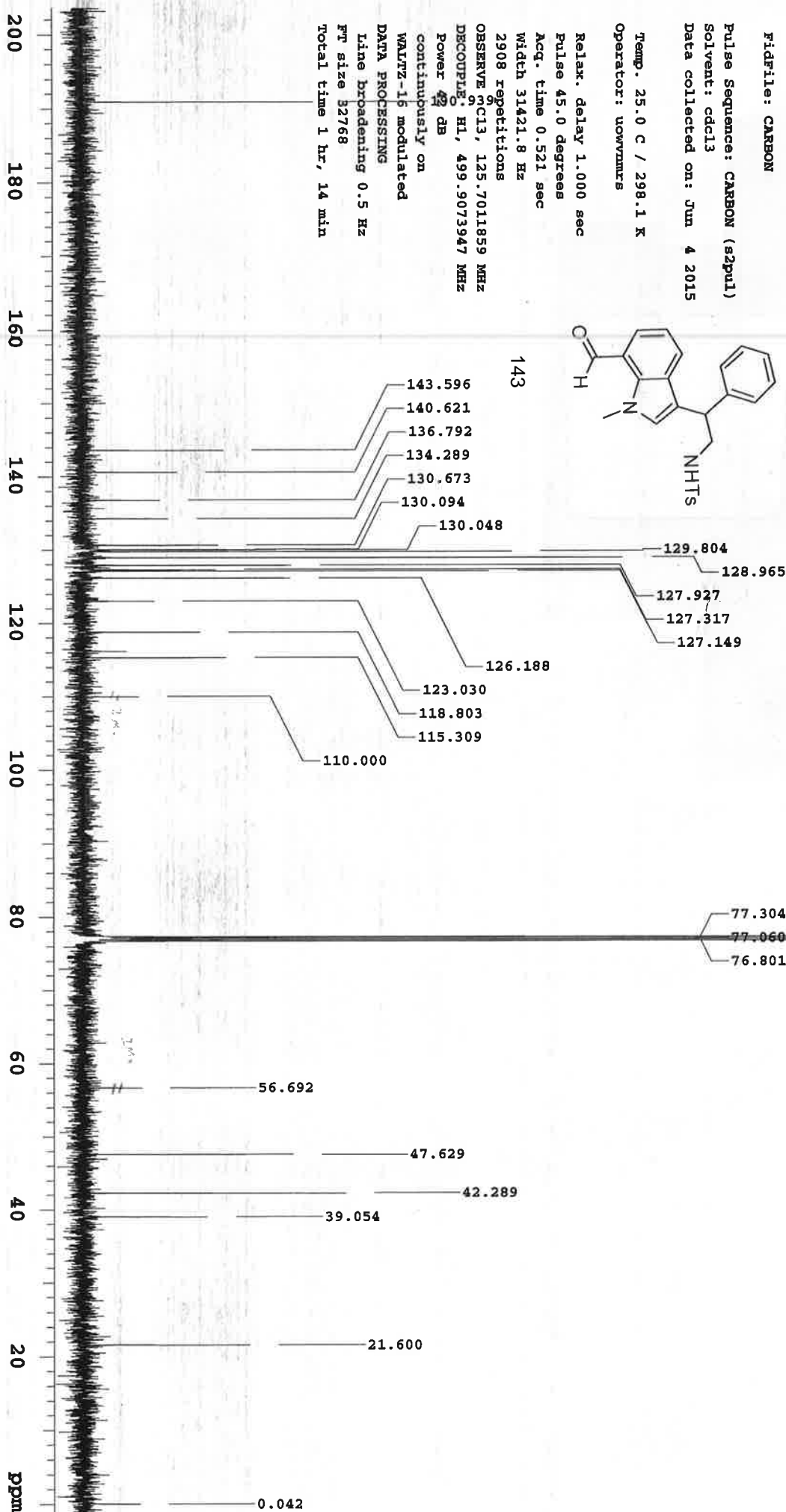
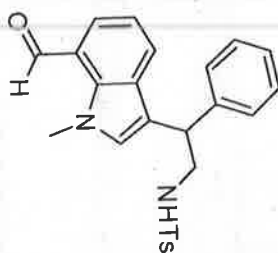
Sample directory:

File: CARBON

Pulse Sequence: CARBON (szpul)
Solvent: cdcl3
Data collected on: Jun 4 2015

Temp. 25.0 C / 298.1 K
Operator: uowvnmrs

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.521 sec
Width 31421.8 Hz
2908 repetitions
OBSERVE ν C13, 125.701859 MHz
DECOUPLE ν H1, 499.9073947 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
line broadening 0.5 Hz
FT size 32768
Total time 1 hr, 14 min

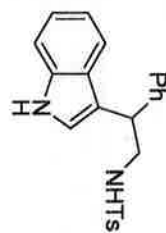


Agilent Technologies

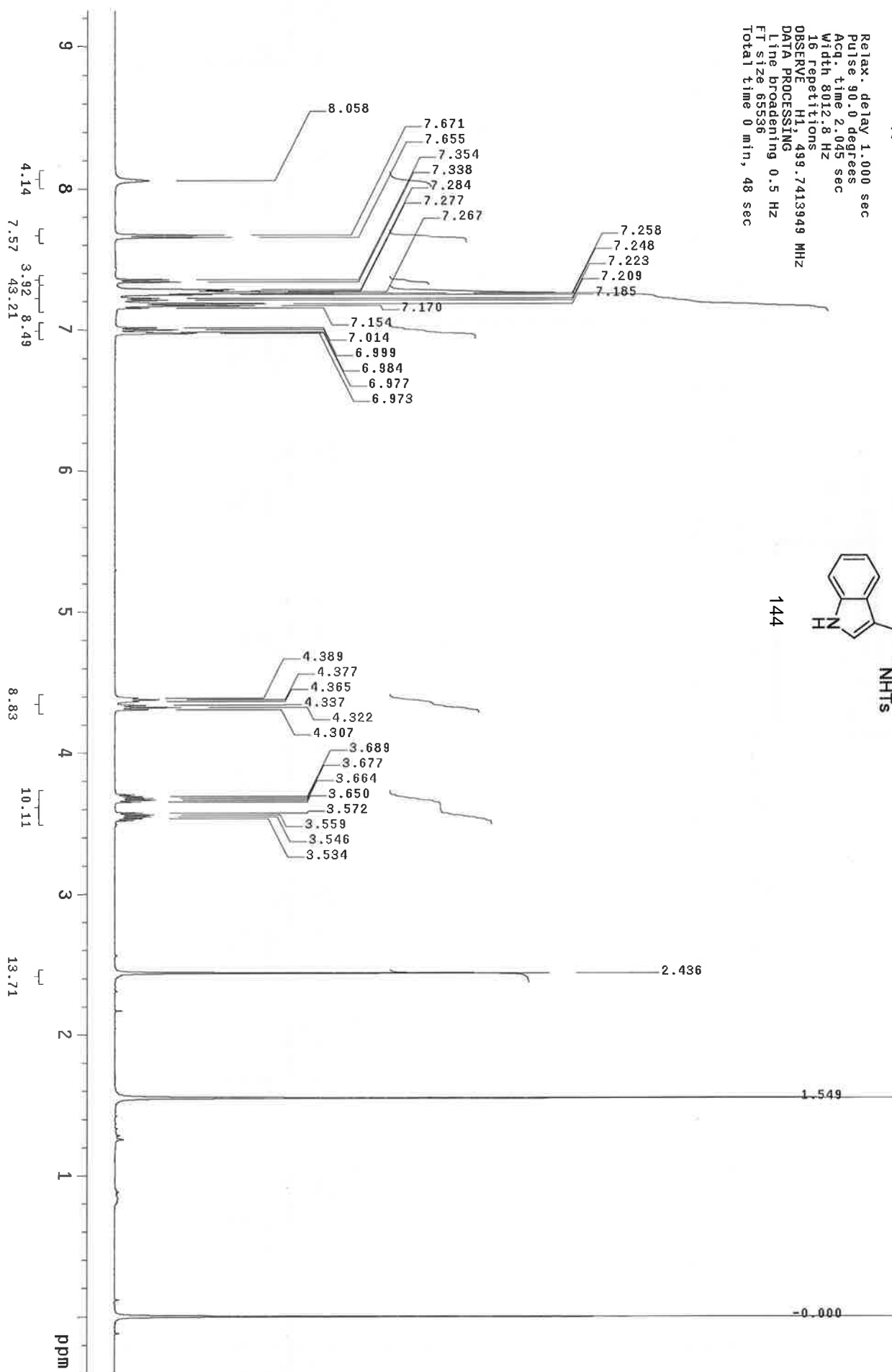
jxy160721_3n_Proton 3n
File: Proton

Pulse Sequence: s2pu1
Solvent: cdcl3
Temp: 25.0 C / 298.1 K
Operator: uowvnmrs
VNMRS-500 "pyne06.domain.com"

Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 2.045 sec
Width 8012.8 Hz
16 repetitions
OBSERVE H1, 499.7413949 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 48 sec



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jxy150618_2.yjx_654_1_13c CARBON

Sample Name:

jxy150618_2.yjx_654_1_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: CARBON

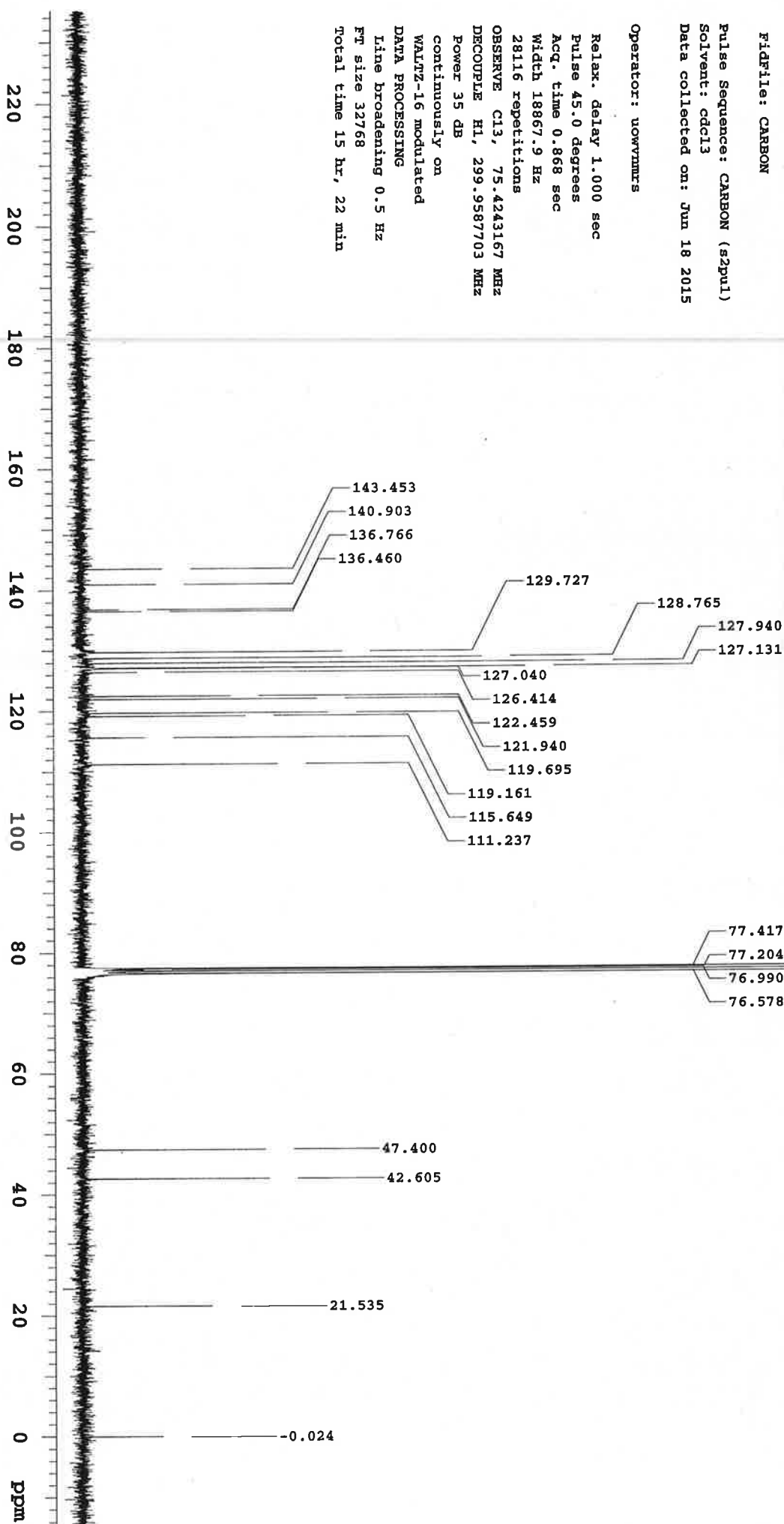
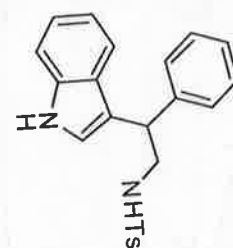
Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jun 18 2015

Operator: uowvnmrs

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
2816 repetitions
OBSERVE C13, 75.4243167 MHz
DECOUPLE H1, 299.9587703 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 15 hr, 22 min



Agilent Technologies

Sample Name: 30

Data Collected on:
ernst.sci.uow.edu.au-inova500
Archive directory:

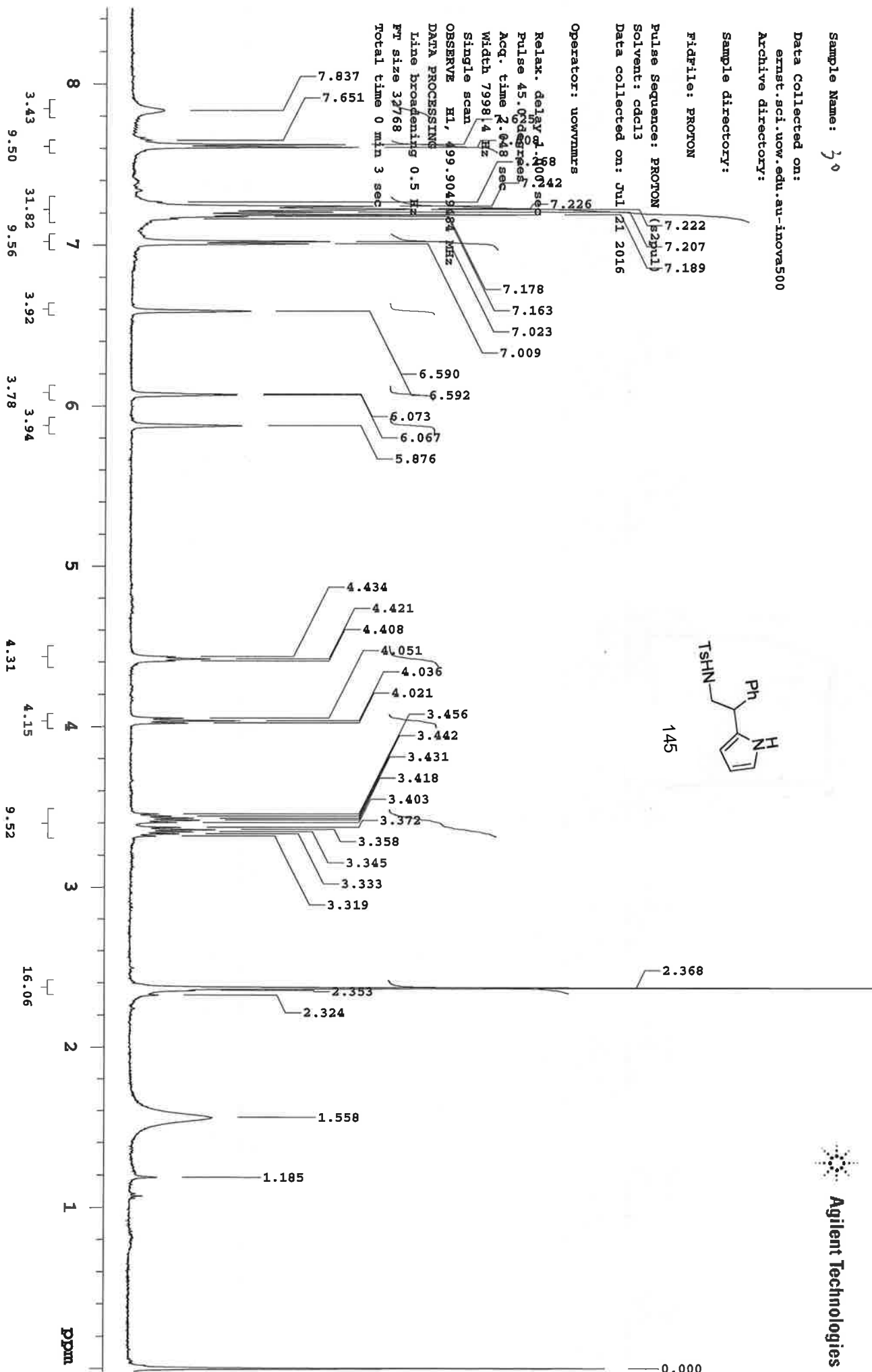
Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jul 21 2016

Operator: uowmms

Relax. delay of 8.000 sec
Pulse 45.0 degrees
Acq. time 2.648 sec
Width 7998.4 Hz
Single scan
OBSERVE H1, 499.9049 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 0 min 3 sec



Agilent Technologies

jxy150626_2_yjk_671_1_13c-CARBON

Sample Name:

jxy150626_2_yjk_671_1_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

/export/home/chempack/vnmrSYS/data

Sample directory:

FIDFile: CARBON

Pulse Sequence: CARBON (s2pul1)

Solvent: cdcl3

Data collected on: Jun 26 2015

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

3296 repetitions

OBSERVE C13, 75.4243921 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

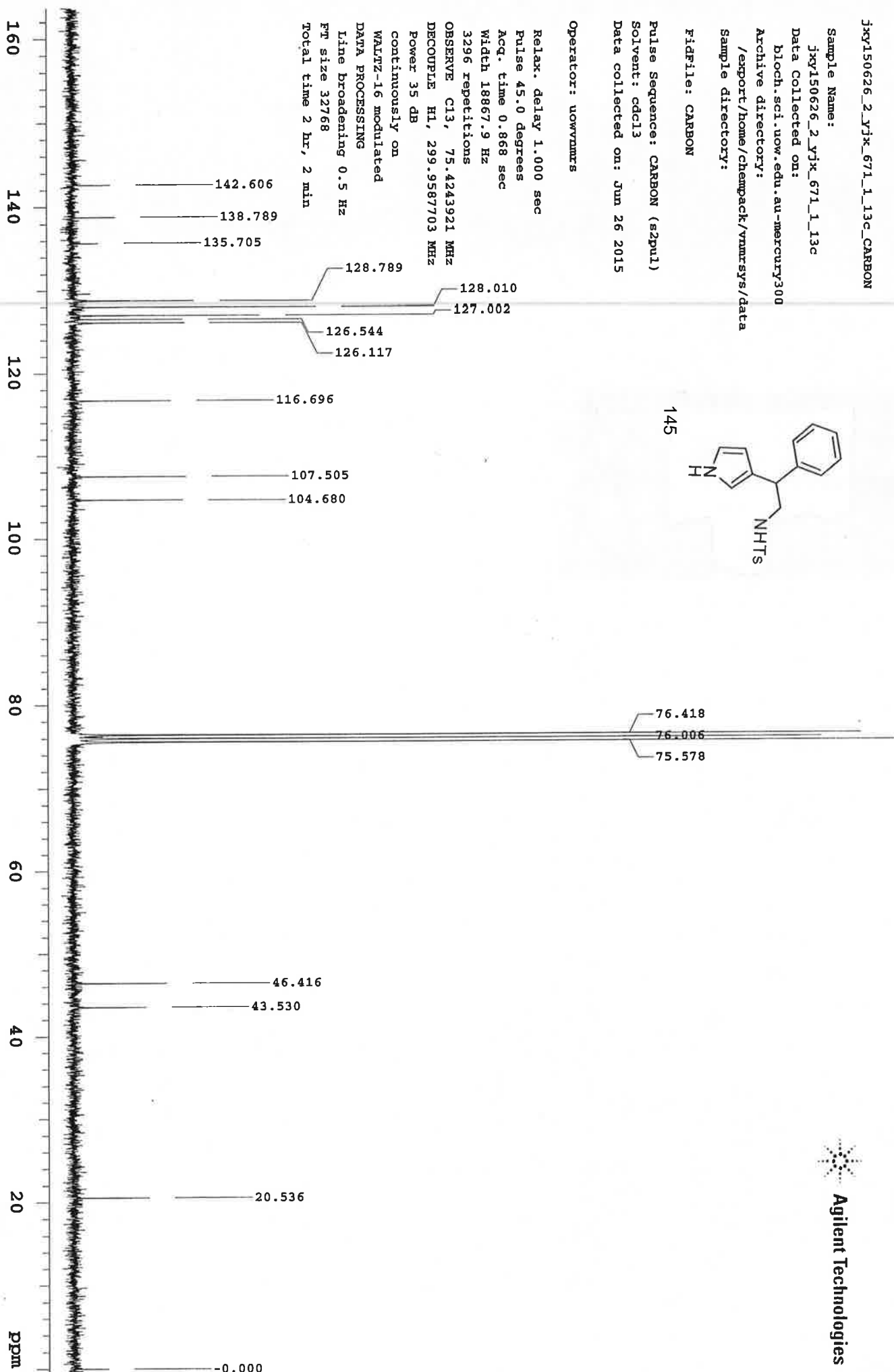
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 2 hr, 2 min



Agilent Technologies

jxy150626_2_yjk_670_1_PROTON

Sample Name:

jxy150626_2_yjk_670_1

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (s2pul1)

Solvent: cdcl3

Data collected on: Jun 26 2015

Operator: uowmurs

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 2.048 sec

Width 7998.4 Hz

16 repetitions

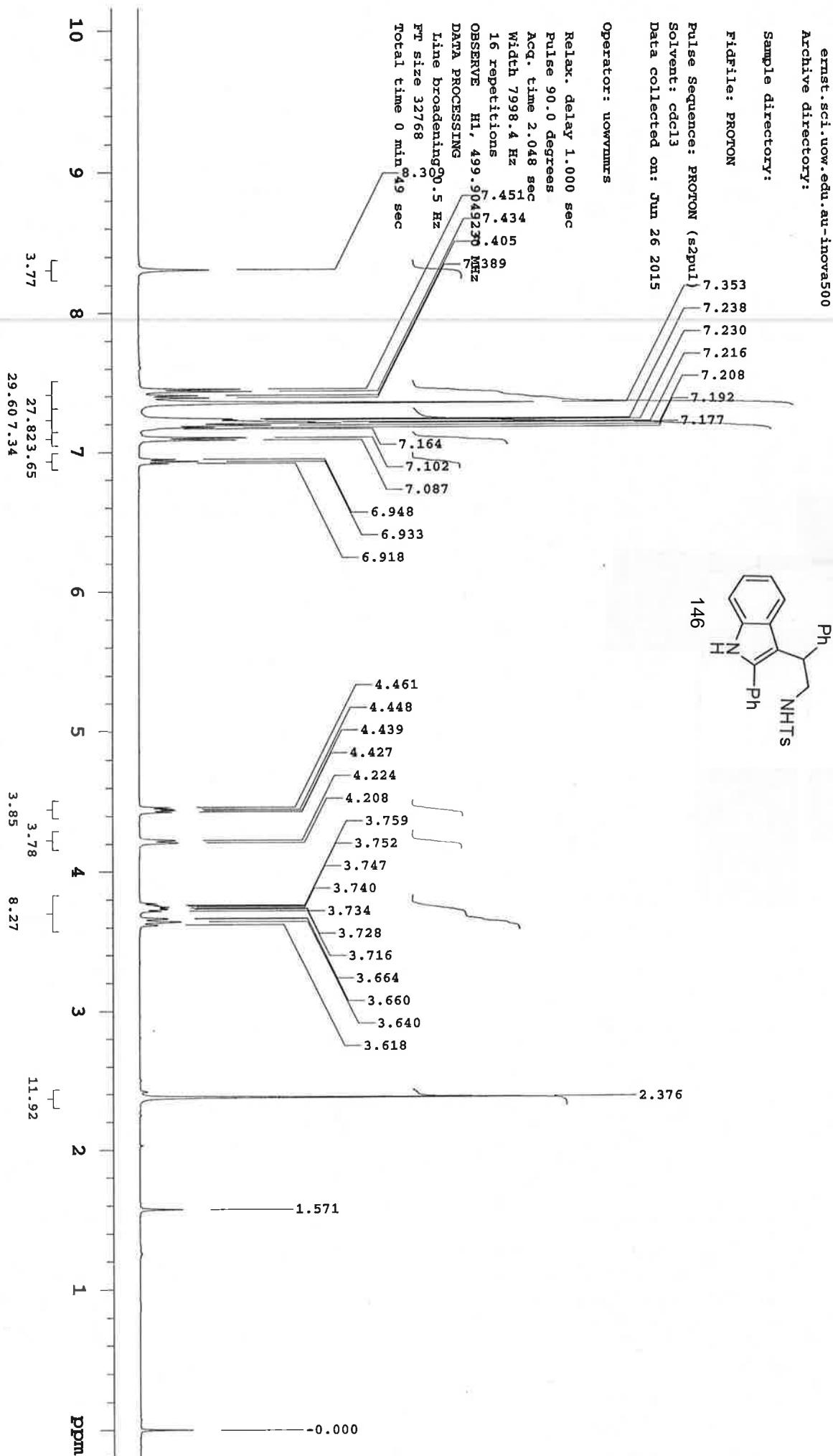
OBSERVE H1, 499.9049230 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 0 min 0.49 sec



Agilent Technologies

jxy150625_2_yjk_670_1_13c_CARBON

Sample Name:

jxy150625_2_yjk_670_1_13c

Data Collected on:

bloch.sci.nov.edu.au-mercury300

Archive directory:

/export/home/chempack/vnmrSYS/data

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jun 25 2015

Operator: uovvnmr

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

2300 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

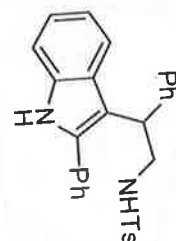
WALTZ-16 modulated

DATA PROCESSING

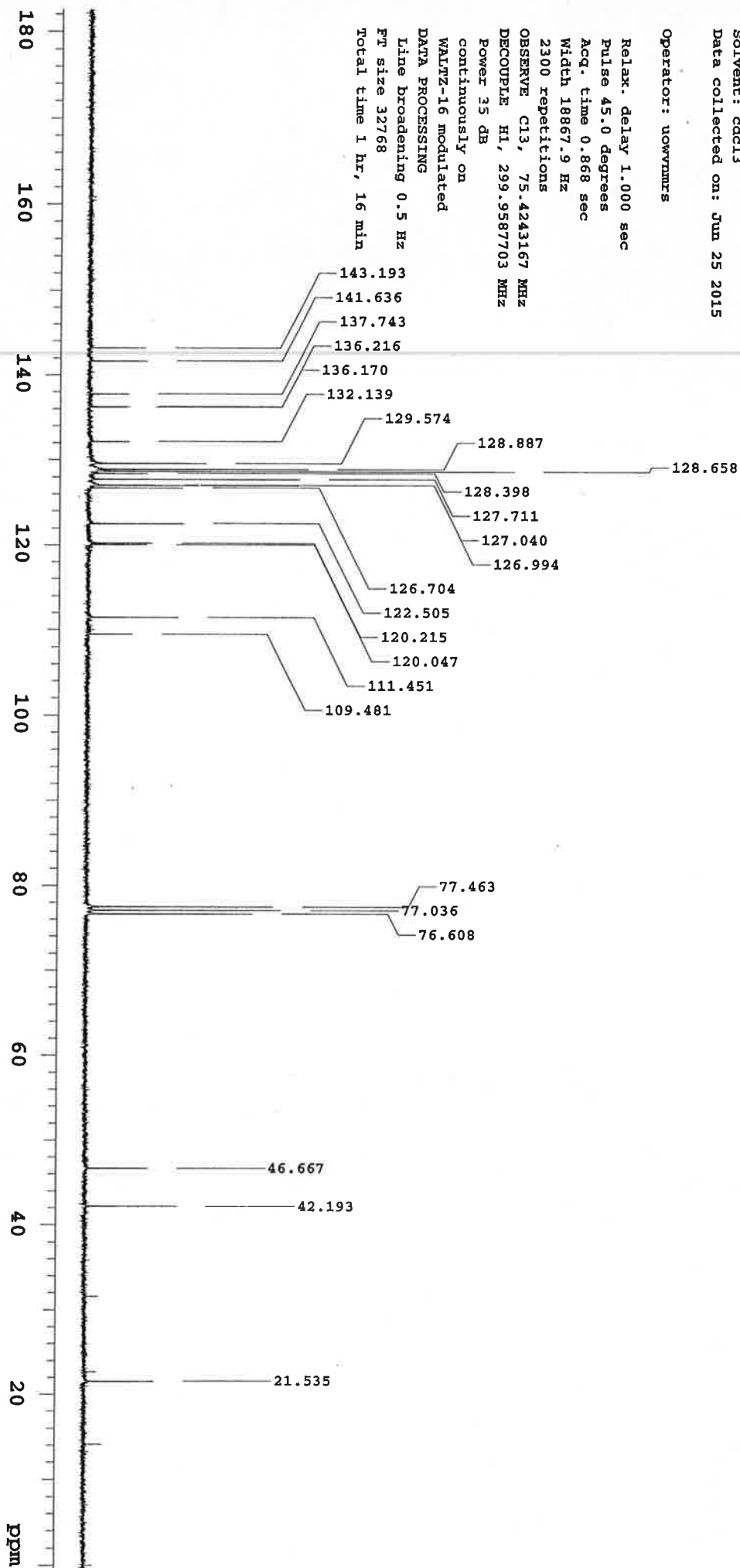
Line broadening 0.5 Hz

FT size 32768

Total time 1 hr, 16 min



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Agilent Technologies

jxy150627_2.yjk_672_1_PROTON

Sample Name:

jxy150627_2.yjk_672_1

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Jun 27 2015

Operator: uowymms

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 2.048 sec

Width 7998.4 Hz

16 repetitions

OBSERVED F1 F2 8049172 MHz

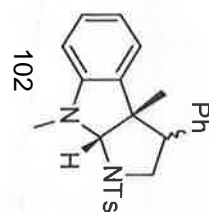
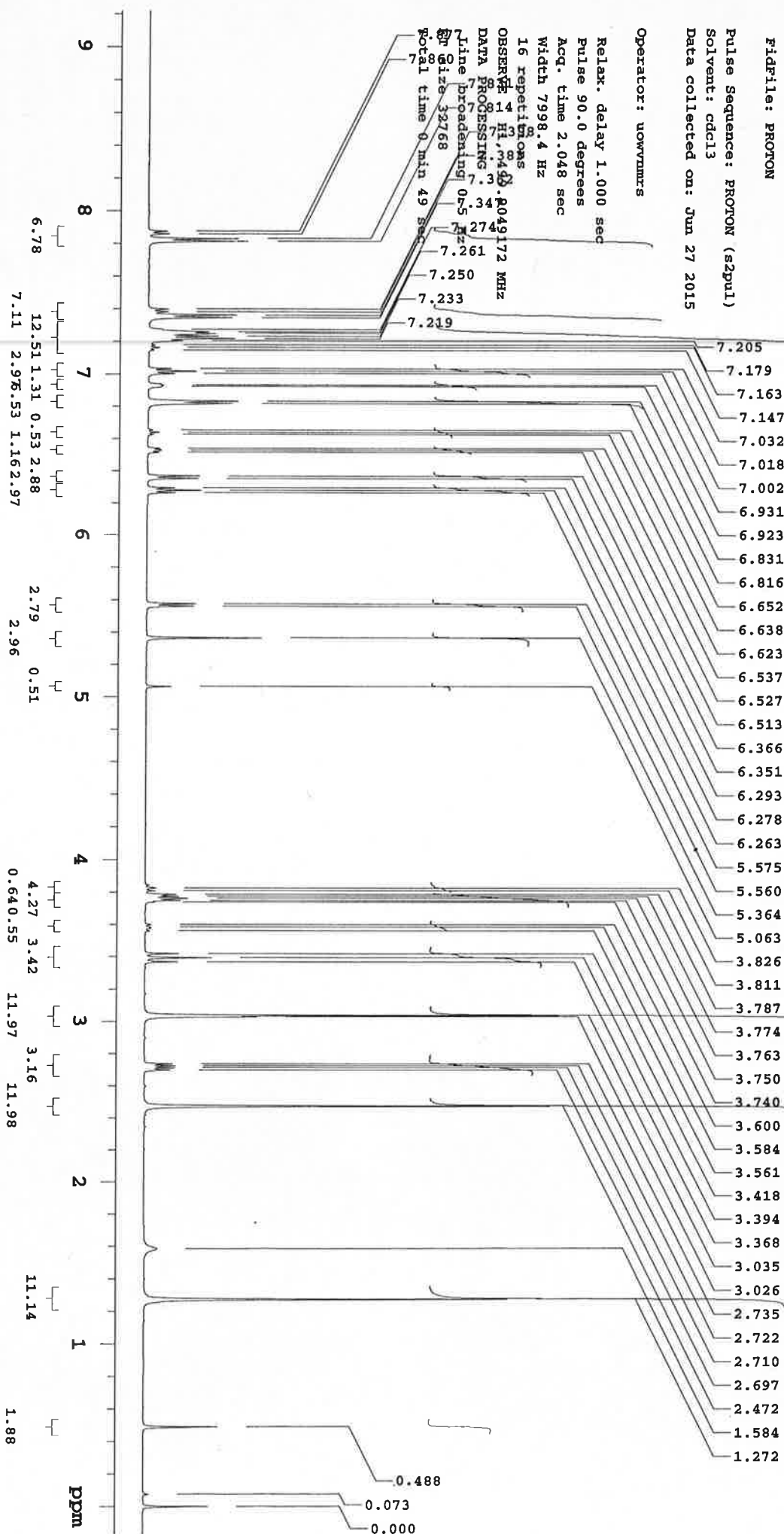
DATA PROCESSING:

Line broadening 0.5 Hz

SI size 32768

SI 0

Total time 0 min 49 sec



Agilent Technologies

jxy150627_2.yjx_672_1_13c CARBON

Sample Name:

jxy150627_2.yjx_672_1_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

/export/home/chempack/vnmrSYS/data

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jun 27 2015

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

4320 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

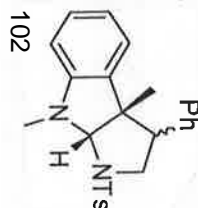
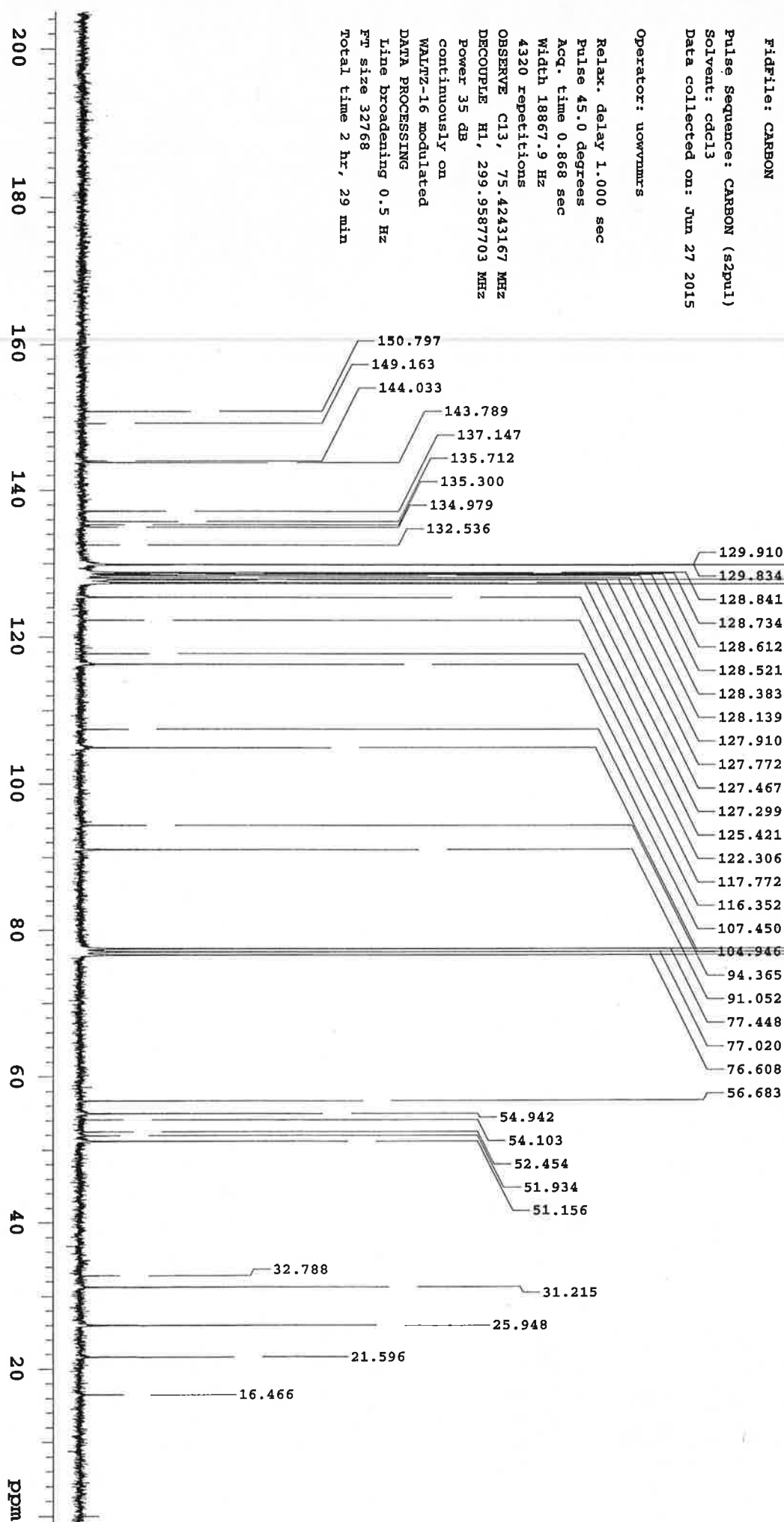
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

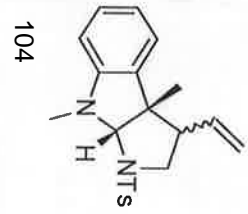
Total time 2 hr, 29 min



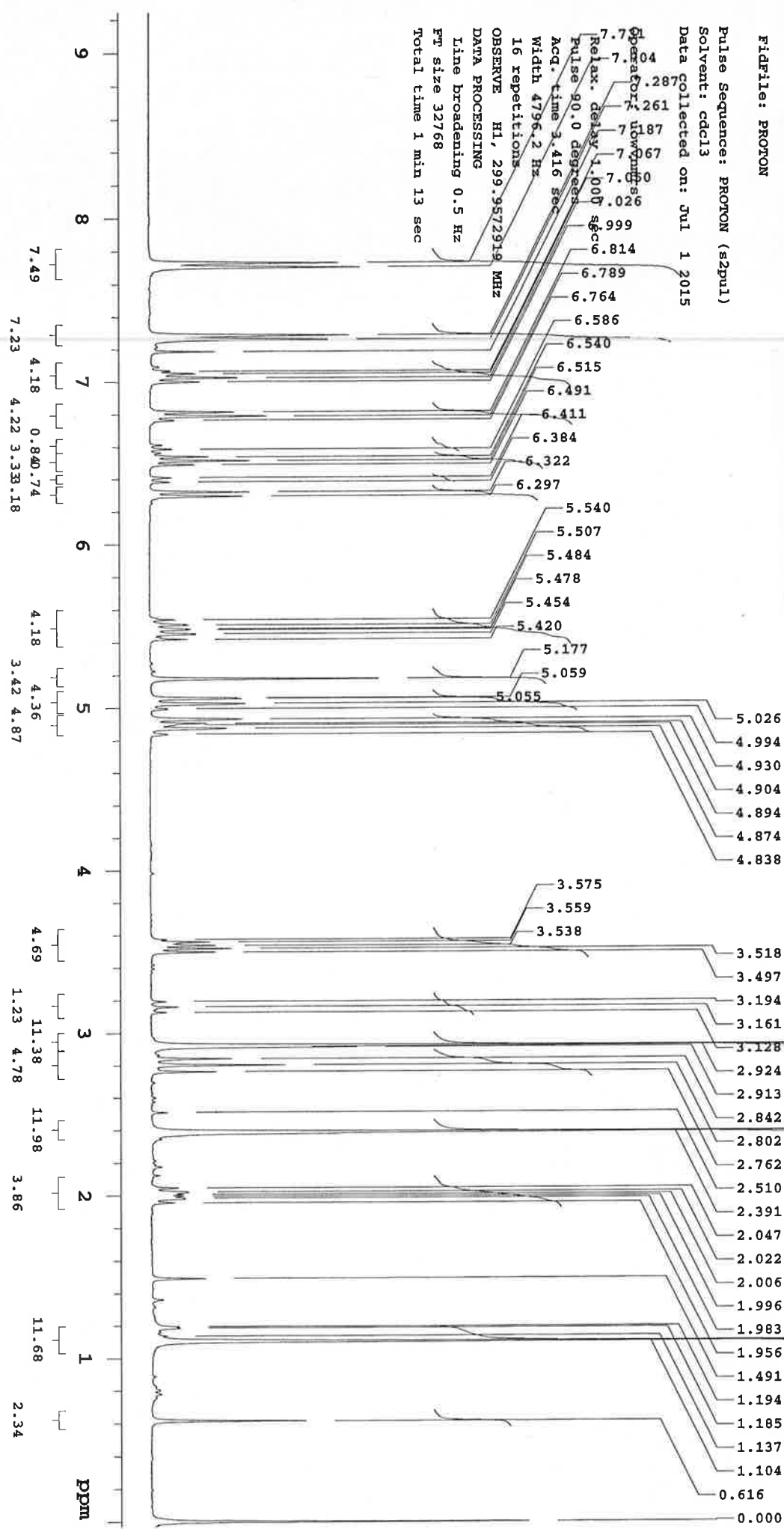
Agilent Technologies

jxy150701_2.yjx_683_1_PROTON

Sample Name:
jxy150701_2.yjx_683_1
Data Collected on:
bloch.sci.uow.edu.au-mercury300
Archive directory:
/export/home/chempack/vnmrSYS/data
Sample directory:



Fidfile: PROTON
Pulse Sequence: PROTON (s2pul1)
Solvent: cdcl3
Data collected on: Jul 1 2015
Operator: jxy150701
Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 3.416 sec
Width 4796.2 Hz
16 repetitions
OBSERVE H1, 299.9572919 MHz
DATA PROCESSING
line broadening 0.5 Hz
FT size 32768
Total time 1 min 13 sec



jxy150701_2.yjk_683_1_13c CARBON

Sample Name:

jxy150701_2.yjk_683_1_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

/export/home/chempack/vnmrSYS/data

Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jul 1 2015

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

3104 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

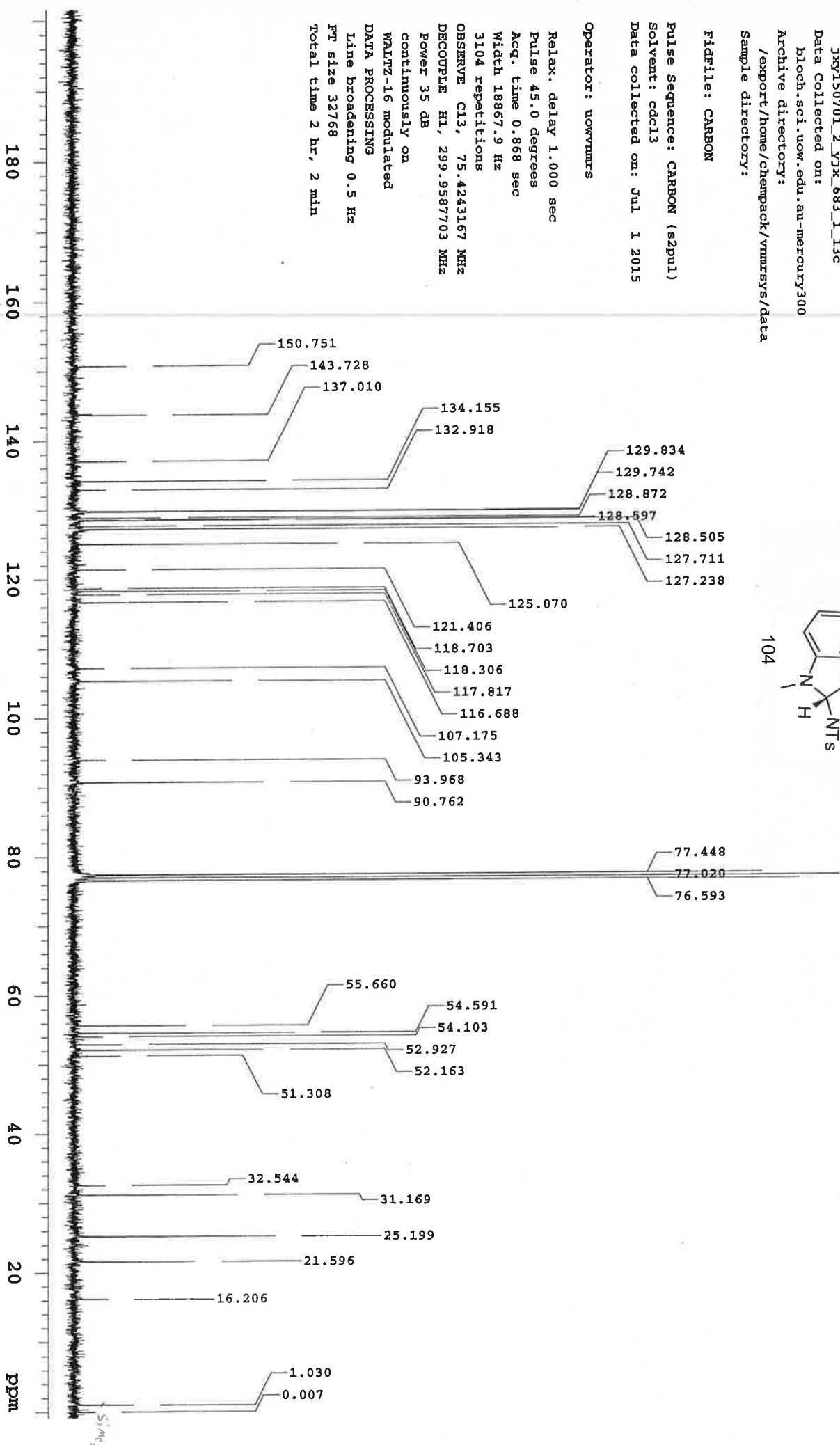
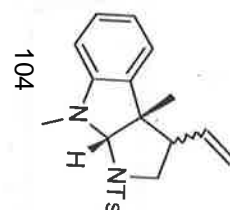
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 2 hr, 2 min



Agilent Technologies

jky150921_2.yjk_729_1-PROTON

Sample Name:

jky150921_2.yjk_729_1

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (s2pml)

Solvent: cdcl3

Data collected on: Sep 21 2015

Operator: uownmrs

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 1.709 sec

Width 4793.9 Hz

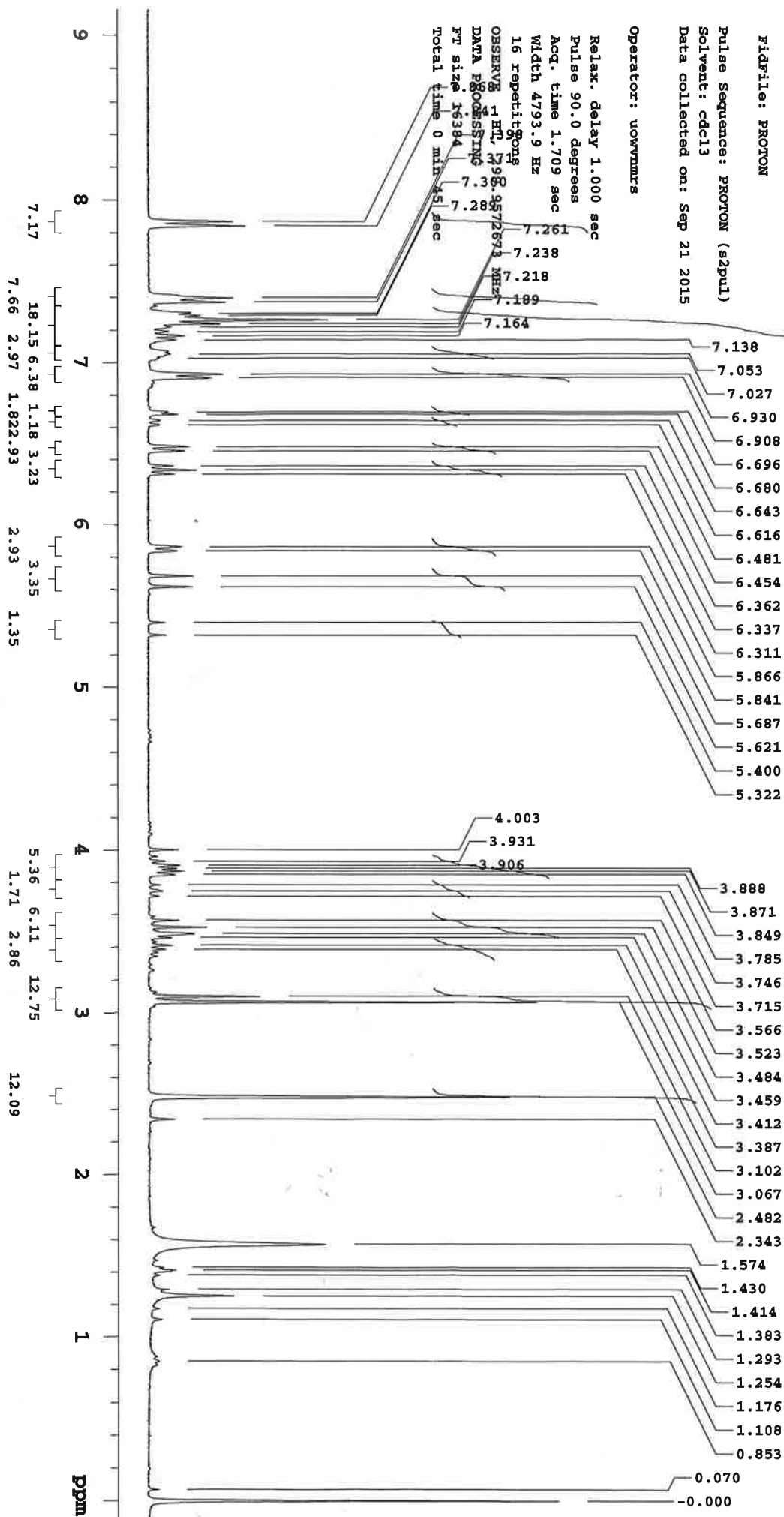
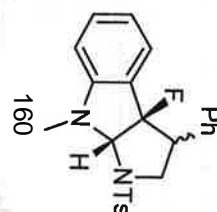
16 repetitions

OBSERVE 1H, 298.15/267.3 KHz

DATA PROCESSING 7

FT size 16384

Total time 0 min 45.5 sec



jxy150926_2_yjk_729_1_13_CARBON

Sample Name:

jxy150926_2_yjk_729_1_13

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (zgpg30)

Solvent: cdcl3

Data collected on: Sep 26 2015

Operator: uowymms

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

37080 repetitions

OBSERVE C13, 75.423561 MHz

DECOUPLE H1, 299958790.0 MHz

Power 35 dB

continuously on

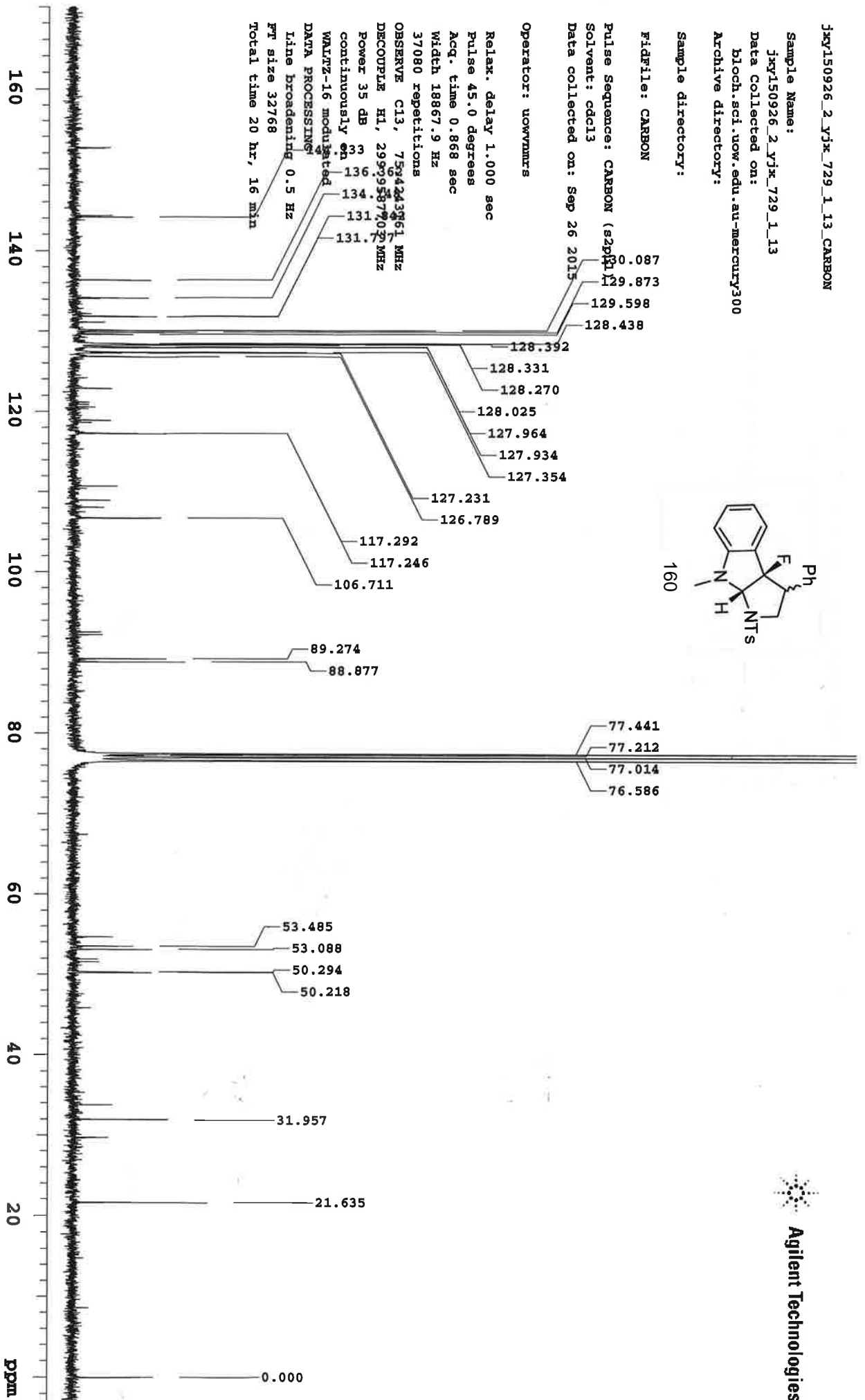
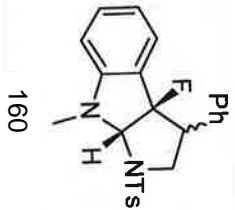
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 20 hr, 16 min



Agilent Technologies

jky150910_2_vjx_727_1_PROTON

Sample Name:

jky150910_2_vjx_727_1

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: jky150910_2_vjx_727_1_PROTON

Pulse Sequence: (PROTON (s2pul))

Solvent: cdcl3

Data collected on: Sep 10 2015

Operator: uownmrs

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 2.048 sec

Width 7898.4 Hz

16 repetitions

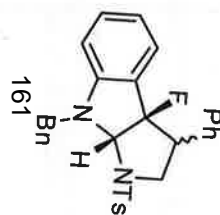
OBSERVE 1H 499.9049177 MHz

DATA PROCESSING

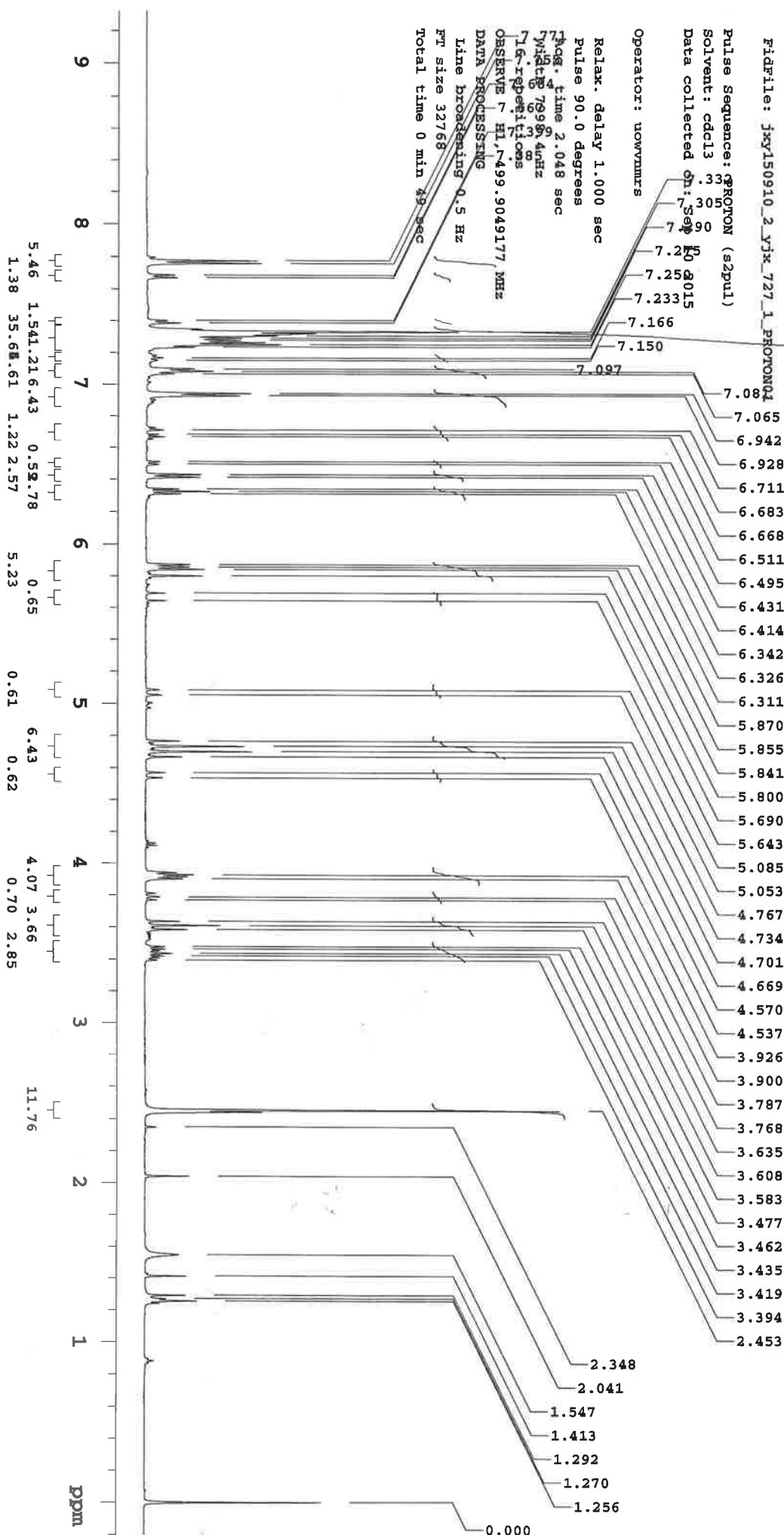
Line broadening 0.5 Hz

FT size 32768

Total time 0 min 49 sec



Agilent Technologies



jky160110_2.yjk_783_1_13c CARBON

Sample Name:

jky160110_2.yjk_783_1_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (szpul)

Solvent: cdcl3

Data collected on: Jan 10 2016

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.521 sec

Width 31421.8 Hz

35088 repetitions

OBSERVE C13, 125.7011859 MHz

DECOUPLE H1, 499.9073947 MHz

Power 42 dB

continuously on

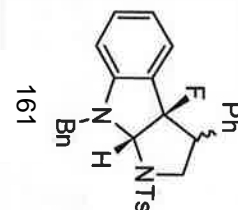
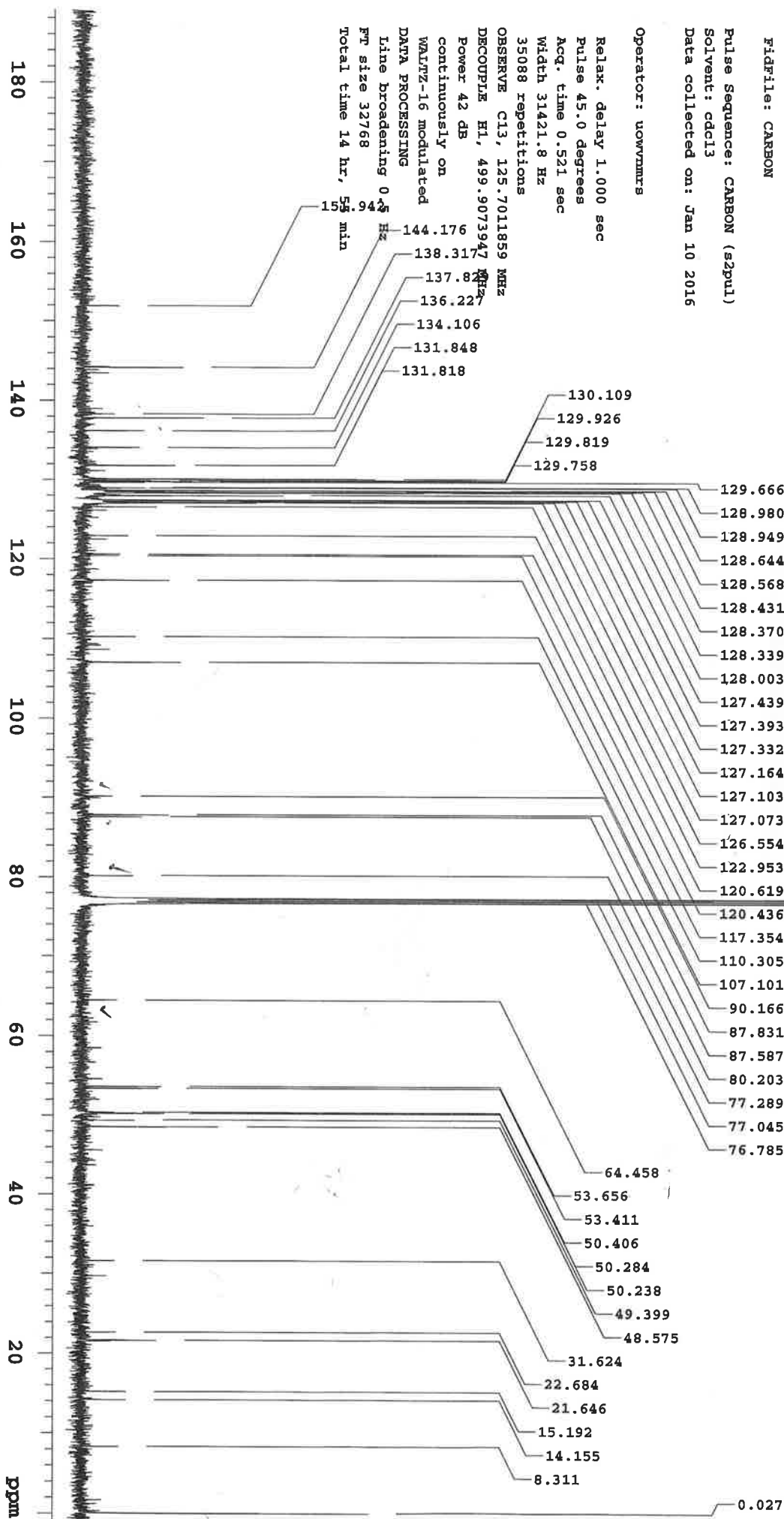
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.4 Hz

FW size 32768

Total time 14 hr, 55 min



Agilent Technologies

jxy160224_2.yjk_727_1.NOESY1D

Sample Name:

jxy160224_2.yjk_727_1

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

FidFile: NOESY1D

Pulse Sequence: NOESY1D

Solvent: cdcl3

Data collected on: Feb 24 2016

Operator: uowymms

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 2.000 sec

Width 4676.7 Hz

64 repetitions

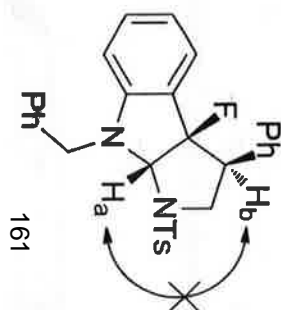
OBSERVE H1, 499.9049158 MHz

DATA PROCESSING

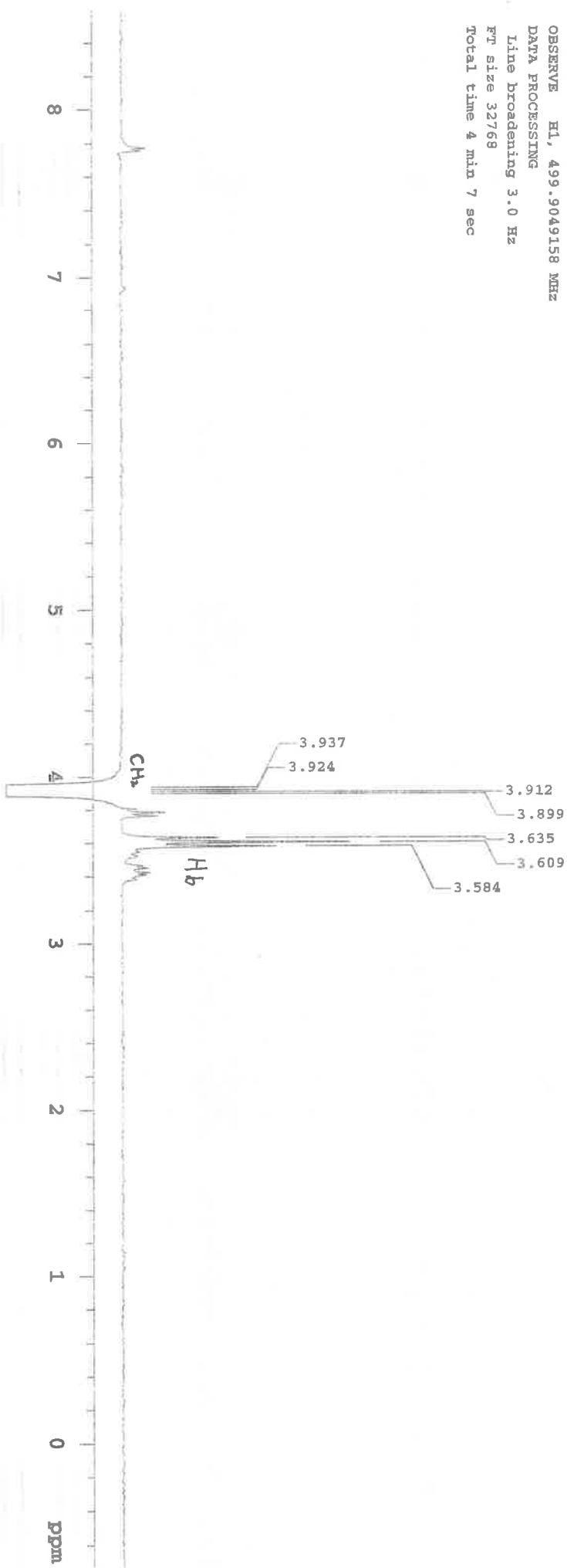
Line broadening 3.0 Hz

FT size 32768

Total time 4 min 7 sec



Agilent Technologies



jxy160224_2_yjk_727_1_NOESY

Sample Name:

jxy160224_2_yjk_727_1

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: NOESY

Pulse Sequence: NOESY

Solvent: cdcl3

Data collected on: Feb 24 2016

Operator: uowymms

Relax. delay 1.000 sec

Acq. time 0.219 sec

Width 4676.7 Hz

2D width 4676.7 Hz

8 repetitions

2 x 250 increments

OBSERVE H1, 499.9049158 MHz

DATA PROCESSING

Line broadening 3.0 Hz

Sq. sine bell 0.219 sec

Shifted by -0.219 sec

F1 DATA PROCESSING

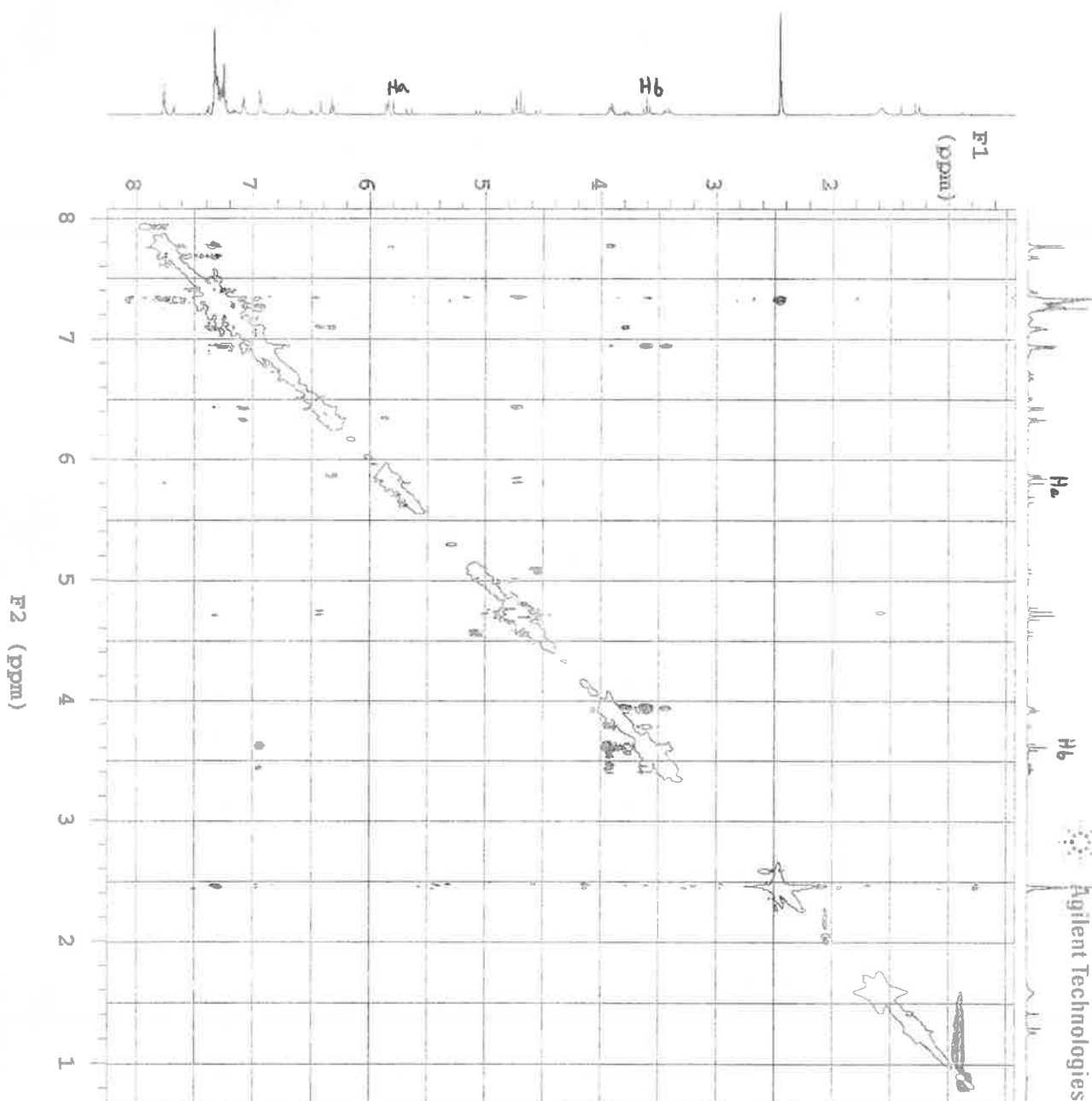
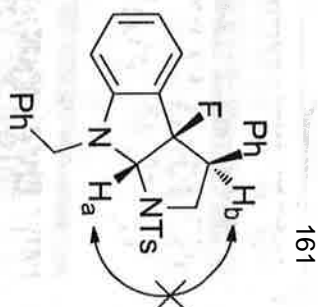
Line broadening 3.0 Hz

Sq. sine bell 0.055 sec

Shifted by -0.055 sec

FT size 2048 x 1024

Total time 1 hr, 37 min



jxy150908_2_vjx_723_1-Proton

File: Proton

Pulse Sequence: s2pu1

Solvent: cdcl3

Temp: 2.0 C / 275.1 K

Operator: uowvmr2

VNMR5-500 "pyne06.domain.com"

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 2.045 sec

Width 8012.8 Hz

16 repetitions

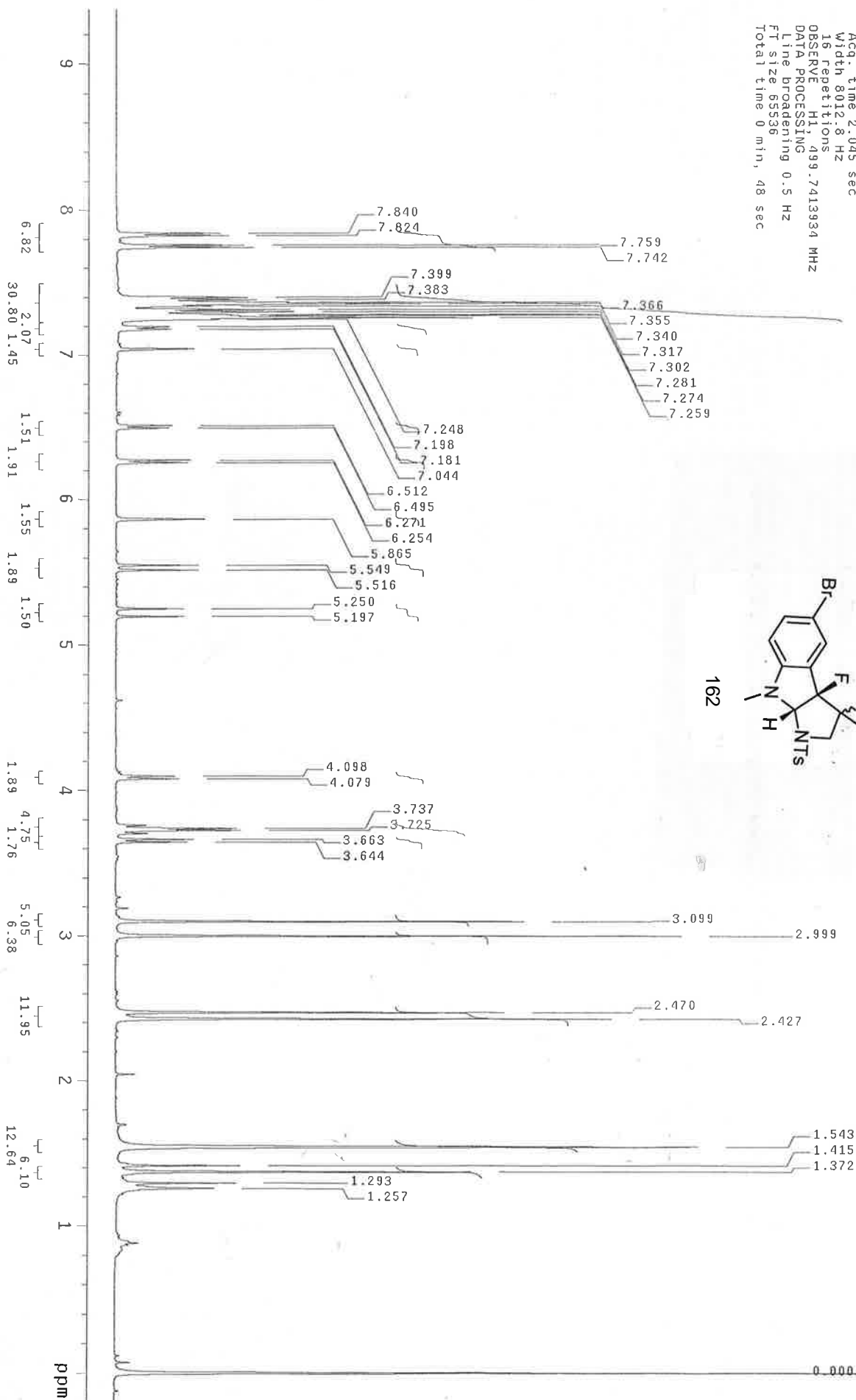
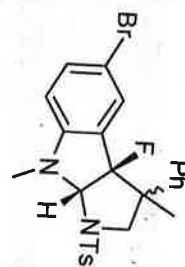
OBSERVE H1, 499.7413934 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 0 min, 48 sec



jxy160113_2_yjk_786_1_13c CARBON

Sample Name:

jxy160113_2_yjk_786_1_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jan 13 2016

Operator: uowwmmr

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

28732 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

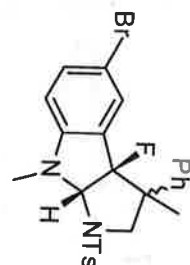
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 15 hr, 42 min

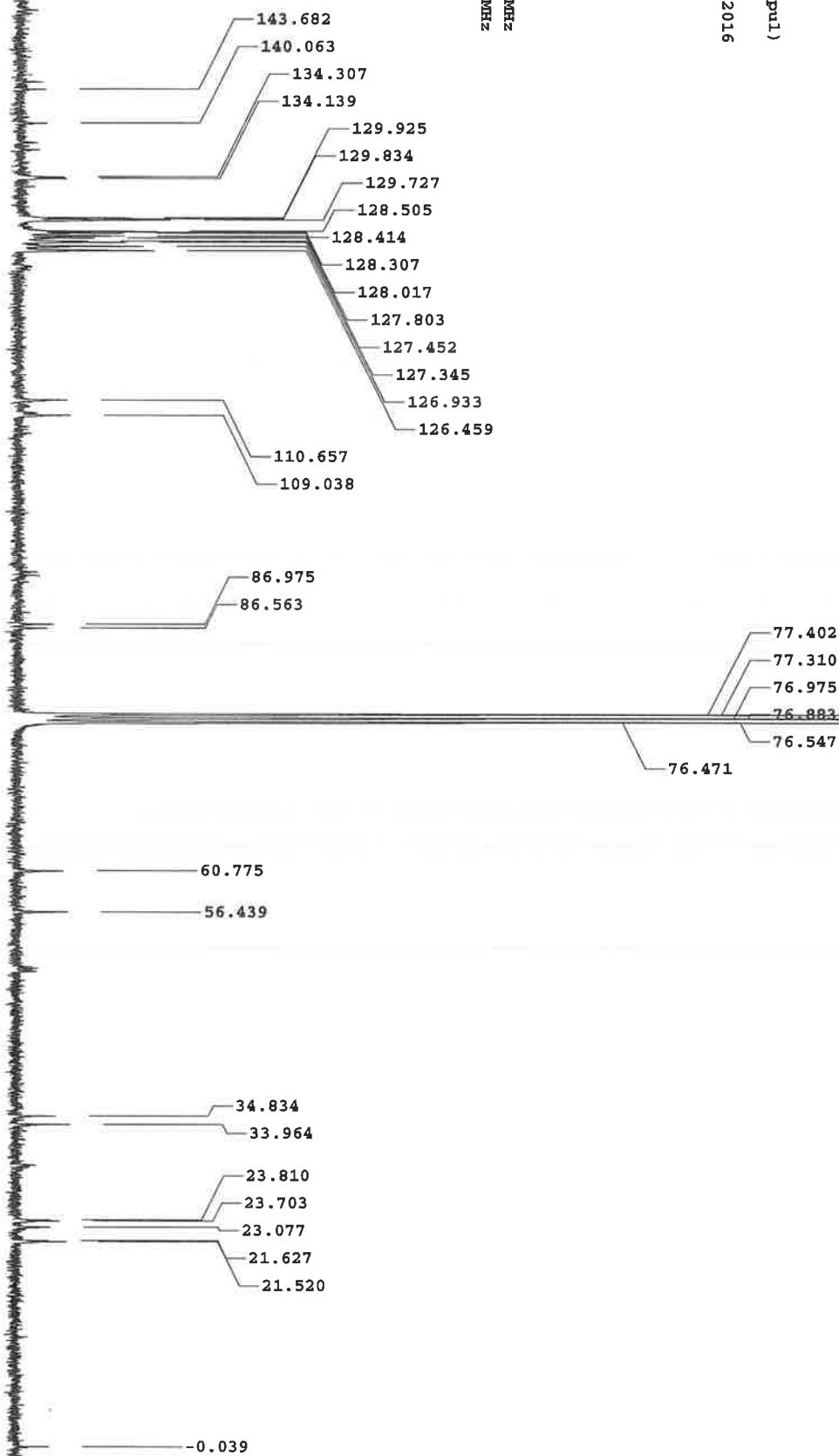


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Agilent Technologies

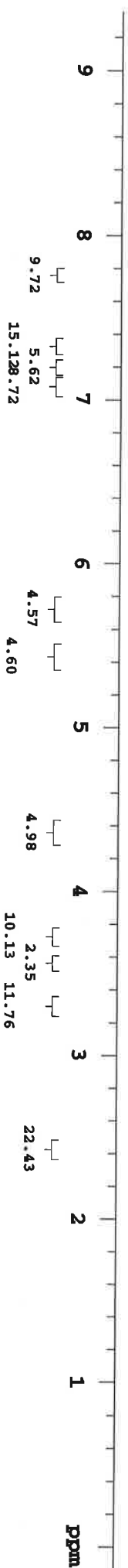
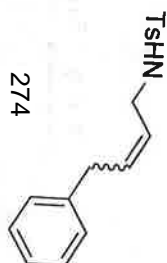
180 160 140 120 100 80 60 40 20 ppm



jky130509_2_yjk_113_3_PROTON

exp4 PROTON

SAMPLE		PRESATURATION	
date	May 9 2013	satmode	n
solvent	cdcl3	wet	n
file	/home/uovvnmr-	SPECIAL	
s/bup_archive/bup_	temp	25.0	
1306xsent/jky13050-	gain	not used	
9_2_yjk_113_3_PROT-	spin	not used	
ON01.fid	hst	0.008	
ACQUISITION			
sw	7998.4	alpha	10.100
at	2.048	il	10.000
np	32768	in	n
fb	4000	dp	n
bs	16	hs	y
d1	1.000	hs	nm
nt	8	lb	0.50
ct	8	fn	not used
TRANSMITTER		PROCESSING	
tn	EL	not used	
sfrq	499.908	DISPLAY	
tof	499.9	-86.4	
tpwr	60	4762.7	
pw	10.100	1018.4	
DECOUPLER		0	
dn	C13	-151.7	
dof	0	-107.8	
dm	nm	PLOT	
decwave	W40_autoxdb	268	
dpwr	37	0	
dmf	32258	50	
	ai	83	
	cdc	ph	



jxzy130513_2_yjk_113_3_13c CARBON

Sample Name:
jxzy130513_2_yjk_113_3_13c
Data Collected on:
ernst.sci.uow.edu.au-inova500
Archive directory:

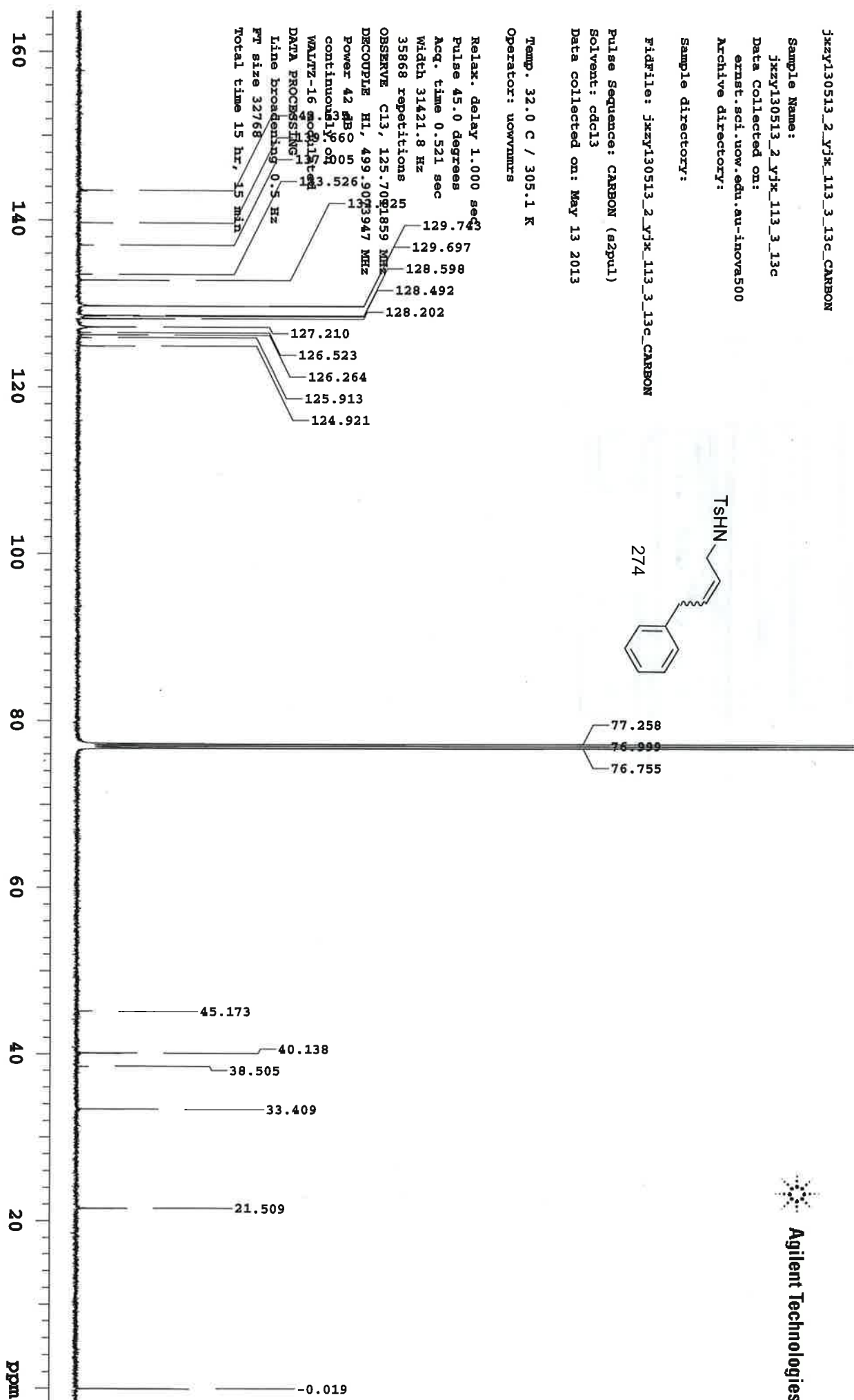
Sample directory:

Fidfile: jxzy130513_2_yjk_113_3_13c CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 13 2013

Temp. 32.0 C / 305.1 K
Operator: uownmrs

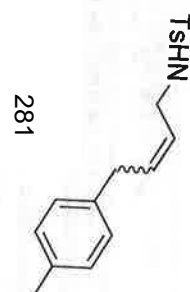
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.521 sec
Width 31421.8 Hz
35868 repetitions
OBSERVE C13, 125.7091859 MHz
DECOUPLE H1, 499.9073947 MHz
Power 42 dB
continuously on
WALTZ-16 modulation
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 15 hr, 15 min



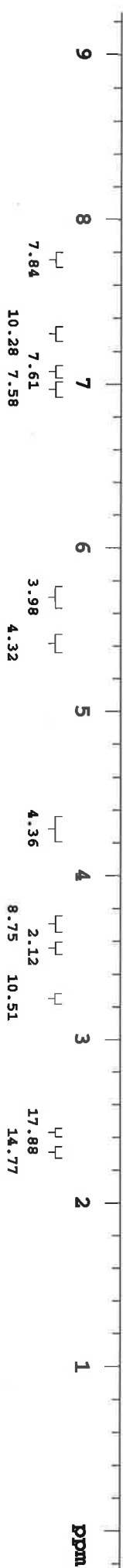
Agilent Technologies

jky130420_2.yjk_132_2_PROTON

exp6 PROTON



SAMPLE PRESATURATION
date Apr 20 2013 satmode n
solvent cdcl3 wet n
file /home/uowvnmr- SPECIAL
s/bup_archive/bup_ temp 25.0
1306sent/jky13042- gain not used
0_2.yjk_132_2_PROT- spin not used
ON01.fid hst 0.008
ACQUISITION pw90 10.100
sw 7998.4 alfa 10.000
at 2.048 flags
np 32768 il n
fb 4000 in n
bs 16 dp y
dl 1.000 hs dn
nt 8
ct 8 lb
TRANSMITTER fn not used
tn H1 DISPLAY
sfreq 499.908 sp -131.3
tof 499.9 wp 4757.8
tpwr 60 ref 1016.4
pw 10.100 refp 0
DECOUPLER xp -157.5
dn C13 lp -103.4
dof 0 PLOT
dm mm wc 268
decwave wa0_autocdb sc 0
dpr 37 vs 48
dmf 32258 th 48
ai cdc ph



jxy130606_2_vjx_132_3_13c_Apt

File: Apt

Pulse Sequence: Apt

Solvent: cdc13

Temp: 25.0 C / 298.1 K

Operator: ucwvnmrs

VNMR5-500 "pyne06.domain.com"

Relax. delay 1.000 sec

1st pulse 90.0 degrees

2nd pulse 135.0 degrees

Acq. time 1.000 sec

Width 30487.8 Hz

26624 repetitions

OBSERVE C13, 125.659960 MHz

DECOUPLE H1, 499.7437041 MHz

Power 45 dB

on during acquisition

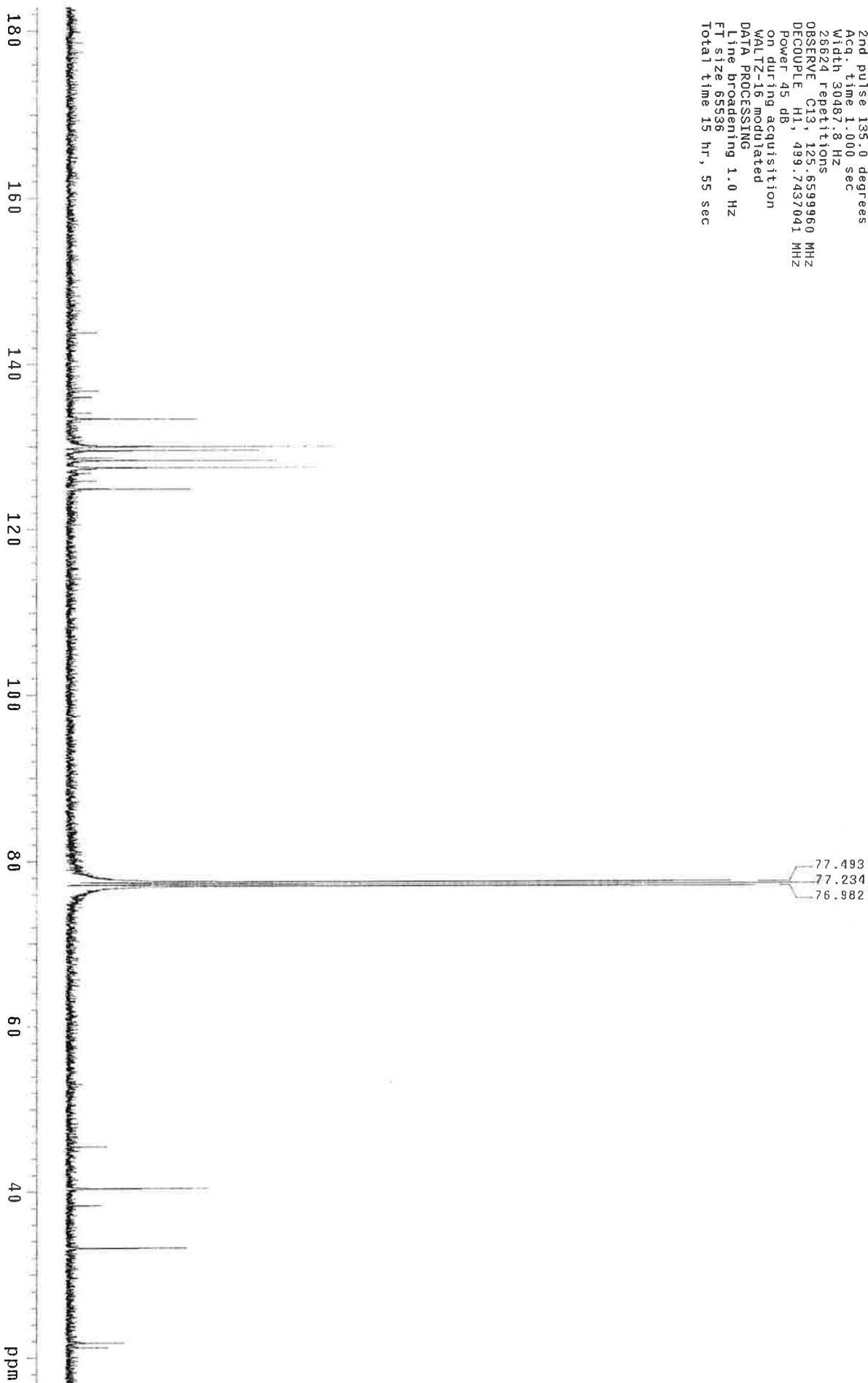
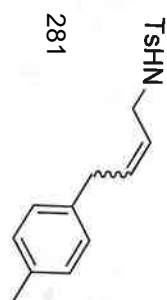
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

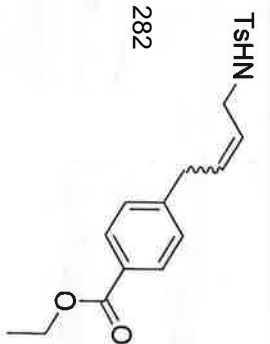
Total time 15 hr, 55 sec



jxy130509_2_yjk_137_3_PROTON

exp1 PROTON

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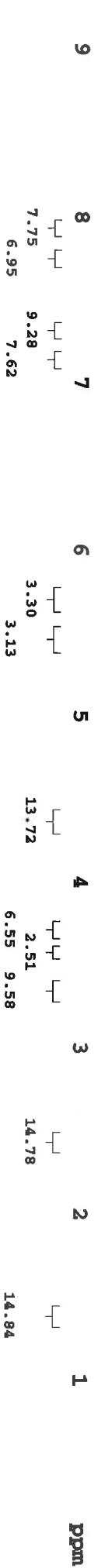


SAMPLE PRESATURATION
 date May 9 2013 satmode n
 solvent cdcl3 wet n
 file /home/uovvnmr- SPECIAL
 s/bup_archive/bup_ temp 25.0
 1306xsent/jxy13050- gain not used
 9_2_yjk_137_3_PROT- spin not used
 ON01.fid hst 0.008
 ACQUISITION pw90 10.100
 sw 7998.4 alfa 10.000
 at 2.048
 np 32768 il
 fb 4000 in n
 bs 16 dp n
 dl 1.000 hs y
 nt 8
 ct 8 lb
 TRANSMITTER fn not used
 tn H1
 sfrq 499.908 sp
 tof 499.9 wp 4705.1
 tpwr 60 rfi 1017.4
 pw 10.100 rfp 0
 DECOUPLER rp -155.1
 dn C13 lp -105.0
 dof 0
 dm nna wc 268
 decwave W40_autocdb sc 0
 dpr 37 vs 91
 dmf 32258 th 151
 ai cdc ph

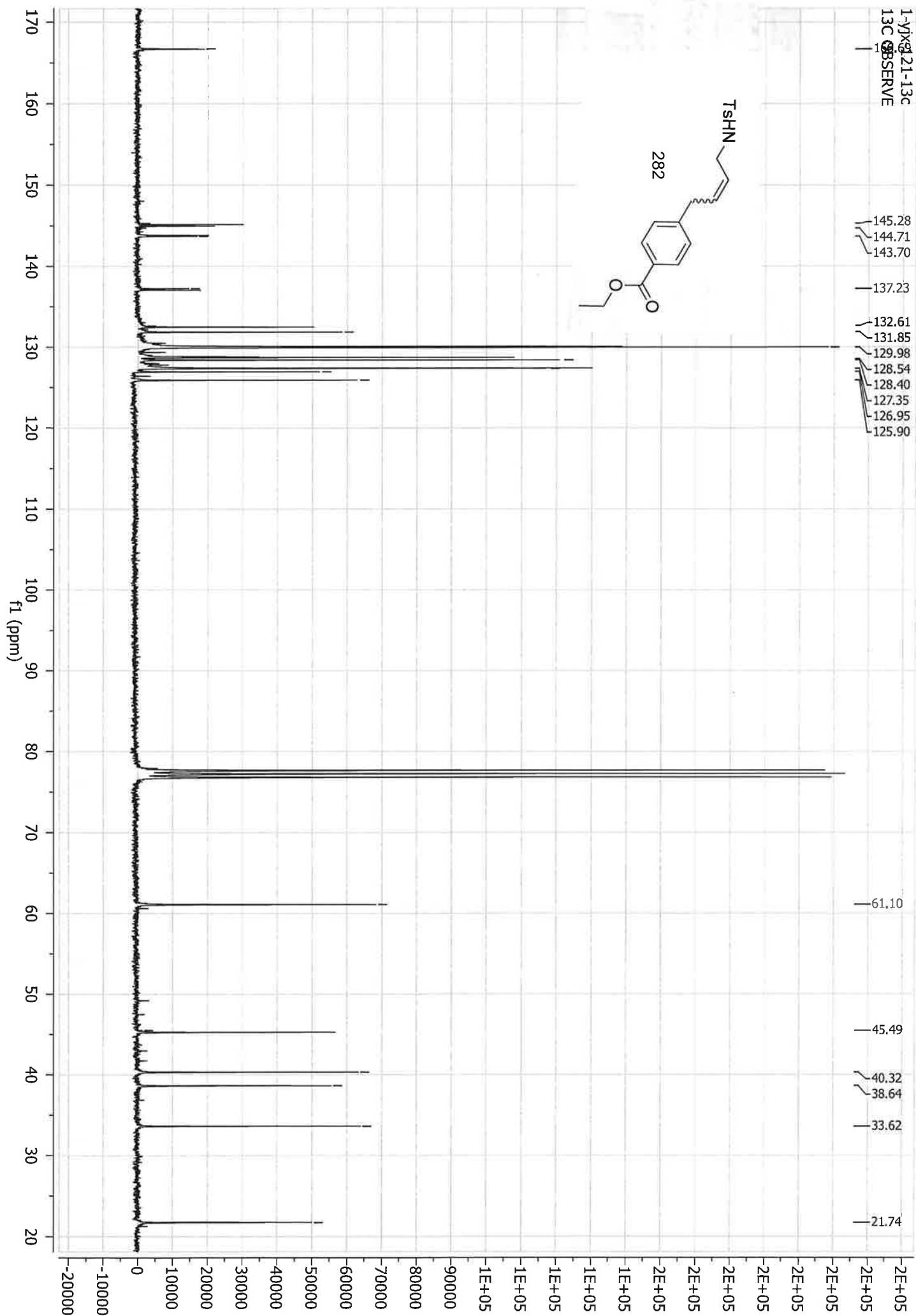
PROCESSING
 not used
 0.50
 2-3C

DISPLAY
 not used
 -80.1
 4705.1
 1017.4
 0
 -155.1
 -105.0

PLOT
 268
 0
 91
 151



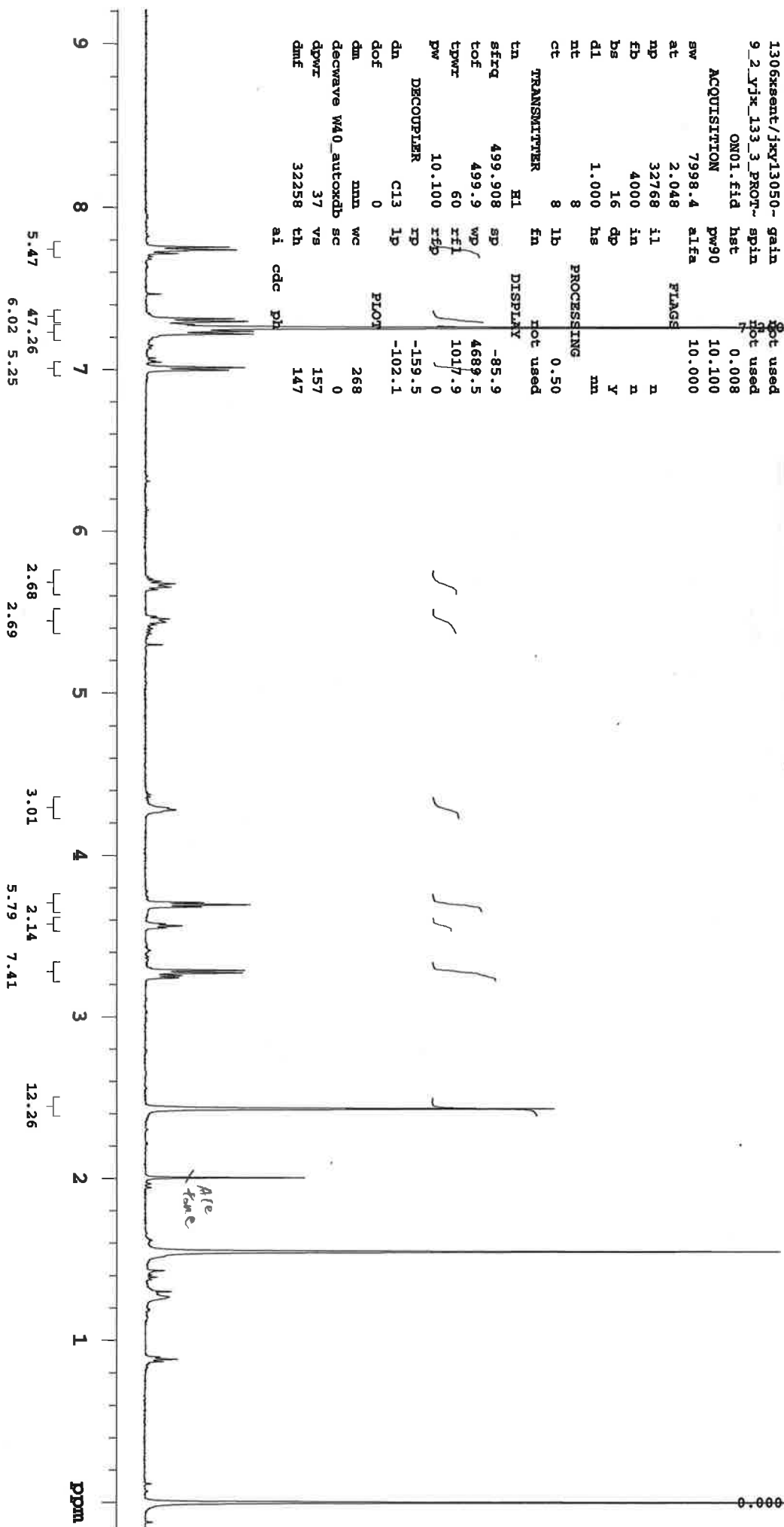
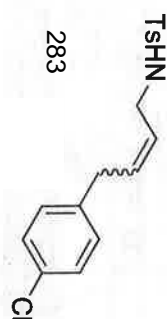
1-ylxg21-13c
13C OBSERVE

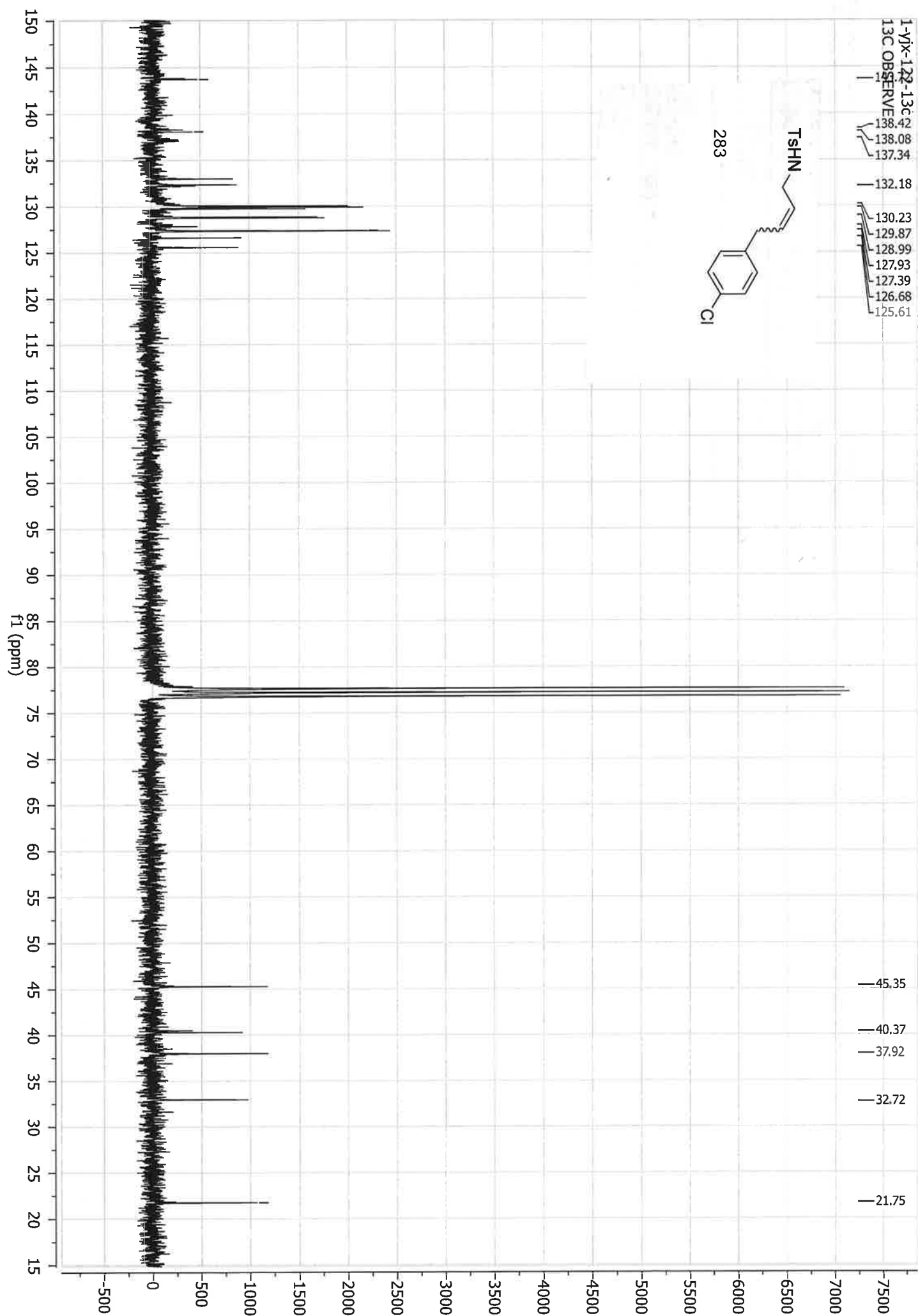


jxy130509_2_yjk_133_3_PROTON

exp4 PROTON

SAMPLE		PRESATURATION	
date	May 9 2013	satmode	n
solvent	cdcl3	wet	n
file	/home/uowvnmr-	SPECIAL	
s/bup_archive/bup_	temp	25.0	
1306xsent/jxy13050-	gain	not used	
9_2_yjk_133_3_PROT-	spin	not used	
ON01.fid	hst	0.008	
ACQUISITION		PROCESSING	
sw	7998.4	alfa	10.100
at	2.048	il	10.000
np	32768	in	n
fb	4000	dp	n
bs	16	hs	y
d1	1.000	nm	
nt	8		
ct	8	lb	0.50
tn	TRANSMITTER	fn	not used
sfreq	499.908	sp	-85.9
tof	499.9	wp	4689.5
tpwr	60	rfl	1017.9
pw	10.100	rfd	0
DECOUPLER		PLOT	
dn	C13	lp	-159.5
dof	0		-102.1
dm	nm	wc	268
decwave	W40_autokdb	sc	0
dpr	37	vs	157
dnt	32258	th	147
	ai	cdc	ph

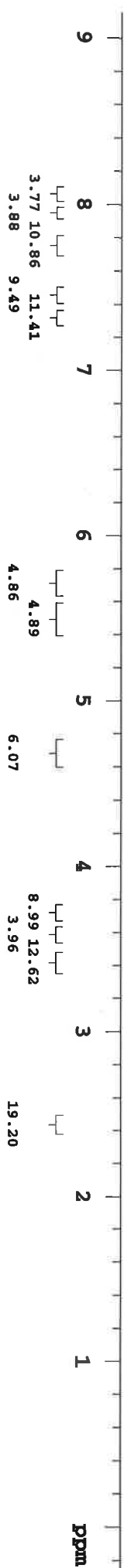
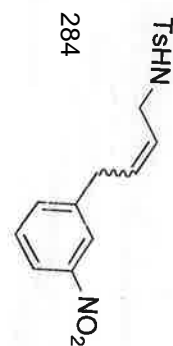




jky130509_2.yjk_141_3_PROTON

expt1 PROTON

SAMPLE PREPARATION
 date May 9 2013 satmode n
 solvent cdcl3 wet n
 file /home/uvnmr- s/bup_archive/bup_ temp 25.0
 1306xsent/jky13050- gain not used
 9_2.yjk_141_3_PROT- spin not used
 ON01.fid hst 0.008
 ACQUISITION pw90 10.100
 sw 7998.4 alfa 10.000
 at 2.048
 up 32768 il/ n
 fb 4000 in n
 bs 16 dp y
 d1 1.000 hs n
 nt 8
 ct 8 lb 0.50
 TRANSMITTER fm not used
 tn H1
 sfreq 499.908 sp -140.6
 tof 499.9 vp 4715.9
 tpwr 60 xfl 1014.9
 pw 10.100 zfp 0
 DECOUPLER xp -148.2
 dn C13 lp -120.7
 dof 0
 dm nmn wc 268
 decwave w40_autokdb sc 0
 dpwr 37 vs 79
 dmf 32258 ei cdc ph 134



jxy130927_2_vjx_141_noe_Noesy1d

File: Noesy1d

Pulse Sequence: NOESY1D

Solvent: cdcl3

Temp: 25.0 C / 298.1 K

Operator: uowvmr

VNMR-500 "pyne06.domain.com"

Relax. delay 1.000 sec

Pulse 90.0 degrees

Mixing 0.500 sec

Acq. time 1.998 sec

Width 8012.8 Hz

64 repetitions

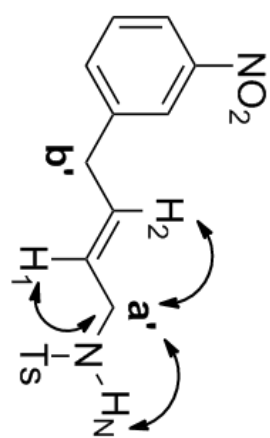
OBSERVE H1, 499.7412053 MHz

DATA PROCESSING

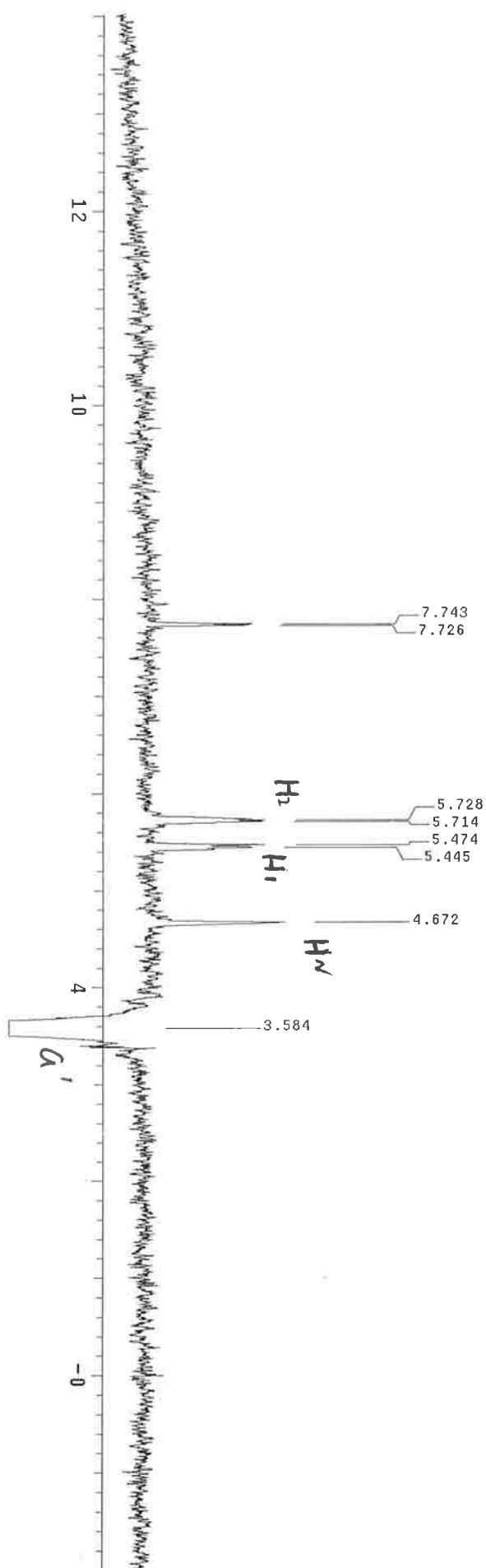
Line broadening 3.0 Hz

FT size 32768

Total time 4 min, 4 sec



Minor *trans*-isomer 284



File: Noesy1d

Pulse Sequence: NOESY1D

Solvent: cdcl3

Temp: 25.0 C / 298.1 K

Operator: uowvmr

VNMR-500 "pyne06.domain.com"

Relax. delay 1.000 sec

Pulse 90.0 degrees

Mixing 0.500 sec

Acq. time 1.998 sec

Width 8012.8 Hz

64 repetitions

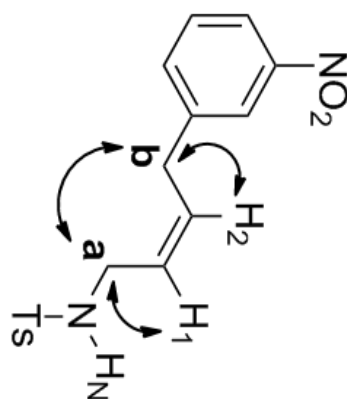
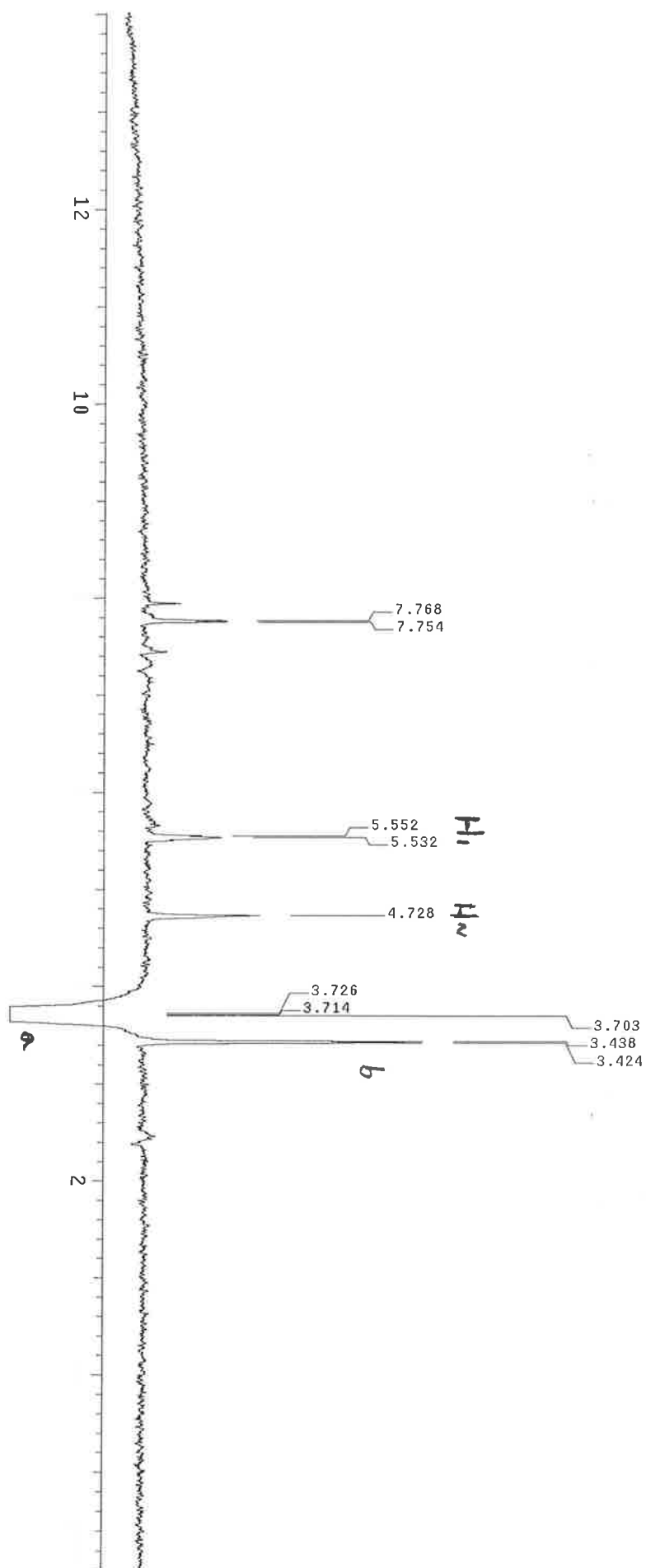
OBSERVE H1, 499.7412053 MHz

DATA PROCESSING

Line broadening 3.0 Hz

FT size 32768

Total time 4 min, 2 sec

Major *cis*-isomer 284

File: Apt

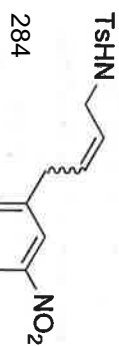
Pulse Sequence: APT

Solvent: cdcl3

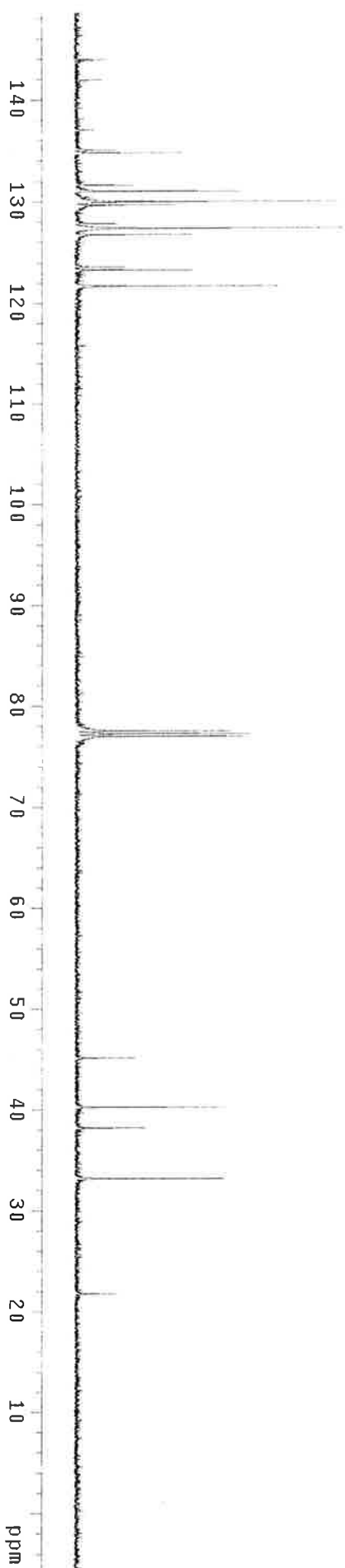
Temp: 25.0 C / 298.1 K

Operator: uowvmr

VMRS-500 "pyne06.domain.com"



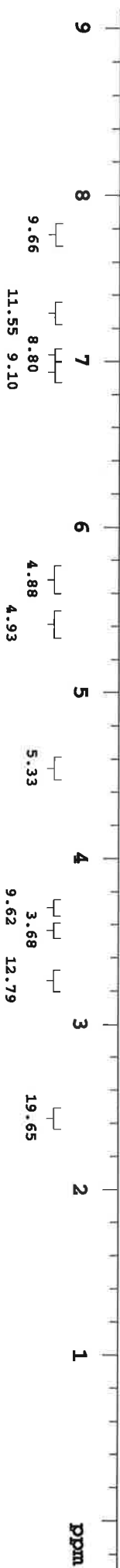
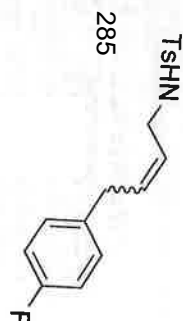
Relax. delay 1.000 sec
1st pulse 90.0 degrees
2nd pulse 135.0 degrees
Acq. time 1.000 sec
Width 30487.8 Hz
1760 repetitions
OBSERVE C13, 125.659960 MHz
DECUPLE H1, 499.7437041 MHz
Power 45 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
F1 size 65536
Total time 59 min, 55 sec



jxy130830_2_yjx_189_3_2ndcolumn_PROTON

exp8 PROTON

SAMPLE PRESATURATION
 date Aug 30 2013 satmode n
 solvent cdcl3 wet n
 file /home/uovvmmr~ SPECIAL
 s/bup_archive/bup_~ temp 25.0
 1309xsent/jxy13083~ gain not used
 0_2_yjx_189_3_2ndc~ spin not used
 column_PROTON01.fid hst 0.008
 ACQUISITION pw90 10.100
 sw 7998.4 alfa 10.000
 at 2.048
 np 32768 il n
 fb 4000 in n
 bs 16 dp y
 dl 1.000 hs n
 nt 14
 ct 14 fn not used
 TRANSMITTER
 tn H1 sp -159.1
 sfrq 499.908 wp 4715.9
 tof 499.9 rfl 1017.9
 tpwr 60 rfp 0
 pw 10.100 xp 150.4
 DECOUPLER lp -105.8
 dn C13
 dof 0 wc 268
 dm nm sc 0
 decwave wa0_autocdb vs 97
 dpwr 37 th 149
 dmf 32258 ai cdc ph



jxy130830_2_vjx_189_3_13c_3_Carbon

File: Carbon

Pulse Sequence: szput1

Solvent: cdc13

Temp. 25.0 C / 298.1 K

Operator: uowvnmrs

VNMR5-500 "pyne06.domain.com"

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 0.537 sec

Width 30487.8 Hz

56756 repetitions

OBSERVE G13, 125.659960 MHz

DECOUPLE H1, 499.7437041 MHz

Power 45 dB

continuously on

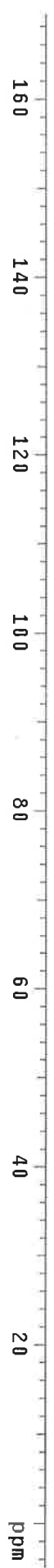
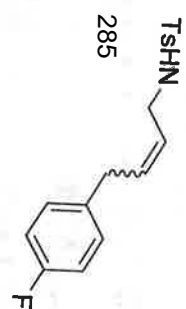
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

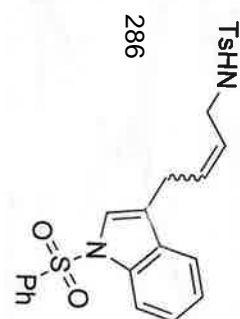
Total time 16 hr, 29 min, 56 sec



jxy130503_2_yjx_149_3_PROTON

expt1 PROTON

SAMPLE PREPARATION
 date May 3 2013 satmode n
 solvent cdcl3 wet n
 file /home/uowvnmr- s/bup_archive/bup_ SPECIAL 25.0
 s/bup_archive/bup_ temp 25.0
 1306xsent/jxy130503- gain not used
 3_2_yjx_149_3_PROT- spin not used
 ON.fid hst 0.008
 ACQUISITION pw90 10.100
 sw 7998.4 alfa 10.000
 at 2.048
 np 32768 il n
 fb 4000 in n
 bs 16 dp y
 dl 1.000 hs nm
 nt 8
 ct 8 lb/ 0.50
 TRANSMITTER fn not used
 tn H1
 afreq 499.908 sp -89.8
 tof 499.9 mp 4752.5
 tpwr 60 ref 1016.4
 pw 10.100 ref 0
 DECOUPLER xp -154.8
 dn C13 lp -106.8
 dof 0 PLOT
 dm 0 wc 268
 decwave w40_autokdb sc 0
 dpwr 37 vs 66
 dmf 32258 th 137
 ai cdc ph



jxy130915_2_vjx_202_2_13c_Carbon

File: Carbon

Pulse Sequence: s2pu1

Solvent: cdcl3

Temp. 25.0 C / 298.1 K

Operator: uowvmrs

VMRS-500 "pyne06.domain.com"

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 0.537 sec

Width 30487.8 Hz

58480 repetitions

OBSERVE C13, 125.659960 MHz

DECUPLE H1, 499.7437041 MHz

Power 45 dB

continuously on

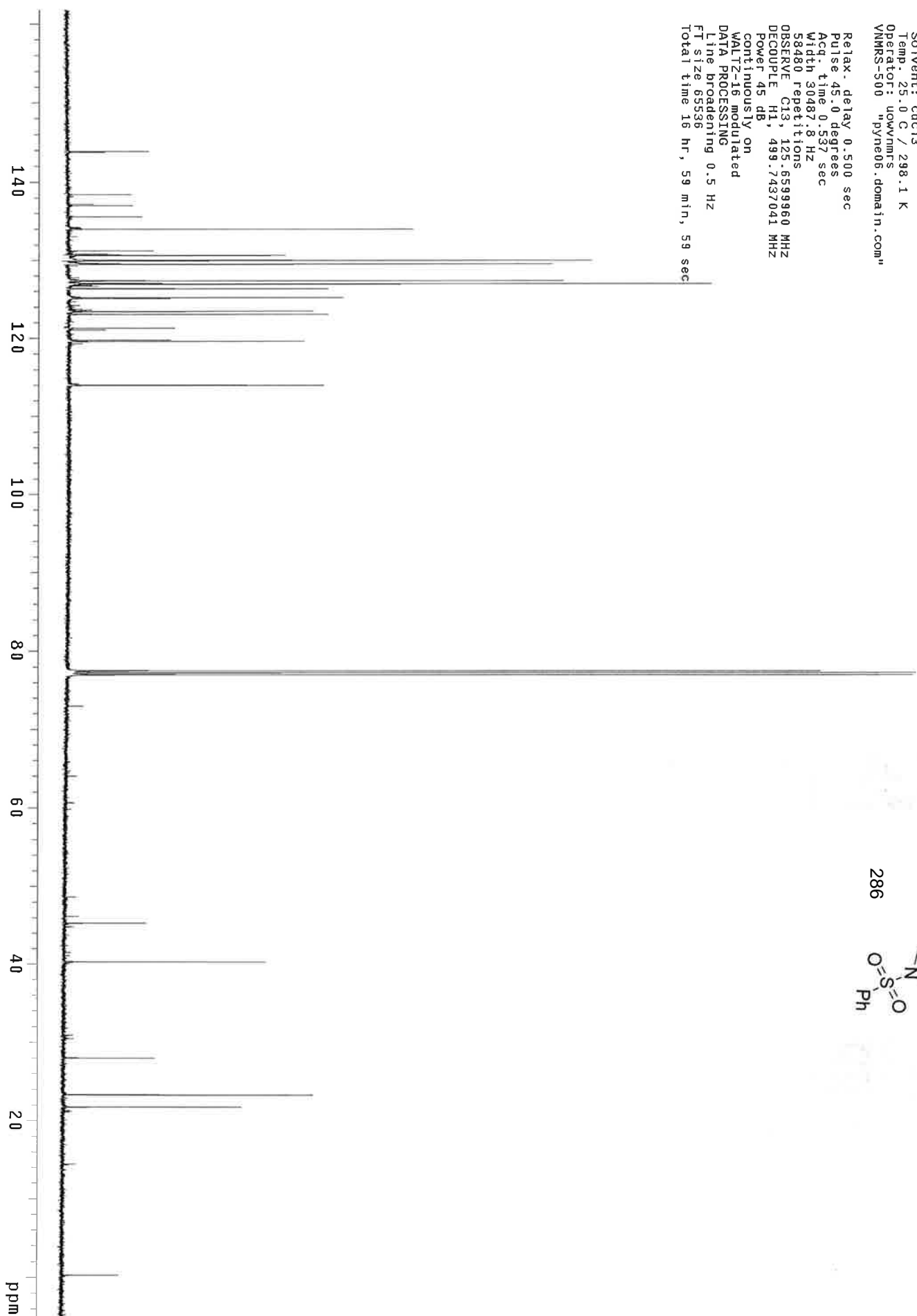
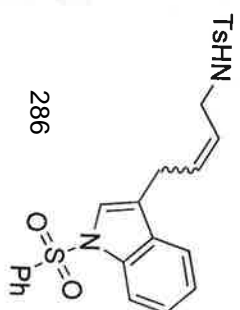
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 16 hr, 59 min, 59 sec



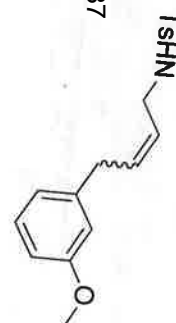
jxy130509_2_yjk_156_3_PROTON

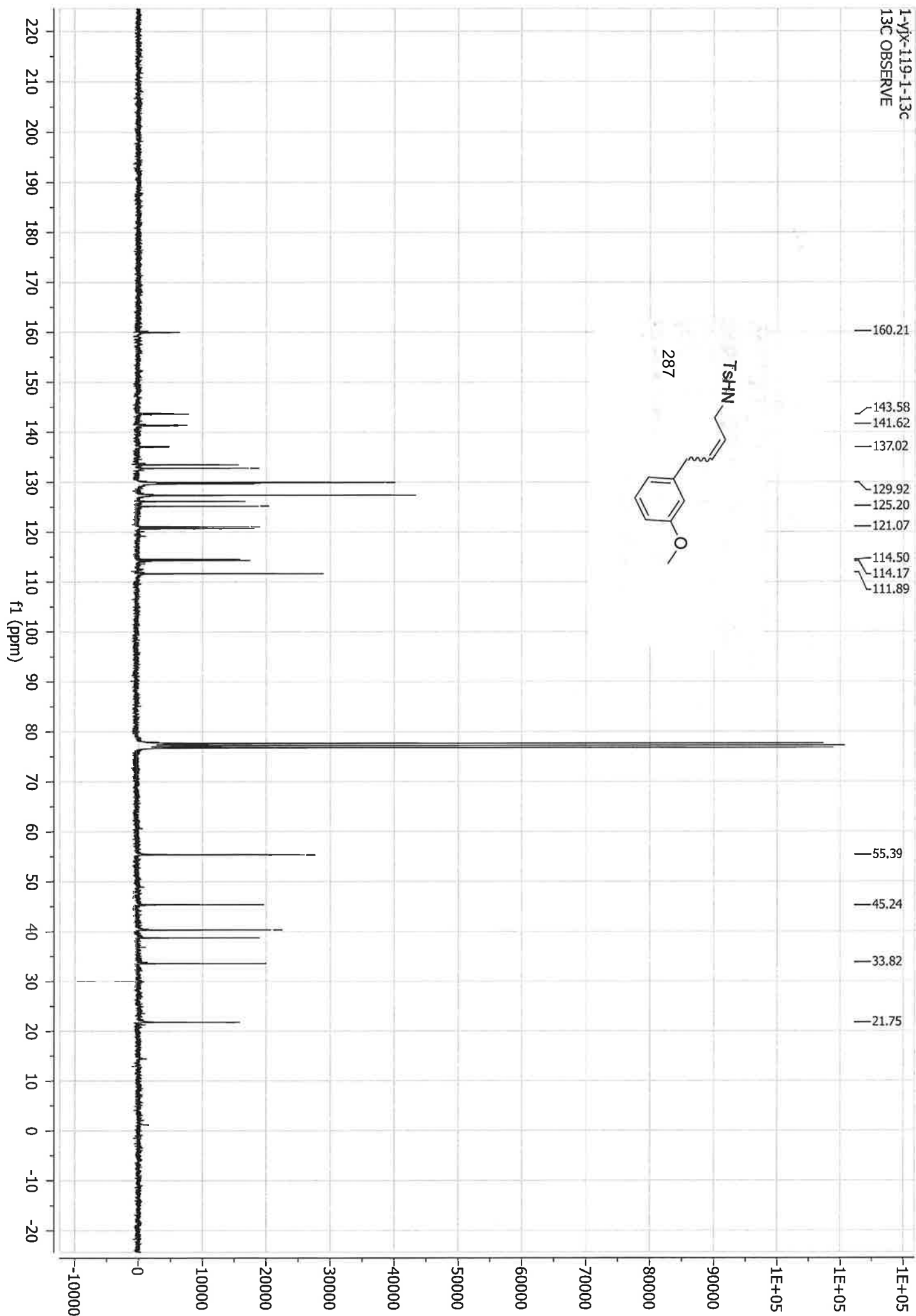
exp1 PROTON

SAMPLE		PRESATURATION	
date	May 9 2013	satmode	n
solvent	cdcl3	wet	n
file	/home/novnmr-	SPECTIL	
s/bup_archive/bup_	temp	25.0	
1306xsent/jxy13050-	gain	not used	
9_2_yjk_156_3_PROT-	spin	not used	
ON.fid	hst	0.008	
ACQUISITION	pw90	10.100	
sw	7998.4	alfa	10.000
at	2.048	FLAGS	
np	32768	il	n
fb	4000	in	n
bs	16	dp	y
d1	1.000	hs	nm
nt	8	PROCESSING	
ct	8	lp	0.50
TRANSMITTER	fa	not used	
tn	H1	DISPLAY	
sfrq	499.908	sp	-112.3
tof	499.9	wp	4694.9
tpwr	60	rf1	1017.9
pw	10.100	rfp	0
DECOUPLER	tp	-154.7	
dn	C13	lp	-108.2
doe	0	PIOT	
dm	nm	wc	268
decwave	W40_autokdb	sc	.0
dpwr	37	vs	102
dmf	32258	th	155
	ai	cdc	ph

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TSHN

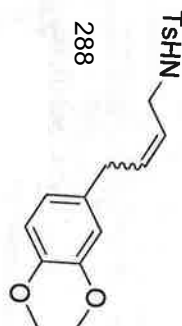




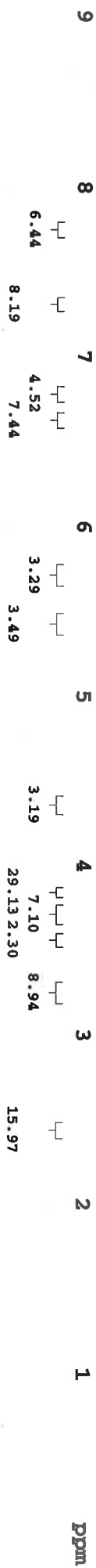
jxy130503_2.yjk_151_1_PROTON

exp1 PROTON

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SAMPLE PREPARATION
 date May 3 2013 satmode n
 solvent cdcl3 wet n
 file /home/ucvnmr- SPECIAL
 s/bup_archive/bup_ temp 25.0
 1306xsent/jxy13050- gain not used
 3_2.yjk_151_1_PROT- spin not used
 ON.fid bat 0.008
 ACQUISITION pw90 10.100
 sw 7998.4 alfa 10.000
 at 2.048
 mp 32768 il n
 fb 4000 in n
 bs 16 dp y
 dl 1.000 hs n
 nt 8
 ct 8 lb 0.50
 TRANSMITTER fn not used
 tn H1
 sfreq 499.908 sp -84.0
 tof 499.9 wp 4658.2
 tpwr 60 xfl 1015.9
 pw 10.100 xfp 0
 DECOUPLER xp -153.0
 dn C13 lp -115.1
 dof 0
 dm 0
 dm nmn wc 268
 decwave w40_autokdb sc 0
 dpwr 37 vs 60
 dmf 32258 th 150
 ai cdc ph



jxy140710_2_yjk_403_cp_PROTON

exp1 PROTON

SAMPLE PRESATURATION

date Jul 10 2014 satmode

solvent cdcl3 wet

file /home/uovvnmr-

s/jxy140710_2_yjk_ temp

403_cp_PROTON02.f1- gain

SPECIAL 25.0

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

not used

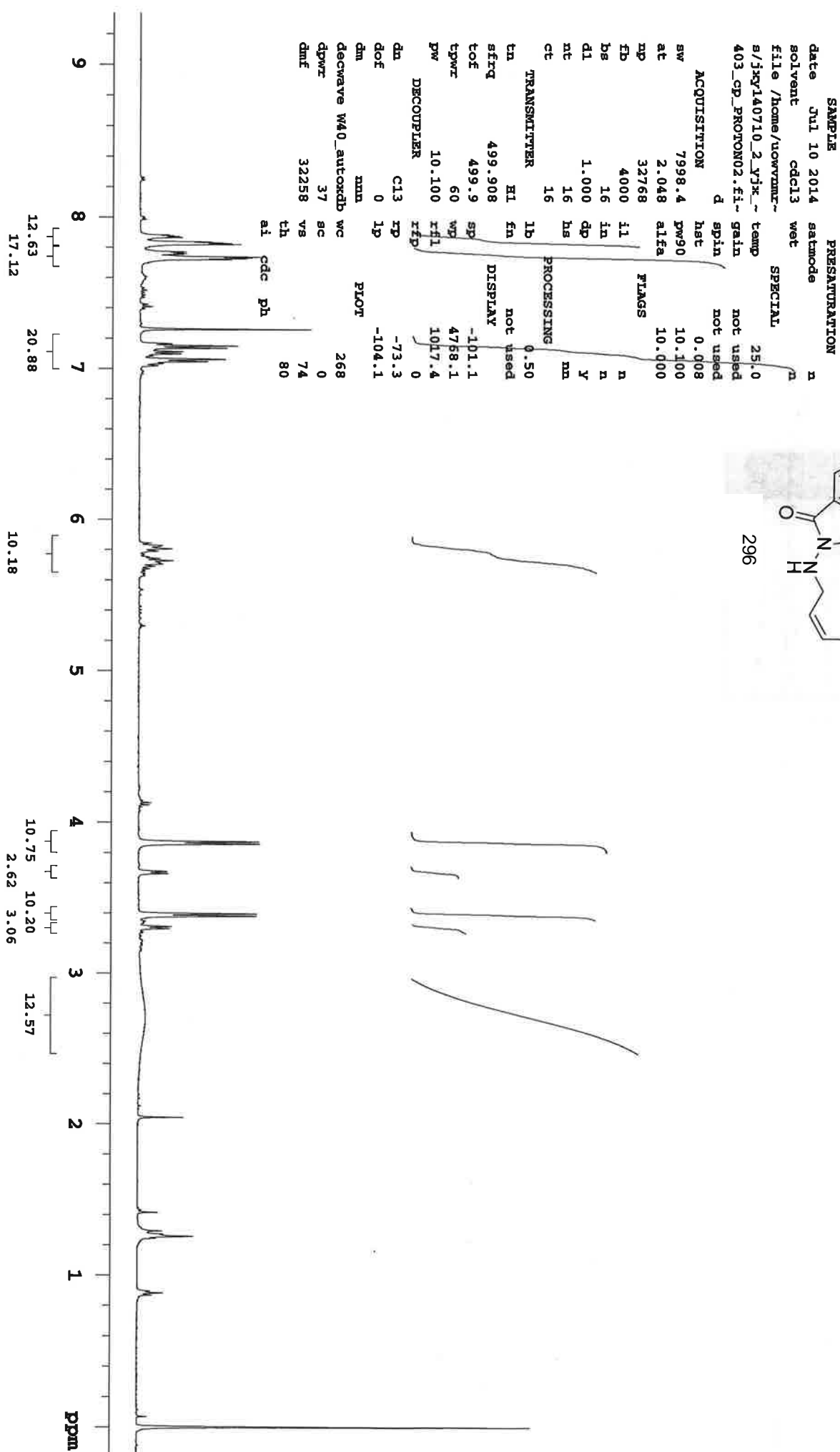
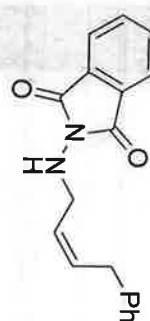
not used

not used

not used

not used

not used



jxy131129_2.y1x_260_3_13c-CARBON

Sample Name:

jxy131129_2.y1x_260_3_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: jxy131129_2.y1x_260_3_13c

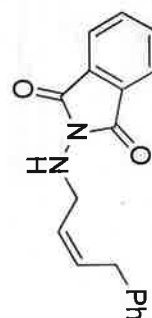
Pulse Sequence:

carbpol (zgpg30)

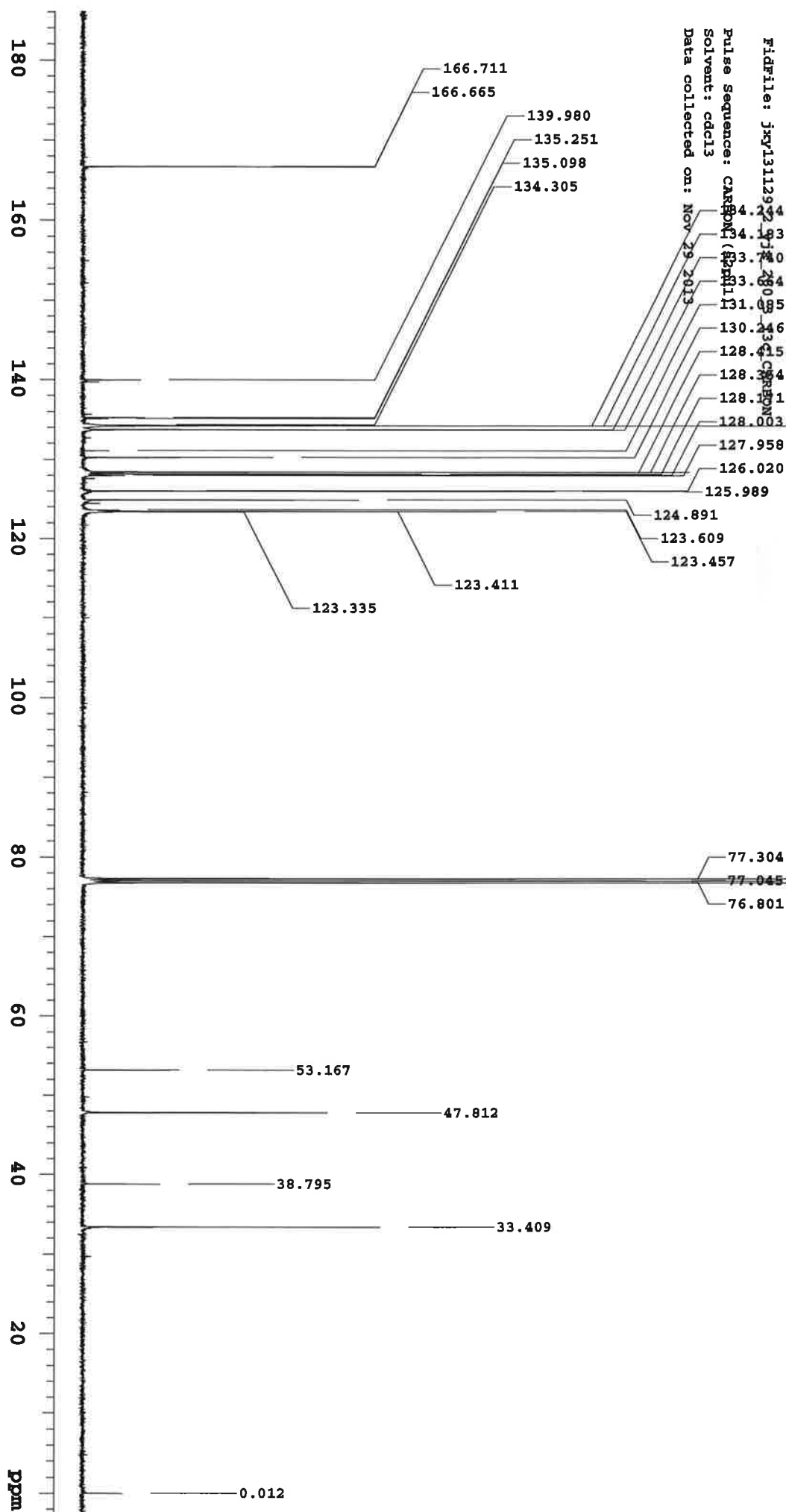
Solvent:

cdcl3

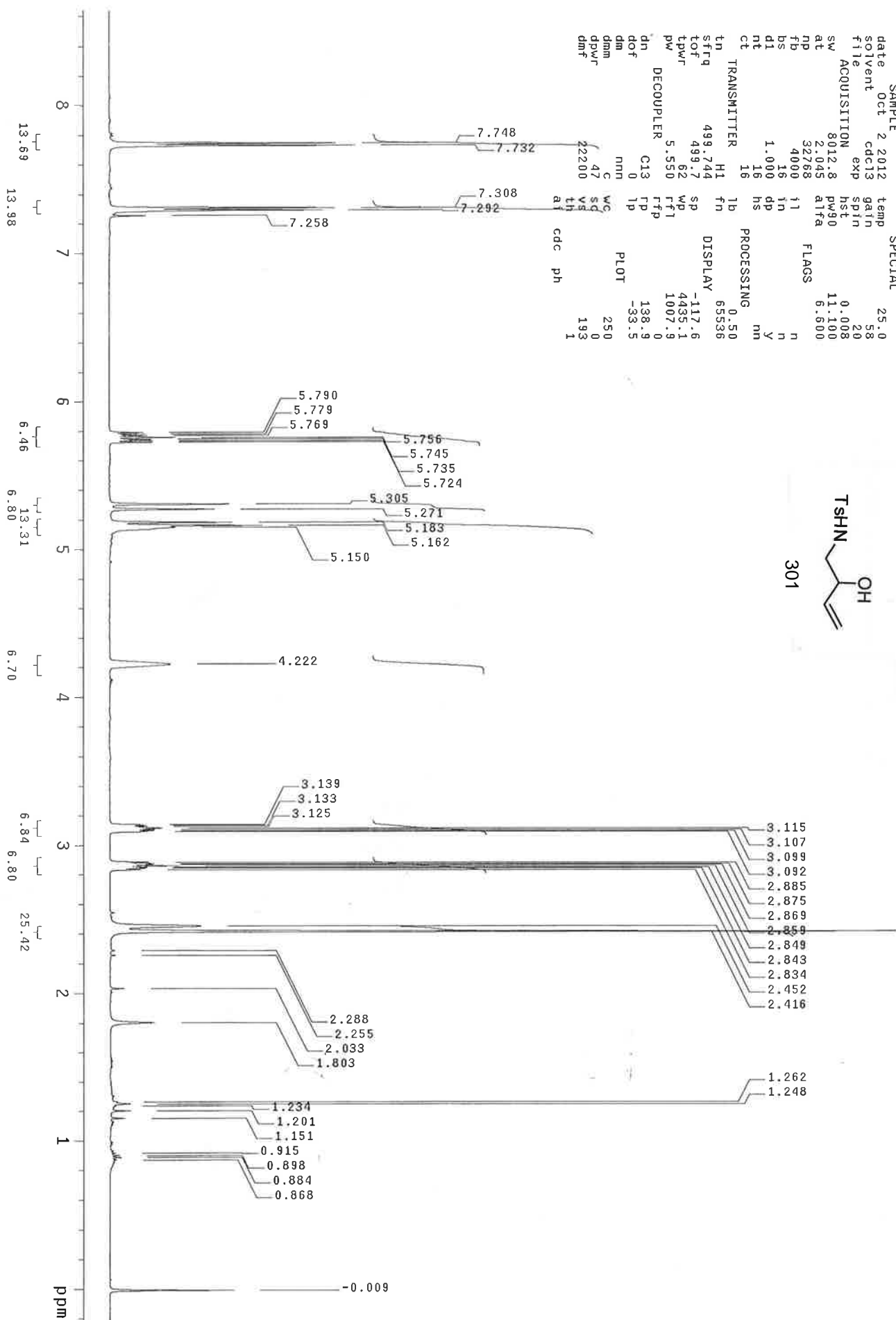
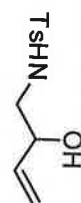
Data collected on: Nov 29 2013



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SAMPLE				SPECIAL			
date	Oct	2	2012	temp	25.0		
solvent		cdcl3		gain	58		
file		exp		spin	20		
ACQUISITION				hst	0.008		
sw		8012.8		pw90	11.100		
at		2.045		alfa	6.500		
np		32768		FLAGS			
fb		4000		i1			
bs		16		i1n			
d1		1.000		hs			
nt		16		dp			
ct		16		PROCESSING			
TRANSMITTER				1b	0.50		
tn		H1		f1n	65536		
strq		499.744		sp	-117.6		
tof		499.7		wp	4435.1		
tpwr		62		rfl1	1007.9		
pw		5.550		rfp	0		
DECOUPLER				1p	138.9		
un		C13		tp	-33.5		
dof		0		PLOT			
dmm		nmn		wc	250		
dpmr		c		sd	0		
dmf		47		vs	193		
		22200		th	1		



jxy160115_2.yjk_hydrolysedvinylaziridine_13c CARBON

Sample Name:

jxy160115_2.yjk_hydrolysedvinylaziridine_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (a2pu1)

Solvent: cdcl3

Data collected on: Jan 15 2016

Operator: uownmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

1248 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 239.9587703 MHz

Power 35 dB

continuously on

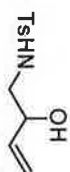
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

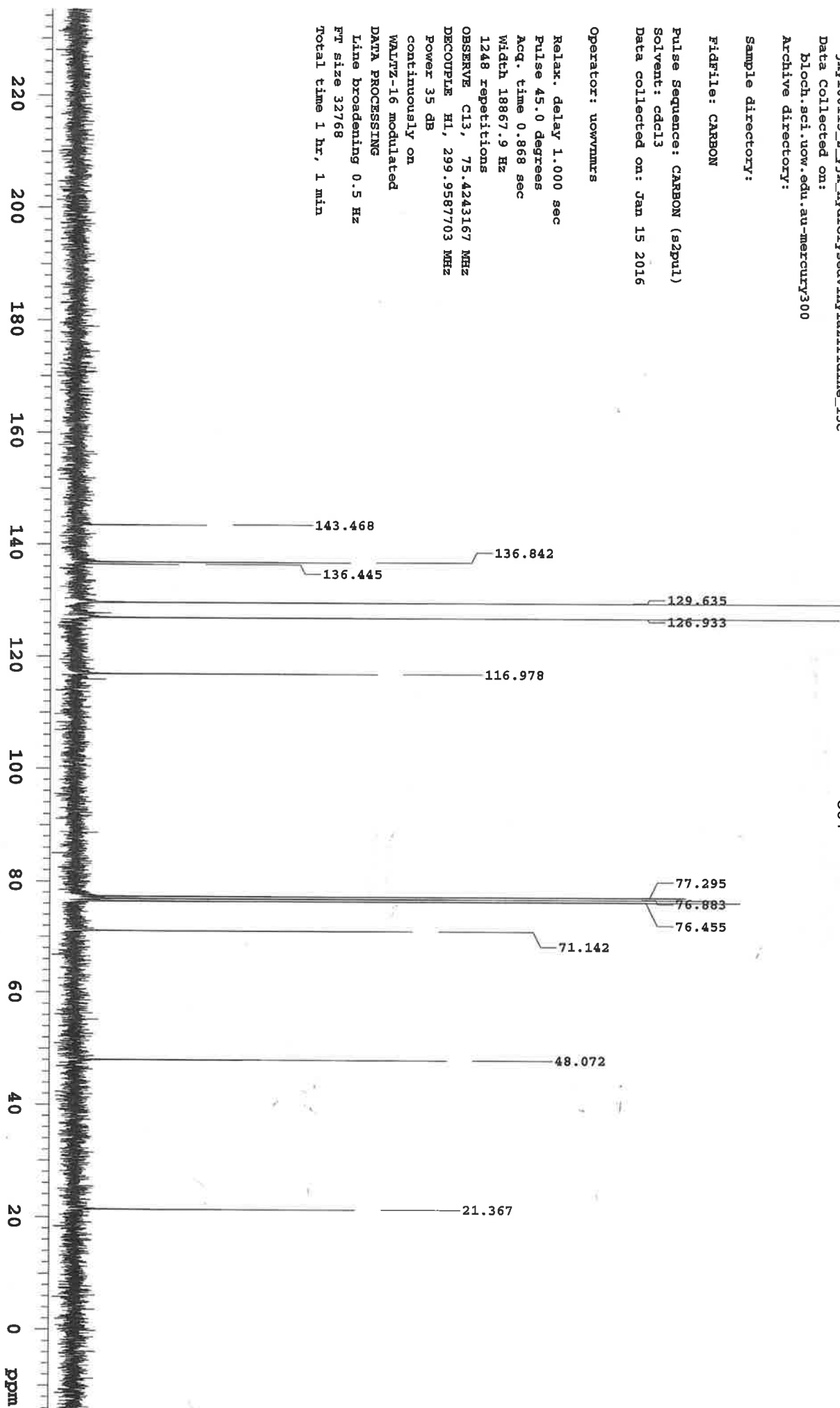
Total time 1 hr, 1 min



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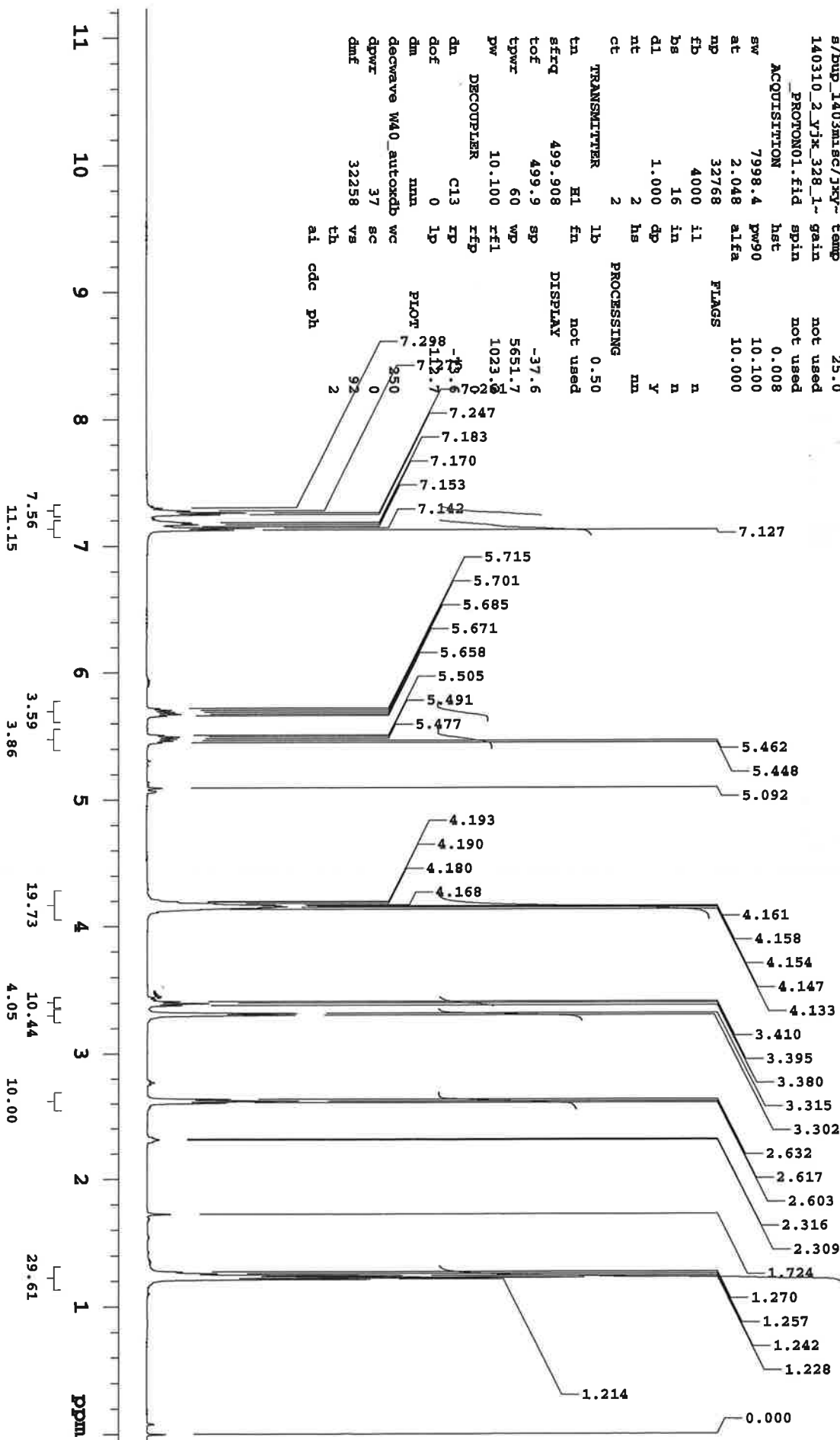
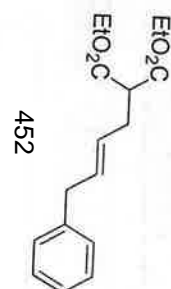
Agilent Technologies



jxy140310_2.yjk_328_1_PROTON

exp5 PROTON

SAMPLE PRESATURATION
date Mar 10 2014 satmode n
solvent cdcl3 wet n
file /home/nowymr~
s/bup_1403m1sc/jxy~
140310_2.yjk_328_1~
PROTON01.fid spin not used
ACQUISITION hsc 0.008
sw 7998.4 pw90 10.100
at 2.048 alfa 10.000
np 32768 FLAGS n
fb 4000 il n
bs 16 in n
dl 1.000 dp y
nt 2 hs n
ct 2 PROCESSING
TRANSMITTER lb 0.50
tn H1 fn not used
sfreq 499.908 DISPLAY
tof 499.9 sp -37.6
tpwr 60 wp 5651.7
pw 10.100 rfl 1023.8
DECOUPLER rfp
dn C13 rp
dof 0 lp
dm nnn
decwave W40_autocdb wc
dppwr 37 sc
dmf 32258 vs
ai cdc ph



jxy140315_2.yjk_328_1_13c CARBON

Sample Name:

jxy140315_2.yjk_328_1_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: jxy140315_2.yjk_328_1_13c CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Mar 15 2014

Temp. 25.0 C / 298.1 K

Operator: uownmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.521 sec

Width 31421.8 Hz

3104 repetitions

OBSERVE C13, 125.7011859 MHz

DECOUPLE H1, 499.9073947 MHz

Power 42 dB

continuously on

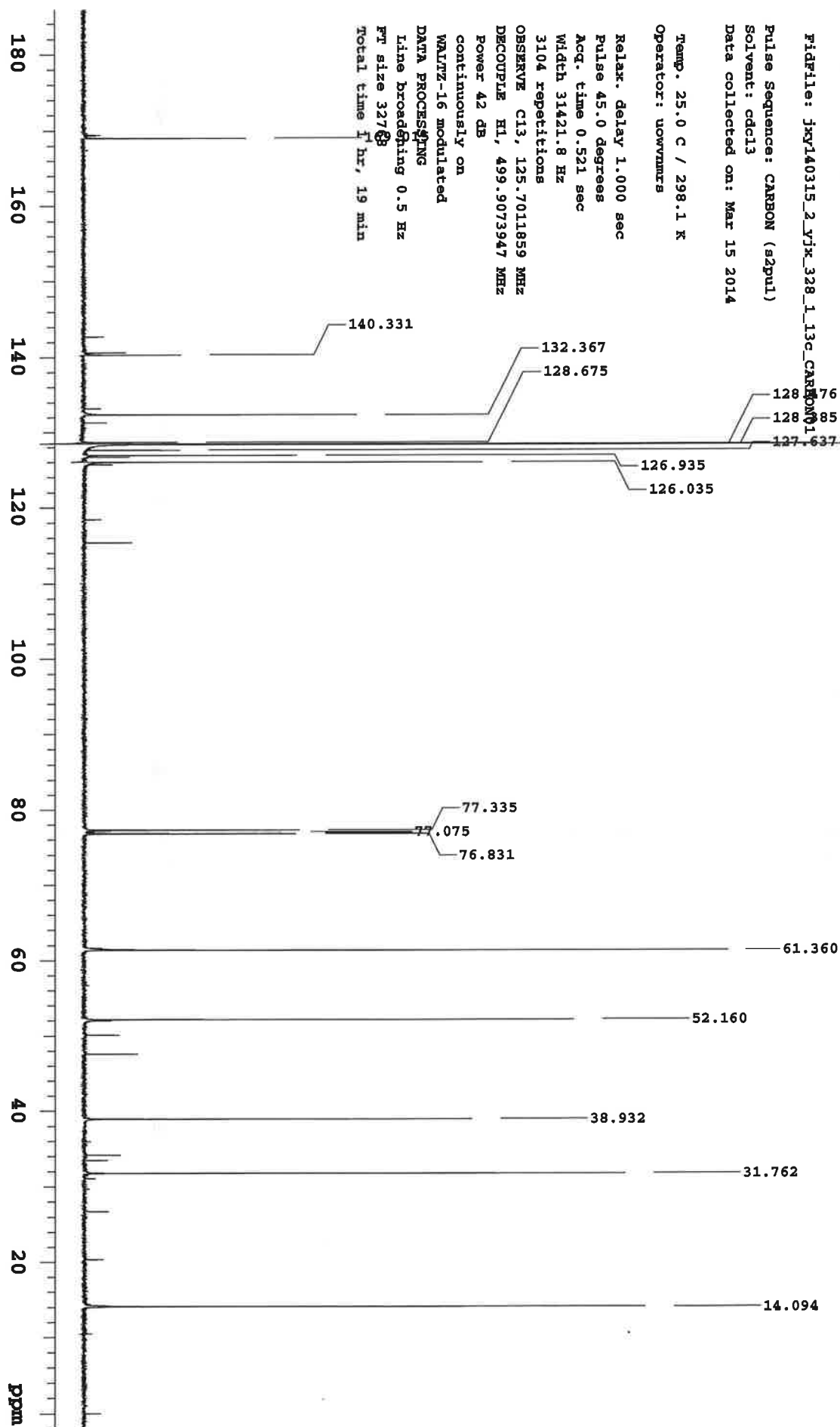
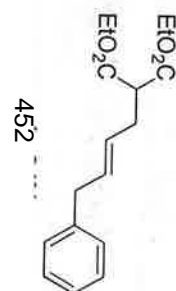
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 1 hr, 19 min



Agilent Technologies

jxy140310_2.yjk_328_1_NMRSTD

Sample Name:

jxy140310_2.yjk_328_1

Data Collected on:

arnst.sci.uow.edu.au-inova500

Archive directory:

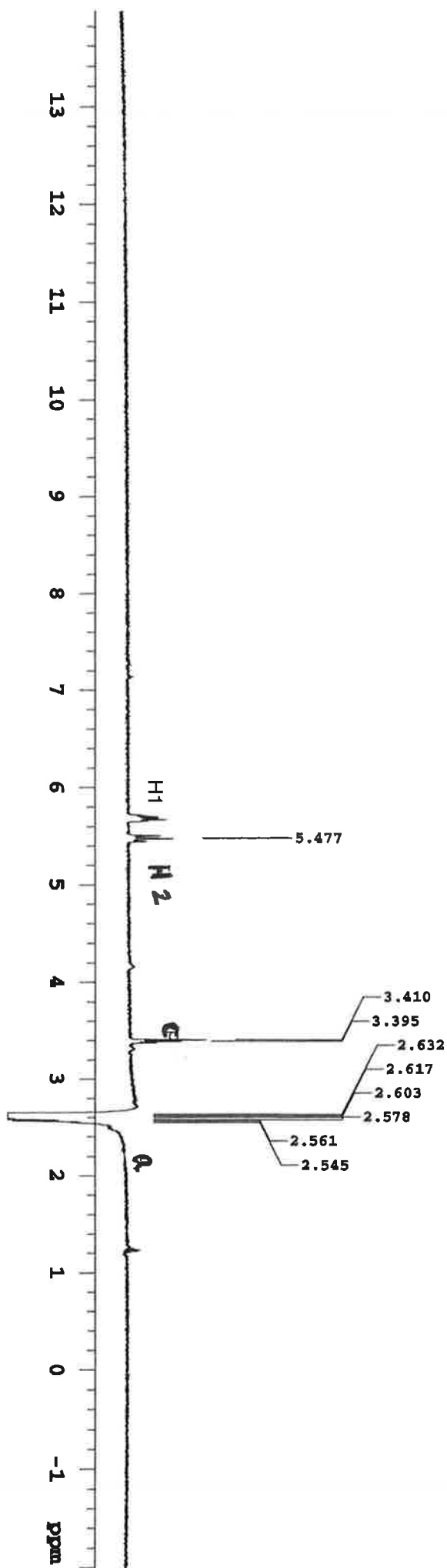
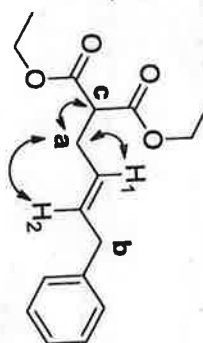
Sample directory:

Fidfile: jxy140310_2.yjk_328_1_NMRSTD01

Pulse Sequence: NOESYD

Solvent: cdcl3

Data collected on: Mar 10 2014



jxy140311_2.yjk_336_1_1_PROTON

exp5 PROTON

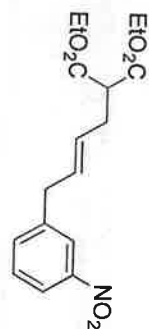
SAMPLE

PRESATURATION

date Mar 11 2014 satmode n
solvent cdcl3 wet n
file /home/uvnmr-
s/bup_1403misc/jxy-
140311_2.yjk_336_1-
_1_PROTON01.fid spin not used
ACQUISITION hst 0.008
sw 7998.4 pw90 10.100
at 2.048 alfa 10.000
np 32768
fb 4000 il n
bs 16 in n
dl 1.000 dp y
nt 6 hs nm

SPECIAL

468



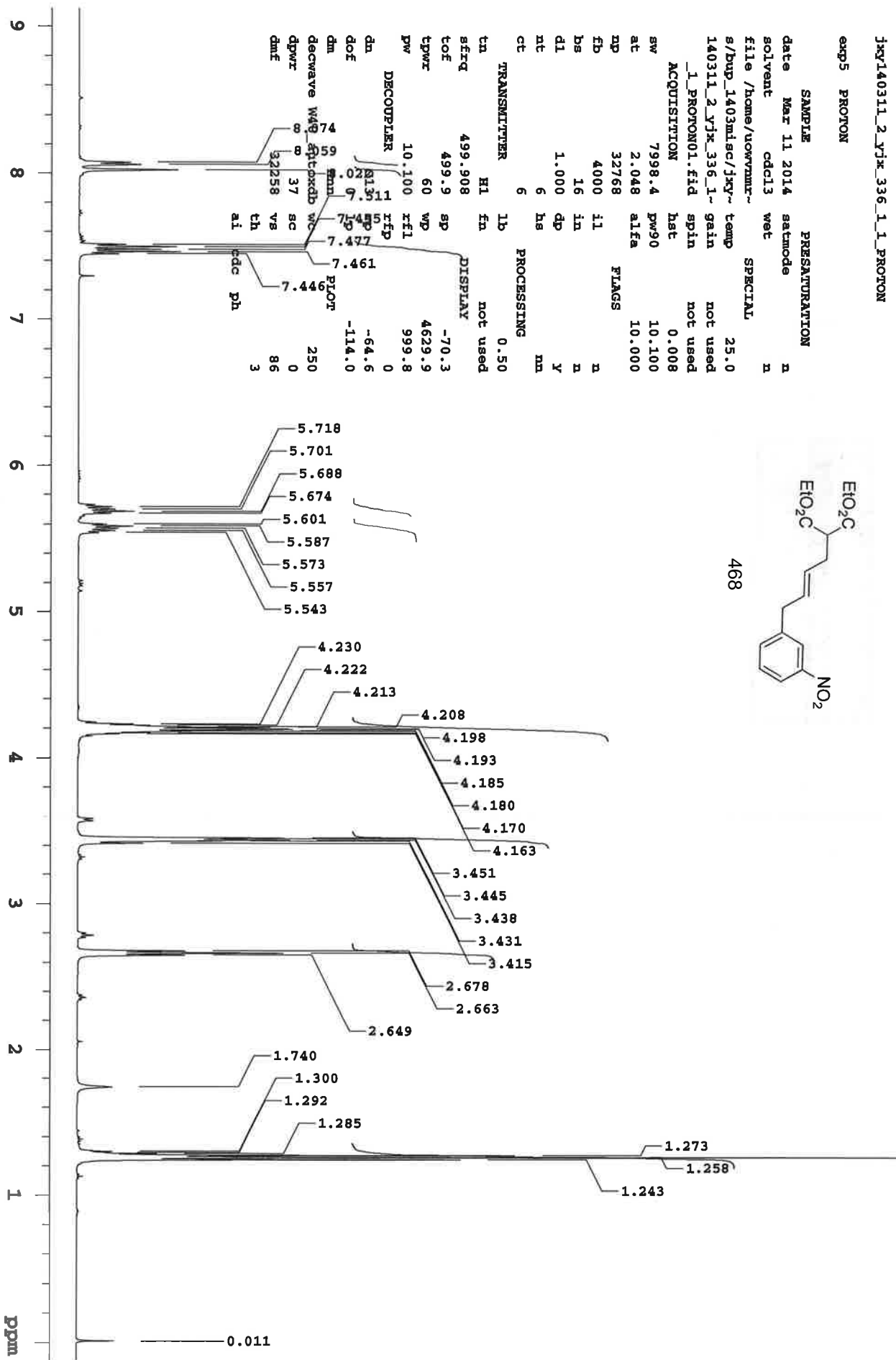
TRANSMITTER

PROCESSING

tn 499.908 H1 fn not used
sfreq 499.9 sp -70.3
tof 60 wp 4629.9
tpwr 10.100 xfl 999.8
pw 11 xfp 0
dn 115 74.461
dof 20 74.446
dm 74 74.427
decouple w4g altokdb vo
dpr 8 37 8c 250
dmf 32258 vs 86
ai cdc ph 3

DISPLAY

0.50
not used



jxy140315_2_vjx_336_1_1_13c CARBON

Sample Name:
jxy140315_2_vjx_336_1_1_13c
Data Collected on:
bloch.sci.ucw.edu.au-mercury300
Archive directory:

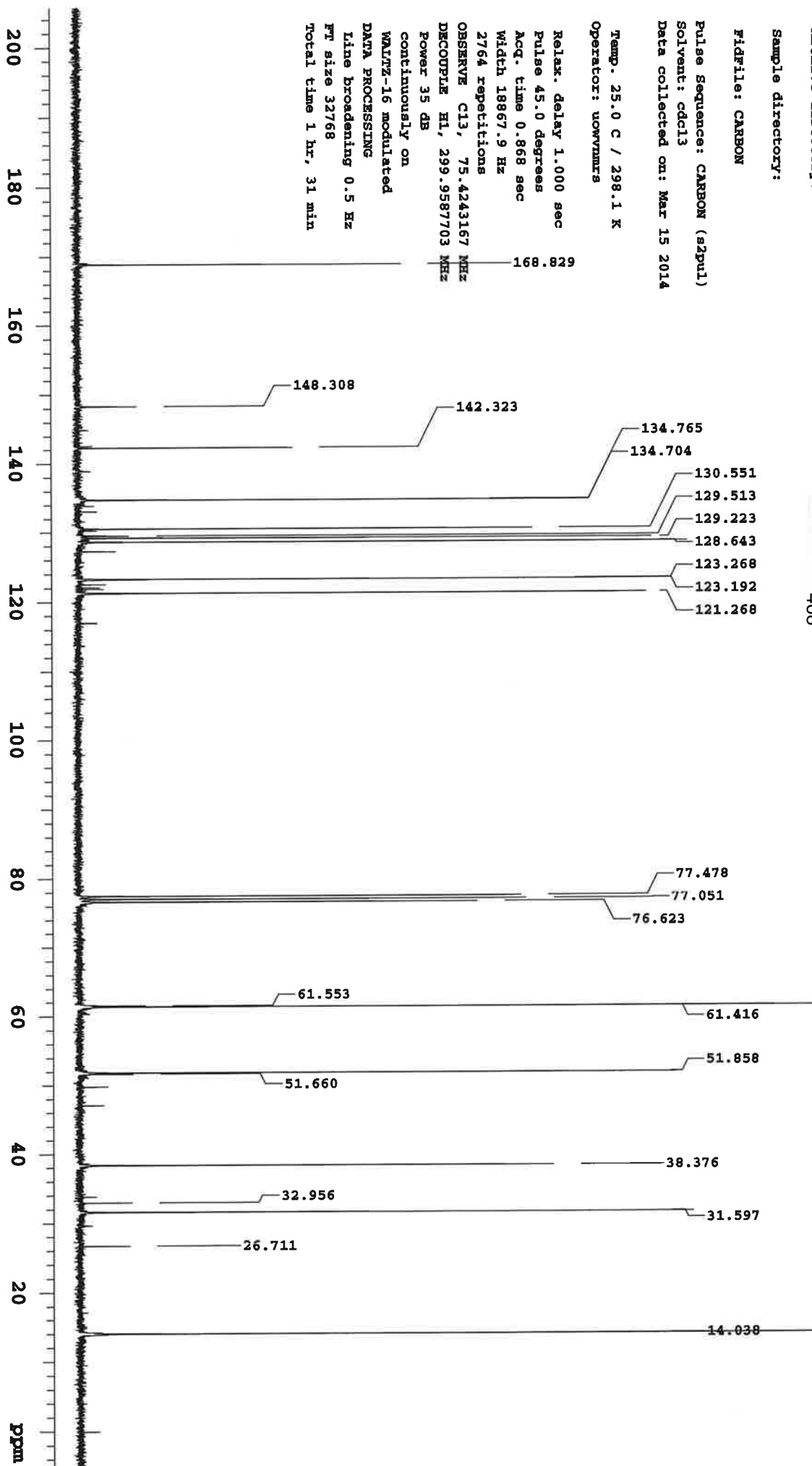
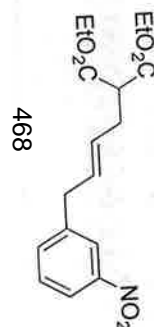
Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (szpu1)
Solvent: cdcl3
Data collected on: Mar 15 2014

Temp. 25.0 C / 298.1 K
Operator: ucwvnmrs

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 1867.9 Hz
2764 repetitions
OBSERVE C13, 75.4243167 MHz
DECOUPLE H1, 299.9587703 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 1 hr, 31 min

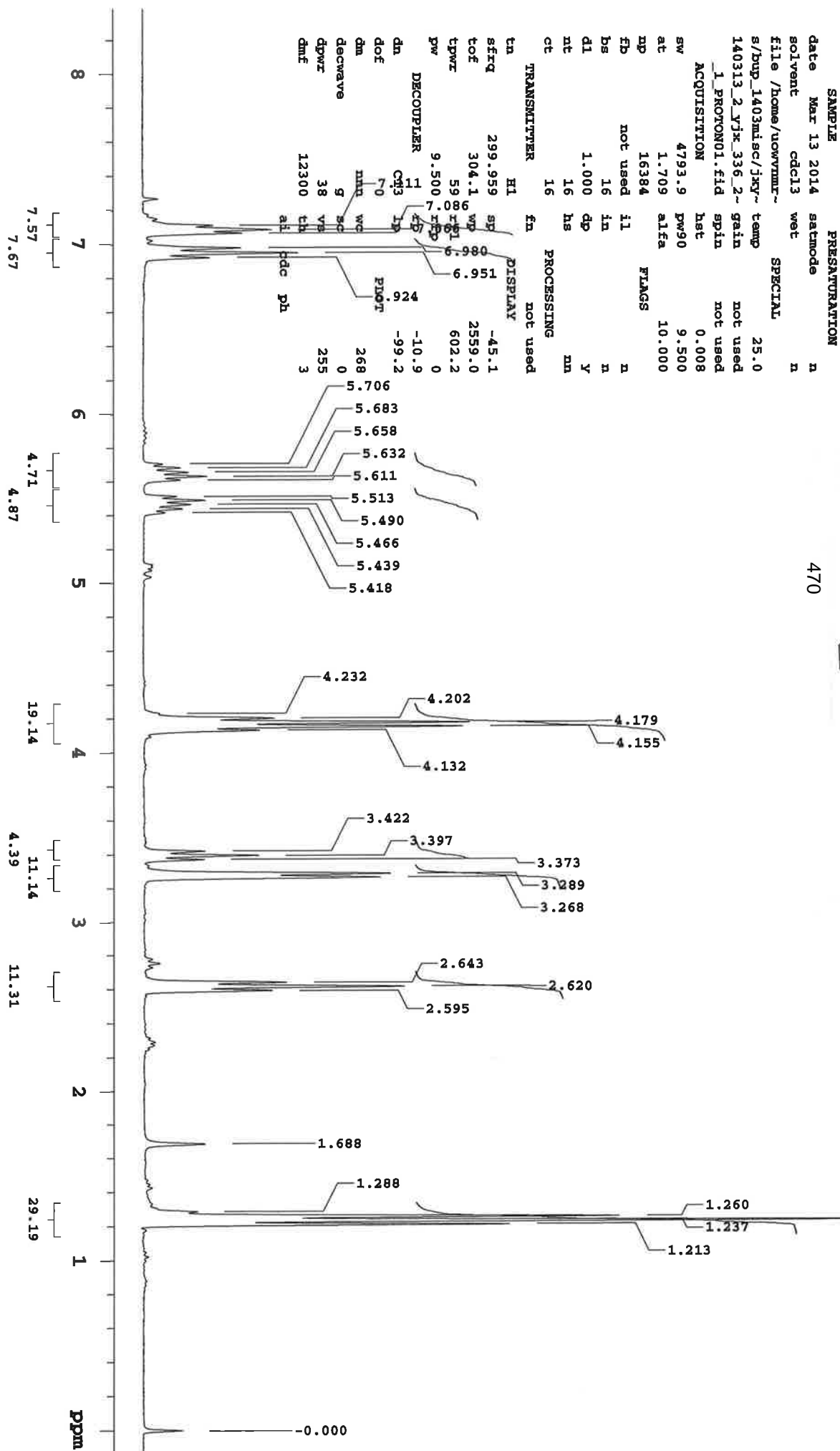
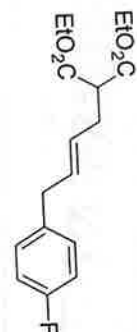


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jxy140313_2_vjk_336_2_1_PROTON

exp2 PROTON

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jxy140315_2_vjx_336_2_1_13c_CARBON

Sample Name:

jxy140315_2_vjx_336_2_1_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

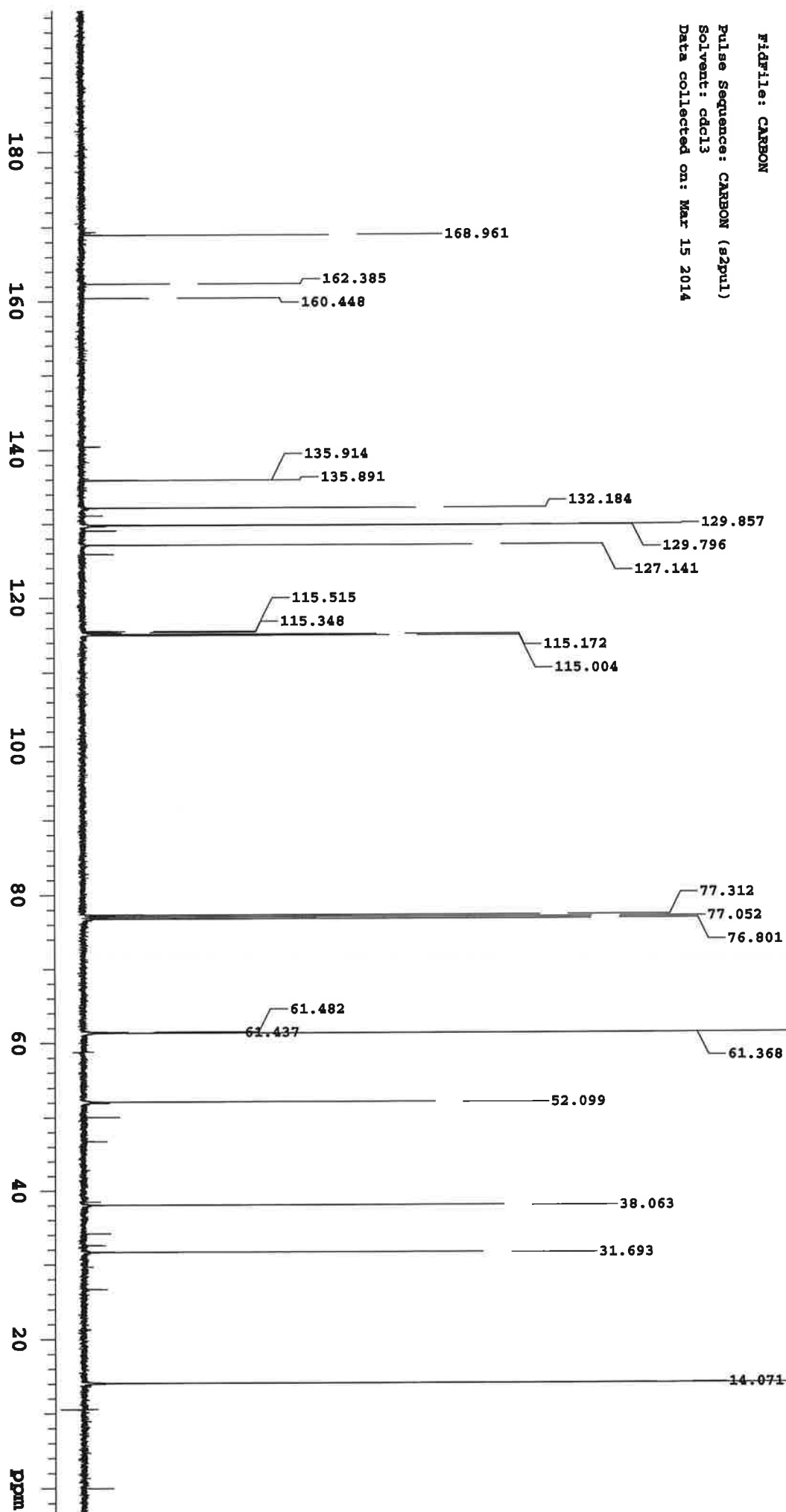
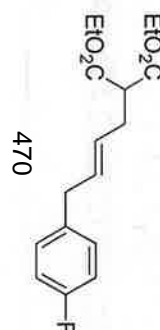
Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Mar 15 2014



jxy140313_2.yjk_336_3_1_PROTON

exp2 PROTON

SAMPLE PRESATURATION

date Mar 13 2014 satmode n

solvent cdcl3 wet n

file /home/novnmr~ SPECIAL

s/bup_1403mlsc/jxy~ temp 25.0

140313_2.yjk_336_3~ gain not used

_1_PROTON01.fid spin not used

ACQUISITION hst 0.008

sw 4793.9 pw90 9.500

at 1.709 alfa 10.000

np 16384 FLAGS

fb not used il n

bs 16 in n

dl 1.000 dp y

nt 16 hs m

ct 16 PROCESSING

tn TRANSMITTER fn not used

sfreq 299.958 MHz DISPLAY

tof 937.5 Hz 53

tpwr 4.59 W 2519.8

pw 79.500 W 596.9

DECOUPLER ffp 0

dm C13 1p -94.6

dof 0 95

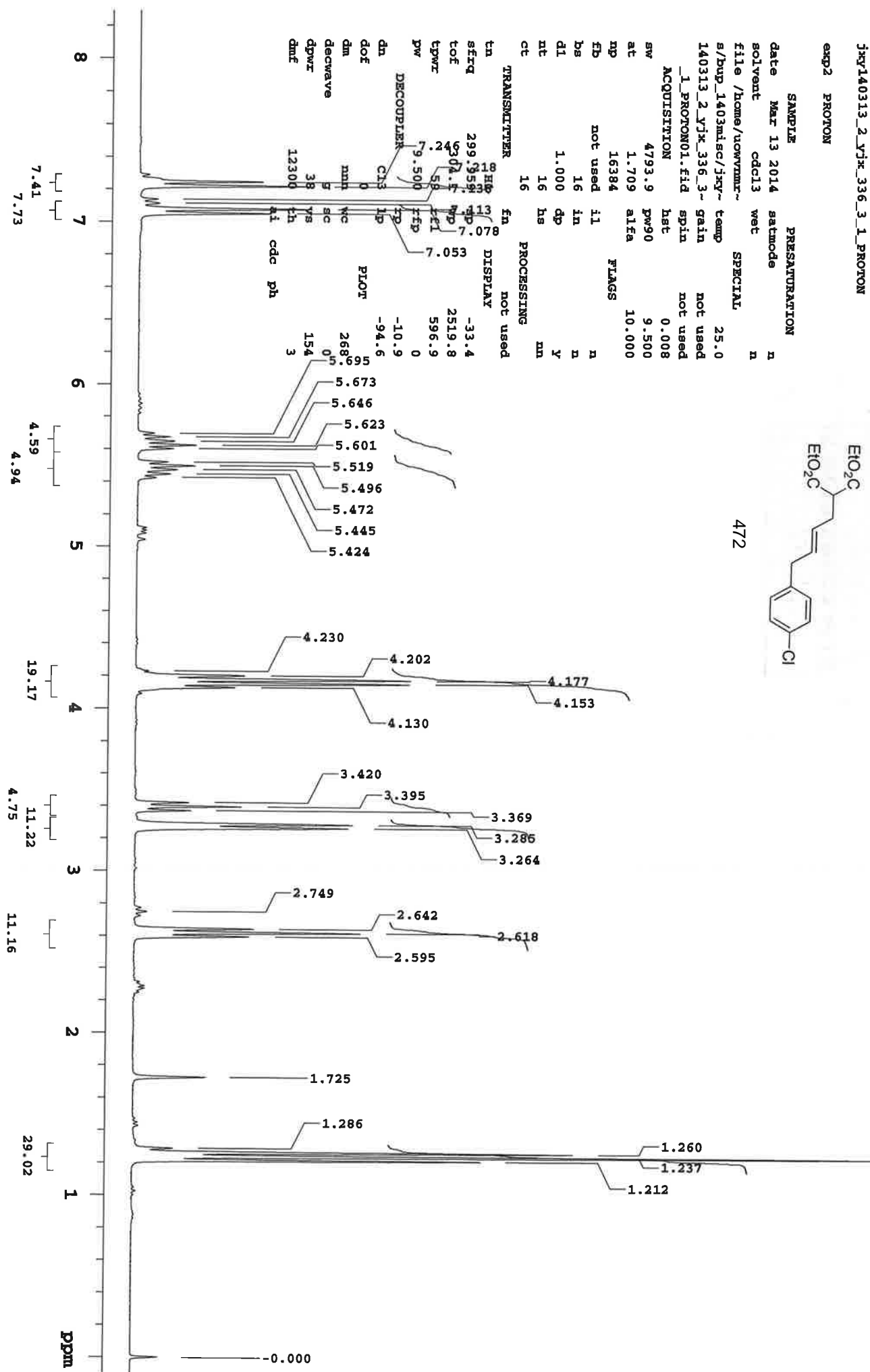
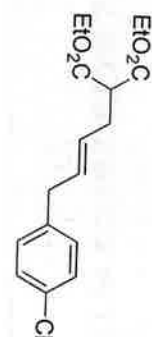
dm nmh 268.0

decwave f sc 0

dpwr 38 vs 154

dnt 12300 ch 3

ai cdcl3 ph



jxy140315_2_yjk_336_3_1_13c CARBON

Sample Name:
jxy140315_2_yjk_336_3_1_13c
Data Collected on:
bloch.sci.uow.edu.au-mercury300
Archive directory:

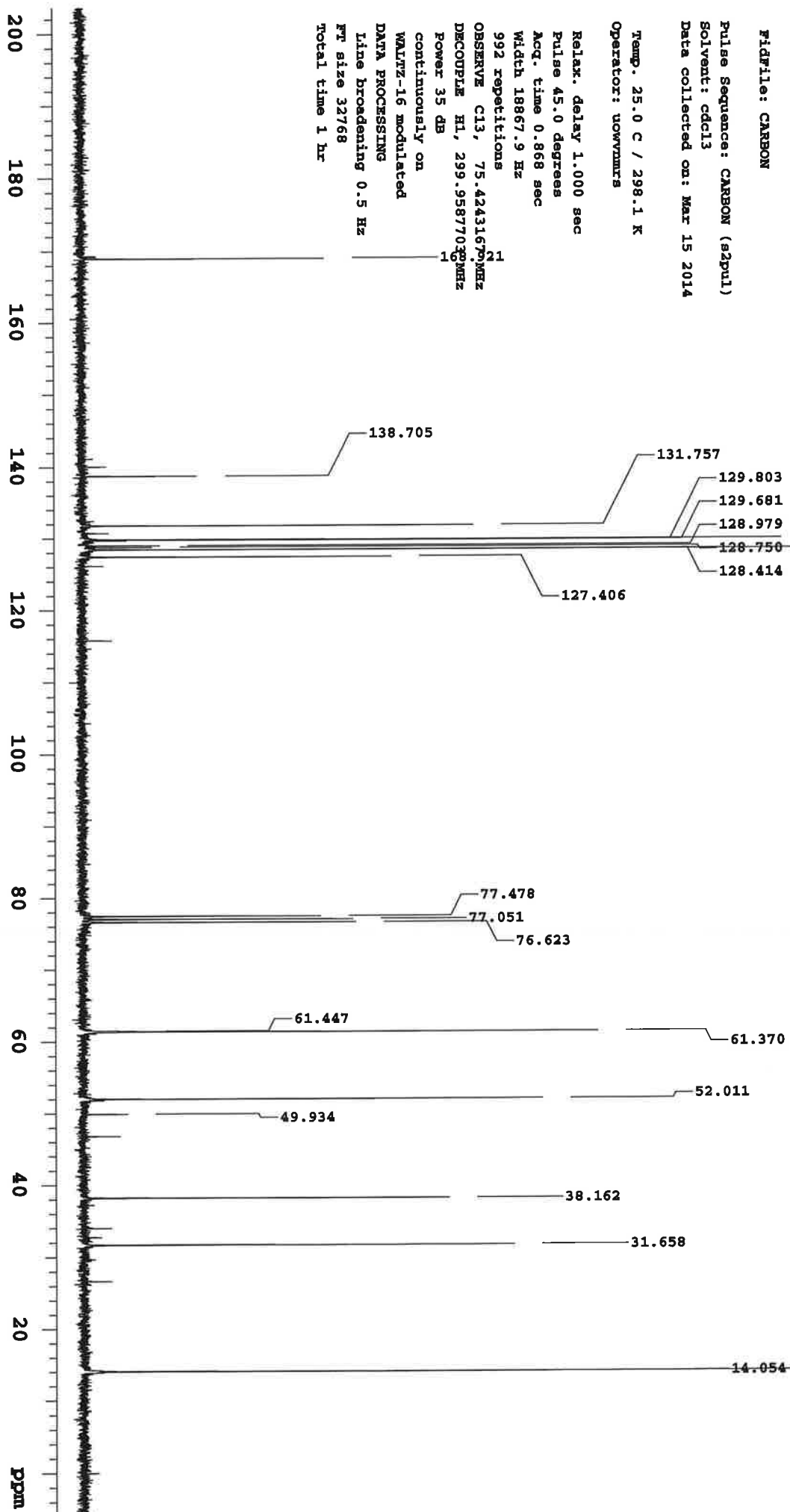
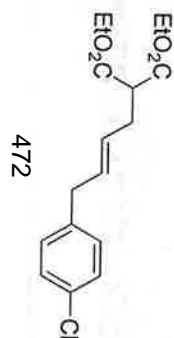
Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (zgpg1)
Solvent: cdcl3
Data collected on: Mar 15 2014

Temp. 25.0 C / 298.1 K
Operator: uowmms

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
992 repetitions
OBSERVE C13, 75.42431670MHz
DECOUPLE H1, 299.95877030MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 1 hr



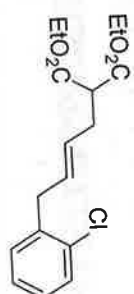
jxy140316_2.yjk_336_4_1_13c CARBON

Sample Name:
jxy140316_2.yjk_336_4_1_13c
Data Collected on:
ernst.sci.uow.edu.au-inova500
Archive directory:

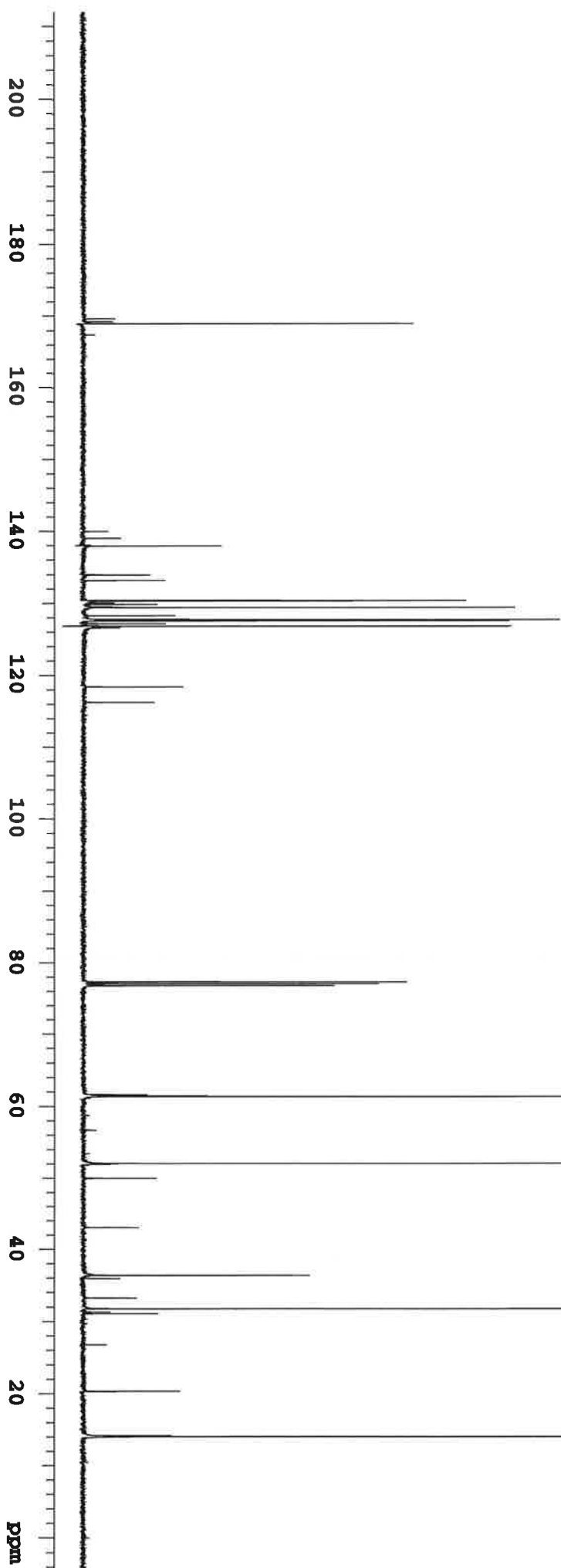
Sample directory:

File: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 16 2014



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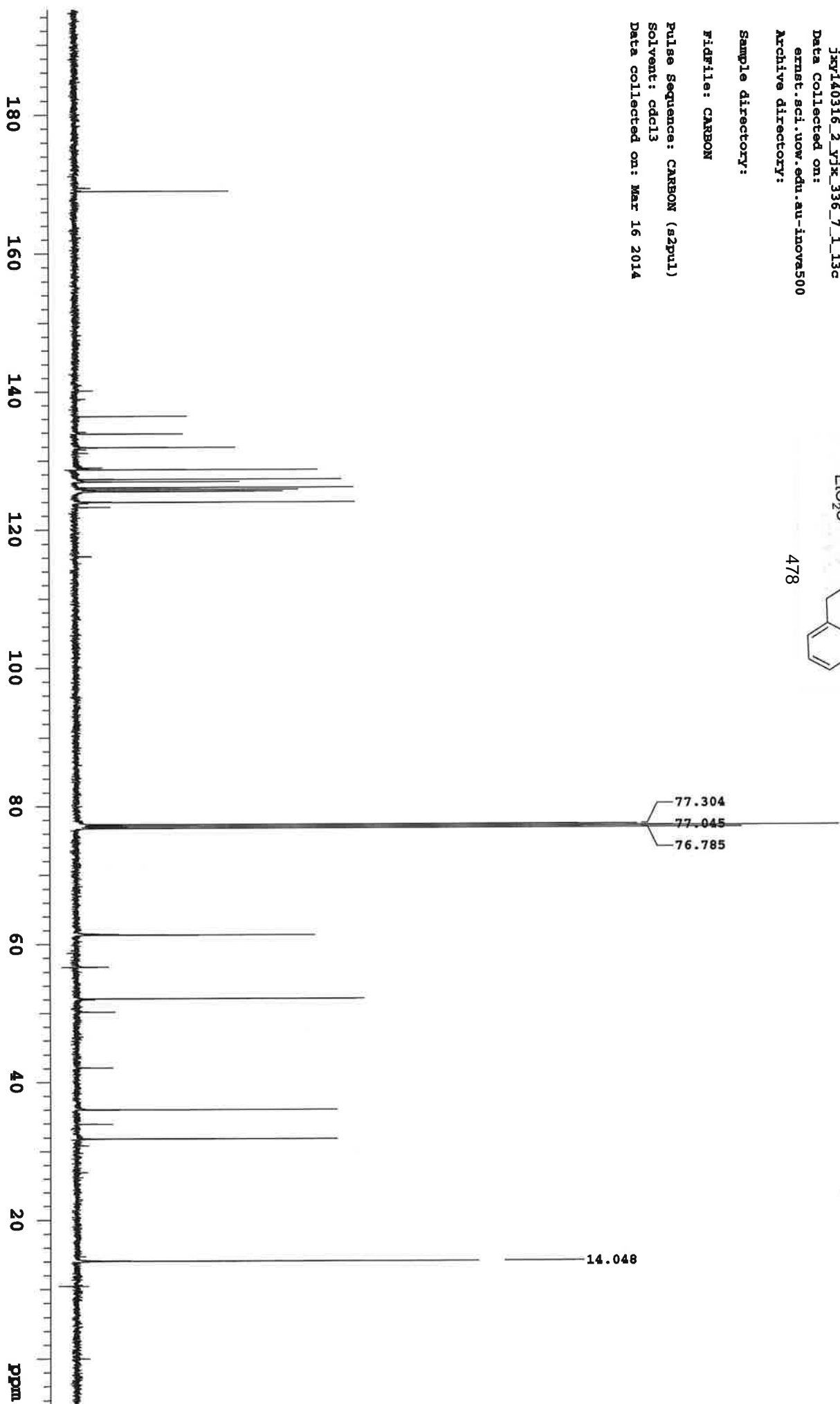
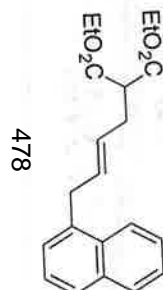
jxy140316_2.yjx_336_7_1_13c CARBON

Sample Name:
jxy140316_2.yjx_336_7_1_13c
Data Collected on:
ernst.sci.uow.edu.au-inova500
Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pu1)
Solvent: cdcl3
Data collected on: Mar 16 2014



exp6 PROTON

SAMPLE	PRESATURATION	n
date	Mar 13 2014	satmode

```
solvent      cdcl3      wet
file /home/uowmr~ SPECIAL
```

s/bup_1403misc/jky~ temp	25.0
140313 2 yix 336 8~ gain	not used

	spin	not used
<u>b</u> PROTON01.fid	spin	not used
ACQUISITION	bst	0.008

NO.	DESCRIPTION	AMOUNT	DATE
1	7998.4	10.100	10.100
2	10.100	10.100	10.100
3	10.100	10.100	10.100
4	10.100	10.100	10.100
5	10.100	10.100	10.100
6	10.100	10.100	10.100
7	10.100	10.100	10.100
8	10.100	10.100	10.100
9	10.100	10.100	10.100
10	10.100	10.100	10.100
11	10.100	10.100	10.100
12	10.100	10.100	10.100
13	10.100	10.100	10.100
14	10.100	10.100	10.100
15	10.100	10.100	10.100
16	10.100	10.100	10.100
17	10.100	10.100	10.100
18	10.100	10.100	10.100
19	10.100	10.100	10.100
20	10.100	10.100	10.100
21	10.100	10.100	10.100
22	10.100	10.100	10.100
23	10.100	10.100	10.100
24	10.100	10.100	10.100
25	10.100	10.100	10.100
26	10.100	10.100	10.100
27	10.100	10.100	10.100
28	10.100	10.100	10.100
29	10.100	10.100	10.100
30	10.100	10.100	10.100
31	10.100	10.100	10.100
32	10.100	10.100	10.100
33	10.100	10.100	10.100
34	10.100	10.100	10.100
35	10.100	10.100	10.100
36	10.100	10.100	10.100
37	10.100	10.100	10.100
38	10.100	10.100	10.100
39	10.100	10.100	10.100
40	10.100	10.100	10.100
41	10.100	10.100	10.100
42	10.100	10.100	10.100
43	10.100	10.100	10.100
44	10.100	10.100	10.100
45	10.100	10.100	10.100
46	10.100	10.100	10.100
47	10.100	10.100	10.100
48	10.100	10.100	10.100
49	10.100	10.100	10.100
50	10.100	10.100	10.100
51	10.100	10.100	10.100
52	10.100	10.100	10.100
53	10.100	10.100	10.100
54	10.100	10.100	10.100
55	10.100	10.100	10.100
56	10.100	10.100	10.100
57	10.100	10.100	10.100
58	10.100	10.100	10.100
59	10.100	10.100	10.100
60	10.100	10.100	10.100
61	10.100	10.100	10.100
62	10.100	10.100	10.100
63	10.100	10.100	10.100
64	10.100	10.100	10.100
65	10.100	10.100	10.100
66	10.100	10.100	10.100
67	10.100	10.100	10.100
68	10.100	10.100	10.100
69	10.100	10.100	10.100
70	10.100	10.100	10.100
71	10.100	10.100	10.100
72	10.100	10.100	10.100
73	10.100	10.100	10.100
74	10.100	10.100	10.100
75	10.100	10.100	10.100
76	10.100	10.100	10.100
77	10.100	10.100	10.100
78	10.100	10.100	10.100
79	10.100	10.100	10.100
80	10.100		

at	2.048	BL1A	10.000
up	32768	FLAGS	

fb	4000	11	m
bs	16	1m	m

dl	1.000	dp	y
nt	13	hs	nn

ct	13	PROCESSING
TRANSMITTER	1b	0.50

tn	H1	fn	not used
400 008			

BLQ	499.506	DISPVAL
tof	499.9	sp
		-53.2

tpwr	60	wp	4599.2
pw	10.100	rf1	1018.4

	DECOUPLER	2	382	0
	C ₇₃	6	7.35	-66.6
da			349	

-113.4

PLOT

7.

1p

70.7

767

.781

dm

dof

decavre	W40	autoxdr	wc
37	334	258	5250

qpwf	3 /	BC
dinf	32258	VS

th
ai
cdc
ph

100

100

100

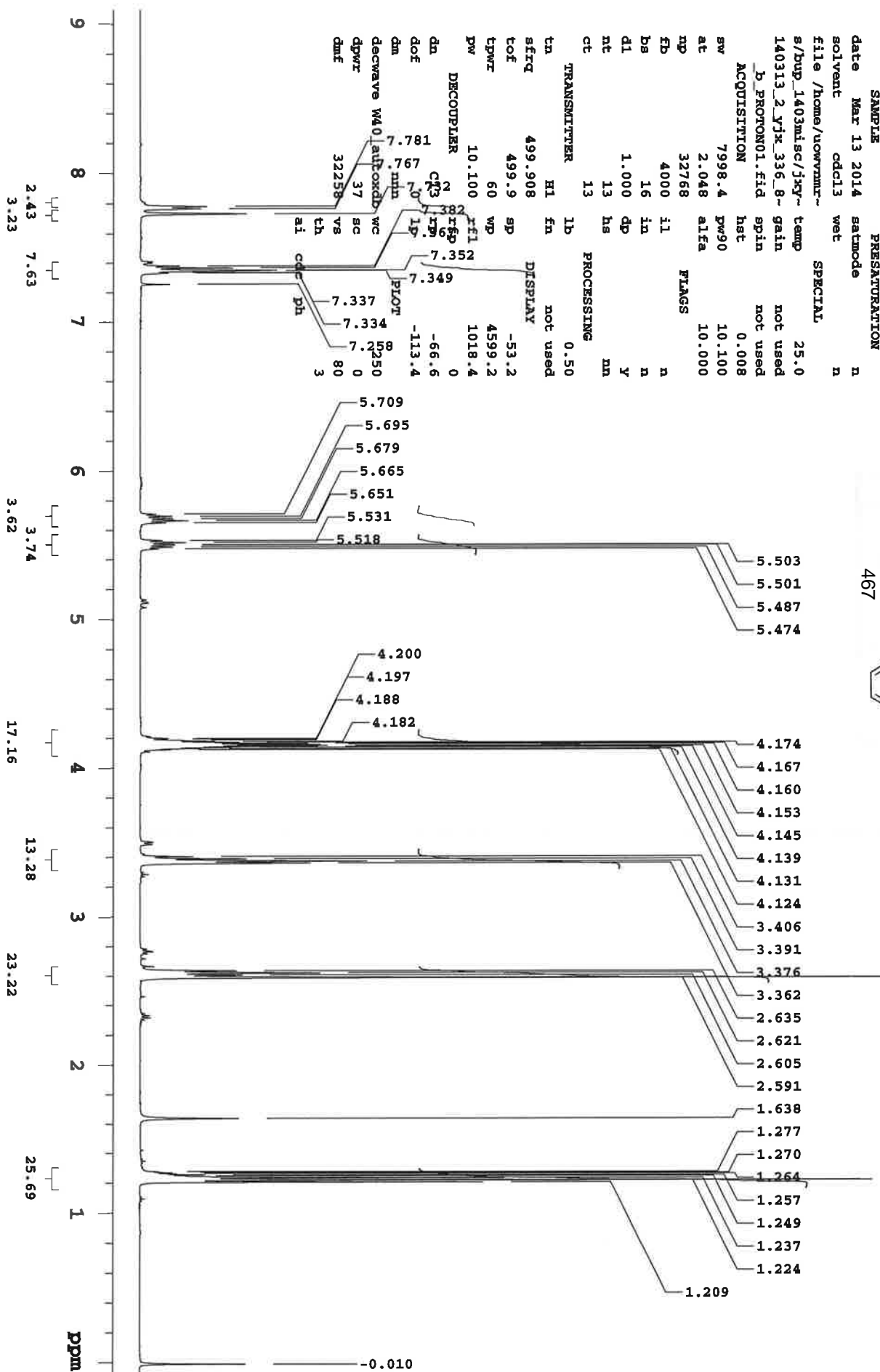
100

[illegible]

1. $\frac{1}{2}$

2.43 7.63
3.33

467

CC(=O)c1ccccc1C/C=C/C(C(=O)OCC)C(=O)OCC

jxy140316_2.yjx_336_8_1_13c CARBON

Sample Name:

jxy140316_2.yjx_336_8_1_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Filefile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Mar 16 2014

Ambient temperature

Operator: uowymms

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

2016 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

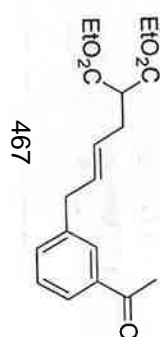
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 1 hr, 29 min



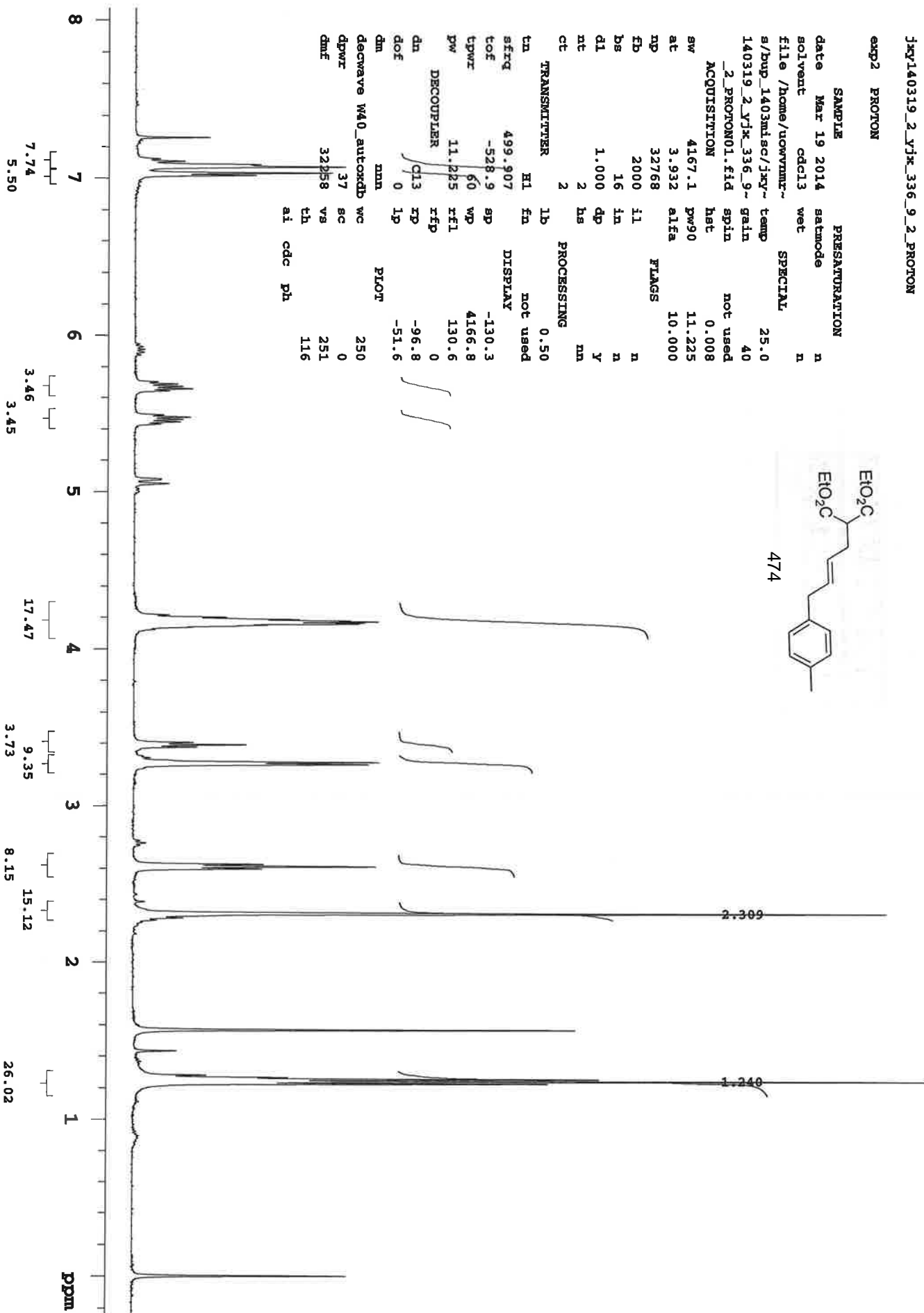
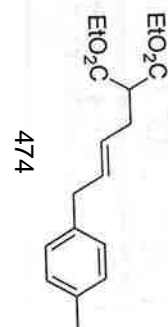
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jky140319_2.yjk_336_9_2_PROTON

exp2 PROTON

SAMPLE		PRESATURATION	
date	Mar 19 2014	satmode	n
solvent	cdcl3	wet	n
file	/home/nowmnr~	SPECIAL	
s/bup	1403mlsc/jky~	temp	25.0
140319_2.yjk_336_9_		gain	40
_2_PROTON01.fid		spin	not used
ACQUISITION		not used	
sw	4167.1	pw90	11.225
at	3.932	alfa	10.000
np	32768	FLAGS	
fb	2000	il	n
bs	16	ln	n
dl	1.000	dp	y
nt	2	hs	nm
ct	2	PROCESSING	
TRANSMITTER		lb	0.50
tn	H1	fn	not used
sfrq	499.907	sp	-130.3
tof	-528.9	wp	4166.8
tpwr	60	rfl	130.6
pw	11.225	rfp	0
DECOUPLER		rp	-96.8
dn	cl3	lp	-51.6
dof	0	PLOT	
dm	nm	wc	250
decwave	W40_autokdb	sc	0
dpwr	37	vs	251
dntf	32858	th	116
	ai	cdc	ph



jxy140319_2_vjk_336_9_2_13c-CARBON

Sample Name:

jxy140319_2_vjk_336_9_2_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

FidFile: jxy140319_2_vjk_336_9_2_13c-CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Mar 19 2014

Temp. 25.0 C / 298.1 K

Operator: uowvnmr

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.521 sec

Width 31421.8 Hz

2324 repetitions

OBSERVE C13, 125.7011859 MHz

DECOUPLE H1, 499.9073947 MHz

Power 42 dB

continuously on

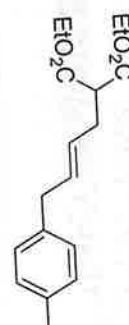
WALTZ-16 modulated

DATA PROCESSING

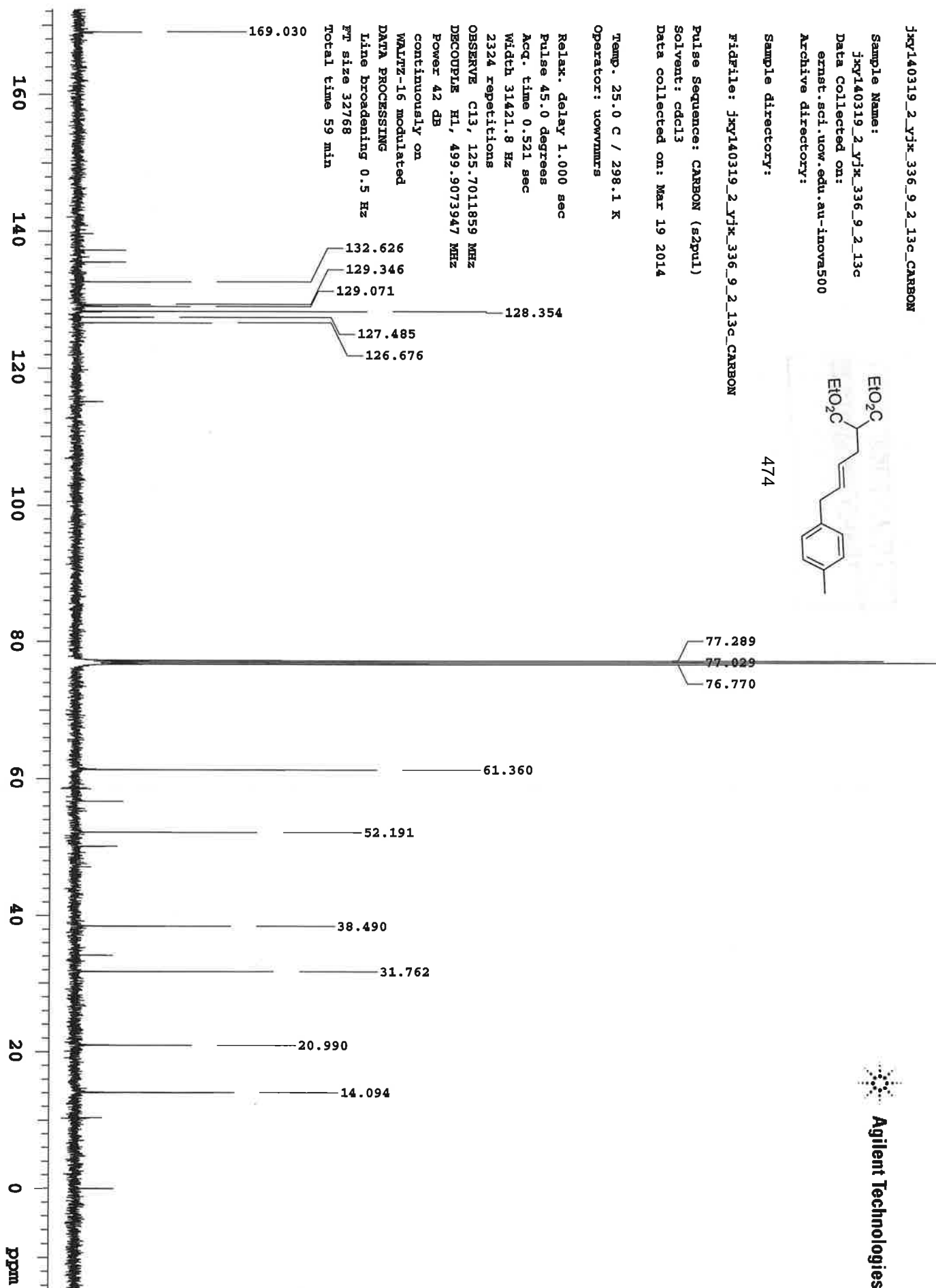
Line broadening 0.5 Hz

FT size 32768

Total time 59 min



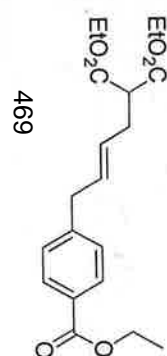
474



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jky140314_2.yjk_336_10_1_PROTON

exp2 PROTON



SAMPLE PRESATURATION

date Mar 14 2014 satmode n

solvent cdc13 wet n

file /home/nowmnr~ SPECIAL

s/bup_1403m1sc/jky~ temp 25.0

140314_2.yjk_336_1~ gain not used

0_1_PROTON01.fid spin not used

ACQUISITION hst 0.008

sw 7998.4 pw90 10.100

at 2.048 alfa 10.000

np 32768 FLAGS

fb 4000 il n

bs 16 in n

dl 1.000 dp y

nt 16 hs na

ct 16 PROCESSING

tn TRANSMITTER lb 0.50

sfreq 499.908 H1 fn not used

toe 499.9 sp -63.0

tpwr 60 wp 4636.8

pw 10.100 rfl 1015.9

DECOUPLER rfp 0

dn C13 rp -68.4

dof 0 lp -103.6

dm 0.000

decouple W40_autocoupling

dpr 7.375 wc 7.215

dmc 32258 vs 7.198

ai th 7.273

ddc ph

53

2

5.519

4.386

4.372

4.357

4.344

4.206

4.202

4.194

4.191

4.186

4.181

4.172

4.166

4.158

4.152

4.144

3.488

3.474

3.413

3.397

3.382

3.374

3.361

2.644

2.629

2.615

1.566

1.401

1.388

1.373

1.283

1.279

1.269

1.265

1.253

1.238

1.230

1.224

1.210

1.195

0.871

0.858

0.001

0.001

0.001

0.001

0.001

0.001

9 8 7 6 5 4 3 2 1 ppm

6.36

6.37

3.06

3.09

7.87

15.07

11.24

7.59

11.89

27.48

jxy140314_2.yjk_336_10_1_CARBON

Sample Name:

jxy140314_2.yjk_336_10_1

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: jxy140314_2.yjk_336_10_1_CARBON1

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Mar 14 2014

Temp. 25.0 C / 298.1 K

Operator: uowymms

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.521 sec

Width 31421.8 Hz

44452 repetitions

OBSERVE C13, 125.7011859 MHz

DECOUPLE H1, 499.9073947 MHz

Power 42.0 dB

continuously on

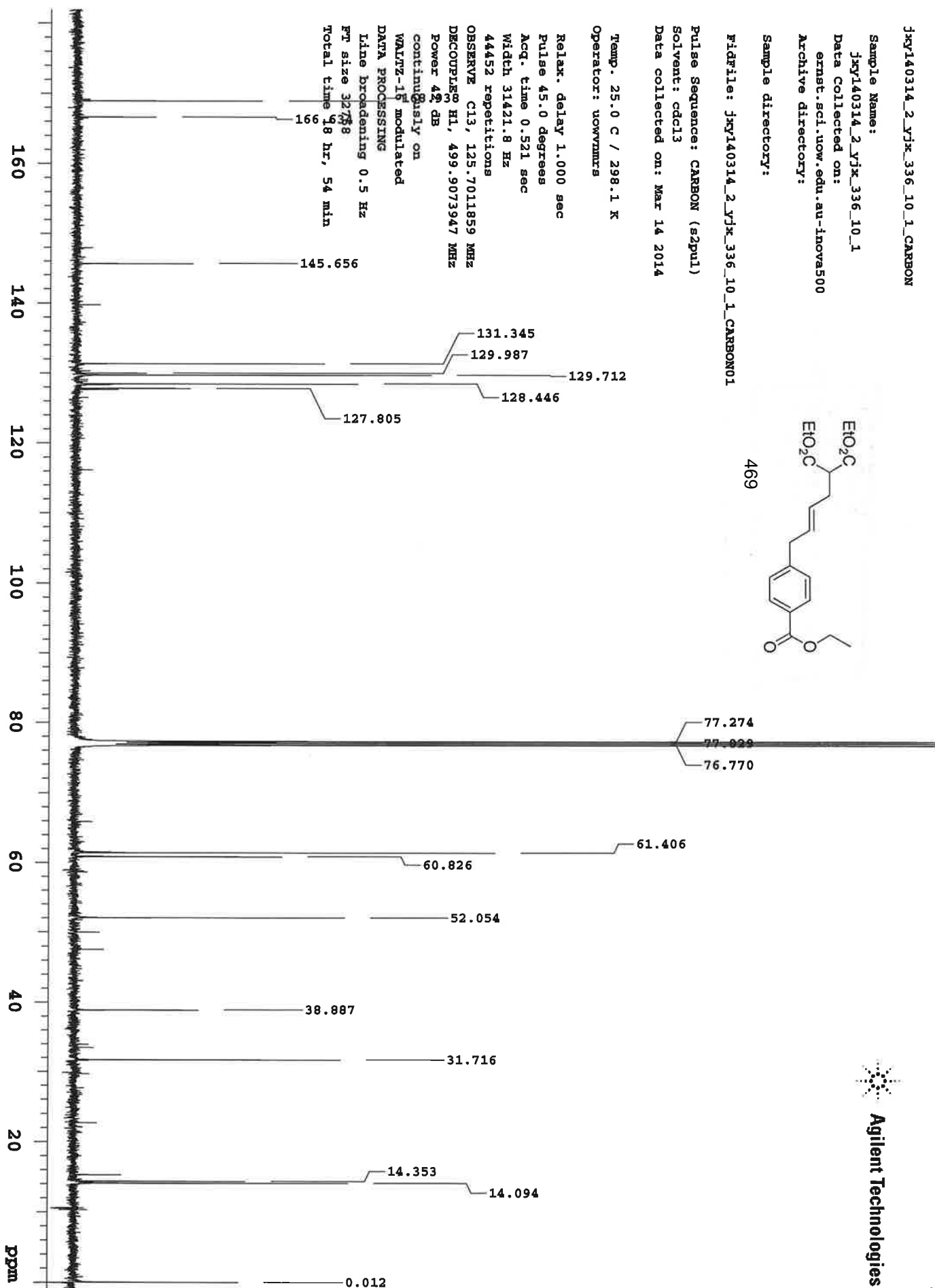
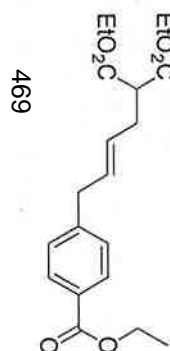
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 98 hr, 54 min



jxy140320_2.yjk_366_11_1_13c_CARBON

Sample Name:

jxy140320_2.yjk_366_11_1_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: jxy140320_2.yjk_366_11_1_13c_CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Mar 20 2014

Temp. 25.0 C / 298.1 K

Operator: ucwvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

2048 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

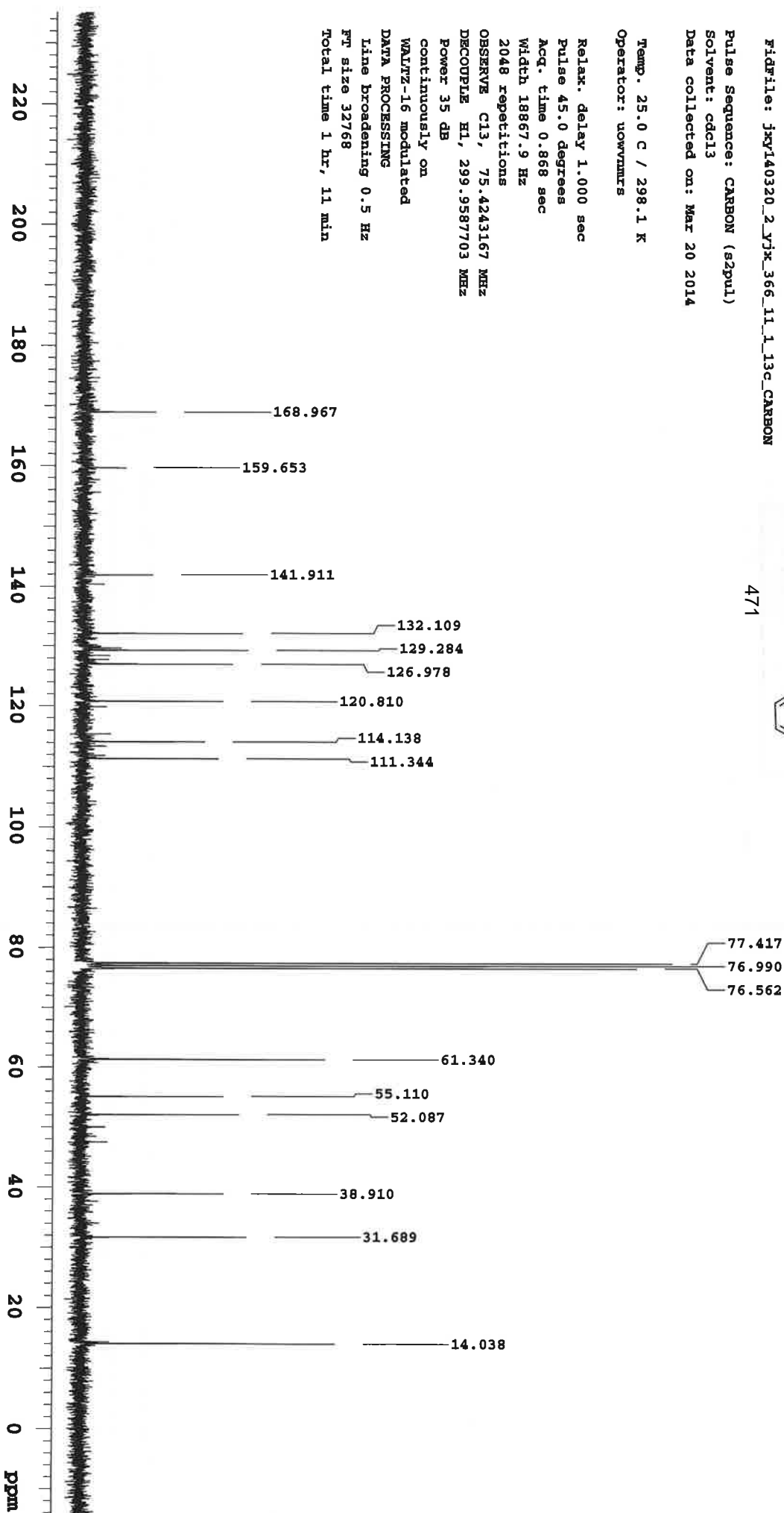
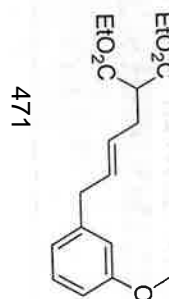
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 1 hr, 11 min



jxy140617_2_yjk_363_12_3_1_PROTON

exp1 PROTON

SAMPLE PRESATURATION

date Jun 17 2014 satmode n

solvent cdcl3 wet n

file /home/nowmr~ SPECIAL

s/jxy140617_2_yjk_~ temp 25.0

336_12_3_1_PROTON0~ gain not used

1.fid spin not used

ACQUISITION

sw 7998.4 pw90 0.008

at 2.048 alfa 10.100

np 32768 FLAGS 10.000

fb 4000 il n

bs 16 ln n

dl 1.000 dp y

nt 16 hs mn

ct 16 PROCESSING 0.50

tn TRANSMITTER H1 fb not used

sfreq 499.908 DISPLAY -107.9

tof 499.9 sp -107.9

tpwr 60 wp 4194.5

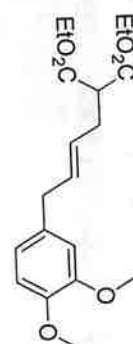
pw 10.100 rfi 1018.4

DECOUPLER C13 rf -89.5

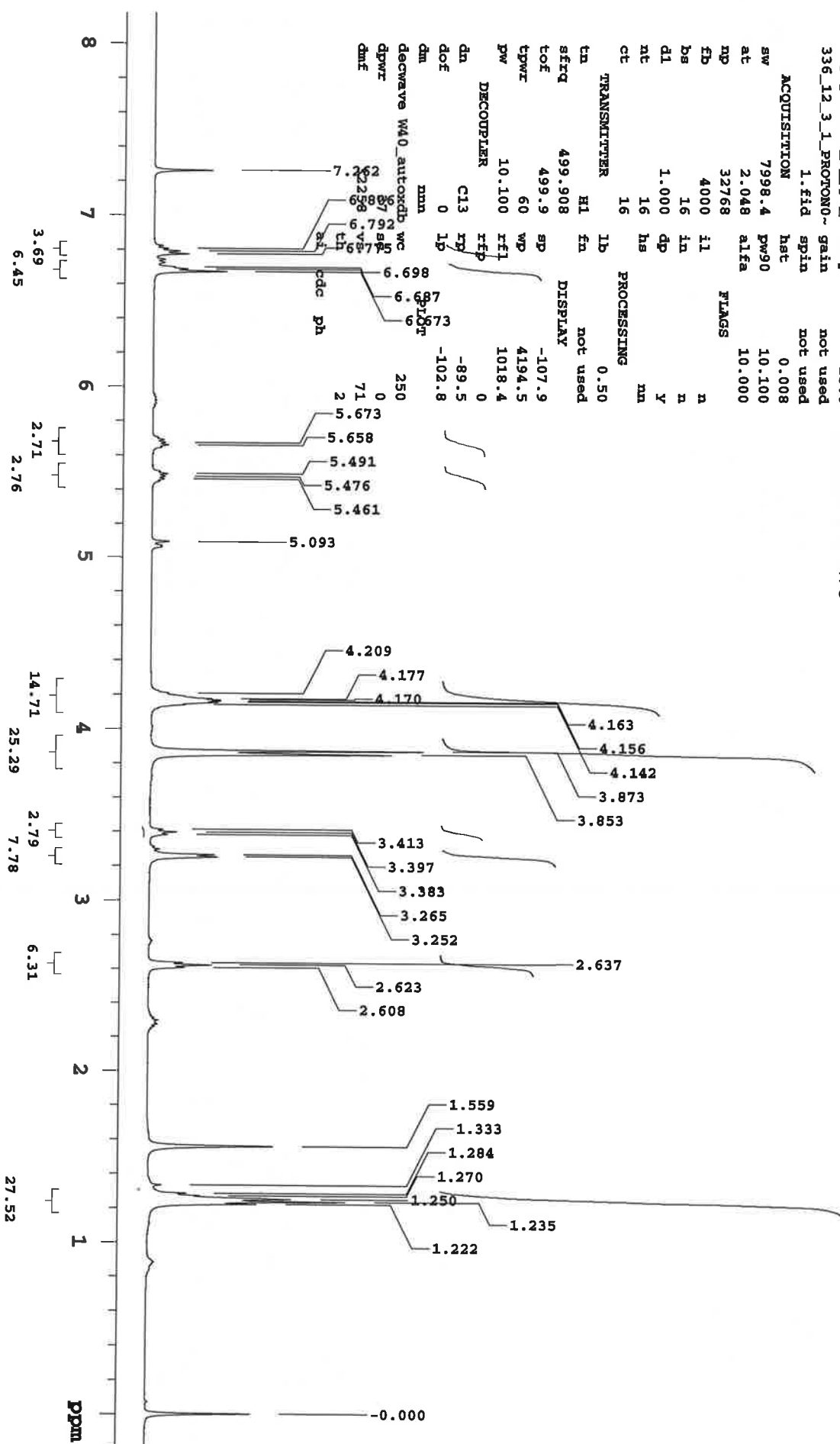
dn 0 lp -102.8

dm decouple W40_autocoupling

dmf



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jxy140315_2_yjk_336_12_1_13c-CARBON

Sample Name:

jxy140315_2_yjk_336_12_1_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: jxy140315_2_yjk_336_12_1_13c-CARBON

Pulse Sequence: CARBON (s2pul1)

Solvent: cdcl3

Data collected on: Mar 15 2014

Temp. 25.0 C / 298.1 K

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.043 sec

Width 31421.8 Hz

34496 repetitions

OBSERVE C13, 125.701869 MHz

DECOUPLE H1, 499.9073947 MHz

Power 42 dB

continuously on

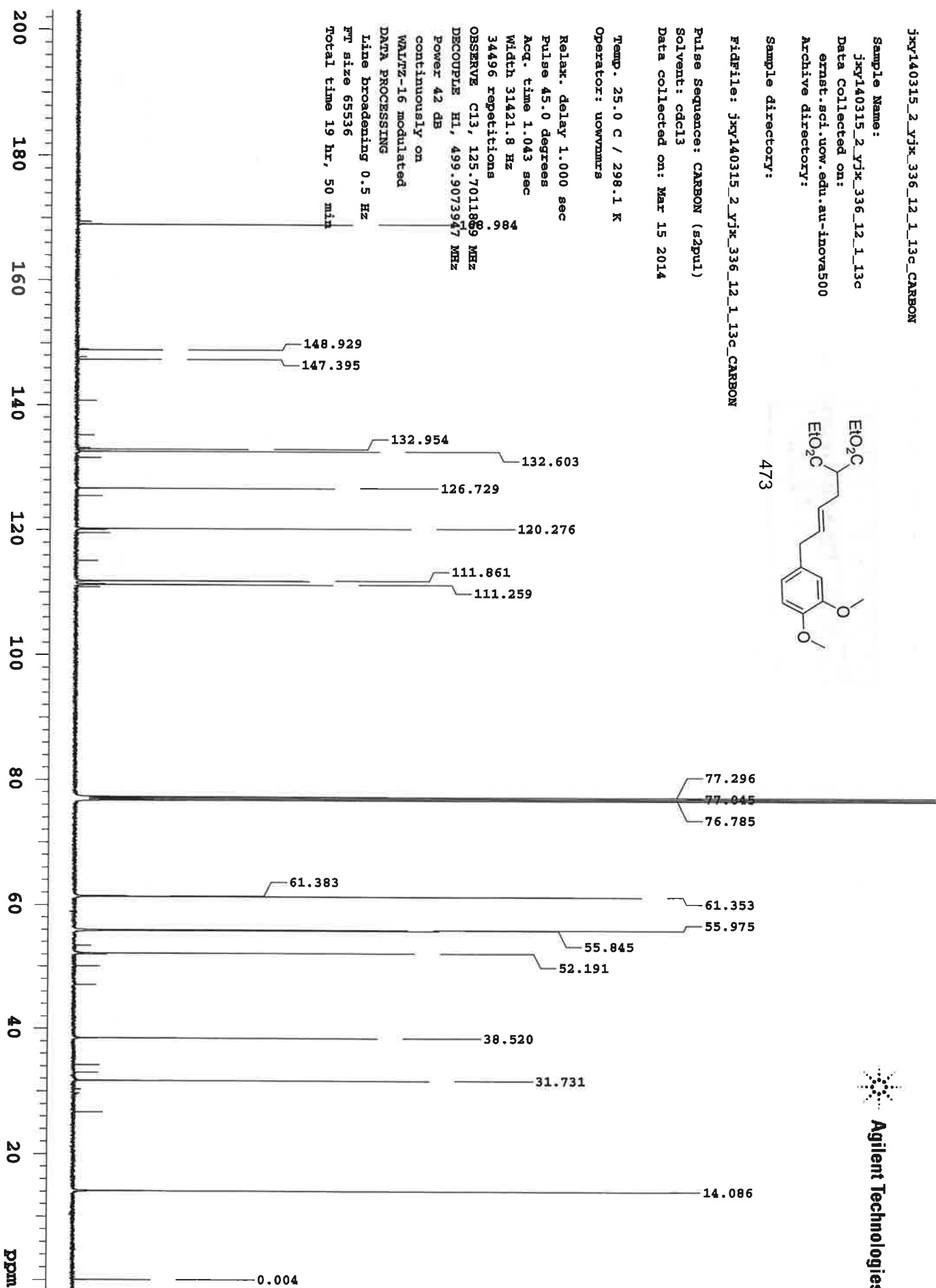
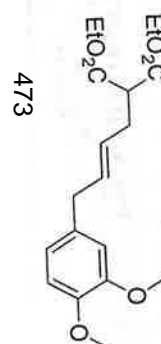
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

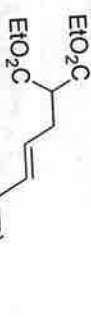
Total time 19 hr, 50 min



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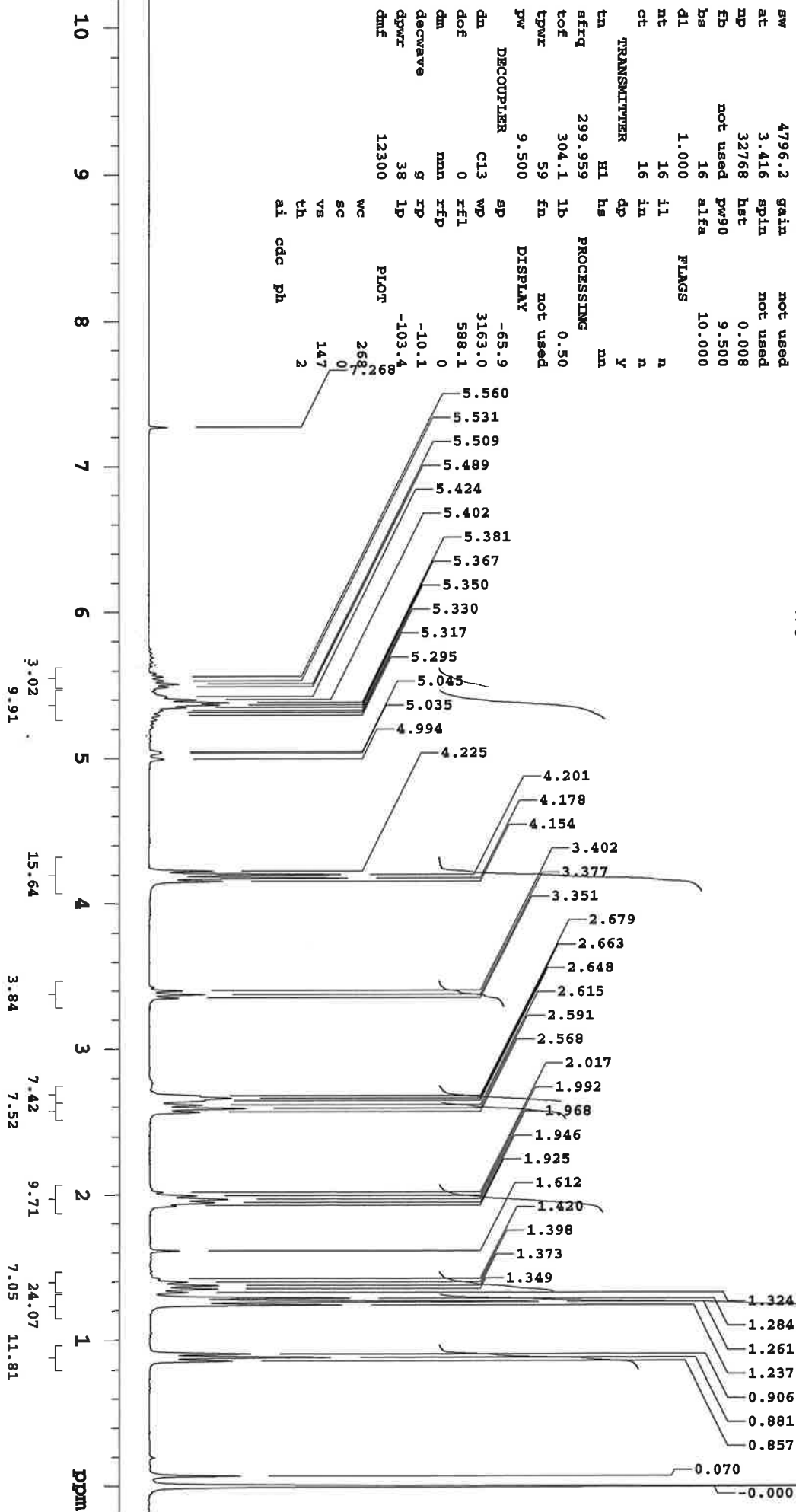
jxy140526_2.yjk_375_1_PROTON

exp1 PROTON



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SAMPLE		PRESATURATION	
date	May 26 2014	satmode	n
solvent	cdcl3	wet	n
file	exp	SPECIAL	n
ACQUISITION		temp	not used
sw	4796.2	gain	not used
at	3.416	spin	not used
np	32768	hst	0.008
fb	not used	pw90	9.500
bs	16	alfa	10.000
d1	1.000	FLAGS	
nt	16	il	n
ct	16	in	n
tn	H1	hs	nm
afreq	299.959	PROCESSING	
tof	304.1	lb	0.50
tpwr	59	fn	not used
pw	9.500	DISPLAY	
DECOUPLER		sp	-65.9
dn	C13	wp	3163.0
dof	0	rfl	588.1
dm	nm	rfp	0
decouple	g	rp	-10.1
dpr	38	lp	-103.4
dmf	12300	PLOT	
		wc	268.0
		sc	0
		vs	
		th	
		ai	cdc
		ph	



```
Sample Name:
jxy140526_2_vjx_375_1_13c
Data Collected on:
  bloch.sci.uow.edu.au-mercury300
Archive directory:
```

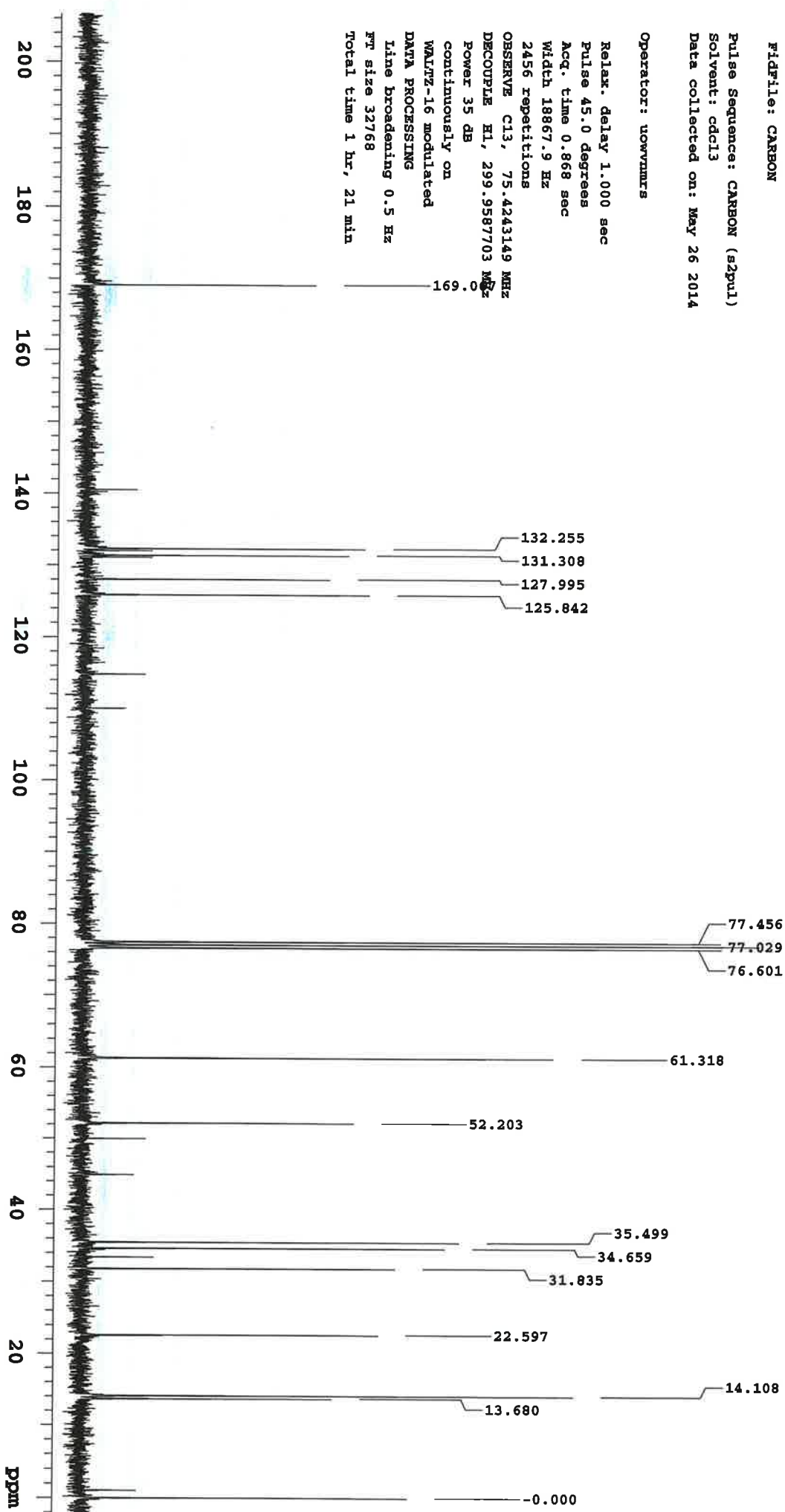
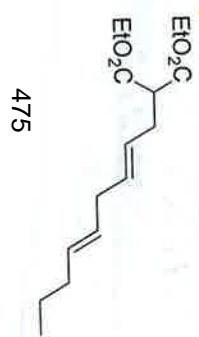
Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 26 2014

Operator: NOWYMIERS

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
2456 repetitions
OBSERVE C13, 75.4243149 MHz
DECUPLE H1, 299.9587703 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 1 hr, 21 min



yjk140429_2.yjk_354_1_PROTON

Sample Name:

yjk140429_2.yjk_354_1

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

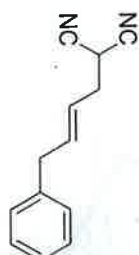
Sample directory:

FIDFile: PROTON

Pulse Sequence: PROTON (s2pul1)

Solvent: cdcl3

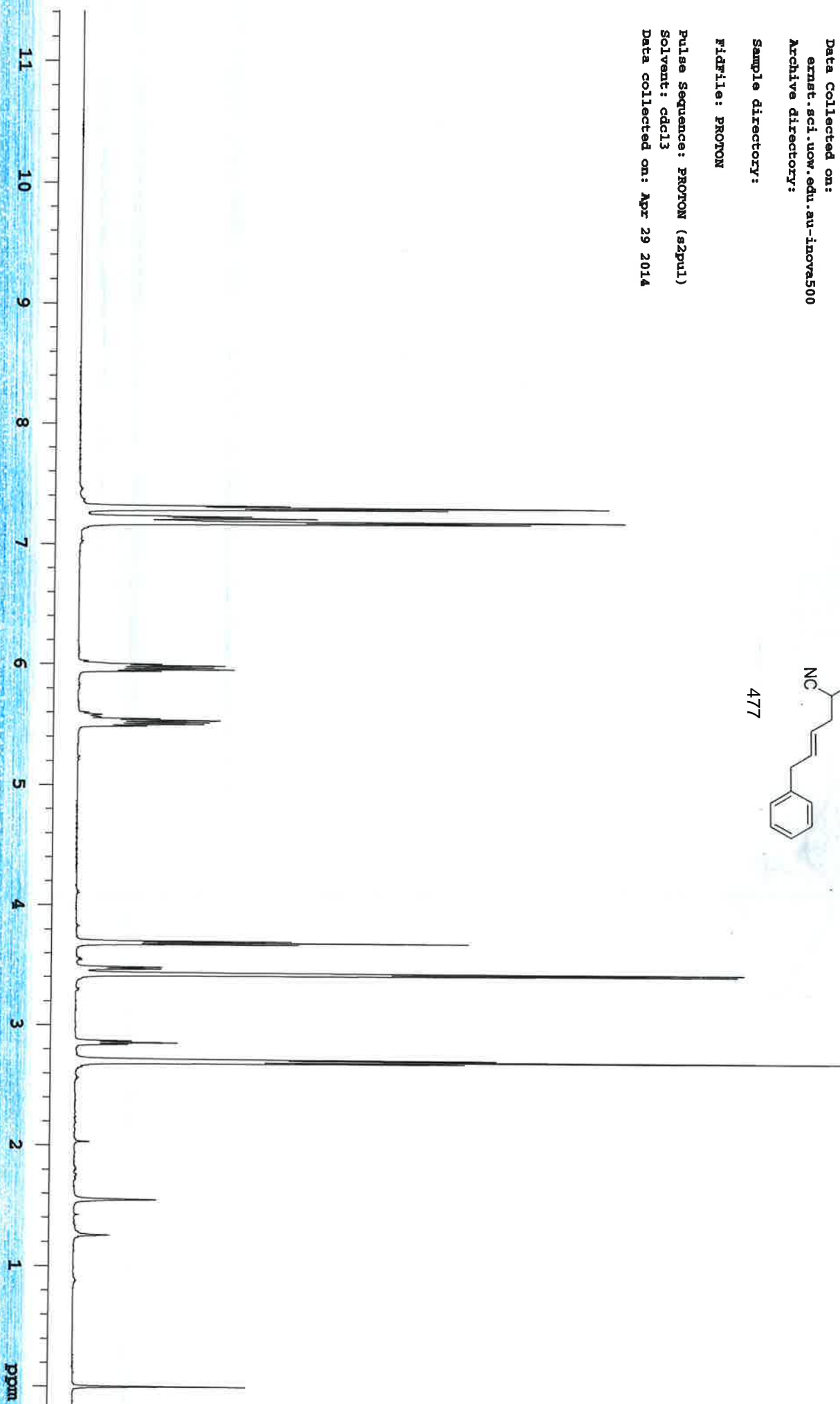
Data collected on: Apr 29 2014



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jxy140429_2_yjk_354_2_CARBON

Sample Name:

jxy140429_2_yjk_354_2

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: jxy140429_2_yjk_354_2_CARBON

Pulse Sequence: CARBON (szpul)

Solvent: cdc13

Data collected on: Apr 29 2014

Temp. 25.0 C / 298.1 K

Operator: uowymms

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.521 sec

Width 31421.8 Hz

1920 repetitions

OBSERVE C13, 125.701859 MHz

DECOUPLE H1, 499.9073947 MHz

Power 42 dB

continuously on

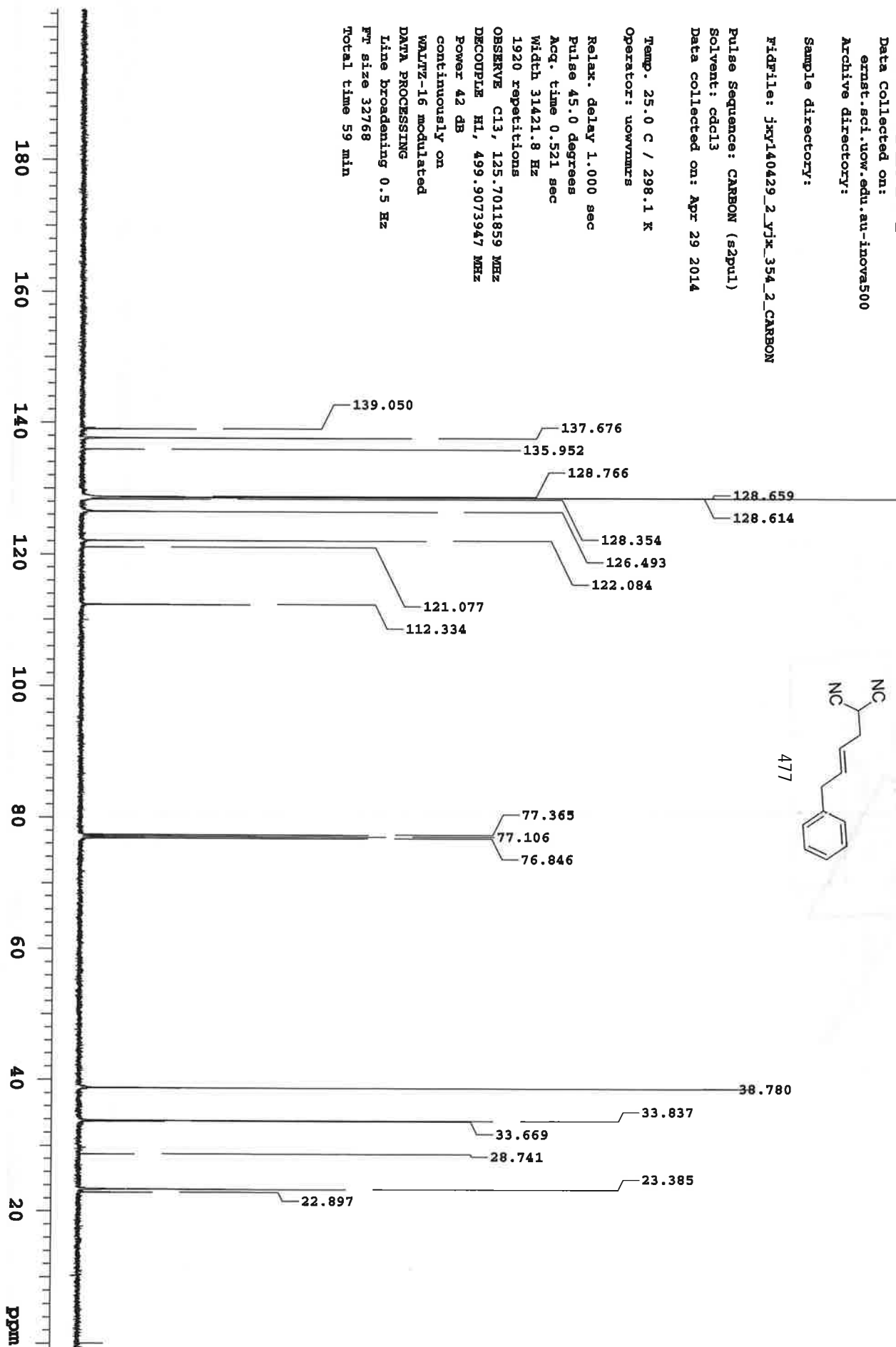
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

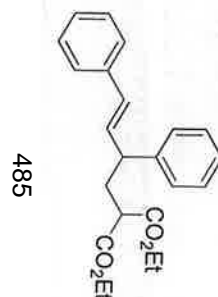
FT size 32768

Total time 59 min

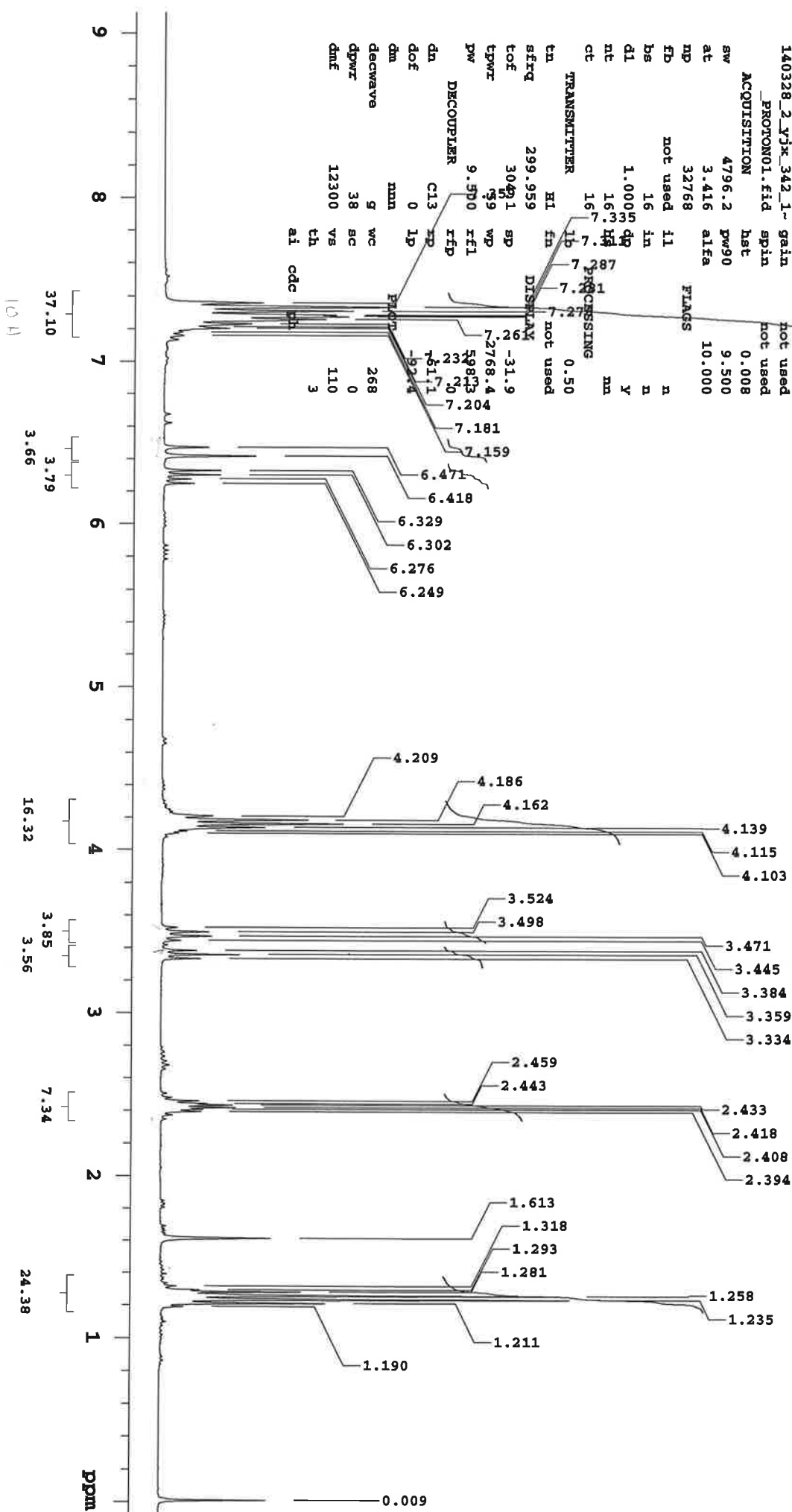


jxy140328_2.yjk_342_1_PROTON

exp7 PROTON



SAMPLE PREPARATION
 date Mar 28 2014 satmode n
 solvent cdc13 wet n
 file /home/ucvnmr- s/bup_1403misc/jxy- temp 25.0
 140328_2.yjk_342_1- gain not used
 _PROTON01.fid spin not used
 ACQUISITION hat 0.008
 sw 4796.2 pw90 9.500
 at 3.416 alfa 10.000
 np 32768
 fb not used 11 n
 bs 16 in n
 dl 1.0000 dp 87 y
 nt 16.744 87 nm
 ct 16.744 87
 TRANSMITTER H1 fn 0.50
 tn 299.959 H1 fn not used
 sfrq 30491 SP 31.9
 tof 99 WP 72768.4
 tpwr 9.590 rfl 59813.0
 pw 9.590 rfd 7.204
 DECOUPLER C13 1p 7.181
 dn 0 1p 7.159
 dof 0 1p 6.471
 dm nm 6.418
 decwa ve 268
 dpr 38 ac 0
 dmf 12300 vs 110
 ai cdc ph 3



jxy140328_2_vjk_342_1_13c-CARBON

Sample Name:

jxy140328_2_vjk_342_1_13c

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Mar 28 2014

Temp. 25.0 C / 298.1 K

Operator: uowmms

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.868 sec

Width 18867.9 Hz

1312 repetitions

OBSERVE C13, 75.4243167 MHz

DECOUPLE H1, 299.9587703 MHz

Power 35 dB

continuously on

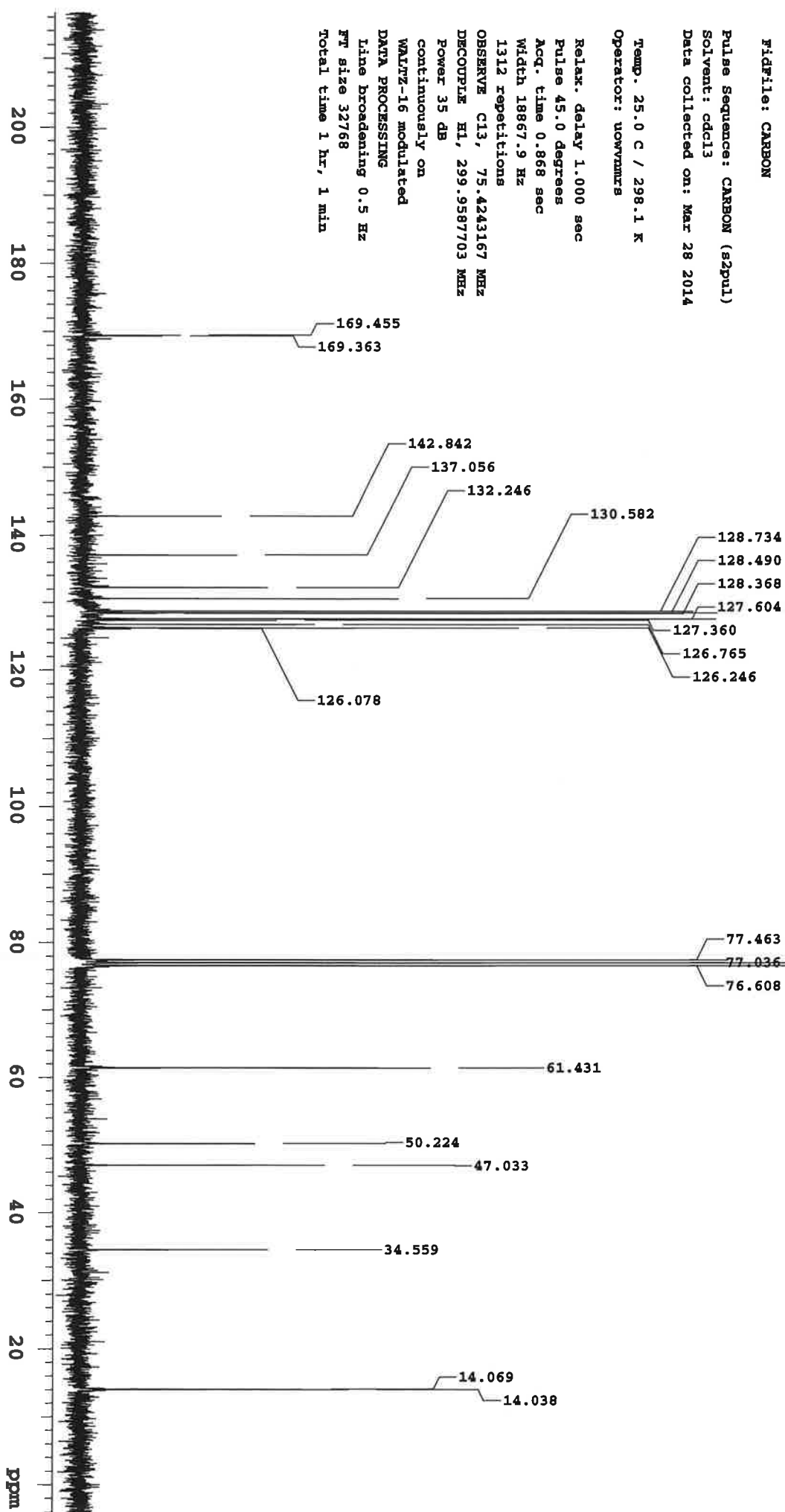
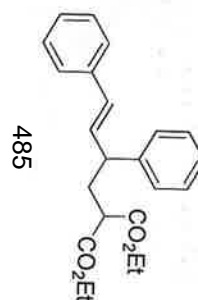
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 1 hr, 1 min



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jxy140328_2_vjk_342_1_gCOSY

Sample Name:

jxy140328_2_vjk_342_1

Data Collected on:

bloch.sei.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: jxy140328_2_vjk_342_1_gCOSY01

Pulse Sequence: gCOSY

Solvent: cdcl3

Data collected on: Mar 28 2014

Temp. 25.0 C / 298.1 K

Operator: uownmrs

Relax. delay 1.000 sec

Acq. time 0.213 sec

Width 4807.7 Hz

2D Width 4807.7 Hz

8 repetitions

250 increments

OBSERVE H1, 299.9572747 MHz

DATA PROCESSING

Line broadening 3.0 Hz

Sq. sine bell 0.106 sec

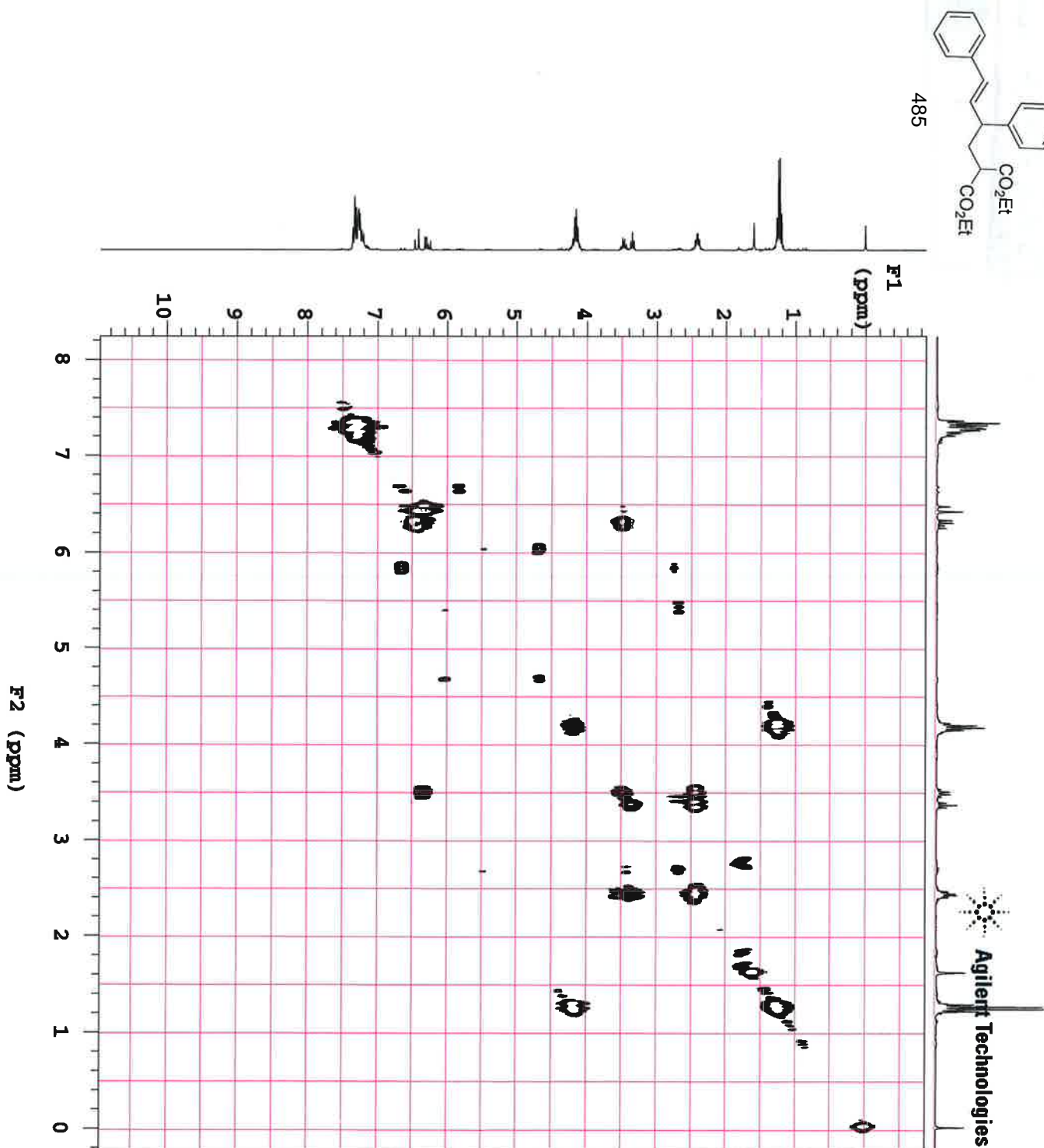
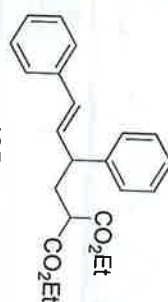
F1 DATA PROCESSING

Line broadening 3.0 Hz

Sq. sine bell 0.027 sec

FT size 2048 x 1024

Total time 45 min



jxy140403_2.yjk_343_2_1_13c CARBON

Sample Name:

jxy140403_2.yjk_343_2_1_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

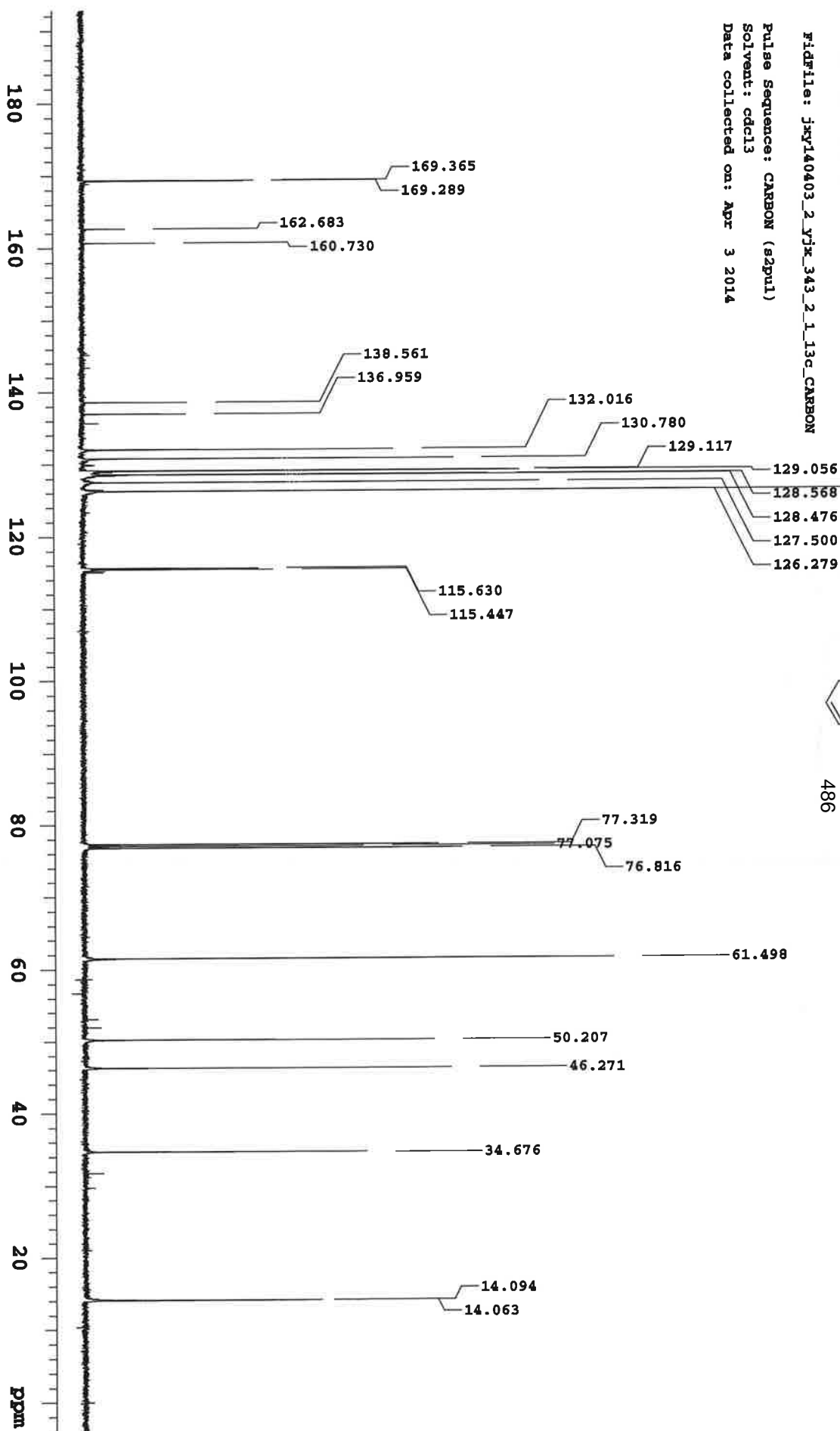
Sample directory:

Filename: jxy140403_2.yjk_343_2_1_13c CARBON

Pulse Sequence: CARBON (s2pu1)

Solvent: cdcl3

Data collected on: Apr 3 2014



expi Proton

SAMPLE SPECIAL

date Apr 5 2014 temp 25.0

solvent cdc13 gain 56

file exp hst not used

ACQUISITION exp spin 0.008

sw 8012.8 pw90 12.825

at 2.045 alfa 6.600

np 32768 flags

fb 4000 i1 n

bs 16 in y

dl 1.000 dp v

nt 16 hs nm

ct 16

TRANSMITTER H1 f1

tn 499.744 fn

stf 499.6 sp

tof 62 wp

tpwr 12.825 rfp

pw DECOUPLER C13 tp

dn 0

dof 0

dm mn

dmm c

dpwr 47

dmf 22200

at th

cds ph

PLDT

WC 250

SC 0

VS 99

TH 4

DISP

-126.4

4675.9

1007.0

6.8

-44.4

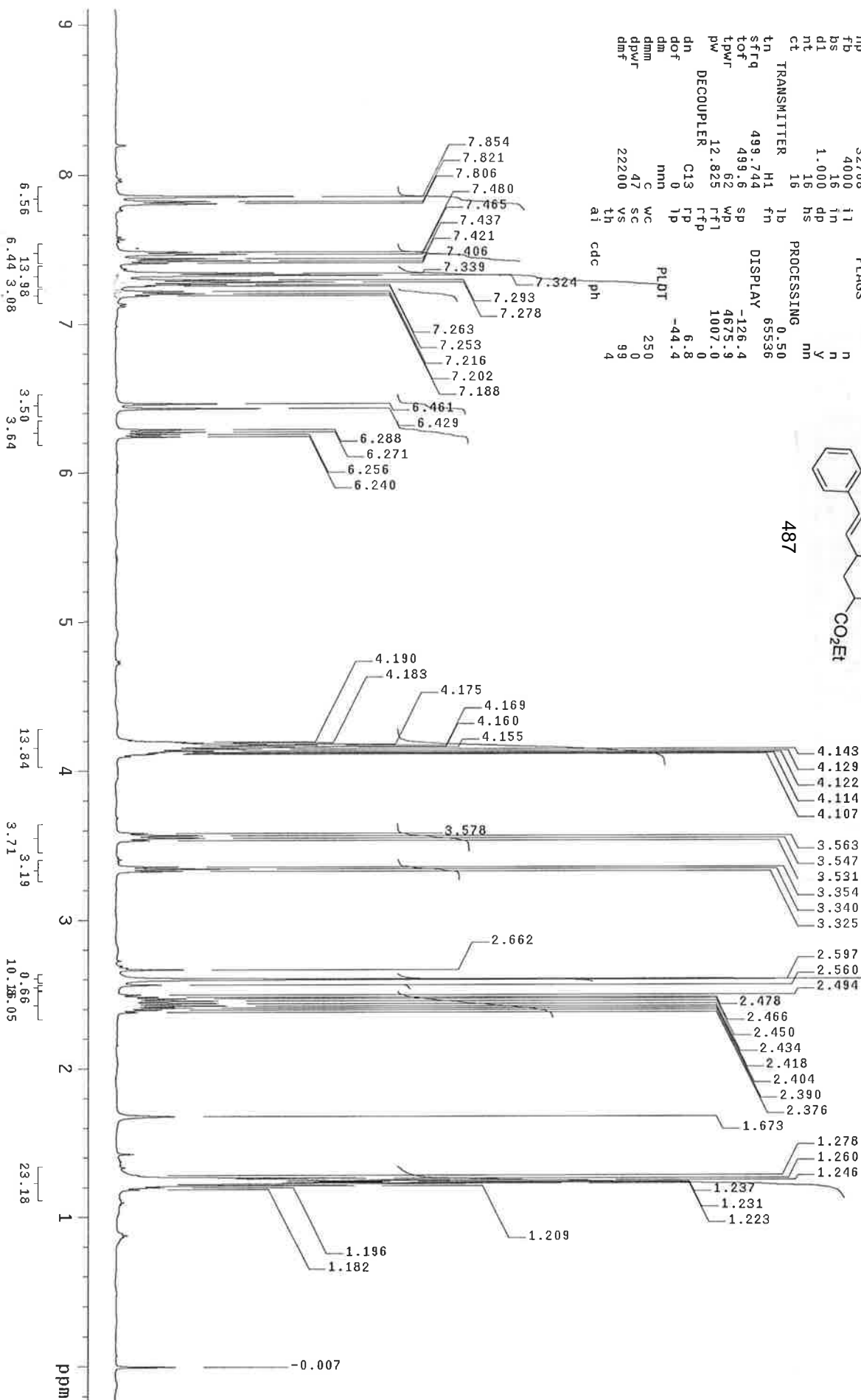
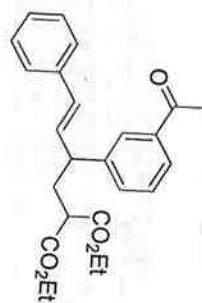
65536

0.50

PROCESSING

nm

487



File: Carbon

Pulse Sequence: s2pu1

Solvent: cdc13

Temp. 25.0 C / 298.1 K

Operator: uowvmms

VNMR5-500 "pyne06.domain.com"

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 0.537 sec

Width 30487.8 Hz

2236 Repetitions

OBSERVE C13, 125.6600437 MHz

DECUPLE H1, 499.7438937 MHz

Power 45 dB

continuously on

WALTZ-16 modulated

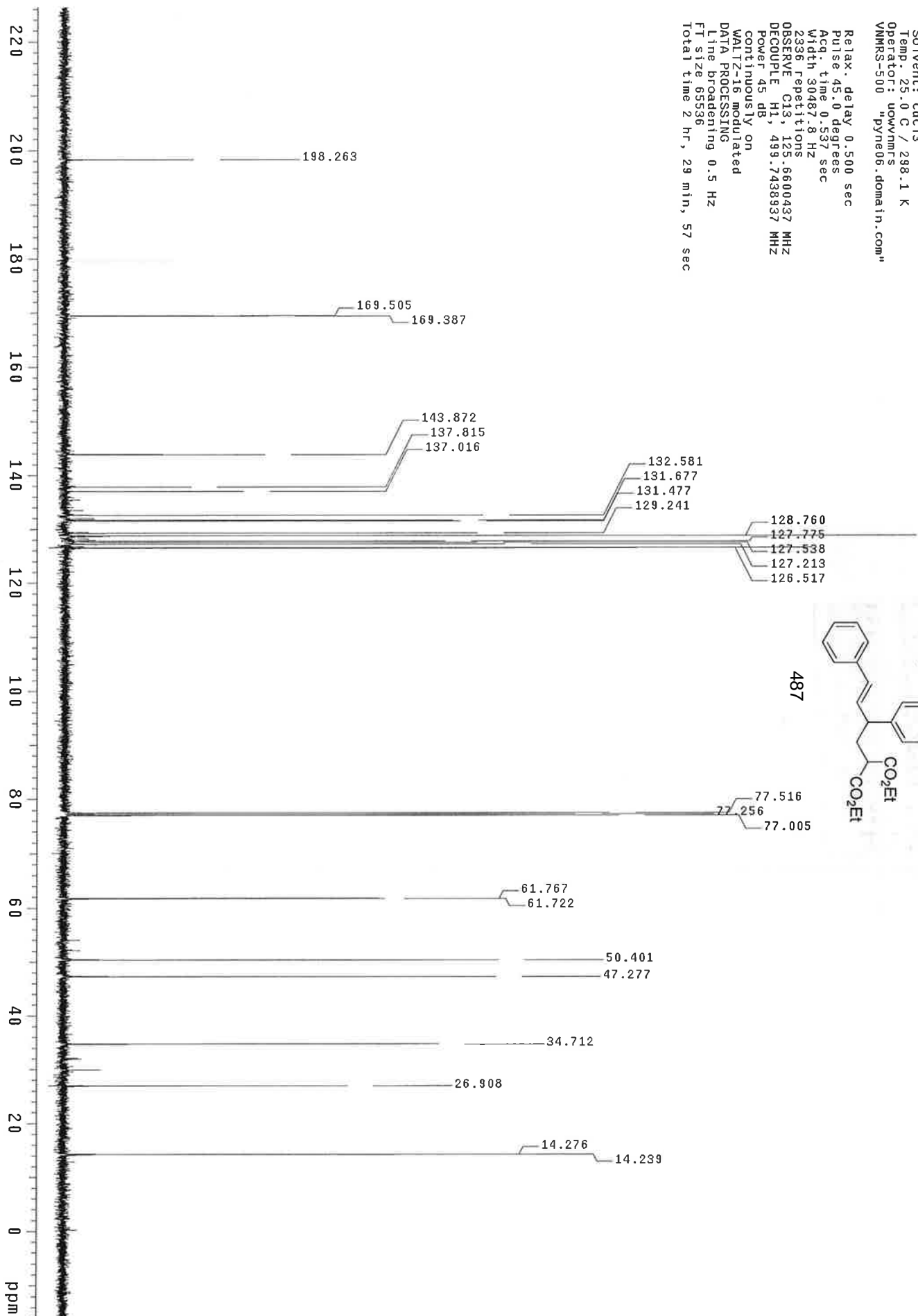
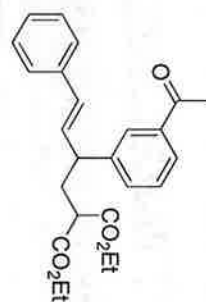
DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 2 hr, 29 min, 57 sec

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jxy140403_2_yjk_343_3_1_PROTON

exp1 PROTON

SAMPLE
date Apr 3 2014
solvent cdcl3
file exp

PRESATURATION
satmode n
wet n
SPECIAL

ACQUISITION
sw 4796.2
at 3.416
np 32768
fb not used
bs 16
dl 1.000
nt 16
ct 16

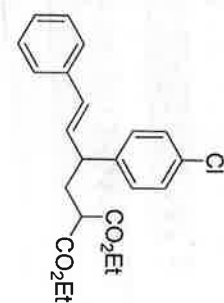
TRANSMITTER
tn H1
sfreq 299.959
tof 304.1
tpwr 59
pw 9.500

DECOUPLER
da 14
dof 13
dm 7
decwave 0
dpr 38
dmf 12300

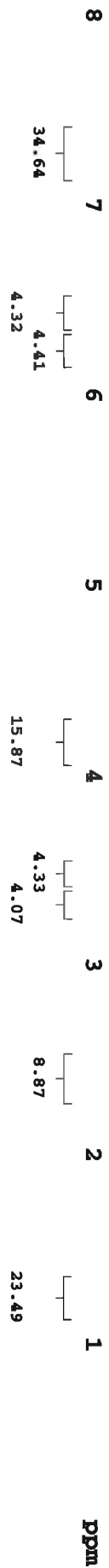
PROCESSING
0.50
not used
nm
7.181

DISPLAY
-63.2
2723.9
596.6
-59.3
-94.0
268
0
282
5

WATER
WC
SC
VS
TH
AI
PH



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jxy140405_2_yjk_343_3_1_13c-CARBON

Sample Name:

jxy140405_2_yjk_343_3_1_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

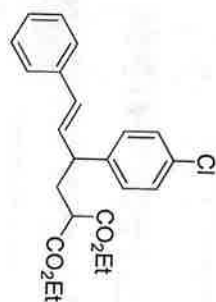
Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul1)

Solvent: cdcl3

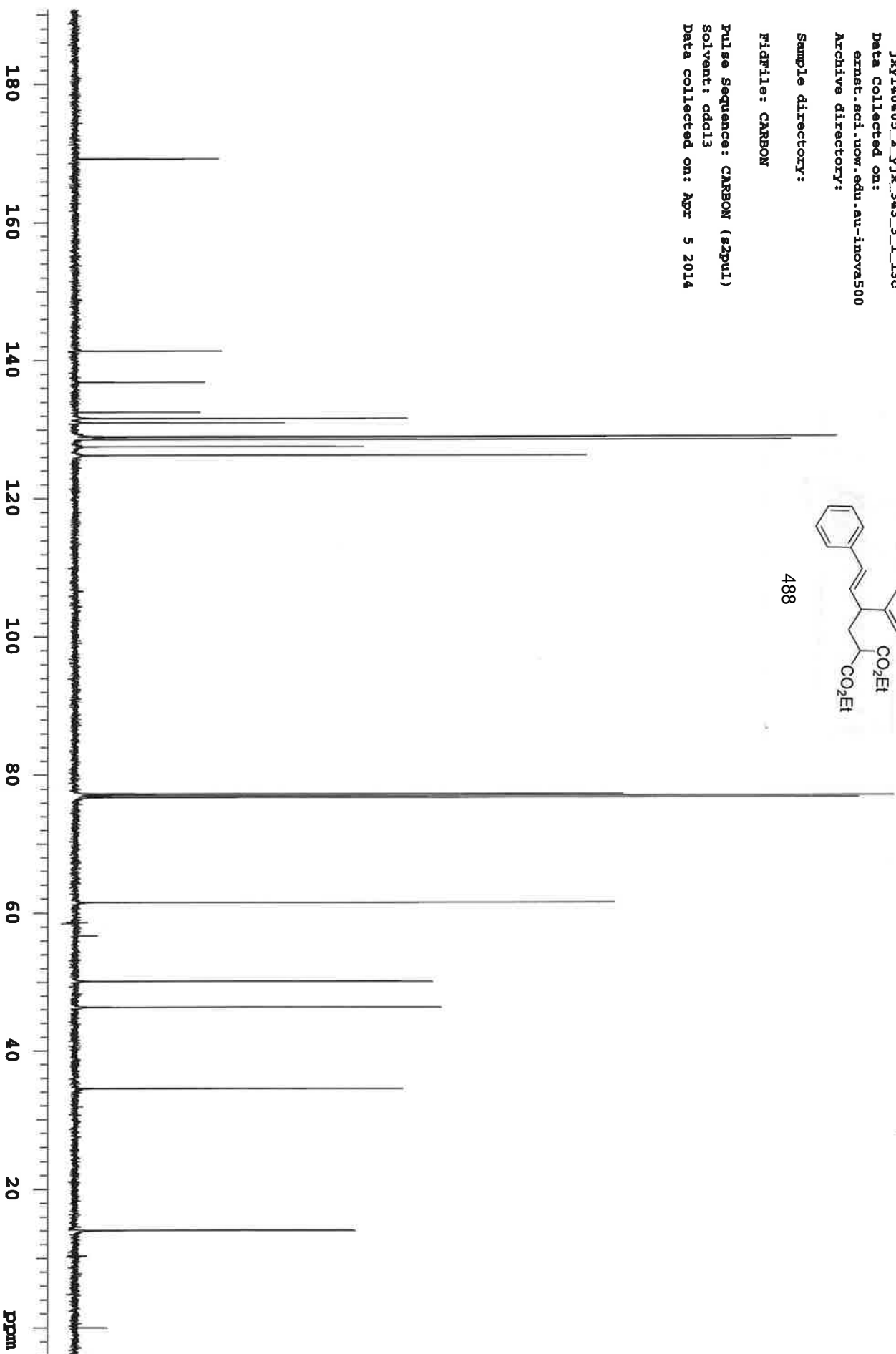
Data collected on: Apr 5 2014



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Agilent Technologies



jxy140405_2_vjk_343_4_1_PROTON

Sample Name:

jxy140405_2_vjk_343_4_1

Data collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

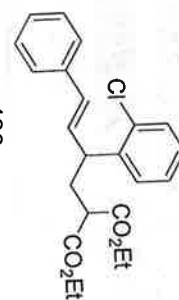
Sample directory:

Fidfile: PROTON

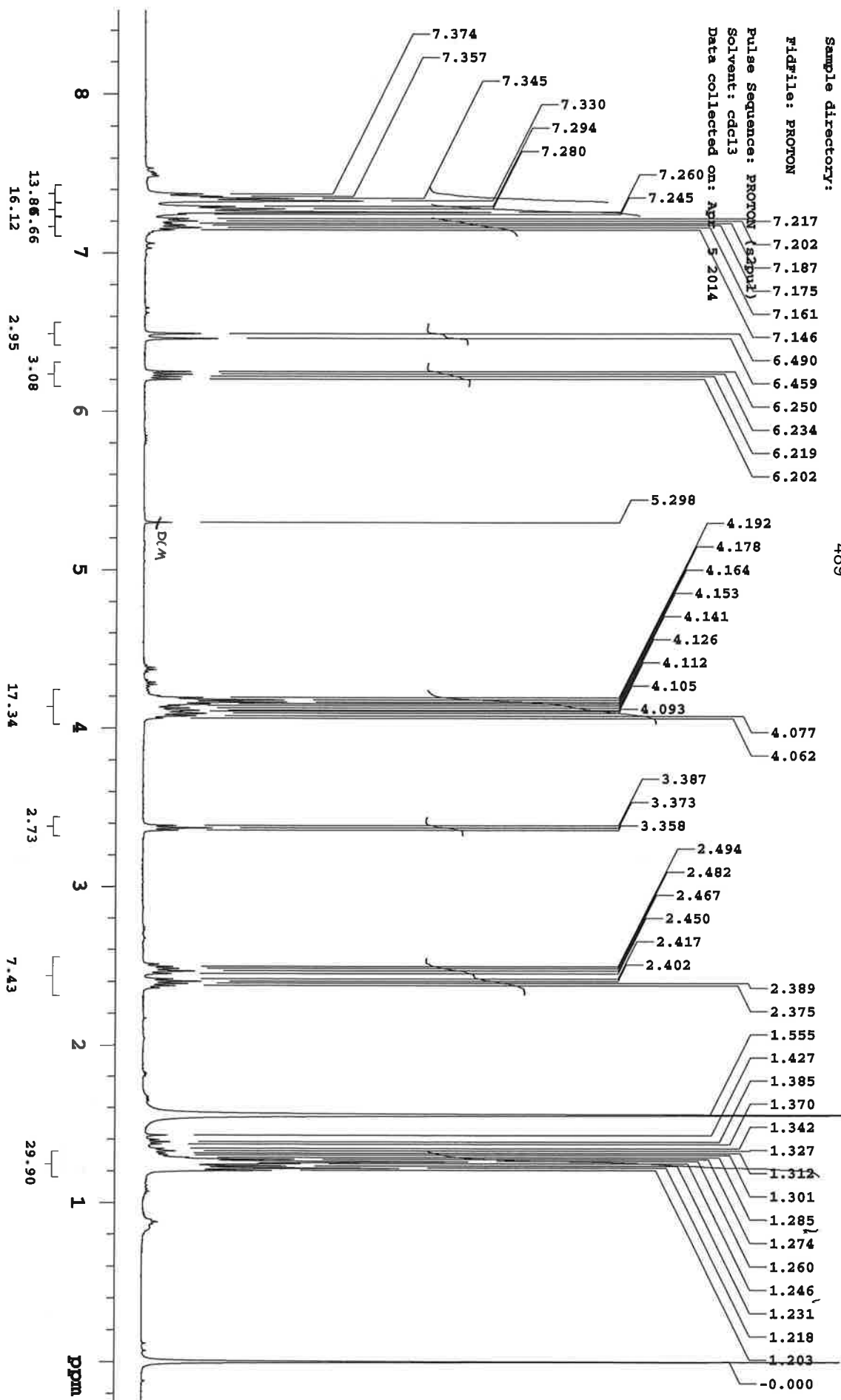
Pulse Sequence: PROTON (g2puz)

Solvent: cdcl3

Data collected on: Apr 5 2014



Agilent Technologies



jxy140405_2-yjk_343_4_1_13c-CARBON

Sample Name:

jxy140405_2-yjk_343_4_1_13c

Data Collected on:

ernst.sci.ucw.edu.au-inova500

Archive directory:

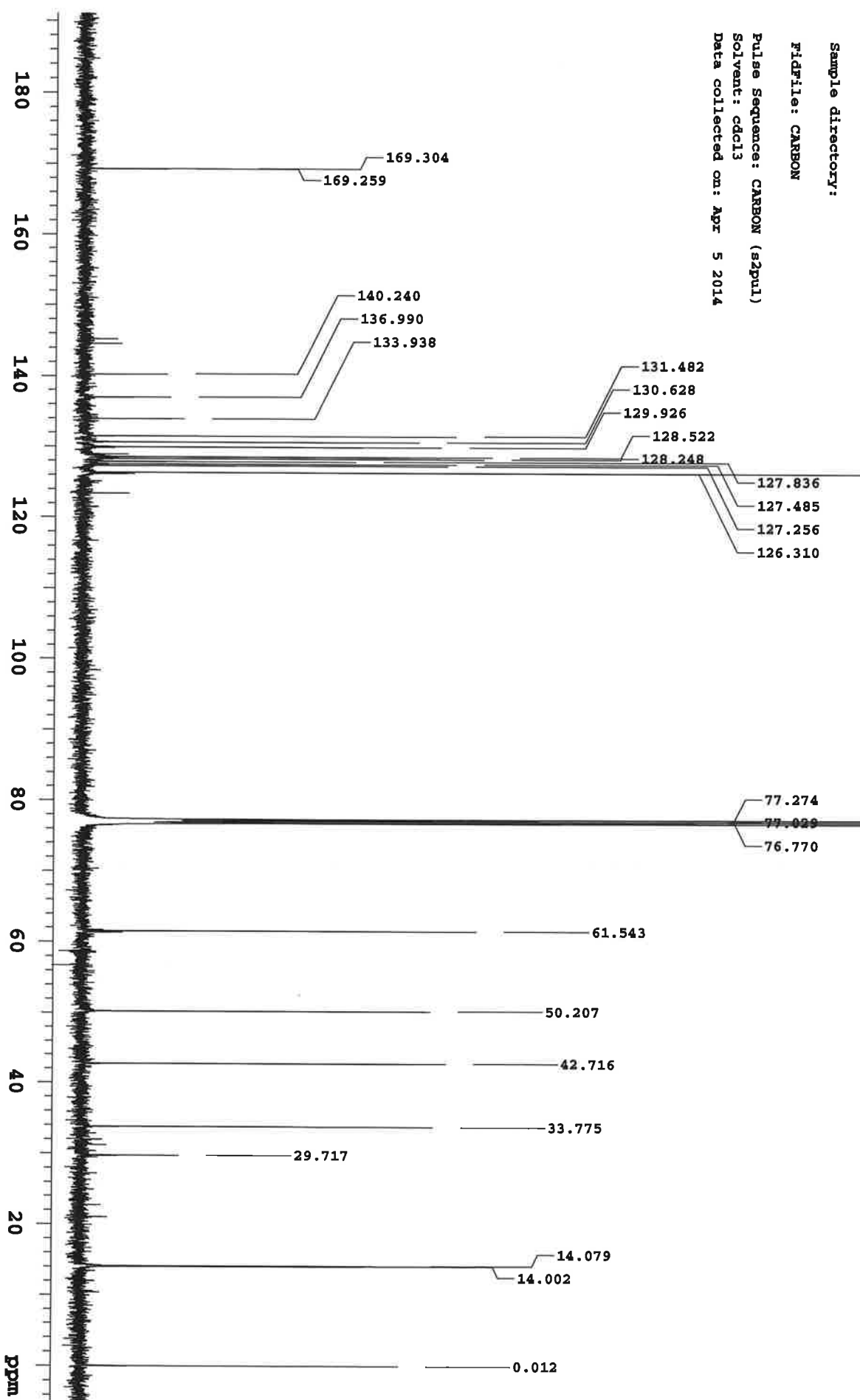
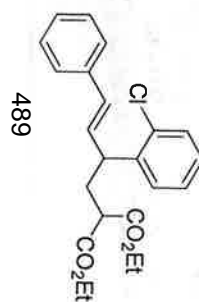
Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Apr 5 2014



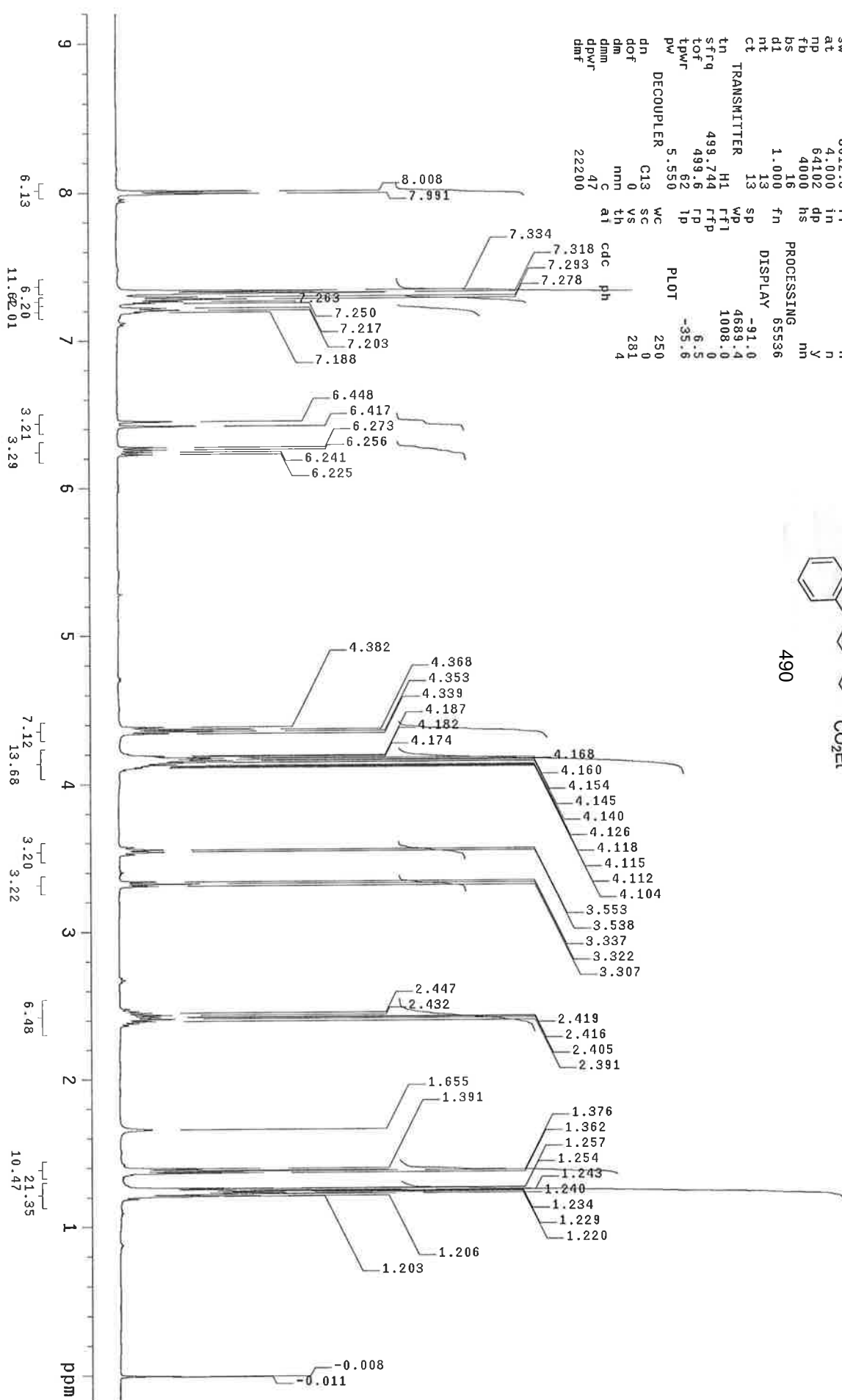
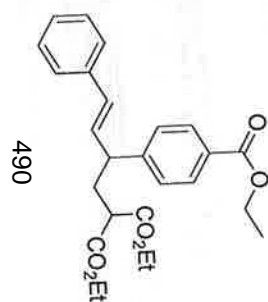
Agilent Technologies

jxy140405_2_yjx_343_8_1-Proton
exp7 Proton

SAMPLE		SPECIAL	
date	Apr 5 2014	temp	25.0
solvent	cdcl3	gain	not used
file	/home/uowvnmr/~sp1n	not used	not used
2/jxy140405_2_yjx_~	hst	0.008	0.008
343_8_1-Proton01.f~	pw90	11.100	11.100
	id	6.600	6.600
	atfa		

ACQUISITION		PROCESSING	
sw	8012.8	in	n
at	4.000	dp	y
np	64102	hs	nm
fb	4000		
bs	16		
d1	1.000	fn	65536
nt	13		
ct	13	sp	-91.0
tn	TRANSMITTER	wp	4689.4
stfrq	499.744	rfl	1008.0
tofr	499.6	rfp	6.5
tpwr	62	tp	-35.6
pw	5.550		

DECOUPLER		PLOT	
dn	C13	sc	250
dof	0	vs	0
dm	nm	th	281
dmm	47		4
dpwr	22200		



File: Carbon

Pulse Sequence: s2pul1

Solvent: cdcl3

Temp: 25.0 C / 298.1 K

Operator: uowvmr's

VMRS-500 "pyne06.domain.com"

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 0.537 sec

Width 30487.8 Hz

3456 repetitions

OBSERVE C13, 125.6600437 MHz

DECOUPLE H1, 499.7438937 MHz

Power 45 dB

continuously on

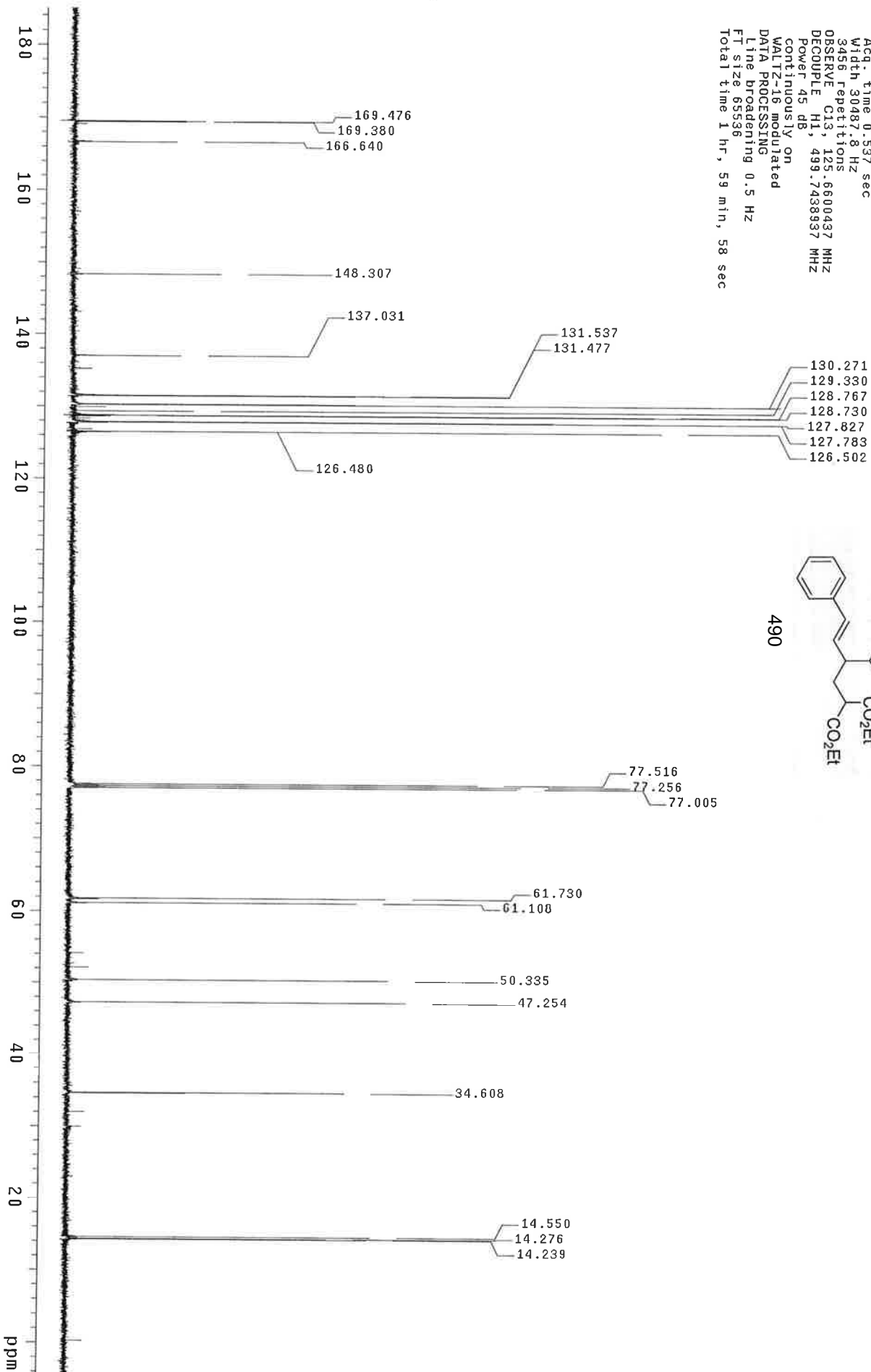
WALTZ-16 modulated

DATA PROCESSING

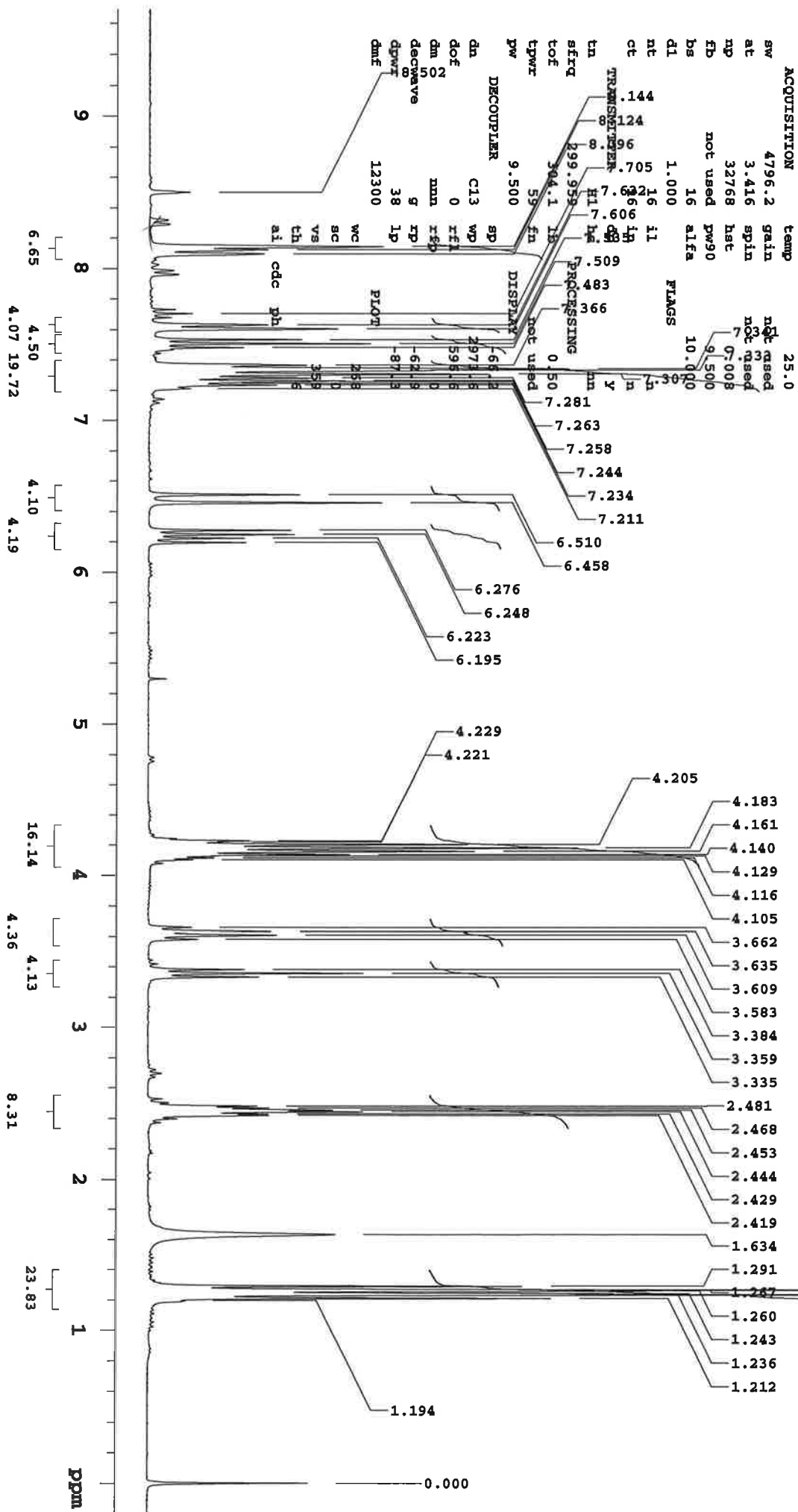
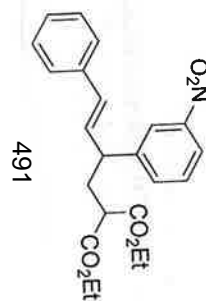
Line broadening 0.5 Hz

FT size 65536

Total time 1 hr, 59 min, 58 sec



SAMPLE		PRESATURATION	
date	Apr 3 2014	satmode	
solvent	cdcl3	wet	
file	exp	SPECIAL	



jxy140403_2_yjk_343_1_13c_CARBON

Sample Name:
jxy140403_2_yjk_343_1_13c
Data Collected on:
bloch.sci.nov.edu.au-mercury300
Archive directory:

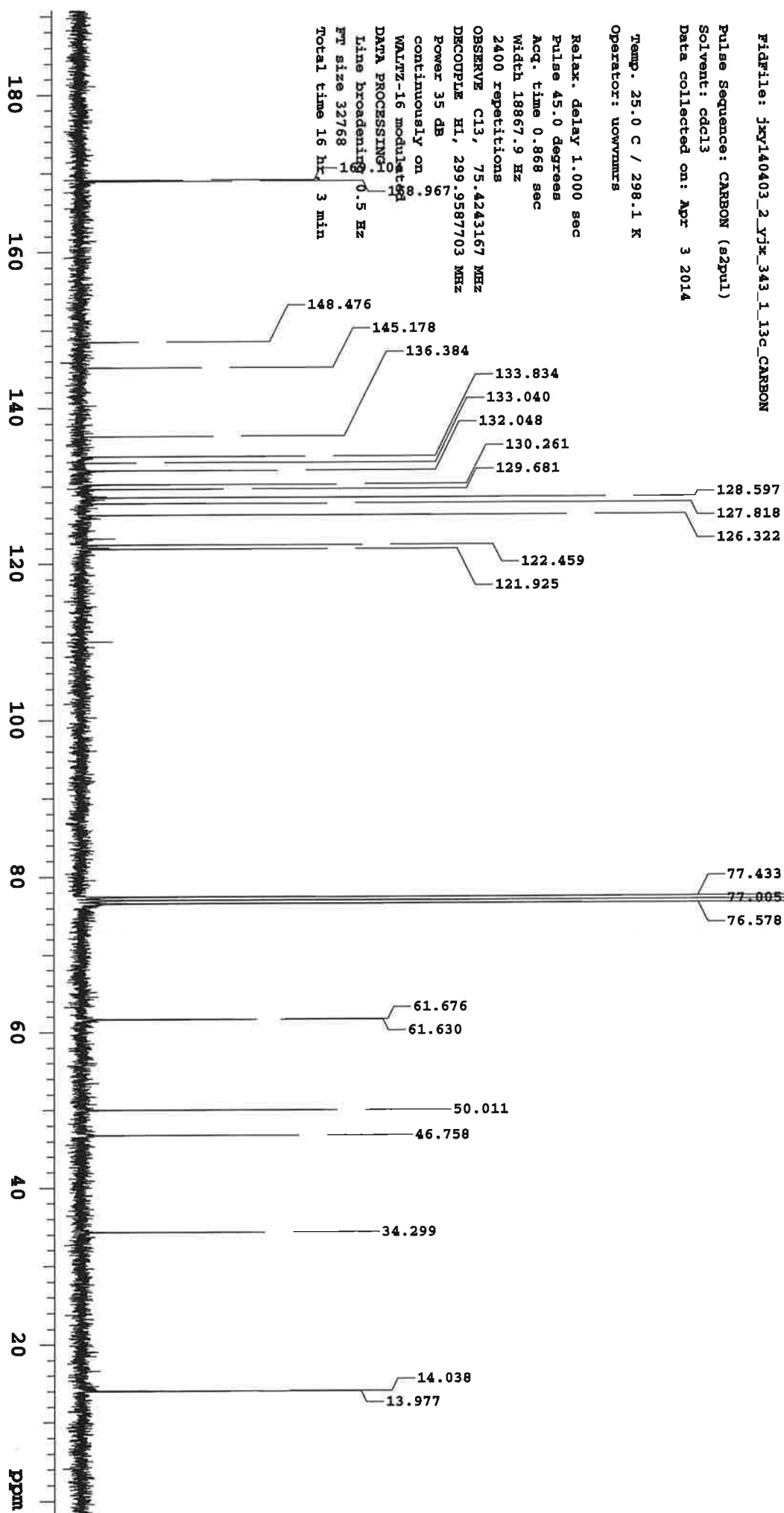
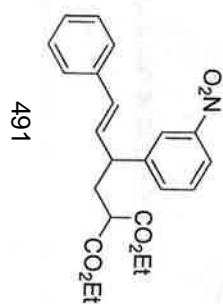
Sample directory:

Fidfile: jxy140403_2_yjk_343_1_13c_CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 3 2014

Temp. 25.0 C / 298.1 K
Operator: uovnmrs

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
2400 repetitions
OBSERVE C13, 75.4243167 MHz
DECOUPLE H1, 299.9587703 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 16 hr, 3 min



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jxy140405_2.yjk_343_7_1_13c CARBON

Sample Name:

jxy140405_2.yjk_343_7_1_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

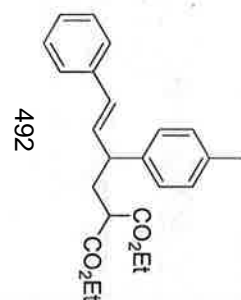
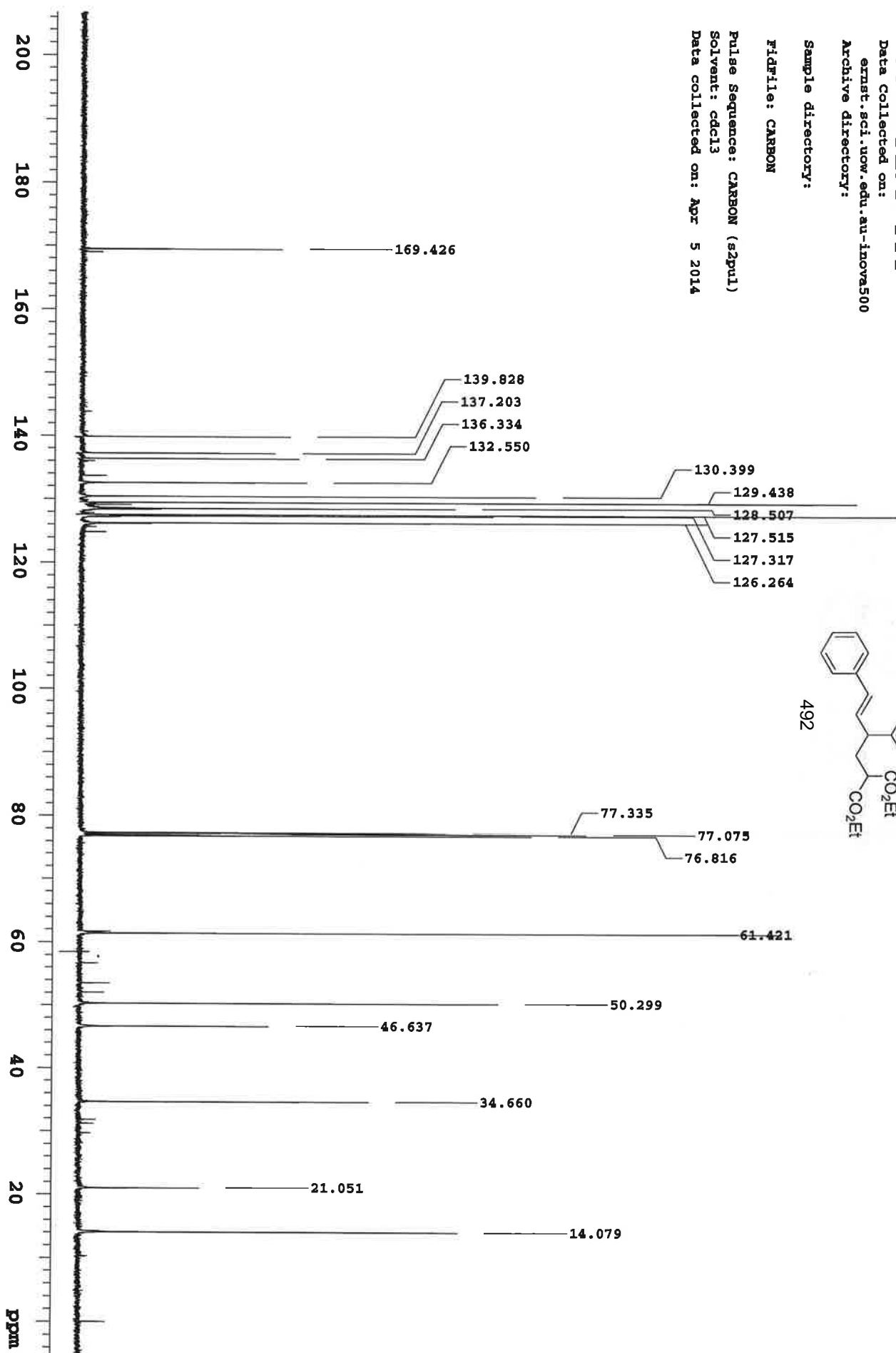
Sample directory:

File: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Apr 5 2014



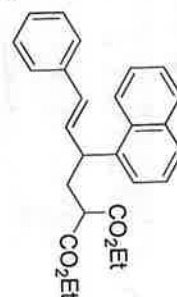
jxy140405_2_yjk_343_5_1_PROTON

exp1 PROTON

SAMPLE PREPARATION

date Apr 5 2014 satmode n
solvent cdc13 wet n
file /home/ucvnmr- s/jxy140405_2_yjk_ temp 25.0
343_5_1_PROTON01.f gain not used

493



ACQUISITION

sw 4796.2 pw90 9.500
at 3.416 alfa 10.000
np 32768
fb not used il n
bs 16 in n
dl 1.000 dp y
nt 16 hs n
ct 16

PROCESSING

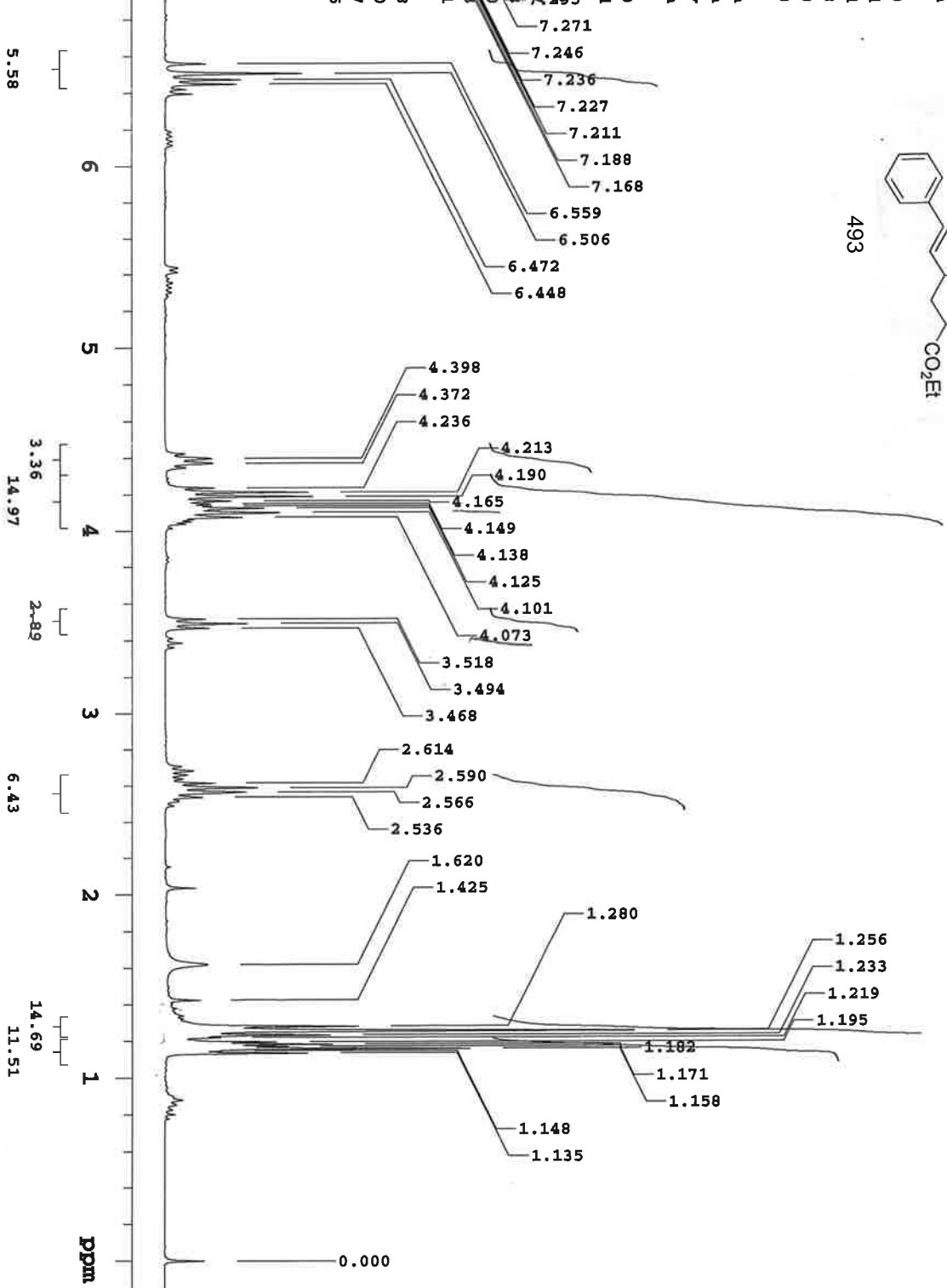
0.50
430
not used

TRANSMITTER

tn H1
sfreq 299.959
to 304.1
tpwr 0
pwr 0
decouple 0
dmf 0

dm 0
decouple 0
dpr 0
dmf 0
C13 0
IP 0
PILOT 0
268
0
127
5

9 8 7 6 5 4 3 2 1
2.94 3.67 5.78.45
3.22 13.07.46 5.58
3.36 14.97
2.89
6.43
14.69
11.51



jxy140405_2_yjx_343_5_1_13c CARBON

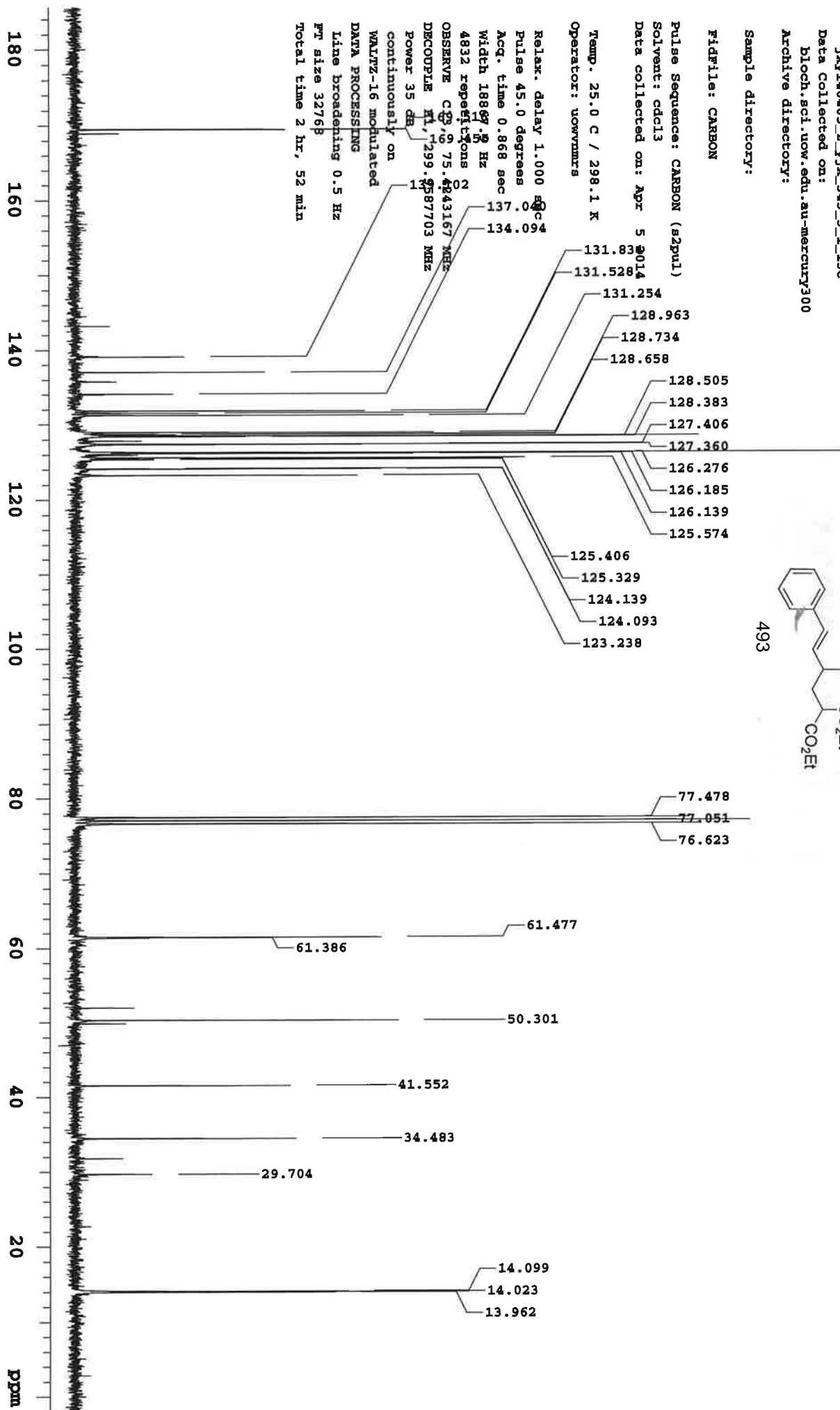
Sample Name:
jxy140405_2_yjx_343_5_1_13c
Data Collected on:
bloch.sci.nov.edu.au-mercury300
Archive directory:

Sample directory:

File: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 5 2014
Temp. 25.0 C / 298.1 K
Operator: novmms

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867 Hz
4832 repetitions
OBSERVE C 75.4243167 MHz
DECOUPLE H 129.7587703 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 2 hr, 52 min



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jxy140525_2_vjx_370_3_PROTON

exp1 PROTON

SAMPLE PRESATURATION

date May 25 2014 satmode n

solvent cdcl3 wet n

file exp SPECIAL

ACQUISITION temp 25.0

sw 7998.4 gain not used

at 2.048 spin not used

np 32768 hsc 0.100

fb 4000 pw90 10.100

bs 16 alfa 10.100

dl 1.000

nt 16 il

ct 16 in

tn H1 hs

sfreq 499.908

tof 499.9 lb

tpwr 60 fn

pw 10.100

DECOUPLE not used

dn 0.100

dof 0.100

dm 0.100

decouple w40 autochk xp

dpr 37 lp

dnt 32258

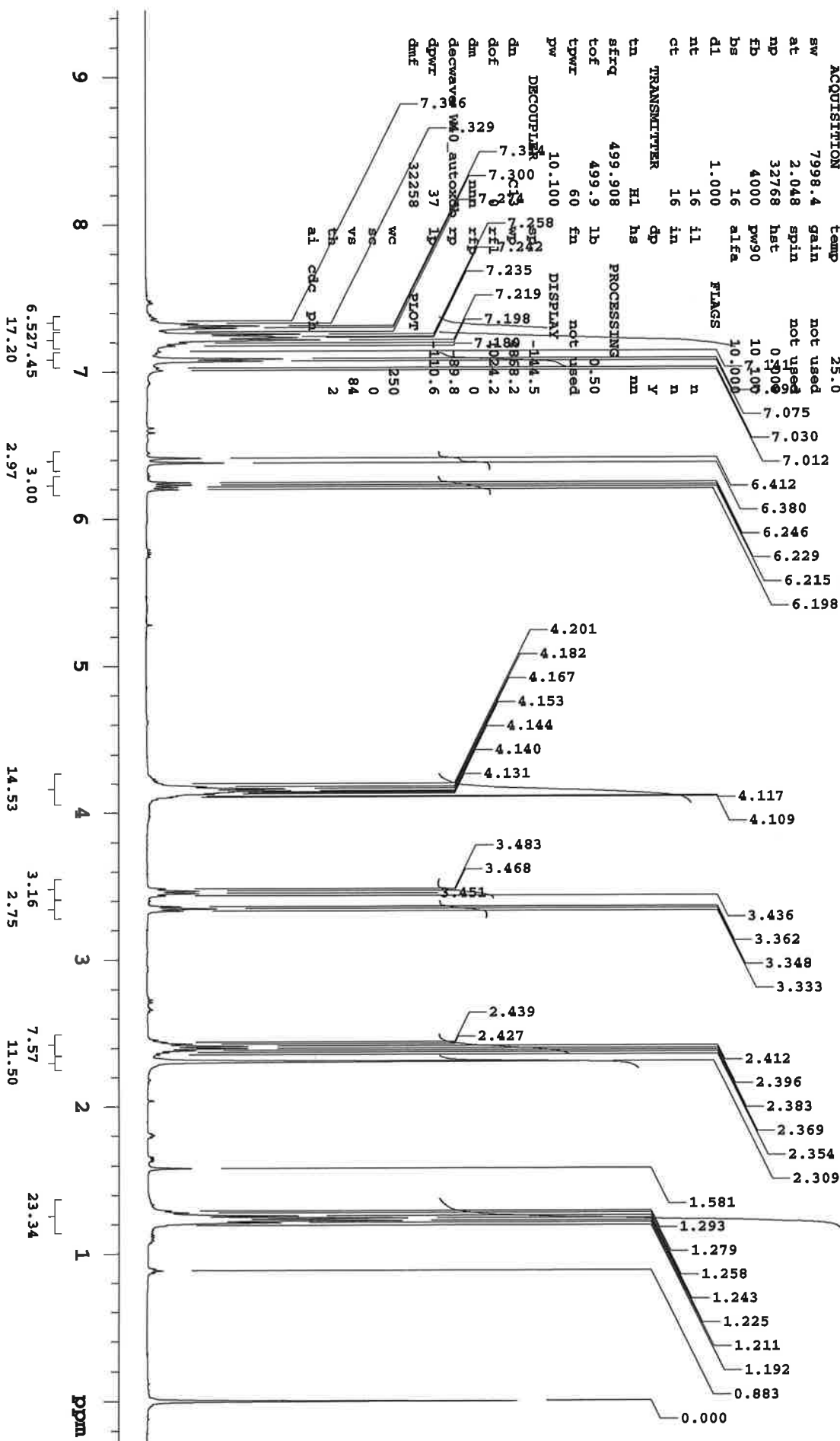
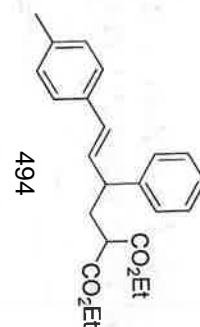
WC

SC

VS

th

al cdc ph



jxy140525_2.yjk_370_3_13c-CARBON

Sample Name:

jxy140525_2.yjk_370_3_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (szpul)

Solvent: cdcl3

Data collected on: May 25 2014

Temp. 25.0 C / 298.1 K

Operator: uownmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.521 sec

Width 31421.8 Hz

4736 repetitions

OBSERVE C13, 125.7011892 MHz

DECOUPLE H1, 499.9073947 MHz

Power 42 dB

continuously on

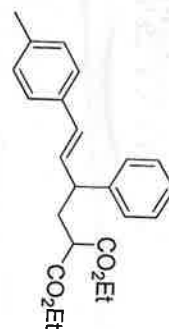
WALTZ-16 modulated

DATA PROCESSING

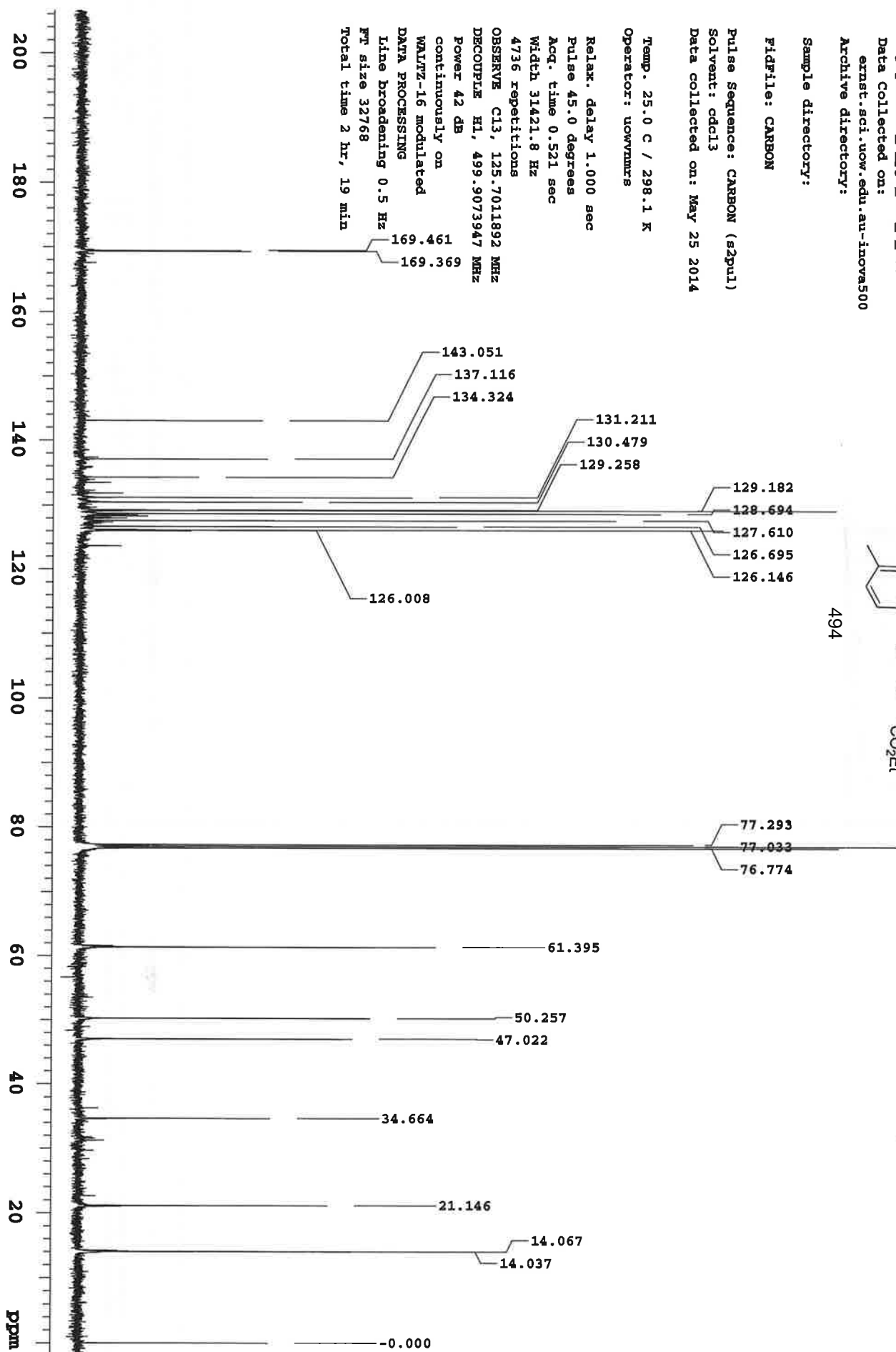
Line broadening 0.5 Hz

FT size 32768

Total time 2 hr, 19 min



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Agilent Technologies

jxy140525_2_vjk_373_2_PROTON

exp1 PROTON

SAMPLE PRESATURATION

date May 25 2014 satmode n

solvent cdcl3 wet n

file exp SPECIAL

ACQUISITION temp 25.0

sv 7998.4 gain not used

at 2.048 spin not used

np 32768 hst 0.008

fb 4000 pw90 10.100

bs 16 alfa 10.000

d1 1.000 FLAGS

nt 16 il n

ct 16 in n

TRANSMITTER H1 hs y

tn 499.908 PROCESSING

sfreq 499.9 fn not used

tof 60 DISPLAY

tpwr 33.3 sp -93.2

pw 100.0 4868.2

DECOUPLER 1 1018.8

7.349 7.191 7.179 7.164

7.143 7.132 7.121 7.110

7.103 7.092 7.081 7.070

7.059 7.048 7.037 7.026

7.015 7.004 6.993 6.982

6.969 6.958 6.947 6.936

6.923 6.912 6.901 6.890

6.877 6.866 6.855 6.844

6.830 6.819 6.808 6.797

6.781 6.770 6.759 6.748

6.732 6.721 6.710 6.699

6.683 6.672 6.661 6.650

6.634 6.623 6.612 6.601

6.585 6.574 6.563 6.552

6.536 6.525 6.514 6.503

6.487 6.476 6.465 6.454

6.425 6.414 6.403 6.392

6.363 6.352 6.341 6.330

6.301 6.290 6.279 6.268

6.236 6.225 6.214 6.203

6.171 6.160 6.149 6.138

6.106 6.095 6.084 6.073

6.041 6.030 6.019 6.008

6.000 5.989 5.978 5.967

5.932 5.921 5.910 5.899

5.864 5.853 5.842 5.831

5.800 5.789 5.778 5.767

5.730 5.719 5.708 5.697

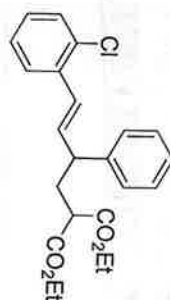
5.660 5.649 5.638 5.627

5.590 5.579 5.568 5.557

5.520 5.509 5.498 5.487

5.450 5.439 5.428 5.417

5.380 5.369 5.358 5.347



495

9 8 7 6 5 4 3 2 1 ppm

3.842.76 3.02
10.28.58

3.38

16.58

3.64 3.17

8.33

26.44

3.386
3.370
3.355

2.427
2.412
2.399

2.467
2.454
2.438

1.562
1.307
1.293
1.285

1.278
1.270
1.257
1.237
1.224
1.210

0.071

-0.000

-0.007

jxy140525_2_vjk_373_2_13c_CARBON

Sample Name:

jxy140525_2_vjk_373_2_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (zgpg3)

Solvent: cdcl3

Data collected on: May 25 2014

Temp. 25.0 C / 298.1 K

Operator: uowmms

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.043 sec

Width 31421.8 Hz

2240 repetitions

OBSERVE C13, 125.7011859 MHz

DECOUPLE H1, 499.9073947 MHz

Power 42 dB

continuously on

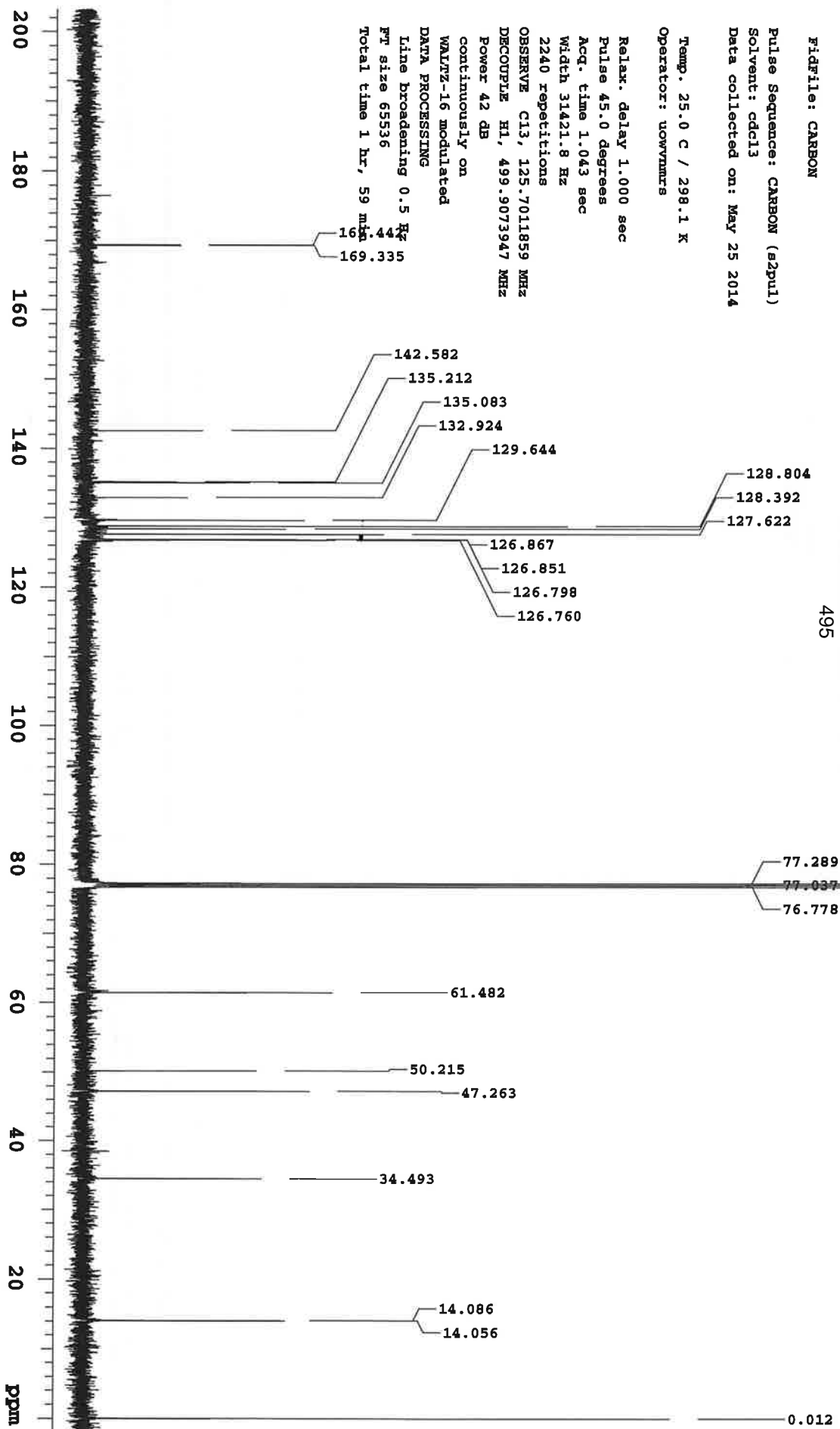
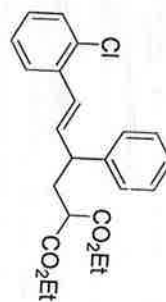
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

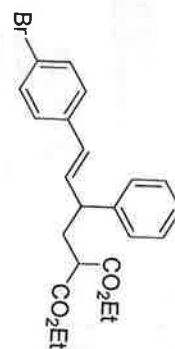
Total time 1 hr, 59 min



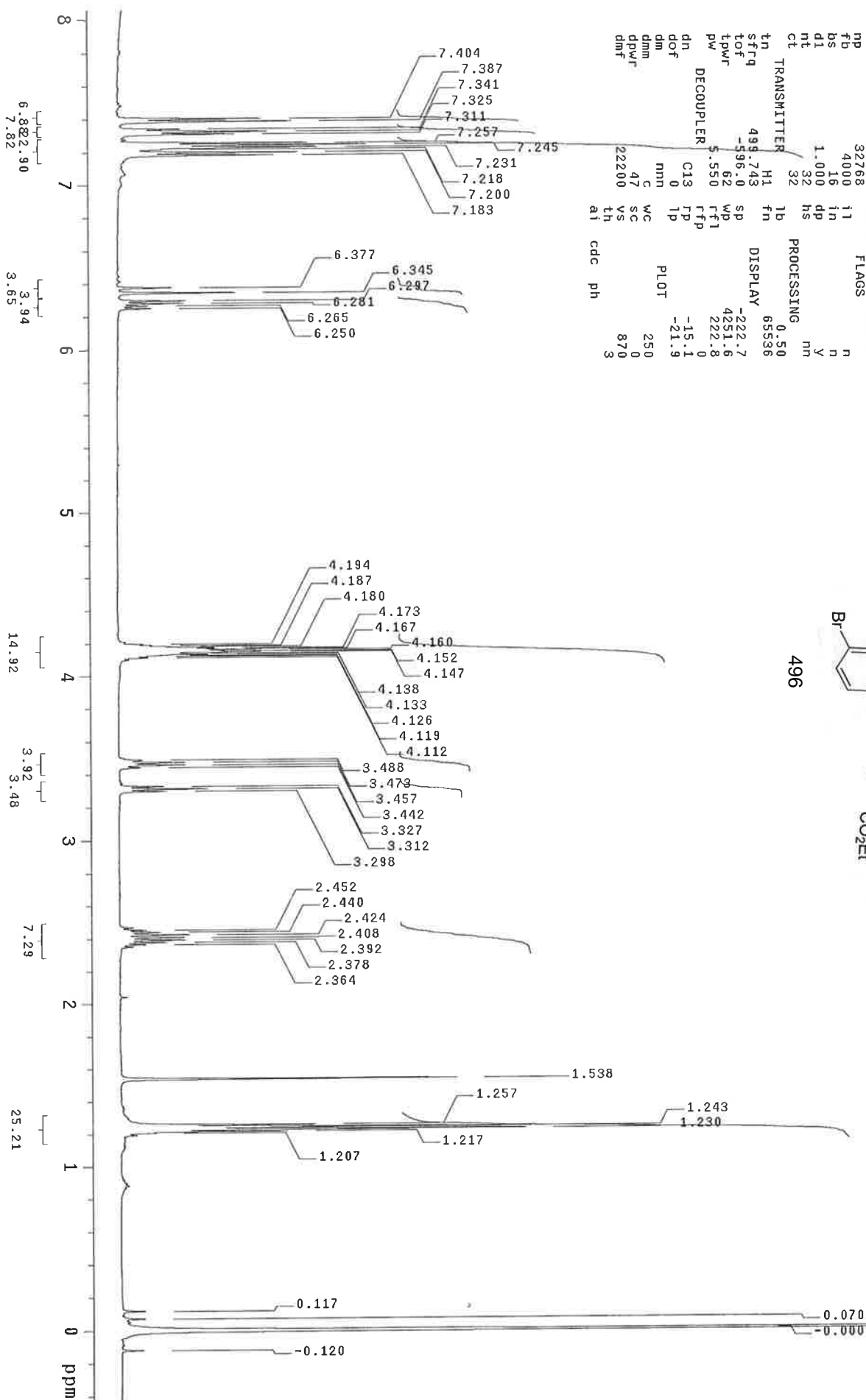
Agilent Technologies

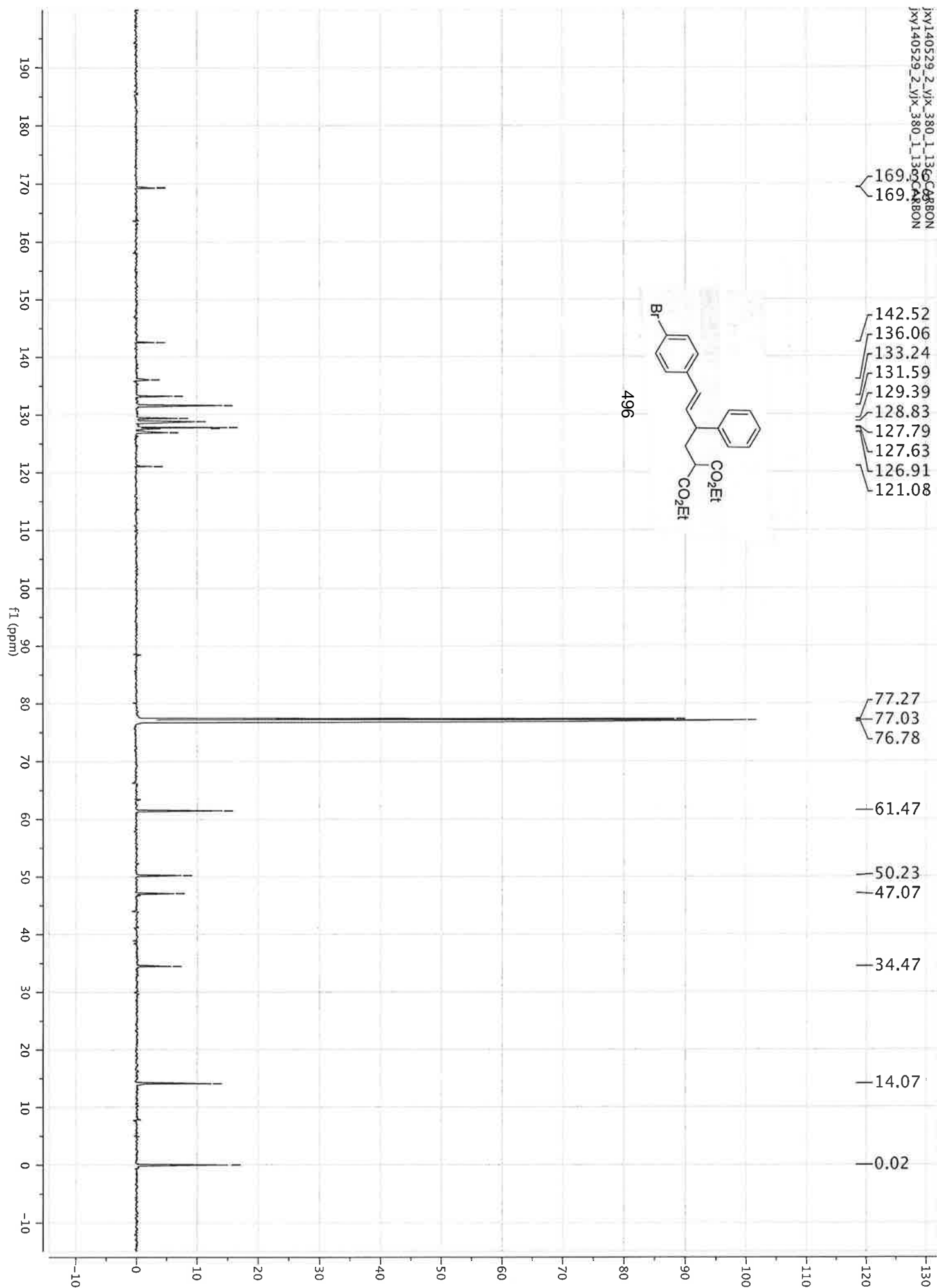
jxy140528_2_vjx_380_1-Proton
expt1 Proton

SAMPLE		SPECIAL	
date	May 28 2014	temp	25.0
solvent	cdcl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	4251.7	pw90	11.100
at	3.854	alfa	6.600
np	32768	flags	
fb	4000		
bs	16		
d1	1.000		
nt	32		
ct	32		
tn	H1	lb	0.50
sfreq	499.743	fn	65536
tofr	-596.0	sp	-222.7
tpwr	62	wp	4251.6
pw	5.550	rfl	222.8
DECOUPLER		rfp	0
dn	C13	tp	-15.1
dof	0	ip	-21.9
dmm	mm	PLOT	
dmm	c	WC	250
dpwr	47	SC	0
dmt	22200	VS	870
tn	al	cdc	ph



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jky140526_2.yjk_379_1_PROTON

exp1 PROTON

SAMPLE PRESATURATION

date May 26 2014 satmode n

solvent cdcl3 wet n

file exp SPECIAL

ACQUISITION temp 25.0

sw 7998.4 gain not used

at 2.048 spin not used

np 32768 hsc 0.008

fb 4000 pw90 10.100

bs 16 alfa 10.000

dl 1.000 FLAGS

nt 16 il n

ct 16 in n

TRANSMITTER dp y

tn H1 hs nm

afreq 499.908 fn

tof 499.9 fn

tpwr 60

pw 10.100

DECOUPLER wp

dn C13

dof 0

dm 7

decouple W40_autokdb

dpwr 37

dmf 32258

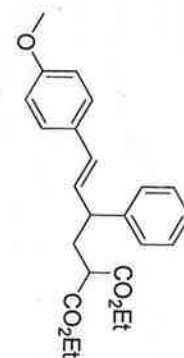
WC 250

SC 0

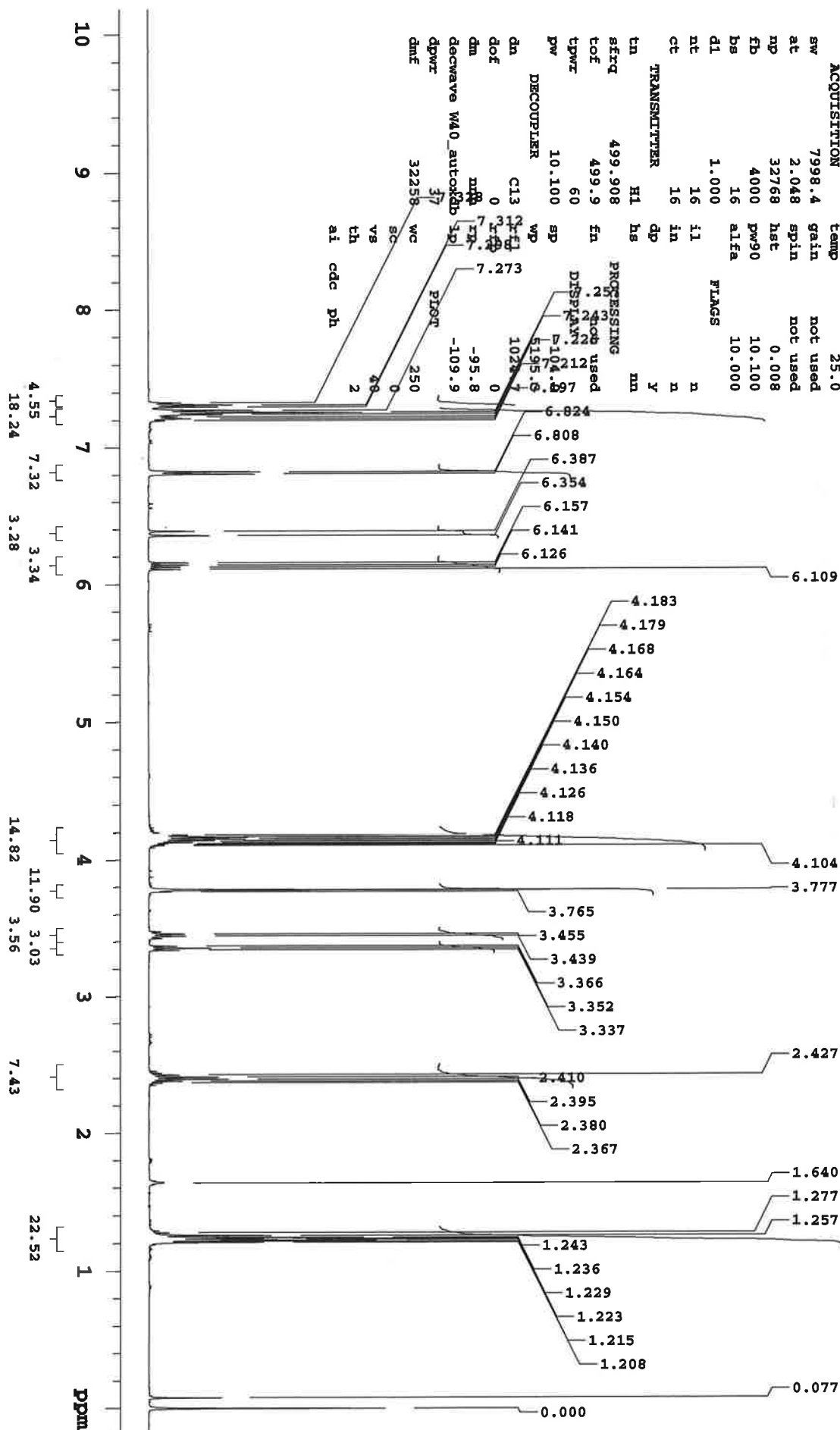
VS 48

TH 2

AI CDC PH



497



jxy140526_2_vjk_373_1_13c-CARBON

Sample Name:

jxy140526_2_vjk_373_1_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (szpul)

Solvent: cdcl3

Data collected on: May 26 2014

Temp. 25.0 C / 298.1 K

Operator: uowvnmrs

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.521 sec

Width 31421.8 Hz

192 repetitions

OBSERVE C13, 125.7011892 MHz

DECOUPLE H1, 499.9073947 MHz

Power 42 dB

continuously on

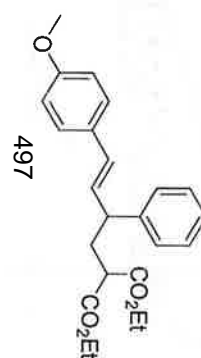
WALTZ-16 modulated

DATA PROCESSING

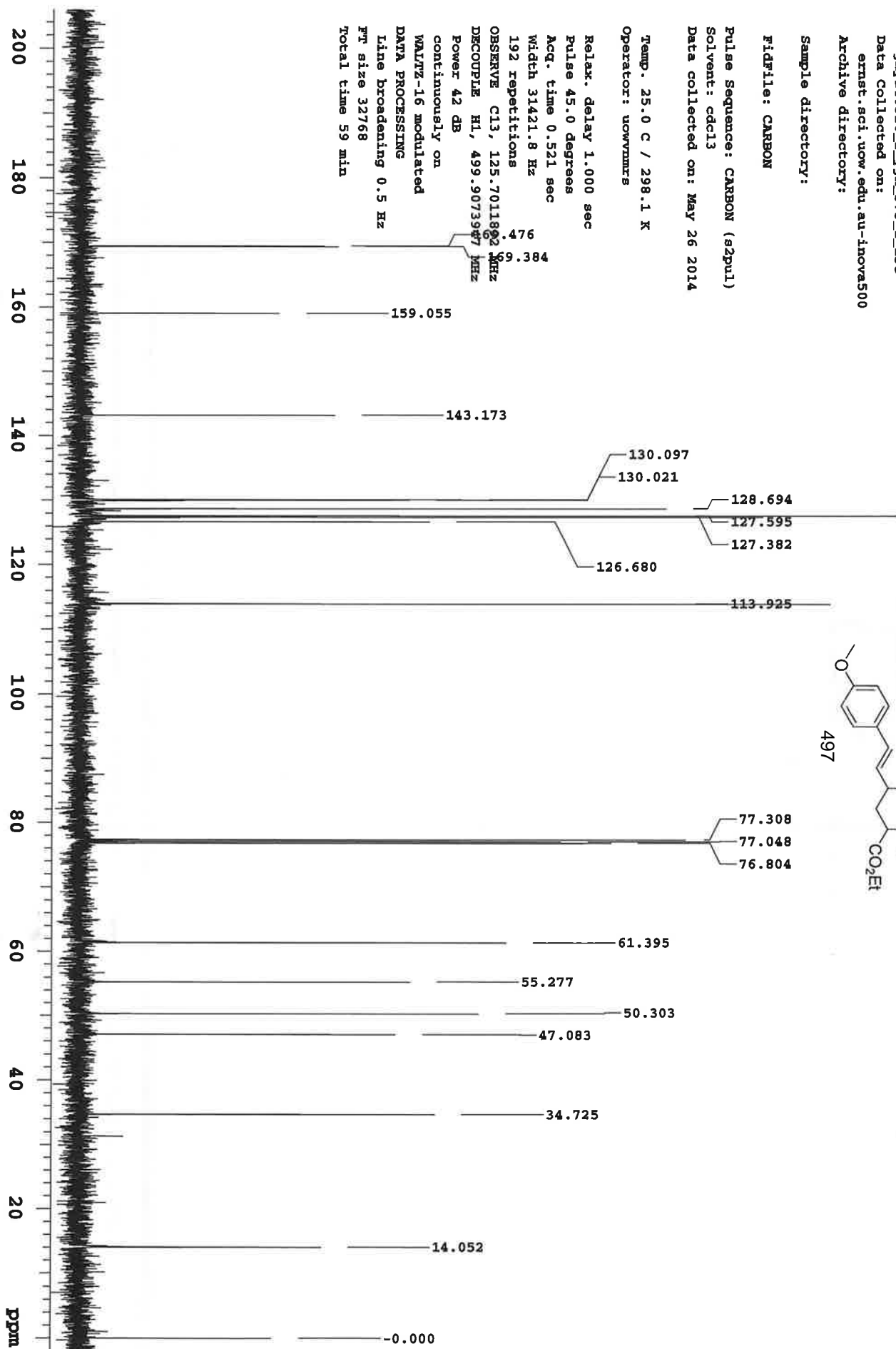
Line broadening 0.5 Hz

FT size 32768

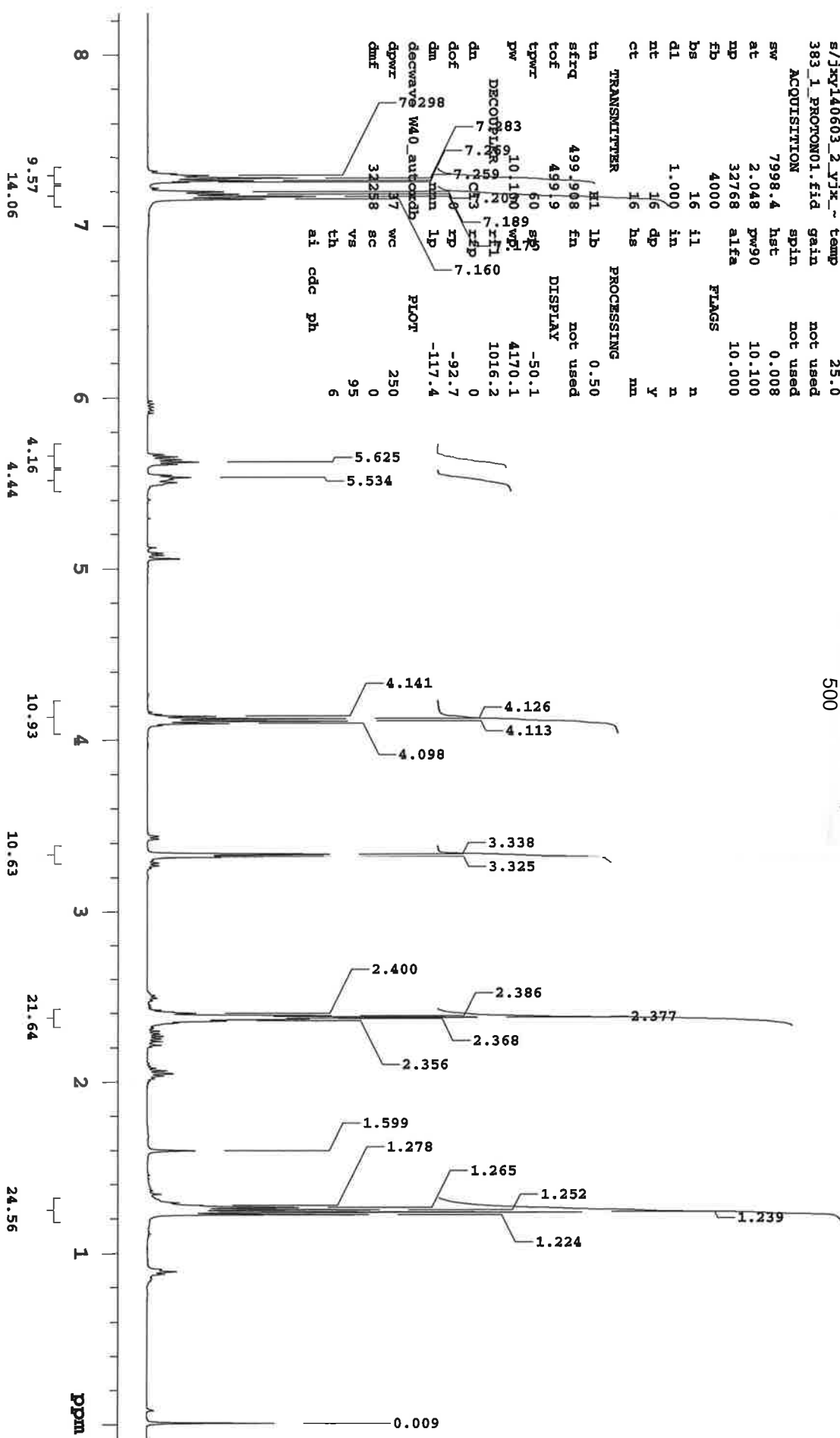
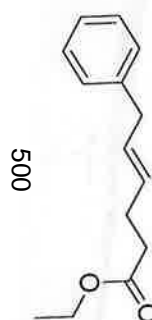
Total time 59 min



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SAMPLE		PRESATURATRON	
date	Jun 3 2014	satmdode	n
solvent	cdcl3	wet	n
file	/home/uowmtr-383_1-PROTON01.fid	SPECIAL	
s/jxy140603_2.yjk	temp	25.0	
acq	gain	not used	
sw	spin	not used	
at	hst	0.008	
np	pw50	10.100	
fb	alfa	10.000	
	4000	FLAGS	
bs	16	11	n
d1	1.000	in	n
nt	16	dp	y
ct	16	bs	nm
TRANSMITTER			
tn	h1	lb	0.50
sfrq	499.908	fn	not used
tcf	499.9	DISPLAY	
tpwr	60	sp	-50.1
pw	8	gwp	4170.1
deco	10	wd	1016.2
dn	3	xtl	0
dof	7	exp	-92.7
dm	7	lp	-117.4
decwa	W40	autocorb	PLOT
dprz	37	wc	250
dmf	34258	sc	0
		vs	95
		th	6
		ai	cdc
		ph	



jxy140603_2_yjk_383_1_13c CARBON

Sample Name:

jxy140603_2_yjk_383_1_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: jxy140603_2_yjk_383_1_13c CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Jun 3 2014

Temp. 25.0 C / 298.1 K

Operator: uowmms

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 0.521 sec

Width 31421.8 Hz

2176 repetitions

OBSERVE C13, 125.7011873 MHz

DECOUPLE H1, 499.9073947 MHz

Power 42 dB

continuously on

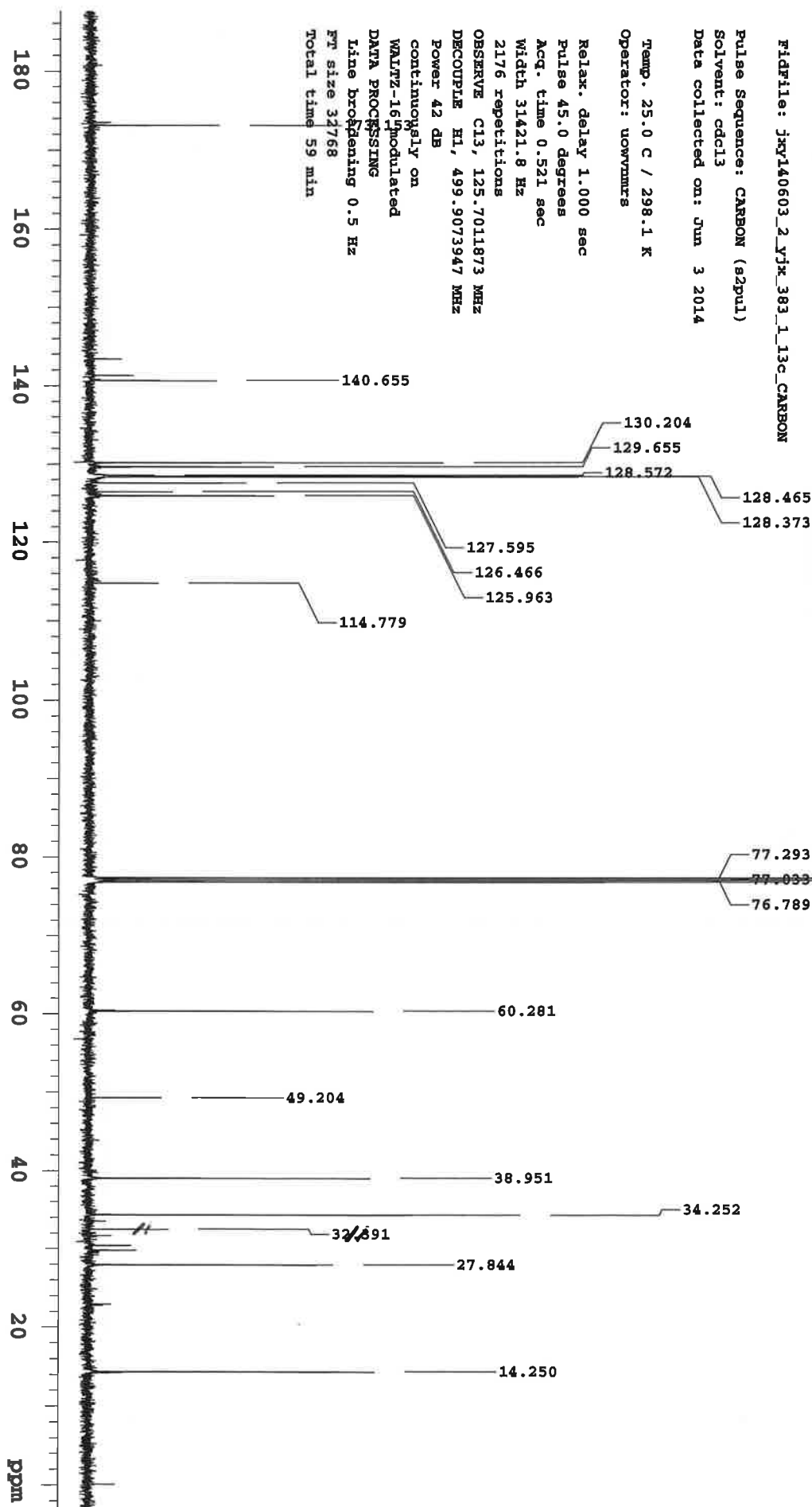
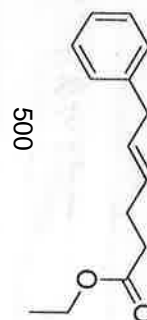
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 59 min



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jxy140626_2_yjk_383_4_gHSQC

Sample Name:

jxy140626_2_yjk_383_4

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: gHSQC

Pulse Sequence: gHSQC

Solvent: cdcl3

Data collected on: Jun 26 2014

Operator: uownmrs

Relax. delay 1.000 sec

Acq. time 0.213 sec

Width 4807.7 Hz

2D Width 12822.6 Hz

16 repetitions

2 x 250 increments

OBSERVE H1, 299.9572747 MHz

DECOUPLE C13, 75.4299735 MHz

Power 38 dB

on during acquisition

off during delay

GARP-1 modulated

DATA PROCESSING

Line broadening 3.0 Hz

Gauss apodization 0.106 sec

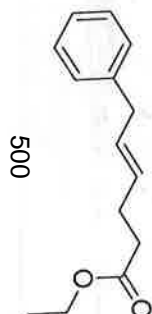
F1 DATA PROCESSING

Line broadening 3.0 Hz

Gauss apodization 0.010 sec

FT size 2048 x 1024

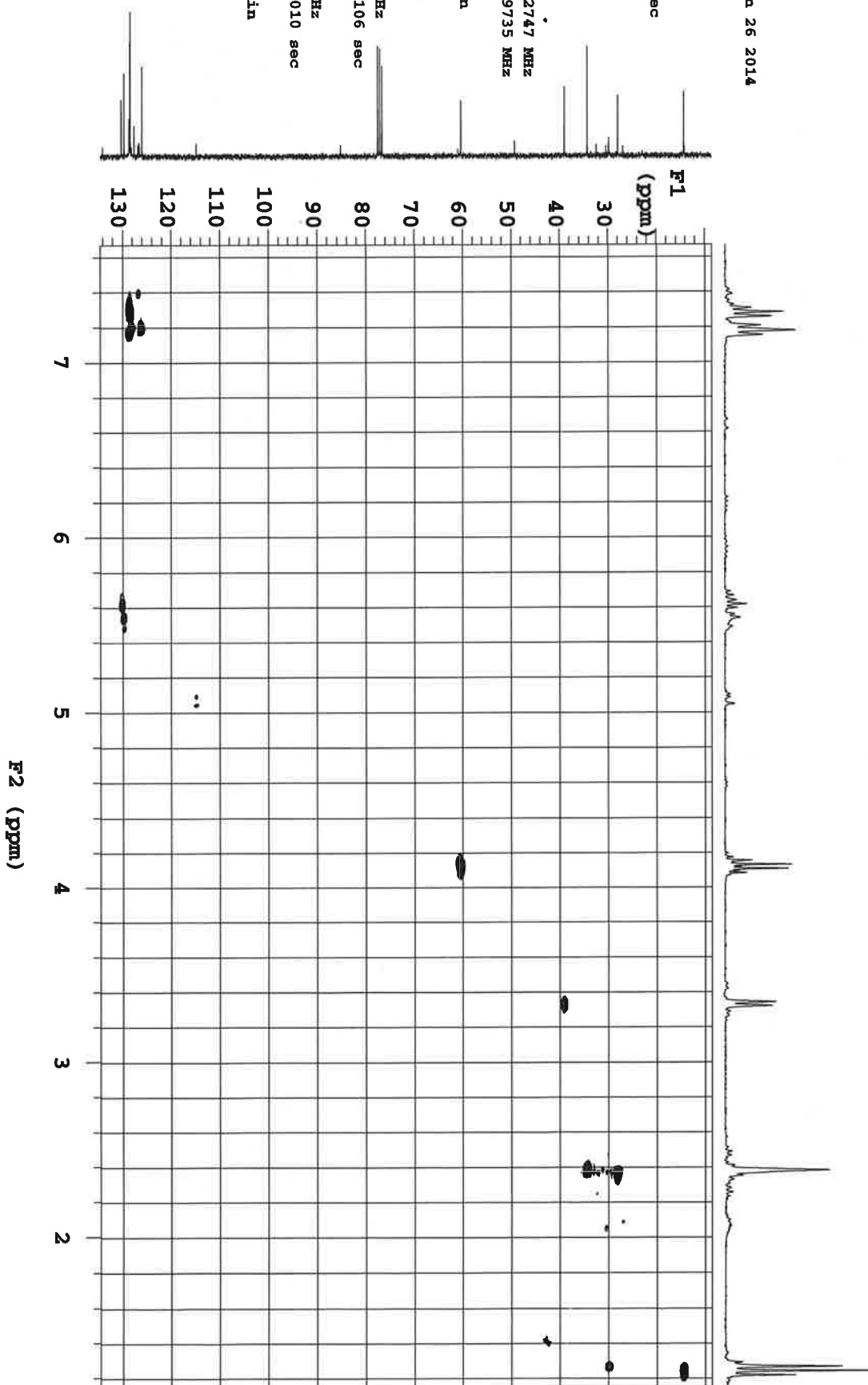
Total time 2 hr, 55 min



500



Agilent Technologies



jxy140626_2_vjx_383_4_gHSQC

Sample Name:

jxy140626_2_vjx_383_4

Data Collected on:

bloch.sci.uow.edu.au-mercury300

Archive directory:

Sample directory:

Fidfile: gHSQC

Pulse Sequence: gHSQC

Solvent: cdcl3

Data collected on: Jun 26 2014

Operator: uownmrs

Relax. delay 1.000 sec

Acq. time 0.213 sec

Width 4807.7 Hz

2D Width 12822.6 Hz

16 repetitions

2 x 250 increments

OBSERVE H1, 299.9572747 MHz

DECOUPLE C13, 75.429735 MHz

Power 38 dB

on during acquisition

off during delay

GARP-1 modulated

DATA PROCESSING

Line broadening 3.0 Hz

Gauss apodization 0.106 sec

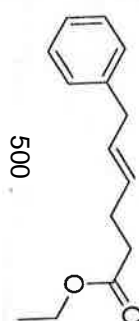
F1 DATA PROCESSING

Line broadening 3.0 Hz

Gauss apodization 0.010 sec

FT size 2048 x 1024

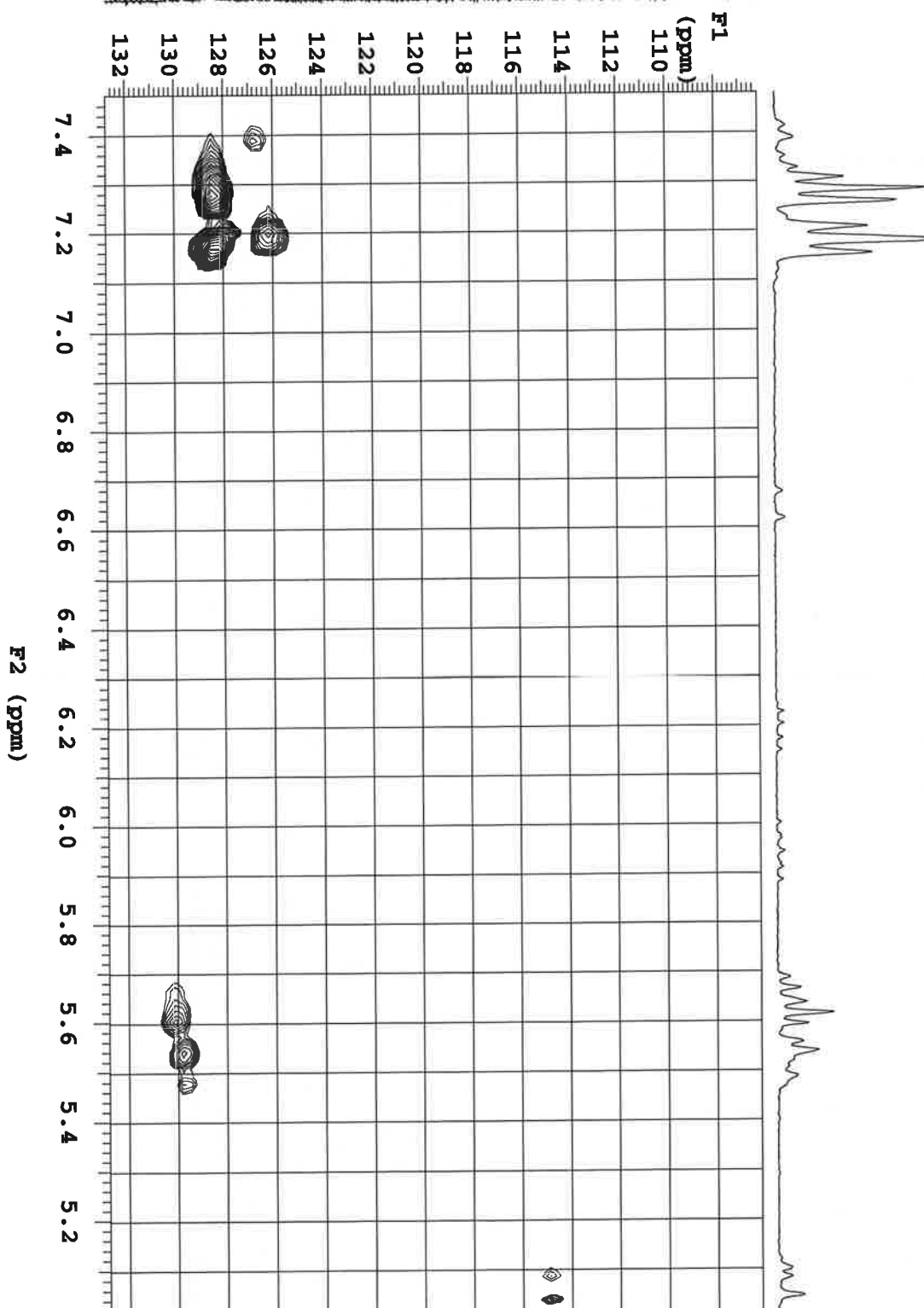
Total time 2 hr, 55 min



500



Agilent Technologies



yjk160728_2.yjk_gdetosyl_PROTON

Sample Name:

yjk160728_2.yjk_gdetosyl

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: PROTON

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Jul 28 2016

Operator: uownmrs

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 2.008 sec

Width 7998.4 Hz

16 repetitions

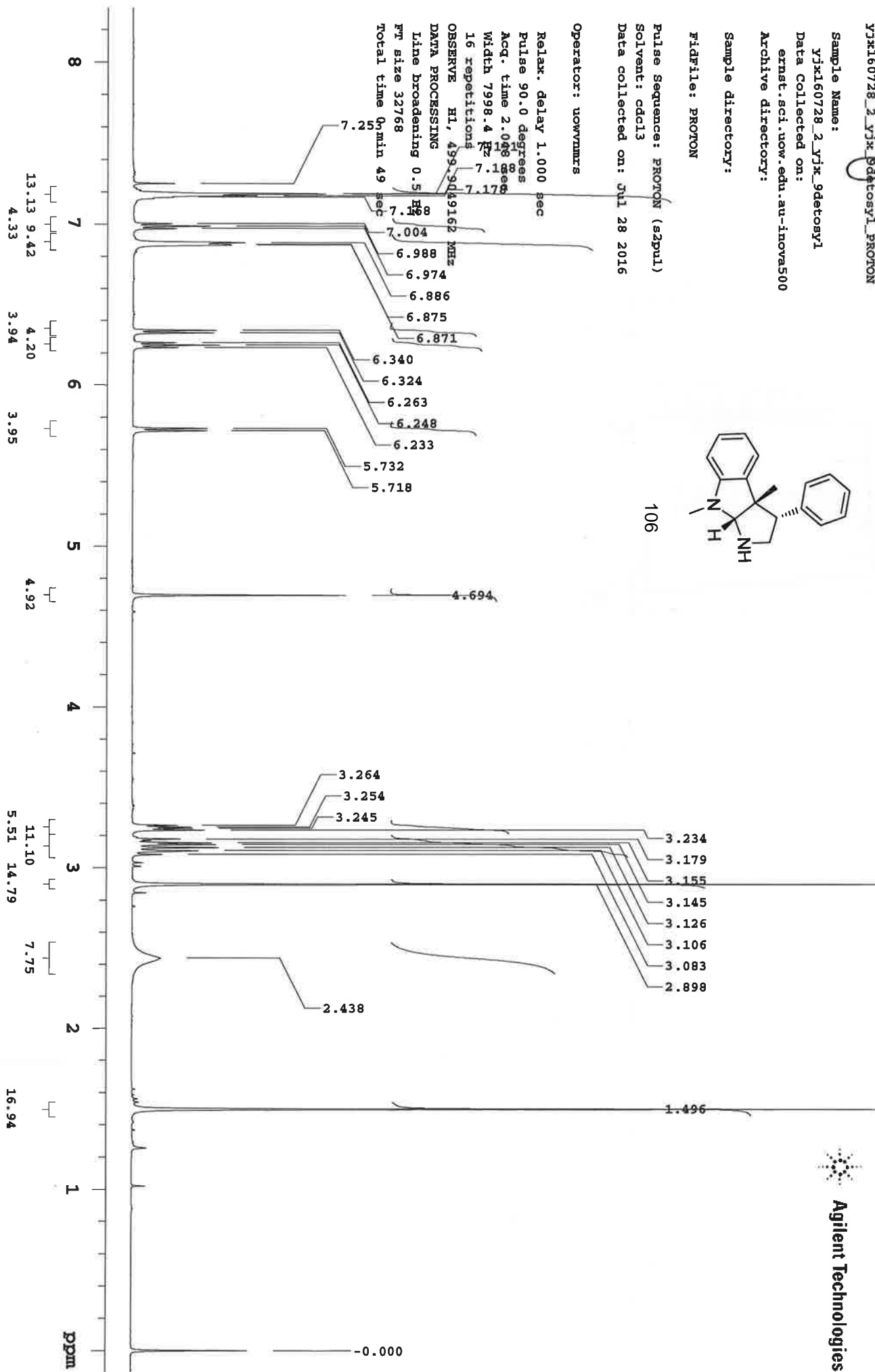
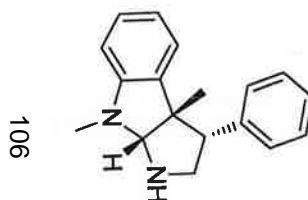
OBSERVE H1, 499.9049162 MHz

DATA PROCESSING

Line broadening 0.5 Hz

FT size 32768

Total time 0min 49 sec



Agilent Technologies

jxy160322_2_yjx_801_2_13c CARBON

Sample Name:

jxy160322_2_yjx_801_2_13c

Data Collected on:

ernst.sci.uow.edu.au-inova500

Archive directory:

Sample directory:

Fidfile: CARBON

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl3

Data collected on: Mar 22 2016

Operator: uowymms

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.043 sec

Width 31421.8 Hz

320 repetitions

OBSERVE C13, 125.701859 MHz

DECOUPLE H1, 499.9073947 MHz

Power 42 dB

continuously on

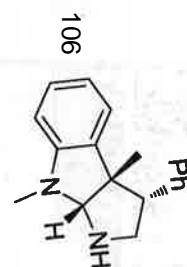
WALTZ-16 modulated

DATA PROCESSING

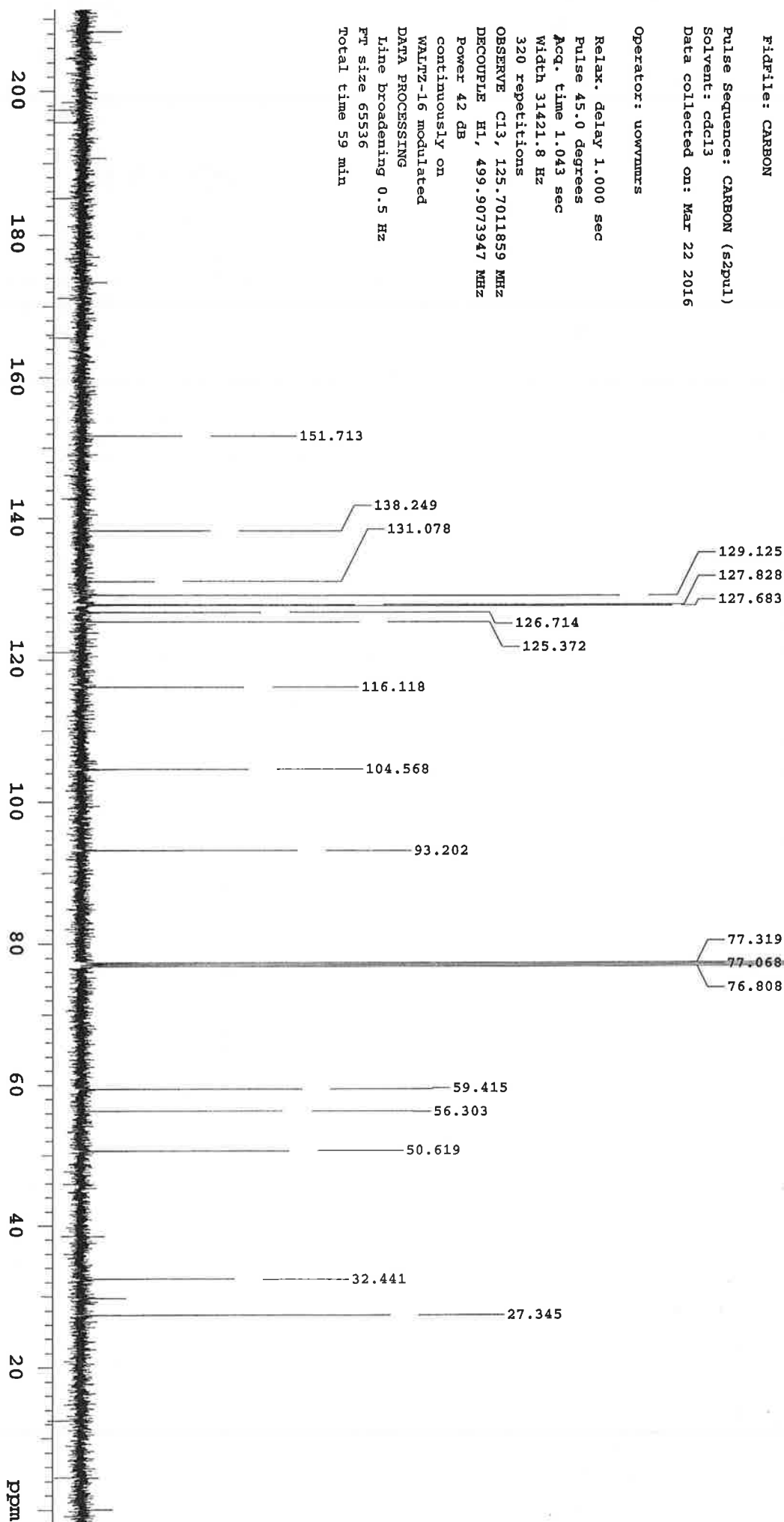
line broadening 0.5 Hz

FT size 65536

Total time 59 min



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