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Enantioselective Functionalizations of Alkenes Using Chiral Phosphoric Acids

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By

Jeffrey Wu

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Committee in charge:
Professor F. Dean Toste, Chair
Professor Peter Vollhardt
Professor Ben de Lumen

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Abstract

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New organocatalytic enantioselective reactions were developed, focusing on using new modes of reactivity with chiral phosphoric acids. Prochiral alkenes and styrenes were explored as substrates for various transformations, including enyne cycloisomerization, hydroamination, halocyclization, and fluorination. The enantioenriched chiral products generated by these methods include heterocycles and allylic fluorides.

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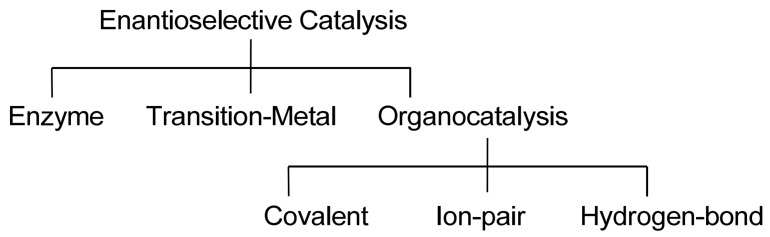
Preface

Enantioselective catalysis continues to advance since the transformations developed by pioneers such as Knowles, Noyori, and Sharpless, who each received the Nobel prize in chemistry in 2001 for their efforts in this field.[1] The ability to distinguish between two enantiotopic faces for the formation of either *R* or *S* (left or right handed) chiral centers has been achieved by biological systems and nature, but only relatively recently has it become within the repertoire of synthetic chemists. Continuing advancements driven by industrial demands as well as academic pursuits have evolved the field into an increasingly diverse and fruitful one. The applications of enantioselective catalysis are diverse, and arguably the most important has been in agrochemicals and pharmaceuticals. Currently, methods identified as useful are often relevant to the construction of moieties commonly found in the molecules desired by these particular industries. The distinctions chemists commonly use to classify the myriad methods can be based on identity of the catalyst, mode of reactivity, or chemical transformation. Historically, transition-metal and enzyme catalysis were the two common branches. The field of enantioselective transition-metal catalysis is further divided depending on the identity of the metal and where it lies on the periodic table; or whether it acts as a Lewis acid, a pi-acid, a redox-active cross-coupling catalyst; or by the transformation from substrate to product.[2]



Scheme 1. A general breakdown of the different classes of enantioselective catalysis.

The advent of enantioselective organocatalysis as the third branch in the field has created a new type of reaction which are distinguished by the *lack* of metals (Scheme 1).[3] Within organocatalysis, several structures and scaffolds have been developed, including but not limited to amines, thioureas, Brønsted acids, N-heterocyclic carbenes, and peptides (Figure 1). They operate *via* hydrogen-bonding interactions, covalent interactions, and ionic interactions.

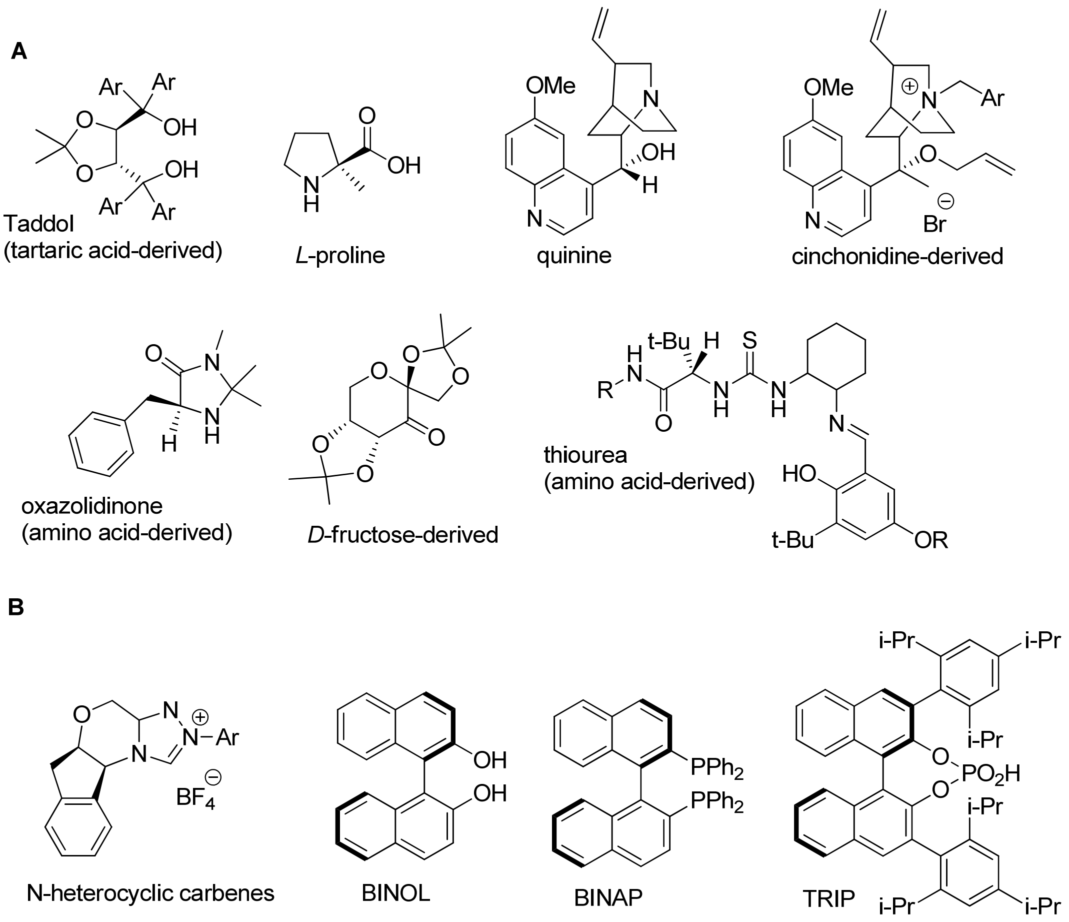


Figure 1. A: Chiral-pool-derived organocatalysts. **B:** Synthetic (resolved) chiral organocatalysts.

Generally, the benefits of organocatalysis from a practical perspective include the avoidance of expensive metals and concomitant contamination, favorable functional group compatibility, stability to air and moisture, and the potential for being more economical.

A broad generalization of enantioselective transition-metal catalyzed methods and enantioselective organocatalytic methods reveals that while seminal examples of the former involve the functionalization of alkenes' unsaturated C-C pi bonds, oxidation, or reduction, seminal examples of the latter involve activation and reaction with unsaturated carbon-heteroatom bonds.[2, 3] This is largely the result of organocatalysis's reliance on hydrogen-bonding interactions or polar ionic interactions, which makes carbon-heteroatom bonds more reasonable substrates. This also presents a limitation in that these interactions are almost impossible to achieve with alkenes.[4] One reasonable solution to the problem of scope, which exists for all types of methods, is the combination of different approaches applied to one method or transformation.[5] For example more recently in our own group, organocatalysts have been used in conjunction with transition-metals, and supramolecular clusters in conjunction with enzymes, allowing for transformations not possible with just one type of catalysis.[6] I explore using an organocatalyst in palladium-catalyzed reactions in the first chapter. However, another approach to solving this problem is to stay within organocatalysis and further develop the catalysts and applications. In the rest of my work, I explore the idea that design of new organocatalysts, and implementation of new approaches with known organocatalysts can successfully functionalize alkenes enantioselectively without the use of metals.

My work has centered on the use of chiral BINOL-derived phosphoric acids. Chiral phosphoric acids have been widely developed and utilized in the last decade, most well represented by the success of TRIP, a commercially available variant first discovered by List and coworkers.[7] Although the first BINOL-derived chiral phosphoric acid catalysts were reported by Terada and Akiyama, TRIP has proved to be the most versatile analog, owing to the 2,4,6-triisopropylphenyl groups in the 3,3'-positions.[8] The initial and still predominant use of these phosphoric acids has been as chiral Brønsted acids, focusing on LUMO lowering of imine and carbonyl groups *via* protonation and resultant hydrogen-bonding with the heteroatom. Many reports have validated this approach to achieving enantioselective nucleophilic attack onto such functional groups. One key in the success is the ability of the phosphate to interact with the protonated substrate as well as the incoming nucleophile, both *via* hydrogen-bonding interactions (Figure 2A).[9]

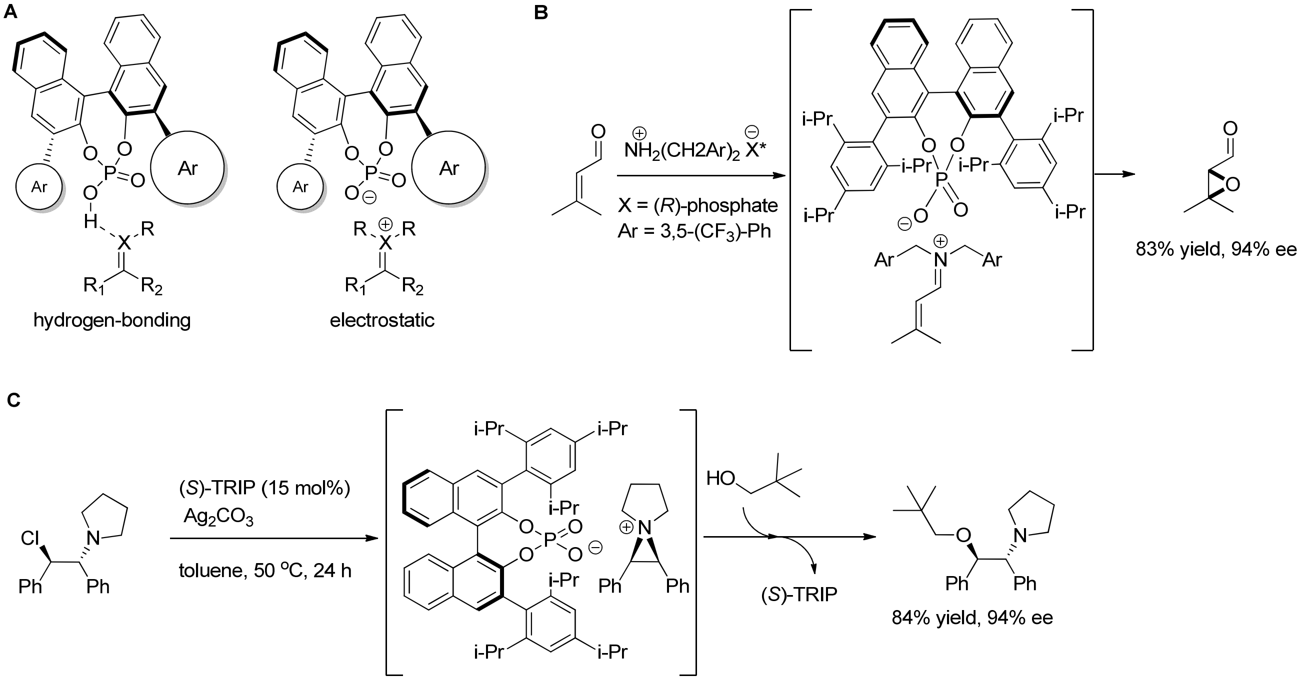


Figure 2. **A:** Two well-precedented activation modes of C-X double bonds. **B:** An example of asymmetric counteranion direct catalysis – an enantioselective epoxidation of enals *via* imminium chiral ion pair. **C**: Toste's TRIP counteranion ion paired with meso-aziridinium intermediate.

In the last five years, an extension in terms of modes of enantioinduction with chiral phosphoric acids has been developed, to rely on ion-pairing of cationic intermediates with chiral phosphates. Generally when used in this fashion, the counteranion phosphate is referred to as a chiral anion (Figure 2B, 2C).[10] However, alkene functionalization is still outside the scope of these transformations because with the necessity of hydrogen-bonding replaced with electrostatic interactions, polar groups are still required. This sub-field of chiral anion catalysis is an important development in the ability to use these organocatalysts in a variety of reactions. In the combination of organocatalysis with transition-metal catalysis, the distinction has been made that the chiral anion in these cases is not necessarily a ligand on the metal, but rather a counterion which is typically achiral such as a halide or borate. Arguably, the genesis for the Toste group's interest in TRIP and its derivatives was Greg Hamilton's project using a chiral counteranion with gold-catalyzed reactions.[6b] An important further development was work by the same colleagues, who showed that a phase-transfer reaction with chiral phosphate solubilizing an achiral silver salt, allowing for chiral ion pairing with a cationic aziridinium intermediate. This was an example of chiral anion catalysis which did not rely on transition-metal reactivity.

These successes were indication that exploring the potential expansion of the roles these types of catalysts play in the reaction could be very fruitful. From there, the Toste group has developed many successful organocatalytic reactions in the last few years, marking a new area of focus. So, as we have found out, chiral phosphoric acids and the derivative phosphate anion can be very versatile in synthesis, and exploitation of their privileged C-2 symmetric structure and bifunctional phosphate group can be achieved with relatively small changes to the catalyst. In short, I aimed to work on these developments, with a thought process which predominantly considers the mode of reactivity, activation, and mechanism, rather than the classification of transformation, product class, or end-user applications. (Of course, working with air- and water-tolerant reactions is highly desirable for any chemist.) As shown in the figure below, I have been able to apply and develop chiral phosphoric acids as catalysts in new methods which incorporate new approaches. Most of these methods continue to utilize the chiral counteranion of chiral phosphoric acids (the *phosphate*). These methods also feature either use as chiral ligands in palladium-catalysis, newly designed covalent catalysts, new halogenating phase-transfer reagents, and directing groups for allylic fluorination (Figure 3).

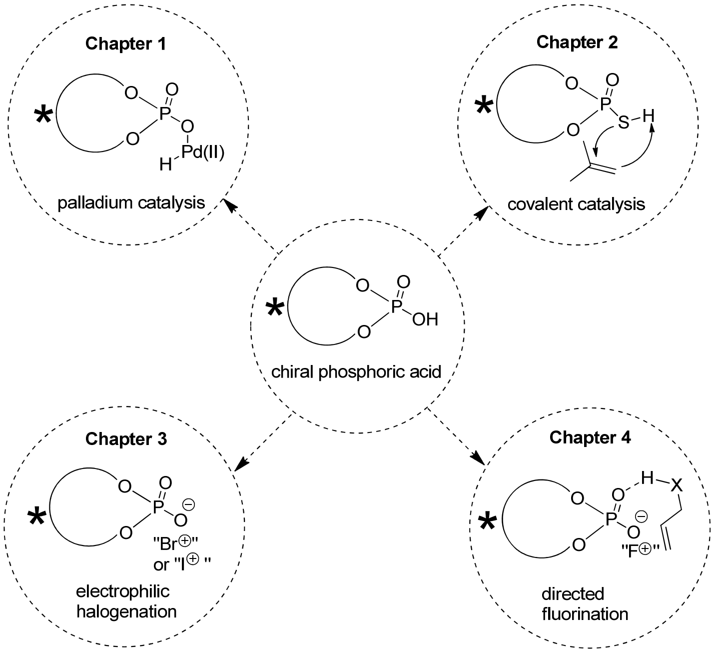


Figure 3. Projects revolving around chiral phosphoric acids includes covalent catalyst design, halogenation reagent design, and implementation of directing groups to interact with chiral phosphates.

Herein I describe the specifics of my work toward further increasing the types of reactions possible with these catalysts for enantioselective reactions with alkenes.[11] Each project chapter will contain a separate introduction which will address more specific precedent based on the transformation developed, and explain how it relates to the general goals described above.

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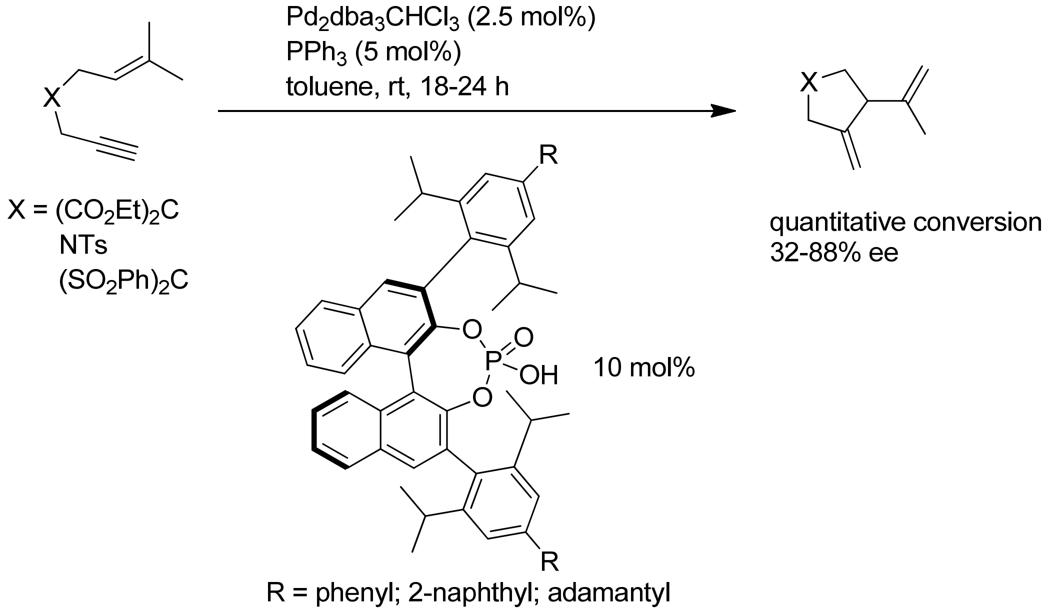
CHAPTER 1: DESIGN OF NEW CHIRAL PHOSPHORIC ACIDS FOR PALLADIUM CATALYZED 1,6-ENYNE CYCLOISOMERIZATION

Abstract

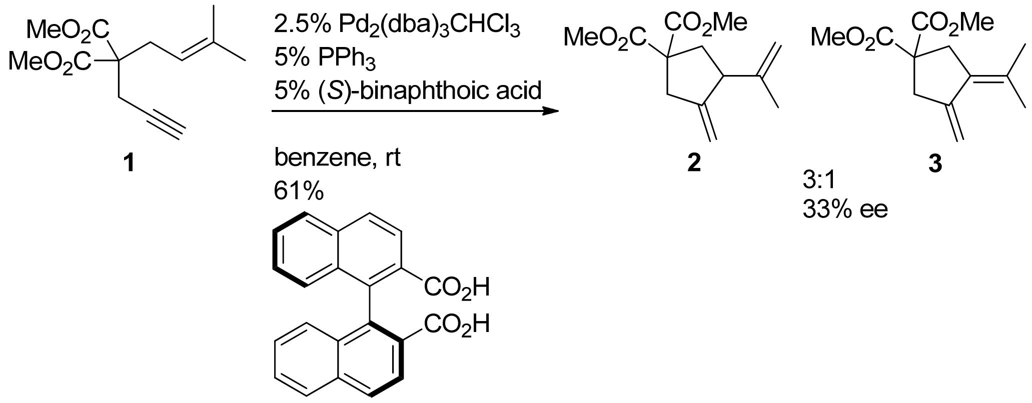
The combination of a chiral phosphoric acid organocatalyst with a palladium (0) source was found to undergo formal oxidative addition, creating a chiral palladium(II) catalyst for 1,6-enyne cycloisomerization, providing chiral carbocycles in good yield and moderate to high enantioselectivity. The development of novel chiral phosphoric acids was instrumental in achieving higher enantioselectivity across a number of substrates. However, the methodology suffered similar disadvantages as previously reported versions of this reaction. Thus, although this approach did not necessarily produce significant progress for this particular transformation, the concept of applying chiral phosphoric acids to palladium catalysis was validated.



Introduction

Although the use of chiral Brønsted acids with palladium catalysis was reported by Trost and co-workers for 1,6-enyne cycloisomerization with encouraging results, developments in chiral Brønsted acid catalysis have not been applied to this reaction. Trost had employed several chiral carboxylic Brönsted acids, of which binaphthoic acid provided **2** with an enantiomeric excess of 33% (Scheme 1).[1] While this concept was applied to the use of TRIP as a counteranion to palladium-intermediates by List and coworkers, examples of the combination of metal-catalysis and organocatalysis are relatively rare.[2] The ability to utilize chiral organocatalysts as ligands or counterions in metal-catalyzed reactions should in theory expand the possibilities for creating catalysts with new or improved reactivity and chiral induction. In our lab, we have explored the use of TRIP in gold-catalysis as a chiral counteranion with impressive results.[3] Interestingly, there was a cooperative effect in choice of chiral ligand and chiral counteranion, which opens the door to finding matched dual-sources of chirality as a viable option for difficult transformations. We saw an opportunity to utilize the aforementioned chiral phosphoric acids to render the cycloisomerization reaction more highly enantioselective, and provide another demonstration of the benefits of combining transition-metal catalysis and organocatalysts.

Due to their abundance in biologically interesting natural products, extensive efforts have been made to develop an efficient method for the synthesis of chiral 5-membered ring structures. Trost reported a 1,6-enyne cycloisomerization reaction that provides an atom-economical and powerful method for the synthesis of cyclic and bicyclic structures. A representative reaction scheme is shown below (Scheme 1). Both ruthenium and palladium catalysts have been investigated, and several methods have been developed to catalyze the reaction efficiently and with a substrate scope that includes 5-membered and 6-membered carbo- and heterocycles.[4]



Scheme 1. Chiral binaphthoic acid induces enantioselectivity.

One plausible mechanism proposed by Trost proceeds *via* hydropalladation of the palladium-enyne complex (Figure 1).[5] First, palladium (0) undergoes formal oxidative addition with the Brönsted acid, generating a catalytically active palladium(II)-hydride species. Complexation of an enyne substrate is followed by hydropalladation of the alkyne, and migratory insertion generates the 5-membered ring structure and the chiral center. Finally, ß-hydride elimination may take place with either of two adjacent hydrogens, providing either the 1,3- or 1,4-diene product.

Since Trost's initial report, other methods of inducing enantioselectivity have been developed, mostly by identifying effective chiral phosphine ligands. Much of the work has been done by Mikami, who has reported high enantioselectivities using axially chiral ligands such as Segphos and other modified BINAP ligands (Figure 2).[6]

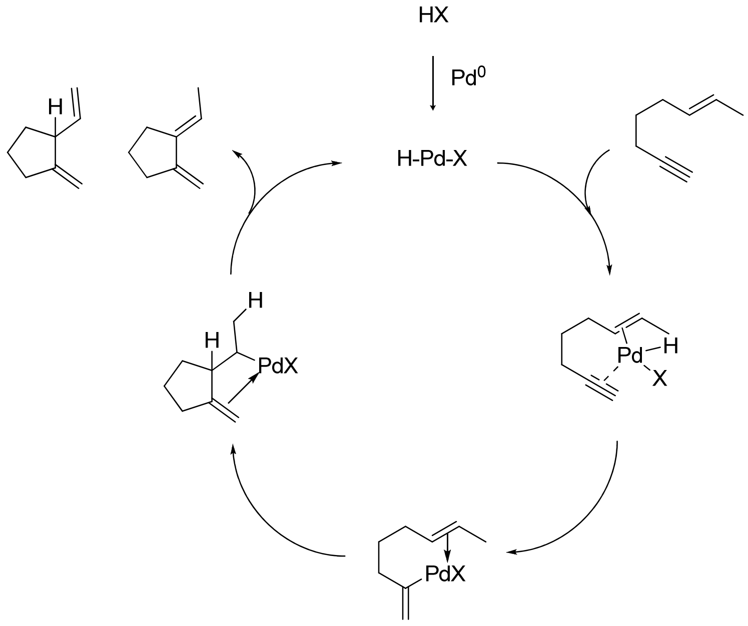
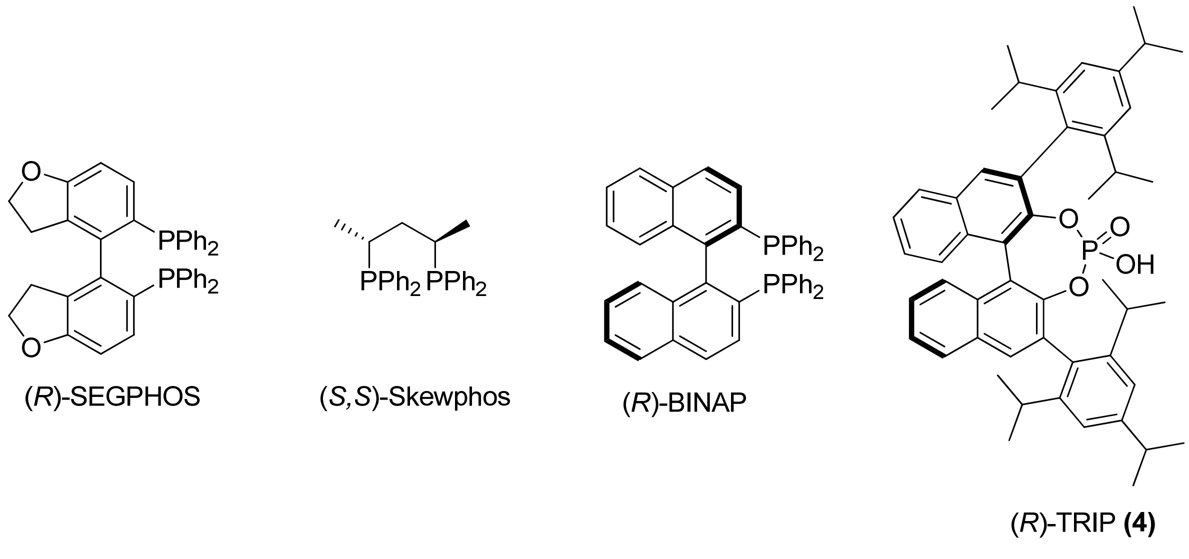


Figure 1. Proposed hydropalladation reaction pathway.



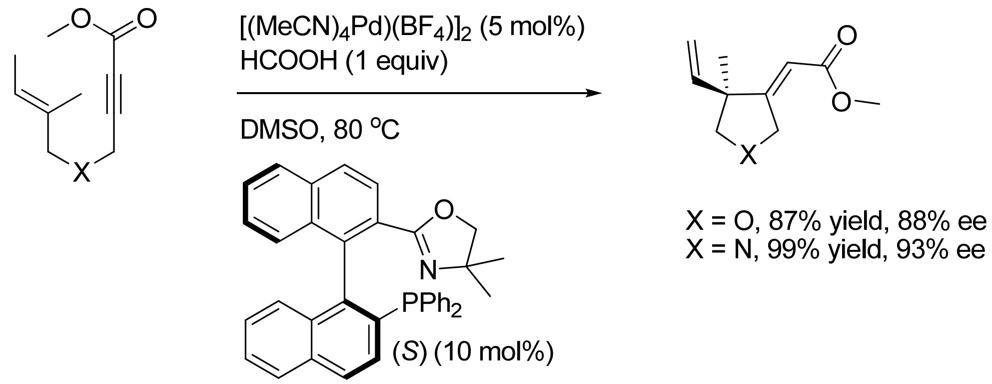
(*R*)-SEGPHOS

(*S,S*)-Skewphos

(*R*)-BINAP

(*R*)-TRIP **(4)**

Figure 2. Chiral ligands used in 1,6-enyne cycloisomerization reactions.

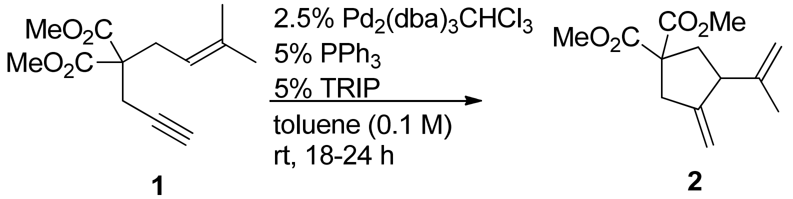


Scheme 2. N,P-ligand as a chiral ligand, achieving high enantioselectivity but limited substrate scope.

In addition, N,P- and Skewphos ligands both provide high enantioselectivity (Scheme 2).[7] However, these methods require highly specific substrates to obtain selectivity, therefore limiting the scope of the reaction. In addition, Ito utilized a chiral diphosphane-palladium complex which achieved enantioselectivity ranging from 34% to 95%, also with a high dependency on the substrate substitution pattern.[9]

Results and Discussion

Since Trost's initial report does not contain a detailed experimental procedure, our studies were initiated by examining the effect of prolonging the stirring time prior to addition of substrate (pre-stirring, Table 1). The combination of palladium (0) pre-catalyst, phosphine ligand, and Brönsted acid, according to the proposed mechanism (Figure 1), generates the catalytically active palladium (II) species. We hypothesized that the some reaction time would be required to generate the chiral active catalyst, and addition of substrate too early might affect the reactivity and selectivity of the transformation.



1 **2** **(1)**

entry	pre-stir time (min)	conv (%)[a]	ee (%)[b]
1	2	25	-[c]
2	5	50	70
3	20	68	81[d]
4	30	12	-[c]
5	45	14	-[c]

[a] Conversion determined by NMR. [b] Enantiomeric excess determined by chiral HPLC. [c] Not determined due to low amount of product. [d] Average of two experiments

Table 1. Dependence on stirring catalyst and ligands prior to addition of substrate.

To test this hypothesis, we performed the cycloisomerization of **1** with different pre-stirring times. Indeed, significantly different results were obtained in experiments performed with 2, 5, 20, 30 and 45 minute pre-stirring times (Table 1). Surprisingly, the reaction was much less successful with a 30 minute or longer stirring time. From these results, a pre-stirring time of 20 minutes was from here on incorporated into our procedure.

The effects of various solvents and palladium sources were investigated (Table 2), which included halogenated, ethereal, and aromatic solvents. Within each class of solvents we obtained different results. However, in all cases, the reaction proceeded with moderate to good conversion, and with moderate to good enantioselectivity. For example, using toluene instead of benzene increased the yield and enantiomeric excess significantly.

entry	solvent	cat.	conv (%)[b]	ee (%)[c]
1	m-xylene	$Pd_2(dba)_3CHCl_3$	76	80
2	toluene	$Pd_2(dba)_3CHCl_3$	68	81
3	benzene	$Pd_2(dba)_3CHCl_3$	35	65
4	MTBE	$Pd_2(dba)_3CHCl_3$	53	70
5	p-dioxane	$Pd_2(dba)_3CHCl_3$	95	78
6	DCE	$Pd_2(dba)_3CHCl_3$	43	-[d]
7	chloroform	$Pd_2(dba)_3CHCl_3$	17	-[d]
8	DCM	$Pd_2(dba)_3CHCl_3$	76	55
9[e]	toluene	$Pd(PPh_3)_4$	76	76
10[e]	m-xylene	$Pd(PPh_3)_4$	99	84
11[e]	p-dioxane	$Pd(PPh_3)_4$	67	74
12	toluene	$Pd(OAc)_2$	99	33

[a] Conditions: Pd (5 mol%), PPh_3 (5 mol%), TRIP (5 mol%), rt,18-24 h. [b] Conversion determined by NMR. [c] Enantiomeric excess determined by chiral HPLC. [d] Not determined due to low amount of product. [e] PPh_3 was not added.

Table 2 [a]**.** Solvent and palladium catalyst optimization of **(1)**.

In our hands, benzene was one of the worst performing solvents for this reaction, despite being the preferred solvent in previously reported studies.[1] With $Pd_2(dba)_3CHCl_3$ as a catalyst, m-xylene and p-dioxane demonstrated increased reactivity compared to toluene; however, they were not beneficial for enantioselectivity. $Pd(OAc)_2$ catalyzed the reaction efficiently but with low enantioselectivity. Interestingly, $Pd(PPh_3)_4$ proved more effective both in reactivity and selectivity, providing the desired product in quantitative yield and 84% ee in m-xylene. Using $Pd(PPh_3)_4$ also has other advantages - for example, no phosphine ligand is added, and therefore no pre-stirring is necessary. We reasoned that when using $Pd_2(dba)_3CHCl_3$, the dibenzylideneacetone needed to be displaced by the phosphine ligand, which is what occurred in the pre-stirring. Interestingly, using a greater than 1:1 ratio of PPh_3 to $Pd_2(dba)_3CHCl_3$ shut down the reaction. When using an old bottle of $Pd(PPh_3)_4$, we obtained quantitative yield and 85% ee in toluene. Unfortunately, we were not able to reproduce this result using a new bottle of $Pd(PPh_3)_4$. This made us cautious of using $Pd(PPh_3)_4$ because there may be trace unidentified palladium species which are catalyzing the reaction. In addition, our initial substrate scope studies demonstrated that $Pd(PPh_3)_4$ did not effectively catalyze the cycloisomerization on substrates with different functional groups. Therefore, all further studies were performed with $Pd_2(dba)_3CHCl_3$ in toluene.

Next, we examined the effect of concentration and amount of chiral phosphoric acid used (Table 3). As the reaction concentration was increased, the reactivity increased dramatically, but with a slightly decreased enantiomeric excess. Doubling the chiral acid loading to 0.10 equivalents increased enantioselectivity from 75% to 85%, which was the optimal result. Thus, both changes in concentration and chiral acid loading provided modest increases in enantioselectivity.

entry	concentration (M)	TRIP (equiv)	conv (%)[b]	ee (%)[c]
1	0.05	0.05	53	81
2	0.10	0.05	74	75
3	0.20	0.05	99	77
4	0.10	0.075	99	78
5	0.10	0.10	99	85

[a] Conditions: $Pd_2(dba)_3CHCl_3$ (2.5 mol%), PPh_3 (5 mol%), toluene, rt,18-24 h.
[b] Conversion determined by NMR. [c] Enantiomeric excess determined by chiral HPLC

Table 3[a]**.** Concentration and catalyst loading optimization of **(1)**.

However, we continued efforts to keep the chiral-inducing element at a low amount, and pursued higher selectivity by exploring novel phosphoric acids which may be more efficient than TRIP. It is unclear whether the low enantioselectivity was a result of undesired background reaction with racemic palladium species, or whether the chiral environment is not discerning between the two diastereomeric transition-states. The increase in enantioselectivity with higher catalyst loading does indicate that the former is probably true.

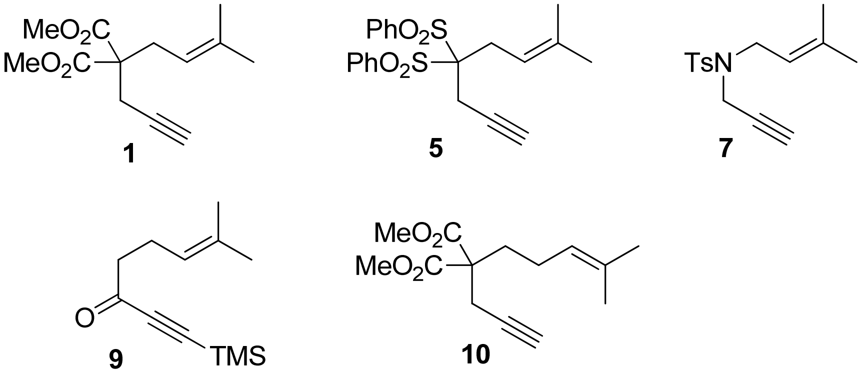
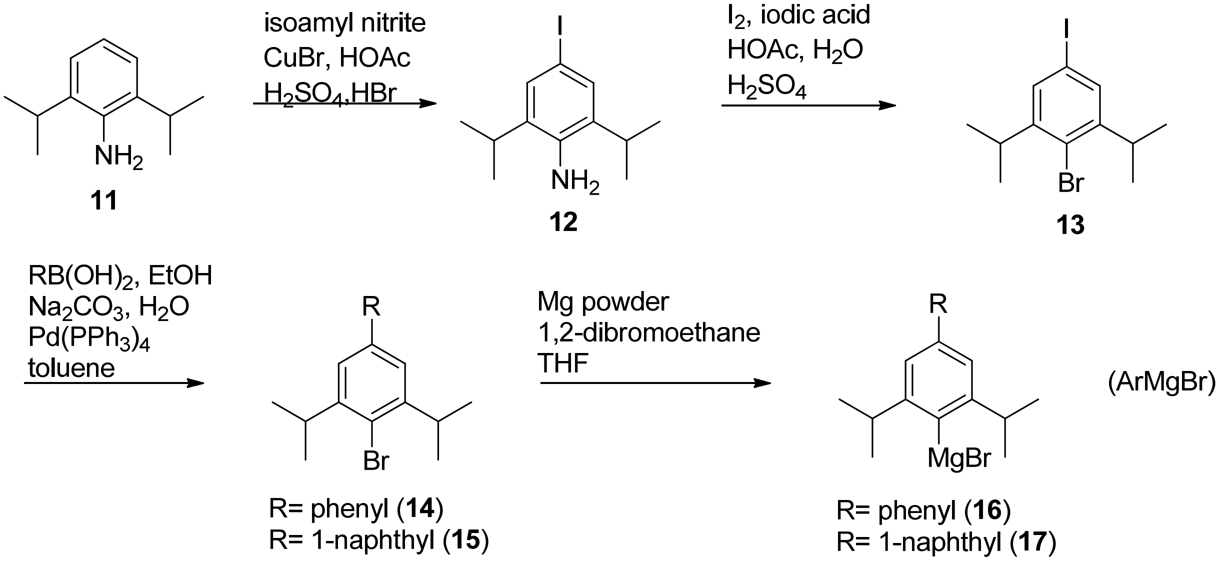


Figure 4. Substrates synthesized for 1,6-enyne cycloisomerization.

With these optimized reaction conditions, we decided to study the substrate scope of this system. Substrates (Figure 4) with different linkers were synthesized following previously reported procedures and subjected to the standard reaction conditions. Initial studies with substrates **9** and **10** were not promising – formation of desired product was not observed in either case when acetic acid was used as the proton source (following Trost's original racemic reaction procedure). The results of the substrate scope study are summarized in Table 4. Both substrates **5** and **7** did not react with high enantioselectivity, achieving only 53% and 17% ee, respectively.

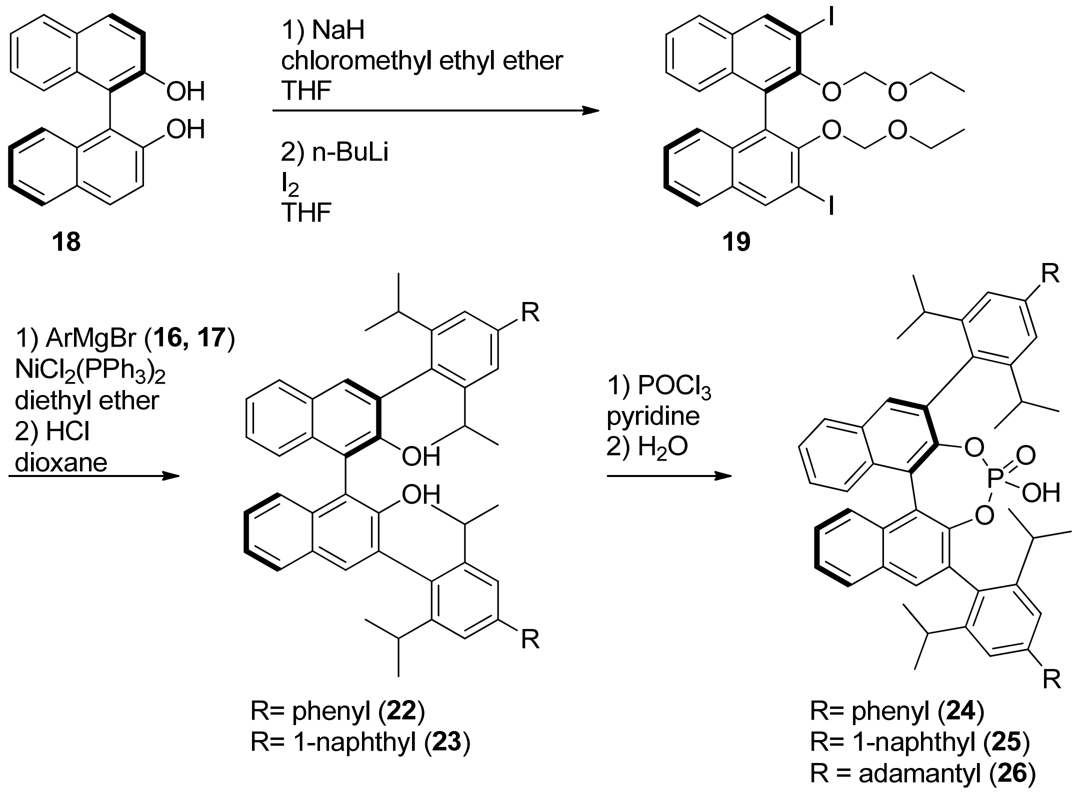
This was not a promising result because our method encountered the same problems as others - specifically, limited substrate scope with regard to substitution patterns on the alkene as well as functional groups in the central tether position. Thus, the TRIP phosphate ligand is not necessarily more versatile than phosphine ligands which were somewhat effective in previous reports.

To address this problem, novel chiral phosphoric acids were synthesized to investigate the effect of minor changes in steric and electronic properties of the chiral phosphoric acid on enantioselectivity and substrate scope. We aimed to extend the chiral information from the 3,3'-positions on the BINOL scaffold and project steric bulk further from the phosphate center. The ionic nature of the phosphate is important for interactions with the metal; however, the phosphate is not interacting with the substrate itself, and thus may be further away from the actual bond-forming event. To this end, analogs of TRIP were synthesized that contained different para-position substitutions (Scheme 4; **24, 25**). A synthetic scheme that utilized an efficient Suzuki coupling reaction, followed by a Kumada coupling reaction, was seen as an expedient way to explore electronic and steric effects at that position.



Scheme 3. Synthesis of aryl Grignard reagents **16** and **17**.

This approach took advantage of the many diversely substituted phenylboronic acids that are commercially available, thereby allowing us to prepare chiral phosphoric acids with substituents of varying steric size without significantly changing the electronic properties. Conversely, we could explore electron-donating and electron-withdrawing substituents without significantly changing the steric properties. For example, comparing a 4-methoxyphenyl substitution with a phenyl substitution keeps the size of the phenyl group but provides a substituent with significantly different electronics. We began by synthesizing para-phenyl and para-1-naphthyl substituted phosphoric acids. The common Suzuki coupling partner **13** was synthesized from commercially available 2,6-diisopropylaniline in two steps. Reaction of **13** with either phenyl boronic acid or 1-naphthyl boronic acid followed by treatment with Mg powder generated aryl Grignard reagents (Kumada coupling partners) **16** and **17** (Scheme 3).

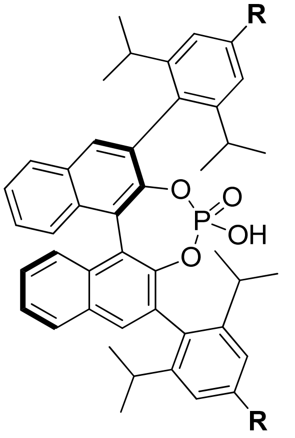


Scheme 4. Synthetic route toward novel chiral phosphoric acids.

These aryl Grignard reagents were coupled with **19**, which was prepared from (*R*)-BINOL **18** in two steps (Scheme 4). The Kumada coupling products were deprotected with HCl to reveal the respective diols (**22, 23**). The phosphoric acids were then obtained by subjecting each diol to $POCl_3$ followed by hydrolysis. With these two novel catalysts (**24, 25**) in hand, we proceeded with substrates **1, 5,** and **7** to determine the impact on substrate scope of phenyl and 1-naphthyl substitutions in the para-position.

Phenyl substituted chiral acid **24** demonstrated an approximately 17% increase in enantioselectivity for substrates with three different linkers. However, the bulkier naphthyl **25** provided similar enantioselectivity as the isopropyl substituted TRIP. Therefore, we have demonstrated that changing the size of the substituent at the para-position does have an effect on enantioselectivity, despite being distant from the phosphoric acid proton.

entry	substrate	chiral acid	R	ee^{a} (%)
1	1	4	i-Pr	83
2	3	4	i-Pr	53
3	5	4	i-Pr	17
4	1	24	Ph	79
5	3	24	Ph	66
6	5	24	Ph	32
7	1	25	naphthyl	73
8	3	25	naphthyl	53
9	5	25	naphthyl	26
10	1	26	adamantyl	- ^{b}
11	3	26	adamantyl	49
12	5	26	adamantyl	19

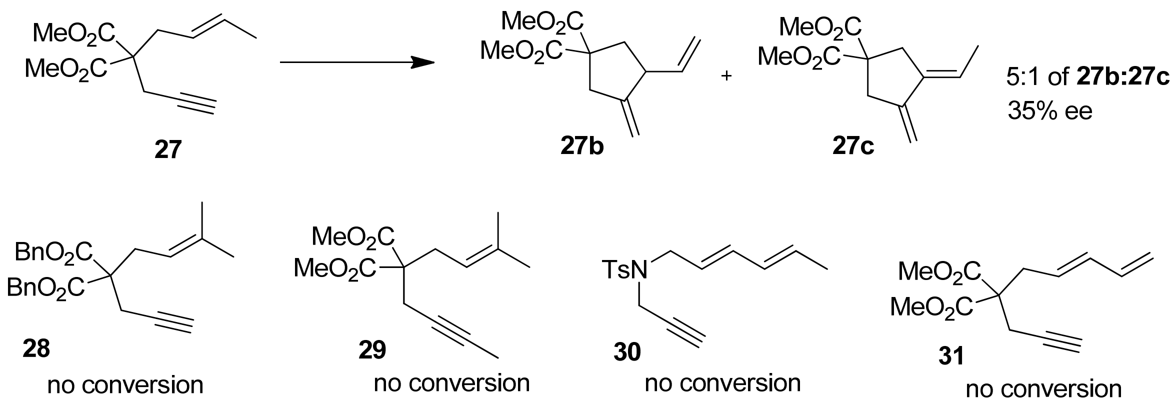


[a] Enantiomeric excess determined by chiral HPLC. [b] Reaction did not proceed.

Table 4. Enantioselectivity of reaction **(1)** using various chiral phosphoric acids.

Installation of the bulky adamantyl group helped probe the steric space at the para-position, while being readily prepared *via* our current synthetic approach. Catalyst **26** was prepared in similar yields and provided enantioselectivity, except in the case of substrate **1** where low conversion was observed. In addition, adamantyl was the sole nonaromatic substituent in the catalyst.

In addition to the substrates reported above, there were diverse compounds found in the literature which did not work for our reaction. Shown below in Figure 5 are substrates which did not undergo the desired cyclization reaction – thus the effective substrate scope is limited to what is presented above. Small changes to the alkene substitution pattern and linker between the alkene and alkyne were not tolerated with our catalytic system, as was the case in most precedented reports of this reaction.



[a] Conditions: $Pd_2(dba)_3CHCl_3$ (2.5 mol%), TRIP (10 mol%), PPh_3 (5 mol%), toluene, rt,18-24 h.
[b] Conversion determined by NMR.

Figure 5[a,b,c]. Additional substrates explored revealed scope limitations.

It is important to note that more recently a report has been published which utilized TRIP as a counterion in iridium-catalyzed cycloisomerization reactions. Although a different metal was used, a similar goal in the combination of BINOL-derived phosphoric acids with the pi-activation of metals for inducing enantioselectivity in enyne cycloisomerization reactions was achieved. In our work, analogs of TRIP were synthesized, and we demonstrated that substitutions in the para-position of the 3,3'-aromatic rings have the potential to improve enantioselectivity. These results are further evidence that BINOL-derived phosphoric acids are not only versatile Brönsted acids, but can also act as sterically and electronically tunable ligands in transition-metal chemistry.

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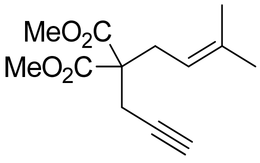
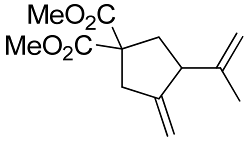
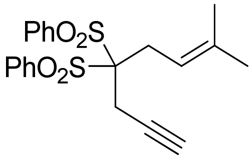


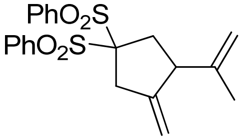
1 **1** was prepared following previously reported methods.[1] Spectroscopic data are consistent with previously reported values. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.909-4.857 (m, 1H), 3.724 (s, 6H), 2.782-2.760 (m, 4H), 1.991 (t, 1H, *J* = 2.7 Hz), 1.683 (s, 3H), 1.639 (s, 3H).



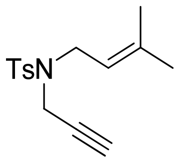
2 $Pd_2(dba)_3CHCl_3$ (0.027 g, 0.0053 mmol, 0.05 equiv), triphenylphosphine (0.0014 g, 0.0053 mmol, 0.05 equiv), and (*S)*-TRIP (0.0048 g, 0.0053 mmol, 0.05 equiv) were stirred in toluene (0.60 mL) for 20 min. A solution of **1** (0.025 g, 0.105 mmol, in 0.4 mL of toluene) was then added by syringe, and the reaction mixture was stirred for 18-24 h at rt. The reaction mixture was purified by silica gel chromatography (3.5% ethyl acetate in hexanes) to afford **2** and starting material **1** as an inseparable mixture. Spectroscopic data is consistent with previously reported values.[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.02 (bs, 1H) 4.84 (bs, 2H), 4.80 (d, 1H, *J* = 2.4 Hz), 3.75-3.72 (m, 6H), 3.31-3.26 (m, 1H), 3.10-3.06 (m, 1H), 2.95-2.90 (m, 1H), 2.55-2.50 (m, 1H), 2.16-2.13 (m, 1H), 1.65 (s, 3H). % ee was determined by HPLC with a Chiralpak AD-H column (99.9% hexane: 0.01% 2-propanol), t_r = 8.752 min for major enantiomer, t_r = 8.016 min for minor enantiomer.



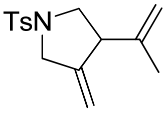
5 Compound **5** was prepared following previously reported methods.[1] Spectroscopic data is consistent with previously reported values. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14-8.12 (m, 4H), 7.74-7.70 (m, 2H), 7.60-7.57 (m, 4H), 5.40 (t, 1H, *J* = 6.4 Hz), 3.18 (d, 2H, *J* = 2.4 Hz), 3.05 (d, 2H, *J* = 6.4 Hz), 2.11 (t, 1H, *J* = 2.8 Hz), 1.77 (s, 3H), 1.58 (d, 3H, *J* = 2.4 Hz).



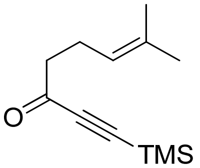
6 Compound **6** was prepared following the procedure described for **2**. Spectroscopic data is consistent with previously reported values.[2] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08-8.02 (m, 4H), 7.75-7.68 (m, 2H), 7.62-7.57 (m, 4H), 4.951 (d, 1H, *J* = 2.1 Hz), 4.86-4.77 (m, 3H), 3.53-3.46 (m, 1H), 3.44-3.15 (m, 2H), 2.64 (d, 2H, *J* = 9.9 Hz), 1.57 (s, 3H). % ee was determined by HPLC with a Chiralpak AD-H column (90% hexane: 10% 2-propanol), t_r = 18.453 min for major enantiomer, t_r = 19.941 min for minor enantiomer.



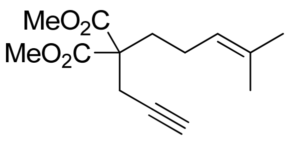
7 Compound **7** was prepared following previously reported methods.[3] Spectroscopic data is consistent with previously reported values. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.74 (d, 2H, J = 8.0 Hz), 7.30 (d, 2H, J = 8.4 Hz), 5.11 (t, 1H, J = 7.2 Hz), 4.07 (d, 2H, J = 2.4 Hz), 3.82 (d, 2H, J = 7.2 Hz), 2.43 (s, 3H), 1.98 (t, 1H, J = 2.4 Hz), 1.73 (s, 3H), 1.68 (s, 3H).



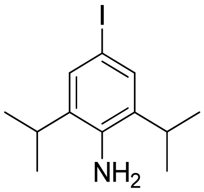
8 Compound **8** was prepared following the procedure described for **2**. Spectroscopic data is consistent with previously reported values.[3] ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.70 (d, 2H, J = 8.1 Hz), 7.33 (d, 2H, J = 8.1 Hz), 5.01-4.99 (m, 1H), 4.87-4.80 (m, 3H), 3.88 (d, 1H, J = 13.8 Hz), 3.81-3.75 (m, 1H), 3.48-3.43 (m, 1H), 3.30 (bt, 1H, J = 7.2 Hz), 3.14-3.08 (m, 1H), 2.43 (s, 3H), 1.58 (s, 3H). % ee was determined by HPLC with a Chiralpak AD-H column (95% hexane: 5% 2-propanol), t_r = 10.955 min for major enantiomer, t_r = 12.485 min for minor enantiomer.



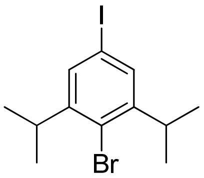
9 Compound **9** was prepared following previously reported methods.[3] Spectroscopic data is consistent with previously reported values. ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.08 (t, 1H, J = 6.8 Hz), 2.59 (t, 2H, J = 7.6 Hz), 2.36 (q, 2H, J = 6.8 Hz), 1.69 (s, 3H), 1.63 (s, 3H), 0.25 (s, 9H).



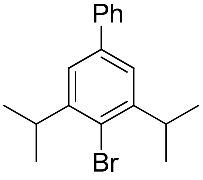
10 Compound **10** was prepared following previously reported methods.[4] Spectroscopic data is consistent with previously reported values. ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.12-5.08 (m, 1H), 3.74 (s, 6H), 2.86 (d, 2H, J = 2.4 Hz), 2.11-2.07 (m, 2H), 2.01 (bs, 1H), 1.92-1.86 (m, 2H), 1.68 (s, 3H), 1.59 (bs, 3H).



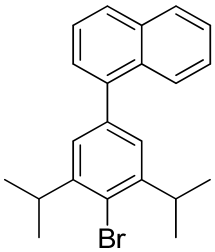
12 Iodine (4.81 g, 1.90 mmol, 0.40 equiv) and iodic acid (1.76 g, 1.02 mmol, 0.215 equiv) were combined in HOAc (75 mL), H_2O (2.0 mL), and H_2SO_4 (conc., 0.50 mL) at rt and stirred for 10 min, followed by addition of 2,6-dimethylaniline (8.40 g, 47.4 mmol). The reaction mixture was heated at 70 °C for 5 h, then returned to room temperature and quenched with 200 mL of K_2CO_3 (sat aq). The reaction mixture was diluted with ethyl acetate and the organic layer was washed with sodium bisulfite (aq), then brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude oil was filtered with a plug of silica gel to provide **12** (12.0 g, 84%). Spectroscopic data is consistent with previously reported values.[5] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27 (s, 2H), 3.73 (bs, 2H), 2.83 (septet, 2H, *J* = 6.9 Hz), 1.23 (d, 12H, *J* = 6.9 Hz).



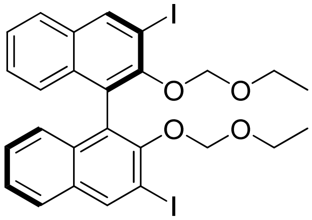
13 Aniline **12** (5.00 g, 16.5 mmol), HOAc (40 mL), and H_2SO_4 (16.5 mL) were stirred at 0 °C for 10 min, followed by dropwise addition of isoamyl nitrite (3.57 g, 30.5 mmol, 1.85 equiv). This mixture was stirred at 0 °C for 30 min and was added to a stirring solution of CuBr (3.31 g, 23.1 mmol, 1.40 equiv) in HBr (reagent grade, 48%, 60mL) at 0 °C. The reaction mixture was stirred at room temperature for 18 h, then poured into ice water. This mixture was extracted with hexanes (3 x 75 mL), and the combined organic layers were sequentially washed with sodium bisulfite (sat aq), HCl (10% v/v aq), then brine. The organic layer was dried over $MgSO_4$, filtered through Celite, and concentrated in vacuo. The crude product was purified by silica gel chromatography (100% hexanes) to provide oil **13** (4.05 g, 66%). Spectroscopic data is consistent with previously reported values.[6] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 2H), 3.43 (septet, 2H, *J* = 6.8 Hz), 1.23 (d, 12H, *J* = 6.8 Hz).



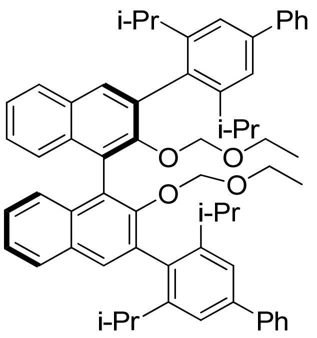
14 Solutions of Na_2CO_3 (0.432 g, 4.08 mmol, 3.0 equiv) in H_2O (2.0 mL) and phenylboronic acid (0.249 g, 2.04 mmol, 1.5 equiv) in ethanol (2.5 mL) were added to **13** (0.500 g, 1.36 mmol) in toluene (6.5 mL) at rt. The reaction mixture was then heated at 70 °C for 18 h, then cooled to rt and partitioned between diethyl ether and H_2O. The aqueous layer was extracted with diethyl ether and the organic layers were combined and washed with NaOH (1 M, aq), then brine. The organic layer was dried over $MgSO_4$, filtered through filter paper, and concentrated in vacuo. Silica gel chromatography (100% hexanes) afforded oil **14** (0.40 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.55 (m, 2H), 7.44 (t, 2H, *J* = 7.8 Hz), 7.38-7.31(m, 3H), 3.52 (septet, 2H, *J* = 6.9 Hz), 1.29 (d, 12H, *J* = 6.0 Hz). ^{13}C NMR (400 MHz, CDCl$_3$): δ 148.18, 141.22, 140.58, 128.90, 127.49, 127.28, 125.96, 123.25, 34.82, 23.25. HRMS calcd for C$_{18}$H$_{21}$Br 316.0827, found 316.0824.



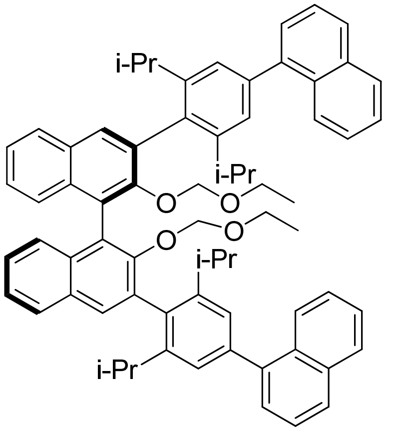
15 Compound **15** was prepared following the procedure described for **14**. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.94-7.85 (m, 3H), 7.56-7.44 (m, 4H), 7.27 (s, 2H), 3.60 (q, 2H, *J* = 7.2 Hz), 1.29 (d, 12H, *J* = 6.8 Hz). ^{13}C NMR (400 MHz, CDCl$_3$): δ 147.65, 139.95, 139.76, 133.85, 133.45, 131.54, 128.38, 127.89, 127.78, 126.84, 126.19, 126.03, 125.89, 125.84, 125.60, 125.40, 34.70, 23.15. HRMS calcd for C$_{22}$H$_{23}$Br$_1$ 366.0983, found 366.0988.



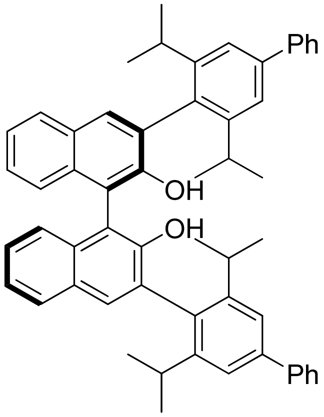
19 To a -78 ^{o}C solution of protected (*R*)-BINOL (4.0 g, 9.9 mmol) in THF (35 mL) was added BuLi (2.5 M in hexanes, 13.9 mL, 13.4 mmol, 3.5 equiv). The reaction mixture was stirred at 0 ^{o}C for 1 h, then cooled to -78 ^{o}C. Iodine (9.40 g, 37.1 mmol, 3.75 equiv) was added and the reaction mixture was warmed to 0 ^{o}C for 45 min. The reaction was then quenched with Na$_2$CO$_3$ (sat aq), and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with Na$_2$CO$_3$ (sat aq), then brine. The organic layer was dried over MgSO$_4$, filtered through filter paper, and concentrated in vacuo to afford crude **19** (90% clean by NMR, 3.60 g, 56%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.55 (s, 2H), 7.79 (d, 2H, *J* = 8.0 Hz), 7.44-7.40 (m, 2H), 7.32-7.18 (m, 2H), 7.18-7.16 (m, 2H), 4.89 (d, 2H, *J* = 5.6 Hz), 4.73 (d, 2H, *J* = 6.0 Hz), 3.12-3.04 (m, 2H), 2.72-2.64 (m, 2H), 0.68-0.66 (m, 6H). ^{13}C NMR (400 MHz, CDCl$_3$): δ 152.23, 139.98, 133.75, 132.19, 127.19, 126.83, 126.46, 126.07, 125.81, 98.12, 92.70, 65.01, 14.41. HRMS calcd for C$_{26}$H$_{24}$O$_4$I$_2$ 653.9764, found 653.9763.



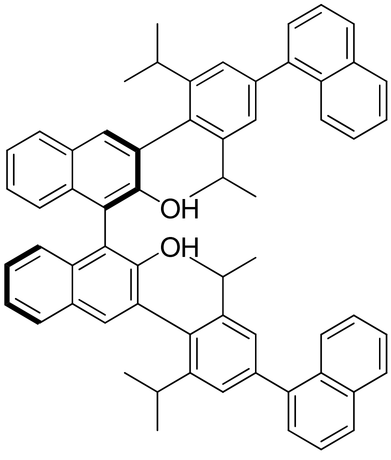
20 To a flame-dried flask, magnesium powder (0.035 g, 1.4 mmol, 1.0 equiv) and THF (2.0 mL) were added, followed by **14** (1 drop) and 1,2-dibromoethane (4 drops). After 5 min, the remainder of **14** (0.430 g, 1.39 mmol) was added dropwise, and the reaction mixture heated at 65 ^{o}C for 16 h. The resulting Grignard solution was cooled to rt and added by syringe to a solution of **19** (0.150 g, 0.23 mmol), $NiCl_2(PPh_3)_2$ (0.018 g, 0.023 mmol, 0.1 equiv) in diethyl ether (3.0 mL), and stirred for 4 h. Solid NH_4Cl was added to the reaction mixture, which was stirred for 5 min, and filtered with Celite. Silica gel chromatography (30-50% methylene chloride in hexanes) afforded **20** (0.110 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96-7.94 (m, 2H), 7.89 (s, 2H), 7.74-7.72 (m, 4H), 7.55-7.39 (m, 16H), 4.40 (s, 4H), 3.00 (septet, 4H, *J* = 6.8 Hz), 2.66-2.47 (m, 4H), 1.44-1.25 (m, 18H), 1.11-1.10 (m, 6H), 0.54 (t, 6H, *J* = 6.8 HZ). ^{13}C NMR (400 MHz, $CDCl_3$): δ 152.44, 148.34, 147.62, 142.09, 140.90, 135.10, 133.86, 133.79, 130.90, 130.43, 128.73, 127.92, 127.24, 127.10, 126.33, 126.22, 126.10, 124.98, 121.95, 121.59, 96.61, 63.75, 31.11, 30.97, 26.00, 25.31, 23.35, 23.20, 14.38.



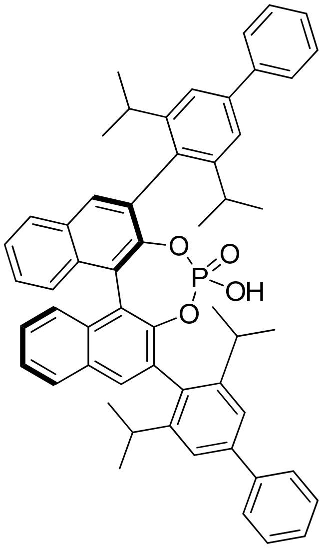
21 Compound **21** was prepared following the procedure described for preparation of **20**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18-8.16 (m, 2H), 8.06-7.99 (m, 8H), 7.68-7.46 (m, 18H), 4.55 (q, 4H, *J* = 5.2 Hz), 3.16-3.11, 3.14 (sextet, 4H, *J* = 6.4 Hz), 2.88-2.77 (m, 4H), 1.48-1.36 (m, 18H), 1.25-1.19 (m, 6H), 0.76-0.72 (m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 152.46, 147.95, 147.18, 141.16, 140.29, 134.93, 134.12, 134.01, 133.93, 131.79, 131.11, 130.55, 128.46, 128.04, 127.56, 126.97, 126.48, 126.25, 126.22, 126.14, 126.04, 125.80, 125.54, 125.10, 124.93, 124.58, 96.74, 63.96, 34.75, 31.17, 31.05, 26.06, 25.37, 25.32, 23.44, 23.34, 14.67.



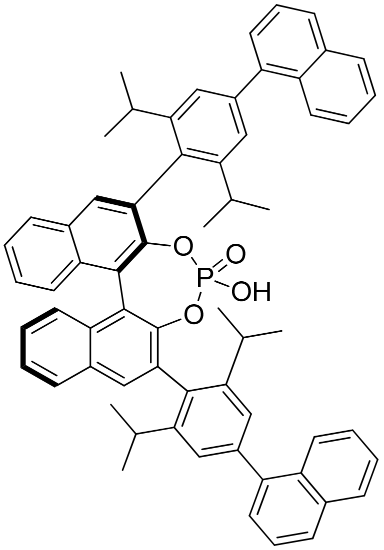
22 To a stirring solution of **20** (0.110 g, 0.126 mmol) in dioxane (2.5 mL) was added HCl (conc., 0.35 mL). The reaction mixture was heated at 60 °C for 8 h, then cooled to rt. The reaction mixture was diluted with methylene chloride, and the organic layer washed with sodium bicarbonate (sat aq), and then brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo to afford crude **22** (0.100 g, 0.132 mmol). This material was used as is in the next step. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.98 (m, 2H), 7.90 (s, 2H), 7.76-7.74 (m, 4H), 7.59-7.36 (m, 16H), 5.08 (s, 2H), 3.01 (quintet, 2H, *J* = 6.8 Hz), 2.86 (quintet, 2H, *J* = 6.8 Hz), 1.385-1.18 (m, 21H), 0.98-0.91 (m, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 150.67, 148.48, 148.42, 141.80, 141.73, 133.49, 132.45, 130.89, 128.16, 128.83, 128.75, 128.41, 127.35, 127.30, 126.97, 124.50, 124.07, 122.22, 122.18, 112.88, 31.08, 31.05, 24.38, 24.31, 23.94, 23.77, 22.84, 22.71. HRMS calcd for $C_{56}H_{54}O_2Li_1$ 765.4278, found 765.4294.



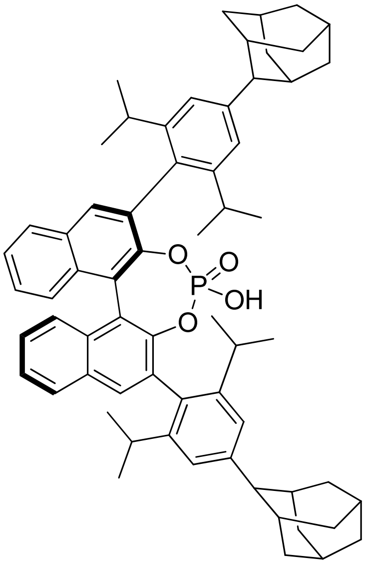
23 Compound **23** was prepared following the procedure described for preparation of **22**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06-8.04 (m, 2H), 7.97-7.88 (m, 7H), 7.60-7.38 (m, 15H), 7.27 (s, 4H), 5.08 (s, 2H), 2.99 (m, 2H), 2.83 (m, 2H), 1.28-1.26 (m, 9H), 1.20-1.16 (m, 9H), 1.12-1.11 (m, 3H), 0.89-0.84 (m, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 150.73, 148.00, 147.93, 141.04, 140.79, 133.95, 133.50, 132.18, 131.69, 130.89, 129.21, 128.95, 128.43, 128.40, 127.64, 127.01, 126.18, 126.08, 125.79, 125.49, 125.11, 124.50, 124.10, 113.00, 34.71, 31.06, 24.35, 24.00, 23.80. HRMS calcd for $C_{64}H_{58}O_2Li_1$ 865.4591 found 865.4607.



24 To a solution of **22** (0.100 g, 0.132 mmol) in pyridine (0.50 mL) was added by syringe $POCl_3$ (0.040 g, 0.26 mmol, 2.0 equiv), and the reaction mixture was heated at 60 °C for 15 h. The reaction mixture was then cooled to 0 °C, charged with 0.1 mL of H_2O, and returned to heating at 60 °C for 7 h. After cooling to rt, the reaction mixture was diluted with methylene chloride, and washed with HCl (10% v/v aq) two times. The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. Silica gel chromatography (0% MeOH in 1:1 methylene chloride: hexanes to 5% MeOH in 1:1 methylene chloride : hexanes) provided a white powder which was then dissolved in methylene chloride and washed with HCl (10% v/v aq). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo to provide **24** (0.070 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96-7.94 (m, 2H), 7.88 (s, 2H), 7.55-7.54 (m, 6H), 7.40-7.26 (m, 14H), 6.07 (brs, 2H), 2.66-2.57 (m, 4H), 1.10 (d, 6H, *J* = 6.4 Hz), 0.99 (d, 6H, *J* = 6.4 Hz), 0.91 (d, 6H, *J* = 6.8 Hz), 0.71 (d, 6H, *J* = 6.4 Hz). ^{13}C NMR (400 MHz, $CDCl_3$): δ 148.61, 148.12, 145.71, 145.62, 141.85, 141.02, 132.85, 132.51, 132.35, 131.78, 130.97, 127.51, 128.24, 127.33, 127.26, 126.98, 126.36, 125.76, 122.24, 122.01, 121.22, 31.07, 30.76, 26.38, 24.88, 23.18, 22.71. ^{31}P NMR (400 MHz, $CDCl_3$): δ 2.96. FTMS calcd for $C_{56}H_{52}O_4P_1$ 819.36, found 819.3603.



25 Compound **25** was prepared following the procedure described for preparation of **24.** ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.00-7.96 (m, 6H), 7.86-7.79 (m, 4H), 7.57-7.54 (m, 4H), 7.40-7.22 (m, 14H), 6.72 (brs, 2H), 2.75-2.67 (m, 4H), 1.12-1.10 (m, 6H), 1.03-1.02 (m, 6H), 0.92-0.91 (m, 6H), 0.73 (brs, 6H). ^{13}C NMR (400 MHz, CDCl$_3$): δ 148.21, 147.60, 145.81, 145.72, 140.77, 140.42, 133.75, 132.70, 132.39, 131.85, 131.57, 131.03, 128.22, 128.07, 127.34, 126.92, 126.44, 126.29, 125.98, 125.82, 125.55, 125.25, 125.18, 124.13, 122.10, 31.10, 30.77, 26.35, 24.91, 23.26, 22.83. ^{31}P NMR (400 MHz, CDCl$_3$): δ 2.93. FTMS calcd for $C_{64}H_{56}O_4P_1$ 919.39, found 919.3893.



26 Compound **26** was prepared following the procedure described for preparation of **24.** ^{1}H NMR (400 MHz, CDCl$_3$): 7.90(m, 2H), 7.88(s, 2H), 7.53-7.52(m, 2H), 7.40-7.36(m, 4H), 7.11-7.06(m, 4H), 2.67-2.52(m, 4H), 2.10 (brs, 6H), 1.92(brs, 12H), 1.75(brs, 6H), 1.05-0.94(m, 18H). ^{13}C NMR (400 MHz, CDCl$_3$): δ 150.6, 147.5, 146.9, 145.9, 145.8, 132.5, 132.4, 131.1, 130.9, 128.1, 127.4, 126.1, 125.6, 122.1, 119.4, 118.4, 43.1, 36.9, 36.3, 31.1, 30.8, 29.7, 29.0, 26.4, 25.1, 23.4, 22.6. ^{31}P NMR (400 MHz, CDCl$_3$): δ 2.48.

Compounds **27-31**, see references below.

References

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2. Porcel S., Echavarren A. M. *Angew. Chem. Int. Ed*. **2007**, *46*, 2672-2676.

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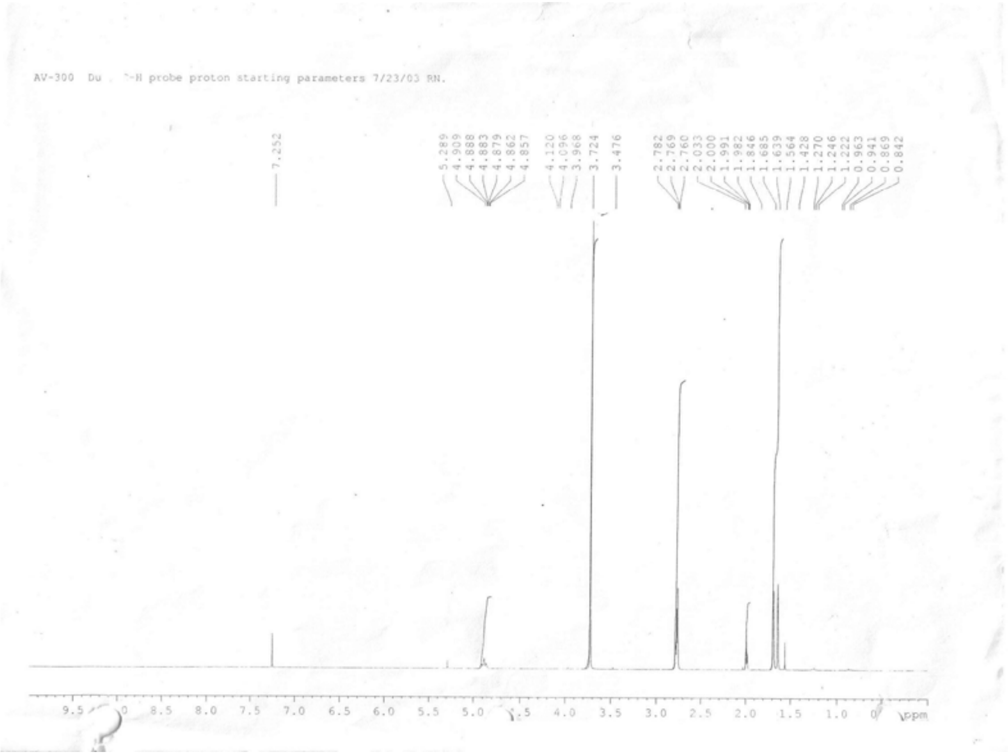
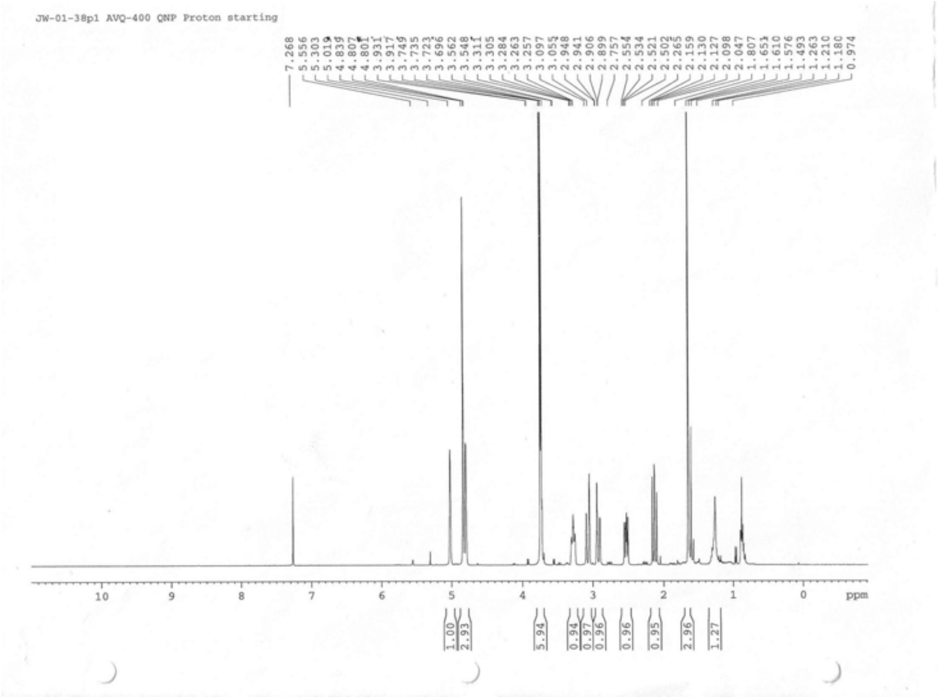
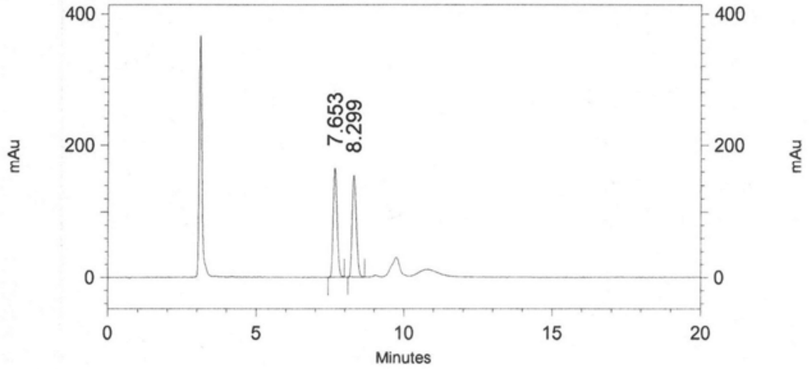
1 ^{1}H NMR



2 ^{1}H NMR



2 HPLC 99.9% Hexanes, 0.01% Isopropylalcohol, Racemic



1: 215 nm, 4 nm Results

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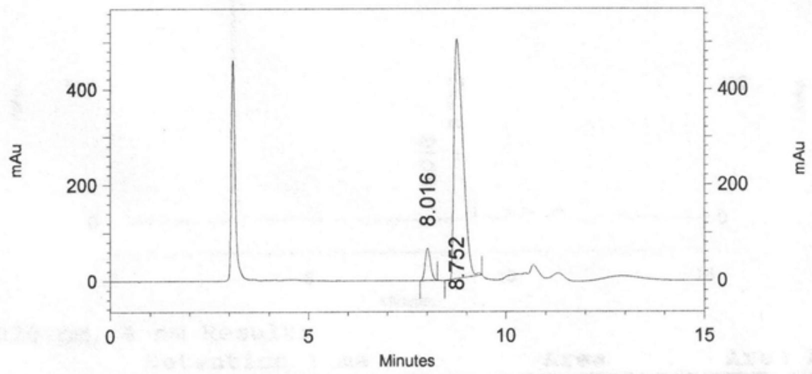
8.299	1540918	49.987

2 HPLC 99.9% Hexanes, 0.01% Isopropylalcohol, Chiral



1: 210 nm, 4 nm Results

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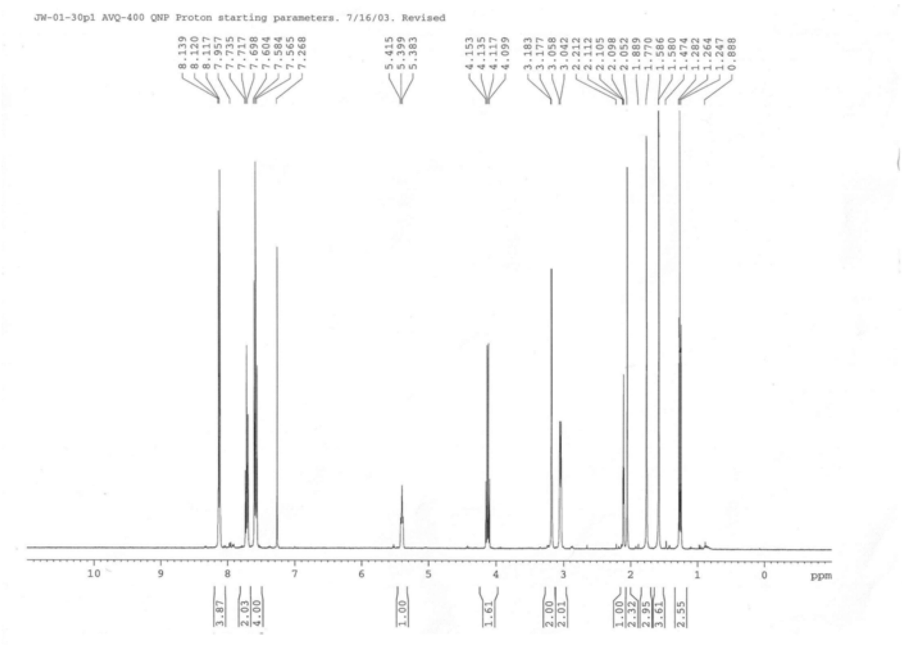
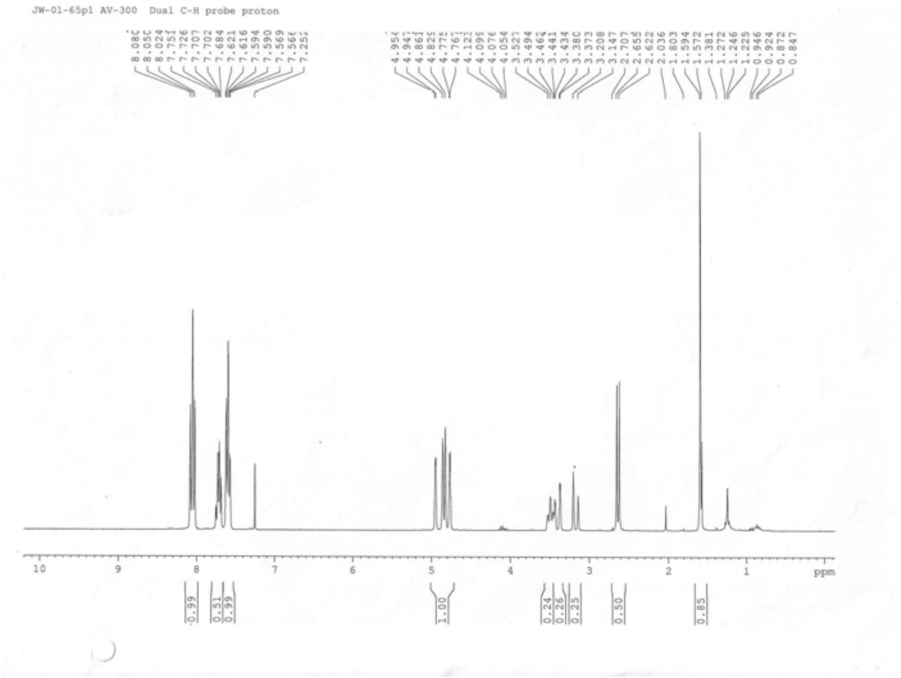
8.752	7839740	92.637

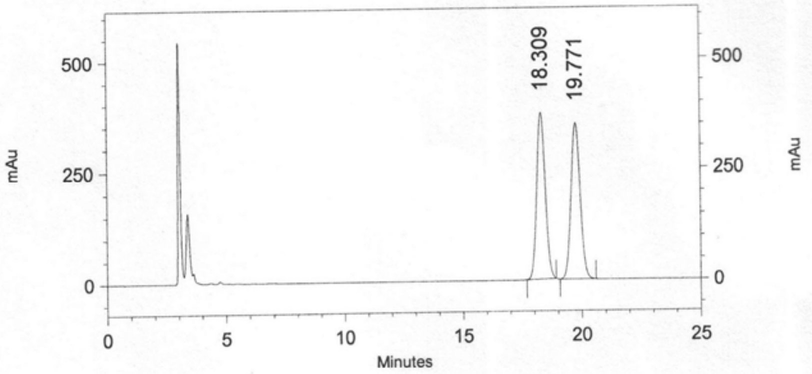
5 ^{1}H NMR



6 ^{1}H NMR



6 HPLC 90% Hexanes, 10% Isopropylalcohol, Racemic



1: 215 nm, 4 nm Results

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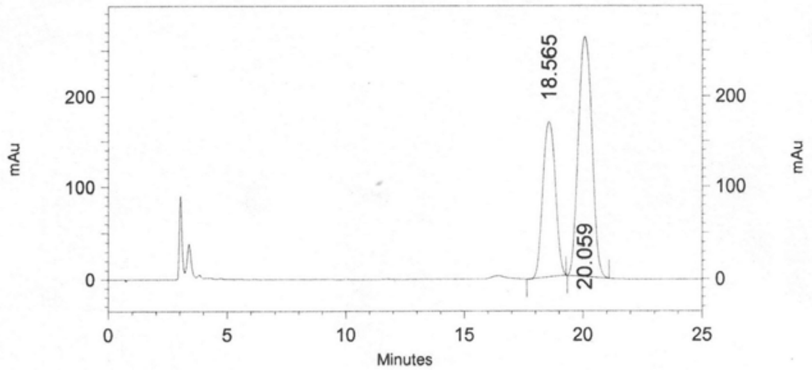
6 HPLC 90% Hexanes, 10% Isopropylalcohol, Chiral



2: 218 nm, 4 nm Results

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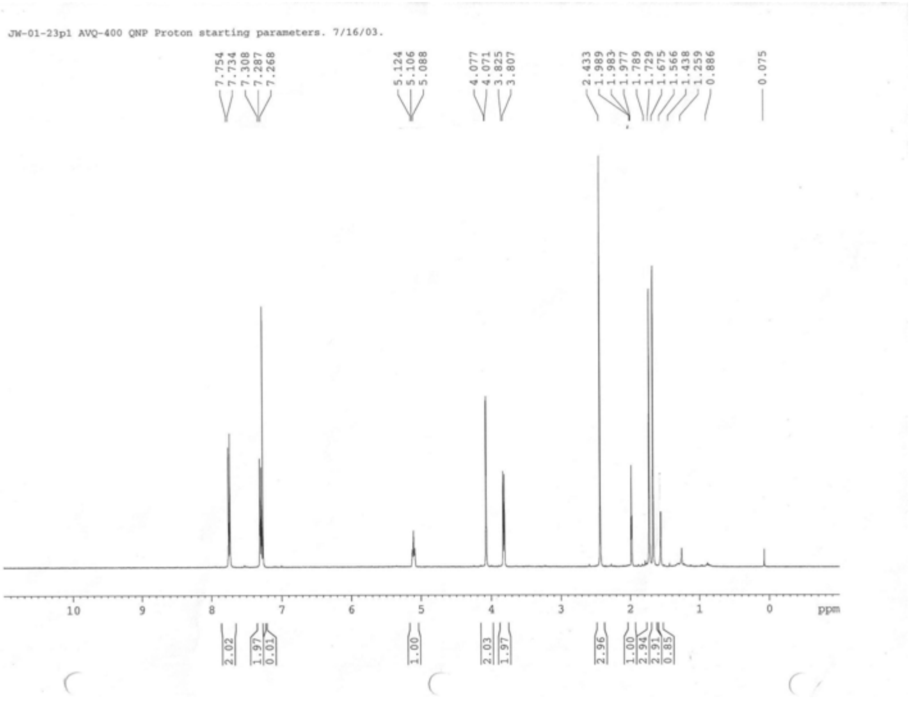
7 ^{1}H NMR



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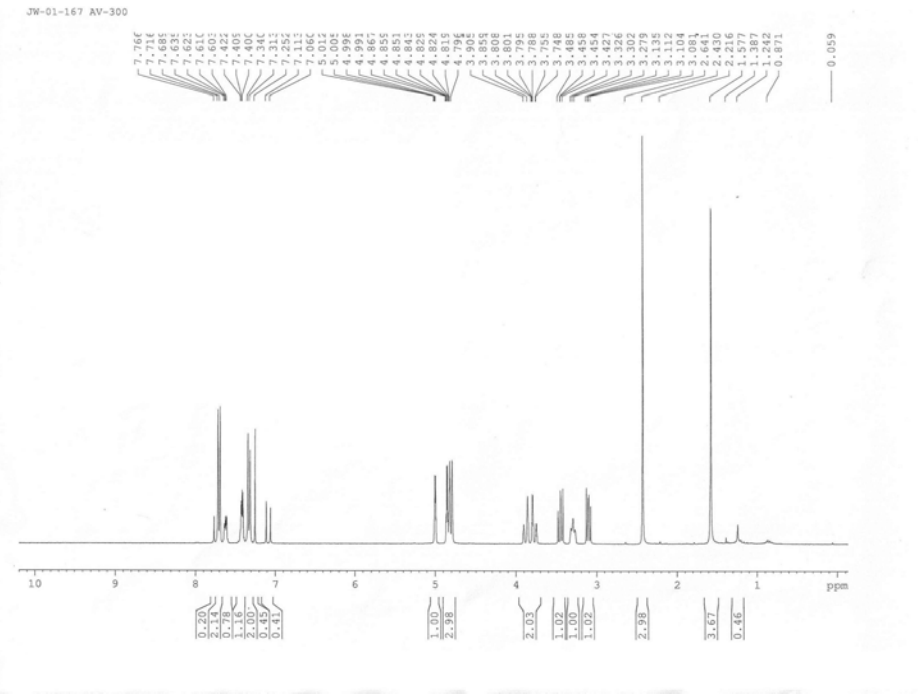
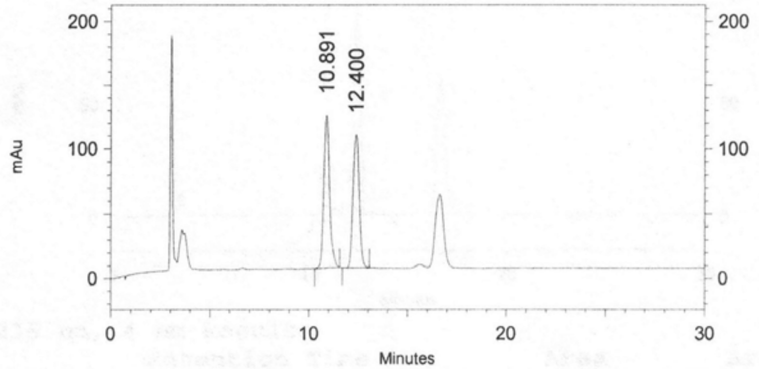


8 HPLC 95% Hexanes, 5% Isopropylalcohol, Racemic



1: 211 nm, 4 nm Results

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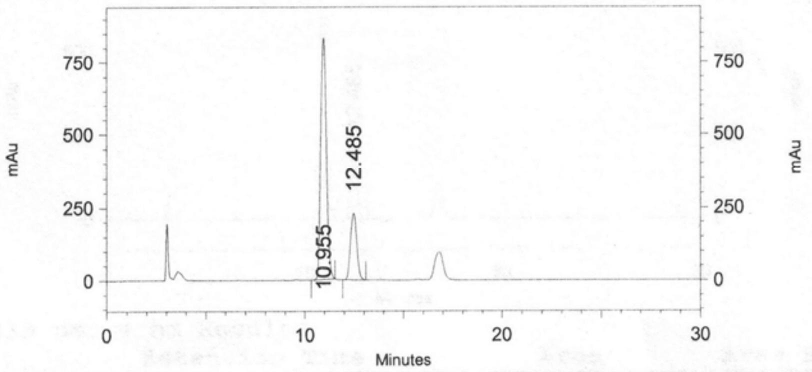
8 HPLC 95% Hexanes, 5% Isopropylalcohol, Chiral



1: 210 nm, 4 nm Results

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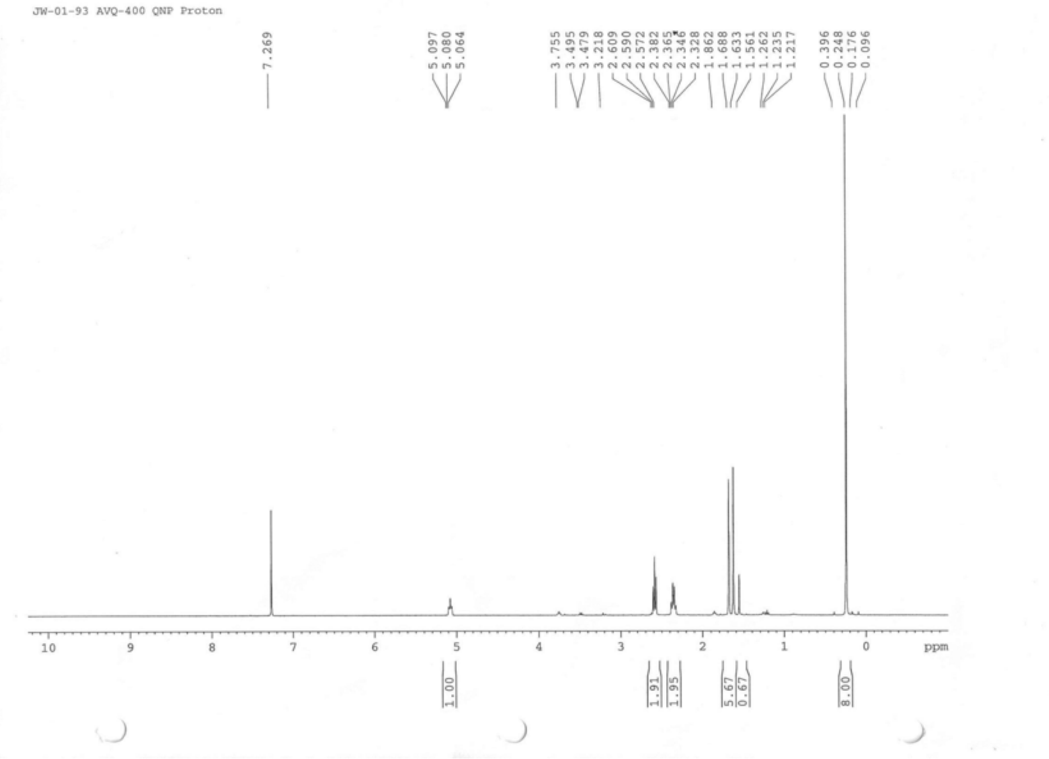
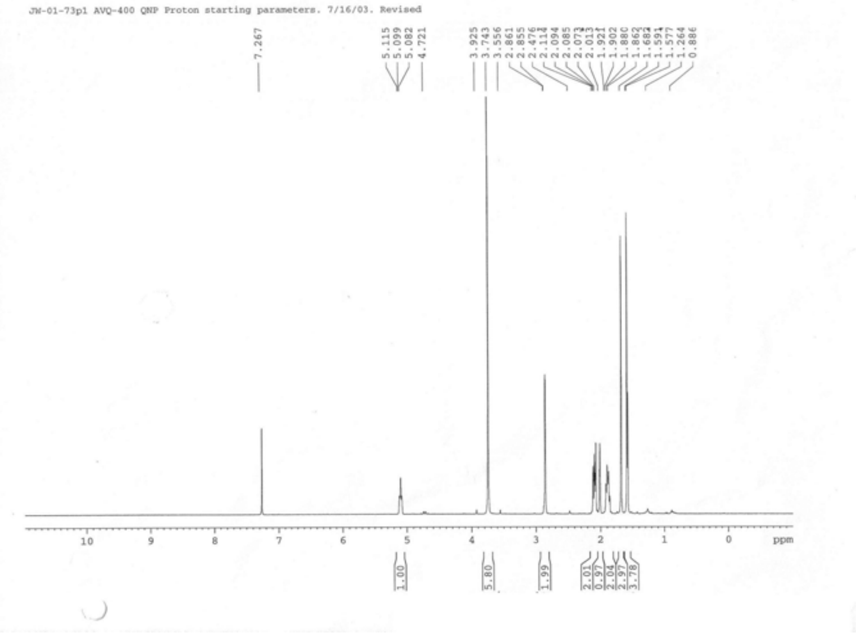
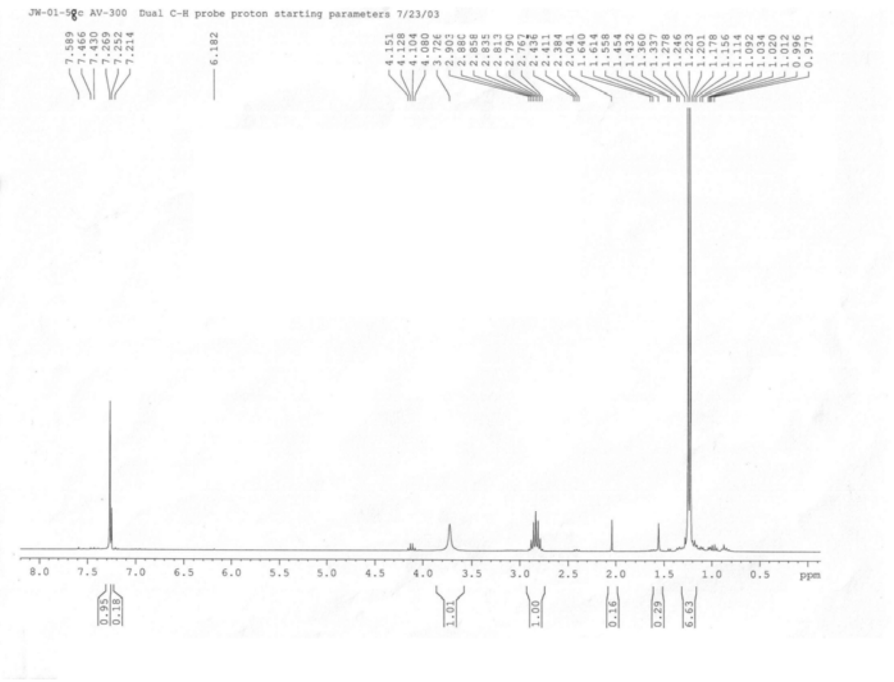
9 ^{1}H NMR



10 ^{1}H NMR



12 ^{1}H NMR



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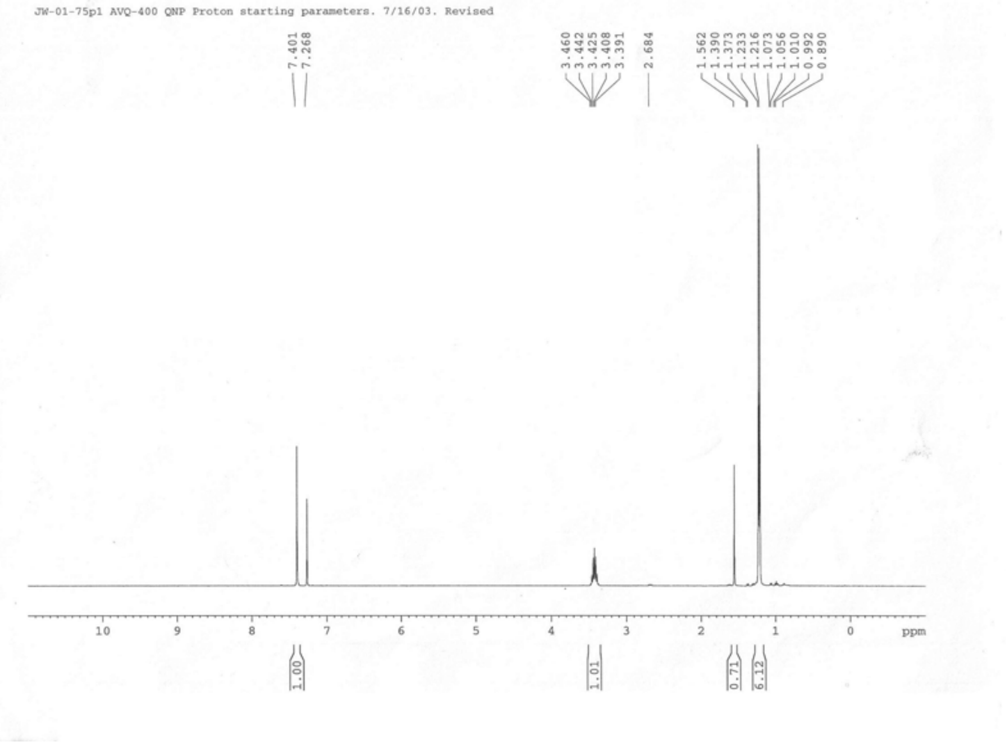

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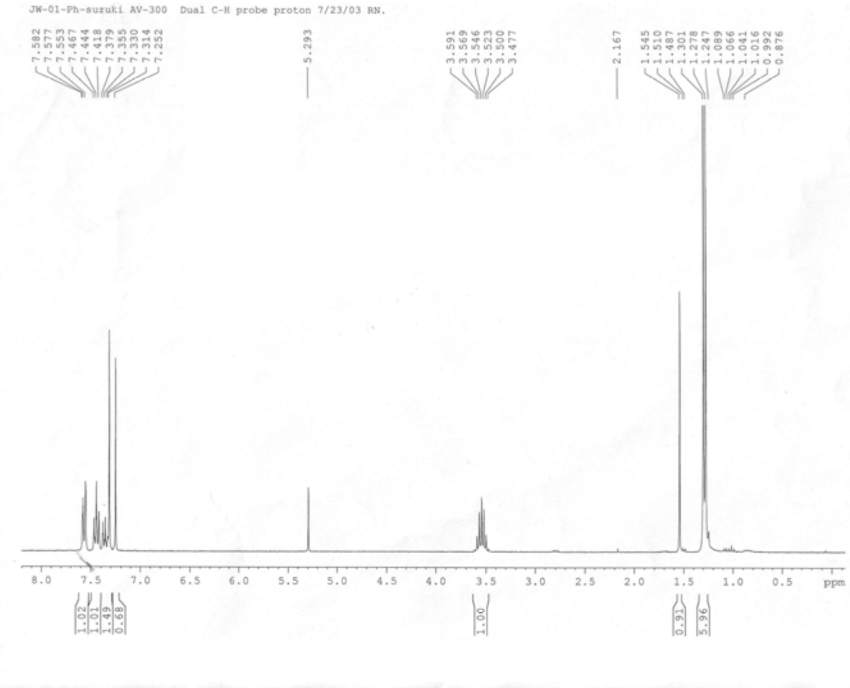
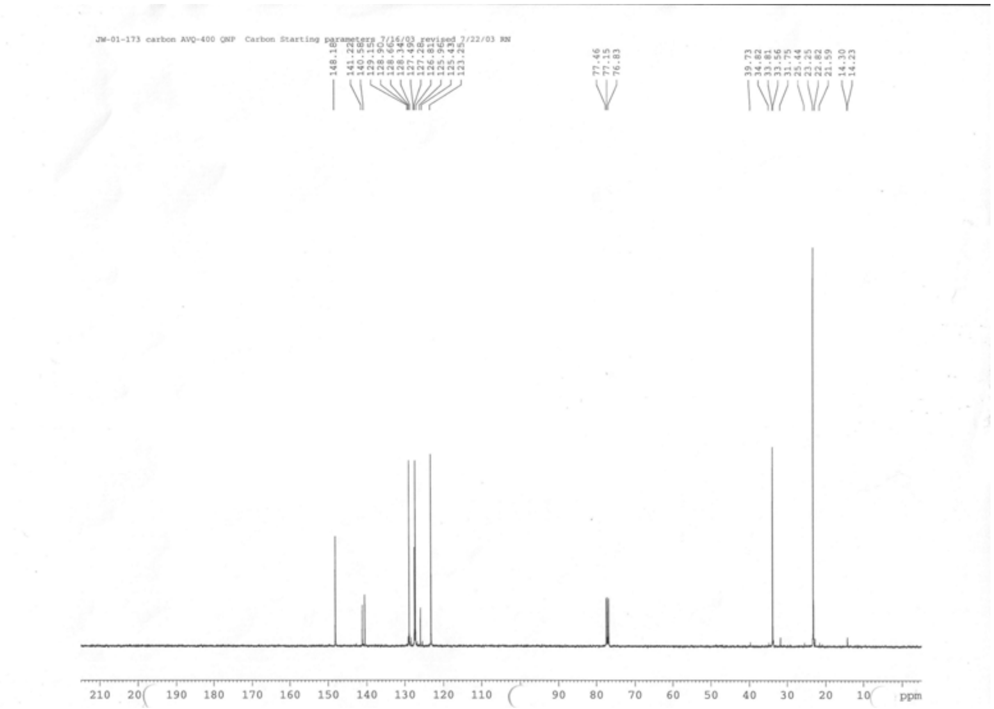
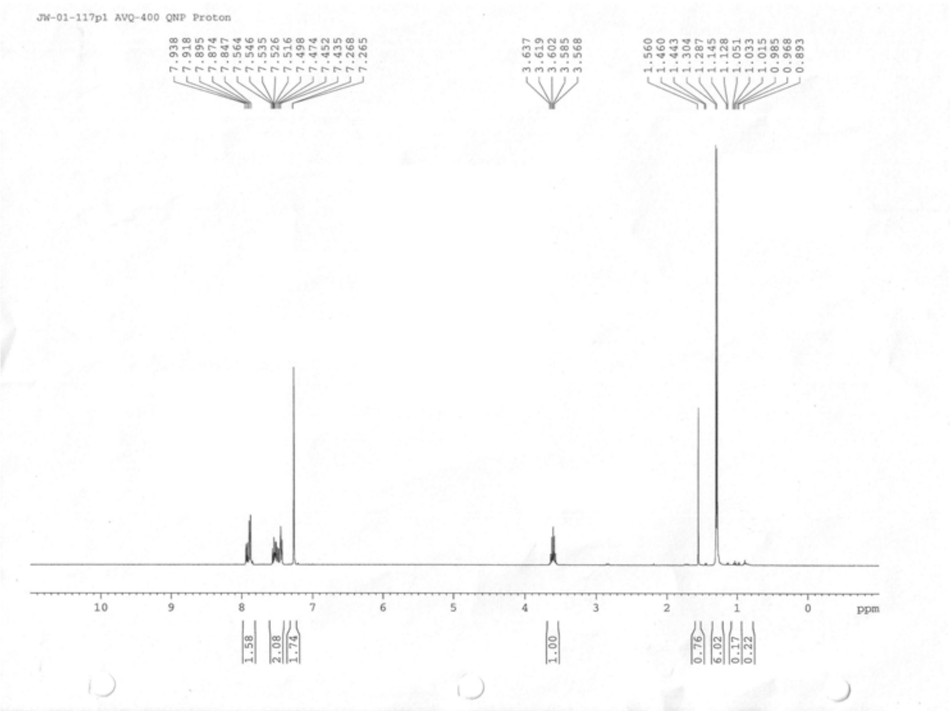


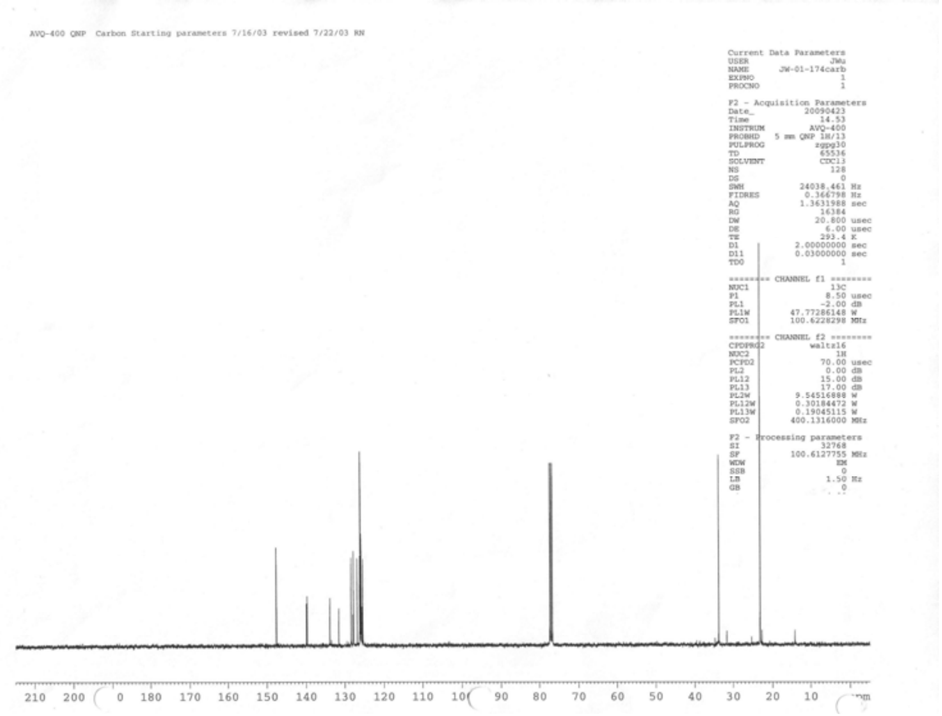
14 ^{13}C NMR



15 ^{1}H NMR



15 ^{13}C NMR



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TD0                   1

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PL1               -2.00 dB
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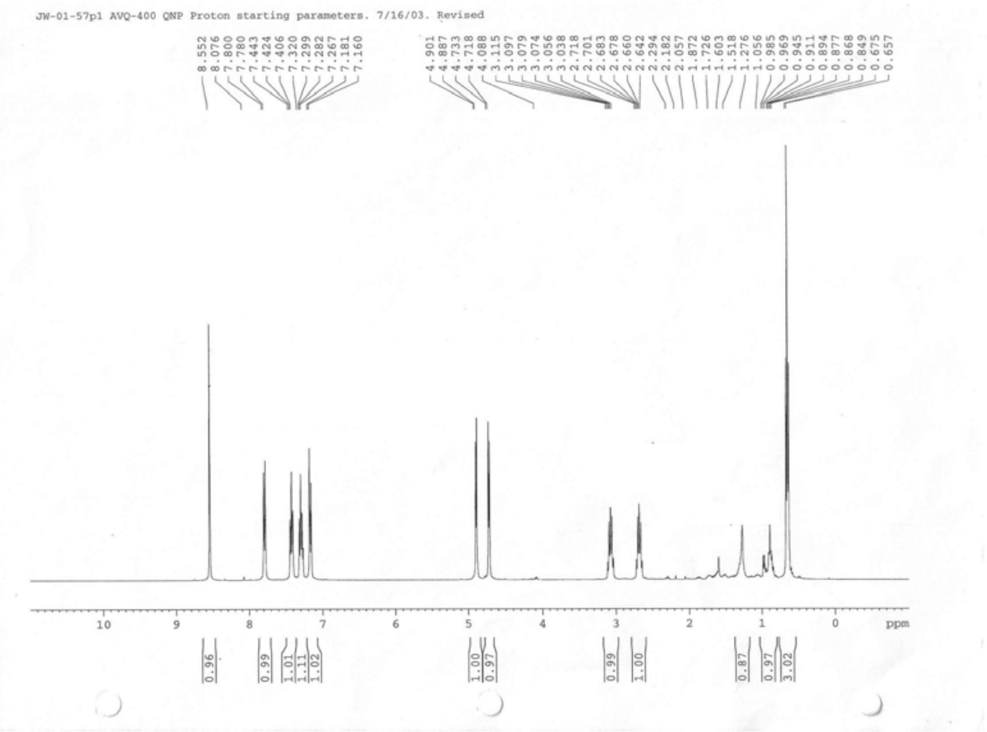

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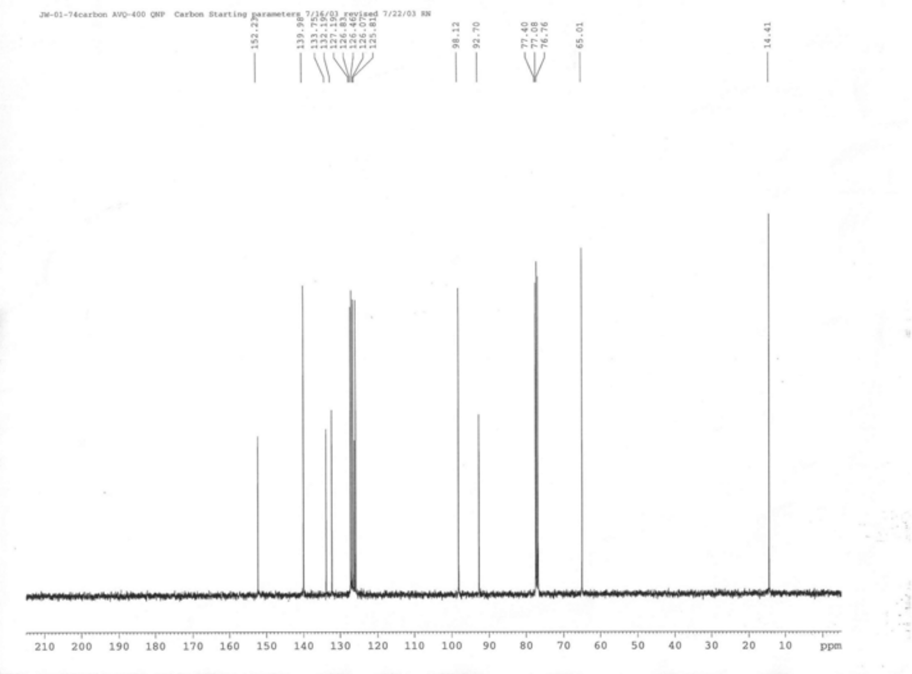

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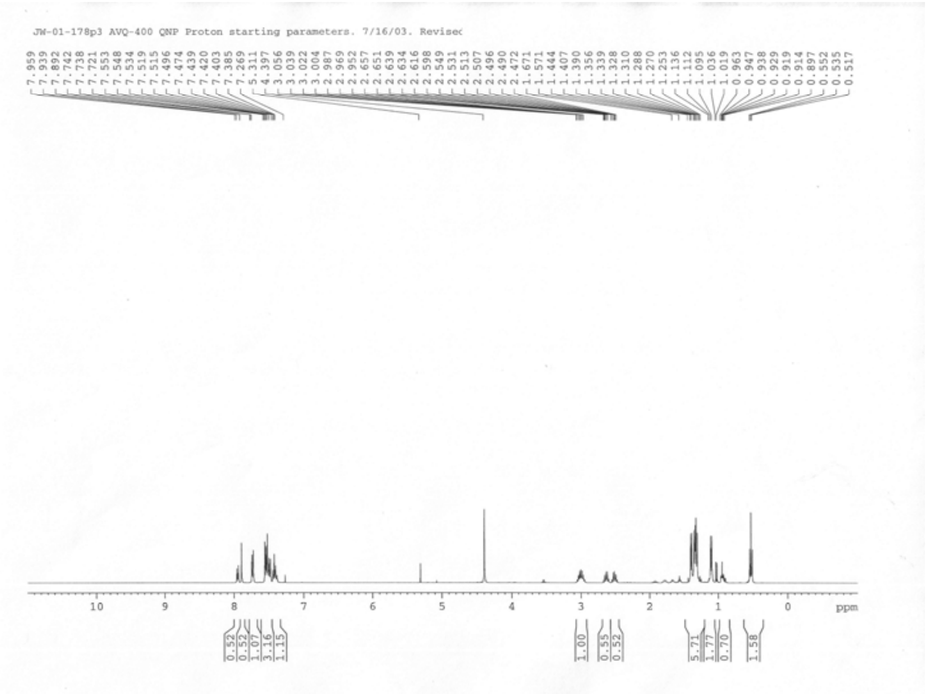

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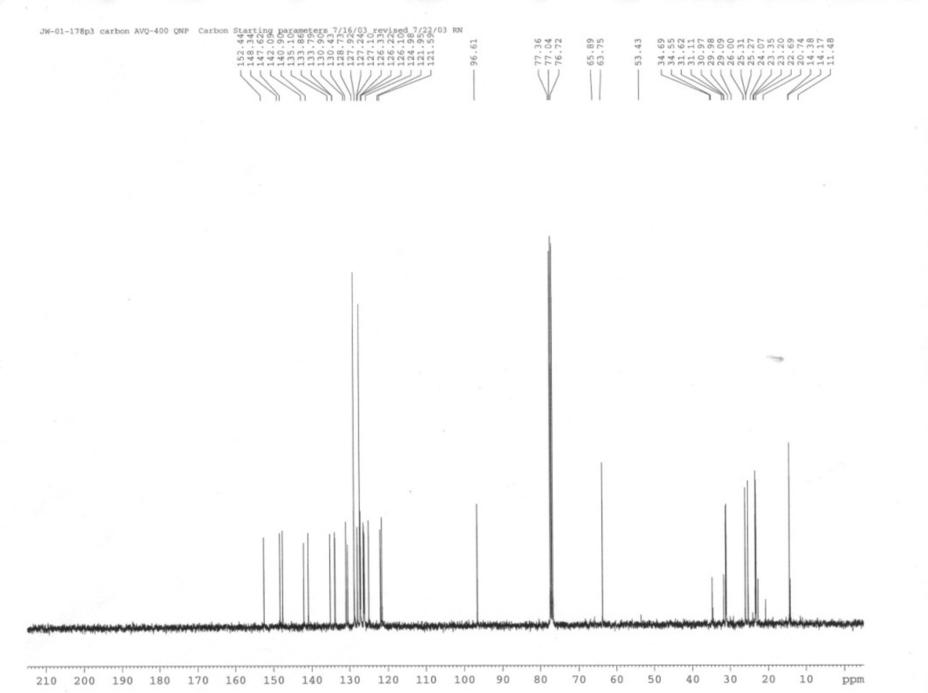

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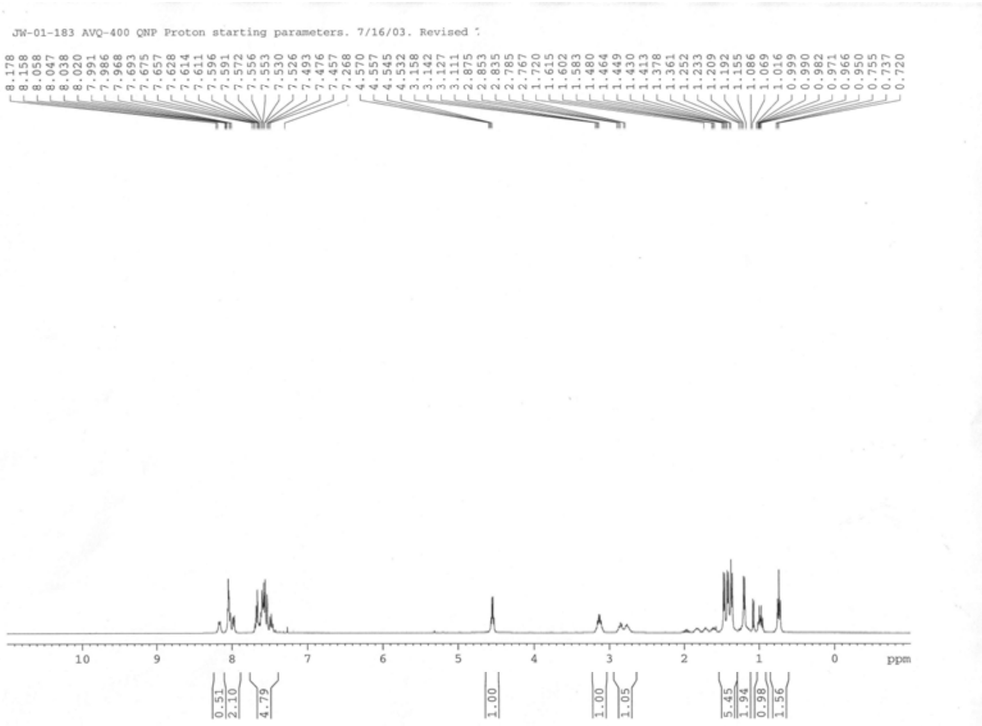

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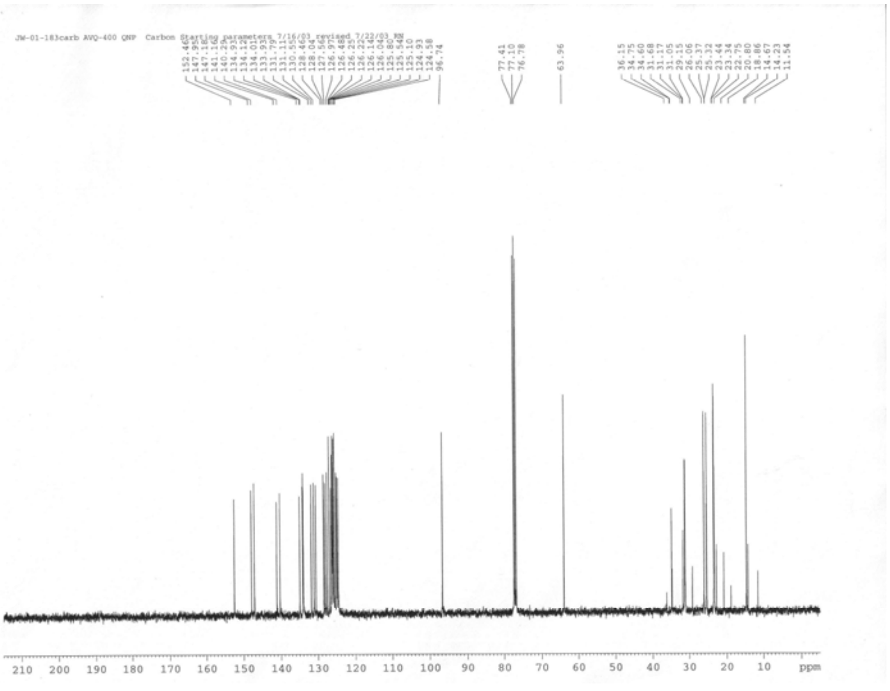

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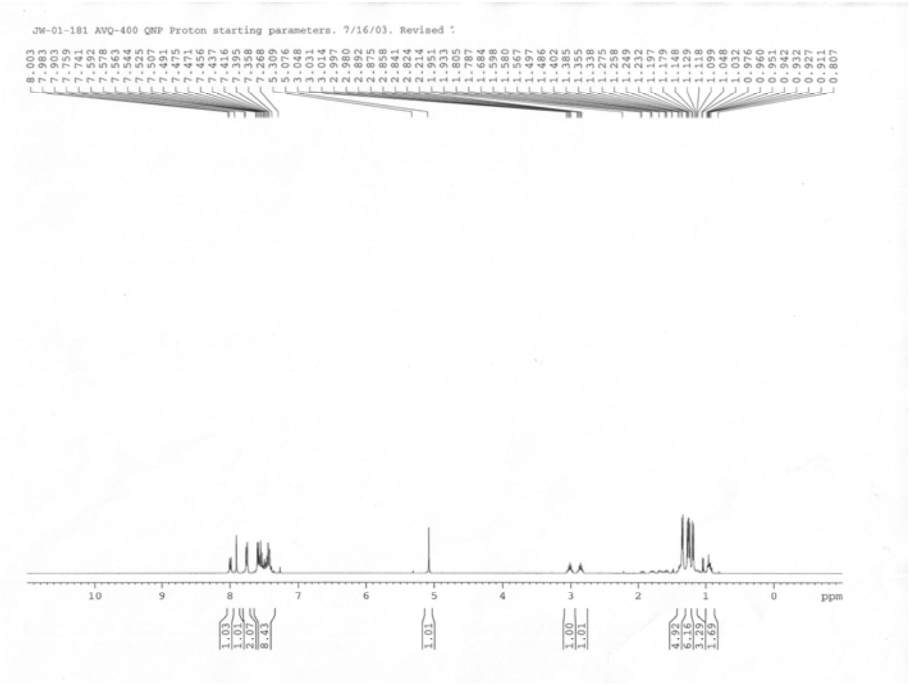

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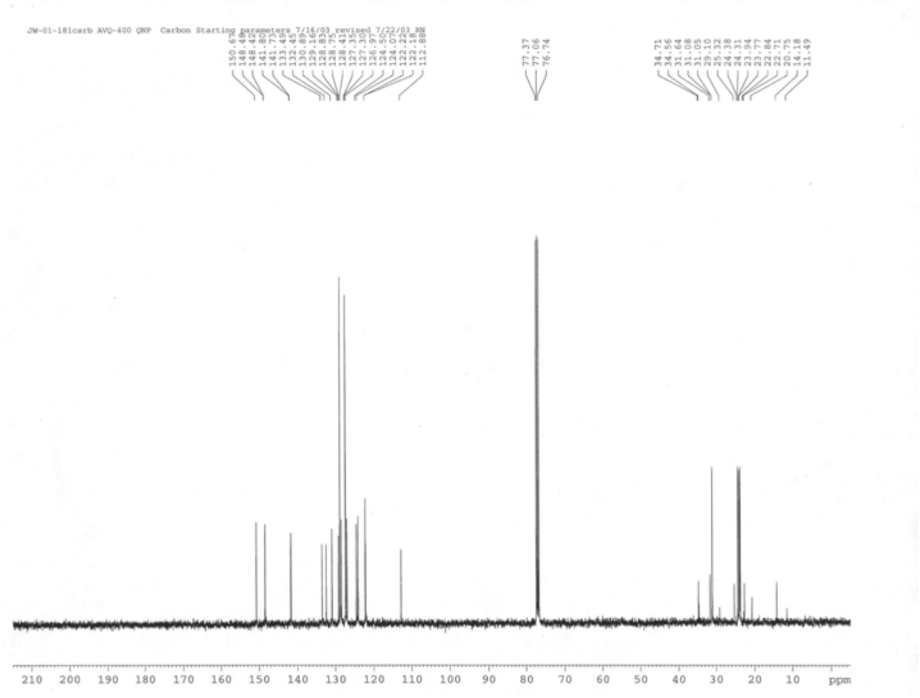

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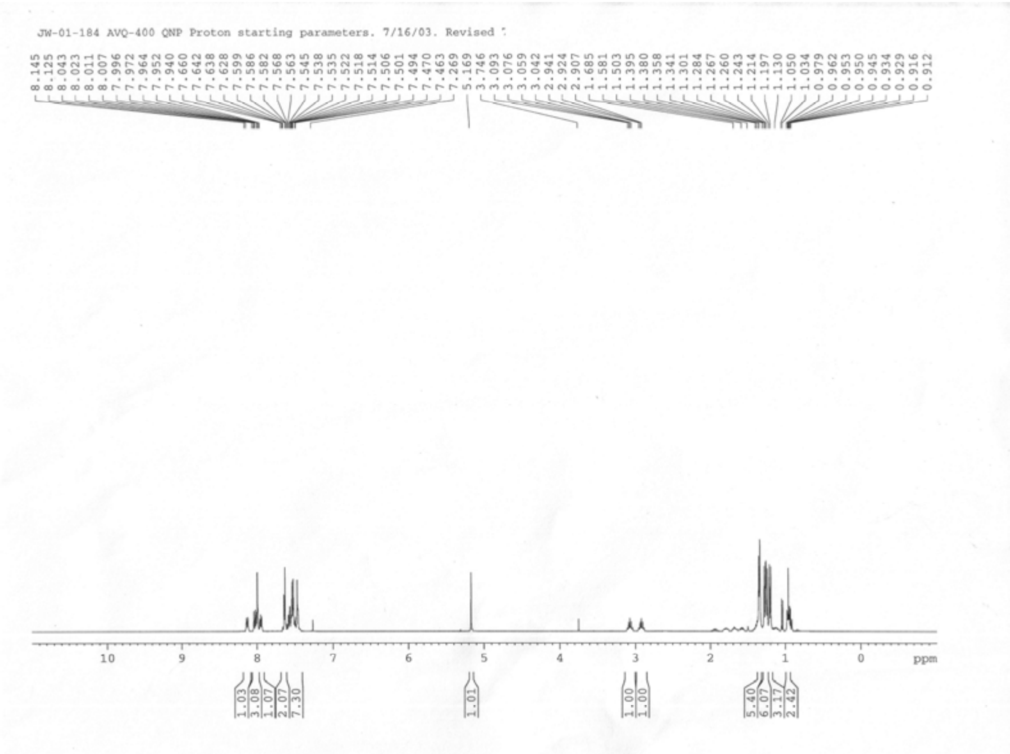

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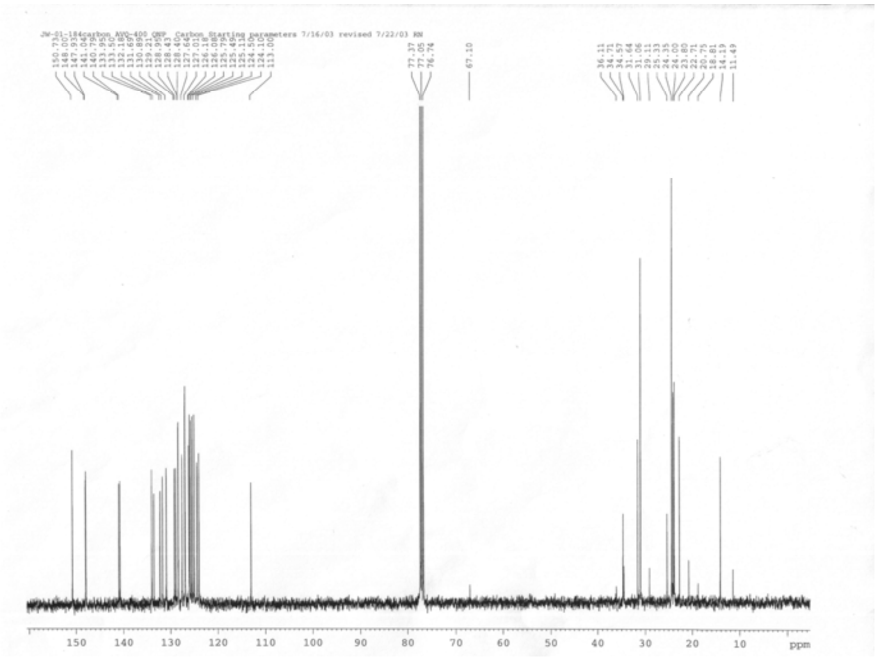
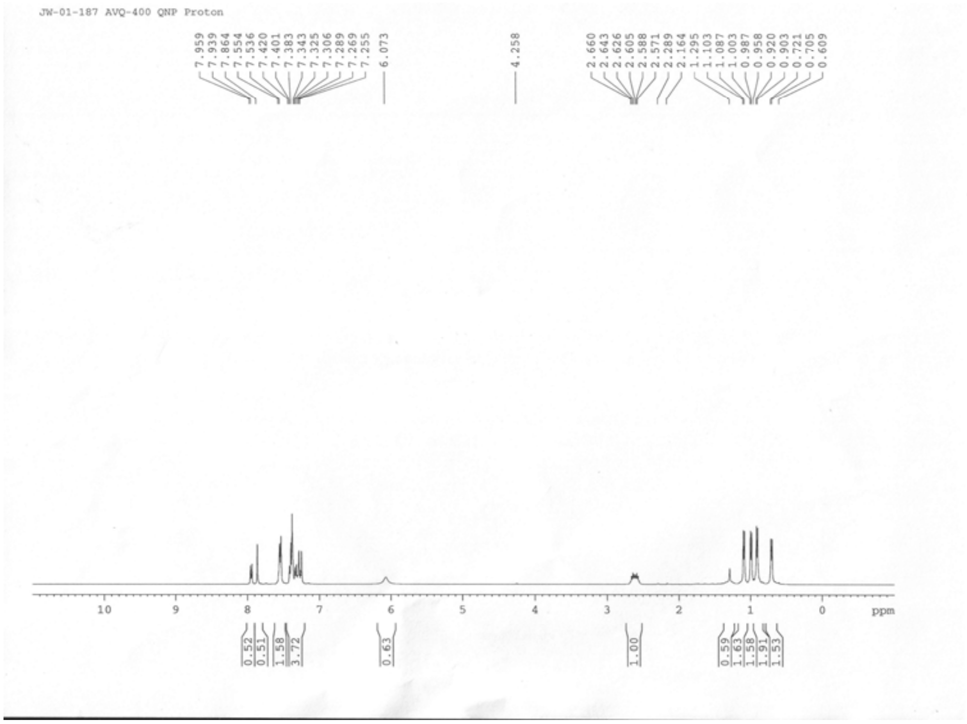


24 ^{1}H NMR



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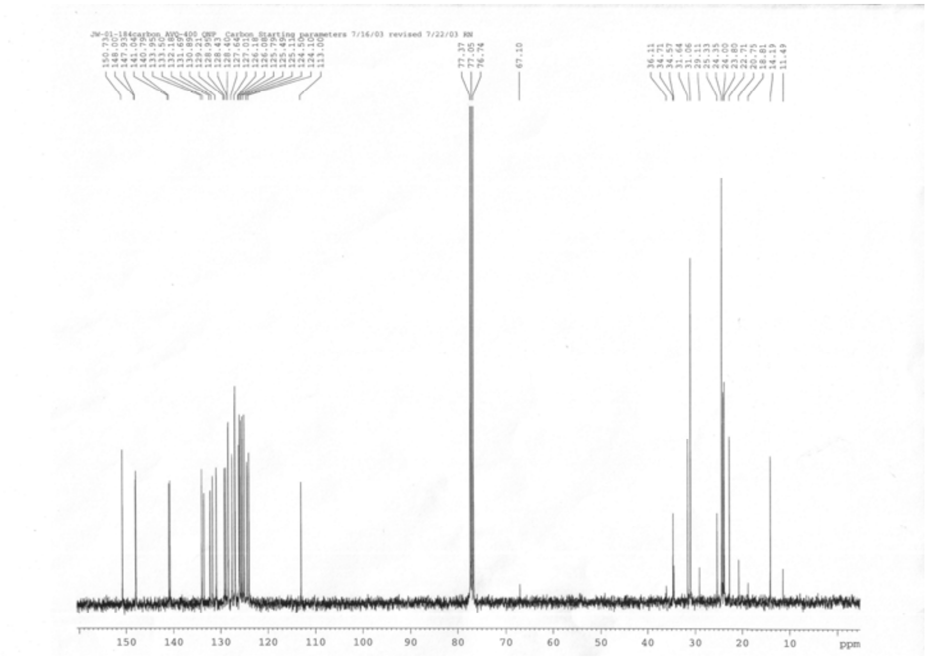

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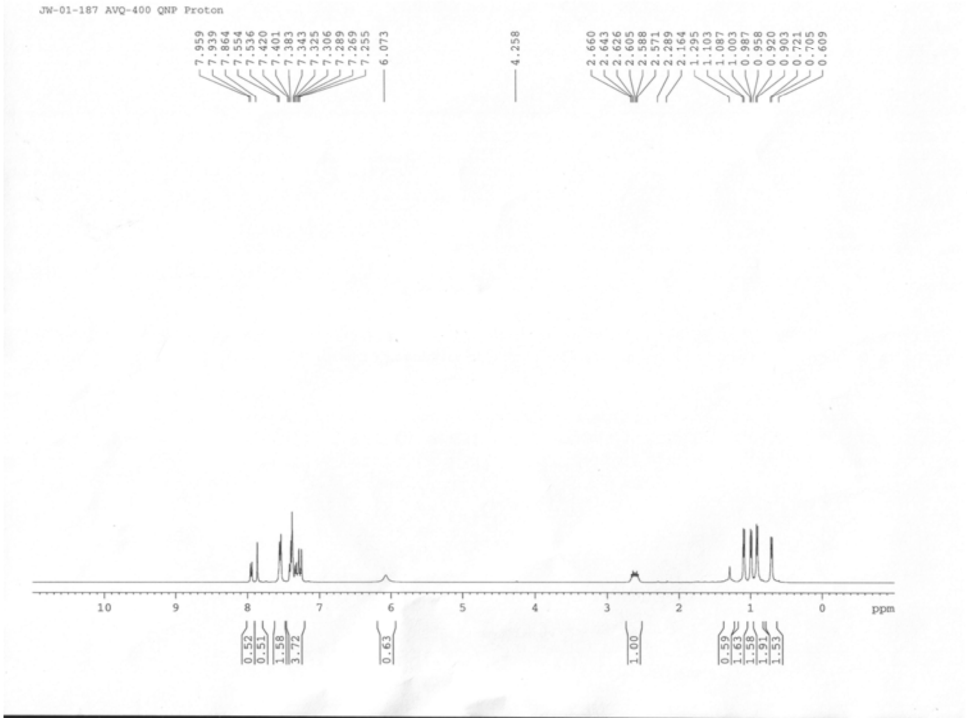

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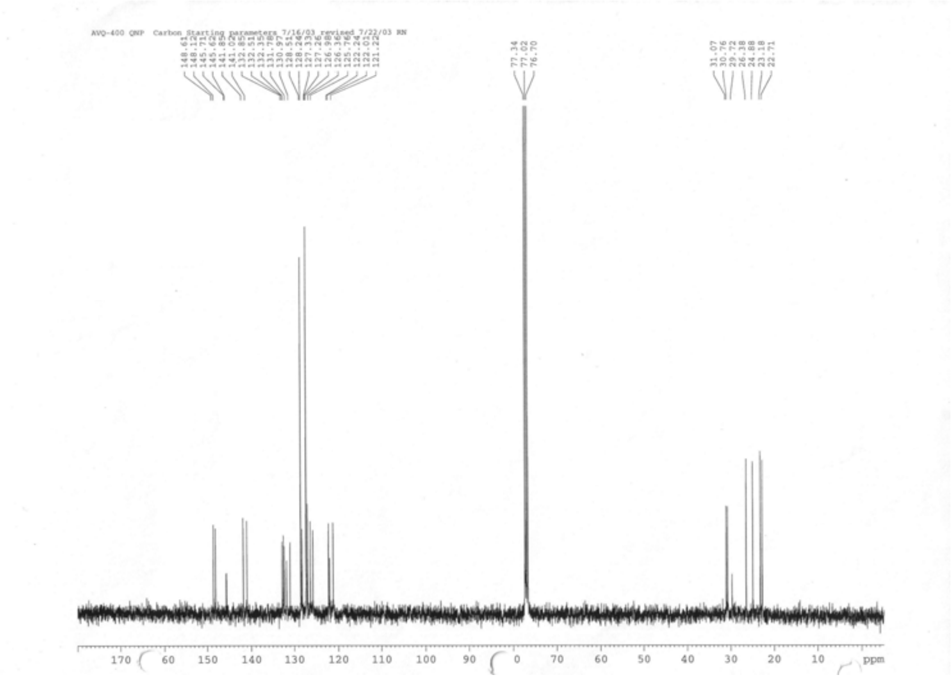

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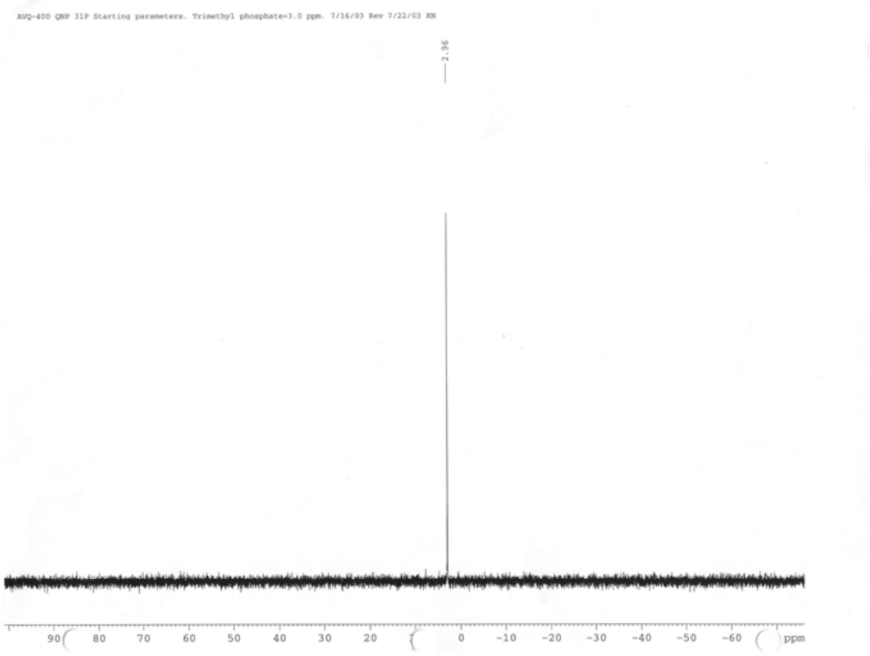
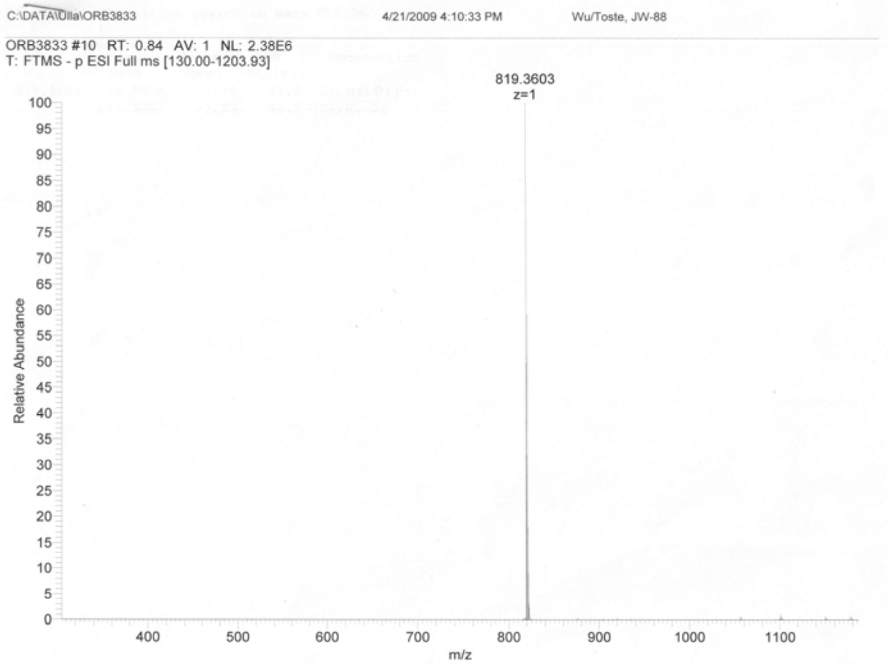


24 FTMS



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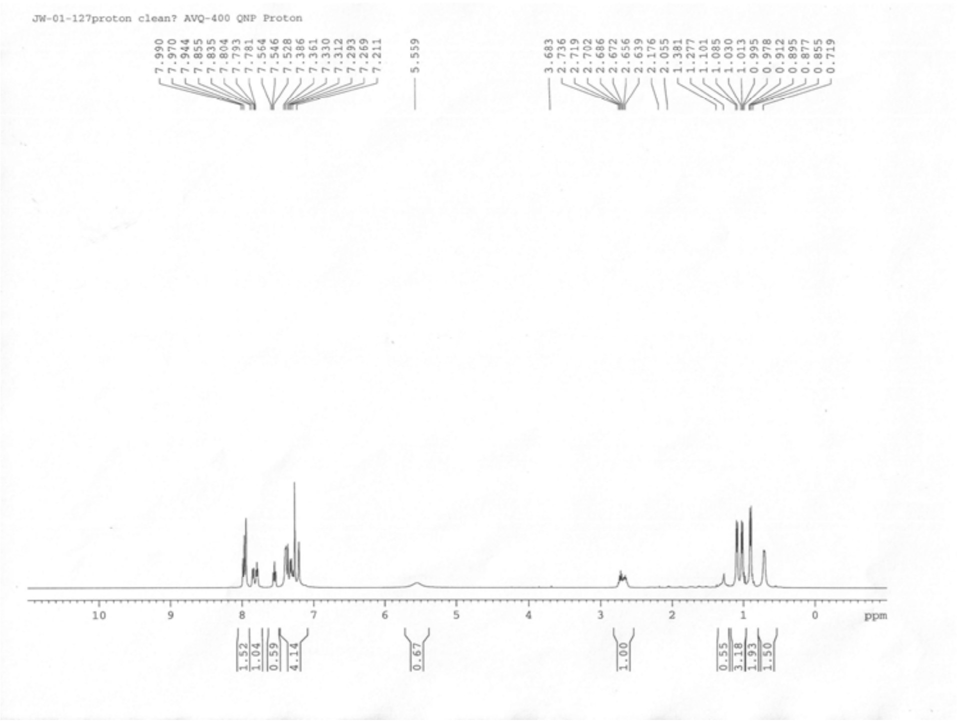
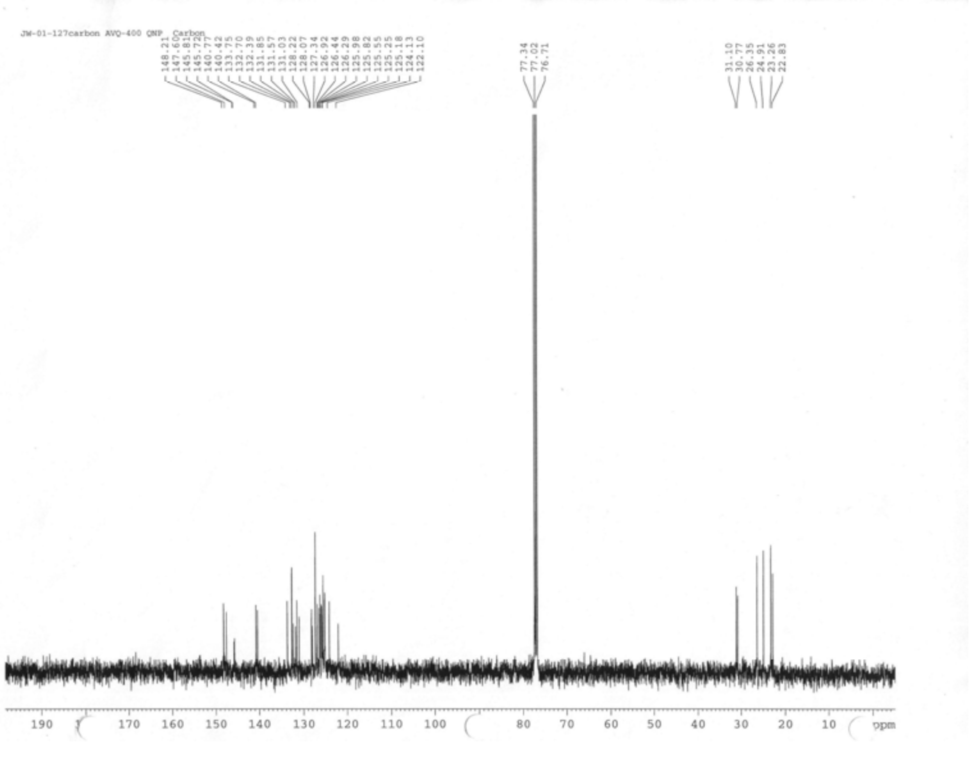


25 ^{13}C NMR



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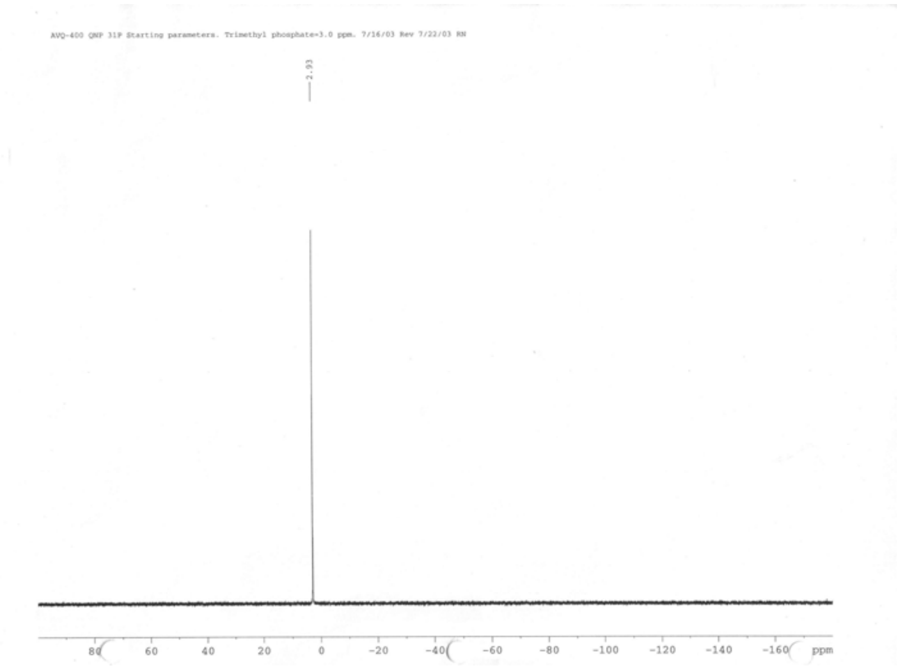
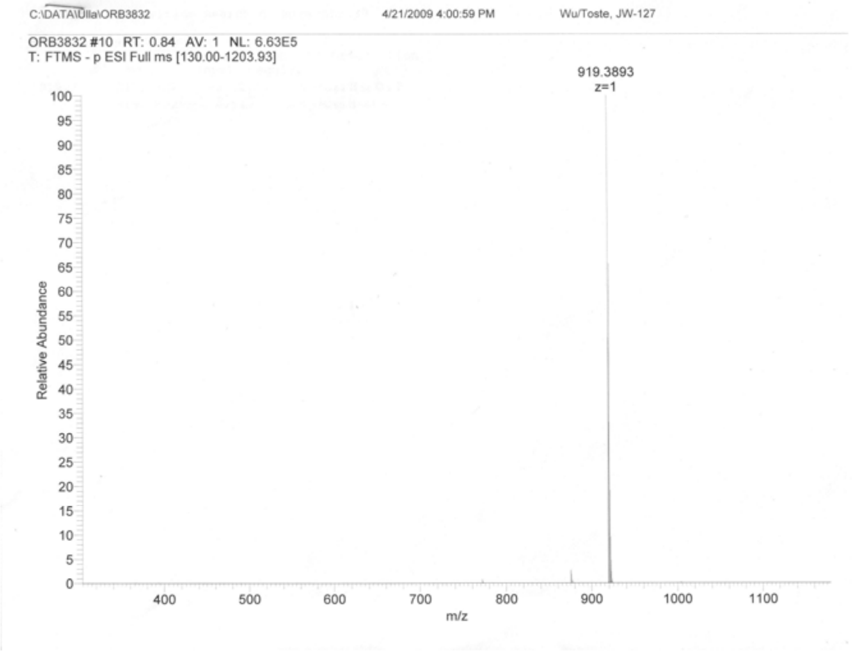
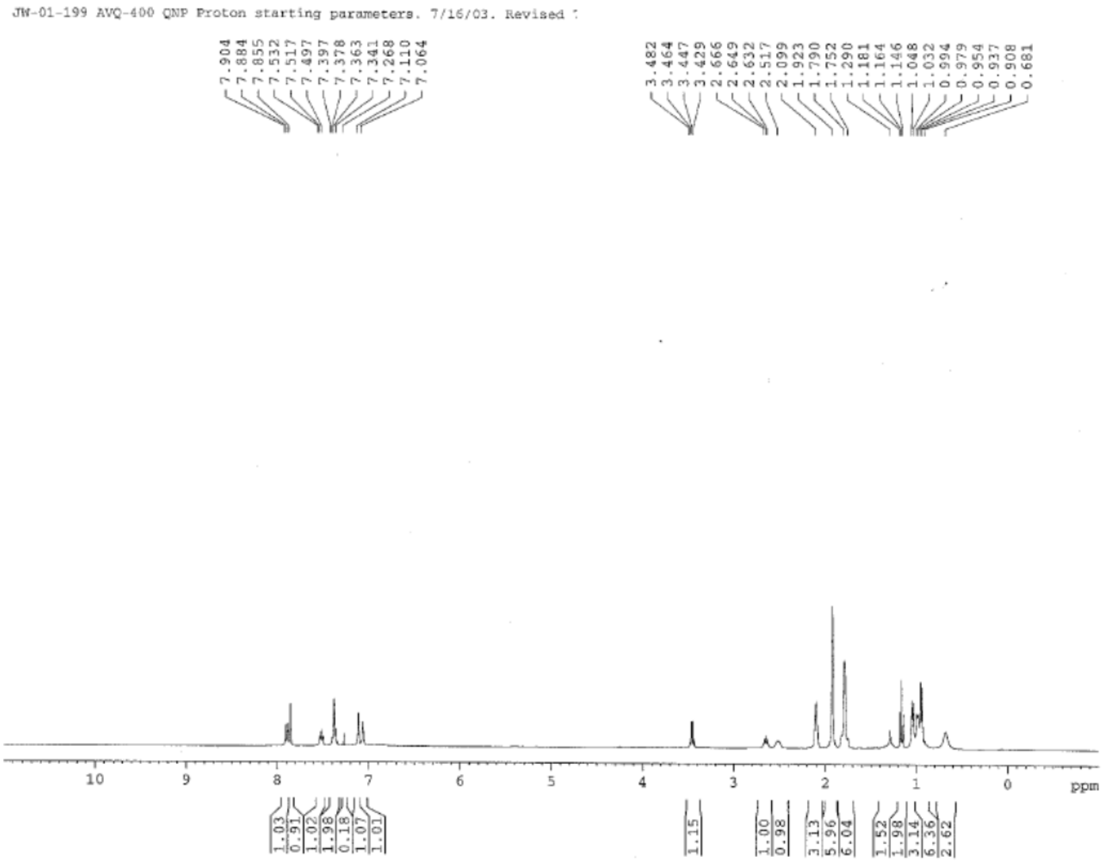


25 FTMS

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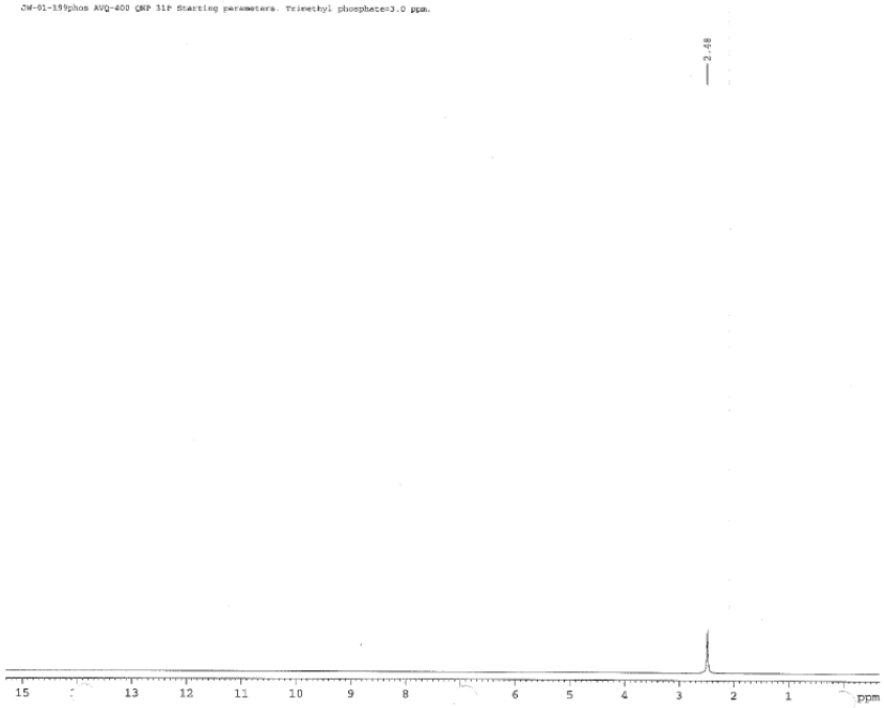
26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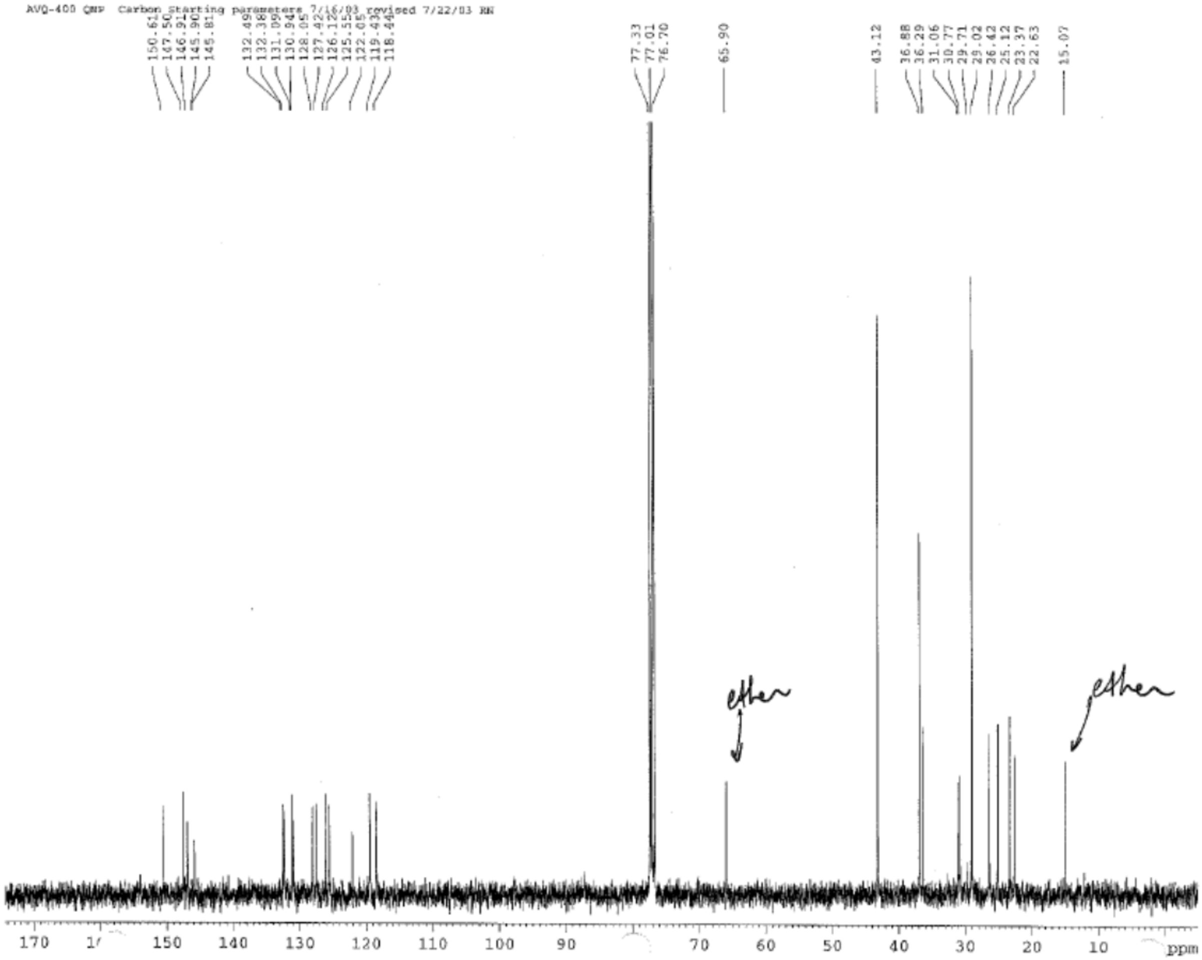
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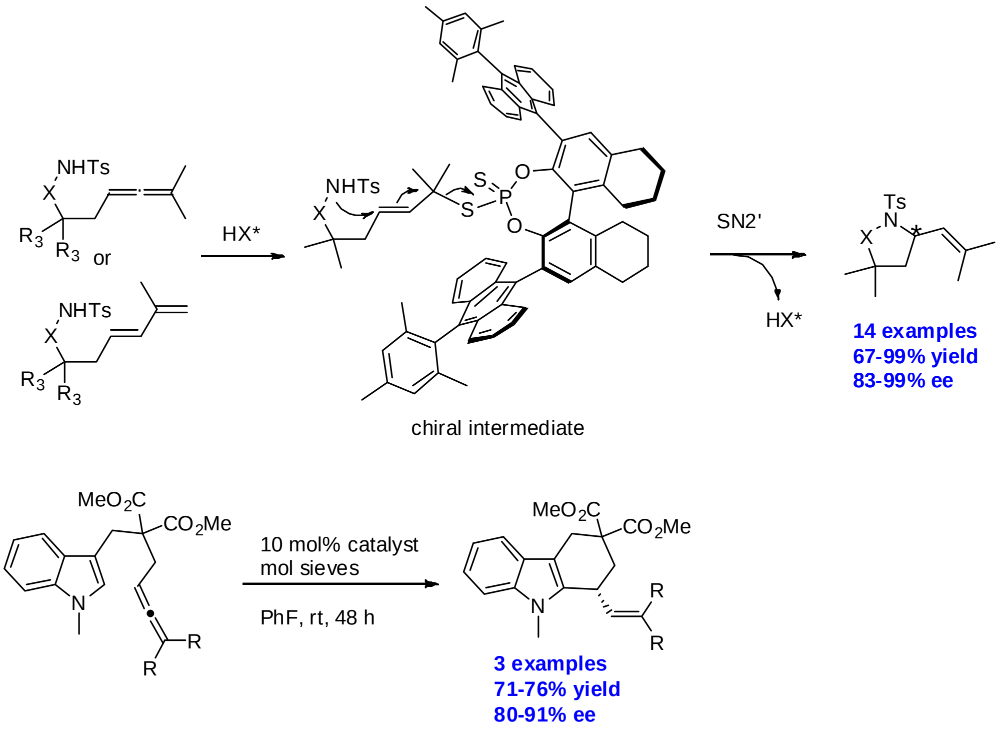
CHAPTER 2: DITHIOPHOSPHORIC ACIDS AS COVALENT CATALYSTS FOR HYDROAMINATION AND HYDROARYLATION OF ALKENES

Abstract

The first organocatalytic enantioselective hydroamination was achieved with newly designed dithiophosphoric acid catalysts. Markovnikov ionic addition of the Brønsted acid catalyst to alkenes resulted in covalent intermediates which then underwent intramolecular enantioselective nucleophilic attack. The substrate scope includes dienes and styrenes, with both amine and carbon nucleophiles. These reactions provided various heterocycles in good to high yield and enantioselectivity, while it was found that probably due to mechanistic and steric considerations, dienes were more successful than styrenes as substrates. However, we believe that the concepts revealed in this work will prove applicable to other asymmetric functionalizations of unsaturated systems.



14 examples
67-99% yield
83-99% ee

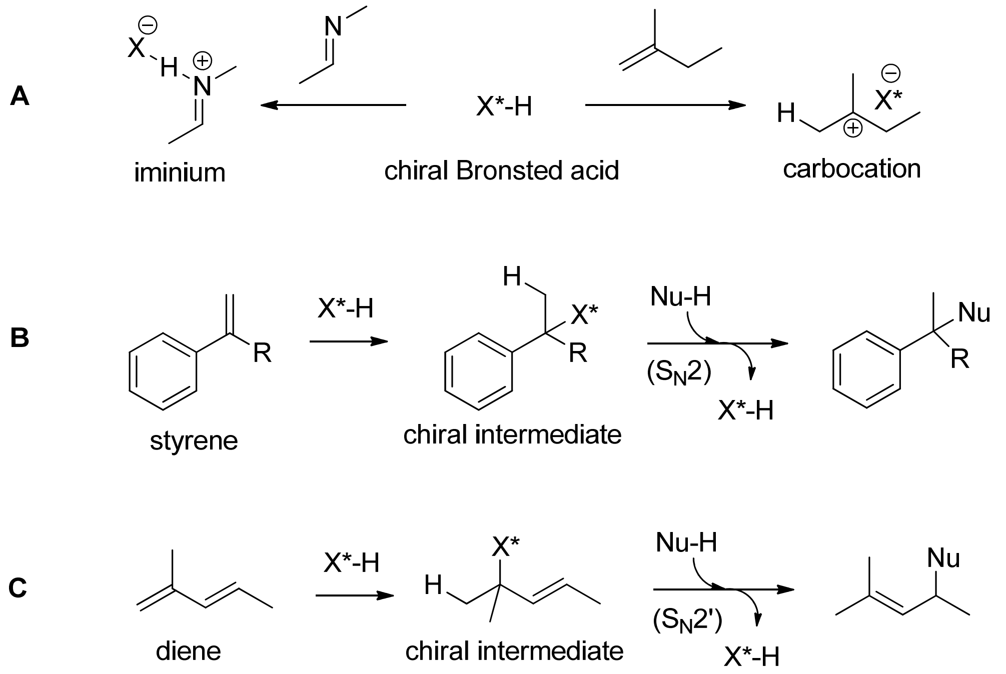
3 examples
71-76% yield
80-91% ee

Introduction

Transition-metal catalysis, through the use of chiral ligands, has mediated functionalization of olefins with high enantioselectivity. In addition, the use of racemic Brønsted acids has also been utilized to catalyze the addition of alcohols and other nucleophiles to olefins. However, the expansion of their reactivity to produce enantioselective products from olefins has been a long-standing challenge. As an illustration of the challenge, the only application toward this type of reaction resulted in low enantioselectivity (17% ee).[1] Organocatalytic methods have become highly desirable because they avoid the use of toxic and expensive metals and are generally insensitive to air and moisture.[2] An organocatalyst capable of achieving asymmetric hydroamination of unactivated olefins would represent not only a potential practical improvement for this important reaction, but also an expansion of the range of transformations amenable to organocatalysis. Typically polar unsaturated bonds are activated by chiral acids, due to the increased basicity as well as the potential for hydrogen bonding. At the time we began work to realize this concept, the general consensus from the organocatalysis community was that chiral Brønsted acids require hydrogen-bonding interaction between the protonated substrate and the conjugate base in order to attain selectivity.[3] A significantly different approach – most likely the design of new catalyst - was needed to achieve the desired enantioselective additions to olefins. There are two main roadblocks to this type of reactivity. First, the acid must be very acidic, such as triflic acid (pKa = -5.9). Second, the intermediate carbocation is planar and generally lacks sufficient attractive interactions with the chiral source and thus cannot provide an energy difference between the two diastereomeric transition states. The first issue of increasing acidity has been previously explored in the design of new catalysts, which are more acidic than the well-precedented BINOL-derived chiral phosphoric acid such as TRIP. Reactions requiring more acidic catalysts have been rendered enantioselective by Yamamoto and others using *N*-triflylphosphoramides and sulfonic acid derivatives.[4] However, these stronger acids have still only been utilized to more highly activate polar functional groups derived from ketones and aldehydes. Instead of solely increasing acidity, we envisioned also increasing the nucleophilicity of the conjugate base, in order to perform an ionic Brønsted acid addition to an alkene to form a covalent intermediate. Ideally this intermediate would mimic the known addition of many simple Brønsted acids such as hydrobromic acid to olefins (Figure 1B). This intermediate with a tethered nucleophile could then undergo intramolecular S_N2 or S_N2' attack, depending on whether a styrene or diene is reacting. Because the chiral catalyst is directly bound to the substrate in the nucleophilic addition step, we hypothesized that the key intermediate is now chiral and could undergo an intramolecular reaction with high enantioselectivity. Although enamine and iminium catalysis also take advantage of covalent catalysis mechanisms, they are a result of condensation with ketones, a mechanism significantly different from addition of a Brønsted acid to an alkene.[5]

The approach we took to increasing the nucleophilicity of the counteranion was to use dithiophosphoric acids. The counterion is expected to be more nucleophilic due to polarizability because of its size.[6] It is precedented that simple dithiophosphoric acids add to dienes efficiently, and chiral dithiophosphoric acids have been synthesized but have not been shown to catalyze any reactions with high enantioselectivity (the best example to date: 7:3 dr, 63% ee).[7, 8]

Furthermore, we aimed to extend this type of covalent catalysis to substrates which bear no hydrogen-bond donors. To demonstrate the lack of reliance on hydrogen-bonding and the vastly different requirements of this type of catalysis, we aimed to look at carbon nucleophiles in the formation of C-C bonds. This type of reaction is even less well-precedented in organocatalysis due to the non-hydrogen bonding nature of both reactive functional groups. We postulated that the chiral intermediate featuring a chiral leaving group could provide enough differentiation between the enantiotopic faces to facilitate highly enantioselective nucleophilic additions.



Scheme 1. Mechanistic distinctions between precedented chiral phosphoric acid activation reactions and our hypothesis for alkene functionalization: **A:** Protonation of an imine with a chiral Brønsted acid leads to a hydrogen-bonded iminium, while protonation of an olefin results in a carbocation which cannot form a hydrogen bond. **B:** Proposed new mechanism where a novel Brønsted chiral acid adds to styrene, then undergoes enantioselective S_N2 displacement. **C:** Proposed new mechanism where a Brønsted chiral acid adds to a diene, then undergoes enantioselective S_N2' displacement.

Results and discussion

The initial foray involved the intramolecular hydroamination reaction of styrenes with nitrogen nucleophiles. The substrate design was straightforward and similar to other hydroamination substrates used in the past by our group and others for metal-catalyzed enantioselective variants; it relied on a benzylic carbocationic intermediate and its potential interaction with the chiral dithiophosphate counteranion. Initial experiments with hydroamination were attemped with a 4-methoxystyrene substrate, with hopes that an electron-donating group would facilitate the initial protonation and interaction with catalyst. In addition to using **7** as a substrate, intermediates **4**, **5**, and **6** were subjected to dithiophosphoric acid catalyst, with **5** providing quantitative conversion and 6% ee while **4** was formed with no enantioselectivity. After obtaining hydroamination in quantitative yield and 7% ee with **7**, unactivated styrenyl substrates (without the methoxy-substituent) were explored.

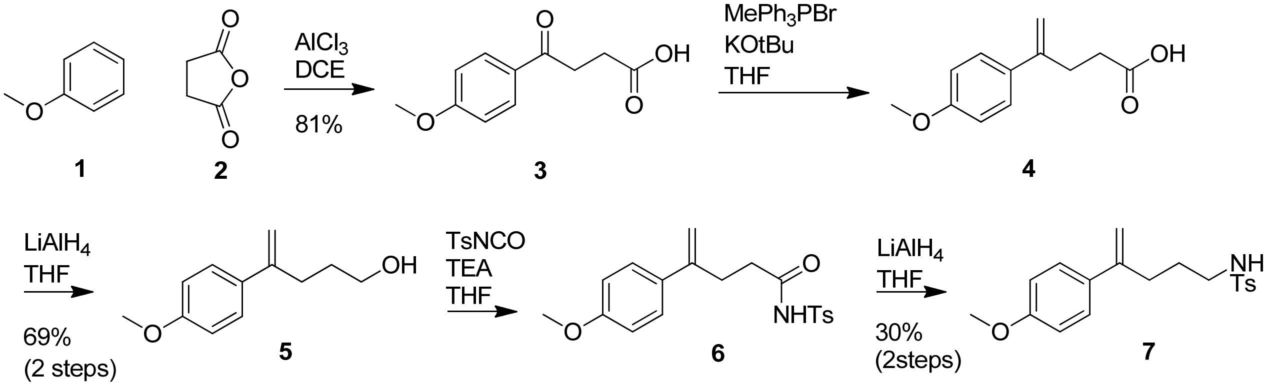
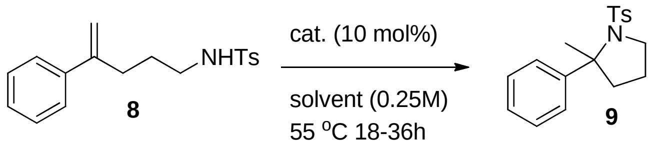


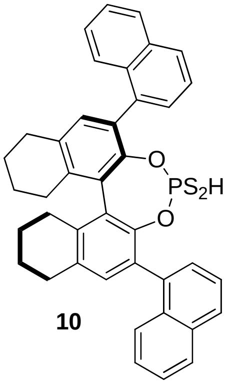
Figure 1. Straight-forward synthesis of styrene substrates for intramolecular hydroamination.

The optimization of the reaction continued with the parent phenyl compound, synthesized in a similar fashion. However, it was found that the methoxy-substitution did indeed provide a larger effect than we anticipated and with the parent compound **8**, heat was required to drive the reaction to completion. Even with slight heating the pyrrolidine product was obtained in 13% ee in benzene. A solvent screen revealed that fluorobenzene as solvent increased enantioselectivity to 19% ee. Various dithiophosphoric acid catalysts were investigated (Table 1). With 3,3'-substituents identical to TRIP, we obtained 7% ee, and with anything larger the reaction was sluggish or did not proceed. This may be due to steric crowding of the quaternary carbon center where nucleophilic attack must occur. In the case of these substrates, it is likely that there is actually not a stable covalent adduct formed, but rather a strongly stabilized benzylic carbocation is ion-paired with the counteranion thiophosphate. Other tethered nucleophiles were explored including alcohol, carboxylic acid, and N-tosylamide. It is common to see the Thorpe-Ingold effect used to improve reactivity in intramolecular reactions; however, in our case the use of dimethyl-substituted linkers was detrimental for reactivity, probably due to the two contiguous quaternary centers in the desired product.



entry[a]	solvent	cat.	ee (%)[b]
1	benzene	**10**	13
2	fluorobenzene	**10**	19
3	fluorobenzene	**11**	-[c]
4	fluorobenzene	**12**	7

[a] Reactions run to >90% completion, monitored by TLC. [b] Enantiomeric excess determined by chiral HPLC. [d] Not determined due to low amount of product.



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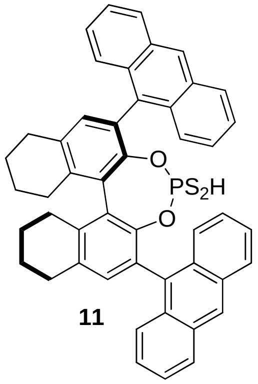

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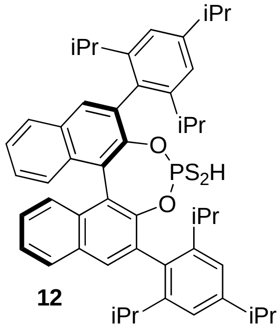

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Table 1. Optimization of reaction conditions and catalyst.

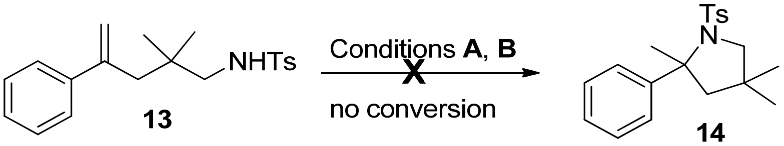
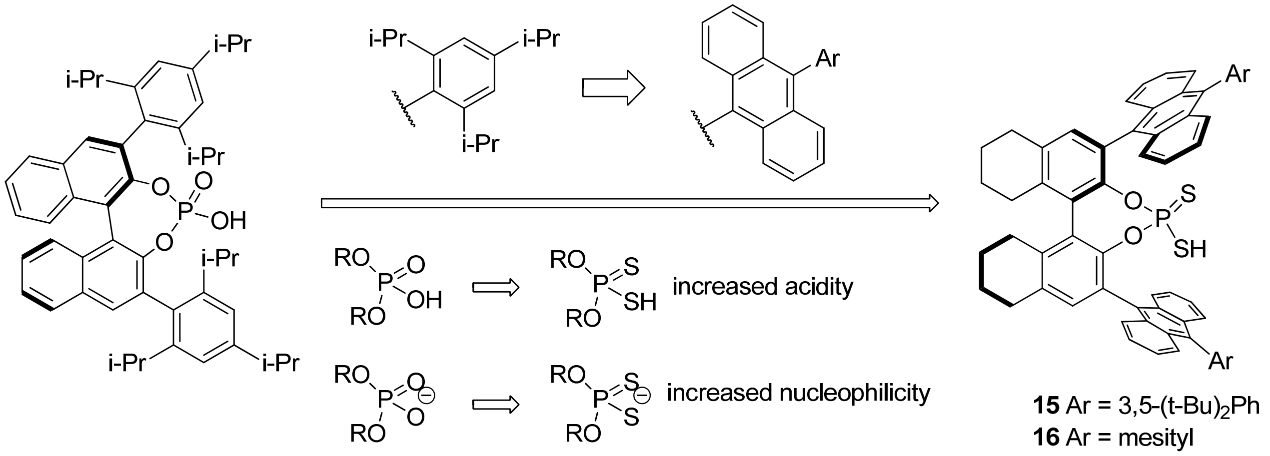


Figure 2. Conditions **A**: Triflic acid in methylene chloride, at room temperature. Conditions **B**: Dithiophosphoric acid catalyst (10 mol%) in fluorobenzene at 55 °C.

From here, I began working on dienes rather than styrenes (Scheme 1B vs. Scheme 1C). Work on 1,3-diene substrates included using fluorobenzene as solvent, and lowering the temperature of the reaction to 15 ºC. Unlike the previous styrene substrates, changing the 3,3′ substituents to anthracenyl groups led to a substantial boost in enantioselectivity, presumably because the projection of chiral information is required due to the less proximal S_N2’ attack. Along these lines, the addition of aryl substituents to the 10-position of the anthracene further increased enantioselectivity in this reaction. The H8-type BINOL backbone also provided improvements in selectivity (entry 5). Thus, we postulate that the change in mechanism (from S_N2 to S_N2’) is critical for success in this type of reaction, because S_N2 displacements are very unlikely at quaternary carbon centers. Notably, both mesityl catalyst **16** and 3,5-t-butylphenyl catalyst **15** provided exceptional enantioselectivity even at room temperature. Both of these catalysts were used in the substrate scope studies.



Scheme 2. Overall modification to design new catalysts includes transition to a more acidic dithiophosphoric acid, and the extension of the 3,3'-position groups.

Various substrates, including modifications to the diene alkyl substituents, and changes in the Thorpe-Ingold linker, were synthesized (Table 2). We found that spirocyclic products as well as dienes with cyclic alkyl substitutions performed well under optimized reaction conditions. In addition, the protecting sulfonyl group could be changed to nosyl.

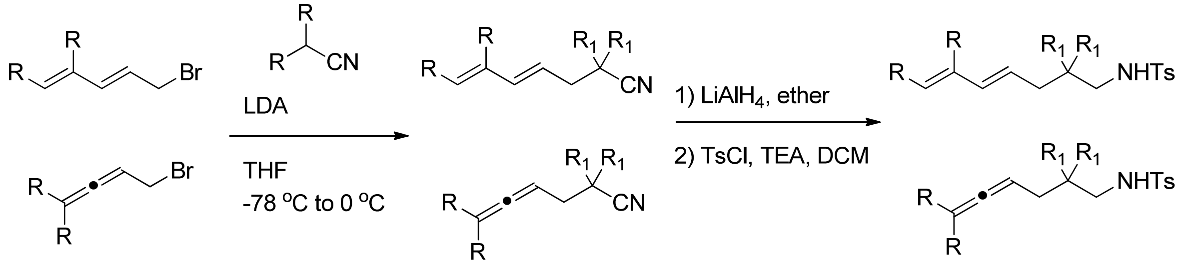


Figure 3. Synthesis of substrates.

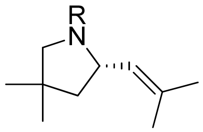
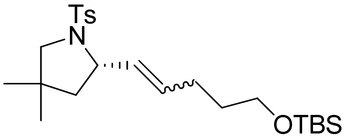
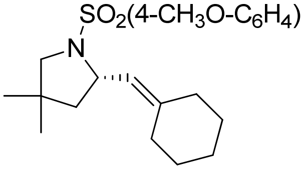
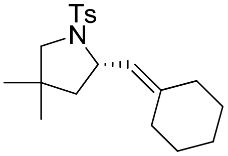
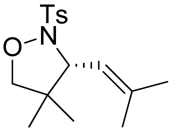
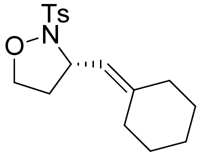
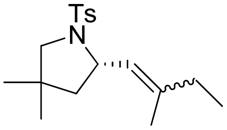
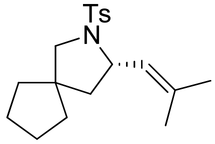
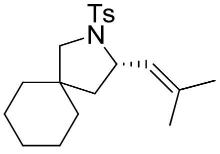
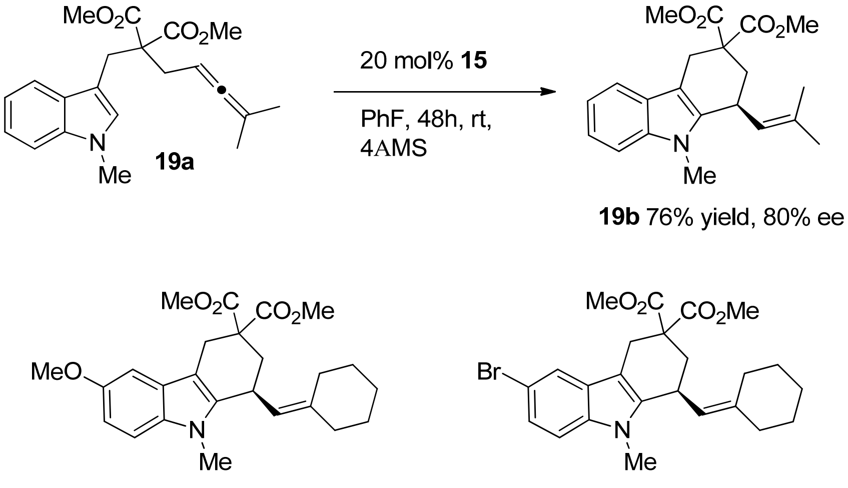
		yield (%)	ee (%)
			
18a	R = SO$_2$-(3,5-CH$_3$)$_2$C$_6$H$_3$	99	92
18b	R = SO$_2$-(4-Cl)C$_6$H$_4$	99	95
18c	R = Ts	99	95
18d	R = Ns	81	90
18e	R = POPh$_2$	99	83
18f		91 (1:3.6)	99 (Z) 91 (E)
18g		67	97
18h		70	94
18i		67	92
18j		70	90
18k		75 (1:2)	99 (Z) 91 (E)
18l		99	96
18m		91	97

Table 2. Substrate scope of hydroamination.

With 1,3- and 1,2-dienes (allenes), we expected similar results, which indeed was observed. They should proceed *via* a common intermediate, which is the chiral covalent adduct. This observation helps verify our mechanistic hypothesis. In addition, we were able to change the nucleophile to hydroxylamines to generate isoxazolidine heterocycles with high enantioselectivity. This stronger nucleophile (due to the alpha-effect) was required in the lone substrate without the gem-dialkyl linker.

To further confirm that the reaction is proceeding by our proposed mechanism, we aimed to observe the covalent intermediate which demonstrates that the dithiophosphoric acid is acting as a covalent chiral Brønsted acid catalyst. Gratifyingly, following the course of the transformation by TOF-MS allowed us to directly observe the covalent intermediate. This work was done with the assistance of the mass spectrometry facility in Stanley Hall. The formation of this intermediate is also supported by literature precedent which has observed addition of dithiophosphoric acids to alkenes and dienes.[7] One possible mechanism consists of a covalent intermediate is being formed, followed by formation of a tight ion pair, which may not observed. We cannot discount this process, but whether the covalent intermediate is directly converted to product or proceeding *via* a more reactive intermediate, the transformation proceeds by a reaction mechanism unprecedented in enantioselective organocatalysis.

As mentioned earlier, we investigated carbon nucleophiles to further demonstrate the potential for this type of transformation. We chose to work with indoles, which are highly nucleophilic, heteroaromatic, and generally alkylate at the 2- or 3-positions, when the nitrogen is protected. Additions of indoles to alkenes have not been demonstrated with organocatalysts.[9] A few substrates were designed and synthesized with similar structural characteristics as the substrates described above. They contained a gem-dimethyl linker in order to keep the Thorpe-Ingold effect, and an indole and allene were tethered to either side. We were gratified to find that indoles do react with high efficiency to form tetrahydrocarbazoles in high yield and enantioselectivity (Figure 3). Notably, there are no hydrogen-bond donors on the nucleophile in this case. Thus the interaction between chiral catalyst and substrate in the form of a covalent bond provides sufficient differentiation between the two diastereomeric transition states. This is a rare example of an enantioselective transformation using chiral Brønsted acids without any hydrogen-bonding capability on either reaction partner. The analogous covalent intermediate between the indole substrate and catalyst was similarly detected by MS studies (See supporting information).



19a

19b 76% yield, 80% ee

20b 75% yield, 91% ee

21b 71% yield, 87% ee

Figure 4. Dithiophosphoric acid catalyzed hydroarylation of indole derivatives.

We have demonstrated that with the design of dithiophosphoric acid catalysts, we were able to achieve organocatalytic hydroamination and hydroarylation. The reaction proceeds *via* a covalent intermediate which is produced in similar fashion as classic Brønsted acid addition to alkenes. This intermediate then undergoes intramolecular nucleophilic attack generating heterocycles in high enantioselectivity. The value in this method is mainly in the demonstration of a new mechanism for chiral Brønsted acid catalysis, allowing for the functionalization of alkenes rather than imines or carbonyls. The further evolution of chiral Brønsted acids, based on the well-precedented TRIP, was explored by using dithiophosphoric acids rather than phosphoric acids, and extension of the 3,3-substituents to a bulkier substituent.

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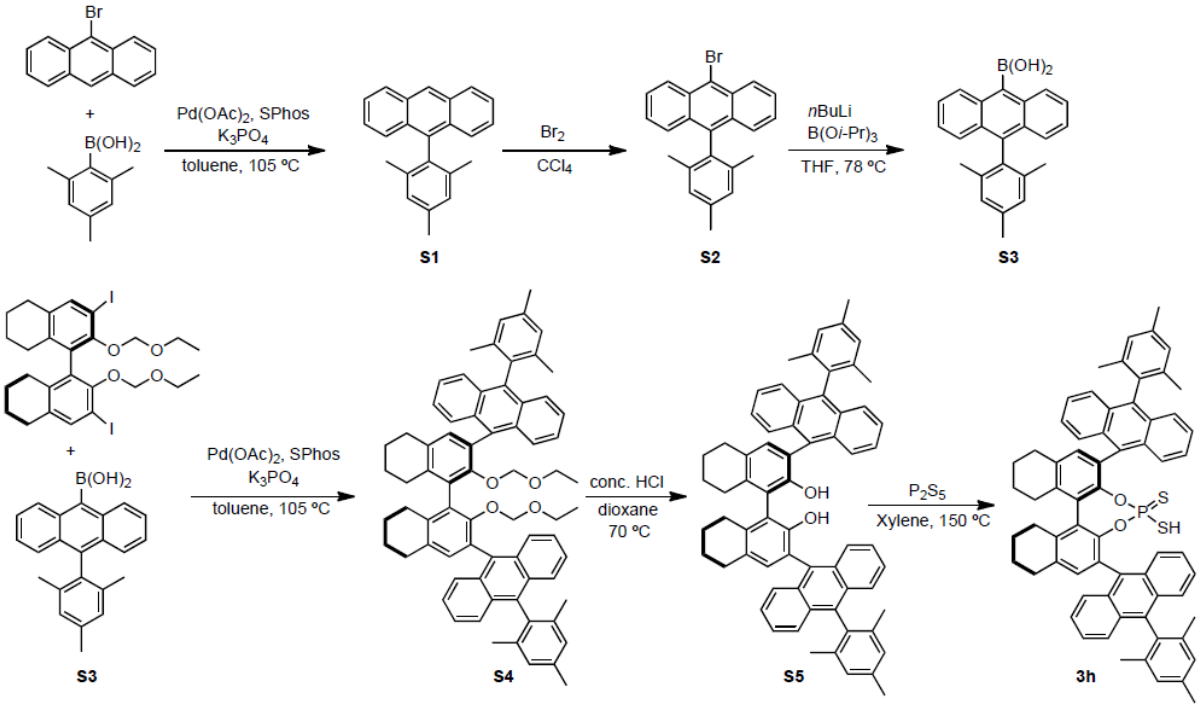
General procedure for acid-catalyzed enantioselective hydroamination reaction. To a 1-dram screw cap vial was added the diene or the allene substrate (0.1 mmol, 1.0 equiv) followed by the dithiophosphoric acid catalyst (0.01 mmol, 0.1 equiv) and activated 4 Å molecular sieves (20 mg). To the mixture was added fluorobenzene 0.5 mL at room temperature. The vial was sealed and allowed to stand at room temperature for 48 h at the indicated temperature. After the reaction was complete, the entire mixture was loaded onto silica gel and the product was eluted with EtOAc/hexanes.



S1: A 100 mL flame-dried round-bottom flask was charged with 9-bromoanthracene (3.81 g, 15 mmol, 1.0 equiv), 2,4,6-trimethylphenylboronic acid (3.69 g, 22.5 mmol, 1.5 equiv), $Pd(OAc)_2$ (101.02 mg, 0.45 mmol, 0.03 equiv), SPhos (369.5 mg, 0.90 mmol, 0.06 equiv), K_3PO_4 (7.96 g, 37.5 mmol, 2.5 equiv), and anhydrous toluene (120 mL). The resulting mixture was subjected to freeze-pump-thaw cycles (3x) and heated at 105 ºC for 18 h. After this time, the reaction mixture was cooled to room temperature and poured over water (50 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 X 50 mL). The organic extracts were combined and dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting dark reddish-brown semi-solid was dissolved in minimal amount of CH_2Cl_2 and triturated with MeOH. The desired product **S1** precipitated as a reddish-brown solid, and was filtered and washed with ice-cold MeOH. The solid mass was dried under high vacuum for 2 h until a constant mass of 4.22 g (96% yield) was obtained. ^1H NMR (300 MHz, $CDCl_3$): δ 8.48 (s, 1H), 8.06 (d, 2H, *J* = 8.4 Hz), 7.50-7.43 (m, 4H), 7.35-7.30 (m, 2H), 7.10 (s, 2H), 2.46 (s, 3H), 1.71 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 137.1, 135.7, 134.5, 131.6, 129.7, 128.6, 128.2, 126.0, 126.0, 125.5, 125.1, 21.2, 20.0.

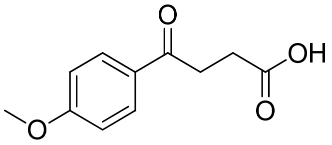
S2: To a flame-dried 250 mL flask was added 9-(2,4,6-trimethylphenyl)-anthracene **(S1)** (3.20 g, 10.8 mmol, 1.0 equiv) and CCl_4 (40 mL). To the resulting solution was added dropwise over 5 minutes Br_2 (612 µL, 11.9 mmol, 1.1 equiv). The reaction mixture was allowed to stir for 15 min at room temperature and quenched with saturated Na_2SO_3 (30 mL). The biphasic mixture was extracted with CH_2Cl_2 (2 X 50 mL) and the combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product **S2** (3.24 g, 73% yield) was obtained by recrystallization from CH_2Cl_2/MeOH as a dark green solid. ^1H NMR (300 MHz, $CDCl_3$): δ 8.63 (d, 2H, *J* = 9.0 Hz), 7.63-7.58 (m, 2H), 7.51 (d, 2H, *J* = 8.7 Hz), 7.40-7.35 (m, 2H), 7.11 (s, 2H), 2.47 (s, 3H), 1.71 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.4, 137.4, 136.6, 134.1, 130.5, 130.5, 128.3, 128.1, 127.0, 126.4, 125.9, 122.2, 21.2, 20.0.

S4: A 100 mL flame-dried round-bottom flask was charged with (*R*)-3,3′-diiodo-5,5′,6,6′,7,7′,8,8′-octahydro-2,2’-bis(ethoxymethyloxy)-1,1’-binaphthyl[1] (818 mg, 1.24 mmol, 1.0 equiv), 9-(2,4,6-trimethylphenyl)10-anthracenylboronic acid (**S3,** 6.0 equiv, prepared by metallation of the bromide precursor (7.41 mmol) using nBuLi (18.5 mmol, 2.5 equiv), THF 250 mL, $B(O\text{-}iPr)_3$ (22.2 mmol, 3.0 equiv) and used as crude material), $Pd(OAc)_2$ (27.8 mg, 0.124 mmol, 0.1 equiv), SPhos (101.5 mg, 0.25 mmol, 0.2 equiv), K_3PO_4 (1.31 g, 6.18 mmol, 2.5 equiv), and anhydrous toluene (25 mL). The resulting mixture was subjected to 3 freeze-pump-thaw cycles and heated at 105 ºC for 18 h. After this time, the reaction mixture was brought to room temperature and poured over water (25 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 X 50 mL). The organic extracts were combined and dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* and the crude product was purified by flash chromatography (5-40% CH_2Cl_2/hexanes) to yield 950.5 mg of **S4** in 77% yield as faint yellow solid. ^1H NMR (300 MHz, $CDCl_3$): δ 8.10 (d, 2H, *J* = 8.7 Hz), 8.00-7.96 (m, 2H), 7.68-7.60 (m, 4H), 7.57-7.52 (m, 2H), 7.46-7.33 (m, 8H), 7.29 (s, 2H), 7.22 (s, 4H), 4.54-4.50 (m, 4H), 2.99 (br, 6H), 2.62-2.45 (m, 12H), 2.01 (m, 8H), 1.90 (s, 6H), 1.87 (s, 6H), 0.70 (t, 6H, *J* = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.2, 137.6, 137.3, 137.1, 137.0, 135.6, 134.8, 133.9, 133.1, 131.6, 130.4, 130.4, 129.4, 129.3, 129.3, 128.2, 127.7, 127.5, 126.0, 125.8, 125.3, 125.1, 96.5, 77.2, 63.8, 29.5, 27.9, 23.4, 23.0, 21.2, 20.1, 20.0, 14.5.

S5: Compound **S4** (840 mg, 0.84 mmol) was suspended in dioxane (50 mL). To the mixture was added conc. HCl (5 mL) and the mixture was heated to 70 ºC for 2 h. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The resulting semi-solid was dissolved in CH_2Cl_2 (70 mL) and washed with water (25 mL) and saturated $NaHCO_3$ (25 mL) and dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by recrystallization from CH_2Cl_2/hexanes to yield 789 mg (94% yield) of the desired product **F** as a faint yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, 2H, *J* = 8.8 Hz), 7.80-7.78 (m, 2H), 7.53-7.46 (m, 6H), 7.40-7.36 (m, 2H), 7.32-7.27 (m, 4H), 7.21 (s, 2H), 7.13 (brs, 4H), 4.70 (s, 2H), 3.72 (s, 2H), 2.90 (m, 4H), 2.80-2.62 (m, 4H), 2.48 (s, 6H), 1.95-1.89 (m, 8H), 1.80 (s, 6H), 1.75 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 137.7, 137.6, 137.1, 136.4, 134.7, 133.2, 131.4, 130.6, 130.5, 129.9, 129.6, 128.3, 126.9, 126.4, 126.2, 125.7, 125.5, 125.5, 125.4, 122.5, 121.0, 67.1, 29.3, 27.5, 23.4, 23.1, 21.3, 20.1, 20.1. HRMS (ESI) calc. for $[M+H]^+$ ($C_{66}H_{59}O_2$) 883.4510, found 883.4493.

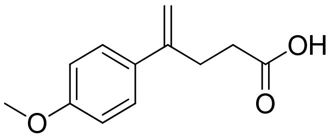
3h: The following procedure is representative for all the dithioacid catalysts used in this study. A flame dried flask was charged with diol **S5** (650 mg, 0.74 mmol, 1.0 equiv), P_2S_5 (81.9 mg, 0.37 mmol, 0.5 equiv), and anhydrous m-xylene (10 mL). The flask was equipped with a condenser and placed in an oil-bath preheated to 150 ºC. The progress of the reaction was monitored by disappearance of the phenolic protons (^{1}H NMR). After 2 h, the reaction was judged complete and allowed to cool to room temperature. The solution was decanted into a flame-dried 100 mL flask and the solvent was evaporated *in vacuo*. The crude product was dissolved in anhydrous CH_2Cl_2 (5 mL) and treated with hexanes (50 mL). At this point, a fine precipitate was observed. The solvent was then partially evaporated until about 2 to 3 mL solvent was left. The precipitate was then collected by filtration and washed with ice-cold hexanes. Following this procedure, the product **16** (617 mg) was obtained as a faint-yellow powder in 85% yield.

3



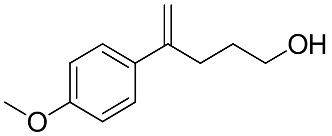
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (d, 2H, *J* = 6.9 Hz), 7.00 (d, 2H, *J* = 9.0 Hz), 3.86(s, 3H), 3.31-3.24 (m, 2H), 2.67 (t, 2H, *J* = 6.3 Hz).

4



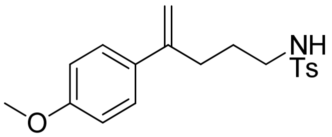
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.35 (m, 2H), 6.96-6.83 (m, 2H), 5.27 (s, 1H), 5.04-5.03 (m, 1H), 2.83 (t, 2H, *J* = 8.0 Hz), 2.56-2.52 (m, 2H).

5



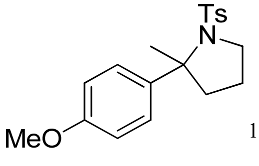
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.35 (m, 2H), 6.88-6.85 (m, 2H), 5.24 (s, 1H), 5.01 (s, 1H), 3.64 (t, 2H, *J* = 6.4 Hz), 2.59 (t, 2H, *J* = 6.8 Hz), 1.75-1.68 (m, 2H), 1.88 (brs, 1H).

7

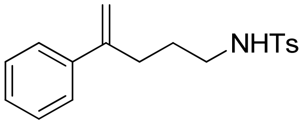


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77-7.71 (m, 2H), 7.29-7.24 (m, 4H), 6.85-6.82 (m, 2H), 5.18 (s, 1H), 4.92 (s, 1H), 4.75 (t, 1H, *J* = 12.4 Hz), 3.81 (s, 3H), 2.97-2.92 (m, 2H), 2.49-2.45 (m, 2H), 2.42 (s, 3H), 1.63-1.56 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 146.3, 143.3, 136.9, 132.8, 129.7, 127.1, 127.0, 113.7, 111.5, 55.3, 42.7, 32.2, 27.9, 21.5.

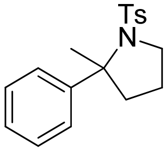
7b



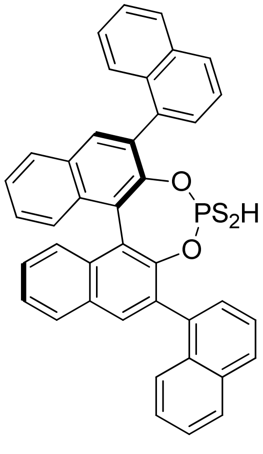
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H, *J* = 8.0 Hz), 7.31-7.27 (m, 2H), 7.27-7.21 (m, 2H), 6.83-6.79 (m, 2H), 3.81 (s, 3H), 3.71-3.55 (m, 2H), 2.41 (s, 3H), 2.16-2.10 (m, 1H), 1.99-1.93 (m, 1H), 1.87 (s, 3H), 1.85-1.84 (m, 2H). Enantiopurity was determined by HPLC analysis (Chiralpak AD column, 92:08 hexanes/ethanol, 1 mL/min) t_R 18.78 min (major), 22.02 min (minor).



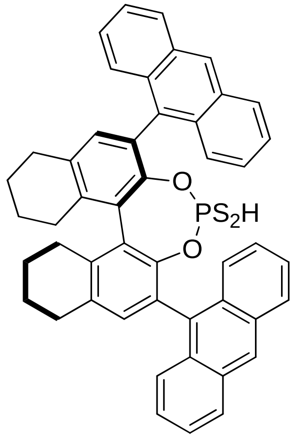
8 ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, 2H, *J* = 8.0 Hz), 7.32-7.29 (m, 7H), 5.25 (s, 1H), 5.01 (s, 1H), 4.57 (t, 1H, *J* = 8.0 Hz), 2.98-2.93 (m, 2H), 2.52-2.49 (m, 2H), 2.43 (s, 3H), 1.63-1.60 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.0, 143.3, 140.5, 136.9, 129.7, 128.4, 127.5, 127.0, 126.0, 113.1, 53.4, 42.7, 32.2, 27.9, 21.5.



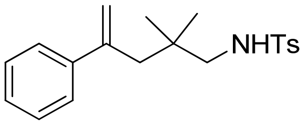
9 ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, 2H, *J* = 8.0 Hz), 7.42-7.39 (m, 2H), 7.32-7.25 (m, 5H), 3.74-3.69 (m, 1H), 3.59-3.53 (m, 1H), 2.42 (s, 3H), 2.18-1.95 (m, 2H), 1.90 (s, 3H), 1.87-1.78 (m, 2H). Enantiopurity was determined by HPLC analysis (Chiralpak AD column, 95:05 hexanes/ethanol, 1 mL/min) t_R 17.52 min (minor), 20.35 min (major).



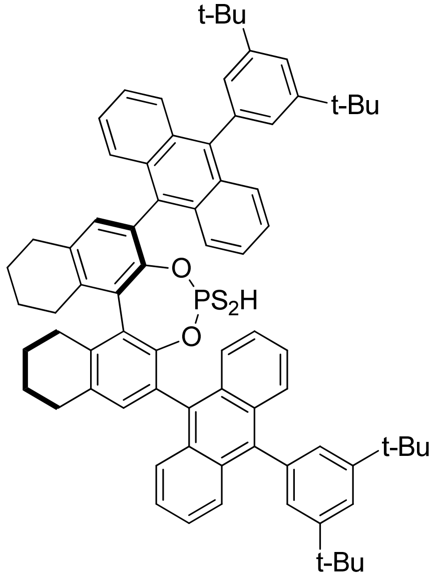
10 NMR analysis of this and related compounds (**3c** and **3d**) is complicated by the presence of multiple conformers due to slow rotation around the 3,3′-biaryl bonds and the unsymmetrical nature of the 1-naphthyl substituent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12-7.33 (m, 24H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 93.4, 93.2, 93.1.



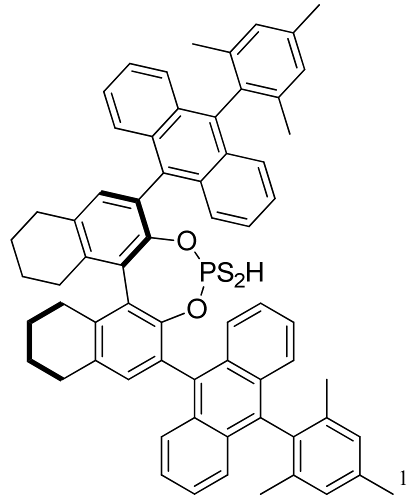
11 ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.47 (s, 2H), 8.04-7.97 (m, 6H), 7.68 (d, 2H, *J* = 8.8 Hz), 7.49-7.27 (m, 10H), 3.13-2.68 (m, 6H), 2.05-1.78 (m, 10H). ^{31}P NMR (162 MHz, CDCl$_3$): δ 90.9. HRMS (ESI) calc. for $[M+H]^+$ ($C_{48}H_{38}O_2PS_2$) 741.2045, found 741.2057.



13 ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.55 (d, 2H, *J* = 8.0 Hz), 7.41-7.25 (m, 7H), 5.27 (s, 1H), 5.03 (s, 1H), 4.52 (t, 1H, *J* = 6.8 Hz), 2.58-2.52 (m, 2H), 2.50 (s, 2H), 2.48 (s, 3H), 0.79 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 154.4, 146.0, 143.3, 143.1, 136.8, 129.6, 128.5, 128.3, 127.4, 126.9, 126.4, 117.6, 55.9, 44.8, 35.2, 25.6, 21.5.



15 ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.11 (d, 2H, *J* = 9.2 Hz), 7.76-7.72 (m, 4H), 7.68 (d, 2H, *J* = 8.0 Hz), 7.56 (s, 2H), 7.46 (s, 2H) 7.37 (t, 2H, *J* = 8.8 Hz), 7.29-7.14 (m, 10H), 3.15-2.96 (m, 6H), 2.78-2.68 (m, 2H), 2.15-1.73 (m, 8H), 1.41 (s, 18H), 1.38 (s, 18H). ^{31}P NMR (162 MHz, CDCl$_3$): δ 91.5. HRMS (ESI) calc. for $[M+H]^+$ ($C_{76}H_{78}O_2PS_2$) 1117.5175, found 1117.5185.

16 

^{1}H NMR (300 MHz, CDCl$_3$): δ 8.09 (d, 2H, *J* = 8.8 Hz), 7.77 (d, 2H, *J* = 8.8 Hz), 7.51-6.99 (m, 18H), 3.13-3.05 (m, 6H), 2.77-2.72 (m, 2H), 2.46 (s, 6H), 2.07-2.01 (m, 8H), 1.83 (s, 6H), 1.60 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 137.3, 137.0, 136.7, 135.7, 134.9, 134.3, 131.0, 130.7, 129.9, 129.6, 129.1, 128.3, 128.1, 128.0, 126.8, 126.1, 126.0, 125.9, 125.6, 125.1, 125.0, 124.5, 29.4, 28.4, 22.8, 22.8, 21.3, 21.2, 20.1, 19.8. ^{31}P NMR (162 MHz, CDCl$_3$): δ 89.7. HRMS (ESI) calc. for [M+H]$^+$ ($C_{66}H_{58}O_2PS_2$) 977.3610, found 977.3617.

Substrates were prepared by the methods of Widenhoefer and coworkers[2] according to the general scheme shown in Supporting Figure 2. Dienyl bromides were prepared by the method of Ollis and coworkers[3].

17c: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.76 (d, 2H, *J* = 7.2 Hz), 7.30 (d, 2H, *J* = 7.2 Hz), 6.09 (d, 1H, *J* = 15.2 Hz), 5.53 (dt, 1H, *J* = 15.2, 7.8 Hz), 5.03 (t, 1H, *J* = 6.8 Hz), 4.88 (s, 1H), 4.86 (s, 1H), 2.66 (d, 2H, *J* = 6.8 Hz), 2.00 (d, 2H, *J* = 7.8 Hz), 1.78 (s, 3H), 0.86 (s, 6H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 162.7, 141.8, 135.9, 131.4, 129.2, 125.8, 115.0, 114.2, 55.6, 52.8, 42.7, 34.6, 25.0, 18.7.

17a: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.50 (s, 2H), 7.17 (s, 1H), 6.09 (d, 1H, *J* = 15.3 Hz), 5.55 (dt, 1H, *J* = 15.3, 7.8 Hz), 5.22 (t, 1H, *J* = 6.8 Hz), 4.87 (s, 1H), 4.85 (s, 1H), 2.67 (d, 2H, *J* = 6.8 Hz), 2.36 (s, 3H), 2.01 (d, 2H, *J* = 7.8 Hz), 1.78 (s, 3H), 0.87 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 142.1, 139.9, 139.3, 136.2, 134.5, 126.2, 124.8, 115.3, 53.1, 43.0, 35.0, 25.2, 21.5, 19.0. HRMS (ESI) calc. for [M+H]$^+$ ($C_{18}H_{28}NO_2S$) 322.1835, found 322.1832.

17b: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.80 (d, 2H, *J* = 8.7 Hz), 7.46 (d, 2H, *J* = 8.7 Hz), 6.08 (d, 1H, *J* = 15.6 Hz), 5.51 (dt, 1H, *J* = 15.6, 7.8 Hz), 5.21 (t, 1H, *J* = 6.8 Hz), 4.87 (s, 1H), 4.85 (s, 1H), 2.66 (d, 2H, *J* = 6.8 Hz), 1.98 (d, 2H, *J* = 7.8 Hz), 1.76 (s, 3H), 0.85 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 142.0, 139.3, 138.7, 136.4, 129.7, 128.8, 125.8, 115.5, 53.1, 42.9, 35.0, 25.2, 18.9. HRMS (ESI) calc. for [M+H]$^+$ ($C_{16}H_{23}ClNO_2S$) 328.1133, found 328.1136.

17h: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.74 (d, 2H, *J* = 8.1 Hz), 7.27 (d, 2H, *J* = 8.1 Hz), 5.94 (d, 1H, *J* = 15.6 Hz), 5.59 (bs, 1H), 5.37 (dt, 1H, *J* = 15.6, 7.5 Hz), 5.09 (t, 1H, *J* = 6.9 Hz), 2.63 (d, 2H, *J* = 6.9 Hz), 2.40 (s, 3H), 2.12-1.98 (m, 4H), 1.94 (d, 2H, *J* = 7.5 Hz), 1.68-1.50 (m, 4H), 0.82 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 143.1, 136.8, 136.5, 135.3, 129.5, 127.8, 127.0, 121.3, 52.7, 42.7, 34.5, 25.6, 24.9, 24.5, 22.5, 22.4, 21.4. HRMS (ESI) calc. for $[M+H]^+$ ($C_{20}H_{30}NO_2S$) 348.1992, found 348.1988.

17k: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.73 (d, 2H, *J* = 8.4 Hz), 7.27 (d, 2H, *J* = 8.4 Hz), 5.98 (d, 1H, *J* = 15.3 Hz), 5.45-5.31 (m, 2H), 4.91 (t, 1H, *J* = 6.8 Hz), 2.64 (d, 2H, *J* = 6.8 Hz), 2.40 (s, 3H), 1.95 (d, 2H, *J* = 7.5 Hz), 1.68 (d, 3H, *J* = 6.9 Hz), 1.64 (s, 3H), 0.83 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 143.1, 137.8, 136.8, 134.1, 129.6, 127.0, 125.3, 121.8, 52.7, 42.7, 34.5, 24.9, 21.4, 13.6, 12.0. HRMS (ESI) calc. for $[M+H]^+$ ($C_{18}H_{28}NO_2S$) 322.1835, found 322.1831.

17k-2: Isolated as about a 6:1 mixture of *E* and *Z* olefin isomers. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.75 (d, 2H, *J* = 8.1 Hz), 7.30 (d, 2H, *J* = 8.1 Hz), 6.03 (d, 1H, *J* = 15.9 Hz), 5.63-5.53 (m, 1H), 4.96-4.86 (m, 2H), 2.66 (d, 2H, *J* = 6.9 Hz), 2.42 (s, 3H), 2.16 (q, 2H, *J* = 7.5 Hz) 1.98 (d, 2H, *J* = 7.5 Hz), 1.05 (t, 3H, *J* = 7.5 Hz), 0.89 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 147.4, 143.2, 136.8, 135.2, 129.6, 127.0, 124.8, 112.9, 52.8, 42.8, 34.6, 24.9, 24.8, 21.5, 12.6.

17f: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.76 (d, 2H, *J* = 8.1 Hz), 7.31 (d, 2H, *J* = 8.1 Hz), 6.02 (d, 1H, *J* = 15.6 Hz), 5.62 (dt, 1H, *J* = 15.6, 7.8 Hz), 4.96 (T, 1H, *J* = 6.8 Hz), 4.90 (app s, 2H), 3.63 (t, 2H, *J* = 6.3 Hz), 2.67 (d, 2H, *J* = 6.8 Hz), 2.43 (s, 3H), 2.22 (t, 2H, *J* = 7.7 Hz), 2.00 (d, 2H, *J* = 7.8 Hz), 1.67 (app quintet, 2H, *J* = 6.9 Hz), 0.90 (s, 9H), 0.87 (s, 6H), 0.06 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 145.9, 143.5, 137.2, 135.4, 130.0, 127.3, 125.5, 114.4, 63.0, 53.7, 53.2, 43.1, 35.0, 31.7, 28.6, 26.2, 25.2, 21.8, 18.6, -5.0. HRMS (ESI) calc. for $[M-H]^+$ ($C_{25}H_{42}NO_3SSi$) 464.2649, found 464.2650.

17l: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.74 (d, 2H, *J* = 8.1 Hz), 7.27 (d, 2H, *J* = 8.1 Hz), 6.09 (d, 1H, *J* = 15.6 Hz), 5.46 (dt, 1H, *J* = 15.6, 7.5 Hz), 5.06 (t, 1H, *J* = 6.7 Hz), 4.85 (s, 1H), 4.83 (s, 1H), 2.70 (d, 2H, *J* = 6.8 Hz), 2.39 (s, 3H), 2.09 (d, 2H, *J* = 7.5 Hz), 1.72 (s, 3H), 1.60-1.45 (m, 4H), 1.45-1.30 (m, 4H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 145.5, 142.1, 137.0, 136.0, 130.0, 127.4, 126.7, 115.3, 50.5, 46.3, 40.8, 35.5, 25.1, 21.8, 18.9. HRMS (ESI) calc. for $[M+H]^+$ ($C_{19}H_{28}NO_2S$) 334.1835, found 334.1834.

17m: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.73 (d, 2H, *J* = 8.1 Hz), 7.27 (d, 2H, *J* = 8.1 Hz), 6.09 (d, 1H, *J* = 15.6 Hz), 5.47 (dt, 1H, *J* = 15.6, 7.8 Hz), 5.89-5.78 (m, 3H), 2.70 (d, 2H, *J* = 6.9 Hz), 2.40 (s, 3H), 2.05 (d, 2H, *J* = 7.8 Hz), 1.73 (s, 3H), 1.42-1.20 (m, 10H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 143.5, 142.1, 137.0, 136.1, 129.9, 127.4, 125.7, 115.4, 53.7, 49.5, 39.4, 37.1, 33.7, 26.3, 21.8, 21.6, 18.9. HRMS (ESI) calc. for $[M+H]^+$ ($C_{20}H_{30}NO_2S$) 348.1992, found 348.1987.

17c-2: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.73 (d, 2H, *J* = 7.7 Hz), 7.29 (d, 2H, *J* = 7.7 Hz), 4.81 (m, 1H), 4.60 (t, 1H, *J* = 7.1 Hz), 2.71 (d, 2H, *J* = 7.1 Hz), 2.42 (s, 3H), 1.83 (d, 2H, *J* = 8.1 Hz), 1.61 (s, 3H), 1.60 (s, 3H), 0.86 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 203.3, 143.3, 137.2, 129.7, 127.1, 94.2, 84.2, 52.5, 39.8, 34.5, 24.8, 21.5, 20.5. HRMS (ESI) calc. for $[M+H]^+$ ($C_{17}H_{26}NO_2S$) 308.1679, found 308.1685.

17d: ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.13-8.07 (m, 1H), 7.88-7.82 (m, 1H), 7.76-7.71 (m, 2H), 5.31 (t, 1H, *J* = 6.9 Hz), 4.88-4.79 (m, 1H), 2.88 (d, 2H, *J* = 6.9 Hz), 1.88 (d, 2H, *J* = 7.8 Hz), 1.63 (s, 3H), 1.62 (s, 3H), 0.90 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 203.4, 147.9, 133.5, 132.7, 131.0, 125.2, 94.2, 83.7, 52.9, 39.6, 34.6, 24.6, 20.4. HRMS (ESI) calc. for $[M+H]^+$ ($C_{16}H_{23}N_2O_4S$) 339.1373, found 339.1377.

17e: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.93-7.86 (m, 4H), 7.52-7.40 (m, 6H), 4.88-4.79 (m, 1H), 2.88 (br, 1H), 2.76 (t, 2H, *J* = 6.9 Hz), 1.88 (d, 2H, *J* = 8.1 Hz), 1.59 (s, 3H), 1.58 (s, 3H), 0.90 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 203.1, 133.4, 132.1, 132.0, 131.7, 128.5, 128.3, 94.0, 84.3, 50.4, 39.9, 34.9, 34.8, 24.7, 20.4. HRMS (ESI) calc. for $[M+H]^+$ ($C_{22}H_{29}NOP$) 354.1981, found 354.1988.

17g: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.79 (d, 2H, *J* = 8.7 Hz), 6.96 (d, 2H, *J* = 8.7 Hz), 4.90-4.81 (m, 2H), 3.85 (s, 3H), 2.68 (d, 2H, *J* = 6.9 Hz), 2.04-1.98 (m, 4H), 1.84 (d, 2H, *J* = 8.1 Hz), 1.57-1.43 (m, 6H), 0.86 (s, 6H).^{13}C NMR (75 MHz, CDCl$_3$) δ 199.8, 162.6, 131.6, 129.0, 114.1, 101.3, 83.9, 55.5, 52.3, 40.1, 34.4, 31.4, 27.2, 25.9, 24.6. HRMS (ESI) calc. for $[M+H]^+$ ($C_{20}H_{30}NO_3S$) 364.1941, found 364.1950.

17i: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.81 (d, 2H, *J* = 8.4 Hz), 7.33 (d, 2H, *J* = 8.4 Hz), 7.07 (s, 1H), 4.87 (app septet, 1H, *J* = 3.0 Hz), 3.79 (s, 2H), 2.49 (s, 3H), 1.65 (s, 3H), 1.64 (s, 3H), 0.97 (s, 6H).^{13}C NMR (75 MHz, CDCl$_3$) δ 200.0, 144.7, 133.7, 129.6, 128.6, 97.3, 96.5, 86.1, 35.8, 25.0, 21.6, 20.6. HRMS (ESI) calc. for $[M+H]^+$ ($C_{16}H_{24}NO_3S$) 310.1471, found 310.1478.

18j: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.81 (d, 2H, *J* = 8.1 Hz), 7.33 (d, 2H, *J* = 8.1 Hz), 7.03 (s, 1H), 4.92-4.86 (m, 1H), 4.01 (t, 2H, *J* = 6.9 Hz), 2.44 (s, 3H), 2.25 (q, 2H, *J* = 6.9 Hz), 2.08-2.02 (m, 4H), 1.60-1.46 (m, 6H).^{13}C NMR (75 MHz, CDCl$_3$) δ 199.0, 144.7, 133.5, 129.6, 128.5, 103.0, 84.1, 31.5, 28.2, 27.3, 26.0, 21.6.

20a: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.14 (d, 1H, *J* = 8.8 Hz), 7.03 (d, 1H, *J* = 2.4 Hz), 6.84 (m, 2H), 4.96 (m, 1H), 3.85 (s, 3H), 3.70 (s, 3H), 3.66 (s, 3H), 3.44 (s, 2H), 2.65 (d, 2H, *J* = 7.6 Hz), 2.13 (m, 4H), 1.60 (m, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 200.5, 171.6, 153.8, 132.0, 128.8, 111.7, 109.8, 107.8, 102.4, 100.9, 83.1, 58.8, 55.9, 52.3, 32.8, 32.7, 31.5, 27.4, 27.1, 26.0.

21a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.25 (d,1H, *J* = 8.4 Hz), 7.11 (d, 1H, *J* = 8.4 Hz), 6.90 (s, 1H), 4.90 (m, 1H), 3.71 (s, 3H), 3.68 (s, 6H), 3.41 (s, 2H), 2.62 (d, 2H, *J* = 7.6 Hz), 2.15 (m, 4H), 1.60 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 171.3, 135.2, 130.1, 129.5, 124.2, 121.6, 112.4, 110.7, 108.0, 102.5, 82.9, 58.5, 52.4, 32.9, 32.7, 31.6, 27.2, 27.1, 26.0.

19a: ^{1}H NMR (400 MHz, $CDCl_3$) δ. 7.57 (d, 1H, *J* = 8.0 Hz), 7.27 (m, 1H), 7.19 (dt, 1H, *J* = 7.2, 0.8 Hz), 7.09 (dt, 1H, *J* = 8.0, 0.8 Hz), 6.86 (s, 1H), 4.96 (m, 1H), 3.73 (s, 3H), 3.67 (s, 6H), 3.48 (s, 2H), 2.63 (d, 2H, *J* = 7.6 Hz), 1.73 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.8, 171.5, 136.6, 128.6, 128.1, 121.4, 118.9, 118.8, 109.1, 108.4, 95.2, 83.4, 58.9, 52.2, 32.6, 32.6, 27.6, 20.6.

18c: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, 2H, *J* = 8.4 Hz), 7.26 (d, 2H, *J* = 8.4 Hz), 5.00 (d, 1H, *J* = 8.5 Hz), 4.34 (app q, 1H, *J* = 8.5 Hz), 3.20 (d, 1H, *J* = 9.9 Hz), 3.10 (d, 1H, *J* = 9.9 Hz), 2.40 (s, 3H), 1.74 (dd, 1H, *J* = 12.6, 7.2 Hz), 1.66 (s, 3H), 1.61 (s, 3H), 1.40 (dd, 1H, *J* = 12.6, 8.5 Hz), 1.03 (s, 3H), 0.77 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 136.8, 133.1, 129.5, 127.7, 126.8, 61.2, 58.0, 48.1, 37.7, 26.7, 26.3, 26.0, 21.8, 18.2. HRMS (ESI) calc. for $[M+H]^+$ ($C_{17}H_{26}NO_2S$) 308.1679, found 308.1675. Enantiopurity was determined by HPLC analysis (Chiralpak AD-H column, 98:2 hexanes/ethanol, 1 mL/min) t_R 8.9 min (minor), 11.6 min (major). Absolute configuration was assigned by comparison with a previous report, and the rest of the products were assigned by analogy[4].

18a: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (s, 2H), 7.15 (s, 1H), 5.01 (d, 1H, *J* = 9 Hz), 4.36 (dd, 1H, *J* = 16.2, 9 Hz), 3.24 (d, 1H, *J* = 9.9 Hz), 3.10 (d, 1H, *J* = 9.9 Hz), 2.36 (s, 6H), 1.75 (dd, 1H, *J* = 12.3, 7.2 Hz), 1.68 (s, 3H), 1.64 (s, 3H), 1.41 (dd, 1H, *J* = 12.3, 9 Hz), 1.04 (s, 3H), 0.81 (s, 3H). NMR (75 MHz, $CDCl_3$) δ 139.1, 138.4, 133.8, 132.8, 126.4, 124.9, 60.8, 57.7, 47.8, 37.3, 26.4, 25.9, 25.6, 21.2, 17.9. HRMS (ESI) calc. for $[M+H]^+$ ($C_{18}H_{28}NO_2S$) 322.1835, found 322.1830. Enantiopurity was determined by HPLC analysis (Chiralpak AS-H column, 99.5:0.5 hexanes/ethanol, 1 mL/min) t_R 11.5 min (minor), 14.5 min (major).

18b: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (dt, 2H, *J* = 8.7, 2.1 Hz), 7.45 (dt, 2H, *J* = 8.7, 2.1 Hz), 4.91 (doublet of septets, 1H, *J* = 9.3, 1.2 Hz), 4.43 (ddd, 1H, *J* = 9.3, 8.7, 7.5 Hz), 3.29 (dd, 1H, *J* = 9.9, 1.2 Hz), 3.09 (d, 1H, *J* = 9.9 Hz), 1.80 (ddd, 1H, *J* = 12.6, 7.5, 1.2 Hz), 1.68 (d, 3H, *J* = 1.2 Hz), 1.62 (d, 3H, *J* = 1.2 Hz), 1.42 (dd, 1H, *J* = 12.6, 8.7 Hz), 1.06 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9, 138.8, 133.9, 129.1, 129.0, 126.2, 61.1, 58.1, 48.1, 37.8, 26.5, 26.3, 25.9, 18.2. Enantiopurity was determined by HPLC analysis (Chiralpak AS-H column, 99:1 hexanes/ethanol, 1 mL/min) t_R 14.1 min (minor), 15.5 min (major).

18h: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, 2H, *J* = 8.1 Hz), 7.28 (d, 2H, *J* = 8.1 Hz), 4.99 (d, 1H, *J* = 9 Hz), 4.41 (dd, 1H, *J* = 16.2, 8.7 Hz), 3.24 (d, 1H, *J* = 9.9 Hz), 3.13 (d, 1H, *J* = 9.9 Hz), 2.42 (s, 3H), 2.30-2.05 (m, 2H), 2.05-1.95 (m, 2H), 1.80-1.32 (m, 8H), 1.05 (s, 3H), 0.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8, 140.6, 136.5, 129.2, 127.4, 123.2, 61.0, 56.9, 37.4, 36.8, 29.0, 28.1, 27.5, 26.7, 26.4, 26.0, 21.5. HRMS (ESI) calc. for $[M+H]^+$ ($C_{20}H_{30}NO_2S$) 348.1992, found 348.1988. Enantiopurity was determined by HPLC analysis (Chiralpak AS-H column, 99:1 hexanes/ethanol, 1 mL/min) t_R 13.4 min (minor), 14.9 min (major).

18k: Using **4d** as starting material, **5d** was isolated as a 4.7:1 mixture of olefin isomers favoring the *E* isomer. Using **4e** as starting material, the product was isolated as a 2:1 mixture of isomers favoring the *Z* isomer. NMR data are reported for the 4.7:1 mixture. The *E* and *Z* isomers were assigned on the basis of a 2D ^{1}H-^{1}H NOESY experiment. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, 2H, *J* = 8.4 Hz), 7.30-7.25 (m, 2H), 5.02-4.96 (m, 1H), 4.45-4.35 (m, 1H), 3.30-3.20 (m, 1H), 3.17-3.09 (m, 1H), 2.41 (s, 3H), 2.24-2.14 (m, 0.18H), 2.07-1.87 (m, 0.18H), 1.91 (q, 1.48H, *J* = 7.4 Hz), 1.76 (ddd, 0.82H, *J* = 12.6, 8.4, 1.2 Hz), 1.80-1.70 (m, 0.18H), 1.67 (d, 2.46H, *J* = 0.9 Hz), 1.62 (d, 0.54H, *J* = 1.2 Hz), 1.47-1.35 (m, 1H), 1.06 (s, 2.46H), 1.05 (s, 0.54H), 1.01 (t, 0.54H, *J* = 7.5 Hz), 0.91 (t, 2.46H, *J* = 7.4 Hz), 0.82 (s, 2.46H), 0.80 (s, 0.54H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8, 137.9, 136.7, 129.2, 127.3, 124.8, 60.9, 57.6, 47.9, 37.4, 32.0, 26.4, 26.0, 21.5, 16.3, 12.0. HRMS (ESI) calc. for $[M+H]^+$ ($C_{18}H_{28}NO_2S$) 322.1835, found 322.1832. Enantiopurity was determined by HPLC analysis (Chiralpak AD-H column, 99.5:0.5 hexanes/ethanol, 1 mL/min) t_R 15.5 min (*Z* diastereomer, minor enantiomer), 17.0 min (*E* diastereomer, minor enantiomer), 18.5 min (*Z* diastereomer, major enantiomer), 26.4 min (*E* diastereomer, major enantiomer).

18f: Isolated as a 78:22 mixture of olefin isomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68-7.64 (m, 2H), 7.28-7.26 (m, 2H), 5.05-5.02 (m, 1H), 5.04 (m, 0.22H), 4.41-4.35 (m, 1H), 3.60 (t, 0.44H, *J* = 6.3 Hz), 3.57 (t, 1.56H, *J* = 6.6 Hz), 3.25-3.20 (m, 1H), 3.14-3.10 (m, 1H), 2.41 (s, 3H), 2.32-2.25 (m, 0.22H), 1.97-1.92 (m, 1.77H), 1.78-1.73 (m, 1.23H), 1.67 (d, 2.34H, *J* = 0.6 Hz), 1.63 (d, 0.66H, *J* = 0.6 Hz), 1.61-1.47 (m, 2H), 1.45-1.39 (m, 1H), 1.05 (s, 2.34H), 1.04 (s, 0.66H), 0.892 (s, 7.02H), 0.888 (s, 1.98H), 0.80 (s, 2.34H), 0.79 (s, 0.66H), 0.06 (s, 4.68H), 0.06 (s, 1.32H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.3, 142.8, 136.5, 136.1, 129.2, 127.4, 127.2, 62.9, 60.8, 57.3, 48.2, 37.4, 31.4, 28.3, 26.4, 25.9, 23.2, 21.5, 18.3, -5.3. HRMS (ESI) calc. for $[M+H]^+$ ($C_{25}H_{44}NO_3SSi$) 466.2806, found 466.2805. Enantiopurity was determined by HPLC analysis after deprotection of the alcohol with tetrabutylammonium fluoride (Regis Technologies Whelk-O1 column, 97:3 hexanes/ethanol, 1 mL/min) t_R 51.4 min (*Z* diastereomer, minor enantiomer), 57.1 min (*Z* diastereomer, major enantiomer), 73.1 min (*E* diastereomer, minor enantiomer), 83.3 min (*E* diastereomer, major enantiomer).

18l: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, 2H, *J* = 8.1 Hz), 7.28 (d, 2H, *J* = 8.1 Hz), 5.06 (d, 1H, *J* = 8.3 Hz), 4.30 (app q, 1H, *J* = 8.3 Hz), 3.26 (d, 1H, *J* = 9.9 Hz), 3.20 (d, 1H, *J* = 9.9 Hz), 2.42 (s, 3H), 1.84 (dd, 1H, *J* = 12.3, 7.2 Hz), 1.68 (s, 3H), 1.64 (s, 3H), 1.63-1.45 (m, 7H), 1.25-1.15 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 136.6, 133.0, 129.5, 127.7, 126.9, 59.8, 58.3, 48.9, 46.4, 37.2, 36.7, 26.0, 24.9, 24.8, 21.8, 18.3. HRMS (ESI) calc. for $[M+H]^+$ ($C_{19}H_{28}NO_2S$) 334.1835, found 334.1832. Enantiopurity was determined by HPLC analysis (Chiralpak AS-H column, 99:1 hexanes/ethanol, 1 mL/min) t_R 20.7 min (minor), 28.1 min (major).

18m: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.67 (d, 2H, *J* = 8.4 Hz), 7.28 (d, 2H, *J* = 8.4 Hz), 5.06 (d, 1H, *J* = 8.5 Hz), 4.30 (app q, 1H, *J* = 8.5 Hz), 3.36 (d, 1H, *J* = 10.2 Hz), 3.10 (d, 1H, *J* = 10.2 Hz), 2.42 (s, 3H), 1.83 (dd, 1H, *J* = 12.63, 7.2 Hz), 1.67 (s, 3H), 1.64 (s, 3H), 1.48-1.22 (m, 9H), 1.10-1.00 (m, 2H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 143.1, 136.4, 132.9, 129.5, 127.7, 126.9, 58.7, 57.3, 46.1, 41.4, 36.8, 34.7, 26.2, 26.0, 24.0, 23.2, 23.2, 21.8, 18.3. HRMS (ESI) calc. for [M+H]$^+$ ($C_{19}H_{28}NO_2S$) 334.1992, found 334.1990. Enantiopurity was determined by HPLC analysis (Chiralpak AS-H column, 99:1 hexanes/ethanol, 1 mL/min) t$_R$ 22.1 min (minor), 28.5 min (major).

18d: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.93-7.87 (m, 1H), 7.63-7.55 (m, 3H), 4.72-4.62 (m, 2H), 3.57 (dd, 1H, *J* = 10.5, 0.6 Hz), 3.16 (d, 1H, *J* = 10.2 Hz), 1.89-1.82 (m, 1H), 1.64 (s, 3H), 1.48-1.44 (m, 1H), 1.39 (s, 3H), 1.09 (s, 3H), 1.07 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 147.7, 135.4, 135.2, 132.8, 131.0, 130.8, 124.5, 123.7, 61.3, 57.8, 47.8, 44.4, 37.5, 25.5, 25.4, 17.7. HRMS (ESI) calc. for [M+H]$^+$ ($C_{16}H_{23}N_2O_4S$) 339.1373, found 339.1376. Enantiopurity was determined by HPLC analysis (Chiralpak IA column, 98:2 hexanes/isopropanol, 1 mL/min) t$_R$ 11.7 min (major), 12.6 min (minor).

18e: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.95-7.81 (m, 4H), 7.44-7.31 (m, 6H), 5.08 (d, 1H, *J* = 9.3 Hz), 4.39 (app quintet, 1H, *J* = 8.4 Hz), 3.05-2.88 (m, 2H), 3.16 (d, 1H, *J* = 10.2 Hz), 1.82 (dd, 1H, *J* = 12.3, 7.5 Hz), 1.42 (dd, 1H, *J* = 12.6, 8.7 Hz), 1.36 (s, 3H), 1.17 (s, 3H), 1.04 (s, 3H), 0.92 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 134.3, 133.6, 132.8, 132.6, 132.3, 131.9, 131.5, 131.1, 131.0, 128.3, 128.2, 127.9, 127.7, 60.1, 56.3, 48.6, 38.8, 26.1, 25.2, 16.7. HRMS (ESI) calc. for [M+H]$^+$ ($C_{22}H_{29}NOP$) 354.1981, found 354.1988. Enantiopurity was determined by HPLC analysis (Chiralpak IA column, 98:2 hexanes/isopropanol, 1 mL/min) t$_R$ 34.5 min (major), 42.4 min (minor).

18g ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.79-7.71 (m, 2H), 7.00-6.92 (m, 2H), 5.00 (d, 9H), 4.39 (dd, 1H, *J* = 16.2, 9 Hz), 3.87 (s, 3H), 3.23 (d, 1H, *J* = 9.9 Hz), 3.13 (d, 1H, *J* = 9.9 Hz), 2.30-1.96 (m, 4H), 1.80-1.33 (m, 8 H), 1.05 (s, 3H), 0.79 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 162.5, 140.4, 131.3, 129.4, 123.3, 113.7, 61.0, 56.8, 55.5, 48.4, 37.3, 36.9, 29.0, 28.2, 27.5, 26.7, 26.4, 26.0. HRMS (ESI) calc. for [M+H]$^+$ ($C_{20}H_{30}NO_3S$) 364.1941, found 364.1934. Enantiopurity was determined by HPLC analysis (Chiralpak AS-H column, 98:2 hexanes/ethanol, 1 mL/min) t$_R$ 25.0 min (minor), 30.1 min (major).

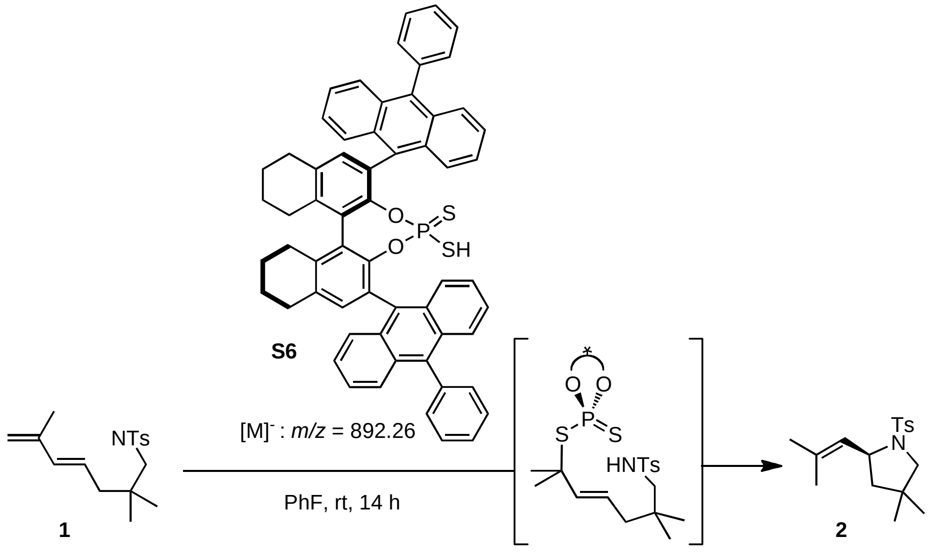
18i: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.88 (d, 2H, *J* = 8.1 Hz), 7.37 (d, 2H, *J* = 8.1 Hz), 5.21 (d, 1H, *J* = 9.6 Hz), 4.17 (d, 1H, *J* = 9.6 Hz), 3.57 (d, 1H, *J* = 8.1 Hz), 3.42 (d, 1H, *J* = 8.1 Hz), 2.46 (s, 3H), 1.83 (s, 3H), 1.76 (s, 3H), 1.08 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 144.8, 137.4, 132.3, 129.6, 129.4, 119.2, 80.3, 66.4, 47.7, 26.3, 21.7, 21.1, 18.3. HRMS (ESI) calc. for [M+H]$^+$ ($C_{16}H_{24}NO_3S$) 310.1471, found 310.1468. Enantiopurity was determined by HPLC analysis (Chiralpak AS-H column, 99:1 hexanes/ethanol, 1 mL/min) t$_R$ 16.3 min (minor), 19.1 min (major).

18j: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, 2H, *J* = 8.1 Hz), 7.34 (d, 2H, *J* = 8.1 Hz), 5.13 (d, 1H, *J* = 8.7 Hz), 5.05-4.97 (m, 1H), 4.08-3.96 (m, 2H), 2.44 (s, 3H), 2.41-1.96 (m, 6H), 1.63-1.55 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 144.0, 133.4, 129.7, 129.3, 120.4, 70.1, 56.7, 37.0, 36.7, 29.3, 28.4, 27.7, 26.7, 21.8. Enantiopurity was determined by HPLC analysis (Chiralpak AS-H column, 98:2 hexanes/ethanol, 1 mL/min) t_R 14.2 min (minor), 29.7 min (major).

20b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, 1H, *J* = 8.8 Hz), 6.97 (d, 1H, *J* = 2.4 Hz), 6.83 (dd, 1H, *J* = 8.8, 2.4 Hz), 5.06 (d, 1H, *J* = 9.2 Hz), 4.11 (q, 1H, *J* = 8.8 Hz), 3.86 (s, 3H), 3.78 (s, 3H), 3.65 (s, 3H), 3.55 (s, 3H), 3.45 (d, 1H, *J* = 15.6 Hz), 3.23 (dd, 1H, *J* = 15.2, 1.6 Hz), 2.66 (ddd, 1H, *J* = 13.6, 6.4, 1.6 Hz), 2.35 (m, 2H), 2.14 (m, 2H), 1.98 (dd, 1H, *J* = 13.6, 9.2 Hz), 1.61 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 171.4, 153.7, 141.1, 136.9, 133.0, 126.7, 123.1, 110.8, 109.2, 105.8, 100.3, 56.0, 54.3, 52.7, 52.6, 37.0, 36.8, 30.3, 28.9, 28.5, 27.7, 27.6, 26.8. Enantiopurity was determined by HPLC analysis (Chiralpak IA column, 98:2 hexanes/isopropanol, 1 mL/min) t_R 19.7 min (minor), 27.2 min (major).

21b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, 1H, *J* = 2.0 Hz), 7.23 (dd, 1H, *J* = 8.8, 2.0 Hz), 7.08 (d, 1H, *J* = 8.8 Hz), 5.04 (d, 1H, *J* = 9.2 Hz), 4.11 (q, 1H, *J* = 9.6 Hz), 3.77 (s, 3H), 3.65 (s, 3H), 3.56 (s, 3H), 3.41 (d, 1H, *J* = 15.2 Hz), 3.19 (dd, 1H, *J* = 15.6, 2.0 Hz), 2.65 (dd, 1H, *J* = 11.6, 4.8 Hz), 2.34 (m, 2H), 2.13 (m, 2H), 1.97 (dd, 1H, *J* = 13.6, 9.2 Hz), 1.61 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 171.2, 141.7, 137.6, 136.3, 128.1, 123.7, 122.5, 120.6, 112.0, 110.0, 106.0, 54.1, 52.8, 52.7, 37.0, 36.8, 30.4, 30.3, 28.9, 28.4, 27.7, 27.4, 26.7. Enantiopurity was determined by HPLC analysis (Chiralpak IA column, 98:2 hexanes/isopropanol, 1 mL/min) t_R 11.4 min (minor), 21.5 min (major).

19b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, 1H, *J* = 7.6 Hz), 7.29 (d, 1H, *J* = 8.0 Hz), 7.22 (t, 1H, *J* = 7.2 Hz), 7.13 (t, 1H, *J* = 7.6 Hz), 5.16 (d, 1H, *J* = 9.2 Hz), 4.11 (q, 1H, *J* = 8.8 Hz), 3.81 (s, 3H), 3.69 (s, 3H), 3.59 (s, 3H), 3.51 (d, 1H, *J* = 8.4 Hz), 3.30 (dd, 1H, *J* = 15.6, 2.0 Hz), 2.73 (ddd, 1H, *J* = 13.6, 6.4, 1.6 Hz), 2.02 (dd, 1H, *J* = 13.2 Hz, 9.2 Hz), 1.88 (s, 3H, 1.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ172.3, 171.3, 137.7, 136.2, 133.3, 126.5, 126.4, 121.0, 118.8, 118.0, 108.6, 106.3, 54.2, 52.7, 52.6, 36.3, 31.2, 30.0, 27.5, 25.6, 17.8. Enantiopurity was determined by HPLC analysis (Chiralpak AS-H column, 99:1 hexanes/isopropanol, 1 mL/min) t_R 8.4 min (major), 9.7 min (minor).



S6

[M]$^-$: *m/z* = 892.26

PhF, rt, 14 h

1

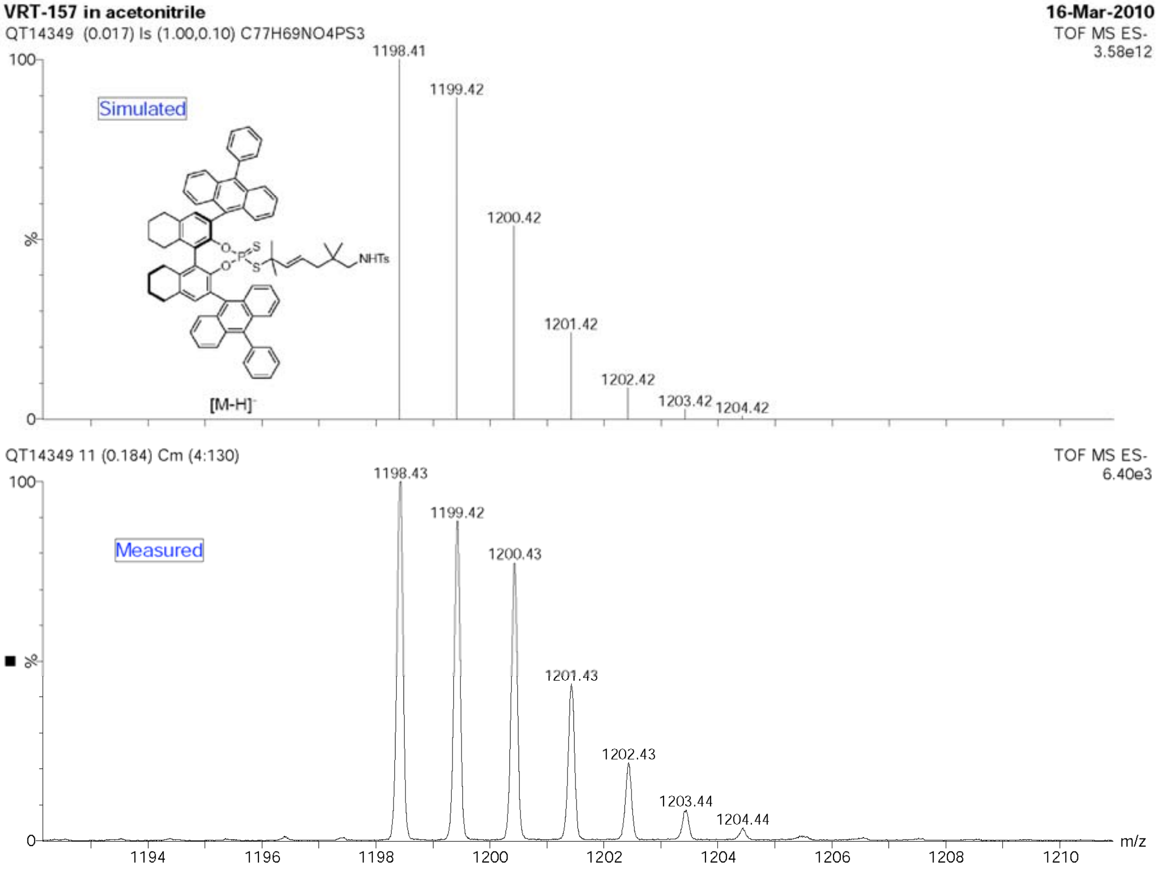
2

[M-H]$^-$: *m/z* = 1198.41

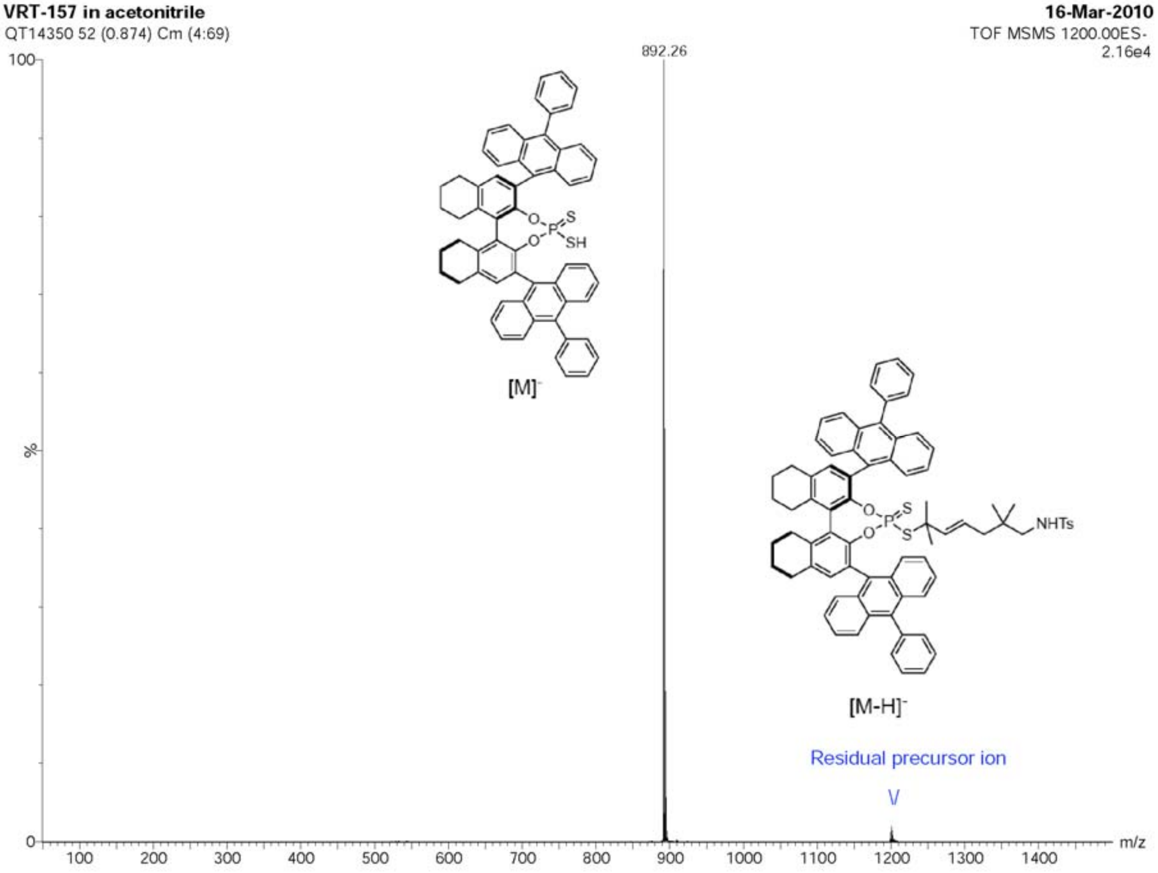
Supporting Figure 3. Reaction analyzed by mass spectrometry.

Studies of reaction intermediate by TOF-MS

A one-dram screw cap vial was charged with catalyst **S6** (0.01 mmol), substrate **1** (0.1 mmol), and fluorobenzene (0.2 mL). The mixture was stirred for 14 h. 0.1 mL of the mixture was diluted with 1 mL CH_3CN, and this solution was analyzed by TOFMS$^-$ (negative mode). A peak fully consistent with the proposed intermediate was observed at 1198.43. The peak had an isotopic distribution in excellent agreement with the theoretical pattern (Supporting Figure 4). This species was then subjected to further ionization (TOFMSMS$^-$), which revealed a fragment corresponding to the regenerated catalyst as the sole negative ion with mass of 892.26 (Supporting Figure 5).



Supporting Figure 4. Comparison of measured and theoretical isotopic mass distributions for the observed intermediate.



Supporting Figure 5. MS/MS of the intermediate ion yields a fragmentation peak corresponding to reformed catalyst.

References

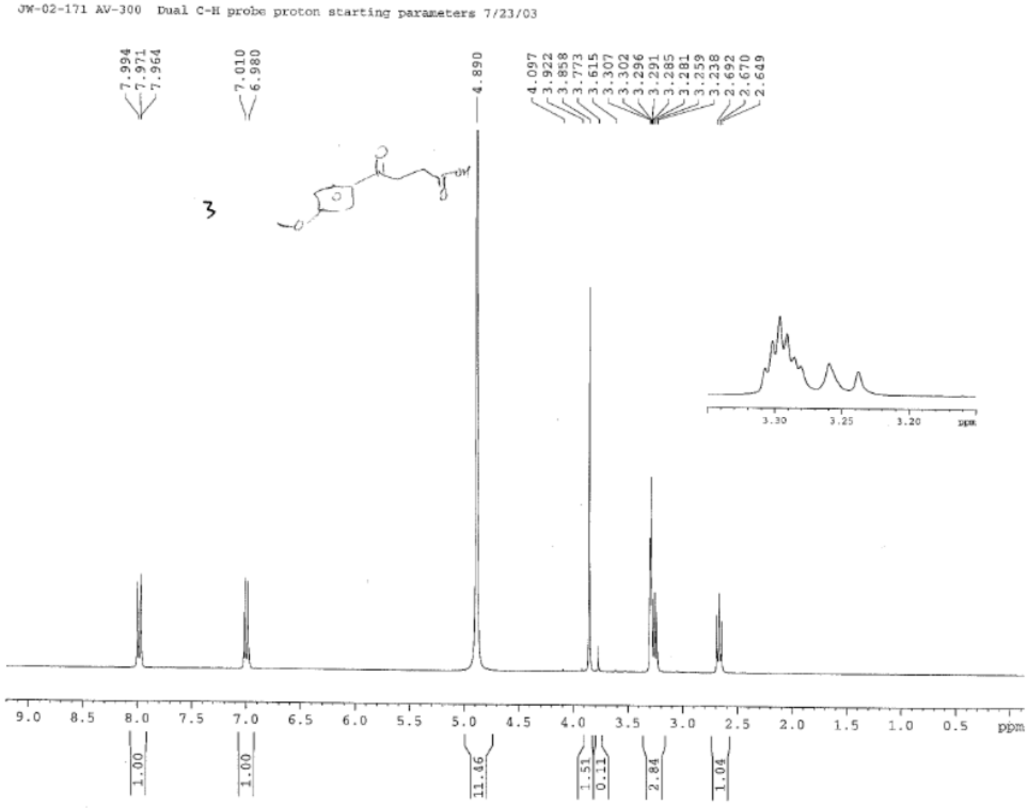
1. Sattely E. S., Meek S. J., Malcolmson S. J., Schrock R. R., Hoveyda A. H. *J. Am. Chem. Soc.* **2009**, *131*, 943–953.

2. Zhang Z., Bender C. F., Widenhoefer R. A. *J. Am. Chem. Soc.* **2007**, *129*, 14148–14149.

3. a) Laird T., Ollis W. D., Sutherland I. O. *J. Chem. Soc., Perkin Trans.* **1980***, 1,* 2033–2048. b) LaLonde, R. L., Sherry B. D., Kang E. J., Toste F. D. *J. Am. Chem. Soc.* **2007**, *129*, 2452–2453.

4. Gironès J., Duran J., Polo A., Real J. *Chem. Commun.* **2003**, 1776-1778.

3 ^{1}H NMR



JW-02-171 AV-300 Dual C-H probe proton starting parameters 7/23/03
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7.964
7.010
6.980
4.890
4.097
3.922
3.858
3.773
3.615
3.307
3.302
3.296
3.291
3.285
3.281
3.259
3.238
2.692
2.670
2.649
3
OH
3.30
3.25
3.20
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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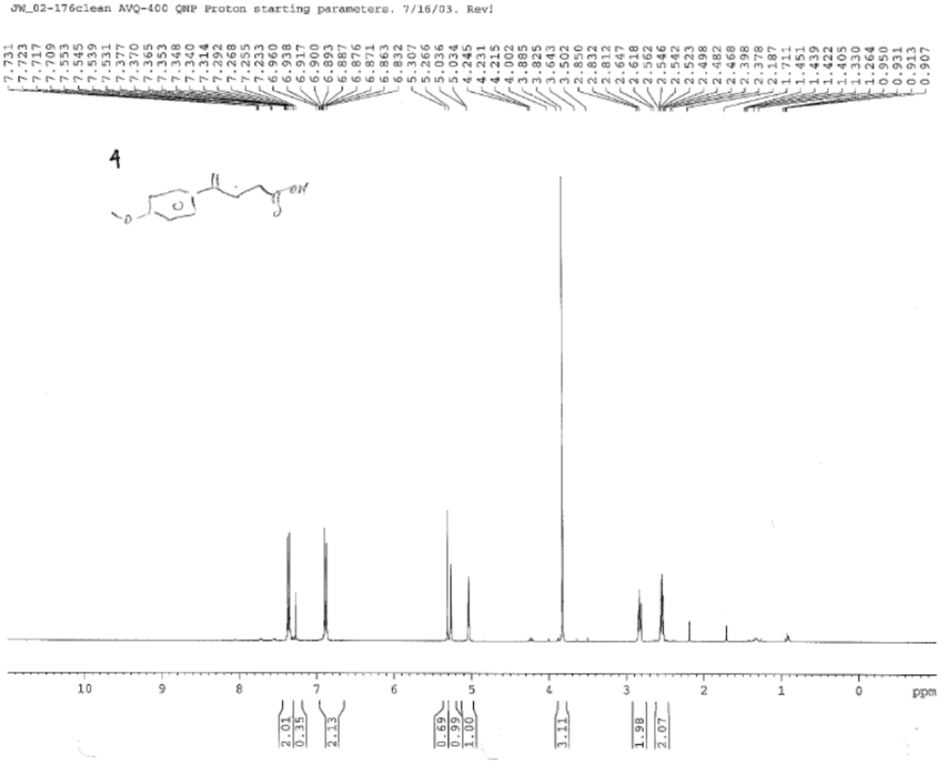
1.00
11.46
1.51
0.11
2.84
1.04



JW_02-176clean AVQ-400 QNP Proton starting parameters. 7/16/03. Rev!
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7.709
7.553
7.545
7.539
7.531
7.377
7.370
7.365
7.353
7.348
7.340
7.314
7.292
7.268
7.255
7.233
6.960
6.938
6.917
6.900
6.893
6.887
6.876
6.871
6.863
6.832
5.307
5.266
5.036
5.034
4.245
4.231
4.215
4.002
3.885
3.825
3.643
3.502
2.850
2.832
2.812
2.647
2.618
2.562
2.546
2.542
2.523
2.498
2.482
2.468
2.398
2.378
2.187
1.711
1.451
1.439
1.422
1.405
1.330
1.264
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0.931
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0.907
4
OH
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8
7
6
5
4
3
2
1
0
ppm
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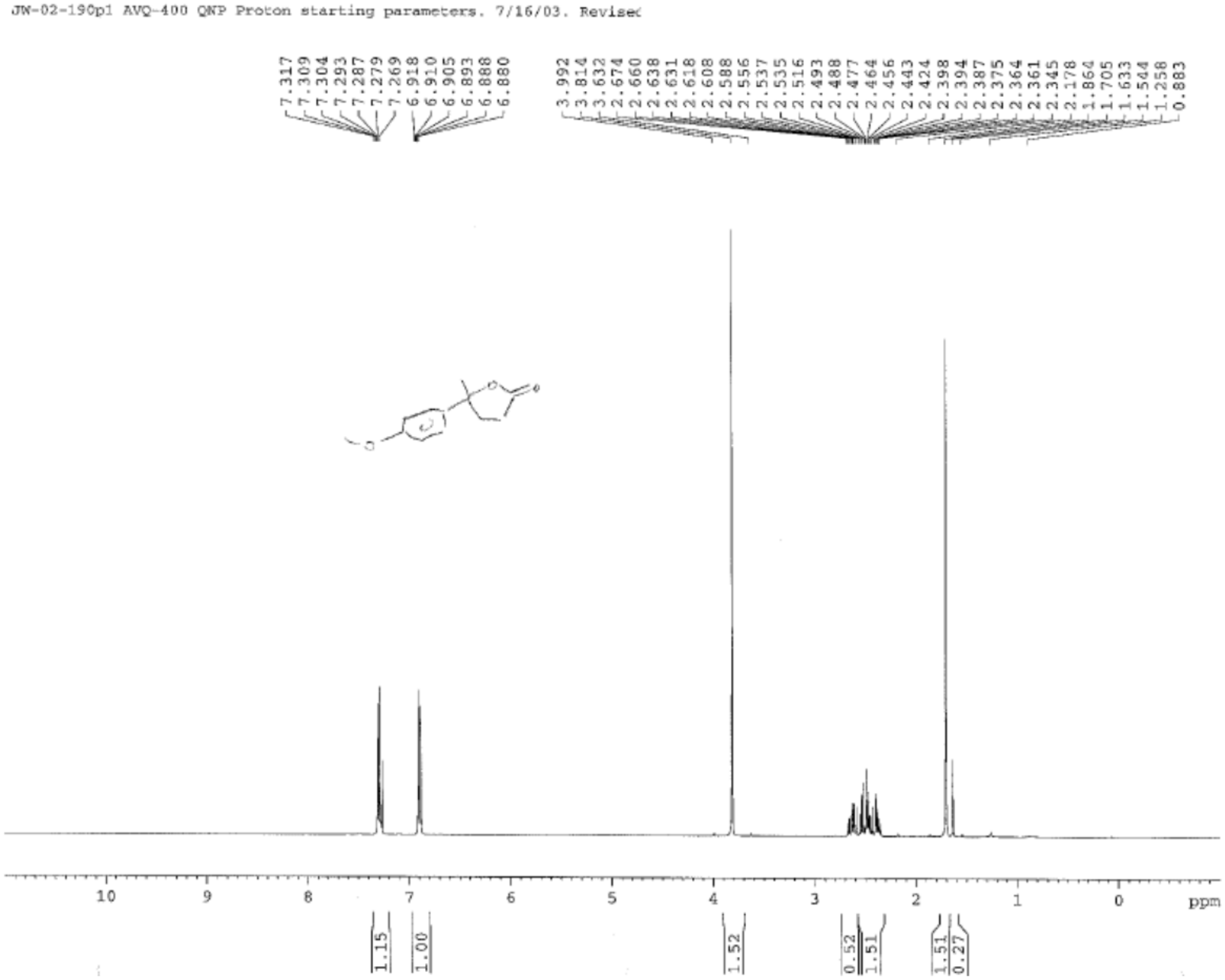
1.98
2.07

4b ^{1}H NMR


JW-02-190p1 AVQ-400 QNP Proton starting parameters. 7/16/03. Revised
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7.293
7.287
7.279
7.269
6.918
6.910
6.905
6.893
6.888
6.880
3.992
3.814
3.632
2.674
2.660
2.638
2.631
2.618
2.608
2.588
2.556
2.537
2.535
2.516
2.493
2.488
2.477
2.464
2.456
2.443
2.424
2.398
2.394
2.387
2.375
2.364
2.361
2.345
2.178
1.864
1.705
1.633
1.544
1.258
0.883
O
10
9
8
7
6
5
4
3
2
1
0
ppm
1.15
1.00
1.52
0.52
1.51
1.51
0.27

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Injection volume:       5 uL
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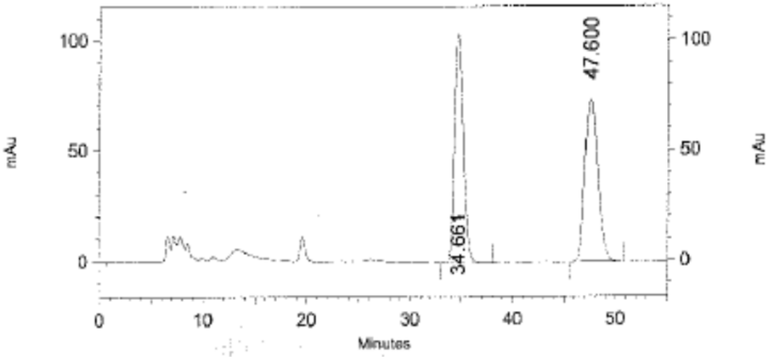

1: 210 nm, 4 nm Results

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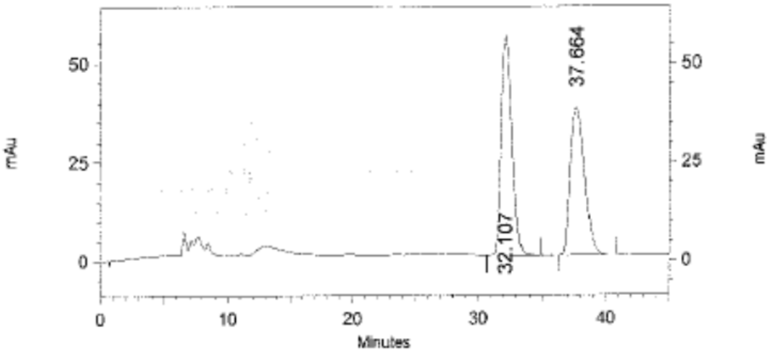

3: 230 nm, 4 nm Results

Retention Time	Area	Area Percent
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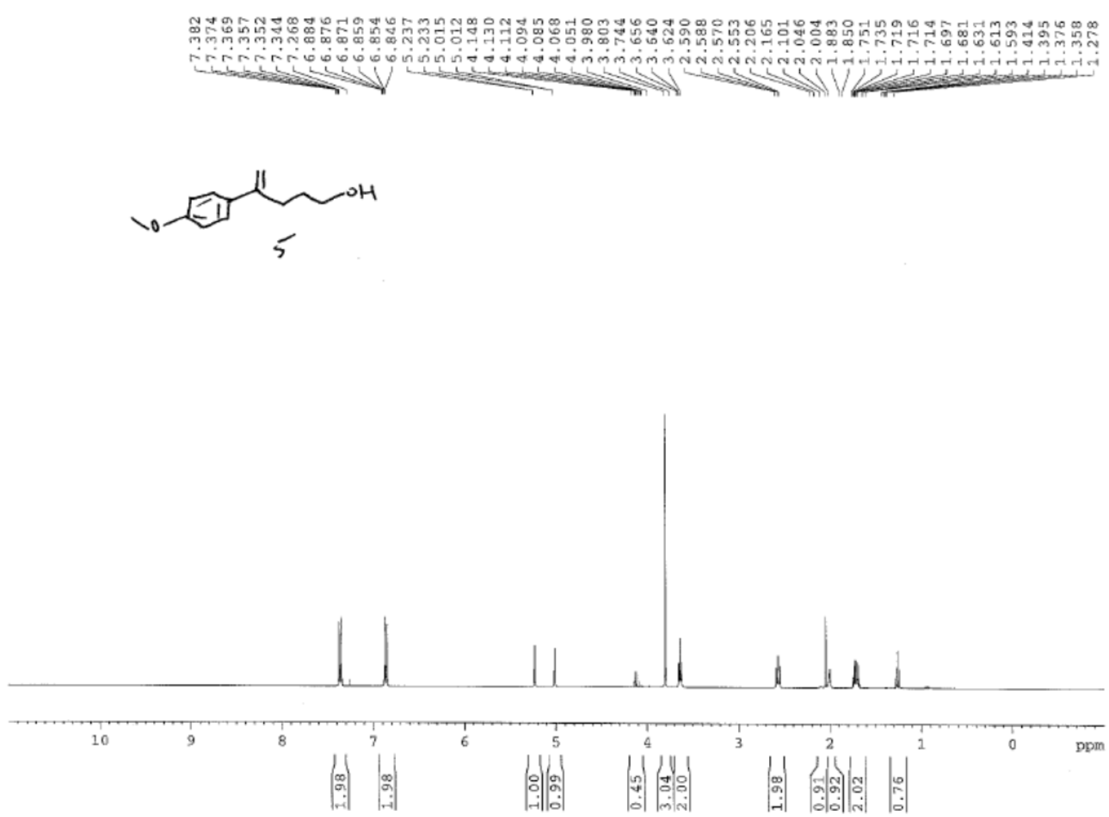
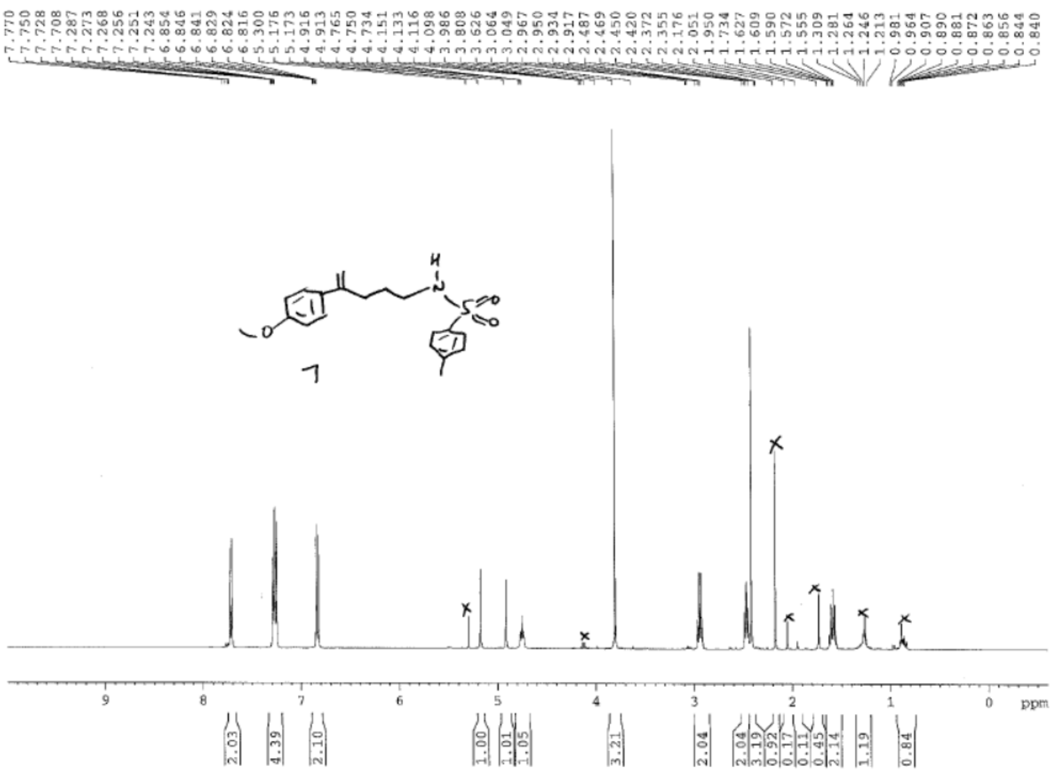
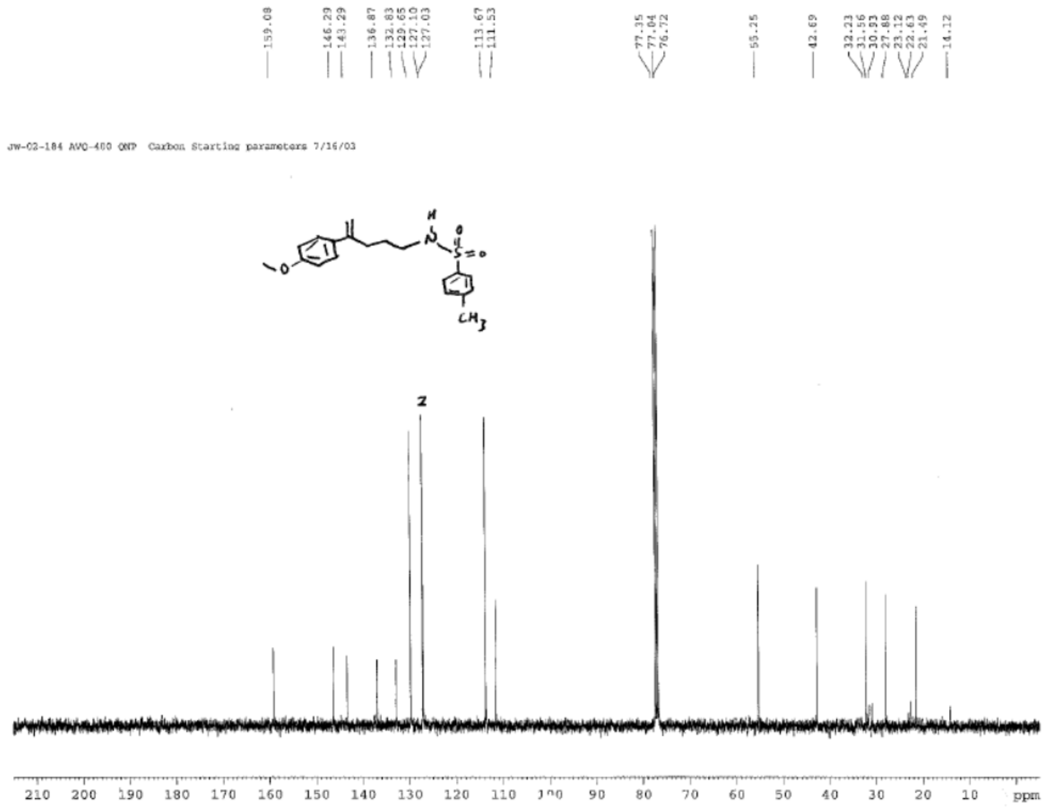
JW-02-175 AVQ-400 QNP Proton starting parameters. 7/16/03. Revised



JW-02-184p1 AVQ-400 QNP Proton starting parameters. 7/16/03. Revised




159.08
146.29
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136.87
132.83
129.65
127.10
127.03
113.67
111.53
77.35
77.04
76.72
55.25
42.69
32.23
31.56
30.93
27.88
23.12
22.63
21.49
14.12
JW-02-184 AVQ-400 QNP Carbon Starting parameters 7/16/03
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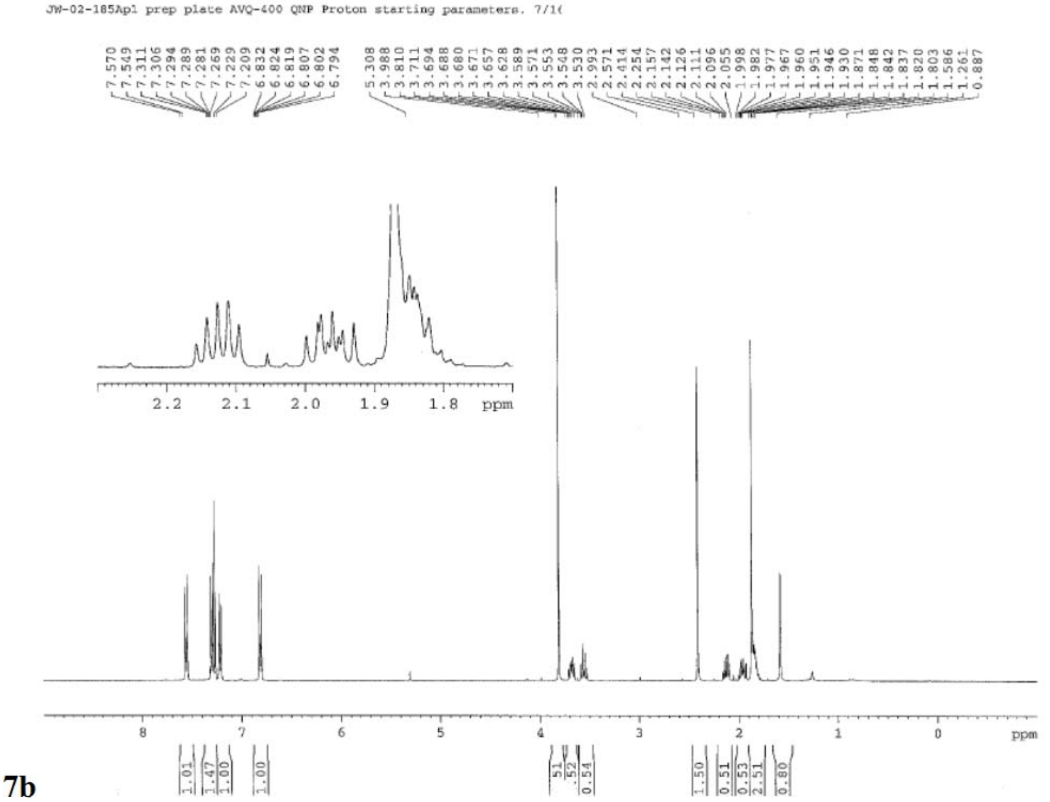
N
S
O
O
CH3
2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


JW-02-185Ap1 prep plate AVQ-400 QNP Proton starting parameters. 7/1(
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7.306
7.294
7.289
7.281
7.269
7.229
7.209
6.832
6.824
6.819
6.807
6.802
6.794
5.308
3.988
3.810
3.711
3.694
3.688
3.680
3.671
3.657
3.628
3.589
3.571
3.553
3.548
3.530
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2.571
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2.254
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2.055
1.998
1.982
1.977
1.967
1.960
1.951
1.946
1.930
1.871
1.848
1.837
1.820
1.803
1.586
1.261
0.887
2.2 2.1 2.0 1.9 1.8 ppm
8 7 6 5 4 3 2 1 0 ppm
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1.47
1.00
1.00
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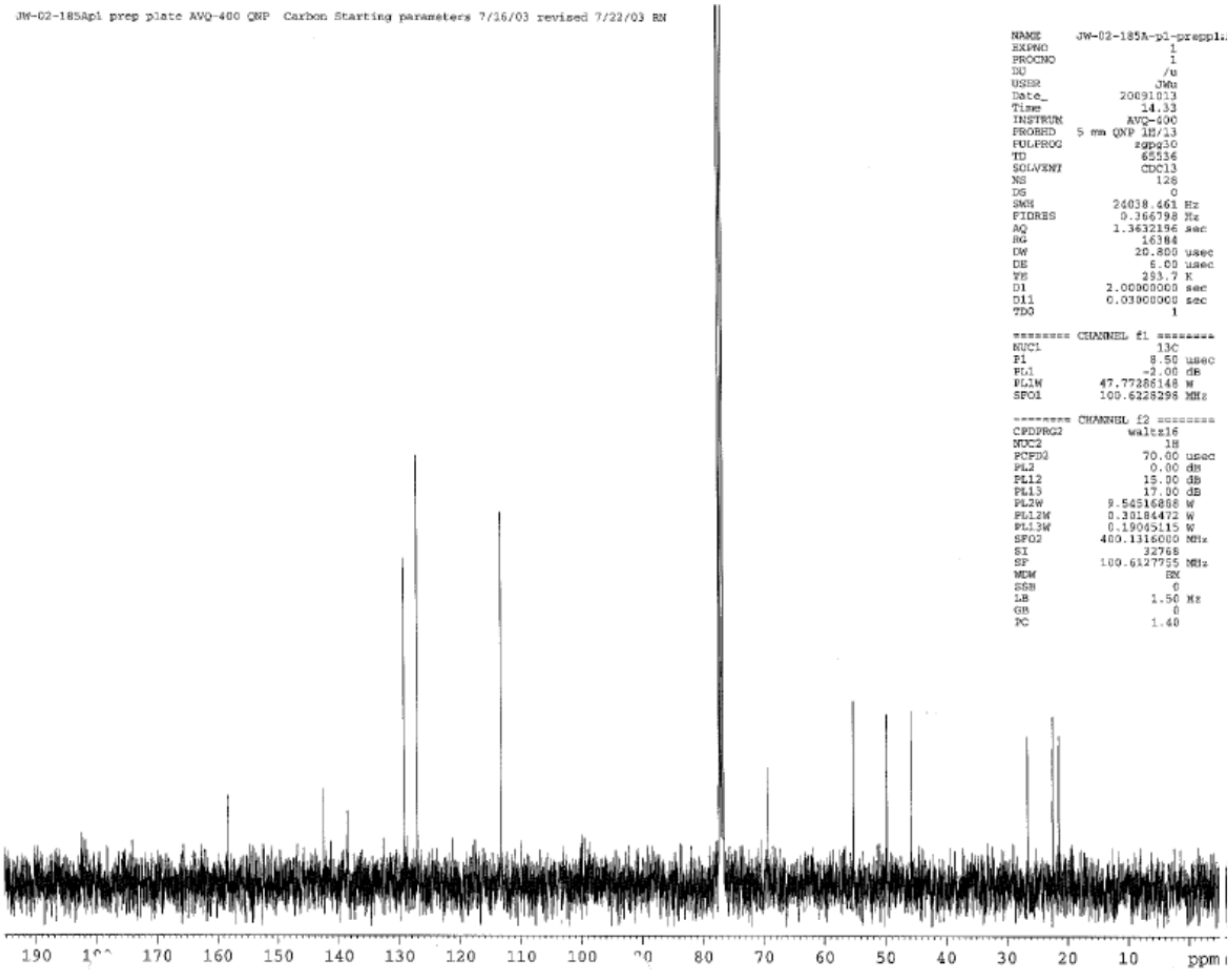
.52
0.54
1.50
0.51
0.53
2.51
0.80

7b


JW-02-185Ap1 prep plate AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7/22/03 BN

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PROCNO                    1
DU                       /u
USER                    JWu
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Time                  14.33
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PROBHD     5 mm QNP 1H/13
PULPROG             zgpg30
TD                    65536
SOLVENT              CDCl3
NS                      128
DS                        0
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FIDRES          0.366798 Hz
AQ             1.3632196 sec
RG                    16384
DW               20.800 usec
DE                 6.00 usec
TE                293.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                       1

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NUC1                    13C
P1                 8.50 usec
PL1               -2.00 dB
PL1W        47.77286148 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2             70.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              17.00 dB
PL2W         9.54516888 W
PL12W        0.30184472 W
PL13W        0.19065115 W
SFO2        400.1316000 MHz
SI                    32768
SF          100.6127755 MHz
WDW                      EM
SSB                       0
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GB                        0
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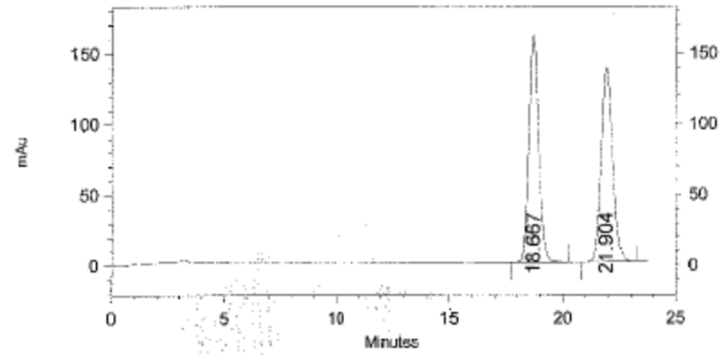

3: 238 nm, 4 nm Results

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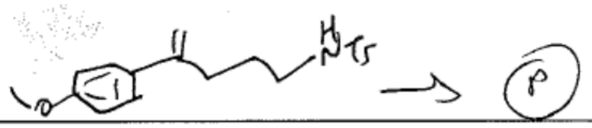

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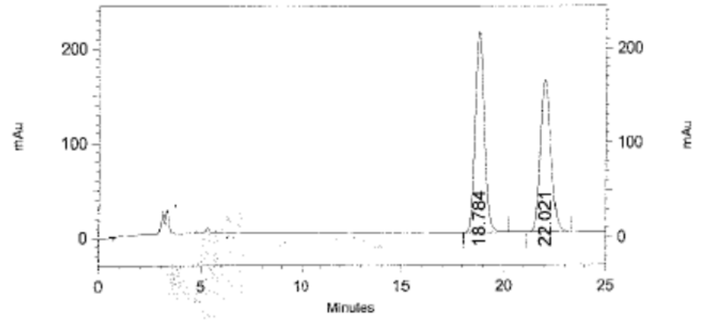

1: 210 nm, 4 nm Results

Retention Time	Area	Area Percent
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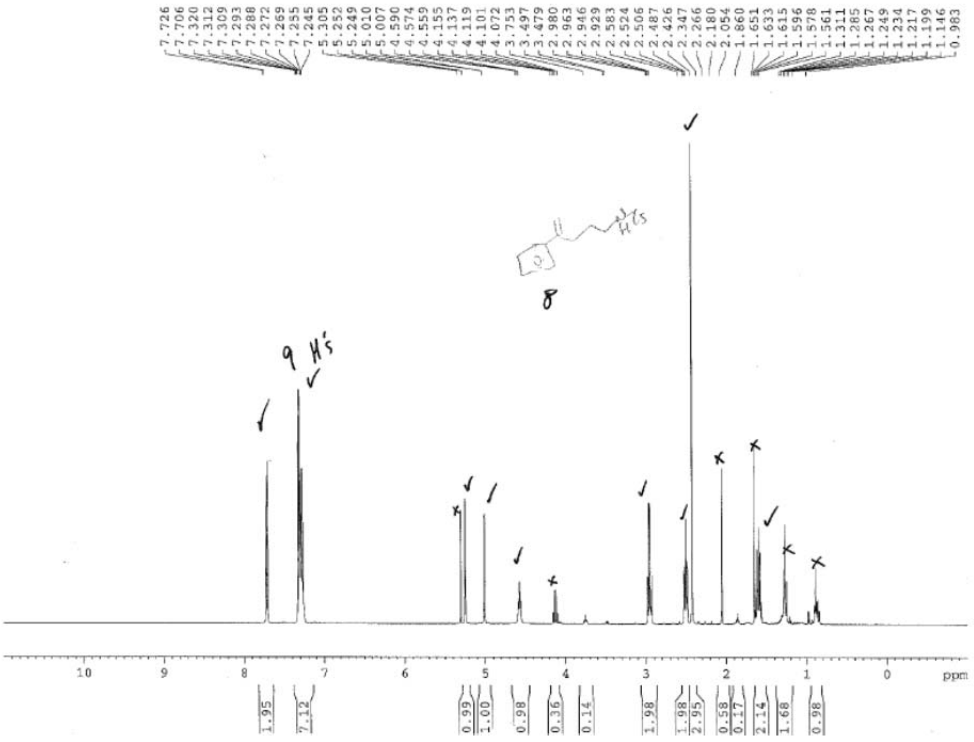
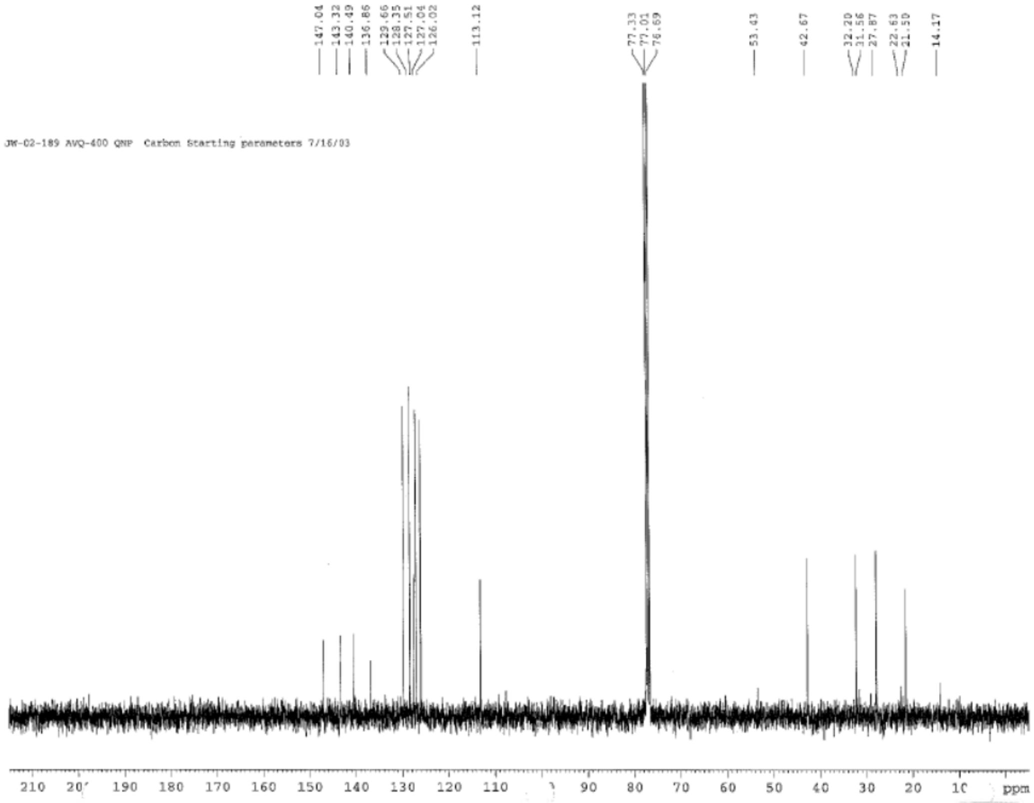
JW-02-189 AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7



8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143.32
140.49
136.86
129.66
128.35
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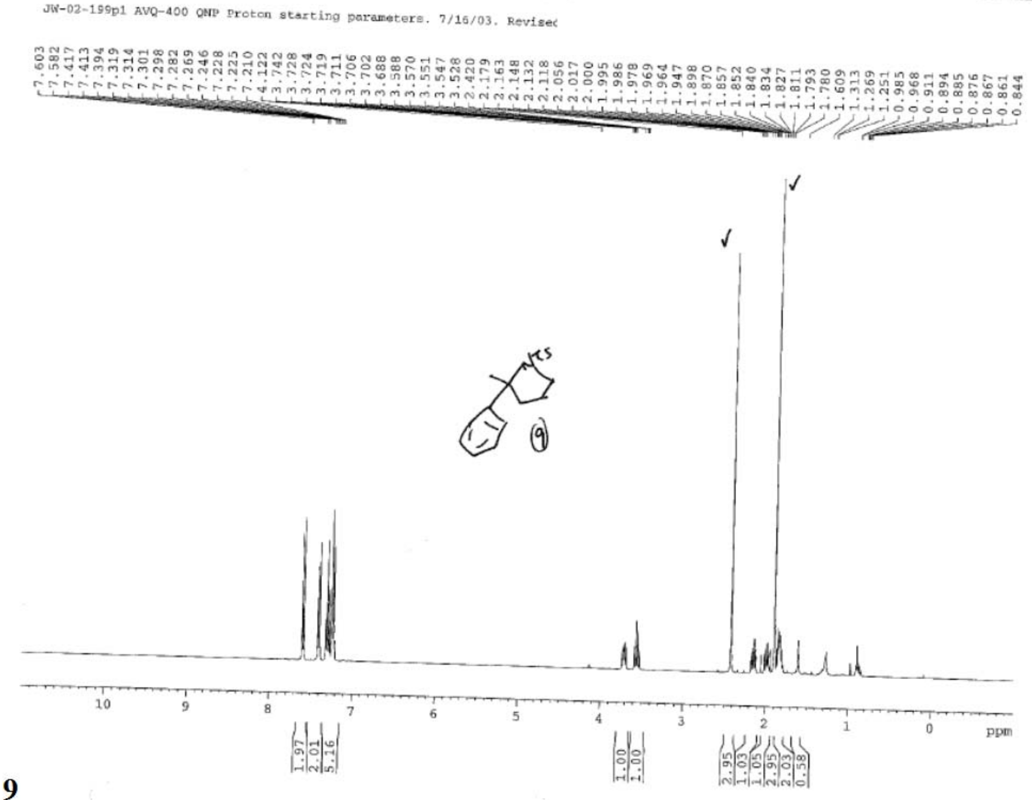
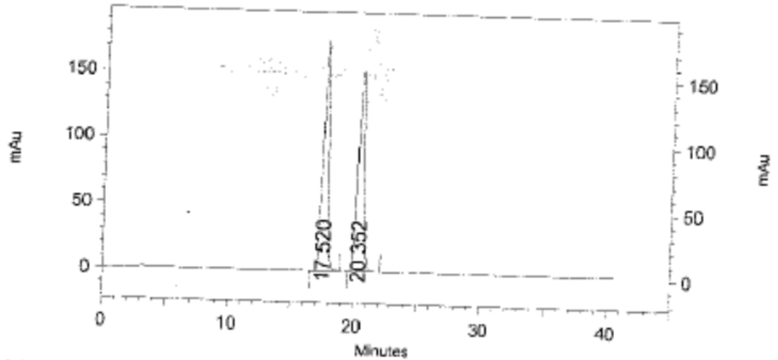
127.04
126.02
113.12
77.33
77.01
76.69
53.43
42.67
32.20
31.56
27.87
22.63
21.50
14.17
JW-02-189 AVQ-400 QNP Carbon Starting parameters 7/16/03
210
20
190
180
170
160
150
140
130
120
110
90
80
70
60
50
40
30
20
10
ppm


JW-02-199p1 AVQ-400 QNP Proton starting parameters. 7/16/03. Revisec
7.603
7.582
7.417
7.413
7.394
7.319
7.314
7.301
7.298
7.282
7.269
7.246
7.228
7.225
7.210
4.122
3.742
3.728
3.724
3.719
3.711
3.706
3.702
3.688
3.588
3.570
3.551
3.547
3.528
2.420
2.179
2.163
2.148
2.132
2.118
2.056
2.017
2.000
1.995
1.986
1.978
1.969
1.964
1.947
1.898
1.870
1.857
1.852
1.840
1.834
1.827
1.811
1.793
1.780
1.609
1.313
1.269
1.251
0.985
0.968
0.911
0.894
0.885
0.876
0.867
0.861
0.844
✓
✓
Ts
9
10
9
8
7
6
5
4
3
2
1
0
ppm
1.97
2.01
5.16
1.00
1.00
2.95
1.03
1.05
2.95
2.03
0.58

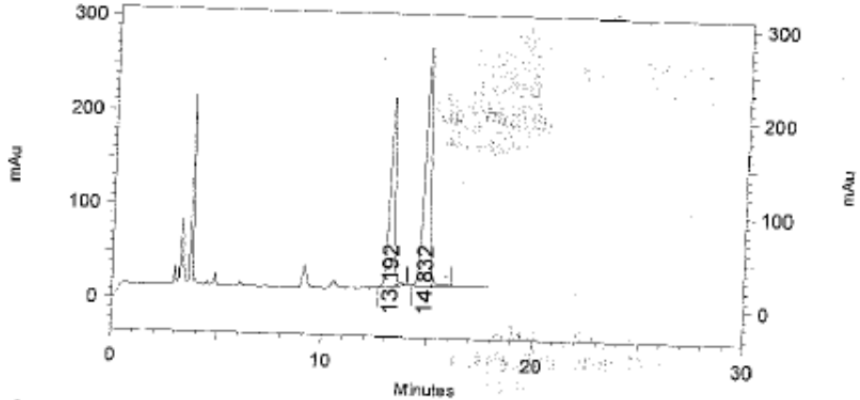
9

Sample ID: **JW-02-199**
Filename:
C:\EZStart\Projects\Default\Data\JWu\JW-02-199_AD9208IP_45min.met10-19-2009
5-15-06 PM.dat Method:
C:\EZStart\Projects\Default\Method\glh\AD\glh_AD9505IP_45min.met
Injection volume: 5 uL



3: 240 nm, 4 nm Results

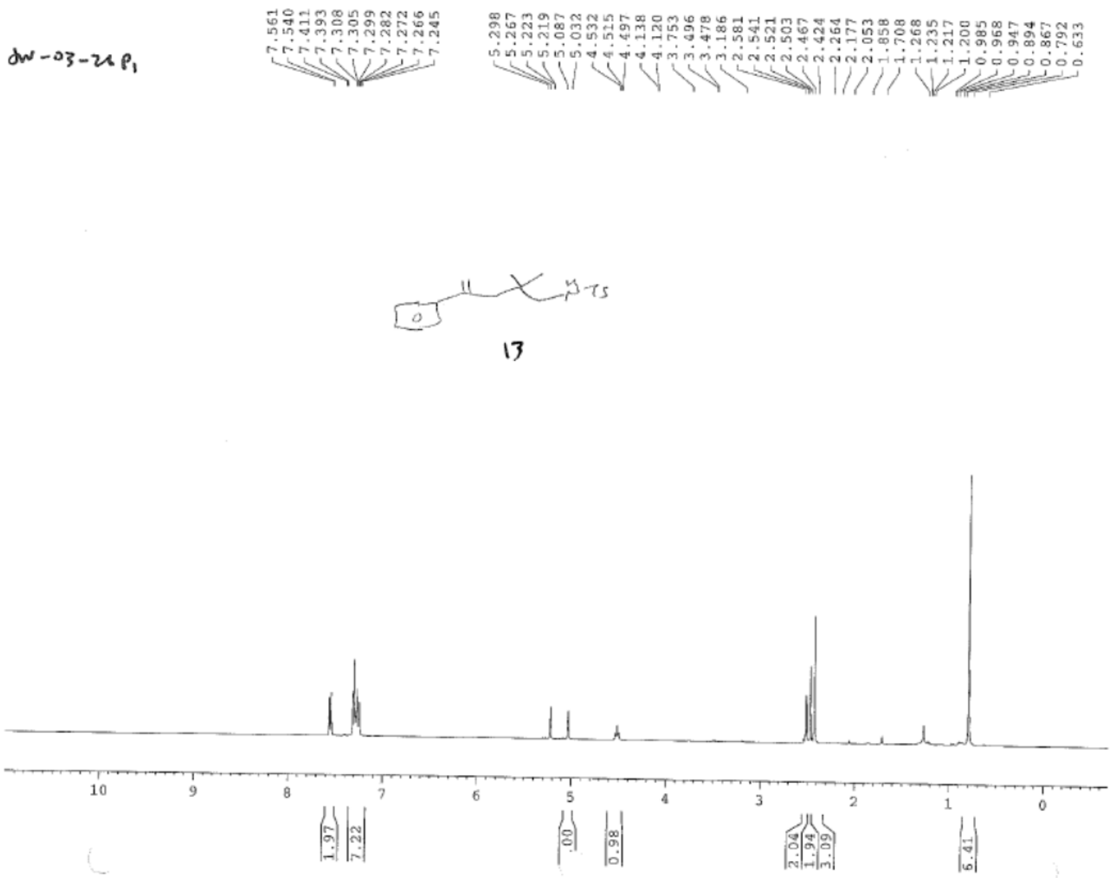
Retention Time	Area	Area Percent
17.520	4871277	49.974
20.352	4876313	50.026

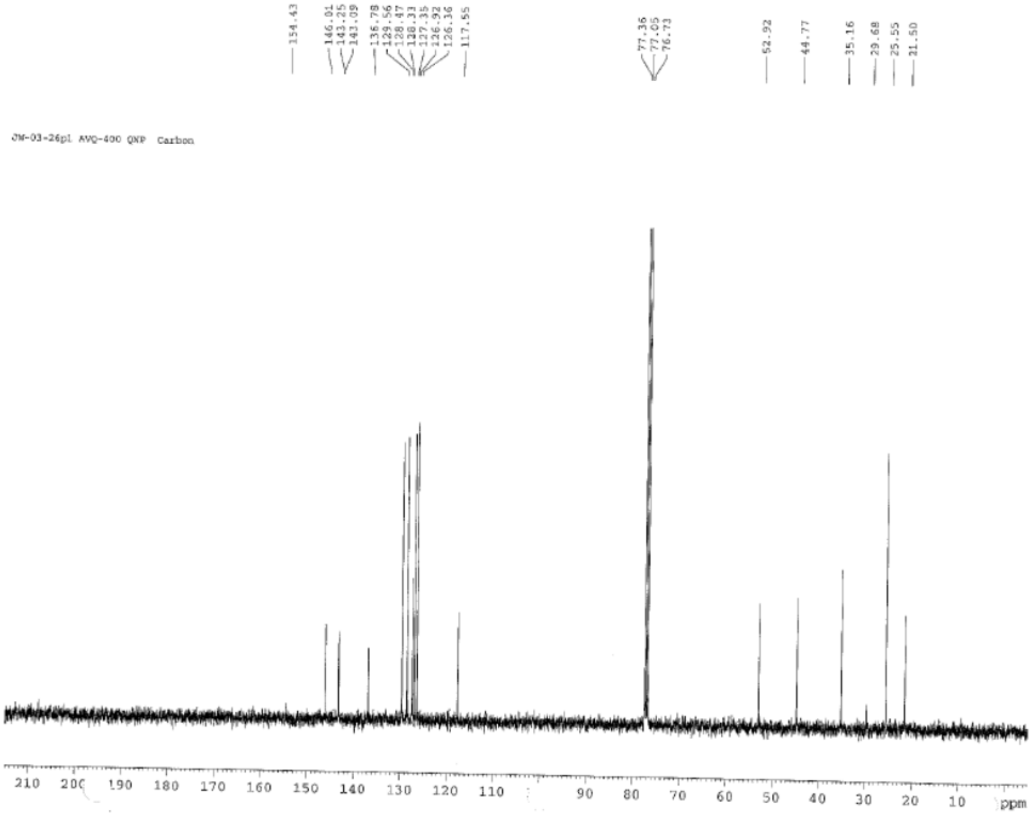


1: 195 nm, 4 nm Results

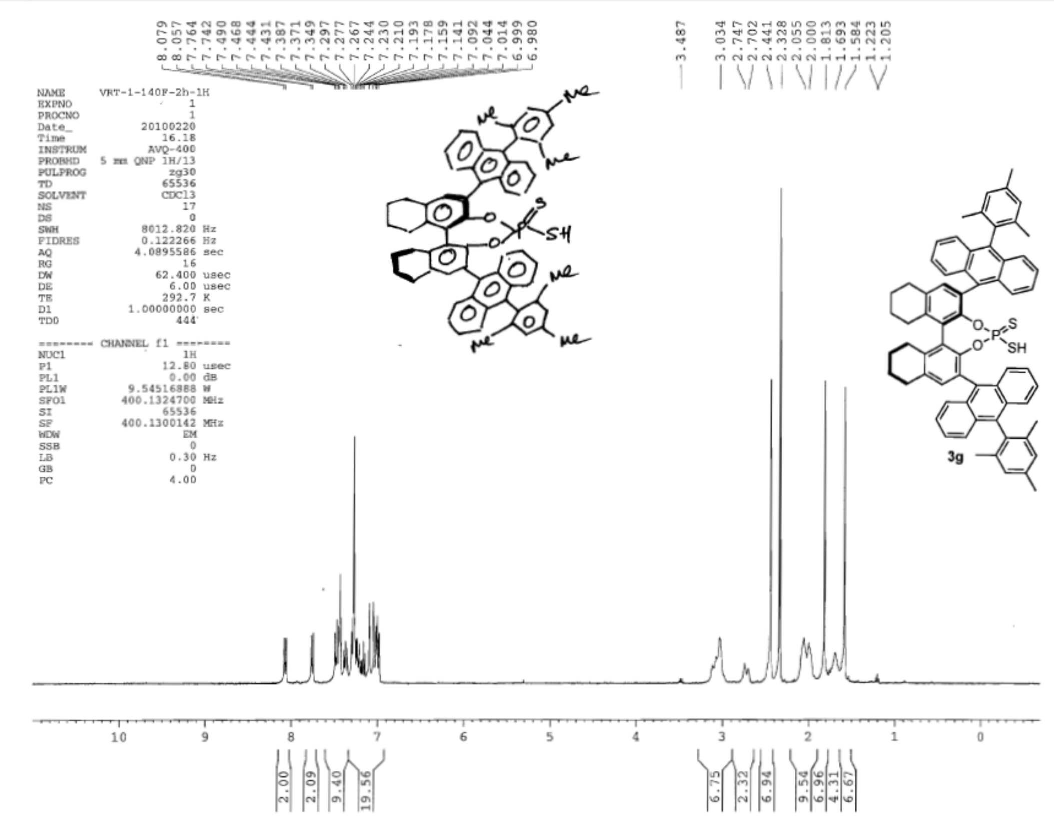
Retention Time	Area	Area Percent	Lambda Max
13.192	3606233	41.371	207
14.832	5110670	58.629	207

JW-03-26 P_1

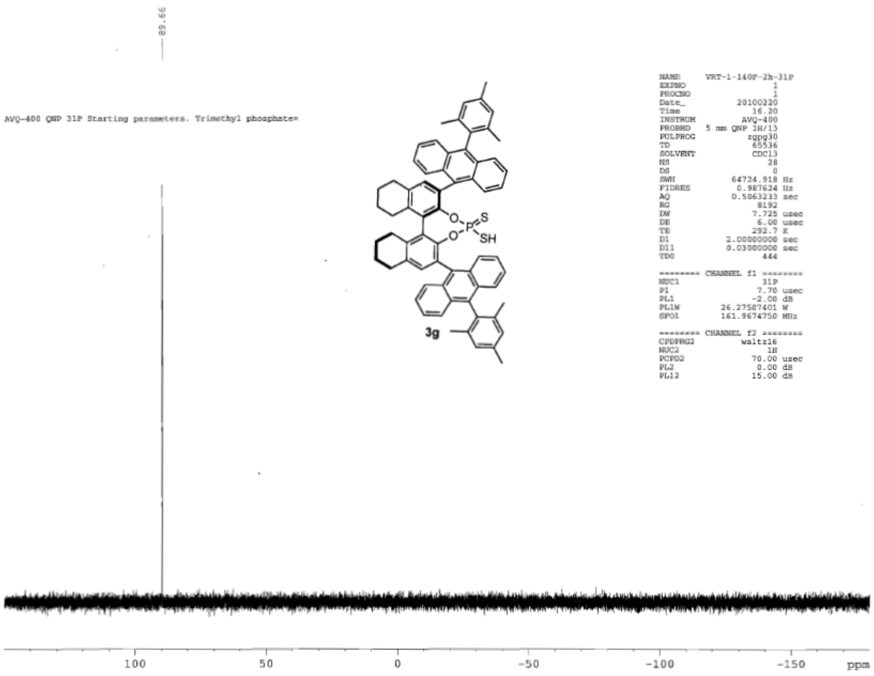

7.561
7.540
7.411
7.393
7.308
7.305
7.299
7.282
7.272
7.266
7.245
5.298
5.267
5.223
5.219
5.087
5.032
4.532
4.515
4.497
4.138
4.120
3.753
3.496
3.478
3.186
2.581
2.541
2.521
2.503
2.467
2.424
2.264
2.177
2.053
1.858
1.708
1.268
1.235
1.217
1.200
0.985
0.968
0.947
0.894
0.867
0.792
0.633
O
N-Ts
13
10
9
8
7
6
5
4
3
2
1
0
1.97
7.22
.00
0.98
2.04
1.94
3.09
6.41


154.43
146.01
143.25
143.09
136.78
129.56
128.47
128.33
127.35
126.92
126.36
117.55
77.36
77.05
76.73
52.92
44.77
35.16
29.68
25.55
21.50
JW-03-26p1 AVQ-400 QNP Carbon
210
200
190
180
170
160
150
140
130
120
110
90
80
70
60
50
40
30
20
10
ppm

16

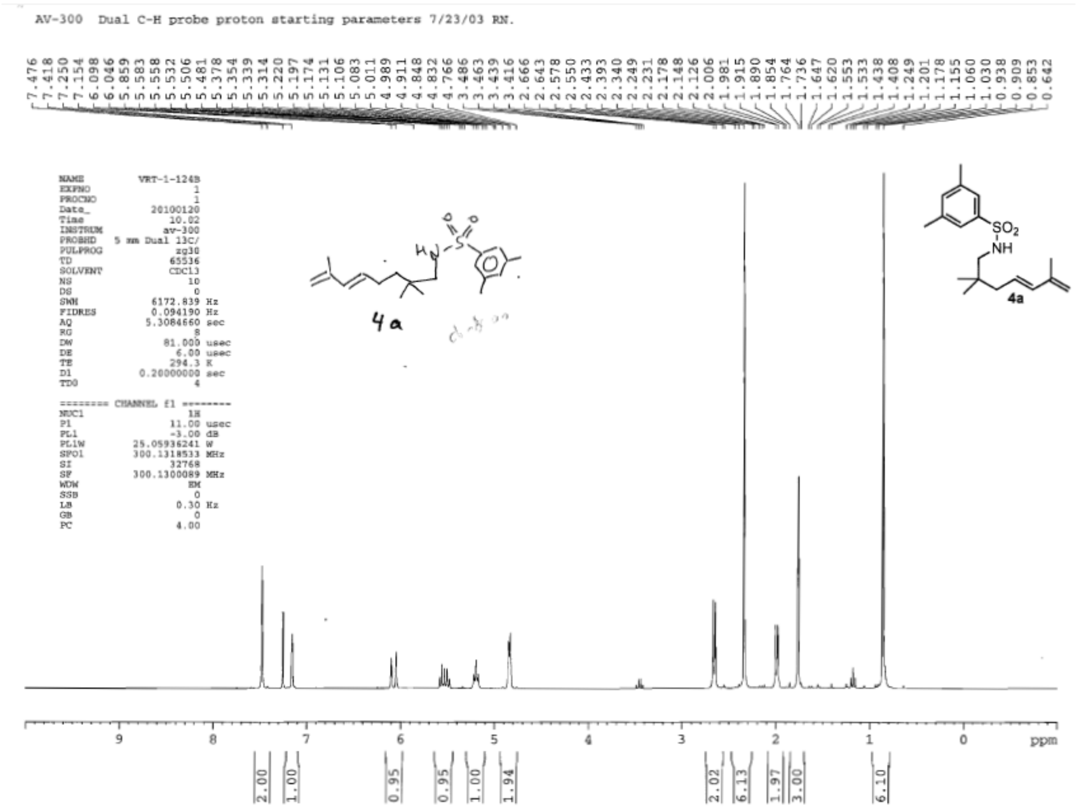


```
NAME       VRT-1-140F-2h-1H
EXPNO                     1
PROCNO                    1
Date_              20100220
Time                  16.18
INSTRUM             AVQ-400
PROBHD     5 mm QNP 1H/13
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       17
DS                        0
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                4.0895586 sec
RG                       16
DW                   62.400 usec
DE                     6.00 usec
TE                    292.7 K
D1               1.00000000 sec
TD0                     444

======== CHANNEL f1 ========
NUC1                     1H
P1                    12.80 usec
PL1                    0.00 dB
PL1W             9.54516888 W
SFO1            400.1324700 MHz
SI                    65536
SF              400.1300142 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     4.00
```

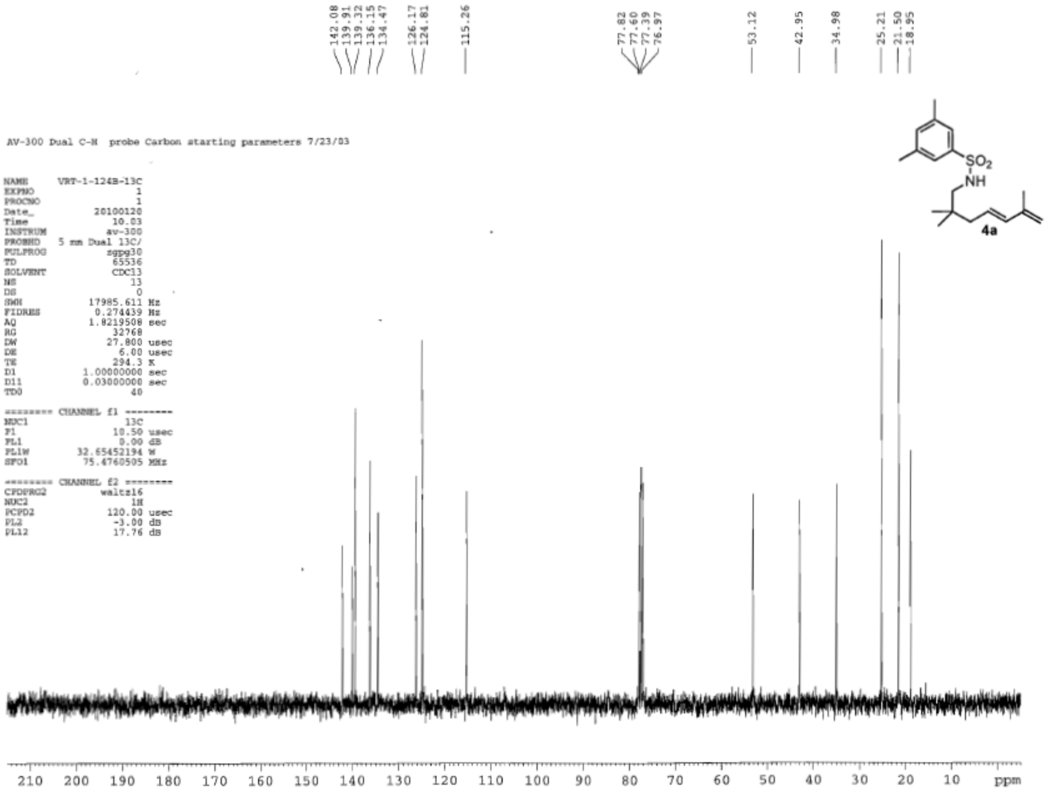


```
AVQ-400 QNP 31P Starting parameters. Trimethyl phosphate=
```

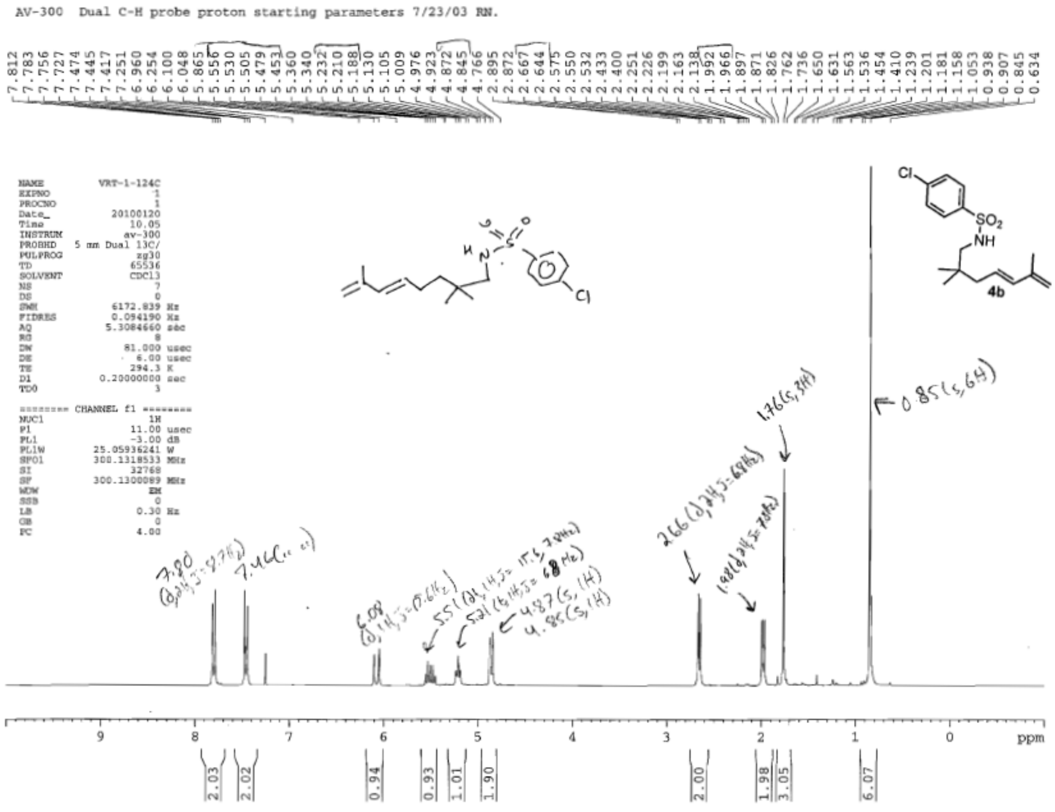
```
NAME       VRT-1-140F-2h-31P
EXPNO                      1
PROCNO                     1
Date_               20100220
Time                   16.20
INSTRUM              AVQ-400
PROBHD      5 mm QNP 1H/13
PULPROG               zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        28
DS                         0
SWH                64724.918 Hz
FIDRES              0.987624 Hz
AQ                 0.5063233 sec
RG                      8192
DW                     7.725 usec
DE                      6.00 usec
TE                     292.7 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                      444

======== CHANNEL f1 ========
NUC1                     31P
P1                      7.70 usec
PL1                    -2.00 dB
PL1W             26.27507401 W
SFO1             161.9674750 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                  70.00 usec
PL2                     0.00 dB
PL12                   15.00 dB
```


AV-300 Dual C-H probe proton starting parameters 7/23/03 RN.
7.476 7.418 7.250 7.154 6.098 6.046 5.859 5.583 5.558 5.532 5.506 5.481 5.378 5.354 5.339 5.314 5.220 5.197 5.174 5.131 5.106 5.083 5.011 4.989 4.911 4.848 4.832 4.766 3.486 3.463 3.439 3.416 2.666 2.643 2.578 2.550 2.433 2.393 2.340 2.249 2.231 2.178 2.148 2.126 2.006 1.981 1.915 1.890 1.854 1.764 1.736 1.647 1.620 1.553 1.533 1.438 1.408 1.249 1.201 1.178 1.155 1.060 1.030 0.938 0.909 0.853 0.642
NAME VRT-1-124B
EXPNO 1
PROCNO 1
Date_ 20100120
Time 10.02
INSTRUM av-300
PROBHD 5 mm Dual 13C/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 10
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 8
DW 81.000 usec
DE 6.00 usec
TE 294.3 K
D1 0.20000000 sec
TD0 4
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -3.00 dB
PL1W 25.05936241 W
SFO1 300.1318533 MHz
SI 32768
SF 300.1300089 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
4a
SO2
NH
4a
9 8 7 6 5 4 3 2 1 0 ppm
2.00 1.00 0.95 0.95 1.00 1.94 2.02 6.13 1.97 3.00 6.10

17a

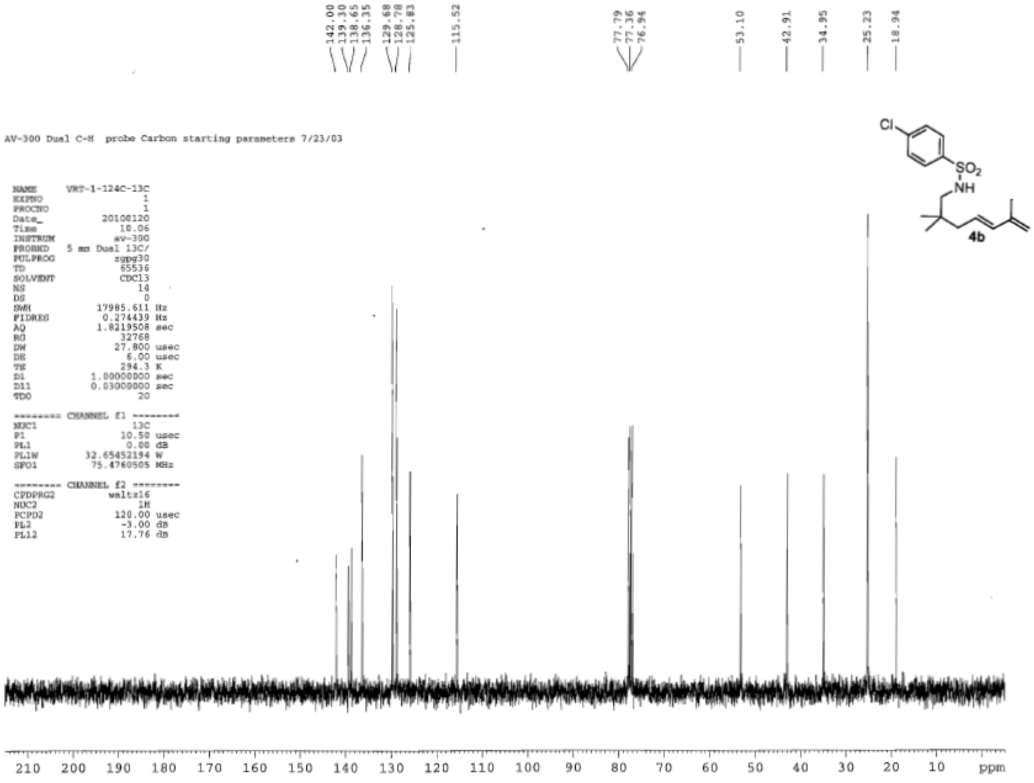

142.08 139.91 139.32 136.15 134.47 126.17 124.81 115.26 77.82 77.60 77.39 76.97 53.12 42.95 34.98 25.21 21.50 18.95
AV-300 Dual C-H probe Carbon starting parameters 7/23/03
NAME VRT-1-124B-13C
EXPNO 1
PROCNO 1
Date_ 20100120
Time 10.03
INSTRUM av-300
PROBHD 5 mm Dual 13C/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 13
DS 0
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 32768
DW 27.800 usec
DE 6.00 usec
TE 294.3 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 40
======== CHANNEL f1 ========
NUC1 13C
P1 10.50 usec
PL1 0.00 dB
PL1W 32.65452194 W
SFO1 75.4760505 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 120.00 usec
PL2 -3.00 dB
PL12 17.76 dB
SO2
NH
4a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

17a



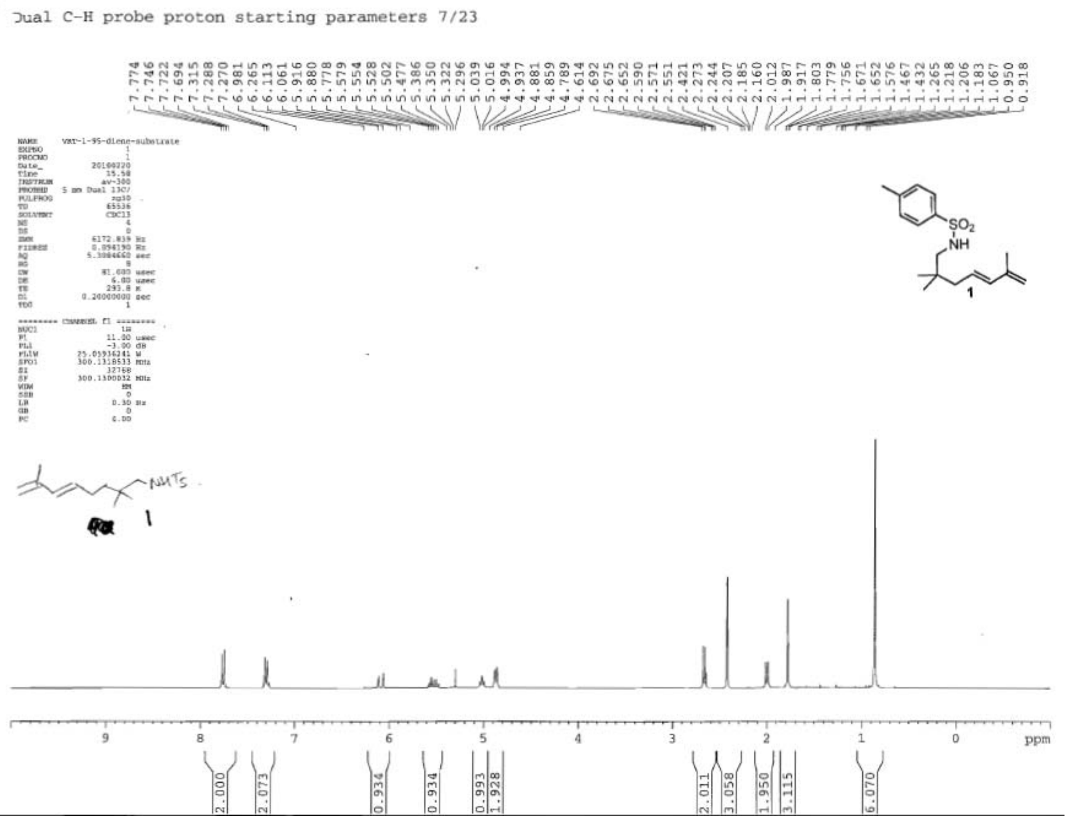
```
AV-300  Dual C-H probe proton starting parameters 7/23/03 RN.

NAME           VRT-1-124C
EXPNO                   1
PROCNO                  1
Date_            20100120
Time                10.05
INSTRUM            av-300
PROBHD   5 mm Dual 13C/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      7
DS                      0
SWH              6172.839 Hz
FIDRES           0.094190 Hz
AQ              5.3084660 sec
RG                      8
DW                 81.000 usec
DE                   6.00 usec
TE                  294.3 K
D1             0.20000000 sec
TD0                     3

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.00 usec
PL1                 -3.00 dB
PL1W          25.05936241 W
SFO1          300.1318533 MHz
SI                  32768
SF            300.1300089 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   4.00
```

17b proton



```
AV-300 Dual C-H  probe Carbon starting parameters 7/23/03

NAME        VRT-1-124C-13C
EXPNO                    1
PROCNO                   1
Date_             20100120
Time                 10.06
INSTRUM             av-300
PROBHD    5 mm Dual 13C/
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      14
DS                       0
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ               1.8219508 sec
RG                   32768
DW                  27.800 usec
DE                    6.00 usec
TE                   294.3 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                     20

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.50 usec
PL1                   0.00 dB
PL1W           32.65452194 W
SFO1           75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               120.00 usec
PL2                  -3.00 dB
PL12                 17.76 dB
```

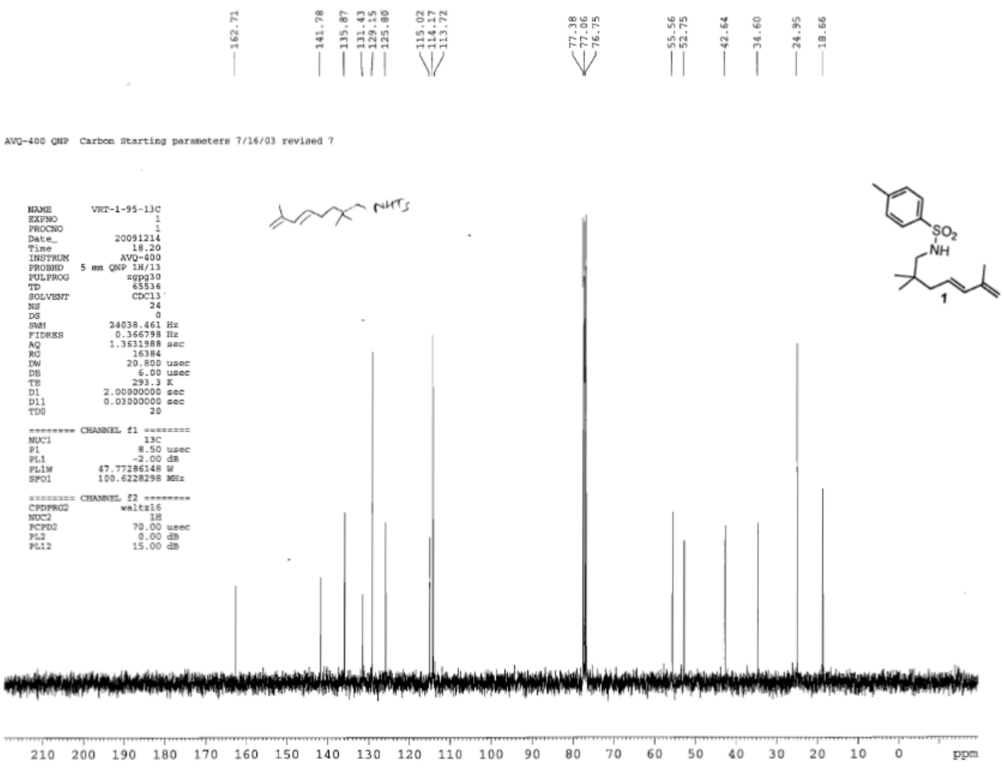
17b carbon



Dual C-H probe proton starting parameters 7/23

```
NAME       VRT-1-95-diene-substrate
EXPNO                     1
PROCNO                    1
Date_              20100220
Time                  15.58
INSTRUM              av-300
PROBHD     5 mm Dual 13C/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        4
DS                        0
SWH                6172.839 Hz
FIDRES             0.094190 Hz
AQ                5.3084660 sec
RG                        8
DW                   81.000 usec
DE                     6.00 usec
TE                    293.8 K
D1               0.20000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    11.00 usec
PL1                   -3.00 dB
PL1W            25.05936241 W
SFO1            300.1318533 MHz
SI                    32768
SF              300.1300032 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     4.00
```

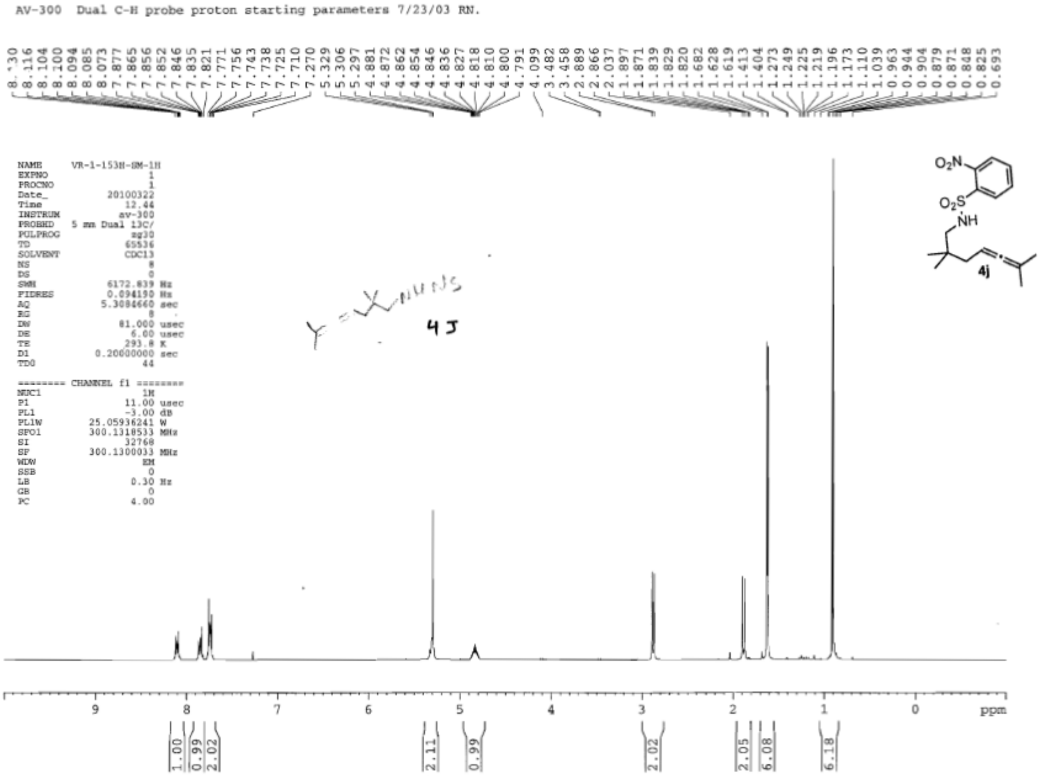
17c proton



AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7

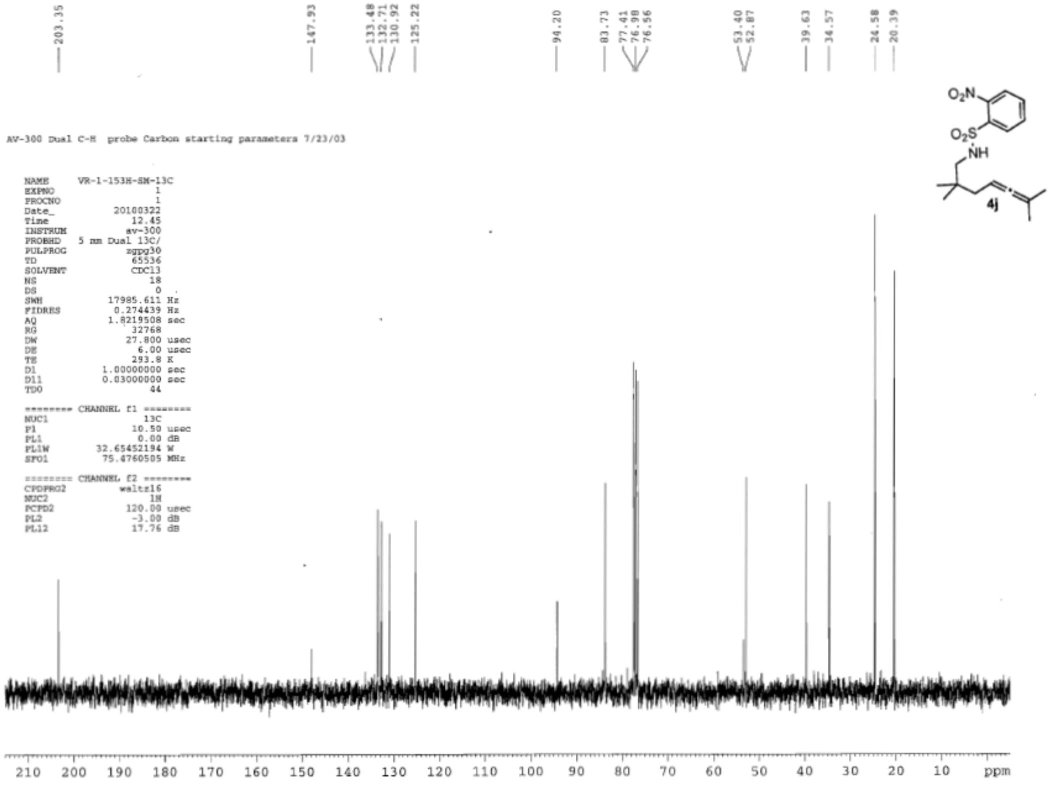
```
NAME           VRT-1-95-13C
EXPNO                     1
PROCNO                    1
Date_              20091214
Time                  18.20
INSTRUM             AVQ-400
PROBHD    5 mm QNP 1H/13
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       24
DS                        0
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631988 sec
RG                    16384
DW                   20.800 usec
DE                     6.00 usec
TE                    293.3 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                      20

======== CHANNEL f1 ========
NUC1                    13C
P1                     8.50 usec
PL1                   -2.00 dB
PL1W            47.77286148 W
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 70.00 usec
PL2                    0.00 dB
PL12                  15.00 dB
```

17c carbon



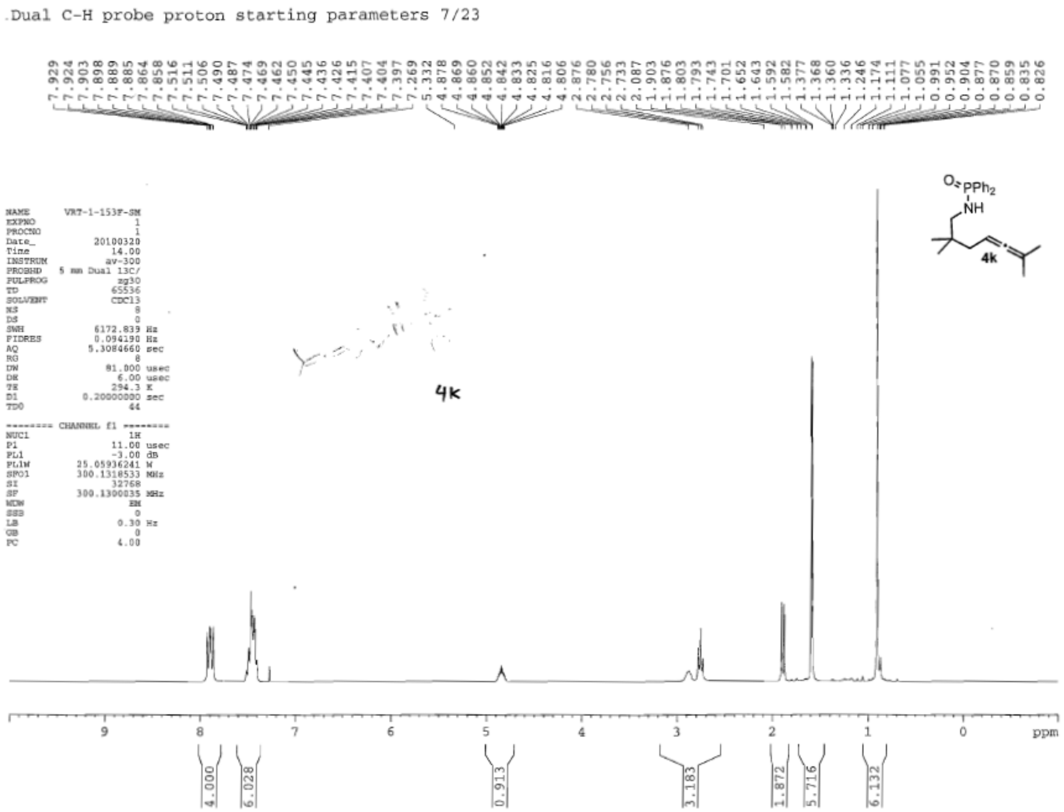
```
NAME       VR-1-153H-SM-1H
EXPNO                    1
PROCNO                   1
Date_             20100322
Time                 12.44
INSTRUM             av-300
PROBHD    5 mm Dual 13C/
PULPROG               zg30
TD                   65536
SOLVENT              CDC13
NS                       8
DS                       0
SWH               6172.839 Hz
FIDRES            0.094190 Hz
AQ               5.3084660 sec
RG                       8
DW                  81.000 usec
DE                    6.00 usec
TE                   293.8 K
D1              0.20000000 sec
TD0                     44

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.00 usec
PL1                  -3.00 dB
PL1W           25.05936241 W
SFO1           300.1318533 MHz
SI                   32768
SF             300.1300033 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00
```

17d proton

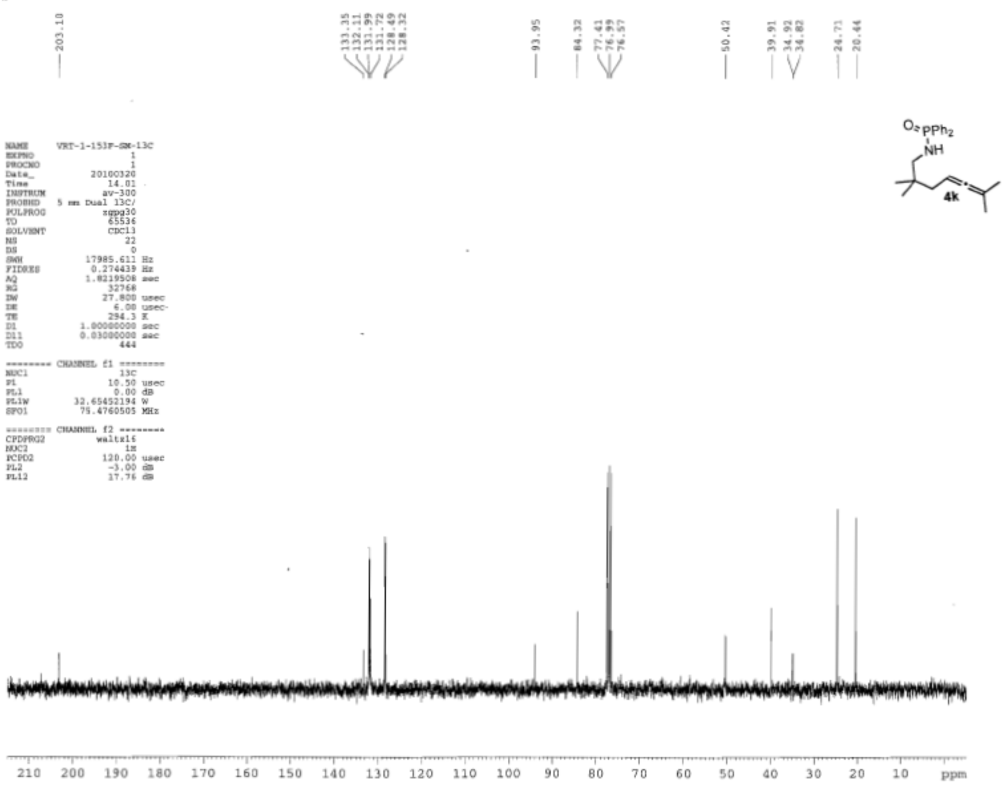


```
NAME       VR-1-153H-SM-13C
EXPNO                    1
PROCNO                   1
Date_             20100322
Time                 12.45
INSTRUM             av-300
PROBHD    5 mm Dual 13C/
PULPROG             zgpg30
TD                   65536
SOLVENT              CDC13
NS                      18
DS                       0
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ               1.8219508 sec
RG                   32768
DW                  27.800 usec
DE                    6.00 usec
TE                   293.8 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                     44

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.50 usec
PL1                   0.00 dB
PL1W           32.65452194 W
SFO1            75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               120.00 usec
PL2                  -3.00 dB
PL12                 17.76 dB
```

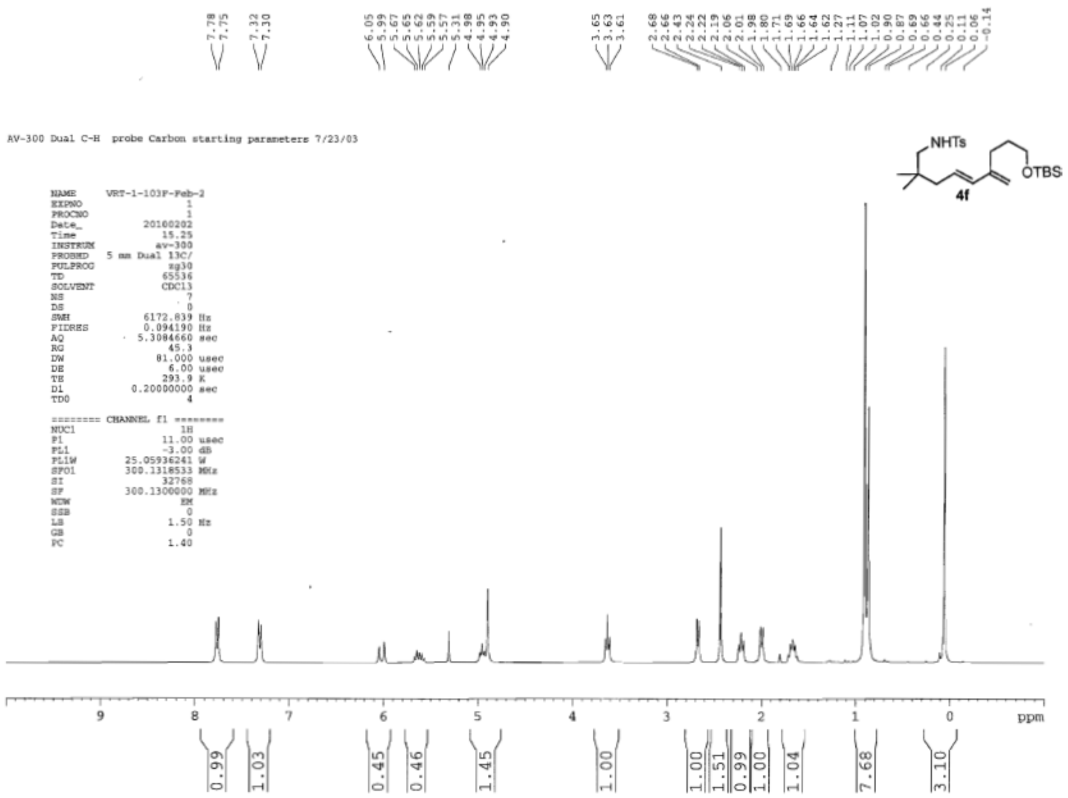
17d carbon



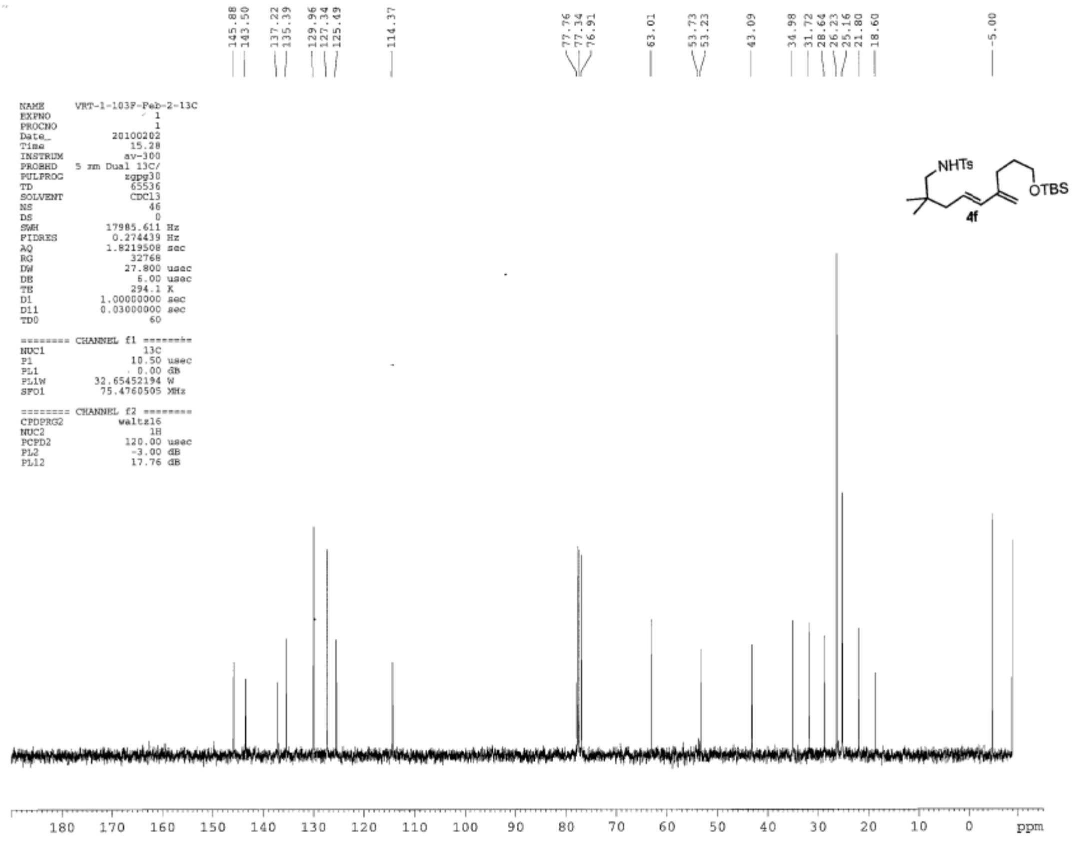
17e proton



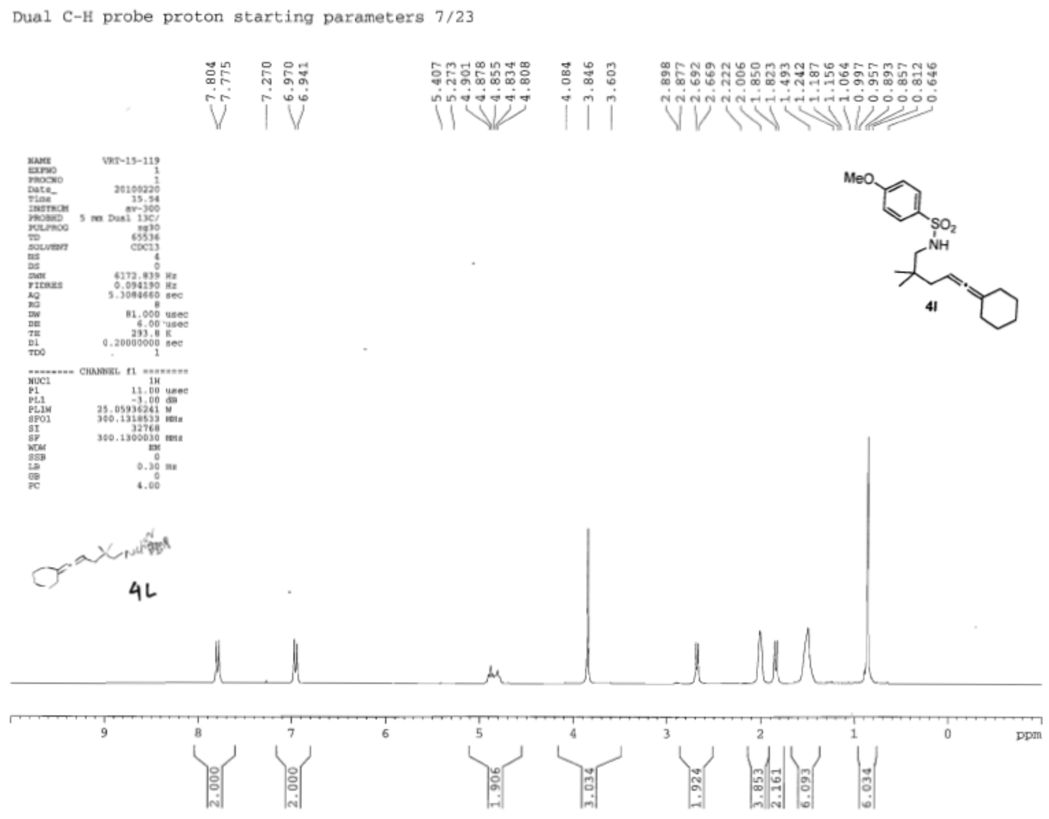
17e carbon



17f proton

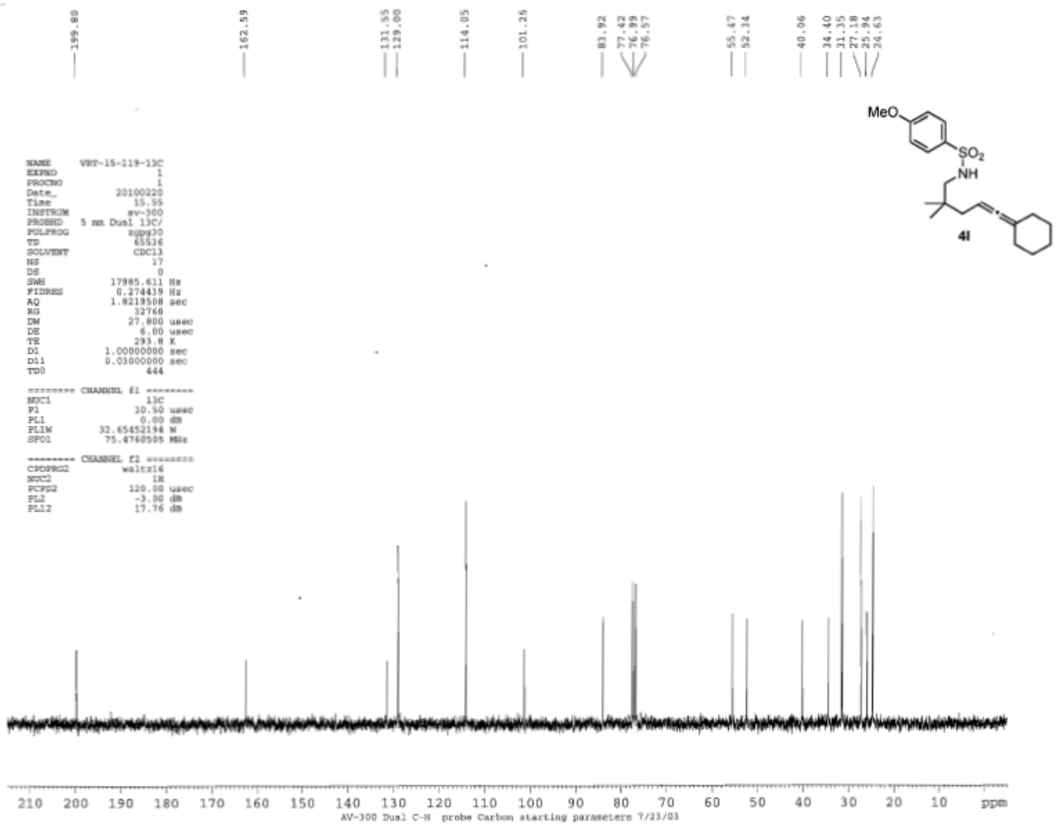


17f carbon



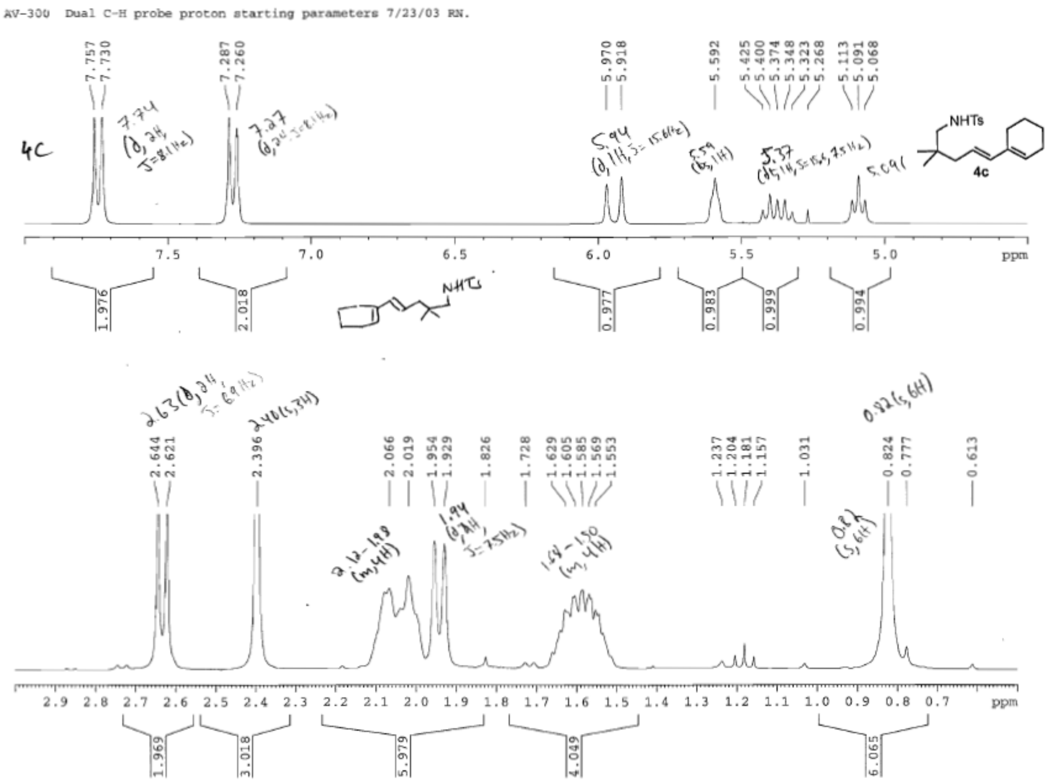
```
NAME          VRT-15-119
EXPNO                  1
PROCNO                 1
Date_           20100220
Time               15.54
INSTRUM           av-300
PROBHD   5 mm Dual 13C/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     4
DS                     0
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ             5.3084660 sec
RG                     8
DW                81.000 usec
DE                  6.00 usec
TE                 293.8 K
D1            0.20000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.00 usec
PL1                -3.00 dB
PL1W         25.05936241 W
SFO1         300.1318533 MHz
SI                 32768
SF           300.1300030 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00
```

17g proton

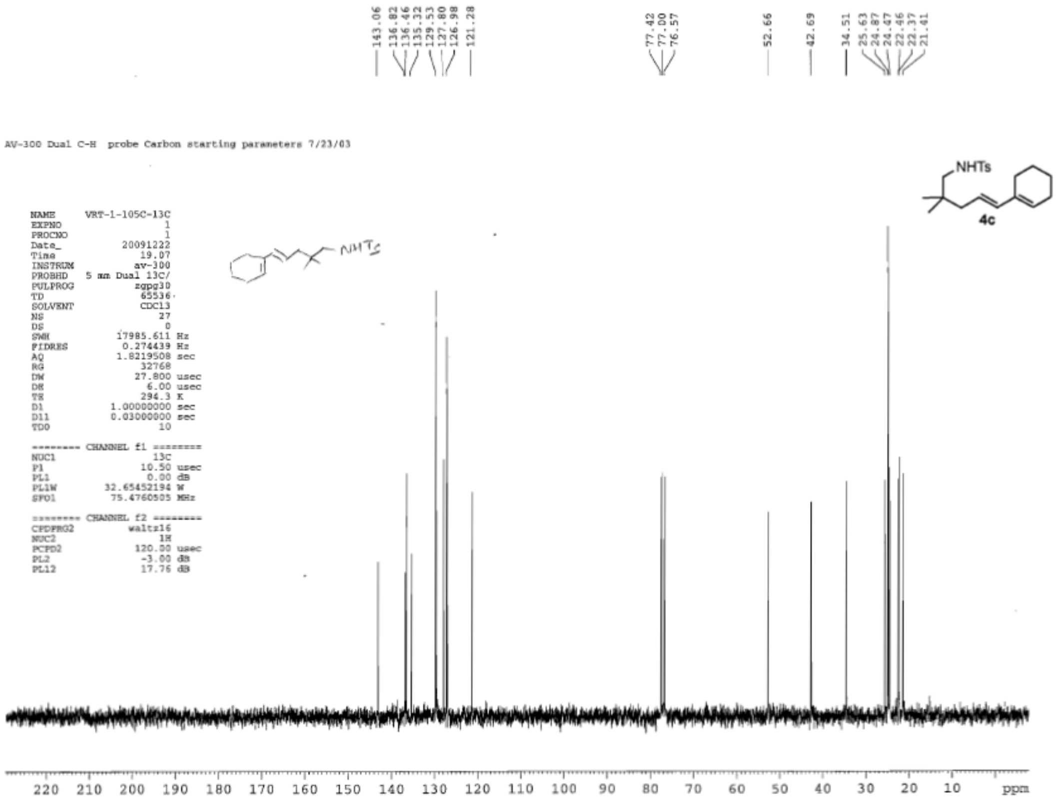


```
NAME      VRT-15-119-13C
EXPNO                  1
PROCNO                 1
Date_           20100220
Time               15.55
INSTRUM           av-300
PROBHD   5 mm Dual 13C/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    17
DS                     0
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                 32768
DW                27.800 usec
DE                  6.00 usec
TE                 293.8 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                  444

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.50 usec
PL1                 0.00 dB
PL1W         32.65452194 W
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2             120.00 usec
PL2                -3.00 dB
PL12               17.76 dB
```

17g carbon

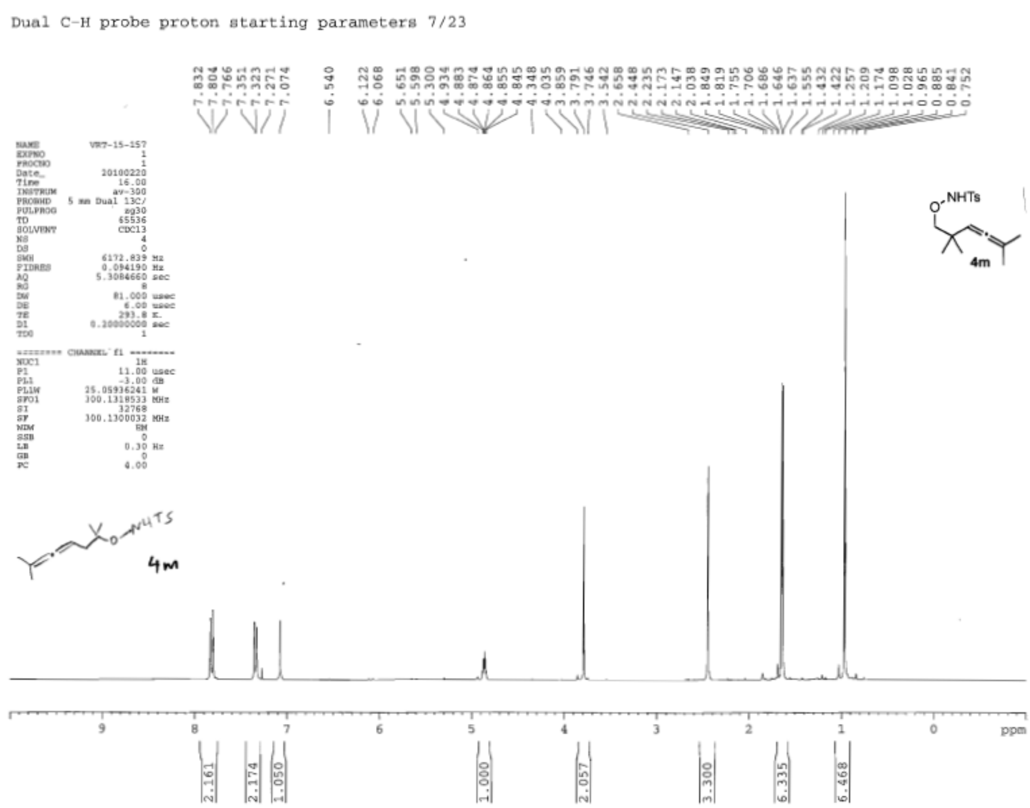


17h proton



```
NAME       VRT-1-105C-13C
EXPNO                   1
PROCNO                  1
Date_            20091222
Time                19.07
INSTRUM            av-300
PROBHD   5 mm Dual 13C/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                     27
DS                      0
SWH             17985.611 Hz
FIDRES           0.274439 Hz
AQ              1.8219508 sec
RG                  32768
DW                 27.800 usec
DE                   6.00 usec
TE                  294.3 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                    10

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.50 usec
PL1                  0.00 dB
PL1W          32.65452194 W
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              120.00 usec
PL2                 -3.00 dB
PL12                17.76 dB
```

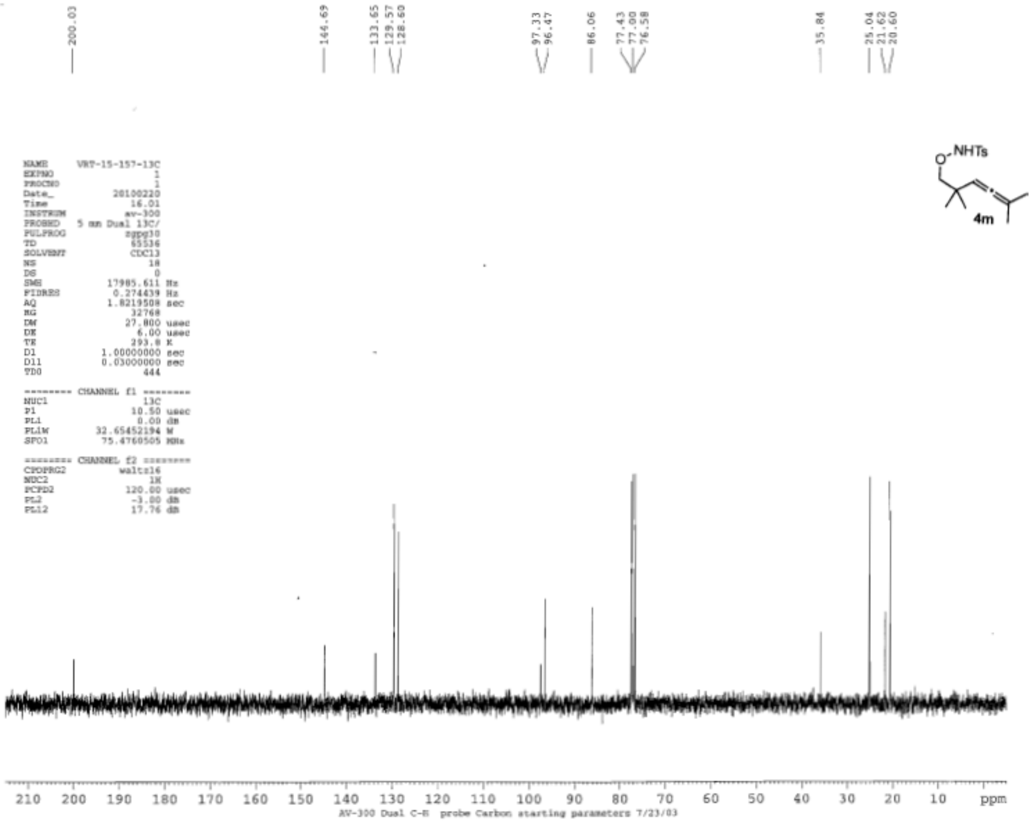
17h carbon



Dual C-H probe proton starting parameters 7/23

```
NAME          VRT-15-157
EXPNO                  1
PROCNO                 1
Date_           20100220
Time               16.00
INSTRUM           av-300
PROBHD   5 mm Dual 13C/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     4
DS                     0
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ             5.3084660 sec
RG                     8
DW                81.000 usec
DE                  6.00 usec
TE                 293.8 K
D1            0.20000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.00 usec
PL1                -3.00 dB
PL1W         25.05936241 W
SFO1         300.1318533 MHz
SI                 32768
SF           300.1300032 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00
```

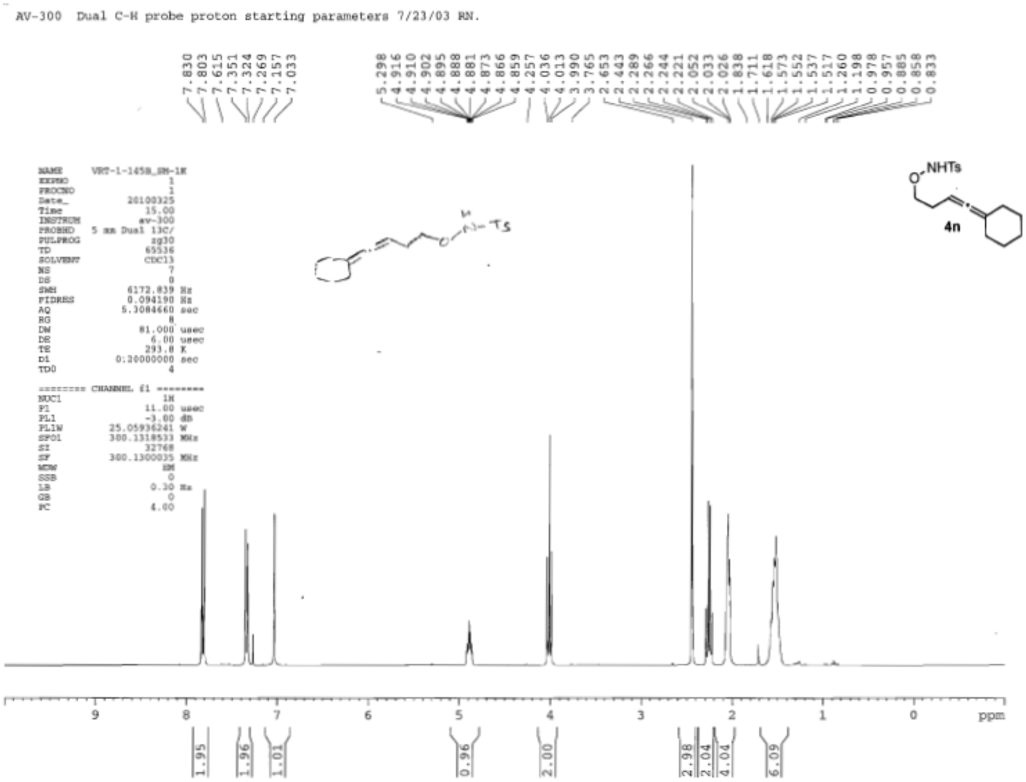
17i proton



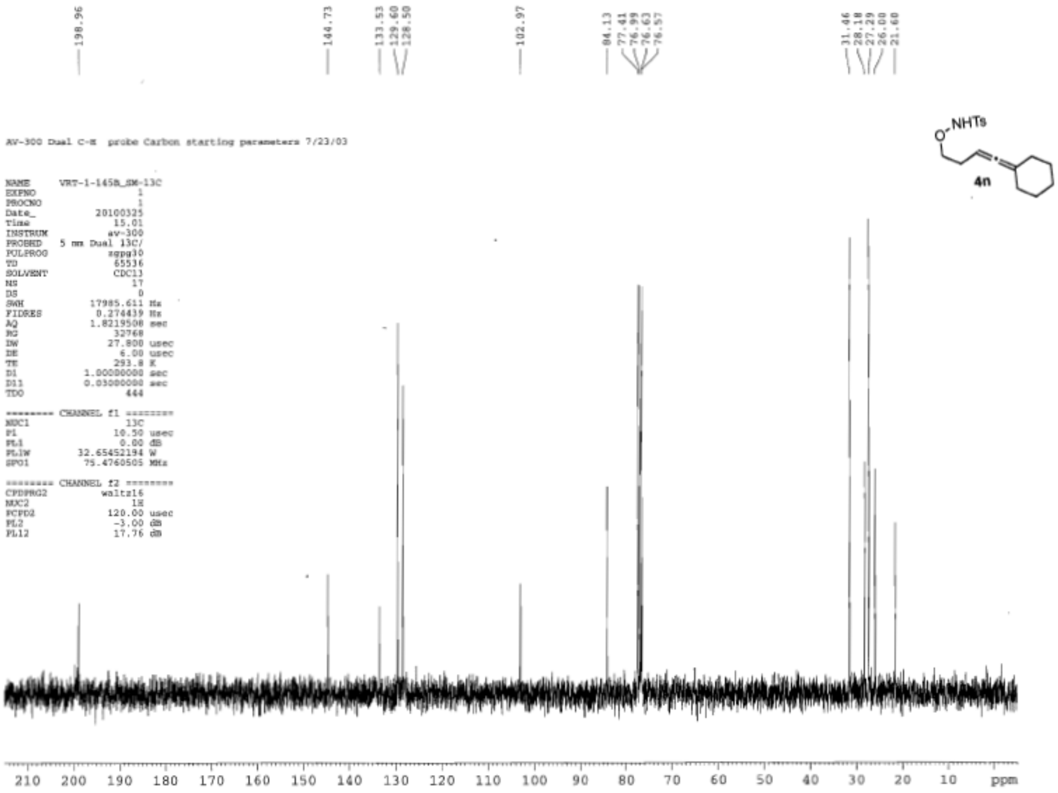
```
NAME      VRT-15-157-13C
EXPNO                  1
PROCNO                 1
Date_           20100220
Time               16.01
INSTRUM           av-300
PROBHD   5 mm Dual 13C/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    18
DS                     0
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                 32768
DW                27.800 usec
DE                  6.00 usec
TE                 293.8 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                  444

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.50 usec
PL1                 0.00 dB
PL1W         32.65452194 W
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             120.00 usec
PL2                -3.00 dB
PL12               17.76 dB
```

AV-300 Dual C-H probe Carbon starting parameters 7/23/03

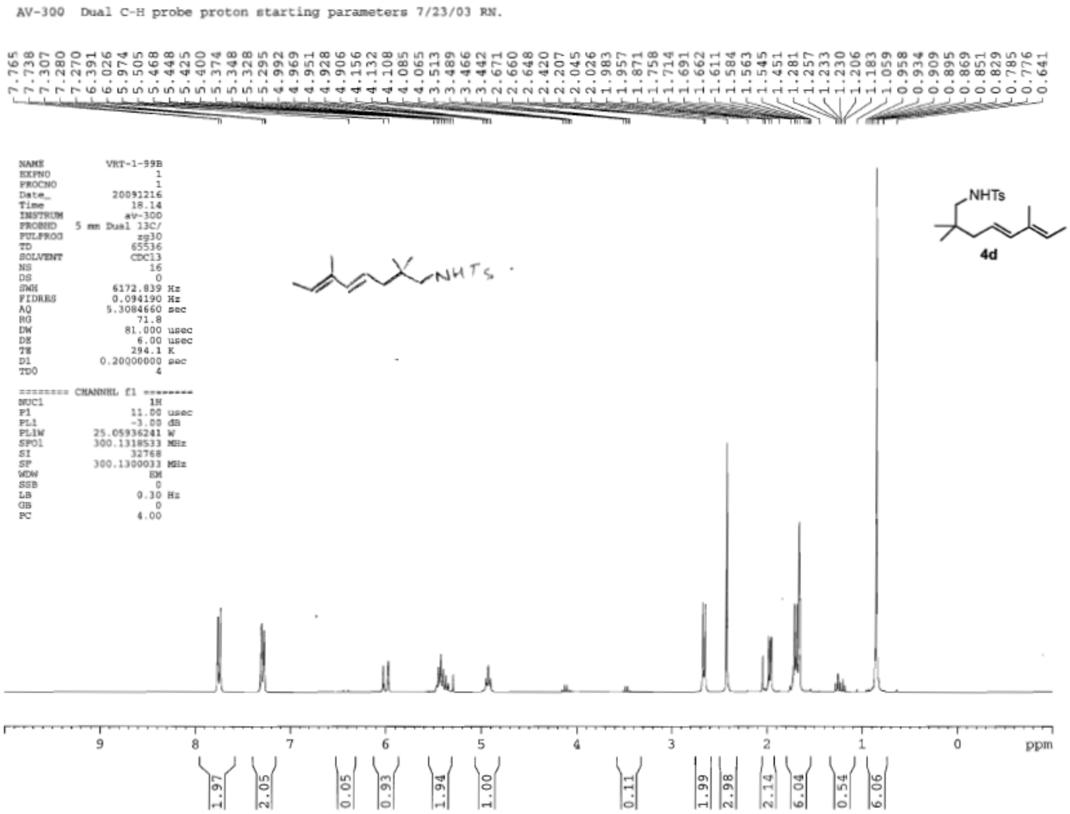
17i carbon



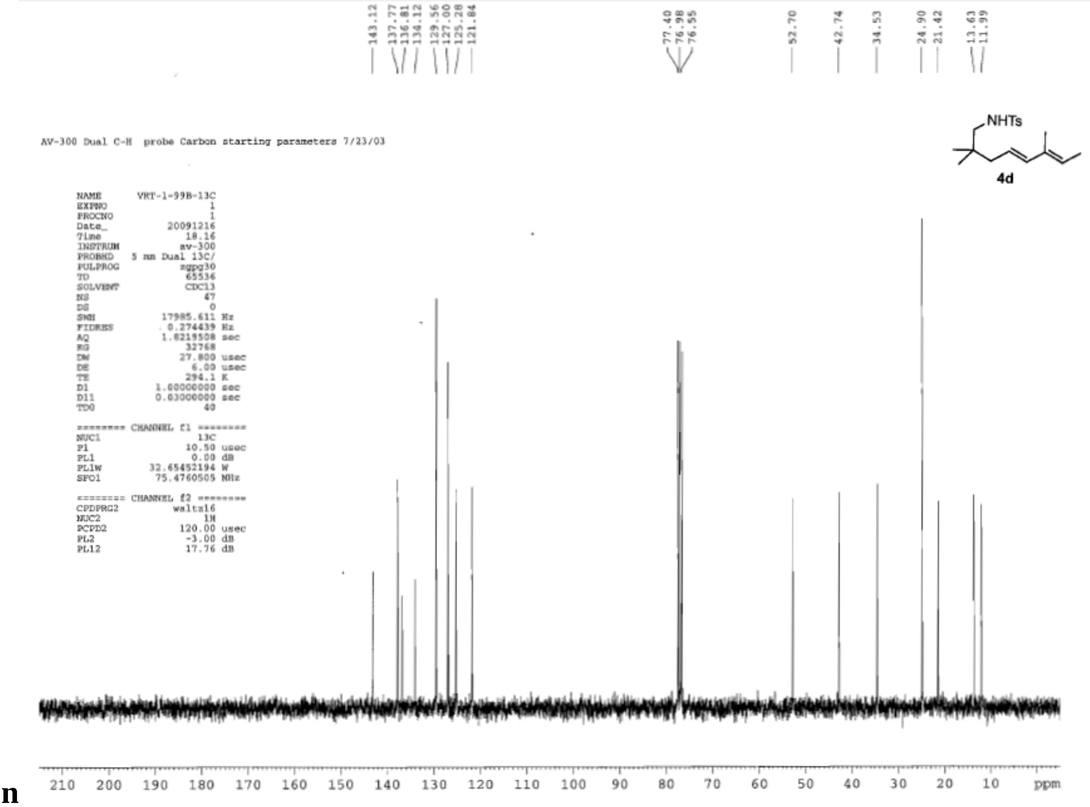
17j proton



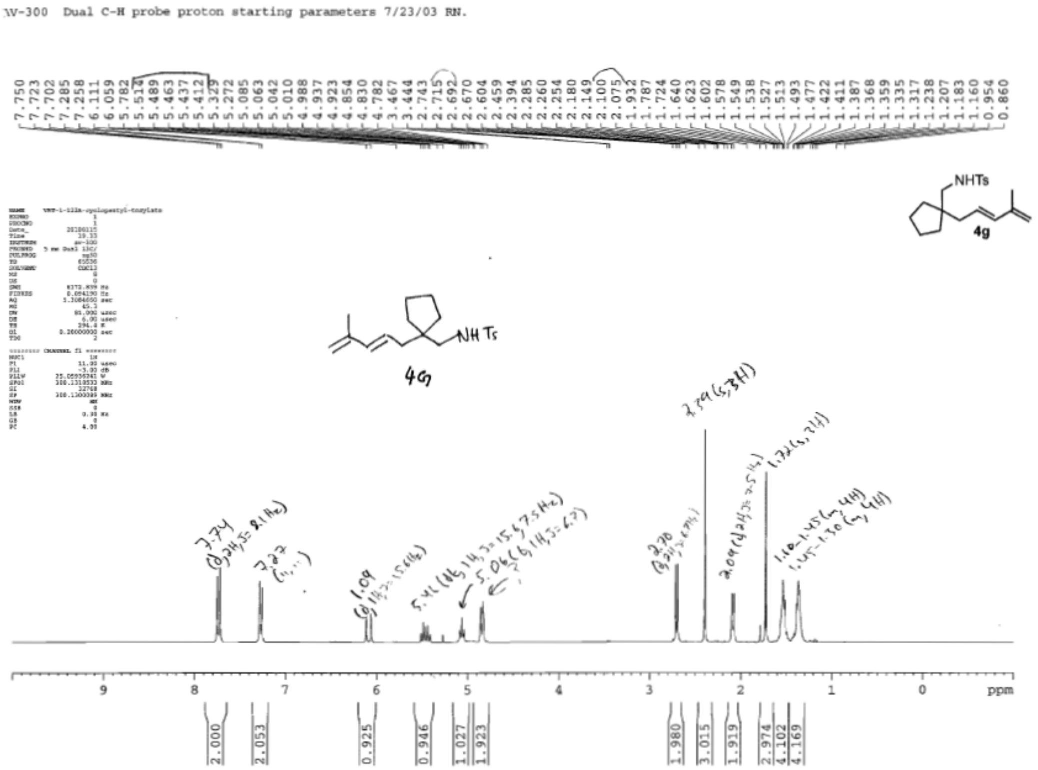
17j carbon



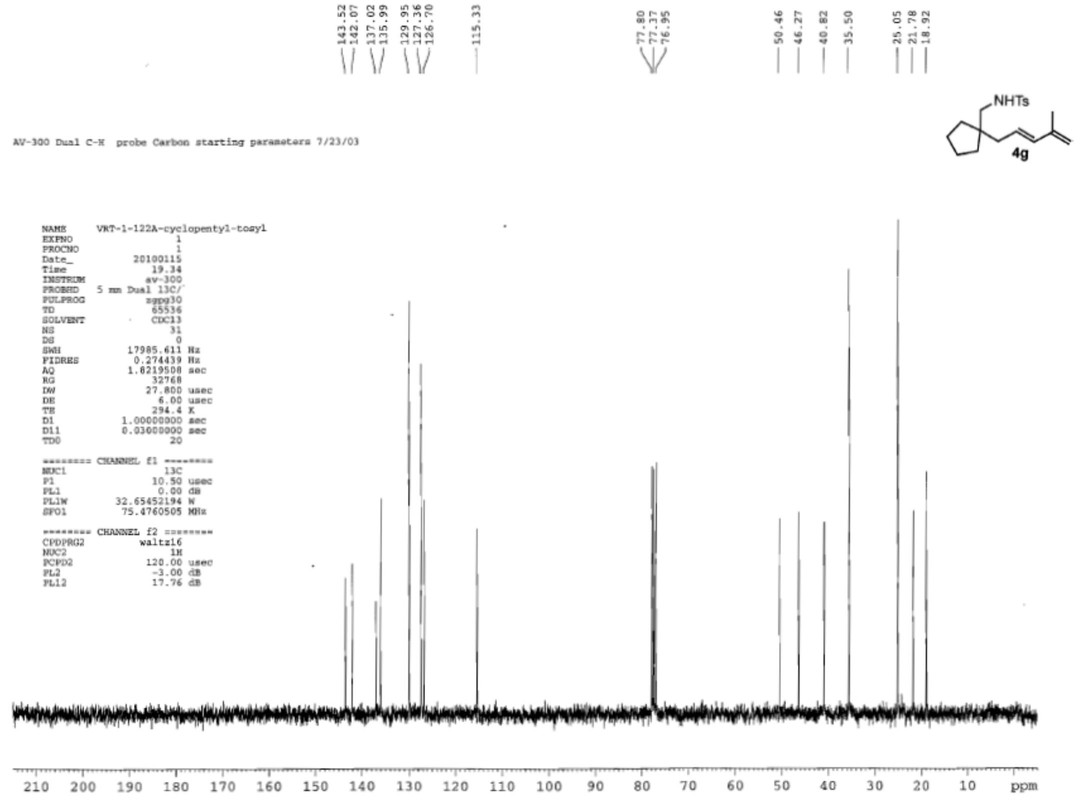
17k proton



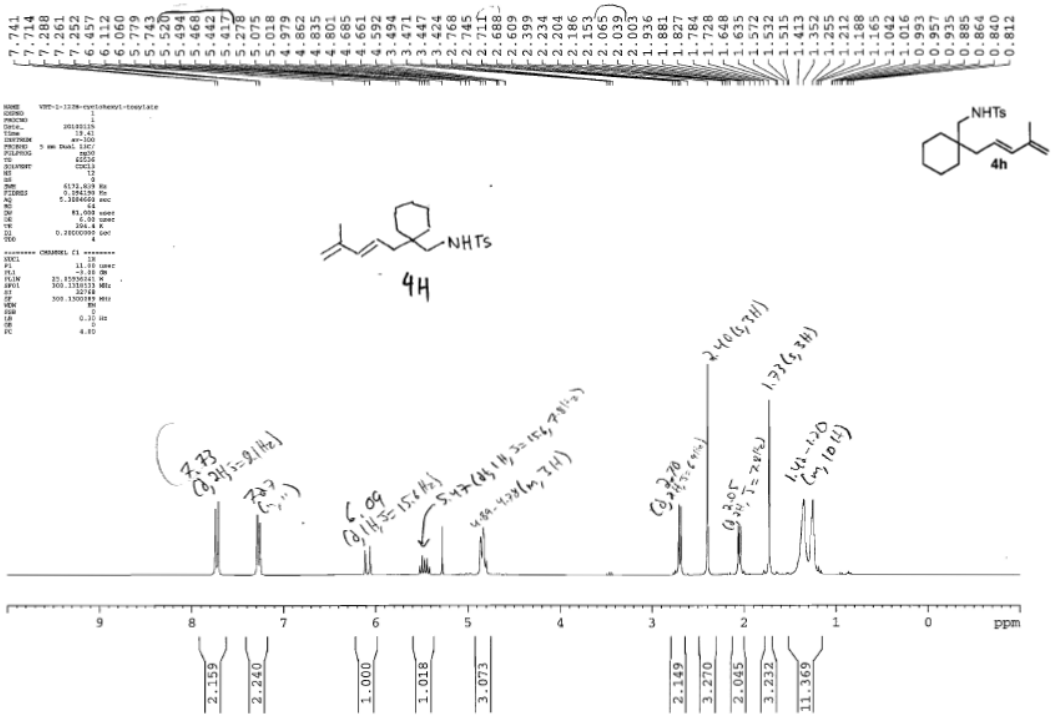
17k carbon



17l proton

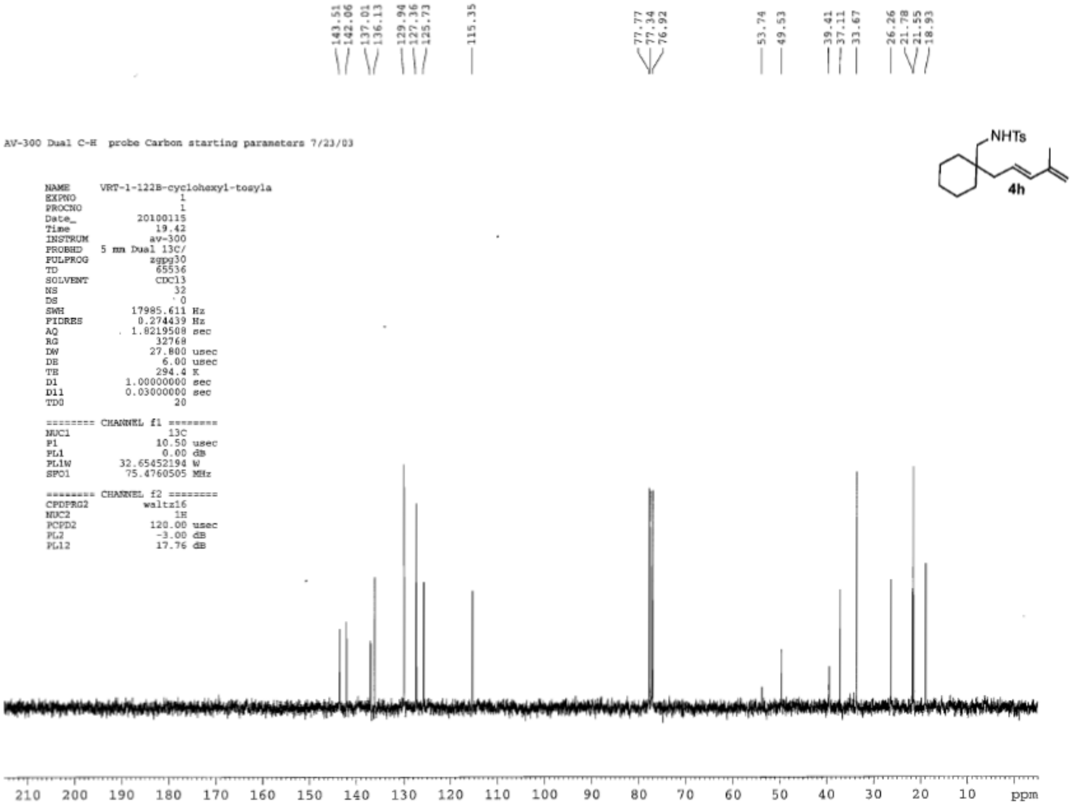


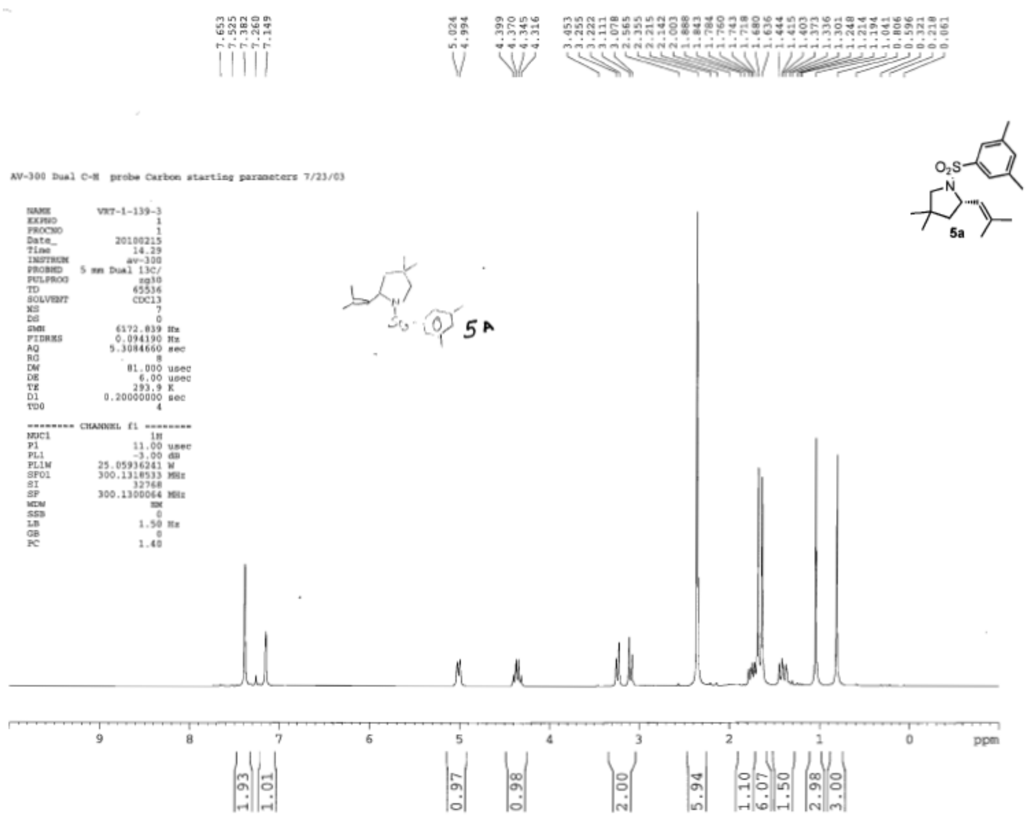
17l carbon



17m proton

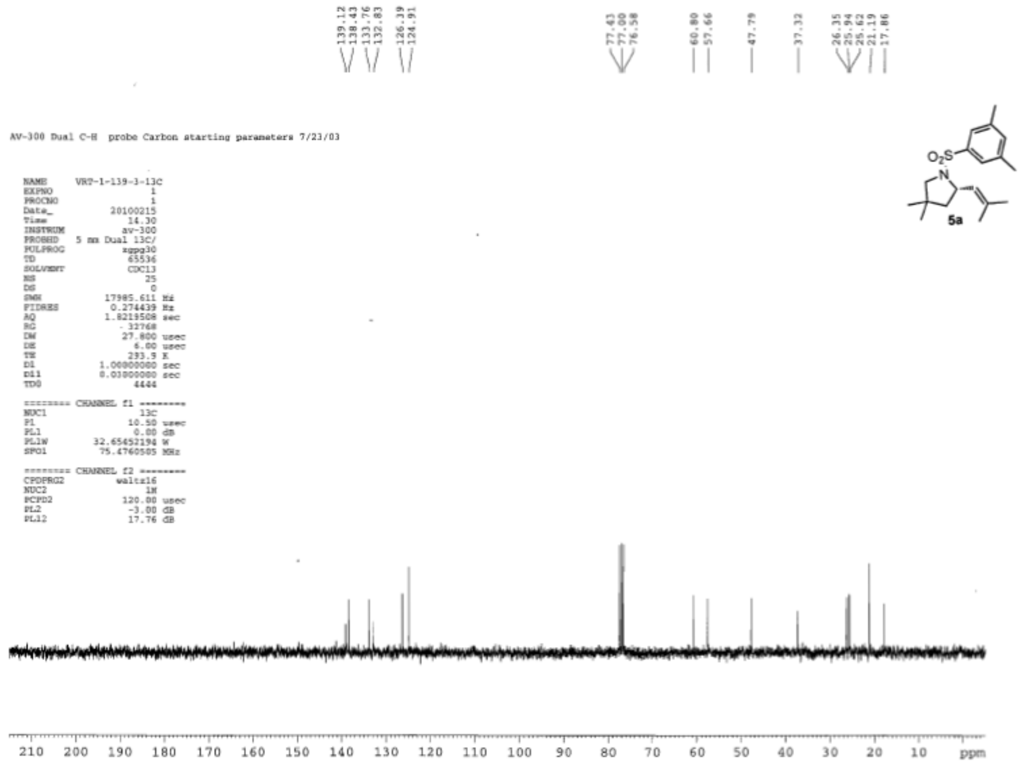
17m carbon





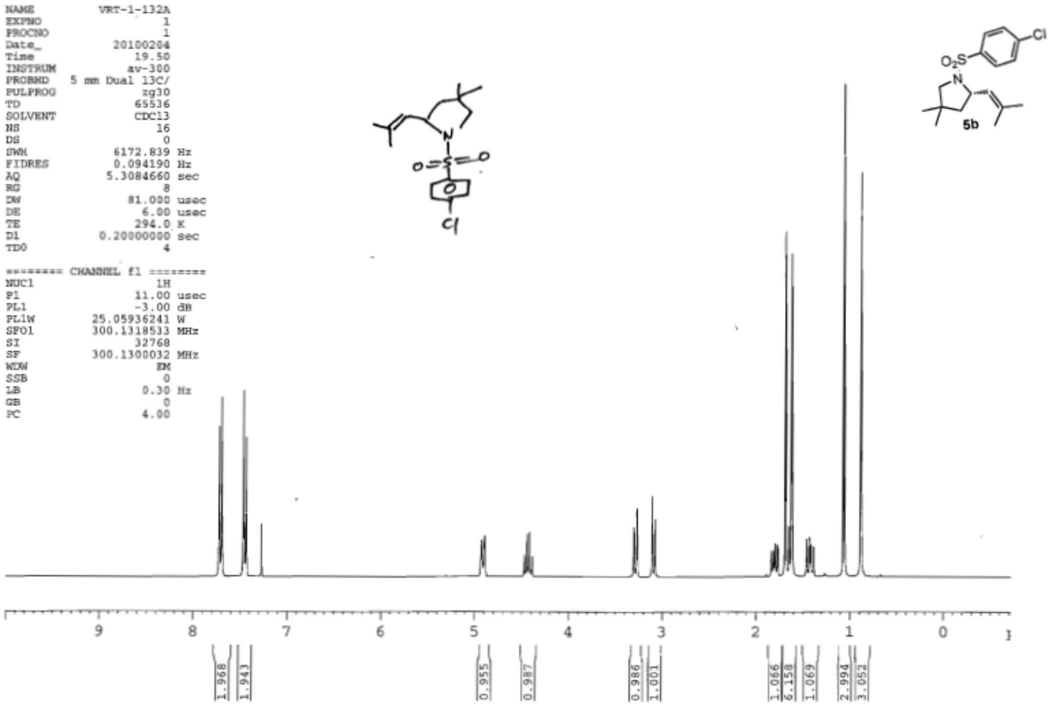
```
AV-300 Dual C-H  probe Carbon starting parameters 7/23/03

NAME          VRT-1-139-3
EXPNO                   1
PROCNO                  1
Date_            20100215
Time                14.29
INSTRUM            av-300
PROBHD    5 mm Dual 13C/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      7
DS                      0
SWH              6172.839 Hz
FIDRES           0.094190 Hz
AQ              5.3084660 sec
RG                      8
DW                 81.000 usec
DE                   6.00 usec
TE                  293.9 K
D1             0.20000000 sec
TD0                     4

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.00 usec
PL1                 -3.00 dB
PL1W          25.05936241 W
SFO1          300.1318533 MHz
SI                  32768
SF            300.1300064 MHz
WDW                    EM
SSB                     0
LB                   1.50 Hz
GB                      0
PC                   1.40
```

18a proton



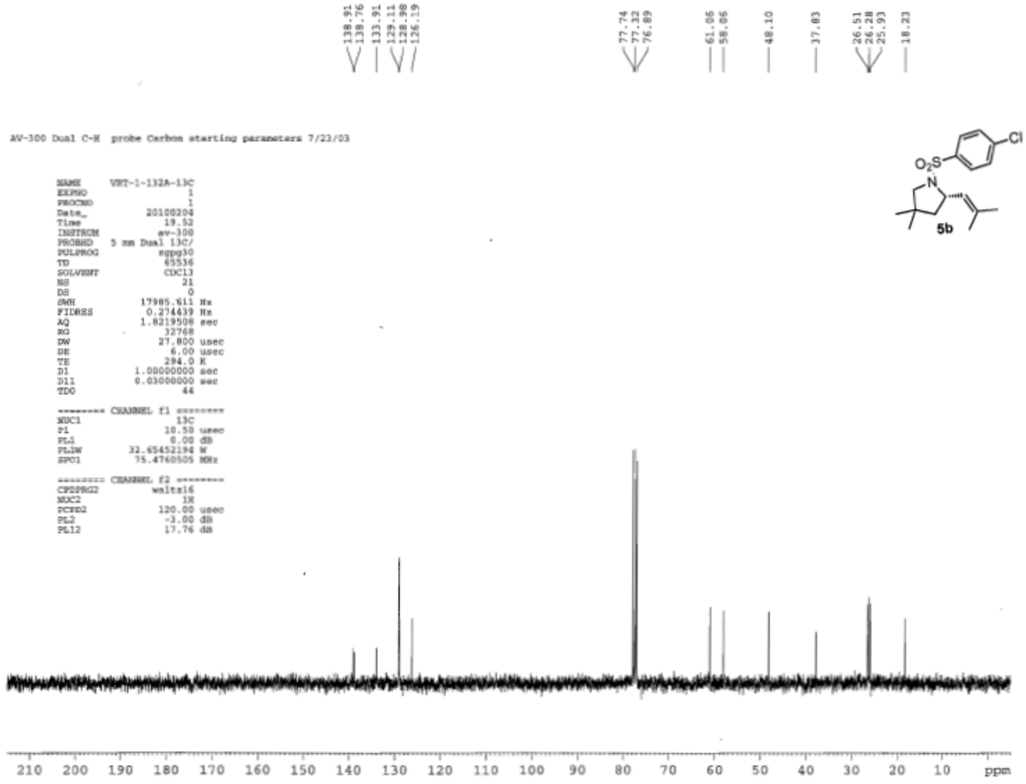
```
AV-300 Dual C-H  probe Carbon starting parameters 7/23/03

NAME      VRT-1-139-3-13C
EXPNO                   1
PROCNO                  1
Date_            20100215
Time                14.30
INSTRUM            av-300
PROBHD    5 mm Dual 13C/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     25
DS                      0
SWH             17985.611 Hz
FIDRES           0.274439 Hz
AQ              1.8219508 sec
RG                  32768
DW                 27.800 usec
DE                   6.00 usec
TE                  293.9 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                  4444

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.50 usec
PL1                  0.00 dB
PL1W          32.65452194 W
SFO1           75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              120.00 usec
PL2                 -3.00 dB
PL12                17.76 dB
```

18a carbon



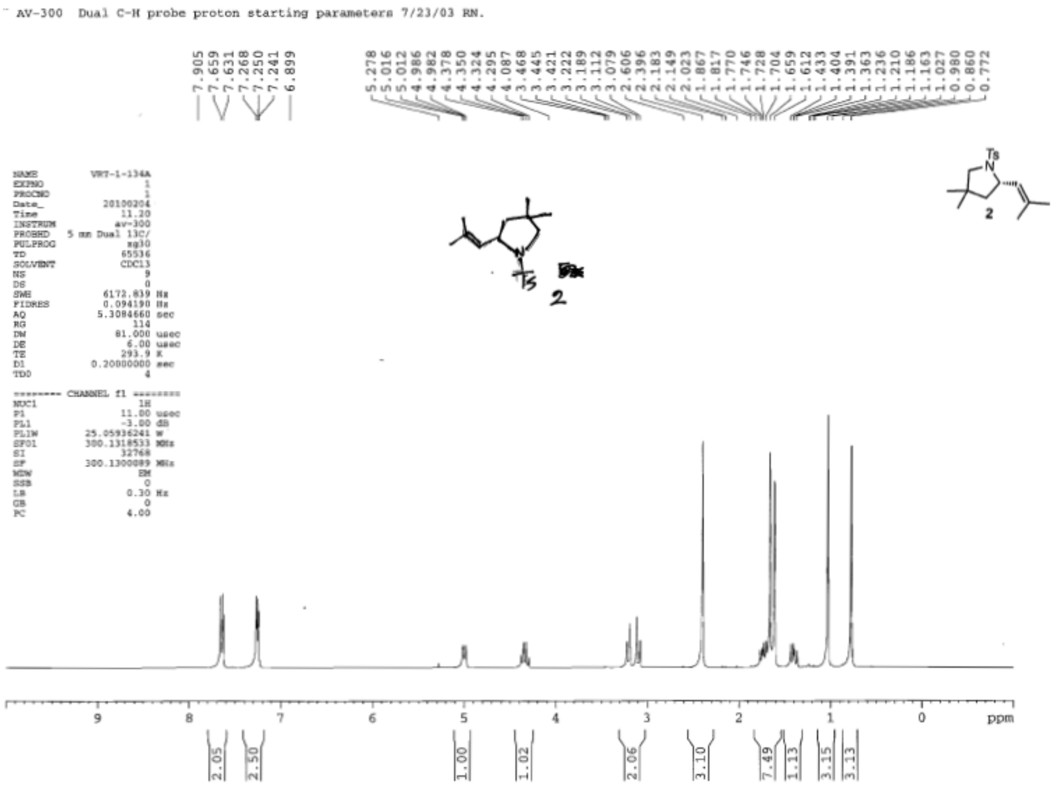
```
NAME          VRT-1-132A
EXPNO                  1
PROCNO                 1
Date_           20100204
Time               19.50
INSTRUM           av-300
PROBHD   5 mm Dual 13C/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ             5.3084660 sec
RG                     8
DW                81.000 usec
DE                  6.00 usec
TE                 294.0 K
D1            0.20000000 sec
TD0                    4

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.00 usec
PL1                -3.00 dB
PL1W         25.05936241 W
SFO1         300.1318533 MHz
SI                 32768
SF           300.1300032 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00
```

18b proton



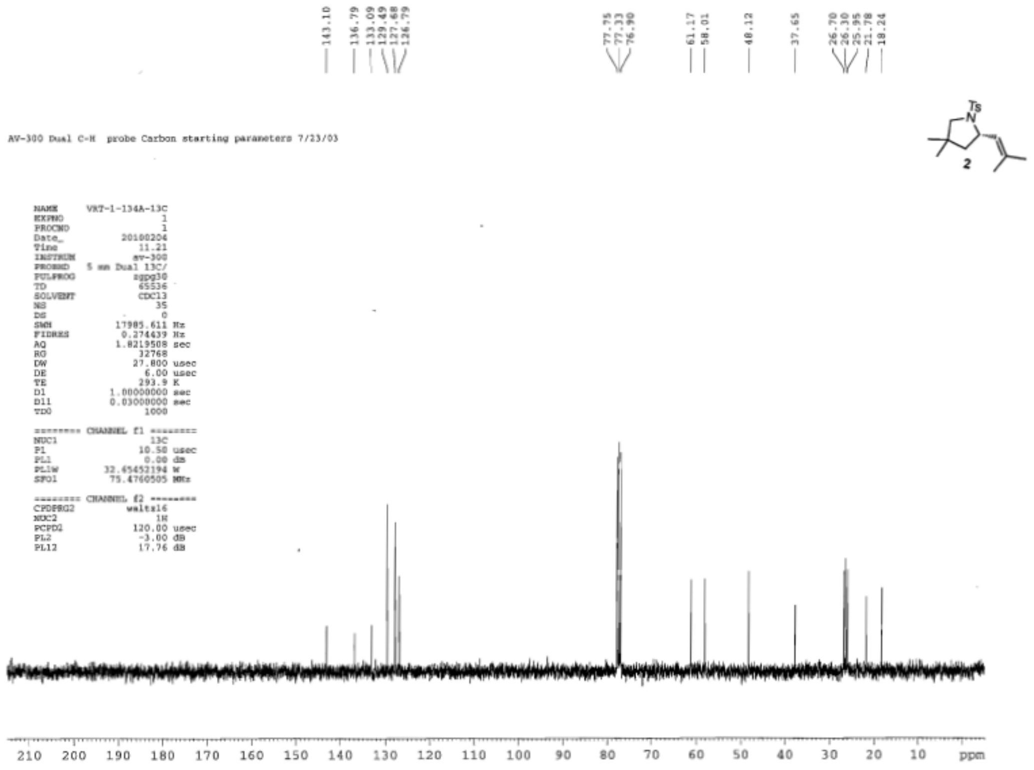
```
AV-300 Dual C-H  probe Carbon starting parameters 7/23/03

NAME       VRT-1-132A-13C
EXPNO                  1
PROCNO                 1
Date_           20100204
Time               19.52
INSTRUM           av-300
PROBHD   5 mm Dual 13C/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    21
DS                     0
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                 32768
DW                27.800 usec
DE                  6.00 usec
TE                 294.0 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                   44

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.50 usec
PL1                 0.00 dB
PL1W         32.65452194 W
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             120.00 usec
PL2                -3.00 dB
PL12               17.76 dB
```

18b carbon



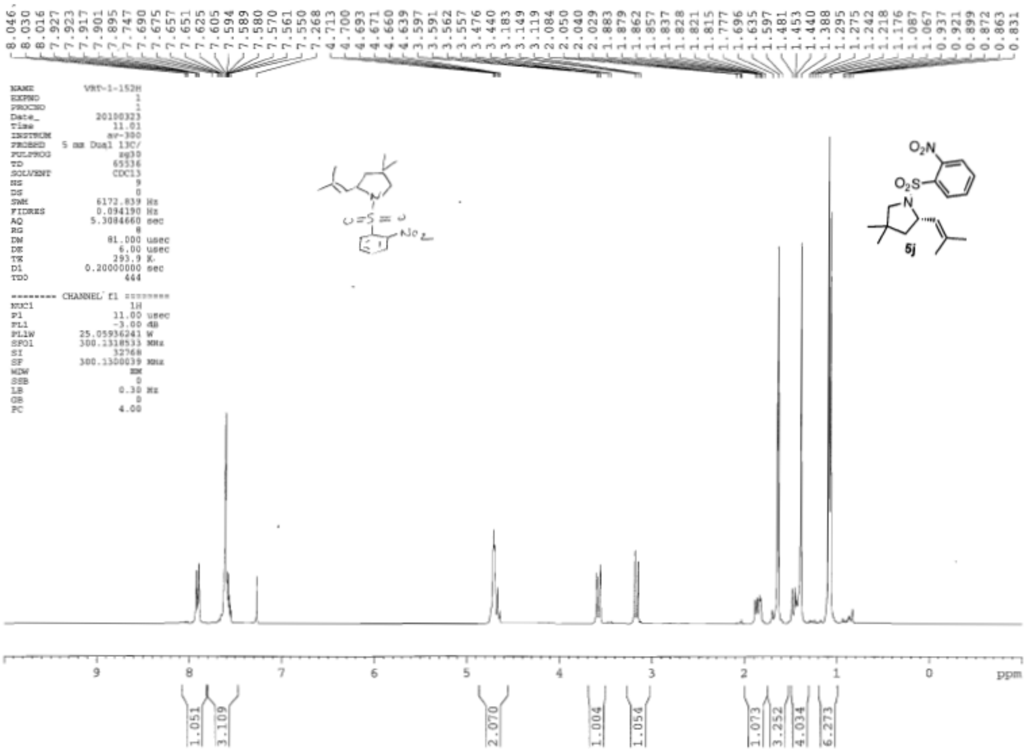
```
NAME        VRT-1-134A
EXPNO                1
PROCNO               1
Date_         20100204
Time             11.20
INSTRUM         av-300
PROBHD   5 mm Dual 13C/
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                   9
DS                   0
SWH           6172.839 Hz
FIDRES        0.094190 Hz
AQ           5.3084660 sec
RG                 114
DW              81.000 usec
DE                6.00 usec
TE               293.9 K
D1          0.20000000 sec
TD0                  4

======== CHANNEL f1 ========
NUC1                1H
P1               11.00 usec
PL1              -3.00 dB
PL1W       25.05936241 W
SFO1       300.1318533 MHz
SI               32768
SF         300.1300089 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                4.00
```

18c proton

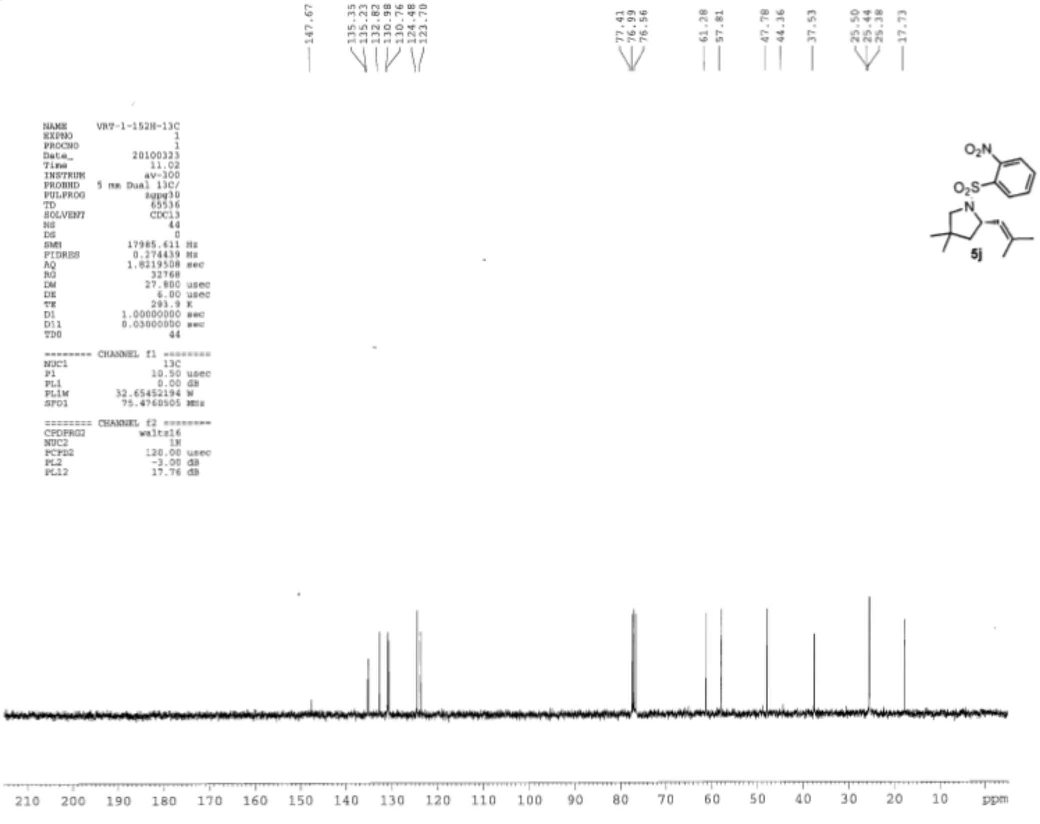


```
NAME     VRT-1-134A-13C
EXPNO                1
PROCNO               1
Date_         20100204
Time             11.21
INSTRUM         av-300
PROBHD   5 mm Dual 13C/
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  35
DS                   0
SWH          17985.611 Hz
FIDRES        0.274439 Hz
AQ           1.8219508 sec
RG               32768
DW              27.800 usec
DE                6.00 usec
TE               293.9 K
D1          1.00000000 sec
D11         0.03000000 sec
TD0               1000

======== CHANNEL f1 ========
NUC1               13C
P1               10.50 usec
PL1               0.00 dB
PL1W       32.45452194 W
SFO1        75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2           120.00 usec
PL2              -3.00 dB
PL12             17.76 dB
```

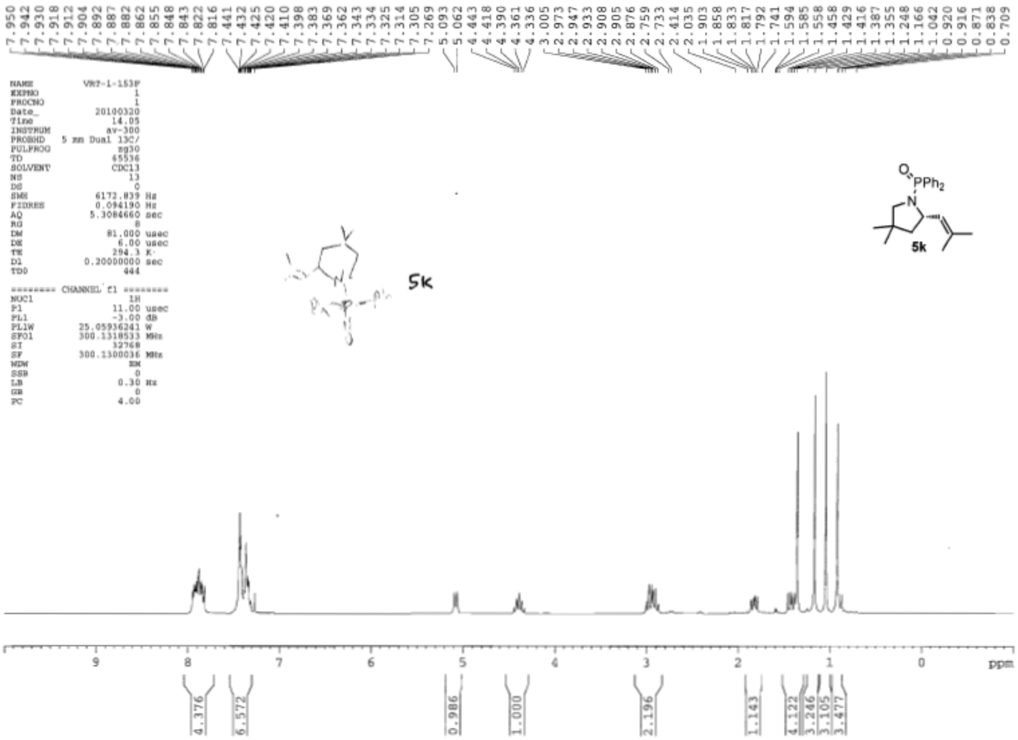
18c carbon



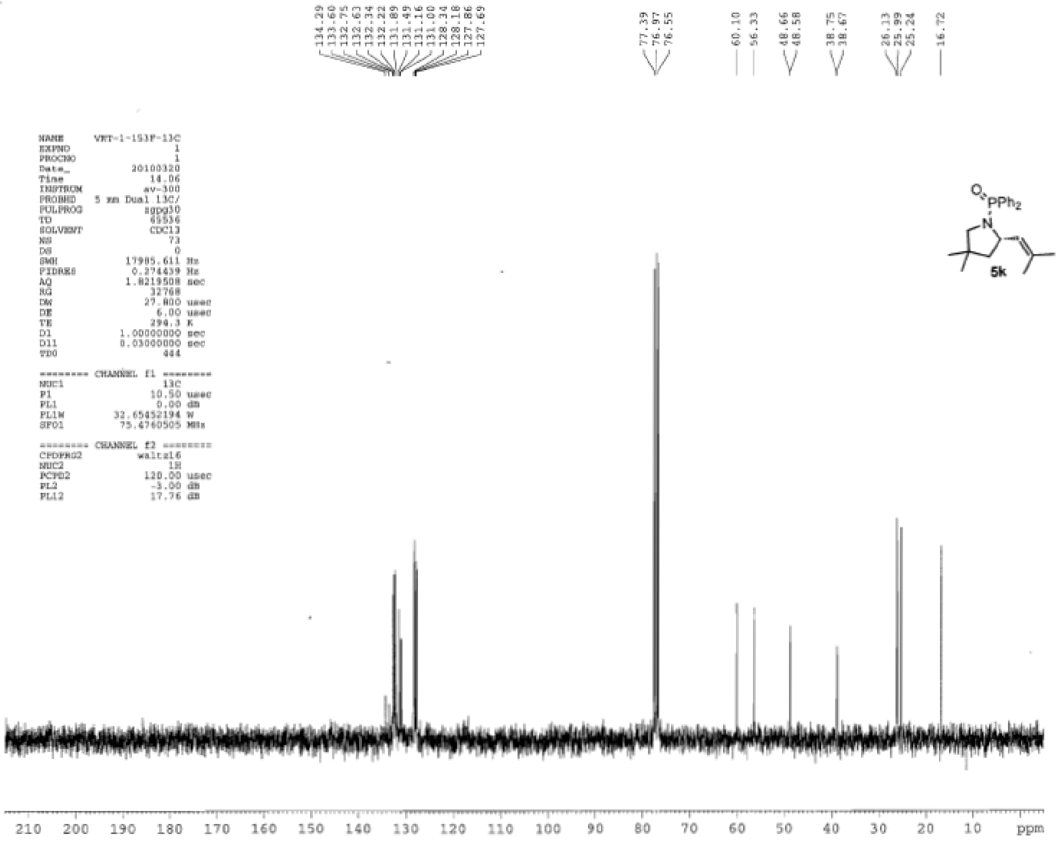
18d proton



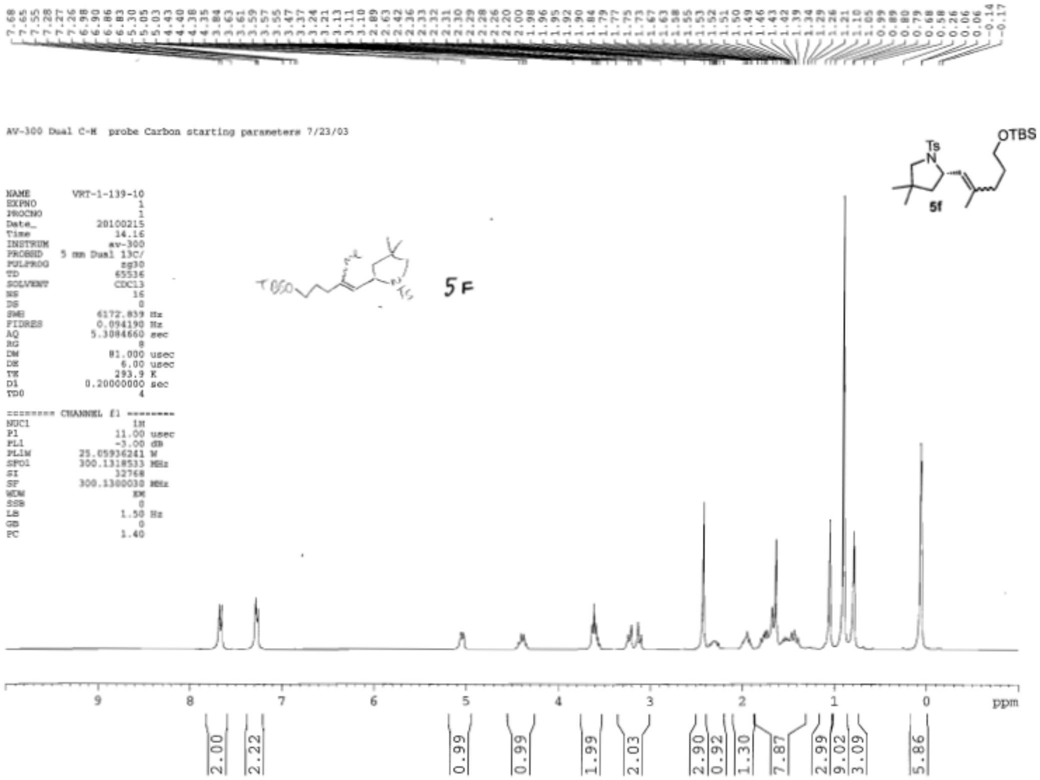
18d carbon



18e proton

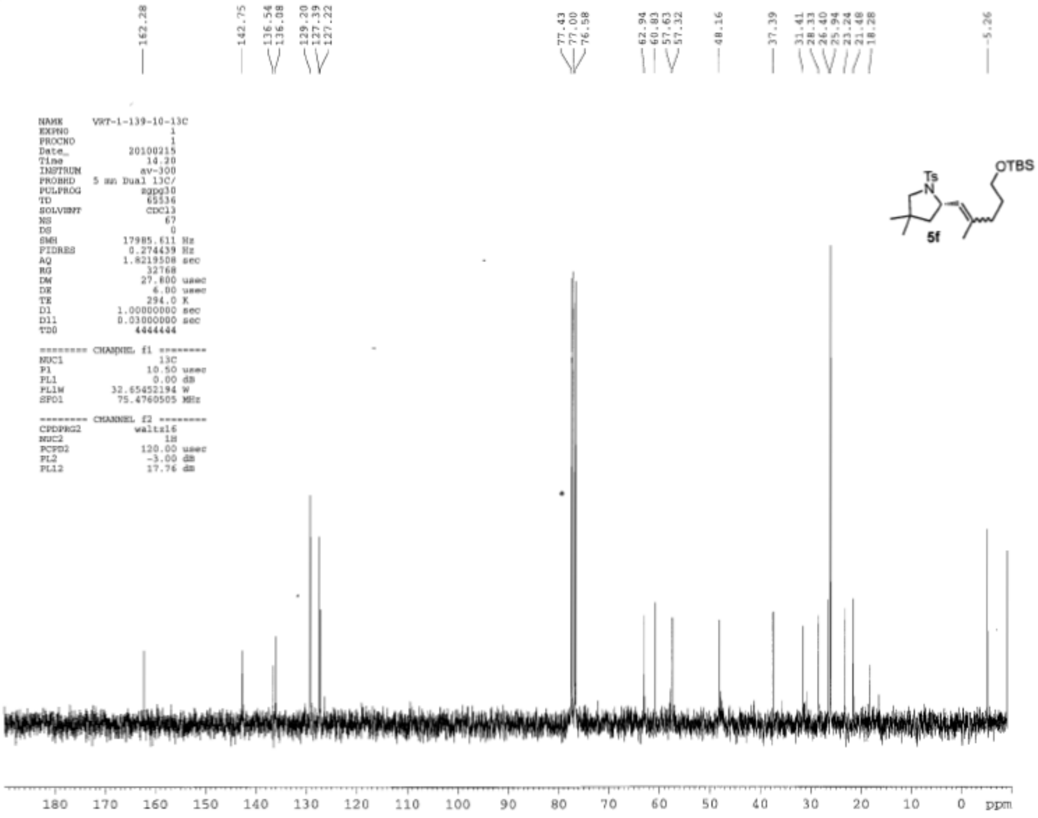


18e carbon



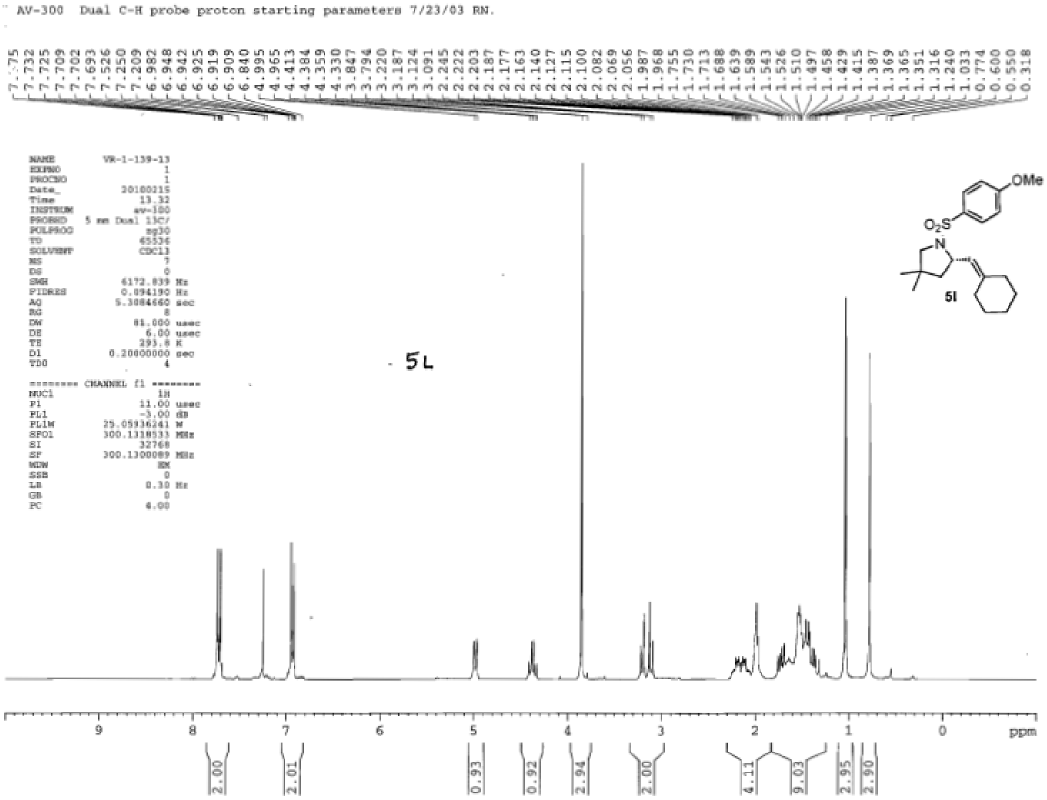
```
AV-300 Dual C-H  probe Carbon starting parameters 7/23/03

NAME         VRT-1-139-10
EXPNO                   1
PROCNO                  1
Date_            20100215
Time                14.16
INSTRUM            av-300
PROBHD   5 mm Dual 13C/
PULPROG              zg30
TD                  65536
SOLVENT             CDC13
NS                     16
DS                      0
SWH              6172.839 Hz
FIDRES           0.094190 Hz
AQ              5.3084660 sec
RG                      8
DW                 81.000 usec
DE                   6.00 usec
TE                  293.9 K
D1             0.20000000 sec
TD0                     4

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.00 usec
PL1                 -3.00 dB
PL1W          25.05936241 W
SFO1          300.1318533 MHz
SI                  32768
SF            300.1300030 MHz
WDW                    EM
SSB                     0
LB                   1.50 Hz
GB                      0
PC                   1.40
```

18f proton

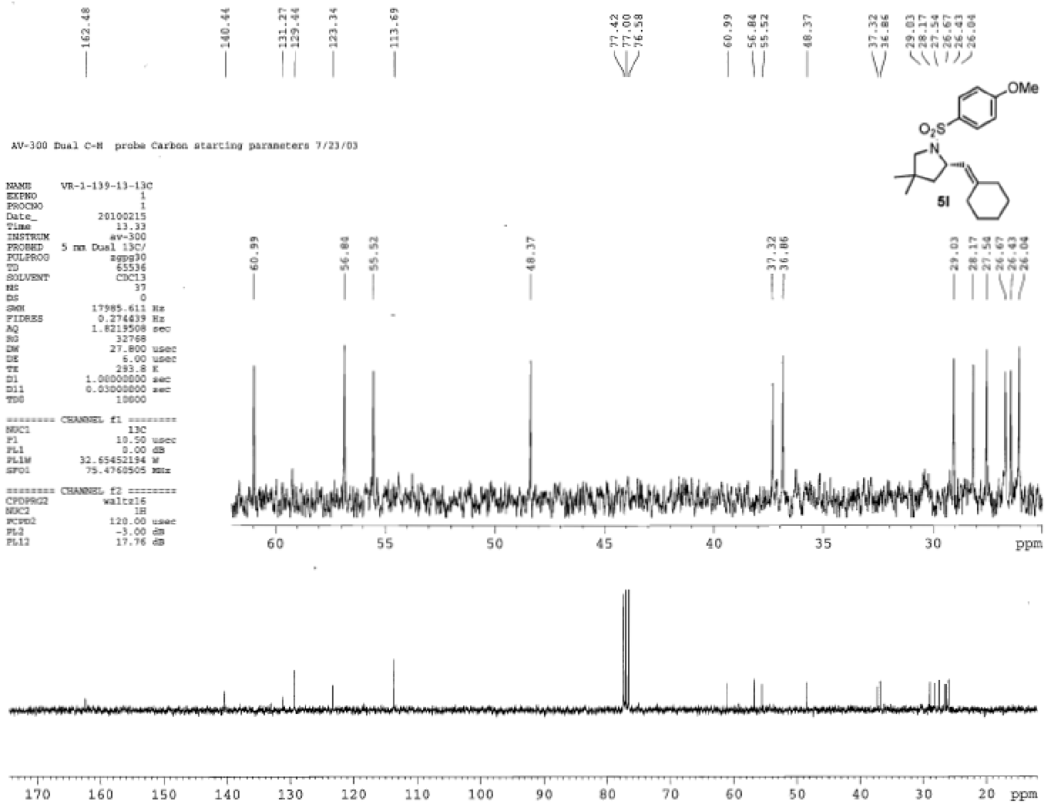


```
NAME      VRT-1-139-10-13C
EXPNO                    1
PROCNO                   1
Date_             20100215
Time                 14.20
INSTRUM             av-300
PROBHD    5 mm Dual 13C/
PULPROG            zgpg30
TD                   65536
SOLVENT              CDC13
NS                      67
DS                       0
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ               1.8219508 sec
RG                   32768
DW                  27.800 usec
DE                    6.00 usec
TE                   294.0 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                4444444

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.50 usec
PL1                   0.00 dB
PL1W           32.65452194 W
SFO1            75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               120.00 usec
PL2                  -3.00 dB
PL12                 17.76 dB
```

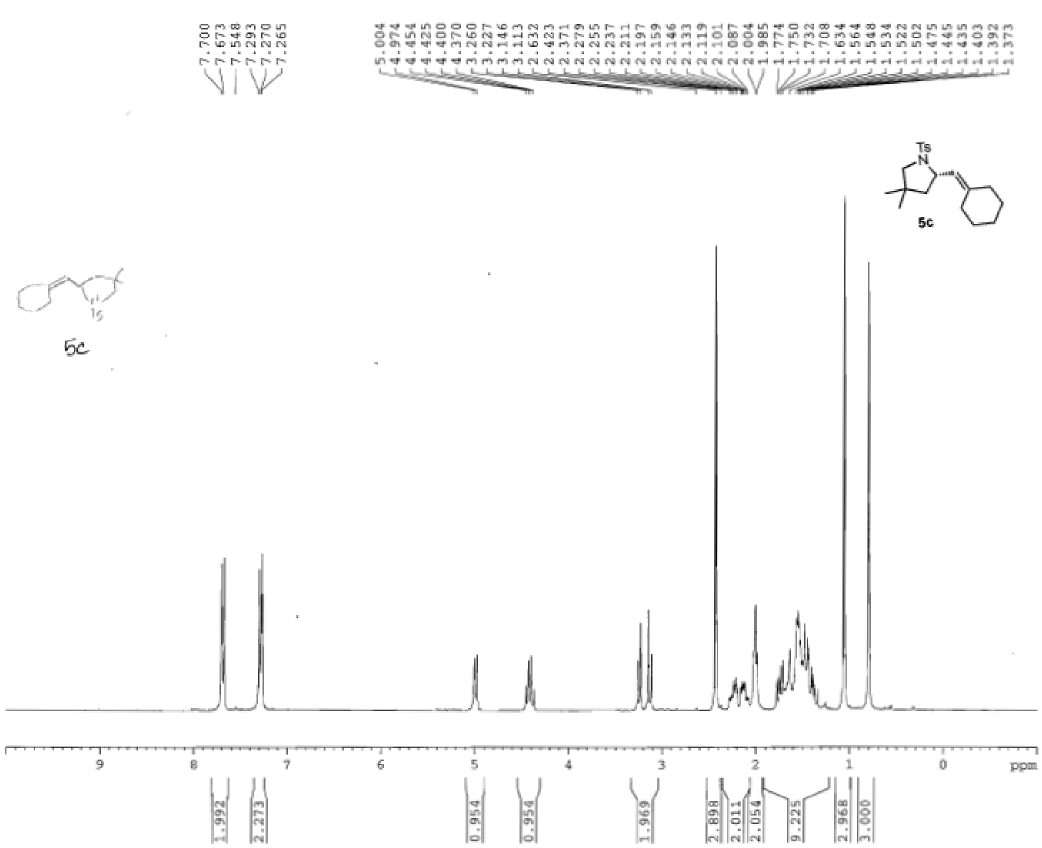
18f carbon



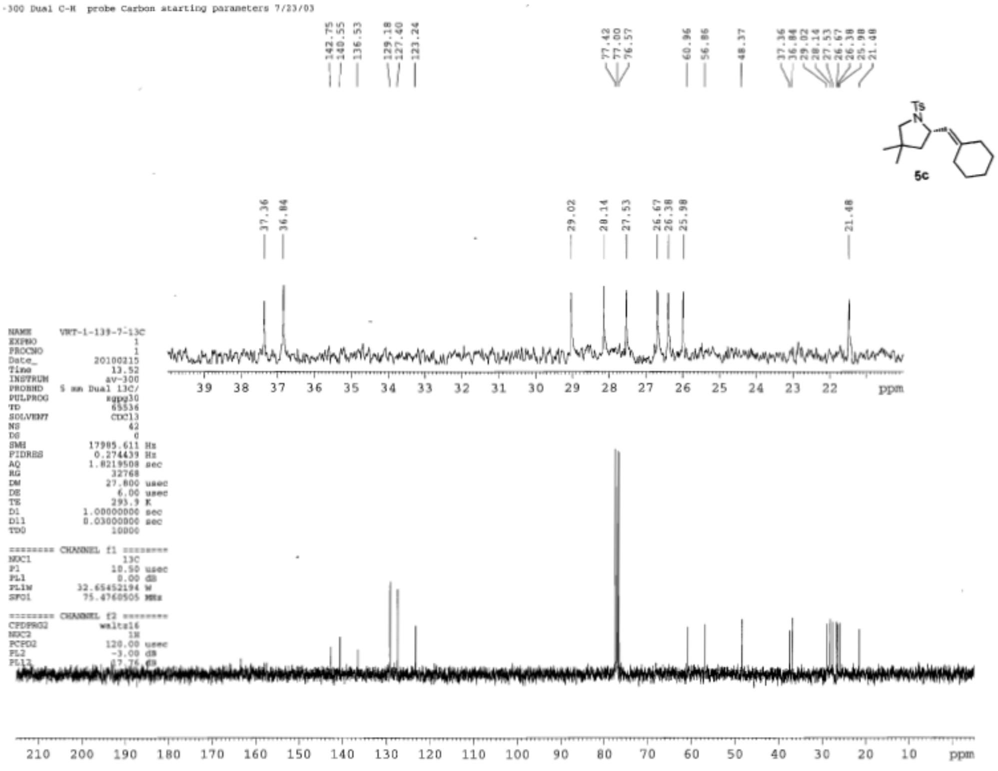
18g proton



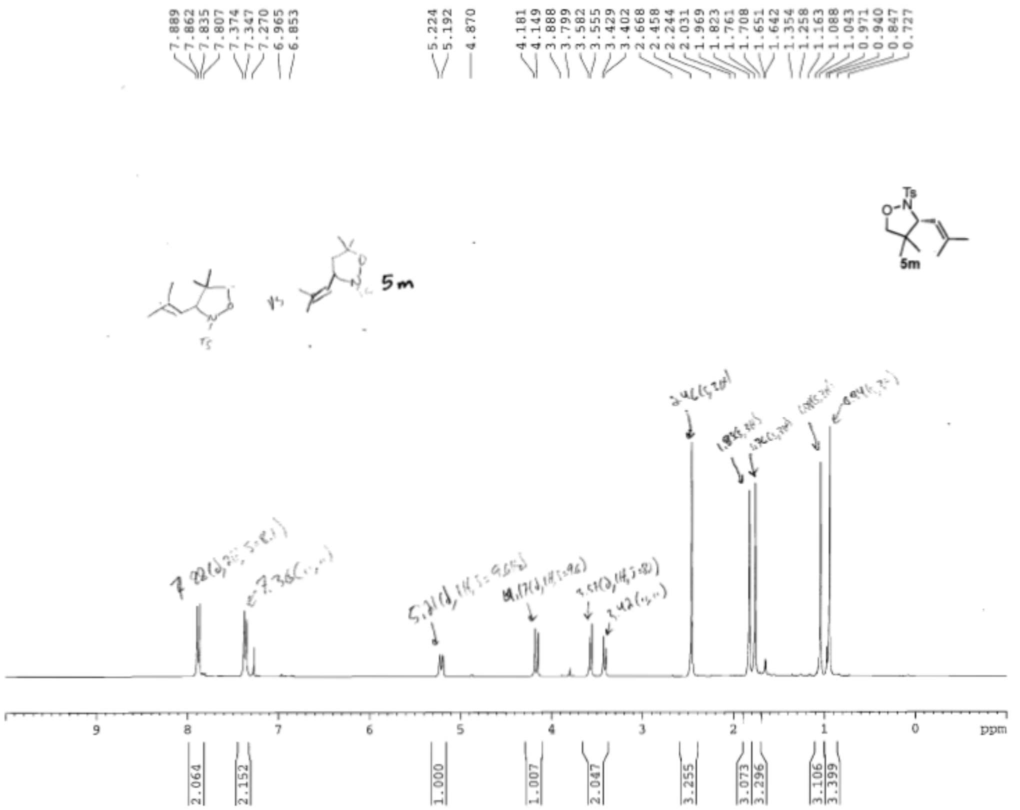
18g carbon



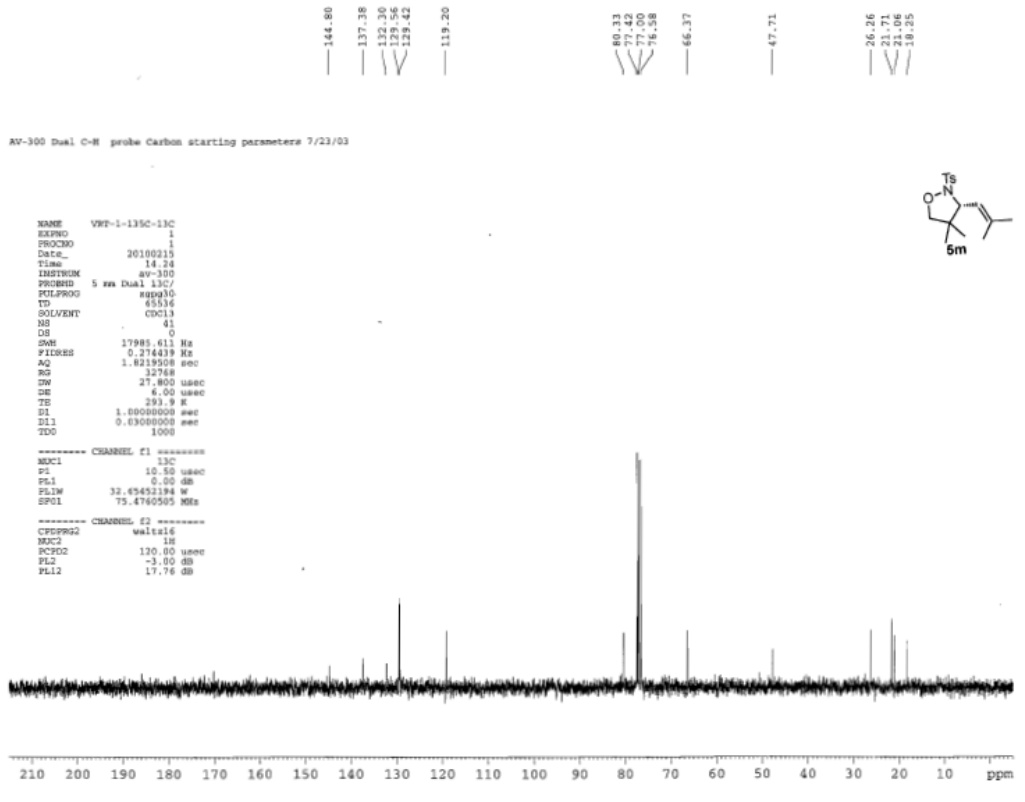
18h proton



18h carbon

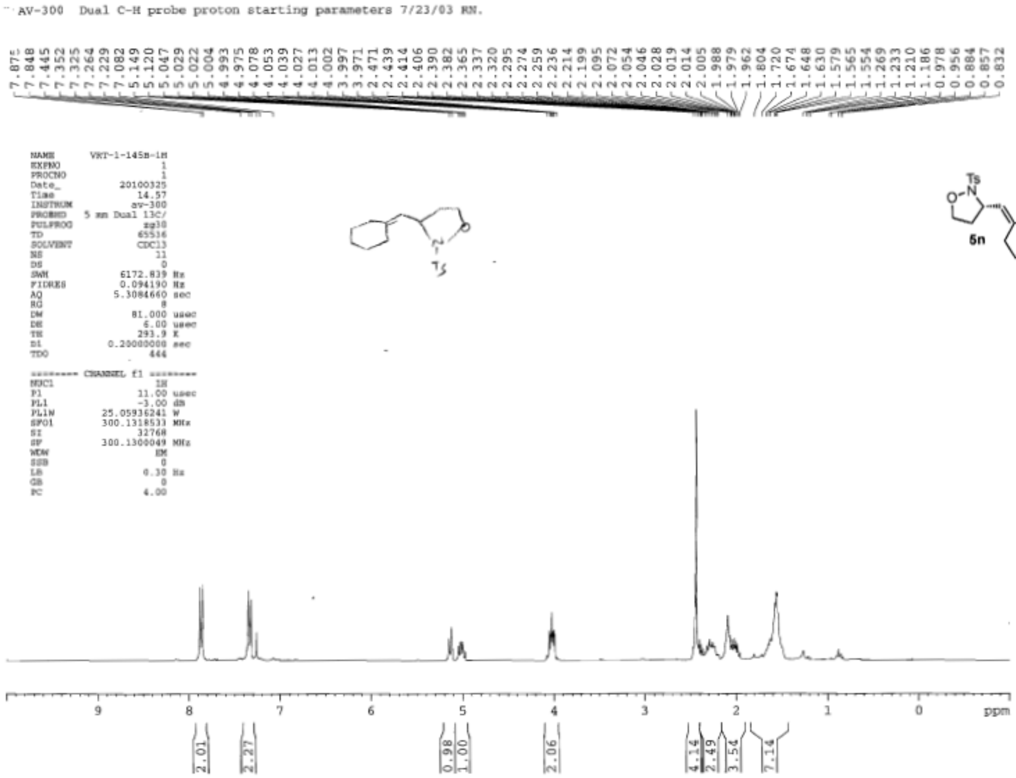


18i proton

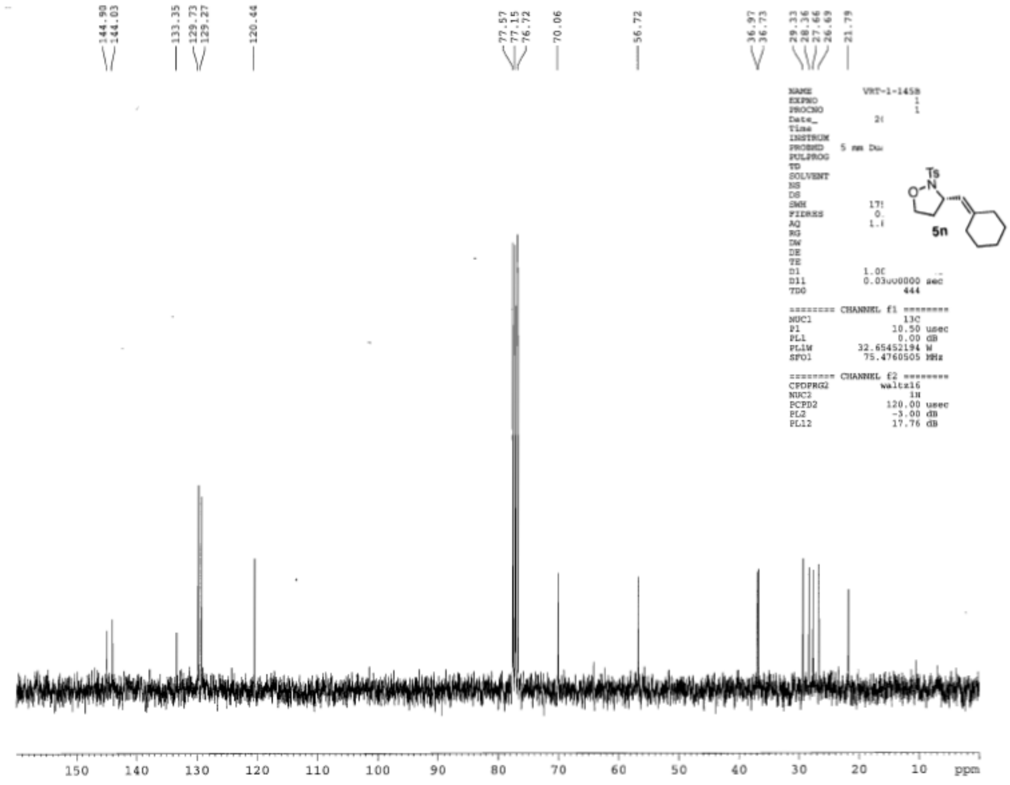


```
AV-300 Dual C-H  probe Carbon starting parameters 7/23/03

NAME        VRT-1-135C-13C
EXPNO                    1
PROCNO                   1
Date_             20100215
Time                 14.24
INSTRUM             av-300
PROBHD     5 mm Dual 13C/
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      41
DS                       0
SWH             17985.611 Hz
FIDRES           0.274439 Hz
AQ              1.8219508 sec
RG                   32768
DW                  27.800 usec
DE                    6.00 usec
TE                   293.9 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                   1000

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.50 usec
PL1                   0.00 dB
PL1W           32.65452194 W
SFO1            75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               120.00 usec
PL2                  -3.00 dB
PL12                 17.76 dB
```

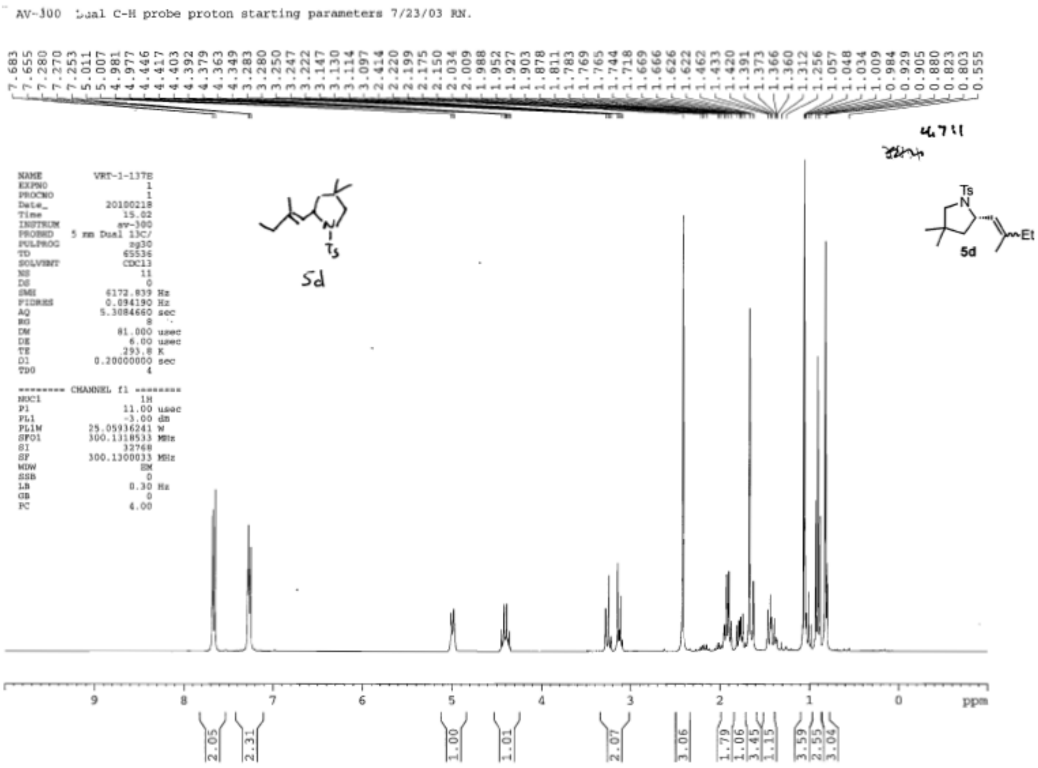
18i carbon



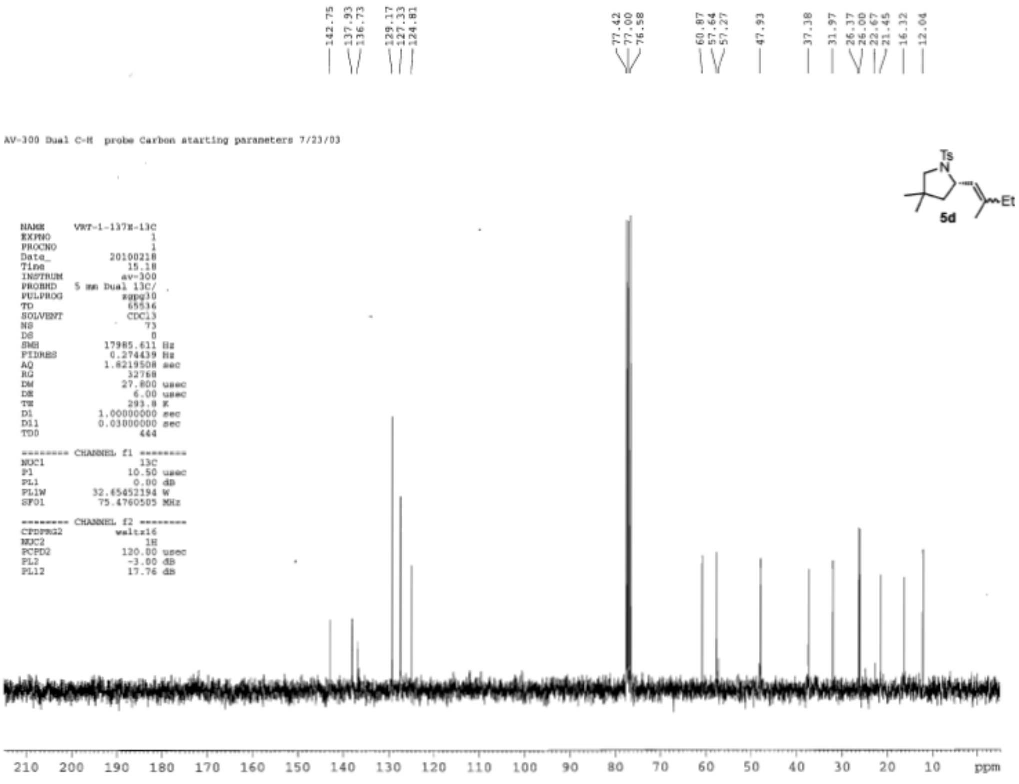
18j proton



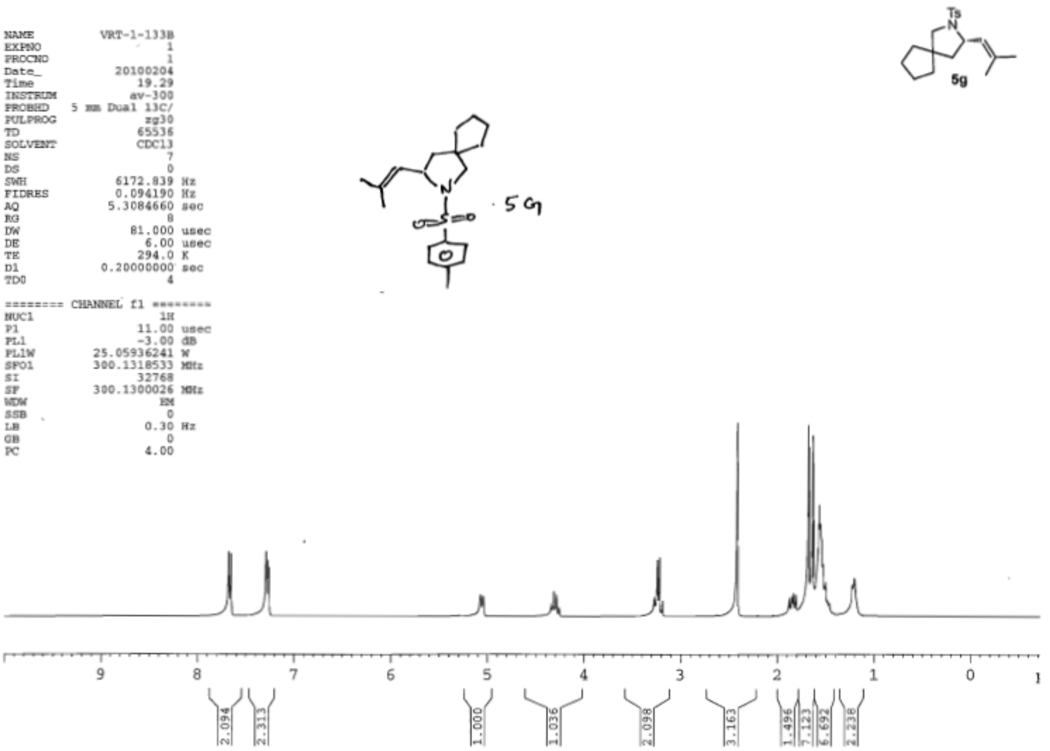
18j carbon



18k proton

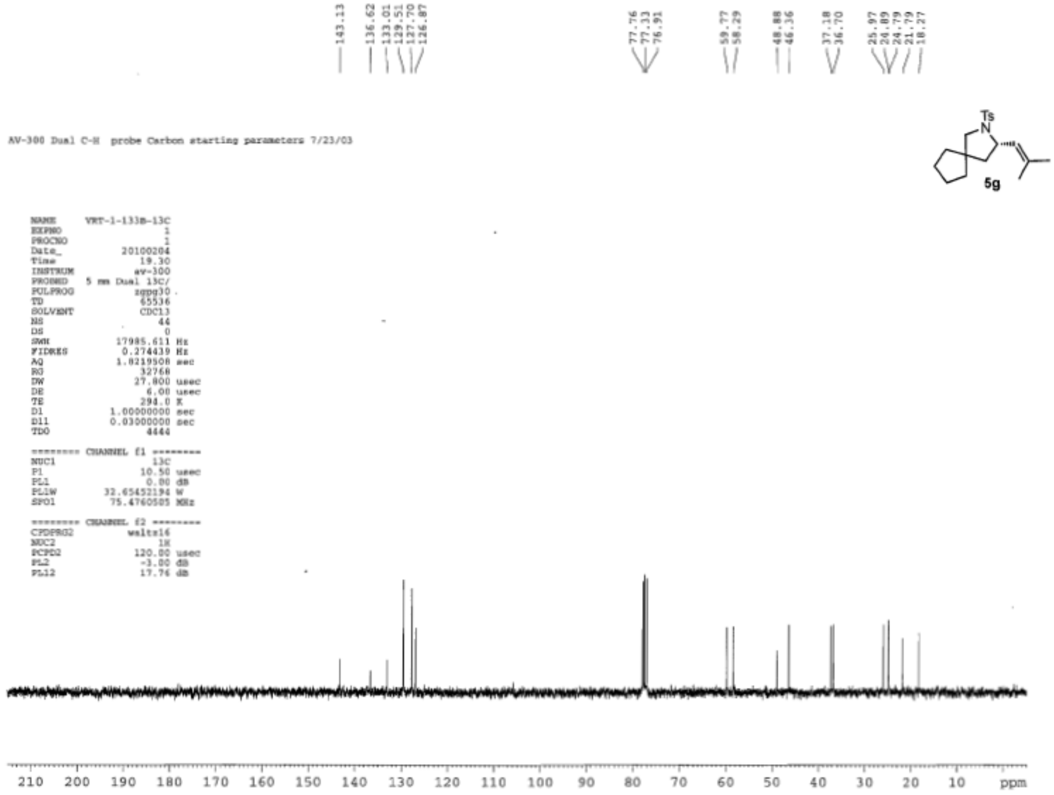


18k carbon



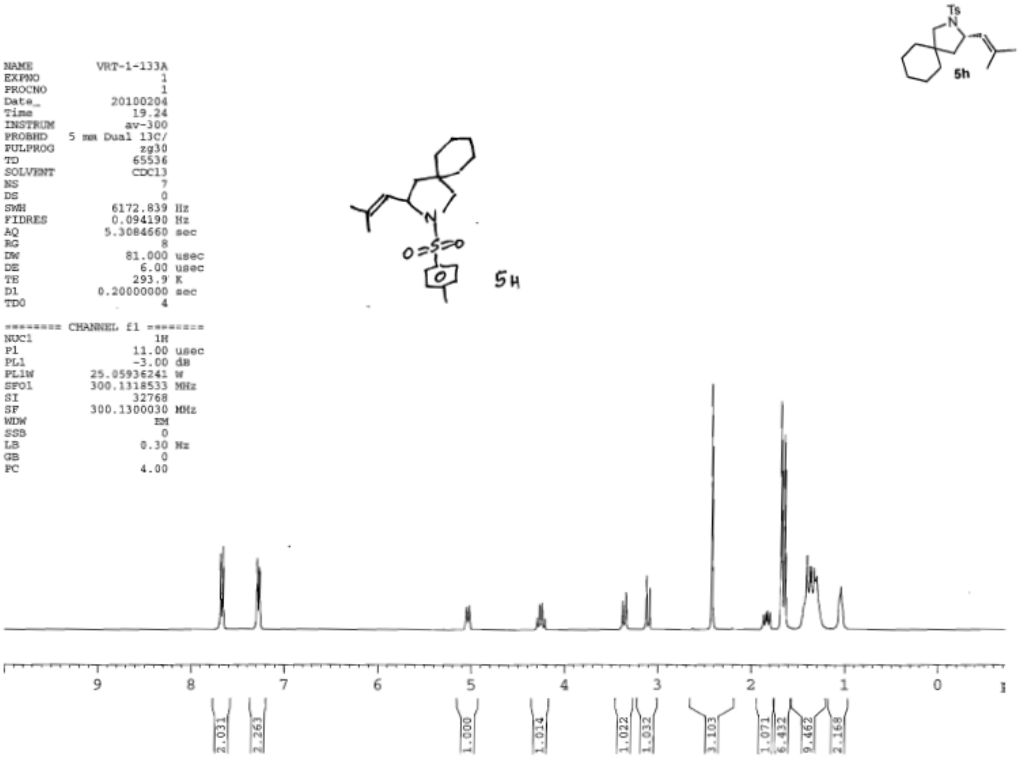
```
NAME           VRT-1-133B
EXPNO                   1
PROCNO                  1
Date_            20100204
Time                19.29
INSTRUM            av-300
PROBHD   5 mm Dual 13C/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      7
DS                      0
SWH              6172.839 Hz
FIDRES           0.094190 Hz
AQ              5.3084660 sec
RG                      8
DW                 81.000 usec
DE                   6.00 usec
TE                  294.0 K
D1             0.20000000 sec
TD0                     4

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.00 usec
PL1                 -3.00 dB
PL1W          25.05936241 W
SFO1          300.1318533 MHz
SI                  32768
SF            300.1300026 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   4.00
```

18l proton



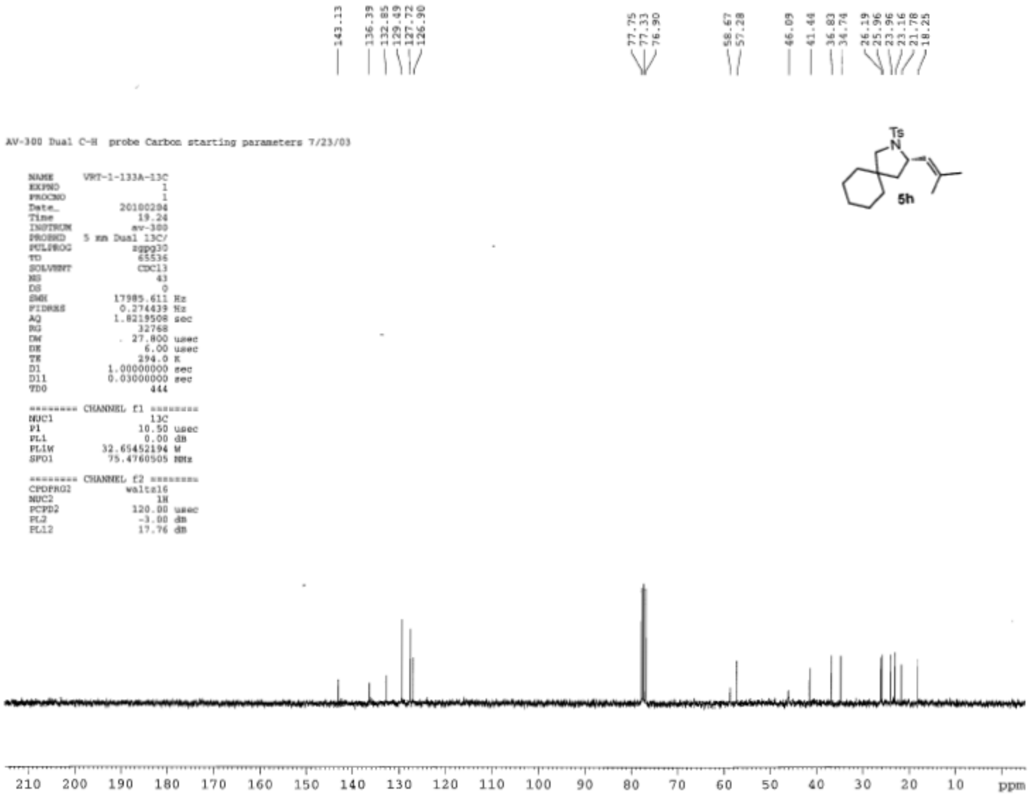
```
AV-300 Dual C-H  probe Carbon starting parameters 7/23/03

NAME      VRT-1-133B-13C
EXPNO                  1
PROCNO                 1
Date_           20100204
Time               19.30
INSTRUM           av-300
PROBHD   5 mm Dual 13C/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    44
DS                     0
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                 32768
DW                27.800 usec
DE                  6.00 usec
TE                 294.0 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                 4444

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.50 usec
PL1                 0.00 dB
PL1W         32.65452194 W
SFO1         75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             120.00 usec
PL2                -3.00 dB
PL12               17.76 dB
```

18l carbon



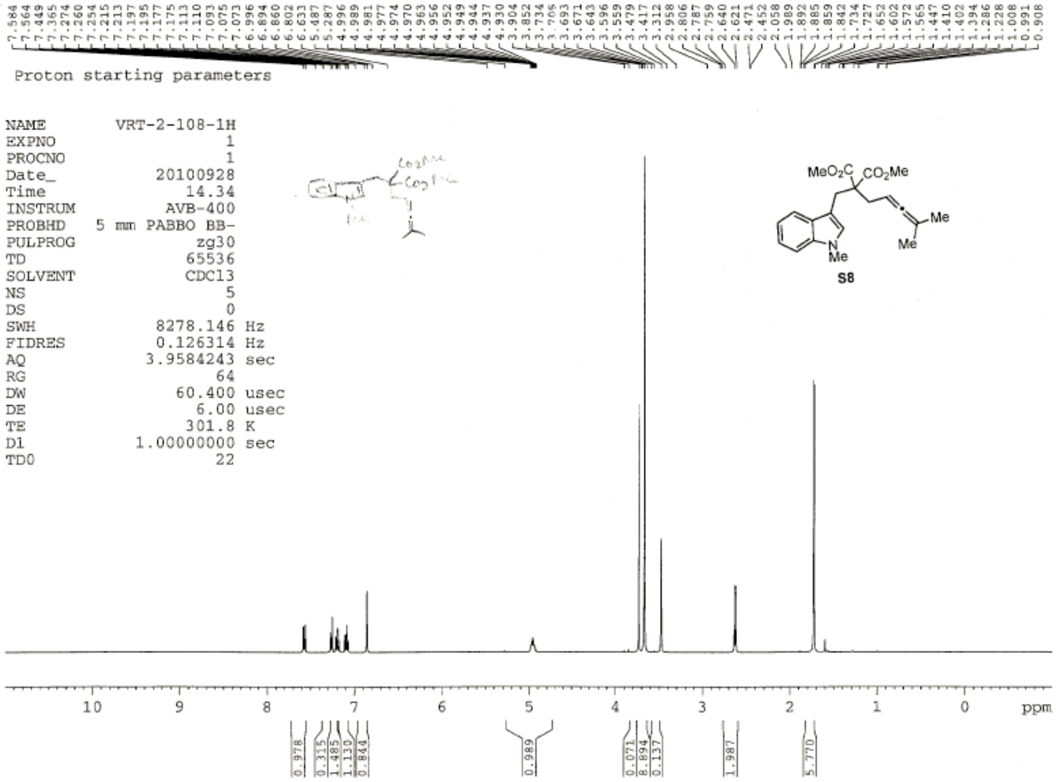
```
NAME           VRT-1-133A
EXPNO                   1
PROCNO                  1
Date_            20100204
Time                19.24
INSTRUM            av-300
PROBHD     5 mm Dual 13C/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      7
DS                      0
SWH              6172.839 Hz
FIDRES           0.094190 Hz
AQ              5.3084660 sec
RG                      8
DW                 81.000 usec
DE                   6.00 usec
TE                  293.9 K
D1             0.20000000 sec
TD0                     4

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.00 usec
PL1                 -3.00 dB
PL1W          25.05936241 W
SFO1          300.1318533 MHz
SI                  32768
SF            300.1300030 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   4.00
```

18m proton



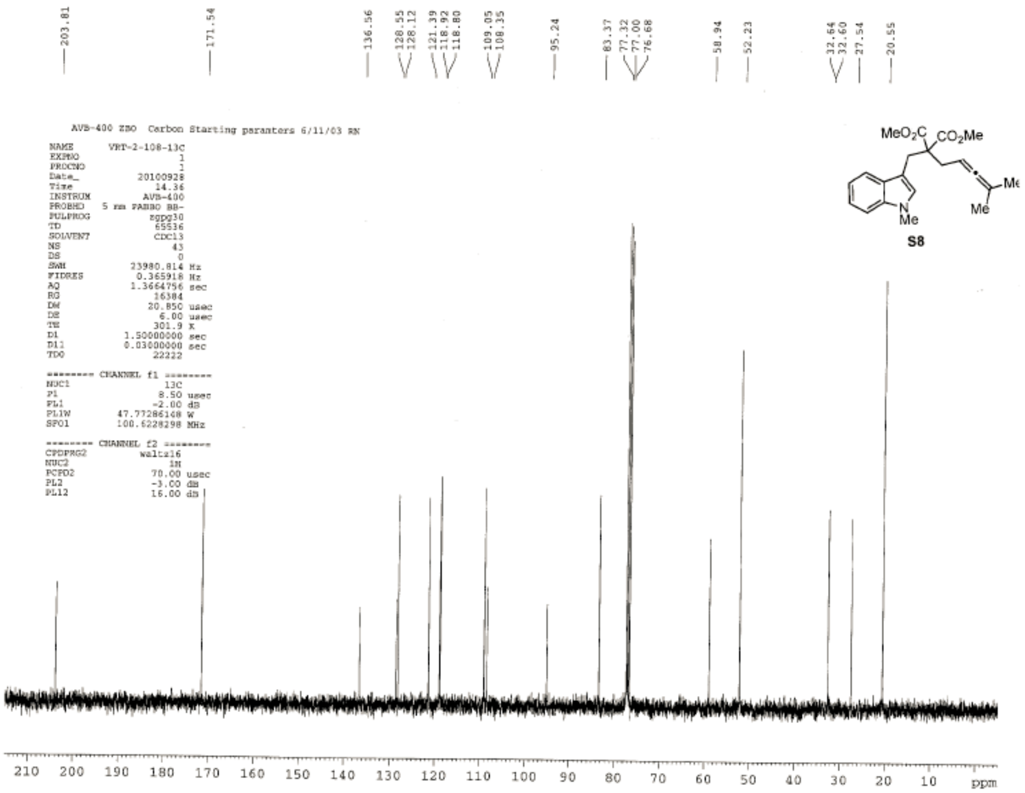
```
AV-300 Dual C-H  probe Carbon starting parameters 7/23/03

NAME       VRT-1-133A-13C
EXPNO                   1
PROCNO                  1
Date_            20100204
Time                19.24
INSTRUM            av-300
PROBHD     5 mm Dual 13C/
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     43
DS                      0
SWH             17985.611 Hz
FIDRES           0.274439 Hz
AQ              1.8219508 sec
RG                  32768
DW               . 27.800 usec
DE                   6.00 usec
TE                  294.0 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                   444

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.50 usec
PL1                  0.00 dB
PL1W          32.65452194 W
SFO1           75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              120.00 usec
PL2                 -3.00 dB
PL12                17.76 dB
```

18m carbon



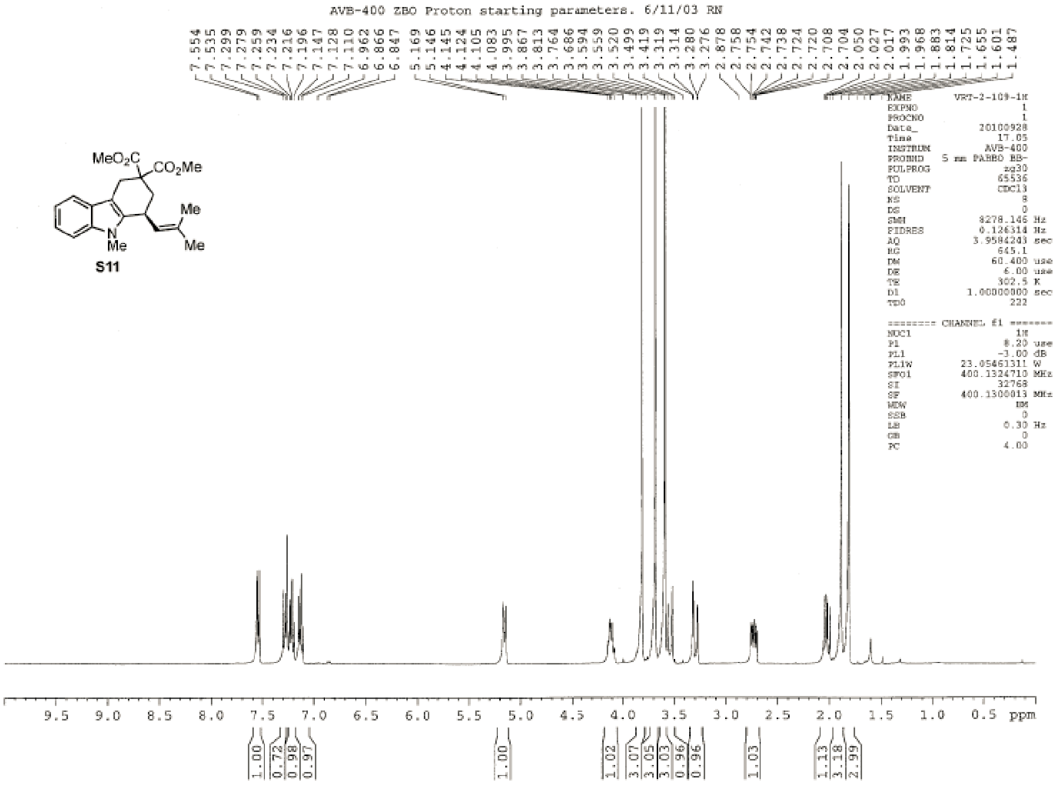
```
Proton starting parameters

NAME         VRT-2-108-1H
EXPNO                   1
PROCNO                  1
Date_            20100928
Time                14.34
INSTRUM           AVB-400
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      5
DS                      0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                     64
DW                 60.400 usec
DE                   6.00 usec
TE                  301.8 K
D1             1.00000000 sec
TD0                    22
```

19a proton

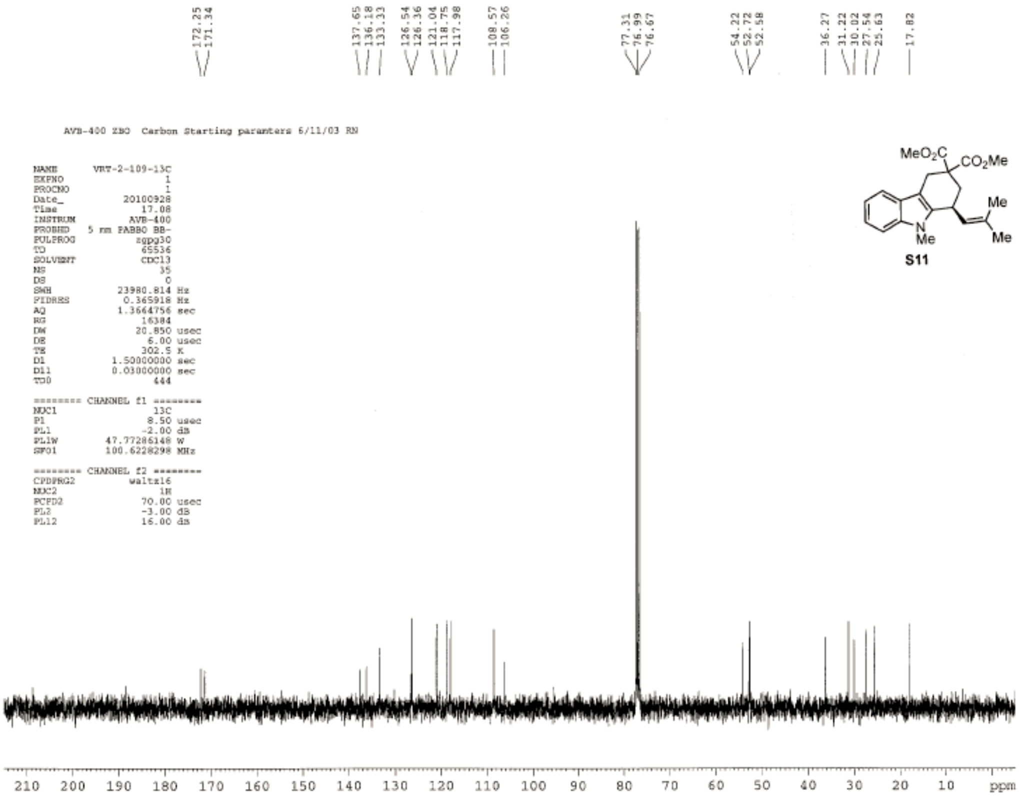


```
AVB-400 ZBO  Carbon Starting paranters 6/11/03 RN

NAME         VRT-2-108-13C
EXPNO                    1
PROCNO                   1
Date_             20100928
Time                 14.36
INSTRUM            AVB-400
PROBHD    5 mm PABBO BB-
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      43
DS                       0
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                   16384
DW                  20.850 usec
DE                    6.00 usec
TE                   301.9 K
D1              1.50000000 sec
D11             0.03000000 sec
TD0                  22222

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.50 usec
PL1                  -2.00 dB
PL1W           47.77286148 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                70.00 usec
PL2                  -3.00 dB
PL12                 16.00 dB
```

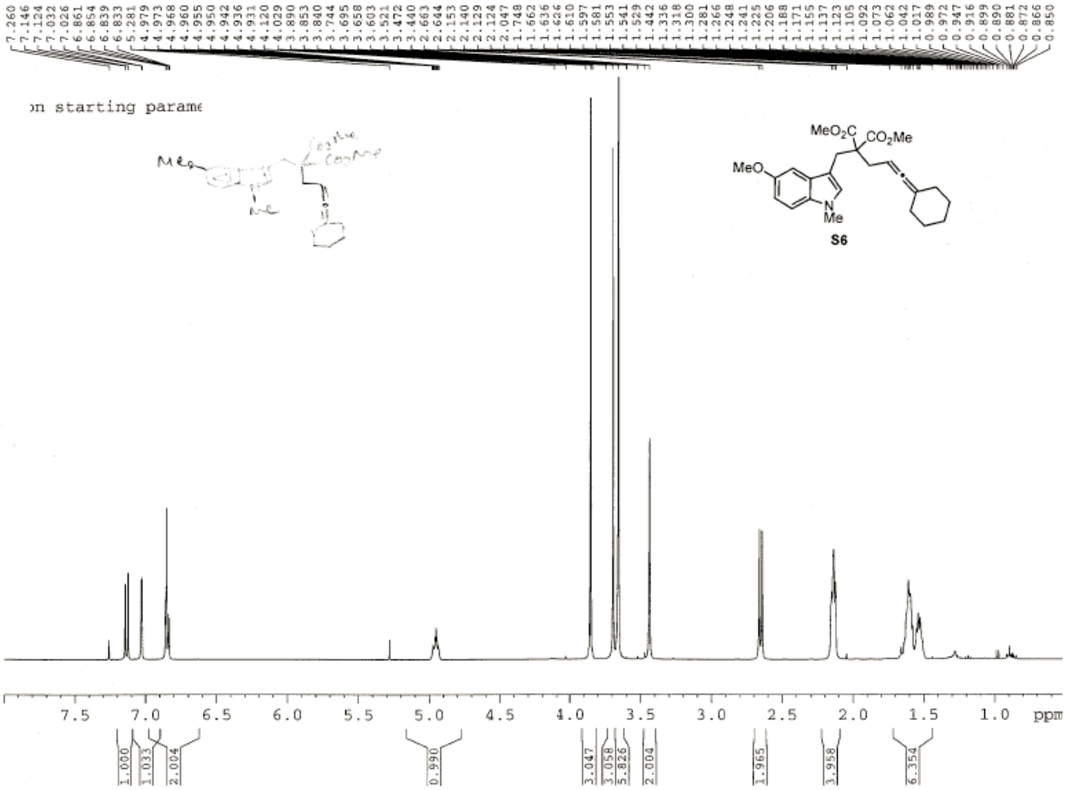
19a carbon



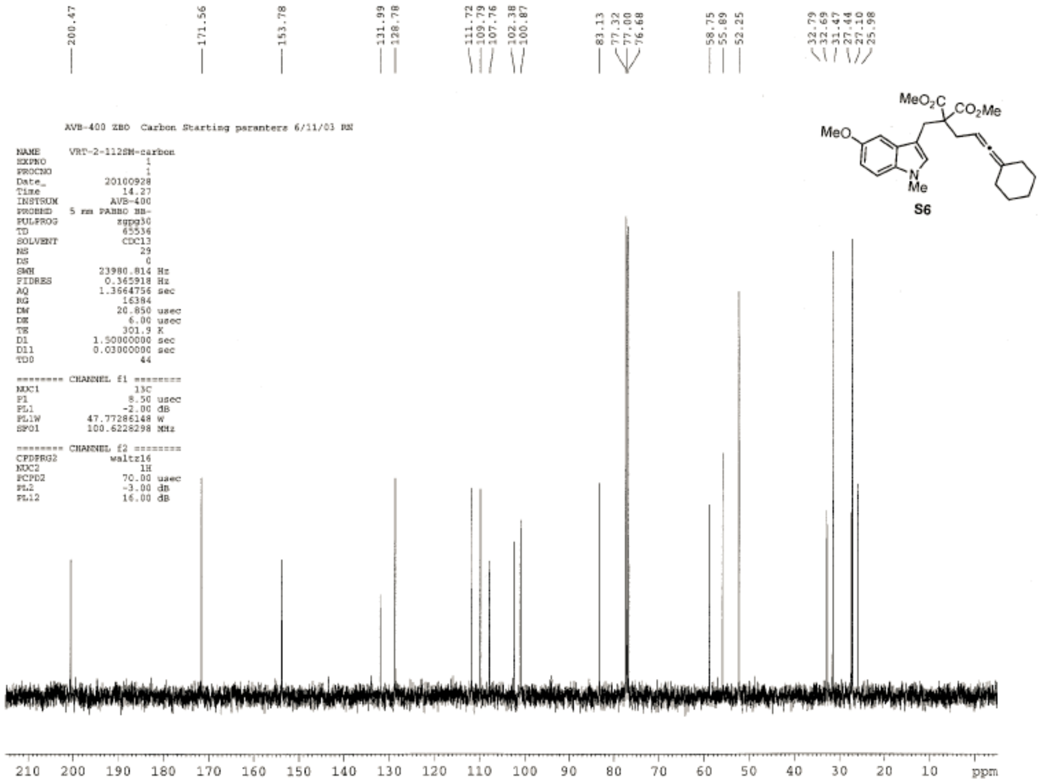
19b proton



19b carbon

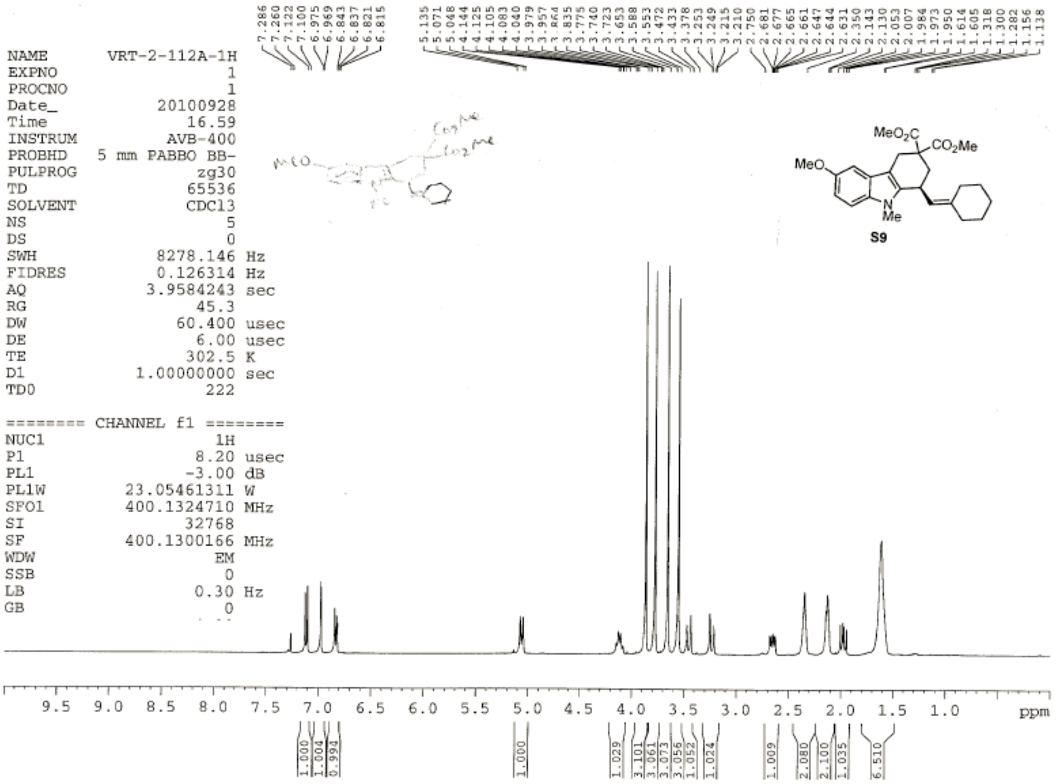


20a proton



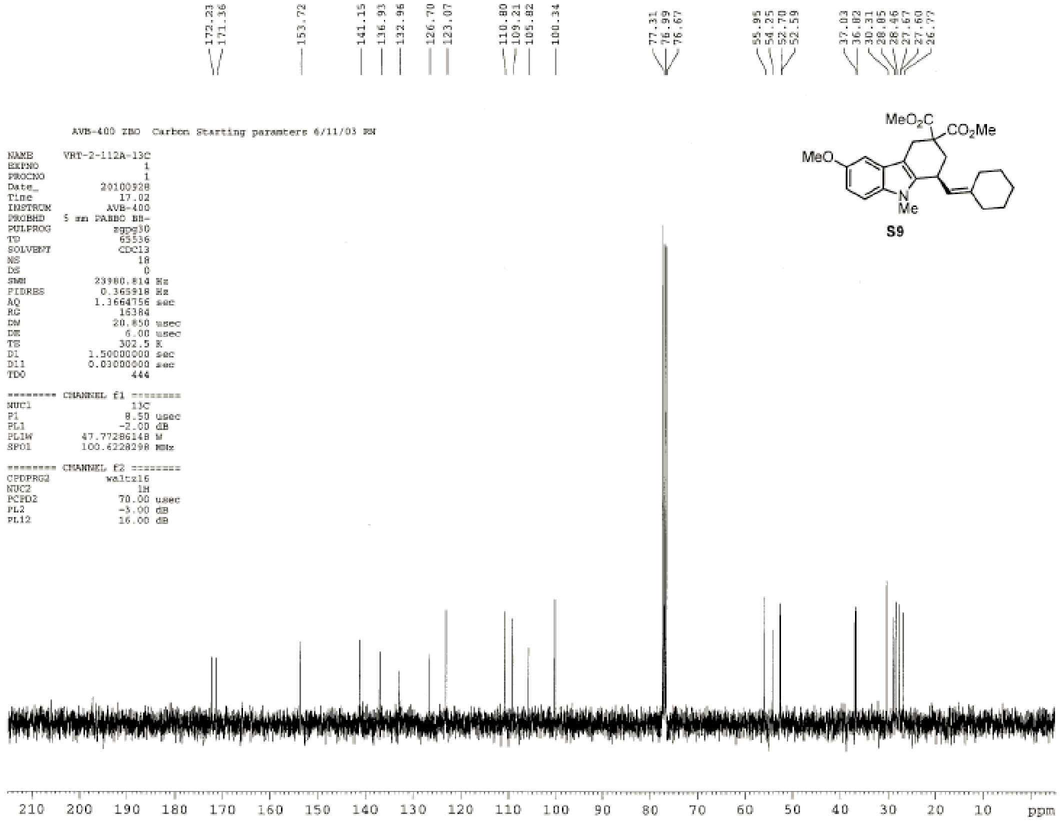
```
AVB-400 ZBO  Carbon Starting paranters 6/11/03 RN

NAME      VRT-2-112SM-carbon
EXPNO                    1
PROCNO                   1
Date_             20100928
Time                 14.27
INSTRUM            AVB-400
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      29
DS                       0
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                   16384
DW                  20.850 usec
DE                    6.00 usec
TE                   301.9 K
D1              1.50000000 sec
D11             0.03000000 sec
TD0                     44

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.50 usec
PL1                  -2.00 dB
PL1W           47.77286148 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                70.00 usec
PL2                  -3.00 dB
PL12                 16.00 dB
```

20a carbon



```
NAME         VRT-2-112A-1H
EXPNO                    1
PROCNO                   1
Date_             20100928
Time                 16.59
INSTRUM            AVB-400
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       5
DS                       0
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ               3.9584243 sec
RG                    45.3
DW                  60.400 usec
DE                    6.00 usec
TE                   302.5 K
D1              1.00000000 sec
TD0                    222

======== CHANNEL f1 ========
NUC1                    1H
P1                    8.20 usec
PL1                  -3.00 dB
PL1W           23.05461311 W
SFO1           400.1324710 MHz
SI                   32768
SF             400.1300166 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
```

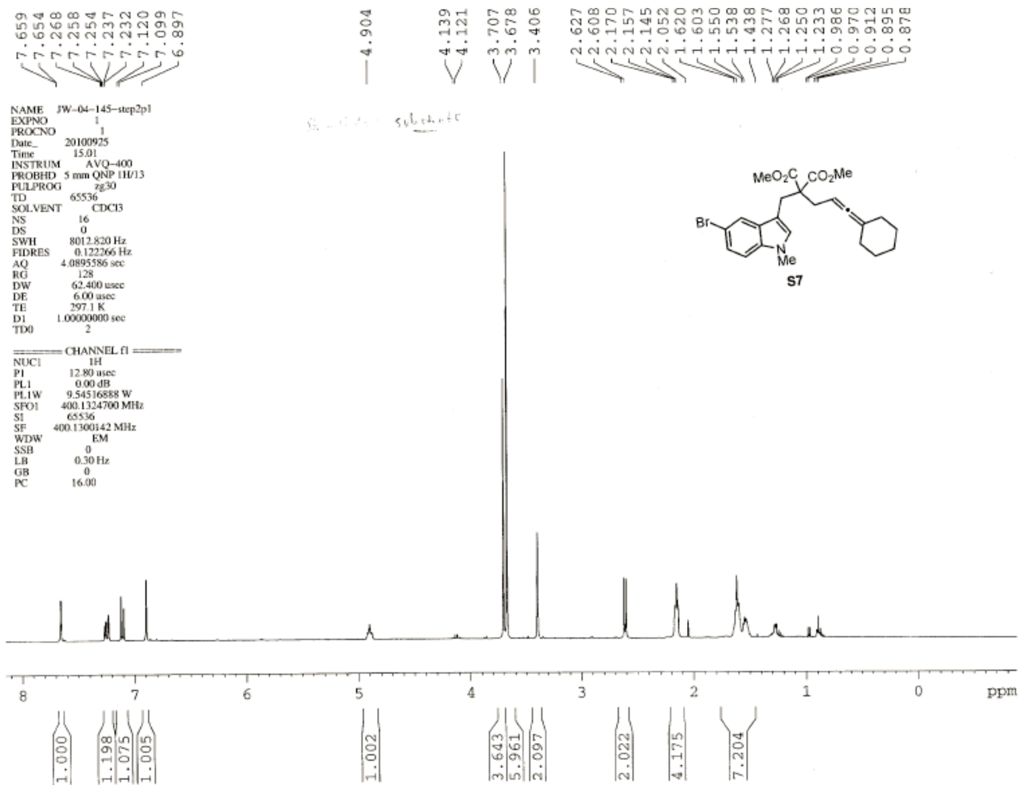
20b proton



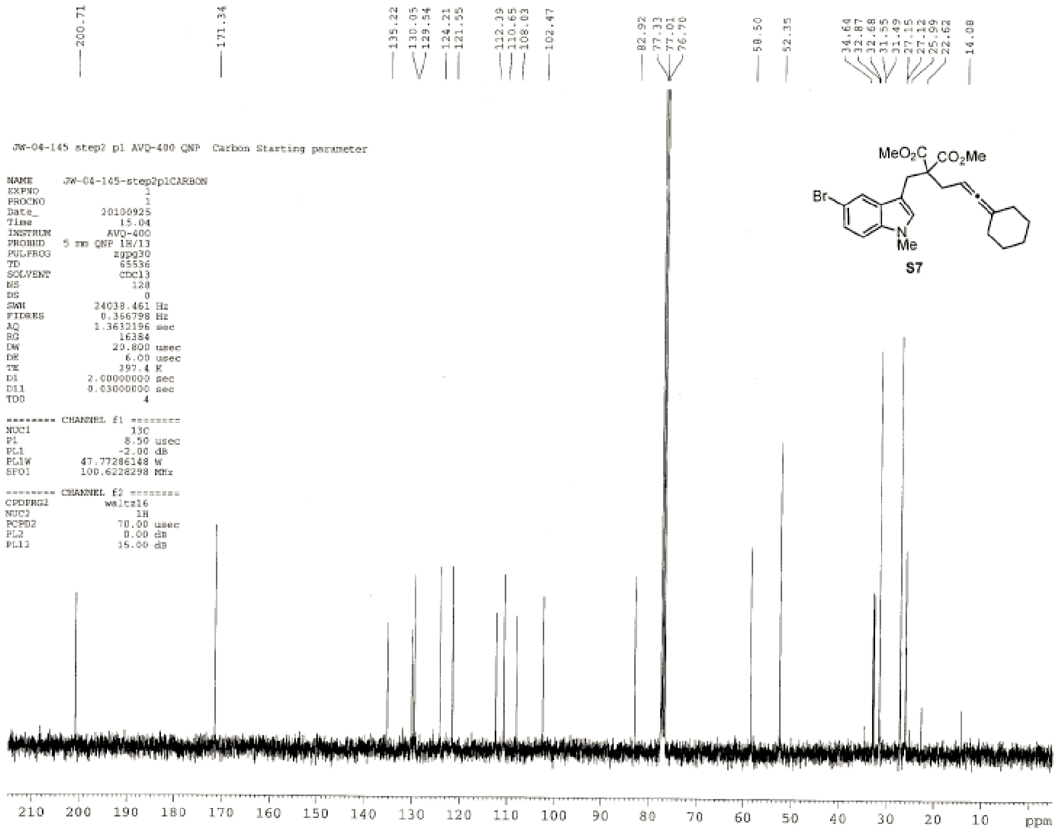
AVB-400 ZBO Carbon Starting paramters 6/11/03 RN

```
NAME      VRT-2-112A-13C
EXPNO                  1
PROCNO                 1
Date_           20100928
Time               17.02
INSTRUM          AVB-400
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    18
DS                     0
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                 16384
DW                20.850 usec
DE                  6.00 usec
TE                 302.5 K
D1            1.50000000 sec
D11           0.03000000 sec
TD0                  444

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.50 usec
PL1                -2.00 dB
PL1W         47.77286148 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              70.00 usec
PL2                -3.00 dB
PL12               16.00 dB
```

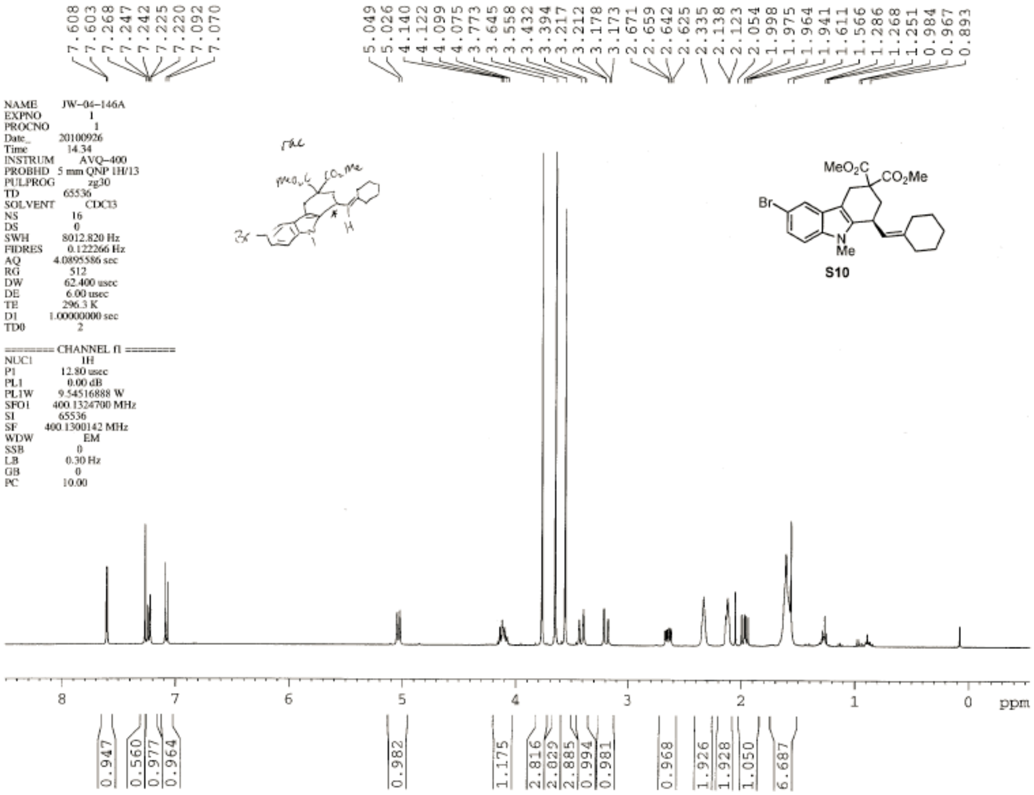
20b carbon



21a proton

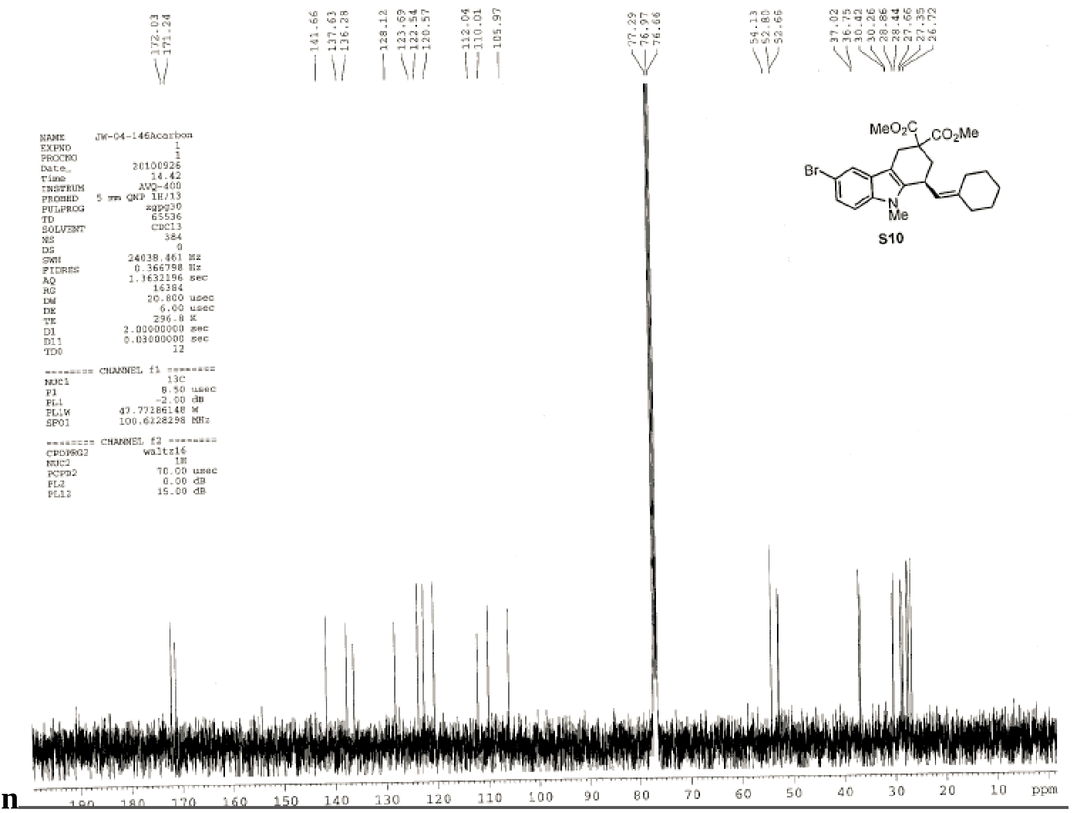


21a carbon



```
NAME      JW-04-146A
EXPNO           1
PROCNO          1
Date_     20100926
Time        14.34
INSTRUM      AVQ-400
PROBHD  5 mm QNP 1H/13
PULPROG        zg30
TD          65536
SOLVENT        CDCl3
NS             16
DS              0
SWH       8012.820 Hz
FIDRES    0.122266 Hz
AQ       4.0895586 sec
RG            512
DW         62.400 usec
DE           6.00 usec
TE          296.3 K
D1      1.00000000 sec
TD0             2

======== CHANNEL f1 ========
NUC1            1H
P1          12.80 usec
PL1          0.00 dB
PL1W     9.54516888 W
SFO1    400.1324700 MHz
SI          65536
SF     400.1300142 MHz
WDW             EM
SSB              0
LB         0.30 Hz
GB               0
PC           10.00
```

21b proton



```
NAME       JW-04-146Acarbon
EXPNO                     1
PROCNO                    1
Date_              20100926
Time                  14.42
INSTRUM             AVQ-400
PROBHD     5 mm QNP 1H/13
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      384
DS                        0
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3632196 sec
RG                    16384
DW                   20.800 usec
DE                     6.00 usec
TE                    296.8 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                      12

======== CHANNEL f1 ========
NUC1                    13C
P1                     8.50 usec
PL1                   -2.00 dB
PL1W            47.77286148 W
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 70.00 usec
PL2                    0.00 dB
PL12                  15.00 dB
```

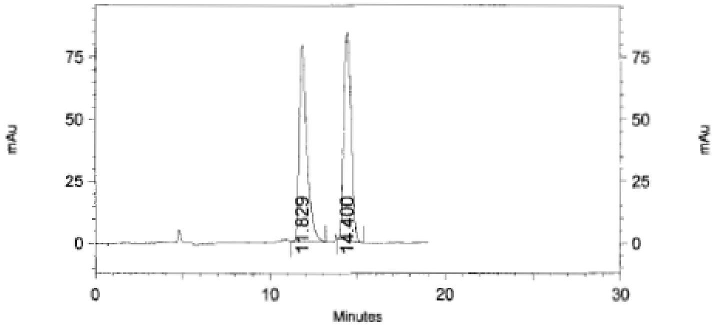
21b carbon

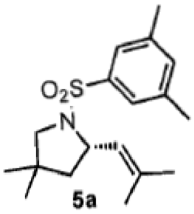
Copies of HPLC traces (racemic on top)

18a

```
        Sample ID:         VRT-1-152D-Rac
         Filename:
C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-152D_Rac-AS99505
-30min.met3-19-2010 4-15-43 PM.dat           Method:
C:\EZStart\Projects\Default\Method\Vivek\AS99505ET-30min.met
Injection volume:        1 uL
```

Description: {Data Description}



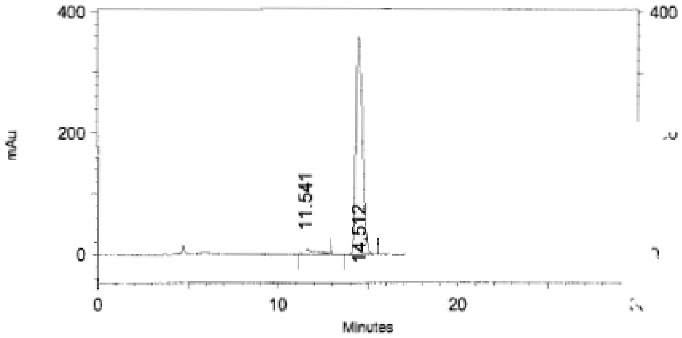


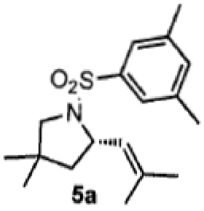
5a

```
1: 230 nm, 4 nm Results
               Retention Time          Area       Area Percent
                       11.829       2417646             49.976
                       14.400       2419995             50.024
```

```
       Sample ID:         VRT-1-152D
        Filename:
C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-152DAS99505-30mi
n.met3-19-2010 4-36-34 PM.dat          Method:
C:\EZStart\Projects\Default\Method\Vivek\AS99505ET-30min.met
Injection volume:        2 uL
```

Description: {Data Description}





5a

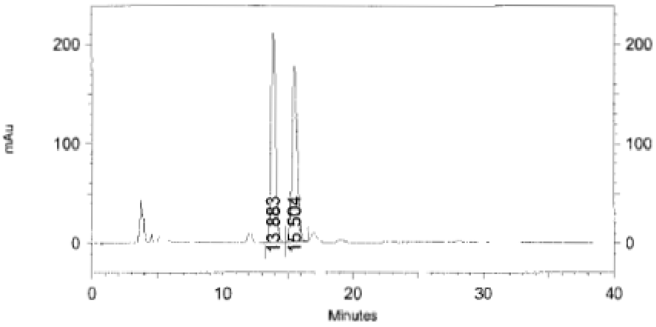
```
4: 220 nm, 4 nm Results
               Retention Time          Area       Area Percent
                       11.541        408348              4.370
                       14.512       8936979             95.630
```

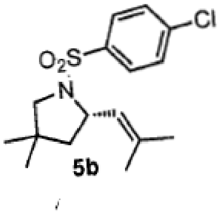
18b

```
      Sample ID:       JW-03-107D
       Filename:
C:\EZStart\Projects\Default\Data\JWu\JW-03-107D_AS9901ET_40min.met3-16-2010
12-34-05 AM.dat            Method:
C:\EZStart\Projects\Default\Method\Vivek\AS9901ET-40min.met
Injection volume:       5 uL
```

```
Description: {Data Description}
```

p-Cl

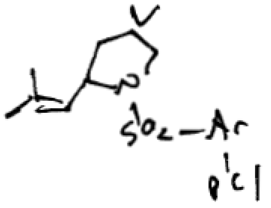


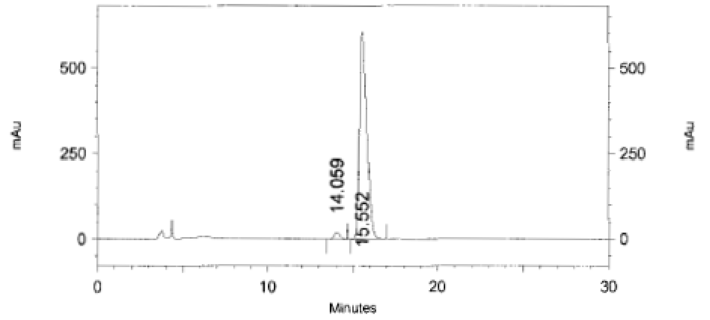


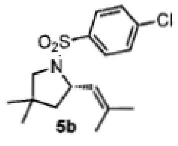
```
1: 210 nm, 4 nm Results
                Retention Time              Area        Area Percent
                        13.883           4987608              50.023
                        15.504           4982970              49.977
```

```
      Sample ID:       JW-03-107Dchiral
       Filename:
C:\EZStart\Projects\Default\Data\JWu\JW-03-107Dchiral_AS9901ET_30min.met3-16
-2010 1-19-42 PM.dat            Method:
C:\EZStart\Projects\Default\Method\Vivek\AS9901Et-30min.met
Injection volume:       5 uL
```

```
Description: {Data Description}
```





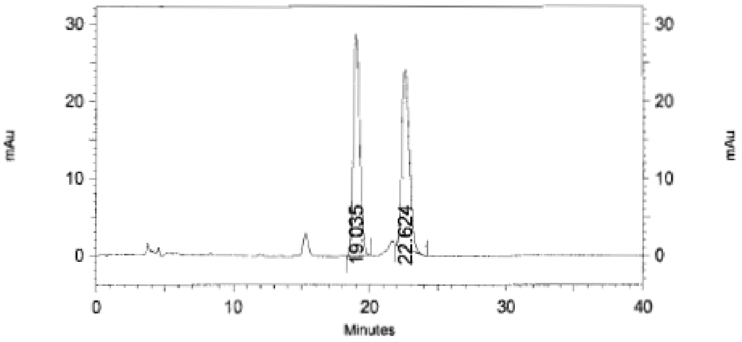


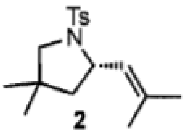
```
1: 210 nm, 4 nm Results
                Retention Time              Area        Area Percent
                        14.059            454706               2.420
                        15.552          18335038              97.580
```

18c

```
       Sample ID:        JW-03-107B
        Filename:
C:\EZStart\Projects\Default\Data\JWu\JW-03-107B_AS9901ET_40min.met3-15-2010
11-20-55 PM.dat           Method:
C:\EZStart\Projects\Default\Method\Vivek\AS9901ET-40min.met
Injection volume:       5 uL
```

Description: {Data Description}





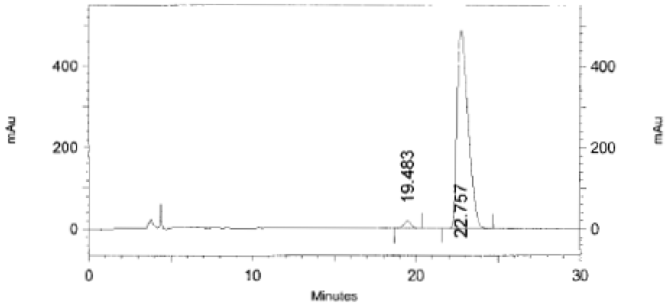
2: 254 nm, 4 nm Results

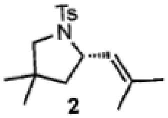
Retention Time	Area	Area Percent
19.035	948215	51.478
22.624	893783	48.522

check w/ Jeff

```
       Sample ID:        JW-03-107Bchiral
        Filename:
C:\EZStart\Projects\Default\Data\JWu\JW-03-107Bchiral_AS9901ET_30min.met3-16
-2010 12-16-41 PM.dat           Method:
C:\EZStart\Projects\Default\Method\Vivek\AS9901Et-30min.met
Injection volume:       5 uL
```

Description: {Data Description}

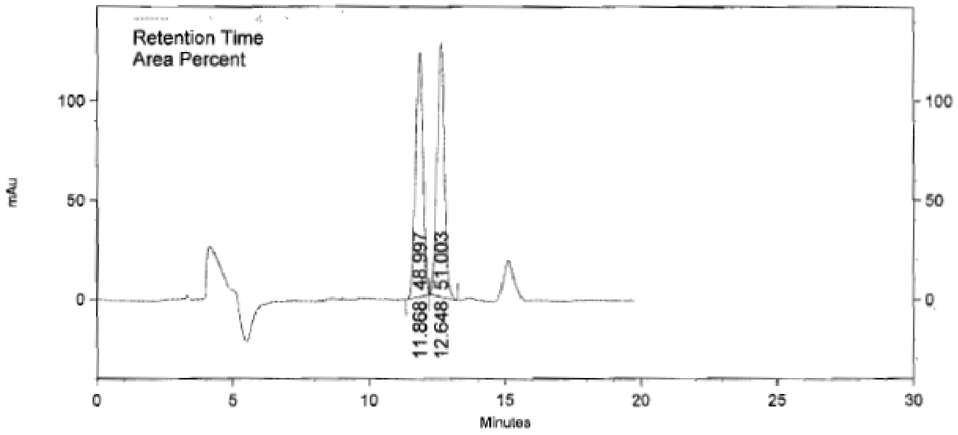


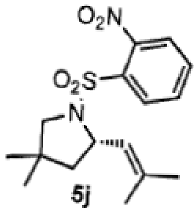


1: 210 nm, 4 nm Results

Retention Time	Area	Area Percent
19.483	591399	2.547
22.757	22628378	97.453

18d

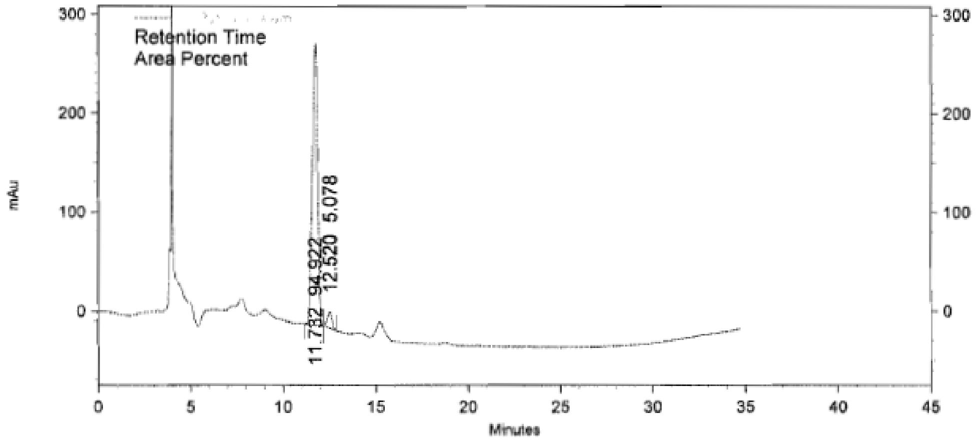


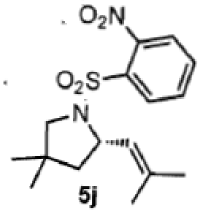


5j

```
3: 280 nm, 4 nm
Results
                     Pk #      Retention Time        Area Percent         Lambda Max
                        1              11.868              48.997                200
                        2              12.648              51.003                201
```

```
C:\EZStart\Projects\Default\Data\glh\VRT-152G_IA995005Et_50min.met3-18-2010
10-51-12 PM.dat
```



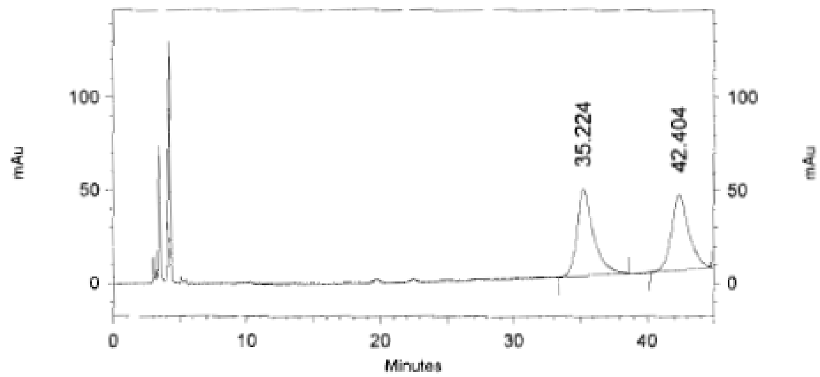


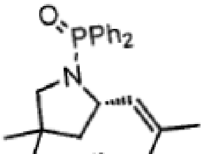
5j

```
1: 255 nm, 4 nm
Results
                     Pk #      Retention Time        Area Percent         Lambda Max
                        1              11.732              94.922                202
                        2              12.520               5.078                205
```

18e

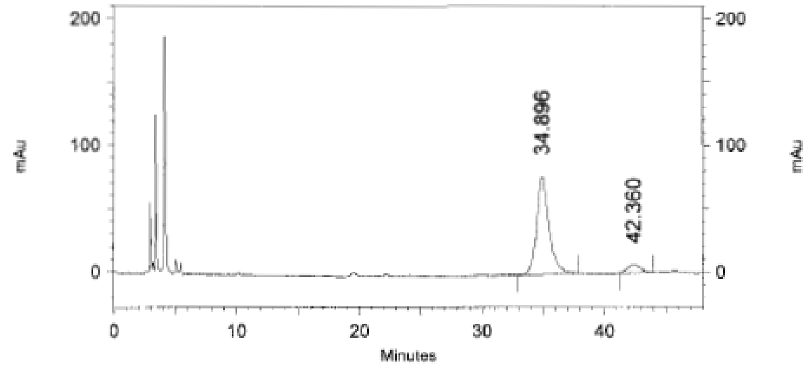
```
 JW-03-107C
C:\EZStart\Projects\Default\Method\wataru\IC 100%D 1ml min 60min.met
 3/17/2010 9:07:14 AM
C:\EZStart\Projects\Default\Data\Jeff\JW-03-107C_IA9802IP_45min3-16-2010
4-38-51 PM.dat
```

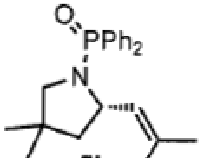




5k

```
 1: 195 nm, 4
 nm Results
  Retention Time            Area   Area Percent    Lambda Max
            35.224       4058715         52.359           206
            42.404       3692945         47.641           205
 JW-03-107Cchiral
C:\EZStart\Projects\Default\Method\wataru\IC 100%D 1ml min 60min.met
 3/17/2010 2:59:32 PM
C:\EZStart\Projects\Default\Data\Jeff\JW-03-107Cchiral.dat
```





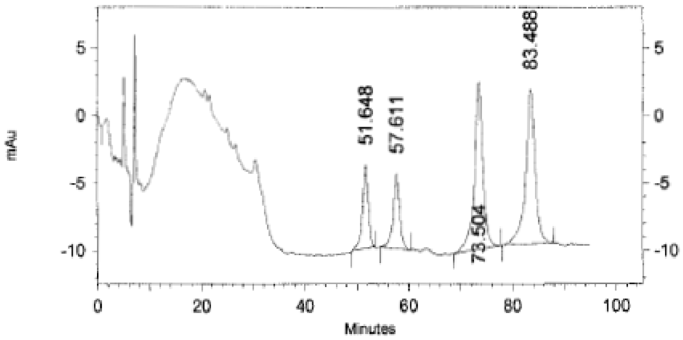
5k

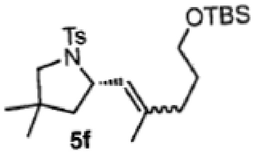
```
 1: 195 nm, 4
 nm Results
  Retention Time            Area   Area Percent    Lambda Max
            34.896       5426707         91.713           206
            42.360        490326          8.287           205
```

18f

```
       Sample ID:        VRT-1-133C-Racemic
        Filename:
C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-133C-RacemicWH97
03ET-90min.met3-20-2010 3-50-04 PM.dat           Method:
C:\EZStart\Projects\Default\Method\Vivek\WH9703ET-90min.met
Injection volume:        1 uL
```

Description: {Data Description}





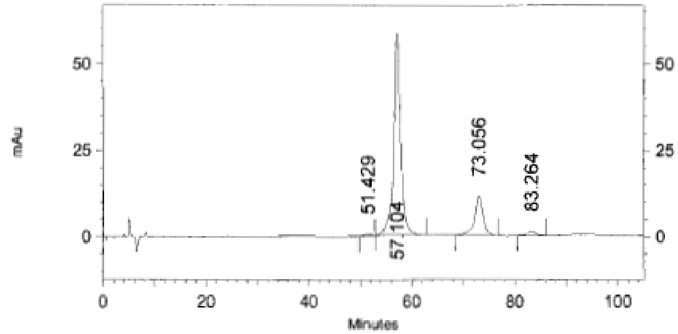
5f

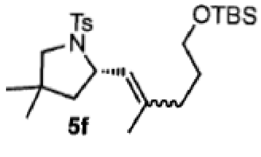
1: 230 nm, 4 nm Results

Retention Time	Area	Area Percent
51.648	475163	12.333
57.611	487115	12.644
73.504	1420619	36.874
83.488	1469762	38.149

```
       Sample ID:        VRT-1-152F
        Filename:
C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-152FWH9703ET-90m
in.met3-20-2010 5-26-36 PM.dat          Method:
C:\EZStart\Projects\Default\Method\Vivek\WH9703ET-90min.met
Injection volume:        1 uL
```

Description: {Data Description}





5f

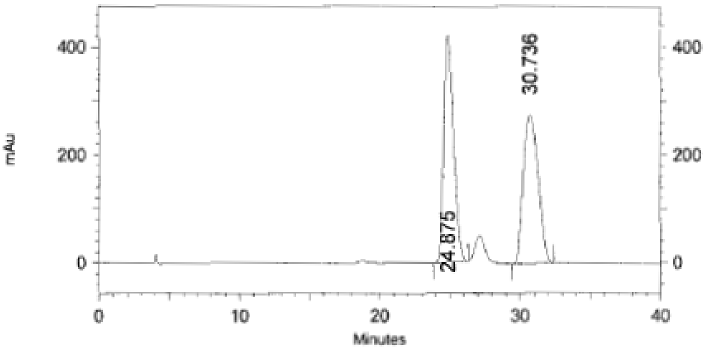
1: 230 nm, 4 nm Results

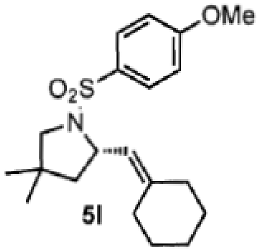
Retention Time	Area	Area Percent
51.429	35226	0.505
57.104	5525286	79.170
73.056	1279889	18.339
83.264	138592	1.986

18g

```
       Sample ID:        VRT-1-154C-Racemic
        Filename:
C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-154C-RacemicAS98
02-40min.met3-19-2010 1-35-31 PM.dat          Method:
C:\EZStart\Projects\Default\Method\Vivek\AS9802-40min.met
Injection volume:        2 uL
```

Description: {Data Description}



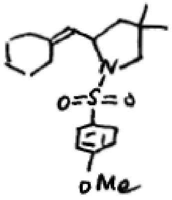


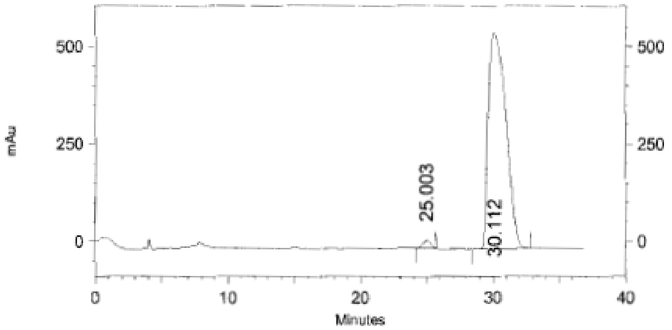
5l

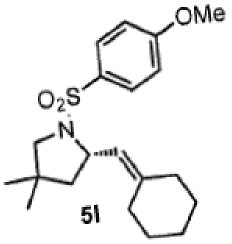
```
  1: 230 nm, 4 nm Results
                    Retention Time              Area        Area Percent
                            24.875          20418087              50.126
                            30.736          20315717              49.874
```

```
       Sample ID:        VRT-1-154C
        Filename:
C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-154C-AS9802-40mi
n.met3-19-2010 2-17-34 PM.dat          Method:
C:\EZStart\Projects\Default\Method\Vivek\AS9802-40min.met
Injection volume:        2 uL
```

Description: {Data Description}







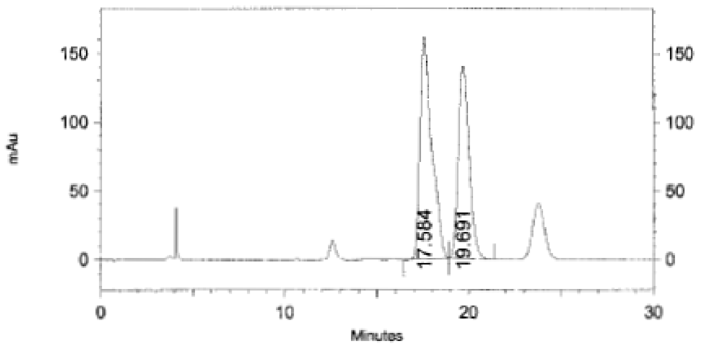
5l

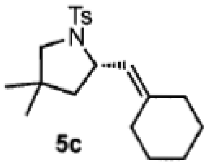
```
  1: 230 nm, 4 nm Results
                    Retention Time              Area        Area Percent
                            25.003            759114               1.467
                            30.112          50996378              98.533
```

18h

```
      Sample ID:        VRT-1-139-7-rac
        Filename:
C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-139-7-racAS9901E
t-30min.met2-15-2010 7-40-36 PM.dat          Method:
C:\EZStart\Projects\Default\Method\Vivek\AS9901Et-30min.met
Injection volume:       5 uL
```

Description: {Data Description}





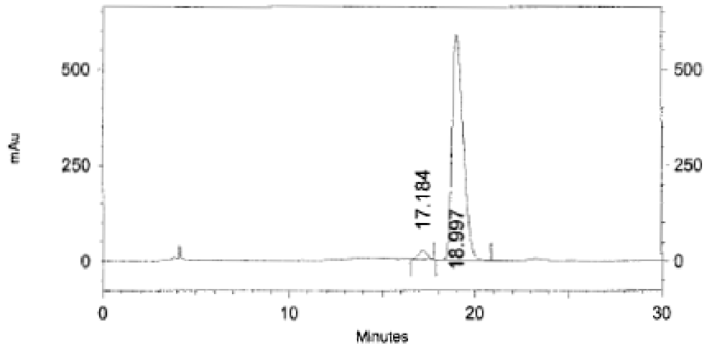
5c

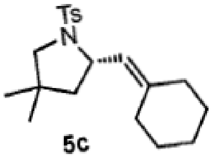
1: 230 nm, 4 nm Results

Retention Time	Area	Area Percent
17.584	7213123	55.650
19.691	5748433	44.350

```
      Sample ID:        VRT-1-139-7
        Filename:
C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-139-7AS9901Et-30
min.met2-15-2010 8-12-29 PM.dat          Method:
C:\EZStart\Projects\Default\Method\Vivek\AS9901Et-30min.met
Injection volume:       5 uL
```

Description: {Data Description}





5c

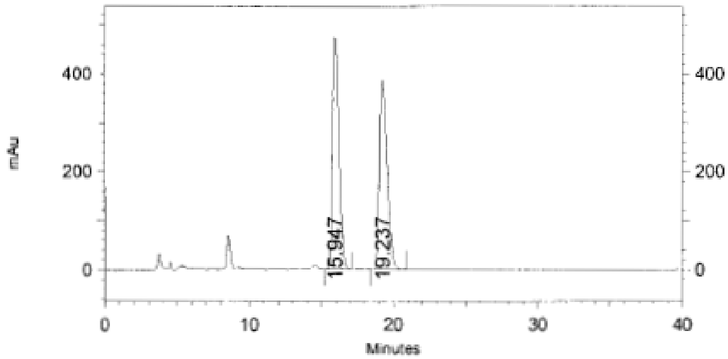
1: 230 nm, 4 nm Results

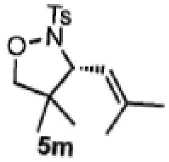
Retention Time	Area	Area Percent
17.184	724444	2.884
18.997	24397158	97.116

18i

```
      Sample ID:       JW-03-108C
       Filename:
C:\EZStart\Projects\Default\Data\JWu\JW-03-108c_AS9901ET_40min.met3-16-2010
10-23-08 PM.dat          Method:
C:\EZStart\Projects\Default\Method\Vivek\AS9901ET-40min.met
Injection volume:       5 uL
```

```
Description: {Data Description}
```

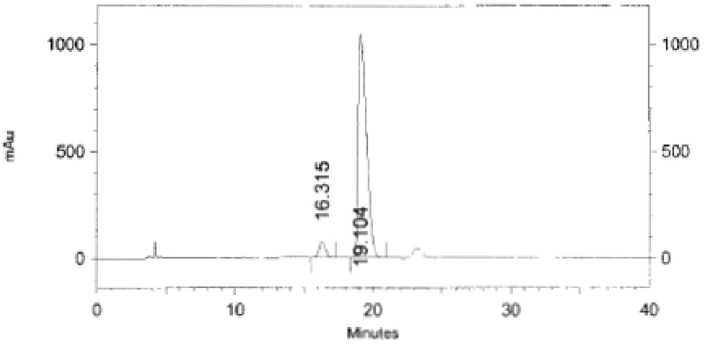


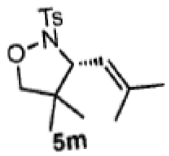


```
1: 210 nm, 4 nm Results
                 Retention Time            Area      Area Percent
                         15.947        14518430            50.435
                         19.237        14268032            49.565
```

```
      Sample ID:       JW-03-108Cchiral
       Filename:
C:\EZStart\Projects\Default\Data\JWu\JW-03-108cChiral_AS9901ET_40min.met3-16
-2010 11-36-11 PM.dat          Method:
C:\EZStart\Projects\Default\Method\Vivek\AS9901ET-40min.met
Injection volume:       5 uL
```

```
Description: {Data Description}
```



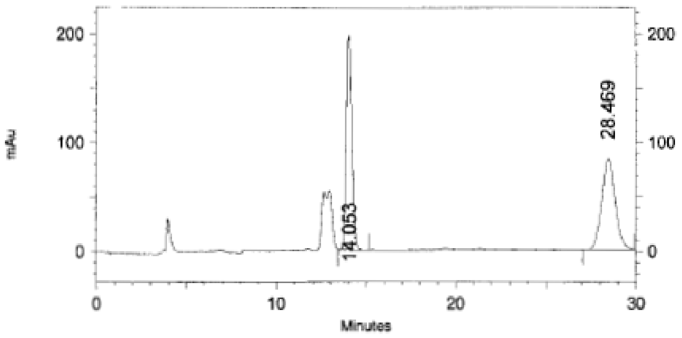


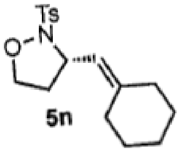
```
1: 210 nm, 4 nm Results
                 Retention Time            Area      Area Percent
                         16.315         2249590             4.827
                         19.104        44353893            95.173
```

18j

```
        Sample ID:        VRT-1-145B-Rac
         Filename:
C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-145B-RacAS9802-3
0min.met2-25-2010 2-55-10 PM.dat           Method:
C:\EZStart\Projects\Default\Method\Vivek\AS9802-30min.met
Injection volume:        5 uL
```

Description: {Data Description}

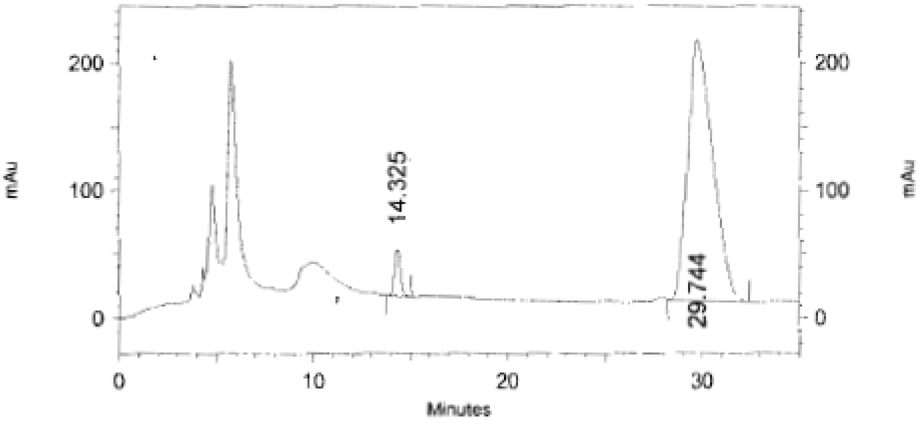




5n

4: 210 nm, 4 nm Results

Retention Time	Area	Area Percent
14.053	4325748	50.024
28.469	4321597	49.976



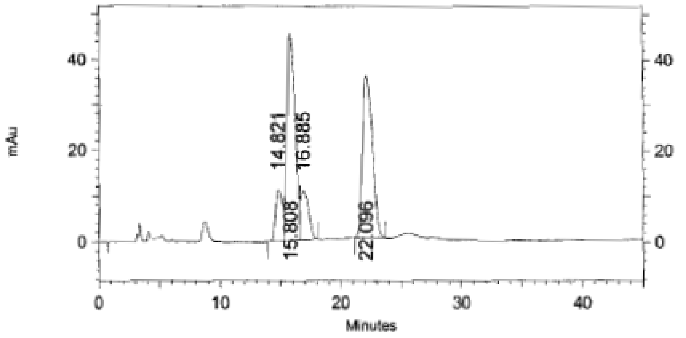
2: 220 nm, 4 nm Results

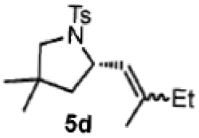
Retention Time	Area	Area Percent
14.325	760475	4.006
29.744	18222910	95.994

18k

```
        Sample ID:          15-174A
         Filename:
C:\EZStart\Projects\Default\Data\Nathan\ns15-174A-12-19-2009 1-19-37
PM-AD995005ET.met.dat           Method:
C:\EZStart\Projects\Default\Method\Nathan\AD995005ET 45min.met
Injection volume:        4 uL
```

Description: {Data Description}





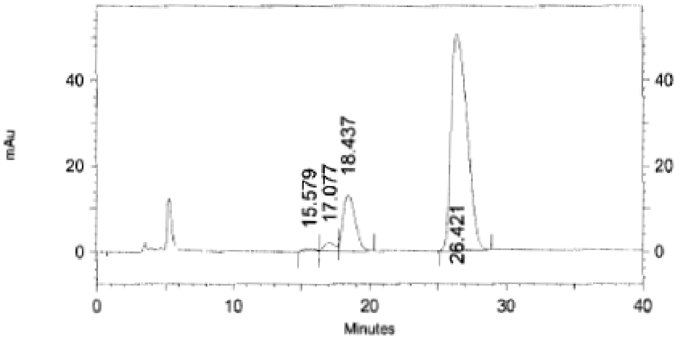
5d

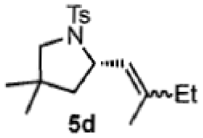
1: 230 nm, 4 nm Results

Retention Time	Area	Area Percent
14.821	443995	8.802
15.808	2067084	40.980
16.885	494466	9.803
22.096	2038556	40.415

```
        Sample ID:          VRT-1-137E
         Filename:
C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-137EVRT-1-136D.m
et2-11-2010 7-29-21 AM.dat           Method:
C:\EZStart\Projects\Default\Method\Vivek\VRt-1-136D.met
Injection volume:        2 uL
```

Description: {Data Description}





5d

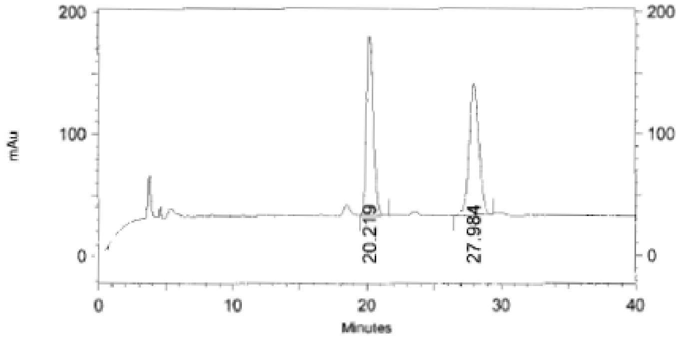
1: 230 nm, 4 nm Results

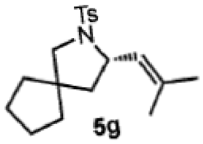
Retention Time	Area	Area Percent
15.579	39375	0.781
17.077	107920	2.139
18.437	803826	15.935
26.421	4093302	81.145

18l

```
        Sample ID:        JW-03-108A
          Filename:
C:\EZStart\Projects\Default\Data\JWu\JW-03-108A_AS9901ET_40min.met3-16-2010
7-57-01 PM.dat           Method:
C:\EZStart\Projects\Default\Method\Vivek\AS9901ET-40min.met
Injection volume:        5 uL
```

```
Description: {Data Description}
```



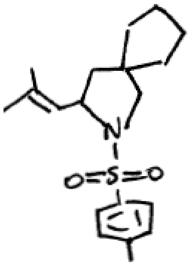


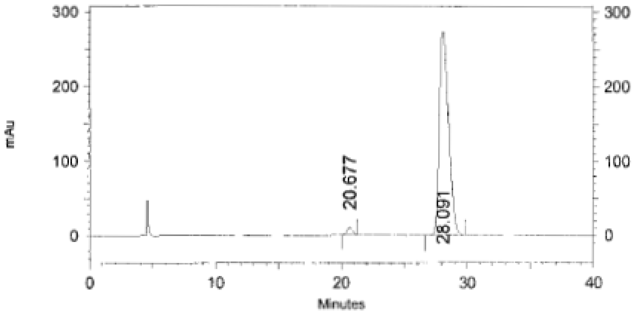
5g

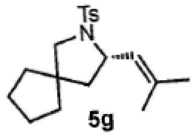
```
     1: 210 nm, 4 nm Results
                    Retention Time          Area          Area Percent
                         20.219           5234845               48.972
                         27.984           5454555               51.028
```

```
        Sample ID:        VRT-1-152B
          Filename:
C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-152BAS9901ET-40m
in.met3-10-2010 10-10-04 PM.dat           Method:
C:\EZStart\Projects\Default\Method\Vivek\AS9901ET-40min.met
Injection volume:        5 uL
```

```
Description: {Data Description}
```







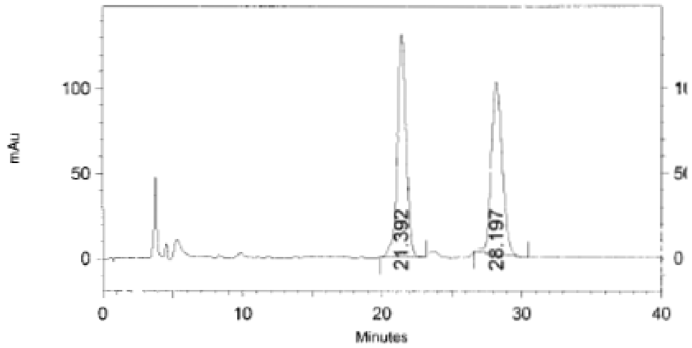
5g

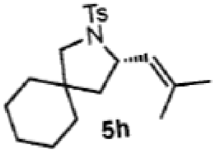
```
     1: 230 nm, 4 nm Results
                    Retention Time          Area          Area Percent
                         20.677            314407                2.202
                         28.091          13964418               97.798
```

18m

Sample ID: **JW-03-108B**
Filename:
C:\EZStart\Projects\Default\Data\JWu\JW-03-107B_AS9901ET_40min.met3-16-2010 9-10-05 PM.dat
Method:
C:\EZStart\Projects\Default\Method\Vivek\AS9901ET-40min.met
Injection volume: 5 uL

Description: {Data Description}





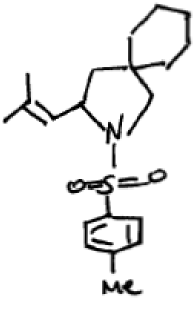
5h

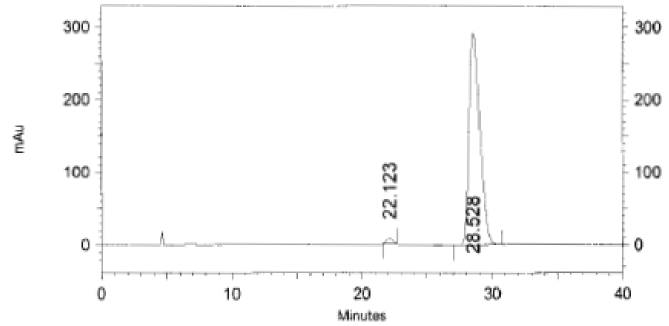
1: 210 nm, 4 nm Results

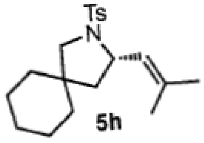
Retention Time	Area	Area Percent
21.392	5735548	50.661
28.197	5585924	49.339

Sample ID: **VRT-1-152A**
Filename:
C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-152AAS9901ET-40min.met3-10-2010 9-28-10 PM.dat
Method:
C:\EZStart\Projects\Default\Method\Vivek\AS9901ET-40min.met
Injection volume: 5 uL

Description: {Data Description}







5h

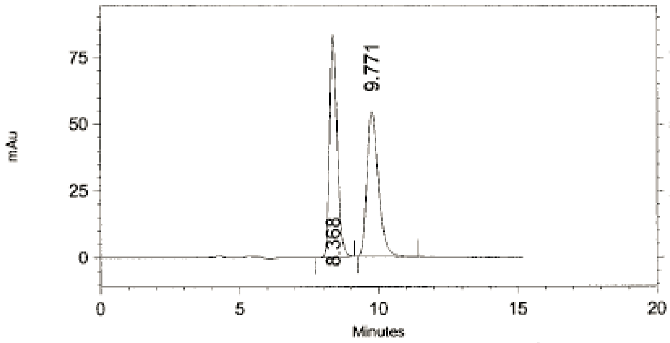
6: 240 nm, 4 nm Results

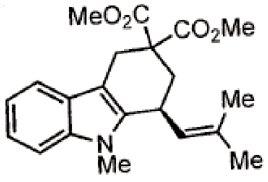
Retention Time	Area	Area Percent
22.123	250463	1.455
28.528	16963043	98.545

19b

```
        Sample ID:        VRT-2-109-Rac
         Filename:
C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-2-109-Rac-AS9901IP
.met9-24-2010 10-40-59 AM.dat           Method:
C:\EZStart\Projects\Default\Method\AS\AS9901IP.met
Injection volume:        1 uL
```

```
Description: {Data Description}
```

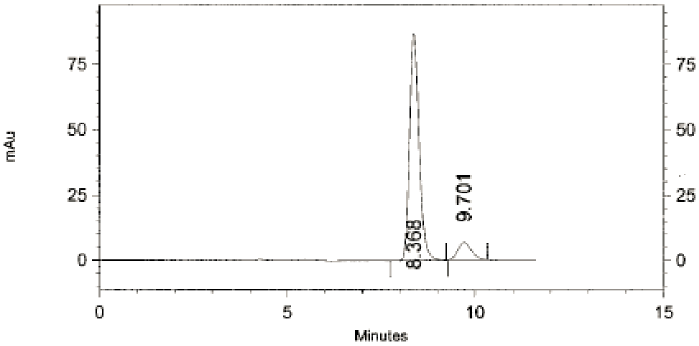


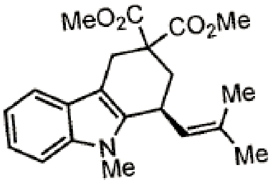


S11

```
3: 277 nm, 4 nm Results
                     Retention Time           Area          Area Percent
                              8.368        1580236                50.323
                              9.771        1559957                49.677
```

```
        Sample ID:        VRT-2-109
         Filename:
C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-2-109-AS9901IP.met
9-24-2010 10-27-39 AM.dat           Method:
C:\EZStart\Projects\Default\Method\AS\AS9901IP.met
Injection volume:        1 uL
```

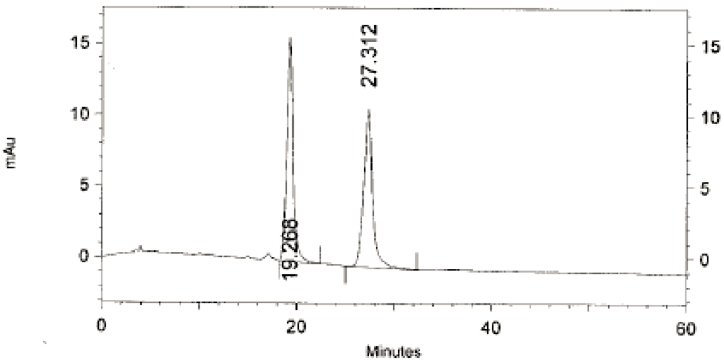


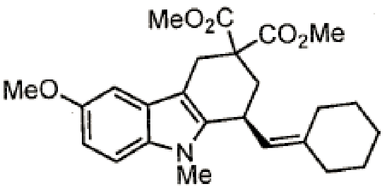


S11

```
3: 277 nm, 4 nm Results
                     Retention Time           Area          Area Percent
                              8.368        1534917                90.022
                              9.701         170135                 9.978
```

20b

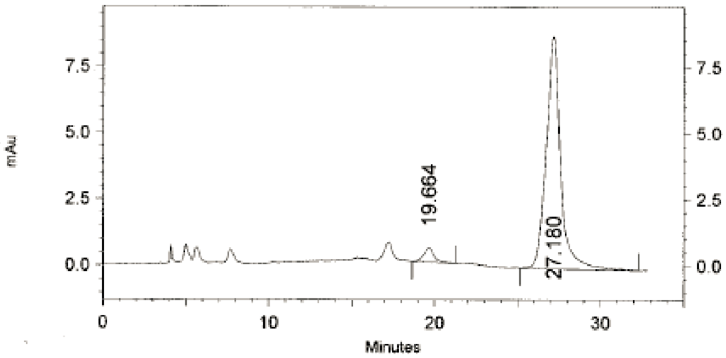




S9

3: 309 nm, 4
nm Results

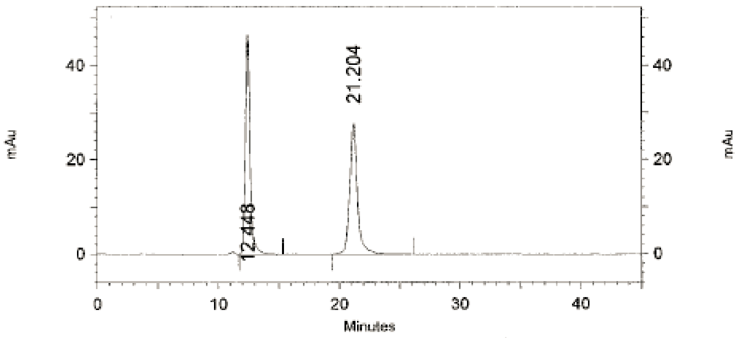
Retention Time	Area	Area Percent	Lambda Max
19.268	695041	49.344	206
27.312	713517	50.656	230

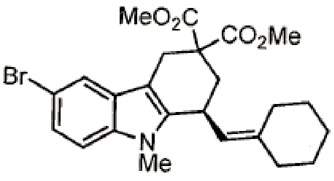


3: 309 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
19.664	24025	4.328	205
27.180	531135	95.672	205

21b

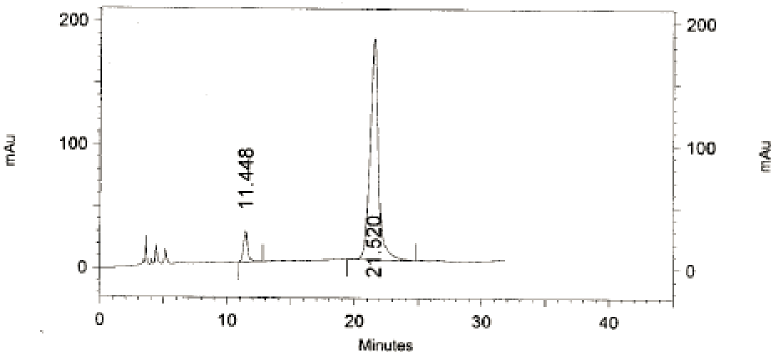


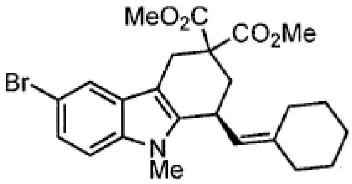


S10

2: 300 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
12.448	1221545	49.602	234
21.204	1241156	50.398	234





S10

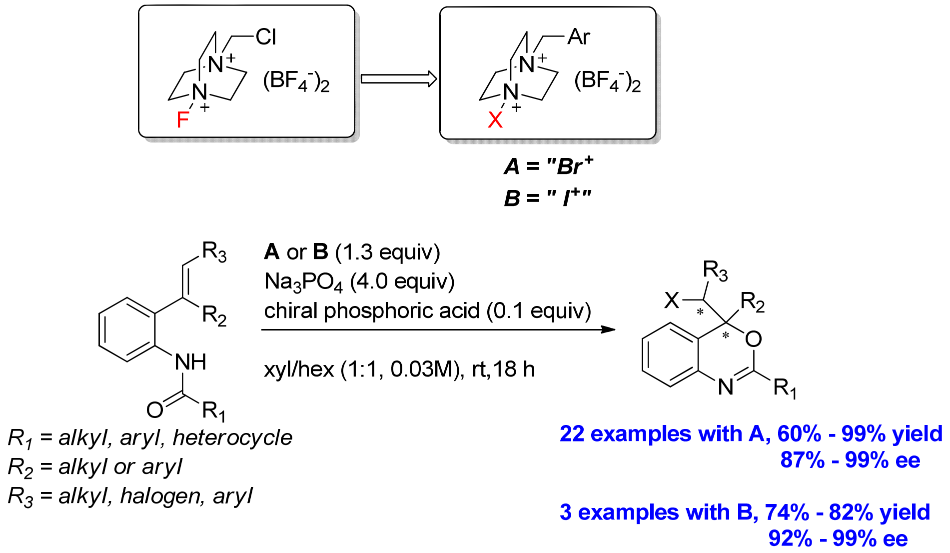
4: 207 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
11.448	573334	6.490	235
21.520	8260898	93.510	235

CHAPTER 3: NEW HALOGENATION REAGENTS DESIGNED FOR CHIRAL ANION PHASE-TRANSFER CATALYSIS: HALOCYCLIZATION

Abstract

New electrophilic halogenation reagents have been designed specifically for use in chiral anion phase-transfer catalysis. The key characteristics of these reagents include low solubility in nonpolar organic solvents, the ability to undergo ion-exchange with chiral phosphates, and bench stability. These ionic reagents include both brominating and iodinating reagents and were shown to react with various alkenes to generate benzoxazines with high enantioselectivity. The amide nucleophile tethered to the arene core is essential for interactions with the chiral ion pair which is generated in-situ by the phase-transfer process. Very wide substrate scope was demonstrated with a variety of alkene substitution patterns. An impressive demonstration of low catalyst loading (0.1 mol%) is also presented, which is generally unseen in organocatalytic reactions.

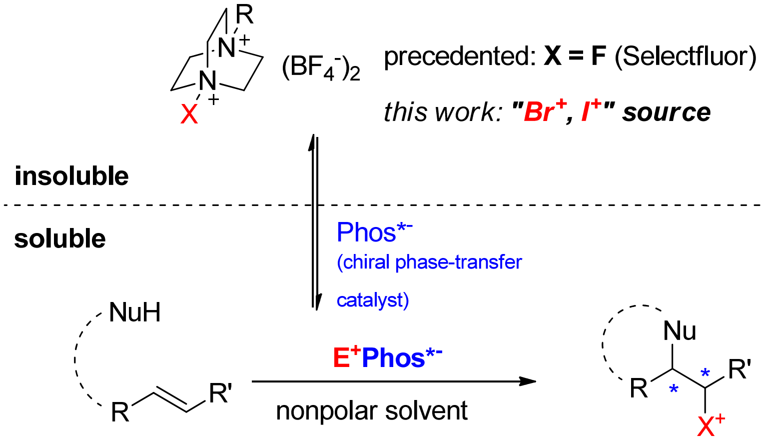


Introduction

In addition to exploring catalyst modifications for enantioselective functionalization of alkenes, this project focused on the development of new reagents for precedented catalytic systems. We demonstrate that while the generation of new modes of reactivity can be achieved by modifications to the catalyst (as shown in chapter 2), new reactions and methods can also be developed by the design of new reagents. Due to the high presence of halogenated chiral motifs in natural products, and importance as synthetic intermediates, we chose to investigate halogenations.[1,2] This work is largely based on the fluorination reactions developed in the Toste group, which rely on the same chiral anion phase-transfer catalytic cycle. However, known bromination and iodination reagents were not found to be amenable in the system – thus, the design of new reagents was required. These transformations present a different challenge from fluorination due to the increased reactivity and electrophilicity of bromination and iodination reagents, which makes achieving enantioselectivity more difficult.

There are a few precedented examples of enantioselective electrophilic addition reactions.[3] Among these types of transformations, metal-catalyzed variants have been developed.[4] Meanwhile, organocatalytic methods generally rely on hydrogen-bonding activation of the electrophilic reagent by chiral hydrogen-bonding catalysts: cinchona alkaloids, chiral diaminocyclohexane derivatives, C_3-symmetric imidazoline derivatives, peptides, and phosphoric acids.[5-9] The success of these methods is due to the increased reactivity of the reagent when in the presence of the catalyst compared with the background racemic reaction which occurs when the substrate and reagent react in the absence of the chiral catalyst. In order to overcome this small difference in reactivity between catalyzed (chiral) and uncatalyzed (racemic) reaction, long reaction times and low temperatures are often employed.

A look at the chiral anion phase-transfer catalytic system that has been developed shows that there is the possibility for "plugging in" various electrophilic salts in place of Selectfluor to achieve a wider range of transformations. Presumably, these reagents would have to have similar characteristics as Selectfluor in terms of solubility and interactions with chiral phosphates.[10] With this in mind, we began the design of new reagents using a DABCO scaffold in order to mimic the reactivity and favorable properties of Selectfluor.



Scheme 1. Proposed expansion of chiral anion phase transfer catalysis from fluorination to bromination and iodination (E^+ = electrophile, Phos$*^-$ = chiral phosphate anion).

Results and Discussion

Beginning with DABCO as a simple modifiable scaffold, and precedented amine-bromine complexes which have been used as brominating and oxidation reagents, we subjected monoalkylated DABCO salts to bromine (Figure 1).[11]

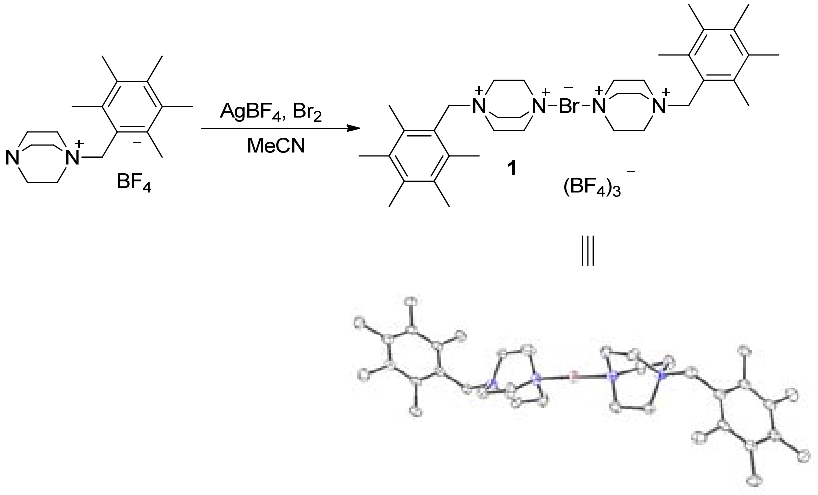
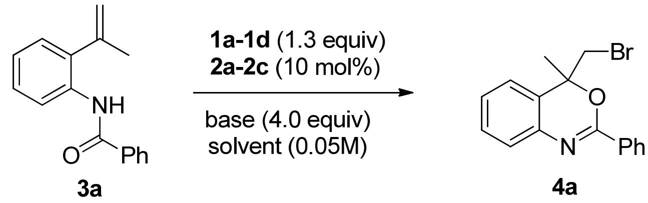


Figure 1. Preparation of reagent **1** and confirmation of structure by X-ray crystallography (ellipsoids at 50% probability level, counterions and H's omitted for clarity).

The bench stability was found to be slightly worse than Selectfluor, and the powder was kept in vials in the -20 °C refrigerator for months. Similar to homogeneous reactions with Selectfluor, reagent **1** was subjected to **3a** and promoted cyclization in high yield and short reaction time. Running the reaction with **3a** in nonpolar solvents such as hexane, toluene, and methylene chloride in the absence of phase-transfer catalyst demonstrated that the insolubility of **1** prevented any background (racemic) reaction. When run in the presence of chiral phase-transfer catalyst **2a,** however, we observed formation of desired product. With these results in hand, we were ready to optimize the reagent and catalyst.

Lipophilicity and electrophilicity were tuned with various changes to the alkyl substituents on the DABCO framework. We postulated that electron-withdrawing substituents could inductively increase electrophilicity of the reagent. Further, highly lipophilic reagent **1d** was found to improve enantioselectivity probably due to increased solubility in the presence of phase-transfer catalyst (Table 1, entries 1-4). Changes to the solvent choice showed that more hydrophobic solvents were beneficial for enantioselectivity (entries 5, 6).



entry	reagent	catalyst	solvent	base	time	conv.[a]	ee[b]
1	**1a**	**2a**	toluene	Na_2CO_3	1 d	82%	59%
2	**1b**	**2a**	toluene	Na_2CO_3	1 d	67%	70%
3	**1c**	**2a**	toluene	Na_2CO_3	1 d	30%	20%
4	**1d**	**2a**	toluene	Na_2CO_3	1 d	67%	83%
5	**1d**	**2a**	*p*-xylene	Na_2CO_3	16 h	62%	86%
6	**1d**	**2a**	p-xyl/hex (1:1)	Na_2CO_3	16 h	90%	89%
7	**1d**	**2a**	hexanes	Na_2CO_3	16 h	21%	60%
8	**1d**	**2b**	p-xyl/hex (1:1)	Na_2CO_3	17 h	90%	89%
9	**1d**	**2c**	p-xyl/hex (1:1)	Na_2CO_3	17 h	90%	91%
10	**1d**	**2c**	p-xyl/hex (1:1)	Na_2CO_3[c]	17 h	100%	90%
11	**1d**	**2c**	p-xyl/hex (1:1)	Na_3PO_4[c]	17 h	100%	92%
12	**1d**[d]	**2c**[e]	p-xyl/hex (1:1)[f]	Na_3PO_4[c]	4 h	100%[g]	94%

[a]Determined by 1H NMR of crude product after workup. [b]Determined by chiral HPLC. [c]Finely ground and dried. [d]Reprecipitated from $MeNO_2$. [e]5 mol%. [f]0.025 M. [g]82% isolated yield.

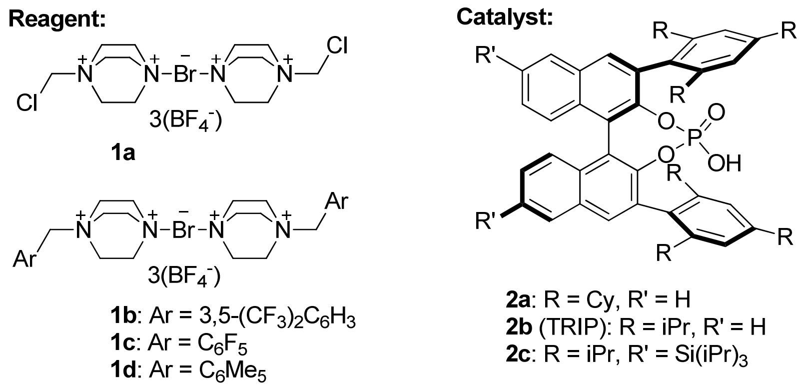


Table 1. Optimization of bromocyclization conditions.

Commonly used phosphoric acid catalyst TRIP (**2b**) provided high enantioselectivities, while the inclusion of 6,6'-TIPS substituents (**2c**, TIPS-TRIP) provided improvements (entries 8, 9) due either to increased solubility in nonpolar solvent, or a slightly different angle between the naphthyl substituents.

After optimization of reaction conditions, we proceeded to investigate the substrate scope by first varying substitutions on the alpha- positions of the styrene. In terms of functional group tolerance, substrates containing silyl ether or alcohol did not undergo side reactions or lack reactivity. In addition, pyridine rather than phenyl derivatives could be subjected to reaction conditions, providing product in high yield and enantioselectivity. Heterocyclic substituents were also well-tolerated, although more polar solvent mesitylene was used in these cases after noticing that results improved when changing the solvent from benzene to toluene to xylene.

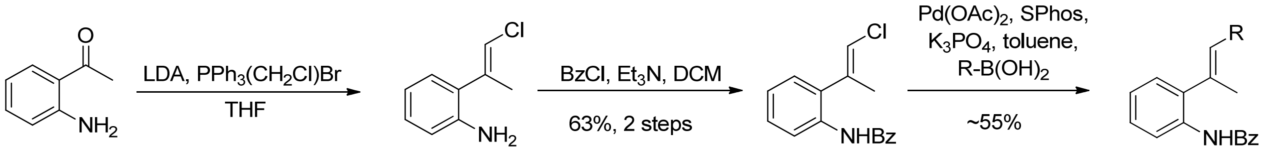


Figure 2. Synthesis of trisubstituted alkenes *via* vinyl chloride and subsequent Suzuki reaction.

We next explored substrates bearing substitution at both α and β positions of the styrenyl system. The vinyl chloride formed *via* a Wittig reaction provided a versatile compound for diversification at the alkene and at the amine. This route was used for compounds **4g – 4i**. Despite forming more than one stereocenter, only one diastereomer was observed in all of these cases. A wide variety of steric and electronic changes were well-tolerated. Thus, although only one type of nucleophile was employed, resulting in only one type of heterocycle, the ability to change every other moiety on the substrate demonstrates a wide tolerance in this reaction regarding with respect to functional groups, steric bulk, and electronic changes.

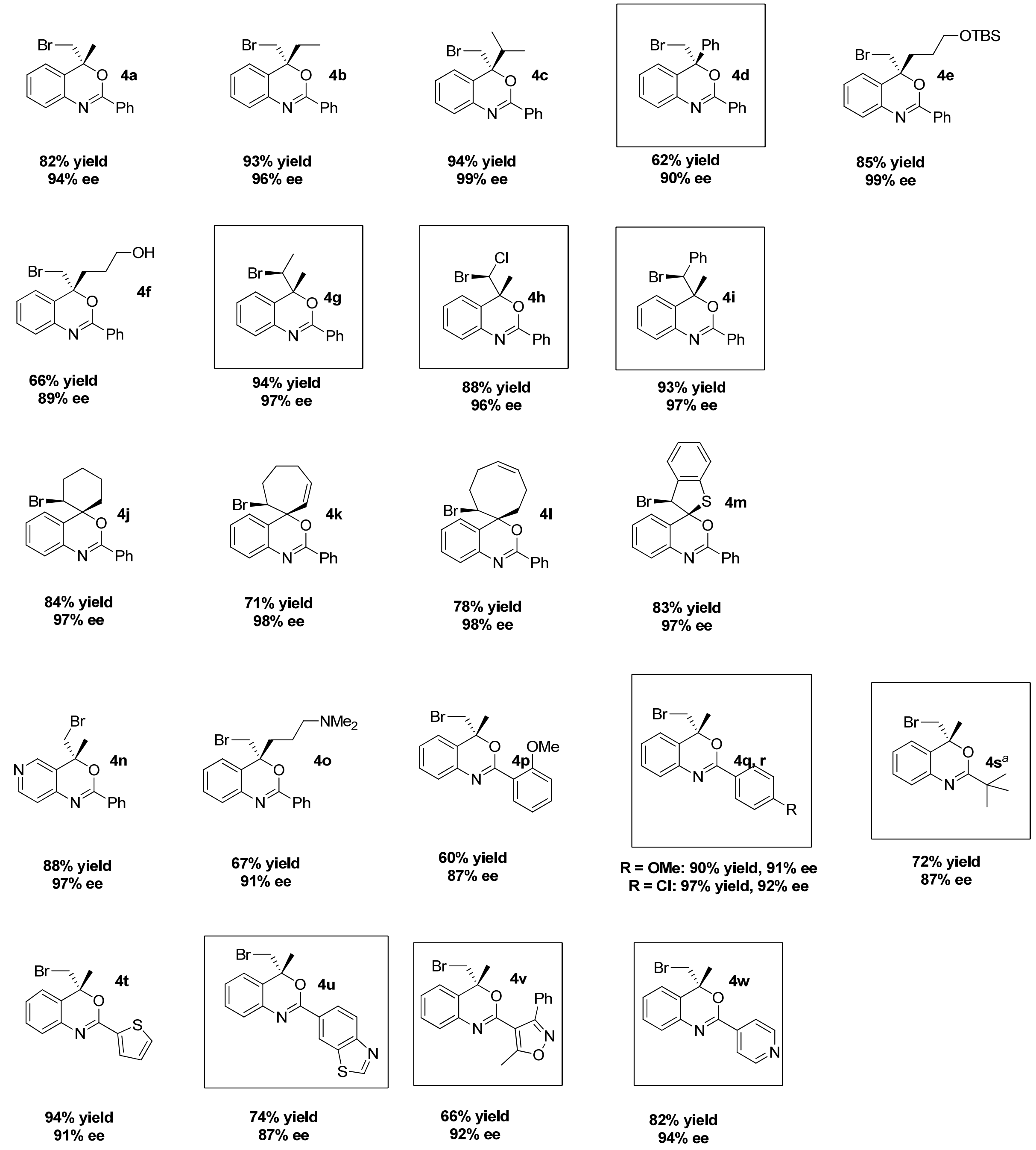
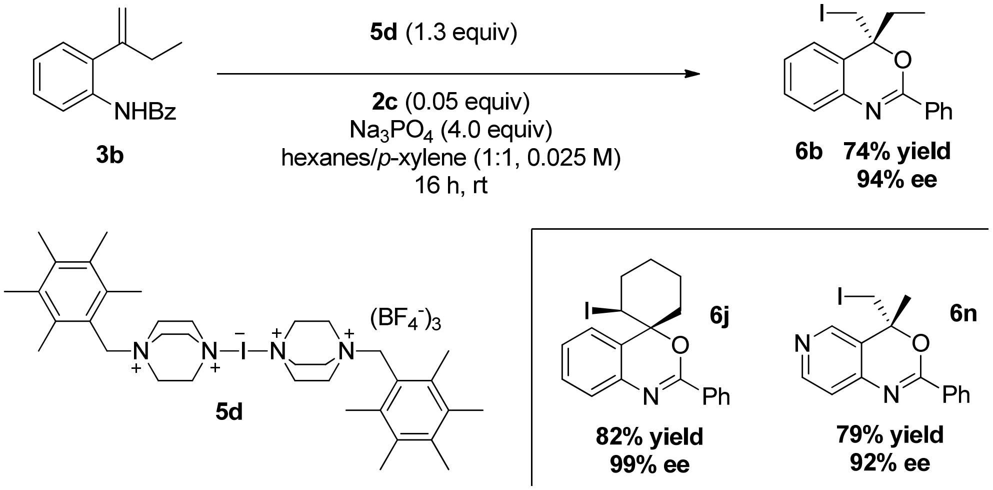


Table 2. Substrate scope of bromocyclization with new reagent **1d**. Conditions: **1d** (1.3 equiv), TIPS-TRIP (5 mol%), Na_3PO_4 (4.0 equiv), *p*-xylene/hexanes (1:1, 0.025 M), 4 h. Enantioselectivities determined by chiral HPLC. ^{a}1.5 equiv **1d** in mesitylene/hexanes (1:1).

The generation of iodination reagents was achieved following a protocol similar to that employed in the synthesis of bromination reagent **1**. After the synthesis of **5d** we investigated various substrates representing a wide range of structures. Without modification of the reaction conditions, we were able to attain iodocyclization products in similar yields and enantioselectivities as the bromocyclization reaction (Scheme 2). This analogous study further demonstrates the ability to design new reagents in a straight-forward manner for use in the chiral anion phase-transfer system.



Scheme 2. Analogous enantioselective electrophilic iodination.

New reagents were designed and synthesized for phase-transfer halocyclization reactions. High enantioselectivities and yields were demonstrated for a variety of compounds including heterocyclic and spirocyclic substrates, and a variety of substitution patterns on the alkene. These reactions were run under air and without the exclusion of moisture, and offers an efficient organocatalytic method for the formation of benzoxazines. The use of a new iodination reagent further highlights the ability to change the reagent in the phase-transfer system without loss of enantioselectivity and yield. Future work in this area may include the design of new electrophilic reagents for non-halogenation reactions, possibly achievable for trifluoromethylation.

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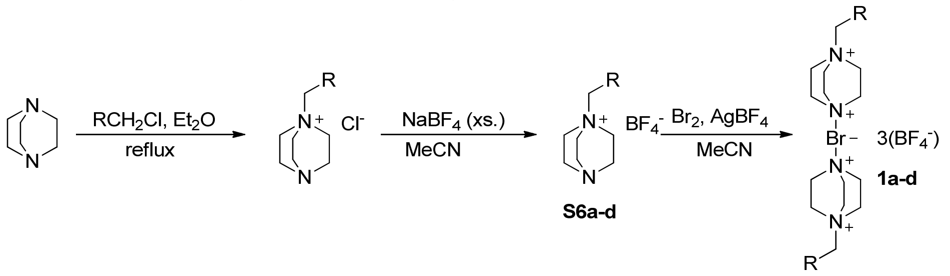
Synthesis of bromination reagents 1a-d and iodination reagent 5d. Reagents **1a-d** were prepared according to the following scheme.



S6d: A solution of 2,3,4,5,6-pentamethylbenzyl chloride (8.61 g, 43.8 mmol, 1.00 equiv) and 1,4-diazabicyclo[2.2.2]octane (4.91 g, 43.8 mmol, 1.00 equiv) in diethyl ether (200 mL) was heated under reflux for 18 h. The resultant white solid was isolated by filtration and washed repeatedly with diethyl ether, air-dried overnight, and used directly in the next step.

The crude product from above and sodium tetrafluoroborate (24.0 g, 219 mmol, 4.99 equiv) were suspended in acetonitrile (300 mL) in an Erlenmeyer flask and sonicated for 2 h with occasional swirling. The reaction mixture was filtered and washed with acetonitrile, and the filtrate was evaporated to dryness. The crude product was purified by recrystallization (EtOH/MeCN) to give the title product (11.6 g, 32.2 mmol, 74%) as a white solid.

^{1}H NMR (300 MHz, CD_3NO_2, ^{1}H res. δ 4.33) δ 4.79 (s, 2H), 3.39-3.30 (m, 6H), 3.19-3.09 (m, 6H), 2.38 (s, 6H), 2.31 (s, 3H), 2.26 (s, 6H). ^{13}C NMR (75 MHz, CD_3NO_2, δ 60.5) δ 126.8, 135.0, 133.5, 120.2, 62.6, 51.2, 44.2, 43.5, 17.4, 15.0. ^{19}F NMR (376 MHz, CD_3NO_2) δ -151.9, -152.0. Anal. calcd. for $C_{19}H_{29}BF_4N_2$: C, 60.01; H, 8.11; N, 7.78, found: C, 60.19; H, 7.79; N, 7.80.

1d: As a precaution, the following procedure was performed with fume hood lights turned off. To an open-flask, stirred solution of **S6d** (1.00 g, 2.78 mmol, 1.00 equiv) and silver tetrafluoroborate (298 mg, 1.53 mmol, 0.55 equiv) in acetonitrile (100 mL) was added bromine (275 mg, 1.72 mmol, 0.62 equiv) in acetonitrile (10 mL) *via* Pasteur pipette over 3 min. The flask was capped, and the reaction mixture was stirred for 5 min after addition was completed, and then vacuum-filtered through a fritted funnel (fine porosity), which was rinsed with additional acetonitrile (50 mL). To the homogeneous filtrate was added dichloromethane (100 mL) and hexanes (200 mL). The resultant suspension was sonicated for 5 min and vacuum-filtered. The precipitate was washed with hexanes and dried by suction for a few minutes to give a very slightly yellow cake of solid. This material may be used directly for bromocyclization without adversely affecting yield or enantioselectivity, although longer reaction times were required. To further purify the reagent, the cake was broken up with a spatula and nitromethane (25 mL) was added to the filter funnel to redissolve the solid. The resultant slightly cloudy solution was vacuum-filtered, and the residue was rinsed with additional nitromethane (25 mL). To the colorless homogeneous filtrate was added dichloromethane (75 mL) and hexanes (100 mL). The resultant suspension was sonicated for 5 min and vacuum-filtered. The precipitate was washed with dichloromethane and then washed thoroughly with hexanes and dried under high vacuum to afford the title product as a colorless and odorless fluffy solid (910 mg, 1.03

mmol, 74%). Crystals suitable for X-ray diffraction were obtained by cooling a saturated solution in nitromethane to -20 °C overnight. *Note:* Reagent **1d** can be stored at -20 °C for at least a month in a tightly sealed vial. However, solutions of **1d** in acetonitrile or nitromethane start to degrade after several hours at room temperature.

^{1}H NMR (600 MHz, CD_3NO_2, ^{1}H res. δ 4.33) δ 4.95 (s, 2H), 3.86 - 3.56 (m, 12H), 2.36 (s, 6H), 2.31 (s, 3H), 2.25 (s, 6H). ^{13}C NMR (151 MHz, CD_3NO_2, δ 60.5) δ 137.7, 135.1, 134.0, 119.2, 63.5, 51.6, 49.6, 17.2, 15.2, 15.0. ^{19}F NMR (376 MHz, CD_3NO_2) δ -151.7, -151.8.

Bromination reagents **1a – 1c** were prepared analogously.

1a: ^{1}H NMR (600 MHz, CD_3NO_2, ^{1}H res. δ 4.33) δ 5.22 (s, 2H), 4.10 - 3.75 (m, 12H).
1b: ^{1}H NMR (600 MHz, CD_3NO_2, ^{1}H res. δ 4.33) δ 8.23 (s, 4H), 8.16 (s, 2H), δ 4.85 (s, 2H), 3.95 - 3.70 (m, 12H).
1c: ^{1}H NMR (300 MHz, CD_3NO_2, ^{1}H res. δ 4.33) δ 4.80 (s, 2H), 4.05 - 3.70 (m, 12H).

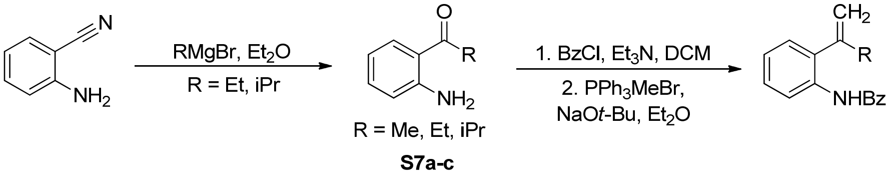
Iodination reagent **5d** was prepared in analogy to bromination reagent **5d**, starting from **S6d (**1.00 g, 2.78 mmol, 1.00 equiv), silver tetrafluoroborate (296 mg, 1.53 mmol, 0.55 equiv), and iodine (424 mg, 1.67 mmol, 0.60 mmol). The reaction mixture was stirred for 15 min, instead of 5 min for the preparation of **1d**. After an identical workup procedure, **5d** was obtained as a very slightly yellow solid (980 mg, 1.05 mmol, 75%), pure enough for use in the iodocyclization reactions. Analytically pure product could be obtained as colorless crystals by cooling a saturated solution of **5d** in nitromethane to -20 °C overnight. Use of the crude product was not detrimental to yield or enantioselectivity of the iodocylization reactions.
^{1}H NMR (500 MHz, CD_3NO_2, ^{1}H res. δ 4.33) δ 4.93 (s, 2H), 3.89 - 3.55 (m, 12H), 2.35 (s, 6H), 2.31 (s, 3H), 2.25 (s, 6H). ^{13}C NMR (126 MHz, CD_3NO_2, δ 60.5) δ 137.6, 135.1, 133.9, 119.1, 63.8, 51.7, 51.0, 17.2, 15.2, 15.0.

General procedure for halocyclizations. Prior to use in halocyclization reactions, sodium phosphate was stirred overnight at 60 °C under high vacuum. To a 4 mL vial was added substrate (0.0421 mmol, 1.00 equiv), **2c** (2.2 mg, 0.00207 mmol, 0.05 equiv), and sodium phosphate (28.0 mg, 0.171 mmol, 4.07 equiv). Solvent (0.84 mL hexanes and 0.84 mL *p*-xylene) was added, followed by **1d** (45.0 mg, 0.0507mmol, 1.20 equiv), and the reaction was stirred using a 1/2'' x 1/8'' octagonal stirbar at 700 rpm. After 4 h (16 h for iodocyclization), the reaction mixture was filtered through Celite with hexanes, and solvent was evaporated under a stream of nitrogen. (More polar products **4f**, **4n**, and **4o** were filtered through silica with ethyl acetate instead.) The residue was purified by preparative thin-layer chromatography to afford the bromocyclization product. Iodocyclization was carried out in an analogous manner.

Halocyclization of 3j with 0.1 mol % catalyst loading. Sodium phosphate was dried and ground as described above immediately before performing the reaction. A stock solution of 2.0 mg **2c** / 2.0 mL hexanes was made, of which 50 µL (0.0469 µmol) was added to **3j** (13.0 mg, 0.0469 mmol), sodium phosphate (31.0 mg), hexanes (0.94 mL), and *p*-xylene (0.89 mL). Brominating reagent **1d** (53.0 mg) was added, and the reaction mixture was stirred for 16 h. Workup as described above afforded **4j** in 86-88% yield (2 runs) and 90-93% ee (4 runs).

Synthesis of substrates. The synthesis of substrates is summarized below.

3a-3c.

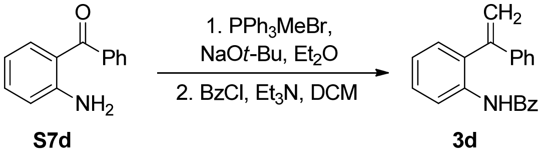


To a stirred solution of Grignard reagent (3.0 equiv; 3.0 M EtMgBr, 1.0 M iPrMgBr) in diethyl ether at 0 °C was added anthranilonitrile (1.0 equiv, 10 - 20 mmol scale) as a solid. The reaction mixture was allowed to warm to room temperature and was stirred overnight. Saturated aqueous NH_4Cl was then cautiously added dropwise by syringe until gas evolution ceased. The reaction mixture was then diluted with water and dichloromethane. Standard aqueous workup (CH_2Cl_2) followed by flash column chromatography (20:1 to 10:1 hexanes/EtOAc) afforded the ketone product **S7b** and **S7c**. 2-Aminoacetophenone (**S7a**) was available commercially and was used as received.

To a solution of **S7a-c** (1.00 equiv) in DCM (0.3 M) was added sequentially triethylamine (1.50 equiv) and benzoyl chloride (1.05 equiv). Water was added after 30 min. Subsequent standard aqueous workup (DCM) followed by recrystallization (EtOAc for **S7a**, **S7b**; hex/EtOAc for **S7c**) afforded the amide product.

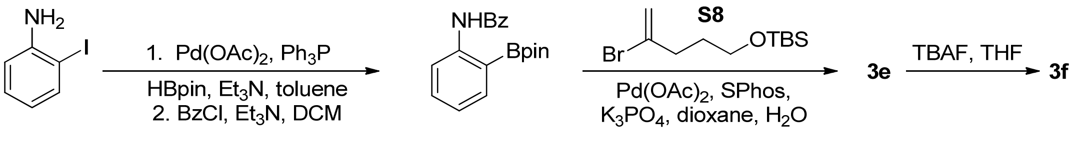
To a stirred suspension of methyltriphenylphosphonium bromide (1.30 equiv) in dry diethyl ether (100 mL for 1.50 g phosphonium salt) at 0 °C was added sodium *t*-butoxide (2.60 equiv). The reaction mixture was stirred for 30 min after which the amide product from above (1.00 equiv) was added. The reaction mixture was allowed to warm to room temperature and then heated at reflux overnight. Saturated aqueous NH_4Cl (5 mL) was added dropwise. Dilution with water and EtOAc, followed by standard aqueous workup (EtOAc) and column chromatography (20:1 to 10:1 hexanes/EtOAc) afforded substrates **3a-3c**.

3d



Amide **3d** was prepared from 2-aminobenzophenone by Wittig olefination followed by benzoylation, using the procedures described for **3a-3c** above.

3e, 3f



To a stirred, degassed solution of 2-iodoaniline (1.00 g, 4.56 mmol), palladium acetate (51 mg, 5 mol%), triphenylphosphine (240 mg, 20 mol%), and triethylamine (2.5 mL, 4.0 equiv) in toluene (5 mL) was added pinacolborane (1.75 g, 3.0 equiv) dropwise by syringe (hydrogen evolution!). Upon cessation of bubbling, the reaction mixture was heated to 90 °C for 2 h. Upon cooling to room temperature, the reaction mixture was filtered through a plug of silica (EtOAc eluent), and the filtrate was concentrated to dryness. Column chromatography (1:1 hexanes/DCM to DCM) afforded 2-aminophenylboronic acid pinacol ester (550 mg, 55%) as an orange solid.

To a solution of the boronic acid pinacol ester from above (550 mg, 1.0 equiv) in DCM (100 mL) was added sequentially triethylamine (0.7 mL) and benzoyl chloride (0.31 mL, 1.05 equiv). After 10 min, water (100 mL) was added. Standard aqueous workup (DCM) followed by crystallization (hexanes/toluene) afforded 2-benzamidophenylboronic acid pinacol ester as a yellow solid.

A mixture of the amide from above (323 mg, 1.0 equiv), **S8** (335 mg, 1.2 equiv), SPhos (41 mg, 10 mol%), potassium phosphate (849 mg, 4.0 equiv), dioxane (5.0 mL), and water (0.5 mL) was degassed. Palladium acetate (11 mg, 5 mol%) was added, and the reaction mixture was once again degassed and then stirred and heated at 90 °C. After 30 min, the reaction mixture was filtered through a plug of silica (DCM eluent), and the filtrate was concentrated to dryness. Column chromatography (20:1 hexanes/EtOAc) afforded **3e** as a yellow oil (321 mg, 81%).

To a stirred solution of amide **3e** (663 mg, 1.0 equiv) in THF (30 mL) at 0 °C was added TBAF (1.84 mL, 1.0 M solution in THF, 1.1 equiv). The reaction mixture was allowed to warm to room temperature and stirring was continued for 30 min. The reaction mixture was diluted with water. Standard aqueous workup (EtOAc) followed by column chromatography (1:1 hexanes/EtOAc) afforded **3f** (460 mg, 96%) as a yellow oil.

3g-3i

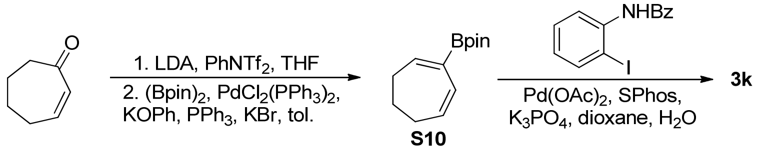
To a stirred solution of diisopropylamine (3.5 mL, 2.5 equiv) in THF (100 mL) was added a 2.5 M *n*-BuLi solution in hexane (10 mL, 2.5 equiv) at -78 °C. The reaction mixture was warmed to 0 °C in an ice bath for 15 min and then cooled back to -78 °C. Chloromethyltriphenylphosphonium bromide (9.78 g, 2.5 equiv) was added, and the reaction mixture was warmed to room temperature for 15 min. The reaction mixture was again cooled to -78 °C, and 2-aminoacetophenone (1.35 g, 10 mmol) was added dropwise. After 18 h, aqueous saturated ammonium chloride was added. Standard aqueous workup (Et_2O) followed by column chromatography afforded (*E*)-2-(1-chloroprop-1-en-2-yl)aniline (**S9)** as a single isomer by NMR.

Triethylamine (1.5 equiv) and benzoyl chloride (0.35 mL, 1.02 equiv) were added dropwise to **S9** (0.5 g, 2.98 mmol) in THF (15 mL) at 0 °C. After 30 min of stirring at room temperature the reaction mixture was filtered and then partitioned between ether and water. The organic layer was dried with magnesium sulfate and concentrated. The crude solid was washed with hexane to provide **3h** as a white solid (0.51g, 63%).

A mixture of amide **3h** (0.1 g, 0.368 mmol), palladium acetate (8 mg, 0.1 equiv), SPhos (0.030 g, 0.2 equiv), phenylboronic acid (0.135 g, 3.0 equiv), and potassium phosphate (finely powdered, 0.39 g, 5 equiv) in toluene (2.5 mL) was degassed, and then stirred vigorously at 70 °C for 18 h. The reaction mixture was then filtered with Celite and partitioned between water and EtOAc and extracted (EtOAc). The combined organic layers were washed with brine and dried with $MgSO_4$. Column chromatography (0-10% ethyl acetate in hexane) provided a product which was suspended in hexane and filtered to provide **3i** as a white solid (0.060 g, 55%).

Amide **3g** was prepared in analogy to **3i**, with trimethylboroxine (2.5 equiv) in place of phenylboronic acid.

3k

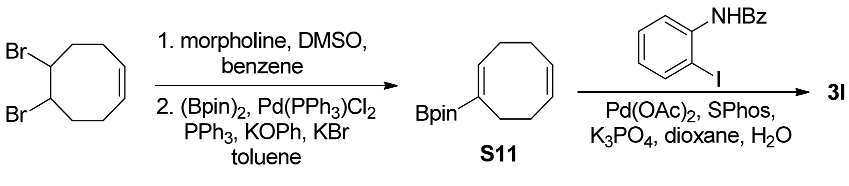


A solution of LDA was prepared by addition of *n*-BuLi (3.40 mL, 1.10 equiv, 2.5 M solution in hexanes) to a stirred solution of diisopropylamine (1.20 mL, 1.10 equiv) in THF (20 mL) at 0 °C and allowing deprotonation to occur over 30 min. The LDA solution was cooled to -78 °C, and a solution of cyclohept-2-en-1-one (0.853 g, 1.00 equiv) in THF (2 mL) was added dropwise. Stirring was continued for 2 h at -78 °C, whereupon a solution of phenyl bistriflimide (2.77 g, 1.00 equiv) was added dropwise. The reaction mixture was allowed to warm to room temperature, with stirring continued for an additional 4 h. Solvent was removed and the residue was extracted with pentane. Column chromatography (pentane) afforded the triflate as a colorless oil (1.3 g).

A mixture of bis(pinacolato)diboron (839 mg, 1.1 equiv), bis(triphenylphosphine)palladium dichloride (63 mg, 3 mol%), triphenylphosphine (47 mg, 6 mol%), potassium phenolate (595 mg, 1.5 equiv), potassium bromide (535 mg, 1.5 equiv), and toluene (20 mL) was degassed, and a solution of the triflate prepared above (727 mg, 1.0 equiv) in toluene (5 mL) was added dropwise by syringe. The reaction mixture was stirred vigorously and heated at 50 °C for 2 h. The crude product was filtered through a short plug of silica (pentane) to afford **S10** (377 mg, 57%), which was essentially pure by ^{1}H NMR (^{1}H NMR (300 MHz, $CDCl_3$) δ 6.81- 6.66 (m, 1H), 6.22 - 6.00 (d, J = 11.7 Hz, 1H), 5.92 - 5.74 (m, 1H), 2.52 - 2.37 (m, 2H), 2.35 - 2.24 (m, 2H), 1.92 - 1.74 (m, 2H), 1.27 (s, 12H)).

A mixture of **S10** (470 mg, 1.5 equiv), SPhos (58 mg, 0.10 equiv), 2-iodobenzamide (460 mg, 1.0 equiv), and potassium phosphate (1.2 g, 4 equiv), dioxane (25 mL), and water (5 mL) was degassed. Palladium acetate (16 mg, 0.05 equiv) was added. The reaction mixture was again degassed and stirred vigorously at 90 °C for 14 h. The reaction mixture was then filtered through a short plug of silica (EtOAc). Solvent was removed, and the residue was purified by column chromatography (10:1 to 6:1 hexanes/EtOAc) to afford **3k** as a yellow oil (270 mg, 66%).

3l



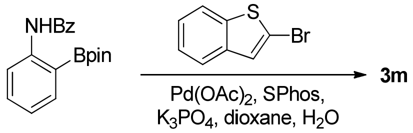
1-Bromo-1,5-cyclooctadiene was prepared by heating a mixture of 5,6-dibromo-1-cyclooctene (16.3 g), DMSO (36 g), and morpholine (26 g) in benzene (40 mL) at reflux for 18 h. The crude reaction mixture was taken up in DCM (100 mL) and washed twice with water (200 mL). Concentration followed by short-path vacuum distillation afforded the diene (1.5 g).

A mixture of the diene prepared above (660 mg), bis(pinacolato)diboron (985 mg), potassium phenolate (700 mg), triphenylphosphine (55 mg) and potassium bromide (628 mg) in toluene was briefly degassed. Bis(triphenylphosphine)palladium dichloride (125 mg) was added.

The reaction mixture was again degassed and stirred vigorously at 60 °C for 7 h. The reaction mixture was then concentrated and subjected directly to column chromatography (pentane to 10:1 pentane:Et_2O) to afford **S11** (ca. 90% pure, 414 mg) as a colorless oil (^{1}H NMR (300 MHz, $CDCl_3$) δ 6.60 - 6.40 (m, 1H), 5.66 - 5.44 (m, 2H), 2.59 - 2.51 (m, 2H), 2.51 - 2.27 (m, 6H), 1.25 (s, 12H)).

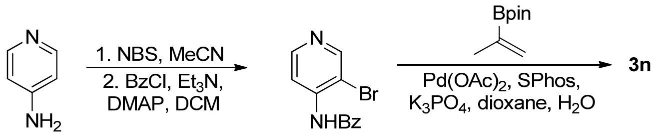
A mixture of **S11** from above (414 mg, ca. 90% pure, 1.35 equiv), SPhos (32 mg, 0.06 equiv), 2-iodobenzamide (420 mg, 1.0 equiv), and potassium phosphate (1.10 g, 4.0 equiv), dioxane (5 mL), and water (0.5 mL) was degassed. Palladium acetate (9 mg, 0.03 equiv) was added. The reaction mixture was again degassed and stirred vigorously at 90 °C for 13 h. The reaction mixture was then filtered through a short plug of silica (EtOAc). Solvent was removed, and the residue was purified by column chromatography (10:1 to 8:1 hexanes/EtOAc) to afford **3l** as a yellow oil (237 mg, 60%).

3m



A mixture of 2-bromobenzothiophene (426 mg, 2.0 equiv), 2-benzamidophenylboronic acid pinacol ester (323 mg, 1.0 equiv), SPhos (41 mg, 10 mol%), potassium phosphate (849 mg, 4.0 equiv), dioxane (5 mL), and water (0.5 mL) was degassed. Palladium acetate (11 mg, 5 mol%) was added, and the reaction mixture was degassed again and heated at 90 °C with vigorous stirring. After 0.5 h, the reaction mixture was allowed to cool and was filtered through a short plug of Celite. Column chromatography (10:1 hexanes/EtOAc) afforded **3m** (242 mg, 73%) as a yellow oil.

3n

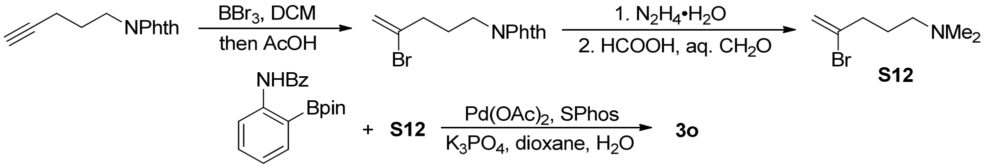


To a stirred solution of 4-aminopyridine (3.00 g, 31.8 mmol) in acetonitrile (150 mL) was added freshly recrystallized NBS (5.67 g, 31.8 mmol) in the dark. The reaction mixture was stirred in the dark for 36h, whereupon solvent was removed, and the resultant residue was partitioned between water and EtOAc. Standard aqueous workup (EtOAc), followed by column chromatography (5:1 to 1:1 hexanes/EtOAc) afforded 4-amino-3-bromopyridine as a colorless solid (2.0 g).

To a stirred solution of 4-amino-3-bromopyridine (1.00 g) in DCM (50 mL) was added sequentially triethylamine (2 mL), benzoyl chloride (812 mg, 1.00 equiv), and DMAP (71 mg, 10 mol%). After 15 min, water was added. Standard aqueous workup (DCM), recrystallization (hexanes/toluene), and column chromatography (2:1 to 1:2 hexanes/EtOAc) afforded the benzoylated product as a white solid (400 mg), which was still slightly impure and used without in the next step without further purification.

A mixture of the amide from above (400 mg), isopropenylboronic acid pinacol ester (364 mg, 1.5 equiv), SPhos (60 mg, 10 mol%), potassium phosphate (1.22 g, 4.0 equiv), dioxane (10 mL) and water (1 mL) was degassed. Palladium acetate (16 mg, 5 mol%) was added, and the reaction mixture was again degassed and heated at 90 °C with vigorous stirring for 16 h. The reaction mixture was then allowed to cool, and filtered through a short plug of silica (EtOAc eluent). Removal of solvent, followed by column chromatography (1:1 to 4:7 hexanes/EtOAc) afforded **3n** (216 mg) as a yellow solid.

3o



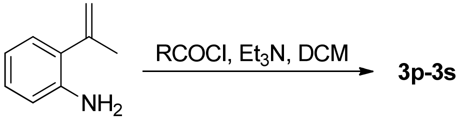
To a stirred solution of 5-phthalimidopent-1-yne (0.778 g, 1.00 equiv) in DCM (10 mL) at -78 °C was added boron tribromide (0.34 mL, 1.00 equiv) over 5 min. The reaction mixture was allowed to warm to room temperature, with stirring continued for 1 h, after which water (3 mL) was added. The reaction mixture was stirred for a further 5 min. Standard aqueous workup (DCM) afforded the crude boronic acid as a yellow-orange oil, which was suspended in hexanes (20 mL) and heated with acetic acid (1 mL) with vigorous stirring at 50 °C overnight. Removal of solvent, followed by column chromatography (20:1 hexanes/EtOAc) afforded the vinyl bromide as a colorless oil.

The vinyl bromide from above and hydrazine hydrate (1.0 mL) were heated at 50 °C in THF (5 mL) with vigorous stirring for 4 h. Gravity filtration with additional THF to remove the hydrazide byproduct and removal of solvent afforded the primary amine as a yellow oil which was used directly in the next step.

A stirred solution of the primary amine from above, formic acid (1.0 mL), and formalin (1.0 mL) in water (5.0 mL) was heated at 90 °C overnight. The reaction mixture was carefully neutralized with saturated NaHCO$_3$ (5.0 mL). Standard aqueous workup (EtOAc) afforded tertiary amine **S12** as a yellow oil (250 mg, 36% over 3 steps), which was essentially pure by ^{1}H NMR (^{1}H NMR (300 MHz, CDCl$_3$) δ 5.73 - 5.50 (m, 1H), 5.45 - 5.34 (m, 1H), 2.46 (t, J = 7.5 Hz, 2H), 2.34 - 2.10 (m, 8H), 1.80 - 1.61 (m, 2H)).

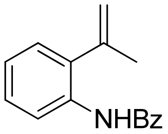
A mixture of **S12** (250 mg, 1.3 equiv), 2-benzamidophenylboronic acid pinacol ester (323 mg, 1.0 equiv), SPhos (41 mg, 10 mol%), potassium phosphate (849 mg, 4.0 equiv), dioxane (10 mL), and water (1.0 mL) was degassed. Palladium acetate (11 mg, 5 mol%) was added, and the reaction mixture was degassed again and heated at 90 °C with vigorous stirring. After 6 h, the reaction mixture was allowed to cool and was filtered through a short plug of Celite. Column chromatography (EtOAc to MeOH gradient) afforded the crude product as a black oil containing only trace impurities (likely palladium). Further purification was achieved by filtration through a short plug of NH silica gel (~3 g, EtOAc eluent) to afford **3o** (200 mg) as a yellow oil.

3p-3s



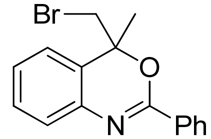
Substrates **3p-3s** were prepared by acylation with the appropriate acyl chloride as outlined in the syntheses for substrates **3a-3c**.

3a



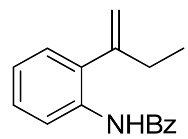
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.53 - 8.44 (m, 2H), 7.84 (d, J = 5.0 Hz, 2H), 7.58-7.53 (m, 1H), 7.52 - 7.47 (m, 2H), 7.36 - 7.31 (m, 1H), 7.21 - 7.16 (m, 1H), 7.15 - 7.10 (m, 1H), 5.49 (s, 1H), 5.13 (s, 1H), 2.12 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 165.2, 143.5, 135.3, 134.2, 133.6, 132.0, 129.0, 128.2, 127.8, 127.1, 124.0, 120.8, 117.0, 24.9. HRMS (ESI+): calcd. for $[C_{16}H_{15}ON+H]^+$: 238.1226, found: 238.1223.

4a



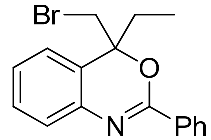
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.26 - 2.19 (m, 2H), 7.54 - 7.49 (m, 1H), 7.49 - 7.44 (m, 2H), 7.40 - 7.34 (m, 2H), 7.28 - 7.22 (m, 1H), 7.20 - 7.16 (m, 1H), 3.78 (d, J = 11.5 Hz, 1H), 3.56 (d, J = 11.5 Hz, 1H), 1.94 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 156.4, 139.2, 132.4, 131.8, 129.8, 128.4, 127.2, 127.0, 125.7, 123.4, 78.2, 39.9, 25.0 (1 resonance missing). HRMS (ESI+): calcd. for $[C_{16}H_{14}ONBr+H]^+$: 316.0332, found: 316.0327.

3b



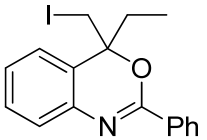
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.55 - 8.49 (m, 1H), 8.44 (s, 1H), 7.84 - 7.76 (m, 2H), 7.58 - 7.43 (m, 3H), 7.36 - 7.30 (m, 1H), 7.17 - 7.08 (m, 2H), 5.48 - 5.45 (m, 1H), 5.13 (s, 1H), 2.45 - 2.36 (m, 2H), 1.10 - 1.00 (m, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 165.1, 149.4, 135.2, 134.6, 133.1, 131.9, 129.0, 128.2, 128.1, 127.0, 123.9, 120.5, 115.1, 31.3, 12.7. HRMS (ESI+): calcd. for $[C_{17}H_{17}ON+H]^+$: 252.1383, found: 252.1380.

4b

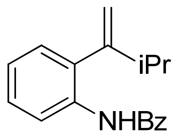


^{1}H NMR (300 MHz, CDCl$_3$) δ 8.23 - 8.15 (m, 2H), 7.55 - 7.41 (m, 3H), 7.37 - 7.30 (m, 2H), 7.27 - 7.19 (m, 1H), 7.12 - 7.07 (m, 1H), 3.79 (d, J = 11.0 Hz, 1H), 3.65 (d, J = 11.0 Hz, 1H), 2.45 - 2.28 (m, 1H), 2.19 - 2.02 (m, 1H), 0.95 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 156.3, 140.0, 132.5, 131.6, 129.5, 128.4, 128.2, 126.8, 125.9, 124.9, 123.7, 81.6, 40.3, 31.0, 8.3. HRMS (ESI+): calcd. for $[C_{17}H_{16}ONBr+H]^+$: 330.0488, found: 330.0483.

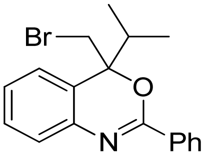
6b



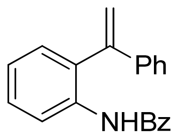
^{1}H NMR (600 MHz, CDCl$_3$) δ 8.22 (d, J = 8.0 Hz, 2H), 7.51 (t, J = 7.0 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H), 7.40 - 7.30 (m, 2H), 7.25 - 7.18 (m, 1H), 7.08 (d, J = 7.5 Hz, 1H), 3.67 (d, J = 11.0 Hz, 1H), 3.57 (d, J = 11.0 Hz, 1H), 2.35 (dq, J = 14.5, 7.5 Hz, 1H), 2.11 (dq, J = 14.5, 7.5 Hz, 1H), 0.94 (t, J = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 156.2, 139.8, 132.5, 131.6, 129.4, 128.4, 128.3, 126.8, 125.9, 125.3, 123.6, 81.1, 32.6, 16.4, 8.7.

3c 

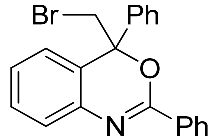
^{1}H NMR (300 MHz, CDCl$_3$) δ 8.52 (d, *J* = 9.0 Hz, 1H), 8.40 (s, 1H), 7.85-7.78 (m, 2H), 7.60-7.45 (m, 3H), 7.38-7.31 (m, 1H), 7.15-7.09 (m, 2H), 5.48-5.44 (m, 1H), 5.14-5.07 (m, 1H), 2.61 (sept, *J* = 7.0 Hz, 1H), 1.10 (d, J = 6 Hz, 6H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 165.0, 153.9, 135.2, 134.9, 133.3, 131.9, 129.0, 128.4, 128.1, 127.0, 123.7, 120.5, 113.8, 35.6, 21.6. HRMS (ESI+): calcd. for [C$_{18}$H$_{19}$ON+H]$^+$: 266.1539, found: 266.1540.

4c 

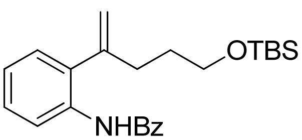
^{1}H NMR (300 MHz, CDCl$_3$) δ 8.20-8.12 (m, 2H), 7.55 - 7.41 (m, 3H), 7.36 - 7.28 (m, 2H), 7.25 - 7.17 (m, 1H), 7.14 - 7.06 (m, 1H), 3.95 (d, *J* = 9.0 Hz, 1H), 3.80 (d, *J* = 9.0 Hz, 1H) 2.48 (sept, *J* = 7.0 Hz, 1H), 1.15 (d, *J* = 7.0 Hz, 3H), 0.96 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 155.9, 139.7, 132.5, 131.5, 129.2, 128.4, 127.9, 126.5, 125.7, 125.1, 123.9, 84.3, 39.7, 37.2, 18.1, 16.1. HRMS (ESI+): calcd. for [C$_{18}$H$_{18}$ONBr+H]$^+$: 344.0645, found: 344.0640.

3d 

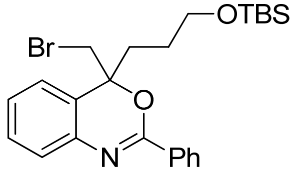
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.50 (d, *J* = 8.0 Hz, 1H), 7.79 (s, 1H), 7.54 - 7.24 (m, 12H), 7.20 (td, *J* = 7.5, 1.0 Hz, 1H), 5.92 (d, *J* = 0.5 Hz, 1H), 5.44 (d, *J* = 0.5 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 165.1, 146.5, 139.1, 135.6, 135.0, 131.8, 131.7, 130.7, 129.2, 129.1, 128.9, 128.7, 126.9, 126.8, 124.4, 121.1, 117.9. HRMS (ESI+): calcd. for [C$_{21}$H$_{17}$ON+H]$^+$: 300.1383, found: 300.1385.

4d 

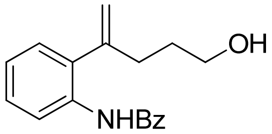
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.42 - 8.20 (m, 2H), 7.58 - 7.42 (m, 5H), 7.42 - 7.29 (m, 5H), 7.29 - 7.17 (m, 1H), 7.16 - 7.04 (m, 1H), 4.25 - 3.99 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 156.1, 140.3, 139.6, 132.3, 131.8, 129.8, 128.8, 128.7, 128.5, 128.4, 126.7, 126.5, 126.1, 125.8, 125.0, 82.3, 37.3. HRMS (ESI+): calcd. for [C$_{21}$H$_{16}$ONBr+H]$^+$: 378.0488, found: 378.0489.

3e 

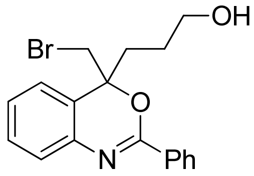
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.52 (d, *J* = 10.0 Hz, 1H), 8.44 (s, 1H), 7.82 (d, *J* = 10.0 Hz, 2H), 7.57 - 7.54 (m, 1H), 7.51 - 7.47 (m, 2H), 7.35 - 7.31 (m, 1H), 7.17 - 7.09 (m, 2H), 5.49 (s, 1H), 5.15 (s, 1H), 3.59 (t, *J* = 5.0 Hz, 2H), 2.58 - 2.42 (m, 2H), 1.67 - 1.59 (m, 2H), 0.85 (s, 9H), 0.01 (s, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 165.1, 147.6, 135.2, 134.7, 132.8, 131.9, 129.0, 128.2, 128.1, 127.0, 123.9, 120.6, 116.3, 62.5, 34.7, 31.2, 26.0, 18.4, -5.2. HRMS (ESI+): calcd. for [C$_{24}$H$_{33}$O$_2$NSi+Na]$^+$: 418.2173, found: 418.2172.

4e 

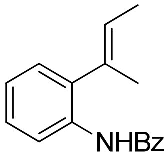
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.20 (d, *J* = 7.5 Hz, 2H), 7.36 - 7.32 (m, 1H), 7.53 - 7.48 (m, 2H) 7.47 - 7.43 (m, 2H), 7.24 - 7.20 (m, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 3.78 (d, *J* = 11 Hz, 1H), 3.65 - 3.58 (m, 3H), 2.44 - 2.35 (m, 1H), 2.24 - 2.15 (m, 1H), 1.69 - 1.61 (m, 1H), 1.58 - 1.48 (m, 1H), 0.88 (s, 9H), 0.01 (d, *J* = 4 Hz, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 156.2, 139.9, 132.5, 131.6, 129.6, 128.4, 128.3, 126.9, 125.9, 125.1, 123.8, 81.3, 62.7, 40.6, 34.3, 27.4, 26.1, 18.4, -5.1_8, -5.2_1. HRMS (ESI+): calcd. for $[C_{22}H_{32}O_2NBrSi+H]^+$:474.1458, found: 474.1466.

3f 

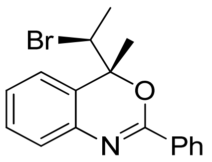
^{1}H NMR (600 MHz, CDCl$_3$) δ 8.52 (s, 1H), 8.45 (d, *J* = 8.2 Hz, 1H), 7.84 - 7.80 (m, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.36 - 7.30 (m, 1H), 7.16 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.12 (td, *J* = 7.5, 1.0 Hz, 1H), 5.49 (s, 1H), 5.15 (s, 1H), 3.64 (t, *J* = 6.0 Hz, 2H), 2.61 - 2.42 (m, 2H), 1.74 - 1.59 (m, 2H), 1.45 (s, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 165.3, 147.3, 135.2, 134.7, 133.0, 131.9, 129.0, 128.3, 128.1, 127.1, 124.1, 121.3, 116.4, 62.6, 34.9, 30.8. HRMS(ESI+): calcd. for $[C_{18}H_{19}O_2N+Na]^+$: 304.1308, found: 304.1310.

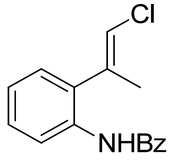
4f 

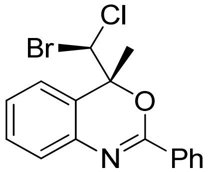
^{1}H NMR (600 MHz, CDCl$_3$) δ 8.19 (d, *J* = 8.0 Hz, 2H), 7.55 - 7.49 (m, 1H), 7.49 - 7.40 (m, 2H), 7.39 - 7.29 (m, 2H), 7.28 - 7.17 (m, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 3.78 (d, *J* = 11.0 Hz, 1H), 3.70 - 3.57 (m, 2H), 2.49 - 2.36 (m, 1H), 2.26 - 2.14 (m, 1H), 1.76 - 1.64 (m, 1H), 1.64 - 1.37 (m, 2H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 156.1, 139.8, 132.4, 131.7, 129.7, 128.4, 128.3, 127.0, 126.0, 124.9, 123.7, 81.2, 62.6, 40.4, 34.3, 27.3. HRMS (ESI+): calcd. for $[C_{18}H_{18}O_2N+H]^+$: 360.0594, found: 360.0597.

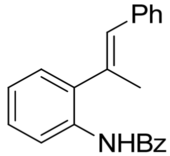
3g 

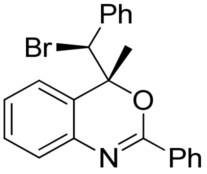
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.48 (d, *J* = 8.0 Hz, 1H), 8.37 (s, 1H), 7.82 (d, *J* = 7.0 Hz, 2H), 7.58 - 7.46 (m, 3H), 7.35 - 7.27 (m, 1H), 7.18 - 7.07 (m, 2H), 5.55 (q, *J* = 6.5 Hz, 1H), 2.00 (s, 3H), 1.87 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 165.0, 135.7, 135.3, 134.5, 133.9, 131.8, 129.0, 128.4, 127.7, 126.9, 126.5, 124.0, 120.6, 18.0, 14.2. HRMS (ESI+): calcd. for $[C_{17}H_{17}ON+H]^+$: 252.1383, found: 252.1383.

4g 
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 - 8.20 (m, 2H), 7.55 - 7.43 (m, 3H), 7.37 - 7.30 (m, 2H), 7.24 - 7.18 (m, 1H), 7.18 - 7.11 (m, 1H), 4.44 (q, *J* = 7.0 Hz, 1H), 1.94 (s, 3H), 1.66 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4, 138.9, 132.3, 131.7, 129.4, 128.5, 128.2, 126.8, 126.7, 125.7, 124.1, 81.6, 57.0, 27.7, 21.0. HRMS (ESI+): calcd. for $[C_{17}H_{16}ONBr+H]^+$: 330.0488, found: 330.0484.

3h 
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.0 Hz, 1H), 7.95 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.61 - 7.55 (m, 1H), 7.54 - 7.49 (m, 2H), 7.40 - 7.35 (m, 1H), 7.19 - 7.13 (m, 2H), 6.22 (s, 1H), 2.16 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3, 136.7, 134.8, 134.8, 132.2, 131.8, 129.1, 129.1, 128.9, 127.0, 124.7, 121.9, 118.8, 19.0. HRMS (ESI+): calcd. for $[C_{16}H_{14}ONCl+H]^+$: 272.0837, found: 272.0837.

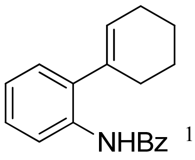
4h 
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 2H), 7.55 - 7.51 (m, 1H), 7.49 - 7.45 (m, 2H), 7.43 - 7.39 (m, 1H), 7.38 - 7.32 (m, 2H), 7.28 - 7.24 (m, 1H), 5.91 (s, 1H), 2.08 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 139.2, 131.9_4, 131.8_9, 130.3, 128.5, 126.8, 125.7_1, 125.6_7, 124.7, 81.7, 65.2, 23.3 (1 resonance missing). HRMS (ESI+): calcd. for $[C_{16}H_{13}ONBrCl+H]^+$:349.9942, found:349.9937.

3i 
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.0 Hz, 1H), 8.45 (s, 1H), 7.82 (d, *J* = 7.5 Hz, 2H), 7.55 - 7.50 (m, 1 H), 7.46 - 7.35 (m, 7H), 7.33 - 7.27 (m, 2H), 7.20 - 7.16 (m, 1H), 6.65 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 136.9, 135.9, 135.7, 135.0, 134.3, 131.9, 131.6, 129.0, 128.9, 128.5, 128.3, 128.1, 127.3, 126.9, 124.3, 121.2, 20.1. HRMS (ESI+): calcd. for $[C_{22}H_{19}ON+H]^+$: 314.1539, found: 314.1539.

4i 
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.5 Hz, 2H), 7.54 - 7.49 (m, 1H), 7.46 - 7.41 (m, 2H), 7.29 - 7.10 (m, 7H), 7.06 - 7.01 (m, 2H), 5.52 (s, 1H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 138.8, 136.8, 132.3, 131.6, 129.9, 129.5, 128.7, 128.3, 128.2,

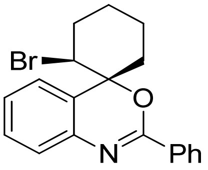
127.70, 126.4, 125.5, 124.9, 82.0, 61.9, 27.5 (1 resonance missing). HRMS (ESI+): calcd. for $[C_{22}H_{18}ONBr+H]^+$: 392.0645, found: 392.0636.

3j



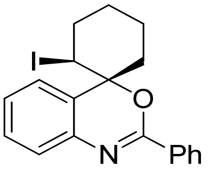
^{1}H NMR (300 MHz, CDCl$_3$) δ 8.62 - 8.43 (m, 2H), 7.92 - 7.76 (m, 2H), 7.63 - 7.44 (m, 3H), 7.37 - 7.23 (m, 1H), 7.21 - 7.05 (m, 2H), 5.96 - 5.78 (m, 1H), 2.39 - 2.13 (m, 4H), 1.94 - 1.64 (m, 4H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 164.9, 136.2, 135.3, 134.6, 134.4, 131.9, 129.0_0, 128.9_6, 128.3, 127.8, 126.9, 123.9, 120.2, 30.3, 25.6, 23.2, 22.2. HRMS (ESI+): calcd. for $[C_{19}H_{19}ON+H]^+$: 278.1539, found: 278.1541.

4j



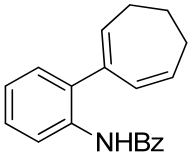
^{1}H NMR (600 MHz, CDCl$_3$) δ 8.22 (d, *J* = 7.5 Hz, 2H), 7.56 - 7.44 (m, 3H), 7.40 - 7.28 (m, 3H), 7.24 (t, *J* = 7.5 Hz, 1H), 4.54 (app. s, 1H), 2.81 (td, *J* = 13.5, 4.5 Hz, 1H), 2.50 - 2.41 (m, 1H), 2.21 - 2.05 (m, 2H), 2.04 - 1.91 (m, 1H), 1.91 - 1.82 (m, 1H), 1.78 - 1.69 (m, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 155.6, 138.9, 132.6, 131.7, 129.3, 128.6, 127.9, 127.8, 126.5, 126.1, 124.9, 79.3, 53.7, 30.1, 29.7, 20.8, 19.7. HRMS (ESI+): calcd. for $[C_{19}H_{18}ONBr+H]^+$: 356.0645, found: 356.0647.

6j

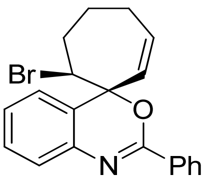


^{1}H NMR (500 MHz, CDCl$_3$) δ 8.22 (d, *J* = 7.0 Hz, 2H), 7.56 - 7.44 (m, 3H), 7.41 - 7.28 (m, 3H), 7.26 - 7.20 (m, 1H), 4.81 (app. s, 1H), 2.88 (td, *J* = 13.0, 4.5 Hz, 1H), 2.44 - 2.31 (m, 1H), 2.24 - 2.09 (m, 2H), 2.01 - 1.73 (m, 4H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 155.9, 138.9, 132.6, 131.8, 129.3, 128.8, 128.6, 127.9, 126.7, 125.9, 124.8, 79.3, 37.0, 31.9, 30.3, 21.5, 21.1. HRMS (ESI+): calcd. for $[C_{19}H_{18}ONI+H]^+$: 404.0506, found: 404.0508.

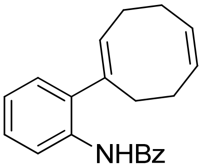
3k



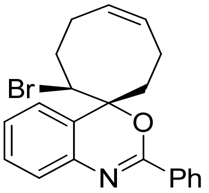
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.49 (d, *J* = 8.0 Hz, 1H), 8.29 (s, 1H), 7.84 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.0 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H) , 6.13-6.02 (m, 2H), 5.88 (d, *J* = 11.5 Hz, 1H), 2.51 - 2.43 (m, 4H), 2.07 - 1.98 (m, 2H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 165.0, 136.2, 136.0, 135.4, 135.3_7, 135.3_5, 135.0, 131.8, 129.1, 128.9, 128.5, 128.1, 127.0, 124.1, 120.4, 31.8, 30.6, 28.1. HRMS (ESI+): calcd. for $[C_{20}H_{19}ON+H]^+$: 290.1539, found: 290.1539.

4k 

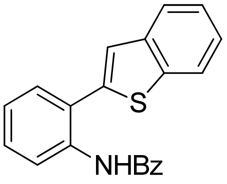
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 – 8.17 (m, 2H), 7.54 – 7.35 (m, 5H), 7.35 - 7.30 (m, 1H), 7.24 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.26 - 6.19 (m, 1H), 6.09 (dd, *J* = 12.0, 2.0 Hz, 1H), 4.57 (dd, *J* = 6.5, 3.0 Hz, 1H), 2.77 - 2.66 (m, 1H), 2.66 - 2.57 (m, 1H), 2.50 - 2.40 (m, 1H), 2.22 – 2.06 (m, 2H), 1.88 - 1.77 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.5, 139.1, 136.3, 132.6, 131.8, 131.7, 129.6, 128.6, 128.0, 127.2, 126.7, 126.1, 125.4, 83.2, 58.4, 33.7, 28.0, 23.3. HRMS (ESI+): calcd. for $[C_{20}H_{18}ONBr+H]^+$: 368.0645, found: 368.0638.

3l 

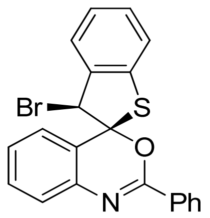
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.0 Hz, 1H), 8.46 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.16 - 7.03 (m, 2H), 5.71 (t, *J* = 7.0 Hz, 1H), 5.59 - 5.51 (m, 1H), 5.50 - 5.41 (m, 1H), 2.70 - 2.53 (m, 4H), 2.51 - 2.35 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 137.9, 135.9, 135.4, 135.0, 131.8, 130.4, 129.6, 129.2, 128.7, 128.6, 127.7, 127.4, 123.7, 120.3, 34.0, 28.4, 27.6, 27.2. HRMS (ESI+): calcd. for $[C_{21}H_{21}ON+H]^+$: 304.1696, found: 304.1695.

4l 

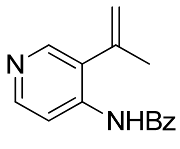
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.5 Hz, 2H), 7.54 - 7.40 (m, 3H), 7.40 - 7.30 (m, 2H), 7.23 (t, *J* = 7.0 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 5.89 - 5.78 (m, 1H), 5.73 - 5.63 (m, 1H), 4.87 (dd, *J* = 12.0, 4.5 Hz, 1H), 3.10 - 2.90 (m, 2H), 2.85 - 2.72 (m, 1H), 2.53 - 2.42 (m, 2H), 2.39 - 2.29 (m, 1H), 2.28 – 2.10 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.4, 139.9, 132.9, 132.5, 131.4, 129.5, 128.4, 127.9, 126.3, 126.0, 125.1, 124.5, 124.2, 85.2, 61.5, 39.1, 34.8, 25.6, 25.2. HRMS (ESI+): calcd. for $[C_{21}H_{20}ONBr+H]^+$: 382.0788, found: 382.0794.

3m 

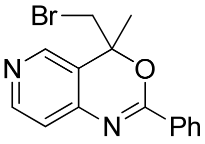
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.0 Hz, 1H), 8.48 (s, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.55 - 7.45 (m, 3H), 7.45 - 7.35 (m, 5H), 7.23 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4, 140.5, 140.2, 139.8, 135.7, 134.7, 132.0, 131.1, 129.9, 129.0, 127.2, 125.0, 125.0, 124.9, 124.6, 124.1, 123.9, 122.5, 121.9. HRMS (ESI+): calcd. for $[C_{21}H_{15}ONS+H]^+$: 330.0947, found: 330.0947.

4m 

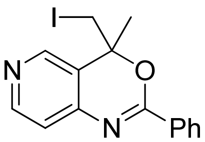
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.94 - 7.89 (m, *J* = 8.3, 2H), 7.71 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.49 - 7.44 (m, 2H), 7.44 - 7.34 (m, 6H), 7.29 – 7.22 (m, 2H), 5.73 (s, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 155.5, 139.2, 138.4, 137.2, 132.1, 131.7, 131.2, 130.3, 128.6, 128.2, 127.9, 127.0, 126.6, 126.4, 125.4, 123.2, 122.2, 102.6, 58.6. HRMS (ESI+): calcd. for $[C_{21}H_{14}ONBrS+H]^+$: 408.0052, found: 408.0050.

3n 

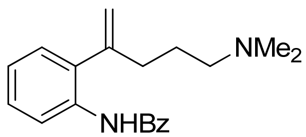
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.57 (s, 1H), 8.51 (d, *J* = 5.5 Hz, 1H), 8.48 (d, *J* = 5.5 Hz, 1H), 8.39 (s, 1H), 7.81 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 5.61 (s, 1H), 5.21 (s, 1H), 2.16 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) 165.6, 149.9, 148.8, 141.3, 140.1, 134.3, 132.6, 129.2, 127.7, 127.1, 119.0, 113.6, 24.8. HRMS (ESI+): calcd. for $[C_{15}H_{14}ON_2+H]^+$: 239.1179, found: 239.1176.

4n 

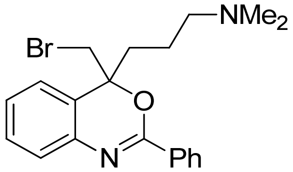
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.57 (d, *J* = 5.0 Hz, 1H), 8.43 (s, 1H), 8.22 (d, *J* = 7.5 Hz, 2H), 7.59 – 7.51 (m, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 5.0 Hz, 1H), 3.77 (d, *J* = 11.5 Hz, 1H), 3.62 (d, *J* = 11.5 Hz, 1H), 1.98 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 160.2, 151.7, 146.0, 145.1, 132.8, 131.6, 128.9, 128.6, 122.6, 119.3, 77.8, 39.6, 25.4. HRMS (ESI+): calcd. for $[C_{15}H_{13}ON_2Br+H]^+$: 317.0284, found: 317.0286.

6n 

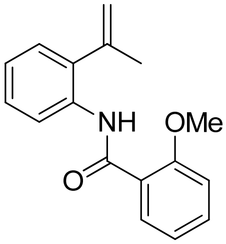
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.56 (d, *J* = 5.0 Hz, 1H), 8.42 (s, 1H), 8.25 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.64 - 7.54 (m, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 5.0 Hz, 1H), 3.67 (d, *J* = 11.0 Hz, 1H), 3.54 (d, *J* = 11.0 Hz, 1H), 1.98 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 160.1, 151.6, 145.8, 145.0, 132.7, 131.5, 129.0, 128.6, 122.7, 119.4, 26.9, 15.0 (1 resonance missing). HRMS (ESI+): calcd. for $[C_{15}H_{13}ON_2I+H]^+$: 365.0145, found: 365.0137.

3o 

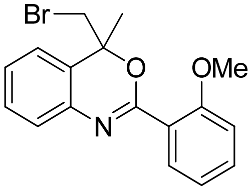
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.47 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 2H), 7.56 - 7.43 (m, *J* = 27.3, 3H), 7.34 - 7.27 (m, 1H), 7.18 - 7.11 (m, 2H), 5.44 (s, 1H), 5.18 (s, 1H), 2.86 - 2.77 (m, 2H), 2.53 (s, 6H), 2.47 (t, *J* = 7.3 Hz, 2H), 1.88 – 1.76 (m, 2H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 165.6, 145.2, 134.5, 134.3, 133.8, 132.1, 129.3, 128.5, 128.4, 127.1, 125.0, 123.3, 117.5, 57.4, 43.0, 34.6, 22.8. HRMS (ESI+): calcd. for $[C_{20}H_{24}ON_2+H]^+$: 309.1961, found: 309.1956.

4o 

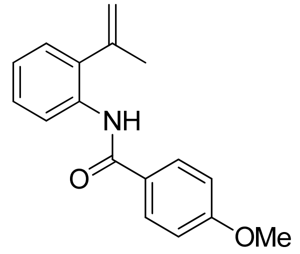
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.19 (d, *J* = 7.5 Hz, 1H), 7.57 - 7.42 (m, 3H), 7.42 - 7.30 (m, 2H), 7.25 - 7.19 (m, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 3.77 (d, *J* = 11.0 Hz, 1H), 3.64 (d, *J* = 11.0 Hz, 1H), 2.43 – 2.08 (m, 10H), 1.69 - 1.54 (m, 1H), 1.54 - 1.40 (m, 1H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 156.2, 139.8, 132.4, 131.6, 129.6, 128.4, 128.2, 126.9, 125.9, 125.0, 123.6, 81.3, 59.3, 45.4, 40.6, 35.8, 22.2. HRMS (ESI+): calcd. for $[C_{20}H_{23}ON_2Br+H]^+$: 387.1067, found: 387.1070.

3p 

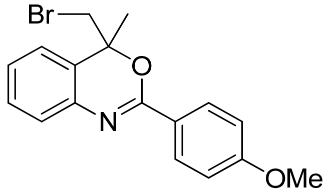
^{1}H NMR (500 MHz, CDCl$_3$) δ 10.13 (s, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.32 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.54 - 7.44 (m, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.20 - 7.06 (m, 3H), 7.02 (d, *J* = 8.5 Hz, 1H), 5.41 (s, 1H), 5.12 - 5.07 (m, 1H), 4.00 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 163.3, 157.3, 143.9, 135.2, 134.3, 133.3, 132.8, 128.0, 123.7, 122.0, 121.6, 121.5, 116.7, 111.4, 55.78, 24.41 (1 resonance missing).

4p 

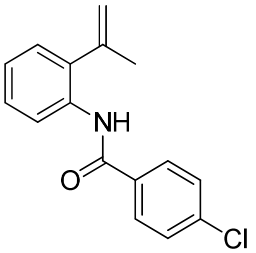
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.76 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.45 - 7.39 (m, 1H), 7.38 - 7.30 (m, 2H), 7.27 - 7.21 (m, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 3.90 (s, 3H), 3.84 (d, *J* = 11.0 Hz, 1H), 3.69 (d, *J* = 11.0 Hz, 1H), 1.90 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 158.6, 157.1, 139.1, 132.2, 131.2, 129.6, 127.0, 126.8, 125.6, 123.7, 122.8, 120.5, 111.9, 79.0, 66.0, 39.6, 25.4.

3q 

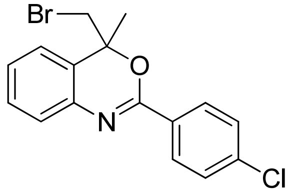
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.56 - 8.31 (m, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 2H), 5.47 (s, 1H), 5.11 (s, 1H), 3.84 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 164.6, 162.4, 143.4, 134.2, 133.5, 128.8, 128.0, 127.7, 127.3, 123.7, 120.8, 116.7, 114.0, 55.4, 24.6.



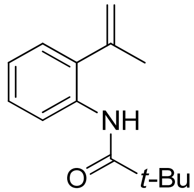
4q ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 9.0 Hz, 2H), 7.39 - 7.28 (m, 2H), 7.24 - 7.14 (m, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H), 3.76 (d, *J* = 11.0 Hz, 1H), 3.53 (d, *J* = 11.0 Hz, 1H), 1.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 156.3, 139.5, 130.3, 129.7, 127.1, 126.5, 125.4, 124.8, 123.3, 113.8, 78.0, 55.6, 39.8, 24.8.



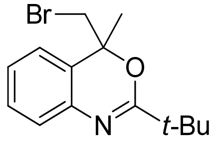
3r ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 - 8.31 (m, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 5.48 (s, 1H), 5.11 (s, 1H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 143.4, 138.2, 133.9, 133.6_1, 133.5_9, 129.3, 128.5, 128.2, 127.8, 124.3, 120.8, 117.0, 24.8.



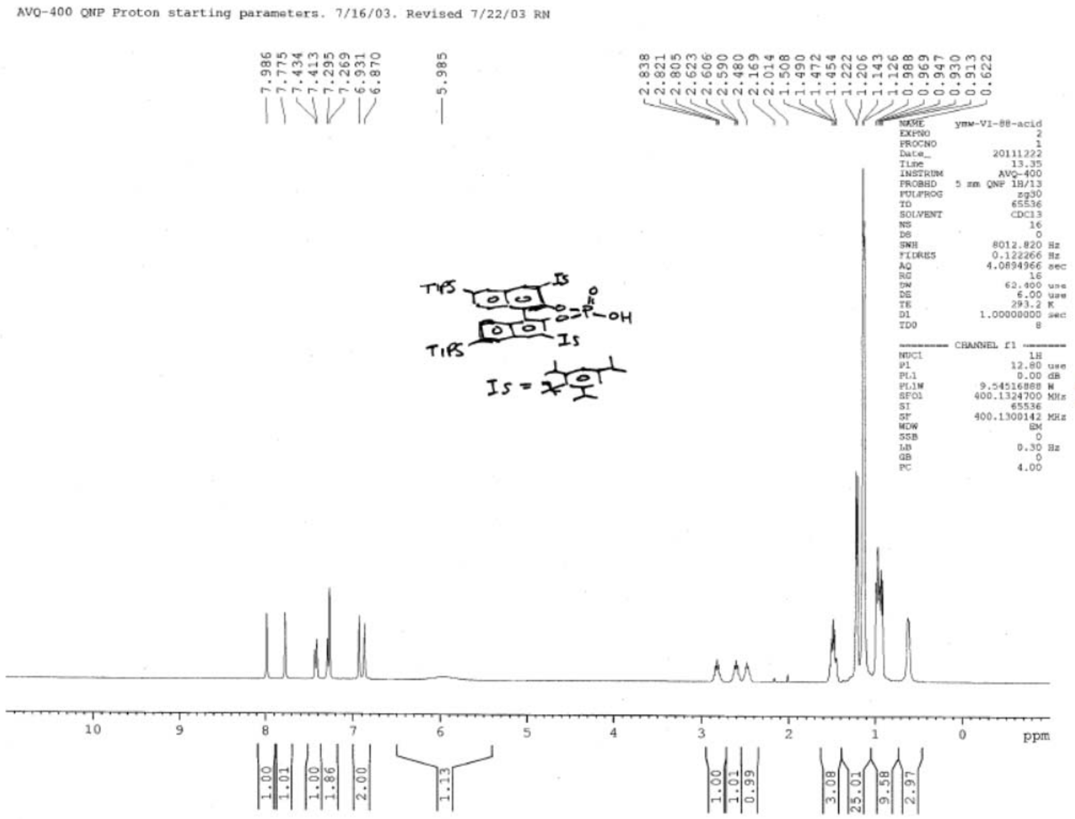
4r ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 - 8.10 (m, 2H), 7.46 - 7.41 (m, 2H), 7.41 - 7.31 (m, 2H), 7.29 - 7.21 (m, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 3.75 (d, *J* = 11.5 Hz, 1H), 3.54 (d, *J* = 11.5 Hz, 1H), 1.93 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.4, 139.0, 138.0, 130.9, 129.8, 129.8, 128.7, 127.2, 127.1, 125.7, 123.4, 78.4, 39.9, 24.9.



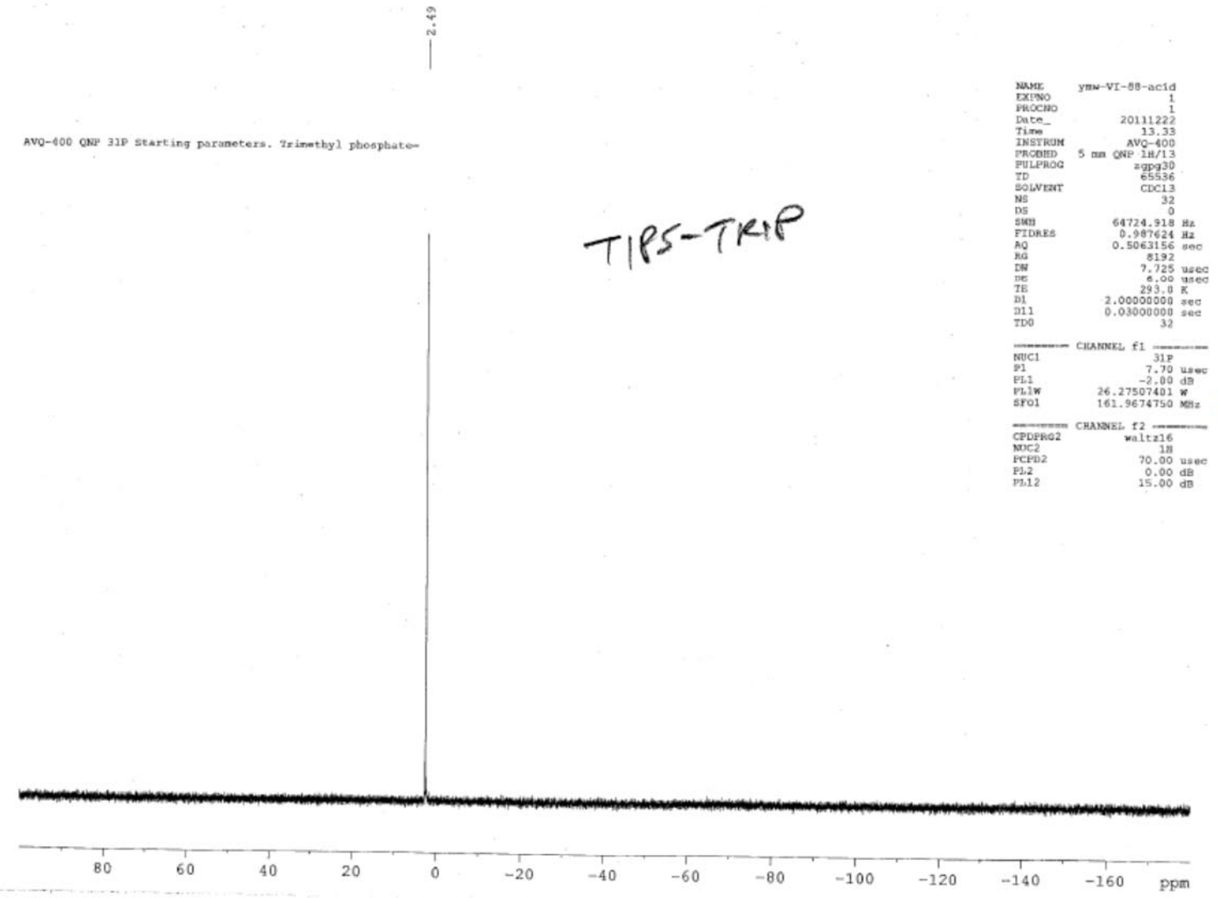
3s ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.3 Hz, 1H), 7.98 (s, 1H), 7.30 - 7.23 (m, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 5.43 (s, 1H), 5.06 - 5.00 (m, 1H), 2.07 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 143.4, 134.3, 133.3, 128.0, 127.6, 123.6, 120.5, 116.8, 40.2, 27.7, 24.6.



4s ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.25 (m, 1H), 7.24 - 7.14 (m, 2H), 7.08 (d, *J* = 7.5 Hz, 1H), 3.64 (d, *J* = 11.0 Hz, 1H), 3.51 (d, *J* = 11.0 Hz, 1H), 1.78 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 139.0, 129.4, 126.5_4, 126.5_1, 125.3, 123.3, 39.9, 37.6, 27.8, 25.4 (1 resonance missing).


AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN
7.986
7.775
7.434
7.413
7.295
7.269
6.931
6.870
5.985
2.838
2.821
2.805
2.623
2.606
2.590
2.480
2.169
2.014
1.508
1.490
1.472
1.454
1.222
1.206
1.143
1.126
0.988
0.969
0.947
0.930
0.913
0.622
NAME ymw-VI-88-acid
EXPNO 2
PROCNO 1
Date_ 20111222
Time 13.35
INSTRUM AVQ-400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 16
DW 62.400 use
DE 6.00 use
TE 293.2 K
D1 1.00000000 sec
TD0 8
======== CHANNEL f1 ========
NUC1 1H
P1 12.80 use
PL1 0.00 dB
PL1W 9.54516888 W
SFO1 400.1324700 MHz
SI 65536
SF 400.1300142 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
TIPS
TIPS
Is
Is
O
O
P
OH
Is =
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.00
1.86
2.00
1.13
1.00
1.01
0.99
3.08
25.01
9.58
2.97

S-2

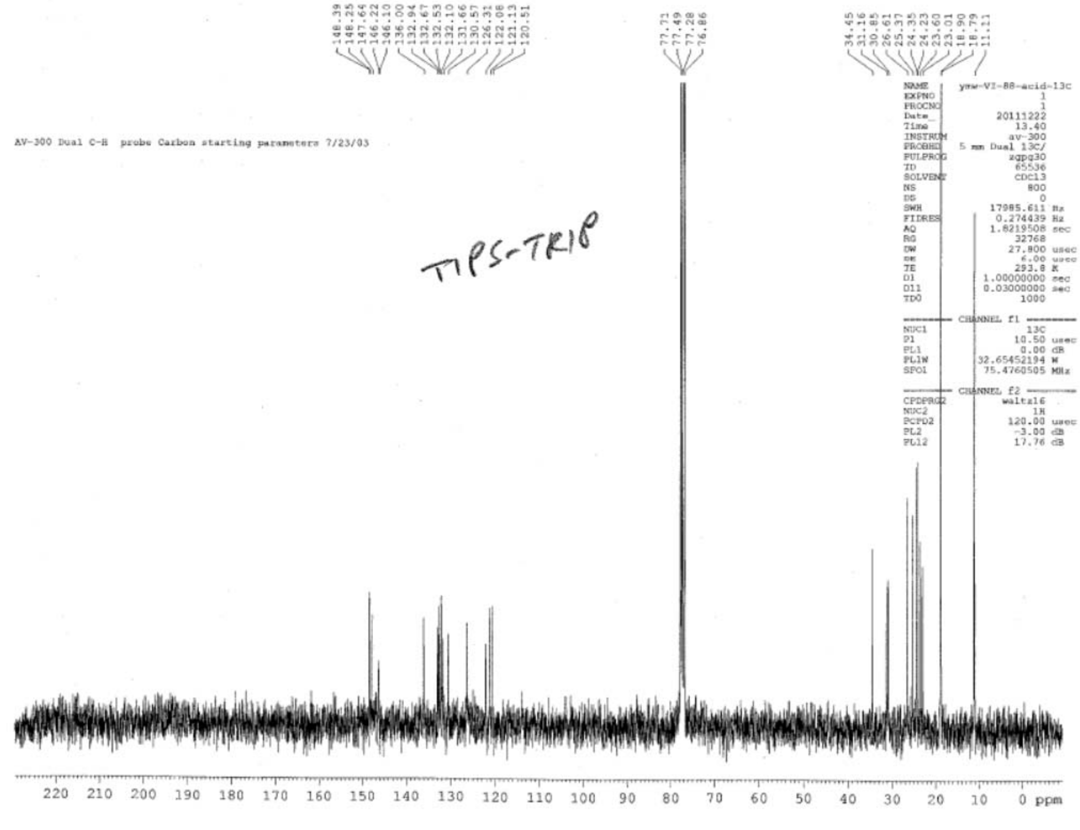


AVQ-400 QNP 31P Starting parameters. Trimethyl phosphate=

TIPS-TRIP

```
NAME       ymw-VI-88-acid
EXPNO                   1
PROCNO                  1
Date_            20111222
Time                13.33
INSTRUM           AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      0
SWH             64724.918 Hz
FIDRES           0.987624 Hz
AQ              0.5063156 sec
RG                   8192
DW                  7.725 usec
DE                   6.00 usec
TE                  293.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    32

========= CHANNEL f1 ========
NUC1                  31P
P1                   7.70 usec
PL1                 -2.00 dB
PL1W          26.27507401 W
SFO1         161.9674750 MHz

========= CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               70.00 usec
PL2                  0.00 dB
PL12                15.00 dB
```

S-3



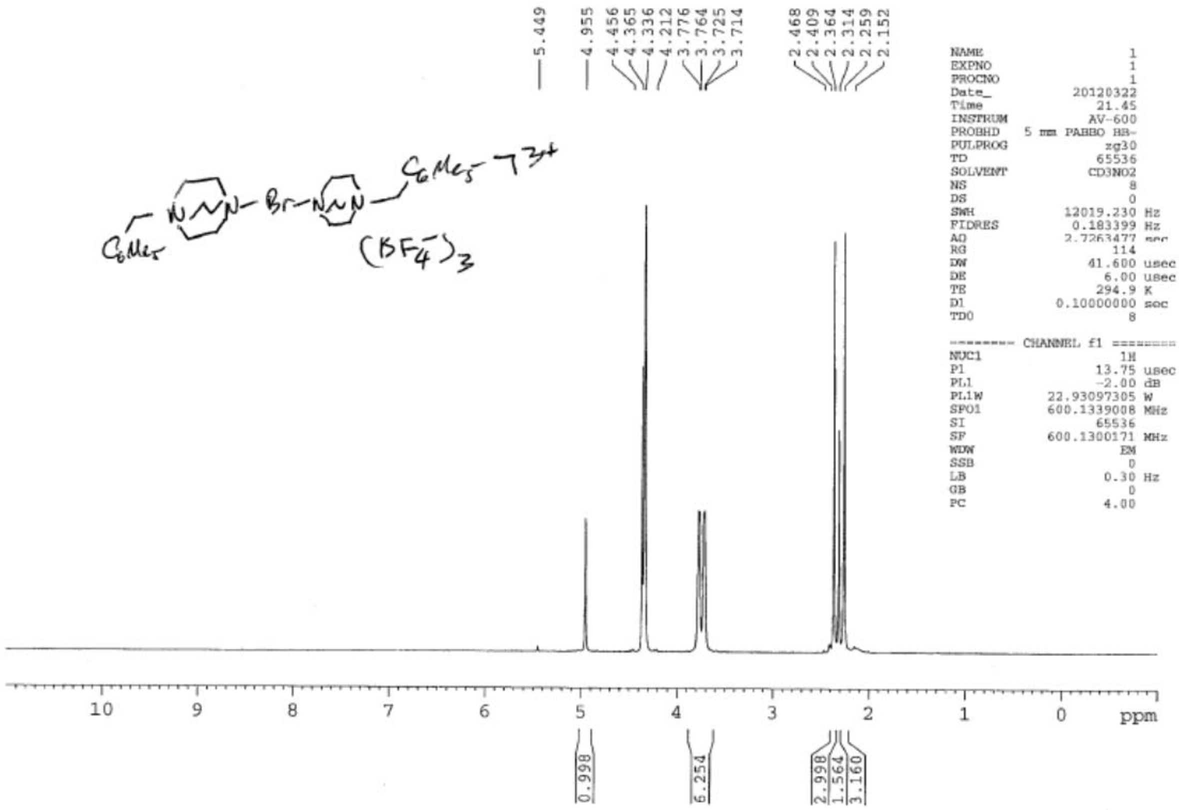
AV-300 Dual C-H probe Carbon starting parameters 7/23/03

TIPS-TRIP

```
NAME       ymw-VI-88-acid-13c
EXPNO                   1
PROCNO                  1
Date_            20111222
Time                13.40
INSTRUM            av-300
PROBHD   5 mm Dual 13C/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    800
DS                      0
SWH             17985.611 Hz
FIDRES           0.274439 Hz
AQ              1.8219508 sec
RG                  32768
DW                 27.800 usec
DE                   6.00 usec
TE                  293.8 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                  1000

========= CHANNEL f1 ========
NUC1                  13C
P1                  10.50 usec
PL1                  0.00 dB
PL1W          32.65452194 W
SFO1          75.4760505 MHz

========= CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              120.00 usec
PL2                 -3.00 dB
PL12                17.76 dB
```

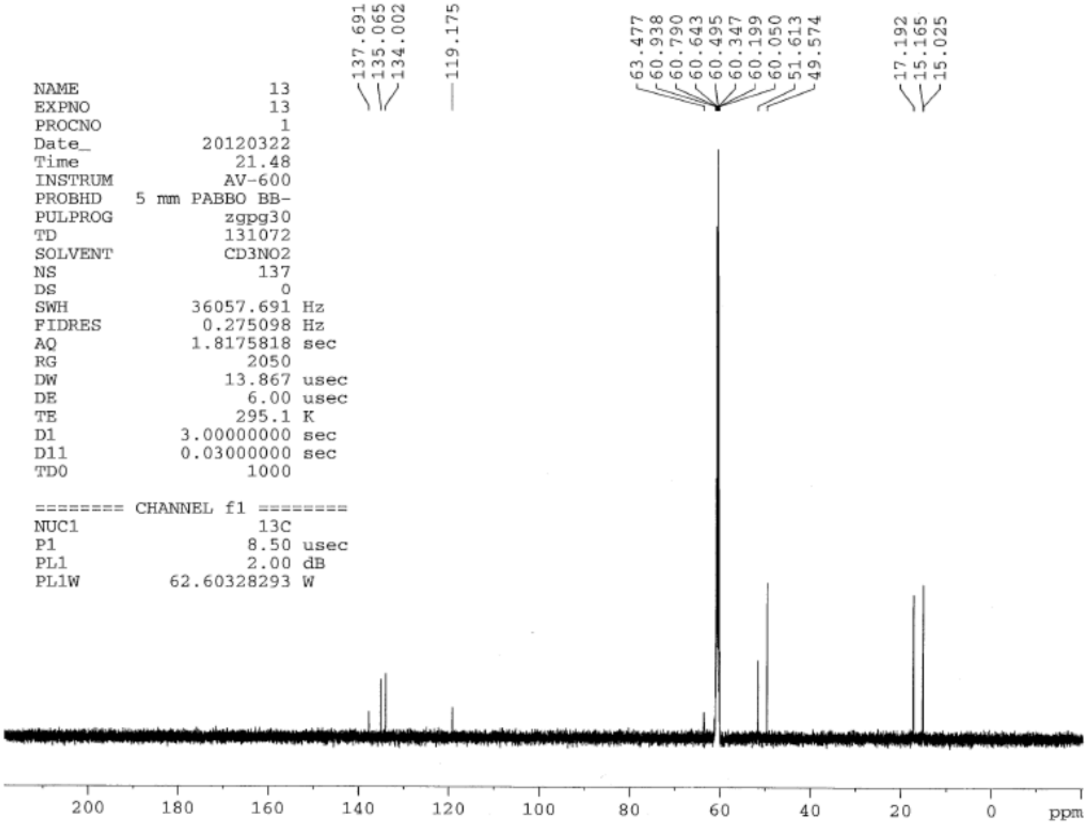
S-4

AV-600 ZBO proton starting parameters 11/16/08 RN

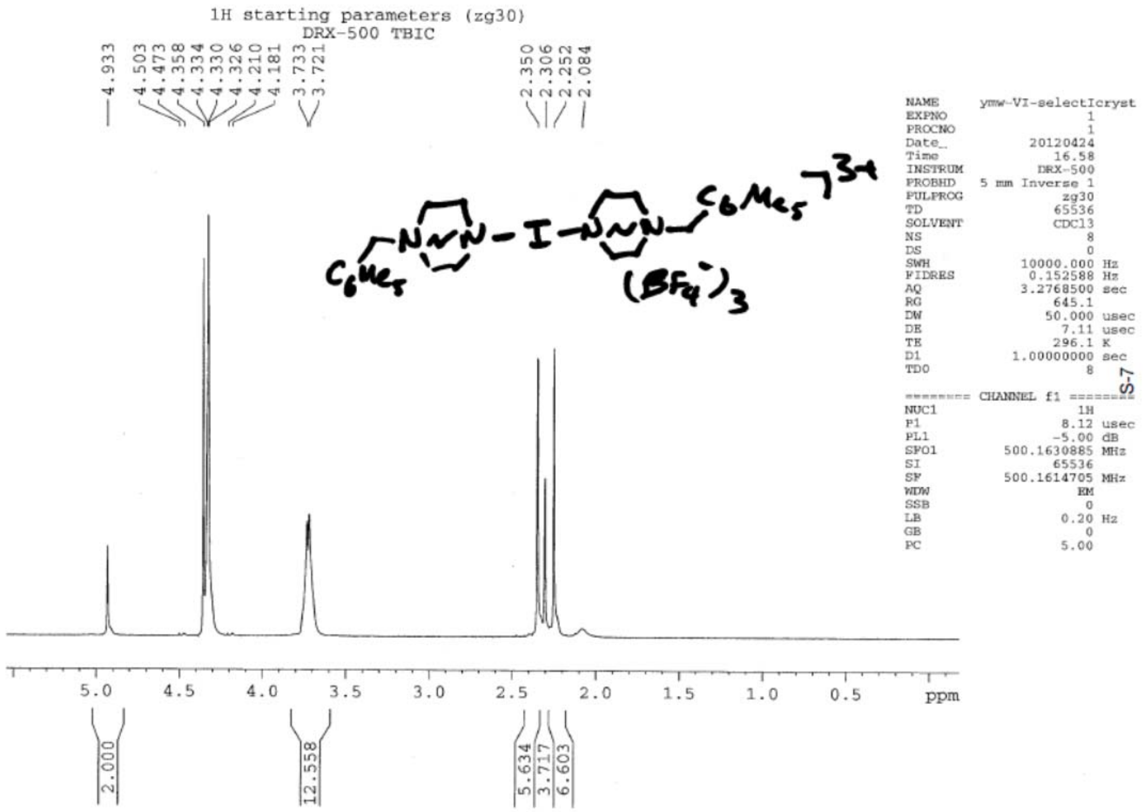


```
NAME                1
EXPNO               1
PROCNO              1
Date_        20120322
Time            21.45
INSTRUM        AV-600
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              65536
SOLVENT        CD3NO2
NS                  8
DS                  0
SWH         12019.230 Hz
FIDRES       0.183399 Hz
AQ          2.7263477 sec
RG                114
DW             41.600 usec
DE               6.00 usec
TE              294.9 K
D1         0.10000000 sec
TD0                 8

======== CHANNEL f1 ========
NUC1               1H
P1              13.75 usec
PL1             -2.00 dB
PL1W      22.93097305 W
SFO1      600.1339008 MHz
SI              65536
SF        600.1300171 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               4.00
```

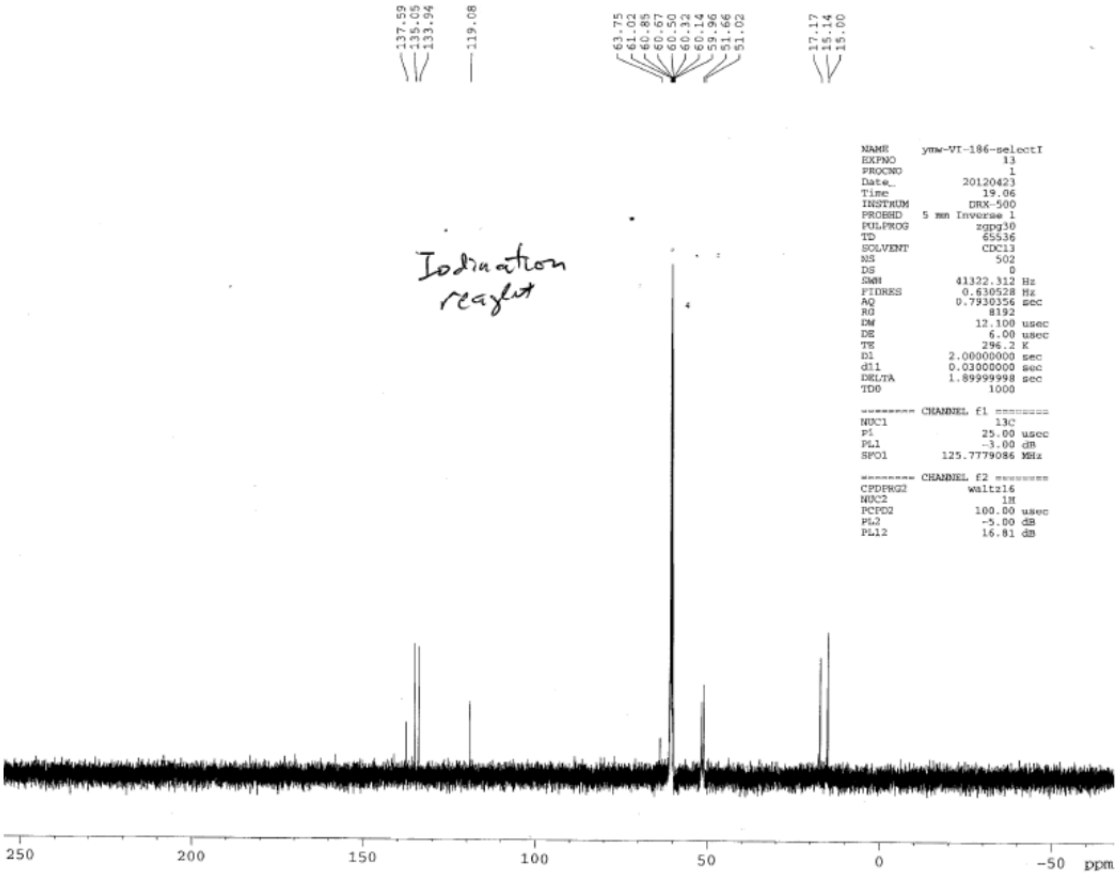
S-5



```
NAME                13
EXPNO               13
PROCNO               1
Date_         20120322
Time             21.48
INSTRUM         AV-600
PROBHD   5 mm PABBO BB-
PULPROG        zgpg30
TD              131072
SOLVENT         CD3NO2
NS                 137
DS                   0
SWH          36057.691 Hz
FIDRES        0.275098 Hz
AQ           1.8175818 sec
RG                2050
DW              13.867 usec
DE                6.00 usec
TE               295.1 K
D1          3.00000000 sec
D11         0.03000000 sec
TD0               1000

======== CHANNEL f1 ========
NUC1               13C
P1                8.50 usec
PL1               2.00 dB
PL1W       62.60328293 W
```

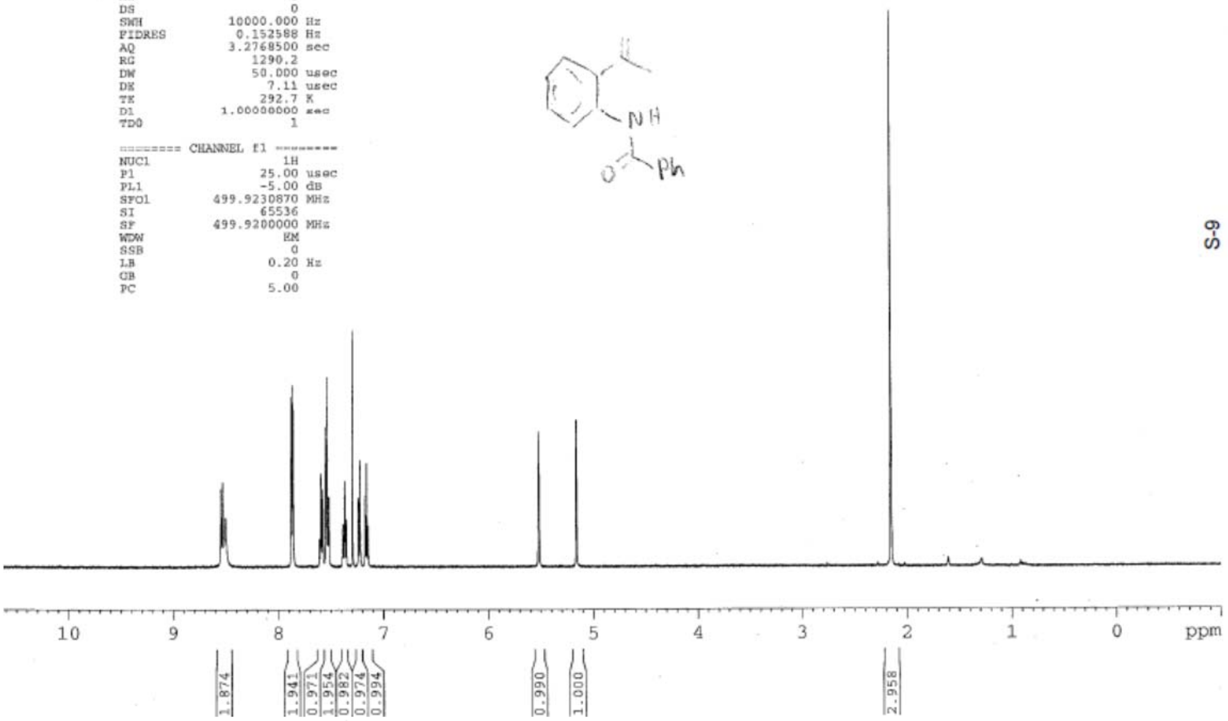


```
NAME        ymw-VI-selectIcryst
EXPNO                     1
PROCNO                    1
Date_              20120424
Time                  16.58
INSTRUM             DRX-500
PROBHD     5 mm Inverse 1
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        0
SWH               10000.000 Hz
FIDRES             0.152588 Hz
AQ                3.2768500 sec
RG                    645.1
DW                   50.000 usec
DE                     7.11 usec
TE                    296.1 K
D1               1.00000000 sec
TD0                       8

======== CHANNEL f1 ========
NUC1                     1H
P1                     8.12 usec
PL1                   -5.00 dB
SFO1            500.1630885 MHz
SI                    65536
SF              500.1614705 MHz
WDW                      EM
SSB                       0
LB                     0.20 Hz
GB                        0
PC                     5.00
```

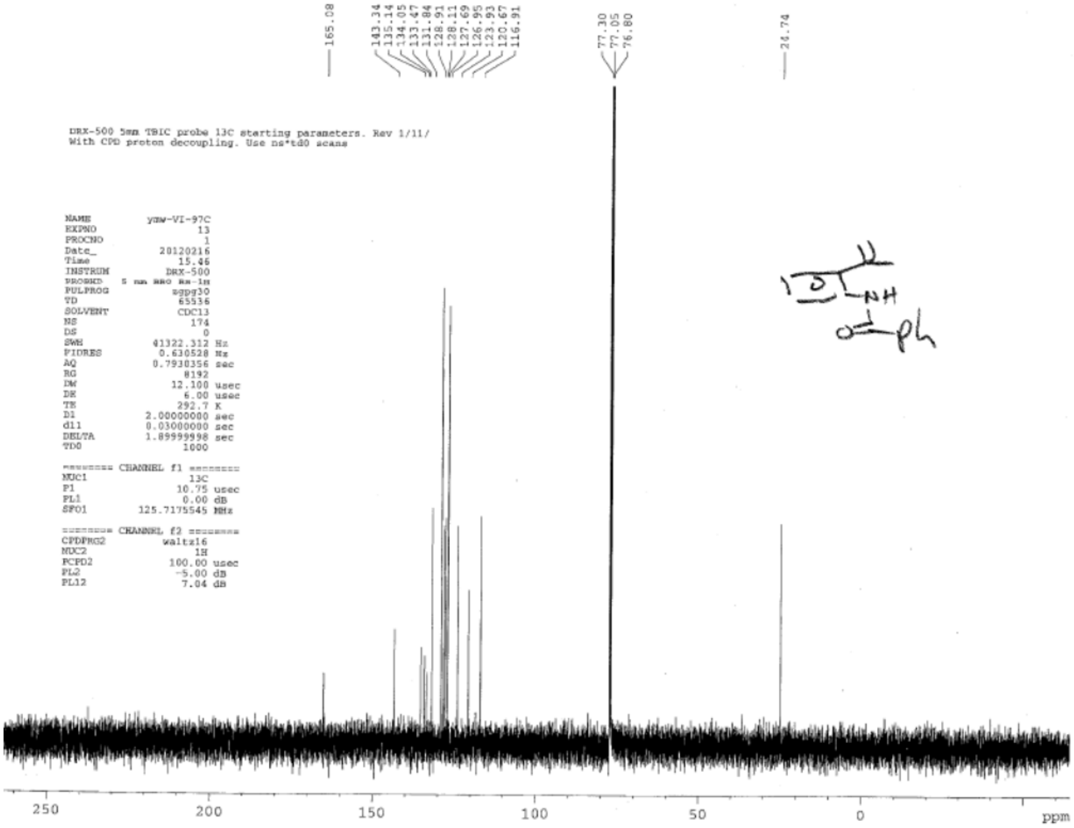


```
NAME        ymw-VI-186-selectI
EXPNO                    13
PROCNO                    1
Date_              20120423
Time                  19.06
INSTRUM             DRX-500
PROBHD     5 mm Inverse 1
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      502
DS                        0
SWH               41322.312 Hz
FIDRES             0.630528 Hz
AQ                0.7930356 sec
RG                     8192
DW                   12.100 usec
DE                     6.00 usec
TE                    296.2 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                    1000

======== CHANNEL f1 ========
NUC1                    13C
P1                    25.00 usec
PL1                   -3.00 dB
SFO1            125.7779086 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                   -5.00 dB
PL12                  16.81 dB
```

```
NAME          ymw-VI-97C
EXPNO                  1
PROCNO                 1
Date_           20120216
Time               15.44
INSTRUM          DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10000.000 Hz
FIDRES          0.152588 Hz
AQ             3.2768500 sec
RG                1290.2
DW                50.000 usec
DE                  7.11 usec
TE                 292.7 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 25.00 usec
PL1                -5.00 dB
SFO1         499.9230870 MHz
SI                 65536
SF           499.9200000 MHz
WDW                   EM
SSB                    0
LB                  0.20 Hz
GB                     0
PC                  5.00
```



S-9



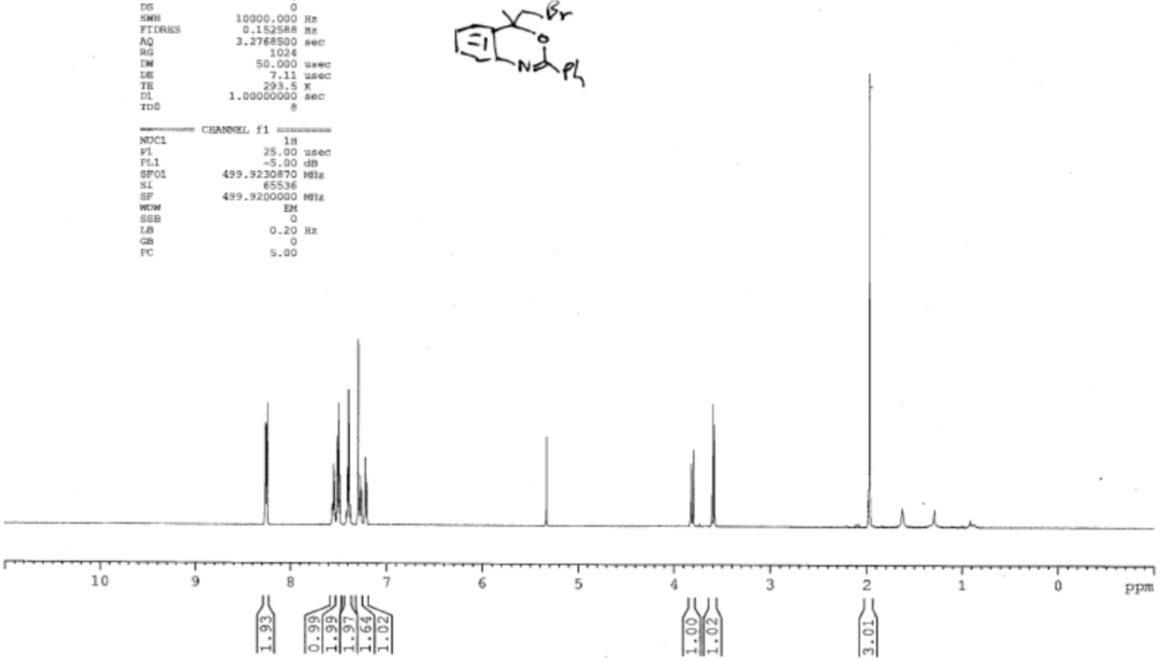
```
DRX-500 5mm TBIC probe 13C starting parameters. Rev 1/11/
With CPD proton decoupling. Use ns*td0 scans
```

```
NAME          ymw-VI-97C
EXPNO                 13
PROCNO                 1
Date_           20120216
Time               15.46
INSTRUM          DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   174
DS                     0
SWH            41322.312 Hz
FIDRES          0.630528 Hz
AQ             0.7930356 sec
RG                  8192
DW                12.100 usec
DE                  6.00 usec
TE                 292.7 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                 1000

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.75 usec
PL1                 0.00 dB
SFO1         125.7175545 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -5.00 dB
PL12                7.04 dB
```

```
1H starting parameters (zg30)
DRX-500 TBIC
```

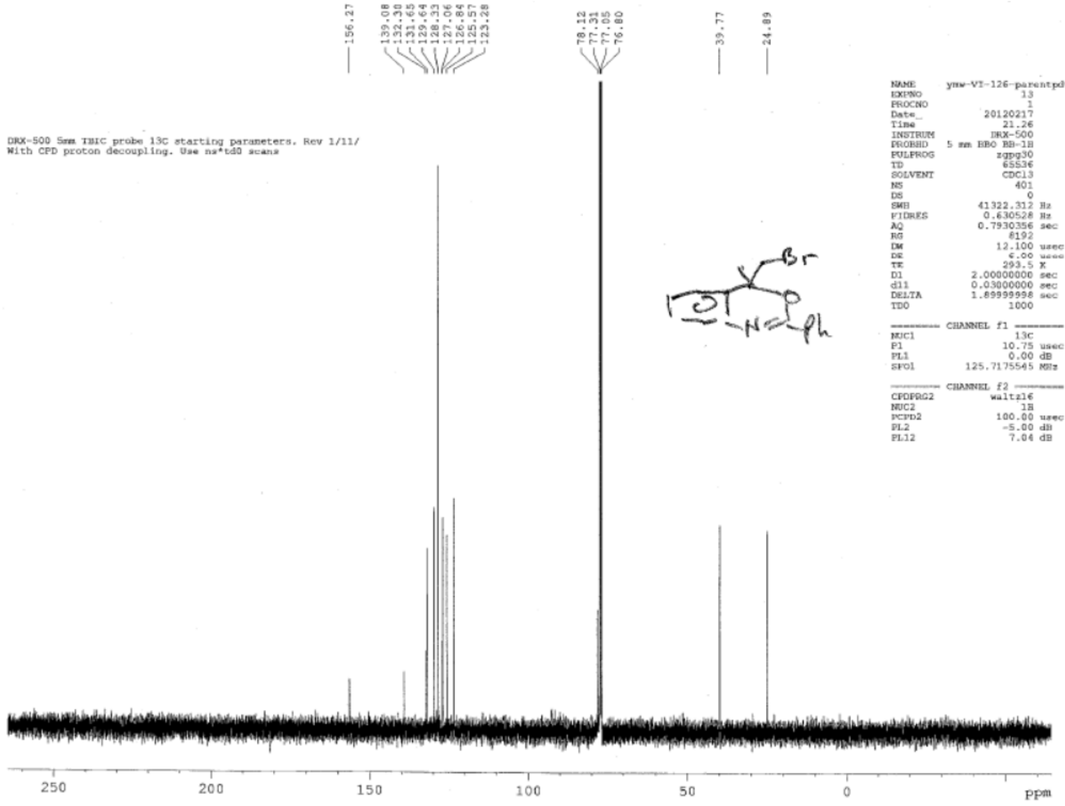
1B

```
NAME       ymw-VI-126-parentpdt
EXPNO                     1
PROCNO                    1
Date_              20120217
Time                  21.25
INSTRUM             DRX-500
PROBHD     5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        0
SWH               10000.000 Hz
FIDRES             0.152588 Hz
AQ                3.2768500 sec
RG                     1024
DW                   50.000 usec
DE                     7.11 usec
TE                    293.5 K
D1               1.00000000 sec
TD0                       8

========== CHANNEL f1 ==========
NUC1                     1H
P1                    25.00 usec
PL1                   -5.00 dB
SFO1            499.9230870 MHz
SI                    65536
SF              499.9200000 MHz
WDW                      EM
SSB                       0
LB                     0.20 Hz
GB                        0
PC                     5.00
```

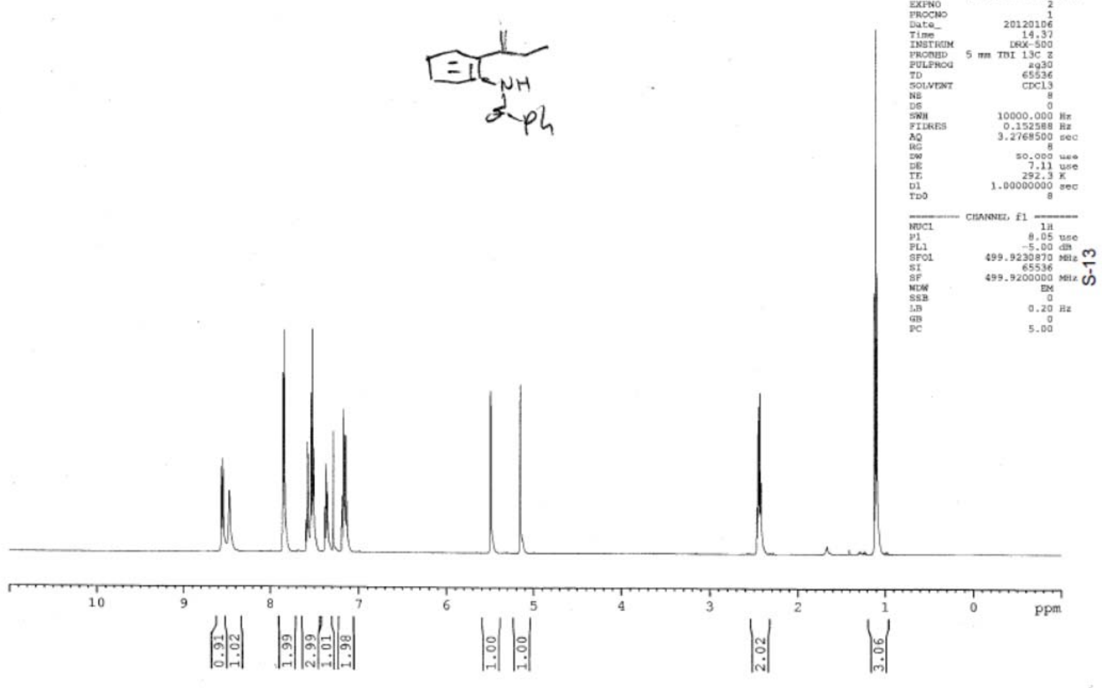


```
DRX-500 5mm TBIC probe 13C starting parameters. Rev 1/11/
With CPD proton decoupling. Use ns*td0 scans
```

```
NAME       ymw-VI-126-parentpdt
EXPNO                    13
PROCNO                    1
Date_              20120217
Time                  21.26
INSTRUM             DRX-500
PROBHD     5 mm BBO BB-1H
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      401
DS                        0
SWH               41322.312 Hz
FIDRES             0.630528 Hz
AQ                0.7930356 sec
RG                     8192
DW                   12.100 usec
DE                     6.00 usec
TE                    293.5 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                    1000

========== CHANNEL f1 ==========
NUC1                    13C
P1                    10.75 usec
PL1                    0.00 dB
SFO1            125.7175545 MHz

========== CHANNEL f2 ==========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                   -5.00 dB
PL12                   7.04 dB
```

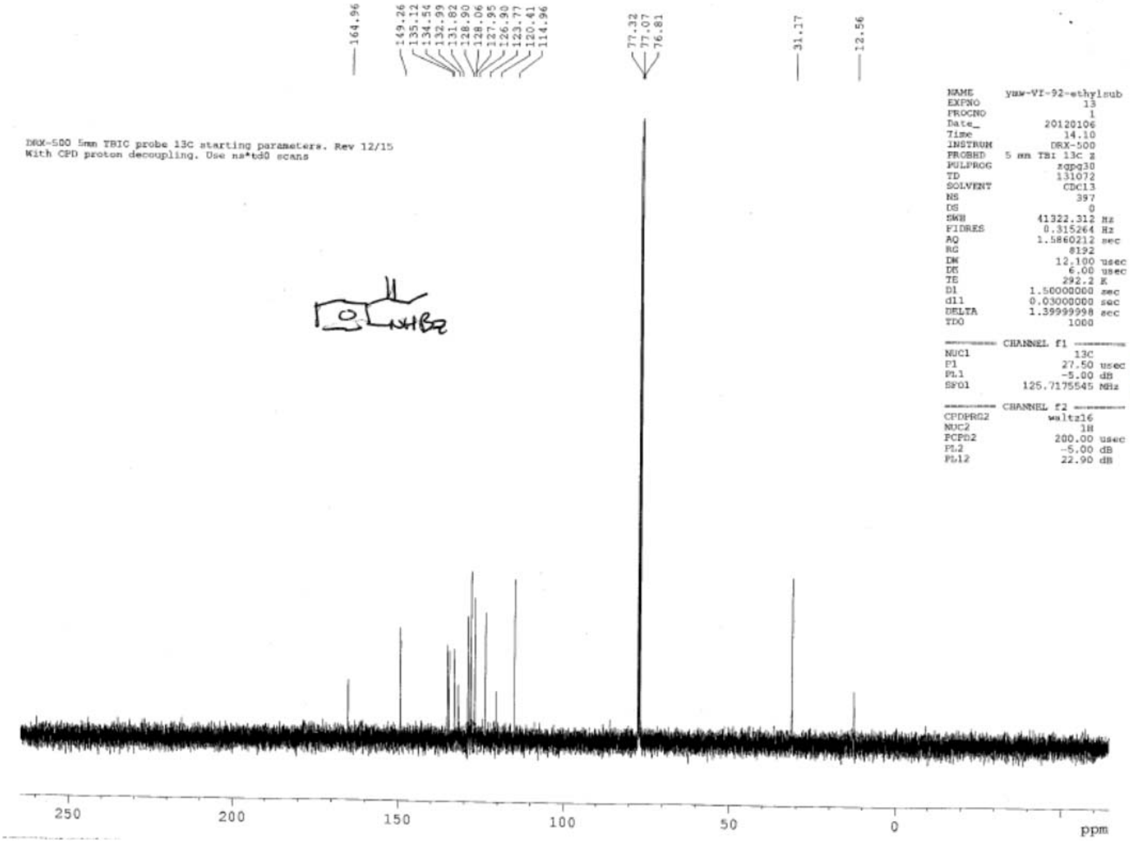


1H starting parameters (zg30)
DRX-500 TBIC



```
NAME      ymw-VI-92-ethylsub
EXPNO                      2
PROCNO                     1
Date_               20120106
Time                   14.37
INSTRUM              DRX-500
PROBHD    5 mm TBI 13C Z
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         8
DS                         0
SWH            10000.000 Hz
FIDRES          0.152588 Hz
AQ             3.2768500 sec
RG                         8
DW                50.000 use
DE                  7.11 use
TE                 292.3 K
D1            1.00000000 sec
TD0                        8

========= CHANNEL f1 ========
NUC1                      1H
P1                  8.05 use
PL1                -5.00 dB
SFO1         499.9230870 MHz
SI                     65536
SF           499.9200000 MHz
WDW                       EM
SSB                        0
LB                  0.20 Hz
GB                         0
PC                      5.00
```

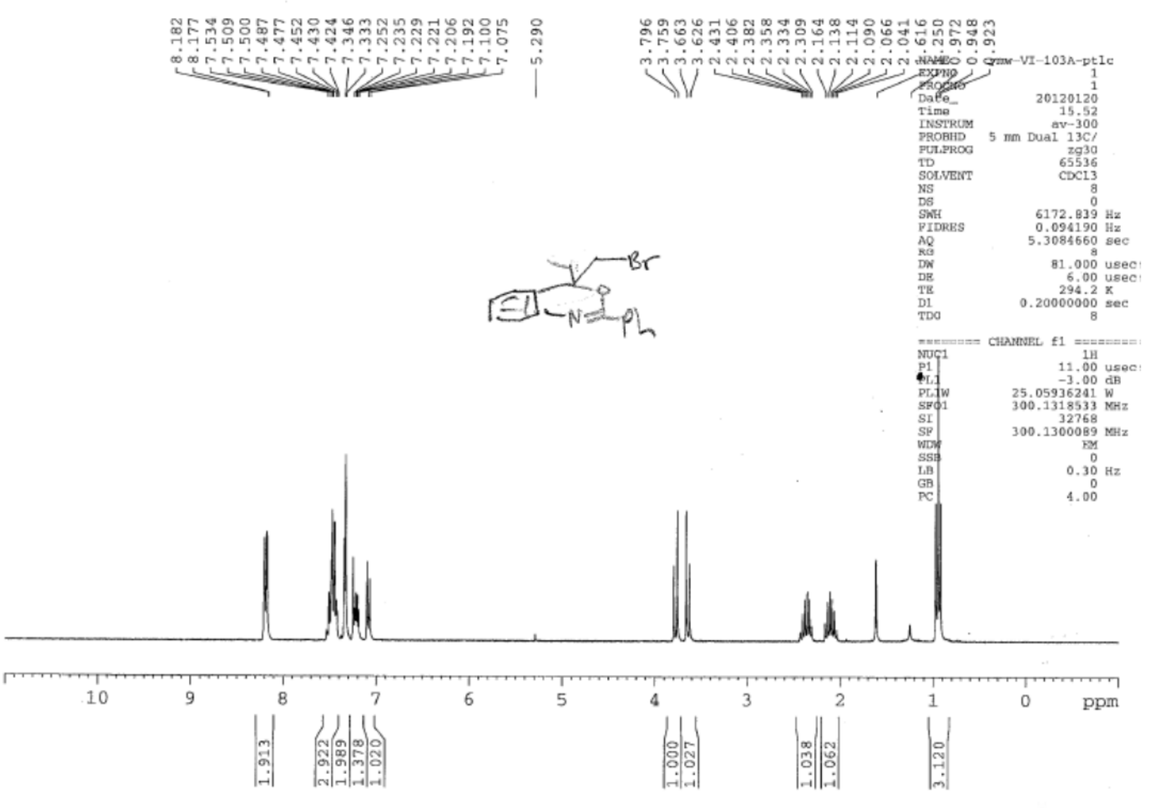
S-13



DRX-500 5mm TBIC probe 13C starting parameters. Rev 12/15
With CPD proton decoupling. Use ns*td0 scans

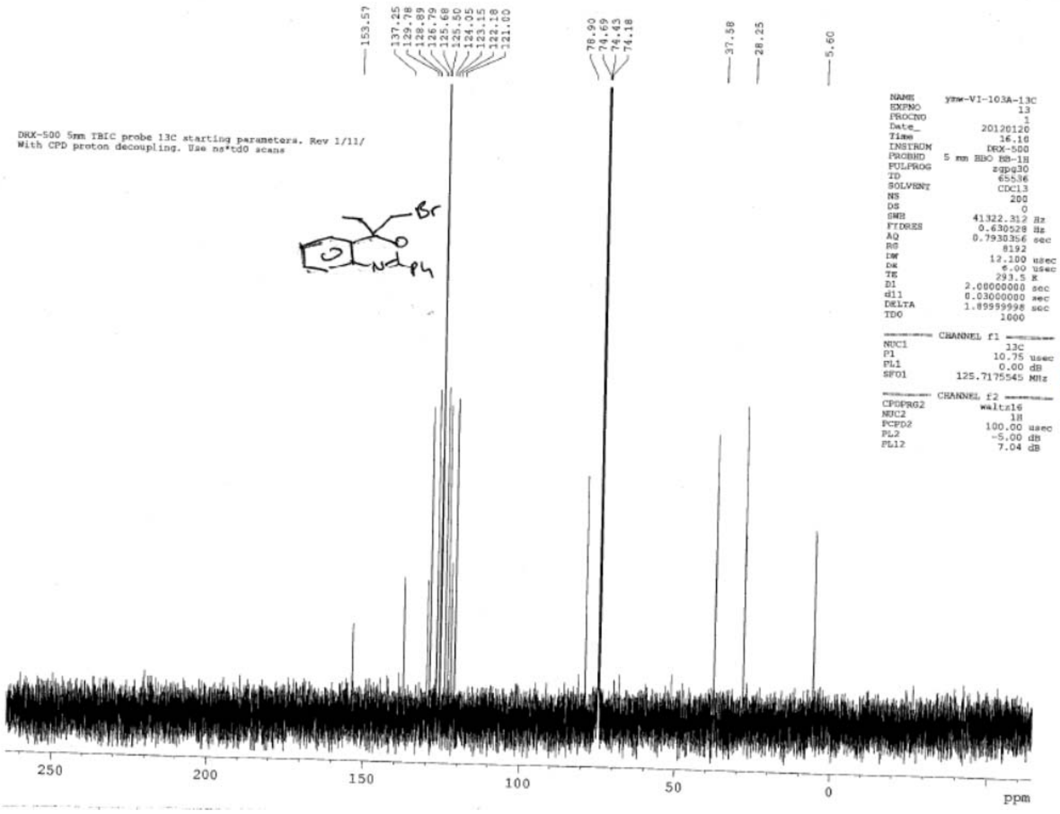
```
NAME      ymw-VI-92-ethylsub
EXPNO                     13
PROCNO                     1
Date_               20120106
Time                   14.10
INSTRUM              DRX-500
PROBHD    5 mm TBI 13C Z
PULPROG               zgpg30
TD                    131072
SOLVENT                CDCl3
NS                       397
DS                         0
SWH            41322.312 Hz
FIDRES          0.315264 Hz
AQ             1.5860212 sec
RG                      8192
DW                12.100 usec
DE                  6.00 usec
TE                 292.2 K
D1            1.50000000 sec
d11           0.03000000 sec
DELTA         1.39999998 sec
TD0                     1000

========= CHANNEL f1 ========
NUC1                     13C
P1                 27.50 usec
PL1                -5.00 dB
SFO1         125.7175545 MHz

========= CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2             200.00 usec
PL2                -5.00 dB
PL12               22.90 dB
```

) Dual C-H probe proton starting parameters 7/23/(



```
NAME        ymw-VI-103A-ptlc
EXPNO                      1
PROCNO                     1
Date_               20120120
Time                   15.52
INSTRUM               av-300
PROBHD     5 mm Dual 13C/
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         8
DS                         0
SWH               6172.839 Hz
FIDRES            0.094190 Hz
AQ               5.3084660 sec
RG                         8
DW                  81.000 usec
DE                    6.00 usec
TE                   294.2 K
D1              0.20000000 sec
TD0                        8

======== CHANNEL f1 ========
NUC1                      1H
P1                     11.00 usec
PL1                    -3.00 dB
PL1W             25.05936241 W
SFO1          300.1318533 MHz
SI                     32768
SF            300.1300089 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      4.00
```

DRX-500 5mm TBIC probe 13C starting parameters. Rev 1/11/
With CPD proton decoupling. Use ns*td0 scans



```
NAME        ymw-VI-103A-13C
EXPNO                    13
PROCNO                    1
Date_              20120120
Time                  16.10
INSTRUM             DRX-500
PROBHD     5 mm BBO BB-1H
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      200
DS                        0
SWH              41322.312 Hz
FIDRES            0.630528 Hz
AQ               0.7930356 sec
RG                     8192
DW                   12.100 usec
DE                     6.00 usec
TE                    293.5 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                    1000

======== CHANNEL f1 ========
NUC1                    13C
P1                    10.75 usec
PL1                    0.00 dB
SFO1         125.7175545 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                   -5.00 dB
PL12                   7.04 dB
```

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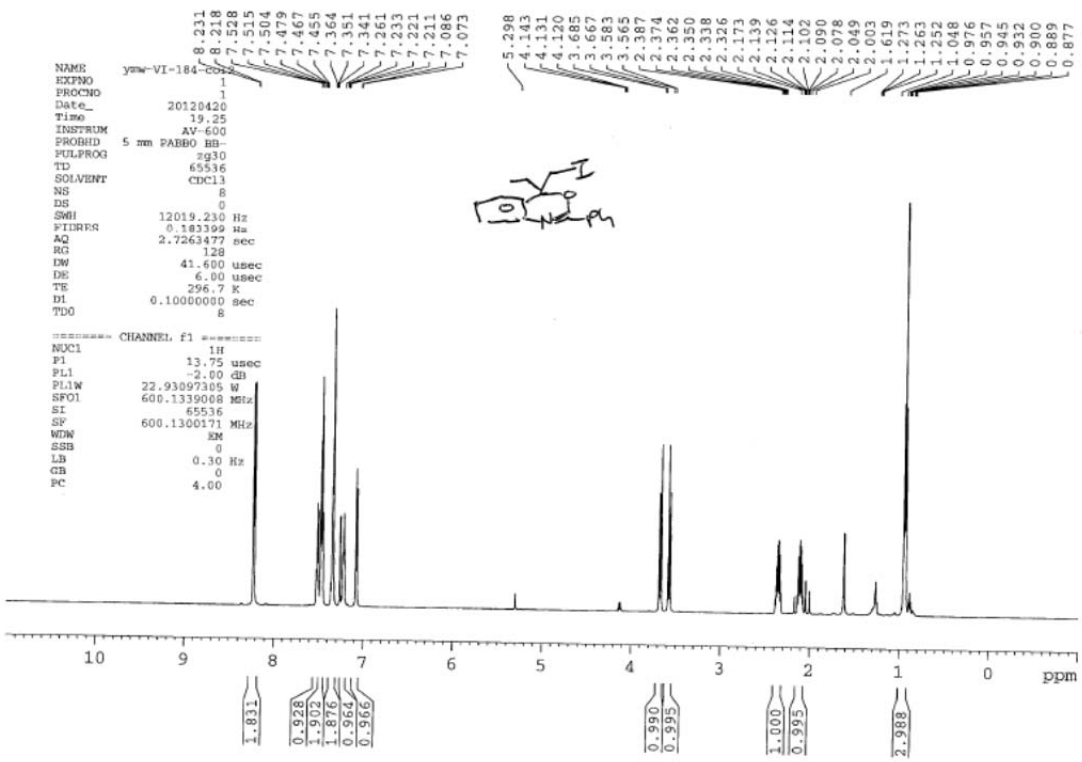
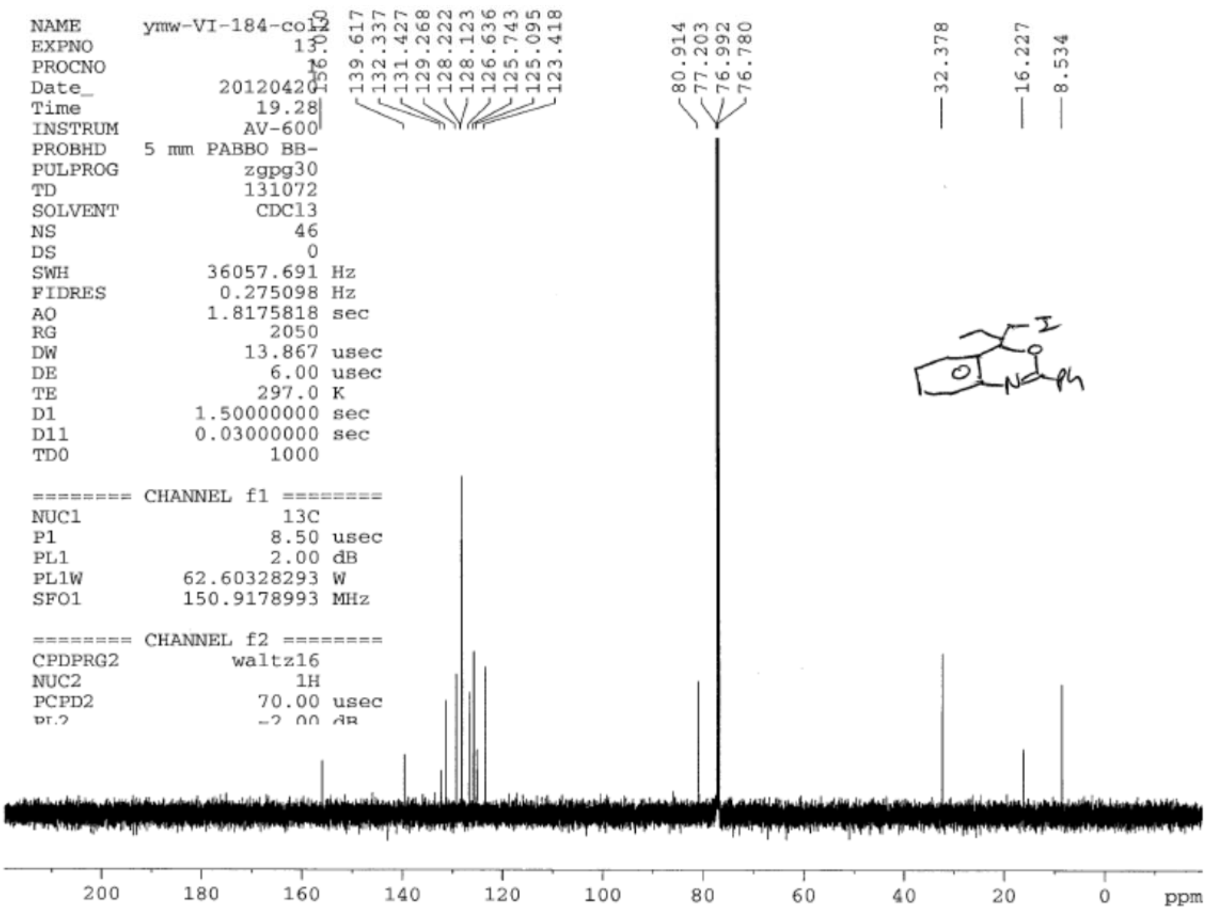
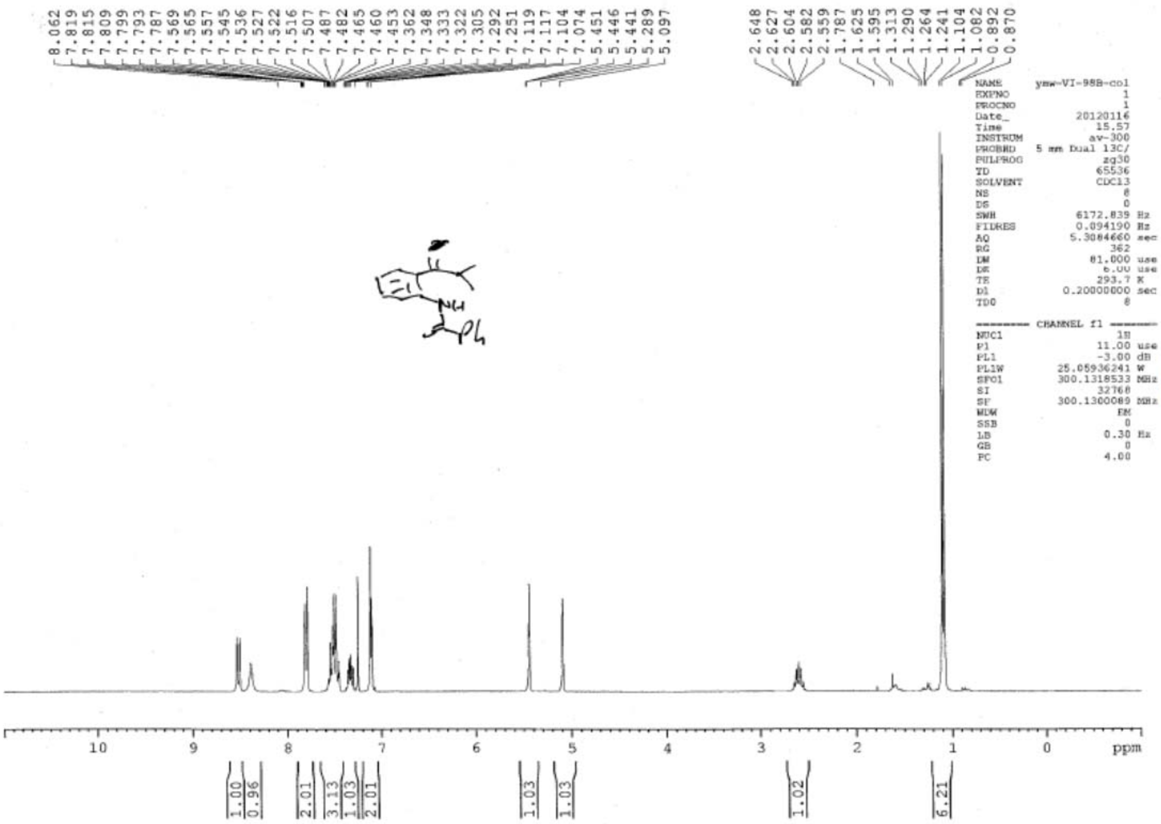
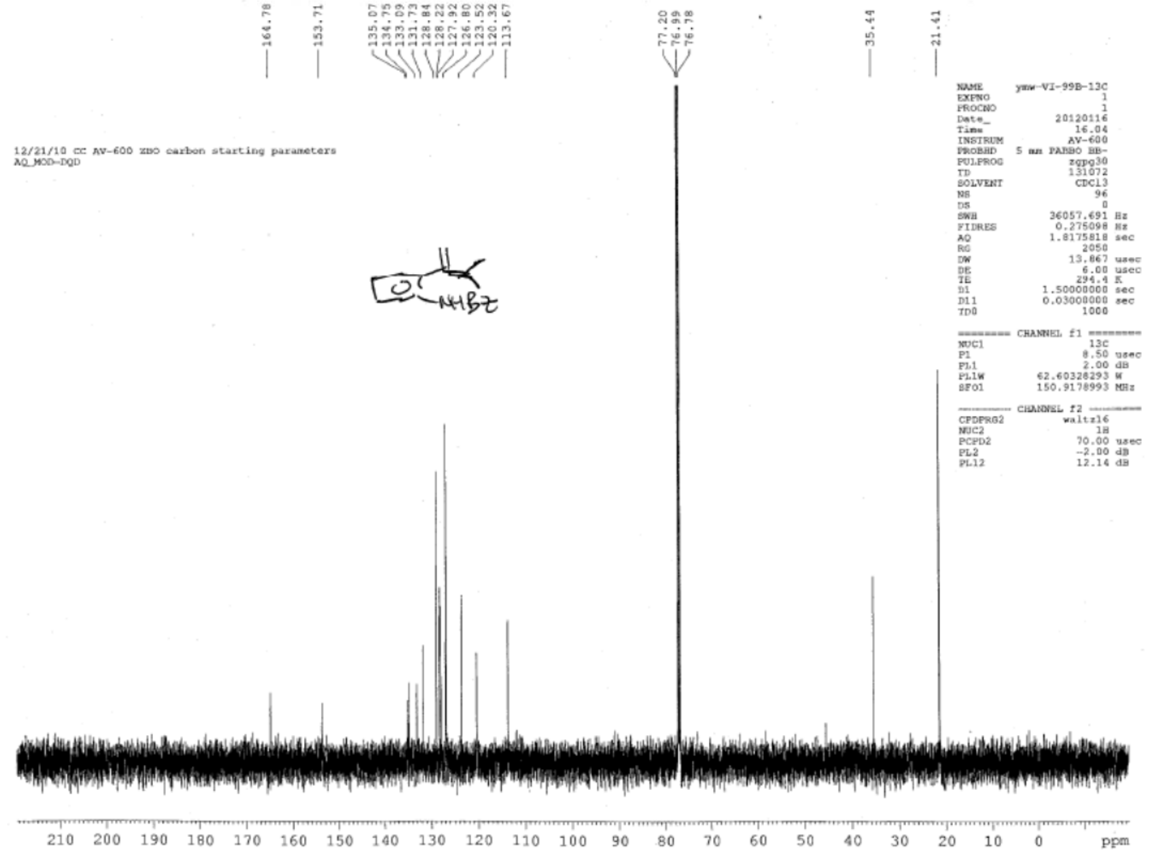
AV-600 ZBO proton starting parameters 11/16/08 RN

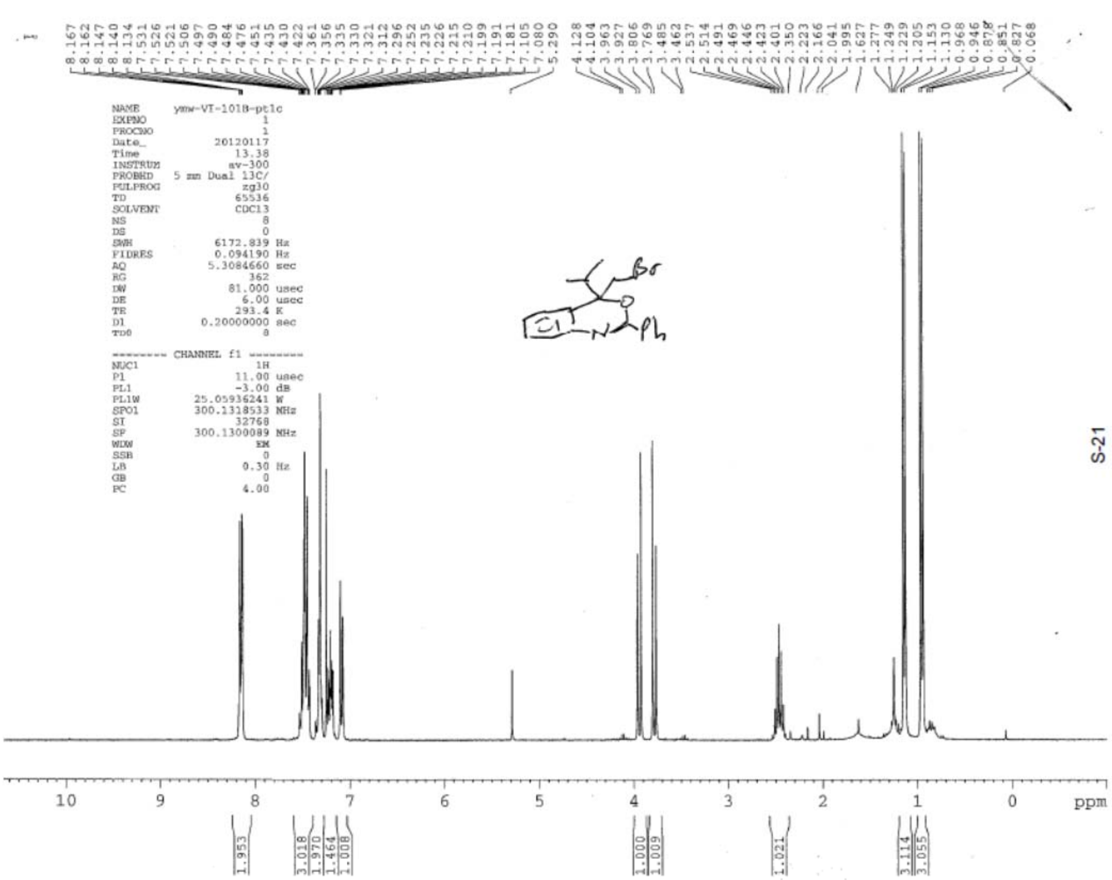


S-17



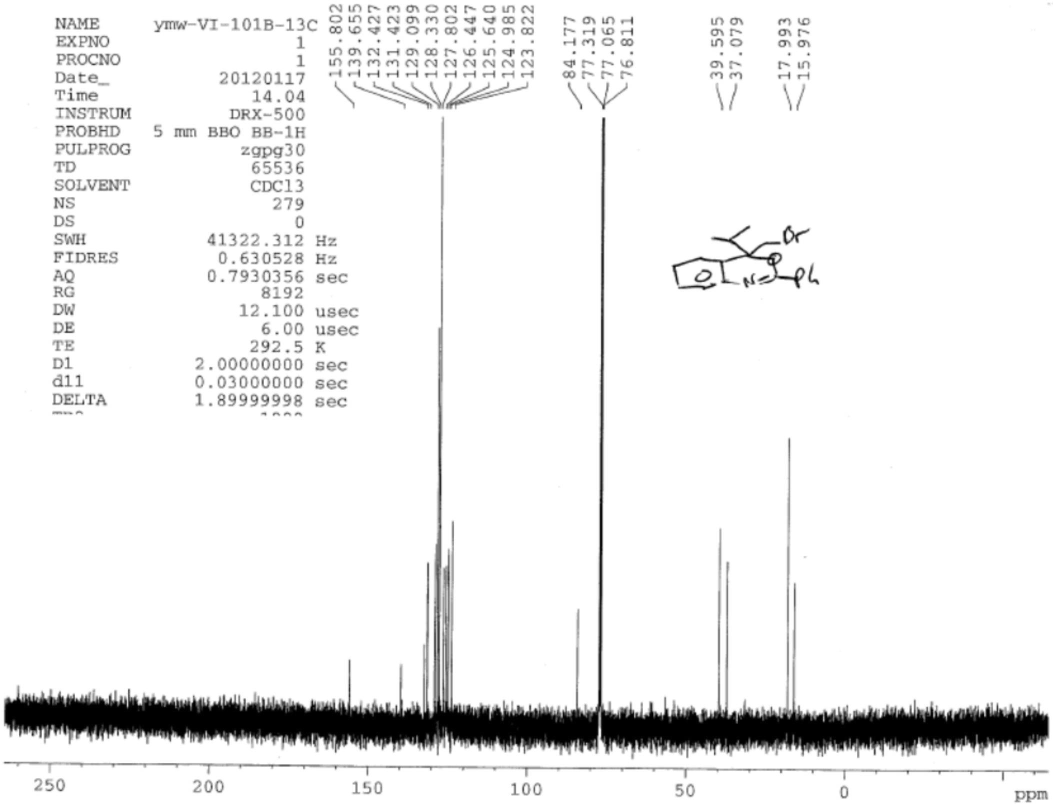

8.062
7.819
7.815
7.809
7.799
7.793
7.787
7.569
7.565
7.557
7.545
7.536
7.527
7.522
7.516
7.507
7.487
7.482
7.465
7.460
7.453
7.362
7.348
7.333
7.322
7.305
7.292
7.251
7.119
7.117
7.104
7.074
5.451
5.446
5.441
5.289
5.097
2.648
2.627
2.604
2.582
2.559
1.787
1.625
1.595
1.313
1.290
1.264
1.241
1.104
1.082
0.892
0.870
NH
Ph
NAME ymw-VI-98B-col
EXPNO 1
PROCNO 1
Date_ 20120116
Time 15.57
INSTRUM av-300
PROBHD 5 mm Dual 13C/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 362
DW 81.000 use
DE 6.00 use
TE 293.7 K
D1 0.20000000 sec
TD0 8
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 use
PL1 -3.00 dB
PL1W 25.05936241 W
SFO1 300.1318533 MHz
SI 32768
SF 300.1300089 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.96
2.01
3.13
1.03
2.01
1.03
1.03
1.02
6.21


164.78
153.71
135.07
134.75
133.09
131.73
128.84
128.22
127.92
126.80
123.52
120.32
113.67
77.20
76.99
76.78
35.44
21.41
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD-DQD
NHBz
NAME ymw-VI-99B-13C
EXPNO 1
PROCNO 1
Date_ 20120116
Time 16.04
INSTRUM AV-600
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 96
DS 0
SWH 36057.691 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 2050
DW 13.867 usec
DE 6.00 usec
TE 294.4 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1000
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 2.00 dB
PL1W 62.60328293 W
SFO1 150.9178993 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 -2.00 dB
PL12 12.14 dB
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

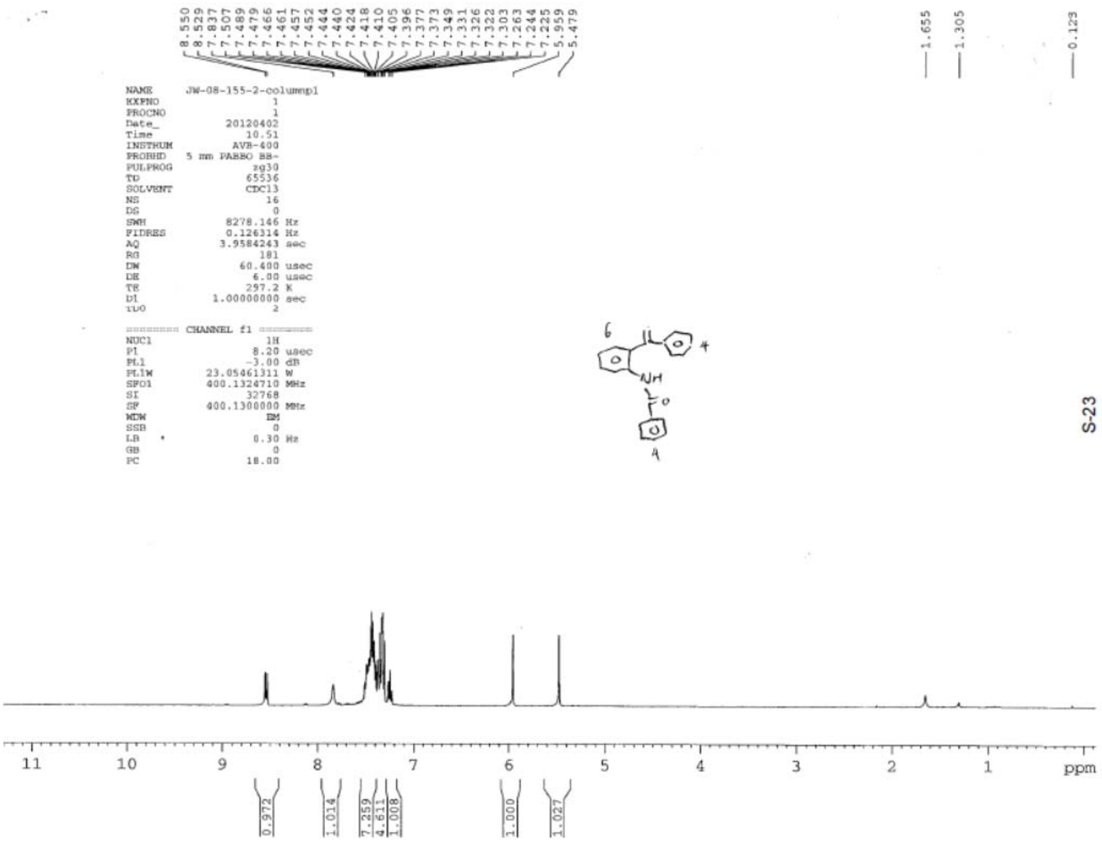


```
NAME        ymw-VI-101B-pt1c
EXPNO                      1
PROCNO                     1
Date_               20120117
Time                   13.38
INSTRUM               av-300
PROBHD      5 mm Dual 13C/
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         8
DS                         0
SWH                 6172.839 Hz
FIDRES              0.094190 Hz
AQ                 5.3084660 sec
RG                       362
DW                    81.000 usec
DE                      6.00 usec
TE                     293.4 K
D1                0.20000000 sec
TD0                        8

======== CHANNEL f1 ========
NUC1                      1H
P1                     11.00 usec
PL1                    -3.00 dB
PL1W             25.05936241 W
SFO1             300.1318533 MHz
SI                     32768
SF               300.1300089 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      4.00
```



```
NAME        ymw-VI-101B-13C
EXPNO                     1
PROCNO                    1
Date_              20120117
Time                  14.04
INSTRUM             DRX-500
PROBHD      5 mm BBO BB-1H
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      279
DS                        0
SWH               41322.312 Hz
FIDRES             0.630528 Hz
AQ                0.7930356 sec
RG                     8192
DW                   12.100 usec
DE                     6.00 usec
TE                    292.5 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
```



```
NAME       JW-08-155-2-columnp1
EXPNO                     1
PROCNO                    1
Date_              20120402
Time                  10.51
INSTRUM             AVB-400
PROBHD     5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                3.9584243 sec
RG                      181
DW                   60.400 usec
DE                     6.00 usec
TE                    297.2 K
D1               1.00000000 sec
TD0                       2

======== CHANNEL f1 ========
NUC1                     1H
P1                     8.20 usec
PL1                   -3.00 dB
PL1W            23.05461311 W
SFO1            400.1324710 MHz
SI                    32768
SF              400.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                    18.00
```

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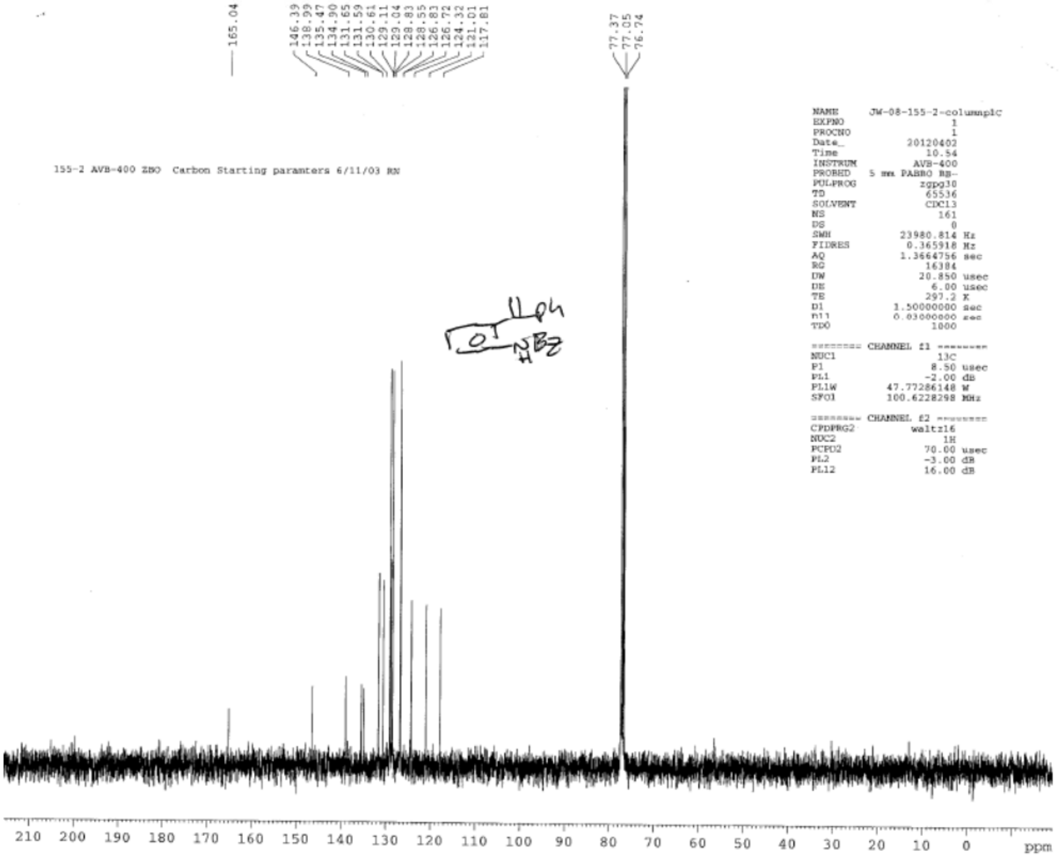
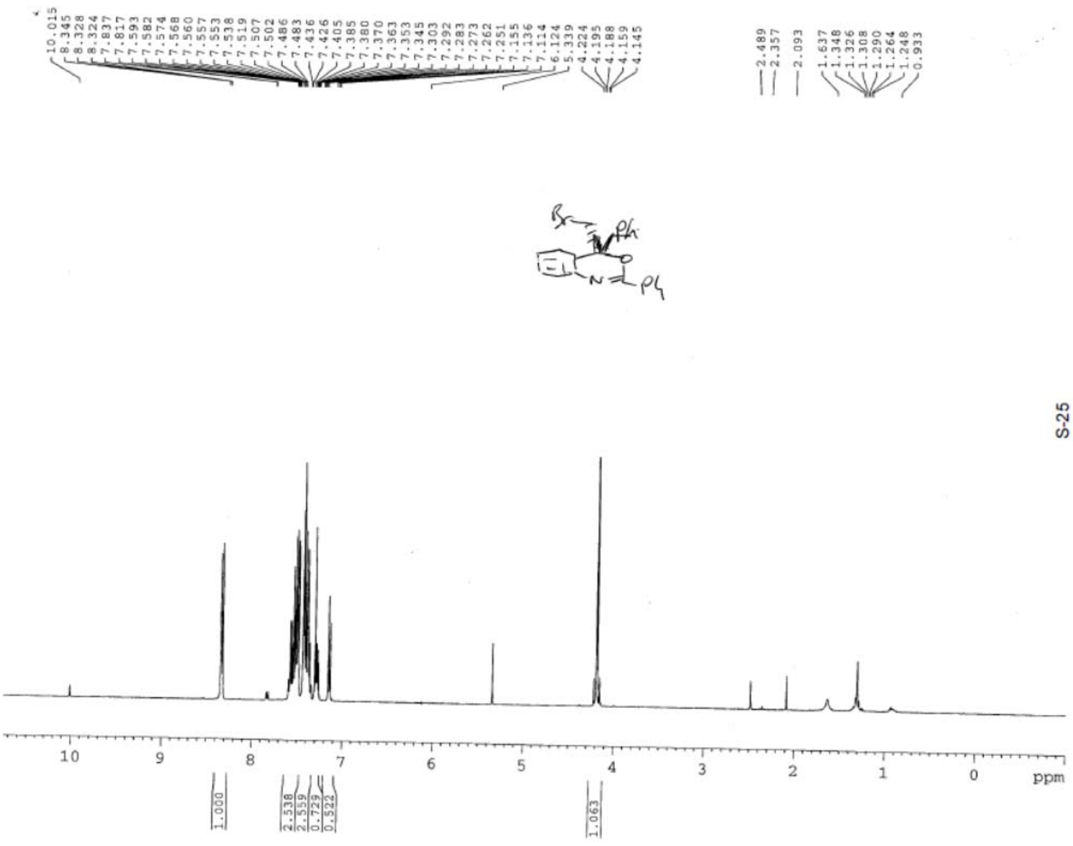


155-2 AVB-400 ZBO Carbon Starting paramters 6/11/03 RN

```
NAME       JW-08-155-2-columnplC
EXPNO                     1
PROCNO                    1
Date_              20120402
Time                  10.54
INSTRUM             AVB-400
PROBHD     5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      161
DS                        0
SWH               23980.814 Hz
FIDRES             0.365918 Hz
AQ                1.3664756 sec
RG                    16384
DW                   20.850 usec
DE                     6.00 usec
TE                    297.2 K
D1               1.50000000 sec
D11              0.03000000 sec
TD0                    1000

======== CHANNEL f1 ========
NUC1                    13C
P1                     8.50 usec
PL1                   -2.00 dB
PL1W            47.77286148 W
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 70.00 usec
PL2                   -3.00 dB
PL12                  16.00 dB
```



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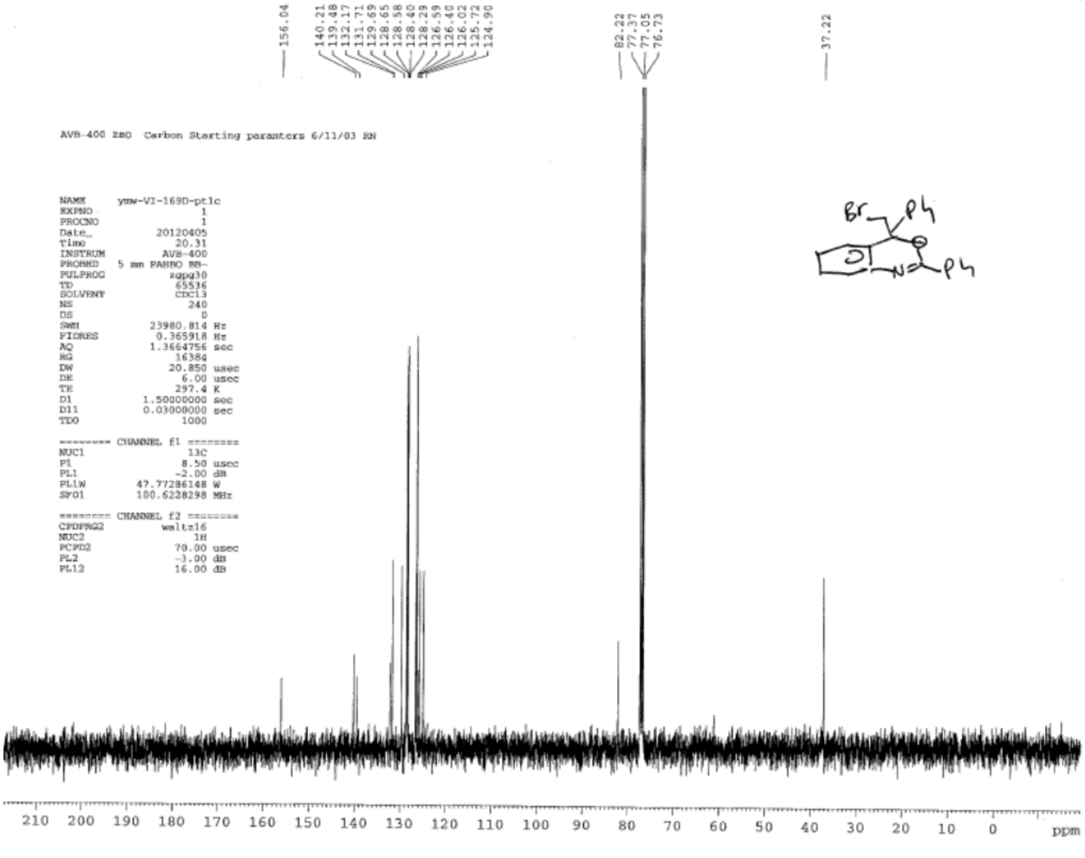


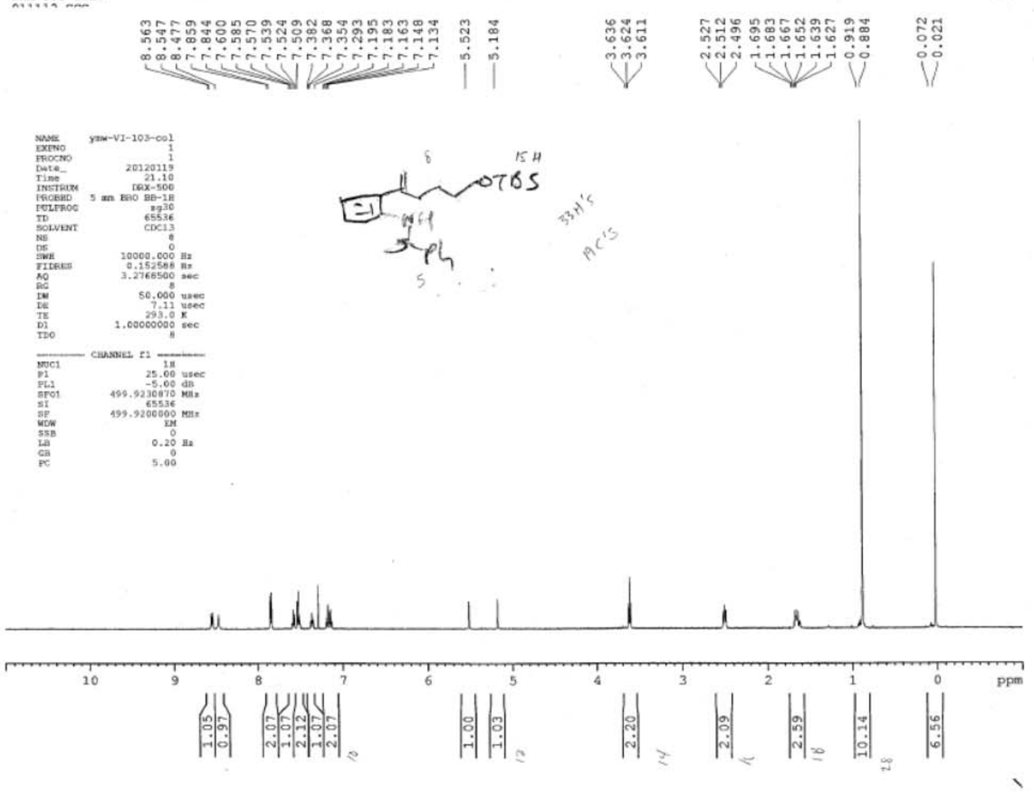
```
AVB-400 zgO  Carbon Starting paramters 6/11/03 RN

NAME        ymw-VI-169D-pt1c
EXPNO                      1
PROCNO                     1
Date_               20120405
Time                   20.31
INSTRUM              AVB-400
PROBHD     5 mm PABBO BB-
PULPROG               zgpg30
TD                     65536
SOLVENT                CDCl3
NS                       240
DS                         0
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ             1.3664756 sec
RG                     16384
DW               20.850 usec
DE                 6.00 usec
TE                   297.4 K
D1            1.50000000 sec
D11           0.03000000 sec
TD0                     1000

======== CHANNEL f1 ========
NUC1                     13C
P1                 8.50 usec
PL1                 -2.00 dB
PL1W          47.77286148 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2             70.00 usec
PL2                 -3.00 dB
PL12                16.00 dB
```

1H starting parameters (zg30)
DRX-500 TBIC



```
NAME         ymw-VI-103-col
EXPNO                     1
PROCNO                    1
Date_              20120119
Time                  21.10
INSTRUM             DRX-500
PROBHD     5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        0
SWH               10000.000 Hz
FIDRES             0.152588 Hz
AQ                3.2768500 sec
RG                        8
DW                   50.000 usec
DE                     7.11 usec
TE                    293.0 K
D1               1.00000000 sec
TD0                       8

======== CHANNEL f1 ========
NUC1                     1H
P1                    25.00 usec
PL1                   -5.00 dB
SFO1            499.9230870 MHz
SI                    65536
SF              499.9200000 MHz
WDW                      EM
SSB                       0
LB                     0.20 Hz
GB                        0
PC                     5.00
```

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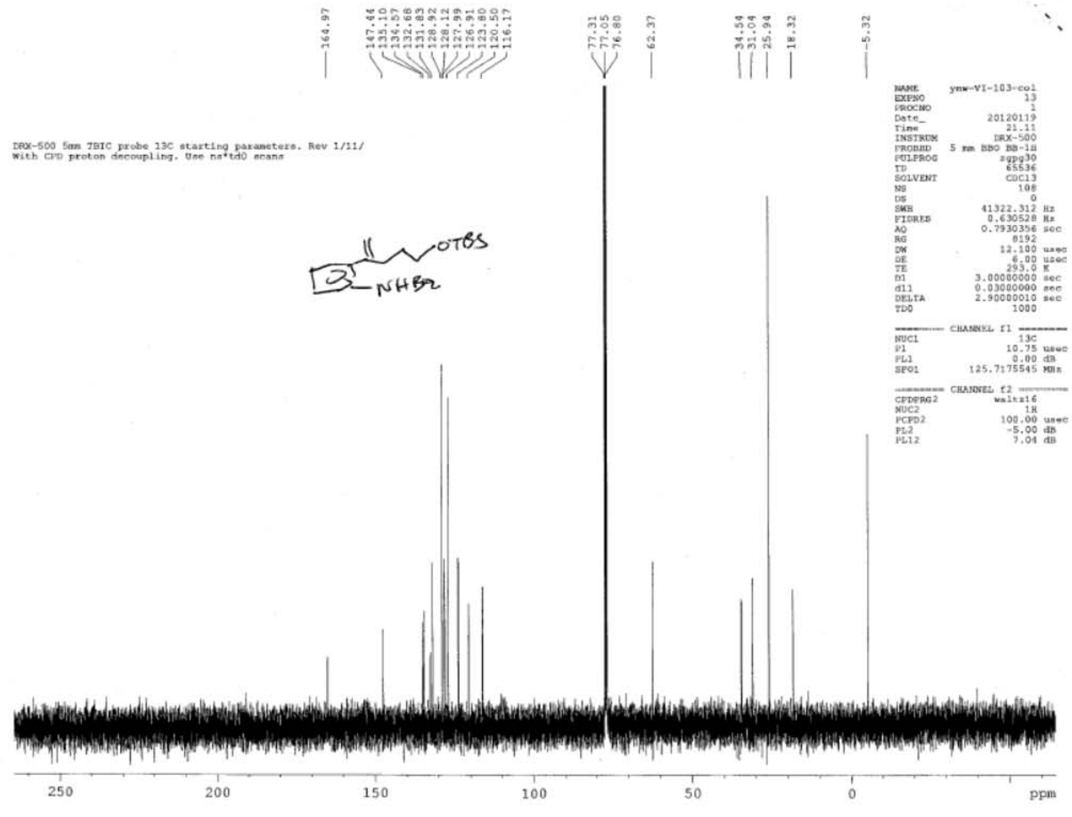
DRX-500 5mm TBIC probe 13C starting parameters. Rev 1/11/
With CPD proton decoupling. Use ns*td0 scans



```
NAME         ymw-VI-103-col
EXPNO                    13
PROCNO                    1
Date_              20120119
Time                  21.11
INSTRUM             DRX-500
PROBHD     5 mm BBO BB-1H
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      108
DS                        0
SWH               41322.312 Hz
FIDRES             0.630528 Hz
AQ                0.7930356 sec
RG                     8192
DW                   12.100 usec
DE                     6.00 usec
TE                    293.0 K
D1               3.00000000 sec
d11              0.03000000 sec
DELTA            2.90000010 sec
TD0                    1000

======== CHANNEL f1 ========
NUC1                    13C
P1                    10.75 usec
PL1                    0.00 dB
SFO1            125.7175545 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                   -5.00 dB
PL12                   7.04 dB
```

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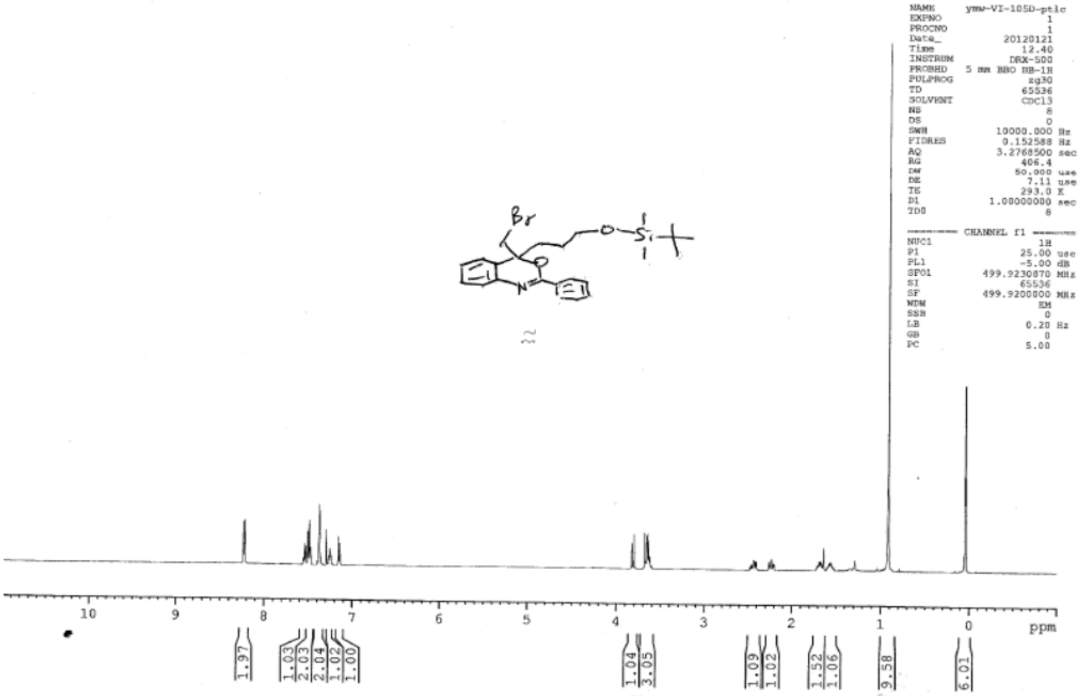
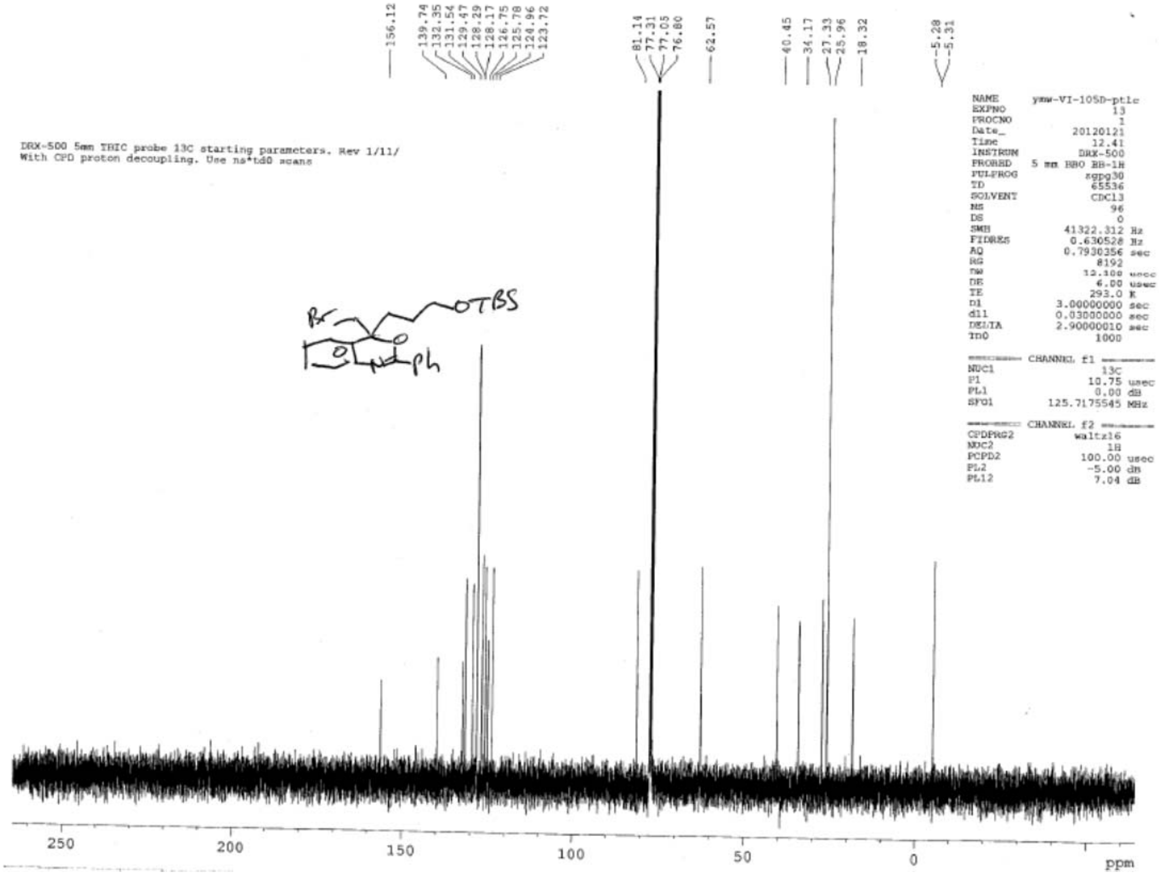
1H starting parameters (zg30)
DRX-500 TBIC



```
NAME      ymw-VI-105D-ptlc
EXPNO                    1
PROCNO                   1
Date_             20120121
Time                 12.40
INSTRUM            DRX-500
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH          10000.000 Hz
FIDRES        0.152588 Hz
AQ           3.2768500 sec
RG                   406.4
DW              50.000 use
DE                7.11 use
TE               293.0 K
D1          1.00000000 sec
TD0                      8

======== CHANNEL f1 ========
NUC1                    1H
P1               25.00 use
PL1              -5.00 dB
SFO1       499.9230870 MHz
SI                   65536
SF         499.9200000 MHz
WDW                     EM
SSB                      0
LB                0.20 Hz
GB                       0
PC                    5.00
```

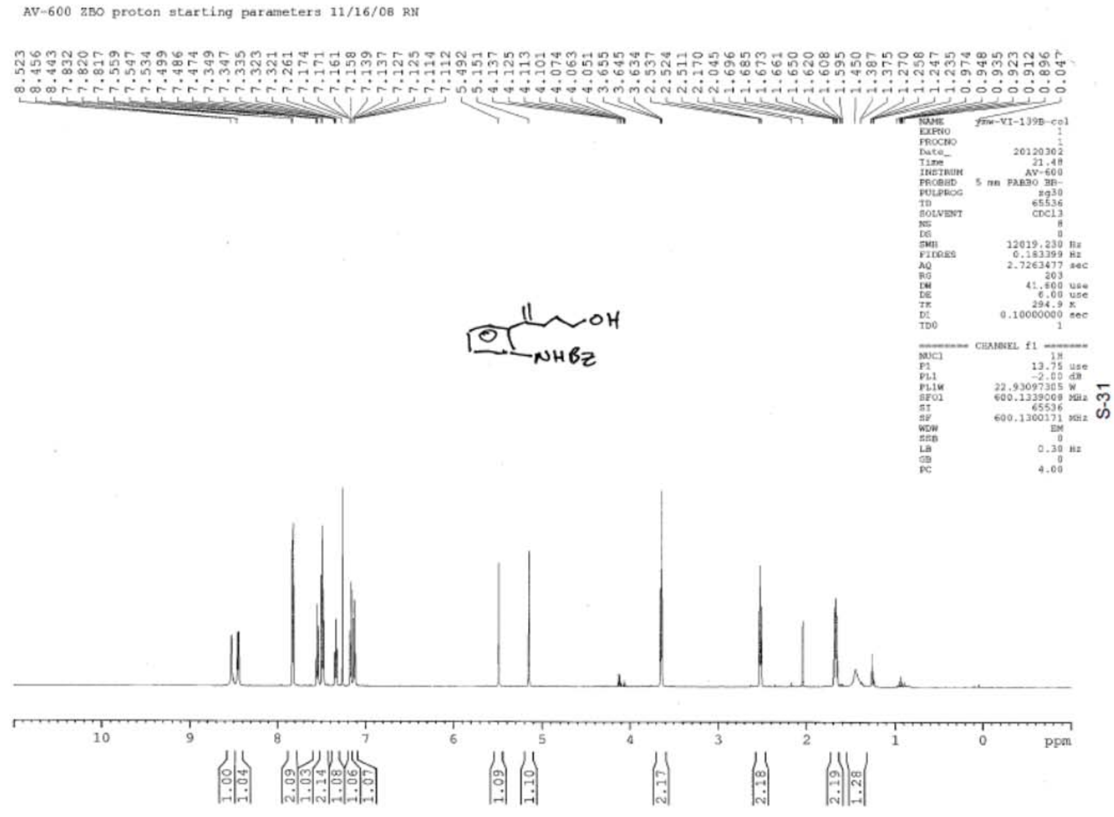


DRX-500 5mm TBIC probe 13C starting parameters. Rev 1/11/
With CPD proton decoupling. Use ns*td0 scans

```
NAME      ymw-VI-105D-ptlc
EXPNO                   13
PROCNO                   1
Date_             20120121
Time                 12.41
INSTRUM            DRX-500
PROBHD    5 mm BBO BB-1H
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      96
DS                       0
SWH          41322.312 Hz
FIDRES        0.630528 Hz
AQ           0.7930356 sec
RG                    8192
DW              12.100 usec
DE                6.00 usec
TE               293.0 K
D1          3.00000000 sec
d11         0.03000000 sec
DELTA       2.90000010 sec
TD0                   1000

======== CHANNEL f1 ========
NUC1                   13C
P1               10.75 usec
PL1               0.00 dB
SFO1       125.7175545 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2           100.00 usec
PL2              -5.00 dB
PL12              7.04 dB
```



```
NAME       ynw-VI-139B-col
EXPNO                    1
PROCNO                   1
Date_             20120302
Time                 21.48
INSTRUM             AV-600
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              12019.230 Hz
FIDRES            0.183399 Hz
AQ               2.7263477 sec
RG                     203
DW                  41.600 use
DE                    6.00 use
TE                   294.9 K
D1              0.10000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   13.75 use
PL1                  -2.00 dB
PL1W           22.93097305 W
SFO1           600.1339008 MHz
SI                   65536
SF             600.1300171 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00
```

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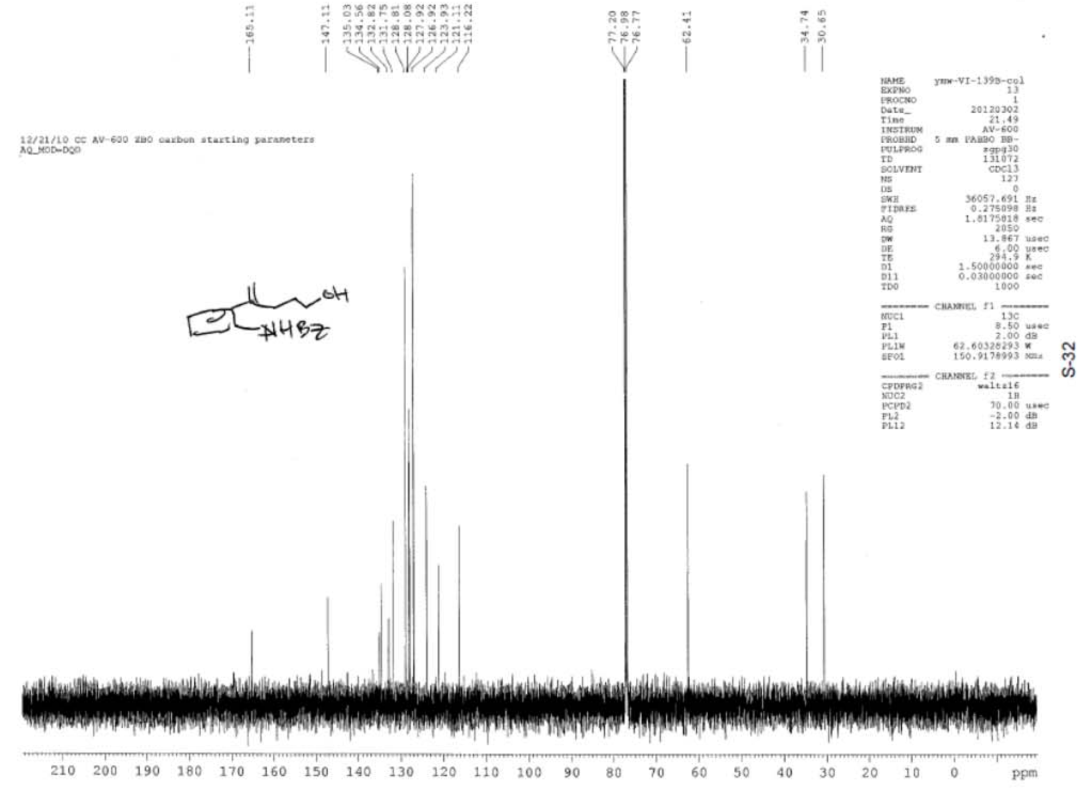

```
NAME       ynw-VI-139B-col
EXPNO                   13
PROCNO                   1
Date_             20120302
Time                 21.49
INSTRUM             AV-600
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  131072
SOLVENT              CDCl3
NS                     127
DS                       0
SWH              36057.691 Hz
FIDRES            0.275098 Hz
AQ               1.8175018 sec
RG                    2050
DW                  13.867 usec
DE                    6.00 usec
TE                   294.9 K
D1              1.50000000 sec
D11             0.03000000 sec
TD0                   1000

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.50 usec
PL1                   2.00 dB
PL1W           62.60328293 W
SFO1           150.9178993 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                70.00 usec
PL2                  -2.00 dB
PL12                 12.14 dB
```

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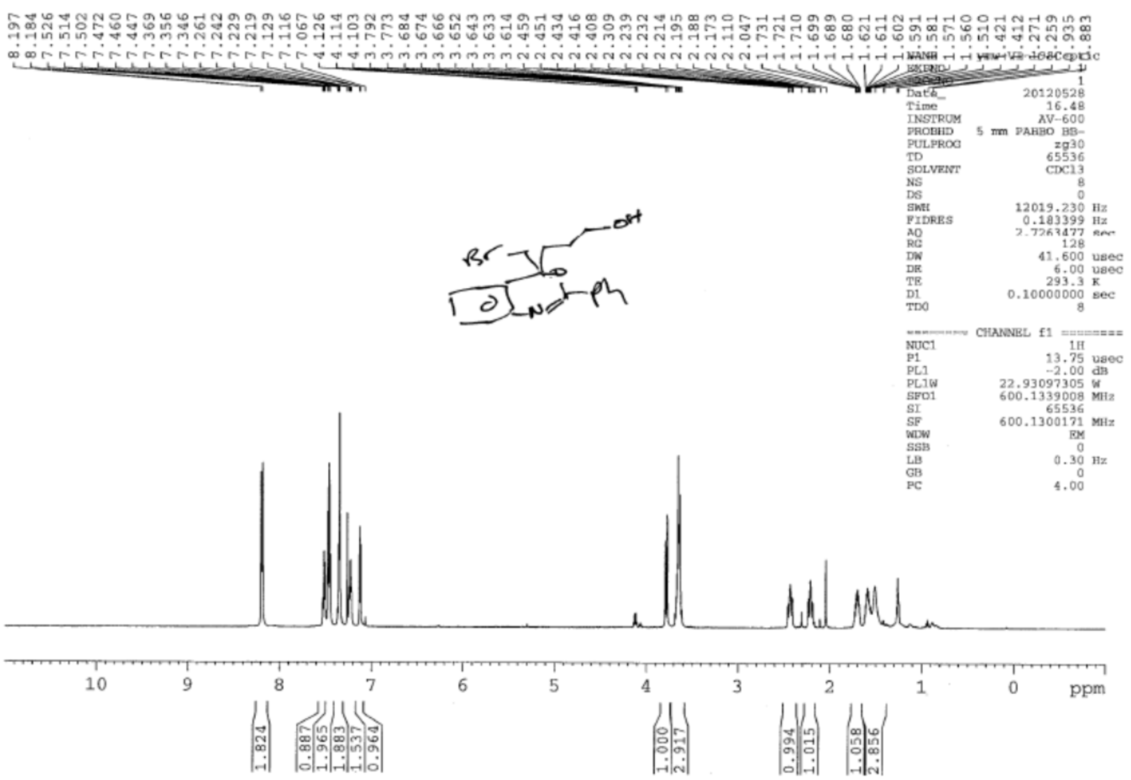
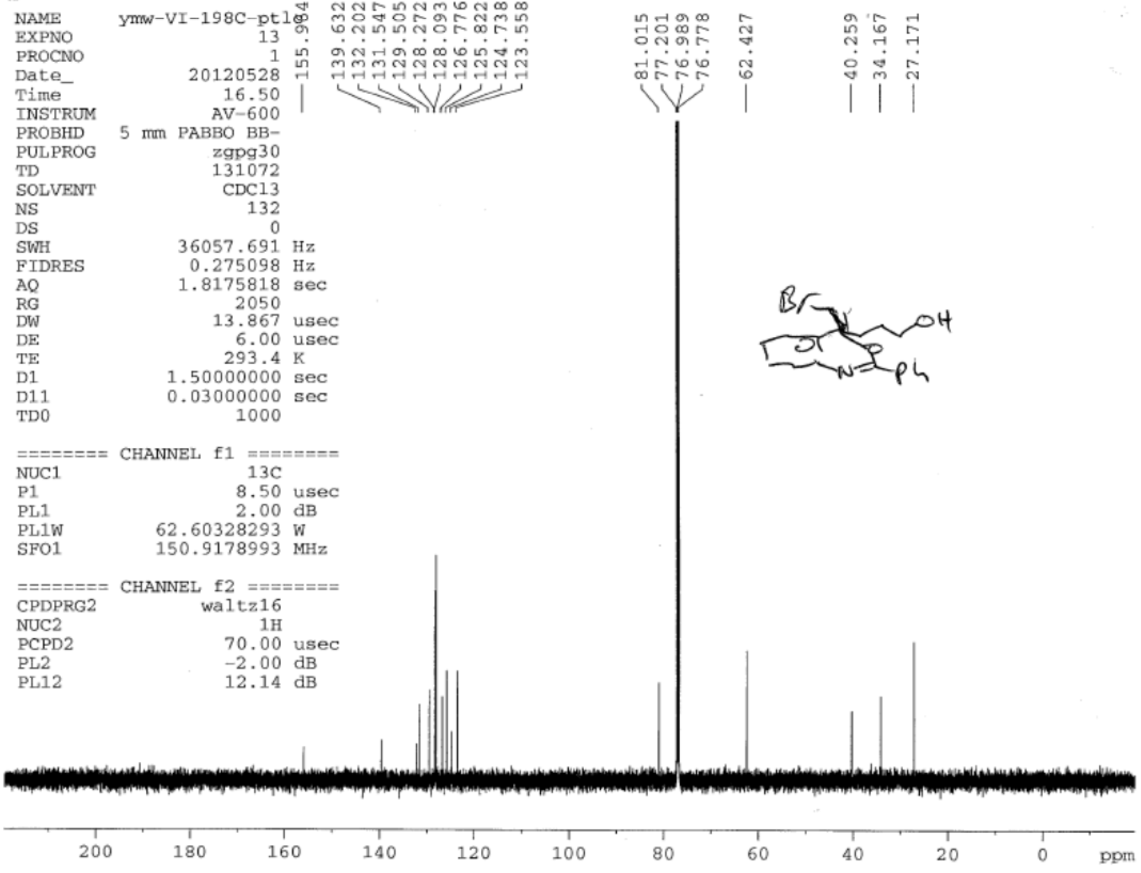
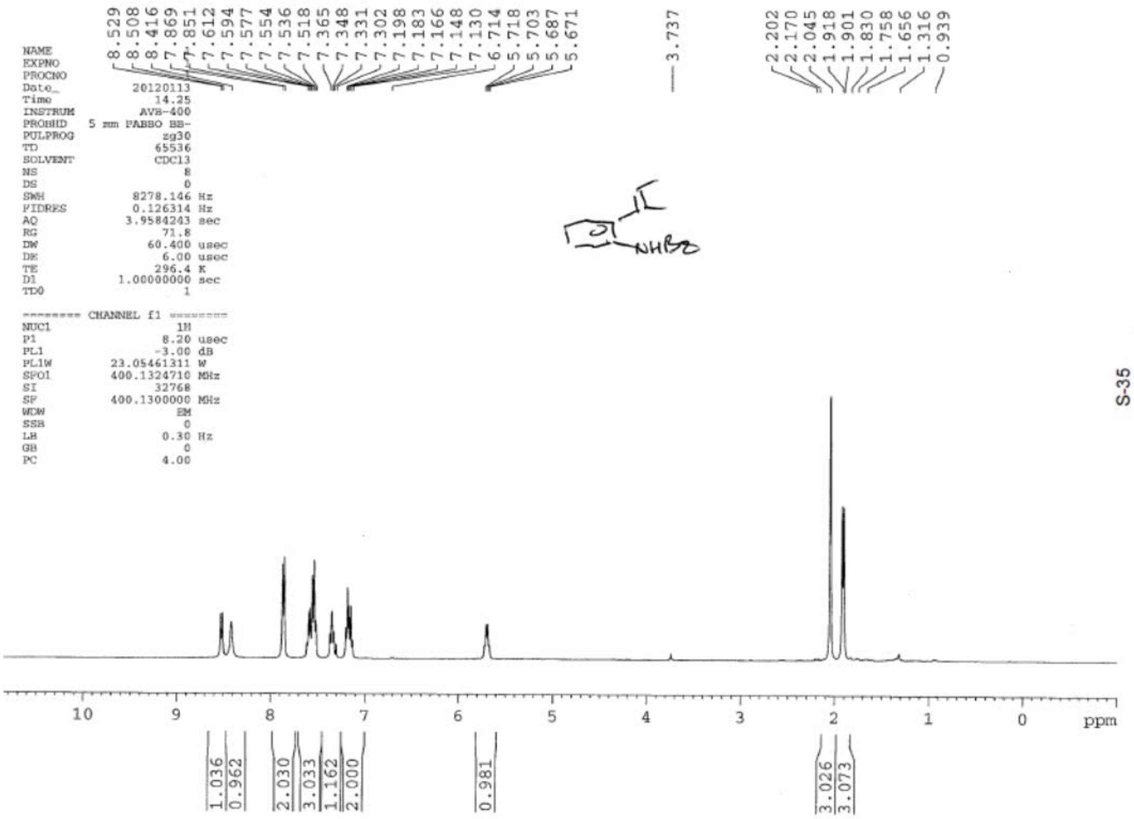
AV-600 ZBO proton starting parameters 11/16/08 RN



```
NAME        ymw-VI-198Cptlc
EXPNO
PROCNO                   1
Date_             20120528
Time                 16.48
INSTRUM             AV-600
PROBHD      5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              12019.230 Hz
FIDRES            0.183399 Hz
AQ               2.7263477 sec
RG                     128
DW                  41.600 usec
DE                    6.00 usec
TE                   293.3 K
D1              0.10000000 sec
TD0                      8

======== CHANNEL f1 ========
NUC1                    1H
P1                   13.75 usec
PL1                  -2.00 dB
PL1W           22.93097305 W
SFO1           600.1339008 MHz
SI                   65536
SF             600.1300171 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00
```



```
NAME        ymw-VI-198C-ptlc
EXPNO                   13
PROCNO                   1
Date_             20120528
Time                 16.50
INSTRUM             AV-600
PROBHD      5 mm PABBO BB-
PULPROG             zgpg30
TD                  131072
SOLVENT              CDCl3
NS                     132
DS                       0
SWH              36057.691 Hz
FIDRES            0.275098 Hz
AQ               1.8175818 sec
RG                    2050
DW                  13.867 usec
DE                    6.00 usec
TE                   293.4 K
D1              1.50000000 sec
D11             0.03000000 sec
TD0                   1000

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.50 usec
PL1                   2.00 dB
PL1W           62.60328293 W
SFO1           150.9178993 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                70.00 usec
PL2                  -2.00 dB
PL12                 12.14 dB
```



```
NAME
EXPNO
PROCNO
Date_           20120113
Time               14.25
INSTRUM         AVB-400
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                  71.8
DW                60.400 usec
DE                  6.00 usec
TE                 296.4 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  8.20 usec
PL1                -3.00 dB
PL1W         23.05461311 W
SFO1         400.1324710 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00
```

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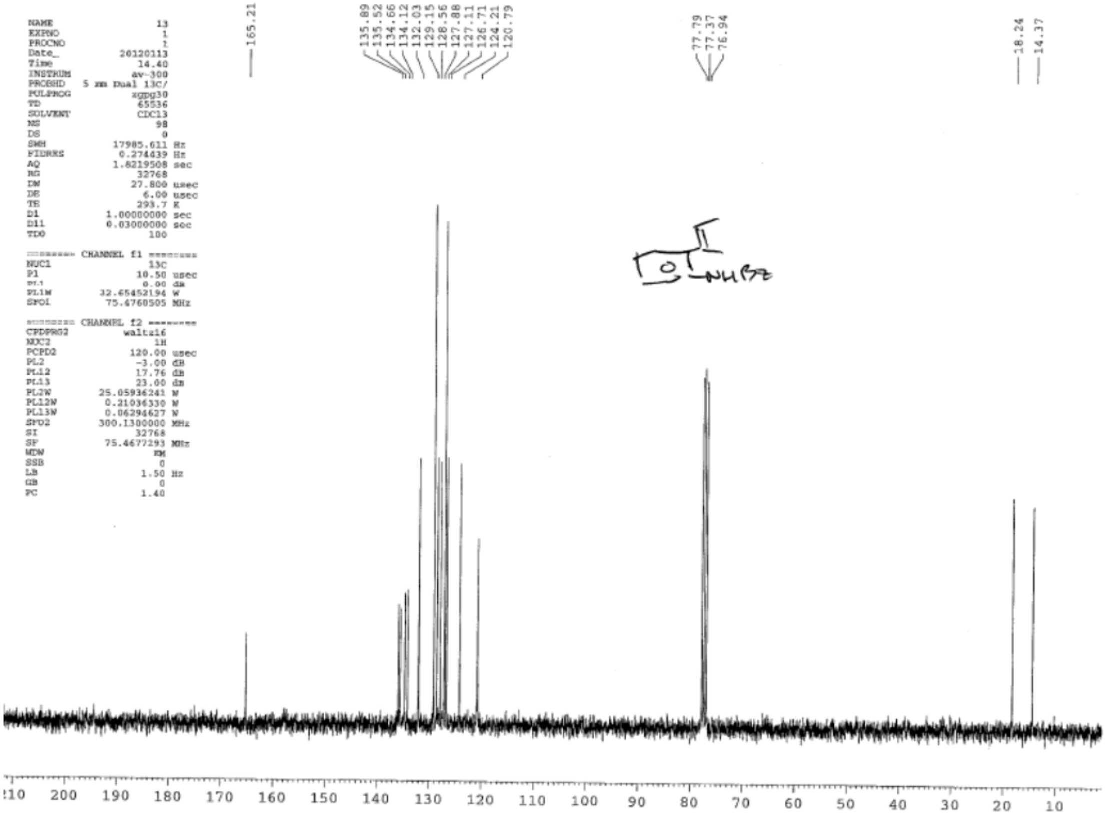
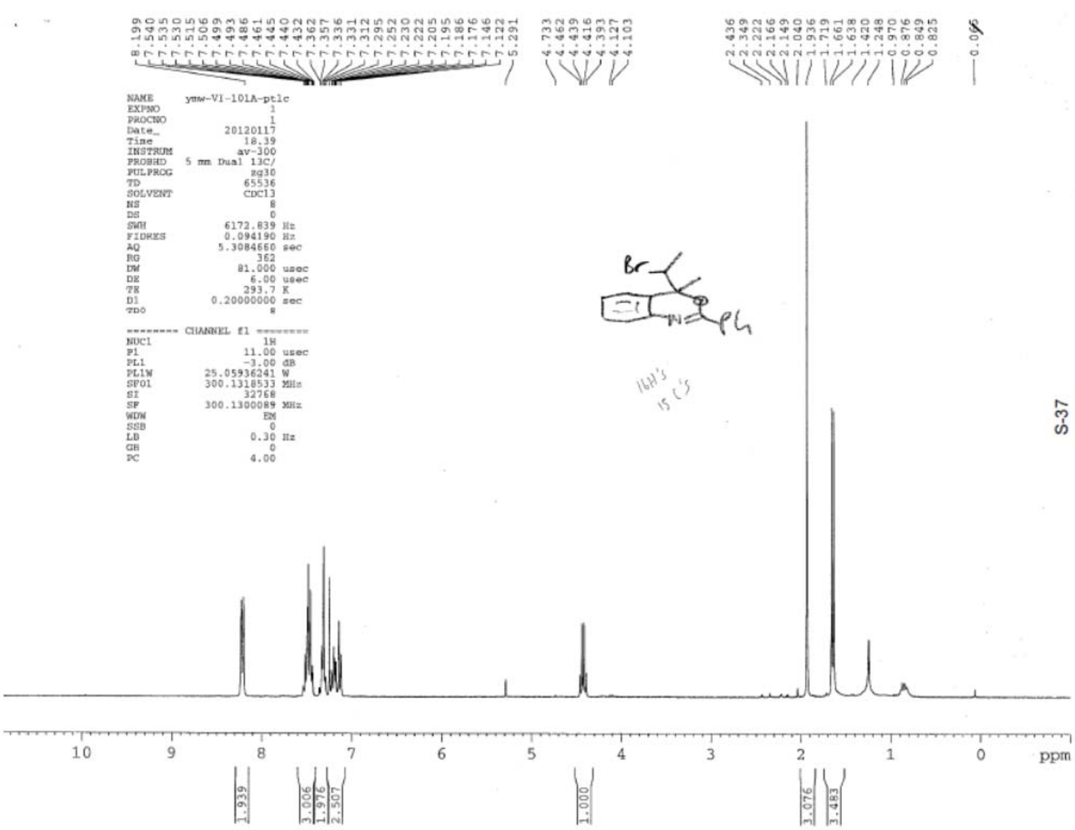
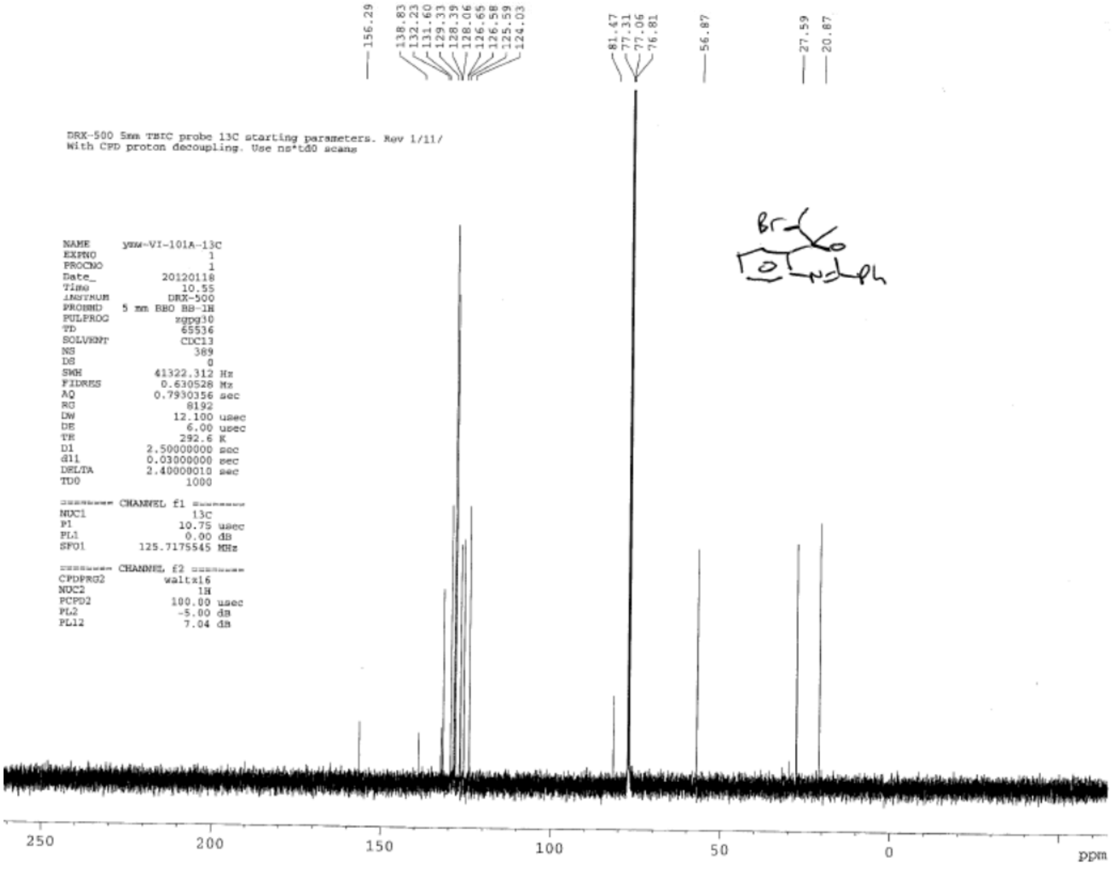


```
NAME                  13
EXPNO                  1
PROCNO                 1
Date_           20120113
Time               14.40
INSTRUM           av-300
PROBHD   5 mm Dual 13C/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    98
DS                     0
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                 32768
DW                27.800 usec
DE                  6.00 usec
TE                 293.7 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                  100

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.50 usec
PL1                 0.00 dB
PL1W         32.65452194 W
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             120.00 usec
PL2                -3.00 dB
PL12               17.76 dB
PL13               23.00 dB
PL2W         25.05936241 W
PL12W         0.21036330 W
PL13W         0.06294627 W
SFO2         300.1300000 MHz
SI                 32768
SF            75.4677293 MHz
WDW                   EM
SSB                    0
LB                  1.50 Hz
GB                     0
PC                  1.40
```

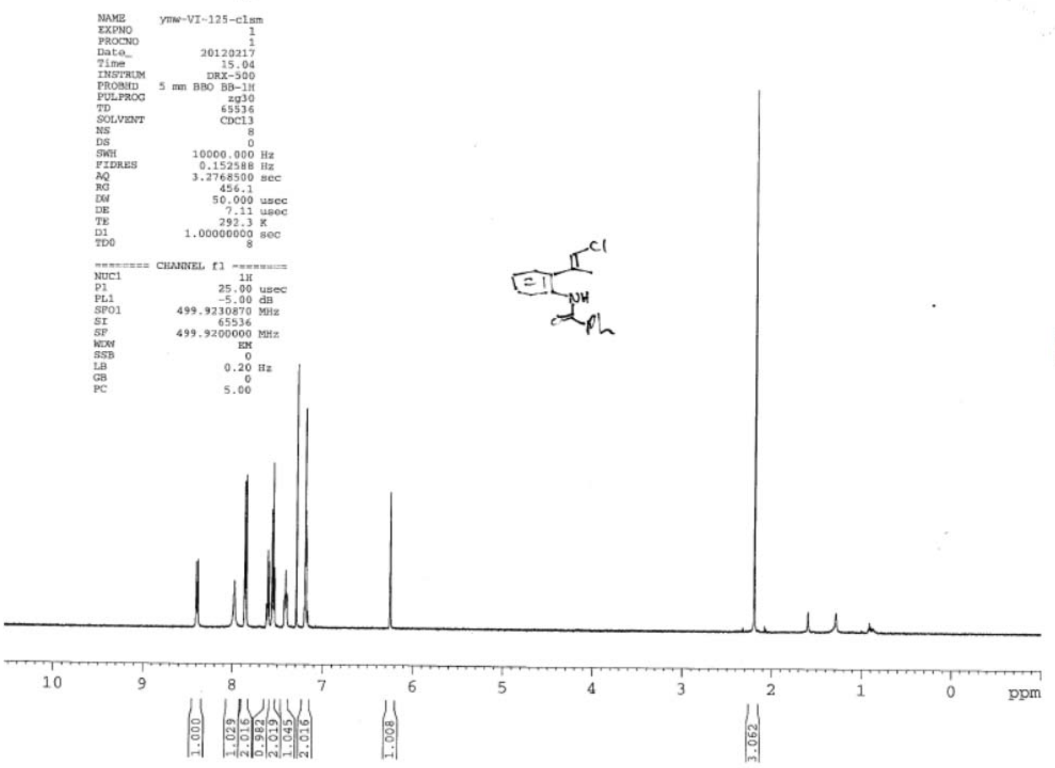


```
NAME       ymw-VI-101A-ptlc
EXPNO                     1
PROCNO                    1
Date_              20120117
Time                  18.39
INSTRUM              av-300
PROBHD     5 mm Dual 13C/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        0
SWH                6172.839 Hz
FIDRES             0.094190 Hz
AQ                5.3084660 sec
RG                      362
DW                   81.000 usec
DE                     6.00 usec
TE                    293.7 K
D1               0.20000000 sec
TD0                       8

======== CHANNEL f1 ========
NUC1                     1H
P1                    11.00 usec
PL1                   -3.00 dB
PL1W            25.05936241 W
SFO1            300.1318533 MHz
SI                    32768
SF              300.1300089 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     4.00
```



```
DRX-500 5mm TBIC probe 13C starting parameters. Rev 1/11/
With CPD proton decoupling. Use ns*td0 scans

NAME       ymw-VI-101A-13C
EXPNO                     1
PROCNO                    1
Date_              20120118
Time                  10.55
INSTRUM             DRX-500
PROBHD     5 mm BBO BB-1H
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      389
DS                        0
SWH               41322.312 Hz
FIDRES             0.630528 Hz
AQ                0.7930356 sec
RG                     8192
DW                   12.100 usec
DE                     6.00 usec
TE                    292.6 K
D1               2.50000000 sec
d11              0.03000000 sec
DELTA            2.40000010 sec
TD0                    1000

======== CHANNEL f1 ========
NUC1                    13C
P1                    10.75 usec
PL1                    0.00 dB
SFO1            125.7175545 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                   -5.00 dB
PL12                   7.04 dB
```

6A



```
NAME         ymw-VI-125-clsm
EXPNO                      1
PROCNO                     1
Date_               20120217
Time                   15.04
INSTRUM              DRX-500
PROBHD       5 mm BBO BB-1H
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         8
DS                         0
SWH               10000.000 Hz
FIDRES             0.152588 Hz
AQ                3.2768500 sec
RG                     456.1
DW                    50.000 usec
DE                      7.11 usec
TE                     292.3 K
D1               1.00000000 sec
TD0                        8

======== CHANNEL f1 ========
NUC1                      1H
P1                     25.00 usec
PL1                    -5.00 dB
SFO1             499.9230870 MHz
SI                     65536
SF               499.9200000 MHz
WDW                       EM
SSB                        0
LB                      0.20 Hz
GB                         0
PC                      5.00
```

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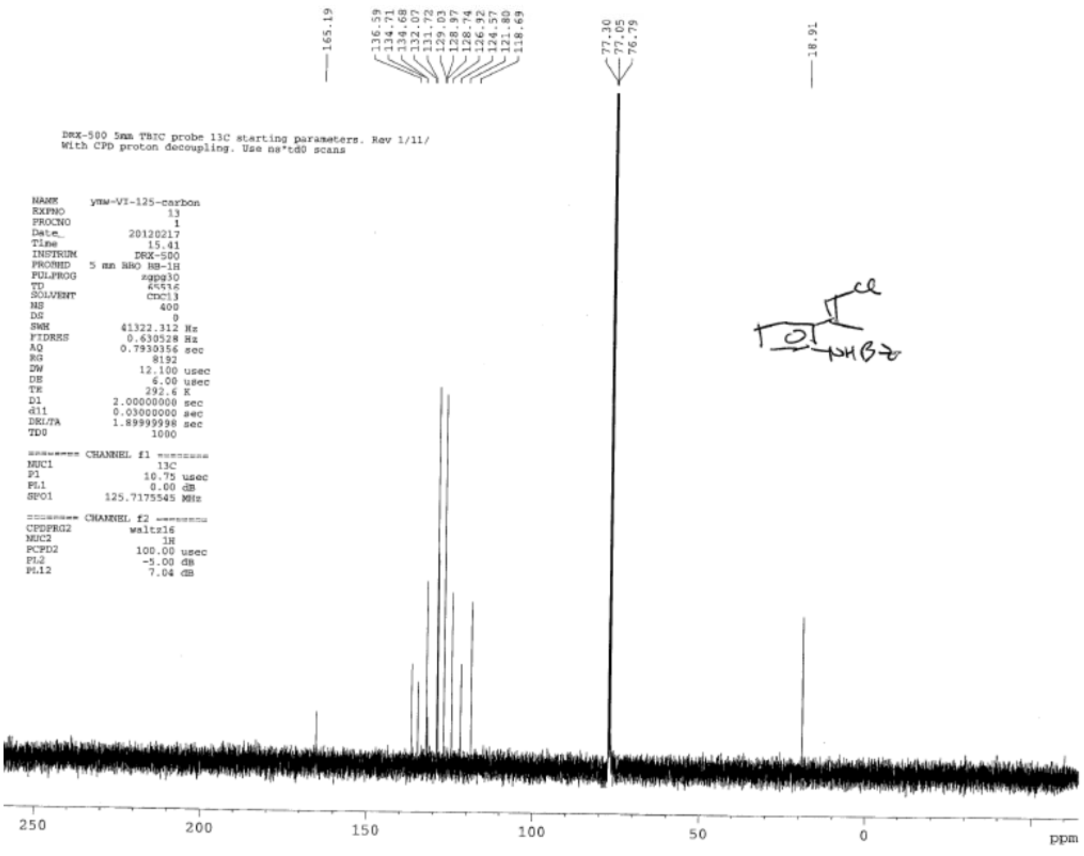
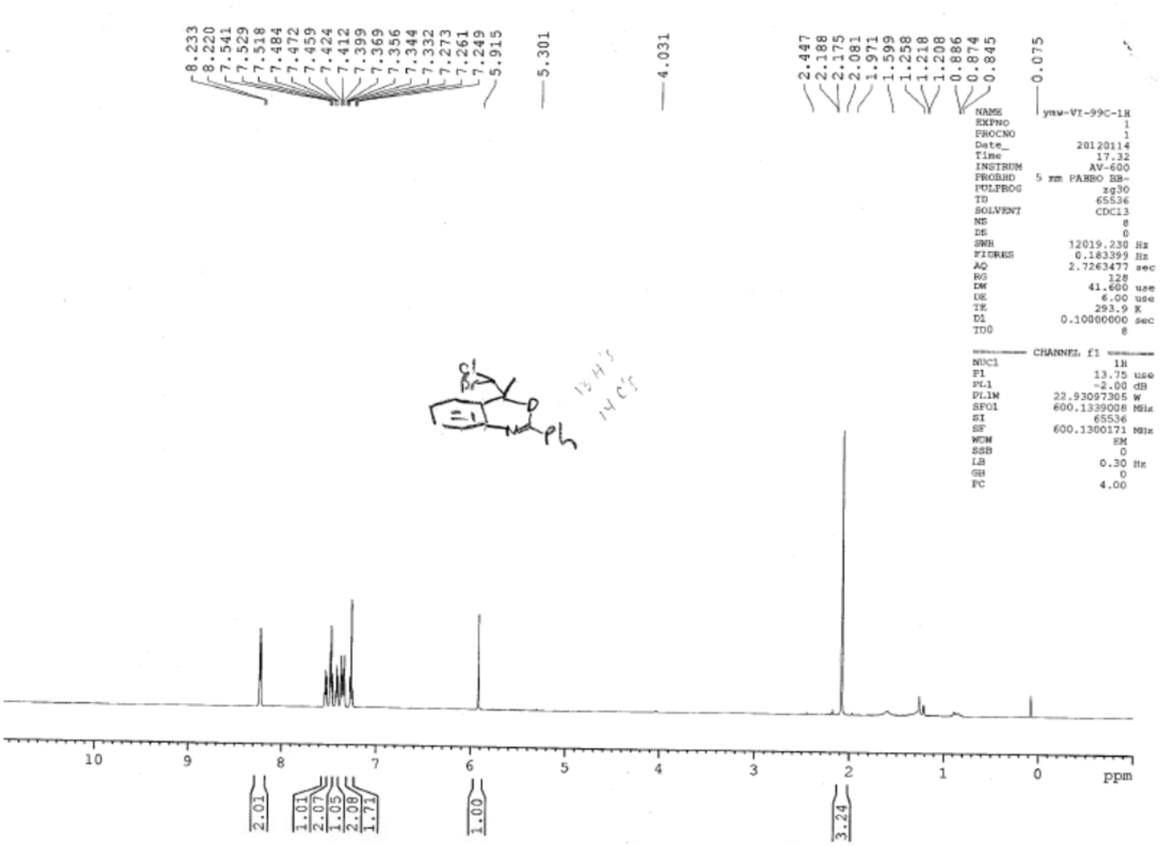


```
DRX-500 5mm TBIC probe 13C starting parameters. Rev 1/11/
With CPD proton decoupling. Use ns*td0 scans
```

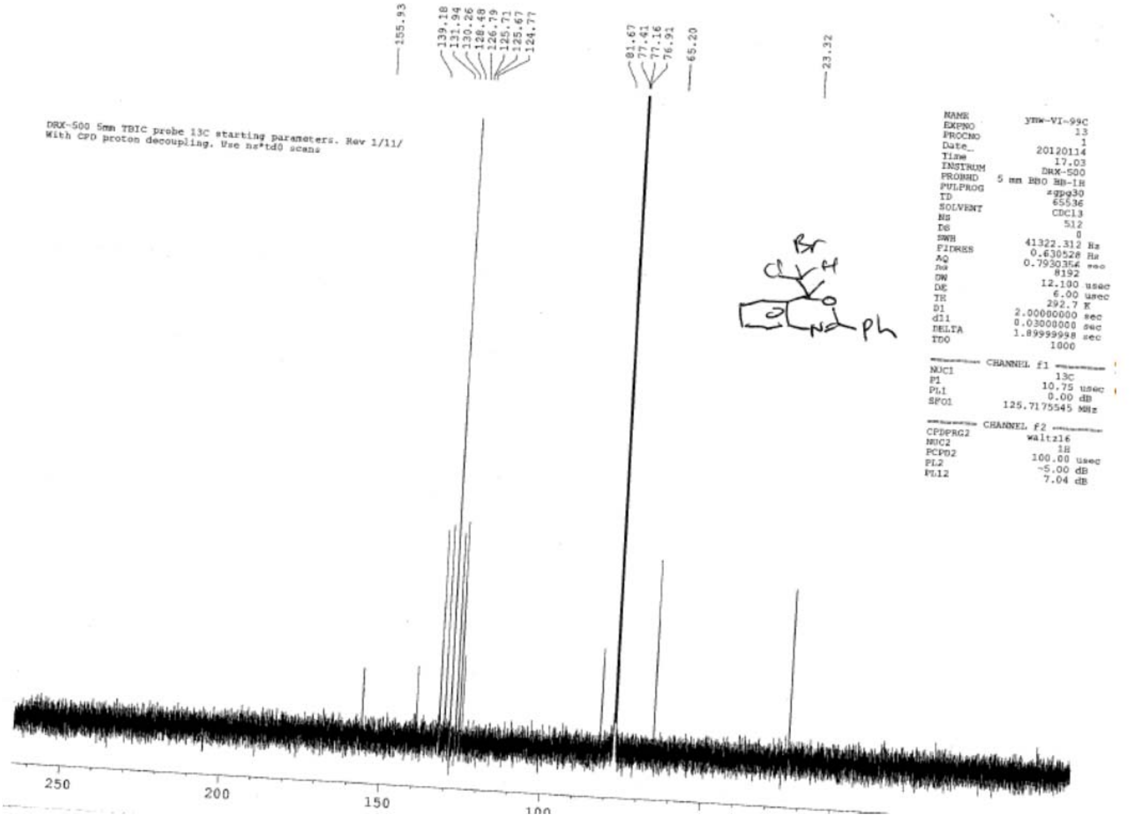
```
NAME         ymw-VI-125-carbon
EXPNO                     13
PROCNO                     1
Date_               20120217
Time                   15.41
INSTRUM              DRX-500
PROBHD       5 mm BBO BB-1H
PULPROG               zgpg30
TD                     65536
SOLVENT                CDCl3
NS                       400
DS                         0
SWH               41322.312 Hz
FIDRES             0.630528 Hz
AQ                0.7930356 sec
RG                      8192
DW                    12.100 usec
DE                      6.00 usec
TE                     292.6 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                     1000

======== CHANNEL f1 ========
NUC1                     13C
P1                     10.75 usec
PL1                     0.00 dB
SFO1             125.7175545 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                 100.00 usec
PL2                    -5.00 dB
PL12                    7.04 dB
```

AV-600 ZBO proton starting parameters 11/16/08 RN

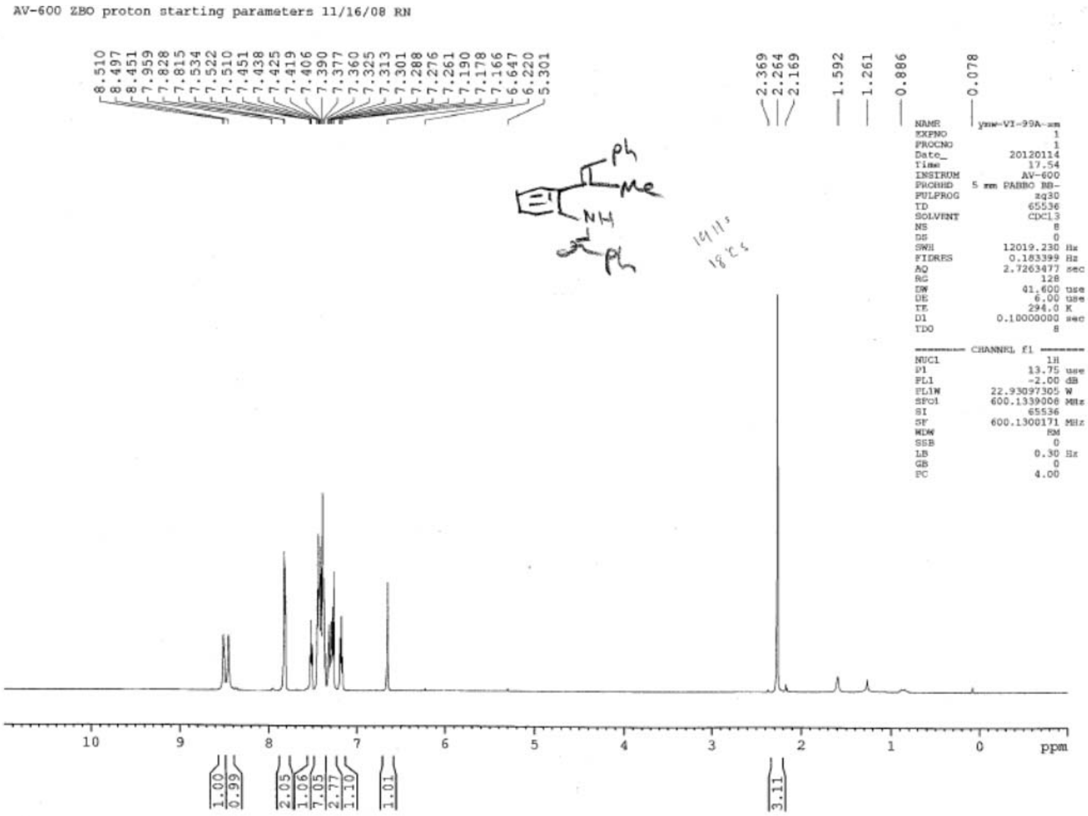


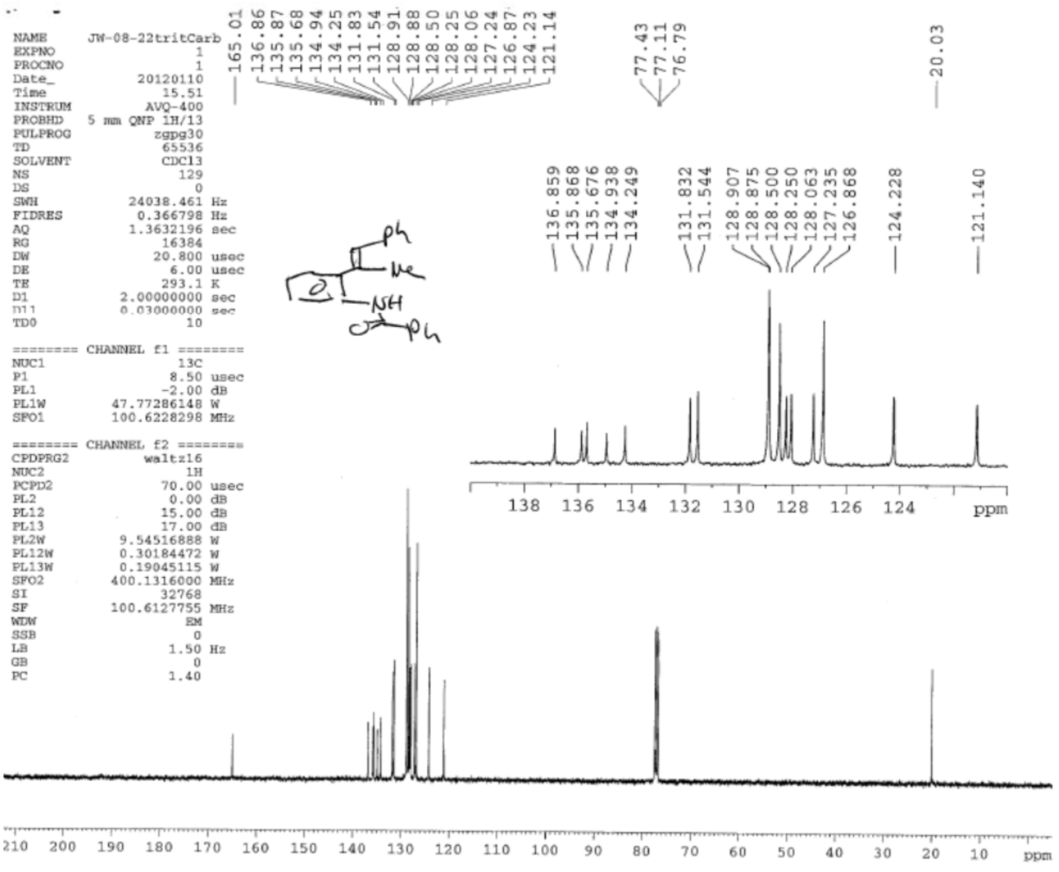
```
NAME        ymw-VI-99C-1H
EXPNO                   1
PROCNO                  1
Date_            20120114
Time                17.32
INSTRUM            AV-600
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH             12019.230 Hz
FIDRES           0.183399 Hz
AQ              2.7263477 sec
RG                    128
DW                 41.600 use
DE                   6.00 use
TE                  293.9 K
D1             0.10000000 sec
TD0                     8

======== CHANNEL f1 ========
NUC1                   1H
P1                  13.75 use
PL1                 -2.00 dB
PL1W          22.93097305 W
SFO1          600.1339008 MHz
SI                  65536
SF            600.1300171 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   4.00
```

DRX-500 5mm TBIC probe 13C starting parameters. Rev 1/11/
With CPD proton decoupling. Use ns*td0 scans

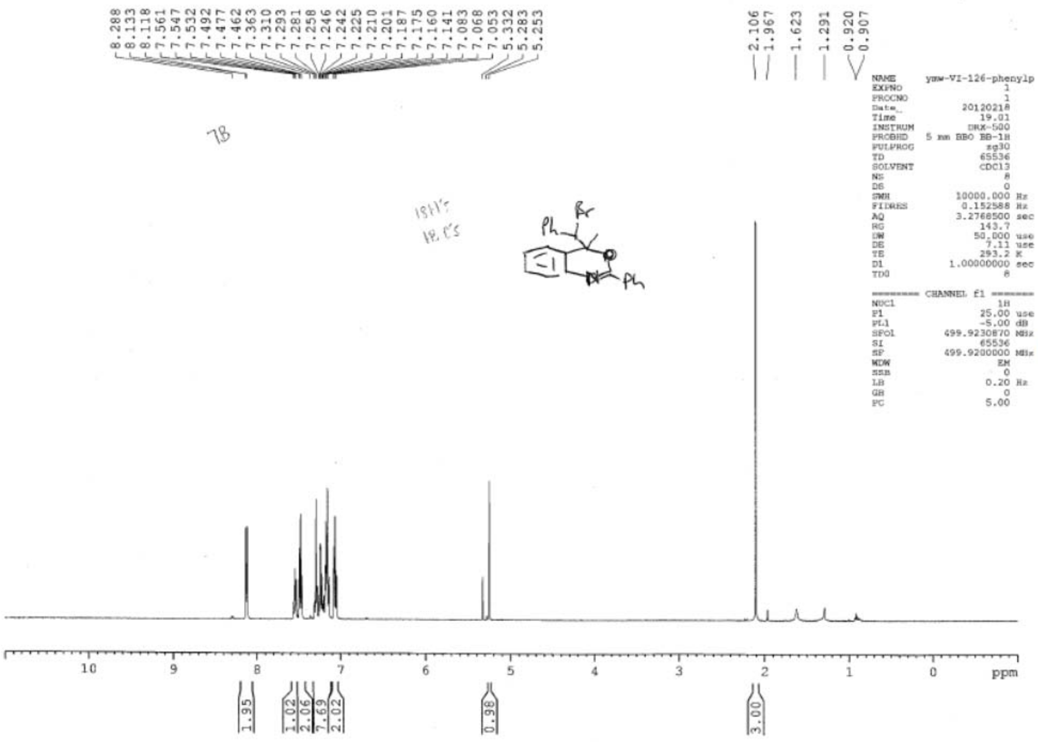


```
NAME           ymw-VI-99C
EXPNO                  13
PROCNO                  1
Date_            20120114
Time                17.03
INSTRUM           DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    512
DS                      0
SWH             41322.312 Hz
FIDRES           0.630528 Hz
AQ              0.7930356 sec
RG                   8192
DW                 12.100 usec
DE                   6.00 usec
TE                  292.7 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                  1000

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.75 usec
PL1                  0.00 dB
SFO1          125.7175545 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -5.00 dB
PL12                 7.04 dB
```


AV-600 ZBO proton starting parameters 11/16/08 RN
8.510
8.497
8.451
7.959
7.828
7.815
7.534
7.522
7.510
7.451
7.438
7.425
7.419
7.406
7.390
7.377
7.360
7.325
7.313
7.301
7.288
7.276
7.261
7.190
7.178
7.166
6.647
6.220
5.301
2.369
2.264
2.169
1.592
1.261
0.886
0.078
Ph
Me
NH
O
Ph
14 H's
18 C's
NAME ynw-VI-99A-sm
EXPNO 1
PROCNO 1
Date_ 20120114
Time 17.54
INSTRUM AV-600
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 128
DW 41.600 use
DE 6.00 use
TE 294.0 K
D1 0.10000000 sec
TDO 8
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 use
PL1 -2.00 dB
PL1W 22.93097305 W
SFO1 600.1339008 MHz
SI 65536
SF 600.1300171 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.99
2.05
1.06
7.05
2.77
1.10
1.01
3.11


NAME JW-08-22tritCarb
EXPNO 1
PROCNO 1
Date_ 20120110
Time 15.51
INSTRUM AVQ-400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 129
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3632196 sec
RG 16384
DW 20.800 usec
DE 6.00 usec
TE 293.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 10
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 47.77286148 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 0.00 dB
PL12 15.00 dB
PL13 17.00 dB
PL2W 9.54516888 W
PL12W 0.30184472 W
PL13W 0.19045115 W
SFO2 400.1316000 MHz
SI 32768
SF 100.6127755 MHz
WDW EM
SSB 0
LB 1.50 Hz
GB 0
PC 1.40
165.01
136.86
135.87
135.68
134.94
134.25
131.83
131.54
128.91
128.88
128.50
128.25
128.06
127.24
126.87
124.23
121.14
77.43
77.11
76.79
20.03
136.859
135.868
135.676
134.938
134.249
131.832
131.544
128.907
128.875
128.500
128.250
128.063
127.235
126.868
124.228
121.140
138
136
134
132
130
128
126
124
ppm
Ph
Me
NH
O
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

1H starting parameters (zg30)
DRX-500 TBIC



```
NAME        ymw-VI-126-phenylp
EXPNO                        1
PROCNO                       1
Date_                 20120218
Time                     19.01
INSTRUM                DRX-500
PROBHD        5 mm BBO BB-1H
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                           8
DS                           0
SWH              10000.000 Hz
FIDRES            0.152588 Hz
AQ               3.2768500 sec
RG                       143.7
DW                  50.000 use
DE                    7.11 use
TE                    293.2 K
D1              1.00000000 sec
TD0                          8

======== CHANNEL f1 ========
NUC1                        1H
P1                   25.00 use
PL1                   -5.00 dB
SFO1           499.9230870 MHz
SI                       65536
SF             499.9200000 MHz
WDW                         EM
SSB                          0
LB                     0.20 Hz
GB                           0
PC                        5.00
```

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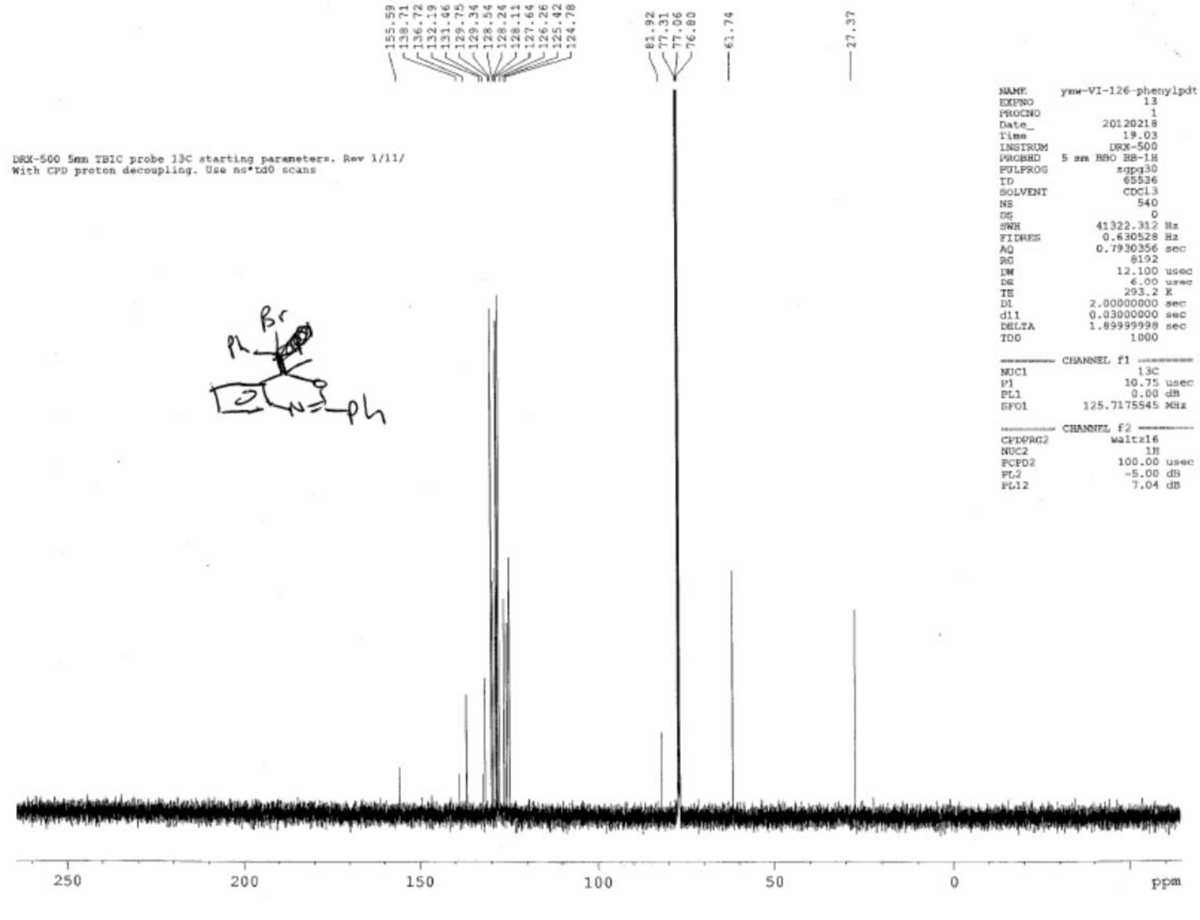
DRX-500 5mm TBIC probe 13C starting parameters. Rev 1/11/
With CPD proton decoupling. Use ns*td0 scans



```
NAME       ymw-VI-126-phenylpdt
EXPNO                       13
PROCNO                       1
Date_                 20120218
Time                     19.03
INSTRUM                DRX-500
PROBHD        5 mm BBO BB-1H
PULPROG                zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         540
DS                           0
SWH              41322.312 Hz
FIDRES            0.630528 Hz
AQ               0.7930356 sec
RG                        8192
DW                 12.100 usec
DE                   6.00 usec
TE                    293.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                       1000

======== CHANNEL f1 ========
NUC1                       13C
P1                 10.75 usec
PL1                   0.00 dB
SFO1           125.7175545 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2             100.00 usec
PL2                   -5.00 dB
PL12                   7.04 dB
```

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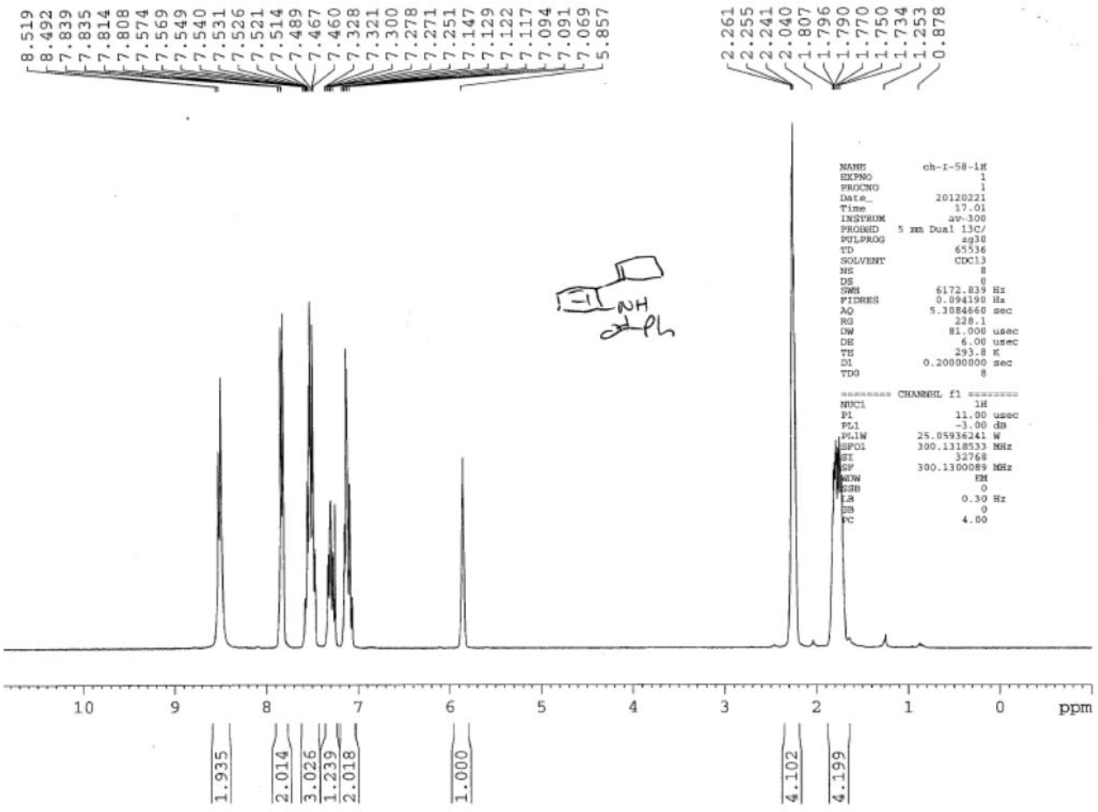
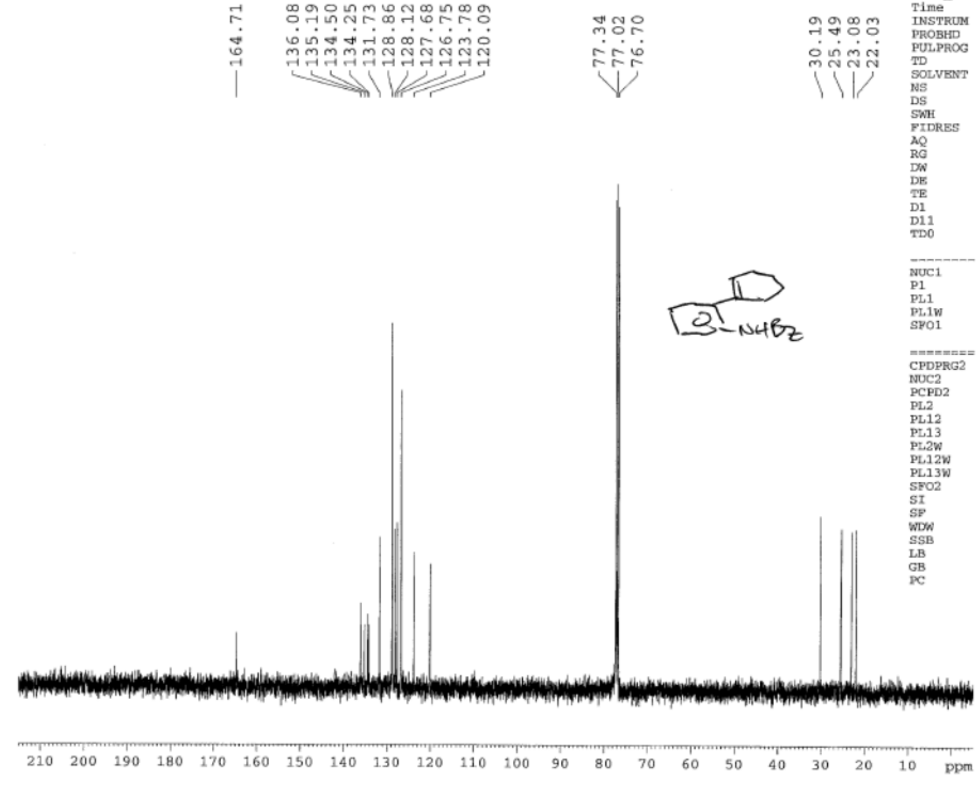
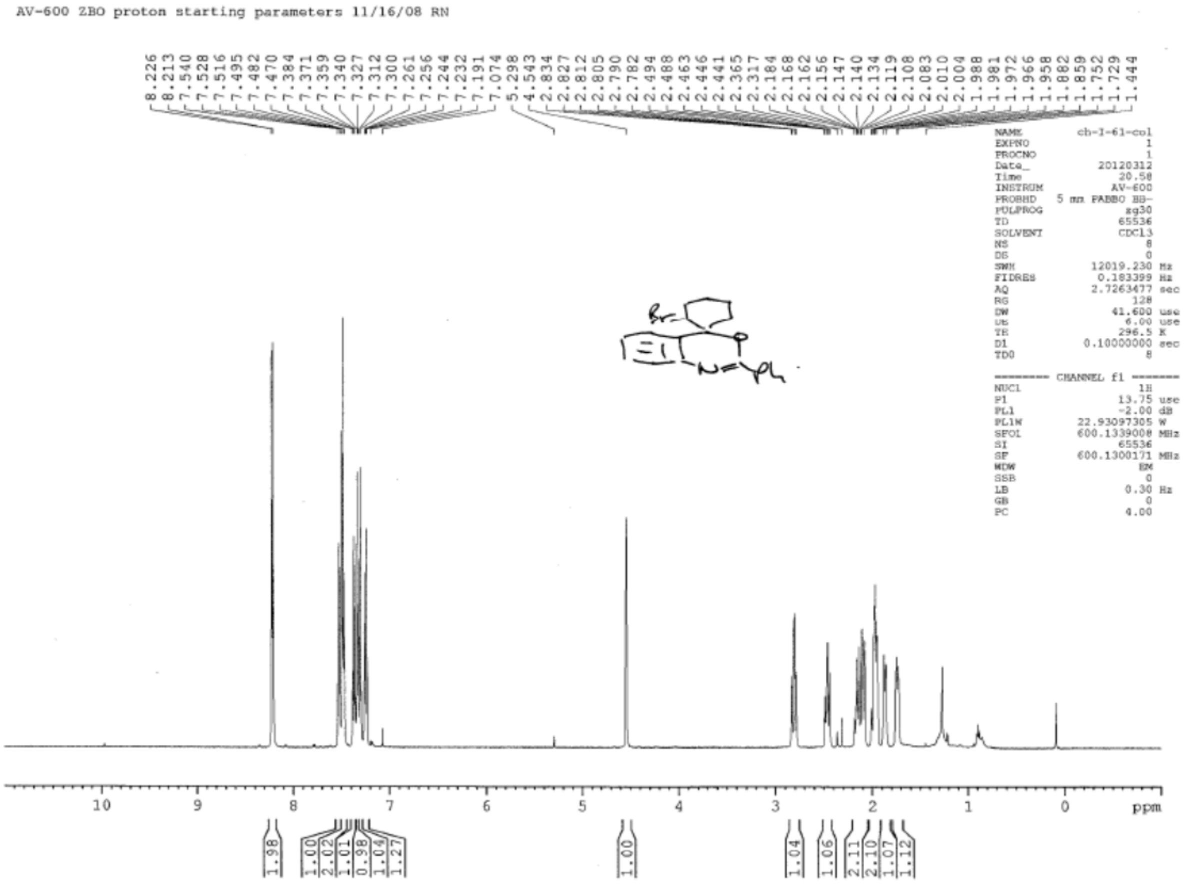


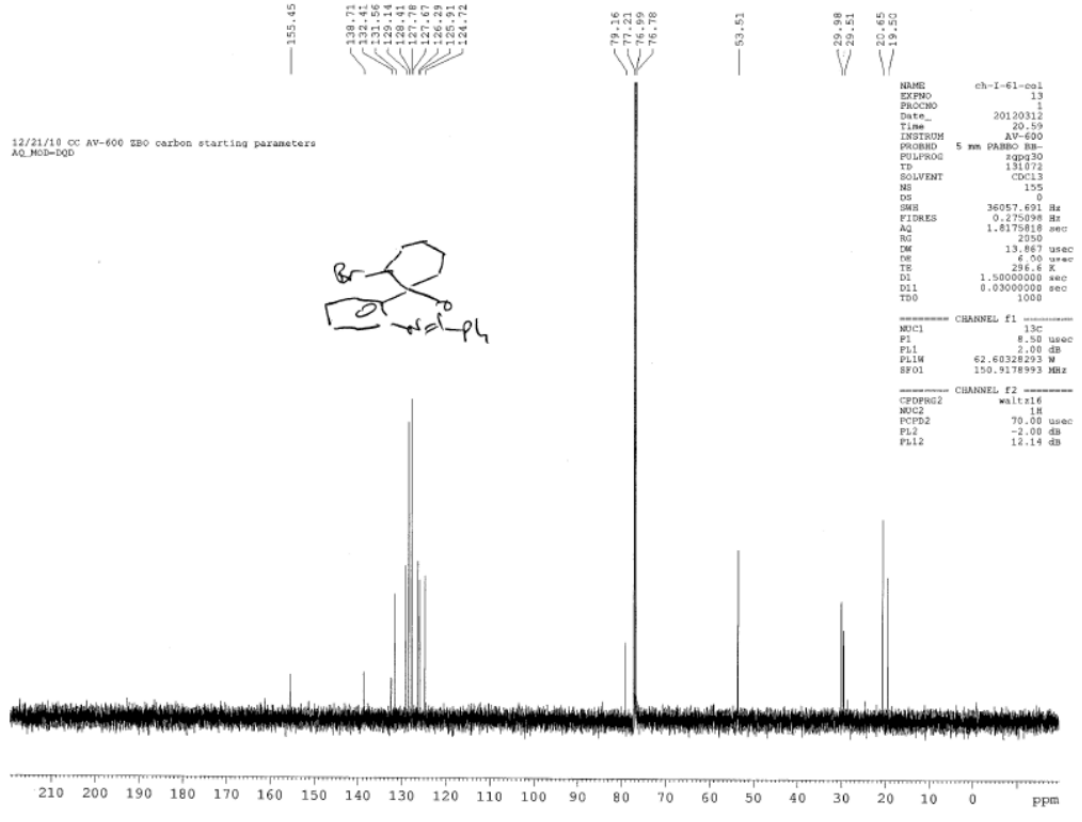
```
NAME             ch-I-58-1H
EXPNO                     1
PROCNO                    1
Date_              20120221
Time                  17.01
INSTRUM              av-300
PROBHD     5 mm Dual 13C/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        0
SWH            6172.839 Hz
FIDRES         0.094190 Hz
AQ            5.3084660 sec
RG                    228.1
DW               81.000 usec
DE                 6.00 usec
TE                293.8 K
D1           0.20000000 sec
TD0                       8

======== CHANNEL f1 ========
NUC1                     1H
P1                11.00 usec
PL1               -3.00 dB
PL1W        25.05936241 W
SFO1        300.1318533 MHz
SI                    32768
SF          300.1300089 MHz
WDW                      EM
SSB                       0
LB                 0.30 Hz
GB                        0
PC                     4.00
```

AVQ-400 QNP Carbon Starting parameters 7/16/03 revis

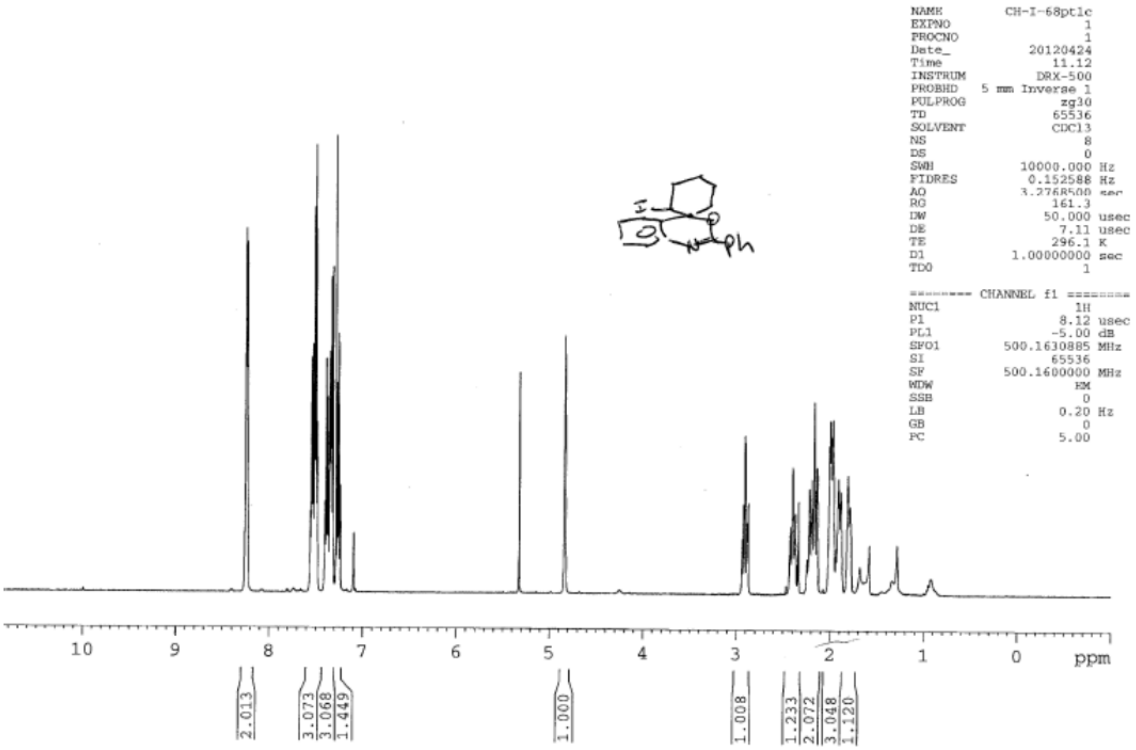


```
NAME                CH-I
EXPNO                  1
PROCNO
Date_            2012022
Time                 16.
INSTRUM            AVQ-4
PROBHD     5 mm QNP 1H/1
PULPROG            zgpg3
TD                  6553
SOLVENT             CDC1
NS                     7
DS
SWH             24038.4
FIDRES           0.3667
AQ               1.36321
RG                  163
DW                  20.8
DE                   6.
TE                  292.
D1            2.000000
D11           0.030000
TD0                  10

-------- CHANNEL f1 --
NUC1                  1
P1                   8.
PL1                  -2.
PL1W          47.7728614
SFO1          100.62282

======== CHANNEL f2 ==
CPDPRG2           waltz1
NUC2                   1
PCPD2               70.
PL2                  0.
PL12                15.
PL13                17.
PL2W          9.545168
PL12W         0.301844
PL13W         0.190451
SFO2          400.13160
SI                  327
SF            100.61277
WDW                    
SSB
LB                   1.
GB
PC                   1.4
```

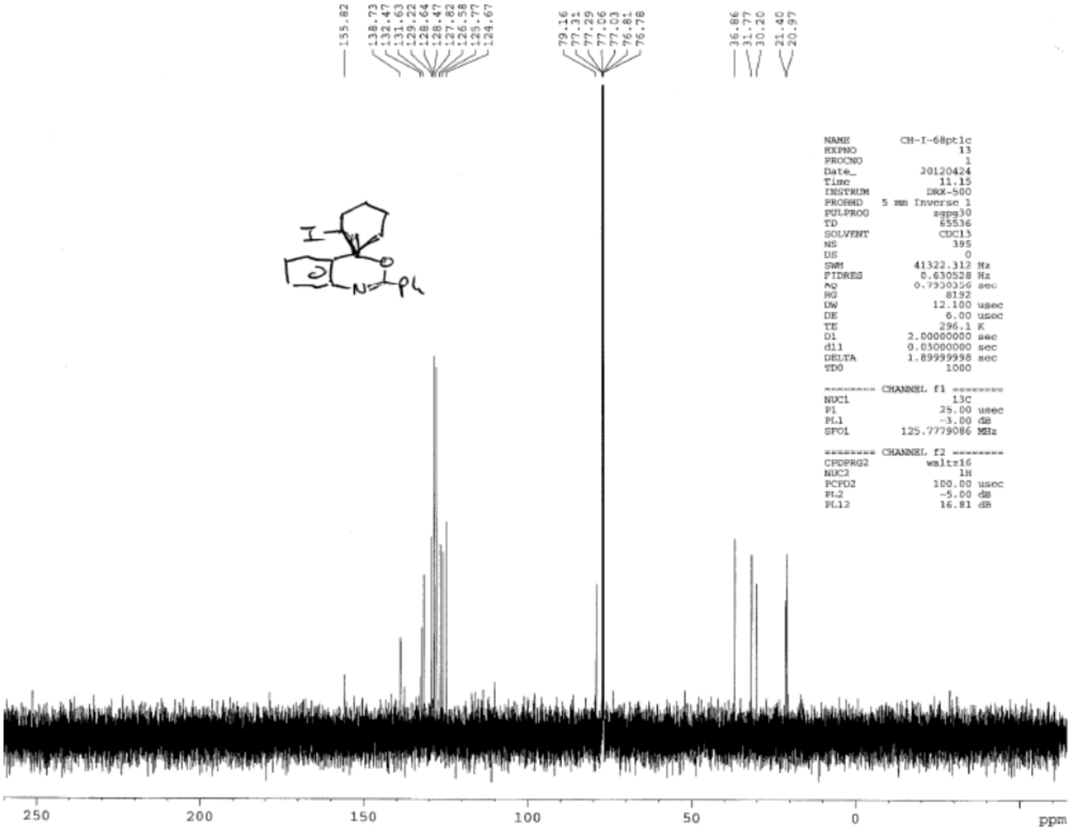

AV-600 ZBO proton starting parameters 11/16/08 RN
8.226 8.213 7.540 7.528 7.516 7.495 7.482 7.470 7.384 7.371 7.359 7.340 7.327 7.312 7.300 7.261 7.256 7.244 7.232 7.191 7.074 5.298 4.543 2.834 2.827 2.812 2.805 2.790 2.782 2.494 2.488 2.463 2.446 2.441 2.365 2.317 2.184 2.168 2.162 2.156 2.147 2.140 2.134 2.119 2.108 2.083 2.010 2.004 1.988 1.981 1.972 1.966 1.958 1.882 1.859 1.752 1.729 1.444
NAME ch-I-61-col
EXPNO 1
PROCNO 1
Date_ 20120312
Time 20.58
INSTRUM AV-600
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 128
DW 41.600 use
DE 6.00 use
TE 296.5 K
D1 0.10000000 sec
TD0 8
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 use
PL1 -2.00 dB
PL1W 22.93097305 W
SFO1 600.1339008 MHz
SI 65536
SF 600.1300171 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
Br
N
Ph
10 9 8 7 6 5 4 3 2 1 0 ppm
1.98 1.00 2.02 1.01 0.98 1.04 1.27 1.00 1.04 1.06 2.11 2.10 1.07 1.12


155.45 138.71 132.41 131.56 129.14 128.41 127.78 127.67 126.29 125.91 124.72 79.16 77.21 76.99 76.78 53.51 29.98 29.51 20.65 19.50
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
NAME ch-I-61-col
EXPNO 13
PROCNO 1
Date_ 20120312
Time 20.59
INSTRUM AV-600
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 155
DS 0
SWH 36057.691 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 2050
DW 13.867 usec
DE 6.00 usec
TE 296.6 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1000
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 2.00 dB
PL1W 62.60328293 W
SFO1 150.9178993 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 -2.00 dB
PL12 12.14 dB
Br
N
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

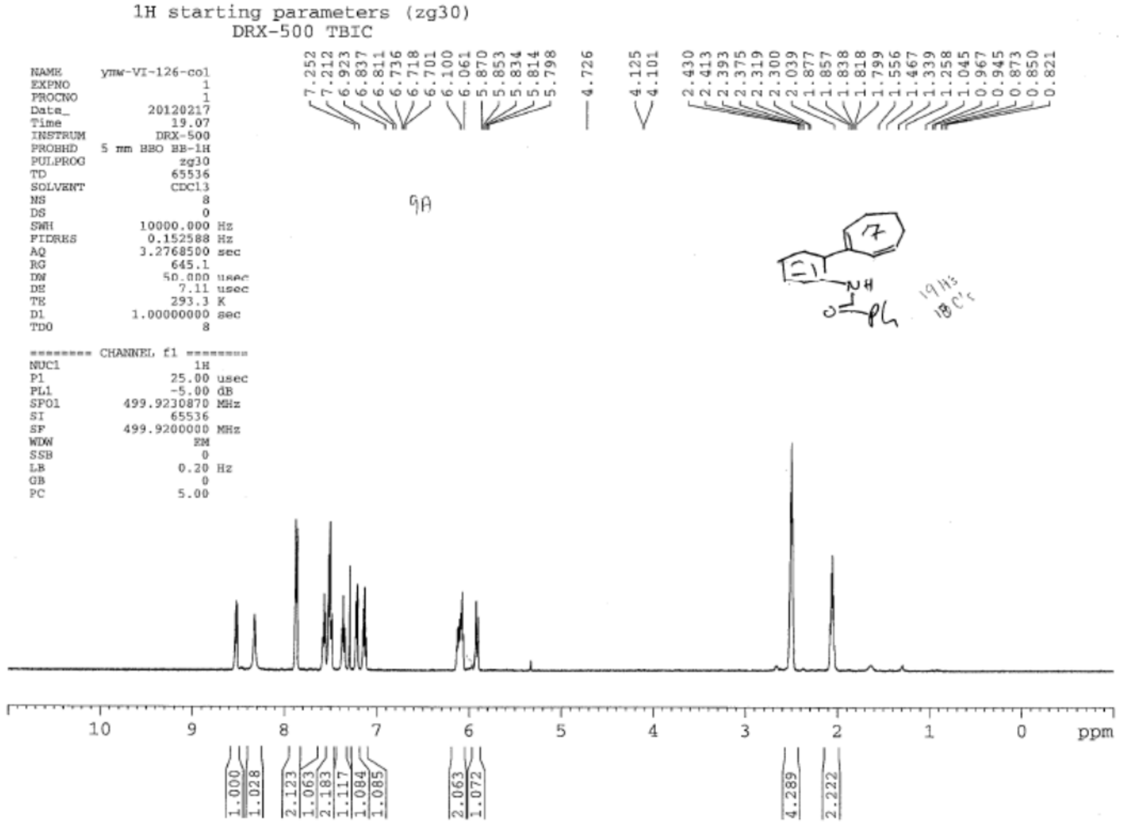
1H starting parameters (zg30)
DRX-500 TBIC



```
NAME              CH-I-68ptlc
EXPNO                       1
PROCNO                      1
Date_                20120424
Time                    11.12
INSTRUM               DRX-500
PROBHD        5 mm Inverse 1
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                          8
DS                          0
SWH                 10000.000 Hz
FIDRES               0.152588 Hz
AQ                  3.2768500 sec
RG                      161.3
DW                     50.000 usec
DE                       7.11 usec
TE                      296.1 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                       8.12 usec
PL1                     -5.00 dB
SFO1              500.1630885 MHz
SI                      65536
SF                500.1600000 MHz
WDW                        EM
SSB                         0
LB                       0.20 Hz
GB                          0
PC                       5.00
```



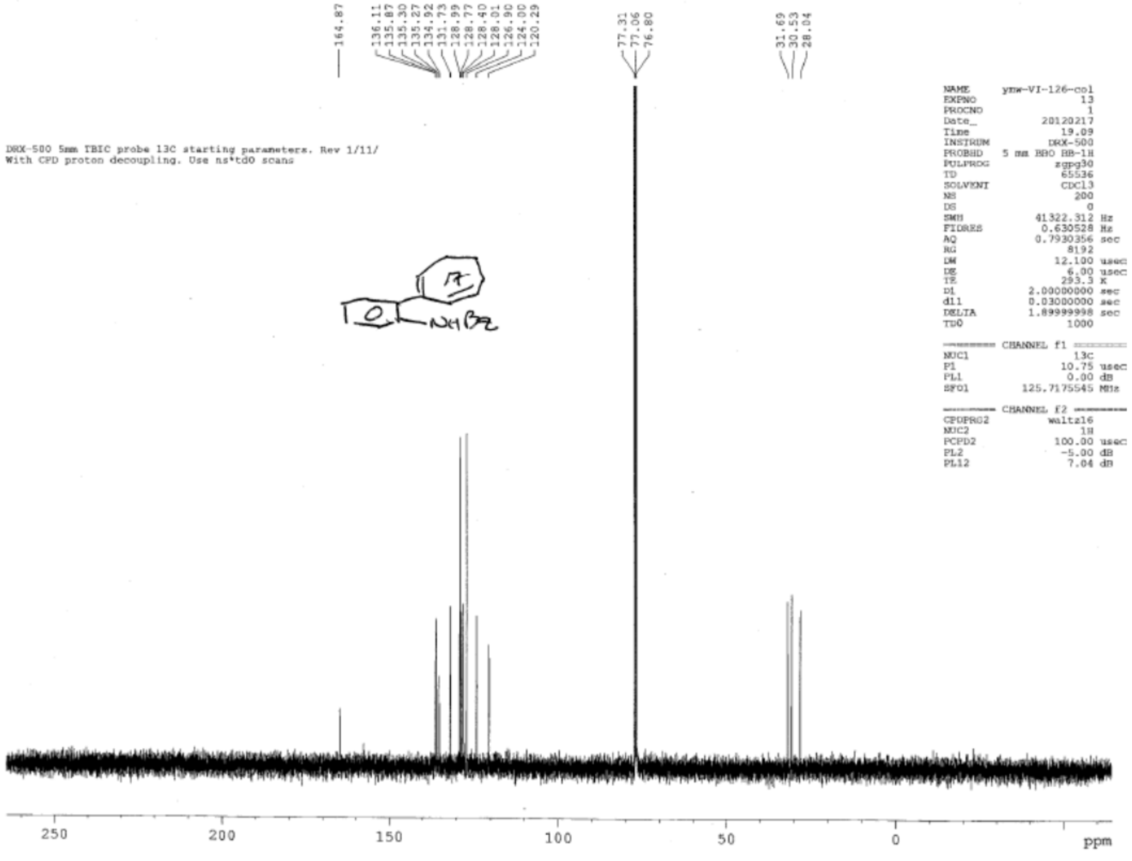
```
NAME              CH-I-68ptlc
EXPNO                      13
PROCNO                      1
Date_                20120424
Time                    11.15
INSTRUM               DRX-500
PROBHD        5 mm Inverse 1
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        395
DS                          0
SWH                 41322.312 Hz
FIDRES               0.630528 Hz
AQ                  0.7930356 sec
RG                       8192
DW                     12.100 usec
DE                       6.00 usec
TE                      296.1 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                      1000

======== CHANNEL f1 ========
NUC1                      13C
P1                      25.00 usec
PL1                     -3.00 dB
SFO1              125.7779086 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                       1H
PCPD2                  100.00 usec
PL2                     -5.00 dB
PL12                    16.81 dB
```



1H starting parameters (zg30)
DRX-500 TBIC

9A

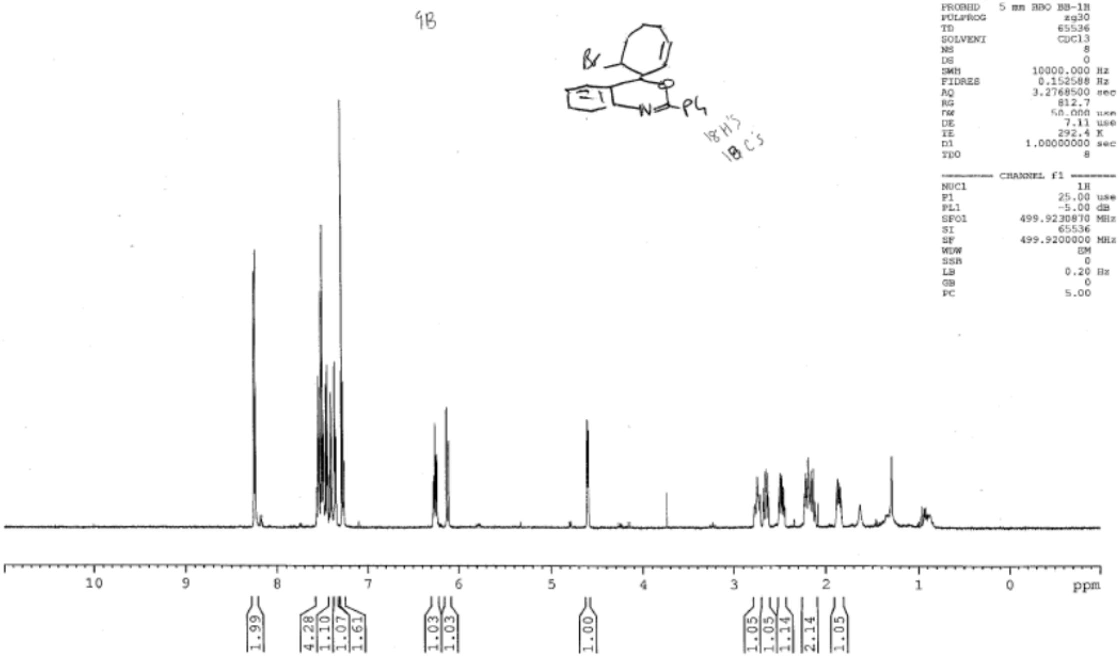
```
NAME      ymw-VI-126-col
EXPNO                  1
PROCNO                 1
Date_           20120217
Time               19.07
INSTRUM          DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10000.000 Hz
FIDRES          0.152588 Hz
AQ             3.2768500 sec
RG                 645.1
DW                50.000 usec
DE                  7.11 usec
TE                 293.3 K
D1            1.00000000 sec
TD0                    8

======== CHANNEL f1 ========
NUC1                  1H
P1                 25.00 usec
PL1                -5.00 dB
SFO1         499.9230870 MHz
SI                 65536
SF           499.9200000 MHz
WDW                   EM
SSB                    0
LB                  0.20 Hz
GB                     0
PC                  5.00
```



DRX-500 5mm TBIC probe 13C starting parameters. Rev 1/11/
With CPD proton decoupling. Use ns*td0 scans

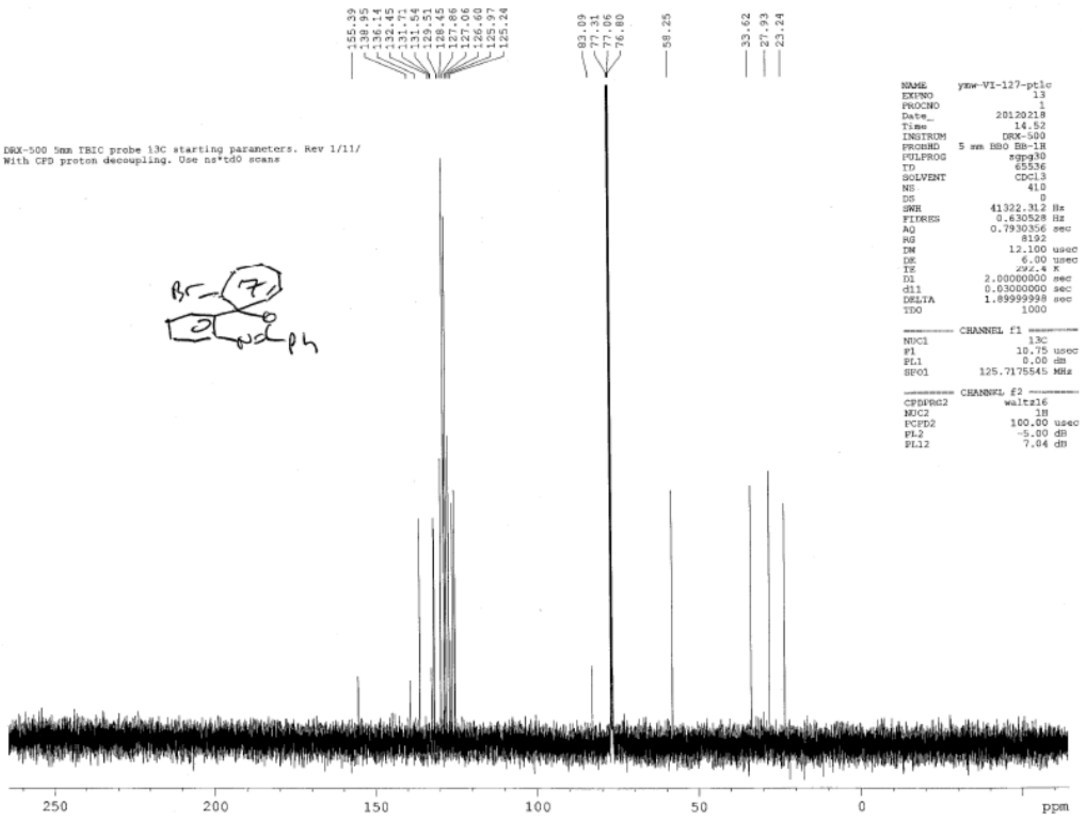
```
NAME      ymw-VI-126-col
EXPNO                 13
PROCNO                 1
Date_           20120217
Time               19.09
INSTRUM          DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   200
DS                     0
SWH            41322.312 Hz
FIDRES          0.630528 Hz
AQ             0.7930356 sec
RG                  8192
DW                12.100 usec
DE                  6.00 usec
TE                 293.3 K
d1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                 1000

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.75 usec
PL1                 0.00 dB
SFO1         125.7175545 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -5.00 dB
PL12                7.04 dB
```

1H starting parameters (zg30)
DRX-500 TBIC

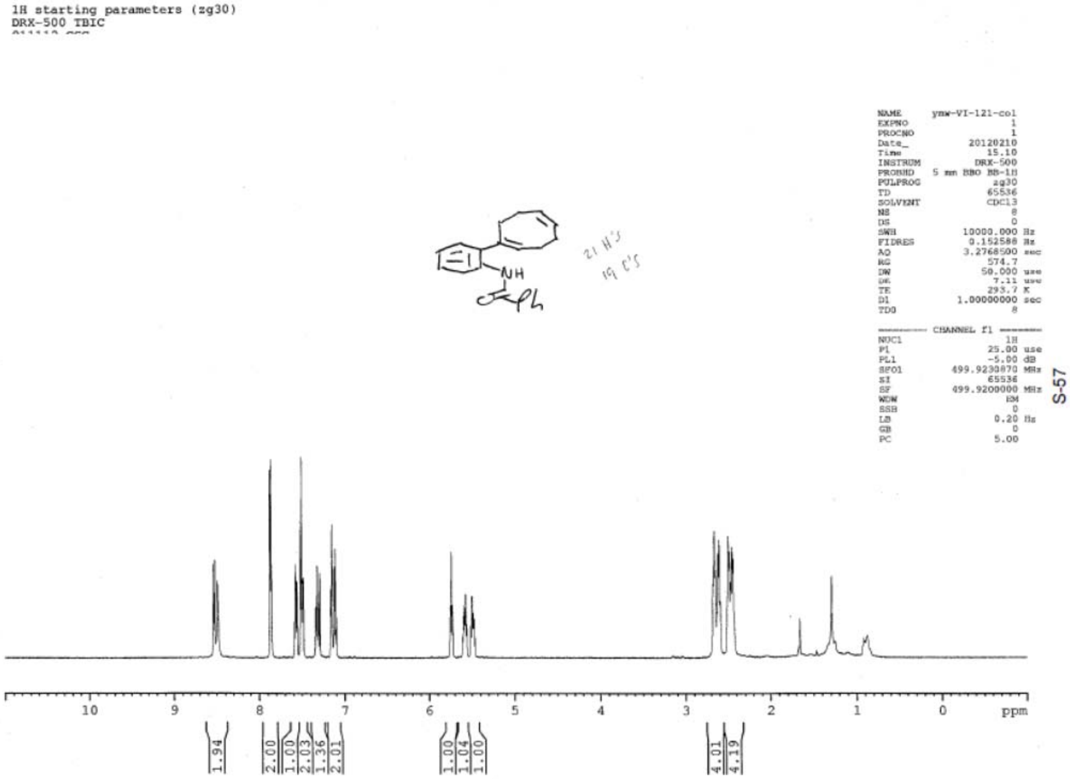


```
NAME       ymw-VI-~~127~~126-ptlc
EXPNO                   1
PROCNO                  1
Date_            20120218
Time                14.51
INSTRUM           DRX-500
PROBHD    5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH            10000.000 Hz
FIDRES          0.152588 Hz
AQ             3.2768500 sec
RG                  812.7
DW                 50.000 use
DE                   7.11 use
TE                  292.4 K
D1            1.00000000 sec
TDO                     8

========== CHANNEL f1 ========
NUC1                   1H
P1                  25.00 use
PL1                 -5.00 dB
SFO1         499.9230870 MHz
SI                  65536
SF           499.9200000 MHz
WDW                    EM
SSB                     0
LB                   0.20 Hz
GB                      0
PC                   5.00
```

DRX-500 5mm TBIC probe 13C starting parameters. Rev 1/11/
With CPD proton decoupling. Use ns*td0 scans



```
NAME       ymw-VI-127-ptlc
EXPNO                  13
PROCNO                  1
Date_            20120218
Time                14.52
INSTRUM           DRX-500
PROBHD    5 mm BBO BB-1H
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    410
DS                      0
SWH            41322.312 Hz
FIDRES          0.630528 Hz
AQ             0.7930356 sec
RG                   8192
DW                 12.100 usec
DE                   6.00 usec
TE                  292.4 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TDO                  1000

========== CHANNEL f1 ========
NUC1                  13C
P1                  10.75 usec
PL1                  0.00 dB
SFO1         125.7175545 MHz

========== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -5.00 dB
PL12                 7.04 dB
```

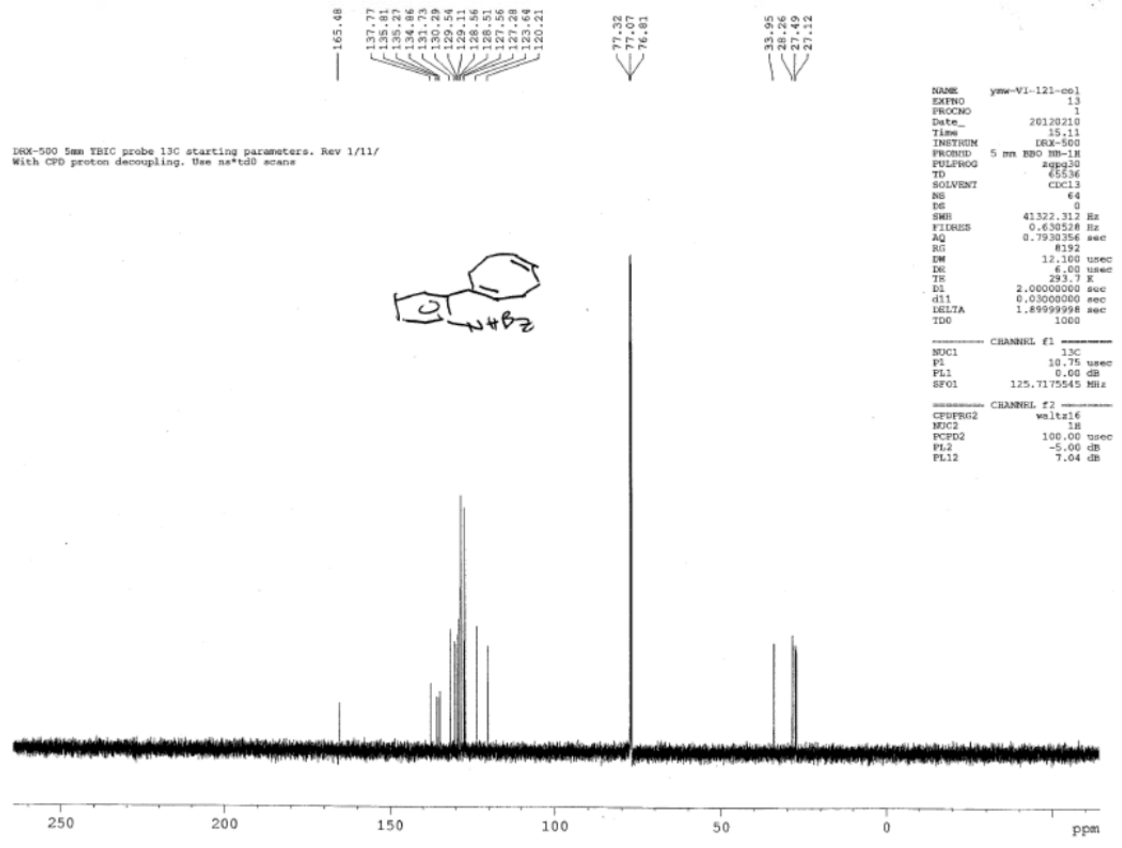


```
1H starting parameters (zg30)
DRX-500 TBIC
```

21 H's
19 C's

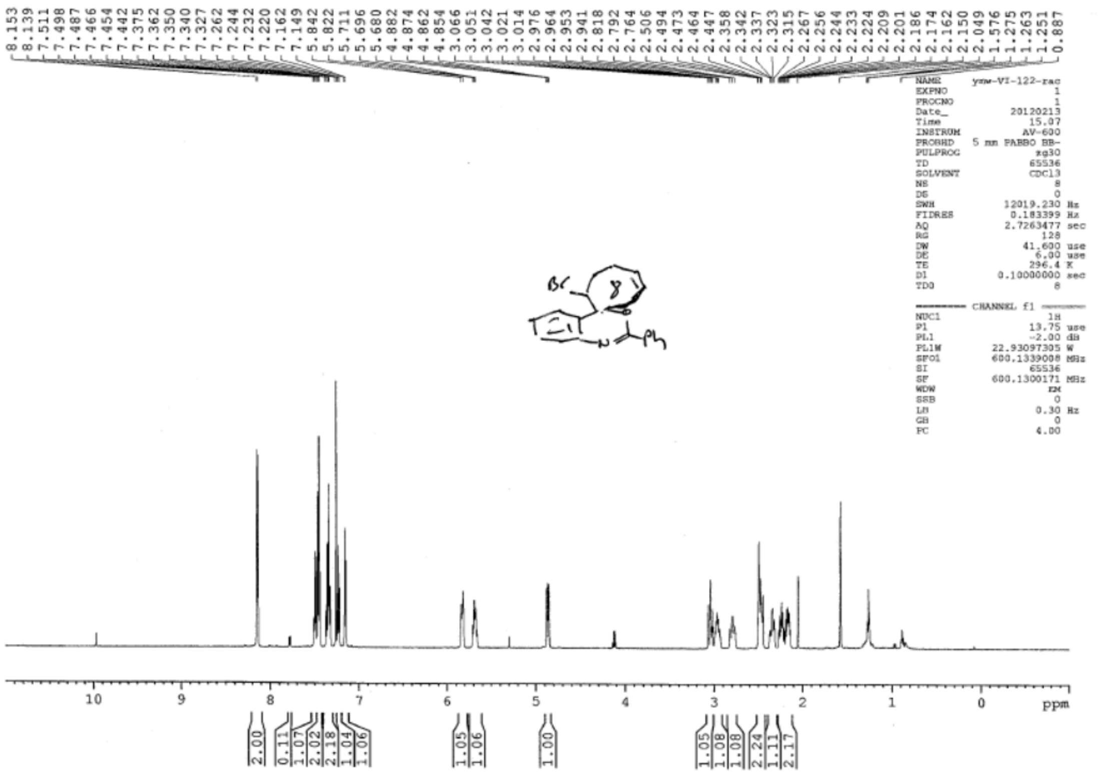
```
NAME       ymw-VI-121-col
EXPNO                   1
PROCNO                  1
Date_            20120210
Time                15.10
INSTRUM           DRX-500
PROBHD    5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH             10000.000 Hz
FIDRES           0.152588 Hz
AQ              3.2768500 sec
RG                  574.7
DW                 50.000 use
DE                   7.11 use
TE                  293.7 K
D1             1.00000000 sec
TD0                     8

========= CHANNEL f1 ========
NUC1                   1H
P1                  25.00 use
PL1                 -5.00 dB
SFO1          499.9230870 MHz
SI                  65536
SF            499.9200000 MHz
WDW                    EM
SSB                     0
LB                   0.20 Hz
GB                      0
PC                   5.00
```

S-57

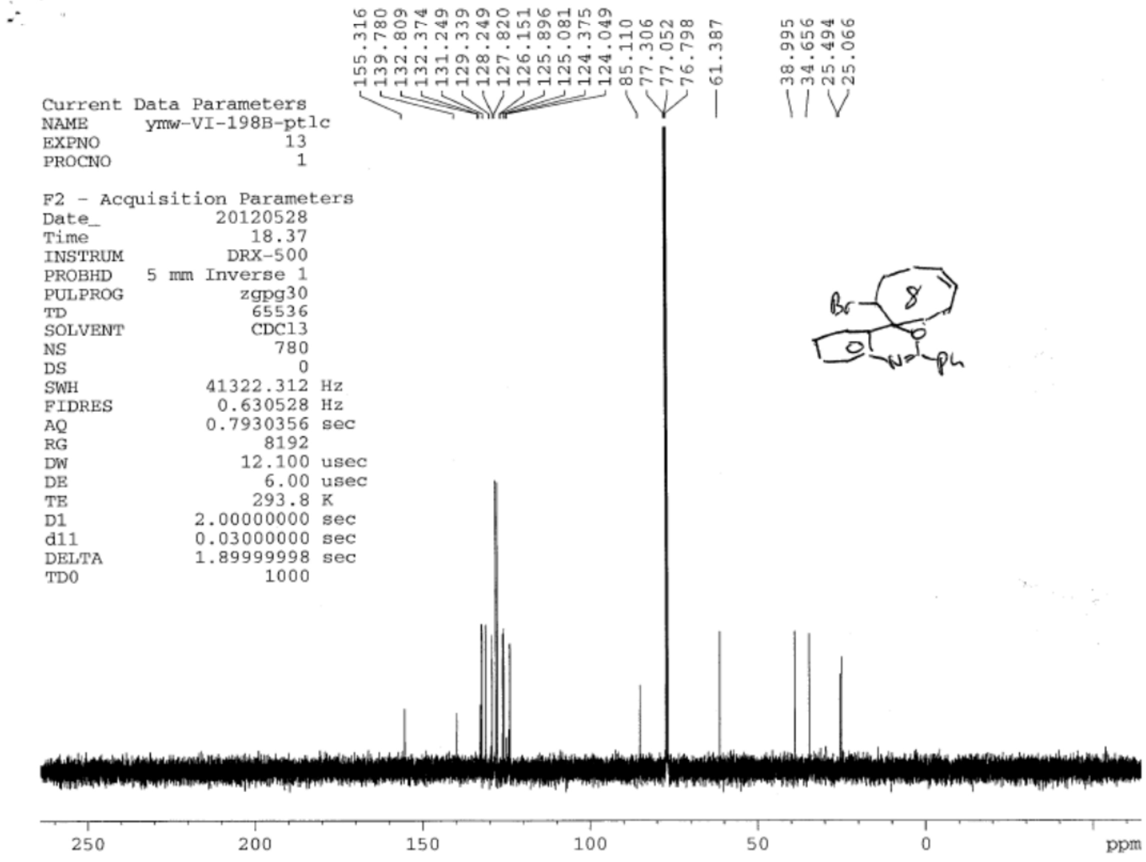


```
DRX-500 5mm TBIC probe 13C starting parameters. Rev 1/11/
With CPD proton decoupling. Use ns*td0 scans
```

```
NAME       ymw-VI-121-col
EXPNO                  13
PROCNO                  1
Date_            20120210
Time                15.11
INSTRUM           DRX-500
PROBHD    5 mm BBO BB-1H
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     64
DS                      0
SWH             41322.312 Hz
FIDRES           0.630528 Hz
AQ              0.7930356 sec
RG                   8192
DW                 12.100 usec
DE                   6.00 usec
TE                  293.7 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                  1000

========= CHANNEL f1 ========
NUC1                  13C
P1                  10.75 usec
PL1                  0.00 dB
SFO1          125.7175545 MHz

========= CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -5.00 dB
PL12                 7.04 dB
```

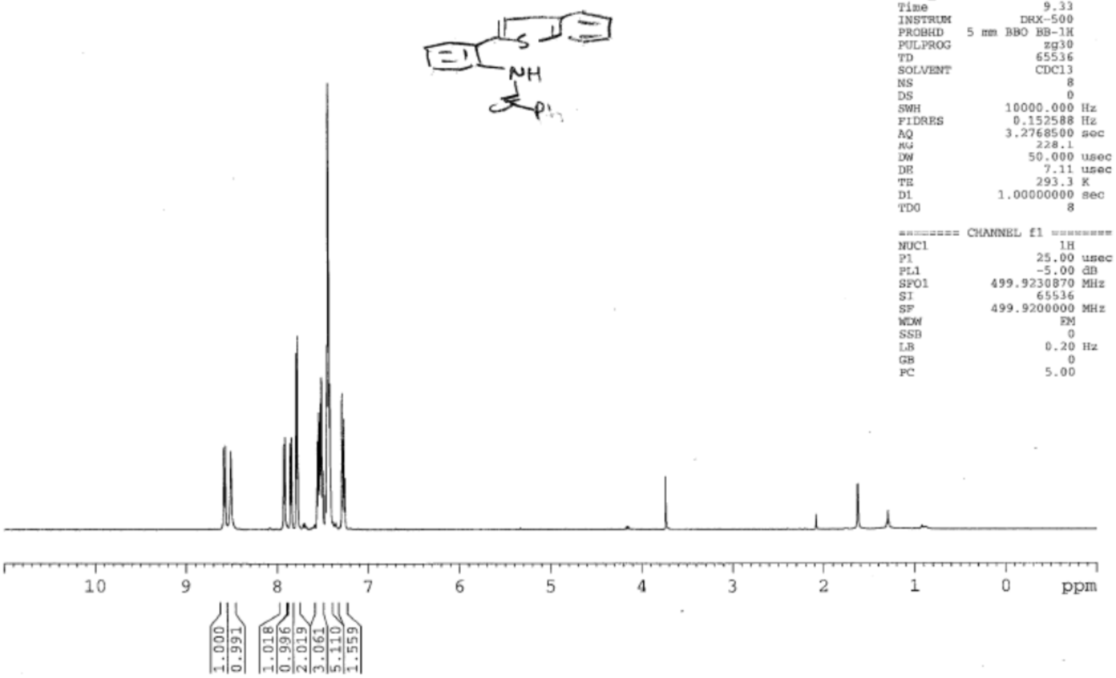


```
NAME        ymw-VI-122-rac
EXPNO                    1
PROCNO                   1
Date_             20120213
Time                 15.07
INSTRUM             AV-600
PROBHD     5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              12019.230 Hz
FIDRES            0.183399 Hz
AQ               2.7263477 sec
RG                     128
DW                  41.600 use
DE                    6.00 use
TE                   296.4 K
D1              0.10000000 sec
TD0                      8

======== CHANNEL f1 ========
NUC1                    1H
P1                   13.75 use
PL1                  -2.00 dB
PL1W           22.93097305 W
SFO1           600.1339008 MHz
SI                   65536
SF             600.1300171 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00
```

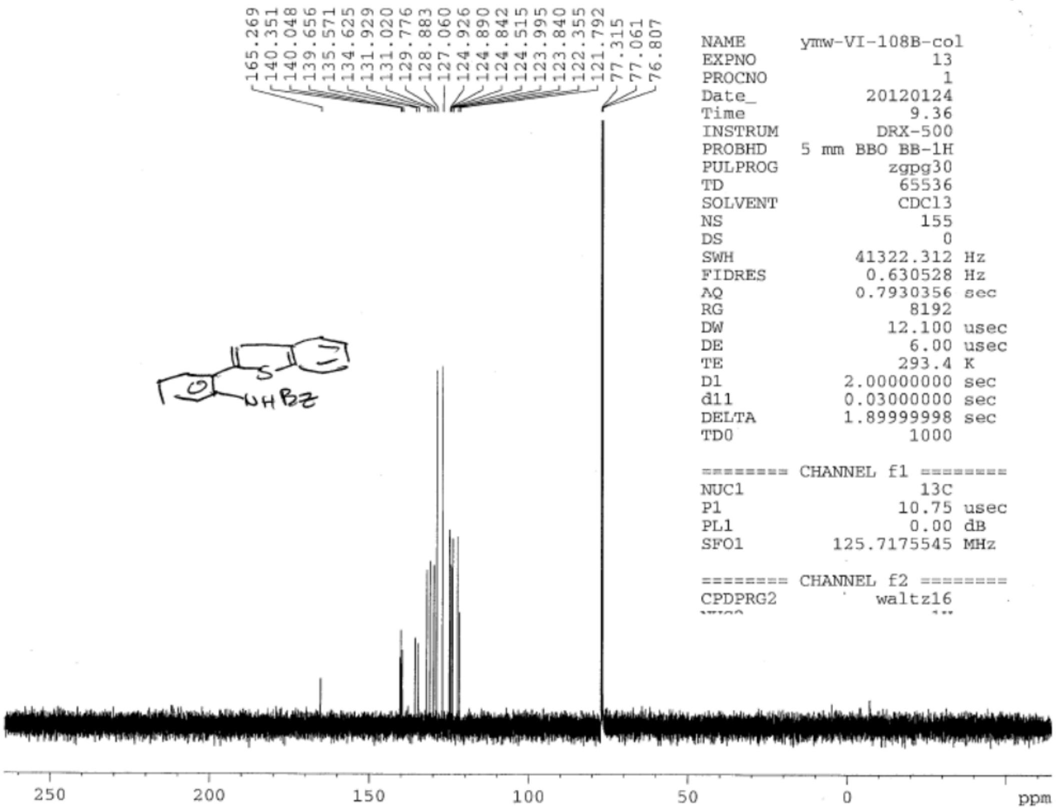


```
Current Data Parameters
NAME       ymw-VI-198B-ptlc
EXPNO                    13
PROCNO                    1

F2 - Acquisition Parameters
Date_              20120528
Time                  18.37
INSTRUM             DRX-500
PROBHD      5 mm Inverse 1
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      780
DS                        0
SWH               41322.312 Hz
FIDRES             0.630528 Hz
AQ                0.7930356 sec
RG                     8192
DW                   12.100 usec
DE                     6.00 usec
TE                    293.8 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                    1000
```

1H starting parameters (zg30)
DRX-500 TBIC

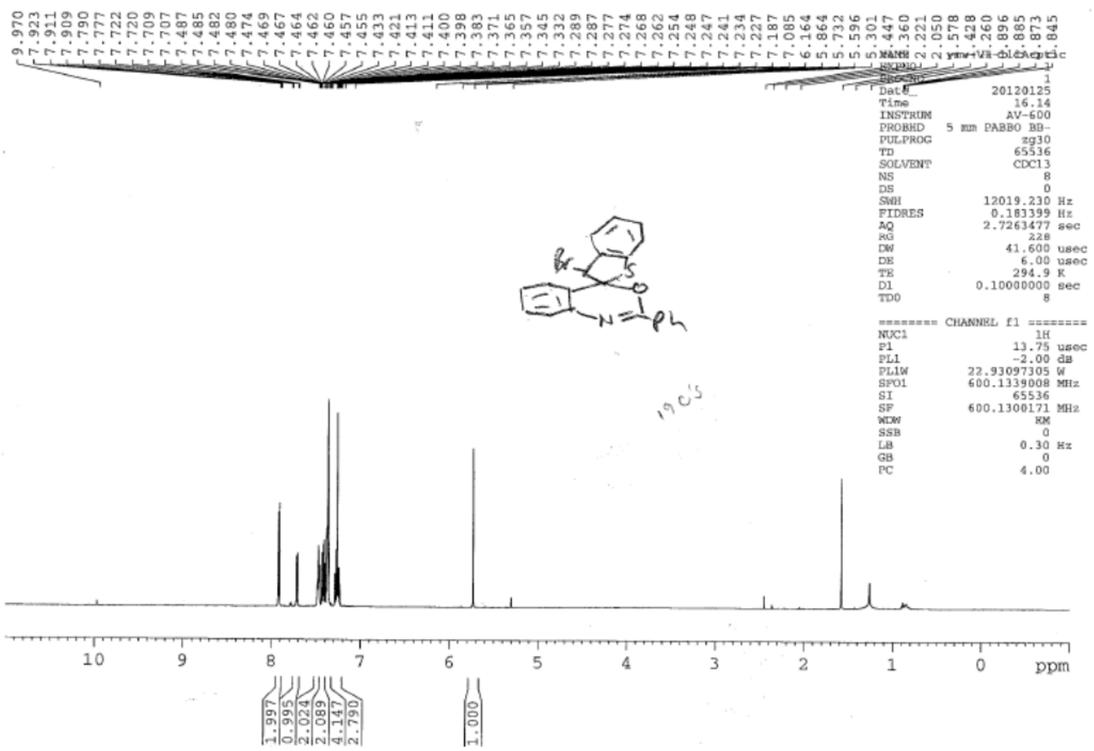


```
NAME       ymw-VI-108B-col
EXPNO                    1
PROCNO                   1
Date_             20120124
Time                  9.33
INSTRUM            DRX-500
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              10000.000 Hz
FIDRES            0.152588 Hz
AQ               3.2768500 sec
RG                   228.1
DW                  50.000 usec
DE                    7.11 usec
TE                   293.3 K
D1              1.00000000 sec
TD0                      8

======== CHANNEL f1 ========
NUC1                    1H
P1                   25.00 usec
PL1                  -5.00 dB
SFO1           499.9230870 MHz
SI                   65536
SF             499.9200000 MHz
WDW                     EM
SSB                      0
LB                    0.20 Hz
GB                       0
PC                    5.00
```

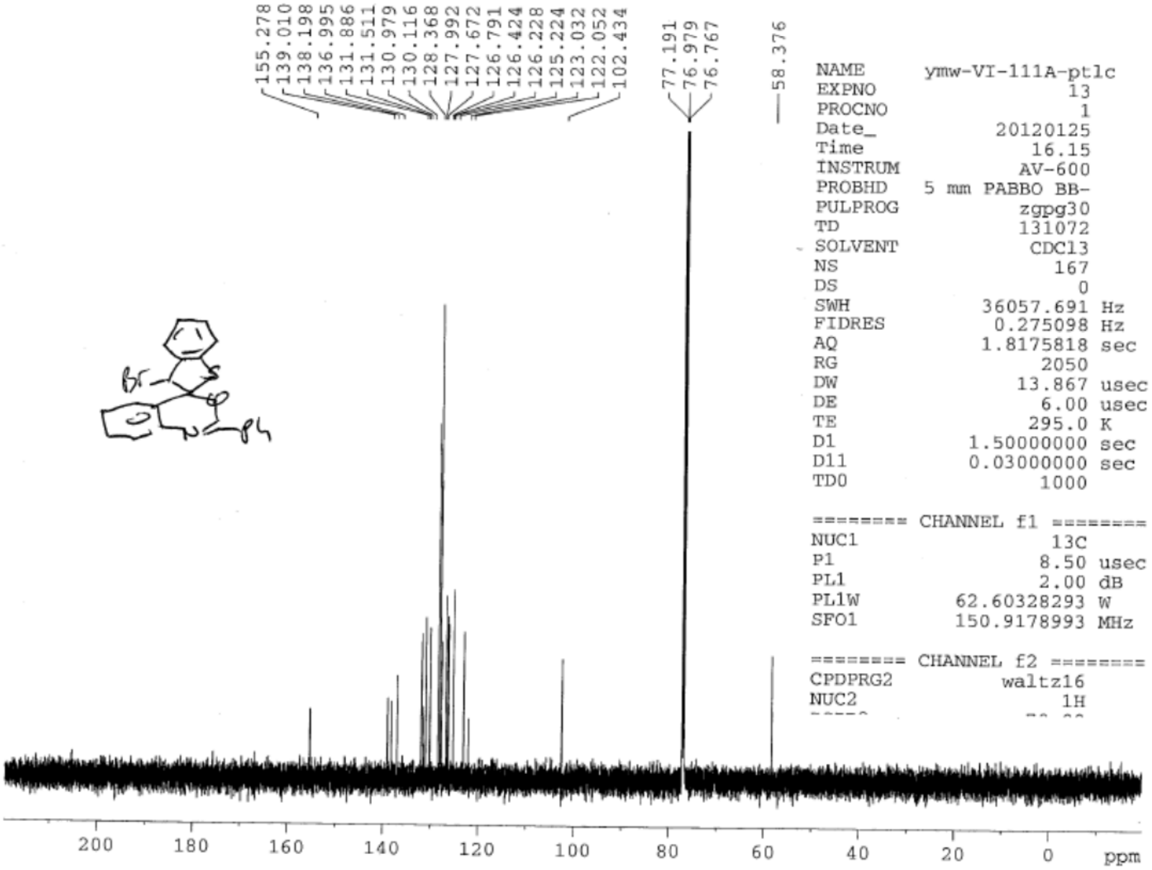


```
NAME       ymw-VI-108B-col
EXPNO                   13
PROCNO                   1
Date_             20120124
Time                  9.36
INSTRUM            DRX-500
PROBHD    5 mm BBO BB-1H
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     155
DS                       0
SWH              41322.312 Hz
FIDRES            0.630528 Hz
AQ               0.7930356 sec
RG                    8192
DW                  12.100 usec
DE                    6.00 usec
TE                   293.4 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                   1000

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.75 usec
PL1                   0.00 dB
SFO1           125.7175545 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
```

AV-600 ZBO proton starting parameters 11/16/08 RN

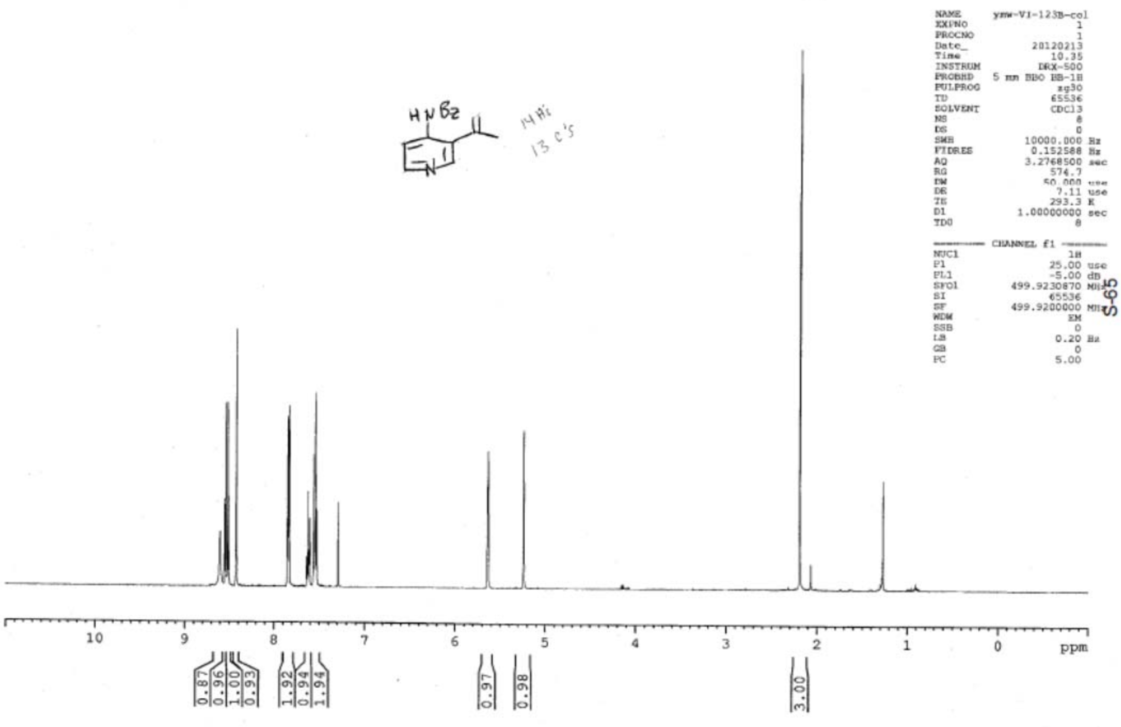


```
NAME      ymw-VI-111A-ptlc
EXPNO                    1
PROCNO                   1
Date_             20120125
Time                 16.14
INSTRUM             AV-600
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              12019.230 Hz
FIDRES            0.183399 Hz
AQ               2.7263477 sec
RG                     228
DW                  41.600 usec
DE                    6.00 usec
TE                   294.9 K
D1              0.10000000 sec
TD0                      8

======== CHANNEL f1 ========
NUC1                    1H
P1                   13.75 usec
PL1                  -2.00 dB
PL1W           22.93097305 W
SFO1           600.1339008 MHz
SI                   65536
SF             600.1300171 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00
```



```
NAME      ymw-VI-111A-ptlc
EXPNO                   13
PROCNO                   1
Date_             20120125
Time                 16.15
INSTRUM             AV-600
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  131072
SOLVENT              CDCl3
NS                     167
DS                       0
SWH              36057.691 Hz
FIDRES            0.275098 Hz
AQ               1.8175818 sec
RG                    2050
DW                  13.867 usec
DE                    6.00 usec
TE                   295.0 K
D1              1.50000000 sec
D11             0.03000000 sec
TD0                   1000

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.50 usec
PL1                   2.00 dB
PL1W           62.60328293 W
SFO1           150.9178993 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
```

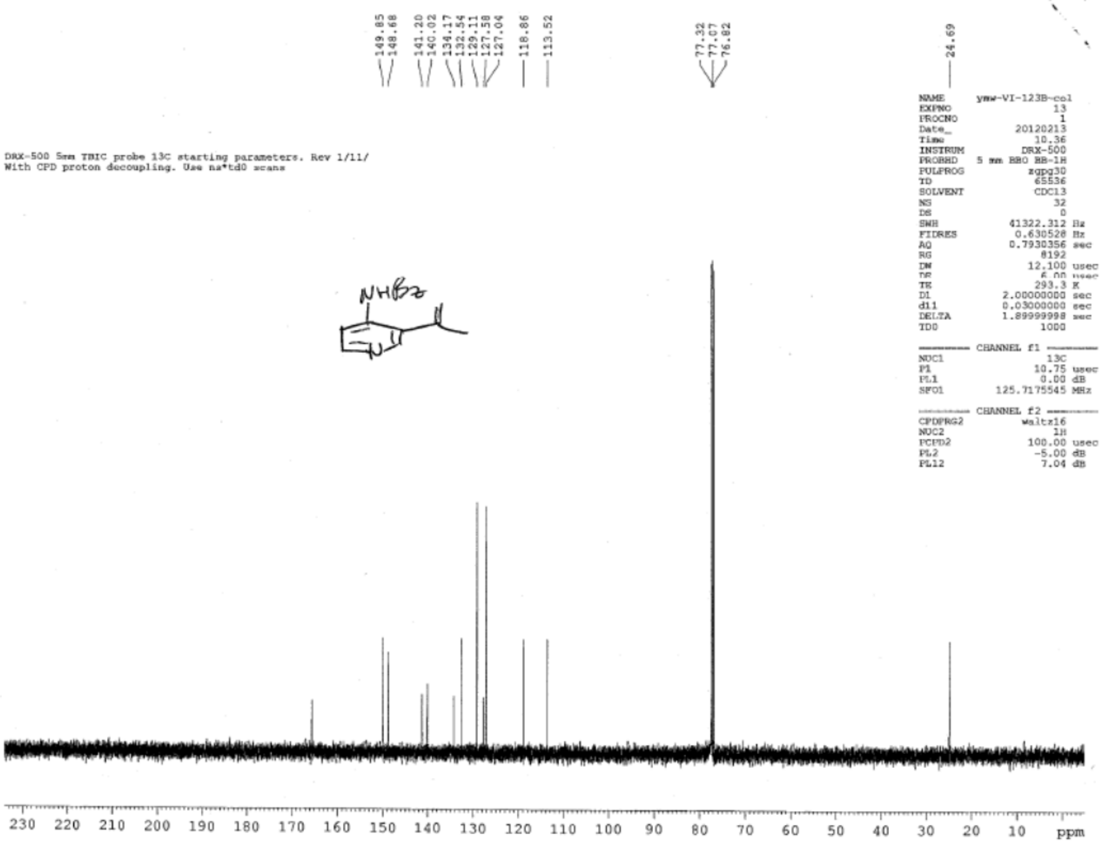
1H starting parameters (zg30)
DRX-500 TBIC



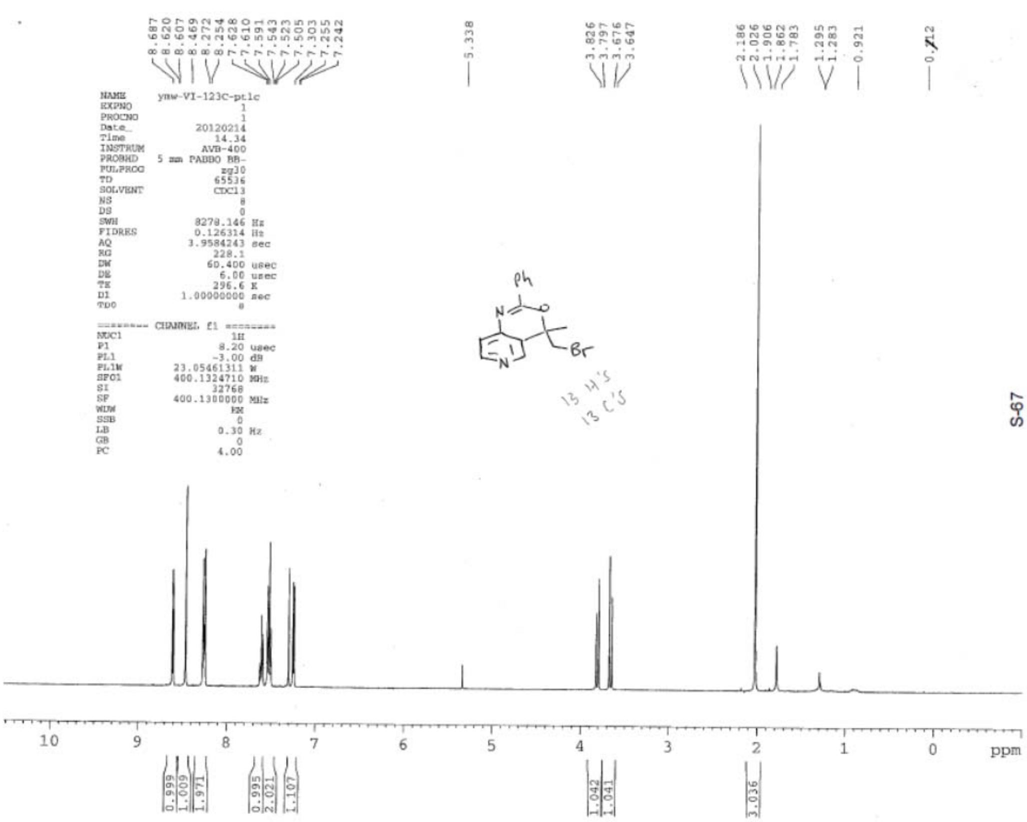
```
NAME       ymw-VI-123B-col
EXPNO                    1
PROCNO                   1
Date_             20120213
Time                 10.35
INSTRUM            DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH             10000.000 Hz
FIDRES           0.152588 Hz
AQ              3.2768500 sec
RG                   574.7
DW                  50.000 use
DE                    7.11 use
TE                   293.3 K
D1             1.00000000 sec
TD0                      8

======== CHANNEL f1 ========
NUC1                    1H
P1                   25.00 use
PL1                  -5.00 dB
SFO1           499.9230870 MHz
SI                   65536
SF             499.9200000 MHz
WDW                     EM
SSB                      0
LB                    0.20 Hz
GB                       0
PC                    5.00
```

S-65

DRX-500 5mm TBIC probe 13C starting parameters. Rev 1/11/
With CPD proton decoupling. Use ns*td0 scans



```
NAME       ymw-VI-123B-col
EXPNO                   13
PROCNO                   1
Date_             20120213
Time                 10.36
INSTRUM            DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       0
SWH             41322.312 Hz
FIDRES           0.630528 Hz
AQ              0.7930356 sec
RG                    8192
DW                  12.100 usec
DE                    6.00 usec
TE                   293.3 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                   1000

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.75 usec
PL1                   0.00 dB
SFO1           125.7175545 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                  -5.00 dB
PL12                  7.04 dB
```



```
NAME       ymw-VI-123C-ptlc
EXPNO                     1
PROCNO                    1
Date_              20120214
Time                  14.34
INSTRUM             AVB-400
PROBHD     5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDC13
NS                        8
DS                        0
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                3.9584243 sec
RG                    228.1
DW                   60.400 usec
DE                     6.00 usec
TE                    296.6 K
D1               1.00000000 sec
TD0                       8

======== CHANNEL f1 ========
NUC1                     1H
P1                     8.20 usec
PL1                   -3.00 dB
PL1W            23.05461311 W
SFO1            400.1324710 MHz
SI                    32768
SF              400.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     4.00
```

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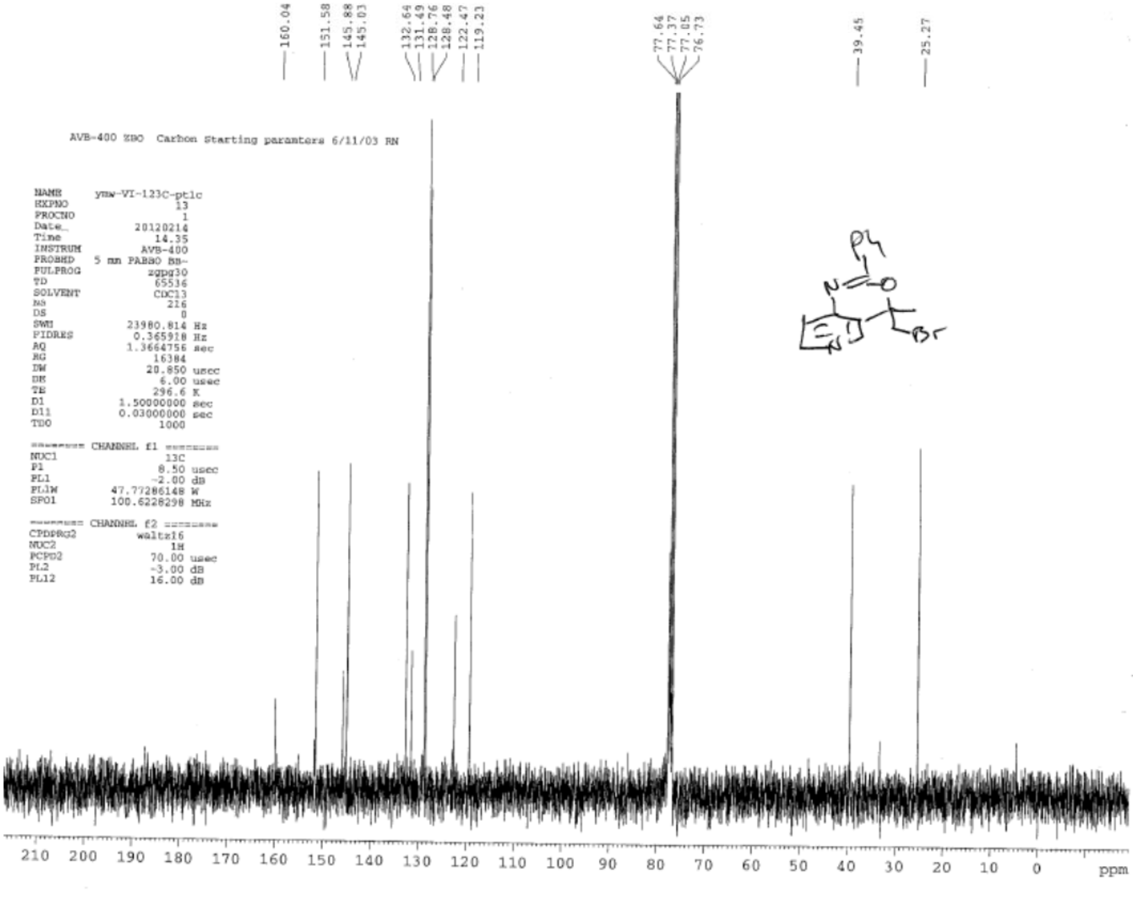
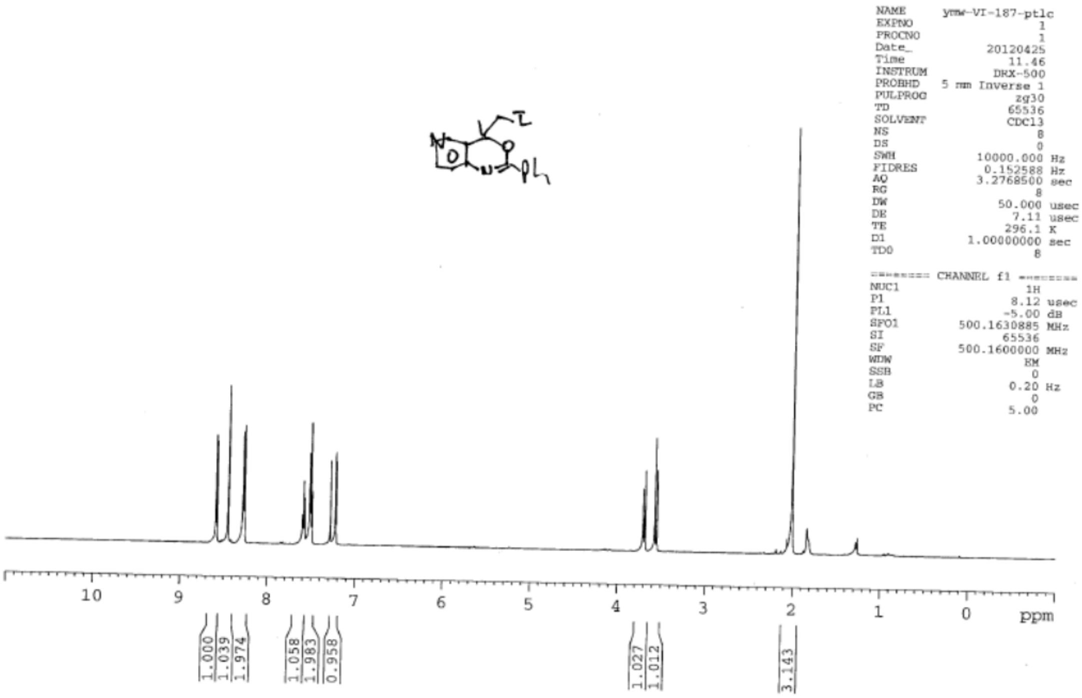
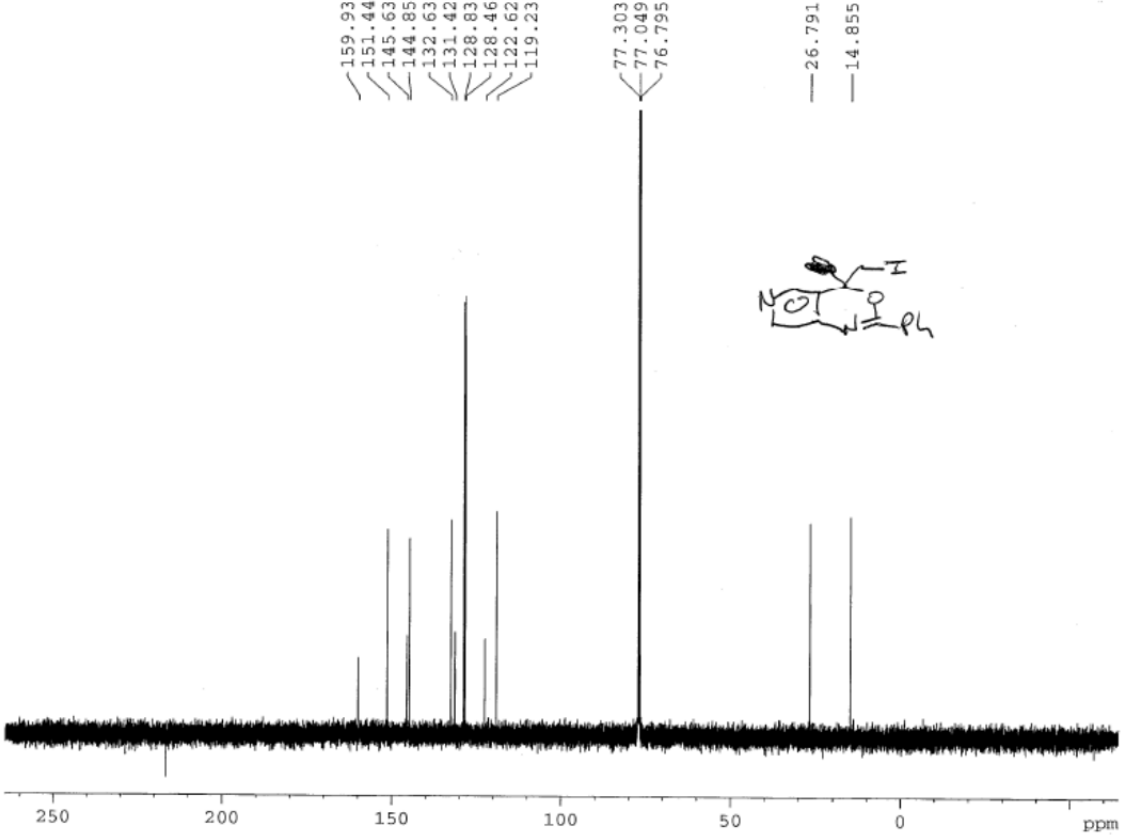


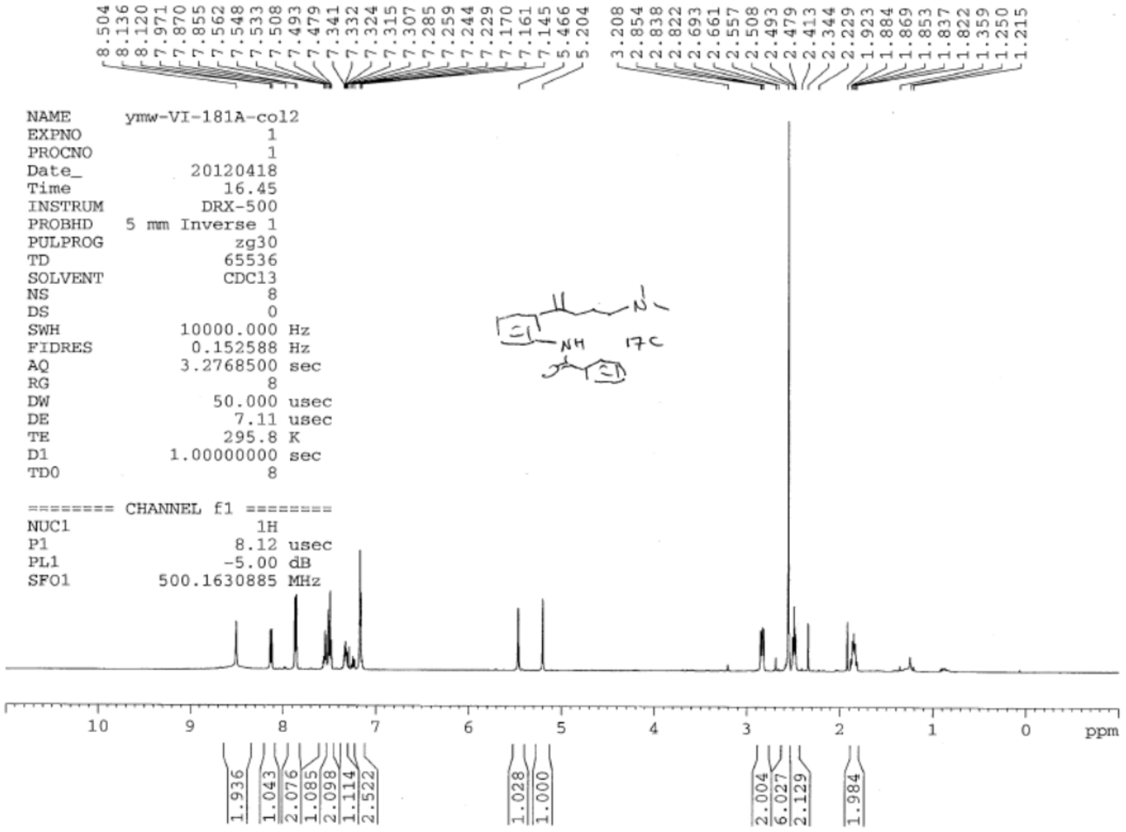
```
AVB-400 ZBO  Carbon Starting paramters 6/11/03 RN

NAME       ymw-VI-123C-ptlc
EXPNO                    13
PROCNO                    1
Date_              20120214
Time                  14.35
INSTRUM             AVB-400
PROBHD     5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDC13
NS                      216
DS                        0
SWH               23980.814 Hz
FIDRES             0.365918 Hz
AQ                1.3664756 sec
RG                    16384
DW                   20.850 usec
DE                     6.00 usec
TE                    296.6 K
D1               1.50000000 sec
D11              0.03000000 sec
TD0                    1000

======== CHANNEL f1 ========
NUC1                    13C
P1                     8.50 usec
PL1                   -2.00 dB
PL1W            47.77286148 W
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 70.00 usec
PL2                   -3.00 dB
PL12                  16.00 dB
```

1H starting parameters (zg30)
DRX-500 TBIC

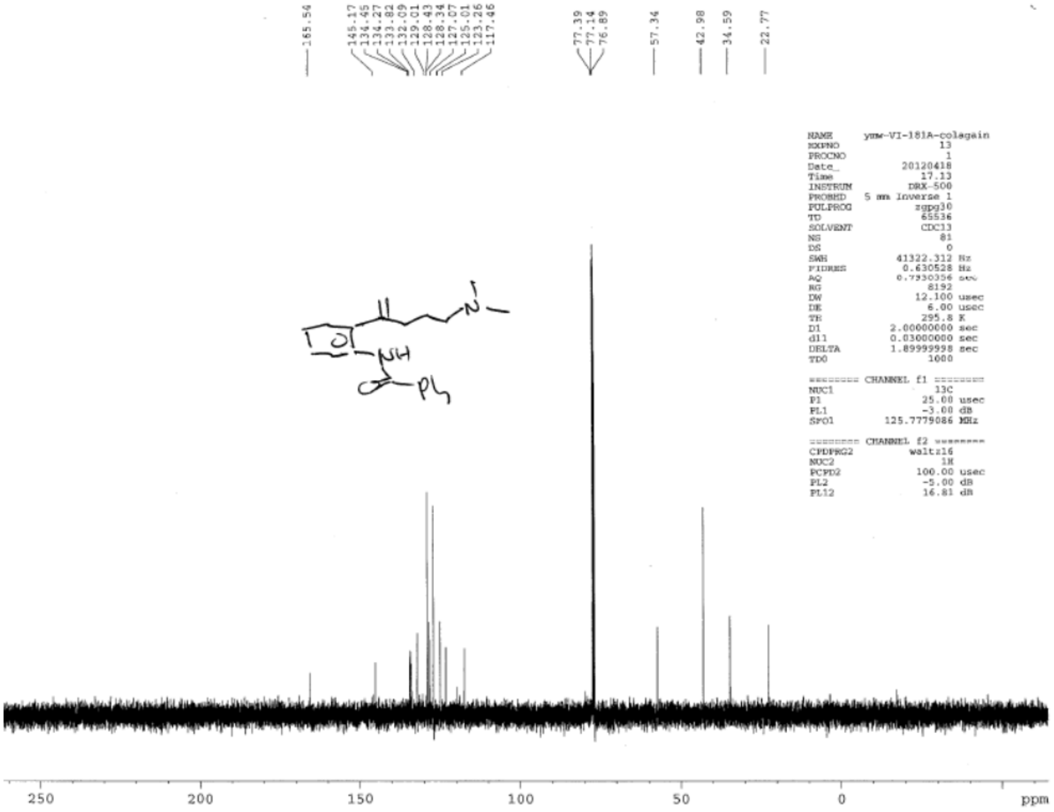


```
NAME        ymw-VI-187-ptlc
EXPNO                     1
PROCNO                    1
Date_              20120425
Time                  11.46
INSTRUM             DRX-500
PROBHD      5 mm Inverse 1
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        0
SWH              10000.000 Hz
FIDRES            0.152588 Hz
AQ               3.2768500 sec
RG                        8
DW                  50.000 usec
DE                    7.11 usec
TE                   296.1 K
D1              1.00000000 sec
TD0                       8

======== CHANNEL f1 ========
NUC1                     1H
P1                     8.12 usec
PL1                   -5.00 dB
SFO1           500.1630885 MHz
SI                    65536
SF             500.1600000 MHz
WDW                      EM
SSB                       0
LB                     0.20 Hz
GB                        0
PC                     5.00
```

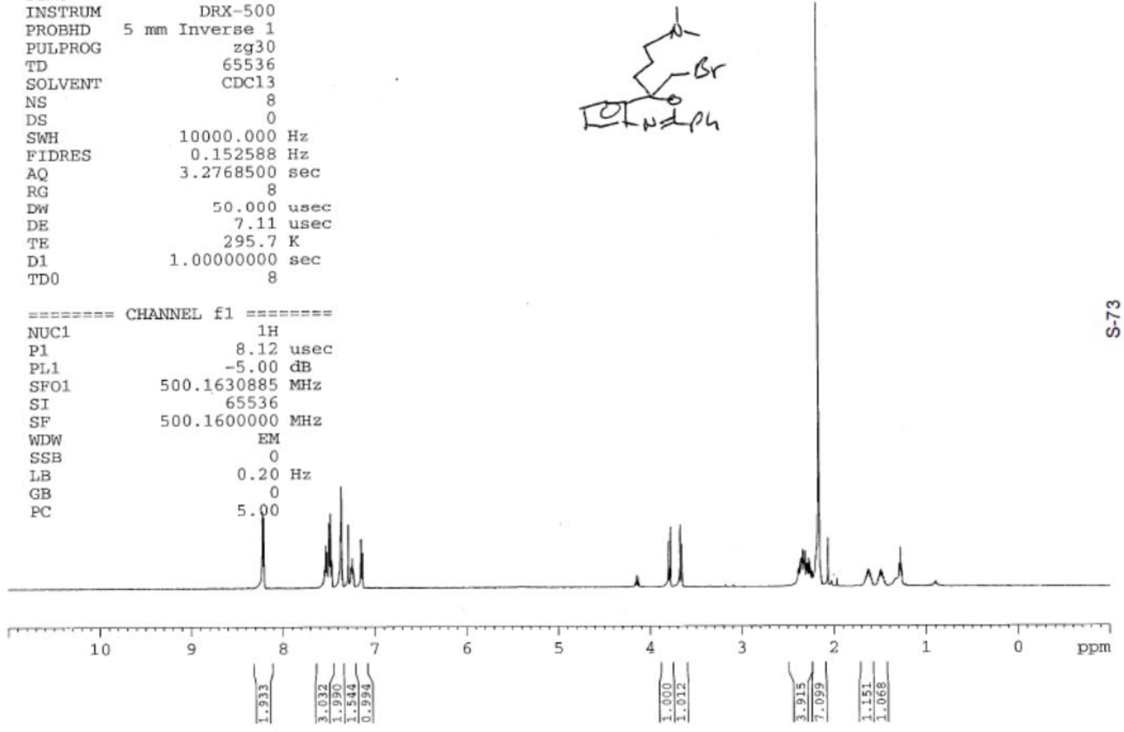




```
NAME        ymw-VI-181A-col2
EXPNO                      1
PROCNO                     1
Date_               20120418
Time                   16.45
INSTRUM              DRX-500
PROBHD      5 mm Inverse 1
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         8
DS                         0
SWH               10000.000 Hz
FIDRES             0.152588 Hz
AQ                3.2768500 sec
RG                         8
DW                    50.000 usec
DE                      7.11 usec
TE                     295.8 K
D1               1.00000000 sec
TD0                        8

======== CHANNEL f1 ========
NUC1                      1H
P1                      8.12 usec
PL1                    -5.00 dB
SFO1           500.1630885 MHz
```



```
NAME        ymw-VI-181A-colagain
EXPNO                     13
PROCNO                     1
Date_               20120418
Time                   17.13
INSTRUM              DRX-500
PROBHD      5 mm Inverse 1
PULPROG              zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        81
DS                         0
SWH               41322.312 Hz
FIDRES             0.630528 Hz
AQ                 0.7930356 sec
RG                      8192
DW                    12.100 usec
DE                      6.00 usec
TE                     295.8 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                     1000

======== CHANNEL f1 ========
NUC1                     13C
P1                     25.00 usec
PL1                    -3.00 dB
SFO1           125.7779086 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                 100.00 usec
PL2                    -5.00 dB
PL12                   16.81 dB
```



```
NAME       ymw-VI-181-rac
EXPNO                   1
PROCNO                  1
Date_            20120418
Time                19.26
INSTRUM           DRX-500
PROBHD     5 mm Inverse 1
PULPROG              zg30
TD                  65536
SOLVENT             CDC13
NS                      8
DS                      0
SWH             10000.000 Hz
FIDRES           0.152588 Hz
AQ              3.2768500 sec
RG                      8
DW                 50.000 usec
DE                   7.11 usec
TE                  295.7 K
D1             1.00000000 sec
TD0                     8

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.12 usec
PL1                 -5.00 dB
SFO1          500.1630885 MHz
SI                  65536
SF            500.1600000 MHz
WDW                    EM
SSB                     0
LB                   0.20 Hz
GB                      0
PC                   5.00
```

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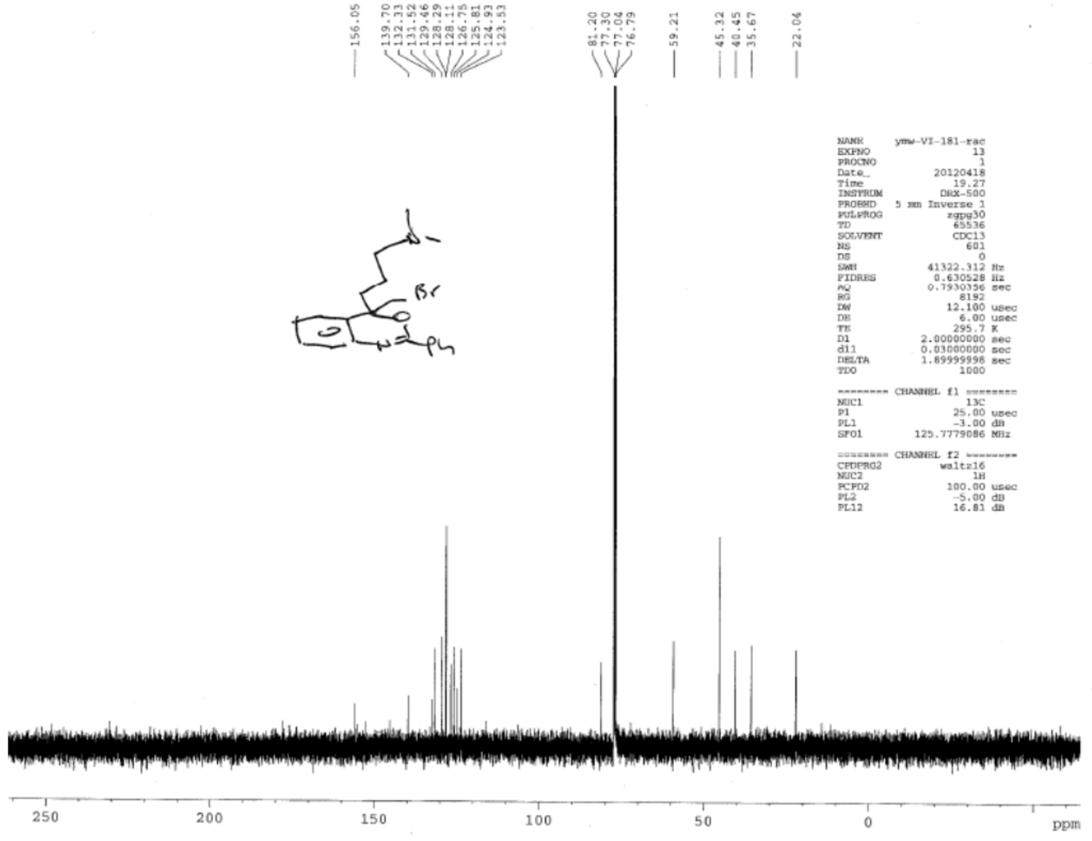


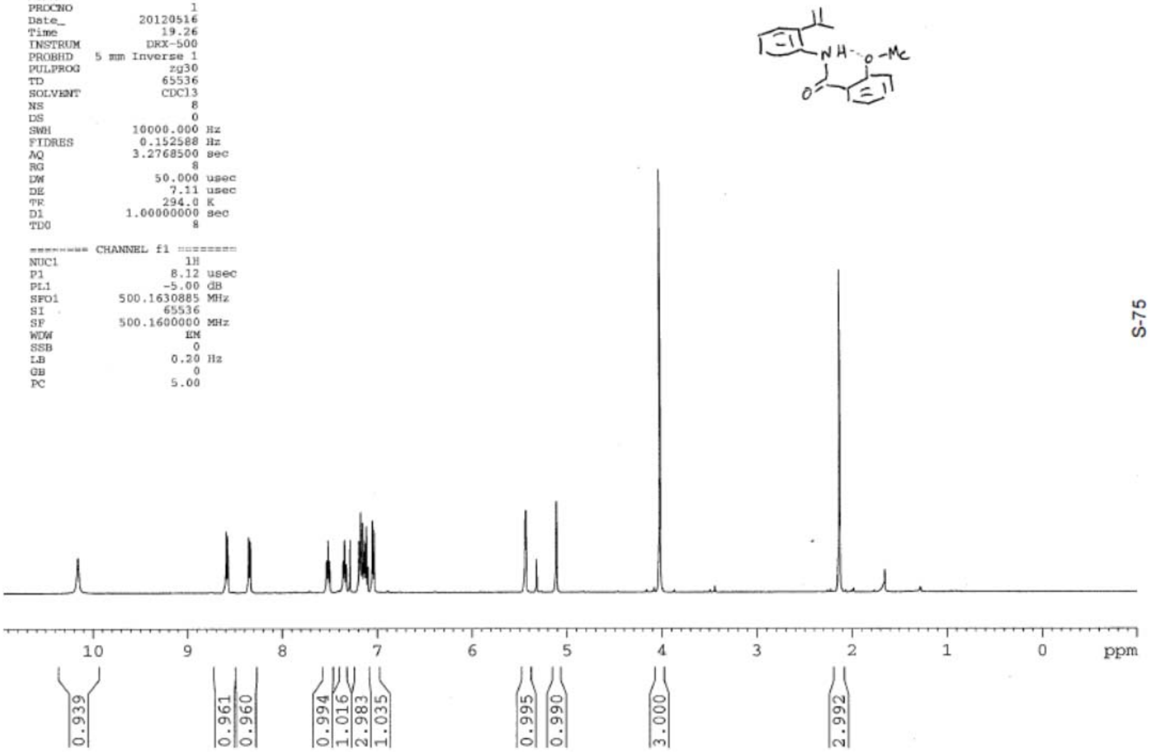
```
NAME       ymw-VI-181-rac
EXPNO                  13
PROCNO                  1
Date_            20120418
Time                19.27
INSTRUM           DRX-500
PROBHD     5 mm Inverse 1
PULPROG            zgpg30
TD                  65536
SOLVENT             CDC13
NS                    601
DS                      0
SWH             41322.312 Hz
FIDRES           0.630528 Hz
AQ              0.7930356 sec
RG                   8192
DW                 12.100 usec
DE                   6.00 usec
TE                  295.7 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                  1000

======== CHANNEL f1 ========
NUC1                  13C
P1                  25.00 usec
PL1                 -3.00 dB
SFO1          125.7779086 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -5.00 dB
PL12                16.81 dB
```

```
NAME       ymw-VI-188-orthoMe
EXPNO                    1
PROCNO                   1
Date_             20120516
Time                 19.26
INSTRUM            DRX-500
PROBHD    5 mm Inverse 1
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              10000.000 Hz
FIDRES            0.152588 Hz
AQ               3.2768500 sec
RG                       8
DW                  50.000 usec
DE                    7.11 usec
TE                   294.0 K
D1              1.00000000 sec
TD0                      8

======== CHANNEL f1 ========
NUC1                    1H
P1                    8.12 usec
PL1                  -5.00 dB
SFO1           500.1630885 MHz
SI                   65536
SF             500.1600000 MHz
WDW                     EM
SSB                      0
LB                    0.20 Hz
GB                       0
PC                    5.00
```



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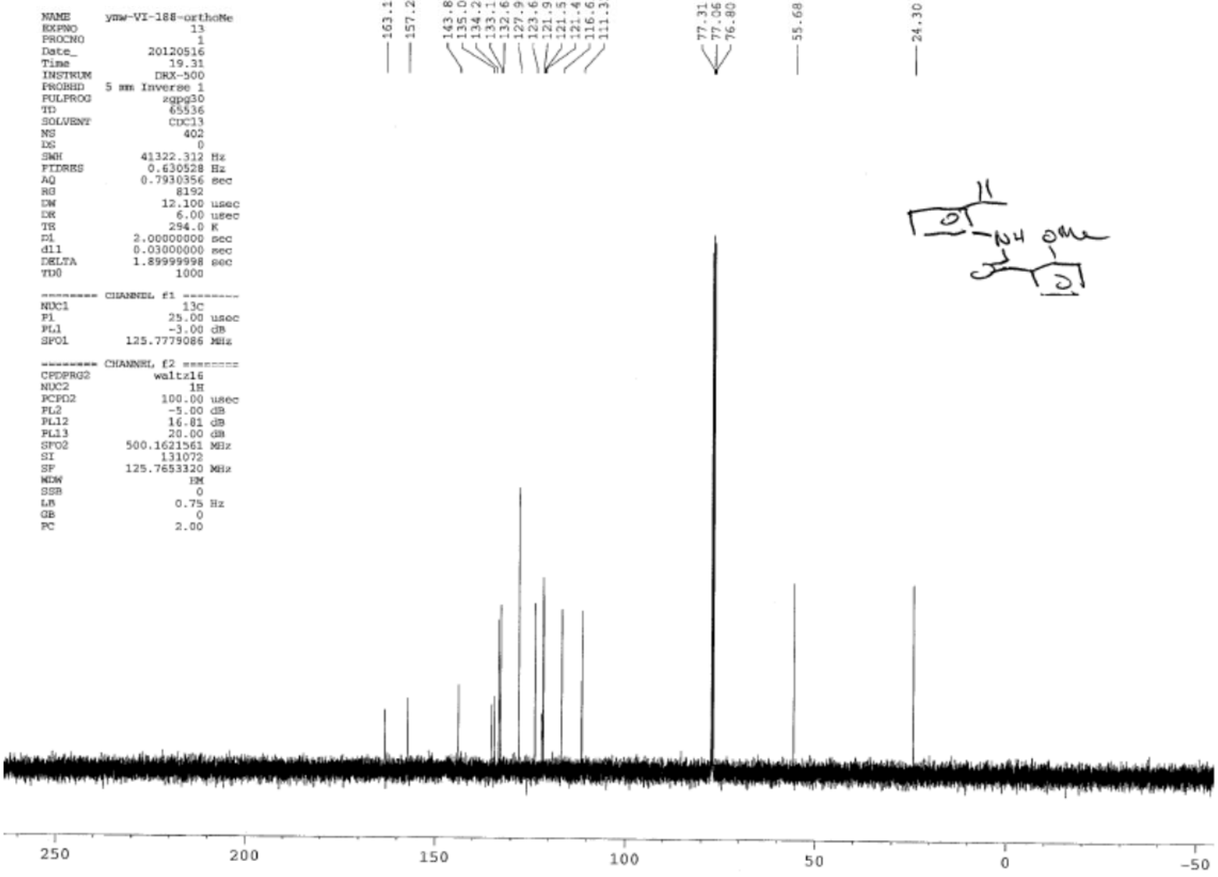
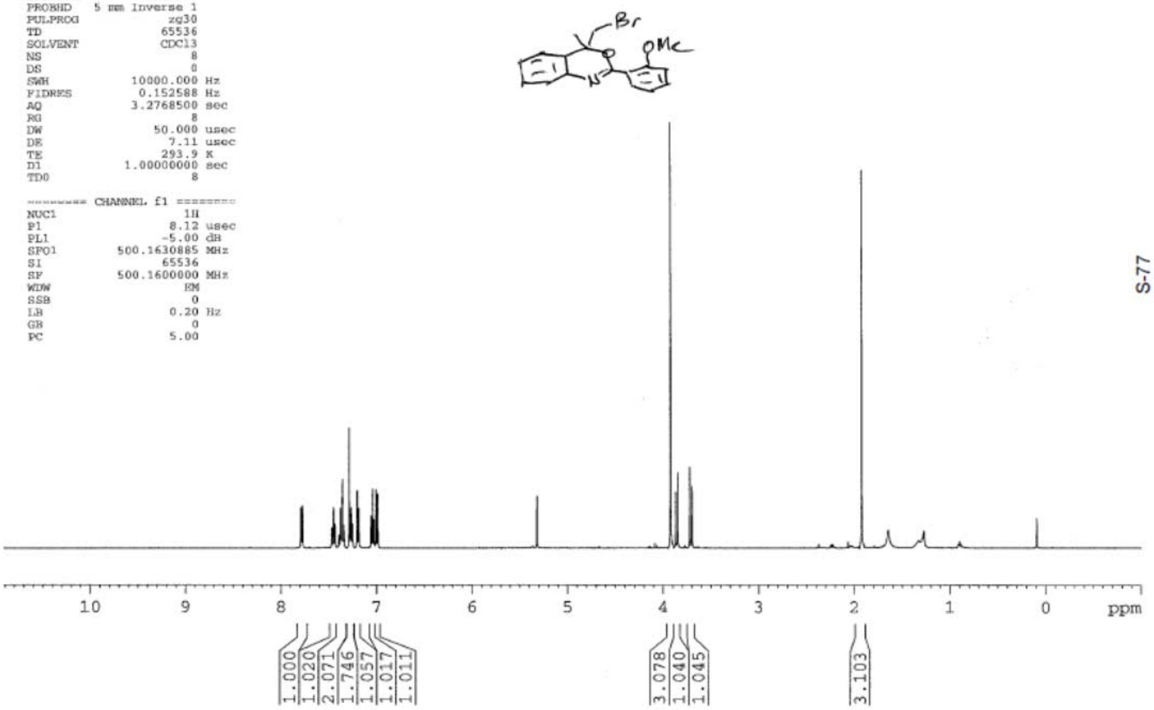
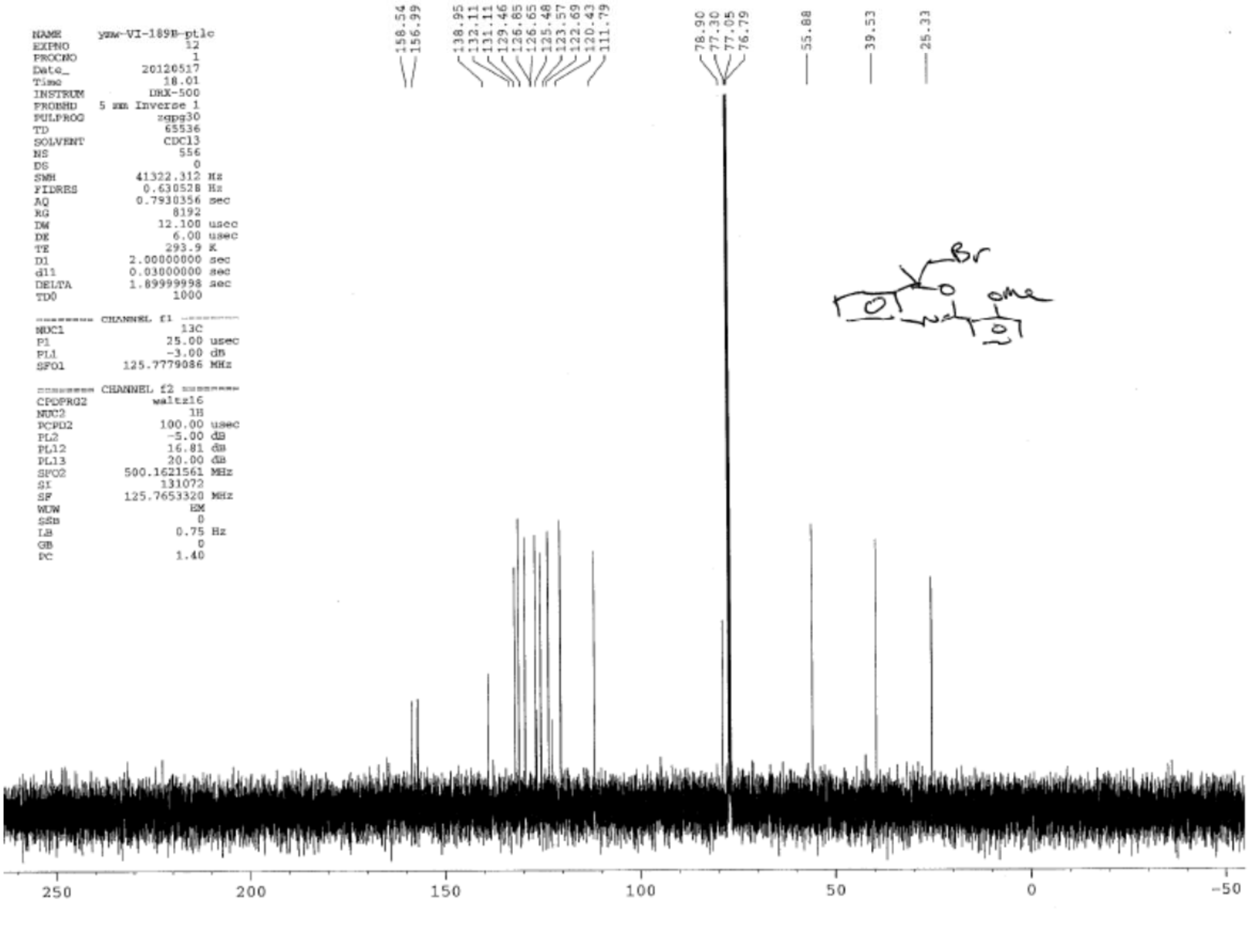
```
NAME       ymw-VI-188-orthoMe
EXPNO                   13
PROCNO                   1
Date_             20120516
Time                 19.31
INSTRUM            DRX-500
PROBHD    5 mm Inverse 1
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     402
DS                       0
SWH              41322.312 Hz
FIDRES            0.630528 Hz
AQ               0.7930356 sec
RG                    8192
DW                  12.100 usec
DE                    6.00 usec
TE                   294.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                   1000

======== CHANNEL f1 ========
NUC1                   13C
P1                   25.00 usec
PL1                  -3.00 dB
SFO1           125.7779086 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                  -5.00 dB
PL12                 16.81 dB
PL13                 20.00 dB
SFO2           500.1621561 MHz
SI                  131072
SF             125.7653320 MHz
WDW                     EM
SSB                      0
LB                    0.75 Hz
GB                       0
PC                    2.00
```

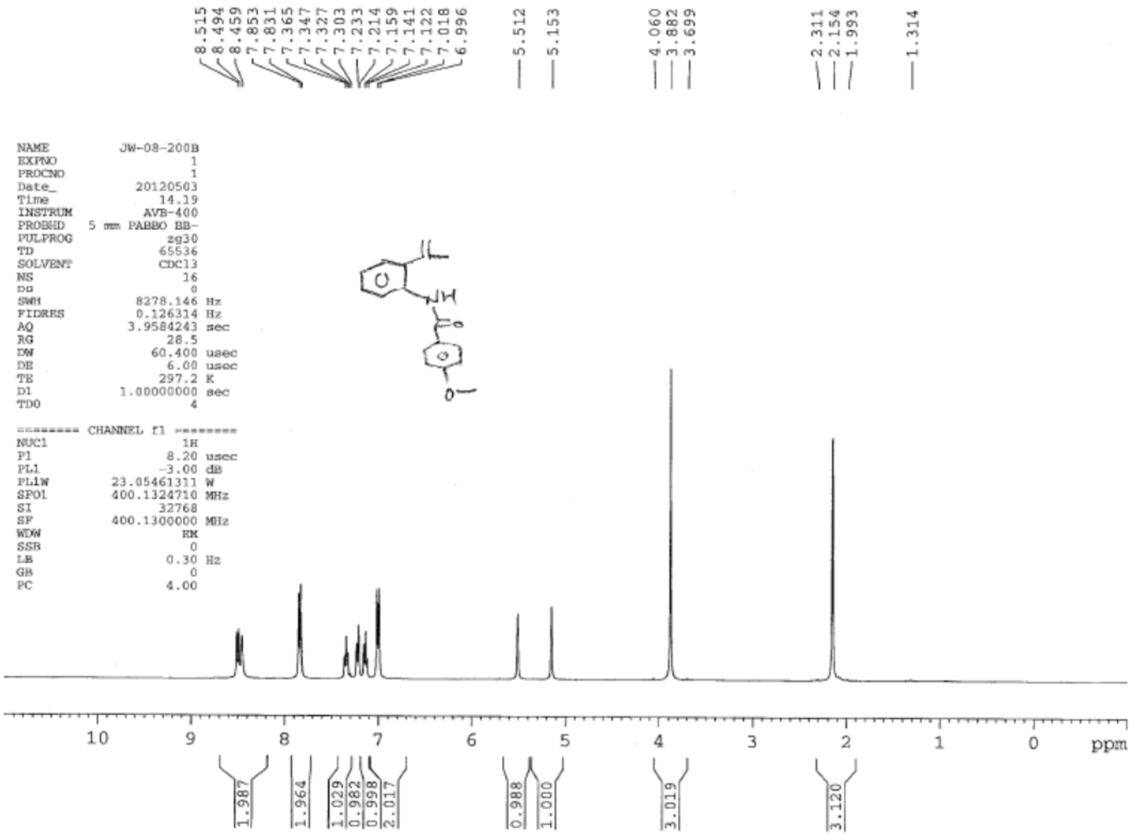


```
NAME       ymw-VI-189B-ptlc
EXPNO                     1
PROCNO                    1
Date_              20120517
Time                  17.47
INSTRUM             DRX-500
PROBHD   5 mm Inverse 1
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        0
SWH               10000.000 Hz
FIDRES             0.152588 Hz
AQ                3.2768500 sec
RG                        8
DW                   50.000 usec
DE                     7.11 usec
TE                    293.9 K
D1               1.00000000 sec
TD0                       8

======== CHANNEL f1 ========
NUC1                     1H
P1                     8.12 usec
PL1                   -5.00 dB
SFO1            500.1630885 MHz
SI                    65536
SF              500.1600000 MHz
WDW                      EM
SSB                       0
LB                     0.20 Hz
GB                        0
PC                     5.00
```

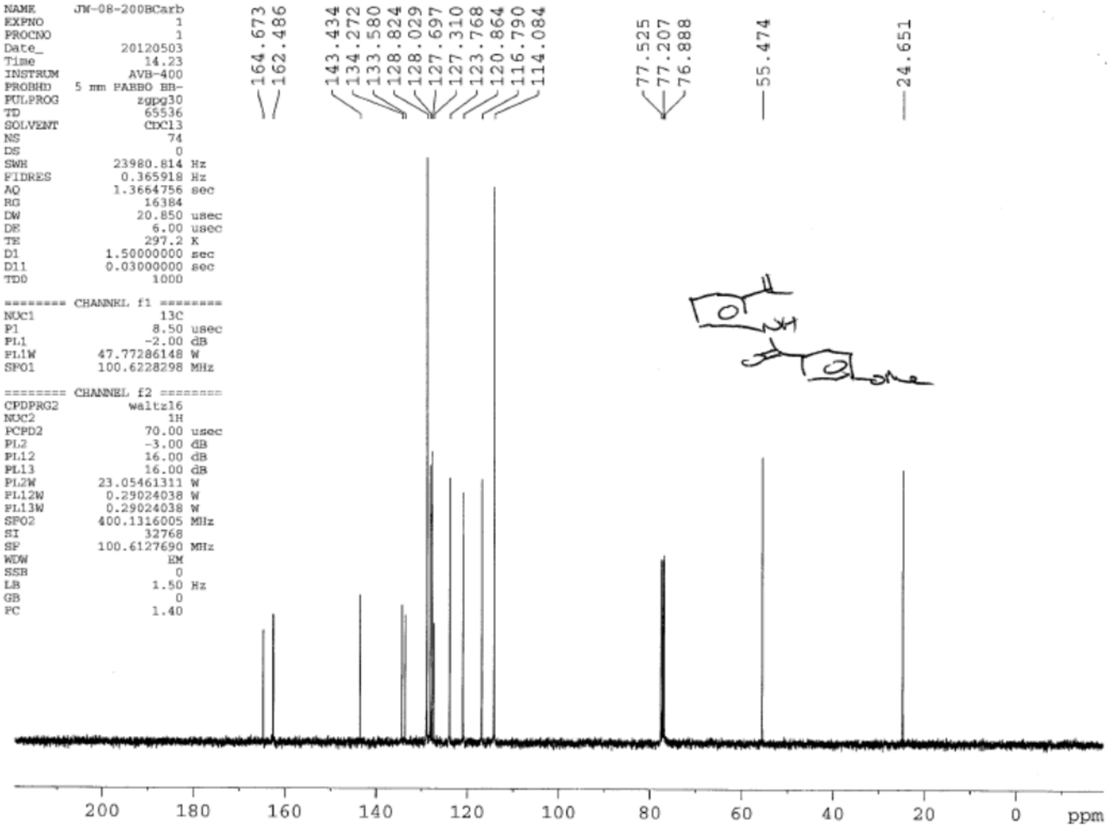


```
NAME       ymw-VI-189B-ptlc
EXPNO                    12
PROCNO                    1
Date_              20120517
Time                  18.01
INSTRUM             DRX-500
PROBHD   5 mm Inverse 1
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      556
DS                        0
SWH               41322.312 Hz
FIDRES             0.630528 Hz
AQ                0.7930356 sec
RG                     8192
DW                   12.100 usec
DE                     6.00 usec
TE                    293.9 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                    1000

======== CHANNEL f1 ========
NUC1                    13C
P1                    25.00 usec
PL1                   -3.00 dB
SFO1            125.7779086 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                   -5.00 dB
PL12                  16.81 dB
PL13                  20.00 dB
SFO2            500.1621561 MHz
SI                   131072
SF              125.7653320 MHz
WDW                      EM
SSB                       0
LB                     0.75 Hz
GB                        0
PC                     1.40
```

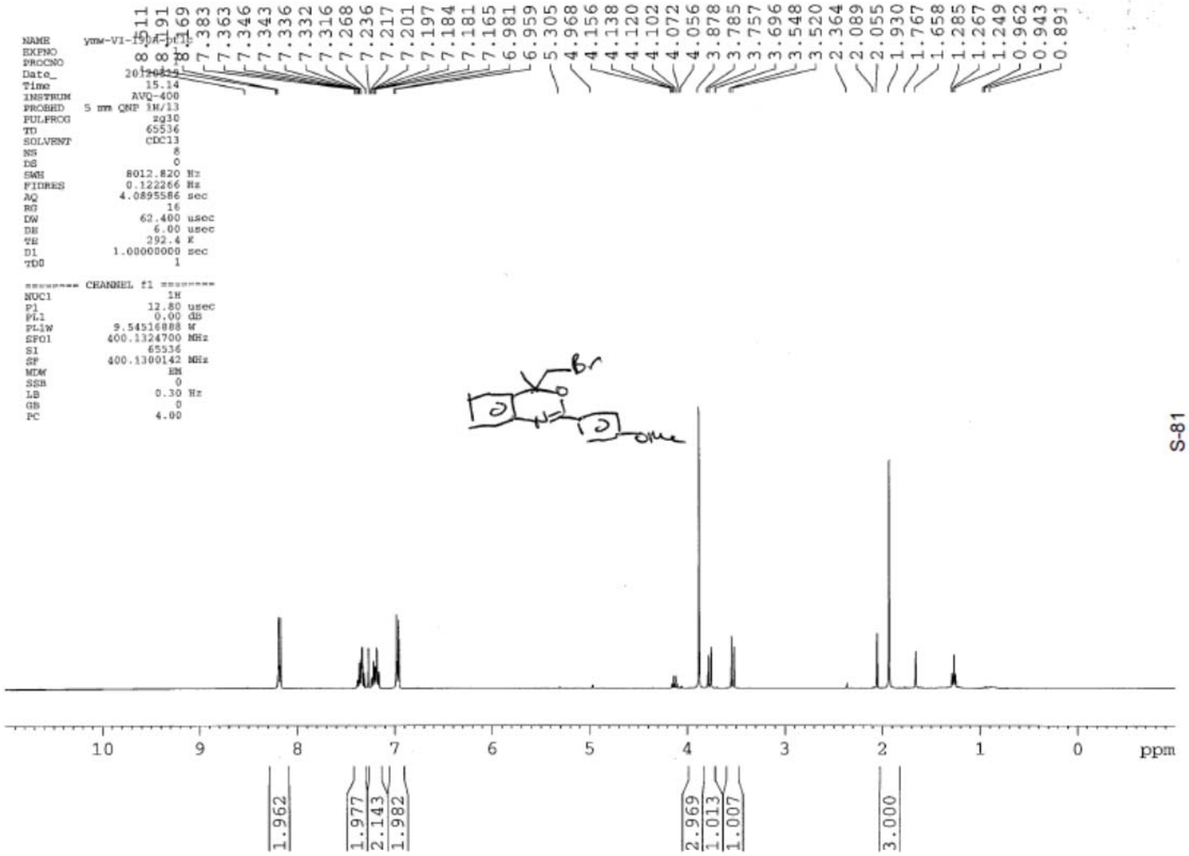




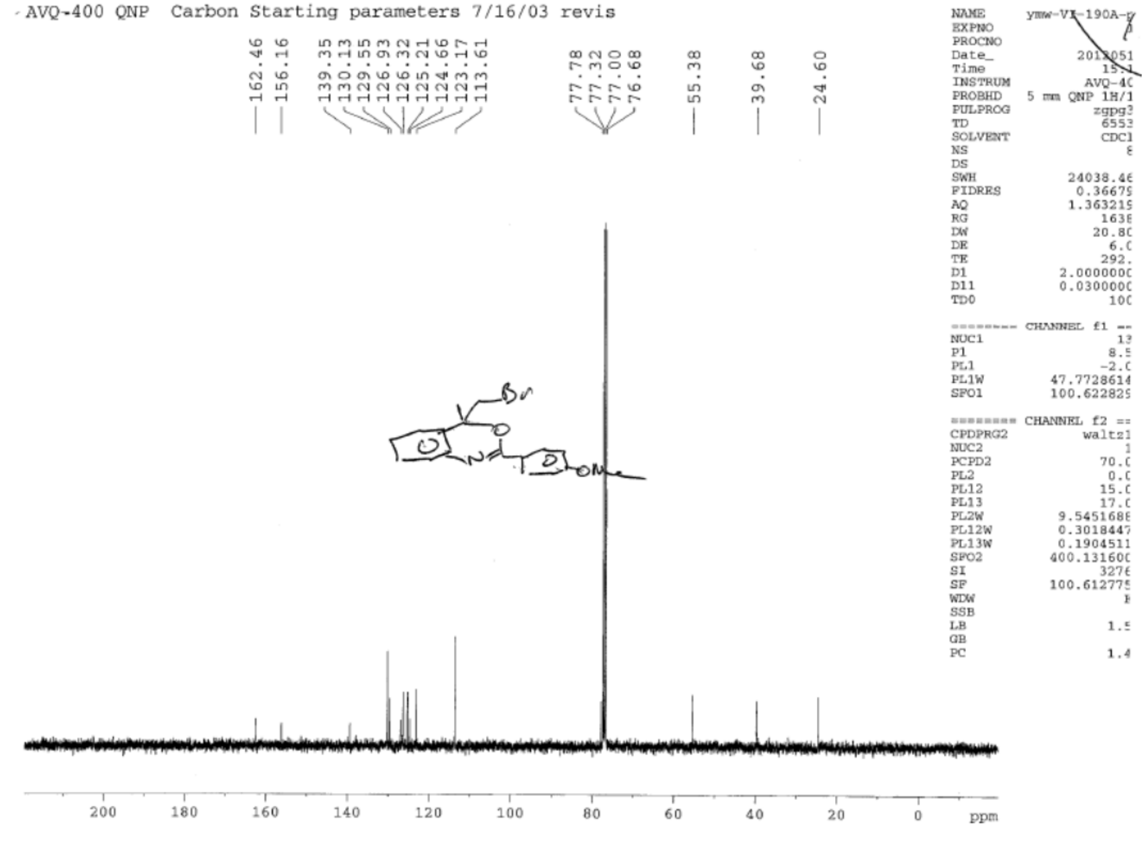
```
NAME          JW-08-200B
EXPNO                  1
PROCNO                 1
Date_           20120503
Time               14.19
INSTRUM          AVB-400
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                  28.5
DW                60.400 usec
DE                  6.00 usec
TE                 297.2 K
D1            1.00000000 sec
TD0                    4

======== CHANNEL f1 ========
NUC1                  1H
P1                  8.20 usec
PL1                -3.00 dB
PL1W         23.05461311 W
SFO1         400.1324710 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00
```



```
NAME      JW-08-200BCarb
EXPNO                  1
PROCNO                 1
Date_           20120503
Time               14.23
INSTRUM          AVB-400
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    74
DS                     0
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                 16384
DW                20.850 usec
DE                  6.00 usec
TE                 297.2 K
D1            1.50000000 sec
D11           0.03000000 sec
TD0                 1000

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.50 usec
PL1                -2.00 dB
PL1W         47.77286148 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              70.00 usec
PL2                -3.00 dB
PL12               16.00 dB
PL13               16.00 dB
PL2W         23.05461311 W
PL12W         0.29024038 W
PL13W         0.29024038 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.50 Hz
GB                     0
PC                  1.40
```

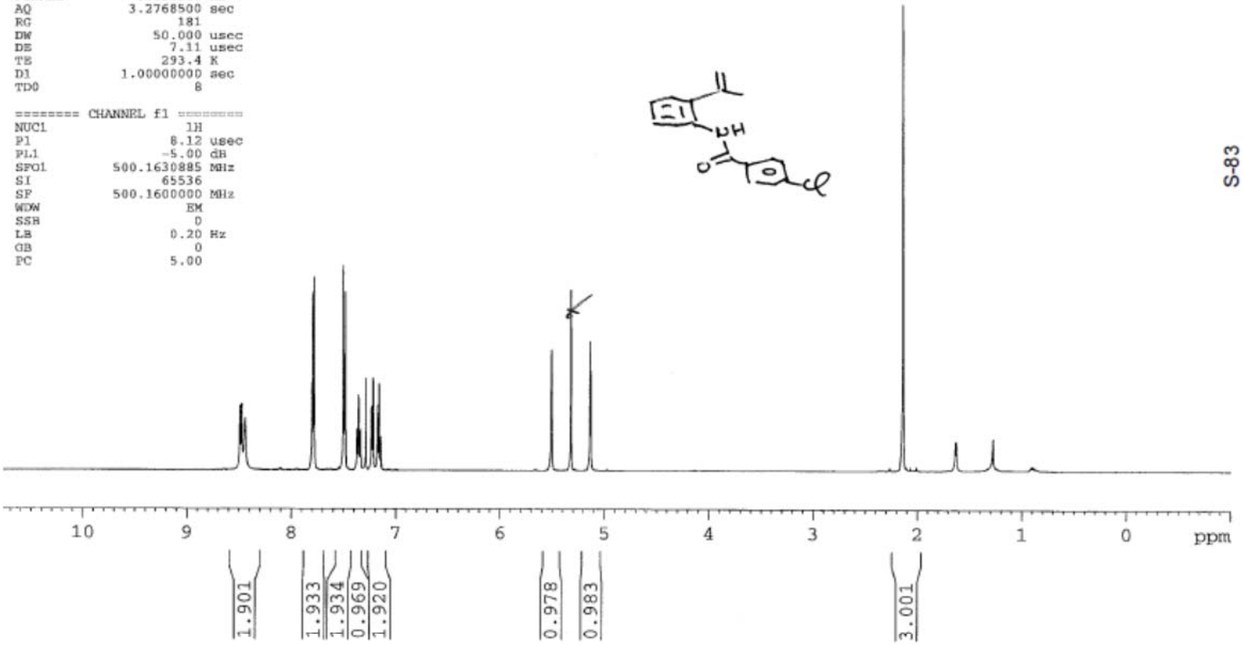


```
NAME       ymw-VI-190A-p
EXPNO
PROCNO
Date_      2012
Time              15.14
INSTRUM         AVQ-400
PROBHD    5 mm QNP 1H/13
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0895586 sec
RG                   16
DW               62.400 usec
DE                 6.00 usec
TE                292.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                12.80 usec
PL1                0.00 dB
PL1W         9.54516888 W
SFO1        400.1324700 MHz
SI                65536
SF          400.1300142 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 4.00
```



```
NAME       ymw-VI-190A-p
EXPNO
PROCNO
Date_            2012051
Time                 15.
INSTRUM           AVQ-40
PROBHD    5 mm QNP 1H/1
PULPROG            zgpg3
TD                  6553
SOLVENT             CDCl
NS                     8
DS
SWH             24038.46
FIDRES           0.36679
AQ              1.363219
RG                  1638
DW                 20.80
DE                   6.0
TE                  292.
D1             2.0000000
D11            0.0300000
TD0                  100

======== CHANNEL f1 --
NUC1                  13
P1                   8.5
PL1                 -2.0
PL1W          47.7728614
SFO1          100.622829

======== CHANNEL f2 ==
CPDPRG2           waltz1
NUC2                   1
PCPD2               70.0
PL2                  0.0
PL12                15.0
PL13                17.0
PL2W           9.5451688
PL12W          0.3018447
PL13W          0.1904511
SFO2          400.131600
SI                  3276
SF            100.612775
WDW                    E
SSB
LB                   1.5
GB
PC                   1.4
```

```
NAME          ymw-VI-chloroamide2
EXPNO                       1
PROCNO                      1
Date_                20120531
Time                    14.49
INSTRUM               DRX-500
PROBHD      5 mm Inverse 1
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                          8
DS                          0
SWH                 10000.000 Hz
FIDRES               0.152588 Hz
AQ                  3.2768500 sec
RG                        181
DW                     50.000 usec
DE                       7.11 usec
TE                      293.4 K
D1                 1.00000000 sec
TD0                         8

======== CHANNEL f1 ========
NUC1                       1H
P1                       8.12 usec
PL1                     -5.00 dB
SFO1              500.1630885 MHz
SI                      65536
SF                500.1600000 MHz
WDW                        EM
SSB                         0
LB                       0.20 Hz
GB                          0
PC                       5.00
```



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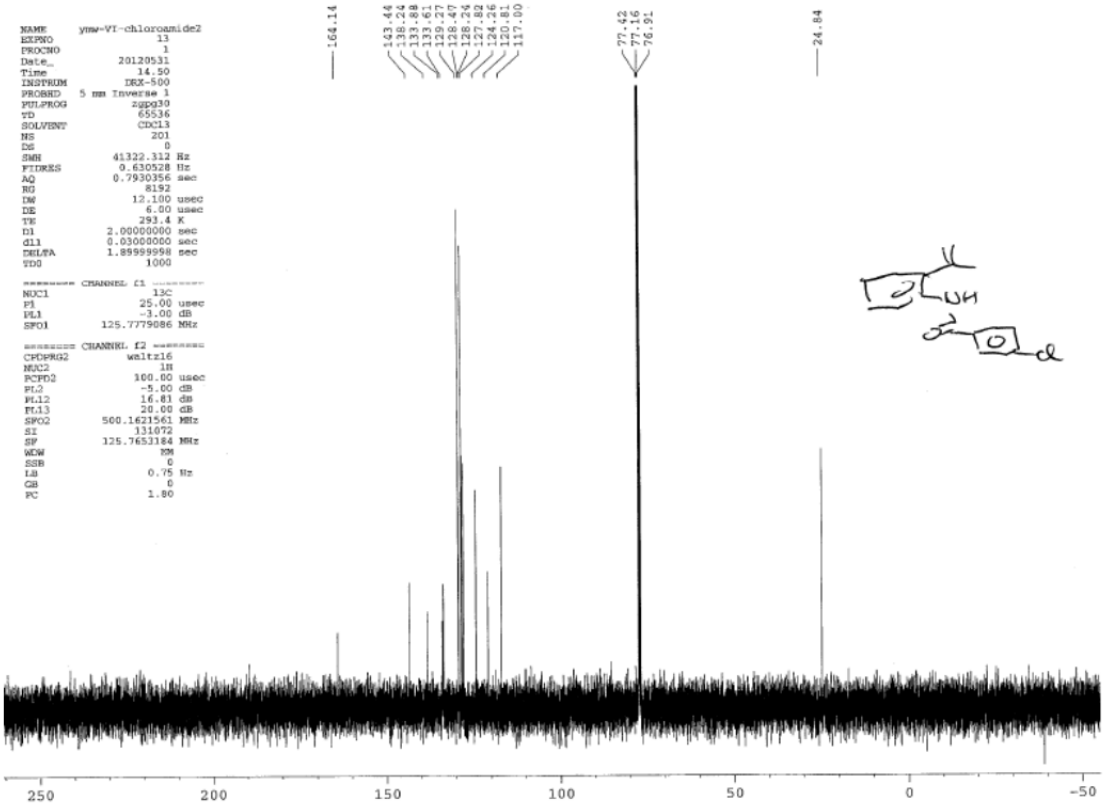
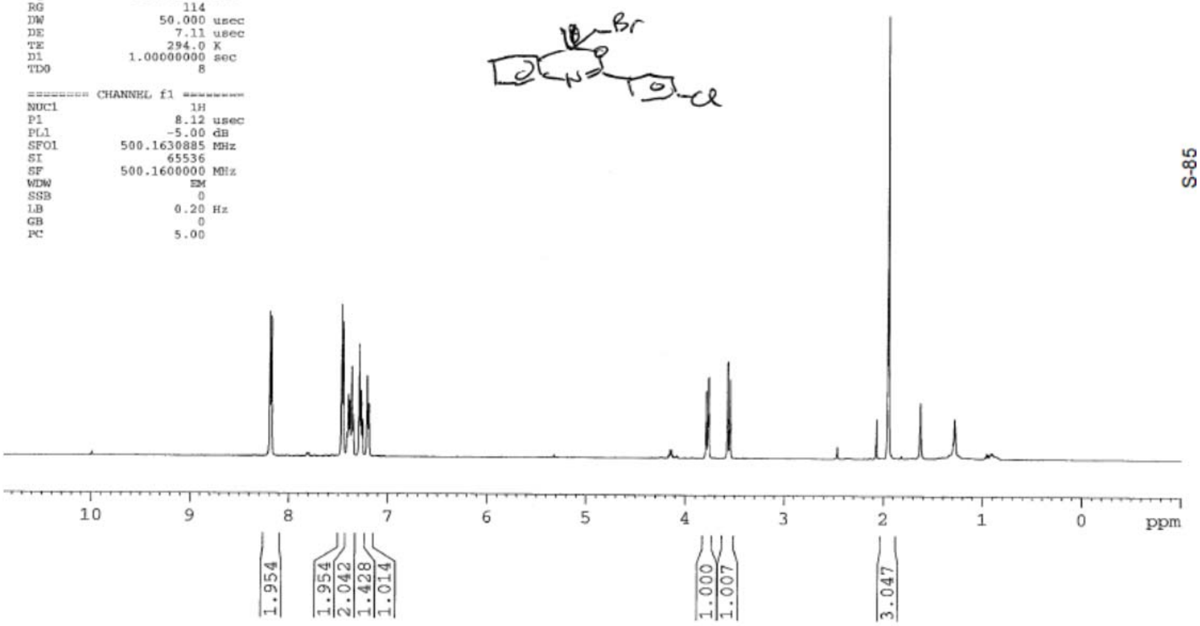
```
NAME          ymw-VI-chloroamide2
EXPNO                      13
PROCNO                      1
Date_                20120531
Time                    14.50
INSTRUM               DRX-500
PROBHD      5 mm Inverse 1
PULPROG               zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        201
DS                          0
SWH                 41322.312 Hz
FIDRES               0.630528 Hz
AQ                  0.7930356 sec
RG                       8192
DW                     12.100 usec
DE                       6.00 usec
TE                      293.4 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                      1000

======== CHANNEL f1 ========
NUC1                      13C
P1                      25.00 usec
PL1                     -3.00 dB
SFO1              125.7779086 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                       1H
PCPD2                  100.00 usec
PL2                     -5.00 dB
PL12                    16.81 dB
PL13                    20.00 dB
SFO2              500.1621561 MHz
SI                     131072
SF                125.7653184 MHz
WDW                        EM
SSB                         0
LB                       0.75 Hz
GB                          0
PC                       1.80
```





```
NAME        ymw-VI-190B-ptlc
EXPNO                      1
PROCNO                     1
Date_               20120519
Time                   16.37
INSTRUM              DRX-500
PROBHD   5 mm Inverse 1
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         8
DS                         0
SWH            10000.000 Hz
FIDRES          0.152588 Hz
AQ             3.2768500 sec
RG                       114
DW                50.000 usec
DE                  7.11 usec
TE                 294.0 K
D1            1.00000000 sec
TD0                        8

======== CHANNEL f1 ========
NUC1                      1H
P1                  8.12 usec
PL1                -5.00 dB
SFO1         500.1630885 MHz
SI                     65536
SF           500.1600000 MHz
WDW                       EM
SSB                        0
LB                  0.20 Hz
GB                         0
PC                      5.00
```

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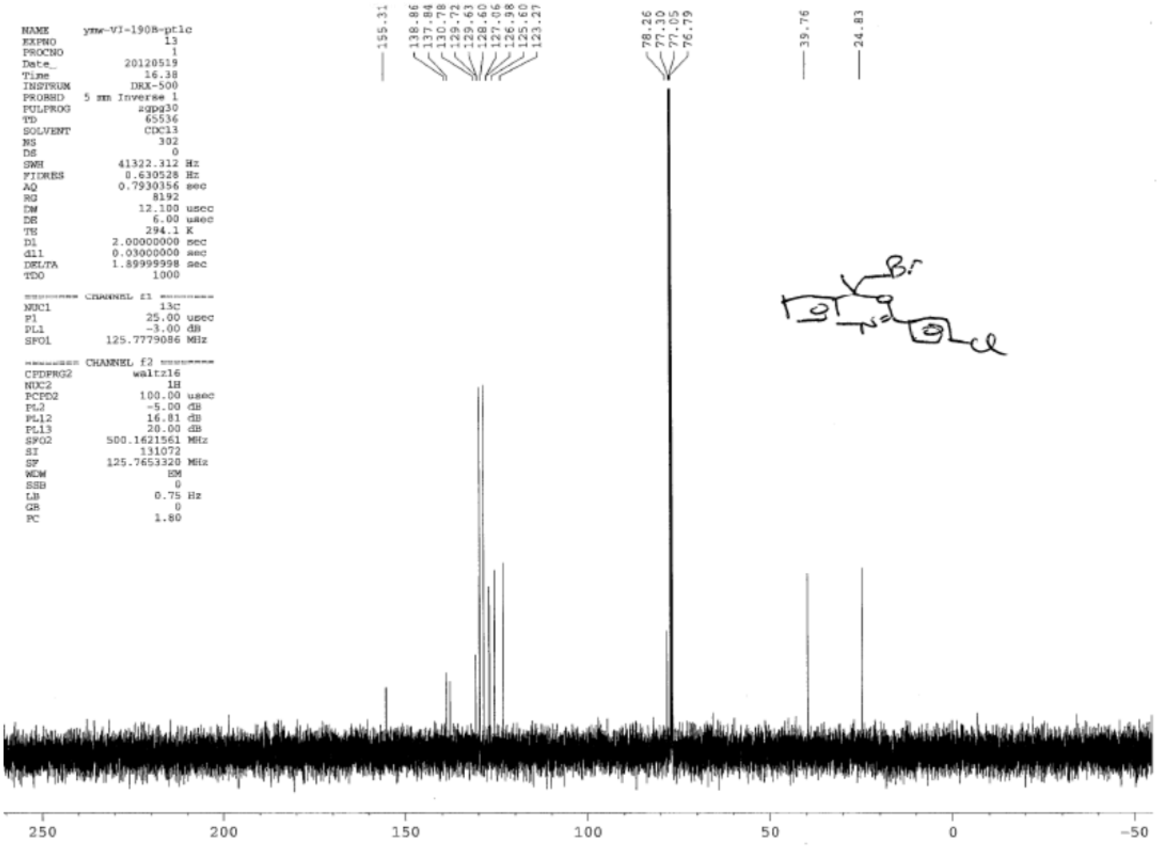
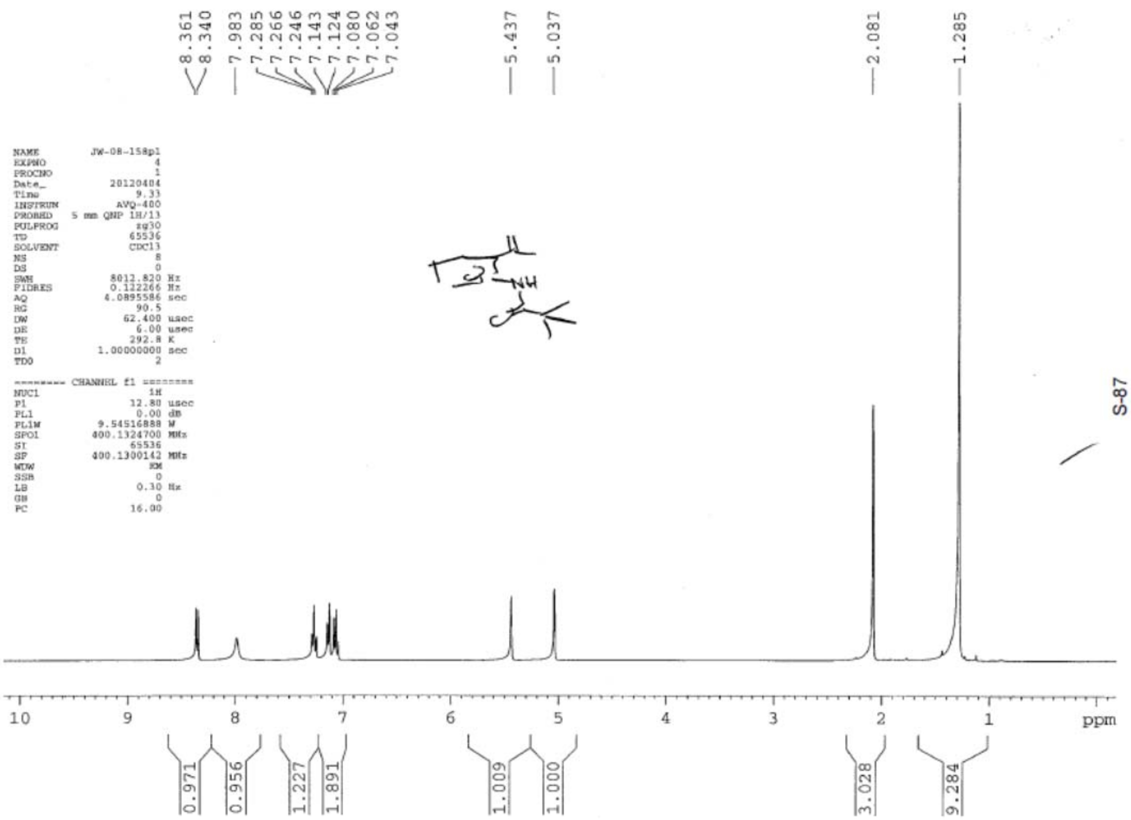
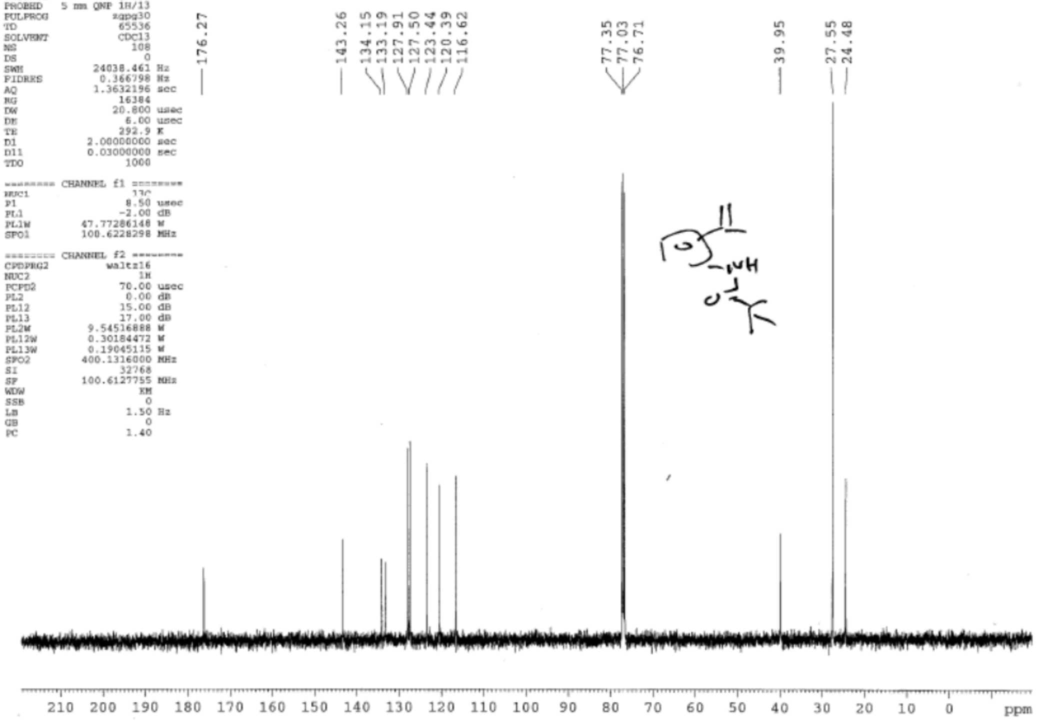


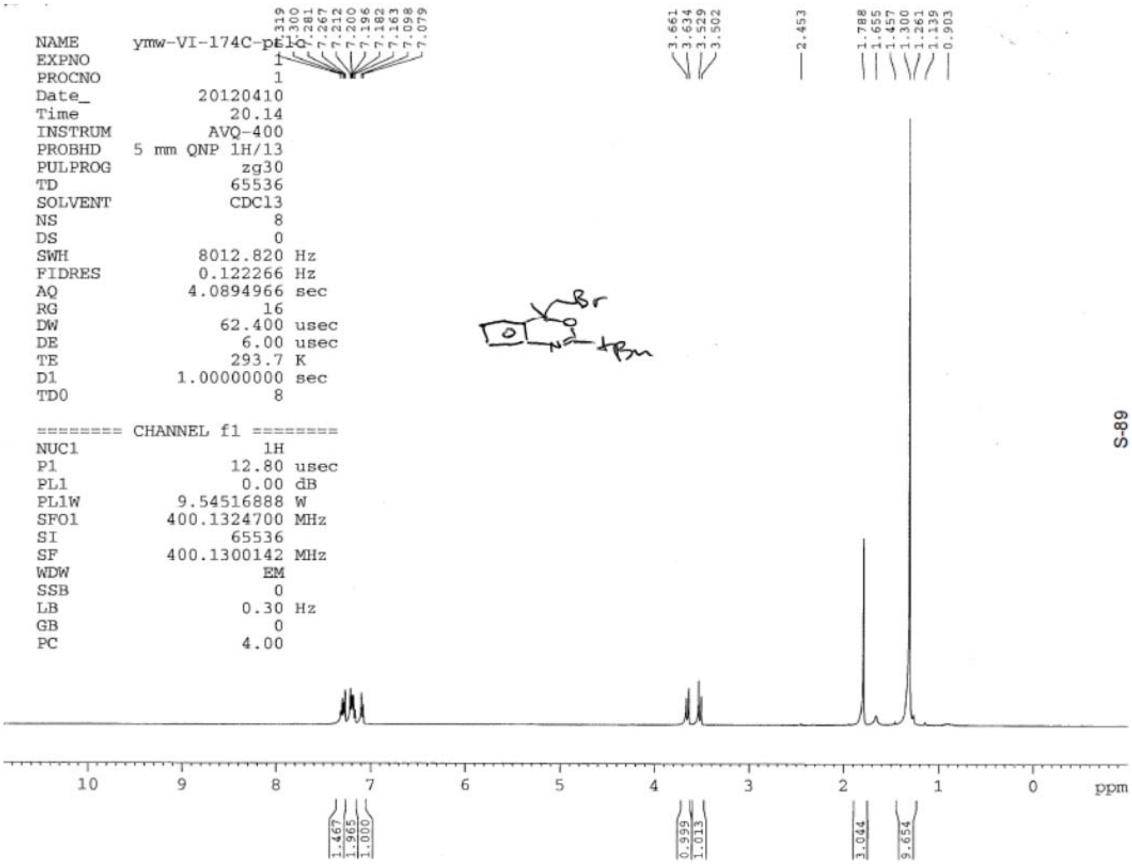
```
NAME        ymw-VI-190B-ptlc
EXPNO                     13
PROCNO                     1
Date_               20120519
Time                   16.38
INSTRUM              DRX-500
PROBHD   5 mm Inverse 1
PULPROG              zgpg30
TD                     65536
SOLVENT                CDCl3
NS                       302
DS                         0
SWH            41322.312 Hz
FIDRES          0.630528 Hz
AQ             0.7930356 sec
RG                      8192
DW                12.100 usec
DE                  6.00 usec
TE                 294.1 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                     1000

======== CHANNEL f1 ========
NUC1                     13C
P1                 25.00 usec
PL1                -3.00 dB
SFO1         125.7779086 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2             100.00 usec
PL2                -5.00 dB
PL12               16.81 dB
PL13               20.00 dB
SFO2         500.1621561 MHz
SI                    131072
SF           125.7653320 MHz
WDW                       EM
SSB                        0
LB                  0.75 Hz
GB                         0
PC                      1.80
```



```
NAME          JW-08-158p1
EXPNO                   4
PROCNO                  1
Date_            20120404
Time                 9.33
INSTRUM           AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG              zg30
TD                  65536
SOLVENT             CDC13
NS                      8
DS                      0
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0895586 sec
RG                   90.5
DW                 62.400 usec
DE                   6.00 usec
TE                  292.8 K
D1             1.00000000 sec
TD0                     2

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.80 usec
PL1                  0.00 dB
PL1W           9.54516888 W
SFO1          400.1324700 MHz
SI                  65536
SF            400.1300142 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                  16.00
```

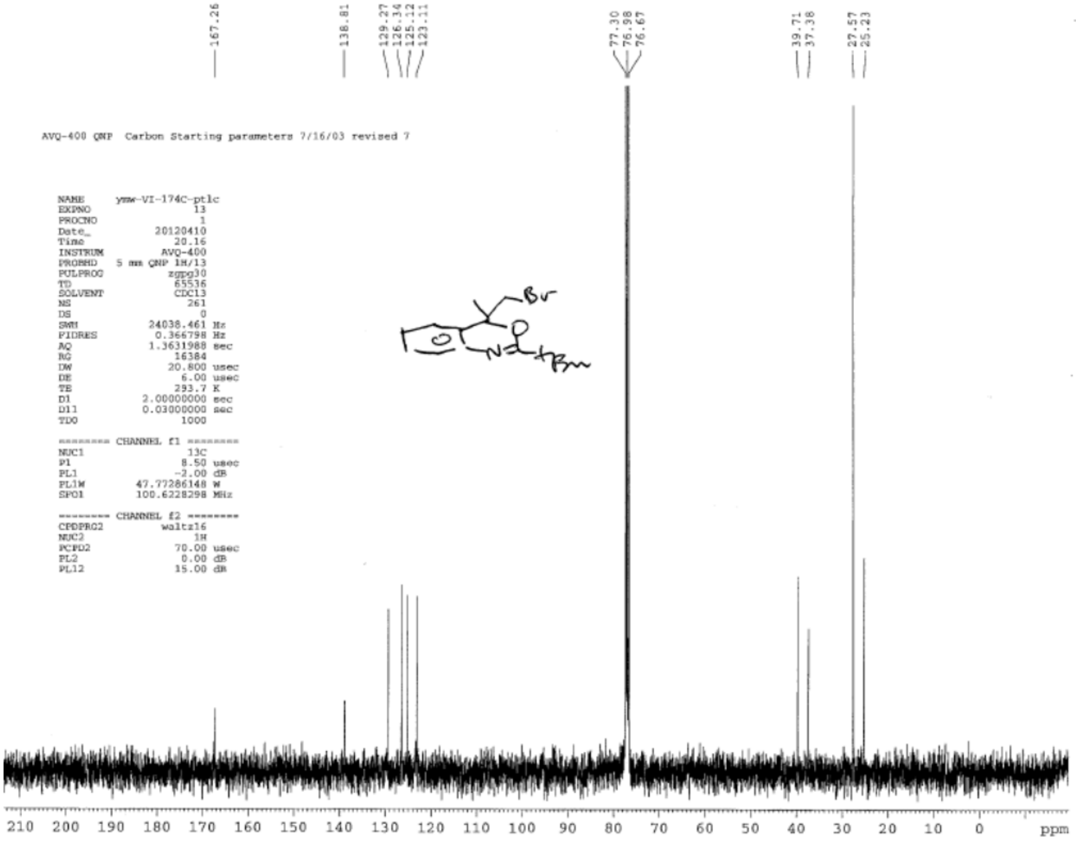


```
NAME         JW-08-158p1C
EXPNO                   4
PROCNO                  1
Date_            20120404
Time                 9.34
INSTRUM           AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG            zgpg30
TD                  65536
SOLVENT             CDC13
NS                    108
DS                      0
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3632196 sec
RG                  16384
DW                 20.800 usec
DE                   6.00 usec
TE                  292.9 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                  1000

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.50 usec
PL1                 -2.00 dB
PL1W          47.77286148 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               70.00 usec
PL2                  0.00 dB
PL12                15.00 dB
PL13                17.00 dB
PL2W           9.54516888 W
PL12W          0.30184472 W
PL13W          0.19045115 W
SFO2          400.1316000 MHz
SI                  32768
SF            100.6127755 MHz
WDW                    EM
SSB                     0
LB                   1.50 Hz
GB                      0
PC                   1.40
```



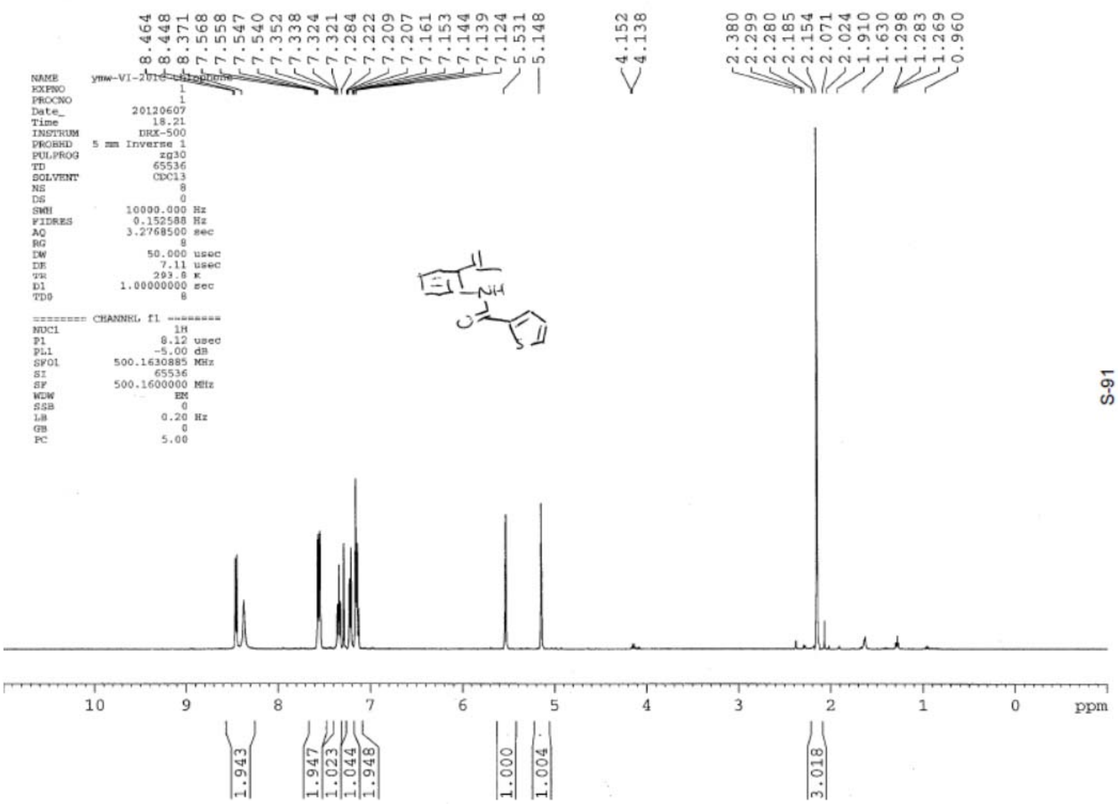
```
NAME      ymw-VI-174C-ptlc
EXPNO                    1
PROCNO                   1
Date_             20120410
Time                 20.14
INSTRUM            AVQ-400
PROBHD    5 mm QNP 1H/13
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                      16
DW                  62.400 usec
DE                    6.00 usec
TE                   293.7 K
D1              1.00000000 sec
TD0                      8

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.80 usec
PL1                   0.00 dB
PL1W            9.54516888 W
SFO1           400.1324700 MHz
SI                   65536
SF             400.1300142 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00
```

S-89



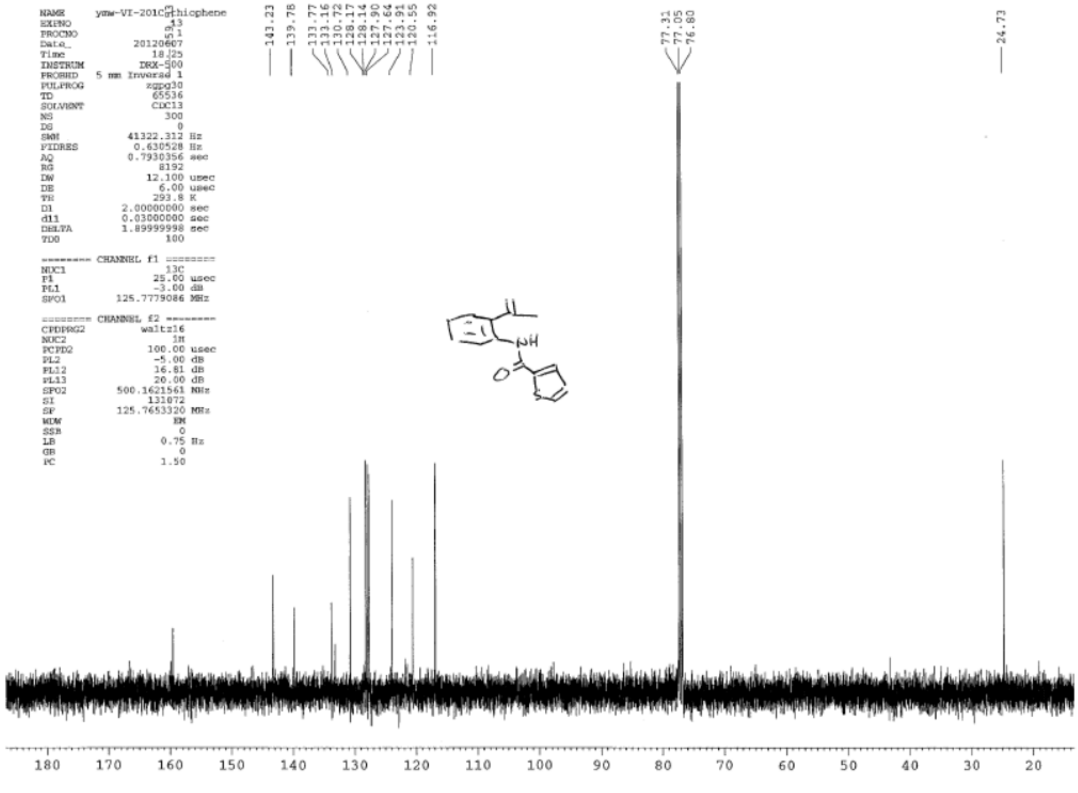
AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7

```
NAME      ymw-VI-174C-ptlc
EXPNO                   13
PROCNO                   1
Date_             20120410
Time                 20.16
INSTRUM            AVQ-400
PROBHD    5 mm QNP 1H/13
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     261
DS                       0
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                   16384
DW                  20.800 usec
DE                    6.00 usec
TE                   293.7 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                   1000

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.50 usec
PL1                  -2.00 dB
PL1W           47.77286148 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                70.00 usec
PL2                   0.00 dB
PL12                 15.00 dB
```

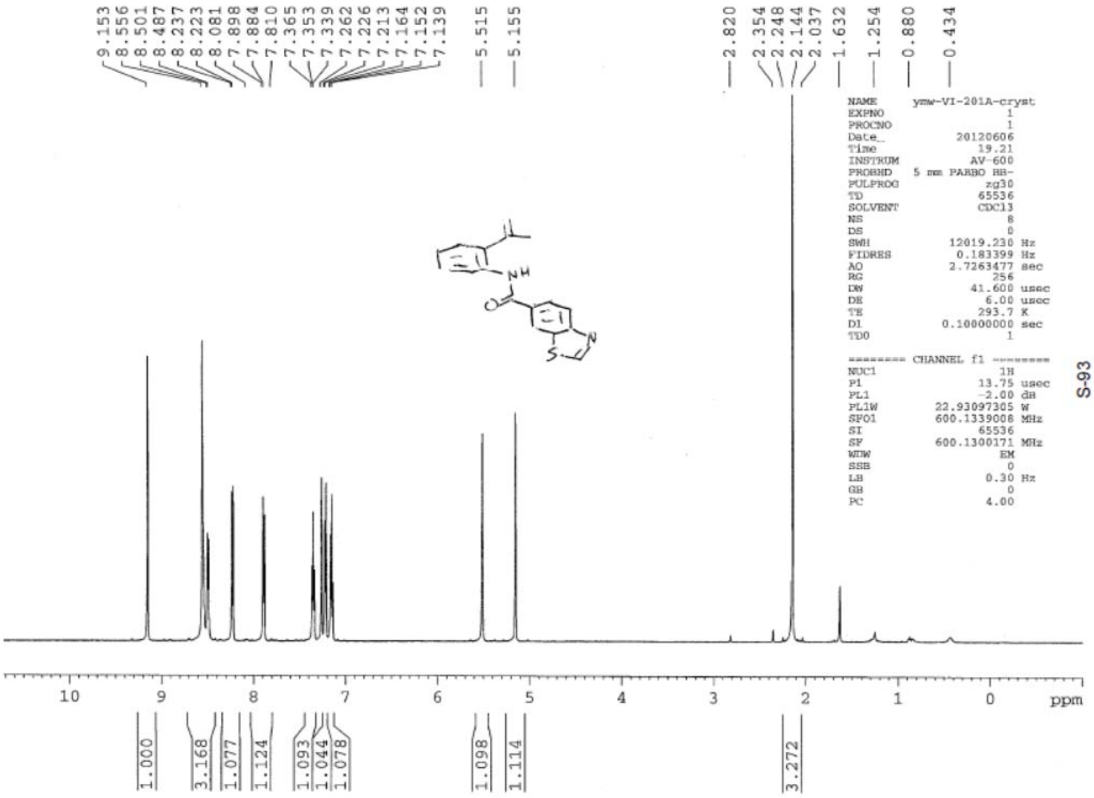


```
NAME       ymw-VI-201C-thiophene
EXPNO                   1
PROCNO                  1
Date_            20120607
Time                18.21
INSTRUM           DRX-500
PROBHD    5 mm Inverse 1
PULPROG              zg30
TD                  65536
SOLVENT             CDC13
NS                      8
DS                      0
SWH             10000.000 Hz
FIDRES           0.152588 Hz
AQ              3.2768500 sec
RG                      8
DW                 50.000 usec
DE                   7.11 usec
TE                  293.8 K
D1             1.00000000 sec
TD0                     8

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.12 usec
PL1                 -5.00 dB
SFO1          500.1630885 MHz
SI                  65536
SF            500.1600000 MHz
WDW                    EM
SSB                     0
LB                   0.20 Hz
GB                      0
PC                   5.00
```

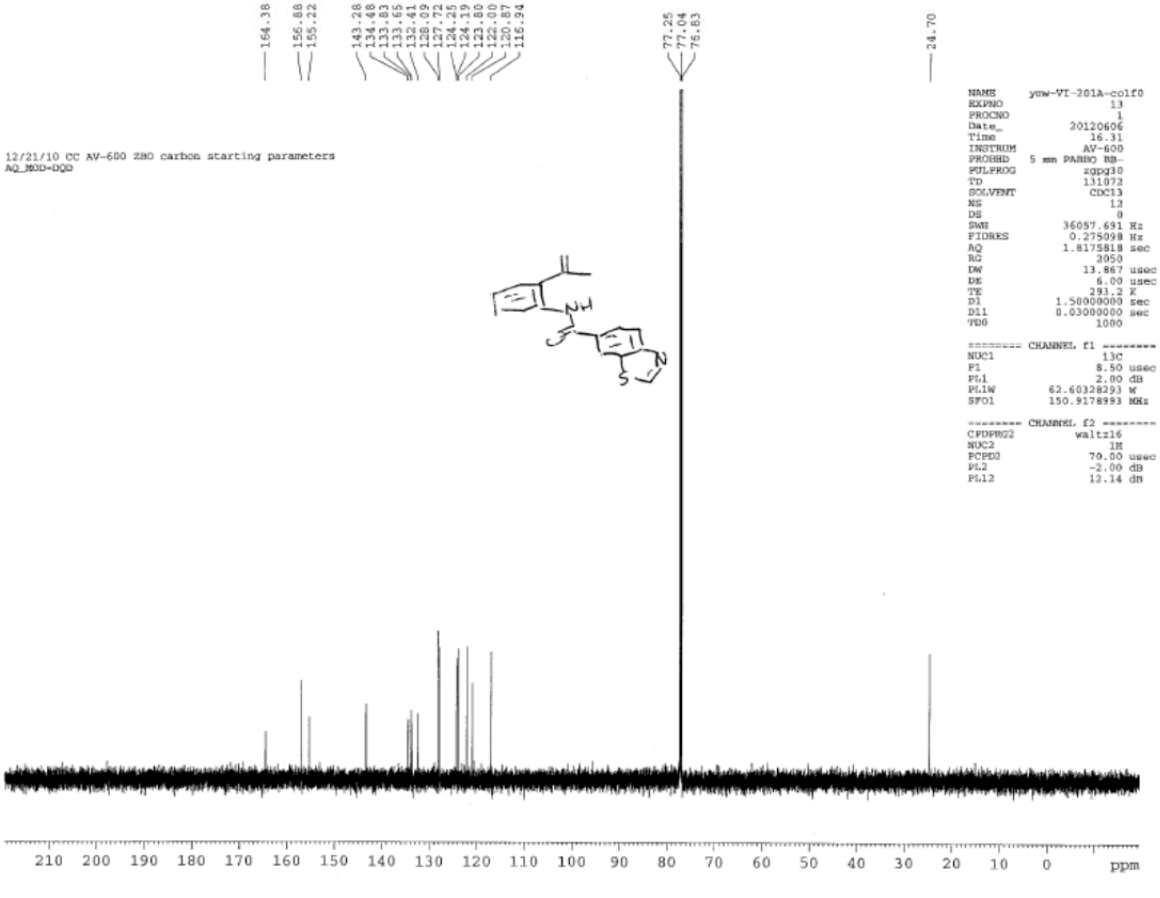
S-91



```
NAME       ymw-VI-201C-thiophene
EXPNO                  13
PROCNO                  1
Date_            20120607
Time                18.25
INSTRUM           DRX-500
PROBHD    5 mm Inverse 1
PULPROG            zgpg30
TD                  65536
SOLVENT             CDC13
NS                    300
DS                      0
SWH             41322.312 Hz
FIDRES           0.630528 Hz
AQ              0.7930356 sec
RG                   8192
DW                 12.100 usec
DE                   6.00 usec
TE                  293.8 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                   100

======== CHANNEL f1 ========
NUC1                  13C
P1                  25.00 usec
PL1                 -3.00 dB
SFO1          125.7779086 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -5.00 dB
PL12                16.81 dB
PL13                20.00 dB
SFO2          500.1621561 MHz
SI                 131072
SF            125.7653320 MHz
WDW                    EM
SSB                     0
LB                   0.75 Hz
GB                      0
PC                   1.50
```

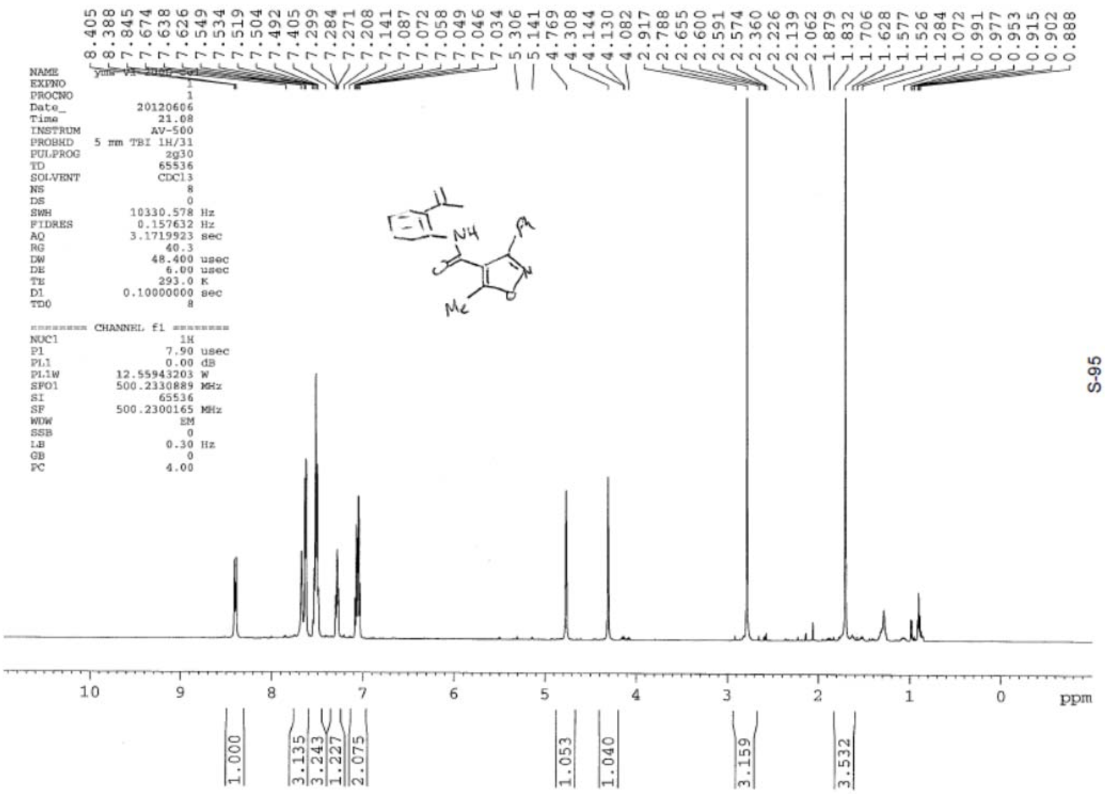


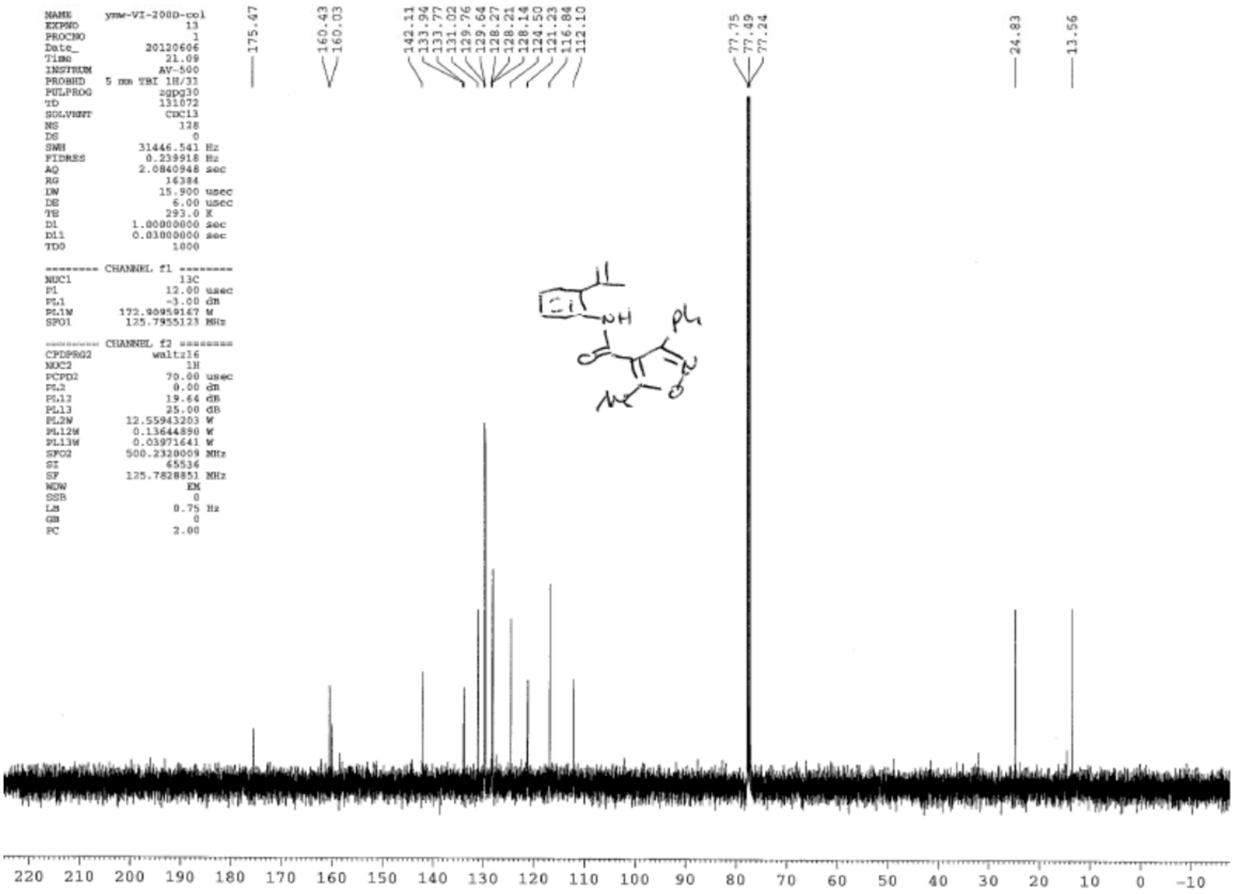
```
NAME       ymw-VI-201A-cryst
EXPNO                      1
PROCNO                     1
Date_               20120606
Time                   19.21
INSTRUM               AV-600
PROBHD      5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         8
DS                         0
SWH             12019.230 Hz
FIDRES           0.183399 Hz
AQ              2.7263477 sec
RG                       256
DW                41.600 usec
DE                  6.00 usec
TE                   293.7 K
D1             0.10000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                 13.75 usec
PL1                  -2.00 dB
PL1W             22.93097305 W
SFO1          600.1339008 MHz
SI                     65536
SF            600.1300171 MHz
WDW                       EM
SSB                        0
LB                   0.30 Hz
GB                         0
PC                      4.00
```

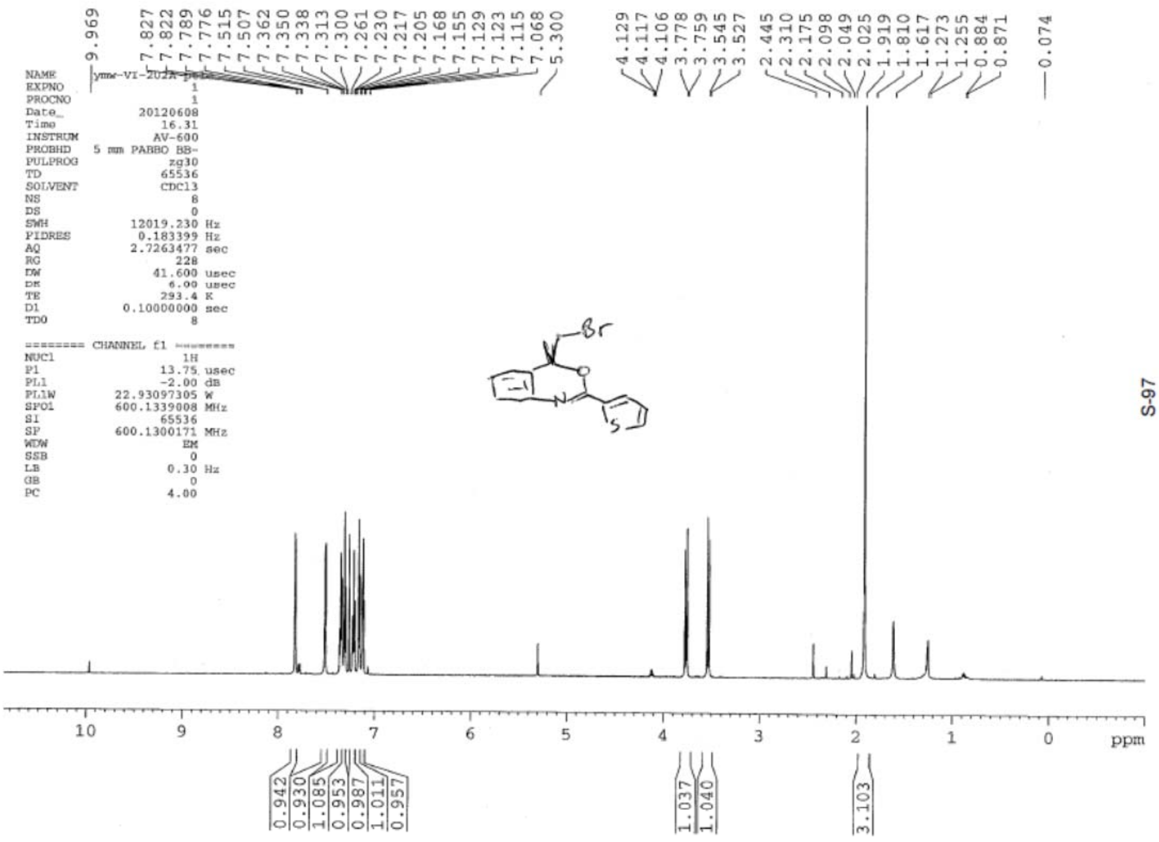


12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD-DQD

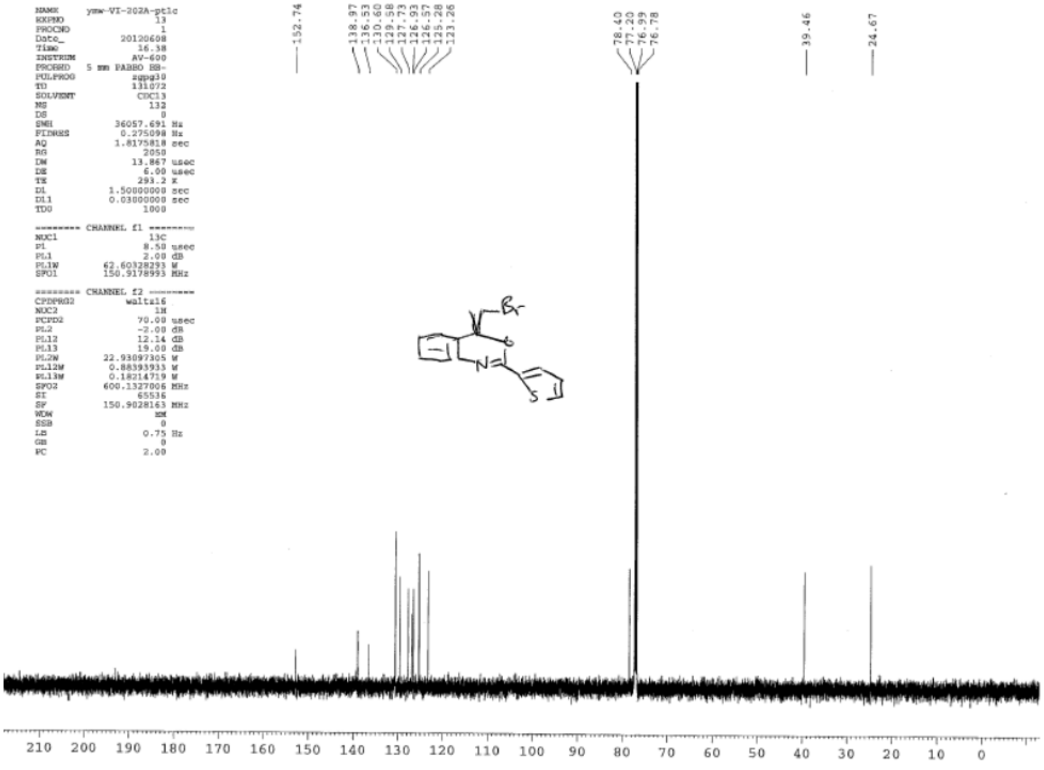
```
NAME        ymw-VI-201A-colf0
EXPNO                      13
PROCNO                      1
Date_                20120606
Time                    16.31
INSTRUM                AV-600
PROBHD       5 mm PABBO BB-
PULPROG               zgpg30
TD                     131072
SOLVENT                 CDCl3
NS                         12
DS                          0
SWH              36057.691 Hz
FIDRES            0.275098 Hz
AQ               1.8175818 sec
RG                       2050
DW                 13.867 usec
DE                   6.00 usec
TE                    293.2 K
D1              1.50000000 sec
D11             0.03000000 sec
TD0                      1000

======== CHANNEL f1 ========
NUC1                      13C
P1                   8.50 usec
PL1                   2.00 dB
PL1W             62.60328293 W
SFO1           150.9178993 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                       1H
PCPD2               70.00 usec
PL2                  -2.00 dB
PL12                 12.14 dB
```


8.405 8.388 7.845 7.674 7.638 7.626 7.549 7.534 7.519 7.504 7.492 7.405 7.299 7.284 7.271 7.208 7.141 7.087 7.072 7.058 7.049 7.046 7.034 5.306 5.141 4.769 4.308 4.144 4.130 4.082 2.917 2.788 2.655 2.600 2.591 2.574 2.360 2.226 2.139 2.062 1.879 1.832 1.706 1.628 1.577 1.526 1.284 1.072 0.991 0.977 0.953 0.915 0.902 0.888
NAME ymw-VI-200D-col
EXPNO 1
PROCNO 1
Date_ 20120606
Time 21.08
INSTRUM AV-500
PROBHD 5 mm TBI 1H/31
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 40.3
DW 48.400 usec
DE 6.00 usec
TE 293.0 K
D1 0.10000000 sec
TD0 8
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 0.00 dB
PL1W 12.55943203 W
SFO1 500.2330889 MHz
SI 65536
SF 500.2300165 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
NH
Ph
N
O
Me
10 9 8 7 6 5 4 3 2 1 0 ppm
1.000 3.135 3.243 1.227 2.075 1.053 1.040 3.159 3.532


NAME ymw-VI-200D-col
EXPNO 13
PROCNO 1
Date_ 20120606
Time 21.09
INSTRUM AV-500
PROBHD 5 mm TBI 1H/31
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 128
DS 0
SWH 31446.541 Hz
FIDRES 0.239918 Hz
AQ 2.0840948 sec
RG 16384
DW 15.900 usec
DE 6.00 usec
TE 293.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1000
======== CHANNEL f1 ========
NUC1 13C
P1 12.00 usec
PL1 -3.00 dB
PL1W 172.98959167 W
SFO1 125.7955123 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 0.00 dB
PL12 19.64 dB
PL13 25.00 dB
PL2W 12.55943203 W
PL12W 0.13644890 W
PL13W 0.03971641 W
SFO2 500.2320009 MHz
SI 65536
SF 125.7828851 MHz
WDW EM
SSB 0
LB 0.75 Hz
GB 0
PC 2.00
175.47
160.43 160.03
142.11 133.94 133.77 131.02 129.76 129.64 128.27 128.21 128.14 124.50 121.23 116.84 112.10
77.75 77.49 77.24
24.83
13.56
NH
Ph
N
O
Me
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

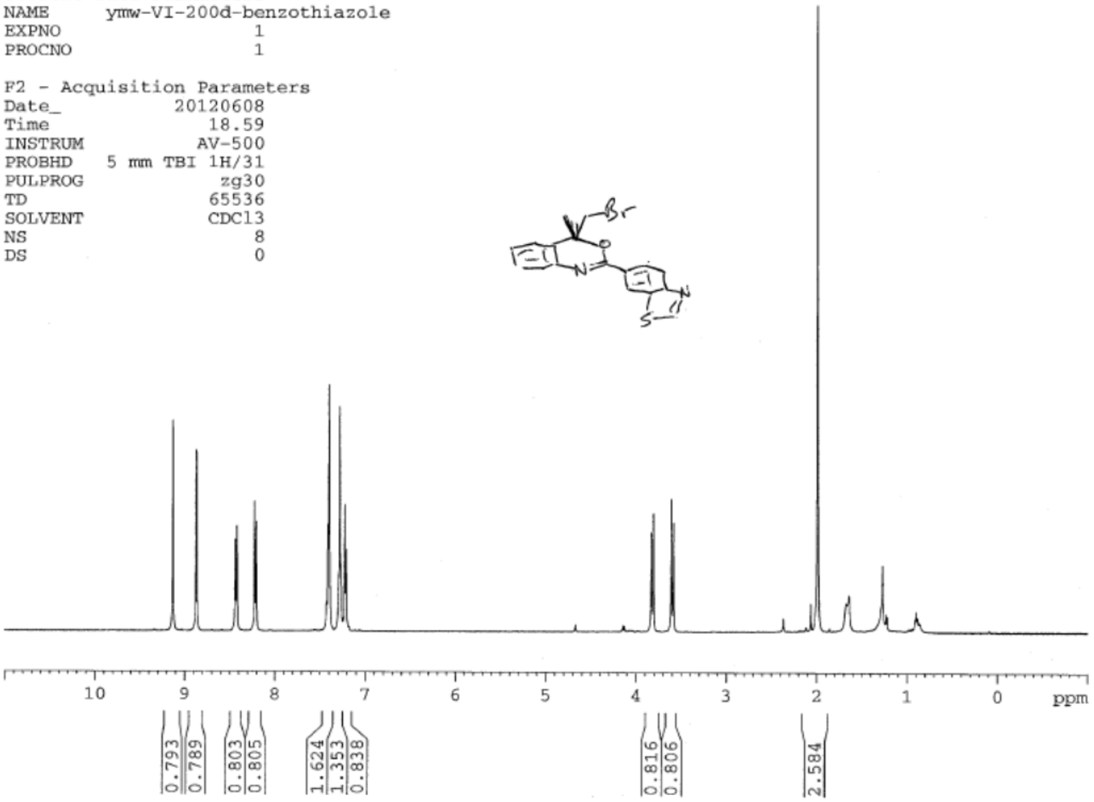


```
NAME      ymw-VI-202A-ptlc
EXPNO                    1
PROCNO                   1
Date_             20120608
Time                 16.31
INSTRUM             AV-600
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              12019.230 Hz
FIDRES            0.183399 Hz
AQ               2.7263477 sec
RG                     228
DW                  41.600 usec
DE                    6.00 usec
TE                   293.4 K
D1              0.10000000 sec
TD0                      8

======== CHANNEL f1 ========
NUC1                    1H
P1                   13.75 usec
PL1                  -2.00 dB
PL1W           22.93097305 W
SFO1           600.1339008 MHz
SI                   65536
SF             600.1300171 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00
```

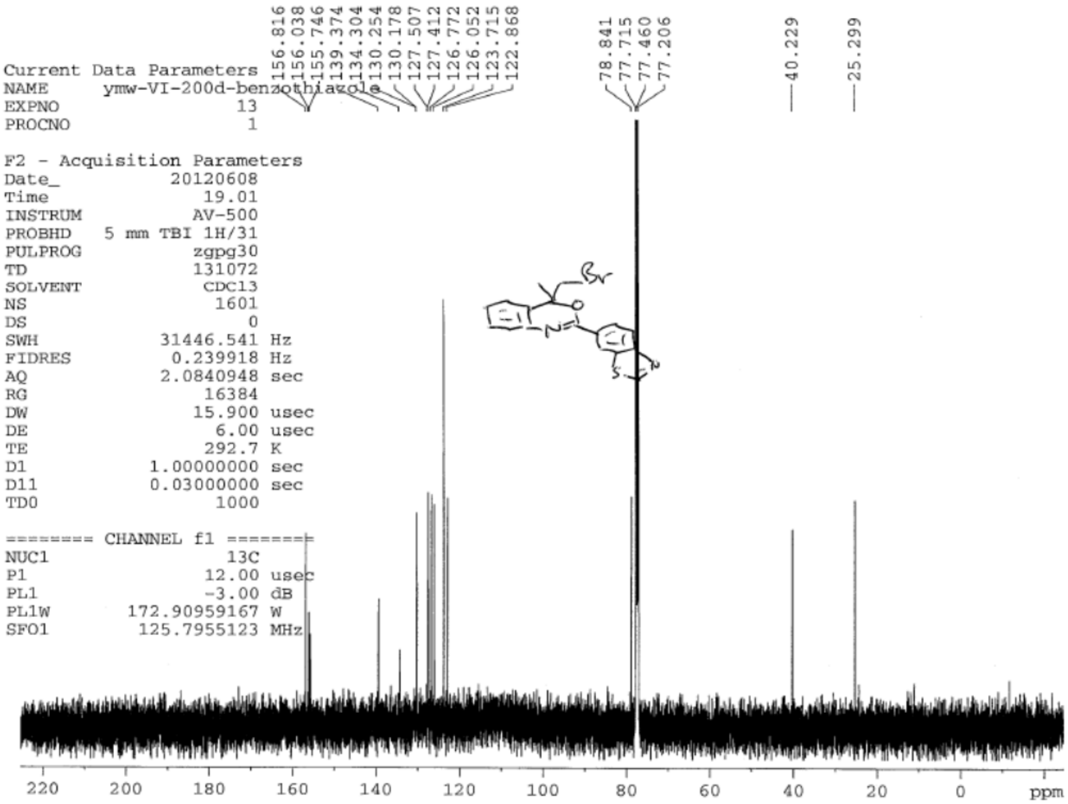


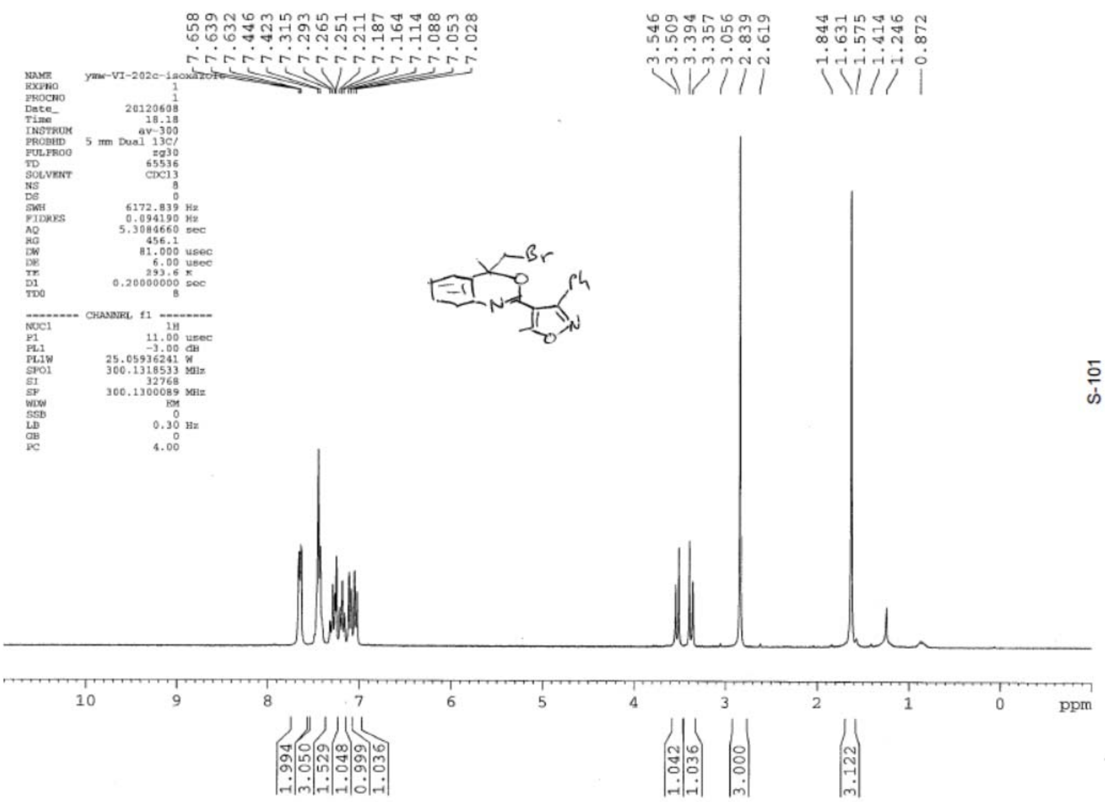
```
NAME      ymw-VI-202A-ptlc
EXPNO                   13
PROCNO                   1
Date_             20120608
Time                 16.38
INSTRUM             AV-600
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                  131072
SOLVENT              CDCl3
NS                     132
DS                       0
SWH              36057.691 Hz
FIDRES            0.275098 Hz
AQ               1.8175818 sec
RG                    2050
DW                  13.867 usec
DE                    6.00 usec
TE                   293.2 K
D1              1.50000000 sec
D11             0.03000000 sec
TD0                   1000

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.50 usec
PL1                   2.00 dB
PL1W           62.60328293 W
SFO1           150.9178993 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                70.00 usec
PL2                  -2.00 dB
PL12                 12.14 dB
PL13                 19.00 dB
PL2W           22.93097305 W
PL12W           0.88393933 W
PL13W           0.18214719 W
SFO2           600.1327006 MHz
SI                   65536
SF             150.9028163 MHz
WDW                     EM
SSB                      0
LB                    0.75 Hz
GB                       0
PC                    2.00
```

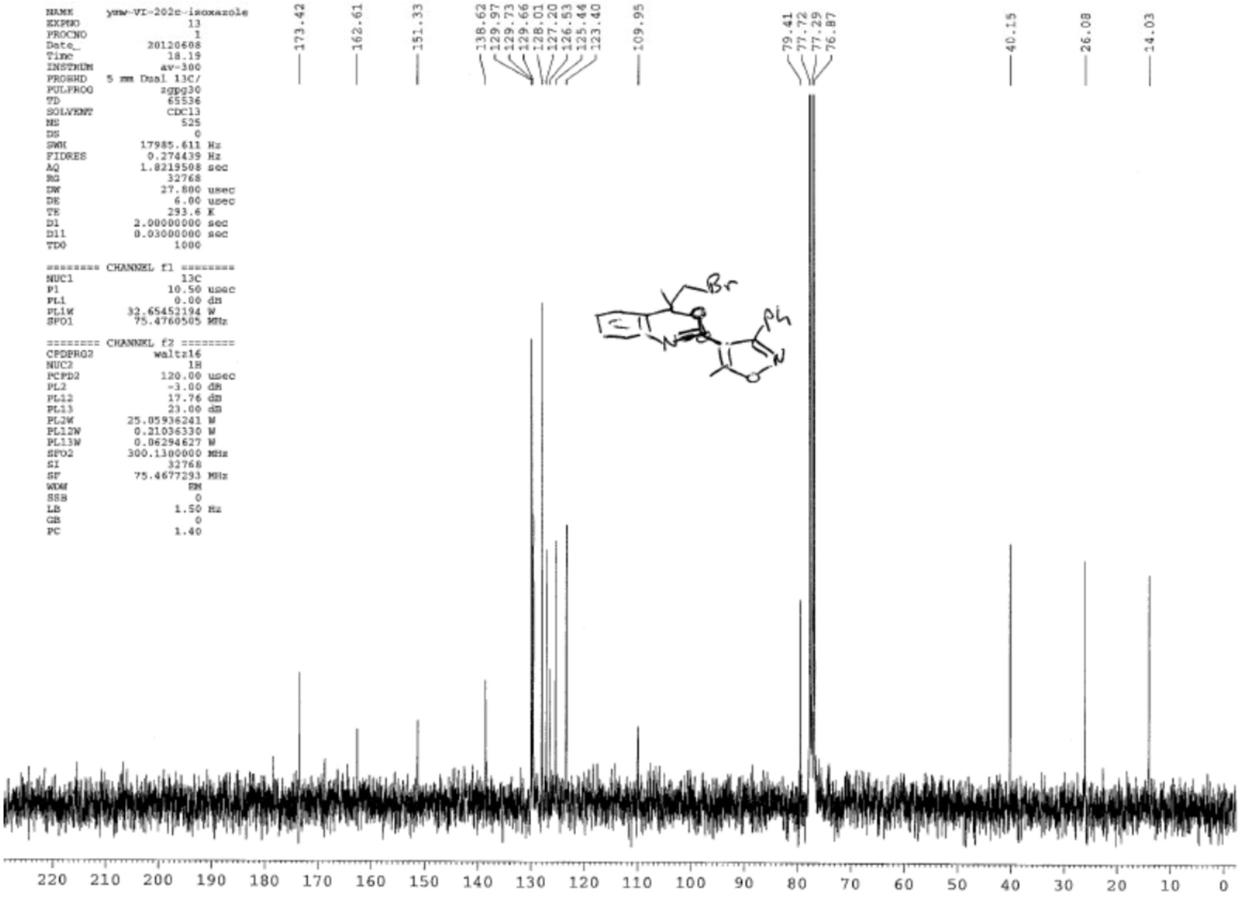
```
Current Data Parameters
NAME      ymw-VI-200d-benzothiazole
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20120608
Time                  18.59
INSTRUM              AV-500
PROBHD   5 mm TBI 1H/31
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        0
```



```
Current Data Parameters
NAME      ymw-VI-200d-benzothiazole
EXPNO                    13
PROCNO                    1

F2 - Acquisition Parameters
Date_              20120608
Time                  19.01
INSTRUM              AV-500
PROBHD   5 mm TBI 1H/31
PULPROG              zgpg30
TD                   131072
SOLVENT               CDCl3
NS                     1601
DS                        0
SWH               31446.541 Hz
FIDRES             0.239918 Hz
AQ                2.0840948 sec
RG                    16384
DW                   15.900 usec
DE                     6.00 usec
TE                    292.7 K
D1               1.00000000 sec
D11              0.03000000 sec
TD0                    1000

======== CHANNEL f1 ========
NUC1                    13C
P1                    12.00 usec
PL1                   -3.00 dB
PL1W        172.90959167 W
SFO1         125.7955123 MHz
```




NAME ymw-VI-202c-isoxazole
EXPNO 1
PROCNO 1
Date_ 20120608
Time 18.18
INSTRUM av-300
PROBHD 5 mm Dual 13C/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 456.1
DW 81.000 usec
DE 6.00 usec
TE 293.6 K
D1 0.20000000 sec
TD0 8
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -3.00 dB
PL1W 25.05936241 W
SFO1 300.1318533 MHz
SI 32768
SF 300.1300089 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
7.658
7.639
7.632
7.446
7.423
7.315
7.293
7.265
7.251
7.211
7.187
7.164
7.114
7.088
7.053
7.028
3.546
3.509
3.394
3.357
3.056
2.839
2.619
1.844
1.631
1.575
1.414
1.246
0.872
Br
Ph
O
N
N
O
10
9
8
7
6
5
4
3
2
1
0
ppm
1.994
3.050
1.529
1.048
0.999
1.036
1.042
1.036
3.000
3.122


NAME ymw-VI-202c-isoxazole
EXPNO 13
PROCNO 1
Date_ 20120608
Time 18.19
INSTRUM av-300
PROBHD 5 mm Dual 13C/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 525
DS 0
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 32768
DW 27.800 usec
DE 6.00 usec
TE 293.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1000
======== CHANNEL f1 ========
NUC1 13C
P1 10.50 usec
PL1 0.00 dB
PL1W 32.65452194 W
SFO1 75.4760505 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 120.00 usec
PL2 -3.00 dB
PL12 17.76 dB
PL13 23.00 dB
PL2W 25.05936241 W
PL12W 0.21036330 W
PL13W 0.06294627 W
SFO2 300.1300000 MHz
SI 32768
SF 75.4677293 MHz
WDW EM
SSB 0
LB 1.50 Hz
GB 0
PC 1.40
173.42
162.61
151.33
138.62
129.97
129.73
129.66
128.01
127.20
126.53
125.44
123.40
109.95
79.41
77.72
77.29
76.87
40.15
26.08
14.03
Br
Ph
O
N
N
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Determination of enantioselectivity:

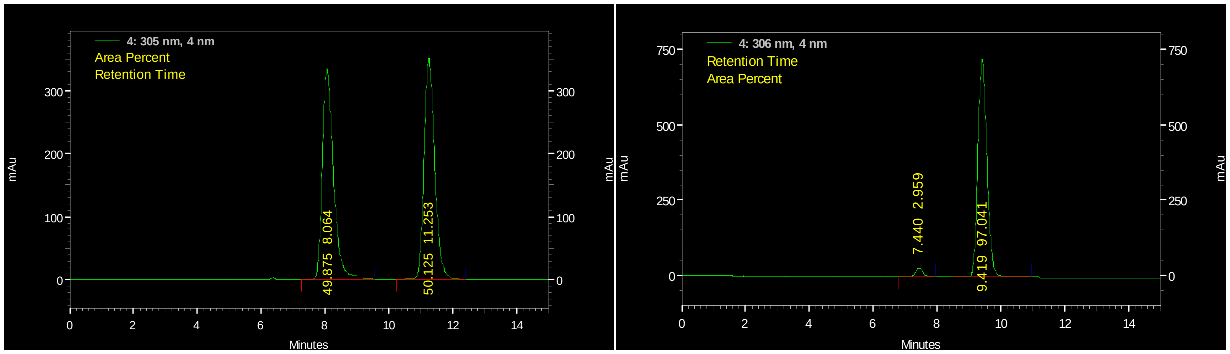
Enantioselectivity was determined by chiral HPLC using Daicel OD-H, AD-H, OJ-H, IA, IB, and IC and the Regis WHELK-O1 columns (0.46 x 25 cm). With the exception of **4f**, **4k**, **4l**, and **4o**, racemic product was generally prepared by reaction with reagent **1d** in acetonitrile under homogeneous conditions. The racemic products **4f**, **4k**, **4l**, and **4o**, we generated by using *rac*-TRIP in place of (*R*)-TIPS-TRIP using the phase-transfer conditions given in "General procedure for halocyclizations."

Chiral HPLC separation conditions and retention times for products:

4a: OD 99:01 hexanes/isopropanol, 1 ml/min, t_m = 7.4 min, t_M = 9.4 min.
4b: OD 99:01 hexanes/isopropanol, 1 ml/min, t_m = 8.3 min, t_M = 9.5 min.
4c: OD 99:01 hexanes/isopropanol, 1 ml/min, t_m = 8.5 min, t_M = 9.7 min.
4d: Two WHELK columns in series, 99:01 hexanes/isopropanol, 0.5 ml/min, t_m = 19.6 min, t_M = 18.0 min.
4e: OD 99:01 hexanes/isopropanol, 1 ml/min, t_m = 6.4 min, t_M = 6.9 min.
4f: OD 92:08 hexanes/isopropanol, 1 ml/min, t_m = 13.5 min, t_M = 15.3 min.
4g: OD 99:01 hexanes/isopropanol, 1 ml/min, t_m = 14.7 min, t_M = 16.6 min.
4h: OD 99:01 hexanes/isopropanol, 1 ml/min, t_m = 7.1 min, t_M = 9.6 min.
4i: OD 99:01 hexanes/isopropanol, 1 ml/min, t_m = 8.5 min, t_M = 11.8 min.
4j: OD 99:01 hexanes/isopropanol, 1 ml/min, t_m = 7.3 min, t_M = 6.5 min.
4k: Two WHELK columns in series, 99:01 hexanes/isopropanol, 0.5 ml/min, t_m = 14.7 min, t_M = 15.8 min.
4l: OD 99:01 hexanes/*n*-butanol, 0.5 ml/min, t_m = 14.8 min, t_M = 11.8 min.
4m: OD 99:01 hexanes/isopropanol, 1 ml/min, t_m = 17.5 min, t_M = 9.9 min.
4n: IB 95:05 (80:1 hexanes/*n*-butylamine)/isopropanol, 1 ml/min, t_m = 12.7 min, t_M = 10.8 min.
4o: OJ 97:03 (80:1 hexanes/*n*-butylamine)/isopropanol, 1 ml/min, t_m = 7.9 min, t_M = 11.8 min.
4p: OD 97:03 hexanes/isopropanol, 1 ml/min, t_m = 6.6 min, t_M = 18.2 min.
4q: OD 98:02 hexanes/isopropanol, 1 ml/min, t_m = 8.9 min, t_M = 13.3 min.
4r: OD 99:01 hexanes/isopropanol, 1 ml/min, t_m = 6.2 min, t_M = 7.1 min.
4s: OD 99:01 hexanes/isopropanol, 1 ml/min, t_m = 4.6 min, t_M = 5.2 min.
6b: OD 99:01 hexanes/isopropanol, 1 ml/min, t_m = 7.1 min, t_M = 8.5 min.
6j: AD 99:01 hexanes/isopropanol, 0.5 ml/min, t_m = 6.2 min, t_M = 7.5 min.
6n: IB 95:05 (80:1 hexanes/*n*-butylamine)/isopropanol, 1 ml/min, t_m = 12.9 min, t_M = 11.6 min.

HPLC traces:

4a: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Area Percent
Retention Time
mAu
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200
100
0
0
2
4
6
8
10
12
14
Minutes
49.875 8.064
50.125 11.253
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Retention Time
Area Percent
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500
250
0
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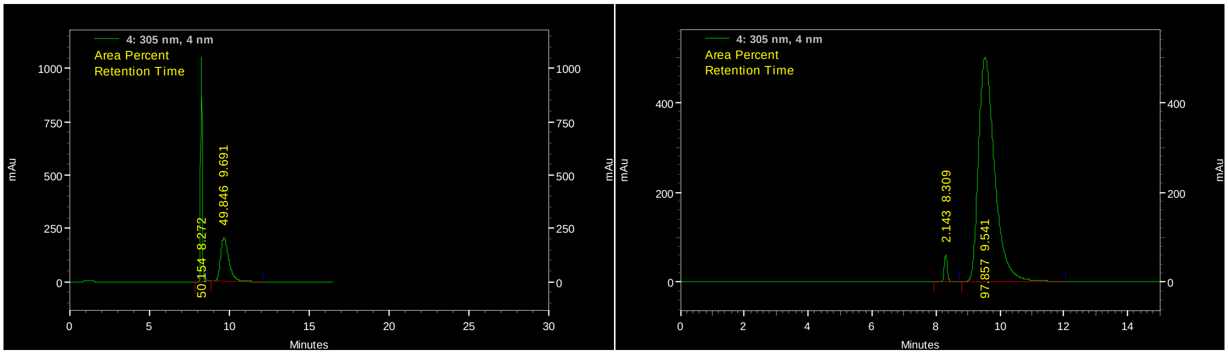
9.419 97.041

4b: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Area Percent
Retention Time
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750
500
250
0
0
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15
20
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Minutes
50.154 8.272
49.846 9.691
4: 305 nm, 4 nm
Area Percent
Retention Time
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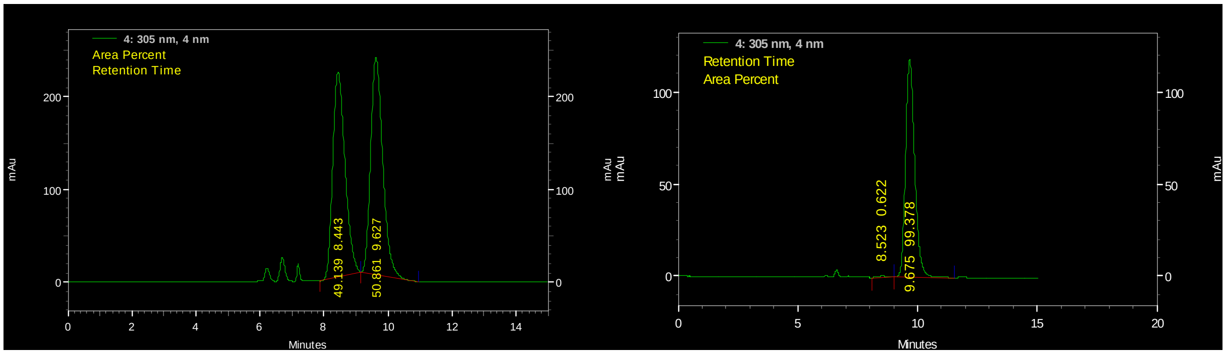
400
200
0
0
2
4
6
8
10
12
14
Minutes
2.143 8.309
97.857 9.541

4c: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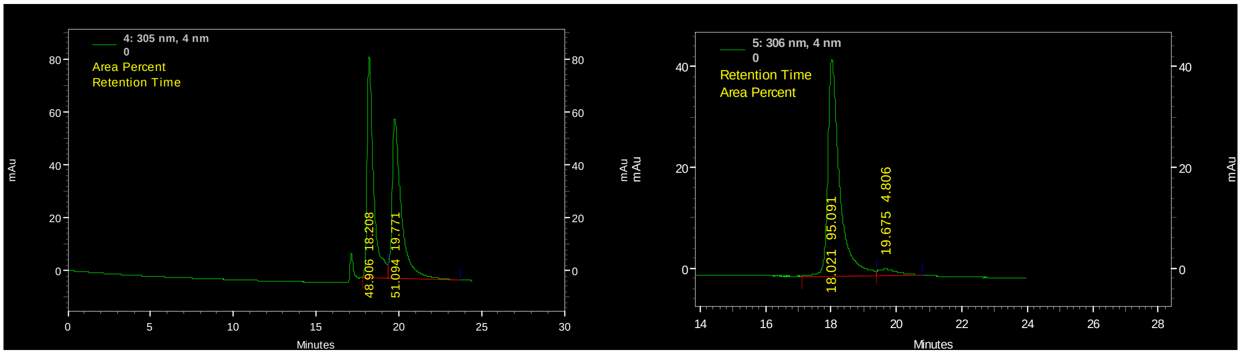
Area Percent
Retention Time
mAu
200
100
0
0
2
4
6
8
10
12
14
Minutes
49.139 8.443
50.861 9.627
4: 305 nm, 4 nm
Retention Time
Area Percent
mAu
100
50
0
0
5
10
15
20
Minutes
8.523 0.622
9.675 99.378

4d: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0
Area Percent
Retention Time
48.906 18.208
51.094 19.771
mAu
Minutes
5: 306 nm, 4 nm
0
Retention Time
Area Percent
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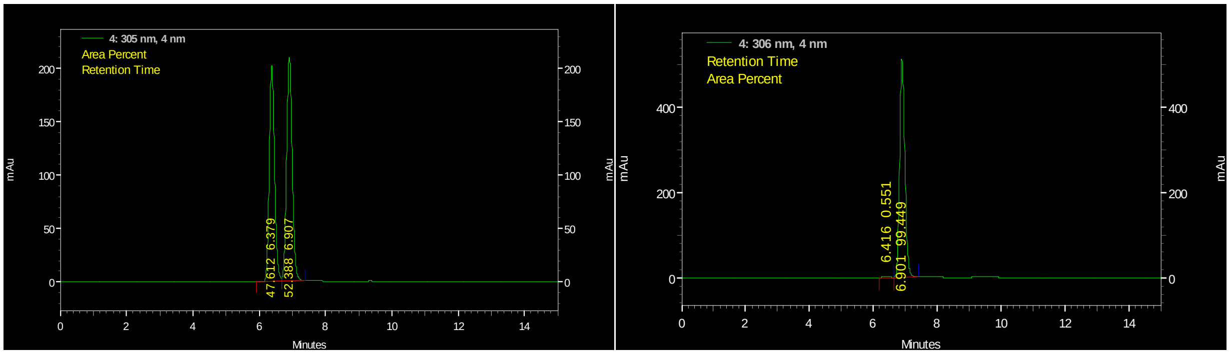
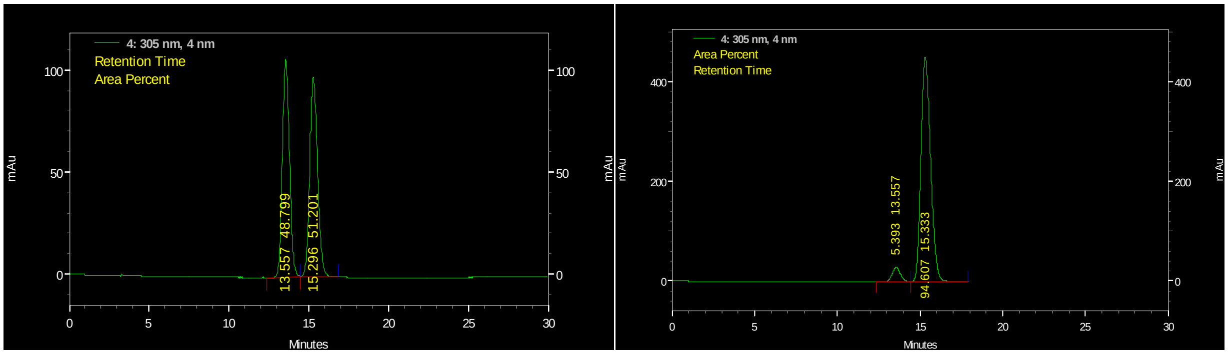
19.675 4.806
mAu
Minutes

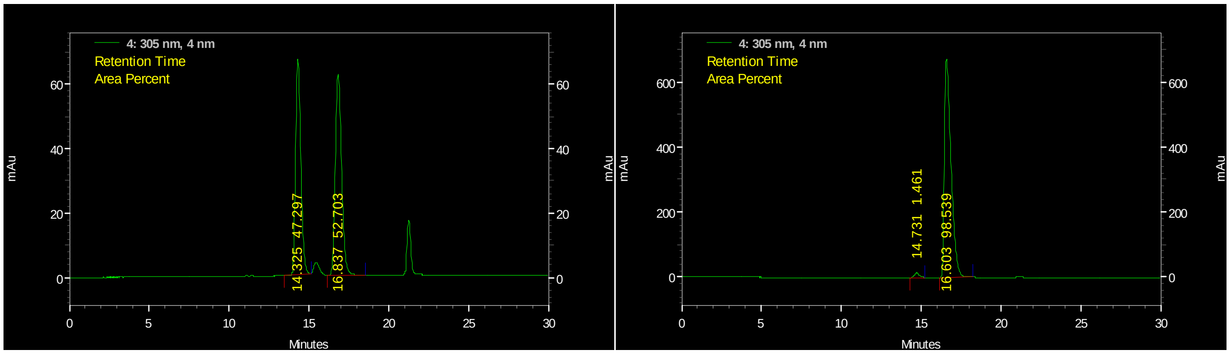
4e:


4: 305 nm, 4 nm
Area Percent
Retention Time
47.612 6.379
52.388 6.907
mAu
Minutes
4: 306 nm, 4 nm
Retention Time
Area Percent
6.416 0.551
6.901 99.449
mAu
Minutes

4f:


4: 305 nm, 4 nm
Retention Time
Area Percent
13.557 48.799
15.296 51.201
mAu
Minutes
4: 305 nm, 4 nm
Area Percent
Retention Time
5.393 13.557
94.607 15.333
mAu
Minutes

4g:


4: 305 nm, 4 nm
Retention Time
Area Percent
14.325 47.297
16.837 52.703
mAu
Minutes
4: 305 nm, 4 nm
Retention Time
Area Percent
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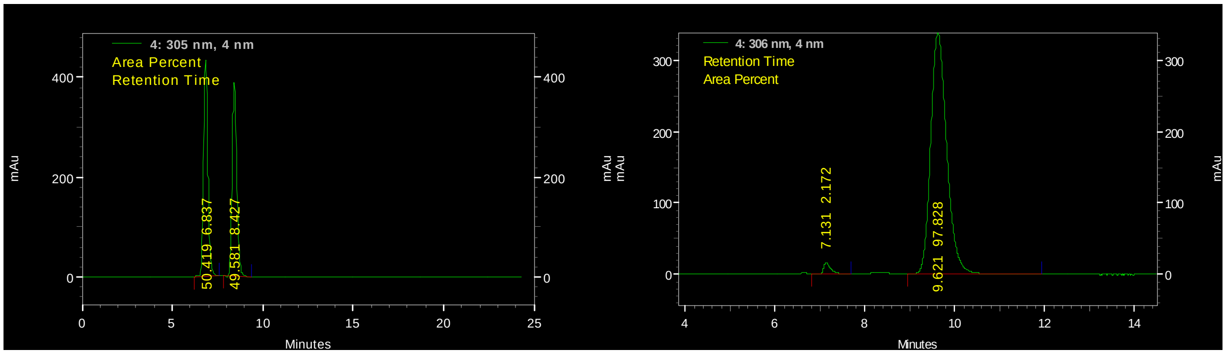
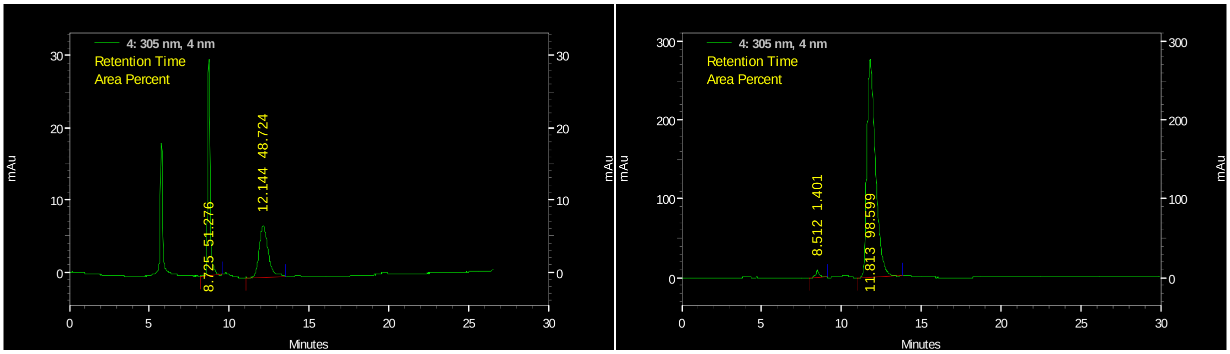
16.603 98.539
mAu
Minutes

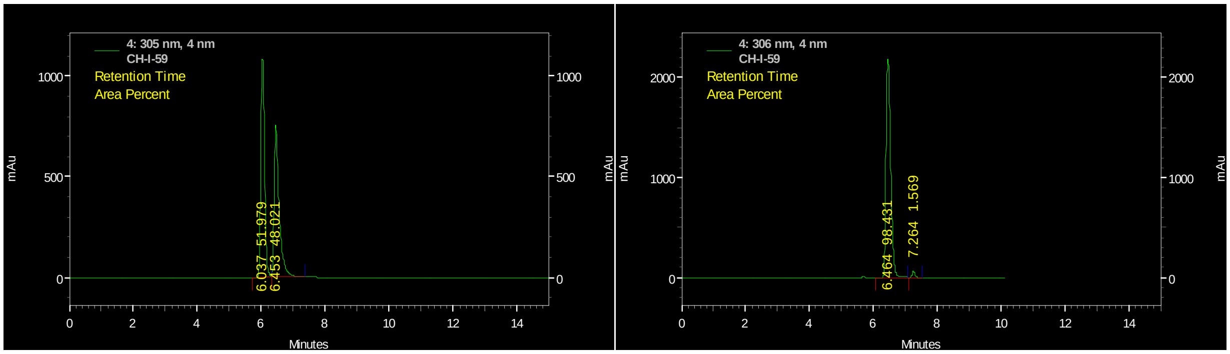
4h:


4: 305 nm, 4 nm
Area Percent
Retention Time
50.419 6.837
49.581 8.427
mAu
Minutes
4: 306 nm, 4 nm
Retention Time
Area Percent
7.131 2.172
9.621 97.828
mAu
Minutes

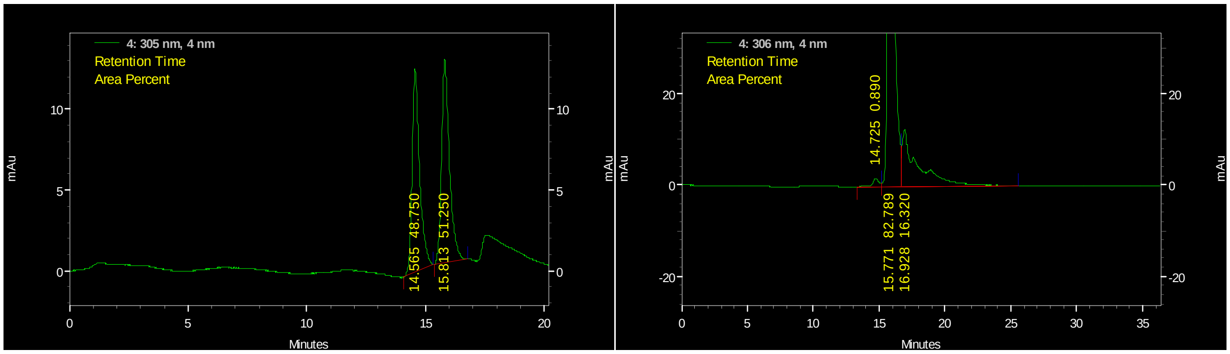
4i


4: 305 nm, 4 nm
Retention Time
Area Percent
8.725 51.276
12.144 48.724
mAu
Minutes
4: 305 nm, 4 nm
Retention Time
Area Percent
8.512 1.401
11.813 98.599
mAu
Minutes

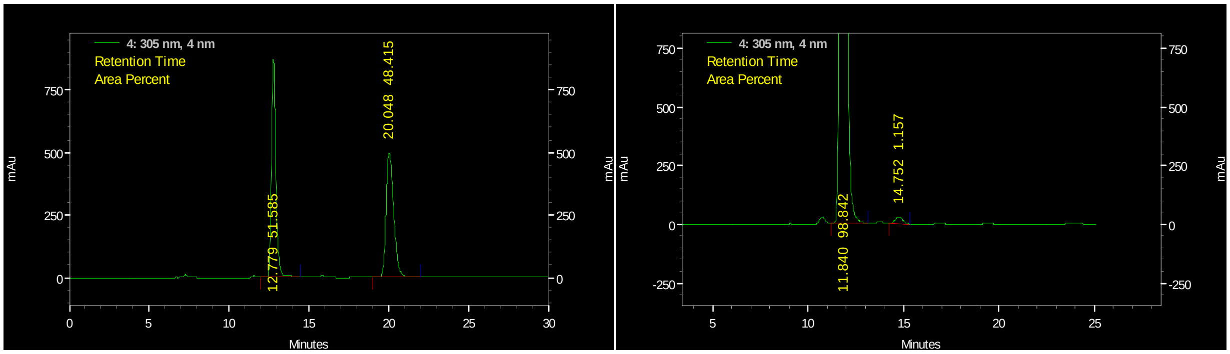
4j:


4: 305 nm, 4 nm
CH-I-59
Retention Time
Area Percent
6.037 51.979
6.453 48.021
mAu
Minutes
4: 306 nm, 4 nm
CH-I-59
Retention Time
Area Percent
6.464 98.431
7.264 1.569
mAu
Minutes

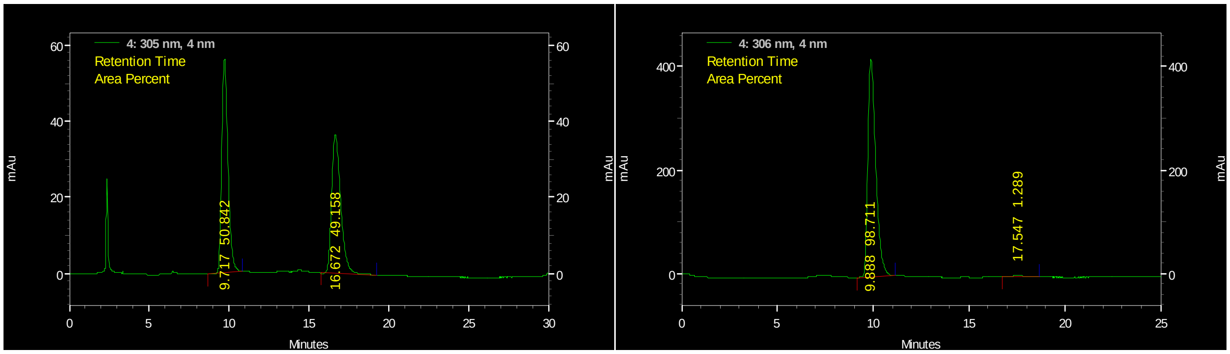
4k:


4: 305 nm, 4 nm
Retention Time
Area Percent
14.565 48.750
15.813 51.250
mAu
Minutes
4: 306 nm, 4 nm
Retention Time
Area Percent
14.725 0.890
15.771 82.789
16.928 16.320
mAu
Minutes

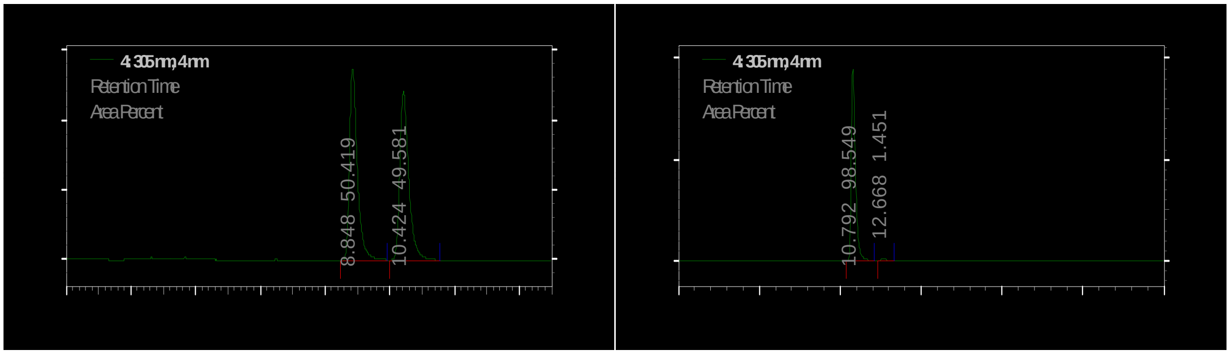
4l:


4: 305 nm, 4 nm
Retention Time
Area Percent
12.779 51.585
20.048 48.415
mAu
Minutes
4: 305 nm, 4 nm
Retention Time
Area Percent
11.840 98.842
14.752 1.157
mAu
Minutes

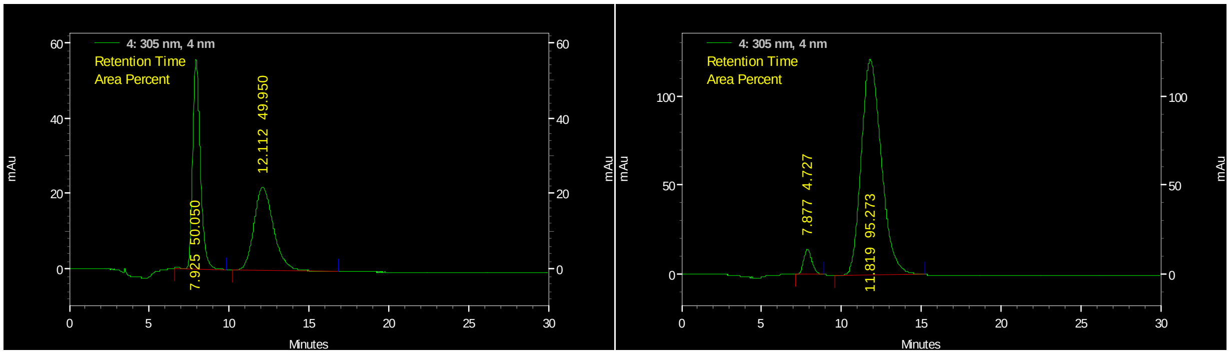
4m:


4: 305 nm, 4 nm
Retention Time
Area Percent
9.717 50.842
16.672 49.158
mAu
Minutes
4: 306 nm, 4 nm
Retention Time
Area Percent
9.888 98.711
17.547 1.289
mAu
Minutes

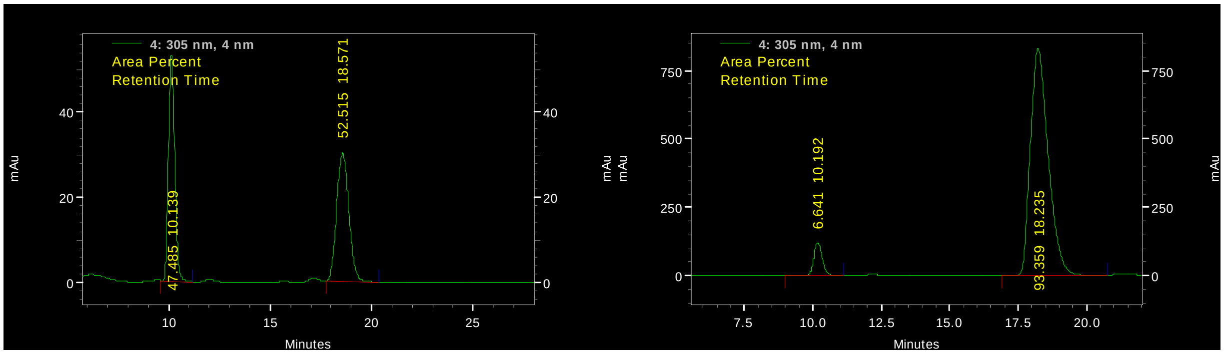
4n:


4: 305 nm, 4 nm
Retention Time
Area Percent
8.848 50.419
10.424 49.581
4: 305 nm, 4 nm
Retention Time
Area Percent
10.792 98.549
12.668 1.451

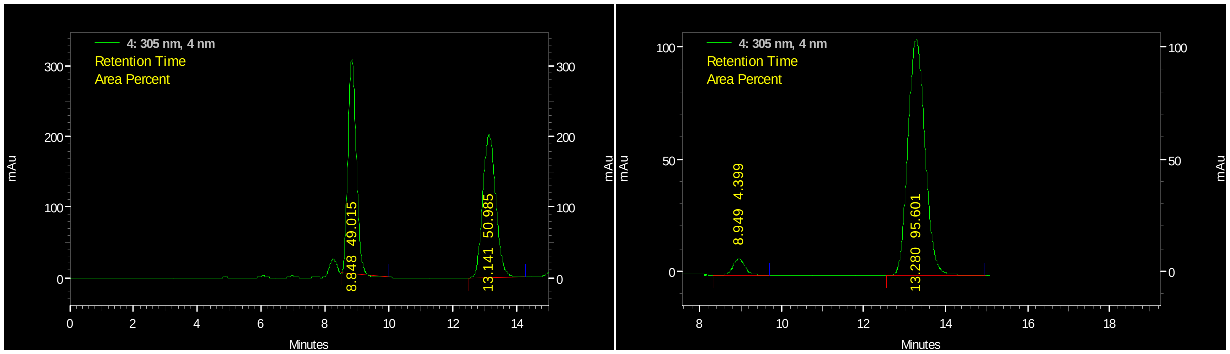
4o:


4: 305 nm, 4 nm
Retention Time
Area Percent
7.925 50.050
12.112 49.950
mAu
Minutes
4: 305 nm, 4 nm
Retention Time
Area Percent
7.877 4.727
11.819 95.273
mAu
Minutes

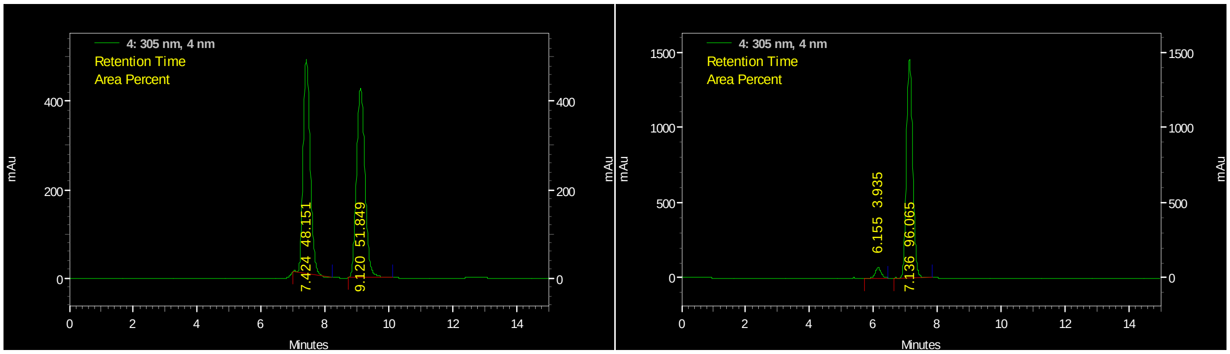
4p:


4: 305 nm, 4 nm
Area Percent
Retention Time
47.485 10.139
52.515 18.571
mAu
0
20
40
10
15
20
25
Minutes
4: 305 nm, 4 nm
Area Percent
Retention Time
6.641 10.192
93.359 18.235
mAu
0
250
500
750
7.5
10.0
12.5
15.0
17.5
20.0
Minutes

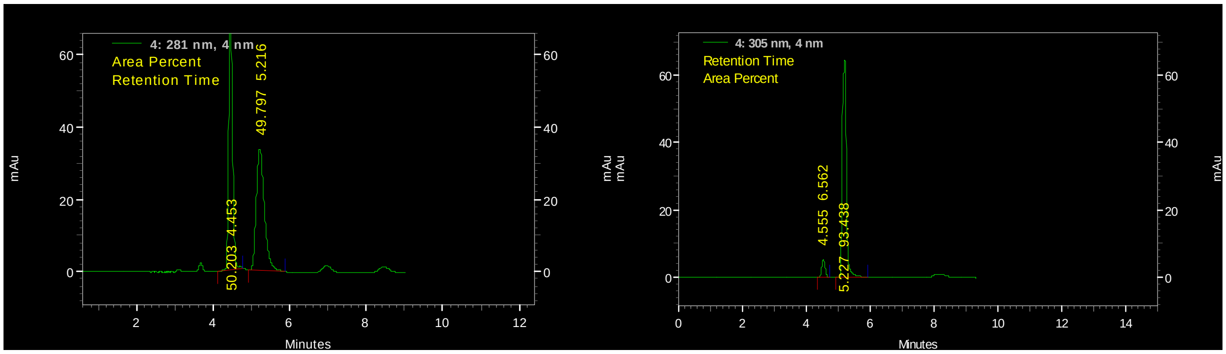
4q:


4: 305 nm, 4 nm
Retention Time
Area Percent
8.848 49.015
13.141 50.985
mAU
0
100
200
300
0
2
4
6
8
10
12
14
Minutes
4: 305 nm, 4 nm
Retention Time
Area Percent
8.949 4.399
13.280 95.601
mAu
0
50
100
8
10
12
14
16
18
Minutes

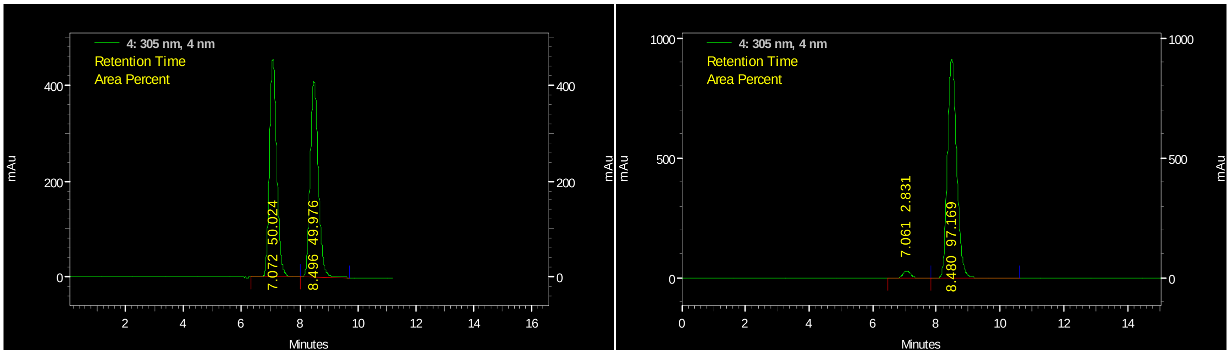
4r:


4: 305 nm, 4 nm
Retention Time
Area Percent
7.424 48.151
9.120 51.849
mAu
0
200
400
0
2
4
6
8
10
12
14
Minutes
4: 305 nm, 4 nm
Retention Time
Area Percent
6.155 3.935
7.136 96.065
mAu
0
500
1000
1500
0
2
4
6
8
10
12
14
Minutes

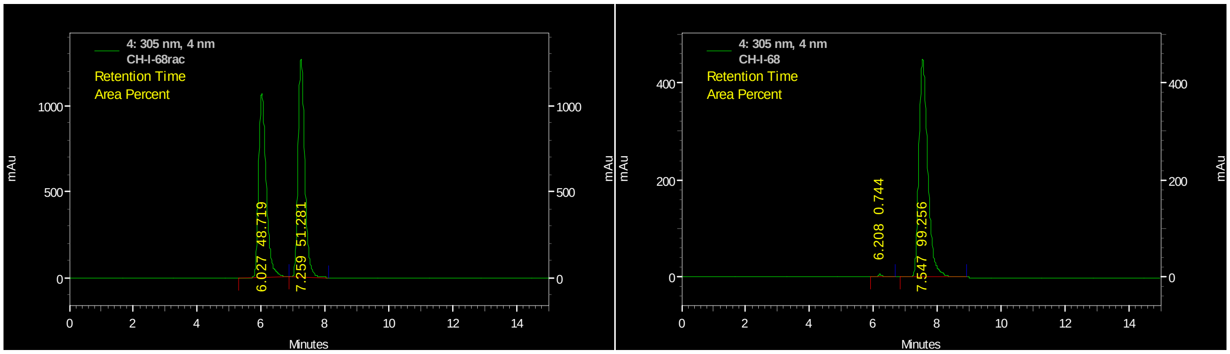
4s:


4: 281 nm, 4 nm
Area Percent
Retention Time
50.203 4.453
49.797 5.216
mAu
Minutes
4: 305 nm, 4 nm
Retention Time
Area Percent
4.555 6.562
5.227 93.438
mAu
Minutes

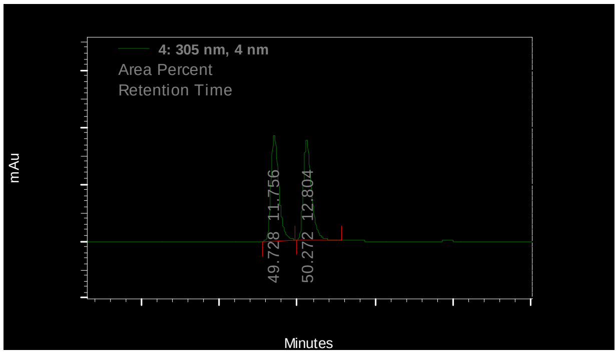
6b:

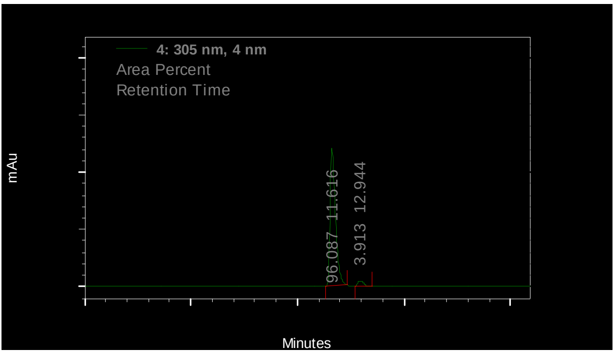

4: 305 nm, 4 nm
Retention Time
Area Percent
7.072 50.024
8.496 49.976
mAu
Minutes
4: 305 nm, 4 nm
Retention Time
Area Percent
7.061 2.831
8.480 97.169
mAu
Minutes

6j:


4: 305 nm, 4 nm
CH-I-68rac
Retention Time
Area Percent
6.027 48.719
7.259 51.281
mAu
Minutes
4: 305 nm, 4 nm
CH-I-68
Retention Time
Area Percent
6.208 0.744
7.547 99.256
mAu
Minutes

6n:

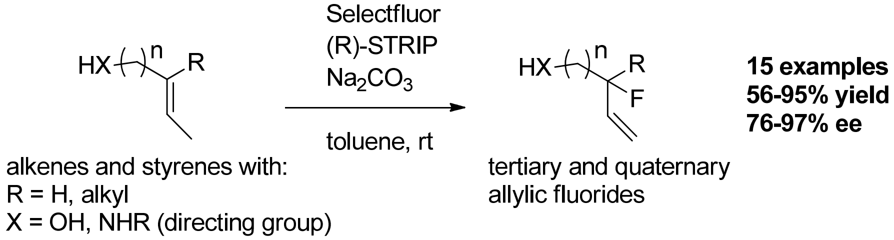

4: 305 nm, 4 nm
Area Percent
Retention Time
mAu
11.756
12.804
49.728
50.272
Minutes

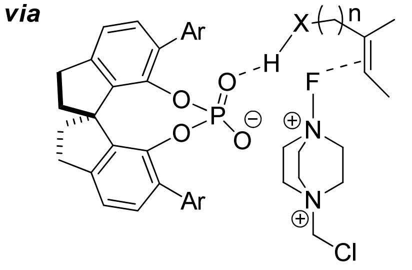

4: 305 nm, 4 nm
Area Percent
Retention Time
mAu
11.616
12.944
96.087
3.913
Minutes

CHAPTER 4: COMBINATION OF CHIRAL ANION PHASE-TRANSFER CATALYSIS AND DIRECTING GROUPS FOR ALKENE FLUORINATION

Abstract:

The combination of directing groups and chiral anion phase-transfer catalysis allows chiral phosphoric acids to catalyze the direct fluorination of alkenes to generate tertiary and quaternary C(sp3)-F bonds, and β-amino- and β–aryl- allylic fluoride moieties. Essentially, a reactive electrophilic chiral ion pair *interacts* with a hydrogen-bond donor directing group but *fluorinates* a remote alkene. A variety of heterocyclic, carbocyclic, and acyclic allylic fluoride products were provided with good to excellent yields and high enantioselectivity. Further, by using two electrophilic salts of differing reactivity, we were able to perform a one-pot, two-step dihalogenation-cyclization reaction sequence utilizing the same catalytic cycle twice.





directing group interaction with chiral
electrophilic fluorinating reagent generated *in-situ*

Introduction

Organocatalysts have largely been developed around the idea that hydrogen-bonding can act as a strong attractive interaction between substrate and catalyst, allowing the creation of a pair of diastereomeric transition states. However, the use of hydrogen-bonding in organocatalysis has not been extended to directing groups (DG). Instead, almost all examples have relied on hydrogen-bonding directly with the reactive functional group. Directing groups (DGs) have been used both in the field of enantioselective transition-metal catalysis and for C-H activation.[1-6] DGs provide the ability to functionalize non-polar bonds (such as alkenes), while maintaining beneficial polar interactions between the substrate and chiral source, by following a similar reactivity model as that described in previous reports of directed reactions (Figure 1).

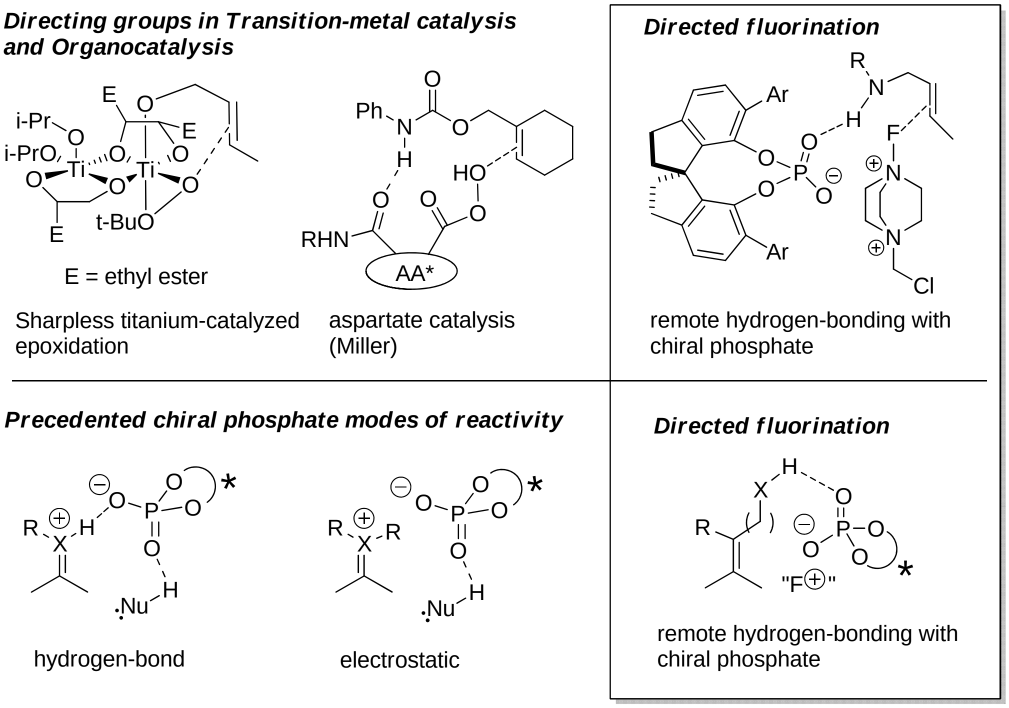


Figure 1. Top: Substrate-catalyst interactions in precedented metal-catalyzed and organocatalytic directed enantioselective reactions with alkenes. Bottom: Modes of activation of polar groups in chiral phosphoric acid catalysis, compared to this work - directed interaction with alkenes.

Within organocatalysis, the Miller research group has developed an enantioselective epoxidation reaction of allylic alcohols using amino acid catalysts featuring aspartate, capable of hydrogen-bonding with a remote alcohol DG (Figure 1).[7] In another mode of catalysis, the Tan group has designed bifunctional *covalent* catalysts which are capable of scaffolding and organizing the transition state to provide enantioselectivity.[8-10]

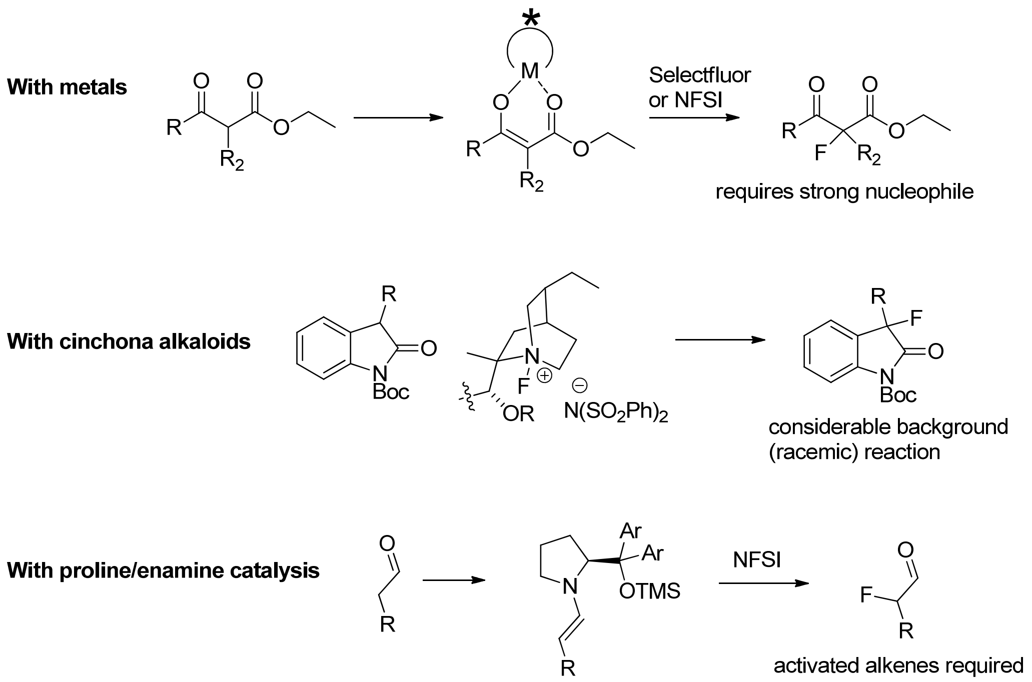


Figure 2. Modes of enantioinduction in electrophilic fluorination.

Both these modes of activation achieve enantioselectivity with catalysts which organize the reactants in the transition state (Figure 1), rather than LUMO-lowering protonation or hydrogen-bonding, which has generally been utilized for substrates containing carbon-heteroatom unsaturated bonds such as carbonyls or imines.[11-13] Generally, chiral phosphoric acids have been predominantly used as Brønsted acids in LUMO-lowering activation of a polar electrophile. It is notable that hydrogen bonding to the incoming nucleophile has also been implicated as a key component of achieving enantioselectivity.[14] Based on the well-established ability of phosphoric acids to hydrogen-bond with substrates, we saw an opportunity to combine transition-state organization catalysis with chiral anion phase-transfer catalysis which was introduced in chapter 3. The hypothesis here is that a remote hydrogen-bonding DG could effectively direct an ion-paired chiral phosphate species for the enantioselective fluorination of alkenes (Figure 1, Bottom).

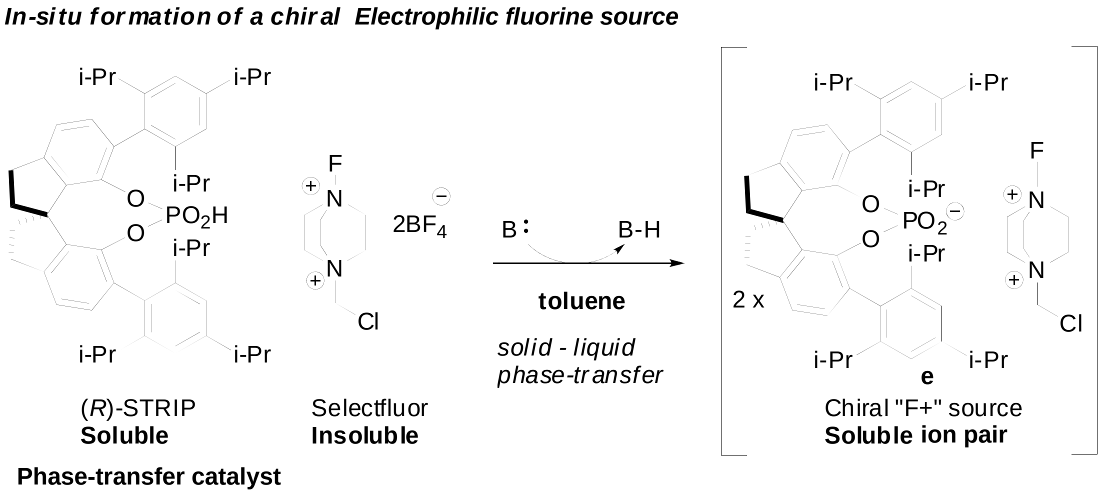


Figure 3. Both solubility and chirality are provided by the organophosphate, when it is ion-paired with the DABCO-derived electrophilic fluorine moiety. In the presence of base, the phosphate is generated in-situ to act as the active catalyst.

Compared with nucleophilic fluorinating reagents which can be used for stereospecific reactions, electrophilic reagents are easier to handle, have a range of reactivity, and are more commonly used in the development of enantioselective fluorination methods (Figure 2). Our recent enantioselective halocyclization methods utilized chiral anion phase-transfer catalysis, in which ion exchange between an insoluble electrophilic salt (such as Selectfluor) and a soluble chiral lipophilic phosphate anion derived from catalysts such as TRIP generates in-situ a chiral electrophilic salt (Figure 3).[15,16] In addition, our reports of enantioselective fluorinations demonstrated that activated alkenes such as enamides react with high enantioselectivity and yield using the same phase-transfer system.[17,18] In both examples, hydrogen-bonding between the reacting functional group (amide) and the phosphate catalyst is hypothesized to facilitate the reaction. The enantioselective synthesis of allylic fluorides has been recently achieved by a few research groups - allylic chlorides undergo palladium-catalyzed nucleophilic fluorination in the presence of silver fluoride, while allylsilanes undergo electrophilic fluorination with NFSI in the presence of cinchona alkaloid catalysts (Figure 4).[19-23] While these are useful advancements in the synthesis of these moieties, they suffer limitations such as the requirement of pre-functionalizing the alkene, as well as the use of transition-metals, and long reaction times – at times requiring up to a week for completion.

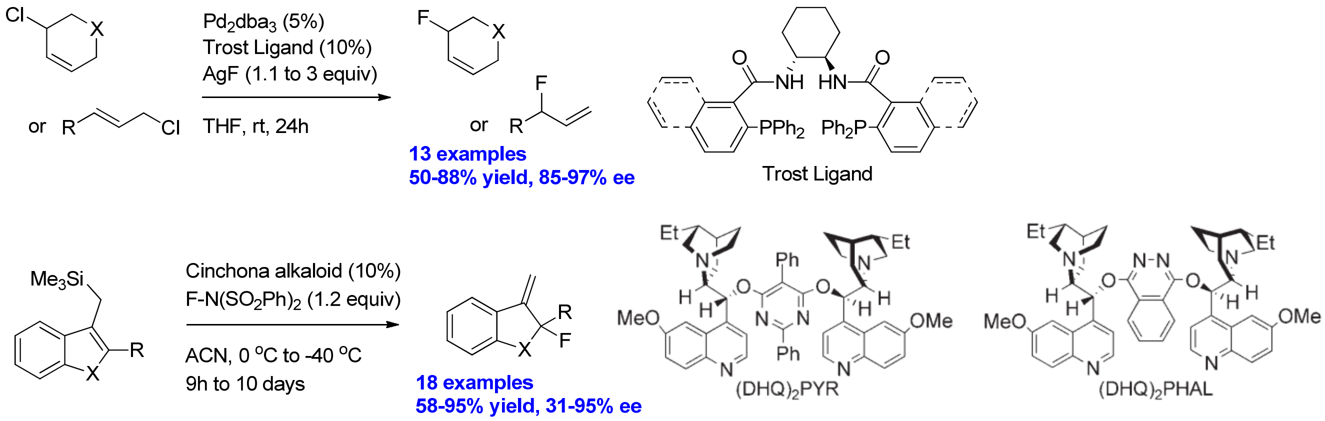


Figure 4. Top: Enantioselective transformation of allylic chlorides to allylic fluorides using palladium-catalysts. Bottom: Organocatalytic enantioselective allylic fluorination using cinchona alkaloids.

On the other hand, the desirable direct fluorination of a variety of alkenes was reported in racemic fashion by Loh and co-workers (Figure 5).[24] This homogeneous reaction required heating, demonstrating the relatively low reactivity of the unactivated alkene toward Selectfluor. Nevertheless, we envisioned that this reaction could be rendered enantioselective by taking advantage of a DG capable of participating in hydrogen-bonding with the phosphate phase-transfer catalyst.

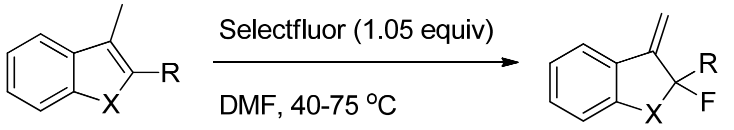
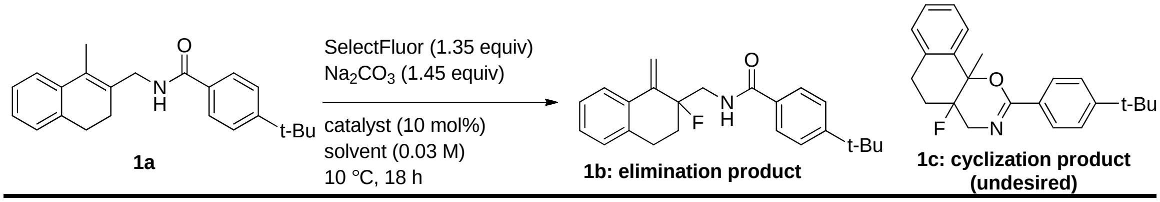


Figure 5. Racemic direct fluorination of alkenes with Selectfluor under homogeneous conditions.

Results and Discussion

Based on the previous success with benzamides in our phase-transfer system, we initially investigated their ability to act as DGs for direct alkene fluorination. Furthermore, we saw this as an opportunity to access enantioenriched tertiary β—fluoroamines, which has been an outstanding challenge for synthetic chemists, while being useful for the development of drug candidates.[25-29] Enantioselective fluorination of substrates with no hydrogen-bond donor containing directing group was attempted with poor results, verifying our initial hypothesis that a directing group with hydrogen-bonding capabilities would be required and beneficial.[24]



1a

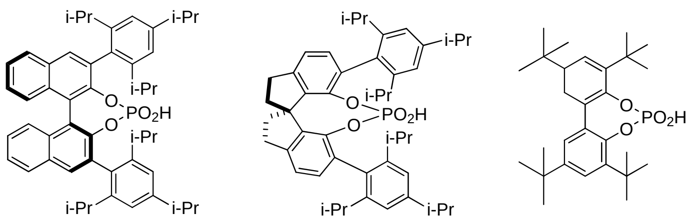
1b: elimination product

1c: cyclization product (undesired)

entry	catalyst	solvent	yield (%)	**1b:1c**	ee (%) **1b (**ee (%) **1c)**
1	(*S*)-**2**	PhF	82	5:1	85 (48)
2	(*S*)-**2**	tol	95	8:1	89
3[a]	(*S*)-**2**	tol	95	8:1	88
4	(*R*)-**3**	tol	95	10:1	90
5	**4**	MeCN	98	1:4	-
6	-	MeCN	98	1:4	-

[a] 3.0 equiv Na_2CO_3

Catalysts:



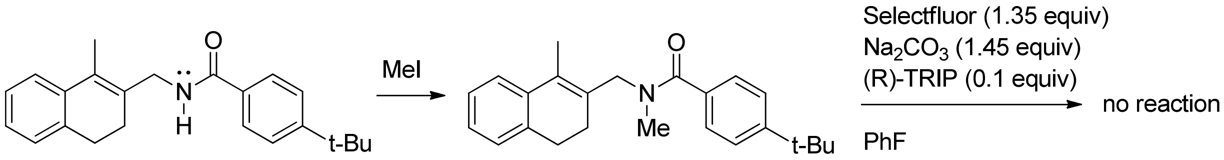
(*S*)-**2** (TRIP)

(*R*)-**3** (STRIP)

achiral **4**

Table 1. Optimization of product distribution and enantioselectivity by catalyst and solvent screening.

Specifically, enantioselectivies no higher than 10% ee were obtained. After the installation of a pendant amide group, fluorination proceeded to provide product **1b** in 82% yield and 85% ee (Table 1, entry 1). Also in accord with our hypothesis that a remote hydrogen-bond donor may be essential to direct fluorination, *N*-methylated amide analog of **1a** gave less than 10% conversion under identical conditions (Figure 6). Interestingly, this is evidence of the amide N-H participating in increasing reactivity as well as selectivity. This is in-line with such observations from covalent catalysis, often referred to as induced-intramolecularity. In principle, the transition-state organization provided by attractive and stabilizing interactions increases reactivity (Figure 6). In other words, it seems like the hydrogen-bonding DG improves both enantioselectivity and reactivity. When the phase-transfer catalyst was left out of the reaction mixture, the fluorination did not proceed, thus verifying that a phase-transfer process is indeed essential, and that there is no background reaction with Selectfluor.



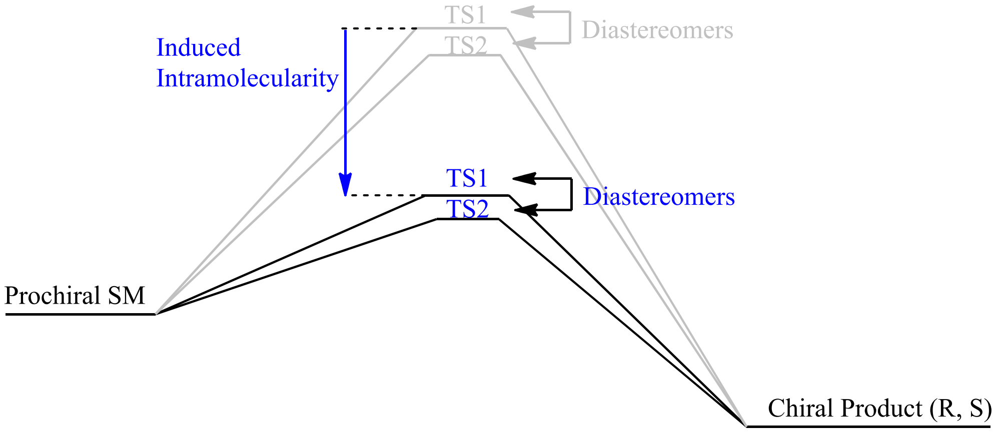


Figure 6. The amide N-H participates in lowering the activation barrier, inducing intramolecularity by hydrogen-bonding. The amide also directs the chiral reagent and is essential for enantioselectivity.

A solvent screen revealed that changing the solvent to toluene helped increase selectivity for the desired allylic fluoride product at the expense of side product **1c** (resulting from nucleophilic attack by the amide) (entry 2). Allylic fluorination and cyclization products could be produced from a common fluorinated carbocationic intermediate as a result of deprotonation or nucleophilic attack. As formation of the C-F bond is presumably enantiodetermining for both, the significantly lower enantioselectivity observed for the cyclization product **1c** (48% ee; Table 1, entry 1) suggest that there is no shared cationic intermediate and that the two reaction pathways are divergent at an earlier stage. In addition we showed that the allylic fluoride could not be produced in greater enantioselectivity through a kinetic resolution (by an elimination reaction of **1c)** in an experiment where we resubjected **2b** to reaction conditions with no observed conversion (Figure 7).

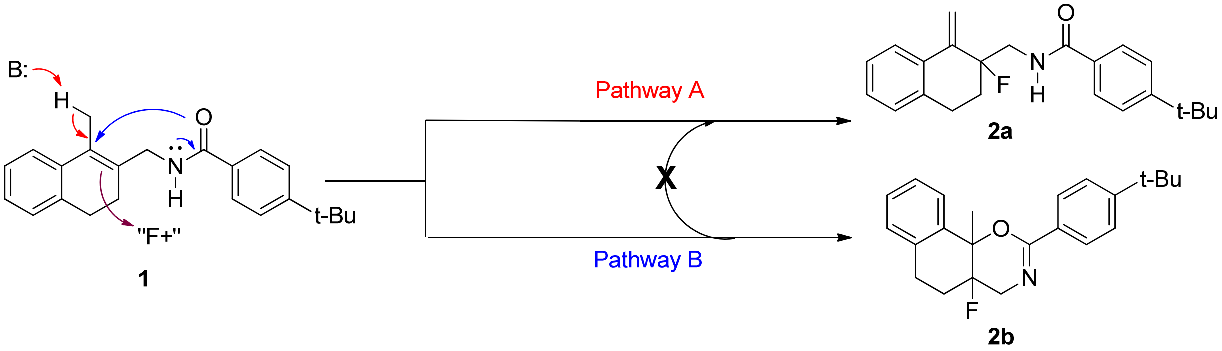
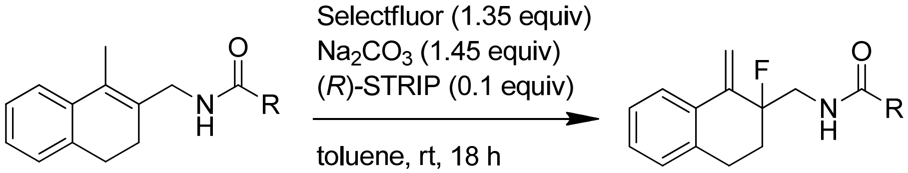


Figure 7. Product does not ring-open to form **2a**, and the two pathways are distinct (no common benzylic carbocation exists).

A catalyst screen revealed that STRIP provided improvements over the commercially available TRIP.[30] The role of the phosphate-directing group interaction is further confirmed by the observation that the undesired cyclization pathway predominates when the reaction was run in acetonitrile under homogeneous conditions (Table 1, entries 5-6). The reactivity under phase-transfer conditions differs greatly from under homogeneous conditions.



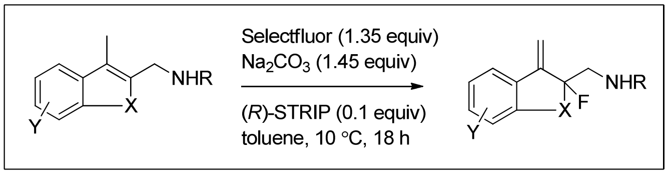
entry	R=	ee (%)	entry	R=	ee (%)
1	Me	30	**5**	CF_2H	30
2	i-Pr	51	**6**	CF_3	82
3	t-Bu	75	**7**	CCl_3	93
4	Ph	92 (76 ^{c})			

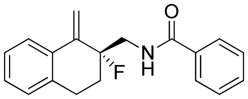
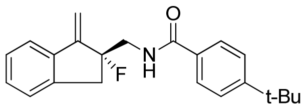
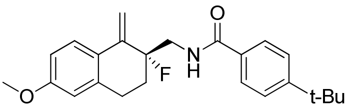
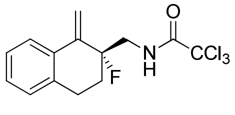
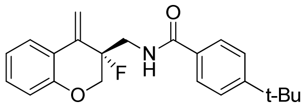
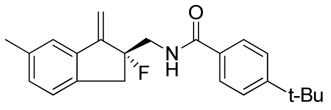
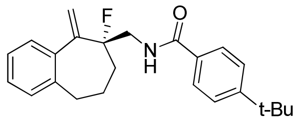
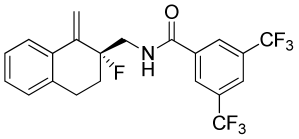
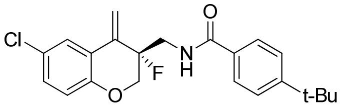
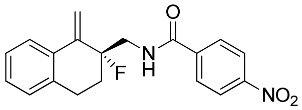
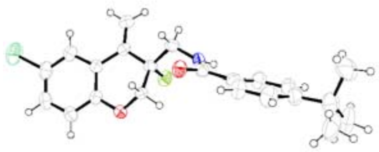
a) ee (%) determined by chiral HPLC. b) Conversion determined by NMR >90% for all entries c) With (*S*)-TRIP rather than (*R*)-STRIP

Table 2. Studies on electronic and steric factors using amide DGs. Enantioselectivity generally increased with steric bulk on the amide.

While we were exploring substrate scope with the tetralone core and other modifications, we undertook a study to determine whether steric and electronic factors were at play in the preferential reactivity of benzamides. In addition, we hoped that the understanding would also help in finding a cleavable directing group rather than being solely able to use benzamides. The ability to use non-benzamide DG would be a step forward for chiral anion phase-transfer catalysis in the Toste group, as well as for this particular method. Various substrates were synthesized with electronic and steric variations (Table 2). Chlorinated and fluorinated acetyl derivatives provided insight into the influence of electronegativity, while increasingly bulky alkyl derivatives revealed the effect of changes in steric bulk. Predictably, increased enantioselectivity tracked well with increased steric bulk (t-Bu > i-Pr > Me; entries 1-3). Identical enantioselectivities were achieved with CH_3 and CHF_2 substituents (entries 1 and 5), but one additional fluorine increased enantioselectivity from 30% to 82% ee (entry 5 vs. 6). We postulate that the rotation of the CHF_2 group can minimize steric interactions which are not possible with the symmetrically bulky CF_3. A further increase in size to CCl_3 (TCA), while decreasing the electron-withdrawing ability, improved enantioselectivity to a synthetically useful 93% ee. In addition, comparison of entries 3 and 4 indicate that a phenyl group, due to either electon-withdrawing or pi-stacking interactions, improves enantioselectivity. We found this to be beneficial also in the development of alcohol derived DGs. Unfortunately, more substantial changes such as the use of p-toluenesulfonamide as the directing group provided product with 67% conversion by NMR analysis and only 18% ee – hence we decided not to investigate any other classes of DG. In addition to being highly efficient for the desired transformation, the TCA group was readily hydrolyzed with potassium hydroxide to provide free amine in 90% yield with no racemization of the fluorinated stereocenter (determined by derivatization of the amine), thus allowing access to primary β-fluoroamines and ability to access a number of amine derivatives not necessarily containing the DGs we have optimized (Figure 10).

Table 3 sums up the various changes we made to the core and amide DG. Good yields and high enantioselectivities were maintained with medium-sized rings (entries 3 and 4). The method tolerates electron-withdrawing and electron-donating groups on the fused benzene ring, even when in an electronically significant (by resonance donation/activation) position (entry 8). Chromanone-derived heterocyclic substrates **9a** and **14a** were fluorinated with good yield and high enantioselectivity (96% ee and 97% ee, respectively) to generate heterocyclic fluorinated products.



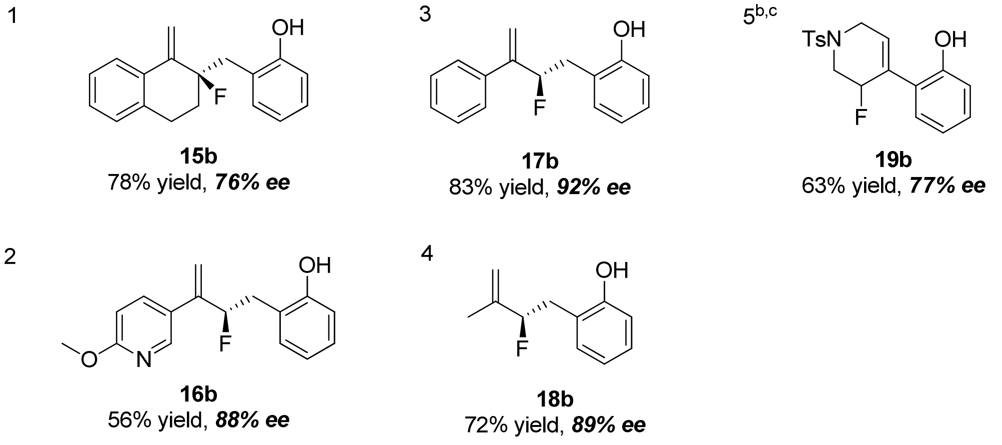
entry	product	entry	product	entry	product
1[b]	 **5b** 88% yield, ***92% ee***	4	 **8b** 65% yield, ***95% ee***	8	 **12b** 60% yield, ***92% ee***
2	 **6b** 72% yield, ***93% ee***	5[a]	 **9b** 57% yield, ***96% ee***	9[a]	 **13b** 63% yield, ***96% ee***
3[a,c]	 **7b** 92% yield, ***93% ee***	6	 **10b** 64% yield, ***97% ee***	10[a]	 **14b** 60% yield, ***97% ee***
		7[b]	 **11b** 66% yield, ***89% ee***		

a) Reaction run at room temperature. b) Product isolated with cyclized by-product in 10:1 ratio.
c) Reaction run for 36 h. d) All stereochemistry defined in analogy to compound **14b** (see Supporting information for crystallography details)

Table 3. Scope of amide DG substrates.

As seen in the amide DGs, pi-stacking or some other electronic effects from an aromatic ring does have an effect. We had recently observed that phenol acts as a competent hydrogen-bond donor in enantioselective fluorination and dearomatization reactions.[31] Specifically, compound **18a** was found to direct fluorination with high enantioselectivity by Robert Phipps, who was exploring dearomatization. Thus, in addition to amides, 2-hydroxyphenyl was serendipitously discovered to be a DG which promotes enantioselective fluorination of a variety of alkenes under identical reaction conditions (Table 4). In the examples shown here, we observe that the presence of more highly substituted double bonds changes the chemoselectivity, and fluorination of the alkene is seen exclusively rather than fluorination of the phenol. Both β-phenolic tertiary and quaternary fluorides with alkyl, aryl, or heteroaryl substituents were obtained with good to high enantioselectivity and yield. Compound **23a,** which contains both an allyl and 3,3-dimethylallyl group ortho- to the hydroxyl, reacts specifically to provide the allylic fluoride in 53% ee, which is a surprising result due to the relatively similar steric bulk of the two faces of the compound. Further, fluorinated piperidine **19b** was obtained in moderate yield and enantioselectivity - a facile synthesis of a scaffold which has been explored in therapeutic agents.[32] This was achieved with a change in catalyst to one previously reported by Du and co-workers – use of TRIP or STRIP with this substrate provided no reactivity. Interestingly, when the hydroxyl group was shifted to be meta- to the alkene, no reaction was seen. In addition, the use of benzamides in the place of the hydroxyl did not provide desired product. The ideal location of the hydroxyl donor is specific, and different from the ideal location of the benzamide donor. In agreement with previous results, conversion was severely diminished (< 10%) when the phenoxy group was methylated, presumably due to the inability of the methyl ether moiety to effectively participate in hydrogen-bonding with the catalysts. Even with these requirements in DG position and identity, we anticipate that the enantioselective construction of β-amino and β-aryl sp3-C-F bonds will still be valuable in drug discovery.[33]

Phenol DG Substrates[a, d]



15b 78% yield, ***76% ee***

17b 83% yield, ***92% ee***

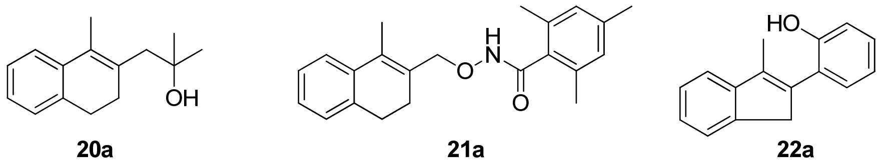
19b 63% yield, ***77% ee***

16b 56% yield, ***88% ee***

18b 72% yield, ***89% ee***

a) Selectfluor (1.35 equiv), Na_2CO_3 (1.45 equiv), (*R*)-STRIP (0.1 equiv), toluene, rt, 18 h. b) Reaction run 36 h. c) Du catalyst (Ref 34) used instead of (*R*)-STRIP. d) All stereochemistry defined in analogy to compound **17b** (see Supporting information for crystallography details).

Table 4. 2-Hydroxylphenyl DG effective for various alkenes.

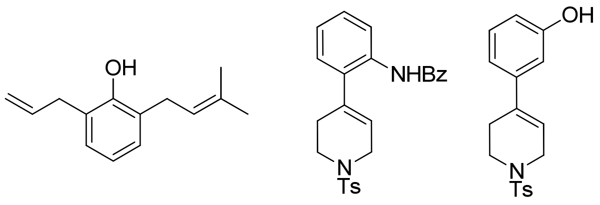


20a 2% ee

21a 34% ee

22a 12% ee

Figure 8. Various hydroxyl-DGs explored. Reaction conditions identical to Table 3. Conversion was followed by NMR, and reactions were run for 24-48 h or until starting material had been completely consumed.



23a
90% yield, 53% ee

24
no reaction

25
no reaction

Figure 9. Substrate with similar ortho-substituents reacted regioselectively and with moderate enantioselectivity. Shift of the hydroxyl-DG, or replacement with benzamide, are both detrimental to reactivity.

Some effort and serendipity was required to identify a suitable DG which was not amine-derived. In the Toste group at this point all of the phase-transfer fluorinations required benzamides. Efforts in expanding this focused on hydroxyl (O-H) based DGs. However, initial results indicated that simple alcohols did not provide high enantioselectivity, maybe due to its small steric parameters or lack of rigidity. First, a bulkier alcohol DG on substrate **15** was found to be ineffective for providing enantioselectivity. Next, benzoylated hydroxylamines were explored in order to mask an alcohol (which would be revealed by deprotection by hydrogenation) as a functional group with the previously successful amide moiety. However, the extended tether length in these cases was detrimental and enantioselectivity was not improved. The incorporation of phenol was investigated with substrate **22** (Figure 8). We explored whether alcohols and amide DG could be interchangeable in analogous substrates **19** and **24**; where a hydroxyl group promoted the reaction, a benzamide with the acidic hydrogen in the exact same position did not promote the reaction. When the hydroxyl-DG was moved from ortho- to meta-, the reaction also did not proceed. Thus, there is specificity regarding hydrogen-bond donor location (Figure 9). Another observation of the difference in reactivity between directing groups was that acyclic substrates were not amenable to amide-directed fluorination - with the benzamide DG, exclusively cyclized product was observed, while with TCA no reaction was observed. Thus, only phenol DG was capable of creating tertiary fluorine-containing carbon centers with these types of substrates.

A tandem reaction was achieved using our previously reported electrophilic bromination reagent **28** to further functionalize the product from the fluorination reaction.[16] This reaction proceeds in two steps, using the same catalytic cycle and phase-transfer process. The important factor is the orthogonal reactivity of the two reagents – Selectfluor does not do the halocyclization, while reagent **28** does. The experiment consisted of subjecting **8a** to the standard fluorination conditions for 18 h ("F+") described above, followed by addition of **28** ("Br+") and an equivalent of base, under air.

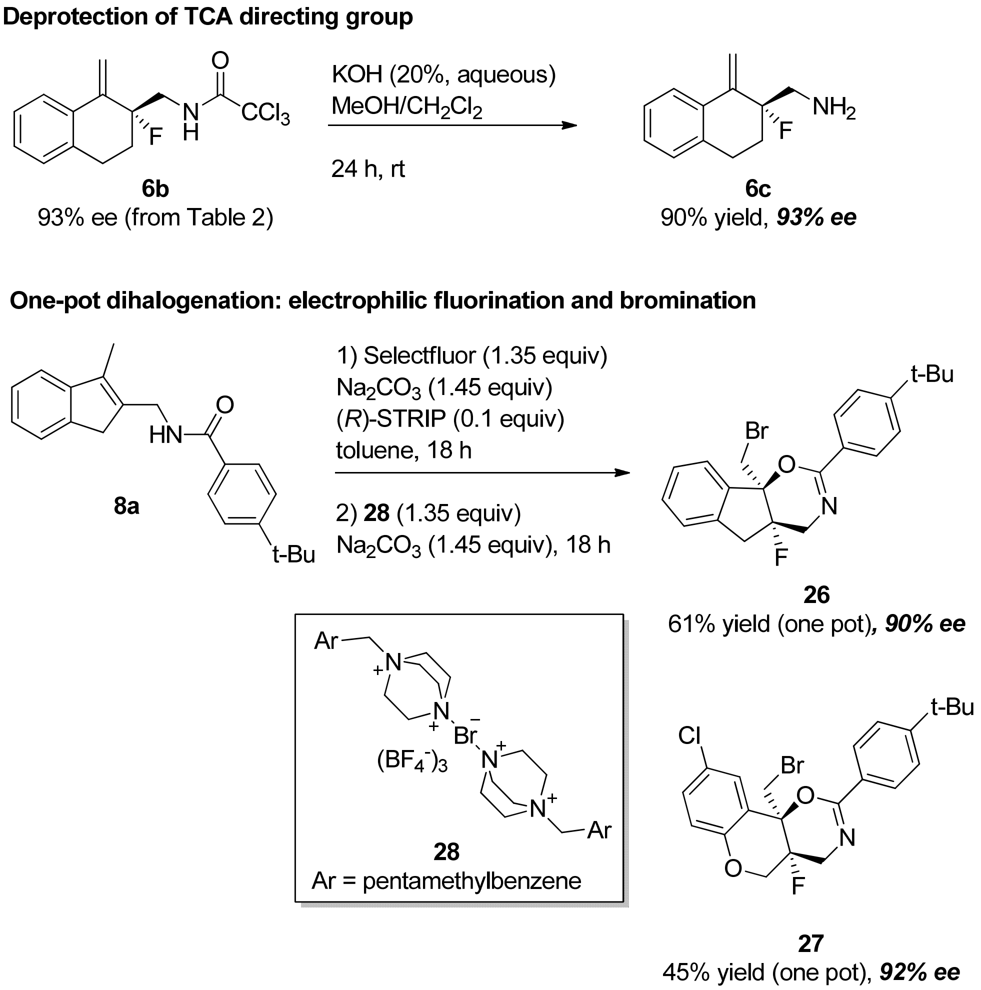


Figure 10. Reactions with enantioenriched allylic fluoride products.

Complex heterocyclic framework of **20** formed in good yield and high diastereo- and enantioselectivity, including two adjacent stereocenters and the incorporation of two different halogen atoms (Figure 10).

An enantioselective allylic fluorination has been achieved through the combination of DG and phase-transfer catalysis. The phosphoric acid catalyst acts both as a phase-transfer catalyst and a hydrogen-bonding catalyst, and allows the chiral electrophilic fluorine source to react with an unactivated alkene. The attractive hydrogen-bonding interaction requires a hydrogen-bond donor DG on the substrate, which we identified as either an amide or phenol. Various substrates were subjected to these reaction conditions with good results – tertiary, quaternary, cyclic and acyclic substrates were successful. Finally, the application of two electrophilic salts in two sequential reactions was achieved in one-pot to generate highly functionalized compounds in high diastereoselectivity and enantioselectivity.

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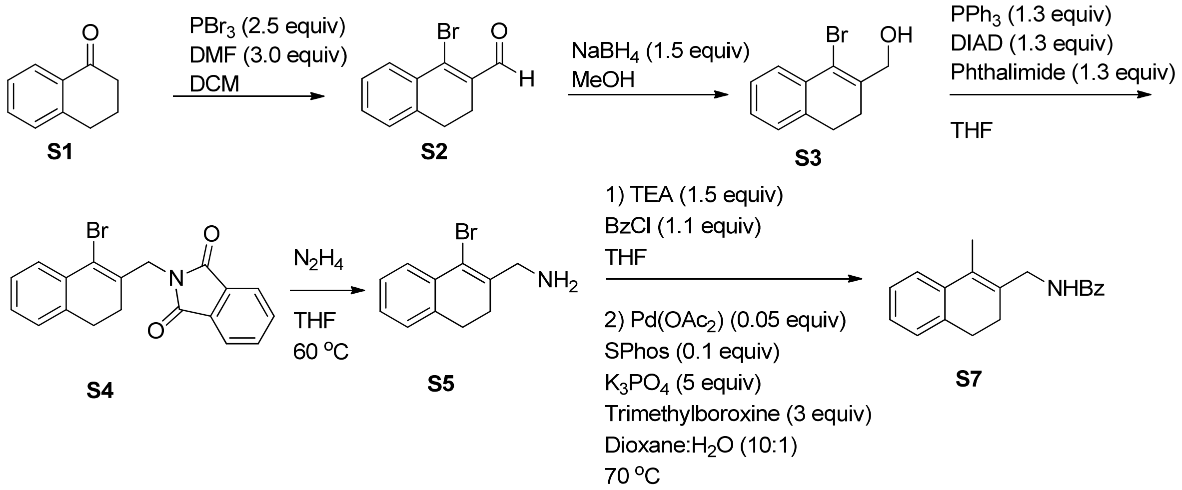
Representative synthesis of substrates



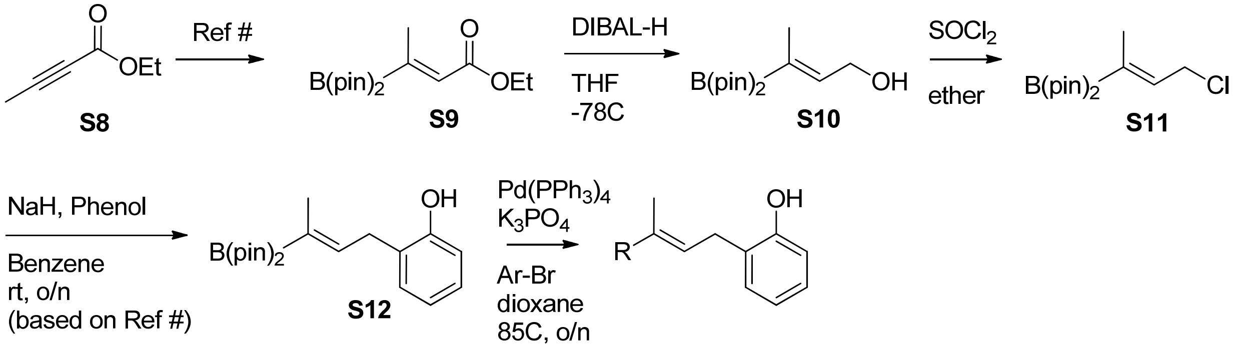
PBr_3 (8mL, 2.5 equiv) was added to DMF (7.8mL, 3.0 equiv) in DCM (150 mL) at 0 ^{o}C then warmed to room temperature for 1.5 h. Starting material tetralone (5g, 33.7mmol) was added as a solution in DCM (15mL), then the mixture was refluxed. The reaction was quenched with water at 0 ^{o}C followed by 20 min of stirring and extraction with DCM. The organic phase was washed with brine and dried with magnesium sulfate. $NaBH_4$ (0.19g, 1 equiv) was added to **S2** (4.94mmol) in MeOH (30mL) at 0 ^{o}C and stirred for one hour. The reaction was warmed up to room temperature and stirred another hour before evaporation of the solvent. The crude mixture was partitioned between methylene chloride and water, and the organic layer separated, dried with magnesium sulfate, and chromatographed (EtOAc: Hex; 3:1) to provide white solid **S3** (88% yield).

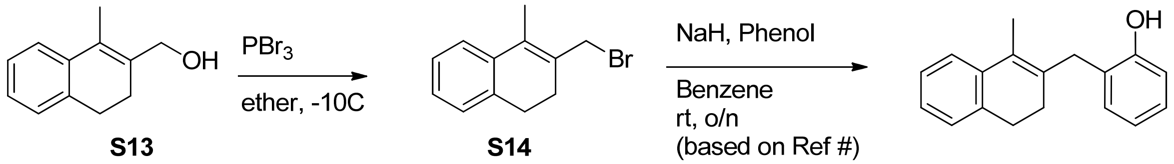
S3 was combined with PPh_3 (1.3 equiv) and phthalimide (1.3 equiv) in THF and cooled to 0 ^{o}C, followed by slow addition (over 30 min.) of DIAD (1.3 equiv). The reaction was warmed up to room temperature and stirred another 2 h, followed by direct silica-gel chromatography (EtOAc: Hex, 4:1) to provide solid S4 (57%).

Hydrazine hydrate (7 equiv) was added to **S4** in THF and heated to 60 ^{o}C for 16 h. The reaction mixture was diluted with methylene chloride and filtered with Celite. The organic layer was washed with water, then brine, and dried with magnesium sulfate to provide amine **S5** (95%).

Triethylamine and benzoyl chloride were added to **S5** in THF at 0 ^{o}C, and warmed up to room temperature immediately. The reaction was stirred for 8 h followed by filtration with Celite. The filtrate was partitioned between ethyl acetate and water, and the organic layer was separated, washed with brine, and dried with magnesium sulfate. Silica gel chromatography (EtOAc: Hex, 4:1) provided **S6** (85%).

$Pd(OAc)_2$ (0.05 equiv), SPhos (0.1 equiv), K_3PO_4 (5 equiv), and trimethylboroxine (3 equiv) were added to **S6** in dioxane:H_2O (10:1, 0.2M) at room temperature, then heated to 70 ^{o}C for 18 h. The reaction mixture was filtered with Celite, followed by extraction with ethyl acetate. The organic layer was washed with ammonium chloride (sat. aq.), followed by water, then brine, and then dried with magnesium sulfate. Chromatography (EtOAc: Hex, 4:1) provided **S7** (80%).





same procedures as above

S9 was prepared from **S8** by a precedented method. Dropwise DIBAL-H addition to a THF solution of **S9** at -78°C followed by stirring for 2 h, the reaction was warmed up to 0 °C and quenched with sodium sulfate decahydrate. Vigorous stirring followed by filtration with Celite provided **S10** as an oil. Purification was done with silica gel column chromatography (0-30% EtOAc in Hexanes); fractions visualized by iodine stain.

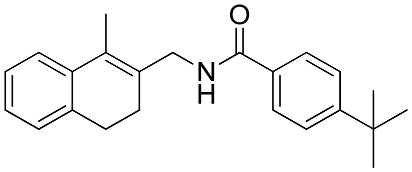
Thionyl chloride was added dropwise to **S10** in ether at 0 °C and the reaction was stirred for 3 h. The reaction was quenched with sodium bicarbonate (saturated aqueous solution) and extracted with ether. The organic layer was washed with brine, dried with magnesium sulfate and used without further purification.

Phenol and sodium hydride were combined at 0 °C in benzene as a slurry. After 15 minutes of stirring, allylic chloride **S11** was added as a solution in benzene. The reaction stirred at rt for 18 h followed by evaporation of solvent, followed by aqueous workup as described in reference X.

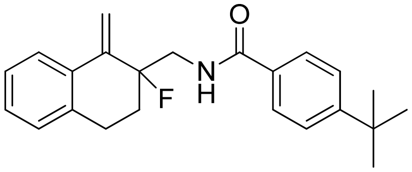
S12 was subjected to Pd(PPh$_3$)$_4$, K$_3$PO$_4$, and ArBr in dioxane under nitrogen at 85°C for 18 h, followed by filtration with Celite. Silica gel column chromatography (0-25% EtOAC in Hexanes) provided substrates.

SOCl$_2$ was added as a solution in DCM to S13 (which was prepared with procedures described on the previous page) in diethyl ether at 0 °C. The reaction was quenched after 3 h at room temperature, with sodium bicarbonate (saturated aqueous solution), then extracted with ether. The organic layer was washed with brine, dried with magnesium sulfate, concentrated and used without further purification.

S14b were prepared following the procedure used with intermediate S11.

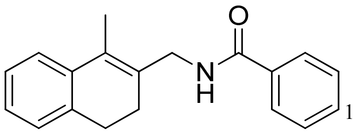


1a ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.73 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.34-7.14 (m, 4H), 6.06 (s, 1H), 4.35 (d, J = 5 Hz, 2H), 2.77 (t, J = 7.5 Hz, 2H), 2.37-2.34 (m, 2H), 2.18 (s, 3H), 1.35 (s, 9H).^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 167.7, 155.0, 136.4, 135.8, 131.9, 131.7, 129.2, 127.2, 126.9, 126.7, 126.5, 125.5, 123.3, 42.2, 35.0, 31.2, 28.5, 26.9, 14.3.
HRMS (ESI) Calcd. [M+H] C23H28ON: 334.2165; found: 334.2170.

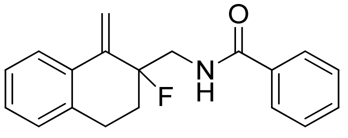


1b ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.75 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 7 Hz, 1H), 7.49 (d, J = 8.5 Hz, 2H), 7.28-7.21 (m, 2H), 7.16-7.15 (m, 1H), 6.47 (s, 1H), 5.75 (s,1H), 5.50 (s, 1H), 4.24-4.13 (m, 1H), 3.48-3.42 (m, 1H), 3.16-3.12 (m, 1H), 2.99-2.94 (m, 1H), 2.26-2.14 (m, 2H), 1.36 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 167.3, 155.2, 143.9, 143.8, 134.9, 132.5, 131.3, 128.9, 128.4, 128.0, 126.8, 126.5, 125.6, 125.1, 124.8, 109.0, 108.9, 97.4, 95.6, 44.8, 44.6, 34.92, 31.1, 30.4, 30.2, 27.0, 26.9. ^{19}F-NMR (376.4 MHz) δ (ppm) –161.0 - –161.2 (m).
HRMS (ESI) Calcd. for [M+H] C23H27ONF: 352.2071; found: 352.2074.
HPLC (ChiralPak IC column) 92:08 (hexane:*i*PrOH) 1mL/min; Tmajor (22.172 min), Tminor (25.260 min)

Catalysts **2-4** are either commercially available or previously reported.

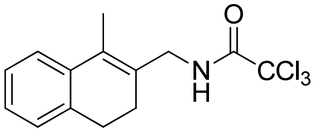


5a ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.79 (d, *J* = 7.0 Hz, 2H), 7.54-7.44 (m, 3H), 7.34-7.32 (m, 1H), 7.26-7.19 (m, 1H), 7.18-7.14 (m, 2H), 6.10 (brs, 1H), 4.36 (d, *J* = 5.5 Hz, 2H), 2.78 (t, *J* = 7.5 Hz, 2H), 2.37 (t, *J* = 7 Hz, 2H), 2.18 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 167.7, 136.3, 135.8, 134.6, 131.6, 131.5, 129.5, 128.7, 127.2, 126.9, 126.8, 126.5, 123.3, 42.4, 28.5, 27.0, 14.3.
HRMS (ESI) Calcd. for [M+H]C_{19}H20ON 278.1539, found: 278.1547.

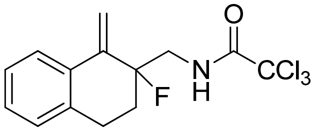


5b ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.81 (d, *J* = 7.5 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.56-7.53 (m, 1H), 7.49-7.46 (m, 2H), 7.26-7.21 (m,2H), 7.16-7.15 (m, 1H), 6.49 (brs, 1H), 5.75 (s, 1H), 5.51 (s, 1H), 4.23-4.13 (m, 1H), 3.50-3.43 (m, 1H), 3.19-3.12 (m, 1H), 2.99-2.96 (m, 1H), 2.27-2.12 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 167.5, 143.9 (d, *J*C–F = 16.3 Hz), 134.9, 134.3, 132.5, 131.7, 129.0, 128.7, 128.5, 128.1, 127.1 (d, *J*C–F = 19.0 Hz), 126.6, 124.9, 109.0 (d, *J*C–F = 11.3 Hz), 97.2, 95.8, 44.8 (d, *J*C–F = 25.0

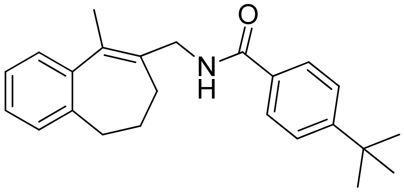
Hz), 30.4 (d, *J*C–F = 21.3 Hz), 27.0 (d, *J*C–F = 11.3 Hz).^{19}F-NMR (376.5 MHz) δ (ppm) –150.03 - -150.06 (m).
HRMS (ESI) Calcd. for [M+H] C_{19}H20ON 296.1445; found: 296.1452.
HPLC (ChiralPak IC column) 92:08(hexane:*i*PrOH) 1mL/min; Tmajor (18.224 min), Tminor (19.572 min)



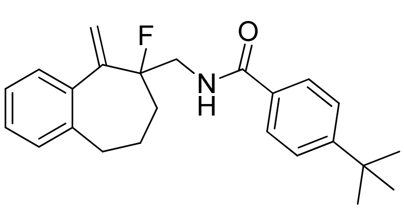
6a ^{1}H-NMR (500MHz, $CDCl_3$) δ (ppm) 7.34-7.24 (m, 2H), 7.21-7.15 (m, 2H), 6.67 (brs, 1H), 4.27 (d, *J* = 5.5 Hz, 2H), 2.79 (t, *J* = 7.5 Hz, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 162.1, 136.0, 135.7, 130.6, 129.7, 127.3, 127.1, 126.6, 123.5, 92.7, 43.8, 28.4, 26.8, 14.3.
Elemental analysis (CHN) est: 52.77% C, 4.43% H, 4.4% N; found: 52.49% C, 4.53% H, 4.51% N.



6b ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.64 (d, *J* = 7.6 Hz, 1H), 7.30-7.24 (m, 2H), 7.19-7.17 (m, 1H), 7.03 (brs, 1H), 5.78 (d, *J* = 3.2 Hz, 1H), 5.52 (s, 1H), 4.01-3.89 (m, 1H), 3.56-3.47 (m, 1H), 3.10-3.02 (m, 2H), 2.28-2.16 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 162.2, 143.2, 143.0, 134.5, 132.2, 132.2, 128.9, 128.6, 126.8, 125.0, 124.9, 109.6, 109.5, 96.7, 94.9, 92.5, 46.2, 46.0, 30.6, 30.4, 26.9, 26.8. ^{19}F-NMR (376.5 MHz) δ (ppm) – 150.59 (m). Elemental analysis (CHN) est: 49.95% C, 3.89% H, 4.16% N; found: 48.96% C, 4.11% H, 3.81% N.
HPLC (ChiralPak IC column) 98:02 (hexane/*i*PrOH) 1mL/min; Tmajor (9.50 min), Tminor (10.90 min).

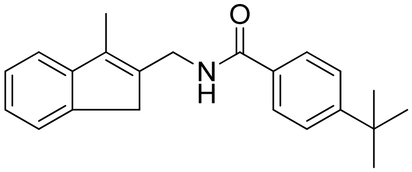


7a ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.73 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.28-7.24 (m, 2H, overlaps $CDCl_3$) 7.17 (d, *J* = 2.4 Hz, 2H), 6.11 (s, 1H), 4.33 (d, *J* = 5.3 Hz, 2H), 2.55 (t, *J* = 7.1 Hz, 2H), 2.17 (s, 3H), 2.13 – 2.02 (m, 2H), 1.93 – 1.86 (m, 2H), 1.34 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 167, 155.0, 143.2, 140.0, 133.5, 132.6, 131.8, 128.5, 126.7, 126.7, 126.5, 126.1, 125.6, 42.2, 35.0, 34.6, 32.1, 31.2, 28.6, 18.3.
HRMS (ESI) Calcd. for [M+H] C24H30ON: 348.2322; found: 348.2330.

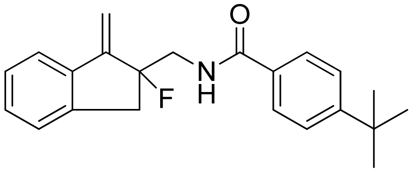


7b ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.93 (d, *J* = 8.0 Hz,

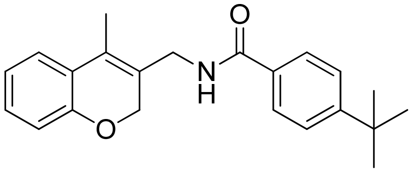
2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.22-7.09 (m, 4H), 6.29 (brs, 1H), 5.64 (s, 1H), 5.22-5.21 (m, 1H), 3.81-3.70 (m, 1H), 3.58-3.45 (m, 1H), 2.82-2.76 (m, 2H), 2.22-1.63 (overlapping multiplets, 4H), 1.35 (s, 9H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) 167.13, 155.11, 151.40, 151.21, 139.54, 139.54, 138.83, 138.78, 131.55, 129.28, 128.88, 128.34, 128.02, 126.76, 126.73, 125.60, 125.30, 114.71, 114.59, 99.07, 97.30, 45.098, 44.89, 38.70, 38.47, 34.96, 31.19, 23.60, 23.49.
^{19}F-NMR (376.5 MHz) δ (ppm) -147.2 (broad multiplet), -149.2 (m), -151.36-151.42 (m); possibly rotamers.
HRMS (ESI) Calcd. for [M+H] C24H29ONF: 366.2228; found: 366.2229.
HPLC (ChiralPak IB column) 95:05 (hexane: *i*PrOH) 1mL/min; Tmajor (9.540 min), Tminor (8.808 min).



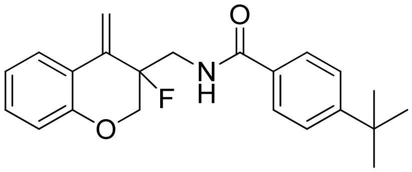
8a ^{1}H-NMR (300 MHz, CDCl$_3$) δ (ppm) 7.72-7.69 (m, 2H), 7.45-7.38 (m, 3H), 7.31-7.30 (m, 2H), 7.20-7.18 (m, 1H), 4.51 (d, *J* = 5.4 Hz, 2H), 3.42 (s, 2H), 2.17 (s, 3H),1.32 (s, 9H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) 167.3, 155.0, 146.4, 142.5, 137.3, 136.2, 131.5, 126.7, 126.3, 125.5, 124.8, 123.4, 118.9, 39.6, 37.5, 34.9, 31.1, 10.4.
HRMS (ESI) Calcd. For C22H26ON: 320.201; found: 320.2015.



8b ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 7.71 (d, *J* = 8.0 Hz, 2H), 7.53-7.46 (m, 3H), 7.27-7.24 (3H), 6.48 (brs, 1H), 5.78 (d, *J* = 4.0 Hz, 1H), 5.44 (s, 1H), 4.16-4.04 (m, 1H), 3.79-3.72 (m, 1H), 3.42-3.21 (m, 2H), 1.35 (s, 9H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) 167.6, 155.3, 149.2, 149.1, 140.7, 137.9, 137.8, 131.3, 129.7, 127.4, 126.9, 125.6, 125.5, 121.1, 107.7, 107.6, 102.7, 100.8, 46.1, 45.8, 40.8, 40.6, 35.0, 31.2. ^{19}F-NMR (376.4 MHz) δ (ppm) –144.78 - –144.81 (m).
HRMS (ESI) Calcd. for C22H25ONF: 338.1915; found: 352.1923.
HPLC (ChiralPak IC column) (90:10 hexane:*i*PrOH) 1mL/min; Tmajor (22.436 min), Tminor (20.620 min).



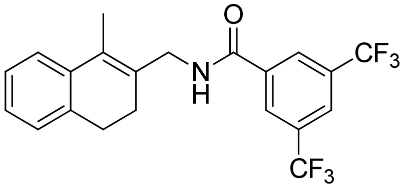
9a ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 7.72 (d, 8.4Hz, 2H), 7.45 (d, 8.4Hz, 2H), 7.27-7.13 (m, 2H), 6.97-6.93 (m, 1H), 6.83 (d, 7.6Hz, 1H), 6.18 (s, 1H), 4.71 (s, 2H), 4.25 (d, 5.6Hz, 2H), 2.11 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) 167.8, 155.2, 153.8, 131.2, 128.9, 127.4, 126.9, 125.6, 125.4, 124.7, 123.9, 121.4, 115.8, 67.0, 38.7, 35.0, 31.2, 12.9.
HRMS (ESI) Calcd. for [M+H] C22H26O2N: 336.1958; found: 336.1963.



9b ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 7.75 (d, *J* = 8.4 Hz, 2H), 7.62-7.60 (m, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.30-7.25 (m, 1H), 7.04-6.96 (m, 2H), 6.43 (brs, 1H), 5.811 (s, 1H), 5.50 (s, 1H), 4.37-4.33 (m, 1H), 4.24-4.12 (m, 2H), 3.82-3.72 (m, 1H), 1.38 (s, 9H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) 167.4, 155.3, 152.9, 138.6, 138.4, 131.2, 130.2, 126.9, 125.6, 124.7, 122.0, 119.3, 117.6, 107.4, 107.3, 68.1, 67.8, 43.4, 43.2, 35.0, 31.2. ^{19}F-NMR (376.4 MHz) δ (ppm) –166.28 - –166.40 (m).

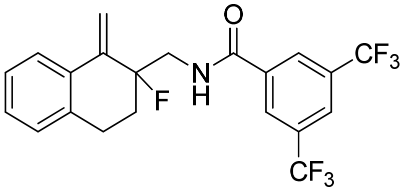
HRMS (ESI) Calcd. for [M+H] C22H25O2NF: 354.1864; found: 354.1874.

HPLC (ChiralPak IC column) 90:10 (hexane/*i*PrOH) 1mL/min; Tmajor (28.140 min), Tminor (31.536 min)



10a ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 8.24 (s, 2H), 8.032 (s, 1H), 7.66 -7.64 (m, 1H), 7.25-7.20 (m, 1H), 7.13-7.11 (m, 1H), 6.51 (brs, 1H), 4.56-4.55 (m, 2H), 2.86 (t, *J* = 8.0 Hz, 2H), 2.57 (ts, *J* = 8.0 Hz, 2H), 1.57 (s, 3H).

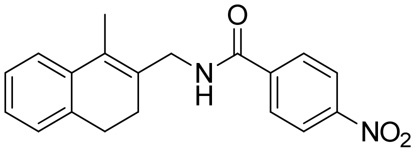
^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) 164.8, 136.5, 136.0, 135.7, 132.7, 132.4, 132.1, 131.8, 130.5, 130.2, 127.3, 127.0, 126.6, 125.1, 125.1, 125.0, 125.0, 124.0, 123.4, 121.8, 42.8, 28.4, 27.1, 14.4. HRMS (ESI) Calcd. For C21H18ONF$_6$: 414.1287, found: 414.1303.



10b ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 8.23 (s, 2H), 8.04 (s, 1H), 7.63-7.61 (m, 1H), 7.26-7.15 (m, 4H), 6.58 (brs, 1H), 5.76 (s, 1H), 5.50 (s, 1H), 4.21 - 4.08 (m, 1H), 3.59-3.51 (m, 1H), 3.13-2.89 (m, 2H), 2.23-2.21 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) 164.6, 143.7, 143.5, 136.3, 134.6, 132.5, 132.3, 132.2, 129.0, 128.6, 127.4, 126.7, 125.3, 124.9, 109.3, 109.2, 96.93, 95.50, 45.2, 45.0, 30.6, 30.4, 26.9, 26.85. ^{19}F-NMR (376.5 MHz) δ (ppm) –62.1 (s), -150.0 (m).

HRMS (ESI) Calcd. for [M+H] C21H17ONF$_7$: 432.119; found: 432.121.

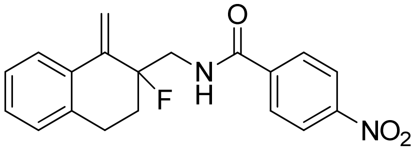
HPLC (ChiralPak IB column) 99:01 (hexane/*i*PrOH) 1mL/min; Tmajor (21.40 min), Tminor (24.99min).



11a ^{1}H-NMR (500 MHz, CDCl$_3$) δ (ppm) 8.33-8.29 (m, 2H), 8.00-7.94 (m, 2H), 7.34-7.28 (m, 1H), 7.26-7.14 (m, 3H), 6.23 (brs, 1H), 4.38-4.37 (m, 2H), 2.87 (t, *J* = 8.0 Hz, 2H), 2.38-2.35 (m, 2H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 165.7,

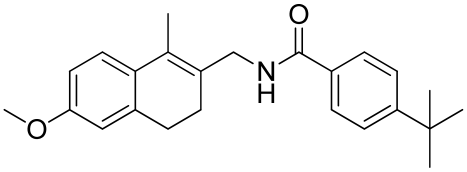
149.6, 140.1, 136.1, 135.7, 130.7, 130.0, 128.2, 127.3, 127.0, 126.6, 123.8, 123.4; 42.7, 28.4, 27.1, 14.3.
HRMS (ESI) Calcd. for [M+H] C19H19O3N2: 323.139; found: 323.1402.

11b



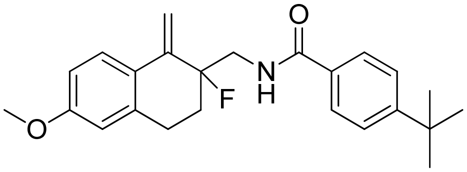
^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 8.32 (d, *J* = 8.8 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.62-7.60 (m, 1H), 7.25-7.15 (m, 4H), 6.50 (brs, 1H), 5.74 (m, 1H), 5.49 (s, 1H), 4.19-4.07 (m, 1H), 3.58-3.48 (m, 1H), 3.19-2.97 (m, 2H), 2.23-2.16 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) 165.5, 149.7, 143.6 (d, *J*C–F = 16.3 Hz), 139.8, 134.6, 132.3 (d, *J*C–F = 16.3 Hz), 128.97-128.61, 128.2, 126.7, 124.9, 124.0, 109.2 (11.3), 96.9, 95.5, 45.1, 44.9, 30.7, 30.5, 27.0, 26.9. ^{19}F-NMR (376.5 MHz) δ (ppm) –150.31 (m).
HRMS (ESI) Calcd. for [M+H] C19H18O3N2F: 341.1296; found: 341.1307.
HPLC (ChiralPak IA column) 90:10 (hexane/*i*PrOH) 1mL/min; Tmajor (15.868 min), Tminor (18.700 min).

12a

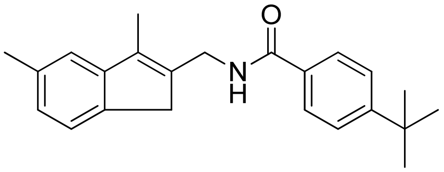


^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 7.74 (d, *J* = 8 Hz, 2H), 7.44-7.42 (m, 2H), 7.27 -7.21 (m, 1H), 6.75-6.70 (m, 2H), 6.33 (brs, 1H), 4.41-4.29 (m, 2H), 3.93 (s, 3H), 2.74-2.7 (t, *J* = 8 Hz, 2H), 2.33-2.31 (m, 2H), 2.12 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) 167.6, 158.3, 154.8, 137.6, 131.7, 129.4, 129.3, 128.8, 126.8, 125.4, 124.5, 113.3, 111.0, 55.2, 42.2, 34.9, 31.1, 28.9, 26.8, 14.2.
HRMS (ESI) Calcd. For C24H30O2N: 364.227, found: 364.228.

12b

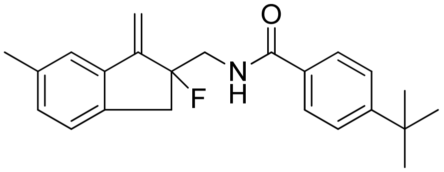


^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 7.77 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.52-7.50 (m, 2H), 6.83-6.81 (m, 1H), 6.67 (s, 1H), 6.48-6.47 (m, 1H), 5.63-5.62 (m, 1H), 5.40 (s, 1H), 4.27-4.14 (m, 1H), 3.84 (s, 3H), 3.50-3.41 (m, 1H), 3.21-3.14 (m, 1H), 2.96-2.92 (m,1H), 2.27-2.13 (m, 2H), 1.39 (s, 9H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) 167.4, 159.7, 155.3, 143.5, 136.4, 131.4, 126.8, 126.3, 125.6, 125.4, 113.6, 112.7, 106.7, 106.6, 55.3, 44.8, 44.6, 35.0, 31.2, 30.3, 30.2, 27.3, 27.2. ^{19}F-NMR (376.5 MHz) δ (ppm) – 150.3 (m).
HRMS (ESI) Calcd. for [M+H] C24H29O2NF: 383.2177; found: 382.2187.
HPLC (ChiralPak IC column) 96:04 (hexane/*i*PrOH) 1mL/min; Tmajor (60.28 min), Tminor (64.92 min).



13a ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 7.72 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.27 (s, 1H), 7.13 (s, 1H), 7.02-7.01 (m, 1H), 6.26 (brs, 1H), 4.51 (d, *J* = 5.6 Hz, 2H), 3.38 (s, 2H), 2.42 (s, 3H), 2.15 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) 167.3, 155.0, 146.6, 139.5, 137.5, 136.2, 135.9, 131.5, 126.7, 125.6, 125.5, 123.1, 119.7, 39.18, 37.6, 34.9, 31.1, 21.5, 10.4.

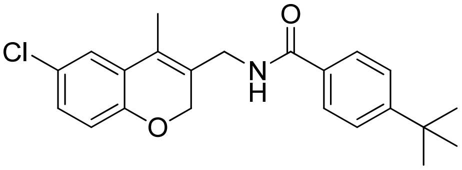
HRMS (ESI) Calcd. For C23H28ON: 334.2165, found: 334.2176.



13b ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 7.72 (d, *J* = 8.0 Hz, 2H), 7.47 (*J* = 8.0 Hz, 2H), 7.33 (s, 1H), 7.11 (s, 2H), 5.75 (d, *J* = 4 Hz, 1H), 5.40 (d, *J* = 4 Hz, 1H), 4.14-4.02 (m, 1H), 3.77-3.7- (m, 1H), 3.36-3.16 (m, 2H), 2.37 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) 167.5, 155.2, 149.2, 149.0, 137.8, 137.7, 137.1, 131.3, 130.7, 126.8, 125.6, 125.1, 121.5, 107.2, 107.1, 102.9, 46.0, 45.8, 40.4, 40.2, 34.9, 31.1, 21.3. ^{19}F-NMR (376.5 MHz) δ (ppm) -144.83 - -145.01(m).

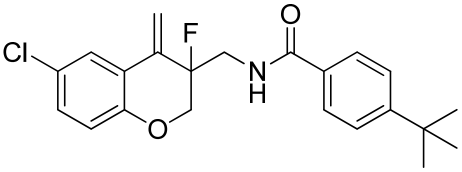
HRMS (ESI) Calcd. for [M+H] C23H27ONF:352.2071; found: 352.2084.

HPLC (ChiralPak IC column) 96:04 (hexane/*i*PrOH) 1mL/min; Tmajor (33.86 min), Tminor (37.06 min).



14a ^{1}H-NMR (300 MHz, CDCl$_3$) δ (ppm) 7.70 (d, *J* = 6.0 Hz, 2H), 7.43 (d, *J* = 8.1 Hz), 7.14 (s, 1H), 7.08-7.05 (m, 1H), 6.75-6.72 (m, 1H), 6.21 (brs, 1H), 4.68 (s, 2H), 4.23 (d, *J* = 5.7 Hz), 2H), 2.06 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm) 168.0, 155.6, 152.6, 131.3, 128.7, 127.1, 127.0, 126.8, 126.5, 126.4, 125.9, 124.1, 117.3, 67.4, 38.9, 35.2, 31.4, 13.1.

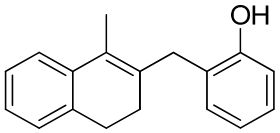
HRMS (ESI) Calcd. For [M+H]C22H24O2NCl: 370.1587; found: 370.1580.

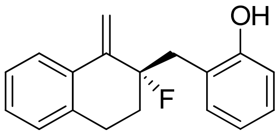


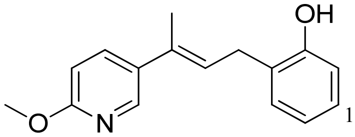
14b ^{1}H-NMR (300 MHz, CDCl$_3$) δ (ppm) 7.71 (d, *J* = 9Hz, 2H), 7.51-7.44 (m, 3H), 7.18-7.14 (m, 1H), 6.38 (brs, 1H), 5.75 (s, 1H), 5.48 (s, 1H), 4.31-25 (m, 1H), 4.19-4.03 (m, 2H), 3.77-3.64 (m, 1H), 1.33 (s, 9H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) 167.38, 155.45, 151.53, 137.58, 137.4, 131.1, 130.1, 127.2, 126.9, 125.6, 124.3, 120.8, 119.1, 108.8, 108.66, 68.13, 67.82, 43.2, 43.0, 35.0, 31.2. ^{19}F-NMR (376.5 MHz) δ (ppm) –166.27 - –166.39 (m).

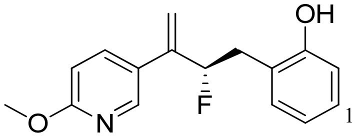
HRMS (ESI) Calcd. for [M+H] C22H24O2NClF: 388.1493; found: 388.1488.

HPLC (ChiralPak IC column) 90:10 (hexane/*i*PrOH) 1mL/min; Tmajor (20.832 min), Tminor (23.336 min).

15a  ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.41-7.40 (m, 1H), 7.32-7.29 (m, 1H), 7.27-7.15 (m, 4H), 6.95-6.93 (m, 1H), 6.88-6.83 (m, 1H), 5.31 (s, 1H), 3.73 (s, 2H), 2.81 (t, *J* = 7.6 Hz, 2H), 2.26-2.23 (t and s overlap, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.4, 136.7, 135.8, 133.8, 130.2, 127.9, 127.6, 127.2, 126.5, 126.3, 125.6, 123.1, 120.9, 116.0, 115.5, 34.4, 28.6, 28.1, 14.5.
HRMS (ESI) Calcd. for [M] C18H18O: 250.1352; found: 250.1351.

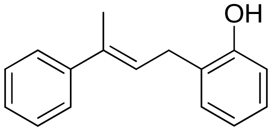
15b  ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.63-7.61 (m, 1H), 7.29-7.13 (m, 4H), 6.97-6.94 (m, 2H), 6.87-6.84 (m, 1H), 5.93 (d, *J* = 21 Hz, 1H), 5.62 (d, *J* = 4.0 Hz, 1H), 5.35 (s, 1H), 3.23-2.99 (m, 4H), 2.22-2.11 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 155.0, 144.9, 144.8, 134.5, 133.1, 133.1, 132.6, 128.8, 128.77, 128.3, 125.13, 125.11, 121.9, 120.6, 117.0, 108.9, 108.8, 100.2, 98.8, 39.0, 38.8, 32.2, 32.0, 27.0, 26.9. ^{19}F-NMR (376.5 MHz) δ (ppm) –137.1 - –137.3 (m).
HRMS (ESI) Calcd. for [M] C18H16OF: 267.1191; found: 267.1192.
HPLC (ChiralPak IC column) 98:02 (hexane/*i*PrOH) 1mL/min; Tmajor (7.72 min), Tminor (8.80 min).

16a  ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.22 (s, 1H), 7.66 (d, J = 2.5 Hz, 1H), 7.19-7.11 (m, 2H), 6.90-6.81 (m, 2H), 6.71 (d, J = 8.5 Hz, 1H), 5.93 (t, J = 3.5 Hz, 1H), 5.60 (s, 1H), 3.93 (s, 3H), 3.57 (d, J = 7.5 Hz, 2H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.1, 153.9, 143.6, 135.3, 133.0, 132.2, 130.0, 127.5, 126.7, 125.4, 120.8, 115.4, 110.1, 53.5, 29.6, 15.7.
HRMS (ESI) Calcd. for [M+H] C16H18O2N: 256.1332; found: 256.1325.

16b  ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 8.26 (s, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.14-7.04 (m, 2H), 6.87-6.75 (m, 3H), 5.79 (s, 1H), 5.73-5.58 (m, 1H), 5.40 (s, 2H), 3.96 (s, 3H), 3.16-2.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.8, 154.1, 144.8, 143.7, 143.5, 137.4, 131.7, 128.3, 127.2, 123.2, 120.7, 115.6, 114.7, 114.6, 110.6, 95.0, 93.3, 53.6, 36.4, 36.2.
^{19}F-NMR (376.5 MHz) δ (ppm) –174.3 - –174.6 (m).
HRMS (ESI) Calcd. for [M+H] C16H17O2NF: 274.1230; found: 274.1238.
HPLC (ChiralPak IC) 98:02 (hexane/*i*PrOH) 1mL/min; Tmajor (9.228 min), Tminor (10.452

min)

17a

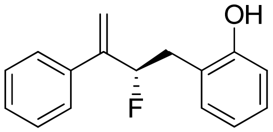


^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 7.43-7.10 (m, 7H), 6.90 (t, J = 9.8 Hz, 1H), 6.80 (d, J = 10.4 Hz, 1H), 5.96(t, J = 8.4 Hz, 1H), 3.57 (d, J = 9.6 Hz, 2H), 2.19 (s, 3H);

^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 154.0, 143.4, 136.9, 130.1, 128.3, 127.6, 127.0, 126.8, 125.8, 125.5, 121.0, 115.6, 29.9, 16.1.

HRMS (EI) Calcd. for [M] C16H16O: 224.1201; found: 224.1204.

17b

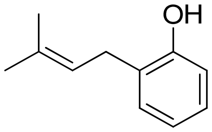


^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 7.45-7.35 (m, 5H), 7.15 (t, J = 7.8 Hz, 1H), 7.03 (d, J = 7.2 Hz, 1H), 6.89-6.82 (m, 2H), 5.77-5.66 (m, 1H), 5.44 (d, J = 12 Hz, 2H), 5.21 (d, J = 8 Hz, 1H), 3.15-2.93 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 154.1, 146.7, 146.5, 138.2, 131.7, 128.5, 128.3, 128.1, 126.8, 123.4, 120.8, 115.9, 114.6, 114.5, 95.6 93.9, 36.4, 36.2, 29.7. ^{19}F-NMR (376.5 MHz) δ (ppm) –173.9 - –174.2 (m).

HRMS (EI) Calcd. for [M] C16H15OF: 242.1107; found: 242.1110.

HPLC (ChiralPak IC) 94:06 (hexane/*i*PrOH) 1mL/min; Tmajor (4.384 min), Tminor (4.612 min).

18a

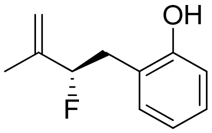


^{1}H-NMR (500 MHz, CDCl$_3$) δ (ppm) 7.15-7.12 (m, 2H), 6.84-6.82 (m, 1H), 6.76 (d, J = 8 Hz, 1H), 5.37-5.34 (m, 1H), 5.16 (s, 1H), 3.39 (d, J = 7 Hz, 2H), 1.81-1.80 (m, 6H).

^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 154.2, 134.5, 130.1, 127.6, 127.3, 122.1, 120.9, 115.8, 29.6, 25.9, 17.9.

HRMS (EI) Calcd. for [M] C11H14O: 162.1045; found: 162.1048.

18b

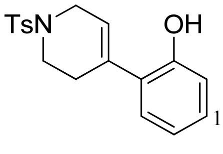


^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 7.17-7.13 (m, 2H), 6.91-6.82 (m, 2H), 5.32 (d, J = 8.4 Hz, 1H), 5.2 (m, 1H), 4.99 (d, J = 21.6 Hz, 2H), 3.09-2.96 (m, 2H), 2.19 (s, 1H), 1.83 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 154.1, 142.8, 142.7, 131.5, 128.3, 123.6, 120.9, 116.0, 113.1, 113.0, 97.5, 95.8, 35.6, 35.4, 17.5, 17.5. ^{19}F-NMR (376.5 MHz) δ (ppm) –173.2 - –173.5 (m).

HRMS (EI) Calcd. for [M] C11H13OF: 180.0950; found: 180.0949.

HPLC (ChiralPak IC) 99:01 (hexane/*i*PrOH) 1mL/min; Tmajor (19.892 min), Tminor (24.844 min).

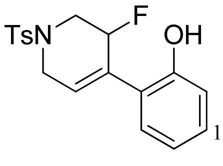
19a



^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.77 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.19 (t, *J* = 6.4 Hz, 1H), 7.04-7.02 (m, 1H), 6.93-6.89 (m, 2H), 5.83 (s, 1H), 5.19 (s, 1H), 3.82-3.81 (m, 2H), 3.40 (t, *J* = 5.6 Hz, 2H), 2.58 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 152.2, 143.9, 134.0, 133.1, 129.8, 128.9, 128.3, 127.8, 122.5, 121.1, 120.6, 115.8, 115.5, 45.0, 43.2, 29.4, 21.6.

HRMS (ESI) Calcd. for [M-1] C18H18O3NS: 328.1013; found: 328.1009.

19b



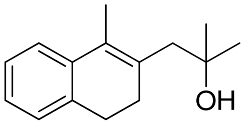
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.77 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.26-7.21 (m, 1H), 7.11-7.09 (m, 1H), 6.95-6.88 (m, 2H), 6.15-6.14 (m, 1H), 5.46-5.34 (m/brs overlap, 2H), 4.16-4.08 (m, 1H), 3.99-3.92 (m, 1H), 3.66-3.53 (m, 1H), 3.31-3.21 (m, 1H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.1, 144.2, 133.2, 132.7, 132.5, 129.9, 129.8, 129.7, 129.6, 129.56, 127.8, 125.0, 120.8, 116.1, 85.85, 84.14, 65.9, 47.7, 47.4, 44.9, 21.6.

^{19}F-NMR (376.5 MHz) δ (ppm) –168.97 (m)

HRMS (ESI) Calcd. for [M-1] C18H17O3NSF: 346.0919; found: 346.0913.

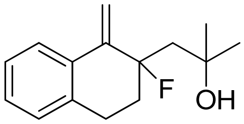
HPLC (ChiralPak IA) 80:20 (hexane/*i*PrOH) 1mL/min; Tmajor (12.38 min), Tminor (14.87 min).

20a



^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.33-7.22 (m, 2H), 7.16-7.14 (m, 2H), 2.76-2.73 (m, 2H), 2.56 (s, 2H), 2.35 (brm, 2H), 2.11-2.107 (m, 3H), 1.33 (s, 6H).

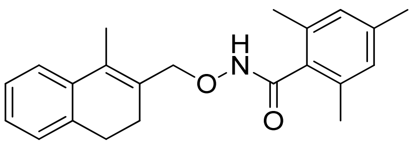
20b



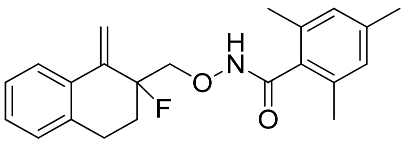
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 7.54-7.52 (m, 1H), 7.24-7.19 (m, 2H), 7.13-7.11 (m, 1H), 5.54 (d, *J* = 4.4 Hz, 1H), 5.47 (s, 1H), 3.03-3.00 (m, 2H), 2.38-2.31 (m, 1H), 2.18-2.10 (m, 1H), 2.02 (s, 2H), 1.28-1.25 (m, 6H). ^{19}F-NMR (376.5 MHz) δ (ppm) –147.57 (s).

HPLC (ChiralPak IA column) 96:04 (hexane/*i*PrOH) 1mL/min; Tmajor (7.22 min), Tminor (8.77 min).

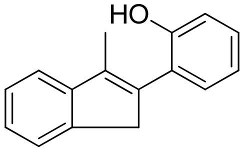
21a

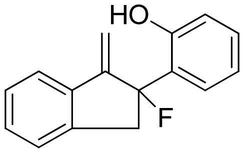


^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.37 (s, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.36-7.23 (m, 4H), 6.81 (s, 2H), 5.00 (s, 2H), 3.55 (s, 2H), 2.25 (s, 6H), 2.20 (s, 3H).

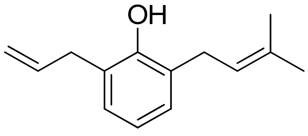
21b  ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 8.60 (s, 1H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.34-7.30 (m, 4H), 6.89 (brs, 2H), 5.82-5.81 (m, 1H), 5.47-5.46 (m, 1H), 4.44-4.23 (m, 2H), 3.75-3.70 (m, 1H), 3.42-3.31 (m, 1H), 2.36 (s, 6H), 2.32 (s, 3H). ^{19}F-NMR (376.5 MHz) δ (ppm) –168.45 - -168.53 (m).

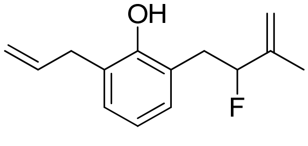
HPLC (ChiralPak OD column) 96:04 (hexane/*i*PrOH) 0.5mL/min; Tmajor (44.7min), Tminor (40.5 min).

22a  ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 7.40-7.37 (m, 1H), 7.30-7.20 (m, 4H), 7.11-7.10 (m, 1H), 7.00-6.93 (m, 2H), 5.14 (s, 1H), 2.96-2.91 (m, 2H), 2.59-2.46 (m, 2H), 1.98 (s, 3H).

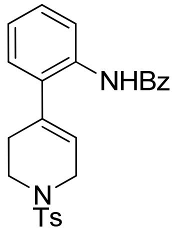
22b  ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 7.72-7.70 (m, 1H), 7.59-7.55 (m, 2H), 7.45-7.19 (m, 5H), 5.85-5.84 (m, 1H), 5.11-5.10 (m, 1H), 4.71-4.67 (m, s overlap, 3H total), 3.19-3.11 (m, 1H), 2.96-2.90 (m, 1H), 2.77-2.72 (m, 1H). ^{19}F-NMR (376.5 MHz) δ (ppm) –134.9-135.0 (m).

HPLC (ChiralPak IB column) 90:10 (hexane/*i*PrOH) 1mL/min; Tmajor (6.78 min), Tminor (6.28 min).

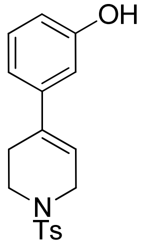
23a  ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 7.02-7.00 (m, 2H), 6.85-6.81 (m, 1H), 6.07-6.02 (m, 1H), 5.33-5.30 (m, 2H), 5.18-5.13 (m, 2H), 3.42-3.36 (m, 4H), 1.79 (s, 6H).

23b  ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 7.06-7.03 (m, 2H), 6.87-6.83 (m, 1H), 6.08-5.98 (m, 1H), 5.44-5.42 (m, 1H), 5.20-5.17 (m, 3H), 5.02 (s, 1H), 4.95 (s, 1H), 3.44 (d, *J* = 7.6 Hz, 2H), 3.07-2.96 (m, 2H), 1.83 (s, 3H). ^{19}F-NMR (376.5 MHz) δ (ppm) –173.62-173.86 (m).

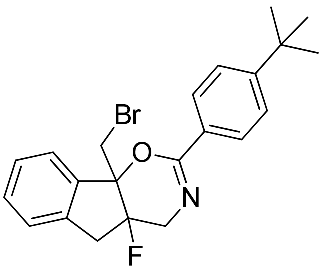
HPLC (ChiralPak IA column) 99:01 (hexane/*i*PrOH) 1mL/min; Tmajor (8.66 min), Tminor (9.02 min).



24 ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 8.33 (d, *J* = 8.4 Hz, 1H), 8.19 (s, 1H), 7.82-7.80 (m, 2H), 7.72-7.70 (m, 2H), 7.59-49 (m, 3H), 7.35-7.31 (m, 3H), 7.14-7.04 (m, 2H), 5.80 (s, 1H), 3.77 (d, *J* = 3.2 Hz, 2H), 3.34 (t, *J* = 5.6 Hz, 2H), 2.52 (brs, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 165.1, 143.9, 134.9, 134.6, 134.4, 133.1, 132.4, 132.0, 129.8, 129.0, 128.5, 128.0, 127.7, 126.9, 124.4, 123.8, 121.6, 45.0, 43.1, 30.2, 24.8, 21.5.



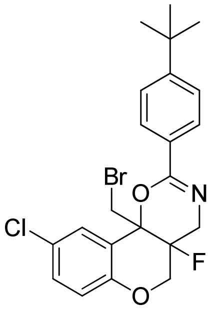
25 ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 7.72 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.88-6.86 (m, 1H), 6.79 (s, 1H), 6.78-6.72 (m, 1H), 5.96 (brs, 1H), 5.01 (s, 1H), 3.76-3.74 (m, 2H), 3.32-3.29 (m, 2H), 2.60-2.57 (m, 2H), 2.44 (s, 3H).



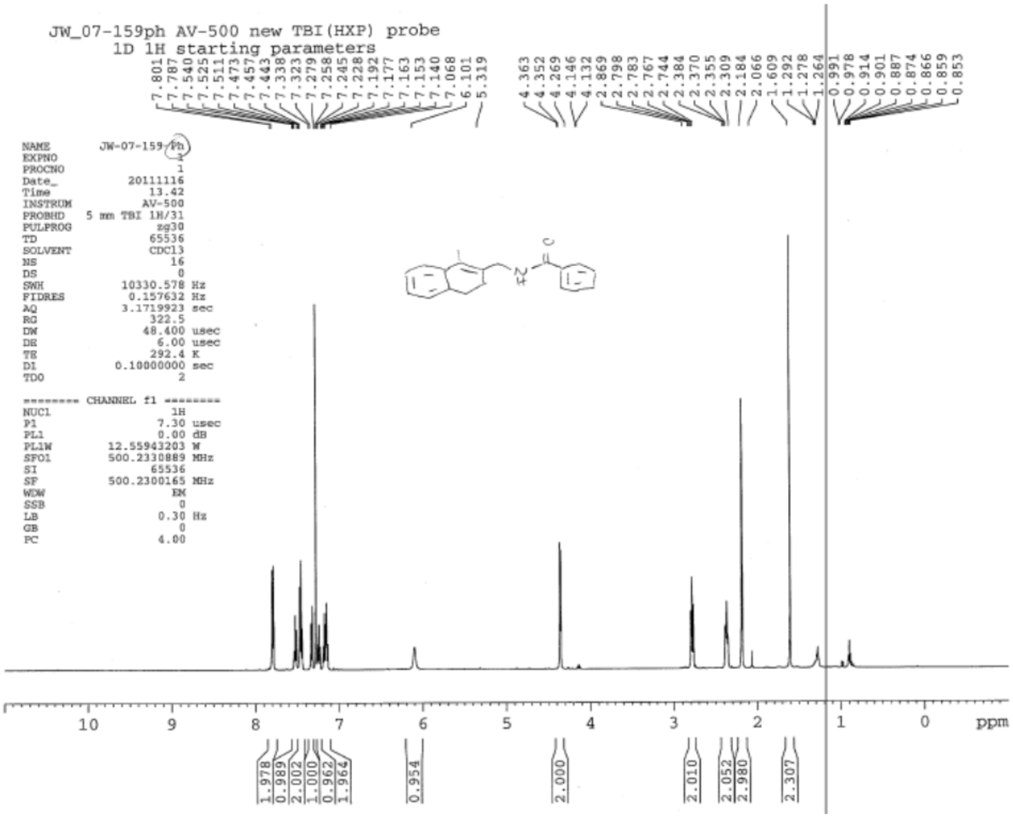
26 ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 8.02 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.47-7.45 (m, 2H), 7.41-7.32 (m, 2H), 7.29 (s, 1H), 4.12 (t, *J* = 16 Hz, 1H), 4.00-3.83 (m, 2H), 3.60-3.46 (m, 2H), 3.28-3.22 (m, 1H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 156.4, 154.5, 141.1, 137.1, 137.06, 130.3, 129.7, 127.6, 127.3, 125.5, 125.4, 125.2, 94.49, 85.25, 85.05, 49.97, 49.71, 40.94, 40.70, 35.19, 35.08, 34.85, 31.16, 30.97. ^{19}F-NMR (376.5 MHz) δ (ppm) –168.45 - -168.53 (m).

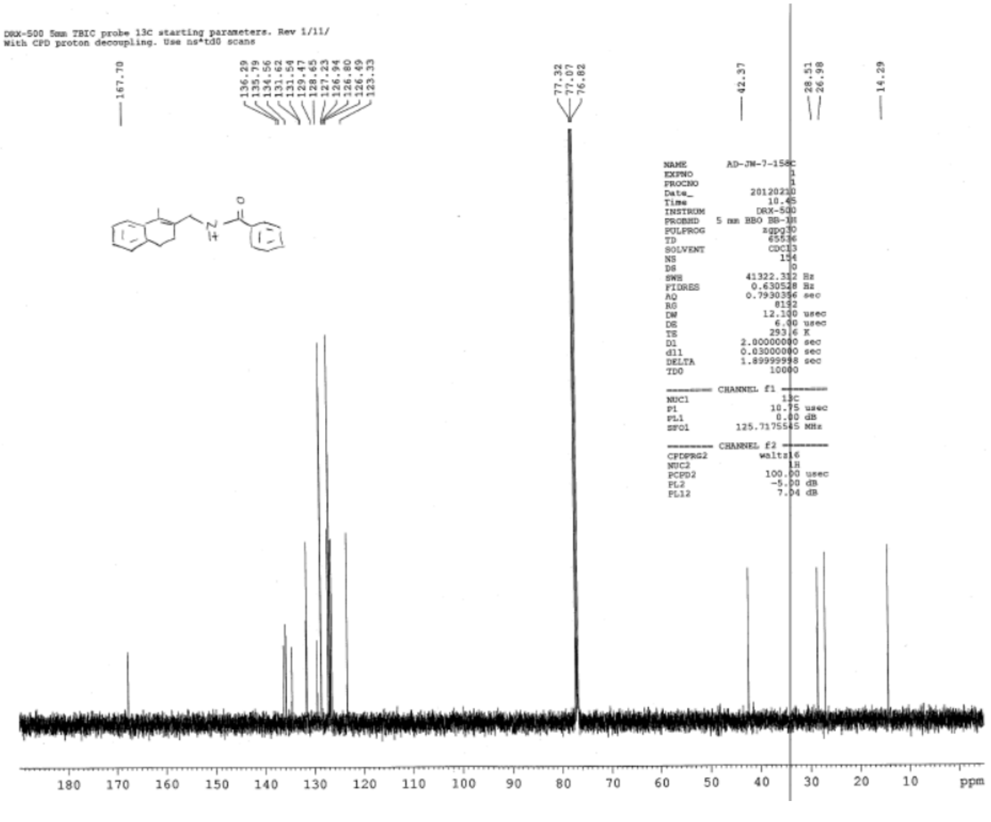
HRMS (ESI) Calcd. for [M+H] C22H24ONFBr: 416.1013; found: 416.1020.

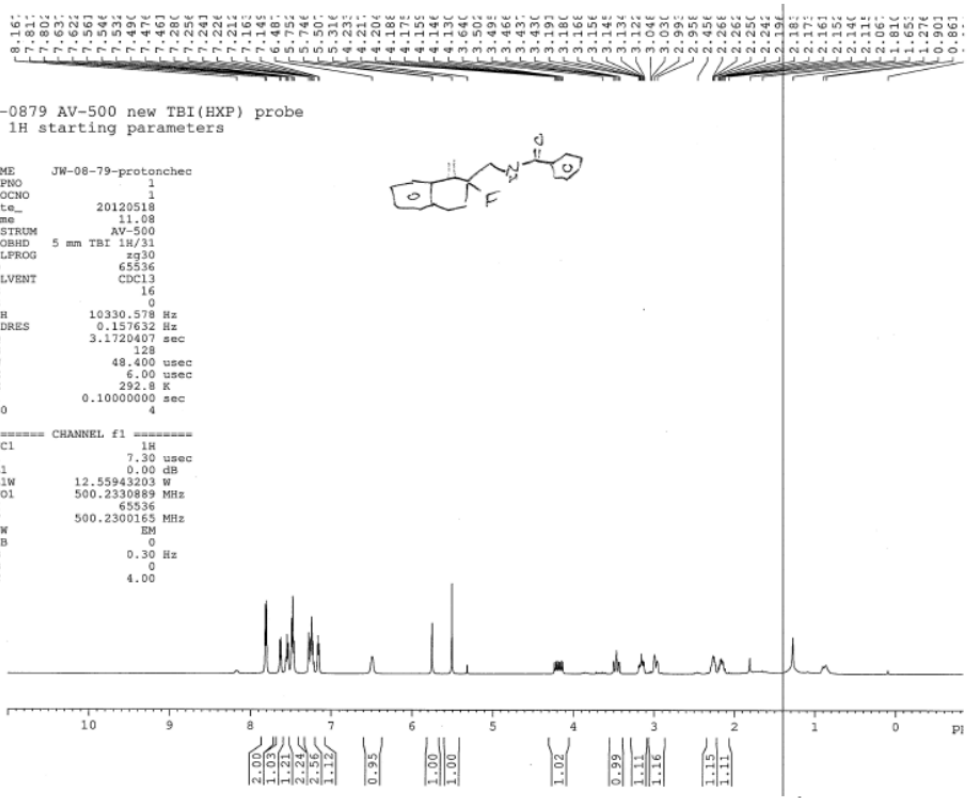
HPLC (ChiralPak IB column) 99:01 (hexane/*i*PrOH) 1mL/min; Tmajor (11.26 min), Tminor (9.252 min).

27 

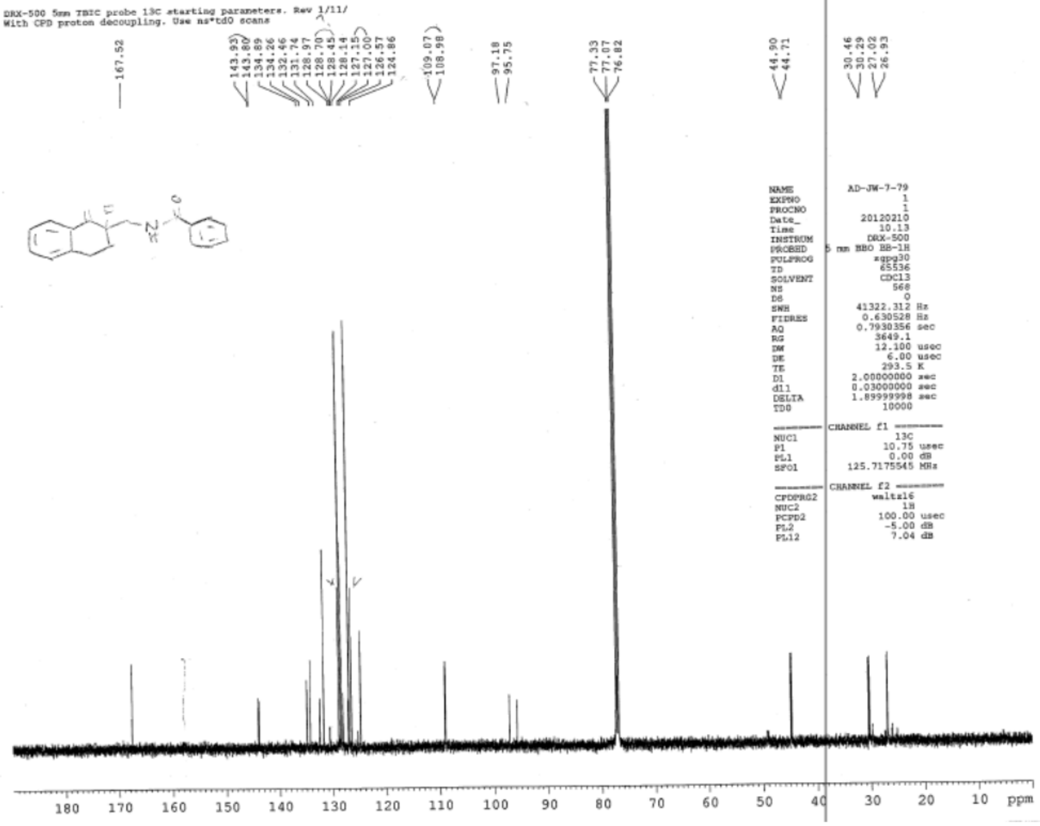
^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm) 8.02(d, *J* = 8.0 Hz, 2H), 7.53-7.48 (m, 3H), 7.26-7.25 (m, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 4.63-4.58 (m, 1H), 4.27-4.25 (m, 1H), 4.21-4.10 (m, 1H), 3.95-3.70 (m, 3H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 154.9, 153.0, 150.5, 131.2, 129.5, 127.5, 127.2, 126.7, 125.5, 123.4, 118.5, 85.8, 84.6, 48.7, 48.6, 36.0, 35.9, 35.1, 31.3. ^{19}F-NMR (376.5 MHz) δ (ppm) –175.20- -175.33 (m).
HRMS (ESI) Calcd. for [M+H] C22H24O2NFBrCl: 466.0575; found: 466.0579.
HPLC (ChiralPak IC column) 98:02 (hexane/*i*PrOH) 1mL/min; Tmajor (6.28 min), Tminor (5.66 min).


JW_07-159ph AV-500 new TBI(HXP) probe
1D 1H starting parameters
7.801 7.787 7.540 7.525 7.511 7.473 7.457 7.443 7.338 7.323 7.279 7.258 7.245 7.228 7.192 7.177 7.163 7.153 7.140 7.068 6.101 5.319
4.363 4.352 4.269 4.146 4.132 2.869 2.798 2.783 2.767 2.744 2.384 2.370 2.355 2.309 2.184 2.066 1.609 1.292 1.278 1.264 0.991 0.978 0.914 0.901 0.887 0.874 0.866 0.859 0.853
NAME JW-07-159-Ph
EXPNO 1
PROCNO 1
Date_ 20111116
Time 13.42
INSTRUM AV-500
PROBHD 5 mm TBI 1H/31
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 322.5
DW 48.400 usec
DE 6.00 usec
TE 292.4 K
D1 0.10000000 sec
TD0 2
======== CHANNEL f1 ========
NUC1 1H
P1 7.30 usec
PL1 0.00 dB
PL1W 12.55943203 W
SFO1 500.2330889 MHz
SI 65536
SF 500.2300165 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
O
N
H
10 9 8 7 6 5 4 3 2 1 0 ppm
1.978 0.989 2.002 1.000 0.962 1.964 0.954 2.000 2.010 2.052 2.980 2.307

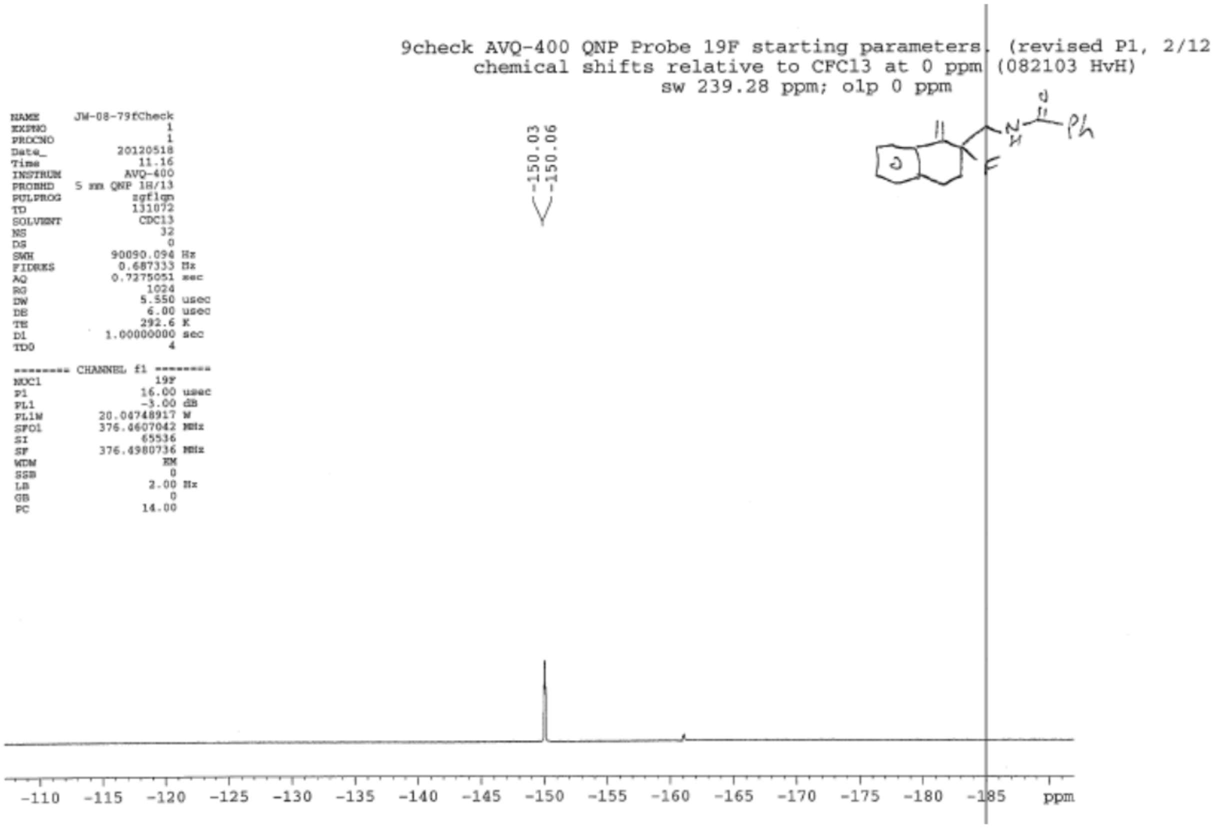

DRX-500 5mm TBIC probe 13C starting parameters. Rev 1/11/
With CPD proton decoupling. Use ns*td0 scans
167.70
136.29 135.79 134.56 131.62 131.54 129.47 128.65 127.23 126.94 126.80 126.49 123.33
77.32 77.07 76.82
42.37
28.51 26.98
14.29
O
N
H
NAME AD-JW-7-158C
EXPNO 1
PROCNO 1
Date_ 20120210
Time 10.45
INSTRUM DRX-500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 154
DS 0
SWH 41322.312 Hz
FIDRES 0.630528 Hz
AQ 0.7930356 sec
RG 8192
DW 12.100 usec
DE 6.00 usec
TE 293.6 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 10000
======== CHANNEL f1 ========
NUC1 13C
P1 10.75 usec
PL1 0.00 dB
SFO1 125.7175545 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -5.00 dB
PL12 7.04 dB
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



```
JW-0879 AV-500 new TBI(HXP) probe
1D 1H starting parameters

NAME       JW-08-79-protonchec
EXPNO                    1
PROCNO                   1
Date_             20120518
Time                 11.08
INSTRUM             AV-500
PROBHD    5 mm TBI 1H/31
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       0
SWH             10330.578 Hz
FIDRES           0.157632 Hz
AQ              3.1720407 sec
RG                     128
DW                  48.400 usec
DE                    6.00 usec
TE                   292.8 K
D1              0.10000000 sec
TD0                      4

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.30 usec
PL1                   0.00 dB
PL1W           12.55943203 W
SFO1           500.2330889 MHz
SI                   65536
SF             500.2300165 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00
```



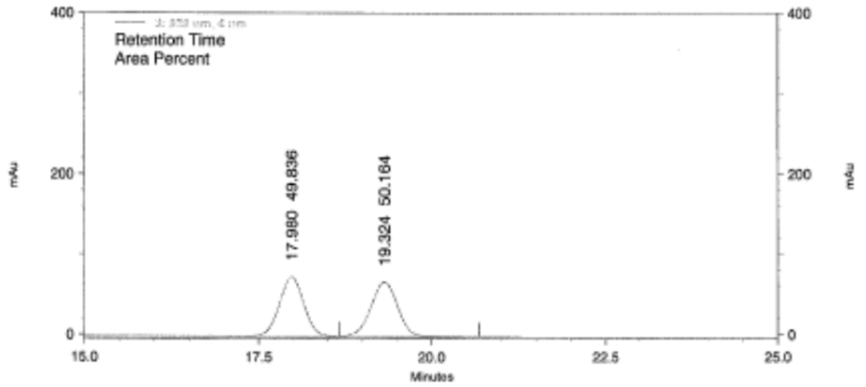
```
DRX-500 5mm TBIC probe 13C starting parameters. Rev 1/11/
With CPD proton decoupling. Use ns*td0 scans

NAME             AD-JW-7-79
EXPNO                     1
PROCNO                    1
Date_              20120210
Time                  10.13
INSTRUM             DRX-500
PROBHD     5 mm BBO BB-1H
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      568
DS                        0
SWH              41322.312 Hz
FIDRES            0.630528 Hz
AQ               0.7930356 sec
RG                   3649.1
DW                   12.100 usec
DE                     6.00 usec
TE                    293.5 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                   10000

======== CHANNEL f1 ========
NUC1                    13C
P1                    10.75 usec
PL1                    0.00 dB
SFO1            125.7175545 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                   -5.00 dB
PL12                   7.04 dB
```



```
9check AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12
     chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
                         sw 239.28 ppm; o1p 0 ppm
```

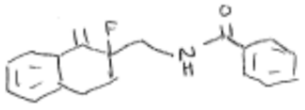
```
NAME       JW-08-79fCheck
EXPNO                   1
PROCNO                  1
Date_            20120518
Time                11.16
INSTRUM           AVQ-400
PROBHD    5 mm QNP 1H/13
PULPROG            zgflqn
TD                 131072
SOLVENT             CDCl3
NS                     32
DS                      0
SWH             90090.094 Hz
FIDRES           0.687333 Hz
AQ              0.7275051 sec
RG                   1024
DW                  5.550 usec
DE                   6.00 usec
TE                  292.6 K
D1             1.00000000 sec
TD0                     4

======== CHANNEL f1 ========
NUC1                  19F
P1                  16.00 usec
PL1                 -3.00 dB
PL1W          20.04748917 W
SFO1          376.4607042 MHz
SI                  65536
SF            376.4980736 MHz
WDM                    EM
SSB                     0
LB                   2.00 Hz
GB                      0
PC                  14.00
```

JW-08-79rac / 07-162

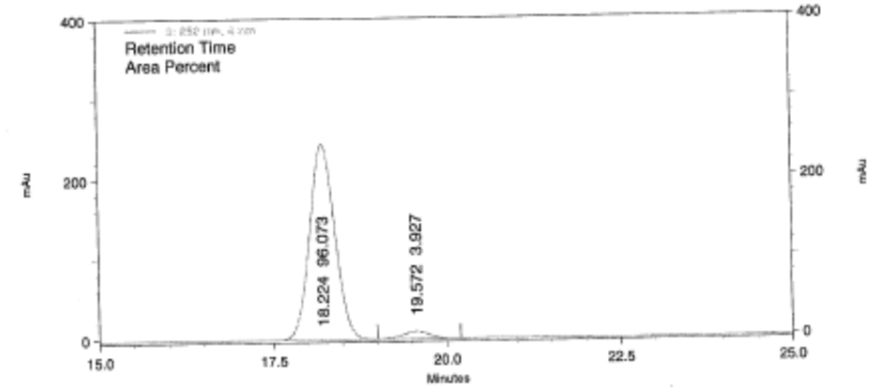


3: 252 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	17.980	49.836	287
2	19.324	50.164	204



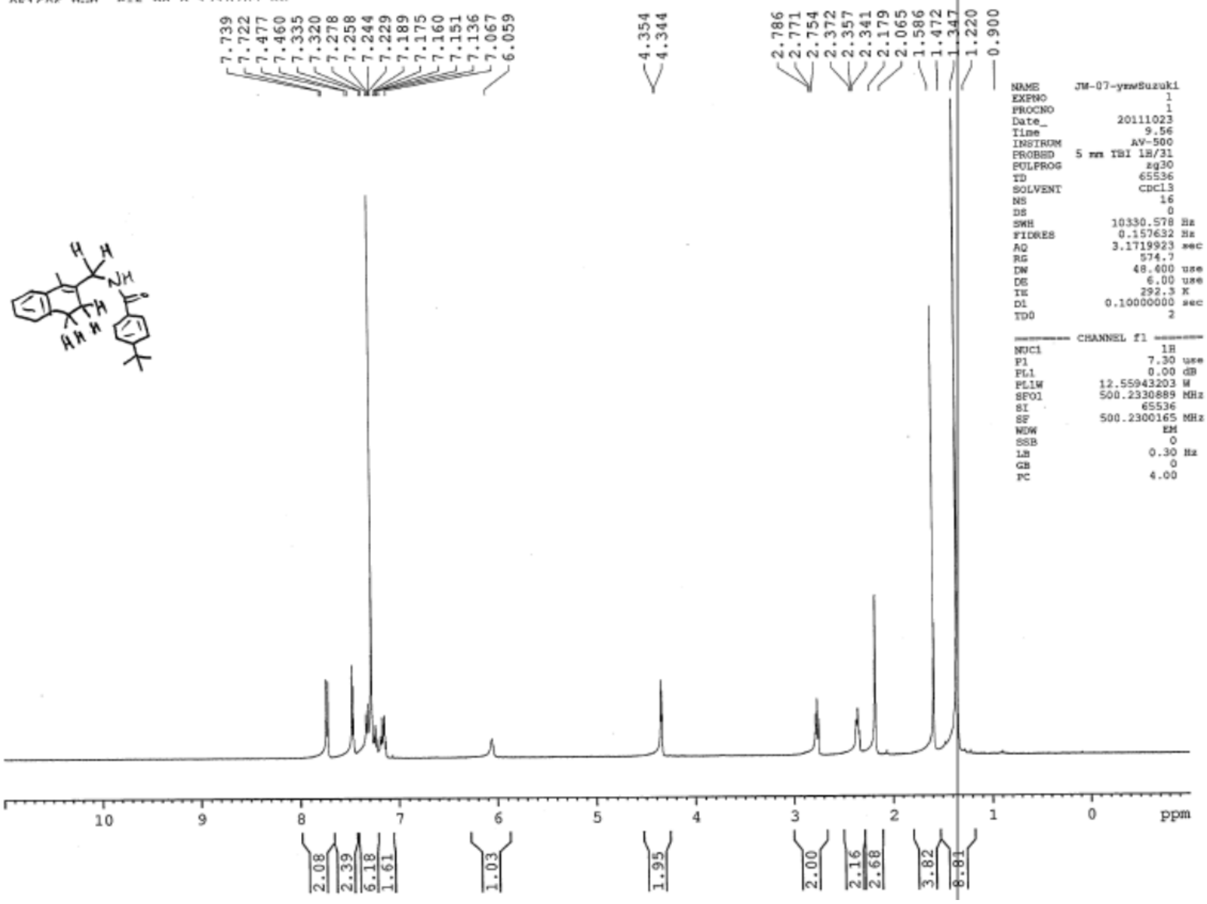
JW-08-79



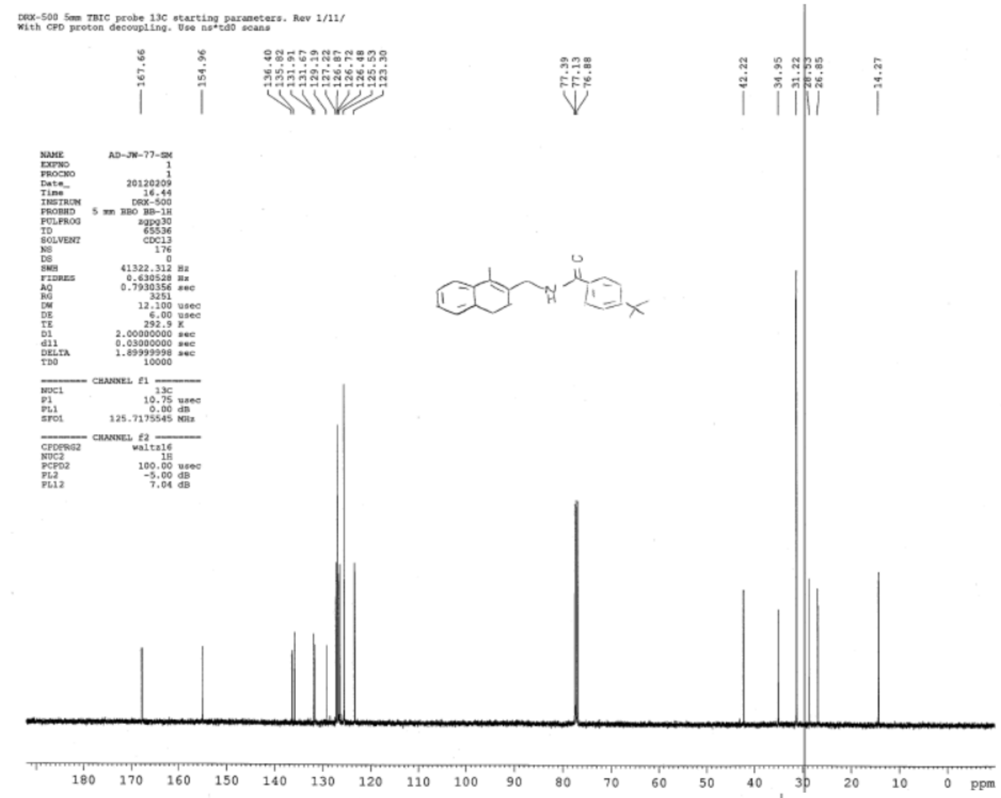
3: 252 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	18.224	96.073	482
2	19.572	3.927	205

JW-07-ymw substrate suzuki AV-500 new TBI(HXP) probe
1D 1H starting parameters

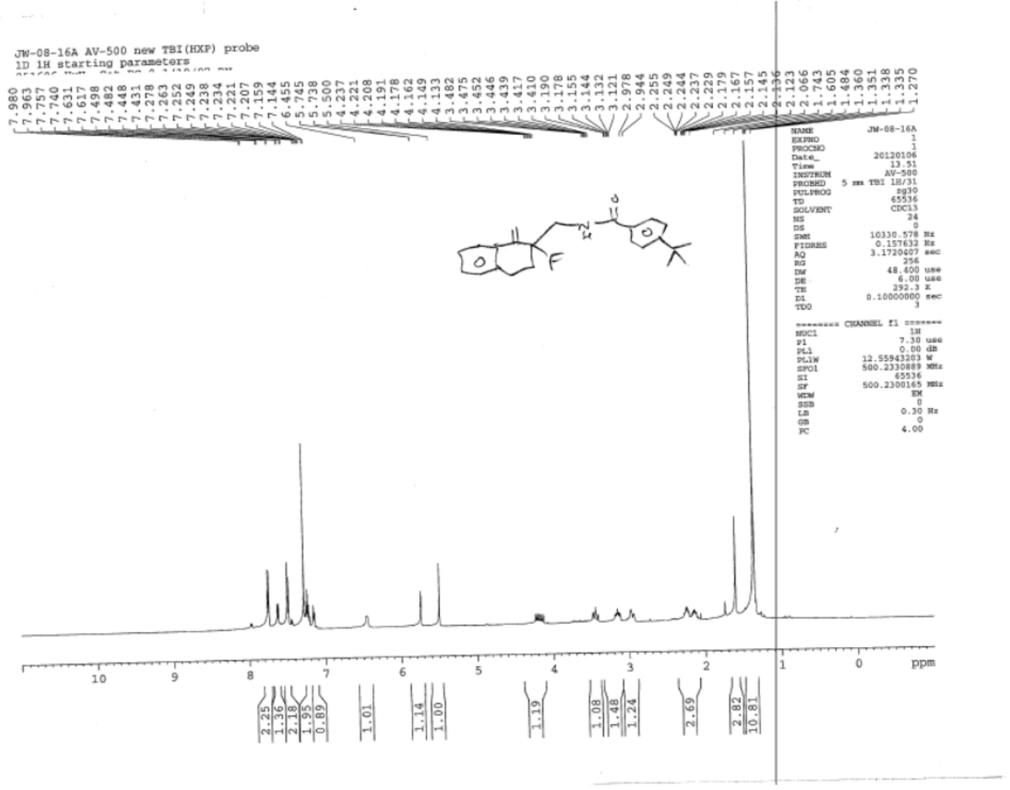


```
NAME       JW-07-ymwSuzuki
EXPNO                    1
PROCNO                   1
Date_             20111023
Time                  9.56
INSTRUM             AV-500
PROBHD   5 mm TBI 1H/31
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       0
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ               3.1719923 sec
RG                   574.7
DW                  48.400 use
DE                    6.00 use
TE                   292.3 K
D1              0.10000000 sec
TD0                      2

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.30 use
PL1                   0.00 dB
PL1W           12.55943203 W
SFO1           500.2330889 MHz
SI                   65536
SF             500.2300165 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00
```



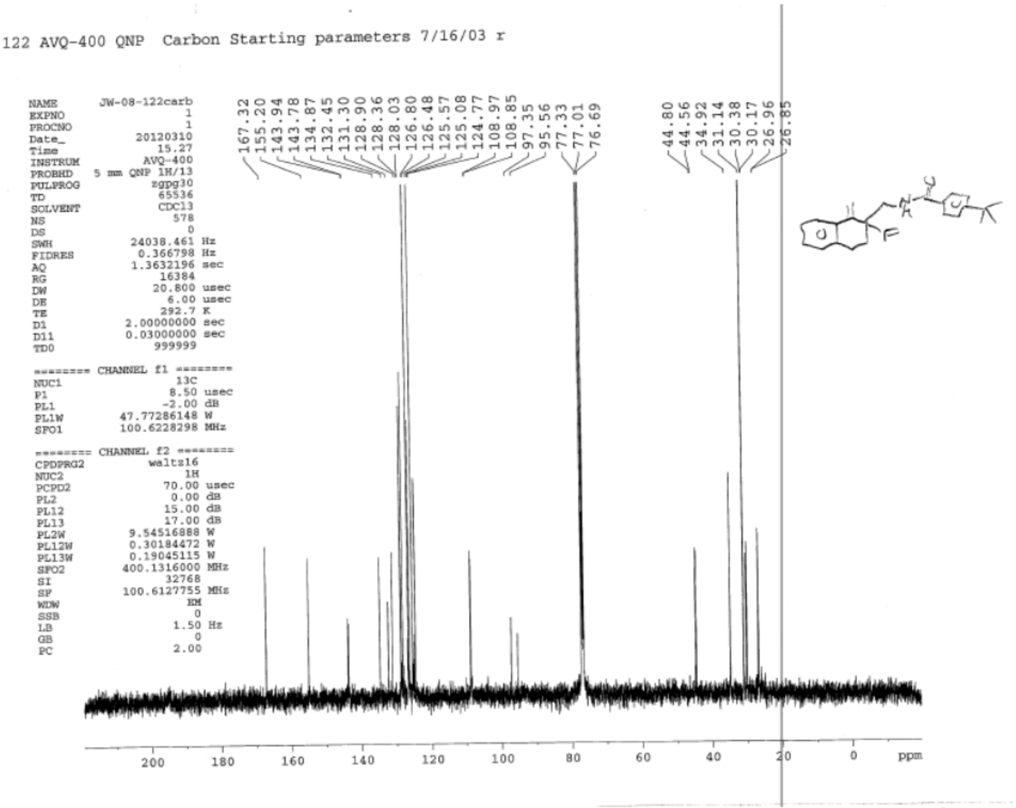
```
DRX-500 5mm TBIC probe 13C starting parameters. Rev 1/11/
With CPD proton decoupling. Use ns*td0 scans
```

```
NAME          AD-JW-77-SM
EXPNO                   1
PROCNO                  1
Date_            20120209
Time                16.44
INSTRUM           DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    176
DS                      0
SWH             41322.312 Hz
FIDRES           0.630528 Hz
AQ              0.7930356 sec
RG                   3251
DW                 12.100 usec
DE                   6.00 usec
TE                  292.9 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                 10000

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.75 usec
PL1                  0.00 dB
SFO1          125.7175545 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -5.00 dB
PL12                 7.04 dB
```



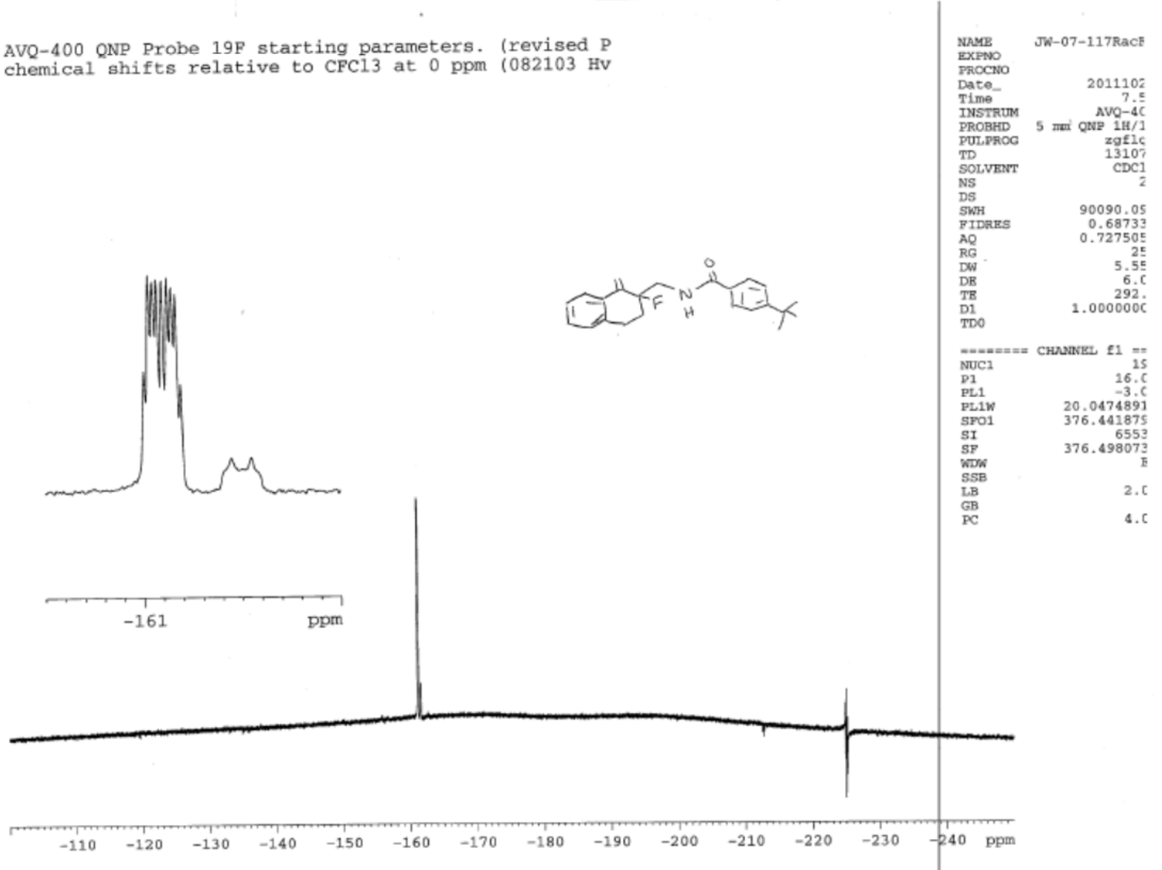
```
JW-08-16A AV-500 new TBI(HXP) probe
1D 1H starting parameters
```

```
NAME          JW-08-16A
EXPNO                 1
PROCNO                1
Date_          20120106
Time              13.51
INSTRUM          AV-500
PROBHD   5 mm TBI 1H/31
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   24
DS                    0
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1720407 sec
RG                  256
DW               48.400 use
DE                 6.00 use
TE                292.3 K
D1           0.10000000 sec
TD0                   3

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.30 use
PL1                0.00 dB
PL1W        12.55943203 W
SFO1        500.2330889 MHz
SI                65536
SF          500.2300165 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 4.00
```



122 AVQ-400 QNP Carbon Starting parameters 7/16/03 r

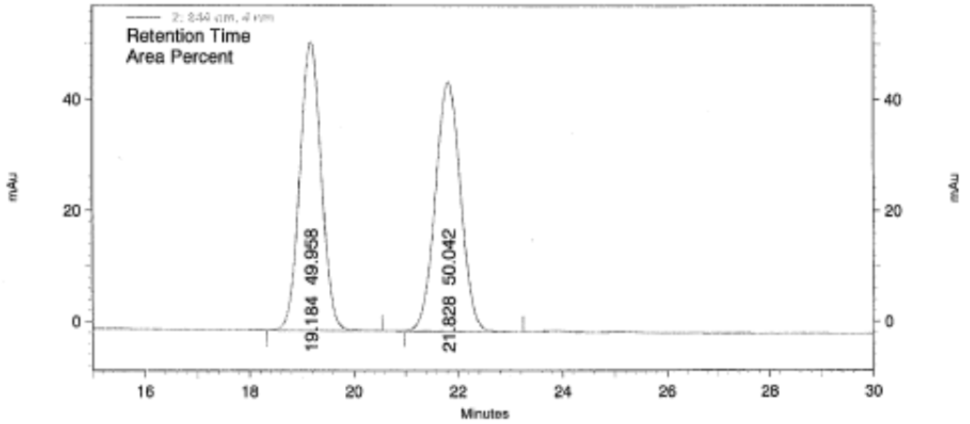
```
NAME          JW-08-122carb
EXPNO                     1
PROCNO                    1
Date_              20120310
Time                  15.27
INSTRUM             AVQ-400
PROBHD     5 mm QNP 1H/13
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     578
DS                       0
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3632196 sec
RG                   16384
DW                  20.800 usec
DE                    6.00 usec
TE                   292.7 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                 999999

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.50 usec
PL1                  -2.00 dB
PL1W           47.77286148 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                70.00 usec
PL2                   0.00 dB
PL12                 15.00 dB
PL13                 17.00 dB
PL2W            9.54516888 W
PL12W           0.30184472 W
PL13W           0.19045115 W
SFO2           400.1316000 MHz
SI                   32768
SF             100.6127755 MHz
WDW                     EM
SSB                      0
LB                    1.50 Hz
GB                       0
PC                    2.00
```



AVQ-400 QNP Probe 19F starting parameters. (revised P
chemical shifts relative to CFCl3 at 0 ppm (082103 Hv

```
NAME          JW-07-117Rac
EXPNO
PROCNO
Date_              201110
Time                  7.
INSTRUM             AVQ-4
PROBHD     5 mm QNP 1H/
PULPROG              zgfl
TD                   1310
SOLVENT              CDC
NS
DS
SWH              90090.0
FIDRES            0.6873
AQ                0.72750
RG                     2
DW                    5.5
DE                    6.
TE                   292.
D1               1.000000
TD0

======== CHANNEL f1 =
NUC1                   1
P1                    16.
PL1                   -3.
PL1W            20.047489
SFO1           376.44187
SI                   655
SF             376.49807
WDW
SSB
LB                    2.
GB
PC                    4.
```

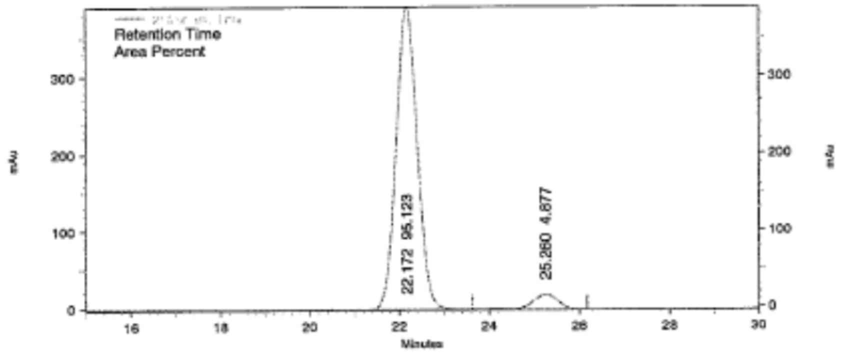
JW-07-119rac_IC9208_30min



2: 244 nm, 4 nm
Results

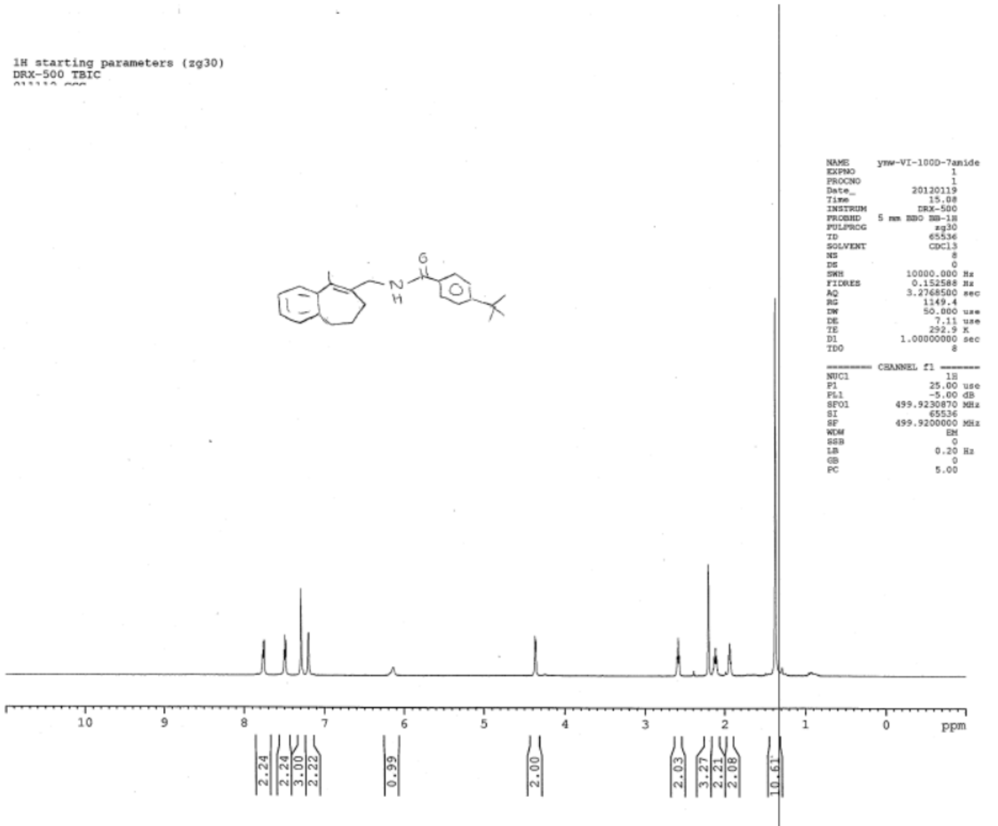
Pk #	Retention Time	Area Percent	Lambda Max
1	19.184	49.958	205
2	21.828	50.042	205

JW-08-16a



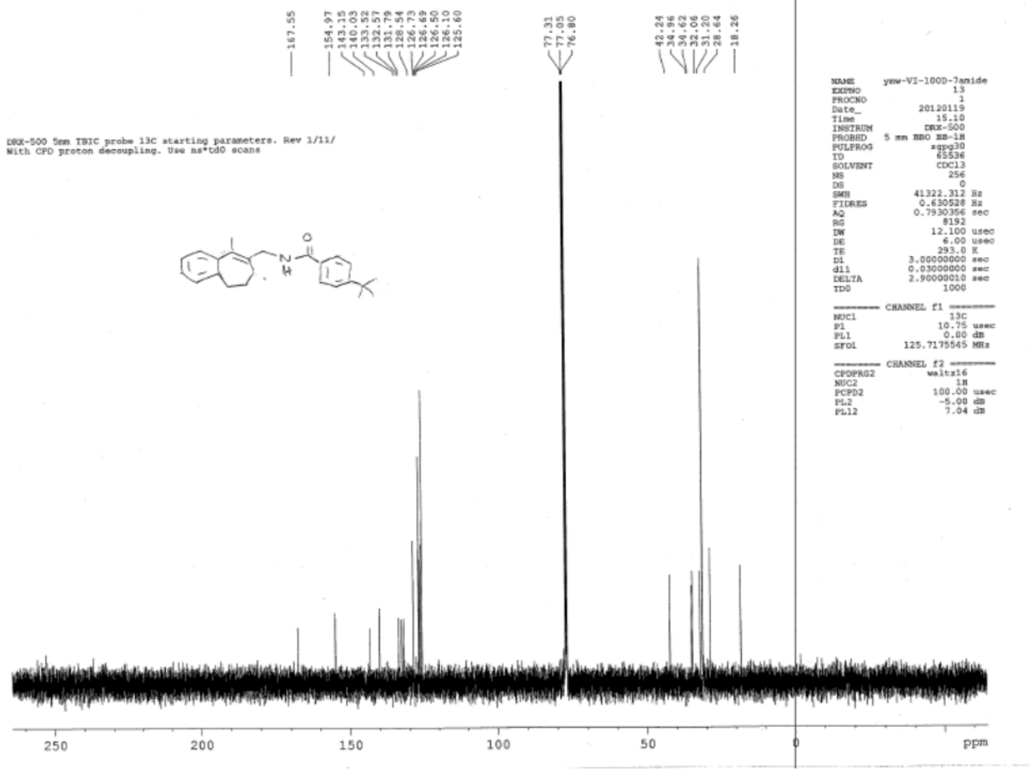
2: 252 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	22.172	95.123	191
2	25.260	4.877	205



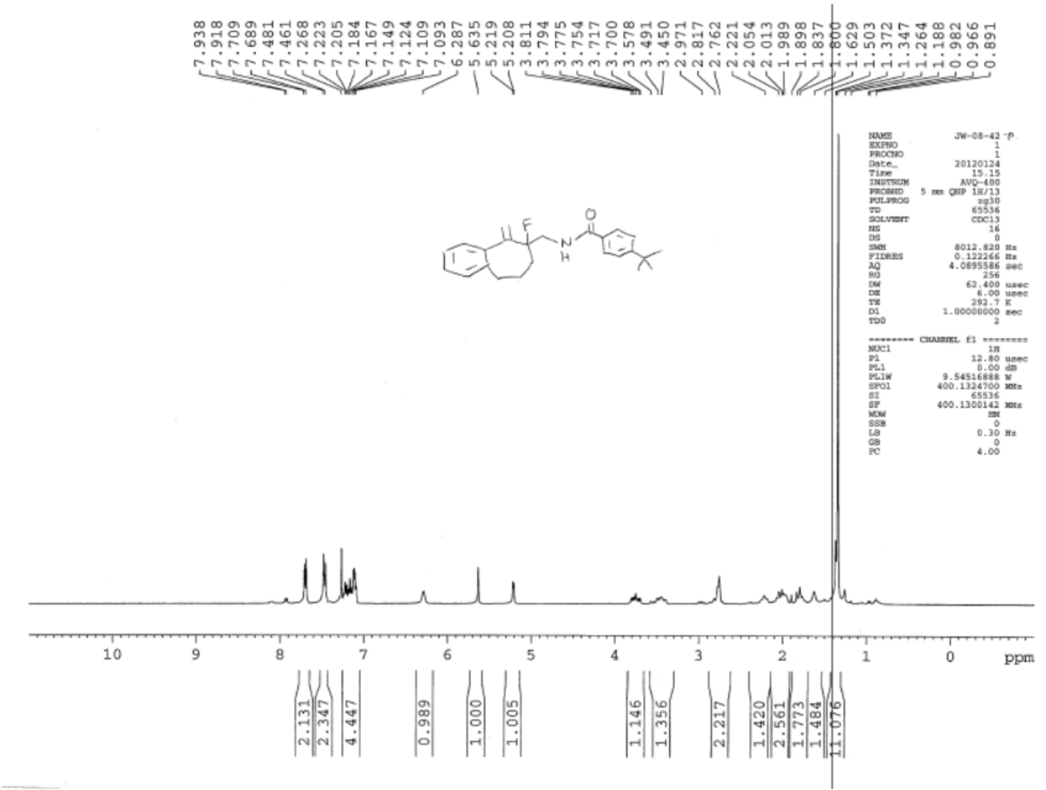
```
1H starting parameters (zg30)
DRX-500 TBIC
```

```
NAME      ymw-VI-100D-7amide
EXPNO                    1
PROCNO                   1
Date_             20120119
Time                 15.08
INSTRUM            DRX-500
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH             10000.000 Hz
FIDRES           0.152588 Hz
AQ              3.2768500 sec
RG                 1149.4
DW                 50.000 use
DE                   7.11 use
TE                  292.9 K
D1             1.00000000 sec
TD0                      8

======== CHANNEL f1 ========
NUC1                    1H
P1                   25.00 use
PL1                  -5.00 dB
SFO1          499.9230870 MHz
SI                   65536
SF            499.9200000 MHz
WDW                     EM
SSB                      0
LB                    0.20 Hz
GB                       0
PC                    5.00
```

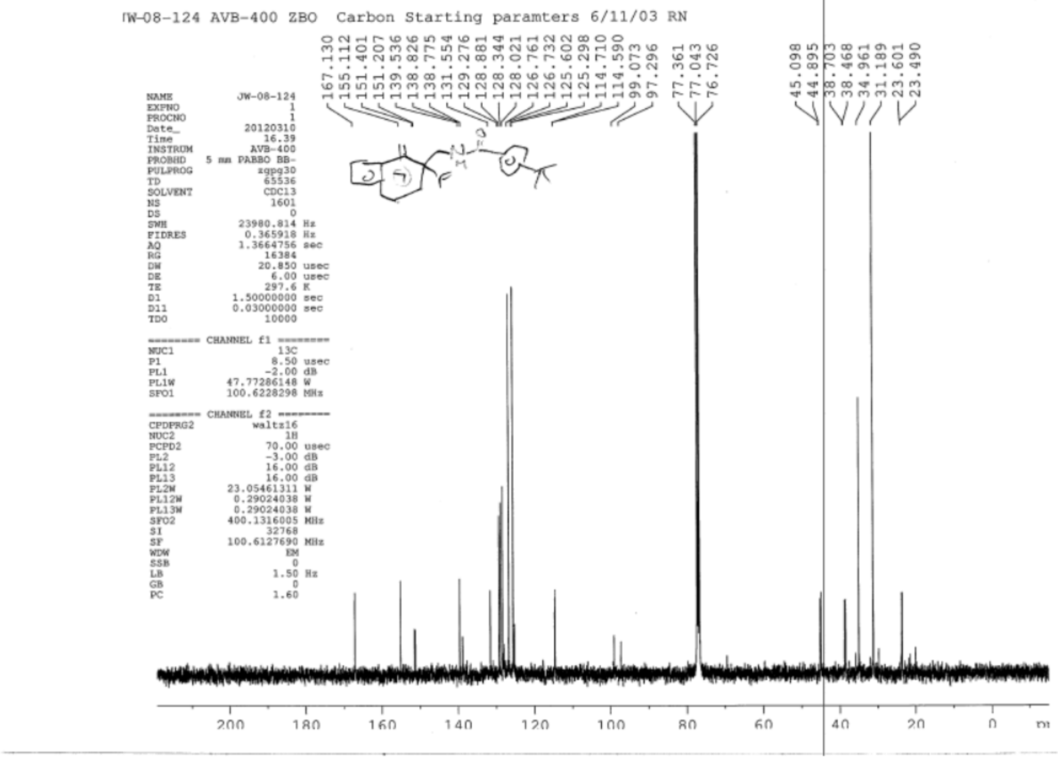


```
DRX-500 5mm TBIC probe 13C starting parameters. Rev 1/11/
With CPD proton decoupling. Use ns*td0 scans
```

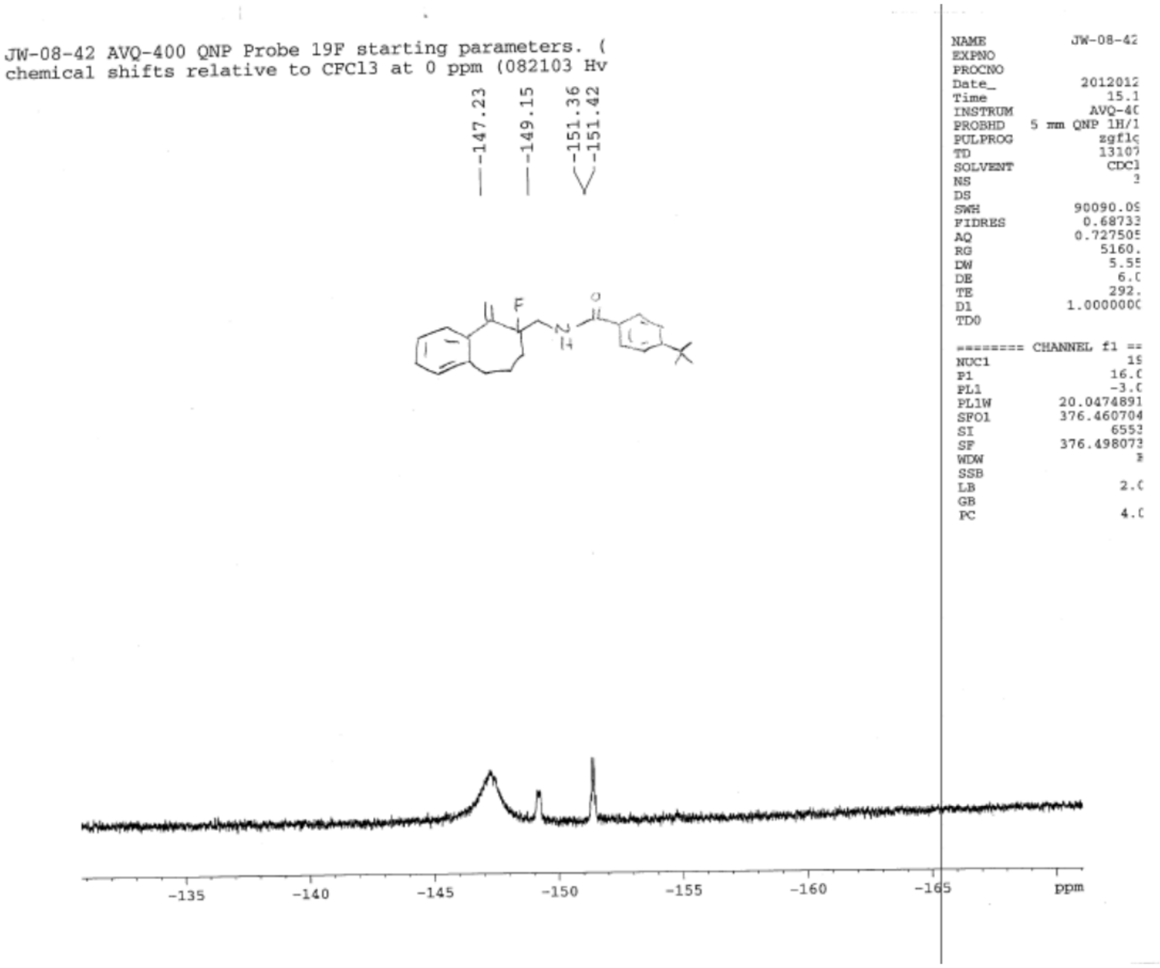
```
NAME      ymw-VI-100D-7amide
EXPNO                   13
PROCNO                   1
Date_             20120119
Time                 15.10
INSTRUM            DRX-500
PROBHD    5 mm BBO BB-1H
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     256
DS                       0
SWH             41322.312 Hz
FIDRES           0.630528 Hz
AQ              0.7930356 sec
RG                    8192
DW                  12.100 usec
DE                    6.00 usec
TE                   293.0 K
D1             3.00000000 sec
d11            0.03000000 sec
DELTA          2.90000010 sec
TD0                   1000

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.75 usec
PL1                   0.00 dB
SFO1          125.7175545 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                  -5.00 dB
PL12                  7.04 dB
```



```
NAME          JW-08-42 -P.
EXPNO                    1
PROCNO                   1
Date_             20120124
Time                 15.15
INSTRUM            AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       0
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0895586 sec
RG                     256
DW                  62.400 usec
DE                    6.00 usec
TE                   292.7 K
D1              1.00000000 sec
TD0                      2

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.80 usec
PL1                   0.00 dB
PL1W            9.54516888 W
SFO1           400.1324700 MHz
SI                   65536
SF             400.1300142 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00
```



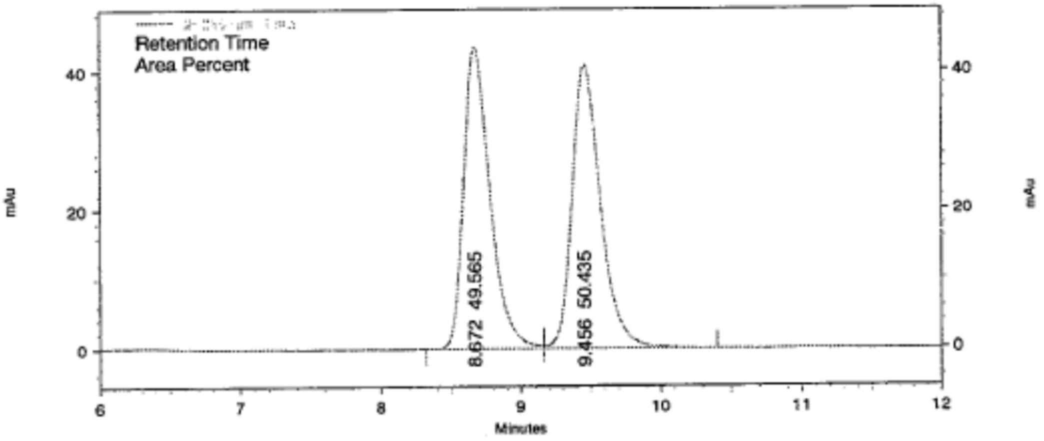
```
W-08-124 AVB-400 ZBO  Carbon Starting paramters 6/11/03 RN

NAME            JW-08-124
EXPNO                   1
PROCNO                  1
Date_            20120310
Time                16.39
INSTRUM           AVB-400
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   1601
DS                      0
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                  16384
DW                 20.850 usec
DE                   6.00 usec
TE                  297.6 K
D1             1.50000000 sec
D11            0.03000000 sec
TD0                 10000

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.50 usec
PL1                 -2.00 dB
PL1W          47.77286148 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               70.00 usec
PL2                 -3.00 dB
PL12                16.00 dB
PL13                16.00 dB
PL2W          23.05461311 W
PL12W          0.29024038 W
PL13W          0.29024038 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.50 Hz
GB                      0
PC                   1.60
```



JW-08-42 AVQ-400 QNP Probe 19F starting parameters. (
chemical shifts relative to CFCl3 at 0 ppm (082103 Hv

```
NAME             JW-08-42
EXPNO
PROCNO
Date_            2012012
Time                15.1
INSTRUM           AVQ-40
PROBHD    5 mm QNP 1H/1
PULPROG            zgflq
TD                 13107
SOLVENT             CDCl
NS                     3
DS
SWH             90090.09
FIDRES           0.68733
AQ              0.727505
RG                 5160.
DW                  5.55
DE                   6.0
TE                  292.
D1             1.0000000
TD0

======== CHANNEL f1 ==
NUC1                  19
P1                  16.0
PL1                 -3.0
PL1W          20.0474891
SFO1          376.460704
SI                  6553
SF            376.498073
WDW                    E
SSB
LB                   2.0
GB
PC                   4.0
```

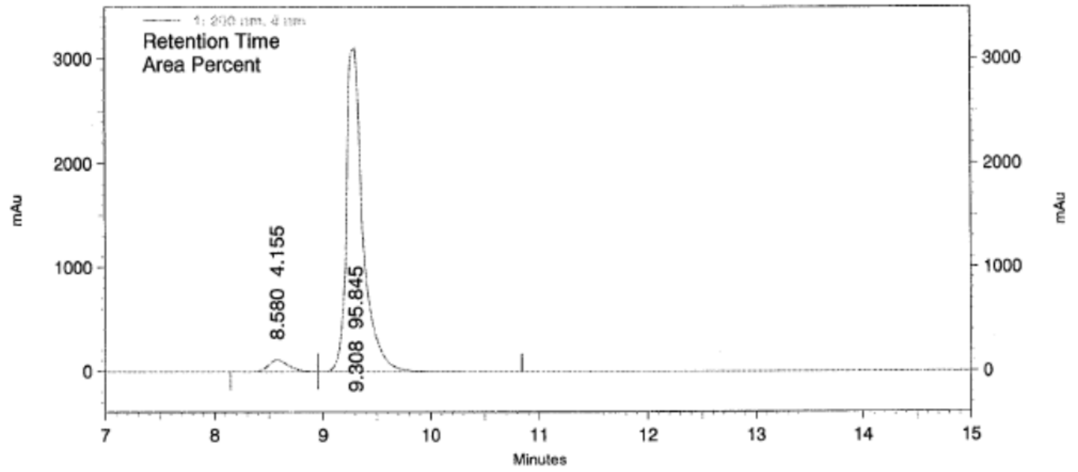
JW-08-42-rac (ad)



2: 255 nm, 4 nm
Results

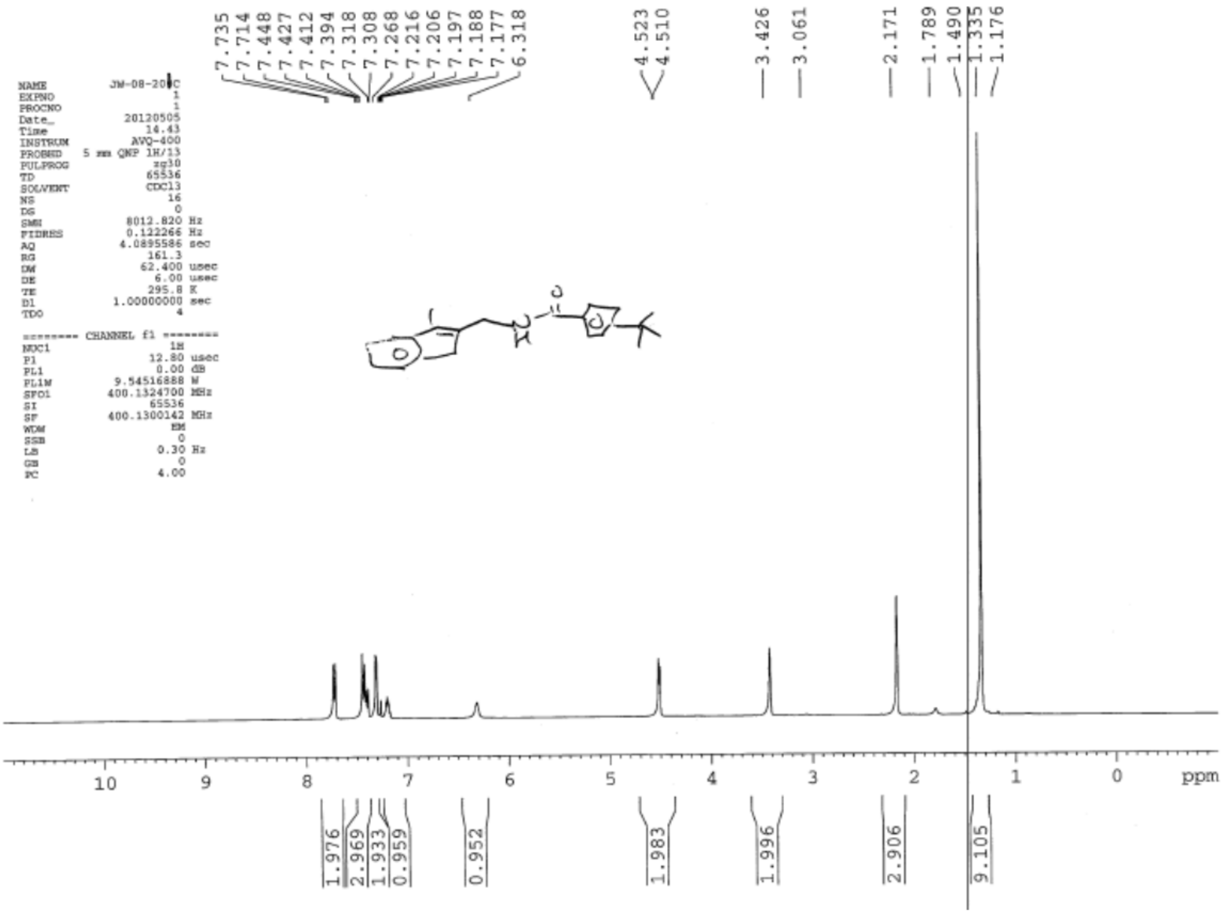
Pk #	Retention Time	Area Percent	Lambda Max
1	8.672	49.565	205
2	9.456	50.435	205

JW-08-124 IB9505_15

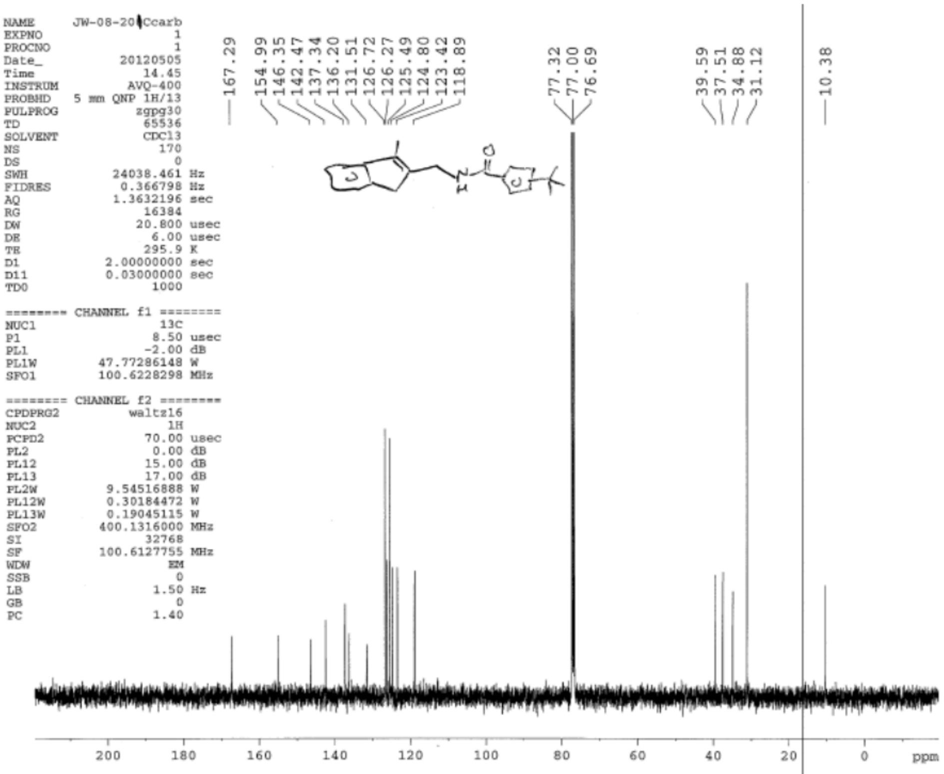


1: 200 nm, 4 nm
Results

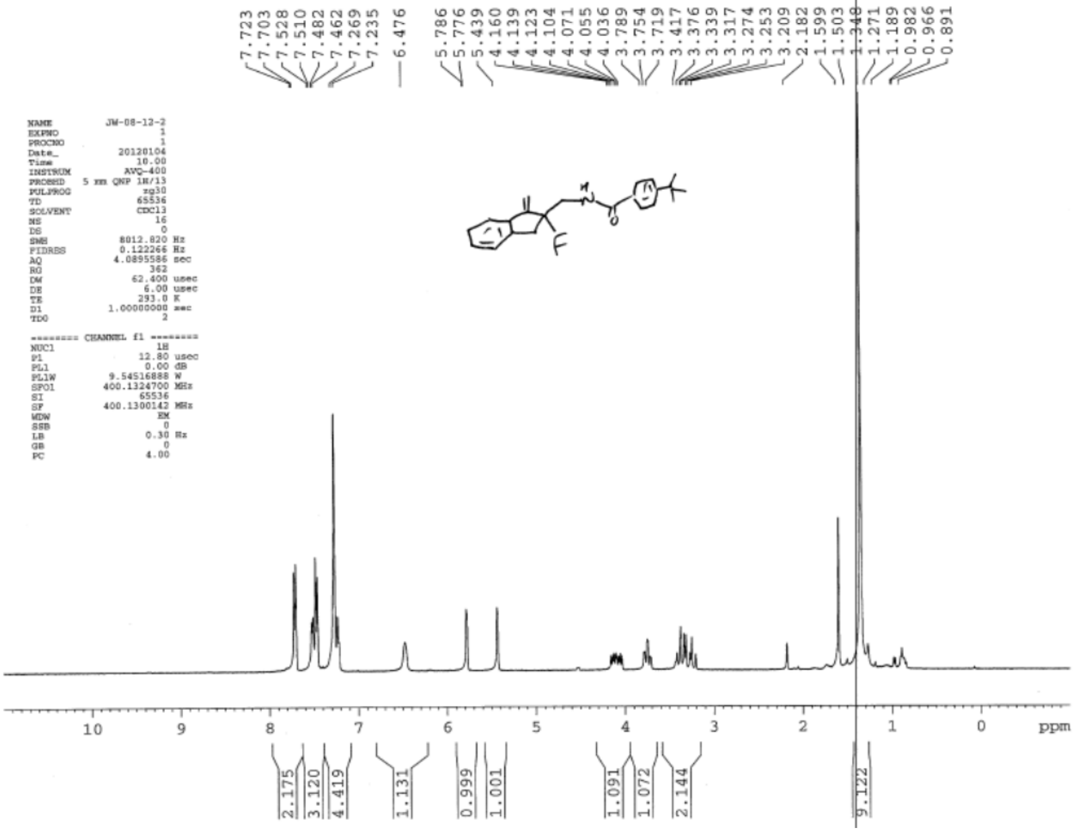
Pk #	Retention Time	Area Percent	Lambda Max
1	8.580	4.155	205
2	9.308	95.845	202



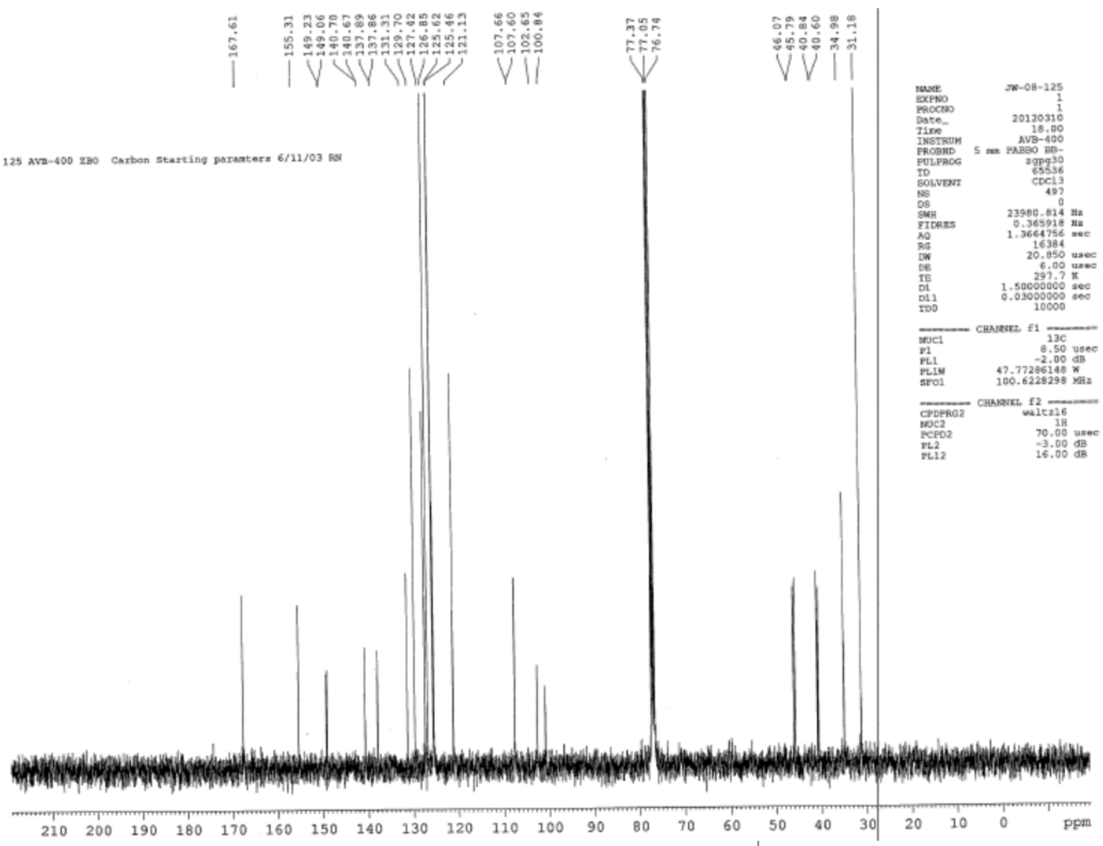
```
NAME          JW-08-20[illegible]C
EXPNO                    1
PROCNO                   1
Date_             20120505
Time                 14.43
INSTRUM            AVQ-400
PROBHD    5 mm QNP 1H/13
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       0
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0895586 sec
RG                   161.3
DW                  62.400 usec
DE                    6.00 usec
TE                   295.8 K
D1             1.00000000 sec
TD0                      4

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.80 usec
PL1                   0.00 dB
PL1W            9.54516888 W
SFO1           400.1324700 MHz
SI                   65536
SF             400.1300142 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00
```

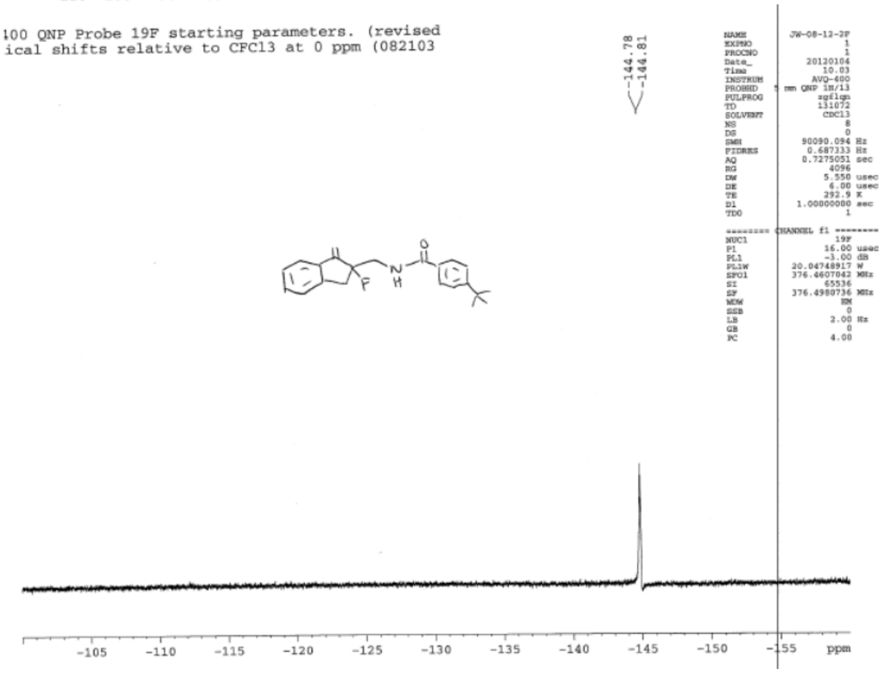


```
NAME       JW-08-20Ccarb
EXPNO                   1
PROCNO                  1
Date_            20120505
Time                14.45
INSTRUM           AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   170
DS                     0
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3632196 sec
RG                 16384
DW                20.800 usec
DE                  6.00 usec
TE                 295.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                 1000

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.50 usec
PL1                -2.00 dB
PL1W         47.77286148 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              70.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               17.00 dB
PL2W          9.54516888 W
PL12W         0.30184472 W
PL13W         0.19045115 W
SFO2         400.1316000 MHz
SI                 32768
SF           100.6127755 MHz
WDW                   EM
SSB                    0
LB                  1.50 Hz
GB                     0
PC                  1.40
```

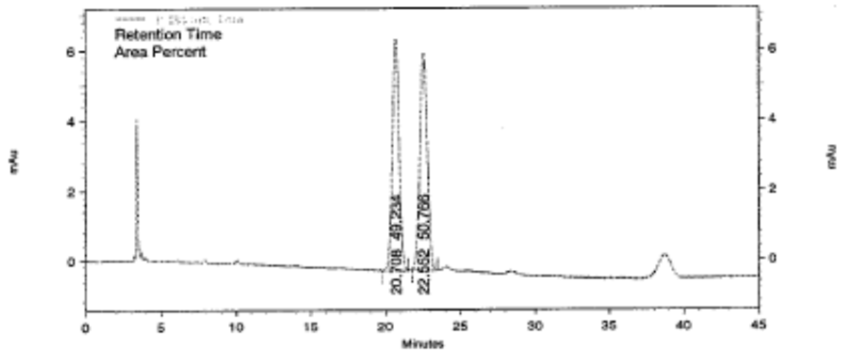


```
NAME         JW-08-12-2
EXPNO                 1
PROCNO                1
Date_          20120104
Time              10.00
INSTRUM         AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0895586 sec
RG                  362
DW               62.400 usec
DE                 6.00 usec
TE                293.0 K
D1           1.00000000 sec
TD0                   2

======== CHANNEL f1 ========
NUC1                 1H
P1                12.80 usec
PL1                0.00 dB
PL1W         9.54516888 W
SFO1        400.1324700 MHz
SI                65536
SF          400.1300142 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 4.00
```


167.61
155.31
149.23
149.06
140.70
140.67
137.89
137.86
131.31
129.70
127.42
126.85
125.62
125.46
121.13
107.66
107.60
102.65
100.84
77.37
77.05
76.74
46.07
45.79
40.84
40.60
34.98
31.18
125 AVB-400 ZBO Carbon Starting paramters 6/11/03 RN
NAME JW-08-125
EXPNO 1
PROCNO 1
Date_ 20120310
Time 18.00
INSTRUM AVB-400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 497
DS 0
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 6.00 usec
TE 297.7 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 10000
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 47.77286148 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 -3.00 dB
PL12 16.00 dB
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


100 QNP Probe 19F starting parameters. (revised
ical shifts relative to CFCl3 at 0 ppm (082103
-144.78
-144.81
NAME JW-08-12-2F
EXPNO 1
PROCNO 1
Date_ 20120104
Time 10.03
INSTRUM AVQ-400
PROBHD 5 mm QNP 1H/13
PULPROG zgflqn
TD 131072
SOLVENT CDCl3
NS 8
DS 0
SWH 90090.094 Hz
FIDRES 0.687333 Hz
AQ 0.7275051 sec
RG 4096
DW 5.550 usec
DE 6.00 usec
TE 292.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 19F
P1 16.00 usec
PL1 -3.00 dB
PL1W 20.04748917 W
SFO1 376.4607042 MHz
SI 65536
SF 376.4980736 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 4.00
O
F
N
H
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
ppm

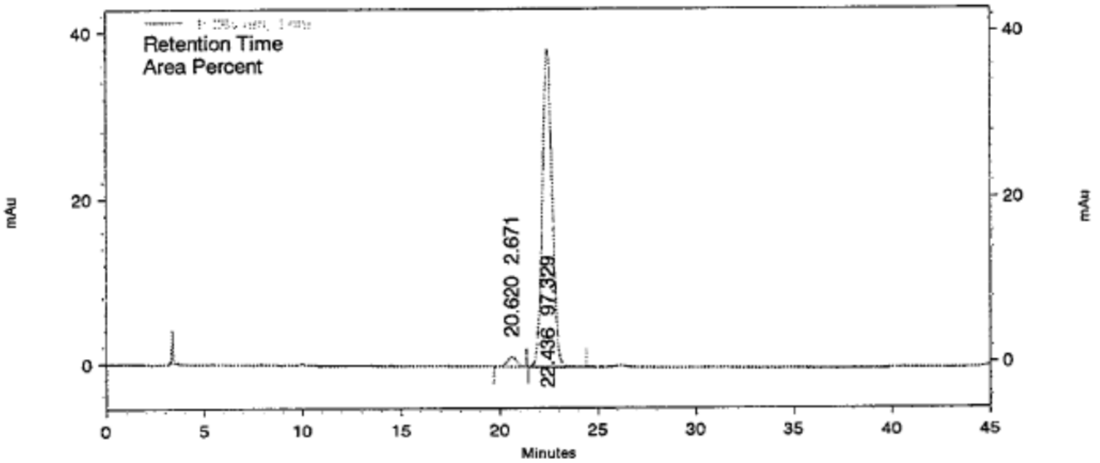
JW-08-31



1: 285 nm, 4 nm
Results

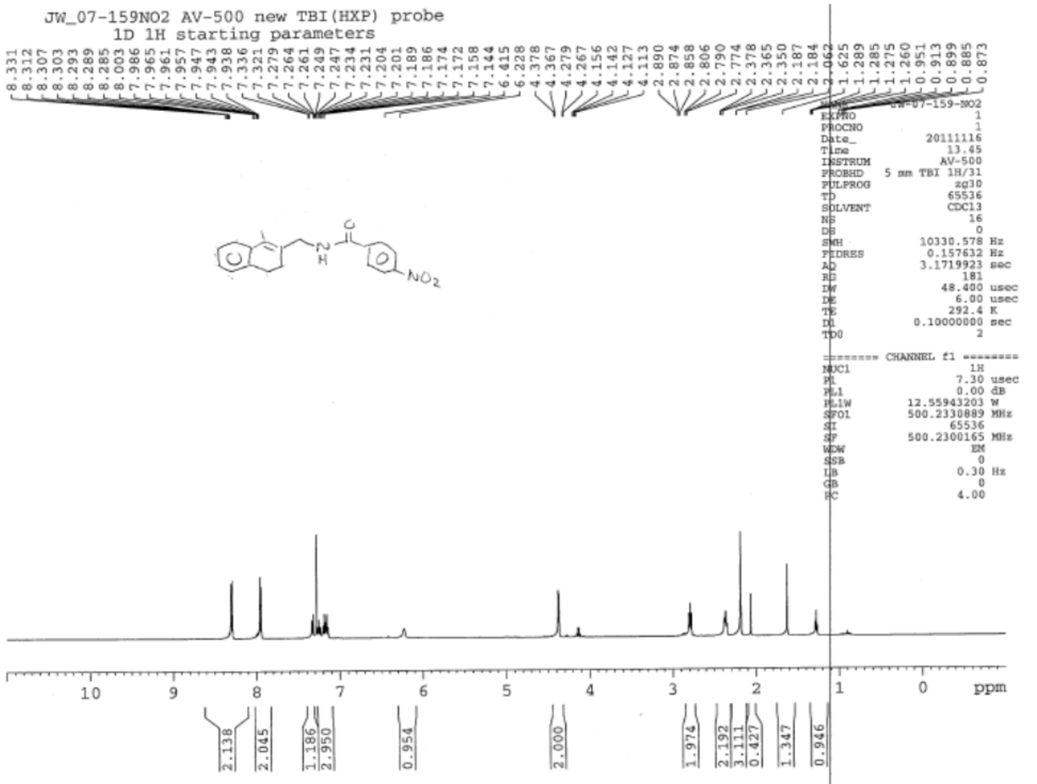
Pk #	Retention Time	Area Percent	Lambda Max
1	20.708	49.234	205
2	22.552	50.766	205

JW-08-31

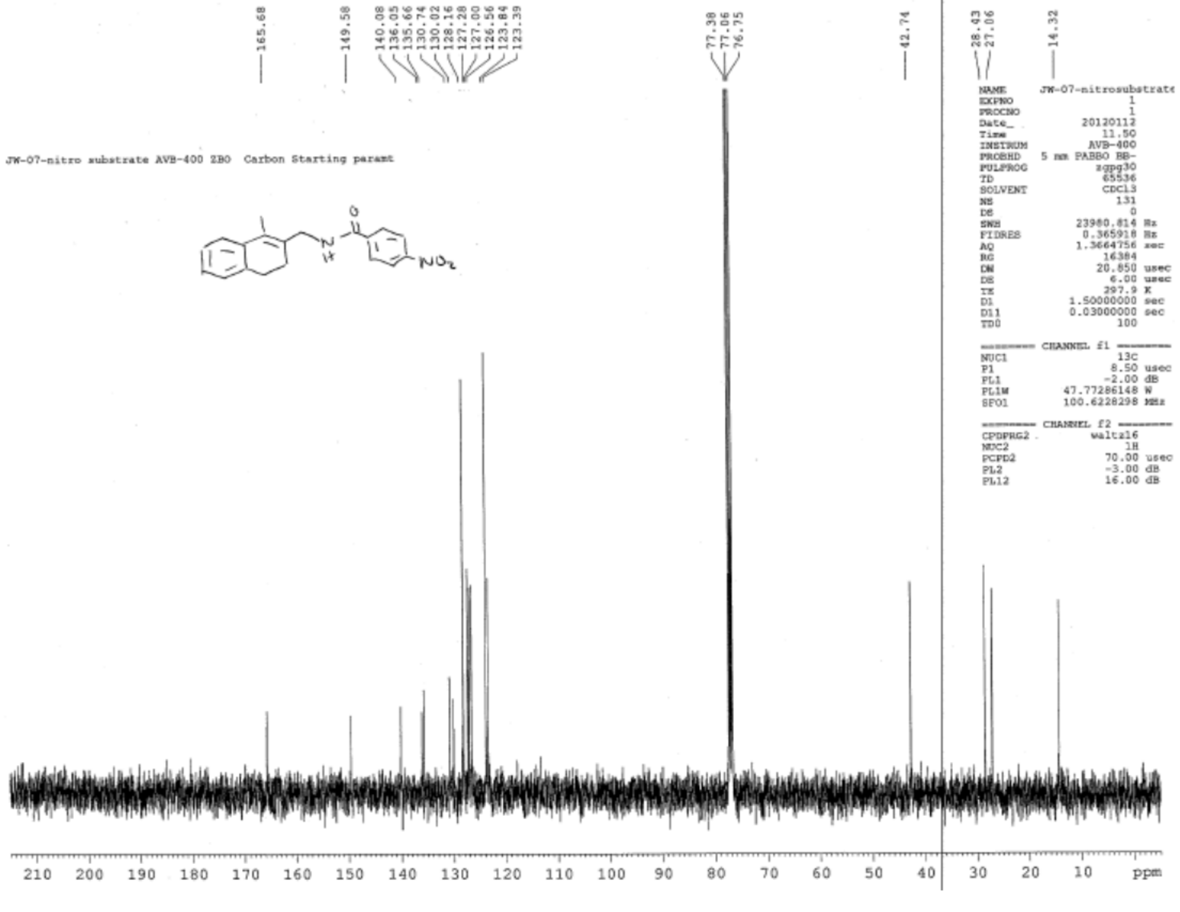


1: 285 nm, 4 nm
Results

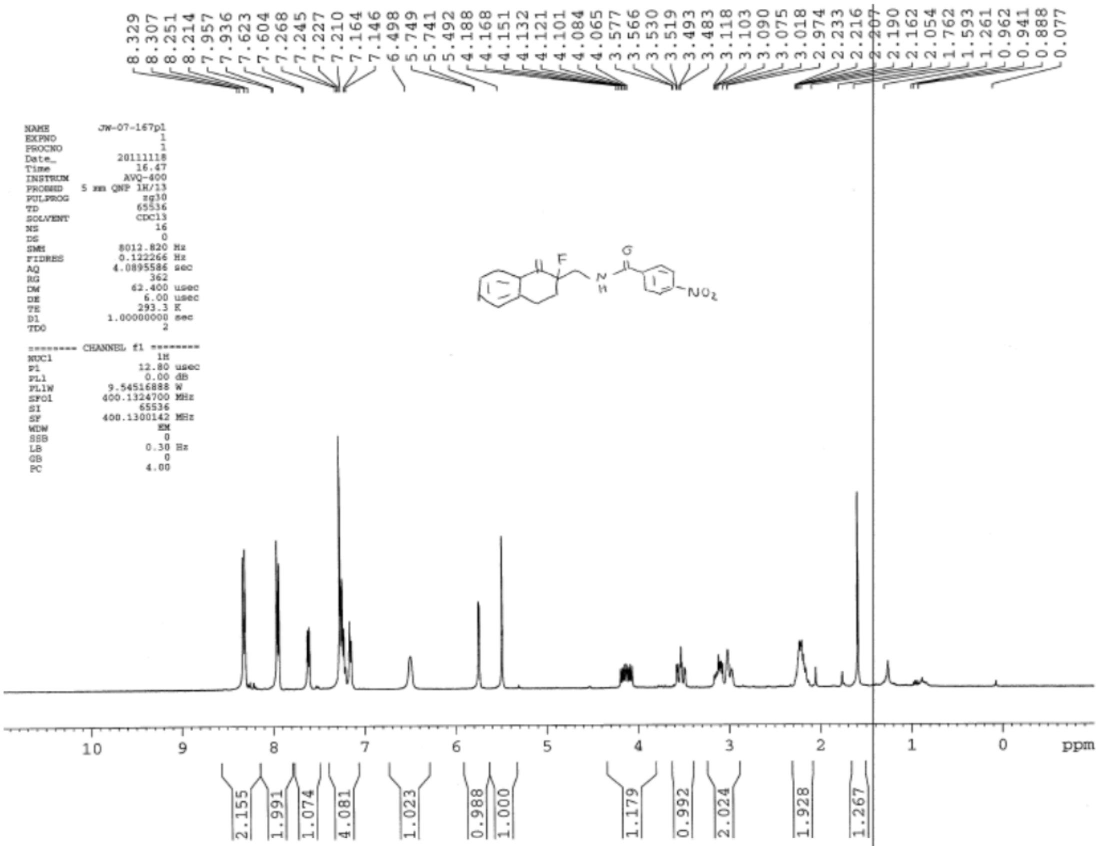
Pk #	Retention Time	Area Percent	Lambda Max
1	20.620	2.671	205
2	22.436	97.329	204


JW_07-159NO2 AV-500 new TBI(HXP) probe
1D 1H starting parameters

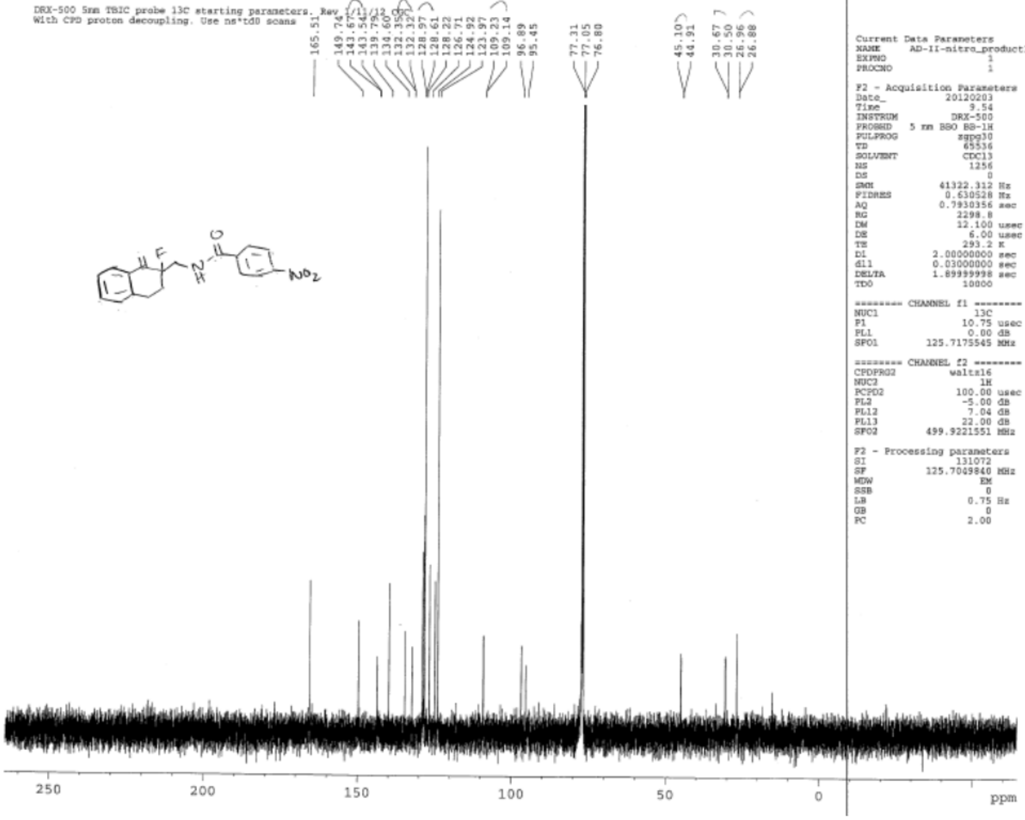
```
NAME       JW-07-159-NO2
EXPNO                  1
PROCNO                 1
Date_           20111116
Time               13.45
INSTRUM           AV-500
PROBHD   5 mm TBI 1H/31
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719923 sec
RG                   181
DW                48.400 usec
DE                  6.00 usec
TE                 292.4 K
D1            0.10000000 sec
TD0                    2

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.30 usec
PL1                 0.00 dB
PL1W         12.55943203 W
SFO1         500.2330889 MHz
SI                 65536
SF           500.2300165 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00
```


JW-07-nitro substrate AVB-400 ZBO Carbon Starting paramt

```
NAME       JW-07-nitrosubstrate
EXPNO                  1
PROCNO                 1
Date_           20120112
Time               11.50
INSTRUM          AVB-400
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   131
DS                     0
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                 16384
DW                20.850 usec
DE                  6.00 usec
TE                 297.9 K
D1            1.50000000 sec
D11           0.03000000 sec
TD0                  100

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.50 usec
PL1                -2.00 dB
PL1W         47.77286148 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              70.00 usec
PL2                -3.00 dB
PL12               16.00 dB
```



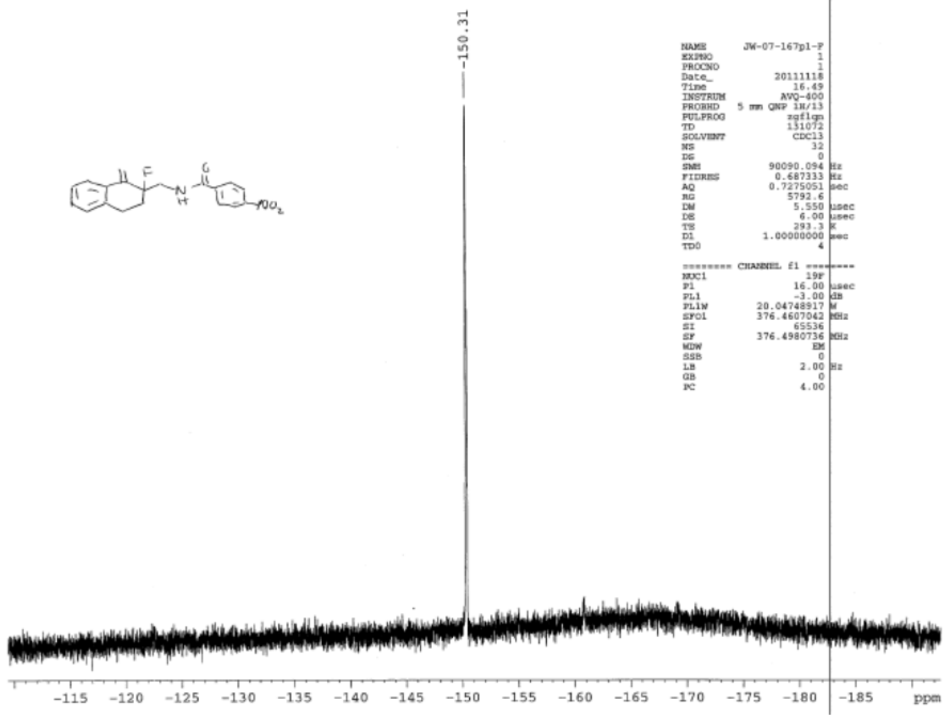
```
NAME          JW-07-167p1
EXPNO                   1
PROCNO                  1
Date_            20111118
Time                16.47
INSTRUM           AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0895586 sec
RG                    362
DW                 62.400 usec
DE                   6.00 usec
TE                  293.3 K
D1             1.00000000 sec
TD0                     2

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.80 usec
PL1                  0.00 dB
PL1W           9.54516888 W
SFO1          400.1324700 MHz
SI                  65536
SF            400.1300142 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   4.00
```



```
DRX-500 5mm TBIC probe 13C starting parameters. Rev 1/11/12 CGC
With CPD proton decoupling. Use ns*td0 scans
```

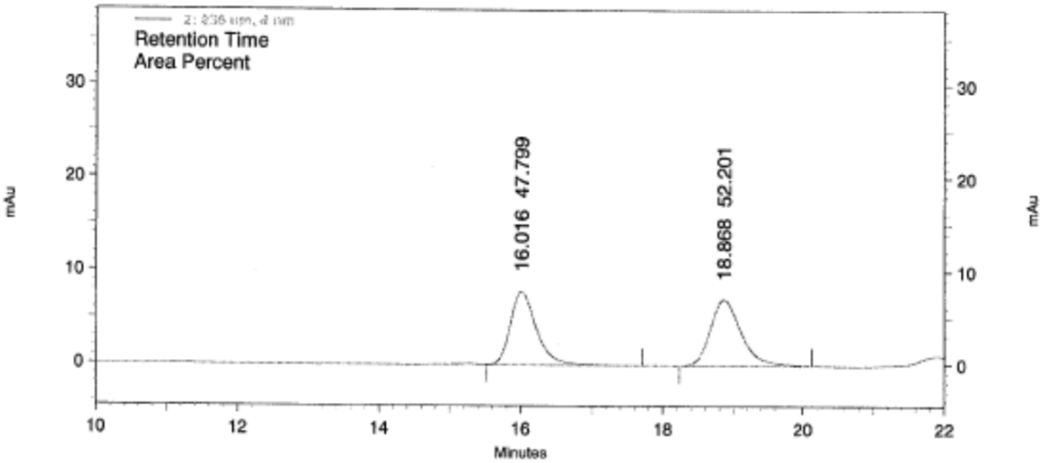
```
Current Data Parameters
NAME      AD-II-nitro_product3
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120203
Time                 9.54
INSTRUM           DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   1256
DS                      0
SWH             41322.312 Hz
FIDRES           0.630528 Hz
AQ              0.7930356 sec
RG                 2298.8
DW                 12.100 usec
DE                   6.00 usec
TE                  293.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                 10000

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.75 usec
PL1                  0.00 dB
SFO1          125.7175545 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -5.00 dB
PL12                 7.04 dB
PL13                22.00 dB
SFO2          499.9221551 MHz

F2 - Processing parameters
SI                 131072
SF            125.7049840 MHz
WDW                    EM
SSB                     0
LB                   0.75 Hz
GB                      0
PC                   2.00
```

```
00 QNP Probe 19F starting parameters. (revised
ical shifts relative to CFC13 at 0 ppm (082103
```



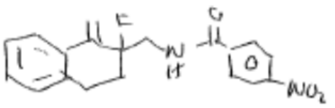
```
NAME          JW-07-167p1-F
EXPNO                     1
PROCNO                    1
Date_              20111118
Time                  16.49
INSTRUM             AVQ-400
PROBHD       5 mm QNP 1H/13
PULPROG              zgflqn
TD                   131072
SOLVENT               CDCl3
NS                       32
DS                        0
SWH               90090.094 Hz
FIDRES             0.687333 Hz
AQ                0.7275051 sec
RG                   5792.6
DW                    5.550 usec
DE                     6.00 usec
TE                    293.3 K
D1               1.00000000 sec
TD0                       4

======== CHANNEL f1 ========
NUC1                    19F
P1                    16.00 usec
PL1                   -3.00 dB
PL1W            20.04748917 W
SFO1            376.4607042 MHz
SI                    65536
SF              376.4980736 MHz
WDW                      EM
SSB                       0
LB                     2.00 Hz
GB                        0
PC                     4.00
```

JW-08-35p

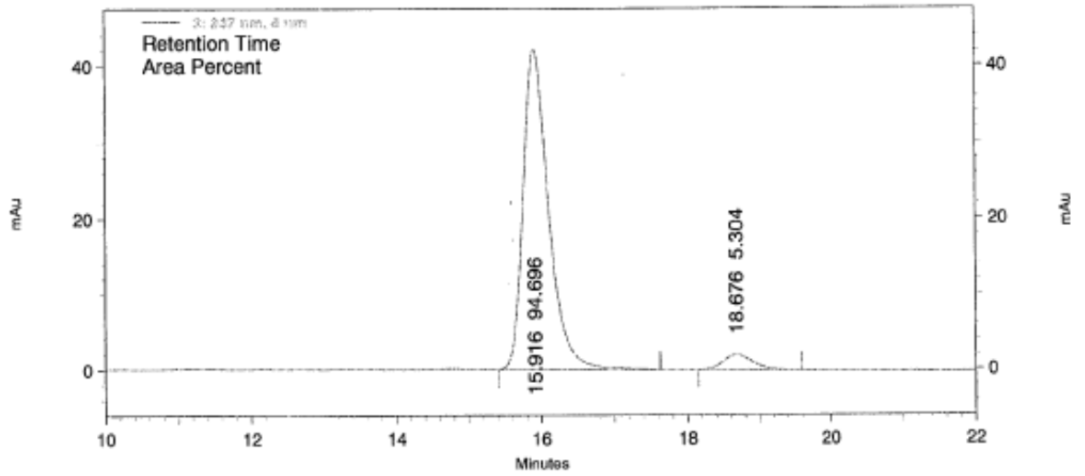


2: 236 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	16.016	47.799	208
2	18.868	52.201	208

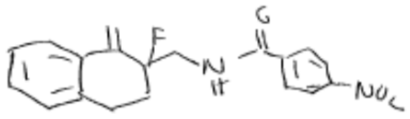


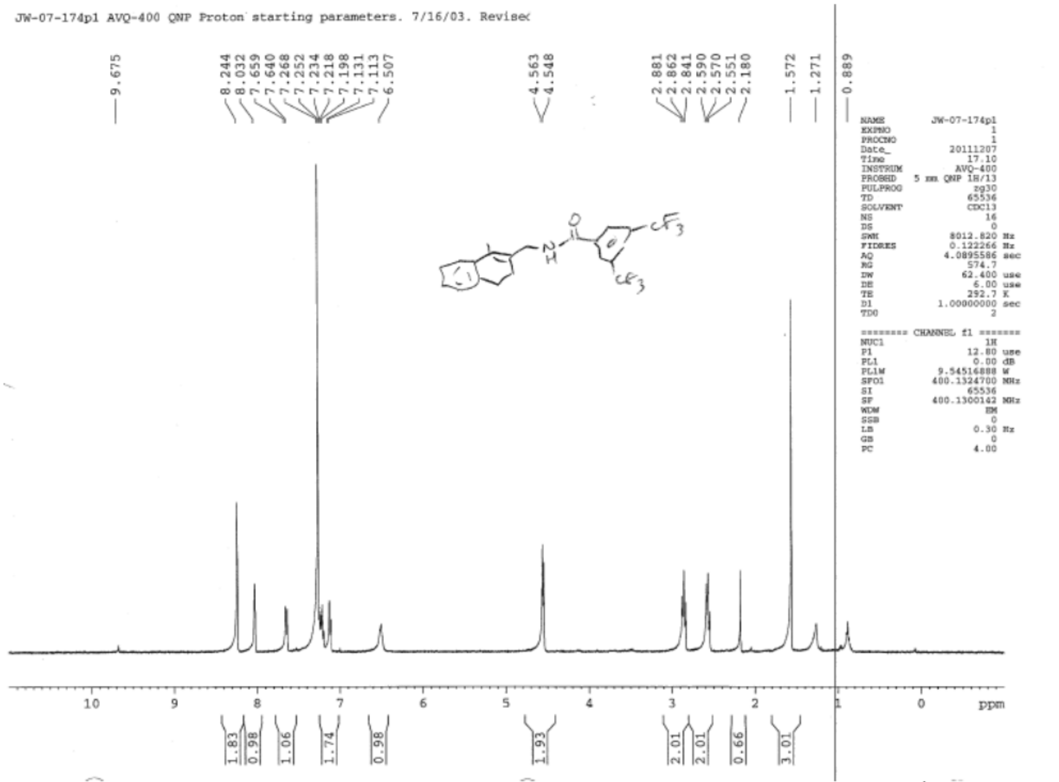
JW-08-35p

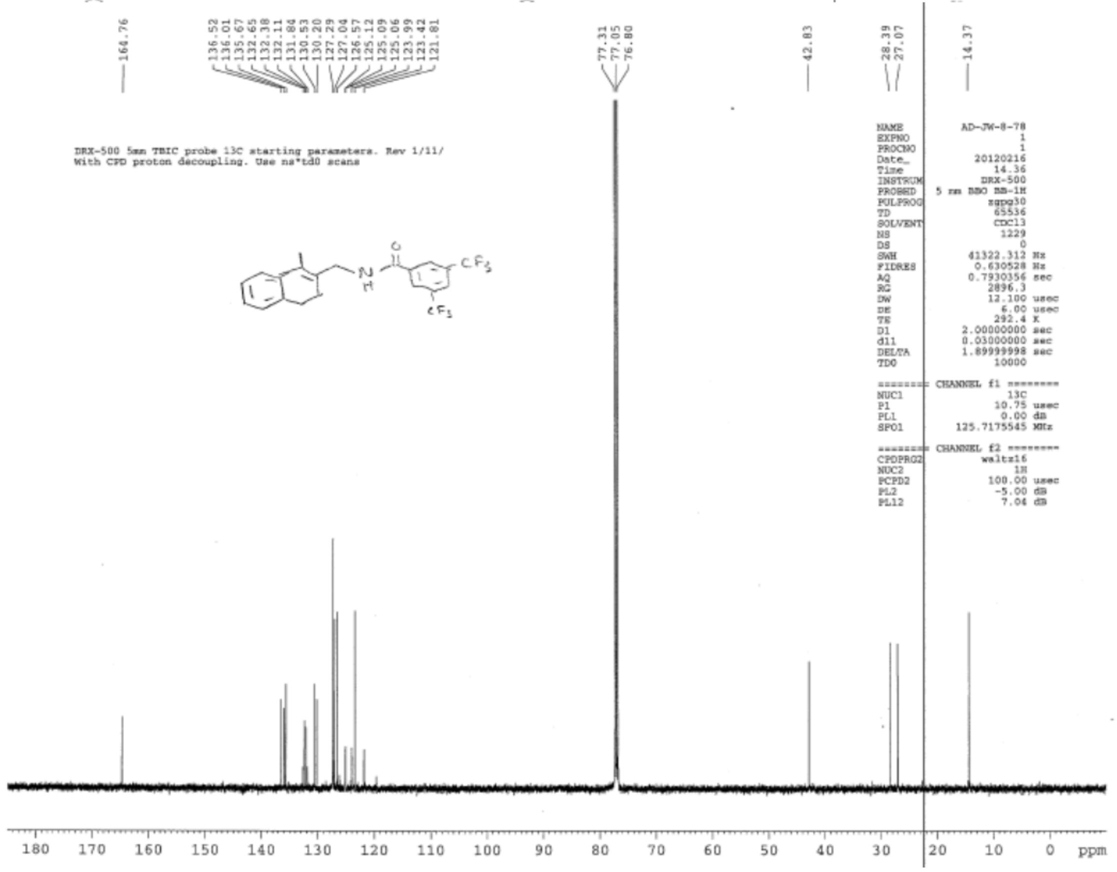


3: 247 nm, 4 nm
Results

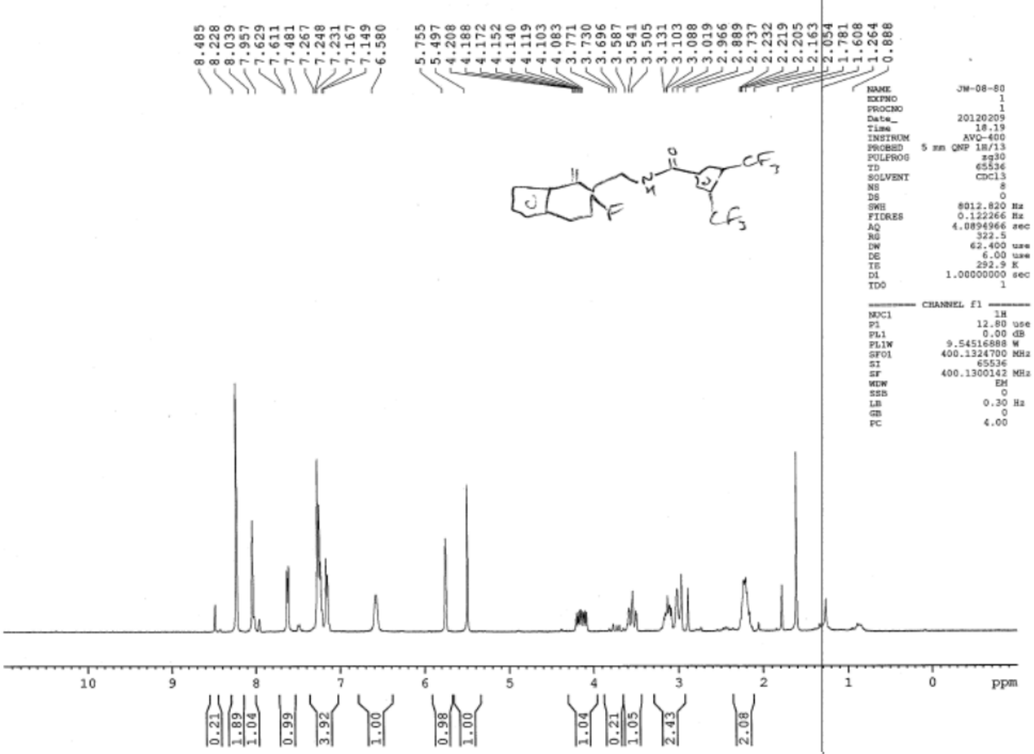
Pk #	Retention Time	Area Percent	Lambda Max
1	15.916	94.696	208
2	18.676	5.304	206




JW-07-174p1 AVQ-400 QNP Proton starting parameters. 7/16/03. Revise(
9.675
8.244
8.032
7.659
7.640
7.268
7.252
7.234
7.218
7.198
7.131
7.113
6.507
4.563
4.548
2.881
2.862
2.841
2.590
2.570
2.551
2.180
1.572
1.271
0.889
NAME JW-07-174p1
EXPNO 1
PROCNO 1
Date_ 20111207
Time 17.10
INSTRUM AVQ-400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0895586 sec
RG 574.7
DW 62.400 use
DE 6.00 use
TE 292.7 K
D1 1.00000000 sec
TD0 2
======== CHANNEL f1 =======
NUC1 1H
P1 12.80 use
PL1 0.00 dB
PL1W 9.54516888 W
SFO1 400.1324700 MHz
SI 65536
SF 400.1300142 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
O
N
H
CF3
CF3
10
9
8
7
6
5
4
3
2
1
0
ppm
1.83
0.98
1.06
1.74
0.98
1.93
2.01
2.01
0.66
3.01

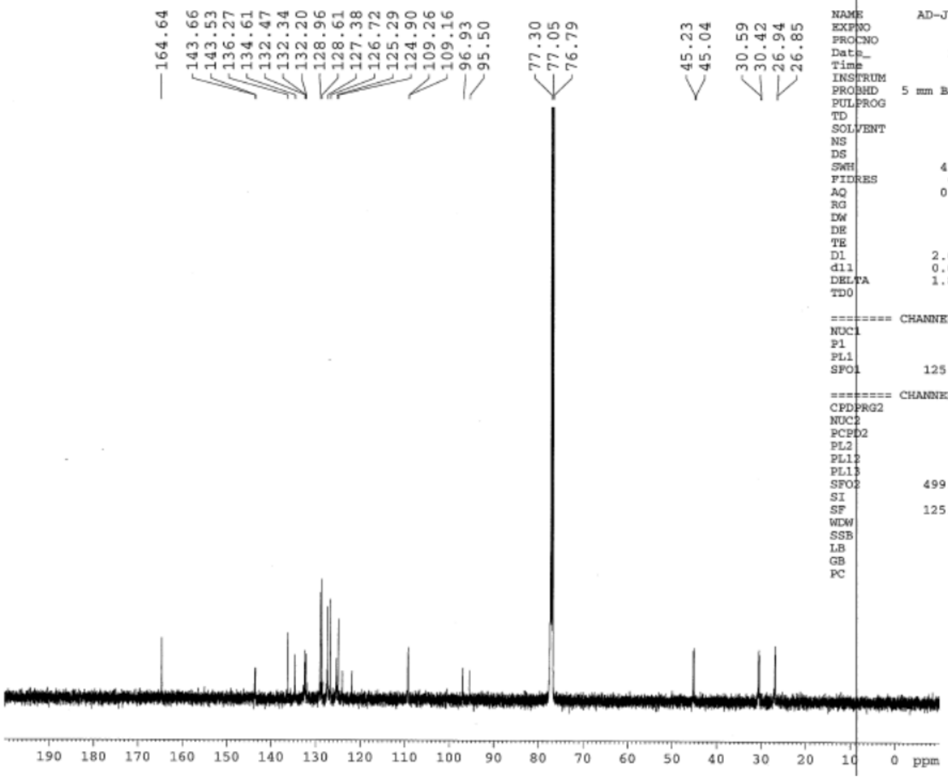

164.76
136.52
136.01
135.67
132.65
132.38
132.11
131.84
130.53
130.20
127.29
127.04
126.57
125.12
125.09
125.06
123.99
123.42
121.81
77.31
77.05
76.80
42.83
28.39
27.07
14.37
DRX-500 5mm TBIC probe 13C starting parameters. Rev 1/11/
With CPD proton decoupling. Use ns*td0 scans
O
N
H
CF3
CF3
NAME AD-JW-8-78
EXPNO 1
PROCNO 1
Date_ 20120216
Time 14.36
INSTRUM DRX-500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1229
DS 0
SWH 41322.312 Hz
FIDRES 0.630528 Hz
AQ 0.7930356 sec
RG 2896.3
DW 12.100 usec
DE 6.00 usec
TE 292.4 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 10000
======== CHANNEL f1 ========
NUC1 13C
P1 10.75 usec
PL1 0.00 dB
SFO1 125.7175545 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -5.00 dB
PL12 7.04 dB
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN

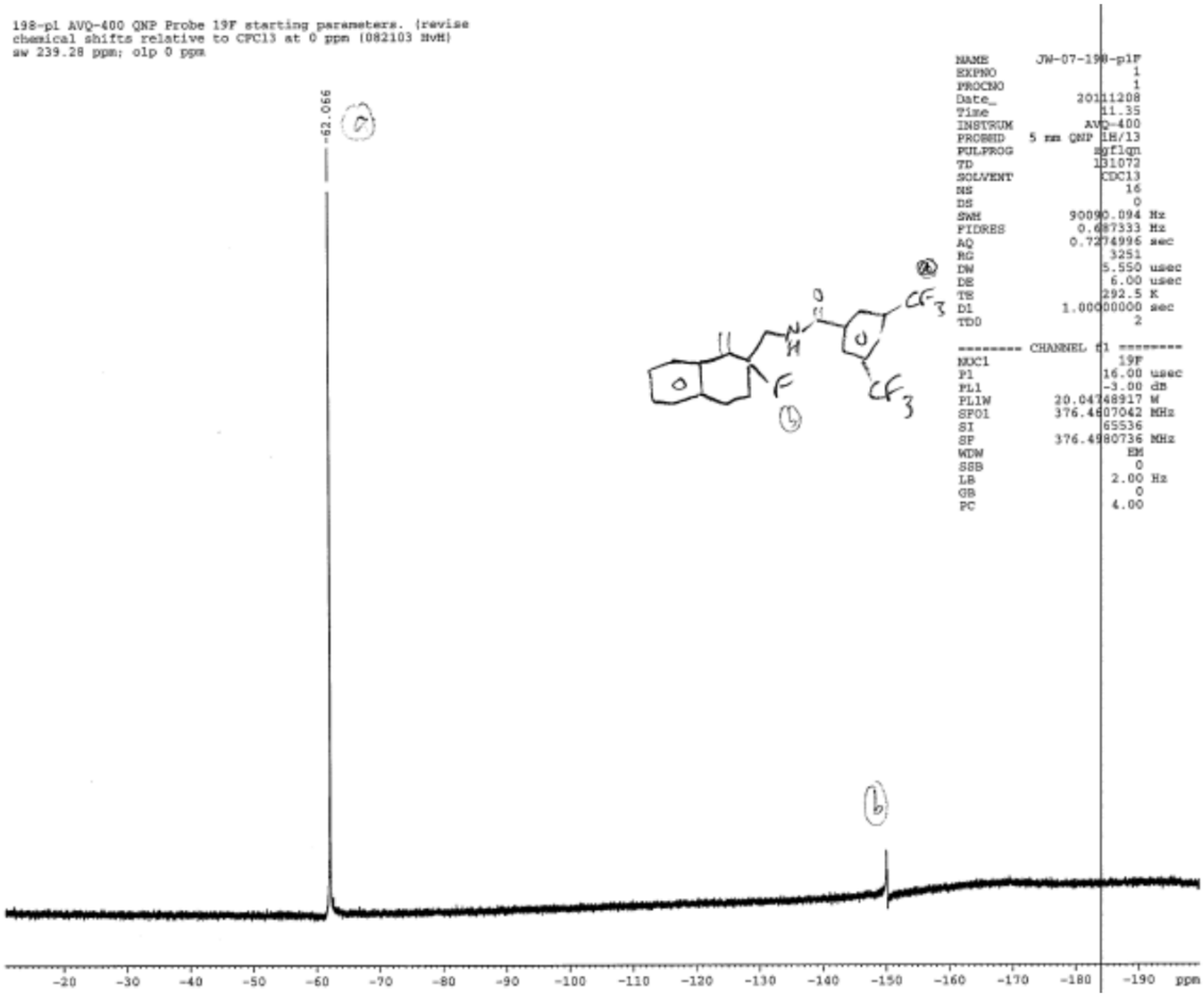


```
NAME              JW-08-80
EXPNO                    1
PROCNO                   1
Date_             20120209
Time                 18.19
INSTRUM            AVQ-400
PROBHD    5 mm QNP 1H/13
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   322.5
DW                  62.400 use
DE                    6.00 use
TE                   292.9 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.80 use
PL1                   0.00 dB
PL1W            9.54516888 W
SFO1         400.1324700 MHz
SI                   65536
SF           400.1300142 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00
```

DRX-500 5mm TBIC probe 13C starting parameters. Rev 1
With CPD proton decoupling. Use ns*td0 scans



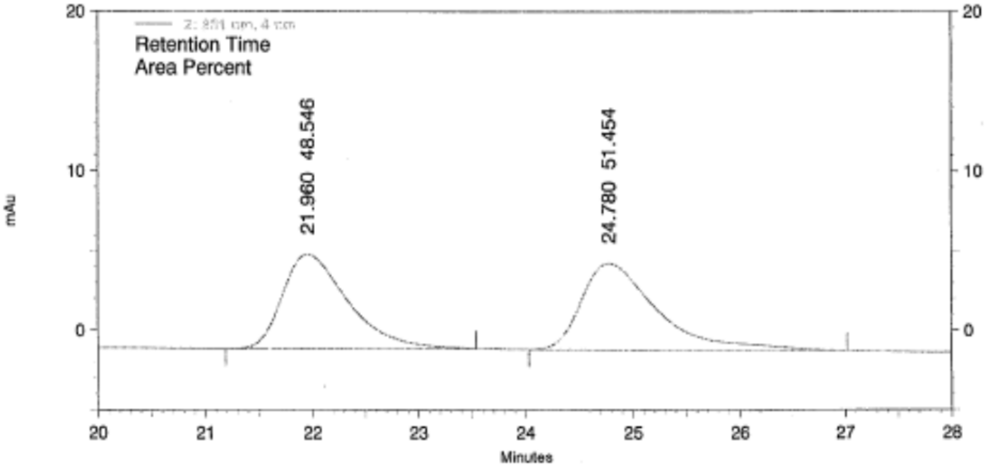
```
NAME          AD-JW-80-CF3
EXPNO                    1
PROCNO                   1
Date_             20120210
Time                 14.05
INSTRUM            DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1099
DS                       0
SWH             41322.312 Hz
FIDRES           0.630528 Hz
AQ              0.7930477 sec
RG                    8192
DW                  12.100 use
DE                    6.00 use
TE                   293.4 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                  10000

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.75 use
PL1                   0.00 dB
SFO1         125.7175545 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 use
PL2                  -5.00 dB
PL12                  7.04 dB
PL13                 22.00 dB
SFO2         499.9221551 MHz
SI                  131072
SF           125.7049840 MHz
WDW                     EM
SSB                      0
LB                    0.75 Hz
GB                       0
PC                    2.40
```



```
198-pl AVQ-400 QNP Probe 19F starting parameters. (revise
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; olp 0 ppm
```

```
NAME        JW-07-198-p1F
EXPNO                   1
PROCNO                  1
Date_            20111208
Time                11.35
INSTRUM           AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG           zgflqn
TD                131072
SOLVENT            CDCl3
NS                     16
DS                      0
SWH           90090.094 Hz
FIDRES         0.687333 Hz
AQ            0.7274996 sec
RG                   3251
DW                  5.550 usec
DE                   6.00 usec
TE                  292.5 K
D1            1.00000000 sec
TD0                     2

======== CHANNEL f1 ========
NUC1                  19F
P1                  16.00 usec
PL1                 -3.00 dB
PL1W          20.04748917 W
SFO1          376.4607042 MHz
SI                  65536
SF            376.4980736 MHz
WDW                    EM
SSB                     0
LB                   2.00 Hz
GB                      0
PC                   4.00
```

JW-08-80rac

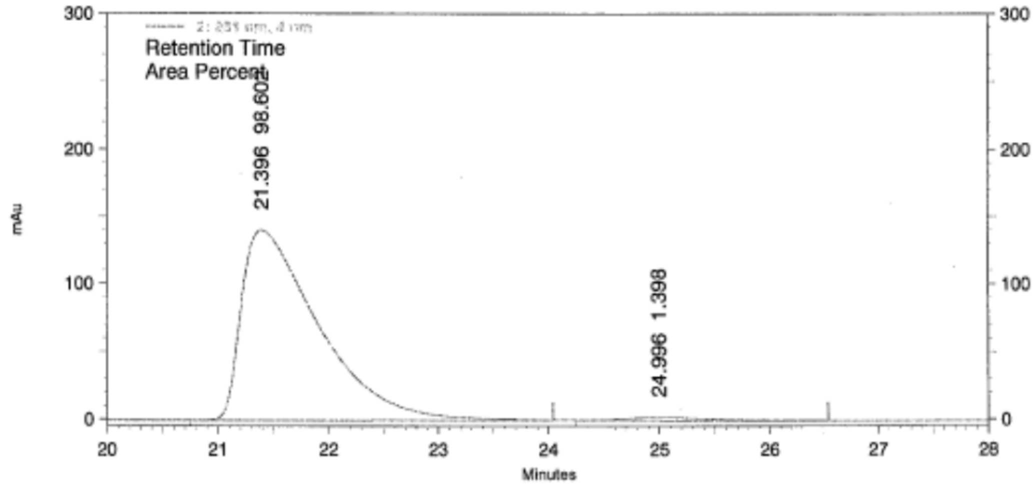


2: 251 nm, 4 nm

Results

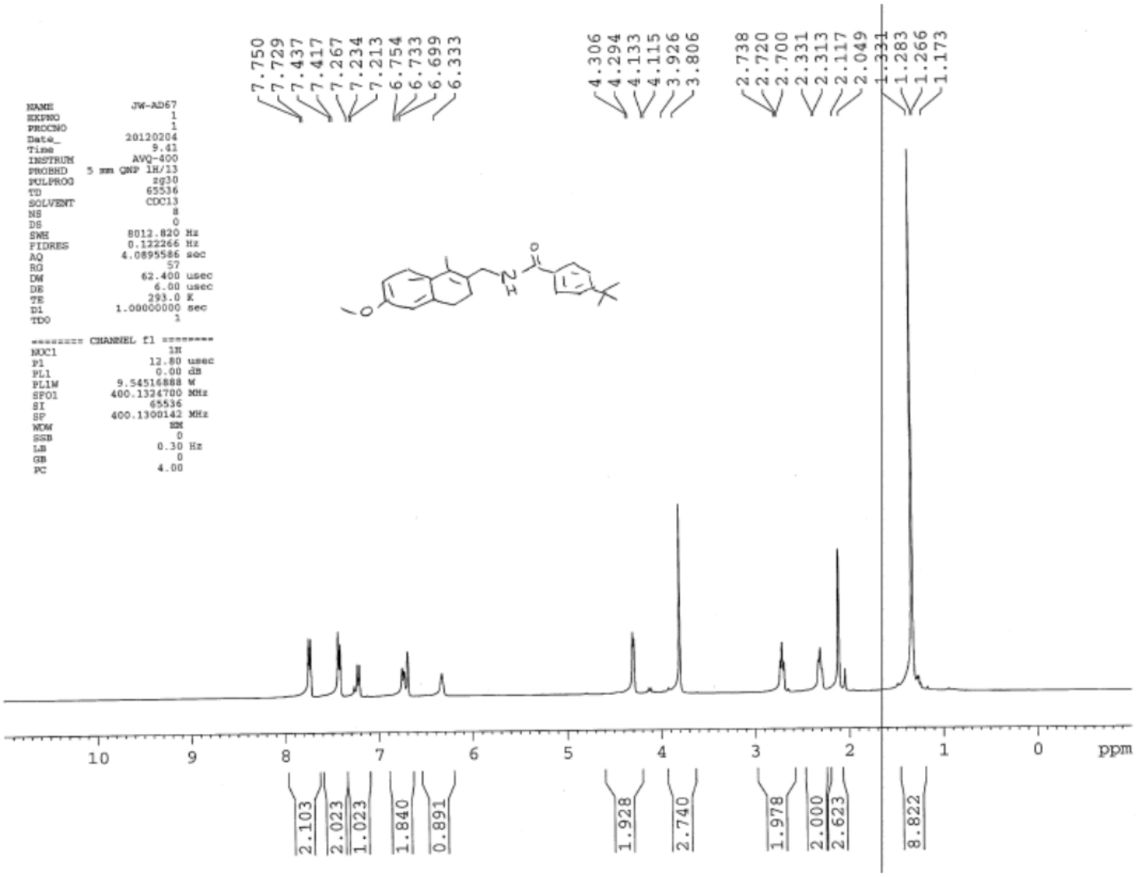
Pk #	Retention Time	Area Percent	Lambda Max
1	21.960	48.546	213
2	24.780	51.454	213

JW-08-80rep-IB9901-30min



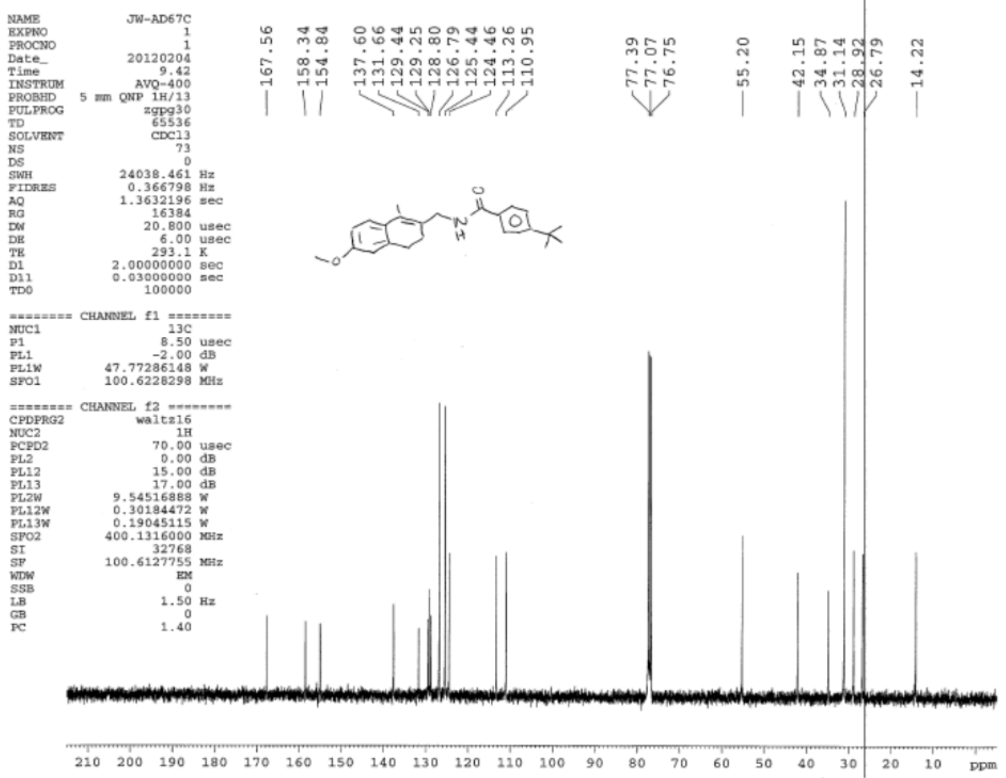
2: 251 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	21.396	98.602	209
2	24.996	1.398	214



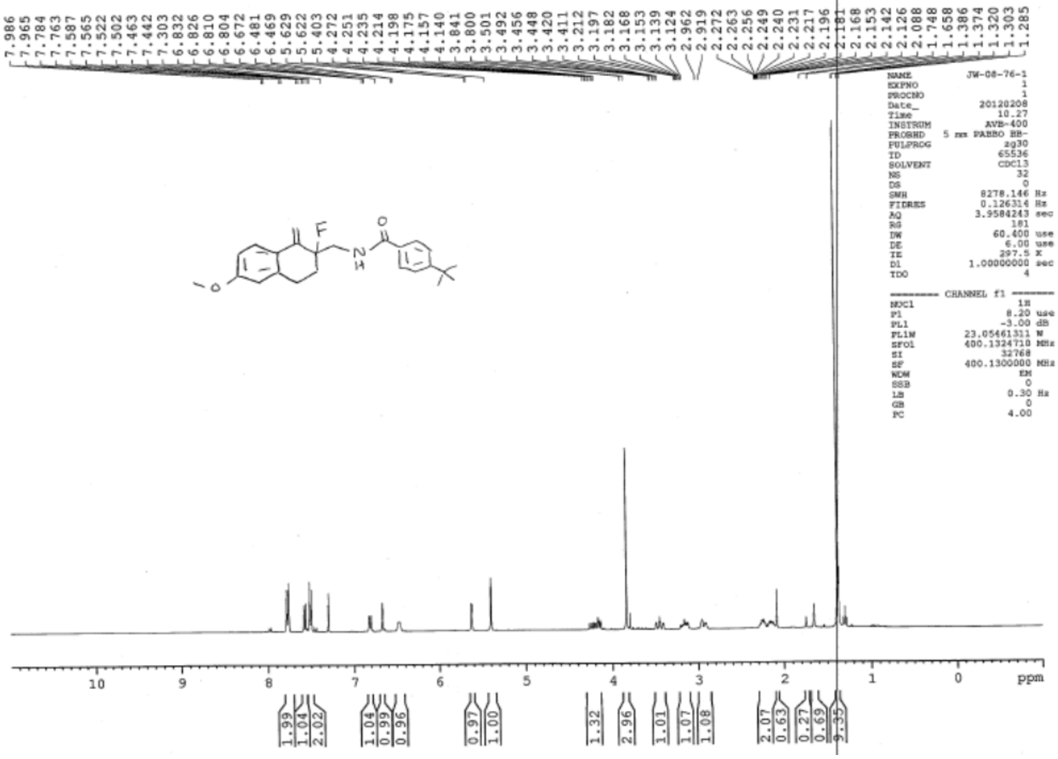
```
NAME          JW-AD67
EXPNO               1
PROCNO              1
Date_        20120204
Time             9.41
INSTRUM       AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG          zg30
TD              65536
SOLVENT         CDCl3
NS                  8
DS                  0
SWH          8012.820 Hz
FIDRES       0.122266 Hz
AQ          4.0895586 sec
RG                 57
DW             62.400 usec
DE               6.00 usec
TE              293.0 K
D1         1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               1H
P1              12.80 usec
PL1              0.00 dB
PL1W       9.54516888 W
SFO1      400.1324700 MHz
SI              65536
SF        400.1300142 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               4.00
```

JW-AD 67 AVQ-400 QNP Carbon Starting parameters 7/16

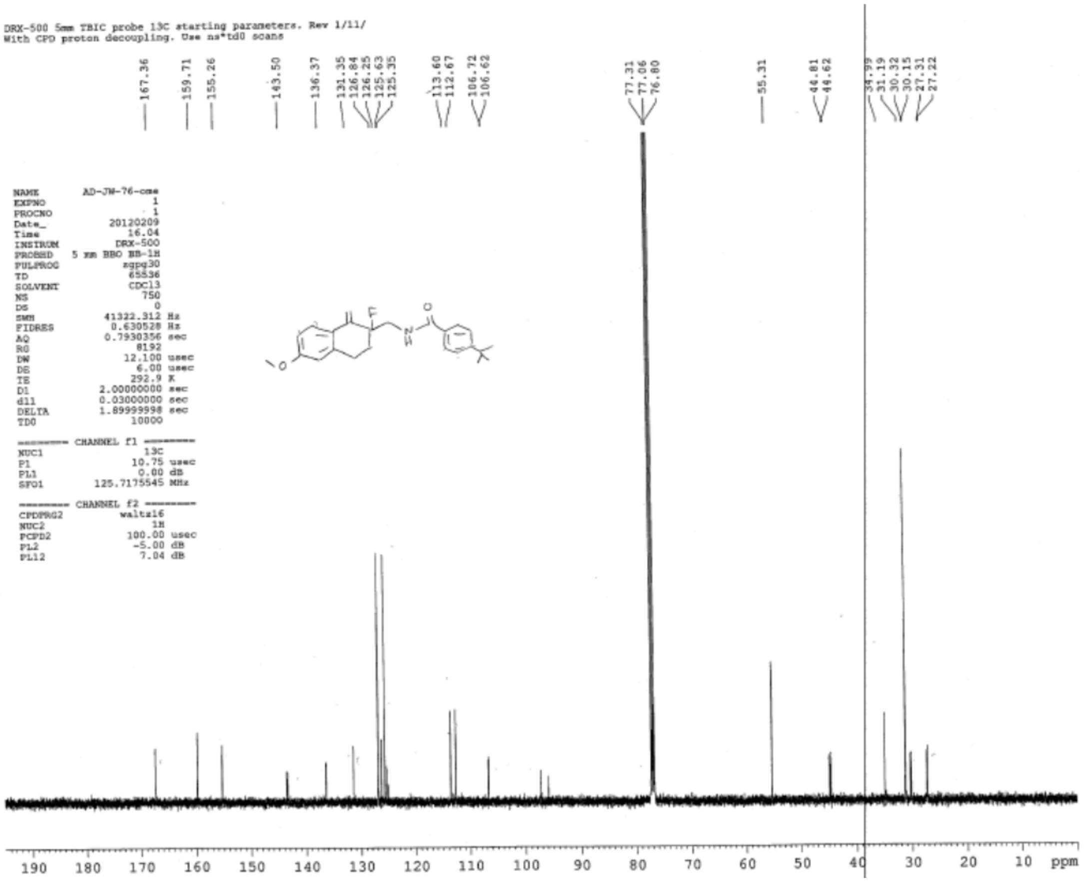


```
NAME          JW-AD67C
EXPNO                1
PROCNO               1
Date_         20120204
Time              9.42
INSTRUM        AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  73
DS                   0
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3632196 sec
RG               16384
DW              20.800 usec
DE                6.00 usec
TE               293.1 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0             100000

======== CHANNEL f1 ========
NUC1               13C
P1                8.50 usec
PL1              -2.00 dB
PL1W       47.77286148 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            70.00 usec
PL2               0.00 dB
PL12             15.00 dB
PL13             17.00 dB
PL2W        9.54516888 W
PL12W       0.30184472 W
PL13W       0.19045115 W
SFO2       400.1316000 MHz
SI               32768
SF         100.6127755 MHz
WDW                 EM
SSB                  0
LB                1.50 Hz
GB                   0
PC                1.40
```

JW-08-76-1 AVB-400 ZBO Proton starting parameters. 6/11/03 RN

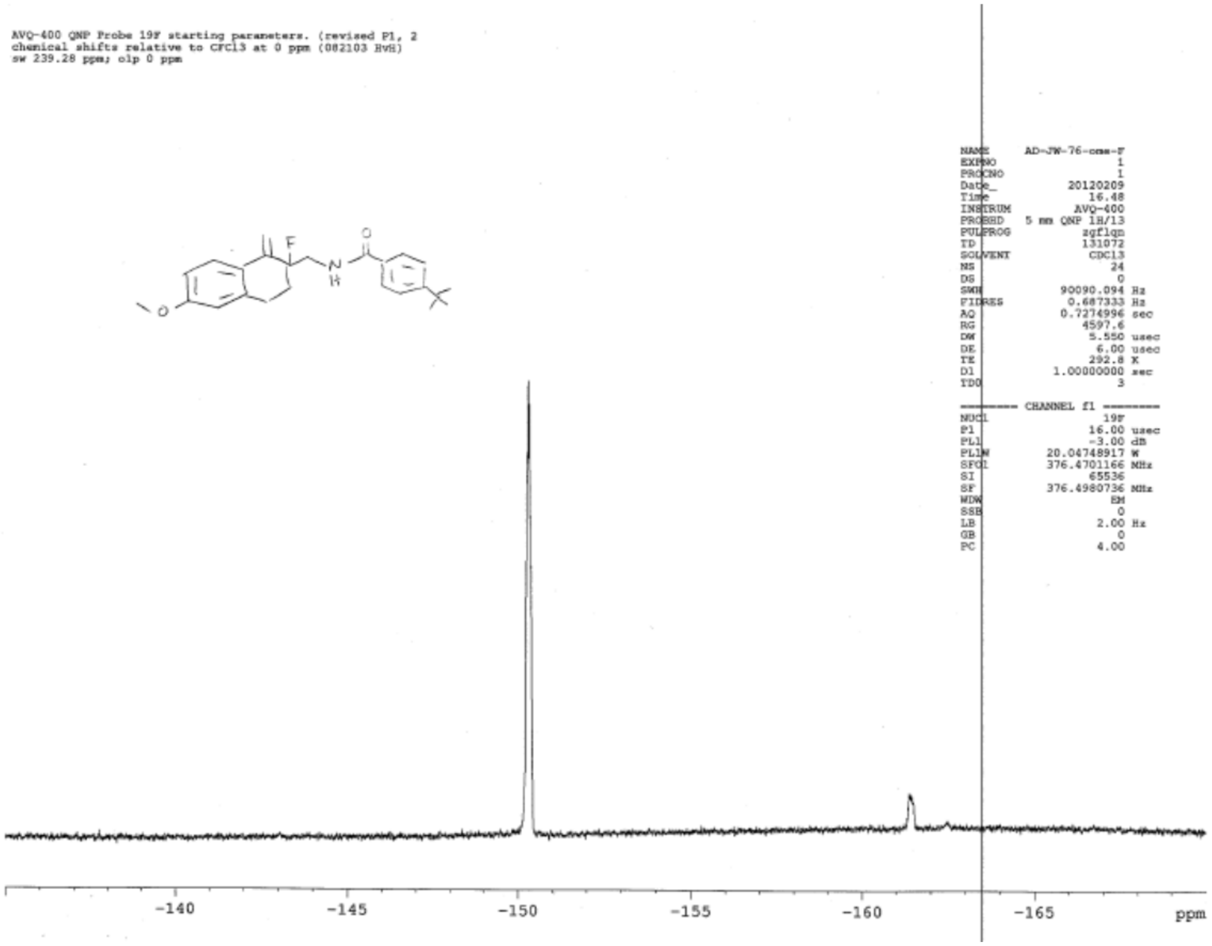


```
NAME         JW-08-76-1
EXPNO                 1
PROCNO                1
Date_          20120208
Time              10.27
INSTRUM         AVB-400
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    0
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                  181
DW               60.400 use
DE                 6.00 use
TE                297.5 K
D1           1.00000000 sec
TD0                   4

======== CHANNEL f1 ========
NUC1                 1H
P1                 8.20 use
PL1               -3.00 dB
PL1W        23.05461311 W
SFO1        400.1324710 MHz
SI                32768
SF          400.1300000 MHz
WDM                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 4.00
```



```
DRX-500 5mm TBIC probe 13C starting parameters. Rev 1/11/
With CPD proton decoupling. Use ns*td0 scans
```

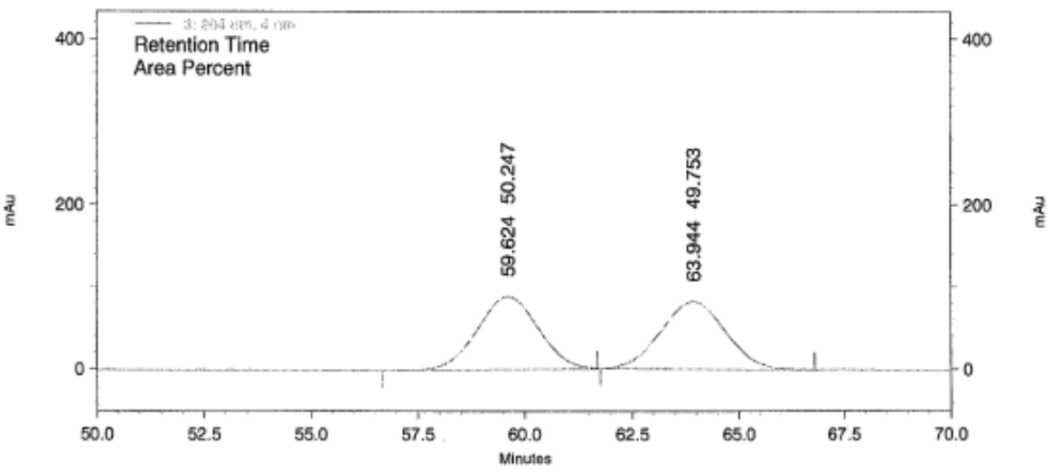
```
NAME          AD-JW-76-ome
EXPNO                    1
PROCNO                   1
Date_             20120209
Time                 16.04
INSTRUM            DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     750
DS                       0
SWH              41322.312 Hz
FIDRES            0.630528 Hz
AQ               0.7930356 sec
RG                    8192
DW                  12.100 usec
DE                    6.00 usec
TE                   292.9 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                  10000

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.75 usec
PL1                   0.00 dB
SFO1           125.7175545 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                  -5.00 dB
PL12                  7.04 dB
```



AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; olp 0 ppm

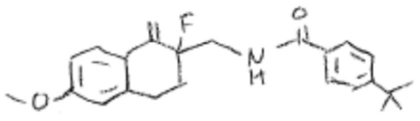
```
NAME       AD-JW-76-cms-F
EXPNO                   1
PROCNO                  1
Date_            20120209
Time                16.48
INSTRUM           AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG            zgflqn
TD                 131072
SOLVENT             CDCl3
NS                     24
DS                      0
SWH             90090.094 Hz
FIDRES           0.687333 Hz
AQ              0.7274996 sec
RG                 4597.6
DW                  5.550 usec
DE                   6.00 usec
TE                  292.8 K
D1             1.00000000 sec
TD0                     3

======== CHANNEL f1 ========
NUC1                  19F
P1                  16.00 usec
PL1                 -3.00 dB
PL1W          20.04748917 W
SFO1          376.4701166 MHz
SI                  65536
SF            376.4980736 MHz
WDW                    EM
SSB                     0
LB                   2.00 Hz
GB                      0
PC                   4.00
```

AD-2-68rac-ic9604-70min

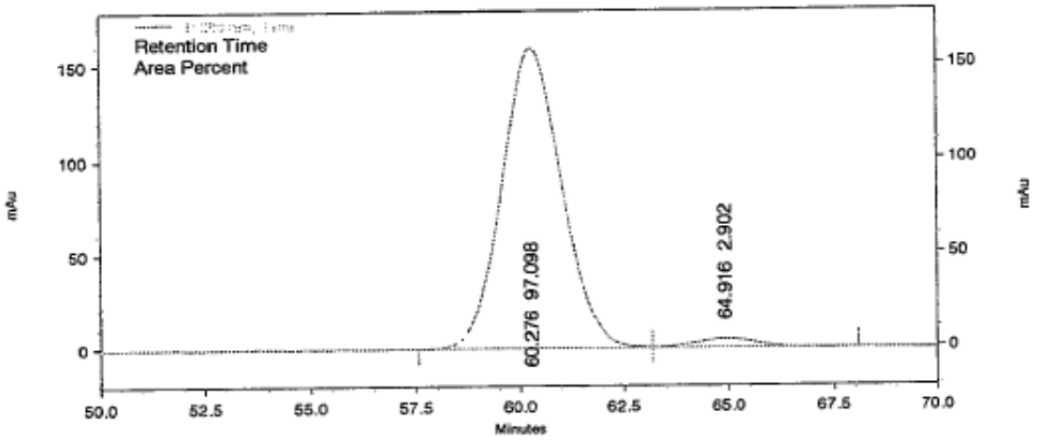


3: 204 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	59.624	50.247	204
2	63.944	49.753	204

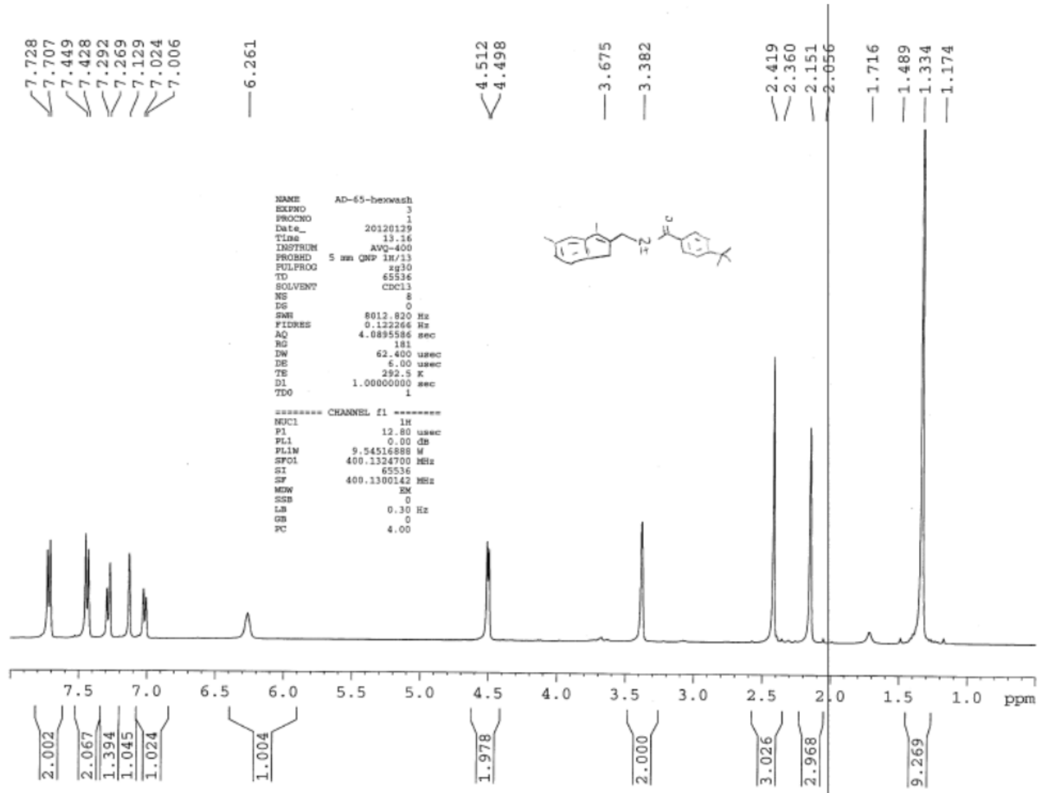


JW-08-76

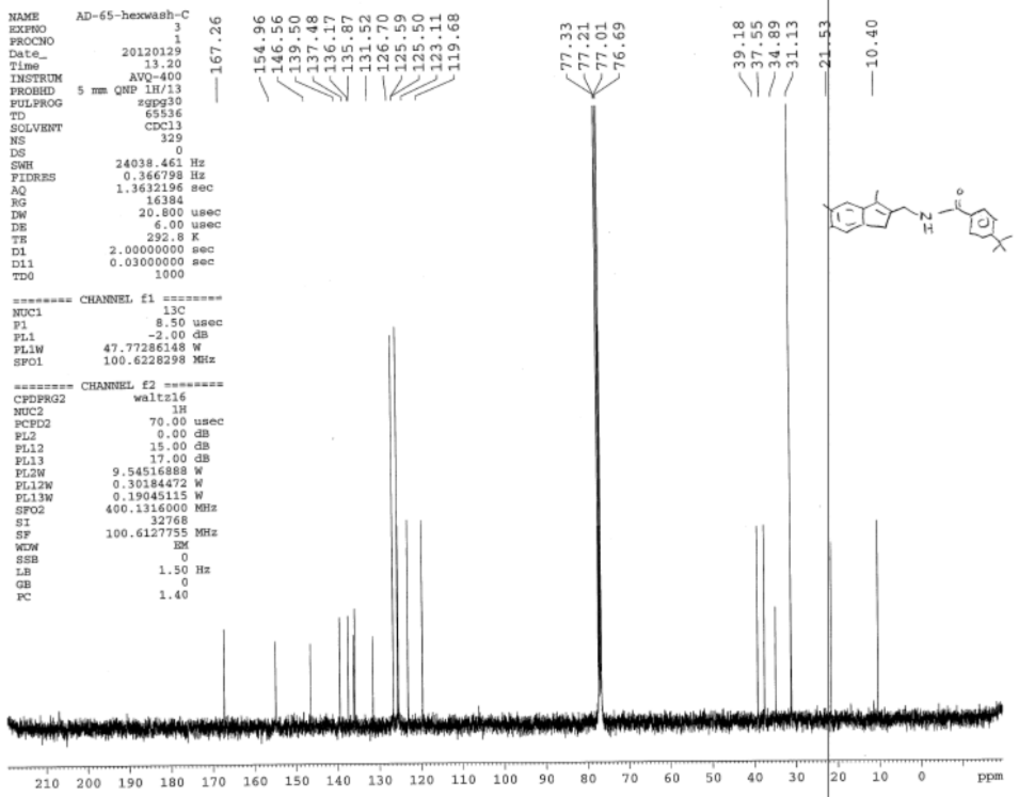


1: 208 nm, 4 nm
Results

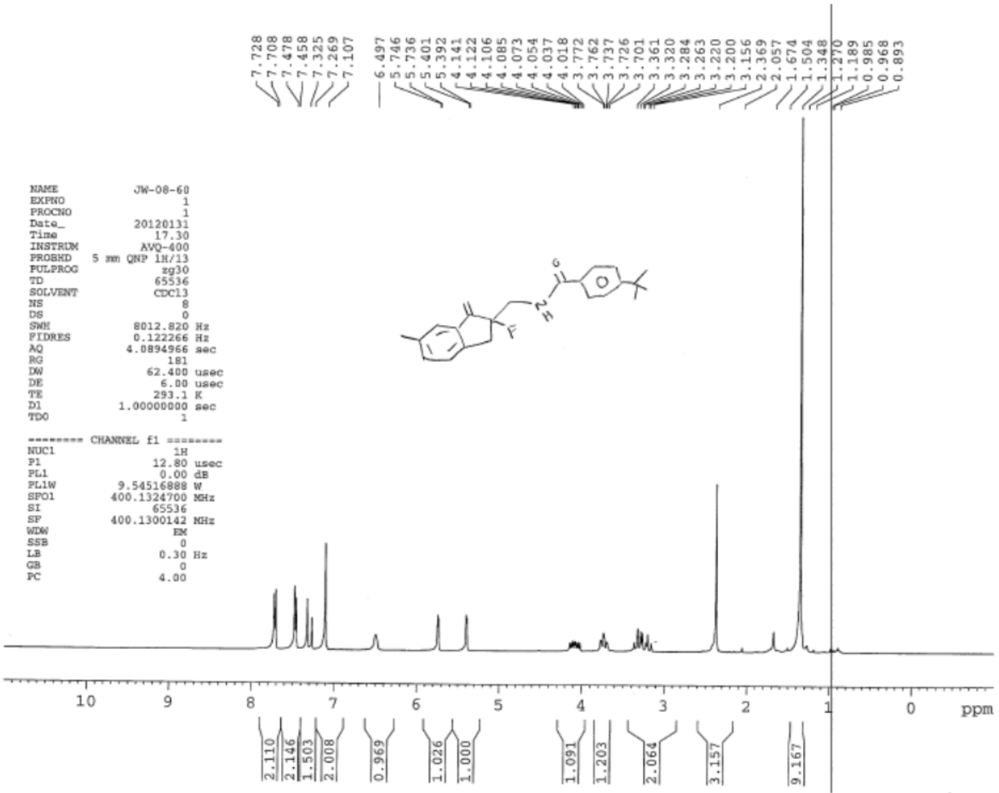
Pk #	Retention Time	Area Percent	Lambda Max
1	60.276	97.098	203
2	64.916	2.902	204



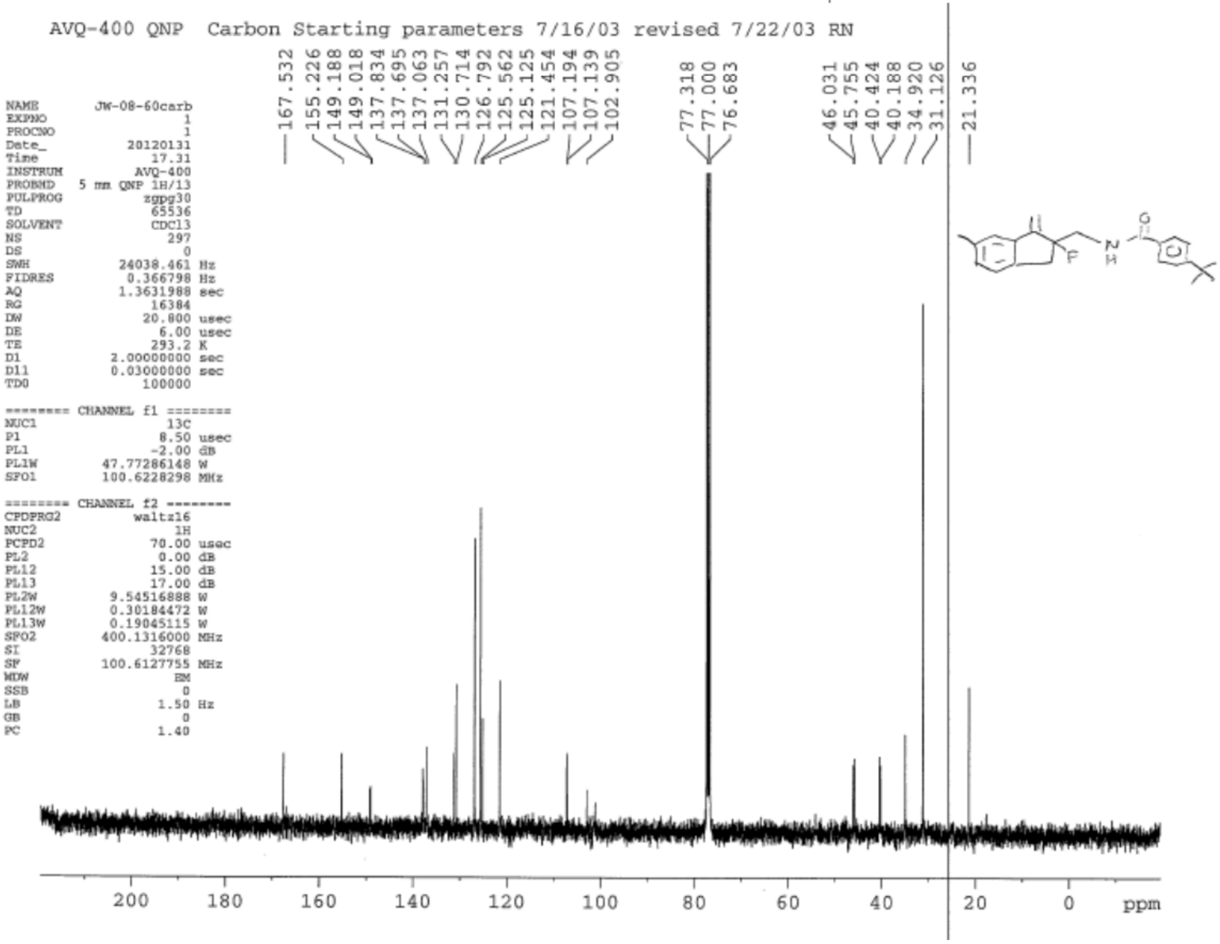
```
NAME          AD-65-hexwash
EXPNO                     3
PROCNO                    1
Date_              20120129
Time                  13.16
INSTRUM            AVQ-400
PROBHD     5 mm QNP 1H/13
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        0
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                4.0895586 sec
RG                      181
DW                   62.400 usec
DE                     6.00 usec
TE                    292.5 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    12.80 usec
PL1                    0.00 dB
PL1W             9.54516888 W
SFO1            400.1324700 MHz
SI                    65536
SF              400.1300142 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     4.00
```



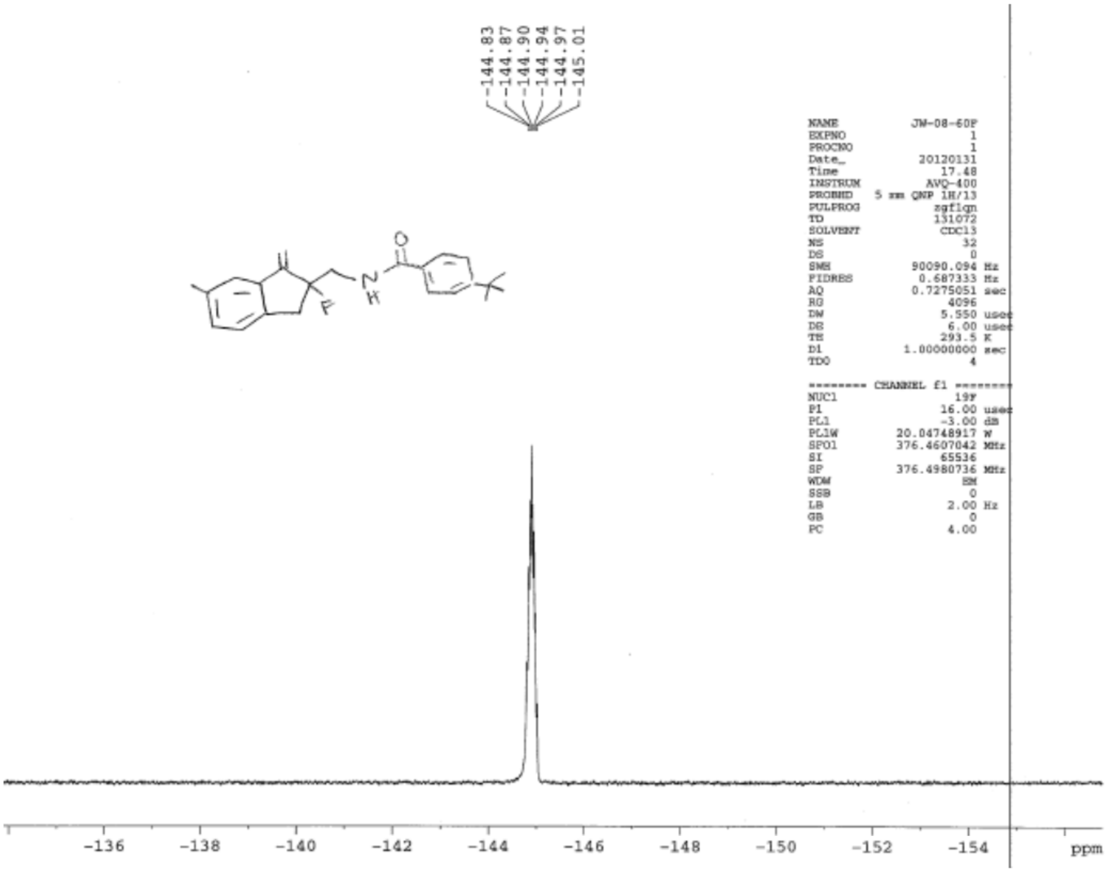
```
NAME          AD-65-hexwash-C
EXPNO                      3
PROCNO                     1
Date_               20120129
Time                   13.20
INSTRUM              AVQ-400
PROBHD      5 mm QNP 1H/13
PULPROG              zgpg30
TD                     65536
SOLVENT                CDCl3
NS                       329
DS                         0
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                 1.3632196 sec
RG                     16384
DW                    20.800 usec
DE                      6.00 usec
TE                     292.8 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                     1000

======== CHANNEL f1 ========
NUC1                     13C
P1                      8.50 usec
PL1                    -2.00 dB
PL1W             47.77286148 W
SFO1             100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                  70.00 usec
PL2                     0.00 dB
PL12                   15.00 dB
PL13                   17.00 dB
PL2W              9.54516888 W
PL12W             0.30184472 W
PL13W             0.19045115 W
SFO2             400.1316000 MHz
SI                     32768
SF               100.6127755 MHz
WDW                       EM
SSB                        0
LB                      1.50 Hz
GB                         0
PC                      1.40
```



```
NAME           JW-08-60
EXPNO                 1
PROCNO                1
Date_          20120131
Time              17.30
INSTRUM         AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                  181
DW               62.400 usec
DE                 6.00 usec
TE                293.1 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                12.80 usec
PL1                0.00 dB
PL1W         9.54516888 W
SFO1        400.1324700 MHz
SI                65536
SF          400.1300142 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 4.00
```

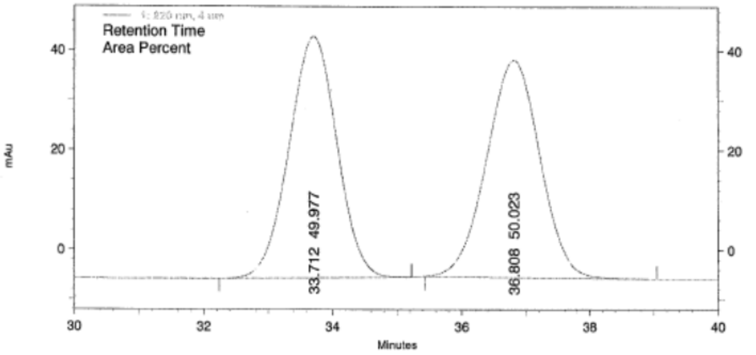

AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7/22/03 RN

```
NAME       JW-08-60carb
EXPNO                 1
PROCNO                1
Date_          20120131
Time              17.31
INSTRUM         AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  297
DS                    0
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                16384
DW               20.800 usec
DE                 6.00 usec
TE                293.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0              100000

======== CHANNEL f1 ========
NUC1                13C
P1                 8.50 usec
PL1               -2.00 dB
PL1W        47.77286148 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             70.00 usec
PL2                0.00 dB
PL12              15.00 dB
PL13              17.00 dB
PL2W         9.54516888 W
PL12W        0.30184472 W
PL13W        0.19045115 W
SFO2        400.1316000 MHz
SI                32768
SF          100.6127755 MHz
WDW                  EM
SSB                   0
LB                 1.50 Hz
GB                    0
PC                 1.40
```



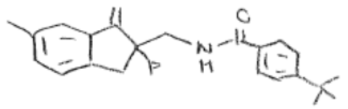
```
NAME          JW-08-60F
EXPNO                 1
PROCNO                1
Date_          20120131
Time              17.48
INSTRUM         AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG          zgflqn
TD               131072
SOLVENT           CDCl3
NS                   32
DS                    0
SWH           90090.094 Hz
FIDRES         0.687333 Hz
AQ            0.7275051 sec
RG                 4096
DW                5.550 use
DE                 6.00 use
TE                293.5 K
D1           1.00000000 sec
TD0                   4

======== CHANNEL f1 =======
NUC1                19F
P1                16.00 use
PL1               -3.00 dB
PL1W        20.04748917 W
SFO1        376.4607042 MHz
SI                65536
SF          376.4980736 MHz
WDW                  EM
SSB                   0
LB                 2.00 Hz
GB                    0
PC                 4.00
```

JW-08-60rac/ADII-66

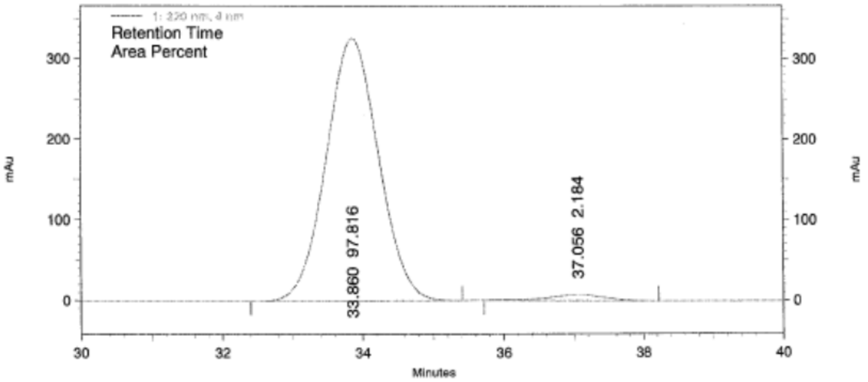


1: 220 nm, 4 nm
Results

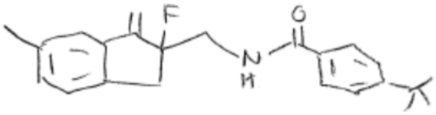
Pk #	Retention Time	Area Percent	Lambda Max
1	33.712	49.977	204
2	36.808	50.023	204

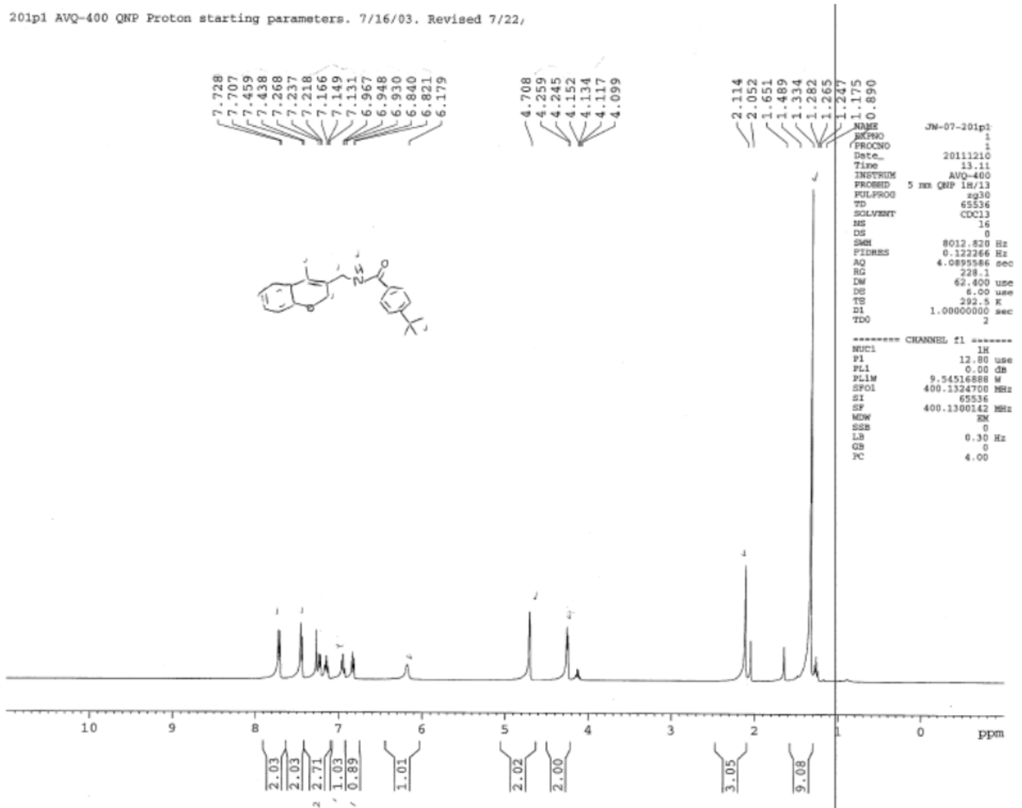


JW-08-60

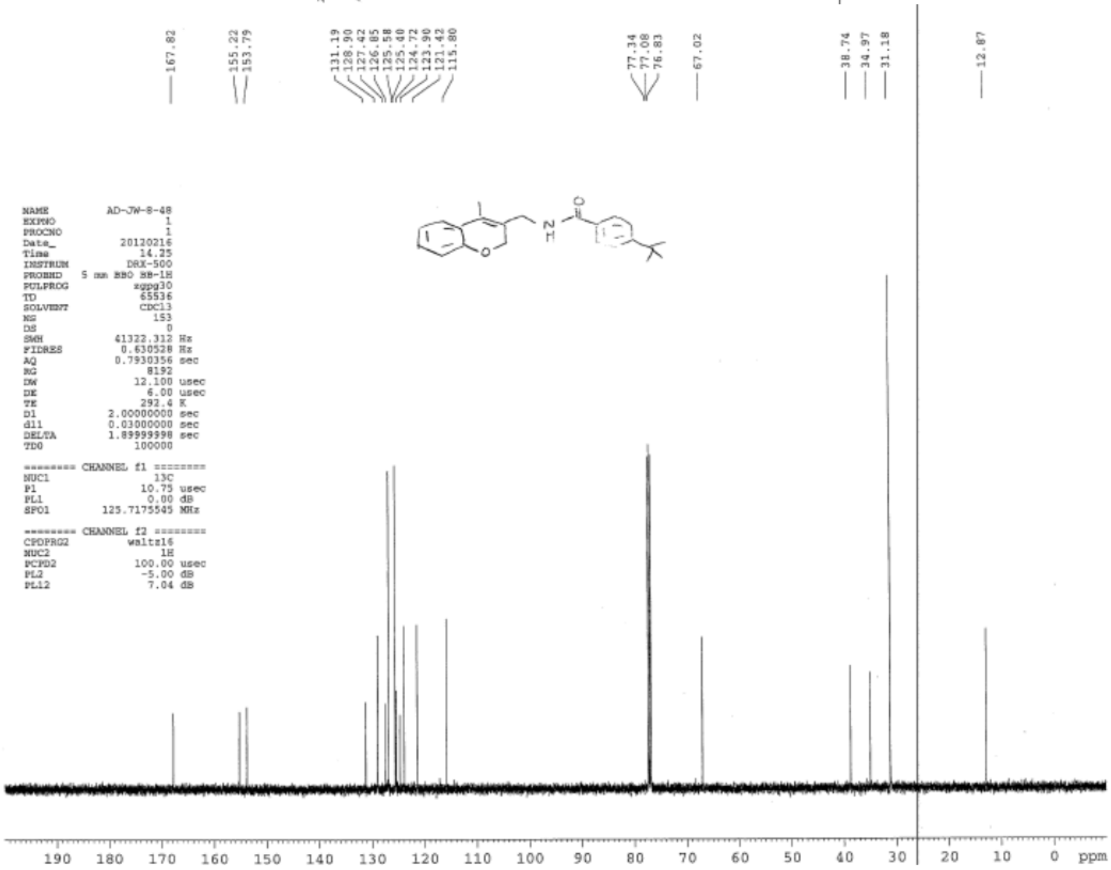


```
1: 220 nm, 4 nm
Results
                  Pk #       Retention Time         Area Percent         Lambda Max
                     1               33.860               97.816                202
                     2               37.056                2.184                204
```

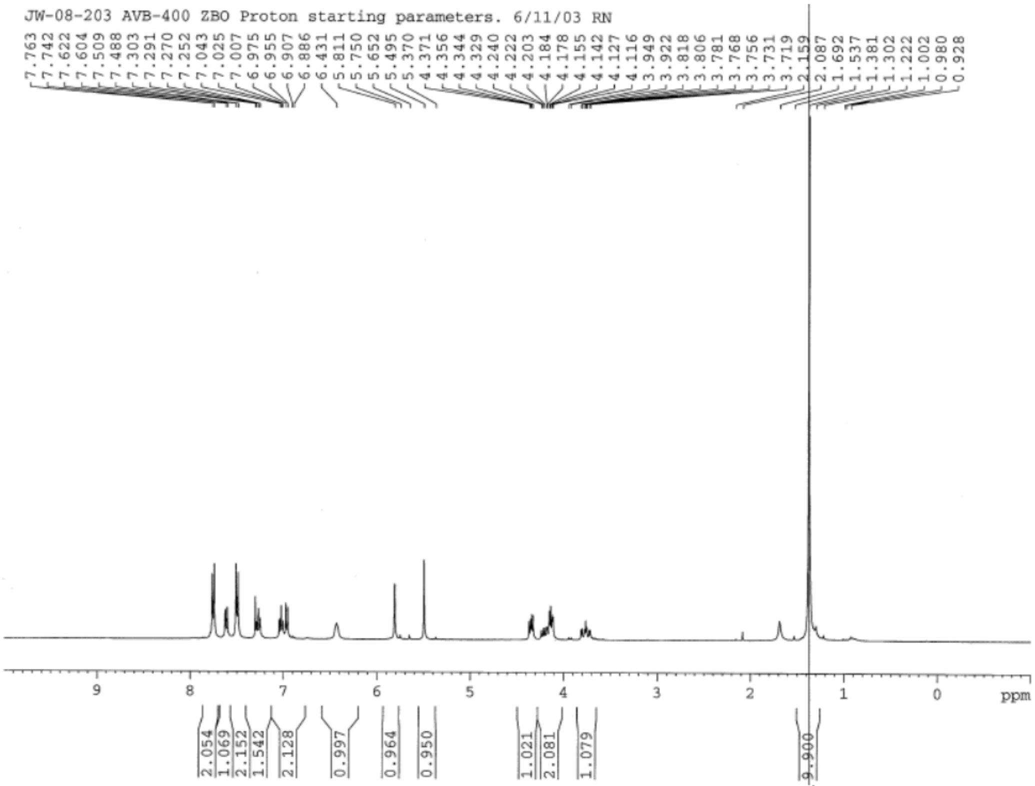


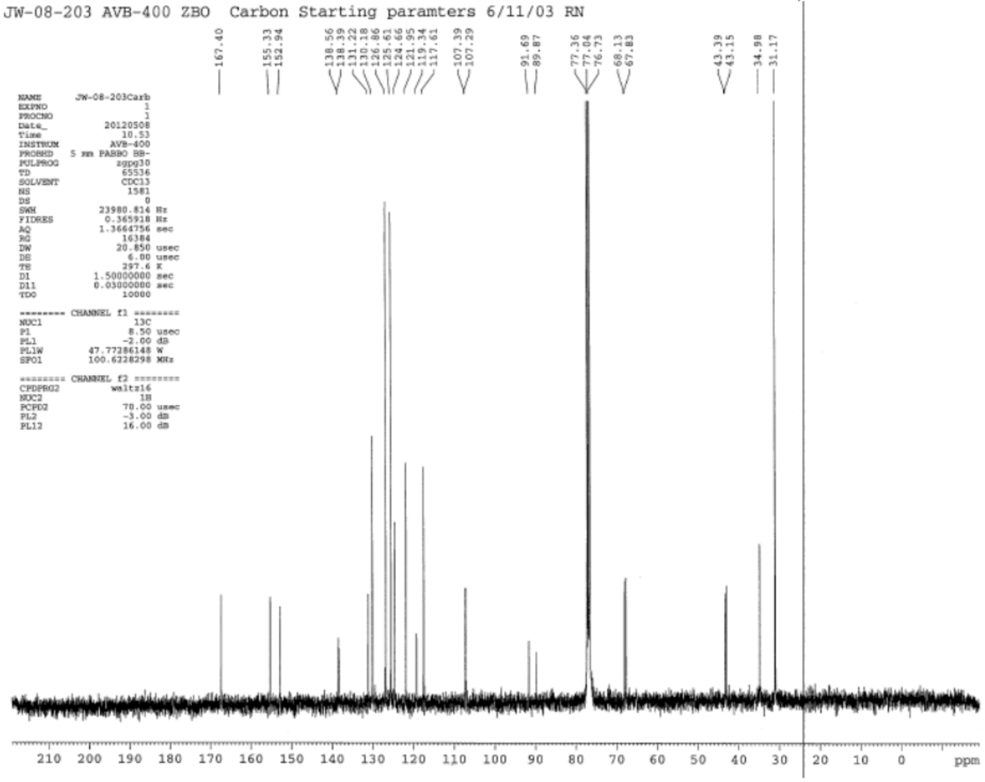


```
NAME          JW-07-201p1
EXPNO                   1
PROCNO                  1
Date_            20111210
Time                13.11
INSTRUM           AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0895586 sec
RG                  228.1
DW                 62.400 use
DE                   6.00 use
TE                  292.5 K
D1             1.00000000 sec
TD0                     2

======== CHANNEL f1 =======
NUC1                   1H
P1                  12.80 use
PL1                  0.00 dB
PL1W           9.54516888 W
SFO1          400.1324700 MHz
SI                  65536
SF            400.1300142 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   4.00
```

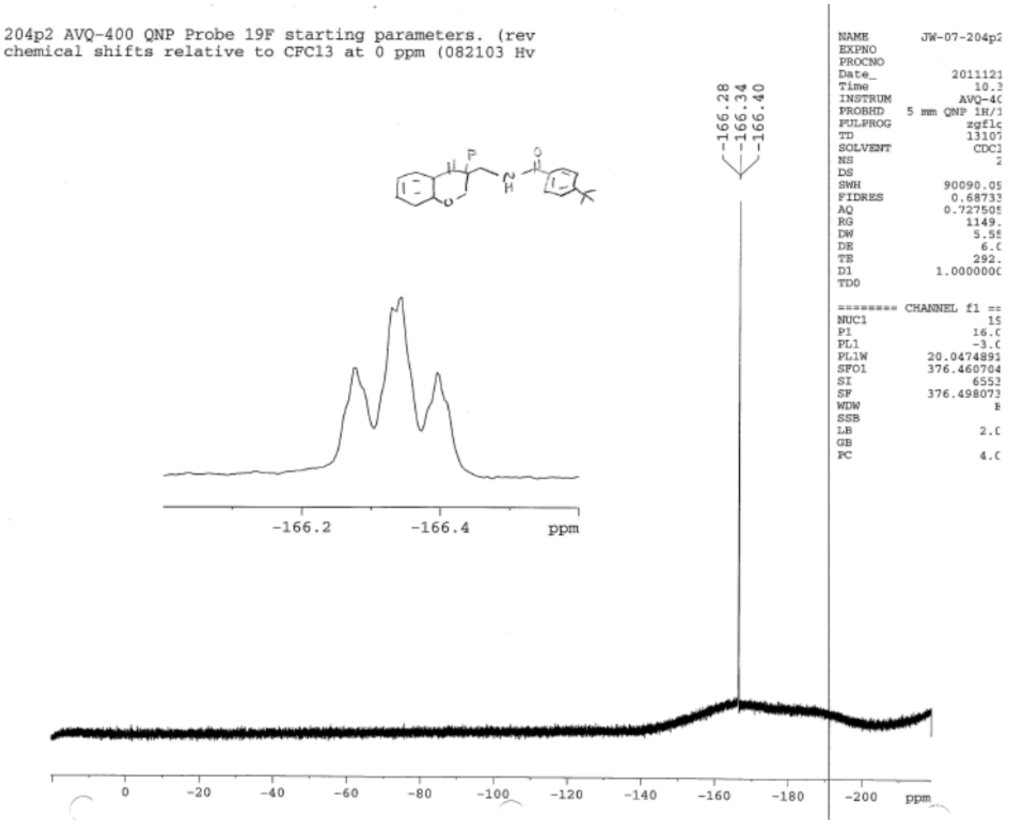


```
NAME           AD-JW-8-48
EXPNO                   1
PROCNO                  1
Date_            20120216
Time                14.25
INSTRUM           DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    153
DS                      0
SWH             41322.312 Hz
FIDRES           0.630528 Hz
AQ              0.7930356 sec
RG                   8192
DW                 12.100 usec
DE                   6.00 usec
TE                  292.4 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                100000

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.75 usec
PL1                  0.00 dB
SFO1          125.7175545 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -5.00 dB
PL12                 7.04 dB
```





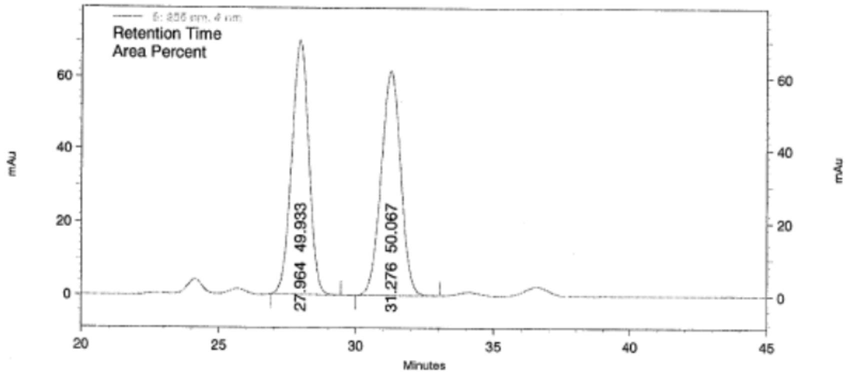
```
NAME          JW-08-203Carb
EXPNO                     1
PROCNO                    1
Date_              20120508
Time                  10.53
INSTRUM             AVB-400
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1581
DS                       0
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                   16384
DW                  20.850 usec
DE                    6.00 usec
TE                   297.6 K
D1              1.50000000 sec
D11             0.03000000 sec
TD0                  10000

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.50 usec
PL1                  -2.00 dB
PL1W           47.77286148 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                70.00 usec
PL2                  -3.00 dB
PL12                 16.00 dB
```



```
204p2 AVQ-400 QNP Probe 19F starting parameters. (rev
chemical shifts relative to CFCl3 at 0 ppm (082103 Hv
```

```
NAME        JW-07-204p2
EXPNO
PROCNO
Date_          2011121
Time              10.3
INSTRUM         AVQ-40
PROBHD   5 mm QNP 1H/1
PULPROG          zgflq
TD               13107
SOLVENT           CDC1
NS                   2
DS
SWH           90090.05
FIDRES         0.68733
AQ            0.727505
RG               1149.
DW                5.55
DE                 6.0
TE                292.
D1           1.0000000
TD0

======== CHANNEL f1 ==
NUC1                19
P1                16.0
PL1               -3.0
PL1W        20.0474891
SFO1        376.460704
SI                6553
SF          376.498073
WDW                  E
SSB
LB                 2.0
GB
PC                 4.0
```

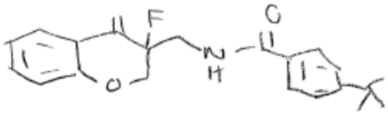
JW-08-59rac/07-204rac



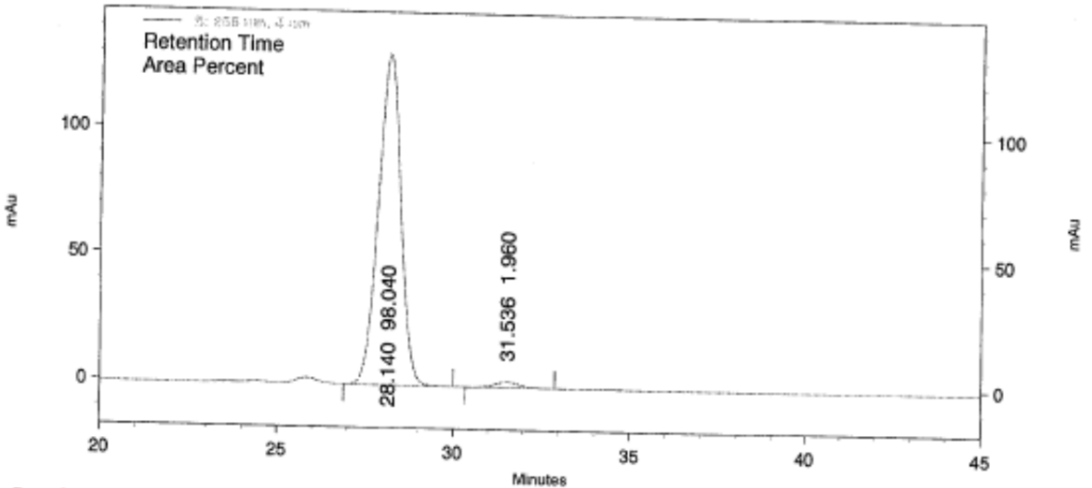
5: 255 nm, 4 nm

Results

Pk #	Retention Time	Area Percent	Lambda Max
1	27.964	49.933	204
2	31.276	50.067	204



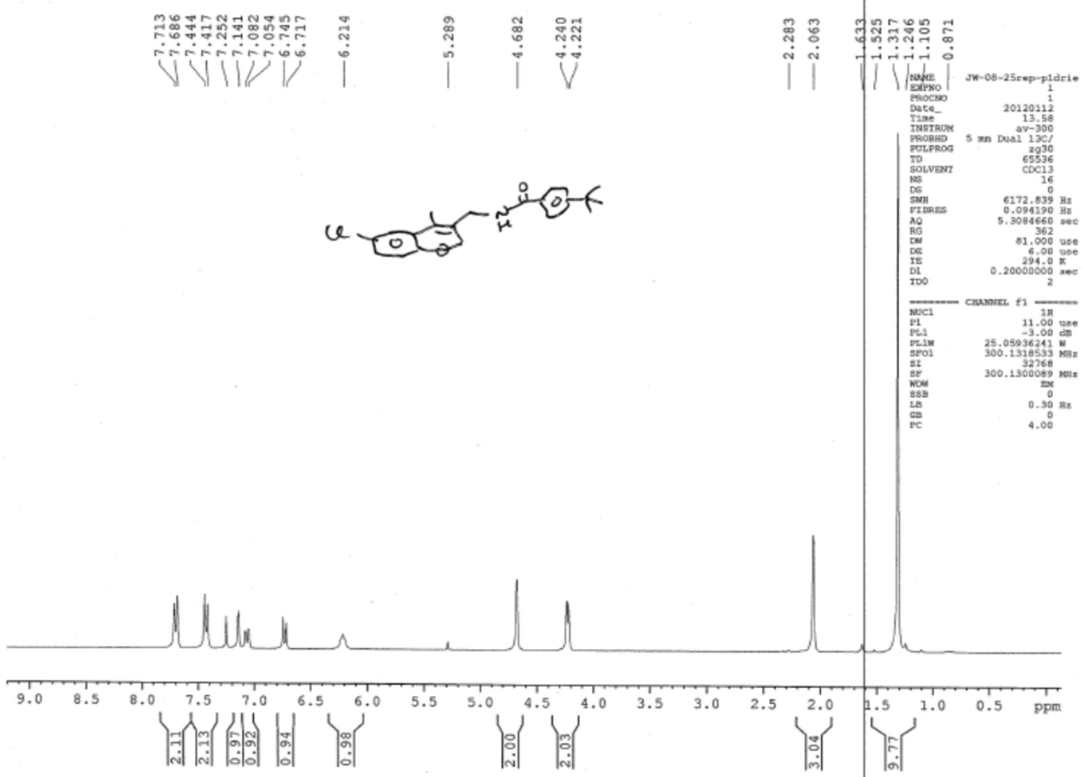
JW-08-59



5: 255 nm, 4 nm
Results

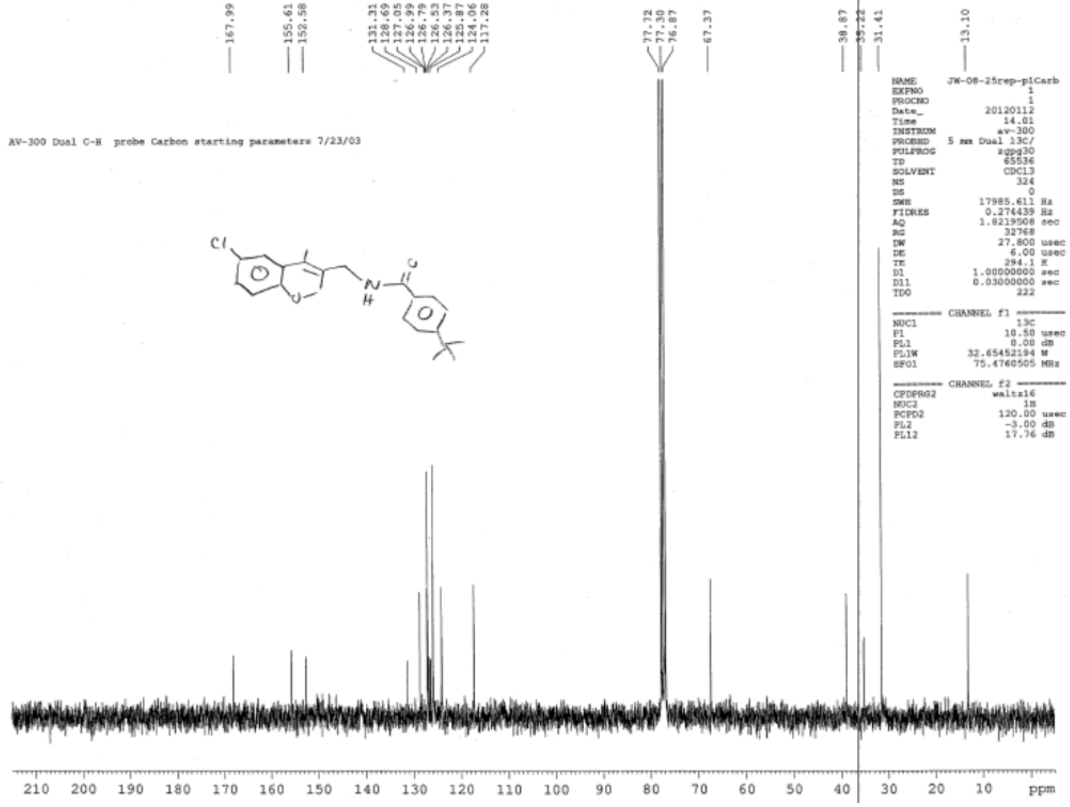
Pk #	Retention Time	Area Percent	Lambda Max
1	28.140	98.040	204
2	31.536	1.960	205

JW-08-25p1 dry AV-300 Dual C-H probe proton starting parameters 7/2

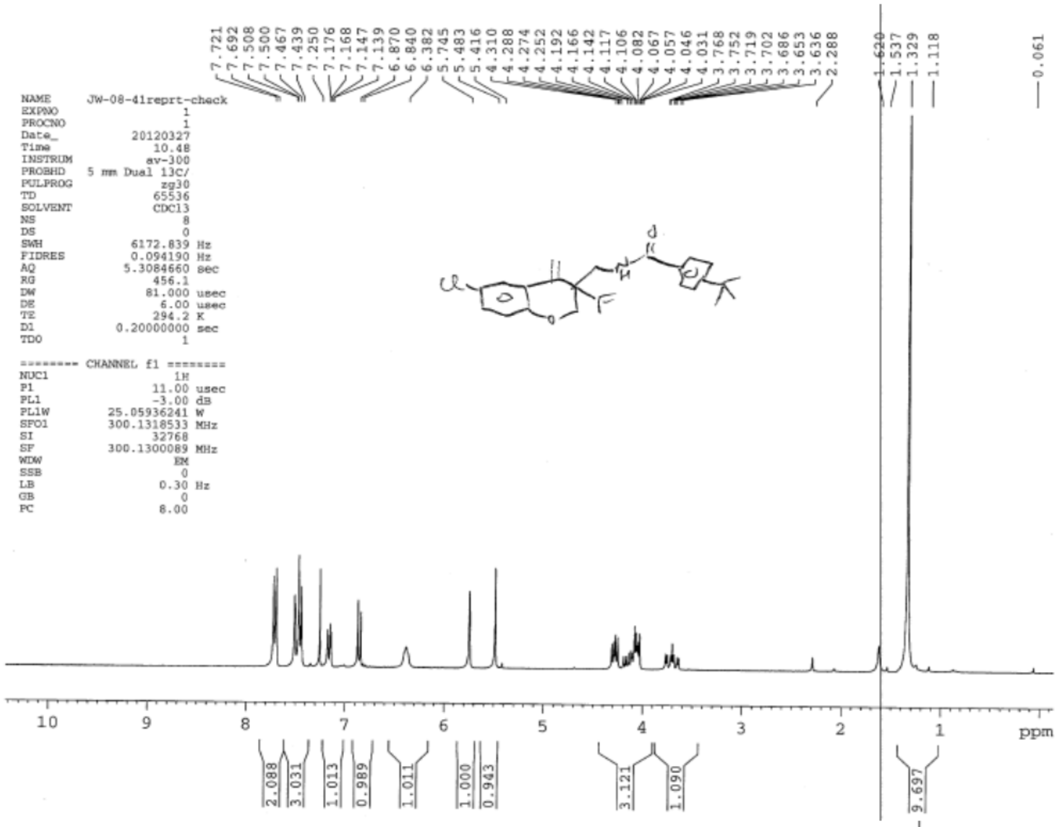


```
NAME         JW-08-25rep-p1drie
EXPNO                     1
PROCNO                    1
Date_              20120112
Time                  13.58
INSTRUM              av-300
PROBHD    5 mm Dual 13C/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                6172.839 Hz
FIDRES             0.094190 Hz
AQ                5.3084660 sec
RG                      362
DW                   81.000 use
DE                     6.00 use
TE                    294.0 K
D1               0.20000000 sec
TD0                       2

======== CHANNEL f1 ========
NUC1                     1H
P1                    11.00 use
PL1                   -3.00 dB
PL1W            25.05936241 W
SFO1            300.1318533 MHz
SI                    32768
SF              300.1300089 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     4.00
```

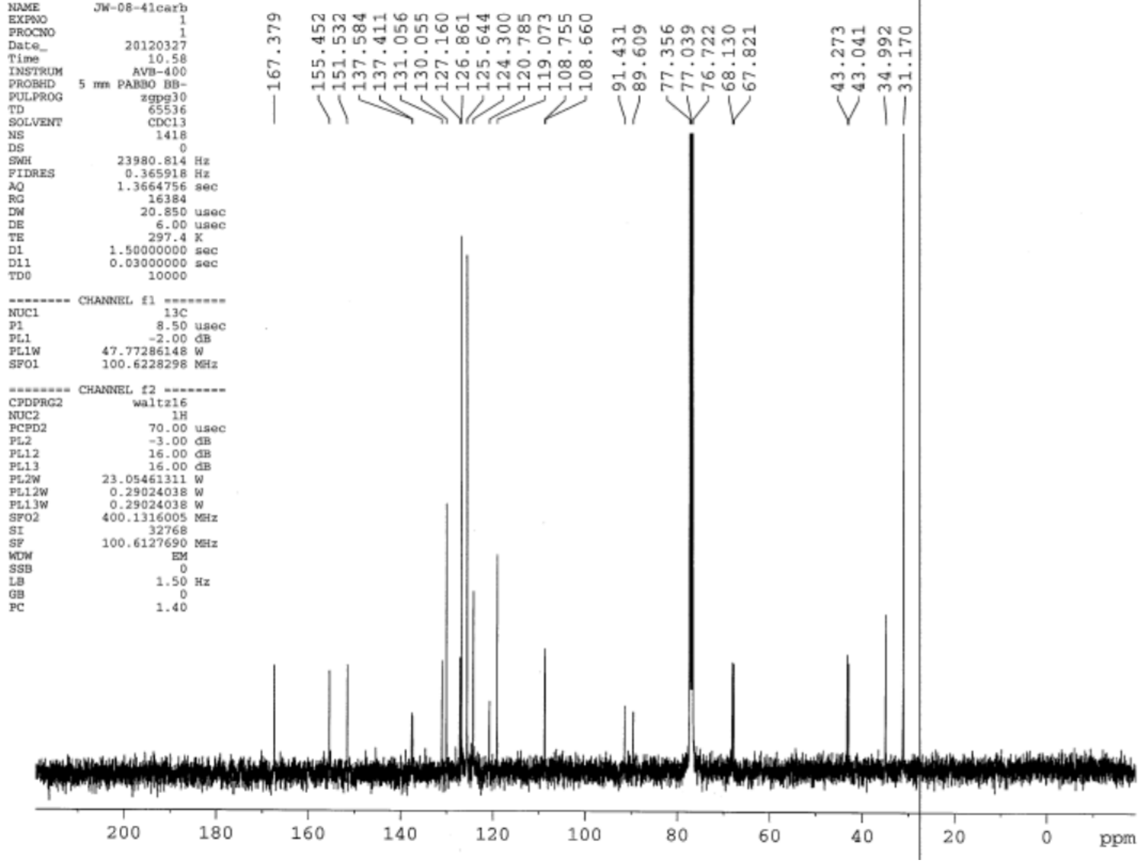
AV-300 Dual C-H probe Carbon starting parameters 7/23/03



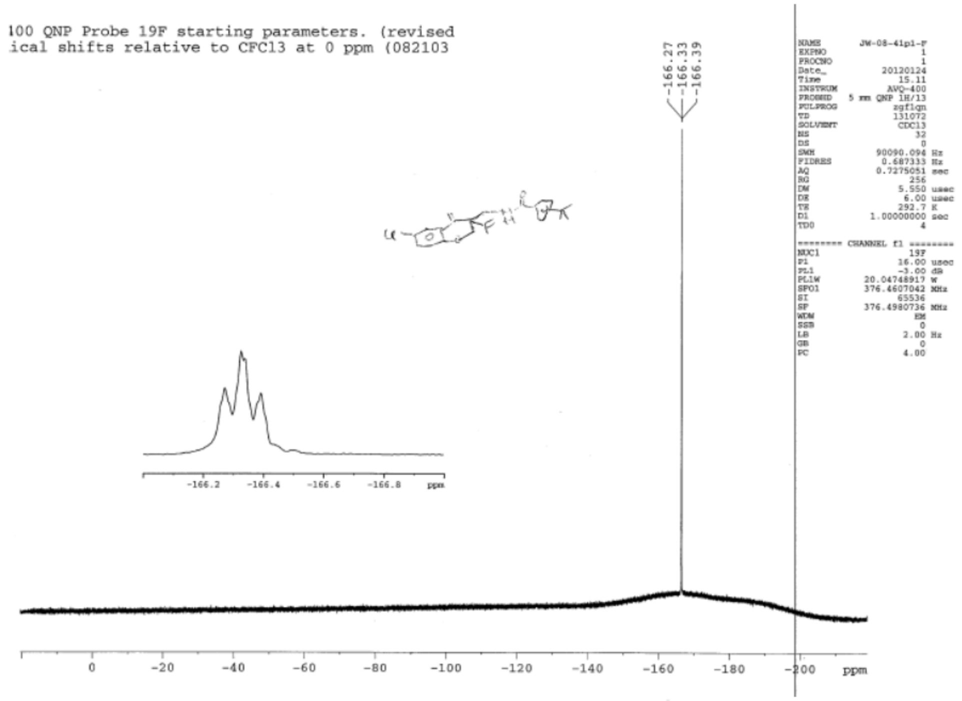
```
NAME         JW-08-25rep-p1Carb
EXPNO                     1
PROCNO                    1
Date_              20120112
Time                  14.01
INSTRUM              av-300
PROBHD    5 mm Dual 13C/
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      324
DS                        0
SWH               17985.611 Hz
FIDRES             0.274439 Hz
AQ                1.8219508 sec
RG                    32768
DW                   27.800 usec
DE                     6.00 usec
TE                    294.1 K
D1               1.00000000 sec
D11              0.03000000 sec
TD0                     222

======== CHANNEL f1 ========
NUC1                    13C
P1                    10.50 usec
PL1                    0.00 dB
PL1W            32.65452194 W
SFO1             75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                120.00 usec
PL2                   -3.00 dB
PL12                  17.76 dB
```



```
NAME       JW-08-41reprt-check
EXPNO                    1
PROCNO                   1
Date_             20120327
Time                 10.48
INSTRUM             av-300
PROBHD    5 mm Dual 13C/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH               6172.839 Hz
FIDRES            0.094190 Hz
AQ               5.3084660 sec
RG                   456.1
DW                  81.000 usec
DE                    6.00 usec
TE                   294.2 K
D1              0.20000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.00 usec
PL1                  -3.00 dB
PL1W           25.05936241 W
SFO1           300.1318533 MHz
SI                   32768
SF             300.1300089 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    8.00
```



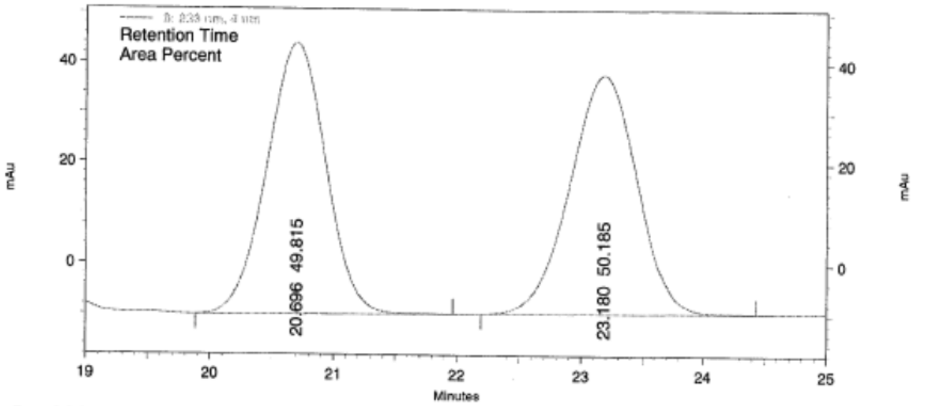
```
NAME          JW-08-41carb
EXPNO                    1
PROCNO                   1
Date_             20120327
Time                 10.58
INSTRUM            AVB-400
PROBHD    5 mm PABBO BB-
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1418
DS                       0
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                   16384
DW                  20.850 usec
DE                    6.00 usec
TE                   297.4 K
D1              1.50000000 sec
D11             0.03000000 sec
TD0                  10000

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.50 usec
PL1                  -2.00 dB
PL1W           47.77286148 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                70.00 usec
PL2                  -3.00 dB
PL12                 16.00 dB
PL13                 16.00 dB
PL2W           23.05461311 W
PL12W           0.29024038 W
PL13W           0.29024038 W
SFO2           400.1316005 MHz
SI                   32768
SF             100.6127690 MHz
WDW                     EM
SSB                      0
LB                    1.50 Hz
GB                       0
PC                    1.40
```



```
100 QNP Probe 19F starting parameters. (revised
ical shifts relative to CFC13 at 0 ppm (082103
```

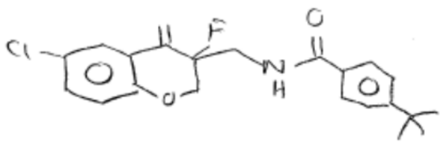
```
NAME          JW-08-41p1-F
EXPNO                    1
PROCNO                   1
Date_             20120124
Time                 15.11
INSTRUM            AVQ-400
PROBHD     5 mm QNP 1H/13
PULPROG             zgflqn
TD                  131072
SOLVENT              CDC13
NS                      32
DS                       0
SWH             90090.094 Hz
FIDRES           0.687333 Hz
AQ              0.7275051 sec
RG                     256
DW                   5.550 usec
DE                    6.00 usec
TE                   292.7 K
D1              1.00000000 sec
TD0                      4

======== CHANNEL f1 ========
NUC1                   19F
P1                   16.00 usec
PL1                  -3.00 dB
PL1W           20.04748917 W
SFO1           376.4607042 MHz
SI                   65536
SF             376.4980736 MHz
WDM                     EM
SSB                      0
LB                    2.00 Hz
GB                       0
PC                    4.00
```

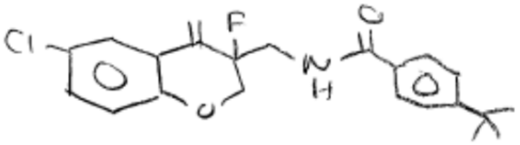
JW-08-28rac



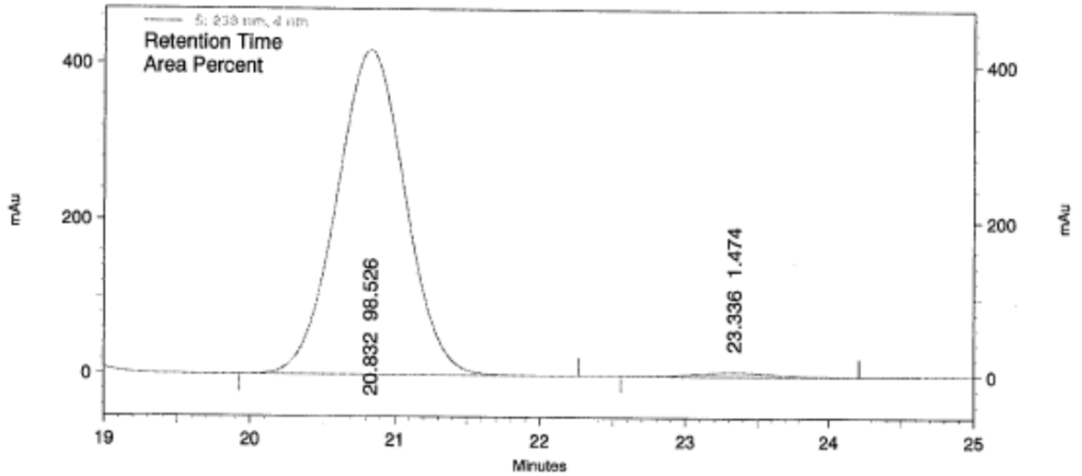
5: 233 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	20.696	49.815	202
2	23.180	50.185	202



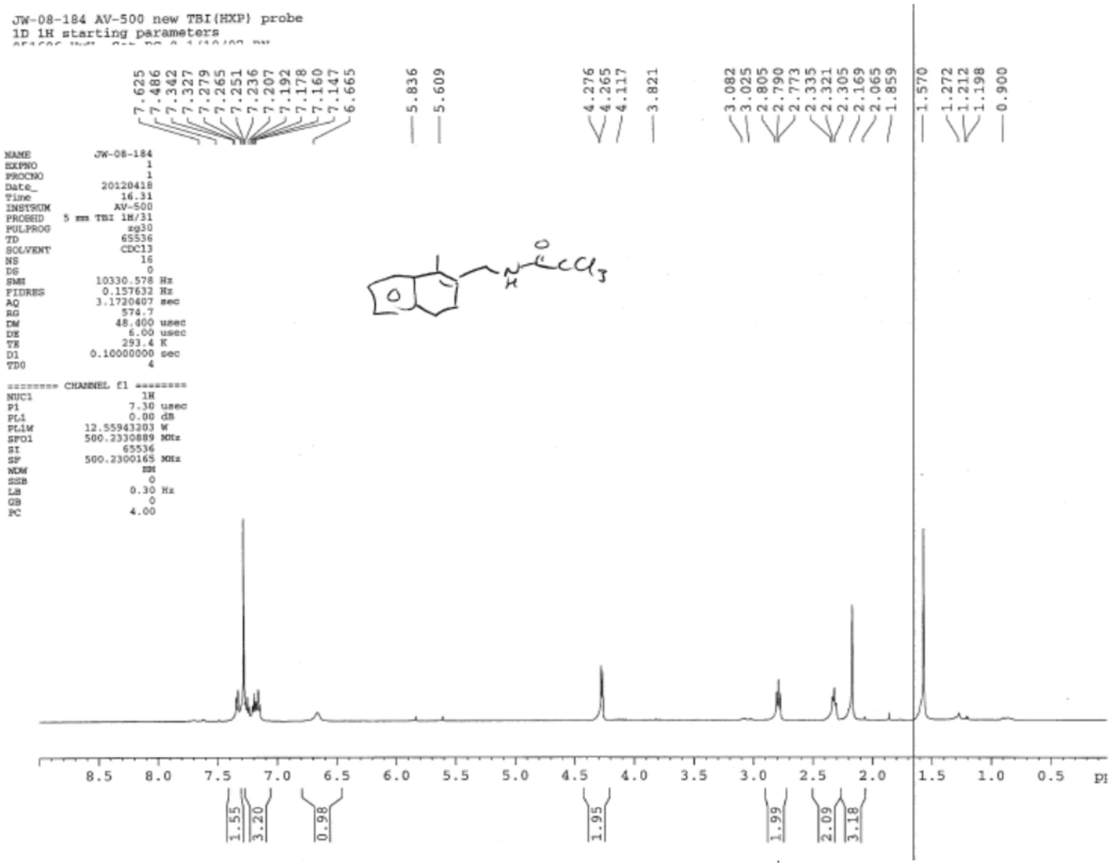


JW-08-41rt

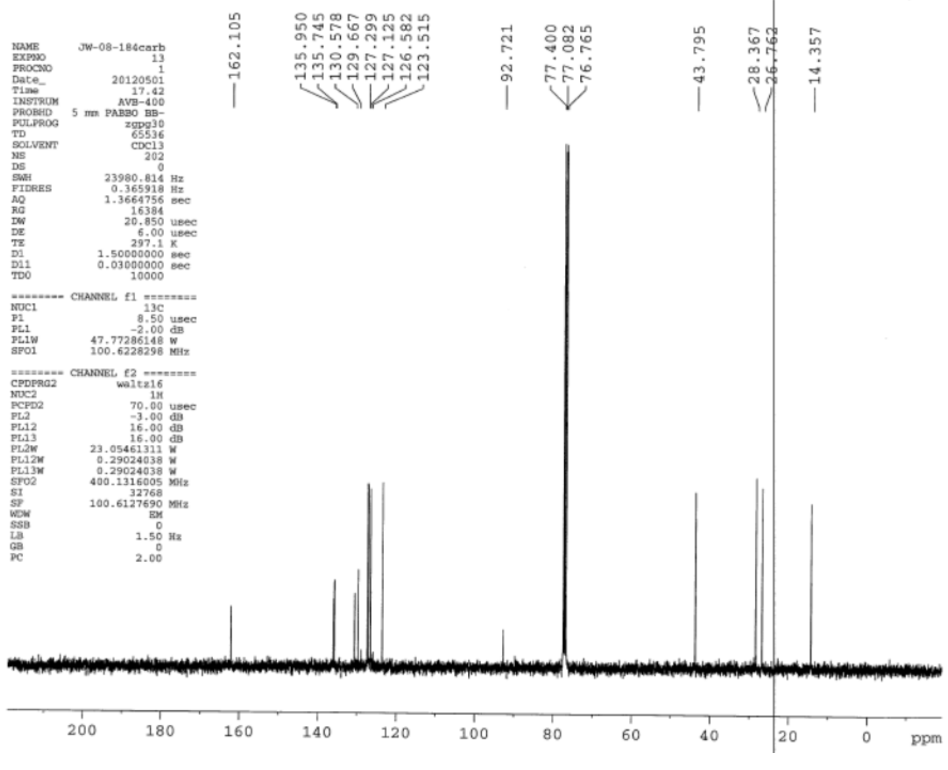


5: 233 nm, 4 nm
Results

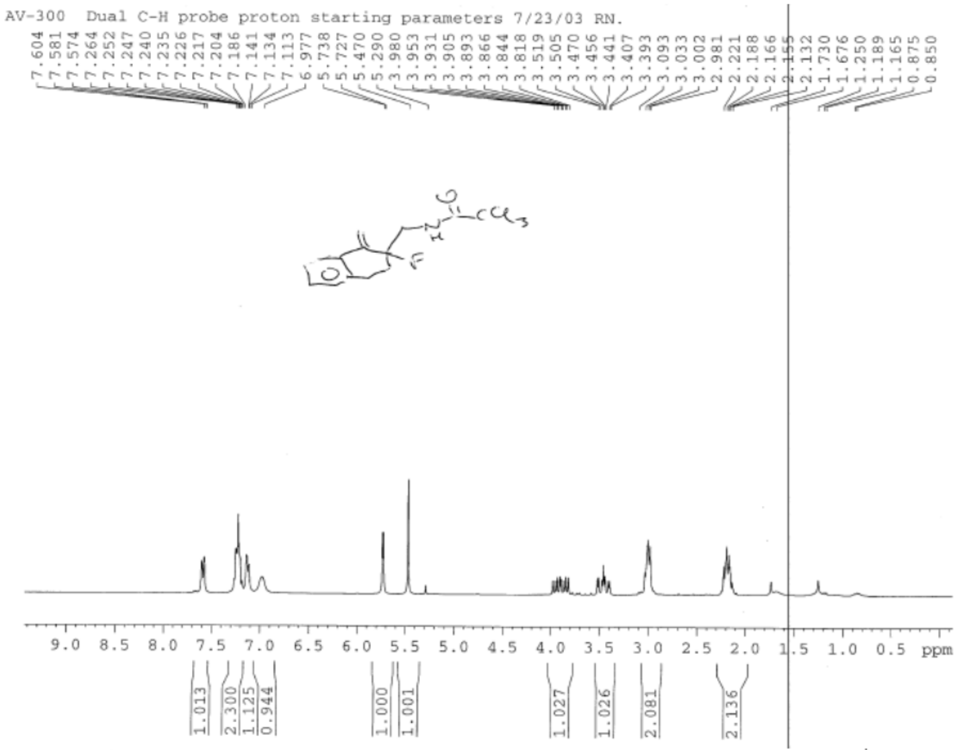
Pk #	Retention Time	Area Percent	Lambda Max
1	20.832	98.526	226
2	23.336	1.474	204

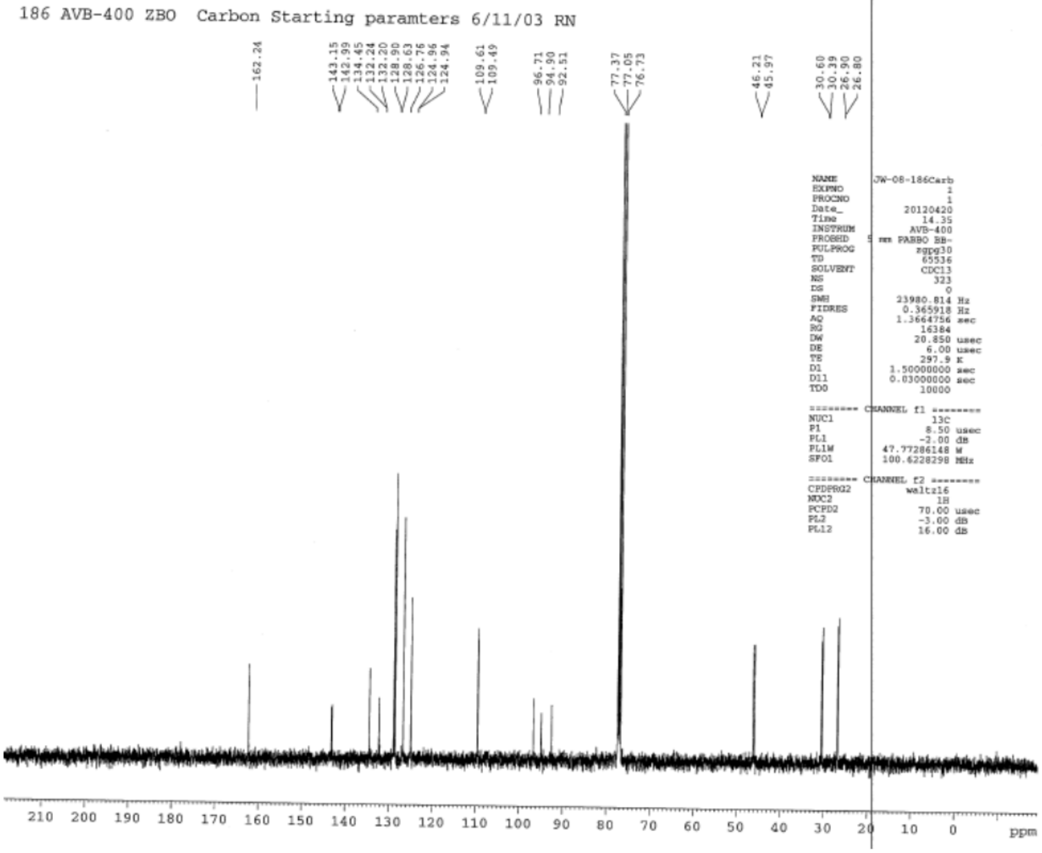


```
JW-08-184 AV-500 new TBI(HXP) probe
1D 1H starting parameters

NAME            JW-08-184
EXPNO                   1
PROCNO                  1
Date_            20120418
Time                16.31
INSTRUM            AV-500
PROBHD   5 mm TBI 1H/31
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1720407 sec
RG                  574.7
DW                 48.400 usec
DE                   6.00 usec
TE                  293.4 K
D1            0.10000000 sec
TD0                     4

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.30 usec
PL1                  0.00 dB
PL1W          12.55943203 W
SFO1          500.2330889 MHz
SI                  65536
SF            500.2300165 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   4.00
```

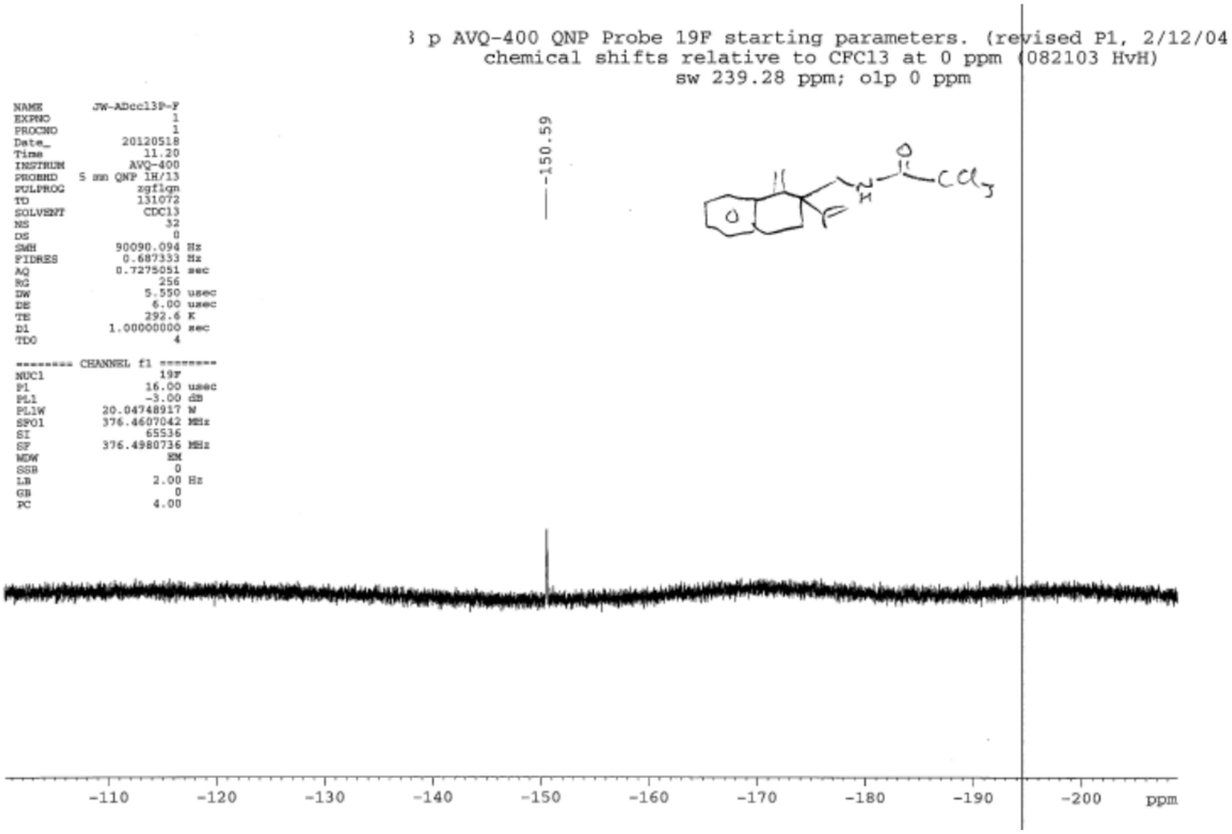


```
NAME         JW-08-184carb
EXPNO                   13
PROCNO                   1
Date_             20120501
Time                 17.42
INSTRUM            AVB-400
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     202
DS                       0
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                   16384
DW                  20.850 usec
DE                    6.00 usec
TE                   297.1 K
D1              1.50000000 sec
D11             0.03000000 sec
TD0                  10000

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.50 usec
PL1                  -2.00 dB
PL1W           47.77286148 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                70.00 usec
PL2                  -3.00 dB
PL12                 16.00 dB
PL13                 16.00 dB
PL2W           23.05461311 W
PL12W           0.29024038 W
PL13W           0.29024038 W
SFO2           400.1316005 MHz
SI                   32768
SF             100.6127690 MHz
WDW                     EM
SSB                      0
LB                    1.50 Hz
GB                       0
PC                    2.00
```


AV-300 Dual C-H probe proton starting parameters 7/23/03 RN.


186 AVB-400 ZBO Carbon Starting paramters 6/11/03 RN

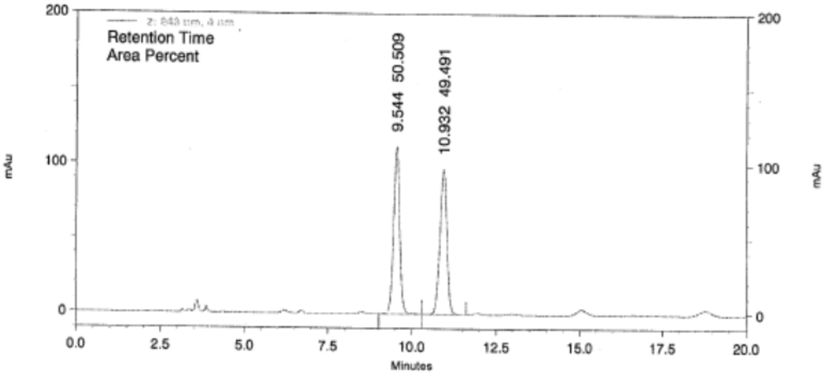
```
NAME          JW-08-186Carb
EXPNO                     1
PROCNO                    1
Date_              20120420
Time                  14.35
INSTRUM             AVB-400
PROBHD       5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      323
DS                        0
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                    16384
DW                   20.850 usec
DE                     6.00 usec
TE                    297.9 K
D1               1.50000000 sec
D11              0.03000000 sec
TD0                   10000

======== CHANNEL f1 ========
NUC1                    13C
P1                     8.50 usec
PL1                   -2.00 dB
PL1W            47.77286148 W
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 70.00 usec
PL2                   -3.00 dB
PL12                  16.00 dB
```



3 p AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04
chemical shifts relative to CFC13 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm

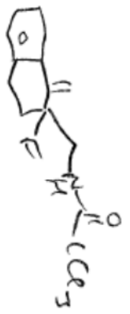
```
NAME          JW-ADccl3P-F
EXPNO                    1
PROCNO                   1
Date_             20120518
Time                 11.20
INSTRUM            AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG             zgflqn
TD                  131072
SOLVENT              CDC13
NS                      32
DS                       0
SWH              90090.094 Hz
FIDRES            0.687333 Hz
AQ               0.7275051 sec
RG                     256
DW                   5.550 usec
DE                    6.00 usec
TE                   292.6 K
D1              1.00000000 sec
TD0                      4

======== CHANNEL f1 ========
NUC1                   19F
P1                   16.00 usec
PL1                  -3.00 dB
PL1W           20.04748917 W
SFO1           376.4607042 MHz
SI                   65536
SF             376.4980736 MHz
WDW                     EM
SSB                      0
LB                    2.00 Hz
GB                       0
PC                    4.00
```

JW-08-117rac IC9802_30min

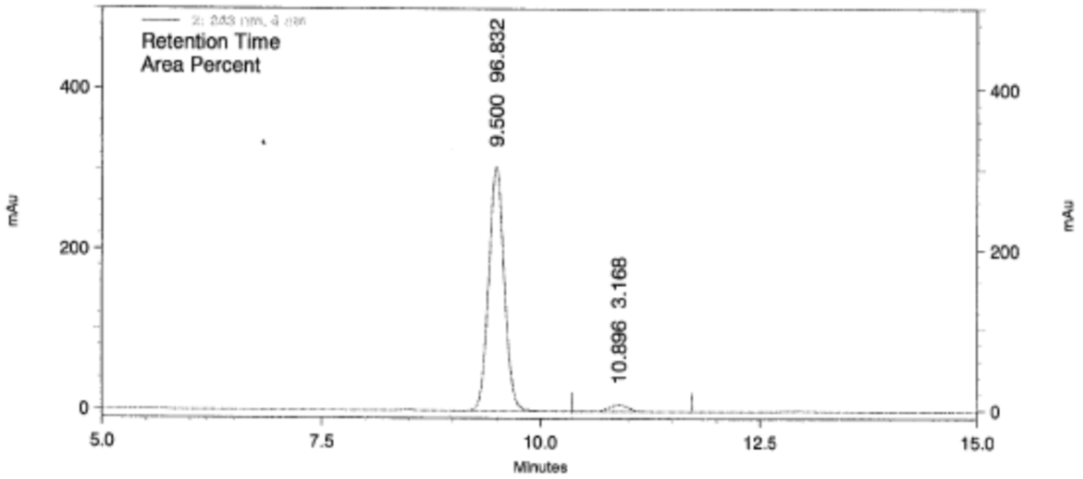


2: 243 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	9.544	50.509	209
2	10.932	49.491	209

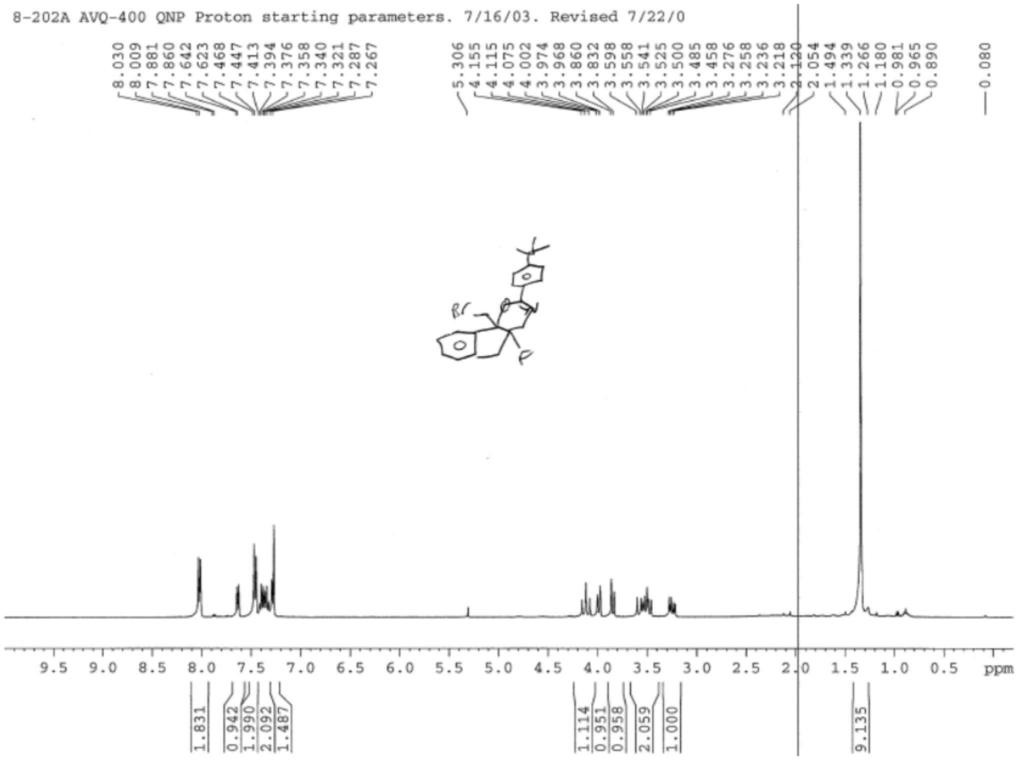


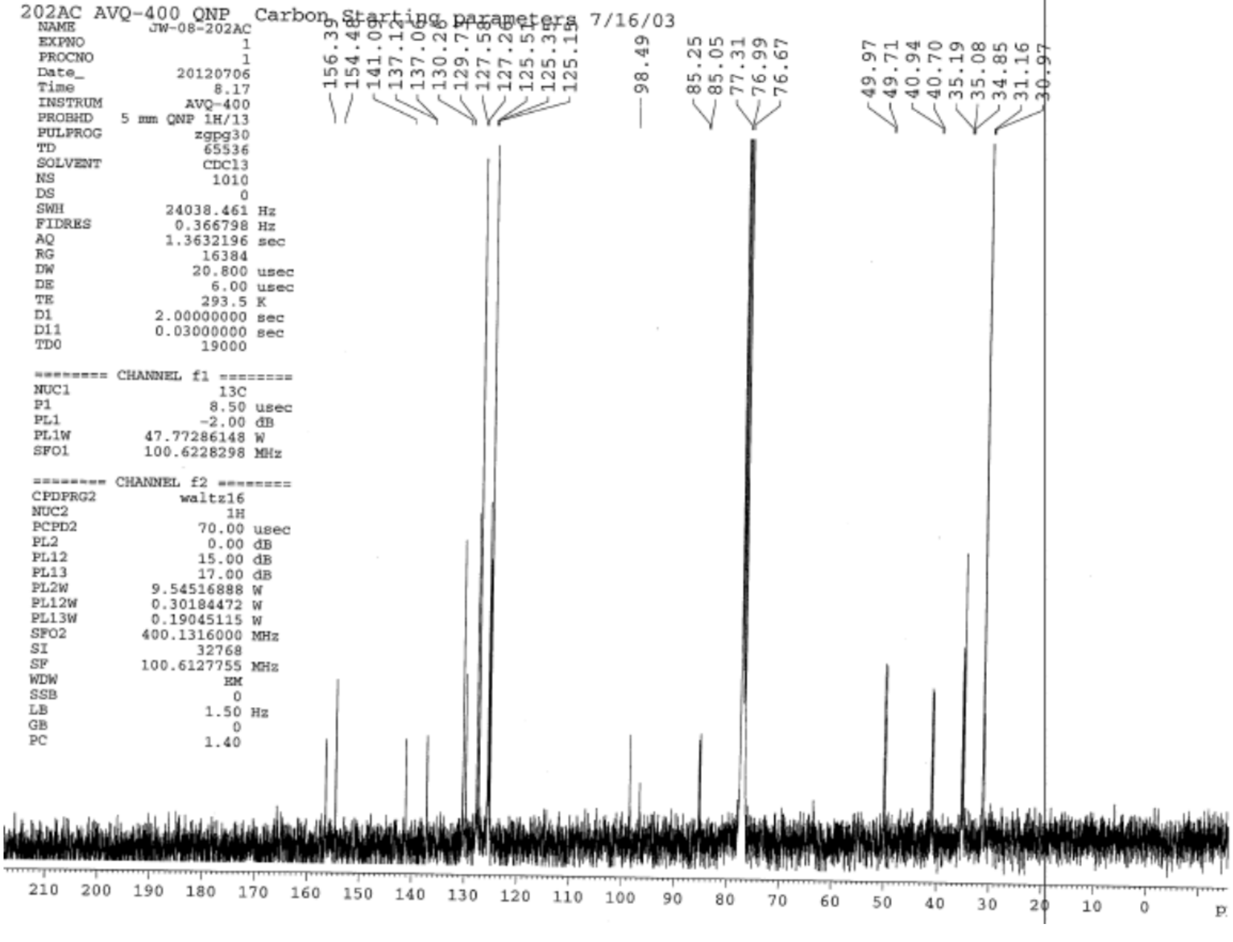
JW-08-121 IC9802_30min

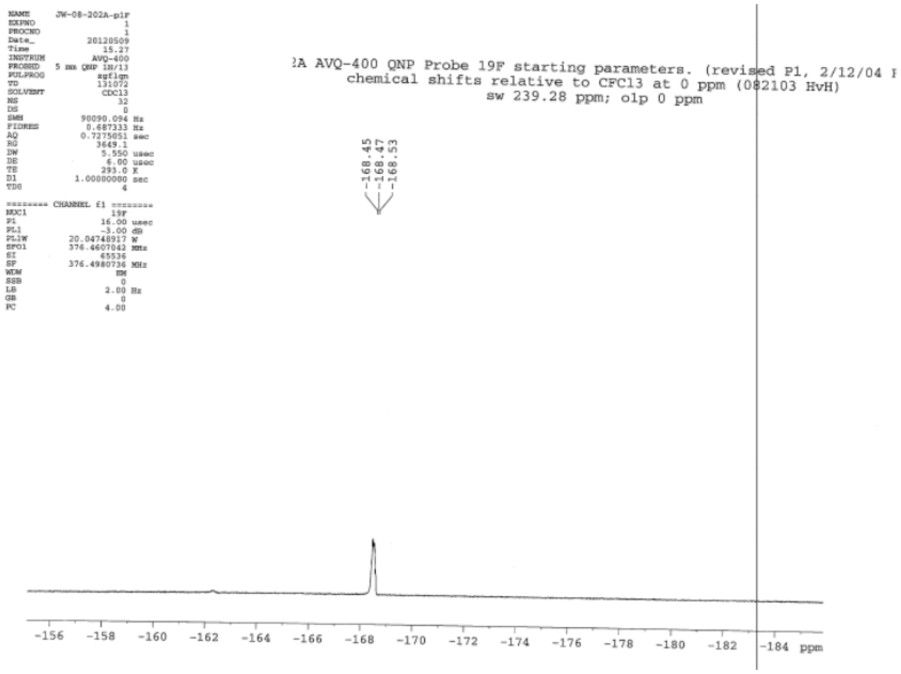


2: 243 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	9.500	96.832	209
2	10.896	3.168	210

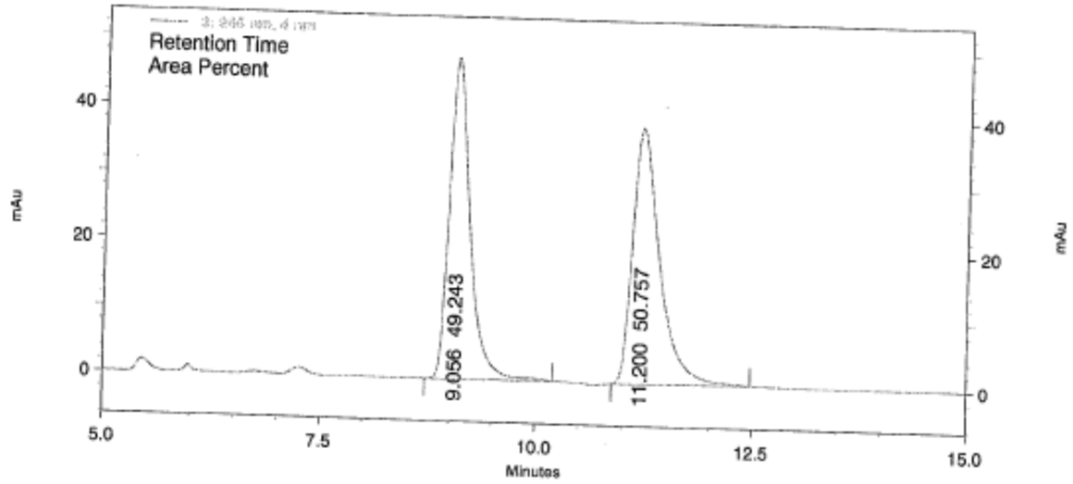

8-202A AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/0
8.030
8.009
7.881
7.860
7.642
7.623
7.468
7.447
7.413
7.394
7.376
7.358
7.340
7.321
7.287
7.267
5.306
4.155
4.115
4.075
4.002
3.974
3.968
3.860
3.832
3.598
3.558
3.541
3.525
3.500
3.485
3.458
3.276
3.258
3.236
3.218
2.120
2.054
1.494
1.339
1.266
1.180
0.981
0.965
0.890
0.080
Br
F
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.831
0.942
1.990
2.092
1.487
1.114
0.951
0.958
2.059
1.000
9.135


202AC AVQ-400 QNP Carbon Starting parameters 7/16/03
NAME JW-08-202AC
EXPNO 1
PROCNO 1
Date_ 20120706
Time 8.17
INSTRUM AVQ-400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1010
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3632196 sec
RG 16384
DW 20.800 usec
DE 6.00 usec
TE 293.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 19000
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 47.77286148 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 0.00 dB
PL12 15.00 dB
PL13 17.00 dB
PL2W 9.54516888 W
PL12W 0.30184472 W
PL13W 0.19045115 W
SFO2 400.1316000 MHz
SI 32768
SF 100.6127755 MHz
WDW EM
SSB 0
LB 1.50 Hz
GB 0
PC 1.40
156.39
154.48
141.09
137.12
137.06
130.26
129.77
127.58
127.26
125.51
125.37
125.15
98.49
85.25
85.05
77.31
76.99
76.67
49.97
49.71
40.94
40.70
35.19
35.08
34.85
31.16
30.97
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
p



```
NAME       JW-08-202A-p1F
EXPNO                   1
PROCNO                  1
Date_            20120509
Time                15.27
INSTRUM           AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG            zgflqn
TD                 131072
SOLVENT             CDC13
NS                     32
DS                      0
SWH             90090.094 Hz
FIDRES           0.687333 Hz
AQ              0.7275051 sec
RG                 3649.1
DW                  5.550 usec
DE                   6.00 usec
TE                  293.0 K
D1             1.00000000 sec
TD0                     4

======== CHANNEL f1 ========
NUC1                  19F
P1                  16.00 usec
PL1                 -3.00 dB
PL1W          20.04748917 W
SFO1          376.4607042 MHz
SI                  65536
SF            376.4980736 MHz
WDW                    EM
SSB                     0
LB                   2.00 Hz
GB                      0
PC                   4.00
```

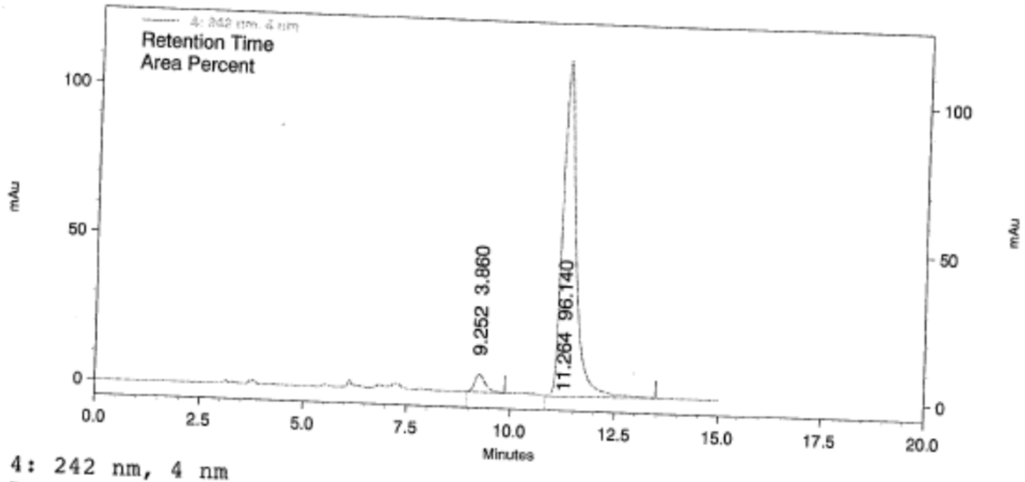
JW-08-207rac- IB9901_15



3: 265 nm, 4 nm
Results

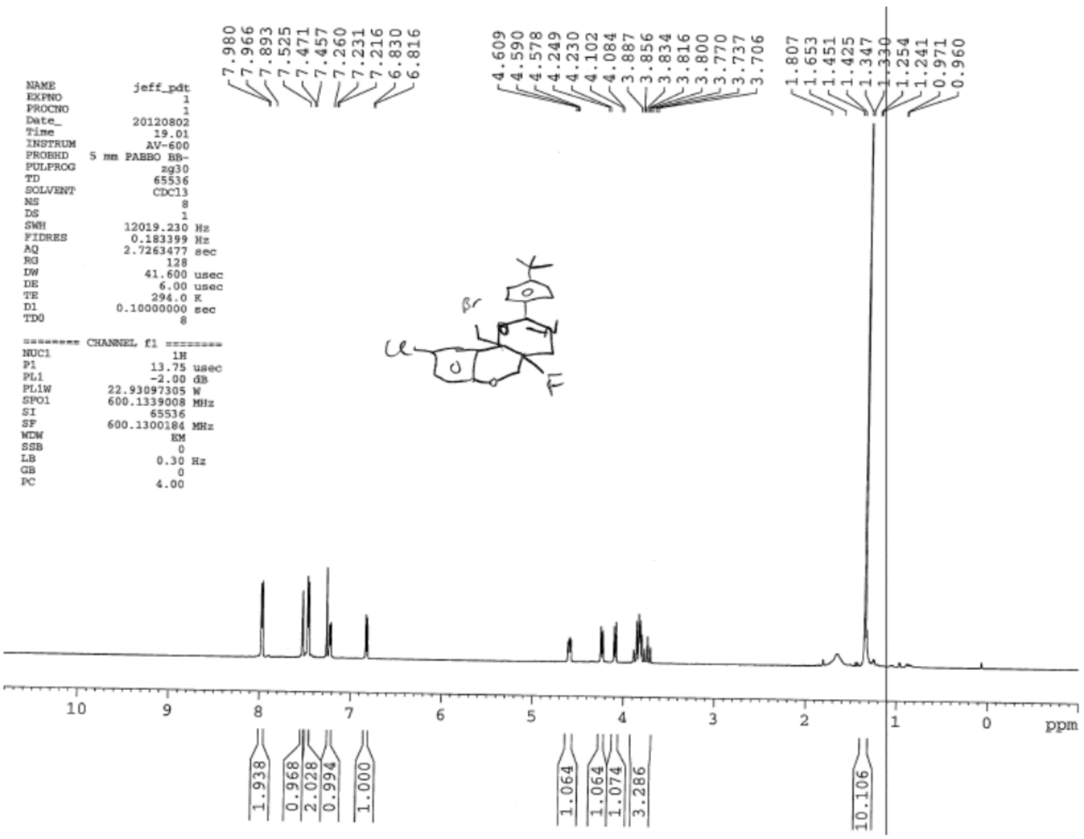
Pk #	Retention Time	Area Percent	Lambda Max
1	9.056	49.243	203
2	11.200	50.757	203

JW-08-202B IB9901

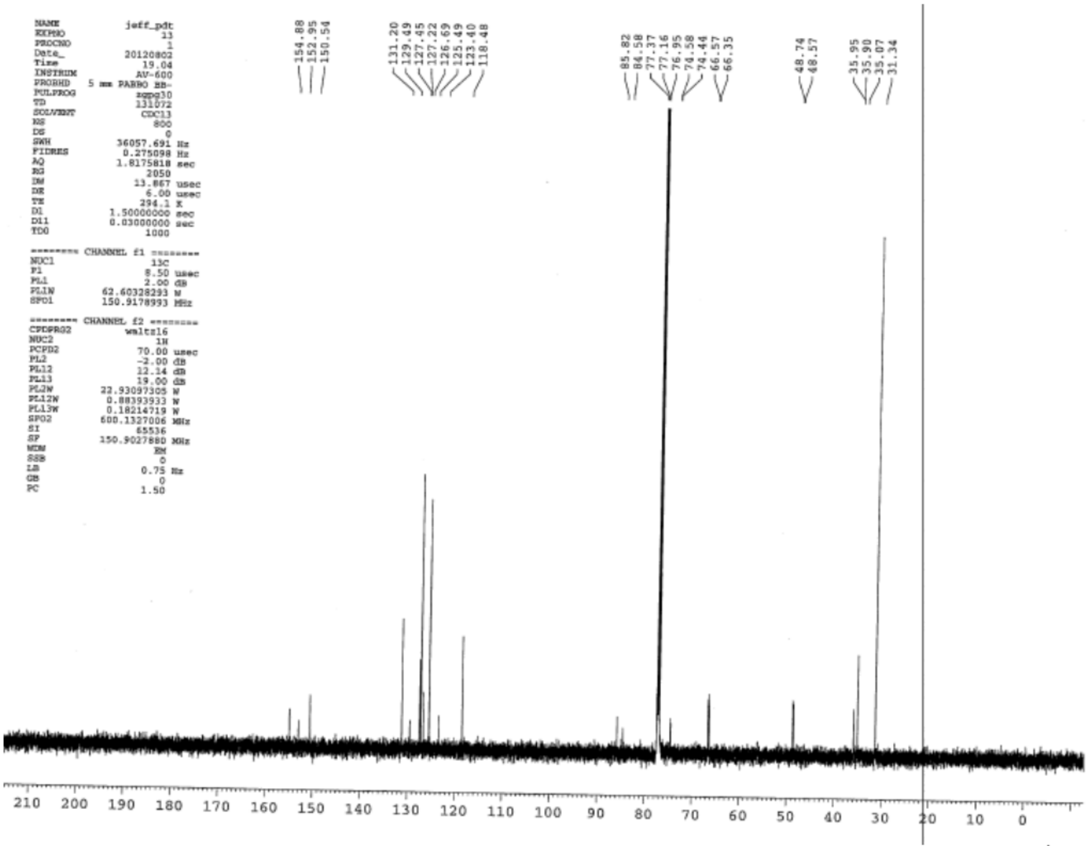


4: 242 nm, 4 nm
Results

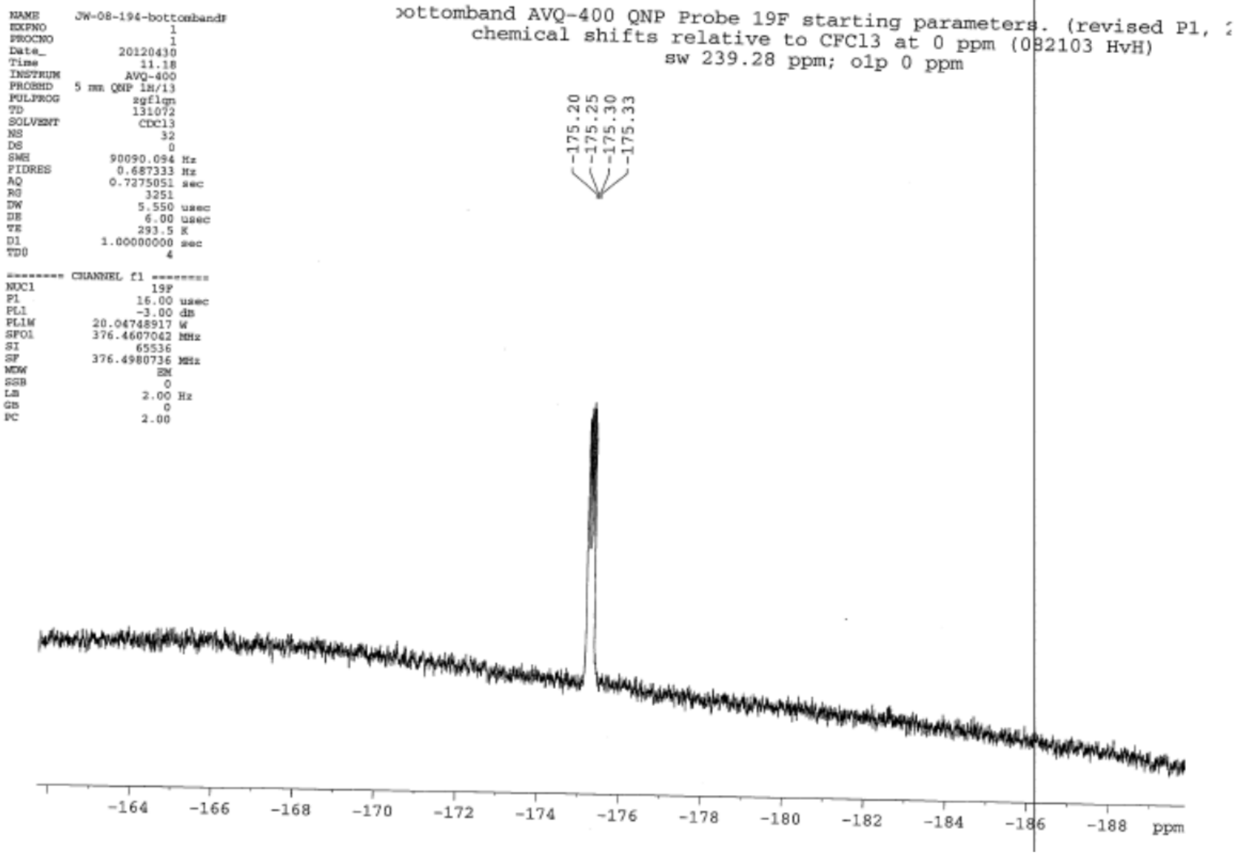
Pk #	Retention Time	Area Percent	Lambda Max
1	9.252	3.860	209
2	11.264	96.140	203



```
NAME              jeff_pdt
EXPNO                    1
PROCNO                   1
Date_             20120802
Time                 19.01
INSTRUM             AV-600
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       1
SWH              12019.230 Hz
FIDRES            0.183399 Hz
AQ               2.7263477 sec
RG                     128
DW                  41.600 usec
DE                    6.00 usec
TE                   294.0 K
D1              0.10000000 sec
TD0                      8

======== CHANNEL f1 ========
NUC1                    1H
P1                   13.75 usec
PL1                  -2.00 dB
PL1W           22.93097305 W
SFO1           600.1339008 MHz
SI                   65536
SF             600.1300184 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00
```



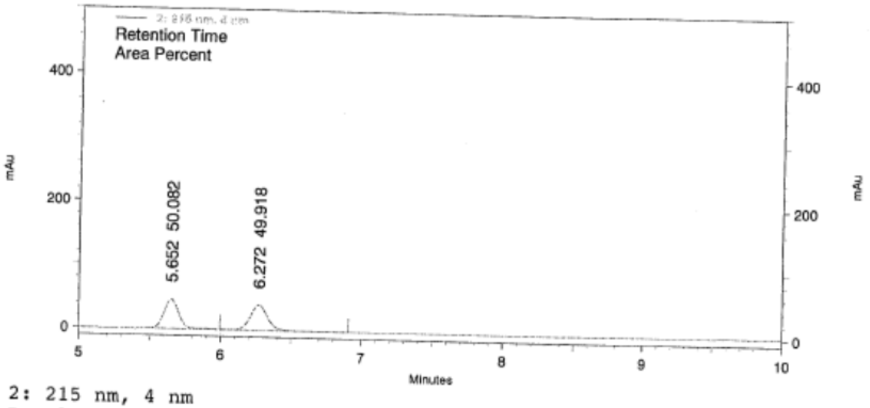
```
NAME           jeff_pdt
EXPNO                13
PROCNO                1
Date_          20120802
Time              19.04
INSTRUM          AV-600
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               131072
SOLVENT           CDCl3
NS                  800
DS                    0
SWH           36057.691 Hz
FIDRES         0.275098 Hz
AQ            1.8175818 sec
RG                 2050
DW               13.867 usec
DE                 6.00 usec
TE                294.1 K
D1           1.50000000 sec
D11          0.03000000 sec
TD0                1000

======== CHANNEL f1 ========
NUC1                13C
P1                 8.50 usec
PL1                2.00 dB
PL1W        62.60328293 W
SFO1        150.9178993 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             70.00 usec
PL2               -2.00 dB
PL12              12.14 dB
PL13              19.00 dB
PL2W        22.93097305 W
PL12W        0.88393933 W
PL13W        0.18214719 W
SFO2        600.1327006 MHz
SI                65536
SF          150.9027880 MHz
WDW                  EM
SSB                   0
LB                 0.75 Hz
GB                    0
PC                 1.50
```



```
NAME     JW-08-194-bottombandF
EXPNO                1
PROCNO               1
Date_         20120430
Time             11.18
INSTRUM        AVQ-400
PROBHD  5 mm QNP 1H/13
PULPROG         zgflqn
TD              131072
SOLVENT          CDCl3
NS                  32
DS                   0
SWH          90090.094 Hz
FIDRES        0.687333 Hz
AQ           0.7275051 sec
RG                3251
DW               5.550 usec
DE                6.00 usec
TE               293.5 K
D1          1.00000000 sec
TD0                  4

======== CHANNEL f1 ========
NUC1               19F
P1               16.00 usec
PL1              -3.00 dB
PL1W       20.04748917 W
SFO1       376.4607042 MHz
SI               65536
SF         376.4980736 MHz
WDW                 EM
SSB                  0
LB                2.00 Hz
GB                   0
PC                2.00
```

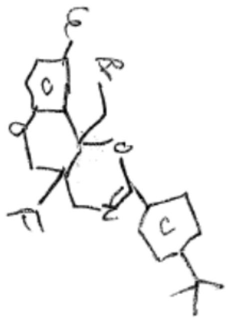
ottomband AVQ-400 QNP Probe 19F starting parameters. (revised P1,
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm

JW-08-194rac IC9802_30min

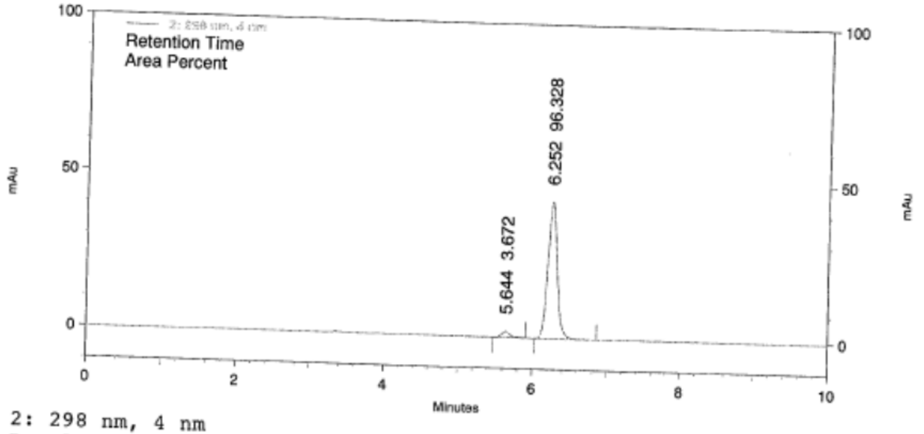


2: 215 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	5.652	50.082	204
2	6.272	49.918	204

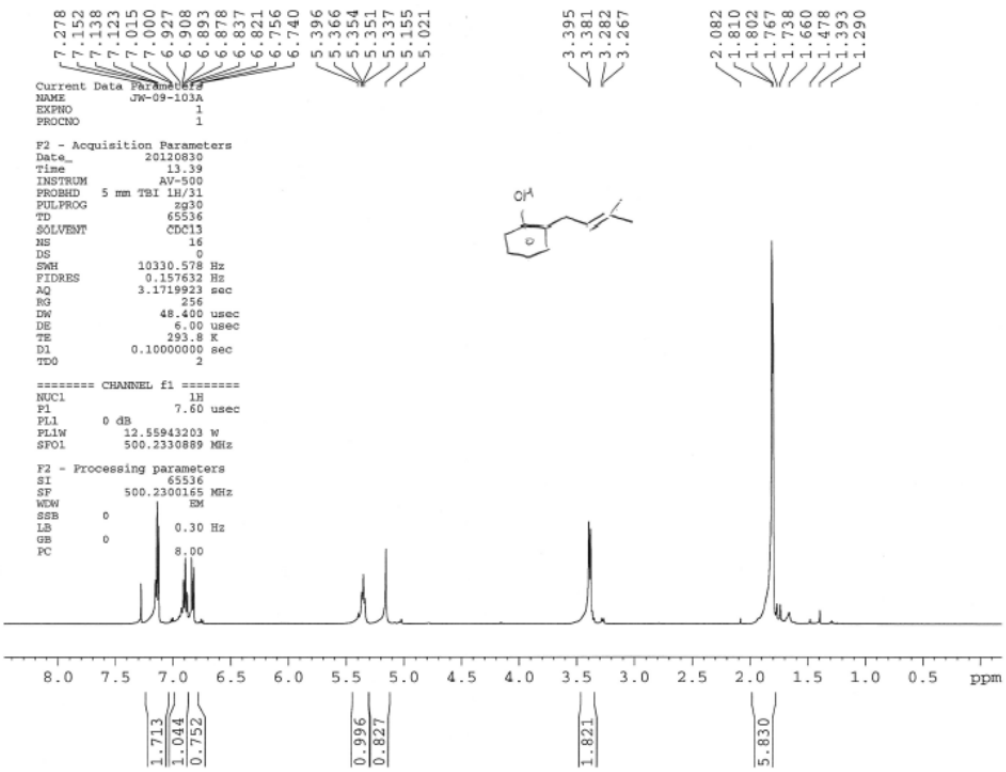


JW-09-6 IC9802_15min

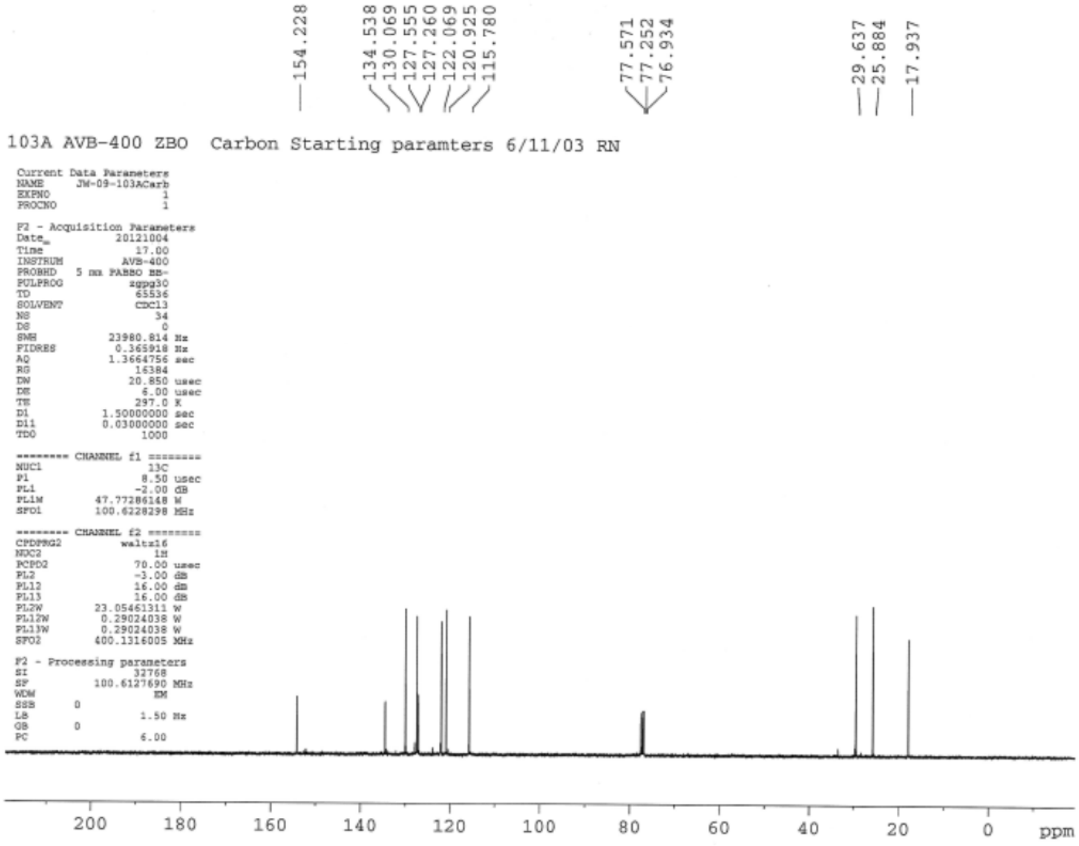


2: 298 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	5.644	3.672	204
2	6.252	96.328	205

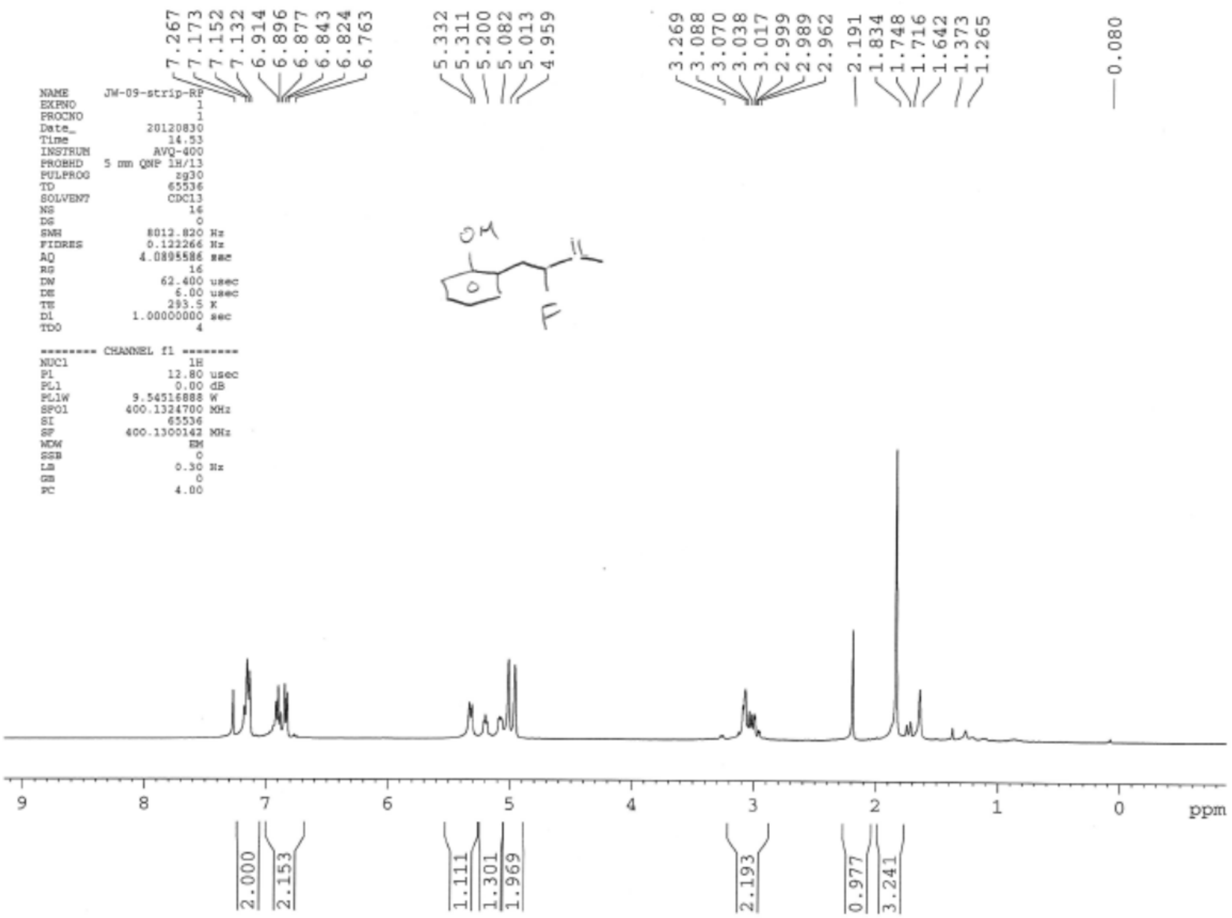


```
Current Data Parameters
NAME         JW-09-103A
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120830
Time              13.39
INSTRUM          AV-500
PROBHD   5 mm TBI 1H/31
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    0
SWH          10330.578 Hz
FIDRES        0.157632 Hz
AQ           3.1719923 sec
RG                  256
DW              48.400 usec
DE                6.00 usec
TE               293.8 K
D1          0.10000000 sec
TD0                   2

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.60 usec
PL1         0 dB
PL1W        12.55943203 W
SFO1        500.2330889 MHz

F2 - Processing parameters
SI                65536
SF          500.2300165 MHz
WDW                  EM
SSB         0
LB                 0.30 Hz
GB          0
PC                 8.00
```

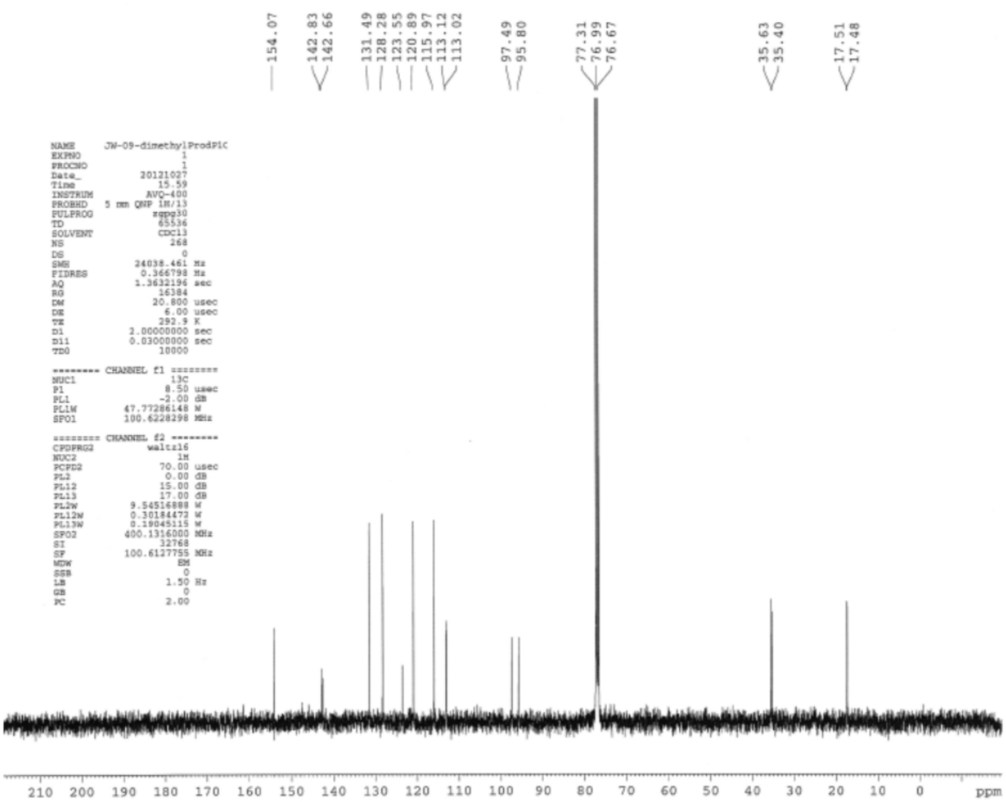


103A AVB-400 ZBO Carbon Starting paramters 6/11/03 RN

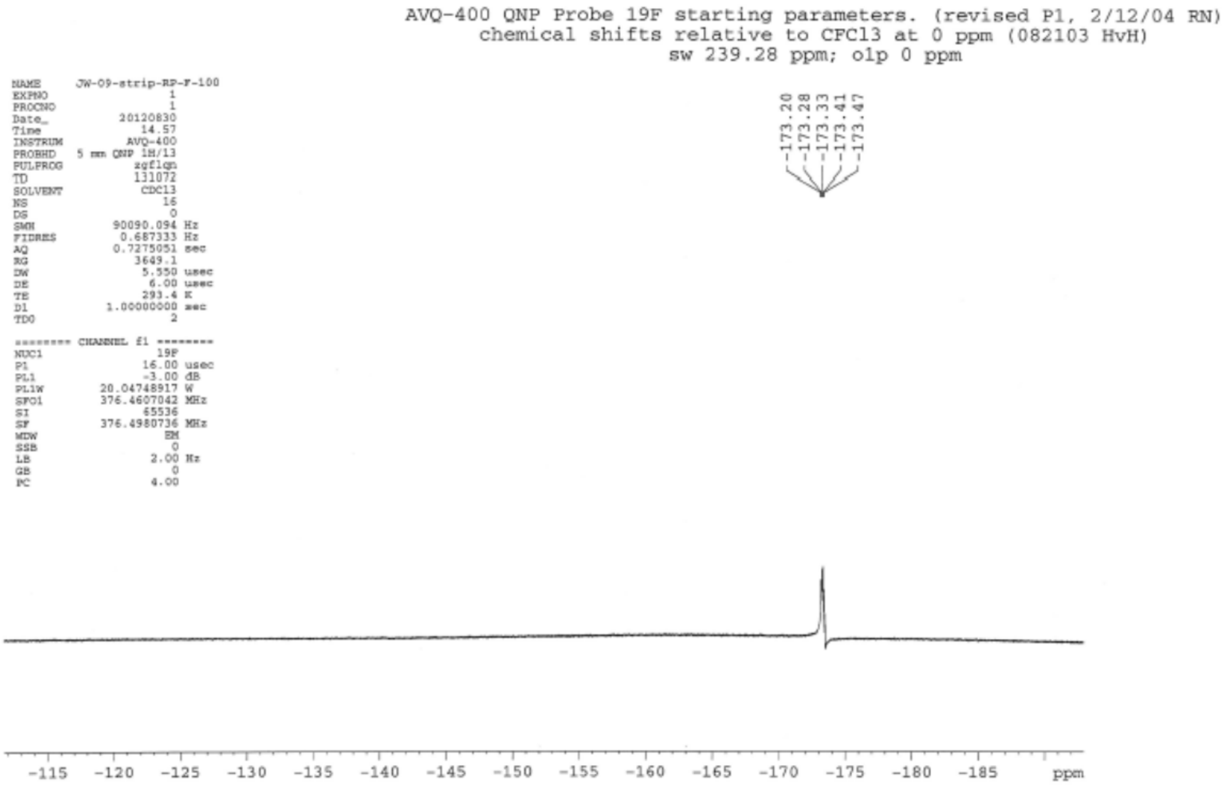
```
Current Data Parameters
NAME     JW-09-103ACarb
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20121004
Time              17.00
INSTRUM         AVB-400
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   34
DS                    0
SWH          23980.814 Hz
FIDRES        0.365918 Hz
AQ           1.3664756 sec
RG                16384
DW              20.850 usec
DE                6.00 usec
TE               297.0 K
D1          1.50000000 sec
D11         0.03000000 sec
TD0                1000

======== CHANNEL f1 ========
NUC1                13C
P1                 8.50 usec
PL1               -2.00 dB
PL1W        47.77286148 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             70.00 usec
PL2               -3.00 dB
PL12              16.00 dB
PL13              16.00 dB
PL2W        23.05461311 W
PL12W        0.29024038 W
PL13W        0.29024038 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB         0
LB                 1.50 Hz
GB          0
PC                 6.00
```



```
NAME       JW-09-strip-RP
EXPNO                   1
PROCNO                  1
Date_            20120830
Time                14.53
INSTRUM           AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG              zg30
TD                  65536
SOLVENT             CDC13
NS                     16
DS                      0
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0895586 sec
RG                     16
DW                 62.400 usec
DE                   6.00 usec
TE                  293.5 K
D1             1.00000000 sec
TD0                     4

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.80 usec
PL1                  0.00 dB
PL1W           9.54516888 W
SFO1          400.1324700 MHz
SI                  65536
SF            400.1300142 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   4.00
```

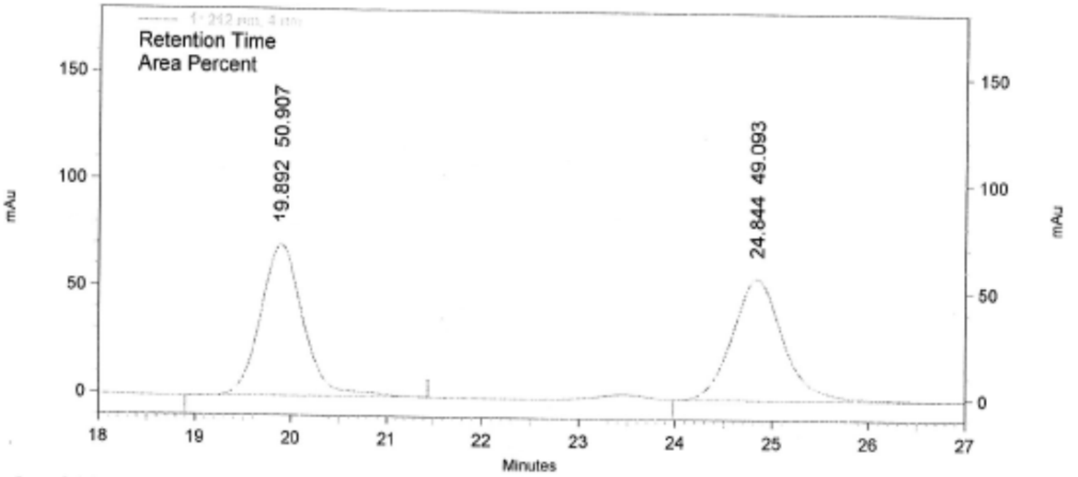


```
NAME       JW-09-dimethylProdP1C
EXPNO                     1
PROCNO                    1
Date_              20121027
Time                  15.59
INSTRUM             AVQ-400
PROBHD     5 mm QNP 1H/13
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      268
DS                        0
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3632196 sec
RG                    16384
DW                   20.800 usec
DE                     6.00 usec
TE                    292.9 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                   10000

======== CHANNEL f1 ========
NUC1                    13C
P1                     8.50 usec
PL1                   -2.00 dB
PL1W            47.77286148 W
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 70.00 usec
PL2                    0.00 dB
PL12                  15.00 dB
PL13                  17.00 dB
PL2W             9.54516888 W
PL12W            0.30184472 W
PL13W            0.19045115 W
SFO2            400.1316000 MHz
SI                    32768
SF              100.6127755 MHz
WDW                      EM
SSB                       0
LB                     1.50 Hz
GB                        0
PC                     2.00
```


AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm

```
NAME       JW-09-strip-RP-F-100
EXPNO                     1
PROCNO                    1
Date_              20120830
Time                  14.57
INSTRUM             AVQ-400
PROBHD     5 mm QNP 1H/13
PULPROG              zgflqn
TD                   131072
SOLVENT               CDCl3
NS                       16
DS                        0
SWH               90090.094 Hz
FIDRES             0.687333 Hz
AQ                0.7275051 sec
RG                   3649.1
DW                    5.550 usec
DE                     6.00 usec
TE                    293.4 K
D1               1.00000000 sec
TD0                       2

======== CHANNEL f1 ========
NUC1                    19F
P1                    16.00 usec
PL1                   -3.00 dB
PL1W            20.04748917 W
SFO1            376.4607042 MHz
SI                    65536
SF              376.4980736 MHz
WDW                      EM
SSB                       0
LB                     2.00 Hz
GB                        0
PC                     4.00
```

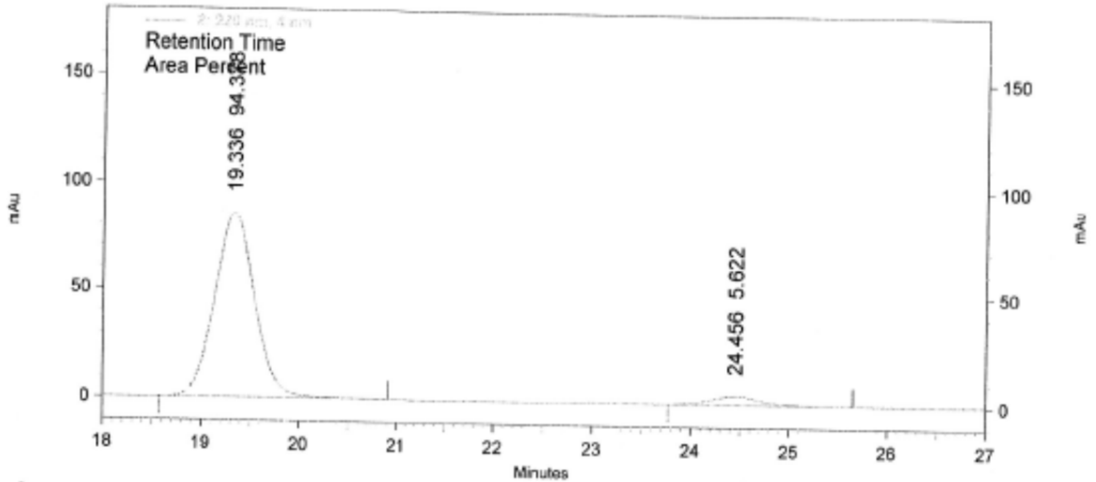
JW-09-102rac ic9901-45



1: 212 nm, 4 nm
Results

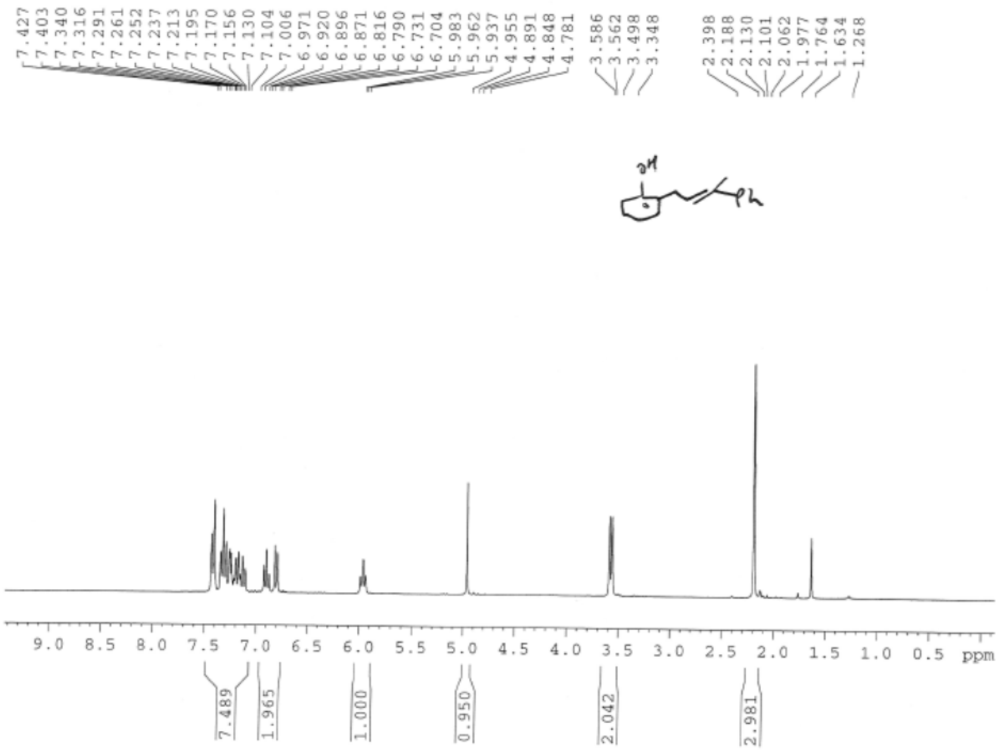
Pk #	Retention Time	Area Percent	Lambda Max
1	19.892	50.907	200
2	24.844	49.093	200

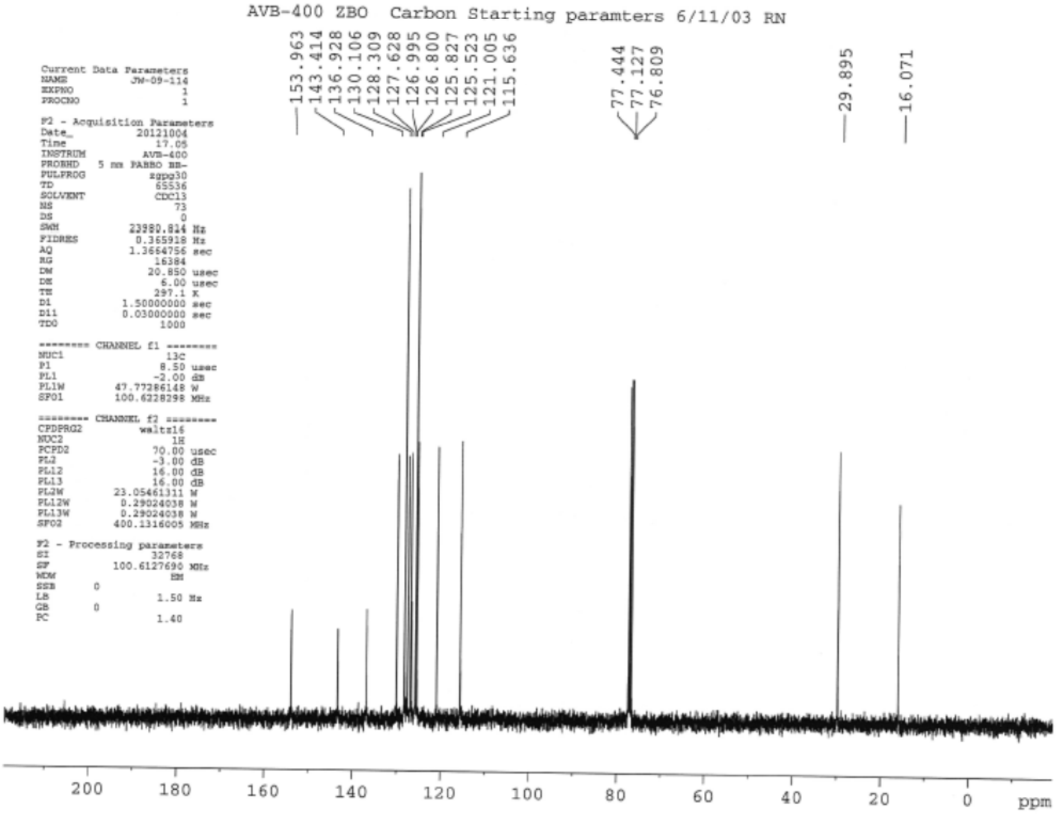
JW-09-102strip ic9901-45



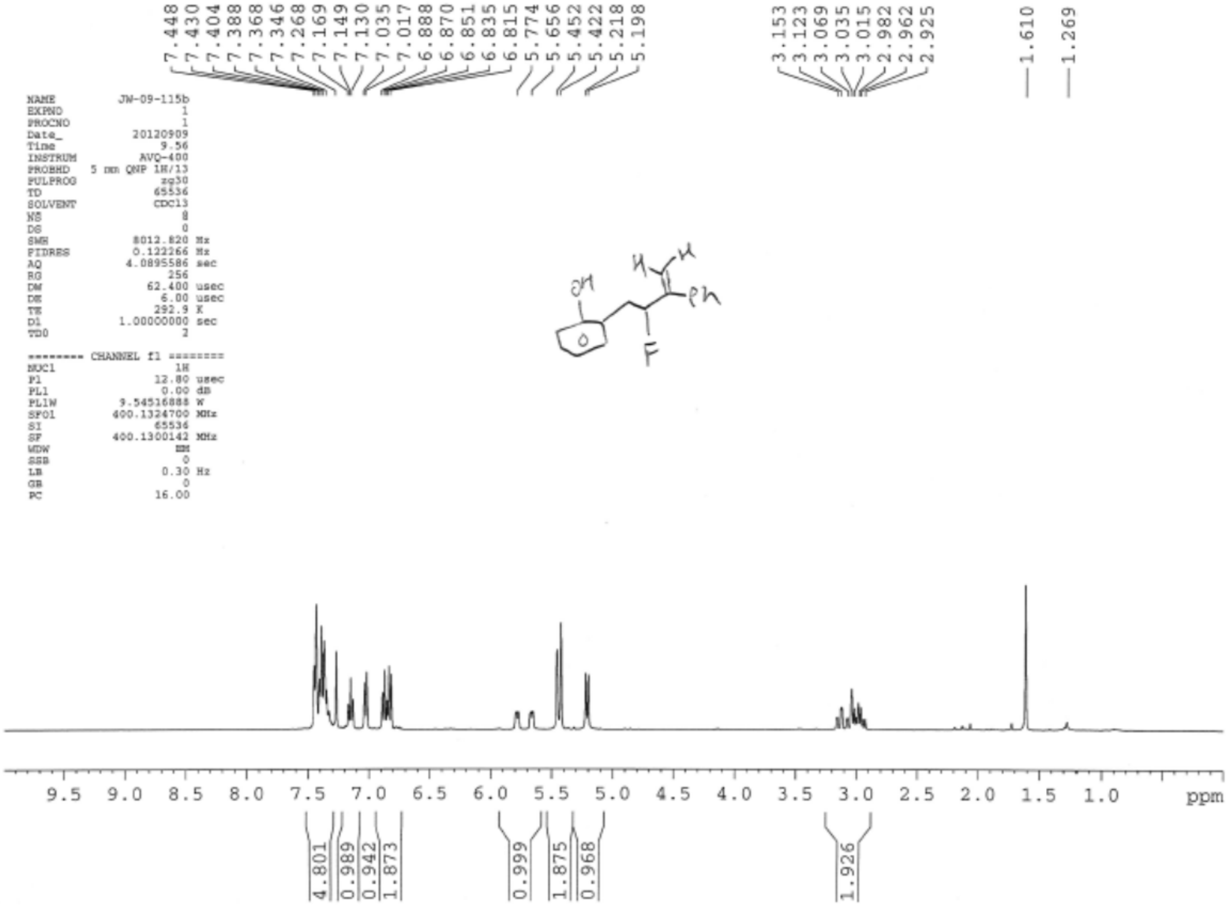
2: 220 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	19.336	94.378	200
2	24.456	5.622	217



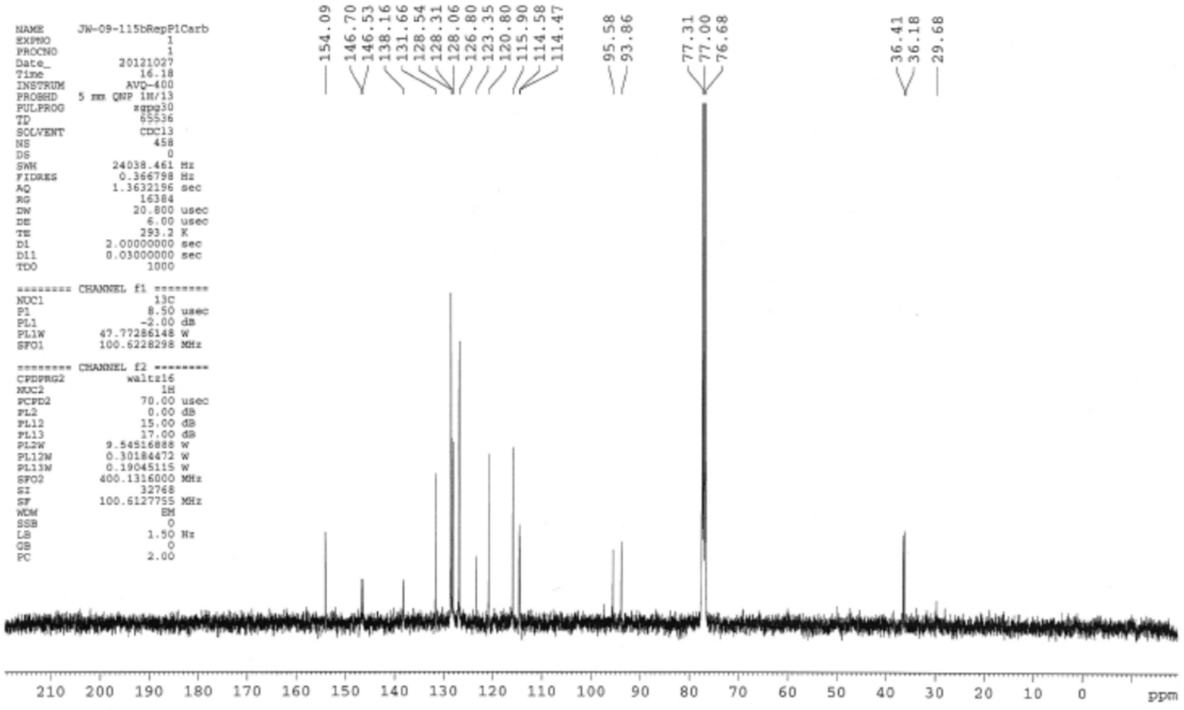

AVB-400 ZBO Carbon Starting paramters 6/11/03 RN

```
Current Data Parameters
NAME            JW-09-114
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121004
Time                17.05
INSTRUM           AVB-400
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    73
DS                     0
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                 16384
DW                20.850 usec
DE                  6.00 usec
TE                 297.1 K
D1            1.50000000 sec
D11           0.03000000 sec
TD0                 1000

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.50 usec
PL1                -2.00 dB
PL1W         47.77286148 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              70.00 usec
PL2                -3.00 dB
PL12               16.00 dB
PL13               16.00 dB
PL2W         23.05461311 W
PL12W         0.29024038 W
PL13W         0.29024038 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB       0
LB                  1.50 Hz
GB        0
PC                  1.40
```

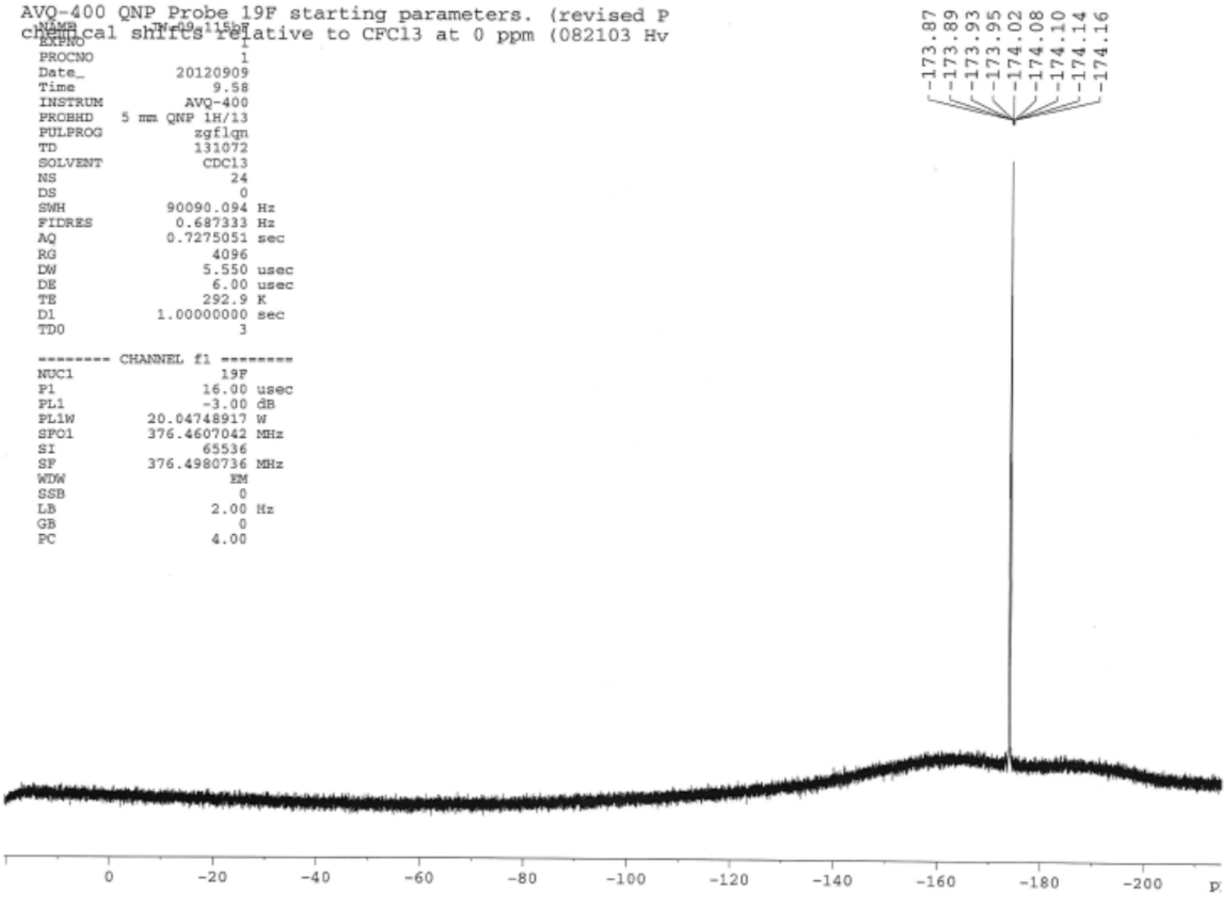


```
NAME          JW-09-115b
EXPNO                  1
PROCNO                 1
Date_           20120909
Time                9.56
INSTRUM          AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0895586 sec
RG                   256
DW                62.400 usec
DE                  6.00 usec
TE                 292.9 K
D1            1.00000000 sec
TD0                    2

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.80 usec
PL1                 0.00 dB
PL1W          9.54516888 W
SFO1         400.1324700 MHz
SI                 65536
SF           400.1300142 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                 16.00
```

55b rep AVQ-400 QNP Carbon Starting parameters 7/16/03 revised 7/2

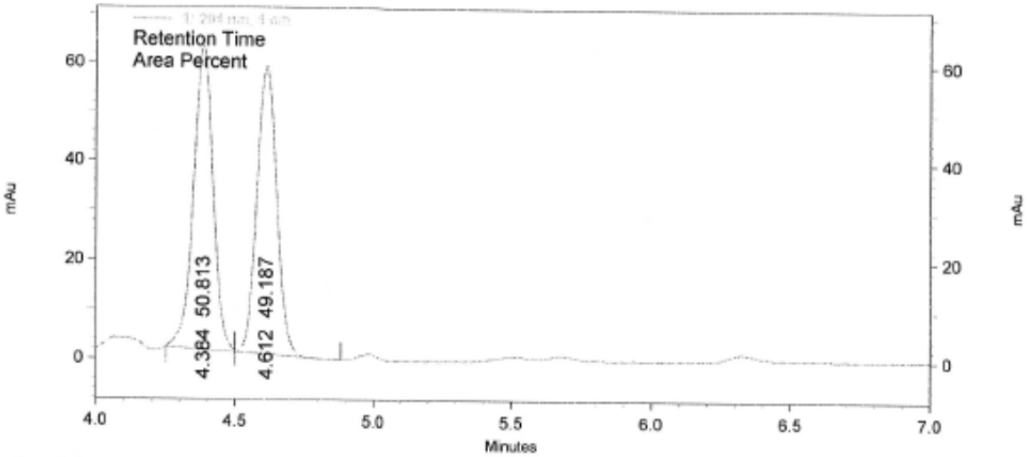


```
NAME     JW-09-115bRepP1Carb
EXPNO                  1
PROCNO                 1
Date_           20121027
Time               16.18
INSTRUM          AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   458
DS                     0
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3632196 sec
RG                 16384
DW                20.800 usec
DE                  6.00 usec
TE                 293.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                 1000

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.50 usec
PL1                -2.00 dB
PL1W         47.77286148 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              70.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               17.00 dB
PL2W          9.54516888 W
PL12W         0.30184472 W
PL13W         0.19045115 W
SFO2         400.1316000 MHz
SI                 32768
SF           100.6127755 MHz
WDW                   EM
SSB                    0
LB                  1.50 Hz
GB                     0
PC                  2.00
```



```
AVQ-400 QNP Probe 19F starting parameters. (revised P
chemical shifts relative to CFCl3 at 0 ppm (082103 Hv
  NAME          JW-09-115bF
  EXPNO                   1
  PROCNO                  1
  Date_            20120909
  Time                 9.58
  INSTRUM           AVQ-400
  PROBHD   5 mm QNP 1H/13
  PULPROG            zgflqn
  TD                 131072
  SOLVENT             CDCl3
  NS                     24
  DS                      0
  SWH          90090.094 Hz
  FIDRES        0.687333 Hz
  AQ           0.7275051 sec
  RG                   4096
  DW              5.550 usec
  DE               6.00 usec
  TE                292.9 K
  D1         1.00000000 sec
  TD0                     3

  ======== CHANNEL f1 ========
  NUC1                  19F
  P1              16.00 usec
  PL1               -3.00 dB
  PL1W       20.04748917 W
  SFO1      376.4607042 MHz
  SI                  65536
  SF        376.4980736 MHz
  WDW                    EM
  SSB                     0
  LB                2.00 Hz
  GB                      0
  PC                   4.00
```

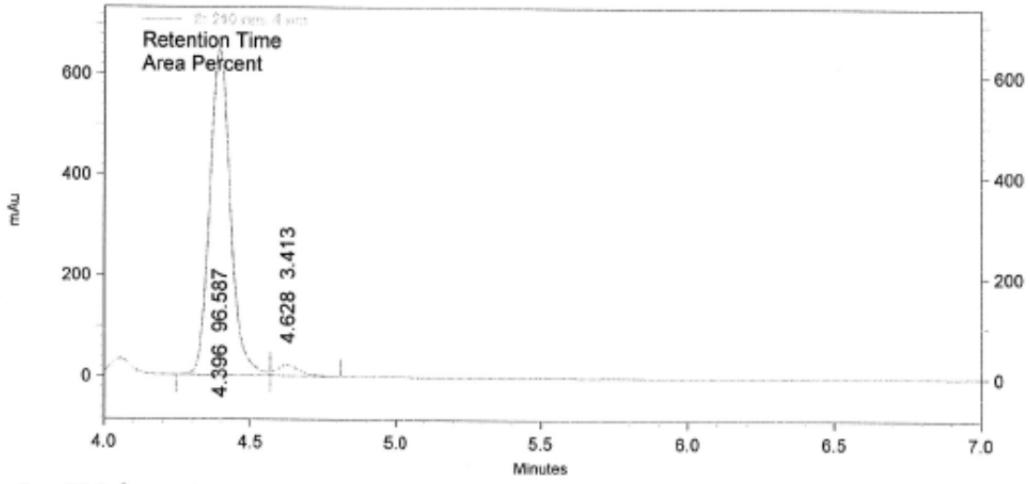
JW-09-115rac- IC9406



1: 204 nm, 4 nm
Results

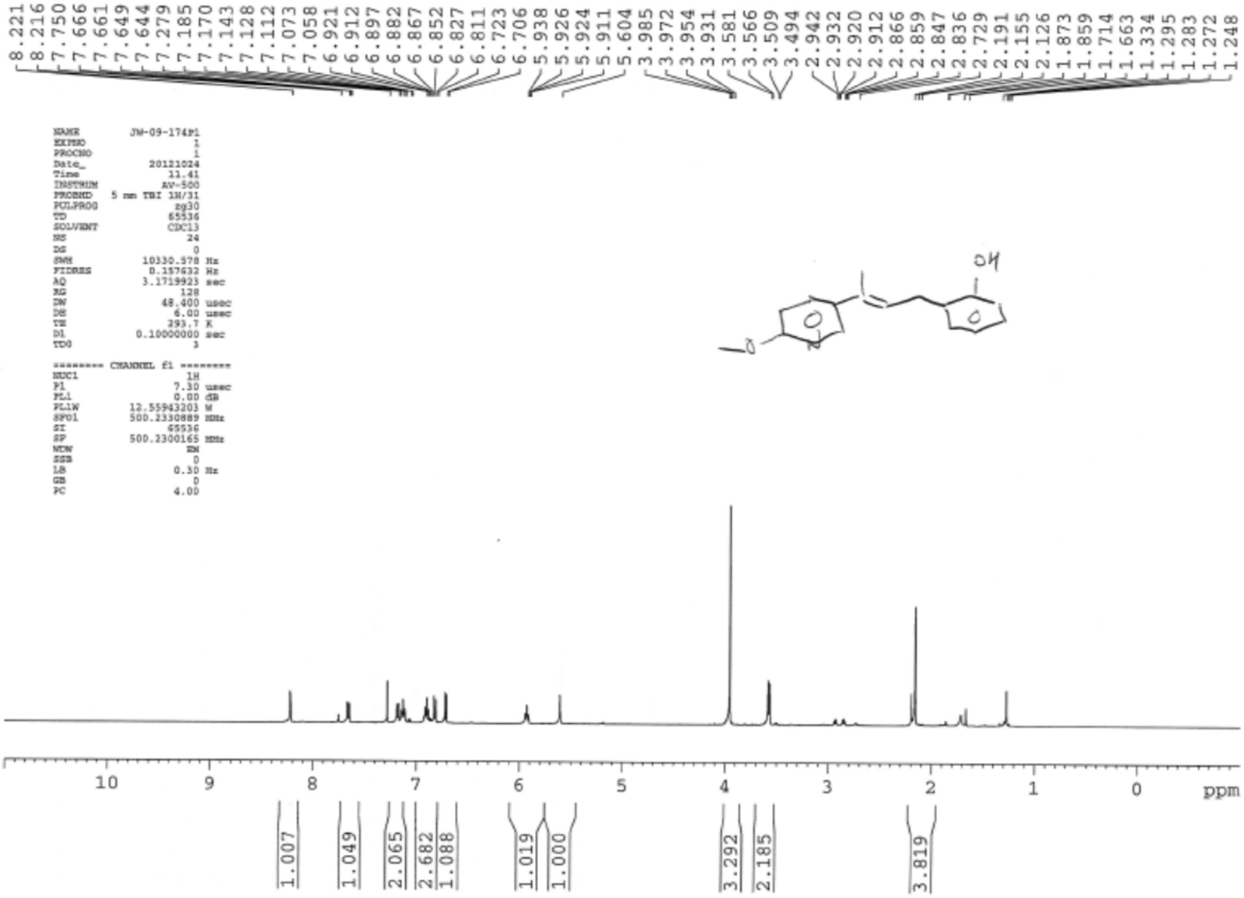
Pk #	Retention Time	Area Percent	Lambda Max
1	4.384	50.813	205
2	4.612	49.187	205

JW-09-115B- IC9406

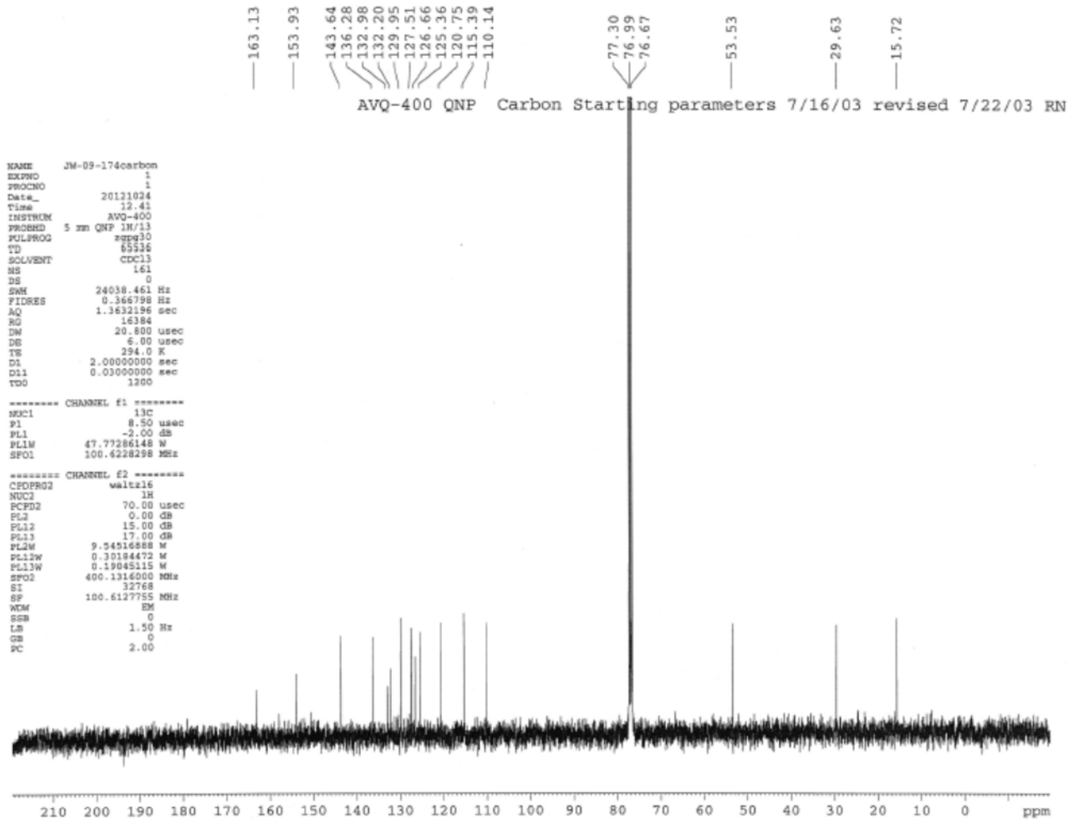


2: 210 nm, 4 nm
Results

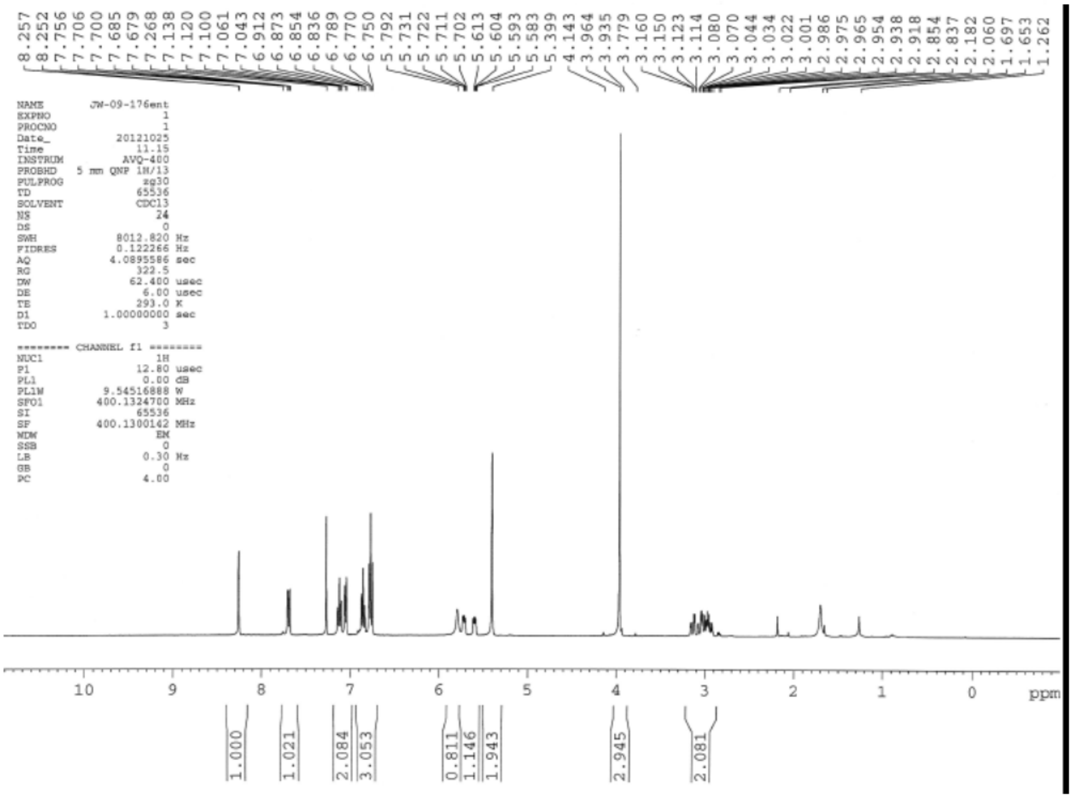
Pk #	Retention Time	Area Percent	Lambda Max
1	4.396	96.587	205
2	4.628	3.413	205



```
NAME        JW-09-174P1
EXPNO                 1
PROCNO                1
Date_          20121024
Time              11.41
INSTRUM          AV-500
PROBHD   5 mm TBI 1H/31
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   24
DS                    0
SWH         10330.578 Hz
FIDRES       0.157632 Hz
AQ          3.1719923 sec
RG                  128
DW             48.400 usec
DE               6.00 usec
TE              293.7 K
D1         0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1               7.30 usec
PL1              0.00 dB
PL1W      12.55943203 W
SFO1      500.2330889 MHz
SI                65536
SF        500.2300165 MHz
WDW                  EM
SSB                   0
LB               0.30 Hz
GB                    0
PC                 4.00
```

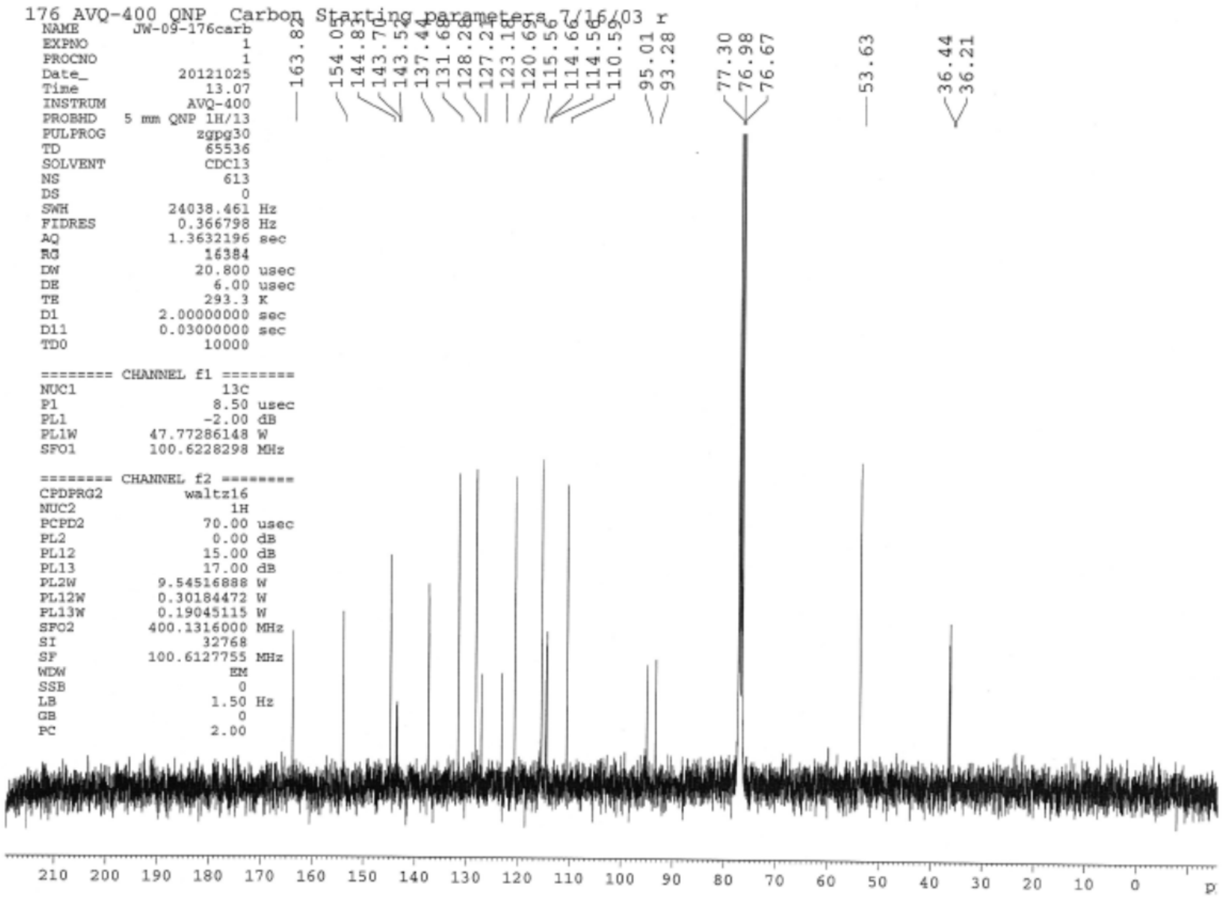


```
NAME        JM-09-174carbon
EXPNO                     1
PROCNO                    1
Date_              20121024
Time                  12.41
INSTRUM             AVQ-400
PROBHD     5 mm QNP 1H/13
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      161
DS                        0
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3632196 sec
RG                    16384
DW                   20.800 usec
DE                     6.00 usec
TE                    294.0 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                    1200

======== CHANNEL f1 ========
NUC1                    13C
P1                     8.50 usec
PL1                   -2.00 dB
PL1W            47.77286148 W
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 70.00 usec
PL2                    0.00 dB
PL12                  15.00 dB
PL13                  17.00 dB
PL2W             9.54516888 W
PL12W            0.30184472 W
PL13W            0.19045115 W
SFO2            400.1316000 MHz
SI                    32768
SF              100.6127755 MHz
WDW                      EM
SSB                       0
LB                     1.50 Hz
GB                        0
PC                     2.00
```



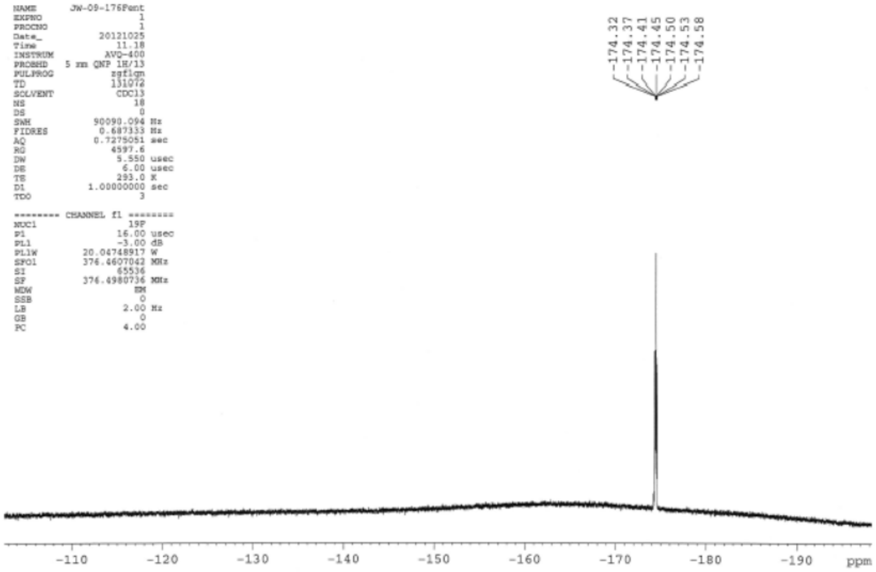
```
NAME        JW-09-176ent
EXPNO                  1
PROCNO                 1
Date_           20121025
Time               11.15
INSTRUM          AVQ-400
PROBHD    5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    24
DS                     0
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0895586 sec
RG                 322.5
DW                62.400 usec
DE                  6.00 usec
TE                 293.0 K
D1            1.00000000 sec
TD0                    3

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.80 usec
PL1                 0.00 dB
PL1W          9.54516888 W
SFO1         400.1324700 MHz
SI                 65536
SF           400.1300142 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00
```

176 AVQ-400 QNP Carbon Starting parameters 7/16/03 r



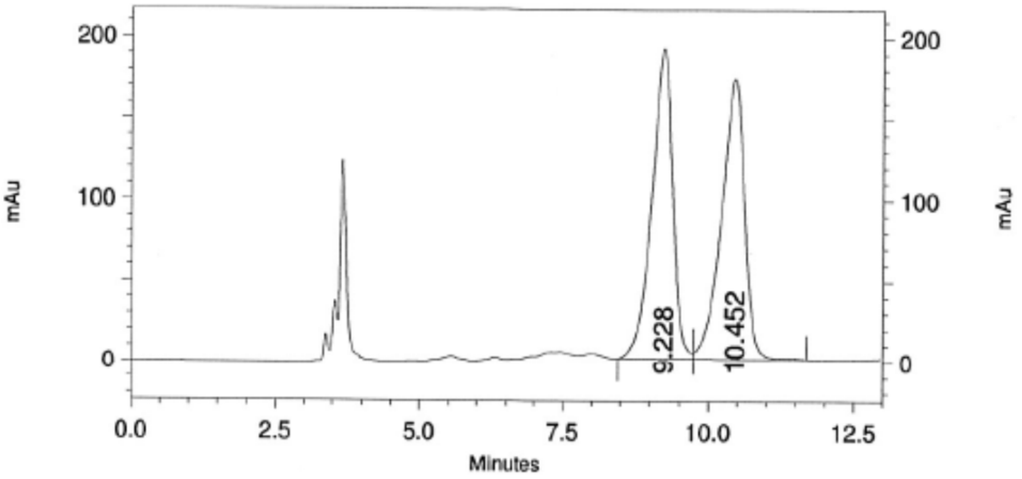
```
NAME          JW-09-176carb
EXPNO                     1
PROCNO                    1
Date_              20121025
Time                  13.07
INSTRUM             AVQ-400
PROBHD     5 mm QNP 1H/13
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     613
DS                       0
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3632196 sec
RG                   16384
DW                  20.800 usec
DE                    6.00 usec
TE                   293.3 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                  10000

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.50 usec
PL1                  -2.00 dB
PL1W           47.77286148 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                70.00 usec
PL2                   0.00 dB
PL12                 15.00 dB
PL13                 17.00 dB
PL2W            9.54516888 W
PL12W           0.30184472 W
PL13W           0.19045115 W
SFO2           400.1316000 MHz
SI                   32768
SF             100.6127755 MHz
WDW                     EM
SSB                      0
LB                    1.50 Hz
GB                       0
PC                    2.00
```

AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm



```
NAME          JW-09-176Fent
EXPNO                     1
PROCNO                    1
Date_              20121025
Time                  11.18
INSTRUM             AVQ-400
PROBHD     5 mm QNP 1H/13
PULPROG             zgflqn
TD                  131072
SOLVENT              CDCl3
NS                      18
DS                       0
SWH              90090.094 Hz
FIDRES            0.687333 Hz
AQ               0.7275051 sec
RG                  4597.6
DW                   5.550 usec
DE                    6.00 usec
TE                   293.0 K
D1              1.00000000 sec
TD0                      3

======== CHANNEL f1 ========
NUC1                   19F
P1                   16.00 usec
PL1                  -3.00 dB
PL1W           20.04748917 W
SFO1           376.4607042 MHz
SI                   65536
SF             376.4980736 MHz
WDW                     EM
SSB                      0
LB                    2.00 Hz
GB                       0
PC                    4.00
```

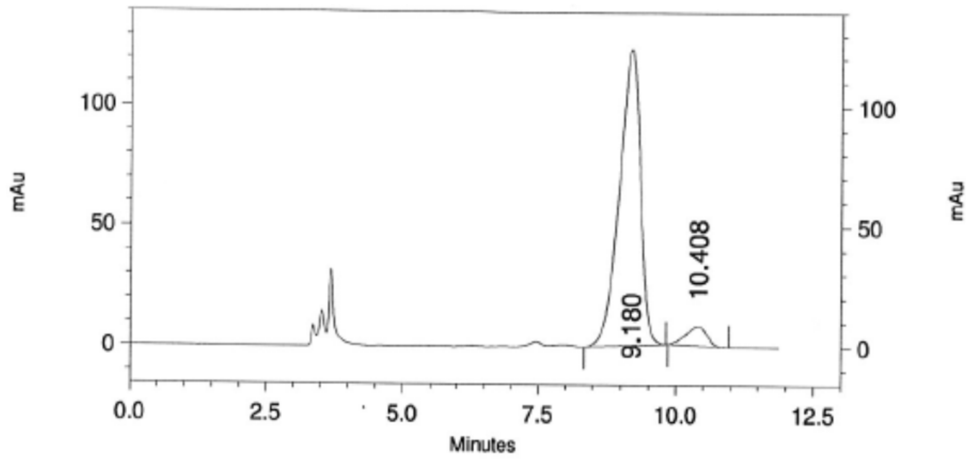
JW-09-176rac



1: 222 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
9.228	4754400	50.011	205
10.452	4752224	49.989	205

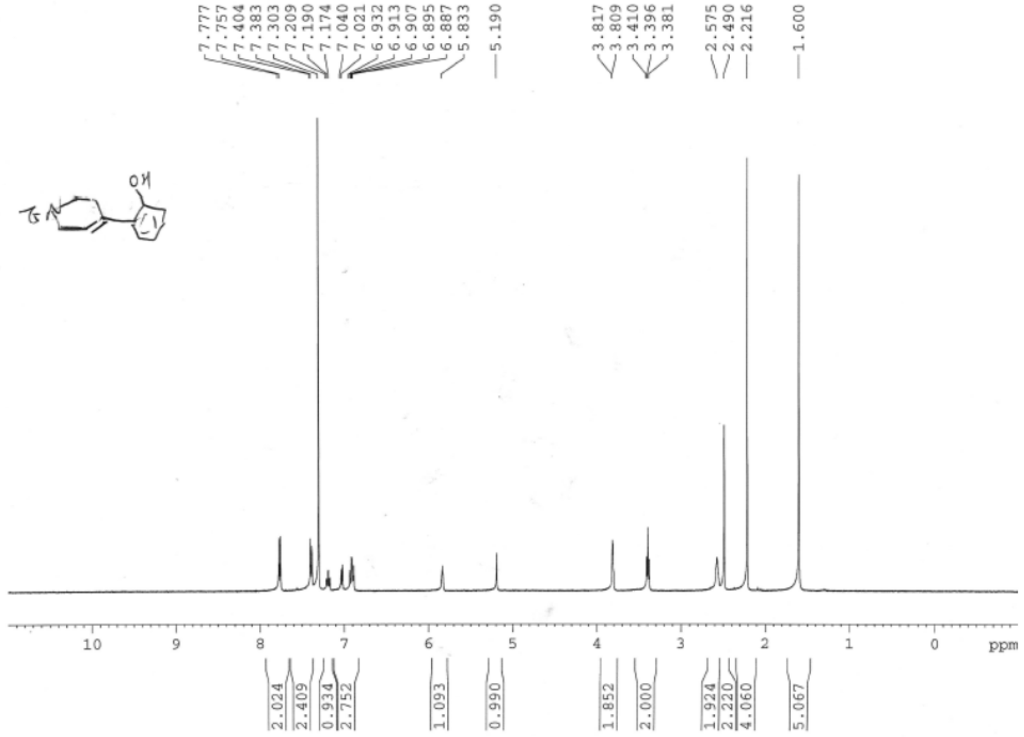
JW-09-176ent

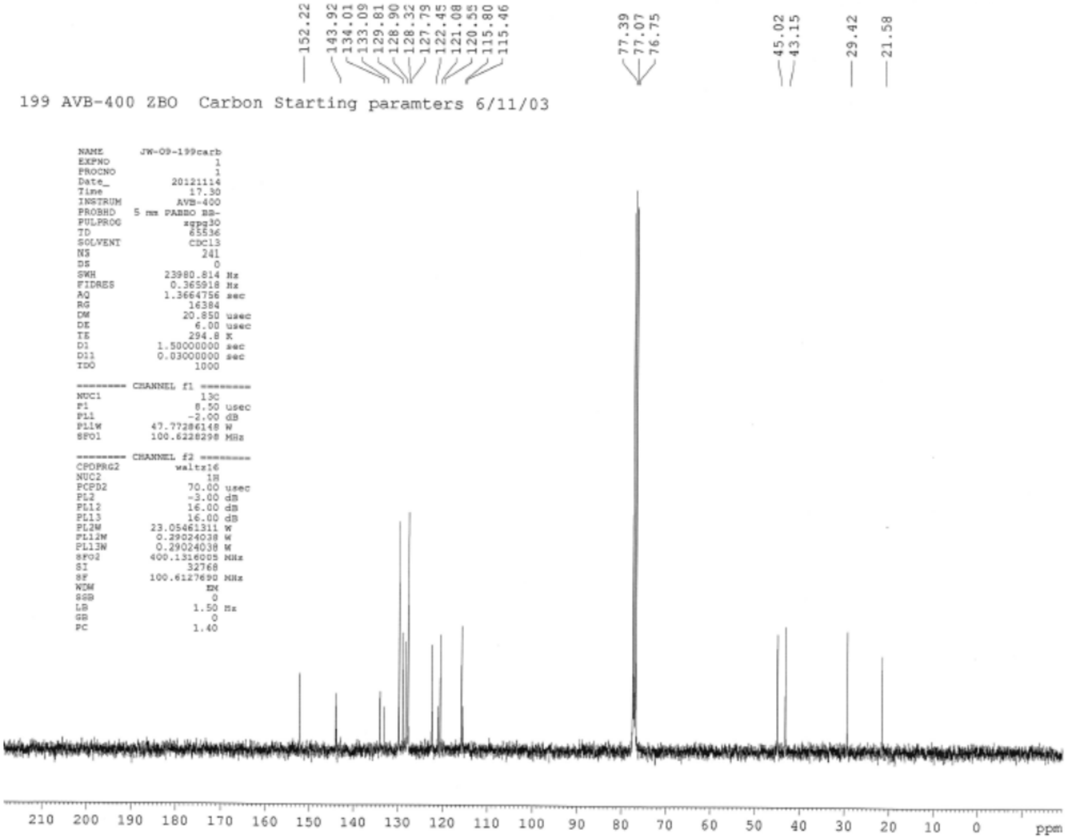


1: 222 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
9.180	3250038	93.910	245
10.408	210767	6.090	246

195 trit AVB-400 ZBO Proton starting parameters. 6/11/03 RN

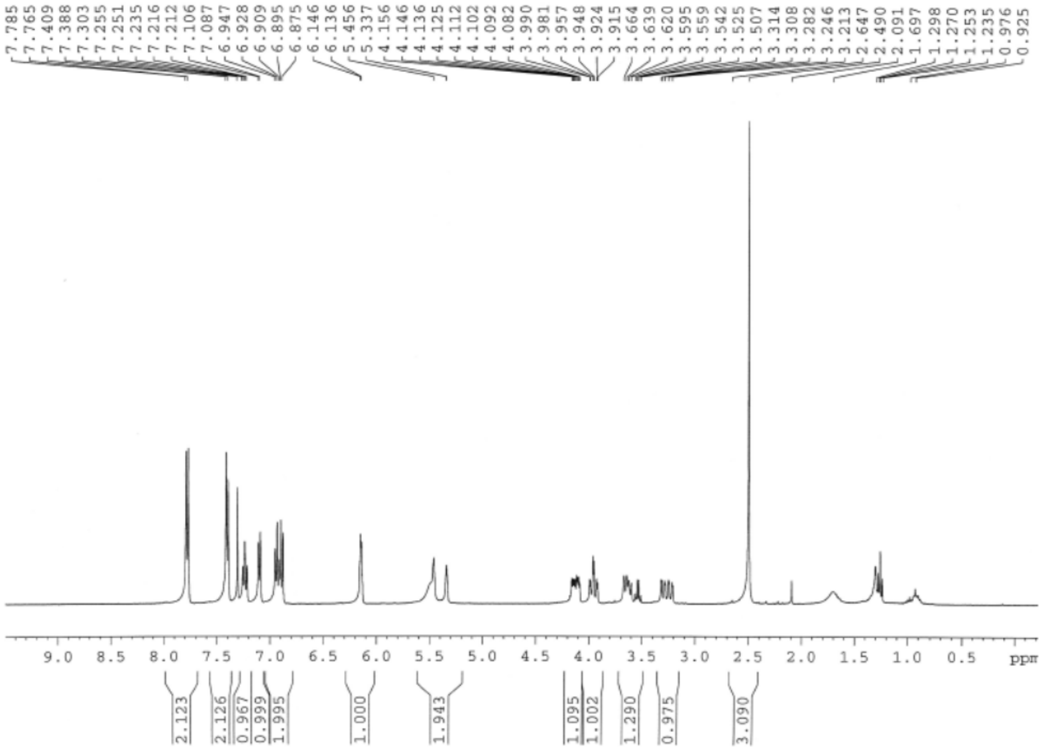




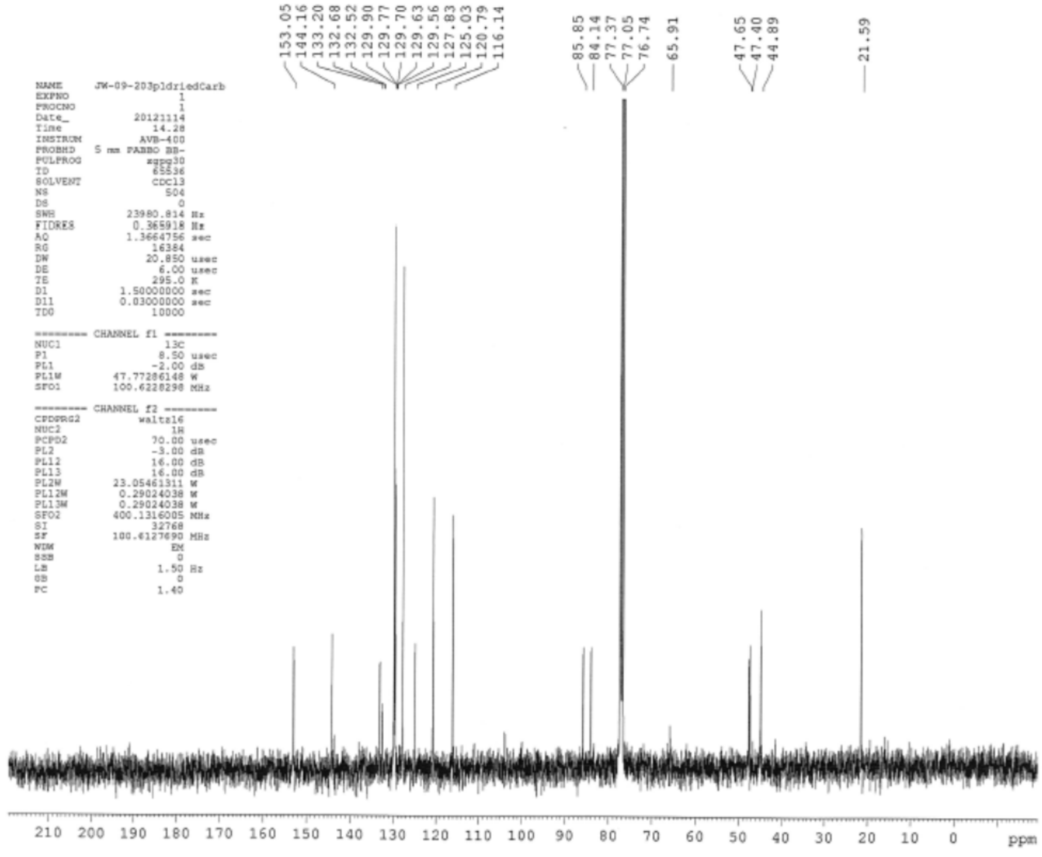
199 AVB-400 ZBO Carbon Starting paramters 6/11/03

```
NAME        JW-09-199carb
EXPNO                   1
PROCNO                  1
Date_            20121114
Time                17.30
INSTRUM           AVB-400
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   241
DS                     0
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                 16384
DW                20.850 usec
DE                  6.00 usec
TE                 294.8 K
D1            1.50000000 sec
D11           0.03000000 sec
TD0                 1000

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.50 usec
PL1                -2.00 dB
PL1W         47.77286148 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              70.00 usec
PL2                -3.00 dB
PL12               16.00 dB
PL13               16.00 dB
PL2W         23.05461311 W
PL12W         0.29024038 W
PL13W         0.29024038 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.50 Hz
GB                     0
PC                  1.40
```

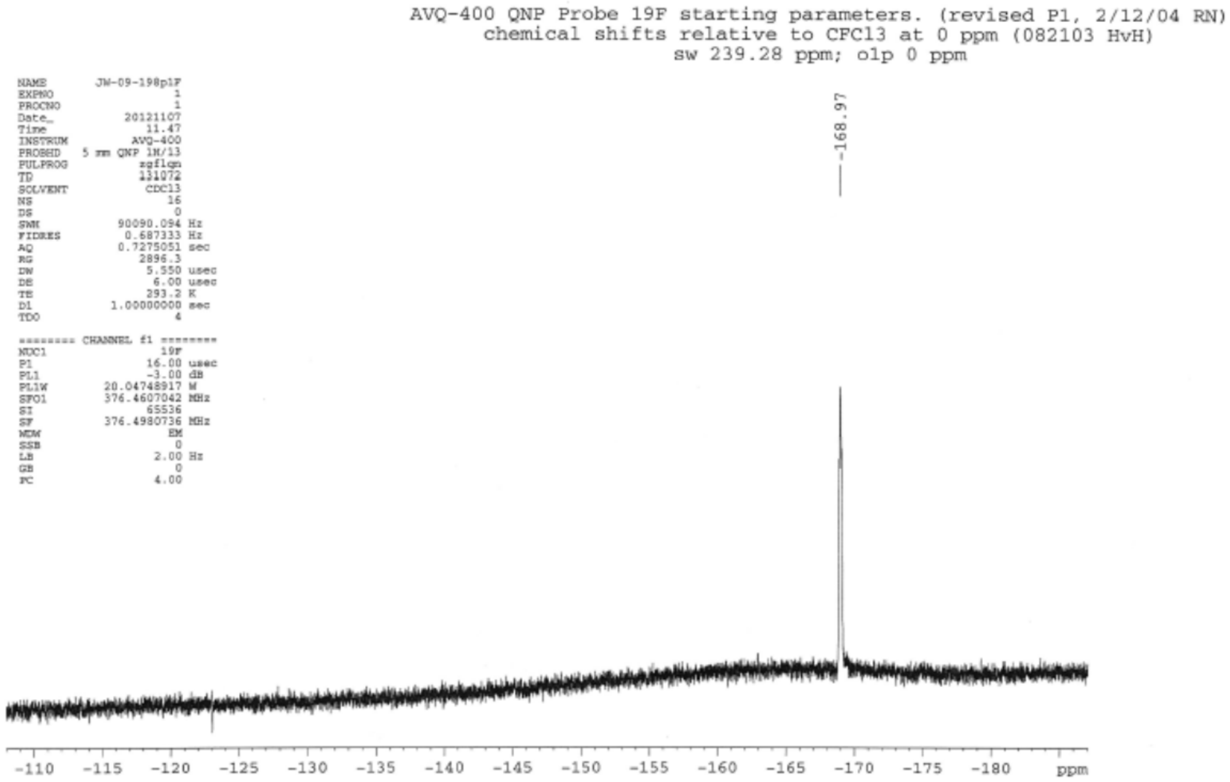
203 AVB-400 ZBO Proton starting parameters. 6/11/03 RN



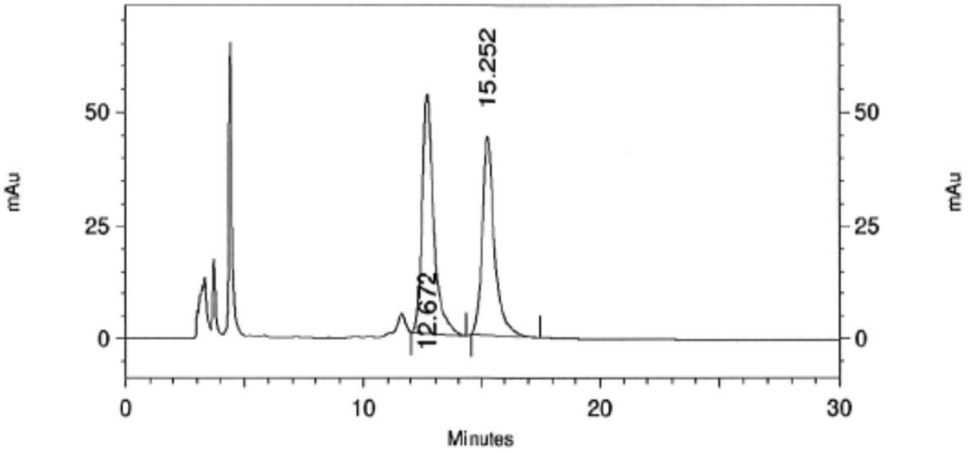
203 AVB-400 ZBO Carbon Starting paramters 6/11/03



```
NAME       JW-09-203pldriedCarb
EXPNO                     1
PROCNO                    1
Date_              20121114
Time                  14.28
INSTRUM             AVB-400
PROBHD     5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      504
DS                        0
SWH               23980.814 Hz
FIDRES             0.365918 Hz
AQ                1.3664756 sec
RG                    16384
DW                   20.850 usec
DE                     6.00 usec
TE                    295.0 K
D1               1.50000000 sec
D11              0.03000000 sec
TD0                   10000

======== CHANNEL f1 ========
NUC1                    13C
P1                     8.50 usec
PL1                   -2.00 dB
PL1W            47.77286148 W
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 70.00 usec
PL2                   -3.00 dB
PL12                  16.00 dB
PL13                  16.00 dB
PL2W            23.05461311 W
PL12W            0.29024038 W
PL13W            0.29024038 W
SFO2            400.1316005 MHz
SI                    32768
SF              100.6127690 MHz
WDW                      EM
SSB                       0
LB                     1.50 Hz
GB                        0
PC                     1.40
```

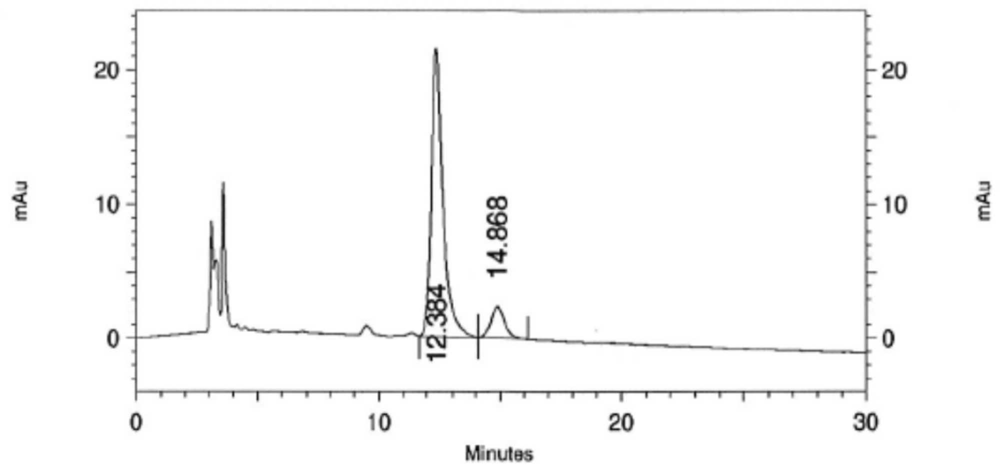


```
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm

NAME          JW-09-198p1F
EXPNO                    1
PROCNO                   1
Date_             20121107
Time                 11.47
INSTRUM            AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG             zgflqn
TD                  131072
SOLVENT              CDCl3
NS                      16
DS                       0
SWH           90090.094 Hz
FIDRES         0.687333 Hz
AQ            0.7275051 sec
RG                  2896.3
DW               5.550 usec
DE                6.00 usec
TE               293.2 K
D1          1.00000000 sec
TD0                      4

======== CHANNEL f1 ========
NUC1                   19F
P1               16.00 usec
PL1              -3.00 dB
PL1W       20.04748917 W
SFO1       376.4607042 MHz
SI                   65536
SF         376.4980736 MHz
WDW                     EM
SSB                      0
LB                2.00 Hz
GB                       0
PC                    4.00
```



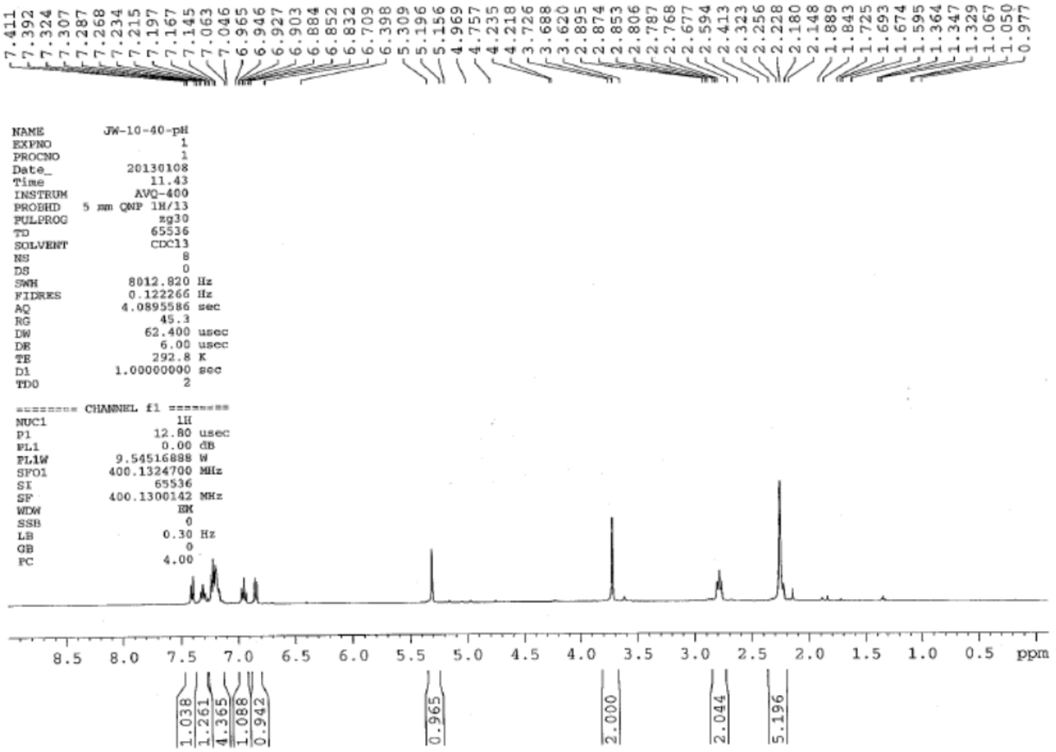
1: 223 nm, 4
nm Results

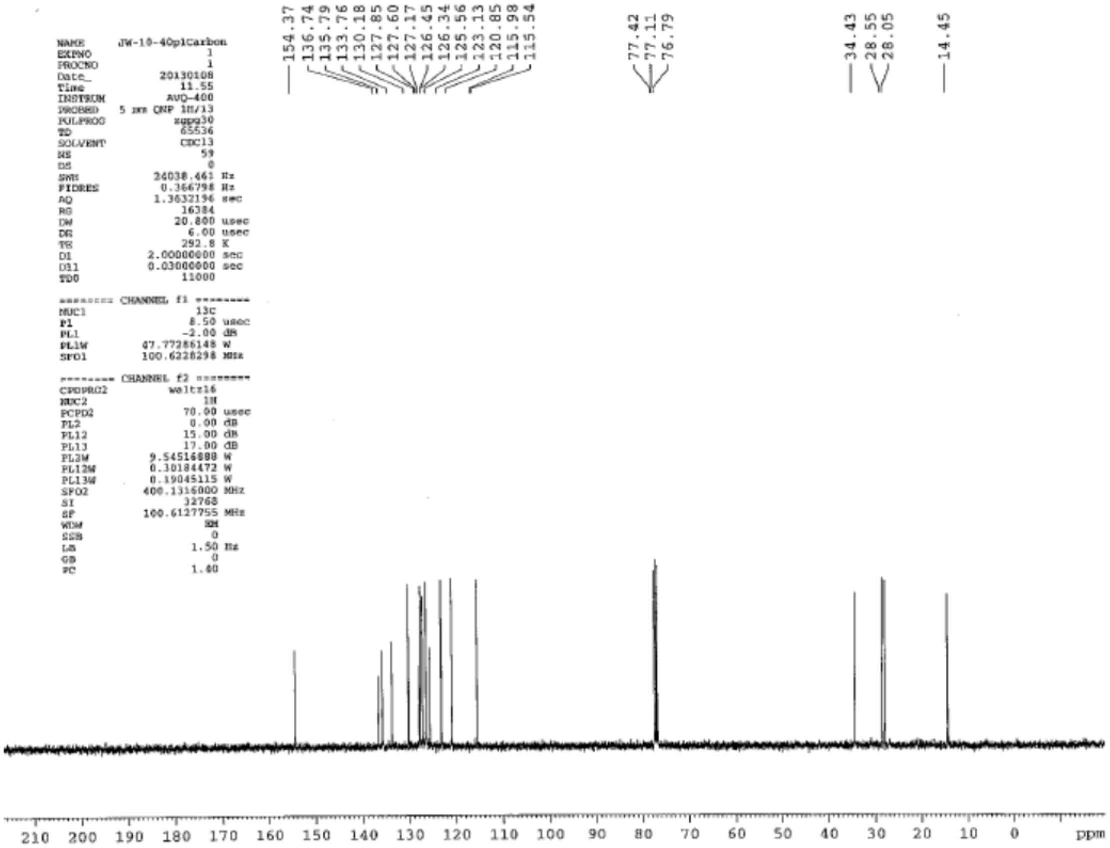
Retention Time	Area	Area Percent	Lambda Max
12.672	1731570	50.077	208
15.252	1726247	49.923	208



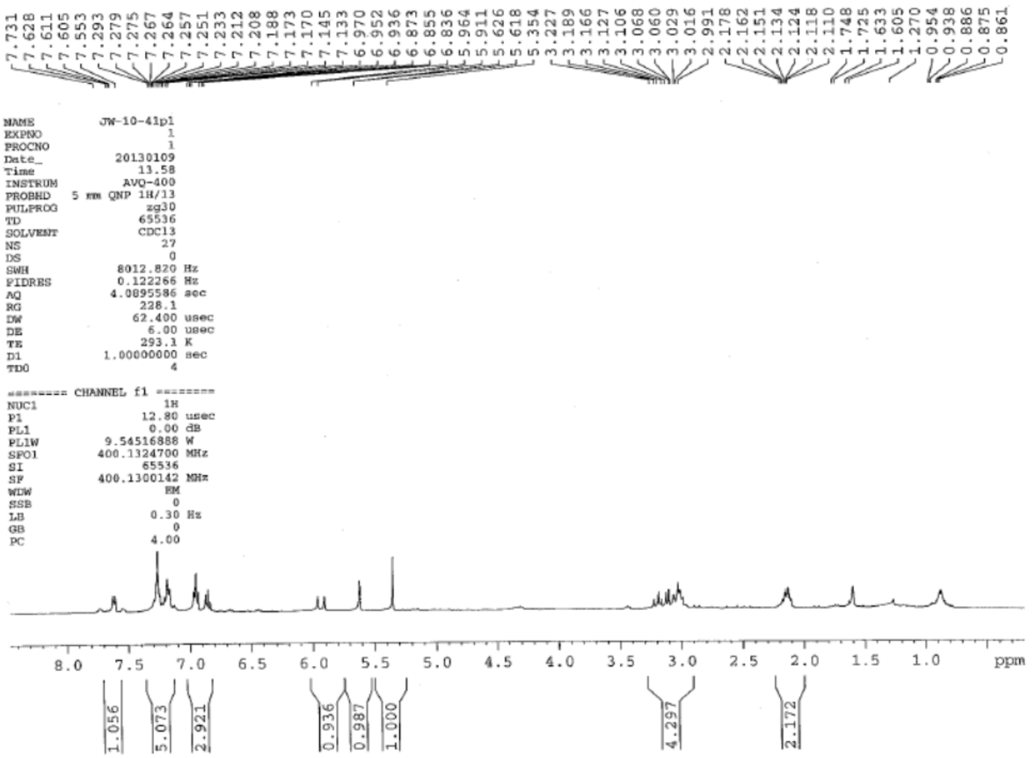
1: 223 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
12.384	685715	88.375	207
14.868	90201	11.625	206

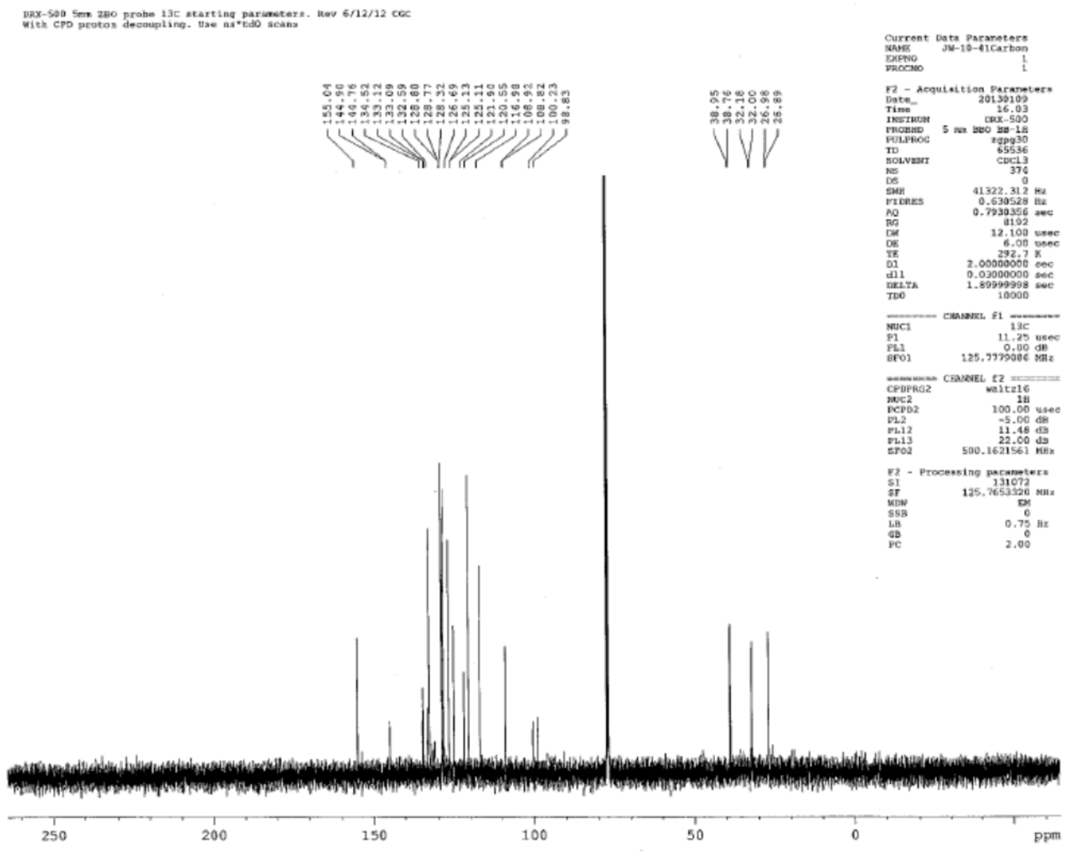




NAME JW-10-40p1Carbon
EXPNO 1
PROCNO 1
Date_ 20130108
Time 11.55
INSTRUM AVQ-400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 59
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3632196 sec
RG 16384
DW 20.800 usec
DE 6.00 usec
TE 292.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 11000
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 47.77286148 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 0.00 dB
PL12 15.00 dB
PL13 17.00 dB
PL2W 9.54516888 W
PL12W 0.30184472 W
PL13W 0.19045115 W
SFO2 400.1316000 MHz
SI 32768
SF 100.6127755 MHz
WDW EM
SSB 0
LB 1.50 Hz
GB 0
PC 1.40
154.37
136.74
135.79
133.76
130.18
127.85
127.60
127.17
126.45
126.34
125.56
123.13
120.85
115.98
115.54
77.42
77.11
76.79
34.43
28.55
28.05
14.45
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



7.731
7.628
7.611
7.605
7.553
7.293
7.279
7.275
7.267
7.264
7.257
7.251
7.233
7.212
7.208
7.188
7.173
7.170
7.145
7.133
6.952
6.970
6.936
6.873
6.855
6.836
5.964
5.911
5.626
5.618
5.354
3.227
3.189
3.166
3.127
3.106
3.068
3.060
3.029
3.016
2.991
2.178
2.162
2.151
2.134
2.124
2.118
2.110
1.748
1.725
1.633
1.605
1.270
0.954
0.938
0.886
0.875
0.861
NAME JW-10-41p1
EXPNO 1
PROCNO 1
Date_ 20130109
Time 13.58
INSTRUM AVQ-400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 27
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0895586 sec
RG 228.1
DW 62.400 usec
DE 6.00 usec
TE 293.1 K
D1 1.00000000 sec
TD0 4
======== CHANNEL f1 ========
NUC1 1H
P1 12.80 usec
PL1 0.00 dB
PL1W 9.54516888 W
SFO1 400.1324700 MHz
SI 65536
SF 400.1300142 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.056
5.073
2.921
0.936
0.987
1.000
4.297
2.172

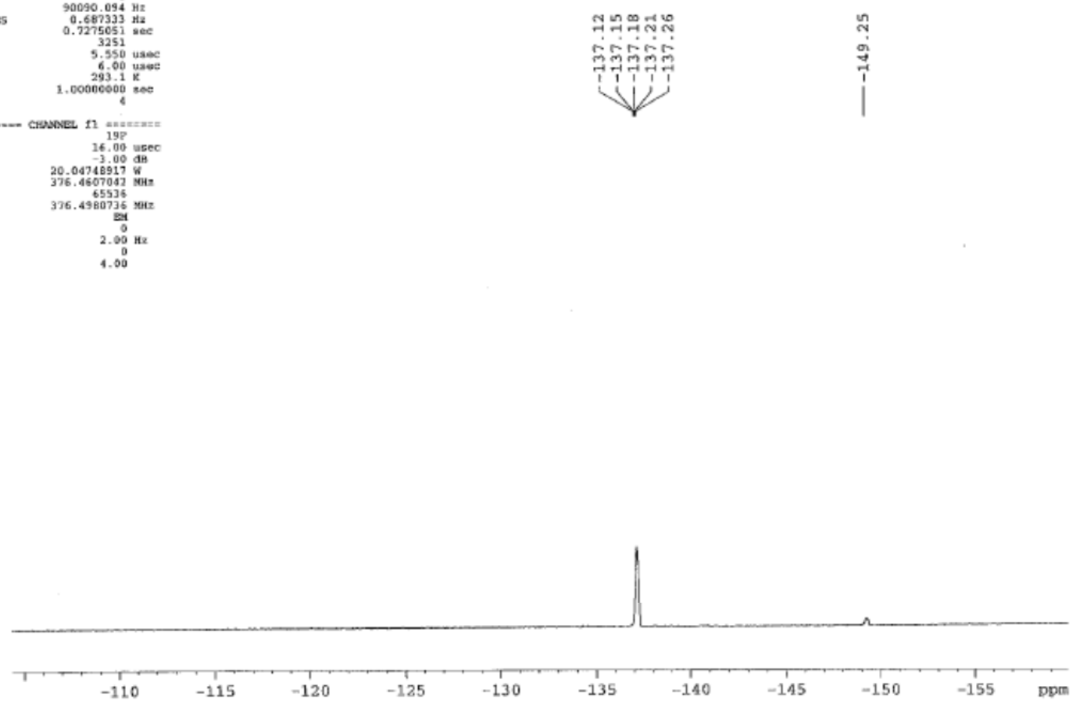


DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans

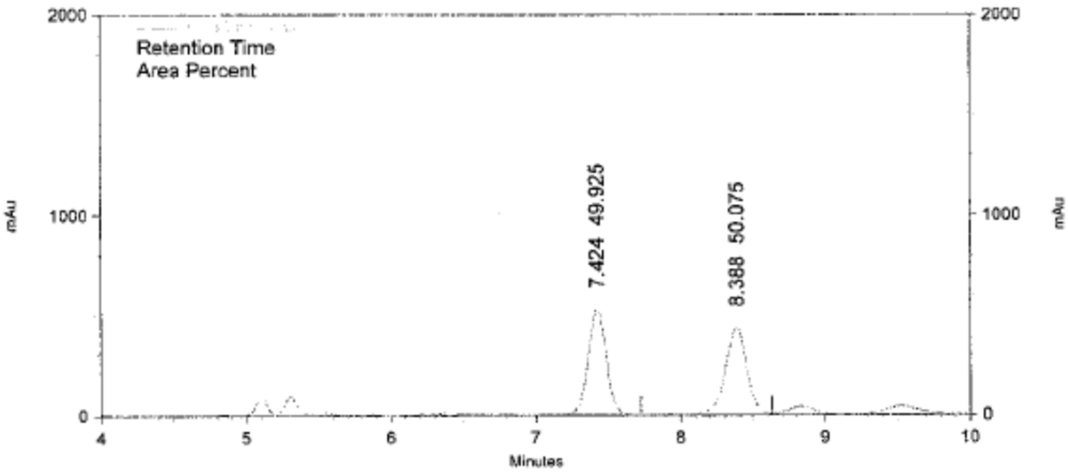
```
Current Data Parameters
NAME       JW-10-41Carbon
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130109
Time                16.03
INSTRUM           DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    374
DS                      0
SWH            41322.312 Hz
FIDRES          0.630528 Hz
AQ             0.7930356 sec
RG                   8192
DW                 12.100 usec
DE                   6.00 usec
TE                  292.7 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                 10000

======== CHANNEL f1 ========
NUC1                  13C
P1                  11.25 usec
PL1                  0.00 dB
SFO1          125.7779086 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -5.00 dB
PL12                11.48 dB
PL13                22.00 dB
SFO2          500.1621561 MHz

F2 - Processing parameters
SI                 131072
SF            125.7653320 MHz
WDW                    EM
SSB                     0
LB                   0.75 Hz
GB                      0
PC                   2.00
```

```
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; olp 0 ppm
```

```
NAME       JW-10-41p1F-300
EXPNO                    1
PROCNO                   1
Date_             20130109
Time                 13.55
INSTRUM            AVQ-400
PROBHD    5 mm QNP 1H/13
PULPROG             zgflqn
TD                  131072
SOLVENT              CDCl3
NS                      32
DS                       0
SWH              90090.094 Hz
FIDRES            0.687333 Hz
AQ               0.7275051 sec
RG                    3251
DW                   5.550 usec
DE                    6.00 usec
TE                   293.1 K
D1              1.00000000 sec
TD0                      4

======== CHANNEL f1 ========
NUC1                   19F
P1                   16.00 usec
PL1                  -3.00 dB
PL1W           20.04748917 W
SFO1           376.4607042 MHz
SI                   65536
SF             376.4980736 MHz
WDW                     EM
SSB                      0
LB                    2.00 Hz
GB                       0
PC                    4.00
```



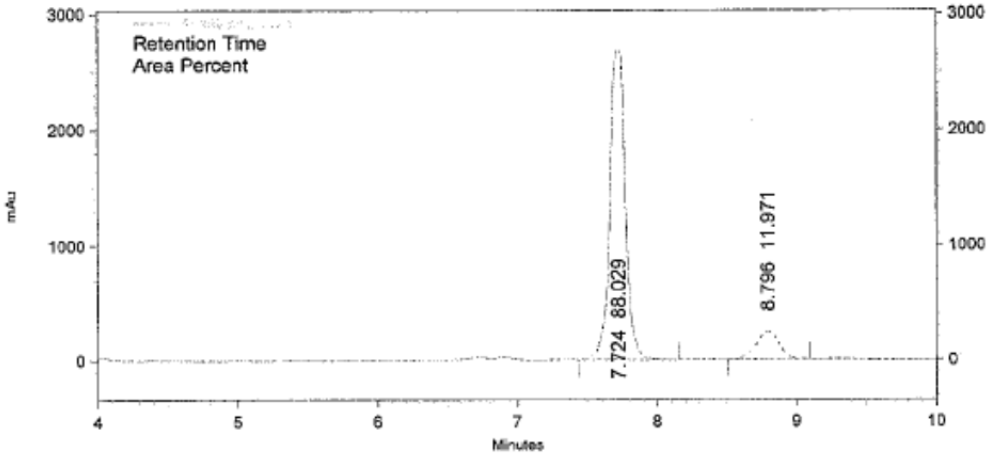
JW-10-41rac



1: 190 nm, 4 nm
Results

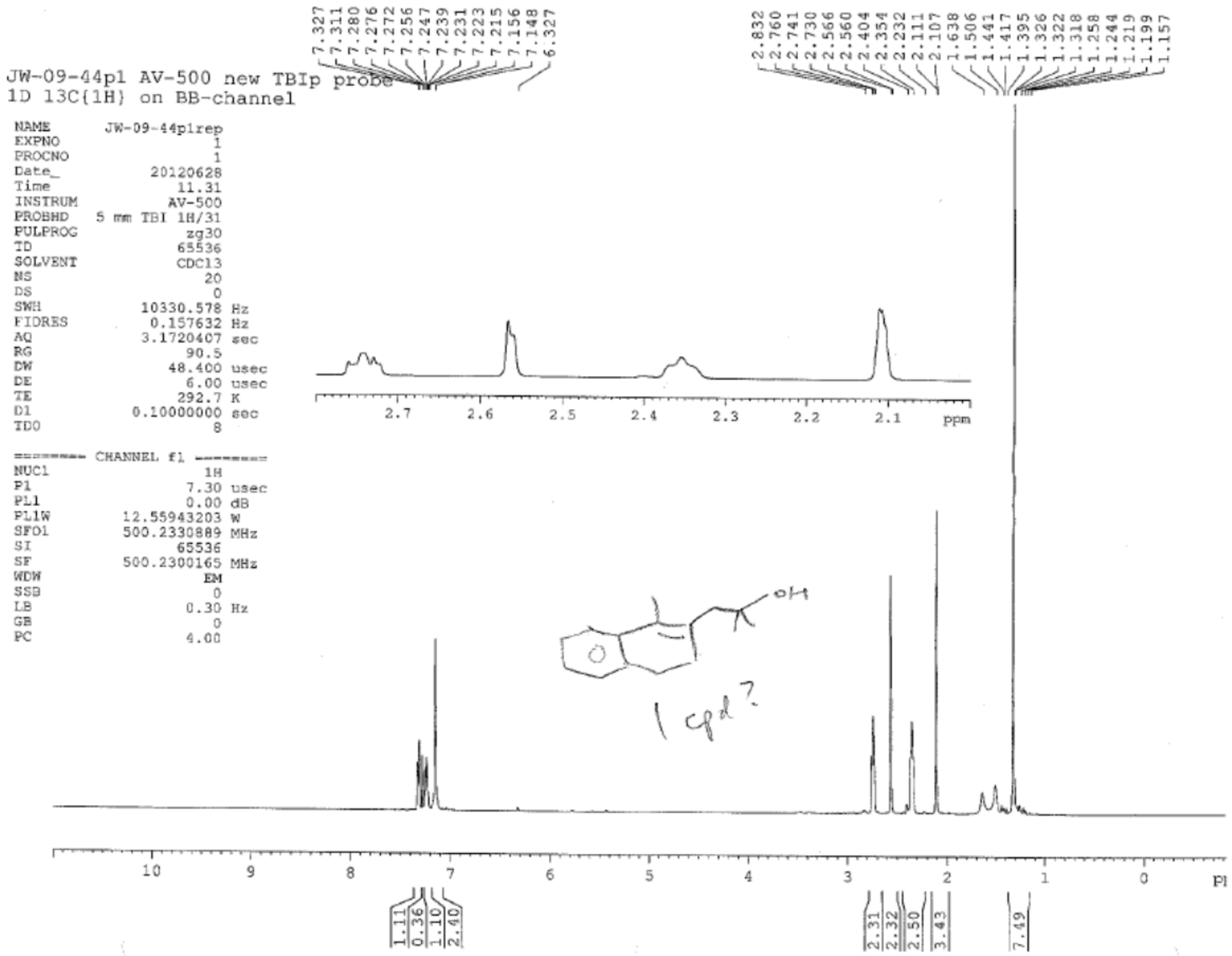
Pk #	Retention Time	Area Percent	Lambda Max
1	7.424	49.925	203
2	8.388	50.075	203

JW-10-41

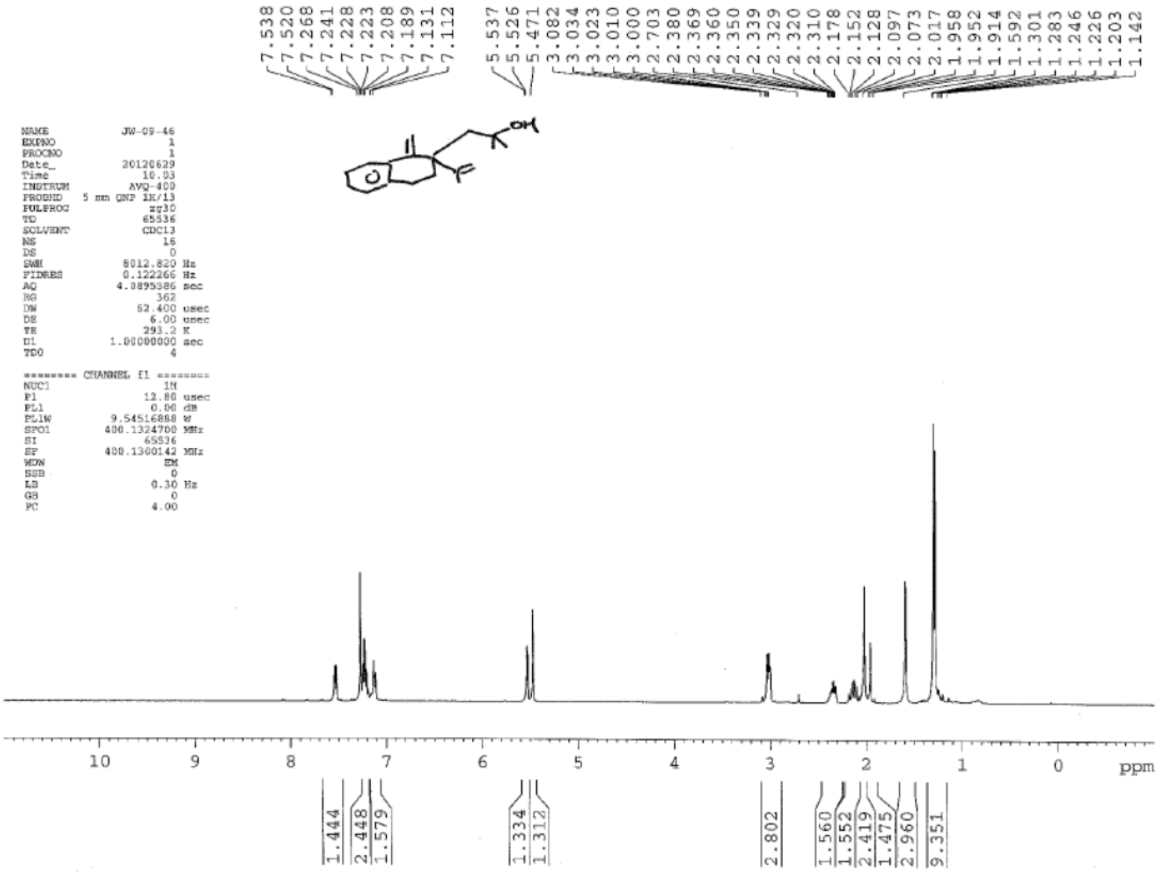


1: 190 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	7.724	88.029	247
2	8.796	11.971	203

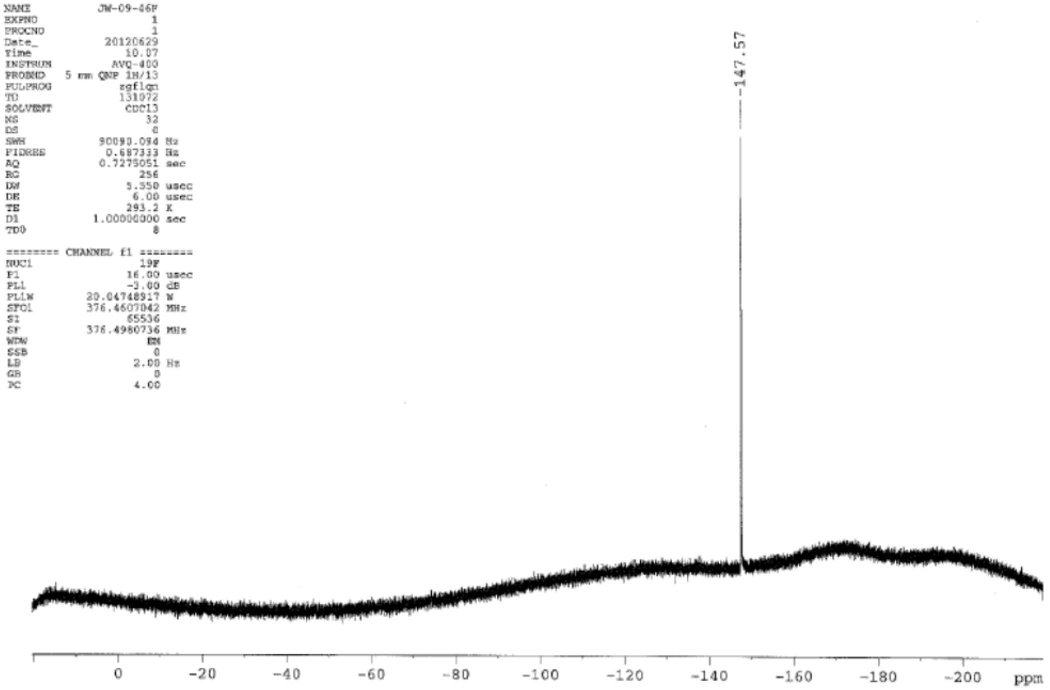


```
NAME          JW-09-44p1rep
EXPNO                     1
PROCNO                    1
Date_              20120628
Time                  11.31
INSTRUM              AV-500
PROBHD     5 mm TBI 1H/31
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       20
DS                        0
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ               3.1720407 sec
RG                     90.5
DW                   48.400 usec
DE                     6.00 usec
TE                    292.7 K
D1               0.10000000 sec
TD0                       8

======== CHANNEL f1 ========
NUC1                     1H
P1                     7.30 usec
PL1                    0.00 dB
PL1W            12.55943203 W
SFO1            500.2330889 MHz
SI                    65536
SF              500.2300165 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     4.00
```



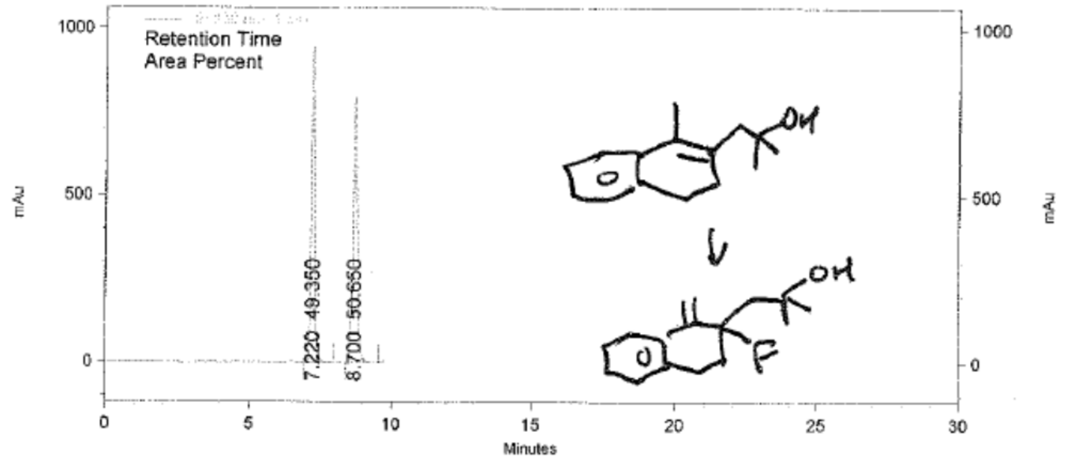
```
NAME          JW-09-46
EXPNO                1
PROCNO               1
Date_         20120629
Time             10.03
INSTRUM        AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   0
SWH           8012.820 Hz
FIDRES        0.122266 Hz
AQ           4.0895386 sec
RG                 362
DW              62.400 usec
DE                6.00 usec
TE               293.2 K
D1          1.00000000 sec
TD0                  4

======== CHANNEL f1 ========
NUC1                1H
P1               12.80 usec
PL1               0.00 dB
PL1W        9.54516888 W
SFO1       400.1324700 MHz
SI               65536
SF         400.1300142 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                4.00
```

46 AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm



```
NAME         JW-09-46F
EXPNO                1
PROCNO               1
Date_         20120629
Time             10.07
INSTRUM        AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG          zgflqn
TD              131072
SOLVENT          CDCl3
NS                  32
DS                   0
SWH          90090.094 Hz
FIDRES        0.687333 Hz
AQ           0.7275051 sec
RG                 256
DW               5.550 usec
DE                6.00 usec
TE               293.2 K
D1          1.00000000 sec
TD0                  8

======== CHANNEL f1 ========
NUC1               19F
P1               16.00 usec
PL1              -3.00 dB
PL1W       20.04748917 W
SFO1       376.4607042 MHz
SI               65536
SF         376.4980736 MHz
WDW                 EM
SSB                  0
LB                2.00 Hz
GB                   0
PC                4.00
```

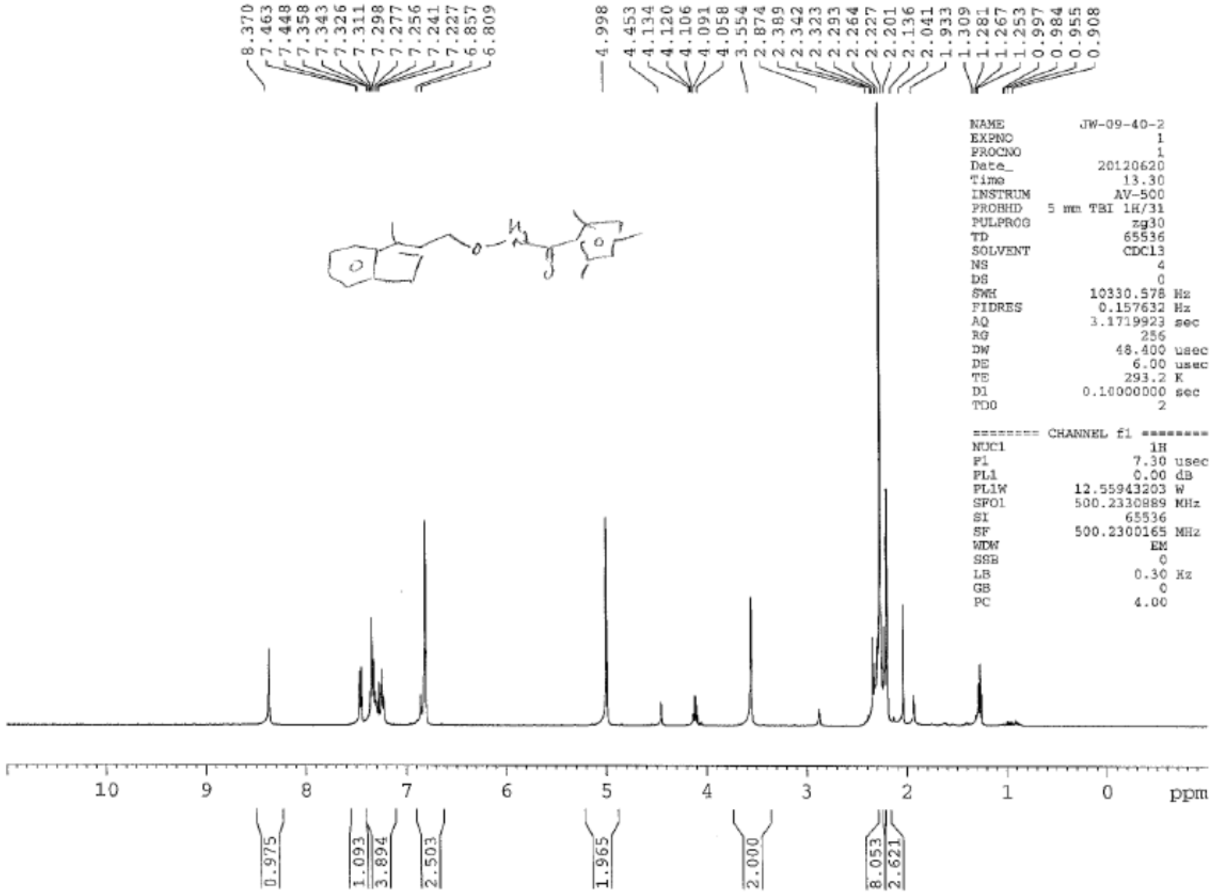
09-46ent ia9604



2: 239 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	7.220	49.350	202
2	8.700	50.650	199

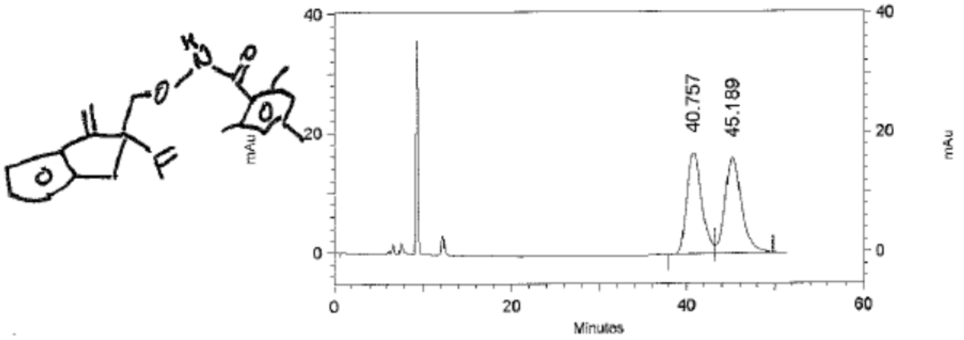
40-2 AV-500 new TBI(HXP) probe
1D 1H starting parameters



```
NAME         JW-09-40-2
EXPNO                 1
PROCNO                1
Date_          20120620
Time              13.30
INSTRUM          AV-500
PROBHD   5 mm TBI 1H/31
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    4
DS                    0
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719923 sec
RG                  256
DW               48.400 usec
DE                 6.00 usec
TE                293.2 K
D1           0.10000000 sec
TD0                   2

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.30 usec
PL1                0.00 dB
PL1W        12.55943203 W
SFO1        500.2330889 MHz
SI                65536
SF          500.2300165 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 4.00
```

Sample ID: **JW-09-41rac**
Filename:
C:\EZStart\Projects\Default\Data\JWu\JW-09-41rac_OD9604_60halfflow.met6-22-2
012 1-17-59 PM.dat Method:
C:\EZStart\Projects\Default\Method\Yiming\OD9604IP_pt5flow_60min.met
Injection volume: 5 uL

Description: {Data Description}

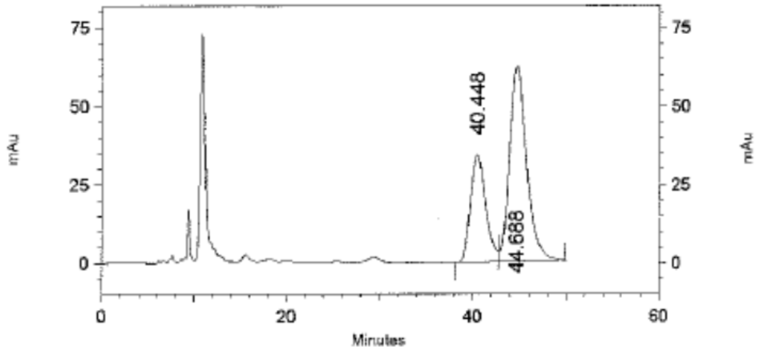


2: 250 nm, 4 nm Results

Retention Time	Area	Area Percent
40.757	1973761	48.733
45.189	2076433	51.267

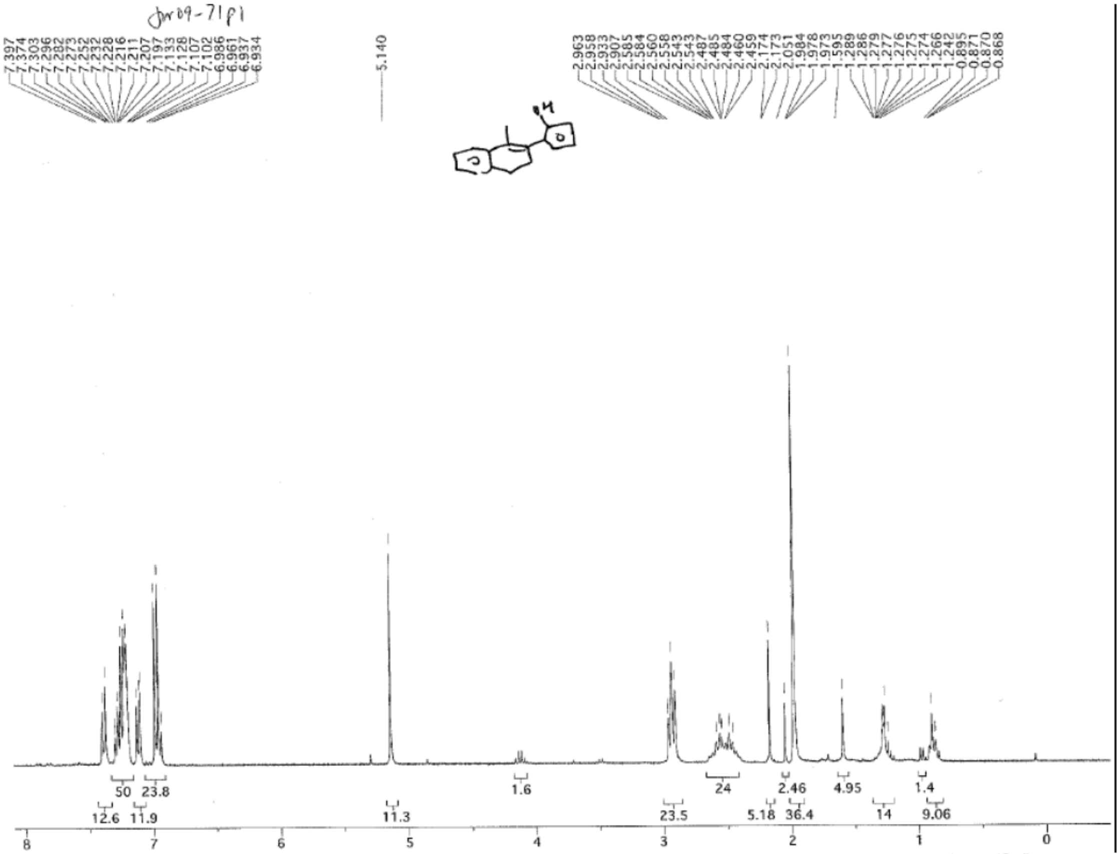
Sample ID: **JW-09-41ent**
Filename:
C:\EZStart\Projects\Default\Data\JWu\JW-09-41ent_OD9604_60halfflow.met6-22-2
012 2-35-51 PM.dat Method:
C:\EZStart\Projects\Default\Method\Yiming\OD9604IP_pt5flow_60min.met
Injection volume: 5 uL

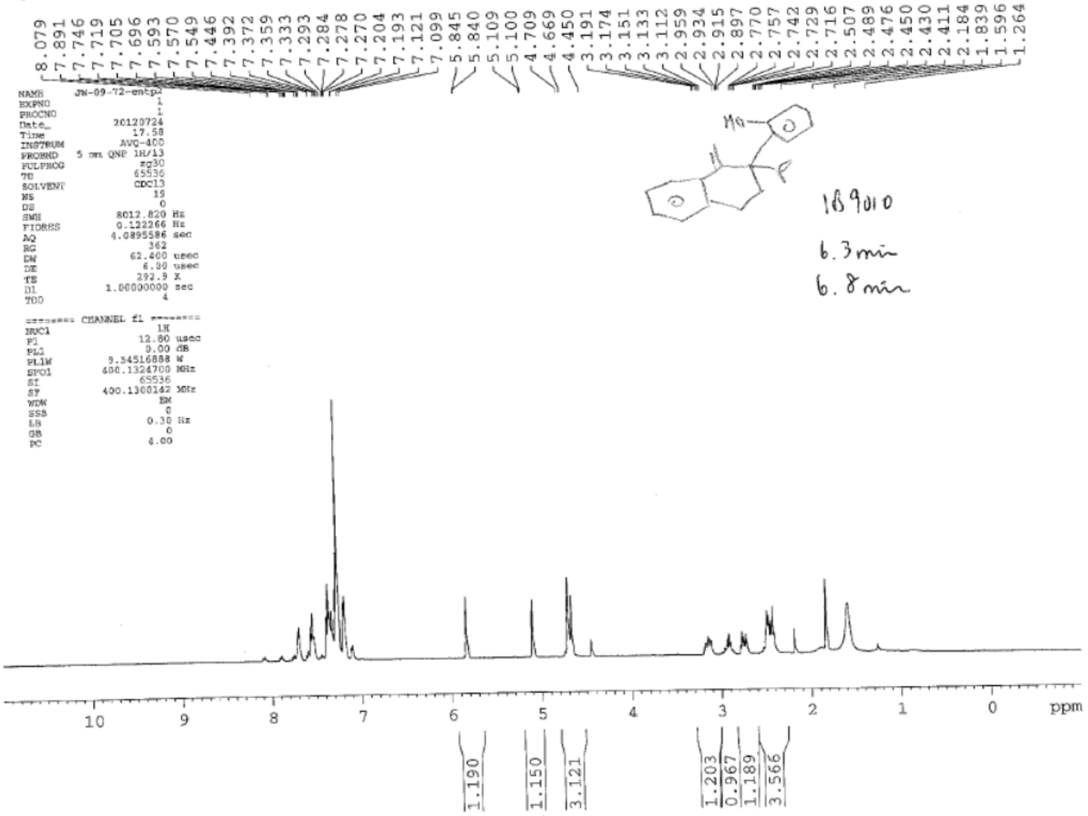
Description: {Data Description}



2: 250 nm, 4 nm Results

Retention Time	Area	Area Percent
40.448	3814523	32.696
44.688	7852100	67.304



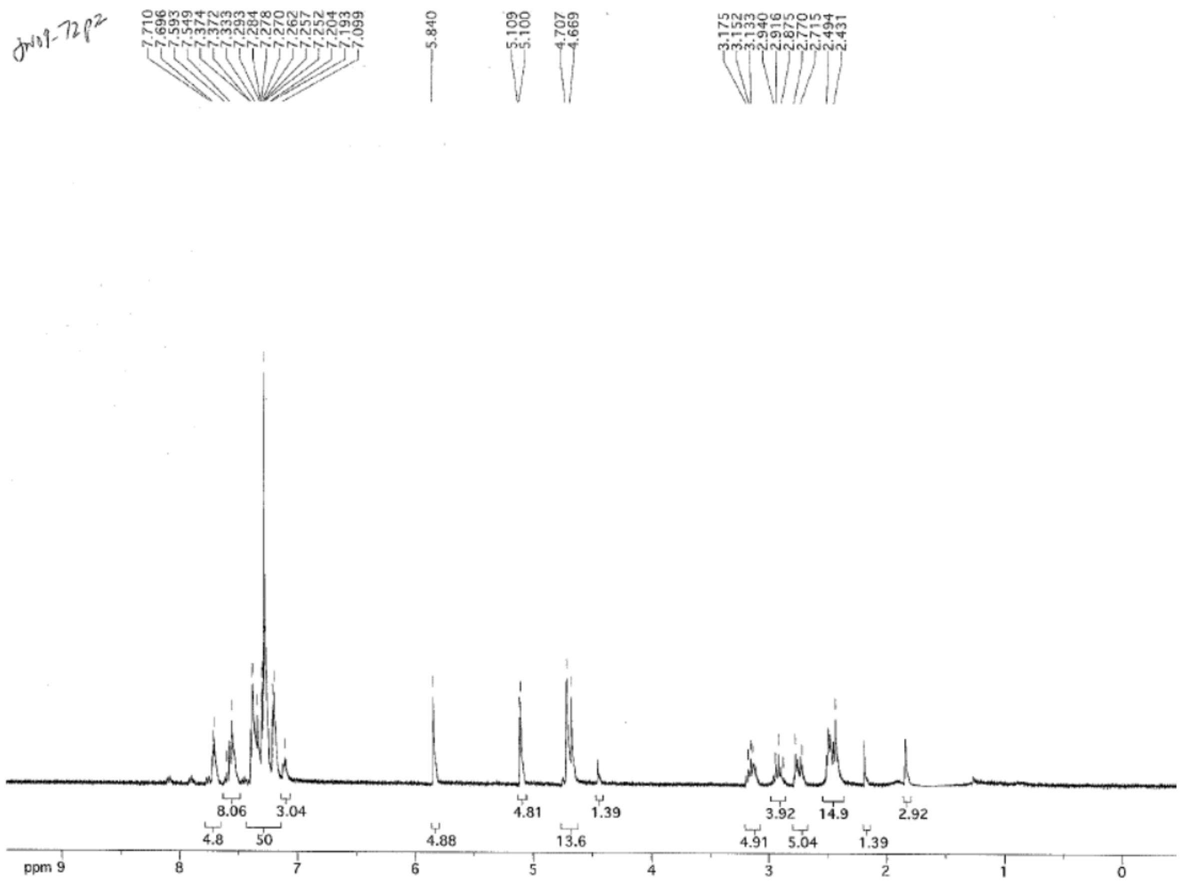


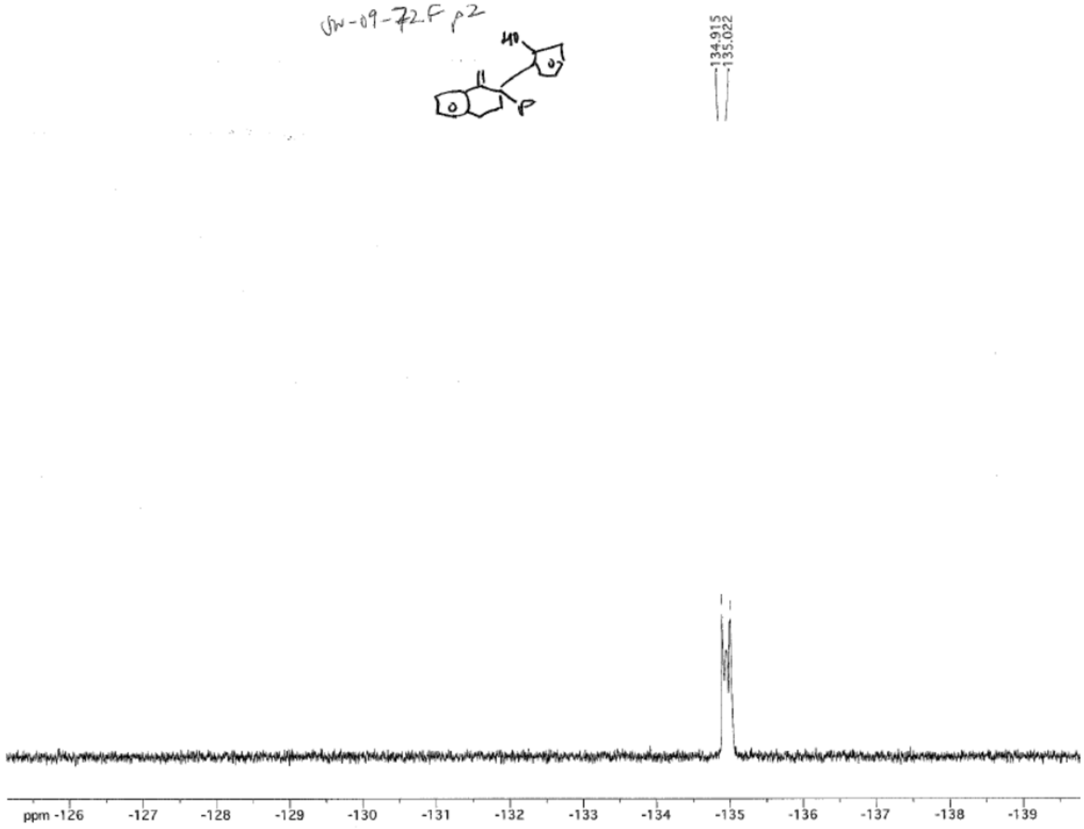
```
NAME        JW-09-72-entp2
EXPNO                    1
PROCNO                   1
Date_             20120724
Time                 17.58
INSTRUM            AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      19
DS                       0
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0895586 sec
RG                     362
DW              62.400 usec
DE                6.00 usec
TE                 292.9 K
D1           1.00000000 sec
TD0                      4

======== CHANNEL f1 ========
NUC1                    1H
P1              12.80 usec
PL1                0.00 dB
PL1W          9.34516888 W
SFO1        400.1324700 MHz
SI                   65536
SF          400.1300142 MHz
WDW                     EM
SSB                      0
LB                 0.30 Hz
GB                       0
PC                    4.00
```

1B9010

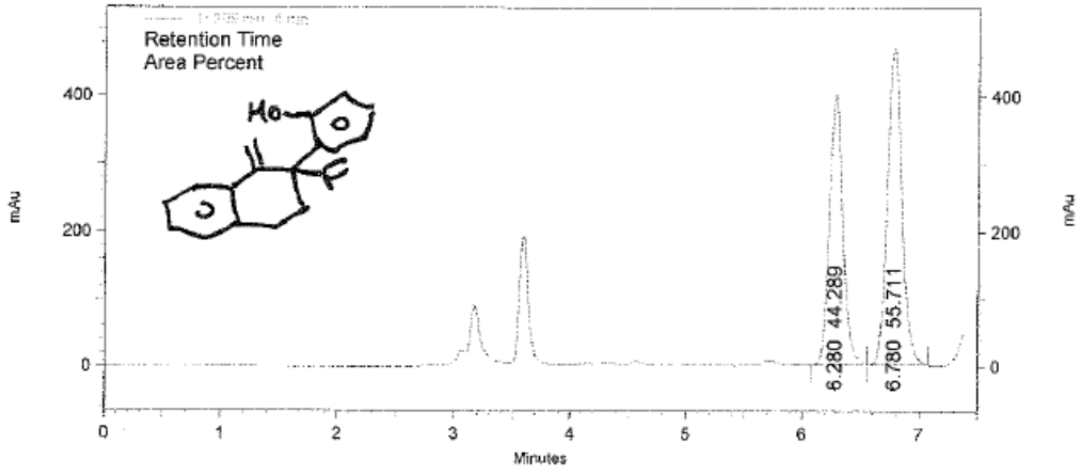
6.3 min

6.8 min


JW09-72p2
7.710
7.696
7.593
7.549
7.374
7.372
7.333
7.293
7.284
7.278
7.270
7.262
7.257
7.252
7.204
7.193
7.099
5.840
5.109
5.100
4.707
4.669
3.175
3.152
3.133
2.940
2.916
2.875
2.770
2.715
2.494
2.431
8.06
3.04
4.81
1.39
3.92
14.9
2.92
4.8
50
4.88
13.6
4.91
5.04
1.39
ppm 9
8
7
6
5
4
3
2
1
0


JW-09-72F p2
HO
O
O
F
134.915
135.022
ppm -126
-127
-128
-129
-130
-131
-132
-133
-134
-135
-136
-137
-138
-139

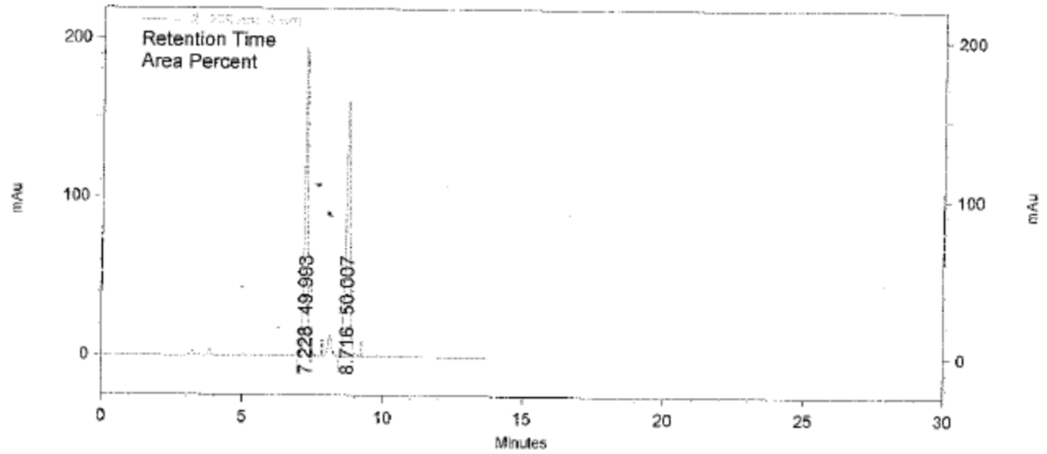
09-72ent 1B9010



1: 205 nm, 4 nm
Results

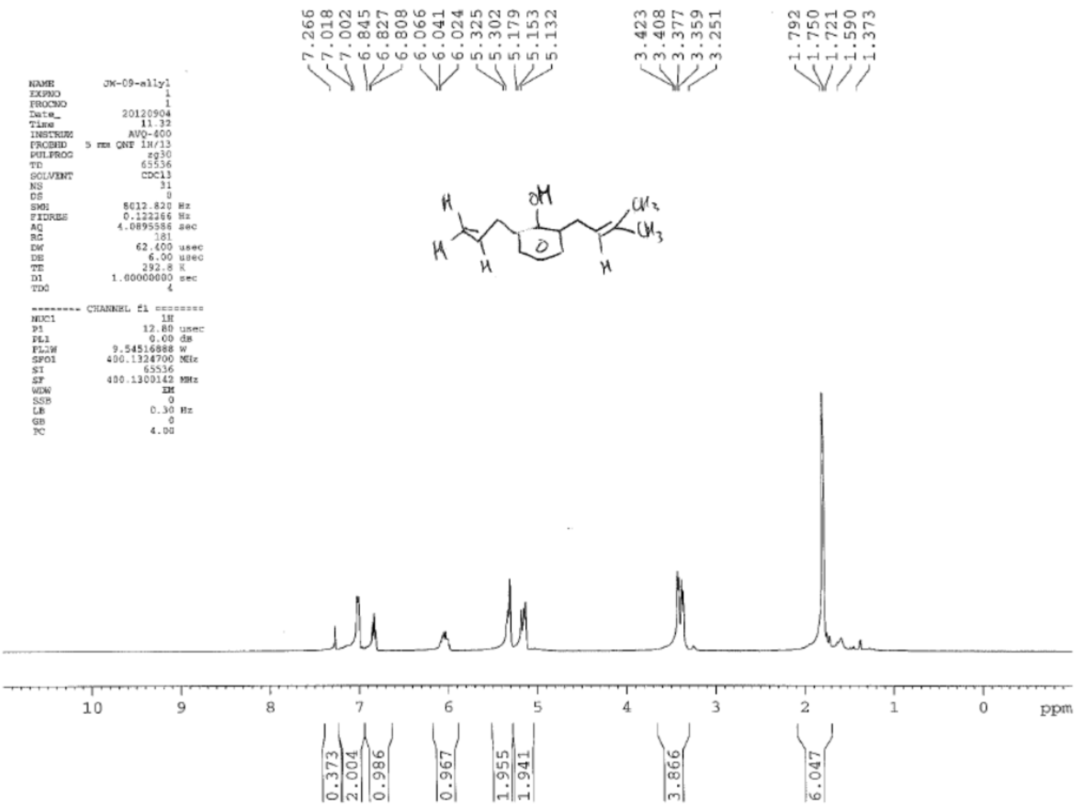
Pk #	Retention Time	Area Percent	Lambda Max
1	6.280	44.289	208
2	6.780	55.711	208

09-45rac

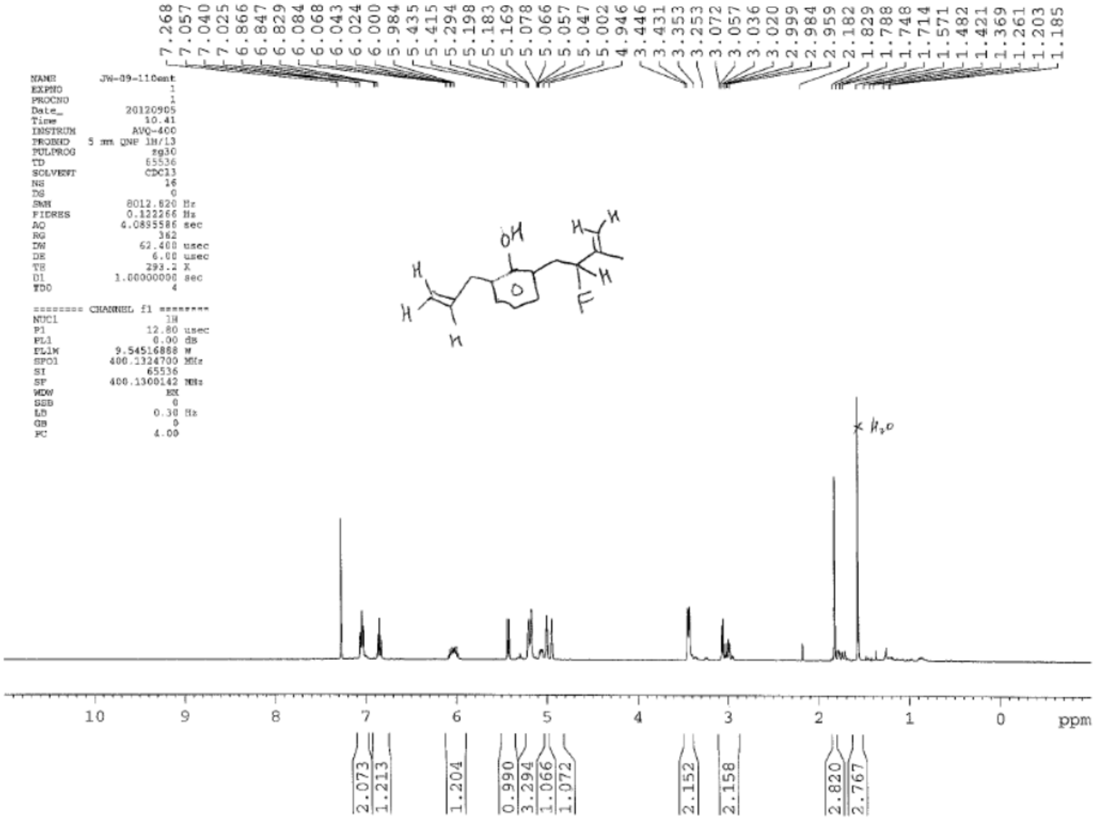


2: 239 nm, 4 nm
Results

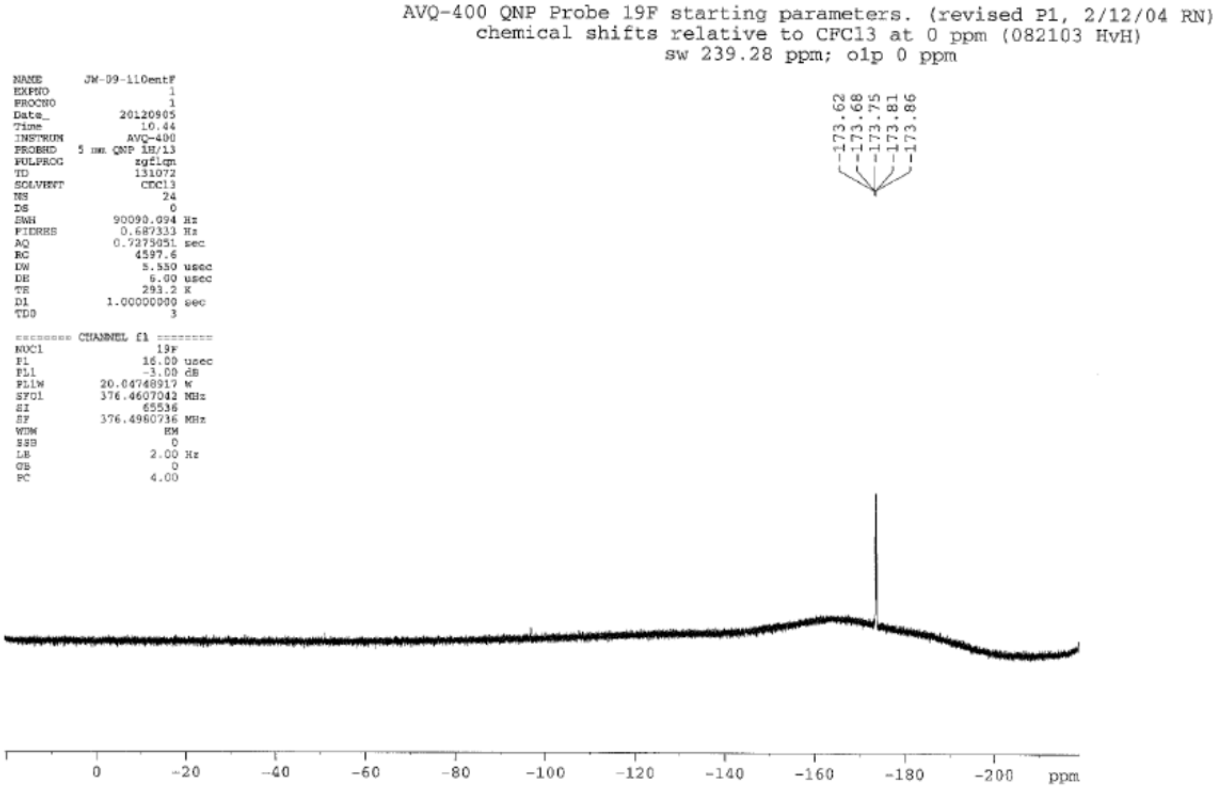
Pk #	Retention Time	Area Percent	Lambda Max
1	7.228	49.993	210
2	8.716	50.007	210



```
NAME          JW-09-allyl
EXPNO                   1
PROCNO                  1
Date_            20120904
Time                11.32
INSTRUM           AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     31
DS                      0
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0895586 sec
RG                    181
DW                 62.400 usec
DE                   6.00 usec
TE                  292.8 K
D1             1.00000000 sec
TD0                     4

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.80 usec
PL1                  0.00 dB
PL1W           9.54516888 W
SFO1          400.1324700 MHz
SI                  65536
SF            400.1300142 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   4.00
```



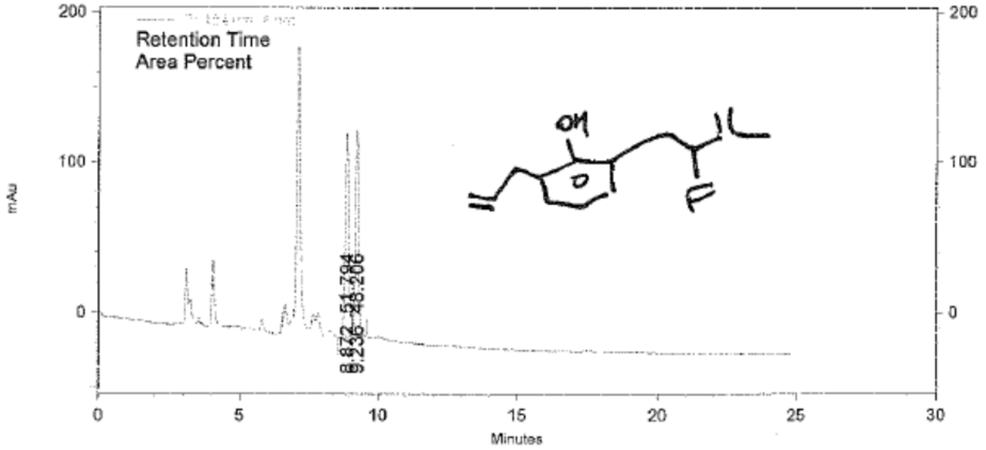
```
NAME         JW-09-110ent
EXPNO                   1
PROCNO                  1
Date_            20120905
Time                10.41
INSTRUM           AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0895586 sec
RG                    362
DW                 62.400 usec
DE                   6.00 usec
TE                  293.2 K
D1             1.00000000 sec
TD0                     4

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.80 usec
PL1                  0.00 dB
PL1W           9.54516888 W
SFO1          400.1324700 MHz
SI                  65536
SF            400.1300142 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   4.00
```



```
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
         chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
                        sw 239.28 ppm; o1p 0 ppm
```

```
NAME           JW-09-110entF
EXPNO                      1
PROCNO                     1
Date_               20120905
Time                   10.44
INSTRUM              AVQ-400
PROBHD      5 mm QNP 1H/13
PULPROG               zgflqn
TD                    131072
SOLVENT                CDCl3
NS                        24
DS                         0
SWH             90090.094 Hz
FIDRES           0.687333 Hz
AQ              0.7275051 sec
RC                    4597.6
DW                  5.550 usec
DE                   6.00 usec
TE                   293.2 K
D1             1.00000000 sec
TD0                        3

======== CHANNEL f1 ========
NUC1                     19F
P1                  16.00 usec
PL1                 -3.00 dB
PL1W          20.04748917 W
SFO1         376.4607042 MHz
SI                     65536
SF           376.4960736 MHz
WDW                       EM
SSB                        0
LB                   2.00 Hz
GB                         0
PC                      4.00
```

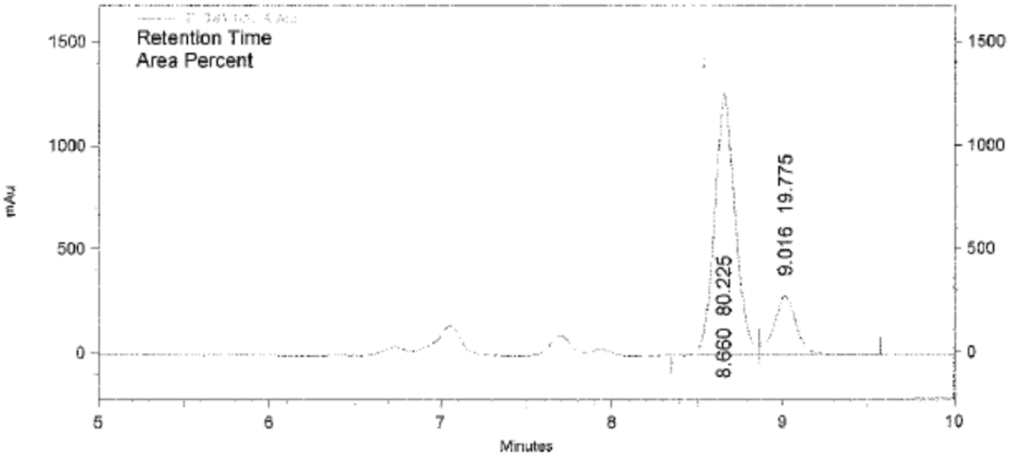
09-110rac



2: 194 nm, 4 nm
Results

Pk #	Retention Time	Area Percent	Lambda Max
1	8.872	51.794	203
2	9.236	48.206	203

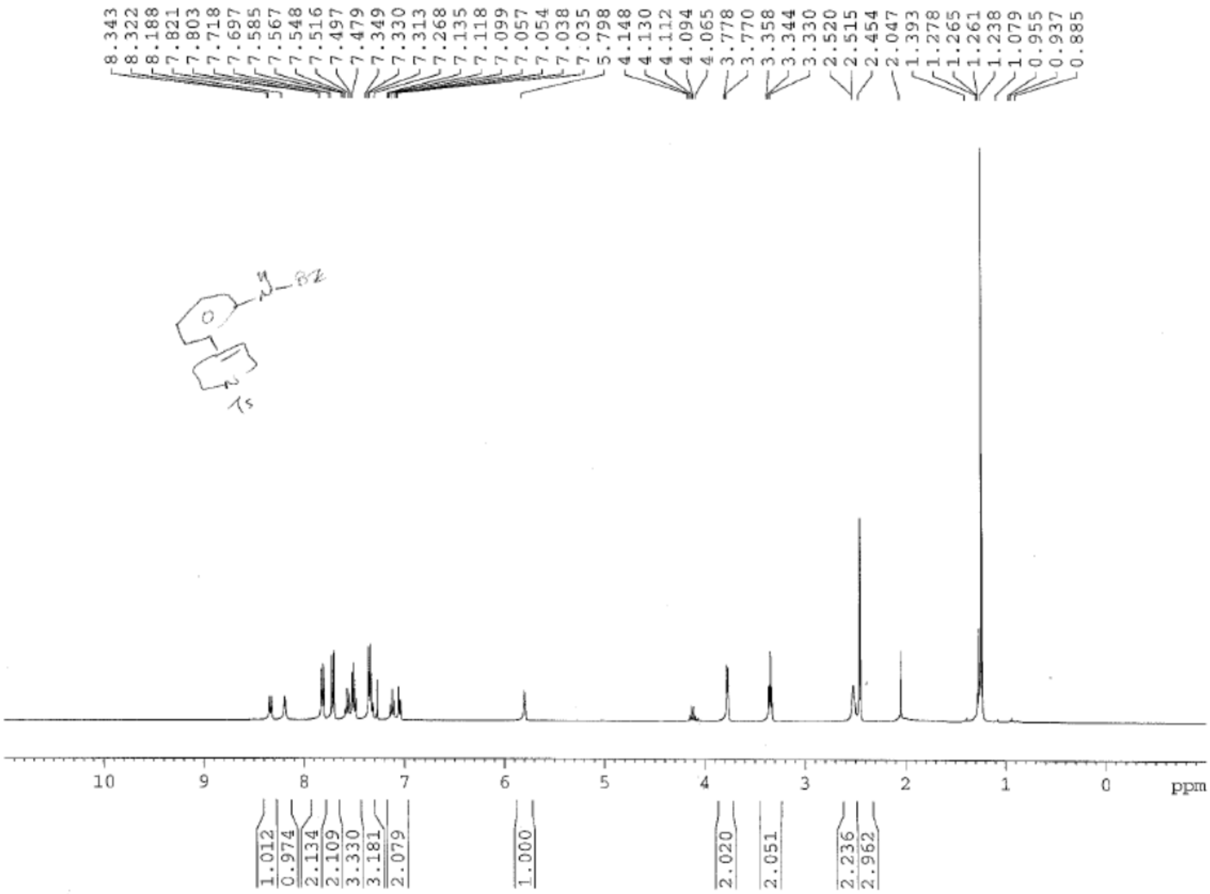
09-110-IA9901

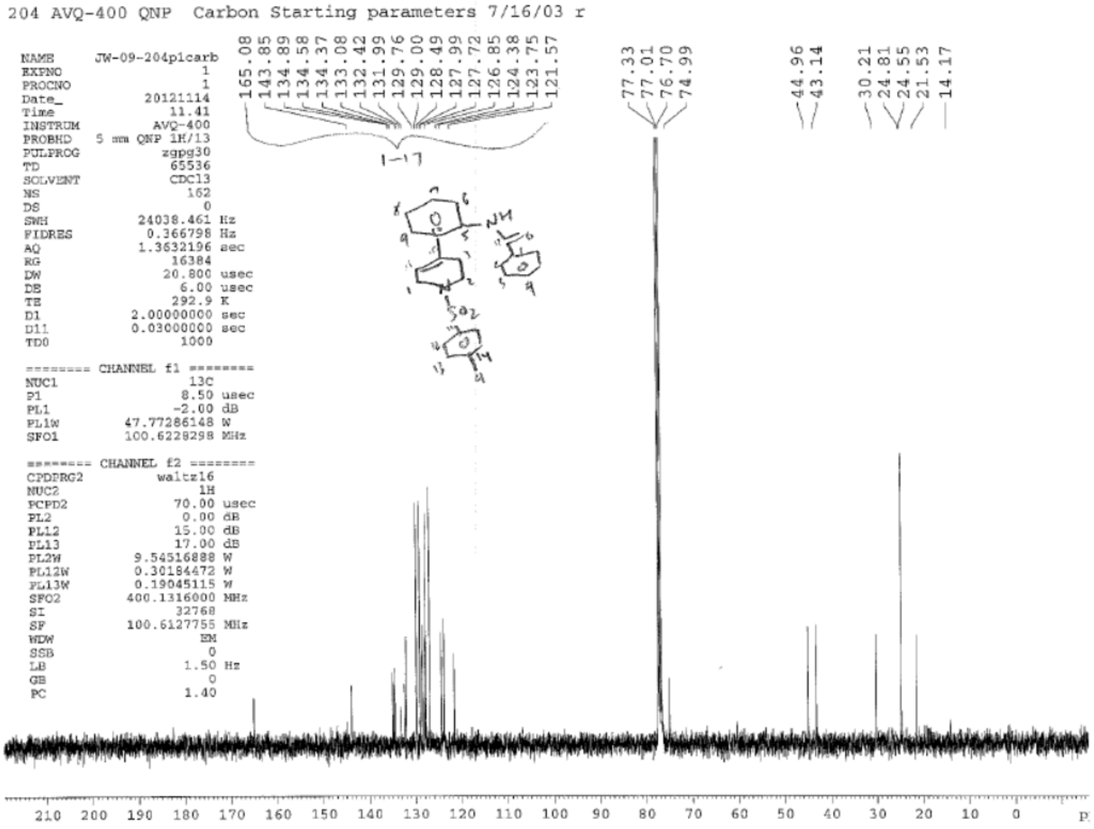


2: 194 nm, 4 nm
Results

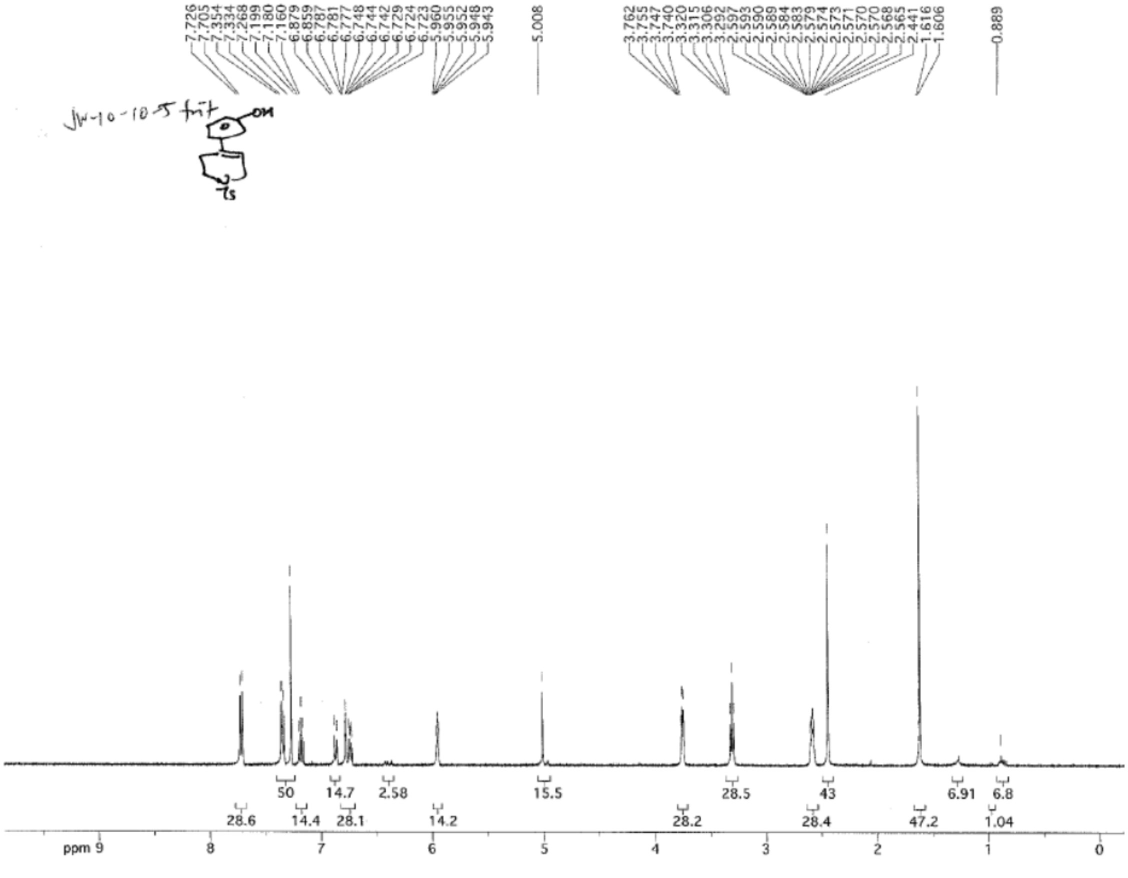
Pk #	Retention Time	Area Percent	Lambda Max
1	8.660	80.225	203
2	9.016	19.775	203

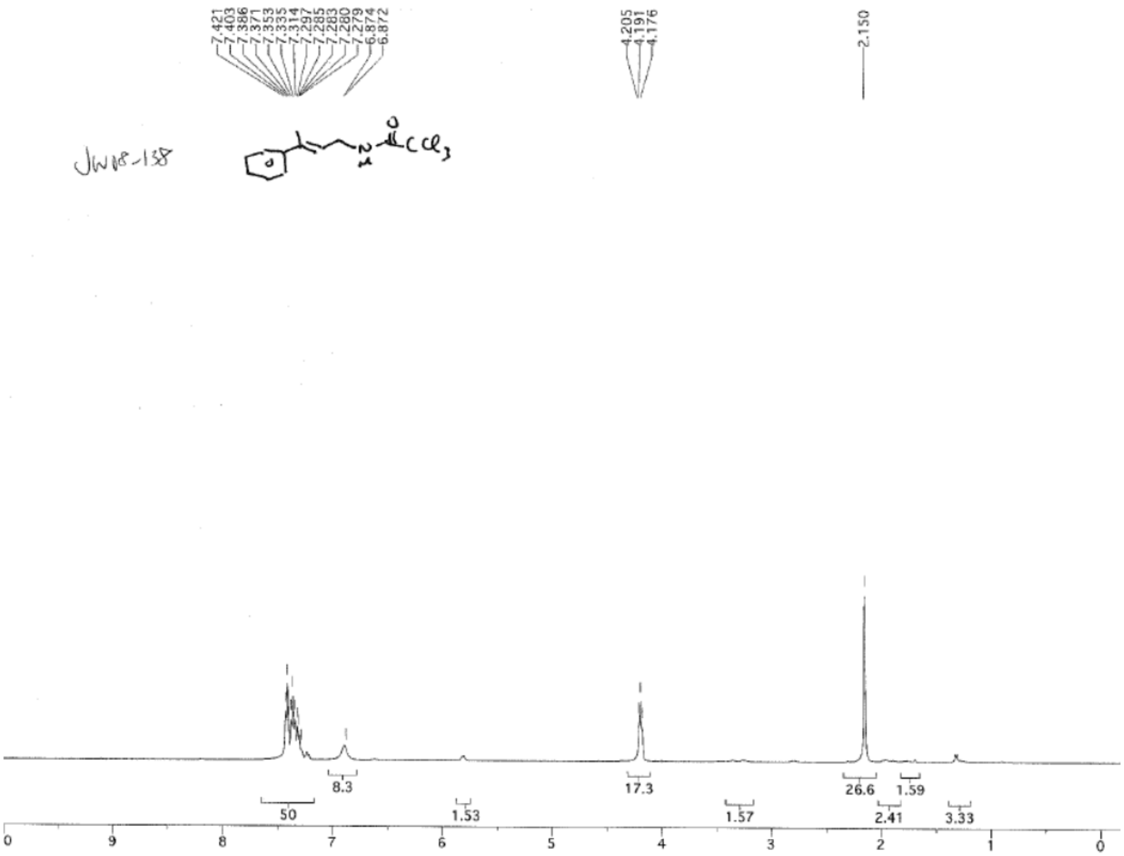
JW-09-204 AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN

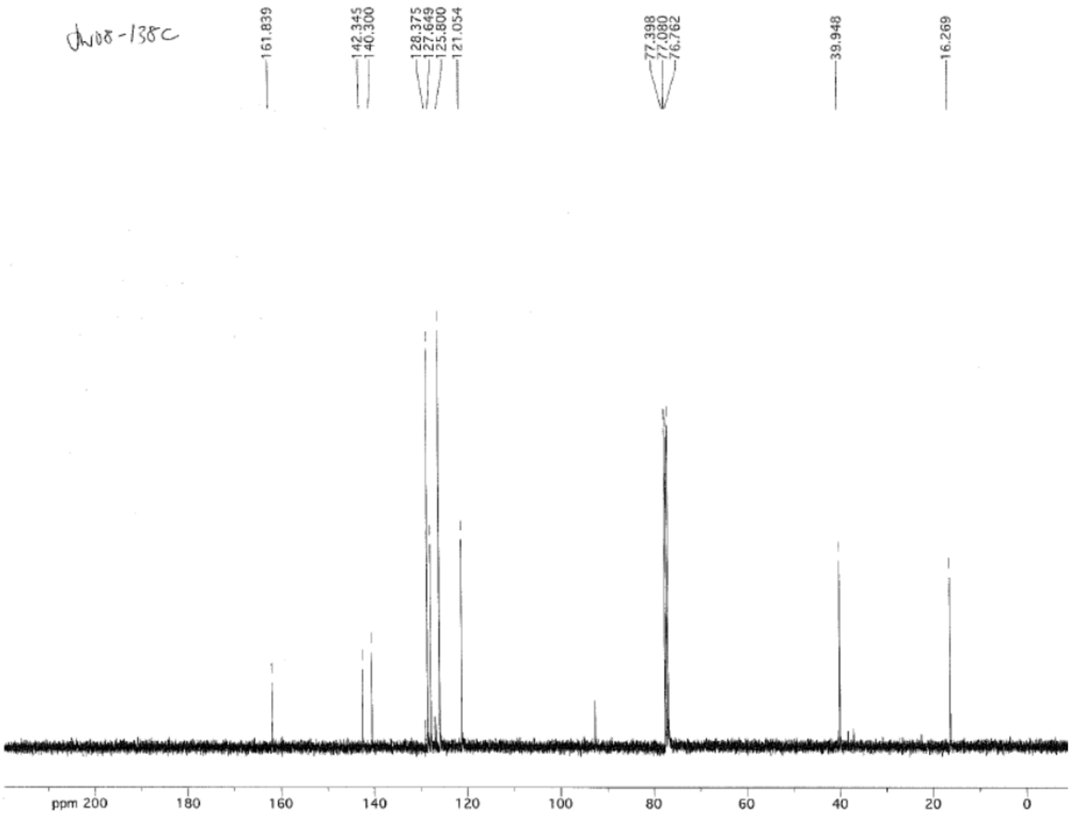


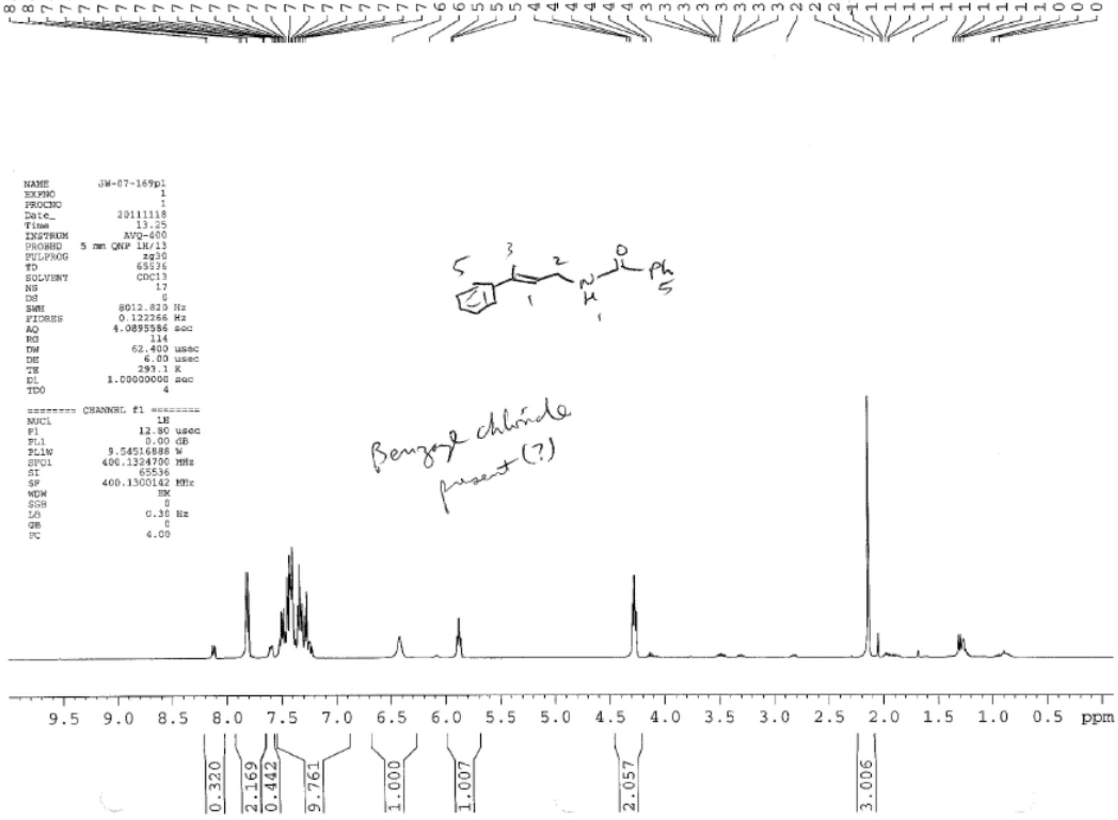


```
NAME       JW-09-204p1carb
EXPNO                    1
PROCNO                   1
Date_             20121114
Time                 11.41
INSTRUM            AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     162
DS                       0
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3632196 sec
RG                   16384
DW                  20.800 usec
DE                    6.00 usec
TE                   292.9 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                   1000

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.50 usec
PL1                  -2.00 dB
PL1W           47.77286148 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                70.00 usec
PL2                   0.00 dB
PL12                 15.00 dB
PL13                 17.00 dB
PL2W            9.54516888 W
PL12W           0.30184472 W
PL13W           0.19045115 W
SFO2           400.1316000 MHz
SI                   32768
SF             100.6127755 MHz
WDW                     EM
SSB                      0
LB                    1.50 Hz
GB                       0
PC                    1.40
```



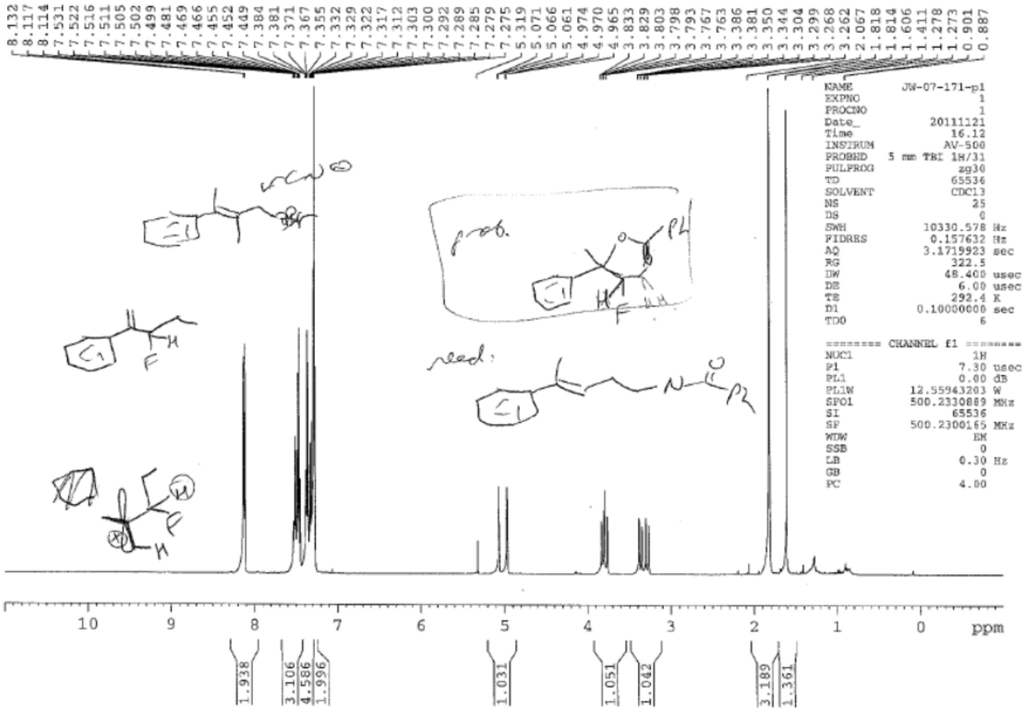

7.421
7.403
7.386
7.371
7.353
7.335
7.314
7.297
7.285
7.283
7.280
7.279
6.874
6.872
4.205
4.191
4.176
2.150
JW08-138
N
H
O
CCl3
8.3
50
1.53
17.3
1.57
26.6
1.59
2.41
3.33
0
9
8
7
6
5
4
3
2
1
0


JW08-138C
161.839
142.345
140.300
128.375
127.649
125.800
121.054
77.398
77.080
76.762
39.948
16.269
ppm 200
180
160
140
120
100
80
60
40
20
0

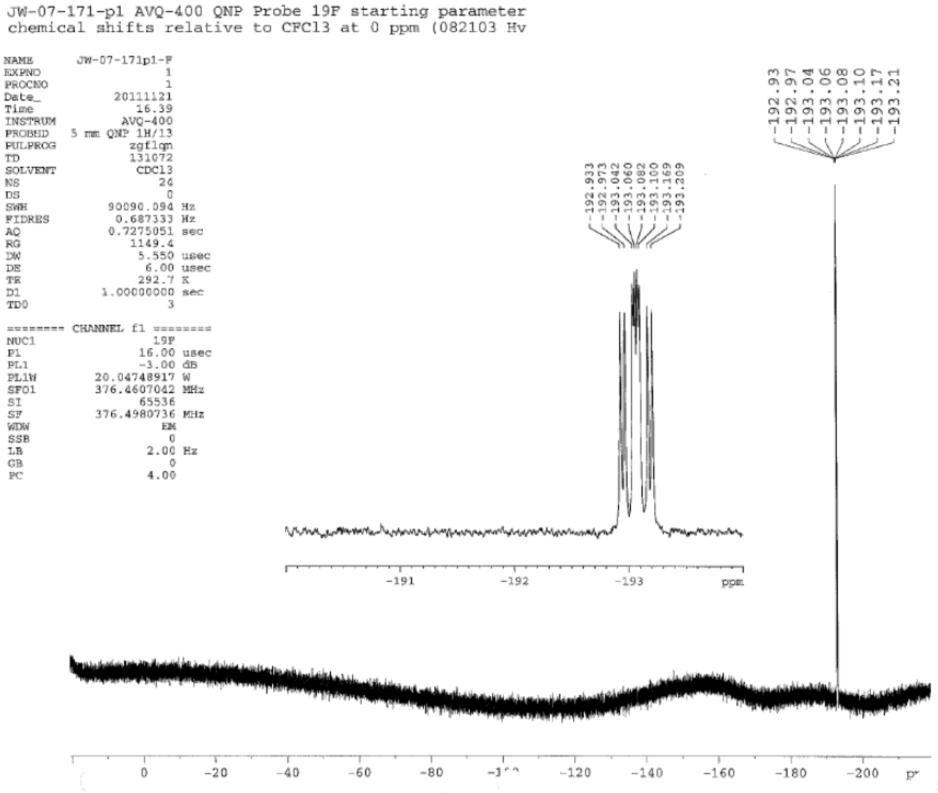


```
NAME          JW-07-169p1
EXPNO                   1
PROCNO                  1
Date_            20111118
Time                13.25
INSTRUM           AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     17
DS                      0
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0895586 sec
RG                    114
DW                 62.400 usec
DE                   6.00 usec
TE                  293.1 K
D1             1.00000000 sec
TD0                     4

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.80 usec
PL1                  0.00 dB
PL1W           9.54516888 W
SFO1          400.1324700 MHz
SI                  65536
SF            400.1300142 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   4.00
```

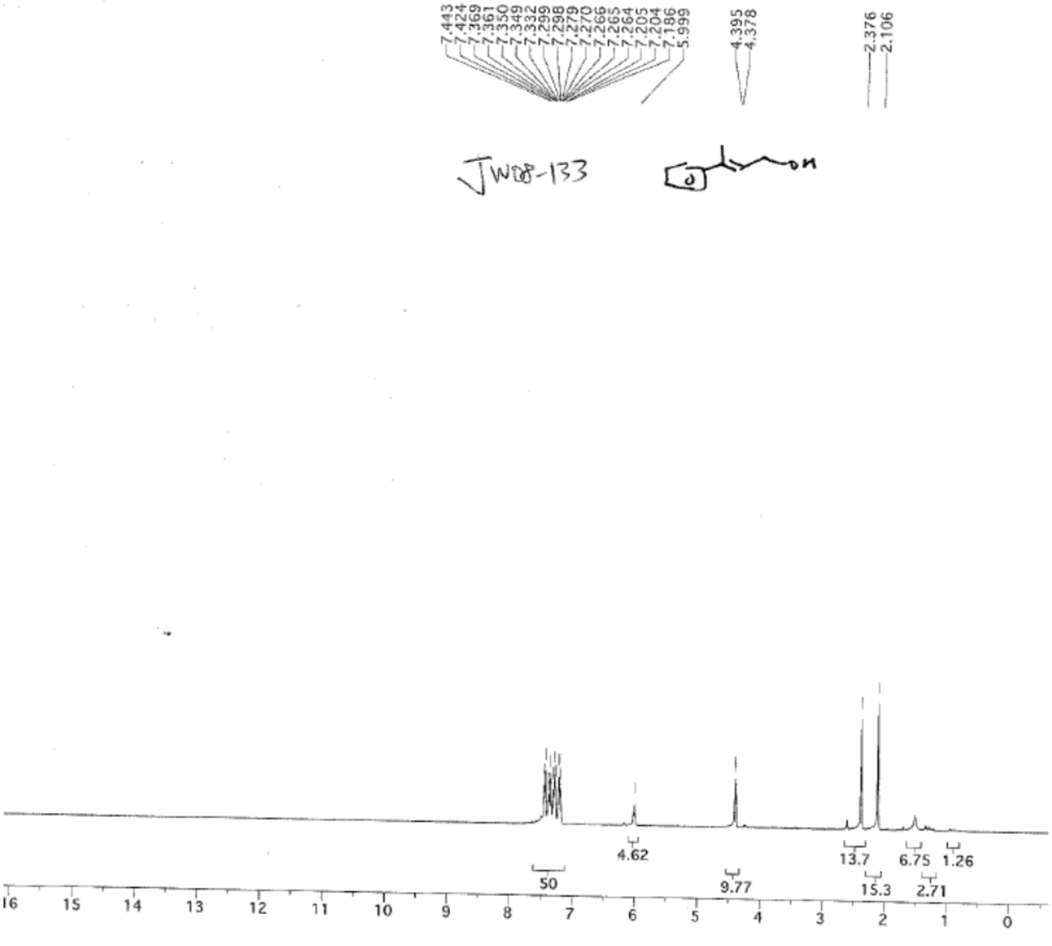
JW-07-171-p1 AV-500 new TBI(HXP) probe
1D 1H starting parameters



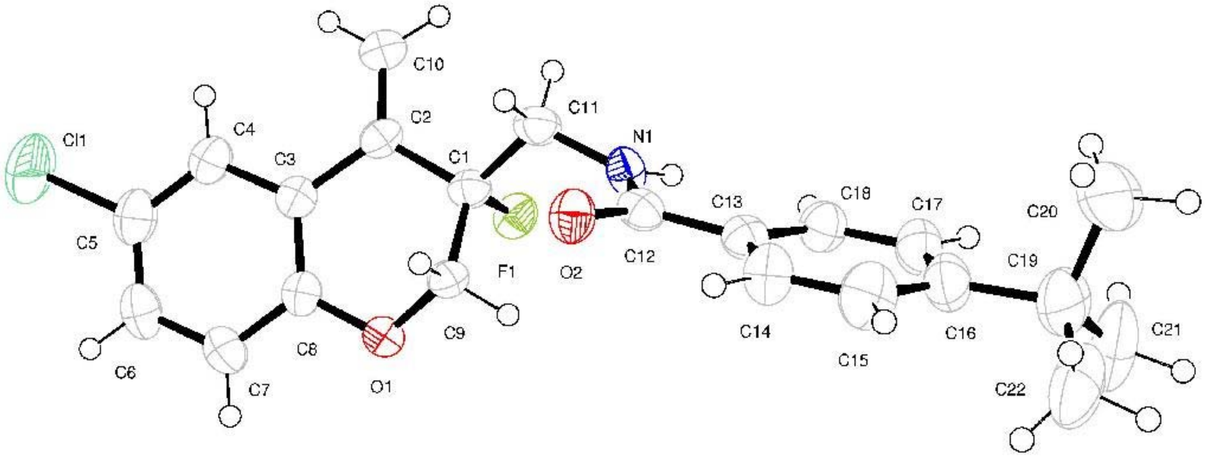
```
NAME          JW-07-171-p1
EXPNO                    1
PROCNO                   1
Date_             20111121
Time                 16.12
INSTRUM             AV-500
PROBHD   5 mm TBI 1H/31
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      25
DS                       0
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ               3.1719923 sec
RG                   322.5
DW                  48.400 usec
DE                    6.00 usec
TE                   292.4 K
D1              0.10000000 sec
TD0                      6

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.30 usec
PL1                   0.00 dB
PL1W           12.55943203 W
SFO1           500.2330889 MHz
SI                   65536
SF             500.2300165 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    4.00
```



```
JW-07-171-p1 AVQ-400 QNP Probe 19F starting parameter
chemical shifts relative to CFCl3 at 0 ppm (082103 Hv

NAME        JW-07-171p1-F
EXPNO                   1
PROCNO                  1
Date_            20111121
Time                16.39
INSTRUM           AVQ-400
PROBHD     5 mm QNP 1H/13
PULPROG            zgflqn
TD                 131072
SOLVENT             CDCl3
NS                     24
DS                      0
SWH             90090.094 Hz
FIDRES           0.687333 Hz
AQ              0.7275051 sec
RG                 1149.4
DW                  5.550 usec
DE                   6.00 usec
TE                  292.7 K
D1             1.00000000 sec
TD0                     3

======== CHANNEL f1 ========
NUC1                  19F
P1                  16.00 usec
PL1                 -3.00 dB
PL1W          20.04748917 W
SFO1          376.4607042 MHz
SI                  65536
SF            376.4980736 MHz
WDW                    EM
SSB                     0
LB                   2.00 Hz
GB                      0
PC                   4.00
```



JW08-133



A colorless plate 0.10 x 0.06 x 0.03 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 10 seconds per frame using a scan width of 1.0°. Data collection was 98.3% complete to 67.00° in □. A total of 22020 reflections were collected covering the indices, -8<=*h*<=9, -14<=*k*<=14, -23<=*l*<=23. 6821 reflections were found to be symmetry independent, with an R_{int} of 0.0431. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P2(1) (No. 4). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SIR-2008) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. Absolute stereochemistry was unambiguously determined to be *R* at C1 and C23, respectively.

Table 1. Crystal data and structure refinement for toste52.

X-ray ID	toste52	
Sample/notebook ID	JW-08-41	
Empirical formula	C22 H23 Cl F N O2	
Formula weight	387.86	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 8.4882(3) Å	□= 90°.
	b = 11.8855(5) Å	□= 96.216(3)°.
	c = 19.4286(8) Å	□ = 90°.
Volume	1948.56(13) Å^3	
Z	4	
Density (calculated)	1.322 Mg/m^3	
Absorption coefficient	1.953 mm^{-1}	
F(000)	816	
Crystal size	0.10 x 0.06 x 0.03 mm^3	
Crystal color/habit	colorless plate	
Theta range for data collection	4.37 to 67.86°.	
Index ranges	-8<=h<=9, -14<=k<=14, -23<=l<=23	
Reflections collected	22020	
Independent reflections	6821 [R(int) = 0.0431]	
Completeness to theta = 67.00°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9437 and 0.8287	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6821 / 1 / 493	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0730, wR2 = 0.1882	
R indices (all data)	R1 = 0.0832, wR2 = 0.2001	
Absolute structure parameter	-0.01(3)	
Largest diff. peak and hole	0.798 and -0.438 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3)
for toste52. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	4214(5)	4439(3)	4535(2)	37(1)
C(2)	4829(5)	4120(4)	3852(2)	38(1)
C(3)	4754(5)	5039(4)	3328(2)	39(1)
C(4)	5340(6)	4891(5)	2687(3)	51(1)
C(5)	5186(7)	5740(6)	2204(3)	62(1)
C(6)	4413(7)	6725(5)	2311(3)	56(1)
C(7)	3870(6)	6904(4)	2953(2)	47(1)
C(8)	4050(5)	6071(4)	3456(2)	40(1)
C(9)	4262(5)	5694(3)	4652(2)	35(1)
C(10)	5316(6)	3090(4)	3738(3)	50(1)
C(11)	5087(6)	3825(4)	5147(2)	43(1)
C(12)	5296(5)	4865(3)	6234(2)	37(1)
C(13)	4874(5)	4903(4)	6955(2)	40(1)
C(14)	5710(6)	5647(5)	7422(3)	51(1)
C(15)	5458(7)	5665(6)	8101(3)	63(1)
C(16)	4361(6)	4971(5)	8368(3)	57(1)
C(17)	3520(6)	4244(5)	7900(3)	54(1)
C(18)	3750(6)	4219(4)	7214(3)	48(1)
C(19)	4109(9)	4941(7)	9146(3)	80(2)
C(20)	5199(19)	4005(11)	9475(4)	166(6)
C(21)	2355(11)	4761(9)	9229(4)	102(3)
C(22)	4550(10)	6092(8)	9482(3)	91(2)
C(23)	-804(5)	6703(3)	4348(2)	38(1)
C(24)	-615(5)	6248(4)	3630(2)	39(1)
C(25)	-157(5)	7111(4)	3131(2)	43(1)
C(26)	-32(6)	6841(5)	2436(3)	52(1)
C(27)	451(7)	7658(6)	1998(3)	62(1)
C(28)	776(7)	8751(5)	2218(3)	60(1)
C(29)	658(6)	9025(4)	2896(3)	54(1)
C(30)	180(5)	8219(4)	3351(3)	45(1)
C(31)	247(5)	7702(3)	4524(2)	41(1)
C(32)	-856(6)	5180(4)	3472(2)	49(1)
C(33)	-581(5)	5820(3)	4927(2)	38(1)
C(34)	586(5)	6545(3)	6039(2)	38(1)
C(35)	264(5)	7014(3)	6729(2)	38(1)
C(36)	-1125(5)	7571(4)	6829(2)	40(1)
C(37)	-1360(5)	7994(4)	7466(3)	45(1)
C(38)	-229(6)	7874(4)	8035(3)	51(1)

C(39)	1176(6)	7332(4)	7931(2)	49(1)
C(40)	1433(5)	6907(4)	7288(2)	43(1)
C(41)	-506(7)	8293(6)	8763(3)	65(2)
C(42)	-837(15)	7315(12)	9203(4)	141(5)
C(43)	-2152(13)	8927(12)	8735(5)	134(5)
C(44)	778(11)	8987(12)	9071(5)	131(4)
N(1)	4551(4)	4093(3)	5807(2)	41(1)
N(2)	-712(4)	6278(3)	5599(2)	39(1)
O(1)	3480(3)	6295(2)	4071(2)	38(1)
O(2)	6346(3)	5460(3)	6043(2)	45(1)
O(3)	39(4)	8557(2)	4013(2)	48(1)
O(4)	1930(3)	6439(3)	5883(2)	44(1)
F(1)	2601(3)	4115(2)	4492(1)	44(1)
F(2)	-2405(3)	7101(2)	4316(1)	46(1)
Cl(1)	5951(3)	5539(2)	1412(1)	94(1)
Cl(2)	678(3)	7284(2)	1137(1)	92(1)

Table 3. Bond lengths [Å] and angles [°] for toste52.

C(1)-F(1)	1.416(5)	C(20)-H(20C)	0.9800
C(1)-C(9)	1.509(5)	C(21)-H(21A)	0.9800
C(1)-C(11)	1.519(6)	C(21)-H(21B)	0.9800
C(1)-C(2)	1.526(6)	C(21)-H(21C)	0.9800
C(2)-C(10)	1.318(6)	C(22)-H(22A)	0.9800
C(2)-C(3)	1.490(6)	C(22)-H(22B)	0.9800
C(3)-C(8)	1.399(6)	C(22)-H(22C)	0.9800
C(3)-C(4)	1.400(6)	C(23)-F(2)	1.434(5)
C(4)-C(5)	1.374(8)	C(23)-C(31)	1.502(6)
C(4)-H(4)	0.9500	C(23)-C(24)	1.521(6)
C(5)-C(6)	1.369(8)	C(23)-C(33)	1.535(6)
C(5)-Cl(1)	1.751(5)	C(24)-C(32)	1.317(7)
C(6)-C(7)	1.394(7)	C(24)-C(25)	1.492(6)
C(6)-H(6)	0.9500	C(25)-C(26)	1.403(7)
C(7)-C(8)	1.388(6)	C(25)-C(30)	1.404(7)
C(7)-H(7)	0.9500	C(26)-C(27)	1.383(8)
C(8)-O(1)	1.364(5)	C(26)-H(26)	0.9500
C(9)-O(1)	1.435(5)	C(27)-C(28)	1.385(9)
C(9)-H(9A)	0.9900	C(27)-Cl(2)	1.763(6)
C(9)-H(9B)	0.9900	C(28)-C(29)	1.370(8)
C(10)-H(10A)	0.9500	C(28)-H(28)	0.9500
C(10)-H(10B)	0.9500	C(29)-C(30)	1.394(7)
C(11)-N(1)	1.441(6)	C(29)-H(29)	0.9500
C(11)-H(11A)	0.9900	C(30)-O(3)	1.364(6)
C(11)-H(11B)	0.9900	C(31)-O(3)	1.419(5)
C(12)-O(2)	1.226(5)	C(31)-H(31A)	0.9900
C(12)-N(1)	1.347(6)	C(31)-H(31B)	0.9900
C(12)-C(13)	1.485(6)	C(32)-H(32A)	0.9500
C(13)-C(18)	1.389(7)	C(32)-H(32B)	0.9500
C(13)-C(14)	1.403(7)	C(33)-N(2)	1.429(6)
C(14)-C(15)	1.358(8)	C(33)-H(33A)	0.9900
C(14)-H(14)	0.9500	C(33)-H(33B)	0.9900
C(15)-C(16)	1.387(8)	C(34)-O(4)	1.218(5)
C(15)-H(15)	0.9500	C(34)-N(2)	1.358(6)
C(16)-C(17)	1.394(8)	C(34)-C(35)	1.504(6)
C(16)-C(19)	1.550(8)	C(35)-C(36)	1.384(6)
C(17)-C(18)	1.368(7)	C(35)-C(40)	1.395(6)
C(17)-H(17)	0.9500	C(36)-C(37)	1.370(7)
C(18)-H(18)	0.9500	C(36)-H(36)	0.9500
C(19)-C(21)	1.529(11)	C(37)-C(38)	1.391(7)
C(19)-C(20)	1.541(11)	C(37)-H(37)	0.9500
C(19)-C(22)	1.545(12)	C(38)-C(39)	1.390(7)
C(20)-H(20A)	0.9800	C(38)-C(41)	1.541(7)
C(20)-H(20B)	0.9800	C(39)-C(40)	1.388(7)

C(39)-H(39)	0.9500
C(40)-H(40)	0.9500
C(41)-C(44)	1.444(11)
C(41)-C(42)	1.487(13)
C(41)-C(43)	1.583(11)
C(42)-H(42A)	0.9800
C(42)-H(42B)	0.9800
C(42)-H(42C)	0.9800
C(43)-H(43A)	0.9800
C(43)-H(43B)	0.9800
C(43)-H(43C)	0.9800
C(44)-H(44A)	0.9800
C(44)-H(44B)	0.9800
C(44)-H(44C)	0.9800
N(1)-H(1)	0.8800
N(2)-H(2)	0.8800

F(1)-C(1)-C(9)	106.7(3)
F(1)-C(1)-C(11)	107.6(3)
C(9)-C(1)-C(11)	110.7(3)
F(1)-C(1)-C(2)	107.5(3)
C(9)-C(1)-C(2)	111.8(4)
C(11)-C(1)-C(2)	112.2(3)
C(10)-C(2)-C(3)	123.9(4)
C(10)-C(2)-C(1)	121.3(4)
C(3)-C(2)-C(1)	114.8(4)
C(8)-C(3)-C(4)	117.9(4)
C(8)-C(3)-C(2)	120.6(4)
C(4)-C(3)-C(2)	121.5(4)
C(5)-C(4)-C(3)	119.9(5)
C(5)-C(4)-H(4)	120.1
C(3)-C(4)-H(4)	120.1
C(6)-C(5)-C(4)	122.4(5)
C(6)-C(5)-Cl(1)	118.6(4)
C(4)-C(5)-Cl(1)	118.9(5)
C(5)-C(6)-C(7)	118.5(5)
C(5)-C(6)-H(6)	120.8
C(7)-C(6)-H(6)	120.8
C(8)-C(7)-C(6)	119.9(5)
C(8)-C(7)-H(7)	120.0
C(6)-C(7)-H(7)	120.0
O(1)-C(8)-C(7)	117.1(4)
O(1)-C(8)-C(3)	121.8(4)
C(7)-C(8)-C(3)	121.2(4)
O(1)-C(9)-C(1)	111.8(3)
O(1)-C(9)-H(9A)	109.3
C(1)-C(9)-H(9A)	109.3
O(1)-C(9)-H(9B)	109.3
C(1)-C(9)-H(9B)	109.3
H(9A)-C(9)-H(9B)	107.9
C(2)-C(10)-H(10A)	120.0
C(2)-C(10)-H(10B)	120.0
H(10A)-C(10)-H(10B)	120.0
N(1)-C(11)-C(1)	114.6(4)
N(1)-C(11)-H(11A)	108.6
C(1)-C(11)-H(11A)	108.6
N(1)-C(11)-H(11B)	108.6
C(1)-C(11)-H(11B)	108.6
H(11A)-C(11)-H(11B)	107.6
O(2)-C(12)-N(1)	120.9(4)
O(2)-C(12)-C(13)	121.7(4)
N(1)-C(12)-C(13)	117.2(4)
C(18)-C(13)-C(14)	117.0(4)
C(18)-C(13)-C(12)	124.7(4)
C(14)-C(13)-C(12)	118.2(4)
C(15)-C(14)-C(13)	121.1(5)
C(15)-C(14)-H(14)	119.5
C(13)-C(14)-H(14)	119.5
C(14)-C(15)-C(16)	122.4(5)
C(14)-C(15)-H(15)	118.8
C(16)-C(15)-H(15)	118.8
C(15)-C(16)-C(17)	116.2(5)
C(15)-C(16)-C(19)	123.2(6)
C(17)-C(16)-C(19)	120.5(5)
C(18)-C(17)-C(16)	122.1(5)
C(18)-C(17)-H(17)	118.9
C(16)-C(17)-H(17)	118.9
C(17)-C(18)-C(13)	121.1(5)
C(17)-C(18)-H(18)	119.5
C(13)-C(18)-H(18)	119.5
C(21)-C(19)-C(20)	113.8(9)
C(21)-C(19)-C(22)	105.9(7)
C(20)-C(19)-C(22)	110.9(7)
C(21)-C(19)-C(16)	110.2(5)
C(20)-C(19)-C(16)	106.3(6)
C(22)-C(19)-C(16)	109.8(6)
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5

H(20B)-C(20)-H(20C)	109.5
C(19)-C(21)-H(21A)	109.5
C(19)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(19)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(19)-C(22)-H(22A)	109.5
C(19)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(19)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
F(2)-C(23)-C(31)	106.6(3)
F(2)-C(23)-C(24)	105.7(3)
C(31)-C(23)-C(24)	111.8(4)
F(2)-C(23)-C(33)	107.3(3)
C(31)-C(23)-C(33)	110.5(4)
C(24)-C(23)-C(33)	114.4(3)
C(32)-C(24)-C(25)	123.8(4)
C(32)-C(24)-C(23)	121.8(4)
C(25)-C(24)-C(23)	114.4(4)
C(26)-C(25)-C(30)	118.3(4)
C(26)-C(25)-C(24)	121.3(4)
C(30)-C(25)-C(24)	120.3(4)
C(27)-C(26)-C(25)	119.3(5)
C(27)-C(26)-H(26)	120.4
C(25)-C(26)-H(26)	120.4
C(26)-C(27)-C(28)	122.1(5)
C(26)-C(27)-Cl(2)	118.4(5)
C(28)-C(27)-Cl(2)	119.4(4)
C(29)-C(28)-C(27)	119.1(5)
C(29)-C(28)-H(28)	120.5
C(27)-C(28)-H(28)	120.5
C(28)-C(29)-C(30)	120.2(5)
C(28)-C(29)-H(29)	119.9
C(30)-C(29)-H(29)	119.9
O(3)-C(30)-C(29)	117.2(4)
O(3)-C(30)-C(25)	121.9(4)
C(29)-C(30)-C(25)	120.9(5)
O(3)-C(31)-C(23)	112.4(4)
O(3)-C(31)-H(31A)	109.1
C(23)-C(31)-H(31A)	109.1
O(3)-C(31)-H(31B)	109.1
C(23)-C(31)-H(31B)	109.1
H(31A)-C(31)-H(31B)	107.9
C(24)-C(32)-H(32A)	120.0
C(24)-C(32)-H(32B)	120.0
H(32A)-C(32)-H(32B)	120.0
N(2)-C(33)-C(23)	113.1(3)
N(2)-C(33)-H(33A)	109.0
C(23)-C(33)-H(33A)	109.0
N(2)-C(33)-H(33B)	109.0
C(23)-C(33)-H(33B)	109.0
H(33A)-C(33)-H(33B)	107.8
O(4)-C(34)-N(2)	122.5(4)
O(4)-C(34)-C(35)	121.7(4)
N(2)-C(34)-C(35)	115.8(4)
C(36)-C(35)-C(40)	118.7(4)
C(36)-C(35)-C(34)	122.8(4)
C(40)-C(35)-C(34)	118.5(4)
C(37)-C(36)-C(35)	120.8(4)
C(37)-C(36)-H(36)	119.6
C(35)-C(36)-H(36)	119.6
C(36)-C(37)-C(38)	121.7(4)
C(36)-C(37)-H(37)	119.2
C(38)-C(37)-H(37)	119.2
C(39)-C(38)-C(37)	117.4(4)
C(39)-C(38)-C(41)	120.2(5)
C(37)-C(38)-C(41)	122.4(5)
C(40)-C(39)-C(38)	121.4(4)
C(40)-C(39)-H(39)	119.3
C(38)-C(39)-H(39)	119.3
C(39)-C(40)-C(35)	120.0(4)
C(39)-C(40)-H(40)	120.0
C(35)-C(40)-H(40)	120.0
C(44)-C(41)-C(42)	112.9(8)
C(44)-C(41)-C(38)	112.4(6)
C(42)-C(41)-C(38)	109.4(6)
C(44)-C(41)-C(43)	111.5(8)
C(42)-C(41)-C(43)	99.8(8)
C(38)-C(41)-C(43)	110.2(5)
C(41)-C(42)-H(42A)	109.5
C(41)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5
C(41)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5
C(41)-C(43)-H(43A)	109.5
C(41)-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43B)	109.5
C(41)-C(43)-H(43C)	109.5

H(43A)-C(43)-H(43C)	109.5
H(43B)-C(43)-H(43C)	109.5
C(41)-C(44)-H(44A)	109.5
C(41)-C(44)-H(44B)	109.5
H(44A)-C(44)-H(44B)	109.5
C(41)-C(44)-H(44C)	109.5
H(44A)-C(44)-H(44C)	109.5
H(44B)-C(44)-H(44C)	109.5
C(12)-N(1)-C(11)	121.7(4)
C(12)-N(1)-H(1)	119.1
C(11)-N(1)-H(1)	119.1
C(34)-N(2)-C(33)	121.8(3)
C(34)-N(2)-H(2)	119.1
C(33)-N(2)-H(2)	119.1
C(8)-O(1)-C(9)	114.5(3)
C(30)-O(3)-C(31)	115.6(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3)for toste52. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2 a^{*2} U^{11} + \ldots + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	36(2)	32(2)	42(2)	-3(2)	4(2)	0(2)
C(2)	31(2)	42(2)	40(2)	-4(2)	5(2)	3(2)
C(3)	38(2)	42(2)	37(2)	-1(2)	5(2)	0(2)
C(4)	60(3)	56(3)	40(2)	-2(2)	14(2)	6(2)
C(5)	78(4)	75(4)	33(2)	2(2)	14(2)	3(3)
C(6)	67(3)	63(3)	39(2)	11(2)	7(2)	-6(2)
C(7)	51(3)	46(2)	44(2)	9(2)	2(2)	0(2)
C(8)	41(2)	45(2)	35(2)	0(2)	6(2)	-2(2)
C(9)	31(2)	36(2)	40(2)	1(2)	7(2)	5(2)
C(10)	56(3)	44(2)	53(3)	-2(2)	14(2)	11(2)
C(11)	51(2)	33(2)	46(2)	-2(2)	5(2)	6(2)
C(12)	29(2)	37(2)	44(2)	5(2)	-2(2)	1(2)
C(13)	32(2)	43(2)	42(2)	2(2)	0(2)	4(2)
C(14)	48(3)	61(3)	44(2)	-2(2)	4(2)	-13(2)
C(15)	60(3)	80(4)	45(3)	-10(3)	-8(2)	-9(3)
C(16)	56(3)	72(3)	44(3)	13(2)	9(2)	8(2)
C(17)	52(3)	61(3)	48(3)	6(2)	12(2)	-2(2)
C(18)	48(3)	50(3)	48(3)	-1(2)	8(2)	-3(2)
C(19)	98(5)	103(5)	36(3)	3(3)	-3(3)	21(4)
C(20)	286(16)	170(10)	42(4)	25(5)	12(6)	136(11)
C(21)	126(7)	131(7)	54(4)	-3(4)	40(4)	-34(6)
C(22)	93(5)	138(7)	41(3)	-9(4)	10(3)	1(5)
C(23)	34(2)	38(2)	43(2)	-2(2)	10(2)	3(2)
C(24)	38(2)	40(2)	41(2)	0(2)	6(2)	6(2)
C(25)	38(2)	47(2)	43(2)	2(2)	2(2)	6(2)
C(26)	56(3)	57(3)	41(2)	-1(2)	1(2)	-9(2)
C(27)	62(3)	84(4)	40(3)	9(3)	1(2)	-9(3)
C(28)	62(3)	65(3)	52(3)	21(2)	1(2)	-5(2)
C(29)	59(3)	47(2)	55(3)	9(2)	5(2)	8(2)
C(30)	43(2)	44(2)	48(3)	0(2)	3(2)	6(2)
C(31)	47(2)	34(2)	42(2)	-4(2)	9(2)	-1(2)
C(32)	58(3)	49(3)	39(2)	-6(2)	11(2)	1(2)
C(33)	35(2)	39(2)	42(2)	-4(2)	10(2)	-1(2)
C(34)	36(2)	33(2)	46(2)	5(2)	11(2)	0(2)
C(35)	41(2)	36(2)	39(2)	1(2)	9(2)	-7(2)
C(36)	36(2)	39(2)	45(2)	0(2)	7(2)	-4(2)
C(37)	38(2)	48(2)	51(3)	-3(2)	13(2)	-2(2)
C(38)	64(3)	48(2)	44(3)	3(2)	19(2)	-1(2)
C(39)	53(3)	59(3)	35(2)	3(2)	5(2)	4(2)
C(40)	37(2)	46(2)	46(2)	2(2)	5(2)	0(2)
C(41)	75(4)	85(4)	35(3)	-5(2)	12(2)	11(3)

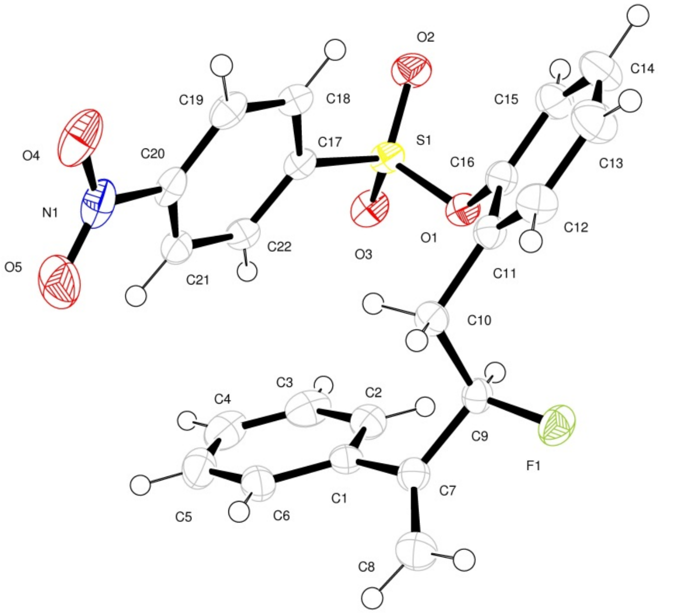
C(42)	187(10)	194(12)	49(4)	-25(6)	45(5)	-94(9)
C(43)	121(7)	212(13)	68(5)	-45(7)	2(5)	60(8)
C(44)	99(6)	200(12)	97(6)	-83(7)	22(5)	-26(7)
N(1)	48(2)	39(2)	36(2)	6(2)	6(1)	-7(2)
N(2)	33(2)	41(2)	43(2)	-1(2)	11(1)	-1(1)
O(1)	41(2)	35(1)	40(2)	3(1)	7(1)	2(1)
O(2)	36(2)	54(2)	44(2)	2(1)	6(1)	-8(1)
O(3)	63(2)	31(1)	54(2)	2(1)	19(2)	0(1)
O(4)	33(2)	52(2)	46(2)	-8(1)	6(1)	-2(1)
F(1)	41(1)	43(1)	48(1)	-7(1)	11(1)	-7(1)
F(2)	42(1)	44(1)	53(2)	0(1)	10(1)	7(1)
Cl(1)	120(1)	122(2)	47(1)	4(1)	35(1)	10(1)
Cl(2)	122(2)	117(2)	38(1)	2(1)	12(1)	-22(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for toste52.

	x	y	z	U(eq)
H(4)	5842	4205	2586	61
H(6)	4251	7273	1954	67
H(7)	3376	7597	3047	57
H(9A)	3743	5874	5071	42
H(9B)	5379	5944	4733	42
H(10A)	5644	2898	3301	60
H(10B)	5337	2539	4093	60
H(11A)	4969	3005	5069	52
H(11B)	6229	4007	5168	52
H(14)	6464	6145	7261	61
H(15)	6056	6173	8404	75
H(17)	2762	3750	8063	64
H(18)	3130	3725	6910	58
H(20A)	5012	3310	9207	250
H(20B)	4972	3876	9952	250
H(20C)	6308	4233	9473	250
H(21A)	2057	3986	9103	152
H(21B)	1712	5283	8926	152
H(21C)	2173	4899	9711	152
H(22A)	4014	6182	9901	136
H(22B)	4217	6695	9154	136
H(22C)	5700	6131	9605	136
H(26)	-276	6103	2268	62
H(28)	1077	9303	1904	72
H(29)	902	9767	3055	64
H(31A)	13	8015	4974	49
H(31B)	1367	7454	4575	49
H(32A)	-739	4920	3018	58
H(32B)	-1146	4669	3813	58
H(33A)	-1388	5222	4831	46
H(33B)	475	5468	4925	46
H(36)	-1925	7660	6451	48
H(37)	-2319	8379	7520	54
H(39)	1978	7251	8309	59
H(40)	2406	6543	7227	52
H(42A)	-756	7550	9689	211
H(42B)	-65	6718	9148	211
H(42C)	-1909	7034	9062	211

H(43A)	-2414	9058	9208	202
H(43B)	-2980	8465	8484	202
H(43C)	-2081	9649	8498	202
H(44A)	415	9431	9448	197
H(44B)	1125	9494	8719	197
H(44C)	1665	8507	9253	197
H(1)	3716	3743	5934	49
H(2)	-1660	6391	5730	46

17b (nosyl-derivative)



A colorless rod 0.060 x 0.040 x 0.040 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 5 seconds per frame using a scan width of 1.0°. Data collection was 100.0% complete to 67.000° in □. A total of 43179 reflections were collected covering the indices, -8<=*h*<=8, -16<=*k*<=16, -26<=*l*<=26. 3685 reflections were found to be symmetry independent, with an R_{int} of 0.0226. Indexing and unit cell refinement indicated a primitive, orthorhombic lattice. The space group was found to be P 21 21 21 (No. 19). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SIR-2011) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2012). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2012. Absolute stereochemistry was unambiguously determined to be *R* at C9.

Table 1. Crystal data and structure refinement for toste72.

X-ray ID	toste72	
Sample/notebook ID	JW-10-NS	
Empirical formula	C22 H18 F N O5 S	
Formula weight	427.43	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 6.8101(4) Å	□= 90°.
	b = 13.2958(8) Å	□= 90°.
	c = 22.2494(14) Å	□ = 90°.
Volume	2014.6(2) $Å^3$	
Z	4	
Density (calculated)	1.409 Mg/m^3	
Absorption coefficient	1.817 mm^{-1}	
F(000)	888	
Crystal size	0.060 x 0.040 x 0.040 mm^3	
Crystal color/habit	colorless rod	
Theta range for data collection	3.873 to 68.334°.	
Index ranges	-8<=h<=8, -16<=k<=16, -26<=l<=26	
Reflections collected	43179	
Independent reflections	3685 [R(int) = 0.0226]	
Completeness to theta = 67.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.841	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3685 / 0 / 271	
Goodness-of-fit on F^2	1.065	
Final R indices [I>2sigma(I)]	R1 = 0.0209, wR2 = 0.0555	
R indices (all data)	R1 = 0.0211, wR2 = 0.0557	
Absolute structure parameter	-0.002(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.178 and -0.217 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3)
for toste72. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5215(3)	12126(1)	1663(1)	26(1)
C(2)	7181(3)	11910(1)	1538(1)	32(1)
C(3)	8374(3)	11480(2)	1974(1)	41(1)
C(4)	7629(4)	11262(2)	2537(1)	47(1)
C(5)	5687(4)	11489(2)	2669(1)	45(1)
C(6)	4491(3)	11913(1)	2238(1)	35(1)
C(7)	3880(3)	12562(1)	1204(1)	26(1)
C(8)	2574(4)	13271(2)	1330(1)	40(1)
C(9)	4009(2)	12090(1)	588(1)	24(1)
C(10)	2945(2)	11083(1)	574(1)	25(1)
C(11)	3181(3)	10524(1)	-11(1)	26(1)
C(12)	1647(3)	10472(1)	-420(1)	33(1)
C(13)	1859(3)	9973(2)	-964(1)	41(1)
C(14)	3613(3)	9505(2)	-1105(1)	42(1)
C(15)	5178(3)	9548(2)	-710(1)	34(1)
C(16)	4936(3)	10053(1)	-170(1)	27(1)
C(17)	5427(2)	8871(1)	1041(1)	24(1)
C(18)	3986(3)	8253(1)	795(1)	26(1)
C(19)	2288(3)	8086(1)	1122(1)	28(1)
C(20)	2111(2)	8537(1)	1679(1)	27(1)
C(21)	3567(3)	9120(1)	1935(1)	28(1)
C(22)	5266(3)	9288(1)	1610(1)	26(1)
N(1)	245(2)	8409(1)	2005(1)	36(1)
O(1)	6555(2)	10168(1)	228(1)	27(1)
O(2)	7819(2)	8428(1)	168(1)	36(1)
O(3)	8948(2)	9643(1)	936(1)	33(1)
O(4)	-903(2)	7769(1)	1825(1)	45(1)
O(5)	-55(3)	8961(1)	2434(1)	51(1)
F(1)	3122(2)	12724(1)	160(1)	34(1)
S(1)	7421(1)	9220(1)	582(1)	26(1)

Table 3. Bond lengths [Å] and angles [°] for toste72.

C(1)-C(2)	1.397(3)	C(12)-H(12)	0.9500
C(1)-C(6)	1.401(2)	C(13)-C(14)	1.383(3)
C(1)-C(7)	1.484(2)	C(13)-H(13)	0.9500
C(2)-C(3)	1.388(3)	C(14)-C(15)	1.381(3)
C(2)-H(2)	0.9500	C(14)-H(14)	0.9500
C(3)-C(4)	1.383(3)	C(15)-C(16)	1.388(2)
C(3)-H(3)	0.9500	C(15)-H(15)	0.9500
C(4)-C(5)	1.388(4)	C(16)-O(1)	1.422(2)
C(4)-H(4)	0.9500	C(17)-C(22)	1.387(2)
C(5)-C(6)	1.377(3)	C(17)-C(18)	1.391(2)
C(5)-H(5)	0.9500	C(17)-S(1)	1.7613(17)
C(6)-H(6)	0.9500	C(18)-C(19)	1.383(3)
C(7)-C(8)	1.326(3)	C(18)-H(18)	0.9500
C(7)-C(9)	1.512(2)	C(19)-C(20)	1.383(3)
C(8)-H(8A)	0.9500	C(19)-H(19)	0.9500
C(8)-H(8B)	0.9500	C(20)-C(21)	1.381(3)
C(9)-F(1)	1.4080(19)	C(20)-N(1)	1.474(2)
C(9)-C(10)	1.523(2)	C(21)-C(22)	1.383(3)
C(9)-H(9)	1.0000	C(21)-H(21)	0.9500
C(10)-C(11)	1.507(2)	C(22)-H(22)	0.9500
C(10)-H(10A)	0.9900	N(1)-O(5)	1.221(2)
C(10)-H(10B)	0.9900	N(1)-O(4)	1.224(2)
C(11)-C(12)	1.387(3)	O(1)-S(1)	1.6002(12)
C(11)-C(16)	1.395(3)	O(2)-S(1)	1.4237(13)
C(12)-C(13)	1.389(3)	O(3)-S(1)	1.4214(14)

C(2)-C(1)-C(6)	118.51(18)	C(8)-C(7)-C(1)	122.97(17)
C(2)-C(1)-C(7)	122.03(16)	C(8)-C(7)-C(9)	121.68(17)
C(6)-C(1)-C(7)	119.45(17)	C(1)-C(7)-C(9)	115.22(14)
C(3)-C(2)-C(1)	120.44(19)	C(7)-C(8)-H(8A)	120.0
C(3)-C(2)-H(2)	119.8	C(7)-C(8)-H(8B)	120.0
C(1)-C(2)-H(2)	119.8	H(8A)-C(8)-H(8B)	120.0
C(4)-C(3)-C(2)	120.3(2)	F(1)-C(9)-C(7)	109.85(13)
C(4)-C(3)-H(3)	119.8	F(1)-C(9)-C(10)	108.04(13)
C(2)-C(3)-H(3)	119.8	C(7)-C(9)-C(10)	110.80(14)
C(3)-C(4)-C(5)	119.7(2)	F(1)-C(9)-H(9)	109.4
C(3)-C(4)-H(4)	120.2	C(7)-C(9)-H(9)	109.4
C(5)-C(4)-H(4)	120.2	C(10)-C(9)-H(9)	109.4
C(6)-C(5)-C(4)	120.4(2)	C(11)-C(10)-C(9)	113.52(14)
C(6)-C(5)-H(5)	119.8	C(11)-C(10)-H(10A)	108.9
C(4)-C(5)-H(5)	119.8	C(9)-C(10)-H(10A)	108.9
C(5)-C(6)-C(1)	120.7(2)	C(11)-C(10)-H(10B)	108.9
C(5)-C(6)-H(6)	119.7	C(9)-C(10)-H(10B)	108.9
C(1)-C(6)-H(6)	119.7	H(10A)-C(10)-H(10B)	107.7

C(12)-C(11)-C(16)	117.14(16)
C(12)-C(11)-C(10)	120.75(16)
C(16)-C(11)-C(10)	122.10(16)
C(11)-C(12)-C(13)	121.20(18)
C(11)-C(12)-H(12)	119.4
C(13)-C(12)-H(12)	119.4
C(14)-C(13)-C(12)	120.12(19)
C(14)-C(13)-H(13)	119.9
C(12)-C(13)-H(13)	119.9
C(15)-C(14)-C(13)	120.30(17)
C(15)-C(14)-H(14)	119.8
C(13)-C(14)-H(14)	119.8
C(14)-C(15)-C(16)	118.60(18)
C(14)-C(15)-H(15)	120.7
C(16)-C(15)-H(15)	120.7
C(15)-C(16)-C(11)	122.61(17)
C(15)-C(16)-O(1)	119.96(16)
C(11)-C(16)-O(1)	117.27(14)
C(22)-C(17)-C(18)	122.60(16)
C(22)-C(17)-S(1)	119.03(13)
C(18)-C(17)-S(1)	118.13(13)
C(19)-C(18)-C(17)	118.58(16)
C(19)-C(18)-H(18)	120.7
C(17)-C(18)-H(18)	120.7
C(20)-C(19)-C(18)	118.27(16)
C(20)-C(19)-H(19)	120.9
C(18)-C(19)-H(19)	120.9
C(21)-C(20)-C(19)	123.46(16)
C(21)-C(20)-N(1)	118.69(16)
C(19)-C(20)-N(1)	117.83(16)
C(20)-C(21)-C(22)	118.35(16)
C(20)-C(21)-H(21)	120.8
C(22)-C(21)-H(21)	120.8
C(21)-C(22)-C(17)	118.64(16)
C(21)-C(22)-H(22)	120.7
C(17)-C(22)-H(22)	120.7
O(5)-N(1)-O(4)	124.62(17)
O(5)-N(1)-C(20)	117.37(17)
O(4)-N(1)-C(20)	118.00(17)
C(16)-O(1)-S(1)	120.46(11)
O(3)-S(1)-O(2)	120.81(8)
O(3)-S(1)-O(1)	103.36(7)
O(2)-S(1)-O(1)	109.54(7)
O(3)-S(1)-C(17)	110.26(8)
O(2)-S(1)-C(17)	109.08(8)
O(1)-S(1)-C(17)	102.05(7)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for toste72. The anisotropic displacement factor exponent takes the form: -2□^{2}[h^2 a^{*2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	32(1)	21(1)	26(1)	-4(1)	-1(1)	-5(1)
C(2)	31(1)	32(1)	33(1)	-2(1)	-6(1)	-4(1)
C(3)	37(1)	35(1)	52(1)	-6(1)	-19(1)	-3(1)
C(4)	68(2)	33(1)	42(1)	1(1)	-32(1)	-9(1)
C(5)	70(2)	37(1)	27(1)	1(1)	-9(1)	-19(1)
C(6)	46(1)	31(1)	28(1)	-4(1)	2(1)	-12(1)
C(7)	26(1)	25(1)	28(1)	1(1)	4(1)	-2(1)
C(8)	43(1)	38(1)	38(1)	-1(1)	6(1)	10(1)
C(9)	22(1)	27(1)	24(1)	4(1)	-1(1)	2(1)
C(10)	21(1)	27(1)	27(1)	0(1)	4(1)	1(1)
C(11)	27(1)	24(1)	27(1)	1(1)	5(1)	-2(1)
C(12)	30(1)	34(1)	35(1)	-1(1)	-1(1)	2(1)
C(13)	43(1)	47(1)	34(1)	-7(1)	-8(1)	0(1)
C(14)	52(1)	45(1)	29(1)	-10(1)	4(1)	0(1)
C(15)	36(1)	34(1)	33(1)	-3(1)	12(1)	1(1)
C(16)	28(1)	27(1)	27(1)	2(1)	3(1)	-3(1)
C(17)	19(1)	20(1)	32(1)	2(1)	2(1)	1(1)
C(18)	27(1)	21(1)	32(1)	0(1)	-1(1)	0(1)
C(19)	23(1)	23(1)	39(1)	6(1)	-5(1)	-3(1)
C(20)	23(1)	23(1)	36(1)	11(1)	3(1)	1(1)
C(21)	32(1)	24(1)	28(1)	3(1)	3(1)	2(1)
C(22)	26(1)	22(1)	31(1)	0(1)	-2(1)	-2(1)
N(1)	29(1)	35(1)	44(1)	17(1)	7(1)	3(1)
O(1)	23(1)	25(1)	32(1)	0(1)	5(1)	0(1)
O(2)	33(1)	31(1)	44(1)	-4(1)	11(1)	6(1)
O(3)	20(1)	32(1)	46(1)	4(1)	2(1)	-1(1)
O(4)	27(1)	42(1)	66(1)	21(1)	3(1)	-6(1)
O(5)	45(1)	58(1)	49(1)	6(1)	22(1)	2(1)
F(1)	38(1)	29(1)	34(1)	6(1)	-11(1)	1(1)
S(1)	20(1)	24(1)	35(1)	0(1)	5(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for toste72.

	x	y	z	U(eq)
H(2)	7705	12059	1152	38
H(3)	9708	11334	1884	50
H(4)	8443	10958	2833	57
H(5)	5179	11352	3058	54
H(6)	3162	12062	2333	42
H(8A)	2462	13522	1728	48
H(8B)	1750	13527	1021	48
H(9)	5420	11986	479	29
H(10A)	3450	10657	905	30
H(10B)	1529	11199	648	30
H(12)	429	10782	-325	40
H(13)	797	9954	-1241	50
H(14)	3743	9153	-1474	50
H(15)	6394	9238	-808	41
H(18)	4165	7953	412	32
H(19)	1270	7672	967	34
H(21)	3405	9397	2326	33
H(22)	6301	9681	1773	32